Solvent-Free Synthesis of 2-Pyrones from Alkynes and Carbon Dioxide Catalyzed by Ni(1,5-cyclooctadiene)$_2$/Trialkylphosphine Catalysts

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Abstract: Solvent-free, efficient, and mild 2-pyrone synthesis by the cycloaddition of alkynes with CO_2 has been achieved under compressed CO_2 with a Ni(cod)$_2$/P(C_4H_9)$_3$ or Ni(cod)$_2$/P(C_8H_{17})$_3$ catalyst; both high yields (up to 98%) and selectivities (up to 99%) are attained. One attractive aspect of these catalysts is their high efficiency at low CO_2 pressures (4 MPa). The applicability of this reaction to a broad range of alkyne substrates and the ease of handling the phosphine ligands are additional merits of the present new catalytic systems in comparison to the previously reported Ni(cod)$_2$/P(CH_3)$_3$ catalyst in supercritical CO_2.

Key words: 2-pyrone derivatives, alkynes, carbon dioxide, Ni(0) complex, solvent-free

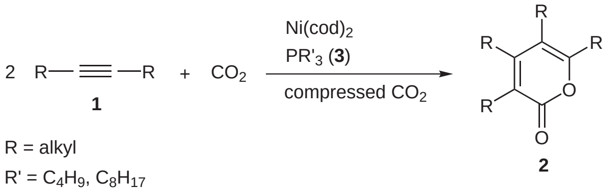
The cycloaddition of alkynes **1** with CO_2 to afford 2-pyrones **2**[1] has drawn much attention from the viewpoints of the utility of 2-pyrone derivatives[2–4] and the chemical fixation of CO_2. Typically a combination of Ni(cod)$_2$ (cod = 1,5-cyclooctadiene) and various phosphines PR'_3 (**3**) are used as catalysts. Two procedures have been reported to be useful for producing 2-pyrones in high yields by catalysis: the first involves a reaction in finely-tuned organic solvents and the second is a reaction in supercritical CO_2 ($scCO_2$) without organic solvents.

Concerning the former approach, Walther et al. reported that the Ni(cod)$_2$/P(C_2H_5)$_3$ catalyst effects the cycloaddition of 3-hexyne (**1a**) with CO_2 to give tetraethyl-2-pyrone (**2a**) quantitatively in THF–acetonitrile.[1b] The presence of acetonitrile is indispensable and plays a critical role in the efficient formation of **2a**. Another characteristic result is the effect of the phosphine ligand: the sterically small trialkylphosphine ligand, P(C_2H_5)$_3$, was effective, but the sterically bulky P(*c*-C_6H_{11})$_3$ was much less effective.

The second approach involves the use of $scCO_2$ both as a solvent and as a substrate. This approach has two significant advantages. The first concerns the role of $scCO_2$ as a suitable 'environmentally benign' alternative for a variety of solvents[5,6] because there is a need to reduce or eliminate toxic chemical wastes and by-products that arise in the course of chemical synthesis and manufacture.[7] The second is related to the role of $scCO_2$ as a substrate, which may improve the reaction rate and the product selectivity.

To the best of our knowledge, only two studies on the Ni(cod)$_2$/phosphine-catalyzed cycloaddition of **1** with CO_2 in $scCO_2$ have been reported and both indicate a remarkable phosphine ligand effect together with a very limited scope of applicable alkyne substrates. Reetz et al. reported that **2a** is formed in 35% yield and ca. 90% selectivity by Ni(cod)$_2$/(C_6H_5)$_2$P(CH_2)$_4$P(C_6H_5)$_2$ catalysis in $scCO_2$.[8,9] Walther et al. used trialkylphosphine ligands instead of (C_6H_5)$_2$P(CH_2)$_4$P(C_6H_5)$_2$ and reported the formation of **2a** in yields of 99% [P(CH_3)$_3$], 53% [P(C_2H_5)$_3$], and 3% [P(C_3H_7)$_3$].[10] The ligand P(CH_3)$_3$ was highly effective for the reaction of **1a**, but was ineffective for the reaction of 2-butyne (4% yield). The result of the reaction of 4-octyne (**1b**) with the Ni(cod)$_2$/P(C_2H_5)$_3$ catalyst was also unsatisfactory (8% yield).

We have studied further the effect of phosphine ligand **3** on the Ni(0)-catalyzed cycloaddition of alkynes **1** with CO_2 to produce 2-pyrones **2** under compressed CO_2 without organic solvents along with improving the substrate scope of the reaction. This communication reports that a catalyst generated from Ni(cod)$_2$ and P(C_4H_9)$_3$ (**3a**) or P(C_8H_{17})$_3$ (**3b**) bearing a long primary alkyl chain, i.e., a Ni(cod)$_2$/P(C_4H_9)$_3$ or Ni(cod)$_2$/P(C_8H_{17})$_3$ catalyst, effects the solvent-free and efficient synthesis of **2** by the cycloaddition of **1** with CO_2 under compressed CO_2. This solvent-free 2-pyrone synthesis is also characterized by being widely applicable to a range of alkyne substrates (Scheme 1).



Scheme 1

The effect of phosphine ligands on the Ni(0)-catalyzed cycloaddition of 3-hexyne (**1a**) with CO_2 is listed in Table 1. A catalyst generated from Ni(cod)$_2$ (10 mol% with respect to **1a**) and P(C_8H_{17})$_3$ (**3b**) (20 mol% with respect to **1a**)

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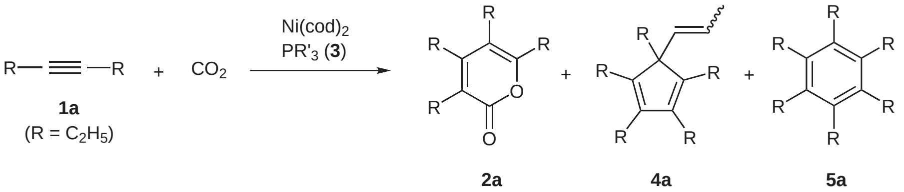
Table 1 The Ni(0)-Catalyzed Cycloaddition of 3-Hexyne (**1a**) with CO_2 under Compressed CO_2[a]



Entry	PR′$_3$ (**3**)	Medium	CO_2 Pressure (MPa)	Conversion (%)[b]	Yield (%)[b]		
					2a	**4a**	**5a**
1	$P(C_4H_9)_3$ (**3a**)	CO_2	15	99	97	<1	<1
2	$P(c\text{-}C_6H_{11})_3$	CO_2	15	61	10	49	<1
3	$P(C_8H_{17})_3$ (**3b**)	THF–CH_3CN[c]	5[d]	100	99	1	<1
4	**3b**	CO_2	15	100	95 (91)	1	<1
5	$P(CH_3)_2(C_6H_5)$	CO_2	20	72	48	13	<1

[a] Conditions: **1a** (2 mmol), $Ni(cod)_2$ (0.2 mmol), **3** (0.4 mmol), 120 °C, 20 h.
[b] Determined by GC analysis on the basis of the alkyne **1**.[13] Isolated yield is shown in parentheses.
[c] THF (5 mL), CH_3CN (5 mL).
[d] CO_2 pressure at 20 °C.

gave tetraethyl-2-pyrone (**2a**) in 99% yield in THF–acetonitrile (1:1) at 120 °C under CO_2 pressure (5 MPa at 20 °C) (Table 1, entry 3). As by-products, the cyclopentadiene-type trimers **4a** were produced in 1% yield and the benzene-type trimer **5a** was barely detected by GC; this result is consistent with a previous report.[1b] Quite interestingly, when this reaction was carried out under compressed CO_2 (15 MPa) in the absence of both THF and acetonitrile, **2a** was obtained nearly quantitatively (95% yield; Table 1, entry 4).[11,12] The alkyne trimers **4a** were formed in very small amounts (1%), and the benzene derivative **5a** was detected only in trace amounts. A reaction employing $P(C_4H_9)_3$ (**3a**) as the ligand also gave **2a** in 97% yield (Table 1, entry 1). In contrast, the use of the $P(CH_3)_2(C_6H_5)$ as the ligand[1b] resulted in both lower yield and selectivity (Table 1, entry 5). The sterically bulky $P(c\text{-}C_6H_{11})_3$ gave **4a** as the main product (49%; Table 1, entry 2). These results show that the trialkylphosphine ligands bearing a long primary alkyl chain such as **3a** and **3b** are effective ligands for the solvent-free Ni(0)-catalyzed cycloaddition of **1a** with CO_2 under compressed CO_2. This ligand effect is new and noteworthy because Walther et al. reported a different ligand effect in $scCO_2$,[10] where the order of decreasing ligand efficiency was $P(CH_3)_3 > P(C_2H_5)_3 > P(C_3H_7)_3$.

Table 2 shows the effect of reaction conditions on the $Ni(cod)_2$/**3a**- and $Ni(cod)_2$/**3b**-catalyzed cycloaddition of **1a** with CO_2 under compressed CO_2. The effect of the CO_2 pressure on the reaction employing ligand **3b** at 120 °C is shown (Table 2, entries 1–6). CO_2 pressures of 4–15 MPa had no significant effect on the yield of **2a** and the selectivity.[13] In all cases, **1a** was completely consumed, and **2a** was obtained in quantitative yield. In particular, it is of great interest that the reaction at 4 MPa gave **2a** in excellent yield (Table 2, entry 2). The reaction at 2 MPa resulted in a slightly lower but satisfactory selectivity (ca. 90%) (Table 2, entry 1). At temperatures as low as 80 °C and 100 °C, the same reaction afforded **2a** in high yields irrespective of the CO_2 pressure (4 and 12 MPa) (Table 2, entries 7–10), where ≥95% selectivity for **2a** was maintained. A reduction in catalyst loading to 5 mol% resulted in a lower reaction rate, but **2a** was obtained in good yield (Table 2, entry 11). The necessity of relatively high catalyst loading to ensure the quantitative formation of **2a**, may be partly correlated with the formation of inactive nickel carbonyl phosphine complexes, as Walther et al. demonstrated for the $Ni(cod)_2/P(C_2H_5)_3$ catalyst under $scCO_2$ conditions.[10] The $Ni(cod)_2$/**3a** catalyst also gave **2a** in high yields over a wide range of CO_2 pressures (Table 2, entries 12 and 13). Noteworthy was the high selectivity (ca. 95%) for **2a** at a CO_2 pressure of 4 MPa, which was similar to **3b**.

Thus, the findings herein demonstrate that the use of **3a** and **3b** as ligands for $Ni(cod)_2$ enables the solvent-free and highly efficient cycloaddition of **1a** with CO_2 under mild reaction conditions. A CO_2 pressure of 4 MPa is sufficient for achieving ≥95% selectivity for **2a**. An additional advantage of the new catalytic systems is the ease of handling **3a** and **3b** in comparison to the reported $P(CH_3)_3$ and $P(C_2H_5)_3$ ligands,[10] since the latter two smell horrible and have pyrophoricity and/or a poorer stability toward oxygen.[14,15]

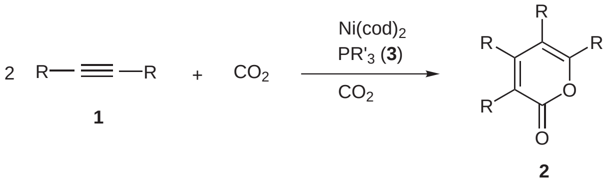
Table 2 The Effect of Reaction Conditions on the Ni(0)-Catalyzed Cycloaddition of 3-Hexyne (**1a**) with CO_2 under Compressed CO_2[a]

Entry	PR′$_3$ (**3**)	Ni(cod)$_2$ (mol%)	Temp (°C)	CO_2 Pressure (MPa)	Time (h)	Conversion (%)[b]	Yield (%)[b] **2a**	**4a**	**5a**
1	**3b**	10	120	2	5	96	76	13	<1
2	**3b**	10	120	4	5	99	90	4	<1
3	**3b**	10	120	7	5	100	93	4	<1
4	**3b**	10	120	9	5	99	95	1	<1
5	**3b**	10	120	11	5	99	97	1	<1
6	**3b**	10	120	15	5	98	92	4	<1
7	**3b**	10	100	4	5	94	86	5	<1
8	**3b**	10	100	12	5	99	98	<1	<1
9	**3b**	10	80	4	5	95	85	6	<1
10	**3b**	10	80	12	5	90	88	<1	<1
11	**3b**	5	100	15	20	72	70	1	<1
12	**3a**	10	120	4	5	97	91	5	<1
13	**3a**	10	120	12	5	99	97	<1	<1

[a] Conditions: **1a** (2 mmol), **3**/Ni(cod)$_2$, 2:1.

[b] Determined by GC analysis on the basis of the alkyne **1**.[13]

Table 3 The Effect of Alkynes on Ni(0)-Catalyzed 2-Pyrone Formation under Compressed CO_2[a]



Entry	R in **1**	PR′$_3$ (**3**)	CO_2 Pressure (MPa)	Conversion (%)[b]	2-Pyrone **2** Yield (%)[b]	Selectivity (%)[b,c]
1	C_3H_7 (**1b**)	**3b**	4	99	91	91
2		**3b**	12	99	98 (96)	>99
3[d]		**3b**	12	76	76	>99
4		**3a**	4	96	66	69
5		**3a**	12	99	95	96
6	C_4H_9 (**1c**)	**3b**	12	61	52	88
7	CH_2OCH_3 (**1e**)	**3b**	18	86	78 (44)	94[e]
8	CH_2OCOCH_3 (**1f**)	**3b**	17	0		
9	$Si(CH_3)_3$ (**1g**)	**3b**	12	17	0	

[a] Conditions: **1** (2 mmol), Ni(cod)$_2$ (0.2 mmol), **3** (0.4 mmol), 120 °C, 5 h.

[b] Determined by GC analysis on the basis of the alkyne **1**.[13] Isolated yields are shown in parentheses.

[c] The selectivity for **2**.[13]

[d] At 100 °C.

[e] Hexa(methoxymethyl)benzene (**5e**) was isolated as the sole by-product (7%).

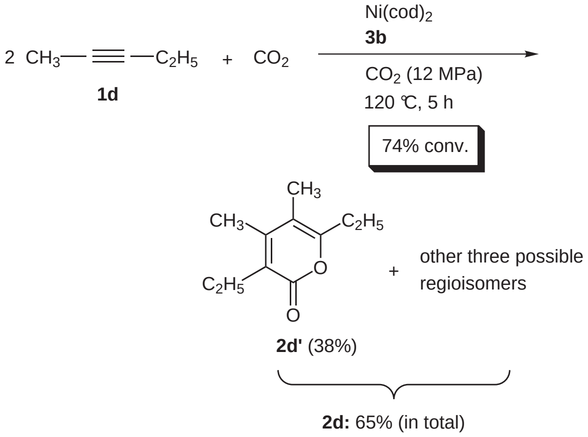
Visual inspection of the reaction mixtures using Ni(cod)$_2$/**3a** or Ni(cod)$_2$/**3b** catalyst (**3**/Ni(cod)$_2$, 2:1) revealed that the reaction does not proceed homogeneously and a dark brown liquid phase is present under the compressed CO_2 phase (2–15 MPa) throughout the reaction. Its volume was approximately equal to the volume sum of the combined Ni(cod)$_2$, **3**, and **2**. In a separate experiment, the solubility of the reaction components and 2-pyrone products in scCO_2 was examined. The alkyne substrates were miscible with scCO_2 while **3b** and the 2-pyrones obtained were not completely soluble in scCO_2; Ni(cod)$_2$ and Ni(cod)$_2$/**3b** were insoluble in scCO_2. These results indicate that the dark brown liquid phase possibly contains an active Ni(0) catalytic species. The efficient 2-pyrone formation at a low CO_2 pressure of 4 MPa where CO_2 exists in the gaseous phase also suggests participation of the above-mentioned liquid phase in the 2-pyrone formation.

As is described in the introductory section, the substrate scope of the 2-pyrone formation by the previously reported Ni(cod)$_2$/P(CH$_3$)$_3$ and Ni(cod)$_2$/P(C$_2$H$_5$)$_3$ catalysts in scCO_2[10] was very limited: the yields of 2-pyrones from 4-octyne (**1b**) and 2-butyne, having a sterically small methyl substituent, were 8% [Ni(cod)$_2$/P(C$_2$H$_5$)$_3$ catalyst] and 4% [Ni(cod)$_2$/P(CH$_3$)$_3$ catalyst], respectively. Therefore, the substrate scope of the solvent-free 2-pyrone formation with Ni(cod)$_2$/**3a** and Ni(cod)$_2$/**3b** catalysts was examined (Table 3).

The reaction of **1b** with CO_2 (12 MPa) in the presence of Ni(cod)$_2$/**3b** (120 °C, 5 h) gave the corresponding 2-pyrone **2b** in 98% yield and >99% selectivity (Table 3, entry 2). The formation of **2b** was confirmed by GC-MS and ^{1}H NMR spectroscopic analyses.[1a] The same reaction at 4 MPa produced **2b** in excellent yield with a slight decrease in selectivity (Table 3, entry 1). Lowering the reaction temperature to 100 °C reduced the yield of **2b**, but the high selectivity was maintained (Table 3, entry 3). On the other hand, the Ni(cod)$_2$/**3a**-catalyzed reaction of **1b** at 120 °C was found to be sensitive to CO_2 pressure. The reaction at 12 MPa proceeded cleanly with 96% selectivity (**2b**), whereas a remarkably decreased selectivity (69%) was observed at 4 MPa (Table 3, entries 4 and 5). 5-Decyne (**1c**) reacted with CO_2 (12 MPa) more slowly than **1a** or **1b**, and gave the corresponding 2-pyrone **2c**[16] with 88% selectivity (Table 3, entry 6).

The Ni(cod)$_2$/**3b** catalyst afforded 2-pyrone **2d** from 2-pentyne (**1d**) having a sterically small methyl substituent with reasonable yield (65%) and satisfactory selectivity (93%) (Scheme 2). 2-Pyrone **2d** obtained consists of four possible regioisomers, among which 3,6-diethyl-4,5-dimethyl-2-pyrone (**2d′**) was found to be the main product (38% yield) following careful isolation by column chromatography and by spectral characterization.[17]

The tolerance of the Ni(cod)$_2$/**3b** catalyst to functionality on the alkynes was briefly examined. The reaction of 1,4-dimethoxy-2-butyne (**1e**) with CO_2 (18 MPa) gave **2e** in 78% yield and 94% selectivity (Table 3, entry 7),[18] indicating that the catalyst tolerates the methoxy functionality. Hexa(methoxymethyl)benzene (**5e**) was obtained as the sole by-product (7%),[19] and cyclopentadiene-type alkyne trimers (**4e**) were not observed. However, 1,4-diacetoxy-2-butyne (**1f**) and bis(trimethylsilyl)acetylene (**1g**) were essentially unreactive under the reaction conditions employed, and these alkynes were recovered from the reaction mixtures (Table 3, entries 8 and 9). The low reactivity of **1f** and **1g** may be due to their electronic nature and the steric bulk of the functional groups, respectively.

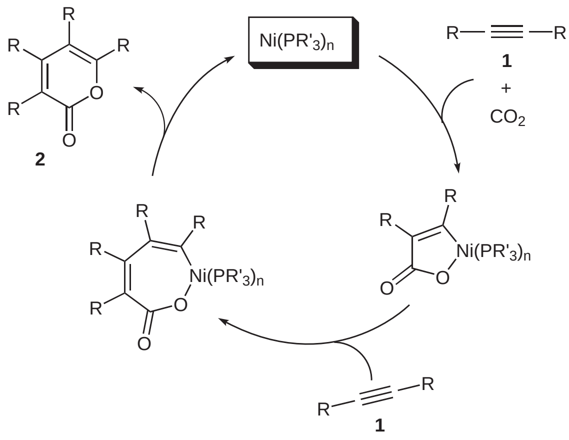


Scheme 2

Thus, the combined results of **1a**, **1b**, **1c**, **1d**, and **1e** revealed that the solvent-free 2-pyrone synthesis with Ni(cod)$_2$/**3b** catalyst under compressed CO_2 can be applied to a broader scope of substrates compared with previously reported Ni(cod)$_2$/P(CH$_3$)$_3$ and P(C$_2$H$_5$)$_3$ catalysts in scCO_2.[10]

The reaction path is reasonably assumed to involve an initial [2 + 2] cycloaddition of the first alkyne molecule with CO_2 (Scheme 3).[10,20] Subsequent insertion of the second alkyne molecule followed by reductive elimination would then release the 2-pyrone product **2** and regenerate the actual catalytic species. Nickel(0) complexes having an electron-rich metal center may promote the coordination of alkynes,[10] the reductive elimination[1d] and, hence, the formation of **2**. The effectiveness of phosphines **3a** and **3b** as ligands, especially at low CO_2 pressure, may be partly attributed to their high electron-donating ability.[21,22]

In summary, solvent-free, efficient, and mild 2-pyrone synthesis by the cycloaddition of alkynes with CO_2 has been achieved under compressed CO_2 with a Ni(cod)$_2$/P(C$_4$H$_9$)$_3$ or Ni(cod)$_2$/P(C$_8$H$_{17}$)$_3$ catalyst; both high yields (up to 98%) and selectivities (up to 99%) are attained. One attractive aspect of these catalysts is their high efficiency at low CO_2 pressures (4 MPa). The applicability of this reaction to a broad range of alkyne substrates and the ease of handling the phosphine ligands are additional merits of the present new catalytic systems in comparison to the previously reported Ni(cod)$_2$/P(CH$_3$)$_3$ catalyst in scCO_2. Expanding the substrate scope and enhancing the performance of the catalyst are currently underway in our laboratory.



Scheme 3

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(9) It has been suggested that this reaction might occur as a multiphase reaction (i.e. between CO$_2$ and catalyst both dissolved in liquid 3-hexyne) and not in scCO$_2$: Dinjus, E. *COST/Dechema Workshop*; Lahnstein Germany, April **1995**.

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(11) **Typical procedure for the Ni(0)-catalyzed cycloaddition of alkynes with CO$_2$:** All manipulations were carried out under a nitrogen or argon atmosphere. Alkyne **1a** (2 mmol), phosphine **3b** (0.4 mmol), and *o*-xylene (40 μL, internal standard for GC analysis) were mixed in a Schlenk tube. Ni(cod)$_2$ (0.2 mmol) was placed in a stainless steel autoclave containing a magnetic stirring bar, and, to this, was added the above mixture via a dry syringe. CO$_2$ (ca. 5 MPa) was quickly introduced, and the autoclave was immersed in an oil bath at 120 °C. When the temperature of the reactor reached the desired temperature (typically after about 10 min), more CO$_2$ was added to achieve the desired pressure of 15 MPa. The time of the second addition of CO$_2$ was considered to be the start of the reaction. The mixture was allowed to stir for 20 h. Then, the vessel was removed from the oil bath, immersed in an ice bath for ca. 1 h, and allowed to cool to ca. 0 °C. Excess CO$_2$ was then slowly vented at ca. 0 °C. The remaining organic liquid was diluted with acetone. The GC analysis of the solution indicated the conversion of **1a** and the yield of **2a** were 100% and 95%, respectively. Acetone was removed by evaporation, and the residue was chromatographed on silica gel (hexanes–EtOAc, 15:1) to give analytically pure **2a** in 91% isolated yield. The product was identified by ^{1}H NMR and GC-MS analyses. The ^{1}H NMR spectrum was identical to the spectral data reported in ref. 1a.

(12) **CAUTION:** Certain alkynes turn immediately brown when they are mixed with trialkylphosphines and the use of such alkynes does not give desired results. The reason for this is unclear at this time, but we recommend the use of the alkynes that cause no color change.

(13) The product yield was determined by GC analysis on the basis of the alkyne **1** employed. Thus, the yield (%) of 2-pyrone **2** = 100 × [(mmol of alkyne component in **2**) / (mmol of **1**)] = 100 × [(2 × mmol of **2**) / (mmol of **1**)]; and the yield (%) of alkyne trimer **4** or **5** = 100 × [(mmol of alkyne component in **4** or **5**) / (mmol of **1**)] = 100 × [(3 × mmol of **4** or **5**) / (mmol of **1**)].
The selectivity for **2** is defined as the mol% of **2** in all of the reaction products and is calculated from the yields of **2**, **4**, and **5** by using the above equations. Thus, the selectivity (%) for **2** = 100 × [(mmol of **2**) / (mmol of **2** + mmol of **4** + mmol of **5**)] = 100 × [(% yield of **2**) / 2] / {[(% yield of **2**) / 2] + [(% yield of **4**) / 3] + [(% yield of **5**) / 3]}.

(14) For safety data for P(CH$_3$)$_3$, see: (a) *Sigma-Aldrich Library of Chemical Safety Data*, Vol. 2; Lenga, R. E., Ed.; Sigma-Aldrich Corp.: Milwaukee, **1995**, 3435C. (b) *Sigma-Aldrich Library of Regulatory & Safety Data*, Vol. 1; Lenga, R. E.; Votoupal, K. L., Eds.; Sigma-Aldrich Corp.: Milwaukee, **1993**, 1087E.

(15) For safety data for P(C$_2$H$_5$)$_3$, see: *Sigma-Aldrich Library of Regulatory & Safety Data*, Vol. 1; Lenga, R. E.; Votoupal, K. L., Eds.; Sigma-Aldrich Corp.: Milwaukee, **1993**, 1087C.

(16) Selected data for compound **2c**: ^{1}H NMR (CDCl$_3$, 270 MHz): δ = 2.36–2.49 (m, 6 H, CH$_2$), 2.24–2.29 (t, *J* = 7.3 Hz, 2 H, CH$_2$), 1.59–1.70 (m, 2 H, CH$_2$), 1.30–1.45 (m, 14 H, CH$_2$), 0.91–1.00 (m, 12 H, CH$_3$). ^{13}C NMR (CDCl$_3$, 67.5 MHz): δ = 163.7 (C=O), 158.1 (C$_{vinyl}$), 154.5 (C$_{vinyl}$), 123.2 (C$_{vinyl}$), 115.4 (C$_{vinyl}$), 33.4 (CH$_2$), 32.1 (CH$_2$), 31.2 (CH$_2$), 30.7 (CH$_2$), 30.1 (CH$_2$), 29.3 (CH$_2$), 27.1 (CH$_2$), 26.6 (CH$_2$), 23.3 (CH$_2$), 23.1 (CH$_2$), 23.0 (CH$_2$), 22.6 (CH$_2$), 14.1 (CH$_3$), 13.93 (CH$_3$), 13.90 (CH$_3$), 13.8 (CH$_3$). HRMS (EI): *m*/*z* calcd for C$_{21}$H$_{36}$O$_2$: 320.2715. Found: 320.2729.

(17) Through careful column chromatography on silica gel (hexanes–EtOAc, 30:1), analytically pure **2d′** could be isolated from the reaction mixture as a colorless oil (15 mg, 8%). ^{1}H NMR (CDCl$_3$, 270 MHz): δ = 2.54 (t, *J* = 7.6 Hz, 2 H, CH$_2$), 2.53 (t, *J* = 7.6 Hz, 2 H, CH$_2$), 2.09 (s, 3 H, CH$_3$), 1.94 (s, 3 H, CH$_3$), 1.19 (t, *J* = 7.6 Hz, 3 H, CH$_3$), 1.07 (t, *J* = 7.6 Hz, 3 H, CH$_3$). ^{13}C NMR (CDCl$_3$, 67.5 MHz): δ = 163.4 (C=O), 157.9 (C$_{vinyl}$), 150.8 (C$_{vinyl}$), 124.4 (C$_{vinyl}$), 110.8 (C$_{vinyl}$), 24.6 (CH$_2$), 20.5 (CH$_2$), 16.3 (CH$_3$), 13.0

(CH_3), 12.8 (CH_3), 12.1 (CH_3). ^{1}H NMR: NOE enhancement (2.8%) between the methyl protons at 1.94 ppm and the methyl protons at 2.09 ppm was observed. HRMS (EI): *m*/*z* calcd for $C_{11}H_{16}O_2$: 180.1146. Found: 180.1144.

(18) Selected data for compound **2e**: ^{1}H NMR ($CDCl_3$, 270 MHz): $\delta = 4.47$ (s, 2 H, CH_2O), 4.45 (s, 2 H, CH_2O), 4.37 (s, 2 H, CH_2O), 4.33 (s, 2 H, CH_2O), 3.42 (s, 3 H, CH_3O), 3.41 (s, 3 H, CH_3O), 3.40 (s, 3 H, CH_3O), 3.37 (s, 3 H, CH_3O). ^{13}C NMR ($CDCl_3$, 67.5 MHz): $\delta = 162.1$ (C=O), 158.6 (C_{vinyl}), 152.1 (C_{vinyl}), 123.7 (C_{vinyl}), 115.4 (C_{vinyl}), 68.6 (CH_2O), 67.0 (CH_2O), 65.6 (CH_2O), 65.1 (CH_2O). HRMS (EI): *m*/*z* calcd for $C_{13}H_{20}O_6$: 272.1260. Found: 272.1257.

(19) Selected data for compound **5e**: ^{1}H NMR ($CDCl_3$, 270 MHz): $\delta = 4.60$ (s, 12 H, CH_2O), 3.41 (s, 18 H, CH_3O). MS (EI): *m*/*z* (%) = 310 (38) [$M^+ - 32$], 295 (100), 265 (42), 233 (30), 203 (23).

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