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Asymmetric azo-ene reactions using the chiral azo-enophile di-(−)-(1*R*,2*S*)-2-phenyl-1-cyclohexyl diazenedicarboxylate

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Abstract

The preparation of di-(−)-(1*R*,2*S*)-2-phenyl-1-cyclohexyl diazenedicarboxylate **4** is described. Reaction of (1*R*,2*S*)-2-phenyl-1-cyclohexanol **1** with excess phosgene in the presence of quinoline afforded chloroformate **2** which was treated directly with hydrazine monohydrate (0.5 equiv.) to afford di-(−)-(1*R*,2*S*)-2-phenyl-1-cyclohexyl diazanedicarboxylate **3**. Oxidization of **3** to the azo-enophile **4** was then readily effected in high yield using *N*-bromosuccinimide and pyridine. The azo-ene reactions of **4** with the alkenes cyclohexene **5**, cyclopentene **6**, *trans*-3-hexene **7** and *trans*-4-octene **8** were carried out using the Lewis acid tin(IV) chloride. Use of cyclohexene **5** afforded the ene adduct **9** in 80% yield with a diastereomeric excess of >97:3 whilst the use of cyclopentene **6**, *trans*-3-hexene **7** and *trans*-4-octene **8** afforded the ene adducts **10** (77%), **11** (71%) and **12** (92%) with a diastereomeric excess of 86:14 in each case. Use of the conjugated aromatic acyclic alkene **13** afforded the product of an ionic addition, namely, chloride **14** in 57% yield. Cleavage of the N–N bond of the ene adduct **9** was effected using lithium in liquid ammonia affording the carbamate **16** in moderate yield.

1. Introduction

The preparation of allylic amines has been limited to the use of sulfur diimido compounds,[1] *N*-sulfonylimines,[2] acylnitroso compounds[3] or *N*-sulfinylbenzenesulfonamides.[4] Whitesell and Yaser[5] have reported asymmetric induction in the allylic amination of alkenes via ene reaction of an *N*-sulfinylcarbamate bearing the chiral auxiliary *trans*-(1*S*)-2-phenylcyclohexanol followed by rearrangement of the ene adducts to allylic carbamates. The azo-ene reaction offers an alternative method for effecting allylic amination in that treatment of an alkene with an azo-diester affords a diacyl hydrazine which upon N–N cleavage furnishes a carbamate. Subsequent hydrolysis of the carbamate provides an allylic amine. Use of chiral diazenedicarboxylates offers an exciting opportunity for development of

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an asymmetric variant of this azo-ene reaction thereby providing a method for stereoselective electrophilic amination. The present study investigates the synthesis of di-(−)-(1*R*,2*S*)-2-phenyl-1-cyclohexyl diazenedicarboxylate **4** and its use as an azo-enophile in reactions with simple alkenes.

The ene reaction[6] provides a powerful method for C–C bond formation with concomitant activation of an allylic C–H bond. A variety of functionalised carbon skeletons can be constructed due to the range of enophiles which can be used; for example carbonyl compounds give homoallylic alcohols[7] and imino derivatives of aldehydes afford homoallylic amines.[8] Milder reaction conditions have been achieved using Lewis acid promoters[9] whilst the use of chiral binaphthol–titanium based Lewis acids developed by Mikami et al.[10] have provided an efficient catalytic asymmetric variant of the carbonyl-ene reaction. A model for the enantioselectivity of this Mikami ene reaction has recently been proposed by Corey et al.[11] invoking complexation of the formyl group with the titanum catalyst and hydrogen bonding of the formyl hydrogen.

Asymmetric carbonyl-ene reactions have also been developed using chiral auxiliaries. Thus, Whitesell et al.[12] have reported excellent asymmetric induction in carbonyl-ene reactions using 8-phenylmenthyl glyoxylates whilst Mikami et al.[13] reported high diastereoselectivity in imino-ene reactions of 1,1-disubstituted alkenes with chiral α-iminoesters bearing the 8-phenylmenthyl auxiliary. More recently, the use of an *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam in asymmetric carbonyl-ene reactions was reported.[14]

Despite the widespread use of chiral glyoxylate enophiles in ene reactions, the synthesis of chiral diazenedicarboxylates as potential chiral electrophilic aminating agents has received little attention. Vederas et al.[15a] synthesized a series of chiral bornyl, isobornyl and menthyl diazenedicarboxylates and reported that their reaction with achiral enolates of esters and *N*,*N*-dimethyl amides afforded α-hydrazino-acid derivatives with little or no selectivity. Attempts[15b] to use a macrocyclic diazenedicarboxylate based on a steroid skeleton was unsuccessful whilst incorporation of a chiral azodicarboxamide unit into a chiral bridging binaphthyl moiety afforded α-hydrazino-acid derivatives with high stereoselectivity in reactions with achiral oxazolidinone anions.[15c] Evans and Nelson[16] have recently reported the elegant use of chiral magnesium bis(sulfonamide) complexes as catalysts for the enantioselective amination of *N*-acyloxazolidinones using achiral diazenedicarboxylates.

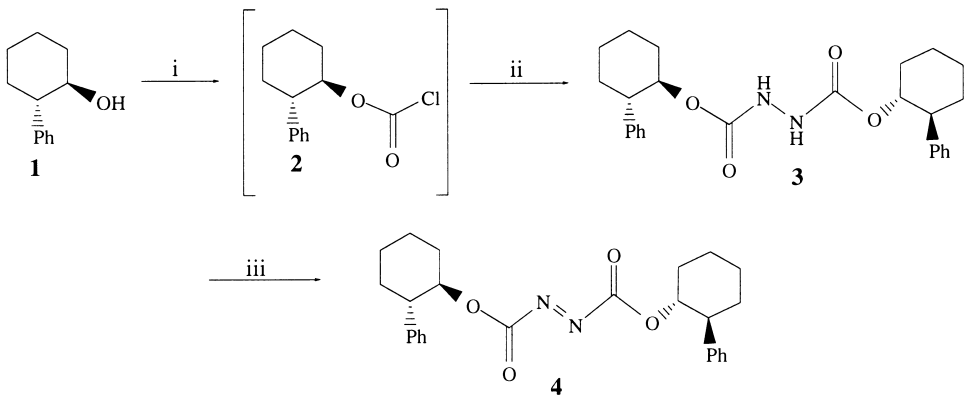
The work carried out by Vederas et al.[15] focused on the electrophilic amination of chiral diazenedicarboxylates with achiral ester enolates. The potential of these aminating agents as chiral azo-enophiles in ene reactions, the subject of our investigations, was not pursued by these authors.

We have reported[17] the use of tin(IV) chloride as a promoter for the azo-ene reaction of diethyl diazenedicarboxylate (DEAD) with alkenes under mild conditions. Cleavage of the N–N bond in the azo-ene adducts was effected using lithium in liquid ammonia. A method for allylic amination was therefore developed which offered an alternative to the use of the more reactive azo-enophile bis(2,2,2-trichloroethyl)azodicarboxylate.[18] Extension of this reaction to the use of a chiral azo-enophile initially focused on the use of di-(−)-menthyl diazenedicarboxylate.[19] However, the level of asymmetric induction achieved in Lewis acid mediated ene reactions with simple alkenes was not impressive. Moreover, it proved difficult to cleave the N–N bond in the menthyl ester azo-ene adducts.

2. Results and discussion

As an extension to our earlier work, we next investigated the use of Whitesell's auxiliary, (−)-(1*R*,2*S*)-2-phenyl-1-cyclohexanol **1**, for development of an asymmetric azo-ene reaction. Chloroacylation of (−)-(1*R*,2*S*)-2-phenyl-1-cyclohexanol **1** with phosgene using triethylamine as the base afforded *N*,*N*-diethylcarbamate **15** in 80% yield whereas use of pyridine as the base and subsequent reaction with

hydrazine monohydrate only afforded the desired diazanedicarboxylate **3** in 11% yield. A successful synthesis of **3** was finally realised when quinoline was used as the base (Scheme 1). The optimum method involved a one-step procedure wherein chloroacylation of **1** by phosgene (3 equiv.) in the presence of quinoline (1.1 equiv.) for 0.5 h afforded the chloroformate **2**. Excess phosgene was removed under reduced pressure and hydrazine monohydrate (0.5 equiv.) and quinoline (1.1 equiv.) were added dropwise and alternately to **2** at 0–10°C over 10–15 min. After stirring at room temperature for 24 h, diazanedicarboxylate **3** was furnished in 74% yield.



Reagents and Conditions: (i) $COCl_2$ (3 equiv.), quinoline (1.1 equiv.), THF, 0.5 h., room temp.; (ii) $NH_2NH_2.H_2O$ (0.5 equiv.), quinoline (1.1 equiv.), 0-10°C, 0.25 h. then room temp, 24 h., 74%; (iii) NBS (1.2 equiv.), py (1.5 equiv.), CH_2Cl_2, 0°C, 0.25 h., 97%.

Scheme 1.

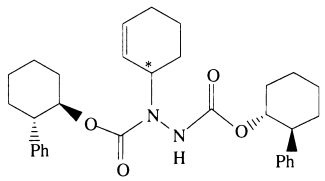
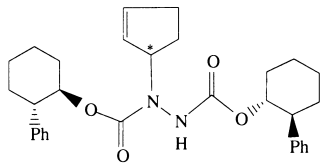
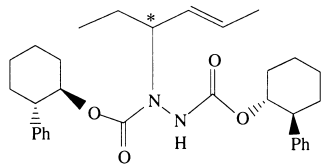
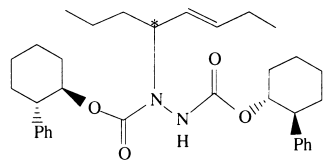
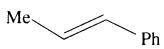
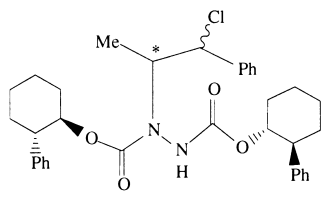
Owing to restricted rotation about the carbamate C–N bond on the NMR timescale, the ^{1}H NMR spectrum for **3** was broad and resolution was poor at 298 K (200 MHz, $CDCl_3$). The resolution was optimized by acquiring the 400 MHz spectrum at 360 K using deuterotoluene as the solvent.

Several oxidants were examined for conversion of the diazanedicarboxylate **3** to the diazenedicarboxylate **4**. Whilst the use of [bis(trifluoroacetoxy)iodo]benzene[20] in dichloromethane at 0°C readily converted **3** to **4**, the diazenedicarboxylate **4** isolated from this reaction proved unstable and underwent conversion back to **3** upon standing at room temperature. Use of bromine and pyridine,[21] fuming nitric acid[17] and *N*-bromosuccinimide[15a] and pyridine all effected smooth conversion of **3** to **4** in 80%, 90% and 97% yields, respectively, and this latter reagent was used routinely.

The ^{1}H NMR spectrum and elemental analysis for azo-enophile **4** were in agreement with the proposed structure and the IR spectrum confirmed the presence of both a C=O stretch (1771 cm^{-1}) and an N=N stretch at (1449 cm^{-1}). With azo-enophile **4** in hand, Lewis acid mediated azo-ene reactions were investigated using a range of alkenes which could only afford one regioisomer of the corresponding ene adduct.

Initial work focused on the ene reaction of **4** with cyclohexene **5** using tin(IV) chloride which had been found to be the optimum Lewis acid in the reaction of di-(−)-menthyl diazanedicarboxylate with alkenes (Table 1).[19] Addition of tin(IV) chloride (1.1 equiv.) to a mixture of enophile **4** and cyclohexene **5** (1.6 equiv.) in dichloromethane at −60°C for 5 min afforded the ene adduct **9** in 80% yield after purification by flash chromatography. Due to hindered rotation about the carbamate C–N bonds the ^{1}H NMR spectrum of adduct **9** acquired at 298 K in deuterated chloroform at 200 MHz, was very broad and complex. The resolution was improved by acquiring the spectrum at elevated temperatures in deuterated toluene and the optimum spectrum resolution was achieved at 380 K. Under these conditions the ^{1}H NMR spectrum

Table 1
Reaction of azo-enophile **4** with alkenes using $SnCl_4$

 **5**	 **9**	80% > 97 : 3
 **6**	 **10**	77% 86 : 14
 **7**	 **11**	71% 86 : 14
 **8**	 **12**	92% 86:14
 **13**	 **14**	57%

established the presence of only one diastereomer within the limits of detection by NMR spectroscopy at 400 MHz (97:3). Further analysis of the ene adduct **9** by HPLC on a Whatman Partisil 5 normal phase silica column using hexane:ethyl acetate (9:1) as eluent confirmed the presence of only one diastereomer, R_t=12 min.

Two double doublets, each integrating for one proton, resonating at δ 2.62 ppm ($J_{2''x,1''ax}$ 10.4, $J_{2''ax,3''ax}$ 10.4, $J_{2''ax,3''eq}$ 3.8) and δ 2.76 ppm ($J_{2''ax,1''ax}$ 10.4, $J_{2''ax,3''ax}$ 10.4, $J_{2''ax,3''eq}$ 3.8) were assigned to the methine protons at C-2″. A broad one-proton singlet at δ 4.66 ppm was assigned to the CHN proton. Two double doublets, each integrating for one proton, resonating at δ 5.06 ppm ($J_{1''ax,2''ax}$

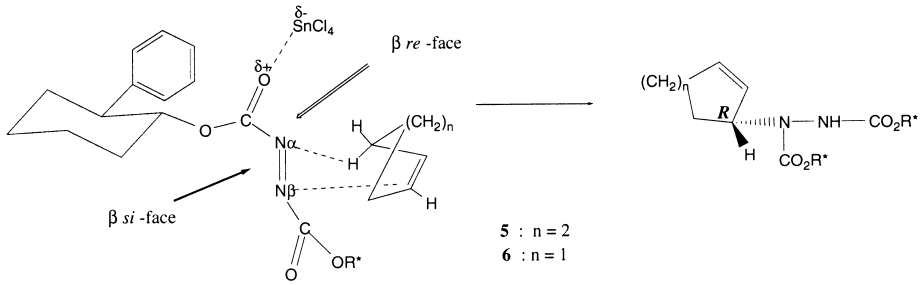


Fig. 1.

10.4, $J_{1''ax,6''ax}$ 10.4, $J_{1''ax,6''eq}$ 4.5) and δ 5.12 ppm ($J_{1''ax,2''ax}$ 10.4, $J_{1''ax,6'ax}$ 10.4, $J_{1''ax,6''eq}$ 4.5) were assigned to the two methine protons at C-1″. In the vinylic region, multiplets at δ 5.38–5.47 ppm and δ 5.65–5.67 ppm, each integrating for one proton, were assigned to the vinylic protons H-3′ and H-2′ respectively. The presence of an NH proton was evident as a singlet at δ 5.58 ppm and a 10-proton multiplet at δ 7.16–7.37 ppm was assigned to the aromatic protons.

The absolute stereochemistry at the newly formed stereogenic carbon of the major diastereomer of the ene adduct **9** can be predicted by analysis of the transition model for the ene reaction (Fig. 1). The (1*R*,2*S*)-2-phenyl-1-cyclohexyl chiral auxiliary adopts a chair conformation with equatorial placement of the bulky phenyl group. Complexation of the carbonyl group to the Lewis acid affords the more stable *s-trans* conformation about the C–N sigma bond. In this conformation the phenyl group shields the $N_β$-*re*-face therefore the cyclic olefin preferentially attacks from the less hindered $N_β$-*si*-face. Ene reaction proceeds through a six-membered cyclic transition state affording the (1′*R*)-diastereomer of the ene adduct. The origin of the diastereocontrol for this reaction is a consequence of the π-stacking of the phenyl group of the auxiliary and the conjugated diazenedicarbonyl moiety.

The tin(IV) chloride promoted azo-ene reaction of **4** with cyclopentene **6** under similar conditions to that used above afforded the ene adduct **10** in 77% yield. In this case two peaks were observed in the HPLC chromatogram [Sorbax Sil normal phase silica column using hexane:ethyl acetate (85:15) as eluent] at R_t=9.5 min and R_t=10 min which upon integration established an 86:14 ratio of diastereomers. This ratio was also in agreement with that obtained from integration of the ^{1}H NMR spectrum of the crude ene adduct **10** acquired at elevated temperature in deuterotoluene at 400 MHz. The major diastereomer was further purified by preparative HPLC.

The diastereomeric ratios observed for the ene adducts obtained after reaction of azo-enophile **4** with the cyclic alkenes, cyclohexene **5** (>97:3) and cyclopentene **6** (86:14), represent a significant improvement over the 1:1 ratio of diastereomers observed in analogous reactions using di-(−)-menthyl diazenedicarboxylate as the azo-enophile.[19]

Encouraged by the promising diastereomeric ratios achieved in the ene reaction of **4** with cyclic alkenes, it was next decided to investigate the use of acyclic alkenes as the ene component. *trans*-3-Hexene **7** and *trans*-4-octene **8** were reacted with **4** using the same conditions as for the analogous reactions with cyclic alkenes. The ene adducts **11** and **12** were isolated in 71% and 92% yield respectively, after flash chromatography. In both cases, HPLC analysis on a Whatman Partisil 5 normal phase column using hexane:ethyl acetate (9:1) as eluent resolved the two diastereomers. For ene adduct **11**, two peaks were observed at R_t=19.5 min and R_t=21.5 min which upon integration established an 86:14 ratio of diastereomers. Similarly for ene adduct **12** two peaks were observed at R_t=20.5 min and R_t=22 min which upon integration also established an 86:14 ratio of diastereomers. Similar diastereomeric ratios were obtained from integration of the ^{1}H NMR spectrum of the crude ene adducts **11** and **12** acquired at 360 K in deuterotoluene at 400 MHz and were significantly better than the ratios observed for the ene

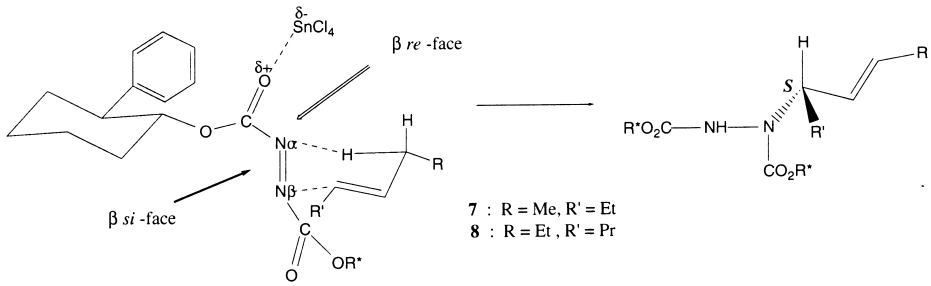


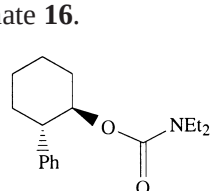
Fig. 2.

reactions of acyclic alkenes **7** and **8** with di-(−)-menthyl diazenedicarboxylate as the azo-enophile (2.5:1 and 2:1 respectively).[19]

The major diastereomers of the ene adducts **11** and **12** were further purified by preparative HPLC. Examination of the transition state model for the ene reaction using *trans*-3-hexene **7** and *trans*-4-octene **8** also allows a prediction of which diastereomer should be the favoured product (Fig. 2).

In view of the successful ene reactions observed with aliphatic cyclic and acyclic alkenes, it was decided to examine the ene reaction of **4** with an acyclic alkene conjugated to an aromatic ring, namely, *trans*-β-methylstyrene **13**. With this more activated alkene, chloride **14** was formed in 57% yield after treatment with tin(IV) chloride under similar conditions to those used for alkenes **5**, **6**, **7** and **8**. Clearly in this system an ionic mechanism involving a stepwise reaction with a carbocation intermediate is operating rather than a pericyclic mechanism.

Given that the best asymmetric induction was observed in the formation of ene adduct **9**, cleavage of the N–N bond of the ene adduct **9** to the carbamate **16** was examined. Lithium in liquid ammonia had been successfully used to cleave the N–N bond in ene adducts formed using DEAD,[17] however, treatment of ene adduct **9** with lithium in liquid ammonia resulted in formation of carbamate **16** in only in 10% yield whereas the use of samarium diiodide was unsuccessful. Use of sodium and liquid ammonia, however, afforded the desired carbamate **16** in 61% yield. The enantiomer of carbamate **16** has been prepared by Whitesell and Yaser,[5] who also demonstrated the facile hydrolysis of allylic *trans*-2-phenylcyclohexyl carbamates to allylic amines under basic conditions. Carbamate **16** was a single diastereomer within the limit of detection by ^{13}C NMR spectroscopy and analytical HPLC as described by Whitesell and Yaser[5] for the enantiomer of carbamate **16**.



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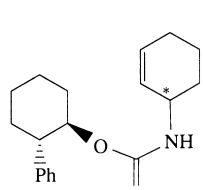

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In summary the work described herein established that the use of a (1*R*,2*S*)-2-phenyl-1-cyclohexyl chiral auxiliary rather than a menthyl ester affords much higher levels of asymmetric induction in the Lewis acid mediated azo-ene reaction however subsequent cleavage of the N–N bond in the ene adduct only proceeds in low yield.

3. Experimental

3.1. General details

Melting points were determined using a Reichert heating stage with microscope and are uncorrected. Elemental analyses were performed at either the Chemical Engineering Faculty, University of Sydney, Sydney, the Central Services Laboratory, Hobart, Tasmania, Australia or the Microanalytical Laboratory, University of Otago, Dunedin, New Zealand. Optical rotations were measured using a PolAAR 2001 polarimeter in chloroform at the temperature and concentration (g/100 mL) indicated. Specific rotations are given in 10^{-1} deg cm^2 g^{-1}. Readings were taken using the 589.3 nm sodium line and a 1 dm cell. Infrared absorption spectra were recorded using a Perkin–Elmer 1600 Series FTIR spectrometer as Nujol mulls or as a thin film on a single sodium chloride plate seated in the apparatus on a custom-made perch. ^{1}H NMR spectra were recorded using a Bruker AC200B spectrometer (200.13 MHz) or a Bruker AM400 spectrometer (400.12 MHz). ^{13}C NMR spectra were recorded on a Bruker AC200 spectrometer (50.3 MHz) at ambient temperatures with complete decoupling. Variable temperature ^{1}H NMR spectra were recorded in deuterotoluene at 360 K or 380 K using toluene as an internal standard. Low resolution mass spectra were recorded on a VG 70-SE, VG 70-250S, VG70-SD or an AEI model MS902 double focusing magnetic sector mass spectrometer with an ionisation potential of 70 eV. The samples were inserted through a solid direct injection probe with a source temperature of 200°C. Chemical ionisation (CI) mass spectra were recorded on a Hewlett–Packard 5989A mass spectrometer using CH_4 as the reagent gas, with the sample dissolved in CH_3OH and injected through an HPLC injection port with the sample passed to the mass spectrometer source at 200°C by a particle beam interface. Liquid secondary ion mass spectra (LSIMS) were recorded on a VG70-SE double focusing magnetic sector mass spectrometer operating with an ionization potential of 20 keV using cesium as a secondary gas. Matrices used for LSIMS sample preparation were *m*-nitrobenzyl alcohol (mnba) and polyethylene glycol. High resolution mass spectra were recorded at a nominal resolution of 5000 or 10000 as appropriate, using EI, CI with ammonia or LSIMS with mnba. High resolution CI and LSIMS mass spectra were recorded at the Central Services Laboratory, Hobart, Australia. Thin layer chromatography (t.l.c) was carried out on Merck precoated aluminium sheets coated with 0.2 mm silica gel 60F254 and flash chromatography on Merck silica gel 60 (230–400 mesh ASTM). Solvent compositions specified are mixed v:v. High performance liquid chromatography (HPLC) was performed using Waters and Associates HPLC instrumentation fitted with a Whatman Partisil 5 normal phase silica column or a Sorbax Sil normal phase silica column (21.5 mm i.d.×25 mm) with a flow rate of 1.5 cm^3/min and hexane–ethyl acetate as eluent (v:v). Hexane was distilled from calcium hydride and tetrahydrofuran was distilled from benzophenone/sodium wire immediately prior to use. Reaction temperatures were maintained at −70°C using dry ice/acetone; −60°C using dry ice/chloroform; −20°C using dry ice/carbon tetrachloride and 0°C using ice/water cooling baths. (−)-(1*R*,2*S*)-2-Phenyl-1-cyclohexanol was prepared from 1-phenylcyclohexene according to the method of Sharpless and King.[22] The ^{1}H NMR spectrum, melting point and optical rotation of the material prepared was in agreement with that reported in the literature.[22]

3.2. Di-(−)-(1R,2S)-2-phenyl-1-cyclohexyl diazane-1,2-dicarboxylate **3**

To phosgene (1.50 mL of a 12.5% w/w solution in benzene, 1.89 mmol) under an atmosphere of nitrogen, were added dropwise and alternately over 10–15 min a solution of (−)-(1*R*,2*S*)-2-phenyl-1-cyclohexanol **1** (100 mg, 0.567 mmol) in dry THF (1 mL) and quinoline (73 μL, 0.62 mmol). The reaction mixture was stirred at room temperature for 30 min. Due to the instability of the chloroformate

2, further purification was not attempted. Unreacted phosgene was removed under reduced pressure to afford the crude chloroformate **2** as a viscous brown oil, δ_H (200 MHz, $CDCl_3$) 1.25–1.70 (4H, m, H-4′, H-5′), 1.76–2.01 (3H, m, H-3′, H-6′), 2.22–2.30 (1H, m, H-6′), 2.74 (1H, ddd, $J_{2'ax,1'ax}$ 10.9, $J_{2'ax,3'ax}$ 10.9, $J_{2'ax,3'eq}$ 4.0, H-2′), 4.98 (ddd, $J_{1'ax,2'ax}$ 10.9, $J_{1'ax,6'ax}$ 10.9, $J_{1'ax,6'eq}$ 4.5, H-1′), 7.21–7.30 (5H, m, Ph); *m/z* (EI) 238 [M^+, 1], 194 [$M-CO_2$, 16], 158 [$M-CHO_2Cl$, 100].

To a solution of the crude chloroformate **2** in dry THF (1 mL) at 0−5°C, were added dropwise and alternately hydrazine monohydrate (14 μL, 0.28 mmol) and quinoline (73 μL, 0.62 mmol) over 10–15 min with stirring under an atmosphere of nitrogen. The reaction mixture was warmed to room temperature for 24 h then extracted with dichloromethane (3×8 mL), washed with water (0.5 mL) and dried over anhydrous sodium sulfate. After removal of solvent under reduced pressure, the residue was purified by flash chromatography using hexane:ethyl acetate (9:1) as eluent to afford the title compound **3** (92 mg, 74%) as a colourless solid, m.p. 43–44°C; $[\alpha]_D$ −37.5 (c 1.07, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 3379 br (NH) and 1718 s (C=O); δ_H (400 MHz, [$^2H_8$]toluene, 360 K) 1.14–1.39 (8H, m, H-4′, H-5′), 1.48–1.52 (2H, m, H-3′), 1.56–1.59 (2H, m, H-3′), 1.69–1.74 (2H, m, H-6′), 2.14–2.18 (2H, m, H-6′), 2.48 (2H, ddd, $J_{2'ax,1'ax}$ 10.9, $J_{2'ax,3'ax}$ 10.9, $J_{2'ax,3'eq}$ 3.8, H-2′), 4.84 (2H, ddd, $J_{1'ax,2'ax}$ 10.5, $J_{1'ax,6'ax}$ 10.5, $J_{1'ax,6'eq}$ 4.4, H-1′), 5.15 (2H, s, NH), 6.95–7.17 (10H, m, 2×Ph); δ_C (50 MHz, $CDCl_3$) 24.7 (CH_2, C-4′), 25.7 (CH_2, C-5′), 32.5 (CH_2, C-3′), 34.2 (CH_2, C-6′), 49.7 (CH, C-2′), 84.6 (CH, C-1′), 126.4, 127.5, 128.3 (CH, C-2′′, C-3′′, C-4′′), 143.3 (quat, C-1′), 155.8 (quat, C=O); *m/z* (CI, CH_4) 437 [$(MH)^+$, 6], 279 [$(MH)-C_{12}H_{14}$, 16], 159 [$(MH)-C_{14}H_{18}N_2O_4$, 100]; [found: $(MH)^+$, 437.2440; $C_{26}H_{32}N_2O_4$ requires *MH*, 437.2443].

3.3. *Di-(−)-(1*R,*2*S*)-2-phenyl-1-cyclohexyl diazene-1,2-dicarboxylate **4***

To a mixture of diazanedicarboxylate **3** (80 mg, 0.184 mmol) and pyridine (22 μL, 0.28 mmol) in dry dichloromethane (1 mL) cooled to 0°C, was added a solution of *N*-bromosuccinimide (40 mg, 0.22 mmol) in dry dichloromethane (0.3 mL). The reaction was protected from light and stirred under an atmosphere of nitrogen at 0–5°C for 15 min The resultant mixture was extracted with dichloromethane (3×15 mL) and washed with water (1 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to afford a yellow oil, which was purified by flash chromatography using hexane:ethyl acetate (9:1) as eluent to give the title compound **4** (78 mg, 97%) as a yellow oil; $[\alpha]_D$ −56.9 (c 0.65, $CHCl_3$); (found: C, 71.6; H, 7.0; N, 6.1; $C_{26}H_{30}N_2O_4$ requires C, 71.9; H, 7.0; N, 6.4%); ν_{max} (thin film)/cm^{-1} 1771 s (C=O), 1449 s (N=N); δ_H (400 MHz, $CDCl_3$) 1.32–1.64 (8H, m, H-4′, H-5′), 1.70–1.93 (6H, m, H-3′, H-6′), 2.10–2.20 (2H, m, H-6′), 2.68 (2H, ddd, $J_{2'ax,1'ax}$ 10.6, $J_{2'ax,3'ax}$ 10.6, $J_{2'ax,3'eq}$ 3.9, H-2′), 5.02 (2H, ddd, $J_{1'ax,2'ax}$ 10.6, $J_{1'ax,6'ax}$ 10.6, $J_{1'ax,6'eq}$ 4.6, H-1′), 7.10–7.40 (10H, m, 2×Ph); δ_C (50 MHz, $CDCl_3$) 24.6 (CH_2, C-4′), 25.4 (CH_2, C-5′), 31.8 (CH_2, C-3′), 33.5 (CH_2, C-6′), 49.2 (CH, C-2′), 81.8 (CH, C-1′), 126.7, 127.4, 128.4 (CH, C-2′′, C-3′′, C-4′′), 141.5 (quat, C-1′′) and 159.6 (quat, C=O); *m/z* (EI) 158 [$M-C_{14}H_{16}N_2O_4$, 95], 91 [$M-C_{19}H_{23}N_2O_4$, 100], 28 [$M-C_{26}H_{30}O_4$, 99].

3.4. *(−)-(1*R,*2*S*)-2-Phenyl-1-cyclohexyl* N,N-*diethylcarbamate **15***

To phosgene (1.50 mL of a 12.5% w/w solution in toluene, 1.70 mmol) was added a solution of (−)-(1*R*,2*S*)-2-phenylcyclohexanol **1** (100 mg, 0.57 mmol) in dry THF (0.8 mL) with stirring under an atmosphere of nitrogen. After 45 min, triethylamine (87 μL, 0.62 mmol) was added dropwise resulting in formation of a white precipitate. The resultant mixture was stirred for 18 h at room temperature under an atmosphere of nitrogen. Excess phosgene and solvent were removed at reduced pressure and the

residue extracted with dichloromethane (3×8 mL) and washed with water (0.5 mL). Purification by flash chromatography using hexane:ethyl acetate (9:1) as eluent afforded the title compound **15** (126 mg, 80%) as a pale yellow oil; $[\alpha]_D$ −56.5 (c 0.32, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 1695 s (C=O); δ_H (200 MHz, $CDCl_3$) 0.85–0.91 (6H, br m, 2×CH_2CH_3), 1.31–1.69 (4H, m, H-4′, H-5′), 1.78–2.02 (2H, m, H-3′), 2.28–2.33 (2H, m, H-6′), 2.71 (1H, ddd, $J_{2'ax,1'ax}$ 11.2, $J_{2'ax,3'ax}$ 11.2, $J_{2'ax,3'eq}$ 3.7, H-2′), 2.97–3.29 (4H, br m, 2×CH_2CH_3), 4.90 (1H, ddd, $J_{1'ax,2'ax}$ 11.2, $J_{1'ax,6'ax}$ 11.2, $J_{1'ax,6'eq}$ 4.1, H-1′), 7.15–7.34 (5H, m, Ph); δ_C (50 MHz, $CDCl_3$) 13.2 (CH_2CH_3), 24.6 (CH_2, C-4′), 25.8 (CH_2, C-5′), 32.3 (CH_2, C-3′), 34.1 (CH_2, C-6′), 40.9 (CH_2CH_3), 50.2 (CH, C-2′), 76.3 (CH, C-1′), 125.9, 127.3, 130.0 (C-2″, C-3″, C-4″), 143.5 (quat, C-1″), 155.2 (quat, C=O); *m/z* (LSIMS, mnba) 276 [$(MH)^+$, 84], 159 [$(MH)-C_5H_{11}NO_2$, 100], 118 [$(MH)-C_{12}H_{14}$, 100]; [found: $(MH)^+$ 276.1969; $C_{17}H_{25}NO_2$ requires *MH*, 276.1885].

3.5. Di-(−)-(1R,2S)-2-phenylcyclohexyl 1-(2′-cyclohexen-1′-yl)-1,2-diazanedicarboxylate **9**

To a solution of diazenedicarboxylate **4** (296 mg, 0.68 mmol) and cyclohexene **5** (86 μL, 0.83 mmol) in dichloromethane (8 mL) cooled to −60°C under an atmosphere of nitrogen, was added tin(IV) chloride (80 μL, 0.68 mmol). After 5 min, the yellow solution turned colourless and water (4 mL) was added. After extraction with dichloromethane (3×25 mL), the combined organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resultant oil was purified by flash chromatography using hexane:ethyl acetate (9:1) as eluent to afford the title compound **9** (281 mg, 80%) as a colourless solid. Further purification by HPLC on a Whatman Partisil 5 normal phase silica column using hexane:ethyl acetate (9:1) as eluent afforded the major diastereomer as a colourless solid, m.p. 138–139°C; $[\alpha]_D$ −3.4 (c 0.65, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 3292 br (NH), 1749 s (C=O), 1713 s (C=O); δ_H (400 MHz, [$^2H_8$]toluene, 380 K) 1.30–1.58 (12H, m, H-5′, H-6′, H-4″, H-5″), 1.59–1.78 (2H, m, H-3″), 1.79–1.90 (4H, m, H-3″, H-4′), 1.91–1.99 (2H, m, H-6″), 2.35–2.44 (2H, m, H-6″), 2.62 (1H, ddd, $J_{2''ax,1''ax}$ 10.4, $J_{2''ax,3''ax}$ 10.4, $J_{2''ax,3''eq}$ 3.8, H-2″), 2.76 (1H, ddd, $J_{2''ax,1''ax}$ 10.4, $J_{2''ax,3''ax}$ 10.4, $J_{2''ax,3''eq}$ 3.8, H-2″), 4.66 (1H, s, CHN), 5.06 (1H, ddd, $J_{1''ax,2''ax}$ 10.4, $J_{1''ax,6''ax}$ 10.4, $J_{1''ax,6''eq}$ 4.5, H-1″), 5.12 (1H, ddd, $J_{1''ax,2''ax}$ 10.4, $J_{1''ax,6''ax}$ 10.4, $J_{1''ax,6''eq}$ 4.5, H-1″), 5.38–5.47 (1H, br m, H-3′), 5.58 (1H, s, NH), 5.65–5.67 (1H, m, H-2′), 7.16–7.37 (10H, m, 2×Ph); *m/z* (LSIMS, mnba), 649 [$(MCs)^+$, 5], 517 [$(MH)^+$, 29], 437 [$(MH)-C_6H_8$, 4], 279 [$(MH)-C_{16}H_{14}O_2$, 17], 159 [$(MH)-C_{20}H_{26}N_2O_4$, 100]; [found $(MH)^+$ 517.3064; $C_{32}H_{40}N_2O_4$ requires *MH*, 517.3068].

3.6. Di-(+)-(1R,2S)-2-phenylcyclohexyl 1-(2′-cyclopenten-1′-yl)-1,2-diazanedicarboxylate **10**

To a solution of diazenedicarboxylate **4** (43 mg, 0.10 mmol) and cyclopentene **6** (14 μL, 0.15 mmol) in dichloromethane (2 mL) cooled to −60°C under nitrogen, was added tin(IV) chloride (13 μL, 0.11 mmol). After 5 min the yellow solution turned colourless and water (0.5 mL) was added. After extraction with dichloromethane (3×5 mL), the combined organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resultant oil was purified by flash chromatography using hexane:ethyl acetate (9:1) as eluent to afford the title compound **10** (37 mg, 77%) as a colourless solid and as an 86:14 mixture of diastereomers. Further purification by HPLC on a Sorbax Sil normal phase silica column using hexane:ethyl acetate (85:15) as eluent afforded the major diastereomer as a colourless solid, m.p. 134–135°C; $[\alpha]_D$ +10.0 (c 0.44, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 3307 br (NH), 1717 br (C=O); δ_H (400 MHz, [$^2H_8$]toluene, 360 K) 1.10–1.41 (8H, m, H-4″, H-5″), 1.48–1.55 (2H, m, H-3″), 1.56–1.66 (2H, m, H-3″), 1.67–1.78 (4H, m, H-5′, H-6″), 1.83–1.87 (1H, m, H-4′), 1.91–1.96 (1H, m, H-4′), 2.18–2.21 (2H, m, H-6″), 2.40–2.47 (1H, ddd, $J_{2''ax,1''ax}$ 10.2, $J_{2''ax,3''ax}$ 10.2, $J_{2''ax,3''eq}$ 3.8, H-2″), 2.60–2.67 (1H, ddd, $J_{2''ax,1''ax}$ 10.2, $J_{2''ax,3''ax}$ 10.2, $J_{2''ax,3''eq}$ 3.8, H-2″), 4.93–5.08 (3H, m,

H-1″, CHN), 5.19–5.31 (1H, m, H-3′), 5.42 (1H, s, NH), 5.56–5.61 (1H, m, H-2′), 6.96–7.18 (10H, m, 2×Ph); *m/z* (LSIMS, mnba) 503 [$(MH)^+$, 44], 437 [$(MH)-C_{26}H_{33}N_2O_4$, 4], 279 [$(MH)-C_{15}H_{12}O_2$, 17], 159 [$(MH)-C_{19}H_{24}N_2O_4$, 100]; [found $(MH)^+$ 503.2902; $C_{31}H_{38}N_2O_4$ requires *MH*, 503.2912].

3.7. Di-(−)-(1R,2S)-2-phenyl-1-cyclohexyl (E)-1-(2′-hexen-4′-yl)-1,2-diazanedicarboxylate **11**

To a solution of diazenedicarboxylate **4** (22 mg, 0.051 mmol) and *trans*-3-hexene **7** (10 μL, 0.081 mmol) in dichloromethane (3 mL) cooled to −60°C under nitrogen, was added tin(IV) chloride (6 μL, 0.051 mmol). After 5 min the yellow solution turned colourless and water (0.5 mL) was added. After extraction with dichloromethane (3×5 mL), the combined organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resultant oil was purified by flash chromatography using hexane:ethyl acetate (9:1) as eluent to afford the title compound **11** (19 mg, 71%) as a colourless oil and as an 86:14 mixture of diastereomers. Further purification by HPLC on a Whatman Partisil 5 normal phase silica column using hexane:ethyl acetate (9:1) as eluent afforded the major diastereomer as a colourless oil; $[\alpha]_D$ −38.9 (c 0.40, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 3385 br (NH), 1754 s (C=O), 1712 s (C=O); δ_H (400 MHz, [$^2H_8$]toluene, 360 K) 0.70 (3H, t, $J_{6'',5''}$ 7.2, H-6″), 1.10–1.39 (10H, m, H-5′, H-4″, H-5″), 1.43 (3H, dq, $J_{1',2'}$ 6.7, $J_{1',3'}$ 1.0, H-1′), 1.50–1.54 (2H, m, H-3″), 1.60–1.64 (2H, m, H−3″), 1.68–1.77 (2H, m, H−6″), 2.18–2.26 (2H, m, H-6″), 2.35 (1H, ddd, $J_{2''ax,1''ax}$ 10.4, $J_{2''ax,3''ax}$ 10.4, $J_{2''ax,3''eq}$ 3.8, H-2″), 2.58 (1H, ddd, $J_{2''ax,1''ax}$ 10.4, $J_{2''ax,3''ax}$ 10.4, $J_{2''ax,3''eq}$ 3.8, H-2″), 4.20 (1H, m, CHN), 4.82 (1H, ddd, $J_{1''ax,2''ax}$ 10.4, $J_{1''ax,6''ax}$ 10.4, $J_{1''ax,6''eq}$ 4.5, H-1″), 4.96–5.14 (2H, m, H-3′, H-1″), 5.17 (1H, dq, $J_{2',3'}$ 18.1, $J_{2',1'}$ 6.4, H-2′), 5.36 (1H, s, NH), 6.97–7.18 (10H, m, 2×Ph); *m/z* (LSIMS, mnba) 519 [$(MH)^+$, 41], 489 [$(MH)-C_2H_5$, 4], 437 [$(MH)-C_6H_9$, 36], 317 [$(MH)-C_{13}H_{14}O_2$, 3], 279 [$(MH)-C_{16}H_{16}O_2$, 27], 159 [$(MH)-C_{20}H_{28}N_2O_4$, 100]; [found: $(MH)^+$, 519.3248; $C_{32}H_{42}N_2O_4$ requires *MH*, 519.3225].

3.8. Di-(−)-(1R,2S)-2-Phenyl-1-cyclohexyl (E)-1-(3′-octen-5′-yl)-1,2-diazanedicarboxylate **12**

To a solution of diazenedicarboxylate **4** (38 mg, 0.087 mmol) and *trans*-4-octene **8** (13 μL, 0.087 mmol) in dichloromethane (2 mL) cooled to −60°C under nitrogen, was added tin(IV) chloride (10 μL, 0.087 mmol). After 5 min the yellow solution turned colourless and water (0.5 mL) was added. After extraction with dichloromethane (3×5 mL), the combined organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resultant oil was purified by flash chromatography using hexane:ethyl acetate (9:1) as eluent to afford the title compound **12** (44 mg, 92%) as a colourless oil and as an 86:14 diastereomeric mixture. Further purification by HPLC on a Whatman Partisil 5 normal phase silica column using hexane:ethyl acetate (9:1) as eluent afforded the major diastereomer as a colourless oil; $[\alpha]_D$ −24.4 (c 0.65, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 3381 br (NH), 1750 s (C=O), 1710 s (C=O); δ_H (400 MHz, [$^2H_8$]toluene, 360 K) 0.80 (3H, t, *J* 7.1, H-1′ or H-8′), 0.85 (3H, t, *J* 7.4, H-8′ or H-1′), 1.07–1.46 (12H, m, H-6′, H-7′, H-4″, H-5″), 1.46–1.55 (2H, m, H-3″), 1.56–1.65 (2H, m, H-3″), 1.66–1.80 (2H, m, H-6″), 1.81 (2H, p, *J* 7.6, H-2′), 2.16–2.25 (2H, m, H-6″), 2.35 (1H, ddd, $J_{2''ax,1''ax}$ 10.9, $J_{2''ax,3''ax}$ 10.9, $J_{2''ax,3''eq}$ 3.9, H-2″), 2.57 (1H, ddd, $J_{2''ax,1''ax}$ 10.5, $J_{2''ax,3''ax}$ 10.5, $J_{2''ax,3''eq}$ 3.9, H-2″), 4.34–4.36 (1H, m, CHN), 4.81 (1H, ddd, $J_{1''ax,2''ax}$ 10.5, $J_{1''ax,6''ax}$ 10.5, $J_{1''ax,6''eq}$ 4.5, H-1″), 4.97 (1H, ddd, $J_{1''ax,2''ax}$ 10.5, $J_{1''ax,6''ax}$ 10.5, $J_{1''ax,6''eq}$ 4.5, H-1″), 5.05 (1H, dd, $J_{4',3'}$ 15.5, $J_{4',5'}$ 7.0, H-4′), 5.29 (1H, ddt, $J_{3',4'}$ 15.5, $J_{3',2'}$ 4.3, $J_{3',5'}$ 0.8, H-3′), 5.38 (1H, s, NH), 6.96–7.20 (10H, m, 2×Ph); *m/z* (LSMIS, mnba), 547 [$(MH)^+$, 27], 437 [$(MH)-C_8H_{14}N_2O_4$, 16], 279 [$(MH)-C_{18}H_{20}O_2$, 21], 159 [$(MH)-C_{22}H_{32}N_2O_4$, 100]; [found: $(MH)^+$, 547.3584; $C_{34}H_{46}N_2O_4$ requires *MH*, 547.3538].

3.9. Di-(1R,2S)-2-phenylcyclohexyl 1-(1′-chloro-1′-phenyl)prop-2′-yl-1,2-diazanedicarboxylate **14**

To a solution of diazenedicarboxylate **4** (39 mg, 0.090 mmol) and *trans*-β-methylstyrene (24 μL, 0.18 mmol) in dichloromethane (2 mL) cooled to −60°C under nitrogen, was added tin(IV) chloride (11 μL, 0.090 mmol). After 5 min the yellow solution turned colourless and water (0.5 mL) was added. After extraction with dichloromethane (3×5 mL), the combined organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resultant oil was purified by flash chromatography using hexane:ethyl acetate (9:1) as eluent to afford the title compound **14** (30 mg, 57%) as a colourless oil; ν_{max} (thin film)/cm^{-1} 3355 br (NH), 1756 s (C=O), 1716 s (C=O); δ_H (400 MHz, [$^2H_8$]toluene, 360 K) 1.19–1.47 (11H, m, H-4″, H-5″, H-3′), 1.48–1.76 (8H, m, H-3″, H-6″), 2.25–2.30 (1H, m, H-2″), 2.56–2.60 (1H, m, H-2″), 4.43 (1H, d, *J* 9.4, H-1′), 4.32–4.75 (1H, br m, H-2′), 4.84 (1H, ddd, $J_{1''ax,2''ax}$ 10.4, $J_{1''ax,6''ax}$ 10.4, $J_{1''ax,6''eq}$ 4.6, H-1″), 5.02 (1H, ddd, $J_{1''ax,2''ax}$ 10.4, $J_{1''ax,6''ax}$ 10.4, $J_{1''ax,6''eq}$ 4.6, H-1″), 5.59 (1H, s, NH), 6.95–7.16 (15H, m, 3×Ph); *m/z* (LSIMS, mnba) 589 [(MH)$^+$, 16], 553 [(MH)−Cl, 0.7], 237 [(MH)−$C_{24}H_{32}O_2$, 30], 159 [(MH)−$C_{23}H_{27}N_2O_4Cl$, 100]; [found: (MH)$^+$, 589.2851; $C_{35}H_{41}ClN_2O_4$ requires *MH*, 589.2836].

3.10. (−)-1-[N-(1R,2S)-2-Phenylcyclohexyloxycarbonylamino]-2-cyclohexene **16**

To anhydrous liquid ammonia (15 mL) cooled to −78°C, was added a solution of the azo-ene adduct **9** (100 mg, 0.19 mmol) in dry THF (5 mL). Freshly cut sodium metal (50 mg, 2.17 mmol) was added to the solution and a permanent blue colour developed. The cold bath was removed and the reaction mixture stirred at reflux (−33°C) for 1.5 h. The reaction was quenched by the addition of solid ammonium chloride (228 mg, 4.26 mmol) and the ammonia was allowed to evaporate. The residue was dissolved in water (5 mL) and extracted with ethyl acetate (3×50 mL). The organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure to afford an oil that was purified by flash chromatography using hexane:ethyl acetate (8:2) as eluent to afford the title compound (35 mg, 61%) as a colourless oil, $[\alpha]_D$ −7.6 (c 0.37, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 3384 br (NH), 1699 s (C=O); δ_H (400 MHz, $CDCl_3$) 1.28–1.93 (12H, br m, H-4′, H-5′, H-6′, H-3″, H-4″, H-5″), 2.20 (2H, br m, H-6″), 2.62 (1H, br m, H-2″), 3.99 (1H, br s, NH), 4.31 (1H, br m, H-1′), 4.90 (1H, ddd, $J_{1''ax,2''ax}$ 10.7, $J_{1''ax,6''ax}$ 10.7, $J_{1''ax,6''eq}$ 4.2, H-1″), 5.53 (1H, br m, H-2′), 5.76 (1H, br m, H-3′), 7.21–7.28 (5H, m, Ph); *m/z* (EI) 299 (M$^+$, 33), 158 (M−$C_7H_{11}NO_2$, 100), 91 (M−$C_{12}H_{18}NO_2$, 77).

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