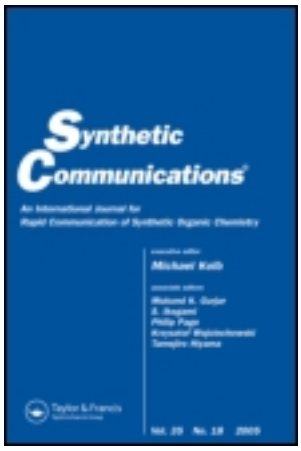

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Studies on the Synthesis of Novel Chiral Naphthylene Bisoxazoline Ligands

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ABSTRACT

The synthesis of chiral C_2-symmetric substituted bisoxazoline ligands containing naphthalene group were investigated. Ethyl 2,3-naphthylene-dicarboxylate reacted with amino alcohols and the resulting amides were treated with $SOCl_2$ and then reacted with Et_3N in toluene to afford the desired bisoxazolines. 2,3-Naphthylenedicarbonitrile reacted with amino alcohol give *N*- (1′-phenyl-2′-hydroxyethyl)-2,3-naphthylenedicarboximide **1**. The 2,3-naphthylenedicarboxylic acid

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reacted with thionyl chloride give the 2,3-Naphthalenedicarboxylic acid cyclic anhydride rather than corresponding 2,3-naphthalenedicarboxylic acid dichloride, the former reacted with amino alcohol also give compound **1**. The later two strategies cannot give the target bisoxazoline.

Key Words: Bisoxazoline; Naphthylene; Synthesis; Amino alcohol.

In recent years, the C_2-symmetric chiral *bis*(oxazolines) are very useful ligands in the catalysis of many reactions. The design and synthesis of new chiral oxazoline ligands and their metal complexes in asymmetric catalytic reaction has inspired many scientists to work with great efforts.[1–8] Our interest has focused on the studies of enantioselective transition-metal catalysis of heterocyclic ligands. In the design of our new ligands it was crucial to have a rigid cyclic backbone. We have chosen system of bisoxazoline containing naphthylene, it has rigid aromatic unit and N coordination sites, the facial selectivity of naphthylene and chiral selectivity of oxazoline may result special enantioselectivity. The size of the chelate in the reaction metal complex of bisoxazolines is an important factor of the catalyst since it will controll the orientation of the substituents on the two oxazolines around the metal ion. The design and synthesis of closely related 1,2-*bis*(2-oxazolinyl)benzene ligands are reported.[9] In this article, we reported the synthesis of new chiral naphthylene bisoxazolines.

Chiral C_2-symmetric substituted bisoxazoline ligands containing naphthylene group were designed in present work considering it has a rigid aromatic unit. The synthesis of naphthylene bisoxazoline was attempted following several of the procedures described above. 2,3-Naphthylenedicarbonitrile **3** can be easily prepared from α,α,α′,α′-tetrabromo-*o*-xylene **2** and fumaronitrile.[10] So, 2,3-naphthylenedicarbonitrile reacted with amino alcohol in chlorobenzene with $ZnCl_2$ may be the convenient way to synthesize the target bisoxazoline. In fact, 2,3-naphthylenedicarbonitrile reacted with *R*-phenylglycinol in chlorobenzene with $ZnCl_2$ as catalyst at 130°C do not give the corresponding bisoxazoline, but give the cyclized five-member ring product, *N*- (1′-phenyl-2′-hydroxyethyl)-2,3-naphthylenedicarboximide **1a** in 53% yield. This cyclized product does not like the reaction product of phthalodinitrile and 2-aminoethanol, which give the 1,3-*bis*-(2-hydroxyethylimino)isoindole as the main product.[11] The 2,3-naphthylenedicarboxylic acid **4**, prepared from α,α,α′,α′-tetrabromo-*o*-xylene and maleic anhydride,[12] reacted with thionyl chloride unexpectedly give the 2,3-Naphthalenedicarboxylic acid

cyclic anhydride **5** rather than corresponding 2,3-Naphthalenedicarboxylic acid dichloride. 2,3-Naphthalenedicarboxylic acid cyclic anhydride **5** reacted with *S*-Leucinol give compound **1c** in 89% yield, this route also can not give the target bisoxazoline. Fortunately, ethyl 2,3-naphthylenedicarboxylate 6 reacted with amino alcohol in the absence of solvent give the corresponding hydroxy amide intermediates **7b** and **7c** in 91 and 85% yield. Treatment of hydroxy amides **7b** and **7c** with MsCl and Et_3N also can not give the target bisoxazoline. Hydroxy amide intermediates **7b** and **7c** were treated with $SOCl_2$ to afford the corresponding chloride intermediate **8b** and **8c** in 61.4 and 15.3% yield. Besides **8c** was formed from the reaction of **7c**, mono cyclized oxazoline **10** was also formed in 46.2% yeild. Compounds **8b** and **8c** was cyclized by treated with Et_3N and toluene to give the desired bisoxazoline **9b** and **9c** in 83.3 and 70.3% yield, respectively (Sch. 1). The difficulty in synthesis of this series of bisoxazoline may be ascribed to the intramolecular and intermolear hydrogen bonding of hydroxy amide intermediate. The hydrogen bonding forbidden the enolization and imino formation is difficult, and thus result in the slowly cyclization process.

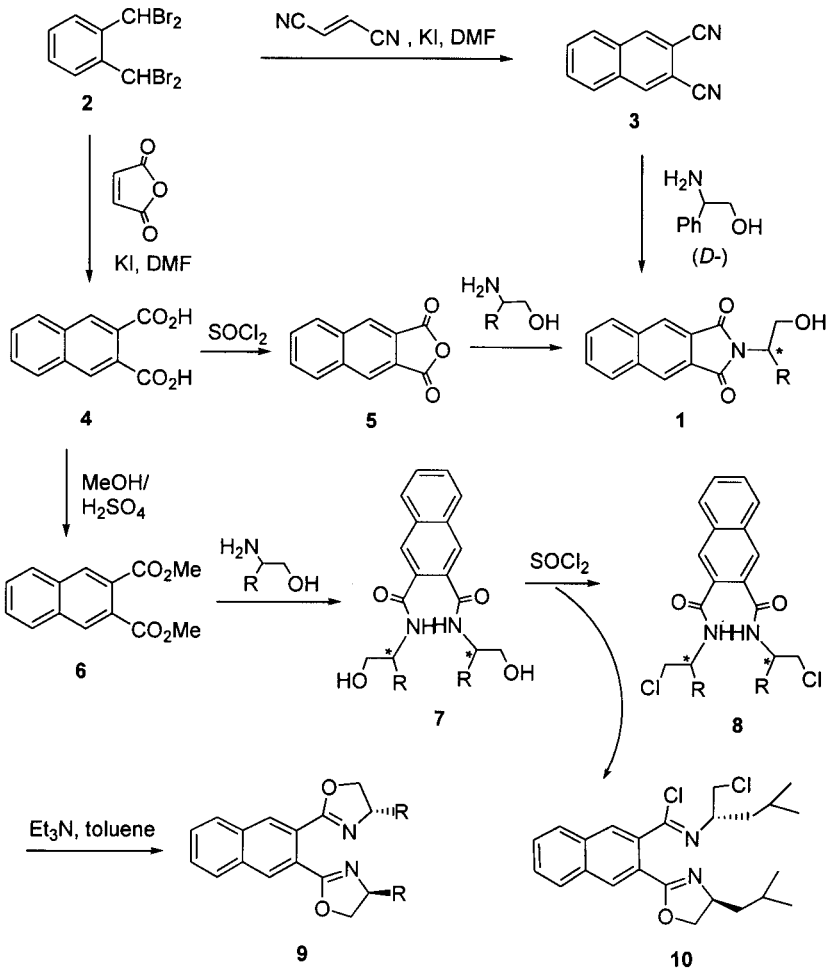
Bisoxazolines have been used as catalysts for the enantioselective synthesis. The application of 2,3-naphthylene bisoxazoline metal complexes as asymmetric catalysts for stereoselective transformations are currently under investigation in our group.

EXPERIMENTAL

Melting points were measured on an XT-4 melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Brucker 400 MHz spectrometer, tetramethylsilane (TMS) serving as internal standard. Infrared spectra were obtained on a Bruker Vector 22 spectrometer. Mass spectra were obtained on a VG-ZAB-HS mass spectrometer. Optical rotations were measured on a Perkin-Elmer 241 MC spectrometer. Elemental analyses were carried out on an Elementar Vario EL instrument. Solvents used were purified and dried by standard procedures.

2,3-Naphthylenedicarbonitrile was prepared from α,α,α′,α′-tetrabromo-*o*-xylene and fumaronitrile according to Lit.[10] 2,3-Naphthylenedicarboxylic acid was prepared from α,α,α′,α′-tetrabromo-*o*-xylene and malic anhydride according to literature procedure.[12]

***N*-[(*R*)-1′-Phenyl-2′-hydroxyethyl]-2,3-naphthylenedicarboximide 1a:** 2,3-naphthylenedicarbonitrile (0.5 g, 2.8 mmol), D-phenylglycinol (0.9 g, 6.6 mmol) and $ZnCl_2$ (0.1 g) in chlorobenzene (30 mL) with heated



a, R = Ph; b, R = *i*-pr; c, R = *i*-Bu

Scheme 1. Synthesis of 2,3-*bis*[(4′s)*R*-oxazolin-2′-yl]napthylene.

at 130°C for 72 h. The solvent was removed under reduced pressure, the residue was treated with water (10 mL) and than extracted with dichloromethane (3 × 20 mL). The layer was separated, and the organic layer was washed with brine and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate–petroleum ether

1:2 v/v) to afford 0.47 g (53%) pure *N*-((*R*)-2-phenylethanol-2-yl)-2,3-naphthylenedicarboximide **1a**. M.p. 154–155°C. $[\alpha]_D^{20} = +50.0^o$ ($c = 0.4$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.18 (1H, s, OH), 4.26 (1H, dd, $J = 4.4$, 16.4 Hz, OCH), 4.77 (1H, dd, $J = 9.8$, 19.4 Hz, CHN), 5.57 (1H, dd, $J = 5.0$, 11.2 Hz, OCH), 7.26–7.37 (3H, m, ArH), 7.50 (2H, d, $J =$ 7.2 Hz, ArH), 7.60–7.64 (2H, m, ArH), 7.89–7.94 (2H, m, ArH), 8.15 (2H, s, ArH). IR (KBr): ν 3453, 3063, 3032, 1762, 1708, 1638, 1515, 1494, 1474, 1455, 1425 cm^{-1}. FABMS: m/z 318 (M + 1, 20), 257 (18), 232 (18), 217 (100). Anal. $C_{20}H_{15}NO_3$, Calcd.: C, 75.70; H, 4.76; N, 4.41; Found: C, 75.53; H, 4.80; N, 4.28.

***N*-[(*S*)-1′-Isobutyl-2′-hydroxyethyl)-2,3-naphthylenedicarboximide 1c:** A solution of 2,3-naphthylenedicarboxylic acid (2.16 g, 10 mmol) and $SOCl_2$ (40 mL) was refluxed for 13 h. The excess $SOCl_2$ was removed under reduced pressure, benzene (10 mL) was added and the solvent was removed again to dryness to afford the 2,3-Naphthalenedicarboxylic acid cyclic anhydride **5** 1.85 g (93.4%). M.p. 248–249°C. ^{1}H NMR ($CDCl_3$): δ 7.82 (2H, dd, $J = 3.2$, 6.2 Hz, ArH), 8.15 (2H, dd, $J = 3.2$, 6.2 Hz, ArH), 8.56 (2H, s, ArH).

To the solution of *S*-leucinol (1.15 g, 9.8 mmol) and Et_3N (3.5 mL) in CH_2Cl_2 (30 mL) was added dropwise a solution of 2,3-naphthalenedicarboxylic acid cyclic anhydride **5** (1.25 g, 6.3 mmol) and stirring at room temperature for 24 h. Then water (50 mL) was added to the reaction vessel and organic phase was separated from reaction mixture. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The organic phase were combined and washed with brine, dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, the crude product was purified by column chromatogrsphy on silica gel (ethyl acetate–methanol 5:2 containing 1% Et_3N) to afford colorless crystals **1c** 1.67g (89%). M.p. 103°C. $[\alpha]_{20}^D = +41.8^o$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.93 (6H, d, $J = 5.6$ Hz, CH_3), 1.10–1.80 (3H, m, CH+CH_2), 3.05–3.20 (1H, m, NCH), 3.38–3.78 (2H, m, CH_2), 4.23 (1H, s, OH), 6.99–7.99 (6H, m, ArH). IR (KBr): ν 3250, 3103, 2957, 2867, 1651, 1627, 1563, 1446, 1313, 1043 cm^{-1}. EIMS: m/z 297 (M^+, 8), 266 (70), 224 (35), 210 (100), 180 (25), 126 (35), 86 (82). HRMS: $C_{18}H_{19}NO_3$, Calcd. 297.13649; Found: 297.13555.

2,3-*Bis*[*N*-(1′*S*)-(1′-isopropyl-2′-hydroxyethyl)-amido]naphthylene 7b: (*S*)-Valinol (1.3 g, 13 mmol) and ethyl 2,3-naphthylenedicarboxylate **6** (1.1 g, 4.4 mmol) were heated at 120°C for 4 h under nitrogen, while generated methanol was removed through a distillation equipment. The crude product was recrystallized from methanol–ethyl acetate to afford colorless solid **7b** 1.6 g (91%). M.p. 215–217°C. $[\alpha]_{20}^D = +37.5^o$ ($c = 0.2$, MeOH). ^{1}H NMR (DMSO): δ 0.94 (12H, d, $J = 6.4$ Hz, CH_3), 1.80–1.98

(2H, m, CH), 3.50 (4H, t, $J = 5.4$ Hz, OCH_2), 3.70–3.80 (2H, m, CH), 4.52 (2H, t, $J = 5.4$ Hz, OH), 7.61 (2H, dd, $J = 3.0$, 6.2 Hz, ArH), 8.01 (2H, dd, $J = 3.2$, 6.2 Hz, ArH), 8.05 (2H, s, ArH), 8.16 (2H, d, $J = 9.0$ Hz, NH). IR (KBr): ν 3308, 2969, 2876, 1650, 1622, 1593, 1537, 1435, 1316, 1032 cm^{-1}. FABMS: m/z 387 (M + 1, 5), 217 (30), 181 (15), 91 (100). Anal. $C_{22}H_{30}N_2O_4$, Calcd.: C, 68.37; H, 7.82; N, 7.25; Found: C, 68.17; H, 7.79; N, 7.21.

2,3-*Bis*[*N*-(1′*S*)-(1′-isobutyl-2′-hydroxyethyl)-amido]naphthylene 7c: Following the same procedure as decribed for **7b**, (*S*)-Leucinol (1.42 g, 12.1 mmol) and ethyl 2,3-naphthylenedicarboxylate **6** (1.4 g, 5.7 mmol) to afford colorless solid **7c** 2.0 g (85%). M.p. 209–210°C. $[\alpha]_{20}^{D} = +11.2^{o}$ (c = 0.6, MeOH); ^{1}H NMR (DMSO): δ 0.91 (12H, dd, $J = 6.6$ Hz, CH_3), 1.31–1.47 (4H, m, CH_2), 1.74–1.84 (2H, m, CH), 3.35–3.53 (4H, m, CH_2), 3.95–4.03 (2H, m, CH), 4.59 (2H, t, $J = 5.8$ Hz, OH), 7.61 (2H, dd, $J = 3.4$, 6.2 Hz, ArH), 7.99 (2H, s, ArH), 8.01 (2H, dd, $J = 3.4$, 6.2 Hz, ArH), 8.12 (2H, d, $J = 8.6$ Hz, NH). IR (KBr): ν 3253, 3103, 2956, 2868, 1650, 1627, 1598, 1567, 1448, 1313, 1044 cm^{-1}. FABMS: m/z 415 (M + 1, 15), 298 (92). Anal. $C_{24}H_{34}N_2O_4$, Calcd.: C, 69.54; H, 8.27; N, 6.76; Found: C, 69.57; H, 8.20; N, 6.78.

2,3-*Bis*[*N*-(1′*S*)-(1′-isopropyl-2′-chloroethyl)-amido]naphthylene 8b: To the suspension of dihydroxy diamide **7b** (0.67 g 1.73 mmol) in the CH_2Cl_2 (20 mL) was added thionyl chloride (1.5 mL, 20 mmol) via syringe. The mixture was kept refluxing for 4 h. The reaction mixture was cooled and poured into the ice-water, the organic phase (CH_2Cl_2) was separated from the mixture. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with 5% $NaHCO_3$ (20 mL), water (20 mL) and brine (20 mL), respectively, dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo to afford the crude product. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether/methanol 5:1:0.2) and recrystallized from ethyl acetate–petroleum ether to afford colorless needles **8b** 0.45 g (61.4%). M.p. 174–176°C. $[\alpha]_{20}^{D} = -89.2^{o}$ (c =0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.05 (6H, d, $J = 4.8$ Hz, $2CH_3$), 1.08 (6H, d, $J = 4.8$ Hz, $2CH_3$), 2.00–2.17 (2H, m, CH), 3.76–3.91 (4H, m, CH_2Cl), 4.12–4.25 (2H, m, CHN), 7.03 (2H, d, $J = 8.8$ Hz, NH), 7.60 (2H, dd, $J = 3.2$, 6.4 Hz, ArH), 7.90 (2H, dd, $J = 3.4$, 6.2 Hz, ArH), 8.15 (2H, s, ArH). IR (KBr): ν 3263, 3056, 2963, 2874, 1639, 1552, 1464, 1316, 1205 cm^{-1}. FABMS: m/z 423 (M + 1, 10), 387 (5), 302 (90), 198 (100). Anal. $C_{22}H_{28}N_2O_2Cl_2$, Calcd.: C, 62.41; H, 6.67; N, 6.62; Found: C, 62.68; H, 6.69; N, 6.61.

2,3-*Bis*[*N*-(1′*S*)-(1′-isobutyl-2′-chloroethyl)-amido]naphthylene 8c: Dihydroxy diamide **7c** (1.1 g 2.6 mmol) and thionyl chloride (2.3 mL,

30.7 mmol) was was treated with procedure as decribed for **8b**. The crude product was purified by column chromatography on silica gel, first eluting with ethyl acetate/petroleum ether (v/v 1:15) to give the product **10** 0.52 g (46.2%). Followed by eluting with ethyl acetate/petroleum ether (v/v 1:6) to afford the colorless plates **8c** 0.18 g (15.3%). M.p. 169–171°C. $[\alpha]_{20}^{D} = -98.3^{o}$ ($c = 0.12$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.00 (6H, d, $J =$ 6.4 Hz, $2CH_3$), 1.01 (6H, d, $J = 6.2$ Hz, $2CH_3$), 1.55–1.64 (4H, m, CH_2), 1.70–1.76 (2H, m, Me_2CH), 3.71 (2H, dd, $J = 3.2$, 11.0 Hz, CH_2Cl), 3.92 (2H, dd, $J = 4.0$, 11.0 Hz, CH_2Cl), 4.48–4.60 (2H, m, CHN), 6.89 (2H, d, $J = 8.2$ Hz, NH), 7.61 (2H, dd, $J = 3.2$, 6.2 Hz, ArH), 7.91 (2H, dd, $J = 3.2$, 6.2 Hz, ArH), 8.13 (2H, s, ArH). IR (KBr): ν 3273, 3065, 2955, 2857, 1642, 1551, 1464, 1312, 1207 cm^{-1}. FABMS: m/z 451 (M + 1, 16), 415 (9), 316 (100), 198 (100). Anal. $C_{24}H_{32}N_2O_2Cl_2$, Calcd.: C, 63.85; H, 7.14; N, 6.21; Found: C, 63.58; H, 7.08; N, 6.20.

Compound 10: M.p. 120–122°C. $[\alpha]_{20}^{D} = -41.6^{o}$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.97 (12H, t, $J = 6.4$ Hz, $4CH_3$), 1.47–1.71 (6H, m, Me_2CH+CH_2), 3.57–3.73 (4H, m, $OCH_2 + CH_2Cl$), 4.37–4.49 (2H, m, CHN), 7.62 (2H, dd, $J = 3.2$, 6.2 Hz, ArH), 8.00 (2H, dd, $J = 3.2$, 6.4 Hz, ArH), 8.46 (2H, s, ArH). ^{13}C NMR ($CDCl_3$): δ 21.81, 23.47, 25.11, 43.12, 48.93, 57.52, 115.99, 123.39, 128.22, 129.35, 135.15. IR (KBr): ν 3065, 2956, 2871, 1735, 1681, 1613, 1509, 1467, 1366, 1271, 937 cm^{-1}. FABMS: m/z 433 (M+1, 34), 332 (21), 315 (100), 197 (100). Anal. $C_{24}H_{30}N_2OCl_2$, Calcd.: C, 66.51; H, 6.98; N, 6.46; Found: C, 66.52; H, 6.88; N, 6.48.

2,3-*Bis*[(4′*S*)-isopropyloxazolin-2′-yl]naphthylene 9b: A 100 mL round-bottom flask with a magnetic stir bar was charged with compound **8b** (277 mg, 0.65 mmol) and Et_3N (0.92 mL, 6.6 mmol) and toluene (25 mL). The solution was stirred under reflux for 12 h. After cooling to room temperature, ethyl acetate (50 mL) was added and the resulting mixture was washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. Purification of the residue by column chromatography on silica gel (ethyl acetate–petroleum ether 1:3) to afford the pure oily product **9b** 0.19 g (83.3%). $[\alpha]_{20}^{D} = -38.7^{o}$ ($c = 0.68$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.99 (6H, d, $J = 6.8$ Hz, $2CH_3$), 1.08 (6H, d, $J = 6.2$ Hz, $2CH_3$), 1.80–2.02 (2H, m, CH), 4.06–4.20 (4H, m, CH_2O), 4.42 (2H, t, $J = 12.8$ Hz, CHN), 7.52 (2H, m, ArH), 7.86–7.90 (2H, m, ArH), 8.29 (2H, s, ArH). IR (KBr): ν 3057, 2959, 2874, 1734, 1656, 1597, 1469, 1347, 1087, 973 cm^{-1}. HRFABMS: $C_{22}H_{27}N_2O_2$, Calcd.: 351.2067; Found: 351.2064.

2,3-*Bis*[(4′*S*)-isobutyloxazolin-2′-yl]naphthylene 9c: Compound **8c** (85 mg, 0.19 mmol) and Et_3N (0.26 mL, 1.9 mmol) was treated with procedure as decribed for **9b**. The crude product was purified by column

chromatography on silica gel (ethyl acetate/petroleum ether 1:6) to give the oily **9c** 50 mg (70.3%). $[\alpha]_{20}^{D} = -16.5^{o}$ ($c = 0.2$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.00 (12H, t, $J = 6.2$ Hz, $4CH_3$), 1.20–1.70 (4H, m, CH_2), 1.70–1.94 (2H, m, Me_2CH), 3.90–4.42 (4H, m, CH_2O), 4.45–4.57 (2H, m, CHN), 7.56 (2H, dd, $J = 3.4$, 6.4 Hz, ArH), 7.88 (2H, dd, $J = 3.4$, 6.4 Hz, ArH), 8.27 (2H, s, ArH). IR (KBr): ν 3055, 2961, 2873, 1733, 1638, 1558, 1460, 1375, 1282 cm^{-1}. HREIMS: $C_{24}H_{30}N_2O_2$, Calcd.: 378.2307; Found: 378.2292.

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