Supporting Information

Rh-Catalyzed [4 + 2] Carbocyclization of 2-Vinylarylaldehydes with Alkenes and Alkynes Leading to Substituted Tetralones and 1-Naphthols

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I. General

Anhydrous CH₂Cl₂ (No. 27,099-7), and (CH₂Cl)₂ (No. 28,450-5) were obtained from Aldrich and used as received. Solvents for the synthesis of substrates were dried over Molecular Sieves 4A (Wako) prior to use. 2-Vinylbenzaldehyde (4a),¹ alkene 2b,² and alkene 2c³ were prepared according to the literatures. All 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 Vinylarylaldehydes

2-Vinynaphthalene-1-carbaldehyde (4b)

\[ \text{O} \]

\[ \text{H} \]

\[ n-\text{BuLi} \text{ (1.58 M in hexane, 1.20 mL, 1.87 mmol) was added to a stirred solution of methyl triphenyl phosphonium iodide (800 mg, 2.00 mmol) in THF (15 mL) at } -78 \degree \text{C, and the resulting mixture was stirred at } -78 \degree \text{C for 1 h. The resulting solution was added dropwise to a stirred solution of 1-bromonaphthalene-2-carbaldehyde (400 mg, 1.70 mmol) at } -78 \degree \text{C, and the mixture was gradually warmed to rt. The reaction was quenched with water and extracted with Et₂O. The organic layer was washed with NaHCO₃ and brine, dried over Na₂SO₄, and concentrated. The residue was purified by silica gel column chromatography (hexane:EtOAc = 20:1), which furnished 1-bromo-2-vinynaphthalene (234 mg, 1.00 mmol, 56% yield).} \]

To a cooled (−78 °C) THF (10 mL) solution of 1-bromo-2-vinynaphthalene (124 mg, 0.532 mmol) was added n-BuLi (1.58 M in hexane, 0.34 mL, 0.532 mmol). After stirring at −65 °C for 1 h, a THF (5 mL) solution of DMF (77.8 mg, 1.06 mmol) was added, and the resulting solution was stirred overnight with gradual warming to rt. The reaction was quenched with water and extracted with Et₂O. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by silica gel column
chromatography (hexane:EtOAc = 30:1), which furnished 4b (40.4 mg, 0.222 mmol, 42% yield) as a pale yellow oil.

IR (neat) 1680, 1061, 921, 828, 758 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 10.71 (s, 1H), 8.84 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.7 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.55–7.37, (m, 3H), 7.32 (dd, J = 17.4, 11.1 Hz, 1H), 5.65–5.51 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 193.4, 141.9, 134.0, 133.7, 132.9, 130.7, 128.8, 128.2, 128.1, 126.5, 125.1, 125.0, 121.7; HRMS (EI) calcd for C₁₃H₁₀O [M]⁺ 182.0732, found 182.0693.

1-Vinylnaphthalene-2-carbaldehyde (4c)

![structure](image)

To a toluene (15 mL) solution of Pd(PPh₃)₄ (44.2 mg, 0.038 mmol) was added 1-bromonaphthalene-2-carbaldehyde (300 mg, 1.28 mmol) and tributylvinylstannane (487 mg, 1.54 mmol) and the resulting solution was refluxed for 12 h. The reaction was quenched with water and extracted with Et₂O. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by silica gel column chromatography (hexane:EtOAc = 40:1), which furnished 4c (233 mg, 1.28 mmol, 99% yield) as a pale red oil.

IR (KBr) 2883, 1673, 949, 825, 752 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 10.46 (s, 1H), 8.19 (dd, J = 8.1, 0.9 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 7.90–7.80 (m, 2H), 7.67–7.53 (m, 2H), 7.39 (dd, J = 17.4, 11.4 Hz, 1H), 6.01 (dd, J = 11.4, 1.5 Hz, 1H), 5.49 (dd, J = 17.4, 1.5 Hz 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 192.6, 143.3, 135.7, 131.5, 131.3, 130.6, 128.8, 128.5, 128.0, 126.9, 126.0, 125.8, 122.9; HRMS (EI) calcd for C₁₃H₁₀O [M]⁺ 182.0732, found 182.0722.

### III. Intermolecular [4 + 2] Carbocyclizations

**General procedure for reactions of 4 and 2 (Table 2, entry 1).** A CH₂Cl₂ (0.3 mL) solution of (R,S)-10 (19.2 mg, 0.030 mmol) was added to a CH₂Cl₂ (0.3 mL) solution of [Rh(cod)₂]BF₄ (12.2 mg, 0.030 mmol) and the mixture was stirred for 5 min. H₂ was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 0.5 h, the resulting solution was concentrated to dryness and dissolved in CH₂Cl₂ (0.5 mL). To this solution was added a CH₂Cl₂ (1.0 mL) solution of 4a (39.6 mg, 0.300 mmol) and 2a (32.7 mg, 0.330 mmol), and washed remaining substrate away by using CH₂Cl₂ (1.5 mL). The mixture was stirred at rt for 48 h. The resulting solution was concentrated and purified by preparative TLC (hexane:EtOAc = 1:1), which furnished 5aa (53.7 mg, 0.232 mmol, 77% yield, 64% ee) as a colorless oil.
(+)-1-Methyl-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid dimethylamide [(+)-5aa]

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\text{Me} \quad \text{O} \quad \text{NMe}_2
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[\alpha]^{25}_D +36.0^\circ \text{ (c 0.980, CHCl}_3, \text{ 64% ee)}; \text{ IR (neat) 2963, 2932, 1685, 1638, 771 cm}^{-1}; ^1H \text{ NMR (CDCl}_3, 300 MHz) \delta 8.04 \text{ (d, } J = 7.8 \text{ Hz, 1H), 7.54 \text{ (t, } J = 7.5 \text{ Hz, 1H), 7.44–7.26 \text{ (m, 2H), 3.43 \text{ (quint, } J = 6.9 \text{ Hz, 1H), 3.33 \text{ (dd, } J = 9.9, 6.9, 4.2 \text{ Hz, 1H), 3.11 \text{ (s, 3H), 2.99 \text{ (s, 3H), 2.89 \text{ (dd, } J = 17.1, 9.9 \text{ Hz, 1H), 2.74 \text{ (dd, } J = 17.1, 4.2 \text{ Hz, 1H), 1.41 \text{ (d, } J = 6.9 \text{ Hz, 3H); } ^13\text{C NMR (CDCl}_3, 75 MHz) } \delta 196.3, 172.9, 146.1, 133.9, 131.4, 127.2, 126.8, 126.7, 44.0, 39.9, 37.4, 35.8, 35.5, 19.5; \text{ HRMS (EI) calcd for } C_{40}H_{37}NO_2 [M–CONMe}_2]^{+} 159.0810, \text{ found 159.0793; CHIRALCEL OD-H, Hexane:i-PrOH = 90:10, 1.0 mL/min, retention times: 10.1 min (major isomer) and 13.4 min (minor isomer).}
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(+)-1-Methyl-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid diisopropylamide [(+)-5ab]

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\text{Me} \quad \text{O} \quad \text{Ni-Pr}_2
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Reaction time: 24 h; Pale yellow oil; [\alpha]^{25}_D +54.4^\circ \text{ (c 1.255, CHCl}_3, \text{ 66% ee); IR (neat) 2967, 2933, 1686, 1633, 1443, 1311 cm}^{-1}; ^1H \text{ NMR (CDCl}_3, 300 MHz) \delta 8.04 \text{ (d, } J = 7.8 \text{ Hz, 1H), 7.54 \text{ (t, } J = 7.8 \text{ Hz, 1H), 7.40 \text{ (d, } J = 7.8 \text{ Hz, 1H), 7.38–7.25 \text{ (m, 1H), 4.05 \text{ (quint, } J = 6.6 \text{ Hz, 1H), 3.75–3.27 \text{ (m, 2H), 3.24–3.08 \text{ (m, 1H), 2.94 \text{ (dd, } J = 16.8, 11.1 \text{ Hz, 1H), 2.69 \text{ (dd, } J = 16.8, 3.9 \text{ Hz, 1H), 1.44–1.32 \text{ (m, 9H), 1.30–1.19 \text{ (m, 6H); } ^13\text{C NMR (CDCl}_3, 75 MHz) } \delta 196.6, 171.7, 146.6, 133.9, 131.4, 126.9, 126.8, 126.4, 48.2, 46.0, 45.7, 41.1, 35.6, 21.4, 21.2, 20.6, 20.3, 18.8; \text{ HRMS (EI) calcd for } C_{40}H_{37}NO_2 [M]^{+} 287.1885, \text{ found 287.1900; CHIRALPAK AD-H, Hexane:i-PrOH = 98:2, 1.0 mL/min, retention times: 27.2 min (minor isomer) and 30.9 min (major isomer).}
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(+)-4-Methyl-3-(pyrrolidine-1-carbonyl)-3,4-dihydro-2H-naphthalen-1-one [(+)-5ac]

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\text{Me} \quad \text{O} \quad \text{N}\text{Me}
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Reaction temperature: 80 °C; Reaction time: 48 h; Colorless oil; [\alpha]^{25}_D +36.3^\circ \text{ (c 2.495, CHCl}_3, \text{ 68% ee); IR (neat) 2925, 2872, 1685, 1635, 1438 cm}^{-1}; ^1H \text{ NMR (CDCl}_3, 300 MHz)
δ 8.04 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.40–7.30 (m, 2H), 3.57–3.38 (m, 5H), 3.13–3.04 (m, 1H), 2.94 (dd, J = 16.5, 10.8 Hz, 1H), 2.75 (dd, J = 16.5, 3.6 Hz, 1H), 2.08–1.82 (m, 4H), 1.41 (d, J = 6.6 Hz, 3H); 13C NMR (CDCl3, 75 MHz) δ 196.5, 171.3, 146.3, 133.9, 131.4, 127.0, 126.8, 126.6, 46.7, 46.6, 45.8, 40.2, 35.3, 26.1, 24.2, 19.0; HRMS (EI) calcd for C16H14NO2 [M]+ 257.1416, found 257.1410; CHIRALCEL OD-H, Hexane:i-PrOH = 90:10, 1.0 mL/min, retention times: 21.3 min (major isomer) and 30.2 min (minor isomer).

(+)-1-Methyl-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid tert-butyl ester [(+)-5ad]

![Chemical structure](image)

Reaction time: 36 h; Colorless oil; [α]25D +4.4° (c 1.080, CHCl3, 70% ee); IR (neat) 2975, 2932, 1725, 1368, 1298, 1153 cm⁻¹; 1H NMR (CDCl3, 300 MHz) δ 8.60–7.98 (m, 1H), 7.56–7.46 (m, 1H), 7.36–7.26 (m, 2H), 3.50–3.38 (m, 1H), 2.98–2.80 (m, 3H), 1.44 (d, J = 6.9 Hz, 3H) 1.31 (s, 9H); 13C NMR (CDCl3, 75 MHz) δ 195.7, 172.7, 146.1, 133.8, 131.3, 127.8, 126.9, 126.8, 81.3, 47.5, 37.4, 35.9, 27.7, 21.0; HRMS (EI) calcd for C16H20O3 [M–Or-Bu]⁺ 187.0759, found 187.0716; CHIRALPAK AD, Hexane:i-PrOH = 95:5, 1.0 mL/min, retention times: 6.4 min (minor isomer) and 7.6 min (major isomer).

(+)-1-Methyl-4-oxo-1,2,3,4-tetrahydrophenanthrene-2-carboxylic acid dimethylamide [(+)-5ba]

![Chemical structure](image)

Reaction time: 48 h; Pale yellow solid; [α]25D +12.5° (c 1.080, CHCl3, 46% ee); Mp 131–132 °C; IR (KBr) 2963, 2932, 1663, 1631, 835, 754 cm⁻¹; 1H NMR (CDCl3, 300 MHz) δ 9.41 (d, J = 8.7 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.68–7.54 (m, 1H), 7.52–7.45 (m, 2H), 3.63 (quint, J = 6.9 Hz, 1H), 3.37–3.25 (m, 1H), 3.14 (s, 3H), 3.18–2.94 (m, 4H), 2.86 (dd, J = 15.9, 4.5 Hz, 1H), 1.48 (d, J = 6.9 Hz, 3H); 13C NMR (CDCl3, 75 MHz) δ 198.3, 172.9, 148.2, 134.7, 132.5, 130.7, 128.8, 128.1, 126.7, 126.2, 126.0, 125.3, 43.6, 41.3, 37.4, 36.8, 35.8, 20.9; HRMS (EI) calcd for C18H17NO2 [M–CONMe2]⁺ 209.0967, found 209.0927; CHIRALPAK AS, Hexane:i-PrOH = 95:5, 1.0 mL/min, retention times: 39.7 min (major isomer) and 47.4 min (minor isomer).

General procedure for reactions of 4a and 11 (Table 4, entry 1). A CH2Cl2 (0.3 mL)
solution of dppp (12.4 mg, 0.030 mmol) was added to a CH₂Cl₂ (0.3 mL) solution of [Rh(cod)₂]BF₄ (12.2 mg, 0.030 mmol) and the mixture was stirred for 5 min. H₂ was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 0.5 h, the resulting solution was concentrated to dryness and dissolved in CH₂Cl₂ (0.3 mL). To this solution was added a CH₂Cl₂ (0.4 mL) solution of 4a (39.6 mg, 0.300 mmol) and 11a (99.8 mg, 0.600 mmol), and washed remaining substrate away by using CH₂Cl₂ (0.3 mL). The mixture was stirred at rt for 36 h. The resulting solution was concentrated and purified by preparative TLC (hexane:EtOAc = 8:1), which furnished 12a (46.9 mg, 0.157 mmol, 52% yield) as a pale yellow solid.

2-Decyl-4-methynaphthalen-1-ol (12a)

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\text{OH} \quad n-C_{10}H_{21} \quad \text{Me}
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Mp 48–49 °C; IR (KBr) 3266, 2954, 2918, 2848, 752 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 8.16–8.13 (m, 1H), 7.91–7.87 (m, 1H), 7.48–7.45 (m, 2H), 7.01 (s, 1H), 5.02 (s, 1H), 2.68 (t, J = 6.9 Hz, 2H), 2.59 (s, 3H), 1.65 (quint, J = 6.9 Hz, 2H), 1.42–1.15 (m, 14H), 0.90–0.85 (m, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 146.5, 132.0, 128.7, 126.2, 125.2, 124.9, 124.7, 124.1, 121.5, 120.8, 31.9, 30.2, 30.0, 29.61, 29.60, 29.58, 29.56, 29.3, 22.7, 18.8, 14.1; HRMS (EI) calcd for C₂₃H₂₁O [M⁺] 298.2297, found 298.2284.

2-(3-Chloropropyl)-4-methynaphthalen-1-ol (12b)

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\text{OH} \quad \text{Cl} \quad \text{Me}
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Reaction time: 36 h; Orange oil; IR (neat) 3312, 2957, 2867, 1634, 1388, 1096, 755 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 8.16–8.11 (m, 1H), 7.92–7.87 (m, 1H), 7.51–7.46 (m, 2H), 7.05 (s, 1H), 5.32 (s, 1H), 3.55 (t, J = 6.9 Hz, 2H), 2.90 (t, J = 6.9 Hz, 2H), 2.58 (s, 3H), 2.13 (quint, J = 6.9 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 147.1, 132.3, 128.5, 126.6, 125.5, 125.1, 124.84, 124.80, 121.5, 118.9, 44.6, 32.7, 26.4, 18.7; HRMS (EI) calcd for C₁₄H₁₅ClO [M⁺] 234.0811, found 234.0788.

2-Benzyl-4-methynaphthalen-1-ol (12c)
Reaction time; 36 h; Pale yellow solid; Mp 72–73 °C; IR (KBr) 3278, 1385, 1091, 752, 701 cm⁻¹; 'H NMR (CDCl₃, 300 MHz) δ 8.18–8.06 (m, 1H), 7.96–7.85 (m, 1H), 7.55–7.40 (m, 2H), 7.35–7.15 (m, 5H), 7.10 (s, 1H), 4.99 (s, 1H), 4.09 (s, 2H), 2.58 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 147.4, 139.4, 132.5, 129.3, 128.8, 128.5, 126.6, 126.5, 125.5, 125.1, 125.0, 124.2, 121.6, 119.4, 36.6, 18.7; HRMS (EI) calcd for C₁₈H₁₆O [M⁺] 248.1201, found 248.1218.

**4-Methyl-2-phenynaphthalen-1-ol (12d)**

Reaction time: 12 h; Yellow oil; IR (neat) 3545, 3061, 1386, 1052, 759 cm⁻¹; 'H NMR (CDCl₃, 300 MHz) δ 8.37–8.26 (m, 1H), 7.98–7.89 (m, 1H), 7.58–7.46 (m, 6H), 7.45–7.36 (m, 1H), 7.19 (s, 1H), 5.70 (s, 1H), 2.63 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 146.2, 137.5, 133.0, 129.5, 129.3, 127.9, 127.7, 126.3, 126.2, 125.2, 124.5, 124.0, 122.9, 120.6, 18.7; HRMS (EI) calcd for C₁₇H₁₄O [M⁺] 234.1045, found 234.1003.

**4-Methyl-2-(4-trifluoromethylphenyl)naphthalen-1-ol (12e)**

Reaction time: 12 h; Pale yellow solid; Mp 54–55 °C; IR (KBr) 3265, 1616, 1323, 844, 759 cm⁻¹; 'H NMR (CDCl₃, 300 MHz) δ 8.34–8.25 (m, 1H), 8.00–7.90 (m, 1H), 7.75 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.60–7.50 (m, 2H), 7.16 (s, 1H), 5.51 (s, 1H), 2.63 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 146.3, 141.49, 141.48, 133.3, 129.7, 127.4, 126.8, 126.7, 126.3(q), 125.5, 124.6, 124.1, 122.7, 122.3, 119.5, 18.7; HRMS (EI) calcd for C₁₈H₁₅F₃O [M⁺] 302.0918, found 302.0883.

**2-(2-Methoxyphenyl)-4-methynaphthalen-1-ol (12f)**
Reaction time: 12 h; Pale yellow solid; Mp 108–109 °C; IR (KBr) 3357, 3067, 1229, 1043, 760 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 8.46–8.37 (m, 1H), 7.97–7.87 (m, 1H), 7.58–7.46 (m, 2H), 7.46–7.33 (m, 2H), 7.22 (s, 1H), 7.14 (dt, J = 7.5, 1.2 Hz, 1H), 7.06 (d, J = 8.4 Hz, 1H), 6.74 (s, 1H), 3.89 (s, 3H), 2.63 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 155.4, 144.7, 133.1, 132.7, 129.2, 129.0, 127.5, 126.3, 126.2, 125.8, 125.1, 123.8, 123.4, 122.2, 118.6, 111.7, 56.3, 18.8; HRMS (El) calcd for C₁₈H₁₆O₂ [M]⁺ 264.1150, found 264.1109.

4-Oxooct-6-enoic acid dimethylamide (13)

Colorless oil; IR (neat) 2920, 1715, 1647, 1399, 967 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 5.65–5.48 (m, 2H), 3.22–3.15 (m, 2H), 3.03 (s, 3H), 2.93 (s, 3H), 2.77 (t, J = 6.6 Hz, 2H), 2.59 (t, J = 6.6 Hz, 2H), 1.75–1.64 (m, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 208.8, 171.6, 129.7, 123.0, 46.9, 37.1, 36.8, 35.5, 27.1, 18.0; HRMS (El) calcd for C₁₀H₁₇NO₂ [M]⁺ 183.1259, found 183.1264.

IV. References

2-Vinylnapthalene-1-carbaldehyde (4b)
1-Vinynaphthalene-2-carbaldehyde (4c)
1-Methyl-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid dimethylamide (5aa)
1-Methyl-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid diisopropylamide (5ab)
4-Methyl-3-(pyrrolidine-1-carbonyl)-3,4-dihydro-2H-naphthalen-1-one (5ac)
1-Methyl-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid tert-butyl ester (5ad)
1-Methyl-4-oxo-1,2,3,4-tetrahydrophenanthrene-2-carboxylic acid dimethylamide (5ba)
2-Decyl-4-methylnaphthalen-1-ol (12a)
2-(3-Chloropropyl)-4-methylnaphthalen-1-ol (12b)
2-Benzyl-4-methylnaphthalen-1-ol (12c)
4-Methyl-2-phenynaphthalen-1-ol (12d)
4-Methyl-2-(4-trifluoromethylphenyl)naphthalen-1-ol (12e)
2-(2-Methoxyphenyl)-4-methylnaphthalen-1-ol (12f)
4-Oxooct-6-enoic acid dimethylamide (13)