Synthesis of Thiophene-Type *S*,*S*- and *N*,*S*-Ligands Derived from (+)-Nopinone

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Abstract: The new chiral thiophene **3** was prepared from (+)-nopinone via a *de novo* construction of the thiophene nucleus. From compound **3** four new *S*,*S*- and *N*,*S*-ligands, namely the C_1-symmetric 2-(thiophen-2-yl)pyridine **7** and the C_2-symmetric 2,2′-bithiophene **5**, 2,6-di(thiophen-2-yl)pyridine **8**, and 2,6-di(thiophen-2-yl)thiophene **9** were synthesized.

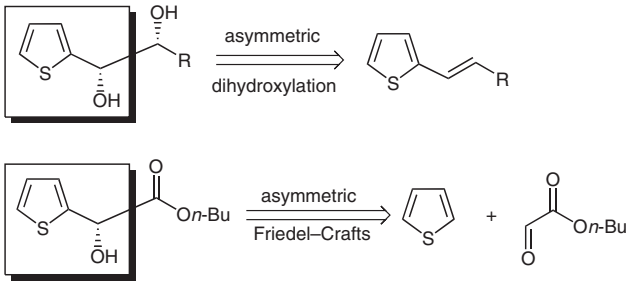
Key words: thiophene, monoterpenes, (+)-nopinone, coupling reactions, palladium catalysts

The thiophene ring can be recognized in various biologically active compounds with applications in medicine[1] or agrochemistry,[2] which often reveal higher activity compared to analogous phenyl-type substituents.[3] Structures containing thiophenes are also useful in the synthesis of new materials[4] applied in organic electronics[5] and as fluorescent biosensors.[6] Moreover, quite stabile S–metal bonds create the possibility of using thiophene derivatives as ligands for metal complexes in catalysis.[7]

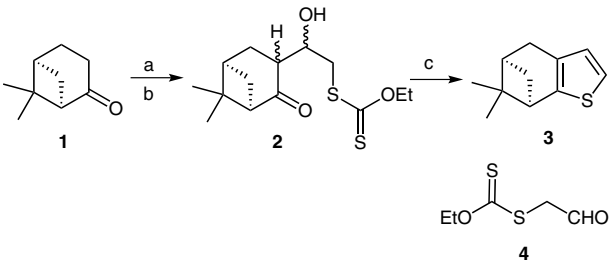
Among chiral ligands, those having almost a stereogenic center close to the coordinating atoms occupy a prominent position. This homotopic property is also present in a number of chiral thiophenes, which have been obtained by classical optical activation methods[8] or by stereodifferentiating metal-catalyzed processes, such as (i) enantioselective conjugate addition,[9](ii) enantioselective Friedel–Crafts reaction,[10] (iii) asymmetric dihydroxylation,[11](iv) enantioselective intramolecular propargylation,[12] and (v) asymmetric intramolecular hydrosilation.[13]

In any case, to obtain these chiral derivatives, a preformed thiophene nucleus is used as starting material, which is converted into the chiral nonracemic product either by reacting on a functional group connected to it, or by generating a stereogenic center via formation of a new heterocycle–carbon bond. These two possible approaches have been pursued to obtain thiophenyl alcohols (Scheme 1).[10,11]

Herein, we report the first synthesis of a chiral nonracemic thiophene with a stereogenic center connected to it, via the *de novo* construction of the heterocycle from a naturally occurring monoterpene. Moreover, the so generated thiophene **3** (Scheme 2) has been used as starting material for a new kind of C_1- and C_2-symmetric chiral thiophene-type *N*,*S*- and *S*,*S*-ligands.



Scheme 1



Scheme 2 *Reagents and conditions*: (a) $LiN(SiMe_3)_2$, THF, –30 °C, then $ZnCl_2$; (b) **4**, THF, –70 °C, 3 h 76%; (c) 1-methylpiperazine, CH_2Cl_2, then concd HCl, 0 °C, 3 h to r.t., overnight, 62%.

The synthesis of the thiophene **3** started from (+)-nopinone (**1**), which was obtained from (–)-β-pinene by oxidative cleavage.[14] Reaction of **1** with lithium bis(trimethylsilyl)amide at –30 °C and then with zinc chloride gave the related zinc enolate, which was condensed with *O*-ethyl *S*-2-oxoethyl carbonodithioate (**4**)[15] to afford a mixture of diastereoisomeric alcohols **2** in 76% yield. Treatment of **2** with 1-methylpiperazine at 0 °C and then with concentrated hydrochloric acid gave the desired thiophene **3** in 62% yield.

With the new chiral thiophene **3** in hand, the use of this compound as starting material for the preparation of potentially useful ligands for metal complexes in enantioselective catalysis was investigated.

Initially, our attention was focused on the C_2-symmetrical 2,2′-bithiophene **5**, seeking a method that would allow the direct dimerization of **3**, so as to avoid procedures requiring the use of the 2-bromo derivative of thiophene **3**. For-

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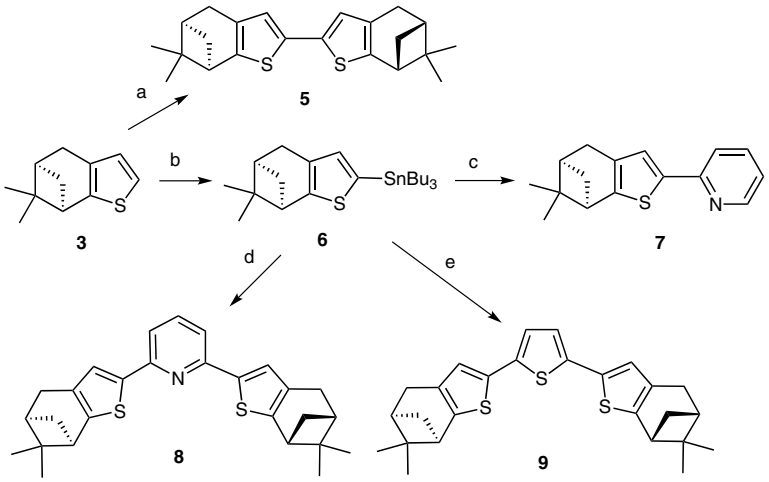

Scheme 3 *Reagents and conditions*: (a) *n*-BuLi, $Me_2NCH_2CH_2NMe_2$, THF, –20 °C, $Fe(acac)_3$, reflux, 6 h, 65%; (b) *n*-BuLi, THF, –40 °C, Bu_3SnCl, ~100% crude; (c) 2-bromopyridine, $Pd(PPh_3)_4$ (5 mol%), DMF, 90 °C, 10 h, 67%; (d) 2,5-dibromopyridine, $Pd(PPh_3)_4$ (5 mol%), DMF, 90 °C, 10 h, 83%; (e) 2,5-dibromothiophene, Pd_2dba_3 (5 mol%), Ph_3P (10 mol%), DMF, 90 °C, 24 h, 62%.

tunately, the method described by Swager and Zhu, for the dimerization of 3,4-ethylenedioxythiophene[16] came to our rescue. Thus, thiophene **3** was treated with the couple *n*-BuLi and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine at –20 °C to give the corresponding lithium derivative, which was added to refluxing THF containing $Fe(acac)_3$ (Scheme 3). Under these reaction conditions the expected 2,2′-bithiophene **5** was formed in 65% yield after six hours.

The preparation of other thiophene-based ligands following a strategy that involves the Stille coupling between a brominated heterocycle and the 2-stannyl derivative of **3** was next examined. Stannylation of thiophene **3** was performed by metalation with *n*-BuLi at –78 °C, followed by treatment with tributylstannyl chloride. In this way, crude 2-tributylstannylthiophene **6** was obtained in quantitative yield (Scheme 3). Attempts to purify the crude material only led to partial destannylation. As already reported by others,[17] trialkylstannylthiophenes exhibit low stability upon silica gel chromatography purification. Fortunately, compound **6** was pure enough to be used in the following step without any additional purification.

Cross-coupling of 2-bromopyridine with stannylthiophene **6** in the presence of 5 mol% of tetrakis(triphenylphosphine)palladium(0) in DMF at 90 °C for 10 hours afforded the 2-(thiophen-2-yl)pyridine **7** in 67% yield (Scheme 3). When the same protocol was applied to 2,5-dibromopyridine and stannylthiophene **6**, the 2,6-di(thiophen-2-yl)pyridine **8** was isolated in 83% yield after 10 hours (Scheme 3). On the other hand, variation of the coupling method was carried out for the cross-coupling of 2,5-dibromothiophene with **6**. Thus, combination of 5 mol% of tris(dibenzylideneacetone)dipalladium(0) as a catalyst precursor and 10 mol% of triphenylphosphine as the ligand in DMF at 90 °C afforded the 2,6-di(thiophen-2-yl)thiophene **9** in 62% yield (Scheme 3).

In conclusion, a new kind of C_1- and C_2-symmetric chiral thiophene-type *S*,*S*- and *N*,*S*- ligands has been synthesized from (+)-nopinone, an inexpensive monoterpene available from the chiral pool. Although the present protocol has been developed to obtain thiophene **3**, a particular example of carbocycle-fused thiophene, it is expected that it may become key to future total syntheses of chiral thiophene-based compounds.

All reagents and solvents were purchased from Aldrich and used as received. Petroleum ether (PE) used was the fraction collected between 40 and 60 °C. THF was distilled from Na-benzophenone ketyl and degassed thoroughly with dry N_2 directly before use. Melting points were determined on a Büchi 510 capillary apparatus and are uncorrected. The NMR spectra were obtained with a Varian VXR-300 spectrometer at 300 for ^1H and 75.4 MHz for ^{13}C. Chemical shifts are reported in ppm downfield from internal Me_4Si in $CDCl_3$. Optical rotations were measured with a Perkin-Elmer 241 polarimeter in a 1 dm tube. Elemental analyses were performed on a Perkin-Elmer 240 B analyzer. TLC was performed on Merck silica gel 60 TLC plates F254 and visualized using UV or phosphomolybdic acid. Flash chromatography was carried out on silica gel (230–400 mesh).

(1*R*,5*R*)-6,6-Dimethylbicyclo[3.1.1]heptan-2-one [(+)-nopinone, **1**] was prepared by oxidation of (–)-β-pinene (99% pure, Aldrich).[7] *O*-Ethyl *S*-2-oxoethyl carbonodithioate (**4**) was obtained according to Waldvogel.[8]

_S_-2-[(1_R_,5_R_)-6,6-Dimethyl-2-oxobicyclo[3.1.1]heptan-3-yl]-2-hydroxyethyl _O_-Ethyl Carbonodithioate (2)

$LiN(SiMe_3)_2$ (13.0 mmol, 13.0 mL of a 1.0 M solution in THF) was added dropwise to cooled (–30 °C) anhyd THF (50 mL). To this solution was then added dropwise a solution of (+)-nopinone (**1**; 1.38 g, 10.0 mol) in THF (18 mL). After 30 min at this temperature, anhyd $ZnCl_2$ (2.04 g, 15.0 mmol) was added portionwise during 1.5 h. The resulting solution was cooled to –70 °C and a solution of *O*-ethyl *S*-2-oxoethyl carbonodithioate (1.81 g, 11.0 mmol) in THF (5 mL) was slowly added during 30 min. After 3 h at –70 °C, AcOH (5 mL), H_2O (7.5 mL), and finally toluene (15 mL) were added in sequence and the solution was allowed to reach slowly r.t. (overnight). The mixture was partitioned between Et_2O (30 mL) and H_2O (20 mL), the organic phase was separated, dried (Na_2SO_4), and the solvent was evaporated. The residue was finally purified by flash chromatography (EtOAc–Et_2O, 6:4) to give **2** as a mixture of diastereomers [the fractions with R_f = 0.52 (EtOAc–Et_2O, 6:4) were collected]; yield: 2.35 g (76%); oil.

^{1}H NMR: δ (significant signals) = 4.66 (q, 2 H, *J* = 7.0 Hz, CH_2O), 4.53 (s, 1 H, OH), 4.05–3.95 (m, 1 H, C*H*OH), 3.74 (dd, *J* = 13.8, 2.4 Hz, 1 H, CHS), 3.28 (dd, *J* = 13.8, 7.5 Hz, 1 H, CHS), 1.45 (t, *J* = 7.0 Hz, 3 H, C*H*$_3$CH$_2$O), 1.35 (s, 3 H), 0.95 (s, 3 H).

Anal. Calcd for $C_{14}H_{22}O_3S_2$: C, 55.60; H, 7.33. Found: C, 55.44; H, 7.38.

(5*R*,7*R*)-5,7-Methano-6,6-dimethyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene (3)

A flask containing 1-methylpiperazine (26 mL) was degassed by bubbling N_2 for a 15 min. Then, the flask was cooled to 0 °C and a solution of **2** (4.26 g, 15.3 mmol) in CH_2Cl_2 (8 mL) was added during 15 min. After stirring for 3 h at 0 °C, aq 37% HCl (39 mL) was added dropwise and the resulting solution was allowed to reach r.t. (overnight). The mixture was taken up with H_2O (50 mL) and the organic phase was separated. The aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic layers were washed several times with H_2O and dried (Na_2SO_4). The solvent was evaporated and the residue was purified by flash chromatography (PE–EtOAc, 95:5) to give pure **3** as a pale-yellow oil; yield: 1.69 g (62%); $[\alpha]_D^{25}$ –60.6 (*c* = 2.11, $CHCl_3$).

IR (neat): 2923, 2360, 1650, 1438, 1382, 1365, 1263, 1153, 1183, 1049, 873, 694 cm^{-1}.

^{1}H NMR: δ = 6.91 (d, *J* = 4.8 Hz, 1 H), 6.83 (d, *J* = 4.8 Hz, 1 H), 2.93–2.74 (m, 3 H), 2.74–2.65 (m, 1 H), 2.35–2.25 (m, 1 H), 1.42–1.36 (overlapping d, 1 H), 1.39 (s, 3 H), 0.66 (s, 3 H).

^{13}C NMR: δ = 143.89, 131.83, 126.47, 119.59, 42.67, 41.53, 41.07, 33.71, 29.99, 26.30, 21.03.

Anal. Calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.91. Found: C, 74.22; H, 7.93.

(5*R*,7*R*,5′*R*,7′*R*)-5,7,5′,7′-Dimethano-6,6,6′,6′-tetramethyl-4,4′,5,5′,6,6′,7,7′-octahydro-2,2′-bibenzo[*b*]thiophene (5)

A solution of tetrahydrobenzo[*b*]thiophene **3** (0.352 g, 2.0 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.233 g, 4.0 mmol) in anhyd THF (7 mL) was cooled to –20 °C under argon. Then, *n*-BuLi (2.0 mmol, 0.8 mL of 2.5 M in hexane) was added dropwise to this solution. After addition, stirring was continued for another 30 min at 0 °C. This solution was then added dropwise (over a period of 30 min) to refluxing THF (7 mL) containing $Fe(acac)_3$ (0.71 g, 2.0 mmol) under argon. After a 6 h at refluxing temperature, the THF was evaporated. The resulting red solid was dissolved in CH_2Cl_2 (10 mL) and quickly passed through a short bed of silica gel using CH_2Cl_2 as the eluent. The CH_2Cl_2 solution was evaporated and the residue was purified by flash chromatography (PE–EtOAc, 95:5) to give pure **5** as a white solid; yield: 0.23 g (65%); mp 173–174 °C; $[\alpha]_D^{25}$ –50.6 (*c* = 0.018, $CHCl_3$).

IR (KBr): 2931, 1538, 1441, 1380, 1365, 1262, 1148, 1133, 1079, 813, 523 cm^{-1}.

^{1}H NMR: δ = 6.83 (s, 1 H), 2.90–2.64 (m, 4 H), 2.31–2.45 (m, 1 H), 1.43 (d, *J* = 9.0 Hz, 1 H), 1.38 (s, 3 H), 0.71 (s, 3 H).

^{13}C NMR: δ = 142.42, 133.09, 132.54, 122.20, 42.73, 41.67, 40.99, 33.74, 30.15, 26.28, 21.10.

Anal. Calcd for $C_{22}H_{26}S_2$: C, 74.52; H, 7.39. Found: C, 74.77; H, 7.42.

(5*R*,7*R*)-5,7-Methano-6,6-dimethyl-2-tributylstannyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene (6)

n-BuLi (2.50 mmol, 1.0 mL of 2.5 M in hexane) was added dropwise to a cooled solution (–78 °C) of tetrahydrobenzo[*b*]thiophene **3** (0.4 g, 2.25 mmol) in anhyd THF (3 mL) under argon. The solution was stirred for 0.5 h and then warmed to –40 °C. Bu_3SnCl (1.0 g, 2.63 mmol) was added at –40 °C, the solution was then warmed to r.t. and the stirring continued for 8 h. The solvent was evaporated and the residue was dissolved in hexanes (22 mL) and filtered. The filtrate was dried in vacuum to afford 1.5 g of stannylated product **6** as a yellow liquid. This compound was used for the next reaction without further purification.

^{1}H NMR: δ = 6.88 (s, 1 H), 2.94–2.87 (m, 2 H), 2.81 (dd, *J* = 16.4, 2.8 Hz, 1 H), 2.69 (dt, *J* = 9.2, 6.0 Hz, 1 H), 1.62–1.53 (m, 6 H), 1.41 (d, *J* = 9.6 Hz, 2 H), 1.38–1.29 (m, 6 H), 1.32 (s, 3 H), 1.09–1.05 (m, 6 H), 0.90 (t, *J* = 5.1 Hz, 9 H), 0.64 (s, 3 H).

(5*R*,7*R*)-5,7-Methano-6,6-dimethyl-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)pyridine (7)

A mixture of 2-bromopyridine (118.5 mg, 0.5 mmol), crude tributylstannylthiophene **6** (0.51 g, 0.55 mmol), $Pd(PPh_3)_4$ (28.8 mg, 0.025 mmol) in anhyd and degassed (by bubbling argon for 15 min) DMF (5 mL) was heated at 90 °C under argon for 10 h. After removal of the DMF under vacuum, the residue was purified by flash chromatography (PE–EtOAc, 95:5) to give pure **7** as a pale-yellow oil; yield: 85.4 mg (67%); $[\alpha]_D^{25}$ –42.8 (*c* = 0.027, $CHCl_3$).

IR (neat): 2929, 1587, 1475, 1431, 1382, 1291, 1172, 1090, 996, 836, 774, 737 cm^{-1}.

^{1}H NMR: δ = 8.50–8.47 (m, 1 H), 7.64–7.52 (m, 2 H), 7.35 (s, 1 H), 7.07–7.01 (m, 1 H), 2.90–2.78 (m, 3 H), 2.78–2.65 (m, 1 H), 2.34–2.26 (m, 1 H), 1.43 (d, *J* = 9.0 Hz, 1 H), 1.40 (s, 3 H), 0.72 (s, 3 H).

^{13}C NMR: δ = 153.14, 149.26, 147.67, 139.19, 136.31, 133.17, 124.53, 120.80, 117.96, 43.00, 41.50, 40.87, 33.51, 30.05, 26.18, 21.00.

Anal. Calcd for $C_{16}H_{17}NS$: C, 75.25; H, 6.71; N, 5.48. Found: C, 75.44; H, 6.76; N, 5.43.

2,6-Bis[(5*R*,7*R*)-5,7-methano-6,6-dimethyl-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl]pyridine (8)

A mixture of 2,6-dibromopyridine (79.0 mg, 0.5 mmol), crude tributylstannylthiophene **6** (0.51 g, 0.55 mmol), $Pd(PPh_3)_4$ (28.8 mg, 0.025 mmol) in anhyd and degassed (by bubbling argon for 15 min) DMF (5 mL) was heated at 90 °C under argon for 10 h. After removal of the DMF under vacuum, the residue was purified by flash chromatography (PE–EtOAc, 95:5) to give pure **8** as a white solid; yield: 0.18 g (83%); mp 214–215 °C; $[\alpha]_D^{25}$ –5.5 (*c* = 0.017, $CHCl_3$).

IR (KBr): 2927, 1561, 1465, 1379, 1271, 1174, 1076, 862, 801, 735 cm^{-1}.

^{1}H NMR: δ = 7.55 (t, *J* = 8.0 Hz, 1 H), 7.39 (s, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 2.90–2.78 (m, 6 H), 2.78–2.69 (m, 2 H), 2.35–2.28 (m, 2 H), 1.44 (d, *J* = 9.0 Hz, 2 H), 1.41 (s, 6 H), 0.73 (s, 6 H).

^{13}C NMR: δ = 152.48, 147.77, 139.60, 136.86, 133.07, 124.50, 115.03, 43.11, 41.61, 40.99, 33.60, 30.16, 26.32, 21.14.

Anal. Calcd for $C_{27}H_{29}NS_2$: C, 75.13; H, 6.77; N, 3.24. Found: C, 74.83; H, 6.73; N, 3.26.

2,5-Bis[(6*R*,7*R*)-5,7-methano-6,6-dimethyl-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl]thiophene (9)

A mixture of 2,5-dibromothiophene (121.0 mg, 0.5 mmol), crude tributylstannylthiophene **6** (0.51 g, 0.55 mmol), Pd_2dba_3 (22.9 mg, 0.025 mmol), and Ph_3P (13.0 mg, 0.05 mmol) in anhyd and degassed (by bubbling argon for 15 min) DMF (5 mL) was heated at 90 °C under argon for 24 h. After removal of the DMF under vacuum, the residue was purified by flash chromatography using PE give pure **9** as a white solid; yield: 0.135 g (62%); mp 164–165 °C; $[\alpha]_D^{25}$ –84.0 (*c* = 0.005, $CHCl_3$).

IR (KBr): 2919, 1524, 1443, 1379, 1364, 1260, 1159, 1133, 1078, 821, 791 cm^{-1}.

^{1}H NMR: δ = 6.92 (s, 2 H), 6.91 (s, 2 H), 2.91–2.67 (m, 8 H) 2.32–2.27 (m, 2 H), 1.44 (d, *J* = 9.0 Hz, 2 H), 1.40 (s, 6 H), 0.73 (s, 6 H).

^{13}C NMR: δ = 143.8, 136.0, 132.9, 132.1, 123.3, 122.8, 42.9, 41.7, 40.9, 33.7, 30.1, 26.3, 21.1.

Anal. Calcd for $C_{26}H_{28}S_3$: C, 71.51; H, 6.46; S, 22.03. Found: C, 71.82; H, 6.49.

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