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Electronic Supplementary Information

for

Dual-Catalytic Decarbonylation of Fatty Acid Methyl Esters to Form Olefins

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1. General Considerations

All manipulations of air and water sensitive compounds were carried out under nitrogen in an MBraun Labmaster glovebox or by using standard Schlenk line techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AX400, AV500 or AM400. Chemical shifts (δ) for ^{1}H NMR spectra were referenced to the residual protons on deuterated chloroform (7.26 ppm) and ^{13}C NMR spectra were referenced to the residual chloroform (77.16 ppm). Mass spectrometry data were recorded on a Bruker BioTOF II ESI/TOF-MS. GC/MS spectral data were collected on a Hewlett Packard HP 6890 Series GC system accompanied by a Hewlett Packard 5973 Mass Selective Detector. The standard method used for all runs involved an initial oven temperature of 50 °C (held for 2 min) followed by a 20 °C min^{-1} ramp to 70 °C (held for 6 min), followed by a final 20 °C min^{-1} ramp to 230 °C (held for 3 min).

2. Materials

Dry and degassed 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) was used as received (Sigma-Aldrich). Liquid alcohols were dried over activated molecular sieves and degassed with three freeze-pump-thaws before bringing them into the glovebox for use. Solid alcohols, ligands, and metals were used as received. $CDCl_3$ was used as received from Cambridge Isotope Laboratories. Palmitic acid (TCI America), oxalyl chloride (Sigma Aldrich), thionyl chloride (Sigma Aldrich), triethylamine (Sigma Aldrich), magnesium sulfate (Sigma Aldrich), and dimethylformamide (Sigma Aldrich) were used as received. Carbon monoxide was used as received. Solvents (methanol, ethyl acetate, and hexanes) were purchased from Sigma Aldrich and used as received. Solvents for air sensitive reactions (tetrahydrofuran and dichloromethane) were purchased from Sigma Aldrich, sparged with ultrahigh purity (UHP) grade argon and passed through columns containing Q-5 and molecular sieves into a Schlenk flask for use.

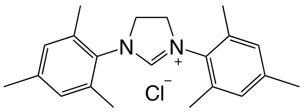
2.1. Structures, names, and vendors for materials used in this study.

Metals:
$Ru_3(CO)_{12}$ (Sigma Aldrich)
[Ru(*p*-cymene)$Cl_2]_2$ (Sigma Aldrich)
Ru(COD)(methylallyl)$_2$ (Acros)
Ru(C_5Me_5) (COD)$_2$Cl (Sigma Aldrich)
$[Ru(CO)_3Cl_2]_2$ (Sigma Aldrich)
$FeCl_2$ (Sigma Aldrich)
$Fe(CO)_3(PPh_3)_2$ (synthesized according to ref[1])
$[(C_5H_5)Fe(CO)_3]_2$ (Strem Chemicals)
$CoCl_2$ (Strem)
$Co_2(CO)_8$ (Strem Chemicals)
$NaCo(CO)_4$ (synthesized according to ref[3])
$Cr(C_6H_6)_2$ (Sigma Aldrich)
$CrCl_3$ (Sigma Aldrich)
$PdCl_2$ (Strem Chemicals)
$Pd(PPh_3)_4$ (Sigma Aldrich)
$Pd_2(dba)_3$ (dba = dibenzylideneacetone)
$NiCl_2$ (Sigma Aldrich)
$Ni(OAc)_2$ (Sigma Aldrich)
$Ni(COD)_2$ (Alfa Aesar)
$Ni(PPh_3)_4$ (synthesized according to ref[2])
$[Rh(COD)Cl]_2$ (Strem Chemicals)
$[Rh(COD)_2]$OTf (Sigma Aldrich)
$VCl_3(THF)_3$ (Aldrich)
$Mn(acac)_2$ (Sigma Aldrich)
$Os_3(CO)_{12}$ (VWR)
$[Ir(COD)Cl]_2$ (Sigma Aldrich)
$Na[(C_5H_5)Mo(CO)_3]$ (Sigma Aldrich)

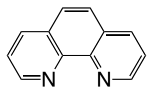
Lewis Acids
$ZnCl_2$ (Fisher Scientific or Sigma Aldrich)
$CuCl_2$ (Strem Chemicals)
Mol sieves (4 angstrom) (Acros)
$InCl_3$ (Sigma Aldrich)
MgO (Sigma Aldrich)
CeO_2 (Sigma Aldrich)
ZnO (Sigma Aldrich)
$LaCl_3$ (Alfa Aesar)
p-TsOH (Sigma Aldrich)
LiCl (Fisher Scientific)
KI (Sigma Aldrich)

NaOAc (Sigma Aldrich) Al(O^{i}Pr)$_3$ (Strem Chemicals)

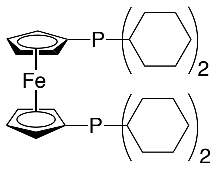
Ligands



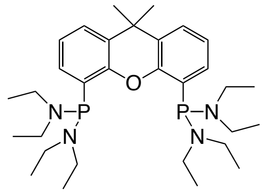
1,3-Bis(2,4,6-trimethylphenyl)
imidazolium chloride
Protonated SIMes
Sigma Aldrich



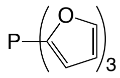
Phenanthroline
L1
(Sigma Aldrich)



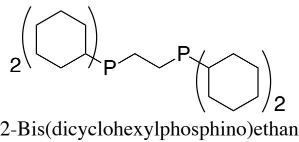
1,1'-Bis(dicyclohexylphosphino)
ferrocene
L2
Alfa Aesar



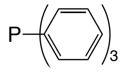
P,P'-(9,9-Dimethyl-9H-xanthene-
4,5-diyl)bis[N,N,N',N'-tetraethyl-
phosphonous diamide]
L3
Sigma Aldrich



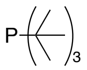
Tri(2-furyl)phosphine
P(furyl)$_3$
Oakwood Products



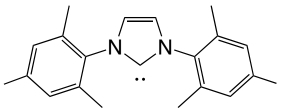
1,2-Bis(dicyclohexylphosphino)ethane
dcype
Alfa Aesar



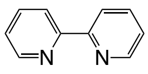
Triphenylphosphine
PPh$_3$
Sigma Aldrich



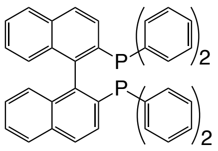
Tri-tert-butylphosphine
P(^{t}Bu)$_3$
(Sigma Aldrich)



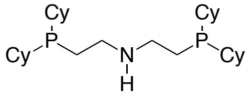
1,3-Bis(2,4,6-trimethylphenyl)-1,3-
dihydro-2H-imidazol-2-ylidene
IMes
Sigma Aldrich



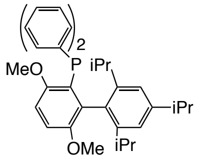
2,2'-Bipyridine
Bipy
Alfa Aesar



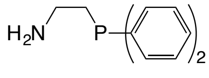
(R)-(+)-2,2'-Bis(diphenyl
phosphino)-1,1'-binaphthyl
BINAP
Alfa Aesar



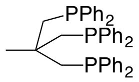
Bis[2-(dicylohexylphosphino)
ethyl]amine
L4
(Strem Chemical)



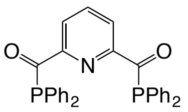
2-(Dicyclohexylphosphino)
3,6-dimethoxy-2',4',6'-triisopropyl-
1,1'-biphenyl
BrettPhos
Sigma Aldrich



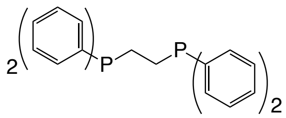
2-(diphenylphosphino)ethylamine
L5
Sigma Aldrich



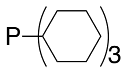
1,1,1-tris(diphenylphosphino
methyl)ethane
L6
Sigma Aldrich



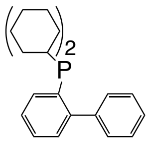
pyridine-2,6-diylbis(diphenyl
phosphino)methanone
L7
(synthesized according to ref[4])



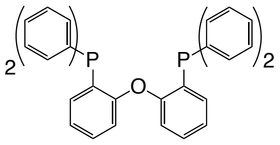
1,2-Bis(diphenylphosphino)ethane
dppe
Sigma Aldrich



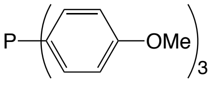
Tricyclohexylphosphine
PCy$_3$
Sigma Aldrich



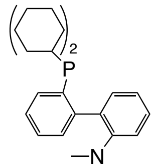
2-(Dicyclohexylphosphino)
biphenyl
CyJohnPhos
Sigma Aldrich



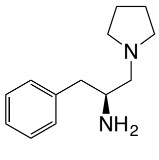
(Oxydi-2,1-
phenylene)bis(diphenylphosphine)
DPEPhos
Sigma Aldrich



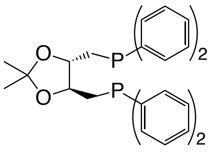
Tris(4-methoxyphenyl)phosphine
P(4-C$_5$H$_4$OMe)
Alfa Aesar



2-Dicyclohexyphosphino-2'-
(N,N-dimethylamino)biphenyl
DavePhos
Matrix Scientific

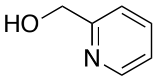


(S)-α-(Phenylmethyl)-1-
pyrrolidinethanamine
L8
Sigma Aldrich

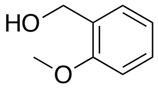


(+)-2,3-*O*-Isopropylidene-,2,3-dihydroxy-
1,4-bis(diphenylphosphino)butane
DIOP
Alfa Aesar

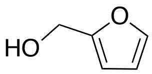
Alcohols



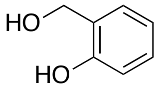
2-pyridine
methanol
Sigma Aldrich



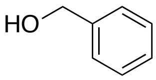
2-methoxybenzyl
alcohol
Alfa Aesar



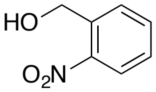
furfuryl
alcohol
Alfa Aesar



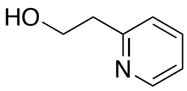
2-hydroxybenzyl
alcohol
Alfa Aesar



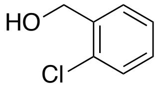
benzyl
alcohol
Sigma Aldrich



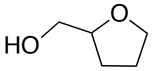
2-nitrobenzyl
alcohol
Acros



2-(2-hydroxyethyl)
pyridine
Sigma Aldrich



2-chlorobenzyl
alcohol
Oakwood



Tetrahydro
furfuryl alcohol
Acros

3. Synthesis

3.1. Synthesis of Methyl Palmitate (2). Palmitic acid (2.99 g, 11.7 mmol, 1.0 equiv) was weighed into a round bottom flask (100 mL). Methanol (~15 mL) was then added to the round bottom and the mixture was stirred at room temperature. Using a syringe, thionyl chloride (0.9 mL, 12.4 mmol, 1.1 equiv) was added dropwise to the reaction mixture. The solution was refluxed overnight (~16 h) at 66 °C. The solvent was removed using a rotary evaporator and the residue was dissolved in ethyl acetate (100 mL). The solution was washed with saturated sodium bicarbonate solution (2 x 50 mL) and brine (1 x 50 mL). The organic layer was then dried with magnesium sulfate, filtered, and concentrated. This process yielded methyl palmitate**2** as a white solid (3.08 g, 97% yield). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 3.66 (s, 3H, OCH_3), 2.30 (t, 2H, *J* = 7.6 Hz, C(O)CH_2), 1.60 (q, 2H, *J* = 7.3 Hz, –CH_2–), 1.33–1.21 (m, 24H, –CH_2–), 0.88 (t, 3H, *J* = 6.9 Hz, CH_3). **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$):** δ 174.45, 51.55, 34.26, 32.08, 29.84, 29.82, 29.80, 29.75, 29.60, 29.51, 29.41, 29.31, 25.11, 22.84, 14.26. **HRMS:** Calculated m/z for $C_{17}H_{34}O_2Na$ = 293.2451, found = 293.2447.

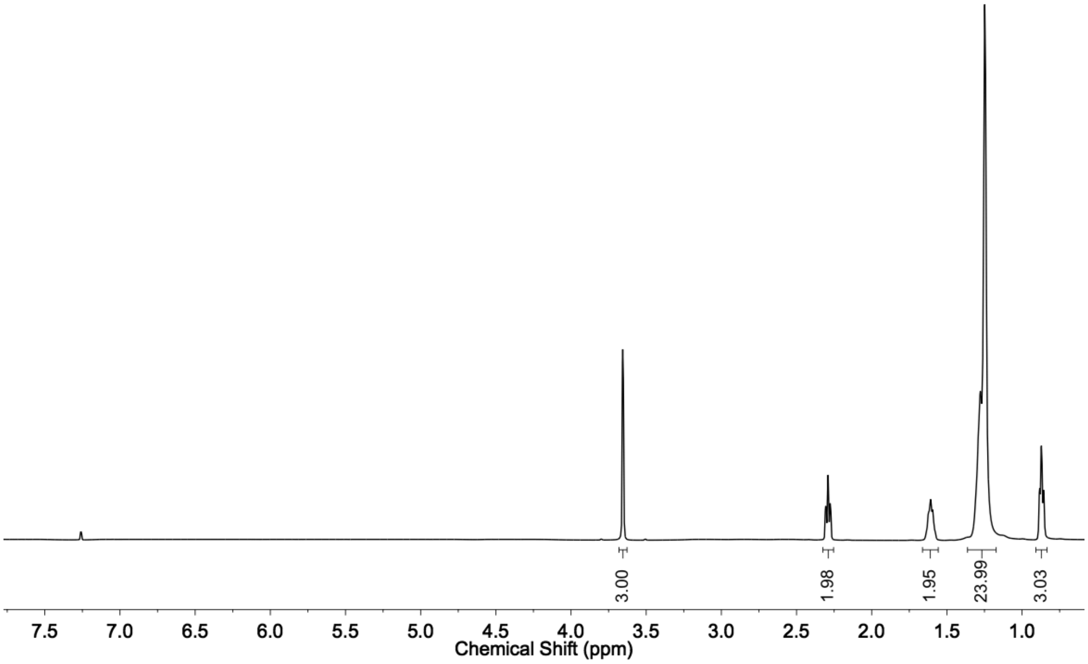


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of methyl palmitate (**2**).

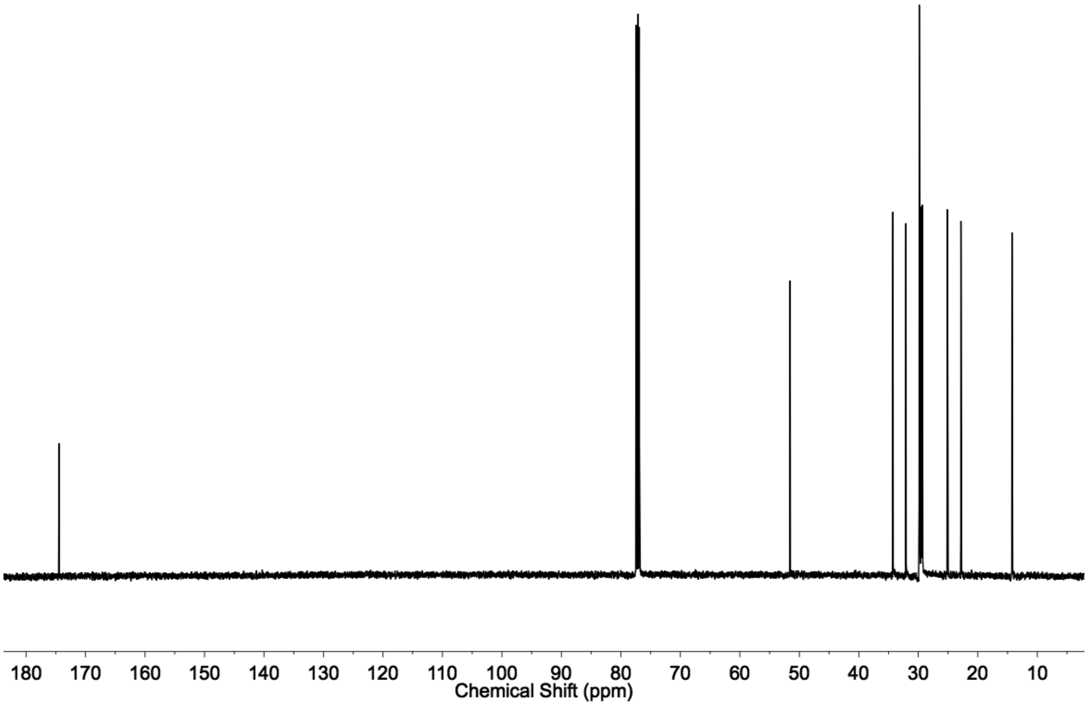


Figure S2. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) spectrum of methyl palmitate (**2**).

3.2. Synthesis of Donor Group Esters. To a stirred solution of palmitic acid (5.0 g, 19.9 mmol, 1.0 equiv) in dry CH_2Cl_2 (*ca.* 50 mL) under N_2 atmosphere was added oxalyl chloride (2.0 mL, 24.0 mmol, 1.2 equiv) dropwise using a syringe followed by DMF (*ca.* 3 drops). The mixture was allowed to stir at room temperature under N_2 for 3 h. After 3 h, solvent was removed under vacuum. The remaining residue was dissolved in dry THF (*ca.* 100 mL). NEt_3 (2.7 mL, 19.4 mmol, 1.0 equiv) and alcohol (22.8 mmol, 1.15 equiv) were added. The reaction was allowed to stir at room temperature for *ca.* 48 h. During this time, the reaction mixture showed the presence of a pale yellow precipitate. The reaction mixture was filtered to remove the precipitate and the filtrate was concentrated on a rotatory evaporator. If the ester obtained was not pure (remaining alcohol present as judged by ^{1}H NMR spectroscopy), the crude product was dissolved in 10% EtOAc in hexanes and filtered through a pad of silica.

Pyridin-2-ylmethyl Palmitate (1). Off-white to tan powder (5.65 g, 82% yield). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.61 (d, 1H, *J* = 4.9 Hz, Ar–*H*), 7.73 (t, 1H, *J* = 7.6 Hz, Ar–*H*), 7.37 (d, 1H, *J* = 7.6 Hz, Ar–*H*), 7.25 (t, 1H, Ar–*H*), 5.25 (s, 2H, Ar–CH_2), 2.42 (t, 2H, *J* = 7.5 Hz, C(O)CH_2), 1.67 (q, 2H, *J* = 7.3 Hz, –CH_2–), 1.36–1.22 (m, 24H, –CH_2–), 0.88 (t, 3H, *J* = 6.8 Hz, CH_3). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$):** δ 173.60, 156.12, 149.57, 136.86, 122.92, 121.87, 66.75, 34.36, 32.06, 29.83, 29.81, 29.79, 29.73, 29.59, 29.50, 29.39, 29.28, 25.07, 22.83, 14.26. **HRMS:** Calculated m/z for $C_{22}H_{37}NO_2Na$ = 370.2716, found = 370.2710.

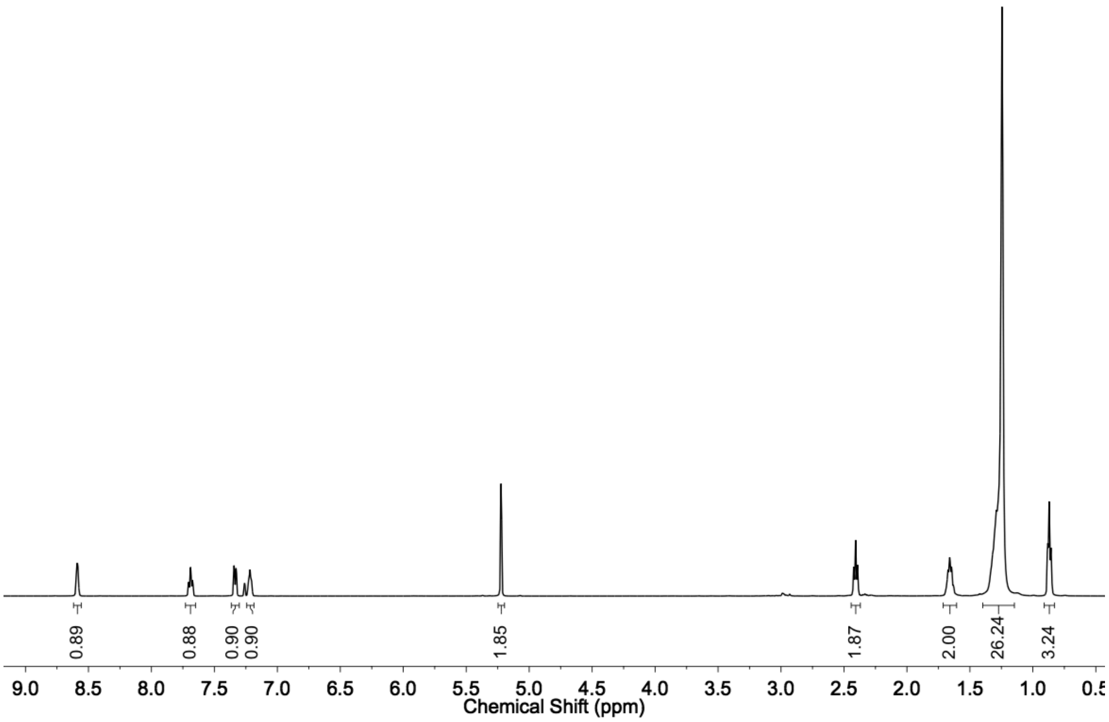


Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of pyridin-2-ylmethyl palmitate (**1**).

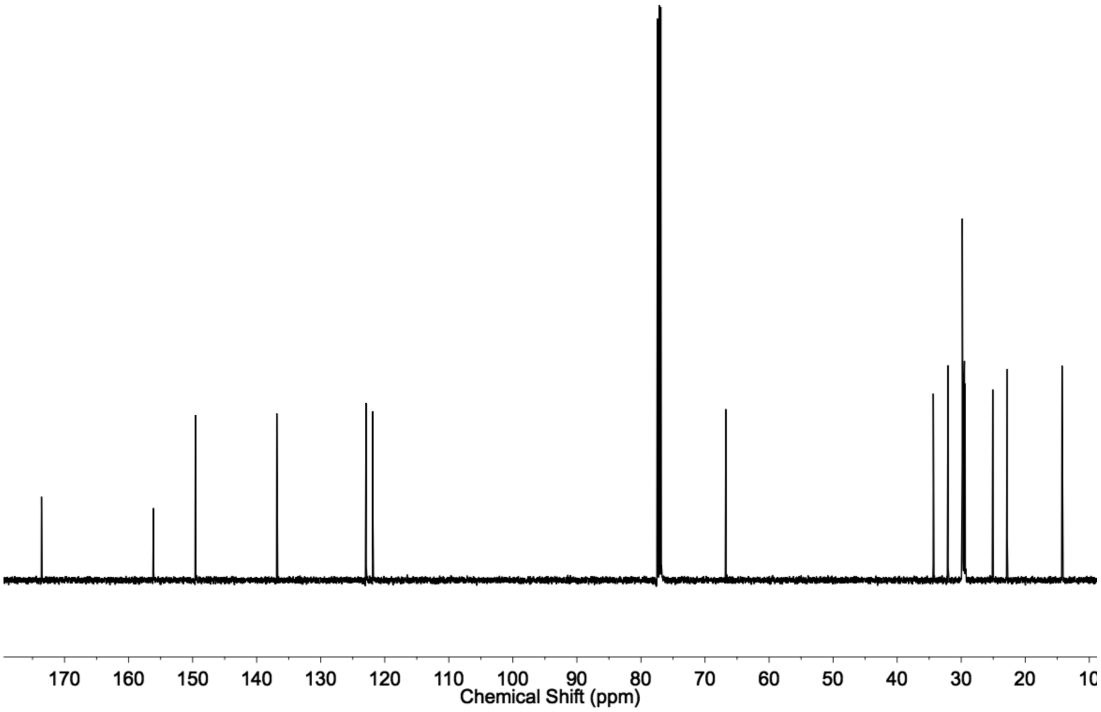


Figure S4. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) spectrum of pyridin-2-ylmethyl palmitate (**1**).

Benzyl Palmitate (4). Performed at a smaller scale (2.0 g palmitic acid) in which all materials are scaled the same as the general method described above. Colorless solid (0.86 g, 32% yield). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 7.42–7.32 (m, 5H, Ar–*H*), 5.14 (s, 2H, Ar–C*H*$_2$), 2.38 (t, 2H, *J* = 7.5 Hz, C(O)C*H*$_2$), 1.66 (q, 2H, *J* = 7.4 Hz, –C*H*$_2$–), 1.42–1.20 (m, 24H, –C*H*$_2$–), 0.91 (t, 3H, *J* = 6.8 Hz, C*H*$_3$). **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$):** δ 173.84, 136.30, 128.67, 128.30, 128.29, 66.19, 34.50, 32.08, 29.85, 29.83, 29.81, 29.74, 29.61, 29.52, 29.40, 29.29, 25.12, 22.85, 14.28. **HRMS:** Calculated m/z for $C_{22}H_{38}O_2Na$ = 369.2764, found = 369.2751.

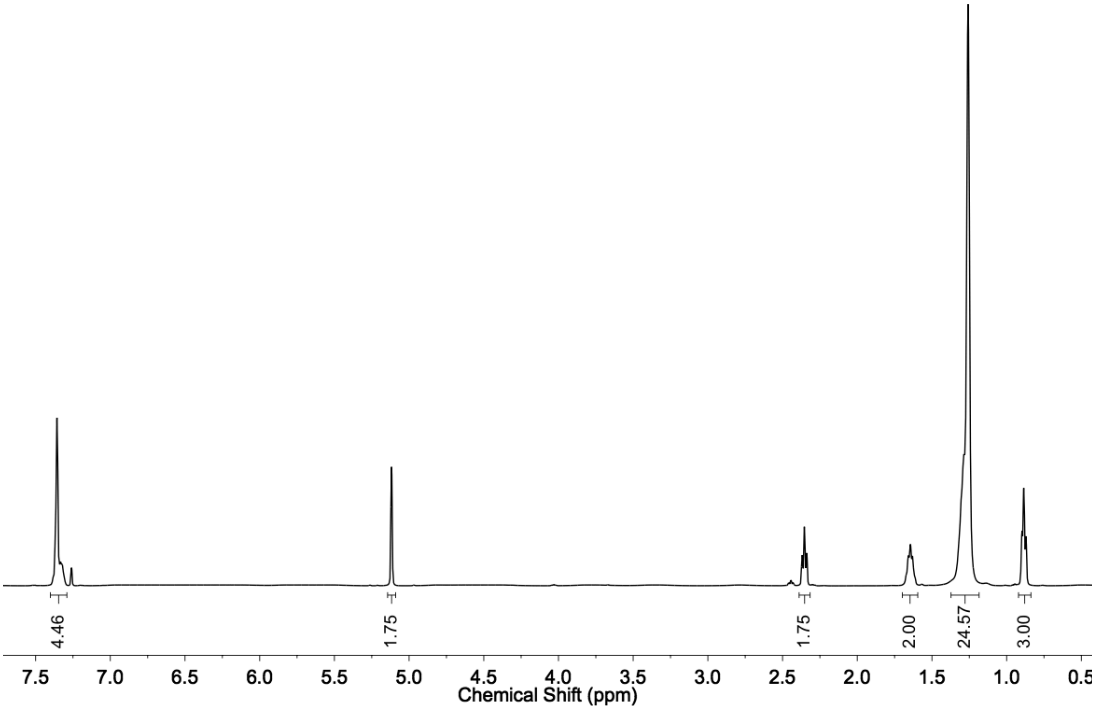


Figure S5. ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of benzyl palmitate (**4**).

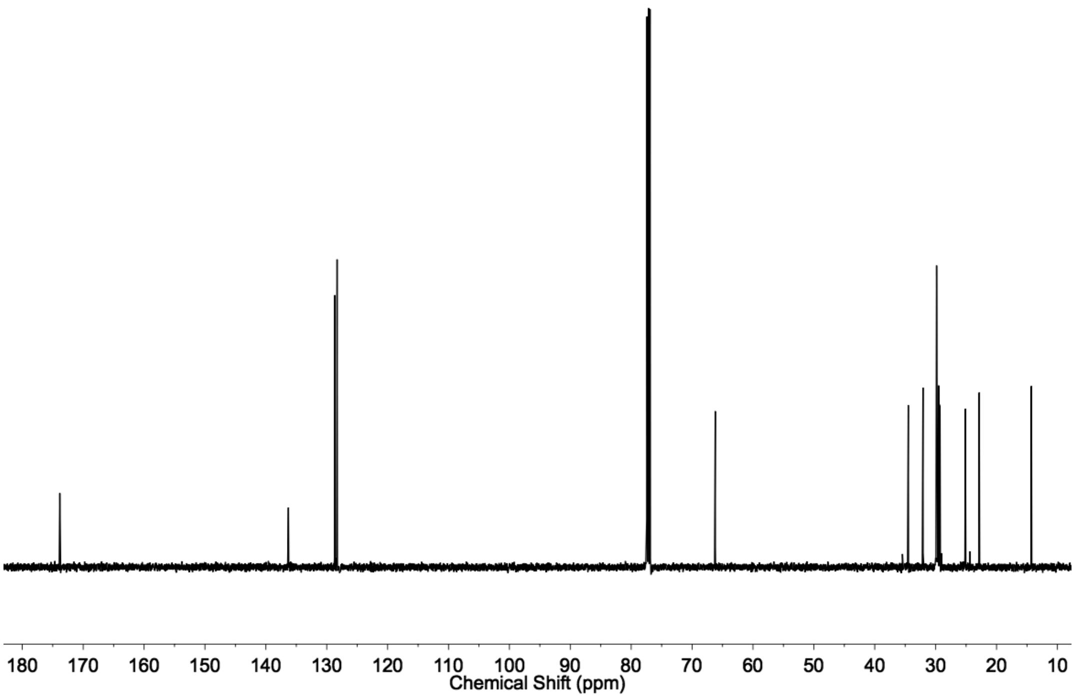


Figure S6. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) spectrum of benzyl palmitate (**4**).

4. High Throughput Experiment Design

4.1 High throughput screening (general procedures). All high throughput experiments were performed using a Freeslate Core Module 3^{TM} (CM3) under a N_2 atmosphere in an MBraun glovebox. Experiments were designed and executed using Library Studio^{TM} and Automation Studio^{TM} software. Reactions were performed in an Al rack containing 96 x 1mL glass vials. Ligands were dispensed as stock solutions in THF, and metal precursors were dispensed as solids or as solutions or slurries in THF (10–20 mg/mL). The solvent was then removed in vacuo using a ThermoSavant Speedvac vacuum centrifuge. Alcohols were added as liquids and then the esters were added as 0.6–1.5M M solutions in DMPU, robotically. The plates were sealed and heated to 180 °C and allowed to react for 18 hours. At the end of the experiments where olefin production was desired, the arrays were removed from the glovebox, cooled and analyzed for the presence of olefins using thin-layer chromatography (TLC, silica on glass as stationary phase, hexanes as mobile phase, and imaged using a potassium permanganate in water dye). For conditions considered promising, ^{1}H NMR experiments were performed on a Bruker AV500 spectrometer for presence of olefins. At the end of the experiments where donor group esters were the desired product, the arrays were removed from the glovebox, cooled and analyzed for the desired ester with ^{1}H NMR spectroscopy.

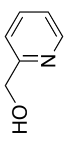
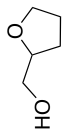
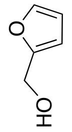
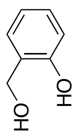
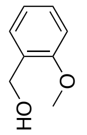
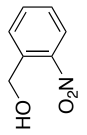
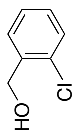
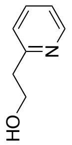
4.2. Results of high throughput screening experiments

Table S1. Screening of 24 different metal complexes and 4 ligands for the decarbonylation of **1**.[a]

	SIMes + KO^{t}Bu	PCy$_3$	Bipy	CyJohnPhos	SIMes + KO^{t}Bu	PCy$_3$	Bipy	CyJohnPhos	
$[RuCl_2(CO)_3]_2$	🟩		🟩						$PdCl_2$
$[Ru(p\text{-}cym)Cl_2]_2$		🟩			🟩	🟩	🟩	🟩	$Pd(PPh_3)_4$
Ru(COD)(methylallyl)$_2$	🟩	🟩	🟩	🟩					$Pd_2(dba)_3$
Cp*Ru(COD)Cl		🟩		🟩					$Ni(OAc)_2$
$FeCl_2$	🟩				🟩	🟩	🟩	🟩	Ni(COD)$_2$
$Fe(CO)_3(PPh_3)_2$						🟩		🟩	[Rh(COD)Cl]$_2$
$[CpFe(CO)_3]_2$		🟩		🟩	🟩	🟩	🟩	🟩	[Rh(COD)$_2$]OTf
$CoCl_2$									$VCl_3(THF)_3$
$Co_2(CO)_8$									$MnCl_2$
$NaCo(CO)_4$					🟩	🟩	🟩	🟩	[Ir(COD)Cl]$_2$
$Cr(C_6H_6)_2$									$Os_3(CO)_{12}$
$CrCl_3$									$Na[CpMo(CO)_3]$

[a] Conditions: pyridin-2-ylmethyl palmitate **1** (0.043 mmol, 1 equiv), metal complex (10 mol % per metal center), and ligand (10 mol %), in DMPU (0.053 mL) were heated at 180 °C for 18 h. Green boxes represent indication of olefin, using TLC, while white boxes had no indication of olefin formation.

Table S2. Screening of 8 directing group alcohols and 12 Lewis acids for the transesterification of **2** to directing group esters.[a]

								
$ZnCl_2$	33 %		9 %	34 %	11 %		19 %	30 %
ZnO	28 %	NA	10 %	31 %	15 %	NA		NA
$CuCl_2$		NA	NA	NA	NA	NA	NA	NA
$Sc(OTf)_3$	14 %					NA	NA	NA
$InCl_3$	29 %				42 %	22 %	31 %	
MgO	25 %		27 %		27 %	NA	NA	NA
CeO_2		NA	NA	NA	NA	NA	NA	NA
TsOH		NA	NA	NA	NA	NA	NA	NA
$Al(OTf)_3$		NA	NA	NA	NA	NA	NA	NA
$LaCl_3$	31 %		37 %		34 %	24 %	32 %	
Mol. Sieves		NA	NA	NA	NA	NA	NA	NA
Al_2O_3		NA	NA	NA	NA	NA	NA	NA

[a]Conditions: methyl palmitate **2** (0.074 mmol, 1 equiv), directing alcohol (1 equiv), and Lewis acid (10 mol %), in DMPU (0.066 mL) were heated at 180 °C for 18 h. Green boxes represent indication of the directing group ester, using ^1H NMR spectroscopy, at the percent conversion written in the box. Blank white boxes represent conditions with <1 % conversion to the directing group ester, and white boxes with NA indicate reactions not studied by ^1H NMR.

Table S3. Screening of 24 different ligands and 4 metal complexes for the decarbonylation of **1**.[a]

	$[CpFe(CO)_3]_2$	$Ni(COD)_2$	$[Rh(COD)_2](OTf)$	$Os_3(CO)_{12}$	$[CpFe(CO)_3]_2$	$Ni(COD)_2$	$[Rh(COD)_2](OTf)$	$Os_3(CO)_{12}$	
No Ligand		🟩	🟩						IMes
dcype		🟩	🟩			🟩			dppe
SIMes + KO^{t}Bu		🟩	🟩			🟩	🟩		BINAP
$P(furyl)_3$		🟩							BrettPhos
DPEPhos	🟩	🟩	🟩				🟩		L5
PCy_3		🟩				🟩	🟩		L6
CyJohnPhos		🟩	🟩			🟩			PPh_3
Bipy						🟩			DIOP
L8									L7
$P(4-C_5H_4OMe)$		🟩							L4
DavePhos			🟩						$P(^tBu)_3$
L1						🟩	🟩	🟩	L3

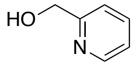
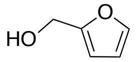
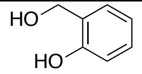
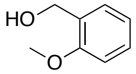
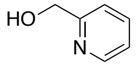
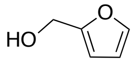
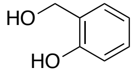
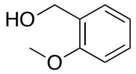
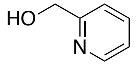
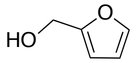
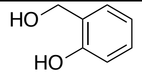
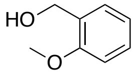
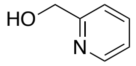
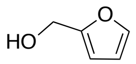
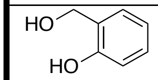
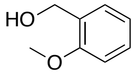
[a] Conditions: pyridin-2-ylmethyl palmitate **1** (0.043 mmol, 1 equiv), metal complex (10 mol % per metal center), and ligand (10 mol %), in DMPU (0.053 mL) were heated at 180 °C for 18 h. Green boxes represent indication of olefin, using TLC, while white boxes had no indication of olefin formation.

Table S4. Screening the effect of Lewis acids on the decarbonylation of **1**.[a]

	$ZnCl_2$	ZnO	$Sc(OTf)_3$	$LaCl_3$	$InCl_3$	MgO
$[Rh(COD)Cl]_2/PCy_3$		🟩	🟩	🟩	🟩	🟩
$[Rh(COD)_2](OTf)/PCy_3$		🟩		🟩	🟩	
$Os_3(CO)_{12}/PCy_3$						
$[CpRu(CO)Cl]_2/PCy_3$						
[Ru(*p*-cymene)$Cl_2]_2/PCy_3$						
$[Ru(CO)_3Cl_2]_2$	🟩	🟩	🟩	🟩	🟩	🟩
$Ni(COD)_2$/SIMes+KO^tBu	🟩		🟩	🟩		🟩
$[CpFe(CO)_3]_2$/bipy						

[a]Conditions: pyridin-2-ylmethyl palmitate **1** (0.058 mmol, 1 equiv), metal complex (10 mol % per metal center), ligand (10 mol %), and Lewis acid (20 mol %) in DMPU (0.072mL) were heated at 180 °C for 18 h. Green boxes represent indication of olefin, using TLC, while white boxes had no indication of olefin formation.

Table S5. Screening promising metal/ligand combinations, directing group alcohols, and Lewis acids for the dual-catalytic decarbonylation of **2**.[a]

	$Ni(COD)_2$/ SIMes + KO^tBu	$[Rh(COD)_2]OTf$ /SIMes + KO^tBu	$[Ru(CO)_3Cl_2]_2$/ SIMes+KO^tBu	$Os_3(CO)_{12}$/ SIMes + KO^tBu	$Ni(COD)_2$/ DPEPhos	$Ni(COD)_2$/ PPh_3	
	🟩	🟩					$ZnCl_2$
					🟩		
							
		🟩			🟩		
			🟩				ZnO
		🟩					
		🟩					
		🟩			🟩		
	🟩						$InCl_3$
	🟩						
	🟩						
	🟩						
						🟩	$LaCl_3$
							
					🟩	🟩	
						🟩	

[a]Conditions: methyl palmitate **2** (0.074 mmol, 1 equiv), metal complex (20 mol % per metal center), ligand (20 mol %), directing group alcohol (0.074 mmol, 1 equiv) and Lewis acid (40 mol %) in DMPU (0.065 mL) were heated at 180 °C for 18 h. Green boxes represent indication of olefin, using TLC, while white boxes had no indication of olefin formation.

5. Representative Bulk Catalysis Reactions

Vial bulk reactions. In a N_2-filled glovebox, an 8 mL vial equipped with a magnetic stir bar was charged with substrate (0.31 mmol, 1.0 equiv), catalyst (15 mol % metal content), ligand (15 mol %), and Lewis acid (25 mol %). Anhydrous DMPU (0.5 mL) was added and the reaction vial was sealed with a Teflon lined cap. The vial was removed from the glovebox and allowed to stir at 190 °C for 20 h in a preheated oil bath. After 20 h, the vial was removed from the oil bath and allowed to cool to room temperature. The reaction was quenched with 1M HCl (*ca.* 7 mL). The solution was extracted with EtOAc (3 x 1 mL). The organic layer was washed with brine (1 x 5 mL) and then dried over $MgSO_4$. $MgSO_4$ was removed and the solvent was removed via rotatory evaporation. The residue was dissolved in minimal $CDCl_3$ and an aliquot was used for analysis by ^1H NMR spectroscopy. Conversion to olefins was determined based on unreacted starting material. All conditions were at least run in duplicate. If two runs did not agree within 5% conversion, additional runs were performed until a statistically reasonable result was obtained. All reactions were performed in vials unless otherwise specified.

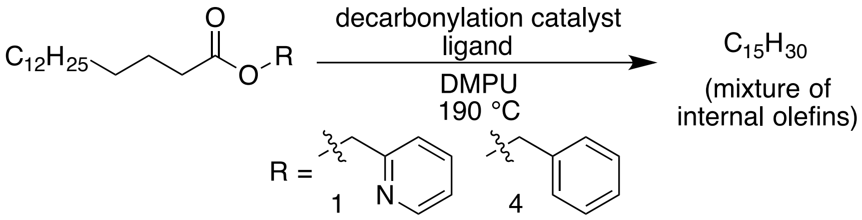
Pressure flask reactions. Reactions were performed analogous to the vial reactions but were performed in 35 mL pressure vessels (Synthware Glassware).

Reflux apparatus reactions. In a glovebox, a 25 mL round bottom flask equipped with a magnetic stir bar was charged with reagents appropriate for the condition studied (described within the tables). Anhydrous DMPU was added. An adapter loaded with a drying agent (molecular sieves, drierite, $MgSO_4$) was added on top of the round bottom flask in some cases, followed by a reflux condenser and a septum. The setup was brought out of the box and added to a Schlenk line under a positive N_2 pressure. The reaction solution was allowed to stir at 190 °C for 20 h in a preheated oil bath with water flow through the reflux condenser. After 20 h, the reaction setup was removed from the oil bath and allowed to cool to room temperature. The reaction was worked up analogous to the vial reactions.

6. Data for Catalysis Reactions

6.1. Decarbonylation

Scheme S1. Proposed decarbonylation reactions of esters.



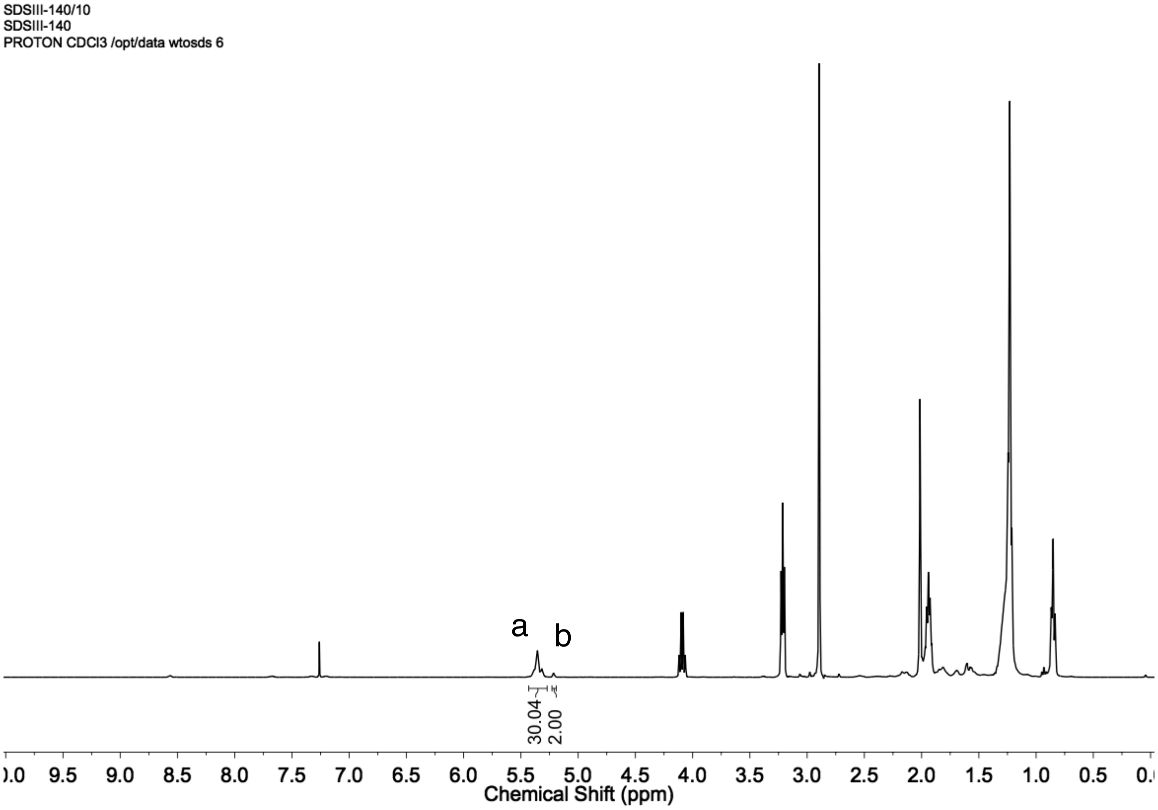


Figure S7. Representative ^{1}H NMR (400 mHz, $CDCl_3$) spectrum of products from decarbonylation (from Table S8, entry 11, where a represents the pentadecene products and b represents pyridin-2-ylmethyl palmitate).

Table S6. Decarbonylation reactions of pyridin-2-ylmethyl palmitate ester (**1**) with metal complexes (without ligands)[a]

entry	catalyst	conv. to olefins[b] (%)
1	$Ru_3(CO)_{12}$	48
2	$PdCl_2$	8
3	$[Rh(COD)Cl]_2$	9
4	$FeCl_2$	<1
5	$Fe(PPh_3)_2(CO)_3$	<1
6	$Ni(PPh_3)_4$	<1
7	$NiCl_2$	<1
8	$Pd(PPh_3)_4$	<1

[a] Conditions: pyridin-2-ylmethyl palmitate **1** (0.31 mmol, 1 equiv) and catalyst (15% metal content) were heated in DMPU at 190 °C for 20 h. Catalyst % is calculated per metal center (i.e. 15% Ru content = 5 mol % $Ru_3(CO)_{12}$). [b] Conversion of ester was determined by ^1H NMR spectroscopy.

Table S7. Decarbonylation reactions of the pyridin-2-ylmethyl palmitate (**1**) with metal complexes and ligands found to be promising in high throughput studies.[a]

entry	catalyst	ligand	conv. to olefins[b] (%)
1	$Ru_3(CO)_{12}$	PPh_3	65
2	$Ru_3(CO)_{12}$	DPPE	<1
3	$Ru_3(CO)_{12}$	SIMes[c]	46
4	$Ru_3(CO)_{12}$	DPEPhos	21
5	$Ru_3(CO)_{12}$	PCy_3	72
6	$[Ru_2(CO)_3Cl_2]_2$	PCy_3	<1
7	$[Ru_2(CO)_3Cl_2]_2$	SIMes[c]	8
8	$[Rh(COD)_2][OTf]$	PCy_3	<1
9	$[Rh(COD)_2][OTf]$	DPEPhos	4
10	$[Rh(COD)_2][OTf]$	CyJohnPhos	6
11	$[Rh(COD)_2][OTf]$	DavePhos	<1
12	$[Rh(COD)_2][OTf]$	BINAP	5
13	$[Rh(COD)_2][OTf]$	L5	<1
14	$[Rh(COD)_2][OTf]$	L3	18
15	$[Rh(COD)_2][OTf]$	dcype	29
16	$[Rh(COD)Cl]_2$	PCy_3	15
17	$Pd(PPh_3)_4$	SIMes[c]	<1
18	$Ni(COD)_2$	PCy3	<1
19	$Ni(COD)_2$	SIMes[c]	2
20	$Ni(COD)_2$	CyJohnPhos	4
21	$Ni(COD)_2$	dcype	5
22	$Ni(COD)_2$	PPh_3	2
23	$Ni(COD)_2$	L3	2
24	$Ni(COD)_2$	dppe	5
25	$Ni(COD)_2$	BINAP	<1
26	$Ni(COD)_2$	DPEPhos	<1
27	$Ni(COD)_2$	DIOP	9
28	$Ni(COD)_2$	L6	9
29	$Ni(COD)_2$	$P(furyl)_3$	9

[a] Conditions: pyridin-2-ylmethyl palmitate **1** (0.31 mmol, 1 equiv), catalyst (15% metal content), and ligand (15 mol %) were heated in DMPU at 190 °C for 20 h. Catalyst % is calculated per metal center (i.e. 15% Ru content = 5 mol % $Ru_3(CO)_{12}$). [b] Conversion of ester was determined by ^1H NMR spectroscopy. [c] SIMes generated by the deprotonation of 1,3-dimesitylimidazolium chloride with 1 equiv KO^tBu.

Table S8. Control decarbonylation reactions of **1** or **4** under various conditions with the $Ru_3(CO)_{12}/PCy_3$ catalyst system.[a]

entry	substrate	conv. to olefins[b] (%)
1[c]	**1**	43
2[d]	**1**	92
3	**4**	2
4[d]	**4**	2
5[e]	**1**	69
6[f]	**1**	62
7[g]	**1**	64
8[h]	**1**	53
9[i]	**1**	12
10[i,j]	**1**	51
11[k]	**1**	95

[a]Conditions unless stated otherwise: substrate **1** or **4** (0.31 mmol, 1 equiv), $Ru_3(CO)_{12}$ (15% metal content), and PCy_3 (15 mol %) were heated in DMPU at 190 °C for 20 h. Catalyst % is calculated per metal center (i.e. 15% Ru content = 5 mol % $Ru_3(CO)_{12}$). [b]Conversion of ester was determined by ^1H NMR spectroscopy. [c]20 mol % 2-pyridinemethanol was added. [d]25 mol % $ZnCl_2$ was added. [e]Three molecular sieves were added to the reaction vessel (4Å). [f]25 mol % ZnO was added. [g]25 mol % $LaCl_3$ was added. [h]30 mol % PCy_3 was added. [i]Lower catalyst and ligand concentrations were used (5 mol % Ru and PCy_3). [j]Reaction was heated for 40 hours. [k]Reaction performed in a 35 mL pressure vessel.

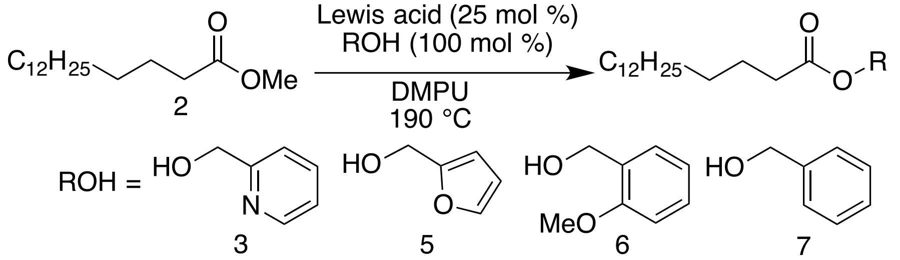
Table S9. Control decarbonylation reactions of **1** in the presence of MeOH.[a]

entry	catalyst	ligand	Conversion to olefins/methyl ester (%)[b]
1	$Ru_3(CO)_{12}$	PCy_3	28 / 42
2[c]	$Ru_3(CO)_{12}$	PCy_3	25 / 69
3[c]	none	none	<1 / 53

[a]Conditions: pyridin-2-ylmethyl palmitate **1** (0.31 mmol, 1 equiv), catalyst (15% metal content), ligand (15 mol %), and MeOH (1 equiv) were heated in DMPU at 190 °C for 20 h. Catalyst % is calculated per metal center (i.e. 15% Ru content = 5 mol % $Ru_3(CO)_{12}$). [b]Conversion of ester was determined by ^1H NMR spectroscopy. [c]25 mol % $ZnCl_2$ was added.

6.2. Transesterification

Scheme S2. Proposed transesterification of methyl palmitate (**2**) with different alcohols to form new esters with donor groups.



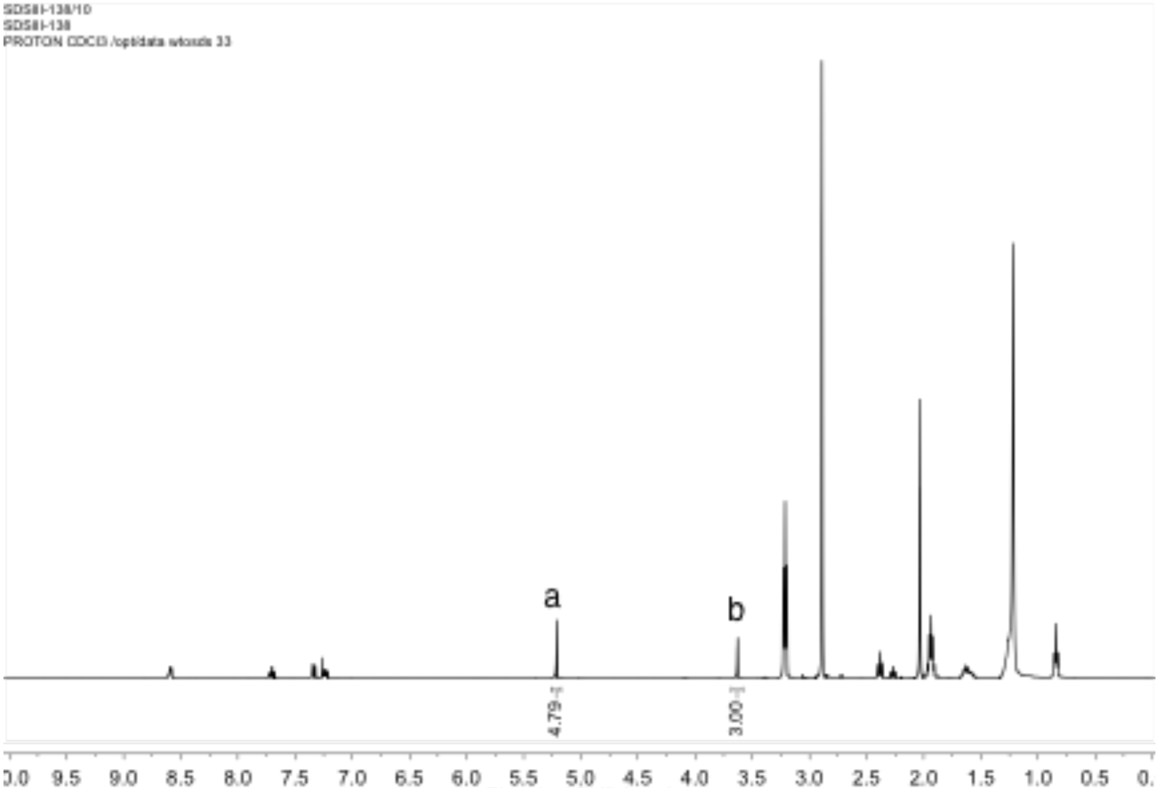


Figure S8. Representative ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of products from transesterification (Table S11, entry 8, where a represents pyridin-2-ylmethyl palmitate and b represents methyl palmitate).

Table S10. Transesterification of methyl palmitate (**2**) and 2-pyridinemethanol (**3**) with various Lewis acids.[a]

entry	Lewis Acid	conv. to **1**[b] (%)
1	none	34
2	$ZnCl_2$	40
3	ZnO	37
4	$LaCl_3$	39
5	$InCl_3$	12
6	LiCl	32
7	KI	20
8	NaOAc	45
9	$Al(O^iPr)_3$	26

[a] Conditions: methyl palmitate **2** (0.31 mmol, 1 equiv), Lewis acid (25 mol %), and 2-pyridinemethanol **3** (100 mol %) in DMPU (0.5 mL) were heated at 190 °C for 20 h. [b] Conversion of methyl ester was determined by ^{1}H NMR spectroscopy.

Table S11. Control reactions for the transesterification of methyl palmitate (**2**) with various alcohols.[a]

entry	Lewis Acid	alcohol	time (h)	conv. to donor ester[b] (%)
1	$ZnCl_2$	**3**	1 h	<1
2	$ZnCl_2$	**3**	2 h	16
3	$ZnCl_2$	**3**	4 h	18
4	$ZnCl_2$	**3**	20 h	40
5[c]	none	**3**	20 h	8
6[c]	$ZnCl_2$	**3**	20 h	16
7[d]	$ZnCl_2$	**3**	20 h	50(44–61)[e]
8[f]	$ZnCl_2$	**3**	20 h	67
9[g]	$ZnCl_2$	**3**	20 h	4
10[h]	$ZnCl_2$	**3**	20 h	32
11	$ZnCl_2$	**7**	20 h	53
12	none	**7**	20 h	27

[a]Conditions unless specified otherwise: methyl palmitate **2** (0.31 mmol, 1 equiv), Lewis acid (25 mol %), and alcohol (100 mol %) in DMPU (0.5 mL) were heated at 190 °C for 20 h. [b]Conversion of methyl ester was determined by ^{1}H NMR spectroscopy. [c]20 mol % 2-pyridinemethanol **3** added. [d]Three molecular sieves were added to the reaction vessel (4Å). [e]Reactions with molecular sieves were often inconsistent, and therefore the average conversion (range of conversions) is reported. [f]Reaction performed in a 35 mL pressure vessel. [g]Reaction heated at 100 °C. [h]Reaction heated at 150 °C.

Table S12. Transesterification reactions of methyl palmitate (**2**) with various alcohols and zinc Lewis acids.[a]

entry	Lewis Acid	alcohol	time (h)	temp (°C)	conv. to donor ester[b] (%)
1	$ZnCl_2$	**5**	20 h	190	5
2	$ZnCl_2$	**5**	20 h	150	10
3	$ZnCl_2$	**6**	20 h	190	44
4	$ZnCl_2$	**6**	20 h	150	12
5	ZnO	**3**	20 h	190	40
6	ZnO	**3**	20 h	150	28
7	ZnO	**5**	20 h	190	36
8	ZnO	**5**	20 h	150	15
9	ZnO	**6**	20 h	190	36
10	ZnO	**6**	20 h	150	31
11	ZnO	**6**	50 h	190	69

[a]Conditions unless specified otherwise: methyl palmitate **2** (0.31 mmol, 1 equiv), Lewis acid (25 mol %), and alcohol (100 mol %) in DMPU (0.5 mL) were heated at 190 °C for 20 h. [b]Conversion of methyl ester was determined by ^{1}H NMR spectroscopy.

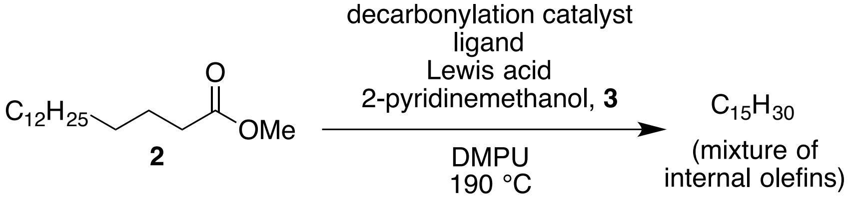
Table S13. Transesterification reactions of methyl palmitate (**2**) with various alcohols and Lewis acids ($InCl_3$ and $LaCl_3$).[a]

entry	Lewis Acid	alcohol	time (h)	temp (°C)	conv. to donor ester[b] (%)
1	$LaCl_3$	**3**	20 h	190	30
2	$LaCl_3$	**3**	20 h	150	25
3	$LaCl_3$	**5**	20 h	190	14
4	$LaCl_3$	**5**	20 h	150	26
5	$LaCl_3$	**6**	20 h	190	60
6	$LaCl_3$	**6**	20 h	150	38
7	$LaCl_3$	**6**	50 h	190	61
8	$InCl_3$	**3**	20 h	190	12
9	$InCl_3$	**3**	20 h	150	20
10	$InCl_3$	**5**	20 h	190	<1
11	$InCl_3$	**5**	20 h	150	<1
12	$InCl_3$	**6**	20 h	190	1
13	$InCl_3$	**6**	20 h	150	11

[a] Conditions: methyl palmitate **2** (0.31 mmol, 1 equiv), Lewis acid (25 mol %), and alcohol (100 mol %) in DMPU (0.5 mL) were heated at 190 °C for 20 h. [b] Conversion of methyl ester was determined by ^1H NMR spectroscopy.

6.3. Dual Catalysis

Scheme S3. Proposed dual-catalytic decarbonylation of methyl palmitate (**2**) to form olefin feedstocks.



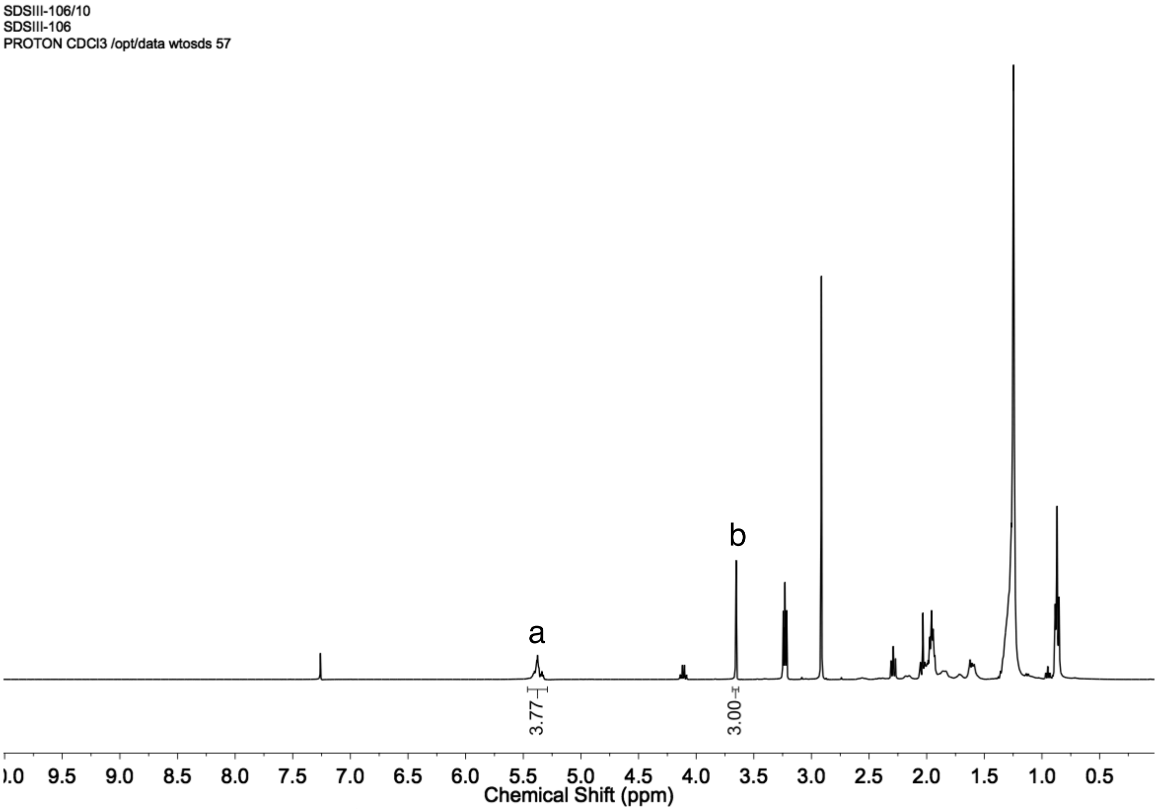


Figure S9. Representative ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of products from dual catalysis (from Table S16, entry 1, where a represents the pentadecene products and b represents methyl palmitate).

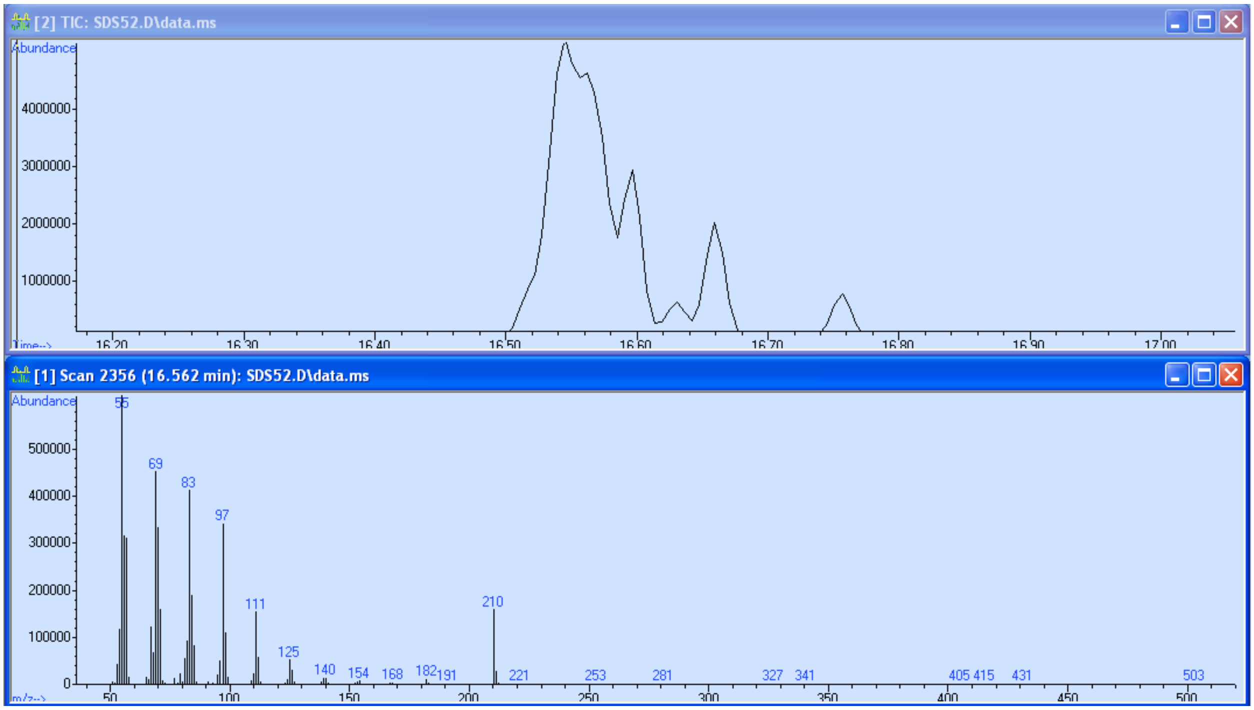


Figure S10. Representative GC-MS of olefin products from dual catalysis (from Table S16, entry 1).

Table S14. Time study of the dual-catalytic decarbonylation of methyl palmitate (**2**) with 2-pyridinemethanol (**3**).[a]

entry	time (h)	conv. to olefin[b] (%)	conv. to **1**[b] (%)
1	2	21	3
2	4	27	<1
3	6	30	1
4	8	32	1
5	14	40	<1
6	20	38	<1
7	24	31	<1
8	30	31	<1
9	40	43	<1

[a]Conditions: methyl palmitate **2** (0.31 mmol, 1 equiv), $ZnCl_2$ (25 mol %), $Ru_3(CO)_{12}$ (15 mol % per metal center), PCy_3 (15 mol %), and 2-pyridinemethanol **3** (20 mol %) in DMPU (0.5 mL) were heated at 190 °C. Catalyst % is calculated per metal center (i.e. 15% Ru content = 5 mol % $Ru_3(CO)_{12}$). [b]Conversion of methyl ester was determined by ^1H NMR spectroscopy.

Table S15. Control reactions of the dual-catalytic decarbonylation of methyl palmitate (**2**).[a]

entry	Lewis Acid (% loading)	alcohol (% loading)	conv. to olefin[b] (%)	conv. to donor ester[b] (%)
1	none	none	<1	<1
2	ZnCl$_2$ (25 %)	none	2	<1
3	none	**3** (20 %)	<1	<1
4	ZnCl$_2$ (50 %)	none	<1	<1
5[c]	ZnCl$_2$ (25 %)	**3** (20 %)	21	<1
6[d]	ZnCl$_2$ (25 %)	**3** (20 %)	44(34– 49)[e]	<1
7[d,f]	ZnCl$_2$ (25 %)	**3** (20 %)	52	<1
8	none	**3** (100 %)	12	6
9	ZnCl$_2$ (25 %)	**7** (20 %)	<1	5
10	ZnCl$_2$ (25 %)	**3** (40 %)	38	2
11	ZnCl$_2$ (25 %)	**3** (80 %)	21	9
12[g]	ZnCl$_2$ (25 %)	**3** (80 %)	37	2
13	ZnCl$_2$ (25 %)	**3** (120 %)	16	19
14[g]	ZnCl$_2$ (25 %)	**3** (120 %)	54	0
15	ZnCl$_2$ (1 equiv)	**3** (20 %)	38	<1
16	ZnCl$_2$ (2 equiv)	**3** (20 %)	<1	<1
17[d,g]	ZnCl$_2$ (25 %)	**3** (20 %)	50(37– 63)[e]	<1
18[h]	ZnCl$_2$ (25 %)	**3** (20 %)	35	<1
19[i]	ZnCl$_2$ (25 %)	**3** (20 %)	33	<1

[a]Conditions unless specified otherwise: methyl palmitate **2** (0.31 mmol, 1 equiv), ZnCl$_2$ (25 mol %), Ru$_3$(CO)$_{12}$ (15 mol % per metal center), PCy$_3$ (15 mol %), and alcohol (20 mol %) in DMPU (0.5 mL) were heated at 190 °C for 20 h. Catalyst % is calculated per metal center (i.e. 15% Ru content = 5 mol % Ru$_3$(CO)$_{12}$). [b]Conversion of methyl ester was determined by ^{1}H NMR spectroscopy. [c]No ligand was used. [d]Three molecular sieves were added to the reaction vessel (4Å). [e]Reactions with molecular sieves were often inconsistent, and therefore the average conversion (range of conversions) is reported. [f]30 mol % Ru$_3$(CO)$_{12}$ and PCy$_3$ were used. [g]Reaction heated for 40 h. [h]Reaction was conducted in an approx. 25 mL Schlenk flask, which was purged with CO gas and sealed prior to heating. [i]Reaction was conducted in a sealed approx. 25 mL Schlenk flask.

Table S16. Dual-catalytic decarbonylation of methyl palmitate (**2**) in a 35 mL pressure vessel.[a]

entry	conv. to olefin[b] (%)	conv. to **1**[b] (%)
1	64	<1
2[c]	48(22– 85)[d]	<1
3[e]	49	<1
4[f]	36	<1
5[c,f]	36(31– 42)[d]	6

[a]Conditions unless specified otherwise: methyl palmitate **2** (0.31 mmol, 1 equiv), $ZnCl_2$ (25 mol %), $Ru_3(CO)_{12}$ (15 mol % per metal center), PCy_3 (15 mol %), and 2-pyridinemethanol **3** (20 mol %) in DMPU (0.5 mL) were heated at 190 °C for 20 h. Catalyst % is calculated per metal center (i.e. 15% Ru content = 5 mol % $Ru_3(CO)_{12}$). [b]Conversion of methyl ester was determined by ^{1}H NMR spectroscopy. [c]Three molecular sieves were added to the reaction vessel (4Å). [d]Reactions with molecular sieves were often inconsistent, and therefore the average conversion (range of conversions) is reported. [e]Reactions were heated for 40 h. [f]Reactions were at 4x the standard scale (1.24 mmol of **2**).

Table S17. Dual-catalytic decarbonylation of methyl palmitate **2** in a 25 mL round bottom flask with a reflux condenser and a drying agent above the reaction solution.[a]

entry	Drying agent above reaction solution	conv. to olefin[b] (%)	conv. to **1**[b] (%)
1	none	47	<1
2[c]	none	31(14– 52)[d]	<1
3[e]	none	38	<1
4	Drierite	51(36– 62)[d]	<1
5	$MgSO_4$	44(36– 48)[d]	<1
6	Molecular Sieves	51(41– 57)[d]	<1

[a]Conditions unless specified otherwise: methyl palmitate **2** (0.31 mmol, 1 equiv), $ZnCl_2$ (25 mol %), $Ru_3(CO)_{12}$ (15 mol % per metal center), PCy_3 (15 mol %), and 2-pyridinemethanol **3** (20 mol %) in DMPU (0.5 mL) were heated at 190 °C for 20 h under N_2 flow and water flowing through the reflux condenser. Catalyst % is calculated per metal center (i.e. 15% Ru content = 5 mol % $Ru_3(CO)_{12}$). [b]Conversion of methyl ester was determined by ^{1}H NMR spectroscopy. [c]Three molecular sieves were added to the reaction vessel (4Å). [d]Reactions with drying agents were often inconsistent, and therefore the average conversion (range of conversions) is reported. [e]Reactions were at 4x the standard scale (1.24 mmol of **2**).

Table S18. Dual-catalytic decarbonylation of methyl palmitate **2** with various alcohols and Lewis acids.[a]

entry	Lewis Acid	alcohol	conv. to olefin[b] (%)	conv. to donor ester[b] (%)
1	$InCl_3$	**3**	4	9
2	LiCl	**3**	15	<1
3	KI	**3**	4	<1
4	NaOAc	**3**	24	13
5[c]	$Al(O^iPr)_3$	**3**	3	<1
6	ZnO	**5**	<1	<1
7	$LaCl_3$	**6**	3	15
8	ZnO	**6**	<1	13
9	$InCl_3$	**6**	<1	<1

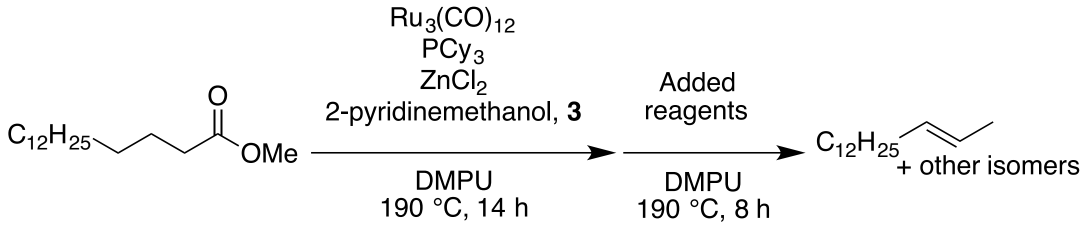
[a]Conditions: methyl palmitate **2** (0.31 mmol, 1 equiv), Lewis acid (25 mol %), $Ru_3(CO)_{12}$ (15 mol % per metal center), PCy_3 (15 mol %), and alcohol (20 mol %) in DMPU (0.5 mL) were heated at 190 °C. Catalyst % is calculated per metal center (i.e. 15% Ru content = 5 mol % $Ru_3(CO)_{12}$). [b]Conversion of methyl ester was determined by ^1H NMR spectroscopy.

Table S19. Dual-catalytic decarbonylation reactions with palmitic acid.[a]

entry	Lewis Acid (mol %)	conv. to olefin[b] (%)	conv. to **1**[b] (%)
1	$ZnCl_2$ (25 %)	4	9
2	none	15	<1
3[c]	$ZnCl_2$ (25 %)	<1	<1

[a]Conditions: palmitic acid (0.31 mmol, 1 equiv), $ZnCl_2$ (25 mol %), $Ru_3(CO)_{12}$ (15 mol % per metal center), PCy_3 (15 mol %), and 2-pyridinemethanol **3** (20 mol %) in DMPU (0.5 mL) were heated at 190 °C. Catalyst % is calculated per metal center (i.e. 15% Ru content = 5 mol % $Ru_3(CO)_{12}$). [b]Conversion of carboxylic acid was determined by ^1H NMR spectroscopy. [c] Three molecular sieves were added to the reaction vessel (4Å).

Table S20. Studying the effect of adding catalytic reagents after 14 h in a 35 mL pressure vessel.[a]



entry	added reagents	conv. to olefin[b] (%)	conv. to **1**[b] (%)
1[c]	none	58	<1
2	$Ru_3(CO)_{12}$ and PCy_3	62	<1
3	$Ru_3(CO)_{12}$, PCy_3, and ZnC_{12}	62	<1
4	$Ru_3(CO)_{12}$, PCy_3, $ZnCl_2$, and **3**	74	<1

[a]Conditions: methyl palmitate **2** (0.31 mmol, 1 equiv), $ZnCl_2$ (25 mol %), $Ru_3(CO)_{12}$ (15 mol % per metal center), PCy_3 (15 mol %), and 2-pyridinemethanol **3** (20 mol %) in DMPU (0.5 mL) were heated at 190 °C for 14 h. The pressure vessel was brought back into the glovebox where reagents were added to the vessel ($ZnCl_2$ (25 mol %), $Ru_3(CO)_{12}$ (15 mol % per metal center), PCy_3 (15 mol %), and 2-pyridinemethanol **3** (20 mol %)). The reaction was heated for an additional 8 h. [c]Reaction was heated only for 14 h total.

7. References

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