# Synthesis and Second-Order Nonlinearities of Chiral Prolinol-Substituted Chromophores

Shang-Shing P. Chou[a]* ( 周善行 ), Chiung-Yi Yu[a] ( 游瓊誼 ),
Hong-Cheu Lin[b†] ( 林宏州 ) and Pao-Keng Yang[c] ( 楊寶賡 )
[a]*Department of Chemistry, Fu Jen Catholic University, Taipei, Taiwan 242, R.O.C.*
[b]*Institute of Chemistry, Academia Sinica, Taipei, Taiwan 115, R.O.C.*
[c]*Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu, Taiwan 300, R.O.C.*

A new series of thiophene- and furan-containing chromophores with a chiral prolinol donor and a sulfone acceptor has been synthesized. The UV-vis absorptions, second-order nonlinear optical properties, and X-ray crystal structures are described.

**Keywords:** Nonlinear optical materials; Chiral; Heterocyclic compounds.

## INTRODUCTION

The potential applications of nonlinear optical (NLO) materials in telecommunications, data storage, and optical information processing have created a need for new materials with very large second-order susceptibilities.[1] We[2] and others[3] have previously demonstrated that heterocyclic chromophores exhibit higher hyperpolarizabilities (μβ) than their benzene analogues. However, it is imperative that nonlinear molecules reside in a noncentrosymmetric environment in order to show this second-order susceptibility. Incorporation of chiral substituent, for example, in *N*-(4-nitrophenyl)-(*L*)-prolinol (NPP)[4a] and 2-(*N*-prolinol)-5-nitropyridine (PNP)[4b] has resulted in a large SHG powder efficiency. Here we report the synthesis of a series of chiral thiophene- and furan-containing chromophores **7**-**10**, **16** and **17** with a prolinol donor and a sulfone acceptor attached to a conjugated system through a π–bridge of C=N. Although the sulfonyl group is not as strong an electron-withdrawing group as the nitro, di- or tri-cyanoethenyl group, it is synthetically more flexible and has greater transparency in the visible spectrum.[5]

## RESULTS AND DISCUSSION

The synthesis of imino dyes **7**-**10** is shown in Scheme I. Alkylation of 4-nitrobenzenethiol **1** gave sulfides **2** which were oxidized by MCPBA to the sulfones **3**. Reduction with stannous chloride gave the aniline derivatives **4**. Treatment of 5-bromo-2-thiophenecarbaldehyde **5a** or its furan analogue **5b** with (*S*)-2-pyrrolidinemethanol (prolinol) gave the aldehydes **6**. The imino dyes **7**-**10** were then prepared in good yields by the condensation of aldehydes **6** with 4-(methylsulfonyl)aniline, 4-(phenylsulfonyl)aniline,[6a] **4a**[6b] or **4b**,[6c] respectively.

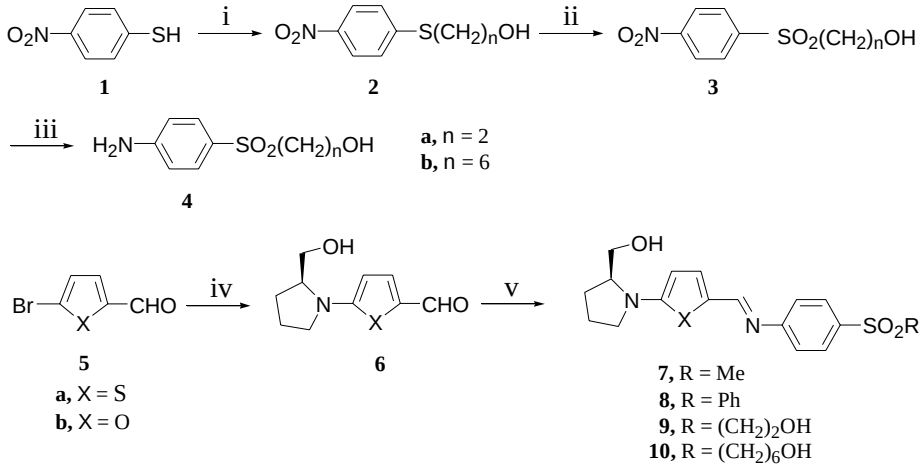
The synthesis of imino dyes **16** and **17** is shown in Scheme II. Reaction of 4-bromo-nitrobenzene **11** with (*S*)-prolinol gave the substitution product **12**.[4a] Reduction with stannous chloride[6c] gave the amine **13**,[6d] which was then condensed with the aldehydes[2] **14** or **15** to give the imines **16** and **17**, respectively, in good yields.

The UV-vis absorptions, molecular hyperpolarizabilities (μβ), second-harmonic generation (SHG) intensities, and decomposition temperatures ($T_d$) of imino dyes **7**-**10**, **16** and **17** are shown in Table 1. To assess the effect of the chiral prolinol group on the NLO properties of these chromophores, the achiral amino compounds **18**-**21**[2] are also included in Table 1 for comparison. The UV-vis absorptions were measured in 1,4-dioxane. The rather low $\lambda_{max}$ values (407-429 nm) of imines **7**-**10**, **16** and **17** indicate their good transparency in the UV-vis spectrum.

The molecular hyperpolarizabilities (μβ) of chromophores **7a**-**10a**, **18** and **19** were measured in dioxane using the electric-field-induced second harmonic generation (EFISH)[7] technique at 1064 nm, and the μβ values of the other chromophores were estimated by solvatochromism.[8] The zero-

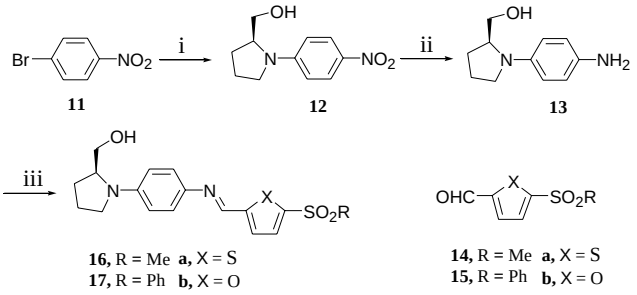
* Corresponding author. Fax: +886-2-29023209; e-mail: chem1004@mails.fju.edu.tw
† Present address: Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan 300, R. O. C.

**Scheme I**




Reagents and conditions: i, Na, $Br(CH_2)_nOH$, EtOH, reflux, 12 h; ii, MCPBA, $CH_2Cl_2$, 0 °C, 2 h; iii, $SnCl_2{\cdot}2H_2O$, EtOH, reflux, 12 h; iv, (*S*)-prolinol, 48% HBr, sealed-tube, 130 °C, 12 h; v, 4-(methylsulfonyl)aniline, 4-(phenylsulfonyl)aniline, **4a** or **4b**, $H_2SO_4$ (2 M), EtOH, rt, 2 h.

**Scheme II**




Reagents and conditions: i, (*S*)-prolinol, $NEt_3$, toluene, reflux, 24 h; ii, $SnCl_2{\cdot}2H_2O$, toluene, reflux, 12 h; iii, **14** or **15**, $H_2SO_4$ (2 M), EtOH, rt, 2 h.

frequency hyperpolarizability ($\mu\beta_0$) was calculated using a two-level model.[9] The Kurtz powder method[10] was used to determine the average SHG intensity at 1064 nm using urea as the reference.

By comparing the $\mu\beta$ values of **7a** and **8a**, it can be seen that the phenylsulfonyl group has a larger effect than the methylsulfonyl group. Consistent with the previous observations,[2] the $\mu\beta$ values of the thiophene compounds **7a**-**10a** are larger than those of the furan analogues **7b**-**10b**. Incorporation of a terminal hydroxyl group in the sulfone moiety also significantly increases the $\mu\beta$ values (for example, **9a** > **10a** > **7a**).

Comparison of the SHG intensities of **7a** and **8a** with those of the achiral amino-substituted imines **18**-**21** is quite revealing. It can be seen that the chiral prolinol group has a very beneficial effect. However, the presence of the prolinol group itself in chromophores **7**-**10**, **16** and **17** does not necessarily lead to high SHG intensities for these compounds. It may not be totally coincident that the furan compounds **7b**-**10b** all exhibit lower SHG values than the thiophene analogues **7a**-**10a**.

In order to understand the reason why the SHG intensity of **8a** is 10 times higher than that of **7a**, the single crystal X-ray structures of **7a** and **8a** were obtained (Fig. 1). Although both of these compounds have a noncentrosymmetric alignment with a $P2_1$ space group, their crystal packings are quite different. The unit cell of crystal **8a** contains two molecules of chromophores, which are almost parallel to each other so that their dipole moments add up. On the other hand, the unit cell of crystal **7a** contains four molecules of chromophores (together with a molecule of dichloromethane) which are arranged almost antiparallel to one another.

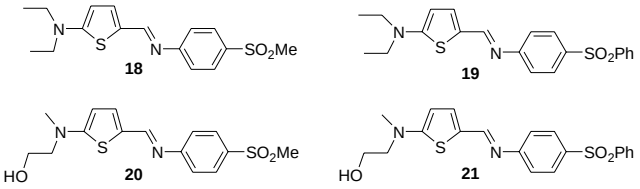
The melting points $T_m$ of these imino dyes were measured by differential scanning calorimetry (DSC) at a heating rate of 20 °C $min^{-1}$. The phenylsulfones have higher $T_m$ than the methylsulfones, and increasing the methylene unit in the sulfonyl group decreases the $T_m$. The decomposition temperatures ($T_d$) of these chromophores are quite high (in most cases greater than 270 °C) as determined by thermogravimetric analysis (TGA) at a heating rate of 10 °C $min^{-1}$. It is interesting to note that imines **7**-**10** have considerably higher $T_d$ than imines **16**-**17**.

In summary, we have successfully synthesized a new

Table 1. UV-vis, Melting Point, Decomposition Temperature, μβ Values, $\mu\beta_0$ Values, Powder SHG Intensity and Space Group for Imino Dyes

| Compound | $\lambda_{max}$ [a] / nm | $\lambda_{cutoff}$ / nm | $T_m$ / °C | $T_d$ / °C | $\mu\beta_{1064}$ / $10^{-48}$esu | $\mu\beta_0$ / $10^{-48}$esu | SHG intensity [d] | space group |
|---|---|---|---|---|---|---|---|---|
| **7a** | 413 | 491 | 116 | 300 | 720[b] | 243 | 1.3 | $P2_1$ |
| **7b** | 407 | 488 | 107 | 301 | 285[c] | 174 | 0.07 | - |
| **8a** | 417 | 519 | 177 | 318 | 1132[b] | 370 | 13 | $P2_1$ |
| **8b** | 416 | 524 | 124 | 269 | 376[c] | 123 | - | - |
| **9a** | 416 | 491 | 115 | 287 | 1300[b] | 430 | 0.3 | - |
| **9b** | 408 | 487 | 106 | 275 | 325[c] | 107 | 0.02 | - |
| **10a** | 416 | 491 | 86 | 317 | 947[b] | 312 | 0.5 | - |
| **10b** | 408 | 488 | 78 | 308 | 90[c] | 31 | 0.07 | - |
| **16a** | 428 | 516 | 114 | 211 | 582[c] | 172 | 1.3 | - |
| **16b** | 412 | 491 | 105 | 196 | 265[c] | 90 | 0 | - |
| **17a** | 429 | 532 | 154 | 226 | 1580[c] | 462 | 0.5 | - |
| **17b** | 419 | 516 | 146 | 240 | 544[c] | 174 | 0.5 | - |
| **18** | 412 | 467 | 98 | 320 | 447[b] | 152 | 0.7 | - |
| **19** | 420 | 476 | 140 | 351 | 488[b] | 156 | $1.5 \times 10^{-2}$ | *P*-1 |
| **20** | 412 | 483 | 151 | 303 | 540[c] | 183 | 0.08 | *P*-1 |
| **21** | 416 | 495 | 158 | 318 | 1513[c] | 495 | 0.8 | - |

[a] Measured in dioxane.
[b] Measured by EFISH with a fundamental wavelength of 1064 nm.
[c] Estimated by solvatochromic method for a fundamental wavelength of 1064 nm.
[d] $I(2\omega)_{sample}/I(2\omega)_{urea}$.




series of thiophene- and furan-containing l chromophores with a chira prolinol donor and a sulfone acceptor. These compounds have good transparency in the UV-vis spectrum, high μβ values and good thermal stability, and should be quite useful for NLO applications. The chiral prolinol group not only can help to induce a noncentrosymmetric alignment, but the pendant hydroxyl group on the prolinol substituent can also be further attached to a polymer chain or converted to other functional groups.

## EXPERIMENTAL SECTION

Infrared spectra were recorded with a FT-IR spectrometer Analect RFX-65. Specific rotations were measured for samples in $CH_2Cl_2$ with a polarimeter Horiba SPEA-300. $^1H$ and $^{13}C$ NMR spectra were measured for samples in $CDCl_3$ with a FT-NMR spectrometer Bruker AC-300 at 300 and 75 MHz, respectively, with tetramethylsilane as the internal standard. High resolution mass spectra were measured with a mass spectrometer JEOL TMS-HX 110. UV-vis absorption spectra were recorded using a Shimadzu UV-160PC spectrophotometer. Elemental analyses were measured by the Perkin-Elmer 2400 (II). Melting points were measured by differential scanning calorimetry (Perkin-Elmer DSC7) except for compounds **6a** and **6b** whose melting points were

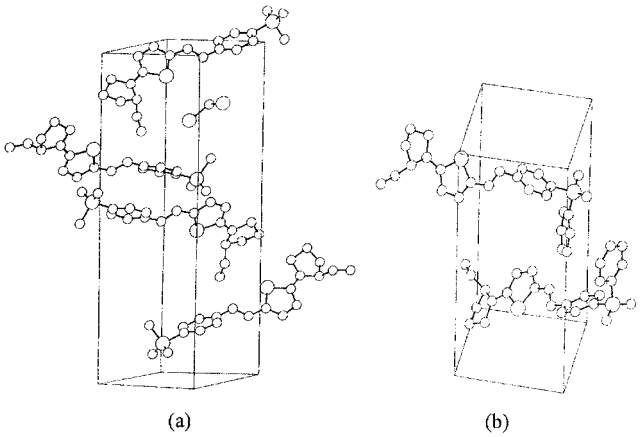



Fig. 1. (a) Packing drawing of compound **7a** (space group $P2_1$); (b) Packing drawing of compound **8a** (space group $P2_1$).

measured with an apparatus Mel-Temp. The silica gel used for flash column chromatography was made by Merck (60 H). All reagents were of reagent grade and were purified prior to use.[11]

**5-[(*S*)-(-)-2-(Hydroxymethyl)pyrrolidinyl]-2-thiophene-carbaldehyde (6a)**

A mixture of 5-bromo-2-thiophenecarbaldehyde **5a** (382 mg, 2.0 mmol), (*S*)-(-)-pyrrolidinemethanol (606 mg, 6.0 mmol), and 48% aq. HBr solution (337 mg, 2.0 mmol) was heated in a sealed tube at 110 °C for 9 h. The mixture was quenched with excess 10% sodium hydroxide solution, and the resulting oil was extracted with methylene chloride (20 mL × 3). The organic layer was dried with magnesium sulfate, and the solvent was removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane 1:1) to give **6a** (296 mg, 70%): mp 108-109 °C. $^1$H NMR ($CDCl_3$) δ 1.99-2.17 (m, 4H), 3.26 (q, *J* = 8.2 Hz, 1H), 3.47 (t, *J* = 8.2 Hz, 1H), 3.59 (m, 1H), 3.77 (m, 2H), 3.79 (m, 1H), 5.96 (d, *J* = 4.5 Hz, 1H), 7.42 (d, *J* = 4.5 Hz, 1H), 9.29 (s, 1H); $^{13}$C NMR ($CDCl_3$) δ 23.87, 28.67, 51.96, 61.87, 64.21, 104.09, 125.65, 140.85, 165.12, 179.57; IR (film) 3422, 2926, 2874, 1621, 1530, 1491, 1403, 1369, 1271, 1058, 978, 927, 661 cm$^{-1}$; HRMS *m/z* calcd for $C_{10}H_{13}NO_2S$ ($M^+$): 211.0667, found 211.0665. Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63. Found: C, 56.83; H, 6.24; N, 6.60%. $[\alpha]_D^{25}$ = -142 (*c* 1.0, $CH_2Cl_2$).

**5-[(*S*)-(-)-2-(Hydroxymethyl)pyrrolidinyl]-2-furaldehyde (6b)**

A mixture of 5-bromo-2-furancarbaldehyde **5b** (345 mg, 2.0 mmol) and (*S*)-(-)-pyrrolidinemethanol (6.0 mmol) was heated in a sealed tube at 110 °C for 9 h. The mixture was quenched with excess 10% sodium hydroxide solution, and the resulting oil was extracted with methylene chloride (20 mL × 3). The organic layer was dried with magnesium sulfate, and the solvent was removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane 1:1) to give **6b** (254 mg, 65%): mp 99-100 °C. $^1$H NMR ($CDCl_3$) δ 1.99-2.01 (m, 4H), 3.36 (q, *J* = 8.2 Hz, 1H), 3.52-3.64 (m, 4H), 4.01 (m, 1H), 5.27 (d, *J* = 4.5 Hz, 1H), 7.18 (d, *J* = 4.5 Hz, 1H), 8.78 (s, 1H); $^{13}$C NMR ($CDCl_3$) δ 23.87, 28.67, 51.96, 61.87, 64.21, 102.09, 132.65, 144.85, 163.11, 170.04; IR (film) 3437, 2938, 2880, 1641, 1579, 1411, 1281, 1039, 910, 764 cm$^{-1}$; HRMS *m/z* calcd for $C_{10}H_{13}NO_3$ ($M^+$): 195.0895, found 195.0895. Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.18. Found: C, 61.47; H, 6.79; N, 7.13%. $[\alpha]_D^{25}$ = -134 (*c* 1.0, $CH_2Cl_2$).

**General Procedure for Imine Formation**

A solution of compound **6a** or **6b** (0.47 mmol), aniline derivative (0.52 mmol) and $H_2SO_{4\,(aq)}$ (0.02 mL, 2 M, 0.047 mmol) in EtOH (5 mL) was stirred at room temperature for 2 h, and an aqueous solution of $Na_2CO_3$ was then added. The solution was evaporated under vacuum and the residue was then extracted with $CH_2Cl_2$ (20 mL × 3). The organic layer was dried with magnesium sulfate, and the solvent was removed. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane 1:1) to give imines **7-10**. Imines **16** and **17** were similarly prepared.

**(*S*)-(-)-5-[(2-Hydroxymethyl)pyrrolidinyl]-2-thiophene-carbaldehyde-4-(methylsulfonyl)phenylimine (7a)**

(693 mg, 95%): mp 116 °C. $^1$H NMR (Acetone-$D_6$) δ 2.09-2.18 (m, 4H), 3.09 (s, 3H), 3.31 (m, 1H), 3.52-3.79 (m, 4H), 4.04 (br, 1H), 6.01 (d, *J* = 3.2 Hz, 1H), 7.32 (d, *J* = 6.7 Hz, 2H), 7.41 (d, *J* = 3.2 Hz, 1H), 7.86 (d, *J* = 6.7 Hz, 2H), 8.50 (s, 1H); $^{13}$C NMR (Acetone-$D_6$) δ 23.66, 28.43. 43.75, 51.59, 61.33, 64.50, 102.64, 121.36, 124.62, 128.53, 136.36, 137.51, 154.30, 157.10,161.58; IR (film) 3468, 3363, 2914, 1602, 1566, 1490, 1285, 1136, 1051, 956, 833, 760 cm$^{-1}$; HRMS *m/z* calcd for $C_{17}H_{20}N_2O_3S_2$ ($M^+$): 364.0915, found 364.0909. $[\alpha]_D^{25}$ = -105 (*c* 1.0, $CH_2Cl_2$).

**(*S*)-(-)-5-[(2-Hydroxymethyl)pyrrolidinyl]-2-furaldehyde-4-(methylsulfonyl)phenylimine (7b)**

(634 mg, 91%): mp 107 °C. $^1$H NMR (Acetone-$D_6$) δ 2.04-2.13 (m, 4H), 3.09 (s, 3H), 3.31 (m, 1H), 3.41-3.57 (m, 4H), 3.94 (m, 1H), 5.36 (d, *J* = 2.8 Hz, 1H), 7.15 (d, *J* = 2.8 Hz, 2H), 7.31 (d, *J* = 6.4 Hz, 2H), 7.86 (d, *J* = 6.4 Hz, 2H), 8.05 (s, 1H); $^{13}$C NMR (Acetone-$D_6$) δ 24.40, 44.61, 49.49, 62.21, 63.41, 86.67, 122.12, 129.43, 137.03, 143.95, 147.17, 158.68, 162.23; IR (film) 3411, 2921, 1625, 1533, 1478, 1302, 1268, 1143, 1023, 949, 839, 759 cm$^{-1}$; HRMS *m/z* calcd for $C_{17}H_{20}N_2O_4S$ ($M^+$): 348.1144, found 348.1132. $[\alpha]_D^{25}$ = -72 (*c* 1.0, $CH_2Cl_2$).

**(*S*)-(-)-5-[(2-Hydroxymethyl)pyrrolidinyl]-2-thiophene-carbaldehyde-4-(phenylsulfonyl)phenylimine (8a)**

(810 mg, 95%): mp 177 °C. $^1$H NMR (Acetone-$D_6$) δ 2.04-2.17 (m, 4H), 3.28 (m, 1H), 3.51-3.69 (m, 4H), 3.99 (m, 1H), 6.00 (d, *J* = 3.2 Hz, 1H), 7.29 (d, *J* = 6.5 Hz, 2H), 7.38 (d, *J* = 3.2 Hz, 1H), 7.62 (m, 3H), 7.90 (d, *J* = 6.5 Hz, 2H), 7.99 (d, *J* = 6.0 Hz, 2H), 8.45 (s, 1H); $^{13}$C NMR (Acetone-$D_6$) δ 24.37, 52.33, 62.01, 65.25, 98.68, 103.53, 122.34, 125.32, 128.05, 129.68, 130.15, 133.74, 137.43, 138.38, 143.66, 155.06, 157.84, 162.49; IR (film) 3522, 2870, 1605, 1566,

1494, 1454, 1274, 1149, 1053, 839, 757 $cm^{-1}$; HRMS *m/z* calcd for $C_{22}H_{22}N_2O_3S_2$ ($M^+$): 426.1072, found 426.1074. Anal. Calcd for $C_{22}H_{22}N_2O_3S_2$: C, 61.95; H, 5.20; N, 6.57. Found: C, 61.59; H, 5.17; N, 6.77. $[\alpha]_D^{25}$ = -105 (*c* 1.0, $CH_2Cl_2$).

**(*S*)-(-)-5-[(2-Hydroxymethyl)pyrrolidinyl]-2-furaldehyde-4-(phenylsulfonyl)phenylimine (8b)**

(763 mg, 93%): mp 124 °C. $^1$H NMR (Acetone-$D_6$) δ 2.03-2.10 (m, 4H), 3.40 (m, 1H), 3.52-3.66 (m, 4H), 3.99 (m, 1H), 5.34 (d, *J* = 3.8 Hz, 1H), 7.12 (d, *J* = 3.8 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.57-7.65 (m, 3H), 7.89 (d, *J* = 8.6 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 3H); $^{13}$C NMR (Acetone-$D_6$) δ 23.50, 28.05, 48.58, 61.32, 62.55, 85.97, 121.52, 127.30, 128.95, 129.43, 133.00, 136.45, 142.87, 143.01, 146.29, 157.73, 161.40; IR (film) 3300, 3089, 1679, 1617, 1589, 1446, 1298, 1271, 1152, 1105, 1024, 850, 731 $cm^{-1}$; HRMS *m/z* calcd for $C_{22}H_{22}N_2O_4S$ ($M^+$): 410.1300, found 410.1296. $[\alpha]_D^{25}$ = -73 (*c* 1.0, $CH_2Cl_2$).

**(*S*)-(-)-5-[(2-Hydroxymethyl)pyrrolidinyl]-2-thiophenecarbaldehyde-4-[(2-hydroxyethyl)sulfonyl]phenylimine (9a)**

(726 mg, 92%): mp 115 °C. $^1$H NMR (Acetone-$D_6$) δ 2.14-2.17 (m, 4H), 3.29-4.09 (m, 11H), 6.00 (d, *J* = 3.1 Hz, 1H), 7.32 (d, *J* = 6.4 Hz, 2H), 7.40 (d, *J* = 3.1 Hz, 1H), 7.85 (d, *J* = 6.4 Hz, 2H), 8.50 (s, 1H); $^{13}$C NMR (Acetone-$D_6$) δ 23.57, 28.33, 51.51, 55.83, 58.29, 61.23, 64.40, 102.62, 121.22, 124.49, 129.18, 135.03, 137.54, 154.22, 157.09, 161.57; IR (film) 3436, 3248, 2923, 1602, 1567, 1446, 1280, 1136, 1033, 847, 736 $cm^{-1}$; HRMS *m/z* calcd for $C_{18}H_{22}N_2O_4S_2$ ($M^+$): 394.1021, found 394.1034. $[\alpha]_D^{25}$ = -105 (*c* 1.0, $CH_2Cl_2$).

**(*S*)-(-)-5-[(2-Hydroxymethyl)pyrrolidinyl]-2-furaldehyde-4-[(2-hydroxyethyl)sulfonyl]phenylimine (9b)**

(643 mg, 86%): mp 106 °C. $^1$H NMR (Acetone-$D_6$) δ 2.04-2.17 (4m), 3.37-3.89 (m, 11H), 5.36 (d, *J* = 3.8 Hz, 1H), 7.16 (d, *J* = 3.8 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 8.05 (s, 1H); $^{13}$C NMR (Acetone-$D_6$) δ 23.44, 28.07, 48.59, 55.87, 58.37, 61.37, 62.63, 85.92, 121.20, 129.27, 134.95, 143.01, 146.32, 157.81, 161.43; IR (film) 3275, 2920, 1627, 1534, 1477, 1400, 1267, 1134,1025, 872, 735 $cm^{-1}$; HRMS *m/z* calcd for $C_{18}H_{22}N_2O_5S$ ($M^+$): 378.1249, found 378.1260. $[\alpha]_D^{25}$ = -72 (*c* 1.0, $CH_2Cl_2$).

**(*S*)-(-)-5-[(2-Hydroxymethyl)pyrrolidinyl]-2-thiophene-carbaldehyde-4-[(6-hydroxyhexyl)sulfonyl]phenylimine (10a)**

(793 mg, 88%): mp 86 °C. $^1$H NMR (Acetone-$D_6$) δ 1.38-1.46 (m, 6H), 1.66 (m, 2H), 2.04-2.17 (m, 4H), 3.14-3.85 (m, 10H), 6.00 (d, *J* = 4.2 Hz, 1H), 7.32 (d, *J* = 6.6 Hz, 2H), 7.41 (d, *J* = 4.2 Hz, 1H), 7.82 (d, *J* = 6.6 Hz, 2H), 8.51 (s, 1H); $^{13}$C NMR (Acetone-$D_6$) δ 22.83, 23.64, 25.22, 27.81, 32.44, 51.57, 55.67, 59.64, 61.28, 61.32, 64.47, 102.63, 121.34, 124.61, 129.24, 134.67, 137.54, 154.31, 157.12, 161.58; IR (film) 3421, 2921, 1626, 1523, 1478, 1399, 1267, 1141, 1023, 872, 748 $cm^{-1}$; HRMS *m/z* calcd for $C_{22}H_{30}N_2O_4S_2$ ($M^+$): 450.1647, found 450.1639. $[\alpha]_D^{25}$ = -87 (*c* 1.0, $CH_2Cl_2$).

**(*S*)-(-)-5-[(2-Hydroxymethyl)pyrrolidinyl]-2-thiophene-carbaldehyde-4-[(6-hydroxyhexyl)sulfonyl]phenylimine (10b)**

(712 mg, 82%): mp 78 °C. $^1$H NMR (Acetone-$D_6$) δ 1.32-1.50 (m, 6H), 1.44 (m, 2H), 2.04-2.15 (m, 4H), 3.13-4.00 (m, 10H), 5.35 (d, *J* = 3.8 Hz, 1H), 7.15 (d, *J* = 3.8 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 8.05 (s, 1H); $^{13}$C NMR (Acetone-$D_6$) δ 23.49, 24.19, 25.89, 28.48, 28.85, 33.10, 49.25, 56.38, 62.01, 62.04, 63.36, 86.58, 121.93, 129.91, 135.18, 143.67, 147.01, 158.39, 162.08;. IR (film) 3434, 2944, 1629, 1545, 1401, 1282, 1136, 1031, 916, 867 $cm^{-1}$; HRMS *m/z* calcd for $C_{22}H_{30}N_2O_5S$ ($M^+$): 434.1875, found 434.1842. $[\alpha]_D^{25}$ = -64 (*c* 1.0, $CH_2Cl_2$).

**(*S*)-(-)-5-(Methylsulfonyl)-2-thiophenecarbaldehyde-4-[(2-hydroxymethyl)pyrrolidinyl]phenylimine (16a)**

(685 mg, 94%): mp 114 °C. $^1$H NMR (Acetone-$D_6$) δ 1.99-2.14 (m, 4H), 3.18 (m, 1H), 3.28 (s, 3H), 3.42 (m, 2H), 3.66 (m, 1H), 3.84 (m, 1H), 6.67 (d, *J* = 6.7 Hz, 2H), 7.31 (d, *J* = 6.7 Hz, 2H), 7.34 (d, *J* = 3.0 Hz, 1H), 7.71 (d, *J* = 3.0 Hz, 1H), 8.81 (s, 1H); $^{13}$C NMR (Acetone-$D_6$) δ 22.96, 28.11, 45.01, 48.47, 60.54, 61.72, 112.18, 123.17, 129.48, 133.45, 137.87, 143.23, 145.50, 147.74, 151.55; IR (film) 3543, 2929, 1610, 1559, 1508, 1290, 1130, 1039, 1010, 965, 820, 765 $cm^{-1}$; HRMS *m/z* calcd for $C_{17}H_{20}N_2O_3S_2$ ($M^+$): 364.0915, found 364.0911. Anal. Calcd for $C_{17}H_{20}N_2O_3S_2$: C, 56.02; H, 5.53; N, 7.69. Found: C, 56.02; H, 5.67; N, 7.51. $[\alpha]_D^{25}$ = -134 (*c* 1.0, $CH_2Cl_2$).

**(*S*)-(-)-5-(Methylsulfonyl)-2-furaldehyde-4-[(2-hydroxy-methyl)pyrrolidinyl]phenylimine (16b)**

(750 mg, 88%): mp 105 °C. $^1$H NMR (Acetone-$D_6$) δ 1.99-2.16 (m, 4H), 3.14 (m, 1H), 3.29 (s, 4H), 3.46 (m, 2H), 3.65 (m, 1H), 3.86 (m, 1H), 6.70 (d, *J* = 6.7 Hz, 2H), 7.09 (d, *J* = 2.8 Hz, 1H), 7.28 (d, *J* = 2.8 Hz, 1H), 7.32 (d, *J* = 6.7 Hz, 2H), 8.53 (s, 1H); $^{13}$C NMR (Acetone-$D_6$) δ 22.75, 27.92, 42.64, 48.24, 60.44, 61.48, 112.05, 112.62, 118.10, 122.92, 138.05, 140.45, 147.66, 150.34, 156.82; IR (film) 3363, 1610, 1522, 1507, 1308, 1153, 1097, 1026, 817, 750 $cm^{-1}$; HRMS *m/z* calcd for $C_{17}H_{20}N_2O_4S$ ($M^+$): 348.1144, found

348.1140. $[\alpha]_D^{25}$ = -110 (*c* 1.0, $CH_2Cl_2$).

**(*S*)-(-)-5-(Phenylsulfonyl)-2-thiophenecarbaldehyde-4-[(2-hydroxymethyl)pyrrolidinyl]phenylimine (17a)**

(679 mg, 90%): mp 154 °C. $^1$H NMR (Acetone-$D_6$) δ 1.95-2.13 (m, 4H), 3.15 (m, 1H), 3.43 (m, 2H), 3.63 (m, 2H), 3.82 (m, 2H), 6.65 (d, *J* = 7.0 Hz, 2H), 7.28 (d, *J* = 7.0 Hz, 2H), 7.38 (d, *J* = 4.0 Hz, 1H), 7.63-7.77 (m, 4H), 8.04 (d, *J* = 7.9 Hz, 2H), 8.77 (s, 1H); $^{13}$C NMR (Acetone-$D_6$) δ 23.75, 28.90, 49.26, 61.35, 62.65, 112.97, 123.99, 125.32, 128.05, 130.39, 130.44, 134.42, 134.65, 138.61, 143.01, 144.58, 146.09, 148.56, 153.25; IR (film) 3375, 2937, 1603, 1571, 1495, 1461, 1345, 1282, 1200, 1140, 1052, 930, 839, 706 $cm^{-1}$; HRMS *m/z* calcd for $C_{22}H_{22}N_2O_3S_2$ ($M^+$): 426.1072, found 426.1071. $[\alpha]_D^{25}$ = -124 (*c* 1.0, $CH_2Cl_2$).

**(*S*)-(-)-5-(Phenylsulfonyl)-2-furaldehyde-4-[(2-hydroxymethyl)pyrrolidinyl]phenylimine (17b)**

(602 mg, 85%): mp 146 °C. $^1$H NMR (Acetone-$D_6$) δ 1.95-2.13 (m, 4H), 3.15 (m, 1H), 3.43 (m, 2H), 3.63 (m, 1H), 3.83 (m, 2H), 6.65 (d, *J* = 6.8 Hz, 2H), 7.07 (d, *J* = 2.8 Hz, 1H), 7.28 (d, *J* = 6.8 Hz, 2H), 7.43 (d, *J* = 2.8 Hz, 1H), 7.62-7.80 (m, 3H), 8.03 (d, *J* = 6.2 Hz, 2H), 8.46 (s, 1H); $^{13}$C NMR (Acetone-$D_6$) δ 23.40, 28.19, 28.19, 48.53, 61.93, 112.22, 112.80, 119.36, 123.16, 127.78, 129.77, 134.18, 138.43, 140.65, 147.91, 150.10, 157.84; IR (film) 3394, 2937, 1717, 1571, 1530, 1494, 1461, 1359, 1285, 1137, 1088, 860, 768 $cm^{-1}$; HRMS *m/z* calcd for $C_{22}H_{22}N_2O_4S$ ($M^+$): 410.1300, found 410.1292. $[\alpha]_D^{25}$ = -103 (*c* 1.0, $CH_2Cl_2$).

**Crystal Data for 7a**

$C_{35}H_{42}Cl_2N_4O_6S_4$, *M* = 813.88, monoclinic, space group $P2_1$, *a* = 8.350(3), *b* = 24.035(6), *c* = 10.075(3) Å, β = 103.56(3)°, *V* = 1965.6(11) $Å^3$, *Z* = 2, $D_c$ = 1.375 g $cm^{-3}$, *F*(000) = 852, μ = 4.1 $cm^{-1}$, crystal size = 0.25 × 0.20 × 0.20 mm. 4389 reflections measured, 2623 unique which were used in all calculations. $R_f$ = 0.039, $R_w$ = 0.039. CCDC 138449.

**Crystal Data for 8a**

$C_{22}H_{22}N_2O_3S_2$, *M* = 426.54, monoclinic, space group $P2_1$, *a* = 6.1649(17), *b* = 7.816(3), *c* = 21.065(4) Å, β = 93.492(19)°, *V* = 1013.1(5) $Å^3$, *Z* = 2, $D_c$ = 1.398 g $cm^{-3}$, *F*(000) = 448, μ = 5.4 $cm^{-1}$, crystal size = 0.50 × 0.40 × 0.05 mm. 1927 reflections measured, 1684 unique which were used in all calculations. $R_f$ = 0.057, $R_w$ = 0.050. CCDC 138448.

**ACKNOWLEDGEMENT**

Financial support of this work by the National Science Council of the Republic of China is gratefully acknowledged (NSC-90-2113-M-030-003).

**REFERENCES**

1. (a) Williams, D. J. *Angew. Chem. Int. Ed.* **1984**, *23*, 690. (b) Chemla, D. S.; Zyss, J. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: Orlando, 1987; vol. 1 and 2. (c) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (d) Marder, S. R.; Sohn, J. E.; Stucky, G. D. *Materials for Nonlinear Opticals: ACS Symposium Series 455*; ACS: Washington, D. C., 1991.
2. (a) Chou, S. S. P.; Sun, D. J.; Lin, H. C.; Yang, P. K. *Chem. Commun*. **1996**, 1045. (b) Chou, S. S. P.; Sun, D. J.; Lin, H. C.; Yang, P. K. *Tetrahedron Lett.* **1996**, *37*, 7279. (c) Chou, S. S. P.; Shen, C. H. *Tetrahedron Lett.* **1997**, *38*, 6407. (d) Chou, S. S. P.; Hsu, G. T.; Lin, H. C. *Tetrahedron Lett.* **1999**, *40*, 2157. (e) Chou, S. S. P.; Yeh, Y. H. *Tetrahedron Lett.* **2001**, *42*, 1309. (f) Sun, D. J. Ph.D. thesis, 1996, Department of Chemistry, Fu Jen Catholic University, Taipei, Taiwan, R.O.C.
3. (a) Rao, V. P.; Jen, A. K.; Wong, K. Y.; Drost, K. J. *Tetrahedron Lett.* **1993**, *34*, 1747. (b) Jen, A. K.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 90. (c) Rao, V. P.; Jen, A. K.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc.,Chem. Commun*. **1993**, 1118.
4. (a) Zyss, J.; Nicoud, J. F.; Coquillay, M. *J. Chem. Phys*. **1984**, *81*, 4160. (b) Sutter, K.; Bosshard, C.; Wang, W. S.; Surmelyand, G.; Günter, P. *Appl. Phys. Lett.* **1988**, *53*, 1779.
5. Ulman, A.; Willand, C. S.; Köhler, W.; Robello, D. S.; Williams, D. J.; Handley, L. *J. Am. Chem. Soc*. **1990**, *112*, 7083.
6. (a) Courtin, A. *Helv. Chim. Acta* **1983**, *66*, 1046. (b) Alonso, D. A.; Najera, C.; Varea, M. *Synthesis* **2003**, 277. (c) Hanken, D. G.; Naujok, R. R.; Gray, J. M.; Corn, R. M. *Anal. Chem.* **1997**, *69*, 240. (d) Piniella, J. F.; Alvarez-Larena, A.; Diaz-Garcia, M. A.; Agullo-Lopez, F.; Ledoux, I.; Zyss, J.; Kato, M.; Kiguchi, M.; Mar Miranda, M.; Montserrat, M.; Soler, E.; Sorribes, S.; Germain, G. *J. Mater. Chem.* **1998**, *8*, 619.
7. Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446.
8. Paley, M. S.; Harris, J. M. *J. Org. Chem*. **1989**, *54*, 3774.
9. Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *67*, 2664.
10. Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798.
11. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; 2nd ed.; Pergamon Press: New York, 1980.