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Catalytic asymmetric synthesis of glycidic amides via chiral sulfur ylides

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Abstract

Reaction of diazoacetamides with aromatic aldehydes in the presence of 20 mol% of chiral binaphthylsulfide and 10 mol% of copper(II) acetylacetonate gave chiral glycidic amides with up to 64% ee. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Chiral glycidic acid derivatives have received much attention as valuable chiral building blocks for several drugs and natural products. For instance, they have been employed in the synthesis of Diltiazem **1** and the side chain of Taxol **2** (Fig. 1).[1] Although many synthetic methods for chiral epoxides have been developed, reports on asymmetric syntheses of chiral glycidic acid derivatives are rare and further investigation is needed. Industrial synthesis of methyl (2*R*,3*S*)-3-(4-methoxyphenyl)glycidate **3** has thus relied on the enzymatic resolution of its racemates.[2] One of the most efficient syntheses of chiral glycidic acid derivatives developed so far is the asymmetric epoxidation of cinnamates with a chiral manganase–salen complex as a catalyst.[1a,b] Although excellent enantioselectivities have been achieved, it requires poorly accessible *cis*-cinnamates as starting materials. As a more direct approach, an asymmetric Darzens reaction using a chiral external ligand has been reported by Koga.[1c] However, a stoichiometric amount of expensive chiral ligand and low temperature (−100°C) are necessary to induce high enantioselectivities. In the search for a more efficient and practical synthesis of chiral glycidic acid derivatives, we envisioned the possible use of the catalytic sulfur ylide reaction.[3] In this report, we describe the first catalytic asymmetric synthesis of glycidic amides via the reaction of aromatic aldehydes with chiral sulfur ylides, which are generated in situ from diazoacetamides in the presence of catalytic amounts of chiral binaphthylsulfide and copper(II) acetylacetonate (Scheme 1).

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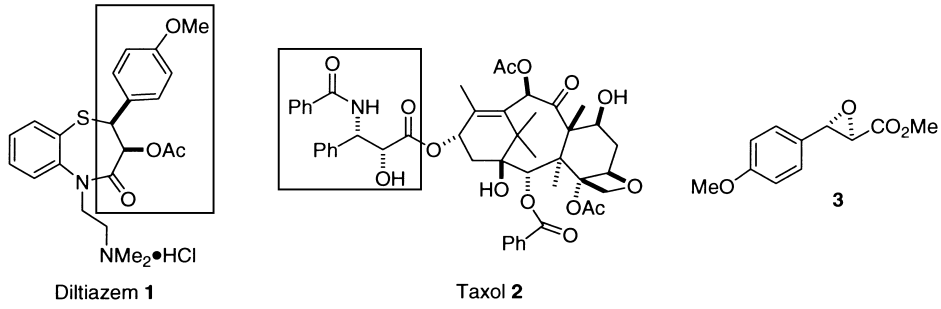
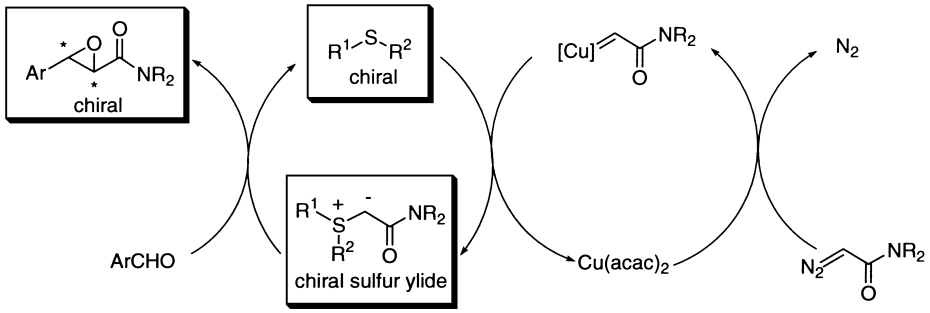


Figure 1.

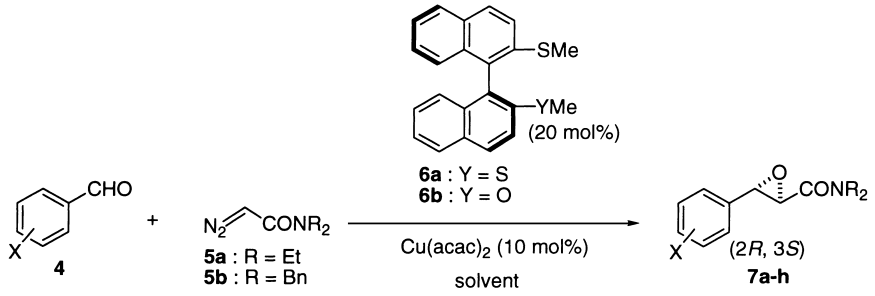


Scheme 1.

2. Results and discussion

The diazoacetamides **5a**,**b** were easily prepared by diazotization of the corresponding glycinamides using the same procedure as for the preparation of ethyl diazoacetate.[4] They were stable enough to be purified by silica gel column chromatography and could be stored in a refrigerator for several weeks without decomposition. For chiral sulfides, binaphthalene type sulfides **6a**,**b**[5] were selected because of their ready accessibility in enantiomerically pure form and ease of optimization. C_2-Symmetric (*S*)-2,2′-bis(methylthio)-1,1′-binaphthalene **6a** was first examined for the epoxidation of *p*-anisaldehyde. The addition of *N*,*N*-diethyl diazoacetamide **5a** to the mixture of *p*-anisaldehyde **6a** (20 mol%) and $Cu(acac)_2$ (10 mol%) in CH_2Cl_2 at ambient temperature gave the desired chiral glycidic amide **7a** in 30% yield and 32% ee exclusively as a *trans* form (Table 1, entry 1). The absolute configuration of the major enantiomer of **7a** was determined by comparison with the authentic sample prepared via amidation of methyl (2*S*,3*R*)-3-(4-methoxyphenyl)glycidate.[6] The use of $Rh_2(OAc)_4$ instead of $Cu(acac)_2$ as a metal catalyst gave a trace of **7a**. The enantioselectivity was dramatically improved by the use of (*S*)-2′-methoxy-2-methylthio-1,1′-binaphthalene **6b** to afford **7a** in 18% yield and 60% ee (entry 2). To improve the yield, the reaction was conducted in acetonitrile at higher temperature.[7] However, improvement of the yield was not observed; instead a lower enantioselectivity was obtained (entry 3). The reaction of benzaldehyde with **5a** also gave chiral glycidic amide **4c** in a low yield (entry 4). The poor yields of **7a**,**b** might be attributed to the poor electrophilicity of the aldehydes. More electrophilic 4-(trifluoromethanesulfonyloxy)benzaldehyde, 4-bromobenzaldehyde and 2-fluorobenzaldehyde with an electron-withdrawing group gave **7c**–**e** in better yields (entries 5, 6, 7). Interestingly, the use of *N*,*N*-dibenzyl diazoacetamide **5b** instead of the *N*,*N*-diethyl counterpart **5a** afforded the corresponding chiral glycidic amide **7f** in a higher yield (54%, entry 8 vs. 41%, entry 7). Moreover, the reaction of **5b** with more electrophilic 2,6-difluorobenzaldehyde gave a good yield and a moderate enantioselectivity (71% yield, 46% ee, entry 9). In order to improve the yield of **7a**, a key intermediate of Diltiazem, we thus

Table 1



Entry[a]	X	Diazoacetamide	Sulfide	Solvent	Product	Yield (%)[b]	ee (%)[c]
1	4-OMe	**5a**	**6a**	CH_2Cl_2	**7a**	30	32
2	4-OMe	**5a**	**6b**	CH_2Cl_2	**7a**	18	60
3	4-OMe	**5a**	**6b**	CH_3CN	**7a**	19	53
4	H	**5a**	**6b**	CH_2Cl_2	**7b**	22	48
5	4-OTf	**5a**	**6b**	CH_2Cl_2	**7c**	34	34
6	4-Br	**5a**	**6b**	CH_2Cl_2	**7d**	43	38
7	2-F	**5a**	**6b**	CH_2Cl_2	**7e**	41	38
8	2-F	**5b**	**6b**	CH_2Cl_2	**7f**	54	39
9	2,6-F	**5b**	**6b**	CH_2Cl_2	**7g**	71	46
10	2-Cl, 4-OMe	**5b**	**6b**	CH_2Cl_2	**7h**	38	44
11	3-Cl, 4-OMe	**5b**	**6b**	CH_2Cl_2	**7i**	25	64 (99)[d]

[a]The reactions were conducted according to the general procedure as described in the text, except for Entry 3, where CH_3CN was employed as a solvent, diazoacetamide was added over 3 h at 60°C under N_2 atmosphere, and the reaction mixture was stirred for 1 h. [b]Isolated yield after silica gel column chromatography. [c]Determined by chiral HPLC (Chiralcel OD, *n*-hexane : *i*-PrOH = 10 : 1, 220 nm, 40°C). [d]The ee value of the product which was recrystallized from *i*-PrOH.

carried out the reaction of 2- or 3-chloro-4-methoxybenzaldehyde with *N*,*N*-dibenzyl diazoacetamide **5b** using catalyst **6b** (entries 10, 11). In both cases, yields better than that given in entry 2 were obtained, as expected. When 3-chloro-4-methoxybenzaldehyde was employed, the enantioselectivity was improved up to 64% ee. Moreover, the ee of the product could be increased to 99% ee by a single recrystallization from *i*-PrOH (entry 11).

As described above, the first asymmetric synthesis of chiral glycidic amides via chiral sulfur ylides was accomplished. The reactions of electron-deficient aldehydes with *N*,*N*-dibenzyl diazoacetamide were found to give high yields of glycidic amide **7**. The enantioselectivities of the reactions were greatly enhanced by the use of mono sulfide **6b** compared to C_2-symmetric bis-sulfide **6a**. Although the enantioselectivities were still moderate, the short route (a single step from the commercially available aromatic aldehyde), ready accessibility of the diazoacetamides, and the chiral binaphthyl sulfides might make this process more advantageous than previously reported methods. Further improvements of the enantioselectivities and considerations of the reaction mechanism are now under investigation.

3. Experimental

Melting points were measured using Büchi melting point apparatus (B-540) and are uncorrected. Optical rotations were measured on a Perkin–Elmer 243 automatic polarimeter. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200 (200 MHz) spectrometer with TMS as an internal standard. IR spectra were recorded on a Perkin–Elmer 1640 spectrophotometer. Mass spectra were obtained on a Hitachi M-2000A double-focusing mass spectrometer and on a Finnigan Mat LCQ. Elemental analyses were measured on a Perkin–Elmer 2400 microanalyzer. Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh, E. Merck).

3.1. N,N-*Diethyl diazoacetamide* ***5a***[4]

A solution of ethyl glycinate hydrochloride (10.0 g, 60.0 mmol) in 14 ml of water was mixed with 36 ml of CH_2Cl_2 and was cooled to −10°C under nitrogen atmosphere. To the biphasic solution was added an ice-cold solution of sodium nitrite (4.97 g, 72 mmol) in 14 ml of water, and then 5% sulfuric acid (5.2 g) was added dropwise below 0°C. The reaction mixture was stirred for 20 minutes below 0°C and extracted with CH_2Cl_2. The extracts were washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by silica gel column chromatography (hexane:AcOEt=4:1) to give **5a** (2.65 g, 31%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.15 (t, *J*=7.2 Hz, 6H), 3.26 (br, 4H), 4.93 (s, 1H); IR (film) 3040, 2977, 2910, 2105, 1640, 1608 cm^{-1}; MS (EI) *m/z* 141 (M^+).

3.2. N,N-*Dibenzyl diazoacetamide* ***5b***[4]

A solution of benzyl glycinate hydrochloride (4.0 g, 13.8 mmol) in 40 ml of water was mixed with 80 ml of CH_2Cl_2 and was cooled to 0°C under nitrogen atmosphere. To the biphasic solution was added an ice-cold solution of sodium nitrite (1.24 g, 17.9 mmol) in 4 ml of water, and then 5% sulfuric acid (1.45 g) was added dropwise at 0°C. The reaction mixture was stirred at rt for 30 minutes and extracted with CH_2Cl_2. The extracts were washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by silica gel column chromatography (hexane:AcOEt=10:1→4:1) to give **5b** (3.45 g, 95%) as a yellow syrup. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.50 (br, 4H), 4.97 (s, 1H), 7.20–7.40 (m, 10H); IR (film) 3440, 3100, 3065, 3024, 2905, 2106, 1609 cm^{-1}; MS (SIMS) *m/z* 266 ($[M+H]^+$).

3.3. (S)-2,2′-*Bis(methylthio)-1,1′-binaphthalene* ***6a***

The compound **6a** was prepared according to the literature.[5b] Mp 202°C [lit.[5b] mp 184–185°C]; $[\alpha]_{436}^{25}$ −43.9 (*c* 1.01, $CHCl_3$) [lit.[5b] (*R*)-form, $[\alpha]_{436}^{25}$ +39.2 (*c* 1, $CHCl_3$)]; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.44 (s, 3H), 7.00 (d, *J*=8.4 Hz, 1H), 7.25 (dt, *J*=1.4, 8.3 Hz, 1H), 7.40 (dt, *J*=1.3, 8.1 Hz, 1H), 7.59 (d, *J*=8.8 Hz, 1H), 7.89 (d, *J*=8.1 Hz, 1H), 7.99 (d, *J*=8.8 Hz, 1H); IR (KBr) 3450, 3040, 2989, 2902, 1617, 1581, 1552, 1500, 1423 cm^{-1}; MS (EI) *m/z* 346 (M^+). Anal. calcd for $C_{22}H_{18}S_2$: C, 76.26; H, 5.14. Found: C, 75.64; H, 5.14.

3.4. (S)-2′-Methoxy-2-methylthio-1,1′-binaphthalene **6b**

The compound **6b** was prepared according to the literature.[5c] Mp 173–174°C; $[\alpha]_D^{25}$ −13.3 (*c* 1.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.38 (s, 3H), 3.76 (s, 3H), 6.99 (d, *J*=8.4 Hz, 1H), 7.10 (d, *J*=8.4 Hz, 1H), 7.17–7.37 (m, 4H), 7.44 (d, *J*=9.0 Hz, 1H), 7.57 (d, *J*=8.7 Hz, 1H), 7.86 (d, *J*=7.7 Hz, 2H), 7.93 (d, *J*=8.7 Hz, 1H), 8.00 (d, *J*=9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 15.9, 56.8, 114.0, 120.9, 123.4, 123.7, 124.8, 125.3, 126.5, 126.7, 128.0, 128.1, 128.3, 129.2, 130.0, 131.3, 131.5, 133.2, 133.4, 136.3, 154.9; IR (KBr) 3030, 2975, 2950, 2920, 2900, 2820, 1618, 1592, 1576, 1552 cm^{-1}; MS (EI) *m/z* 330 (M^+). Anal. calcd for $C_{22}H_{18}OS$: C, 79.96; H, 5.49. Found: C, 78.83; H, 5.16.

3.5. Preparation of the authentic sample of (2R,3S)-N,N-diethyl 3-(4-methoxyphenyl)glycidamide **7a**

To a solution of (2*R*,3*S*)-*N*-ethyl 3-(4-methoxyphenyl)glycidamide[6] (100 mg, 0.452 mmol) in 1 ml of DMF was added NaH (62.5% in oil, 19 mg, 0.458 mmol) at 0°C, and the mixture was stirred for 30 minutes. Iodoethane (155 μl, 0.904 mmol) was then added, and the mixture was stirred at 0°C for 30 minutes. The reaction was quenched by adding saturated aqueous NH_4Cl, and the mixture was extracted with diethyl ether. The ethereal layer was washed with brine and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by silica gel column chromatography (hexane:AcOEt=2:1) to give **7a** as a colorless oil (69 mg, 61%), which was solidified in a freezer. Recrystallization of the solid from hexane–diethyl ether gave a pure sample as colorless crystals. Mp 55°C; $[\alpha]_D^{23}$ −103 (*c* 1.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.3–1.25 (m, 6H), 3.38–3.57 (m, 4H), 3.58 (d, *J*=1.9 Hz, 1H), 3.82 (s, 3H), 4.04 (d, *J*=1.9 Hz, 1H), 6.90 (d, *J*=8.8 Hz, 2H), 7.25 (d, *J*=8.8 Hz, 2H); IR (KBr) 2973, 2920, 1650, 1608, 1581, 1517 cm^{-1}; MS (EI) *m/z* 249 (M^+). Anal. calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.38; N, 5.50. Found: C, 67.45; H, 7.68; N, 5.62.

3.6. Typical procedure of asymmetric epoxidation of arylaldehydes via chiral sulfur ylide: (2R,3S)-N,N-diethyl 3-(4-methoxyphenyl)glycidamide **7a**

Diazoacetamide **5a** (212 mg, 1.5 mmol) in 0.5 ml of CH_2Cl_2 was added to the solution of *p*-anisaldehyde (136 mg, 1 mmol), chiral sulfide **6b** (66 mg, 0.2 mmol, 20 mol%) and $Cu(acac)_2$ (26 mg, 0.1 mmol) in 0.5 ml of CH_2Cl_2 at rt over 5 h under a nitrogen atmosphere. After stirring the mixture for 3 days, the mixture was evaporated and the residue was purified by silica gel column chromatography to give the epoxide **7a** (46 mg, 18% yield, 60% ee) and the sulfide **6b** (50 mg, 76% recovery). The epoxide **7a** prepared by this procedure had ^{1}H NMR, IR and mass spectra in good agreement with the authentic sample. The ee of the epoxide **7a** prepared by this method was determined by chiral HPLC (Chiralcel OD, hexane:*i*-PrOH=10:1, 220 nm, 40°C). The absolute configuration of the main enantiomer was assigned by comparing the retention time in HPLC with that of the authentic sample of (2*R*,3*S*)-**7a**.

3.6.1. (2R,3S)-N,N-Diethyl 3-phenylglycidamide **7b**

22% yield, 48% ee. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.14–1.25 (m, 6H), 3.39–3.55 (m, 4H), 3.59 (d, *J*=1.9 Hz, 1H), 4.10 (d, *J*=2.2 Hz, 1H), 7.30–7.37 (m, 5H); IR (film) 3025, 2976, 2920, 2860, 1654, 1590, 1476, 1465, 1400 cm^{-1}; MS (EI) *m/z* 219 (M^+).

*3.6.2. (2*R,*3*S*)*-N,N-*Diethyl 3-(4-trifluoromethanesulfonyloxyphenyl)glycidamide* ***7c***

34% yield, 34% ee. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.11–1.27 (m, 6H), 3.46 (q, *J*=7.3 Hz, 4H), 3.54 (d, *J*=1.9 Hz, 1H), 4.16 (d, *J*=1.9 Hz, 1H), 7.29 (d, *J*=9.5 Hz, 2H), 7.43 (d, *J*=8.8 Hz, 2H); IR (film) 3050, 2978, 2915, 1656, 1595, 1495, 1477, 1457, 1445, 1425 cm^{-1}; MS (EI) *m/z* 367 (M^+).

*3.6.3. (2*R,*3*S*)*-N,N-*Diethyl 3-(4-bromophenyl)glycidamide* ***7d***

43% yield, 38% ee. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.12–1.28 (m, 6H), 3.39–3.51 (m, 4H), 3.53 (d, *J*=1.9 Hz, 1H), 4.06 (d, *J*=1.8 Hz, 1H), 7.21 (d, *J*=8.5 Hz, 2H), 7.50 (d, *J*=8.5 Hz, 2H); IR (KBr) 2970, 2925, 1650, 1485, 1465, 1444, 1431, 1419 cm^{-1}; MS (EI) *m/z* 299 (M^+, ^{81}Br), 297 (M^+, ^{79}Br).

*3.6.4. (2*R,*3*S*)*-N,N-*Diethyl 3-(2-fluorophenyl)glycidamide* ***7e***

41% yield, 38% ee. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.14–1.27 (m, 6H), 3.32–3.57 (m, 4H), 3.61 (d, *J*=2.0 Hz, 1H), 4.32 (d, *J*=1.8 Hz, 1H), 7.03–7.20 (m, 2H), 7.25–7.38 (m, 2H); IR (film) 2977, 2920, 2860, 1656, 1610, 1581, 1485, 1459, 1402 cm^{-1}; MS (EI) *m/z* 237 (M^+).

*3.6.5. (2*R,*3*S*)*-N,N-*Dibenzyl 3-(2-fluorophenyl)glycidamide* ***7f***

54% yield, 39% ee. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.71 (d, *J*=1.9 Hz, 1H), 4.40 (d, *J*=1.8 Hz, 1H), 4.56 (s, 2H), 4.65 (s, 2H), 6.98–7.39 (m, 14H); IR (film) 3075, 3050, 3020, 1662, 1614, 1501, 1582, 1496, 1467, 1453, 1400 cm^{-1}; MS (EI) *m/z* 361 (M^+).

*3.6.6. (2*R,*3*S*)*-N,N-*Dibenzyl 3-(2,6-difluorophenyl)glycidamide* ***7g***

71% yield, 46% ee. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.27 (d, *J*=2.2 Hz, 1H), 4.32 (d, *J*=2.2 Hz, 1H), 4.66 (m, 4H), 3.85 (t, *J*=8.3 Hz, 2H), 7.18–7.39 (m, 11H); IR (film) 3040, 3031, 2900, 1664, 1620, 1580, 1488, 1471, 1444, 1400 cm^{-1}; MS (EI) *m/z* 379 (M^+).

*3.6.7. (2*R,*3*S*)*-N,N-*Dibenzyl 3-(2-chloro-4-methoxyphenyl)glycidamide* ***7h***

38% yield, 44% ee. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.56 (d, *J*=2.0 Hz, 1H), 3.78 (s, 3H), 4.44 (d, *J*=1.9 Hz, 1H), 4.53–4.60 (m, 3H), 4.73 (d, *J*=14.8 Hz, 1H), 6.76 (dd, *J*=2.5, 8.6 Hz, 1H), 6.89 (d, *J*=2.5 Hz, 1H), 7.10–7.39 (m, 11H); IR (KBr) 1662, 1598 cm^{-1}; MS (SIMS) *m/z* 408 ($[M+H]^+$).

*3.6.8. (2*R,*3*S*)*-N,N-*Dibenzyl 3-(3-chloro-4-methoxyphenyl)glycidamide* ***7i***

25% yield, 64% ee. Recrystallization of the 64% ee product from *i*-PrOH provided **7i** having 99% ee. mp 125°C; $[\alpha]_D^{23}$ −62.0 (*c* 1.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.62 (d, *J*=1.9 Hz, 1H), 3.88 (s, 3H), 4.02 (d, *J*=1.9 Hz, 1H), 4.54–4.63 (m, 3H), 4.74 (d, *J*=14.6 Hz, 1H), 6.84 (d, *J*=8.4 Hz, 1H), 7.03–7.32 (m, 12H); IR (KBr) 1661 cm^{-1}; MS (ESI) *m/z* 408 ($[M+H]^+$). Anal. calcd for $C_{24}H_{22}ClNO_3$: C, 70.67; H, 5.44; N, 3.43. Found: C, 70.50; H, 5.39; N, 3.25.

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