An Innovative Synthesis of Unsymmetrical Tetrahydrobinaphthyls, Binaphthyls with a Phenyl Spacer, and Tetrahydroazabinaphthyls through Ring Transformation Reactions of 6-Naphthyl-2-pyrones†

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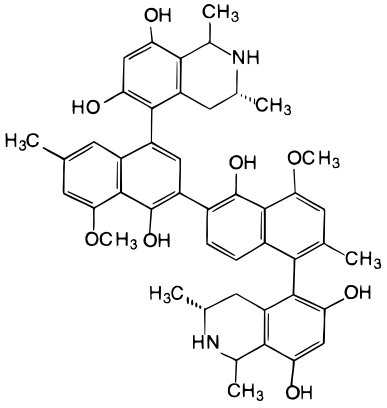
An innovative approach to the synthesis of unsymmetrical tetrahydrobinaphthyls (**3**), binaphthyls with a phenyl spacer (**5**), and tetrahydroazabinaphthyls (**7**) is delineated and illustrated from functionalized 3-(carbomethoxy)-4-(methylthio)-6-naphthyl-2*H*-pyran-2-one through base-catalyzed ring transformation reactions.

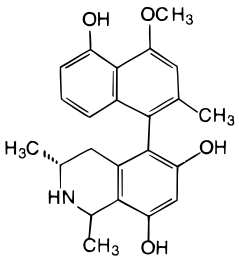
Binaphthyl systems, particularly those suffering hindered rotation, not only are the central building blocks in a large number of natural products and pharmaceuticals but are also useful as chiral reagents[1] and crown ethers,[2] as chiral host molecules for inclusion compounds,[3] and as chiral phases for chromatography.[4] Recently numerous natural products with an azabinaphthyl system such as michellamine (I), korupensamine (II), and ancistrocladine (III) have been reported to have anti-HIV[5] and antitumor[6] activities.

Continuously increasing pressure to devise new synthetic approaches to the highly important biaryl systems has borne fruit in recent years. The reductive dimerization of aryl iodides in the presence of copper bronze is one of the oldest methods[7] for the synthesis of a symmetrical biaryl system.

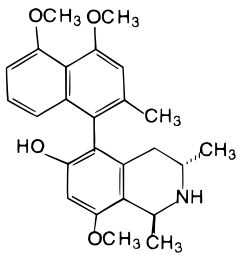
Ni complexes have been also used as coupling reagents to produce[8] biaryls in high yield at 40−50 °C. Complementary to the Ullmann reaction, oxidative coupling of electron-rich aromatic phenols also led to the formation[9] of biaryls having limited preparative use. A convenient and efficient synthesis[10] of biaryls has been developed via coupling of arylthallium bis(trifluoroacetate) with a catalytic amount of lithium tetrachloropalladate or ruthenium(IV) tetrakis(trifluoroacetate)[11,12] as coupling



I
(Michellamine)



II
(Korupensamine)



III
(Ancistrocladine)

reagents. Palladium-catalyzed cross-coupling between the electrophilic compounds Ar−X (X being mainly Br, I, and OTf) and the organometallic species Ar−M (M being mainly Mg, Zn, Sn, and B) is a versatile synthetic route for C−C bond formation.[13] The palladium-catalyzed arylboronic acid coupling[14] (Suzuki reaction) has become increasingly popular due to the commercial availability

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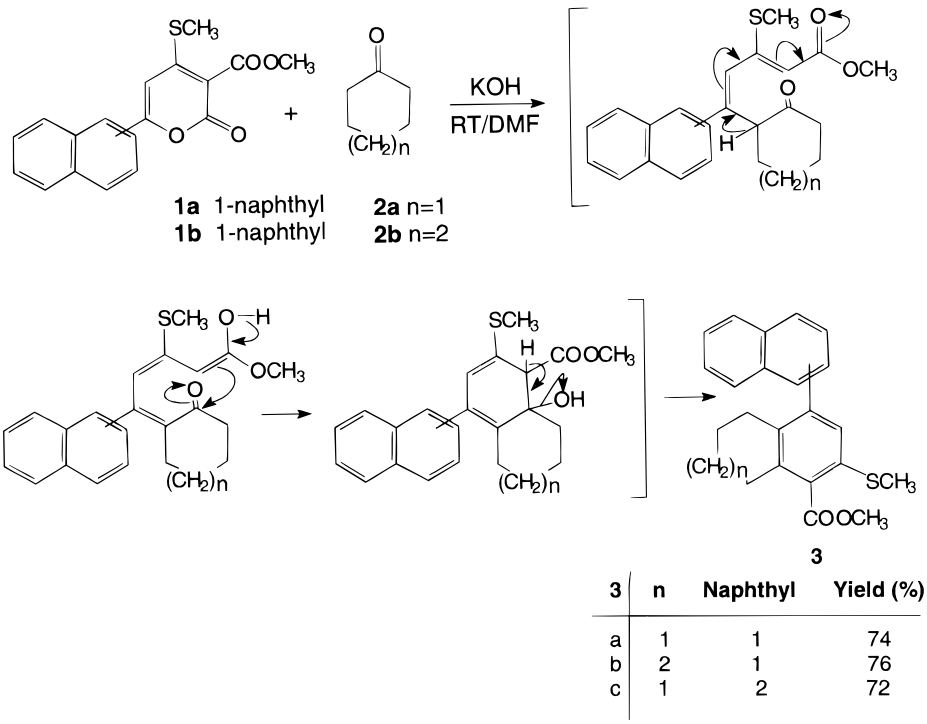
Scheme 1



3

3	n	Naphthyl	Yield (%)
a	1	1	74
b	2	1	76
c	1	2	72

of arylboronic acids, easy workup, and tolerance of the reaction to aqueous media. A recent improvement of the Suzuki coupling has been the introduction of a phosphine-free catalytic system.[15] Despite the versatility of Suzuki-type cross coupling, it has the disadvantage of coupling of arylboronic acid with a phenyl group of a triphenylphosphine stabilizing ligand as a side reaction to the desired coupling of the arylboronic acid with an aryl bromide[16] and also self-coupling of aryl groups of arylboronic acid in the case of slow cross-coupling.[17−19]

Despite numerous known cross-coupling reactions for the construction of biaryls, Meyers[20] developed an efficient route for the synthesis of unsymmetrical biaryl systems through an oxazoline-mediated coupling reaction. Besides its limitations to certain substitution patterns and the difficulty of obtaining some Grignard reagents, it is highly useful in natural products synthesis.[21]

We report here a highly convenient and efficient synthesis of unsymmetrical biaryls as an alternative for the Suzuki reaction through base-induced ring transformation reactions of 6-naphthyl-3-(carbomethoxy)-4-(methylthio)-2*H*-pyran-2-one[22](**1**) from aryl ketone. This reaction in many ways is superior to the existing procedures available for the construction of biaryls with respect to its (1) versatility and compatibility, (2) mild reaction conditions, (3) use of inexpensive reactants, (4) high yields and easy workup, and (5) possibility for enlargement of ring size in one of the aromatic halves at will (the reaction fails when 2-substituted ketones are used as the source of the carbanion).

The substrate needed for the transformation reactions is 3-(carbomethoxy)-4-(methylthio)-6-naphthyl-2*H*-pyran-2-one (**1**), having the three electrophilic centers C^2, C^4, and C^6 in which C^6 is highly susceptible to nucleophilic attack. This transformation is basically initiated by the attack of a carbanion generated in situ from a ketone by alkali-metal hydroxide in DMF at the C^6 position in pyran-2-one (**1**), with ring opening followed by decarboxylation and intramolecular condensation−cyclization involving the keto group with concomitant elimination of water, offering biaryls. This is a one-pot reaction in which an equimolar mixture of pyran-2-one (**1**), alicyclic ketone (**2**), and powdered KOH in DMF is stirred at ambient temperature for 35 h under an inert atmosphere. After the reaction mixture is poured into ice water, the solution is neutralized with 10% HCl and the precipitate thus obtained is filtered and purified by column chromatography as unsymmetrical biaryls such as the 1-naphthyl-1′-benzocycloalkanes **3a**,**b** and the 2-naphthyl-1′-benzocycloalkane **3c** (Scheme 1). Besides the synthesis of functionalized unsymmetrical 1,1′-tetrahydrobinaphthyl and 2,1′-binaphthyl, application of this reagent was extended to the synthesis of binaphthyls with a phenyl spacer (**5a**,**b**) from the reaction of 3-(carbomethoxy)-4-(methylthio)-6-(1-naphthyl)-2*H*-pyran-2-one (**1a**) and 1-

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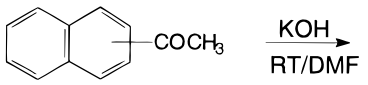
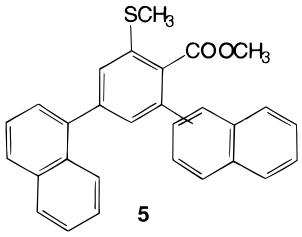
Scheme 2



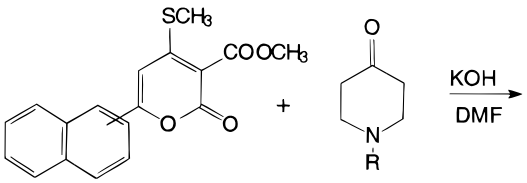
4a 1-naphthyl
4b 2-naphthyl



5

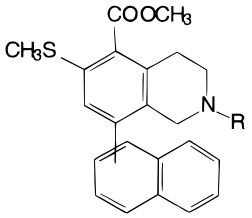
5	Naphthyl	Yield (%)
a	1	68
b	2	65

Scheme 3



1

6a R=$COOC_2H5$
6b R=$C_6H_5CH_2$



7

7	R	Naphthyl	Yield (%)
a	$COOC_2H_5$	1	72
b	$COOC_2H_5$	2	69
c	$C_6H_5CH_2$	1	78
d	$C_6H_5CH_2$	2	74

or 2-acetylnaphthalene. In all of the cases the desired compounds were isolated in high yields (Scheme 2) and characterized by their elemental and spectroscopic analyses. Attempts were also made to synthesize aza analogues of binaphthyl from the reaction of **1** and N-substituted 4-piperidone (**6**), and the desired compounds (**7a**−**d**) were isolated in high yields (Scheme 3). The spectroscopic data for all the synthesized compounds were in agreement with their proposed structures. The mechanism for the formation of binaphthyls from **1** is depicted in Scheme 1. Other compounds that were synthesized (**3a**−**c**, **5a**,**b**, and **7a**−**d**) followed the same course of reaction.

In summary, an innovative one-pot route for the synthesis of unsymmetrical tetrahydrobinaphthyls, binaphthyls with a phenyl spacer, and tetrahydroazabinaphthyls has been developed. The yield in each case is highly compatible and comparable to that reported in the literature. This procedure also provides a new method of introducing the functional group in the molecule at a specific position.

Experimental Section

Melting points are uncorrected. The reagent grade reaction solvents such as DMSO and DMF were further dried by distillation over calcium hydride. Cyclohexanone, cycloheptanone, 1-carboethoxy-4-piperidone, and 1-benzyl-4-piperidone were purchased from Aldrich. TLC was performed on precoated silica gel plastic plates and visualized by UV irradiation, exposure to iodine vapors, or spraying with $KMnO_4$ solution. IR spectra of liquid samples were run neat, and solids were run as KBr pellets. ^{1}H NMR spectra were recorded at 200 and 300 MHz in $CDCl_3$ with tetramethylsilane as internal reference. Chemical shifts and coupling constants (J) are reported in δ (ppm) and in Hz, respectively. Mass spectra were collected at 70 eV by electron impact. Elemental analyses (C, H, and N) were performed at RSIC, Central Drug Research Institute, Lucknow, India.

1-(Carbomethoxy)-2-(methylthio)-4-(1-naphthyl)benzocyclohexane (3a). A mixture of **1a** (0.33 g, 1 mmol), cyclohexanone (0.10 g, 1 mmol), and powdered KOH (0.11 g, 2 mmol) was stirred in dry DMSO (8 mL) at ambient temperature for 35 h. After completion of the reaction, the mixture was poured into ice−water and acidified with 10% HCl. The precipitate was collected and purified on a silica gel column using chloroform−hexane (1:2) as eluent: colorless oil, yield 0.27 g (74%). IR (neat): ν 1728 cm^{-1} (CO). MS: m/z 362 (M^+, 49), 330 (100), 297 (15). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.65−1.68 (m, 2H, CH_2), 1.78−1.81 (m, 2H, CH_2), 2.45 (s, 3H, CH_3), 2.56−2.60 (m, 2H, CH_2), 2.78−2.82 (m, 2H, CH_2), 3.97 (s, 3H, CH_3), 7.17 (s, 1H, Ar H), 7.39 (d, 1H, J = 7.9 Hz, Ar H), 7.50−7.53 (m, 2H, Ar H), 7.71 (s, 1H, Ar H), 7.84−7.89 (m, 3H, Ar−H). Anal. Calcd for $C_{23}H_{22}O_2S$: C, 76.21; H, 6.12. Found: C, 76.43; H, 6.23.

1-(Carbomethoxy)-2-(methylthio)-4-(1-naphthyl)benzocycloheptane (3b). This compound was synthesized by stirring a mixture of **1a** (0.33 g, 1 mmol) and cycloheptanone (0.12 g, 1 mmol) as described above. Mp: 85−87 °C. IR (KBr): ν 1728 cm^{-1} (CO). MS: m/z 376 (M^+, 100), 344 (74), 311 (14). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.56−1.59 (m, 2H, CH_2), 1.70−1.75 (m, 2H, CH_2), 1.76−1.81 (m, 2H, CH_2), 2.45 (s, 3H, CH_3), 2.71−2.75 (m, 2H, CH_2), 2.76−2.80 (m, 2H, CH_2), 3.98 (s, 3H, CH_3), 7.17 (s, 1H, Ar H), 7.38 (d, 2H, J = 8.0 Hz, Ar H), 7.50−7.54 (m, 2H, Ar H), 7.71 (s, 1H, Ar H), 7.85−7.91 (m, 3H, Ar H). Anal. Calcd for $C_{24}H_{24}O_2S$: C, 76.56; H, 6.42. Found: C, 76.61; H, 6.43.

1-(Carbomethoxy)-2-(methylthio)-4-(2-naphthyl)benzocyclohexane (3c). The title compound was synthesized by stirring a reaction mixture of **1b** (0.33 g, 1 mmol), cyclohexanone (0.12 g,1 mmol), and powdered KOH (0.11 g, 2 mmol) in dry DMSO (8 mL) for 35 h and isolated as described for **3a**. Mp: 104−106 °C. IR (KBr): ν 1728 cm^{-1} (CO). MS: m/z 362 (M^+, 62), 330 (100), 296 (20). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.66−1.74 (m, 2H, CH_2), 1.78−1.86 (m, 2H, CH_2), 2.46 (s, 3H, CH_3), 2.58−2.62 (m, 2H, CH_2), 2.80−2.84 (m, 2H, CH_2), 3.99 (s, 3H, CH_3), 7.20 (s, 1H, Ar H), 7.42 (d, 2H, J = 8.0 Hz, Ar H), 7.53−7.56 (m, 2H, Ar H), 7.74 (s, 1H, Ar H), 7.87−7.93 (m, 3H, Ar H). Anal. Calcd for $C_{23}H_{22}O_2S$: C, 76.21; H, 6.12. Found: C, 76.28; H, 6.17.

Methyl 2,4-Bis(1-naphthyl)-6-(methylthio)benzoate (5a). A mixture of **1a** (0.33 g, 1 mmol), 1-acetylnaphthalene (**4a**, 0.18 g, 1 mmol), and powdered KOH (0.11 g, 2 mmol) was stirred in DMF (8 mL) for 33 h at ambient temperature. After completion, the reaction mixture was poured into ice−water and acidified with 10% HCl. The precipitate was collected and purified on a silica gel column using hexane−chloroform (4:1) as eluent: colorless oil. IR (neat): ν 1726 cm^{-1} (CO) MS: m/z 434 (M^+, 34), 404 (31), 372 (22). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.56 (s, 3H, CH_3), 3.66 (s, 3H, CH_3), 7.45−7.60 (m, 9H, Ar

H), 7.82−7.93 (m, 7H, Ar H). Anal. Calcd for $C_{29}H_{22}O_2S$: C, 80.15; H, 5.10. Found: C, 80.19; H, 5.16.

Methyl 2-(2-Naphthyl)-4-(1-naphthyl)-6-(methylthio)-benzoate (5b). This compound was synthesized from the reaction of **1a** (0.33 g, 1 mmol), 2-acetylnaphthalene (**4b**; 0.18 g, 1 mmol), and powdered KOH (0.11 g, 2 mmol) in dry DMF (8 mL) under an inert atmosphere at room temperature and isolated according to the procedure described for **5a**: colorless oil. IR (neat): ν 1726 cm^{-1} (CO). MS: *m*/*z* 434 (M^+, 56), 403 (52), 372 (28). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.63 (s, 3H, CH_3), 3.62 (s, 3H, CH_3), 7.50−7.65 (m, 7H, Ar H), 7.76 (s, 1H, Ar H), 7.78 (s, 1H, Ar H), 7.84−7.97 (m, 6H, Ar H), 8.09 (s, 1H, Ar H). Anal. Calcd for $C_{29}H_{22}O_2S$: C, 80.15; H, 5.10. Found: C, 80.29; H, 5.23.

2-(Carboethoxy)-5-(carbomethoxy)-6-(methylthio)-8-(1-naphthyl)-1,2,3,4-tetrahydroisoquinoline (7a). A mixture of **1a** (0.33 g, 1 mmol), 1-carboethoxy-4-piperidone (**6a**; 0.17 g, 1 mmol), and powdered KOH (0.11 g, 2 mmol) in dry DMF (8 mL) was stirred at room temperature for 34 h under an inert atmosphere. After completion, the reaction mixture was poured into ice−water and acidified with 10% HCl. The precipitate was collected and purified on silica gel column using chloroform-hexane (1:1) as eluent: colorless oil. IR (neat): ν 1692 (CO), 1726 cm^{-1} (CO). MS: *m*/*z* 434 (M^+, 13), 406 (26), 374 (15). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.21 (t, 3H, J = 7.2 Hz, CH_3), 2.46 (s, 3H, CH_3), 2.91 (t, 2H, J = 6.1, CH_2), 3.67 (t, 2H, J = 6.0 Hz, CH_2), 3.98 (s, 3H, CH_2), 4.09 (q, 2H, J = 7.2 Hz, CH_2), 4.46 (s, 2H, CH_2), 7.19 (s, 1H, Ar H), 7.41(d, 1H, J = 7.0 Hz, Ar H), 7.50−7.56 (m, 3H, Ar H), 7.90−7.94 (m, 3H, Ar H). Anal. Calcd for $C_{25}H_{25}NO_4S$: C, 68.94; H, 5.79; N, 3.22. Found: C, 68.99; H, 5.86; N, 3.31.

2-(Carboethoxy)-5-(carbomethoxy)-6-(methylthio)-8-(2-naphthyl)-1,2,3,4-tetrahydroisoquinoline (7b). This compound was synthesized by stirring a reaction mixture of **1b** (0.66 g, 2 mmol), **6a** (0.34 g, 2 mmol), and powdered KOH (0.22 g, 4 mmol) in dry DMF (15 mL) and isolated according to the procedure described for **7a**: colorless oil. IR (neat): ν 1697 (CO), 1728 cm^{-1} (CO). MS: *m*/*z* 435 (M^+, 41), 406 (100), 374 (52), 301 (17), 259 (32). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (t, 3H, J = 7.2 Hz, CH_3), 2.46 (s, 3H, CH_3), 2.89 (t, 2H, J = 6.0 Hz, CH_2), 3.67 (t, 2H, J = 6.0 Hz, CH_2), 3.98 (s, 3H, CH_3), 4.08 (q, 2H, J = 7.2 Hz, CH_2), 4.46 (s, 2H, CH_2), 7.19 (s, 1H, Ar H), 7.39 (t, 1H, J = 6.9 Hz, Ar H), 7.53−7.57 (m, 2H, Ar H), 7.73 (s, 1H, Ar H), 7.86−7.95 (m, 3H, Ar H). Anal. Calcd for $C_{25}H_{25}NO_2S$: C, 68.94; H, 5.79; N, 3.22. Found: C, 69.07; H, 5.81; N, 3.27.

2-Benzyl-5-(carbomethoxy)-6-(methylthio)-8-(1-naphthyl)-1,2,3,4-tetrahydroisoquinoline (7c). A mixture of **1a** (0.33 g, 1 mmol), 1-benzyl-4-piperidone (**6b**; 0.19 g, 1 mmol), and powdered KOH (0.11 g, 2 mmol) in dry DMF (8 mL) was stirred at room temperature for 30 h under an inert atmosphere. After completion, the reaction mixture was poured into ice−water and acidified with 10% HCl. The reaction mixture was extracted with chloroform. An organic layer was separated out and evaporated to dryness. The crude product was purified on a silica gel column using chloroform−hexane (1:2) as eluent: colorless oil. IR (neat): ν 1728 cm^{-1} (CO). MS: *m*/*z* 453 (M^+, 88), 395 (25). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 3H, CH_3), 2.65 (t, 2H, J = 6.3 Hz, CH_2), 2.89 (t, 2H, J = 6.1 Hz, CH_2), 3.52 (s, 2H, CH_2), 3.56 (s, 3H, CH_2), 3.94 (s, 3H, CH_3), 7.16 (s, 1H, Ar H), 7.25 (s, 2H, Ar H), 7.36 (d, 1H, J = 7.7 Hz, Ar H), 7.40 (d, 1H, J = 7.7 Hz, Ar H), 7.50−7.55 (m, 3H, Ar H), 7.71 (s, 1H, Ar H), 7.83−7.91 (m, 4H, Ar H). Anal. Calcd for $C_{29}H_{27}NO_2S$: C, 76.79; H, 6.00; N, 3.09. Found: C, 76.85; H, 6.06; N, 3.11.

2-Benzyl-5-(carbomethoxy)-6-(methylthio)-8-(2-naphthyl)-1,2,3,4-tetrahydroisoquinoline (7d). This compound was synthesized by stirring a reaction mixture of **1b** (0.66 g, 2 mmol) and **6b** (0.38 g, 2 mmol) in dry DMF (15 mL) in the presence of powdered KOH (0.22 g, 4 mmol), and the product was isolated according to the procedure described for **7c**: colorless oil. IR (neat): ν 1726 cm^{-1} (CO). MS: *m*/*z* 453 (M^+, 49), 395 (16). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.44 (s, 3H, CH_3), 2.64 (t, 2H, J = 6.1 Hz, CH_2), 2.89 (t, 2H, J = 6.1 Hz, CH_2), 3.54 (s, 2H, CH_2), 3.56 (s, 3H, CH_2), 3.96 (s, 3H, CH_3), 7.15 (s, 1H, Ar H), 7.24−7.26 (m, 3H, Ar H), 7.38 (d, 1H, J = 7.7 Hz, Ar H), 7.50−7.56 (m, 3H, Ar H), 7.71(s, 1H, Ar H), 7.83−7.90 (m, 4H, Ar H). Anal. Calcd for $C_{29}H_{27}NO_2S$: C, 76.79; H, 6.00; N, 3.09. Found: C, 76.89; H, 6.11; N, 3.18.

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