Pd-Catalyzed Coupling of β–Hydroxy α–Diazocarbonyl Compounds with Aryl Iodides: A Migratory Insertion/β-Hydroxy Elimination Sequence

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General All reactions were performed under a nitrogen atmosphere in a flame-dried reaction flask. All solvents were distilled prior to use. THF and toluene were dried over Na before use. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. 1H NMR and 13CNMR spectra were recorded on Varian 300 or Brucker ARX 400 spectrometer in CDCl3 solution and the chemical shifts were reported in parts per million (d) relative to internal standard TMS (0 ppm). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

General Procedure for the Preparation of Ethyl 2-Diazo-3-hydroxy Carboxylates. 1

\[
\text{R}^\prime\text{R} \quad + \quad \text{OEt} \quad \text{LDA} \quad \text{-78 }^\circ\text{C} \quad \text{HO} \quad \text{N}_2 \quad \text{CO}_2\text{Et}
\]

A cold (-10 °C) solution of lithium diisopropylamide [prepared by the addition of n-butyllithium in hexane (10 mL of a 2.5 M solution) to a solution of diisopropylamine (2.5 g) in THF (15 mL)] was added during 30 min to a stirred solution of the appropriate ketone (20 mmol) and ethyl diazoacetate (20 mmol) at -78 °C. The mixture was allowed to stir at -78 °C for 2 h, at which time the reaction was quenched with a saturated NH₄Cl solution and extracted with ether. The combined organic extracts were washed with saturated aqueous NaHCO₃ solution and brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude residue was subjected to flash silica gel chromatography to afford the pure ethyl 2-diazoo-3-hydroxy carboxylate.
General Procedure for the Pd-Catalyzed Reactions

Pd$_2$(dba)$_3$ (2.5 mol%, 11.3 mg), 2-(dicyclohexylphosphino)-2',4',6'-triisopropylbiphenyl (Xphos, 10 mol%, 23.7 mg) and aryl iodide (0.6 mmol) were suspended in THF (3 mL) in a 10 mL Schlenk tube under nitrogen. Then diisopropylamine (0.22 mL, 1.5 mmol) and α-hydroxyl diazo compound (0.5 mmol) were added. The resulting solution was stirred at 70 °C for 24 h. After cooling to room temperature, the resulting mixture was filtered through a short path of silica gel, eluting with ethyl acetate. The volatile compounds were removed *in vacuo* and the crude residue was purified by column chromatography (SiO$_2$, hexane).

Spectral Data

Ethyl 2-Diazo-2-(1-hydroxycyclopentyl)acetate (1)$^1$

![Structure 1]

IR (neat) 3460, 2967, 2089, 1697, 1370, 1301, 1108, 750 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.25 (t, $J = 7.2$ Hz, 3H), 1.67-1.92 (m, 6H), 2.01-2.09 (m, 2H), 3.26 (s, 1H), 4.25 (q, $J = 7.2$ Hz, 2H).

Ethyl 2-Diazo-2-(1-hydroxycyclohexyl)acetate (5a)$^2$

![Structure 5a]

IR (neat) 3468, 2972, 2091, 1695, 1374, 4, 1109, 752 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.27 (t, $J = 7.2$ Hz, 3H), 1.32-1.90 (m, 10H), 3.32 (s, 1H), 4.26 (q, $J = 7.2$ Hz, 2H).

Ethyl 2-Diazo-2-(1-hydroxy-4-methylcyclohexyl)acetate (5b)

![Structure 5b]

IR (neat) 3483, 2926, 2088, 1673, 1370, 1297, 1114, 1079, 744 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.93 (d, $J = 5.6$ Hz, 3H), 1.28 (t, $J = 7.2$ Hz, 3H), 1.40-1.69 (m, 7H), 2.04-2.07 (m, 2H), 3.47 (s, 1H), 4.23 (q, $J = 7.2$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.5, 22.2, 29.8, 31.9, 36.1, 60.8, 69.1, 167.5.
Ethyl 2-(4-tert-butyl-1-hydroxycyclohexyl)-2-diazoacetate (5c)

IR (neat) 2949, 2868, 2087, 1681, 1366, 1291, 1084, 747 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.83 (s, 9H), 0.89-1.06 (m, 3H), 1.27 (t, J = 7.2 Hz, 3H), 1.50-1.60 (m, 2H), 1.69-1.74 (m, 2H), 2.24-2.29 (m, 2H), 3.51 (s, 1H), 4.22 (q, J = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.25, 14.28, 24.2, 27.3, 27.4, 32.0, 36.9, 46.8, 60.6, 71.8, 166.9.

Ethyl 2-Diazo-2-(1-hydroxy-4-phenylcyclohexyl)acetate (5d)

IR (neat) 3477, 2933, 2088, 1686, 1368, 1302, 1099, 746, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.30 (t, J = 7.2 Hz, 3H), 1.57-1.78 (m, 4H), 1.97-2.03 (m, 2H), 2.20-2.23 (m, 2H), 2.51-2.57 (m, 1H), 3.59 (s, 1H), 4.26 (q, J = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.6, 28.9, 36.6, 43.7, 61.0, 68.9, 126.2, 127.0, 128.5, 146.7, 167.5.

Ethyl 2-Diazo-3-ethyl-3-hydroxypentanoate (5e)

IR (neat) 3368, 2977, 2094, 1671, 1370, 1310, 1085, 1048, 908, 734 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.94 (t, J = 7.2 Hz, 6H), 1.29 (t, J = 7.2 Hz, 3H), 1.75 (t, J = 7.2 Hz, 4H), 3.83 (s, 1H), 4.22 (q, J = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 8.1, 14.5, 31.5, 60.9, 74.0, 167.8.

Ethyl 2-Diazo-3-hydroxy-3-methylpentanoate (5f)

IR (neat) 3473, 2977, 2091, 1673, 1370, 1307, 1081, 745 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.94 (t, J = 7.2 Hz, 2H), 4.18 (q, J = 7.2 Hz, 2H), 4.35 (s, 1H), 7.25-7.34 (m, 3H), 7.47-7.49 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 8.8, 14.5, 25.2, 34.5, 60.9, 71.6, 167.5.

Ethyl 2-Diazo-3-hydroxy-3-phenylbutanoate (5g)

IR (neat) 3324, 2974, 2362, 2090, 1676, 1307, 1049, 731 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.21 (t, J = 7.2 Hz, 3H), 1.70 (s, 3H), 4.18 (q, J = 7.2 Hz, 2H), 4.35 (s, 1H), 7.25-7.34 (m, 3H), 7.47-7.49 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.4, 29.2, 61.1, 73.3, 124.7, 127.7, 128.5, 146.3, 167.0.
Ethyl 2-Cyclopentylidene-2-(4-methoxyphenyl)acetate (3)

IR (film) 2952, 1705, 1608, 1511, 1245, 1206, 1038, 834 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.21 (t, $J = 7.2$ Hz, 3H), 1.57-1.62 (m, 2H), 1.72-1.79 (m, 2H), 2.21 (t, $J = 7.2$ Hz, 2H), 2.84 (t, $J = 7.2$ Hz, 2H), 3.81 (s, 3H), 4.15 (q, $J = 7.2$ Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 7.08 (d, $J = 8.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.5, 26.0, 26.9, 34.1, 35.4, 55.3, 60.2, 113.5, 125.4, 130.5, 131.6, 158.4, 162.4, 167.9; MS (70 eV) m/z (%) 260 (100) ($M^+$), 231(25), 214(66), 203(9), 185(94), 171(19), 159(23); HRMS (ESI) calcd for C$_{16}$H$_{21}$O$_3$ [(M+H)$^+$] 261.1485, found: 261.1484.

Ethyl 2-Cyclohexylidene-2-(4-methoxyphenyl)acetate (6a)

IR (film) 2930, 2854, 1711, 1607, 1509, 1261, 1244, 1188, 1033, 836 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.22 (t, $J = 7.2$ Hz, 3H), 1.54-1.69 (m, 6H), 2.01 (t, $J = 6.2$ Hz, 2H), 2.48 (t, $J = 6.2$ Hz, 2H), 3.79 (s, 3H), 4.16 (q, $J = 7.2$ Hz, 2H), 6.86 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.3, 26.5, 28.32, 28.36, 32.0, 32.8, 55.3, 60.5, 113.6, 127.3, 129.8, 130.6, 148.3, 158.6, 169.7; MS (70 eV) m/z (%): 274 (100) ($M^+$), 245(11), 228(87), 217(11), 199(89), 184(19), 171(29), 159(24); HRMS (ESI) calcd for C$_{17}$H$_{23}$O$_3$ [(M+H)$^+$] 275.1641, found: 275.1644.

Ethyl 2-Cyclohexylidene-2-phenylacetate (6b)

IR (film) 2927, 2854, 1712, 1510, 1448, 1260, 1188, 1035, 732 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.22 (t, $J = 7.2$ Hz, 3H), 1.54-1.72 (m, 6H), 2.08 (t, $J = 6.2$ Hz, 2H), 2.52 (t, $J = 6.2$ Hz, 2H), 4.16 (q, $J = 7.2$ Hz, 2H), 7.19-7.34 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 26.3, 28.22, 28.25, 32.0, 32.6, 60.4, 126.9, 127.6, 128.0, 129.4, 137.4, 148.9, 169.2; MS (70 eV) m/z (%): 244 (100) ($M^+$), 229(12), 212(91), 183(64), 169(36), 155(36); HRMS (ESI) calcd for C$_{16}$H$_{21}$O$_2$ [(M+H)$^+$] 245.1536, found: 245.1529.
Ethyl 2-Cyclohexylidene-2-p-tolylacetate (6c)

IR (film) 2928, 2854, 1712, 1444, 1260, 1218, 1187, 1106, 1037, 919, 773, 700 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.23 (t, \(J = 7.2\) Hz, 3H), 1.56-1.74 (m, 6H), 2.12 (t, \(J = 6.2\) Hz, 2H), 2.36 (s, 3H), 2.51 (t, \(J = 6.2\) Hz, 2H), 4.18 (q, \(J = 7.2\) Hz, 2H), 7.10-7.17 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.1, 21.1, 26.4, 28.20, 28.23, 31.9, 32.6, 60.4, 127.5, 128.8, 129.2, 134.4, 136.5, 148.3, 169.4; MS (70 eV) \(m/z\) (%): 258 (100) (M\(^+\)), 229(12), 212(91), 183(64), 169(36), 155(36); HRMS (ESI) calcd for C\(_{17}\)H\(_{23}\)O\(_2\) [(M+H)\(^+\)] 259.1692, found: 259.1687.

Ethyl 2-Cyclohexylidene-2-m-tolylacetate (6d)

IR (film) 2927, 2855, 1713, 1447, 1261, 1203, 1037, 732 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.22 (t, \(J = 7.2\) Hz, 3H), 1.54-1.71 (m, 6H), 2.09 (t, \(J = 6.4\) Hz, 2H), 2.33 (s, 3H), 2.48 (t, \(J = 6.4\) Hz, 2H), 4.16 (q, \(J = 7.2\) Hz, 2H), 6.99-7.26 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.2, 21.4, 26.4, 28.22, 28.26, 32.0, 32.7, 60.4, 126.4, 127.7, 127.8, 127.9, 137.2, 137.6, 148.2, 169.4; MS (70 eV) \(m/z\) (%): 258 (92) (M\(^+\)), 229(12), 212(100), 203(9), 183(54), 169(46), 155(35); HRMS (ESI) calcd. for C\(_{17}\)H\(_{23}\)O\(_2\) [(M+H)\(^+\)] 259.1692, found: 259.1687.

Ethyl 2-Cyclohexylidene-2-o-tolylacetate (6e)

IR (film) 2928, 2855, 1709, 1448, 1261, 1200, 1184, 1104, 1035, 909, 733 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.19 (t, \(J = 7.2\) Hz, 3H), 1.52-1.74 (m, 6H), 1.89-1.93 (m, 2H), 2.23 (s, 3H), 2.66-2.70 (m, 2H), 4.14 (q, \(J = 7.2\) Hz, 2H), 7.08-7.20 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.1, 19.7, 26.4, 28.0, 28.2, 31.9, 32.6, 60.1, 125.4, 126.3, 127.1, 129.6, 129.8, 136.8, 137.6, 151.6, 168.4; MS (70 eV) \(m/z\) (%) 258(100) (M\(^+\)), 229(7), 212(61), 183(56), 169(22), 155(25); HRMS (ESI) calcd for C\(_{17}\)H\(_{23}\)O\(_2\) [(M+H)\(^+\)] 259.1692, found: 259.1686.
**Ethyl 2-Cyclohexylidene-2-(2,3-dimethylphenyl)acetate (6f)**

IR (film) 2927, 2854, 1710, 1448, 1262, 1198, 1094, 1033, 764, 731 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.14 (t, \(J = 7.2\) Hz, 3H), 1.43-1.69 (m, 6H), 1.82-1.86 (m, 2H), 2.09 (s, 3H), 2.24 (s, 3H), 2.58-2.61 (m, 2H), 4.07 (q, \(J = 7.2\) Hz, 2H), 6.89-7.02 (m, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.2, 16.3, 20.5, 26.4, 27.9, 28.3, 32.0, 32.5, 60.2, 125.1, 126.9, 127.6, 128.7, 135.4, 136.6, 137.6, 150.7, 168.7; MS (70 eV) \(m/z\) (%): 272 (100) (M\(^+\)), 257(5), 243(6), 226(86), 211(10), 197(45), 183(41), 169(19), 155(42); HRMS (ESI) calcd for C\(_{18}\)H\(_{25}\)O\(_2\) [(M+H)+] 273.1849, found: 273.1845.

**Ethyl 2-(Biphenyl-4-yl)-2-cyclohexylideneacetate (6g)**

IR (film) 2929, 2854, 1714, 1485, 1447, 1264, 1186, 1034, 769, 697 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.20 (t, \(J = 7.2\) Hz, 3H), 1.53-1.87 (m, 6H), 2.11 (t, \(J = 6.4\) Hz, 2H), 2.49 (t, \(J = 6.4\) Hz, 2H), 4.15 (q, \(J = 7.2\) Hz, 2H), 7.21-7.31 (m, 3H), 7.37-7.41 (m, 2H), 7.51-7.57 (m, 4H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.2, 26.4, 27.5, 28.2, 32.1, 32.7, 60.5, 126.8, 127.0, 127.2, 127.3, 128.7, 129.8, 136.4, 139.7, 140.8, 149.0, 169.3; MS (70 eV) \(m/z\) (%): 320 (100) (M\(^+\)), 291(8), 274(88), 245(46), 231(11), 217(35), 205(23), 191(25), 178(21), 165(27), 152(15); HRMS (ESI) calcd for C\(_{22}\)H\(_{25}\)O\(_2\) [(M+H)+] 321.1849, found: 321.1844.

**Ethyl 2-(4-Chlorophenyl)-2-cyclohexylideneacetate (6h)**

IR (film) 2929, 2854, 1712, 1448, 1260, 1188, 1035, 732 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.21 (t, \(J = 7.2\) Hz, 3H), 1.53-1.71 (m, 6H), 2.05 (t, \(J = 6.4\) Hz, 2H), 2.53 (t, \(J = 6.4\) Hz, 2H), 4.15 (q, \(J = 7.2\) Hz, 2H), 7.12 (d, \(J = 8.4\) Hz, 2H), 7.29 (d, \(J = 8.4\) Hz, 2H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.1, 26.3, 28.2, 32.2, 32.5, 60.5, 126.5, 128.3, 130.8, 132.9, 136.0, 150.4, 168.7; MS (70 eV) \(m/z\) (%): 278 (76) (M\(^+\)), 249(15), 232(100), 203(39), 191(6), 182(12), 169(67), 153(15); HRMS (ESI) calcd for C\(_{18}\)H\(_{20}\)ClO\(_2\) [(M+H)+] 279.1146, found: 279.1139.
Ethyl 2-Cyclohexylidene-2-(naphthalen-1-yl)acetate (6i)

IR (film) 2929, 2854, 1709, 1532, 1263, 1199, 1091, 1031, 779 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.04 (t, \(J = 7.2\) Hz, 3H), 1.39-1.42 (m, 2H), 1.53-1.56 (m, 2H), 1.72-1.85 (m, 4H), 2.68-2.75 (m, 2H), 4.03 (q, \(J = 7.2\) Hz, 2H), 7.27-7.29 (m, 1H), 7.39-7.43 (m, 3H), 7.74-7.90 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.1, 26.4, 28.2, 28.4, 32.2, 32.9, 60.3, 125.2, 125.3, 125.6, 125.7, 125.9, 127.2, 127.5, 128.1, 132.5, 133.6, 135.7, 152.8, 168.7; MS (70 eV) \(m/z\) (%): 294(100) (M\(^+\)), 265(19), 248(81), 219(73), 205(20), 191(58), 178(57), 165(65), 153(35); HRMS (ESI) calcd for C\(_{20}\)H\(_{23}\)O\(_2\) [(M+H\(^+\)] 295.1692, found: 295.1687.

Ethyl 2-Cyclohexylidene-2-(4-methoxy-2-nitrophenyl)acetate (6j)

IR (film) 2927, 2853, 1712, 1617, 1531, 1352, 1263, 1191, 1035, 733 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.24 (t, \(J = 7.2\) Hz, 3H), 1.56-1.71 (m, 6H), 2.07 (t, \(J = 6.0\) Hz, 2H), 2.58 (t, \(J = 6.0\) Hz, 2H), 3.97 (s, 3H), 4.16 (q, \(J = 7.2\) Hz, 2H), 7.05 (d, \(J = 8.4\) Hz 1H), 7.37 (dd, \(J = 8.4, 1.6\) Hz, 1H), 7.70 (d, \(J = 2.0\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.3, 26.3, 28.3, 32.6, 56.6, 60.8, 113.2, 125.1, 126.9, 130.2, 135.5, 139.3, 152.0, 152.5, 168.4; MS (70 eV) \(m/z\) (%) 319 (13) (M\(^+\)), 302(100), 285(3), 273(23), 256(6), 244(8), 228(18), 210(10), 199(28), 184(7), 169(12), 153(10); HRMS (ESI) calcd. for C\(_{17}\)H\(_{22}\)NO\(_5\) [(M+H\(^+\)] 320.1492, found: 320.1489.

Ethyl 2-(4-Methoxyphenyl)-2-(4-methylcyclohexylidene)acetate (6k)

IR (film) 2952, 2923, 2850, 1731, 1607, 1510, 1457, 1244, 1185, 1034, 835 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.91 (d, \(J = 6.4\) Hz, 3H), 1.22 (t, \(J = 7.2\) Hz, 3H), 1.57-1.74 (m, 6H), 1.80-1.87 (m, 1H), 2.39-2.42 (m, 1H), 2.90-2.94 (m 1H), 3.80 (s, 3H), 4.16 (q, \(J = 7.2\) Hz, 2H), 6.86 (d, \(J = 8.4\) Hz, 2H), 7.12 (d, \(J = 8.4\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.3, 21.8, 31.4, 32.1, 32.5, 36.3, 36.4, 55.3, 60.6, 113.6, 127.4, 129.9, 130.6, 140.8, 158.7, 169.7; MS (70 eV) \(m/z\) (%): 288 (100) (M\(^+\)), 259(11), 242(89), 213(67), 187(11), 171(39); HRMS (ESI) calcd for C\(_{18}\)H\(_{24}\)NaO\(_3\) [(M+Na\(^+\)]
311.1617, found: 311.1616.

**Ethyl 2-(4-tert-Butylecyclohexylidene)-2-(4-methoxyphenyl)acetate (6l)**

IR (film) 2949, 2968, 2087, 1681, 1366, 1291, 1084, 1058, 747 cm⁻¹; 
¹H NMR (400 MHz, CDCl₃) δ 0.85 (s, 9H), 1.21-1.25 (m, 4H), 1.75-2.03 (m, 6H), 2.46-2.50 (m, 1H), 3.01-3.04 (m, 1H), 2.90-2.94 (m, 1H), 3.80 (s, 3H), 4.16 (q, J = 7.2 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.3, 27.7, 28.9, 29.0, 31.9, 32.5, 32.6, 41.8, 55.3, 60.6, 113.6, 127.0, 129.9, 130.7, 148.6, 158.6, 169.7; MS (70 eV) m/z (%): 330 (100) (M⁺), 315(2), 301(5), 284(95), 269(5), 256(21), 241(11), 227(22), 199(89), 185(18), 172(19); HRMS (ESI) calcd for C₂₁H₃₁O₃ [(M+H)⁺] 331.2267, found: 331.2266.

**Ethyl 2-(4-Methoxyphenyl)-2-(4-phenylcyclohexylidene)acetate (6m)**

IR (film) 2952, 2923, 2850, 1713, 1713, 1509, 1457, 1244, 1185, 1034, 835 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.24 (t, J = 7.2 Hz, 3H), 1.53-1.59 (m, 1H), 1.71-1.75 (m, 1H), 1.93-2.10 (m, 4H), 2.68-2.80 (m, 2H), 3.09-3.12 (m, 1H), 3.81 (s, 3H), 4.18 (q, J = 7.2 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 7.16-7.22 (m, 5H), 7.27-7.31(m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.3, 31.8, 32.5, 35.3, 35.4, 55.3, 60.7, 113.7, 126.2, 126.9, 128.5, 128.7, 129.6, 130.6, 146.3, 146.8, 158.8, 169.6; MS (70 eV) m/z (%): 350 (100) (M⁺), 304(39), 277(22), 194(21), 173(41), 159(22); HRMS (ESI) calcd for C₂₃H₂₆NaO₃ [(M+Na)⁺] 373.1774, found: 373.1779.

**Ethyl 3-Ethyl-2-(4-methoxyphenyl)pent-2-enoate (6n)**

IR (film) 2966, 2917, 1712, 1607, 1509, 1244, 1204, 1105, 1032, 836, 808 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.94 (t, J = 7.6 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H), 2.01 (q, J = 7.2 Hz, 2H), 2.40 (q, J = 7.2 Hz, 2H), 3.80 (s, 3H), 4.14 (q, J = 7.2 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 12.9, 13.4, 14.3, 25.6, 25.8, 55.3, 60.4, 113.6, 127.8, 129.6, 130.5, 152.9, 158.6, 169.3; MS (70 eV) m/z (%):
262 (100) (M⁺), 233(16), 216(83), 205(19), 197(83), 187(83), 173(56), 159(83); HRMS (ESI) calcd for C₁₆H₂₃O₃ [(M+H)+] 263.1641, found: 263.1637.

**Ethyl 2-(4-Methoxyphenyl)-3-methylpent-2-enoate (6o, E/Z isomers E:Z=1:2.5)**

IR (film) 2929, 1711, 1510, 1245, 1208, 1031, 836, 733 cm⁻¹; 
¹H NMR (400 MHz, CDCl₃) δ 1.14 (t, J = 7.6 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H), 1.68 (s, 3H), 2.38 (q, J = 7.2 Hz, 2H), 3.81 (s, 3H), 4.14 (q, J = 7.2 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 12.6, 13.1, 14.3, 19.6, 19.9, 29.1, 29.4, 55.3, 60.51, 60.54, 113.6, 129.7, 130.4, 130.5, 130.6, 147.4, 148.4, 158.6, 169.3; MS (70 eV) m/z (%): 248 (100) (M⁺), 219(6), 202(62), 191(23), 173(95), 159(72); HRMS (ESI) calcd for C₁₅H₂₁O₃ [(M+H)+] 249.1485, found: 249.1481.

**References**
