Supporting Information

Rhodium-Catalyzed Enantio- and Diastereoselective Intramolecular [2 + 2 + 2]
Cycloaddition of Unsymmetrical Dienynes

Hiromi Sagae, a Keiichi Noguchi, b Masao Hirano, a and Ken Tanaka* a

a Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

b Instrumentation Analysis Center, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

I. General

Anhydrous CH₂Cl₂ (No. 27099-7) and anhydrous (CH₂Cl)₂ (No. 28450-5) were obtained from Aldrich and used as received. Solvents for the synthesis of substrates were dried over Molecular Sieves 4A (Wako) prior to use. Ligands, (R)-H₈-BINAP and (R)-Segphos, were obtained from Takasago International Corporation. All other reagents were obtained from commercial sources and used as received. All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried glassware with magnetic stirring.

II. Synthesis of Unsymmetrical Dienynes

4-Methyl-N-(2-methylallyl)-N-[4-(2-methylallyloxy)but-2-ynyl]benzenesulfonamide (1a). 4-Methyl-N-(2-methylallyl)-benzenesulfonamide (0.530 g, 2.35 mmol) and triphenylphosphine (0.561 g, 2.14 mmol) were dissolved in THF (20 mL). To this were added 4-(2-methylallyloxy)but-2-yn-1-ol (0.300 g, 2.14 mmol) dropwise and then diisopropyl azadicarboxylate (0.433 g, 2.14 mmol) in a portion at 0 °C. The resulting mixture was stirred at room temperature for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 15:1), which furnished 1a (0.724 g, 2.08 mmol, 97% yield) as a colorless oil.

IR (neat) 2977, 2917, 2853, 1422, 1348, 1163, 1097, 904, 659 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.74 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 4.96 (s, 2H), 4.90 (s, 2H), 4.09 (s, 2H), 4.05 (s, 2H), 3.06 (s, 2H), 2.94 (s, 2H), 2.89 (s, 2H), 2.83 (s, 2H), 2.74 (s, 2H), 2.67 (s, 2H), 2.61 (s, 2H), 2.58 (s, 2H), 2.51 (s, 2H), 2.46 (s, 2H), 2.42 (s, 2H), 2.38 (s, 2H), 2.35 (s, 2H), 2.32 (s, 2H), 2.29 (s, 2H), 2.26 (s, 2H), 2.23 (s, 2H), 2.21 (s, 2H), 2.19 (s, 2H), 2.17 (s, 2H), 2.15 (s, 2H), 2.13 (s, 2H), 2.11 (s, 2H), 2.09 (s, 2H), 2.07 (s, 2H), 2.05 (s, 2H), 2.03 (s, 2H), 2.01 (s, 2H), 1.99 (s, 2H), 1.97 (s, 2H), 1.95 (s, 2H), 1.93 (s, 2H), 1.91 (s, 2H), 1.89 (s, 2H), 1.87 (s, 2H), 1.85 (s, 2H), 1.83 (s, 2H), 1.81 (s, 2H), 1.79 (s, 2H), 1.77 (s, 2H), 1.75 (s, 2H), 1.73 (s, 2H), 1.71 (s, 2H), 1.69 (s, 2H), 1.67 (s, 2H), 1.65 (s, 2H), 1.63 (s, 2H), 1.61 (s, 2H), 1.59 (s, 2H), 1.57 (s, 2H), 1.55 (s, 2H), 1.53 (s, 2H), 1.51 (s, 2H), 1.49 (s, 2H), 1.47 (s, 2H), 1.45 (s, 2H), 1.43 (s, 2H), 1.41 (s, 2H), 1.39 (s, 2H), 1.37 (s, 2H), 1.35 (s, 2H), 1.33 (s, 2H), 1.31 (s, 2H), 1.29 (s, 2H), 1.27 (s, 2H), 1.25 (s, 2H), 1.23 (s, 2H), 1.21 (s, 2H), 1.19 (s, 2H), 1.17 (s, 2H), 1.15 (s, 2H), 1.13 (s, 2H), 1.11 (s, 2H), 1.09 (s, 2H), 1.07 (s, 2H), 1.05 (s, 2H), 1.03 (s, 2H), 1.01 (s, 2H), 0.99 (s, 2H), 0.97 (s, 2H), 0.95 (s, 2H), 0.93 (s, 2H), 0.91 (s, 2H), 0.89 (s, 2H), 0.87 (s, 2H), 0.85 (s, 2H), 0.83 (s, 2H), 0.81 (s, 2H), 0.79 (s, 2H), 0.77 (s, 2H), 0.75 (s, 2H), 0.73 (s, 2H), 0.71 (s, 2H), 0.69 (s, 2H), 0.67 (s, 2H), 0.65 (s, 2H), 0.63 (s, 2H), 0.61 (s, 2H), 0.59 (s, 2H), 0.57 (s, 2H), 0.55 (s, 2H), 0.53 (s, 2H), 0.51 (s, 2H), 0.49 (s, 2H), 0.47 (s, 2H), 0.45 (s, 2H), 0.43 (s, 2H), 0.41 (s, 2H), 0.39 (s, 2H), 0.37 (s, 2H), 0.35 (s, 2H), 0.33 (s, 2H), 0.31 (s, 2H), 0.29 (s, 2H), 0.27 (s, 2H), 0.25 (s, 2H), 0.23 (s, 2H), 0.21 (s, 2H), 0.19 (s, 2H), 0.17 (s, 2H), 0.15 (s, 2H), 0.13 (s, 2H), 0.11 (s, 2H), 0.09 (s, 2H), 0.07 (s, 2H), 0.05 (s, 2H), 0.03 (s, 2H), 0.01 (s, 2H), 0.00 (s, 2H).
3.83 (t, \( J = 1.8 \text{ Hz}, 2 \text{H} \)), 3.74 (t, \( J = 1.8 \text{ Hz}, 2 \text{H} \)), 3.72 (s, 2H), 2.42 (s, 3H), 1.77 (s, 3H), 1.70 (s, 3H); \(^{13}\text{C} \text{ NMR (CDCl} _3, 75 \text{ MHz}) \) \( \delta 143.3, 141.3, 139.2, 136.1, 129.3, 127.8, 115.4, 112.9, 81.6, 78.7, 73.3, 56.8, 52.5, 35.8, 21.5, 19.7, 19.4; \) HRMS (ESI) calcd for \( \text{C}_19\text{H}_{23}\text{NO}_3\text{SNa} \) [M+Na]\(^+\) 370.1453, found 370.1428.

**4-Methyl-N-(3-methylbut-3-enyl)-N-[4-[(2-methylprop-3-enyl)(toluene-4-sulfonyl)amino]but-2-ynyl]benzenesulfonamide (1b).** To a \( \text{CH}_3\text{CN} \) (10 mL) solution of \( 4\)-methyl-N-(3-methylbut-3-enyl)benzenesulfonamide\(^3\) (0.255 g, 1.07 mmol) was added \( \text{K}_2\text{CO}_3 \) (0.148 g, 1.07 mmol). The resulting mixture was stirred at room temperature for 30 min. \( N\)-(4-Chlorobut-2-ynyl)-4-methyl-N-(2-methylprop-2-enyl)benzenesulfonamide\(^4\) (0.300 g, 0.97 mmol) was added, and the resulting mixture was stirred at 80 °C for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over \( \text{Na}_2\text{SO}_4 \), and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 10:1), which furnished 1b (0.450 g, 0.874 mmol, 90% yield) as a colorless solid.

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\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{TsN} & \quad \text{NTs}
\end{align*}
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Mp 87.1–87.3 °C; IR (neat) 2974, 2920, 2868, 1443, 1348, 1161, 1096, 905, 661 cm\(^{-1}\); \(^1\text{H} \text{ NMR (CDCl} _3, 300 \text{ MHz}) \) \( \delta 7.67 \) (d, \( J = 8.4 \text{ Hz}, 2 \text{H} \)), 7.61 (d, \( J = 8.4 \text{ Hz}, 2 \text{H} \)), 7.30 (d, \( J = 8.4 \text{ Hz}, 2 \text{H} \)), 7.26 (d, \( J = 8.4 \text{ Hz}, 2 \text{H} \)), 4.90 (s, 1H), 4.78 (s, 1H), 4.72 (s, 1H), 4.66 (s, 1H), 3.87 (s, 2H), 3.82 (s, 2H), 3.52 (s, 2H), 3.12 (t, \( J = 7.5 \text{ Hz}, 2 \text{H} \)), 2.44 (s, 3H), 2.41 (s, 3H), 2.12 (t, \( J = 7.5 \text{ Hz}, 2 \text{H} \)), 1.71 (s, 6H); \(^{13}\text{C} \text{ NMR (CDCl} _3, 75 \text{ MHz}) \) \( \delta 143.6, 143.5, 141.9, 139.0, 135.9, 135.8, 129.4, 129.3, 127.4, 115.2, 112.3, 78.2, 78.1, 52.3, 44.4, 36.0, 35.6, 35.3, 22.0, 21.42, 21.40, 19.5; \) HRMS (FAB) calcd for \( \text{C}_{27}\text{H}_{35}\text{N}_2\text{O}_4\text{S}_2 \) [M+H]\(^+\) 515.2038, found 515.2068.

**4-Methyl-N-[4-(2-methylallyloxy)but-2-ynyl]-N-(3-methylbut-3-enyl)benzenesulfonamide (1c).** This compound (0.584 g, 1.62 mmol, 76% yield) was prepared from 4-(2-methylallyloxy)-2-butyn-1-ol\(^2\) (0.300 g, 2.14 mmol) and 4-methyl-N-(3-methylbut-3-enyl)benzenesulfonamide\(^3\) (0.562 g, 2.35 mmol) by the procedure described for 1b.

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\begin{align*}
\text{TsN} & \quad \text{Me} \\
\text{Me} & \quad \text{O}
\end{align*}
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Colorless oil; IR (neat) 3075, 2973, 2920, 1453, 1347, 1162, 1098, 901, 660 cm\(^{-1}\); \(^1\text{H} \text{ NMR (CDCl} _3, 300 \text{ MHz}) \) \( \delta 7.74 \) (d, \( J = 8.4 \text{ Hz}, 2 \text{H} \)), 7.28 (d, \( J = 8.4 \text{ Hz}, 2 \text{H} \)), 4.90 (s, 2H), 4.80 (s, 1H), 

S2
4.74 (s, 1H), 4.19 (t, J = 1.8 Hz, 2H), 3.88 (t, J = 1.8 Hz, 2H), 3.75 (s, 2H), 3.31 (t, J = 7.5 Hz, 2H), 2.41 (s, 3H), 2.29 (t, J = 7.5 Hz, 2H), 1.76 (s, 3H), 1.69 (s, 3H); \(^1\)H NMR (CDCl\(_3\), 300 MHz)  \(\delta\) 143.3, 142.1, 141.2, 139.4, 127.7, 112.9, 112.4, 81.6, 78.9, 73.4, 56.8, 44.6, 36.5, 35.9, 22.1, 21.5, 19.4; HRMS (ESI) calcd for C\(_{24}\)H\(_{27}\)NO\(_3\)SNa [M+Na\(^+\)] 384.1609, found 384.1624.

4-Methyl-N-((2-methylallyl)-N-[3-[2-(2-methylallyloxy)phenyl]prop-2-ynyl]benzenesulfonamide (1d). To a solution of 1-iodo-2-(2-methylallyloxy)benzene\(^5\) (0.344 g, 1.26 mmol) in \(i\)-Pr\(_2\)NH (20 mL) were added PdCl\(_2\)(PPh\(_3\))\(_2\) (16 mg, 0.023 mmol) and CuI (8.7 mg, 0.046 mmol). 4-Methyl-N-((2-methylallyl)-N-prop-2-ynylbenzenesulfonamide\(^6\) (0.300 g, 1.14 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na\(_2\)SO\(_4\), and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 20:1), which furnished 1d (0.353 g, 0.862 mmol, 76% yield) as a yellow solid.

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\text{Me} \quad \text{NTs} \\
\text{H} \\
\text{O} \\
\text{Me} \\
\text{Me} \\
\text{NTs}
\]

Mp 55.6–56.0 °C; IR (neat) 3079, 2974, 2918, 1597, 1492, 1444, 1348, 1163, 903, 754, 658 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz)  \(\delta\) 7.77 (d, \(J = 8.4\) Hz, 2H), 7.23 (ddd, \(J = 7.5, 7.5, 1.8\) Hz, 1H), 7.19 (d, \(J = 8.4\) Hz, 2H), 6.92 (dd, \(J = 7.5, 1.8\) Hz, 1H), 6.81 (ddd, \(J = 7.5, 7.5, 1.8\) Hz, 1H), 6.78 (dd, \(J = 7.5, 1.8\) Hz, 1H), 5.10–5.03 (m, 2H), 5.03–4.94 (m, 2H), 4.41 (s, 2H), 4.30 (s, 2H), 3.81 (s, 2H), 2.27 (s, 3H), 1.80 (s, 3H), 1.79 (s, 3H); \(^1\)C NMR (CDCl\(_3\), 75 MHz)  \(\delta\) 159.2, 143.2, 140.3, 139.3, 136.1, 133.4, 129.6, 129.4, 127.8, 120.2, 115.5, 112.8, 112.0, 85.6, 82.2, 72.0, 52.5, 36.7, 21.3, 19.8, 19.3; HRMS (ESI) calcd for C\(_{24}\)H\(_{27}\)NO\(_3\)SNa [M+Na\(^+\)] 432.1607, found 432.1607.

N-Allyl-4-methyl-N-[3-[2-(2-methylallyloxy)phenyl]prop-2-ynyl]benzenesulfonamide (1e). This compound (0.725 g, 1.83 mmol, 57% yield) was prepared from 1-iodo-2-(2-methylallyloxy)benzene\(^5\) (0.959 g, 3.50 mmol) and N-allyl-4-methyl-N-prop-2-ynylbenzenesulfonamide\(^7\) (0.800 g, 3.20 mmol) by the procedure described for 1d.

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\text{Me} \quad \text{NTs} \\
\text{H} \\
\text{O} \\
\text{Me} \\
\text{Me} \\
\text{NTs}
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Yellow solid: mp 32.2–32.5 °C; IR (neat) 2980, 2919, 2865, 1491, 1445, 1348, 1162, 897, 754, 664 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz)  \(\delta\) 7.76 (d, \(J = 8.4\) Hz, 2H), 7.24 (ddd, \(J = 7.5, 7.5, 1.8\) Hz,
1H), 7.20 (d, J = 8.4 Hz, 2H), 6.95 (dd, J = 7.5, 1.8 Hz, 1H), 6.81 (ddd, J = 7.5, 7.5, 1.8 Hz, 1H), 6.78 (dd, J = 7.5, 1.8 Hz, 1H), 5.79 (ddt, J = 17.1, 10.2, 6.3 Hz, 1H), 5.34 (dd, J = 17.1, 1.8 Hz, 1H), 5.24 (dd, J = 10.2, 1.8 Hz, 1H), 5.11–5.02 (m, 1H), 5.02–4.91 (m, 1H), 4.42 (s, 2H), 4.35 (s, 2H), 3.90 (d, J = 6.3 Hz, 2H), 2.28 (s, 3H), 1.80 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 159.2, 143.3, 140.3, 136.0, 133.4, 132.1, 129.6, 129.4, 127.8, 120.3, 120.0, 112.8, 112.0, 85.6, 82.2, 77.2, 72.0, 49.1, 37.0, 21.4, 19.3; HRMS (FAB) calcd for C$_{23}$H$_{26}$NO$_3$S [M+H]$^+$ 396.1633, found 396.1635.

2- Allyl-2-(3-[2-(2-methylallyloxy)phenyl]prop-2-ynyl)malonic acid diethyl ester (1f). This (1.09 g, 2.83 mmol, 62% yield) was prepared from 1-iodo-2-(2-methylallyloxy)benzene$^5$ (1.50 g, 5.47 mmol) and 2-allyl-2-prop-2-ynyl-malonic acid diethyl ester$^6$ (1.10 g, 4.56 mmol) by the procedure described for 1d.

Yellow oil: IR (neat) 3078, 2980, 2935, 1735, 1492, 1445, 1289, 1215, 909, 753 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.33 (dd, J = 7.5, 1.8 Hz, 1H), 7.21 (ddd, J = 7.5, 7.5, 1.8 Hz, 1H), 6.86 (ddd, J = 7.5, 7.5, 1.8 Hz, 1H), 6.82 (dd, J = 7.5, 1.8 Hz, 1H), 5.70 (ddt, J = 17.4, 10.2, 7.5 Hz, 1H), 5.21 (dd, J = 17.4, 1.8 Hz, 1H), 5.13 (dd, J = 10.2, 1.8 Hz, 1H), 5.14–5.07 (m, 1H), 5.01–4.94 (m, 1H), 4.47 (s, 2H), 4.21 (qq, J = 6.9 Hz, 4H), 3.07 (s, 2H), 2.75 (d, J = 12.3, Hz, 2H), 1.84 (s, 3H), 1.25 (t, J = 6.9 Hz, 6H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 169.9, 159.2, 140.6, 133.6, 132.1, 129.1, 120.4, 119.6, 113.0, 112.7, 112.2, 88.3, 79.7, 72.0, 61.5, 57.1, 36.5, 23.8, 19.3, 14.1; HRMS (ESI) calcd for C$_{23}$H$_{26}$O$_2$Na [M+Na]$^+$ 407.1834, found 407.1828.

1-(3-Allyloxyprop-1-ynyl)-2-(2-methylallyloxy)benzene (1g). To a solution of 1-iodo-2-(2-methylallyloxy)benzene$^5$ (2.00 g, 7.3 mmol) in i-Pr$_2$NH (40 mL) were added PdCl$_2$(PPh$_3$)$_2$ (103 mg, 0.147 mmol) and CuI (55.7 mg, 0.292 mmol). Propargyl alcohol (0.409 g, 7.30 mmol) was added dropwise and the resulting mixture was stirred at 60 °C for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na$_2$SO$_4$, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 20:1), which furnished 3-[2-(2-methylallyloxy)phenyl]prop-2-yn-1-ol (1.02 g, 5.05 mmol, 69% yield) as a colorless oil.

To a THF (20 mL) solution of 3-[2-(2-methylallyloxy)phenyl]prop-2-yn-1-ol (0.400 g, 2.00 mmol) was added NaH (0.576 g, 2.40 mmol) at 0 °C, and the resulting mixture was stirred at room temperature for 30 min. 3-Bromopropene (0.363 g, 3.00 mmol) was added, and the resulting mixture was stirred at room temperature for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na$_2$SO$_4$, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc
= 50:1), which furnished 1g (0.208 g, 0.858 mmol, 43% yield) as a yellow oil.

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\text{O} & \\
\text{O} & \\
\text{Me} & \\
\end{align*}
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IR (neat) 3078, 2977, 2916, 1491, 1445, 1262, 1086, 1013, 907, 752 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 7.41 (dd, \(J = 7.5, 1.8\) Hz, 1H), 7.26 (dd, \(J = 7.5, 7.5, 1.8\) Hz, 1H), 6.89 (ddd, \(J = 7.5, 7.5, 1.8\) Hz, 1H), 6.85 (dd, \(J = 7.5, 1.8\) Hz, 1H), 6.08 (dd, \(J = 7.5, 1.8\) Hz, 1H), 5.95 (ddt, \(J = 15.9, 11.1, 5.7\) Hz, 1H), 5.34 (dd, \(J = 15.9, 1.5\) Hz, 1H), 5.22 (dd, \(J = 11.1, 1.5\) Hz, 1H), 5.18–5.13 (m, 1H), 5.02–4.96 (m, 1H), 4.49 (s, 2H), 4.43 (s, 2H), 4.16 (d, \(J = 5.7\) Hz, 2H), 1.85 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 159.3, 140.5, 134.2, 133.6, 129.6, 120.5, 117.7, 112.6, 112.4, 112.2, 89.1, 82.7, 72.1, 70.4, 58.1, 19.3; HRMS (ESI) calcd for C\(_{16}\)H\(_{18}\)O\(_2\)Na [M+Na\(^+\)] 265.1205, found 265.1203.

1-Allyloxy-2-[3-(2-methylallyloxy)prop-1-ynyl]benzene (1h). This compound (0.452 g, 1.87 mmol, 68% yield) was prepared from 1-allyloxy-2-iodobenzene\(^9\) (0.853 g, 3.28 mmol) and 2-methyl-3-prop-2-ynooxypropene\(^10\) (0.300 g, 2.73 mmol) by the procedure described for 1d.

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Yellow oil; IR (neat) 3077, 2917, 2850, 2364, 1491, 1445, 1264, 1085, 997, 927, 752 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 6.90 (dd, \(J = 7.5, 1.2\) Hz, 1H), 7.26 (dd, \(J = 7.5, 7.5, 1.2\) Hz, 1H), 6.07 (ddt, \(J = 17.1, 10.2, 5.1\) Hz, 1H), 5.47 (ddd, \(J = 17.1, 4.8, 1.8\) Hz, 1H), 5.29 (ddd, \(J = 10.2, 4.8, 1.8\) Hz, 1H), 5.08–5.00 (m, 1H), 4.97–4.88 (m, 1H), 4.61 (dt, \(J = 4.8, 1.8\) Hz, 2H), 4.41 (s, 2H), 4.08 (s, 2H), 1.78 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 159.2, 141.6, 133.6, 133.0, 129.6, 120.6, 117.4, 112.9, 112.5, 112.3, 89.3, 82.5, 73.4, 69.2, 57.9, 19.6; HRMS (ESI) calcd for C\(_{16}\)H\(_{18}\)O\(_2\)Na [M+Na\(^+\)] 265.1205, found 265.1203.

[2-(2-Methylallyloxy)phenyl]propynoic acid 2-methylallyl ester (1i). To a CH\(_3\)CN (20 mL) solution of 3-(2-hydroxyphenyl)propynoic acid\(^11\) (0.400 g, 2.47 mmol) was added K\(_2\)CO\(_3\) (0.683 g, 4.94 mmol), and the resulting mixture was stirred at room temperature for 30 min. 3-Bromo-2-methylpropene (0.367 g, 2.72 mmol) was added, and the resulting mixture was stirred at room temperature for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na\(_2\)SO\(_4\), and concentrated. The
residue was purified by silica gel column chromatography (hexane/EtOAc = 20:1), which furnished 1i (0.523 g, 1.93 mmol, 78% yield) as a yellow oil.

IR (neat) 2919, 2326, 2220, 1709, 1491, 1446, 1301, 1175, 1011, 904, 752 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.54 (dd, J = 7.5, 1.5 Hz, 1H), 7.38 (ddd, J = 7.5, 7.5, 1.5 Hz, 1H), 6.94 (ddd, J = 7.5, 7.5, 1.5 Hz, 1H), 6.88 (dd, J = 7.5, 1.5 Hz, 1H), 5.26–5.17 (m, 1H), 5.09–5.04 (m, 1H), 5.04–4.95 (m, 2H), 4.65 (s, 2H), 4.51 (s, 2H), 1.86 (s, 3H), 1.81 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 160.8, 154.0, 140.0, 139.1, 134.7, 132.2, 120.6, 113.7, 112.6, 112.2, 109.3, 84.5, 83.6, 72.0, 69.0, 19.4, 19.2; HRMS (FAB) calcd for C₁₇H₁₄O₃ [M+H]⁺ 271.1334, found 271.1340.

N-Alllyl-4-methyl-N-[3-[2-(2-methylallyloxymethyl)phenyl]prop-2-ynyl]benzenesulfonamide (1j). To a EtOH (40 mL) solution of NaBH₄ (0.310 g, 8.18 mmol) was added dropwise N-allyl-N-[3-[2-formylphenyl]prop-2-ynyl]-4-methylbenzenesulfonamide¹² (2.22 g, 6.29 mmol) at 0 °C, and the resulting mixture was stirred at 0 °C for 2 h. The reaction was quenched with water and extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 20:1), which furnished N-allyl-N-[3-[2-hydroxyethylphenyl]prop-2-ynyl]-4-methylbenzenesulfonamide (2.03 g, 5.70 mmol, 91% yield) as a colorless oil.

To a THF (20 mL) solution of N-allyl-N-[3-[2-hydroxyethylphenyl]prop-2-ynyl]-4-methylbenzenesulfonamide (1.00 g, 2.81 mmol) was added NaH (0.0812 g, 3.38 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 15 min. 3-Bromo-2-methylpropene (0.456 g, 3.38 mmol) was added at 0 °C, and the resulting mixture was stirred at room temperature for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by preparative TLC (hexane/EtOAc = 10:1), which furnished N-allyl-4-methyl-N-[3-[2-(2-methylallyloxymethyl)phenyl]prop-2-ynyl]benzenesulfonamide (50.2 mg, 0.0127 mmol, 5% yield, unoptimized) as a colorless oil.

IR (neat) 2918, 2853, 2367, 1349, 1164, 1092, 897, 760, 663 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.75 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 7.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 8.1 Hz, 2H), 7.16 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 7.5 Hz, 1H), 5.80 (ddt, J = 16.5, 9.9, 6.3 Hz,
III. Intramolecular [2 + 2 + 2] Cycloaddition of Unsymmetrical Diynes

**General Procedure (Table 1, entry 1).** Under an Ar atmosphere, a CH₂Cl₂ (1.0 mL) solution of (R)-H₃-BINAP (6.3 mg, 0.010 mmol) was added to a CH₂Cl₂ (1.0 mL) solution of [Rh(cod)]BF₃ (4.1 mg, 0.010 mmol) at room temperature, and the solution was stirred at room temperature for 5 min. H₂ (1 atm) was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 0.5 h, the resulting solution was concentrated to dryness and the residue was dissolved in CH₂Cl₂ (0.5 mL). To this solution was added a (CH₂Cl₂) solution of 1b (102.9 mg, 0.200 mmol). The solution was stirred at 80 °C for 3 h. The resulting solution was concentrated and purified by preparative TLC (hexane/EtOAc = 2:1), which furnished the mixture of 2b and 3b [102.9 mg, 0.200 mmol, >99% yield, 2b/3b = 1:2.4, 4% ee (2b), 99% ee (3b)] as a colorless oil.

3a,5a-Dimethyl-2,8-bis-(toluene-4-sulfonyl)-2,3,3a,4,5,5a,6,7,8,9-decahydro-1H-pyrrolo[3,4-h]isoquinoline [2b/3b = 1:2.4, Table 1, entry 1, >99% yield, 4% ee (2b), 99% ee (3b)].

![Structure of 2b and 3b]

[α]D +12.1° [acetone, c 1.430, a mixture of 2b (4% ee) and 3b (99% ee)]; IR (neat) 3398, 2926, 2864, 2368, 2367, 1344, 1160, 1093, 942, 815, 667 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) 2b: δ 7.74 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 7.8 Hz, 2H), 7.42–7.21 (m, 4H), 4.05 (d, J = 14.1 Hz, 1H), 3.91 (d, J = 14.1 Hz, 2H), 3.62–3.53 (m, 1H), 3.44 (d, J = 8.7 Hz, 1H), 2.93 (d, J = 12.9 Hz, 1H), 2.74–2.56 (m, 1H), 2.49 (d, J = 8.7 Hz, 1H), 2.44 (s, 3H), 2.41 (s, 3H), 1.66–1.31 (m, 4H), 1.20–1.10 (m, 2H), 1.07 (s, 3H), 0.94 (s, 3H); 3b: δ 7.74 (d, J = 7.8 Hz, 2H), 7.65 (d, J = 7.8 Hz, 2H), 7.42–7.21 (m, 4H), 3.94 (d, J = 12.9 Hz, 2H), 3.81 (d, J = 12.9 Hz, 1H), 3.76–3.65 (m, 1H), 3.40 (d, J = 9.3 Hz, 1H), 2.95 (d, J = 12.6 Hz, 1H), 2.81 (d, J = 9.3 Hz, 1H), 2.74–2.56 (m, 1H), 2.45 (s, 3H), 2.44 (s, 3H), 1.66–1.31 (m, 6H), 0.83 (s, 3H), 0.81 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 143.5, 143.44, 134.40, 137.0, 135.4, 134.3, 133.6, 129.8, 129.6, 128.8, 127.7, 127.5, 127.4, 127.3, 61.2, 61.0, 60.3, 48.6, 47.8, 44.8, 44.0, 42.4, 42.3, 41.5, 41.3, 39.3, 37.5, 34.8, 34.6, 33.1, 32.9, 29.8, 28.4, 25.1, 24.3, 23.6, 22.9, 21.5, 21.4, 21.0, 14.1; HRMS (FAB) calcd for C₃₂H₂₇NO₃S₃Na[M+H]^⁺ 515.2038, found 515.2045; CHIRALPAK AD, hexane/2-ProOH = 95:5, 1.0 mL/min, retention times: 110.6 min (minor cis-isomer), 125.4 min (minor trans-isomer), 159.7 min (major cis-isomer), and 240.0 min (major trans-isomer).
(+)-3a,5a-Dimethyl-7-(toluene-4-sulfonyl)-3,3a,4,5,5a,6,7,8-octahydro-1H-2-oxa-7-aza-as-indacene [(+)-2a, eq 1, 81 % yield, 38 % ee].

![Chemical Structure](image)

Colorless oil; [α]$_D^{25}$ +10.8° (acetone, c 3.140, 38 % ee); IR (neat) 3390, 2962, 2925, 2866, 2326, 1453, 1345, 1166, 1093, 1053, 817, 669 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.71 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 4.27 (d, $J = 13.2$ Hz, 1H), 4.06 (d, $J = 13.2$ Hz, 1H), 3.84 (d, $J = 13.2$ Hz, 1H), 3.83 (d, $J = 7.8$ Hz, 1H), 3.62 (d, $J = 13.2$ Hz, 1H), 3.32 (d, $J = 9.3$ Hz, 1H), 3.12 (d, $J = 7.8$ Hz, 1H), 2.70 (d, $J = 9.3$ Hz, 1H), 2.43 (s, 3H), 1.73–1.42 (m, 2H), 1.33–1.05 (m, 2H), 1.10 (s, 3H), 1.00 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 143.5, 137.5, 133.8, 130.3, 129.6, 127.4, 79.8, 67.5, 59.0, 47.9, 41.2, 40.3, 30.1, 29.6, 26.0, 23.7, 21.5; HRMS (ESI) calcd for C$_{19}$H$_{25}$NO$_3$SNa [M+Na]$^+$ 370.1453, found 370.1433; CHIRALPAK AD-H, hexane:2-PrOH = 95:5, 1.0 mL/min, retention times: 27.6 min (major isomer) and 32.8 min (minor isomer).

(+)-3a,5a-Dimethyl-7-(toluene-4-sulfonyl)-3,3a,4,5,5a,6,7,8-octahydro-1H-2-oxa-7-aza-as-indacene [(+)-3a, eq 1, 17 % yield, 93 % ee].

![Chemical Structure](image)

Colorless oil; [α]$_D^{25}$ +7.9° (acetone, c 0.965, 93 % ee); IR (neat) 3390, 2966, 2933, 2862, 2366, 1456, 1343, 1161, 1094, 1041, 817, 669 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.72 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 4.30 (d, $J = 12.3$ Hz, 1H), 4.06 (d, $J = 12.3$ Hz, 1H), 3.89 (d, $J = 12.6$ Hz, 1H), 3.77 (d, $J = 7.5$ Hz, 1H), 3.64 (d, $J = 12.6$ Hz, 1H), 3.47 (d, $J = 9.0$ Hz, 1H), 3.25 (d, $J = 7.5$ Hz, 1H), 2.84 (d, $J = 9.0$ Hz, 1H), 2.43 (s, 3H), 1.73–1.42 (m, 4H), 1.04 (s, 3H), 0.88 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 143.4, 135.4, 134.7, 129.6, 129.4, 127.3, 80.3, 66.5, 61.2, 47.7, 42.2, 41.7, 29.5, 28.2, 24.7, 24.2, 21.5; HRMS (ESI) calcd for C$_{19}$H$_{25}$NO$_3$SNa [M+Na]$^+$ 370.1453, found 370.1441; CHIRALPAK AD-H, hexane:2-PrOH = 95:5, 1.0 mL/min, retention times: 27.5 min (minor isomer) and 32.0 min (major isomer).

(+)-Dimethyl-8-(toluene-4-sulfonyl)-1,3,3a,4,5,5a,6,7,8,9-decahydro-furo[3,4-h]isoquinoline [(+)-2c, Table 1, entry 2, 24 % yield, 45 % ee].

![Chemical Structure](image)

Colorless solid; mp 139.1–139.3 °C; [α]$_D^{25}$ +67.1° (acetone, c 0.830, 45 % ee); IR (neat) 3390, 2925, 2853, 2366, 2327, 1349, 1156, 1092, 1053, 923, 678 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.66 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 4.49 (d, $J = 13.2$ Hz, 1H), 4.41 (dd, $J = 13.2$, 1.2 Hz, 1H), 3.90 (dd, $J = 12.6$, 1.2 Hz, 1H), 3.77 (d, $J = 7.8$ Hz, 1H), 3.73–3.62 (m, 1H), 3.27 (d,
\[ J = 7.8 \text{ Hz, 1H}, 2.99 \text{ (d, } J = 12.6 \text{ Hz, 1H}), 2.73 \text{ (dt, } J = 12.6, 3.3 \text{ Hz, 1H}), 2.44 \text{ (s, 3H), } 1.89-1.70 \text{ (m, 2H), } 1.65-1.41 \text{ (m, 2H), } 1.29-1.18 \text{ (m, 2H), } 1.09 \text{ (s, 3H), } 0.99 \text{ (s, 3H); } ^{13}\text{C NMR (CDCl}_3, 75 \text{ MHz)} \delta 143.5, 141.1, 133.6, 129.6, 127.6, 126.5, 81.0, 67.9, 44.3, 42.6, 42.1, 37.9, 35.0, 33.2, 28.7, 25.2, 22.9, 21.5; \text{ HRMS (ESI) calcd for } C_{26}H_{22}NO_3\text{SNa [M+Na}^+ \text{] 384.1609, found } 384.1596; \text{ CHIRALPAK AD-H, hexane/2-PrOH = 95:5, 1.0 mL/min, retention times: 37.9 min (minor isomer) and 41.1 min (major isomer).}

\[(3aR,5aS)-(+)\text{-3a,5a-Dimethyl-8-(toluene-4-sulfonyl)-1,3,3a,4,5,5a,6,7,8,9-decahydro-furo[3,4-\text{h}]isoquinoline [(3aR,5aS)-(+)\text{-3c, Table 1, entry 2, 75% yield, >99% ee].}

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{TsN} & \quad \text{O}
\end{align*}
\]

Colorless solid; mp 131.2–131.5 °C; [\alpha]_{D}^{25} +51.5° (acetone, c 2.100, >99% ee); IR (neat) 3394, 2966, 2928, 2857, 2368, 2327, 1456, 1349, 1156, 1092, 1031, 676 cm\(^{-1}\); \(^1\text{H NMR (CDCl}_3, 300 \text{ MHz) } \delta 7.66 \text{ (d, } J = 8.1 \text{ Hz, 2H), } 7.32 \text{ (d, } J = 8.1 \text{ Hz, 2H), } 4.50 \text{ (dd, } J = 12.6, 1.2 \text{ Hz, 1H), } 4.24 \text{ (d, } J = 12.6 \text{ Hz, 1H), } 3.91 \text{ (dd, } J = 12.6, 1.2 \text{ Hz, 1H), } 3.76 \text{ (d, } J = 7.5 \text{ Hz, 1H), } 3.80-3.67 \text{ (m, 1H), } 3.24 \text{ (d, } J = 7.5 \text{ Hz, 1H), } 3.09 \text{ (d, } J = 12.6 \text{ Hz, 1H), } 2.69 \text{ (dt, } J = 12.6, 3.9 \text{ Hz, 1H), } 2.44 \text{ (s, 3H), } 1.67-1.30 \text{ (m, 6H), } 1.09 \text{ (s, 3H), } 0.90 \text{ (s, 3H); } ^{13}\text{C NMR (CDCl}_3, 75 \text{ MHz) } \delta 143.4, 139.2, 133.9, 129.6, 127.6, 125.3, 80.8, 67.1, 45.0, 42.4, 41.9, 39.4, 35.1, 33.3, 27.2, 23.8, 22.9, 21.5; \text{ HRMS (ESI) calcd for } C_{25}H_{22}NO_3\text{SNa [M+Na}^+ \text{] 384.1609, found } 384.1609; \text{ CHIRALPAK AD-H, hexane/2-PrOH = 90:10, 1.0 mL/min, retention times: 14.1 min (minor isomer) and 23.8 min (major isomer). The absolute configuration was determined by X-ray crystallographic analysis (CCDC 673294).}

\[(+)-3a,5a-Dimethyl-2-(toluene-4-sulfonyl)-1,2,3,3a,4,5,5a,6-octahydro-7-oxa-2-azacyclopenta[c]phenanthrene [(+)-2d, Table 1, entry 3, 98% yield, 94% ee].

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{O} & \quad \text{NTs}
\end{align*}
\]

Colorless solid; mp 136.0–136.2 °C; [\alpha]_{D}^{25} +2.5° (acetone, c 0.680, 94% ee); IR (neat) 3394, 2925, 2864, 2369, 2331, 1485, 1341, 1233, 1164, 1094, 666 cm\(^{-1}\); \(^1\text{H NMR (CDCl}_3, 300 \text{ MHz) } \delta 7.67 \text{ (d, } J = 8.1 \text{ Hz, 2H), } 7.25 \text{ (d, } J = 8.1 \text{ Hz, 2H), } 7.15 \text{ (ddd, } J = 7.8, 6.3, 1.2 \text{ Hz, 1H), } 6.90 \text{ (dd, } J = 6.3, 1.2 \text{ Hz, 2H), } 6.77 \text{ (dd, } J = 7.8, 1.2 \text{ Hz, 1H), } 4.48 \text{ (d, } J = 14.4 \text{ Hz, 1H), } 3.94 \text{ (d, } J = 14.4 \text{ Hz, 1H), } 3.84 \text{ (d, } J = 10.2 \text{ Hz, 1H), } 3.77 \text{ (d, } J = 10.2 \text{ Hz, 1H), } 3.45 \text{ (d, } J = 9.3 \text{ Hz, 1H), } 2.65 \text{ (d, } J = 9.3 \text{ Hz, 1H), } 2.40 \text{ (s, 3H), } 1.79 \text{ (ddd, } J = 12.3, 3.9, 3.9 \text{ Hz, 1H), } 1.66 \text{ (ddd, } J = 12.3, 3.9, 3.9 \text{ Hz, 1H), } 1.47 \text{ (ddd, } J = 12.3, 3.9, 3.9 \text{ Hz, 1H), } 1.25 \text{ (ddd, } J = 12.3, 3.9, 3.9 \text{ Hz, 1H), } 1.17 \text{ (s, 3H), } 1.08 \text{ (s, 3H); } ^{13}\text{C NMR (CDCl}_3, 75 \text{ MHz) } \delta 153.0, 143.4, 133.8, 133.5, 129.7, 129.6, 128.8, 128.3, 127.4, 120.9, 119.9, 115.9, 75.5, 60.1, 50.2, 42.7, 31.5, 30.3, 30.0, 25.3, 24.4, 21.5; \text{ HRMS (FAB) calcd for } C_{24}H_{28}NO_3\text{S [M+H}^+ \text{] 410.1790, found 410.1750; CHIRALPAK AD-H,}

S9
hexane/2-PrOH = 95:5, 1.0 mL/min, retention times: 15.7 min (major isomer) and 19.1 min (minor isomer).

(3aR,5aS)-(+) -5a-Methyl-2-(toluene-4-sulfonyl)-1,2,3,3a,4,5,5a,6-octahydro-7-oxa-2-aza-cyclopenta[c]phenanthrene [(3aR,5aS)-(+) -2e, Table 1, entry 5, 89% yield, 99% ee].

Orange solid; mp 172.1–172.5 °C; [α]D25 +23.3° (acetone, c 2.470, 99% ee); IR (neat) 3062, 2927, 2865, 2370, 2318, 1484, 1449, 1343, 1233, 1161, 1094, 758, 666 cm−1; 1H NMR (CDCl3, 300 MHz) δ 7.67 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.16 (ddd, J = 8.1, 6.3, 1.2 Hz, 1H), 7.03–6.84 (m, 2H), 6.78 (ddd, J = 8.1, 1.2 Hz, 1H), 4.41 (ddd, J = 14.4, 1.2 Hz, 1H), 3.94 (dd, J = 14.4, 1.2 Hz, 1H), 3.85 (d, J = 10.2 Hz, 1H), 3.82 (d, J = 8.4 Hz, 1H), 3.76 (d, J = 8.4 Hz, 1H), 2.83–2.66 (m, 1H), 2.55 (dd, J = 16.2, 8.4 Hz, 1H), 2.40 (s, 3H), 1.92–1.79 (m, 1H), 1.67–1.50 (m, 2H), 1.13–0.95 (m, 1H), 1.07 (s, 3H); 13C NMR (CDCl3, 75 MHz) δ 153.0, 143.4, 133.4, 130.2, 130.1, 129.7, 128.7, 128.0, 127.5, 121.0, 120.0, 116.0, 75.6, 60.3, 52.5, 51.1, 40.4, 32.6, 31.7, 24.9, 23.4; HRMS (ESI) calcd for C23H24NO3SNa [M+Na]+ 418.1453, found 418.1450; CHIRALPAK AD-H, hexane/2-PrOH = 95:5, 1.0 mL/min, retention times: 20.2 min (major isomer) and 26.8 min (minor isomer). The absolute configuration was determined by X-ray crystallographic analysis (CCDC 673295).

(+) -5a-Methyl-3,3a,4,5,5a,6-hexahydro-1H-7-oxacyclopenta[c]phenanthrene-2,2-dicarboxylic acid diethyl ester [(+) -2f, Table 1, entry 7, 87% yield, 97% ee].

Colorless oil; [α]D25 +81.9° (acetone, c 3.665, 97% ee); IR (neat) 3413, 2928, 2368, 2327, 1731, 1254, 1232, 1176, 1065, 747 cm−1; 1H NMR (CDCl3, 300 MHz) δ 7.29 (dd, J = 8.1, 1.5Hz, 1H), 7.11 (dd, J = 8.1, 1.5, 1.5 Hz, 1H), 6.88 (ddd, J = 8.1, 1.5, 1.5 Hz, 1H), 6.78 (dd, J = 8.1, 1.5 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 4.13 (q, J = 7.2 Hz, 2H), 4.03 (d, J = 10.2 Hz, 1H), 3.84 (d, J = 10.2 Hz, 1H), 3.50 (d, J = 17.7 Hz, 1H), 3.67 (dd, J = 17.7, 1.8 Hz, 1H), 2.70–2.46 (m, 2H), 1.92 (ddt, J = 9.0, 4.5, 4.5 Hz, 1H), 1.80–1.68 (m, 1H), 1.66–1.57 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H), 1.24–1.13 (m, 1H), 1.09 (s, 3H); 13C NMR (CDCl3, 75 MHz) δ 172.3, 171.7, 153.1, 134.9, 129.0, 128.7, 127.9, 122.2, 119.5, 115.8, 76.3, 61.6, 61.5, 58.9, 41.2, 39.7, 38.9, 33.3, 32.1, 25.7, 25.1, 14.0, 13.9; HRMS (ESI) calcd for C23H20O3Na [M+Na]+ 407.1834, found 407.1834; CHIRALPAK AD-H, hexane/2-PrOH = 98:2, 1.0 mL/min, retention times: 7.3 min (minor isomer) and 8.0 min (major isomer).
(+)-5a-Methyl-3,3a,4,5,5a,6-hexahydro-1H-2,7-dioxa-cyclopenta[c]phenanthrene [(+)-2g, Table 1, entry 9, 95% yield, 93% ee].

![Chemical structure](attachment:image.png)

Colorless oil; [α]$_D^{25} +72.4^\circ$ (acetone, c 2.265, 93% ee); IR (neat) 3357, 2927, 2862, 2365, 2331, 1484, 1449, 1231, 1042, 758 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.20–7.08 (m, 1H), 6.96–6.74 (m, 3H), 4.82 (d, $J = 13.5$ Hz, 1H), 4.45 (d, $J = 13.5$ Hz, 1H), 4.20 (dd, $J = 16.2$, 8.1 Hz, 1H), 4.06 (d, $J = 10.2$ Hz, 1H), 3.88 (d, $J = 10.2$ Hz, 1H), 3.19 (dd, $J = 16.2$, 8.1 Hz, 1H), 2.88–2.67 (m, 1H), 1.97–1.85 (m, 1H), 1.74–1.65 (m, 2H), 1.18–1.03 (m, 1H), 1.16 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 153.0, 134.8, 128.3, 128.1, 127.9, 121.7, 119.9, 116.1, 75.9, 72.9, 70.1, 41.7, 33.3, 31.9, 25.3, 22.9; HRMS (FAB) calcd for C$_{116}$H$_{162}$O$_2$ [M+H]$^+$ 243.1385, found 265.1404; CHIRALPAK AD-H, hexane/2-ProOH = 95:5, 1.0 mL/min, retention times: 6.5 min (minor isomer) and 8.5 min (major isomer).

4-(4,4-Dimethylidihydrofuran-3-ylidene)-3-methyl-4H-chromene [4, Table 1, entry 10, 70% yield (E/Z = 1:3.3)].

![Chemical structures](attachment:image.png)

Colorless oil; IR (neat) 3360, 2961, 2368, 2327, 1475, 1452, 1229, 1124, 1080, 959, 760 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) E-isomer: δ 7.24–7.14 (m, 1H), 7.14–6.97 (m, 3H), 6.67 (d, $J = 1.2$ Hz, 1H), 4.63 (s, 2H), 3.51 (s, 2H), 2.07 (d, $J = 1.2$ Hz, 3H), 1.36 (s, 6H); Z-isomer: δ 7.43 (dd, $J = 7.5$, 1.2 Hz, 1H), 7.24–7.14 (m, 1H), 7.14–6.97 (m, 2H), 6.60 (d, $J = 1.2$ Hz, 1H), 4.67 (s, 2H), 3.47 (s, 2H), 1.90 (d, $J = 0.2$ Hz, 3H), 1.18 (s, 6H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 153.4, 141.0, 140.5, 140.1, 139.9, 128.6, 127.5, 127.0, 126.5, 126.4, 124.3, 122.5, 122.0, 120.94, 120.90, 116.5, 115.6, 115.5, 115.3, 83.1, 83.0, 77.4, 73.52, 73.49, 65.4, 42.9, 42.5, 24.9, 23.6, 19.0, 16.8; HRMS (FAB) calcd for C$_{16}$H$_{16}$O$_2$ [M+H]$^+$ 243.1385, found 243.1421. The double bond geometry was determined by NOE experiments shown the above structures.

3a,5a-Dimethyl-3,3a,4,5,5a,6-hexahydro-2,7-dioxa-cyclopenta[c]phenanthren-1-one [2i/3i = 14:1, Table 1, entry 11, 57% yield, 96% ee (2i), >99% ee (3i)].

![Chemical structures](attachment:image.png)
Yellow solid; mp 155.7–156.1 °C; [α]25°D +170.9° (acetone, c 0.895, a mixture of 2i (96% ee) and 3i (>99% ee)] IR (neat) 3398, 2954, 2370, 2327, 1769, 1489, 1265, 1222, 1058, 1025, 755 cm⁻¹; 1H NMR (CDCl₃, 300 MHz) 2i: δ 7.72 (dd, J = 7.8, 1.5 Hz, 1H), 7.07 (ddd, J = 7.8, 7.5, 1.5 Hz, 1H), 6.92 (ddd, J = 7.8, 7.5, 1.5 Hz, 1H), 6.83 (dd, J = 7.5, 1.5 Hz, 1H), 4.20 (d, J = 9.3 Hz, 1H), 4.11 (d, J = 10.2 Hz, 1H), 3.97 (d, J = 9.3 Hz, 1H), 3.78 (d, J = 10.2 Hz, 1H), 1.61 (d, J = 4.5 Hz, 1H), 1.56 (d, J = 4.5 Hz, 1H), 1.51 (s, 3H), 1.26 (d, J = 5.4 Hz, 1H), 1.20 (s, 3H), 1.03 (d, J = 5.4 Hz, 1H); 3i: δ 7.07 (ddd, J = 7.8, 7.5, 1.5 Hz, 1H), 6.92 (ddd, J = 7.8, 7.5, 1.5 Hz, 1H), 6.83 (dd, J = 7.5, 1.5 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 4.31 (d, J = 10.2 Hz, 1H), 4.26 (d, J = 10.2 Hz, 1H), 4.09 (d, J = 10.2 Hz, 1H), 3.72 (d, J = 10.2 Hz, 1H), 1.61 (d, J = 4.5 Hz, 1H), 1.58 (s, 3H), 1.56 (d, J = 4.5 Hz, 1H), 1.26 (d, J = 5.4 Hz, 1H), 1.14 (s, 3H), 1.03 (d, J = 5.4 Hz, 1H); 13C NMR (CDCl₃, 75 MHz) δ 152.8, 129.0, 126.1, 126.0, 121.4, 117.6, 71.4, 66.8, 30.2, 29.9, 28.8, 24.1, 24.0, 18.0, 16.5, 14.9; HRMS (ESI) calcd for C₁₇H₁₉O₃ [M+H]+ 293.1154, found 293.1148; CHIRALPAK AD-H, hexane/2-PrOH = 95:5, 1.0 mL/min, retention times: 11.6 min (major cis-isomer), 13.8 min (minor cis-isomer), 14.3 min (minor trans-isomer), and 17.9 min (major trans-isomer).

(+)-5,7,7a,8,9,10-hexahydro-10,11-(N-(4-methylphenylsulfonyl)methanaminomethano)-7a-methyl-Dibenz[c,e]oxepin [(+)2i, Table 1, entry 12, 81% yield, 98% ee].

Yellow solid; mp 118.2–118.4 °C; [α]25°D +12.7° (acetone, c 1.035, 98% ee); IR (neat) 3360, 2925, 2853, 2370, 2326, 1770, 1457, 1340, 1160, 1095, 811, 762, 667 cm⁻¹; 1H NMR (CDCl₃, 300 MHz) δ 7.60 (d, J = 8.1 Hz, 2H), 7.30–7.18 (m, 4H), 7.15–7.10 (m, 1H), 7.02–6.97 (m, 1H), 4.47 (d, J = 13.2 Hz, 1H), 4.11 (d, J = 13.2 Hz, 1H), 4.05 (d, J = 14.4 Hz, 1H), 3.86–3.73 (m, 1H), 3.68 (d, J = 11.7 Hz, 1H), 3.61 (d, J = 11.7 Hz, 1H), 3.40 (d, J = 14.4 Hz, 1H), 2.73–2.60 (m, 2H), 2.43 (s, 3H), 1.92–1.81 (m, 1H), 1.59–1.48 (m, 2H), 1.37–1.20 (m, 1H), 0.83 (s, 3H); 13C NMR (CDCl₃, 75 MHz) δ 143.3, 139.7, 138.6, 136.2, 134.3, 133.8, 129.8, 129.6, 127.83, 127.78, 127.43, 127.37, 84.6, 74.7, 54.0, 50.6, 40.1, 37.3, 35.0, 25.5, 22.8, 21.5; HRMS (ESI) calcd for C₂₅H₂₇NO₃SNa [M+Na]+ 432.1609, found 432.1612; CHIRALPAK AD-H, hexane/2-PrOH = 90:10, 1.0 mL/min, retention times: 20.8 min (major isomer) and 27.3 min (minor isomer).

IV. References

4-Methyl-N-(2-methylallyl)-N-[4-(2-methylallyloxy)but-2-ynyl]benzenesulfonamide (1a)
4-Methyl-N-(3-methylbut-3-enyl)-N-{4-[(2-methylprop-3-enyl)(toluene-4-sulfonyl)amino] but-2-ynyl}benzenesulfonamide (1b)
4-Methyl-N-[4-(2-methylallyloxy)but-2-ynyl]-N-(3-methylbut-3-enyl)benzenesulfonamide (1c)
4-Methyl-N-(2-methylallyl)-N-(3-[2-(2-methylallyloxy)phenyl]prop-2-ynyl)benzenesulfonamide (1d)
N-Allyl-4-methyl-N-\(3-[2-(2\text{methylallyloxy})\text{phenyl}]\text{prop-2-ynyl}\)benzenesulfonamide (1e)
2-Alllyl-2-(3-[2-(2-methylallyloxy)phenyl]prop-2-ynyl)malonic acid diethyl ester (1f)
1-(3-Allyloxyprop-1-ynyl)-2-(2-methylallyloxy)benzene (1g)
1-Allyloxy-2-[3-(2-methylallyloxy)prop-1-ynyl]benzene (1h)
[2-(2-Methylallyloxy)phenyl]propynoic acid 2-methylallyl ester (1i)
\[ \text{N-Allyl-4-methyl-N-}[3-(2-(2-methylallyloxymethyl)phenyl)prop-2-ynyl]benzenesulfonamide (1j)} \]
3a,5a-Dimethyl-7-(toluene-4-sulfonyl)-3,3a,4,5,5a,6,7,8-octahydro-1H-2-oxa-7-aza-as-indacene (2a)
3a,5a-Dimethyl-7-(toluene-4-sulfonyl)-3,3a,4,5,5a,6,7,8-octahydro-1H-2-oxa-7-aza-as-indane (3a)
3a,5a-Dimethyl-2,8-bis-(toluene-4-sulfonyl)-2,3,3a,4,5,5a,6,7,8,9-decahydro-1H-pyrrolo[3,4-h]isoquinoline (2b/3b)
Dimethyl-8-(toluene-4-sulfonyl)-1,3,3a,4,5,5a,6,7,8,9-decahydro-furo[3,4-h]isoquinoline (2c)
3a,5a-Dimethyl-8-(toluene-4-sulfonyl)-1,3,3a,4,5,5a,6,7,8,9-decahydro-furo[3,4-h]isoquinoline (3c)
3a,5a-Dimethyl-2-(toluene-4-sulfonyl)-1,2,3,3a,4,5,5a,6-octahydro-7-oxa-2-azacyclopenta[c]phenanthrene (2d)
5a-Methyl-2-(toluene-4-sulfonyl)-1,2,3,3a,4,5,5a,6-octahydro-7-oxa-2-aza-cyclopenta[c]phenanthrene (2e)
5a-Methyl-3,3a,4,5,5a,6-hexahydro-1H-7-oxacyclopenta[c]phenanthrene-2,2-dicarboxylic acid diethyl ester (2f)
5a-Methyl-3,3a,4,5,5a,6-hexahydro-1\textit{H}-2,7-dioxa-cyclopenta[c]phenanthrene (2g)
4-(4,4-Dimethyldihydrofuran-3-ylidene)-3-methyl-4H-chromene (4)
3a,5a-Dimethyl-3a,3,4,5a,6-hexahydro-2,7-dioxa-cyclopenta[c]phenanthren-1-one (2i/3i)
5,7a,8,9,10-hexahydro-10,11-(N-(4-methylphenylsulfonyl)methaniminomethano)-7a-methyl-Dibenzo[c,e]oxepin (2j)