Supporting Information

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1. Experimental procedures and spectroscopic data

1.1 General information

All reactions were carried out under an inert atmosphere of dry N₂ in Schlenk tube. Solvents were purified by standard method. Unless otherwise specified, the anhydrous DCE distilled form the refluxing mixture with CaH₂ was used. MeOH and AcOH were A. R. pure and used as received from commercial sources without further purification. ¹H, ¹³C, ¹⁹F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ¹H; 100 MHz for ¹³C; 376 MHz for ¹⁹F), ¹H NMR and ¹³C NMR chemical shifts were determined relative to internal standard TMS at 0 δ 0.0 and ¹⁹F NMR chemical shifts were determined relative to CFCl₃ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra (MS) were obtained using LTQ FTICR DART and ESI mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

1.2 Preparation of substrates 1a-1v

1.2.1 Preparation of substrates 1a-1o

For the synthesis of substrates 1a – 1o, the general procedure was described using substrate 1a as example.

S2a: Et₃N (9.15 g, 90.6 mmol) was added dropwise into a solution of methyl prolinate hydrochloride S1a (5.0 g, 30.2 mmol) and TsCl (5.18 g, 27.2 mmol) in dichloromethane (DCM, 150 mL) cooling with ice bath. The reaction was stirred at 0 °C and monitored by TLC. After the TsCl was completely consumed in about 3 h, the reaction mixture was poured into ice water and extracted with DCM (2 × 100 mL). The organic phase was washed with 1M HCl (2 × 50 mL), brine and dried with anhydrous Na₂SO₄. The solvent was distilled using rotary evaporator to obtain S2a (6.78 g, 88%) without further purification.
**S3a**: Under N₂ atmosphere, the solution of i-PrMgBr (17.6 mL, 52.8 mmol) in 2-methyltetrahydrofuran (3 mol/L) was added dropwise into the suspension of Ts-protected methyl prolinate **S2a** (5.0 g, 17.6 mmol) and N, O-dimethylhydroxylamine hydrochloride (2.58 g, 26.4 mmol) in anhydrous THF (150 mL) at -40 °C with vigorous stir. After the complete consumption of **S2a** (determined by TLC, about 2 h), the reaction was quenched by 100 mL saturated NH₄Cl (aq), and extracted with ethyl acetate (EtOAc, 3 × 100 mL). The organic phase was washed with brine and dried with anhydrous Na₂SO₄, the solvent was removed by rotary evaporator to obtain **S3a** (5.2g, 95%) without further purification.

**S4a**: Under N₂ atmosphere, n-BuLi (0.9 mL, 2.2 mmol, 2.5 M) in hexane was added dropwise into the solution of phenylacetylene (245 mg, 2.4 mmol) in anhydrous THF (10 mL) at -78 °C. After stir for 1 h, the Weinreb amide **S3a** (625 mg, 2.0 mmol) dissolved in THF (2 mL) was added dropwise into the reaction mixture. After the reaction temperature raised to room temperature, the reaction was quenched using saturated 20 mL NH₄Cl (aq), and extracted with EtOAc (2 × 20 mL). The organic phase was washed with brine and dried with anhydrous Na₂SO₄, the solvent was removed by rotary evaporator. **S4a** (565 mg, 80%) was obtained after purified by chromatography (SiO₂; PE: EA = 5: 1) to yield 1a (328 mg, 60%).

**2-(4-phenylbut-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1a)**

Pale white solid, m.p. = 76 - 77 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 8.2 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 4H), 7.26 (d, J = 2.4 Hz, 1H), 5.68 (s, 1H), 5.57 (s, 1H), 4.39 (dd, J = 8.1, 2.9 Hz, 1H), 3.50 (dd, J = 9.8, 7.3, 4.1 Hz, 1H), 3.34 (dt, J = 9.6, 7.4 Hz, 1H), 2.40 (s, 3H), 2.00 – 2.08 (m, 1H), 1.98 – 1.88 (m, 1H), 1.84 – 1.75 (m, 1H), 1.75 – 1.65 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 135.5, 132.2, 131.5, 129.6, 128.4, 128.3, 127.5, 122.9, 122.3, 90.9, 87.5, 63.7, 49.1, 31.9, 24.0, 21.5. IR (KBr, cm⁻¹) 305, 2976, 2874, 1822, 1597, 1490, 1444, 1347, 1159, 1065, 1008, 912, 845, 691, 588; HRMS (DART) Calcd for C₂₁H₂₅NO₃S (M+H)⁺ 352.1366, found 352.1366.

**2-(4-(p-toly)but-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1b)**

Pale white solid, m.p. = 68 - 69 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, J = 8.2 Hz, 2H), 7.34 – 7.11 (m, 4H), 7.03 (d, J = 7.9 Hz, 2H), 5.59 (s, 1H), 5.47 (s, 1H), 4.32 (dd, J = 7.9, 2.5 Hz, 1H), 3.42 (dd, J = 11.2, 7.4, 4.1 Hz, 1H), 3.30 – 3.13 (m, 1H), 2.32 (s, 3H), 2.27 (s, 3H), 2.00 – 1.91 (m, 1H), 1.91 – 1.81 (m, 1H), 1.76 – 1.67 (m, 1H), 1.67 – 1.58 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 138.6, 135.6, 132.2, 131.4, 129.6, 129.1, 127.5, 121.9, 119.8, 91.1, 86.8, 63.8, 49.0,
31.9, 24.0, 21.5; IR (KBr, cm\(^{-1}\)) 3029, 2975, 2873, 2199, 1663, 1599, 1347, 1159, 1093, 816, 671, 548; HRMS (DART) Calcd for C\(_{22}\)H\(_{30}\)NO\(_2\)S (M+H\(^+\)) 366.1522, found 366.1522.

2-(4-(4-(tert-butylyphenyl)but-1-en-3-yn-2-yl)-1-tosylpyrroolidine (1c)

White solid, m.p. = 83 - 84 °C, purified by chromatography (PE/EA = 5/1, \(R_f = 0.4\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.76 (d, \(J = 8.2\) Hz, 2H), 7.39 – 7.34 (m, 6H), 5.68 (s, 1H), 5.57 (s, 1H), 4.53 – 3.45 (m, 1H), 3.50 (ddd, \(J = 9.8, 7.3, 4.1\) Hz, 1H), 3.34 (dt, \(J = 9.6, 7.4\) Hz, 1H), 2.40 (s, 3H), 2.08 – 1.99 (m, 1H), 1.98 – 1.88 (m, 1H), 1.84 – 1.75 (m, 1H), 1.75 – 1.65 (m, 1H), 1.30 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.7, 143.3, 135.5, 132.3, 131.3, 129.6, 127.5, 125.3, 121.9, 119.9, 91.1, 86.9, 63.8, 49.1, 34.8, 31.9, 31.2, 24.0, 21.5; IR (KBr, cm\(^{-1}\)) 3034, 2962, 2870, 2201, 1916, 1812, 1598, 1503, 1461, 1399, 1193, 1159, 1063, 1008, 907, 836, 815, 671, 588, 548; HRMS (DART) Calcd for C\(_{22}\)H\(_{30}\)NO\(_2\)S (M+H\(^+\)) 408.1992, found 408.1994.

2-(4-(4-methoxyphenyl)but-1-en-3-yn-2-yl)-1-tosylpyrroolidine (1d)

Yellow solid, m.p. = 85 - 86 °C, purified by chromatography (PE/EA = 5/1, \(R_f = 0.3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.75 (d, \(J = 8.1\) Hz, 2H), 7.32 – 7.25 (m, 4H), 7.07 – 6.73 (m, 2H), 5.64 (s, 1H), 5.52 (s, 1H), 4.38 (d, \(J = 7.7\) Hz, 1H), 3.79 (s, 3H), 3.53 – 3.44 (m, 1H), 3.32 (dd, \(J = 16.2, 8.4\) Hz, 1H), 2.38 (s, 3H), 2.02 (ddd, \(J = 16.5, 8.7, 5.8\) Hz, 1H), 1.92 (dt, \(J = 23.0, 8.1\) Hz, 1H), 1.82 – 1.73 (m, 1H), 1.73 – 1.63 (m, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 159.7, 143.3, 135.5, 133.0, 132.4, 129.6, 127.4, 121.5, 115.0, 114.0, 91.0, 86.2, 63.8, 55.3, 49.1, 31.9, 23.9, 21.5; IR (KBr, cm\(^{-1}\)) 3060, 2956, 2840, 2194, 1720, 1601, 1510, 1344, 1250, 1092, 1030, 911, 736, 589, 548; HRMS (DART) Calcd for C\(_{22}\)H\(_{30}\)FNO\(_2\)S (M+H\(^+\)) 382.1471, found 382.1471.

2-(4-(4-fluorophenyl)but-1-en-3-yn-2-yl)-1-tosylpyrroolidine (1e)

Yellow solid, m.p. = 82 - 83 °C, purified by chromatography (PE/EA = 5/1, \(R_f = 0.4\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.75 (d, \(J = 8.2\) Hz, 2H), 7.38 – 7.32 (m, 2H), 7.29 (d, \(J = 8.1\) Hz, 2H), 7.04 – 6.95 (m, 2H), 5.68 (s, 1H), 5.57 (s, 1H), 4.37 (dd, \(J = 8.1, 2.9\) Hz, 1H), 3.50 (ddd, \(J = 10.0, 7.3, 4.1\) Hz, 1H), 3.33 (dt, \(J = 9.7, 7.4\) Hz, 1H), 2.40 (s, 3H), 2.06 – 1.97 (m, 1H), 1.97 - 1.87 (m, 1H), 1.84 – 1.75 (m, 1H), 1.75 – 1.65 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.5 (d, \(J_{C,F} = 249.8\) Hz), 143.3, 135.4, 133.4 (d, \(J_{C,F} = 8.3\) Hz), 132.1, 129.6, 127.5, 122.4, 119.0 (d, \(J_{C,F} = 3.5\) Hz), 115.6 (d, \(J_{C,F} = 22.1\) Hz), 89.8, 87.2, 63.7, 49.1, 32.0, 23.9, 21.5. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -110.65. IR (KBr, cm\(^{-1}\)) 3062, 2976, 2926, 2874, 2204, 1918, 1596, 1490, 1346, 1158, 1091, 1101, 817, 737, 707, 589, 547; HRMS (DART) Calcd for C\(_{22}\)H\(_{28}\)FNO\(_2\)S (M+H\(^+\)) 370.1272, found 370.1272.

2-(4-(4-chlorophenyl)but-1-en-3-yn-2-yl)-1-tosylpyrroolidine (1f)

Yellow solid, m.p. = 79 - 80 °C, purified by chromatography (PE/EA = 5/1, \(R_f = 0.4\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.67 (d, \(J = 8.2\) Hz, 2H), 7.34 – 7.25 (m, 6H), 5.72 (s, 1H), 5.60 (s, 1H), 4.38 (dd, \(J = 8.0, 2.8\) Hz, 1H), 3.54 – 3.46 (m, 1H), 3.39 – 3.28 (m, 1H), 2.40 (s, 3H), 2.02 (ddd, \(J = 14.6, 6.8, 3.6\) Hz, 1H), 1.93 (ddd, \(J = 18.7, 11.4, 5.5\) Hz, 1H), 1.79 (ddd, \(J = 16.4, 11.6, 8.0\) Hz, 1H), 1.70 (ddd, \(J = 11.3, 6.9, 3.0\) Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.4, 135.4, 134.4, 132.7, 132.0, 129.6, 128.6, 127.4, 122.7, 121.4.
89.8, 88.5, 63.6, 49.1, 32.0, 23.9, 21.5. IR (KBr, cm⁻¹) 3063, 2976, 2926, 2874, 2204, 1918, 1724, 1670, 1490, 1345, 1158, 1091, 1011, 817, 736, 589, 547; HRMS (DART) Calcd for C₂₁H₂₃ClNO₃S (M+H)⁺ 386.0976, found 386.0975.

2-(4-(4-bromophenyl)but-1-en-3-yne-2-yl)-1-tosylpyrrolidine (1g)

Yellow solid, m.p. = 85 - 86 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); ¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.72 (m, 2H), 7.46 – 7.41 (m, 1H), 7.38 – 7.34 (m, 1H), 7.30 (m, 3H), 7.25 – 7.19 (m, 1H), 5.72 – 5.66 (m, 1H), 5.60 – 5.55 (m, 1H), 4.42 – 4.34 (m, 1H), 3.53 – 3.45 (m, 1H), 3.42 – 3.27 (m, 1H), 2.40 – 2.38 (m, 3H), 2.08 – 1.88 (m, 2H), 1.83 – 1.76 (m, 1H), 1.75 – 1.65 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.4, 143.3, 135.6, 135.4, 132.9, 132.1, 132.0, 131.6, 131.5, 129.62, 129.59, 128.4, 128.3, 127.5, 122.9, 122.8, 122.6, 122.3, 121.9, 90.9, 89.8, 88.6, 87.5, 63.7, 63.6, 49.1, 32.0, 24.0, 23.9, 21.5.; IR (KBr, cm⁻¹) 3062, 2975, 2874, 2202, 1597, 1486, 1346, 1157, 1068, 1008, 817, 707, 577, 547; HRMS (DART) Calcd for C₂₁H₂₃BrNO₃S (M+H)⁺ 430.0471, found 430.0470.

2-(4-(m-tolyl)but-1-en-3-yne-2-yl)-1-tosylpyrrolidine (1h)

Colorless viscous liquid, purified by chromatography (PE/EA = 5/1, Rf = 0.4); ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.15 – 7.09 (m, 1H), 5.68 (s, 1H), 5.57 (s, 1H), 4.39 (dd, J = 8.1, 3.2 Hz, 1H), 3.54 – 3.46 (m, 1H), 3.42 – 3.27 (m, 1H), 2.39 (s, 6H), 2.06 – 1.99 (m, 1H), 1.99 – 1.88 (m, 1H), 1.82 – 1.76 (m, 1H), 1.73 – 1.60 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 138.0, 135.5, 132.1, 132.0, 129.6, 129.3, 128.6, 128.2, 127.5, 122.7, 122.2, 91.1, 87.1, 63.8, 49.1, 31.9, 24.0, 21.5, 21.2. IR (KBr, cm⁻¹) 3062, 3024, 2975, 2736, 2121, 1811, 1665, 1597, 1485, 1454, 1400, 1380, 1093, 1063, 846, 758, 711, 667, 620, 588, 548; HRMS (DART) Calcd for C₂₂H₂₄NO₃S (M+H)⁺ 366.1522, found 366.1522.

2-(4-(o-tolyl)but-1-en-3-yne-2-yl)-1-tosylpyrrolidine (1i)

Colourless viscous liquid, purified by chromatography (PE/EA = 5/1, Rf = 0.4); ¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.62 (m, 2H), 7.33 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.15 – 7.09 (m, 1H), 5.68 (s, 1H), 5.57 (s, 1H), 4.39 (dd, J = 8.1, 3.2 Hz, 1H), 3.53 – 3.46 (m, 1H), 3.42 – 3.27 (m, 1H), 2.39 (s, 6H), 2.10 – 2.02 (m, 1H), 2.00 – 1.88 (m, 1H), 1.86 – 1.76 (m, 1H), 1.73 – 1.60 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 140.0, 135.5, 132.3, 131.9, 129.6, 129.4, 128.4, 127.5, 125.5, 122.7, 122.0, 91.3, 89.9, 63.8, 49.1, 31.20, 24.0, 21.5, 20.7. IR (KBr, cm⁻¹) 3029, 2953, 2924, 2872, 2735, 2415, 2307, 2198, 1915, 1724, 1668, 1599, 1494, 1449, 1379, 1159, 1092, 1063, 1007, 910, 816, 736, 707, 669, 587, 525, 492; HRMS (DART) Calcd for C₂₂H₂₄NO₃S (M+H)⁺ 366.1522, found 366.1522.

2-(4-(naphthalen-2-yl)but-1-en-3-yne-2-yl)-1-tosylpyrrolidine (1j)

White solid, m.p. = 117 - 118 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); ¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 1H), 7.83 – 7.71 (m, 5H), 7.52 – 7.45 (m, 2H), 7.40 (dd, J = 8.5, 1.3 Hz, 1H), 7.27 (d, J = 8.1 Hz, 2H), 5.72 (s, 1H), 5.62 (s, 1H), 4.44 (dd, J = 8.1, 2.8 Hz, 1H), 3.57 – 3.49 (m, 1H), 3.42 – 3.31 (m, 1H), 2.36 (s, 3H), 2.12 – 2.03 (m, 1H), 2.02 – 1.92 (m, 1H), 1.87 – 1.75 (m, 1H), 1.76 – 1.67 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 135.6, 132.9, 132.8, 132.2, 131.4, 129.6, 128.2, 128.0, 127.8, 127.7, 127.5,
126.8, 126.6, 122.5, 120.2, 91.4, 87.8, 63.8, 49.1, 32.0, 24.0, 21.5. \textbf{IR} (KBr, cm$^{-1}$) 3056, 2974, 2925, 2873, 1920, 1813, 1597, 1449, 1400, 1346, 1268, 1191, 1159, 1094, 1064, 1008, 908, 860, 816, 749, 708, 673, 588, 548, 475; \textbf{HRMS} (DART) Calcd for C$_2$H$_2$NO$_2$S (M+H)$^+$ 402.1522, found 402.1521.

2-(4-(thiophen-3-yl)but-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1k)

Yellow viscous liquid, purified by chromatography (PE/EA = 5/1, R$_f$ = 0.4); \textbf{1}$H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J$ = 8.1 Hz, 2H), 7.38 (d, $J$ = 1.9 Hz, 1H), 7.34 – 7.19 (m, 3H), 7.05 (d, $J$ = 4.9 Hz, 1H), 5.68 (s, 1H), 5.56 (s, 1H), 4.36 (d, $J$ = 7.8 Hz, 1H), 3.56 – 3.41 (m, 1H), 3.35 – 3.27 (m, 1H), 2.40 (s, 3H), 2.05 – 1.97 (m, 1H), 1.96 – 1.84 (m, 1H), 1.82 – 1.63 (m, 2H). \textbf{13}$C$ NMR (101 MHz, CDCl$_3$) $\delta$ 143.4, 135.3, 132.1, 129.7, 129.6, 128.8, 127.5, 125.4, 122.2, 121.9, 87.0, 86.1, 63.7, 49.1, 31.9, 23.9, 21.5. \textbf{IR} (KBr, cm$^{-1}$) 3107, 2952, 2926, 2873, 1921, 1721, 1669, 1597, 1493, 1448, 1379, 1255, 1191, 1159, 1094, 1063, 1008, 909, 845, 815, 783, 742, 707, 670, 626, 588, 548; \textbf{HRMS} (DART) Calcd for C$_{19}$H$_{20}$NO$_2$S (M+H)$^+$ 358.0930, found 358.0930.

2-(4-cyclopropylbut-1-en-3-yn-2-yl)-1-tosylpyrrolidine (II)

Yellow viscous liquid purified by chromatography (PE/EA = 5/1, R$_f$ = 0.4); \textbf{1}$H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J$ = 8.2 Hz, 2H), 7.30 (d, $J$ = 8.0 Hz, 2H), 5.51 (t, $J$ = 1.3 Hz, 1H), 5.36 (s, 1H), 4.27 – 4.21 (m, 1H), 3.47 – 3.49 (m, 1H), 3.33 – 3.24 (m, 1H), 2.43 (s, 3H), 1.98 – 1.79 (m, 2H), 1.73 – 1.60 (m, 2H), 1.33 – 1.25 (m, 1H), 0.83 – 0.75 (m, 2H), 0.68 – 0.62 (m, 2H). \textbf{13}$C$ NMR (101 MHz, CDCl$_3$) $\delta$ 143.2, 135.5, 132.3, 129.5, 127.4, 120.8, 95.0, 73.8, 63.8, 48.9, 31.7, 23.8, 21.5, 8.5, 7.0. \textbf{IR} (KBr, cm$^{-1}$) 3093, 2977, 2874, 1922, 1814, 1673, 1589, 1493, 1450, 1400, 1346, 1194, 1159, 1093, 1006, 872, 847, 815, 760, 736, 588, 547; \textbf{HRMS} (DART) Calcd for C$_{19}$H$_{22}$NO$_2$S (M+H)$^+$ 316.1366, found 316.1366.

2-(dec-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1m)

Yellow viscous liquid, purified by chromatography (PE/EA = 5/1, R$_f$ = 0.4); \textbf{1}$H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J$ = 8.0 Hz, 2H), 7.32 (d, $J$ = 7.9 Hz, 2H), 5.54 (s, 1H), 5.40 (s, 1H), 4.27 (d, $J$ = 7.6 Hz, 1H), 3.52 – 3.40 (m, 1H), 3.30 (dd, $J$ = 17.1, 7.5 Hz, 1H), 2.44 (s, 3H), 2.26 (t, $J$ = 7.0 Hz, 2H), 2.02 – 1.83 (m, 2H), 1.76 – 1.61 (m, 2H), 1.54 – 1.45 (m, 2H), 1.35 (m, 6H), 0.91 (t, $J$ = 6.8 Hz, 3H). \textbf{13}$C$ NMR (101 MHz, CDCl$_3$) $\delta$ 143.2, 135.5, 132.4, 129.5, 127.5, 120.7, 92.1, 78.6, 63.9, 49.0, 31.7, 31.3, 28.6, 23.8, 22.6, 21.5, 19.3, 14.1. \textbf{IR} (KBr, cm$^{-1}$) 3028, 2929, 2858, 1614, 1598, 1493, 1458, 1379, 1244, 1191, 1094, 1008, 903, 815, 758, 708, 588, 548; \textbf{HRMS} (DART) Calcd for C$_{32}$H$_{32}$NO$_2$S (M+H)$^+$ 360.1992, found 360.1992.

2-(4-phenylbut-1-en-3-yn-2-yl)-1-tosylpiperidine (1n)

Yellow viscous liquid, purified by chromatography (PE/EA = 5/1, R$_f$ = 0.4); \textbf{1}$H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J$ = 8.0 Hz, 2H), 7.38 (m, 2H), 7.32 – 7.28 (m, 3H), 7.26 (d, $J$ = 8.1 Hz, 2H), 5.69 (s, 1H), 5.55 (s, 1H), 4.85 – 4.76 (m, 1H), 3.78 (dt, $J$ = 14.2, 2.9 Hz, 1H), 3.18 (dd, $J$ = 13.5, 2.9 Hz, 1H), 2.40 (s, 3H), 2.28 – 2.20 (m, 1H), 1.67 – 1.45 (m, 5H). \textbf{13}$C$ NMR (101 MHz, CDCl$_3$) $\delta$ 143.0, 138.4, 131.4, 129.6, 129.5, 128.4, 128.3, 127.0, 123.7, 122.9, 91.0, 88.2, 55.9, 41.6, 27.8, 24.4, 21.5, 19.1. \textbf{IR} (KBr, cm$^{-1}$) 3060, 2942, 2861, 2361, 1666, 1598, 1491, 1446, 1378, 1337, 1217, 1188, 1156, 1109, 1053, 961, 938, 917, 855, 815, 758, 735, 709, 692, 661, 617, 575, 547; \textbf{HRMS} (DART) Calcd for C$_{32}$H$_{32}$NO$_2$S (M+H)$^+$ 366.1522, found 366.1521.
For the synthesis of 1o, \( \text{CH}_3\text{CH}_2\text{PPh}_3\text{Br} \) was used instead of \( \text{CH}_3\text{PPh}_3\text{Br} \) in the last step.

**2-(1-phenylpent-3-en-1-yn-3-yl)-1-tosylpyrrolidine (1o)**

Yellow viscous liquid, purified by chromatography (PE/EA = 5/1, \( R_f = 0.4 \)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.77 – 7.71 (m, 2H), 7.35 – 7.19 (m, 7H), 6.14 (q, \( J = 6.8 \) Hz, 0.2H), 6.03 (dd, \( J = 7.5, 5.4 \) Hz, 0.8H), 4.37 (dd, \( J = 8.1, 3.0 \) Hz, 0.8H), 2.36 (s, 0.6H), 2.33 (s, 2.4H), 2.20 – 1.92 (m, 3H), 1.91 (s, 1.5H), 1.89 (s, 1.5H), 1.80 – 1.68 (m, 1H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 142.9, 136.7, 134.2, 131.3, 131.2, 129.4, 129.3, 128.3, 128.2, 128.1, 127.8, 127.4, 127.3, 125.7, 123.5, 89.1, 88.2, 85.8, 57.3, 49.1, 49.0, 32.5, 32.1, 25.3, 24.2, 21.4, 16.0, 14.0. IR (KBr, cm\(^{-1}\)) 3031, 2925, 2871, 2362, 2340, 1596, 1490, 1442, 1440, 1344, 1244, 1200, 1158, 1094, 1068, 986, 814, 757, 691, 666, 589, 547; HRMS (DART) Calcd for C\(_{22}\)H\(_{24}\)NO\(_2\)S (M+H)\(^{+}\) 366.1522, found 366.1521.

### 1.2.2 Preparation of substrates 1p–1v

For the synthesis of substrates 1p – 1v, the general procedure was described using substrate 1p as example.

**S2p:** Et\(_3\)N (4.21 g, 41.7 mmol) was added dropwise into a solution of phenylalanine methyl ester hydrochloride S1p (3.0 g, 13.9 mmol) and TsCl (2.38 g, 12.5 mmol) in DCM (100 mL) cooling with ice bath. The reaction was stirred at 0 °C and monitored by TLC. After the TsCl was completely consumed, the reaction mixture was poured into ice water and extracted with DCM (2 × 100 mL). The organic phase was washed with 1M HCl (2 × 50 mL), brine and dried with anhydrous Na\(_2\)SO\(_4\). The solvent was removed using rotary evaporator to obtain S2p (4.03 g, 87%) without further purification.

**S3p:** A solution of Ts-protected phenylalanine methyl ester S2p (3.0 g, 9.0 mmol) and iodomethane (1.53 g, 10.8 mmol) in acetone (50 mL) was added K\(_2\)CO\(_3\) (2.49 g, 18.0 mmol), the reaction mixture was stirred at 60 °C overnight. The reaction was then filtrated and the solvent was distillled using rotary evaporator to obtain S3p (2.91 g, 93%) without further purification.

**S4p:** Under N\(_2\) atmosphere, the solution of i-PrMgBr (5.8 mL, 17.3 mmol) in 2-methyltetrahydrofuran (3 M) was added dropwise into the suspension of S3p (2 g, 5.7 mmol) and N,O-dimethylhydroxylamine hydrochloride (843 mg, 8.64 mmol) in anhydrous THF at -40 °C with vigorous stir. After the complete consumption of S3p (determined by TLC, about 2 h), the reaction was quenched by 20 mL saturated NH\(_4\)Cl (aq), and extracted with EtOAc (2 × 50 mL). The organic phase was washed with brine and dried with anhydrous Na\(_2\)SO\(_4\), the solvent was removed by rotary evaporator to obtain S4p (1.36 g, 63%) without further purification.
**S5p**: Under N₂ atmosphere, n-BuLi (0.9 mL, 2.2 mmol, 2.5 M) in hexane was added dropwise into the solution of phenylacetylene (245 mg, 2.4 mmol) in anhydrous THF (10 mL) at -78 °C. After stir for 1 h, the Weinreb amide S4p (753 mg, 2 mmol) dissolved in THF (2 mL) was added dropwise into the reaction mixture. After the reaction temperature raised to room temperature, the reaction was quenched using saturated NH₄Cl (aq), and extracted with EtOAc. The organic phase was washed with brine and dried with anhydrous Na₂SO₄, the solvent was removed by rotary evaporator. The desired S5p (417 mg, 50%) was obtained after purified by chromatography (SiO₂, PE: EA = 6: 1).

**1p**: Under N₂ atmosphere, n-BuLi (0.5 mL, 1.1 mmol, 2.5 M) in hexane was added dropwise into the suspension of CH₃PPhBr (428 mg, 1.2 mmol) in anhydrous THF at -40 °C. The reaction mixture was stirred for 1 h until it turned to clear orange solution. After S5p (417 mg, 1.0 mmol) dissolved in anhydrous THF was added into the reaction dropwise, the reaction temperature was raised to 0 °C and maintained until the entire consumption of S5p. And then the reaction was quenched using 5 mL saturated NH₄Cl (aq), and extracted with EtOAc (2 × 20 mL). The organic phase was washed with brine and dried with anhydrous Na₂SO₄, the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography (SiO₂, PE: EA = 6: 1) to yield 1p (174 mg, 42%).

**N,N′-dimethyl-N-(3-methylene-1,5-diphenylpent-4-yn-2-yl)benzenesulfonamide (1p)**

Pale white solid, m. p. = 93 - 94 °C, purified by chromatography (PE/EA = 6/1, Rf = 0.5); ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.48 (m, 4H), 7.39 – 7.35 (3H), 7.33 – 7.25 (m, 5H), 7.17 (d, J = 8.0 Hz, 2H), 5.63 (s, 1H), 5.51 (s, J = 9.5, 1H), 5.11 (t, J = 7.7 Hz, 6.5 Hz, 1H), 3.30 (dd, J = 14.0, 7.8 Hz, 1H), 2.99 (s, 3H), 2.96 (dd, J = 13.9, 7.7 Hz, 1H), 2.38 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.0, 137.7, 136.8, 131.6, 129.5, 129.0, 129.3, 128.7, 128.5, 127.4, 126.7, 125.4, 122.8, 89.1, 82.3, 37.3, 29.6, 21.5. IR (KBr, cm⁻¹): 3061, 3029, 2926, 1951, 1808, 1667, 1599, 1492, 1453, 1400, 1336, 1219, 1158, 1088, 1042, 976, 926, 885, 847, 814, 779, 757, 694, 663, 617, 589, 548; HRMS (DART) Calcd for C₂₆H₂₆NO₂S (M+H)⁺ 416.1679, found 416.1676.

**N-benzyl-4-methyl-N-(3-methylene-1,5-diphenylpent-4-yn-2-yl)benzenesulfonamide (1q)**

Pale white solid, m.p. = 102 - 103 °C, purified by chromatography (PE/EA = 6/1, Rf = 0.5); ¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.61 (m, 2H), 7.39 (dd, J = 7.3, 2.2 Hz, 2H), 7.29 (s, 5H), 7.25 – 7.13 (m, 6H), 7.13 – 7.08 (m, 4H), 5.46 (d, J = 1.2 Hz, 1H), 5.19 (s, 1H), 4.85 (dd, J = 10.1, 4.9 Hz, 1H), 4.79 (d, J = 16.1 Hz, 1H), 4.63 (d, J = 16.1 Hz, 1H), 2.98 (qd, J = 13.7, 7.5 Hz, 2H), 2.28 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.1, 138.2, 138.1, 137.9, 131.6, 129.4, 129.3, 128.7, 128.45, 128.43, 128.41, 128.3, 127.5, 127.4, 127.2, 126.5, 122.7, 92.1, 88.4, 63.6, 48.8, 39.5, 21.5. IR (KBr, cm⁻¹): 3062, 3029, 2955, 2926, 2857, 1949, 1808, 1737, 1600, 1493, 1454, 1399, 1338, 1289, 1204, 1158, 1092, 1028, 979, 920, 888, 850, 813, 778, 756, 696, 665, 635, 594, 546; HRMS (DART) Calcd for C₂₆H₂₆NO₂S (M+H)⁺ 492.1992, found 492.1990.

**N-allyl-4-methyl-N-(3-methylene-1,5-diphenylpent-4-yn-2-yl)benzenesulfonamide (1r)**

Yellow liquid, purified by chromatography (PE/EA = 6/1, Rf = 0.5); ¹H NMR (400 MHz, CDCl₃) δ 7.49 (dd, J = 8.3, 1.6 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.19 – 7.16 (m, 3H), 7.13 (d, J = Hz, 4H), 7.09 – 7.06 (m, 1H), 7.00 (d, J = 8.0 Hz, 2H), 5.80 – 5.63 (m, 1H), 5.40 (s, 1H), 5.28 – 5.20 (m, 1H), 5.10 (dt, J = 17.1, 1.7 Hz, 1H), 4.96 (dd, J = 10.1, 1.6
N,4-dimethyl-N-(2-methylene-1,4-diphenylbut-3-yn-1-yl)benzenesulfonamide (1s)

Yellow liquid, purified by chromatography (PE/EA = 6/1, Rf = 0.5); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, J = 8.3 Hz, 2H), 7.35 – 7.15 (m, 12H), 5.95 (s, 1H), 5.73 (d, J = 1.2 Hz, 1H), 5.46 (d, J = 1.4 Hz, 1H), 2.78 (s, 3H), 2.36 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.1, 136.8, 136.8, 131.4, 129.5, 129.2, 128.6, 128.4, 128.2, 127.9, 127.4, 125.6, 122.7, 92.0, 88.2, 64.6, 31.2, 21.5. IR (KBr, cm\(^{-1}\)) 3061, 3029, 2856, 1910, 1811, 1736, 1653, 1599, 1508, 1494, 1451, 1401, 1338, 1261, 1211, 1162, 1087, 1019, 970, 949, 918, 843, 814, 741, 701, 674, 657, 608, 588, 573, 547; HRMS (DART) Calcd for \(C_{26}H_{23}NO_2S\) (M+H\(^+\)) 442.1835, found 442.1834.

N,4-dimethyl-N-(2-methylene-1-phenyl-4-(p-toly)but-3-yn-1-yl)benzenesulfonamide (1t)

Yellow liquid, purified by chromatography (PE/EA = 6/1, Rf = 0.5); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, J = 8.1 Hz, 2H), 7.32 – 7.26 (m, 5H), 7.21 (d, J = 7.9 Hz, 2H), 7.05 (q, J = 8.0 Hz, 4H), 5.94 (s, 1H), 5.70 (s, 1H), 5.43 (s, 1H), 2.78 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.1, 136.8, 136.8, 131.4, 129.5, 129.2, 128.6, 128.4, 128.2, 127.9, 127.4, 125.6, 122.7, 92.0, 88.2, 64.6, 31.2, 21.5. IR (KBr, cm\(^{-1}\)) 3061, 3029, 2856, 1910, 1811, 1736, 1653, 1599, 1508, 1494, 1451, 1401, 1338, 1261, 1211, 1162, 1087, 1019, 970, 949, 918, 843, 814, 741, 701, 674, 657, 608, 588, 573, 547; HRMS (DART) Calcd for \(C_{26}H_{23}NO_2S\) (M+H\(^+\)) 416.1679, found 416.1677.

N-(4-(4-methoxyphenyl)-2-methylene-1-phenylbut-3-yn-1-yl)-N,4-dimethylbenzenesulfonamide (1u)

Yellow liquid, purified by chromatography (PE/EA = 6/1, Rf = 0.4); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.76 (d, J = 8.3 Hz, 2H), 7.36 – 7.29 (m, 5H), 7.25 (d, J = 8.0 Hz, 2H), 7.19 – 7.11 (m, 2H), 6.80 (d, J = 8.8 Hz, 2H), 5.97 (s, 1H), 5.72 (t, J = 1.2 Hz, 1H), 5.44 (t, J = 1.4 Hz, 1H), 3.80 (s, 3H), 2.81 (s, 3H), 2.40 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 159.8, 143.1, 136.9, 136.5, 132.9, 129.4, 129.3, 128.6, 128.4, 127.8, 127.4, 124.8, 114.8, 113.9, 92.1, 87.0, 84.5, 55.3, 31.2, 21.5. IR (KBr, cm\(^{-1}\)) 3031, 2956, 2925, 2851, 1917, 1665, 1599, 1571, 1509, 1454, 1400, 1336, 1305, 1288, 1249, 1162, 1108, 1087, 1029, 970, 949, 919, 832, 812, 738, 701, 674, 658, 608, 575; HRMS (DART) Calcd for \(C_{26}H_{23}NO_2S\) (M+H\(^+\)) 432.1628, found 432.1626.

N-(4-(4-fluorophenyl)-2-methylene-1-phenylbut-3-yn-1-yl)-N,4-dimethylbenzenesulfonamide (1v)

Yellow liquid, purified by chromatography (PE/EA = 6/1, Rf = 0.4); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.64 (d, J = 8.2 Hz, 2H), 7.25 – 7.12 (m, 7H), 7.12 – 7.06 (m, 2H), 6.85 (t, J = 8.7 Hz, 2H), 5.87 (s, 1H), 5.65 (d, J = 1.2 Hz, 1H), 5.38 (t, J = 1.3 Hz, 1H), 2.68 (s, 3H), 2.29 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.6 (d, J\(_{C-F}\) = 250.1 Hz), 143.2, 136.8

59
(d, $J_{CF} = 15.3$ Hz), 133.3 (d, $J_{CF} = 8.4$ Hz), 129.5, 129.1, 128.6, 128.4, 127.9, 127.4, 125.5, 118.8 (d, $J_{CF} = 3.5$ Hz), 115.5 (d, $J = 22.2$ Hz), 90.88, 87.86, 64.59, 31.10, 21.48. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -110.45. IR (KBr, cm$^{-1}$) 3063, 3031, 2955, 2925, 2854, 1736, 1671, 1597, 1505, 1452, 1400, 1338, 1228, 1161, 1088, 1017, 969, 950, 919, 837, 812, 739, 701, 676, 658, 607, 588, 573; HRMS (DART) Calcd for C$_{25}$H$_{23}$NFO$_2$S (M+H)$^+$ 420.1428, found 420.1426.

4-methoxy-N-methyl-N-(2-methylene-1,4-diphenylbut-3-yn-1-yl)benzenesulfonamide (1w)

Yellow liquid, purified by chromatography (PE/EA = 6/1, $R_f$ = 0.3); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 8.8$ Hz, 2H), 7.37 – 7.20 (m, 12H), 6.92 (d, $J = 8.8$ Hz, 2H), 5.98 (s, 1H), 5.77 (s, 1H), 5.50 (s, 1H), 3.83 (s, 3H), 2.81 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.7, 136.9, 131.5, 131.4, 129.5, 129.2, 128.5, 128.4, 128.2, 127.8, 125.6, 122.7, 114.0, 92.0, 88.2, 64.6, 55.5, 31.1. IR (KBr, cm$^{-1}$) 3062, 3030, 2930, 2842, 2566, 2054, 1957, 1899, 1723, 1672, 1596, 1579, 1495, 1413, 1338, 1304, 1259, 1159, 1112, 1090, 1026, 951, 919, 835, 819, 757, 693, 669, 629, 614, 589, 558; HRMS (DART) Calcd for C$_{25}$H$_{24}$NO$_3$S (M+H)$^+$ 418.1471, found 418.1471.
1.3 Optimization of the reaction conditions

Table S1. Optimization of the reaction conditions of 2[a]

<table>
<thead>
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<th>Entry</th>
<th>Cat.</th>
<th>Solvent</th>
<th>T (ºC)</th>
<th>2a[b]</th>
<th>2a[c]</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PPh₃AuCl/AgBF₄</td>
<td>DCE</td>
<td>25</td>
<td>17</td>
<td>4</td>
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<tr>
<td>2</td>
<td>PtCl₂</td>
<td>DCE</td>
<td>60</td>
<td>30</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>PdCl₂(CH₃CN)₂</td>
<td>DCE</td>
<td>80</td>
<td>-</td>
<td>-</td>
<td>degradation</td>
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<tr>
<td>4[d]</td>
<td>In(OTf)₃</td>
<td>DCE</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>n.r.</td>
</tr>
<tr>
<td>5</td>
<td>tBuPhosAuCl/AgBF₄</td>
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<td>trace</td>
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<td>85% SM</td>
</tr>
<tr>
<td>6</td>
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<td>25</td>
<td>56</td>
<td>13</td>
<td>-</td>
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<tr>
<td>7</td>
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<td>9</td>
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<td>11</td>
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<tr>
<td>14</td>
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<td>DCE</td>
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<td>73</td>
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<td>DCE</td>
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<td>63</td>
<td>11</td>
<td>MeOH 2eq</td>
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<td>45</td>
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<td>-</td>
<td>-</td>
<td>Toluene 2 eq</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>n.r.</td>
</tr>
<tr>
<td>22</td>
<td>AgNTf₂</td>
<td>DCE</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>n.r.</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.1 mmol), 1 mL Solvent, N₂ atmosphere, 12 h, full conversion unless the yield of recovered starting material was noted. [b] Isolated yield. [c] The yield of 2a' was determined by ¹H NMR spectrum of the crude product. [d] 10 mol%.
Table S2. Optimization of the reaction conditions of 3[a]

<table>
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<tr>
<th>Entry</th>
<th>Oxidation (eq)</th>
<th>Additive</th>
<th>T (°C)</th>
<th>3a[b]</th>
<th>note</th>
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</thead>
<tbody>
<tr>
<td>1[c]</td>
<td>DDQ (2.0)</td>
<td>MeOH 20 μL</td>
<td>25</td>
<td>20</td>
<td>75% SM</td>
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<tr>
<td>2[c]</td>
<td>SeO₂ (2.0)</td>
<td>MeOH 20 μL</td>
<td>25</td>
<td>-</td>
<td>degradation</td>
</tr>
<tr>
<td>3[c]</td>
<td>TCQ (2.0)</td>
<td>MeOH 20 μL</td>
<td>25</td>
<td>-</td>
<td>90% SM</td>
</tr>
<tr>
<td>4</td>
<td>DDQ (2.2)</td>
<td>HOAc 40 μL</td>
<td>40</td>
<td>28</td>
<td>20% 3a’</td>
</tr>
<tr>
<td>5</td>
<td>DDQ (2.2)</td>
<td>MeOH 20 μL/ AcOH 40 μL</td>
<td>40</td>
<td>66</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>DDQ (3.0)</td>
<td>MeOH 20 μL/ AcOH 40 μL</td>
<td>40</td>
<td>46</td>
<td>-</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.1 mmol), 1 mL Solvent, N₂ atmosphere, 4 h, full conversion unless the yield of recovered starting material was noted. [b] Isolated yield. [c] 5 mol% catalyst.

Table S3. Attempts to trap the azafulvenium intermediate[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>NuH (2.0 eq)</th>
<th>3′[b]</th>
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<tbody>
<tr>
<td>1</td>
<td>1,3,5-trimethoxybenzene</td>
<td>n.d.</td>
</tr>
<tr>
<td>2</td>
<td>Anisole</td>
<td>n.d.</td>
</tr>
<tr>
<td>3</td>
<td>Dimethyline</td>
<td>n.d.</td>
</tr>
<tr>
<td>4</td>
<td>Dimethyl malonate</td>
<td>n.d.</td>
</tr>
<tr>
<td>5</td>
<td>Saccharin</td>
<td>n.d.</td>
</tr>
<tr>
<td>6</td>
<td>AcOH</td>
<td>34%</td>
</tr>
<tr>
<td>7</td>
<td>=TMS</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.1 mmol), 1 mL Solvent, N₂ atmosphere, 12 h [b] Isolated yield.

1.4 General procedure for the synthesis of 2a – 2w

In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added IPrAuCl (5 mol%) and AgNTf₂ (5 mol %) in dry dichloroethane (DCE, 1 mL). After stirred for 5 min, the substrate 1 was added. The mixture was stirred at 40 °C until the starting material was completely consumed (monitored by TLC). Then the solvent was evaporated by rotary evaporator, and the residue was
purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product 2.

7-methyl-5-phenyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (2a)

74%, 52 mg, pale white solid, m.p. = 184 - 185 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.3); 1H NMR (400 MHz, CDCl3) δ 7.53 (d, J = 8.1 Hz, 2H), 7.46 – 7.29 (m, 5H), 7.15 (d, J = 8.0 Hz, 2H), 3.71 (t, J = 7.1 Hz, 2H), 2.79 (t, J = 7.2 Hz, 2H). 2.42 (q, J = 7.2 Hz, 2H), 2.36 (s, 3H), 2.24 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 142.4, 141.9, 134.6, 131.4, 131.0, 130.6, 129.1, 128.4, 127.7, 126.5, 121.5, 110.1, 45.9, 26.8, 23.2, 21.4, 11.0; IR (KBr, cm⁻¹) 3058, 2959, 2923, 2859, 1541, 1447, 1401, 1339, 1310, 1229, 1159, 1136, 1088, 1060, 1019, 921, 854, 736, 700, 655, 617, 574, 540; HRMS (DART) Calcd for C21H22NO2S (M+H)⁺ 352.1366, found 352.1365.

7-methyl-5-(p-tolyl)-6-tosyl-2,3-dihydro-1H-pyrrolizine (2b)

66%, 48 mg, pale white solid, m.p. = 161-162 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.3); 1H NMR (400 MHz, CDCl3) δ 7.55 (d, J = 8.2 Hz, 2H), 7.30 – 7.18 (m, 4H), 7.16 (d, J = 8.1 Hz, 2H), 3.71 (t, J = 7.1 Hz, 2H), 2.79 (t, J = 7.3 Hz, 2H), 2.42 (m, 5H), 2.37 (s, 3H), 2.23 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 142.3, 142.0, 138.3, 134.4, 131.6, 130.4, 128.5, 128.0, 126.5, 121.3, 110.0, 45.9, 26.7, 23.1, 21.4, 11.0; IR (KBr, cm⁻¹) 3024, 2958, 2923, 2864, 2745, 2584, 1912, 1798, 1735, 1701, 1652, 1596, 1531, 1492, 1460, 1417, 1394, 1337, 1311, 1233, 1211, 1182, 1159, 1137, 1114, 1088, 1058, 1018, 946, 914, 862, 815, 723; HRMS (DART) Calcd for C22H23NO2S (M+H)⁺ 366.1522, found 366.1523.

5-(4-(tert-butyl)phenyl)-7-methyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (2c)

69%, 42 mg, white solid, m.p. = 193 - 194 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); 1H NMR (400 MHz, CDCl3) δ 7.49 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 3.70 (t, J = 7.1 Hz, 2H), 2.77 (t, J = 7.2 Hz, 2H), 2.39 (q, J = 7.2 Hz, 2H), 2.33 (s, 3H), 2.21 (s, 3H), 1.35 (s, 9H). 13C NMR (101 MHz, CDCl3) δ 151.3, 142.2, 141.8, 134.3, 131.6, 130.2, 129.0, 127.8, 126.6, 124.6, 121.3, 110.2, 46.0, 34.7, 31.4, 26.8, 23.1, 21.4, 11.0; IR (KBr, cm⁻¹) 3061, 2959, 2925, 2865, 2746, 1913, 1731, 1648, 1597, 1558, 1530, 1460, 1417, 1396, 1363, 1338, 1311, 1268, 1234, 1200, 1181, 1160, 1137, 1114, 1087, 1058, 1017, 968, 915, 863, 731, 664; HRMS (DART) Calcd for C22H23NO2S (M+H)⁺ 408.1992, found 408.1991.

5-(4-methoxyphenyl)-7-methyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (2d)

75%, 43 mg, yellow solid, m.p. = 131-132 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.2); 1H NMR (400 MHz, CDCl3) δ 7.53 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H), 3.71 (t, J = 7.1 Hz, 2H), 2.78 (t, J = 7.3 Hz, 2H), 2.41 (q, J = 7.4 Hz, 2H), 2.36 (s, 3H), 2.23 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 159.7, 142.3, 142.0, 134.2, 131.8, 131.4, 129.1, 126.5, 123.2, 121.3, 113.2, 110.0, 55.3, 45.8, 26.7, 23.1, 21.4, 11.0; IR (KBr, cm⁻¹) 3098, 2924, 2854, 1746, 2538, 1718, 1653, 1611, 1574, 1530, 1462, 1441, 1422, 1398, 1338, 1289, 1249, 1177, 1059, 1027, 966, 914, 861, 733, 704, 665, 592; HRMS (DART) Calcd for C22H23NO2S (M+H)⁺ 382.1471, found 382.1470.
5-(4-fluorophenyl)-7-methyl-6-tosyl-2,3-dihydro-1H-pyrrlizine (2e)

70%, 38mg, white solid, m.p. = 169 - 170 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); 1H NMR δ 7.52 (d, J = 8.3 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.16 (d, J = 8.1 Hz, 2H), 7.14 – 7.07 (m, 2H), 3.70 (t, J = 7.1 Hz, 2H), 2.80 (t, J = 7.3 Hz, 2H), 2.43 (q, J = 7.3 Hz, 2H), 2.37 (s, 3H), 2.23 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 162.8 (d, JCF = 248.1 Hz), 142.5, 141.7, 134.7, 132.4 (d, JCF = 8.3 Hz), 130.2, 129.2, 126.9, 126.5, 121.7, 114.9 (d, JCF = 21.6 Hz), 110.2, 45.9, 26.7, 23.1, 21.5, 10.9; 19F NMR (376 MHz, CDCl3) δ -112.94. IR (KBr, cm⁻¹) 3063, 2956, 2923, 2861, 1912, 1735, 1650, 1598, 1527, 1462, 1421, 1393, 1338, 1300, 1225, 1158, 1136, 1088, 1057, 1016, 966, 914, 862, 841, 812, 725, 704, 666, 619, 573; HRMS (DART) Calcd for C21H21FNO3S (M+H)+ 370.1272, found 370.1272.

5-(4-chlorophenyl)-7-methyl-6-tosyl-2,3-dihydro-1H-pyrrlizine (2f)

68%, 39mg, yellow solid, m.p. = 190 - 191 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); 1H NMR (400 MHz, CDCl3) δ 7.54 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 3.71 (t, J = 7.1 Hz, 2H), 2.79 (t, J = 7.3 Hz, 2H), 2.42 (p, J = 7.3 Hz, 2H), 2.37 (s, 3H), 2.22 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 142.6, 141.6, 135.0, 134.6, 131.9, 123.0, 129.4, 128.3, 128.1, 126.5, 121.9, 110.4, 46.0, 26.7, 23.1, 21.5, 10.9. IR (KBr, cm⁻¹) 2955, 2855, 1920, 1773, 1736, 1718, 1685, 1651, 1597, 1561, 1541, 1458, 1416, 1385, 1339, 1309, 1233, 1159, 1136, 1088, 1055, 1014, 947, 915, 862, 834, 812, 721, 703, 666, 619, 574; HRMS (DART) Calcd for C21H21ClNO3S (M+H)+ 386.0976, found 386.0974.

5-(4-bromophenyl)-7-methyl-6-tosyl-2,3-dihydro-1H-pyrrlizine (2g)

67%, 43 mg, yellow solid, m.p. = 189 - 190 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); 1H NMR δ 7.57 – 7.51 (m, 3H), 7.43 – 7.35 (m, 1H), 7.29 – 7.22 (m, 2H), 7.20 – 7.12 (m, 2H), 3.71 (t, J = 7.1 Hz, 2H), 2.79 (t, J = 7.2 Hz, 2H), 2.48 – 2.34 (m, 3H), 2.23 (m, 3H). 13C NMR (101 MHz, CDCl3) δ 142.6, 141.6, 141.3, 135.1, 134.6, 132.2, 131.0, 130.6, 123.0, 129.8, 129.2, 129.1, 128.4, 127.8, 126.5, 125.0, 122.9, 121.9, 110.4, 110.1, 46.0, 26.7, 23.2, 21.5, 10.9. IR (KBr, cm⁻¹) 3060, 2957, 2923, 2856, 2747, 1511, 1493, 1458, 1416, 1340, 1311, 1233, 1159, 1137, 1088, 1071, 1011, 968, 916, 862, 833, 812, 736, 701, 668, 616, 574; HRMS (DART) Calcd for C21H21BrNO3S (M+H)+ 430.0471, found 430.0471.

7-methyl-5-(4-tolyl)-6-tosyl-2,3-dihydro-1H-pyrrlizine (2h)

60%, 33 mg, white solid, m.p. = 158 - 159 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); 1H NMR (400 MHz, CDCl3) δ 7.52 (d, J = 8.2 Hz, 2H), 7.30 – 7.23 (m, 1H), 7.19 (m, 1H), 7.16 – 7.09 (m, 4H), 3.69 (t, J = 7.1 Hz, 2H), 2.77 (t, J = 7.3 Hz, 2H), 2.37 (m, 8H), 2.22 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 142.3, 141.9, 137.2, 134.5, 131.6, 131.2, 130.8, 129.2, 129.0, 127.6, 126.6, 121.4, 110.1, 45.9, 26.8, 23.1, 21.4, 11.0. IR (KBr, cm⁻¹) 3062, 2960, 2925, 2865, 1734, 1597, 1529, 1460, 1417, 1363, 1338, 1311, 1234, 1160, 1137, 1087, 1058, 1017, 915, 863, 840, 813, 735, 703, 663, 617, 573; HRMS (DART) Calcd for C22H24NO4S (M+H)+ 366.1522, found 366.1522.
7-methyl-5-(naphthalen-2-yl)-6-tosyl-2,3-dihydro-1H-pyrrolizine (2j)

72%, 43 mg, white solid, m.p. = 164 - 165 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); ¹H NMR (400 MHz, CDCl₃) δ 7.84 (m, 3H), 7.78 (s, 1H), 7.49 (m, 5H), 7.08 (d, J = 8.1 Hz, 2H), 3.72 (t, J = 7.1 Hz, 2H), 2.80 (t, J = 7.3 Hz, 2H), 2.40 (p, J = 7.2 Hz, 2H), 2.31 (s, 3H), 2.25 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 142.4, 141.8, 134.8, 133.0, 132.7, 131.3, 129.8, 129.1, 128.5, 128.3, 128.2, 127.7, 127.2, 126.6, 126.5, 126.2, 121.9, 110.3, 46.0, 26.8, 23.2, 21.4, 11.0. IR (KBr, cm⁻¹) 3054, 2956, 2923, 2858, 2746, 1917, 1729, 1630, 1494, 1442, 1407, 1334, 1309, 1291, 1188, 1159, 1156, 1086, 1057, 1018, 950, 899, 865, 816, 747, 701, 664, 614, 573; HRMS (DART) Calcd for C₂₅H₂₃NO₂S (M+H)⁺ 402.1522, found 402.1523.

7-methyl-5-(thiophen-3-yl)-6-tosyl-2,3-dihydro-1H-pyrrolizine (2k)

75%, 40 mg, white solid, m.p. = 189 - 190 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 2.6 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.16 – 7.07 (m, 3H), 3.75 (t, J = 7.1 Hz, 2H), 2.77 (d, J = 7.2 Hz, 2H), 2.40 (p, J = 7.0 Hz, 2H), 2.33 (s, 3H), 2.23 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 142.4, 141.7, 134.7, 130.4, 129.5, 129.1, 126.4, 126.3, 126.1, 124.5, 121.4, 110.6, 46.2, 26.7, 23.1, 21.4, 11.1. IR (KBr, cm⁻¹) 3104, 2955, 2923, 1719, 1595, 1555, 1492, 1416, 1335, 1300, 1232, 1181, 1156, 1136, 1087, 1061, 1019, 922, 870, 837, 809, 735, 698, 622, 622, 575; HRMS (DART) Calcd for C₁₉H₁₈NO₂S (M+H)⁺ 358.0930, found 358.0930.

5-cyclopropyl-7-methyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (2l)

78%, 37 mg, white solid, m.p. = 135 - 136 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 3.86 (t, J = 7.0 Hz, 2H), 2.64 (t, J = 7.3 Hz, 2H), 2.39 (d, J = 6.6 Hz, 5H), 2.12 (m, 4H), 0.94 (q, J = 5.5, 4.9 Hz, 2H), 0.70 (q, J = 5.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 142.4, 142.2, 133.3, 132.2, 129.2, 126.4, 121.4, 109.6, 46.3, 27.2, 22.5, 21.5, 10.8, 7.2, 6.6. IR (KBr, cm⁻¹) 2929, 2854, 2662, 1613, 1598, 1448, 1349, 1192, 1159, 1094, 1063, 1008, 903, 846, 815, 707, 588, 547; HRMS (DART) Calcd for C₁₉H₂₁NO₂S (M+H)⁺ 351.1636, found 351.1634.

5-hexyl-7-methyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (2m)

48%, 34 mg, white solid, m.p. = 121 - 122 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 7.9 Hz, 2H), 3.83 (t, J = 7.0 Hz, 2H), 2.93 – 2.85 (m, 2H), 2.70 (t, J = 7.2 Hz, 2H), 2.42 (d, J = 15.2 Hz, 5H), 2.08 (s, 3H), 1.55 (q, J = 7.7 Hz, 2H), 1.41 – 1.21 (m, 6H), 0.90 (t, J = 5.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 142.4, 142.2, 133.3, 132.2, 129.3, 126.4, 118.8, 109.0, 45.0, 31.6, 30.2, 29.4, 26.9, 26.0, 22.8, 22.6, 21.5, 14.1, 10.7. IR (KBr, cm⁻¹) 2955, 2927, 2853, 2216, 1915, 1705, 1598, 1493, 1439, 1381, 1345, 1299, 1184, 1159, 1133, 1084, 1015, 916, 813, 767, 670, 576; HRMS (DART) Calcd for C₂₁H₂₆NO₂S (M+H)⁺ 360.1992, found 360.1992.

1-methyl-3-phenyl-2-tosyl-5,6,7,8-tetrahydroindolizine (2n)

42%, 23 mg, white solid, m.p. = 180 - 181 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 6.6 Hz, 3H), 7.27 – 7.23 (m, 2H), 7.15 (d, J = 8.1 Hz, 2H), 3.48 (s, 2H), 2.67 (s, 2H), 2.37 (s, 3H), 2.22 (s, 3H), 1.85 – 1.76 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 142.4, 141.8, 134.6,
7-ethyl-5-phenyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (2o)

45%, 25 mg, white solid, m.p. = 160 - 161 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); 1H NMR (400 MHz, CDCl3) δ 7.47 (d, J = 8.2 Hz, 2H), 7.39 - 7.30 (m, 5H), 7.30 (d, J = 8.1 Hz, 2H), 3.67 (t, J = 7.1 Hz, 2H), 2.84 (t, J = 7.3 Hz, 2H), 2.75 (q, J = 7.5 Hz, 2H), 2.39 (p, J = 7.1 Hz, 2H), 2.33 (s, 3H), 1.18 (t, J = 7.5 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 142.2, 142.0, 133.9, 131.3, 131.1, 130.7, 129.0, 128.4, 127.7, 126.6, 121.0, 116.9, 45.6, 26.8, 23.9, 21.4, 18.8, 15.1. IR (KBr, cm⁻¹) 3061, 2963, 2926, 2870, 2071, 1913, 1674, 1597, 1515, 1492, 1448, 1404, 1351, 1300, 1259, 1230, 1160, 1138, 1091, 1023, 967, 920, 863, 811, 759, 736, 707, 665, 615, 575; HRMS (DART) Calcd for C27H23NO3S (M+H)+ 366.1522, found 366.1521.

2-benzyl-1,3-dimethyl-5-phenyl-4-tosyl-1H-pyrrole (2p)

53%, 33 mg, pale white solid, m.p. = 147 - 148 °C, purified by chromatography (PE/EA = 6/1, Rf = 0.5); 1H NMR (400 MHz, CDCl3) δ 7.42 - 7.34 (m, 3H), 7.31 - 7.24 (m, 2H), 7.23 - 7.17 (m, 2H), 7.14 (d, J = 8.1 Hz, 1H), 3.95 (s, 2H), 3.03 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 142.4, 141.7, 138.3, 136.7, 131.3, 130.7, 129.1, 128.8, 128.6, 127.9, 127.8, 126.6, 126.5, 119.2, 116.4, 31.8, 30.2, 21.5, 10.5. IR (KBr, cm⁻¹) 3060, 3028, 2925, 1915, 1805, 1736, 1653, 1599, 1520, 1493, 1461, 1386, 1311, 1233, 1181, 1144, 1096, 1074, 1018, 970, 923, 838, 813, 762, 733, 703, 661, 614, 589, 563; HRMS (DART) Calcd for C28H25NO3S (M+H)+ 416.1679, found 419.1679.

1,2-dibenzyl-3-methyl-5-phenyl-4-tosyl-1H-pyrrole (2q)

49%, 36 mg, pale white solid, m.p. = 167 - 168 °C, purified by chromatography (PE/EA = 6/1, Rf = 0.5); 1H NMR (400 MHz, CDCl3) δ 7.52 (d, J = 8.2 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.28 - 7.10 (m, 12H), 6.96 (d, J = 7.2 Hz, 2H), 6.71 - 6.66 (m, 2H), 4.60 (s, 2H), 3.74 (s, 2H), 2.38 (s, 3H), 2.36 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 142.5, 141.6, 138.5, 137.4, 137.3, 131.3, 130.3, 129.1, 128.8, 128.7, 128.6, 127.8, 127.7, 127.3, 126.7, 126.5, 125.5, 119.9, 117.2, 47.9, 30.0, 21.5, 10.6. IR (KBr, cm⁻¹) 3061, 3028, 2926, 1925, 1807, 1736, 1600, 1521, 1494, 1454, 1396, 1356, 1312, 1181, 1157, 1135, 1090, 1060, 1028, 973, 919, 849, 812, 763, 735, 699, 667, 606, 588, 566, 540; HRMS (DART) Calcd for C32H29NO3S (M+H)+ 492.1992, found 492.1990.

1-allyl-2-benzyl-3-methyl-5-phenyl-4-tosyl-1H-pyrrole (2r)

49%, 36 mg, pale white solid, m.p. = 167 - 168 °C, purified by chromatography (PE/EA = 6/1, Rf = 0.5); 1H NMR (400 MHz, CDCl3) δ 7.52 (d, J = 8.2 Hz, 2H), 7.42 (m, 1H), 7.36 (t, J = 7.4 Hz, 2H), 7.31 (m, 2H), 7.27 - 7.15 (m, 5H), 7.06 (d, J = 7.3 Hz, 2H), 5.67 - 5.47 (m, 1H), 5.70 - 5.49 (m, 1H), 5.04 (d, J = 10.4 Hz, 1H), 4.66 (d, J = 17.1 Hz, 1H), 4.05 - 3.97 (m, 2H of of CH2-CH=), 3.94 (s, 2H), 2.39 (s, 3H), 2.36 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 142.5, 141.7, 138.6, 136.8, 133.6, 131.3, 130.5, 129.1, 128.9, 128.7, 128.3, 127.8, 127.6, 126.7, 126.5, 119.6, 116.8, 116.4, 46.7, 29.9, 21.5, 10.5. IR (KBr, cm⁻¹) 3061, 3027, 2925, 2854, 1719,
The structure of the product 2r about the migration group was determined with the reference of ref S2. Org. Chem. 2013, 78, 7588-7587.

The chemical shift of the methylene in the allyl of product 2 is consistent with the product 2b from ref S2, which was very similar to 2r.
2-(4-fluorophenyl)-1,4-dimethyl-5-phenyl-3-tosyl-IH-pyrrrole (2v)

64%, 40 mg, pale white solid, m. p. = 147 – 148 °C, purified by chromatography (PE/EA = 6/1, Rf = 0.4). 1H NMR (400 MHz, CDCl3) δ 7.52 (d, J = 8.1 Hz, 2H), 7.46 – 7.36 (m, 3H), 7.32 – 7.24 (m, 4H), 7.17 (d, J = 8.1 Hz, 2H), 7.12 (t, J = 8.6 Hz, 2H), 3.10 (s, 3H), 2.37 (s, 3H), 2.21 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 163.1 (d, Jc-/s= 249.0 Hz), 142.7, 141.4, 135.6, 133.2 (d, Jc-/F = 8.3 Hz), 132.5, 131.1, 130.9, 129.2, 128.5, 128.2, 126.8, 120.3, 116.8, 115.1 (d, Jc-/C = 21.7 Hz), 33.1, 21.5, 10.9. 19F NMR (376 MHz, CDCl3) δ -110.45. IR (KBr, cm⁻¹) 3060, 2955, 2925, 2855, 1895, 1733, 1653, 1599, 1530, 1493, 1464, 1381, 1312, 1228, 1181, 1147, 1099, 1079, 1015, 968, 921, 864, 838, 812, 768, 732, 705, 664, 641, 622, 590, 574; HRMS (DART) Calcd for C25H23NFO2S (M+H)⁺ 420.1428, found 420.1426.

3-((4-methoxyphenyl)sulfonyl)-1,4-dimethyl-2,5-diphenyl-IH-pyrrrole (2w)

60%, 38 mg, pale white solid, m. p. = 155 – 156 °C, purified by chromatography (PE/EA = 6/1, Rf = 0.3); 1H NMR (400 MHz, CDCl3) δ 7.58 (d, J = 8.7 Hz, 2H), 7.49 – 7.37 (m, 6H), 7.33 (m, 4H), 6.84 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H), 3.12 (s, 3H), 2.25 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 162.4, 136.6, 136.4, 132.2, 131.3, 131.3, 130.9, 128.9, 128.4, 128.1, 128.0, 120.4, 116.6, 113.7, 55.5, 33.1, 10.9. IR (KBr, cm⁻¹) 3060, 2957, 2926, 2844, 1899, 1729, 1695, 1595, 1495, 1463, 1411, 1381, 1311, 1297, 1258, 1179, 1144, 1102, 1074, 1022, 922, 853, 833, 802, 759, 736, 702, 671, 593, 562; HRMS (ESI) Calcd for C23H22NO2S (M+H)+ 418.1471, found 418.1482.

1.4 General procedure for the synthesis of 2a'', 2p'' and 2s''.

Taking 2a'' as an example: in a Schlenk tube with a magnetic bar under nitrogen atmosphere was added IPrAuCl (5 mol%), AgNTf₂ (5 mol%) in dry dichloroethane (DCE, 2 mL). After stirred for 5 min, the substrate 1a (or 1p, 1s) (0.2 mmol) was added. The mixture was stirred at 40 °C until the starting materia was completely consumed (monitored by TLC). Then the solvent was evaporated by rotary evaporator to get the crude products.

Under N₂ atmosphere, PBr₃ (0.2 mmol, 1 eq) in hexane was added dropwise into the solution of DMF (2 mmol, 1 eq) in anhydrous CHCl₃ (2 mL) at 0 °C. The reaction mixture was stirred for 1 h before the addition of the solution of crude product in CHCl₃ obtained in the previous step. The reaction temperature was raised to room temperature and maintained for 2 h. After the reaction completed, the reaction mixture was poured into ice saturated NaHCO₃ (aq.) with violent stirring. The mixture was extracted with DCM, and the organic phase was washed with brine and dried with anhydrous Na₂SO₄. Then the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography (SiO₂; PE: EA = 5: 1) to obtain 2a'' as a white solid (8 mg, 11%).
5-phenyl-7-(tosylmethyl)-2,3-dihydro-1H-pyrrolizine-6-carbaldehyde (2a")

11%, 8 mg, white solid, m.p. = 145 - 146 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.2); 1H NMR (400 MHz, CDCl3) δ 9.34 (s, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.51 – 7.38 (m, 3H), 7.33 – 7.28 (m, 2H), 7.24 (d, J = 8.2 Hz, 2H), 4.77 (s, 2H), 3.96 (t, J = 7.1 Hz, 2H), 3.03 (t, J = 7.4 Hz, 2H), 2.61 – 2.48 (m, 2H), 2.40 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 186.6 144.2, 140.9, 138.8, 136.2, 129.7, 129.4, 129.2, 128.8, 128.7, 123.9, 101.4, 53.19, 46.1, 27.2, 23.5, 21.6. IR (KBr, cm⁻¹) 3062, 3028, 2955, 2923, 2851, 2736, 1796, 1796, 1735, 1652, 1601, 1541, 1525, 1488, 1459, 1388, 1361, 1314, 1136, 1085, 1025, 973, 912, 834, 814, 741, 700, 647, 621, 547; HRMS (DART) Calcd for C25H22NO3 (M+H)+ 380.1315, found 380.1316.

5-benzyl-1-methyl-2-phenyl-4-(tosylmethyl)-1H-pyrrole-3-carbaldehyde (2p")

15%, 13 mg, white solid, m.p. = 117 - 118 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.2); 1H NMR (400 MHz, CDCl3) δ 9.29 (s, 1H), 7.78 (d, J = 8.1 Hz, 2H), 7.5 – 7.45 (m, 3H), 7.36 – 7.27 (m, 6H), 7.25 (t, J = 7.3 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 4.87 (s, 2H), 4.32 (s, 2H), 3.27 (s, 3H), 2.44 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 186.6, 144.6, 144.3, 137.6, 136.4, 134.8, 131.0, 129.2, 128.9, 128.8, 128.5, 127.9, 126.7, 120.8, 107.8, 52.6, 32.1, 30.2, 21.6. IR (KBr, cm⁻¹) 3071, 3021, 2966, 2923, 2766, 1793, 1765, 1632, 1600, 1541, 1489, 1461, 1366, 1361, 1315, 1211, 1037, 1025, 973, 834, 814, 742, 701, 647, 624, 544; HRMS (DART) Calcd for C22H20NO3 (M+H)+ 444.1628, found 444.1626.

1-methyl-2,5-diphenyl-4-(tosylmethyl)-1H-pyrrole-3-carbaldehyde (2s")

10%, 8 mg, white solid, m.p. = 107 - 108 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.2); 1H NMR (400 MHz, CDCl3) δ 9.38 (s, 1H), 7.70 (d, J = 8.1 Hz, 2H), 7.54 – 7.44 (m, 8H), 7.43 – 7.40 (m, 2H), 7.25 – 7.22 (m, 2H), 4.68 (s, 2H), 3.30 (s, 3H), 2.41 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 186.5, 144.4, 144.0, 137. 9, 136.9, 131.0, 130.98, 129.6, 129.3, 129.2, 129.0, 128.9, 128.8, 128.6, 128.6, 121.2, 107.7, 53.3, 33.3, 21.6. IR (KBr, cm⁻¹) 3061, 2955, 2924, 2852, 1659, 1526, 1484, 1456, 1382, 1315, 1178, 1145, 1084, 969, 934, 800, 763, 702, 658, 593, 555, 511; HRMS (DART) Calcd for C30H28NO3S (M+H)+ 430.1471, found 430.1472.

1.5 General procedure for the Synthesis of 3

In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added IPrAuCl (10 mol%), AgNTf2 (10 mol%), MeOH (30 µL) and AcOH (60 µL) in dry dichloroethane (DCE, 1.5 mL). After stirred for 5 min, the substrate 1 (0.15 mmol), 2, 3-dicyano-5, 6-dichlorobenzoquinone (DDQ, 0.33 mmol) were added respectively. The mixture was stirred at 40 °C until the starting materials was completely consumed monitored by TLC. After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product.
5-phenyl-6-tosyl-2, 3-dihydro-1H-pyrrolizine-7-carbaldehyde (3a)

66%, 36 mg, yellow solid, m. p. = 173 – 174 °C, purified by chromatography (PE/EA = 3/1, Rf = 0.3); 1H NMR (400 MHz, CDCl3) δ 10.46 (s, 1H), 7.43 (m, 5H), 7.31 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 3.73 (t, J = 7.3 Hz, 2H), 3.17 (t, J = 7.4 Hz, 2H), 2.54 – 2.43 (m, 2H), 2.34 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 187.5, 144.6, 143.3, 140.7, 132.9, 130.5, 129.4, 128.4, 128.1, 126.8, 124.2, 115.5, 46.3, 26.3, 26.1, 21.5. IR (KBr, cm⁻¹) 3061, 2922, 2852, 1893, 1719, 1657, 1599, 1543, 1491, 1465, 1428, 1398, 1363, 1302, 1181, 1141, 1085, 1057, 1024, 968, 923, 887, 848, 812, 783, 763, 735, 700, 666, 575; HRMS (DART) Calcd for C25H20NO6S (M+H)⁺ 366.1158, found 366.1157.

5-(p-tolyl)-6-tosyl-2, 3-dihydro-1H-pyrrolizine-7-carbaldehyde (3b)

73%, 41 mg, pale white solid, m. p. = 180 – 181 °C, purified by chromatography (PE/EA = 3/1, Rf = 0.3); 1H NMR (400 MHz, CDCl3) δ 10.46 (s, 1H), 7.49 (d, J = 8.1 Hz, 2H), 7.24 (m, 4H), 7.16 (d, J = 8.1 Hz, 2H), 3.74 (t, J = 7.3 Hz, 2H), 3.18 (t, J = 7.5 Hz, 2H), 2.50 (m, 2H), 2.45 (s, 3H), 2.37 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 187.4, 144.6, 143.3, 140.8, 139.5, 133.2, 130.4, 129.4, 128.8, 126.8, 125.9, 124.0, 115.4, 46.2, 26.3, 26.1, 21.5; IR (KBr, cm⁻¹) 3028, 2957, 2923, 1918, 1662, 1597, 1490, 1429, 1404, 1363, 1307, 1235, 1210, 1182, 1142, 1085, 1052, 1018, 968, 922, 887, 817, 737, 703, 666, 604, 577, 541; HRMS (DART) Calcd for C25H20NO6S (M+H)⁺ 380.1315, found 380.1313.

5-(4-(tert-butyl)phenyl)-6-tosyl-2,3-dihydro-1H-pyrrolizine-7-carbaldehyde (3c)

57%, 36 mg, white solid, m.p. = 195 - 196 °C, purified by chromatography (PE/EA = 3/1, Rf = 0.4); 1H NMR (400 MHz, CDCl3) δ 10.48 (s, 1H), 7.43 (dd, J = 8.0, 5.2 Hz, 4H), 7.23 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 3.76 (t, J = 7.3 Hz, 2H), 3.18 (t, J = 7.5 Hz, 2H), 2.58 – 2.42 (m, 2H), 2.35 (s, 3H), 1.39 (s, 9H). 13C NMR (101 MHz, CDCl3) δ 187.6, 152.6, 144.5, 143.2, 140.5, 133.1, 130.2, 129.3, 126.9, 125.8, 125.0, 124.0, 115.5, 46.3, 34.8, 31.3, 26.3, 26.2, 21.5; IR (KBr, cm⁻¹) 3061, 2961, 2871, 1662, 1597, 1543, 1488, 1429, 1399, 1364, 1305, 1236, 1204, 1180, 1143, 1115, 1084, 1053, 1017, 922, 887, 841, 812, 735, 702, 666, 601, 577; HRMS (ESI) Calcd for C25H20NO6S (M+H)⁺ 422.1784, found 422.1796.

5-(4-methoxyphenyl)-6-tosyl-2, 3-dihydro-1H-pyrrolizine-7-carbaldehyde (3d)

75%, 43 mg, white solid, m. p. = 129 -130 °C, purified by chromatography (PE/EA = 3/1, Rf = 0.2); 1H NMR (400 MHz, CDCl3) δ 10.45 (s, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 3.87 (s, 3H), 3.72 (t, J = 7.3 Hz, 2H), 3.16 (t, J = 7.5 Hz, 2H), 2.48 (m, 2H), 2.34 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 187.5, 160.5, 144.5, 143.3, 140.8, 133.0, 131.9, 129.4, 126.8, 123.9, 120.9, 115.4, 113.6, 55.3, 46.2, 26.3, 26.1, 21.4; IR (KBr, cm⁻¹) 3033, 2960, 2931, 1900, 1667, 1596, 1493, 1422, 1400 1361, 1307, 1232, 1211, 1180, 1142, 1085, 1042, 1010, 968, 922, 888, 813, 737, 700, 666, 604, 577, 541; HRMS (ESI) Calcd for C25H23NO6S (M+H)⁺ 396.1264, found 396.1277.

5-(4-bromophenyl)-6-tosyl-2,3-dihydro-1H-pyrrolizine-7-carbaldehyde (3e)

61%, 41 mg, yellow solid, m. p. = 190 - 191 °C, purified by chromatography (PE/EA = 3/1, Rf = 0.3); 1H NMR δ 10.43 (s, 1H), 7.57 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.19 (m, 4H), 3.74 (t, J = 7.3 Hz, 2H), 3.16 (t, J = 7.5 Hz,
5-(4-fluorophenyl)-6-tosyl-2, 3-dihydro-1H-pyrrolizine-7-carbaldehyde (3f)

\[
\begin{align*}
\text{HNMR} & \quad \delta 10.47 (s, 1H), 7.46 (d, J = 8.1 \text{ Hz}, 2H), 7.32 (dd, J = 8.2, 5.5 \text{ Hz}, 2H), 7.15 (m, 4H), 3.74 (t, J = 7.3 \text{ Hz}, 2H), 3.19 (t, J = 7.5 \text{ Hz}, 2H), 2.57 – 2.45 (m, 2H), 2.37 (s, 3H). \quad \text{IR} (\text{KBr, cm}^{-1}) 3063, 2959, 2922, 1910, 1662, 1599, 1542, 1488, 1430, 1403, 1365, 1304, 1229, 1181, 1142, 1084, 1051, 1015, 921, 887, 842, 814, 735, 702, 667, 605, 576, 540; \quad \text{HRMS} (\text{ESI}) \quad \text{Caled for C}_{21} \text{H}_{16} \text{BrNO}_{3} \text{S} (\text{M}^+). \quad 444.0264, \text{ found 444.0275.}
\end{align*}
\]

5-(4-chlorophenyl)-6-tosyl-2, 3-dihydro-1H-pyrrolizine-7-carbaldehyde (3g)

\[
\begin{align*}
\text{HNMR} & \quad \delta 10.43 (s, 1H), 7.46 (d, J = 8.1 \text{ Hz}, 2H), 7.41 (d, J = 8.3 \text{ Hz}, 2H), 7.26 (d, J = 6.4 \text{ Hz}, 2H), 7.16 (d, J = 8.1 \text{ Hz}, 2H), 3.73 (t, J = 7.3 \text{ Hz}, 2H), 3.16 (t, J = 7.5 \text{ Hz}, 2H), 2.57 – 2.44 (m, 2H), 2.36 (s, 3H). \quad \text{IR} (\text{KBr, cm}^{-1}) 3060, 2959, 2922, 1914, 1663, 1597, 1544, 1485, 1465, 1430, 1399, 1365, 1307, 1232, 1181, 1142, 1088, 1050, 1014, 968, 921, 886, 837, 814, 735, 706, 667, 600, 675, 575, 540; \quad \text{HRMS} (\text{ESI}) \quad \text{Caled for C}_{21} \text{H}_{15} \text{ClNO}_{3} \text{S} (\text{M}^+). \quad 400.0769, \text{ found 400.0779.}
\end{align*}
\]

5-(naphthalen-2-y1)-6-tosyl-2,3-dihydro-1H-pyrrolizine-7-carbaldehyde (3h)

\[
\begin{align*}
\text{HNMR} & \quad \delta 10.50 (s, 1H), 7.89 (t, J = 8.4 \text{ Hz}, 2H), 7.84 (d, J = 7.1 \text{ Hz}, 1H), 7.77 (d, J = 1.6 \text{ Hz}, 1H), 7.62 – 7.52 (m, 2H), 7.44 (d, J = 8.2 \text{ Hz}, 2H), 7.40 – 7.35 (m, 1H), 7.06 (d, J = 8.1 \text{ Hz}, 2H), 3.75 (t, J = 7.3 \text{ Hz}, 2H), 3.19 (t, J = 7.5 \text{ Hz}, 2H), 2.55 – 2.41 (m, 2H), 2.30 (s, 3H). \quad \text{IR} (\text{KBr, cm}^{-1}) 3055, 2959, 2924, 2926, 1661, 1698, 1543, 1497, 1454, 1428, 1402, 1369, 1305, 1222, 1142, 1084, 1053, 1017, 951, 922, 899, 867, 817, 754, 734, 663, 603, 574; \quad \text{HRMS} (\text{ESI}) \quad \text{Caled for C}_{25} \text{H}_{22} \text{NO}_{3} \text{S} (\text{M}^+). \quad 416.1315, \text{ found 416.1326.}
\end{align*}
\]

5-(thiophen-3-y1)-6-tosyl-2,3-dihydro-1H-pyrrolizine-7-carbaldehyde (3i)

\[
\begin{align*}
\text{HNMR} & \quad \delta 10.48 (s, 1H), 7.44 (m, J = 8.3 \text{ Hz}, 3H), 7.38 (dd, J = 4.8, 3.0 \text{ Hz}, 1H), 7.13 (d, J = 8.1 \text{ Hz}, 2H), 7.08 (d, J = 4.9 \text{ Hz}, 1H), 3.80 (t, J = 7.3 \text{ Hz}, 2H), 3.16 (t, J = 7.5 \text{ Hz}, 2H), 2.60 – 2.42 (m, 2H), 2.34 (s, 3H). \quad \text{IR} (\text{KBr, cm}^{-1}) 3055, 2959, 2924, 2926, 1661, 1698, 1543, 1497, 1454, 1428, 1402, 1369, 1305, 1222, 1142, 1084, 1053, 1017, 951, 922, 899, 867, 817, 754, 734, 663, 603, 574; \quad \text{HRMS} (\text{ESI}) \quad \text{Caled for C}_{25} \text{H}_{22} \text{NO}_{3} \text{S} (\text{M}^+). \quad 416.1315, \text{ found 416.1326.}
\end{align*}
\]
115.7, 46.6, 26.3, 26.2, 21.5. \textbf{IR} (KBr, cm$^{-1}$) 3105, 2958, 2923, 1661, 1596, 1540, 1492, 1431, 1381, 1350, 1304, 1232, 1193, 1142, 1084, 1059, 1017, 930, 878, 808, 734, 702, 661, 606, 573; \textbf{HRMS} (ESI) Calcd for C$_{10}$H$_{18}$NO$_3$S (M+H)$^+$ 372.0723, found 372.0732.

5-hexyl-6-tosyl-2,3-dihydro-1H-pyrrolizin-7-carbaldehyde (3j)

24%, 13 mg, white solid, m.p. = 109 – 110 °C, purified by chromatography (PE/EA = 5/1, $R_f$ = 0.2); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.24 (s, 1H), 7.77 (d, $J$ = 8.1 Hz, 2H), 7.27 (d, $J$ = 5.0 Hz, 2H), 3.89 (t, $J$ = 7.3 Hz, 2H), 3.08 (t, $J$ = 7.5 Hz, 2H), 2.96 – 2.82 (m, 2H), 2.58 – 2.47 (m, 2H), 2.39 (s, 3H), 1.58 – 1.46 (m, 2H), 1.33 (m, 6H), 0.89 (t, $J$ = 6.5 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 186.7, 144.5, 143.4, 141.3, 135.2, 129.7, 126.6, 121.7, 114.8, 45.5, 31.5, 29.7, 29.3, 26.3, 25.9, 25.5, 22.5, 21.5, 14.0. \textbf{IR} (KBr, cm$^{-1}$) 3108, 2955, 2927, 2857, 2719, 1652, 1540, 1474, 1414, 1388, 1287, 1192, 1143, 975, 862, 824, 726, 636, 578, 543; \textbf{HRMS} (ESI) Calcd for C$_{19}$H$_{28}$NO$_3$S (M+H)$^+$ 374.1784, found 374.1796.

5-hexanoyl-2,3-dihydro-1H-pyrrolizin-7-carbaldehyde (3j’)

33%, 11 mg, viscous liquid, purified by chromatography (PE/EA = 5/1, $R_f$ = 0.4); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.79 (s, 1H), 7.32 (s, 1H), 4.37 (t, $J$ = 7.3 Hz, 2H), 3.11 (d, $J$ = 7.6 Hz, 2H), 2.74 (t, $J$ = 7.5 Hz, 2H), 2.67 – 2.50 (m, 2H), 1.83 – 1.65 (m, 2H), 1.48 – 1.30 (m, 4H), 0.92 (t, $J$ = 6.1 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ \textbf{IR} (KBr, cm$^{-1}$) 3108, 2955, 2927, 2857, 2719, 1652, 1540, 1474, 1414, 1388, 1287, 1192, 1143, 975, 862, 824, 726, 636, 578, 543; \textbf{HRMS} (ESI) Calcd for C$_{14}$H$_{26}$NO$_3$ (M+H)$^+$ 234.1489, found 234.1494.

(2-benzyl-1-methyl-5-phenyl-4-tosyl-1H-pyrrol-3-yl)methanol (3k’)

The crude mixture obtained from the general preparation procedure of 3k was concentrated by rotary evaporator. The residue was dissolved in 2 mL methanol at 0 °C before NaBH$_4$ (0.3 mmol, 2 eq) was added. The reaction mixture was stirred for another 30 min before quenched with saturated NH$_4$Cl solution and extracted with DCM. Then the organic phase was washed with brine and dried with anhydrous Na$_2$SO$_4$, and the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography.

48%, 31 mg, white solid, m.p. = 161 – 162 °C, purified by chromatography (PE/EA = 3/1, $R_f$ = 0.3); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 – 7.30 (m, 3H), 7.30 – 7.19 (m, 4H), 7.14 (t, $J$ = 7.3 Hz, 1H), 7.04 (t, $J$ = 8.5 Hz, 6H), 4.71 (d, $J$ = 6.9 Hz, 2H), 3.98 (s, 2H), 3.59 (t, $J$ = 7.1 Hz, 1H), 2.97 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.0, 140.8, 137.7, 137.6, 131.2, 129.9, 129.7, 129.2, 129.1, 128.8, 128.1, 128.0, 126.70, 126.67, 121.2, 119.3, 55.6, 31.9, 30.2, 21.5. \textbf{IR} (KBr, cm$^{-1}$) 3061, 3028, 2954, 2924, 1731, 1598, 1524, 1493, 1465, 1386, 1294, 1234, 1164, 1138, 1071, 981, 914, 841, 814, 761, 732, 701, 668, 590, 541; \textbf{HRMS} (ESI) Calcd for C$_{28}$H$_{32}$NO$_3$NaS (M+Na)$^+$ 454.1447, found 454.1456.
1.6 Control experiment

1.6.1 Crossover experiment

In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added IPrAuCl (5 mol%) and AgNTf$_2$ (5 mol %) in dry dichloroethane (DCE, 1 mL). After stirred for 5 min, the substrates 1t (0.12 mmol) and 2w (0.1 mmol) were added. The mixture was stirred at 40 °C until the starting material was completely consumed (monitored by TLC). Then the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute. The yield of products were calculated based on the isolated yield of 2t.

Comparison of the $^1$H NMR spectras of crude reaction mixtures (Figure S1) illustrated that there was no crossover product.

Figure S1. The $^1$H NMR spectras of crude reaction mixtures (top: the mixture of crossover experiment; middle: the reaction mixture with 1t as starting material; down: the reaction mixture with 1t as starting material.)
1.6.2 Oxidation experiment of 2a

(1): In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added 2a (0.1 mmol), methanol (20 μL) and DDQ (0.2 mmol) in dichloroethane (1 mL). The mixture was stirred at room temperature until the starting material was completely consumed (monitored by TLC, about 6 h). After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product.

(2): In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added 2a (0.1 mmol), AcOH (250 μL) and DDQ (0.25 mmol) in dichloroethane (1 mL). The mixture was stirred at room temperature until the starting materials was completely consumed (monitored by TLC, about 4 h). After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product.

(3): In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added IPrAuCl (10 mol%) and AgNTf₂ (10 mol %) in dry dichloroethane (DCE, 1 mL). After stirred for 5 min, the substrates 2a (0.1 mmol), DDQ (0.22 mmol), AcOH (40 μL) and MeOH (20 μL) were added respectively. The mixture was stirred at 40 °C until the starting materials was completely consumed. After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product.

1-methoxy-7-methyl-5-phenyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (4a)

60%, 22 mg, white solid, m.p. = 99 - 100 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.4); ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 8.2 Hz, 2H), 7.43 – 7.30 (m, 5H), 7.12 (d, J = 8.1 Hz, 2H), 4.68 (d, J = 5.0 Hz, 1H), 3.92 (ddd, J = 11.2, 9.0, 6.9 Hz, 1H), 3.59 (ddd, J = 11.0, 8.7, 1.9 Hz, 1H), 3.34 (s, 3H), 2.54 (ddd, J = 14.6, 9.7, 5.7 Hz, 1H), 2.43 (dd, J = 13.6, 6.6 Hz, 1H), 2.36 (s, 3H), 2.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 142.5, 141.5, 133.6, 132.5, 130.5, 130.4, 129.1, 128.7, 127.8, 126.6, 122.1, 75.0, 56.3, 44.2, 35.0, 21.4, 11.3. IR (KBr, cm⁻¹) 3061, 2957, 2925, 2855, 2360, 1700, 1620, 1598, 1519, 1492, 1449, 1408, 1341,
1300, 1226, 1139, 1089, 1019, 967, 923, 846, 811, 734, 702, 655, 583, 543; HRMS (DART) Caled for C$_2$H$_2$O$_2$NS (M+H)$^+$ 382.1471, found 382.1470.

**7-methyl-5-phenyl-6-tosyl-2,3-dihydro-1H-pyrrolizin-1-one (4b)**

72%, 26 mg, white solid, m.p. = 206 - 207 °C, purified by chromatography (PE/EA = 5/1, R$_f$ = 0.3); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 – 7.41 (m, 5H), 7.32 (d, $J$ = 6.8 Hz, 2H), 7.13 (d, $J$ = 8.1 Hz, 2H), 3.96 (t, $J$ = 6.5 Hz, 2H), 2.98 (t, $J$ = 6.5 Hz, 2H), 2.60 (s, 3H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 189.0, 143.4, 140.4, 137.4, 130.2, 129.7, 129.3, 128.6, 128.6, 128.3, 127.2, 126.8, 122.9, 41.1, 38.7, 21.5, 10.3. IR (KBr, cm$^{-1}$) 3061, 2977, 2946, 2890, 2370, 1720, 1670, 1577, 1494, 1421, 1330, 1226, 1130, 1083, 1014, 900, 846, 811, 734, 702, 655, 523, 533; HRMS (DART) Caled for C$_2$H$_2$O$_2$NS (M+H)$^+$ 366.1158, found 366.1158.

### 1.6.3 Transformation of 1a to 3a' and 3a

![Reaction Scheme](image)

**3a':** In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added IPrAuCl (5 mol%), and AgNTf$_2$ (5 mol%) in dry dichloroethane (DCE, 1 mL). After stirred for 5 min, the 1a and AcOH (20 μL), DDQ (1.2 eq) was added respectively. The mixture was stirred until the starting materials was completely consumed monitored by TLC. After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product.

**3a:** In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added 3a' and DDQ (1.2 eq) in dry dichloroethane (DCE, 1 mL). MeOH (20 μL) and AcOH (20 μL) was added and mixture was stirred at 40 °C until the starting materials was completely consumed monitored by TLC. After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product.

**((5-phenyl-6-tosyl-2,3-dihydro-1H-pyrrolizin-7-yl)methyl acetate (3a'))**

31%, 13 mg, white solid, m.p. = 150 - 151 °C, purified by chromatography (PE/EA = 5/1, R$_f$ = 0.2); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (d, $J$ = 8.0 Hz, 2H), 7.43 – 7.36 (m, 3H), 7.31 (d, $J$ = 6.8 Hz, 2H), 7.10 (d, $J$ = 8.0 Hz, 2H), 5.32 (s, 2H), 3.70 (t, $J$ = 7.1 Hz, 2H), 2.93 (t, $J$ = 7.3 Hz, 2H), 2.41 (dd, $J$ = 14.5, 7.2 Hz, 2H), 2.33 (s, 3H), 2.02 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.0, 142.6, 141.5, 137.8, 132.4, 130.6, 130.2, 129.0, 128.8, 127.9, 126.8, 122.1, 109.3, 58.1, 46.1, 26.5, 23.9, 21.4, 21.1. IR (KBr, cm$^{-1}$) 3062, 2956, 2853, 1734, 1646, 1598, 1520, 1488, 1460, 1401, 1382, 1364, 1307, 1232, 1161, 1061, 1020, 952, 921, 853, 808, 701, 658, 573, 541, 491; HRMS (ESI) Caled for C$_{23}$H$_{25}$O$_2$NaNS (M+Na)$^+$ 432.1248, found 432.1249.
1.6.4 Control reaction for the conversion of 3j to 3j′

![Chemical Structure Image]

In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added IPrAuCl (10 mol%), AgNTf₂ (10 mol%), MeOH (10 μL) and AcOH 20 μL in dry dichloroethane (DCE, 0.5 mL). After stirred for 5 min, the 3j (0.05mmol), 2, 3-dicyano-5, 6-dichlorobenzoquinone (DDQ, 0.33 mmol) were added respectively. The reaction was stirred at 40 °C for 12h.

1.7 Derivatization reactions of 3a

In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added DCM and MeOH (0.6 mL and 0.4 mL) and K₂CO₃ (0.15 mmol), and then the 3a (0.1 mmol) and Bestmann Reagent[1] (0.12 mmol) were added respectively. The mixture was stirred at room temperature until the starting materials was completely consumed monitored by TLC. After that, the solvent was filtered and evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 5/1) to afford the pure product.

7-ethynyl-5-phenyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (5a)

85%, 31 mg, white solid, m.p. = 214 - 215 °C, purified by chromatography (PE/EA = 5/1, Rᵥ = 0.4); 1H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 8.2 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.37 (m, 2H), 7.21 (d, J = 8.1 Hz, 2H), 3.75 (t, J = 7.1 Hz, 2H), 3.28 (s, 1H), 2.96 (t, J = 7.4 Hz, 2H), 2.52 – 2.41 (m, 2H), 2.39 (s, 3H). 13C NMR (101 MHz, CDCl₃) δ 143.3, 142.9, 141.0, 131.6, 130.4, 129.9, 129.2, 129.0, 128.0, 127.2, 124.8, 95.7, 80.8, 76.2, 46.6, 26.4, 24.3, 21.5. IR (KBr, cm⁻¹) 3225, 3060, 2957, 2922, 2853, 2108, 1666, 1596, 1554, 1521, 1487, 1463, 1387, 1315, 1233, 1158, 1137, 1084, 1020, 918, 809, 735, 702, 666, 575, 540; HRMS (ESI) Calcd for C₂₂H₂₀O₂NS (M+H)⁺ 362.1209, found 362.1216.

Under N₂ atmosphere, n-BuLi (1.1 eq, 2.5 M) in hexane was added dropwise into the suspension of CH₃PPh₃Br (1.2 eq) in anhydrous THF (1 mL) at 0 °C. After stir for 1h, 3a (0.1 mmol) dissolved in THF (0.5 mL) was added dropwise into the reaction mixture. After the reaction temperature raised to room temperature, the reaction was quenched using saturated NH₄Cl (aq), and extracted with EtOAc. The organic phase was washed with brine and dried with anhydrous Na₂SO₄, then the solvent was removed by rotary evaporator. 5e was obtained after purified by chromatography (SiO₂, EA: PE = 1: 5, Rᵥ = 0.5).
5-phenyl-6-tosyl-7-vinyl-2,3-dihydro-1H-pyrrolizine (5b)

72%, 26 mg, white solid, m.p. = 163 - 164 °C, purified by chromatography (PE/EA = 5/1, Rf = 0.5); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.49 (d, \(J = 7.8\) Hz, 2H), 7.44 – 7.27 (m, 6H), 7.12 (d, \(J = 7.7\) Hz, 2H), 5.22 (m, 2H), 3.69 (t, \(J = 7.0\) Hz, 2H), 2.97 (t, \(J = 7.1\) Hz, 2H), 2.54 – 2.39 (m, 2H), 2.33 (s, 3H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 142.5, 141.8, 134.9, 131.8, 130.6, 130.5, 129.2, 128.9, 128.7, 127.8, 126.6, 120.8, 113., 113.0, 45.7, 26.7, 25.6, 21.4. IR (KBr, cm\(^{-1}\)) 3301, 3061, 2956, 2923, 2855, 1731, 1619, 1599, 1518, 1488, 1461, 1391, 1317, 1294, 1231, 1180, 1141, 1086, 1037, 1019, 999, 920, 893, 861, 839, 810, 700, 663, 581, 539; HRMS (ESI) Calcd for C\(_{22}\)H\(_{22}\)O\(_2\)N\(_2\)S (M+H)\(^+\) 364.1366, found 364.1378.

2. References:


3. X-Ray diffraction analysis

3.1 Crystal data and structure refinement for 2a

Identification code 2a
Empirical formula C21 H21 N O2 S
Formula weight 351.45
Temperature 100.00(10) K
Wavelength 1.54184 Å
Crystal system monoclinic
Space group C 1 2/c 1
Unit cell dimensions
\( a = 31.1655(5) \) Å \( \alpha = 90^\circ \).
\( b = 8.49460(10) \) Å \( \beta = 98.752(2)^\circ \).
\( c = 13.3472(2) \) Å \( \gamma = 90(4)^\circ \).
Volume 3492.37(9) Å\(^3\)
3.2 Crystal data and structure refinement for 3e

<table>
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<th>Identification code</th>
<th>3e (CCDC 1836652)</th>
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<td>Empirical formula</td>
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<tr>
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<tr>
<td>Temperature</td>
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<tr>
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<tr>
<td>Space group</td>
<td>P2₁/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 8.6549(5) Å, α = 90°.</td>
</tr>
<tr>
<td></td>
<td>b = 18.2100(11) Å, β = 94.769(5)°.</td>
</tr>
</tbody>
</table>
**Volume** | 1870.96(18) Å³
---|---
**Z** | 4
**Density (calculated)** | 1.577 Mg/m³
**Absorption coefficient** | 1.7223 mm⁻¹
**F(000)** | 904
**Crystal size** | 0.160 x 0.140 x 0.120 mm³
**Theta range for data collection** | 4.446 to 74.477°
**Index ranges** | -10≤h≤7, -22≤k≤20, -12≤l≤14
**Reflections collected** | 9309
**Independent reflections** | 3679 [R(int) = 0.0766]
**Completeness to theta = 66.97°** | 99.74%
**Absorption correction** | spherical harmonics
**Max. and min. transmission** | 1.000 and 0.552
**Refinement method** | Full-matrix least-squares on F²
**Data / restraints / parameters** | 3679 / 0 / 245
**Goodness-of-fit on F²** | 1.017
**Final R indices [I>2sigma(I)]** | R₁ = 0.0759, wR₂ = 0.2101
**R indices (all data)** | R₁ = 0.0832, wR₂ = 0.2302
**Extinction coefficient** | n/a
**Largest diff. peak and hole** | 1.31 and -1.54 e.Å⁻³
4. Copies of NMR spectra

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1a
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1b
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1c
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1d
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (101 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of substrate 1e
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1f
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (101 MHz, CDCl$_3$) and spectrum of substrate 1g
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1h
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate $\text{1i}$
$\text{H NMR (400 MHz, CDCl}_3\text{) and }^{13}\text{C NMR (101 MHz, CDCl}_3\text{) spectrum of substrate 1f}$
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1k
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 11
$^1$H NMR (400 MHz, CDCl₃) and $^{13}$C NMR (101 MHz, CDCl₃) spectrum of substrate 1m
$^{1}$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1n
1H NMR (400 MHz, CDCl₃) and 13C NMR (101 MHz, CDCl₃) spectrum of substrate 1o
$\text{H NMR (400 MHz, CDCl}_3\text{) and }^{13}\text{C NMR (101 MHz, CDCl}_3\text{) spectrum of substrate 1p}$
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1q
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1q

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1r
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1s
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1t
$^{1}$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1u
\[ ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3), \ ^{13}\text{C NMR} \ (101 \text{ MHz, CDCl}_3) \text{ and } 19\text{F NMR} \ (376 \text{ MHz, CDCl}_3) \]
spectrum of substrate 1v
$\textbf{1v}$

---

$\textbf{1v}$
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 1w
\(^1\)H NMR (400 MHz, CDCl\(_3\)) and \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) spectrum of substrate 2a
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate $2b$. 

![Spectrum](image-url)
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2c
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2d
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (101 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of substrate 2e
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2f
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2g
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2h
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2j
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2k
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2l
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate $2m$
$^{1}$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2n
$\text{H NMR (400 MHz, CDCl}_3\text{) and } ^{13}\text{C NMR (101 MHz, CDCl}_3\text{) spectrum of substrate 2o}$
$^{1}H$ NMR (400 MHz, CDCl$_3$) and $^{13}C$ NMR (101 MHz, CDCl$_3$) spectrum of substrate 2p
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2q
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2r
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2s
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2t
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2u
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (101 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of substrate 2v
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 2w
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 3a
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 3b
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate $3c$
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 3d
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 3e
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (101 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of substrate 3f
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 3g
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 3h
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 3i
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of substrate 3j
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of product 3j$'$
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of product $3k'$
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of product 2a''
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of product 2p$''$
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of product 2s$^{**}$
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of product 4a
$\text{H NMR (400 MHz, CDCl}_3\text{) and } ^{13}\text{C NMR (101 MHz, CDCl}_3\text{) spectrum of product 4b}$
$^{1}$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of product 5a
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of product 5b
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of product 3a'}