Supporting Information for OL

Efficient Synthesis of 1,3,5-Trisubstituted (Pyrrol-2-yl)acetic Acid Esters via Dual Nucleophilic Reactions of Sulfonamides or Carbamate with 4-Trimethylsiloxy-(5*E*)-hexen-2-ynoates: Lewis Acid-Catalyzed S_N1 and Intramolecular Michael Addition

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Experimental Section

*General procedure for the preparation of 4,6-disubstituted ethyl 4-trimethylsiloxy-(5*E*)-hexen-2-ynoate: the following procedure for the synthesis of **1a** is representative.*

Ethyl 4-methyl-6-phenyl-4-(trimethylsiloxy)-(5*E*)-hexen-2-ynoate (1a). To a solution of ethyl propiolate (1.26 mL, 12.3 mmol) in THF (50 mL) was added BuLi (1.56 M in hexane, 7.9 mL, 12.3 mmol) at $-78\text{ }^{\circ}\text{C}$. After stirring at $-78\text{ }^{\circ}\text{C}$ for 15 min, benzalacetone was added to the mixture at $-78\text{ }^{\circ}\text{C}$. The reaction was stirred at $-78\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$ for 4.5 h and quenched by the addition of saturated aqueous solution of NH₄Cl. The mixture was extracted with EtOAc. The combined organic layers were dried over Na₂SO₄ and concentrated to give an oil, which was purified by CC to provide 2-propynyl alcohol (1.43 g, 86 %). To a solution of this alcohol (1.43 g, 5.85 mmol) in THF (50 mL) were added imidazole (2.39 g, 35.1 mmol) and chlorotrimethylsilane (2.25 mL, 17.6 mmol) at $0\text{ }^{\circ}\text{C}$, and the mixture was stirred at room temperature for 30 min. The reaction was quenched by the addition of water and the mixture was extracted with EtOAc. The combined organic layers were dried over Na₂SO₄ and concentrated to give an oil, which was purified by CC to provide **1a** (1.59 g, 85 %, 2 steps: 74 %) as a yellow gum; ¹H NMR δ 0.23 (s, 9H), 1.33 (t, 3H, $J = 7.1\text{ Hz}$), 1.68 (s, 3H), 4.27 (q, 2H, $J = 7.1\text{ Hz}$), 6.21 (d, 1H, $J = 15.8\text{ Hz}$), 6.77 (d, 1H, $J = 15.8\text{ Hz}$), 7.20–7.45 (m, 5H); ¹³C NMR δ 1.8, 14.0, 32.0, 62.0, 69.2, 77.5, 88.9, 126.8, 127.9, 128.6, 129.1, 132.7, 136.1, 153.5; $R_f = 0.80$ (hexane : EtOAc = 3 : 1); exact mass, m/z 316.14955 (calcd for C₁₈H₂₄O₃Si m/z 316.14947).

*Spectroscopic data for **1b–j** with yield (not optimized).*

Ethyl 4-isopropyl-6-phenyl-4-(trimethylsiloxy)-(5*E*)-hexen-2-ynoate (1b). Yield: 33 %; ¹H NMR δ 0.91 (s, 9H), 0.96 (d, 3H, $J = 6.9\text{ Hz}$), 1.03 (d, 3H, $J = 6.6\text{ Hz}$), 1.33 (t, 3H, $J = 7.1\text{ Hz}$), 1.85–2.05 (m, 1H), 4.26 (q, 2H, $J = 7.1\text{ Hz}$), 6.11 (d, 1H, $J = 15.9\text{ Hz}$), 6.75 (d, 1H, $J = 15.9\text{ Hz}$), 7.20–7.45 (m, 5H); ¹³C NMR δ 1.7, 14.0, 17.1, 17.4, 40.3, 62.0, 76.5, 79.5, 87.6, 126.7, 127.9, 128.6, 130.7, 131.1, 136.3, 153.5; $R_f = 0.53$ (hexane : EtOAc = 3 : 1).

Ethyl 4,6-diphenyl-4-(trimethylsiloxy)-(5*E*)-hexen-2-ynoate (1c). Yield: 82 %; ¹H NMR δ 0.23 (s, 9H), 1.34 (t, 3H, $J = 7.1\text{ Hz}$), 4.29 (q, 2H, $J = 7.1\text{ Hz}$), 6.25 (d, 1H, $J = 15.7\text{ Hz}$), 6.88 (d, 1H, $J = 15.7$

Hz), 7.20–7.45 (m, 8H), 7.50–7.70 (m, 2H); ^{13}C NMR δ 1.6, 13.9, 62.0, 74.0, 79.8, 87.3, 125.6, 125.7, 126.8, 126.8, 127.9, 128.0, 128.2, 128.3, 128.5, 128.6, 128.9, 129.0, 132.6, 132.7, 135.8, 143.0, 153.2; R_f = 0.80 (hexane:EtOAc = 3:1); exact mass, m/z 378.16502 (calcd for $\text{C}_{23}\text{H}_{26}\text{O}_3\text{Si}$ m/z 378.16512).

Ethyl 4-isopropyl-6-(2-bromophenyl)-4-(trimethylsiloxy)-(5E)-hexen-2-ynoate (1d). Yield: 88 %; ^1H NMR δ 0.24 (s, 9H), 1.01 (d, 3H, J = 6.6 Hz), 1.44 (s, 3H, J = 6.6 Hz), 1.33 (t, 3H, J = 7.1 Hz), 1.85–2.05 (m, 1H), 4.26 (q, 2H, J = 7.1 Hz), 6.08 (d, 1H, J = 15.7 Hz), 7.05–7.18 (m, 2H), 7.20–7.35 (m, 1H), 7.40–7.60 (m, 2H); ^{13}C NMR δ 1.7, 14.0, 17.1, 17.4, 40.2, 62.0, 76.1, 79.4, 87.5, 124.0, 127.2, 127.5, 129.0, 129.7, 133.0, 134.1, 136.5, 153.3; R_f = 0.75 (hexane : EtOAc = 3 : 1).

Ethyl 6-phenyl-4-(3,4-dimethoxyphenyl)-4-(trimethylsiloxy)-(5E)-hexen-2-ynoate (1e). Yield: 40 %; ^1H NMR δ 0.22 (s, 9H), 1.33 (t, 3H, J = 7.1 Hz), 3.88 (s, 3H), 3.89 (s, 3H), 4.28 (q, 2H, J = 7.1 Hz), 6.25 (d, 1H, J = 15.7 Hz), 6.82 (s, 1H, J = 7.1 Hz), 7.05–7.45 (m, 7H); ^{13}C NMR δ 1.5, 1.6, 14.0, 55.9, 55.9, 62.1, 73.8, 79.7, 87.6, 109.3, 110.7, 118.2, 126.9, 128.0, 128.6, 129.0, 132.8, 135.7, 136.0, 148.8, 153.4; R_f = 0.13 (hexane : EtOAc = 3 : 1); exact mass, m/z 438.18630 (calcd for $\text{C}_{25}\text{H}_{30}\text{O}_5\text{Si}$ m/z 438.18625).

Ethyl 4-isopropyl-6-(4-methoxyphenyl)-4-(trimethylsiloxy)-(5E)-hexen-2-ynoate (1f). Yield: 75 %; ^1H NMR δ 0.19 (s, 9H), 0.96 (d, 3H, J = 6.9 Hz), 1.04 (d, 1H, J = 6.6 Hz), 1.34 (t, 3H, J = 7.1 Hz), 1.80–2.00 (m, 1H), 3.82 (s, 3H), 4.27 (q, 2H, J = 7.1 Hz), 5.98 (d, 1H, J = 15.9 Hz), 6.70 (d, 1H, J = 15.9 Hz), 6.80–6.95 (m, 2H), 7.30–7.40 (m, 2H); ^{13}C NMR δ 1.7, 14.0, 17.1, 17.4, 40.3, 55.3, 62.0, 79.4, 87.9, 114.0, 127.9, 128.9, 129.0, 130.2, 153.5, 159.4; R_f = 0.63 (hexane : EtOAc = 3 : 1).

Ethyl 4-isopropyl-6-(4-chlorophenyl)-4-(trimethylsiloxy)-(5E)-hexen-2-ynoate (1g). Yield: 72 %; ^1H NMR δ 0.12 (s, 9H), 0.97 (d, 3H, J = 6.9 Hz), 1.04 (d, 3H, J = 6.6 Hz), 1.34 (t, 3H, J = 7.1 Hz), 1.85–2.00 (m, 1H), 4.27 (q, 2H, J = 7.1 Hz), 6.10 (d, 1H, J = 15.9 Hz), 6.71 (d, 1H, J = 15.9 Hz), 7.20–7.40 (m, 5H); ^{13}C NMR δ 1.7, 14.0, 17.1, 17.3, 40.2, 62.0, 76.4, 79.6, 87.4, 127.9, 128.8, 129.5, 131.8, 133.5, 134.7, 153.4; R_f = 0.70 (hexane : EtOAc = 3 : 1); exact mass, m/z 378.14176 (calcd for $\text{C}_{20}\text{H}_{27}\text{ClO}_3\text{Si}$ m/z 378.14180).

Ethyl 6-cyclohexyl-4-(4-methoxyphenyl)-4-(trimethylsiloxy)-(5E)-hexen-2-ynoate (1h). Yield: 51 %; ^1H NMR δ 0.19 (s, 9H), 1.00–2.10 (m, 11H), 1.31 (t, 3H, J = 7.1 Hz), 3.80 (s, 3H), 4.24 (q, 2H, J = 7.1 Hz), 5.49 (dd, 1H, J = 1.1, 15.5 Hz), 6.80–6.95 (m, 2H), 7.35–7.50 (m, 2H); ^{13}C NMR δ 1.7, 13.9, 25.9, 26.0, 32.3, 32.5, 39.9, 55.1, 61.8, 73.6, 79.2, 88.3, 113.3, 126.8, 131.1, 135.8, 136.1, 153.4, 159.0; R_f = 0.75 (hexane : EtOAc = 3 : 1).

Ethyl 6-cyclohexyl-4-phenyl-4-(trimethylsiloxy)-(5E)-hexen-2-ynoate (1i). Yield: 41 %; ^1H NMR δ 0.20 (s, 9H), 1.00–2.10 (m, 11H), 1.31 (t, 3H, J = 7.1 Hz), 4.25 (q, 2H, J = 7.1 Hz), 5.50 (dd, 1H, J = 1.4, 15.4 Hz), 8.79 (dd, 1H, J = 6.7, 15.4 Hz), 7.20–7.40 (m, 3H), 7.40–7.60 (m, 2H); ^{13}C NMR δ 1.8, 14.0, 25.9, 26.1, 32.4, 32.5, 40.0, 62.0, 74.0, 79.4, 88.2, 125.6, 127.6, 128.1, 131.1, 136.5, 143.8, 153.4; R_f = 0.80 (hexane : EtOAc = 3 : 1); exact mass, m/z 384.21211 (calcd for $\text{C}_{23}\text{H}_{32}\text{O}_3\text{Si}$ m/z 384.21207).

Ethyl 6-cyclohexyl-4-methyl-4-(trimethylsiloxy)-(5E)-hexen-2-ynoate (1j). Yield: 40%; ^1H -

NMR δ 0.17 (s, 9H), 1.00–2.10 (m, 11H), 1.31 (t, 3H, J = 6.7, 15.7 Hz), 1.54 (s, 3H), 4.24 (q, 2H, J = 7.1 Hz), 5.43 (dd, 1H, J = 1.4, 15.7 Hz), 5.80 (dd, 1H, J = 6.7, 15.7 Hz); R_f = 0.32 (hexane:EtOAc = 5:1).

General procedure for one-pot preparation of pyrroles (3) with sulfonamides (2): the following procedure for the synthesis of 3h is representative.

Ethyl (1-benzenesulfonyl-3,5-diphenylpyrrol-2-yl)acetate (3h). To a solution of silyl ether **1c** (69 mg, 0.18 mmol) and benzenesulfonamide (42 mg, 0.27 mmol) in dichloromethane (2 mL) was added trimethylsilyl trifluoromethanesulfonate (0.005 mL, 0.028 mmol) at -30 °C. The reaction was stirred at -30 °C for 1 h and quenched by the addition of saturated aqueous solution of NaHCO_3 at 0 °C. The mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated to give an oil, which was purified by CC to provide **3h** (77 mg, 96 %) as a yellow gum; IR (neat): 2891, 1737 cm^{-1} ; ^1H NMR δ 1.34 (t, 3H, J = 7.1 Hz), 4.04 (s, 2H), 4.30 (q, 2H, J = 7.1 Hz), 6.26 (s, 1H), 7.05–7.60 (m, 15H); ^{13}C NMR δ 14.2, 34.1, 61.0, 116.0, 126.2, 127.1, 127.2, 127.3, 128.2, 128.8, 129.9, 131.3, 131.5, 133.3, 134.3, 137.1, 139.4, 171.6; R_f = 0.33 (hexane : EtOAc = 3 : 1); exact mass, m/z 445.13471 (calcd for $\text{C}_{26}\text{H}_{23}\text{NO}_4\text{S}$ m/z 445.13478).

Spectroscopic data for 3a–g,i–o with reaction time and yield (not optimized).

Ethyl (1-benzenesulfonyl-3-methyl-5-phenylpyrrol-2-yl)acetate (3a). Yellow gum; Yield: 55 %; Reaction time: 1 h; IR (neat): 3020, 1732 cm^{-1} ; ^1H NMR δ 1.32 (t, 3H, J = 7.1 Hz), 2.02 (s, 3H), 3.98 (s, 2H), 4.24 (q, 2H, J = 7.1 Hz), 5.97 (s, 1H), 7.05–7.50 (m, 10H); ^{13}C NMR δ 11.3, 14.2, 32.7, 61.0, 117.9, 123.9, 126.7, 126.9, 127.1, 127.9, 128.5, 131.0, 132.0, 133.2, 137.0, 139.4, 170.8; R_f = 0.27 (hexane : EtOAc = 3 : 1); exact mass, m/z 383.11920 (calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_4\text{S}$ m/z 383.11913).

Ethyl [3-methyl-5-phenyl-1-(p-toluenesulfonyl)pyrrol-2-yl]acetate (3b). Red gum; Yield: 81 %; Reaction time: 1 h; IR (neat): 2981, 1736 cm^{-1} ; ^1H NMR δ 1.32 (t, 3H, J = 7.1 Hz), 2.01 (s, 3H), 3.97 (s, 2H), 4.24 (q, 2H, J = 7.1 Hz), 5.97 (s, 1H), 7.00–7.40 (m, 9H); ^{13}C NMR δ 11.3, 14.2, 21.5, 32.7, 60.9, 117.9, 123.8, 126.6, 126.9, 127.1, 127.2, 127.8, 129.1, 129.6, 130.9, 132.2, 137.0, 144.1, 170.8; R_f = 0.20 (hexane : EtOAc = 3 : 1).

Ethyl [1-(4-methoxybenzenesulfonyl)-3-methyl-5-phenylpyrrol-2-yl]acetate (3c). Yellow gum; Yield: 52 %; Reaction time: 3 h; IR (neat): 2981, 1736 cm^{-1} ; ^1H NMR δ 1.32 (t, 3H, J = 7.1 Hz), 2.01 (s, 3H), 3.79 (s, 3H), 3.97 (s, 2H), 4.24 (t, 2H, J = 7.1 Hz), 5.97 (s, 1H), 6.65–6.75 (m, 2H), 7.10–7.30 (m, 7H); ^{13}C NMR δ 11.3, 14.2, 32.8, 55.5, 60.9, 113.6, 117.7, 123.6, 126.5, 127.1, 127.8, 129.2, 131.0, 131.0, 132.2, 136.8, 163.2, 171.0; R_f = 0.38 (hexane : EtOAc = 3 : 1); Anal. Calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_5\text{S}$: C, 63.90; H, 5.61; Found: C, 63.88; H, 5.60.

Ethyl (1-benzenesulfonyl-3-isopropyl-5-phenylpyrrol-2-yl)acetate (3d). Yellow gum; Yield: 62 %; Reaction time: 1 h; IR (neat): 2962, 1735 cm^{-1} ; ^1H NMR δ 1.15 (d, 6H, J = 6.9 Hz), 1.31 (t, 3H, J = 7.1 Hz), 2.75–2.85 (m, 1H), 4.00 (s, 1H), 4.23 (q, 2H, J = 7.1 Hz), 6.06 (s, 1H), 7.05–7.50 (m, 9H); ^{13}C NMR δ 14.2, 23.3, 25.3, 32.6, 60.9, 114.0, 125.1, 126.7, 127.1, 127.9, 128.4, 130.9, 132.2, 133.1,

135.3, 137.6, 139.3, 170.9; $R_f = 0.27$ (hexane : EtOAc = 3 : 1).

Ethyl [3-isopropyl-5-phenyl-1-(*p*-toluenesulfonyl)pyrrol-2-yl]acetate (3e). Yellow gum; Yield: 69 %; Reaction time: 3 h; IR (neat): 2962, 1738 cm^{-1} ; ^1H NMR δ 1.14 (d, 6H, $J = 6.9$ Hz), 1.30 (t, 3H, $J = 7.1$ Hz), 2.34 (s, 3H), 2.65–2.90 (m, 1H), 3.98 (s, 2H), 4.22 (q, 2H, $J = 7.1$ Hz), 6.05 (s, 1H), 7.00–7.40 (m, 9H); ^{13}C NMR δ 14.2, 21.5, 23.3, 25.3, 32.6, 60.9, 133.9, 125.0, 126.8, 127.1, 129.0, 130.9, 132.4, 135.2, 136.5, 137.6, 144.0, 170.9; $R_f = 0.27$ (hexane : EtOAc = 3 : 1); exact mass, m/z 425.16600 (calcd for $\text{C}_{24}\text{H}_{27}\text{NO}_4\text{S}$ m/z 425.16608).

Ethyl [3-isopropyl-1-(4-methoxybenzenesulfonyl)-5-phenylpyrrol-2-yl]acetate (3f). Yellow gum; Yield: 72 %; Reaction time: 1 h; IR (neat): 2962, 1736 cm^{-1} ; ^1H NMR δ 1.14 (d, 6H, $J = 6.9$ Hz), 1.31 (t, 3H, $J = 7.1$ Hz), 2.70–2.90 (m, 1H), 3.79 (s, 3H), 3.98 (s, 2H), 4.24 (q, 2H, $J = 7.1$ Hz), 6.04 (s, 1H), 6.65–6.75 (m, 2H), 7.10–7.30 (m, 7H); ^{13}C NMR δ 14.2, 23.3, 25.3, 32.6, 55.5, 60.9, 113.5, 113.8, 125.0, 127.1, 127.8, 129.2, 130.9, 131.2, 132.5, 135.0, 137.4, 163.2, 171.1; $R_f = 0.17$ (hexane : EtOAc = 3 : 1).

Ethyl (3-isopropyl-1-methanesulfonyl-5-phenylpyrrol-2-yl)acetate (3g). Yellow gum; Yield: 39 %; Reaction time: 2 h; IR (neat): 2964, 1736 cm^{-1} ; ^1H NMR δ 1.25 (d, 6H, $J = 6.9$ Hz), 1.36 (t, 3H, $J = 7.1$ Hz), 2.75–2.90 (m, 1H), 3.98 (s, 2H), 4.26 (q, 2H, $J = 7.1$ Hz), 6.29 (s, 1H), 7.40–7.60 (m, 5H); ^{13}C NMR δ 14.2, 23.3, 25.3, 32.1, 41.0, 61.0, 114.5, 124.5, 127.4, 128.3, 130.8, 132.5, 135.2, 137.1, 171.4; $R_f = 0.33$ (hexane : EtOAc = 3 : 1); exact mass, m/z 349.13471 (calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_4\text{S}$ m/z 349.13478).

Ethyl [3,5-diphenyl-1-(*p*-toluenesulfonyl)pyrrol-2-yl]acetate (3i). Red gum; Yield: 89 %; Reaction time: 15 h; IR (neat): 3061, 1736 cm^{-1} ; ^1H NMR δ 1.28 (t, 3H, $J = 7.1$ Hz), 2.28 (s, 3H), 3.96 (s, 2H), 4.23 (q, 2H, $J = 7.1$ Hz), 6.19 (s, 1H), 6.95–7.45 (m, 14H); ^{13}C NMR δ 14.2, 21.6, 34.1, 61.1, 116.0, 126.1, 126.4, 127.1, 127.3, 128.1, 128.5, 128.8, 129.2, 129.7, 129.9, 131.3, 131.7, 134.3, 136.5, 137.1, 144.4, 171.7; $R_f = 0.22$ (hexane : EtOAc = 3 : 1); exact mass, m/z 459.15021 (calcd for $\text{C}_{27}\text{H}_{25}\text{NO}_4\text{S}$ m/z 459.15043).

Ethyl [1-(4-methoxybenzenesulfonyl)-3,5-diphenylpyrrol-2-yl]acetate (3j). Yellow gum; Yield: 94 %; Reaction time: 3 h; IR (neat): 3022, 1732 cm^{-1} ; ^1H NMR δ 1.34 (t, 3H, $J = 7.1$ Hz), 3.80 (s, 3H), 4.02 (s, 2H), 4.30 (q, 2H, $J = 7.1$ Hz), 6.25 (s, 1H), 6.65–6.75 (m, 2H), 7.10–7.45 (m, 12H); ^{13}C NMR δ 14.3, 34.1, 55.6, 61.0, 113.7, 115.8, 126.0, 127.1, 127.2, 128.1, 128.5, 128.8, 129.5, 129.7, 131.1, 131.4, 131.8, 134.4, 131.8, 134.4, 137.0, 163.4, 171.8; $R_f = 0.07$ (hexane : EtOAc = 3 : 1).

Ethyl [1-(4-nitrobenzenesulfonyl)-3,5-diphenylpyrrol-2-yl]acetate (3k). Yellow gum; Yield: 31 %; Reaction time: 3 h; IR: 2983, 1736 cm^{-1} ; ^1H NMR δ 1.34 (t, 3H, $J = 7.1$ Hz), 4.02 (s, 2H), 4.30 (q, 2H, $J = 7.1$ Hz), 6.30 (s, 2H), 7.05–7.75 (m, 12H), 8.05–8.20 (m, 2H); ^{13}C NMR δ 14.2, 34.2, 61.3, 116.8, 123.7, 126.4, 127.5, 127.7, 128.7, 128.7, 130.8, 131.1, 131.4, 133.7, 137.0, 144.4, 150.2, 171.9; $R_f = 0.33$ (hexane : EtOAc = 3 : 1); exact mass, m/z 490.11100 (calcd for $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_6\text{S}$ m/z 490.11986).

Ethyl (1-methanesulfonyl-3,5-diphenylpyrrol-2-yl)acetate (3l). Yellow gum; Yield: 64 %; Reaction time: 2 h; IR (neat): 2181, 1736 cm^{-1} ; ^1H NMR δ 1.33 (t, 3H, $J = 7.1$ Hz), 2.99 (s, 3H), 3.95 (s,

3H), 4.26 (q, 2H, $J = 7.1$ Hz), 6.43 (s, 1H), 7.25–7.55 (m, 10H); ^{13}C NMR δ 14.2, 33.6, 41.6, 61.1, 116.8, 125.5, 127.4, 127.5, 128.6, 128.7, 128.8, 130.2, 131.1, 131.9, 134.1, 136.9, 172.0; $R_f = 0.30$ (hexane : EtOAc = 3 : 1).

Ethyl [1-benzensulfinyl-5-(2-bromophenyl)-3-isopropylpyrrol-2-yl]acetate (3m). Yellow gum; Yield: 71 %; Reaction time: 1 h; IR (neat): 2962, 1738 cm^{-1} ; ^1H NMR δ 1.15 (d, 3H, $J = 4.4$ Hz), 1.17 (d, 3H, $J = 4.4$ Hz), 1.29 (t, 3H, $J = 7.1$ Hz), 2.70–2.90 (m, 1H), 3.99 (s, 2H), 4.20 (q, 2H, $J = 7.1$ Hz), 6.16 (s, 1H), 7.10–7.60 (m, 9H); ^{13}C NMR δ 14.2, 23.4, 23.5, 25.3, 32.3, 60.9, 114.7, 124.2, 125.9, 126.5, 127.1, 128.8, 129.7, 132.1, 133.4, 134.0, 134.3, 139.7, 170.7; $R_f = 0.50$ (hexane : EtOAc = 3:1).

Ethyl [5-(2-bromophenyl)-3-isopropyl-1-(p-toluenesulfonyl)pyrrol-2-yl]acetate (3n). Yellow gum; Yield: 59 %; Reaction time: 2 h; IR (neat): 2962, 1738 cm^{-1} ; ^1H NMR δ 1.14 (d, 3H, $J = 4.4$ Hz), 1.17 (d, 3H, $J = 4.4$ Hz), 1.28 (t, 3H, $J = 7.1$ Hz), 2.37 (s, 3H), 2.70–2.85 (m, 1H), 3.97 (s, 2H), 4.19 (q, 2H, $J = 7.1$ Hz), 6.14 (s, 1H), 7.10–7.50 (m, 8H); ^{13}C NMR δ 14.2, 21.6, 23.4, 23.5, 25.3, 32.2, 60.9, 114.5, 124.0, 125.9, 126.5, 127.1, 129.3, 129.6, 132.1, 133.6, 133.9, 134.0, 134.2, 136.8, 144.3, 170.7; $R_f = 0.50$ (hexane : EtOAc = 3 : 1); exact mass, m/z 503.07688 (calcd for $\text{C}_{24}\text{H}_{26}\text{BrNO}_4\text{S}$ m/z 503.07659).

Ethyl [1-(4-methoxybenzenesulfonyl)-3-(3,4-dimethoxyphenyl)-5-phenylpyrrol-2-yl]acetate (3o). Yellow gum; Yield: 45 %; Reaction time: 2 h; IR (neat): 2990, 1736 cm^{-1} ; ^1H NMR δ 1.33 (t, 3H, $J = 7.1$ Hz), 3.80 (s, 3H), 3.87 (s, 3H), 3.90 (s, 3H), 4.01 (s, 2H), 4.28 (q, 2H, $J = 7.1$ Hz), 6.23 (s, 1H), 6.65–6.75 (m, 2H), 6.85–7.00 (m, 3H), 7.05–7.40 (m, 8H); ^{13}C NMR δ 14.3, 34.3, 55.6, 55.8, 55.9, 61.0, 111.2, 112.1, 113.7, 115.8, 121.0, 125.7, 127.1, 127.2, 128.1, 129.5, 129.8, 131.0, 131.3, 131.7, 137.0, 148.4, 148.8, 163.4, 172.1; $R_f = 0.10$ (hexane : EtOAc = 2 : 1); exact mass, m/z 535.16627 (calcd for $\text{C}_{29}\text{H}_{29}\text{NO}_7\text{S}$ m/z 535.16647).

General procedure for the preparation of ethyl 6-[N-(benzyloxycarbonyl)amino]-4-hexen-2-ynoates 6: the following procedure for the synthesis of 6c is representative.

Ethyl 6-(N-benzyloxycarbonyl)amino-4,6-diphenyl-(4Z)-hexen-2-ynoate (6c). To a solution of silyl ether **1c** (62 mg, 0.16 mmol) and benzyl carbamate (37 mg, 0.25 mmol) in dichloromethane (1.6 mL) was added trimethylsilyl trifluoromethanesulfonate (0.005 mL, 0.028 mmol) at -30 °C. The reaction was stirred at -30 °C for 1 h and quenched by the addition of saturated aqueous solution of NaHCO_3 at 0 °C. The mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated to give an oil, which was purified by CC to provide **6c** (59 mg, 82 %) as a red gum. ^1H NMR δ 1.35 (t, 3H, $J = 7.1$ Hz), 4.29 (q, 2H, $J = 7.1$ Hz), 5.14 (s, 2H), 5.25–5.40 (m, 1H), 5.85–6.00 (m, 1H), 6.71 (d, 1H, $J = 9.1$ Hz), 7.20–7.45 (m, 13H), 7.50–7.60 (m, 2H); ^{13}C NMR δ 14.0, 55.9, 62.2, 67.0, 81.9, 122.6, 126.2, 126.6, 128.0, 128.1, 128.5, 128.6, 128.7, 129.0, 135.4, 136.2, 139.8, 141.5, 153.6, 155.4; $R_f = 0.30$ (hexane : EtOAc = 3 : 1).

Spectroscopic data for 6a,b–d–f with reaction time and yield (not optimized).

Ethyl 6-(N-benzyloxycarbonyl)amino-4-methyl-6-phenyl-(4Z)-hexen-2-ynoate (6a). Red gum;

Yield: 53 %; Reaction time: 30 min; ^1H NMR δ 1.32 (t, 3H, $J = 7.1$ Hz), 1.93 (s, 3H), 4.25 (q, 2H, $J = 7.1$ Hz), 5.12 (s, 2H), 5.10–5.30 (m, 1H), 5.60–5.80 (m, 1H), 6.05 (d, 1H, $J = 7.4$ Hz), 7.20–7.40 (m, 10H); ^{13}C NMR δ 14.0, 22.2, 55.6, 62.0, 66.9, 83.8, 117.7, 126.4, 127.8, 128.1, 128.4, 128.9, 136.3, 140.2, 142.0, 153.7, 155.4; $R_f = 0.30$ (hexane : EtOAc = 3 : 1).

Ethyl 6-(*N*-benzyloxycarbonyl)amino-4-isopropyl-6-phenyl-(4*Z*)-hexen-2-ynoate (6b). Red gum; Yield: 58 %; Reaction time: 1 h; IR (neat): 2966, 2210, 1709 cm^{-1} ; ^1H NMR δ 1.00–1.20 (m, 6H), 1.32 (t, 3H, $J = 7.1$ Hz), 2.30–2.60 (m, 1H), 4.27 (t, 2H, $J = 7.1$ Hz), 5.12 (s, 2H), 5.37 (s, 1H), 5.70–5.85 (m, 1H), 6.05 (d, 1H, $J = 8.0$ Hz), 7.20–7.70 (m, 10H); ^{13}C NMR δ 14.0, 21.4, 21.4, 34.7, 55.3, 61.9, 66.8, 82.4, 126.3, 127.6, 128.0, 128.4, 128.7, 129.2, 136.2, 139.1, 140.4, 153.7; $R_f = 0.40$ (hexane : EtOAc = 3 : 1); exact mass, m/z 405.19385 (calcd for $\text{C}_{25}\text{H}_{27}\text{NO}_4$ m/z 405.19401).

Ethyl 6-(*N*-benzyloxycarbonyl)amino-4-isopropyl-6-(4-methoxyphenyl)-(4*Z*)-hexen-2-ynoate (6d). Yellow gum; Yield: 86 %; Reaction time: 30 min; IR (neat): 3334, 2934, 2210 cm^{-1} ; ^1H NMR δ 1.05–1.20 (m, 6H), 1.32 (t, 3H, $J = 7.1$ Hz), 2.35–2.50 (m, 1H), 3.79 (s, 3H), 4.24 (q, 2H, $J = 7.1$ Hz), 5.12 (s, 2H), 5.10–5.25 (m, 1H), 5.66 (dd, 1H, $J = 7.1, 8.8$ Hz), 6.04 (d, 1H, $J = 8.5$ Hz), 6.80–6.90 (m, 2H), 7.15–7.40 (m, 7H); ^{13}C NMR δ 14.1, 21.4, 21.5, 34.7, 54.8, 55.2, 61.9, 66.9, 82.6, 114.2, 127.6, 128.0, 128.4, 128.9, 132.6, 136.3, 139.5, 153.8, 159.1; $R_f = 0.27$ (hexane : EtOAc = 3 : 1); exact mass, m/z 435.20428 (calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_5$ m/z 435.20457).

Ethyl 6-(*N*-benzyloxycarbonyl)amino-4-isopropyl-6-(4-chlorophenyl)-(4*Z*)-hexen-2-ynoate (6e). Yellow gum; Yield: 57 %; Reaction time: 30 min; ^1H NMR δ 1.05–1.20 (m, 6H), 1.32 (t, 3H, $J = 7.1$ Hz), 2.35–2.50 (m, 1H), 4.25 (q, 2H, $J = 7.1$ Hz), 5.11 (s, 2H), 5.10–5.30 (m, 1H), 5.60–5.75 (m, 1H), 5.99 (d, 1H, $J = 8.8$ Hz), 7.20–7.45 (m, 9H); ^{13}C NMR δ 14.0, 21.4, 21.5, 34.8, 54.8, 62.1, 67.0, 82.1, 127.8, 128.1, 128.4, 128.7, 129.0, 130.0, 133.5, 136.2, 138.3, 139.2, 153.6, 155.3; $R_f = 0.28$ (hexane : AcOEt = 3 : 1).

Ethyl 6-(*N*-benzyloxycarbonyl)amino-6-cyclohexyl-4-(4-methoxyphenyl)-(4*Z*)-hexen-2-ynoate (6f). Red gum; Yield: 53 %; Reaction time: 30 min; IR (neat): 3368, 2929, 2212, 1705 cm^{-1} ; ^1H NMR δ 1.33 (t, 3H, $J = 7.1$ Hz), 1.00–1.35 (m, 5H), 1.50–1.95 (m, 6H), 3.82 (s, 3H), 4.27 (q, 2H, $J = 6.9$ Hz), 4.45–4.70 (m, 1H), 4.99 (s, 1H), 5.10 (s, 1H), 6.25–6.45 (m, 1H), 6.80–6.95 (m, 2H), 7.20–7.40 (m, 7H); ^{13}C NMR δ 14.1, 26.0, 26.0, 26.2, 29.2, 42.7, 55.3, 62.0, 66.8, 82.8, 113.9, 122.2, 127.4, 128.1, 128.4, 136.4, 140.0, 159.9; $R_f = 0.27$ (hexane : EtOAc = 3 : 1); exact mass, m/z 475.23600 (calcd for $\text{C}_{29}\text{H}_{33}\text{NO}_5$ m/z 475.23587).

General procedure for the preparation of (N-benzyloxycarbonyl)pyrroles (7).

To a solution of enyne **6** (0.28 mmol) in THF (3.0 mL) was added sodium hydride (0.38 mmol) at 0 °C. The reaction was stirred at 0 °C for 30 min—1 h and quenched by the addition of saturated aqueous solution of NH_4Cl . The mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated to give an oil, which was purified by CC to provide **7**.

Spectroscopic data for 7a–f with reaction time and yield (not optimized).

Ethyl (1-benzyloxycarbonyl-3-methyl-5-phenylpyrrol-2-yl)acetate (7a). Red gum; Yield: 87 %; Reaction time: 1 h; ^1H NMR δ 1.28 (t, 3H, $J = 7.1$ Hz), 2.08 (s, 3H), 3.91 (s, 2H), 4.18 (q, 2H, $J = 7.1$ Hz), 5.12 (s, 2H), 6.11 (s, 1H), 6.90–7.05 (m, 2H), 7.20–7.40 (s, 8H); ^{13}C NMR δ 11.0, 14.2, 32.3, 60.8, 68.6, 115.9, 121.2, 124.8, 126.9, 127.7, 128.2, 128.3, 128.4, 134.2, 134.5, 134.9, 151.5, 170.8; $R_f = 0.40$ (hexane : EtOAc = 3:1); exact mass, m/z 377.16252 (calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_4$ m/z 377.16271).

Ethyl (1-benzyloxycarbonyl-3-isopropyl-5-phenylpyrrol-2-yl)acetate (7b). Red gum; Yield: 96 %; Reaction time: 1 h; ^1H NMR δ 1.24 (d, 3H, $J = 6.9$ Hz), 1.29 (t, 3H, $J = 7.1$ Hz), 2.80–3.00 (m, 1H), 3.95 (s, 2H), 4.18 (q, 2H, $J = 7.1$ Hz), 5.14 (s, 2H), 6.21 (s, 1H), 6.90–7.05 (m, 2H), 7.20–7.40 (m, 8H); ^{13}C NMR δ 14.2, 21.6, 25.1, 32.0, 60.7, 68.6, 111.9, 123.2, 126.8, 127.7, 128.2, 128.2, 128.3, 132.6, 134.2, 134.7, 135.2, 151.7, 170.8; $R_f = 0.70$ (hexane : EtOAc = 3 : 1).

Ethyl (1-benzyloxycarbonyl-3,5-diphenylpyrrol-2-yl)acetate (7c). Red gum; Yield: 75 %; Reaction time: 1 h; ^1H NMR δ 1.26 (t, 3H, $J = 7.1$ Hz), 3.96 (s, 2H), 4.17 (q, 2H, $J = 7.1$ Hz), 5.12 (s, 2H), 6.33 (s, 1H), 6.85–7.05 (m, 2H), 7.05–7.45 (m, 13H); ^{13}C NMR δ 14.2, 33.3, 61.0, 69.0, 114.6, 124.7, 126.9, 127.2, 127.8, 128.1, 128.3, 128.3, 128.5, 128.6, 128.6, 134.1, 134.3, 134.8, 135.5, 151.6, 171.1; $R_f = 0.63$ (hexane : EtOAc = 3 : 1); exact mass, m/z 439.17808 (calcd for $\text{C}_{28}\text{H}_{25}\text{NO}_4$ m/z 439.17836).

Ethyl [1-benzyloxycarbonyl-3-isopropyl-5-(4-methoxyphenyl)pyrrol-2-yl]acetate (7d). Yellow gum; Yield: 94 %; Reaction time: 30 min; ^1H NMR δ 1.17 (d, 6H, $J = 6.9$ Hz), 1.23 (t, 3H, $J = 7.1$ Hz), 2.70–2.90 (m, 1H), 3.79 (s, 3H), 3.87 (s, 2H), 4.10 (q, 2H, $J = 7.1$ Hz), 5.08 (s, 2H), 6.75–6.80 (m, 2H), 7.10–7.30 (m, 5H); ^{13}C NMR δ 14.1, 23.6, 25.1, 32.1, 55.1, 60.1, 68.5, 111.4, 113.1, 122.7, 128.2, 128.3, 129.6, 132.5, 134.3, 134.9, 151.7, 151.7, 158.6, 170.9; $R_f = 0.53$ (hexane : EtOAc = 3 : 1); exact mass, m/z 435.20409 (calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_5$ m/z 435.20457).

Ethyl 1-benzyloxycarbonyl-3-isopropyl-5-(4-chlorophenyl)pyrrol-2-yl]acetate (7e). Yellow gum; Yield: 78 %; Reaction time: 30 min; ^1H NMR δ 1.18 (d, 6H, $J = 6.9$ Hz), 1.25 (t, 3H, $J = 7.1$ Hz), 2.75–2.90 (m, 1H), 3.89 (s, 2H), 4.14 (q, 2H, $J = 7.1$ Hz), 5.08 (s, 2H), 6.13 (s, 1H), 6.95–7.05 (m, 2H), 7.10–7.20 (m, 3H); ^{13}C NMR δ 12.4, 23.6, 25.1, 32.1, 60.8, 68.9, 112.3, 123.6, 127.8, 128.3, 128.5, 129.7, 132.8, 133.2, 133.9, 134.0, 151.4, 170.7; $R_f = 0.63$ (hexane : EtOAc = 3 : 1); exact mass, m/z 439.15526 (calcd for $\text{C}_{25}\text{H}_{26}\text{ClNO}_4$ m/z 439.15504).

Ethyl [1-benzyloxycarbonyl-3-(4-methoxyphenyl)-5-cyclohexylpyrrol-2-yl]acetate (7f). Yellow gum; Yield: 53 %; Reaction time: 40 min; ^1H NMR δ 1.22 (t, 3H, $J = 7.1$ Hz), 1.10–1.35 (m, 5H), 1.50–1.80 (m, 3H), 1.90–2.05 (m, 5H), 3.05–3.15 (m, 1H), 3.82 (s, 3H), 4.10 (q, 2H, $J = 7.1$ Hz), 5.32 (s, 2H), 6.05 (d, 1H, $J = 0.6$ Hz), 6.80–6.95 (m, 2H), 7.20–7.50 (m, 7H); ^{13}C NMR δ 14.2, 26.3, 26.5, 33.8, 34.0, 37.2, 55.2, 60.7, 69.0, 109.7, 113.8, 122.3, 127.5, 127.8, 128.6, 128.8, 129.1, 129.7, 142.4, 151.6, 158.5, 171.5; $R_f = 0.47$ (hexane : EtOAc = 3 : 1).

Nuclear magnet resonance spectral charts (^1H and ^{13}C) for pyrroles **3a–o** obtained from **1** and sulfonamides **2** in a one step reaction are shown in the following fifteen pages.

3g

3n

Nuclear magnet resonance spectral charts (^1H and ^{13}C) for pyrroles **7a–f** obtained from **1** and benzyl carbamate in two steps are shown in the following six pages.

7d

7e

7f