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Synthesis of unusual amino acids: *N*-(*tert*-butoxycarbonyl)-L-vinyl glycine and *N*-(*tert*-butoxycarbonyl)-L-homophenylalanine†

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Abstract—The synthesis of the unusual amino acids *N*-(*tert*-butoxycarbonyl)-L-vinyl glycine and *N*-(*tert*-butoxycarbonyl)-L-homophenylalanine starting from commercially available D-xylose via an alkylative fragmentation method is described.

1. Introduction

Unusual amino acids continue to be the targets of much synthetic interest.[1] Optically active, non-proteinogenic amino acids deserve particular attention because of their documented and potential biological activities.[2] Obviously there is a demand for the synthesis of uncommon amino acids in enantiomerically pure form both for pure and applied organic and bioorganic chemistry. In principle, the design of general strategies for enantiopure amino acids is a challenge for the synthetic organic chemist. Hence, there is considerable interest in α-amino acids, both from pharmaceutical and mechanistic viewpoints.[3]

Vinyl glycine, the simplest β,γ-unsaturated-α-amino acid, is a plant toxin,[4] which has attracted considerable interest both as an irreversible inhibitor of pyridoxal phosphate-linked aspartate amino transferase as well as a chiral building block for the elaboration of complex natural products.[5] Various methods have been reported in the literature for the synthesis of vinyl glycine both in racemic and enantiomerically pure form.[6] However, the utility of this amino acid is hampered by the difficulties involved in its synthesis in enantiomerically pure form, which are often complicated by rearrangement of the double bond to the α,α-position or by an increased tendency for racemisation.

Similiarly, L-homophenylalanine, which may be viewed as a homologue of naturally occurring amino acid phenylalanine, is a new agent of pharmacological interest.[7] However, the number of procedures available for the synthesis of L-homophenylalanine[8] is limited. Herein, we describe the full details of a common strategy for the synthesis of these two unusual amino acids, with the key reaction involving alkylative fragmentation of a sugar tosylhydrazone (vide infra).[9]

2. Results and discussion

Carbohydrates, which are abundant in nature, are considered as the main stream of nature's 'chiral pool'. For the synthesis of *N*-(*tert*-butoxycarbonyl)-L-vinyl glycine **I** and *N*-(*tert*-butoxycarbonyl)-L-homophenylalanine **II**, we chose the inexpensive and readily available pentose sugar, D-xylose, as the chiral starting material. According to our retrosynthetic analysis (Scheme 1), the key chiral allyl alcohols **6** and **10** could be obtained by alkylative elimination of the tosylhydrazone of D-xylose **3**. This unprecedented alkylative fragmentation of an α-*O*-tosylhydrazone is studied in detail by our group.[9] The hydroxyl group becomes a precursor for the introduction of the amino group with inversion and the 1,2-*O*-isopropylidine would then be cleaved to the –COOH group with the loss of one carbon atom.

Accordingly, D-xylose was converted to its ethylmercaptal derivative[10] using ethanethiol in concentrated HCl, and was further converted to the di-*O*-isopropylidine-D-xylose-diethyl dithioacetal[11] using standard

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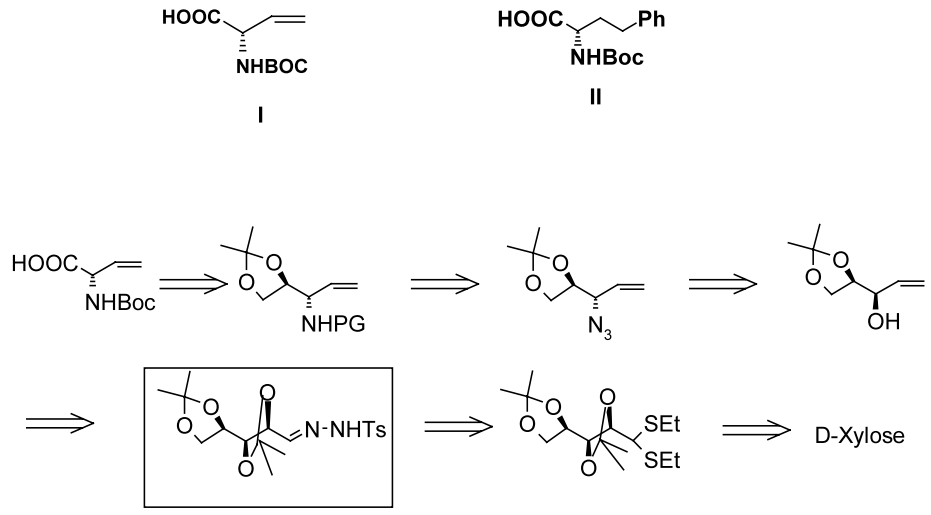
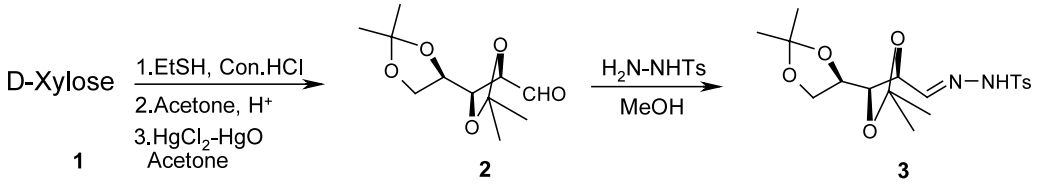


Scheme 1.

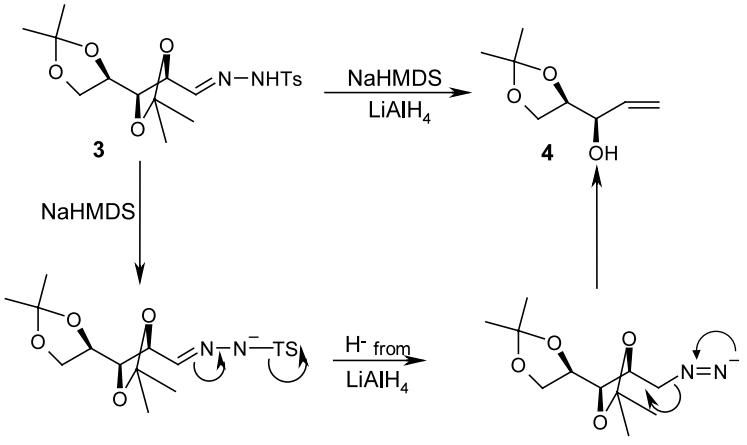
reported procedure (Scheme 2). Thioacetal was then treated with $HgCl_2$ and HgO in acetone–H_2O[12] to afford the unstable aldehyde **2**, which was immediately derivatised with *p*-toluenesulfonyl hydrazine in methanol to afford the corresponding tosylhydrazone **3**.

Exposure of the hydrazone **3** to sodium hexamethyldisilazide (NaHMDS) and $LiAlH_4$ in THF as solvent furnished allyl alcohol **4** in 52% yield by an alkylative fragmentation process,[9] wherein the first equivalent of non-nucleophilic base NaHMDS abstracts a proton from the nitrogen and hydride from $LiAlH_4$ adds to the olefinic carbon with elimination of a nitrogen molecule, *p*-toluenesulfonic acid and acetone (Scheme 3).

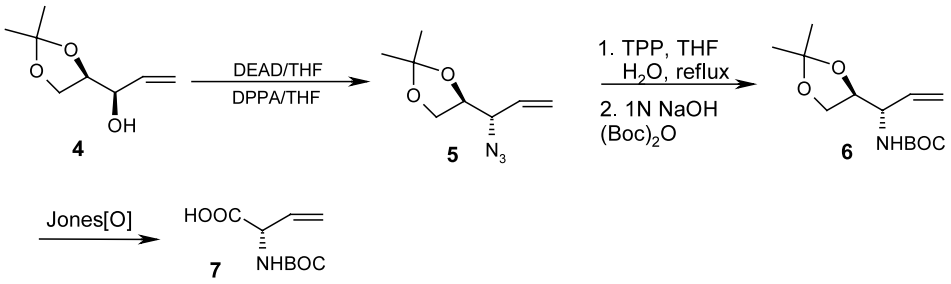
Alcohol **4** was then converted to azide **5** under Mitsunobu conditions[13] using TPP/DEAD (diethyl azodicarboxylate)/DPPA (diphenyl phosporyl azide) in THF. The azide group was reduced to an amine (TPP, H_2O in THF),[14] which was further protected in a single pot transformation as its *tert*-butyl carbamate derivative **6** by treatment with 1N aqueous NaOH and $(Boc)_2O$ (Scheme 4).



Scheme 2.



Scheme 3.



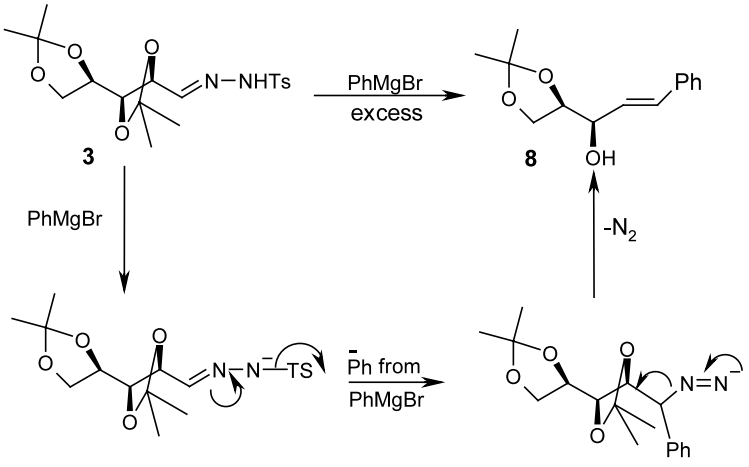
Scheme 4.

Oxidation of the Boc-protected isopropylidine moiety **6** with Jones' reagent[15] provided the carboxylic acid **7**, again in one pot, the ^{1}H NMR spectrum of which showed resonances at 4.11 ppm as a doublet due to the α-protons. The remaining protons resonated at their respective positions. The specific rotation of this compound was determined as $[\alpha]_D^{25}=+2.6$ (*c* 1.5, MeOH) [lit.[16] $[\alpha]_D^{25}=+2.8$ (*c* 4, MeOH)].

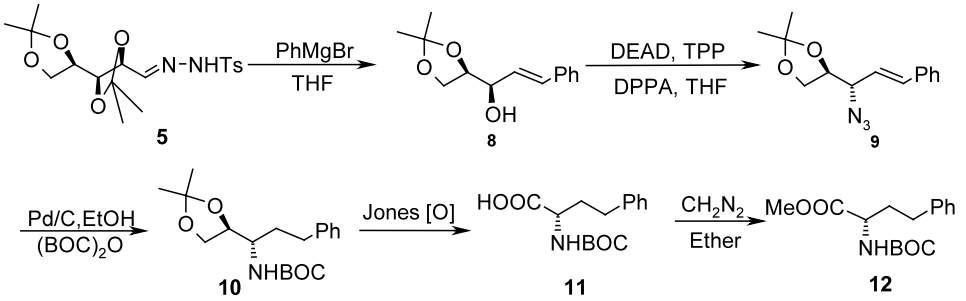
As per our synthetic plan, we began the synthesis of L-homophenylalanine from D-xylose as the chiral template. In an initial attempt, D-xylose was converted to the desired hydrazone precursor **3**, in a series of four transformations as depicted in Scheme 2. Exposure of the hydrazone **3** to Grignard reaction with PhMgBr in THF as solvent, furnished the allyl alcohol **8** in 56% yield through an alkylative fragmentation process[9] (Scheme 5).

The alcohol was then converted to azide **8** under Mitsunobu conditions using TPP/DEAD (diethyl azodicarboxylate)/DPPA (diphenylphosporyl azide) in THF (Scheme 6). The azide was reduced to an amine function by catalytic hydrogenation with palladium–carbon under hydrogen gas, which on in situ treatment with $(Boc)_2O$ afforded the NH-Boc isopropylidene **10** in one pot.

Oxidation of the Boc-protected isopropylidine **10** with Jones' reagent then provided carboxylic acid **11** again in a single step. The specific rotation of this compound was also obtained $[\alpha]_D^{25}=+5.8$ (*c* 0.9, EtOH) and other spectral features were comparable [lit.[17] value $[\alpha]_D^{25}=+6.0$ (*c* 1, EtOH)]. Finally, the structure of this unnatural amino acid was confirmed by preparing its methyl ester derivative **14** through treatment of the acid with an ethereal solution of diazomethane at 0°C. The specific



Scheme 5.



Scheme 6.

rotation of the compound was determined to be $[\alpha]_D^{25} = -13.1$ (*c* 1, MeOH) and other spectral features were also comparable [lit.[18] $[\alpha]_D^{25} = -14.7$ (*c* 1.2, MeOH)].

3. Conclusion

In conclusion, we have developed a novel procedure for the preparation of *N*-(*tert*-butoxycarbonyl)-L-vinyl glycine and *N*-(*tert*-butoxycarbonyl)-L-homophenylalanine from D-xylose via fragmentation of sugar hydrazones, which is convenient and flexible and can conveniently be used in the synthesis of molecules of biological and pharmaceutical interests.

4. Experimental

4.1. General

All solvents and reagents were purified by standard techniques. Column chromatography was performed on SiO_2 (60–120 mesh). IR spectra were recorded on Perkin–Elmer 683 spectrophotometer. Optical rotations were obtained on Jasco Dip 360 digital polarimeter. Melting points (uncorrected) were obtained using a Buchi 535 melting point apparatus. NMR spectra were recorded on a Varian Gemini 200 or Varian Unity 400 using TMS as the internal standard. Chemical shifts (δ) are reported in ppm, coupling constants (J) are reported in Hz. Mass spectra were obtained on a Finnegan-MAT 1020B (70 eV).

4.1.1. D-Xylose-(2*R*,3*R*,4*R*)-5-di-*O*-isopropylidene-[4-(methylphenyl)sulfonyl]hydrazone 3. 2,3,4,5-Di-*O*-isopropylidene-D-xylose aldehyde[12] **2** (1.7 g, 7.39 mmol) was dissolved in methanol (20 mL) and to this solution was added *p*-toluenesulfonylhydrazine (1.38 g, 7.39 mmol) and stirred for 6 h at room temperature under nitrogen. Methanol was evaporated under reduced pressure and the residue was triturated with petroleum ether (15 mL). The resulting white solid was then filtered and dried to yield tosyl hydrazone **3** (2.49 g, 72%). ^{1}H NMR ($CDCl_3$): δ 1.24–1.38 (3s, 12H), 2.40 (s, 3H), 3.25–4.0 (series of m, 5H), 7.10 (d, $J = 6.5$ Hz, 1H), 7.30 (d, $J = 7.8$ Hz, 2H, aromatic protons), 7.70 (d, $J = 7.8$ Hz, 2H, aromatic protons), 11.20 (s, 1H); mp: 153–155°C; IR ($CHCl_3$): 1630 cm^{-1}; $[\alpha]_D^{25}$: +48 (*c* 0.6, $CHCl_3$); HRMS: calcd for $C_{18}H_{26}N_2O_6$ 398.4732. Found. 398.4725.

4.1.2. (3*R*)-Hydroxy-(4*R*)-5-isopropylidine-1-pentene 4. The tosyl hydrazone of 2,3,4,5-di-*O*-isopropylidene-D-xylose **3** (1.152 g, 1 mmol) was placed in an oven-dried, nitrogen flushed 100 mL flask fitted with a septum inlet and a magnetic stirrer bar. The flask was charged with dry THF (30 mL) and cooled to 0°C. NaHMDS (1 M solution, 1 mL, 1 mmol) was added dropwise over 3 min, followed by addition of $LiAlH_4$ (0.225 g, 2 mmol) at once under a stream of N_2 at the same temperature and allowed to stir at room temperature for 8 h. Saturated aqueous Na_2SO_4 solution was added and the reaction mixture was extracted with ether, washed with water, brine, dried (Na_2SO_4) and solvent was evaporated under reduced pressure. The product was isolated by column chromatography (1:10 ethyl acetate–hexane as eluent) to furnish **4** as a colourless liquid (0.237 g, 52%). ^{1}H NMR ($CDCl_3$): δ 1.31 and 1.42 (2s, 6H), 2.20–2.32 (bs, 1H), 3.68–3.80 (m, 1H), 3.90–4.02 (m, 3H), 5.15–5.41 (dd, 2H, $J = 11.2$, 17.9 Hz), 5.67–5.85 (m, 1H); IR ($CHCl_3$): 3500 cm^{-1}, $[\alpha]_D^{25}$: +6.2 (*c* 1, $CHCl_3$); HRMS: calcd for $C_8H_{14}O_3$ 158.1968. Found 158.1937.

4.1.3. (3*S*)-Azido-(4*R*)-5-isopropylidene-1-pentene 5. To a solution of PPh_3 (2.72 g, 10.4 mmol) in dry THF (30 mL) under a nitrogen atmosphere at −20°C was added diethyl azodicarboxylate (1.45 mL, 10.4 mmol) dropwise. After stirring for 10 min, a solution of alcohol **4** (1.5 g, 9.5 mmol) in THF (10 mL) was added slowly. The reaction mixture was stirred for 30 min at the same temperature and then cooled to 0°C and diphenyl phosphoryl azide (2.45 mL, 11.3 mmol) was added dropwise and the reaction mixture was stirred for 6 h at room temperature, after which it was quenched with water and extracted with ethyl acetate (50 mL, 2×25 mL). The combined extracts were washed with brine, dried (Na_2SO_4), concentrated and the residue was purified by silica gel column chromatography to afford azide **5** as a colourless viscous liquid (1.21 g, 70%). ^{1}H NMR ($CDCl_3$): δ 1.35 and 1.44 (2s, 6H), 3.75–4.15 (series of m, 4H), 5.25–5.40 (2H, dd, $J = 10.1$, 18.5 Hz), 5.90–6.01 (m, 1H); IR (neat): 2105, 1600 cm^{-1}; HRMS: calcd for $C_{18}H_{13}N_3O_2$ 183.2098. Found 183.1995.

4.1.4. (3*S*)-[(*tert*-Butoxycarbonyl)amino]-(4*R*)-5-isopropylidene-1-pentene 6. A solution of **5** (0.95 g, 5.19 mmol) and TPP (1.35 g, 5.19 mmol) in THF (15 mL) was heated under reflux for 2 h. After cooling, water (1 mL) was added and the mixture was stirred overnight at room temperature. To the reaction mixture, 10% aq. NaOH solution (5 mL) was added and the flask was cooled to 0°C. $(Boc)_2O$ (1.35 g, 6.2 mmol) in THF (5 mL) was added dropwise and the same temperature was maintained for 4 h. The reaction mixture was extracted with ethyl acetate (3×10 mL) and the combined extracts were washed with water, brine and dried (Na_2SO_4). Concentration and purification by column chromatography provided **6** as a viscous oil (0.97 g, 73% yield). ^{1}H NMR ($CDCl_3$): δ 1.35 and 1.40 (2s, 6H), 1.52 (s, 9H), 3.71–4.51 (series of m, 4H), 5.15 (bd, 1H), 5.55–5.60 (m, 3H); IR ($CHCl_3$): 1679, 3283 cm^{-1}; $[\alpha]_D^{25}$: −35.3 (C1, $CHCl_3$); HRMS: calcd for $C_{13}H_{23}NO_4$ 257.329. Found 257. 298.

4.1.5. (2*S*)-[*N*-(*tert*-Butoxycarbonyl)amino]-3-pentenoic acid 7. To a solution of **6** (0.5 g, 1.57 mmol) in alcohol-free acetone (10 mL) at 0°C, freshly prepared Jones reagent (1 mL) was added dropwise. After stirring for 2 h at room temperature, excess of Jones reagent was quenched with isopropanol. Acetone was removed and extracted with ethyl acetate (4×10 mL). The extracts were dried (Na_2SO_4), concentrated and purified by column chromatography to afford **7** as a highly viscous liquid (0.226 g, 58%). ^{1}H NMR ($CDCl_3$): δ 1.49 (s, 9H), 4.75 (bd, 1H), 5.32–6.10 (m, 3H); IR ($CHCl_3$): 1637,

2995 cm^{-1}; $[\alpha]_D^{25}$: +2.6 (*c* 1.5, MeOH); HRMS: calcd for $C_9H_{15}NO_4$ 201.2218. Found 201.2025.

4.1.6. 1-Phenyl-(3*R*)-hydroxy-(4*R*)-5-isopropylidene-1-pentene 8. To a solution of PhMgBr [freshly prepared from PhBr (9.45 mL, 0.09 mmol) and magnesium (2.33 g, 0.096 mmol)] in ether (200 mL) at 0°C was added dropwise a solution of **3** (11.94 g, 0.03 mmol) in a mixed solvent of THF (100 mL) and ether (50 mL) for 30 min with constant stirring under a nitrogen atmosphere. The reaction mixture was slowly warmed up to room temperature and stirred for an additional 4 h. The reaction mixture was quenched with saturated aq. solution of NH_4Cl and the organic layer was separated and washed with water, brine and dried (Na_2SO_4). After concentration and column chromatography, allyl alcohol **8** was obtained as a colourless syrupy liquid (3.93 g, 56%). ^1H NMR ($CDCl_3$): δ 1.35 and 1.41 (2S, 6H), 2.45 (m, 1H, -OH), 3.65–4.12 (series of m, 3H), 4.32–4.48 (m, 1H), 5.62 (dd, $J=9.2$, 13.3 Hz, 1H), 6.68 (d, $J=13.3$, 1H), 7.20–7.38 (m, 5H, aromatic); IR (neat): 3500 cm^{-1}; $[\alpha]_D^{25}$:+21.2 (*c* 0.5, $CHCl_3$), HRMS: calcd for $C_{14}H_{18}O_3$ 234.2944. Found 238.2543.

4.1.7. 1-Phenyl-(3*S*)-azido-(4*R*)-5-isopropylidene-1-pentene 9. To a solution of TPP (4.32 g, 16.35 mmol) in dry THF (40 mL) under a nitrogen atmosphere, –20°C was added diethyl azodicarboxylate (2.56 mL, 16.5 mmol) dropwise. After stirring for 10 min, alcohol **8** (3.51 g, 15 mmol) in THF (20 mL) was added slowly. The reaction mixture was stirred for 30 min at the same temperature and then allowed to come to 0°C and diphenyl phosphoryl azide (3.9 mL, 18 mmol) was added dropwise. After stirring for 6 h at room temperature, the reaction mixture was quenched with water and extracted with ethyl acetate (100 mL, 2×50 mL). The combined extracts were washed with brine, dried (Na_2SO_4), concentrated and the residue was purified by silica gel column chromatography to afford azide **9** as a colourless viscous liquid (2.86 g, 74%). ^1H NMR ($CDCl_3$): δ 1.35 and 1.44 (2S, 6H), 3.78–4.28 (series of m, 4H), 6.13 (dd, $J=8.1$, 13.7 Hz, 1H), 6.66 (dd, $J=5.5$, 13.7 Hz), 7.22 –7.45 (m, 5H, aromatic); IR (neat): 2105, 1600 cm^{-1}; $[\alpha]_D^{25}$: −13.5 (*c* 1.0, $CHCl_3$), HRMS: calcd for $C_{14}H_{17}N_3O_2$ 259.3072. Found 259. 2975.

4.1.8. 1-Phenyl-(3*S*)-[*N*-(*tert*-butoxycarbonyl)amino]-(4*R*)-5-isopropylidene-1-pentene 10. A solution of azide **9** (1 g, 3.86 mmol) in absolute ethanol (30 mL) was added and hydrogenated over 10% Pd/C (10 mg) at room temperature at 1 atm pressure for 24 h. The reaction was analysed to check for completion by TLC. A solution of $(Boc)_2O$ (0.925 g, 4.24 mmol) in EtOH (5 mL) was added in one portion and stirring was continued for another 6 h, then the catalyst was removed by filtration through Celite. The filtrate was concentrated to furnish amine **10** as a syrup after column chromatography (0.838 g, 65%). ^1H NMR ($CDCl_3$): δ 1.35 and 1.45 (2S, 6H), 1.47 (s, 9H), 1.80–1.92 (m, 2H), 2.60–2.82 (m, 2H), 3.61–4.15 (series of m, 3H), 4.65 (bd, 1H), 7.15–7.42 (m, 5H, aromatic); IR (neat): 1638 cm^{-1}; HRMS: calcd for $C_{19}H_{27}NO_4$ 333.4276. Found 333.4156.

4.1.9. (2*S*)-[(*tert*-Butoxycarbonyl)amino]-4-phenylbutanoic acid 11. To a solution of **10** (0.5 g, 1.5 mmol) in alcohol-free acetone (10 mL) at 0°C freshly prepared Jones' reagent (1 mL) was added dropwise. After stirring for 24 h at room temperature, excess Jones' reagent was quenched with isopropanol. Acetone was removed on a rotavapor and to the residue, water was added and extracted with ethyl acetate (4×10 mL). The extracts were dried (Na_2SO_4), concentrated and purified by column chromatography to afford **11** as a highly viscous liquid (0.208 g, 50%). ^1H NMR ($CDCl_3$): δ 1.51 (S, 9H), 1.93–2.33 (m, 2H), 2.65 (t, 2H, $J=4.76$ Hz), 4.26–4.42 (m, 1H), 5.12 (bd, 1H), 7.1–7.35 (m, 5H, aromatic); ^{13}C NMR ($CDCl_3$): 176.5, 157, 140.6, 143.3, 126.0, 80, 54, 34.2, 31.5, 28.1, IR (neat): 1720, 2975, 3400 cm^{-1}; $[\alpha]_D^{25}=+5.8$ (*c* 1, EtOH); HRMS: calcd for $C_{15}H_{19}NO_4$ 277.2194. Found. 277.2085.

4.1.10. (2*S*)-[*N*-(*tert*-Butoxycarbonyl)amino]-4-phenylmethyl butanoate 12. A 25 mL round-bottomed flask was charged with ether (6 mL) and 50% aq. KOH solution (6 mL) and chilled to −5°C using coolant. To this well stirred cooled solution, NMO (82 mg, 0.8 mmol) was added portionwise. After stirring for 5 min, the yellow ether layer was separated and dried over KOH. The yellow ethereal solution of diazomethane was added to the cooled solution of **11** (0.05 g, 0.16 mmol) in ether (5 mL) and the mixture was allowed to stir for 30 min. Ether was removed and the residue was purified by silica gel column chromatography to afford methyl ester **12** as a syrupy liquid (0.05 g, 96% yield). ^1H NMR ($CDCl_3$): δ 1.48 (S, 9H), 2.08–2.21 (m, 2H), 2.62 (t, 2H, $J=5$ Hz), 3.79 (s, 3H), 4.20–4.40 (m, 1H), 5.05 (bd, 1H), 7.15–7.3 (m, 5H, aromatic), IR (neat): 1635, 1732 cm^{-1}; $[\alpha]_D^{25}=-13.1$ (*c* 1, MeOH), HRMS: calcd for $C_{16}H_{21}NO_4$ 291.3462. Found. 291. 3123.

Acknowledgements

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