Supporting Information

Addition of Amines to Triple Bond in α,α,α -Trichloromethyl Propargyl Mesylate: Synthesis of α,α -Dichloromethyl Enaminones and Preparation of 2-Phenyl-4-dichloromethyl-quinolines

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General Experimental Procedures:

Infrared (IR) spectra were determined with a FT IR spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded at 300 MHz in CDCl_3 using TMS as an internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Mass spectra were obtained by the EI method. Microanalyses were carried out at a Heraeus Rapid-CHNO instrument. All moisture sensitive reaction were done under an argon atmosphere in oven dried ($150\text{ }^\circ\text{C}$) glassware. Flash chromatography was performed using silica gel H (10-40 μm). Standard reagents and solvents were purified according to known procedures

1-Trichloromethyl-3-phenyl-2-propyn-1-ol (**1a**):

To a solution of ZnCl_2 (181 mg, 0.50 mmol) and triethylamine (104 μL , 0.75 mmol) in dried toluene (1 mL) was added phenyl acetylene (1.1 mmol) under argon atmosphere for 2 h at $25\text{ }^\circ\text{C}$. Then chloral (98 μL , 1 mmol) was introduced by syringe. The mixture was stirred overnight at rt and poured into the saturated NH_4Cl (10 mL). The mixture was extracted with EtOAc (15 mL x 3). And dried with NaSO_4 . After removal of solvent, the crude product was purified by flash chromatography on silica gel (Hexane: EtOAc = 15:1) to afford the trichloromethyl propargylic alcohol **1a** in 93% yield. FTIR (neat) 3377, 2242, 1491, 1073, 823 cm^{-1} ; ^1H NMR δ = 7.50 (m, 2H), 7.37 (m, 3H), 5.06 (s, 1H), 3.38 (s, 1H); ^{13}C NMR δ = 132.2, 129.6, 128.7, 121.4, 101.3, 88.3, 83.2, 76.0; MS (EI) m/e 248(M^+ , 1.5), 131(100)

1-Tribromomethyl-3-phenyl-2-propyn-1-ol (1b): Compound **1b** was prepared according the procedure for preparing **1a** using bromal. FTIR (neat) 3533, 3398, 2237, 1490, 1069, 756 cm^{-1} ; ^1H NMR δ = 7.52 (m, 2H), 7.35 (m, 3H), 5.03 (d, J = 9.0 Hz, 1H), 3.38 (d, J = 9.0 Hz, 1H); MS (EI) m/e 382(M^+ , 0.8), 131(100)

1-Trichloromethyl-3-phenyl-2-propyn-1-ol mesylate (2a): To a solution of the 1-trichloromethyl-3-phenyl-2-propyn-1-ol (7.936 g, 32 mmol) in 40 mL CH_2Cl_2 was added Et_3N (6.7 mL, 48 mmol) and mesyl chloride (3.2 mL, 41 mmol) in $-5\text{--}0\text{ }^\circ\text{C}$. After stirring for 1 h, the reaction mixture was warmed to room temperature. The reaction was monitored with TLC (hexane: EtOAc=15:1) and completed in 5-6 h. Saturated NH_4Cl aqueous was added to the reaction mixture. The mixture was extracted with

CH₂Cl₂ (40 mL X 2). The organic layer was dried with Na₂SO₄ and concentrated under vacuum to give the 1-trichloromethyl-3- phenyl-2-propyn-1-ol mesylate **2a** in quant yield. FTIR (neat): 2236, 1491, 1355, 1175cm⁻¹; ¹H NMR δ = 7.55-7.52 (m, 2H), 7.44-7.35 (m, 3H), 5.83 (s, 1H), 3.27 (s, 3H); ¹³C NMR δ = 132.4, 132.0, 130.5, 128.8, 120.4, 96.5, 91.1, 79.5, 39.9; MS (EI) *m/e* 326(M⁺, 8.9), 290(8.0), 209(100), 181(87.8), 131(57.4); Anal. Calcd for C₁₁H₉Cl₃O₃S: C, 40.49; H, 2.76. Found: C, 40.58; H, 2.73.

Spectral characterization data for enaminones 3:

1,1-dichloro-4-benzylamino-4-phenylbut-3-en-2-one (3a). FTIR (neat): 3197, 1604, 1586, 1570, 1487, 1339 cm⁻¹; ¹H NMR δ = 11.12 (br s, 1H), 7.50-7.18 (m, 10H), 5.90 (s, 1H), 5.49 (s, 1H), 4.43 (d, *J* = 6.3 Hz, 2H); ¹³C NMR δ = 185.0, 169.7, 137.5, 134.4, 130.5, 129.1, 129.0, 128.0, 127.8, 127.2, 91.2, 70.8, 49.1; MS (EI) *m/e* 319(M⁺, 7.6), 284(8.6), 248(10.7), 236(100), 91(93.3); Anal. Calcd for C₁₇H₁₅NCl₂O: C, 63.95; H, 4.70; N, 4.38. Found: C, 64.12; H, 4.82; N, 4.28.

1,1-dichloro-4-allylamino-4-phenylbut-3-en-2-one (3b). FTIR (neat): 3196, 1606, 1569, 1486, 1334 cm⁻¹; ¹H NMR δ = 10.85 (br s, 1H), 7.51-7.35 (m, 5H), 5.90 (s, 1H), 5.88-5.76 (m, 1H), 5.46 (s, 1H), 5.30-5.23 (m, 1H), 5.22-5.18 (m, 1H), 3.87-3.82 (m, 2H); ¹³C NMR δ = 184.5, 169.5, 134.0, 133.4, 130.1, 128.6, 127.4, 117.0, 90.7, 70.4, 47.2; MS (EI) *m/e* 269(M⁺, 11.5), 234(14.9), 186(100), 104(18.4); Anal. Calcd for C₁₃H₁₃NCl₂O: C, 58.00; H, 4.83; N, 5.20. Found: C, 57.87; H, 4.82; N, 5.20.

1,1-dichloro-4-(1-methoxycarbonyl)ethylamino-4-phenylbut-3-en-2-one (3c). FTIR (neat): 2955, 1747, 1607, 1569, 1486, 1360 cm⁻¹; ¹H NMR δ = 10.81 (br d, *J* = 9.4 Hz, 1H), 7.48-7.41 (m, 3H), 7.35-7.30 (m, 2H), 5.90 (s, 1H), 5.47 (s, 1H), 4.16 (dd, *J* = 9.5 and 2.5 Hz, 1H), 3.71 (s, 3H), 1.45 (d, *J* = 7.4 Hz, 3H); ¹³C NMR δ = 185.1, 171.9, 168.1, 135.8, 134.1, 130.1, 128.7, 127.2, 91.6, 70.3, 52.9, 52.6, 19.7; MS (EI) *m/e* 315(M⁺, 6.1), 256(10.8), 232(100), 202(15.6), 172(28.9); HRMS (EI) calcd for C₁₄H₁₅NCl₂O₃: 315.0446. Found, 315.0447.

1,1-dichloro-4-cyclohexylmethylamino-4-phenylbut-3-en-2-one (3d). FTIR (neat): 2856, 1652, 1516, 1402, 1176cm⁻¹; ¹H NMR δ = 7.45-7.41 (m, 3H), 7.17-7.14 (m, 2H), 5.65 (s, 1H), 5.51 (s, 1H), 3.20 (m, 1H), 2.99 (s, 3H), 1.70-1.42 (m, 8H), 1.02 (m, 2H);

MS (EI) m/e 325(M+, 12.4), 290(14.7), 242(56.8), 214(94.7), 160(36.5), 118(100);

1,1-dichloro-4-phenylamino-4-phenylbut-3-en-2-one (3e). FTIR (KBr): 1608, 1568, 1484, 1350, 1222, 1130, 767 cm^{-1} ; ^1H NMR δ = 12.21 (br s, 1H), 7.43-7.33 (m, 5H), 7.19-7.04 (m, 3H), 6.80 (d, J = 7.5 Hz, 2H), 5.98 (s, 1H), 5.76 (s, 1H); ^{13}C NMR δ = 184.7, 163.7, 137.3, 133.4, 129.2, 127.8, 127.5, 127.2, 124.1, 122.6, 92.4, 69.3; MS (EI) m/e 305(M+, 5.9), 222(100); HRMS (EI) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{NCl}_2\text{O}$: 306.0469. Found, 306.0447.

1,1-dichloro-4-(4-methoxyphenyl)amino-4-phenylbut-3-en-2-one (3f). FTIR (KBr): 1610, 1570, 1513, 1470, 1348, 1250, 1031 cm^{-1} ; ^1H NMR δ = 12.23 (br s, 1H), 7.39-7.31 (m, 5H), 6.77-6.67 (m, 4H), 5.97 (s, 1H), 5.71 (s, 1H), 3.73 (s, 3H); ^{13}C NMR (Acetone- d_6) δ = 185.1, 165.1, 157.7, 134.9, 131.6, 130.4, 128.9, 128.7, 128.6, 125.7, 114.3, 92.9, 70.9, 55.1; MS (EI) m/e 336(M+, 16.7), 253(100), 237(10.6), 210(34.6); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{15}\text{NCl}_2\text{O}_2$: 335.0465. Found, 335.0480. Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{NCl}_2\text{O}_2$: C, 60.90; H, 4.48; N, 4.18. Found: C, 60.77; H, 4.40; N, 3.84.

1,1-dichloro-4-(2-methoxyphenyl)amino-4-phenylbut-3-en-2-one (3g). FTIR (KBr): 1606, 1562, 1479, 1351, 1262, 1033 cm^{-1} ; ^1H NMR δ = 12.09 (br s, 1H), 7.41-7.31 (m, 5H), 7.01 (m, 1H), 6.86 (m, 1H), 6.59 (m, 1H), 6.41 (m, 1H), 5.97 (s, 1H), 5.74 (s, 1H), 3.87 (s, 3H); ^{13}C NMR δ = 184.3, 163.1, 150.3, 134.0, 129.1, 127.5, 126.9, 126.4, 124.7, 122.7, 118.9, 109.9, 92.7, 69.4, 54.6; MS (EI) m/e 335(M+, 10.9), 252(100), 237(69.6); HRMS (EI) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{16}\text{NCl}_2\text{O}_2$: 336.0549. Found, 335.0553.

1,1-dichloro-4-(4-methylphenyl)amino-4-phenylbut-3-en-2-one (3h). FTIR (KBr): 1608, 1591, 1566, 1484, 1341, 1212 cm^{-1} ; ^1H NMR δ = 12.21 (br s, 1H), 7.40-7.32 (m, 5H), 6.95 (d, J = 8.2 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 5.96 (s, 1H), 5.72 (s, 1H), 2.24 (s, 3H); ^{13}C NMR δ = 185.4, 164.9, 135.7, 135.1, 134.5, 130.1, 129.4, 128.5, 128.3, 123.5, 93.1, 70.4, 20.8; MS (EI) m/e 319(M+, 6.2), 306(9.4), 236(100), 220(7.6); HRMS (EI) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{16}\text{NCl}_2\text{O}$: 320.0611. Found, 320.0604.

1,1-dichloro-4-(4-fluorophenyl)amino-4-phenylbut-3-en-2-one (3i). FTIR (KBr): 1614, 1585, 1568, 1507, 1482, 1347, 1211 cm^{-1} ; ^1H NMR δ = 12.14 (br s, 1H), 7.41-7.29 (m, 5H), 6.88-6.75 (m, 4H), 5.96 (s, 1H), 5.76 (s, 1H); ^{13}C NMR δ = 186.0, 165.0, 161.7, 134.5, 130.4, 128.7, 128.4, 125.5, 125.4, 115.9, 115.6, 93.4, 70.3; MS (EI)

m/e 323(M⁺, 9.6), 240(100); HRMS (EI) calcd for C₁₆H₁₂NCl₂FO: 323.0274. Found, 323.0280.

1,1-dichloro-4-(4-trifluoromethoxyphenyl)amino-4-phenylbut-3-en-2-one (3j).

FTIR (KBr): 1612, 1515, 1272, 1260, 1200, 1156, 743 cm⁻¹; ¹H NMR δ = 12.12 (br s, 1H), 7.43-7.30 (m, 5H), 7.00 (m, 2H), 6.79 (m, 2H), 5.96 (s, 1H), 5.79 (s, 1H); ¹³C NMR δ = 186.2, 164.4, 146.0, 137.1, 134.0, 130.5, 128.8, 128.2, 124.6, 121.4, 94.0, 70.2; MS (EI) m/e 389(M⁺, 5.4), 306(100); HRMS (EI) [M+H]⁺calcd for C₁₇H₁₃NCl₂F₃O₂: 390.0272. Found, 390.0270.

Spectral characterization data for quinoline compounds 4:

4-dichloromethyl-2-phenylquinoline (4a). FTIR (KBr): 2970, 1599, 1350, 765 cm⁻¹; ¹H NMR δ = 8.29-8.20 (m, 5H), 7.83 (m, 1H), 7.66 (m, 1H), 7.54 (m, 3H), 7.40(s, 1H); ¹³C NMR δ = 156.1, 147.8, 142.7, 137.8, 129.7, 128.9, 128.7, 127.9, 126.4, 126.0, 121.6, 121.2, 115.4, 67.3; MS (EI) m/e 287(M⁺, 100), 252(84.6), 217(64.8), 189(14.4), 108(26.3); Anal. Calcd for C₁₆H₁₁NCl₂: C, 66.90; H, 3.83; N, 4.88. Found: C, 66.58; H, 3.86; N, 4.60.

4-dichloromethyl-6-methoxy-2-phenylquinoline (4b). FTIR (KBr): 1621, 1497, 1358, 1213, 1021, 740 cm⁻¹; ¹H NMR δ = 8.18-8.14 (m, 4H), 7.57-7.42 (m, 5H), 7.30 (s, 1H), 4.01 (s, 3H); ¹³C NMR δ = 158.0, 154.6, 145.1, 142.1, 139.0, 132.3, 129.4, 128.9, 127.2, 123.4, 122.4, 116.7, 101.3, 69.0, 55.7; MS (EI) m/e 317(M⁺, 64.3), 282(100), 267(6.3), 238(15.7), 204(20.3); HRMS (EI) [M+H]⁺calcd for C₁₇H₁₄NCl₂O: 318.0443. Found, 318.0447. Anal. Calcd for C₁₇H₁₃NCl₂O: C, 64.35; H, 4.10; N, 4.41. Found: C, 64.14; H, 4.20; N, 4.33.

4-dichloromethyl-8-methoxy-2-phenylquinoline (4c). FTIR (KBr): 1611, 1552, 1471, 1413, 1264, 1148, 744 cm⁻¹; ¹H NMR δ = 8.33 (s, 1H), 8.23-8.20 (m, 2H), 7.72 (m, 1H), 7.60-7.47 (m, 4H), 7.37 (s, 1H), 7.13 (d, J = 8.1 Hz, 1H), 4.12 (s, 3H); ¹³C NMR δ = 155.1, 154.9, 142.7, 139.8, 137.9, 128.5, 127.8, 126.5, 126.4, 122.4, 115.9, 113.1, 107.3, 67.4, 55.2; MS (EI) m/e 317(M⁺, 81.2), 282(100), 253(44.4), 217(63.7), 189(29.0), 109(54.1); Anal. Calcd for C₁₇H₁₃NCl₂O: C, 64.35; H, 4.10; N, 4.41. Found: C, 64.15; H, 4.14; N, 4.11.

4-dichloromethyl-6-methyl-2-phenylquinoline (4d). FTIR (KBr): 1601, 1552, 1449,

1349, 822, 711 cm^{-1} ; ^1H NMR δ = 8.24 (s, 1H), 8.19-8.13 (m, 3H), 7.93 (s, 1H), 7.63-7.48 (m, 4H), 7.38 (s, 1H), 2.62 (s, 3H); ^{13}C NMR δ = 156.2, 147.4, 143.0, 138.9, 137.2, 132.2, 130.4, 129.5, 128.8, 127.3, 122.2, 121.4, 116.4, 68.3, 22.1; MS (EI) m/e 301(M^+ , 88.5), 266(100), 230(53.6), 202(14.5), 115(44.6); Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{NCl}_2$: C, 67.78; H, 4.32; N, 4.65. Found: C, 67.48; H, 4.47; N, 4.40.

1,1-dichloro-4-phenyl-but-1-en-3-yn-2-ol mesylate (5a). To a solution of 1-trichloromethyl-3-phenyl-2-propyn-1-ol mesylate (326 mg, 1 mmol) in DMF was added Et_3N (153 μL , 1.1 mmol). The reaction mixture was stirring at 55-60 $^\circ\text{C}$ for 3 h. After cooling to room temperature, the reaction mixture was quenched with saturated NH_4Cl aqueous. The mixture was extracted with EtOAc (10 mL X 3). The organic layer was dried with Na_2SO_4 and concentrated under vacuum to give the mesylate **5a**. FTIR (neat): 2202, 1489, 1381, 1191, 1135, 985, 968, 792, 757 cm^{-1} ; ^1H NMR δ = 7.53-7.50 (m, 2H), 7.44-7.38 (m, 3H), 3.32 (s, 3H); ^{13}C NMR δ = 131.7, 130.2, 128.6, 128.0, 126.9, 120.4, 101.2, 79.0, 39.9; MS (EI) m/e 290(M^+ , 36.5), 212(33.8), 183(55.6), 129(100); HRMS (EI) calcd for $\text{C}_{11}\text{H}_8\text{Cl}_2\text{O}_3\text{S}$: 289.9575. Found, 289.9571.

1,1-dibromo-4-phenyl-but-1-en-3-yn-2-ol mesylate (5b). Compound **5b** was prepared according the procedure for preparing **5a**. FTIR (neat): 2205, 1378, 1188, 940, 788 cm^{-1} ; ^1H NMR δ = 7.55-7.52 (m, 2H), 7.41-7.38 (m, 3H), 3.33 (s, 3H); MS (EI) m/e 380(M^+ , 32.0), 302(39.8), 273(56.3), 129(100); HRMS (EI) calcd for $\text{C}_{11}\text{H}_8\text{Br}_2\text{O}_3\text{S}$: 377.8561. Found, 377.8570.

1,1-dibromo-4-phenyl-but-1-en-3-yn-2-ol triflate (5c). To a solution of 1-tribromomethyl-3-phenyl-2-propyn-1-ol (380 mg, 1 mmol) in CH_2Cl_2 (3 mL) was added Et_3N (347 μL , 2.5 mmol). The reaction mixture was cooled to -70 $^\circ\text{C}$. To this mixture was added Tf_2O (310 mg, 1.1 mmol). After stirring for 1 h, the reaction mixture was warmed to room temperature. The mixture was quenched with saturated NH_4Cl aqueous after stirring for 4 h. The resulting mixture was extracted with CH_2Cl_2 (10 mL X 3). The organic layer was dried with Na_2SO_4 . After removal of solvent, the crude product was purified by flash chromatography on silica gel (Hexane: EtOAc = 15:1) to afford the triflate **5c**. FTIR (neat): 2208, 1431, 1219, 1137, 935 cm^{-1} ; ^1H NMR δ = 7.56-6.79 (m, 5H); ^{19}F NMR δ = -73.5 (s, 3F); MS (EI) m/e 432(M^+ , 4.6),

286(37.2), 273(40.6), 126(100); HRMS (EI) calcd for $C_{11}H_5Br_2O_3SF_3$: 431.8277.

Found, 431.8259.

Figure 1. X-ray Analysis of Compound 3d