Stereoselective Synthesis of Chiral 3-Aryl-1-Alkynes from Bromoallenes and Heterocuprates.

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General remarks. Infrared absorption spectra (FTIR) were recorded as neat films, and only noteworthy absorptions (cm⁻¹) are listed. NMR spectra were recorded in CDCl₃ solution at 300 or 200 MHz (¹H) and 50.3 MHz (¹³C). Chemical shifts were determined relative to internal Si(CH₃)₄ (δ = 0 ppm) and coupling constants *J* are in Hz. GC analyses were performed on a chromatograph equipped with a flame ionisation detector (FID), using a SiO₂ “Wide Bore” column (DB1, 30m × 0.53mm, 5μm) and helium as carrier gas. Preparative GC were performed with SE-30 and Carbowax 20M as stationary phases (3m × 0.8cm columns). Optical rotations were measured with an automatic polarimeter, using standard cuvettes (*l* = 0.1 and 1dm). Analytical thin-layer chromatography (TLC) was performed on aluminium sheets precoated (0.25 mm) with silica gel and preparative column chromatography on Fluka silica gel 60 (230-400 mesh). Microanalyses were accomplished at the Faculty of Pharmacy, Pisa University.

All air- or moisture-sensitive reactions were carried out in flame-dried glassware under a dry argon or nitrogen atmosphere. Solvents were reagent-grade materials, purified by standard methods, redistilled and stored under argon. The racemic 1-bromo-1,2-dienes, **1a-e**, were made and purified as previously described (70-85% yield)¹ from the appropriate propargylic alcohols. (S)-1-bromo-1,2-dienes, **(S)-1a-d**, were synthesized from the optically active (R)-carbinols² by reacting the corresponding methanesulfonate esters with LiCuBr₂ or Li₂CuBr₃.^{1c,d} The enantiomeric purities of compounds **(S)-1a-d** (Table 2) were determined by GC analyses on a Cydex-B chiral column [25m × 0.33mm, 0.25μm heptakis(2,3,6-tri-O-methyl)-β-cyclodextrin as stationary phase] and/or ¹H NMR in CD₃OD as solvent and heptakis(2,3,6-tri-O-methyl)-β-cyclodextrin as chiral solvating agent.^{2e,3} The arylbromocuprates **2** were prepared by adding, at 0°C, 1 molar equivalent of ArMgBr to a well stirred tetrahydrofuran (THF) solution of LiCuBr₂, made from stoichiometric amounts of cuprous bromide

and lithium bromide; stirring was continued at 0°C for 30 min, and the mixture then used *immediately*. The aryl Grignard reagents ArMgBr were prepared in THF from the corresponding arylbromides, generally purchased from Fluka, and standardized by titration methods. 4-Bromo-*iso*-butylbenzene was obtained by a published procedure⁴ starting from commercially available *iso*-butylbenzene. Zinc cyanocuprates **5** were prepared by stirring, at -10°C, the alkylzinc-chlorides RZnCl with a stoichiometric amount of a THF solution of CuCN·2LiCl;⁵ stirring was continued at 0°C during 30 min, then the mixture was used *immediately*. The starting alkylzinc-chlorides were obtained by transmetallation with ZnCl₂ of the corresponding Grignard reagents, prepared in diethyl ether or THF by commercially available bromides or chlorides. The Grignard reagents from 3-chloro-1-propanol⁶ (entries 4 and 5 in Table 3) and 4-bromo-1-trimethylsilyl-1-butyne⁷ (entry 8 in Table 3,) were prepared in THF according to previously reported procedures. 4-Bromo-1-trimethylsilyl-1-butyne was synthesized by a published procedure starting from 3-butyne-1-ol.⁸ (+)-Dehydroabietylamine was a commercial product, purified by a published procedure.⁹ Commercial lithium chloride, lithium bromide, cuprous bromide, cuprous cyanide, heptakis(2,3,6-tri-O-methyl)- β -cyclodextrin, (R)-1-(1-naphthyl)ethylamine and other chemicals were used as purchased.

Spectroscopic and analytical data for all new acetylenic derivatives **3**

All compounds showed characteristic IR bands in the 3295-3310 cm⁻¹ ($\equiv$ C-H stretching), 2100-2110 cm⁻¹ (C $\equiv$ C stretching), and 630-645 cm⁻¹ ($\equiv$ C-H bending) regions.

3-[4-(2-Methylpropyl)phenyl]-1-butyne (3ad): ¹H NMR δ 0.89 (d, J = 6.6 Hz, 6H), 1.50 (d, J = 7.0 Hz, 3H), 1.84 (m, 1H), 2.25 (d, J = 2.5 Hz, 1H), 2.45 (d, J = 7.2 Hz, 2H), 3.74 (dq, J = 2.5, 7.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H); ¹³C NMR δ 22.2, 24.1, 30.1, 31.1, 44.9, 69.9 ($\equiv$ CH), 87.4 (-C $\equiv$), 126.6, 129.4, 140.0, 140.3; GC-MS(EI) m/z (rel int) 186 (M⁺, 47), 171 (27), 143 (100), 129 (77), 128 (64), 115 (16), 91 (14), 77 (8), 63 (6), 51 (5). Anal. Calcd. for C₁₄H₁₈: C, 90.26; H, 9.74. Found: C, 90.30; H, 9.70.

3-(2-Methoxyphenyl)-1-butyne (3ae): ^1H NMR δ 1.43 (d, $J = 7.0$ Hz, 3H), 2.19 (d, $J = 2.4$ Hz, 1H), 3.79 (s, 3H), 4.19 (dq, $J = 2.4, 7.0$ Hz, 1H), 6.80-7.60 (m, 4H); ^{13}C NMR δ 22.5, 25.1, 55.2, 69.2 ($\equiv\text{CH}$), 87.6 ($-\text{C}\equiv$), 110.4, 120.8, 127.7, 127.9, 131.1, 156.2; GC-MS(EI) m/z (rel int) 160 (M^+ , 43), 145 (100), 127 (13), 115 (59), 102(17), 91 (36), 77 (17), 63 (14), 51 (14). Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{O}$: C, 82.46; H, 7.55. Found: C, 82.48; H, 7.56.

3-(1-Naphthyl)-1-butyne (3ai): ^1H NMR δ 1.60 (d, $J = 7.0$ Hz, 3H), 2.28 (d, $J = 2.5$ Hz, 1H), 4.46 (dq, $J = 2.5, 7.0$ Hz, 1H), 7.30-8.20 (m, 7H); ^{13}C NMR δ 22.9, 28.0, 70.4 ($\equiv\text{CH}$), 87.2 ($-\text{C}\equiv$), 123.0, 124.2, 125.6, 125.7, 126.1, 127.7, 129.1, 130.5, 134.1, 138.3; GC-MS(EI) m/z (rel int) 180 (M^+ , 25), 179 (24), 165 (100), 89 (7), 83 (6). Anal. Calcd. for $\text{C}_{14}\text{H}_{12}$: C, 93.29; H, 6.71. Found: C, 93.28; H, 6.72.

3-(2-Naphthyl)-1-butyne (3aj): ^1H NMR δ 1.57 (d, $J = 7.1$ Hz, 3H), 2.32 (d, $J = 2.5$ Hz, 1H), 3.91 (dq, $J = 2.5, 7.1$ Hz, 1H), 7.46 (m, 3H), 7.80 (m, 4H); ^{13}C NMR δ 23.9, 31.6, 70.4 ($\equiv\text{CH}$), 87.0 ($-\text{C}\equiv$), 125.2, 125.5, 125.8, 126.2, 127.7, 127.9, 128.4, 132.6, 133.6, 140.1; GC-MS(EI) m/z (rel int) 180 (M^+ , 50), 165 (100), 152 (4), 115 (7), 89 (10), 83 (7), 76 (7), 63 (5). Anal. Calcd. for $\text{C}_{14}\text{H}_{12}$: C, 93.29; H, 6.71. Found: C, 93.32; H, 6.68.

3-[(6-Methoxy)-2-naphthyl]-1-butyne (3ak): ^1H NMR δ 1.58 (d, $J = 7.1$ Hz, 3H), 2.31 (d, $J = 2.4$ Hz, 1H), 3.90 (dq, $J = 2.4, 7.1$ Hz, 1H), 3.91 (s, 3H), 7.12-7.76 (m, 6H); ^{13}C NMR δ 24.0, 31.4, 55.2, 70.2 ($\equiv\text{CH}$), 87.2 ($-\text{C}\equiv$), 105.6, 119.0, 125.4, 126.0, 127.3, 129.3, 129.5, 133.6, 137.9, 157.7; GC-MS(EI) m/z (rel int) 210 (M^+ , 64), 195 (100), 165 (10), 152 (24). Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{O}$: C, 85.68; H, 6.71. Found: C, 85.71; H, 6.73.

3-(2-Methoxyphenyl)-4,4-dimethyl-1-pentyne (3be): ^1H NMR δ 0.98 (s, 9H), 2.11 (d, $J = 2.6$ Hz, 1H), 3.76 (s, 3H), 4.15 (d, $J = 2.6$ Hz, 1H), 6.80-7.50 (m, 4H); ^{13}C NMR δ 27.1, 35.4, 39.8, 55.0, 69.7

($\equiv\text{CH}$), 86.5 ($-\text{C}\equiv$), 110.2, 120.1, 127.9, 129.6, 130.7, 157.0; GC-MS(EI) m/z (rel int) 202 (M^+ , 11), 187 (23), 172 (6), 146 (29), 145 (42), 131 (100), 115 (44), 102 (21), 91 (32), 76 (13), 57 (95). Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}$: C, 83.12; H, 8.97. Found: C, 83.15; H, 9.00.

3-(4-Methoxyphenyl)-4,4-dimethyl-1-pentyne (3bf): ^1H NMR δ 0.96 (s, 9H), 2.24 (d, $J = 2.6$ Hz, 1H), 3.37 (d, $J = 2.6$ Hz, 1H), 3.79 (s, 3H), 6.83 (m, 2H), 7.23 (m, 2H); ^{13}C NMR δ 27.3, 34.7, 48.6, 55.1, 71.2 ($\equiv\text{CH}$), 85.7 ($-\text{C}\equiv$), 113.1, 130.6, 134.8, 158.7; GC-MS(EI) m/z (rel int) 202 (M^+ , 11), 187 (5), 146 (49), 145 (100), 131 (7), 102 (9), 57 (28). Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}$: C, 83.12; H, 8.97. Found: C, 83.17; H, 8.99.

3-(4-Dimethylaminophenyl)-4,4-dimethyl-1-pentyne (3bh): ^1H NMR δ 0.96 (s, 9H), 2.21 (d, $J = 2.6$ Hz, 1H), 2.93 (s, 6H), 3.33 (d, $J = 2.6$ Hz, 1H), 6.73 (m, 2H), 7.24 (m, 2H); GC-MS(EI) m/z (rel. int.) 215 (M^+ , 8), 158 (100), 142 (10), 115 (7). Anal. Calcd. for $\text{C}_{15}\text{H}_{21}\text{N}$: C, 83.67; H, 9.83; N, 6.50. Found: C, 83.65; H, 9.82; N, 6.53.

3-(1-Naphthyl)-4,4-dimethyl-1-pentyne (3bi): ^1H NMR δ 1.03 (s, 9H), 2.22 (d, $J = 2.5$ Hz, 1H), 4.48 (d, $J = 2.5$ Hz, 1H), 7.40-8.30 (m, 7H); ^{13}C NMR δ 27.9, 36.4, 42.6, 70.6 ($\equiv\text{CH}$), 86.7 ($-\text{C}\equiv$), 124.0, 125.3, 125.5, 126.2, 127.9, 128.1, 129.3, 131.7, 132.5, 134.0; GC-MS(EI) m/z (rel int) 222 (M^+), 207 (25), 165 (79), 164 (32), 163 (55), 141 (21), 139 (14), 126 (13), 67 (32), 57 (71), 41 (100). Anal. Calcd. for $\text{C}_{17}\text{H}_{18}$: C, 91.84; H, 8.16. Found: C, 91.88; H, 8.12.

3-(2-Naphthyl)-4,4-dimethyl-1-pentyne (3bj): ^1H NMR δ 1.03 (s, 9H), 2.30 (d, $J = 2.4$ Hz, 1H), 3.59 (d, $J = 2.4$ Hz, 1H), 7.40-7.90 (m, 7H); ^{13}C NMR δ 27.5, 35.1, 46.9, 71.6 ($\equiv\text{CH}$), 85.4 ($-\text{C}\equiv$), 125.8, 126.0, 127.2, 127.7, 128.0, 128.1, 128.4, 132.6, 133.1, 136.6; GC-MS(EI) m/z (rel int) 222 (M^+ , 7), 207 (12), 165 (100), 152 (8), 128 (10), 57 (45), 41 (30). Anal. Calcd. for $\text{C}_{17}\text{H}_{18}$: C, 91.84; H, 8.16. Found: C, 91.91; H, 8.09.

3-(2-Methoxyphenyl)-3-methyl-1-pentyne (3ce): ^1H NMR δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.72 (s, 3H), 1.92 (q, $J = 7.0$ Hz, 2H), 2.33 (s, 1H), 3.73 (s, 3H), 6.80-7.40 (m, 4H); GC-MS(EI) m/z (rel int) 188 (M^+ , 11), 159 (73), 144 (100), 128 (14), 115 (45), 103(6), 91 (8), 77 (19), 63 (16), 51 (22). Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 82.94; H, 8.57. Found: C, 83.00; H, 8.60.

3-(4-Methoxyphenyl)-3-methyl-1-pentyne (3cf): ^1H NMR δ 0.86 (t, $J = 7.3$ Hz, 3H), 1.55 (s, 3H), 1.79 (q, $J = 7.3$ Hz, 2H), 2.36 (s, 1H), 3.76 (s, 3H), 6.85 (m, 2H), 7.43 (m, 2H); ^{13}C NMR δ 9.5, 29.6, 36.8, 40.1, 55.0, 71.1 ($\equiv\text{CH}$), 89.6 ($-\text{C}\equiv$), 113.5, 127.2, 137.1, 158.3; GC-MS(EI) m/z (rel int) 188 (M^+ , 13), 159 (100), 115 (10). Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 82.94; H, 8.57. Found: C, 83.01; H, 8.60.

3-(1-Naphthyl)-3-methyl-1-pentyne (3ci): ^1H NMR δ 0.96 (t, $J = 7.4$ Hz, 3H), 1.83 (s, 3H), 1.94 (m, 2H), 2.40 (s, 1H), 7.36-8.30 (m, 7H); ^{13}C NMR δ 9.4, 28.0, 34.7, 39.3, 71.5 ($\equiv\text{CH}$), 90.6 ($-\text{C}\equiv$), 123.9, 125.0, 125.2, 125.6, 126.5, 128.4, 129.4, 131.2, 134.8, 135.0; GC-MS(EI) m/z (rel int) 208 (M^+ , 14), 193 (17), 179 (100), 178 (29), 165 (7), 152 (9).

3-(2-Naphthyl)-3-methyl-1-pentyne (3cj): ^1H NMR δ 0.88 (t, $J = 7.4$ Hz, 3H), 1.65 (s, 3H), 1.91 (q, $J = 7.4$ Hz, 2H), 2.45 (s, 1H), 7.37-8.03 (m, 7H); ^{13}C NMR δ 9.6, 29.6, 36.4, 41.0, 71.7 ($\equiv\text{CH}$), 89.3 ($-\text{C}\equiv$), 124.4, 125.0, 125.7, 126.1, 127.5, 127.9, 128.2, 132.3, 133.4, 142.2; GC-MS(EI) m/z (rel int) 208 (M^+ , 9), 179 (100), 165 (6), 152 (12), 128 (7), 51 (7). Anal. Calcd. for $\text{C}_{16}\text{H}_{16}$: C, 92.26; H, 7.74. Found: C, 92.30; H, 7.70.

3-(2-Ethylphenyl)-3,4,4-trimethyl-1-pentyne (3db): ^1H NMR δ 0.92 (s, 9H), 1.17 (t, $J = 7.5$ Hz, 3H), 1.69 (s, 3H), 2.27 (s, 1H), 2.57 (q, $J = 7.5$, 2H), 7.10 (m, 4H). GC-MS(EI) m/z (rel int) 214 (M^+), 199 (19), 164 (22), 157 (55), 143 (60), 142 (42), 129 (15), 57 (100), 41 (38). Anal. Calcd. for $\text{C}_{16}\text{H}_{22}$: C, 89.65; H, 10.35. Found: C, 89.59; H, 10.41.

3-(4-Ethylphenyl)-3,4,4-trimethyl-1-pentyne (3dc): ^1H NMR δ 0.89 (s, 9H), 1.15 (t, $J = 7.6$ Hz, 3H), 1.56 (s, 3H), 2.24 (s, 1H), 2.55 (q, $J = 7.6$ Hz, 2H), 7.03 (m, 2H), 7.36 (m, 2H); ^{13}C NMR δ 15.4, 23.4, 26.3, 28.3, 36.9, 47.0, 70.9 ($\equiv\text{CH}$), 90.3 ($-\text{C}\equiv$), 126.4, 128.5, 139.7, 142.1. GC-MS(EI) m/z (rel int) 214 (M^+ , 10), 199 (30), 184 (15), 158 (62), 157 (84), 143 (41), 142 (27), 129 (19), 128 (7), 57 (100), 41 (36). Anal. Calcd. for $\text{C}_{16}\text{H}_{22}$: C, 89.65; H, 10.35. Found: C, 89.66; H, 10.34.

3-(2-Methoxyphenyl)-3,4,4-trimethyl-1-pentyne (3de): ^1H NMR δ 0.99 (s, 9H), 1.83 (s, 3H), 2.35 (s, 1H), 3.72 (s, 3H), 6.80-7.40 (m, 4H); ^{13}C NMR δ 24.4, 26.4, 38.4, 48.2, 55.0, 71.0 ($\equiv\text{CH}$), 91.6 ($-\text{C}\equiv$), 112.4, 119.7, 128.1, 130.0, 133.2, 158.7; GC-MS(EI) m/z (rel int) 201 (M^+ -15, 16), 186 (10), 159 (44), 145 (100), 144 (89), 128 (10), 115 (54), 91 (22), 77 (11), 65 (12), 57 (42), 41 (46). Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}$: C, 83.28; H, 9.32. Found: C, 83.31; H, 9.32.

3-(4-Methoxyphenyl)-3,4,4-trimethyl-1-pentyne (3df): ^1H NMR δ 0.95 (s, 9H), 1.63 (s, 3H), 2.32 (s, 1H), 3.78 (s, 3H), 6.75-7.60 (m, 4H); ^{13}C NMR δ 23.3, 26.0, 36.9, 46.5, 55.0, 70.9 ($\equiv\text{CH}$), 90.3 ($-\text{C}\equiv$), 112.4, 129.7, 134.8, 158.2; GC-MS(EI) m/z (rel int) 216 (M^+ , 9), 201 (6), 187 (5), 160 (65), 159 (100), 145 (16), 128 (10), 115 (30), 89 (5), 77 (6), 57 (19), 41 (17). Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}$: C, 83.28; H, 9.32. Found: C, 83.40; H, 9.34.

3-(4-Fluorophenyl)-3,4,4-trimethyl-1-pentyne (3dg): ^1H NMR δ 0.96 (s, 9H), 1.64 (s, 3H), 2.35 (s, 1H), 6.97 (m, 2H), 7.50 (m, 2H); ^{13}C NMR δ 23.3, 26.0, 36.9, 46.8, 71.3 ($\equiv\text{CH}$), 89.9 ($-\text{C}\equiv$), 113.8 (d, $J_{\text{CF}} = 21$ Hz), 130.3 (d, $J_{\text{CF}} = 7.7$ Hz), 138.4 (d, $J_{\text{CF}} = 3.4$ Hz), 161.7 (d, $J_{\text{CF}} = 245$ Hz); GC-MS(EI) m/z (rel int) 204 (M^+ , 4), 201 (6), 189 (10), 174 (6), 161 (7), 148 (62), 147 (50), 146 (24), 133 (21), 109 (6), 75 (6), 57 (100), 41 (33). Anal. Calcd. for $\text{C}_{14}\text{H}_{17}\text{F}$: C, 82.31; H, 8.39. Found: C, 82.27; H, 8.40.

3-(4-Dimethylaminophenyl)-3,4,4-trimethyl-1-pentyne (3dh): ^1H NMR δ 0.96 (s, 9H), 1.62 (s, 3H), 2.30 (s, 1H), 2.93 (s, 6H), 6.74 (m, 2H), 7.24 (m, 2H); GC-MS(EI) m/z (rel int) 229 (M^+ , 4), 214 (1), 199 (1), 172 (100), 156 (4), 128 (4). Anal. Calcd. for $\text{C}_{16}\text{H}_{23}\text{N}$: C, 83.79; H, 10.11; N, 6.11. Found: C, 83.70; H, 10.09; N, 6.21.

3-(2-Naphthyl)-3,4,4-trimethyl-1-pentyne (3dj): ^1H NMR δ 1.01 (s, 9H), 1.76 (s, 3H), 2.41 (s, 1H), 7.40-7.90 (m, 7H); GC-MS(EI) m/z (rel int) 236 (M^+ , 9), 180 (66), 179 (100), 178 (40), 165 (24), 152 (9), 128 (10), 115 (6), 57 (41), 41 (24). Anal. Calcd. for $\text{C}_{18}\text{H}_{20}$: C, 91.47; H, 8.53. Found: C, 91.45; H, 8.55.

3-[(6-Methoxy)-2-naphthyl]-3,4,4-trimethyl-1-pentyne (3dk): ^1H NMR δ 0.93 (s, 9H), 1.67 (s, 3H), 2.33 (s, 1H), 3.89 (s, 3H), 7.03-7.82 (m, 6H); GC-MS(EI) m/z (rel int) 266 (M^+ , 8) 209 (100), 165 (13), 57 (8). Anal. Calcd. for $\text{C}_{19}\text{H}_{22}\text{O}$: C, 85.67; H, 8.32. Found: C, 85.70; H, 8.35.

Spectroscopic and analytical data for all new allenic derivatives 4:

All compounds showed a characteristic IR band in the $1945\text{-}1955\text{ cm}^{-1}$ region ($\text{C}=\text{C}=\text{C}$ stretching).

1-[4-(2-Methylpropyl)phenyl]-1,2-butadiene (4ad): GC-MS(EI) m/z (rel int) 186 (M^+ , 39), 143 (100), 128 (55), 115 (13), 91 (6), 77 (4), 51 (4).

1-(2-Methoxyphenyl)-1,2-butadiene (4ae): ^1H NMR δ 1.76 (dd, $J = 3.3, 7.0\text{ Hz}$, 3H), 3.77 (s, 3H), 5.49 (m, 1H), 6.50 (dq, $J = 3.3, 7.0\text{ Hz}$, 1H), 6.80-7.60 (m, 4H); GC-MS(EI) m/z (rel int) 160 (M^+ , 25), 145 (100), 128 (13), 117 (34), 115 (71), 102(24), 91 (37), 75 (12), 63 (20), 51 (18).

1-(1-Naphthyl)-1,2-butadiene (4ai): ^1H NMR δ 1.78 (dd, $J = 3.2, 7.1$ Hz, 3H), 5.52 (m, 1H), 6.76 (dq, $J = 3.2, 7.1$ Hz, 1H), 7.30-8.20 (m, 7H); ^{13}C NMR δ 13.9, 88.5 ($\underline{\text{CH}}=\text{C}=\text{}$), 90.6 ($=\text{C}=\underline{\text{CH}}$), 123.7, 125.4, 125.7, 126.0, 127.4, 128.7, 131.0, 131.4, 134.0, 208.0 ($=\text{C}=\text{}$); GC-MS(EI) m/z (rel int) 180 (M^+ , 49), 179 (66), 165 (100), 152 (16), 89 (15), 83 (6), 76 (11), 63 (6). Anal. Calcd. for $\text{C}_{14}\text{H}_{12}$: C, 93.29; H, 6.71. Found: C, 93.09; H, 6.89.

1-(2-Naphthyl)-1,2-butadiene (4aj): ^1H NMR δ 1.84 (dd, $J = 3.2, 7.2$ Hz, 3H), 5.61 (m, 1H), 6.27 (dq, $J = 3.2, 7.0$ Hz, 1H), 7.35-7.85 (m, 7H); GC-MS(EI) m/z (rel int) 180 (M^+ , 81), 165 (100), 152 (10), 139 (5), 115 (7), 89 (15), 83 (5), 76 (12), 63 (5), 51 (4).

1-[(6-Methoxy)-2-naphthyl]-1,2-butadiene (4ak): ^1H NMR δ 1.82 (dd, $J = 3.2, 7.0$ Hz, 3H), 3.91 (s, 3H), 5.60 (m, 1H), 6.24 (dq, $J = 3.2, 7.0$ Hz, 1H), 7.10-7.80 (m, 6H); MS(EI) m/z (rel int) 210 (M^+ , 70), 195 (100), 165 (35), 152 (8), 139 (3), 89 (10).

1-(2-Methoxyphenyl)-4,4-dimethyl-1,2-pentadiene (4be): ^1H NMR δ 1.12 (s, 9H), 3.81 (s, 3H), 5.53 (d, $J = 6.4$ Hz, 1H), 6.60 (d, $J = 6.4$ Hz, 1H), 6.80-7.50 (m, 4H); ^{13}C NMR δ 30.2, 32.5, 55.4, 90.0 ($\underline{\text{CH}}=\text{C}=\text{}$), 106.2 ($=\text{C}=\underline{\text{CH}}$), 111.0, 120.8, 123.4, 127.7, 130.7, 156.1, 203.1 ($=\text{C}=\text{}$); GC-MS(EI) m/z (rel int) 202 (M^+ , 40), 187 (39), 172 (9), 159 (7), 145 (34), 131 (100), 115 (58), 102 (32), 91 (30), 77 (19), 57 (83). Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}$: C, 83.12; H, 8.97. Found: C, 82.98; H, 8.95.

1-(4-Methoxyphenyl)-4,4-dimethyl-1,2-pentadiene (4bf): ^1H NMR δ 1.11 (s, 9H), 3.80 (s, 3H), 5.54 (d, $J = 6.3$ Hz, 1H), 6.15 (d, $J = 6.3$ Hz, 1H), 6.80-7.30 (m, 4H); ^{13}C NMR δ 30.1, 32.4, 55.2, 95.6 ($\underline{\text{CH}}=\text{C}=\text{}$), 106.9 ($=\text{C}=\underline{\text{CH}}$), 114.2, 127.6, 131.1, 158.7, 202.1 ($=\text{C}=\text{}$); GC-MS(EI) m/z (rel int) 202 (M^+ , 43), 187 (12), 145 (100), 131 (6), 115 (6), 102 (8), 77 (6), 57 (39).

1-(4-Dimethylaminophenyl)-4,4-dimethyl-1,2-pentadiene (4bh): ^1H NMR δ 1.11 (s, 9H), 2.93 (s, 6H), 5.53 (d, J = 6.4 Hz, 1H), 6.60 (d, J = 6.4 Hz, 1H), 6.69 (m, 2H), 7.18 (m, 2H); GC-MS(EI) m/z (rel int) 215 (M^+ , 30), 200(7), 158 (100), 142 (9), 115 (8).

1-(1-Naphthyl)-4,4-dimethyl-1,2-pentadiene (4bi): ^1H NMR δ 1.16 (s, 9H), 5.62 (d, J = 6.4 Hz, 1H), 6.91 (d, J = 6.4 Hz, 1H), 7.44-8.32 (m, 7H); ^{13}C NMR δ 30.3, 32.8, 92.9 ($\text{CH}=\text{C}=\text{}$), 106.2 ($=\text{C}=\text{CH}$), 123.8, 125.0, 125.9, 126.0 (2C), 127.5, 128.9, 131.1, 134.3, 136.0, 204.5 ($=\text{C}=\text{}$); GC-MS(EI) m/z (rel int) 222 (M^+ , 16), 207 (45), 192 (10), 179 (31), 165 (100), 164 (27), 163 (35), 152 (24), 139 (14), 115 (14), 89 (8), 75 (8), 57 (50), 41 (45). Anal. Calcd. for $\text{C}_{17}\text{H}_{18}$: C, 91.84; H, 8.16. Found: C, 91.73; H, 8.21.

1-(2-Naphthyl)-4,4-dimethyl-1,2-pentadiene (4bj): ^1H NMR δ 1.16 (s, 9H), 5.64 (d, J = 6.3 Hz, 1H), 6.37 (d, J = 6.3 Hz, 1H), 7.40-7.90 (m, 7H); ^{13}C NMR δ 96.6 ($\text{CH}=\text{C}=\text{}$), 107.2 ($=\text{C}=\text{CH}$), 203.5 ($=\text{C}=\text{}$); GC-MS(EI) m/z (rel int) 222 (M^+ , 26), 207 (47), 192 (12), 179 (30), 165 (100), 164 (40), 152 (20), 139 (10), 89 (6), 57 (52).

1-(2-Methoxyphenyl)-3-methyl-1,2-pentadiene (4ce): ^1H NMR δ 1.05 (t, J = 7.4 Hz, 3H), 1.79 (d, J = 3.0 Hz, 3H), 2.07 (dq, J = 3.0, 7.4 Hz, 2H), 3.78 (s, 3H), 6.50 (m, 1H), 6.70-7.50 (m, 4H); ^{13}C NMR δ 12.1, 18.5, 26.9, 55.4, 88.1 ($\text{C}=\text{C}=\text{}$), 104.6 ($=\text{C}=\text{CH}$), 110.9, 120.7, 124.5, 127.5 (2C), 156.1, 202.9 ($=\text{C}=\text{}$); GC-MS(EI) m/z (rel int) 188 (M^+ , 26), 173 (100), 159 (40), 158 (34), 144(20), 131 (39), 115 (56), 102 (9), 91 (45), 89 (22), 77 (25), 63 (23). Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 82.94; H, 8.57. Found: C, 82.86; H, 8.60.

1-(4-Methoxyphenyl)-3-methyl-1,2-pentadiene (4cf): ^1H NMR δ 1.05 (t, J = 7.3 Hz, 3H), 1.79 (d, J = 3.0 Hz, 3H), 2.07 (dq, J = 3.0, 7.3 Hz, 2H), 3.74 (s, 3H), 6.05 (m, 1H), 6.81 (m, 2H), 7.19 (m, 2H); ^{13}C NMR δ 12.1, 18.6, 27.1, 55.1, 93.9 ($\text{C}=\text{C}=\text{}$), 105.3 ($=\text{C}=\text{CH}$), 114.1, 127.5, 128.6, 158.6,

201.9 (=C=); GC-MS(EI) m/z (rel int) 188 (M^+ , 31), 173 (100), 159 (38), 158 (40), 144 (16), 115 (42), 91 (18).

1-(1-Naphthyl)-3-methyl-1,2-pentadiene (4ci): ^1H NMR δ 1.10 (t, J = 7.3 Hz, 3H), 1.86 (d, J = 3.0 Hz, 3H), 2.13 (dq, J = 3.0, 7.3 Hz, 2H), 6.78 (m, 1H), 7.37-8.28 (m, 7H); ^{13}C NMR δ 12.1, 18.7, 27.1, 91.0 ($\text{C}=\text{C}=\text{}$), 104.2 ($=\text{C}=\text{CH}$), 123.8, 125.1, 125.6, 125.7, 125.9, 127.1, 128.7, 131.0, 132.4, 134.1, 204.3 (=C=); GC-MS(EI) m/z (rel int) 208 (M^+ , 53), 193 (45), 179 (100), 178 (40), 165 (14), 152 (17), 89 (6). Anal. Calcd. for $\text{C}_{16}\text{H}_{16}$: C, 92.26; H, 7.74. Found: C, 92.17; H, 7.83.

1-(2-Naphthyl)-3-methyl-1,2-pentadiene (4cj): ^1H NMR δ 1.08 (t, J = 7.3 Hz, 3H), 1.85 (d, J = 3.0 Hz, 3H), 2.12 (dq, J = 3.0, 7.3 Hz, 2H), 6.26 (m, 1H), 7.36-7.85 (m, 7H); ^{13}C NMR δ 12.1, 18.7, 27.1, 94.9 ($\text{C}=\text{C}=\text{}$), 105.8 ($=\text{C}=\text{CH}$), 124.8, 125.1, 125.4, 126.2, 127.7, 127.8, 128.2, 132.6, 133.9, 134.0, 203.3 (=C=); GC-MS(EI) m/z (rel int) 208 (M^+ , 49), 193 (46), 179 (100), 178 (93), 165 (21), 151 (29), 139 (11), 115 (14), 99 (6), 91 (6), 76 (16), 63 (13), 51 (11). Anal. Calcd. for $\text{C}_{16}\text{H}_{16}$: C, 92.26; H, 7.74. Found: C, 92.13; H, 7.85.

1-(2-Ethylphenyl)-3,4,4-trimethyl-1,2-pentadiene (4db): ^1H NMR δ 1.05 (s, 9H), 1.16 (t, J = 7.6 Hz, 3H), 1.73 (d, J = 2.9 Hz, 3H), 2.55 (q, J = 7.6 Hz, 2H), 6.20 (q, J = 2.9, 1H), 7.10 (m, 4H); GC-MS(EI) m/z (rel int) 214 (M^+ , 25), 199 (24), 184 (7), 171 (6), 157 (68), 143 (28), 142 (20), 129 (7), 57 (100). Anal. Calcd. for $\text{C}_{16}\text{H}_{22}$: C, 89.65; H, 10.35. Found: C, 89.51; H, 10.47.

1-(4-Ethylphenyl)-3,4,4-trimethyl-1,2-pentadiene (4dc): ^1H NMR δ 1.05 (s, 9H), 1.14 (t, J = 7.6 Hz, 3H), 1.71 (d, J = 2.9 Hz, 3H), 2.54 (q, J = 7.6 Hz, 2H), 5.95 (q, J = 2.9 Hz, 1H), 7.07 (m, 4H); ^{13}C NMR δ 14.7, 15.7, 28.6, 29.2, 34.2, 93.9 ($\text{C}=\text{C}=\text{}$), 112.4 ($=\text{C}=\text{CH}$), 126.3, 128.1, 133.6, 142.4, 201.5 (=C=); GC-MS(EI) m/z (rel int) 214 (M^+ , 32), 199 (35), 184 (12), 171 (4), 157 (72), 143 (30), 142 (20), 129 (11), 57 (100).

1-(4-Dimethylaminophenyl)-3,4,4-trimethyl-1,2-pentadiene (4dh): ^1H NMR δ 1.20 (s, 9H), 1.86 (d, $J = 2.8$ Hz, 3H), 2.98 (s, 6H), 6.08 (q, $J = 2.8$ Hz, 1H), 6.80 (m, 2H), 7.27 (m, 2H) ; GC-MS(EI) m/z (rel int) 229 (M^+ , 26), 214 (18), 172 (100), 156 (7), 129(10).

1-[(6-Methoxy)-2-naphthyl]-3,4,4-trimethyl-1,2-pentadiene (4dk): ^1H NMR δ 1.16 (s, 9H), 1.85 (d, $J = 2.8$ Hz, 3H), 3.91 (s, 3H), 6.20 (q, $J = 2.8$ Hz, 1H), 7.09-7.69 (m, 6H); GC-MS(EI) m/z (rel int) 266 (M^+ , 26) 209 (100), 165 (12), 57 (14), 41 (6).

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