

Supplementary material

Efficient preparation of novel N-propargylic β -enaminones from the reaction of β -alkoxyvinyltrihalomethyl[carboxy]ketones and propargylamines

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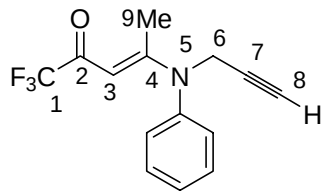
Contents

¹H, ¹³C-NMR and GC-MS data of compounds **6-11**

S2

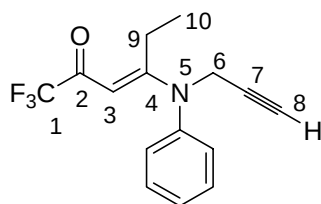
Spectral Data

(*E*)-1,1,1-Trifluoro-4-(phenyl-*N*-1-propyn-3-ylamino)-pent-3-en-2-one (6a)



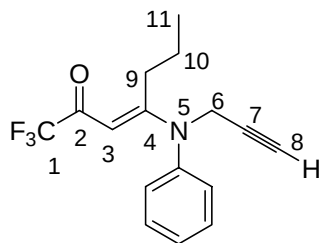
mp 68-70 °C (Yield 95%); ^1H NMR (200 MHz, CDCl_3): δ (J , Hz) 2.40 (s, 4H, H8, H9), 4.38 (d, $^4J_{\text{H-H}} = 2.3$, 2H, H6), 5.54 (s, 1H, H3), 7.24-7.19 (m, 2H, Ph), 7.53-7.37 (m, 3H, Ph); ^{13}C NMR (50 MHz, CDCl_3): δ (J , Hz) 18.8 (C9), 43.2 (C6), 74.3 (C8), 76.2 (C7), 90.1 (C3), 117.4 (q, $^1J_{\text{C-F}} = 292.4$ Hz, CF_3), 143.1, 130.0, 128.7, 126.9 (Ph), 167.2 (C4), 176.6 (q, $^2J_{\text{C-F}} = 31.0$, C=O); MS: m/z % = 267 (M^+ , 70), 198 (100), 170 (90), 118 (80), 77 (70); IR (KBr, ν , cm^{-1}): 3243, 2118, 1657, 1534. Anal. calcd. for $\text{C}_{14}\text{H}_{12}\text{F}_3\text{NO}$: C, 62.92; H, 4.53; N, 5.24. Found: C, 63.01; H, 4.44; N, 5.08 %.

(*E*)-1,1,1-Trifluoro-4-(phenyl-*N*-1-propyn-3-ylamino)-hex-3-en-2-one (6b)



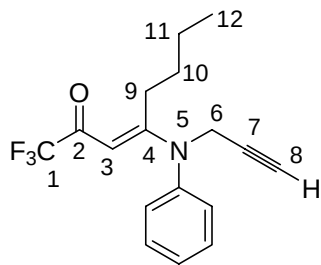
mp 54-56 °C (Yield 83%); ^1H NMR (CDCl_3 , 400 MHz): δ (J , Hz) 1.09 (t, 3H, $J = 7.3$, H10), 2.42 (t, 1H, $^4J = 2.4$, H8), 2.84 (q, 2H, H9), 4.35 (d, 2H, $^4J = 2.4$, H6), 5.48 (s, 1H, H3), 7.24-7.26 (m, 2H, H-Ar), 7.41-7.56 (m, 3H, H-Ar); ^{13}C NMR (CDCl_3 , 100 MHz): δ (J , Hz) 12.2 (C10), 24.1 (C9), 43.2 (C6), 74.3 (C8), 76.3 (C7), 88.8 (C3), 117.5 (q, $^1J = 292.4$, CF_3), 127.1, 128.8, 129.8, 142.7 (C-Ar), 172.7 (C4), 175.5 (q, $^2J = 31.0$, C=O); MS: m/z (%) = 281 (M^+ , 60), 266 (50), 212 (100), 77 (15). Anal. calcd. for $\text{C}_{15}\text{H}_{14}\text{F}_3\text{NO}$: C, 64.05; H, 5.02; N, 4.98. Found: C, 64.01; H, 5.14; N, 4.87 %.

(E)-1,1,1-Trifluoro-4-(phenyl-N-1-propyn-3-ylamino)-hept-3-en-2-one (6c)



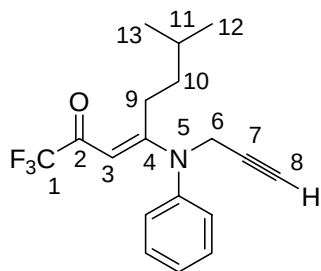
m.p. 60-62 °C (Yield 90%); ^1H NMR (400 MHz, CDCl_3): δ (J, Hz) 0.88 (t, 3H, H11), 1.51 (sex, 2H, H10), 2.42 (t, 1H, $^4J = 2.4$, H8), 2.75 (b s, 2H, H9), 4.35 (d, 2H, $^4J = 2.4$, H6), 5.50 (s, 1H, H3), 7.22-7.26 (m, 2H, H-Ar), 7.41-7.50 (m, 3H, H-Ar); ^{13}C NMR (100 MHz, CDCl_3): δ (J, Hz) 14.1 (C11), 21.8 (C10), 32.6 (C9), 43.3 (C6), 74.3 (C8), 76.4 (C7), 89.4 (C3), 117.5 (q, $^1J = 292.7$, CF_3), 127.2, 128.8, 129.9, 142.9 (C-Ar), 171.4 (C4), 175.8 (q, $^2J = 31.4$, $\text{C}=\text{O}$); MS (EI, 70eV): m/z (%) 295 (M^+ , 30), 266 (100), 226 (30), 77 (10). Anal. calcd. for $\text{C}_{16}\text{H}_{16}\text{F}_3\text{NO}$: C, 65.08; H, 5.46; N, 4.74. Found: C, 65.01; H, 5.34; N, 4.58 %.

(E)-1,1,1-Trifluoro-4-(phenyl-N-1-propyn-3-ylamino)-oct-3-en-2-one (6d)



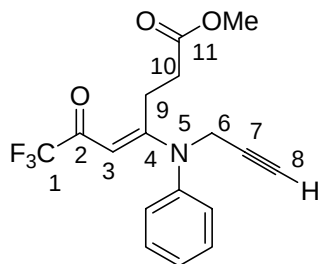
m.p. 59-60 °C (Yield 91%); ^1H NMR (400 MHz, CDCl_3): δ (J, Hz) 0.78 (t, 3H, $J = 7.1$, H12), 1.28 (sex, 2H, H11), 1.47 (quin, 2H, H10), 2.42 (t, 1H, $^4J = 2.4$, H8), 2.78 (b s, 2H, H9), 4.34 (d, 2H, $^4J = 2.4$, H6), 5.48 (s, 1H, H3), 7.26-7.23 (m, 2H, H-Ar), 7.49-7.40 (m, 3H, H-Ar); ^{13}C NMR (100 MHz, CDCl_3): δ (J, Hz) 13.3 (C12), 22.7 (C11), 30.1 (C10), 30.5 (C9), 43.3 (C6), 74.3 (C8), 76.4 (C7), 89.3 (C3), 117.5 (q, $^1J_{\text{C-F}} = 292$, CF_3), 127.3, 128.8, 129.9, 142.9 (C-Ar), 171.6 (C4), 175.7 (q, $^2J_{\text{C-F}} = 30$, C2); MS (EI, 70eV): m/z (%) 309 (M^+ , 30), 266 (100), 240 (30), 169 (20), 77 (15). Anal. calcd. for $\text{C}_{17}\text{H}_{18}\text{F}_3\text{NO}$: C, 66.01; H, 5.87; N, 4.53. Found: C, 66.21; H, 5.74; N, 4.23 %.

(E)-1,1,1-Trifluoro-7-methyl-4-(phenyl-N-1-propyn-3-ylamino)-oct-3-en-2-one (6e)



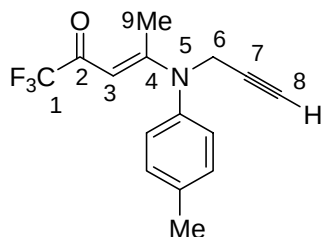
m.p. 113-114 °C (Yield 88%); ^1H NMR (400 MHz, CDCl_3): δ (J , Hz) 0.74 (d, 6H, H12, H13), 1.38 (m, 2H, H10), 1.69 (m, 1H, H11), 2.42 (t, 1H, $J = 2.3$, H8), 2.80 (b s, 2H, H9), 4.34 (d, 2H, $^4J = 2.4$, H6), 5.50 (s, 1H, H3), 7.24 (d, 2H, H-Ar), 7.48-7.42 (m, 3H, H-Ar); ^{13}C NMR (100 MHz, CDCl_3): δ (J , Hz) 21.8 (C12, C13), 28.3 (C10), 28.8 (C9), 36.6 (C11), 43.3 (C6), 74.3 (C8), 76.4 (C7), 89.2 (C3), 117.6 (q, $^1J_{\text{C-F}} = 296$, CF_3), 127.4, 128.8, 129.9, 142.9 (C-Ar), 171.8 (C4), 175.8 (q, $^2J_{\text{C-F}} = 30$, C=O); MS (EI, 70eV): m/z (%) 232 (M^+ , 25), 266 (100), 170 (35), 77 (10). Anal. calcd. for $\text{C}_{18}\text{H}_{20}\text{F}_3\text{NO}$: C, 66.86; H, 6.23; N, 4.33. Found: C, 67.01; H, 6.40; N, 4.08 %.

(E)-Methyl-6,6,6-trifluoro-5-oxo-3-(phenyl-N-1-propyn-3-ylamino)-hex-3-enoate (6f)



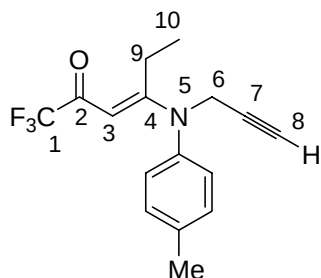
m.p. 74-76 °C (Yield 75%); ^1H NMR (400 MHz, CDCl_3): δ (J , Hz) 2.43 (t, 1H, $J = 2.3$, H8), 2.56 (b s, 2H, H9), 3.10 (m, 2H, H10), 3.62 (s, 3H, OMe), 4.40 (d, $^4J = 2.4$, 2H, H6), 5.54 (s, 1H, H3), 7.50-7.21 (m, 5H, H-Ar); ^{13}C NMR (100 MHz, CDCl_3): δ (J , Hz) 26.3 (C9), 31.7 (C10), 43.7 (C6), 51.7 (OMe), 74.6 (C8), 76.2 (C7), 90.1 (C3), 117.3 (q, $^1J_{\text{C-F}} = 292$, CF_3), 142.8, 130.2, 129.1, 127.1 (C-Ar), 169.4 (C4), 172.3 (C11), 176.1 (q, $^2J_{\text{C-F}} = 32$, C2); MS (EI, 70eV): m/z (%) 339 (M^+ , 45), 266 (100), 210 (10), 77 (10). Anal. calcd. for $\text{C}_{17}\text{H}_{16}\text{F}_3\text{NO}_3$: C, 60.18; H, 4.75; N, 4.13. Found: C, 60.11; H, 4.63; N, 4.02 %.

(E)-1,1,1-Trifluoro-4-(N-1-propyn-3-yl-4-tolyl-amino)-pent-3-en-2-one (7a)



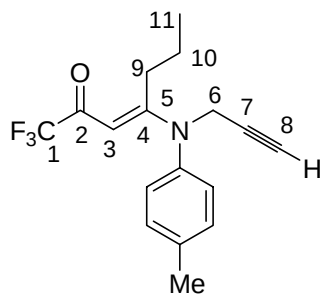
mp 88-90 °C (Yield 86%); ^1H NMR (200 MHz, CDCl_3): δ (J , Hz) 2.40 (b s, 4H, H8, H9), 2.44 (b s, 3H, $\text{CH}_3\text{-Ph}$), 2.40 (m, 1H, H8), 4.35 (d, $^4J_{\text{H-H}} = 2.4$ Hz, 2H, H6), 5.54 (s, 1H, H3), 7.10 (d, $J = 8.3$ Hz, 2H, Ph), 7.26 (d, $J = 8.0$, 2H, Ph); ^{13}C NMR (50 MHz, CDCl_3): δ (J , Hz) 18.6 (C9), 20.9 ($\text{CH}_3\text{-Ph}$), 43.2 (C6), 74.2 (C8), 76.3 (C7), 89.9 (C3), 117.5 (q, $^1J_{\text{C-F}} = 292.7$, CF_3), 140.5, 138.8, 130.5, 126.5 (Ph), 167.4 (C4), 177.8 (q, $^2J_{\text{C-F}} = 31.4$, C=O); MS: m/z % = 281 (M^+ , 43); 212 (100); 184 (43); 91 (20); IR (KBr, ν , cm^{-1}): 3246, 2120, 1649, 1545. Anal. calcd. for $\text{C}_{15}\text{H}_{14}\text{F}_3\text{NO}$: C, 64.05; H, 5.02; N, 4.98. Found: C, 64.01; H, 5.24; N, 5.06 %.

(E)-1,1,1-Trifluoro-4-(N-1-propyn-3-yl-4-tolyl-amino)-hex-3-en-2-one (7b)



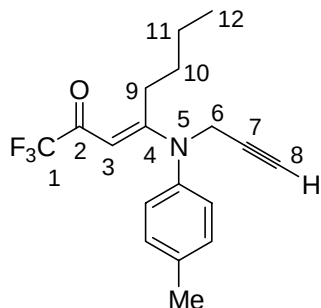
Oil (Yield 90%); ^1H NMR (400 MHz, CDCl_3): δ (J , Hz) 1.08 (b t, 3H, H10), 2.39 (s, 3H, $\text{CH}_3\text{-Ar}$), 2.42 (t, 1H, $^4J = 2.4$, 1H, H8), 2.82 (b s, 2H, H9), 4.33 (d, 2H, $^4J = 2.4$, H6), 5.48 (s, 1H, H3), 7.12 (d, 2H, H-Ar), 7.26 (d, 2H, H-Ar); ^{13}C NMR (100 MHz, CDCl_3): δ (J , Hz) 12.3 (C10), 20.9 ($\text{CH}_3\text{-Ar}$), 24.2 (C9), 43.4 (C6), 74.2 (C8), 76.4 (C7), 88.7 (C3), 117.5 (q, $^1J = 292.7$, CF_3), 126.9, 130.5, 138.9, 140.2 (C-Ar), 173.1 (C4), 175.5 (q, $^2J = 31.4$, C=O); MS (EI, 70eV): m/z (%) 295 (M^+ , 60), 280 (45), 226 (100), 91 (10). Anal. calcd. for $\text{C}_{16}\text{H}_{16}\text{F}_3\text{NO}$: C, 65.08; H, 5.46; N, 4.74. Found: C, 65.27; H, 5.44; N, 4.98 %.

(E)-1,1,1-Trifluoro-4-(N-1-propyn-3-yl-4-tolyl-amino)-hept-3-en-2-one (7c)



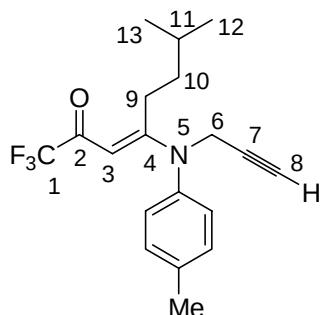
Oil (Yield 88%); ^1H NMR (200 MHz, CDCl_3): δ (J, Hz) 0.92-0.85 (m, 3H, H11), 1.57-1.46 (t, 2H, H10), 2.40 (s, 4H, H8, $\text{CH}_3\text{-Ph}$), 2.75 (b s, 2H, H9), 4.33 (d, $^4J_{\text{H-H}} = 2.3$, 2H, H6), 5.49 (s, 1H, H3), 7.11 (d, $J = 8.3$, Ph), 7.26 (d, $J = 8.0$, Ph); ^{13}C NMR (50 MHz, CDCl_3): δ (J, Hz) 14.1 (C11), 20.9 ($\text{CH}_3\text{-Ph}$), 32.6, 21.8 (C9, C10), 43.4 (C6), 74.2 (C8), 76.4 (C7), 89.1 (C3), 117.5 (q, $^1J_{\text{C-F}} = 292.7$, CF_3), 140.3, 138.8, 130.4, 126.8 (Ph), 171.7 (C4), 175.7 (q, $^2J_{\text{C-F}} = 31.4$, C=O); MS: m/z % = 309 (M^+ , 95), 280 (100), 240 (70), 168 (40). IR (KBr, ν , cm^{-1}): 3308, 2964, 2110, 1657, 1541. Anal. calcd. for $\text{C}_{17}\text{H}_{18}\text{F}_3\text{NO}$: C, 66.01; H, 5.87; N, 4.53. Found: C, 65.93; H, 5.63; N, 4.39 %.

(E)-1,1,1-Trifluoro-4-(N-1-propyn-3-yl-4-tolyl-amino)-oct-3-en-2-one (7d)



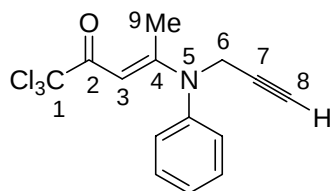
m.p. 60-62 $^{\circ}\text{C}$ (Yield 86%); ^1H NMR (400 MHz, CDCl_3): δ (J, Hz) 0.80 (m, 3H, H12), 1.29 (m, 2H, H11), 1.46 (m, 2H, H10), 2.40 (s, 4H, H8, $\text{CH}_3\text{-Ar}$), 2.78 (b s, 2H, H9), 4.32 (d, 2H, $^4J = 2.3$, H6), 5.48 (s, 1H, H3), 7.11 (d, 2H, H-Ar), 7.26 (d, 2H, H-Ar); ^{13}C NMR (100 MHz, CDCl_3): δ (J, Hz) 13.4 (C12), 21.0 (C11), 22.8 ($\text{CH}_3\text{-Ar}$), 30.6 (C10), 33.9 (C9), 43.5 (C6), 74.3 (C8), 77.1 (C7), 89.2 (C3), 117.9 (q, $^1J_{\text{C-F}} = 292$, CF_3), 127.0, 130.6, 139.0, 140.4 (C-Ar), 172.0 (C4), 175.7 (q, $^2J_{\text{C-F}} = 31.4$, C=O); MS (EI, 70eV): m/z (%) 324 ($\text{M}^+ + \text{H}$, 10), 323 (35), 280 (100), 254 (30), 183 (35), 168 (50), 91 (15). Anal. calcd. for $\text{C}_{18}\text{H}_{20}\text{F}_3\text{NO}$: C, 66.86; H, 6.23; N, 4.33. Found: C, 66.81; H, 6.44; N, 4.30 %.

(E)-1,1,1-Trifluoro-7-methyl-4-(N-1-propyn-4-tolyl-3-ylamino)-3-octen-2-one (7e)



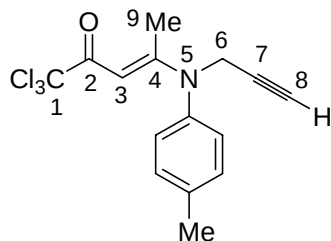
m.p. 80-82 °C (Yield 80%); ^1H NMR (400 MHz, CDCl_3): δ (J, Hz) 0.97 (d, 6H, H12, H13), 1.38 (m, 2H, H10), 1.71 (m, 2H, H11), 2.40 (s, 4H, H8, $\text{CH}_3\text{-Ar}$), 2.80 (b s, 2H, H9), 4.32 (d, 2H, $^4J = 2.3$, H6), 5.50 (s, 1H, H3), 7.20 (d, 2H, H-Ar), 7.26 (d, 2H, H-Ar); ^{13}C NMR (100 MHz, CDCl_3): δ (J, Hz) 21.1 (C12, C13), 22.0 ($\text{CH}_3\text{-Ar}$), 28.5 (C10), 30.5 (C9), 37.0 (C11), 43.8 (C6), 74.4 (C8), 77.1 (C7), 89.6 (C3), 118.4 (q, $^1J_{\text{C-F}} = 292$, CF_3), 127.2, 131.1, 139.2, 140.5 (C-Ar), 172.4 (C4), 177.0 (q, $^2J_{\text{C-F}} = 30$, C=O); MS (EI, 70eV): m/z (%) 337 (M^+ , 35), 280 (100), 268 (40), 182 (45), 168 (75). Anal. calcd. for $\text{C}_{19}\text{H}_{22}\text{F}_3\text{NO}$: C, 67.64; H, 6.57; N, 4.15. Found: C, 67.61; H, 6.48; N, 3.98 %.

(E)-1,1,1-Trichloro-4-(phenyl-N-1-propyn-3-ylamino)-pent-3-en-2-one (8a)



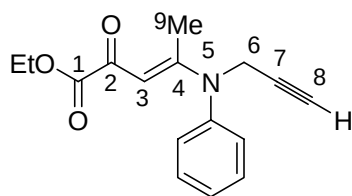
Oil (Yield 90%); ^1H NMR (400 MHz, CDCl_3): δ (J, Hz) 2.40 (s, 3H, H9), 2.42 (t, $^4J = 2.4$, 1H, H8), 4.38 (d, 2H, $^4J_{\text{H-H}} = 2.4$, H6), 5.98 (s, 1H, H3), 7.21-7.25 (m, 2H, H-Ar), 7.38-7.49 (m, 3H, H-Ar); ^{13}C NMR (100 MHz, CDCl_3): δ (J, Hz) 18.4 (C9), 43.1 (C6), 74.1 (C8), 76.7 (C7), 88.7 (C3), 99.0 (CCl_3), 127.1, 128.4, 129.9, 143.4 (H-Ar), 166.2 (C4), 179.4 (C=O); MS (EI, 70eV): m/z (%) 315 (M^+ , 10), 198 (100), 77 (10). Anal. calcd. for $\text{C}_{14}\text{H}_{12}\text{Cl}_3\text{NO}$: C, 53.11; H, 3.82; N, 4.42. Found: C, 53.01; H, 3.94; N, 4.48 %.

(E)-1,1,1-Trichloro-4-(N-1-propyn-3-yl-4-tolyl-amino)-pent-3-en-2-one (9a)



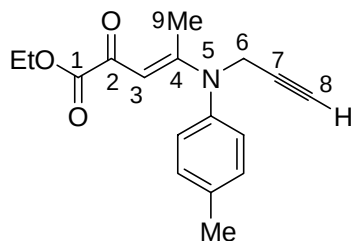
m.p. 93-95 °C (Yield 80%); ^1H NMR (400 MHz, CDCl_3): δ (J , Hz) 2.39 (s, 7H, H8, H9, $\text{CH}_3\text{-Ar}$), 4.36 (d, 2H, $^4J = 2.4$, H6), 5.97 (s, 1H, H3), 7.10 (d, 2H, H-Ar), 7.25 (d, 2H, H-Ar); ^{13}C NMR (100 MHz, CDCl_3): δ (J , Hz) 18.7 (C9), 21.2 ($\text{CH}_3\text{-Ar}$), 43.5 (C6), 74.2 (C8), 77.5 (C7), 88.8 (C3), 99.3 (CCl_3), 126.8, 130.7, 138.6, 141.1 (C-Ar), 166.7 (C4), 179.7 (C=O); MS (EI, 70eV): m/z (%) 329 (M^+ , 15), 212 (100), 91 (5). Anal. calcd. for $\text{C}_{15}\text{H}_{14}\text{Cl}_3\text{NO}$: C, 54.49; H, 4.27; N, 4.24. Found: C, 54.31; H, 4.34; N, 4.08 %.

(E)-Ethyl-4-(phenyl-N-1-propyn-3-ylamino)-2-oxo-pent-3-enoate (10a)



m.p. 83-85 °C (Yield 70%); ^1H NMR (200 MHz, CDCl_3): δ (J , Hz) 1.34 (t, $^3J_{\text{H-H}} = 7.1$, 3H, OCCCH_3), 2.43 (s, 3H, H9, H8), 4.26 (q, $^3J_{\text{H-H}} = 7.1$, 2H, OCH_2), 4.40 (d, $^4J_{\text{H-H}} = 2.2$, 2H, H6), 6.14 (s, 1H, H3), 7.22 (d, $J = 6.6$, 2H, Ph), 7.50-7.36 (m, 3H, Ph); ^{13}C NMR (50 MHz, CDCl_3): δ (J , Hz) 13.9 (OCCCH_3), 18.7 (C9), 43.1 (C6), 61.6 (OCH_2), 73.9 (C8), 76.8 (C7), 94.2 (C3), 143.5, 130, 128.5, 127.3 (Ph), 164.7 (C1), 165.4 (C4), 178.5 (C=O); MS: m/z % = 271 (M^+ , 70), 198 (20), 169 (100), 77 (10); IR (KBr, ν , cm^{-1}): 3240, 2111, 1720, 1654, 1540. Anal. calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.71; H, 6.34; N, 5.08 %.

(E)-Ethyl-4-(N-1-propyn-3-yl-4-tolyl-amino)-2-oxo-pent-3-enoate (11a)



m.p. 74-76 °C (Yield 75%); ¹H NMR (CDCl₃, 400 MHz): δ (J, Hz) 1.35 (t, 3H, OCCH₃), 2.40 (s, 4H, H8, H9), 2.42 (s, 3H, CH₃-Ar), 4.27 (q, 2H, OCH₂), 4.36 (d, 2H, ⁴J = 2.3, H6), 6.13 (s, 1H, H3), 7.10 (d, 2H, H-Ar), 7.25 (d, 2H, H-Ar); ¹³C NMR (CDCl₃, 100 MHz): δ (J, Hz) 14.0 (OCCH₃), 18.6 (C9), 21.0 (CH₃-Ar), 43.1 (C6), 61.5 (OCH₂), 73.8 (C8), 77.0 (C7), 94.0 (C3), 126.9, 130.4, 138.4, 140.9 (C-Ar), 164.7 (C1), 165.6 (C4), 178.4 (C=O); MS: m/z (%) = 285 (M⁺, 80), 212 (100), 91 (70). Anal. calcd. for C₁₇H₁₉NO₃: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.49; H, 6.64; N, 5.01 %.