General and Selective Olefination of Aldehydes and Ketones Catalyzed by a Cobalt(II) Porphyrin Complex

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The Co(II) porphyrin complex Co(TPP) is an efficient and versatile catalyst for selective olefination of carbonyl compounds, including aldehydes and activated and unactivated ketones, with ethyl diazoacetate (EDA) in the presence of triphenylphosphine. The catalytic reactions of aldehydes and activated ketones can be carried out in a one-pot fashion with the use of a stoichiometric amount of diazo reagents, affording olefins in high yields and high *E* selectivity. In the case of unactivated ketones, a substoichiometric amount of benzoic acid is required to promote the catalytic reactions.

Introduction

The classic approach for constructing carbon−carbon double bonds in organic synthesis involves the use of the Wittig reaction and its many variants.[1] Despite their wide successes in numerous applications, several aspects of Wittig reactions warrant further improvements. In particular, Wittig reactions usually require stepwise formation of phosphorane precursors under basic conditions. To this end, there has been growing research interest in developing new methodologies that can directly use easily accessible diazo compounds[2] for in situ generation of the phosphorane under neutral conditions. Several transition-metal complexes, including Mo, Re, Ru, Rh, and Fe, have been demonstrated to be effective catalysts for selective olefination of aldehydes with suitable diazo compounds in the presence of tertiary phosphines.[3] More importantly, this transition-metal-based catalytic approach also provides a possibility to develop efficient asymmetric olefination processes.[4]

Recently, we have developed practical catalytic systems, based on Fe(TPP)Cl and Ru(TPP)(CO), for highly selective olefination of a wide variety of aldehydes with ethyl diazoacetate (EDA) in the presence of triphenylphosphine under mild conditions.[5] Applying the Fe(III) and Ru(II) porphyrin complex based methodologies to trifluoromethyl ketones, we reported the stereoselective synthesis of β-trifluoromethyl α,β-unsaturated esters from EDA and *tert*-butyl diazoacetate (*t*-BDA).[6] With substoichiometric amounts of benzoic acid as a promoter, we also demonstrated for the first time that unactivated ketones could also be olefinated with diazo compounds to afford the corresponding olefins.[7] In our continuing quest for a more general and practical catalytic system for the olefination process, we discovered that the cost-effective Co(II) porphyrin complex Co(TPP) (Figure 1) is an efficient and versatile catalyst for selective olefination of a variety of carbonyl compounds, including aldehydes and activated and unactivated ketones, with diazo compounds (Scheme 1). Herein, we report these results along with the observed differences between Co(TPP) and Fe(TPP)Cl systems. To the best of our knowledge, this represents the first

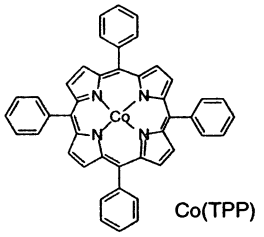
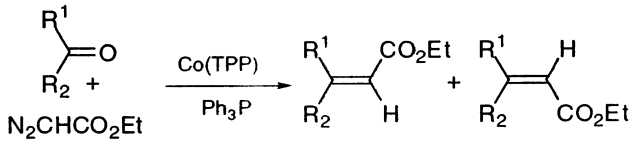


Figure 1. Structure of Co(TPP).

Scheme 1. Olefination of Carbonyl Compounds by Co(TPP)



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(1) (a) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863. (b) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263. (c) Cristau, H.-J. *Chem. Rev.* **1994**, *94*, 1299.

(2) (a) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091. (b) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*; Wiley: New York, 1998. (c) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911.

(3) (a) Aggarwal, V. K.; Fulton, J. R.; Sheldon, C. G.; de Vicente, J. *J. Am. Chem. Soc.* **2003**, *125*, 6034. (b) Santos, A. M.; Romão, C. C.; Kühn, F. E. *J. Am. Chem. Soc.* **2003**, *125*, 2414. (c) Zhang, X.; Chen, P. *Chem. Eur. J.* **2003**, *9*, 1852. (d) Cheng, G.; Mirafzal, G. A.; Woo, L. K. *Organometallics* **2003**, *22*, 1468. (e) Mirafzal, G. A.; Cheng, G.; Woo, L. K. *J. Am. Chem. Soc.* **2002**, *124*, 176. (f) Grasa, G. A.; Moore, Z.; Martin, K. L.; Stevens, E. D.; Nolan, S. P.; Paquet, V.; Lebel, H. *J. Organomet. Chem.* **2002**, *658*, 126. (g) Lebel, H.; Paquet, V. *Org. Lett.* **2002**, *4*, 1671. (h) Lebel, H.; Paquet, V.; Proulx, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2887. (i) Fujimura, O.; Honma, T. *Tetrahedron Lett.* **1998**, *39*, 625. (j) Ledford, B. E.; Carreira, E. M. *Tetrahedron Lett.* **1997**, *38*, 8125. (k) Herrmann, W. A.; Roesky, P. W.; Wang, M.; Scherer, W. *Organometallics* **1994**, *13*, 4531. (l) Herrman, W. A.; Wang, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1641. (m) Lu, X.; Fang, H.; Ni, Z. *J. Organomet. Chem.* **1989**, *373*, 77.

(4) (a) Rein, T.; Reiser, O. *Acta Chem. Scand.* **1996**, *50*, 369. (b) Li, A.-H.; Dai, L.-X.; Aggarwal, V. K. *Chem. Rev.* **1997**, *97*, 2341. (c) Rein, T.; Pederson, T. M. *Synthesis* **2002**, *5*, 579.

(5) Chen, Y.; Huang, L.; Ranade, M. A.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 3714.

(6) Chen, Y.; Huang, L.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 5925.

(7) Chen, Y.; Huang, L.; Zhang, X. P. *Org. Lett.* **2003**, *5*, 2493.

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Table 1. Olefination of Aldehydes with EDA Catalyzed by Co(TPP)[a]

entry	RCHO[b]	[Co] (mol %)	temp (°C)	time (h)[c]	yield (%)[d]	*E*/*Z*[e]
1	**a**	2.0	80	2	84 (72)	95/5
2[f]	**a**	2.0	80	2	27 (21)	94/6
3	**a**	2.0	22	2	27 (29)	99/1
4	**a**	2.0	80	4	85 (73)	94/6
5	**a**	2.0	80	8	91 (87)	94/6
6	**a**	2.0	80	12	91 (83)	94/6
7	**a**	4.0	80	12	99 (94)	94/6
8	**a**	1.0	80	12	68 (−)	93/7
9	**a**	0.5	80	12	50 (−)	93/7
10[g]	**a**	4.0	80	12	91 (85)	96/4
11[g]	**a**	2.0	80	12	43 (−)	95/5
12	**b**	2.0	80	12	99 (89)	93/7
13	**b**	4.0	80	12	99 (95)	89/11
14	**c**	2.0	80	12	84 (80)	98/2
15	**c**	4.0	80	12	99 (94)	97/3
16	**d**	2.0	80	12	88 (75)	99/1
17	**d**	4.0	80	12	88 (86)	95/5
18	**e**	2.0	80	12	49 (42)	99/1
19	**e**	4.0	80	12	62 (−)	96/4
20	**e**	8.0	80	12	80 (74)	94/6
21	**f**	2.0	80	12	99 (93)	95/5
22	**f**	4.0	80	12	90 (90)	95/5
23	**g**	2.0	80	12	99 (86)	99/1
24	**g**	4.0	80	12	99 (89)	96/4
25	**h**	2.0	80	12	99 (88)	99/1
26	**i**	2.0	80	12	97 (83)	94/6
27	**i**	4.0	80	12	91 (86)	90/10
28	**j**	2.0	80	12	84 (72)	90/10
29	**j**	4.0	80	12	88 (81)	89/11
30	**k**	2.0	80	12	88 (80)	98/2
31	**k**	4.0	80	12	90 (88)	97/3

[a] Reactions were carried out in toluene under N_2 with 1.0 equiv of aldehyde, 1.2 equiv of EDA, 1.2 equiv of PPh_3, and a catalytic amount of Co(TPP). Concentration: 0.5 mmol of aldehyde/2 mL of toluene. [b] The structures of the aldehydes are shown in Figure 2. [c] Reaction times have not been optimized. [d] The first yields were determined by GC. Yields in parentheses represent isolated yields of >95% purity as determined by GC and ^{1}H NMR. [e] The ratio of *E* to *Z* isomers was determined by GC or ^{1}H NMR. [f] The reaction was carried out in air. [g] The reaction was carried out in THF.

examples of cobalt-catalyzed olefinations of carbonyl compounds.

Results and Discussion

We first evaluated the catalytic activity of Co(TPP) for olefination of benzaldehyde (Table 1). Under the typical catalytic conditions (using 2 mol % catalyst at 80 °C in toluene for 2 h) that are effective for the Fe(TPP)Cl system,[5] Co(TPP) showed a modest catalytic activity, affording the desired olefin in 84% yield (isolated yield 72%; Table 1, entry 1). This moderate yield was dramatically decreased when the reaction was carried out in air (Table 1, entry 2) or at room temperature (Table 1, entry 3). However, a noticeable increase in yields was observed when the reactions were allowed to proceed for longer times (Table 1, entries 4−6). While the same effect was diminished when lower catalyst loadings were employed (Table 1, entries 8 and 9), near-quantitative yields were achieved when the reaction was performed for 12 h using 4 mol % Co(TPP) (Table 1, entry 7). Different from the Fe(TPP)Cl system,[5] THF was found to be an inferior solvent, especially at relatively lower catalyst loadings (Table 1, entries 10 and 11). Together, these results indicate that the catalytic rates of olefination were slower by Co(TPP) than by Fe(TPP)Cl. However, with reasonable catalyst loadings (2−4 mol %) and reaction times (8−12 h), Co(TPP) could effectively catalyze the olefination reaction of benzaldehyde in excellent yield and stereoselectivity.

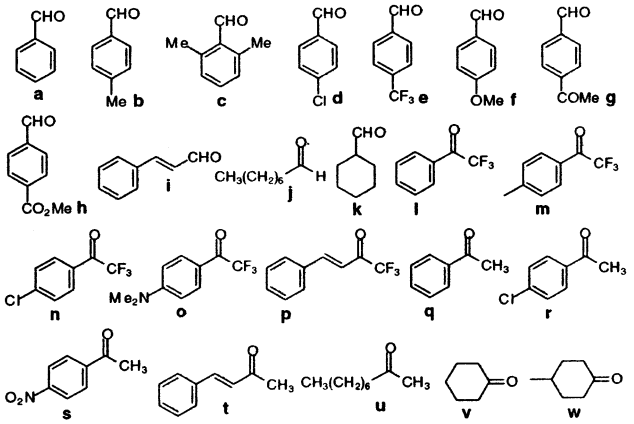


Figure 2. Structures of carbonyl substrates.

Using the above catalytic conditions, we then examined the scope of Co(TPP)-mediated olefination with a variety of aldehydes (Figure 2, substrates **a**−**k**). As shown in Table 1, the catalytic reaction is suitable for a wide scope of aldehyde substrates, affording the desired olefin in excellent yields and *E* selectivities. For example, 4-methylbenzaldehyde and sterically hindered 2,6-dimethylbenzaldehyde could be quantitatively olefinated (Table 1, entries 12−15). Benzaldehyde derivatives containing functional groups were well tolerated (Table 1, entries 23−25). While electron-rich 4-methoxybenzaldehyde was converted in excellent yields (Table 1, entries 21 and 22), electron-poor benzaldehydes were surprisingly found to be less reactive (Table 1, entries 16−20),[8] suggesting possible substrate inhibition via interaction between Co(TPP) and electron-poor benzaldehydes.[3d] The catalytic system is also suitable to nonaromatic aldehydes such as α,*β*-unsaturated cyclic and aliphatic aldehydes (Table 1, entries 26−31).

β-Trifluoromethyl α,*β*-unsaturated esters are a class of important compounds which have found numerous applications in organic, materials, medicinal, and agricultural chemistry, owing to their unique physical, chemical, and biological properties.[9] We were interested in extending the current Co(TPP)-mediated olefination to trifluoromethyl ketones for their synthesis. Initial experiments were conducted with trifluoroacetophenone as a substrate. The results showed that the yield of the desired ethyl 4,4,4-trifluoro-3-phenylbut-2-enoate was improved, along with the use of an increased amount of the catalyst until it reached the best at ∼4 mol % loading; the effect of reaction times was not obvious (Table 2, entries 1−8). As observed in the cases of aldehydes, THF was a poorer solvent than toluene for the reaction (Table 2, entry 9). Further improvement was achieved when the reactions were carried out at higher temperatures (Table 2, entries 10 and 11). For example, at 120 °C for 12 h, a 96% yield (isolated yield:

(8) When electron-poor benzaldehydes were used, the corresponding azine byproducts were observed, the amount of which increased along with the decreases in yields of the desired olefination products.

(9) (a) Bégué, J.-P.; Bonnet-Delpon, D.; Chennoufi, A.; Ourevitch, M.; Ravikumar, K. S.; Rock, M. H. *J. Fluorine Chem.* **2001**, *107*, 275. (b) Lin, P.; Jiang, J. *Tetrahedron* **2000**, *56*, 3635. (c) Schofield, H. *J. Fluorine Chem.* **1999**, *100*, 7. (d) Welch, J. T. *Tetrahedron* **1987**, *4*, 3123.

Table 2. Olefination of Activated Ketones with EDA Catalyzed by Co(TPP)[a]

entry	$RC(O)CF_3$[b]	[Co] (mol %)	temp (°C)	time (h)[c]	yield (%)[d]	*E*/*Z*[e]
1	**l**	0.5	80	12	37 (−)	87/13
2	**l**	1.0	80	12	57 (−)	88/12
3	**l**	2.0	80	12	75 (−)	88/12
4	**l**	2.0	80	1	74 (−)	88/12
5	**l**	4.0	80	12	93 (88)	91/9
6	**l**	4.0	80	24	93 (−)	90/10
7	**l**	6.0	80	12	94 (−)	90/10
8	**l**	7.4	80	12	94 (−)	88/12
9[f]	**l**	2.0	80	12	19 (−)	90/10
10	**l**	4.0	120	12	94 (−)	84/16
11	**l**	2.0	120	12	96 (90)	84/16
12	**m**	2.0	80	12	87 (−)	88/12
13	**m**	4.0	80	12	98 (92)	90/10
14	**m**	4.0	80	24	99 (−)	88/12
15	**m**	4.0	120	12	99 (94)	88/12
16	**n**	2.0	80	12	61 (−)	93/7
17	**n**	4.0	80	12	75 (74)	92/8
18	**n**	4.0	80	24	77 (−)	91/9
19	**n**	4.0	120	12	88 (86)	88/12
20	**o**	2.0	80	12	86 (−)	88/12
21	**o**	4.0	80	12	90 (81)	89/11
22	**o**	4.0	80	24	93 (90)	91/9
23	**o**	4.0	120	12	90 (−)	86/14
24	**p**	2.0	80	12	55 (−)	98/2
25	**p**	4.0	80	12	69 (64)	99/1
26	**p**	4.0	80	24	74 (−)	99/1
27	**p**	4.0	120	12	74 (69)	99/1

[a] Reactions were carried out in toluene under N_2 with 1.0 equiv of ketone, 1.2 equiv of EDA, 1.2 equiv of PPh_3, and a catalytic amount of Co(TPP). Concentration: 0.5 mmol of ketone/2 mL of toluene. [b] The structures of the activated ketones are shown in Figure 2. [c] Reaction times have not been optimized. [d] The first yields were determined by GC. Yields in parentheses represent isolated yields of >95% purity as determined by GC and ^1H NMR. [e] The ratio of *E* to *Z* isomers was determined by GC or ^1H NMR. [f] The reaction was carried out in THF.

Table 3. Olefination of Unactivated Ketones with EDA Catalyzed by Co(TPP)[a]

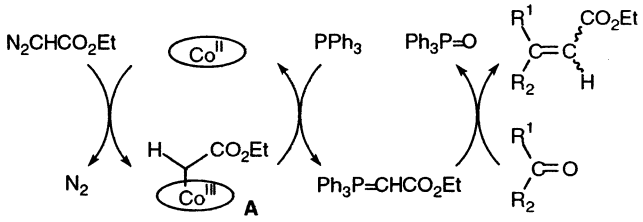
entry	$RC(O)CH_3$[b]	[Co] (mol %)	temp (°C)	time (h)[c]	yield (%)[d]	*Z*/*E*[e]
1	**q**	2.0	80	12	20 (−)	61/39
2	**q**	4.0	80	24	34 (−)	62/38
3	**q**	4.0	120	24	36 (−)	60/40
4	**q**	4.0	80	48	46 (45)	59/41
5	**q**	8.0	80	48	47 (−)	59/41
6	**r**	2.0	80	12	34 (−)	69/31
7	**r**	4.0	120	24	60 (59)	61/39
8	**r**	4.0	80	48	47 (−)	66/34
9	**s**	2.0	80	12	66 (−)	69/31
10	**s**	4.0	80	24	77 (74)	70/30
11	**s**	4.0	120	24	70 (−)	68/32
12	**s**	4.0	80	48	73 (−)	68/32
13	**t**	2.0	80	12	46 (−)	68/32
14	**t**	4.0	80	24	58 (−)	72/28
15	**t**	4.0	120	24	73 (70)	68/32
16	**t**	4.0	80	48	58 (−)	70/30
17	**u**	4.0	80	24	39 (−)	59/41
18	**u**	4.0	120	24	57 (50)	62/38
19	**u**	4.0	80	48	47 (−)	60/40
20	**v**	2.0	80	12	65 (−)	
21	**v**	4.0	80	24	68 (−)	
22	**v**	4.0	80	48	73 (−)	
23	**v**	2.0	120	12	80 (−)	
24	**v**	4.0	120	24	85 (82)	
25	**w**	2.0	80	12	60 (−)	
26	**w**	4.0	80	48	70 (−)	
27	**w**	4.0	120	24	74 (68)	

[a] Reactions were carried out in toluene under N_2 with 1.0 equiv of ketone, 1.2 equiv of EDA, 1.2 equiv of PPh_3, and a catlytic amount of Co(TPP) in the presence of 0.5 equiv of benzoic acids. Concentration: 0.5 mmol of ketone/2 mL toluene. [b] The structures of the unactivated ketones are shown in Figure 2. [c] Reaction times have not been optimized. [d] The first yields were determined by GC. Yields in parentheses represent isolated yields of >95% purity, as determined by GC and ^1H NMR. [e] The ratio of *Z* to *E* isomers was determined by GC or ^1H NMR.

90%) of ethyl 4,4,4-trifluoro-3-phenylbut-2-enoate was obtained using 2 mol % Co(TPP), although a slight decease in *E* selectivity was observed (Table 2, entry 11). Using 2−4 mol % of Co(TPP) at 80−120 °C for 12−24 h, a variety of trifluoromethyl ketones (Figure 2, substrates **l**−**p**), including electron-neutral (Table 2, entries 12−15), electron-poor (Table 2, entries 16−19), and electron-rich (Table 2, entries 20−23) trifluoroacetophenone derivatives as well as α,*β*-unsaturated trifluoromethyl ketone (Table 2, entries 24−27), were effectively transformed into the desired *β*-trifluoromethyl α,*β*-unsaturated esters.

When unactivated ketones (Figure 2, substrates **q**−**w**) were used as substrates, however, no yields or very low yields of the desired olefins were found. As discovered previously,[7,10] these reactions could be remarkably promoted by substoichiometric amounts of acid. The previously unsuccessful reaction of acetophenone could now be effected to produce the desired ethyl 3-phenyl-2-butenoate in 20% yield upon the addition of 0.5 equiv of benzoic acids (Table 3, entry 1).[11] This yield could be further doubled or tripled through the use of more catalyst, higher reaction temperatures, or longer reaction times (Table 3, entries 2−5). Under similar conditions, different types of normal ketones (Figure 2, substrates **q**−**w**) were successfully olefinated, although

Scheme 2. Possible Olefination Mechanism by Co(TPP)



the yields and stereoselectivities were generally lower than for the reactions of aldehydes and activated ketones (Tables 1−3). Examples include acetophenone derivatives (Table 3, entries 6−12), α,*β*-unsaturated ketones (Table 3, entries 13−16), aliphatic ketones (Table 3, entries 17−19), and cyclic ketones (Table 3, entries 20−27).

The current Co(TPP)-based catalytic system presumably proceeds through a metallocarbene-phosphorane mechanism that was proposed for other metalloporphyrin systems.[3d−e,5−7] As illustrated in Scheme 2, the Co(II) center of Co(TPP) reacts with the diazo reagent to afford the neutral cobalt−carbene intermediate **A** with concomitant release of nitrogen. Carbene transfer from intermediate **A** to Ph_3P yields a phosphorane and regenerates the active Co(TPP) to continue the catalytic cycle. In a way similar to the classic Wittig reaction,[1] the resulting phosphorane reacts with cabonyl compounds to form the desired alkene and $Ph_3P{=}O$. The

(10) Ruchardt, C.; Eichler, S.; Panse, P. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 619.
(11) In the absence of Co(TPP), no desired olefins were observed when benzoic acids were added.

activation of simple ketones by benzoic acid operates possibly via protonation of the carbonyl oxygen, which would make the carbonyl group a better electrophile toward reaction with phosphorane.[7] While it is well-known that Fe and Ru porphyrins can form carbene complexes and mediate carbene transfer reactions, cobalt porphyrin carbene complexes and their carbene transfer reactions have not been firmly established. Our efforts to elucidate the nature of the cobalt porphyrin carbene intermediate **A** have so far been inconclusive. Among several possible structures, the intermediate **A** could be considered as a cobalt(III)−carbene complex having a Co−C single bond with carbon-based radical character, an unusual metal−carbene structure that was recently proposed for 3-oxobutylideneaminato−cobalt- and salen−cobalt-based cyclopropanation systems.[12]

Conclusions

In summary, we have demonstrated the first cobalt-catalyzed selective olefination of carbonyl compounds with diazo reagents. The commercially available Co(TPP)-based system is effective for a wide range of aldehydes and activated and unactivated ketones. We are currently working to further widen the scope of the reaction to include other carbonyl compounds such as esters and amides. Continuing efforts are underway to elucidate the underlying mechanism of the new catalytic process, including the characterization of catalytic intermediates.

Experimental Section

General Considerations. All reactions were carried out in oven-dried glassware using standard Schlenk techniques. Toluene and tetrahydrofuran were freshly distilled from sodium/benzophenone under a nitrogen atmosphere. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as supplied. All other solvents were of liquid chromatography grade quality, purchased from Fisher Scientific and used as supplied. Aldehydes and ketones were purchased from Acros Organics, Aldrich Chemical Co., and Lancaster and used without further purification. Triphenylphosphine and Co(TPP) were supplied by Strem Chemical Co or Midcentury Chemicals. Ethyl diazoacetate (EDA) was obtained from Aldrich Chemical Co. Benzoic acid was purchased from Acros Organics. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Varian Mercury 300 spectrometer and referenced with respect to internal TMS standard or residual solvent. GC/GC-MS analysis was performed using a Hewlett-Packard G 1800B GCD System apparatus equipped with an HP-5MS capillary column (HP 19091S-433, 5% phenyl methyl siloxane, 30 m × 250 μm × 0.25 μm nominal) under the following conditions: helium 1 mL/min (constant flow mode), injector 250 °C (split mode), detector EI, oven 50 °C (4 min), 10 °C/min (23 min), 280 °C (2 min) unless otherwise specified. Thin-layer chromatography was carried out on E. Merck silica gel 60 F-254 TLC plates.

General Procedures for Aldehyde and Fluorine-Containing Ketone Olefination Reactions (Solid Aldehydes and Fluorine-Containing Ketones). A specified mole percent of Co(TPP), 1.2 equiv of triphenylphosphine, and 1.0 equiv of aldehyde (**c**, **d**, **g**, and **h**) or fluorine-containing ketone (**o**) (0.5 mmol) were placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screw cap and a rubber septum, evacuated, and back-filled with nitrogen. Then the solvent (2 mL) was added via syringe, followed by 1.2 equiv of EDA. The tube was purged with nitrogen for 2 min, and its contents were stirred at constant temperature in an oil bath. After the reaction was finished, the resulting mixture was cooled to room temperature and concentrated. The residue was purified by flash silica gel chromatography to give the product.

General Procedures for Aldehyde and Fluorine-Containing Ketone Olefination Reactions (Liquid Aldehydes and Fluorine-Containing Ketones). A specified mole percent of Co(TPP) and 1.2 equiv of triphenylphosphine were placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screw cap and a rubber septum, evacuated, and back-filled with nitrogen. One equivalent of aldehyde (**a**, **b**, **e**, **f**, **i**−**k**) or fluorine-containing (**l**−**n**, **p**) (0.5 mmol) was added via syringe, followed by solvent (2 mL) and 1.2 equiv of EDA. The tube was purged with nitrogen for 2 min, and its contents were stirred at constant temperature in an oil bath. After the reaction was finished, the resulting mixture was cooled to room temperature and concentrated. The residue was purified by flash silica gel chromatography to give the product.

General Procedures for Ketone Olefination Reactions. A specified mole percent of Co(TPP), 1.2 equiv of triphenylphosphine, and 0.5 equiv of benzoic acid were placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screw cap and a rubber septum, evacuated, and back-filled with nitrogen. One equivalent of ketone (**q**, **r**, **u**−**w**) (0.5 mmol) was added via syringe (**s** and **t** were added in the Schlenk tube before it was evacuated and back-filled with nitrogen.), followed by solvent (2 mL) and 1.2 equiv of EDA. The tube was purged with nitrogen for 2 min, and its contents were stirred at constant temperature in an oil bath. After the reaction was finished, the resulting mixture was cooled to room temperature and concentrated. The residue was purified by flash silica gel chromatography to give the product.

Ethyl (*E*)-3-phenyl-2-propenoate[5,13] (Table 1, entries 1−11) was synthesized from benzaldehyde (**a**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, 1H, J = 15.9 Hz), 7.50 (m, 2H), 7.36 (m, 3H), 6.42 (d, 1H, J = 15.9 Hz), 4.25 (q, 2H, J = 7.2 Hz), 1.32 (t, 3H, J = 7.2 Hz).

Ethyl (*E*)-3-(4-methylphenyl)-2-propenoate[5,13] (Table 1, entries 12 and 13) was synthesized from 4-methylbenzaldehyde (**b**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, 1H, J = 16.2 Hz), 7.40 (d, 2H, J = 7.8 Hz), 7.16 (d, 2H, J = 8.1 Hz), 6.38 (d, 1H, J = 15.9 Hz), 4.24 (q, 2H, J = 7.2 Hz), 2.35 (s, 3H), 1.32 (t, 3H, J = 7.2 Hz).

Ethyl (*E*)-3-(2,6-dimethylphenyl)-2-propenoate[5,14] (Table 1, entries 14 and 15) was synthesized from 2,6-dimethylbenzaldehyde (**c**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, 1H, J = 16.5 Hz), 7.06 (m, 3H), 6.07 (d, 1H, J = 16.5 Hz), 4.28 (q, 2H, J = 7.2 Hz), 2.34 (s, 6H), 1.35 (t, 3H, J = 7.2 Hz).

Ethyl (*E*)-3-(4-chlorophenyl)-2-propenoate[5,13] (Table 1, entries 16 and 17) was synthesized from 4-chlorobenzaldehyde (**d**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, 1H, J = 15.9 Hz), 7.42 (d, 2H, J = 8.4 Hz), 7.32 (d, 2H, J = 8.4 Hz), 6.38 (d, 1H, J = 16.2 Hz), 4.24 (q, 2H, J = 7.2 Hz), 1.31 (t, 3H, J = 7.2 Hz).

Ethyl (*E*)-3-(4-(trifluoromethyl)phenyl)-2-propenoate[5,13] (Table 1, entries 18−20) was synthesized from 4-(trifluoromethyl)tolualdehyde (**e**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, 1H, J = 15.9 Hz), 7.62 (s, 4H), 6.49 (d, 1H, J = 15.9 Hz), 4.26 (q, 2H, J = 7.2 Hz), 1.33 (t, 3H, J = 7.2 Hz).

Ethyl (*E*)-3-(4-methoxyphenyl)-2-propenoate[5,13] (Table 1, entries 21 and 22) was synthesized from 4-methoxybenzaldehyde (**f**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, 1H, J =

(12) Ikeno, T.; Iwakura, I.; Yamada, T. *J. Am. Chem. Soc.* **2002**, *124*, 15152.

(13) Huang, Z.; Ye, S.; Xia, W.; Yu, Y.; Tang, Y. *J. Org. Chem.* **2002**, *67*, 3096.

(14) Li, X,; Wu, H.; Hruby, V. J. *Tetrahedron: Asymmetry* **1995**, *6*, 83.

15.9 Hz), 7.43 (d, 2H, J = 8.7 Hz), 6.86 (d, 2H, J = 8.7 Hz), 6.27 (d, 1H, J = 15.9 Hz), 4.22 (q, 2H, J = 7.2 Hz), 3.79 (s, 3H), 1.30 (t, 3H, J = 7.2 Hz).

Ethyl (*E*)-3-(4-acetylphenyl)-2-propenoate[5,15] (Table 1, entries 23 and 24) was synthesized from 4-acetylbenzaldehyde (**g**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (d, 2H, J = 8.4 Hz), 7.65 (d, 1H, J = 15.9 Hz), 7.56 (d, 2H, J = 8.4 Hz), 6.48 (d, 1H, J = 16.2 Hz), 4.23 (q, 2H, J = 7.2 Hz), 2.57 (s, 3H), 1.30 (t, 3H, J = 6.9 Hz).

Ethyl (*E*)-3-((4-methoxycarbonyl)phenyl)-2-propenoate[5,16] (Table 1, entry 25) was synthesized from methyl 4-formylbenzoate (**h**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, 2H, J = 8.1 Hz), 7.62 (d, 1H, J = 15.9 Hz), 7.51 (d, 2H, J = 8.1 Hz), 6.45 (d, 1H, J = 16.2 Hz), 4.21 (q, 2H, J = 7.2 Hz), 3.86 (s, 3H), 1.28 (t, 3H, J = 7.2 Hz).

Ethyl (*E*,*E*)-5-phenylpenta-2,4-dienoate[5,13] (Table 1, entries 26 and 27) was synthesized from *trans*-cinnamaldehyde (**i**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.5−6.8 (m, 8H), 5.98 (d, 1H, J = 15.0 Hz), 4.22 (q, 2H, J = 7.2 Hz), 1.31 (t, 3H, J = 7.2 Hz).

Ethyl (*E*)-2-decenoate[5,17] (Table 1, entries 28 and 29) was synthesized from octylaldehyde (**j**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.93 (dt, 1H, J = 15.3, 7.2 Hz), 5.77 (d, 1H, J = 15.6 Hz), 4.15 (q, 2H, J = 7.2 Hz), 2.15 (m, 2H), 1.41 (m, 2H), 1.24 (m, 11H), 0.84 (t, 3H, J = 7.2 Hz).

Ethyl (*E*)-3-cyclohexyl-2-propenoate[5,18] (Table 1, entries 30 and 31) was synthesized from cyclohexanecarboxaldehyde (**k**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92 (dd, 1H, J = 16.1, 6.9 Hz), 5.76 (d, 1H, J = 16.1 Hz), 4.18 (q, 2H, J = 7.2 Hz), 2.12 (m, 1H), 1.75 (m, 5H), 1.29 (t, 3H, J = 7.2 Hz), 1.16 (m, 5H).

Ethyl (*E*)-4,4,4-trifluoro-3-phenylbut-2-enoate[6,19] (Table 2, entries 1−11) was synthesized from α,α,α-trifluoroacetophenone (**l**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (m, 3H), 7.24 (m, 2H), 6.55 (q, 1H, J = 1.5 Hz), 3.98 (q, 2H, J = 6.9 Hz), 0.99 (t, 3H, J = 6.9 Hz).

Ethyl (*E*)-4,4,4-trifluoro-3-(4-methylphenyl)but-2-enoate[6,20] (Table 2, entries 12−15) was synthesized from 4-(trifluoroacetyl)toluene (**m**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 (s, 4H), 6.58 (q, 1H, J = 1.5 Hz), 4.06 (q, 2H, J = 7.2 Hz), 2.37 (s, 3H), 1.09 (t, 3H, J = 7.2 Hz).

Ethyl (*E*)-4,4,4-trifluoro-3-(4-chlorophenyl)but-2-enoate[6,21] (Table 2, entries 16−19) was synthesized from 4′-chloro-2,2,2-trifluoroacetophenone (**n**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (d, 2H, J = 8.4 Hz), 7.23 (d, 2H, J = 8.7 Hz), 6.62 (q, 1H, J = 1.2 Hz), 4.06 (q, 2H, J = 6.9 Hz), 1.11 (t, 3H, J = 7.2 Hz).

Ethyl (*E*)-4,4,4-trifluoro-3-(4-(dimethylamino)phenyl)-but-2-enoate[6,22] (Table 2, entries 20−23) was synthesized from 4′-(dimethylamino)-2,2,2-trifluoroacetophenone (**o**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20 (d, 2H, J = 9.0 Hz), 6.68 (d, 2H, J = 9.3 Hz), 6.48 (q, 1H, J = 1.5 Hz), 4.10 (q, 2H, J = 7.2 Hz), 2.98 (s, 6H), 1.15 (t, 3H, J = 7.2 Hz).

Ethyl 5-phenyl-3-(trifluoromethyl)penta-(2*E*,4*E*)-dienoate[6,23] (Table 2, entries 24−27) was synthesized from *trans*-1,1,1-trifluoro-4-phenyl-3-buten-2-one (**p**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (d, 1H, J = 17.1 Hz), 7.56−7.31 (m, 5H), 7.13 (dd, 1H, J = 17.1, 2.1 Hz), 6.29 (q, 1H, J = 0.6 Hz), 4.27 (q, 2H, J = 7.2 Hz), 1.33 (t, 3H, J = 7.2 Hz).

Ethyl 3-phenyl-2-butenoate[7,24] (Table 3, entries 1−5) was synthesized from acetophenone (**q**). *E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46−7.49 (m, 2H), 7.35−7.39 (m, 3H), 6.2 (q, 1H, J = 1.5 Hz), 4.21 (q, 2H, J = 7.2 Hz), 2.57 (d, 3H, J = 1.5 Hz), 1.31 (t, 3H, J = 7.2 Hz). *Z* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30−7.38 (m, 2H), 7.19−7.22 (m, 3H), 5.90 (q, 1H, J = 1.2 Hz), 3.99 (q, 2H, J = 7.2 Hz), 2.16 (d, 3H, J = 1.5 Hz), 1.07 (t, 3H, J = 7.2 Hz).

Ethyl 3-(4-chlorophenyl)-2-butenoate[7,25] (Table 3, entries 6−8) was synthesized from 4-chloroacetophenone (**r**). *E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, 2H, J = 8.4 Hz), 7.33 (d, 2H, J = 8.4 Hz), 6.11 (q, 1H, J = 1.5 Hz), 4.20 (q, 2H, J = 7.2 Hz), 2.53 (d, 3H, J = 1.5 Hz), 1.31 (t, 3H, J = 7.2 Hz). *Z* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, 2H, J = 8.4 Hz), 7.14 (d, 2H, J = 8.4 Hz), 5.90 (q, 1H, J = 1.5 Hz), 4.00 (q, 2H, J = 7.2 Hz), 2.13 (d, 3H, J = 1.5 Hz), 1.11 (t, 3H, J = 7.2 Hz).

Ethyl 3-(4-nitrophenyl)-2-butenoate[7,26] (Table 3, entries 9−12) was synthesized from 4-nitroacetophenone (**s**). *E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, 2H, J = 9.0 Hz), 7.52 (d, 2H, J = 8.7 Hz), 6.19 (s, 1H), 4.20 (q, 2H, J = 7.2 Hz), 2.54 (d, 3H, J = 1.2 Hz), 1.30 (t, 3H, J = 7.2 Hz). *Z* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, 2H, J = 8.7 Hz), 7.31 (d, 2H, J = 9.0 Hz), 5.96 (q, 1H, J = 1.2 Hz), 3.97 (q, 2H, J = 7.2 Hz), 2.15 (d, 3H, J = 1.5 Hz), 1.08 (t, 3H, J = 7.2 Hz).

Ethyl 3-methyl-5-phenyl-2,4-pentadieneoate[7,27] (Table 3, entries 13−16) was synthesized from *trans*-4-phenyl-3-buten-2-one (**t**). *Z*,*E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (d, 1H, J = 16.5 Hz), 7.51−7.54 (m, 2H), 7.24−7.35 (m, 3H), 6.90 (d, 1H, J = 16.2 Hz), 5.74 (s, 1H), 4.19 (q, 2H, J = 7.2 Hz), 2.11 (d, 3H, J = 1.2 Hz), 1.30 (t, 3H, J = 7.2 Hz). *E*,*E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.48 (m, 2H), 7.26−7.38 (m, 3H), 6.94 (d, 1H, J = 16.2 Hz), 6.81 (d, 1H, J = 16.2 Hz), 5.89 (s, 1H), 4.19 (q, 2H, J = 7.2 Hz), 2.40 (d, 3H, J = 1.5 Hz), 1.30 (t, 3H, J = 7.2 Hz).

Ethyl 3-methyl-decenoate[7,28] (Table 3, entries 17−19) was synthesized from 2-nonanone (**u**). *Z* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.61 (q, 1H, J = 1.2 Hz), 4.11 (q, 2H, J = 7.2 Hz), 2.58 (m, 2H), 1.85 (d, 3H, J = 1.2 Hz), 1.24−1.48 (m, 13H), 0.85 (t, 3H, J = 7.2 Hz). *E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.63 (q, 1H, J = 1.5 Hz), 4.12 (q, 2H, J = 7.2 Hz), 2.12 (d, 3H, J = 1.5 Hz), 2.10 (m, 2H), 1.26−1.49 (m, 13H), 0.85 (t, 3H, J = 6.9 Hz).

Ethyl cyclohexylideneacetate[7,29] (Table 3, entries 20−24) was synthesized from cyclohexanone (**v**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.57 (s, 1H), 4.10 (q, 2H, J = 7.2 Hz), 2.79 (m, 2H), 2.16 (m, 2H), 1.58 (m, 6H), 1.24 (t, 3H, J = 7.2 Hz).

Ethyl (4-methylcyclohexylidene)acetate[7,30] (Table 3, entries 25−27) was synthesized from 4-methylcyclohexanone (**w**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.57 (s, 1H), 4.11 (q, 2H, J = 6.9 Hz), 3.68−3.75 (m, 1H), 2.13−2.25 (m, 2H), 1.79−1.97 (m, 3H), 1.55−1.67 (m, 1H), 1.24 (t, 3H, J = 7.2 Hz), 1.03−1.19 (m, 2H), 0.88 (d, 3H, J = 6.6).

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(15) Butt, G.; Topsom, R. D. *Spectrochim. Acta, Part A* **1982**, *38*, 649.
(16) Bozell, J. J.; Vogt, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 2655.
(17) Ando, K. *J. Org. Chem.* **1997**, *62*, 1934.
(18) Barrett, A. G. M.; Doubleday: W. W.; Tustin, G. J. *Tetrahedron* **1996**, *52*, 15325.
(19) Shen, Y.; Gao, S. *J. Org. Chem.* **1993**, *58*, 4564.
(20) Pan, R.-Q.; Wang, P.-A.; Deng, M.-Z. *Heteroat. Chem.* **2002**, *13*, 287.
(21) Gong, Y.; Kato, K.; Kimoto, H. *J. Fluorine Chem.* **2000**, *105*, 169.
(22) Il'chenko, A. Y.; Koval'chuk, R. E.l Yagupol'skii, L. M. *Zh. Org. Khim.* **1977**, *13*, 1992.
(23) Shen, Y.; Zhang, Z.; Sun, J. *J. Fluorine Chem.* **2001**, *111*, 189.
(24) Kobayashi, Y.; William, A. D.; Mizojiri, R. *J. Organomet. Chem.* **2002**, *653*, 91.
(25) Allan, R. D.; Tran, H. *Aust. J. Chem.* **1981**, *34*, 2641.
(26) Kagabu, S.; Shimizu, Y.; Ito, C.; Moriya, K. *Synthesis* **1992**, *9*, 830.
(27) Albaugh-Roberston, P.; Katzenellenbogen, J. A. *J. Org. Chem.* **1983**, *48*, 5288.
(28) Spinella, A.; Fortunati, T.; Soriente, A. *Synlett* **1997**, 93.
(29) (a) Katritzky, A. R.; Ignatchenko, A. V.; Lan, X.; Lang, H.; Stevens, C. V. *Tetrahedron* **1994**, *50*, 6005. (b) Srikrishna, A.; Kumar, P. P. *Tetrahedron* **2000**, *56*, 8189.
(30) Rekowski, P.; Lammek, B. *Pol. J. Chem.* **1987**, *61*, 907.