A Study of Fluoro-carbonyls for the Baylis-Hillman Reaction

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Physical data for the functionalized allylic alcohols prepared via Baylis-Hillman reaction of fluoroaldehydes and ketones

4,4,4-Trifluoro-3-hydroxy-2-methylenebutanal (3a). Yield: 40%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3445, 1685; ¹H NMR (300MHz, CDCl₃) δ (ppm): 4.13 (d, $J=6.93$ Hz, 1H, OH), 4.97 (quint, $J=6.6$ Hz, 1H, HO-CH), 6.44 (s, 1H, C=CH), 6.78 (s, 1H, C=CH), 9.55 (s, 1H, CHO); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 66.9 (q, $J=32.9$ Hz, C-OH), 123.8 (q, $J=282.4$ Hz, CF₃), 139.7 (C=CH₂), 142.8 (C=CH₂), 193.0 (C=O); ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -79.79 (d, $J=7.1$ Hz); MS (EI) m/z (relative intensity) 136 (M-H₂O, 28), 55 (C₃H₃O⁺, 100); (CI) m/z 155 (M+H); HRMS: calcd for C₅H₃OF₃ (m-H₂O) m/z 136.0136, obsd m/z 136.0137.

5,5,5-Trifluoro-4-hydroxy-3-methylene-2-pentanone (3b). Yield: 65%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3439, 1678; ¹H NMR (300MHz, CDCl₃) δ (ppm) 2.36 (s, 3H, COCH₃), 4.52 (d, $J=7.2$ Hz, 1H, OH), 4.99 (quint, $J=6.87$ Hz, 1H, HO-CH), 6.34 (s, 1H, C=CH), 6.42 (s, 1H, C=CH); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm) 25.87 (COCH₃), 68.5 (q, $J=32.6$ Hz, C-OH), 124.1 (q, $J=282.8$ Hz, CF₃), 131.5 (C=CH₂), 141.6 (C=CH₂), 199.6 (C=O); ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm) -79.63 (d, $J=6.27$ Hz); MS (EI) m/z (relative intensity) 153 (M-CH₃, 3), 43 (CH₃CO⁺, 100); (CI) m/z 169 (M+H); HRMS: calcd for C₆H₈O₂F₃ (M+H) m/z 168.0398, obsd m/z 168.0390.

Ethyl 4,4,4-Trifluoro-3-hydroxy-2-methylenebutanoate (3c). Yield: 20%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3465, 1701, 1631; ¹H NMR (300MHz, CDCl₃) δ (ppm): 1.27 (t, $J=7.14$ Hz, 3H, OCH₂CH₃), 4.22 (q, $J=7.14$ Hz, 2H, OCH₂CH₃), 4.62 (broad s, 1H, OH), 4.91 (quint, $J=6.57$ Hz, 1H, HO-CH), 6.12 (s, 1H, C=CH), 6.52 (s, 1H, C=CH); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm) 13.75 (OCH₂CH₃), 61.69 (OCH₂CH₃), 69.15 (q, $J=32.5$ Hz, C-OH), 123.98 (q, $J=282.8$ Hz, CF₃), 131.0 (C=CH₂), 134.1 (C=CH₂), 165.7 (C=O), ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -79.74 (d, $J=6.8$ Hz); MS (EI) m/z (relative intensity) 153 (M-OEt, 90), 83 (100); (CI) m/z 199 (M+H).

4,4,5,5,6,6,6-heptafluoro-3-hydroxy-2-methylenehexanal (5a). Yield: 50%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3459, 1685; ¹H NMR (300MHz, CDCl₃) δ (ppm): 4.03 (m, 1H, OH), 5.15 (m, 1H, HO-CH), 6.46 (s, 1H, C=CH), 6.75 (s, 1H, C=CH), 9.57 (s, 1H, CHO); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 65.94 (m, C-OH), 103.5-123.9 (m, C₃F₇), 140.4 (C=CH₂), 142.8 (C=CH₂), 193.3 (C=O); ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -82.5 (t, $J=9.0$ Hz, 2F), -120.1 (m, 3F), -126.4- -129.2 (m, 4F); MS (EI) m/z (relative intensity) 236 (M-H₂O, 9), 85 (100) (CI) m/z 255 (M+H); HRMS: calcd for C₇H₃OF₇ (M-H₂O) m/z 236.0072, obsd m/z 236.0071.

5,5,6,6,7,7,7-heptafluoro-4-hydroxy-3-methylene-2-heptanone (5b). Yield: 70%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3439, 1678 cm⁻¹; ¹H NMR (300MHz, CDCl₃) δ (ppm): 2.36 (s, 3H, COCH₃),

4.59 (d, $J=8.2$ Hz, 1H, OH), 5.15 (m, 1H, HO-CH), 6.29 (s, 1H, C=CH), 6.43 (s, 1H, C=CH); ^{13}C NMR (75.5 MHz, CDCl_3) δ (ppm): 25.79 (COCH_3), 68.34 (m, C-OH), 106.0-124.4 (m, C_3F_7), 131.96 (C=CH₂), 141.32 (C=CH₂), 200.17 (C=O); ^{19}F NMR (282 MHz, CDCl_3) δ (ppm): -82.69 (t, $J=10.0$ Hz, 2F), -119.8 (m, 3F), -126.4- -129.4 (m, 4F); MS (EI) (relative intensity) m/z 248 (M-HF, 2), 43 (CH_3CO^+ , 100); (CI) m/z 269 (M+H); HRMS: calcd for $\text{C}_8\text{H}_8\text{O}_2\text{F}_7$ (M+H) m/z 269.0413, obsd m/z 269.0418.

4-(2',3',4',5',6'-pentafluorophenyl)-4-hydroxy-3-methylene-2-butanone (7b). Yield: 70%. IR (CHCl_3) ν_{max} cm^{-1} : 3439, 1675, 1648; ^1H NMR (300MHz, CDCl_3) δ (ppm): 2.35 (s, 3H, COCH_3), 3.39 (d, $J=5.6$ Hz, 1H, OH), 5.89 (d, $J=4.7$ Hz, 1H HO-CH), 6.30 (s, 1H, C=CH), 6.35 (s, 1H, C=CH); ^{13}C NMR (75.5 MHz, CDCl_3) δ (ppm): 26.11 (COCH_3), 63.77 (C-OH), 115.3 (m), 127.2 (C=CH₂), 135.6-143.5 (m), 146.8 (C=CH₂), 199.35 (C=O); ^{19}F NMR (282 MHz, CDCl_3) δ (ppm): -143.77 (m, 2F), -156.4 (t, $J=22$ Hz, 1F), -163.67 (m, 2F).

Ethyl 3-(2',3',4',5',6'-pentafluorophenyl)-3-hydroxy-2-methylenepropanoate (7c). Yield: 70%. IR (CHCl_3) ν_{max} cm^{-1} : 3453, 1705, 1651; ^1H NMR (300MHz, CDCl_3) δ (ppm): 1.25 (t, $J=7.14$ Hz, 3H, OCH_2CH_3), 4.15 (m, 2H, OCH_2CH_3), 4.76 (broad s, 1H, OH), 5.87 (s, 1H, HO-CH), 6.09 (s, 1H, C=CH), 6.47 (s, 1H, C=CH); ^{13}C NMR (75.5 MHz, CDCl_3) δ (ppm): 13.76 (OCH_2CH_3), 61.36 (OCH_2CH_3), 64.0 (C-OH), 126.55 (C=CH₂), 5.68 (C=CH₂), 136-148 (m, aromatic), 165.5 (C=O); ^{19}F NMR (282 MHz, CDCl_3) δ (ppm): -143.78 (m, 2F), -156.2 (m, 1F), -163.8 (m, 2F); MS (EI) m/z (relative intensity) 296 (M^+ , 37), 279 (M-OH, 50), 55 ($\text{C}_3\text{H}_3\text{O}^+$, 100); (CI) m/z 297 (M+H).

3-(2',3',4',5',6'-pentafluorophenyl)-3-hydroxy-2-methylenepropionitrile (7d). Yield: 75%. IR (CHCl_3) ν_{max} cm^{-1} : 3445, 2231, 1651; ^1H NMR (300MHz, CDCl_3) δ (ppm): 3.30 (d, $J=7.14$ Hz, 1H, OH), 5.69 (d, $J=6.9$ Hz, 1H, HO-CH), 6.20 (d, $J=1.95$ Hz, 1H, C=CH), 6.29 (d, $J=2.1$ Hz, 1H, C=CH); ^{13}C NMR (75.5 MHz, CDCl_3) δ (ppm): 64.62 (C-OH), 115.99 (CN), 122.7 (C=CH₂), 131.3 (C=CH₂), 136-148 (m, aromatic); ^{19}F NMR (282 MHz, CDCl_3) δ (ppm): -143.7 (m, 2F), -153.2 (m, 1F), -161.9 (m, 2F).

4,4,4-Trifluoro-3-hydroxy-3-methyl-2-methylenebutanal (9a). Yield: 12%. IR (CHCl_3) ν_{max} cm^{-1} : 3432, 1685; ^1H NMR (300MHz, CDCl_3) δ (ppm): 1.57 (s, 3H, CH_3), 5.63 (s, 1H, OH), 6.37 (s, 1H, C=CH), 6.69 (s, 1H, C=CH), 9.54 (s, 1H, CHO); ^{13}C NMR (75.5 MHz, CDCl_3) δ (ppm): 21.26 (CH_3), 75.25 (q, $J=30.10$ Hz, C-OH), 125.08 (q, $J=286.2$, CF_3), 140.9 (C=CH₂), 145.03 (C=CH₂), 195.5 (C=O); ^{19}F NMR (282 MHz, CDCl_3) δ (ppm): -83.17 (s); MS (EI) m/z (relative intensity) 150 (m- H_2O , 11), 43 (CH_3CO^+ , 100) (CI) m/z 169 (M+H); HRMS: calcd for $\text{C}_6\text{H}_8\text{O}_2\text{F}_3$ (M+H) m/z 169.0476, obsd m/z 169.0471.

4,4,4-Trifluoro-3-hydroxy-3-methyl-2-methylenebutyronitrile (9d). Yield: 10%. IR (CHCl_3) ν_{max} cm^{-1} : 3425, 2250; ^1H NMR (300MHz, CDCl_3) δ (ppm): 69 (s, 3H, CH_3), 2.94 (s, 1H, OH), 6.32 (s, 1H, C=CH), 6.42 (s, 1H, C=CH); ^{13}C NMR (75.5 MHz, CDCl_3) δ (ppm): 21.65 (CH_3), 73.7 (q, $J=30.5$ Hz, C-OH), 115.7 (CN), 122.0 (C=CH₂), 124.2 (q, $J=286.0$, CF_3), 135.1 (C=CH₂); ^{19}F NMR (282 MHz, CDCl_3) δ (ppm): -82.55 (s); MS (EI) m/z (relative intensity) 150 (m- CH_3 , 4), 54 ($\text{C}_3\text{H}_4\text{N}^+$, 100) (CI) m/z 166 (M+H); HRMS: calcd for $\text{C}_6\text{H}_7\text{OF}_3\text{N}$ (M+H) m/z 166.0480, obsd m/z 166.0475.

Ethyl 4,4,4-Trifluoro-3-hydroxy-3-phenyl-2-methylenebutanoate (11c). Yield: 70%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3439, 1698, 1621; ¹H NMR (300MHz, CDCl₃) δ (ppm): 1.24 (t, J =7.11 Hz, 3H, OCH₂CH₃), 4.17 (m, 2H, OCH₂CH₃), 5.69 (s, 1H, OH), 6.13 (s, 1H, C=CH), 6.63 (s, 1H, C=CH), 7.39 (m, 3H, aromatic), 7.60 (m, 2H, aromatic); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 13.85 (OCH₂CH₃), 61.99 (OCH₂CH₃), 79.17 (q, J =28.95 Hz, C-OH), 124.2 (q, J =285.3 Hz, CF₃), 126.9, 128.3, 128.7, 128.9, 136.4, 137.2, 167.1 (C=O); ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -76.71 (s); MS (EI) m/z (relative intensity) 257 (m-OH, 8.5), 205 (m-CF₃, 75), 105 (C₆H₅CO⁺, 100) (CI) m/z 275 (M+H, 100) 257 (M-H₂O, 51); HRMS: calcd for C₁₃H₁₃O₃F₃ (M⁺) m/z 274.0817, obsd m/z 274.0826.

4,4,4-Trifluoro-3-hydroxy-3-phenyl-2-methylenebutyronitrile (11d). Yield: 94%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3379, 2240; ¹H NMR (300MHz, CDCl₃) δ (ppm): 3.72 (s, 1H, OH), 6.30 (s, 1H, C=CH), 6.38 (s, 1H, C=CH), 7.44 (m, 3H, aromatic), 7.58 (m, 2H, aromatic); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 77.7 (q, J =29.76 Hz, C-OH), 115.79 (CN), 122.6, 124.0 (q, J =287.0 Hz, CF₃), 126.6, 128.9, 129.9, 134.5, 134.9; ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -76.32 (s); MS (EI) m/z (relative intensity) 227 (m⁺, 26), 105 (C₆H₅CO⁺, 100) (CI) m/z 284 (M+C₄H₉ from isobutene, 100) 228 (M+H, 67); HRMS: calcd for C₁₁H₈OF₃N (M⁺) m/z 227.0558, obsd m/z 227.0556.

Ethyl 4,4,4-Trifluoro-3-hydroxy-3-(2-thiophenyl)-2-methylenebutanoate (13c) Yield: 65%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3346, 1692, 1618; ¹H NMR (300MHz, CDCl₃) δ (ppm): 1.31 (t, J =7.14 Hz, 3H, OCH₂CH₃), 4.27 (m, 2H, OCH₂CH₃), 6.06 (s, 1H, C=CH), 6.60 (s, 1H, C=CH), 6.73 (s, 1H, OH), 7.01 (m, 1H, aromatic), 7.13 (m, 1H, aromatic), 7.36 (m, 1H, aromatic); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 14.01 (CH₂CH₃), 62.29 (OCH₂CH₃), 77.74 (q, J =30.33 Hz, C-OH), 124.05 (q, J =286.15 Hz, CF₃), 126.77, 126.93, 130.6, 135.5, 141.42, 167.43 (C=O); ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -78.25 (s); MS (EI) m/z (relative intensity) 280 (M⁺, 20), 263 (M-OH, 15.5), 111 (100) (CI) m/z 281 (M+H, 2), 263 (M+H-H₂O, 100); HRMS: calcd for C₁₁H₁₁O₃F₃S (M⁺) m/z 280.0381, obsd m/z 280.0391.

4,4,4-Trifluoro-3-hydroxy-3-(2-thiophenyl)-2-methylenebutyronitrile (13d). Yield: 82%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3359, 2237, 1618; ¹H NMR (300MHz, CDCl₃) δ (ppm): 3.78 (broad s, 1H, OH), 6.36 (s, 1H, C=CH), 6.48 (s, 1H, C=CH), 7.06 (m, 1H, aromatic), 7.30 (m, 1H, aromatic), 7.43 (m, 1H, aromatic); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 76.24 (q, J =31.0 Hz, C-OH), 115.41 (CN), 121.716, 123.5 (q, J =286.8 Hz, CF₃), 127.5, 127.8, 135.6, 137.8; ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -78.23 (s); MS (EI) m/z (relative intensity) 233 (m⁺, 33), 111 (100) (CI) m/z 234 (m+H); HRMS: calcd for C₉H₆OF₃NS (M⁺) m/z 233.0122, obsd m/z 233.0118.

N-(2-ethoxycarbonylethyl)-3-(trifluoroacetyl)indole (15c). Yield: 80%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 1728, 1668, 1615; ¹H NMR (300MHz, CDCl₃) δ (ppm): 1.21 (t, J =7.14 Hz, 3H, OCH₂CH₃), 2.90 (t, J =6.45 Hz, 2H, COCH₂), 4.13 (q, J =7.14 Hz, 2H, OCH₂CH₃), 4.53 (t, J =6.54 Hz, 2H, N-CH₂), 7.38 (m, 3H, aromatic), 8.05 (m, 1H, N-CH=C), 8.38 (m, 1H, aromatic); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 13.98 (OCH₂CH₃), 34.22 (COCH₃), 42.9 (N-CH₂), 61.30 (OCH₂CH₃), 109.67, 110.15, 117.10 (q, J =290.98 Hz, CF₃), 122.67, 123.99, 124.72, 127.06, 136.29, 138.22, 170.44 (COOCH₂CH₃), 174.88 (q, J =33.95 Hz, CO-CF₃); ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -73.71 (s); MS (EI) m/z (relative intensity) 313 (M⁺, 46), 244 (M-

CF₃, 100); (CI) m/z 314 (M+H); HRMS: calcd for C₁₅H₁₄O₃F₃N (M⁺) m/z 313.0926, obsd m/z 313.0925.

N-(2-cyanoethyl)-3-(trifluoroacetyl)indole (15d). Yield: 82%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 2235, 1671, 1651; ¹H NMR (300MHz, CDCl₃) δ (ppm): 2.96 (t, *J*=6.72 Hz, 2H, H₂C-CN), 4.56 (t, *J*=6.80 Hz, 2H, H₂C-N), 7.43 (m, 3H, aromatic), 8.03 (s, 1H, N-CH=C), 8.44 (m, 1H, aromatic); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 19.07 (H₂C-CN), 43.12 (N-CH₂), 109.45, 116.13 (CN), 123.2, 124.5, 125.2, 126.7, 127.1, 136.7, 136.75, 135.85; ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -73.927 (s); MS (EI) m/z (relative intensity) 266 (M⁺, 38), 197 (M-CF₃, 100); (CI) m/z 267 (M+H); HRMS: calcd for C₁₃H₉OF₃N₂ (M⁺) m/z 266.0667, obsd m/z 266.0666.

Ethyl 4-Chloro-4,4-difluoro-3-hydroxy-3-phenyl-2-methylenebutanoate (18c). Yield: 68%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3386, 1695, 1621; ¹H NMR (300MHz, CDCl₃) δ (ppm): 1.24 (t, *J*=7.11 Hz, 3H, OCH₂CH₃), 4.18 (m, 2H, OCH₂CH₃), 6.13 (s, 1H, OH), 6.19 (s, 1H, C=CH), 6.66 (s, 1H, C=CH), 7.38 (m, 3H, aromatic), 7.65 (m, 2H, aromatic); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 13.87 (OCH₂CH₃), 62.08 (OCH₂CH₃), 82.16 (t, *J*=25.14 Hz, C-OH), 129.90 (t, *J*=299.9 Hz, CF₂Cl), 127.4, 128.1, 128.9, 129.4, 136.7, 137.6, 167.5 (C=O); ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -61.03; MS (EI) m/z (relative intensity) 273 (M-OH, 0.2), 105 (C₆H₅CO⁺, 100) (CI) m/z 291 (M+H); HRMS: calcd for C₁₃H₁₃O₃F₂Cl (M⁺) m/z 290.0521, obsd m/z 290.0529.

4-Chloro-4,4-Difluoro-3-hydroxy-3-phenyl-2-methylenebutyronitrile (18d). Yield: 90%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3379, 2237, 1611; ¹H NMR (300MHz, CDCl₃) δ (ppm): 3.81 (s, 1H, OH), 6.31 (s, 1H, C=CH), 6.43 (s, 1H, C=CH), 7.43 (m, 3H, aromatic), 7.65 (m, 2H, aromatic); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 80.71 (t, *J*=25.37, C-OH), 116.12 (CN), 123.06, 126.82, 128.79, 129.79, 129.8 (t, *J*=302.7 Hz, CF₂Cl), 135.32, 135.44; ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -61.01. MS (EI) m/z (relative intensity) 158 (M-CF₂Cl, 88), 105 (C₆H₅CO⁺, 100) (CI) m/z 244 (M+H); HRMS: calcd for C₁₁H₉OF₂ClN (M+H) m/z 244.0341, obsd m/z 244.0343.

3-Trifluoromethyl-3-hydroxy-2-methylene-5-phenyl-4-pentynal (20a). Yield: 54%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3399, 2250, 1682, 1618; ¹H NMR (300MHz, CDCl₃) δ (ppm): 5.88 (s, 1H, OH), 6.54 (s, 1H, C=CH), 7.02 (s, 1H, C=CH), 7.37 (m, 3H, aromatic), 7.50 (m, 2H, aromatic), 9.66 (s, 1H, CHO); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 74.00 (q, *J*=33.91 Hz, C-OH), 81.94 (C≡C), 88.54 (C≡C), 120.65, 123.28 (q, *J*=287.13, CF₃), 128.52, 129.76, 132.08, 133.99, 141.63, 193.77 (C=O); ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -81.53 (s); MS (EI) m/z (relative intensity) 254 (M⁺, 0.9), 237 (M-OH, 1.5), 185 (M-CF₃, 100) (CI) m/z 255 (M+H); HRMS: calcd for C₁₃H₉O₂F₃ (M⁺) m/z 254.0555, obsd m/z 254.0557.

4-Trifluoromethyl-4-hydroxy-2-methylene-6-phenylhex-5yn-2-one (20b). Yield: 50%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3326, 2250, 1668, 1618; ¹H NMR (300MHz, CDCl₃) δ (ppm): 2.49 (s, 3H, COCH₃), 6.59 (s, 1H, C=CH), 6.83 (s, 1H, C=CH), 6.99 (s, 1H, OH), 7.36 (m, 3H, aromatic), 7.52 (m, 2H, aromatic); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 27.71 (CH₃), 75.98 (q, *J*=32.87 Hz, C-OH), 82.61 (C≡C), 88.18 (C≡C), 120.95, 123.55 (q, *J*=287.65 Hz, CF₃), 128.46, 129.42, 132.04, 135.11, 139.86; ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -81.10 (s); MS (EI) m/z (relative intensity) 268 (M⁺, 22), 199 (M-CF₃, 65), 97 (C₅H₆O₂⁺, 100) (CI) m/z 269 (M+H); HRMS: calcd for C₁₄H₁₁O₂F₃ (M⁺) m/z 268.0711, obsd m/z 268.0709.

Ethyl 3-Trifluoromethyl-3-hydroxy-2-methylene-5-phenyl-4-pentynoate (20c). Yield: 75%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3339, 2237, 1695, 1618; ¹H NMR (300MHz, CDCl₃) δ (ppm): 1.36 (t, *J*=7.14 Hz, 3H, OCH₂CH₃), 4.33 (q, *J*=7.11 Hz, 2H, OCH₂CH₃), 6.64 (s, 1H, C=CH), 6.72 (s, 1H, C=CH), 6.78 (s, 1H, OH), 7.39 (m, 3H, aromatic), 7.52 (m, 2H, aromatic); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 13.93 (OCH₂CH₃), 62.38 (OCH₂CH₃), 74.66 (q, *J*=32.9 Hz, C-OH), 82.56 (C=C), 88.04 (C=C), 121.0, 123.5 (q, *J*=287.6 Hz, CF₃), 128.4, 129.5, 132.1, 133.0, 134.0, 167.02 (C=O); ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -81.31 (s); MS (EI) *m/z* (relative intensity) 298 (M⁺, 7), 281 (M-OH, 9), 253 (M-OEt, 8), 129 (C₉H₅O⁺, 100) (CI) *m/z* 299 (M+H); HRMS: calcd for C₁₅H₁₃O₃F₃ (M⁺) *m/z* 298.0817, obsd *m/z* 298.0819.

3-Trifluoromethyl-3-hydroxy-2-methylene-5-phenyl-4-pentynonitrile (20d). Yield: 40%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3352, 2231, 1598; ¹H NMR (300MHz, CDCl₃) δ (ppm): 4.07 (s, 1H, OH), 6.39 (s, 1H, C=CH), 6.64 (s, 1H, C=CH), 7.35 (m, 3H, aromatic), 7.51 (m, 2H, aromatic); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 71.33 (q, *J*=33.68 Hz, C-OH), 80.3 (C=C), 90.4 (C=C), 115.01 (CN), 120.0, 120.07, 122.25 (q, *J*=287.3, CF₃), 128.3, 130.1, 132.15, 136.38; ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -81.19 (s); MS (EI) *m/z* (relative intensity) 251 (M⁺, 9), 182 (M-CF₃, 51), 129 (C₉H₅O⁺, 100) (CI) *m/z* 308 (M+C₄H₉ from isobutene, 100) 252 (M+H, 21); HRMS: calcd for C₁₃H₈OF₃N (M⁺) *m/z* 251.0558, obsd *m/z* 251.0555.

3-Heptafluoropropyl-3-hydroxy-2-methylene-5-phenyl-4-pentynal (22a). Yield: 50%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3386, 2251, 1681, 1618; ¹H NMR (300MHz, CDCl₃) δ (ppm): 6.13 (s, 1H, OH), 6.59 (s, 1H, C=CH), 7.09 (s, 1H, C=CH), 7.38 (m 3H, aromatic), 7.49 (m, 2H, aromatic), 9.68 (s, 1H, CHO); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 75.28 (t, *J*=28.0 Hz), 81.92 (d, *J*=7.5 Hz), 89.72, 105.6-123.9 (m), 120.72, 128.51, 129.75, 131.97, 141.56, 143.05, 194.25 (C=O); ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -82.39 (t, *J*=10.16 Hz, 3F), -115.5- -116.6 (m, 1F), -119.7- -120.8 (m, 1F), -122.8- -125.0 (m, 2F); MS (EI) *m/z* (relative intensity) 337 (M-OH, 3), 185 (95), 83 (100); (CI) *m/z* 355 (M+H); HRMS: calcd for C₁₅H₉O₂F₇ (M⁺) *m/z* 354.0491, obsd *m/z* 354.0493.

4-Heptafluoropropyl-4-hydroxy-2-methylene-6-phenylhex-5yn-2-one (22b). Yield: 46%. IR (CHCl₃) $\nu_{\max}$ cm⁻¹: 3299, 2237, 1668, 1618; ¹H NMR (300MHz, CDCl₃) δ (ppm): 2.50 (s, 3H, COCH₃), 6.61 (s, 1H, C=CH), 6.85 (s, 1H, C=CH), 7.31 (s, 1H, OH), 7.37 (m, 3H, aromatic), 7.49 (m, 2H, aromatic); ¹³C NMR (75.5 MHz, CDCl₃) δ (ppm): 27.75 (COCH₃), 82.6 (d, *J*=7.2 Hz), 89.45, 114.5- -120.1 (m), 121.02, 128.47, 129.56, 131.91, 135.50, 139.57, 203.37 (C=O); ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -82.39 (t, *J*=10.50 Hz, 3F), -114.9- -115.9 (m, 1F), -119.0- -120.2 (m, 1F), -122.8- -125.2 (m, 2F); MS (EI) *m/z* (relative intensity) 368 (M⁺, 12), 199 (M-C₃F₇, 60), 97 (100); (CI) *m/z* 369 (M+H); HRMS: calcd for C₁₆H₁₁O₂F₇ (M⁺) *m/z* 368.0647, obsd *m/z* 368.0657.

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