

Supporting Information

Selective Palladium-Catalyzed Carbonylation of Alkynes: An Atom-Economic Synthesis of 1,4-Dicarboxylic Acid Diesters

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Contents

General Informations.....	2
Experimental sections.....	2
1. Syhthesis of new ligands L1-L4.....	2
2. Selective Palladium-Catalyzed Carbonylation of Alkynes.....	5
2.1 General procedure	5
2.2 Optimization of reaction conditions	6
2.3 Characterization of the products.....	11
References	32
NMR Spectra.....	33

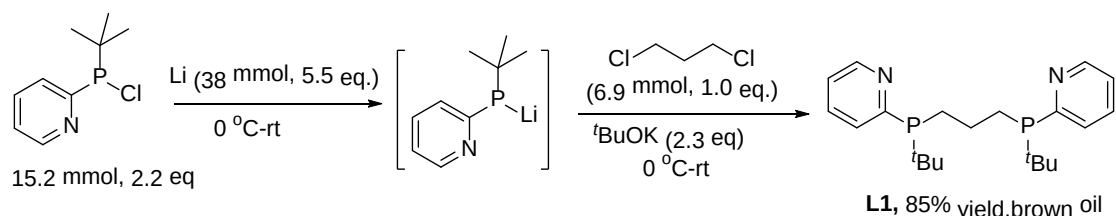
General Informations:

All commercial reagents were ordered from Alfa Aesar, Aldrich, TCI or Strem. Unless otherwise statement, commercial reagents were used without purification. Air- and moisture-sensitive syntheses were performed under argon atmosphere in heating gun vacuum dried glassware. Analytical data of literature known compounds were in accord with reported data. NMR spectra were recorded on Bruker Avance 300 (300 MHz) NMR spectrometers. 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. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). High resolution mass spectra (HRMS) were recorded on Agilent 6210 Time-of-Flight LC/MS (Agilent) with electrospray ionization (ESI). The data are given as mass units per charge (m/z) and intensities of signals are given in brackets. For GC analyses, HP 6890 chromatograph with a 29 m HP5 column was used.

Experimental sections

1. Synthesis of new ligands L1-L4.

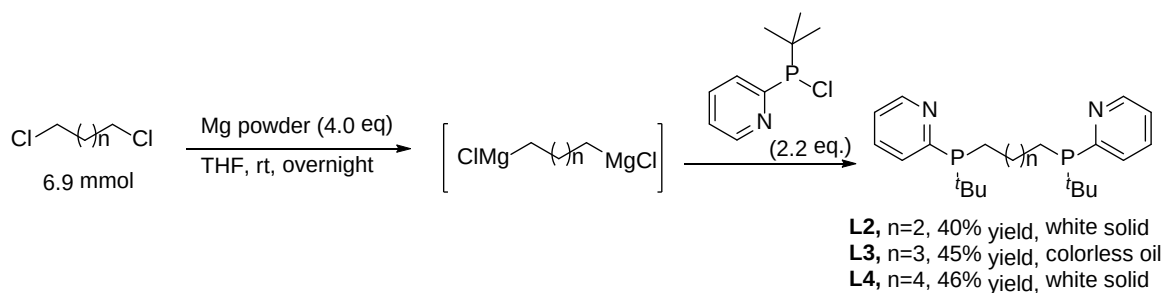
The ligand **L1** was synthesized according to following procedure:



General procedure for 1,3-bis(tert-butyl(pyridin-2-yl)phosphanyl)propane (L1): Lithium (270 mg, 38 mmol) was added slowly to the solution of 2-(tert-butylchlorophosphanyl)pyridine in 30 mL THF under argon at 0 °C, and the solution became red slowly. The mixture was stirred at room temperature overnight. The potassium *tert*-butoxide (1.8 g, 16 mmol) and 1,3-dichloropropane were added to the mixture at 0 °C under argon, and the mixture was further stirred over 24 h. Degassed water (1.0 mL) was added to quench the reaction and the solvent was removed under vacuum. Degassed water (20 mL) and diethyl ether (50 mL) were added and the organic phase was separated. The aqueous phase was extracted three times with diethyl ether (3×10 mL) and the combined organic phase was dried over sodium sulfate

anhydrous, filtered and the solvent was removed under reduced pressure. Then the residue was further purified by flash chromatograph using the degassed ethyl acetate as the eluent to afford the ligand as brown oil (2.3 g, 85% yield). ^1H NMR (300 MHz, CD_2Cl_2) δ 8.57-8.51 (m, 2H), 7.44-7.40 (m, 4H), 7.06-7.00 (m, 2H), 2.44-2.34 (m, 2H), 1.55-1.37 (m, 4H), 0.87 (d, $J = 11.4$ Hz, 9H), 0.86 (d, $J = 11.4$ Hz, 9H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2) δ 162.12, 162.02, 161.93, 161.83, 149.70, 149.66, 149.62, 149.58, 134.47, 134.36, 130.94, 130.87, 130.49, 130.43, 122.42, 122.41, 29.50, 29.48, 29.33, 29.31, 27.70, 27.53, 24.44, 24.27, 24.19, 24.02, 23.93, 23.77, 22.53, 22.40, 22.36, 22.34, 22.22, 22.21, 22.17, 22.04 ppm; ^{31}P NMR (121 MHz, CD_2Cl_2) δ 6.31, 6.14 ppm; HRMS (ESI): Calcd. for $\text{C}_{21}\text{H}_{32}\text{N}_2\text{P}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 397.19329, Found: 397.19404.

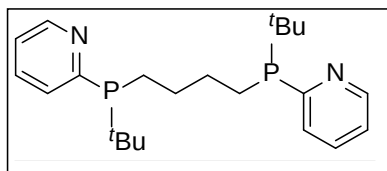
The ligands **L2-L4** were synthesized according to following procedure:



General procedure: Mg powder (675 mg, 27.8 mmol, 4 eq) was heated at 90 °C for 45 minutes. After cooling to room temperature 2 grains of iodine were added and dissolved in 20 ml of THF. The suspension was stirred for 10 minutes until the yellow color of iodine disappeared. Then the THF solution was decanted and the activated magnesium powder was washed 2 times with 1-2 ml of THF. After fresh THF (20 mL) was added again a solution of α,α' -dichloro-*o*-xylene (1.21 g, 6.9 mmol in 70 ml THF) was slowly dropped with the syringe pump at room temperature. The THF mixture turned slowly dark and stirred overnight. The unreacted magnesium powder was filtered off from the reaction mixture. 2-(tert-butylchlorophosphanyl)pyridine solution (3.05 g, 15.2 mmol in 10 mL THF) was cooled to -60 °C under argon. Then the fresh Grignard solution was slowly added dropwise at this temperature with the syringe pump. The mixture was allowed to room temperature and stirred overnight. Degassed water (1.0 mL) was added to quench the reaction. After removal of THF in vacuum, 20 mL of degassed water and 20 ml of ether were added into the residue and two separated clear phases observed. The aqueous phase was extracted with ether (10 mL x 2). After the combined organic phase was dried with anhydrous Na_2SO_4 , the ether was removed

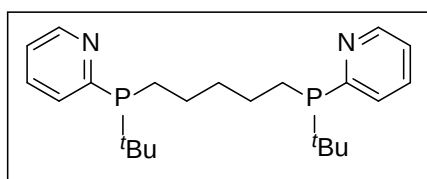
under high vacuum. The residue was dissolved in 5 mL MeOH under heating on a water bath and filtered through celite. After cooling at -28 °C overnight the desired ligand was afforded.

1,4-bis(tert-butyl(pyridin-2-yl)phosphanyl)butane (L2)



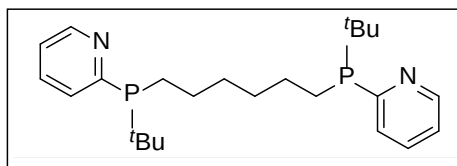
White solid, 40% yield, ^1H NMR (300 MHz, CD_2Cl_2) δ 8.58-8.55 (m, 2H), 7.53-7.47 (m, 2H), 7.42-7.37 (m, 2H), 7.11-7.06 (m, 2H), 2.24-2.20 (m, 2H), 1.42-1.39 (m, 6H), 0.89 (s, 9H), 0.85 (s, 9H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2) δ 162.15, 161.95, 149.68, 149.59, 134.49, 134.38, 130.94, 130.50, 122.43, 29.42, 29.24, 28.89, 28.64, 28.47, 27.59, 27.42, 20.08, 19.90 ppm; ^{31}P NMR (121 MHz, CD_2Cl_2) δ 7.49, 7.39 ppm; HRMS (ESI): Calcd. for $\text{C}_{22}\text{H}_{34}\text{N}_2\text{P}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 411.20894, Found: 411.20891.

1,5-bis(tert-butyl(pyridin-2-yl)phosphanyl)pentane (L3)



Colorless oil, 45% yield, ^1H NMR (300 MHz, CD_2Cl_2) δ 8.58-8.55 (m, 2H), 7.49-7.42 (m, 4H), 7.10-7.04 (m, 2H), 2.27-2.18 (m, 2H), 1.40-1.29 (m, 8H), 0.89-0.85 (m, 18H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2) δ 162.22, 162.19, 162.03, 161.99, 149.68, 149.66, 149.60, 149.59, 134.48, 134.37, 130.93, 130.88, 130.49, 130.45, 122.41, 29.41, 29.24, 27.62, 27.45, 26.52, 26.35, 26.28, 20.11, 20.07, 19.94, 19.89 ppm; ^{31}P NMR (121 MHz, CD_2Cl_2) δ 7.47, 7.41 ppm; HRMS (ESI): Calcd. for $\text{C}_{23}\text{H}_{36}\text{N}_2\text{P}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 425.22459, Found: 425.22440.

1,6-bis(tert-butyl(pyridin-2-yl)phosphanyl)hexane (L4)

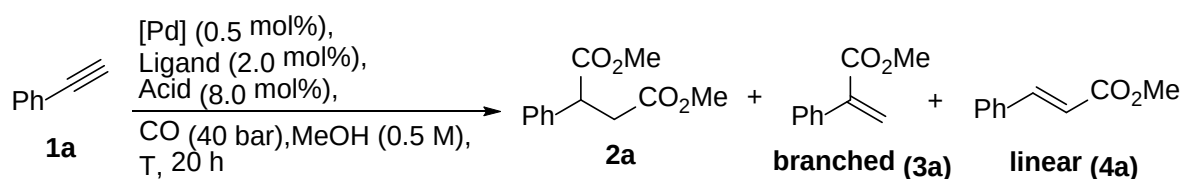


White solid, 46% yield, ^1H NMR (300 MHz, CD_2Cl_2) δ 8.58-8.55 (m, 2H), 7.52-7.46 (m, 2H), 7.42-7.40 (m, 2H), 7.11-7.06 (m, 2H), 2.24-2.17 (m, 2H), 1.33-1.29 (m, 10H), 0.90 (s, 9H),

0.86 (s, 9H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2) δ 162.23, 162.04, 149.66, 149.59, 134.48, 134.37, 130.89, 130.45, 122.41, 31.28, 31.11, 29.39, 27.60, 27.43, 26.86, 26.62, 20.22, 20.05 ppm; ^{31}P NMR (121 MHz, CD_2Cl_2) δ 7.48 ppm; HRMS (ESI): Calcd. for $\text{C}_{24}\text{H}_{38}\text{N}_2\text{P}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 439.24024, Found: 439.24072.

2. Selective Palladium-Catalyzed Carbonylation of Alkynes

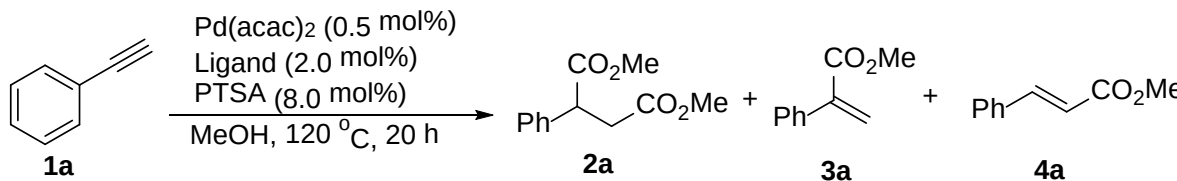
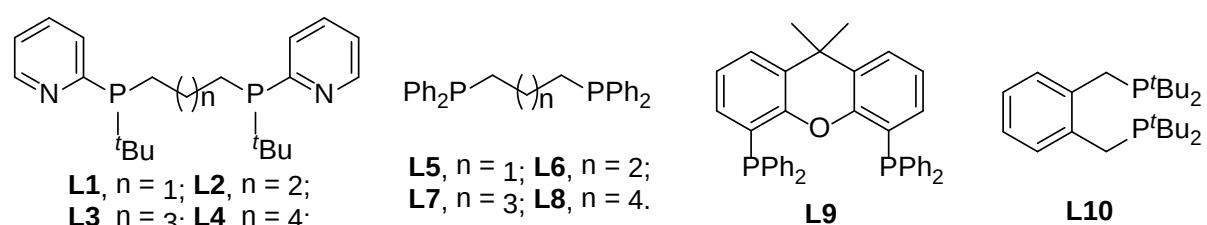
2.1 General procedure



A 4 mL screw-cap vial was charged with Palladium salts (0.5 mol% in terms of Pd atom), Ligand (2.0 mol%), Acid (8.0 mol% in terms of H atom), and an oven-dried stirring bar. The vial was closed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a needle. Then, the vial was evacuated under vacuum and recharged with argon for three times. After MeOH (2.0 ml) and alkyne (1.0 mmol) were injected by syringe; the vial was fixed in an alloy plate and put into Paar 4560 series autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave is flushed with carbon monoxide for three times and carbon monoxide was charged to 40 bar. The reaction was heated under specified temperature for 20 hours. Afterwards, the autoclave was cooled to room temperature and the pressure was carefully released. Isooctane (100 μL) was added into the reaction as internal standard. A sample of the mixture was analyzed by gas chromatography. Pure product could be obtained by column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1).

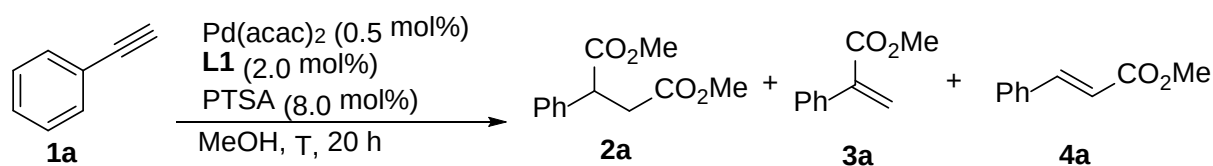
2.2 Optimization of reaction conditions

Table S1. The effect of ligand^a

				
				
entry	ligand	Conv.(%)	2a/3a/4a	GC Yield of 2a (%)
1	L1	>99	88/5/7	88(88 ^b)
2	L2	>99	40/26/30	38
3	L3	>99	0/91/9	0
4	L4	>99	0/89/11	0
5	L5	>99	41/6/53	29
6	L6	>99	6/41/53	<5
7	L7	76	0/77/23	0
8	L8	74	0/83/17	0
9	L9	>99	68/2/30	60
18	L10	>99	5/1/ 94	<5 (90 ^c)

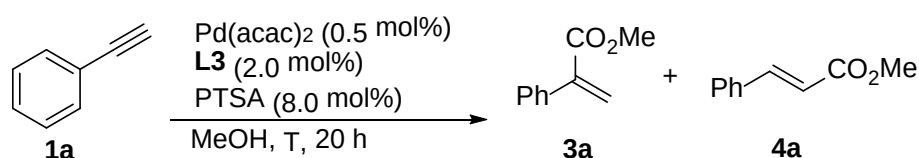
[a]. Standard reaction conditions: **1a** (1.0 mmol), Pd(acac)₂ (0.005 mmol, 0.5 mol%), Ligand (0.02 mmol, 2 mol%), PTSA (16 mg, 8 mol%), MeOH (2.0 mL), CO (40 atm), 120 °C, 20 h; the conversion, the ratio of **2a/3a/4a** and GC yield of **2a** were determined by GC analysis with isooctane as the internal standard. [b]. Isolated yield for **2a**. [c] Isolated yield for **3a**.

Table S2. The effect of reaction temperature^a



entry	T (°C)	Conv.(%)	2a/3a/4a	GC Yield of 2 (%)
1	120	>99	88/5/7	88
2	100	>99	95/2/3	94(94) ^b
3	80	>99	92/1/7	92
4	60	>99	78/1/21	76

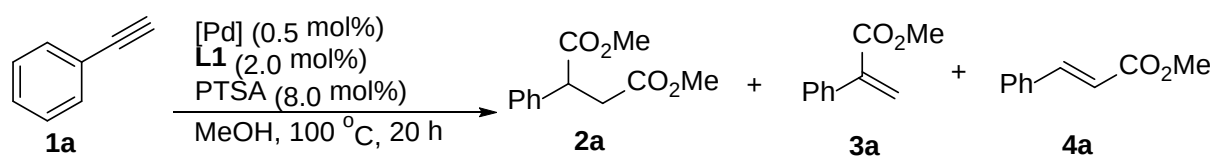
[a]. Standard reaction conditions: **1a** (1.0 mmol), Pd(acac)₂ (0.005 mmol, 0.5 mol%), Ligand (0.02 or 0.04 mmol, 2 or 4 mol%), PTSA (16 mg, 8 mol%), MeOH (2.0 mL), CO (40 atm), 20 h at specified temperature; the conversion, the ratio of **2a/3a/4a** and GC yield of **2a** were determined by GC analysis with isooctane as the internal standard. [b]. Isolated yield for **2a**.



entry	T (°C)	Conv.(%)	3a/4a	GC Yield of 3a (%)
1	120	>99	92/8	86
2	100	>99	94/6	88
3	80	>99	95/5	92(90) ^b
4	60	30	89/11	28

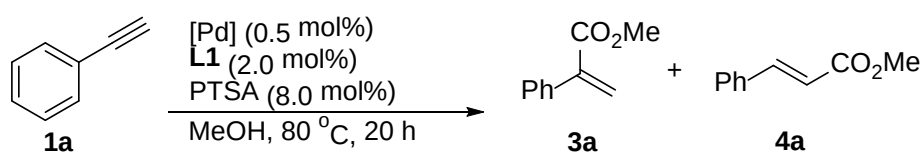
[a]. standard reaction conditions: **1a** (1.0 mmol), Pd(acac)₂ (0.005 mmol, 0.5 mol%), Ligand (0.02 mmol, 2.0 mol%), PTSA (16 mg, 8 mol%), MeOH (2.0 mL), CO (40 atm), 20 h at specified temperature; the conversion, the ratio of **3a/4a** and GC yield of **3a** were determined by GC analysis with isooctane as the internal standard. [b]. Isolated yield for **3a**.

Table S3. The effect of palladium precursor^a



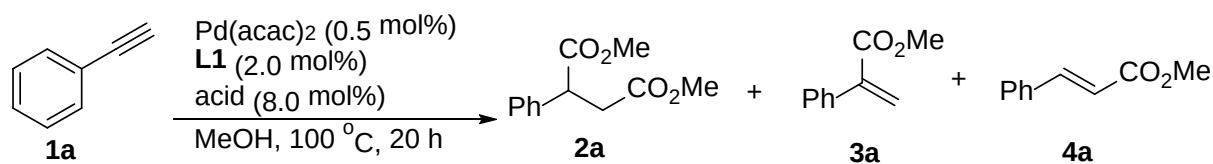
entry	Pd salts	Conv.(%)	2a/3a/4a	GC Yield of 2a (%)
1	Pd(acac) ₂	>99	95/2/3	94
2	PdCl ₂	>99	90/3/7	87
3	Pd ₂ (dba) ₃	>99	86/2/12	84
4	Pd(OAc) ₂	>99	95/2/3	94
5	Pd(TFA) ₂	>99	87/3/10	85
6	Pd(cod)Cl ₂	>99	88/3/9	86
7	Pd(MeCN) ₂ Cl ₂	>99	88/4/8	87

[a]. Standard reaction conditions: **1a** (1.0 mmol), [Pd] (0.005 mmol in terms of Pd atom, 0.5 mol%), **L1** (0.02 mmol, 2.0 mol%), PTSA (16 mg, 8 mol%), MeOH (2.0 mL), CO (40 atm), 20 h at 100 °C; the conversion, the ratio of **2a/3a/4a** and GC yield of **2a** were determined by GC analysis with isooctane as the internal standard.



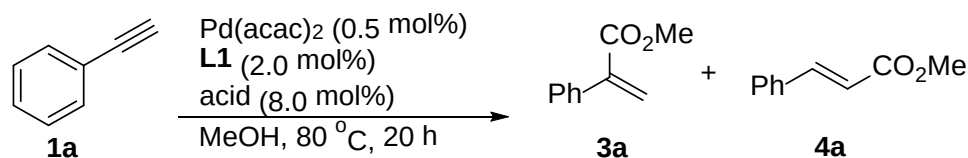
entry	Pd salts	Conv.(%)	3a/4a	GC Yield of 3a (%)
1	Pd(acac) ₂	>99	95/5	92 (90 ^b)
2	PdCl ₂	17	67/33	11
3	Pd ₂ (dba) ₃	>99	93/7	91
4	Pd(OAc) ₂	>99	95/5	91

[a]. Standard reaction conditions: **1a** (1.0 mmol), [Pd] (0.005 mmol in terms of Pd atom, 0.5 mol%), **L3** (0.02 mmol, 2.0 mol%), PTSA (16 mg, 8 mol%), MeOH (2.0 mL), CO (40 atm), 20 h; the conversion, the ratio of **2a/3a** and GC yield of **3a** were determined by GC analysis with isooctane as the internal standard. [b] Isolated yield for **3a**.

Table S4. The effect of acid^a

entry	Acid (x)	Conv.(%)	2a/3a/4a	GC Yield of 2a (%)
1	HOAc (8)	>99	3/80/17	trace
2	CF ₃ SO ₃ H (8)	>99	61/5/34	60
3	H ₂ SO ₄ (4)	>99	92/2/6	90
4	PTSA (8)	>99	95/2/3	94
5	PTSA (4)	>99	93/1/6	91
6	PTSA (16)	>99	86/5/9	83

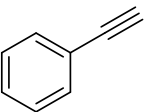
[a]. Standard reaction conditions: **1a** (1.0 mmol), Pd(acac)₂ (0.005 mmol, 0.5 mol%), **L1** (0.02 mmol, 2.0 mol%), acid, MeOH (2.0 mL), CO (40 atm), 20 h at 100 °C; the conversion, the ratio of **2a/3a/4a** and GC yield of **2a** were determined by GC analysis with isooctane as the internal standard.



entry	Acid (x)	Conv.(%)	3a/4a	GC Yield of 3a (%)
1	HOAc (8)	66	56/44	65
2	CF ₃ SO ₃ H (8)	>99	95/5	92
3	H ₂ SO ₄ (4)	>99	93/7	92
4	PTSA (8)	>99	95/5	92 (90 ^b)
5	PTSA (4)	>99	91/9	92
6	PTSA (16)	>99	95/5	88

[a]. Standard reaction conditions: **1a** (1.0 mmol), Pd(acac)₂ (0.005 mmol, 0.5 mol%), **L3** (0.02 mmol, 2.0 mol%), acid, MeOH (2.0 mL), CO (40 atm), 20 h; the conversion, the ratio of **2a/3a** and GC yield of **3a** were determined by GC analysis with isooctane as the internal standard. [b] Isolated yield for **3a**.

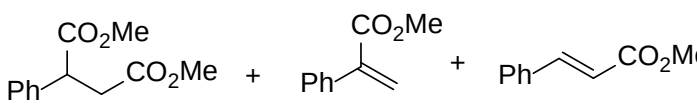
Table S5. The effect of catalyst loading^a



1a

Pd(acac)₂ (x mol%)
L1 (y mol%)
 PTSA (z mol%)

 MeOH, 100 °C, 20 h



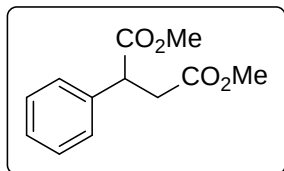
2a + **3a** + **4a**

entry	x/y/z	Conv.(%)	2a/3a/4a	GC Yield of 2a (%)
1	0.5/2/8	>99	95/1/4	94
2 ^b	0.5/2/8	>99	95/1/4	94
3	1/4/16	>99	>99/<1	99(98 ^c)
4 ^b	1/4/16	>99	>99/<1	99

[a]. Standard reaction conditions: **1a** (1.0 mmol), Pd(acac)₂ (x mol%), **L1** (y mol%), PTSA (z mol%), MeOH (2.0 mL), CO (40 atm), 20 h at 100 °C; the conversion, the ratio of **2a/3a/4a** and GC yield of **2a** were determined by GC analysis with isooctane as the internal standard. [b] Pd(OAc)₂ was used instead of Pd(acac)₂. [c] Isolated yield for **2a**.

2.3 Characterization of the products

dimethyl 2-phenylsuccinate (2a)¹



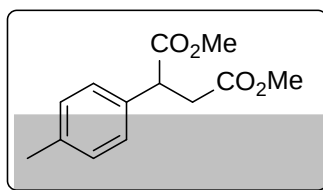
217 mg, 98% yield, 1.0 mmol scale, white solid. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.36-7.24 (m, 5H), 4.11 (dd, *J* = 9.0, 6.0 Hz, 1H), 3.66 (s, 6H), 3.22 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.67 (dd, *J* = 15.0, 6.0 Hz, 1H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 173.35, 171.89, 137.71, 128.86, 127.71, 127.65, 52.25, 51.77, 47.08, 37.60 ppm;

HRMS (ESI): Calcd. for C₁₂H₁₄O₄Na [M+Na]⁺: 245.07843, Found: 245.07815.

dimethyl 2-(p-tolyl)succinate (2b)¹



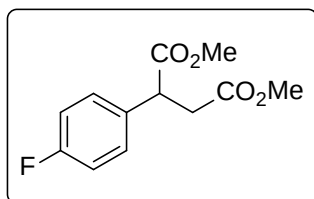
222 mg, 94% yield, 1.0 mmol scale, yellow oil. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.21-7.10 (m, 4H), 4.08 (dd, *J* = 9.0, 6.0 Hz, 1H), 3.68 (s, 6H), 3.22 (dd, *J* = 18.0, 9.0 Hz, 1H), 2.67 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.34 (s, 3H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 173.57, 172.01, 137.36, 134.70, 129.57, 127.58, 52.27, 51.80, 46.68, 37.65, 21.04 ppm;

HRMS (ESI): Calcd. for C₁₃H₁₆O₄Na [M+Na]⁺: 259.09408, Found: 259.09382.

dimethyl 2-(4-fluorophenyl)succinate (2c)²



233 mg, 97% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

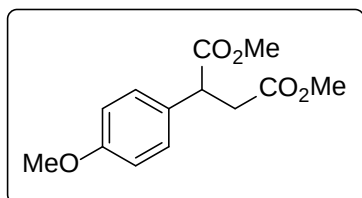
¹H NMR (300 MHz, CDCl₃) δ 7.27-7.22 (m, 2H), 7.03-6.96 (m, 2H), 4.07 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.65 (s, 6H), 3.16 (dd, *J* = 18.0, 9.0 Hz, 1H), 2.65 (dd, *J* = 18.0, 6.0 Hz, 1H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 173.21, 171.71, 162.18 (d, *J*_(F,C) = 245.2 Hz), 133.40 (d, *J*_(F,C) = 3.0 Hz), 129.36 (d, *J*_(F,C) = 6.8 Hz), 115.72 (d, *J*_(F,C) = 21.8 Hz), 52.33, 51.82, 46.27, 37.57 ppm;

¹⁹F NMR (282 MHz, CDCl₃) δ -114.69 ppm.

HRMS (ESI): Calcd. for C₁₂H₁₃FO₄Na [M+Na]⁺: 263.06901, Found: 263.06876.

dimethyl 2-(4-methoxyphenyl)succinate (2d)¹



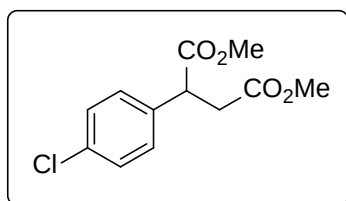
239 mg, 95% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 10/1.

¹H NMR (300 MHz, CDCl₃) δ 7.20-7.16 (m, 2H), 6.86-6.81 (m, 2H), 4.02 (dd, *J* = 9.0, 6.0 Hz, 1H), 3.75 (s, 3H), 3.64 (s, 6H), 3.16 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.63 (dd, *J* = 15.0, 6.0 Hz, 1H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 173.60, 171.93, 159.65, 129.69, 128.74, 114.22, 55.14, 52.17, 51.72, 46.22, 37.66 ppm.

HRMS (ESI): Calcd. for C₁₃H₁₆O₅Na [M+Na]⁺: 275.08899, Found: 275.08861.

dimethyl 2-(4-chlorophenyl)succinate (2e)¹



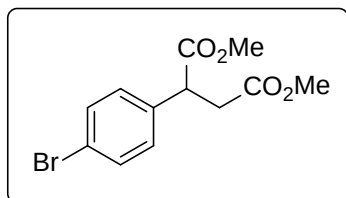
223 mg, 87% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.31-7.20 (m, 4H), 4.07 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 3.17 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.66 (dd, *J* = 15.0, 6.0 Hz, 1H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 172.96, 171.61, 136.14, 133.58, 129.15, 129.01, 52.40, 51.87, 46.44, 37.41 ppm.

HRMS (ESI): Calcd. for C₁₂H₁₃ClO₄Na [M+Na]⁺: 279.03946, Found: 279.03928.

dimethyl 2-(4-bromophenyl)succinate (2f)¹



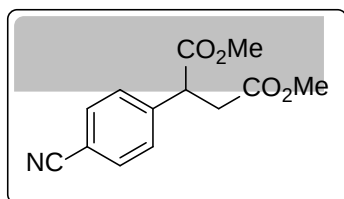
258 mg, 86% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.46-7.41 (m, 2H), 7.18-7.14 (m, 2H), 4.06 (dd, *J* = 9.0, 6.0 Hz, 1H), 3.66-3.65 (m, 6H), 3.16 (dd, *J* = 18.0, 9.0 Hz, 1), 2.65 (dd, *J* = 18.0, 6.0 Hz, 1H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 172.86, 171.58, 136.66, 131.97, 129.51, 121.69, 52.43, 51.88, 46.51, 37.34 ppm.

HRMS (ESI): Calcd. for C₁₂H₁₃BrO₄Na [M+Na]⁺: 322.98894, Found: 322.98855.

dimethyl 2-(4-cyanophenyl)succinate (2g)¹



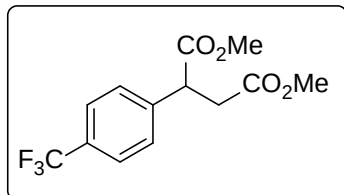
210 mg, 85% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.62-7.58 (m, 2H), 7.41-7.37 (m, 2H), 4.14 (dd, *J* = 9.0, 6.0 Hz, 1H), 3.65 (s, 3H), 3.63 (s, 3H), 3.16 (dd, *J* = 18.0, 9.0 Hz, 1H), 2.68 (dd, *J* = 18.0, 6.0 Hz, 1H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 172.22, 171.26, 142.84, 132.62, 128.74, 118.39, 111.71, 52.61, 51.98, 47.06, 37.05 ppm;

HRMS (ESI): Calcd. for C₁₃H₁₃NO₄Na [M+Na]⁺: 270.07368, Found: 270.07324.

dimethyl 2-(4-(trifluoromethyl)phenyl)succinate (2h)²



267 mg, 92% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

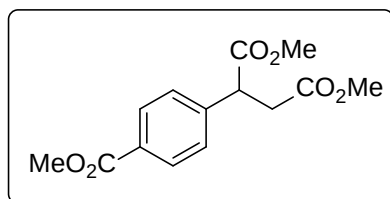
¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, *J* = 6.0 Hz, 2H), 7.42 (d, *J* = 6.0 Hz, 2H), 4.18 (dd, *J* = 9.0, 6.0 Hz, 1H), 3.68-3.67 (m, 6H), 3.22 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.70 (dd, *J* = 18.0, 6.0 Hz, 1H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 172.63, 171.48, 141.63 (q, *J* = 1.5 Hz, 1C), 129.97 (q, *J* = 32.3 Hz, 1C), 128.24, 128.79 (q, *J* = 3.8 Hz, 1C), 123.96 (q, *J* = 270.8 Hz, 1C), 52.46, 51.88, 46.89, 37.25 ppm;

¹⁹F NMR (282 MHz, CDCl₃) δ -62.76 ppm.

HRMS (ESI): Calcd. for C₁₃H₁₃F₃O₄Na [M+Na]⁺: 313.06581, Found: 313.06603.

dimethyl 2-(4-(methoxycarbonyl)phenyl)succinate (2i)³



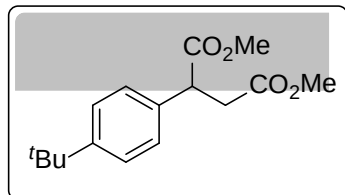
249 mg, 89% yield, 1.0 mmol scale, white solid. Eluent: pentane/ethyl acetate = 15/1.

¹H NMR (300 MHz, CDCl₃) δ 7.97-7.93 (m, 2H), 7.34-7.30 (m, 2H), 4.12 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.85 (s, 3H), 3.63 (s, 3H), 3.61 (s, 3H), 3.17 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.65 (dd, *J* = 18.0, 6.0 Hz, 1H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 172.66, 171.51, 166.48, 142.64, 130.07, 129.56, 127.83, 52.40, 52.03, 51.83, 47.00, 37.22 ppm;

HRMS (ESI): Calcd. for C₁₄H₁₆O₆Na [M+Na]⁺: 303.08391, Found: 303.08346.

dimethyl 2-(4-(tert-butyl)phenyl)succinate (2j)³



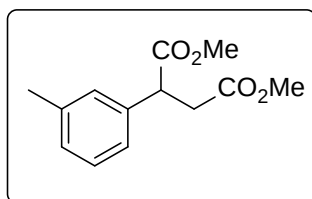
264 mg, 95% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.36-7.33 (m, 2H), 7.23-7.20 (m, 2H), 4.08 (dd, *J* = 9.0, 6.0 Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 3.22 (dd, *J* = 18.0, 9.0 Hz, 1H), 2.66 (dd, *J* = 15.0, 6.0 Hz, 1H), 1.31 (s, 9H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 173.51, 171.99, 150.43, 134.63, 127.33, 125.77, 52.16, 51.71, 46.58, 37.62, 34.44, 31.28 ppm.

HRMS (ESI): Calcd. for C₁₆H₂₂O₄Na [M+Na]⁺: 301.14103, Found: 301.14064.

dimethyl 2-(m-tolyl)succinate (2k)²



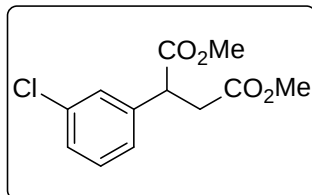
224 mg, 95% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.24-7.19 (m, 1H), 7.11-7.06 (m, 3H), 4.07 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.67-3.66 (m, 6H), 3.21 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.66 (dd, *J* = 15.0, 6.0 Hz, 1H), 2.34 (s, 3H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 173.45, 171.91, 138.53, 137.64, 128.75, 128.42, 128.38, 124.74, 52.22, 51.74, 47.01, 37.64, 21.23 ppm.

HRMS (ESI): Calcd. for C₁₃H₁₆O₄Na [M+Na]⁺: 259.09408, Found: 259.09365.

dimethyl 2-(3-chlorophenyl)succinate (2l)



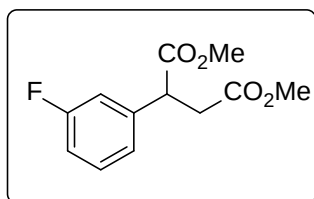
230 mg, 90% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.20-7.14 (m, 3H), 7.11-7.06 (m, 1H), 3.98 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.59 (s, 3H), 3.57 (s, 3H), 3.10 (dd, *J* = 18.0, 9.0 Hz, 1H), 2.58 (dd, *J* = 15.0, 6.0 Hz, 1H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 172.75, 171.56, 139.56, 134.60, 130.10, 127.96, 127.90, 125.99, 52.44, 51.87, 46.70, 37.33 ppm.

HRMS (ESI): Calcd. for C₁₂H₁₃ClO₄Na [M+Na]⁺: 279.03946, Found: 279.03903.

dimethyl 2-(3-fluorophenyl)succinate (2m)²



221 mg, 92% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

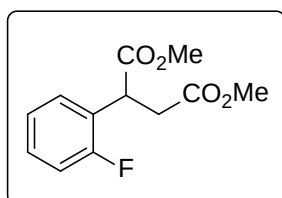
¹H NMR (300 MHz, CDCl₃) δ 7.23-7.16 (m, 1H), 6.99-6.84 (m, 3H), 4.01 (dd, *J* = 9.0, 6.0 Hz, 1H), 3.58 (s, 3H), 3.57 (s, 3H), 3.10 (dd, *J* = 18.0, 9.0 Hz, 1H), 2.58 (dd, *J* = 18.0, 6.0 Hz, 1H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 172.82, 171.61, 162.85 (d, *J* = 245.2 Hz, 1C), 139.98 (d, *J* = 7.5 Hz, 1C), 130.36 (d, *J* = 8.2 Hz, 1C), 123.48 (d, *J* = 3.0 Hz, 1C), 114.86 (d, *J* = 13.5 Hz, 1C), 114.57 (d, *J* = 12.0 Hz, 1C), 52.38, 51.83, 46.74 (d, *J* = 2.25 Hz, 1C), 37.34 ppm;

¹⁹F NMR (282 MHz, CDCl₃) δ -112.29 ppm;

HRMS (ESI): Calcd. for C₁₂H₁₃FO₄Na [M+Na]⁺: 263.06901, Found: 263.06905.

dimethyl 2-(2-fluorophenyl)succinate (2n)



202 mg, 84% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

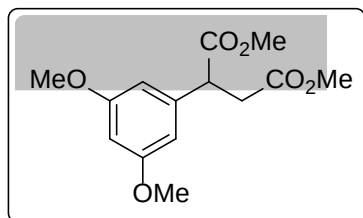
¹H NMR (300 MHz, CDCl₃) δ 7.29-7.21 (m, 2H), 7.12-7.01 (m, 2H), 4.40 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 3.19 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.65 (dd, *J* = 15.0, 6.0 Hz, 1H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 172.65, 171.72, 160.32 (d, *J* = 246.0 Hz, 1C), 129.31 (d, *J* = 10.5 Hz, 1C), 129.28 (d, *J* = 1.5 Hz, 1C), 125.08 (d, *J* = 14.2 Hz, 1C), 124.46 (d, *J* = 3.8 Hz, 1C), 115.76 (d, *J* = 21.8 Hz, 1C), 52.41, 51.84, 40.46 (d, *J* = 2.2 Hz, 1C), 36.46 (d, *J* = 0.75 Hz, 1C) ppm;

^{19}F NMR (282 MHz, CDCl_3) δ -117.57 ppm;

HRMS (ESI): Calcd. for $\text{C}_{12}\text{H}_{13}\text{FO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 263.06901, Found: 263.06866.

dimethyl 2-(3,5-dimethoxyphenyl)succinate (2o)



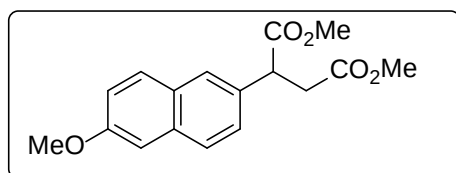
265 mg, 94% yield, 1.0 mmol scale, white solid. Eluent: pentane/ethyl acetate = 5/1.

^1H NMR (300 MHz, CDCl_3) δ 6.40 (s, 2H), 6.35-6.34 (m, 1H), 3.99 (dd, J = 12.0, 6.0 Hz, 1H), 3.74 (s, 6H), 3.65 (s, 3H), 3.64 (s, 3H), 3.16 (dd, J = 15.0, 9.0 Hz, 1H), 2.63 (dd, J = 15.0, 6.0 Hz, 1H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 173.14, 171.88, 161.02, 139.79, 105.76, 99.41, 55.22, 52.30, 51.78, 47.18, 37.49 ppm;

HRMS (ESI): Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$: 305.09956, Found: 305.09912.

dimethyl 2-(6-methoxynaphthalen-2-yl)succinate (2p)



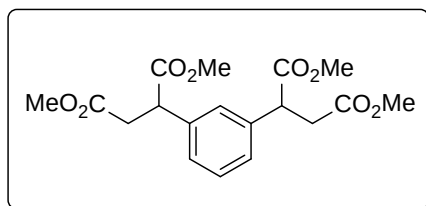
266 mg, 88% yield, 1.0 mmol scale, white solid. Eluent: pentane/ethyl acetate = 10/1.

^1H NMR (300 MHz, CDCl_3) δ 7.61-7.55 (m, 3H), 7.28-7.24 (m, 1H), 7.06-6.99 (m, 2H), 4.13 (dd, J = 12.0, 6.0 Hz, 1H), 3.78 (s, 3H), 3.57 (s, 6H), 3.20 (dd, J = 15.0, 9.0 Hz, 1H), 2.65 (dd, J = 18.0, 6.0 Hz, 1H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 173.59, 172.04, 157.87, 133.94, 132.74, 129.34, 128.90, 127.51, 126.52, 126.08, 119.26, 105.57, 55.30, 52.39, 51.89, 47.04, 37.68 ppm.

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 325.10464, Found: 325.10412.

tetramethyl 2,2'-(1,3-phenylene)disuccinate (2q)



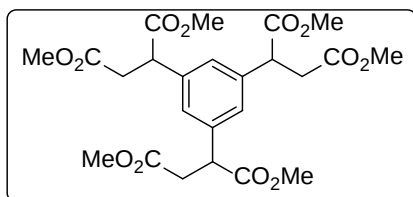
158 mg, 86% yield, 0.5 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 10/1.

^1H NMR (300 MHz, CDCl_3) δ 7.24-7.19 (m, 1H), 7.13-7.10 (m, 3H), 4.00 (dd, J = 12.0, 6.0 Hz, 1H), 3.59 (s, 12H), 3.08 (m, 2H), 2.57 (dd, J = 18.0, 6.0 Hz, 1H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 173.09, 171.75, 138.31, 129.38, 127.39, 126.91, 52.34, 51.84, 46.91, 37.53 ppm;

HRMS (ESI): Calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_8\text{Na}$ $[\text{M}+\text{Na}]^+$: 389.12069, Found: 389.12042.

hexamethyl 2,2',2''-(benzene-1,3,5-triyl)trisuccinate (2r)



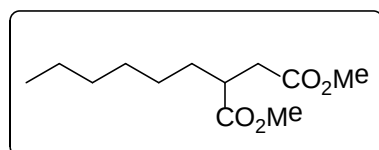
160 mg, 63% yield, 0.5 mmol scale, white solid. Eluent: pentane/ethyl acetate = 10/1.

^1H NMR (300 MHz, CDCl_3) δ 7.03 (s, 3H), 3.99 (dd, J = 9.0, 6.0 Hz, 1H), 3.61 (s, 9H), 3.60 (s, 9H), 3.09 (dd, J = 15.0, 9.0 Hz, 1H), 2.55 (dd, J = 15.0, 6.0 Hz, 1H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 172.80, 171.59, 138.90, 126.47, 52.38, 51.86, 46.79, 37.51 ppm.

HRMS (ESI): Calcd. for $\text{C}_{24}\text{H}_{30}\text{O}_{12}\text{Na}$ $[\text{M}+\text{Na}]^+$: 533.16295, Found: 533.16315.

dimethyl 2-hexylsuccinate (2s)⁴



216 mg, 94% yield (product/isomers = 75/25), 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

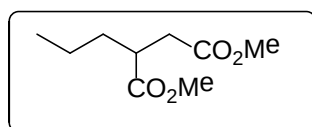
^1H NMR (300 MHz, CDCl_3) δ 3.62-3.59(m, 6H), 2.76-2.22 (m, 3H), 1.60-1.51 (m, 2H), 1.47-1.07 (m, 8H), 0.82-0.78 (m, 3H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 175.33, 172.29, 51.59, 51.54, 41.04, 35.68, 31.84, 31.48, 28.93, 26.77, 22.43, 13.89 ppm;

DEPT 135 NMR (75 MHz, CDCl_3) δ 51.99 (+), 51.55 (+), 41.04 (+), 35.68 (-), 31.84 (-), 31.48 (-), 28.93 (-), 26.77 (-), 22.43 (-), 13.89 (+) (CH and CH_3 : +, positive; CH_2 : -, negative).

HRMS (ESI): Calcd. for $\text{C}_{12}\text{H}_{22}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 253.14103, Found: 253.14083.

dimethyl 2-propylsuccinate (2t)⁵



165 mg, 88% yield (product/isomers = 75/25), 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

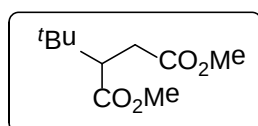
^1H NMR (300 MHz, CDCl_3) δ 3.65-3.61 (m, 6H), 2.71-2.22 (m, 3H), 1.65-1.22 (m, 4H), 1.14-1.09 (m, 1H), 0.89-0.84 (m, 2H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 175.38, 172.34, 51.61, 51.60, 40.89, 35.73, 34.01, 20.09, 13.37 ppm;

DEPT 135 NMR (75 MHz, CDCl_3) δ 51.65 (+), 51.61 (+), 40.89 (+), 35.73 (-), 34.01(-), 20.09 (-), 13.74 (+) (CH and CH_3 : +, positive; CH_2 : -, negative).

HRMS (ESI): Calcd. for $\text{C}_9\text{H}_{16}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 211.09408, Found: 211.09405.

dimethyl 2-(tert-butyl)succinate (2u)¹



178 mg, 88% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

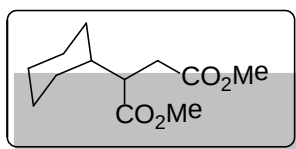
^1H NMR (300 MHz, CDCl_3) δ 3.64 (s, 3H), 3.61 (s, 3H), 2.74 (dd, J = 15.0, 12.0 Hz, 1H), 2.62 (dd, J = 12.0, 3.0 Hz, 1H), 2.44 (dd, J = 18.0, 3.0 Hz, 1H), 0.92 (s, 9H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 174.57, 173.01, 51.64, 51.22, 51.14, 32.53, 27.71 ppm;

DEPT 135 NMR (75 MHz, CDCl_3) δ 51.64 (+), 51.22 (+), 51.15 (+), 32.53 (-), 27.71 (+) (CH and CH_3 : +, positive; CH_2 : -, negative).

HRMS (ESI): Calcd. for $\text{C}_{10}\text{H}_{18}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 225.10973, Found: 225.10934.

dimethyl 2-cyclohexylsuccinate (2v)⁶



223 mg, 98% yield (product/isomers = 91/9), 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

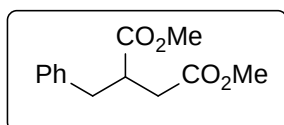
^1H NMR (300 MHz, CDCl_3) δ 3.67-3.60 (m, 6H), 2.68-2.65 (m, 2H), 2.45-2.38 (m, 1H), 1.72-1.53 (m, 6H), 1.19-0.95 (m, 5H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 174.83, 172.82, 51.60, 51.45, 46.92, 39.87, 33.14, 30.54, 30.07, 26.22, 26.06 ppm;

DEPT 135 NMR (75 MHz, CDCl_3) δ 51.60 (-), 51.45 (-), 46.92 (-), 39.87 (-), 33.14 (+), 30.53 (+), 30.07 (+), 26.22 (+), 26.06 (+) (CH and CH_3 : -, negative; CH_2 : +, positive).

HRMS (ESI): Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 251.12538, Found: 251.12501.

dimethyl 2-benzylsuccinate (2w)⁴



227 mg, 96% yield (product/isomers = 82/18), 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

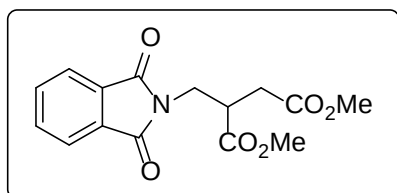
^1H NMR (300 MHz, CDCl_3) δ 7.32-7.14 (m, 5H), 3.67-3.62 (m, 6H), 3.20-3.09 (m, 2H), 3.05-2.64 (m, 2H), 2.45-2.25 (m, 1H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 174.69, 172.20, 138.14, 128.98, 128.53, 126.70, 51.85, 51.68, 43.01, 37.71, 34.89 ppm;

DEPT 135 NMR (75 MHz, CDCl_3) δ 128.99 (+), 128.53 (+), 126.70 (+), 51.85 (+), 51.68 (+), 43.01 (+), 37.71 (-), 34.89 (-) (CH and CH_3 : +, positive; CH_2 : -, negative).

HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 259.09408, Found: 259.09357.

dimethyl 2-((1,3-dioxoisindolin-2-yl)methyl)succinate (2x)



283 mg, 93% yield, 1.0 mmol scale, white solid. Eluent: pentane/ethyl acetate = 10/1.

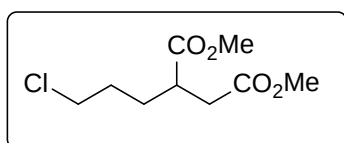
^1H NMR (300 MHz, CDCl_3) δ 7.80-7.76 (m, 2H), 7.72-7.66 (m, 2H), 4.01-3.83 (m, 2H), 3.64 (s, 3H), 3.59 (s, 3H), 3.23-3.20 (m, 1H), 2.76-2.68 (m, 1H), 2.52 (dd, J = 15.0, 6.0 Hz, 1H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 172.50, 171.53, 167.93, 134.14, 131.76, 123.35, 52.34, 51.83, 40.41, 38.60, 33.30 ppm;

DEPT 135 NMR (75 MHz, CDCl_3) δ 134.14 (+), 123.35 (+), 52.34 (+), 51.83 (+), 40.41 (+), 38.60 (-), 33.30 (-) (CH and CH_3 : +, positive; CH_2 : -, negative).

HRMS (ESI): Calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}_6\text{Na}$ $[\text{M}+\text{Na}]^+$: 328.07916, Found: 328.07889.

dimethyl 2-(3-chloropropyl)succinate (2y)



204 mg, 92% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 10/1.

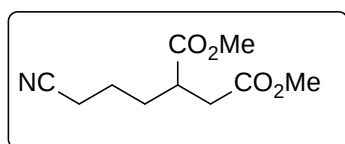
^1H NMR (300 MHz, CDCl_3) δ 3.66 (s, 3H), 3.63 (s, 3H), 3.51-3.47 (m, 2H), 2.87-2.78 (m, 1H), 2.70 (dd, J = 15.0, 9.0 Hz, 1H), 2.41 (dd, J = 18.0, 6.0 Hz, 1H), 1.81-1.63 (m, 4H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 174.73, 172.01, 51.86, 51.73, 44.29, 40.42, 35.79, 29.87, 29.05 ppm;

DEPT 135 NMR (75 MHz, CDCl_3) δ 51.86 (+), 51.73 (+), 44.30 (-), 40.43 (+), 35.79 (-), 29.87 (-), 29.05 (-) (CH and CH_3 : +, positive; CH_2 : -, negative).

HRMS (ESI): Calcd. for $\text{C}_9\text{H}_{15}\text{ClO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 245.05511, Found: 245.05499.

dimethyl 2-(3-cyanopropyl)succinate (2z)⁸



192 mg, 90% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 10/1.

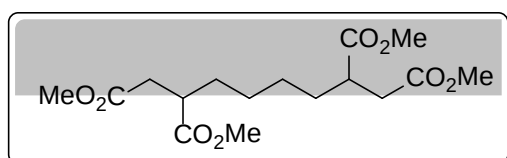
^1H NMR (300 MHz, CDCl_3) δ 3.65 (s, 3H), 3.62 (s, 3H), 2.86-2.77 (m, 1H), 2.69 (dd, J = 15.0, 9.0 Hz, 1H), 2.44-2.30 (m, 3H), 1.77-1.57 (m, 4H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 174.37, 171.85, 119.12, 51.97, 51.81, 40.35, 35.70, 30.57, 22.96, 16.89 ppm;

DEPT 135 NMR (75 MHz, CDCl_3) δ 51.98 (-), 51.81 (-), 40.35 (-), 35.70 (+), 30.57 (+), 22.96 (+), 16.89 (+) (CH and CH_3 : -, negative; CH_2 : +, positive).

HRMS (ESI): Calcd. for $\text{C}_{10}\text{H}_{15}\text{NO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 236.08933, Found: 236.08927.

tetramethyl octane-1,2,7,8-tetracarboxylate (2aa)



260 mg, 75% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 10/1.

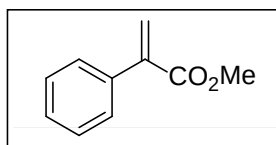
^1H NMR (300 MHz, CDCl_3) δ 3.65 (s, 6H), 3.62 (s, 6H), 2.77-2.61 (m, 4H), 3.38 (dd, J = 15.0, 6.0 Hz, 2H), 1.62-1.41 (m, 4H), 1.27-1.07 (m, 4H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 175.19, 172.25, 51.77, 51.70, 40.96, 35.71, 31.58, 26.66 ppm;

DEPT 135 NMR (75 MHz, CDCl_3) δ 51.75 (+), 51.68 (+), 40.96 (+), 35.72 (-), 31.57 (-), 26.64 (-) (CH and CH_3 : +, positive; CH_2 : -, negative).

HRMS (ESI): Calcd. for $\text{C}_{16}\text{H}_{26}\text{O}_8\text{Na}$ $[\text{M}+\text{Na}]^+$: 369.15199, Found: 369.15168.

methyl 2-phenylacrylate (3a)⁸

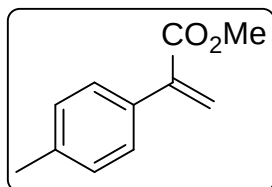


141 mg, 87% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

^1H NMR (300 MHz, CDCl_3) δ 7.49-7.38 (m, 5H), 6.41 (d, J = 1.2 Hz, 1H), 5.94 (d, J = 1.2 Hz, 1H), 3.86 (s, 3H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 167.25, 141.37, 136.75, 128.31, 128.20, 128.14, 126.83, 52.17 ppm.

methyl 2-(p-tolyl)acrylate (3b)⁸

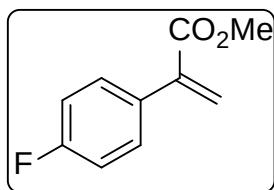


120 mg, 68% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

^1H NMR (300 MHz, CDCl_3) δ 7.38-7.34 (m, 2H), 7.23-7.19 (m, 2H), 6.36 (d, J = 1.2 Hz, 1H), 5.91 (d, J = 1.2 Hz, 1H), 3.86 (s, 3H), 2.41 (s, 3H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 167.47, 141.18, 138.09, 133.85, 128.86, 128.18, 126.17, 52.18, 21.22 ppm;

methyl 2-(4-fluorophenyl)acrylate (3c)⁹

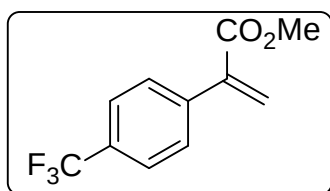


149 mg, 83% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.45-7.38 (m, 2H), 7.09-7.03 (m, 2H), 6.38 (d, *J* = 1.2 Hz, 1H), 5.89 (d, *J* = 1.2 Hz, 1H), 3.84 (s, 3H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 167.01, 162.71 (d, *J* = 246 Hz, 1C), 140.17, 132.73 (d, *J* = 3.8 Hz, 1C), 130.10 (d, *J* = 8.2 Hz, 1C), 126.95, 115.04 (d, *J* = 21.8 Hz, 1C), 52.24 ppm.

methyl 2-(4-(trifluoromethyl)phenyl)acrylate (3d)¹⁰

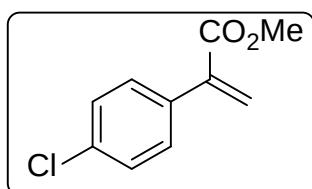


126 mg, 55% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.52-7.48 (m, 2H), 7.43-7.39 (m, 2H), 6.36 (d, *J* = 1.2 Hz, 1H), 5.84 (d, *J* = 1.2 Hz, 1H), 3.72 (s, 3H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 166.48, 140.24 (q, *J* = 1.5 Hz, 1C), 140.17, 130.22 (q, *J* = 32.2 Hz, 1C), 128.74, 128.60, 125.06 (q, *J* = 3.8 Hz, 1C), 124.08 (q, *J* = 270 Hz, 1C), 52.34 ppm.

methyl 2-(4-chlorophenyl)acrylate (3e)⁸

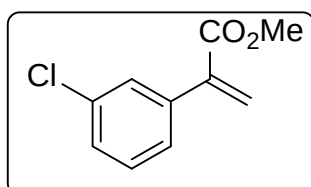


149 mg, 76% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

^1H NMR (300 MHz, CDCl_3) δ 7.29-7.21 (m, 4H), 6.30 (d, $J = 1.2$ Hz, 1H), 5.81 (d, $J = 1.2$ Hz, 1H), 3.73 (s, 3H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 166.81, 140.14, 135.10, 134.22, 129.68, 128.31, 127.40, 52.30 ppm;

methyl 2-(3-chlorophenyl)acrylate (3f)⁹

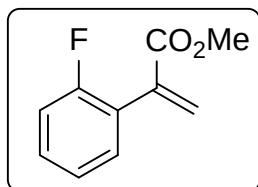


137 mg, 70% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

^1H NMR (300 MHz, CDCl_3) δ 7.33-7.32(m, 1H), 7.24-7.17 (m, 3H), 6.32 (d, $J = 0.9$ Hz, 1H), 5.82 (d, $J = 0.9$ Hz, 1H), 3.73 (s, 3H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 166.62, 140.08, 138.42, 133.98, 129.35, 128.46, 128.26, 127.94, 126.56, 52.32 ppm;

methyl 2-(2-fluorophenyl)acrylate (3g)¹¹

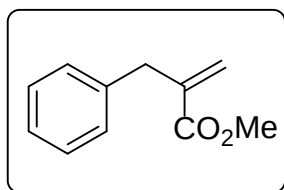


163 mg, 91% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

^1H NMR (300 MHz, CDCl_3) δ 7.25-7.14 (m, 2H), 7.05-6.92 (m, 2H), 6.40 (d, $J = 0.9$ Hz, 1H), 5.77 (d, $J = 0.9$ Hz, 1H), 3.68 (s, 3H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 166.52, 159.9 (d, $J = 246.0$ Hz, 1C), 136.54, 130.78 (d, $J = 3.0$ Hz, 1C), 130.10 (d, $J = 8.2$ Hz, 1C), 129.25 (d, $J = 1.5$ Hz, 1C), 125.11 (d, $J = 15.0$ Hz, 1C), 123.98 (d, $J = 3.8$ Hz, 1C), 115.46 (d, $J = 21.8$ Hz, 1C), 52.27 ppm.

methyl 2-benzylacrylate (3h)¹²



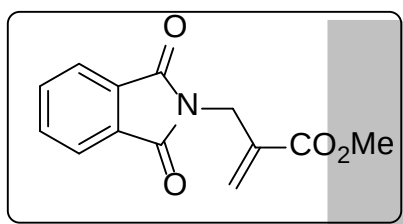
123 mg, 70% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.34-7.22 (m, 5H), 6.28 (m, 1H), 6.50 (m, 1H), 3.77 (s, 3H), 3.68 (s, 2H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 167.36, 140.15, 138.71, 129.05, 128.45, 126.37, 126.25, 51.88, 38.09 ppm;

DEPT 135 NMR (75 MHz, CDCl₃) δ 129.06 (+), 128.45 (+), 126.38 (+), 126.26(-), 51.88 (+), 38.09 (-) (CH and CH₃: +, positive; CH₂: -, negative).

methyl 2-((1,3-dioxoisindolin-2-yl)methyl)acrylate (3i)²²



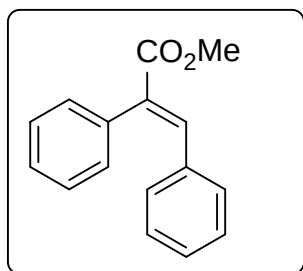
171 mg, 70% yield, 1.0 mmol scale, white solid. Eluent: pentane/ethyl acetate = 10/1.

¹H NMR (300 MHz, CDCl₃) δ 7.89-7.84 (m, 2H), 7.76-7.72 (m, 2H), 6.31 (dt, *J* = 1.2, 0.3 Hz, 1H), 5.58 (dt, *J* = 1.2, 0.3 Hz, 1H), 4.55 (t, *J* = 1.2 Hz, 2H), 3.78 (s, 3H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 167.67, 165.70, 134.35, 134.16, 131.94, 126.02, 123.45, 52.12, 38.24 ppm;

DEPT 135 NMR (75 MHz, CDCl₃) δ 134.16 (+), 126.03 (-), 123.45 (+), 52.12 (+), 38.25 (-) (CH and CH₃: +, positive; CH₂: -, negative).

methyl (E)-2,3-diphenylacrylate (3j)¹³

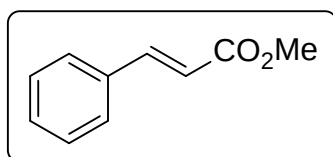


174 mg, 73% yield, 1.0 mmol scale, white solid. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.96 (s, 1H), 7.45-7.41 (m, 3H), 7.32-7.11 (m, 7H), 3.85 (s, 3H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 168.33, 140.60, 135.96, 134.66, 132.53, 130.69, 129.82, 129.14, 128.73, 128.28, 127.92, 52.44 ppm;

methyl cinnamate (4a)¹⁴

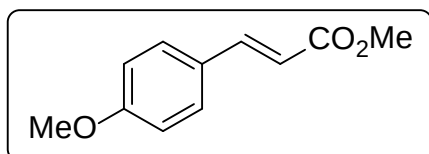


146 mg, 90% yield, 1.0 mmol scale, white solid. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.70 (d, *J* = 15.9 Hz, 1H), 7.52-7.48 (m, 2H), 7.39-7.35 (m, 2H), 6.45 (d, *J* = 16.2 Hz, 1H), 3.80 (s, 3H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 167.31, 144.81, 134.38, 130.27, 128.87, 128.07, 117.81, 51.61 ppm.

methyl (E)-3-(4-methoxyphenyl)acrylate (4b)¹⁵

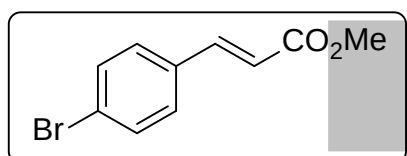


154 mg, 80% yield, 1.0 mmol scale, white solid. Eluent: pentane/ethyl acetate = 15/1.

^1H NMR (300 MHz, CDCl_3) δ 7.55 (d, $J = 15.9$ Hz, 1H), 7.39-7.34 (m, 2H), 6.81-6.78 (m, 2H), 6.21 (d, $J = 15.9$ Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 167.71, 161.39, 144.49, 129.71, 127.10, 115.25, 114.31, 55.33, 51.53 ppm;

methyl (E)-3-(4-bromophenyl)acrylate (4c)¹⁶

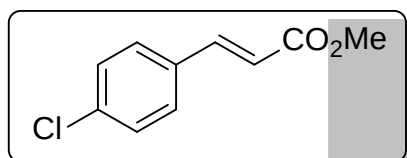


211 mg, 88% yield, 1.0 mmol scale, white solid. Eluent: pentane/ethyl acetate = 20/1.

^1H NMR (300 MHz, CDCl_3) δ 7.52 (d, $J = 16.2$ Hz, 1H), 7.43-7.40 (m, 2H), 7.30-7.19 (m, 2H), 6.33 (d, $J = 16.2$ Hz, 1H), 3.71 (s, 3H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 167.09, 143.43, 133.28, 132.12, 129.43, 124.53, 118.50, 51.78 ppm;

methyl (E)-3-(4-chlorophenyl)acrylate (4d)¹⁵

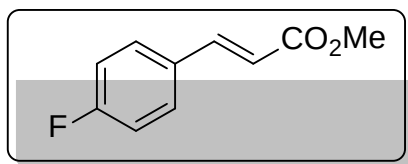


168 mg, 86% yield, 1.0 mmol scale, white solid. Eluent: pentane/ethyl acetate = 20/1.

^1H NMR (300 MHz, CDCl_3) δ 7.54 (d, $J = 16.2$ Hz, 1H), 7.36-7.34 (m, 2H), 7.27-7.24 (m, 2H), 6.31 (d, $J = 15.9$ Hz, 1H), 3.71 (s, 3H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 167.10, 143.36, 136.18, 132.86, 129.21, 129.15, 118.38, 51.76 ppm;

methyl (E)-3-(4-fluorophenyl)acrylate (4e)¹⁷

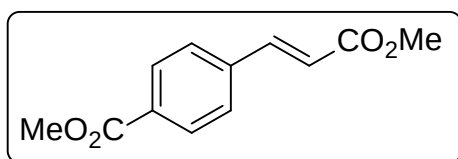


164 mg, 91% yield, 1.0 mmol scale, white solid. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, *J* = 16.2 Hz, 1H), 7.43-7.37 (m, 2H), 7.01-6.93 (m, 2H), 6.26 (d, *J* = 16.2 Hz, 1H), 3.70 (s, 3H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 167.21, 163.87 (d, *J* = 249.0 Hz, 1C), 143.48, 130.62 (d, *J* = 3.0 Hz, 1C), 129.91 (d, *J* = 9.0 Hz, 1C), 117.55 (d, *J* = 2.2 Hz, 1C), 116.00 (d, *J* = 21.8 Hz, 1C), 51.66 ppm;

methyl (E)-4-(3-methoxy-3-oxoprop-1-en-1-yl)benzoate (4f)¹⁸

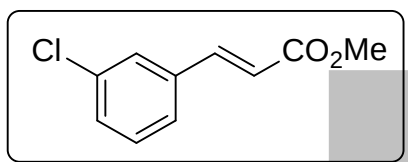


200 mg, 91% yield, 1.0 mmol scale, white solid. Eluent: pentane/ethyl acetate = 10/1.

¹H NMR (300 MHz, CDCl₃) δ 7.99-7.95 (m, 2H), 7.63 (d, *J* = 15.9 Hz, 1H), 7.52-7.48 (m, 2H), 6.44 (d, *J* = 15.9 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 3H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 166.92, 166.39, 143.31, 138.57, 131.39, 130.09, 127.89, 120.18, 52.26, 51.86 ppm;

methyl (E)-3-(3-chlorophenyl)acrylate (4g)¹⁶

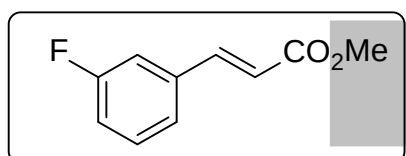


165 mg, 84% yield, 1.0 mmol scale, white solid. Eluent: pentane/ethyl acetate = 20/1.

^1H NMR (300 MHz, CDCl_3) δ 7.51 (d, $J = 15.9$ Hz, 1H), 7.39-7.38 (m, 1H), 7.29-7.17 (m, 3H), 6.33 (d, $J = 15.9$ Hz, 1H), 3.71 (s, 3H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 166.92, 143.17, 136.18, 134.88, 130.11, 130.10, 127.77, 126.22, 119.26, 51.79 ppm.

methyl (E)-3-(3-fluorophenyl)acrylate (4h)¹⁹



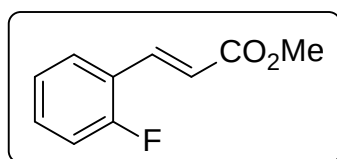
131 mg, 73% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

^1H NMR (300 MHz, CDCl_3) δ 7.54 (d, $J = 15.6$ Hz, 1H), 7.29-7.09 (m, 3H), 7.01-6.94 (m, 1H), 6.33 (d, $J = 15.9$ Hz, 1H), 3.71 (s, 3H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 166.98, 162.98 (d, $J = 245.2$ Hz, 1C), 143.40 (d, $J = 3.0$ Hz, 1C), 136.61 (d, $J = 7.5$ Hz, 1C), 130.42 (d, $J = 8.2$ Hz, 1C), 124.05 (d, $J = 3.0$ Hz, 1C), 119.19, 117.11 (d, $J = 21.0$ Hz, 1C), 114.27 (d, $J = 21.8$ Hz, 1C), 51.77 ppm;

^{19}F NMR (282 MHz, CDCl_3) δ -112.52 ppm;

methyl (E)-3-(2-fluorophenyl)acrylate (4i)²⁰



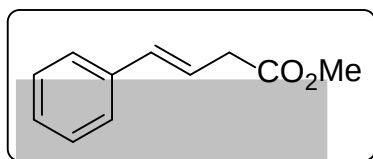
164 mg, 91% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

^1H NMR (300 MHz, CDCl_3) δ 7.72 (d, $J = 16.5$ Hz, 1H), 7.55-7.50 (m, 1H), 7.39-7.31 (m, 1H), 7.18-7.06 (m, 2H), 6.54 (d, $J = 16.2$ Hz, 1H), 3.81 (s, 3H) ppm;

^{13}C NMR (75 MHz, CDCl_3) δ 167.19, 161.32 (d, $J = 252$ Hz, 1C), 137.40 (d, $J = 3.0$ Hz, 1C), 131.68 (d, $J = 9.0$ Hz, 1C), 129.02 (d, $J = 3.0$ Hz, 1C), 124.42 (d, $J = 3.8$ Hz, 1C), 122.42 (d, $J = 12.0$ Hz, 1C), 120.35 (d, $J = 6.8$ Hz, 1C), 116.16 (d, $J = 21.8$ Hz, 1C) 51.73 ppm;

^{19}F NMR (282 MHz, CDCl_3) δ -114.42 ppm;

methyl (E)-4-phenylbut-3-enoate (4j)²¹



105 mg, 60% yield, 1.0 mmol scale, colorless oil. Eluent: pentane/ethyl acetate = 20/1.

¹H NMR (300 MHz, CDCl₃) δ 7.29-6.98 (m, 5H), 6.39 (dt, *J* = 15.9, 1.2 Hz, 1H), 6.20 (dt, *J* = 15.9, 6.9 Hz, 1H), 3.61 (s, 3H), 3.15 (dd, *J* = 6.9, 1.2 Hz, 2H) ppm;

¹³C NMR (75 MHz, CDCl₃) δ 171.98, 136.84, 133.50, 128.56, 127.59, 126.31, 121.69, 51.92, 38.23 ppm;

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