Synthesis of 2-Substitued 3-Aroylindenes via Palladium-Catalyzed Carbonylative Cyclization of Diethyl 2-(2-(1-alkynyl)phenyl)malonates with Aryl Halides

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General Remarks:
Column chromatography was carried out on silica gel. \( ^1 \)H NMR spectra were recorded on 300 MHz or 400 MHz in CDCl\(_3\) and \( ^{13} \)C NMR spectra were recorded on 75 MHz or 100 MHz in CDCl\(_3\) using TMS as internal standard. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm\(^{-1}\). Melting points were determined on a microscopic apparatus and were uncorrected. All new compounds were further characterized by element analysis; copies of their \( ^1 \)H NMR and \( ^{13} \)C NMR spectra are provided. Unless otherwise stated, all aryl halides were purchased from commercial suppliers and used without further purification.

Starting Materials:
Diethyl (2-iodophenyl)malonate, ethyl (2-iodophenyl)(phenylsulfonyl)acetate, and ethyl 2-cyano-2-(2-iodophenyl)acetate were prepared according to the literature.\(^1\) Starting materials \( 1a, 1d, 1e, 1f, \) and \( 1g \) have been previously reported.\(^2\) \( 1b, 1c, \) and \( 1h \) were prepared according to previous literature procedures.\(^2\)

Synthesis of Diethyl 2-(2-(2-(4-methoxyphenyl)ethynyl)phenyl)malonate, 1b.
To a solution of diethyl (2-iodophenyl)malonate (0.36 g, 1.0 mmol) and 1-ethynyl-4-methoxybenzene (0.16 g, 1.2 mmol) in Et\(_3\)N (4.0 mL) was added PdCl\(_2\)(PPh\(_3\))\(_2\) (14 mg, 0.02 mmol, 2 mol %). The mixture was stirred for 5 min and CuI (2 mg, 0.01 mmol, 1 mol %) was added. The resulting mixture was then stirred under an argon atmosphere at room temperature for 12 h. The ammonium salt was removed by filtration, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to afford \( 1b \) 0.34 g (92 %) as an oil, which solidified upon cooling: mp 49-51 °C; \( ^1 \)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.55-7.44 (m, 4H), 7.36-7.30 (m, 2H), 6.90-6.87 (d, \( J = 8.7 \) Hz, 2H), 5.38 (s, 1H), 4.28-4.20 (m, 4H), 3.81 (s, 3H), 1.28-1.23 (t, \( J = 7.2 \) Hz, 6H); \( ^{13} \)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 168.1 (2 C), 159.8, 134.6, 133.0 (2 C), 131.7, 128.4, 128.2, 127.8, 123.9, 114.8, 113.9 (2 C), 94.6, 85.5, 61.8 (2 C), 56.0, 55.2, 14.0 (2 C); IR (KBr, cm\(^{-1}\)) 3453, 2982, 2214, 1734, 1604, 1512, 1251, 1031; Anal.Calcd for C\(_{22}\)H\(_{22}\)O\(_5\): C, 72.12; H, 6.05. Found: C, 72.37; H, 6.08.

Synthesis of Diethyl 2-(2-(2-(4-nitrophenyl)ethynyl)phenyl)malonate, 1c.
The \( 1c \) was prepared by the same method. But employing diethyl (2-iodophenyl)malonate (0.36 g, 1.0 mmol) and 1-ethynyl-4-methoxybenzene (0.16 g, 1.2 mmol) in Et\(_3\)N (4.0 mL) was added PdCl\(_2\)(PPh\(_3\))\(_2\) (14 mg, 0.02 mmol, 2 mol %). The mixture was stirred for 5 min and CuI (2 mg, 0.01 mmol, 1 mol %) was added. The resulting mixture was then stirred under an argon atmosphere at room temperature for 12 h. The ammonium salt was removed by filtration, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to afford \( 1c \) 0.34 g (92 %) as a solid: mp 73-75 °C; \( ^1 \)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 8.25-8.22 (d, \( J = 8.7 \) Hz, 2H), 7.71-7.68 (d, \( J = 8.7 \) Hz, 2H), 7.61-7.59 (d, \( J = 7.5 \) Hz, 1H), 7.53-7.50 (d, \( J = 7.5 \) Hz, 1H), 7.46-7.34 (m, 2H), 5.30 (s, 1H), 4.28-4.20 (m, 4H), 1.29-1.25 (t, \( J = 6.9 \) Hz, 6H); \( ^{13} \)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 167.8 (2 C), 159.8, 134.6, 133.0 (2 C), 131.7, 128.4, 128.2, 127.8, 123.9, 114.8, 113.9 (2 C), 94.6, 85.5, 61.8 (2 C), 56.0, 55.2, 14.0 (2 C); IR (KBr, cm\(^{-1}\)) 3450, 2984, 2217, 1734, 1604, 1512, 1251, 1031; Anal.Calcd for C\(_{22}\)H\(_{22}\)O\(_5\): C, 66.13; H, 5.02; N 3.67. Found: C, 66.12; H, 4.97; N, 3.61.

Synthesis of Ethyl 2-cyano-2-(2-(2-phenylethynyl)phenyl)acetate, 1h.
The \( 1h \) was prepared by the same method. But employing ethyl 2-cyano-2-(2-iodophenyl)acetate (0.32 g, 1.0 mmol) and phenylacetylene (0.12 g, 1.2 mmol) at room temperature for 12 h afforded \( 1h \) 0.25 g (87 %) as a yellow oil. \( 1h: ^1 \)H
NMR (300 MHz, CDCl₃) δ 7.61-7.54 (m, 4H), 7.44-7.36 (m, 5H), 5.29 (s, 1H), 4.27-4.20 (q, J = 6.9 Hz, 2H), 1.24-1.19 (t, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 164.6, 132.5, 131.8, 131.5 (2 C), 129.1, 129.0, 128.9, 128.5, 128.4, 125.8, 123.1, 122.2, 115.5, 95.9, 85.6, 63.3, 42.2, 13.8; IR (KBr, cm⁻¹) 3472, 2985, 2251, 2218, 1746, 1496, 1214, 1027; Anal. Calcd for C₁₉H₁₅NO₂: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.65; H, 4.98; N, 4.76

References

General Procedure for the Preparation of 2-Substituted 3-Aroylindenes
To a solution of diethyl 2-(2-(2-phenylethynyl)phenyl)malonate 1a (67.2 mg, 0.20 mmol) in CH₃CN (2.0 mL) was added K₂CO₃ (55.2 mg, 0.40 mmol). The mixture was stirred for 10 min and Pd₂(dba)₃·CHCl₃ (10.4 mg, 0.01 mmol, 5 mol %), organic halides (0.24 mmol) was added. The mixture was flushed with CO and fitted with a CO-filled balloon (caution!). The reaction mixture was heated to 80 °C with vigorous stirring for the specified time, the reaction mixture was cooled to room temperature, quenched with a saturated aqueous solution of ammonium chloride, and the mixture was extracted with EtOAc. The combined organic extracts were washed with water and saturated brine. The organic layers were dried over Na₂SO₄ and filtered. Solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford corresponding 2-substituted 3-aroylindenes.

Diethyl 3-(4-chlorobenzoyl)-2-phenyl-1H-indene-1,1-dicarboxylate 3aa:
The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 78.7 mg (83%) of the indicated compound as a solid: mp 96-98 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.91-7.88 (d, J = 8.7 Hz, 2H), 7.73-7.70 (m, 1H), 7.39-7.28 (m, 5H), 7.24-7.21 (d, J = 8.7 Hz, 2H), 7.18-7.14 (m, 3H), 4.25-4.11 (m, 4H), 1.13-1.08 (t, J = 7.2 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 193.7, 167.3 (2 C), 146.1, 142.7, 141.6, 140.6, 140.0, 134.5, 133.4, 131.0 (2 C), 129.3 (2 C), 129.1, 128.7 (2 C), 127.9 (2 C), 127.3, 124.6 (2 C), 121.4, 72.5, 62.3 (2 C), 13.7 (2 C); IR (KBr, cm⁻¹) 3448, 2983, 1732, 1661, 1587, 1464, 1223, 1092, 1051; Anal. Calcd for C₂₈H₂₃ClO₅: C, 70.81; H, 4.88. Found: C, 70.72; H, 4.74.

Diethyl 3-(4-(methoxycarbonyl)benzoyl)-2-phenyl-1H-indene-1,1-dicarboxylate 3ab: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 89.6 mg (90%) of the indicated compound as a solid: mp 128-130 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.01-7.98 (d, J = 8.1 Hz, 2H), 7.92-7.89 (d, J = 8.7 Hz, 2H), 7.74-7.72
Diethyl 3-(4-nitrobenzoyl)-2-phenyl-1H-indene-1,1-dicarboxylate 3ac: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 72.8 mg (75%) of the indicated compound as a solid: mp 82-84 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.06, (s, 4H), 7.75-7.73 (dd, $J = 1.2$, 6.3 Hz, 1H), 7.47-7.37 (m, 3H), 7.29-7.26 (m, 2H), 7.14-7.12 (m, 3H), 4.26-4.14 (m, 4H), 1.15-1.10 (t, $J = 7.2$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 193.0, 167.1 (2 C), 150.0, 148.4, 142.1, 140.9 (2 C), 140.5, 133.3, 130.4 (3 C), 129.5 (2 C), 129.2, 128.0 (2 C), 127.5, 124.8, 123.4 (2 C), 121.5, 72.7, 62.4 (2 C), 13.7 (2 C); IR (KBr, cm$^{-1}$) 3451, 2984, 1731, 1663, 1528, 1464, 1346, 1219, 1050; Anal.Calcd for C$_{28}$H$_{23}$NO$_7$: C, 69.27; H, 4.78; N 2.89. Found: C, 69.51; H, 4.58; N, 2.66.

Diethyl 3-(4-(trifluoromethyl)benzoyl)-2-phenyl-1H-indene-1,1-dicarboxylate 3ad: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 84.3 mg (83%) of the indicated compound as a solid: mp 89-91 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05-8.03 (dd, $J = 8.0$, 0.8 Hz, 2H), 7.74-7.72 (m, 1H), 7.52-7.50 (dd, $J = 8.0$, 0.8 Hz, 2H), 7.40-7.35 (m, 3H), 7.30-7.28 (m, 2H), 7.15-7.12 (m, 3H), 4.25-4.14 (m, 4H), 1.13-1.10 (t, $J = 7.2$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 193.8, 167.2 (2 C), 147.2, 142.5, 141.5, 140.7, 139.1, 134.4 (q, $J_{C-F}^2 = 32.2$ Hz, 1C), 133.5, 129.9 (2 C), 129.5 (2 C), 129.2, 128.7, 127.9 (2 C), 127.4, 126.1 (q, $J_{C-F}^1 = 264.1$ Hz, 1C), 125.3 (2 C), 124.8, 121.5, 72.8, 62.3 (2 C), 13.7 (2 C); IR (KBr, cm$^{-1}$) 3455, 2984, 1733, 1665, 1464, 1324, 1223, 1132, 1067; Anal.Calcd for C$_{29}$H$_{23}$F$_3$O$_5$: C, 68.50; H, 4.56. Found: C, 68.43; H, 4.78.

Diethyl 3-(4-methylbenzoyl)-2-phenyl-1H-indene-1,1-dicarboxylate 3ae: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 47.2 mg (52%) of the indicated compound as a solid: mp 115-117 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.89-7.86 (d, $J = 7.8$ Hz, 2H), 7.72-7.69 (m, 1H), 7.35-7.27 (m, 5H), 7.17-7.13 (m, 3H), 7.09-7.06 (d, $J = 8.4$ Hz, 2H), 4.25-4.11 (m, 4H), 2.29 (s, 3H), 1.31 (s, 3H), 1.12 (t, $J = 7.2$ Hz, 6H).
Diethyl 3-(4-methoxybenzoyl)-2-phenyl-1H-indene-1,1-dicarboxylate 3af: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 39.5 mg (42%) of the indicated compound as a solid: mp 91-93 °C; 1H NMR (300 MHz, CDCl3) δ 7.98-7.95 (m, 2H), 7.72-7.69 (dd, J = 1.2, 7.5 Hz, 1H), 7.37-7.27 (m, 5H), 7.18-7.14 (m, 3H), 6.77-6.74 (d, J = 8.7 Hz, 2H), 4.25-4.11 (m, 4H), 3.77 (s, 3H), 1.13-1.08 (m, 6H); 13C NMR (75 MHz, CDCl3) δ 193.5, 167.5 (2 C), 163.9, 144.3, 143.2, 142.4, 140.7, 133.6, 132.1 (2 C), 129.2, 129.1, 129.0, 128.3, 127.8 (2 C), 127.0, 124.5 (2 C), 121.3, 113.6 (2 C), 72.4, 62.2 (2 C), 55.3, 13.7 (2 C); IR (KBr, cm⁻¹) 3448, 2983, 1731, 1662, 1450, 1225, 1051; Anal.Calcd for C29H26O6: C, 76.35; H, 5.49. Found: C, 76.26; H, 5.36.

Diethyl 3-benzoyl-2-phenyl-1H-indene-1,1-dicarboxylate 3ag: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 53.7 mg (61%) of the indicated compound as a solid: mp 94-96 °C; 1H NMR (300 MHz, CDCl3) δ 7.97-7.95 (m, 2H), 7.73-7.70 (m, 1H), 7.44-7.24 (m, 8H), 7.15-7.12 (m, 3H), 4.25-4.09 (m, 4H), 1.13-1.08 (t, J = 6.9 Hz, 6H); 13C NMR (75 MHz, CDCl3) δ 195.0, 167.4 (2 C), 145.6, 143.0, 142.1, 140.6, 136.1, 133.6 (2 C), 129.6 (2 C), 129.3 (2 C), 128.1, 128.5, 128.3 (2 C), 127.8 (2 C), 127.1, 124.5, 121.4, 72.5, 62.2 (2 C), 13.7 (2 C); IR (KBr, cm⁻¹) 3444, 2983, 1731, 1654, 1597, 1463, 1234, 1168, 1051; Anal.Calcd for C29H26O5: C, 74.03; H, 5.57. Found: C, 74.25; H, 5.45.

Diethyl 3-(3-methylbenzoyl)-2-phenyl-1H-indene-1,1-dicarboxylate 3ah: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 46.3 mg (51%) of the indicated compound as a solid: mp 98-100 °C; 1H NMR (300 MHz, CDCl3) δ 7.80-7.69 (m, 3H), 7.37-7.35 (m, 5H), 7.34-7.21 (m, 1H), 7.15-7.12 (m, 4H), 4.25-4.12 (m, 4H), 2.27 (s, 3H), 1.13-1.08 (t, J = 7.2 Hz, 6H); 13C NMR (75 MHz, CDCl3) δ 195.1, 167.5 (2 C), 145.3, 143.0, 142.3, 140.6, 138.0, 136.0, 134.4, 133.7, 129.9, 129.3 (2 C), 129.0, 128.4, 128.2, 127.7 (2 C), 127.2, 127.1, 124.5, 121.4, 72.5,
Diethyl 3-(3-chlorobenzoyl)-2-phenyl-1H-indene-1,1-dicarboxylate 3ai: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 84.4 mg (89%) of the indicated compound as a solid: mp 109-111 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.90 (s, 1H), 7.83-7.81 (d, $J$ = 7.5 Hz, 1H), 7.73-7.71 (d, $J$ = 7.2 Hz, 1H), 7.40-7.28 (m, 6H), 7.21-7.14 (m, 4H), 4.25-4.12 (m, 4H), 1.13-1.08 (t, $J$ = 7.2 Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 193.5, 167.3 (2 C), 146.8, 142.5, 141.4, 140.6, 137.7, 134.5, 133.5, 133.3, 129.6 (2 C), 129.3 (2 C), 129.1, 128.8, 127.9 (2 C), 127.7, 127.3, 124.6, 121.4, 72.5, 62.3 (2 C), 13.7 (2 C); IR (KBr, cm$^{-1}$) 3452, 2983, 1731, 1661, 1569, 1465, 1218, 1050; Anal.Calcd for C$_{28}$H$_{23}$ClO$_5$: C, 70.81; H, 4.88. Found: C, 70.76; H, 4.92.

Diethyl 3-(3-nitrobenzoyl)-2-phenyl-1H-indene-1,1-dicarboxylate 3aj: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 82.5 mg (85%) of the indicated compound as a solid: mp 120-122 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.70-8.69 (d, $J$ = 1.8 Hz, 1H), 8.27-8.19 (m, 2H), 7.76-7.74 (d, $J$ = 7.2 Hz, 1H), 7.50-7.35 (m, 4H), 7.29-7.27 (m, 2H), 7.12-7.10 (m, 3H), 4.26-4.17 (m, 4H), 1.14-1.09 (t, $J$ = 7.2 Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 192.2, 167.0 (2 C), 148.4, 147.8, 142.0, 140.6, 137.5, 134.8, 133.4, 129.4 (4 C), 129.1, 129.0, 127.9 (2 C), 127.5, 127.3, 124.7, 124.6, 121.5, 72.7, 62.5 (2 C), 13.7 (2 C); IR (KBr, cm$^{-1}$) 3452, 2983, 1731, 1664, 1533, 1465, 1351, 1221, 1050; Anal.Calcd for C$_{28}$H$_{23}$NO$_7$: C, 69.27; H, 4.78; N 2.89. Found: C, 69.34; H, 4.62; N, 2.69.

Diethyl 3-(2-methylbenzoyl)-2-phenyl-1H-indene-1,1-dicarboxylate 3ak: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 56.3 mg (62%) of the indicated compound as a solid: mp 72-74 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.71-7.69 (d, $J$ = 7.5 Hz, 1H), 7.61-7.58 (d, $J$ = 8.1 Hz, 1H), 7.49-7.46 (d, $J$ = 6.9 Hz, 1H), 7.42-7.31 (m, 2H), 7.24-7.20 (m, 3H), 7.18-7.05 (m, 4H), 6.98-6.93 (m, 1H), 4.22-4.09 (m, 4H), 2.57 (s, 3H), 1.11-1.07 (t, $J$ = 7.2 Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 196.7, 167.3 (2 C), 147.0, 143.8, 142.8, 140.5, 139.2, 136.8, 133.8, 131.8,
Diethyl 3-(2-(methoxycarbonyl)benzoyl)-2-phenyl-1H-indene-1,1-dicarboxylate 3al: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 77.7 mg (78%) of the indicated compound as an oil: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.88-7.85 (d, \(J = 7.5\) Hz, 1H), 7.68-7.65 (d, \(J = 7.8\) Hz, 1H), 7.56-7.53 (m, 1H), 7.50-7.44 (m, 1H), 7.39-7.32 (m, 2H), 7.27-7.17 (m, 2H), 7.15-7.08 (m, 2H), 7.03-6.97 (m, 3H), 4.19-4.08 (m, 4H), 3.58 (s, 3H), 1.11-1.06 (m, 6H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 194.6, 167.6, 167.0 (2 C), 149.4, 142.9, 142.5, 140.1, 139.8, 133.3, 130.9, 130.7, 130.6, 129.7 (2 C), 129.6, 129.2, 129.0, 128.2, 127.2 (3 C), 124.4, 122.6, 73.5, 62.2 (2 C), 52.5, 13.7 (2 C); IR (KBr, cm\(^{-1}\)) 3449, 2984, 1759, 1638, 1410, 1228, 1054; Anal.Calcd for C\(_{30}\)H\(_{26}\)O\(_7\): C, 72.28; H, 5.26. Found: C, 72.28; H, 5.13.

Diethyl 2-phenyl-3-(2-thienylcarbonyl)-1H-indene-1,1-dicarboxylate 3am: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 58.0 mg (65%) of the indicated compound as a solid: mp 151-153 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.71-7.69 (m, 1H), 7.63-7.62 (m, 1H), 7.56-7.54 (m, 1H), 7.42-7.27 (m, 5H), 7.23-7.19 (m, 3H), 6.87-6.84 (m, 1H), 4.24-4.12 (m, 4H), 1.12-1.07 (m, 6H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 186.9, 167.4, 167.0 (2 C), 145.3, 143.5, 142.6, 142.1, 140.6, 136.0, 135.3, 133.6, 129.3 (2 C), 129.1, 128.6, 128.0, 127.9 (2 C), 127.2, 124.5, 121.3, 72.4, 62.3 (2 C), 13.7 (2 C); IR (KBr, cm\(^{-1}\)) 3449, 2984, 1733, 1661, 1455, 1254, 1101, 1049; Anal.Calcd for C\(_{26}\)H\(_{22}\)O\(_5\)S: C, 69.94; H, 4.97. Found: C, 69.83; H, 5.16.

Diethyl 3-(4-(methoxycarbonyl)benzoyl)-2-(4-methoxyphenyl)-1H-indene-1,1-dicarboxylate 3bb: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 84.5 mg (80%) of the indicated compound as an oil: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.02-7.99 (d, \(J = 9.0\) Hz, 2H), 7.93-7.90 (d, \(J = 8.1\) Hz, 2H), 7.71-7.69 (m, 1H), 7.40-7.31 (m, 3H), 7.24-7.21 (m, 2H), 6.66-6.30 (d, \(J = 9.3\) Hz, 2H), 4.26-4.12 (m, 4H), 3.89 (s, 3H), 3.69 (s, 3H), 1.16-1.11 (m, 6H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 194.5, 167.5 (2 C), 166.2, 159.9, 147.1, 142.7, 140.4, 139.9, 139.6, 133.8, 131.0 (2 C), 129.5 (4 C), 129.1, 127.0, 125.7, 124.5, 121.2, 113.3 (2 C), 72.4, 62.3 (2 C), 55.1, 52.4, 13.8 (2 C); IR (KBr, cm\(^{-1}\)) 3432, 2918, 1727, 1657, 1510, 1253, 1111,
Diethyl 3-(4-(methoxycarbonyl)benzoyl)-2-(4-nitrophenyl)-1H-indene-1,1-dicarboxylate 3cb: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 101.0 mg (93%) of the indicated compound as an oil, which solidified upon cooling: mp 48-50 °C; 1H NMR (300 MHz, CDCl3) δ 8.04-7.95 (m, 6H), 7.80-7.77 (m, 1H), 7.53-7.49 (m, 2H), 7.44-7.40 (m, 2H), 7.36-7.28 (m, 1H), 4.29-4.17 (m, 4H), 3.89 (s, 3H), 1.19-1.15 (t, J = 7.2 Hz, 6H); 13C NMR (75 MHz, CDCl3) δ 193.6, 166.7 (2 C), 165.7, 147.2, 144.7, 142.8, 141.8, 140.4, 140.2, 138.7, 134.6, 130.1 (2 C), 129.7 (2 C), 129.3 (3 C), 128.2, 125.0, 123.0 (2 C), 121.9, 72.6, 62.7 (2 C), 52.4, 13.8 (2 C); IR (KBr, cm⁻¹) 3441, 2984, 1728, 1520, 1347, 1281, 1221, 1111, 1048; Anal.Calcd for C30H25NO9: C, 66.29; H, 4.64; N 2.58. Found: C, 66.38; H, 4.62; N, 2.79.

Diethyl 3-(4-(methoxycarbonyl)benzoyl)-2-(4-bromophenyl)-1H-indene-1,1-dicarboxylate 3db: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 98.0 mg (85%) of the indicated compound as a solid: mp 101-103 °C; 1H NMR (300 MHz, CDCl3) δ 8.01-7.94 (m, 4H), 7.74-7.71 (m, 1H), 7.40-7.32 (m, 3H), 7.29-7.26 (m, 2H), 7.20-7.16 (m, 2H), 4.26-4.14 (m, 4H), 3.90 (s, 3H), 1.17-1.12 (t, J = 6.9 Hz, 6H); 13C NMR (75 MHz, CDCl3) δ 194.1, 167.1 (2 C), 166.0, 144.9, 142.3, 142.2, 140.4, 139.1, 134.3, 132.4, 131.1 (2 C), 130.8 (2 C), 129.7 (2 C), 129.4 (2 C), 129.2, 127.6, 124.8, 123.1, 121.5, 72.5, 62.5 (2 C), 52.4, 13.8 (2 C); IR (KBr, cm⁻¹) 3435, 2983, 1728, 1662, 1463, 1280, 1220, 1110, 1049; Anal.Calcd for C30H25BrO7: C, 62.40; H, 4.36. Found: C, 62.32; H, 4.47.

Diethyl 3-(4-(methoxycarbonyl)benzoyl)-2-cyclohexenyl-1H-indene-1,1-dicarboxylate 3eb: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 70.3 mg (70%) of the indicated compound as an oil: 1H NMR (400 MHz, CDCl3) δ 8.11-8.08 (m, 2H), 8.00-7.98 (m, 2H), 7.64-7.62 (d, J = 8.0 Hz, 1H), 7.48-7.46 (d, J = 7.6 Hz, 1H), 7.39-7.34 (m, 1H), 7.31-7.28 (m, 1H), 5.66 (s, 1H), 4.29-4.17 (m, 4H), 3.95 (s, 3H), 2.12-2.11 (m, 2H), 1.73-1.72 (m, 2H), 1.37-1.20 (m, 8H), 1.12-1.08 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 194.2, 167.2 (2 C), 166.3, 152.4, 142.0, 140.4, 140.2, 134.9, 134.1, 133.3, 129.6, 129.5 (2 C), 128.9, 128.4 (2 C), 126.9, 124.7, 121.3, 70.9, 62.2 (2 C), 52.3, 27.9, 25.9, 22.1, 21.1, 13.9 (2 C); IR (KBr,
Diethyl 3-(4-(methoxycarbonyl)benzoyl)-2-pentyl-1H-indene-1,1-dicarboxylate 3fb: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 59.0 mg (60%) of the indicated compound as an oil: 1H NMR (300 MHz, CDCl3) δ 8.16-8.13 (d, J = 8.7 Hz, 2H), 8.04-8.01 (d, J = 8.7 Hz, 2H), 7.67-7.64 (m, 1H), 7.27-7.25 (m, 2H), 7.01-6.99 (m, 1H), 4.30-4.21 (m, 4H), 3.96 (s, 3H), 2.56-2.51 (t, J = 8.4 Hz, 2H), 1.37-1.35 (m, 2H), 1.32-1.27 (t, J = 7.2 Hz, 6H), 1.15-1.12 (m, 4H), 0.78-0.73 (t, J = 6.6 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ 194.2, 167.5 (2 C), 166.1, 149.6, 142.9, 140.9, 140.1, 139.4, 134.4, 129.9 (2 C), 129.3 (2 C), 128.7, 126.4, 124.9, 120.5, 72.4, 62.3 (2 C), 52.5, 31.9, 29.4, 28.4, 22.0, 13.9 (2 C), 13.8; IR (KBr, cm-1) 3431, 2957, 1728, 1669, 1464, 1282, 1219, 1169, 1109, 1048; Anal. Calcd for C29H32O7: C, 70.71; H, 6.55. Found: C, 70.63; H, 6.46.

General Procedure for the Preparation of 2-Phenyl 3-Aroylindenes, 3gb.

To a solution of ethyl 2-((2-(2-phenylethynyl)phenyl)-2-(phenylsulfonyl)acetate 1g (80.8 mg, 0.20 mmol) in CH3CN (2.0 mL) was added K2CO3 (55.2 mg, 0.40 mmol). The mixture was stirred for 10 min and Pd2(dba)3.CHCl3 (10.4 mg, 0.01 mmol, 5 mol %), organic halides (0.24 mmol) was added. The mixture was flushed with CO and fitted with a CO-filled balloon (caution!). The reaction mixture was heated to 80 °C with vigorous stirring for the specified time, the reaction mixture was cooled to room temperature, quenched with a saturated aqueous solution of ammonium chloride, and the mixture was extracted with EtOAc. The combined organic extracts were washed with water and saturated brine. The organic layers were dried over Na2SO4 and filtered. Solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford corresponding 2-phenyl 3-arylidene 3gb.

Ethyl 3-(4-(methoxycarbonyl)benzoyl)-2-phenyl-1-(phenylsulfonyl)-1H-indene-1-carboxylate 3gb: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 62.3 mg (55%) of the indicated compound as a solid: mp 172-174 °C; 1H NMR (300 MHz, CDCl3) δ 8.01-7.98 (m, 1H), 7.87-7.85 (d, J = 8.1 Hz, 2H), 7.77-7.41 (d, J = 8.4 Hz, 2H), 7.56-7.52 (m, 1H), 7.46-7.39 (m, 2H), 7.23-7.05 (m, 10H), 4.56-4.48 (m, 1H), 4.42-4.34 (m, 1H), 3.87 (s, 3H), 1.37-1.32 (t, J = 7.2 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ 193.5, 165.9, 165.1, 144.2, 142.9, 142.7, 138.8, 136.9, 135.5, 134.1 (2 C), 131.7, 130.4, 129.9 (2 C), 129.7 (2 C), 129.5 (2 C), 129.4, 129.2 (2 C), 127.9 (2 C), 127.8 (2 C), 127.6, 126.1, 121.5, 84.8, 63.3, 52.4, 13.9; IR (KBr, cm-1) 3433, 2925, 1728, 1664, 1443, 1282, 1219, 1153, 1111, 1021; Anal. Calcd for
General Procedure for the Preparation of 2-Phenyl 3-Aroylindenes, 3hb.

To a solution of ethyl 2-cyano-2-(2-(2-phenylethynyl)phenyl)acetate 1h (57.8 mg, 0.20 mmol) in CH₃CN (2.0 mL) was added K₂CO₃ (55.2 mg, 0.40 mmol). The mixture was stirred for 10 min and Pd₂(dba)₃·CHCl₃ (10.4 mg, 0.01 mmol, 5 mol %), organic halides (0.24 mmol) was added. The mixture was flushed with CO and fitted with a CO-filled balloon (caution!). The reaction mixture was heated to 80 °C with vigorous stirring for the specified time, the reaction mixture was cooled to room temperature, quenched with a saturated aqueous solution of ammonium chloride, and the mixture was extracted with EtOAc. The combined organic extracts were washed with water and saturated brine. The organic layers were dried over Na₂SO₄ and filtered. Solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford corresponding 2-phenyl 3-aroylindene 3hb.

C₃₃H₂₆O₇S: C, 69.95; H, 4.63. Found: C, 70.15; H, 4.68.

Ethyl 3-(4-(methoxycarbonyl)benzoyl)-1-cyano-2-phenyl-1H-indene-1-carboxylate 3hb: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 58.6 mg (65%) of the indicated compound as a solid: mp 137-139 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.03-7.96 (m, 4H), 7.76-7.73 (m, 1H), 7.49-7.33 (m, 5H), 7.25-7.22 (m, 3H), 4.41-4.35 (m, 1H), 4.27-4.21 (m, 1H), 3.90 (s, 3H), 1.26-1.22 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 193.4, 165.9, 165.0, 143.1, 142.4, 141.6, 138.8, 138.7, 134.5, 131.1, 130.5, 129.8 (3 C), 129.4 (2 C), 128.9 (2 C), 128.4 (3 C), 123.2, 122.3, 115.6, 64.1, 58.9, 52.5, 13.9; IR (KBr, cm⁻¹) 3431, 2924, 1744, 1663, 1440, 1282, 1222, 1112, 1015; Anal.Calcd for C₂₈H₂₁NO₅: C, 74.49; H, 4.69; N 3.10. Found: C, 74.36; H, 4.62; N, 2.97.
C$_2$H$_5$O$_2$C

Ph

$\text{NO}_2$

3ac
\[ \text{3af} \]
$C_2H_5O_2C\text{Ph}$

$\text{NO}_2$
C₆H₅O₂C₅SO₂Ph

3gb