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# **Electronic Supplementary Information**

# Highly-Functionalized Arene Synthesis Based on Palladium on Carbon-Catalyzed Aqueous Dehydrogenation of Cyclohexadienes and Cyclohexenes

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# **1. General Information.**

10% Pd/C was supplied by the N. E. Chemcat Corporation (Tokyo, Japan). H<sub>2</sub>O, THF and toluene as solvents were purchased from a commercial source and used without further purification. Flash column chromatography was performed with Silica Gel 60 N (Kanto Chemical Co., Inc., 63–210 µm spherical, neutral). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a ECA 500 spectrometer at room temperature in CDCl<sub>3</sub> as a solvent and internal standard (<sup>1</sup>H NMR:  $\delta$ = 7.26; <sup>13</sup>C NMR:  $\delta$ = 77.0 for CDCl<sub>3</sub>, <sup>1</sup>H NMR:  $\delta$ = 2.49; <sup>13</sup>C NMR:  $\delta$ = 39.5 for DMSO-*d*<sub>6</sub>) with tetramethylsilane as an internal standard. IR spectra were recorded by a Brucker FT-IR ALPHA. The Pd leaching was analysed by ICP-OES using SPS5520 (SII Nano

Technology, Tokyo, Japan). ESI high resolution mass spectra (HRMS) were measured by a Shimadzu hybrid IT-TOF mass spectrometer. Melting points were measured by a SANSYO SMP-300 melting point apparatus.

# 2. Preparation of substrates.

- 2-1. Synthesis of 1,3-dutadienes (1)
- 2-1-1. Genaral procedure A



To a suspension of methyltriphenylphosphonium bromide (6.0 mmol) in THF (30 mL) was added *n*-BuLi (2.3 mL: 2.6 M in *n*-hexane, 3.6 mmol) at 0 °C under argon. After stirring for 15 min, a cinnamaldehyde derivative (6.0 mmol) was added. The reaction mixture was warmed to room temperature and the progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was quenched with sat. NH<sub>4</sub>Cl aq. (10 mL) and extracted with EtOAc (10 mL  $\times$  2). The combined organic layers were dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding 1-aryl-1,3-butadiene derivative (1).

(*E*)-1-Phenyl-1,3-butadiene (1a)

*trans*-Cinnamaldehyde (0.66 g, 5.0 mmol) was used as a substrate and 1a (0.65 g, 5.0 mmol) was obtained in quantitative yield after purification by silica-gel column chromatography (only *n*-hexane).

Colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.44 (d, *J* = 7.5 Hz, 2H), 7.32 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.23 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.80 (dd, *J* = 10.0, 16.0 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.53—6.48 (m, 1H), 5.34 (d, *J* = 16.0 Hz, 1H), 5.18 (d, *J* = 10.0 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 1.

#### (E)-1-(Buta-1,3-dien-1-yl)-4-methoxybenzene (1c)



4-Methoxycinnamaldehyde (0.81 g, 5.0 mmol) was used as a substrate and 1c (0.52 g, 3.2 mmol) was obtained in 65% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 50/1).

Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.34 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 6.67 (dd, J = 10.4, 15.2 Hz, 1H), 6.52 (d, J = 10.4 Hz, 1H), 6.50—6.44 (m, 1H), 5.28 (d, J = 16.0 Hz, 1H), 5.11 (d, J = 9.2 Hz, 1H), 3.81 (s, 3H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 1.

### (E)-4-(Buta-1,3-dien-1-yl)-N,N-dimethylaniline (1d)



4-*N*,*N*-Dimethylaminocinnamaldehyde (0.53 g, 3.0 mmol) was used as a substrate and **d** (0.52 g, 3.0 mmol) was obtained in 99% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 15/1).

Yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.30 (d, J = 8.5 Hz, 2H), 6.68 (d, J = 8.5 Hz, 2H), 6.65—6.60 (m, 1H), 6.52—6.47 (m, 2H), 5.22 (d, J = 16.0 Hz, 1H), 5.04 (d, J = 10.0 Hz, 1H), 2.97 (s, 6H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 2.

#### (E)-1-(Buta-1,3-dien-1-yl)-4-nitrobenzene (1f)



4-Nitrocinnamaldehyde (0.89 g, 5.0 mmol) was used as a substrate and **1f** (0.44 g, 2.5 mmol) was obtained in 51% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 15/1).

Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.18 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 6.93 (dd, J = 10.5, 15.0 Hz, 1H), 6.61 (d, J = 15.0 Hz, 1H), 6.58—6.50 (m, 1H), 5.48 (d, J = 17.5 Hz, 1H), 5.35 (d, J = 10.0 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 3.

#### (E)-1-(Buta-1,3-dien-1-yl)-4-bromobenzene (1h)



4-Bromocinnamaldehyde (0.69 g, 3.3 mmol) was used as a substrate and **1h** (0.46 g, 2.2 mmol)

was obtained in 67% yield after purification by silica-gel column chromatography (only *n*-hexane).

Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.43 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 6.77 (dd, J = 10.0, 16.0 Hz, 1H), 6.53—6.45 (m, 2H), 5.36 (d, J = 17.0 Hz, 1H), 5.21 (d, J = 10.0 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 1.

#### (E)-1-(Buta-1,3-dien-1-yl)-4-fluorobenzene (1j)



4-Fluorocinnamaldehyde (0.60 g, 4.0 mmol) was used as a substrate and 1j (0.47 g, 3.1 mmol) was obtained in 79% yield after purification by silica-gel column chromatography (only *n*-hexane).

Colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.37 (dd, J = 6.0, 8.5 Hz, 2H), 7.01 (t, J = 8.5 Hz, 2H), 6.71 (dd, J = 10.5, 15.5 Hz, 1H), 6.54—6.46 (m, 2H), 5.33 (d, J = 17.5 Hz, 1H), 5.18 (d, J = 10.0 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 1.

# (Z)-2-Bromo-1-phenyl-1,3-butadiene (1n)



 $\alpha$ -Bromocinnamaldehyde (1.10 g, 5.0 mmol) was used as a substrate and **1n** (0.47 g, 2.2 mmol) was obtained in 45% yield after purification by silica-gel column chromatography (only *n*-hexane).

Colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.70 (d, J = 8.0 Hz, 2H), 7.40—7.37 (m, 2H), 7.33—7.30 (m, 1H), 6.99 (s, 1H), 6.52 (dd, J = 10.5, 16.0 Hz, 1H), 5.74 (d, J = 16.0 Hz, 1H), 5.35 (d, J = 10.5 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 4.

#### (*E*)-1-(2-furyl)-1,3-butadiene (1q)



4-(2-Furyl)-3-buten-2-one (0.61 g, 5.0 mmol) was used as a substrate and 1q (0.54 g, 4.5 mmol) was obtained in 90% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 50/1).

Colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.37 (d, J = 2.0 Hz, 1H), 6.71 (dd, J = 11.0, 15.5 Hz, 1H), 6.48—6.35 (m, 3H), 6.28 (d, J = 3.5 Hz, 1H), 5.33 (d, J = 17.0 Hz, 1H), 5.16 (d, J = 10.5 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 5.

# 2,3-Diphenyl-1,3-butadiene (1v)



Benzil (0.53 g, 2.5 mmol) was used as a substrate. Methyltriphenylphosphonium bromide (2.14 g, 6 mmol), *n*-BuLi (2.3 mL: 2.6 M in *n*-hexane, 6.0 mmol) and THF (30 mL) were used and **1v** (0.49 g, 2.4 mmol) was obtained in 87% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 100/1).

Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.44—7.42 (m, 2H), 7.32—7.27 (m, 6H), 5.58 (d, J = 2.5 Hz, 2H), 5.35 (d, J = 2.5 Hz, 2H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 6.

#### 2-1-2. Genaral procedure B



Step 1: To a round-bottomed flask were added allyl bromide (60.49 g, 500 mmol), triphenylphosphine (65.57 g, 250 mmol), and toluene (125 mL) under argon, and the reaction mixture was refluxed at 130 °C. After stirring for 9 h, the reaction mixture was cooled to room temperature and passed through a filter paper [Kiriyama, No. 5C (1  $\mu$ m), diameter = 60 mm]. The obtained colorless solid was washed with toluene (30 mL), and dried in a desiccator under vacuum for overnight to give the allyltriphenylphosphonium bromide.

# Allyltriphenylphosphonium bromide

# P+Ph<sub>3</sub>Br

Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.88—7.83 (m, 6H), 7.81—7.77 (m, 3H), 7.73—7.67 (m, 6H), 5.75—5.67 (m, 1H), 5.60 (dd, J = 4.5, 16.0 Hz, 1H), 5.39 (dd, J = 6.0, 10.5

Hz, 1H), 4.85 (dd, J = 6.0, 16.0 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 7.

Step 2: To a suspension of allyltriphenylphosphonium bromide (2.30 g, 6.0 mmol) in THF (30 mL) was added n-BuLi (2.3 mL: 2.6 M in *n*-hexane, 6.0 mmol) at 0 °C under argon. After stirring for 15 min, a benzaldehyde derivative (5.0 mmol) was added. The reaction mixture was warmed to room temperature and the progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was quenched with sat. NH<sub>4</sub>Cl aq. (10 mL) and extracted with EtOAc (10 mL  $\times$  2). The combined organic layers were dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding 1-aryl-1,3-butadiene derivative (1).

#### (E or Z)-4-(Buta-1,3-dien-1-yl)biphenyl (1b)



4-Phenyl-benzaldehyde (0.91 g, 5.0 mmol) was used as a substrate and **1b** (0.87 g, 4.2 mmol) was obtained in 85% yield after purification by silica-gel column chromatography (n-hex/EtOAc = 30/1).

E/Z mixture was obtained. E/Z ratio = 48/52

Colorless solid; <sup>1</sup>H NMR of *E* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.64—7.58 (m, 4H), 7.51—7.42 (m, 4H), 7.38—7.35 (m, 1H), 6.88—6.83 (m, 1H), 6.64—6.50 (m, 2H), 5.38 (d, *J* = 17.5 Hz, 1H), 5.21 (d, *J* = 10.0 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 8. <sup>1</sup>H NMR of *Z* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.64—7.58 (m, 4H), 7.51—7.42 (m, 4H), 7.38—7.35 (m, 1H), 7.02—6.94 (m, 1H), 6.64—6.50 (m, 1H), 6.32 (t, *J* = 11.5 Hz, 1H), 5.43 (d, *J* = 17.5 Hz, 1H), 5.28 (d, *J* = 10.0 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 8.

#### (*E* or *Z*)-1-[4-(Carbomethoxy)phenyl]-1,3-butadiene (1e)



Methyl terephthalaldehydate (4.10 g, 25.0 mmol) was used as a substrate and **1e** (3.81 g, 20.0 mmol) was obtained in 80% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 20/1).

# E/Z mixture was obtained. E/Z ratio = 26/74

Cololess oil; <sup>1</sup>H NMR of *E* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.98 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 6.91—6.81 (m, 1H), 6.60—6.51 (m, 2H), 5.41 (d, *J* = 17.0 Hz, 1H), 5.26 (d, *J* = 10.5 Hz, 1H), 3.91 (s, 3H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 9. <sup>1</sup>H NMR of *Z* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.01 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 6.91—6.81 (m, 1H), 6.47 (d, *J* = 11.5 Hz, 1H), 6.34 (dd, *J* = 11.5, 11.5 Hz, 1H), 5.44 (d, *J* = 16.5 Hz, 1H), 5.30 (d, *J* = 11.5 Hz, 1H), 3.92 (s, 3H). *Z* isomer is unknown compound but the two isomers were inseparable.

# (*E* or *Z*)-1-(Buta-1,3-dien-1-yl)-4-cyanobenzene (1g)



4-Cyanobenzaldehyde (0.66 g, 5.0 mmol) was used as a substrate and **1g** (0.27 g, 1.8 mmol) was obtained in 35% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 10/1).

E/Z mixture was obtained. E/Z ratio = 48/52

Colorless oil; <sup>1</sup>H NMR of *E* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.58 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 6.87 (dd, *J* = 10.5, 15.5 Hz, 1H), 6.55—6.47 (m, 2H), 5.48—5.42 (m, 1H), 5.33—5.29 (m, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 10. <sup>1</sup>H NMR of *Z* isomer (500 MHz, CDCl<sub>3</sub>): 7.61 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 6.77 (dt, *J* = 10.5, 16.5 Hz, 1H), 6.43—6.34 (m, 2H), 5.48—5.42 (m, 1H), 5.33—5.29 (m, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 11.

#### (E or Z)-1-(Buta-1,3-dien-1-yl)-4-chlorobenzene (1i)



4-Chlorobenzaldehyde (0.70 g, 5.0 mmol) was used as a substrate and **1i** (0.33 g, 2.0 mmol) was obtained in 41% yield after purification by silica-gel column chromatography (only *n*-hexane). E/Z mixture was obtained. E/Z ratio = 48/52

Colorless oil; <sup>1</sup>H NMR of *E* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.34—7.24 (m, 4H), 6.87—6.74 (m, 1H), 6.54—6.46 (m, 2H), 5.43—5.34 (m, 1H), 5.28—5.20 (m, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 1. <sup>1</sup>H NMR of *Z* isomer (500 MHz, CDCl<sub>3</sub>): 7.34—7.24 (m, 4H), 6.87—6.74 (m, 1H), 6.41—6.39 (m, 1H), 6.31—6.26 (m, 1H), 5.43—5.34 (m, 1H), 5.28—5.20 (m, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the

reference 12.

(*E* or *Z*)-1-(Buta-1,3-dien-1-yl)-2-methoxybenzene (11)

2-Methoxybenzaldehyde (0.82 g, 6.0 mmol) was used as a substrate and **11** (0.74 g, 4.6 mmol) was obtained in 77% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 30/1).

E/Z mixture was obtained. E/Z ratio = 23/77

Colorless oil; <sup>1</sup>H NMR of *E* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.48 (dd, *J* = 2.0, 7.5 Hz, 1H), 7.28—7.20 (m, 1H), 6.96—6.76 (m, 4H), 6.56—6.51 (m, 1H), 5.31 (d, *J* = 17.5 Hz, 1H), 5.15 (d, *J* = 10.5 Hz, 1H), 3.87 (s, 3H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 1. <sup>1</sup>H NMR of *Z* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.31 (d, *J* = 7.5 Hz, 1H), 7.28—7.20 (m, 1H), 6.96—6.76 (m, 3H), 6.60 (d, *J* = 11.5 Hz, 1H), 6.32 (dd, *J* = 11.5, 11.5 Hz, 1H), 5.36 (d, *J* = 17.5 Hz, 1H), 5.19 (d, *J* = 9.5 Hz, 1H), 3.84 (s, 3H). *Z* isomer is unknown compound but the two isomers were inseparable.

# (*E* or *Z*)-1-(Buta-1,3-dien-1-yl)-3-methoxybenzene (1m)



3-Methoxybenzaldehyde (082 g, 6.0 mmol) was used as a substrate and 1m (0.67 g, 4.2 mmol) was obtained in 69% yield after purification by silica-gel column chromatography (only *n*-hexane).

#### E/Z mixture was obtained. E/Z ratio = 24/76

Colorless oil; <sup>1</sup>H NMR of *E* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.24 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.95—6.90 (m, 2H), 6.88 (s, 1H), 6.54 (d, *J* = 17.0 Hz, 1H), 6.54—6.47 (m, 1H), 5.35 (d, *J* = 17.0 Hz, 1H), 5.19 (d, *J* = 9.5 Hz, 1H), 3.83 (s, 3H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 1. <sup>1</sup>H NMR of *Z* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.26 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.91—6.90 (m, 1H), 6.86 (s, 1H), 6.81 (dd, *J* = 2.5, 7.5 Hz, 1H), 6.44 (d, *J* = 11.5 Hz, 1H), 6.26 (dd, *J* = 11.5, 11.5 Hz, 1H), 5.38 (d, *J* = 16.0 Hz, 1H), 5.23 (d, *J* = 11.5 Hz, 1H), 3.82 (s, 3H). *Z* isomer is unknown compound but the two isomers were inseparable.

(*E* or *Z*)-1-(2-thienyl)-1,3-butadiene (1r)



2-Thiophenecarboxaldehyde (0.34 g, 3.0 mmol) was used as a substrate. Potassium *tert*-butoxide (0.67 g, 6.0 mmol) was used instead of *n*-BuLi. Allyltriphenylphosphonium bromide (3.45 g, 9.0 mmol) was used and **1r** (0.40 g, 2.9 mmol) was obtained in 98% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 30/1).

E/Z mixture was obtained. E/Z ratio = 49/51

Yellow oil; <sup>1</sup>H NMR of *E* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.18—7.10 (m, 1H), 7.04—6.96 (m, 2H), 6.72—6.58 (m, 2H), 6.45 (ddd, *J* = 10.0, 10.0, 16.5 Hz, 1H), 5.31 (d, *J* = 16.5 Hz, 1H), 5.16 (d, *J* = 10.0 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 3. <sup>1</sup>H NMR of *Z* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.23 (d, *J* = 4.5 Hz, 1H), 7.18—7.10 (m, 1H), 7.04—6.96 (m, 2H), 6.50 (d, *J* = 11.5 Hz, 1H), 6.14 (dd, *J* = 11.5, 11.5 Hz, 1H), 5.42 (d, *J* = 16.5 Hz, 1H), 5.31 (d, *J* = 11.5 Hz, 1H). *Z* isomer is unknown compound but the two isomers were inseparable.

#### (*E* or *Z*)-1-Benzyl-1,3-butadiene (1x)



Phenylacetaldehyde (1.20 g, 10.0 mmol) was used as a substrate and 1x (1.02 g, 7.1 mmol) was obtained in 71% yield after purification by silica-gel column chromatography (*n*-pen/Et<sub>2</sub>O = 50/1).

E/Z mixture was obtained. E/Z ratio = 48/52

Colorless oil; <sup>1</sup>H NMR of *E* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.32—7.29 (m, 2H), 7.23—7.20 (m, 3H), 6.35 (dt, *J* = 10.5, 17.0 Hz, 1H), 6.17—6.10 (m, 1H), 5.89—5.83 (m, 1H), 5.23—5.13 (m, 1H), 5.02 (d, *J* = 9.0 Hz, 1H), 3.44 (d, *J* = 6.5 Hz, 2H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 13. <sup>1</sup>H NMR of *Z* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.32—7.29 (m, 2H), 7.23—7.20 (m, 3H), 6.79 (dt, *J* = 10.5, 16.5 Hz, 1H), 6.17—6.10 (m, 1H), 5.66—5.61 (m, 1H), 5.30 (dd, *J* = 1.5, 16.5 Hz, 1H), 5.23—5.13 (m, 1H), 3.56 (d, *J* = 8.0 Hz, 2H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 13.

## 2-1-3. Synthetic procedures of 1-(buta-1,3-dienyl)-4-vinylbenzene (1k).



Step 1: To a round bottomed flask were added 4-bromobenzaldehyde (1.85 g, 10.0 mmol), acrolein (0.8 mL, 12.0 mmol), palladium(II) diacetate (22.4 mg, 0.1 mmol, 1 mol%), tetra-*n*-butylammonium chloride (5.6 mL, 20.0 mmol), sodium hydrogen carbonate (1.26 g, 15 mmol) and DMF (50 mL) at room temperature under argon, and the reaction mixture was heated to 80 °C. After stirring for 40 h, the reaction mixture was cooled to room temperature and passed through a celite pad. The filtrate was extracted with EtOAc (30 mL × 3). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-EtOAc (2/1) as a mixed eluent to give 4-formylcinnamaldehyde (0.86 g, 5.38 mmol) in 54% yield.

4-Formylcinnamaldehyde



Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  10.05 (s, 1H), 9.76 (d, J = 7.5 Hz, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 16.0 Hz, 1H), 6.81 (dd, J = 7.5, 16.0 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 14.

Step 2: To a suspension of allyltriphenylphosphonium bromide (4.8 mmol) in THF (24 mL) was added *n*-BuLi (1.8 mL: 2.6 M in *n*-hexane, 4.8 mmol) at 0 °C under argon. After stirring for 15 min, 4-formylcinnamaldehyde (2.0 mmol) was added into the reaction mixture. The reaction mixture was warmed at room temperature. After stirring for 8 h, the reaction was quenched with sat. NH<sub>4</sub>Cl aq. (1 mL) and extracted with EtOAc (10 mL  $\times$  2). The combined organic layers were dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane- EtOAc (50/1) as a mixed eluent to give 1-(buta-1,3-dienyl)-4-vinylbenzene (**1k**: 0.11 g, 0.71 mmol) in 36% yield.

(E)-1-(Buta-1,3-dienyl)-4-vinylbenzene (1k)

Colorless solid; M.p. 55—58 °C; IR (ATR) cm<sup>-1</sup>: 3016, 1627, 1508, 1002; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.37 (s, 4H), 6.79 (dd, J = 10.5, 17.0 Hz, 1H), 6.70 (dd, J = 10.5, 17.0 Hz, 1H), 6.55 (d, J = 17.0 Hz, 1H), 6.51 (ddd, J = 10.5, 10.5, 17.0 Hz, 1H), 5.75 (d, J = 17.0 Hz, 1H), 5.34 (d, J = 17.0 Hz, 1H), 5.24 (d, J = 10.5 Hz, 1H), 5.18 (d, J = 10.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  137.2, 136.9, 136.7, 136.4, 132.5, 130.0, 126.6, 126.5, 117.7, 113.7.

# 2-1-4. Synthetic procedure of 1-[(*E*)-3-bromobuta-1,3-dienyl]benzene (10).



Based on reference 15: To a solution of triphenyl phosphite (7.43 mL, 28.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (80 mL) were added bromine (5.0 g, 31.3 mmol), trimethylamine (4.75 mL, 33.8 mmol), and 4-phenylbut-3-en-2-one (3.80 mL, 26.0 mmol) at -60 °C under Ar. The reaction mixture was warmed to room temperature. After stirring for 24 h, the reaction mixture was refluxed at 60 °C. After stirring for a further 2 h, the reaction mixture was cooled to room temperature and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-EtOAc (50/1) as a mixed eluent to give 1-[(*E*)-3-bromobuta-1,3-dienyl]benzene (**10**: 3.02 g, 14.5 mmol) in 56% yield.

# 3-[tert-Buthyl(dimethyl)silyloxy]-1-phenylbuta-1,3-diene (10)



Yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.46 (d, J = 7.5 Hz, 2H), 7.35 (dd, J = 7.5, 7.5 Hz, 2H), 7.30—7.27 (m, 1H), 6.94 (d, J = 15.5 Hz, 1H), 6.73 (d, J = 15.5 Hz, 1H), 5.93 (d, J = 1.0 Hz, 1H), 5.71 (d, J = 1.0 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 15.

2-1-5. Synthetic procedure of 3-[*tert*-buthyl(dimethyl)silyloxy]-1-phenylbuta-1,3-diene (1p).



To a solution of 4-phenylbut-3-en-2-one (1.47 g, 10.0 mmol), *tert*-butyl(dimethyl)silyl chloride (1.54 g, 10.2 mmol), and sodium iodide (1.51 g, 10.0 mmol) in MeCN (10 mL) was added triethylamine (1.67 mL, 12.0 mmol) at room temperature under argon. The reaction mixture was warmed to 45 °C. After stirring for 24 h, the reaction mixture was cooled to room temperature and added to sat. NaHCO<sub>3</sub> aq. (10 mL). The solution was extracted with *n*-hexane (30 mL  $\times$  2). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-NEt<sub>3</sub> (100/1) as a mixed eluent to give 3-[*tert*-Buthyl(dimethyl)silyloxy]-1-phenylbuta-1,3-diene (**1p**: 1.59 g, 6.1 mmol) in 61% yield.

3-[tert-Buthyl(dimethyl)silyloxy]-1-phenylbuta-1,3-diene (1p).



Colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.42 (d, *J* = 7.5 Hz, 2H), 7.33 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.24 (t, *J* = 7.5, 7.5 Hz, 1H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 4.45 (s, 1H), 4.42 (s, 1H), 1.02 (s, 6H), 0.22 (s, 6H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 16.

# 2-1-6. Synthetic procedure of (Z)-1,3-diphenyl-1,3-butadiene (1s).



Step 1: To a solution of α-Bromocinnamaldehyde (4.49 g, 20.0 mmol) in Et<sub>2</sub>O (30 mL) was

added lithium aluminium hydride (1.52g, 40.0 mmol) at 0 °C under argon. After stirring for 48 h, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (10 mL  $\times$  2). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-EtOAc (3/1) as a mixed eluent to give (*E*)-2,3-diphenylprop-2-en-1ol (3.46 g, 16.6 mmol) in 83% yield.

(E)-2,3-diphenylprop-2-en-1ol



Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.36—7.30 (m, 3H), 7.24—7.22 (m, 2H), 7.13—7.10 (m, 3H), 7.01—6.99 (m, 2H), 4.47 (d, J = 4.5 Hz, 2H), 1.67 (brs, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 17.

Step 2: To a round-bottomed flask was added (*E*)-2,3-diphenylprop-2-en-1-ol (2.10 g, 10.0 mmol), TEMPO (0.16 g, 1.0 mmol), (diacetoxyiodo)benzene (3.22 g, 10.0 mmol) and MeCN (8 mL) at 0 °C under argon. After stirring for 24 h, the reaction was quenched with sat. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aq. and extracted with EtOAc (10 mL  $\times$  2). The combined organic layers were dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-EtOAc (5/1) as a mixed eluent to give (*E*)-2,3-diphenyl-propenal (1.03 g, 0.49 mmol) in 49% yield.

(E)-2,3-diphenyl-2-propenal



Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  9.78 (s, 1H), 7.44—7.37 (m, 4H), 7.32—7.28 (m, 1H), 7.25—7.19 (m, 6H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 18.

Step 3: To a suspension of allyltriphenylphosphonium bromide (1.29 g, 3.6 mmol) in THF (18 mL) was added *n*-BuLi (1.4 mL: 2.6 M in *n*-hexane, 3.6 mmol) at 0 °C under argon. After stirring for 15 min, (*E*)-2,3-diphenyl-propenal (0.62 g, 3.0 mmol) was added into the reaction mixture. The reaction mixture was warmed at room temperature. After stirring for 4 h, the reaction mixture was quenched with sat.  $NH_4Cl$  aq. (1 mL) and extracted with EtOAc (10 mL ×

2). The combined organic layers were dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-EtOAc (50 /1) as a mixed eluent to give (Z)-1,3-diphenyl-1,3-butadiene (**1s**: 0.61 g, 2.92 mmol) in 97% yield.

(Z)-1,3-diphenyl-1,3-butadiene (1s)



Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.42—7.34 (m, 3H), 7.19 (dd, J = 1.5, 8.0 Hz, 2H), 7.12—7.08 (m, 3H), 6.91 (dd, J = 2.5, 7.0 Hz, 2H), 6.75 (dd, J = 10.5, 17.5 Hz, 1H), 6.62 (s, 1H), 5.17 (d, J = 10.5 Hz, 1H), 4.85 (d, J = 17.5 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 6.

### 2-1-7. Synthetic procedure of [(1E)-3-phenylbuta-1,3-dien-1-yl]benzene (1t)



Step 1: To a round-bottomed flask was added  $\alpha$ -methylstyrene (4.73 g, 40.0 mmol), *N*-bromosuccinimide (7.83g, 44.0 mmol), and CH<sub>3</sub>Cl (6 mL) at room temperature under argon, and the reaction mixture was refluxed at 90 °C. After 5 h, the reaction mixture was cooled to room temperature and passed through a celite pad. The filtrate was concentrated in vacuo. To the residue were added triphenylphosphine (10.49 g, 40.0 mmol) and toluene (40 mL) under argon at room temperature. After stirring for 24 h, the reaction mixture was passed through a filter paper [Kiriyama, No. 5C (1 µm), diameter = 60 mm]. The obtained colorless solid was washed with toluene (30 mL) and *n*-hexane (30 mL), and dried in a desiccator under vacuum for overnight to give triphenyl(2-phenyl-2-propenyl)phosphonium bromide (10.8 g, 23.5 mmol) in 59% yield..

#### Triphenyl(2-phenyl-2-propenyl)phosphonium bromide

P+Ph₃Br⁻

Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.79–7.75 (m, 6H), 7.69–7.66 (m, 3H), 7.57–7.53 (m, 6H), 7.23–7.21 (m, 2H), 7.10–7.06 (m, 3H), 5.49 (s, 1H), 5.48 (s, 1H), 5.27 (d, J = 15.5 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 19.

Step 2: To a suspension of triphenyl(2-phenyl-2-propenyl)phosphonium bromide (1.66 g, 3.6 mmol) in THF (18 mL) was added *n*-BuLi (1.4 mL: 2.6 M in *n*-hexane, 3.6 mmol) at 0 °C under argon. After stirring for 15 min, benzaldehyde (0.32 g, 3.0 mmol) was added into the reaction mixture. The reaction mixture was warmed to room temperature. After stirring for 3 h, the reaction mixture was quenched with sat. NH<sub>4</sub>Cl aq. (1 mL) and extracted with EtOAc (30 mL × 2). The combined organic layers were dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-EtOAc (50 /1) as a mixed eluent to give [(*E* or *Z*)-3-phenylbuta-1,3-dien-1-yl]benzene (**1t**: 0.24 g, 1.14 mmol) in 38% yield.

[(*E* or *Z*)-3-phenylbuta-1,3-dien-1-yl]benzene (1t)



E/Z mixture was obtained. E/Z ratio = 33/67

Colorless oil; <sup>1</sup>H NMR of *E* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.47 (d, *J* = 6.5 Hz, 1H), 7.39—7.02 (m, 7H), 7.16—7.08 (m, 2H), 7.04 (d, *J* = 16.0 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 5.41 (s, 1H), 5.23 (s, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 19. <sup>1</sup>H NMR of *Z* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.47 (d, *J* = 6.5 Hz, 1H), 7.39—7.02 (m, 7H), 7.16—7.08 (m, 2H), 6.63 (d, *J* = 12.0 Hz, 1H), 6.37 (d, *J* = 12.0 Hz, 1H), 5.53 (s, 1H), 5.26 (s, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 20.

#### 2-2. Synthesis of 1,4-cyclohexadienes (3)

2-1-1. General procedure C



To a round bottomed flask were added 1-aryl-1,3-butadiene derivative and dimethyl acetylenedicarboxylate (1: 3.0 mmol) and H<sub>2</sub>O (30 mL) at room temperature under argon and the reaction mixture was warmed to 50 °C. After stirring for 12 h, the reaction mixture was cooled to room temperature and extracted with EtOAc (10 mL  $\times$  2). The combined organic layers were dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding dimethyl 3-arylcyclohexa-1,4-diene-1,2-dicarboxylate (**3**).

# 2-2-2. General procedure D



To a round bottomed flask were added 1,3-butadiene derivative (1: 3.0 mmol), dimethyl acetylenedicarboxylate (3.0 mmol) and toluene (30 mL) at room temperature under argon and the reaction mixture was refluxed at 130 °C. After stirring for 12 h, the reaction mixture was cooled to room temperature and extracted with EtOAc (10 mL  $\times$  2). The combined organic layers were dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding dimethyl 3-arylcyclohexa-1,4-diene-1,2-dicarboxylate (3).

# 2-2-3. General procedure E



To a round bottomed flask were added 1-aryl-1,3-butadiene derivative (1: 0.5 mmol) and dimethyl acetylenedicarboxylate (0.5 mmol) at room temperature under argon and the reaction mixture was warmed to 50 °C. After stirring for 12 h, the reaction mixture was cooled to room temperature and purified by silica-gel column chromatography to give the corresponding dimethyl 3-arylcyclohexa-1,4-diene-1,2-dicarboxylate (3).

# 2-2-4. General procedure F



Based on reference 21: To a solution of  $CoBr_2(dppe)$  (0.1 mmol), zinc (0.2 mmol), and zinc iodide (0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) were added 1-3-butadiene derivative (**3**: 2.0 mmol) and alkynes (2.0 mmol) at room temperature under argon. The progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was passed through a short pass silica-gel column chromatography using only *n*-hexane as an eluent. The filtrate was concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding 1,4-cyclohexadiene derivatives (**3**).

#### Dimethyl 3-phenylcyclohexa-1,4-diene-1,2-dicarboxylate (3a)



Synthesized according to the general procedure C; **1a** (0.39 g, 3.0 mmol) was used as a substrate and **3a** (0.78 g, 2.9 mmol) was obtained in 96% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.31–7.28 (m, 2H), 7.23–7.18 (m, 3H), 5.83–5.74 (m, 2H), 4.40–4.37 (m, 1H), 3.77 (s, 3H), 3.53 (s, 3H), 3.28–3.25 (m, 1H), 3.04–2.97 (m, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 22.

# Dimethyl 3-(4':4''-biphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (3b)



Synthesized according to the general procedure A; **1b** (0.83 g, 4.0 mmol) was used as a substrate and **3b** (0.38 g, 1.1 mmol) was obtained in 27% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Colorless solid; M.p. 56—58 °C; IR (ATR) cm<sup>-1</sup>: 3029, 2950, 1721, 1678, 1642, 1486, 1434, 1363, 1255, 1193, 1157, 1114, 1067, 1007; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.57—7.55 (m, 2H), 7.52 (dt, *J* = 2.0, 8.0 Hz, 2H), 7.43—7.40 (m, 2H), 7.34—7.31 (m, 1H), 7.27—7.24 (m, 2H), 5.86—5.82 (m, 1H), 5.80—5.76 (m, 1H), 4.45—4.41 (m, 1H), 3.78 (s, 3H), 3.55 (s, 3H), 3.29—3.22 (m, 1H), 3.06—2.99 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.1, 168.1, 140.7, 140.4, 140.0, 136.5, 131.3, 128.7, 128.7, 127.4, 127.2, 127.0, 121.3, 52.3, 52.0, 43.6, 27.4; ESI-HRMS m/z: 371.1254 ([M+Na]<sup>+</sup>); C<sub>22</sub>H<sub>20</sub>O<sub>4</sub>Na: 371.1254.

# Dimethyl 3-(4'-methoxyphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (3c)



Synthesized according to the general procedure C; **1c** (0.16 g, 1.0 mmol) was used as a substrate and **3c** (0.27 g, 0.9 mmol) was obtained in 90% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Colorless solid; M.p. 62—65 °C; IR (ATR) cm<sup>-1</sup>: 2951, 2838, 1718, 1677, 1641, 1584, 1509, 1434, 1388, 1364, 1301, 1245, 1175, 1143, 1109, 1056, 1032; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.10 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.82—5.78 (m, 1H), 5.74—5.71 (m, 1H, 4.35—4.31 (m, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.54 (s, 3H), 3.26—3.18 (m, 1H), 3.02—2.95 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.4, 167.9, 158.6, 137.5, 133.4, 130.2, 129.4, 127.5, 121.0, 114.0, 55.2, 52.3, 52.0, 43.2, 27.2; ESI-HRMS m/z: 325.1044 ([M+Na]<sup>+</sup>); C<sub>17</sub>H<sub>18</sub>O<sub>5</sub>Na: 325.1046.

# Dimethyl 3-(4'-*N*,*N*-dimethylaminophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (3d)



Synthesized according to the general procedure E; **1g** (86.6 mg, 0.5 mmol) was used as a substrate and **3d** (139.8 mg, 0.44 mmol) was obtained in 89% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Yellow oil; IR (ATR) cm<sup>-1</sup>: 2950, 1724, 1644, 1634, 1613, 1519, 1505, 1453, 1434, 1353, 1259, 1204, 1163, 1066; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.04 (d, *J* = 9.0 Hz, 2H), 6.66 (d, *J* = 9.0 Hz, 2H), 5.80—5.76 (m, 1H), 5.75—5.71 (m, 1H), 4.30—4.26 (m, 1H), 3.76 (s, 3H), 3.56 (s, 3H), 3.25—3.18 (m, 1H), 3.01—2.93 (m, 1H), 2.91 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.6,

168.0, 149.7, 138.2, 129.4, 129.0, 128.9, 127.8, 120.7, 112.7, 52.2, 51.9, 43.2, 40.6, 27.1; ESI-HRMS m/z: 338.1363 ( $[M+Na]^+$ ); C<sub>18</sub>H<sub>21</sub>NO<sub>4</sub>Na: 338.1363.

## Trimethyl 3-phenylcyclohexa-1,4-diene-1,2,4'-tricarboxylate (3e)



Synthesized according to the general procedure C; **1e** (0.94 g, 5.0 mmol) was used as a substrate and **3e** (0.68 g, 2.1 mmol) was obtained in 41% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1).

Yellow oil; IR (ATR) cm<sup>-1</sup>: 2952, 1717, 1642, 1608, 1435, 1417, 1364, 1310, 1252, 1192, 1178, 1157, 1103, 1066, 1020; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.95 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.86—5.83 (m, 1H), 5.73—5.70 (m, 1H), 4.46—4.43 (m, 1H), 3.89 (s, 3H), 3.79 (s, 3H), 3.51 (s, 3H), 3.28—3.21 (m, 1H), 3.06—2.99 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.0, 167.7, 166.8, 146.7, 135.3, 132.3, 130.0, 129.0, 128.4, 126.7, 121.7, 52.3, 52.1, 52.0, 43.8, 27.6; ESI-HRMS m/z: 353.0995 ([M+Na]<sup>+</sup>); C<sub>18</sub>H<sub>18</sub>O<sub>6</sub>Na: 353.0996.

# Dimethyl 3-(4'-nitrophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (3f)



Synthesized according to the general procedure C; **1f** (0.14 g, 0.8 mmol) was used as a substrate and **3f** (0.19 g, 0.6 mmol) was obtained in 75% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Yellow oil; IR (ATR) cm<sup>-1</sup>: 2952, 1721, 1679, 1642, 1596, 1519, 1434, 1347, 1257, 1193, 1157, 1108, 1066; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.15 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 5.90—5.86 (m, 1H), 5.72—5.69 (m, 1H), 4.53—4.49 (m, 1H), 3.79 (s, 3H), 3.54 (s, 3H), 3.29—3.22 (m, 1H), 3.09—3.02 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.0, 167.1, 149.1, 147.0, 133.9, 133.7, 129.2, 126.2, 123.9, 122.2, 52.4, 52.1, 43.4, 27.7; ESI-HRMS m/z: 340.0795 ([M+Na]<sup>+</sup>); C<sub>16</sub>H<sub>15</sub>NO<sub>6</sub>Na: 340.0792.

# Dimethyl 3-(4'-cyanophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (3g)



Synthesized according to the general procedure D; **1g** (0.16 g, 1.0 mmol) was used as a substrate and **3g** (0.11 g, 0.38 mmol) was obtained in 38% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 4/1).

Colorless solid; M.p. 84—87 °C; IR (ATR) cm<sup>-1</sup>: 2952, 2228, 1718, 1679, 1434, 1250, 1192, 1156, 1057, 1004; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.60 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.89—5.87 (m, 1H), 5.72—5.70 (m, 1H), 4.48—4.45 (m, 1H), 3.80 (s, 3H), 3.56 (s, 3H), 3.30—3.22 (m, 1H), 3.09—3.02 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.0, 167.3, 147.0, 134.0, 133.6, 132.5, 129.2, 126.3, 122.2, 118.7, 111.1, 52.2, 52.1, 43.7, 27.7; ESI-HRMS m/z: 320.0893 ([M+Na]<sup>+</sup>); C<sub>17</sub>H<sub>15</sub>NO<sub>4</sub>Na: 320.0893.

# Dimethyl 3-(4'-bromophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (3h)



Synthesized according to the general procedure C; **1h** (0.78 g, 3.8 mmol) was used as a substrate and **3h** (0.21 g, 0.60 mmol) was obtained in 16% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Colorless solid; M.p. 98—99 °C; IR (ATR) cm<sup>-1</sup>: 3038, 2950, 1722, 1679, 1642, 1588, 1486, 1434, 1405, 1364, 1257, 1191, 1157, 1144, 1103, 1068, 1011; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.41 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 5.83—5.81 (m, 1H), 5.71—5.69 (m, 1H), 4.36—4.35 (m, 1H), 3.78 (s, 3H), 3.55 (s, 3H), 3.26—3.19 (m, 1H), 3.04—2.97 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.0, 167.8, 140.5, 135.7, 131.9, 131.7, 130.1, 127.0, 121.5, 121.1, 52.3, 52.0, 43.3, 27.4; ESI-HRMS m/z: 373.0047 ([M+Na]<sup>+</sup>); C<sub>16</sub>H<sub>15</sub>O<sub>4</sub>BrNa: 373.0046.

#### Dimethyl 3-(4'-chlorophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (3i)



Synthesized according to the general procedure D; 1i (0.16 g, 1.0 mmol) was used as a substrate and 3i (0.08 g, 0.2 mmol) was obtained in 26% yield after purification by silica-gel column

chromatography (n-hex/EtOAc = 5/1).

Colorless solid; M.p. 97—99 °C; IR (ATR) cm<sup>-1</sup>: 2951, 1723, 1680, 1642, 1490, 1434, 1364, 1257, 1192, 1157, 1090, 1068, 1015; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.26 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 5.85—5.81 (m, 1H), 5.72—5.69 (m, 1H), 4.38—4.35 (m, 1H), 3.78 (s, 3H), 3.55 (s, 3H), 3.26—3.19 (m, 1H), 3.05—2.97 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.0, 167.9, 139.9, 135.9, 132.9, 131.8, 129.7, 128.8, 127.0, 121.5, 52.3, 52.0, 43.3, 27.4; ESI-HRMS m/z: 329.0551 ([M+Na]<sup>+</sup>); C<sub>16</sub>H<sub>15</sub>O<sub>4</sub>ClNa: 329.0551.

Dimethyl 3-(4'-fluorophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (3j)



Synthesized according to the general procedure E; 1j (74.1 mg, 0.5 mmol) was used as a substrate and 3j (130.1 mg, 0.4 mmol) was obtained in 90 % yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Colorless solid; M.p. 52—54 °C; IR (ATR) cm<sup>-1</sup>: 2952, 1720, 1680, 1642, 1602, 1506, 1455, 1434, 1364, 1307, 1251, 1221, 1155, 1120, 1096, 1064, 1014; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.17—7.13 (m, 2H), 6.99—6.95 (m, 2H), 5.84—5.80 (m, 1H), 5.73—5.70 (m, 1H), 4.39—4.35 (m, 1H), 3.77 (s, 3H), 3.54 (s, 3H), 3.26—3.19 (m, 1H), 3.04—2.96 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.1, 167.9, 161.9 (d, *J* = 244.5 Hz), 137.1, 136.6, 131.1, 129.9 (d, *J* = 8.4 Hz) 127.2, 121.4, 115.4 (d, *J* = 20.3 Hz), 52.3, 52.0, 43.2, 27.3; ESI-HRMS m/z: 313.0849 ([M+Na]<sup>+</sup>); C<sub>16</sub>H<sub>15</sub>O<sub>4</sub>FNa: 313.0847.

Dimethyl 3-(4'-vinylphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (3k)



Synthesized according to the general procedure C; 1k (0.10 g, 0.6 mmol) was used as a substrate and 3k (0.93 g, 0.3 mmol) was obtained in 48% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1).

Colorless solid; M.p. 73—76 °C; IR (ATR) cm<sup>-1</sup>: 2951, 1719, 1641, 1509, 1435, 1364, 1256, 1193, 1157, 1115, 1067; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.33 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.67 (dd, *J* = 10.5, 17.5 Hz, 1H), 5.84—5.72 (m, 2H), 5.71 (d, *J* = 17.5 Hz, 1H), 5.22 (d, *J* = 10.5, 1H), 4.38—4.36 (m, 1H), 3.77 (s, 3H), 3.54 (s, 3H), 3.27—3.20 (m, 1H),

3.04—2.97 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 168.1, 168.0, 140.9, 136.5, 136.5, 136.4, 131.2, 128.5, 127.3, 126.5, 121.2, 113.8, 52.3, 52.0, 43.7, 27.4; ESI-HRMS m/z: 321.1099 ([M+Na]<sup>+</sup>); C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>Na: 321.1097.

Dimethyl 3-(2'-methoxyphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (3l)



Synthesized according to the general procedure D; **11** (0.52 g, 4.0 mmol) was used as a substrate and **31** (0.34 g, 1.1 mmol) was obtained in 28 % yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1).

Colorless oil; IR (ATR) cm<sup>-1</sup>: 2951, 2839, 1719, 1678, 1641, 1597, 1490, 1460, 1434, 1364, 1242, 1192, 1159, 1105, 1052, 1027; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.19 (ddd, J = 1.5, 7.5, 7.5 Hz, 1H), 7.09 (dd, J = 1.5, 7.5 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 5.78—5.75 (m, 1H), 5.75—5.72 (m, 1H), 4.91—4.88 (m, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.57 (s, 3H), 3.20—3.13 (m, 1H), 3.04—2.97 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.3, 168.0, 156.6, 137.1, 131.3, 129.6, 129.1, 128.1, 126.9, 120.9, 110.6, 55.6, 52.2, 51.9, 36.9, 27.2; ESI-HRMS m/z: 325.1047 ([M+Na]<sup>+</sup>); C<sub>17</sub>H<sub>18</sub>O<sub>5</sub>Na: 325.1046.

# Dimethyl 3-(3'-methoxyphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (3m)



Synthesized according to the general procedure D; **1m** (0.52 g, 4.0 mmol) was used as a substrate and **3m** (0.38 g, 1.3 mmol) was obtained in 31 % yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1).

Colorless oil; IR (ATR) cm<sup>-1</sup>: 2952, 1719, 1642, 1599, 1485, 1435, 1364, 1255, 1193, 1144, 1055, 1008; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.21 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.79—6.75 (m, 2H), 6.73—6.72 (m, 1H), 5.83—5.80 (m, 1H), 5.76—5.73 (m, 1H), 4.38—4.34 (m, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.55 (s, 3H), 3.26—3.19 (m, 1H), 3.03—2.96 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.2, 168.0, 159.8, 142.9, 136.7, 131.1, 129.6, 127.3, 121.3, 120.7, 114.2, 112.4, 55.2, 52.3, 52.0, 44.0, 27.4; ESI-HRMS m/z: 325.1044 ([M+Na]<sup>+</sup>); C<sub>17</sub>H<sub>18</sub>O<sub>5</sub>Na: 325.1046.

# Dimethyl 4-bromo-3-phenylcyclohexa-1,4-diene-1,2-dicarboxylate (3n)



Synthesized according to the general procedure C; 1n (0.21 g, 1.0 mmol) was used as a substrate and 3n (0.27 g, 0.8 mmol) was obtained in 77% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Colorless solid; M.p. 75—76 °C; IR (ATR) cm<sup>-1</sup>: 2951, 1725, 1673, 1492, 1454, 1434, 1365, 1252, 1192, 1156, 1061, 1032; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.34—7.31 (m, 2H), 7.30—7.27 (m, 1H), 7.22—7.20 (m, 2H), 6.23 (dd, J = 4.0, 4.0 Hz, 1H), 4.52 (dd, J = 7.0, 7.0 Hz, 1H), 3.77 (s, 3H), 3.54 (s, 3H), 3.34 (ddd, J = 4.0, 7.0, 23.5 Hz, 1H), 3.13 (ddd, J = 4.0, 7.0, 23.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  167.5, 166.8, 138.9, 136.2, 129.8, 128.7, 127.9, 124.5, 122.3, 52.4, 52.2, 51.2, 30.2; ESI-HRMS m/z: 373.0046 ([M+Na]<sup>+</sup>); C<sub>16</sub>H<sub>15</sub>O<sub>4</sub>BrNa: 373.0046.

# Dimethyl 5-bromo-3-phenylcyclohexa-1,4-diene-1,2-dicarboxylate (30)



Synthesized according to the general procedure E; **10** (0.63 g, 3.0 mmol) was used as a substrate and **30** (0.51 g, 1.5 mmol) was obtained in 48% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 10/1).

Brown oil; IR (ATR) cm<sup>-1</sup>: 3028, 2951, 1719, 1673, 1647, 1492, 1454, 1433, 1368, 1248, 1191, 1157, 1081, 1051, 1032, 1002; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.33—7.30 (m, 2H), 7.27—7.25 (m, 1H), 7.17—7.15 (m, 2H), 6.10 (ddd, *J* = 2.0, 2.0, 4.0 Hz, 1H), 4.45 (ddd, *J* = 4.0, 7.5, 7.5 Hz, 1H), 3.78 (s, 3H), 3.61 (ddd, *J* = 2.0, 7.5, 23.0 Hz, 1H), 3.52 (s, 3H), 3.35 (ddd, *J* = 2.0, 7.5, 23.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  167.7, 166.4, 139.3, 136.9, 129.3, 128.8, 128.4, 128.3, 127.7, 116.5, 52.5, 52.1, 47.2, 35.9; ESI-HRMS m/z: 373.0046 ([M+Na]<sup>+</sup>); C<sub>16</sub>H<sub>15</sub>O<sub>4</sub>BrNa: 373.0046.

# Dimethyl 5-tert-butyldimethylsilyloxy-3-phenyl-1,4-diene-1,2-dicarboxylate (3p)



Synthesized according to the general procedure E; **1p** (0.26 g, 1.0 mmol) was used as a substrate and **3p** (0.17 g, 0.4 mmol) was obtained in 42% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 10/1).

Colorless oil; IR (ATR) cm<sup>-1</sup>: 2954, 1722, 1686, 1436, 1385, 1263, 1208, 1035 ;<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.28 (dd, *J* = 7.0, 7.0 Hz, 2H), 7.23—7.19 (m, 1H), 7.17 (dd, *J* = 1.5, 7.0 Hz, 2H), 4.88 (ddd, *J* = 1.5, 1.5, 3.5 Hz, 1H), 4.49 (ddd, *J* = 3.5, 7.5, 7.5 Hz, 1H), 3.76 (s, 3H), 3.50 (s, 3H), 3.23 (ddd, *J* = 1.5, 7.5, 22.5 Hz, 1H), 2.95 (ddd, *J* = 1.5, 7.5, 22.5 Hz, 1H), 0.92 (s, 9H), 6.02 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.4, 166.9, 146.3, 141.7, 138.7, 128.5, 128.2, 127.1, 104.5, 52.3, 51.9, 46.1, 31.2, 25.6, 17.9, -4.5; ESI-HRMS m/z: 425.1755 ([M+Na]<sup>+</sup>); C<sub>22</sub>H<sub>30</sub>O<sub>5</sub>SiNa: 425.1755.

# Dimethyl 3-(2'-furyl)cyclohexa-1,4-diene-1,2-dicarboxylate (3q)



Synthesized according to the general procedure E; 1q (0.12 g, 1.0 mmol) was used as a substrate and 3q (0.25 g, 0.96 mmol) was obtained in 96% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Yellow oil; IR (ATR) cm<sup>-1</sup>: 2952, 1719, 1681, 1644, 1501, 1434, 1388, 1363, 1247, 1194, 1171, 1146, 1114, 1056, 1010; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.32 (d, *J* = 3.0 Hz, 1H), 6.28 (dd, *J* = 3.0, 3.0 Hz, 1H), 6.09 (d, *J* = 3.0 Hz, 1H), 5.89—5.85 (m, 1H), 5.80—5.77 (m, 1H), 4.58—4.54 (m, 1H), 3.77 (s, 3H), 3.66 (s, 3H), 3.22—3.15 (m, 1H), 2.99—2.92 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.1, 167.7, 153.4, 142.2, 134.4, 131.8, 124.2, 122.9, 110.4, 106.7, 52.3, 52.2, 37.5, 27.2; ESI-HRMS m/z: 285.0732 ([M+Na]<sup>+</sup>); C<sub>14</sub>H<sub>14</sub>O<sub>5</sub>Na: 285.0733.

#### Dimethyl 3-(2'-thienyl)cyclohexa-1,4-diene-1,2-dicarboxylate (3r)



Synthesized according to the general procedure E; 1r (0.14 mg, 1.0 mmol) was used as a substrate and 3r (0.11 g, 0.40 mmol) was obtained in 40% yield after purification by silica-gel

column chromatography (n-hex/EtOAc = 5/1).

Colorless oil; IR (ATR) cm<sup>-1</sup>: 2952, 1719, 1643, 1435, 1253, 1158, 1065; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.18 (d, J = 5.0 Hz, 1H), 6.91 (dd, J = 3.5, 5.0 Hz, 1H), 6.58 (d, J = 3.5 Hz, 1H), 5.88—5.82 (m, 2H), 4.75—4.71 (m, 1H), 3.76 (s, 3H), 3.63 (s, 3H), 3.24—3.18 (m, 1H), 3.00—2.94 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  167.9, 167.8, 144.7, 135.8, 131.3, 126.8, 126.8, 125.4, 125.0, 121.8, 52.3, 52.0, 38.4, 27.2; ESI-HRMS m/z: 301.0505 ([M+Na]<sup>+</sup>); C<sub>14</sub>H<sub>14</sub>O<sub>4</sub>SNa: 301.0505.

Dimethyl 3',6'-dihydro-[1,3':4',1''-terphenyl]-1',2'-dicarboxylate (3s)



Synthesized according to the general procedure D; **1s** (0.52 g, 2.5 mmol) was used as a substrate and 3s (0.83 g, 2.4 mmol) was obtained in 95% yield after purification by silica-gel column chromatography (n-hex/EtOAc = 5/1).

Colorless solid; M.p. 118—120 °C; IR (ATR) cm<sup>-1</sup>: 3027, 2950, 1718, 1643, 1492, 1433, 1374, 1261, 1227, 1146, 1067, 1032, 1002; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.26—7.10 (m, 10H), 6.15 (dd, J = 2.5, 5.0 Hz, 1H), 4.90 (dd, J = 6.0, 6.0 Hz, 1H), 3.78 (s, 3H), 3.60 (s, 3H), 3.47 (ddd, J = 2.5, 6.0, 23.5 Hz, 1H), 3.25 (ddd, J = 5.0, 6.0, 23.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.1, 167.9, 140.4, 139.8, 138.0, 137.8, 130.0, 128.5, 128.4, 128.2, 127.3, 127.1, 126.3, 120.6, 52.3, 52.1, 46.5, 28.9; ESI-HRMS m/z: 371.1248 ([M+Na]<sup>+</sup>); C<sub>22</sub>H<sub>20</sub>O<sub>4</sub>Na: 371.1254.

# Dimethyl 3',6'-dihydro-[1,3':5',1''-terphenyl]-1',2'-dicarboxylate (3t)



Synthesized according to the general procedure D; **1t** (0.41 g, 2.0 mmol) was used as a substrate and **3t** (0.13 g, 0.4 mmol) was obtained in 19% yield after purification by silica-gel column chromatography (n-hex/EtOAc = 3/1).

Colorless oil; IR (ATR) cm<sup>-1</sup>: 3027, 2950, 1719, 1674, 1643, 1599, 1492, 1434, 1381, 1333, 1263, 1229, 1190, 1157, 1085, 1058, 1031, 1002; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.45—7.43 (m,

2H), 7.36—7.28 (m, 5H), 7.25—7.21 (m, 3H), 6.15 (ddd, J = 1.5, 1.5, 3.5 Hz, 1H), 4.59 (ddd, J = 3.5, 7.5, 7.5 Hz, 1H), 3.82 (s, 3H), 3.65 (ddd, J = 1.5, 7.5, 23.0 Hz, 1H), 3.57 (s, 3H), 3.42 (ddd, J = 1.5, 7.5, 23.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.1, 167.9, 141.1, 139.3, 131.2, 131.0, 128.7, 128.5, 127.7, 127.3, 125.2, 123.9, 52.4, 52.0, 45.6, 29.4; ESI-HRMS m/z: 371.1255 ([M+Na]<sup>+</sup>); C<sub>22</sub>H<sub>20</sub>O<sub>4</sub>Na: 371.1254.

## Dimethyl 3',6'-dihydro-[1,3':6',1''-terphenyl]-1',2'-dicarboxylate (3u)



Synthesized according to the general procedure D; 1u (0.61 g, 3.0 mmol) was used as a substrate and 3u (1.0 g, 3.0 mmol) was obtained in quantitative yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.36—7.33 (m, 4H), 7.30—7.27 (m, 6H), 5.79 (d, *J* = 2.0 Hz, 2H), 4.47 (d, *J* = 2.0 Hz, 2H), 3.56 (s, 6H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 23.

#### Dimethyl 3',6'-dihydro-[1,1':2',1''-terphenyl]-4',5'-dicarboxylate (3v)



Synthesized according to the general procedure E; 1v (0.21 g, 1.0 mmol) was used as a substrate and 3v (0.26 g, 0.75 mmol) was obtained in 75% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.13—7.10 (m, 6H), 7.01 (d, *J* = 8.0 Hz, 4H), 3.81 (s, 6H), 3.48 (s, 4H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 24.

#### Dimethyl 4,5-dimethylcyclohexa-1,4-diene-1,2-dicarboxylate (3w)

Synthesized according to the general procedure C; 2,3-Dimethyl-1,3-butadiene (w: 0.72 g, 5.0 mmol) was used as a substrate and **3w** (1.1 g, 4.9 mmol) was obtained in 98% yield after purification by silica-gel column chromatography (n-hex/EtOAc = 10/1).

Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  3.78 (s, 6H), 2.92 (s, 4H), 1.66 (s, 6H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 25.

#### Dimethyl 3-benzylcyclohexa-1,4-diene-1,2-dicarboxylate (3x)



Synthesized according to the general procedure E; 1q (0.43 g, 3.0 mmol) was used as a substrate and 3x (0.09 g, 0.3 mmol) was obtained in 10% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 10/1).

Colorless oil; IR (ATR) cm<sup>-1</sup>: 2951, 1718, 1639, 1495, 1435, 1254, 1194, 1149 1060; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.27—7.25 (m, 2H), 7.21—7.18 (m, 1H), 7.17—7.15 (m, 2H), 5.69—5.65 (m, 1H), 5.59—5.56 (m, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.51—3.47 (m, 1H), 2.96 (dd, *J* = 4.5, 13.5 Hz, 1H), 2.84—2.78 (m, 1H), 2.72—2.64 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.7, 168.0, 138.0, 137.2, 132.8, 129.6, 128.0, 126.6, 126.2, 122.8, 52.2, 52.2, 40.9, 39.1, 27.5; ESI-HRMS m/z: 309.1096 ([M+Na]<sup>+</sup>); C<sub>17</sub>H<sub>18</sub>O<sub>4</sub>Na: 309.1097.

# (4,5-Dimethyl-1,4-cyclohexadien-1-yl)benzene (3z)



Synthesized according to the general procedure F; **1w** (0.23 mL, 2.0 mmol) and ethynylbenzene (0.20 g, 2.0 mmol) were used as a substrate and **3z** (0.21 g, 1.1 mmol) was obtained in 57% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 100/1). Colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.43 (d, *J* = 8.0 Hz, 2H), 7.33 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.24 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.13—6.12 (m, 1H), 3.01—2.83 (m, 4H), 1.74 (s, 3H), 1.71

(s, 3H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 26.

# (4,5-Dimethyl-2-trimethylsilyl-1,4-cyclohexadien-1-yl)benzene (3aa)



Synthesized according to the general procedure F; **1w** (0.23 mL, 2.0 mmol) and 1-phenyl-2-(trimethylsilyl)acetylene (0.35 g, 2.0 mmol) were used as a substrate and **3aa** (0.091 g, 0.36 mmol) was obtained in 18% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 100/1).

Colorless oil; IR (ATR) cm<sup>-1</sup>: 2953, 2911, 2860, 2803, 1625, 1598, 1489, 1441, 1419, 1381, 1245, 1095, 1069, 1031, 1005; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.31—7.28 (m, 2H), 7.25—7.24 (m, 1H), 7.14—7.12 (m, 2H), 2.84—2.79 (m, 4H), 1.70 (s, 3H), 1.65 (s, 3H), -0.22 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  146.4, 145.6, 130.8, 128.1, 127.9, 126.6, 123.3, 123.1, 41.5, 37.5, 18.1, -0.4; ESI-HRMS m/z: 279.1536 ([M+Na]<sup>+</sup>); C<sub>17</sub>H<sub>24</sub>SiNa: 279.1539.

#### 1,2,3-Triphenyl-1,4-cyclohexadien (3ab)



Synthesized according to the general procedure F; **1a** (0.26 g, 2.0 mmol) diphenylacetylene (0.36 g, 2.0 mmol) were used as a substrate and **3ab** (0.22 g, 0.73 mmol) was obtained in 36% yield after purification by silica-gel column chromatography (n-hex/EtOAc = 100/1).

Colorless solid; M.p. 129—130 °C; IR (ATR) cm<sup>-1</sup>: 3025, 1489, 1452, 1442, 1071; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.21—7.18 (m, 2H), 7.15—7.09 (m, 5H), 7.06—7.04 (m, 3H), 6.97—6.91 (m, 3H), 6.78—6.74 (m, 2H), 5.99—5.93 (m, 2H), 4.39—4.35 (m, 1H), 3.47—3.41 (m, 1H), 3.13—3.07 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  143.9, 142.6, 141.6, 136.0, 133.0, 129.6, 129.5, 128.8, 128.5, 128.2, 127.6, 127.3, 126.2, 126.0, 125.8, 123.0, 49.0, 33.2; ESI-HRMS m/z: 331.1436 ([M+Na]<sup>+</sup>); C<sub>24</sub>H<sub>20</sub>Na: 331.1457.

### 2-2-5. Synthetic procedure of 3-phenylcyclohexa-1,4-diene-1,2-dicarboxylic acid (3y)



To a round bottomed flask were added **3a** (68.1 mg, 0.25 mmol), sodium hydroxide (40.0 mg, 1.0 mmol), ethanol (1.5 mL) and H<sub>2</sub>O (0.5 mL) at room temperature under argon and the reaction mixture was refluxed at 100 °C. After stirring for 6 h, the reaction mixture was cooled to room temperature and concentrated in vacuo. To the residue was added 1N HCl aq. (5 mL) and the solution was passed through a filter paper [Kiriyama, No. 5C (1  $\mu$ m), diameter = 40 mm]. The filtrated solid was washed with *n*-hexane (10 mL × 5) and dried in a desiccator under vacuum for overnight to give 3-phenylcyclohexa-1,4-diene-1,2-dicarboxylic acid (**3y**: 30.7 mg, 0.13 mmol) in 50% yield.

#### 3-Phenylcyclohexa-1,4-diene-1,2-dicarboxylic acid (3y)



Colorless solid; M.p. 206—209 °C; IR (ATR) cm<sup>-1</sup>: 2874, 1675, 1584, 1402, 1280, 1153, 1070; <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  12.39 (brs, 2H), 7.47 (d, J = 7.5 Hz, 2H), 7.33 (dd, J = 7.5, 7.5 Hz, 2H), 7.28—7.25 (m, 1H), 7.11—7.09 (m, 1H), 6.13—6.11 (m, 1H), 4.56—4.53 (m, 1H), 3.11—3.09 (m, 1H); <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  172.2, 167.1, 139.7, 137.3, 134.2, 128.3, 128.2, 127.3, 126.2, 123.4, 44.2, 28.2; ESI-HRMS m/z: 267.0632 ([M+Na]<sup>+</sup>); C<sub>14</sub>H<sub>12</sub>O<sub>4</sub>Na: 267.0628.

# 2-2-6. Synthetic procedure of 1-phenyl-1,4-dihydronaphthalene (3ac)



To a solution of cesium fluoride (0.19 g, 1.25 mmol) in MeCN (2.5 mL) were added 3a (65.1 mg, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (146  $\mu$ L, 0.6 mmol) at room temperature under argon. The reaction mixture was refluxed at 80 °C. After stirring for 12 h, the reaction was quenched with H<sub>2</sub>O (1 mL) and extracted with EtOAc (10 mL × 2). The

combined organic layers were dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-EtOAt (100/1) as a mixed eluent to give 1-phenyl-1,4-dihydronaphthalene (**3ac**: 68.2 mg, 0.33 mmol) in 66% yield.

# 1-Phenyl-1,4-dihydronaphthalene (3ac)



Colorless solid; M.p. 44—47 °C; IR (ATR) cm<sup>-1</sup>: 3060, 3026, 2864, 2820, 1600, 1492, 1453, 1423, 1074, 1030, 1018; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.28 (dd, J = 7.5, 7.5 Hz, 2H), 7.21—7.13 (m, 5H), 7.09 (dd, J = 7.5, 7.5 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 6.04—6.01 (m, 1H), 5.97—5.94 (m, 1H), 4.64—4.63 (m, 1H), 3.61—3.57 (m, 1H) 3.50—3.45 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  146.2, 137.5, 133.6, 129.5, 129.4, 128.5, 128.4, 128.3, 126.2, 126.2, 126.0, 123.7, 45.9, 29.8; ESI-HRMS m/z: 205.1017 ([M-H]<sup>-</sup>); C<sub>16</sub>H<sub>13</sub>: 205.1023.

#### 2-3. Synthesis of cyclohexenes (3')

2-3-1. Synthetic procedure of dimethyl 1,2-dimethylcyclohexene-4,5-dicarboxylate (3'a and 3'b)



To a round bottomed flask were added 2,3-dimethyl-1,3-butadiene (**1w**: 0.41 mL, 3.6 mmol), dimethyl maleate or dimethyl fumarate (**2'a** or **2'b**: 0.43 g, 3.0 mmol) and toluene (3 mL) at room temperature under argon and the reaction mixture was warmed to 50 °C. After stirring for 24 h, the reaction mixture was cooled to room temperature and extracted with EtOAc (10 mL  $\times$  2). The combined organic layers were dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding dimethyl 1,2-dimethylcyclohexene-4,5-dicarboxylate (**3'**).

### Dimethyl 1,2-dimethylcyclohexene-4,5-cis-dicarboxylate (3'a)



**1w** (0.41 mL, 3.6 mmol) and dimethyl maleate (0.43 g, 3.0 mmol) were used as substrates and **3'a** (0.07 g, 0.30 mmol) was obtained in 10% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Colorless oil; IR (ATR) cm<sup>-1</sup>: 2951, 2915, 1730, 1435, 1356, 1308, 1199, 1171, 1118, 1058, 1023; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  3.66 (s, 6H), 2.98 (t, *J* = 5.5 Hz, 2H), 2.43 (dd, *J* = 4.0, 16.0 Hz, 2H), 2.24 (dd, *J* = 4.0, 16.0 Hz, 2H), 1.61 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  173.9, 123.8, 51.7, 40.3, 31.7, 18.8; ESI-HRMS m/z: 249.1095 ([M+Na]<sup>+</sup>); C<sub>12</sub>H<sub>18</sub>O<sub>4</sub>: 249.1097.

#### Dimethyl 1,2-dimethylcyclohexene-4,5-trans-dicarboxylate (3'b)



**1w** (0.41 mL, 3.6 mmol) and dimethyl fumarate (0.43 g, 3.0 mmol) were used as a substrate and **3'a** (0.57 g, 2.5 mmol) was obtained in 85% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Colorless solid; M.p. 52—54 °C; IR (ATR) cm<sup>-1</sup>: 2952, 2915, 2843, 1733, 1436, 1362, 1320, 1257, 1237, 1194, 1175, 1156, 1119, 1069, 1010; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 3.68 (s, 3H), 2.83—2.80 (m, 2H), 2.28—2.12 (m, 4H), 1.61 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 175.4, 123.8, 51.8, 42.0, 34.1, 18.6; ESI-HRMS m/z: 249.1093 ([M+Na]<sup>+</sup>); C<sub>12</sub>H<sub>18</sub>O<sub>4</sub>: 249.1097.

### 2-3-2. Synthetic procedure of dimethyl 3-phenylcyclohexene-4,5-cis-dicarboxylate (3'c)



To a round bottomed flask were added 1-phenyl-1,3-butadiene (1a: 0.39 g, 3.0 mmol), dimethyl maleate (2'a: 0.43 g, 3.0 mmol) and toluene (3 mL) at room temperature under argon and the reaction mixture was refluxed at 130 °C. After stirring for 24 h, the reaction mixture was cooled to room temperature and extracted with EtOAc (10 mL  $\times$  2). The combined organic layers were dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-EtOAt (5/1) as a mixed eluent to give the unseparated diasteromixture of dimethyl 3-phenylcyclohexene-4,5-*cis*-dicarboxylate (3'c: 0.31 g, 1.14 mmol) in 38% yield.

# Dimethyl 3-phenylcyclohexene-4,5-cis-dicarboxylate (3'c)



Colorless oil; IR (ATR) cm<sup>-1</sup>: 3027, 2950, 1730, 1492, 1434, 1383, 1299, 1196, 1162, 1081, 1031; <sup>1</sup>H NMR of 3,4-*trans* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.35—7.28 (m, 3H), 7.18—7.17 (m, 2H), 6.03 (dddd, *J* = 3.0, 5.5, 8.0, 10.5 Hz, 1H), 5.79 (ddd, *J* = 1.0, 2.0, 10.5 Hz, 1H), 3.87 (dd, *J* = 2.0, 6.5 Hz, 1H), 3.69 (s, 3H), 3.43 (dd, *J* = 3.5, 6.5 Hz, 1H), 3.19 (s, 3H), 3.03 (ddd, *J* = 3.5, 6.0, 11.5 Hz, 1H), 2.91—2.83 (m, 1H), 2.47—2.46 (m, 1H); <sup>1</sup>H NMR of 3,4-*cis* isomer (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.35—7.28 (m, 3H), 7.24—7.21 (m, 2H), 5.98 (ddd, *J* = 1.5, 3.0, 10.0 Hz, 1H), 5.72 (dddd, *J* = 2.0, 4.5, 6.5, 10.0 Hz, 1H), 4.08 (dd, *J* = 1.5, 3.5 Hz, 1H), 3.70 (s, 3H), 3.65 (s, 3H), 3.23 (dd, *J* = 3.5, 3.5 Hz, 1H), 2.79 (ddd, *J* = 3.5, 6.5, 9.5 Hz, 1H), 2.61 (dddd, *J* = 2.0, 4.5, 9.5, 19.0 Hz, 1H), 2.45—2.43 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  174.0, 173.9, 172.8, 171.6, 143.0, 141.4, 128.5, 128.4, 128.2, 128.0, 127.6, 127.1, 126.8, 126.8, 126.6, 52.0, 51.9, 51.8, 50.8, 47.7, 45.9, 43.7, 42.1, 41.7, 36.3, 24.7, 24.6; ESI-HRMS m/z: 297.1098 ([M+Na]<sup>+</sup>); C<sub>16</sub>H<sub>18</sub>O<sub>4</sub>: 297.1097.

# 2-3-3. Synthetic procedure of dimethyl methylcyclohexene-3,4-*trans*-dicarboxylate (3'd)



To a round bottomed flask were added isoprene (0.24 mL, 2.4 mmol), dimethyl fumarate (0.29 g, 2.0 mmol) and toluene (2 mL) at room temperature under argon and the reaction mixture was refluxed at 130 °C. After stirring for 6 h, the reaction mixture was cooled to room temperature and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-EtOAt (5/1) as a mixed eluent to give dimethyl methylcyclohexene-3,4-*trans*-dicarboxylate (**3'd**: 0.33 g, 1.54 mmol) in 77% yield.

Dimethyl methylcyclohexene-3,4-trans-dicarboxylate (mixture) (3'd)

Colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  5.38 (s, 1H), 3.69 (s, 3H), 3.69 (s, 3H), 2.88 (dt, *J* = 6.0, 11.0 Hz, 1H), 2.79 (dt, *J* = 6.0, 11.0 Hz, 1H), 2.40—2.36 (m, 1H), 2.29—2.25 (m, 1H), 2.18—2.10 (m, 2H), 1.67 (s, 3H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 27.

#### 2-3-4. Synthetic procedure of 3,4-dimethylcyclohexenecarboxylic acid (3'e)



To a round bottomed flask were added 1w (0.27 mL, 2.4 mmol), acrylic acid (0.14 g, 2.0 mmol) and toluene (2 mL) at room temperature under argon and the reaction mixture was refluxed at 130 °C. After stirring for 6 h, the reaction mixture was cooled to room temperature and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-EtOAt (1/1) as a mixed eluent to give 3,4-dimethylcyclohexenecarboxylic acid (**3'e**: 0.12 g, 0.79 mmol) in 40% yield.

3,4-Dimethylcyclohexenecarboxylic acid (3'e)



Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  11.03 (brs, 1H), 2.60–2.55 (m, 1H), 2.55–2.13 (m, 2H), 2.08–1.97 (m, 3H), 1.71–1.64 (m, 1H) 1.63 (s, 3H), 1.61 (s, 3H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 28.

# 2-3-5. Synthetic procedure of dicarboxylic acid derivatives (3'g and 3'h) for the reactions shown in S59



To a round bottomed flask were added **3'a** or **3'b** (56.6 mg, 0.25 mmol) and sodium hydroxide (40.0 mg, 1.0 mmol), ethanol (1.5 mL) and H<sub>2</sub>O (0.5 mL) at room temperature under argon and the reaction mixture was refluxed at 100 °C. After stirring for 6 h, the reaction mixture was

cooled to room temperature and concentrated in vacuo. To the residue was added 1N HCl aq. (5 mL) and the solution was passed through a filter paper [Kiriyama, No. 5C (1  $\mu$ m), diameter = 40 mm]. The filtrated solid was washed with *n*-hexane (10 mL × 5) and dried in a desiccator under vacuum for overnight to give the corresponding dicarboxylic acid derivatives (**3'g** or **3'h**).

1,2-Dimethylcyclohexene-4,5-cis-dicarboxylic acid (3'g)



**3'a** (56.6 mg, 0.25 mmol) was used as a substrate and **3'g** (38.9 mg, 0.20 mmol) was obtained in 79% yield.

Colorless solid; M.p. 197—201 °C; IR (ATR) cm<sup>-1</sup>: 2881, 2859, 1687, 1419, 1343, 1318, 1297, 12696, 1245, 1215, 1171, 1120, 1042; <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  12.17 (brs, 2H), 22.84—2.81 (m, 2H), 2.33—2.29 (m, 2H), 2.18—2.14 (m, 2H), 1.56 (s, 6H); <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  174.6, 123.7, 39.4, 31.9, 18.9; ESI-HRMS m/z: 221.0788 ([M+Na]<sup>+</sup>); C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>Na: 221.0784.

### 1,2-Dimethylcyclohexene-4,5-trans-dicarboxylic acid (3'h)

CO<sub>2</sub>H .CO2H

**3'b** (56.6 mg, 0.25 mmol) was used as a substrate and **3'h** (41.2 mg, 0.21 mmol) was obtained in 83% yield.

Colorless solid; M.p. 220—224 °C; IR (ATR) cm<sup>-1</sup>: 2911, 2836, 1698, 1419, 1318, 1294, 1259, 1234, 1202, 1125; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 12.22 (brs, 2H), 2.55—2.53 (m, 2H), 2.19—2.16 (m, 2H), 2.04—2.00 (m, 2H), 1.58 (s, 6H); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 175.9, 123.7, 41.6, 33.7, 18.5; ESI-HRMS m/z: 221.0788 ([M+Na]<sup>+</sup>); C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>Na: 221.0784.

### 2-4. Synthetic procedure of dodecyl acrylate (6)



To a solution of acrylic acid (0.69 mL, 10.0 mmol) in toluene (40 mL) was were added 1-dodecanol (2.2 g, 12.0 mmol), hydroquinone (0.11g, 1.0 mmol), and *p*-toluenesulfonic acid (0.57 g, 3.0 mmol) at room temperature under argon and the reaction mixture was refluxed at 130 °C. After stirring for 4 h, the reaction mixture was cooled to room temperature and extracted with EtOAc (20 mL × 2). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-EtOAc (30/1) as a mixed eluent to give dodecyl acrylate (**6**: 1.83 g, 7.6 mmol) in 76% yield.

**Dodecyl acrylate (6)** 

Colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.39 (dd, J = 1.0, 17.5 Hz, 1H), 6.12 (dd, J = 10.0, 17.5 Hz, 2H), 5.81 (dd, J = 1.0, 10.0 Hz, 1H), 4.14 (t, J = 6.5 Hz, 2H), 1.69—1.63 (m, 2H), 1.39—1.26 (m, 18H), 0.88 (t, J = 6.5 Hz, 3H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 29.

# 3. Typical procedures in dehydrogenation and application3-1. Typical procedure in Pd/C-catalyzed dehydrogenation



To a solution of 1,4-cyclohexadiene derivative (**3**: 0.1 mmol, 1.0 equiv.) in H<sub>2</sub>O (1 mL) were added 10% Pd/C (5.3 mg, 0.005 mmol, 5 mol%) and acrylic acid (34.3  $\mu$ L, 0.5 mmol, 5.0 equiv.) under argon. The reaction mixture was refluxed at 80~150 °C. After an adequate reaction time, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Pd/C. The filtrate was extracted with EtOAc (10 mL × 3). The combined organic layers were washed sat. NaHCO<sub>3</sub> aq. (10 mL × 3), dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding arene derivatives (**4**).

# 3-2. Typical procedure in one-pot synthesis



To a mixture of 1,3-butadiene derivative (1: 0.2 mmol, 1.0 equiv.) and alkyne (2: 0.24 mmol, 1.2 equiv.) was heated at 50 °C under argon. After stirring for 12 h, to the reaction mixture were added 10% Pd/C (21.2 mg, 0.02 mmol, 10 mmol%), acrylic acid (68.6  $\mu$ L, 1.0 mmol, 5.0 equiv.) and H<sub>2</sub>O (2 mL) and the air inside was replaced with Ar (ballon) by three vaccum/Ar cycles. The reaction mixture was refluxed at 120 °C. After an adequate reaction time, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Pd/C. The filtrate was extracted with EtOAc (10 mL × 3). The combined organic layers were washed sat. NaHCO<sub>3</sub> aq. (10 mL × 3), dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding arene derivatives (4).

# **3-3.** Typical procedure in chemical modification of arene derivatives into diol derivatives



To a solution of phthalic acid dimethyl ester derivatives (4: 1.0 mmol) in anhydrous THF (1 mL) was added LiAlH<sub>4</sub> (0.15 g, 4.0 mmol) at 0 °C under argon. After stirring for 24 h at room temperature, the reaction was quenched with H<sub>2</sub>O (0.1 mL), 15% NaOH aq. (0.1 mL), and H<sub>2</sub>O (0.3 mL) and passed through a celite pad. The filtrate was concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding diol derivatives (8).

# **3-4.** Typical procedure in chemical modification of diol derivatives into phthalan derivative


To a solution of diol derivatives (8: 0.2 mmol) in anhydrous cyclopentyl methyl ether (CPME: 1 mL) was added sodium hydride (16.0 mg, 0.4 mmol, 60% oil suspension) at 0 °C under argon. After stirring for 10 min, trimethyl phosphate (57.4  $\mu$ L, 0.5 mmol) was added and the reaction mixture was warmed to room temperature. After further stirring for 24 h, the mixture was quenched with H<sub>2</sub>O (1 mL) and extracted with AcOEt (10 mL x 3). The combined organic layers were dried over MgSO4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give corresponding phthalan derivatives (9).

# 4. Optimization of Pd/C-catalyzed dehydrogenation

# 4-1. Optimization of Pd/C-catalyzed dehydrogenation of cyclohexadiene derivatives

CO <sub>2</sub> Me CO <sub>2</sub> Me	catalyst solvent		D <sub>2</sub> Me CO <sub>2</sub> Me +	CO <sub>2</sub> Me CO <sub>2</sub> Me
entry	catalyst	4w 5w yield (%)		
		3w	<b>4</b> w	5w
1	10% Pd/C	0	74	25
2	10% Pt/C	27	59	12
3	10% Ru/C	85	15	<1
4	10% Rh/C	44	26	3
5	10% Ni/C	95	5	<1
6	10% Au/C	15	85	<1

Table S1. Catalyst efficiency.<sup>a</sup>

 $^a$  Reaction conditions: 3w (0.1 mmol, 1.0 equiv.), catalyst (0.005 mmol, 5 mol%) in H\_2O (1 mL) under Ar at 120  $^o$ C for 6h.

	CO <sub>2</sub> Me CO <sub>2</sub> Me	catalyst additive solvent	CO <sub>2</sub> Me CO <sub>2</sub>	Me (		D₂Me CO₂Me
	3a		4a		5a	
entry	catalyst	additive (x equiv.)	solvent	yield (%)		
				3a	4a	5a
1	10% Pd/C	_	H <sub>2</sub> O	0	70	27
2	5% Pd/C	—	H <sub>2</sub> O	0	68	24
3	$10\% Pd/Al_2O_3$		$H_2O$	0	73	27
4	$Pd(OAc)_2$	_	H <sub>2</sub> O	0	65	31
5	Pd(PPh <sub>3</sub> ) <sub>4</sub>		$H_2O$	0	67	29
6	10% Pd/C		<i>i</i> -PrOH	0	66	29
7	10% Pd/C		acetone	0	46	22
8	10% Pd/C	_	cyclohexene	0	77	19
9	10% Pd/C		toluene	0	66	39
10	10% Pd/C		MeCN	0	68	32
11	10% Pd/C	methyl acrylate (5)	H <sub>2</sub> O	0	92	8
12	10% Pd/C	acrylic acid (5)	H <sub>2</sub> O	0	>99	<1
13	10% Pd/C	dimethyl maleate (5)	H <sub>2</sub> O	37	55	<1
14	10% Pd/C	dimethyl maleate (1)	H <sub>2</sub> O	<1	96	3

Table S2. Solvent and additive efficiency.<sup>a</sup>

<sup>a</sup> Reaction conditions: **3a** (0.1 mmol, 1.0 equiv.), catalyst (0.005 mmol, 5 mol%), and additive in solvent (1 mL) under Ar at 120 °C for 6h.

# 4-2. Optimization of one-pot synthesis

Table S3. Optimization of one-pot synthesis.<sup>a</sup>



<sup>a</sup>Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.) and **2** (x equiv.) in  $H_2O$  (y mL) under Ar at 50 °C for 12 h. Then, 10% Pd/C (0.02 mmol, 10 mol%), acrylic acid (z equiv.) and  $H_2O$  (total 2 mL) at 120 °C under Ar.

# 5. Spectroscopic data of synthesized products

Biphenyl-2,3-dicarboxylic acid dimethyl ester (4a)



**3a** (27.3 mg, 0.1 mmol) was used as a substrate and **4a** (27.0 g, 0.1 mmol) was obtained in >99% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 10/1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.00 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.55—7.51 (m, 2H), 7.41—7.36 (m, 5H), 3.91 (s, 3H), 3.67 (s, 3H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 30.

#### Dimethyl [1,1':4',1''-terphenyl]-2,3-dicarboxylate (4b)



**3b** (34.8 mg, 0.1 mmol) was used as a substrate and **4b** (34.4 mg, 0.099 mmol) was obtained in 99% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 2/1). Colorless solid; M.p. 130—133 °C; IR (ATR) cm<sup>-1</sup>: 3029, 2950, 1723, 1590, 1487, 1454, 1434, 1397, 1306, 1266, 1204, 1151, 1119, 1067, 1008; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.20 (d, *J* = 8.0 Hz, 1H), 7.65—7.64 (m, 4H), 7.61—7.60 (m, 1H), 7.57—7.53 (m, 1H), 7.48—7.45 (m, 4H), 7.37 (t, *J* = 7.5 Hz, 1H), 3.93 (s, 3H), 3.72 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  169.3, 166.2, 140.7, 140.4, 140.1, 138.1, 134.7, 134.2, 129.2, 129.0, 129.0, 128.8, 128.1, 127.5, 127.1, 127.0, 52.6, 52.4; ESI-HRMS m/z: 369.1097 ([M+Na]<sup>+</sup>); C<sub>22</sub>H<sub>18</sub>O<sub>4</sub>Na: 369.1097.

### Dimethyl 4'-methoxy-[1,1'-biphenyl]-2,3-dicarboxylate (4c)



**3c** (30.2 mg, 0.1 mmol) was used as a substrate and **4c** (29.8 mg, 0.099 mmol) was obtained in 99% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.97 (dd, J = 2.0, 7.5 Hz, 1H), 7.54—7.48 (m, 2H), 7.30 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H), 3.84 (s, 3H), 3.70 (s, 3H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 31.

Dimethyl 4'-N,N-dimethylamino-[1,1'-biphenyl]-2,3-dicarboxylate (4d)



**3d** (31.5 mg, 0.1 mmol) was used as a substrate and **4d** (30.0 mg, 0.096 mmol) was obtained in 96% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1). Yellow solid; M.p. 143—146 °C; IR (ATR) cm<sup>-1</sup>: 2949, 1725, 1611, 1588, 1526, 1447, 1433, 1356, 1311, 1268, 1203, 1151, 1118, 1068; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.93 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.54 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.48 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.24 (d, *J* = 9.0 Hz, 2H), 6.74 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H), 3.74 (s, 3H), 2.99 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  169.8, 166.4, 150.0, 140.7, 134.5, 134.3, 129.3, 129.0, 128.0, 127.9, 126.9, 112.1, 52.5, 52.3, 40.4; ESI-HRMS m/z: 314.1386 ([M+Na]<sup>+</sup>); C<sub>18</sub>H<sub>19</sub>NO<sub>4</sub>Na: 314.1387.

### Trimethyl [1,1'-biphenyl]-2,3,4'-tricarboxylate (4e)



**3e** (33.0 mg, 0.1 mmol) was used as a substrate and **4e** (31.2 mg, 0.095 mmol) was obtained in 95% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1). Colorless solid; M.p. 151—153 °C; IR (ATR) cm<sup>-1</sup>: 2953, 2256, 1718, 1643, 1609, 1436, 1364, 1275, 1193, 1179, 1159, 1113, 1068, 1020; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.08 (d, *J* = 8.0 Hz, 2H), 8.05—8.02 (m, 1H), 7.56—7.55 (m, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 3.67 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.9, 166.8, 166.0, 143.8, 139.5, 134.6, 133.9, 129.6, 129.6, 129.5, 129.3, 128.7, 128.3, 52.7, 52.4, 52.2; ESI-HRMS m/z: 351.0839 ([M+Na]<sup>+</sup>); C<sub>18</sub>H<sub>16</sub>O<sub>6</sub>Na: 351.0839.

# Dimethyl 4'-nitoro-[1,1'-biphenyl]-2,3-dicarboxylate (4f)



**3f** (31.7 mg, 0.1 mmol) was used as a substrate and **4f** (31.2 g, 0.099 mmol) was obtained in 99% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1).

Yellow solid; M.p. 101—102 °C; IR (ATR) cm<sup>-1</sup>: 2952, 2924, 2851, 1723, 1600, 1588, 1518, 1455, 1432, 1402, 1347, 1308, 1258, 1204, 1151, 1120, 1066, 1015; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.27 (d, *J* = 8.5 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.61—7.54 (m, 4H), 3.93 (s, 3H), 3.70 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.7, 165.8, 147.6, 145.8, 138.2, 134.6, 133.6, 130.1, 129.7, 129.6, 128.6, 123.5, 52.8, 52.6; ESI-HRMS m/z: 338.0635 ([M+Na]<sup>+</sup>); C<sub>16</sub>H<sub>13</sub>NO<sub>6</sub>Na: 338.0635.

Dimethyl 4'-cyano-[1,1'-biphenyl]-2,3-dicarboxylate (4g)



**3g** (30.6 mg, 1.0 mmol) was used as a substrate and **4g** (28.0 g, 0.92 mmol) was obtained in 92% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1). Colorless solid; M.p. 131—133 °C; IR (ATR) cm<sup>-1</sup>: 2952, 2229, 1728, 1609, 1589, 1454, 1433, 1307, 1272, 1205, 1152, 1121, 1066; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.06 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.58 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.52—7.48 (m, 3H), 3.92 (s, 3H), 3,69 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.7, 165.8, 143.9, 138.6, 134.6, 133.7, 132.1, 129.9, 129.5, 129.4, 128.5, 118.5, 111.9, 52.8, 52.6; ESI-HRMS m/z: 318.0737 ([M+Na]<sup>+</sup>); C<sub>17</sub>H<sub>13</sub>NO<sub>4</sub>Na: 318.0737.

### Dimethyl 4'-bromo-[1,1'-biphenyl]-2,3-dicarboxylate (4h)



**3h** (35.1 mg, 0.1 mmol) was used as a substrate and **4h** (31.8 mg, 0.091 mmol) was obtained in 91% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1). Colorless solid; M.p. 102—104 °C; IR (ATR) cm<sup>-1</sup>: 2950, 1727, 1592, 1494, 1454, 1432, 1392, 1308, 1270, 1204, 1152, 1120, 1065, 1011; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.02 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.54—7.51 (m, 4H), 7.25—7.24 (m, 2H), 3.92 (s, 3H), 3.70 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  169.0, 166.0, 139.3, 138.1, 134.6, 134.0, 131.5, 130.2, 129.3, 129.2, 128.2, 122.4, 52.7, 52.5; ESI-HRMS m/z: 370.9889 ([M+Na]<sup>+</sup>); C<sub>16</sub>H<sub>13</sub>O<sub>4</sub>BrNa: 370.9889.

### Dimethyl 4'-chloro-[1,1'-biphenyl]-2,3-dicarboxylate (4i)



**3i** (30.7 mg, 0.1 mmol) was used as a substrate and 4i (28.7 mg, 0.094 mmol) was obtained in 94% yield after purification by silica-gel column chromatography (hex/EtOAc = 5/1). Colorless solid; M.p. 96—100 °C IR (ATR) cm<sup>-1</sup>: 2950, 1723, 1493, 1454, 1433, 1308, 1266, 1203, 1151, 1120, 1092, 1065, 1015; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.02 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.55—7.50 (m, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 3.92 (s, 3H), 3.70 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  169.1, 166.0, 139.2, 137.6, 134.7, 134.2, 134.0, 129.9, 129.3, 129.2, 128.5, 128.1, 52.7, 52.4; ESI-HRMS m/z: 327.0395 ([M+Na]<sup>+</sup>); C<sub>16</sub>H<sub>13</sub>O<sub>4</sub>ClNa: 327.0395.

Dimethyl 4'-fluoro-[1,1'-biphenyl]-2,3-dicarboxylate (4j)



**3j** (29.0 mg, 0.1 mmol) was used as a substrate and **4j** (28.2 mg, 0.098 mmol) was obtained in 98% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1). Colorless solid; M.p. 80—83 °C; IR (ATR) cm<sup>-1</sup>: 2999, 2952, 1724, 1605, 1512, 1455, 1432, 1307, 1267, 1223, 1203, 1151, 1119, 1097, 1065, 1015; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.01—8.00 (m, 1H), 7.52—7.51 (m, 2H), 7.35—7.32 (m, 2H), 7.11—7.07 (m, 2H), 3.91 (s, 3H), 3.69 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  169.1, 166.0, 162.6 (d, *J* = 245.6 Hz), 139.5, 135.1, 134.8, 134.2, 130.3 (d, *J* = 8.3 Hz), 129.2, 129.0, 128.0, 115.3 (d, *J* = 21.5 Hz), 52.6, 52.4; ESI-HRMS m/z: 311.0693 ([M+Na]<sup>+</sup>); C<sub>16</sub>H<sub>13</sub>O<sub>4</sub>FNa: 311.0690.

#### Dimethyl 4'-vinyl-[1,1'-biphenyl]-2,3-dicarboxylate (4k)



**3k** (29.8 mg, 0.1 mmol) was used as a substrate and **4k** (0.089 mmol) and recovered **3k** (0.011 mol) were obtained as a mixture (**4k** : **3k** = 89 : 11) in nearly quantitative yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

11% of inseparable starting substrate (3k) was contaminated. Main spectra derived from 4k were depicted below.

IR (ATR) cm<sup>-1</sup>: 2956, 1723, 1630, 1421, 1369, 1256, 1193, 1151, 1111, 1067; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.00 (dd, J = 2.0, 7.5 Hz, 1H), 7.56—7.51 (m, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 6.75 (dd, J = 10.5, 17.5 Hz, 1H), 5.80 (d, J = 17.5 Hz, 1H), 5.30 (d, J = 10.5 Hz, 1H), 3.91 (s, 3H), 3.70 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  169.3, 166.2, 140.2, 138.6, 137.1, 136.3, 134.6, 134.1, 129.2, 128.9, 128.8, 128.5, 126.2, 114.4, 52.6, 52.4; ESI-HRMS m/z: 319.0942 ([M+Na]<sup>+</sup>); C<sub>18</sub>H<sub>16</sub>O<sub>4</sub>Na: 319.0941.

Dimethyl 2'-methoxy-[1,1'-biphenyl]-2,3-dicarboxylate (4l)



**3j** (30.2 mg, 0.1 mmol) was used as a substrate and **4l** (29.8 mg, 0.099 mmol) was obtained in 99% yield after purification by silica-gel column chromatography (n-hex/EtOAc = 3/1). Colorless solid; M.p. 115—116 °C; IR (ATR) cm<sup>-1</sup>: 2951, 1725, 1602, 1587, 1498, 1464, 1434, 1309, 1257, 1201, 1150, 1116, 1064, 1045, 1026; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.94 (dd, *J* = 2.5, 7.0 Hz, 1H), 7.53—7.48 (m, 2H), 7.34 (dt, *J* = 1.8, 8.0 Hz, 1H), 7.19 (dd, *J* = 1.5, 7.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.94 (dd, *J* = 8.0 Hz, 1H), 3.89 (s, 3H), 3.73 (s, 3H), 3.61 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.9, 166.6, 156.5, 137.5, 135.0, 130.7, 129.5, 128.8, 128.7, 128.6, 127.8, 120.3, 110.8, 55.5, 52.5, 52.1; ESI-HRMS m/z: 323.0893 ([M+Na]<sup>+</sup>); C<sub>17</sub>H<sub>16</sub>O<sub>5</sub>Na: 323.0890.

Dimethyl 3'-methoxy-[1,1'-biphenyl]-2,3-dicarboxylate (4m)



**3m** (30.2 mg, 0.1 mmol) was used as a substrate and **4m** (28.6 g, 0.095 mmol) was obtained in 95% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1). Colorless oil; IR (ATR) cm<sup>-1</sup>: 3001, 2950, 2837, 1722, 1585, 1490, 1463, 1433, 1308, 1261, 1227, 1200, 1177, 1149, 1117, 1091, 1065, 1039; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.00 (dd, *J* = 1.0, 7.5 Hz, 1H), 7.57—7.50 (m, 2H), 7.32—7.29 (m, 1H), 6.95 (dd, *J* = 1.5, 6.5 Hz, 1H), 6.92—6.91 (m, 2H), 3.91 (s, 3H), 3.82 (s, 3H), 3.70 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ 

169.2, 166.1, 159.3, 140.5, 140.4, 134.6, 134.1, 129.3, 129.1, 129.0, 128.0, 121.0, 114.0, 113.7, 55.2, 52.6, 41.4; ESI-HRMS m/z: 323.0891 ( $[M+Na]^+$ ); C<sub>17</sub>H<sub>16</sub>O<sub>5</sub>Na: 323.0890.

Biphenyl-6-bromo-2,3-dicarboxylic acid dimethyl ester (4n)



**3n** (35.1 mg, 0.1 mmol) was used as a substrate and **4n** (30.7 mg, 0.088 mmol) was obtained in 88% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1). Colorless solid; M.p. 83—87 °C; IR (ATR) cm<sup>-1</sup>: 2952, 1727, 1698, 1567, 1433, 1409, 1295, 1273, 1196, 1161, 1103, 1070;<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.87 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.43—7.40 (m, 3H), 7.24—7.22 (m, 2H), 3.90 (s, 3H), 3.52 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  167.8, 165.4, 140.9, 137.5, 137.2, 133.4, 130.2, 129.7, 129.4, 128.4, 127.9, 126.4, 52.7, 52.3; ESI-HRMS m/z: 370.9890 ([M+Na]<sup>+</sup>); C<sub>16</sub>H<sub>13</sub>O<sub>4</sub>BrNa: 370.9889.

Biphenyl-5-bromo-2,3-dicarboxylic acid dimethyl ester (40)



**3o** (35.1 mg, 0.1 mmol) was used as a substrate and **4o** (31.3 mg, 0.090 mmol) was obtained in 90% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1). Colorless oil; IR (ATR) cm<sup>-1</sup>: 2978, 1729, 1577, 1439, 1304, 1268, 1241, 1204, 1123, 1070; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.13 (d, *J* = 2.0 Hz, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.42—7.37 (m, 3H), 7.35—7.33 (m, 2H), 3.92 (s, 3H), 3.66 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.5, 164.9, 142.4, 137.8, 136.8, 133.6, 131.7, 129.7, 128.4, 128.4, 123.0, 52.9, 52.4; ESI-HRMS m/z: 370.9889 ([M+Na]<sup>+</sup>); C<sub>16</sub>H<sub>13</sub>O<sub>4</sub>BrNa: 370.9889.

#### Biphenyl-5-tert-butyldimethylsilyloxy-2,3-dicarboxylic acid dimethyl ester (4p)



**3p** (40.3 mg, 0.1 mmol) was used as a substrate and **4p** (27.6 mg, 0.069 mmol) was obtained in 69% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1). Dimethyl 5-hydroxybiphenyl-2,3-dicarboxylate (7.7 mg, 0.027 mmol) was obtained in 27% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1).

Colorless solid; M.p. 79—84 °C; IR (ATR) cm<sup>-1</sup>: 2953, 2860, 1727, 1587, 1469, 1431, 1342, 1261, 1193, 1169, 1115, 1067, 1012; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.42 (d, *J* = 2.0 Hz, 1H), 7.41—7.34 (m, 5H), 7.00 (d, *J* = 2.0 Hz, 1H), 3.90 (s, 3H), 3.64 (s, 3H), 1.00 (s, 9H), 0.24 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  169.3, 166.1, 155.9, 142.2, 139.2, 129.9, 128.3, 128.2, 127.8, 127.8, 125.5, 120.2, 52.6, 52.2, 25.5, 18.1, -4.5; ESI-HRMS m/z: 423.1598 ([M+Na]<sup>+</sup>); C<sub>22</sub>H<sub>28</sub>O<sub>5</sub>SiNa: 423.1598.

### Dimethyl 5-hydroxybiphenyl-2,3-dicarboxylate



**3p** (40.3 mg, 0.1 mmol) was used as a substrate and dimethyl 5-hydroxybiphenyl-2,3-dicarboxylate (7.7 mg, 0.027 mmol) was obtained in 27% yield after purification by silica-gel column chromatography (n-hex/EtOAc = 3/1).

Colorless solid; M.p. 103—105 °C; IR (ATR) cm<sup>-1</sup>: 3289, 2954, 1718, 1698, 1601, 1584, 1425, 1335, 1265, 1228, 1189, 1170, 1118, 1064; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.40 (d, *J* = 2.5 Hz, 1H), 7.39—7.36 (m, 3H), 7.34—7.33 (m, 2H), 6.99 (d, *J* = 2.5 Hz, 1H), 5.48 (brs, 1H), 3.89 (s, 3H), 3.64 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  170.0, 166.2, 156.2, 142.5, 139.0, 130.0, 128.3, 128.3, 127.9, 126.8, 120.9, 115.7, 52.7, 52.5; ESI-HRMS m/z: 309.0733 ([M+Na]<sup>+</sup>); C<sub>16</sub>H<sub>14</sub>O<sub>5</sub>Na: 309.0733.

#### Dimethyl 3-(2-furyl)phthalate (4q)



**3q** (26.2 mg, 0.1 mmol) was used as a substrate and **4q** (24.5 g, 0.094 mmol) was obtained in 94% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1). Colorless solid; M.p. 49—52 °C; IR (ATR) cm<sup>-1</sup>: 2954, 1723, 1594, 1498, 1434, 1287, 1260, 1219, 1204, 1151, 1121, 1065, 1020; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.96 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.53—7.50 (m, 2H), 6.64 (d, *J* = 3.5 Hz, 1H), 6.48—6.47 (m, 1H), 3.95 (s, 3H), 3.91 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 169.6, 165.7, 150.4, 143.0, 131.8, 130.8, 129.2, 129.1, 128.7, 128.1, 111.8, 108.7, 52.7, 52.6; ESI-HRMS m/z: 283.0574 ([M+Na]<sup>+</sup>); C<sub>14</sub>H<sub>12</sub>O<sub>5</sub>Na: 283.0577.

# Dimethyl 3-(2-thienyl)phthalate (4r)



**3r** (27.8 mg, 0.1 mmol) was used as a substrate and **4r** (24.5 mg, 0.089 mmol) was obtained in 89% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1).

Yellow oil; IR (ATR) cm<sup>-1</sup>: 2951, 1725, 1589, 1455, 1434, 1285, 1202, 1151, 1119, 1067, 1035; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.00 (d, *J* =7.5 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.49 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.37 (d, *J* = 4.5 Hz, 1H), 7.15 (d, *J* = 4.5 Hz, 1H), 7.06 (dd, *J* = 4.5, 4.5 Hz, 1H); 3.91 (s, 3H), 3.81 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  169.2, 165.7, 139.8, 134.7, 134.6, 132.9, 129.4, 129.1, 128.0, 127.5, 127.1, 126.7, 52.6, 51.5; ESI-HRMS m/z: 299.0349 ([M+Na]<sup>+</sup>); C<sub>14</sub>H<sub>12</sub>O<sub>4</sub>SNa: 299.0349.

### Dimethyl [1,1':2',1''-terphenyl]-3',4'-dicarboxylate (4s)



**3s** (34.8 mg, 0.1 mmol) was used as a substrate and **4s** (33.8 mg, 0.098 mmol) was obtained in 98% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1). Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.08 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.19—7.16 (m, 6H), 7.10—7.08 (m, 2H), 7.06—7.04 (m, 2H), 3.93 (s, 3H), 3.57 (s, 3H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 32.

# Dimethyl [1,1':3',1''-terphenyl]-4',5'-dicarboxylate (4t)



**3t** (34.8 mg, 0.1 mmol) was used as a substrate and **4t** (31.8 mg, 0.092 mmol) was obtained in 92% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1). Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.24 (d, *J* = 2.0 Hz, 1H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.66—7.64 (m, 2H), 7.48 (t, *J* = 7.0 Hz, 2H), 7.44—7.39 (m, 6H) 3.95 (s, 3H), 3.70 (s, 3H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 33.

# Dimethyl [1,1':4',1''-terphenyl]-2',3'-dicarboxylate (4u)



**3u** (34.8 mg, 0.1 mmol) was used as a substrate and **4u** (33.6 mg, 0.097 mmol) was obtained in 97% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1). Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.52 (s, 2H), 7.44—7.36 (m, 10H), 3.61 (s, 6H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 34.

### Dimethyl [1,1':2',1''-terphenyl]-4',5'-dicarboxylate (4v)



**3v** (34.8 mg, 0.1 mmol) was used as a substrate and **4v** (30.7 g, 0.89 mmol) was obtained in 89% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 2/1). Colerless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.79 (s, 2H), 7.24—7.23 (m, 6H), 7.14—7.13 (m, 4H), 3.94 (s, 6H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 32.

#### 4,5-Dimethylphthalic acid dimethyl ester (4w)

CO<sub>2</sub>Me CO<sub>2</sub>Me

**3w** (22.4 mg, 0.1 mmol) was used as a substrate and **4w** (22.1 mg, 0.099 mmol) was obtained in 99% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1). Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.48 (s, 2H), 3.88 (s, 6H), 2.31 (s, 6H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 35.

### **3-Benzylphthalic acid dimethyl ester (4x)**



**3x** (28.6 mg, 0.1 mmol) was used as a substrate and **4x** (25.6 mg, 0.090 mmol) was obtained in 90% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1). Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.87 (dd, J = 1.5, 8.0 Hz, 1H), 7.39—7.27 (m, 4H), 7.21 (dd, J = 7.5, 7.5 Hz, 1H), 7.16 (d, J = 7.5 Hz, 2H), 4.02 (s, 2H), 3.89 (s, 3H), 3.85 (s, 3H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 30.

### Biphenyl-2,3-dicarboxylic acid (4y)



**3y** (24.4 mg, 0.1 mmol) was used as a substrate and **4y** (22.0 mg, 0.091 mmol) was obtained in 91% yield after purification by silica-gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 5/1). Colorless solid; <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  7.89 (dd, J = 2.0, 7.5 Hz, 2H), 7.60—7.54 (m, 2H), 7.45—7.37 (m, 5H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 36.

# 3,4-Dimethylbiphenyl (4z)



**3z** (18.4 mg, 0.1 mmol) was used as a substrate and **4z** (17.1 mg, 0.094 mmol) was obtained in 94% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 100/1).

Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.62 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 7.5 Hz, 2H), 7.39 (s, 1H), 7.37—7.34 (m, 2H), 7.25 (dd, J = 7.5 Hz, 1H), 2.37 (s, 3H), 2.35 (s, 3H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 37.

# 3,4-Dimethyl-2-trimethylsilyl-biphenyl (4aa)



**3aa** (25.6 mg, 0.1 mmol) was used as a substrate and **4aa** (23.4 mg, 0.092 mmol) was obtained in 92% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 100/1). Colorless oil; IR (ATR) cm<sup>-1</sup>: 2952, 1473, 1443, 1379, 1247, 1088; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.42—7.38 (m, 4H), 7.34—7.32 (m, 2H), 7.09 (s, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 0.04 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  147.0, 144.4, 137.0, 136.0, 135.4, 134.5, 131.0, 129.4, 127.6, 126.8, 19.6, 19.4, 0.6; ESI-HRMS m/z: 277.1393 ([M+Na]<sup>+</sup>); C<sub>17</sub>H<sub>22</sub>SiNa: 277.1383.

### 1,2,3-Triphenylbenzene (4ab)



**3ab** (30.8 mg, 0.1 mmol) was used as a substrate and **4ab** (28.9 mg, 0.094 mmol) was obtained in 94% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 50/1). Coloress solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.49—7.43 (m, 3H), 7.17—7.13 (m, 6H), 7.09—7.07 (m, 4H), 6.99—6.95 (m, 3H), 6.84—6.82 (m, 2H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 38.

#### 1-Phenylnaphthalene (4ac)



**3ac** 20.6 mg, 0.1 mmol) was used as a substrate and **4ac** (19.2 mg, 0.094 mmol) was obtained in 94% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 100/1). Coloress oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.92 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.56—7.49 (m, 6H), 7.47—7.43 (m, 3H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 37.

### 4-Methylphthalic acid dimethyl ester (4ad)



**3'd** (21.2 mg, 0.1 mmol) was used as a substrate and **4ad** (20.3 mg, 0.098 mmol) was obtained in 98% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1). Colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.67 (d, *J* = 8.0 Hz, 1H), 7.46 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 2.40 (s, 3H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 38.

### 3,4-Dimethylbenzoic acid (4ae)



**3'g** (15.4 mg, 0.1 mmol) was used as a substrate and **4ae** (13.8 mg, 0.092 mmol) was obtained in 92% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 1/1). Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.89 (s, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 39.

#### [2-(Hydroxymethyl)-3-phenylphenyl]methanol (8a)



**4a** (0.27 g, 1.0 mmol) was used as a substrate and **8a** (0.16 g, 0.75 mmol) was obtained in 75% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 1/1). Colorless solid; M.p. 100—101 °C; IR (ATR) cm<sup>-1</sup>: 3316, 3059, 3024, 2883, 1495, 1461, 1434, 1191, 1104, 1006; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.45—7.41 (m, 4H), 7.40—7.36 (m, 3H), 7.35—7.31 (m, 1H), 4.83 (s, 2H), 4.65 (s, 2H), 3.21 (brs, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 143.5, 140.9, 140.4, 136.9, 130.6, 129.4, 129.1, 128.2, 128.1, 127.2, 65.1, 60.0; ESI-HRMS m/z: 237.0886 ([M+Na]<sup>+</sup>); C<sub>14</sub>H<sub>14</sub>O<sub>2</sub>Na: 237.0886.

# [2-(Hydroxymethyl)-3-furylphenyl]methanol (8b)



**4q** (0.26 g, 1.0 mmol) was used as a substrate and **8b** (0.15 g, 0.73 mmol) was obtained in 73% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 1/1).

Colorless oil; IR (ATR) cm<sup>-1</sup>: 3330, 2978, 1455, 1157, 1004; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.55 (d, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.31 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 3.0 Hz, 1H), 6.50 (dd, *J* = 2.0, 3.0 Hz, 1H), 4.72 (s, 4H), 3.78 (brs, 1H), 3.61 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  152.7, 142.6, 140.9, 135.9, 132.0, 129.1, 128.6, 128.3, 111.5, 109.3, 64.4, 59.8; ESI-HRMS m/z: 227.0679 ([M+Na]<sup>+</sup>); C<sub>12</sub>H<sub>12</sub>O<sub>3</sub>Na: 227.0679.

1,1':2',1''-Terphenyl-3',4'-diyldimethanol (8c)



**4s** (0.35 g, 1.0 mmol) was used as a substrate and **8c** (0.23 g, 0.81 mmol) was obtained in 81% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 1/1).

Colorless solid; M.p. 143—144 °C; IR (ATR) cm<sup>-1</sup>: 3329, 3056, 3025, 2884, 1601, 1492, 1443, 1409, 1278, 1084, 1028, 1008; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.46 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.24—7.18 (m, 3H), 7.14—7.09 (m, 5H), 7.02—7.00 (m, 2H), 4.89 (s, 2H), 4.59 (s, 2H), 2.94 (brs, 1H), 2.74 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  142.3, 141.7, 141.5, 139.3, 139.0, 137.7, 130.6, 130.0, 129.7, 129.1, 127.7, 127.5, 126.8, 126.3, 65.0, 60.3; ESI-HRMS m/z: 313.1198 ([M+Na]<sup>+</sup>); C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>Na: 313,1199.

# 1,1':5',1"-Terphenyl-2',3'-diyldimethanol (8d)



**4t** (0.17 g, 0.5 mmol) was used as a substrate and **8d** (0.096 g, 0.33 mmol) was obtained in 66% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 1/1). Colorless solid; M.p. 119—122 °C; IR (ATR) cm<sup>-1</sup>: 3340, 3019, 3008, 2892, 1598, 1497, 1439, 1076; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.63—7.60 (m, 3H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.49—7.35 (m, 8H), 4.90 (s, 2H), 4.69 (s, 2H), 3.20 (brs, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  144.0, 141.0, 140.9, 140.1, 135.8, 129.4, 129.1, 128.8, 128.3, 128.2, 127.8, 127.6, 127.4, 127.1, 65.3, 59.9; ESI-HRMS m/z: 313.1200 ([M+Na]<sup>+</sup>); C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>Na: 313.1199.

1,1':4',1''-Terphenyl-2',3'-diyldimethanol (8e)



**4u** (0.35 g, 1.0 mmol) was used as a substrate and **8e** (0.25 g, 0.87 mmol) was obtained in 87% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 1/1). Colorless solid; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.48—7.42 (m, 8H), 7.41—7.37 (m, 2H), 7.33 (s, 2H), 4.70 (s, 4H), 3.24 (brs, 2H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 23.

# 1,1':2',1''-Terphenyl-4',5'-diyldimethanol (8f)



**4v** (34.7 mg, 0.1 mmol) was used as a substrate and **8f** (24.1 mg, 0.083 mmol) was obtained in 83% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 1/1).

Colorless solid; M.p. 117—118 °C; IR (ATR) cm<sup>-1</sup>: 3337, 3319, 1481, 1445, 1026, 1008; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.44 (s, 2H), 7.22—7.20 (s, 6H), 7.14—7.13 (m, 4H), 4.86 (d, *J* = 5.5 Hz, 4H), 2.73 (brs, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  140.7, 138.4, 132.2, 129.8, 128.0, 126.7, 64.1; ESI-HRMS m/z: 313.1196 ([M+Na]<sup>+</sup>); C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>Na: 313.1199.

#### 1,3-Dihydro-4-phenylisobenzofuran (9a)



**8a** (42.9 mg, 0.2 mmol) was used as a substrate and **9a** (29.1 g, 0.15 mmol) was obtained in 75% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 20/1). Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.47—7.41 (m, 4H), 7.40—7.33 (m, 3H), 7.25 (d, *J* = 7.0 Hz, 1H), 5.22 (s, 2H), 5.19 (s, 2H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 40.

### 1,3-Dihydro-4-furylisobenzofuran (9b)



**8b** (40.8 mg, 0.2 mmol) was used as a substrate and **9b** (33.0 mg, 0.18 mmol) was obtained in 89% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 20/1). Colorless solid; M.p. 49—53 °C; IR (ATR) cm<sup>-1</sup>: 2853, 1604, 1501, 1464, 1368, 1218, 1157, 1098, 1048, 1020; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.61 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 1.0 Hz, 1H), 7.32 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.15 (d, *J* = 7.0 Hz, 1H), 6.52—6.50 (m, 2H), 5.35 (s, 2H), 5.16 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  152.7, 142.3, 140.1, 134.4, 127.8, 124.9, 123.0, 119.6, 111.7, 106.9, 74.3, 73.4; ESI-HRMS m/z: 185.0624 ([M-H]<sup>-</sup>); C<sub>12</sub>H<sub>11</sub>O<sub>2</sub>: 185.0608.

# 1,3-Dihydro-4,5-diphenylisobenzofuran (9c)



**8c** (58.1 mg, 0.2 mmol) was used as a substrate and **9c** (41.6 g, 0.15 mmol) was obtained in 76% yield after purification by silica-gel column chromatography (hex/EtOAc = 20/1).

Colorless solid; M.p. 125—127 °C; IR (ATR) cm<sup>-1</sup>: 2921, 2851, 1459, 1448, 1439, 1421, 1376, 1362, 1319, 1258, 1101, 1079, 1067, 1040, 1026; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.39 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.25—7.17 (m, 6H), 7.12—7.10 (m, 2H), 7.08—7.06 (m, 2H), 5.24 (s, 2H), 5.02 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  140.8, 140.1, 138.9, 138.8, 134.5, 130.0, 129.9, 129.4, 128.0, 127.7, 126.8, 126.4, 119.9, 74.0, 73.7; ESI-HRMS m/z: 273.1291 ([M+H]<sup>+</sup>); C<sub>20</sub>H<sub>17</sub>O: 273.1274.

1,3-Dihydro-4,6-diphenylisobenzofuran (9d)



**8d** (58.1 mg, 0.2 mmol) was used as a substrate and **9d** (43.0 g, 0.16 mmol) was obtained in 79% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm<sup>-1</sup>: 3029, 2847, 1599, 1547, 1498, 1466, 1440, 1364, 1315, 1187, 1112, 1076, 1048; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.63 (dd, *J* = 1.0, 8.0 Hz, 2H), 7.55 (s, 1H), 7.47—7.44 (m, 7H), 7,40—7.36 (m, 2H), 5.25 (s, 2H), 5.24 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  141.6, 141.0, 140.8, 140.0, 136.3, 136.2, 128.8, 128.7, 127.9, 127.6, 127.5, 127.2, 126.8, 118.6, 73.7, 73.4; ESI-HRMS m/z: 273.1291 ([M+H]<sup>+</sup>); C<sub>20</sub>H<sub>17</sub>O: 273.1274.

### 1,3-Dihydro-4,7-diphenylisobenzofuran (9e)



**8e** (58.1 mg, 0.2 mmol) was used as a substrate and **9e** (27.6 mg, 0.10 mmol) was obtained in 51% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 20/1). Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.48—7.36 (m, 12H), 5.26 (s, 4H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 41.

#### 1,3-Dihydro-5,6-diphenylisobenzofuran (9f)



**8f** (14.5 mg, 0.05 mmol) was used as a substrate and **9f** (10.5 g, 0039 mmol) was obtained in 77% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 20/1). Colorless solid; M.p. 131—133 °C; IR (ATR) cm<sup>-1</sup>: 3435, 3026, 2849, 1599, 1473, 1447, 1364, 1048; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.31 (s, 2H), 7.22—7.19 (m, 6H), 7.13—7.12 (m, 4H), 5.21 (s, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  141.4, 140.1, 138.6, 129.9, 127.9, 126.5, 123.0, 73.4; ESI-HRMS m/z: 273.1291 ([M+H]<sup>+</sup>); C<sub>20</sub>H<sub>17</sub>O: 273.1274.

### 6. Metal leaching test.

To a solution of dimethyl 3-phenylcyclohexa-1,4-diene-1,2-dicarboxylate (**3a**: 1.4 g, 5.0 mmol) in H<sub>2</sub>O (50 mL) were added 10% Pd/C (266 mg, 0.25 mmol), acrylic acid (4.5 mL, 50 mmol) under argon. The reaction mixture was refluxed at 120 °C for 6 h. After stirring for 6 h, the reaction mixture was cooled to room temperature. The reaction mixture was passed through a filter paper [Kiriyama, No. 5C (1  $\mu$ m), diameter = 40 mm] and the catalyst was washed with H<sub>2</sub>O (20 mL × 5) and AcOEt (20 mL × 5). The filtrate was extracted with AcOEt (20 mL × 2). The combined organic layers were washed sat. NaHCO<sub>3</sub> aq. (20 mL × 2), dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was dissolved in EtOAc, and the aqueous layer was diluted with H<sub>2</sub>O to 100 mL, respectively. The Pd leaching in each layers was measured by ICP-OES. A very small amount of residual Pd species was detected in aqueous layer (4.0 ppm), while no palladium was detected in organic layer.

#### 7. Reuse test.

To a test tube were added dimethyl 3-phenylcyclohexa-1,4-diene-1,2-dicarboxylate (**3a**: 27.2 mg, 0.1 mmol), 10% Pd/C (5.3 mg, 0.005 mmol), acrylic acid (34.3  $\mu$ L, 0.5 mmol), and H<sub>2</sub>O (1 mL), then the system was sealed with a septum. The air inside was replaced with argon (balloon) by three vacuum/argon cycles. The test tube was placed on an organic reactor, ChemiStation (EYELA, Tokyo Rikakikai Co., Ltd., Tokyo, Japan), and the mixture was

refluxed (80 °C outer temperature). After 6 h, the reaction mixture was cooled to room temperature. The reaction mixture was passed through a filter paper [Kiriyama, No. 5C (1  $\mu$ m), diameter = 40 mm] and the catalyst was washed with H<sub>2</sub>O (10 mL × 5) and MeOH (10 mL × 5). The filtrate was extracted with EtOAc (20 mL × 2). The combined organic layers were washed sat. NaHCO<sub>3</sub> aq. (20 mL × 2), dried over MgSO<sub>4</sub>, and concentrated in vacuo. The filtrated catalysts were further washed with MeOH (50 mL) and water (50 mL) and dried in a desiccator under vacuum overnight, then the recovered catalyst was used for the next run. The results of reuse test are summarized in the Table S4.

Table S4. Reuse test of Pd/C in dehydrogenation.<sup>a</sup>

	CO <sub>2</sub> Me CO <sub>2</sub> Me	$\frac{10\% \text{ Pd/C}}{\text{Acrylic acid}}$	CO <sub>2</sub> Me CO <sub>2</sub> Me
Run	yield (%)		Recovered Pd/C (%)
	<b>3</b> a	4a	
$1^{st}$	0	>99	>99
$2^{nd}$	4	96	98
3 <sup>rd</sup>	6	92	>99

<sup>a</sup> Reaction conditions: **3a** (0.1 mmol, 1.0 equiv.), 10% Pd/C (0.005 mmol, 5 mol%), and acrylic acid (0.5 mmol, 5.0 equiv.) in  $H_2O$  (1 mL) under Ar at 80 °C for 6 h.

# 8. Mechanism study

#### 8-1. GC/TCD analysis (eq. 2)

To a solution of dimethyl 3-phenylcyclohexa-1,4-diene-1,2-dicarboxylate (3a: 0.27 g, 1.0 mmol) in H<sub>2</sub>O (10 mL) was added 10% Pd/C (53.3 mg, 0.05 mmol) under argon. The reaction mixture was refluxed at 80 °C. After stirring for 6 h, the reaction mixture was cooled to room temperature. The inside gasses were analyzed by GC/TCD and H<sub>2</sub> gas was detected. The reaction mixture was passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Pd/C. The filtrate was extracted with EtOAc (10 mL  $\times$  3). The combined organic layers

were washed sat. NaHCO<sub>3</sub> aq. (10 mL  $\times$  3), dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-EtOAc (5/1) as a mixed eluent to give the mixture (0.27 g) of biphenyl-2,3-dicarboxylic acid dimethyl ester (4a: 0.69 mmol, 69% yield) and dimethyl 3-phenylcyclohexa-1,2-dicarboxylate (**5a**: 0.30 mmol, 30% yield).

# **3-2.** Tracer test of acrylic acid derivatives (eq. 3)

To a solution of dimethyl 3-phenylcyclohexa-1,4-diene-1,2-dicarboxylate (3a: 27.2 mg, 0.1 mmol) in H<sub>2</sub>O (1 mL) was added 10% Pd/C (5.3 mg, 0.005 mmol) and dodecyl acrylate (6: 112.2 mg, 0.5 mmol) as a H<sub>2</sub> acceptor under argon. The reaction mixture was refluxed at 120 °C. After stirring for 6 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Pd/C. The filtrate was extracted with EtOAc (10 mL  $\times$  3). The combined organic layers were washed sat. NaHCO<sub>3</sub> aq. (10 mL  $\times$ 3), dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-EtOAc (20/1) as а mixed eluent to give biphenyl-2,3-dicarboxylic acid dimethyl ester (4a: 25.6 mg, 0.095 mmol, 95% yield) and the mixture of dodecyl acrylate (6: 0.414 mmol) and dodecyl propionate (7: 0.077 mmol).

**Dodecyl propionate (7)** 

0.*n*-C<sub>12</sub>H<sub>25</sub>

Colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  4.05 (t, *J* = 7.5 Hz, 2H), 2.31 (q, *J* = 7.5 Hz, 2H), 1.61—1.58 (m, 2H), 1.36—1.27 (m, 18H), 1.13 (t, *J* = 7.5 Hz, 1H), 0.87 (t, *J* = 7.5 Hz, 1H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 42.



# 3-3. Consideration of stereochemistry (3'c-[cis] and 3'c-[trans]: eq. 5)

To a solution of dimethyl 3-phenylcyclohexene-4,5-*cis*-dicarboxylate (**3**°**c**: 27.4 mg, 0.1 mmol) in H<sub>2</sub>O (1 mL) was added 10% Pd/C (10.6 mg, 0.01 mmol, 10 mol%) and acrylic acid (68.6  $\mu$ L, 1.0 mmol) under argon. The reaction mixture was refluxed at 120 °C. After stirring for 24 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Pd/C. The filtrate was extracted with EtOAc (10 mL × 3). The combined organic layers were washed sat. NaHCO<sub>3</sub> aq. (10 mL × 3), dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-EtOAc (5/1) as a mixed eluent to give the mixture of biphenyl-2,3-dicarboxylic acid dimethyl ester (**4a**: 0.044 mmol, 44% yield) and the recovered dimethyl 3-phenylcyclohexene-4,5-*cis*-dicarboxylate (**3'c-**[*cis*]: 0.048 mmol, 48% yield).



# 9. Limitation of substrates.

# 9-1. Scope of cyclohexene derivatives as a starting material



# 9-2. Scope of cyclohexane derivatives as a starting material



### 10. References.

(1) D. A. Mundal, K. E. Lutz, R. J. Thomson, Org. Lett. 2009, 11, 465-468.

(2) J. Barluenga, M. Tomas-Gamasa, F. Aznar, C. Valdes, *Adv. Synth. Catal.* **2010**, *352*, 3235-3240.

(3) K. S. Madden, S. David, J. P. Knowles, A. Whiting, *Chem. Commun.* 2015, 51, 11409-11412.

- (4) N. Chinkov, S. Majumdar, I. Marek, J. Am. Chem. Soc. 2003, 125, 13258-13264.
- (5) A. L. Watkins, C. R. Landis, Org. Lett. 2011, 13, 164-167.
- (6) M. Ohashi, I. Takeda, M. Ikawa, S. Ogoshi, J. Am. Chem. Soc. 2011, 133, 18018-18021.
- (7) N. Marco, A. Fredi, T. Parella, Chem. Commun. 2015, 51, 3262-3265.
- (8) F. A. Khan, B. M. Budanur, Tetrahedron 2015, 71, 7600-7607.
- (9) J. M. Landesberg, M. A. Slam, M. Mandel, J. Org. Chem. 1981, 46, 5025-5027.
- (10) T. Chatterjee, R. Dey, B. C. Ranu, New J. Chem. 2011, 35, 1103-1110.
- (11) Q. Wang, M. E. Khoury, M. Schlosser, Chem. Eur. J. 2000, 6, 420-426.
- (12) D. F. Schneider, A. C. Venter, Synth. Commun. 1999, 29, 3067-3081.

(13) W. M. Dean, M. Siauciulis, T. E. Storr, W. Lewis, R. A. Stockman, *Angew. Chem. Int. Ed.* **2016**, *55*, 10013-10016.

- (14) G. Battistuzzi, S. Cacchi, G. Fabrizi, Org. Lett. 2003, 5, 777-780.
- (15) A. Spaggiari, D. Vaccari, P. Davoli, G. Torre, F. Prati, J. Org. Chem. 2007, 72, 2216-2219.
- (16) E. Lestini, K. Robertson, C. D. Murphy, F. Paradisi, Synth. Commun. 2012, 42, 1864-1876.
- (17) M. H. Babu, G. R. Kumar, R. Kant, M. S. Reddy, Chem. Commun. 2017, 53, 3894-3897.
- (18) Z. Zhang, Q. Wang, C. Chen, Z. Han, Xiu-Qin Dong, X. Zhang, Org. Lett. 2016, 18, 3290-3293.
- (19) J. Mulzer, G. Bruntrup, U. Kuhl, G. Hartz, Chem. Ber. 1982, 115, 3453-3469.
- (20) Y. Al-Jawaheri, M. C. Kimber, Org. Lett. 2016, 18, 3502-3505.
- (21) G. Hilt, K. I. Smolko, Angew. Chem. Int. Ed. 2003, 42, 2795-2797.
- (22) T. Shibata, D. Fujiwara, K. Endo, Org. Biomol. Chem. 2008, 6, 464-467.

(23) D. Thirion, C. Poriel, J. Rault-Berthelot, F. Barriere, O. Jeannin, *Chem. Eur. J.* 2010, *16*, 13646-13658.

- (24) H. Jiang, L. He, X. Li, H. Chen, W. Wu, W. Fu, Chem. Commun. 2013, 49, 9218-9220.
- (25) I. Kaur, W. Jia, R. P. Kopreski, S. Selvarasah, M. R. Dokmeci, C. Pramanik, N. E. McGruer, G. P. Miller, *J. Am. Chem. Soc.* **2008**, *130*, 16274-16386.
- (26) R. Chopra, K. Sharma, M. Kumar, V. Bhalla, J. Org. Chem. 2016, 81, 1039-1046.
- (27) Y. K. Choughule, A. V. Patwardgan, Orient. J. Chem. 2016, 32, 921-926.
- (28) C. K. Malik, R. N. Yadav, M. G. B. Drew, S. Ghosh, J. Org. Chem. 2009, 74, 1957-1963.
- (29) P. Dutta, J. Dey, A. Shome, P. K. Das, Int. J. Pharm. 2011, 414, 298-311.

(30) H. Hara, M. Hirano, K. Tanaka, Tetrahedron 2009, 65, 5093-5101.

- (31) L. Huamg, D. Hackenberger, L. J. Gooben, Angew. Chem. Int. Ed. 2015, 54, 12607-12611.
- (32) C. Feng, X. Wang, Bi-Qin Wang, Ke-Qing Zhao, P. Hu, Zhang-Jie Shi, *Chem. Commun.* 2012, 48, 356-358.
- (33) Yun-Yun Yang, Wang-Ge Shou, Yan-Guang Wang, Synth. Commun. 2006, 36, 1383-1390.
- (34) S. Li, M. Aljhdli, H. Thakellapalli, B. Farajidizaji, Y. Zhang, N. G. Akhmedov, C. Milsmann, B. V. Popp, K. K. Wang, *Org. Lett.* **2017**, *19*, 4078-4081.
- (35) S. Li, H. Qu, L. Zhou, K. Kanno, Q. Guo, B. Shen, T. Takahashi, Org. Lett. 2009, 11, 3318-3321.
- (36) Y. Cheng, X. Gu, P. Li, Org. Lett. 2013, 15, 2664-2667.
- (37) R. Sebastian, E. Peter, S. Muhammad, S. Anke, L. Peter, *Tetrahedron* 2016, 72, 1083-1094.
- (38) B. Bozic-Weber, E. C. Constable, N. Hostettler, C. E. Housecroft, R. Sc hi¥mitt, E. Schonhofer, *Chem. Commun.* **2012**, *48*, 5727-5729.
- (39) V. Venkateswarlu, K. A. A. Kumar, S. Gupta, D. Singh, R. A. Vishwakarma, S. D. Sawant, *Org. Biomol. Chem.* **2015**, *13*, 7973-7978.
- (40) B. A. Seigal, M. H. An, M. L. Snapper, Angew. Chem. Int. Ed. 2005, 44, 4929-4932.
- (41) F. E. McDonald, V. Smolentsev, Org. Lett. 2002, 4, 745-748.
- (42) Hoang-Phuong. Nguyen, S. Znifeche, M. Baboulene, Synth. Commun. 2004, 34, 2085-2093.

**11.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the newly synthesized substrates and products <sup>1</sup>H NMR of 1-(Buta-1,3-dienyl)-4-vinylbenzene (1k)



<sup>13</sup>C NMR of 1-(Buta-1,3-dienyl)-4-vinylbenzene (1k)



<sup>1</sup>H NMR of dimethyl 3-phenylcyclohexa-1,4-diene-1,2-dicarboxylate (**3a**)



<sup>1</sup>H NMR of dimethyl 3-(4':4''-biphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3b**)



<sup>13</sup>C NMR of dimethyl 3-(4':4''-biphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3b**)



<sup>1</sup>H NMR of dimethyl 3-(4'-methoxyphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3c**)



<sup>13</sup>C NMR of dimethyl 3-(4'-methoxyphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3c**)



<sup>1</sup>H NMR of dimethyl 3-(4'-*N*,*N*-dimethylaminophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3d**)



<sup>13</sup>C NMR of dimethyl 3-(4'-*N*,*N*-dimethylaminophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3d**)



<sup>1</sup>H NMR of trimethyl 3-phenylcyclohexa-1,4-diene-1,2,4'-tricarboxylate (**3e**)



<sup>13</sup>C NMR of trimethyl 3-phenylcyclohexa-1,4-diene-1,2,4'-tricarboxylate (**3e**)



<sup>1</sup>H NMR of dimethyl 3-(4'-nitorophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3f**)



<sup>13</sup>C NMR of dimethyl 3-(4'-nitorophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3f**)



<sup>1</sup>H NMR of dimethyl 3-(4'-cyanophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3g**)



<sup>13</sup>C NMR of dimethyl 3-(4'-cyanophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3g**)



<sup>1</sup>H NMR of dimethyl 3-(4'-bromophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3h**)



<sup>13</sup>C NMR of dimethyl 3-(4'-bromophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3h**)



<sup>1</sup>H NMR of dimethyl 3-(4'-chlorophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3i**)



<sup>13</sup>C NMR of dimethyl 3-(4'-chlorophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3i**)



<sup>1</sup>H NMR of dimethyl 3-(4'-fluorophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3j**)


<sup>13</sup>C NMR of dimethyl 3-(4'-fluorophenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3**j)



<sup>1</sup>H NMR of dimethyl 3-(4'-vinylphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3**k)



<sup>13</sup>C NMR of dimethyl 3-(4'-vinylphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (3k)



<sup>1</sup>H NMR of dimethyl 3-(2'-methoxyphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3**I)



<sup>13</sup>C NMR of dimethyl 3-(2'-methoxyphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3**I)



<sup>1</sup>H NMR of dimethyl 3-(3'-methoxyphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3m**)



<sup>13</sup>C NMR of dimethyl 3-(3'-methoxyphenyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3m**)



<sup>1</sup>H NMR of dimethyl 4-bromo-3-phenylcyclohexa-1,4-diene-1,2-dicarboxylate (**3n**)



<sup>13</sup>C NMR of dimethyl 4-bromo-3-phenylcyclohexa-1,4-diene-1,2-dicarboxylate (**3n**)



<sup>1</sup>H NMR of dimethyl 5-bromo-3-phenylcyclohexa-1,4-diene-1,2-dicarboxylate (**30**)



<sup>13</sup>C NMR of dimethyl 5-bromo-3-phenylcyclohexa-1,4-diene-1,2-dicarboxylate (**3o**)



<sup>1</sup>H NMR of dimethyl 5-*tert*-butyldimethylsilyloxy-3-phenyl-1,4-diene-1,2-dicarboxylate (**3p**)



<sup>13</sup>C NMR of dimethyl 5-*tert*-butyldimethylsilyloxy-3-phenyl-1,4-diene-1,2-dicarboxylate (**3p**)



<sup>1</sup>H NMR of dimethyl 3-(2'-furyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3q**)



<sup>13</sup>C NMR of dimethyl 3-(2'-furyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3q**)



<sup>1</sup>H NMR of dimethyl 3-(2'-thienyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3r**)



<sup>13</sup>C NMR of dimethyl 3-(2'-thienyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**3r**)



<sup>1</sup>H NMR of dimethyl 3',6'-dihydro-[1,3':4',1"-terphenyl]-1',2'-dicarboxylate (**3s**)



<sup>13</sup>C NMR of dimethyl 3',6'-dihydro-[1,3':4',1"-terphenyl]-1',2'-dicarboxylate (**3s**)



<sup>1</sup>H NMR of dimethyl 3',6'-dihydro-[1,3':5',1"-terphenyl]-1',2'-dicarboxylate (**3t**)



<sup>13</sup>C NMR of dimethyl 3',6'-dihydro-[1,3':5',1"-terphenyl]-1',2'-dicarboxylate (**3t**)



<sup>1</sup>H NMR of dimethyl 3',6'-dihydro-[1,3':6',1"-terphenyl]-1',2'-dicarboxylate (**3u**)



<sup>1</sup>H NMR of dimethyl 3',6'-dihydro-[1,1':2',1"-terphenyl]-4',5'-dicarboxylate (**3v**)



<sup>1</sup>H NMR of dimethyl 4,5-dimethylcyclohexa-1,4-diene-1,2-dicarboxylate (**3**w)



<sup>1</sup>H NMR of dimethyl 3-benzylcyclohexa-1,4-diene-1,2-dicarboxylate (**3x**)



<sup>13</sup>C NMR of dimethyl 3-benzylcyclohexa-1,4-diene-1,2-dicarboxylate (**3x**)



<sup>1</sup>H NMR of 3-phenylcyclohexa-1,4-diene-1,2-dicarboxylic acid (**3y**)



<sup>13</sup>C NMR of 3-phenylcyclohexa-1,4-diene-1,2-dicarboxylic acid (**3y**)



<sup>1</sup>H NMR of (4,5-dimethyl-1,4-cyclohexadien-1-yl)benzene (**3z**)



<sup>1</sup>H NMR of (4,5-dimethyl-2-trimethylsilyl-1,4-cyclohexadien-1-yl)benzene (**3aa**)



<sup>13</sup>C NMR of (4,5-dimethyl-2-trimethylsilyl-1,4-cyclohexadien-1-yl)benzene (**3aa**)



<sup>1</sup>H NMR of 1,2,3-triphenyl-1,4-cyclohexadien (**3ab**)



## <sup>13</sup>C NMR of 1,2,3-triphenyl-1,4-cyclohexadien (**3ab**)



## <sup>1</sup>H NMR of 1-phenyl-1,4-dihydronaphthalene (**3ac**)



<sup>13</sup>C NMR of 1-phenyl-1,4-dihydronaphthalene (**3ac**)



<sup>1</sup>H NMR of dimethyl 1,2-dimethylcyclohexene-4,5-*cis*-dicarboxylate (**3'a**)



<sup>13</sup>C NMR of dimethyl 1,2-dimethylcyclohexene-4,5-*cis*-dicarboxylate (**3'a**)



<sup>1</sup>H NMR of dimethyl 1,2-dimethylcyclohexene-4,5-*trans*-dicarboxylate (**3'b**)



<sup>13</sup>C NMR of dimethyl 1,2-dimethylcyclohexene-4,5-*trans*-dicarboxylate (**3'b**)



<sup>1</sup>H NMR of dimethyl 3-phenylcyclohexene-4,5-*trans*-dicarboxylate (**3'c**)



<sup>13</sup>C NMR of dimethyl 3-phenylcyclohexene-4,5-*trans*-dicarboxylate (**3'c**)



<sup>1</sup>H NMR of dimethyl methylcyclohexene-3,4-*trans*-dicarboxylate (**3'd**)



<sup>1</sup>H NMR of 3,4-dimethylcyclohexenecarboxylic acid (**3'e**)



 $^1\mathrm{H}$  NMR of 1,2-dimethylcyclohexene-4,5-cis-dicarboxylic acid (3'g)



<sup>13</sup>C NMR of 1,2-dimethylcyclohexene-4,5-*cis*-dicarboxylic acid (**3'g**)



<sup>1</sup>H NMR of 1,2-dimethylcyclohexene-4,5-*trans*-dicarboxylic acid (**3'h**)



<sup>13</sup>C NMR of 1,2-dimethylcyclohexene-4,5-*trans*-dicarboxylic acid (**3'h**)



<sup>1</sup>H NMR of biphenyl-2,3-dicarboxylic acid dimethyl ester (**4a**)



<sup>1</sup>H NMR of dimethyl [1,1':4',1''-terphenyl]-2,3-dicarboxylate (4b)



<sup>13</sup>C NMR of dimethyl [1,1':4',1''-terphenyl]-2,3-dicarboxylate (**4b**)



<sup>1</sup>H NMR of dimethyl 4'-methoxy-[1,1'-biphenyl]-2,3-dicarboxylate (**4c**)



<sup>1</sup>H NMR of dimethyl 4'-*N*,*N*-dimethylamino-[1,1'-biphenyl]-2,3-dicarboxylate (**4d**)



<sup>13</sup>C NMR of dimethyl 4'-*N*,*N*-dimethylamino-[1,1'-biphenyl]-2,3-dicarboxylate (**4d**)



<sup>1</sup>H NMR of trimethyl [1,1'-biphenyl]-2,3,4'-tricarboxylate (**4e**)



<sup>13</sup>C NMR of trimethyl [1,1'-biphenyl]-2,3,4'-tricarboxylate (**4e**)



<sup>1</sup>H NMR of dimethyl 4'-nitoro-[1,1'-biphenyl]-2,3-dicarboxylate (**4f**)



<sup>13</sup>C NMR of dimethyl 4'-nitoro-[1,1'-biphenyl]-2,3-dicarboxylate (**4f**)



<sup>1</sup>H NMR of dimethyl 4'-cyano-[1,1'-biphenyl]-2,3-dicarboxylate (**4g**)



<sup>13</sup>C NMR of dimethyl 4'-cyano-[1,1'-biphenyl]-2,3-dicarboxylate (4g)



<sup>1</sup>H NMR of dimethyl 4'-bromo-[1,1'-biphenyl]-2,3-dicarboxylate (**4h**)



<sup>13</sup>C NMR of dimethyl 4'-bromo-[1,1'-biphenyl]-2,3-dicarboxylate (**4h**)



<sup>1</sup>H NMR of dimethyl dimethyl 4'-chloro-[1,1'-biphenyl]-2,3-dicarboxylate (**4i**)



<sup>13</sup>C NMR of dimethyl 4'-chloro-[1,1'-biphenyl]-2,3-dicarboxylate (**4i**)



<sup>1</sup>H NMR of dimethyl 4'-fluoro-[1,1'-biphenyl]-2,3-dicarboxylate (**4j**)



<sup>13</sup>C NMR of dimethyl 4'-fluoro-[1,1'-biphenyl]-2,3-dicarboxylate (**4**j)



<sup>1</sup>H NMR of dimethyl 4'-vinyl-[1,1'-biphenyl]-2,3-dicarboxylate (4k)



<sup>13</sup>C NMR of dimethyl 4'-vinyl-[1,1'-biphenyl]-2,3-dicarboxylate (4k)



<sup>1</sup>H NMR of dimethyl 2'-methoxy -[1,1'-biphenyl]-2,3-dicarboxylate (4I)



<sup>13</sup>C NMR of dimethyl 2'-methoxy -[1,1'-biphenyl]-2,3-dicarboxylate (**4**I)



<sup>1</sup>H NMR of dimethyl 3'-methoxy -[1,1'-biphenyl]-2,3-dicarboxylate (**4m**)



<sup>13</sup>C NMR of dimethyl 3'-methoxy -[1,1'-biphenyl]-2,3-dicarboxylate (**4m**)



<sup>1</sup>H NMR of biphenyl-6-bromo-2,3-dicarboxylic acid dimethyl ester (**4n**)


$^{13}$ C NMR of biphenyl-6-bromo-2,3-dicarboxylic acid dimethyl ester (4n)



<sup>1</sup>H NMR of biphenyl-5-bromo-2,3-dicarboxylic acid dimethyl ester (**4o**)



<sup>13</sup>C NMR of biphenyl-5-bromo-2,3-dicarboxylic acid dimethyl ester (**4o**)



<sup>1</sup>H NMR of biphenyl-5-*tert*-butyldimethylsilyloxy-2,3-dicarboxylic acid dimethyl ester (**4p**)



<sup>13</sup>C NMR of biphenyl-5-*tert*-butyldimethylsilyloxy-2,3-dicarboxylic acid dimethyl ester (**4p**)



<sup>1</sup>H NMR of dimethyl 5-hydroxybiphenyl-2,3-dicarboxylate



<sup>13</sup>C NMR of dimethyl 5-hydroxybiphenyl-2,3-dicarboxylate



<sup>1</sup>H NMR of dimethyl 3-(2-furyl)phthalate (4q)



<sup>13</sup>C NMR of dimethyl 3-(2-furyl)phthalate (4q)



<sup>1</sup>H NMR of dimethyl 3-(2-thienyl)phthalate (**4r**)



<sup>13</sup>C NMR of dimethyl 3-(2-thienyl)phthalate (**4r**)



<sup>1</sup>H NMR of dimethyl [1,1':2',1''-terphenyl]-3',4'-dicarboxylate (**4s**)





<sup>1</sup>H NMR of dimethyl [1,1':3',1''-terphenyl]-4',5'-dicarboxylate (4t)

<sup>1</sup>H NMR of dimethyl [1,1':4',1''-terphenyl]-2',3'-dicarboxylate (4u)





 $^1\text{H}$  NMR of dimethyl [1,1':2',1''-terphenyl]-4',5'-dicarboxylate (4v)

<sup>1</sup>H NMR of 4,5-dimethylphthalic acid dimethyl ester (4w)



<sup>1</sup>H NMR of 3-benzylphthalic acid dimethyl ester (4x)



# <sup>1</sup>H NMR of biphenyl-2,3-dicarboxylic acid (**4**y)



## <sup>1</sup>H NMR of 3,4-dimethylbiphenyl (4z)



## <sup>1</sup>H NMR of 3,4-dimethyl-2-trimethylsilyl-biphenyl (4aa)



<sup>13</sup>C NMR of 3,4-dimethyl-2-trimethylsilyl-biphenyl (4aa)



<sup>1</sup>H NMR of 1,2,3-triphenylbenzene (**4ab**)



## <sup>1</sup>H NMR of 1-phenylnaphthalene (**4ac**)



### <sup>1</sup>H NMR of 3,4-dimethylbenzoic acid (4ad)



<sup>1</sup>H NMR of 3,4-dimethylbenzoic acid (4ae)



<sup>1</sup>H NMR of [2-(hydroxymethyl)-3-phenylphenyl]methanol (8a)



<sup>13</sup>C NMR of [2-(hydroxymethyl)-3-phenylphenyl]methanol (8a)



<sup>1</sup>H NMR of [2-(hydroxymethyl)-3-furylphenyl]methanol (8b)







<sup>1</sup>H NMR of 1,1':2',1"-terphenyl-3',4'-diyldimethanol (8c)



<sup>13</sup>C NMR of 1,1':2',1"-terphenyl-3',4'-diyldimethanol (8c)



<sup>1</sup>H NMR of 1,1':5',1"-terphenyl-2',3'-diyldimethanol (8d)



<sup>13</sup>C NMR of 1,1':5',1"-terphenyl-2',3'-diyldimethanol (8d)



<sup>1</sup>H NMR of 1,1':4',1"-terphenyl-2',3'-diyldimethanol (8e)







<sup>13</sup>C NMR of 1,1':2',1"-terphenyl-4',5'-diyldimethanol (8f)



<sup>1</sup>H NMR of 1,3-dihydro-4-phenylisobenzofuran (9a)



<sup>1</sup>H NMR of 1,3-dihydro-4-furylisobenzofuran (9b)



<sup>13</sup>C NMR of 1,3-dihydro-4-furylisobenzofuran (9b)



<sup>1</sup>H NMR of 1,3-dihydro-4,5-diphenylisobenzofuran (**9c**)



<sup>13</sup>C NMR of 1,3-dihydro-4,5-diphenylisobenzofuran (9c)



<sup>1</sup>H NMR of 1,3-dihydro-4,6-diphenylisobenzofuran (9d)



<sup>13</sup>C NMR of 1,3-dihydro-4,6-diphenylisobenzofuran (9d)



<sup>1</sup>H NMR of 1,3-dihydro-4,7-diphenylisobenzofuran (9e)



<sup>1</sup>H NMR of 1,3-dihydro-5,6-diphenylisobenzofuran (9f)



<sup>13</sup>C NMR of1,3-dihydro-5,6-diphenylisobenzofuran (9f)

