Convenient Method for the Synthesis of 6,6′-Diacyl-1,1′-bi-2-naphthyl Ethers

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Abstract: Acylation of 1,1′-bi-2-naphthol (BINOL) ethers using Lewis acids aluminum(III) chloride and titanium(IV) chloride gave the corresponding 6,6′-diacyl derivatives in good yields.

Key words: chiral 1,1′-bi-2-naphthol, acylation, aluminum(III) chloride, titanium(IV) chloride, acyl-bi-2-naphthyl ether

Optically active 1,1′-bi-2-naphthol (BINOL, **1**) (Figure 1) derivatives have been used both catalytically and stoichiometrically in various asymmetric transformations.[1] There has been immense interest in modified BINOL ligands as the outcome of a given asymmetric transformation depends on both the steric and the electronic properties of the chiral ligand. Several 6,6′-disubstituted 1,1′-bi-2-naphthol derivatives have been found to be useful in asymmetric transformations.[2,3] For example, the La–Li complex of 6,6′-dimethyl-1,1′-bi-2-naphthol was used as an asymmetric catalyst for the nitro-aldol reaction[2] and a chiral 6,6′-dibromo-1,1′-bi-2-naphthol–zirconium catalyst used for enantioselective Mannich-type reaction.[3]

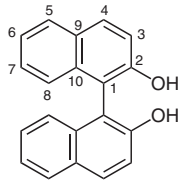

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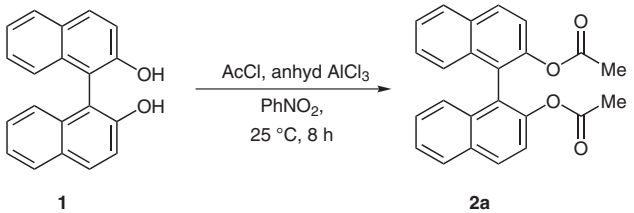
Figure 1

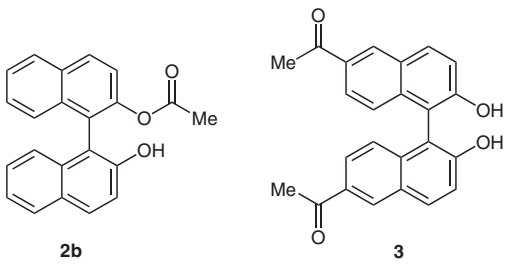
Previously, a simple method for the resolution of racemic 1,1′-bi-2-naphthol using boric acid and (+)-(*R*)-α-methylbenzylamine or (*S*)-proline was reported from this laboratory.[4] Racemic BINOL was also resolved with an optically active aminonaphthol and boric acid in acetonitrile solvent.[5] Chiral 1,1′-bi-2-naphthol in alliance with boric acid was utilized for the purification of diastereomeric amino alcohol derivatives[6] and for the resolution of (±)-*trans*-2-pyrrolidinylcyclohexanol and its methyl ether derivative.[7] Intramolecular oxidative coupling of phenylacetic acid esters of enantiomerically pure 1,1′-bi-2-naphthol was achieved by preparing the corresponding titanium ester enolates with the titanium(IV) chloride/triethylamine reagent system.[8] Convenient methods were developed for the preparation of chiral 1,1′-bi-2-naphthol derived amino ethers through the opening of aziridinium ion intermediates derived from *trans* (±)-2-pyrrolidin-1-ylcyclohexanol.[9] During these investigations, we became interested in the synthesis of 6,6′-diacyl-1,1′-binaphthyl ether derivatives for further synthetic exploitation. The 6,6′-positions of 1,1′-bi-2-naphthol can be selectively functionalized. The most common precursor for the synthesis of 6,6′-disubstituted BINOL ligands described in the literature is 6,6′-dibromo-1,1′-bi-2-naphthol. This derivative is prepared by electrophilic aromatic bromination of BINOL.[10] A variety of 6,6′-disubstituted BINOLs were prepared using 6,6′-dibromo-1,1′-bi-2-naphthol.[11] However, there is no direct method available to obtain 6,6′-diacyl-1,1′-bi-2-naphthyl ether derivatives.[12] We wish to report here a convenient method for the synthesis of these derivatives.

Initially, we examined the acylation of 1,1′-bi-2-naphthol (**1**) using various Lewis acids like anhydrous aluminum(III) chloride, titanium(IV) chloride, or zirconium(IV) chloride. For example, we have observed that the reaction of 1,1′-bi-2-naphthol (**1**) with acetyl chloride in the presence of aluminum(III) chloride in nitrobenzene at 25 °C for eight hours gave the diester derivative **2a** in 95% yield (Scheme 1) instead of the desired diketone **3** (Figure 2).



1 **2a** 95%

Scheme 1



2b **3**

Figure 2

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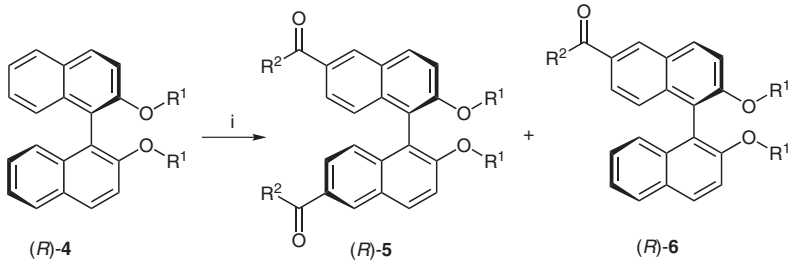


Scheme 2 *Reagents and conditions* (R^1 = pentyl): (i) R^2OCl, CH_2Cl_2, $TiCl_4$, r.t., 24 h.

We have made efforts to carry out the Fries rearrangement of the diester **2a** in a separate step using the Lewis acid aluminum(III) chloride in carbon disulfide at 50 °C to obtain **3**; these attempts were not successful. Also, acylation of diester **2a** did not proceed further in the presence of aluminum(III) chloride in nitrobenzene at 25 °C. In this run, only the starting material **2a** was obtained along with the monoester **2b** in 35% yield.

Fortunately, protection of the hydroxy groups of BINOL **1** gave good results in the acylations. When the reaction was carried out using the pentyl-protected 1,1′-bi-2-naphthol (*R*)-**4**, the mono- (*R*)-**6** and diacylated (*R*)-**5** derivatives were obtained in acceptable yields (Scheme 2). The acylation reaction was carried out using four equivalents of acetyl chloride and pentyl-protected optically active (+)-(*R*)-1,1′-bi-2-naphthol (*R*)-**4** in the presence of titanium(IV) chloride in dichloromethane at 25 °C for 24 hours. Both the 6,6′-diacyl-1,1′-bi-2-naphthol derived ether (*R*)-**5a** and the 6-acyl-1,1′-bi-2-naphthol derived ether (*R*)-**6a** were obtained in 64% and 22% yields, respectively. The results of the acylation of 1,1′-bi-2-naphthol derived ether (*R*)-**4** are summarized in Table 1.

Table 1 Acylation of (*R*)-**4** Using Titanium(IV) Chloride[a,b]

Entry	R^2	(*R*)-**5**	Yield[c] (%)	(*R*)-**6**	Yield[c] (%)
1	Me	(*R*)-**5a**	64	(*R*)-**6a**	22
2	Et	(*R*)-**5b**	66	(*R*)-**6b**	20
3	Ph	(*R*)-**5c**	62	(*R*)-**6c**	21
4	Bn	(*R*)-**5d**	66	(*R*)-**6d**	16

[a] R^1 = pentyl.
[b] The products were identified by IR, ^{1}H NMR, ^{13}C NMR, MS data.
[c] All reactions were carried out using: (*R*)-**4** (2.5 mmol), R^2COCl (10 mmol), $TiCl_4$ (2.2 mL of $TiCl_4$–CH_2Cl_2, 1:1 soln) (10 mmol); isolated yields are based on (*R*)-**4**.

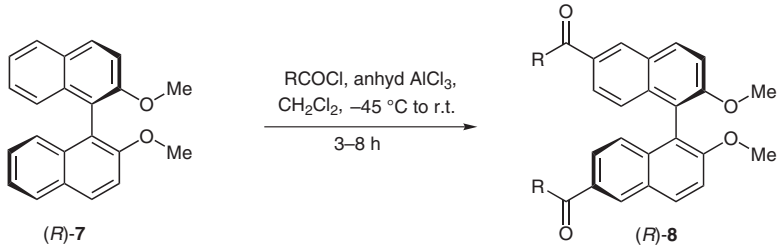
The acylation of methyl-protected 1,1′-bi-2-naphthol (*R*)-**7** failed when titanium(IV) chloride was used as the Lewis acid. However, (+)-(*R*)-2,2′-dimethoxy-1,1′-binaphthyl [(*R*)-**7**] was successfully acylated with acetyl chloride in the presence of anhydrous aluminum(III) chloride in nitrobenzene at 0 °C to give the diketone in 84% yield.

To avoid difficulties in removing nitrobenzene from the reaction mixture, we examined the reaction in dichloromethane solvent. When the reaction was carried out using four equivalents of acetyl chloride and (*R*)-**7** in dichloromethane at –45 °C, the desired diketone (*R*)-**8a** was obtained in 87% yield (Scheme 3). The reaction was also carried out using various acid chlorides and the corresponding diketones were obtained in good yields. The results are summarized in Table 2.

Table 2 Synthesis of (*R*)-**8** Using Various Acid Chlorides[a]

Entry	R	Temp.	Time (h)	(*R*)-**8**	Yield[b] (%)
1	Me	–45 °C	3	(*R*)-**8a**	87
2	Et	0 °C	3	(*R*)-**8b**	78
3	*i*-Pr	r.t.	5	(*R*)-**8c**	75
4	CH_2Cl	r.t.	5	(*R*)-**8d**	72
5	4-$O_2NC_6H_4CH_2$	r.t.	8	(*R*)-**8e**	68
6	Ph	r.t.	5	(*R*)-**8f**	75
7	4-MeC_6H_4	r.t.	5	(*R*)-**8g**	72
8	4-$MeOC_6H_4$	r.t.	8	(*R*)-**8h**	70
9	1-naphthyl	r.t.	8	(*R*)-**8i**	71

[a] All reactions were carried out using: (*R*)-**7** (5 mmol), anhyd $AlCl_3$ (20 mmol), RCOCl (20 mmol), CH_2Cl_2 (30 mL).
[b] The products were identified by IR, ^{1}H NMR, ^{13}C NMR, and MS data; yields are for isolated products.



Scheme 3

The acylation of optically active, as well as racemic, 1,1′-bi-2-naphthyl ethers using anhydrous aluminum(III) chloride gave the corresponding 6,6′-diacyl products (*R*)-**8a–i** in good yields. Both mono- and diacyl products were formed when the acylation was carried out using titanium(IV) chloride. The 6,6′-dibromo-1,1′-bi-2-naphthol ethers have been used in the synthesis of various monomeric and polymeric derivatives.[13] The methods described here for the synthesis of acyl derivatives of BINOL ethers have good potential for further synthetic exploitation as these derivatives can serve as precursors for the preparation of various substituted 1,1′-bi-2-naphthyl derivatives.[13,14]

Melting points were determined using a Superfit capillary point apparatus and are uncorrected. IR (KBr) spectra were recorded on Jasco FT-IR spectrophotometer model 5300 and IR (neat) spectra were recorded on Shimadzu FT-IR spectrophotometer model 8300 with polystyrene as reference. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Bruker Avance 400 spectrometer with $CDCl_3$ as solvent and TMS as reference. Elemental analyses were carried out using a Perkin-Elmer elemental analyzer model 240C and Thermo Finnigan analyzer series Flash EA 1112. Mass spectral analyses were carried out on VG 7070H mass spectrometer using EI technique at 70 eV. Optical rotations were measured in JASCO DIP-370 Digital polarimeter (readability = ± 0.001°). Column chromatography was carried out using Acme silica gel (100–200 mesh). CH_2Cl_2 was dried by distillation over CaH_2. All the acid chlorides, anhydrous aluminium(III) chloride and titanium(IV) chloride were supplied by E Merck (India).

2,2′-Bis(pentyloxy)-1,1′-binaphthyl [(*R*)-4]

A suspension of (+)-(*R*)-1,1′-bi-2-naphthol (5.0 g, 17.4 mmol) in MeCN (50 mL) stirred under N_2 was added K_2CO_3 (6.0 g, 43.5 mmol) and $C_5H_{11}Br$ (6.5 mL, 52.2 mmol), and the mixture was refluxed at 85 °C for 24 h. The solvent was removed under vacuum and the mixture was diluted with CH_2Cl_2 (30 mL). The organic layer was further washed with H_2O and brine and dried (anhyd Na_2SO_4). After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–EtOAc, 97:3) to give (*R*)-**4** (7.03 g, 95%) as a viscous liquid.

$[\alpha]_D^{25}$ +53.7 (*c* 0.6, $CHCl_3$).

IR (neat): 2930, 2868, 1622, 1593, 1145, 1086 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.8 Hz, 2 H), 7.88 (d, *J* = 8.1 Hz, 2 H), 7.44 (d, *J* = 8.9 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 7.22–7.19 (m, 4 H), 3.98–3.94 (m, 4 H), 1.41–1.39 (m, 4 H), 1.07–0.95 (m, 8 H), 0.78 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 156.7, 136.5, 132.3, 131.3, 130.6, 127.9, 125.5, 124.3, 119.6, 115.6, 69.2, 29.7, 28.9, 27.8, 22.1, 13.0.

LCMS: *m*/*z* = 427 (M + 1).

2,2′-Dimethoxy-1,1′-binaphthyl [(*R*)-7]

A suspension of (+)-(*R*)-1,1′-bi-2-naphthol (5.0 g, 17.4 mmol) was heated at 40 °C in acetone (150 mL) to give a homogeneous soln. To this soln stirred under N_2 was added K_2CO_3 (8.0 g, 58 mmol) and MeI (5.3 mL, 84 mmol). The mixture was refluxed for 24 h. An additional portion of MeI (1.7 mL, 28 mmol) was added, and the mixture was further refluxed for an additional 12 h. The solvent was removed and H_2O (150 mL) was added. The mixture was allowed to stir for 8 h and filtered and the solid was dissolved in CH_2Cl_2 (50 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined CH_2Cl_2 layers were successively washed with H_2O and brine and dried (anhyd Na_2SO_4). The solvent was evaporated to give (*R*)-**7** (5.3 g, 97%) as a white powder; mp 204–206 °C.

$[\alpha]_D^{25}$ +57.54 (*c* 1, $CHCl_3$).

IR (KBr): 2955, 2837, 1618, 1249, 1147, 1089 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 9.2 Hz, 2 H), 7.85 (d, *J* = 8.2 Hz, 2 H), 7.46 (d, *J* = 9.2 Hz, 2 H), 7.33–7.19 (m, 4 H), 7.10 (d, *J* = 8.2 Hz, 2 H), 3.76 (s, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 155.0, 134.0, 131.1, 129.8, 129.4, 128.2, 119.6, 114.2, 56.9.

LCMS: *m*/*z* = 315 (M + 1).

6,6′-Diacyl-2,2′-bis(pentyloxy)-1,1′-binaphthyls (*R*)-5; General Procedure

The acid chloride (10 mmol) and $TiCl_4$ (1.1 mL, 10 mmol) were taken in CH_2Cl_2 (30 mL) under N_2 . The mixture was stirred for 20 min at 25 °C. To this mixture was added (*R*)-**4** (2.5 mmol) and it was stirred at 25 °C for 24 h. The reaction was quenched with H_2O, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined organic layers were washed with brine (10 mL) and dried (anhyd Na_2SO_4). The solvent was removed and the residue was column chromatographed (silica gel, EtOAc–hexane, 4:96) to give compounds (*R*)-**5** as highly viscous materials.

6,6′-Diacetyl-2,2′-bis(pentyloxy)-1,1′-binaphthyl [(*R*)-5a]

Yield: 64%.

$[\alpha]_D^{25}$ –14.3 (*c* 1.00, $CHCl_3$).

IR (neat): 3063, 2953, 1682, 1618, 1273, 1051 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 2 H), 8.07 (d, *J* = 8.8 Hz, 2 H), 7.76 (d, *J* = 8.8 Hz, 2 H), 7.46 (d, *J* = 8.8 Hz, 2 H), 7.16 (d, *J* = 8.8 Hz, 2 H), 4.01–3.92 (m, 4 H), 2.66 (s, 6 H), 1.43–1.40 (t, *J* = 7.2 Hz, 4 H), 1.04 –0.88 (m, 8 H), 0.63 (t, *J* = 6.8 Hz, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 197.9, 156.7, 136.5, 132.3, 131.3, 130.6, 127.9, 125.5, 124.3, 119.6, 115.6, 69.2, 29.7, 28.9, 27.8, 26.6, 22.1, 13.0.

LCMS: *m*/*z* = 511 (M + 1).

6-Acetyl-2,2′-bis(pentyloxy)-1,1′-binaphthyl [(*R*)-6a]

Yield: 22%.

$[\alpha]_D^{25}$ +32.8 (*c* 1.00, $CHCl_3$).

IR (neat): 3055, 2934, 2872, 1680, 1618, 1051 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50–7.11 (m, 11 H), 4.01–3.91 (m, 4 H), 2.67 (s, 3 H), 1.28–1.22 (m, 4 H), 1.04–0.98 (m, 4 H), 0.94–0.88 (m, 4 H), 0.63 (t, *J* = 6.8 Hz, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 198.0, 156.9, 154.6, 145.9, 136.8, 134.1, 132.4, 131.1, 130.53, 129.4, 129.3, 128.9, 128.0, 127.0, 126.3, 126.0, 125.2, 124.2, 123.5, 120.7, 119.9, 117.9, 117.2, 116.0, 115.6, 69.7, 29.1, 28.0, 26.6, 22.2, 13.9.

LCMS: *m*/*z* = 469 (M + 1).

2,2′-Bis(pentyloxy)-6,6′-dipropanoyl-1,1′-binaphthyl [(*R*)-5b]

Yield: 66%.

$[\alpha]_D^{25}$ –18.2 (*c* 1.00, $CHCl_3$).

IR (neat): 3063, 2932, 2868, 1684, 1618, 1041 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (s, 2 H), 8.07 (d, *J* = 8.8 Hz, 2 H), 7.77 (d, *J* = 8.8 Hz, 2 H), 7.46 (d, *J* = 8.8 Hz, 2 H), 7.15(d, *J* = 8.8 Hz, 2 H), 4.01–3.92 (m, 4 H), 3.09 (q, *J* = 7.2 Hz, 4 H), 1.43–1.40 (m, 4 H), 1.26 (t, *J* = 6.8 Hz, 6 H), 1.03–0.88 (m, 8 H), 0.63 (t, *J* = 6.8 Hz, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 200.6, 156.6, 136.4, 132.0, 131.3, 129.9, 128.0, 125.5, 124.41, 119.4, 115.6, 69.3, 31.7, 28.9, 27.8, 22.1, 13.9, 8.5.

LCMS: *m*/*z* = 539 (M + 1).

2,2′-Bis(pentyloxy)-6-propanoyl-1,1′-binaphthyl [(*R*)-6b]
Yield: 20%.

$[\alpha]_D^{25}$ +41.2 (*c* 1.00, $CHCl_3$).

IR (neat): 3055, 2934, 2872, 1680, 1618, 1051 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54–7.19 (m, 11 H), 4.05–3.65 (m, 4 H), 3.06 (q, *J* = 7.2 Hz, 4 H), 1.53–1.42 (m, 4 H), 1.31 (t, *J* = 6.8 Hz, 3 H), 1.29–1.23 (m, 4 H), 1.10–0.72 (m, 4 H), 0.66 (t, *J* = 6.8 Hz, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 200.3, 156.6, 154.4, 136.6, 134.0, 131.9, 130.9, 129.7, 129.3, 129.2, 127.9, 127.8, 126.1, 125.8, 125.1, 124.0, 123.3, 120.4, 119.6, 115.7, 115.3, 69.4, 31.5, 29.0, 27.8, 22.0, 13.7, 8.4.

LCMS: *m*/*z* = 483 (M + 1).

6,6′-Dibenzoyl-2,2′-bis(pentyloxy)-1,1′-binaphthyl [(*R*)-5c]
Yield: 62%.

$[\alpha]_D^{25}$ –10.0 (*c* 1.00, $CHCl_3$).

IR (neat): 3061, 2955, 2870, 1653, 1616, 1051 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35–7.26 (m, 20 H), 4.04–3.97 (m, 4 H), 1.46 (t, *J* = 6.8 Hz, 4 H), 1.09–0.95 (m, 8 H), 0.68 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 196.6, 156.7, 138.3, 136.3, 132.6, 132.5, 132.1, 130.0, 128.4, 127.8, 126.2, 125.5, 119.7, 115.7, 69.3, 29.7, 28.9, 27.9, 22.1, 13.9.

LCMS: *m*/*z* = 635 (M + 1).

6-Benzoyl-2,2′-bis(pentyloxy)-1,1′-binaphthyl [(*R*)-6c]
Yield: 21%.

$[\alpha]_D^{25}$ +39.7 (*c* 1.00, $CHCl_3$).

IR (neat): 3063, 2953, 2870, 1616, 1464, 1089 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33–7.30 (m, 16 H), 4.02–3.91 (m, 4 H), 1.43 (t, *J* = 6.8 Hz, 4 H), 1.27–0.92 (m, 8 H), 0.67 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 196.7, 156.7, 154.5, 138.4, 136.5, 134.5, 134.1, 133.7, 132.5, 132.3, 132.0, 130.9, 130.6, 130.2, 130.0, 129.4, 129.3, 128.9, 128.5, 128.2, 127.9, 127.8, 127.3, 126.2, 126.0, 125.8, 123.5, 120.6, 19.8, 115.9, 115.6, 69.6, 69.3, 29.1, 28.9, 27.9, 27.8, 22.2, 22.1, 13.9.

LCMS: *m*/*z* = 531 (M + 1).

2,2′-Bis(pentyloxy)-6,6′-bis(phenylacetyl)-1,1′-binaphthyl [(*R*)-5d]
Yield: 66%.

$[\alpha]_D^{25}$ +33.7 (*c* 1.00, $CHCl_3$).

IR (neat): 3050, 2926, 1675, 1610, 1469, 939 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73–7.13 (m, 20 H), 4.38 (s, 4 H), 4.03–3.97 (m, 4 H), 1.04 (t, *J* = 6.0 Hz, 4 H), 1.06–0.92 (m, 8 H), 0.65 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 197.5, 156.8, 136.6, 135.0, 131.5, 129.8, 129.5, 129.0, 128.7, 128.0, 126.8, 125.7, 124.8, 119.6, 115.6, 69.2, 45.4, 28.9, 27.8, 22.1, 13.9.

LCMS: *m*/*z* = 663 (M + 1).

2,2′-Bis(pentyloxy)-6-(phenylacetyl)-1,1′-binaphthyl [(*R*)-6d]
Yield: 16%.

$[\alpha]_D^{25}$ +23.8 (*c* 1.00, $CHCl_3$).

IR (neat): 3059, 2932, 1672, 1618, 1269, 1051 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22–8.66 (m, 16 H), 4.40 (s, 2 H), 4.08–3.94 (m, 4 H), 1.47 (t, *J* = 7.2 Hz, 4 H), 0.96–1.09 (m, 8 H), 0.71 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 197.4, 157.0, 154.6, 144.5, 136.8, 135.2, 134.2, 131.8, 131.2, 130.9, 129.3, 129.3, 128.7, 128.6, 128.4, 128.01, 126.8, 126.3, 126.1, 125.2, 124.6, 123.6, 121.2, 115.9, 115.5, 69.4, 45.5, 29.0, 27.9, 22.2, 14.1.

LCMS: *m*/*z* = 543 (M – 1).

6,6′-Diacetyl-2,2′-dimethoxy-1,1′-binaphthyl [(*R*)-8a]; Typical Procedure
Anhyd $AlCl_3$ (2.66 g, 20 mmol) and AcCl (1.42 mL, 20 mmol) were added to CH_2Cl_2 (30 mL) at 0 °C. To this mixture, (*R*)-**7** (1.57 g, 5 mmol) was added, and the mixture was stirred at –45 °C for 3 h. The mixture was poured into ice-cold H_2O and it was shaken with CH_2Cl_2 (25 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL) and the combined organic phases were washed with brine (10 mL) and dried (anhyd Na_2SO_4). The solvent was removed and the residue was column chromatographed (silica gel, hexane–EtOAc, 80:20); yield: 1.73 g (87%); mp 184–186 °C.

$[\alpha]_D^{25}$ –100.3 (*c* 1.00, $CHCl_3$).

IR (KBr): 2935, 2837, 1666, 1614, 1174, 1057 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (s, 2 H), 8.13 (d, *J* = 9.2 Hz, 2 H), 7.76 (d, *J* = 8.2 Hz, 2 H), 7.52 (d, *J* = 8.2 Hz, 2 H), 7.11 (d, *J* = 9.2 Hz, 2 H), 3.80 (s, 6 H), 2.68 (s, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 195.3, 154.5, 133.7, 129.9, 129.1, 128.1, 125.4, 122.7, 122.0, 116.2, 111.8, 54.0, 24.0.

LCMS: *m*/*z* = 399 (M + 1).

Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 78.25; H, 5.53.

2,2′-Dimethoxy-6,6′-dipropanoyl-1,1′-binaphthyl [(*R*)-8b]
Yield: 78%; mp 156–158 °C.

$[\alpha]_D^{25}$ –86.4 (*c* 0.5, $CHCl_3$).

IR (KBr): 2966, 2839, 1678, 1616, 1172, 1041 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (s, 2 H), 8.15 (d, *J* = 8.8 Hz, 2 H), 7.81 (d, *J* = 8.8 Hz, 2 H), 7.55 (d, *J* = 8.8 Hz, 2 H), 7.14 (d, *J* = 8.8 Hz, 2 H), 3.79 (s, 6 H), 3.12 (q, *J* = 7.2 Hz, 4 H), 1.29 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 200.6, 157.0, 136.2, 132.3, 131.6, 130.0, 128.1, 125.4, 124.6, 118.9, 114.4, 56.6, 31.7, 8.5.

LCMS: *m*/*z* = 427 (M + 1).

Anal. Calcd for $C_{28}H_{26}O_4$: C, 78.85; H, 6.14. Found: C, 78.73; H, 6.15.

2,2′-Dimethoxy-6,6′-bis(2-methylpropanoyl)-1,1′-binaphthyl [(*R*)-8c]
Yield: 75%; mp 126–128 °C.

$[\alpha]_D^{25}$ –90.6 (*c* 0.5, $CHCl_3$).

IR (KBr): 2968, 2841, 1674, 1616, 1271, 1062 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (s, 2 H), 8.16 (d, *J* = 9.0 Hz, 2 H), 7.80 (d, *J* = 8.9 Hz, 2 H), 7.55 (d, *J* = 9.0 Hz, 2 H), 7.15 (d, *J* = 8.9 Hz, 2 H), 3.83 (s, 6 H), 3.72 (m, *J* = 6.8 Hz, 2 H), 1.28 (d, *J* = 6.8 Hz, 12 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 204.2, 157.0, 136.2, 131.6, 131.5, 130.2, 128.2, 125.5, 118.9, 114.4, 56.6, 35.2, 19.4.

LCMS: *m*/*z* = 455 (M + 1).

Anal. Calcd for $C_{30}H_{30}O_4$: C, 79.27; H, 6.65. Found: C, 79.34; H, 6.77.

6,6′-Bis(chloroacetyl)-2,2′-dimethoxy-1,1′-binaphthyl [(*R*)-8d]
Yield: 72%; mp 178–180 °C.

$[\alpha]_D^{25}$ –42.0 (*c* 0.2, $CHCl_3$).

IR (KBr): 2935, 2841, 1695, 1682, 1616, 1350 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.5 (s, 2 H), 7.91–7.89 (d, *J* = 8.4 Hz, 2 H), 7.57–7.55 (d, *J* = 8.4 Hz, 2 H), 7.50–7.48 (d, *J* = 8.7 Hz, 2 H), 7.28–7.26 (d, *J* = 8.7 Hz, 2 H), 4.79 (s, 4 H), 3.79 (s, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 193.6, 155.5, 134.6, 129.6, 128.1, 127.9, 126.8, 125.7, 124.8, 123.6, 114.3, 56.7, 50.6.

LCMS: *m*/*z* = 468 (M + 1).

Anal. Calcd for $C_{26}H_{20}Cl_2O_4$: C, 66.82; H, 4.31; Cl, 15.17. Found: C, 66.79; H, 4.33; Cl, 15.09.

2,2′-Dimethoxy-6,6′-bis[(4-nitrophenyl)acetyl]-1,1′-binaphthyl [(*R*)-8e]
Yield: 68%; mp 156–158 °C.

$[\alpha]_D^{25}$ –54.2 (*c* 1.00, $CHCl_3$).

IR (KBr): 2939, 2839, 1674, 1606, 1514, 1344 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.6 (s, 2 H), 8.2–7.06 (m, 16 H), 4.51 (s, 4 H), 3.82 (s, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 195.6, 157.5, 154.9, 147.0, 142.4, 136.7, 133.7, 131.4, 129.2, 128.1, 126.5, 124.8, 123.7, 119.7, 118.4, 114.7.

LCMS: *m*/*z* = 641 (M + 1).

Anal. Calcd for $C_{38}H_{28}N_2O_8$: C, 71.24; H, 4.41; N, 4.37. Found: C, 71.20; H, 4.45; N, 4.39.

6,6′-Dibenzoyl-2,2′-dimethoxy-1,1′-binaphthyl [(*R*)-8f]
Yield: 75%; mp 152–154 °C.

$[\alpha]_D^{25}$ –52.3 (*c* 0.6, $CHCl_3$).

IR (KBr): 2935, 2835, 1718, 1653, 1616, 1062 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 2 H), 8.10 (d, *J* = 8.9 Hz, 2 H), 7.86 (m, *J* = 8.2 Hz, 4 H), 7.74 (d, *J* = 8.7 Hz, 2 H), 7.60 (d, *J* = 7.7 Hz, 2 H), 7.54 (m, *J* = 8.7 Hz, 4 H), 7.50 (d, *J* = 7.7 Hz, 2 H), 7.20 (d, *J* = 8.9 Hz, 2 H), 3.83 (s, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 196.2, 155.1, 143.6, 138.7, 133.4, 129.5, 128.9, 128.4, 127.5, 126.7, 126.6, 125.7, 125.3, 125.2, 119.4, 114.4.

LCMS: *m*/*z* = 523 (M + 1).

Anal. Calcd for $C_{36}H_{26}O_4$: C, 82.74; H, 5.01. Found: C, 82.59; H, 5.04.

2,2′-Dimethoxy-6,6′-bis(4-methylbenzoyl)-1,1′-binaphthyl [(*R*)-8g]
Yield: 72%; mp 128–130 °C.

$[\alpha]_D^{25}$ –67.2 (*c* 0.6, $CHCl_3$).

IR (KBr): 2935, 2843, 1763, 1651, 1616, 1041 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (s, 2 H), 8.10–7.16 (m, 16 H), 3.82 (s, 6 H), 2.45 (s, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 196.2, 156.9, 142.9, 135.9, 135.4, 132.9, 132.3, 131.4, 130.2, 128.9, 127.8, 126.5, 125.2, 118.9, 114.3, 56.6, 21.6.

LCMS: *m*/*z* = 551 (M + 1).

Anal. Calcd for $C_{38}H_{30}O_4$: C, 82.89; H, 5.49. Found: C, 82.65; H, 5.42.

2,2′-Dimethoxy-6,6′-bis(4-methoxybenzoyl)-1,1′-binaphthyl [(*R*)-8h]
Yield: 70%; mp 132–134 °C.

$[\alpha]_D^{25}$ –65.2 (*c* 1.00, $CHCl_3$).

IR (KBr): 2964, 2847, 1768, 1643, 1599, 1022 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 2 H), 8.12 (d, *J* = 9.0 Hz, 2 H), 7.92 (d, *J* = 8.6 Hz, 4 H), 7.70 (d, *J* = 8.8 Hz, 2 H), 7.56 (d, *J* = 9.0 Hz, 2 H), 7.22 (d, *J* = 8.8 Hz, 2 H), 7.02 (d, *J* = 8.6 Hz, 4 H), 3.92 (s, 6 H), 3.72 (s, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 195.3, 163.0, 156.8, 135.8, 133.3, 132.5, 131.8, 131.3, 130.6, 127.8, 127.6, 126.5, 125.2, 118.9, 114.4, 113.6, 113.5.

LCMS: *m*/*z* = 583 (M + 1).

Anal. Calcd for $C_{38}H_{30}O_6$: C, 78.33; H, 5.19. Found: C, 78.39; H, 5.12.

2,2′-Dimethoxy-6,6′-di-1-naphthoyl-1,1′-binaphthyl [(*R*)-8i]
Yield: 71%; mp 138–140 °C.

$[\alpha]_D^{25}$ –52.4 (*c* 0.6, $CHCl_3$).

IR (KBr): 2937, 2843, 1768, 1685, 1602, 1265 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 4 H), 8.28–7.26 (m, 20 H), 3.74 (s, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 173.0, 156.2, 143.9, 134.6, 134.0, 133.7, 132.9, 131.8, 130.9, 130.4, 129.6, 129.1, 128.6, 128.3, 127.9, 127.6, 127.2, 126.6, 118.7, 118.6, 114.6.

LCMS: *m*/*z* = 623 (M + 1).

Anal. Calcd for $C_{44}H_{30}O_4$: C, 84.87; H, 4.86. Found: C, 84.65; H, 4.89.

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