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Simple preparation of enantiomeric Michael adducts of thiophenol to chalcones: easily available new chiral building blocks

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Abstract—A facile and enantioselective method for the multigram preparation of the title compounds is described. The Michael addition of thiophenols to chalcones catalyzed by (+)-cinchonine, followed by crystallization, led to the corresponding adducts **2** in up to >95% e.e. The stereoselective Beckmann rearrangement of the oxime of (+)-1,3-diphenyl-3-phenylsulfanylpropan-1-one **2a** gives the anilide of (*R*)-(+)-3-phenyl-3-phenylsulfanylpropanoic acid (as determined by X-ray analysis) and alcoholysis leads to the corresponding enantiomerically pure ethyl ester.

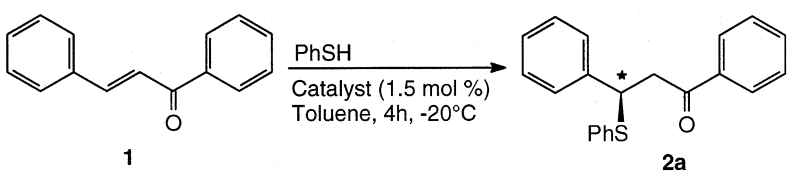
1. Introduction

Catalytic asymmetric synthesis is a very attractive method for the preparation of chiral building blocks, necessary for the construction of more complex molecular structures. Among catalytic reactions, considerable attention has been focused on the enantioselective conjugate addition of sulfur nucleophiles to α,β-unsaturated carbonyl compounds, thus providing a new stereogenic carbon center at the β-position.[1] However, only a limited number of successful examples have been reported. In early studies, Wynberg et al. examined the Michael reaction catalyzed by chiral β-amino alcohols, including cinchona alkaloids,[2] but the enantioselectivities attained did not reach a desirable level. The only exception was the catalyzed cinchonine addition of thiophenol to di-*iso*-propyl maleate.[3] More recently, high enantiomeric excesses (e.e.s) have been obtained in some cases; however, these required the use of complex catalyst systems.[4]

During our recent work on the catalytic application of metal complexes of salicylidene β-amino alcohols,[5] we tested the asymmetric conjugate addition of thiophenol to enone. For comparison, we also examined cinchonine, quinine and quinidine. Herein, we report the obtained results that were elaborated into a simple procedure for the preparation of optically pure adducts. We also demonstrate their utility for further, stereoselective transformation.

2. Results and discussion

Firstly, in the addition of thiophenol to 2-cyclohexenone catalyzed by 1.5 mol% of cinchonine, we observed 59% e.e.[5b] (versus 54% e.e. obtained by Hiemstra and Wynberg).[2] Then, we examined a similar reaction with *trans*-chalcone; the respective results are shown in Scheme 1. The addition of thiophenol to *trans*-chalcone in the presence of chiral amines has



1 2a

Scheme 1.

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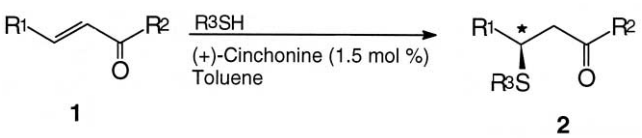
already been studied; however, to date, no cinchonine was used and the reported enantioselectivities were unsatisfactory.[6] Thus, our results demonstrated that (+)-cinchonine is the best catalyst for this reaction. The highest e.e. of 80% was observed for the addition run on a 0.1 mol scale in toluene for a 5.6 mM catalyst concentration at −20°C (Table 1). The observed dependency of the e.e. on catalyst concentration and temperature is similar to that described in earlier reports.[2,6b]

4-Substituted thiophenols and benzyl mercaptan added to the ring-substituted chalcones in 54–73% e.e. and excellent chemical yields. Moreover, we observed that the recrystallization of crude adducts **2a**, **2c**, **2e** and **2f** gave mostly racemic crystals and the concentration of mother liquors allowed isolation of the correspondingly enriched (+)-enantiomers (Scheme 2). In the case of **2a**, a single crystallization was sufficient to isolate an enantiomerically pure product in 70% total yield (>95% e.e., no opposite enantiomer detected by ^{1}H NMR using Eu(hfc)$_3$). Since we are dealing here with a substance forming a racemic compound in the solid state (higher mp), not a conglomerate, the composition at the eutectic point should be very close to a pure enantiomer. This is regarded as an extreme, but not uncommon case, where one may expect high enantiomeric enrichment by crystallization leaving the enantioenriched, lower melting material in the mother liquor.[7] In two other cases (**2b** and **2g**), the (+)-enantiomers melted at higher temperatures than the corresponding racemates and could be obtained from the crystallizing material. In the case of **2d**, almost no enrichment on crystallization was observed. The absolute configuration of (+)-**2** was assigned tentatively (*R*), as it is correlated to the (*R*)-(+)-product obtained by the well-known enantioselective east reduction of β-oxoester and subsequent inversion at the created stereogenic center.[8] However, in the course of this study, we proved this configuration more directly (see Table 2).

Table 1.

Catalyst[a]	Temperature (°C)	Yield (%)	E.e. (%)
Cinchonidine	−20	99	14
Quinine	−20	98	17
Cinchonine	−20	96–98	64, 70,[b] 80[c]
Cinchonine	0	91	38
Cinchonine	−70	80	50

[a] Applied in a 1.5 mol% amount (conc. 4.2 mM), 2 mmol reaction scale.
[b] For the reaction with 3.0 mol% (conc. 8.4 mM) catalyst, 2 mmol reaction scale.
[c] For the reaction with 1.5 mol% (conc. 5.6 mM) catalyst, 0.1 mol reaction scale.



Scheme 2.

Thus, the reasonably high enantioselectivity of the addition and successful crystallization gave optically pure adducts **2** and now these compounds can be regarded as easily available in multigram quantities. In order to test their possible synthetic applications, ketone (+)-**2a** was converted to oxime (+)-**3**. Reduction of this product with $NaBH_4/TiCl_4$[15] gave a diastereomeric mixture of amine **4** (d.r. 65:35). The oxime was subjected to the reaction induced by thionyl chloride and the chemo- and stereoselective Beckmann rearrangement[16] gave the anilide of (+)-3-phenyl-3-sulfinylpropanoic acid **5**. Its alcoholysis furnished the corresponding ethyl ester **6**, a known chiral building block, useful for the synthesis of biologically active products.[8,17] X-Ray analysis of a single crystal of (+)-**5** proves the (*R*) configuration of its stereogenic center (Fig. 1). Thus, the absolute configuration (*R*) of (+)-**2** adducts is also confirmed by analogy (Scheme 3).

Table 2.

2	R^1	R^2	R^3	Adduct		Crystallization				
						(*R*)-Isomer				Racemate
				Yield (%)	E.e. (%)	Yield (%)	E.e. (%)	$[\alpha]_D^{20}$	mp (°C)	mp, lit. mp (°C)
a	Ph	Ph	Ph	99	80	70	>95	+136	96–97	118.5–119, 119–120[a]
b	*p*-$MeOC_6H_4$	Ph	Ph	99	73	72	93	+148	87.2–88	82–84.5, 86.8[b]
c	Ph	Ph	*p*-$MeOC_6H_4$	98	58	44	94	+109	91.5–92	115.5–117 (EtOH)
d	Ph	Ph	*p*-MeC_6H_4	97	65		67	+98	102–106	–, 110–111[c]
e	Ph	Ph	*p*-ClC_6H_4	96	54	13	77	+119	97.5–99.5	99.5–101.5, 103[d]
f	Ph	Ph	CH_2Ph	65	64	20	92	+138	57–59	68–70, 71[e], 72–73[c]
g	Ph	*tert*-Bu	Ph	84	27	19	>95	+175	103–104	85–89, 86–88[f]

[a] lit.[9]; [b] lit.[10]; [c] lit.[11]; [d] lit.[12]; [e] lit.[13]; [f] lit.[14]

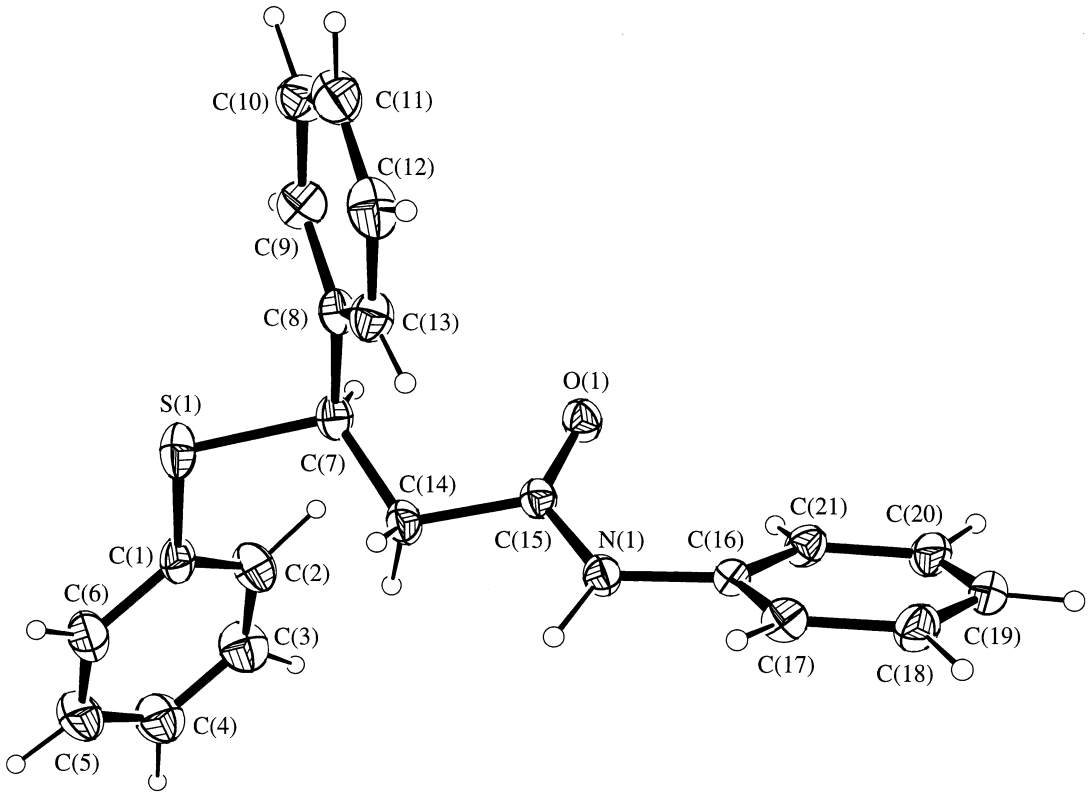
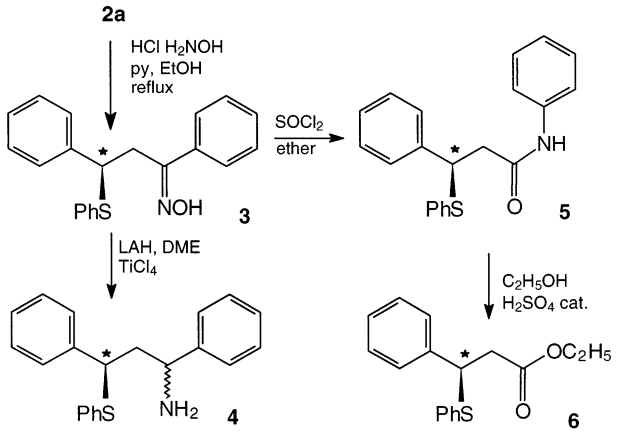


Figure 1. ORTEP view of molecule **5**. Thermal ellipsoids were drawn on the 25% probability level. Hydrogen atoms were diminished for clarity.



Scheme 3.

In conclusion, the method described in this paper offers a convenient route to some enantioenriched Michael adducts obtained in the catalytic presence of (+)-cinchonine in good yield and often excellent e.e. from the readily available chalcones and thiophenols. Work on further synthetic applications of the prepared chiral ketones is underway.

3. Experimental

3.1. General

Melting points were determined using a Boetius hot-stage apparatus and are uncorrected. IR spectra were reordered on a Zeiss–Jena Specord 75 spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured on a Bruker CPX (300 MHz) spectrometer using TMS as an internal standard. GC/MS spectra were determined on a Hewlett–Packard 5890 II gas chromatograph (25 m capillary column) with a Hewlett–Packard mass spectrometer 5971A operating on the electron-impact mode (70 eV). Optical rotations at 578 nm were measured using an Optical Activity Ltd. model AA-5 automatic polarimeter. Separations of products by chromatography were performed on silica gel 60 (230–400 mesh) purchased from Merck. TLC analyses were performed using silica gel 60 precoated plates (Merck).

3.2. X-Ray crystallographic data

Colorless crystals of **5** suitable for X-ray diffraction studies were grown by dissolving the compound in an *n*-hexane/methylene chloride mixture, and then by the slow evaporation at rt. Monoclinic, $P2_1$, $a=8.0552(9)$, $b=5.1806(5)$, $c=20.8294(18)$ Å, $\beta=96.732(9)°$, $V=863.23(15)$ Å^3, $Z=2$, $\mu=0.194$ mm^{-1}, $F(000)=352$, CCD camera, 5088 reflections collected, 2567 unique reflections, 2362 observed unique reflections, $R_{int}=0.0347$, SHELXL-97,[18] $R_1=0.050$ and $wR_2=0.129$ for $I>2\sigma(I)$, $R_1=0.054$ and $wR_2=0.132$ for all data, $S=1.17$, $\rho_{max}=0.46$, $\rho_{min}=-0.34$ e Å^{-3}, Flack absolute structure parameter $x=0.05(12)$.

Crystallographic data (excluding structure factors) for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 165607. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

3.3. Preparation of the chiral Michael adducts 2

A solution of the appropriate chalcone (2.0 mmol) in dry toluene (4 mL) was added to a stirred solution of cinchonine (8.8 mg, 1.5% mol) in dry toluene (2 mL). This mixture was stirred for 15 min at rt and cooled to −20°C. Then a solution of thiophenol (0.226 mL, 2.2 mmol) in dry toluene (1 mL) was added dropwise. The resulting mixture was kept for 4–24 h (monitored by TLC) at −20°C under argon, then quenched with 1N HCl (4 mL) and extracted with Et_2O (2×2 mL). The combined extracts were washed with 10% NaOH, brine, dried over Na_2SO_4 and the solvent was evaporated. The crude product obtained was chemically pure **2** (by ^{1}H NMR) The e.e. of the adduct was determined by ^{1}H NMR with ca. equimolar amount of Eu(hfc)$_3$ as a chiral shift reagent.

The products were enantioenriched by recrystallization from hexane/methylene chloride. For **2a** and **2c–f** the enantiomeric forms were isolated from the mother liquors and had lower mp's than the corresponding racemic crystals. For **2b** and **2g**, the enantioenriched crystals were separated and had higher mp's than the respective racemates (see Scheme 2).

3.3.1. (*R*)-(+)-1,3-Diphenyl-3-phenylsulfanylpropan-1-one 2a. Yield 70%, after recrystallization, mp 96–97°C; ^{1}H NMR (300 MHz, $CDCl_3$): 3.62 (m†, J_1=17.2 Hz, J_2=11.1 Hz, J_3=7.4 Hz, 2H, CH_2), 4.95 (t, J=7.1 Hz, 1H, *CH), 7.18–7.56 (m, 13H, ArH), 7.88 (d, J=7.5 Hz, 2H, ArH); ^{1}H NMR (CCl_4, Eu(hfc)$_3$): *CH, $\Delta\delta$ 0.077; IR (KBr): 3058, 1679, 1581, 1450, 1231, 738, 698 cm^{-1}; $[\alpha]_D^{20}$=+136 (1.02, CH_2Cl_2), >95% e.e. The reported value of $[\alpha]_D^{20}$=+127.2±7.6 (CH_2Cl_2), extrapolated for 100% e.e.[6b]

3.3.2. (*R*)-(+)-3-(4-Methoxyphenyl)-1-phenyl-3-phenylsulfanylpropan-1-one 2b. Yield 72%, recrystallized twice, mp 87.2–88.0°C; ^{1}H NMR (300 MHz, $CDCl_3$): 3.58 (m†, J_1=17.1 Hz, J_2=15.0 Hz, J_3=7.1 Hz, 2H, CH_2), 3.75 (s, 3H, OMe), 4.92 (dd, J_1=8.2 Hz, J_2=6.0 Hz, 1H, *CH), 6.78 (d, J=8.6 Hz, 2H, ArH), 7.21–7.56 (m, 10H, ArH), 7.86 (d, J=7.4 Hz, 2H, ArH); ^{1}H NMR (CCl_4, Eu(hfc)$_3$): *CH, $\Delta\delta$ 0.128 ppm, $[\alpha]_D^{20}$=+148 (0.98, CH_2Cl_2), 93% e.e.

3.3.3. (*R*)-(+)-3-(4-Methoxyphenylsulfanyl)-1,3-diphenylpropan-1-one 2c. Yield 44%, recrystallized twice, mp 91.5–92.0°C; ^{1}H NMR (300 MHz, $CDCl_3$): 3.58 (dd, J_1=7.1 Hz, J_2=3.0 Hz, 2H, CH_2), 3.76 (s, 3H, OMe), 4.78 (t, J=7.1 Hz, 1H, *CH), 6.75 (d, J=8.8 Hz, 2H, ArH), 7.17–7.25 (m, 7H, ArH), 7.42 (t, J=7.5 Hz, 2H, ArH), 7.54 (t, J=7.3 Hz, 1H, ArH), 7.87 (d, J=7.8 Hz, 2H, ArH); ^{1}H NMR (CCl_4, Eu(hfc)$_3$): *CH, $\Delta\delta$ 0.048 ppm, $[\alpha]_D^{20}$=+109 (1.02, CH_2Cl_2), 94% e.e.

3.3.4. (*R*)-(+)-3-(4-Methyl-phenylsulfanyl)-1,3-diphenylpropan-1-one 2d. Yield 97%, recrystallized twice, mp 102–106°C; ^{1}H NMR (300 MHz, $CDCl_3$): 2.29 (s, 3H, CH_3), 3.59 (m†, J_1=17.1 Hz, J_2=9.9 Hz, J_3=7.1 Hz, 2H, CH_2), 4.87 (t, J=7.1 Hz, 1H, *CH), 7.02 (d, J=7.9 Hz, 2H, ArH), 7.17–7.32 (m, 7H, ArH), 7.42 (t, J=7.5 Hz, 2H, ArH), 7.53 (t, J=7.4 Hz, 1H, ArH), 7.86 (d, J=7.4 Hz, 2H, ArH); ^{1}H NMR (CCl_4, Eu(hfc)$_3$): *CH, $\Delta\delta$ 0.107 ppm, $[\alpha]_D^{20}$=+95 (1.10, CH_2Cl_2), 65% e.e.

3.3.5. (*R*)-(+)-3-(4-Chlorophenylsulfanyl)-1,3-diphenylpropan-1-one 2e. Yield 13%, recrystallized twice, mp 97.5–99.5°C; ^{1}H NMR (300 MHz, $CDCl_3$): 3.59 (dd, J_1=6.9 Hz, J_2=5.0 Hz, 2H, CH_2), 4.91 (t, J=7.0 Hz, 1H, *CH), 7.16–7.32 (m, 9H, ArH), 7.44 (t, J=7.5 Hz, 2H, ArH), 7.55 (t, J=7.3 Hz, 1H, ArH), 7.88 (d, J=7.3 Hz, 2H, ArH); ^{1}H NMR (CCl_4, Eu(hfc)$_3$): *CH, $\Delta\delta$ 0.083 ppm, $[\alpha]_D^{20}$=+119 (1.78, CH_2Cl_2), 77% e.e.

3.3.6. (*R*)-(+)-3-Benzylsulfanyl-1,3-diphenylpropan-1-one 2f. Yield 20%, recrystallized three times, mp 57–59°C; ^{1}H NMR (300 MHz, CCl_4): 3.01 (d, J=7.0 Hz, 2H, (S)CH_2), 3.10 (m†, J_1=13.5 Hz, J_2=13.3 Hz, 2H, CH_2), 3.99 (t, J=6.9 Hz, 1H, *CH), 6.76–7.09 (m, 13H, ArH), 7.44 (d, J=7.8 Hz, 2H, ArH); ^{1}H NMR (CCl_4, Eu(hfc)$_3$): *CH, $\Delta\delta$ 0.095 ppm, $[\alpha]_D^{20}$=+138 (1.04, CH_2Cl_2), 92% e.e.

3.3.7. (*R*)-(+)-4,4-Dimethyl-1-phenyl-1-phenylsulfanylpentan-3-one 2g. Yield 19%, recrystallized four times, mp 103–104°C; ^{1}H NMR (300 MHz, $CDCl_3$): 0.99 (s, 9H, *tert*-Bu), 3.08 (m†, J_1=21.8 Hz, J_2=17.3 Hz, J_3=7.1 Hz, 2H, CH_2), 4.78 (dd, J_1=8.0 Hz, J_2=6.2 Hz, 1H, *CH), 7.15–7.28 (m, 10H, ArH); ^{1}H NMR (CCl_4, Eu(hfc)$_3$): *CH, $\Delta\delta$ 0.045, $[\alpha]_D^{20}$=+175 (1.04, CH_2Cl_2), >95% e.e.

3.4. Preparation of the oxime 3

A solution of **2a** (3.184 g, 10.0 mmol) in abs. ethanol (90 mL) was treated with NH_2OH·HCl (3.972 g, 57.2 mmol) and dry pyridine (13.2 mL, 163.6 mmol). The reaction mixture was stirred under reflux for 3.5 h, then the solvent and pyridine were removed under reduced pressure. The residue was dissolved in ether (15 mL) and washed with water, dried over Na_2SO_4, and evaporated. The product was purified by column chromatography on silica gel, R_f=0.63 (*tert*-BuOMe/$CHCl_3$, 1.0:1.0).

3.4.1. (*R*)-(+)-1,3-Diphenyl-3-phenylsulfanylpropan-1-one oxime 3. Yield 99%; oil; ^{1}H NMR (300 MHz, $CDCl_3$): 3.43 (dd, J_1=7.8 Hz, J_2=4.5 Hz, 2H, CH_2), 4.60 (t, J=7.9 Hz, 1H, *CH), 7.15–7.37 (m, 15H, ArH), 8.18 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): 33.6 (C-2), 49.8 (C-3), 126.6, 127.2, 127.4, 127.5, 127.6,

† The reported J values are those observed from the splitting patterns in the spectrum and may not reflect the true coupling constant values.

127.8, 127.9, 128.2, 128.4, 128.5, 128.7, 129.1, 129.2, 132.4, 133.0, 134.6, 135.4, 140.7 (phenyl moiety), 157.3 (C-1); IR (film): 3231, 3059, 1583, 1481, 1439, 1324, 1078, 1026, 916, 749, 696 cm^{-1}; $[\alpha]_D^{20}=+105$ (1.48, CH_2Cl_2).

3.5. Reduction of the oxime 3 to amine 4

A solution of **3** (1.110 g, 3.33 mmol) in anhydrous DME (3.5 mL) was added dropwise to an ice-cooled, stirred mixture of $TiCl_4$ (7.0 mmol) and $NaBH_4$ (0.53 g, 14 mmol) in anhydrous DME (15 mL). Stirring was continued for 20 h at rt and then the reaction was quenched by the addition of water (30 mL) with ice cooling. The mixture was basified with 25% aq. NH_3 and then extracted with Et_2O (2×30 mL). The extract was washed with brine and dried over Na_2SO_4. The solvent was evaporated and the product was purified by column chromatography on silica gel, $R_f=0.18$ (*tert*-BuOMe/$CHCl_3$/hexane, 1.0:1.0:1.0).

3.5.1. (3*R*)-1,3-Diphenyl-3-phenylsulfanylpropylamine 4 (diastereomeric ratio 65:35). Yield 40%; crystallized on standing; ^1H NMR (300 MHz, CCl_4): 1.04 (br s, 2H, NH_2), 1.81 (dd, $J_1=14.7$ Hz, $J_2=7.6$ Hz, 2H, CH_2), 3.41 and 3.57 (dd, $J_1=8.3$ Hz, $J_2=5.9$ Hz, t, $J=6.8$ Hz, 1H, (N)CH), 3.71 and 3.87 (t, $J=7.6$ Hz; dd, $J_1=8.5$ Hz, $J_2=6.7$ Hz, 1H, (S)CH), 6.73–6.89 (m, 15H, ArH); IR (film): 3370, 3060, 2927, 1583, 1492, 1453, 1025, 747, 699 cm^{-1}; MS (EI, 70 eV): m/z (%)=319 (1) [M^+], 302(25), 209(27), 208(19), 109(14), 106(100), 79 (100), 77(22), 51(7); $[\alpha]_D^{20}=+168$ (0.96, MeOH).

3.6. Beckmann rearrangement of 3

In a dry test tube was placed oxime **3** (0.333 g, 1 mmol) and anhydrous ether (5 mL). The solution was cooled to −20°C and $SOCl_2$ (0.22 mL, 3.0 mol) was added dropwise. The resulting mixture was stirred at 0°C for 5–10 min and then the solvent was evaporated under reduced pressure. The ice-water mixture was added to the residue and shaken. The reaction mixture was neutralized with satd aq. $NaHCO_3$ and extracted with Et_2O (2×5 mL). The ether solution was washed with water and dried ($MgSO_4$). After removal of the solvent the crude product was purified by chromatography.

3.6.1. (*R*)-(+)-3-Phenyl-3-phenylsulfanylpropionic acid anilide 5. Yield 78%; mp 109.2–110°C (hexane, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$): 2.87 ($m^\dagger$, $J_1=14.9$ Hz, $J_2=14.7$ Hz, $J_3=7.5$ Hz, 2H, CH_2), 4.69 (t, $J=7.4$ Hz, 1H, *CH), 6.97–7.34 (m, 16H, ArH and NH); IR (KBr): 3338, 1660, 1600, 1532, 1441, 743, 692 cm^{-1}; $[\alpha]_D^{20}=+122$ (1.0, CH_2Cl_2). Anal. calcd for $C_{21}H_{19}NOS$ (333.45): C, 75.65; H, 5.75; N, 4.20; S, 9.60. Found: C, 75.40; H, 6.00; N, 4.40; S, 9.88%. For X-ray analysis, see Section 3.2.

3.7. Alcoholysis of the anilide 5

A solution of **5** (0.100 g, 0.3 mmol) in abs. EtOH (3 mL) with two drops of conc. H_2SO_4 was placed in a reaction ampoule. The sealed ampoule was heated at 90°C for 5 days. Thereafter, the solvent was evaporated and the residue was dissolved in ether (5 mL). The resultant solution was washed with water, satd aq. $NaHCO_3$, brine and dried (Na_2SO_4). After evaporation the product was purified by column chromatography on silica gel, $R_f=0.65$ (*tert*-BuOMe/$CHCl_3$/hexane, 2.5:2.0:10.0).

3.7.1. (*R*)-(+)-Ethyl-3-phenylsulfanyl-3-phenylpropionate 6. Yield 71%; oil; ^1H NMR (300 MHz, $CDCl_3$): 1.15 (t, $J=7.1$ Hz, 3H, CH_3), 2.94 (dd, $J_1=7.8$ Hz, $J_2=3.1$ Hz, 2H, CH_2), 4.01–4.09 (dq, $J_1=7.1$ Hz, $J_2=2.1$ Hz, 2H, CH_2 (CH_3)), 4.65 (t, $J=7.8$ Hz, 1H, *CH), 7.23–7.33 (m, 10H, ArH), IR (film): 3061, 2981, 1735, 1583, 1439, 1371, 1250, 1149, 1025, 749, 696 cm^{-1}; MS (EI, 70 eV): m/z (%)=286 (11) [M^+], 177 (28), 135 (100), 109 (30), 105 (59), 91 (21), 77 (30), 65 (20), 51 (15); $[\alpha]_D^{20}=+132$ (1.0, $CHCl_3$), >95% e.e., lit.[8] $[\alpha]_D^{20}=+129.5$ ($CHCl_3$) and lit.[17] $[\alpha]_D^{20}=+138.3$ ($CHCl_3$).

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