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Novel Concise Synthesis of (–)-Clausenamide†

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A six-step synthesis of (–)-clausenamide is described. Optically pure (*R*,*E*)-1,3-diphenylallylic alcohol was acetylated and then subjected to an Ireland-Claisen rearrangement, giving the *γ*,*δ*-unsaturated acid, which underwent a substrate-induced stereoselective bromolactonization to afford the expected all-equatorial substituted bromo-*δ*-lactone. An unusual chemo-selective aminolysis of the lactone resulted in the formation of a *γ*,*δ*-epoxy-amide in stereospecific manner. Base-promoted cyclization of this intermediate and the subsequent Davis oxidation furnished the synthesis, delivering the final product in ＞99% *ee* and up to 34% overall yield.

Keywords (–)-clausenamide, diastereoselective synthesis, Ireland-Claisen rearrangement, diastereoselective bromolactonization, bromo-*δ*-lactone aminolysis

Introduction

Clausenalansium (*Lour*) skeels, also named *Wampee*, is a species of fruit tree commonly grown in southern China. It has been known to local people for centuries that aqueous extract from the leaves of *Wampee* is a useful folk medicine to ease jaundice (or icterus), a symptom often related to liver disorders. Phytochemical study on the species was first carried out in our laboratory in the 1980s, resulting in the identification of several novel biosynthetically related amide natural products **1**—**5** (Figure 1).[1] Whereas most of the isolated compounds indeed showed considerable hepatoprotective effects *in vitro*,[2] racemic clausenamide (±)-**1** was of additional interest due to its remarkable learning and memory enhancive effects. With four chiral centers in clausenamide, it is not surprising that the two enantiomers were found to display different biological activities in later studies.[3] (–)-Clausenamide, of which the configuration was determined to be 3*S*,4*R*,5*R*,6*S*, was able to exert significant neuroprotective effect against *β*-amyloid in cellular models and potentiate synaptic transmission in the dentate gyrus of rats, while its (＋)-enantiomer proved to be ineffective. Presently, (–)-**1** is under human clinical trial in China for its potential in the treatment of Alzheimer's disease.

Ironically, clausenamide is racemic in nature,[1] hence the access to its (–)-enantiomer is solely dependent on chemical synthesis. Shortly after Hartwig's contribution to the first total synthesis of (±)-**1** and its (＋)-enantiomer in 1987,[4] we developed a significantly shorter biomimetic approach to the racemate (Scheme 1).[5] The high efficiency of our synthesis owes to a base-promoted cyclization of 2,3-epoxy-cinnamic amide **6** to give clausenamidone **7**, which was then stereoselectively reduced to produce (±)-**1**. Currently, pilot scale preparation of (–)-**1** is carried out in our laboratory through optical resolution of **7**. In addition to our progress, other groups[6-10] also accomplished elegant asymmetric syntheses of (–)- or (＋)-**1**. As a continuation of our endeavor to develop more efficient synthesis of clausenamide-type compounds,[11] we report herein a recently finished concise synthesis of (–)-**1**.

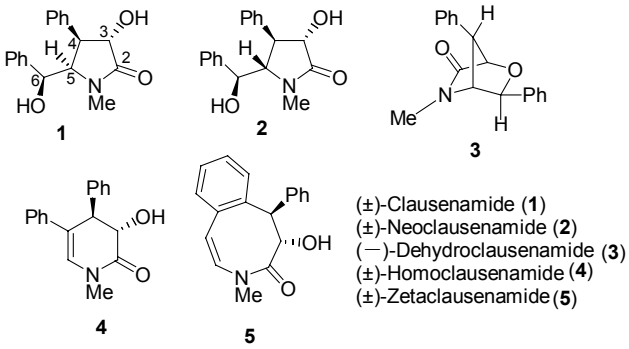

Figure 1 Structures of clausenamide and its biosynthetic relatives.

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† Dedicated to Professor Guoqiang Lin on the occasion of his 70th birthday.

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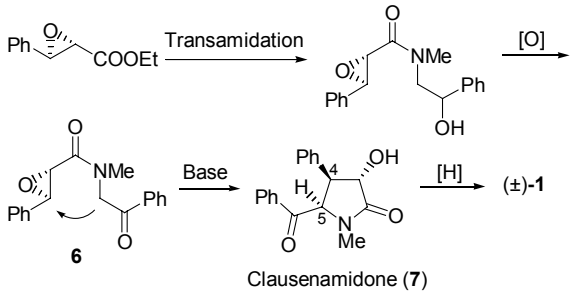
Results and Discussion

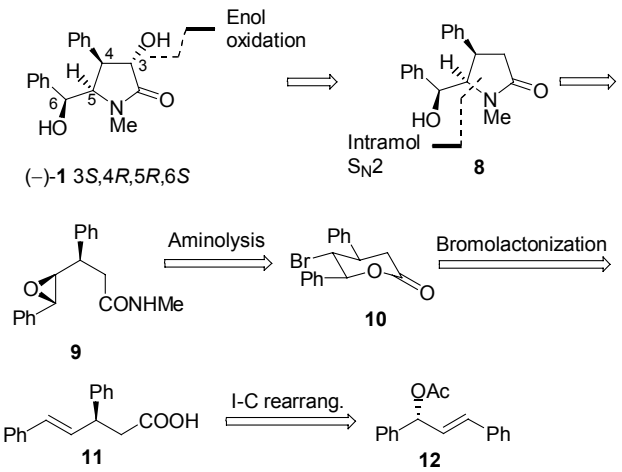
As aforementioned, (−)-**1** has been synthesized using a variety of asymmetric approaches, and (−)-clausenamidone ((−)-**7**, Scheme 1) was frequently involved as the key precursor for the final product. A notable defect of this intermediate, however, is the presence of an enolizable proton at C^5 that could inevitably lead to partial epimerization, forming its 4,5-*trans* diastereomer.[5] For this reason, asymmetric synthesis of (−)-**1** without involving the intermediacy of **7**, given its step- and cost-efficiency comparable to previous works, is highly desirable.

Scheme 1 Previously reported biomimetic synthesis of clausenamide[5]



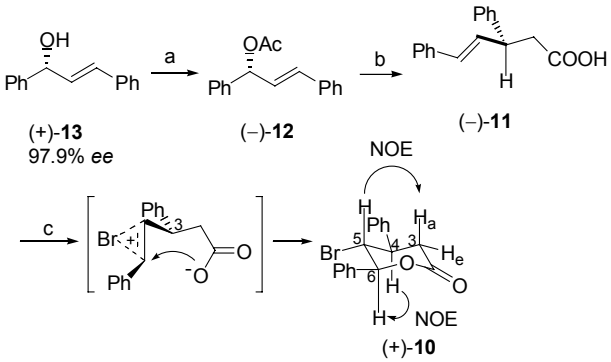
Our retro-synthetic analysis of (−)-**1** (Scheme 2) started with detaching of the C^3-OH based on the known oxidation of **8**[4] and its isomer[11] in their lithium enolate forms. An amide-nitrogen participated intramolecular S_N2 epoxide ring-opening of **9**[12] was then projected to bring up the *γ*-lactam framework. Further deduction from *γ*,*δ*-epoxy-amide (**9**) clearly suggested the intermediacy of acid **11**. However, concerns on the industrial feasibility of this synthetic route precluded us from using modern asymmetric epoxidation techniques to synthesize compound **9**. Alternatively, we assumed an unusual aminolysis of *δ*-lactone **10** that would plausibly lead to the *in situ* installation of the epoxide function along with the formation of *N*-methyl amide moiety in compound **9**. The lactone **10** in turn is possibly achievable by a substrate-induced bromolactonization of acid **11**.[13] Foreseeably, the asymmetric synthesis of chiral acid **11** should be easy, because Ireland-Claisen rearrangement of **12** is known to give the compound in high yield,[14] though in racemic form; while optically pure (*R*,*E*)-1,3-diphenyl-allylic alcohol, the close equivalent to **12**, has been synthesized using several different protocols.[15]

Scheme 2 Retro-synthesis of (−)-clausenamide



According to the synthetic plan, (*R*,*E*)-1,3-diphenyl-allylic alcohol (+)-**13** (Scheme 3, 97.9% *ee* based on HPLC) was prepared through the known kinetic resolution of (±)-**13**[15a] under standard Sharpless asymmetric epoxidation conditions, and then converted into *R*-configured (−)-**12** in 92% yield with acetic anhydride in the presence of pyridine. The subsequent Ireland-Claisen rearrangement of (−)-**12** was effected by applying excessive LDA (3.0 equiv.) and TMSCl (2.5 equiv.) as previously described[14] to give *S*-configured (−)-**11** in 85% yield. The coupling constant of the two olefin protons (J = 16.0 Hz) confirmed the formation of *trans*-isomer.

Scheme 3 Synthesis and bromolactonization of (−)-**11**

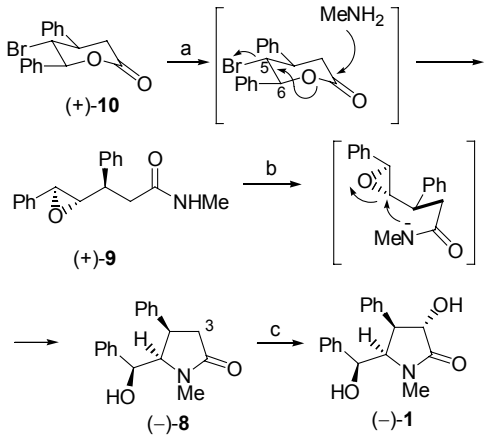


Reagents and conditions: (a) Ac_2O, pyridine, DMAP, r.t., 92%; (b) LDA, TMSCl, THF, −78 °C, 85%; (c) NBS, 4 Å MS, CH_2Cl_2, r.t., 79%.

With (−)-**11** in hand, we were ready to examine its stereochemical behavior in the bromolactonization step. Formation of lactone **10** with all-equatorial substitutions is theoretically predicted on considering the allylic strain governed conformational bias of the substrate, which keeps the C^3-H co-planar to the C=C double bond. Delightfully, our experimental results turned out to be consistent with this prediction, and (+)-**10** was produced in 79% yield without detecting other isomers when (−)-**11** was treated with NBS in the presence of grounded 4 Å molecular sieves. The stereochemistry of (+)-**10** was assigned on the basis of the following NMR studies. Vicinal coupling constant $J_{4,5}$ (10.0 Hz) and $J_{5,6}$ (10.4 Hz) suggested all the three protons at 4-, 5-, and 6-positions are in axial orientations in this chair-like six-membered cyclic molecule. The coupling constants of two 3-Hs with 4-H ($J_{3a,4}$ = 9.6 Hz and $J_{3e,4}$ = 6.4 Hz), as well as the strong NOE observed between 4-H and 6-H, also confirmed the axial 4-H.

Successful establishment of the expected stereochemistry in compound (+)-**10** provided the entrance to **9**. Apparently, there are two electrophilic sites in (+)-**10**, namely the brominated C^5 and the lactone carbonyl, but a known example reported by Falentin *et al.*[16] suggested the latter was more reactive upon exposure to primary amine. Indeed, treatment of (+)-**10** in methanol with methylamine, *in situ* generated by reacting its hydrochloric salt with K_2CO_3, led preferentially to the nucleophilic lactone ring-opening and subsequently triggered an epoxide ring-closure to afford (+)-**9**, despite that the yield (50%) was not satisfying. Further optimization of the aminolysis conditions was attempted and (+)-**9** was finally obtained in 80% yield by using Et_3N instead of K_2CO_3.

Scheme 4 Completion of the synthesis



Reagents and conditions: (a) $MeNH_2$•HCl, Et_3N, MeOH, r.t., 80%; (b) *t*-BuOK, *t*-BuOH, 45 ˚C, 88%; (c) LDA, Davis oxidant, THF, −78 ˚C, 80%.

Cyclization of (+)-**9** proved to be straight forward. After heating of the epoxy-amide with potassium *tert*-butoxide (2.0 equiv.) at 45 ˚C for 2 h in *tert*-butanol, 3-deoxy-clausenamide (−)-**8** was obtained in 88% yield, which showed identical NMR to that of our previously prepared sample.[17] As expected, the final introduction of C^3-OH was furnished by treatment of (−)-**8** with LDA and Davis oxidant to deliver (−)-**1** in 80% yield after chromatography or 50% yield after recrystallization from ethyl acetate. Both samples showed >99% *ee* by HPLC and identical ^{1}H NMR spectra to the authentic sample in our hand. Optical rotation [$[\alpha]_D^{20}$ −144.2 (*c* 0.55, CH_3OH)] and melting point (159.5−161.2 ℃) of the recrystallized sample were also in agreement with the previous data.[3c]

Conclusions

(−)-Clausenamide, a promising anti-Alzheimer drug candidate, was synthesized in 6 steps from *R*-(+)-1,3-diphenylallylic alcohol ((+)-**13**) in 34% (or 22% after recrystallization) overall yield. In comparison to our previously developed biomimetic approach, this synthetic route is of similar step-economy, but superior in terms of stereoselectivity and overall yield. Because 1,3-diphenylallylic alcohol and a wide variety of its substituted derivatives are possibly available in large quantity with high optical purity through asymmetric catalytic hydrogenation or chiral ligand induced asymmetric addition, a new version of process research on (−)-clausenamide and the generation of an expanded library of (−)-clausenamide analogues are ongoing in our laboratory.

Experimental

General information

THF and CH_2Cl_2 were dried over Al_2O_3 absorbent prior to use. Flash chromatography was performed on 200−300 mesh silica gel. NMR spectra were recorded at ambient temperature in $CDCl_3$ using Oxford MERCURY 400 and Bruker AV500-III spectrometers. High resolution mass spectroscopy was performed using electrospray ionization (ESI) in either positive or negative ionization as stated. Enantiomeric excess was determined by HPLC analysis on chiral pak AS-H or AD-H columns. All commercially available chemicals were purchased from Aldrich Chemical Co., JK Chemicals, or Alfa Aesar Organics and used as received unless otherwise specified. Chiral starting material (+)-**13** was prepared according to literature method[15a] and purified by flash chromatography.

Preparation of (−)-(*R*)-1,3-diphenylallyl acetate (−)-12

(*R*,*E*)-(+)-1,3-Diphenylallylic alcohol (+)-**13** (1.1 g, 5.2 mmol) was placed in a round bottom flask equipped with a magnetic stir bar and septum. Pyridine (0.5 mL, 6.3 mmol), acetic anhydride (3 mL) and catalytic DMAP (122 mg, 1.0 mmol) were successively added under argon. The reaction mixture was stirred overnight at room temperature and diluted with ethyl acetate (50 mL). The diluted solution was poured into saturated aqueous $NaHCO_3$ (50 mL) and vigorously stirred for 20 min. The resulting biphasic mixture was then separated, and the aqueous phase was extracted with ethyl acetate (50 mL×3). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residual yellow oil was purified by flash chromatography (SiO_2, hexanes/ethyl acetate, V∶V=9∶1) to give colorless oil (−)-**12** (1.2 g, 92%).[18] $[\alpha]_D^{20}$ −4.78 (*c* 0.80, $CHCl_3$) [lit:[18] $[\alpha]_D^{20}$ −4.9 (*c* 1.0, $CHCl_3$)]; ^{1}H NMR[17] (400 MHz, $CDCl_3$) δ: 7.42−7.24 (m, 10H), 6.63 (d, J=15.6 Hz, 1H), 6.44 (d, J=6.4 Hz, 1H), 6.36 (dd, J_1=6.8 Hz, J_2=16.0 Hz, 1H), 2.14 (s, 3H).

Preparation of (−)-(*S*,*E*)-3,5-diphenylpent-4-enoic acid (−)-11

LDA (4.8 mL, 2 mol•L^{-1} in THF, 9.6 mmol) was added to a stirred solution of (−)-**12** (800 mg, 3.2 mmol) in THF (20 mL) at −78 ℃ and stirred for 10 min.

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TMSCl (870 mg, 8.1 mmol) was dropwisely added in neat through a syringe at −78 ℃, and stirring was continued for 1 h. The reaction mixture was then allowed to slowly warm up to room temperature and stirred for 30 h. Solid TBAF (4.0 g, 12.2 mmol) was added to the mixture and stirring was continued for additional 8 h. The reaction was then quenched with water (20 mL) and aqueous HCl (1 mol•L^{-1}, 6 mL), and extracted with ethyl acetate (20 mL×3). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure to give colorless oil. The crude material was purified by flash chromatography (SiO_2, hexanes/ethyl acetate, V∶V=10∶1) to give white solid (−)-**11** (680 mg, 85%). $[\alpha]_D^{20}$ +21.2 (c 0.20, CH_3OH); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34−7.20 (m, 10H), 6.44 (d, J=16.0 Hz, 1H), 6.33 (dd, J_1=7.2 Hz, J_2=16.0 Hz, 1H), 4.01−4.03 (m, 1H), 2.88−2.85 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 176.6, 142.3, 137.0, 131.7, 130.3, 128.7, 138.5, 127.5, 127.4, 126.9, 126.3, 44.6, 40.2; FT-IR (KBr) v: 1303, 1707, 3025 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}O_2$ $[M-H]^-$ 251.1078, found 251.1099.

Preparation of (4*R*,5*R*,6*S*)-5-bromo-4,6-diphenyltetrahydropyran-2-one (+)-10

N-Bromosuccinimide (240 mg, 1.0 mmol) was added in one portion to a stirred mixture of (−)-**11** (300 mg, 1.0 mmol) and grounded 4 Å molecular sieves (30 mg) in CH_2Cl_2 (5 mL) at room temperature. Vigorous stirring of the resulting suspension was continued for 4 h, it was then filtered, and the combined filtrate was concentrated under reduced pressure. The resultant white solid paste was triturated with *n*-hexanes (10 mL), filtered, and the combined filtrate was concentrated under reduced pressure to afford essentially pure white solid (+)-**10** (450 mg, 79%). $[\alpha]_D^{20}$ +42.2 (c 0.58, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43−7.27 (m, 10H), 5.46 (d, J=10.0 Hz, 1H), 4.29 (t, J=10.4 Hz, 1H), 3.60−3.66 (m, 1H), 3.19 (dd, J_1=6.4 Hz, J_2=17.6 Hz, 1H), 2.90 (dd, J_1=9.6 Hz, J_2=17.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 169.0, 140.7, 136.4, 129.5, 129.1, 128.6, 128.0, 127.7, 127.1, 85.2, 53.5, 47.3, 37.8; FT-IR (KBr) v: 1016, 1249, 1730, 3033 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{16}BrO_2$ $[M+H]^+$ 331.0333/333.0312, found 331.0323/333.0306.

Preparation of (*R*)-*N*-methyl-3-phenyl-3-((2*S*,3*S*)-3-phenyloxiran-2-yl)propanamide (+)-9

Methylamine hydrochloride (54 mg, 0.80 mmol) and Et_3N (340 mg, 3.4 mmol) was added to a solution of (+)-**10** (220 mg, 0.67 mmol) in methanol (5 mL). The reaction mixture was stirred for 5 h at room temperature. Aqueous HCl (1 mol•L^{-1}, 5 mL) was then added under stirring and the mixture was extracted with CH_2Cl_2 (10 mL×3). The combined organic layers were washed with brine (10 mL×3), dried over Na_2SO_4 and concentrated under reduced pressure to give a white solid (+)-**9** (150 mg, 80%).

This material was used without further purification in the next step. An analytical sample of (+)-**5** was obtained by chromatography (SiO_2, hexanes/ethyl acetate, V∶V=3∶1). $[\alpha]_D^{20}$ +17.2 (c 0.39, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (d, J=7.2 Hz, 2H), 7.38−7.34 (m, 8H), 5.44 (br s, 1H), 4.60 (dd, J_1=2.8 Hz, J_2=9.6 Hz, 1H), 4.33 (d, J=10 Hz, 1H), 4.16−4.21 (m, 1H), 2.83 (dd, J_1=8.8 Hz, J_2=14.8 Hz, 1H), 2.77 (d, J=2.4 Hz, 3H), 2.68 (dd, J_1=6.4, J_2=14.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 171.4, 141.9, 138.6, 129.7, 128.4, 128.1, 127.5, 127.2, 75.6, 63.4, 42.0, 41.7, 26.4; FT-IR (KBr) v: 699, 1645, 3031, 3308 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{20}NO_2$ $[M+H]^+$ 282.1489, found 282.1490.

Prparation of (4*R*,5*R*)-5-((*R*)-hydroxy(phenyl)-methyl)-1-methyl-4-phenyl-pyrrolidin-2-one (−)-8

A solution of (+)-**9** (130 mg, 0.46 mmol) and potassium *tert*-butoxide (104 mg, 0.92 mmol) in *tert*-butanol (3 mL) was heated at 45 ℃ for 3 h under stirring, then diluted with water (15 mL) and extracted with CH_2Cl_2 (10 mL×3). The combined organic layers were washed with brine (10 mL×3), dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash chromatography (SiO_2, acetone/hexane, V∶V=1∶5) to give white solid (−)-**8** (115 mg, 88%).[17] $[\alpha]_D^{20}$ −114 (c 0.38, $CHCl_3$) [lit:[17] $[\alpha]_D^{20}$ −119.7 (c 0.8, $CHCl_3$)]; ^{1}H NMR[16] (400 MHz, $CDCl_3$) δ: 7.38−7.19 (m, 8H), 6.89−6.92 (m, 2H), 4.73 (d, J=5.2 Hz, 1H), 4.16 (t, J=7.2 Hz, 1H), 3.84−3.93 (m, 1H), 2.75 (s, 3H), 2.36 (d, J=10 Hz, 2H).

Preparation of (−)-clausenamide (−)-1

A solution of (−)-**10** (100 mg, 0.36 mmol) in THF (5 mL) was added slowly to a stirred solution of LDA (0.65 mL, 2 mol•L^{-1} in THF, 1.3 mmol) at −78 ℃ through a syringe. Stirring was continued for 20 min, then a solution of Davis oxidant (370 mg, 1.4 mmol) in THF (1 mL) was dropwisely added at −78 ℃. The resulting mixture was stirred for additional 30 min at −78 ℃ and quenched with saturated aqueous NH_4Cl (3 mL). After warmed up to room temperature, the biphasic mixture was separated and the aqueous layer was extracted with methylene chloride (15 mL×3). The organic layers were combined, washed with brine (15 mL×3), dried over Na_2SO_4 and concentrated under reduced pressure to give colorless oil. This material was purified by flash chromatography (SiO_2, acetone/hexanes, V∶V=1∶5) to afford a white solid (−)-**1** (85 mg, 80%).[3c] ^{1}H NMR (400 MHz, CD_3OD) δ: 7.21−7.14 (m, 5H), 7.09−7.01 (m, 3H), 6.66 (d, J=7.2 Hz, 2H), 4.73 (s, 1H), 4.33 (d, J=8.4 Hz, 1H), 3.95 (d, J=11.2 Hz, 1H), 3.60 (t, J=8.8 Hz, 1H), 3.11 (s, 3H); ^{13}C NMR (126 MHz, CD_3OD) δ: 177.3, 141.3, 136.8, 129.9, 129.2, 128.8, 128.5, 128.4, 127.9, 74.2, 70.8, 67.5, 51.4, 31.5.

Crystalline (−)-**1** (53 mg, 50%) was obtained from a solution of this sample in ethyl acetate (2 mL). m.p. 159.5−161.2 ℃ (lit:[3c] 160−162 ℃); $[\alpha]_D^{20}$ −144.2

(c 0.55, methanol) [lit:[3c] $[\alpha]_D^{20}$ −144.2 (c 0.8, methanol)]; FT-IR (KBr) ν: 1602, 1686, 3215, 3408 cm^{-1}.

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