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Synthesis of Biaryl Compounds Using Tandem Ruthenium-Catalyzed Ring-Closing Metathesis

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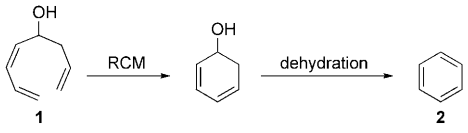
Abstract: Tandem ring-closing enyne metathesis (RCEM)/ring-closing olefin metathesis (RCM) of tetraenynes with Grubbs second-generation catalyst, followed by elimination, was found to be a new and efficient synthetic approach to biaryl compounds. A preliminary asymmetric version of this approach, which used homochiral Ru–alkylidene catalysts, is also presented.

Keywords: aromatic compounds · asymmetric synthesis · metathesis · ring closure · synthesis design

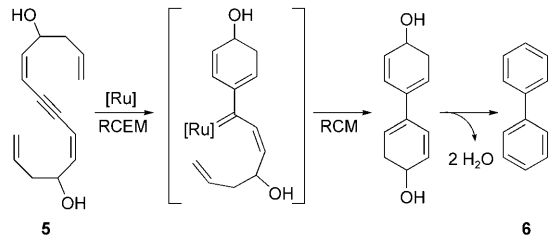
Introduction

Modern synthetic organic chemistry has sufficient flexibility to construct acyclic compounds selectively. Therefore, the construction of aromatic rings from acyclic precursors is an attractive approach to obtain substituted aromatic compounds without the formation of inseparable regioisomers.[1] Recently, a considerable number of studies have been conducted on the synthesis of aromatic compounds by using ruthenium-catalyzed ring-closing olefin metathesis[2,3] (RCM).[4,5] The reason for this is clearly the great reliability of RCM as a cyclization reaction. In the past few years, we have focused our efforts on this field[6] and reported that substituted benzenes **2** and styrenes **4** can be synthesized by the RCM/dehydration of 1,5,7-octatrien-4-ols **1** [Eq. (1)][6e] and the ring-closing enyne metathesis[7] (RCEM)/dehydration of 1,5-octadien-7-yn-4-ols **3** [Eq. (2)],[6j] respectively. On the basis of those studies, we report here a new synthetic strategy that yields biaryl compounds **6** from tetraenynes **5**, in which two rings are consecutively constructed by the RCEM/RCM/elimination sequence[8] (Scheme 1).[9]



(1)

(2)



Scheme 1. Synthesis of biaryl compounds **6** by tandem RCEM/RCM/dehydration of **5**.

Results and Discussion

Our retrosynthetic analysis of substrates **5** is outlined in Scheme 2. First, we prepared dienynedials **7** by the Sonogashira coupling between two well-known building blocks, β-halo-α,β-unsaturated aldehydes **8**[10] and 2-penten-4-ynal **9**.

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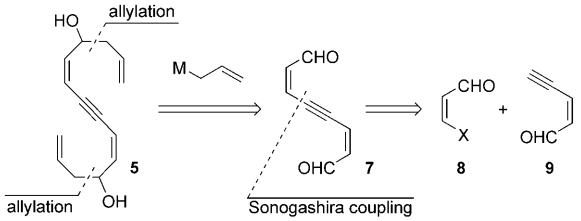
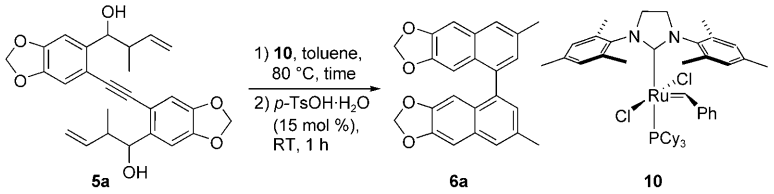


Scheme 2. Retrosynthetic analysis of substrates **5**.

Then, we carried out double allylation of resulting coupling products **7** to furnish desired substrates **5**.[11]

We first surveyed the reaction conditions for the synthesis of 1,1′-binaphthyl compound **6a** from **5a** that was chosen as the model substrate (Table 1). To our delight, when RCEM/RCM of **5a** with 2.5 mol% Grubbs second-generation catalyst **10**[12] under an ethylene atmosphere[6j,13] at 80 °C for 2 h, followed by dehydration with a catalytic amount of *p*-toluenesulfonic acid, was carried out, desired **6a** was obtained, although the conversion was low (Table 1, entry 1). Even though we prolonged the reaction time to 4 h, no significant improvement was observed in terms of product yield (entry 2). As the catalyst decomposition is likely responsible for the low conversion, we next examined the influence of catalyst loading. We were pleased to see that the product yield gradually increased with increasing catalyst loading (entries 3–5). Although the reaction also proceeded under a nitrogen atmosphere, the yield was lower than that under an ethylene atmosphere (entry 4 vs. 6).

Table 1. Survey of reaction conditions for synthesis of 1,1′-binaphthyl compound **6a**.[a]

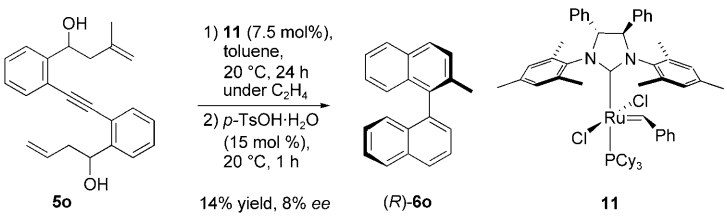


Entry	**10** [mol%]	Atmosphere	*t* [h]	Yield [%][b]
1	2.5	C_2H_4	2	36
2	2.5	C_2H_4	4	39
3	5.0	C_2H_4	2	61
4	7.5	C_2H_4	2	74
5	15	C_2H_4	2	87
6	7.5	N_2	2	53

[a] Ring-closing metathesis was carried out with **5a** and ruthenium catalyst **10** in toluene at 80 °C. The reaction mixture was treated with *p*-toluenesulfonic acid (15 mol%) at RT for 1 h. [b] Isolated yield by silica gel chromatography.

With these basic data, we examined the generality of the synthetic approach to biaryl compounds. Examples of the synthesis of symmetrically substituted biaryl compounds and nonsymmetrically substituted biaryl compounds are listed in entries 1–10 and entries 11–20 in Table 2, respectively. The reaction of **5b** that has no methyl groups at the R^3 and $R^{3'}$ positions with **10** (7.5 mol%) proceeded well and desired product **6b** was obtained in a higher yield than that of **5a** (entry 3 vs. 1). The reaction of **5c** with ethyl groups at the R^4 and $R^{4'}$ positions also proceeded to give **6c** in 79% yield (entry 4). On the other hand, the synthesis of **6d** that has methyl groups at the R^2 and $R^{2'}$ positions was unsuccessful. The cyclization of **5d** did not occur at all (entry 5). Whereas the reaction of fluorine-containing substrate **5e** proceeded to give **6e** in moderate yield (entry 6), the reaction of **5f** gave bibenzothiophene **6f** in high yield (entry 7). The introduction of ester groups at R^3 and $R^{3'}$ positions was also accomplished, but slow cyclization gave rise to low yields (entries 8 and 9). One surprising result was that substrate **5h** is unreactive in this system (entry 10). Considering the problem-free synthesis of analogous product **6a** (entry 1), the cyclization seemed to have suffered seriously from steric interactions between the two methoxy groups at the 7- and 7′-positions of **6h**. In conformity with this view, the synthesis of nonsymmetrically substituted biaryl compound **6i**, the structure of which is the same as that of **6h** except for the hydrogen at 7′-position, proceeded without any problems (entry 11). The reactions of **5j** and **5k** produced nonsymmetrically substituted biaryl compounds **6j** and **6k**, respectively (entries 12 and 13). Although the reaction of **5l** with a methyl ester group at the R^3 position was slightly slow as predicted, **6l** was obtained in higher yields than **6g** (entries 8 and 9 vs. 14 and 15). Difficulties arose in the cyclization of **5m** and **5n** with a substituent at the R^2 position, and corresponding products **6m** and **6n** were not isolated at all (entries 16 and 17). However, the reaction of **5o** exceptionally gave **6o** in spite of possession of a methyl group at the R^2 position (entries 18 and 19). The last example is the formation of 1-arylnaphthalene. Despite the slow reaction and the low yield, desired product **6p** was isolated (entry 20).

We next examined the application of the method to asymmetric synthesis (Scheme 3). When the reaction of **5o** was carried out with homochiral Ru–alkylidene catalyst **11**,[14]



Scheme 3. Asymmetric synthesis of 1,1′-binaphthyl compound **6o** using homochiral Ru–alkylidene catalyst **11**.

Table 2. Synthesis of biaryl compounds **6** by tandem RCEM/RCM/dehydration of **5**.[a]

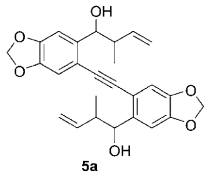
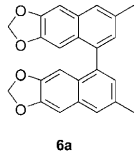
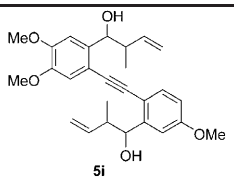
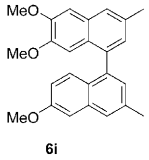
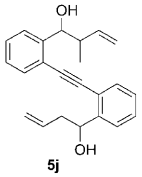
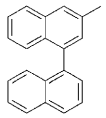
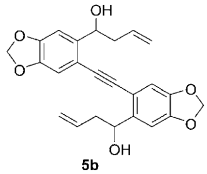
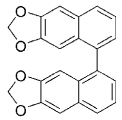
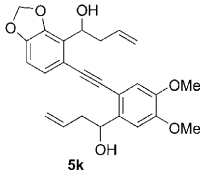
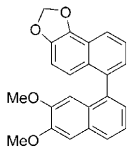
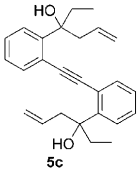
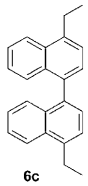
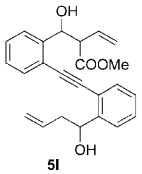
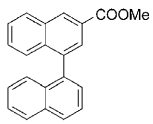
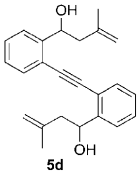
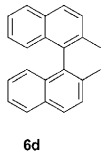
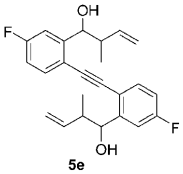
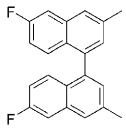
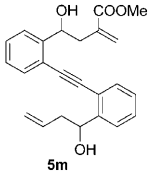
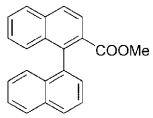
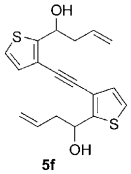
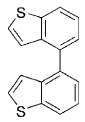
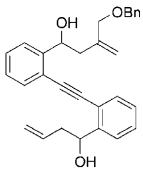
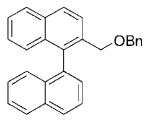
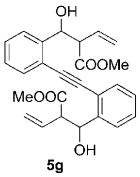
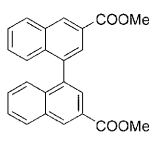
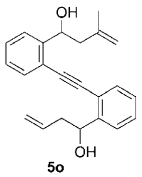
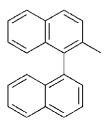
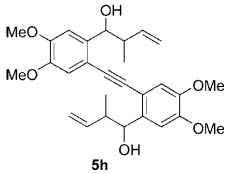
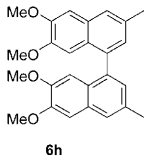
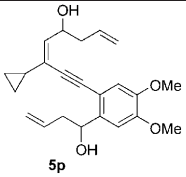
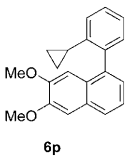
Entry	Substrate	Product	Conditions[b]	Yield [%][c]	Entry	Substrate	Product	Conditions[b]	Yield [%][c]
1	 5a	 6a	**10** (7.5 mol %)	74	11	 5i	 6i	**10** (7.5 mol %)	90
2			**10** (15 mol %)	87	12	 5j	 6j	**10** (7.5 mol %)	76
3	 5b	 6b	**10** (7.5 mol %)	85	13	 5k	 6k	**10** (7.5 mol %)	77
4	 5c	 6c	**10** (7.5 mol %)	79	14	 5l	 6l	**10** (7.5 mol %)	41
5	 5d	 6d	**10** (7.5 mol %)	0	15			**10** (15 mol %)	64
6	 5e	 6e	**10** (7.5 mol %)	54	16	 5m	 6m	**10** (7.5 mol %)	0
7	 5f	 6f	**10** (7.5 mol %)	88	17	 5n	 6n	**10** (7.5 mol %)	0
8	 5g	 6g	**10** (7.5 mol %)	7	18			**10** (7.5 mol %)	67
9			**10** (15 mol %)	25	19	 5o	 6o	**10** (7.5 mol %)[d]	41

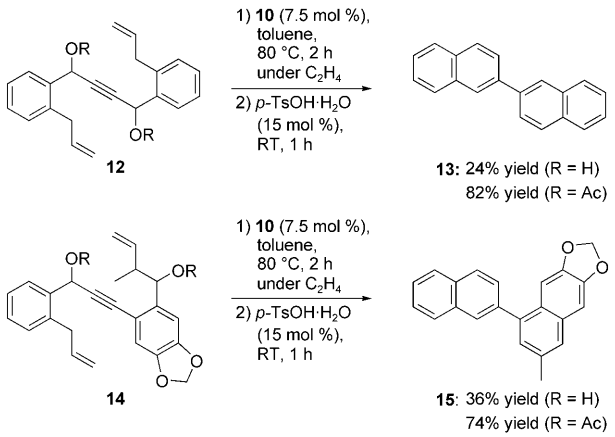
Table 2. (Continued)

Entry	Substrate	Product	Conditions[b]	Yield [%][c]	Entry	Substrate	Product	Conditions[b]	Yield [%][c]
10	 5h	 6h	**10** (7.5 mol %)	0	20	 5p	 6p	**10** (7.5 mol %)	16

[a] Ring-closing metathesis was carried out with **5** and ruthenium catalyst **10** in toluene for 2 h. The reaction mixture was treated with *p*-toluenesulfonic acid (15 mol %) at RT for 1 h. [b] Reactions were carried out at 80 °C. [c] Isolated yield by silica gel chromatography. [d] Reaction carried out at RT.

8 % *ee* of (*R*)-**6o** was obtained in 14 % yield. Despite the insufficient result, this preliminary investigation demonstrates the possibility of applying RCM to the asymmetric synthesis of axial chiral biaryl compounds.

Finally, we applied this method to the synthesis of 2,2′- and 1,2′-binaphthyl compounds (Scheme 4). As a result, newly prepared substrates **12** and **14** were successfully converted into desired products **13** and **15** by the RCEM/RCM/elimination sequence, respectively.[15]



Scheme 4. Synthesis of 2,2′-binaphthyl compound **13** and 1,2′-binaphthyl compound **15** by tandem RCEM/RCM/elimination of **12** and **14**, respectively.

Conclusion

In conclusion, we have developed a new synthetic approach to biaryl compounds by utilizing the RCEM/RCM/dehydration sequence. The method employed for the synthesis of biaryl compounds is remarkably different from the conventional method represented by the cross-coupling reaction. Although the method was found to be strongly dependent on the substituents of the substrates when Grubbs second-generation catalyst was used, we believe that future development of active catalysts would increase the potential of this method.

Experimental Section

General: All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under prepurified argon. NMR spectra were recorded using a JEOL JNM LA-500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C), an ECA-500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C), an LA-400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C), and an ECS-400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) at the Chemical Analysis Center, Chiba University. Chemical shifts are reported in δ [ppm] referenced to an internal $SiMe_4$ standard for ^{1}H NMR spectroscopy and [D]chloroform ($\delta = 77.0$ ppm) for ^{13}C NMR spectroscopy. High-resolution mass spectra were recorded using Thermo Fisher Scientific Exactive Orbitrap mass spectrometers at the Chemical Analysis Center, Chiba University. Optical rotations were measured using a JASCO P-1020 polarimeter. In the HRMS data, APCI stands for atmospheric pressure chemical ionization.

Materials: Toluene was distilled with sodium benzophenone ketyl under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. Ruthenium complexes **10**[12b] and **11**[14] were prepared according to the reported procedures. *p*-Toluenesulfonic acid monohydrate was used as received.

General procedure for the preparation of biaryl compounds 6, 13, or 15: Catalyst **10** (7.5 or 15 mol %) was added in one portion to a solution of **5**, **12**, or **14** in toluene (0.01 M), which was then filled with ethylene gas in three cycles. The reaction mixture was heated to 80 °C and stirred for 2 h under the ethylene atmosphere. After cooling to room temperature, the reaction mixture was treated with *p*-toluenesulfonic acid monohydrate (15 mol %) and stirred for 1 h at room temperature. The mixture was concentrated under reduced pressure and purified by silica gel column chromatography or preparative thin-layer chromatography (PTLC) on silica gel to afford **6**, **13**, or **15**.

7,7′-Dimethyl-5,5′-binaphtho[2,3-*d*][1,3]dioxole (6a): Compound **5a** (28.7 mg, 0.0662 mmol), **10** (8.4 mg, 0.00993 mmol), and toluene (6.6 mL) were used. The crude mixture was purified by silica gel column chromatography (chloroform/hexane = 2:1) to afford **6a** (21.4 mg, 87 %). M.p. 290–291 °C; ^{1}H NMR ($CDCl_3$): $\delta = 2.49$ (s, 6H), 5.92 (s, 4H), 6.60 (s, 2H), 7.11 (s, 2H), 7.14 (s, 2H), 7.51 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 21.37$, 100.83, 102.71, 103.46, 126.12, 127.72, 128.23, 130.91, 133.47, 137.82, 147.06, 147.43 ppm; HRMS (ESI): *m*/*z*: calcd for $C_{24}H_{19}O_4$: 371.1278 [M^+ +H]; found: 371.1267.

5,5′-Binaphtho[2,3-*d*][1,3]dioxole (6b): Compound **5b** (55.4 mg, 0.136 mmol), **10** (8.7 mg, 0.0102 mmol), and toluene (13.6 mL) were used. The crude mixture was purified by silica gel column chromatography (chloroform/hexane = 2:3) to afford **6b** (39.5 mg, 85 %). M.p. 261–264 °C; ^{1}H NMR ($CDCl_3$): $\delta = 5.95$ (s, 4H), 6.63 (s, 2H), 7.20 (s, 2H), 7.30 (d, J = 7.0 Hz, 2H), 7.42 (dd, J = 7.7, 7.3 Hz, 4H), 7.74 ppm (d, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 100.99$, 102.83, 104.04, 124.03, 126.27, 126.87, 129.78, 130.75, 137.97, 147.47, 147.79 ppm; HRMS (APCI): *m*/*z*: calcd for $C_{22}H_{14}O_4$: 342.0887 [M^+]; found: 342.0879.

4,4′-Diethyl-1,1′-binaphthyl (6c): Compound **5c** (58.8 mg, 0.157 mmol), **10** (10.0 mg, 0.0118 mmol), and toluene (15.7 mL) were used. The crude mixture was purified by silica gel column chromatography (chloroform/hexane = 1:2) to afford **6c** (38.3 mg, 79%). The ^{1}H and ^{13}C NMR spectra were consistent with those reported previously.[16]

6,6′-Difluoro-3,3′-dimethyl-1,1′-binaphthyl (6e): Compound **5e** (95.9 mg, 0.251 mmol), **10** (16.0 mg, 0.0188 mmol), and toluene (25.1 mL) were used. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 15:1) to afford **6e** (42.7 mg, 54%). ^{1}H NMR ($CDCl_3$): δ = 2.67 (s, 6H), 6.98 (td, J = 8.7, 2.4 Hz, 2H), 7.22–7.33 (m, 4H), 7.44 (dd, J = 9.8, 2.5 Hz, 2H), 7.63 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): δ = 21.64, 110.43 (d, J = 20.1 Hz), 115.35 (d, J = 25.1 Hz), 126.34 (d, J = 5.0 Hz), 128.08, 128.79 (d, J = 9.0 Hz), 129.23 (d, J = 3.0 Hz), 134.72 (d, J = 9.0 Hz), 136.33, 138.19, 160.73 ppm (d, J = 245.5 Hz); HRMS (FAB): m/z: calcd for $C_{22}H_{16}F_2$: 318.1220 [M^+]; found: 318.1213.

4,4′-Bibenzo[*b*]thiophene (6f): Compound **5f** (75.9 mg, 0.230 mmol), **10** (14.6 mg, 0.0173 mmol), and toluene (23.0 mL) were used. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to afford **6f** (53.6 mg, 88%). ^{1}H NMR ($CDCl_3$): δ = 7.07 (dd, J = 5.7, 0.8 Hz, 2H), 7.34 (d, J = 5.5 Hz, 2H), 7.38–7.44 (m, 4H), 7.92 ppm (ddd, J = 7.0, 2.1, 0.6 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 121.91, 123.74, 124.23, 125.42, 126.18, 136.42, 138.57, 140.23 ppm; HRMS (APCI): m/z: calcd for $C_{16}H_{11}S_2$: 267.0297 [M^++H]; found: 267.0289.

Dimethyl 1,1′-binaphthyl-3,3′-dicarboxylate (6g): Compound **5g** (31.6 mg, 0.0727 mmol), **10** (9.3 mg, 0.0109 mmol), and toluene (7.3 mL) were used. The crude mixture was purified by PTLC on silica gel (chloroform only) to afford **6g** (6.8 mg, 25%); known compound.[17] ^{1}H NMR ($CDCl_3$): δ = 3.98 (s, 6H), 7.36 (d, J = 8.0 Hz, 2H), 7.39–7.43 (m, 2H), 7.55 (td, J = 7.9, 1.3 Hz, 2H), 8.07 (d, J = 8.3 Hz, 2H), 8.10 (s, 2H), 8.74 (s, 2H) ppm.

6,6′,7-Trimethoxy-3,3′-dimethyl-1,1′-binaphthyl (6i): Compound **5i** (82.1 mg, 0.188 mmol), **10** (12.0 mg, 0.0141 mmol), and toluene (18.8 mL) were used; The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 4:1) to afford **6i** (62.9 mg, 90%). ^{1}H NMR ($CDCl_3$): δ = 2.51 (s, 3H), 2.54 (s, 3H), 3.52 (s, 3H), 3.91 (s, 3H), 4.00 (s, 3H), 6.65 (s, 1H), 6.89 (dd, J = 9.2, 2.5 Hz, 1H), 7.12 (s, 1H), 7.14 (d, J = 2.4 Hz, 1H), 7.18 (d, J = 1.9 Hz, 1H), 7.20 (d, J = 1.5 Hz, 1H), 7.29 (d, J = 9.2 Hz, 1H), 7.55 (s, 1H), 7.59 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 21.46, 21.68, 55.21, 55.56, 55.78, 105.30, 105.48, 105.97, 117.45, 125.40, 125.75, 126.24, 126.41, 127.71, 128.07, 128.31, 129.63, 133.26, 135.08, 135.68, 137.08, 138.65, 148.73, 149.41, 157.55 ppm; HRMS (APCI): m/z: calcd for $C_{25}H_{25}O_3$: 373.1798 [M^++H]; found: 373.1784.

3-Methyl-1,1′-binaphthyl (6j): Compound **5j** (50.9 mg, 0.153 mmol), **10** (9.7 mg, 0.0115 mmol), and toluene (15.3 mL) were used. The crude mixture was purified by PTLC on silica gel (hexane/EtOAc = 10:1) to afford **6j** (31.0 mg, 76%). M.p. 120–124 °C; ^{1}H NMR ($CDCl_3$): δ = 2.55 (s, 3H), 7.19 (t, J = 7.6 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.32 (d, J = 7.6 Hz, 2H), 7.36–7.50 (m, 4H), 7.56 (t, J = 7.5 Hz, 1H), 7.70 (s, 1H), 7.83 (d, J = 8.3 Hz, 1H), 7.92 ppm (d, J = 7.9 H, 2H); ^{13}C NMR ($CDCl_3$): δ = 21.65, 125.07, 125.35, 125.75, 125.83, 125.92, 126.34, 126.59, 126.82, 127.47, 127.74, 127.80, 128.11, 130.06, 131.14, 132.84, 133.49, 133.77, 134.92, 138.29, 138.51 ppm; HRMS (APCI): m/z: calcd for $C_{21}H_{17}$: 269.1325 [M^++H]; found: 269.1318.

6-(6,7-Dimethoxynaphthalen-1-yl)naphtha[1,2-*d*][1,3]dioxole (6k): Compound **5k** (72.3 mg, 0.171 mmol), **10** (10.9 mg, 0.0128 mmol), and toluene (17.1 mL) were used. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 2:1) to afford **6k** (47.5 mg, 77%). M.p. 110–115 °C; ^{1}H NMR ($CDCl_3$): δ = 3.54 (s, 3H), 4.01 (s, 3H), 6.18 (dd, J = 8.6, 1.5 Hz, 2H), 6.67 (s, 1H), 6.99 (d, J = 17.4 Hz, 1H), 7.01 (d, J = 17.4 Hz, 1H), 7.20 (s, 1H), 7.29–7.37 (m, 2H), 7.42 (dd, J = 8.3, 7.3 Hz, 1H), 7.54 (dd, J = 8.5, 7.0 Hz, 1H), 7.77 (d, J = 8.3 Hz, 1H), 7.90 ppm (d, J = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 55.55, 55.81, 101.67, 105.13, 106.45, 110.16, 119.38, 120.12, 120.82, 123.79, 125.82, 126.16, 126.26, 128.29, 129.13, 129.42, 137.06, 139.35, 141.28, 143.07, 149.39, 149.41 ppm; HRMS (APCI): m/z: calcd for $C_{23}H_{19}O_4$: 359.1278 [M^++H]; found: 359.1265.

Methyl 1,1′-binaphthyl-3-carboxylate (6l): Compound **5l** (42.5 mg, 0.113 mmol), **10** (14.4 mg, 0.0169 mmol), and toluene (11.3 mL) were used. The crude mixture was purified by PTLC on silica gel (chloroform/hexane = 1:1) to afford **6l** (22.4 mg, 64%). M.p. 146–151 °C; ^{1}H NMR ($CDCl_3$): δ = 3.97 (s, 3H), 7.26–7.35 (m, 2H), 7.36–7.44 (m, 2H), 7.45–7.50 (m, 2H), 7.50–7.56 (m, 1H), 7.59 (dd, J = 8.1, 7.2 Hz, 1H), 7.96 (t, J = 9.2 Hz, 2H), 8.06 (d, J = 8.3 Hz, 1H), 8.10 (d, J = 1.5 Hz, 1H), 8.72 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 52.27, 125.39, 125.92, 126.16, 126.32, 126.61, 126.63, 127.02, 127.05, 127.91, 128.25, 128.39, 129.68, 130.94, 132.68, 132.75, 133.56, 135.06, 137.60, 139.00, 167.26 ppm; HRMS (APCI): m/z: calcd for $C_{22}H_{17}O_2$: 313.1223 [M^++H]; found: 313.1211.

2-Methyl-1,1′-binaphthyl (6o): Compound **5o** (48.1 mg, 0.145 mmol), **10** (9.3 mg, 0.0109 mmol), and toluene (14.5 mL) were used. The crude mixture was purified by silica gel column chromatography (chloroform/hexane = 1:2) to afford **6o** (25.8 mg, 67%). The ^{1}H and ^{13}C NMR spectra were consistent with those reported previously.[18] The reaction was also carried out with **5o** (30.0 mg, 0.0902 mmol), homochiral Ru–alkylidene catalyst **11a** (6.8 mg, 0.00677 mmol, 7.5 mol%), and toluene (9.0 mL, 0.01 M) at 20 °C for 24 h. The crude mixture was purified by PTLC on silica gel (chloroform/hexane = 1:2) to afford (*R*)-**6o** (3.3 mg, 14%, 8% *ee*). $[\alpha]_D^{20} = -6.09$ (c = 0.250, $CHCl_3$);[19] HPLC (Daicel Chiralcel OJ); hexane/EtOH/MeOH = 1000:5:3.5, 1.0 mL min^{-1}; t_R (*R*) = 7.6 min, t_R (*S*) = 11.8 min.[20]

1-(2-Cyclopropylphenyl)-6,7-dimethoxynaphthalene (6p): Compound **5p** (257 mg, 0.697 mmol), **10** (44.4 mg, 0.0523 mmol), and toluene (69.7 mL) were used. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 4:1) to afford **6p** (34.5 mg, 16%). ^{1}H NMR ($CDCl_3$): δ = 0.54–0.63 (m, 4H), 1.40–1.48 (m, 1H), 3.76 (s, 3H), 4.01 (s, 3H), 6.87 (s, 1H), 6.92 (d, J = 7.7 Hz, 1H), 7.18 (s, 1H), 7.23–7.26 (m, 2H), 7.29 (dd, J = 7.2, 0.9 Hz, 1H), 7.34 (ddd, J = 8.4, 5.0, 3.7 Hz, 1H), 7.40 (dd, J = 8.2, 6.9 Hz, 1H), 7.69 ppm (d, J = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 9.56, 9.79, 13.12, 55.59, 55.80, 77.20, 105.31, 106.46, 122.51, 123.83, 125.08, 125.68, 125.74, 127.73, 128.01, 129.24, 130.24, 138.26, 140.63, 142.20, 149.28 ppm; HRMS (ESI): m/z: calcd for $C_{21}H_{21}O_2$: 305.1536 [M^++H]; found: 305.1526.

2,2′-Binaphthalene (13): Compound **12b** (32.8 mg, 0.0815 mmol), **10** (5.2 mg, 0.00611 mmol), and toluene (8.2 mL) were used. The crude mixture was purified by silica gel column chromatography (dichloromethane/hexane = 1:4) to afford **13** (17.1 mg, 82%). The ^{1}H and ^{13}C NMR spectra were consistent with those reported previously.[21]

7-Methyl-5-(naphthalen-2-yl)naphtho[2,3-*d*][1,3]dioxole (15): Compound **14b** (21.5 mg, 0.0467 mmol), **10** (3.0 mg, 0.00350 mmol), and toluene (4.7 mL) were used. The crude mixture was purified by PTLC on silica gel (dichloromethane/hexane = 1:2) to afford **15** (10.8 mg, 74%). M.p. 190–192 °C; ^{1}H NMR ($CDCl_3$): δ = 2.50 (s, 3H), 5.97 (s, 2H), 7.11 (s, 1H), 7.15 (s, 1H), 7.21 (s, 1H), 7.46–7.60 (m, 4H), 7.84–7.96 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): δ = 21.37, 100.93, 102.30, 103.63, 125.96, 126.12, 126.24, 126.77, 127.70, 128.02, 128.28, 128.44, 131.22, 132.49, 133.40, 133.49, 138.68, 139.21, 147.28, 147.41 ppm; HRMS (APCI): m/z: calcd for $C_{22}H_{17}O_2$: 313.1223 [M^++H]; found: 313.1218.

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