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LEWIS ACID PROMOTED DIASTEREOSELECTIVE MANNICH REACTION OF β -LACTAM – TETHERED ALDIMINES WITH 1-METHOXY-1-TRIMETHYLSILOXY-2,2-DIMETHYLETHENE

Katarina Vazdar, Davor Margetić, and Ivan Habuš*

Ruđer Bošković Institute, Bijenička c. 54, P.O. Box 180, HR-10002 Zagreb,
Croatia
ihabus@irb.hr

Dedicated to Professor Francis Johnson on the occasion of his 80th birthday

Abstract – Lewis acid (ZnI_2) – promoted Mannich reaction of azetidin-2-one – tethered aldimines **3a-r** with silylenol ether **4** in toluene at $-20\text{ }^\circ\text{C}$ afforded a diastereomeric mixture of β -amino acid esters **5a-r/6a-r**. The effect of the amount of zinc(II) iodide, equimolar (100 mol%) and catalytic (20 mol%), on the chemical yield and the product stereoisomeric ratio was studied. The diastereoselective Mannich reaction of imine **3a** with silylenol ether **4** at low temperature ($-20\text{ }^\circ\text{C}$) in toluene under equimolar zinc(II) iodide catalysis provided the best chemical yield – 99% combined with the highest diastereoselectivity of β -amino acid esters **5a/6a** – 85:15%. Furthermore, the influence of various groups on azetidin-2-one – tethered imines **3a-r** (R^1 = phenyl, ferrocenyl; R^2 = alkyl, aryl, ferrocenyl) has been applied in the Mannich reaction leading to the formation of two stereoisomers of β -amino acid esters **5a-r/6a-r** with diastereomeric ratio varying from 92:8 to 59:41%.

INTRODUCTION

Mannich reaction, in the modern organic synthesis, represents an excellent tool for the C–C bond construction that makes it a favorable choice in natural product synthesis.¹ However, the application of the Mannich reaction in organic synthesis is often accompanied by numerous disadvantages, especially in the design of asymmetric variants of the reaction.² Nevertheless, numerous synthetic variants of the

Mannich reaction were developed during the 20th century,³⁻⁸ ensuring the production of Mannich bases with high enantiomeric and diastereomeric purity.⁹⁻¹⁷ One of these methods is the stereoselective Lewis acid promoted condensation of silylenol ethers to imines, an indirect route to enantio- and diastereo-enriched β -amino acids, first described by Ojima and coworkers.¹⁸

Monocyclic β -lactam derivatives occupy a central place among medicinally important compounds due to their diverse and interesting antibiotic activities.^{19,20} Consequently, the development of their synthesis and application as novel biologically active compounds has been of considerable interest to the scientific community in the past few decades.²¹⁻²⁵ Their potential is also recognized in the field of amino acid and peptide synthesis, where they provide access to non – protein α - and β -amino acids and their peptides.²⁶⁻²⁹

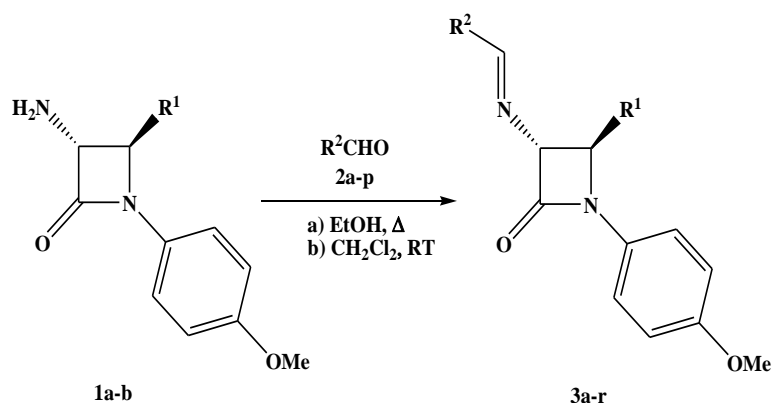
The synergy of two excellent stereoselective methods: (i) chiral ester enolate – imine condensation strategy^{13,29,30} that was applied to the asymmetric synthesis of *trans*-3-amino- β -lactams^{29,31} and (ii) Lewis acid promoted Mannich condensation of the β -lactam – tethered aldimines with silyl enol ethers^{18,32} provides multifunctional compounds, e.g. diamino acids and diamino alcohols. The multifunctional compounds of this type can serve as valuable precursors for exploration in the field of peptidomimetics,^{28,33,34} enzyme inhibition,^{25,35} and the synthesis of macrocyclic compounds.^{36,37}

In continuation of our research in the field of β -lactam chemistry^{31,32,38-40} we further explored β -lactams as synthons and chiral precursors in diastereoselective synthesis. We report here the study on the chemical yield and diastereoselectivity of the Lewis acid – promoted Mannich reaction of azetidin-2-one – tethered aldimines **3a-r** with 1-methoxy-1-trimethylsilyloxy-2,2-dimethylethene **4**.

RESULTS AND DISCUSSION

We applied lithium chiral ester enolate – imine condensation strategy^{13,30,34,41} to the asymmetric synthesis^{29,31} of *trans*-3-amino- β -lactams **1a-b**. Treatment of *trans*-3-amino- β -lactams **1a-b** with a variety of aldehydes **2a-p** in boiling ethanol followed by stirring in dichloromethane at room temperature in the presence of sodium sulfate provided^{32,38} the corresponding imines **3a-r** (Scheme 1). Aryl and ferrocenyl imines **3a-j** and **3m-r** (isolated yields vary from 62 to 89%, Table 1) were purified by recrystallization, while alkyl imines **3k-l** (¹H NMR spectra calculated yields: 63 and 61%) were generated³⁸ in dichloromethane at room temperature, filtered, evaporated to dryness, and as such applied in the next reaction step.

1-Methoxy-1-trimethylsilyloxy-2,2-dimethylethene **4** was used in the Mannich reaction with azetidin-2-one – tethered imines **3a-r**. We studied the Mannich reaction of imine **3a** and silylenol ether **4** in the presence of equimolar (100 mol%) and catalytic (20 mol%) amount of zinc(II) iodide in toluene at low

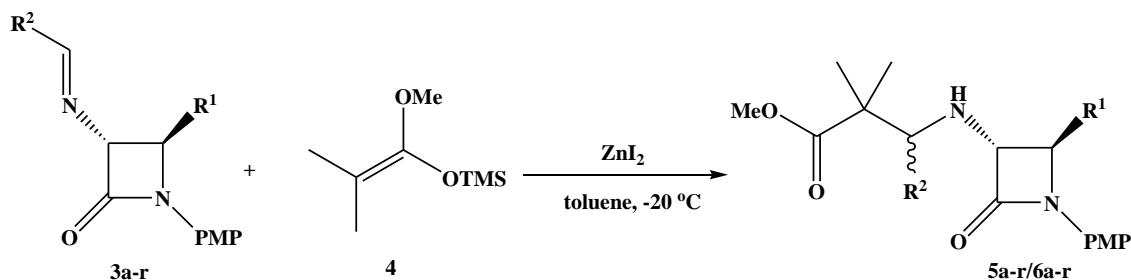


Scheme 1

Table 1. Yields of imines **3a-r**

Entry	Imine	R ¹	R ²	Yield (%)
1	3a	C ₆ H ₅	C ₆ H ₅	82
2	3b	C ₆ H ₅	4-MeOC ₆ H ₄	72
3	3c	C ₆ H ₅	3,4-(MeO) ₂ C ₆ H ₃	78
4	3d	C ₆ H ₅	4-FC ₆ H ₄	89
5	3e	C ₆ H ₅	4-CF ₃ C ₆ H ₄	64
6	3f	C ₆ H ₅	2-NO ₂ C ₆ H ₄	82
7	3g	C ₆ H ₅	3-NO ₂ C ₆ H ₄	58
8	3h	C ₆ H ₅	4-NO ₂ C ₆ H ₄	83
9	3i	C ₆ H ₅	<i>trans</i> -C ₆ H ₅ CH=CH	84
10	3j	C ₆ H ₅	3-pyridyl	84
11	3k	C ₆ H ₅	Me ₃ C	63
12	3l	C ₆ H ₅	cyclohexyl	61
13	3m	C ₆ H ₅	2-furyl	86
14	3n	C ₆ H ₅	5-C ₆ H ₅ -2-furyl	76
15	3o	C ₆ H ₅	5-Me-2-furyl	85
16	3p	C ₆ H ₅	Fc	78
17	3q	Fc	C ₆ H ₅	62
18	3r	Fc	4-CF ₃ C ₆ H ₄	71

(−20 °C) and room temperature (RT), Scheme 2, Table 2. Diastereoselectivities were reasonable but chemical yield of the reaction depended on the amount of zinc(II) iodide and temperature. We found that zinc(II) iodide provided the best chemical yield (99%) combined with the highest diastereoselectivity (85:15%) using equimolar amount of zinc(II) iodide at −20 °C, while at RT the reaction only proceeded with the equimolar amount of zinc(II) iodide and moderate stereoselectivity (72:28%) (Table 2, entry 1). We continued our research studying the influence of various groups on imine **3** (R¹ = phenyl, ferrocenyl; R² = alkyl, aryl, ferrocenyl) on diastereomeric ratio and product yield of the reaction.



Scheme 2

Table 2. Yield and diastereoselectivity dependency in the Mannich reaction of imines **3a-r** and silylenol ether **4** in toluene at $-20\text{ }^{\circ}\text{C}$ on the amount of zinc(II) iodide and R^1 and R^2 substituents

Entry	Imine	Product	R^1	R^2	20 mol% ZnI_2		100 mol% ZnI_2	
					Yield (%)	$^{\text{c}}5:6$	Yield (%)	$^{\text{c}}5:6$
1	3a	5a/6a	C_6H_5	C_6H_5	66 ^b -	78:22 -	99 ^b 99	85:15 72:28
2	3b	5b/6b	C_6H_5	4-MeOC $_6\text{H}_4$	86	72:28	83	81:19
3	3c	5c/6c	C_6H_5	3,4-(MeO) $_2\text{C}_6\text{H}_3$	97	87:13	97	88:12
4	3d	5d/6d	C_6H_5	4-FC $_6\text{H}_4$	56	86:14	90	90:10
5	3e	5e/6e	C_6H_5	4-CF $_3\text{C}_6\text{H}_4$	68	88:12	87	92:8
6	3f	5f/6f	C_6H_5	2-NO $_2\text{C}_6\text{H}_4$	34	70:30	51	83:17
7	3g	5g/6g	C_6H_5	3-NO $_2\text{C}_6\text{H}_4$	72	60:40	93	77:23
8	3h	5h/6h	C_6H_5	4-NO $_2\text{C}_6\text{H}_4$	77	86:14	98	87:13
9	3i	5i/6i	C_6H_5	<i>trans</i> -C $_6\text{H}_5\text{CH}=\text{CH}$	91	85:15	96	92:8
10	3j	5j/6j	C_6H_5	3-pyridyl	-	-	97	71:29
11	3k	5k/6k	C_6H_5	Me $_3\text{C}$	-	-	-	-
12	3l	5l/6l	C_6H_5	cyclohexyl	-	-	-	-
13	3m	5m/6m	C_6H_5	2-furyl	68	59:41	80	66:34
14	3n	5n/6n	C_6H_5	5-C $_6\text{H}_5$ -2-furyl	70	76:24	79	83:17
15	3o	5o/6o	C_6H_5	5-Me-2-furyl	36	72:28	43	76:24
16	3p	^a5p/6p	C_6H_5	Fc	78	69:31	65	62:38
17	3q	5q/6q	Fc	C_6H_5	21	55:45	48	59:41
18	3r	5r/6r	Fc	4-CF $_3\text{C}_6\text{H}_4$	46	68:32	52	79:21

^aRef. 32; ^bReaction performed at RT; ^cThe diastereomeric ratio was determined by integration of well-resolved signals in the ^1H NMR spectra of the crude reaction mixtures before purification and confirmed by RP-HPLC (Figure 1).

A variety of the substituents (Table 2, entries 1-9) on phenyl ring at the R^2 - position generated high chemical yields (83 to 99%) except for $\text{R}^2 = 2\text{-NO}_2\text{C}_6\text{H}_4$ (entry 6, 51%). The best diastereomeric ratios (90:10 and 92:8%) were obtained with $\text{R}^2 = 4\text{-FC}_6\text{H}_4$, $4\text{-CF}_3\text{C}_6\text{H}_4$ (entries 4-5) and $\text{R}^2 = \textit{trans}\text{-C}_6\text{H}_5\text{CH}=\text{CH}$ (92:8%, entry 9). Interestingly, the *o*-, *m*-, and *p*-position of NO_2 - group on the phenyl ring (entries 6-8) significantly affected the product chemical yield **5g-i/6g-i** (51, 93, and 98%) and the stereoselectivity 83:17 and 77:23%, respectively. The phenyl displacement with $\text{R}^2 = 3\text{-pyridyl}$ (entry 10)

and alkyl-substituents ($R^2 = \textit{tert}$ -butyl, cyclohexyl; entries 11-12) resulted in moderate stereoselectivity (71:29%) in combination with high chemical yield for **5j/6j** (97%), while complete failure in the product formation was observed for **5k-l/6k-l**. The substituents, e.g. 2-furyl, 5-phenyl-2-furyl, and 5-methyl-2-furyl, at the R^2 -position in **5m-o/6m-o** resulted with chemical yield's drop from 80 to 43% (Table 2, entries 13-15) and low to moderate stereoselectivities 66:34 and 83:17%, respectively. The combination of aryl and ferrocenyl substituents at the R^1 - and R^2 -position resulted in moderate chemical yields and stereoselectivities (Table 2, entries 16-18). A fine balance between steric and electronic factors of the substituents at the R^1 - and R^2 -position on the β -lactam ring is needed in order to achieve high chemical yield in combination with excellent stereoselectivity. This balance has been the most probably achieved with $R^1 = \text{phenyl}$ and $R^2 = 4\text{-FC}_6\text{H}_4$, $4\text{-CF}_3\text{C}_6\text{H}_4$, and $\textit{trans}\text{-C}_6\text{H}_5\text{CH}=\text{CH}$, (Table 2, entries 4, 5, and 9).

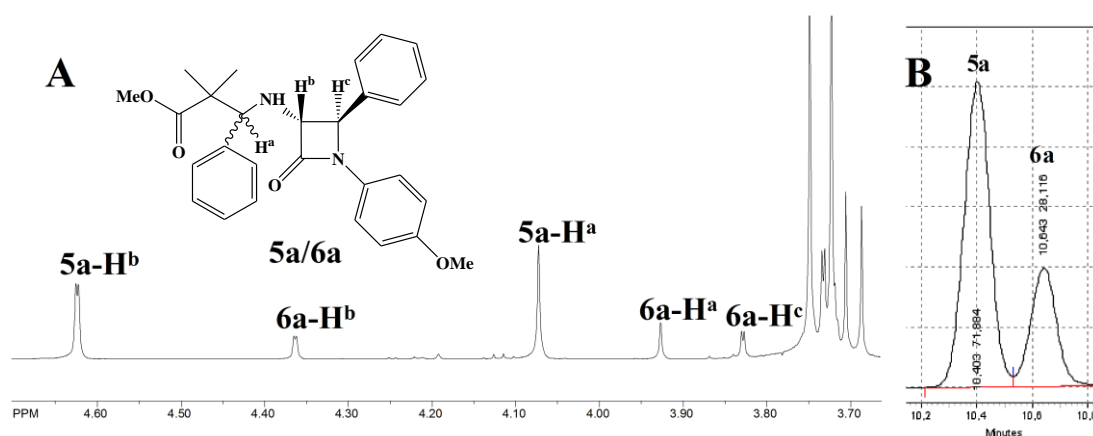


Figure 1. (A) ^1H NMR spectra of C3 H^a , C3' H^b , and C4' H^c well – resolved proton signals and (B) RP-HPLC profile of **5a/6a** diastereomeric mixture.

Although the reaction mechanism in the Lewis acid promoted diastereoselective Mannich reaction is unknown, the diastereoselectivity might be rationalized assuming that firstly imine with zinc reagent adopts the chelate conformation, followed by the nucleophilic attack which might occur from the less hindered side. Analogous mechanistic rationale was offered by Wu and Ishimaru for Cu^{42} and ZnOTf_2^{43} catalyzed reactions, or by Takahashi,⁴⁴ Enders,⁴⁵ and Gálvez⁴⁶ (Figure 2). The assumption that the first mechanistic step is chelation of ZnI_2 catalyst to imine and carbonyl lone pairs is supported in this study by the experiment without ZnI_2 catalyst, in which case no reaction took place.

To elucidate the origins of diastereoselection of the Mannich reaction, a computational study was performed, with the density functional theory method B3LYP/LanL2dz. The structures of imines and ZnI_2

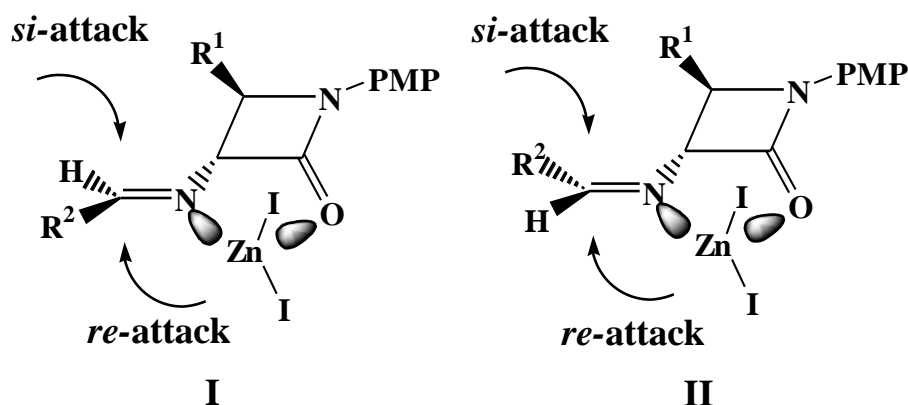


Figure 2. The proposed transition states **I** and **II** for the chelated β -lactam-imine and ZnI_2 complexes according to Enders.⁴⁵

conjugation of imine bond with aromatic substituent at the R^2 -position (as illustrated for $3\text{e}@\text{ZnI}_2$, Figure 3(A)). The complex structures which have substituents at the R^2 -position more distant from substituent at the R^1 -position were calculated as energetically favorable (Figure 2, **I**) by 8.1 kJ mol^{-1} . The orientations of PMP and substituents at the R^1 -position govern the approach of nucleophilic reagent mainly from the *si*-face, leading to (*S*)-product. This conclusion was further corroborated by the molecular orbital analysis. For example, Figure 3(B) depicts LUMO for $3\text{e}@\text{ZnI}_2$, while Figure 4 depicts its LUMO plotted on the electron density isosurface. The inspection of these surfaces reveals that the combination of stereoelectronic factors causes the preferential attack to the *re*-face of imine system. Analysis of Mulliken charge distribution and molecular orbital coefficients on imine bond indicated that the change in the electronic nature of substituent at the R^2 -position does not correlate solely with the increase in diastereoselection.

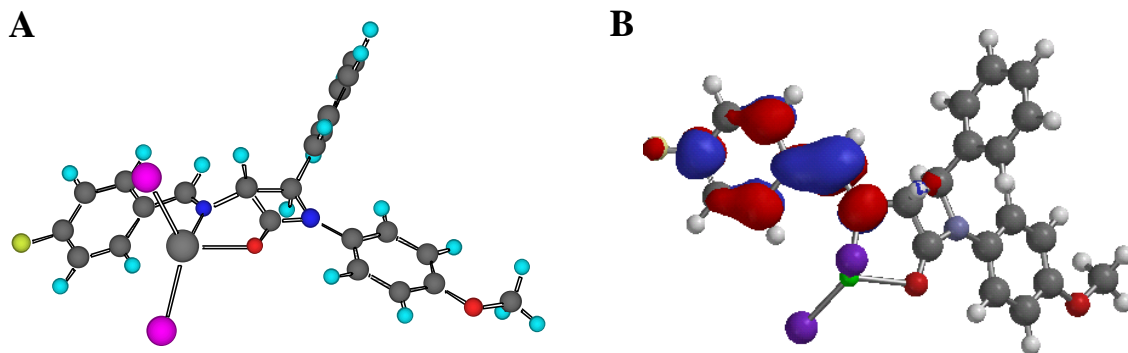


Figure 3. (A) B3LYP/LanL2dz optimized structure of $3\text{e}@\text{ZnI}_2$; (B) LUMO of $3\text{e}@\text{ZnI}_2$ (isovalue = 0.032)

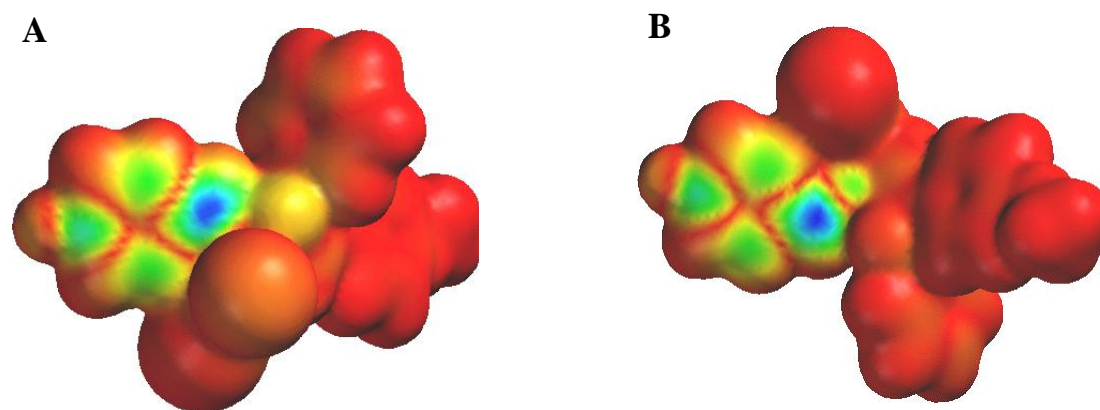


Figure 4. LUMO of $3e@ZnI_2$ plotted on electron density isosurface (isovalue = 0.002 electrons/ au^3), (A) *si*-face, (B) *re*-face

CONCLUSION

The study was focused on the Lewis acid (ZnI_2) – promoted diastereoselective Mannich reaction of the β -lactam – tethered aldimines $3a-r$ with 1-methoxy-1-trimethylsilyloxy-2,2-dimethylethene **4** in toluene at $-20\text{ }^\circ\text{C}$ that afforded a diastereomeric mixture of β -amino acid esters $5a-r/6a-r$. The effect of the amount of zinc(II) iodide, equimolar (100 mol%) and catalytic (20 mol%) on the chemical yield and the product stereoisomeric ratio was studied. The diastereoselective Mannich reaction of imine **3a** with silylenol ether **4** at low temperature ($-20\text{ }^\circ\text{C}$) in toluene under equimolar zinc(II) iodide catalysis provided the best chemical yield – 99% combined with the highest diastereoselectivity of β -amino acid esters $5a/6a$ – 85:15%. Furthermore, the influence of various groups on azetidin-2-one – tethered imines $3a-r$ (R^1 = phenyl, ferrocenyl; R^2 = alkyl, aryl, ferrocenyl) has been applied in the Mannich reaction leading to the formation of two stereoisomers of β -amino acid esters $5a-r/6a-r$ with diastereomeric ratio varying from 92:8 to 59:41%.

To elucidate the origins of diastereoselection of the Mannich reaction, a computational study was performed, with the density functional theory method B3LYP/LanL2dz. The structures of imines and ZnI_2 complexes $3a-3r@ZnI_2$ were fully optimized, and they adopt distorted tetrahedral geometry and full conjugation of imine bond with aromatic substituent at the R^2 -position (as illustrated for $3e@ZnI_2$, Figure 3(A)). The complex structures which have substituents at the R^2 -position more distant from substituent at the R^1 -position were calculated as energetically favorable (Figure 2, I) by 8.1 kJ mol^{-1} . The orientations of PMP and substituents at the R^1 -position govern the approach of nucleophilic reagent mainly from the *si*-face, leading to (*S*)-product. This conclusion was further corroborated by the molecular orbital analysis.

Analysis of Mulliken charge distribution and molecular orbital coefficients on imine bond indicated that the change in the electronic nature of substituent at the R²-position does not correlate solely with the increase in diastereoselection.

EXPERIMENTAL

Melting points were determined on a Reichert Thermovar 7905 apparatus and are not corrected. The IR spectra were recorded on a PerkinElmer Spectrum RX I FT-IR System spectrometer (KBr pellets technique) (PerkinElmer Instruments, Norwalk, CT, USA). The ¹H and ¹³C NMR spectra (in CDCl₃ at RT) were measured on a Bruker AV 300 and/or AV 600 spectrometer (Bruker BioSpin GmbH., Rheinstetten, Germany), δ is given in ppm relative to tetramethylsilane as the internal reference. Microanalysis was performed on a PE 2400 Series II CHNS/O Analyzer (PerkinElmer Instruments, Shelton, CT, USA). Optical rotations: Optical Activity Automatic Polarimeter AA-10 in 1 dm cell; *c* in g/100 mL (Optical Activity Ltd., Ramsey, England). Column chromatography on silica gel 60, 70-230 mesh, 60 Å (E. Merck, Darmstadt, Germany) was performed at RT. Thin layer chromatography was carried out on TLC aluminium sheets, 20 × 20 cm, silica gel 60 F₂₅₄ and preparative thin layer chromatography on PLC plates, 20 × 20 cm, silica gel 60 F₂₅₄, 1 mm (E. Merck). RP-HPLC analysis was performed on a HPLC System (Dr. ing. Herbert Knauer GmbH., Berlin, Germany) supplied with UV/VIS WellChrom Diode Array Detector K-2800 using Knauer 5 μm Kromasil C18 (reversed phase) 4.0 x 250 mm HPLC column operated at RT and flow rate 1 mL/min; Method I (for compounds **5a/6a**, **5f-j/6f-j**, **5m-p/6m-p**, and **5r/6r**) – linear gradient of water containing 9% AccQTag Eluent A Concentrate (Solvent A) and acetonitrile (solvent B): 40% A + 60% B, 0 min; 5% A + 95% B, 17 min; 40% A + 60% B, 3 min. Method II (for compounds **5b/6b**) – isocratic gradient of water containing 0,1% formic acid (solvent A) and methanol containing 0,1% formic acid (solvent B) in ratio 35:65, 80 min. Method III (for compounds **5c/6c** and **5q/6q**) – isocratic gradient of water containing 0,1% formic acid (solvent A) and methanol containing 0,1% formic acid (solvent B) in ratio 40:60, 80 min. NP-HPLC analysis was performed on a Knauer HPLC System using Nucleosil 100-5 (normal phase), 5 μm, 4.6 x 250 mm HPLC column (Macherey-Nagel GmbH & Co. KG, Düren, Germany) operated at RT and flow rate 1 mL/min. Method IV (for compounds **5d-e/6d-e**) – isocratic gradient of hexane (solvent A) and 2-propanol (solvent B) in ratio 98:2, 10 min. LC-MS analysis of compounds **5a-j/6a-j** and **5m-o/6m-o** was performed on an Agilent 1200 LC-MS System equipped with an Agilent Diode Array Detector and an Agilent 6410 Triple Quadrupole Mass Spectrometer Detector applying electrospray ionization (ESI) (Agilent Technologies Inc., Wilmington, DE, USA) and Agilent Zorbax, C18 (reversed phase), 3.5 μm, 4.6 x 75 mm HPLC column (Agilent Technologies Inc.) operated at RT and flow rate 0.5 mL/min. Separation was achieved

applying an isocratic gradient of water containing 0.1% formic acid (solvent A) and acetonitrile (solvent B) in ratio of 30:70, 60 min. High resolution mass spectra (HRMS) of compounds **5i/6i**, **5n-o/6n-o**, **5q/6q** and **5r/6r** were obtained on a matrix-assisted laser desorption/ionization-time-of-flight 4700 Proteomics Analyzer MALDI-TOF/TOF Mass Spectrometer (Applied Biosystems, Foster City, CA, USA) equipped with Nd:YAG laser operating at 355 nm and firing rate of 200 Hz in positive ion reflector mode, 1600 shots per spectrum was taken with mass range 100 - 900 Da, focus mass 400 Da and delay time 500 ns. Vitamin B6 and azithromycin were used for external mass calibration.

Geometrical optimizations were carried out employing B3LYP hybrid functional DFT method (Becke's 3 parameter functional with the non-local correlation provided by the expression of Lee *et al.*)⁴⁷ employing LANL2DZ basis set. Calculations were performed using *Gaussian03* suite of programs,⁴⁸ implemented on dual core Opteron 240 personal computer under Linux operating system and computer cluster Isabella at the University of Zagreb Computing Center. Harmonic vibration frequencies were calculated for all localized stationary structures to verify whether they are true minima.

trans-3-Amino- β -lactams **1a-b** were prepared according to the literature,^{29,31} while homochiral β -lactam – tethered aldimines **3a-h**, **3j-l**, and **3p-q** were prepared according to the literature proceeding.³⁸ Synthesis and structure determination of methyl (3*S*)- **5p** and (3*R*)-(*trans*-(3'*R*,4'*R*))-3-amino-1-(4-methoxyphenyl)-2-oxo-4-phenylazetid-3-yl)-2,2-dimethyl-3-ferrocenylpropanoate **6p** is described in the literature.³²

Preparation of azetid-2-one – tethered imines **3i**, **3m-o**, and **3r**

General Procedure. – A mixture of *trans*-3-amino- β -lactams **1a-b** and aldehydes **2e**, **2i**, and **2m-o** was dissolved in anhydrous EtOH (5.0 mL), heated under reflux for 12 h and cooled, evaporated to dryness, redissolved in CH₂Cl₂ (5.0 mL) and stirred at room temperature over anhydrous sodium sulfate (100.0 mg) for additional 30 min. Sodium sulfate was filtered off, washed with CH₂Cl₂ (3 × 5 mL) and filtrate evaporated to dryness. Imines **3i**, **3m-o**, and **3r** were recrystallized from a proper solvent.

(3*R*,4*R*)-1-(4-Methoxyphenyl)-4-phenyl-3-(*trans*-phenylalylideneamino)-2-oxoazetid-3-yl)-2,2-dimethyl-3-ferrocenylpropanoate, **3i**

Obtained from **1a** (150 mg, 5.6 × 10⁻¹ mmol) and **2i** (81.3 mg, 77.4 μ L, 6.15 × 10⁻¹ mmol) as white crystals (from CH₂Cl₂ – petroleum ether (bp 40-70 °C)), 179 mg (83.7%), *R*_f = 0.46 (EtOAc – petroleum ether in ratio 1:2), mp 176-178 °C; [α]_D +325.3 (*c* 0.3074, CH₂Cl₂); IR (KBr) ν_{\max} /cm⁻¹: 3057, 3021, 2996, 2924, 1751, 1631, 1604, 1513, 1458, 1450, 1441, 1398, 1360, 1296, 1247, 1170, 1146, 1114, 827, 757; ¹H NMR (300 MHz, CDCl₃) δ /ppm: 3.74 (s, 3H, OMe, PMP), 4.57 (bs, 1H, C4, β -lactam), 5.11 (d, 1H, *J* = 1.83 Hz, C3, β -lactam), 6.79 (d, 2H, *J* = 9.03 Hz, C3 and C5, PMP), 6.93 (dd, 1H, *J*₁ = 15.98 Hz, *J*₂ = 8.45 Hz, CH=CH-CH=N), 7.05 (d, 1H, *J* = 16.00 Hz, CH=CH-CH=N), 7.27 (d, 2H, *J* = 8.88 Hz, C2

and C6, PMP), 7.35-7.50 (m, 10H, Ph, β -lactam and Ph, cinnamaldehyde), 8.17 (dd, 1H, $J_1 = 8.45$ Hz, $J_2 = 0.59$ Hz, CH=CH-CH=N); ^{13}C NMR (75 MHz, CDCl_3) δ /ppm: 55.38 (OMe, PMP), 63.75 (C4, β -lactam), 83.38 (C3, β -lactam), 114.32 (C3 and C5, PMP), 118.76 (C2 and C6, PMP), 126.22 (C2 and C6, Ph, β -lactam), 127.48 (C2 and C6, Ph, cinnamaldehyde and CH=CH-CH=N), 128.69 (C4, Ph, β -lactam), 128.87 (C3 and C5, Ph, cinnamaldehyde), 129.18 (C3 and C5, Ph, β -lactam), 129.61 (C4, Ph, cinnamaldehyde), 130.83 (C1, Ph, β -lactam), 135.36 (C1, Ph, cinnamaldehyde), 136.66 (C1, PMP), 144.15 (CH=CH-CH=N), 156.27 (C4, PMP), 163.18 (CO), 166.18 (CH=N). Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_2$ ($M_r = 372.43$): C 78.51, H 5.80, N 7.32%. Found: C 78.41, H 5.84 N 7.28%.

(3R,4R)-3-((Furan-2-yl)methylideneamino)-1-(4-methoxyphenyl)-4-phenyl-2-oxoazetidine, **3m**

Obtained from **1a** (100 mg, 3.72×10^{-1} mmol) and **2m** (39.4 mg, $34.0 \mu\text{L}$, 4.10×10^{-1} mmol) as orange crystals (from CH_2Cl_2 – petroleum ether (bp 40-70 °C)), 110 mg (85.5%), $R_f = 0.27$ (EtOAc – petroleum ether in ratio 1:3), mp 85-87 °C; $[\alpha]_D +283.02$ (c 0.0530; CH_2Cl_2); IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3029, 2894, 2838, 1737, 1642, 1586, 1561, 1511, 1455, 1444, 1389, 1296, 1246, 1170, 1153, 1065, 1026, 835, 760, 697; ^1H NMR (300 MHz, CDCl_3) δ /ppm: 3.74 (s, 3H, OMe, PMP), 4.61 (bs, 1H, C4, β -lactam), 5.22 (d, 1H, $J = 1.68$ Hz, C3, β -lactam), 6.51 (dd, 1H, $J_1 = 3.45$ Hz, $J_2 = 1.73$ Hz, C4, furyl), 6.79 (d, 2H, $J = 8.97$ Hz, C3 and C5, PMP), 6.84 (d, 1H, $J = 3.42$ Hz, C3, furyl), 7.26 (d, 2H, $J = 8.97$ Hz, C2 and C6, PMP), 7.34-7.40 (m, 5H, Ph), 7.56 (s, 1H, C5, furyl), 8.21 (s, 1H, CH=N); ^{13}C NMR (75 MHz, CDCl_3) δ /ppm: 55.36 (OMe, PMP), 63.65 (C4, β -lactam), 83.23 (C3, β -lactam), 111.95 (C3, furyl), 114.28 (C3 and C5, PMP), 116.64 (C4, furyl), 118.76 (C2 and C6, PMP), 126.25 (C2 and C6, Ph, β -lactam), 128.68 (C4, Ph, β -lactam), 129.13 (C3 and C5, Ph, β -lactam), 130.74 (C1, Ph, β -lactam), 136.57 (C1, PMP), 145.65 (C5, furyl), 150.85 (C2, furyl), 152.45 (CH=N), 156.24 (C4, PMP), 162.85 (CO, β -lactam). Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_3$ ($M_r = 346.39$): C 72.82, H 5.24, N 8.09%. Found: C 72.41, H 5.67 N 8.01%.

(3R,4R)-3-((5-Phenylfuran-2-yl)methylideneamino)-1-(4-methoxyphenyl)-4-phenyl-2-oxoazetidine, **3n**

Obtained from **1a** (92 mg, 3.4×10^{-1} mmol) and **2n** (65 mg, 3.8×10^{-1} mmol) as orange crystals (from CH_2Cl_2 – petroleum ether (bp 40-70 °C)), 110 mg (76.3%), $R_f = 0.26$ (EtOAc – petroleum ether in ratio 1:3), mp 62-65 °C; $[\alpha]_D +300.0$ ($c = 0.050$; CH_2Cl_2); IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3031, 2927, 1751, 1631, 1584, 1511, 1480, 1450, 1388, 1297, 1247, 1143, 1027, 921, 828, 762, 691; ^1H NMR (300 MHz, CDCl_3) δ /ppm: 3.74 (s, 3H, OMe, PMP), 4.64 (d, 1H, $J = 0.96$ Hz, C4, β -lactam), 5.23 (d, 1H, $J = 1.83$ Hz, C3, β -lactam), 6.76 (d, 1H, $J = 3.60$ Hz, C3, furyl), 6.79 (d, 2H, $J = 9.06$ Hz, C3 and C5, PMP), 6.95 (d, 1H, $J = 3.60$ Hz, C4, furyl), 7.28 (d, 2H, $J = 9.03$ Hz, C2 and C6, PMP), 7.30-7.45 (m, 8H, 5H, Ph, β -lactam and 3H, Ph, furyl), 7.78 (d, 2H, $J = 7.08$ Hz, Ph, furyl), 8.23 (d, 1H, $J = 0.72$ Hz, CH=N); ^{13}C -NMR (75 MHz,

CDCl₃) δ /ppm: 55.38 (OMe, PMP), 63.65 (C4, β -lactam), 83.60 (C3, β -lactam), 107.37 (C3, furyl), 114.30 (C3 and C5, PMP), 118.37 (C4, furyl), 118.77 (C2 and C6, PMP), 124.76 (C2 and C6, Ph, furyl), 126.30 (C2 and C6, Ph, β -lactam), 128.59 (C4, Ph, furyl), 128.67 (C4, Ph, β -lactam), 128.71 (C3 and C5, Ph, furyl), 129.15 (C3 and C5, Ph, β -lactam), 129.66 (C1, Ph, furyl), 130.83 (C1, Ph, β -lactam), 136.67 (C1, PMP), 150.46 (C2, furyl), 152.60 (CH=N), 156.23 (C4, PMP), 157.03 (C5, furyl), 163.18 (CO). Anal. Calcd for C₂₇H₂₂N₂O₃ (M_r = 422.49): C 76.76, H 5.25, N 6.63%. Found: C 76.51, H 5.60, N 6.24%.

(3R,4R)-3-((5-Methylfuran-2-yl)methylideneamino)-1-(4-methoxyphenyl)-4-phenyl-2-oxoazetidine, 3o

Obtained from **1a** (100 mg, 3.73 x 10⁻¹ mmol) and **2o** (45.1 mg, 40.8 μ L, 4.10 x 10⁻¹ mmol) as orange crystals (from CH₂Cl₂ – petroleum ether (bp 40-70 °C)), 115 mg (85.1%), R_f = 0.22 (EtOAc – petroleum ether in ratio 1:3), mp 181-182 °C; $[\alpha]_D$ +280.58 (c 0.0891, CH₂Cl₂); IR (KBr) ν_{\max} /cm⁻¹: 3060, 3034, 2955, 2916, 2881, 2838, 1742, 1637, 1583, 1528, 1510, 1468, 1455, 1446, 1430, 1394, 1362, 1296, 1280, 1246, 1177, 1168, 1153, 1089, 1078, 1065, 1020, 944, 837, 806, 781, 750, 700; ¹H NMR (300 MHz, CDCl₃) δ /ppm: 2.39 (s, 3H, Me, furyl), 3.74 (s, 3H, OMe, PMP), 4.57 (d, 1H, J = 0.48 Hz, C4, β -lactam), 5.22 (d, 1H, J = 1.77 Hz, C3, β -lactam), 6.12 (dd, 1H, J_1 = 3.27 Hz, J_2 = 0.78 Hz, C3, furyl), 6.72 (d, 1H, J = 0.60 Hz, C4, furyl), 6.78 (d, 2H, J = 9.03 Hz, C3 and C5, PMP), 7.25 (d, 2H, J = 8.97 Hz, C2 and C6, PMP), 7.35-7.39 (m, 5H, Ph), 8.40 (d, 1H, J = 0.51 Hz, CH=N); ¹³C NMR (75 MHz, CDCl₃) δ /ppm: 14.00 (CH₃, furyl), 55.36 (OMe, PMP), 63.62 (C4, β -lactam), 83.56 (C3, β -lactam), 108.57 (C3, furyl), 114.27 (C3 and C5, PMP), 118.73 (C2 and C6, PMP), 119.02 (C4, furyl), 126.27 (C2 and C6, Ph, β -lactam), 128.62 (C4, Ph, β -lactam), 129.11 (C3 and C5, Ph, β -lactam), 130.81 (C1, Ph, β -lactam), 136.71 (C1, PMP), 149.49 (C2, furyl), 152.30 (CH=N), 156.18 (C4, PMP), 156.79 (C5, furyl), 163.15 (CO). Anal. Calcd for C₂₂H₂₀N₂O₃ (M_r = 360.41): C 73.32, H 5.59, N 7.77%. Found: C 73.26, H 5.94 N 7.72%.

(3R,4R)-4-Ferrocenyl-3-(4-trifluoromethylbenzylideneamino)-1-(4-methoxyphenyl)-2-oxoazetidine, 3r

Obtained from **1b** (100 mg, 2.66 x 10⁻¹ mmol) and **2e** (50.8 mg, 40.0 μ L, 2.92 x 10⁻¹ mmol) as brown crystals (from CH₂Cl₂ – petroleum ether (bp 40-70 °C)), 100 mg (70.9%), R_f = 0.51 (CH₂Cl₂), mp 145-147 °C; $[\alpha]_D$ +41.67 (c 0.048, CH₂Cl₂); IR (KBr) ν_{\max} /cm⁻¹: 3468, 2905, 2841, 1744, 1646, 1586, 1560, 1541, 1511, 1464, 1444, 1395, 1326, 1298, 1245, 1164, 1131, 1064, 1029, 1016, 942, 920, 777, 598; ¹H NMR (CDCl₃) δ /ppm: 3.74 (s, 3H, OMe, PMP), 4.23 (s, 5H, Fc), 4.27 (m, 2H, Fc), 4.32 (m, 1H, Fc), 4.44 (m, 1H, Fc), 5.00 (d, 1H, J = 1.98 Hz, C4, β -lactam), 5.17 (d, 1H, J = 1.44 Hz, C3, β -lactam), 6.80 (d, 2H, J = 9.00 Hz, C3 and C5, PMP), 7.34 (d, 2H, J = 9.06 Hz, C2 and C6, PMP), 7.70 (d, 2H, J = 8.16 Hz, C2 and C6, 4-CF₃C₆H₄), 7.96 (d, 2H, J = 8.10 Hz, C3 and C5, 4-CF₃C₆H₄), 8.73 (s, 1H, CH=N); ¹³C NMR

(CDCl₃) δ /ppm: 55.42 (OMe, PMP), 60.91 (C4, β -lactam), 66.39, 68.34, 68.64, 69.82, 70.71 (Fc), 80.51 (C3, β -lactam), 82.87 (C3, β -lactam), 114.25 (C3 and C5, PMP), 119.09 (C2 and C6, PMP), 124.72 (CF₃), 125.67 (d, J = 3.60 Hz, C3 and C5, 4-CF₃C₆H₄), 128.72 (C2 and C6, 4-CF₃C₆H₄), 130.78 (C1, Ph, 4-CF₃C₆H₄), 132.89 (d, J = 32.90 Hz, C4, 4-CF₃C₆H₄), 138.71 (C1, PMP), 156.40 (C4, PMP), 162.32 (CH=N), 163.28 (CO). Anal. Calcd for C₂₈H₂₃N₂O₂F₃Fe (M_r = 532.35): C 63.18, H 4.35, N 5.26%. Found: C 63.07, H 4.72, N 5.21%.

Preparation of β -amino acid esters **5a-r/6a-r**

General Procedure. – A solution of imine **3a-r** in anhydrous toluene (4.0 mL) was added dropwise to a suspension of zinc(II) iodide in toluene (1.0 mL), under stirring for 15 minutes at -20 °C. Silylenol ether **4** was added to the reaction mixture and was left to stir for 6 h at -20 °C and then at RT for overnight. The reaction mixture was poured into EtOAc (20 mL) containing a saturated solution of sodium bicarbonate (10 mL). A mixture of the products was further extracted with EtOAc (2 \times 20 mL), and the combined extracts (60 mL) were dried over anhydrous sodium sulfate, filtered, and the filtrate was evaporated to dryness. The crude products **5a-r/6a-r** were purified by column chromatography on silica gel using a mixture of EtOAc – petroleum ether in ratios 1:2, 1:3, 1:5 or 3:1 as eluents.

Methyl (3*S*/3*R*)-(trans-(3'*R*,4'*R*)-3-amino-1-(4-methoxyphenyl)-2-oxo-4-phenylazetididin-3-yl)-2,2-dimethyl-3-phenylpropanoate, **5a/6a**

Obtained from (3*R*,4*R*)-**3a** (15 mg, 4.2×10^{-2} mmol) and silylenol ether **4** (8.0 mg, 9.4 μ L, 4.6×10^{-2} mmol) and zinc(II) iodide (13.4 mg, 4.2×10^{-2} mmol) as a diastereomeric mixture **5a/6a**, 19.2 mg (99.4%), R_f = 0.22 (EtOAc – petroleum ether in ratio 1:3). RP-HPLC analysis (method I) of diastereomeric mixture showed ratio of **5a/6a** – 85:15% (**5a**, 10.50 min and **6a**, 10.86 min). LC-MS for C₂₈H₃₀N₂O₄ (M_r = 458.56008): calcd. m/z [M+H]⁺ 459.23, found 459.30 (**5a**, 16.58 min) and 459.30 (**6a**, 20.65 min); IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3337, 2936, 1740, 1514, 1454, 1389, 1298, 1251, 1185, 1132, 1065, 1028, 824, 697; ¹H NMR (300 MHz, CDCl₃) δ /ppm: 1.05 (s, 3H, CMe₂, **6a**), 1.07 (s, 3H, CMe₂, **5a**), 1.15 (bs, 6H, CMe₂, **5a/6a**), 2.60 (bs, 2H, NH, β -lactam, **5a/6a**), 3.69 (s, 3H, COOMe, **5a**), 3.70 (s, 3H, OMe, PMP, **5a**), 3.72 (s, 3H, COOMe, **6a**), 3.73 (m, 1H, C4, β -lactam, **6a**), 3.75 (s, 3H, OMe, PMP, **6a**), 3.83 (d, 1H, J = 1.74 Hz, C3, β -lactam, **5a**), 3.93 (s, 1H, PhCHN, **5a**), 4.07 (s, 1H, PhCHN, **6a**), 4.36 (d, 1H, J = 1.38 Hz, C4, β -lactam, **5a**), 4.62 (d, 1H, J = 1.56 Hz, C3, β -lactam, **6a**), 6.60 (dd, 2H, J_1 = 7.65 Hz, J_2 = 1.26 Hz, C3 and C5, PMP, **6a**), 6.72 (d, 2H, J = 9.12 Hz, C3 and C5, PMP, **5a**), 6.75 (d, 2H, J = 9.09 Hz, C2 and C6, PMP, **6a**), 7.11 (d, 2H, J = 8.94 Hz, C3 and C5, PMP, **5a**), 7.15-7.34 (m, 20H, Ph, β -lactam and PhCHN, **5a/6a**); ¹³C NMR (75 MHz, CDCl₃) δ /ppm: 18.82 (CMe₂, **6a**), 20.10 (CMe₂, **5a**), 23.79 (CMe₂, **5a**), 24.46 (CMe₂, **6a**), 47.46 (CMe₂, **6a**), 47.66 (CMe₂, **5a**), 51.99 (COOMe, **5a**), 52.09 (COOMe, **6a**), 55.35 (OMe,

PMP, **5a**), 55.38 (OMe, PMP, **6a**), 64.45 (C4, β -lactam, **6a**), 65.20 (C4, β -lactam, **5a**), 66.62 (C3, β -lactam, **6a**), 68.95 (C3, β -lactam, **5a**), 73.72 (PhCHN, **6a**), 76.38 (PhCHN, **5a**), 114.17 (C3 and C5, PMP, **5a**), 114.22 (C3 and C5, PMP, **6a**), 118.59 (C2 and C6, PMP, **5a**), 118.65 (C2 and C6, PMP, **6a**), 125.61 (C2 and C6, Ph, β -lactam, **5a**), 125.69 (C2 and C6, Ph, β -lactam, **6a**), 127.70 (C4, Ph, β -lactam, **6a**), 127.81 (C4, Ph, β -lactam, **5a**), 127.89 (C4, PhCHN, **5a**), 127.95 (C2 and C6, PhCHN, **6a**), 128.06 (C2 and C6, PhCHN, **5a**), 128.11 (C4, PhCHN, **6a**), 128.56 (C3 and C5, PhCHN, **5a**), 128.89 (C3 and C5, PhCHN, **6a**), 128.92 (C3 and C5, Ph, β -lactam, **6a**), 129.10 (C3 and C5, Ph, β -lactam, **5a**), 130.95 (C1, Ph, β -lactam, **5a/6a**), 136.71 (C1, PMP, **5a**), 137.17 (C1, PMP, **6a**), 138.19 (C1, PhCHN, **6a**), 140.08 (C1, PhCHN, **5a**), 155.97 (C4, PMP, **5a**), 156.03 (C4, PMP, **6a**), 165.37 (CO, β -lactam, **6a**), 165.51 (CO, β -lactam, **5a**), 177.18 (COOMe, **5a**), 177.64 (COOMe, **6a**). Anal. Calcd for C₂₈H₃₀N₂O₄ (**5a/6a**, M_r = 458.56): C 73.34, H 6.59, N 6.11%. Found: C 73.12, H 6.61, N 6.06%.

Methyl (3S/3R)-(trans-(3'R,4'R)-3-amino-1-(4-methoxyphenyl)-2-oxo-4-phenylazetididin-3-yl)-2,2-dimethyl-3-(4-methoxyphenyl)propanoate, 5b/6b

Obtained from (3R,4R)-**3b** (15 mg, 3.9 x 10⁻² mmol), silylenol ether **4** (7.5 mg, 8.7 μ L, 4.3 x 10⁻² mmol) and zinc(II) iodide (12.4 mg, 3.9 x 10⁻² mmol) as a diastereomeric mixture **5b/6b**, 15.7 mg (82.5%), R_f = 0.17 (EtOAc – petroleum ether in ratio 1:3). RP-HPLC analysis (method II) of diastereomeric mixture showed ratio of **5b/6b** – 81:19% (**5b**, 64.55 min and **6b**, 68.95 min). LC-MS for C₂₉H₃₂N₂O₅ (M_r = 488.58646): calcd. m/z [M+H]⁺ 489.24, found 489.30 (**5b**, 14.24 min) and 489.30 (**6b**, 17.28 min); IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3339, 2950, 2835, 1735, 1610, 1584, 1560, 1513, 1456, 1387, 1299, 1249, 1178, 1134, 1069, 1032, 831, 748, 570; ¹H NMR (300 MHz, CDCl₃) δ /ppm: 1.04 (s, 3H, CMe₂, **5b**), 1.06 (s, 3H, CMe₂, **6b**), 1.14 (s, 3H, CMe₂, **5b**), 1.26 (s, 3H, CMe₂, **6b**), 2.46 (bs, 2H, NH, β -lactam, **5b/6b**), 3.68 (s, 3H, COOMe, **6b**), 3.71 (s, 3H, OMe, PMP, propanoate, **6b**), 3.72 (s, 3H, COOMe, **5b**), 3.73 (s, 3H, OMe, PMP, β -lactam, **6b**), 3.74 (s, 3H, OMe, PMP, propanoate, **5b**), 3.76 (s, 3H, OMe, PMP, β -lactam, **5b**), 3.81 (d, 1H, J = 1.83 Hz, C4, β -lactam, **6b**), 3.84 (s, 1H, C4, β -lactam, **5b**), 3.89 (s, 1H, CHN, **6b**), 4.03 (s, 1H, CHN, **5b**), 4.37 (d, 1H, J = 1.71 Hz, C3, β -lactam, **6b**), 4.63 (d, 1H, J = 1.71 Hz, C3, β -lactam, **5b**), 6.66-6.86 (m, 4H, 2H, C3 and C5, PMP, propanoate and 2H, C3 and C5, PMP, β -lactam, **5b/6b**), 7.05-7.32 (m, 16H, 10H, Ph, β -lactam, **5b/6b**, 2H, C2 and C6, PMP, propanoate, **5b**, and 4H, C2 and C6, PMP, β -lactam, **5b/6b**), 7.84 (dd, J_1 = 8.81 Hz, J_2 = 1.97 Hz, 2H, C2 and C6, PMP, propanoate, **6b**); ¹³C NMR (75 MHz, CDCl₃) δ /ppm: 18.87 (CMe₂, **5b**), 20.12 (CMe₂, **6b**), 23.72 (CMe₂, **6b**), 24.43 (CMe₂, **5b**), 47.54 (CMe₂, **5b**), 47.73 (CMe₂, **6b**), 51.96 (COOMe, **6b**), 52.06 (COOMe, **5b**), 55.15 (OMe, PMP, propanoate, **5b**), 55.23 (OMe, PMP, propanoate, **6b**), 55.28 (OMe, PMP, β -lactam, **6b**), 55.38 (OMe, PMP, β -lactam, **5b**), 64.57 (C4, β -lactam, **5b**), 65.18 (C4, β -lactam, **6b**), 66.05 (C3, β -lactam, **5b**), 68.33 (C3, β -lactam, **6b**), 73.66 (CHN, **5b**), 76.19 (CHN, **6b**), 113.31 (C3 and C5, PMP, propanoate, **5b**),

113.40 (C3 and C5, PMP, propanoate, **6b**), 114.17 (C3 and C5, PMP, β -lactam, **6b**), 114.22 (C3 and C5, PMP, β -lactam, **5b**), 118.58 (C2 and C6, PMP, β -lactam, **6b**), 118.65 (C2 and C6, PMP, β -lactam, **5b**), 125.69 (C2 and C6, PMP, propanoate, **5b/6b**), 127.92 (C4, Ph, β -lactam, **6b**), 128.09 (C4, Ph, β -lactam, **5b**), 128.55 (C2 and C6, Ph, β -lactam, **6b**), 128.93 (C2 and C6, Ph, β -lactam, **5b**), 129.92 (C3 and C5, Ph, β -lactam, **5b**), 130.07 (C3 and C5, Ph, β -lactam, **6b**), 13.97 (C1, Ph, β -lactam, **5b**), 131.02 (C1, Ph, β -lactam, **6b**), 131.88 (C1, PMP, propanoate, **5b**), 131.92 (C1, PMP, propanoate, **6b**), 136.78 (C1, PMP, β -lactam, **6b**), 137.23 (C1, PMP, β -lactam, **5b**), 155.96 (C4, PMP, β -lactam, **6b**), 156.02 (C4, PMP, β -lactam, **5b**), 159.06 (C4, PMP, propanoate, **5b**), 159.29 (C4, PMP, propanoate, **6b**), 165.49 (CO, β -lactam, **5b**), 165.53 (CO, β -lactam, **6b**), 176.92 (COOMe, **6b**), 177.76 (COOMe, **5b**). Anal. Calcd for $C_{29}H_{32}N_2O_5 \times 1.5 H_2O$ (**5b/6b**, $M_r = 515.61$): C 67.56, H 6.84, N 5.43%. Found: C 67.36, H 7.24, N 5.56%.

Methyl (3S/3R)-(trans-(3'R,4'R)-3-amino-1-(4-methoxyphenyl)-2-oxo-4-phenylazetididin-3-yl)-2,2-dimethyl-3-(3,4-dimethoxyphenyl)propanoate, 5c/6c

Obtained from (3R,4R)-**3c** (15 mg, 3.6×10^{-2} mmol), silylenol ether **4** (7.0 mg, 8.0 μ L, 4.0×10^{-2} mmol) and zinc(II) iodide (11.5 mg, 3.6×10^{-2} mmol) as a diastereomeric mixture **5c/6c**, 18.0 mg (96.6%), $R_f = 0.31$ (EtOAc – petroleum ether in ratio 1:2). RP-HPLC analysis (method III) of diastereomeric mixture showed ratio of **5c/6c** – 88:12% (**6c**, 66.12 min and **5c**, 69.72 min). LC-MS for $C_{30}H_{34}N_2O_6$ ($M_r = 518.61284$): calcd. m/z $[M+H]^+$ 519.25, found 519.30 (**5c**, 8.93 min) and 519.30 (**6c**, 10.13 min); IR (KBr) ν_{max}/cm^{-1} : 3630, 3449, 2952, 2836, 1740, 1654, 1605, 1590, 1560, 1513, 1458, 1388, 1299, 1247, 1180, 1142, 1068, 1027, 830, 700, 520; 1H NMR (300 MHz, $CDCl_3$) δ/ppm : 1.06 (s, 3H, CMe_2 , **5c**), 1.09 (s, 3H, CMe_2 , **6c**), 1.16 (s, 3H, CMe_2 , **6c**), 1.18 (s, 3H, CMe_2 , **5c**), 2.60 (bs, 2H, NH, β -lactam, **5c/6c**), 3.69 (s, 3H, COOMe, **6c**), 3.71 (s, 3H, 3,4-(MeO) $_2C_6H_3$, **6c**), 3.72 (s, 3H, COOMe, **5c**), 3.75 (bs, 6H, 3H, 3,4-(MeO) $_2C_6H_3$, and 3H, OMe, PMP, **5c**), 3.78 (s, 3H, OMe, PMP, **6c**), 3.79 (s, 3H, 3,4-(MeO) $_2C_6H_3$, **6c**), 3.83 (s, 3H, 3,4-(MeO) $_2C_6H_3$, **5c**), 3.88 (d, 1H, $J = 1.71$ Hz, C4, β -lactam, **6c**), 3.91 (s, 1H, C4, β -lactam, **5c**), 3.95 (s, 1H, CHN, **6c**), 4.01 (s, 1H, CHN, **5c**), 4.37 (d, 1H, $J = 1.47$ Hz, C3, β -lactam, **6c**), 4.63 (d, 1H, $J = 1.44$ Hz, C3, β -lactam, **5c**), 6.64-6.77 (m, 10H, 2x2H, C3 and C5, PMP and 2x3H, 3,4-(MeO) $_2C_6H_3$, **5c/6c**), 7.16-7.30 (m, 14H, 2x5H, Ph, β -lactam and 2x2H, C2 and C6, PMP, **5c/6c**); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm : 19.06 (CMe_2 , **5c**), 20.34 (CMe_2 , **6c**), 23.80 (CMe_2 , **6c**), 24.50 (CMe_2 , **5c**), 47.45 (CMe_2 , **5c**), 47.65 (CMe_2 , **6c**), 52.00 (COOMe, **6c**), 52.09 (COOMe, **5c**), 55.37 (OMe, PMP, **5c/6c**), 55.76 (3,4-(MeO) $_2C_6H_3$, **5c**), 55.79 (3,4-(MeO) $_2C_6H_3$, **5c**), 55.90 (3,4-(MeO) $_2C_6H_3$, **6c**), 55.95 (3,4-(MeO) $_2C_6H_3$, **6c**), 64.52 (C4, β -lactam, **5c**), 65.10 (C4, β -lactam, **6c**), 66.45 (C3, β -lactam, **5c**), 68.73 (C3, β -lactam, **6c**), 73.72 (CHN, **5c**), 76.11 (CHN, **6c**), 110.53 (C5, 3,4-(MeO) $_2C_6H_3$, **5c**), 110.62 (C5, 3,4-(MeO) $_2C_6H_3$, **6c**), 112.05 (C6, 3,4-(MeO) $_2C_6H_3$, **5c**), 112.29 (C6, 3,4-(MeO) $_2C_6H_3$, **6c**), 114.18 (C3 and

C5, PMP, **6c**), 114.22 (C3 and C5, PMP, **5c**), 118.54 (C2 and C6, PMP, **6c**), 118.63 (C2 and C6, PMP, **5c**), 121.09 (C2, 3,4-(MeO)₂C₆H₃, **5c**), 121.16 (C2, 3,4-(MeO)₂C₆H₃, **6c**), 125.73 (C2 and C6, Ph, β-lactam, **5c/6c**), 128.03 (C4, Ph, β-lactam, **6c**), 128.12 (C4, Ph, β-lactam, **5c**), 128.54 (C3 and C5, Ph, β-lactam, **6c**), 128.93 (C3 and C5, Ph, β-lactam, **5c**), 130.57 (C1, Ph, β-lactam, **5c**), 130.92 (C1, Ph, β-lactam, **6c**), 130.97 (C1, 3,4-(MeO)₂C₆H₃, **5c**), 130.99 (C1, 3,4-(MeO)₂C₆H₃, **6c**), 132.09 (C3, 3,4-(MeO)₂C₆H₃, **6c**), 132.38 (C3, 3,4-(MeO)₂C₆H₃, **5c**), 136.90 (C1, PMP, **6c**), 137.31 (C1, PMP, **5c**), 148.37 (C4, 3,4-(MeO)₂C₆H₃, **5c**), 148.39 (C4, 3,4-(MeO)₂C₆H₃, **6c**), 156.04 (C4, PMP, **5c**), 156.10 (C4, PMP, **6c**), 165.54 (CO, β-lactam, **5c**), 165.57 (CO, β-lactam, **6c**), 177.39 (COOMe, **6c**), 177.72 (COOMe, **5c**). Anal. Calcd for C₃₀H₃₄N₂O₆ x 0.5H₂O (**5c/6c**, *M_r* = 527.62): C 68.29, H 6.69, N 5.31%. Found: C 68.56, H 7.08, N 5.24%.

Methyl (3*S*/3*R*)-(trans-(3'*R*,4'*R*)-3-amino-1-(4-methoxyphenyl)-2-oxo-4-phenylazetididin-3-yl)-2,2-dimethyl-3-(4-fluorophenyl)propanoate, **5d/6d**

Obtained from (3*R*,4*R*)-**3d** (12.5 mg, 3.3 x 10⁻² mmol), silylenol ether **4** (6.4 mg, 7.4 μL, 3.7 x 10⁻² mmol) and zinc(II) iodide (11.9 mg, 3.3 x 10⁻² mmol) as a diastereomeric mixture **5d/6d**, 14.3 mg (90.2%), *R_f* = 0.34 (EtOAc – petroleum ether in ratio 1:3). NP-HPLC analysis (method IV) of diastereomeric mixture showed ratio of **5d/6d** – 90:10% (**5d**, 7.65 min and **6d**, 8.13 min). LC-MS for C₂₈H₂₉N₂O₄F (*M_r* = 476.55054): calcd. *m/z* [M+H]⁺ 477.22, found 477.30 (**5d**, 17.25 min) and 477.30 (**6d**, 20.58 min); IR (KBr) *v*_{max}/cm⁻¹: 3334, 3069, 2981, 2950, 2834, 1741, 1654, 1637, 1604, 1560, 1514, 1458, 1390, 1352, 1300, 1276, 1248, 1191, 1169, 1149, 1130, 1092, 1070, 1037, 1016, 934, 866, 810, 784, 745, 668, 618; ¹H NMR (300 MHz, CDCl₃) δ/ppm: 1.04 (s, 3H, CMe₂, **5d**), 1.07 (s, 3H, CMe₂, **6d**), 1.15 (s, 3H, CMe₂, **5d**), 1.22 (s, 3H, CMe₂, **6d**), 2.48 (bs, 2H, NH, β-lactam, **5d/6d**), 3.69 (s, 3H, COOMe, **6d**), 3.71 (s, 3H, OMe, PMP, **6d**), 3.73 (bs, 4H, COOMe and C4, β-lactam, **5d**), 3.74 (s, 3H, OMe, PMP, **5d**), 3.79 (d, 1H, *J* = 1.26 Hz, C4, β-lactam, **6d**), 3.96 (s, 1H, CHN, **6d**), 4.08 (s, 1H, CHN, **5d**), 4.38 (d, 1H, *J* = 0.84 Hz, C3, β-lactam, **6d**), 4.64 (s, 1H, C3, β-lactam, **5d**), 6.71-6.77 (m, 4H, 2x2H, C3 and C5, PMP, **5d/6d**), 6.91 (t, 2H, *J*₁ = *J*₂ = 8.57 Hz, C3 and C5, 4-FC₆H₄, **5d**), 7.00 (t, 2H, *J*₁ = *J*₂ = 8.63 Hz, C3 and C5, 4-FC₆H₄, **6d**), 7.11-7.32 (m, 18H, 2x5H, Ph, β-lactam, 2x2H, C2 and C6, PMP and 2x2H, C2 and C6, 4-FC₆H₄, **5d/6d**); ¹³C NMR (75 MHz, CDCl₃) δ/ppm: 18.83 (CMe₂, **5d**), 20.17 (CMe₂, **6d**), 23.69 (CMe₂, **6d**), 24.37 (CMe₂, **5d**), 47.37 (CMe₂, **5d**), 47.43 (CMe₂, **6d**), 52.07 (COOMe, **5d**), 52.16 (COOMe, **6d**), 55.39 (OMe, PMP, **5d**), 55.47 (OMe, PMP, **6d**), 64.65 (C4, β-lactam, **5d**), 65.09 (C4, β-lactam, **6d**), 66.03 (C3, β-lactam, **5d**), 68.24 (C3, β-lactam, **6d**), 73.68 (CHN, **5d**), 75.93 (CHN, **6d**), 114.21 (C3 and C5, PMP, **6d**), 114.25 (C3 and C5, PMP, **5d**), 114.86 (d, *J* = 84.91 Hz, C3 and C5, 4-FC₆H₄, **5d/6d**), 118.57 (C2 and C6, PMP, **6d**), 118.65 (C2 and C6, PMP, **5d**), 125.64 (C2 and C6, Ph, β-lactam, **5d/6d**), 128.10 (C4, Ph, β-lactam, **6d**), 128.21 (C4, Ph, β-lactam, **5d**), 128.99 (C3 and C5, Ph, β-lactam, **5d**), 129.11 (C3 and

C5, Ph, β -lactam, **6d**), 130.43 (d, $J = 32.08$ Hz, C2 and C6, 4-FC₆H₄, **5d**), 130.59 (d, $J = 32.68$ Hz, C2 and C6, 4-FC₆H₄, **6d**), 130.88 (C1, Ph, β -lactam, **5d/6d**), 133.74 (d, $J = 13.42$ Hz, C1, 4-FC₆H₄, **5d/6d**), 137.12 (C1, PMP, **5d/6d**), 156.09 (C4, PMP, **5d**), 156.13 (C4, PMP, **6d**), 163.91 (C4, 4-FC₆H₄, **5d/6d**), 165.30 (CO, β -lactam, **5d/6d**), 177.50 (COOMe, **5d**), 177.83 (COOMe, **6d**). Anal. Calcd for C₂₈H₂₉N₂O₄F x H₂O (**5d/6d**, $M_r = 494.57$): C 68.00, H 6.32, N 5.66%. Found: C 67.85, H 6.69, N 5.72%.

Methyl (3S/3R)-(trans-(3'R,4'R)-3-amino-1-(4-methoxyphenyl)-2-oxo-4-phenylazetid-3-yl)-2,2-dimethyl-3-(4-trifluoromethylphenyl)propanoate, 5e/6e

Obtained from (3R,4R)-**3e** (12.0 mg, 2.83×10^{-2} mmol), silylenol ether **4** (5.4 mg, 6.3 μ L, 3.1×10^{-2} mmol) and zinc(II) iodide (9.0 mg, 2.83×10^{-2} mmol) as a diastereomeric mixture **5e/6e**, 12.9 mg (86.8%), $R_f = 0.22$ (EtOAc – petroleum ether in ratio 1:3). NP-HPLC analysis (method IV) of diastereomeric mixture showed ratio of **5e/6e** – 92:8% (**5e**, 7.07 min and **6e**, 7.80 min). LC-MS for C₂₉H₂₉N₂O₄F₃ ($M_r = 526.55845$): calcd. m/z [M+H]⁺ 527.22, found 527.30 (**5e**, 27.82 min) and 527.30 (**6e**, 32.72 min); IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3347, 2953, 1743, 1654, 1618, 1560, 1514, 1467, 1421, 1391, 1327, 1299, 1249, 1167, 1129, 1095, 1068, 1035, 1017, 932, 829, 749, 682; ¹H NMR (300 MHz, CDCl₃) δ /ppm: 1.06 (s, 3H, CMe₂, **5e**), 1.11 (s, 3H, CMe₂, **6e**), 1.16 (bs, 6H, CMe₂, **5e/6e**), 2.64 (bs, 2H, NH, β -lactam, **5e/6e**), 3.66 (d, 1H, $J = 1.65$ Hz, C4, β -lactam, **5e**), 3.71 (s, 3H, COOMe, **6e**), 3.73 (s, 3H, COOMe, **5e**), 3.76 (s, 6H, OMe, PMP, **5e/6e**), 3.79 (s, 1H, C4, β -lactam, **6e**), 4.01 (s, 1H, CHN, **6e**), 4.16 (s, 1H, CHN, **5e**), 4.35 (d, 1H, $J = 1.62$ Hz, C3, β -lactam, **6e**), 4.65 (d, 1H, $J = 1.65$ Hz, C3, β -lactam, **5e**), 6.64 (d, 2H, $J = 9.24$ Hz, C3 and C5, PMP, **6e**), 6.76 (d, 2H, $J = 9.06$ Hz, C3 and C5, PMP, **5e**), 7.15-7.33 (m, 18H, 2x5H, Ph, β -lactam, 2x2H, C2 and C6, PMP and 2x2H, C3 and C5, 4-CF₃C₆H₄, **5e/6e**), 7.49 (d, 2H, $J = 8.07$ Hz, C2 and C6, 4-CF₃C₆H₄, **5e**), 7.57 (d, 2H, $J = 6.84$ Hz, C2 and C6, 4-CF₃C₆H₄, **6e**); ¹³C NMR (75 MHz, CDCl₃) δ /ppm: 16.52 (CMe₂, **6e**), 18.86 (CMe₂, **5e**), 20.37 (CMe₂, **6e**), 24.42 (CMe₂, **5e**), 47.29 (CMe₂, **5e/6e**), 52.25 (COOMe, **5e/6e**), 55.38 (OMe, PMP, **5e/6e**), 64.81 (C4, β -lactam, **5e**), 64.89 (C4, β -lactam, **6e**), 66.44 (C3, β -lactam, **5e/6e**), 73.65 (CHN, **5e**), 75.97 (CHN, **6e**), 114.21 (C3 and C5, PMP, **6e**), 114.26 (C3 and C5, PMP, **5e**), 118.59 (C2 and C6, PMP, **6e**), 118.66 (C2 and C6, PMP, **5e**), 124.88 (d, $J = 3.90$ Hz, C3 and C5, 4-CF₃C₆H₄, **5e**), 124.89 (d, $J = 10.89$ Hz, C3 and C5, 4-CF₃C₆H₄, **6e**), 125.49 (C2 and C6, Ph, β -lactam, **6e**), 125.61 (C2 and C6, Ph, β -lactam, **5e**), 127.43 (CF₃, **5e/6e**), 128.30 (C4, Ph, β -lactam, **5e**), 128.38 (C4, Ph, β -lactam, **6e**), 128.69 (C3 and C5, Ph, β -lactam, **5e**), 129.05 (C3 and C5, Ph, β -lactam, **6e**), 129.31 (C2 and C6, 4-CF₃C₆H₄, **5e**), 129.53 (C2 and C6, 4-CF₃C₆H₄, **6e**), 130.80 (C1, Ph, β -lactam, **5e**), 130.86 (C1, Ph, β -lactam, **6e**), 131.62 (C4, 4-CF₃C₆H₄, **5e/6e**), 136.99 (C1, PMP, **5e/6e**), 142.43 (C1, 4-CF₃C₆H₄, **5e**), 142.45 (C1, 4-CF₃C₆H₄, **6e**), 156.14 (C4, PMP, **5e/6e**), 165.05 (CO, β -lactam, **5e/6e**), 177.22 (COOMe, **5e/6e**). Anal. Calcd for C₂₉H₂₉N₂O₄F₃ x 0.5 H₂O (**5e/6e**, $M_r = 535.57$): C 65.04, H 5.65, N 5.23%. Found: C 65.16, H 6.06, N 5.23%.

Methyl (3*S*/3*R*)-(trans-(3'*R*,4'*R*)-3-amino-1-(4-methoxyphenyl)-2-oxo-4-phenylazetididin-3-yl)-2,2-dimethyl-3-(2-nitrophenyl)propanoate, 5f/6f

Obtained from (3*R*,4*R*)-**3f** (15.0 mg, 3.74×10^{-2} mmol), silylenol ether **4** (7.16 mg, 8.33 μ L, 4.11×10^{-2} mmol) and zinc(II) iodide (11.9 mg, 3.74×10^{-2} mmol) as a diastereomeric mixture **5f/6f**, 9.50 mg (50.5%), $R_f = 0.10$ (EtOAc – petroleum ether in ratio 1:3). RP-HPLC analysis (method I) of diastereomeric mixture showed ratio of **5f/6f** – 83:17% (**6f**, 8.41 min and **5f**, 8.81 min). LC-MS for $C_{28}H_{29}N_3O_6$ ($M_r = 503.55768$): calcd. m/z $[M+H]^+$ 504.21, found 504.30 (**6f**, 10.78 min) and 504.30 (**5f**, 11.81 min); IR (KBr) ν_{max}/cm^{-1} : 3650, 3340, 3030, 2955, 2839, 1735, 1608, 1512, 1458, 1356, 1298, 1248, 1130, 1030, 893, 852, 833, 746, 699; 1H NMR (300 MHz, $CDCl_3$) δ/ppm : 1.08 (s, 3H, CMe_2 , **5f**), 1.11 (s, 3H, CMe_2 , **5f**), 1.16 (s, 3H, CMe_2 , **6f**), 1.26 (s, 3H, CMe_2 , **6f**), 2.76 (bs, 2H, NH, β -lactam, **5f/6f**), 3.67 (s, 3H, $COOMe$, **6f**), 3.70 (s, 3H, OMe , PMP, **6f**), 3.71 (s, 1H, C4, β -lactam, **5f**), 3.73 (s, 3H, $COOMe$, **5f**), 3.74 (s, 3H, OMe , PMP, **5f**), 4.07 (d, 1H, $J = 1.83$ Hz, C4, β -lactam, **6f**), 4.47 (d, 1H, $J = 1.80$ Hz, C3, β -lactam, **6f**), 4.74 (d, 1H, $J = 1.53$ Hz, C3, β -lactam, **6f**), 4.81 (s, 1H, CHN, **6f**), 5.04 (s, 1H, CHN, **5f**), 6.71 (d, 2H, $J = 9.03$ Hz, C3 and C5, PMP, **6f**), 6.78 (d, 2H, $J = 8.43$ Hz, C3 and C5, PMP, **5f**), 7.11 (d, 2H, $J = 9.00$ Hz, C2 and C6, PMP, **6f**), 7.20 (d, 2H, $J = 9.00$ Hz, C2 and C6, PMP, **5f**), 7.23-7.42 (m, 10H, Ph, β -lactam, **5f/6f**), 7.58-7.67 (m, 6H, 2- $NO_2C_6H_4$, **5f/6f**), 7.75-7.83 (m, 2H, 2- $NO_2C_6H_4$, **5f/6f**); ^{13}C -NMR (75 MHz, $CDCl_3$) δ/ppm : 19.35 (CMe_2 , **5f**), 21.03 (CMe_2 , **6f**), 23.63 (CMe_2 , **6f**), 23.82 (CMe_2 , **5f**), 47.79 (CMe_2 , **6f**), 47.88 (CMe_2 , **5f**), 52.24 ($COOMe$, **6f**), 52.31 ($COOMe$, **5f**), 55.38 (OMe , PMP, **5f/6f**), 59.02 (C4, β -lactam, **5f**), 60.64 (C4, β -lactam, **6f**), 64.74 (C3, β -lactam, **6f**), 65.22 (C3, β -lactam, **5f**), 73.53 (CHN, **5f**), 75.75 (CHN, **6f**), 114.16 (C3 and C5, PMP, **6f**), 114.25 (C3 and C5, PMP, **5f**), 118.64 (C2 and C6, PMP, **6f**), 118.75 (C2 and C6, PMP, **5f**), 124.21 (C3, 2- $NO_2C_6H_4$, **5f/6f**), 125.59 (C2 and C6, Ph, β -lactam, **6f**), 125.85 (C2 and C6, Ph, β -lactam, **5f**), 128.19 (C6, 2- $NO_2C_6H_4$, **6f**), 128.26 (C6, 2- $NO_2C_6H_4$, **5f**), 128.54 (C4, Ph, β -lactam, **5f**), 128.68 (C4, Ph, β -lactam, **6f**), 128.94 (C3 and C5, Ph, β -lactam, **5f**), 129.11 (C3 and C5, Ph, β -lactam, **6f**), 129.70 (C4, 2- $NO_2C_6H_4$, **5f**), 130.06 (C4, 2- $NO_2C_6H_4$, **6f**), 130.86 (C1, Ph, β -lactam, **5f/6f**), 131.71 (C5, 2- $NO_2C_6H_4$, **6f**), 132.23 (C5, 2- $NO_2C_6H_4$, **5f**), 133.43 (C1, 2- $NO_2C_6H_4$, **5f/6f**), 136.61 (C1, PMP, **5f/6f**), 151.21 (C2, 2- $NO_2C_6H_4$, **5f**), 151.56 (C2, 2- $NO_2C_6H_4$, **6f**), 156.13 (C4, PMP, **5f/6f**), 164.96 (CO, β -lactam, **5f/6f**), 176.65 ($COOMe$, **5f/6f**). Anal. Calcd for $C_{28}H_{29}N_3O_6$ (**5f/6f**, $M_r = 503.56$): C 66.79, H 5.81, N 8.34%. Found: C 66.49, H 6.18, N 8.03%.

Methyl (3*S*/3*R*)-(trans-(3'*R*,4'*R*)-3-amino-1-(4-methoxyphenyl)-2-oxo-4-phenylazetididin-3-yl)-2,2-dimethyl-3-(3-nitrophenyl)propanoate, 5g/6g

Obtained from (3*R*,4*R*)-**3g** (10.0 mg, 2.49×10^{-2} mmol), silylenol ether **4** (4.8 mg, 5.6 μ L, 2.74×10^{-2} mmol) and zinc(II) iodide (7.95 mg, 2.49×10^{-2} mmol) as a diastereomeric mixture **5g/6g**, 11.7 mg (93.3%), $R_f = 0.21$ (EtOAc – petroleum ether in ratio 1:3). RP-HPLC analysis (method I) of

diastereomeric mixture showed ratio of **5g/6g** – 77:23% (**6g**, 12.34 min and **5g**, 12.76 min). LC-MS for $C_{28}H_{29}N_3O_6$ ($M_r = 503.55768$): calcd. m/z $[M+H]^+$ 504.21, found 504.30 (**6g**, 12.28 min) and 504.30 (**5g**, 13.71 min); IR (KBr) ν_{max}/cm^{-1} : 3650, 3334, 2949, 1735, 1654, 1618, 1585, 1528, 1512, 1458, 1349, 1247, 1131, 1029, 829, 698; 1H NMR (600 MHz, $CDCl_3$) δ/ppm : 1.09 (s, 3H, CMe_2 , **5g**), 1.14 (s, 3H, CMe_2 , **5g**), 1.17 (s, 3H, CMe_2 , **6g**), 1.19 (s, 3H, CMe_2 , **6g**), 2.70 (bs, 2H, NH, β -lactam, **5g/6g**), 3.71 (s, 3H, COOMe, **6g**), 3.72 (bs, 6H, COOMe, **5g** and OMe, PMP, **6g**), 3.74 (s, 1H, C4, β -lactam, **5g**), 3.75 (s, 1H, C4, β -lactam, **6g**), 3.76 (s, 3H, OMe, PMP, **5g**), 4.16 (s, 1H, CHN, **6g**), 4.22 (s, 1H, CHN, **5g**), 4.45 (d, 1H, $J = 1.68$ Hz, C3, β -lactam, **6g**), 4.68 (d, 1H, $J = 1.56$ Hz, C3, β -lactam, **5g**), 6.73 (d, 2H, $J = 9.00$ Hz, C3 and C5, PMP, **6g**), 6.75 (d, 2H, $J = 9.06$ Hz, C3 and C5, PMP, **5g**), 6.79 (d, 2H, $J = 6.78$ Hz, 3- $NO_2C_6H_4$, **5g/6g**), 7.11 (d, 2H, $J = 9.06$ Hz, C2 and C6, PMP, **5g**), 7.13-7.32 (m, 12H, 2x5H, Ph, β -lactam, **5g/6g** and 2H, C2 and C6, PMP, **6g**), 7.42-7.48 (m, 2H, 3- $NO_2C_6H_4$, **5g/6g**), 7.59-7.62 (m, 2H, 3- $NO_2C_6H_4$, **5g/6g**), 7.98-8.16 (m, 2H, 3- $NO_2C_6H_4$, **5g/6g**); ^{13}C NMR (150 MHz, $CDCl_3$) δ/ppm : 19.23 (CMe_2 , **5g**), 20.50 (CMe_2 , **6g**), 23.60 (CMe_2 , **6g**), 24.24 (CMe_2 , **5g**), 47.24 (CMe_2 , **6g**), 47.26 (CMe_2 , **5g**), 52.28 (COOMe, **6g**), 52.35 (COOMe, **5g**), 55.38 (OMe, PMP, **6g**), 55.39 (OMe, PMP, **5g**), 64.63 (C4, β -lactam, **5g**), 65.00 (C4, β -lactam, **6g**), 66.52 (C3, β -lactam, **6g**), 68.27 (C3, β -lactam, **5g**), 73.83 (CHN, **5g**), 75.35 (CHN, **6g**), 114.26 (C3 and C5, PMP, **6g**), 114.29 (C3 and C5, PMP, **5g**), 118.60 (C2 and C6, PMP, **6g**), 118.66 (C2 and C6, PMP, **5g**), 122.90 (C4, 3- $NO_2C_6H_4$, **6g**), 122.92 (C4, 3- $NO_2C_6H_4$, **5g**), 123.84 (C2, 3- $NO_2C_6H_4$, **6g**), 124.04 (C2, 3- $NO_2C_6H_4$, **5g**), 125.45 (C2 and C6, Ph, β -lactam, **6g**), 125.50 (C2 and C6, Ph, β -lactam, **5g**), 128.34 (C4, Ph, β -lactam, **6g**), 128.42 (C4, Ph, β -lactam, **5g**), 128.79 (C3 and C5, Ph, β -lactam, **6g**), 128.87 (C6, 3- $NO_2C_6H_4$, **6g**), 128.99 (C6, 3- $NO_2C_6H_4$, **5g**), 129.13 (C3 and C5, Ph, β -lactam, **5g**), 130.73 (C1, Ph, β -lactam, **6g**), 130.74 (C1, Ph, β -lactam, **5g**), 134.71 (C5, 3- $NO_2C_6H_4$, **5g**), 135.28 (C5, 3- $NO_2C_6H_4$, **6g**), 136.40 (C1, PMP, **6g**), 136.82 (C1, PMP, **5g**), 140.60 (C1, 3- $NO_2C_6H_4$, **5g**), 142.44 (C1, 3- $NO_2C_6H_4$, **6g**), 147.89 (C3, 3- $NO_2C_6H_4$, **5g**), 148.13 (C3, 3- $NO_2C_6H_4$, **6g**), 156.14 (C4, PMP, **5g**), 156.20 (C4, PMP, **6g**), 164.86 (CO, β -lactam, **5g**), 165.39 (CO, β -lactam, **6g**), 176.40 (COOMe, **6g**), 176.88 (COOMe, **5g**). Anal. Calcd for $C_{28}H_{29}N_3O_6$ (**5g/6g**, $M_r = 503.56$): C 66.79, H 5.81, N 8.34%. Found: C 66.99, H 6.06, N 7.99%.

Methyl (3S/3R)-(trans-(3'R,4'R)-3-amino-1-(4-methoxyphenyl)-2-oxo-4-phenylazetididin-3-yl)-2,2-dimethyl-3-(4-nitrophenyl)propanoate, 5h/6h

Obtained from (3R,4R)-**3h** (15.0 mg, 3.74×10^{-2} mmol), silylenol ether **4** (7.16 mg, 8.33 μ L, 4.11×10^{-2} mmol) and zinc(II) iodide (11.9 mg, 3.74×10^{-2} mmol) as a diastereomeric mixture **5h/6h**, 18.4 mg (97.6%), $R_f = 0.11$ (EtOAc – petroleum ether in ratio 1:3). RP-HPLC analysis (method I) of diastereomeric mixture showed ratio of **5h/6h** – 87:13% (**5h**, 9.44 min and **6h**, 9.80 min). LC-MS for $C_{28}H_{29}N_3O_6$ ($M_r = 503.55768$): calcd. m/z $[M+H]^+$ 504.21, found 504.30 (**6h**, 13.05 min) and 504.30 (**5h**,

14.32 min); IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3362, 3341, 2950, 1734, 1654, 1636, 1605, 1560, 1508, 1458, 1388, 1346, 1247, 1131, 1030, 853, 828, 748, 698; ^1H NMR (300 MHz, CDCl_3) δ/ppm : 1.08 (s, 3H, CMe_2 , **5h**), 1.17 (s, 3H, CMe_2 , **5h**), 1.22 (s, 3H, CMe_2 , **6h**), 1.24 (s, 3H, CMe_2 , **6h**), 2.69 (bs, 2H, NH, β -lactam, **5h/6h**), 3.64 (bs, 2H, C4, β -lactam, **5h/6h**), 3.71 (s, 3H, COOMe, **6h**), 3.72 (s, 3H, OMe, PMP, **6h**), 3.73 (s, 3H, COOMe, **5h**), 3.76 (s, 3H, OMe, PMP, **6h**), 4.16 (s, 1H, CHN, **6h**), 4.22 (s, 1H, CHN, **5h**), 4.43 (d, 1H, $J = 1.41$ Hz, C3, β -lactam, **6h**), 4.67 (d, 1H, $J = 1.56$ Hz, C3, β -lactam, **5h**), 6.71-6.82 (m, 4H, C3 and C5, PMP, **5h/6h**), 7.11 (d, 2H, $J = 9.03$ Hz, C2 and C6, PMP, **6h**), 7.17 (d, 2H, $J = 9.00$ Hz, C2 and C6, PMP, **5h**), 7.19-7.34 (m, 10H, Ph, β -lactam, **5h/6h**), 7.38 (d, 2H, $J = 8.64$ Hz, C2 and C6, 4- $\text{NO}_2\text{C}_6\text{H}_4$, **5h**), 7.47 (d, 2H, $J = 8.70$ Hz, C2 and C6, 4- $\text{NO}_2\text{C}_6\text{H}_4$, **6h**), 8.10 (d, 2H, $J = 8.67$ Hz, C3 and C5, 4- $\text{NO}_2\text{C}_6\text{H}_4$, **5h**), 8.15 (d, 2H, $J = 8.76$ Hz, C3 and C5, 4- $\text{NO}_2\text{C}_6\text{H}_4$, **6h**); ^{13}C -NMR (75 MHz, CDCl_3) δ/ppm : 19.09 (CMe_2 , **5h**), 20.40 (CMe_2 , **6h**), 21.30 (CMe_2 , **6h**), 24.34 (CMe_2 , **5h**), 47.24 (CMe_2 , **6h**), 47.29 (CMe_2 , **5h**), 52.37 (COOMe, **5h/6h**), 55.38 (OMe, PMP, **6h**), 55.48 (OMe, PMP, **5h**), 64.80 (C4, β -lactam, **5h**), 66.44 (C3, β -lactam, **5h**), 68.19 (C4, β -lactam, **6h**), 69.25 (C3, β -lactam, **6h**), 73.77 (CHN, **5h**), 75.32 (CHN, **6h**), 114.28 (C3 and C5, PMP, **5h/6h**), 118.56 (C2 and C6, PMP, **6h**), 118.66 (C2 and C6, PMP, **5h**), 123.11 (C3 and C5, 4- $\text{NO}_2\text{C}_6\text{H}_4$, **5h/6h**), 125.53 (C2 and C6, Ph- β -lactam, **5h/6h**), 128.42 (C4, Ph, β -lactam, **5h**), 128.83 (C4, Ph, β -lactam, **6h**), 129.12 (C3 and C5, Ph, β -lactam, **5h/6h**), 129.85 (C2 and C6, 4- $\text{NO}_2\text{C}_6\text{H}_4$, **5h**), 129.86 (C2 and C6, 4- $\text{NO}_2\text{C}_6\text{H}_4$, **6h**), 130.67 (C1, Ph, β -lactam, **5h/6h**), 136.88 (C1, PMP, **5h/6h**), 146.07 (C1, 4- $\text{NO}_2\text{C}_6\text{H}_4$, **5h/6h**), 147.58 (C4, 4- $\text{NO}_2\text{C}_6\text{H}_4$, **5h/6h**), 156.13 (C4, PMP, **6h**), 156.19 (C4, PMP, **5h**), 164.85 (CO, β -lactam, **5h**), 165.06 (CO, β -lactam, **6h**), 176.90 (COOMe, **5h/6h**). Anal. Calcd for $\text{C}_{28}\text{H}_{29}\text{N}_3\text{O}_6$ (**5h/6h**, $M_r = 503.56$): C 66.79, H 5.81, N 8.34%. Found: C 66.99, H 6.09, N 8.01%.

Methyl (3S/3R)-(trans-(3'R,4'R)-3-amino-1-(4-methoxyphenyl)-2-oxo-4-phenylazetididin-3-yl)-2,2-dimethyl-3-(trans-2-phenylethenyl)propanoate, 5i/6i

Obtained from (3R,4R)-**3i** (15.0 mg, 3.9×10^{-2} mmol), silylenol ether **4** (7.50 mg, $8.71 \mu\text{L}$, 4.3×10^{-2} mmol) and zinc(II) iodide (12.5 mg , 3.9×10^{-2} mmol) as a diastereomeric mixture **5i/6i**, 18.1 mg (95.8%), $R_f = 0.30$ (EtOAc – petroleum ether in ratio 1:2). RP-HPLC analysis (method I) of diastereomeric mixture showed ratio of **5i/6i** – 92:8% (**5i**, 16.30 min and **6i**, 17.48 min). LC-MS for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_4$ ($M_r = 484.59816$): calcd. m/z $[\text{M}+\text{H}]^+$ 485.24, found 485.30 (**5i**, 25.73 min) and 485.30 (**6i**, 31.03 min); IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3630, 3568, 2927, 1735, 1686, 1654, 1648, 1637, 1560, 1542, 1509, 1458, 1388, 1247, 1131, 829, 747, 697; ^1H NMR (600 MHz, CDCl_3) δ/ppm : 1.06 (s, 3H, CMe_2 , **5i**), 1.08 (s, 3H, CMe_2 , **6i**), 1.16 (s, 3H, CMe_2 , **6i**), 1.18 (s, 3H, CMe_2 , **5i**), 1.77 (bs, 1H, NH, β -lactam, **6i**), 2.55 (bs, 1H, NH, β -lactam, **5i**), 3.72 (s, 3H, COOMe, **6i**), 3.74 (bs, 6H, 3H, COOMe, **5i** and 3H, OMe, PMP, **6i**), 3.78 (d, 1H, $J = 1.92$ Hz, C4, β -lactam, **5i**), 3.78 (bs, 1H, C4, β -lactam, **6i**), 3.82 (s, 3H, OMe, PMP, **5i**), 3.91 (s, 1H,

CHN, **6i**), 4.01 (s, 1H, CHN, **5i**), 4.37 (d, 1H, $J = 1.80$ Hz, C3, β -lactam, **6i**), 4.63 (d, 1H, $J = 1.86$ Hz, C3, β -lactam, **5i**), 6.64 (d, 1H, $J = 1.74$ Hz, PhCH=CH-, **5i**), 6.69 (d, 1H, $J = 1.86$ Hz, PhCH=CH-, **6i**), 6.71 (d, 1H, $J = 1.92$ Hz, PhCH=CH-, **5i**), 6.72 (d, 2H, $J = 9.18$ Hz, C3 and C5, PMP, **6i**), 6.73- 6.75 (m, 1H, PhCH=CH-, **5i**), 6.75 (d, 2H, $J = 9.12$ Hz, C3 and C5, PMP, **5i**), 7.11 (d, 2H, $J = 9.06$ Hz, C2 and C6, PMP, **6i**), 7.17 (d, 2H, $J = 9.06$ Hz, C2 and C6, PMP, **5i**), 7.19-7.33 (m, 20H, 2x5H, Ph, β -lactam and 2x5H, PhCH=CH-, **5i/6i**); ^{13}C NMR (150 MHz, CDCl_3) δ /ppm: 19.07 (CMe_2 , **5i**), 20.34 (CMe_2 , **6i**), 23.80 (CMe_2 , **6i**), 24.49 (CMe_2 , **5i**), 47.45 (CMe_2 , **5i**), 47.65 (CMe_2 , **6i**), 51.99 (COOMe , **6i**), 52.08 (COOMe , **5i**), 55.79 (OMe, PMP, **5i**), 55.91 (OMe, PMP, **6i**), 64.52 (C4, β -lactam, **5i**), 65.10 (C4, β -lactam, **6i**), 66.45 (C3, β -lactam, **5i**), 68.74 (C3, β -lactam, **6i**), 73.73 (CHN, **5i**), 76.12 (CHN, **6i**), 110.54 (PhCH=CH-, **5i**), 110.63 (PhCH=CH-, **6i**), 112.06 (PhCH=CH-, **5i**), 112.31 (PhCH=CH-, **6i**), 114.23 (C3 and C5, PMP, **5i**), 114.36 (C3 and C5, PMP, **6i**), 118.54 (C2 and C6, PMP, **6i**), 118.63 (C2 and C6, PMP, **5i**), 121.09 (C2 and C6, PhCH=CH-, **5i**), 121.17 (C2 and C6, PhCH=CH-, **6i**), 125.73 (C2 and C6, Ph, β -lactam, **5i/6i** and C3 and C5, PhCH=CH-, **5i/6i**), 128.02 (C4, PhCH=CH-, **6i**), 128.12 (C4, PhCH=CH-, **5i**), 128.54 (C4, Ph, β -lactam, **5i**), 128.62 (C4, Ph, β -lactam, **6i**), 128.93 (C3 and C5, Ph, β -lactam, **5i/6i**), 130.58 (C1, Ph, β -lactam, **5i**), 130.93 (C1, Ph, β -lactam, **6i**), 136.78 (C1, PMP, **6i**), 137.32 (C1, PMP, **5i**), 148.39 (C1, PhCH=CH-, **5i/6i**), 156.04 (C4, PMP, **5i/6i**), 165.53 (CO, β -lactam, **5i**), 165.60 (CO, β -lactam, **6i**), 177.71 (COOMe , **5i/6i**). HRMS for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_4$ (**5i/6i**, $M_r = 484.59816$): calcd. m/z $[\text{M}+\text{Na}]^+$ 507.2254, found 507.2236.

Methyl (3S/3R)-(trans-(3'R,4'R)-3-amino-1-(4-methoxyphenyl)-2-oxo-4-phenylazetididin-3-yl)-2,2-dimethyl-3-(3-pyridyl)propanoate, 5j/6j

Obtained from (3R,4R)-**3j** (15.0 mg, 4.2×10^{-2} mmol), silylenol ether **4** (8.05 mg, 9.36 μL , 4.62×10^{-2} mmol) and zinc(II) iodide (13.4 mg, 4.2×10^{-2} mmol) as a diastereomeric mixture **5j/6j**, 18.7 mg (96.8%), $R_f = 0.65$ (EtOAc – petroleum ether in ratio 3:1). RP-HPLC analysis (method I) of diastereomeric mixture showed ratio of **5j/6j** – 71:29% (**6j**, 8.45 min and **5j**, 8.76 min). LC-MS for $\text{C}_{27}\text{H}_{29}\text{N}_3\text{O}_4$ ($M_r = 459.54778$): calcd. m/z $[\text{M}+\text{H}]^+$ 460.22, found 460.30 (**5j**, 2.04 min) and 460.30 (**6j**, 2.23 min); IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3629, 3332, 3031, 2981, 2952, 2843, 1739, 1588, 1574, 1514, 1456, 1392, 1370, 1299, 1251, 1184, 1134, 1112, 1068, 1029, 967, 830, 752, 699; ^1H NMR (300 MHz, CDCl_3) δ /ppm: 1.07 (s, 3H, CMe_2 , **5j**), 1.17 (s, 3H, CMe_2 , **5j**), 1.22 (s, 3H, CMe_2 , **6j**), 1.24 (s, 3H, CMe_2 , **6j**), 2.64 (bs, 2H, NH, β -lactam, **5j/6j**), 3.66 (bs, 1H, C4, β -lactam, **5j**), 3.71 (s, 3H, COOMe , **5j**), 3.72 (bs, 6H, 3H, COOMe and 3H, OMe, PMP, **6j**), 3.76 (s, 3H, OMe, PMP, **5j**), 3.79 (s, 1H, C4, β -lactam, **6j**), 4.02 (s, 1H, CHN, **6j**), 4.13 (s, 1H, CHN, **5j**), 4.40 (d, 1H, $J = 1.71$ Hz, C3, β -lactam, **6j**), 4.68 (d, 1H, $J = 1.71$ Hz, C3, β -lactam, **5j**), 6.71-6.76 (d, 4H, C3 and C5, PMP, **5j/6j**), 7.09-7.33 (m, 16H, 2x5H, Ph, β -lactam, 2x2H, C2 and C6, PMP and 2x1H, Py, **5j/6j**), 7.62-7.66 (m, 2H, Py, **5j/6j**), 8.31 (d, 1H, $J = 1.89$ Hz, Py, **5j**), 8.47 (dd, 1H,

$J_1 = 4.73$ Hz, $J_2 = 1.51$ Hz, Py, **5j**), 8.51 (d, 1H, $J = 1.93$ Hz, Py, **6j**), 8.56 (dd, 1H, $J_1 = 4.64$ Hz, $J_2 = 1.55$ Hz, Py, **6j**); ^{13}C NMR (75 MHz, CDCl_3) δ/ppm : 18.85 (CMe_2 , **5j**), 20.20 (CMe_2 , **6j**), 23.64 (CMe_2 , **6j**), 24.33 (CMe_2 , **5j**), 47.31 (CMe_2 , **5j**), 47.41 (CMe_2 , **6j**), 52.19 (COOMe , **6j**), 52.27 (COOMe , **5j**), 55.35 (OMe, PMP, **6j**), 55.37 (OMe, PMP, **5j**), 64.54 (C4, β -lactam, **5j**), 64.80 (C3, β -lactam, **5j**), 65.04 (C4, β -lactam, **6j**), 66.72 (C3, β -lactam, **6j**), 73.63 (CHN, **5j**), 75.72 (CHN, **6j**), 114.21 (C3 and C5, PMP, **6j**), 114.25 (C3 and C5, PMP, **5j**), 118.58 (C2 and C6, PMP, **6j**), 118.66 (C2 and C6, PMP, **5j**), 123.04 (C5, Py, **6j**), 123.11 (C5, Py, **5j**), 125.46 (C2 and C6, Ph, β -lactam, **6j**), 125.52 (C2 and C6, Ph, β -lactam, **5j**), 128.22 (C4, Ph, β -lactam, **6j**), 128.39 (C4, Ph, β -lactam, **5j**), 128.81 (C3 and C5, Ph, β -lactam, **6j**), 129.11 (C3 and C5, Ph, β -lactam, **5j**), 130.76 (C1, Ph, β -lactam, **5j/6j**), 133.65 (C1, Py, **5j**), 135.49 (C1, Py, **6j**), 135.94 (C6, Py, **5j**), 136.40 (C1, PMP, **6j**), 136.52 (C6, Py, **6j**), 136.87 (C1, PMP, **5j**), 149.23 (C2, Py, **6j**), 149.30 (C2, Py, **5j**), 150.55 (C4, Py, **6j**), 150.68 (C4, Py, **5j**), 156.14 (C4, PMP, **5j/6j**), 164.97 (CO, β -lactam, **5j**), 165.24 (CO, β -lactam, **6j**), 177.10 (COOMe , **5j/6j**). Anal. Calcd for $\text{C}_{27}\text{H}_{29}\text{N}_3\text{O}_4$ (**5j/6j**, $M_r = 459.55$): C 70.57, H 6.36, N 9.14%. Found: C 70.28, H 6.39, N 9.13%.

Methyl (3S/3R)-(trans-(3'R,4'R)-3-amino-1-(4-methoxyphenyl)-2-oxo-4-phenylazetididin-3-yl)-2,2-dimethyl-3-(furan-2-yl)propanoate, 5m/6m

Obtained from (3R,4R)-**3m** (15.0 mg, 4.33×10^{-2} mmol), silylenol ether **4** (8.30 mg, $9.65 \mu\text{L}$, 4.76×10^{-2} mmol) and zinc(II) iodide (13.8 mg, 4.33×10^{-2} mmol) as a diastereomeric mixture **5m/6m**, 15.5 mg (80.0%), $R_f = 0.39$ (EtOAc – petroleum ether in ratio 1:3). RP-HPLC analysis (method I) of diastereomeric mixture showed ratio of **5m/6m** – 66:34% (**6m**, 13.38 min and **5m**, 13.62 min). LC-MS for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_5$ ($M_r = 448.5214$): calcd. m/z $[\text{M}+\text{H}]^+$ 449.21, found 449.30 (**6m**, 11.52 min) and 449.30 (**5m**, 12.14 min); IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3752, 3320, 3065, 3035, 2953, 2852, 2346, 1740, 1706, 1587, 1514, 1456, 1396, 1369, 1299, 1251, 1185, 1134, 1068, 1030, 966, 831, 752, 733, 698; ^1H NMR (600 MHz, CDCl_3) δ/ppm : 1.11 (s, 3H, CMe_2 , **5m**), 1.12 (s, 3H, CMe_2 , **6m**), 1.20 (s, 3H, CMe_2 , **6m**), 1.24 (s, 3H, CMe_2 , **5m**), 2.51 (bs, 1H, NH, β -lactam, **5m**), 2.59 (bs, 1H, NH, β -lactam, **6m**), 3.68 (s, 3H, COOMe , **6m**), 3.71 (s, 3H, OMe, PMP, **6m**), 3.73 (s, 3H, COOMe , **5m**), 3.74 (s, 3H, OMe, PMP, **5m**), 3.81 (d, 1H, $J = 1.80$ Hz, C4, β -lactam, **5m**), 3.92 (d, 1H, $J = 1.50$ Hz, C4, β -lactam, **6m**), 4.03 (s, 1H, CHN, **6m**), 4.06 (s, 1H, CHN, **5m**), 4.37 (d, 1H, $J = 1.74$ Hz, C3, β -lactam, **6m**), 4.58 (d, 1H, $J = 1.68$ Hz, C3, β -lactam, **5m**), 6.04 (d, 1H, $J = 3.06$ Hz, C3, furyl, **5m**), 6.13 (d, 1H, $J = 2.94$ Hz, C3, furyl, **6m**), 6.26 (dd, 1H, $J_1 = 3.12$ Hz, $J_2 = 1.83$ Hz, C4, furyl, **5m**), 6.39 (dd, 1H, $J_1 = 3.12$ Hz, $J_2 = 1.83$ Hz, C4, furyl, **6m**), 6.73 (d, 2H, $J = 9.06$ Hz, C3 and C5, PMP, **6m**), 6.76 (d, 2H, $J = 9.06$ Hz, C3 and C5, PMP, **5m**), 6.95-6.97 (m, 1H, C5, furyl, **5m**), 7.15 (d, 2H, $J = 9.12$ Hz, C2 and C6, PMP, **6m**), 7.18 (d, 2H, $J = 9.12$ Hz, PMP, **5m**), 7.24-7.35 (m, 10H, Ph, β -lactam, **5m/6m**), 7.42 (m, 1H, C5, furyl, **6m**); ^{13}C NMR (150 MHz, CDCl_3) δ/ppm : 19.46 (CMe_2 , **5m**), 20.46 (CMe_2 , **6m**), 23.26 (CMe_2 , **6m**), 23.79 (CMe_2 , **5m**), 47.51

(CMe₂, **5m**), 47.88 (CMe₂, **6m**), 51.98 (COOMe, **6m**), 52.06 (COOMe, **5m**), 55.37 (OMe, PMP, **6m**), 55.40 (OMe, PMP, **5m**), 60.78 (C4, β-lactam, **5m**), 61.84 (C4, β-lactam, **6m**), 63.95 (C3, β-lactam, **6m**), 64.98 (C3, β-lactam, **5m**), 73.72 (CHN, **5m**), 76.13 (CHN, **6m**), 108.89 (C5, furyl, **6m**), 109.20 (C5, furyl, **5m**), 110.06 (C4, furyl, **5m**), 110.48 (C5, furyl, **6m**), 114.20 (C3 and C5, PMP, **6m**), 114.25 (C3 and C5, PMP, **6m**), 118.64 (C2 and C6, PMP, **5m/6m**), 125.81 (C2 and C6, Ph, β-lactam, **5m**), 125.90 (C2 and C6, Ph, β-lactam, **6m**), 128.18 (C4, Ph, β-lactam, **6m**), 128.74 (C4, Ph, β-lactam, **5m**), 128.74 (C3 and C5, Ph, β-lactam, **6m**), 129.02 (C3 and C5, Ph, β-lactam, **5m**), 130.93 (C1, Ph, β-lactam, **6m**), 130.97 (C1, Ph, β-lactam, **5m**), 137.07 (C1, PMP, **6m**), 137.21 (C1, PMP, **5m**), 141.77 (C3, furyl, **6m**), 142.16 (C3, furyl, **5m**), 152.51 (C2, furyl, **5m**), 153.65 (C2, furyl, **6m**), 156.01 (C4, PMP, **6m**), 156.07 (C4, PMP, **5m**), 164.84 (CO, β-lactam, **5m**), 165.19 (CO, β-lactam, **6m**), 176.64 (COOMe, **6m**), 176.90 (COOMe, **5m**). Anal. Calcd for C₂₆H₂₈N₂O₅ (**5m/6m**, *M_r* = 448.52): C 69.63, H 6.29, N 6.25%. Found: C 69.79, H 6.44, N 6.21%.

Methyl (3S/3R)-(trans-(3'R,4'R)-3-amino-1-(4-methoxyphenyl)-2-oxo-4-phenylazetididin-3-yl)-2,2-dimethyl-3-(5-phenylfuran-2-yl)propanoate, 5n/6n

Obtained from (3R,4R)-**3n** (15.0 mg, 3.55 x 10⁻² mmol), silylenol ether **4** (6.82 mg, 7.92 μL, 3.91 x 10⁻² mmol) and zinc(II) iodide (11.3 mg, 3.55 x 10⁻² mmol) as a diastereomeric mixture **5n/6n**, 14.7 mg (78.7%), *R_f* = 0.23 (EtOAc – petroleum ether in ratio 1:3). RP-HPLC analysis (method I) of diastereomeric mixture showed ratio of **5n/6n** – 83:17% (**6n**, 16.36 min and **5n**, 16.70 min). LC-MS for C₃₂H₃₂N₂O₅ (*M_r* = 524.61976): calcd. *m/z* [M+Na]⁺ 547.22, found 547.30 (**6n**, 30.94 min) and 547.30 (**5n**, 34.61 min); IR (KBr) *v*_{max}/cm⁻¹: 3447, 2924, 2852, 1734, 1676, 1513, 1458, 1388, 1249, 1133, 1027, 830, 762, 692; ¹H NMR (300 MHz, CDCl₃) δ/ppm: 1.18 (s, 3H, CMe₂, **5n**), 1.27 (s, 3H, CMe₂, **6n**), 1.29 (s, 3H, CMe₂, **6n**), 1.31 (s, 3H, CMe₂, **5n**), 2.59 (bs, 2H, NH, β-lactam, **5n/6n**), 3.70 (s, 3H, COOMe, **6n**), 3.72 (s, 3H, COOMe, **5n**), 3.76 (bs, 6H, OMe, PMP, **5n/6n**), 3.91 (d, 1H, *J* = 1.92 Hz, C4, β-lactam, **5n**), 3.98 (d, 1H, *J* = 1.92 Hz, C4, β-lactam, **6n**), 4.04 (s, 1H, CHN, **6n**), 4.11 (s, 1H, CHN, **5n**), 4.44 (d, 1H, *J* = 1.38 Hz, C3, β-lactam, **6n**), 4.63 (d, 1H, *J* = 1.44 Hz, C3, β-lactam, **5n**), 6.13 (d, 1H, *J* = 3.24 Hz, C3, furan, **5n**), 6.34 (d, 1H, *J* = 3.24 Hz, C3, furan, **6n**), 6.52 (d, 1H, *J* = 3.24 Hz, C4, furan, **5n**), 6.59 (d, 1H, *J* = 3.24 Hz, C4, furan, **6n**), 6.70 (d, 2H, *J* = 9.00 Hz, C3 and C5, PMP, **6n**), 6.76 (d, 2H, *J* = 9.00 Hz, C3 and C5, PMP, **5n**), 7.12 (d, 2H, *J* = 9.00 Hz, C2 and C6, PMP, **6n**), 7.19 (d, 2H, *J* = 9.00 Hz, C2 and C6, PMP, **5n**), 7.23-7.45 (m, 16H, 2x5H, Ph, β-lactam, **5n/6n** and 2x3H, furan, **5n/6n**), 7.56 (d, 2H, *J* = 7.98 Hz, Ph-furan, **5n**), 7.64 (d, 2H, *J* = 7.98 Hz, Ph-furan, **6n**); ¹³C NMR (75 MHz, CDCl₃) δ/ppm: 19.61 (CMe₂, **5n**), 20.37 (CMe₂, **6n**), 23.06 (CMe₂, **5n**), 23.87 (CMe₂, **6n**), 47.38 (CMe₂, **5n**), 47.70 (CMe₂, **6n**), 52.11 (COOMe, **5n**), 52.15 (COOMe, **6n**), 55.34 (OMe, PMP, **6n**), 55.39 (OMe, PMP, **5n**), 60.90 (C4, β-lactam, **5n**), 62.36 (C4, β-lactam, **6n**), 63.95 (C3, β-lactam, **5n**), 65.46 (C3, β-lactam, **6n**), 73.72 (CHN,

5n), 76.20 (CHN, **6n**), 105.44 (C3, furan, **5n**), 105.49 (C3, furan, **6n**), 110.92 (C4, furan, **5n**), 111.25 (C3, furan, **6n**), 114.18 (C3 and C5, PMP, **6n**), 114.25 (C3 and C5, PMP, **5n**), 118.65 (C2 and C6, PMP, **5n/6n**), 123.64 (C2 and C6, Ph, furan, **5n/6n**), 125.82 (C2 and C6, Ph, β -lactam, **5n**), 125.89 (C2 and C6, Ph, β -lactam, **6n**), 127.32 (C4, Ph, furan, **6n**), 127.35 (C4, Ph-furan, **5n**), 128.13 (C4, Ph, β -lactam, **6n**), 128.27 (C4, Ph, β -lactam, **5n**), 128.63 (C3 and C5, Ph, furan, **5n**), 128.72 (C3 and C5, Ph, furan, **6n**), 128.75 (C3 and C5, Ph, β -lactam, **6n**), 129.04 (C3 and C5, Ph, β -lactam, **5n**), 130.53 (C1, Ph, furan, **5n**), 130.66 (C1, Ph, furan, **6n**), 130.67 (C1, Ph, β -lactam, **6n**), 130.95 (C1, Ph, β -lactam, **5n**), 136.91 (C1, PMP, **6n**), 137.20 (C1, PMP, **5n**), 152.20 (C2, furan, **5n**), 153.44 (C2, furan, **6n**), 153.49 (C5, furan, **6n**), 153.64 (C5, furan, **5n**), 156.08 (C4, PMP, **5n/6n**), 164.83 (CO, β -lactam, **5n**), 164.89 (CO, β -lactam, **6n**), 176.85 (COOMe, **5n**), 177.12 (COOMe, **6n**). HRMS for $C_{32}H_{32}N_2O_5$ ($M_r = 524.61976$): calcd. m/z $[M+Na]^+$ 547.2203, found 547.2221.

Methyl (3S/3R)-(trans-(3'R,4'R)-3-amino-1-(4-methoxyphenyl)-2-oxo-4-phenylazetididin-3-yl)-2,2-dimethyl-3-(5-methylfuran-2-yl)propanoate, 5o/6o

Obtained from (3R,4R)-**3o** (15.0 mg, 4.16×10^{-2} mmol), silylenol ether **4** (7.98 mg, 9.28 μ L, 4.58×10^{-2} mmol) and zinc(II) iodide (13.3 mg, 4.16×10^{-2} mmol) as a diastereomeric mixture **5o/6o**, 8.24 mg (42.8%), $R_f = 0.23$ (EtOAc – petroleum ether in ratio 1:3). RP-HPLC analysis (method I) of diastereomeric mixture showed ratio of **5o/6o** – 76:24% (**6o**, 15.47 min and **5o**, 15.68 min). LC-MS for $C_{27}H_{30}N_2O_5$ ($M_r = 462.54838$): calcd. m/z $[M+H]^+$ 463.22, found 463.30 (**6o**, 15.96 min) and 463.30 (**5o**, 16.82 min); IR (KBr) ν_{max}/cm^{-1} : 3402, 2975, 1738, 1514, 1457, 1388, 1299, 1250, 1135, 1089, 1049, 880, 832, 787, 748, 700; 1H NMR (300 MHz, $CDCl_3$) δ/ppm : 1.10 (s, 3H, CMe_2 , **5o**), 1.11 (s, 3H, CMe_2 , **6o**), 1.25 (s, 3H, CMe_2 , **5o**), 1.26 (s, 3H, CMe_2 , **6o**), 2.22 (s, 3H, Me, furan, **5o**), 2.30 (s, 3H, Me, furan, **6o**), 2.47 (bs, 2H, NH, β -lactam, **5o/6o**), 3.68 (s, 3H, COOMe, **6o**), 3.72 (s, 3H, OMe, PMP, **6o**), 3.73 (s, 3H, COOMe, **5o**), 3.74 (s, 3H, OMe, PMP, **5o**), 3.84 (d, 1H, $J = 1.80$ Hz, C4, β -lactam, **5o**), 3.92 (s, 1H, CHN, **6o**), 3.94 (bs, 1H, C4, β -lactam, **6o**), 3.96 (s, 1H, CHN, **5o**), 4.40 (d, 1H, $J = 1.71$ Hz, C3, β -lactam, **6o**), 4.60 (d, 1H, $J = 1.74$ Hz, C3, β -lactam, **5o**), 5.81 (dd, 1H, $J_1 = 2.95$ Hz, $J_2 = 0.92$ Hz, C3, furan, **5o**), 5.87 (d, 1H, $J = 3.06$ Hz, C4, furan, **5o**), 5.95 (dd, 1H, $J_1 = 2.97$ Hz, $J_2 = 0.84$ Hz, C3, furan, **6o**), 6.00 (d, 1H, $J = 3.03$ Hz, C4, furan, **6o**), 6.72-6.79 (m, 4H, C3 and C5, PMP, **5o/6o**), 7.14 (m, 4H, C2 and C6, PMP, **5o/6o**), 7.23-7.37 (m, 10H, Ph, β -lactam, **5o/6o**); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm : 13.58 (Me, furan, **5o**), 13.65 (Me, furan, **6o**), 19.46 (CMe_2 , **5o**), 20.49 (CMe_2 , **6o**), 23.27 (CMe_2 , **6o**), 23.82 (CMe_2 , **5o**), 47.40 (CMe_2 , **5o**), 47.77 (CMe_2 , **6o**), 51.91 (COOMe, **6o**), 52.01 (COOMe, **5o**), 55.37 (OMe, PMP, **5o**), 55.41 (OMe, PMP, **6o**), 60.77 (C4, β -lactam, **5o**), 62.00 (C4, β -lactam, **6o**), 63.89 (C3, β -lactam, **5o**), 65.07 (C3, β -lactam, **6o**), 73.60 (CHN, **5o**), 76.24 (CHN, **6o**), 105.90 (C3, furan, **5o**), 106.34 (C3, furan, **6o**), 109.55 (C4, furan, **6o**), 110.10 (C4, furan, **5o**), 114.20 (C3 and C5, PMP, **6o**), 114.25 (C3 and C5,

PMP, **5o**), 118.64 (C2 and C6, PMP, **5o/6o**), 125.85 (C2 and C6, Ph, β -lactam, **5o**), 125.95 (C2 and C6, Ph, β -lactam, **6o**), 128.12 (C4, Ph, β -lactam, **6o**), 128.22 (C4, Ph, β -lactam, **5o**), 128.73 (C3 and C5, Ph, β -lactam, **6o**), 129.00 (C3 and C5, Ph, β -lactam, **5o**), 131.00 (C1, Ph, β -lactam, **6o**), 131.03 (C1, Ph, β -lactam, **5o**), 137.15 (C1, PMP, **6o**), 137.31 (C1, PMP, **5o**), 150.32 (C2, furan, **5o**), 151.36 (C2, furan, **6o**), 151.75 (C5, furan, **6o**), 151.85 (C5, furan, **5o**), 156.06 (C4, PMP, **6o**), 156.06 (C4, PMP, **5o**), 164.96 (CO, β -lactam, **5o**), 165.33 (CO, β -lactam, **6o**), 177.03 (COOMe, **6o**), 177.33 (COOMe, **5o**). HRMS for $C_{27}H_{30}N_2O_5$ (**5o/6o**, $M_r = 462.54838$): calcd. m/z $[M+Na]^+$ 485.2047, found 485.2061.

Methyl (3*S*/3*R*)-(trans-(3'*R*,4'*R*)-3-amino-4-ferrocenyl-1-(4-methoxyphenyl)-2-oxoazetidin-3-yl)-2,2-dimethyl-3-phenylpropanoate, **5q/6q**

Obtained from (3*R*,4*R*)-**3q** (15.0 mg, 3.23×10^{-2} mmol), silylenol ether **4** (6.19 mg, 7.20 μ L, 3.55×10^{-2} mmol) and zinc(II) iodide (10.3 mg, 3.23×10^{-2} mmol) as a diastereomeric mixture **5q/6q**, 8.80 mg (48.1%), $R_f = 0.27$ (EtOAc – petroleum ether in ratio 1:4). RP-HPLC analysis (method III) of diastereomeric mixture showed ratio of **5q/6q** – 59:41% (**5q**, 3.12 min and **6q**, 3.95 min). IR (KBr) ν_{max}/cm^{-1} : 3630, 3468, 2925, 1735, 1685, 1654, 1637, 1560, 1542, 1508, 1458, 1246, 705; 1H NMR (300 MHz, $CDCl_3$) δ/ppm : 1.13 (s, 3H, CMe_2 , **5q**), 1.15 (s, 3H, CMe_2 , **6q**), 1.21 (s, 3H, CMe_2 , **6q**), 1.22 (s, 3H, CMe_2 , **5q**), 2.59 (bs, 2H, NH, β -lactam, **5q/6q**), 3.71 (s, 3H, COOMe, **6q**), 3.73 (s, 3H, COOMe, **5q**), 3.74 (s, 3H, OMe, PMP, **6q**), 3.77 (s, 3H, OMe, PMP, **5q**), 3.83-3.84 (m, 1H, Fc, **6q**), 3.85-3.87 (m, 1H, Fc, **5q**), 3.90-3.91 (m, 1H, Fc, **5q**), 3.99 (d, 1H, $J = 1.92$ Hz, C4, β -lactam, **6q**), 4.03 (s, 5H, Fc, **5q**), 4.05-4.08 (m, 4H, Fc, **5q/6q**), 4.09 (s, 5H, Fc, **6q**), 4.10 (s, 1H, Fc, **6q**), 4.13 (s, 1H, Fc, **5q**), 4.15 (d, 1H, $J = 2.67$ Hz, C4, β -lactam, **5q**), 4.28 (s, 1H, CHN, **6q**), 4.30 (d, 1H, $J = 1.65$ Hz, C3, β -lactam, **5q**), 4.50 (d, 1H, $J = 2.01$ Hz, C3, β -lactam, **6q**), 4.53 (s, 1H, CHN, **5q**), 6.79 (d, 2H, $J = 9.03$ Hz, C3 and C5, PMP, **6q**), 6.83 (d, 2H, $J = 9.00$ Hz, C3 and C5, PMP, **5q**), 7.22-7.24 (m, 4H, C2 and C6, PMP, **5q/6q**), 7.26 (s, 5H, Ph, **5q**), 7.40 (s, 5H, Ph, **6q**); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm : 19.33 (CMe_2 , **5q**), 20.07 (CMe_2 , **6q**), 24.09 (CMe_2 , **6q**), 24.30 (CMe_2 , **5q**), 47.22 (CMe_2 , **6q**), 47.44 (CMe_2 , **5q**), 52.06 (COOMe, **5q/6q**), 55.42 (OMe, PMP, **6q**), 55.45 (OMe, PMP, **5q**), 59.45 (C4, β -lactam, **5q**), 59.90 (C4, β -lactam, **6q**), 66.15 (C3, β -lactam, **5q**), 66.21 (C3, β -lactam, **6q**), 66.58 (Fc, **5q**), 66.78 (Fc, **6q**), 67.57 (Fc, **5q**), 67.80 (Fc, **6q**), 68.32 (Fc, **6q**), 68.48 (Fc, **5q**), 68.53 (Fc, **5q**), 68.61 (Fc, **5q**), 68.80 (Fc, **6q**), 69.43 (Fc, **5q**), 70.74 (CHN, **6q**), 72.01 (CHN, **5q**), 84.29 (C1, Fc, **6q**), 85.92 (C1, Fc, **5q**), 114.15 (C3 and C5, PMP, **6q**), 114.19 (C3 and C5, PMP, **5q**), 119.23 (C2 and C6, PMP, **6q**), 119.85 (C2 and C6, PMP, **5q**), 127.89 (C4, Ph, **6q**), 127.92 (C4, Ph, **5q**), 128.04 (C2 and C6, Ph, **6q**), 128.16 (C2, C6, Ph, **5q**), 129.15 (C3 and C5, Ph, **5q**), 129.48 (C3 and C5, Ph, **6q**), 130.65 (C1, Ph, **5q**), 130.97 (C1, Ph, **6q**), 138.92 (C1, PMP, **6q**), 139.11 (C1, PMP, **5q**), 156.12 (C4, PMP, **6q**), 156.38 (C4, PMP, **5q**), 165.97 (CO, β -lactam, **5q**), 166.77

(CO, β -lactam, **6q**), 177.42 (COOMe, **5q**), 177.61 (COOMe, **6q**). HRMS for $C_{32}H_{34}N_2O_4Fe$ (**5q/6q**, $M_r = 566.48324$): calcd. m/z $[M+H]^+$ 567.1941, found 567.1931.

Methyl (3*S*/3*R*)-(trans-(3'*R*,4'*R*)-3-amino-4-ferrocenyl-1-(4-methoxyphenyl)-2-oxoazetidin-3-yl)-2,2-dimethyl-3-(4-trifluoromethylphenyl) propanoate, **5r/6r**

Obtained from (3*R*,4*R*)-**3r** (15.0 mg, 2.81×10^{-2} mmol), silylenol ether **4** (5.40 mg, 6.30 μ L, 3.1×10^{-2} mmol) and zinc(II) iodide (9.0 mg, 2.81×10^{-2} mmol) as a diastereomeric mixture **5r/6r**, 9.30 mg (52.0%), $R_f = 0.29$ (EtOAc – petroleum ether in ratio 1:4). RP-HPLC analysis (method I) of diastereomeric mixture showed ratio of **5r/6r** – 79:21% (**5r**, 14.27 min and **6r**, 14.83 min). IR (KBr) ν_{max}/cm^{-1} : 3630, 3448, 2926, 1735, 1654, 1618, 1560, 1542, 1512, 1459, 1326, 1248, 1126, 1068, 829, 618; 1H NMR (300 MHz, $CDCl_3$) δ/ppm : 1.15 (s, 3H, CMe₂, **5r**), 1.17 (s, 3H, CMe₂, **5r**), 1.21 (s, 3H, CMe₂, **6r**), 1.26 (s, 3H, CMe₂, **6r**), 2.65 (bs, 2H, NH, β -lactam, **5r/6r**), 3.72 (s, 3H, COOMe, **6r**), 3.75 (bs, 6H, 3H, COOMe, **5r** and 3H, OMe, PMP, **6r**), 3.77 (s, 3H, OMe, PMP, **5r**), 3.86 (m, 1H, Fc, **5r**), 3.93 (m, 1H, Fc, **6r**), 4.05 (s, 5H, Fc, **5r**), 4.07-4.13 (m, 12H, 10H, Fc, **5r/6r**, 1H, Fc, **6r** and 1H, C4, β -lactam, **5r**), 4.23 (bs, 2H, 1H, CHN, **5r** and 1H, C4, β -lactam, **6r**), 4.30 (d, 1H, $J = 1.68$ Hz, C3, β -lactam, **5r**), 4.51 (d, 1H, $J = 1.98$ Hz, C3, β -lactam, **6r**), 4.63 (s, 1H, CHN, **6r**), 6.79 (d, 2H, $J = 9.00$ Hz, C3 and C5, PMP, **6r**), 6.83 (d, 2H, $J = 8.97$ Hz, C3 and C5, PMP, **5r**), 7.22-7.25 (m, 4H, C2 and C6, PMP, **5r/6r**), 7.56 (d, 2H, $J = 8.07$ Hz, C3 and C5, 4- $CF_3C_6H_4$, **5r**), 7.57-7.60 (m, 2H, C3 and C5, 4- $CF_3C_6H_4$, **6r**), 7.63 (d, 2H, $J = 7.53$ Hz, C2 and C6, 4- $CF_3C_6H_4$, **6r**), 7.56 (d, 2H, $J = 8.19$ Hz, C2 and C6, 4- $CF_3C_6H_4$, **5r**); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm : 19.53 (CMe₂, **5r**), 20.17 (CMe₂, **6r**), 24.05 (CMe₂, **6r**), 24.24 (CMe₂, **5r**), 47.04 (CMe₂, **6r**), 47.31 (CMe₂, **5r**), 52.12 (COOMe, **6r**), 52.23 (COOMe, **5r**), 55.36 (OMe, PMP, **6r**), 55.44 (OMe, PMP, **5r**), 59.86 (C4, β -lactam, **5r**), 59.98 (C4, β -lactam, **6r**), 66.09 (C3, β -lactam, **5r**), 66.18 (C3, β -lactam, **6r**), 66.30 (Fc, **6r**), 66.42 (Fc, **5r**), 67.72 (Fc, **5r**), 67.96 (Fc, **6r**), 68.45 (Fc, **6r**), 68.55 (Fc, **5r**), 68.58 (Fc, **5r**), 68.59 (Fc, **5r**), 69.03 (Fc, **6r**), 69.49 (Fc, **6r**), 70.35 (CHN, **6r**), 71.94 (CHN, **5r**), 83.85 (C1, Fc, **6r**), 85.42 (C1, Fc, **5r**), 114.19 (C3 and C5, PMP, **6r**), 114.23 (C3 and C5, PMP, **5r**), 119.23 (C2 and C6, PMP, **6r**), 119.88 (C2 and C6, PMP, **5r**), 124.08 (d, $J = 271.88$ Hz, CF_3 , **5r/6r**), 125.02 (d, $J = 3.49$ Hz, C3 and C5, 4- $CF_3C_6H_4$, **6r**), 125.11 (d, $J = 3.50$ Hz, C3 and C5, 4- $CF_3C_6H_4$, **5r**), 129.54 (C2 and C6, 4- $CF_3C_6H_4$, **5r**), 129.85 (C2 and C6, 4- $CF_3C_6H_4$, **6r**), 129.96 (C1, 4- $CF_3C_6H_4$, **6r**), 130.01 (C1, 4- $CF_3C_6H_4$, **5r**), 130.42 (C1, PMP, **5r**), 130.81 (C1, PMP, **6r**), 143.26 (C4, 4- $CF_3C_6H_4$, **6r**), 143.69 (C4, 4- $CF_3C_6H_4$, **5r**), 156.23 (C4, PMP, **6r**), 156.50 (C4, PMP, **5r**), 165.72 (CO, β -lactam, **5r**), 166.45 (CO, β -lactam, **6r**), 176.95 (COOMe, **5r**), 177.15 (COOMe, **6r**). HRMS for $C_{33}H_{33}N_2O_4F_3Fe$ (**5r/6r**, $M_r = 634.48161$): calcd. m/z $[M+Na]^+$ 657.1635, found 657.1611.

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