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Graphical Abstract

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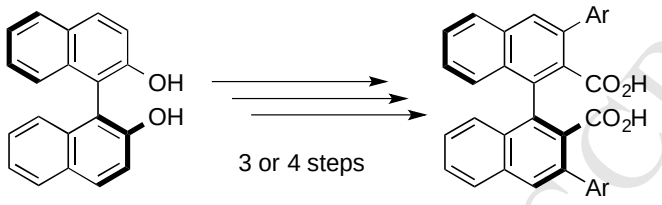

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ABSTRACT

3,3'-Disubstituted 1,1'-binaphthyl-2,2'-dicarboxylic acids (**1**) were synthesized in three or four steps from commercially available BINOL via carbon dioxide fixation with organolithium to incorporate the carboxylic acid moieties, followed by either carboxylate-directed *ortho*-C–H arylation or Suzuki cross-coupling. This method provides easy access to various types of axiially chiral dicarboxylic acids, which should be useful for studies of chiral Brønsted acid-catalyzed asymmetric reactions.

1. Introduction

Chiral Brønsted acid catalysis is a major research target in the field of asymmetric organocatalysis.[1] Since the asymmetric Mukaiyama-aldol reaction and Mannich-type reactions were independently reported by Akiyama's and Terada's groups in 2004,[2] binaphthol-derived chiral phosphoric acids have been widely used as chiral Brønsted acid catalysts.[3] In contrast, little work has been done on asymmetric catalysis with chiral carboxylic acids. Momiyama and Yamamoto reported a highly enantioselective nitroso aldol reaction with a chiral mandelic acid analog in 2005.[4] In 2007, Hashimoto and Maruoka developed a chiral dicarboxylic acid having a 1,1'-binaphthyl framework,[5] which catalyzed various C–C bond-forming reactions.[6]

Despite the great potential of axially chiral dicarboxylic acids,[6] 3,3'-disubstituted 1,1'-binaphthyl-2,2'-dicarboxylic acids (**1**) have seen only limited application, probably due to the unavailability of a cost-effective and concise synthetic method. Although the original synthetic route to **1** is reliable,[5] there is much room for improvement in terms of atom and step economy. First, the starting 1,1'-binaphthyl-2,2'-dicarboxylic acid (**2**) was prepared from 1-bromo-2-methylnaphthalene in six steps, including optical resolution of racemic **2** with chiral 1-(cyclohexyl)ethyl-1-amine according to Seki's procedure (Scheme 1).[7] From the viewpoint of atom economy, a procedure that does not require a resolution process would be more favorable. Second, Maruoka's synthesis of **1** required five steps from **2**, i.e., 1) acid chloride formation, 2) trimethylsilyl(TMS)ethyl ester formation with expensive 2-trimethylsilylethanol, 3) *ortho*-magnesiation followed by bromination, 4) Suzuki-Miyaura cross-coupling to install aryl groups at the 3,3' positions, and 5) deprotection of the TMSethyl group.[5,6] We thought that C–H functionalization might be an effective approach to reduce the number of steps.

BINOL is an important chiral source that is commercially available at reasonable cost, and we thought that it might be suitable for a more efficient synthesis of **2**. Several relevant reactions have been reported, though these methods have some drawbacks. In 1993, Takaya reported a palladium-catalyzed carbonylation of BINOL-ditriflate to give the corresponding methyl ester, but this method requires toxic CO gas and relatively expensive triflating reagents.[8] In 2006, Schlosser reported a unique method utilizing Wittig [1,2]-rearrangement of a di-allylated BINOL derivative, although several additional steps are required to generate the carboxylic acid.[9] As for CO_2 fixation, Hoshi and Hagiwara synthesized **2** from chiral 2,2'-dibromo-1,1'-binaphthyl via lithiation with *t*-BuLi, though the starting bromide is more expensive than BINOL, and partial racemization was observed when *n*-BuLi was used.[10]

On the other hand, we have been investigating catalytic asymmetric halo-functionalization of alkenes.[11] In this context, we became interested in using a chiral dicarboxylic acid framework in the design of novel halogenation catalysts. Therefore, we needed to devise a practical protocol for rapid preparation of various derivatives. Considering the structure of **1**, we planned a synthetic strategy consisting of two stages: 1) construction of 1,1'-binaphthyl-2,2'-dicarboxylic acid from BINOL and 2) substitution at the 3,3'-positions. We envisaged that a short-step synthesis of **1** would be possible if we could

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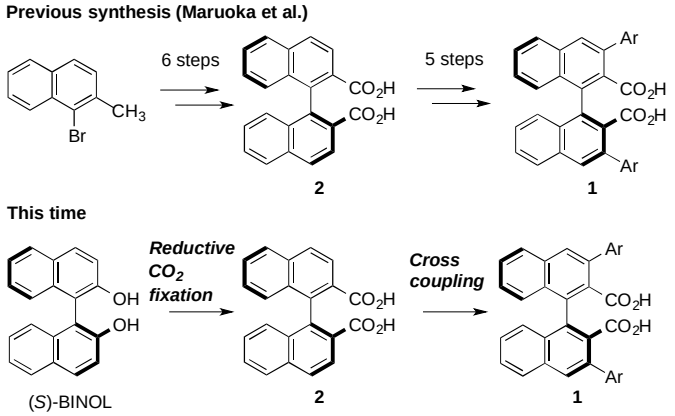
achieve facile incorporation of CO_2 to afford **2** and combine it with directed palladium-catalyzed *ortho*-C–H functionalization, which has been actively investigated. In this report, we disclose a short-step synthesis of chiral 3,3'-disubstituted 1,1'-binaphthyl-2,2'-dicarboxylic acid derivatives (**1**) from commercially available BINOL.

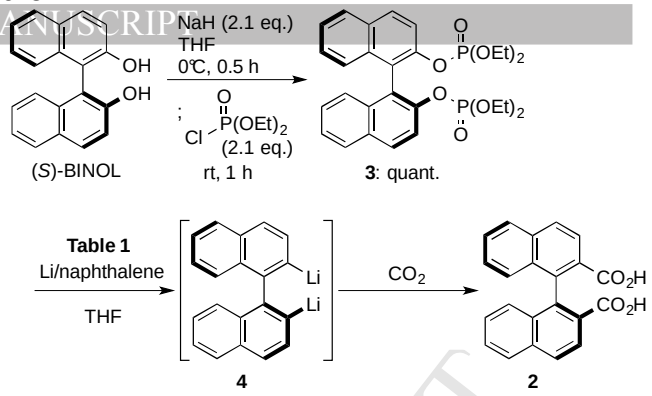


Scheme 1. Our synthetic plan

2. Results and discussions

Aiming first at the preparation of 1,1'-binaphthyl-2,2'-dicarboxylic acid (**2**), the backbone of our target compound (Scheme 1), we focused on reaction of organolithium species with CO_2. To apply this transformation to our synthesis, 1,1'-binaphthyl-2,2'-dilithium (**4**) should be generated *in situ* under mild conditions (Scheme 2). Although there is no report on the generation of such dilithium species from a BINOL derivative, with the exception of 2,2'-dibromo-1,1'-binaphthyl, [10] boronation and iodination via lithiation by reduction of an aryl diethyl phosphate with lithium-naphthalenide has been reported.[12,13] With reference to these reports, we examined reductive CO_2 fixation onto the binaphthyl backbone via lithium-naphthalenide reduction after phosphate formation on BINOL.

As shown in Scheme 2, the hydroxyl groups of BINOL reacted smoothly with diethyl chlorophosphate to provide **3** in quantitative yield. Optimization of the reaction conditions for dilithiation of **3** and CO_2 fixation was conducted (Table 1). Six equivalents of lithium naphthalenide was enough to generate the dilithium species **4** (entries 1-3). The reactions at 0 °C and room temperature resulted in low yield of **2**, and this was attributed to deprotonation of THF by the generated organolithium species to give the corresponding protonated by-product (entries 4 and 5). In addition, it was found that the reduction time for the generation of **4** was important: a longer or shorter reaction time afforded only moderate yield (entries 6-8). Based on these results, we selected the conditions of entry 2 as the optimal reaction conditions. To our delight, the reaction could be carried out on a 2 g scale without difficulty, providing the desired di-acid in 89% isolated yield (entry 9). It should be noted that the reaction occurred without significant loss of enantiomer excess (99% ee), as confirmed by HPLC analysis.[10]



Scheme 2. Reductive CO_2 fixation of **3**

Table 1. Optimization of the conditions for di-lithiation of **3**[a]

Entry	Li/naphthalene (equiv.)	Temp. (°C)	Time (h)	Yield of **2** (%)[b]
1	4	-78	0.5	12
2	6	-78	0.5	82
3	8	-78	0.5	82
4	6	0	0.5	9
5	6	rt	0.5	5
6	6	-78	0.25	44
7	6	-78	1	68
8	6	-78	2	54
9[c]	6	-78	0.5	89

[a] The reactions were carried out in THF on a 0.5 mmol scale, unless otherwise mentioned.

[b] Isolated yield.

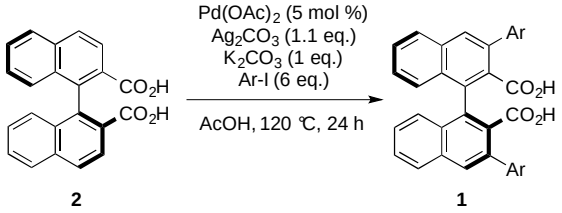
[c] Run with 2 g (3.5 mmol) of **3**.

Having established a highly efficient route to 1,1'-binaphthyl-2,2'-dicarboxylic acid (**2**), we next turned our attention to functionalization at the 3,3' positions. Inspired by recent advances in C–H activation chemistry,[14] we planned to examine palladium-catalyzed C–H coupling reactions. It was encouraging that the carboxylate group had been reported to act as a directing group in palladium-catalyzed *ortho*-C–H arylation of benzoic acid derivatives with aryl boronates and/or aryl iodides.[15] Furthermore, some of these reactions were applicable to sterically hindered benzoic acids with a substituent at the other *ortho*-position.

According to Yu's procedure,[15a] the dicarboxylic acid **2** was subjected to oxidative C–H coupling reaction with phenyl boronate in the presence of benzoquinone and Ag_2CO_3 in *t*-BuOH (Scheme 3). But, even when the amount of the reagents and reaction time were increased, the reaction was not complete, resulting in the formation of a mono-functionalized product with recovery of the starting material. Therefore, we next examined the reaction with iodobenzene. Daugulis disclosed carboxylate-directed *ortho*-C–H coupling reactions of benzoic acid derivatives using the combination of $Pd(OAc)_2$ and AgOAc in AcOH,[15b] but this reaction did not work in our case. Larrosa subsequently reported a catalytic system that is also applicable to 2-substituted benzoic acids by suppressing protodecarboxylation of the carboxyl group.[15c] According to their protocol, *ortho*-C–H coupling reaction of **2** was carried out with a catalytic amount of

$Pd(OAc)_2$ in the presence of Ag_2CO_3 and K_2CO_3 (Table 2). When 4 equivalents of iodobenzene with respect to **2** (2 equivalents for each CO_2H group) was used, the desired compound **1a** was obtained in 64% yield after 24 hours (entry 1). The chemical yield was further improved when the amount of iodobenzene was increased, and **1a** was obtained in 81% yield. Under these reaction conditions, other iodoarenes underwent the desired coupling reaction, affording the products **1b** and **1c** without difficulty (entries 3,4), although a sterically hindered iodoarene could not be used (entry 5). In contrast to alkyl-substituted iodoarenes, compounds having either electron-donating or electron-withdrawing groups did not react well under the optimized conditions (Table 2, entries 6,7), although the reason for this is not clear.

Table 2. C-H di-arylation of **2** using Ar-I[a]



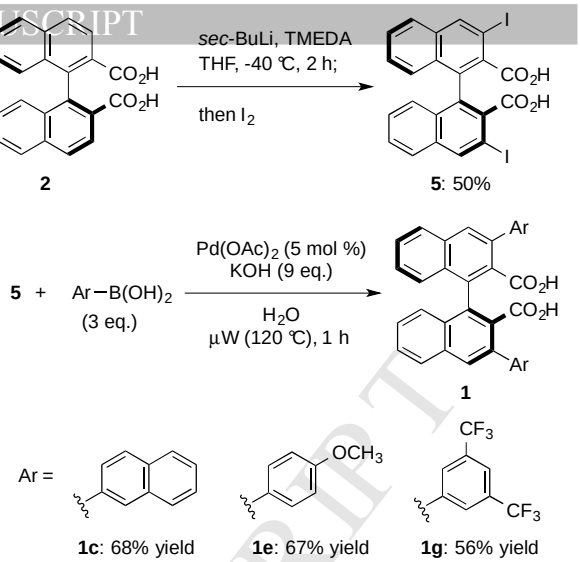
Entry	Ar	1	Yield of **1** (%)[b]
1[c]	C_6H_5	**1a**	64
2	C_6H_5	**1a**	81
3	3,5-Me_2-C_6H_3	**1b**	91
4	2-naphthyl	**1c**	46
5	2,4,6-Me_3-C_6H_2	**1d**	n.r.
6	4-MeO-C_6H_4	**1e**	34
7	4-Cl-C_6H_4	**1f**	<10

[a] The reactions were carried out with $Pd(OAc)_2$ (5 mol %), Ag_2CO_3 (1.1 equiv.), K_2CO_3 (1 equiv.) and iodoarene (6 equiv.) in AcOH on a 0.25 mmol scale, unless otherwise mentioned.

[b] Isolated yield.

[c] 4 equivalents of PhI were used.

In place of C–H activation, we expected that cross-coupling reactions of 3,3'-dihalo-1,1'-binaphthyl-2,2'-dicarboxylic acid with semi-metal reagents such as aryl boronic acid should work well, since several examples of cross-coupling reaction of 2-halobenzoic acids with aryl boronic acids have been reported.[16] To this end, we modified Yang's protocol for the synthesis of 3,3'-dihalogenated variants via the formation of the tetra-anion species, since their method provided low yields when the reaction was carried out at low temperature (–90 °C).[17] To our delight, treatment of **2** with *sec*-BuLi/TMEDA[18] at –40 °C and subsequent iodination with molecular iodine afforded di-iodide **5** in 50% isolated yield (Scheme 3). Under the micro-wave conditions,[16,19] Suzuki-Miyaura cross-coupling of **5** with aryl boronic acids including compounds having heterofunctional groups proceeded without difficulty to afford the coupling products **1c, 1e** and **1g** in good yield. This method is supplementary to the above-mentioned direct C–H arylation, which would provide facile access to a wide variety of 1,1'-binaphthyl-2,2'-dicarboxylic acids **1**.



Scheme 3. Suzuki-Miyaura cross-coupling reaction of **5**

3. Conclusion

We have established an efficient synthetic method for the preparation of chiral 3,3'-disubstituted 1,1'-binaphthyl-2,2'-dicarboxylic acids from commercially available BINOL. The key steps are reductive CO_2 fixation of aryl phosphate and C–H functionalization at the *ortho*-position of the carboxyl group. In the case of heterofunctionalized coupling partners, the synthesis was achieved by way of Suzuki-Miyaura cross-coupling reaction. We believe that this straightforward synthetic method will facilitate applications of chiral 1,1'-binaphthyl-2,2'-dicarboxylic acids as asymmetric organocatalysts.

4. Experimental section

4.1. General

^1H and ^{19}F NMR spectra were measured on a JEOL JNM-ECA-500 spectrometer at 500 and 470 MHz, respectively. ^{13}C NMR spectra were recorded on a JEOL JNM-ECA-500 spectrometer at 125 MHz. Chemical shifts are reported downfield from TMS (= 0) or a solvent[20] for ^1H NMR. For ^{13}C NMR, chemical shifts are reported in the scale relative to a solvent.[20] For ^{19}F NMR, chemical shifts are reported in the scale relative to a $CFCl_3$ external standard (0 ppm). Infrared spectra were measured on a Shimazu IRPrestige-21; only diagnostic absorptions are listed below. ESI-MS was taken on Bruker micrOTOF-QII-$_{RSL}$. Column chromatography was performed with silica gel N-60 (40-100 □m) purchased from Kanto Chemical Co., Inc.. TLC analysis was performed on Silica gel 60 F_{254}-coated glass plates (Merck). Visualization was accomplished by means of ultraviolet (UV) irradiation at 254 nm or by spraying 12-molybdo(VI)phosphoric acid ethanol solution as the developing agent.

*4.2. Synthesis of (S)-1,1'-binaphthyl-2,2'-bis(diethylphosphate) **3***[21]

To a solution of (*S*)-BINOL (1.0 g, 3.5 mmol) in THF (10 mL) was added NaH (60% in oil, 0.3 g, 7.5 mmol) at 0 °C. The mixture was stirred for 30 min, then diethyl chlorophosphate (1.1 mL, 7.6 mmol) was added, and stirring was continued for 30 min at room temperature. The reaction was quenched with aqueous saturated NH_4Cl and the mixture was extracted with ethyl

acetate. The organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 1/1) to provide the diethylphosphate **3** as a colorless solid (1.95 g, quant.); $[\alpha]_D^{20}$ -5.1 (*c* 0.85, $CHCl_3$); ^{1}H NMR (500 MHz, $CDC1_3$): δ = 0.85 (t, *J* = 6.3 Hz, 6H), 1.06 (t, *J* = 6.3 Hz, 6H), 3.46-3.52 (m, 4H), 3.67-3.79 (m, 4H), 7.27-7.33 (m, 4H), 7.42-7.45 (m, 2H), 7.79 (d, *J* = 9.2 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDC1_3$): δ = 15.5, 15.7, 64.0, 64.3, 119.1, 121.5, 125.3, 126.1, 126.9, 127.8, 129.9, 130.7, 133.5, 146.7; IR ($CHCl_3$): 3061, 2931, 2911, 1624, 1593, 1508, 1475, 1394, 1361, 1265, 1165, 1066, 1011, 868, 854, 816 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{32}O_8P_2Na$ *m/z* 581.1465 $[M+Na]^+$, found 581.1481.

*4.3. Reductive CO_2 fixation of **3** to provide (S)-1,1'-binaphthyl-2,2'-dicarboxylic acid **2***

Lithium (20.8 mg, 3.0 mmol) and naphthalene (384.5 mg, 3.0 mmol) were weighed into a flask, which had been flame-dried under vacuum. The flask was evacuated and refilled with argon, and THF (5 mL) was added to it. The mixture was stirred for 3 h at room temperature, then cooled to -78 °C. A solution of **3** (279.3 mg, 0.5 mmol) in THF (5 mL) was slowly added to the mixture using a cannula. After stirring for 30 min, carbon dioxide was bubbled to the reaction mixture. Stirring was continued for 2 h, then the mixture was allowed to warm to room temperature, and the reaction was quenched with aqueous 1 N HCl. The whole was extracted with diethyl ether, and then 1 N NaOH was added to the organic phase. The resulting aqueous layer was washed with diethyl ether. The aqueous phase was acidified with 1 N HCl, and extracted with ethyl acetate. The organic phase was washed with brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 4/1 with 1% AcOH) to give the dicarboxylic acid **2** (140.3 mg, 82%) as a colorless solid. The obtained compound was identified by comparison of the analytical data with reported values.[10] The optical purity of the product was determined to be >99% by chiral HPLC analysis; $[\alpha]_D^{26}$ -76.4 (*c* 0.90, $CHCl_3$, >99% ee sample); ^{1}H NMR (500 MHz, $CDC1_3$): δ = 6.90 (d, *J* = 8.6 Hz, 2H), 7.13-7.16 (m, 2H), 7.46-7.50 (m, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.6 Hz, 2H), 8.13 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDC1_3$): δ = 125.5, 126.5, 126.6, 127.4, 127.8, 128.0, 132.8, 135.3, 141.8, 172.1; IR ($CHCl_3$): 1703, 1597, 1470, 1285 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{13}O_4$ *m/z* 341.0808 $[M-H]^-$, found 341.0805. Daicel CHIRALCEL OD-H (ϕ 0.46 cm x 25 cm), *n*-hexane/EtOH = 90/10 with 1% CF_3CO_2H, flow rate 1.0 mL/min, detection at 254 nm, t_R = 9.1 min (*R*), 12.7 min (*S*).

4.4. Typical experimental procedure for Pd-catalyzed C–H coupling at the ortho-position of the carboxylic acid using iodoarenes

Compound **2** (85.6 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 10 mol %), Ag_2CO_3 (76 mg, 1.1 equiv.), and K_2CO_3 (35 mg, 1 equiv.) were weighed into a Schlenk tube with J Young greaseless stopcock, which had been flame-dried under vacuum. The tube was evacuated and back-filled with argon. Then, AcOH (0.13 mL) and iodobenzene (167 µL, 6 equiv.) were added. The mixture was stirred for 24 h at 120 °C, then allowed to cool to room temperature, and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 4/1 with 1% AcOH) to provide **1a** (100 mg, 81%) as a colorless solid.

*4.4.1. (S)-1,1'-binaphthyl-3,3'-diphenyl-2,2'-dicarboxylic acid (**1a**)*[5,6c]

Analytical data for this compound were identical with reported data: $[\alpha]_D^{20}$ -16.6 (*c* 0.90, $CHCl_3$); ^{1}H NMR (500 MHz, $CDC1_3$): δ = 7.13 (d, *J* = 8.6 Hz, 2H), 7.30-7.34 (m, 2H), 7.40-7.43 (m, 2H), 7.45-7.49 (m, 4H), 7.51-7.55 (m, 2H), 7.60 (d, *J* = 7.4 Hz, 4H), 7.95 (d, *J* = 8.0 Hz, 2H), 8.04 (s, 2H); ^{13}C NMR (125 MHz, $CDC1_3$): δ = 126.7, 127.7, 127.9, 128.0, 128.2, 128.6, 128.7, 130.3, 131.3, 132.2, 132.9, 133.7, 136.3, 139.9, 171.4; IR ($CHCl_3$): 3061, 2928, 2855, 1748, 1662, 1454, 1373, 1273, 1109, 897 cm^{-1}; HRMS (ESI) calcd. for $C_{34}H_{21}O_4$ *m/z* 493.1434 $[M-H]^-$, found 493.1414.

*4.4.2. (S)-1,1'-binaphthyl-3,3'-bis(3,5-dimethylphenyl)-2,2'-dicarboxylic acid (**1b**)*

$[\alpha]_D^{20}$ 1.2 (*c* 2.26, $CHCl_3$); ^{1}H NMR (500 MHz, $CDC1_3$): δ = 2.38 (s, 12H), 7.04 (s, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 7.20 (s, 4H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 2H), 8.00 (s, 2H); ^{13}C NMR (125 MHz, $CDC1_3$): δ = 21.3, 126.5, 126.6, 127.5, 127.8, 128.1, 129.5, 130.1, 131.2, 132.3, 132.7, 133.6, 136.5, 138.0, 139.9, 171.8; IR ($CHCl_3$): 2922, 1746, 1668, 1602, 1363, 1288, 895, 852 cm^{-1}; HRMS (ESI) calcd. for $C_{38}H_{29}O_4$ *m/z* 549.2060 $[M-H]^-$, found 549.2033.

*4.4.3. (S)-1,1'-binaphthyl-3,3'-bis(2-naphthyl)-2,2'-dicarboxylic acid (**1c**)*

$[\alpha]_D^{20}$ 74.2 (*c* 0.49, $CHCl_3$); ^{1}H NMR (500 MHz, $CDC1_3$): δ = 7.18 (d, *J* = 8.6 Hz, 2H), 7.33 (dt, *J* = 1.2, 7.5 Hz, 2H), 7.50-7.76 (m, 7H), 7.70 (dd, *J* = 1.8, 8.6 Hz, 2H), 7.88-7.93 (m, 7H), 7.96 (d, *J* = 8.0 Hz, 2H), 8.06 (s, 2H), 8.12 (s, 2H); ^{13}C NMR (125 MHz, $CDC1_3$): δ = 126.2, 126.4, 126.7, 126.8, 127.6, 127.7, 127.9, 128.1, 128.2, 130.5, 131.3, 132.7, 132.9, 133.0, 133.3, 133.6, 136.2, 137.5, 172.0; IR ($CHCl_3$): 3057, 2928, 2855, 1748, 1668, 1456, 1362, 1271, 895, 858 cm^{-1}; HRMS (ESI) calcd. for $C_{42}H_{25}O_4$ *m/z* 593.1747 $[M-H]^-$, found 593.1737.

*4.5. Diiodination of 1,1'-binaphthyl-2,2'-dicarboxylic acid **2** to give **5***[17]

To a solution of **2** (684 mg, 2 mmol) and TMEDA (2 mL, 13.4 mmol) in THF (10 mL) was added *sec*-BuLi solution in cyclohexane (1.0 M, 12 mL, 12 mmol) at -40 °C. The mixture was stirred for 2 h at -40 °C, and then iodine (2g, 15.8 mmol) solution in THF (10 mL) was added to it. The solution was stirred for additional 2 h at -40 °C, then quenched with aqueous $Na_2S_2O_3$ and extracted with ethyl acetate after acidifying with 1N HCl. The organic layer was dried over Na_2SO_4, and filtered. The filtrate was evaporated under reduced pressure and the residue was re-dissolved in MeOH. Silica gel was added to the mixture and the organic solvent was removed under reduced pressure. The compound was purified by column chromatography on silica gel (hexane/ethyl acetate = 1/1 with 1% AcOH) to provide **5** (0.59 g, 50%). Analytical data for the isolated compound were identical with reported values: $[\alpha]_D^{20}$ -117.3 (*c* 0.72, $CHCl_3$); ^{1}H NMR (500 MHz, CD_3OD): δ = 7.07 (d, *J* = 8.5 Hz, 2H), 7.36-7.39 (m, 2H), 7.55-7.58 (m, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 8.68 (s, 2H); ^{13}C NMR (125 MHz, CD_3OD): δ = 89.0, 129.0, 129.1, 129.6, 129.9, 133.8, 135.2, 136.7, 140.1, 142.0, 172.4; IR ($CHCl_3$): 1749, 1711, 1364 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{11}I_2O_4$ *m/z* 592.8741 $[M-H]^-$, found 592.8763.

*4.6. Typical experimental procedure for Suzuki-Miyaura coupling of **5***

Compound **5** (29.7 mg, 0.05 mmol), $Pd(OAc)_2$ (0.5 mg, 5 mol %), and 2-naphthylboronic acid (25.8 mg, 0.15 mmol) were weighed into a Schlenk flask. Water (1 mL) was added. After stirring for 10 min at room temperature, KOH (25.2 mg, 0.45 mmol) was added to the mixture. The mixture was heated up under micro-wave irradiation to 120 °C for 1 h, and then extracted with ethyl acetate after acidifying with 1N HCl. The organic layer was dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 4/1 with 1% AcOH) to provide **1c** (20.1 mg, 68%) as a colorless solid.

*4.6.1. (S)-1,1'-binaphthyl-3,3'-bis(4-methoxyphenyl)-2,2'-dicarboxylic acid (**1e**)*

$[\alpha]_D^{20}$ 27.9 (*c* 1.64, $CHCl_3$); ^{1}H NMR (500 MHz, $CDC1_3$): δ = 3.86 (s, 6H), 6.99 (td, *J* = 2.9, 9.2 Hz, 4H), 7.12 (d, *J* = 8.6 Hz, 2H), 7.30 (dt, *J* = 1.1, 7.5 Hz, 2H), 7.50-7.53 (m, 6H), 7.93 (d, *J* = 8.6 Hz, 2H), 8.00 (s, 2H); ^{13}C NMR (125 MHz, $CDC1_3$): δ = 55.3, 114.1, 126.6, 127.4, 127.9, 128.1, 129.8, 130.1, 131.0, 132.3, 132.3, 132.7, 133.7, 135.8, 159.3, 171.9; IR ($CHCl_3$): 2936, 2839, 1744, 1611, 1514, 1240, 1036, 835 cm^{-1}; HRMS (ESI) calcd. for $C_{36}H_{25}O_6$ *m/z* 553.1646 $[M-H]^-$, found 553.1625.

*4.6.2. (S)-1,1'-binaphthyl-3,3'-bis[3,5-bis(trifluoromethyl) phenyl]-2,2'-dicarboxylic acid (**1g**)*[5]

Analytical data for this compound were identical with reported values: $[\alpha]_D^{20}$ -30.5 (*c* 0.58, $CHCl_3$); ^{1}H NMR (500 MHz, CD_3OD): δ = 7.11 (d, *J* = 8.5 Hz, 2H), 7.35-7.38 (m, 2H), 7.55-7.58 (m, 2H), 8.01 (s, 2H), 8.09 (d, *J* = 8.5 Hz, 2H), 8.19 (s, 2H), 8.28 (s, 4H); ^{13}C NMR (125 MHz, CD_3OD): δ = 122.9, 125.8 (q, *J* = 271.8 Hz), 128.6 (q, *J* = 8.3 Hz), 129.4, 129.8, 130.5, 131.3, 132.4 (q, *J* = 3.6 Hz), 133.6 (q, *J* = 33.4 Hz), 134.3, 134.6, 135.4, 135.6, 138.1, 145.8, 175.5; ^{19}F NMR (375 MHz, CD_3OD): δ = -64.1 (s); IR ($CHCl_3$): 1749, 1667, 1377, 1280, 1184, 1142 cm^{-1}; HRMS (ESI) calcd. for $C_{38}H_{17}F_{12}O_4$ *m/z* 765.0930 $[M-H]^-$, found 765.0941.

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