Supporting Information

for

Efficient Synthesis of Biindenylidene Derivatives via a Domino-Heck Type Double Cyclization of Diaryldienynes

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General: All reactions were carried out in well-dried glassware under an N₂ or Ar atmosphere. Dichloromethane, benzene, diethylamine, and acetonitrile were distilled from CaH₂ under an N₂ atmosphere. Anhydrous DMF was used as it was received from Wako chemicals, Japan. ¹H NMR (400 or 300 or 270 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a JEOL JNM-AL-400, or a Varian Mercury 300, or a JEOL JNM-EX-270 spectrometer in CDCl₃. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane or CHCl₃ (δ = 77.0) for ¹³C NMR spectra. IR spectra were recorded as a neat film on a JASCO FTIR-410 spectrometer. Preparative HPLC separation was accomplished by a JAILC-908 chromatograph using 600 mm X 20 mm JAIGEL-1H and 2H GPC columns with CHCl₃ as an eluent.

General procedure for the synthesis of diaryldienynes (1b-f): The aldehydes (**5b-e**) were converted to the corresponding 1,1-dibromoalkene by the published method.¹ The dibromoalkenes were then transformed to the corresponding (Z)-bromostyrenes (**6b-e**) by a method similar to that reported by Uenishi.² The Sonogashira coupling of **6** with **7** was performed as follows: To a stirred mixture of (Z)-bromostyrene (**6**) (1 equiv), PdCl₂(PPh₃)₂ (0.01 equiv) and CuI (0.02 equiv) in Et₂NH was added slowly (dropwise addition) a solution of the enyne **7** (1.1 equiv) under a nitrogen atmosphere. The mixture was stirred at room temperature for 1 to 5 h, depending on the substrate. The progress of the reactions was monitored by TLC and GC (occasionally). After completion of the reaction, the mixture was diluted with water and ether. The resulting mixture was extracted with ether, washed with 1N HCl and brine, dried (MgSO₄) and filtered. Evaporation of the filtrate provided a residue which was purified by a flash chromatography (hexane 100%) to give (Z,Z)-diaryldienynes **1b-e** and their corresponding (E,Z) isomers in a very good yield (79 to 90%). In most cases, minor amount of the dimer of enyne **7** was formed as a side product. Compound **1f** was synthesized in a similar manner. Pure (Z,Z) isomers of **1b-f** were obtained by subjection of the

isomeric mixtures to a recyclable preparative HPLC.

(Z,Z)-1-(2-Bromophenyl)-6-(p-tolyl)-1,5-hexadien-3-yne (1b). Pale yellow solid. Mp: 41-42 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.31 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.59 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.24-7.20 (m, 1H), 7.13 (td, *J* = 7.8, 1.6 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 12.0 Hz, 1H), 6.62 (d, *J* = 12.0 Hz, 1H), 6.05 (dd, *J* = 12.0, 3.2 Hz, 1H), 5.80 (dd, *J* = 12.0, 3.2 Hz, 1H), 2.34 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 138.90, 138.60, 136.93, 135.82, 133.53, 132.65, 129.52, 129.50, 128.96 (2C), 128.42 (2C), 127.10, 124.07, 109.92, 106.13, 94.76, 93.39, 21.48; IR (KBr) 2924, 2847, 1550, 1508, 1465, 1436, 1023, 823, 767 cm⁻¹; MS (EI) *m/z*: 322, 324 (both for M⁺, 33), 228 (M⁺-Br-CH₃, 100), 129 (50). HRMS (EI) calcd for C₁₉H₁₅Br: 322.0357, 324.0339. Found: 322.0343, 324.0349.

(Z,Z)-1-(2-Bromophenyl)-6-(p-anisyl)-1,5-hexadien-3-yne (1c). Yellowish oil. ¹H NMR (CDCl₃, 400 MHz) δ 8.32 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.79-7.75 (m, 2H), 7.60 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.23 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.13 (td, *J* = 8.0, 1.6 Hz, 1H), 6.96 (d, *J* = 11.6 Hz, 1H), 6.81-6.77 (m, 2H), 6.58 (d, *J* = 12.0 Hz, 1H), 6.06 (dd, *J* = 11.6, 2.8 Hz, 1H), 5.74 (dd, *J* = 12.0, 2.8 Hz, 1H), 3.81 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 159.68, 138.43, 136.79, 135.93, 132.68, 129.99 (2C), 129.55, 129.51, 129.28, 127.13, 124.06, 113.66 (2C), 110.01, 104.67, 94.96, 93.14, 55.27; IR (neat) 2929, 2835, 2165, 1604, 1509, 1436, 1257, 1174, 1025, 837, 767 cm⁻¹; MS (EI) *m/z*: 338, 340 (both for M⁺, 85), 259 (M⁺-Br, 28), 215 (100). HRMS (EI) calcd for C₁₉H₁₅BrO: 338.0306, 340.0288. Found: 338.0308, 340.0304.

(Z,Z)-1-(2-Bromophenyl)-6-(4-cyanophenyl)-1,5-hexadien-3-yne (1d). Colorless needles. Mp: 87-88 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.15 (dd, *J* = 6.6, 2.7 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.63 (dd, *J* = 6.6, 2.2 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.21-7.15 (m, 2H), 7.03 (d, *J* = 11.7 Hz, 1H), 6.63 (d, *J* = 11.7 Hz, 1H), 6.06-6.00 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 140.24, 138.76, 136.48, 135.80, 132.86, , 132.01 (2C), 129.93, 129.62, 128.72 (2C), 127.02, 124.12, 118.73, 111.48, 111.02, 109.45, 95.62, 92.97; IR (KBr) 3083, 3059, 2961, 2224, 1603, 1503, 1466, 1436, 1188, 1025, 846, 770, 740 cm⁻¹; MS (EI) *m/z*: 333, 335 (both for M⁺, 15), 254 (M⁺-Br, 100). HRMS (EI) calcd for C₁₉H₁₂BrN: 333.0153, 335.0135. Found: 333.0150, 335.0126. Anal. Calcd for C₁₉H₁₂BrN: C, 68.28; H, 3.62; N, 4.19. Found: C, 68.19; H, 3.34; N, 4.10.

(Z,Z)-1-(2-Bromophenyl)-6-[4-(trifluoromethyl)phenyl]-1,5-hexadien-3-yne (1e). Colorless oil. ¹H NMR (CDCl₃, 400 MHz) δ 8.19 (dd, *J* = 7.5, 2.1 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.61 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.19-7.10 (m, 2H), 7.01 (d, *J* = 11.7 Hz, 1H), 6.66 (d, *J* = 12.0 Hz, 1H), 6.04 (dd, *J* = 11.7, 3.2 Hz, 1H), 5.98 (dd, *J* = 12.0, 3.2 Hz, 1H); ¹³C NMR (CDCl₃, 100

(MHz) δ 139.38, 138.26, 137.07, 135.79, 132.79, 129.91 (q, J = 32.2 Hz), 129.84, 129.59, 128.53 (2C), 127.07, 125.19 (q, J = 3.7 Hz, 2C), 124.08, 123.94 (q, J = 269.7 Hz), 109.87, 109.55, 94.62, 93.36; IR (neat) 3065, 3026, 1615, 1468, 1435, 1325, 1167, 1125, 1065, 1024, 848, 768 cm^{-1} ; MS (EI) m/z : 376, 378 (both for M^+ , 30), 297 (M^+ -Br, 52), 228 (M^+ -Br- CF_3 , 100). HRMS (EI) calcd for $\text{C}_{19}\text{H}_{12}\text{BrF}_3$: 376.0074. Found: 376.0048.

(Z,Z)-1-(2-Bromophenyl)-6-(1-naphthyl)-1,5-hexadien-3-yne (1f). Colorless solid. Mp: 55-57 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 8.15 (d, J = 7.2 Hz, 1H), 8.11 (dd, J = 7.8, 1.4 Hz, 1H), 8.04-8.01 (m, 1H), 7.87-7.84 (m, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.54-7.48 (m, 3H), 7.40 (d, J = 11.6 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.04 (td, J = 7.6, 1.6 Hz, 1H), 6.94-6.92 (m, 1H), 6.91 (d, J = 12.0 Hz, 1H), 6.10 (dd, J = 11.6, 2.8 Hz, 1H), 5.94 (dd, J = 12.0, 2.8 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 137.01, 136.79, 135.57, 133.47, 132.86, 132.57, 131.22, 129.49, 129.29, 128.85, 128.53, 126.97, 126.38, 126.20, 125.79, 125.29, 124.04, 123.58, 109.78, 109.65, 94.27, 92.30; IR (KBr) 3057, 1606, 1586, 1557, 1506, 1464, 1433, 1340, 1021, 946, 798, 776, 751 cm^{-1} ; MS (EI) m/z : 358, 360 (both for M^+ , 65), 278 (100). HRMS (EI) calcd for $\text{C}_{22}\text{H}_{15}\text{Br}$: 358.0357, 360.0339. Found: 358.0376, 360.0323.

(1Z, 5E)-1-(2-Bromophenyl)-6-(p-anisyl)-1,5-hexadien-3-yne (9). Colorless oil, which solidified on standing in a refrigerator. Mp: 77-79 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 8.34 (dd, J = 7.8, 1.4 Hz, 1H), 7.59 (dd, J = 7.8, 0.8 Hz, 1H), 7.36 (d, J = 5.9 Hz, 1H), 7.34 (d, J = 8.8 Hz, 2H), 7.15 (td, J = 7.8, 1.7 Hz, 1H), 6.95 (d, J = 12.0 Hz, 1H), 6.89 (d, J = 16.1 Hz, 1H), 6.86 (d, J = 8.8 Hz, 2H), 6.19 (dd, J = 16.1, 2.7 Hz, 1H), 5.99 (dd, J = 12.0, 2.7 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 160.16, 141.41, 136.38, 135.91, 132.70, 129.48, 129.42, 128.99 (2C), 127.69, 126.89, 124.26, 114.16 (2C), 109.93, 105.61, 94.14, 89.01, 55.36; IR (neat) 2963, 2927, 2833, 2173, 1600, 1508, 1435, 1246, 1173, 1023, 950, 847, 768, 757 cm^{-1} ; MS (EI) m/z : 338, 340 (both for M^+ , 80), 259 (M^+ -Br, 22), 215 (100). HRMS (EI) calcd for $\text{C}_{19}\text{H}_{15}\text{BrO}$: 338.0306, 340.0288. Found: 338.0307, 340.0311.

(1E, 5Z)-1-(2-Bromophenyl)-6-(1-naphthyl)-1,5-hexadien-3-yne (10). Colorless solid. Mp: 54-55 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 8.28 (d, J = 7.2 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.89-7.86 (m, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.57-7.49 (m, 5H), 7.46 (d, J = 11.6 Hz, 1H), 7.28-7.24 (m, 1H), 7.25 (d, J = 15.8 Hz, 1H), 7.12 (td, J = 8.0, 1.6 Hz, 1H), 6.26 (dd, J = 15.8, 2.8 Hz, 1H), 6.13 (dd, J = 11.6, 2.8 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 139.80, 136.45, 135.95, 133.53, 133.15, 132.78, 131.37, 129.63, 128.85, 128.58, 127.45, 126.45, 126.17 (2C), 125.72, 125.19, 123.73, 123.52, 110.96, 109.64, 94.13, 91.19; IR (KBr) 3046, 1507, 1465, 1436, 1340, 1023, 950, 800, 778, 746 cm^{-1} ; MS (EI) m/z : 358, 360 (both for M^+ , 45), 276 (100). HRMS (EI) calcd for $\text{C}_{22}\text{H}_{15}\text{Br}$: 358.0357, 360.0339. Found: 358.0368, 360.0310.

General procedure for the domino-Heck double cyclization reaction: A flame-dried flask was loaded with palladium acetate (20 mol%), triphenylphosphine (40 mol%), anhydrous potassium carbonate (3 equiv), and tetrabutylammonium bromide (1 equiv). A dilute solution (0.01M) of diaryldieneyne **1a-f** was then added to the flask, the resulting mixture was heated to 80 °C for 20 minutes and the reaction temperature was maintained at 80 °C until the reaction was complete. The reaction was cooled to room temperature, water and ether was added sequentially. The mixture was extracted with ether for three times. Organic layers were combined together and washed with brine, dried over MgSO₄, and filtered. The filtrate was evaporated to give a dark residue, which was purified by column chromatography to yield the corresponding products.

(E)-1,1'-Biindenylidene (3a). Orange solid. ¹H NMR (CDCl₃, 300 MHz) δ 7.96-7.93 (m, 2H), 7.43 (d, *J* = 5.6 Hz, 2H), 7.32-7.18 (m, 6H), 7.05 (d, *J* = 5.6 Hz, 2H). Spectral data are identical with those of literature.^{3,4}

(E)-6-Methyl-1,1'-biindenylidene (3b). Reddish solid. Mp: 80-82 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.93 (d, *J* = 7.2 Hz, 1H), 7.75 (s, 1H), 7.44 (d, *J* = 5.6 Hz, 1H), 7.34 (d, *J* = 5.6 Hz, 1H), 7.31-7.29 (m, 1H), 7.25 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.22-7.19 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.05 (m, 1H), 7.04 (d, *J* = 5.6 Hz, 1H), 7.00 (d, *J* = 5.6 Hz, 1H), 2.42 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 143.48, 141.42, 140.97, 140.67, 137.20, 136.85, 136.22, 135.83, 135.47, 128.77, 128.14, 127.18, 126.42, 126.31, 125.68, 125.04, 121.71, 121.43, 21.91; IR (KBr) 2924, 2853, 1734, 1541, 1448, 1369, 1243, 875, 818, 751 cm⁻¹; MS (EI) *m/z*: 242 (M⁺, 6), 205 (100). HRMS (EI) calcd for C₁₉H₁₄: 242.1096. Found: 242.1110.

(E)-6-Methoxy-1,1'-biindenylidene (3c). Orange solid. Mp: >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.92 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.37 (d, *J* = 5.6 Hz, 1H), 7.30-7.18 (m, 3H), 7.28 (d, *J* = 5.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 5.6 Hz, 1H), 6.98 (d, *J* = 5.6 Hz, 1H), 6.76 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.87 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 158.58, 143.44, 141.26, 140.62, 138.71, 136.81, 136.51, 136.24 (2C), 135.96, 128.18, 126.87, 125.71, 125.04, 121.93, 121.74, 113.78, 111.69, 55.77; IR (KBr) 2925, 2853, 1699 (w), 1586, 1451, 1374, 1285, 1229, 1032, 821, 756 cm⁻¹; MS (EI) *m/z*: 258 (M⁺, 100), 225 (32). HRMS (EI) calcd for C₁₉H₁₄O: 258.1045. Found: 258.1035.

(E)-6-Trifluoromethyl-1,1'-biindenylidene (3e). Orange solid. Mp: 72-73 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.14 (s, 1H), 7.93 (d, *J* = 7.3 Hz, 1H), 7.60 (d, *J* = 5.6 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 5.6 Hz, 1H), 7.32 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.29 (dd, *J* = 7.3,

1.0 Hz, 1H), 7.23 (td, $J = 7.3, 1.7$ Hz, 1H), 7.12 (d, $J = 5.6$ Hz, 1H), 7.10 (d, $J = 5.6$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 146.39, 143.58, 142.94, 139.23, 137.68, 136.91, 136.51, 134.73, 129.62, 128.92, 127.6 (q, $J = 31.5$ Hz), 126.68, 126.12, 125.31, 125.23 (q, $J = 4.1$ Hz), 124.60 (q, $J = 271.2$ Hz), 122.10, 121.49, 121.37 (q, $J = 4.1$ Hz); IR (KBr) 2960, 2924, 2853, 1732 (w), 1614, 1540, 1452, 1374, 1330, 1262, 1155, 1111 (s, br), 1052, 824, 801, 746 cm^{-1} ; MS (EI) m/z : 296 (M^+ , 100), 226 ($\text{M}^+ - \text{CF}_3$, 36). HRMS (EI) calcd for $\text{C}_{19}\text{H}_{11}\text{F}_3$: 296.0813. Found: 296.0788.

(*E*)-11-(1-Indenylidene)-11H-cyclopenta[*a*]naphthalene (3f). Brownish solid. Mp: >300 °C. ^1H NMR (CDCl_3 , 270 MHz) δ 8.10 (d, $J = 8.6$ Hz, 1H), 8.05 (dd, $J = 7.9, 1.0$ Hz, 1H), 8.00 (dd, $J = 6.6, 1.6$ Hz, 1H), 7.83 (dd, $J = 7.3, 2.0$ Hz, 1H), 7.68 (d, $J = 8.6$ Hz, 1H), 7.55 (d, $J = 5.7$ Hz, 1H), 7.51 (d, $J = 5.6$ Hz, 1H), 7.50-7.41 (m, 3H), 7.33-7.19 (m, 2H), 7.24 (d, $J = 5.6$ Hz, 1H), 7.10 (d, $J = 5.7$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 143.59, 143.20, 141.91, 140.64, 137.05, 136.83, 133.66, 133.09, 132.91, 128.67, 128.22, 127.59, 127.38, 126.20, 126.13, 126.08, 125.93, 125.57, 125.34, 123.82, 122.85, 121.88; IR (KBr) 3048, 1698, 1506, 1451, 1407, 1371, 1189, 794, 755, 721 cm^{-1} ; MS (EI) m/z : 278 (M^+ , 100), 226 (60). HRMS (EI) calcd for $\text{C}_{22}\text{H}_{14}$: 278.1096. Found: 278.1090.

Spectral data of the acetates (side products): The acetates (**4a-f**) were obtained as inseparable mixtures of two isomers. Spectral data were recorded from the mixtures.

[(*E*)- α -Acetoxy-cinnamylidene]indene (4a; mixture of *E* and *Z* isomers). Partly solidified orange oil. ^1H NMR (CDCl_3 , 300 MHz; 57:43 mixture of two isomers) δ 7.80-7.15 (m, 10H including 7.68 (d, $J = 15.9$ Hz, 0.57H), the signals of the corresponding minor isomer was overlapped), 6.99-6.60 (m, 3H including 6.96 (d, $J = 15.6$ Hz, 0.43H), 6.90 (d, $J = 6.0$ Hz, 0.57H), 6.85 (d, $J = 6.0$ Hz, 0.57H), 6.82 (d, $J = 15.9$ Hz, 0.57H), 6.81 (d, $J = 5.7$ Hz, 0.43H), 6.58 (d, $J = 5.7$ Hz, 0.43H)), 2.53-2.43 (m, 3H including 2.53 (s, $3 \times 0.57\text{H}$), 2.43 (s, $3 \times 0.43\text{H}$)); IR (KBr) 2925, 1761 (s), 1612, 1448, 1373, 1192 (s), 953, 753, 694 cm^{-1} ; MS (EI) m/z : 288 (M^+ , 45), 246 ($\text{M}^+ - \text{Ac} + \text{H}$, 100), 245 ($\text{M}^+ - \text{Ac}$, 45), 215(29). HRMS (EI) calcd for $\text{C}_{20}\text{H}_{16}\text{O}_2$: 288.1150. Found: 288.1133.

[(*E*)- α -Acetoxy-*p*-methylnamylidene]indene (4b; mixture of *E* and *Z* isomers). Orange solid. ^1H NMR (CDCl_3 , 400 MHz; 82:18 mixture of two isomers) δ 7.80-7.15 (m, 9H including 7.80-7.77 (m, 0.82H), 7.64 (d, $J = 15.6$ Hz, 0.82H), the signals of the corresponding minor isomer was overlapped, 7.46 (d, $J = 8.0$ Hz, $2 \times 0.82\text{H}$), 7.42 (d, $J = 8.0$ Hz, $2 \times 0.18\text{H}$)), 6.95-6.56 (m, 3H including 6.93 (d, $J = 15.6$ Hz, 0.82H), 6.90 (d, $J = 5.6$ Hz, 0.18H), 6.85 (d, $J = 5.6$ Hz, 0.18H), 6.81 (d, $J = 5.6$ Hz, 0.82H), 6.79 (d, $J = 15.6$ Hz, 0.18H), 6.58 (d, $J = 5.6$ Hz, 0.82H)), 2.53-2.34 (m, 6H ($3\text{H} \times 2$) including 2.53 (s, $3 \times 0.18\text{H}$), 2.43 (s, $3 \times 0.82\text{H}$), 2.39 (s, $3 \times 0.82\text{H}$), 2.34 (s, $3 \times 0.18\text{H}$)); IR (KBr) 2919, 1754 (s), 1614, 1593, 1446, 1368, 1302, 1204 (s), 1179 (s), 1020, 956, 804, 741

cm⁻¹; MS (EI) *m/z*: 302 (M⁺, 25), 260 (M⁺-Ac+H, 100), 245 (15), 215(25). HRMS (EI) calcd for C₂₁H₁₈O₂: 302.1307. Found: 302.1279.

[(*E*)- α -Acetoxy-*p*-methoxycinnamylidene]indene (4c; mixture of *E* and *Z* isomers). Orange solid. ¹H NMR (CDCl₃, 400 MHz; 74:26 mixture of two isomers) δ 7.79-6.57 (m, 12H including 7.79-7.76 (m, 0.74H), 7.60 (d, *J* = 7.2 Hz, 0.26H), 7.55 (d, *J* = 15.6 Hz, 0.74H), 7.52-7.49 (m, 2 $\times$ 0.74H), 7.47-7.45 (m, 2 $\times$ 0.26H), 6.84 (d, *J* = 5.6 Hz, 0.26H), 6.79 (d, *J* = 5.2 Hz, 0.74H), 6.76 (d, *J* = 15.6 Hz, 0.26H), 6.58 (d, *J* = 5.2 Hz, 0.74H), two doublets of coupling constant 15.6 for the major and minor isomers and a doublet of coupling constant 5.6 for minor isomer were overlapped in this region also), 3.85-3.83 (m, 3H including 3.85 (s, 3 $\times$ 0.74H), 3.84 (s, 3 $\times$ 0.26 H), 2.52-2.42 (m, 3H including 2.52 (s, 3 $\times$ 0.26H), 2.42 (s, 3 $\times$ 0.74 H)); IR (KBr) 2930, 1752 (s), 1592 (s), 1510, 1447, 1369, 1255, 1172 (s), 1034, 952, 821, 750 cm⁻¹; MS (EI) *m/z*: 318 (M⁺, 26), 276 (M⁺-Ac+H, 44), 135 (72), 85(100). HRMS (EI) calcd for C₂₁H₁₈O₃: 318.1256. Found: 318.1247.

[(*E*)- α -Acetoxy-*p*-cyanocinnamylidene]indene (4d; mixture of *E* and *Z* isomers). Partly solidified orange oil. ¹H NMR (CDCl₃, 400 MHz; 57:43 mixture of two isomers) δ 7.81-6.54 (m, 12H including 7.75 (d, *J* = 15.6 Hz, 0.57H), 7.42 (d, *J* = 15.8 Hz, 0.43H), 6.91 (d, *J* = 15.6 Hz, 0.57H), 6.89 (d, *J* = 5.6 Hz, 0.43H), 6.84 (d, *J* = 5.6 Hz, 0.57H), 6.76 (d, *J* = 15.8 Hz, 0.43H), 6.55 (d, *J* = 5.6 Hz, 0.43H), one doublet (*J* = 5.6 Hz) of the major isomer was overlapped), 2.54-2.44 (m, 3H including 2.54 (s, 3 $\times$ 0.43H), 2.44 (s, 3 $\times$ 0.57 H)); IR (KBr) 2923, 2852, 2224, 1760 (s), 1613, 1448, 1370, 1174 (s), 1015, 959, 753 cm⁻¹; MS (EI) *m/z*: 313 (M⁺, 15), 271 (M⁺-Ac+H, 100), 240 (10). HRMS (EI) calcd for C₂₁H₁₅NO₂: 313.1103. Found: : 313.1088.

[(*E*)- α -Acetoxy-*p*-(trifluoromethyl)cinnamylidene]indene (4b; mixture of *E* and *Z* isomers). Orange solid. ¹H NMR (CDCl₃, 300 MHz; 77:23 mixture of two isomers) δ 7.76-6.55 (m, 12H including 7.74 (d, *J* = 15.9 Hz, 0.77H), 7.65 (s, 4 $\times$ 0.77H), 7.62 (s, 4 $\times$ 0.23 H), 7.40 (d, *J* = 15.9 Hz, 0.23H), 6.95 (d, *J* = 15.9 Hz, 0.77H), 6.83 (d, *J* = 5.4 Hz, 0.77H), 6.80 (d, *J* = 15.9 Hz, 0.23H), 6.56 (d, *J* = 5.4 Hz, 0.77H), two doublets for indenyl part of the minor isomer were overlapped), 2.54-2.43 (m, 3H including 2.54 (s, 3 $\times$ 0.23H), 2.43 (s, 3 $\times$ 0.77 H)); IR (KBr) 2921, 1752 (s), 1618, 1542, 1449, 1369, 1327 (s), 1195 (br), 1107, 1066, 947, 822, 748 cm⁻¹; MS (EI) *m/z*: 356 (M⁺, 13), 314 (M⁺-Ac+H, 100), 313 (M⁺-Ac,14). HRMS (EI) calcd for C₂₁H₁₅F₃O₂: 356.1024. Found: 356.1012.

[(2*E*)-3-(1-Naphthyl)-2-propenylidene]indene (4f; mixture of *E* and *Z* isomers). Brownish colored partly solidified oil. ¹H NMR (CDCl₃, 270 MHz; 65:35 mixture of two isomers) δ 8.14-6.61 (m, 15H including 8.11 (d, *J* = 8.2 Hz, 0.65H), 7.70 (d, *J* = 8.6 Hz, 0.65H), 7.36 (d, *J* = 14.2 Hz,

0.65H), 7.11 (d, $J = 5.6$ Hz, 0.65H), 6.89 (d, $J = 14.2$ Hz, 0.35H), 6.87 (d, $J = 14.2$ Hz, 0.65H), 6.84 (d, $J = 5.6$ Hz, 0.35H), 6.62 (d, $J = 5.6$ Hz, 0.65H), due to low concentration of sample, the signals of the minor isomer was vague and two doublets for the minor isomer were overlapped which could not be assigned), 2.60-2.50 (m, 3H including 2.60 (s, 3×0.35 H), 2.50 (s, 3×0.65 H)); IR (KBr) 2925, 1767 (s), 1713, 1604, 1508, 1449, 1371, 1180 (s), 793,, 755 cm^{-1} ; MS (EI) m/z : 338 (M^+ , 30), 296 (M^+ -Ac+H, 100), 278 (M^+ -OAc, 35). HRMS (EI) calcd for $\text{C}_{24}\text{H}_{18}\text{O}_2$: 338.1307. Found: 338.1308.

References:

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8000.0 Hz
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21.7 C
CDCL3
0.00 ppm
0.05 Hz
22

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EXMOD
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SCANS
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SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
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