Drastic effect of bidentate phosphine ligands on Pd-catalyzed hydroarylation of ethyl propiolate: a simple route to arylbutadienes

Juzo Oyamada and Tsugio Kitamura*
Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, 1 Honjo-machi, Saga 840-8502, Japan

General
All the reactions were carried out in dry Pyrex tubes capped with rubber septa and stirred with magnetic stirring bars. Thin layer chromatography (TLC) analyses were carried out using TLC aluminum sheet (Silica gel 60 F254, Merck). Silica gel column chromatography was carried out using Silica Gel 60 (spherical, 63-210 m) from Kanto Chemical Co., Inc. 1H and 13C NMR spectra were recorded on a JEOL JNM-AL 300 FT-NMR using tetramethylsilane (TMS) as an internal standard. Melting points were measured with a YANACO micro melting apparatus and are not corrected. Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000. GC analyses were performed on a Shimadzu GC-14B equipped with a flame ionization detector using capillary column (DB-1, 15 m x 0.53 mm i.d. x 1.5 mm film thickness, J&W Scientific). GC yields were determined using n-heptadecane or n-pentadecane as an internal standard. Mass spectra were measured on a Shimadzu GC/MS 5020A. Elemental analyses were performed by the Service Center of the Elemental Analysis of Organic Compounds, Faculty of Science, Kyushu University.

Materials
All of arenes (1), ethyl propiolate (2) and solvent used in the reaction were commercially available and used as received without further purification. Pd(OAc)2 (Aldrich), AgOAc (Kanto Chemical Co., Inc.), bis(diphenylphosphino)methane (dppm) (Aldrich), 1,2-bis(diphenylphosphino)ethane (dppe) (Wako Pure Chemical Industries, Ltd.), 1,2-bis(diphenylphosphino)propane (dppp) (Wako Pure Chemical Industries, Ltd.) and triphenylphosphine (Wako Pure Chemical Industries, Ltd.) were purchased and used as received. Pd(dppe)(OAc)2, Pd(dppp)(OAc)2, Pd(PPh3)2(OAc)2 and Pd(dppe)2(OAc)2 were prepared from Pd(OAc)2 and the corresponding phosphine according to the literature. PdCl2(PhCN)2 was prepared from PdCl2 and benzonitrile according to the literature. Pd(dppm)Cl2 was prepared from PdCl2(PhCN)2 and dppe according to the reported method.

Optimization of reaction conditions of the Pd(dppe)(OAc)2-catalyzed reaction of mesitylene (1a) with ethyl propiolate (2)
After a mixture of Pd(dppe)(OAc)2 (0.005 mmol), mesitylene (1a), trifluoroacetic acid (TFA) and CH2Cl2 was stirred on an ice/water bath for 10 min, ethyl propiolate (2) was added to the cold mixture (the amounts of starting materials and solvents were described in Table 1). Again, the mixture was stirred on an ice/water bath for 5 min. Then, the mixture was stirred at 30 °C. After 5 h, n-heptadecane (ca. 0.15g) as an internal standard was added to the reaction mixture. Then, the mixture was poured into water (20 mL), neutralized by NaHCO3, and extracted with Et2O (20 mL + 10 mL x 2). The ethereal layer was analyzed by GC to determine the yields of the products and conversion of 1a.
Effect of a phosphine ligand of a Pd catalyst in the reaction of mesitylene (1a) with ethyl propiolate (2)

After a mixture of a Pd catalyst (0.005 mmol), mesitylene (1a) (2 mmol), TFA (0.25 mL) and CH₂Cl₂ (0.75 mL) was stirred on an ice/water bath for 10 min, ethyl propiolate (2) (2 mmol) was added to the cold mixture. Again, the mixture was stirred on an ice/water bath for 5 min. Then, the mixture was stirred at 30°C. After 5 h, n-heptadecane (ca. 0.15g) as an internal standard was added to the reaction mixture. After the mixture became homogeneous by addition of CH₂Cl₂ (ca. 0.5 mL), a portion of the mixture was poured into water (ca. 1 mL), neutralized by NaHCO₃, and extracted with Et₂O (1 mL). The ethereal layer was analyzed by GC to determine the yields of the products and conversion of 1a.

In the case of Pd(dppm)(OAc)₂, the catalyst was prepared in situ from Pd(dppm)Cl₂ and AgOAc. The procedure is as follows: a mixture of Pd(dppm)Cl₂ (0.005 mmol) and AgOAc (0.02 mmol) in TFA and CH₂Cl₂ was stirred at room temperature for 30 min (the amounts of solvents were described in Table 2). After mesitylene (2 mmol) was added to the mixture, the mixture was stirred on an ice/water bath for 10 min. After addition of ethyl propiolate (2 mmol), the mixture was stirred on an ice/water bath for 5 min. Then, the mixture was stirred at 30°C.

General procedure for Pd(dppe)(OAc)₂-catalyzed reaction of an arene with ethyl propiolate (2)

After a mixture of Pd(dppe)(OAc)₂ (0.005 mmol), an arene (2 mmol), TFA and CH₂Cl₂ was stirred on an ice/water bath for 10 min, ethyl propiolate (2) (2 mmol) was added to the cold mixture (the amounts of solvents were described in Table 3). Again, the mixture was stirred on an ice/water bath for 5 min. Then, the mixture was stirred at 30°C. After the reaction, the mixture was poured into water (20 mL), neutralized by NaHCO₃, and extracted with CH₂Cl₂ (20 mL + 10 mL x 3). The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using ethyl acetate/hexane as eluent, affording arylbutadiene 4 along with cinnamate 3.

General procedure for Pd(dppm)(OAc)₂-catalyzed reaction of an arene with ethyl propiolate (2)

A mixture of Pd(dppm)Cl₂ (0.005 mmol) and AgOAc (0.02 mmol) in TFA and CH₂Cl₂ was stirred at room temperature for 30 min (the amounts of solvents were described in Table 3). After an arene (2 mmol) was added to the mixture, the mixture was stirred on an ice/water bath for 10 min. After addition of ethyl propiolate (2 mmol), the mixture was stirred on an ice/water bath for 5 min. Then, the mixture was stirred at 30°C. After the reaction, the mixture was poured into water (20 mL), neutralized by NaHCO₃, and extracted with CH₂Cl₂ (20 mL + 10 mL x 3). The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using ethyl acetate/hexane as eluent, affording arylbutadiene 4 along with cinnamate 3.

All products were characterized by ¹H and ¹³C NMR. In addition, new compounds were characterized by elemental analyses, IR and Mass spectra. The stereochemistry of arylbutadiene 4 was determined by coupling constant in ¹H NMR spectra and differential NOE experiments showing 20-24% enhancement in intensity (see, an example at page S32).
Ethyl (2Z)-3-(2,4,6-trimethylphenyl)prop-2-enoate (3a)\(^7\)

![Chemical Structure](image)

Colorless liquid. \(^1\)H NMR (300MHz, CDCl\(_3\)): \(\delta\) 1.10 (t, \(J = 7.1\) Hz, 3H, CH\(_3\)), 2.16 (s, 6H, CH\(_3\)), 2.27 (s, 3H, CH\(_3\)), 4.03 (q, \(J = 7.1\) Hz, 2H, CH\(_2\)), 6.11 (d, \(J = 12.0\) Hz, 1H, vinyl), 6.84 (s, 2H, aryl), 7.02 (d, \(J = 12.0\) Hz, 1H, vinyl). \(^{13}\)C NMR (75MHz, CDCl\(_3\)): \(\delta\) 13.94, 20.11, 21.01, 59.92, 122.77, 127.78, 132.77, 134.44, 136.65, 144.13, 165.47.

Ethyl (2Z)-3-(pentamethylphenyl)prop-2-enoate (3b)\(^7\)

![Chemical Structure](image)

Colorless crystals. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 1.10 (t, \(J = 7.1\) Hz, 3H, CH\(_3\)), 2.14 (s, 6H, CH\(_3\)), 2.20 (s, 6H, CH\(_3\)), 2.22 (s, 3H, CH\(_3\)), 4.02 (q, \(J = 7.1\) Hz, 2H, CH\(_2\)), 6.13 (d, \(J = 11.9\) Hz, 1H, vinyl), 7.13 (d, \(J = 11.9\) Hz, 1H, vinyl). \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta\) 13.95, 16.35, 16.74, 17.59, 59.76, 122.09, 129.73, 131.87, 133.20, 133.93, 146.48, 165.39.

Ethyl (2Z)-3-(2,3,5,6-tetramethylphenyl)prop-2-enoate (3c)\(^7\)

![Chemical Structure](image)

Colorless liquid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 1.07 (t, \(J = 7.1\) Hz, 3H, CH\(_3\)), 2.08 (s, 6H, CH\(_3\)), 2.21 (s, 6H, CH\(_3\)), 4.00 (q, \(J = 7.1\) Hz, 2H, CH\(_2\)), 6.14 (d, \(J = 11.9\) Hz, 1H, vinyl), 6.90 (s, 1H, aryl), 7.09 (d, \(J = 11.9\) Hz, 1H, vinyl). \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta\) 13.86, 16.47, 19.93, 59.80, 122.44, 130.21, 130.51, 133.02, 135.69, 145.59, 165.43.

Ethyl (2Z)-3-(3-hydroxy-2,4,6-trimethylphenyl)prop-2-enoate (3d)\(^7\)

![Chemical Structure](image)

Colorless liquid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 1.12 (t, \(J = 7.1\) Hz, 3H, CH\(_3\)), 2.09 (s, 6H, CH\(_3\)), 2.17 (s, 3H, CH\(_3\)), 4.04 (q, \(J = 7.1\) Hz, 2H, CH\(_2\)), 4.65 (brs, 1H, OH), 6.13 (d, \(J = 11.9\) Hz, 1H, vinyl), 6.79 (s, 1H, aryl), 7.00 (d, \(J = 11.9\) Hz, 1H, vinyl). \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta\) 12.95, 13.93, 15.84, 19.51, 59.99, 120.23, 121.93, 122.72, 126.03, 129.09, 134.20, 144.07, 149.77, 165.42.

S3
Ethyl (2Z)-3-(3-bromo-2,4,6-trimethylphenyl)prop-2-enoate (3e)

Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$): δ 1.09 (t, $J = 7.1$ Hz, 3H, CH$_3$), 2.11 (s, 3H, CH$_3$), 2.30 (s, 3H, CH$_3$), 2.40 (s, 3H, CH$_3$), 4.02 (q, $J = 7.1$ Hz, 2H, CH$_2$), 6.13 (d, $J = 11.9$ Hz, 1H, vinyl), 6.93 (s, 1H, aryl), 7.02 (d, $J = 11.9$ Hz, 1H, vinyl). $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 13.88, 19.91, 21.24, 23.91, 60.07, 123.24, 125.02, 129.27, 133.18, 134.34, 134.58, 136.92, 143.59, 165.17.

Ethyl (2Z)-3-(2-methoxynaphthalen-1-yl)prop-2-enoate (3f)

Light yellow liquid. $^1$H NMR (300 MHz, CDCl$_3$): δ 0.86 (t, $J = 7.1$ Hz, 3H, CH$_3$), 3.90 (q, $J = 7.1$ Hz, 2H, CH$_2$), 3.91 (s, 3H, OCH$_3$), 6.32 (d, $J = 11.9$ Hz, 1H, vinyl), 7.26 (d, $J = 9.0$ Hz, 1H, naphthyl), 7.26 (d, $J = 11.9$ Hz, 1H, vinyl), 7.32 (dd, $J = 6.9, 8.1$ Hz, 1H, naphthyl), 7.42 (dd, $J = 6.9, 8.4$ Hz, 1H, naphthyl), 7.77 (d, $J = 8.1$ Hz, 1H, naphthyl), 7.77 (d, $J = 8.4$ Hz, 1H, naphthyl), 7.81 (d, $J = 9.0$ Hz, 1H, naphthyl). $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 13.62, 56.27, 59.84, 112.77, 119.19, 123.51, 123.94, 124.28, 126.53, 128.16, 128.63, 129.68, 131.91, 137.44, 153.52, 165.94. MS (EI, m/z): 256 (M$^+$, 40), 225 (15), 211 (15), 197 (33), 183 (100), 168 (38), 153 (29), 139 (44). IR (neat, cm$^{-1}$): 3058 (w), 2980 (m), 2840 (w), 1725 ($\nu$(C=O), s), 1623 (m), 1592 (m), 1510 (m), 1466 (m), 1268 (s), 1184 (s), 1086 (m), 1025 (m), 808 (m), 749 (m). Anal. Calcd for C$_{16}$H$_{16}$O$_3$: C, 74.98; H, 6.29. Found: C, 75.00; H, 6.30.

Ethyl (2Z)-3-(naphthalen-1-yl)prop-2-enoate (3g)

Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$): δ 1.00 (t, $J = 7.1$ Hz, 3H, CH$_3$), 4.00 (q, $J = 7.1$ Hz, 2H, CH$_2$), 6.23 (d, $J = 12.1$ Hz, 1H, vinyl), 7.41-7.50 (m, 4H, naphthyl), 7.54 (d, $J = 12.1$ Hz, 1H, vinyl), 7.80-7.90 (m, 3H, naphthyl). $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 13.77, 60.09, 122.77, 124.36, 124.95, 125.79, 126.19, 126.48, 128.49, 128.66, 131.04, 133.00, 133.22, 141.80, 165.88.

Ethyl (2Z)-3-(2,5-dimethylphenyl)prop-2-enoate (3i)

Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$): δ 1.15 (t, $J = 7.1$ Hz, 3H, CH$_3$), 2.23 (s, 3H, CH$_3$), 2.30 (s, 3H, CH$_3$), 4.09 (q, $J = 7.1$ Hz, 2H, CH$_2$), 6.00 (d, $J = 12.1$ Hz, 1H, vinyl), 7.00-7.07 (m, 2H, aryl), 7.08 (d, $J = 12.1$ Hz, 1H, vinyl), 7.12 (s, 1H, aryl). $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 13.92, 19.29, 20.85, 60.02, 120.99, 129.06, 129.24, 129.52, 132.59, 134.44, 134.86, 142.81, 166.07.
Diethyl (2Z,2′Z)-3,3’-(2,4,6-trimethylbenzene-1,3-diyl)bisprop-2-enoate (5a)

\[
\text{EtO}_2\text{C} \begin{array}{c}
\text{CO}_2\text{Et} \\
\text{CO}_2\text{Et}
\end{array} \]

Colorless liquid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 1.12 (t, \(J = 7.1\) Hz, 6H, CH\(_3\)), 2.05 (s, 3H, CH\(_3\)), 2.15 (s, 6H, CH\(_3\)), 4.03 (q, \(J = 7.1\) Hz, 4H, CH\(_2\)), 6.12 (d, \(J = 11.9\) Hz, 2H, vinyl), 6.88 (s, 1H, aryl), 7.03 (d, \(J = 11.9\) Hz, 2H, vinyl). \(^13\)C NMR (75MHz, CDCl\(_3\)): \(\delta\) 13.98, 17.66, 20.17, 59.90, 122.68, 128.36, 130.97, 132.98, 133.46, 144.40, 165.38.

Diethyl (2E,4Z)-4-(2,4,6-trimethylbenzylidene)pent-2-enedioate (4a)

\[
\begin{array}{c}
\text{CO}_2\text{Et} \\
\text{CO}_2\text{Et}
\end{array} \]

Colorless liquid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 0.90 (t, \(J = 7.1\) Hz, 3H, CH\(_3\)), 1.32 (t, \(J = 7.1\) Hz, 3H, CH\(_3\)), 2.15 (s, 6H, CH\(_3\)), 2.26 (s, 3H, CH\(_3\)), 2.26 (s, 3H, CH\(_3\)), 3.99 (q, \(J = 7.1\) Hz, 2H, CH\(_2\)), 4.25 (q, \(J = 7.1\) Hz, 2H, CH\(_2\)), 6.22 (d, \(J = 15.9\) Hz, 1H, vinyl), 6.83 (s, 2H, aryl), 7.15 (s, 1H, vinyl), 7.46 (d, \(J = 15.9\) Hz, 1H, vinyl). \(^13\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta\) 13.44, 14.24, 20.08, 20.94, 60.49, 60.70, 120.72, 127.81, 132.05, 134.40, 135.15, 137.29, 141.36, 143.06, 166.03, 166.80. MS (EI, m/z (relative intensity)): 316 (M\(^+\), 8), 271 (27), 243 (59), 225 (40), 213 (28), 197 (77), 183 (36), 159 (100), 157 (76), 141 (34), 128 (46), 115 (29). IR (neat, cm\(^{-1}\)): 2981 (m), 1720 (\(\nu\) (C=O), s), 1623 (m), 1454 (m), 1407 (m), 1384 (m), 1362 (m), 1309 (s), 1233 (s), 1164 (s), 1023 (m), 989 (m), 861 (m).

Diethyl (2E,4Z)-4-(pentamethylbenzylidene)pent-2-enedioate (4b)

\[
\begin{array}{c}
\text{CO}_2\text{Et} \\
\text{CO}_2\text{Et}
\end{array} \]

Colorless crystals. Mp. 79-81°C (MeOH). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 0.87 (t, \(J = 7.1\) Hz, 3H, CH\(_3\)), 1.32 (t, \(J = 7.1\) Hz, 3H, CH\(_3\)), 1.32 (t, \(J = 7.1\) Hz, 3H, CH\(_3\)), 2.12 (s, 6H, CH\(_3\)), 2.18 (s, 6H, CH\(_3\)), 2.22 (s, 3H, CH\(_3\)), 2.22 (s, 3H, CH\(_3\)), 3.97 (q, \(J = 7.1\) Hz, 2H, CH\(_2\)), 4.25 (q, \(J = 7.1\) Hz, 2H, CH\(_2\)), 6.20 (d, \(J = 15.8\) Hz, 1H, vinyl), 7.26 (s, 1H, vinyl), 7.49 (d, \(J = 15.8\) Hz, 1H, vinyl). \(^13\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta\) 13.40, 14.26, 16.19, 16.66, 17.78, 60.47, 60.52, 120.41, 130.36, 132.04, 132.44, 133.98, 134.44, 141.47, 145.25, 166.01, 166.83. MS (EI, m/z (relative intensity)): 344 (M\(^+\), 22), 299 (25), 271 (100), 256 (52), 225 (45), 198 (72), 185 (57), 141 (22), 128 (17), 115 (14). IR (KBr, cm\(^{-1}\)): 2989 (m), 2907 (m), 1713 (\(\nu\)(C=O), s), 1623 (m), 1454 (m), 1407 (m), 1384 (m), 1362 (m), 1309 (s), 1233 (s), 1164 (s), 1023 (m), 989 (m), 861 (m).

Diethyl (2E,4Z)-4-(2,3,5,6-tetramethylbenzylidene)pent-2-enedioate (4c)

\[
\begin{array}{c}
\text{CO}_2\text{Et} \\
\text{CO}_2\text{Et}
\end{array} \]

Colorless liquid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 0.84 (t, \(J = 7.1\) Hz, 3H, CH\(_3\)), 1.32 (t, \(J = 7.1\) Hz,
3H, CH3), 2.06 (s, 6H, CH3), 2.20 (s, 6H, CH3), 3.95 (q, J = 7.1 Hz, 2H, CH2), 4.25 (q, J = 7.1 Hz, 2H, CH2), 6.22 (d, J = 15.9 Hz, 1H, vinyl), 6.90 (s, 1H, aryl), 7.22 (s, 1H, vinyl), 7.49 (d, J = 15.9 Hz, 1H, vinyl). 13C NMR (75.5 MHz, CDCl3): δ 13.34, 14.26, 16.63, 19.78, 60.51, 60.54, 120.62, 130.86, 130.92, 134.18, 134.93, 140.34, 144.42, 165.99, 166.83. MS (EI, m/z (relative intensity)): 330 (M+, 30), 285 (36), 257 (100), 242 (53), 211 (75), 197 (46), 185 (89), 183 (89), 171 (87), 153 (43), 141 (41), 128 (36), 115 (29). IR (neat, cm⁻¹): 2981 (m), 2938 (m), 1719 (ν(C=O), s), 1628 (m), 1467 (m), 1378 (m), 1313 (m), 1284 (m), 1224 (m), 1180 (s), 1033 (m), 981 (m), 866 (m).


Diethyl (2E,4Z)-4-(3-hydroxy-2,4,6-trimethylbenzylidene)pent-2-enedioate (4d)

Yellow viscous liquid. ¹H NMR (300 MHz, CDCl3): δ 0.92 (t, J = 7.1 Hz, 3H, CH3), 1.32 (t, J = 7.1 Hz, 3H, CH3), 2.11 (s, 3H, CH3), 2.29 (s, 3H, CH3), 2.37 (s, 3H, CH3), 3.99 (q, J = 7.1 Hz, 2H, CH2), 4.24 (q, J = 7.1 Hz, 2H, CH2), 6.25 (d, J = 15.9 Hz, 1H, vinyl), 6.92 (s, 1H, aryl), 7.13 (s, 1H, vinyl), 7.46 (d, J = 15.9 Hz, 1H, vinyl). 13C NMR (75.5 MHz, CDCl3): δ 13.46, 129.33, 133.84, 135.06, 137.58, 140.89, 142.10, 165.64, 166.67. MS (EI, m/z (relative intensity)): 332 (M⁺, 75), 287 (43), 271 (57), 259 (57), 244 (59), 229 (35), 213 (93), 199 (56), 185 (100), 173 (68), 157 (36), 141 (40), 128 (47), 115 (46). IR (neat, cm⁻¹): 3494 (O-H, s), 2982 (m), 1720 (ν(C=O), s), 1625 (m), 1476 (m), 1377 (m), 1312 (s), 1181 (s), 1101 (m), 1030 (m), 981 (m), 865 (m). Anal. Calcd for C19H24O5: C, 68.66; H, 7.28. Found: C, 68.39; H, 7.29.

Diethyl (2E,4Z)-4-(3-bromo-2,4,6-trimethylbenzylidene)pent-2-enedioate (4e)

Colorless liquid. ¹H NMR (300 MHz, CDCl3): δ 0.90 (t, J = 7.1 Hz, 3H, CH3), 1.32 (t, J = 7.1 Hz, 3H, CH3), 1.69 (s, 1H, OH), 2.11 (s, 3H, CH3), 2.29 (s, 3H, CH3), 2.37 (s, 3H, CH3), 3.99 (q, J = 7.1 Hz, 2H, CH2), 4.24 (q, J = 7.1 Hz, 2H, CH2), 6.25 (d, J = 15.9 Hz, 1H, vinyl), 6.92 (s, 1H, aryl), 7.13 (s, 1H, vinyl), 7.46 (d, J = 15.9 Hz, 1H, vinyl). 13C NMR (75.5 MHz, CDCl3): δ 13.46, 129.33, 133.84, 135.06, 137.58, 140.89, 142.10, 165.64, 166.67. MS (EI, m/z): 396 (M⁺, 90), 394 (M⁺, 9), 351 (15), 349 (15), 242 (82), 224 (37), 213 (33), 196 (100), 156 (47), 153 (55), 141 (38), 128 (32) 115 (31). IR (neat, cm⁻¹): 2981 (m), 1720 (ν(C=O), s), 1629 (m), 1451 (m), 1378 (m), 1312 (m), 1223 (m), 1181 (s), 1033 (m), 980 (m), 866 (m). Anal. Calcd for C19H23BrO5: C, 57.73; H, 5.86. Found: C, 57.72; H, 5.86.

Diethyl (2E,4Z)-4-[(2-methoxynaphthalen-1-yl)methylidene]pent-2-enedioate (4f)
Light yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): δ 0.75 (t, $J = 7.1$ Hz, 3H, CH$_3$), 1.33 (t, $J = 7.1$ Hz, 3H, CH$_3$), 3.90 (s, 3H, OCH$_3$), 3.91 (q, $J = 7.1$ Hz, 2H, CH$_2$), 4.26 (d, $J = 7.1$ Hz, 2H, CH$_2$), 6.39 (d, $J = 15.8$ Hz, 1H, vinyl), 7.24 (d, $J = 9.2$ Hz, 1H, aryl), 7.35 (dd, $J = 6.9, 8.1$ Hz, 1H, aryl), 7.47 (dd, $J = 6.9, 8.4$ Hz, 1H, aryl), 7.50 (s, 1H, vinyl), 7.59 (d, $J = 15.8$ Hz, 1H, vinyl), 7.78 (d, $J = 8.1$ Hz, 1H, aryl), 7.79 (d, $J = 8.4$ Hz, 1H, aryl), 7.84 (d, $J = 9.2$ Hz, 1H, aryl). $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 13.28, 14.23, 56.00, 60.35, 60.41, 112.50, 118.20, 120.29, 123.59, 123.80, 127.04, 128.28, 128.59, 130.73, 132.09, 133.86, 137.64, 142.51, 154.22, 166.18, 166.98. MS (EI, m/z (relative intensity)): 354 (M$^+$, 32), 280 (100), 235 (67), 208 (51), 165 (37), 139 (26). IR (KBr, cm$^{-1}$): 2981 (m), 2936 (m), 2839 (m), 1713 ($\nu$(C=O), s), 1619 (m), 1589 (m), 1510 (m), 1468 (m), 1407 (m), 1367 (m), 1256 (s), 1176 (s), 1048 (m), 1022 (m), 978 (m), 1048 (m), 1022 (m), 978 (m), 1048 (m), 1022 (m), 978 (m), 1048 (m), 1022 (m), 978 (m). Anal. Calcd for C$_{21}$H$_{22}$O$_5$: C, 71.17; H, 6.26. Found: C, 71.13; H, 6.26.

Diethyl (2$^E$,4$^Z$)-4-(naphthalen-1-ylmethylidene)pent-2-enedioate (4g)

Yellow viscous liquid. $^1$H NMR (300 MHz, CDCl$_3$): δ 0.91 (t, $J = 7.1$ Hz, 3H, CH$_3$), 1.33 (t, $J = 7.1$ Hz, 3H, CH$_3$), 4.05 (q, $J = 7.1$ Hz, 2H, CH$_2$), 4.26 (q, $J = 7.1$ Hz, 2H, CH$_2$), 6.18 (d, $J = 15.8$ Hz, 1H, vinyl), 7.38-7.58 (m, 5H, napht hyl and vinyl), 7.65 (s, 1H, vinyl), 7.82-7.96 (m, 3H, naphthyl). $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 13.56, 14.27, 60.59, 61.14, 120.96, 124.09, 125.07, 126.23, 126.69, 128.58, 129.57, 131.20, 132.45, 133.22, 134.25, 138.97, 141.90, 166.67, 167.02. MS (EI, m/z (relative intensity)): 324 (M$^+$, 13), 251 (38), 250 (28), 223 (18), 205 (55), 179 (100), 165 (24), 152 (16). IR (neat, cm$^{-1}$): 3059 (m), 2982 (m), 1714 ($\nu$(C=O), s), 1622 (m), 1463 (m), 1380 (m), 1313 (m), 1229 (m), 1179 (s), 1048 (m), 1022 (m), 978 (m), 859 (m), 813 (m). Anal. Calcd for C$_{20}$H$_{20}$O$_4$: C, 74.06; H, 6.21. Found: C, 73.96; H, 6.20.

Diethyl (2$^E$,4$^Z$)-4-(2,5-dimethylbenzylidene)pent-2-enedioate (4h)

Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$): δ 1.11 (t, $J = 7.1$ Hz, 3H, CH$_3$), 1.32 (t, $J = 7.1$ Hz, 3H, CH$_3$), 2.26 (s, 3H, CH$_3$), 2.29 (s, 3H, CH$_3$), 4.17 (q, $J = 7.1$ Hz, 2H, CH$_2$), 4.24 (q, $J = 7.1$ Hz, 2H, CH$_2$), 6.08 (d, $J = 15.9$ Hz, 1H, vinyl), 7.02-7.09 (m, 3H, aryl), 7.14 (s, 1H, vinyl), 7.42 (d, $J = 15.9$ Hz, 1H, vinyl). $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 13.70, 14.29, 19.34, 20.79, 60.52, 61.17, 120.23, 128.28, 129.94, 130.08, 132.51, 133.74, 133.93, 135.09, 139.09, 142.32, 166.73, 167.29. MS (EI, m/z (relative intensity)): 302 (M$^+$, 9), 257 (31), 229 (87), 211 (39), 201 (44), 183 (97), 157 (100), 141 (51), 128 (55), 115 (47). IR (neat, cm$^{-1}$): 2981 (m), 1719 ($\nu$(C=O), s), 1622 (m), 1463 (m), 1380 (m), 1313 (m), 1229 (m), 1179 (s), 1036 (m), 978 (m), 861 (m), 813 (m). Anal. Calcd for
Diethyl (2E,4Z)-4-[3-{(Z)-2-(ethoxycarbonyl)ethenyl}-2,4,6-trimethylbenzylidene]pent-2-enedioate (4i)

Colorless viscous liquid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.96 (t, $J = 7.1$ Hz, 3H, CH$_3$), 1.14 (t, $J = 7.1$ Hz, 3H, CH$_3$), 1.32 (t, $J = 7.1$ Hz, 3H, CH$_3$), 2.04 (s, 3H, CH$_3$), 2.15 (s, 6H, CH$_3$), 4.01 (q, $J = 7.1$ Hz, 2H, CH$_2$), 4.03 (q, $J = 7.1$ Hz, 2H, CH$_2$), 4.24 (q, $J = 7.1$ Hz, 2H, CH$_2$), 6.13 (d, $J = 11.9$ Hz, 1H, vinyl), 6.22 (d, $J = 15.9$ Hz, 1H, vinyl), 6.87 (s, 1H, aryl), 6.99 (d, $J = 11.9$ Hz, 1H, vinyl), 7.15 (s, 1H, vinyl), 7.46 (d, $J = 15.9$ Hz, 1H, vinyl).

Tetraethyl (2E,4Z,2'E,4'Z)-4,4'-[2,4,6-trimethylbenzene-1,3-diylid(Z)methylidyene]bispent-2-enedioate (4j)

Light yellow viscous liquid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.99 (t, $J = 7.1$ Hz, 6H, CH$_3$), 1.32 (t, $J = 7.1$ Hz, 6H, CH$_3$), 2.04 (s, 3H, CH$_3$), 2.15 (s, 6H, CH$_3$), 4.03 (q, $J = 7.1$ Hz, 4H, CH$_2$), 4.25 (q, $J = 7.1$ Hz, 4H, CH$_2$), 6.21 (d, $J = 15.9$ Hz, 2H, vinyl), 6.86 (s, 1H, aryl), 7.11 (s, 2H, vinyl), 7.46 (d, $J = 15.9$ Hz, 2H, vinyl).

References


