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SYNTHESIS OF PHENOL AND NAPHTHOL DERIVATIVES FROM FURFURAL†

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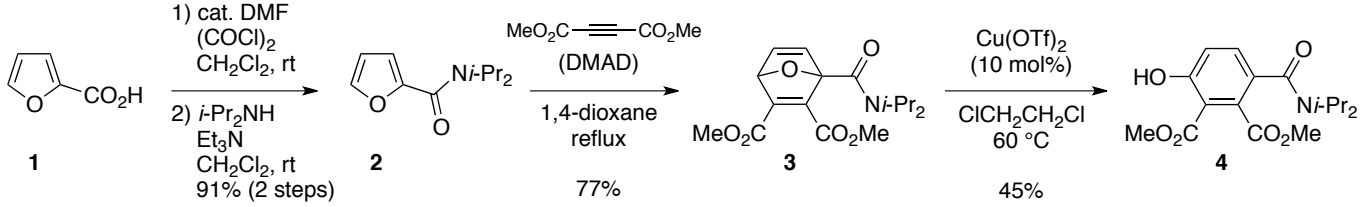
†This paper is dedicated to Professor Dr. Kiyoshi Tomioka on celebration of his 70th birthday.

Abstract – Synthesis of phenol and naphthol derivatives was performed from furfural derivatives through cycloaddition with an alkyne and benzyne, respectively. Lewis acid-promoted ring opening of the cycloadducts led to the formation of the corresponding phenol and naphthol derivatives. Amide-directed C–H alkenylation and arylation gave functionalized π-conjugated naphthalene derivatives.

Benzene and naphthalene are basic constituents of π-conjugated functional materials.[1] These aromatic compounds have been obtained mainly by fossil oil. Recently, tremendous efforts have been devoted to production of biomass-derived aromatic compounds; however, the lack of a reliable synthetic method has hampered its widespread use. Among plant-derived compounds, furfural (2-formylfuran) is attracting a great deal of attention as a non-edible biomass.[2] This compound is readily obtained from xylose and contains the reactive furan and aldehyde moieties. Several research groups have utilized furfural as a starting material for the synthesis of resins,[3] pesticides,[4] and fuels[5] by transformation of the furan ring. In our previous work, we converted the formyl group in furfural to thiazole, oxazole, and benzoxazole for the synthesis of novel π-extended furan derivatives.[6] Herein, we report the construction of phenol and naphthol frameworks from furfural derivatives by cycloaddition with DMAD and benzyne followed by Lewis acid-promoted ring opening of the oxabicyclic cycloadducts. In addition, an alkenyl group or an aryl group was introduced by the amide-directed rhodium-catalyzed C–H functionalization to provide π-conjugated naphthalene derivatives.

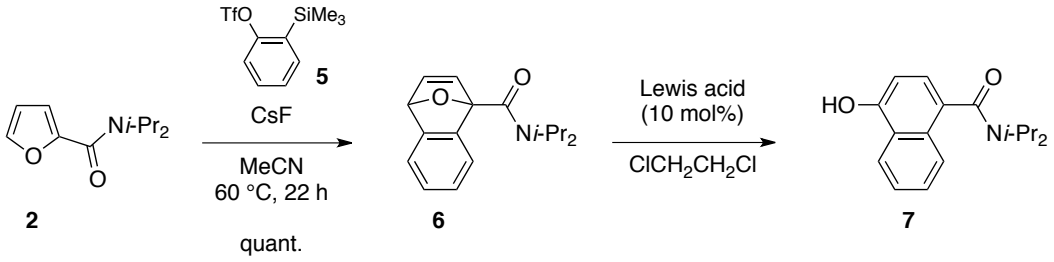
We first investigated the formation of the phenol ring from commercially available and inexpensive furan carboxylic acid **1**, which is obtained by oxidation of furfural. Because an amide moiety on an aromatic ring is effective for the transition metal-catalyzed aromatic C–H functionalization[7] and transformed to various functional groups,[8] we converted carboxylic acid **1** to the corresponding diisopropylamide **2** through the corresponding acid chloride in 91% yield over 2 steps (Scheme 1). The furan derivative underwent the key cycloaddition when DMAD[9] (dimethyl acetylenedicarboxylate) was used as a dienophile to provide oxabicyclic compound **3** in 77% yield. Subsequent ring opening was performed in the presence of catalytic $Cu(OTf)_2$[10] as a Lewis acid under the heating conditions, which led to the formation of the functionalized phenol **4** in 45% yield in a regioselective manner.



Scheme 1. Formation of a functionalized phenol through cycloaddition of a furyl amide and DMAD

Having found the suitable Lewis acid for the ring opening of oxabicyclic compound **3** bearing the amide moiety, we then applied the method to a benzo-fused system.[11] A mixture of furyl amide **2** and benzyne precursor **5**[12] in acetonitrile was treated with CsF at 60 °C to provide the desired adduct **6** in quantitative yield. With this compound in hand, we examined the optimal reaction conditions using $Cu(OTf)_2$. After the reaction mixture was heated at 80 °C for 20 h, the starting cycloadduct **6** was completely consumed. But, several unidentified byproducts were observed and none of the desired naphthol **7** was isolated (Table 1, entry 1). A lower reaction temperature (40 °C) provided naphthol **7**, albeit in low yield with recovery of cycloadduct **6** (entry 2). The yield of the desired product **7** was significantly reduced at room temperature (entry 3). Switching the Lewis acid to AgOTf[13] improved the yield of the product even at elevated temperature. While the reaction was performed in the presence of AgOTf at 40 °C for 4 days to provide naphthol **7** in 39% yield, the yield was increased to 85% at 60 °C for the same reaction time (entries 4 and 5). In addition, we also conducted the same reaction at 70 °C and 80 °C and found that starting cycloadduct **6** was consumed within 24 h to give the corresponding naphthol **7** in comparable yields (entries 6 and 7).

Table 1. Lewis acid-promoted ring opening of benzo-fused oxabicyclic compound

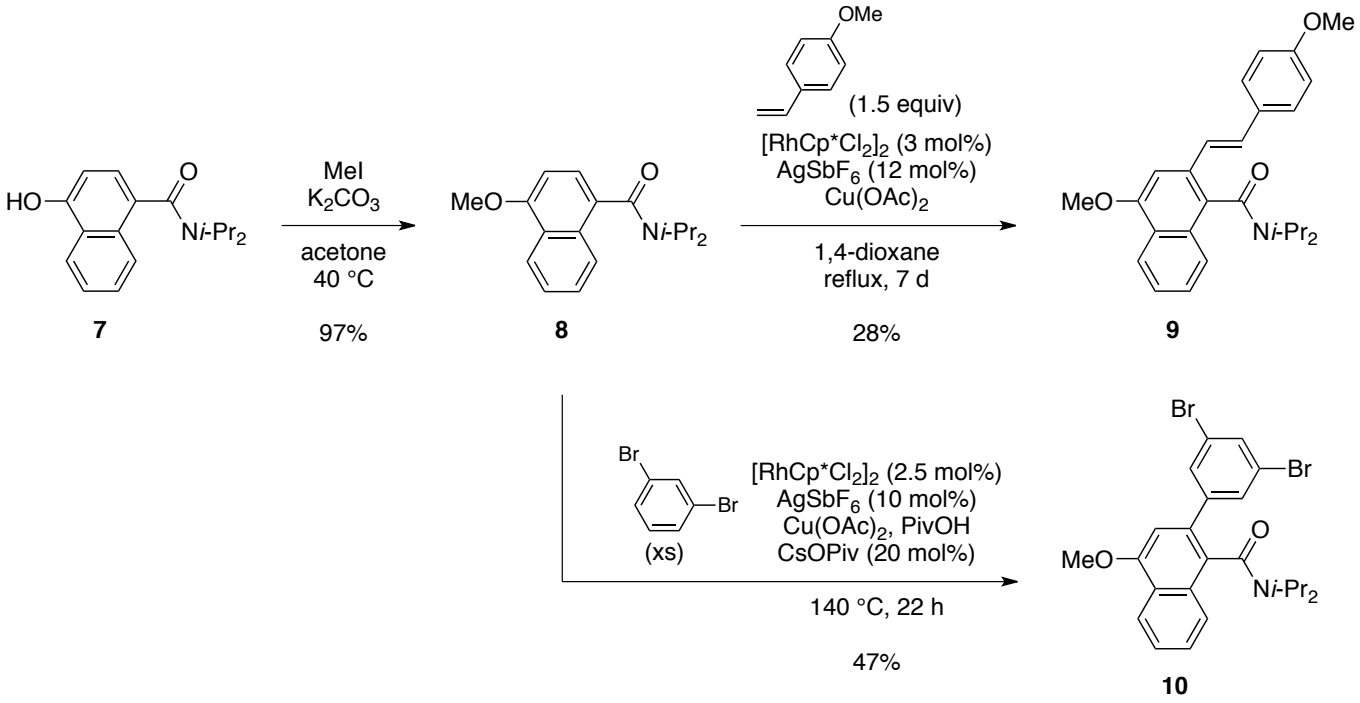


entry	Lewis acid	temperature (°C)	reaction time	yield [%][a]
1	$Cu(OTf)_2$	80	20 h	–[b]
2	$Cu(OTf)_2$	40	22 h	27
3	$Cu(OTf)_2$	rt	7 d	–[c]
4	AgOTf	40	4 d	39
5	AgOTf	60	4 d	85
6	AgOTf	70	24 h	79
7	AgOTf	80	24 h	86

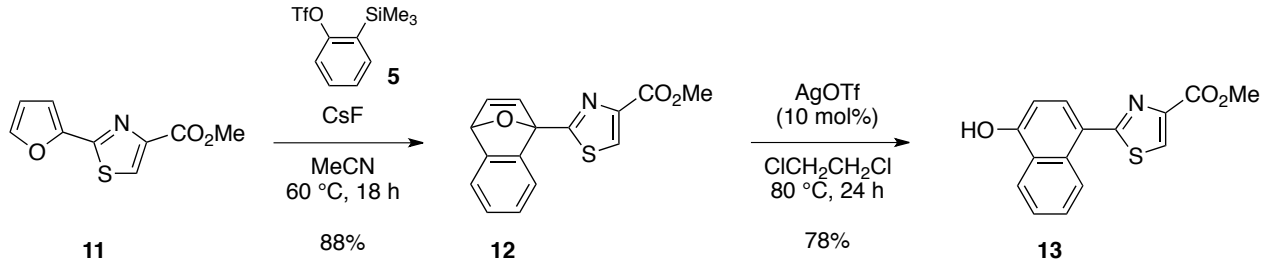
[a] Isolated yield. [b] Complex mixture. [c] Trace (<5%).

The naphthol derivative **7** thus obtained was converted to its methyl ether **8** for the amide-directed C–H functionalization (Scheme 2). Subjection of naphthalene **8** to the reported Rh-catalyzed conditions[14] yielded the desired π-conjugated coupling product **9** in 28% yield. In addition to the styryl group, an aryl group was introduced under the modified conditions. The use of excess amount of 1,3-dibromobenzene resulted in the formation of the corresponding product **10** in moderate yield. The two bromo groups can be converted to various functional groups.

The established method proved to be effective for the synthesis of thiazole-conjugated naphthalene **13**, because thiazole unit is contained in fluorescent materials and serves as a good directing group for C–H arylation[15] (Scheme 3). Thus, the known furylthiazole **11**,[6,16] which was synthesized from furfural in our group, underwent the cycloaddition smoothly to provide the adduct **12** in 88% yield. Catalytic AgOTf facilitated subsequent ring opening of the oxabicyclic structure to give thiazole-conjugated naphthalene **13** in 78% yield.



Scheme 2. Rhodium-catalyzed C–H functionalization using an amide as a directing group



Scheme 3. Synthesis of thiazole-conjugated naphthol

In summary, synthesis of phenol and naphthol derivatives was achieved from the biomass-derived furfural derivatives through cycloaddition with DMAD and benzyne. AgOTf proved to be effective for the ring opening of the benzo-fused cycloadducts bearing the electron-withdrawing amide group. The resulting naphthol derivative underwent the amide-directed C–H functionalization to give functionalized π-conjugated naphthalene derivatives. The established method was also applicable to the synthesis of the thiazole-conjugated naphthol.

EXPERIMENTAL

General Remarks: Analytical thin layer chromatography (TLC) was performed on Merck 60 F_{254} aluminum sheets precoated with a 0.25 mm thickness of silica gel. Melting points (mp) were measured on

a Yanaco MP-J3 and are uncorrected. Infrared (IR) spectra were recorded on a Bruker Alpha with an ATR attachment (Ge) and are reported in wave numbers (cm^{-1}). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on a JEOL ECZ400 spectrometer. Chemical shifts for ^{1}H NMR are reported in parts per million (ppm) downfield from tetramethylsilane with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 ppm, tetramethylsilane: δ 0 ppm) and coupling constants are in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, and br = broad. Chemical shifts for ^{13}C NMR are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm). High-resolution mass spectra (HRMS) were performed on a JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. Unless otherwise stated, all reactions were conducted in flame-dried glassware under an inert atmosphere of nitrogen. All work-up and purification procedures were carried out with reagent-grade solvents in air. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Flash column chromatography was performed on Wakogel® C-300 (45–75 μm, Wako Pure Chemical Industries, Ltd.). Recycling preparative SEC-HPLC was performed with LC-9201 (Japan Analytical Industry Co., Ltd.) equipped with preparative SEC columns (JAI-GEL-1H and JAI-GEL-2H). Anhydrous THF was purchased from Wako Pure Chemical Industries, Ltd.

***N*,*N*-Diisopropylfuran-2-carboxamide (2):** A 200-mL round bottomed flask equipped with a Teflon-coated magnetic stirring bar was charged with 2-furancarboxylic acid (**1**) (1.12 g, 10.0 mmol, 1.0 equiv), 1,2-dichloroethane (33 mL), oxalyl chloride (943 μL, 11 mmol, 1.1 equiv), and DMF (5 drops) at 0 °C. The solution was warmed to room temperature and stirred for 1 h. After removal of the solvent, the resulting acid chloride was used directly to the next reaction. A 200-mL round bottomed flask equipped with a Teflon-coated magnetic stirring bar, a three-way cock, and a rubber septum was charged with the crude acid chloride and 1,2-dichloroethane (25 mL) under nitrogen atmosphere. After cooling to 0 °C, the solution was treated with a 1,2-dichloroethane solution (10 mL) of diisopropylamine (1.69 mL, 12 mmol, 1.2 equiv) and Et_3N (1.80 mL, 13 mmol, 1.3 equiv). The resulting mixture was stirred at room temperature for 2 h, at which time the reaction mixture was treated with 1 M hydrochloric acid. After partitioned, the aqueous layer was extracted twice with Et_2O. The combined organic extracts were washed twice with hydrochloric acid, saturated aqueous sodium hydrogen carbonate, brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/Et_2O = 5:1) to afford the corresponding amide **2** (1.77 g, 9.08 mmol, 91% over 2 steps) as a colorless oil. IR (ATR, cm^{-1}): 1622, 1486, 1436, 1372, 1331, 1197, 1159, 1037, 1009, 814, 754, 617, 597 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45–7.40 (m, 1H), 6.83

(dd, *J* = 3.2, 1.2 Hz, 1H), 6.44 (dd, *J* = 3.2, 2.0 Hz, 1H), 4.60–3.41 (br, 2H), 1.38 (br, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.1, 149.3, 142.7, 113.7, 110.7, 48.1, 20.7; HRMS (DART$^+$) Calcd for $C_{11}H_{18}NO_2$ $[M+H]^+$: 196.1338; found: *m/z* 196.1344.

Dimethyl 1-(diisopropylcarbamoyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (3). A 20-mL Schlenk tube with a Teflon-coated magnetic stirring bar and a rubber septum was charged with furan **2** (383 mg, 1.96 mmol, 1.0 equiv), 1,4-dioxane (2 mL), and DMAD (0.31 mL, 2.1 mmol, 1.1 equiv) under nitrogen atmosphere. The solution was heated at reflux for 24 h, at which time the reaction mixture was treated with water. After partitioned, the aqueous layer was extracted twice with Et_2O. The combined organic extracts were washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/Et_2O = 3:2) to afford the corresponding cycloadduct **3** (510 mg, 1.51 mmol, 77%) as a colorless solid. Mp 89–91 °C; IR (ATR, cm^{-1}): 1737, 1720, 1635, 1433, 1316, 1255, 1202, 1124, 966, 789, 773, 684; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57 (d, *J* = 5.6 Hz, 1H), 7.16 (dd, *J* = 5.6, 2.0 Hz, 1H), 5.74 (d, *J* = 2.0 Hz, 1H), 4.52–4.40 (m, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.50–3.36 (m, 1H), 1.44 (d, *J* = 6.4 Hz, 3H), 1.43 (d, *J* = 6.4 Hz, 3H), 1.12 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.4, 162.9, 162.5, 155.6 150.0, 144.8, 142.1, 97.3, 85.0, 52.4, 52.3, 48.6, 46.6, 20.9, 20.3, 20.1, 20.0; HRMS (DART$^+$) Calcd for $C_{17}H_{24}NO_6$ $[M+H]^+$: 338.1604; found: *m/z* 338.1615.

Dimethyl 3-(diisopropylcarbamoyl)-6-hydroxyphthalate (4): A 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with **3** (169 mg, 0.501 mmol, 1.0 equiv), $Cu(OTf)_2$ (18 mg, 0.050 mmol, 10 mol%), and 1,2-dichloroethane (5 mL) under nitrogen atmosphere. The resulting mixture was stirred at 60 °C for 46 h. After cooling to room temperature, the reaction mixture was treated with water. After partitioned, the aqueous layer was extracted twice with $CHCl_3$. The combined organic extracts were washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/Et_2O = 3:2, gradient) to afford phenol **4** (75.8 mg, 0.225 mmol, 45%) as a colorless solid. Mp 146–148 °C; IR (ATR, cm^{-1}): 3209, 2970, 2927, 1743, 1727, 1611, 1583, 1475, 1446, 1371, 1350, 1307, 1255, 1233, 1208, 1105, 1015; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.81 (br s, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 3.81–3.69 (m, 1H), 3.56–3.36 (m, 1H), 1.57–1.40 (m, 6H), 1.24–1.07 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.2, 168.0, 167.9, 161.0, 133.4, 131.5, 129.6, 119.1, 110.6, 53.1, 52.6, 51.3, 45.9, 20.3 (CH_3 x 4); HRMS (DART$^+$) Calcd for $C_{17}H_{24}NO_6$ $[M+H]^+$: 338.1604; found: *m/z* 338.1610.

***N*,*N*-Diisopropyl-1,4-epoxynaphthalene-1(4*H*)-carboxamide (6):** A 50-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with **2** (583 mg, 3.0 mmol, 1.0 equiv), cesium fluoride (1.64 g, 10.8 mmol, 3.6 equiv), **5** (874 μL, 3.6 mmol, 1.2 equiv) and MeCN (3 mL) under nitrogen atmosphere. The solution was stirred at 60 °C for 22 h, at which time the reaction mixture was treated with brine. After partitioned, the aqueous layer was extracted twice with Et_2O. The combined organic extracts were washed with water, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane to hexane/Et_2O = 1:1, gradient) to afford the corresponding cycloadduct **6** (846 mg, quant) as a colorless solid. Mp 92–94 °C; IR (ATR, cm^{-1}): 1629, 1477, 1469, 1453, 1356, 1203, 1018, 768, 747, 718, 645, 613; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (d, *J* = 5.2 Hz, 1H) 7.33–7.29 (m, 1H), 7.28–7.23 (m, 1H), 7.04–6.94 (m, 3H), 5.77 (d, *J* = 2.0 Hz, 1H), 4.57–4.45 (m, 1H), 3.52–3.39 (m, 1H), 1.57 (d, *J* = 6.8 Hz, 3H), 1.50 (d, *J* = 6.8 Hz, 3H), 1.10 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.3, 149.1, 148.5, 144.8, 141.7, 125.5, 125.1, 120.4, 120.2, 93.4, 83.2, 48.2, 46.7, 20.9 (CH_3 x 2), 20.33, 20.30; HRMS (DART$^+$) Calcd for $C_{17}H_{22}NO_2$ $[M+H]^+$: 272.1651; found: *m*/*z* 272.1660.

4-Hydroxy-*N*,*N*-diisopropyl-1-naphthamide (7): A 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with **6** (271.4 mg, 1.0 mmol, 1.0 equiv) and 1,2-dichloroethane (10 mL) under nitrogen atmosphere. AgOTf (25.7 mg, 0.10 mmol, 10 mol%) was added to the Schlenk tube and the resulting mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with THF (5 mL) and filtered through a pad of celite. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by trituration with hexane to afford naphthol **7** (232 mg, 0.855 mmol, 86%) as a colorless solid. Mp 237–240 °C; IR (ATR, cm^{-1}): 1597, 1578, 1447, 1371, 1345, 1041, 820, 769, 669, 625, 604; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.42–7.36 (m, 1H), 7.33–7.27 (m, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.29 (d, *J* = 7.6 Hz, 1H), 3.75–3.52 (m, 2H), 1.83–1.47 (m, 6H), 1.03 (d, *J* = 6.4 Hz, 3H), 1.02 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.3, 153.1, 130.8, 127.5, 126.8, 125.8, 124.9, 124.2, 123.1, 122.9, 109.5, 51.6, 46.4, 20.9 (CH_3 x 2), 20.8 (CH_3 x 2); HRMS (DART$^+$) Calcd for $C_{17}H_{22}NO_2$ $[M+H]^+$: 272.1651; found: *m*/*z* 272.1653.

***N*,*N*-Diisopropyl-4-methoxy-1-naphthamide (8):** A 300-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with **7** (400 mg, 1.47 mmol, 1.0 equiv), potassium carbonate (2.037 g, 14.7 mmol, 10 equiv), iodomethane (918 μL, 14.7 mmol, 10 equiv) , and acetone (14.7 mL). The solution was stirred at 40 °C for 6 h, at which time the reaction mixture was

treated with water. The aqueous layer was extracted twice with Et_2O. The combined organic extracts were washed with water, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to afford methyl ether **8** (408 mg, 1.43 mmol, 97%) as a pale yellow solid. Mp 120–122 °C; IR (ATR, cm^{-1}): 1633, 1622, 1584, 1442, 1371, 1337, 1269, 1242, 1088, 812, 770, 668; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.31–8.24 (m, 1H), 7.83–7.76 (m, 1H), 7.55–7.44 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.01 (s, 3H), 3.74–3.52 (m, 2H), 1.71 (d, *J* = 6.8 Hz, 3H), 1.64 (d, *J* = 6.8 Hz, 3H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.5, 155.5, 130.9, 129.5, 127.3, 125.7, 125.6, 124.8, 122.6, 122.4, 103.1, 55.7, 51.2, 46.0, 21.0, 20.9, 20.8 (CH_3 x 2); HRMS ($DART^+$) Calcd for $C_{18}H_{24}NO_2$ $[M+H]^+$: 286.1807; found: *m*/*z* 286.1807.

(*E*)-*N*,*N*-Diisopropyl-4-methoxy-2-(4-methoxystyryl)-1-naphthamide (9): A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with **8** (142.5 mg, 0.50 mmol, 1.0 equiv), 4-methoxystyrene (100.6 μL, 0.75 mmol, 1.5 equiv), $[RhCp^*Cl_2]_2$ (4.6 mg, 7.5 μmol, 1.5 mol%), $AgSbF_6$ (10.3 mg, 0.030 mmol, 6.0 mol%), $Cu(OAc)_2$ (190.7 mg, 1.05 mmol, 2.1 equiv), and anhydrous 1,4-dioxane (2.5 mL) under nitrogen atmosphere. The solution was stirred at 100 °C for 24 h, at which time $[RhCp^*Cl_2]_2$ (4.6 mg, 7.5 μmol, 1.5 mol%), $AgSbF_6$ (10.3 mg, 0.030 mmol, 6.0 mol%) were added to the Schlenk tube at room temperature and the resulting mixture was stirred at 100 °C for 6 days, at which time the reaction mixture was treated with water. After partitioned, the aqueous layer was extracted twice with Et_2O. The combined organic extracts were washed with water, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/Et_2O = 4:1) followed by SEC-HPLC to afford the corresponding product **9** (59.0 mg, 0.14 mmol, 28%) as a pale yellow solid. Mp 196–197 °C; IR (ATR, cm^{-1}): 1623, 1606, 1592, 1511, 1453, 1372, 1333, 1316, 1276, 1245, 1175, 1112, 833; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.53–7.40 (m, 4H), 7.25 (d, *J* = 16.6 Hz, 1H), 7.13 (d, *J* = 16.6 Hz, 1H), 7.09 (s, 1H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.07 (s, 3H), 3.82 (s, 3H), 3.68–3.53 (m, 2H), 1.80 (d, *J* = 6.8 Hz, 6H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.7, 159.6, 155.2, 131.2, 130.7, 130.0, 129.7, 127.9, 127.8, 127.5, 125.6, 125.4, 124.9, 124.1, 122.3, 114.3, 99.7, 55.6, 55.4, 51.3, 46.2, 21.1, 20.8, 20.7 (CH_3 x 2); HRMS ($DART^+$) Calcd for $C_{27}H_{32}NO_3$ $[M+H]^+$: 418.2382; found: *m*/*z* 418.2394.

2-(3,5-Dibromophenyl)-*N*,*N*-diisopropyl-4-methoxy-1-naphthamide (10): A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with naphthalene **8** (28.5 mg, 0.10 mmol, 1.0 equiv), 1,3-dibromobenzene (500 μL), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 μmol, 2.5 mol%), $AgSbF_6$ (3.4 mg, 0.010 mmol, 10 mol%), $Cu(OAc)_2$ (40.0 mg, 0.22 mmol, 2.2 equiv),

pivalic acid (11.2 mg, 0.11 mmol, 1.1 equiv), and cesium pivalate (4.7 mg, 0.020 mmol, 20 mol%) under nitrogen atmosphere. The mixture was stirred at 140 °C for 22 h, at which time the reaction mixture was treated with water. After partitioned, the aqueous layer was extracted twice with Et_2O. The combined organic extracts were washed with water, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane to hexane/Et_2O = 10:1, gradient) followed by preparative TLC (hexane/Et_2O = 2:1) to afford the corresponding product **10** (24.2 mg, 0.047 mmol, 47%) as a pale yellow solid. Mp 174–176 °C; IR (ATR, cm^{-1}): 1622, 1581, 1545, 1442, 1369, 1318, 1116, 1102, 1046, 801, 766, 744, 679, 645, 633; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.30–8.26 (m, 1H), 7.84 (d, 1H, *J* = 8.0 Hz), 7.82–7.78 (m, 2H), 7.71–7.65 (m, 1H), 7.61–7.47 (m, 2H), 6.74 (s, 1H), 4.06 (s, 3H), 3.43 (sept, *J* = 6.6 Hz, 1H), 3.34 (sept, *J* = 6.6 Hz, 1H), 1.71 (d, *J* = 6.8 Hz, 3H), 1.40 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H), 0.47 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.7, 155.6, 144.2, 133.1, 131.7, 131.42, 131.38, 127.9, 127.7, 126.3, 125.5, 125.4, 122.9, 122.2, 104.4, 55.9, 51.1, 46.2, 21.5, 20.8, 20.2, 20.1; HRMS ($DART^+$) Calcd for $C_{24}H_{26}{}^{81}Br_2NO_2$ $[M+H]^+$: 522.0289; found: *m*/*z* 522.0286.

Methyl 2-(1,4-epoxynaphthalen-1(4*H*)-yl)thiazole-4-carboxylate (12): A 50-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with **11** (418 mg, 2.00 mmol, 1.0 equiv), cesium fluoride (1.09 g, 7.18 mmol, 3.6 equiv), **5** (716 mg, 2.40 mmol, 1.2 equiv), and MeCN (2 mL) under nitrogen atmosphere. The solution was stirred at 60 °C for 18 h, at which time the reaction mixture was treated with water. After partitioned, the aqueous layer was extracted twice with Et_2O. The combined organic extracts were washed with water, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/Et_2O = 5:1 to 3:2, gradient) to afford the corresponding cycloadduct **12** (500 mg, 1.75 mmol, 88%) as a colorless solid. Mp 86–89 °C; IR (ATR, cm^{-1}): 1734, 1438, 1346, 1217, 1098, 990, 940, 922, 901, 861, 777, 757, 696; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.31 (s, 1H), 7.38–7.32 (m, 2H), 7.31–7.27 (m, 1H), 7.14 (dd, *J* = 5.6, 2.0 Hz, 1H), 7.05–6.96 (m, 2H), 5.88 (d, *J* = 2.0 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5, 161.9, 149.0, 148.3, 147.5, 143.7, 143.6, 128.9, 125.7, 125.5, 120.6, 120.3, 91.5, 83.1, 52.7; HRMS ($DART^+$) Calcd for $C_{15}H_{12}NO_3S$ $[M+H]^+$: 286.0538; found: *m*/*z* 286.0525.

Methyl 2-(4-hydroxynaphthalen-1-yl)thiazole-4-carboxylate (13): A 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with **12** (143 mg, 0.501 mmol, 1.0 equiv), AgOTf (13 mg, 0.051 mmol, 10 mol%), and 1,2-dichloroethane (5 mL) under nitrogen atmosphere. The resulting mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the

reaction mixture was treated with water. After partitioned, the aqueous layer was extracted twice with $CHCl_3$. The combined organic extracts were washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/Et_2O = 3:2, gradient) to afford naphthol **13** (111 mg, 0.389 mmol, 78%) as a colorless solid. Mp 126–128 °C; IR (ATR, cm^{-1}): 3294, 1685, 1579, 1503, 1462, 1371, 1358, 1327, 1272, 1259, 1230, 1175, 1063, 989, 815, 753, 739; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.57 (d, *J* = 8.4 Hz, 1H), 8.28 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.58–7.45 (m, 3H), 6.80 (d, *J* = 8.0 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.2, 162.4, 154.6, 146.9, 131.9, 129.7, 128.1, 128.0, 125.6, 125.1, 125.0, 122.4, 122.2, 108.8, 52.8; HRMS ($DART^+$) Calcd for $C_{15}H_{12}NO_3S$ $[M+H]^+$: 286.0538; found: *m/z* 286.0527.

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