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# Catalysis of Intramolecular Morita–Baylis–Hillman and Rauhut–Currier Reactions by Fluorous Phosphines; Facile Recovery by Liquid/Solid Organic/Fluorous Biphase Protocols Involving Precipitation, Teflon® Tape, and Gore-Rastex® Fiber

Florian O. Seidel[a] and John A. Gladysz[a,b,*]

[a] Institut für Organische Chemie and Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestraße 42, 91054 Erlangen, Germany

[b] Department of Chemistry, Texas A&M University, PO Box 30012, College Station, Texas 77842-3012, USA
Fax: (+1)-979-845-5629; e-mail: gladysz@mail.chem.tamu.edu

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**Abstract:** The fluorous phosphine $P[(CH_2)_3R_{f8}]_3$ [**1**, $R_{f8} = (CF_2)_7CF_3$; 10 mol%] catalyzes intramolecular Morita–Baylis–Hillman reactions of $O=CH(CH_2)_nCH=CH(C=O)R$ [$n$/R = 2/Ph (**2a**), 2/S-*i*-Pr, 3/*p*-tol] in acetonitrile at 60–72 °C. Upon cooling, **1** precipitates and is recycled. The products $HOCH(CH_2)_nCH=C(C=O)R$ are isolated from the supernatant (78–96%). The educt *i*-$PrS(C=O)CH=CH(CH_2)_2CH=CH(C=O)S$-*i*-Pr similarly undergoes a Rauhut–Currier reaction to give *i*-$PrS(C=O)CH_2CH(CH_2)_2CH=C(C=O)S$-*i*-Pr (71–73%). In the case of **2a**, reactions are also conducted in the presence of Teflon® tape or Gore-Rastex® fiber. The catalyst now precipitates onto the fluoropolymer support, mechanically facilitating recycling. For each reaction, three to five cycles are conducted. HPLC or GC monitoring of the rates show low activity losses, with Gore-Rastex® fiber giving better results than Teflon® tape, presumably due to a higher surface area.

**Keywords:** fluorous phase; Morita–Baylis–Hillman reaction; organocatalysis; phosphines; Rauhut–Currier reaction; recycling

## Introduction

Among the many methods for catalyst recovery and recycling, those involving fluorous systems continue to develop and evolve.[1] This now familiar approach utilizes "ponytails" or phase tags such as $(CH_2)_mR_{fn}$ [$R_{fn} = (CF_2)_{n-1}CF_3$] to render catalysts fluorophilic, enabling their recovery in orthogonal fluorous phases. The initial applications of this technique utilized perfluoroalkane solvents,[2] in which most organic compounds have little or no solubility. In subsequent refinements, the lengths of the $R_{fn}$ segments were used to modulate catalyst solubilities in organic solvents, such that homogeneous conditions could be achieved at elevated temperatures, with near quantitative catalyst precipitation at room temperature or below.[3,4] We then introduced the concurrent use of solid fluoropolymer supports, providing a locus for deposition.[3,5] In conceptually related recycling efforts, others have applied fluorous silica gel.[6–10]

In two feasibility studies, we described (1) the use of Teflon® shavings as a mechanical support for recycling the fluorous phosphine $P[(CH_2)_2R_{f8}]_3$, which is an effective Lewis base or nucleophilic catalyst for additions of alcohols to propiolate esters (*n*-octane, 65 °C),[3] and (2) the use of Teflon® tape as an adsorbent for recycling a rhodium hydrosilylation catalyst derived from $ClRh\{P[(CH_2)_2R_{f6}]_3\}_3$ (dibutyl ether, 55 °C).[5] We were naturally interested in broadening the applicability of these protocols, and evaluating a wider range of fluoropolymer supports.

Earlier, we noted that the phosphine $P[(CH_2)_3R_{f8}]_3$ (**1**),[11] which contains an additional methylene spacer between the phosphorus atom and the $R_{f8}$ segments, is a much stronger Lewis base and more active catalyst for alcohol additions to propiolates.[3,12] Accordingly, we sought to examine its efficacy with and recoverability from other types of reactions catalyzed by phosphorus Lewis bases.[13–17] Thus, intramolecular Morita–Baylis–Hillman and Rauhut–Currier reactions of olefinic dicarbonyl compounds were selected for investigation. Such transformations have been previously studied by several groups,[16,17] and in separate efforts we have developed chiral rhenium-containing phosphorus Lewis base catalysts that effect enantioselective cyclizations.[14]

## Results and Discussion

For screening purposes, the aldehydic α,β-unsaturated ketone $O{=}CH(CH_2)_2CH{=}CH(C{=}O)Ph$ (**2a**)[14,16b] was chosen. As shown in Figure 1, **A**, **1** (10 mol%) and a 0.0500 M $CH_3CN$ solution of **2a** (2.00 mL) were combined in a vial under argon. Catalyst **1** did not seem to dissolve.[18] The mixture was heated at 60–64 °C (sand bath) and appeared to become homogeneous (0.0050 M in **1**). Aliquots were assayed by HPLC.[19] The previously reported intramolecular Morita–Baylis–Hillman product **2b** gradually formed, reaching 81% yield after 9 h and 85% yield after 24 h. The mixture was cooled to room temperature (3 h) and then −30 °C (overnight). Catalyst **1** precipitated, mostly on the sides of the vial. The product solution was carefully removed by syringe and evaporated to dryness. A $^1H$ NMR spectrum of the residue ($CDCl_3$) indicated an 85% yield of **2b**, as assayed by integration of the signals at $\delta = 6.68$ and 5.30 *versus* the total phenyl signals.

The vial containing precipitated **1** was washed with $CH_3CN$ and dried under vacuum (see Figure 2, **A**), and then charged with 1.92 mL of a 0.0500 M solution of **2a** in $CH_3CN$ as above. Four additional cycles were conducted, each with 0.080 mL less of the 0.0500 M solution than the previous cycle (1.84, 1.76, 1.68 mL) to exactly compensate for the catalyst removed in the aliquots. The data in Figure 1, **A** indicate an excellent retention of activity. After the fifth cycle, the catalyst residue was dissolved in $CF_3C_6H_5$, and analyzed by $^1H$ and $^{31}P$ NMR. This showed a 76:24 ratio of **1** and the corresponding phosphine oxide $O{=}P[(CH_2)_3R_{f8}]_3$ (*ca.* 2% in parallel experiments analyzed after the first cycle).[11,20] Control experiments established that the oxide, which was independently synthesized, is not an active catalyst under similar conditions.

The preceding sequence was repeated in the presence of fluoropolymer supports. The first experiments utilized 0.160 g segments (*ca.* 550 × 12 mm) of Teflon® tape (Figure 2, **B** and **C**). After each cycle, the tape was removed, washed with $CH_3CN$ (4 × 1.5 mL), and dried under vacuum (Figure 2, **D**). After the fifth cycle, the catalyst residue was dissolved in $CF_3C_6H_5$. Analysis by $^1H$ and $^{31}P$ NMR indicated a 75:25 ratio of **1** and the corresponding oxide. As shown in Figure 1, **B**, the yield of **2b** after the first cycle was quite close to that in Figure 1, **A** (82 *vs.* 85%), but activity was not as well maintained in subsequent cycles. Possible rationales are offered below.

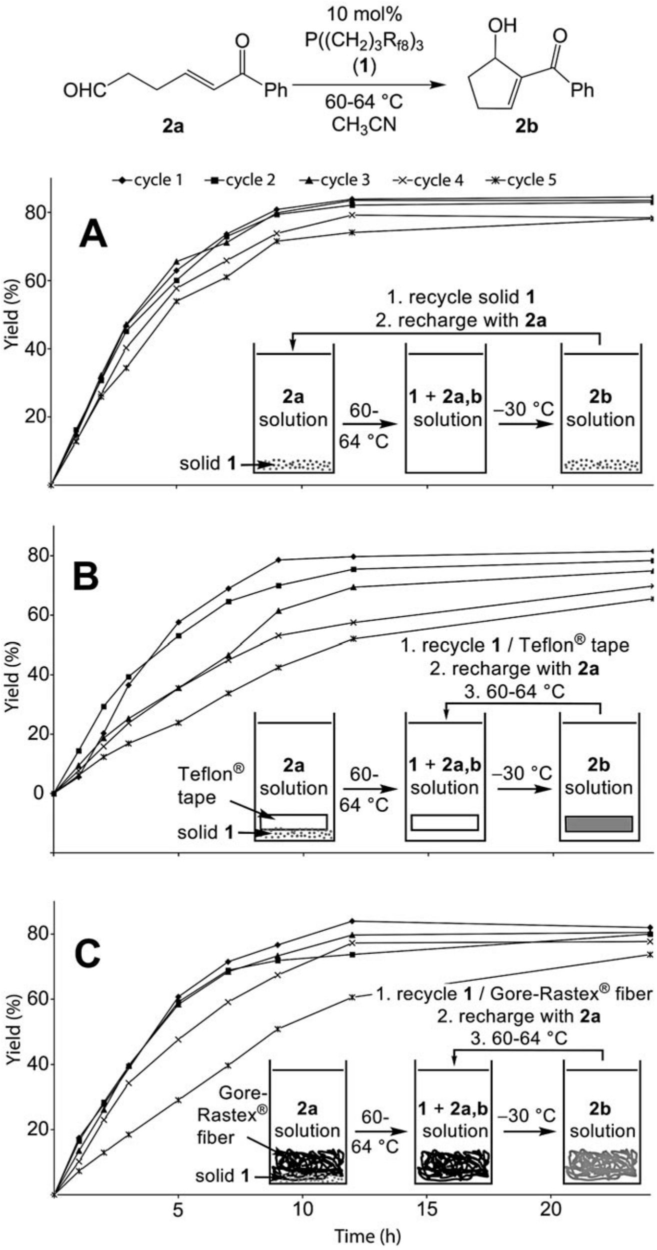


**Figure 1.** Yield of **2b** as a function of cycle: **A** (*top*), catalyst recovery *via* precipitation; **B** (*middle*), catalyst recovery *via* precipitation onto Teflon® tape; **C** (*bottom*), catalyst recovery *via* precipitation onto Gore-Rastex® fiber.

Next, an analogous sequence was conducted in the presence of a plug of Gore-Rastex® fiber (0.160 g),[21] as illustrated in Figure 2, **E–G**. This material can be viewed as a porous modification of Teflon®, consistent with the "breathable" nature of commercial outdoor garments based upon it. The data in Figure 1, **C** show a tangible improvement over those with Teflon® tape, with the retention of activity over the first four cycles very close to that achieved with precipitation alone. After the final cycle, $^1H$ and $^{31}P$ NMR analyses indicated a 63:37 ratio of **1** and the corresponding oxide.

The generality of the protocol in Figure 1, **A** was tested with additional substrates. As shown in Figure 3, the aldehydic α,β-unsaturated thioester and ketone $O{=}CH(CH_2)_2CH{=}CH(C{=}O)S$-*i*-Pr (**3a**)[14] and $O{=}CH(CH_2)_3CH{=}CH(C{=}O)$-*p*-tol (**4a**)[14] smoothly converted to the five- and six-membered carbocycles **3b** and **4b** at 60–64 °C and 70–72 °C, respectively. The

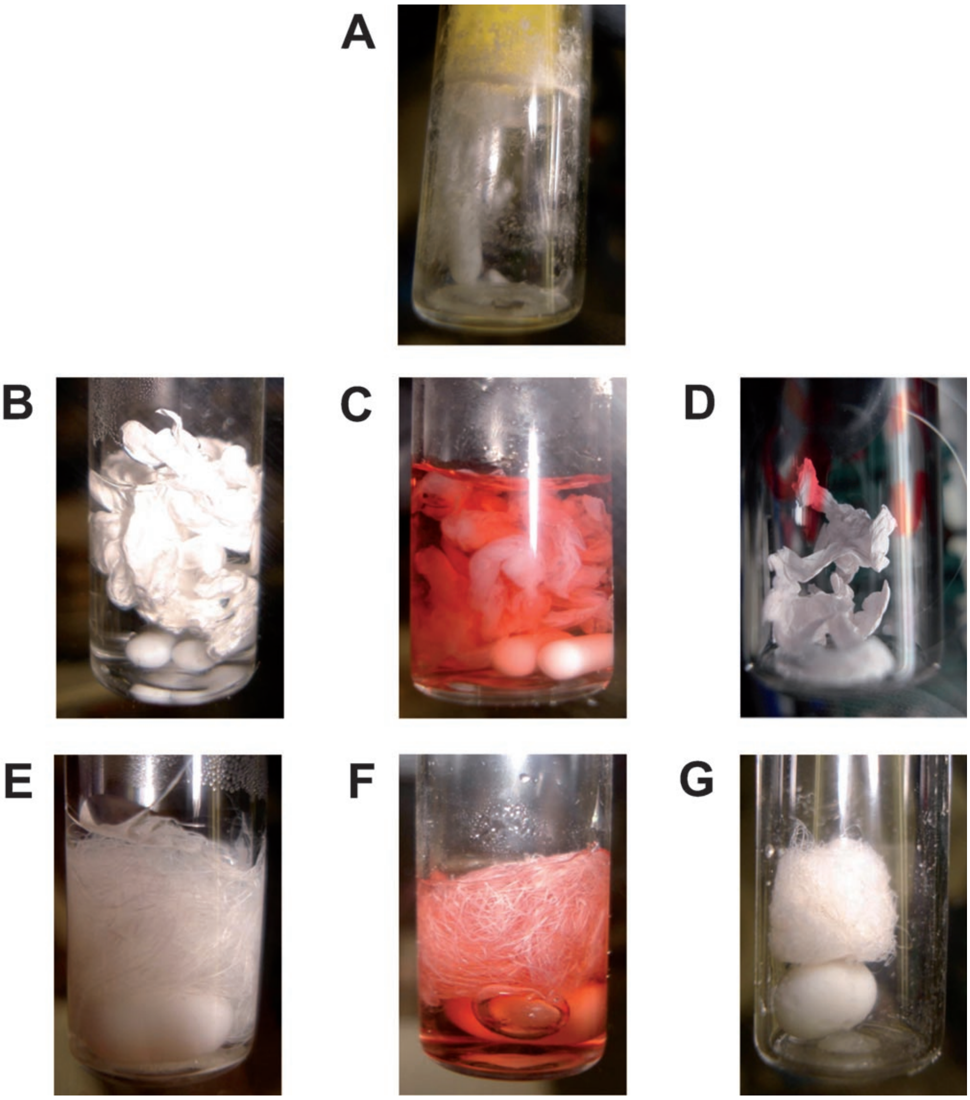


**Figure 2.** Photographs representative of the recycling sequences in Figure 1. **A** (Figure 1, A). Precipitate prior to start of cycle 2. **B** (Figure 1, B). Reaction mixture and Teflon® tape prior to the start of cycle 1. **C** (Figure 1, B). Reaction mixture after cycle 1. **D** (Figure 1, B). Catalyst coated Teflon® tape prior to adding the reaction mixture for cycle 2. **E** (Figure 1, C). Reaction mixture and Gore-Rastex® fiber prior to the start of cycle 1. **F** (Figure 1, C). Reaction mixture after cycle 1. **G** (Figure 1, C). Catalyst coated Gore-Rastex® fiber prior to adding the reaction mixture for cycle 2.

former reaction was monitored by GC *versus* an internal standard; the latter was monitored by HPLC as above. The yields of **3b** ranged from 95–96% at the end of each cycle, and those of **4b** from 79–81%. In both cases there was good retention of activity, although the shape of the plot for the final cycle with **4b** suggests 1–2 measurement artifacts.

Finally, the protocol in Figure 1, **A** was extended to the bis(thioester) *i*-PrS(CO)CH=CH(CH$_2$)$_2$CH=CH(CO)S-*i*-Pr (**5a**),[14] which is capable of a vinylogous version of the preceding transformations, the Rauhut–Currier reaction. GC analyses showed the formation of the cyclic dicarbonyl compound **5b**, with yields of 71–73% at the end of each cycle (Figure 3, *bottom*). The starting **5a** was consumed, and several by-products formed. In any event, the retention of activity was excellent. All of the cyclized products were purified by column chromatography, and characterized by NMR ($^1$H, $^{13}$C) and IR spectroscopy as summarized in the experimental section. For **3b**–**5b**, which have not been reported outside of our research group, elemental analyses are also given.

Importantly, two other groups have developed fluorous catalyst systems for *inter*molecular (aza)-Morita–Baylis–Hillman reactions.[22,23] One family (**I**) features a chiral phosphorus Lewis base. Although high *ee* values have been reported, no recycling has to our knowledge been carried out. The other (**II**) features a fluorous ytterbium Lewis acid that is used in conjunction with a stoichiometric amount of a fluorous pyri-

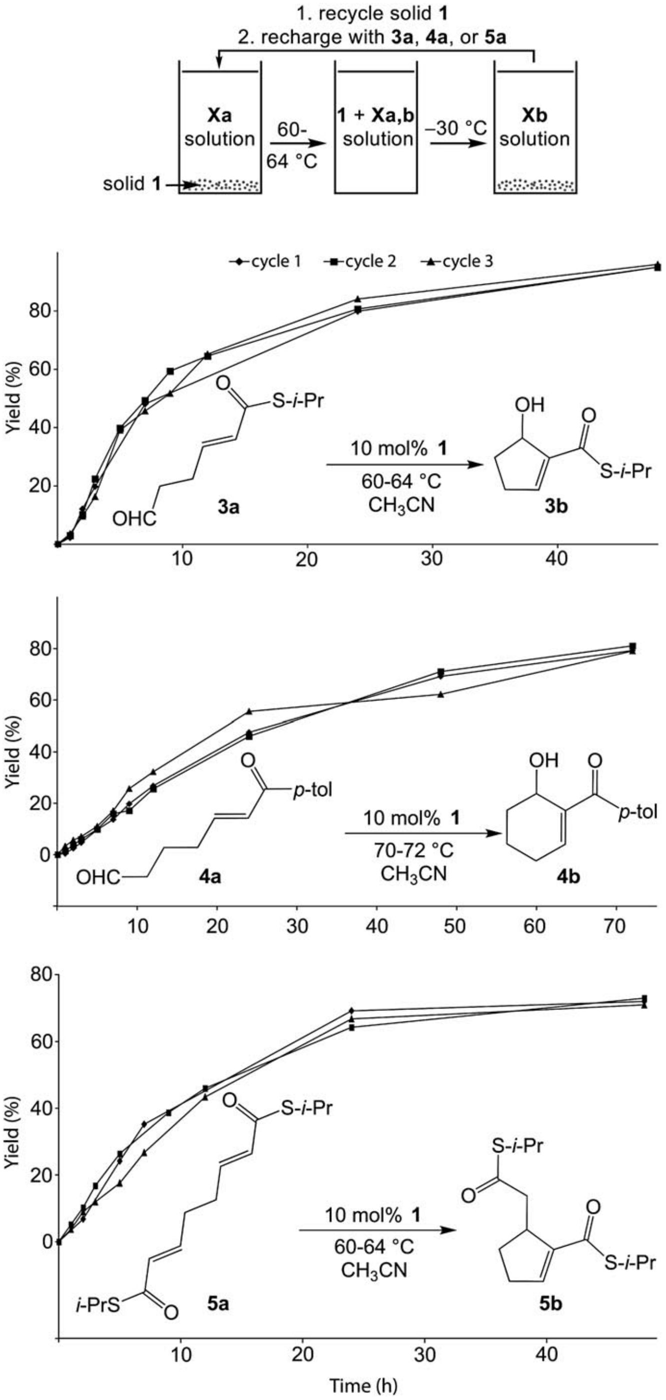
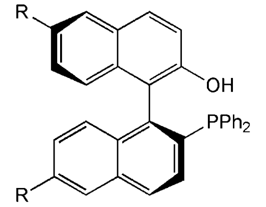
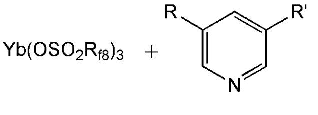


**Figure 3.** Yields of **3b**, **4b**, and **5b** as a function of cycle, with catalyst recovery *via* precipitation.



**I**

R = $CH_2CH_2R_{f6}$, $Si(CH_2CH_2R_{f6})_3$



**II**

R/R' = $COOCH_2CH_2R_{f8}$/H
R/R' = $CH(CH_2CH_2R_{f8})_2$/H
R = R' = $COOCH_2CH_2R_{f8}$

dine. This system could be recycled with particularly high efficiency.

## Conclusions

In summary, the above experiments provide additional examples of the facile and efficient recovery of thermomorphic fluorous catalysts by precipitation from organic solvents. They also significantly extend the number of catalyst systems demonstrated to be recyclable by precipitation onto Teflon® tape,[5,24] and provide the first use of Gore-Rastex® fiber for recovery. The latter fluoropolymer gives slightly better results, consistent with a greater surface area. Although recycling *via* unassisted precipitation appears to be most efficient, there is an obvious mechanical convenience in simply being able to "fish out" a catalyst and immediately apply it again. We speculate that the higher catalyst loading associated with these reactions, as opposed to the rhodium systems reported earlier (10 mol% *vs.* 0.15 mol%),[5] may "saturate" the polymer surface, leading to small losses in the washing steps. Efforts to clarify these points, as well as additional examples of all of the preceding types of protocols, will be described in forthcoming publications.[25]

## Experimental Section

### General Data

NMR spectra were recorded on Bruker 300 MHz or 400 MHz spectrometers at ambient probe temperature (27 °C) and referenced to the residual solvent signal ($^1H$: $CHCl_3$, 7.26 ppm; $^{13}C$: $CDCl_3$, 77.0 ppm). IR spectra were recorded on an ASI React IR®-1000 spectrometer. HPLC analyses were conducted with a ThermoQuest instrument package (pump/autosampler/detector P4000/AS3000/UV6000 LP; Column: Macherey–Nagel, Nucleosil 100–5). GC analyses were conducted with a ThermoQuest TRACE GC 2000 instrument with FID and an Optima-5–0.25 µm capillary column. Column chromatography was conducted using silica gel 60M (Macherey–Nagel). The Gore-Rastex® fiber (30 den) was obtained as a sample from Gore corporation (http://www.gore.com/en_xx/products/fabrics/sewing/rastex_weave_datasheet.html).

Chemicals were treated as follows: $CH_3CN$ and $CH_2Cl_2$, distilled from $CaH_2$ under $N_2$, with $CH_3CN$ for catalysis furthermore freeze-pump-thaw degassed (3×); $CF_3C_6H_5$ freeze-pump-thaw degassed (3×); ethyl acetate and pentane for column chromatography, distilled and stored over molecular sieves; isopropyl alcohol (Roth) and hexanes (Fischer) for HPLC, and $CDCl_3$ (99.8%, Deutero GmbH), used as received.

### Recycling Sequence A (Figure 1, A)

A vial was charged with $O{=}CHCH_2CH_2CH{=}CH(C{=}O)Ph$ (**2a**;[16b] 0.0188 g, 0.100 mmol), evacuated (1 h, 1×

$10^{-2}$ mbar), filled with $N_2$, and transferred into an argon glove box. The vial was further charged with $P[(CH_2)_3R_{f8}]_3$ (**1**;[11] 0.0141 g, 0.010 mmol) and $CH_3CN$ (2.00 mL) to give a 0.0500 M solution of **2a**. The mixture was heated at 60–64 °C (sand bath) with stirring. Aliquots were periodically removed (0.010 mL), diluted with $CH_3CN$ (1.50 mL) and analyzed by HPLC (98:2 v/v hexanes/isopropyl alcohol, flow = 0.5 mL $min^{-1}$, 270 nm, $SiO_2$). After 24 h, the mixture was cooled to room temperature (3 h) and then −30 °C (overnight). The supernatant was carefully separated from the precipitated **1** by syringe, taken to dryness, and dissolved in $CDCl_3$. A $^1H$ NMR spectrum was recorded. The yield of **2b** was calculated by integration of the signals at $\delta = 6.68$ and 5.30 *versus* all phenyl signals.

The precipitated **1** was washed with $CH_3CN$ (0.5 mL) and dried under oil pump vacuum. The vial was recharged with a 0.0500 M $CH_3CN$ solution of **2a** (1.92 mL) and the above procedure repeated. The volume was decreased by 0.080 mL for each cycle to compensate for the catalyst lost in the aliquots. After the final cycle, the catalyst was washed with $CH_3CN$ (0.5 mL), dried under oil pump vacuum, and dissolved in degassed $CF_3C_6H_5$. Then $^{31}P$ and $^1H$ NMR spectra were recorded (data: see text).

### Recycling Sequence B (Figure 1, B)

A vial was charged with **2a** (0.0188 g, 0.100 mmol), evacuated (1 h, $1 \times 10^{-2}$ mbar), filled with $N_2$, and transferred into an argon glove box. The vial was further charged with **1** (0.0141 g, 0.010 mmol), Teflon® tape (0.160 g, ca. 550 × 12 mm) and $CH_3CN$ (2.00 mL) to give a 0.0500 M solution of **2a**. The mixture was heated at 60–64 °C (sand bath) with stirring. Aliquots were periodically analyzed per sequence A. After 24 h, the mixture was cooled to room temperature (3 h) and then −30 °C (overnight). The supernatant was carefully separated from the coated Teflon® tape by syringe, taken to dryness, and analyzed per sequence A.

The coated Teflon® tape was washed with $CH_3CN$ (4 × 1.5 mL) and dried under oil pump vacuum. Another vial was charged with a 0.0500 M $CH_3CN$ solution of **2a** (1.92 mL) and the coated Teflon® tape. The above procedure was repeated. The volume was decreased by 0.080 mL for each cycle to compensate for the catalyst lost in the aliquots. After the final cycle, the Teflon® tape was washed with $CH_3CN$ (4 × 1.5 mL) and dried under oil pump vacuum, and the coating dissolved in degassed $CF_3C_6H_5$. Then $^{31}P$ and $^1H$ NMR spectra were recorded (data: see text).

### Recycling Sequence C (Figure 1, C)

This was conducted identically to sequence B, using Gore-Rastex® fiber (0.160 g) in place of Teflon® tape.

### Product Characterization

Cyclized products were purified by silica gel column chromatography and characterized as follows.

$HO\overline{CH(CH_2)_2CH{=}C}(C{=}O)Ph$ (**2b**)[16b] was obtained (7:3 v/v ethyl acetate/pentane) as a pale yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 7.78$–7.75 (m, *o*-Ph, 2 H), 7.59–7.54 (m, *p*-Ph, 1 H), 7.48–7.44 (m, *m*-Ph, 2 H), 6.68 (dd, CHH′C*H*=C, $^3J_{H,H} = 3.0$ Hz and 2.8 Hz, 1 H), 5.32–5.28 (m, HOC*H*, 1 H), 3.28 (br s, *H*O, 1 H), 2.80–2.71 (m, HOCHC*H*H′, 1 H), 2.56–2.48 (m, HOCHCH*H*′, 1 H), 2.40–2.31 (m, C*H*H′CH=C, 1 H), 1.97–1.89 (m, CH*H*′CH=C, 1 H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 194.9$ [s, CH=C(*C*=O)], 149.0 [s, CH=*C*(C=O)], 144.5 [s, *C*H=C(C=O)], 138.1 (s, *i*-Ph), 132.4 (s, *p*-Ph), 128.9, 128.3 (2 s, *o*-, *m*-Ph), 76.5 (s, HO*C*H), 31.7, 31.3 (2 s, 2 $CH_2$); IR (thin film): ν = 3450 (br, $\nu_{OH}$), 1633 (s, $\nu_{C=O}$), 1598 $cm^{-1}$ (s, $\nu_{C=C}$).

$HO\overline{CH(CH_2)_2CH{=}C}(C{=}O)S$-*i*-Pr (**3b**) was obtained (3:2 v/v ethyl acetate/pentane) as a colorless oil. Anal. calcd. (%) for $C_9H_{14}O_2S$ (186.1): C 58.03, H 7.58, S 17.21; found: C 57.63, H 7.71, S 16.78; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 6.89$ (dd, $^3J_{H,H} = 2.8$ Hz and 2.8 Hz, CHH′C*H*=C, 1 H), 5.16–5.13 (m, HOC*H*, 1 H), 3.74 [sept, $^3J_{H,H} = 7.2$ Hz, $CH(CH_3)_2$, 1 H], 2.78 (br s, *H*O, 1 H), 2.73–2.62 (m, HOCHC*H*H′, 1 H), 2.46–2.27 (m, CH*H*′CH=C, HOCHCH*H*′, 2 H), 1.91–1.82 (m, C*H*H′CH=C, 1 H), 1.39 [d, $CH(CH_3)_2$, $^3J_{H,H} = 7.2$ Hz, 6 H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 190.1$ [s, CH=C(*C*=O)], 145.2 [s, *C*H=C(C=O)], 144.4 [s, CH=*C*(C=O)], 75.7 (s, HO*C*H), 34.3 [s, $CH(CH_3)_2$], 31.8 (s, $HOCHCH_2$), 30.9 (s, $CH_2CH{=}C$), 23.0 [s, $CH(CH_3)_2$]; IR (thin film): ν = 3450 (br, $\nu_{OH}$), 1648 (s, $\nu_{C=O}$), 1613 $cm^{-1}$ (s, $\nu_{C=C}$).

$HO\overline{CH(CH_2)_3CH{=}C}(C{=}O)$-*p*-tol (**4b**) was obtained (4:1 v/v ethyl acetate/pentane) as a pale yellow oil. Anal. calcd. (%) for $C_{14}H_{16}O_2$ (216.1): C 77.75, H 7.46; found: C 77.18, H 7.53; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 7.58$ (d, $^3J_{H,H} = 8.2$ Hz, $C_6H_4$, *o* to C=O, 2 H), 7.24 (d, $^3J_{H,H} = 8.2$ Hz, $C_6H_4$, *m* to C=O, 2 H), 6.70 (t, $^3J_{H,H} = 3.9$ Hz, C*H*=C, 1 H), 4.72–4.69 (m, HOC*H*, 1 H), 3.55 (br s, *H*O, 1 H), 2.41 (s, $CH_3$, 3 H), 2.42–2.18, 1.97–1.82, 1.69–1.60 (3 m, 3 C*HH*′, 6 H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 199.1$ [s, CH=C(*C*=O)], 146.2 (s, $C_6H_4$, *p* to C=O), 142.7 [s, *C*H=C(C=O)], 139.9 [s, CH=*C*-(C=O)], 135.0 (s, $C_6H_4$, *i* to C=O), 129.6, 128.9 (2 s, $C_6H_4$, *o*, *m* to C=O), 64.2 (s, HO*C*H), 21.6 (s, $CH_3$), 29.7, 26.3, 17.5 (3 s, 3 $CH_2$); IR (thin film): ν = 3460 (br, $\nu_{OH}$), 1633 (s, $\nu_{C=O}$), 1606 $cm^{-1}$ (s, $\nu_{C=C}$).

*i*-$PrS(C{=}O)CH_2\overline{CH(CH_2)_2CH{=}C}(C{=}O)S$-*i*-Pr (**5b**) was obtained (1:9 v/v ethyl acetate/pentane) as a tan liquid. Anal. calcd. (%) for $C_{14}H_{22}O_2S_2$ (286.1): C 58.70, H 7.74, S 22.39; found: C 58.52, H 7.62, S 22.41; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 6.81$–6.78 [m, C*H*=C(C=O), 1 H], 3.72 [sept, $^3J_{H,H} = 7.0$ Hz, $CH(CH_3)_2$, 1 H], 3.67 [sept, $^3J_{H,H} = 7.0$ Hz, $CH(CH_3)_2'$, 1 H], 3.53–3.44 (m, C*H*CHH′CHH′, 1 H), 3.08 [dd, $^2J_{H,H} = 15.2$ Hz, $^3J_{H,H} = 3.3$ Hz, (C=O)C*H*H′, 1 H], 2.48 [dd, $^2J_{H,H} = 15.2$ Hz, $^3J_{H,H} = 10.2$ Hz, (C=O)CH*H*′, 1 H], 2.60–2.41 (m, CHCHH′C*HH*′, 2 H), 2.25–2.15, 1.84–1.76 (2 m, CHC*HH*′CHH′, 2 H), 1.32 [d, $^3J_{H,H} = 7.0$ Hz, $CH(CH_3)_2$, 6 H], 1.29 [d, $^3J_{H,H} = 7.0$ Hz, $CH(CH_3)_2'$, 6 H]; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 198.3$ [s, $(C{=}O)CH_2$], 188.8 [s, CH=C(*C*=O)], 146.7 [s, *C*H=C(C=O)], 143.1 [s, CH=*C*(C=O)], 47.8 [s, $(C{=}O)CH_2$], 42.0 (s, $CHCH_2CH_2$), 34.5, 34.3 [2 s, $CH(CH_3)_2$ and $CH(CH_3)_2'$], 31.6 (s, $CHCH_2CH_2$), 29.1 (s, $CHCH_2CH_2$), 23.15, 22.97, 22.94, 22.91 {4 s, $CH(CH_3)(CH_3)'$ and $[CH(CH_3)(CH_3)']'$}; IR (thin film): ν = 1683 (s, $\nu_{C=O}$), 1652 (s, $\nu_{C=O}$), 1613 $cm^{-1}$ (s, $\nu_{C=C}$).

### Syntheses of Educts $O{=}CH(CH_2)_nCH{=}CH(C{=}O)R$

A flask was charged with a solution of a dialdehyde (*n* = 2, succinaldehyde;[26] 3, glutaraldehyde[27]) in $CH_2Cl_2$ (40.0 mL, 0.300 M, 12.0 mmol) and cooled to 0 °C. Then the ylide $Ph_3PCH(C{=}O)R$ (5.80 mmol) dissolved in $CH_2Cl_2$ (10 mL) was added dropwise with stirring. The mixture was allowed to warm to room temperature overnight. The solvent was removed and the residue was extracted with ether (3 × 20 mL). The ether was removed, and the products were purified by silica gel column chromatography and characterized as summarized below.

The known ylides $Ph_3PCH(C{=}O)Ph$[28] and $Ph_3PCH(C{=}O)$-*p*-tol[29] were prepared by an alternative procedure.[30] The new ylide $Ph_3PCH(C{=}O)S$-*i*-Pr was synthesized analogously to the SEt homolog.[31] Additional details are provided elsewhere.[32]

$O{=}CHCH_2CH_2CH{=}CH(C{=}O)Ph$ (**2a**)[16b] was obtained (7:3 v/v ethyl acetate/pentane) as a slightly yellow liquid; yield: 0.643 g (3.42 mmol, 59%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 9.79$ (s, O=C*H*, 1 H), 7.91 (d, $^3J_{H,H} = 7.6$ Hz, *o*-Ph, 2 H), 7.54 (t, $^3J_{H,H} = 7.6$ Hz, *p*-Ph, 1 H), 7.44 (dd, $^3J_{H,H} = 7.6$ Hz and 7.6 Hz, *m*-Ph, 2 H), 7.00 (dt, $^3J_{H,H} = 14.2$ Hz and 6.3 Hz, $CH_2CH{=}CH$, 1 H), 6.90 (dt, $^3J_{H,H} = 14.2$ Hz, $^4J_{H,H} = 1.3$ Hz, $CH_2CH{=}CH$, 1 H), 2.77–2.62 (m, $O{=}CHCH_2$, $CH_2CH{=}CH$, 4 H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 200.4$ (s, O=*C*H), 190.4 [s, (*C*=O)Ph], 146.6 (s, $CH_2CH{=}CH$), 137.6 (s, *i*-Ph), 132.8 (s, *p*-Ph), 128.54, 128.51 (2 s, *o*-, *m*-Ph), 126.7 (s, $CH_2CH{=}CH$), 41.9 (s, $O{=}CHCH_2$), 24.9 (s, $CH_2CH{=}CH$); IR (thin film): $\nu = 1721$ (s, $\nu_{C=O}$), 1669 (s, $\nu_{C=O}$), 1619 cm$^{-1}$ (s, $\nu_{C=C}$).

$O{=}CHCH_2CH_2CH{=}CH(C{=}O)S$-*i*-Pr (**3a**) was obtained (1:4 v/v ethyl acetate/pentane) as a colorless oil; yield: 0.766 g (4.11 mmol, 71%). Anal. calcd. (%) for $C_9H_{14}O_2S$ (186.1): C 58.03, H 7.58, S 17.21; found: C 57.82, H 7.78, S 16.80; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 9.78$ (s, O=C*H*, 1 H), 6.82 (dt, $^3J_{H,H} = 15.5$ Hz and 6.8 Hz, $CH_2CH{=}CH$, 1 H), 6.08 (d, $^3J_{H,H} = 15.5$ Hz, $CH_2CH{=}CH$, 1 H), 3.70 (sept, $^3J(H,H) = 7.0$ Hz, $CH(CH_3)_2$, 1 H), 2.63 (t, $^3J(H,H) = 7.0$ Hz, $O{=}CHCH_2$, 2 H), 2.50 (dt, $^3J_{H,H} = 6.9$ Hz and 6.9 Hz, $CH_2CH{=}CH$, 2 H), 1.31 (d, $^3J_{H,H} = 7.0$ Hz, $CH(CH_3)_2$, 6 H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 200.6$ (s, O=*C*H), 190.2 [s, (*C*=O)S], 141.9 (s, $CH_2CH{=}CH$), 129.7 (s, $CH_2CH{=}CH$), 41.8 (s, $O{=}CHCH_2$), 34.5 [s, $CH(CH_3)_2$], 24.3 (s, $CH_2CH{=}CH$), 23.0 [s, $CH(CH_3)_2$]; IR (thin film): $\nu = 1725$ (s, $\nu_{C=O}$), 1664 (s, $\nu_{C=O}$), 1629 cm$^{-1}$ (s, $\nu_{C=C}$).

$O{=}CHCH_2CH_2CH_2CH{=}CH(C{=}O)$-*p*-tol (**4a**) was obtained (1:3 v/v ethyl acetate/pentane) as a slightly yellow liquid; yield: 0.689 g (3.19 mmol, 55%). Anal. calcd. (%) for $C_{14}H_{16}O_2$ (216.1): C 77.75, H 7.46; found: C 77.18, H 7.53; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 9.80$ (s, O=C*H*, 1 H), 7.84 (d, $^3J_{H,H} = 8.1$ Hz, $C_6H_4$, *o* to C=O, 2 H), 7.27 (d, $^3J_{H,H} = 8.1$ Hz, $C_6H_4$, *m* to C=O, 2 H), 7.00 (dt, $^3J_{H,H} = 15.5$ Hz and 6.8 Hz, $CH_2CH{=}CH$, 1 H), 6.32 (d, $^3J_{H,H} = 15.5$ Hz, $CH_2CH{=}CH$, 1 H), 2.53 (t, $^3J_{H,H} = 7.5$ Hz, $O{=}CHCH_2$, 2 H), 2.42 (s, $CH_3$, 3 H), 2.36 (dt, $^3J_{H,H} = 7.5$ Hz and 7.5 Hz, $CH_2CH{=}CH$, 2 H), 1.88 (tt, $^3J_{H,H} = 7.5$ Hz and 7.5 Hz, $O{=}CHCH_2CH_2$, 2 H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 202.0$ (s, O=*C*H), 190.4 [s, (*C*=O)(*p*-tol)], 147.7 (s, $CH_2CH{=}CH$), 143.9 (s, $C_6H_4$, *p* to C=O), 135.6 (s, $C_6H_4$, *i* to C=O), 129.7, 129.1 (2 s, $C_6H_4$, *o*, *m* to C=O), 127.0 (s, $CH_2CH{=}CH$), 43.5 (s, $O{=}CHCH_2$), 32.3 (s, $CH_2CH{=}CH$), 22.1 (s, $O{=}CHCH_2CH_2$), 20.9 (s, $CH_3$); IR (thin film): $\nu = 1722$ (s, $\nu_{C=O}$), 1668 (s, $\nu_{C=O}$), 1621 cm$^{-1}$ (s, $\nu_{C=C}$).

### *i*-PrS(C=O)CH=CHCH$_2$CH$_2$CH=CH(C=O)S-*i*-Pr (5a)

A round-bottom flask was charged with a solution of succinaldehyde[26] in $CH_2Cl_2$ (17.0 mL, 0.300 M, 5.20 mmol). Then $Ph_3PCH(C{=}O)S$-*i*-Pr (4.16 g, 11.0 mmol) dissolved in $CH_2Cl_2$ (5 mL) was added with stirring. After 1 d, the solvent was removed by rotary evaporation. The residue was chromatographed (silica gel column, 1:9 v/v ethyl acetate/pentane) to give **5a** as a colorless solid that can be recrystallized from hexanes at −20 °C; yield: 1.19 g (4.16 mmol, 80%). Anal. calcd. (%) for $C_{14}H_{22}O_2S_2$ (286.1): C 58.70, H 7.74, S 22.39; found: C 58.35, H 7.55, S 22.25; $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 6.81$ (dt, $^3J_{H,H} = 15.4$ and 6.10 Hz, $CH_2CH{=}CH$, 2 H), 6.07 (d, $^3J_{H,H} = 15.4$ Hz, $CH_2CH{=}CH$, 2 H), 3.69 [sept, $^3J_{H,H} = 7.0$ Hz, $CH(CH_3)_2$, 2 H], 2.33 (d, $^3J_{H,H} = 5.6$ Hz, $CH_2CH{=}CH$, 4 H), 1.31 [d, $^3J_{H,H} = 7.0$ Hz, $CH(CH_3)_2$, 12 H]; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 189.8$ (s, *C*=O), 142.3 (s, $CH_2CH{=}CH$), 129.6 (s, $CH_2CH{=}CH$), 34.5 [s, $CH(CH_3)_2$], 30.3 (s, $CH_2CH{=}CH$), 23.0 [s, $CH(CH_3)_2$]; IR (powder film): $\nu = 1683$ (s, $\nu_{C=O}$), 1652 cm$^{-1}$ (s, $\nu_{C=C}$).

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