1. Analytical Methods

NMR spectra were recorded on Bruker Avance 300 (300 MHz) and Bruker Avance 400(400 MHz) NMR spectrometers. Chemical shifts δ (ppm) are given relative to solvent: references for CDCl₃ were 7.26 ppm (¹H NMR) and 77.16 ppm (¹³C NMR). ¹³C NMR spectra were acquired on a broad band decoupled mode. Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet) and br. s (broad singlet). All measurements were carried out at room temperature unless otherwise stated. For GC analyses, HP 6890 chromatograph with a 29 m HP5 column was used. The products were isolated from the mixture by following column chromatography on silica gel 60, 0.064-0.2 mm, 70-230 mesh (Merk). Linear to branched ratios were determined by GC analysis of the crude reaction mixture.

2. Materials and Methods

All commercial reagents were ordered from Acros Organics, Alfa Aesar, or Sigma Aldrich. Dry solvents were prepared according to standard procedures.¹ Air- and moisture-sensitive syntheses were performed under argon atmosphere in glassware after heat gun-dried under vacuum. Analytical data of literature known compounds were in accord with reported data.

3. General Procedure for the Alkoxycarbonylation of Olefins

Alkoxycarbonylation experiments were carried out in a 300 mL autoclave which can be placed with five 12 mL vials. Generally, additives and LIKATphos (when more than 0.1 mol% of LIKATphos was used) were weighed and added into the vials with a small stirring bar in glovebox. LIKATphos solution (when 0.1 mol% of LIKATphos was used), palladium precursor solution, alcohol solvent and olefin substrates were added by syringe under argon atmosphere. The autoclave was flushed by nitrogen gas three times and then twice with carbon monoxide. Carbon monoxide was pressurized at room temperature then the autoclave was heated to 120 °C for 20 hours with 600 rpm stirring speed. To terminate the reaction, the autoclave was cooled by 0 °C ice water. Isooctane (57 mg) was added as internal standard, then the solution was filter by celite and analyzed by gas chromatography. Specially, palladium precursor in alcohol solution was used in fresh preparation every time. Firstly, 0.01 mmol of palladium precursor (1.0 mol% to 1.0 mmol substrate) was weight to a Schlenk flask in glovebox, then diluted in 20 mL of alcohol solvent. Heating and ultrasonic treatments were applied to make sure all the palladium precursor was dissolved. Second step, 2 mL of this solution was transferred to another Schlenk flask with 8 mL of the corresponding alcohol. For 0.001 mol% palladium loading reaction, 100 µL of the solution was employed. For 0.0001 mol% palladium loading reaction, the solution of second step was diluted in to 1/10, 1 mL of solution was added to 9 mL alcohol in anther Schlenk flask, 100 µL of this solution was applied.

Methoxycarbonylation of ethylene was carried out in a brand new 100 mL autoclave. LIKATphos (9.2 mg) and PTSA·H₂O (15.8 mg) were weighed and added to the autoclave in the glovebox. Methanol (10 mL) and Pd(dba)₂ methanol solution (100 μ L, 7.9 × 10⁻⁵ M) were added into the autoclave under argon flow. Then ethylene (5 bar) and CO (35 bar) were filled. The reaction was conducted at 120 °C for 22 hours then quenched by ice water. The sample was analyzed by GC using isooctane (166 μ L, 1.0 mmol) as internal standard.

Calculation of palladium concentration in ppm:

Example: Using 0.001 mol% of palladium in 1 mmol scale reactions.

The mass percentage of palladium metal in methanol solution is expressed below:

 $\frac{mass of Pd}{mass in total} \times 10^{6} ppm$ $= \frac{1.0 \times 10^{-8} mol \times 106.42 \frac{g}{mol}}{2 mL \times 0.792 \frac{g}{mL} + 0.112 g + 0.002 g + 0.004 g} \times 10^{6} = 0.6$ ppm

4. Supplemental experiments

Table S1. "Homeopathic" palladium-catalysed alkoxycarbonylation of 1-octene using $Pd_2(dba)_3$ in 8 hours.

1 octopo	Pd ₂ (dba) ₃ LIKATphos						
1-octene	PTSA	•H ₂ O (2.0 mol%)		°C ₆ H ₁₃ کېر ک	+ octe	ne isomers	
1a	CO (40 bar), 8 h			2a	3a		
Entry	[Pd] (mol%)	L (mol%)	Temp. (°C)	2a (%)	n/i	3a (%)	
1	0.0005	0.5	130	85	72/28	14	
2	0.001	0.5	130	90	73/27	9	
3	0.002	0.5	130	92	73/27	7	
4	0.003	0.5	130	99	73/27	<1	
5	0.003	0.1	130	80	72/28	20	
6	0.004	0.1	130	98	73/27	2	

Reaction conditions: **1a** (1.0 mmol), PTSA·H₂O (2.0 mol%), MeOH (2 mL in total), CO (40 bar), 8 hours. The yields and n/i are determined by GC analysis using isooctane as internal standard.

Table S2. "Homeopath	nic" palladium-catalysed	alkoxycarbonylation	of 1-octene	using
$Pd(dba)_2$: effect of CO	pressure.			-

1 aatana	Pd(dba) ₂ (0.001 mol%) LIKATphos (0.5 mol%)				
1-octene -	PTSA•H ₂ O (2.0 mol%)	-	ⁿ C ₆ H ₁₃ , ¹ O +	- octene isomers	
1a	CO, 20 h		2a	3a	
Entry	CO (bar)	2a (%)	n/i	3a (%)	
1	40	94	72/28	5	
2	30	75	72/28	25	
3	20	68	71/29	32	

Reaction conditions: **1a** (1.0 mmol), $Pd(dba)_2$ (0.001 mol%, ca. 0.6 ppm), $PTSA \cdot H_2O$ (2.0 mol%), MeOH (2 mL in total), 2 hours. The yields and n/i are determined by GC analysis using isooctane as internal standard.



1 actors			LIKATphos (0.5 mol%)	~	
1-oclene	+	aniline	$PTSA \cdot H_2O$ (2.0 mol%)		ⁿ C _e H ₁₃ N N
1.0 mmol		1.0 mmol	THF (2 mL)		^o nd H
< 1 % conversion	า		CO (40 bar), Ź0 h		n.u.

Scheme S1. "Homeopathic" palladium-catalysed hydroxycarbonylation and aminocarbonylation of 1-octene: exploration.

5. NMR data of products



Methyl 3-phenylpropanoate (2b) & methyl 2-phenylpropanoate (2b'), 2b:2b' = 70:30

¹H NMR (300 MHz, CDCl₃) δ /pm: **2b**: 7.28-7.13 (m, 5H), 3.62 (s, 3H), 2.91 (t, *J* = 7.8 Hz, 2 H), 2.59 (t, *J* = 7.8 Hz, 2 H); **2b**': 7.28-7.13 (m, 5H), 3.68 (q, *J* = 7.2 Hz, 1H), 3.61 (s, 3H), 1.46 (d, *J* = 7.2 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃) δ /pm:175.07, 173.41, 140.65, 140.60, 128.73, 128.60, 128.52, 128.36, 127.55, 127.22, 126.35, 52.09, 51.68, 45.50, 35.79, 31.03, 18.69.



Methyl nonanoate (2c) & branched isomers, n:i = 73:27

2c: ¹H NMR (300 MHz, CDCl₃) δ/ppm: 3.66 (s, 3H), 2.23 (t, *J* = 15.1 Hz)], 1.64-1.59 (m, 2H), 1.27-1.26 (m, 12 H), 0.90-0.85 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ/ppm: 174.49, 51.57, 34.26, 31.94, 29.25, 29.29, 29.25, 25.09, 22.77, 14.22.

Methyl undecanoate (2d) & branched isomers, n:i = 77:23

2d: ¹H NMR (300 MHz, CDCl₃) δ/ppm: 3.63 (s, 3H), 2.28 (t, *J* = 15.1 Hz, 2H), 1.62-1.57 (m, 2H), 1.26-1.24 (m, 14H), 0.88-0.84 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ/ppm: 174.41, 51.34, 34.21, 31.91, 29.66, 29.57, 29.42, 29.37, 29.27, 25.07, 22,79, 14.20.

Methyl hexanoate (2e) & branched isomers, n:i = 77:23

2e: ¹H NMR (300 MHz, CDCl₃) δ/ppm: 3.64 (s, 3H), 2.28 (t, *J* = 13.7 Hz, 2H), 1.62-1.59 (m, 2H), 1.31-1.26 (m, 4H), 0.89-0.85 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ/ppm: 174.43, 51.52, 34.17, 31.42, 24.75, 22.43, 13.99.

Methyl 3,5,5-trimethylhexanoate (2f)

¹H NMR (300 MHz, CDCl₃) δ/ppm: 3.63 (s, 3H), 2.28 (m, 1H), 2.06 (m, 1H), 1.21 (m, 1H), 1.09 (m, 1H), 0.94 (d, J = 6.5 Hz, 3H), 0.88 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ/ppm: 173.67, 51.37, 50.63, 43.92, 31.15, 30.01, 27.10, 22.81.

0 L

Methyl 4,4-dimethylpentanoate (2g)

¹H NMR (300 MHz, CDCl₃) δ/ppm: 3.65 (s, 3H), 2.30 (m, 2H), 1.56-1.51 (m, 2H), 0.88 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ/ppm: 175.00, 51.65, 38.73, 30.17, 30.02, 29.10.

Methyl 3,4-dimethylpentanoate (2h)

¹H NMR (300 MHz, CDCl₃) δ/ppm: 3.64 (s, 3H), 2.32 (dd, *J* = 14.8, 5.2 Hz, 1H), 2.05 (dd, *J* = 14.7, 9.2 Hz, 1H), 1.88-1.83 (m, 1H), 1.59-1.51 (m, 1H), 0.86-0.81 (m, 9H); ¹³C NMR (75 MHz, CDCl₃) δ/ppm: 174.30, 51.47, 39.09, 36.00, 32.17, 19.89, 18.35, 15.93.

Methyl cyclohexanecarboxylate (2i)

¹H NMR (300 MHz, CDCl₃) δ/ppm: 3.64 (s, 3H), 2.33-2-23 (m, 1H), 1.90-1.85 (m, 2H), 1.76-1.69 (m, 2H), 1.65-1.59 (m, 1H), 1.48-1.35 (m, 2H), 1.33-1.16 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ/ppm: 176.70, 51.54, 43.21, 29.12, 25.85, 25.55.

Methyl cyclooctanecarboxylate (2j)

¹H NMR (300 MHz, CDCl₃) δ/ppm: 3.65 (s, 3H), 2.56-2-47 (m, 1H), 1.91-1.82 (m, 2H), 1.75-1.48 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 177.95, 51.65, 43.61, 28.87, 26.88, 26.25, 25.36.

Methyl bicyclo[2.2.1]heptane-2-carboxylate (2k)

¹H NMR (300 MHz, CDCl₃) δ/ppm: 3.62 (s, 3H), 2.46-2.44 (m, 1H), 2.31-2.26 (m, 2H), 1.84-1.76 (m, 1H), 1.50-1.40 (m, 4H), 1.24-1.10 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 176.62, 51.64, 46.41, 40.97, 36.53, 36.08, 34.21, 29.53, 28.69.

Methyl 3-(4-methoxyphenyl)propanoate (21) & methyl 2-(4-methoxyphenyl)propanoate (21')

21:21' = 63:27

¹H NMR (300 MHz, CDCl₃) δ /ppm: **2I**: 7.25-7.20 (m, 2H), 6.87-6.82 (m, 2H), 3.79 (s, 3H), 3.69 (s, 3H), 2.90 (t, *J* = 7.8 Hz, 2H), 2.60 (t, *J* = 7.8 Hz, 2H); **2I**': 7.25-7.20 (m, 2H), 6.87-6.82 (m, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 3.69 (m, 1H), 1.48 (d, *J* = 7.3 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃) δ /ppm: 175.35, 173.49, 158.77, 158.16, 132.74, 132.66, 129.46, 129.31, 128.55, 114.09, 113.98, 113.87, 55.31, 52.05, 51.65, 44.62, 36.09, 30.18, 18.74.

Methyl 3-(4-chlorophenyl)propanoate (2m)

¹H NMR (300 MHz, CDCl₃) δ /ppm: 7.29-7.26 (m, 2H), 7.16-7.13 (m, 2H), 3.69 (s, 3H), 2.94 (t, *J* = 15.35 Hz, 2H), 2.62 (t, *J* = 7.61 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ /ppm:174.15, 139.05, 132.16, 129.16, 128.75, 128.71, 51.78, 35.60, 30.35.

Methyl 4-(1,3-dioxoisoindolin-2-yl)butanoate (2n) and methyl 3-(1,3-dioxoisoindolin-2-yl)-2methylpropanoate (2n'), 2n:2n' = 80:20

2n: ¹H NMR (300 MHz, CDCl₃) δ /ppm: 7.81-7-78 (m, 2H), 7.69-7.66 (m, 2H), 3.71 (t, *J* = 6.8 Hz, 2H), 3.60 (s, 3H), 2.34 (t, *J* = 7.4 Hz, 2H), 2.02-1.93 (pent, *J* = 7.1 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ /ppm: 173.07, 168.34, 134.07, 131.95, 123.38, 51.70, 37.19, 31.32, 23.91.

Methyl 4-(4-methoxyphenyl)butanoate (20) and methyl 3-(4-methoxyphenyl)-2-methylpropanoate (20')

20:20' = 81:19

20: ¹H NMR (300 MHz, CDCl₃) δ/ppm: 7.11-7.08 (m, 2H), 6.84-6.81 (m, 2H), 3.78 (s, 3H), 3.66 (s, 3H), 2.59 (t, *J* = 15.12 Hz, 2H), 2.31 (t, *J* = 14.96 Hz, 2H), 1.97-1.87 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ/ppm: 174.09, 157.98, 133.51, 129.46, 113.83, 55.32, 51.57, 34.29, 33.42, 26.82.

Dimethyl decanedioate (**2p**) & branched isomers, n:i = 63:37

2p: ¹H NMR (300 MHz, CDCl₃) δ/ppm (dimethyl decanedioate): 3.59 (s, 6H), 2.23 (t, 7.5 Hz, 4 H), 1.57-1.52 (m, 4 H), 1.24 (m, 8 H); ¹³C NMR (75 MHz, CDCl₃) δ/ppm: 174.19, 51.26, 33.95, 29.04, 24.85, 17.07.

Ethyl nonanoate (2q) & branched isomers, n:i = 75:25

2q: ¹H NMR (300 MHz, CDCl₃) δ/ppm: 4.11 (q, *J* = 7.12 Hz, 2H), 2.27 (t, *J* =7.55, 2H), 1.60 (m, 2H), 1.28-1.11 (m, 13H), 0.88-0.85 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ/ppm: 174.05, 60.17, 34.52, 31.93, 29.36, 29.31, 29.28, 25.12, 22.76, 14.37, 14.21.

O O & branched isomers

Butyl nonanoate (2r) & branched isomers, n:i = 74:26

2r: ¹H NMR (300 MHz, CDCl₃) δ/ppm: 4.05 (t, *J* = 6.66 Hz, 2H), 2.26 (t, *J* = 7.52 Hz, 2H), 1.62-1.54 (m, 4H), 1.39-1.10 (m, 12H), 0.94-0.83 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ/ppm: 174.10, 64.08, 34.51, 31.82, 29.29, 29.27, 29.24, 25.14, 22.70, 19.27, 17.22, 14.16, 13.81.

Ethyl 3-phenylpropanoate (2s) & ethyl 2-phenylpropanoate (2s'), 2s:2s' = 58:42

¹H NMR (300 MHz, CDCl₃) δ /ppm: **2s**: 7.27-7.14 (m, 5H), 4.21-4.03 (m, 2H), 2.91 (t, *J* = 7.8 Hz, 2 H), 2.57 (t, *J* = 7.8 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H); **2s**': 7.27-7.14 (m, 5H), 4.21-4.03 (m, 2H), 3.71 (q, *J* = 7.2 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ /ppm:174.64, 173.01, 140.80, 140.68, 128.67, 128.57, 128.40, 127.56, 127.14, 126.32, 45.65, 36.06, 31.08, 31.08, 18.70, 14.30, 14.21.

Butyl 3-phenylpropanoate (2t) & butyl 2-phenylpropanoate (2t'), 2t:2t' = 64:36

¹H NMR (300 MHz, CDCl₃) δ /ppm: **2t**: 7.27-7.14 (m, 5H), 4.04-4.00 (m, 2H), 2.90 (t, J = 7.8 Hz, 2H), 2.58 (t, J = 7.8 Hz, 2H), 1.57-1.47 (m, 2H), 1.32-1.21 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H); **2t**²: 7.27-7.14 (m, 5H), 4.04-4.00 (m, 2H), 3.67 (q, J = 7.2 Hz, 1H), 1.46 (d, J = 7.2 Hz, 3H), 1.57-1.47 (m, 2H), 1.32-1.21 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ /ppm: 174.64, 173.01, 140.80, 140.68, 128.67, 128.57, 128.40, 127.56, 127.14, 126.32, 60.81, 60.50, 45.66, 36.05, 31.08, 18.70, 14.31, 14.21.

6. NMR Spectra of Products

Methyl 3-phenylpropanoate (**2b**) & methyl 2-phenylpropanoate (**2b'**) ¹H NMR (300 MHz, CDCl₃):

~S 9 ~

0 & branched isomers

Methyl nonanoate (**2c**) & branched isomers ¹H NMR (300 MHz, CDCl₃):

Methyl undecanoate (2d) & branched isomers

¹H NMR (300 MHz, CDCl₃):

O O & branched isomers

Methyl hexanoate (2e) & branched isomers ¹H NMR (300 MHz, CDCl₃):

Methyl 3,5,5-trimethylhexanoate (**2f**) ¹H NMR (300 MHz, CDCl₃):

Methyl 4,4-dimethylpentanoate (**2g**) ¹H NMR (300 MHz, CDCl₃):

¹³C NMR (75 MHz, CDCl₃):

Methyl 3,4-dimethylpentanoate (2h) ¹H NMR (300 MHz, CDCl₃):

 $Methyl \ cyclohexane carboxylate \ (2i)$

¹H NMR (300 MHz, CDCl₃):

Methyl cyclooctanecarboxylate (**2j**) ¹H NMR (300 MHz, CDCl₃):

Methyl bicyclo[2.2.1]heptane-2-carboxylate (2k) ¹H NMR (300 MHz, CDCl₃):

Methyl 3-(4-methoxyphenyl)propanoate (21) & methyl 2-(4-methoxyphenyl)propanoate (21') ¹H NMR (300 MHz, CDCl₃):

Methyl 3-(4-chlorophenyl)propanoate (2m)

¹H NMR (300 MHz, CDCl₃):

~S 20 ~

Methyl 4-(1,3-dioxoisoindolin-2-yl)butanoate (2n) and methyl 3-(1,3-dioxoisoindolin-2-yl)-2-methylpropanoate (2n')

¹H NMR (300 MHz, CDCl₃):

~S 21 ~

Methyl 4-(4-methoxyphenyl)butanoate (20) and methyl 3-(4-methoxyphenyl)-2-methylpropanoate (20')

¹H NMR (300 MHz, CDCl₃):

~S 22 ~

Dimethyl decanedioate (**2p**) & branch isomers ¹H NMR (300 MHz, CDCl₃):

Ethyl 3-phenylpropanoate (2s) & ethyl 2-phenylpropanoate (2s') ¹H NMR (300 MHz, CDCl₃):

Butyl 3-phenylpropanoate (2t) & butyl 2-phenylpropanoate (2t') ¹H NMR (300 MHz, CDCl₃):

Reference

¹ Purification of Laboratory Chemical (Eds: Perrin, D. D.; Armarego, W. L. F.-). Pergamon Press, Oxford, **1988** *3*.