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CAL-B Catalyzed Alkoxycarbonylation of A-Ring Stereoisomeric Synthons of 1α,25-Dihydroxyvitamin D_3 and 1α,25-Dihydroxy-19-*nor*-previtamin D_3: A Comparative Study. First Regioselective Chemoenzymatic Synthesis of 19-*nor*-A-Ring Carbonates.

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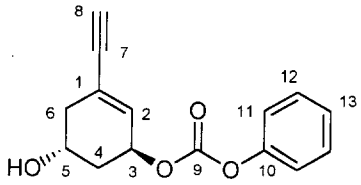
SUPPLEMENTARY MATERIAL (page 1 of 7 pages)

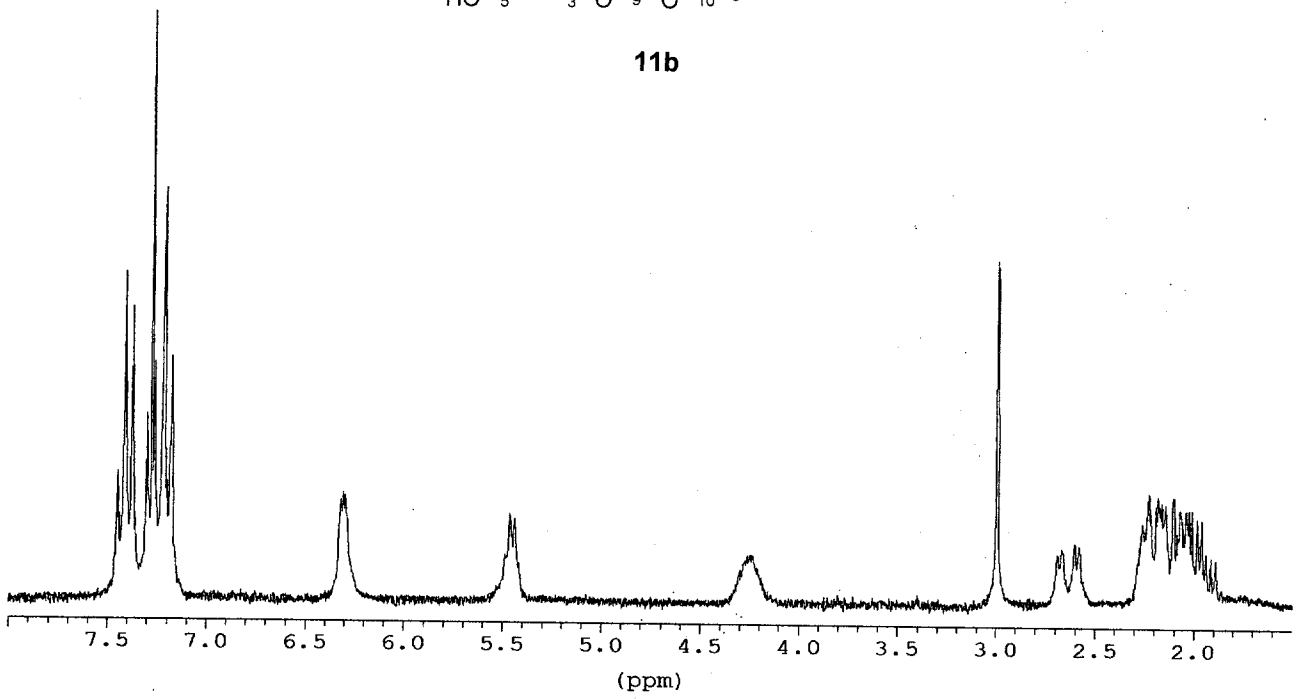
General Spectroscopic and Experimental Data

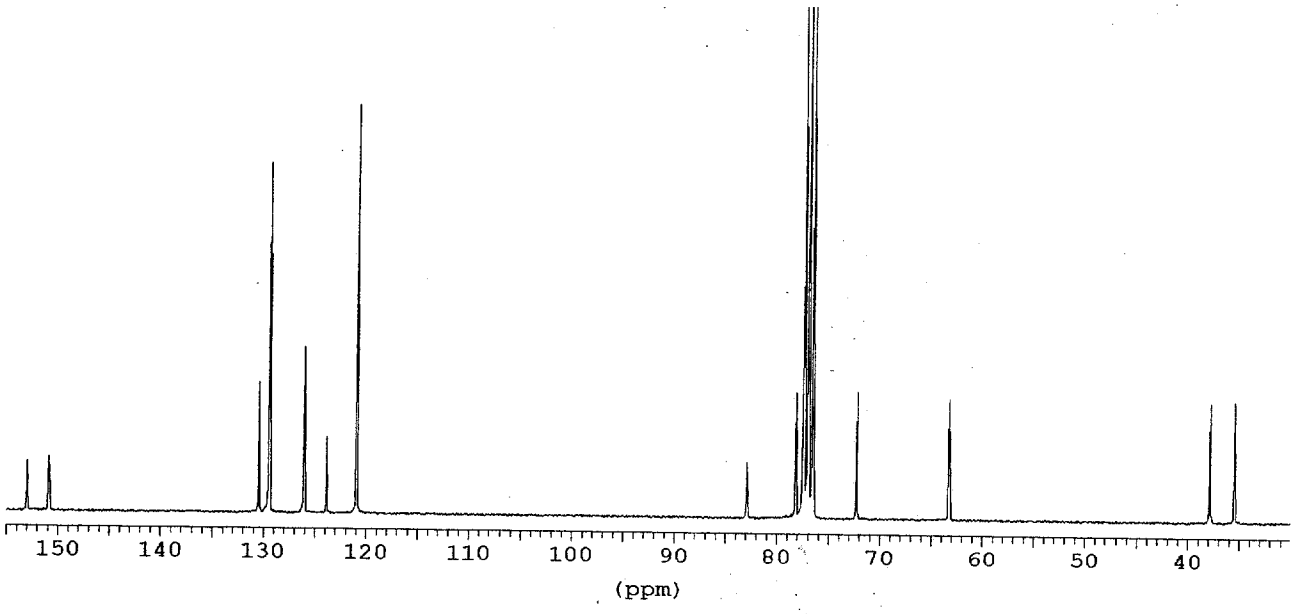
Melting points were taken on samples in open capillary tubes and are uncorrected. IR spectra were recorded on an Infrared Fourier Transform spectrophotometer using NaCl plates. Flash chromatography was performed using silica gel 60 (230-400 mesh). ^{1}H-, ^{13}C-NMR, and DEPT were obtained using AC-200 (^{1}H, 200.13 MHz and ^{13}C, 50.3 MHz), AC-300 (^{1}H, 300.13 MHz and ^{13}C, 75.5 MHz), or DPX-300 (^{1}H, 300.13 MHz and ^{13}C, 75.5 MHz) spectrometers for routine experiments. AMX-400 spectrometer operating at 400.13 and 100.61 MHz for ^{1}H and ^{13}C, respectively, was used for the acquisition of ^{1}H-^{1}H homonuclear (COSY and NOESY) and ^{1}H-^{13}C heteronuclear (HMQC and HMBC) correlations. EI or ESI$^+$ were used to record mass spectra (MS).

(3*S*,5*R*)- and (3*R*,5*S*)-1-Ethynyl-5-hydroxy-3-(phenoxy)carbonyloxy-1-cyclohexene (11b and 14b). R_f (5% ^{i}PrOH/Hex): 0.3. IR (NaCl): υ 3482, 3281, 2932, 2863, 2097, 1766, and 1598 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 1.90-2.26 (m, 3H, 2H4+H6), 2.63 (dd, 1H, H6, $|^2J_{HH}|$ 17.4, J_{HH} 5.2 Hz), 2.99 (s, 1H, H8), 4.25 (m, 1H, H5), 5.44 (m, 1H, H3), 6.30 (m, 1H, H2), and 7.21-7.41 (m, 5H, ArH). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 35.4, 37.8 (C4, C6), 63.2, 72.2 (C3, C5), 78.2 (C8), 82.9 (C7), 120.9 (C11), 123.8 (C1), 126.1 (C13), 129.4 (C12), 130.4 (C2), 150.9 (C10), and 153.0 (C9). Anal. Calcd. (%) for $C_{15}H_{14}O_4$: C, 69.8; H, 5.5. Found: C, 69.5; H, 5.7. MS (ESI$^+$, *m/z*): 281 $[M+Na]^+$.

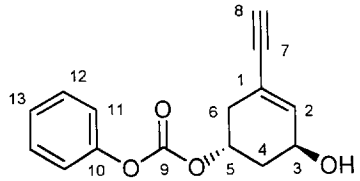


11b

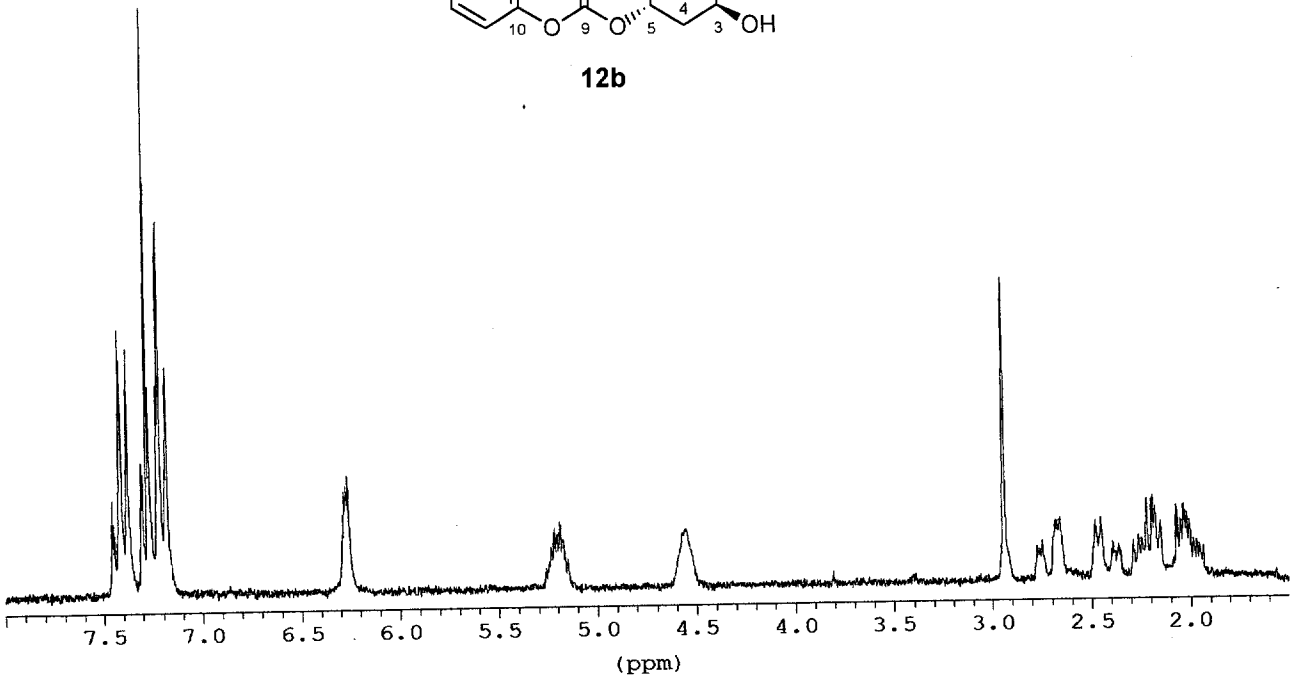


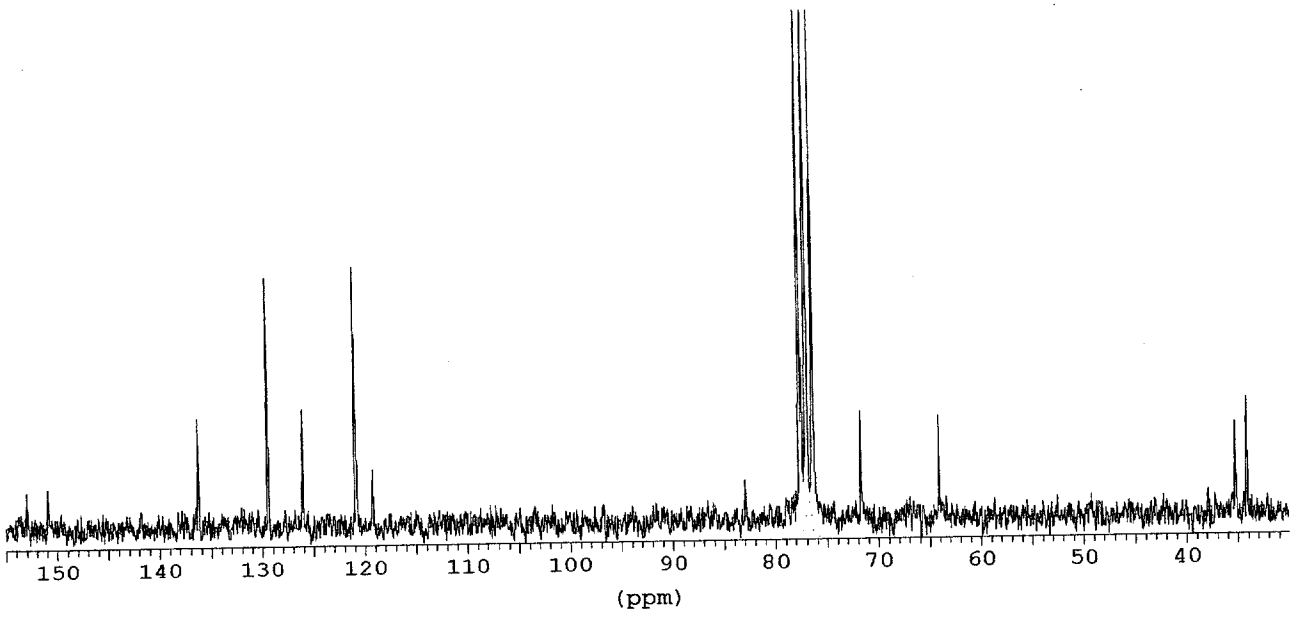


(3*S*,5*R*)- and (3*R*,5*S*)-1-Ethynyl-3-hydroxy-5-(phenoxy)carbonyloxy-1-cyclohexene (12b and 15b). R_f (5% ^{i}PrOH/Hex): 0.3. IR (NaCl): υ 3391, 3295, 2929, 2857, 2092, 1760, and 1592 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 2.02 (m, 1H, H4), 2.22 (m, 1H, H4), 2.42 (ddd, 1H, H6, $|^2J_{HH}|$ 17.9, J_{HH} 5.9, 1.8 Hz), 2.71 (ddd, 1H, H6, $|^2J_{HH}|$ 17.9, J_{HH} 5.1, 2.3 Hz), 2.94 (s, 1H, H8), 4.54 (m, 1H, H3), 5.19 (m, 1H, H5), 6.25 (m, 1H, H2), and 7.21-7.41 (m, 5H, ArH). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 34.1, 35.2 (C4, C6), 64.1, 71.6 (C3, C5), 77.4, 82.9 (C7, C8), 119.2 (C1), 120.9 (C11), 126.0 (C13), 129.4 (C12), 136.2 (C2), 150.9 (C10), and 152.9 (C9). Anal. Calcd. (%) for $C_{15}H_{14}O_4$: C, 69.8; H, 5.5. Found: C, 69.5; H, 5.3. MS (ESI$^+$, *m/z*): 281 $[M+Na]^+$.

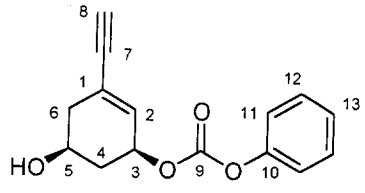


12b

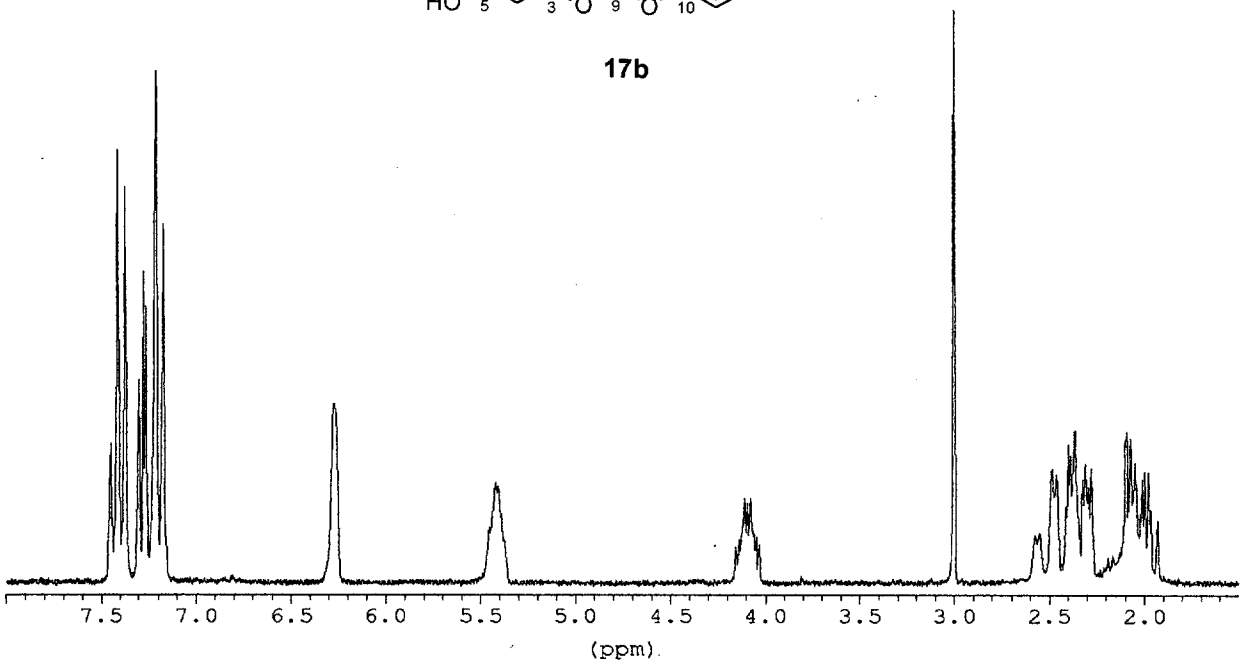


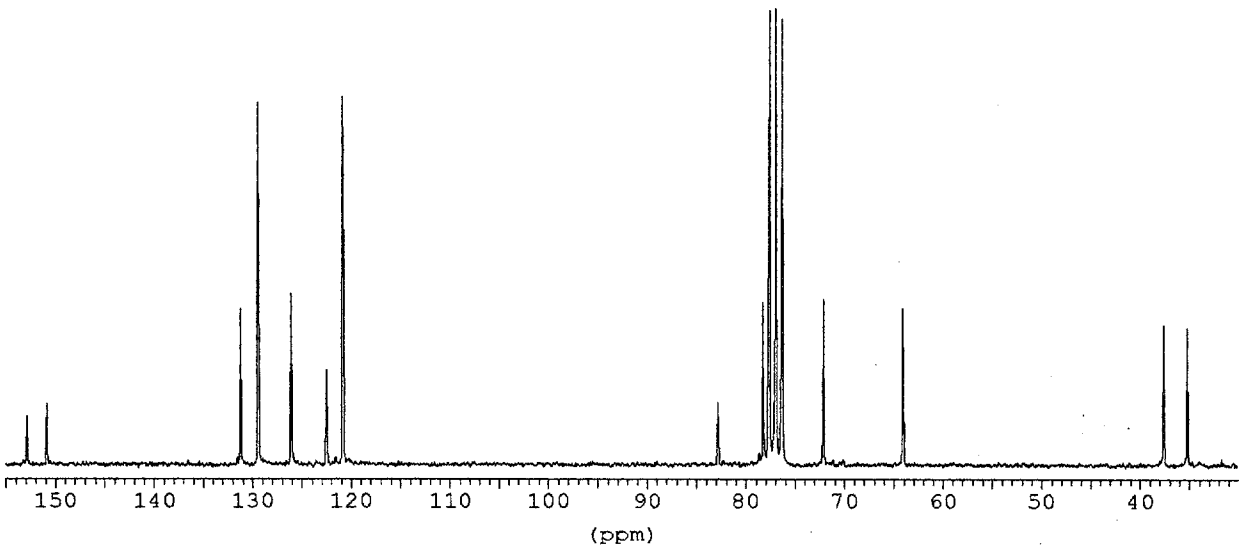


(3*S*,5*S*)- and (3*R*,5*R*)-1-Ethynyl-5-hydroxy-3-(phenoxy)carbonyloxy-1-cyclohexene (17b and 20b). R_f (5% ^{i}PrOH/Hex): 0.3. IR (NaCl): υ 3430, 3284, 3057, 2946, 2098, 1757, and 1630 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 1.93-2.10 (m, 2H, H4), 2.28-2.57 (m, 2H, H6), 3.00 (s, 1H, H8), 4.09 (m, 1H, H5), 5.41 (m, 1H, H3), 6.27 (m, 1H, H2), and 7.17-7.45 (m, 5H, ArH). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 35.2, 37.6 (C4, C6), 64.1 (C5), 72.1 (C3), 78.7 (C8), 82.9 (C7), 120.9 (C11), 122.5 (C1), 126.1 (C13), 129.4 (C12), 131.2 (C2), 150.9 (C10), and 152.9 (C9). Anal. Calcd. (%) for $C_{15}H_{14}O_4$: C, 69.8; H, 5.5. Found: C, 69.9; H, 5.2. MS (ESI$^+$, *m/z*): 281 $[M+Na]^+$.

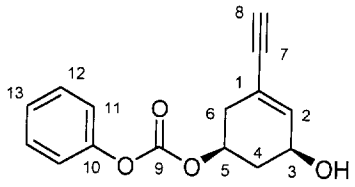


17b

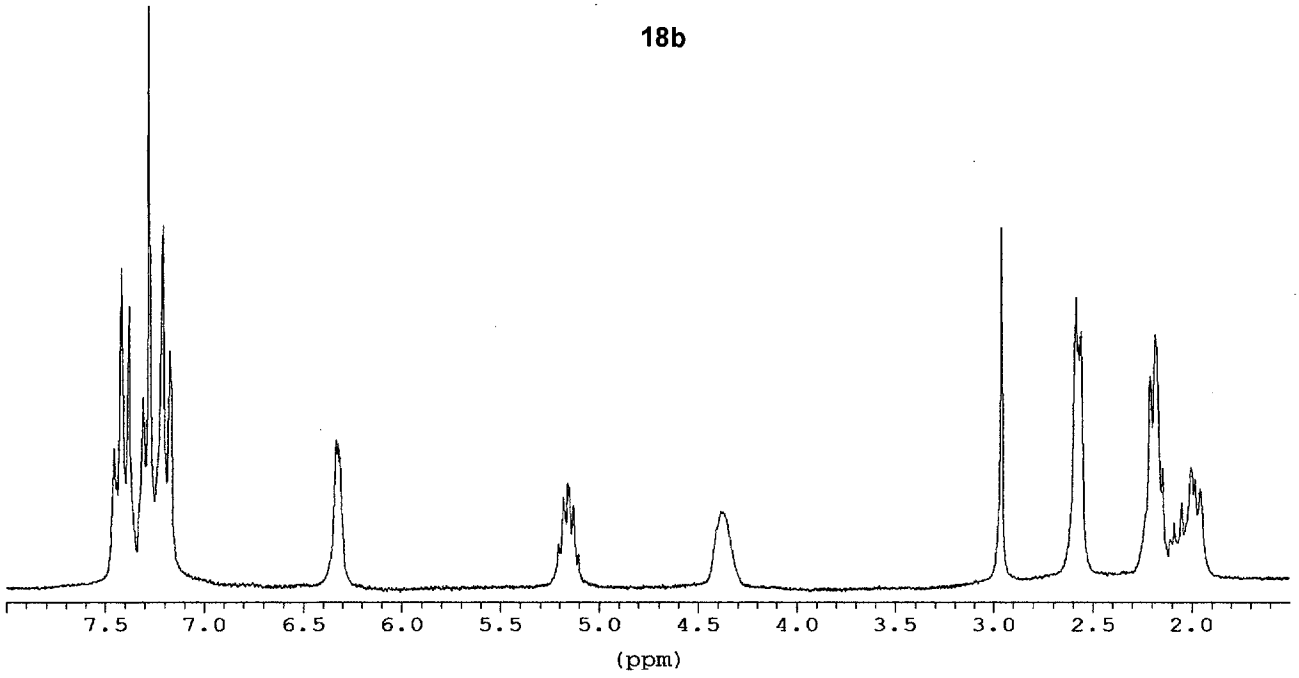


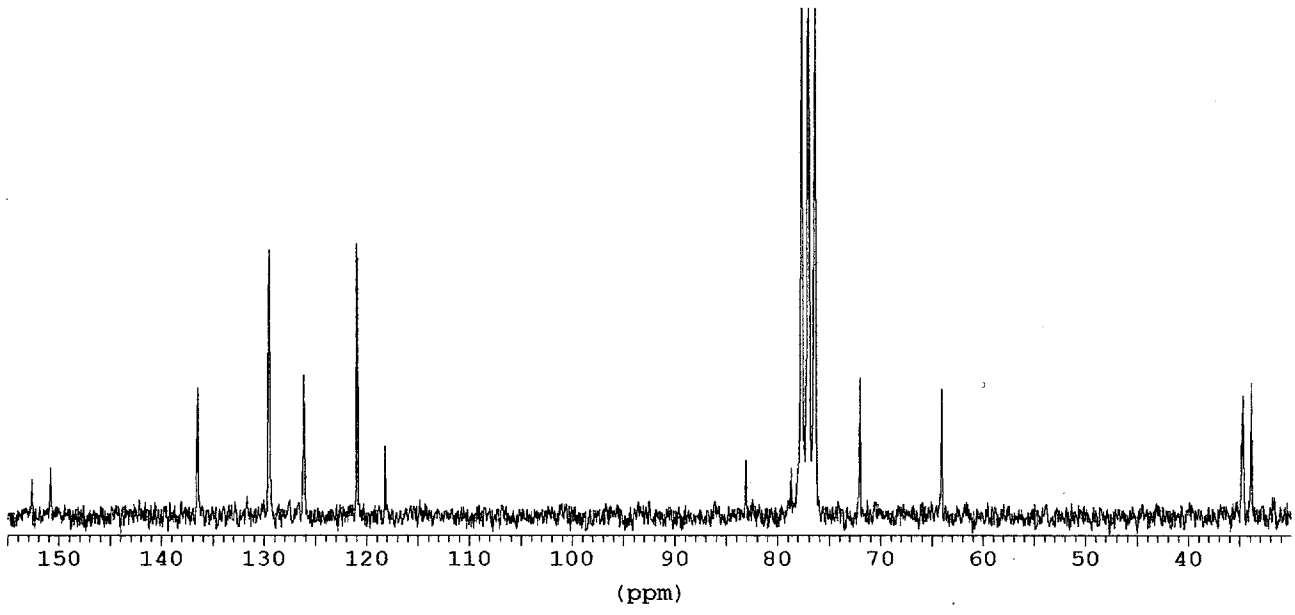


(3*S*,5*S*)- and (3*R*,5*R*)-1-Ethynyl-3-hydroxy-5-(phenoxy)carbonyloxy-1-cyclohexene (18b and 21b). R_f (5% ^{i}PrOH/Hex): 0.3. IR (NaCl): υ 3391, 3294, 2929, 2091, 1764, and 1598 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 1.95-2.21 (m, 2H, 2H4), 2.57 (m, 2H, 2H6), 2.96 (s, 1H, H8), 4.37 (m, 1H, H3), 5.15 (m, 1H, H5), 6.32 (m, 1H, H2), and 7.16-7.42 (m, 5H, ArH). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 33.8, 34.7 (C4, C6), 64.0, 72.0 (C3, C5), 78.6, 83.0 (C7, C8), 118.2 (C1), 120.9 (C11), 126.1 (C13), 129.5 (C12), 136.5 (C2), 150.8 (C10), and 152.6 (C9). Anal. Calcd. (%) for $C_{15}H_{14}O_4$: C, 69.8; H, 5.5. Found: C, 70.0; H, 5.5. MS (ESI$^+$, *m/z*): 281 $[M+Na]^+$.

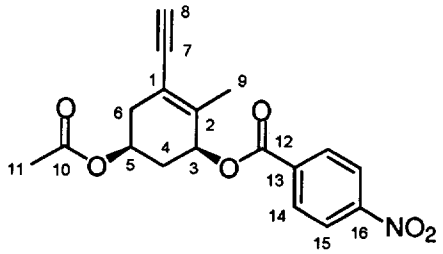


18b





(3*S*,5*S*)- and (3*R*,5*R*)- 5-Acetoxy-1-ethynyl-2-methyl-3-[(4-nitrophenyl)carbonyloxy] cyclohex-1-ene (26 and 29). R_f (10% EtOAc/hex): 0.13; IR (NaCl): υ 3290, 3312, 2945, 2858, 2095, 1729, 1528, and 1439 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.95 (s, 3H, H9), 1.98 (s, 3H, H11), 2.12 (ddd, 1H, H4, $^2J_{HH}$ 13.9, $^3J_{HH}$ 8.3, $^3J_{HH}$ 6.1 Hz), 2.31 (ddd, 1H, H4, $^2J_{HH}$ 13.5, $^3J_{HH}$ 5.7, $^3J_{HH}$ 3.1 Hz), 2.43 (m, 1H, H6), 2.58 (d, 1H, H6, $^2J_{HH}$ 17.0 Hz), 3.21 (s, 1H, H8), 5.08 (m, 1H, H5), 5.70 (apparent t, 1H, H3, $^3J_{HH}$ ~5.6 Hz), 8.19 (d, 2H, H15, $^3J_{HH}$ 2.2 Hz), and 8.21 (d, 2H, H14, $^3J_{HH}$ 2.2 Hz); ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 18.0 (C9), 21.1 (C11), 32.6 (C4), 34.7 (C6), 65.7 (C5), 71.0 (C3), 82.1 (C8+C7, assigned by HMQC and HMBC experiments), 116.6 (C1), 123.5 (C14), 130.6 (C15), 135.3 (C13), 138.7 (C2), 150.5 (C16), 164.0 (C12), and 170.2 (C10); Anal. Calcd. (%) for $C_{18}H_{17}NO_6$: C, 62.95; H, 4.99; N, 4.08. Found: C, 62.8; H, 5.1; N, 4.1; MS (ESI$^+$, *m/z*): 366 $[M+Na]^+$.



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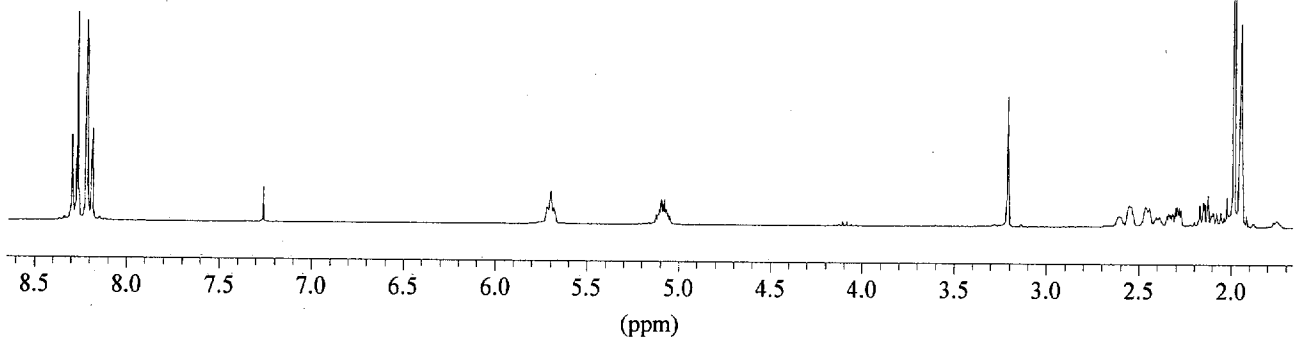
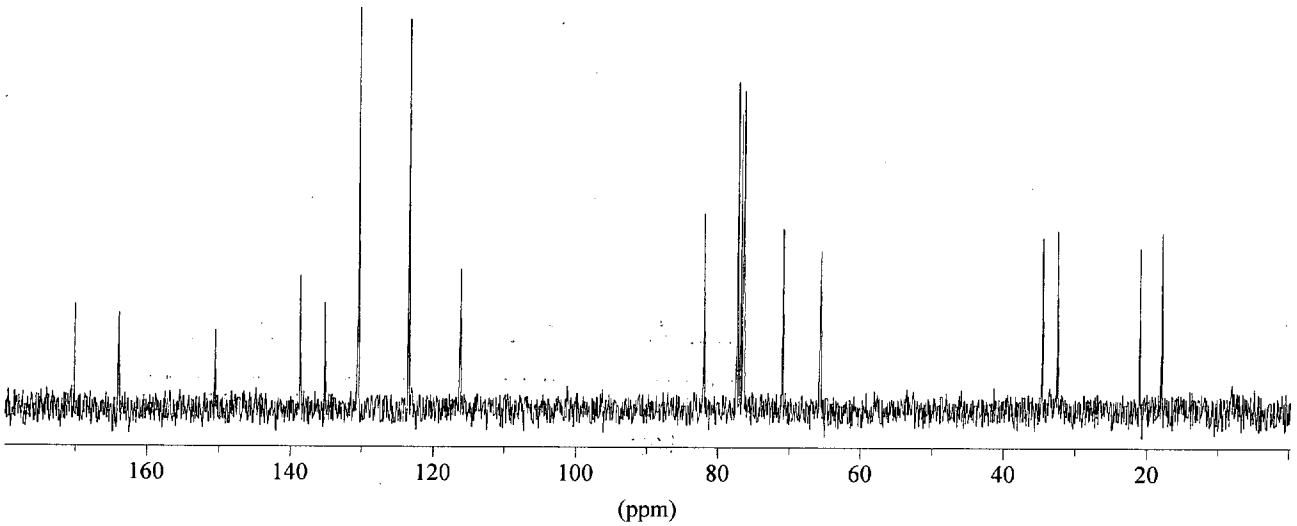
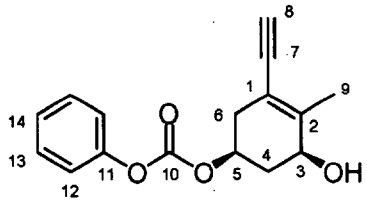




(3*S*,5*S*)- and (3*R*,5*R*)-1-Ethynyl-3-hydroxy-2-methyl-5-(phenoxycarbonyloxy)cyclohex-1-ene (32a and 33a). R_f (20% EtOAc/hex): 0.30; IR (NaCl): υ 3430, 3289, 2925, 2854, 2091, 1759, 1592, 1494, and 1362 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 1.70 (br s, 1H, OH), 2.09 (s, 3H, H9), 2.13 (m, 1H, H4), 2.30 (ddd, 1H, H4, $^2J_{HH}$ 14.6, $^3J_{HH}$ 6.4, $^3J_{HH}$ 4.1 Hz), 2.59 (m, 2H, H6), 3.16 (s, 1H, H8), 4.13 (m, 1H, H3), 5.17 (m, 1H, H5), and 7.15-7.45 (m, 5H, ArH); ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 18.6 (C9), 34.5, 34.7 (C4+C6), 67.2 (C3), 72.2 (C5), 81.1 (C8), 82.6 (C7), 112.1 (C1), 120.9 (C12), 126.1 (C14), 129.5 (C13), 143.5 (C2), 150.8 (C11), and 152.6 (C10); Anal. Calcd. (%) for $C_{16}H_{16}O_4$: C, 70.56; H, 5.93. Found: C, 70.5; H, 6.0; MS (ESI$^+$, *m/z*): 272 $[M]^+$, 295 $[M+Na]^+$, and 311 $[M+K]^+$.



32a