Supporting Information

An Newly-designed PE-supported Arsine for efficient and Practical Catalytic Wittig Olefination

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General Information All reactions were carried out under N_2 unless otherwise noted. All carbonyl compounds and solvents were purified according to standard methods unless otherwise noted.

¹H NMR spectra were recorded on a VARIAN Mercury 300 MHz or VARIAN Mercury 400 MHz spectrometer in chloroform-d. All signals are reported in ppm with the internal TMS signal at 0.0 ppm or chloroform signal at 7.26 ppm as a standard. The data are reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). ¹³C NMR spectra signals are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

Fe(TCP)Cl was synthesized according to literature procedure.^[1]

Entry	Catalyst (mol%)	Substrates	Conv. (%) ^{<i>a,b</i>}
1^c	As(<i>n</i> -Bu) ₃ (20)	<>>⊂⊃=0 1b	trace
2^c	As(n-Bu) ₃ (20)	O ₽h ↓ Ph 1h	trace
3^d	AsPh ₃ (20)	○ 1b	<5
4^d	AsPh ₃ (100)	○ 1b	31 (31)
5^d	AsPh ₃ (20)	Ph Ph 1h	NR
6^e	"BuTe-PEG-TeBu" (2.0)	○ 1b	19
7^e	"BuTe-PEG-TeBu" (2.0)	O Ph [⊥] Ph 1h	NR
8^{f}	P;O Ph (10)	○ 1b	trace
9 ^f	P ^C _{Ph} (100)	<>>⊖=0 1b	trace
10^{f}	P_{Ph}^{O}	Ph Ph 1h	NR

Table S1	. Ylide	Olefination	of Ketones	Using	Different	Catalysts
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^{*a*} Determined by ¹H NMR. ^{*b*} Isolated yields in brackets. ^{*c*} Ketones (1.0 mmol), As(*n*-Bu)₃ (49 mg, 0.2 mmol), P(OPh)₃ (0.31 mL, 1.2 mmol), Ethyl bromoacetate (0.13 mL, 1.2 mmol), K₂CO₃ (165.6 mg, 1.2 mmol), CH₃CN/THF (4.0/0.5 mL), rt, 36 h; ^{*d*} Ketones (0.6 mmol), AsPh₃ (cat.), Fe(TCP)Cl (2.5 mg, 0.5 mol%), Na₂S₂O₄ (210 mg, 1.2 mmol), EDA (136.8 mg, 1.2 mmol), Toluene/H₂O (2.0/2.5 mL), 80 °C, 8 h; ^{*e*} Ketones (1.0 mmol), Ethyl bromoacetate (0.16 mL, 1.4 mmol), ^{*n*}BuTe-PEG-TeBu^{*n*} (74.7 mg, 2.0 mol%), P(OPh)₃ (0.36 mL, 1.4 mmol), K₂CO₃ (179.6 mg, 1.3 mmol), Toluene (4.0 mL), 80 °C, 52 h; ^{*f*} Ketones (1.0 mmol), 3-methyl-1-phenyl- phospholane 1-oxide (cat.), methyl bromoacetate (199 µL, 1.3 mmol), Na₂CO₃ (159 mg, 1.5 mmol), Ph₂SiH₂ (225 µL, 1.2 mmol), Toluene (0.33 mL), 100 °C, 24 h.

Part I General Procedure of Preparation of PE-1 and PE-2^[2]



To a solution of 'Bu₃Al-protreated diphenyl(undec-10-enyl)arsine (4.6 g, 12 mmol, 1.0 M in toluene) was added MMAO (15 mL, 28.5 mmol, Al/Ti molar ratio: 1000, 7 wt% Al in heptane) under 1 atm of ethylene atmosphere, followed by toluene (total volume of the solution, 120 mL). At 30°C, complex **S1** (1.6 mg, 2.8 µmol, 0.35 µmol/mL in toluene) was added and the polymerization was carried out for 30 minutes, quenched with concentrated HCl in ethanol (HCl/EtOH, 1/20, v/v, 5 mL) and the resulting mixture was poured into HCl-ethanol (HCl/EtOH, 1/20, v/v, 700 mL) and further stirred for 2 hours. The precipitated polymer was collected, washed with ethanol, and dried *in vacuo* at 60 °C overnight affording **PE-1** 2.2 g; M_ŋ: 3.4 kg/mol. The content of arsonium: 5.2 mol%.

PE-2 was synthesized by a similar procedure except under 10 atm of ethylene atmosphere, yield 3.2 g. M_{η} : 230 kg/mol. The content of Arsonium: 0.39 mol %.

Part II General Procedures for Wittig Reaction

1. Procedure for Iron(III) Porphyrin and PE-1-Catalyzed Olefination Reaction of Ketones.

Procedure A: A mixture of Fe(TCP)Cl (6.3 mg, 0.007 mmol), **PE-1** (53.5 mg, 0.024 mmol) and ketone (3.0 mmol) in toluene (2.0 mL) was heated to 110 °C and a mixture of EDA (684 mg, 6.0 mmol) and PMHS (0.25 mL, 3.9 mmol) in toluene (1.0 mL) was added within 12 h via a syringe pump. After the reaction was complete, the resulting mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography (silica gel) to give the product.

Ethyl 4,4,4-trifluoro-3-phenylbut-2-enoate(3a)^[3]:



97% yield. E/Z = 95/5. *E*-isomer: ¹H NMR (400 MHz,CDCl₃/TMS) δ 7.43-7.38 (m,

3H), 7.29-7.26 (m, 2H), 6.60 (d, J = 1.2 Hz, 1H), 4.04 (q, J = 7.2 Hz, 2 H), 1.06 (t, J = 7.2 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃/TMS): δ -67.6 (s, 3F).

Ethyl 2-cyclohexylideneacetate (3b)^[4]:

98% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 5.60 (s, 1H), 4.14 (q, J = 7.2 Hz, 2H), 2.83-2.81 (m, 2H), 2.21-2.17 (t, J = 5.4 Hz, 2H), 1.65-1.61 (m, 6H), 1.28 (t, J = 7.2 Hz, 3H).

Ethyl 2-(tetrahydropyran-4-ylidene)acetate (3c)^[5]:



95% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 5.69 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.80-3.72 (m, 4H), 3.03-2.99 (m, 2H), 2.35-2.31 (m, 2H), 1.28 (t, *J* = 7.5 Hz, 3H).

Procedure B: A mixture of Fe(TCP)Cl (6.3 mg, 0.007 mmol), **PE-1** (80.3 mg, 0.09 mmol) and ketone (3.0 mmol) in toluene (2.0 mL) was heated to 110 °C and a solution of EDA (855 mg, 7.5 mmol) and PMHS (0.25 mL, 3.9 mmol) in toluene (1.0 mL) were added within 15 h via a syringe pump. After the reaction was complete, the resulting mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography (silica gel) to give the product.

Ethyl 2-cyclopentylideneacetate (3d)^[4]:



93% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 5.80 (t, J = 2.1 Hz, 1H), 4.15 (q, J = 7.5 Hz, 2H), 2.79-2.74 (m, 2H), 2.44 (t, J = 7.2 Hz, 2H), 1.80-1.61 (m, 4H), 1.27 (t, J = 7.2 Hz, 3H).

Procedure C: A mixture of Fe(TCP)Cl (6.3 mg, 0.0075 mmol), **PE-1** (107 mg, 0.12mmol) and ketone (3.0 mmol) in toluene (2.0 mL) was heated to 110 °C and a solution of EDA (1026 mg, 6.0 mmol) and PMHS (0.25 mL, 3.9 mmol) in toluene

(1.0 mL) was added within 18 h *via* a syringe pump. After the reaction was complete, the resulting mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography (silica gel) to give the product.

Ethyl 3-methyl-5-phenylpenta-2,4-dienoate (3e)^[4]:



81% Yield. E/Z = 60/40. ¹H NMR (300 MHz, CDCl₃): δ 8.42 (d, J = 16.2 Hz, 0.40H),
7.56-7.28 (m, 5H), 6.97-6.78 (m, 1.6H), 5.91 (s, 0.60H), 5.75 (s, 0.40H), 4.24-4.16 (m,
2H), 2.41 (s, 1.8 H), 2.13 (s, 1.2H), 1.34-1.28 (m, 3H).

Ethyl 3-methylhepta-2,6-dienoate (3f)^[6]:



83% yield. E/Z = 63/37. ¹H NMR (300 MHz, CDCl₃/TMS): δ 5.89-5.72 (m, 1H), 5.67 (s, 1H) , 5.07-4.95 (m, 2H), 4.18-4.00 (m, 2H), 2.72 (t, *J* = 7.5 Hz, 0.74H), 2.27-2.20 (m, 3.26H), 2.16 (s, 1.9H), 1.89 (d, *J* = 1.2 Hz, 1.1 H), 1.30-1.25 (m, 3 H).

(*E*)-ethyl 3-(4-fluorophenyl)but-2-enoate (3g)^[7]:



81% yield. E/Z = 83/17. (*E*)-*isomer*: ¹H NMR (300 MHz, CDCl₃/TMS): δ 7.48-7.44 (m, 2 H), 7.09-7.03 (m, 2 H) , 6.10 (s, 1H), 4.22 (q, J = 6.9 Hz, 2 H), 2.56 (s, 3 H), 1.32 (t, J = 6.9 Hz, 3 H). ¹⁹F NMR (282 MHz, CDCl₃/TMS): δ -112.96 (m, 1F).

Procedure D: A mixture of Fe(TCP)Cl (6.3 mg, 0.0075 mmol), **PE-1** (214 mg, 0.24 mmol) and benzophenone (546 mg, 3.0 mmol) in toluene (2.0 mL) was heated to 110 ^oC and then a solution of EDA (1368 mg, 12 mmol) and PMHS (0.25mL, 3.9 mmol) and toluene (1.0 mL) was added within 48 h via a syringe pump. After the reaction was complete, the resulting mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography (silica gel) to give 487 mg ethyl

3,3-diphenylacrylate.

Ethyl 3,3-diphenylacrylate(3h)^[8]:



64% yield. ¹H NMR (300 MHz, CDCl₃/TMS): δ 7.39-7.20 (m, 10H), 6.37 (s, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 1.11 (t, *J* = 7.2 Hz, 3H).

Procedure for PE-1-catalyzed Olefination Reaction of Ketones With Diazo Acetophenone: A mixture of Fe(TCP)Cl (6.3 mg, 0.0075 mmol), **PE-1** (107 mg, 0.12 mmol) and substrate (3.0 mmol) in toluene (1.0 mL) was heated to 110 °C and a mixture of diazo acetophenone (1095 mg, 2.5 mmol) and PMHS (0.25 mL, 3.9 mmol) in toluene (3.0 mL) was added within 38 h via a syringe pump. After the reaction was complete, the resulting mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography (silica gel) to give the product.

(*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-one (3i)^[9]:



98% yield. E/Z = 95/5. *E*-isomer: ¹H NMR (300 MHz, CDCl₃/TMS): δ 7.83-7.80 (m, 2H), 7.55-7.50 (m, 1H), 7.42-7.37 (m, 2H), 7.30-7.26 (m, 6H). ¹⁹F NMR (282 MHz, CDCl₃/TMS): δ = -66.7 (s, 3F).

Procedure for PE-1-Catalyzed Olefination Reaction of Ketones With Ethyl 2-diazopropanoate: A mixture of Fe(TCP)Cl (6.3 mg, 0.0075 mmol), **PE-1** (107 mg, 0.12 mmol) and substrate (3.0 mmol) in toluene (1.0 mL) was heated to 110 °C and a solution of 2-diazo ethyl propionate (1.15 g, 9.0 mmol) and PMHS (0.25 mL, 3.9 mmol) in toluene (0.5 mL) was added within 36 h via a syringe pump. After the reaction was complete, the resulting mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography (silica gel) to give

the product.

(*E*)-ethyl 4,4,4-trifluoro-2-methyl-3-phenylbut-2-enoate (3j)^[10]:

94% yield. E/Z = 93/7. *E*- isomer: ¹H NMR (300 MHz, CDCl₃/TMS): δ 7.36-7.29 (m, 3H), 7.22-7.19 (m, 2H), 3.86 (q, *J* = 6.9 Hz, 2H), 2.24 (q, *J* = 2.4, 3H), 0.81 (t, *J* = 7.2 Hz, 3H). ¹⁹F NMR (282 MHz, CDCl₃/TMS): δ = -55.63 (d, *J* = 3.1 Hz, 3F).

Ethyl 2-cyclohexylidenepropanoate (3k)^[11]:



84%. ¹H NMR (300 MHz, CDCl₃/TMS): δ 4.23-4.14 (m, 2H), 2.42-2.40 (m, 2H), 2.22-2.20 (m, 2H), 1.86 (s, 3H), 1.60-1.57 (m, 6H), 1.30 (t, *J* = 7.2 Hz, 3H).

Ethyl 2-(tetrahydropyran-4-ylidene)propanoate (31)^[12]:



85%. ¹H NMR (400 MHz, CDCl₃/TMS): δ 4.20 (q, *J* = 7.2 Hz, 2H), 3.75-3.69 (m, 4H), 2.69-2.66 (m, 2H), 2.40-2.36 (m, 2H), 1.88 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

2. Procedure for 0.05 mol% Iron(III) Porphyrin and PE-1-Catalyzed Olefination Reaction.

A mixture of Fe(TCP)Cl (6.1 mg, 0.0072 mmol), **PE-1** (10.7 mg, 0.012 mmol) and **4a** (3.26 mL, 24.0 mmol) in toluene (4.0 mL) was heated to 110 °C and a solution of EDA (8.2 g, 72.0 mmol), PMHS (2.2 mL, 36.0 mmol) in toluene(2.0 mL) was added within 98 h via a syringe pump. After the reaction was complete, the resulting mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography (silica gel) to give the product in 87% yield.

(E)-ethyl 3-(naphthalen-5-yl)acrylate (5a)^[13]:



99% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 8.53 (d, *J* = 15.6 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.91-7.86 (m, 2H), 7.75 (d, *J* = 6.9 Hz, 1H), 7.61-7.46 (m, 3H), 6.53 (d, *J* = 15.9 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H).

3. General Procedure for Iron(III) Porphyrin and PE-1-Catalyzed Olefination Reaction of Aldehydes.

A mixture of Fe(TCP)Cl (6.3 mg, 0.007 mmol), **PE-1** (21.4 mg, 0.024 mmol) and **4** (3.0 mmol) in toluene (2.0 mL) was heated to 110 °C and then a solution of EDA (560 mg, 4.8 mmol) and PMHS (0.25 mL, 3.9 mmol) in toluene (1.0 mL) were added within 12 h via a syringe pump. After the reaction was complete, the resulting mixture was cooled to room temperature and was concentrated. The residue was chromatographized on silica gel to give the product.

(*E*)-ethyl 3-(2-nitrophenyl)acrylate(5b)^[13]:



95% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 8.13-8.02 (m , 2H), 7.70-7.64 (m, 2H), 7.58-7.53(m, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 4.29 (q, *J* = 7.5 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H).

(E)-ethyl 3-(2,6-dichlorophenyl)acrylate(5c)^[14]:

98% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 7.79 (d , *J* = 16.5 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.21-7.16 (m, 1H), 6.59 (d, *J* = 16.5 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 6.9 Hz, 3H).

(*E*)-ethyl 3-(2,4-dichlorophenyl)acrylate (5d)^[14]:



99% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 8.01 (d , *J* = 15.9 Hz, 1H), 7.56 (d , *J* = 8.7 Hz, 1H), 7.45 (d, *J* = 1.8 Hz, 1H), 7.29-7.26 (m, 1H), 6.42 (d, *J* = 16.2 Hz, 1H), 4.28 (q, *J* = 7.5 Hz, 2H), 1.35 (t, *J* = 6.9 Hz, 3H).

(E)-ethyl 3-(4-chlorophenyl)acrylate (5e)^[14]:

99% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 7.63 (d, *J* = 16.5 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 6.41 (d, *J* = 16.2 Hz, 1H), 4.27 (q, *J* = 7.5 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H).

(E)-ethyl 3-(4-bromophenyl)acrylate (5f)^[14]:

99% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 7.61 (d, J = 16.5 Hz, 1H), 7.52 (d, J = 7.5 Hz, 2H), 7.38 (d, J = 7.8 Hz, 2H), 6.42 (d, J = 15.9 Hz, 1H), 4.26 (q, J = 6.8 Hz, 2H), 1.34 (t, J = 7.8 Hz, 3H).

(*E*)-ethyl 3-(4-(trifluoromethyl)phenyl)acrylate (5g)^[14]:

96% yield. ¹H NMR (400 MHz,CDCl₃/TMS) δ 7.72-7.61 (m, 5H), 6.51 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 6.8 Hz, 3H). ¹⁹F NMR (282 MHz, CDCl₃/TMS): δ -63.3 (s, 3F).

(E)-ethyl 3-(4-nitrophenyl)acrylate(5h)^[13]:

99% yield. ¹H NMR (300 MHz, CDCl₃/TMS) δ 8.25 (d, J = 8.7 Hz, 2H), 7.74-7.67 (m, 3H), 6.57 (d, J = 15.9 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H).
(E)-ethyl 3-(4-cyanophenyl) acrylate(5i)^[15]:



99% yield. ¹H NMR (400 MHz,CDCl₃/TMS) δ 7.72-7.61 (m, 5H), 6.51 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H).

(*E*)-ethyl 3-(3-nitrophenyl)acrylate(5j)^[13]:



98% yield. ¹H NMR (400 MHz,CDCl₃/TMS) δ 8.39 (s, 1H), 8.24-8.22 (m, 1H), 7.83 (d, J = 7.2 Hz, 1H), 7.72 (d, J = 16.0 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 6.57 (d, J = 16.0 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H).

(E)-ethyl 3-(3-chlorophenyl)acrylate(5k)^[16]:

CO₂Et

99% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 7.61 (d, *J* = 15.6 Hz, 1H), 7.52 (s, 1H), 7.41-7.29 (m, 3H), 6.44 (d, *J* = 16.2 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.5 Hz, 3H).

(E)-ethyl 3-(2-chlorophenyl)acrylate (5l)^[16]:

CO₂Et

98% yield. ¹H NMR (400 MHz,CDCl₃/TMS) δ 8.09 (d, J = 16.0 Hz, 1H), 7.63-7.61 (m, 1H), 7.43-7.41 (m, 1H), 7.32-7.26 (m, 2H), 6.43 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.6 Hz, 2H), 1.35 (t, J = 7.6 Hz, 3H).

(E)-ethyl 3-(p-tolyl)acrylate (5m)^[14]:

CO₂Et

99% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 7.67 (d, *J* = 15.0 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 9.0 Hz, 2H), 6.39 (d, *J* = 16.5 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.33 (t, *J* = 6.3 Hz, 3H).

(*E*)-ethyl 3-(4-methoxyphenyl)acrylate (5n)^[14]:

97% yield. ¹H NMR (300 MHz, CDCl₃/TMS) δ 7.64 (d, *J* = 16.2 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.31 (d, *J* = 16.2 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).

(E)-ethyl 3-(2,4-dimethylphenyl)acrylate (50)^[17]:

94% yield. ¹H NMR (300 MHz, CDCl₃/TMS) δ 7.64 (d, *J* =15.6 Hz, 1H), 7.26-7.30 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.39 (d, *J* = 15.9 Hz, 1H), 4.26 (q, *J* = 7.8 Hz, 2H), 2.28 (s, 6H), 1.33 (t, *J* = 7.5 Hz, 3H).

(E)-ethyl cinnamate (5p)^[14]:

99% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 7.69 (d, J = 15.9 Hz, 1H), 7.54-7.52 (m, 2H), 7.40-7.38 (m, 3H), 6.44 (d, J = 16.5 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 6.3 Hz, 3H).

(E)-ethyl 3-(furan-2-yl)acrylate (5q)^[14]:

98% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 7.48-7.40 (m, 2H), 6.61 (d, J = 3.3 Hz, 1H), 6.47 (dd, J = 1.8 Hz, 3.3 Hz, 1H), 6.32 (d, J = 15.6 Hz, 1H), 4.24 (q, J = 7.5 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H).

(2E,4E)-Ethyl 5-phenylpenta-2,4-dienoate (5r)^[16]:

96% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 7.50-7.28 (m, 5H), 6.94-6.82 (m, 2H), 5.99 (d, J = 15.3 Hz, 1H), 4.23 (q, J = 6.9 Hz, 2H), 1.32 (t, J = 6.9 Hz, 3H).

(*E*)-ethyl 5-phenylpent-2-enoate (5s)^[18]:

97% yield. ¹H NMR (400 MHz,CDCl₃/TMS) δ 7.32-7.28 (m, 2H), 7.22-7.17 (m, 3H), 7.04-6.97 (m, 1H), 5.85 (dt, *J* = 1.6 Hz, 16.0 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.78 (t, *J* = 6.8 Hz, 2H), 2.55-2.49 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).

(E)-ethyl 4-phenylpent-2-enoate(5t)^[19]:



98% yield. ¹H NMR (300 MHz,CDCl₃/TMS) δ 7.35-7.18 (m, 5H), 7.11 (dd, J = 6.9, 15.6 Hz, 1H), 5.80 (dt, J = 1.2 Hz, 15.6 Hz, 1H), 4.18 (q, J = 6.9 Hz, 2H), 3.62 (m, 1H), 1.43 (d, J = 7.2 Hz, 3H), 1.28 (t, J = 6.9 Hz, 3H).

(E)-ethyl 3-cyclohexylacrylate (5u)^[14]:



98% yield. ¹H NMR (400 MHz,CDCl₃/TMS) δ 6.92 (dd, *J* = 6.8, 16.0 Hz, 1H), 5.76 (dd, *J* = 15.6, 1.2 Hz, 1H), 4.18 (q, *J* = 6.8 Hz, 2 H), 2.17-2.09 (m, 1 H), 1.78-1.65 (m, 5 H), 1.34-1.09 (m, 8 H).

(E)-ethyl dec-2-enoate(5v)^[14]:

94% yield. ¹H NMR (400 MHz,CDCl₃/TMS) δ 7.02-6.92 (m, 1H), 5.81(d, *J* = 16.2 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.23-2.15 (m, 2H), 1.50-1.40 (m, 2H), 1.31-1.27 (m, 11 H), 0.88 (t, *J* = 7.2 Hz, 3H).

(E)-ethyl 6-(benzyloxy)hex-2-enoate(5w)^[20]:

BnO____CO2Et

93% yield. ¹H NMR (400 MHz,CDCl₃/TMS) δ 7.37-7.25 (m, 5H), 7.02-6.92 (m, 1H),

5.82 (dt, J = 15.6, 1.5 Hz, 1H), 4.49 (s, 2H), 4.18 (q, J = 7.2 Hz, 2H), 3.48 (t, J = 6.0

Hz, 2H), 2.35-2.27 (m, 2H), 1.82-1.72 (m, 2H), 1.28 (t, *J* = 7.5 Hz, 3H).

(S) -(*E*)-ethyl 3-(2,2-dimethyl-1,3-dioxolan-4-yl)acrylate (5x)^[21]:



87% yield. ¹H NMR (400 MHz,CDCl₃/TMS) δ 6.88 (dd, J = 15.6, 5.6 Hz, 1H), 6.10 (dd, J = 15.2, 1.6 Hz, 1H), 4.70-4.64 (m, 1H), 4.24-4.17 (m, 3H), 3.68 (dd, J = 8.4, 7.8 Hz, 1H), 1.45 (s, 3H), 1.41 (s, 3H), 1.30 (t, J = 6.8 Hz, 3H). Ee was determined by HPLC (OJ-H, Hexane/*i*-PrOH = 99/1, 0.6 mL/min, 230 nm; t_r(major) = 15.73 min, t_r(minor) = 13.56 min) 100% ee.

(S)-Tert-butyl-4-((*E*)-2-(ethoxycarbonyl)vinyl)-2,2-dimethyloxazolidine-3-carbox ylate (5y)^[22]:



99% yield. ¹H NMR (400 MHz,CDCl₃/TMS) δ 6.89-6.80 (m, 1H), 5.97-5.87 (m, 1H), 4.58-4.39 (m, 1H), 4.22-4.19 (m, 2H), 4.11-4.07 (m, 1H), 3.80 (dd, J = 9.6, 2.4 Hz, 1H), 1.64-1.42 (m, 15H), 1.31-1.27 (m, 3H). Ee of **5**y was determined by HPLC (Amy lose, Hexane/*i*-PrOH = 98.5/1.5, 0.6 mL/min, 230 nm; t_r(major) = 15.12 min, t_r(minor) = 19.88 min) 94% ee.

General Procedure for Iron(III) Porphyrin and PE-1-Catalyzed Olefination Reaction of Diazo Acetophenone: A mixture of Fe(TCP)Cl (6.3 mg, 0.007 mmol), PE-1 (26.8 mg, 0.03 mmol) and substrate (3.0 mmol) in toluene (1.0 mL) was heated to 110 °C. Then a solution of diazo acetophenone (701 mg, 4.8 mmol) and PMHS (0.25 mL, 3.9 mmol) in toluene (2.0 mL) was added within 12 h via a syringe pump. After the reaction was complete, the resulting mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography (silica gel) to give the product. (*E*)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (5e')^[16]:



98% yield. ¹H NMR (300 MHz, CDCl₃/TMS): δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.77 (d, *J* = 15.6 Hz, 1H), 7.60-7.49 (m, 6H), 7.40 (d, *J* = 8.4 Hz, 2H).

(*E*)-1-phenyloct-2-en-1-one (5v')^[23]:



95% yield. ¹H NMR (300 MHz, CDCl₃/TMS): δ 7.94-7.91 (m, 2H), 7.58-7.44 (m, 3H), 7.12-7.02 (m, 1H), 6.90-6.84 (m, 1H), 2.35-2.78 (m, 2H), 1.57-1.48 (m, 2H), 1.38-1.29 (m, 8H), 0.889-0.86 (m, 3H).

General Procedure for Iron(III) Porphyrin and PE-1-Catalyzed Olefination Reaction of 2-Diazo Ethyl Propionate: A mixture of Fe(TCP)Cl (6.3 mg, 0.0075 mmol), PE-1 (26.8 mg, 0.03mmol) and substrate (3.0 mmol) in toluene (2.0 mL) was heated to 110 °C and a mixture of 2-diazo ethyl propionate (768 mg, 6.0 mmol) and PMHS (0.25 mL, 3.9 mmol) in toluene(1.0 mL) were added within 15 h via a syringe pump. After the reaction was complete, the resulting mixture was cooled to room temperature, concentrated. The residue was purified by flash chromatography (silica gel) to give the product.

(E)-ethyl 3-(4-chlorophenyl)-2-methylacrylate (5e")^[24]:

94% yield. ¹H NMR (400 MHz, CDCl₃/TMS): δ 7.54 (s, 1H), 7.29-7.23 (m, 4H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.01 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H).

(*E*)-ethyl 2-methyloct-2-enoate $(5v^{"})^{[23]}$:

.CO₂Et

94% yield. E/Z = 79/21, ¹H NMR (300 MHz, CDCl₃/TMS): 6.76 (t, J = 7.2 Hz,

0.79H), 5.92 (t, *J* = 7.5 Hz, 0.21H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.47-2.40 (m, 0.42H), 2.20-2.12 (m, 1.58H), 1.89 (s, 0.63H), 1.83 (s, 2.37H), 1.48-1.27(m, 12H) , 0.90-0.86 (m, 3 H).

4. Procedure for Iron(III) Porphyrin and PE-2-Catalyzed Olefination Reaction.

Fe(TCP)Cl (6.3 mg, 0.007 mmol), **PE-2** (181 mg, 0.024 mmol) and **4e** (420 mg, 3.0 mmol) were mixed in a Schlenk tube. The tube was evacuated and backfilled with nitrogen. Toluene (2.0 mL) was added and the reaction mixture was heated to 110 °C. To this solution was added a mixtute of EDA (0.56 g, 4.8 mmol) and PMHS (0.25 mL, 3.9 mmol) in toluene (1.0 mL) within 18 h *via* a syringe pump or in portions. The mixture was further stirred at 110 °C until **4e** disappeared (determined by ¹H NMR). The resulting mixture was cooled to room temperature and EtOH (10 mL), petroleum ether (10 mL) was added sequentially to precipitate the polymer (overnight at room temperature). The precipitated polymer (**PE-2**) was collected and washed by ethyl acetate (3 \times 10 mL), dried under reduced pressure and reused as catalyst in the next run. The filtrate was collected and concentrated to give the crude product **5e**, which was purified by column chromatography on silica gel with PE/EA (30/1) to afford the product.

5. Synthesis of (*E*)-2-ethylhexyl 3-(4-methoxyphenyl)-acrylate^[25]:

A mixture of Fe(TCP)Cl (4.2 mg, 0.005 mmol), **PE-1** (17.9 mg, 0.002 mmol) and **4n** (272 mg, 2.0 mmol) in toluene (1.0 mL) was heated to 110 $^{\circ}$ C and a solution of **6** (713 mg, 3.6 mmol), PMHS (0.18 mL, 2.6 mmol) in toluene (1.0 mL) was added within 20 h via a syringe pump. After the reaction was complete, the resulting mixture was cooled to room temperature, concentrated. The residue was purified by flash chromatography (silica gel) to give the product **7**, yield 569 mg (98 %).



Yield: 569.3 mg (98%). ¹H NMR (300 MHz, CDCl₃/TMS): δ 7.63 (d, J =15.9 Hz,

1H), 7.48 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.32 (d, *J* = 15.9 Hz, 1H), 4.14-4.08 (m, 2H), 3.83 (s, 3H), 1.68-1.61(m, 1H), 1.46-1.33 (m, 8H), 0.95-0.88 (m, 6H).

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Part III NMR Spectra of the Compounds and Copolymers









5x **HPLC** : Sample Name : wp-1258-3-rac-OJ-H-0. Injection Volume : 10 uL Description: OJ-H(250), Hex/iPrOH=99/1, 0.6 mL : wp-1258-3-rac-OJ-H-0.6-99 : 10 uL

<Chromatogram>

1Det.A Ch1/230nm

			PeakTable		
Detector A	Ch1 230nm				
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.558	2464526	60522	50.148	56.638
2	15.606	2449977	46336	49.852	43.362
Total		4914503	106858	100.000	100,000

: wp-1254-1-Chiral-OJ-H-0.6-99 : 10 uL Sample Name Injection Volume Discription: OJ-H(250), Hex/iPrOH=99/1, 0.6 mL/min

<Chromatogram>

PeakTable						
Detector A Ch1 230nm						
Peak#	Ret. Time	Area	Height	Area %	Height %	
1	15.729	21332168	310140	100.000	100.000	
Total		21332168	310140	100.000	100.000	

Sample Name : wp-lcr-1331-1 Injection Volume : 10 uL Descrption: Amy lose(250), Hex/iPrOH = 98.5/1.5, 0.6 mL/h

<Chromatogram>

1Det.A Ch1/230nm

Injection Volume : 10 uL Description: Amy-lose(250), Hex/iPrOH = 98.5/1.5, 0.6 mL/h

<Chromatogram>

				Peak rable		
	Detector A	Ch1 230nm				
ĺ	Peak#	Ret. Time	Area	Height	Area %	Height %
	1	15.120	27956232	295045	96.935	96.084
	2	19.875	883956	12025	3.065	3.916
	Total		28840188	307070	100.000	100.000