Supporting information for:

**Reductive Cyclization of 1,6- and 1,7-Enynes Catalyzed by Iron Complexes**
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I. General Information
Ether, THF, dioxane and toluene were distilled from sodium benzophenone ketyl prior to use. DCM was distilled from calcium hydride. Diethylzinc (Et₂Zn) (1.0 mol/L in toluene) was purchased from Energy Chemical. The other commercial available chemicals were used as received. NMR spectra were recorded on a Bruker-400 instrument. ¹H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm), ¹³C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, CDCl₃). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, q = quadruplet. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. High-resolution mass spectra (HRMS) were recorded on EI-TOF (electrospray ionization-time of flight).

Enynes 1a-1, 1b-1, 1c-1, 1d-1, 1e-1, 1f-1g-1, 1h-1, 1i-1, 1j-1, 1k-1, 1l-1, 1m-1, 1n-1, 1o-1, 1p-1, 1q-1, 1r-1, 1s-1, 1t-1, 1u-1, 1v-1, 1w-1, 1x-1, 1y-1, 1aa-12 are known compounds and have been synthesized according to the reported methods. Their ¹H NMR data are reported as reference. Iron complex I-13, iron complex II-14, iron complex III-15 and iron complex IV-16 are known compounds and have been synthesized according to the reported methods. Iron complex V have been synthesized according to the same methods of iron complex IV.
II. Optimizations of Reductive Cyclization

Table S1_Reaction Conditions

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<th>Recovery (%)ᵃ</th>
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ᵃYields determined by ¹H NMR analysis using TMSPh as an internal standard.

Table S2_Reaction Conditions

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ᵇYields determined by ¹H NMR analysis using TMSPh as an internal standard. ᵇno toluene.
III. Procedures for Synthesis of Enynes

\[ \text{N-allyl-N-(3-(4-(hydroxymethyl)phenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1p):} \]

To a solution of ethyl 4-(3-N-allyl-4-methylbenzenesulfonamido)-1-ynyl)benzoate (1.5765 g, 4.0 mmol) in THF (50 mL) was added dropwise dibal-H (8 mL, 1.5 M in toluene, 12 mmol) at -78 °C over 30 minutes, and then the mixture was stirred at room temperature overnight. The mixture was cooled to 0 °C, and a solution of Rochelle salt was added dropwise over a period of 30 minutes. The mixture was stirred at room temperature. The organic layer was separated. The aqueous layer was extracted with ether (3 x 20 mL), and the combined organic layer was washed with brine (20 mL), dried over Na₂SO₄, and concentrated under vacuo. The crude residue was purified by flash chromatography on silica gel (Hexane:EtOAc = 10:1) to give 1p (1.2925 g, 92% yield) as a colorless oil.

IR (neat): 3534, 2920, 2867, 1645, 1598, 1491, 1442 cm⁻¹; \(^1\)H NMR: (400 MHz, CDCl₃) \(\delta\) 7.76 (d, \(J = 8.1\) Hz, 2H), 7.30-7.20 (m, 4H), 7.05 (d, \(J = 8.1\) Hz, 2H), 5.86-5.72 (m, 1H), 5.38-5.23 (m, 2H), 4.66 (d, \(J = 5.6\) Hz, 2H), 4.29 (s, 2H), 3.88 (d, \(J = 6.4\) Hz, 2H), 2.34 (s, 3H), 2.14-2.02 (m, 1H); \(^13\)C NMR: (100 MHz, CDCl₃) \(\delta\) 143.5, 141.2, 135.8, 131.9, 131.5, 129.5, 127, 126.5, 121.2, 119.9, 85.5, 81.6, 64.6, 49.2, 36.6, 21.4; HRMS (EI) calculated for [C₂₃H₂₁NO₃S]⁺ requires \(m/z\) 526.2658, found \(m/z\) 526.2654.

(E)-N-allyl-N-(3-(4-(1-(2,6-diisopropylphenyl)imino)ethyl)phenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1r): To a solution of N-(3-(4-acetylphenyl)prop-2-yn-1-yl)-N-allyl-4-methylbenzenesulfonamide (1.1501 g, 3.0 mmol), 2,6-diisopropylaniline (679 \(\mu\)L, 3.6 mmol) in dry toluene (50 mL) was added 4-methylbenzenesulfonic acid (0.0332 g, 0.15 mmol) at room temperature and refluxed at 110 °C overnight. The solvent was removed under vacuo, and the crude residue was purified by flash chromatography on silica gel (Hexane : EtOAc = 10:1) to give 1r (0.3029 g, 19% yield) as a yellow oil.

IR (neat): 3066, 2922, 2865, 1644, 1598, 1491, 1442 cm⁻¹; \(^1\)H NMR: (400 MHz, CDCl₃) \(\delta\) 7.92 (d, \(J = 8.1\) Hz, 2H), 7.79 (d, \(J = 8.1\) Hz, 2H), 7.28 (d, \(J = 8.0\) Hz, 2H), 7.20-7.12 (m, 4H), 7.11-7.05 (m, 1H), 5.89-5.74 (m, 2H), 5.40-5.20 (m, 2H), 4.34 (s, 2H), 3.91 (d, \(J = 6.3\) Hz, 2H), 2.75-2.63 (m, 2H), 2.36 (s, 3H), 2.07 (s, 3H), 1.13 (dd, \(J = 7.1, 4.3\) Hz, 12H); \(^13\)C NMR: (100 MHz, CDCl₃) \(\delta\) 163.9, 146.5, 143.5, 138.7, 136.0, 135.8, 132.0, 131.5, 129.5, 127.8, 126.8, 124.2, 123.5, 123.0, 120.0, 85.4, 83.7, 49.3, 36.8, 28.2, 23.1, 22.8, 21.4, 17.9; HRMS (EI) calculated for [C₃₃H₂₃N₂O₂S]⁺ requires \(m/z\) 526.2654, found \(m/z\) 526.2658.

N-allyl-4-methyl-N-(5-phenylpenta-2,4-diyn-1-yl)benzenesulfonamide (1u): To a solution of N-allyl-N-(3-iodoprop-2-yn-1-yl)-4-methylbenzenesulfonamide (0.6239 g, 1.8 mmol), Phenylacetylene (240 \(\mu\)L, 2.1 mmol), Pd(PPh₃)₃Cl (0.0363 g, 0.045 mmol) and Cul (0.0171 g, 0.09 mmol) in dry CH₂CN (5 mL) under nitrogen atmosphere was added NEt₃ (1 mL) at room temperature and stirred for 5 h. The solvent was removed under vacuo, and the crude residue was purified by flash chromatography on silica gel (Hexane: EtOAc = 10:1) to give 1u (0.1244 g, 20% yield) as a colorless oil.

IR (neat): 3066, 2922, 2865, 1644, 1598, 1491, 1442 cm⁻¹; \(^1\)H NMR: (400 MHz, CDCl₃) \(\delta\) 7.76 (d, \(J = 8.2\) Hz, 2H), 7.47-7.41 (m, 2H), 7.40-7.29 (m, 5H), 5.81-7.69 (m, 1H), 5.37-5.23 (m, 2H), 4.22 (s, 2H), 3.84 (d, \(J = 6.3\) Hz, 2H), 2.40 (s, 3H); \(^13\)C NMR:
(100 MHz, CDCl₃) δ 143.8, 135.5, 132.5, 131.8, 129.6, 129.4, 128.4, 127.7, 121.2, 120.3, 75.5, 73.0, 70.2, 49.4, 36.8, 21.6; HRMS (EI) calculated for [C₁₂H₁₀NO₂S]⁺ requires m/z 349.1137, found m/z 349.1132.

1-(4-(allyloxy)but-1-yn-1-yl)-4-methoxybenzene (1ab): To a suspension of NaH (0.7686 g, 19.14 mmol) in THF (135 mL) was added dropwise a solution of 4-(4-methoxyphenyl)but-3-yn-1-ol (2.8109 g, 15.95 mmol) in THF (15 mL) at 0 °C over a period of 30 minutes, and then the mixture was stirred at room temperature until the evolution of hydrogen gas subsided. The mixture was cooled to 0 °C, and a solution of allyl bromide (1.62 mL, 19.14 mmol) in THF (10 mL) was added dropwise over a period of 30 minutes. The mixture was stirred at room temperature overnight and checked by TLC. After the reaction was completed, water (20 mL) was added slowly at 0 °C, and the organic layer was separated. The aqueous layer was extracted with ether (3 x 30 mL), and the combined organic layers were washed with brine (40 mL), dried over Na₂SO₄, and concentrated under vacuo. The crude residue was purified by flash chromatography on silica gel (Hexane:EtOAc = 150:1~50:1) to give 1ab (2.2464 g, 65% yield) as a yellow oil. IR (neat): 2909, 2840, 1647, 1607, 1510, 1463 cm⁻¹; ¹H NMR: (400 MHz, CDCl₃) δ 7.33 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 5.99-5.87 (m, 1H), 5.36-5.27 (m, 1H), 5.24-5.16 (m, 1H), 4.05 (d, J = 5.4 Hz, 2H), 3.79 (s, 3H), 3.64 (t, J = 7.2 Hz, 2H), 2.69 (t, J = 7.2 Hz, 2H); ¹³C NMR: (100 MHz, CDCl₃) δ 159.2, 134.7, 132.9, 117.0, 115.8, 113.8, 85.0, 81.2, 71.9, 68.6, 55.2, 20.8; HRMS (EI) calculated for [C₁₄H₁₆O₂]⁺ requires m/z 216.1150, found m/z 216.1148.

1-(4-(allyloxy)but-1-yn-1-yl)-4-chlorobenzene (1ac): To a suspension of NaH (0.3184 g, 7.89 mmol) in THF (60 mL) was added dropwise a solution of 4-(4-chlorophenyl)but-3-yn-1-ol (1.1879 g, 6.58 mmol) in THF (10 mL) at 0 °C over a period of 30 minutes, and then the mixture was stirred at room temperature until the evolution of hydrogen gas subsided. The mixture was cooled to 0 °C, and a solution of allyl bromide (0.67 mL, 7.89 mmol) in THF (8 mL) was added dropwise over a period of 30 minutes. The mixture was stirred at room temperature overnight and checked by TLC. After the reaction was completed, water (20 mL) was added slowly at 0 °C, and the organic layer was separated. The aqueous layer was extracted with ether (3 x 30 mL), and the combined organic layers were washed with brine (40 mL), dried over Na₂SO₄, and concentrated under vacuo. The crude residue was purified by flash chromatography on silica gel (Hexane:EtOAc = 200:1) to give 1ac (0.7918 g, 55% yield) as a yellow oil. IR (neat): 2910, 2862, 1647, 1593, 1489 cm⁻¹; ¹H NMR: (400 MHz, CDCl₃) δ 7.32 (d, J = 8.6 Hz, 2H), 7.27-7.22 (m, 2H), 5.99-5.87 (m, 1H), 5.36-5.27 (m, 1H), 5.24-5.17 (m, 1H), 4.05 (d, J = 5.6 Hz, 2H), 3.64 (t, J = 7.0 Hz, 2H), 2.69 (t, J = 7.0 Hz, 2H); ¹³C NMR: (100 MHz, CDCl₃) δ 134.5, 133.7, 132.8, 128.5, 122.1, 117.2, 87.8, 80.4, 71.9, 68.3, 20.8; HRMS (EI) calculated for [C₁₃H₁₃OCl]⁺ requires m/z 220.0655, found m/z 220.0657.
IV. Reductive Cyclization of Enynes

**General procedure A for Reductive Cyclization:** To a 25 mL flame-dried Schlenk flask cooled under Ar, iron complex I (0.025 mmol) and Et₂Zn (1.25 mL, 1.0 M in toluene) were added. After stirring for 5 min, I (0.5 mmol) was added to the above solution. The reaction mixture was stirred at room temperature for 1.5 h. The reaction was quenched by addition of a saturated solution of NH₄Cl (5 mL) at -78 °C, then warmed to room temperature gradually and stirred for 2 hour. The mixture were extracted with Ether (3×10 mL). The combined organic phases were dried over Na₂SO₄, and then concentrated in vacuo. The residue was purified by column chromatography with silica gel (ethyl acetate:pentane = 1:10) to give 2.

**General procedure B for Reductive Cyclization:** To a 25 mL flame-dried Schlenk flask cooled under Ar, iron complex I (0.025 mmol) and Et₂Zn (1.25 mL, 1.0 M in toluene) were added. After stirring for 5 min, I (0.5 mmol) was added to the above solution. The reaction mixture was stirred at room temperature for 1.5 h. The reaction was quenched by addition of EtOH (5 mL) at room temperature, then filtered through a plug of silica gel by Ether. The filtrate was concentrated in vacuo, and the residue was purified by column chromatography with silica gel (ethyl acetate:pentane = 1:10) to give 2.

(Z)-3-benzylidene-4-methyltetrahydrofuran (2a) \(^{17}\) (General procedure A): The reaction with iron complex I (0.0158 g, 0.028 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and (3-allyloxy)prop-1-yn-1-ylbenzene (1a) (87 μL, 0.5 mmol) afforded 2a (0.0625 g, 72%) as a colorless oil, Z/E > 20/1. \(^1\)H NMR: (400 MHz, CDCl₃) \(\delta\) 7.38-7.30 (m, 2H), 7.24-7.18 (m, 1H), 7.18-7.08 (m, 2H), 6.30 (d, \(J\) = 2.2 Hz, 1H), 4.80-4.54 (m, 2H), 4.08 (t, \(J\) = 7.9 Hz, 1H), 3.39 (t, \(J\) = 8.1 Hz, 1H), 2.98-2.84 (m, 1H), 1.22 (d, \(J\) = 6.9 Hz, 3H); \(^13\)C NMR: (100 MHz, CDCl₃) \(\delta\) 146.5, 137.4, 128.5, 127.9, 126.5, 119.9, 74.3, 70.3, 39.8, 16.4.

(Z)-1-benzyl-3-benzylidene-4-methylpyrrolidine (2b) (General procedure B): The reaction with iron complex I (0.0149 g, 0.026 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and N-benzyl-N-(3-phenylprop-2-yn-1-yl)prop-2-en-1-amine (1b) (125 μL, 0.5 mmol) afforded 2b (0.1216 g, 92%) as a colorless oil, Z/E > 20/1. IR (neat): 3059, 2961, 1688, 1599, 1493, 1450 cm\(^{-1}\); \(^1\)H NMR: (400 MHz, CDCl₃) \(\delta\) 7.45-7.21 (m, 7H), 7.21-7.12 (m, 3H), 6.22 (d, \(J\) = 2.1 Hz, 1H), 3.84-3.75 (m, 1H), 3.69 (s, 2H), 3.39-3.29 (m, 1H), 3.00 (t, \(J\) = 7.9 Hz, 1H), 2.95-2.83 (m, 1H), 2.11 (t, \(J\) = 8.2 Hz, 1H), 1.20 (d, \(J\) = 6.5 Hz, 3H); \(^13\)C NMR: (100 MHz, CDCl₃) \(\delta\) 147.4, 138.9, 138.1, 128.7, 128.28, 128.26, 127.8, 126.9, 126.0, 120.3, 61.2, 60.6, 58.5, 39.2, 18.0; HRMS (EI) calculated for \([\text{C}_{10}\text{H}_{12}\text{N}^+]\) requires \(m/z\) 263.1674, found \(m/z\) 263.1671.

(Z)-3-benzylidene-1,4-dimethylpyrroline (2c) (General procedure B): The reaction with iron complex I (0.0146 g, 0.025 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and N-methyl-N-(3-phenylprop-2-yn-1-yl)prop-2-en-1-amine (1c) (98 μL, 0.5 mmol) afforded 2c (0.0686 g, 73%) as a colorless oil, Z/E > 20/1. IR (neat): 2960, 2932, 2770, 1691, 1660, 1494, 1448 cm\(^{-1}\); \(^1\)H NMR: (400 MHz, CDCl₃) \(\delta\) 7.36-7.28 (m, 2H), 7.24-7.14 (m, 3H), 6.21 (d, \(J\) = 2.2 Hz, 1H), 3.75 (dd, \(J\) = 1.1, 14.6 Hz, 1H), 3.34-3.26 (m, 1H), 3.04-2.84 (m, 2H), 2.42 (s, 3H), 2.11 (t, \(J\) = 8.0 Hz, 1H), 1.22 (d, \(J\) = 6.7 Hz, 3H); \(^13\)C NMR: (100 MHz, CDCl₃) \(\delta\) 147.7, 138.1,
128.3, 127.9, 126.1, 120.2, 63.6, 60.5, 42.6, 39.8, 18.0; HRMS (EI) calculated for [C_{13}H_{17}N]⁺ requires m/z 187.1361, found m/z 187.1363.

(Z)-3-benzylidene-4-methyl-1-tosylpyrrolidine (2d)\(^{17}\) (General procedure B): The reaction with iron complex I (0.0151 g, 0.027 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and N-allyl-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1d) (0.1643 g, 0.5 mmol) afforded 2d (0.1251 g, 76%) as a white solid, Z/E > 20/1. \(^{1}H\) NMR: (400 MHz, CDCl₃) δ 7.72 (d, J = 8.2 Hz, 2H), 7.40-7.28 (m, 4H), 7.26-7.20 (m, 1H), 7.14 (d, J = 7.5 Hz, 2H), 6.22 (d, J = 2.0 Hz, 1H), 4.29-4.20 (m, 1H), 4.09-4.01 (m, 1H), 3.60-3.51 (m, 1H), 2.93-2.81 (m, 1H), 2.73 (t, J = 8.7 Hz, 1H), 2.41 (s, 3H), 1.17 (d, J = 6.7 Hz, 3H); \(^{13}C\) NMR: (100 MHz, CDCl₃) δ 143.6, 141.8, 136.5, 132.9, 129.7, 128.5, 128.0, 127.7, 126.9, 122.0, 53.8, 50.8, 39.1, 21.5, 16.9.

(E)-diethyl-3-benzylidene-4-methylcyclopentane-1,1-dicarboxylate (2e)\(^{18}\) (General procedure A): The reaction with iron complex I (0.0161 g, 0.028 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and diethyl 2-allyl-2-(3-phenylprop-2-yn-1-yl)malonate (1e) (0.1642 μL, 0.5 mmol) afforded 2e (0.1059 g, 63%) as a colorless oil, Z/E > 20/1. \(^{1}H\) NMR: (400 MHz, CDCl₃) δ 7.36-7.27 (m, 4H), 7.23-7.13 (m, 1H), 6.22 (d, J = 2.2 Hz, 1H), 4.26-4.10 (m, 4H), 3.42-3.32 (m, 1H), 3.25-3.16 (m, 1H), 2.85-2.70 (m, 1H), 2.65-2.54 (m, 1H), 1.76 (t, J = 12.4 Hz, 1H), 1.32-1.15 (m, 9H); \(^{13}C\) NMR: (100 MHz, CDCl₃) δ 171.8, 171.7, 146.3, 137.9, 128.23, 128.18, 126.1, 121.4, 61.5, 59.1, 41.3, 39.0, 38.8, 18.3, 14.0, 13.9.

(Z)-3-(2-methoxybenzylidene)-4-methyl-1-tosylpyrrolidine (2f)\(^{14}\) (General procedure B): The reaction with iron complex I (0.0156 g, 0.028 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and N-allyl-N-(3-(2-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1f) (0.1808 g, 0.5 mmol) afforded 2f (0.1522 g, 84%) as a white solid, Z/E > 20/1. \(^{1}H\) NMR: (400 MHz, CDCl₃) δ 7.69 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.26-7.20 (m, 1H), 7.06 (d, J = 7.5 Hz, 1H), 6.95 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 6.48 (d, J = 2.1 Hz, 1H), 4.20-4.12 (m, 1H), 4.04-3.95 (m, 1H), 3.80 (s, 3H), 3.59-3.51 (m, 1H), 2.94-2.81 (m, 1H), 2.75 (t, J = 8.2 Hz, 1H), 2.41 (s, 3H), 1.17 (d, J = 6.7 Hz, 3H); \(^{13}C\) NMR: (100 MHz, CDCl₃) δ 156.5, 143.5, 141.7, 133.1, 129.6, 128.6, 128.4, 127.7, 125.5, 120.4, 116.7, 110.5, 55.4, 54.0, 50.6, 39.0, 21.5, 17.0.

(Z)-3-(3-methoxybenzylidene)-4-methyl-1-tosylpyrrolidine (2g)\(^{15}\) (General procedure B): The reaction with iron complex I (0.0140 g, 0.025 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and N-allyl-N-(3-(3-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1g) (0.1779 g, 0.5 mmol) afforded 2g (0.1318 g, 74%) as a white solid, Z/E > 20/1. \(^{1}H\) NMR: (400 MHz, CDCl₃) δ 7.71 (d, J = 8.2 Hz, 2H), 7.35-7.23 (m, 3H), 6.79 (dd, J = 8.3, 2.3 Hz, 1H), 6.73 (d, J = 7.7 Hz, 1H), 6.66 (s, 1H), 6.19 (d, J = 2.2 Hz, 1H), 4.52-4.18 (m, 1H), 4.09-3.99 (m, 1H), 3.81 (s, 3H), 3.59-3.51 (m, 1H), 2.92-2.80 (m, 1H), 2.72 (t, J = 8.8 Hz, 1H), 2.41 (s, 3H), 1.16 (d, J = 6.6 Hz, 3H); \(^{13}C\) NMR: (100 MHz, CDCl₃) δ 159.6, 143.6, 142.2, 137.9, 132.9, 129.7, 129.5, 127.7, 122.0, 120.4, 114.0, 112.3, 55.2, 53.8, 50.8, 39.0, 21.5, 16.9.
(Z)-3-(4-methoxybenzylidene)-4-methyl-1-toslylpyrrolidine (2h)

The reaction with iron complex I (0.0141 g, 0.025 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and N-allyl-N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonyamide (1h) (0.1762 g, 0.5 mmol) afforded 2h (0.1408 g, 79%) as a white solid, Z/E > 20/1. ¹H NMR: (400 MHz, CDCl₃) δ 7.72 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.15 (d, J = 2.1 Hz, 1H), 4.26-4.17 (m, 1H), 4.07-3.97 (m, 1H), 3.82 (s, 3H), 3.57-3.49 (m, 1H), 2.91-2.78 (m, 1H), 2.71 (t, J = 8.8 Hz, 1H), 2.41 (s, 3H), 1.15 (d, J = 6.7 Hz, 3H); ¹³C NMR: (100 MHz, CDCl₃) δ 158.5, 143.5, 139.5, 133.0, 129.7, 129.32, 129.30, 127.7, 121.4, 114.0, 55.3, 53.9, 50.8, 39.0, 21.5, 16.9.

(Z)-3-methyl-4-(4-methylbenzylidene)-1-toslylpyrrolidine (2i)

The reaction with iron complex I (0.0152 g, 0.027 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and N-allyl-4-methyl-N-(3-(p-tolyl)prop-2-yn-1-yl)benzenesulfonyamide (1i) (0.1706 g, 0.5 mmol) afforded 2i (0.1353 g, 79%) a colorless oil, Z/E > 20/1. IR (neat): 2968, 2924, 1596, 1512, 1335 cm⁻¹; ¹H NMR: (400 MHz, CDCl₃) δ 7.72 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.18 (d, J = 2.0 Hz, 1H), 4.27-4.19 (m, 1H), 4.08-4.00 (m, 1H), 3.58-3.50 (m, 1H), 2.92-2.77 (m, 1H), 2.71 (t, J = 8.3 Hz, 1H), 2.41 (s, 3H), 2.34 (s, 3H), 1.15 (d, J = 6.7 Hz, 3H); ¹³C NMR: (100 MHz, CDCl₃) δ 143.5, 140.7, 136.8, 133.7, 133.0, 129.7, 129.2, 128.0, 127.7, 121.9, 53.8, 50.8, 39.0, 21.5, 21.1, 16.9. HRMS (EI) calculated for [C₂₀H₂₃NO₂S]⁺ requires m/z 341.1450, found m/z 341.1451.

(Z)-3-(4-chlorobenzylidene)-4-methyl-1-toslylpyrrolidine (2j)

The reaction with iron complex I (0.0147 g, 0.026 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and N-allyl-N-(3-(4-chlorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonyamide (1j) (0.1802 g, 0.5 mmol) afforded 2j (0.1248 g, 69%) as a white solid, Z/E > 20/1. ¹H NMR: (400 MHz, CDCl₃) δ 7.71 (d, J = 8.2 Hz, 2H), 7.36-7.27 (m, 4H), 7.06 (d, J = 8.3 Hz, 2H), 6.17 (d, J = 2.0 Hz, 1H), 4.24-4.15 (m, 1H), 4.04-3.94 (m, 1H), 3.60-3.51 (m, 1H), 2.92-2.80 (m, 1H), 2.72 (t, J = 8.9 Hz, 1H), 2.42 (s, 3H), 1.16 (d, J = 6.7 Hz, 3H); ¹³C NMR: (100 MHz, CDCl₃) δ 143.7, 142.6, 135.0, 132.8, 132.7, 129.7, 129.2, 128.7, 127.7, 120.9, 53.7, 50.7, 39.1, 21.5, 16.8.

(Z)-3-(4-bromobenzylidene)-4-methyl-1-toslylpyrrolidine (2k)

The reaction with iron complex I (0.0142 g, 0.025 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and N-allyl-N-(3-(4-chlorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonyamide (1k) (0.2074 g, 0.5 mmol) afforded 2k (0.1484 g, 71%) as a colorless oil, Z/E > 20/1. IR (neat): 3062, 2965, 2929, 1597, 1488, 1453, 1344 cm⁻¹; ¹H NMR: (400 MHz, CDCl₃) δ 7.71 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 6.15 (d, J = 1.7 Hz, 1H), 4.19 (d, J = 14.8 Hz, 1H), 3.98 (d, J = 14.8 Hz, 1H), 3.59-3.51 (m, 1H), 2.91-2.80 (m, 1H), 2.72 (t, J = 8.5 Hz, 1H), 2.41 (s, 3H), 1.16 (d, J = 6.8 Hz, 3H); ¹³C NMR: (100 MHz, CDCl₃) δ 143.7, 142.8, 135.4, 132.9, 131.6, 129.7, 129.5, 127.7, 121.0, 120.8, 53.7, 50.7, 39.1, 21.5, 16.8; HRMS (EI) calculated for [C₁₉H₁₃BrNO₂SBr]⁺ requires m/z 405.0398, found m/z 405.0393.
(Z)-3-methyl-1-tosyl-4-(4-(trifluoromethyl)benzylidene)pyrrolidine (2l)\(^7\) (General procedure B): The reaction with iron complex I (0.0148 g, 0.026 mmol), Et\(_2\)Zn (1.25 mL, 1.0 M in toluene) and N-allyl-4-methyl-N-(3-(4-((trifluoromethyl)phenyl)-prop-2-yn-1-yl)benzenesulfonamide (1l) (0.1983 g, 0.5 mmol) afforded 2l (0.1502 g, 75%) as a white solid, Z/E > 20/1. \(^1\)H NMR: (400 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, \(J = 8.2\) Hz, 2H), 7.59 (d, \(J = 8.1\) Hz, 2H), 7.32 (d, \(J = 8.0\) Hz, 2H), 7.23 (d, \(J = 8.0\) Hz, 2H), 6.30-6.22 (m, 1H), 4.28-4.18 (m, 1H), 4.07-3.95 (m, 1H), 3.62-3.52 (m, 1H), 2.96-2.84 (m, 1H), 2.75 (t, \(J = 9.0\) Hz, 1H), 2.42 (s, 3H), 1.18 (d, \(J = 6.7\) Hz, 3H); \(^13\)C NMR: (100 MHz, CDCl\(_3\)) \(\delta\) 144.7, 143.8, 140.0, 132.8, 129.8, 128.2, 127.7, 125.5 (q, \(J = 3.8\) Hz), 120.9, 53.7, 50.7, 39.2, 21.5, 16.8.

(Z)-4-((4-methyl-1-tosylpyrrolidin-3-ylidene)methyl)benzonitrile (2m) (General procedure B): The reaction with iron complex I (0.0141 g, 0.025 mmol), Et\(_2\)Zn (1.25 mL, 1.0 M in toluene) and N-allyl-N-(3-(4-(cyanophenyl)-4-methylbenzenesulfonamide (1m) (0.1782 g, 0.5 mmol) afforded 2m (0.0845 g, 47%) a colorless oil, Z/E > 20/1. Recovery 1m (0.0478 g, 27%). IR (neat): 2967, 2871, 2226, 1662, 1602, 1344 cm\(^{-1}\); \(^1\)H NMR: (400 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, \(J = 8.1\) Hz, 2H), 7.63 (d, \(J = 8.1\) Hz, 2H), 7.33 (d, \(J = 8.1\) Hz, 2H), 7.22 (d, \(J = 8.1\) Hz, 2H), 6.24 (d, \(J = 2.0\) Hz, 1H), 4.26-4.19 (m, 1H), 4.06-3.97 (m, 1H), 3.62-3.54 (m, 1H), 2.99-2.85 (m, 1H), 2.75 (t, \(J = 8.5\) Hz, 1H), 2.43 (s, 3H), 1.19 (d, \(J = 6.7\) Hz, 3H); \(^13\)C NMR: (100 MHz, CDCl\(_3\)) \(\delta\) 146.2, 143.9, 140.9, 132.7, 132.3, 129.8, 128.5, 127.7, 120.8, 118.7, 110.3, 53.6, 50.8, 39.4, 21.5, 16.8; HRMS (El) calculated for [C\(_{20}\)H\(_{19}\)N\(_3\)O\(_3\)S]+ requires \(m/z\) 352.1245, found \(m/z\) 352.1243.

(Z)-ethyl 4-((4-methyl-1-tosylpyrrolidin-3-ylidene)methyl)benzoate (2n)\(^d\) (General procedure B): The reaction with iron complex I (0.0161 g, 0.028 mmol), Et\(_2\)Zn (1.25 mL, 1.0 M in toluene) and ethyl 4-(3-(N-allyl-4-methylphenylsulfonamido)prop-1-yn-1-yl)benzate (1n) (0.2001 g, 0.5 mmol) afforded 2n (0.1481 g, 74%) as a white solid, Z/E > 20/1. \(^1\)H NMR: (400 MHz, CDCl\(_3\)) \(\delta\) 8.01 (d, \(J = 8.2\) Hz, 2H), 7.72 (d, \(J = 8.0\) Hz, 2H), 7.32 (d, \(J = 8.2\) Hz, 2H), 7.19 (d, \(J = 8.2\) Hz, 2H), 6.26 (d, \(J = 1.8\) Hz, 1H), 4.38 (q, \(J = 7.2\) Hz, 2H), 4.30-4.20 (m, 1H), 4.08-3.99 (m, 1H), 3.62-3.53 (m, 1H), 2.96-2.84 (m, 1H), 2.74 (t, \(J = 8.9\) Hz, 1H), 2.42 (s, 3H), 1.41 (t, \(J = 7.1\) Hz, 3H), 1.18 (d, \(J = 6.6\) Hz, 3H); \(^13\)C NMR: (100 MHz, CDCl\(_3\)) \(\delta\) 166.2, 144.6, 143.7, 140.8, 132.8, 129.79, 129.75, 128.8, 127.9, 127.7, 121.4, 61.0, 53.7, 50.8, 39.3, 21.5, 16.8, 14.3.

(Z)-1-(4-((4-methyl-1-tosylpyrrolidin-3-ylidene)phenyl)ethanone (2o) (General procedure B): The reaction with iron complex I (0.0141 g, 0.025 mmol), Et\(_2\)Zn (1.25 mL, 1.0 M in toluene) and N-allyl-N-(3-(4-formylphenyl)-prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1o) (0.1915 g, 0.5 mmol) afforded 2o (0.0787 g, 41%) as a colorless oil, Z/E > 20/1. IR (neat): 2966, 2929, 1679, 1601, 1344, 1268 cm\(^{-1}\); \(^1\)H NMR: (400 MHz, CDCl\(_3\)) \(\delta\) 7.94 (d, \(J = 8.2\) Hz, 2H), 7.72 (d, \(J = 8.2\) Hz, 2H), 7.32 (d, \(J = 8.1\) Hz, 2H), 7.22 (d, \(J = 8.1\) Hz, 2H), 6.27 (d, \(J = 1.9\) Hz, 1H), 4.30-4.20 (m, 1H), 4.10-4.00 (m, 1H), 3.62-3.58 (m, 1H), 2.98-2.84 (m, 1H), 2.74 (t, \(J = 8.5\) Hz, 1H), 2.61 (s, 3H), 2.42 (s, 3H), 1.19 (d, \(J = 6.7\) Hz, 3H); \(^13\)C NMR: (100 MHz, CDCl\(_3\)) \(\delta\) 197.4,
(Z)-(4-((methyl-1-toslyphyrroldin-3-yllidene)methyl)phénylmethanol (2p) (General procedure B): The reaction with iron complex I (0.0155 g, 0.027 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and 4-allyl-N-3-(4-(hydroxymethyl)phényl)prop-2-yn-1-yl)-4-methylbenzenesulfonyamide (1p) (0.1791 g, 0.5 mmol) afforded 2p (0.1017 g, 56%) as a colorless oil, Z/E > 20/1. IR (neat): 3522, 2965, 2927, 1598, 1453, 1340 cm⁻¹; ¹H NMR: (400 MHz, CDCl₃) δ 7.71 (d, J = 8.3 Hz, 2H), 7.38-7.28 (m, 4H), 7.13 (d, J = 8.0 Hz, 2H), 6.21 (d, J = 2.2 Hz, 1H), 4.69 (d, J = 4.0 Hz, 2H), 4.28-4.19 (m, 1H), 4.08-3.98 (m, 1H), 3.60-3.51 (m, 1H), 2.94-2.81 (m, 1H), 2.72 (t, J = 8.5 Hz, 1H), 2.41 (s, 3H), 1.95-1.85 (m, 1H), 1.16 (d, J = 6.7 Hz, 3H); ¹³C NMR: (100 MHz, CDCl₃) δ 143.6, 141.8, 139.6, 135.9, 132.9, 128.2, 127.7, 127.1, 121.7, 64.9, 53.8, 50.8, 39.1, 21.5, 16.8; HRMS (EI) calculated for [C₁₄H₁₃NO₂S]⁺ requires m/z 357.1399, found m/z 357.1400.

(Z)-3-(3,5-dimethylbenzyldienyl)-4-methyl-1-toslyphyroldine (2q) (General procedure A): The reaction with iron complex I (0.0142 g, 0.025 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and 4-allyl-N-3-(3,5-dimethylphényl)prop-2-yn-1-yl)-4-methylbenzenesulfonyamide (1q) (0.1768 g, 0.5 mmol) afforded 2q (0.1310 g, 73%) as a white solid, Z/E > 20/1. Recovery 1r (0.0532 g, 31%). ¹H NMR: (400 MHz, CDCl₃) δ 7.71 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.88 (s, 1H), 6.75 (s, 2H), 6.15 (d, J = 1.7 Hz, 1H), 4.24 (d, J = 15.2 Hz, 1H), 4.05 (d, J = 15.2 Hz, 1H), 3.58-3.50 (m, 1H), 2.88-2.76 (m, 1H), 2.71 (t, J = 8.5 Hz, 1H), 2.41 (s, 3H), 2.31 (s, 6H), 1.14 (d, J = 6.6 Hz, 3H); ¹³C NMR: (100 MHz, CDCl₃) δ 143.5, 141.2, 138.0, 136.5, 133.1, 129.7, 128.7, 127.7, 125.9, 122.2, 53.8, 50.6, 39.0, 21.5, 21.3, 16.9.

(E)-2,6-diisopropyl-N-(1-(4-((Z)-(4-methyl-1-toslyphyroldin-3-yllidene)methylphényl)enyl)enylidenediyl)aniline (2r) (General procedure B): The reaction with iron complex I (0.0096 g, 0.0162 mmol), Et₂Zn (0.81 mL, 1.0 M in toluene) and (E)-N-allyl-N-3-(3-(4-(1-(2,6-diisopropylphénylimino)ethyl)phényl)prop-2-yn-1-yl)-4-methylbenzenesulfonyamide (1r) (0.1716 g, 0.326 mmol) afforded 2r (0.0825 g, 48%) as a colorless oil, Z/E > 20/1. Recovery 1r (0.0532 g, 31%). IR (neat): 2963, 2872, 1635, 1597, 1451, 1345 cm⁻¹; ¹H NMR: (400 MHz, CDCl₃) δ 8.02 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 7.27-7.21 (m, 2H), 7.15 (d, J = 7.2 Hz, 2H), 7.11-7.04 (m, 1H), 6.29 (d, J = 1.6 Hz, 1H), 4.29 (d, J = 14.9 Hz, 1H), 4.09 (d, J = 14.9 Hz, 1H), 3.58 (dd, J = 7.5, 8.6 Hz, 1H), 2.97-2.85 (m, 1H), 2.80-2.70 (m, 3H), 2.42 (s, 3H), 2.09 (s, 3H), 1.23-1.10 (m, 15H); ¹³C NMR: (100 MHz, CDCl₃) δ 164.2, 146.7, 143.6, 134.4, 138.6, 137.5, 136.0, 132.9, 129.7, 128.0, 127.7, 127.3, 123.3, 122.9, 121.6, 53.8, 50.9, 39.2, 28.2, 23.2, 22.9, 21.5, 18.0, 16.9; HRMS (EI) calculated for [C₃₃H₄₀N₂O₂S]⁺ requires m/z 528.2811, found m/z 528.2811.

(Z)-3-methyl-4-(naphthalen-1-ylmethylene)-1-toslyphyroldine (2s) (General procedure B): The reaction with iron complex I (0.0147 g, 0.026 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and
**N-allyl-4-methyl-N-(3-(naphthalen-1-yl)prop-2-yn-1-yl)benzene-sulfonamide (1s)** (0.1139 g, 0.3 mmol) afforded 2s (0.00883 g, 73%) as a white solid, Z/E > 20/1. $^1$H NMR: (400 MHz, CDCl$_3$) $\delta$ 7.89-7.81 (m, 2H), 7.77 (d, $J$ = 8.2 Hz, 1H), 7.62 (d, $J$ = 8.2 Hz, 2H), 7.53-7.40 (m, 3H), 7.27-7.17 (m, 3H), 6.78 (d, $J$ = 1.6 Hz, 1H), 4.16-4.06 (m, 1H), 3.92-3.81 (m, 1H), 3.69-3.60 (m, 1H), 3.01-2.89 (m, 1H), 2.79 (t, $J$ = 8.6 Hz, 1H), 2.37 (s, 3H), 1.28 (d, $J$ = 6.6 Hz, 3H); $^{13}$C NMR: (100 MHz, CDCl$_3$) $\delta$ 144.0, 143.5, 133.6, 133.5, 133.1, 131.3, 129.6, 128.5, 127.8, 127.6, 126.0, 125.9, 125.7, 125.4, 124.1, 119.5, 54.3, 50.5, 38.5, 21.5, 16.8.

(Z)-3-methyl-4-((thiophen-2-ylmethylene)-1-tosylpyrroloidine (2t)$^7$ (General procedure B): The reaction with iron complex I (0.0144 g, 0.025 mmol), Et$_2$Zn (1.25 mL, 1.0 M in toluene) and N-allyl-4-methyl-N-(3-(thiophen-2-yl)prop-2-yn-1-yl)benzenesulfonamide (1s) (0.1686 g, 0.5 mmol) afforded 2s (0.1294 g, 78%) as a white solid, Z/E > 20/1. $^1$H NMR: (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J$ = 8.2 Hz, 1H), 7.36-7.27 (m, 3H), 7.05-7.00 (m, 1H), 6.90-6.85 (m, 1H), 6.40 (d, $J$ = 1.8 Hz, 1H), 4.24-4.14 (m, 1H), 4.04-3.96 (m, 1H), 3.62-3.54 (m, 1H), 2.95-2.83 (m, 1H), 2.72 (t, $J$ = 8.8 Hz, 1H), 2.42 (s, 3H), 1.15 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR: (100 MHz, CDCl$_3$) $\delta$ 143.7, 140.3, 132.5, 129.7, 127.8, 127.4, 126.2, 125.5, 115.0, 54.5, 51.3, 38.7, 21.5, 16.7.

(Z)-3-methyl-4-(3-phenylprop-2-yn-1-ylidene)-1-tosylpyrroloidine (2u) (General procedure B): The reaction with iron complex I (0.0049 g, 0.0075 mmol), Et$_2$Zn (0.38 mL, 1.0 M in toluene) and N-allyl-4-methyl-N-(5-phenylpenta-2,4-diyn-1-yl)benzenesulfonamide (1u) (0.0524 g, 0.15 mmol) afforded 2u (0.0215 g, 41%) a colorless oil, Z/E > 20/1. IR (neat): 3060, 2965, 2928, 1597, 1490, 1451, 1399 cm$^{-1}$; $^1$H NMR: (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J$ = 7.8 Hz, 2H), 7.45-7.39 (m, 2H), 7.38-7.30 (m, 5H), 5.52 (d, 1H), 4.18 (d, $J$ = 16.2 Hz, 1H), 4.00 (d, $J$ = 16.2 Hz, 1H), 3.62 (t, $J$ = 8.0 Hz, 1H), 2.88-2.69 (m, 2H), 2.44 (s, 3H), 1.10 (d, $J$ = 6.6 Hz, 3H); $^{13}$C NMR: (100 MHz, CDCl$_3$) $\delta$ 155.1, 143.7, 132.7, 131.4, 129.8, 128.4, 127.8, 123.0, 101.9, 95.0, 85.3, 55.1, 52.0, 37.9, 21.5, 16.3; HRMS (EI) calculated for [C$_9$H$_{12}$NO$_2$S]$^+$ requires m/z 351.1293, found m/z 351.1295.

(Z)-3-hexylidene-4-methyl-1-tosylpyrroloidine (2v)$^4$ (General procedure B): The reaction with iron complex I (0.0141 g, 0.025 mmol), Et$_2$Zn (1.25 mL, 1.0 M in toluene) and N-allyl-4-methyl-N-(oct-2-yn-1-yl)benzenesulfonamide (1v) (0.1615 g, 0.5 mmol) afforded 2v (0.1217 g, 75%) as a colorless oil, Z/E > 20/1. $^1$H NMR: (400 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J$ = 8.1 Hz, 2H), 7.33 (d, $J$ = 8.1 Hz, 2H), 5.20-5.10 (m, 1H), 3.92-3.82 (m, 1H), 3.75-3.66 (m, 1H), 3.56-3.46 (m, 1H), 2.70-2.58 (m, 2H), 2.43 (s, 3H), 1.91-1.82 (m, 2H), 1.36-1.15 (m, 6H), 1.01 (d, $J$ = 6.1 Hz, 3H), 0.87 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR: (100 MHz, CDCl$_3$) $\delta$ 143.4, 139.4, 132.8, 129.6, 127.7, 121.9, 55.0, 49.6, 37.1, 31.3, 29.1, 28.8, 22.4, 21.5, 16.6, 13.9.

(Z)-3-(cyclopropylmethylene)-4-methyl-1-tosylpyrroloidine (2w) (General procedure A): The reaction with iron complex I (0.0150 g, 0.027 mmol), Et$_2$Zn (1.25 mL, 1.0 M in toluene) and N-allyl-N-(3-cyclopropylprop-2-yn-1-yl)-4-methylbenzenesulfonamide (1w) (0.1490 g, 0.5 mmol) afforded 2w (0.0900 g, 60%) as a colorless oil, Z/E > 20/1. IR (neat): 2965, 2870, 1597, 1453, 1343 cm$^{-1}$; $^1$H NMR: (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J$ = 8.2 Hz, 2H), 7.33 (d, $J$ = 8.0 Hz, 2H), 4.63-4.52 (m, 1H), 4.06-3.96 (m, 1H), 3.90-3.81 (m, 1H),

S-10
3.57-3.47 (m, 1H), 2.70-2.57 (m, 2H), 2.44 (s, 3H), 1.20-1.09 (m, 1H), 0.98 (d, J = 6.1 Hz, 3H), 0.77-0.67 (m, 2H), 0.35-0.25 (m, 2H); $^1$C NMR: (100 MHz, CDCl$_3$) δ 143.4, 138.1, 132.9, 129.6, 127.8, 125.4, 55.0, 49.9, 37.2, 21.5, 16.5, 11.0, 6.8, 6.7. HRMS (EI) calculated for [C$_{10}$H$_{16}$NO$_2$Si]$^+$ requires m/z 291.1293, found m/z 291.1290.

(Z)-3-methyl-1-tosyl-4-((trimethylsilylmethylene)pyrrolidine (2x)$^{11}$ (General procedure A): The reaction with iron complex I (0.0156 g, 0.028 mmol), Et$_2$Zn (1.25 mL, 1.0 M in toluene) and N-allyl-4-methyl-N-(3-(trimethylsilyl)prop-2-yn-1-yl)benzenesulfonylamide (1x) (0.1669 g, 0.5 mmol) afforded 2x (0.1509 g, 90%) as a colorless oil, Z/E > 20/1. IR (neat): 2956, 1637, 1598, 1494, 1454 cm$^{-1}$; $^1$H NMR: (400 MHz, CDCl$_3$) δ 7.69 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 5.30 (d, J = 1.6 Hz, 1H), 3.93 (dd, J = 14.7, 2.0 Hz, 1H), 3.71 (d, J = 14.7 Hz, 1H), 3.59-3.54 (m, 1H), 2.68-2.56 (m, 2H), 2.42 (s, 3H), 1.00 (d, J = 6.0 Hz, 3H), 0.04 (s, 9H); $^1$C NMR: (100 MHz, CDCl$_3$) δ 157.1, 143.5, 132.6, 129.6, 127.7, 119.5, 54.3, 51.5, 39.9, 30.8, 21.4, 16.1, -0.7; HRMS (EI) calculated for [C$_{14}$H$_{14}$NO$_2$Si]$^+$ requires m/z 323.1375, found m/z 323.1379.

3-methyl-4-methylene-1-tosylpyrrolidine (2y)$^{19}$ (General procedure B): The reaction with iron complex I (0.0148 g, 0.026 mmol), Et$_2$Zn (1.25 mL, 1.0 M in toluene) and N-allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonylamide (1y) (0.1263 g, 0.5 mmol) afforded 2y (0.0754 g, 60%) as a colorless oil, Z/E > 20/1. $^1$H NMR: (400 MHz, CDCl$_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 4.90 (d, J = 1.9 Hz, 1H), 4.85 (d, J = 1.9 Hz, 1H), 3.99-3.90 (m, 1H), 3.79-3.69 (m, 1H), 3.63-3.57 (m, 1H), 2.75-2.60 (m, 2H), 2.43 (s, 3H), 1.04 (d, J = 6.2 Hz, 3H); $^1$C NMR: (100 MHz, CDCl$_3$) δ 149.3, 143.6, 132.9, 129.6, 127.8, 106.0, 55.1, 52.1, 37.4, 21.5, 16.0;

(Z)-4-benzylidene-3-methyl-2-phenyltetrahydrofuran (2z) (General procedure A): The reaction with iron complex I (0.0147 g, 0.026 mmol), Et$_2$Zn (1.25 mL, 1.0 M in toluene) and 3-(1-(phenylallyl)oxy)prop-1-yn-1-yl)benzene (1z) (0.1229 g, 0.5 mmol) afforded 2z (0.0807 g, 65%) as a colorless oil, Z/E > 20/1, dr > 20/1. IR (neat): 3029, 2963, 2867, 1600, 1493, 1452 cm$^{-1}$; $^1$H NMR: (400 MHz, CDCl$_3$) δ 7.45-7.29 (m, 7H), 7.25-7.14 (m, 4H), 6.27 (d, J = 2.4 Hz, 1H), 5.02-4.98 (m, 1H), 4.78-4.70 (m, 1H), 4.30 (d, J = 9.5 Hz, 1H), 2.78-2.66 (m, 1H), 1.20 (d, J = 6.6 Hz, 3H); $^1$C NMR: (100 MHz, CDCl$_3$) δ 146.2, 140.4, 137.2, 128.5, 128.4, 128.01, 127.97, 126.59, 126.56, 119.9, 87.2, 70.3, 47.8, 14.2. HRMS (EI) calculated for [C$_{11}$H$_{16}$O]$^+$ requires m/z 250.1358, found m/z 250.1357.

(E)-4-benzylidene-3-methylenehydro-2H-pyran (2aa)$^{10}$ (General procedure A): The reaction with iron complex I (0.0138 g, 0.024 mmol), Et$_2$Zn (1.25 mL, 1.0 M in toluene) and (4-(allyloxy)but-1-yn-1-yl)benzene (1aa) (0.0931 g, 0.5 mmol) afforded 2aa (0.0460 g, 49%) as a colorless oil, Z/E > 20/1. IR (neat): 2959, 2845, 1651, 1599, 1491, 1462, 1447 cm$^{-1}$; $^1$H NMR: (400 MHz, CDCl$_3$) δ 7.36-7.28 (m, 2H), 7.24-7.15 (m, 3H), 6.31 (s, 1H), 3.91-3.84 (m, 1H), 3.81-3.74 (m, 1H), 3.59-3.49 (m, 1H), 3.36-3.26 (m, 1H), 2.76-2.66 (m, 1H), 2.54-2.43 (m, 1H), 2.39-2.30 (m, 1H), 1.14 (d, J = 6.8 Hz, 3H); $^1$C NMR: (100 MHz, CDCl$_3$) δ 142.2, 137.8, 129.0, 128.1, 126.2, 121.6, 75.1, 69.1, 38.7, 29.5, 14.8. HRMS (EI) calculated for [C$_{16}$H$_{14}$O]$^+$ requires m/z 188.1201, found m/z 188.1203.
**General procedure**

- **A:** The reaction with iron complex I (0.0149 g, 0.026 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and 1-(4-(allyloxy)but-1-yn-1-yl)-4-methoxybenzene (1ab) (0.1100 g, 0.5 mmol) afforded 2ab (0.0565 g, 51%) as a colorless oil, Z/E > 20/1. IR (neat): 2958, 2839, 1608, 1511, 1463 cm⁻¹; ¹H NMR: (400 MHz, CDCl₃) δ 7.11 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 6.25 (s, 1H), 3.90-3.72 (m, 5H), 3.58-3.49 (m, 1H), 3.35-2.56 (m, 1H), 2.75-2.65 (m, 1H), 2.52-2.41 (m, 1H), 2.39-2.28 (m, 1H), 1.13 (d, J = 6.7 Hz, 3H);¹³C NMR: (100 MHz, CDCl₃) δ 158.0, 140.9, 130.2, 130.0, 121.0, 113.6, 75.1, 69.0, 55.2, 38.7, 29.4, 14.9. HRMS (EI) calculated for [C₁₃H₁₈O₂]⁺ requires m/z 218.1307, found m/z 218.1306.

![Chemical Structure](image)

**Enantioselective Reaction**

(E)-4-(4-chlorobenzylidene)-3-methyltetrahydro-2H-pyran (2ac) (General procedure A): The reaction with iron complex I (0.0152 g, 0.027 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and 1-(4-(allyloxy)but-1-yn-1-yl)-4-chlorobenzene (1ac) (0.1040 g, 0.5 mmol) afforded 2ac (0.0461 g, 44%) as a colorless oil, Z/E > 20/1. IR (neat): 2960, 2843, 1651, 1592, 1490, 1463, 1382 cm⁻¹; ¹H NMR: (400 MHz, CDCl₃) δ 7.28 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 6.25 (s, 1H), 3.91-3.84 (m, 1H), 3.82-3.74 (m, 1H), 3.67-3.48 (m, 1H), 3.34-3.26 (m, 1H), 2.70-2.61 (m, 1H), 2.53-2.42 (m, 1H), 2.37-2.27 (m, 1H), 1.13 (d, J = 6.8 Hz, 3H);¹³C NMR: (100 MHz, CDCl₃) δ 143.0, 136.1, 131.9, 130.2, 128.3, 120.4, 75.0, 68.9, 38.7, 29.4, 14.7. HRMS (EI) calculated for [C₁₃H₁₄ClO]⁺ requires m/z 222.0811, found m/z 222.0809.

**V. Deuteroinsertion Study**

Quenched by D₂O:

(Z)-1-benzyl-3-benzylidene-4-methylpyrrolidine (2b) (General procedure B): The reaction with iron complex I (0.0153 g, 0.026 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and 1b (125 μL, 0.5 mmol) afforded 2b (0.1168 g, 89%) as a colorless oil, Z/E > 20/1. ¹H NMR: (400 MHz, CDCl₃) δ 7.45-7.21 (m, 7H), 7.21-7.12 (m, 3H), 6.22 (d, J = 2.1 Hz, 0.3H), 3.84-3.75 (m, 1H), 3.69 (s, 2H), 3.39-3.29 (m, 1H), 3.00 (t, J = 7.9 Hz, 1H), 2.95-2.83 (m, 1H), 2.11 (t, J = 8.2 Hz, 1H), 1.20 (d, J = 6.5 Hz, 2H).

Quenched by MeOD:

(Z)-1-benzyl-3-benzylidene-4-methylpyrrolidine (2b) (General procedure B): The reaction with iron complex I (0.0141 g, 0.025 mmol), Et₂Zn (1.25 mL, 1.0 M in toluene) and 1b (125 μL, 0.5 mmol) afforded 2b (0.1115 g, 85%) as a colorless oil, Z/E > 20/1. ¹H NMR: (400 MHz, CDCl₃) δ 7.45-7.21 (m, 7H), 7.21-7.12 (m, 3H), 6.22 (d, J = 2.1 Hz, 0.31H), 3.84-3.75 (m, 1H), 3.69 (s, 2H), 3.39-3.29 (m, 1H), 3.00 (t, J = 7.9 Hz, 1H), 2.95-2.83 (m, 1H), 2.11 (t, J = 8.2 Hz, 1H), 1.20 (d, J = 6.5 Hz, 2H).

VI Enantioselective Reaction

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5-12
To a 25 mL flame-dried Schlenk flask cooled under Ar, iron complex V (0.0117 g, 0.025 mmol) and Et₂Zn (1.25 mL, 1.0 M in toluene) were added. After stirring for 5 min, 1b (0.1319 g, 0.5 mmol) was added to the above solution. The reaction mixture was stirred at 25 °C for 1.5 h. The reaction was quenched by addition of a saturated solution of EtOH (5 mL) at -78 °C, then warmed to room temperature gradually and stirred for 2 hour. The filtrate was concentrated in vacuo, and the residue was purified by column chromatography with silica gel (ethyl acetate : petroleum = 1 : 10) to give 2b (0.0884 g, 66%) as colorless oil, Z/E > 20/1. The analysis data are same as above.

\[ \text{[} \alpha \text{]}_{D}^{20} = -11.5 \text{ (c = 0.98, CHCl}_3\text{)}} \]; 39% ee, determined by HPLC, HPLC conditions: Chiralcel OD-H, n-hexane/i-PrOH = 90/10, 1.0 mL/min, n = 254 nm, tr 4.4 (major), 6.0 (minor).

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**1^13C NMR**

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400 MHz, CDCl₃
OMe

lab

$^{13}$C NMR

100 MHz, CDCl$_3$
\[ \text{S22} \]
13C NMR
100 MHz, CDCl$_3$
Ph

2a

$^1$H NMR
400 MHz, CDCl$_3$
\[ \text{Ph} \]

2a

\(^{13}\text{C NMR}\)

100 MHz, CDCl\textsubscript{3}
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100 MHz, CDCl$_3$
$\text{Ph}$

$\text{H}_3\text{C} - \text{N}$

$\text{2c}$

$^1\text{H NMR}$

400 MHz, CDCl$_3$
$^{13}$C NMR
100 MHz, CDCl$_3$
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400 MHz, CDCl$_3$

2d

Ph

TsN

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EtO$_2$C

Ph

EtO$_2$C
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100 MHz, CDCl$_3$
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7.750 & \quad 7.729 \\
7.333 & \quad 7.313 \\
7.246 & \quad 7.230 \\
7.163 & \quad 7.145 \\
7.097 & \quad 7.081 \\
7.077 & \quad 7.060 \\
6.295 & \quad 6.291 \\
4.303 & \quad 4.267 \\
4.110 & \quad 4.073 \\
3.603 & \quad 3.584 \\
3.581 & \quad 3.562 \\
2.918 & \quad 2.901 \\
2.885 & \quad 2.783 \\
2.761 & \quad 2.743 \\
2.727 & \quad 2.710 \\
2.418 & \quad 2.095 \\
1.680 & \quad 1.204 \\
1.187 & \quad 1.164 \\
1.150 & \quad 1.134
\end{align*}$

$\begin{align*}
1.96 & \quad 2.71 \\
1.97 & \quad 1.99 \\
1.98 & \quad 0.99 \\
1.99 & \quad 1.08 \\
0.99 & \quad 1.00 \\
1.02 & \quad 1.01 \\
1.01 & \quad 1.04 \\
1.04 & \quad 2.98 \\
2.97 & \quad 2.92 \\
2.92 & \quad 14.96
\end{align*}$

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400 MHz, CDCl$_3$
$^{13}$C NMR
100 MHz, CDCl$_3$
$^{1}$H NMR
400 MHz, CDCl$_3$
$^{13}$C NMR
100 MHz, CDCl$_3$
$^{13}$C NMR
100 MHz, CDCl$_3$
$^{13}$C NMR
100 MHz, CDCl$_3$
1H NMR
400 MHz, CDCl₃
|-----|---------|---------|---------|---------|---------|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|

**$^{13}$C NMR**

100 MHz, CDCl$_3$
$^{1}\text{H NMR}$

400 MHz, CDCl$_3$
2x

$^{13}$C NMR

100 MHz, CDCl$_3$
$^1$H NMR
400 MHz, CDCl$_3$
\[ \text{\( ^1\)H NMR} \]

400 MHz, CDCl\textsubscript{3}
$^{13}$C NMR

100 MHz, CDCl$_3$
2aa

$^1$H NMR

400 MHz, CDCl$_3$
$^{13}$C NMR
100 MHz, CDCl₃
$^{1}$H NMR
400 MHz, CDCl$_3$
\(^{13}\)C NMR
100 MHz, CDCl\(_3\)
$^{1}$H NMR
400 MHz, CDCl$_3$
$^{13}$C NMR
100 MHz, CDCl$_3$
89% yield
BnN

Ph

D (69% D)

D (>99% D)

85% yield

S84
**VX HPLC Spectra**

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描述：OD-H, n-hex, iPrOH+90/10, 1.0 ml/min, 254 nm

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