

Palladium(II), silver(I), and gold(I) complexes of a new class of chiral bicyclic [1,2,3]-triazolooxazine derived *N*-heterocyclic carbenes (NHCs): Synthesis, structure and application studies



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ABSTRACT

A new class of chiral bicyclic [1,2,3]-triazolooxazine derived *N*-heterocyclic carbene (NHC) ligands was synthesised in its enantiopure form from commercially available, cheap amino acid without undertaking any chiral resolution. In particular, the bicyclic *N*-heterocyclic carbene precursor, (*S*)-7-benzyl-6,6-(R^1)₂-2- R^2 -[1,2,3]-triazolooxazinium iodide [$R^1 = R^2 = \text{Me}$ (**1a**); $R^1 = \text{H}$, $R^2 = \text{Me}$ (**2a**); $R^1 = \text{H}$, $R^2 = \text{Et}$ (**3a**)] salts were conveniently prepared by the *N*-alkylation reactions of the corresponding [1,2,3]-triazolooxazine derivatives with alkyl iodides in ca. 37–73% yields. The copper mediated [3 + 2] cycloaddition reaction of the PhCH₂CH(N₃)CR₂OH (R = H, Me) azido alcohol compounds and propargyl bromide gave the desired [1,2,3]-triazolooxazines. These chiral bicyclic [1,2,3]-triazolooxazine derived *N*-heterocyclic carbene ligands were characterised in the form of its silver (NHC)AgCl (**1-3b**), gold (NHC)AuCl (**1-3c**), and the palladium (NHC)₂PdCl₂ (**1-3d**) and the PEPPSI type (NHC)PdI₂(NC₅H₅) (**1-3e**) complexes (NHC = (*S*)-7-benzyl-6,6-(R^1)₂-2- R^2 -[1,2,3]-triazolooxazin-3-ylidene; $R^1 = \text{H}$, Me and $R^2 = \text{Me}$, Et; PEPPSI = Pyridine Enhanced Precatalyst Preparation Stabilisation and Initiation).

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1. Introduction

The boundaries of conventional singlet *N*-heterocyclic carbenes (NHCs), first reported by Arduengo in 1991 [1,2] and primarily of the imidazole framework [3–6], are melting and expanding to various exotic and complex architectures having specialized attributes. Consequently, in the last decade, there has been a tremendous explosion in the report of various kinds of singlet carbene ligands ranging from charge separated mesoionic ones (MICs) [7,8] to their neutral counterparts, stabilised over a variety of multi cyclic ring structures to the heteroatom stabilised acyclic derivatives [9,10]. In this regard, exciting frameworks containing bicyclic and tricyclic *N*-heterocyclic carbenes with chiral substituents having restricted rotation have been developed [11] with the intent of higher asymmetric induction in chiral catalysis, a field that remains largely unexplored even though the achiral version has been studied exhaustively. While much of the literature involves organocatalytic applications of the in situ generated singlet carbe-

nes of these bicyclic and tricyclic ring systems [11], only a handful of examples report the use of well-defined transition metal based singlet carbene complexes of these ligands for asymmetric catalysis. Notable are the gold complexes of an axially chiral bicyclic [1,2,4]-triazole based *N*-heterocyclic carbene ligand, namely, [2-(adamantyl)-5-(2-*R*-naphthalen-1-yl)-[1,2,4]-triazoloisoquinolin-3-ylidene]AuCl [R = Me, cyclohexyl] that carried out enantioselective Diels–Alder cycloaddition reactions in high yields (48–88%) and enantioselectivities (63–99% *ee*) [12]. Similarly, a series of chiral bicyclic [2-(R^1)-5-(R^2)-pyrrolo-imidazol-2-ylidene](COD)IrCl [R¹ = CH₂Ph, CHPh₂, CH(C₆H₄OCH₃)₂, CH(C₆H₄CF₃)₂; CH(C₆H₄CH₃)₂; R² = Ph, 1,3,5-(CH₃)₃C₆H₂, 2,6-(*i*-Pr)₂C₆H₃, 2,4,6-(C₆H₁₁)₃C₆H₂] type catalysts performed the asymmetric transfer hydrogenation of ketones in presence of *t*-BuOK in *i*-propanol at a low catalyst loading of 0.1 mol % in high yields (ca. 55–98%) and enantioselectivities (ca. 77–97% *ee*) at 70 °C in 1 h of reaction time [13,14]. Despite high asymmetric induction, a major drawback of these aforementioned catalyst systems arises from their synthetic protocol that calls for a tedious chiral resolution of the racemic ligand for asymmetric catalysis applications.

In this regard, we became interested in developing a variety of multi-cyclic singlet carbene platforms having restricted rotation of the chiral auxiliary with the intent of achieving higher asymmetric

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induction. Hence we have reported the rhodium(I) and iridium(I) complexes of the chiral bicyclic oxazolidine-fused *N*-heterocyclic carbene ligands, namely, [3-*R*-6-methyl-7-phenyl-imidazooxazol-5-ylidene]M(COD)Cl (*R* = *s*-Bu, *i*-Bu, *i*-Pr; M = Rh, Ir) [15] and the rhodium(I) and iridium(I) complexes of the C₂-symmetric chiral tricyclic bioxazoline fused imidazole derived *N*-heterocyclic carbene ligand, namely, [3,7-di-*R*-7-dioxazoloimidazol-5-ylidene]M(COD)Cl [*R* = *s*-Bu, *i*-Bu, *i*-Pr; M = Rh [16], Ir [17]], which were synthesised in a multistep sequence in their enantiopure forms starting from the commercially available cheap chiral amino acids without requiring any chiral optical resolution. Continuing further along the line, we also set out to explore the catalytic potential of other late transition metals mainly silver, gold and palladium in asymmetric catalysis using the new chiral bicyclic *N*-heterocyclic carbene platforms we are designing.

In connection with this, notable are our efforts in performing Michael addition reaction, particularly under base-free bifunctional catalysis condition using a variety of transition metal carbene complexes, namely that of nickel and iron, both in achiral [18–20] and chiral fashions [21–23]. Michael addition provides a classical platform for the construction of C–C bonds in organic synthesis [24–26]. Hence building up on our earlier results, we decided to explore the utility of palladium chiral bicyclic [1,2,3]-triazolooxazine derived *N*-heterocyclic carbene (NHC) complexes in asymmetric Michael addition reaction.

Here in this manuscript we report a new class of chiral bicyclic [1,2,3]-triazolooxazine derived *N*-heterocyclic carbene (NHC) ligands along with their silver(I) (**1–3**)b, gold(I) (**1–3**)c, palladium (II) (**1–3**)d and (**1–3**)e complexes (Fig. 1). The palladium (**2–3**)d and (**2–3**)e complexes were explored for asymmetric Michael addition reaction.

2. Results and discussions

A new class of chiral bicyclic [1,2,3]-triazolooxazoline based *N*-heterocyclic carbene namely, (*S*)-7-benzyl-6,6-(*R*¹)₂-2-*R*²-[1,2,3]-triazolooxazin-3-ylidene [*R*¹ = H, Me; *R*² = Me, Et] was designed with the intent of probing its utility in homogenous asymmetric catalysis and was synthesised by a multi-step sequence (Scheme 1) starting from commercially available cheap chiral amino acid precursor. The strategy involved preparation of these chiral bicyclic [1,2,3]-triazolooxazoline based *N*-heterocyclic carbene ligands in their enantiopure form without any tedious chiral resolution protocol.

The dimethyl *N*-heterocyclic carbene precursor **1a** and its dihydro counterparts (**2–3**)a were synthesised from the dimethyl (*S*)-7-benzyl-6, 6-(Me)₂-[1,2,3]-triazolooxazine and dihydro (*S*)-7-benzyl-6, 6-(H)₂-[1,2,3]-triazolooxazine respectively. The reaction of these [1,2,3]-triazolooxazines with methyl or ethyl iodides in refluxing CH₃CN produced the desired *N*-heterocyclic carbene precursors, **1a** (61%), **2a** (73%) and **3a** (37%) in respective yields. Notable are the [1,2,3]-triazolooxazin-3-ium (C₂HN₃) resonances that appeared at δ 9.38 ppm (**1a**), δ 9.29 ppm (**2a**) and δ 9.30 ppm (**3a**) in the ¹H NMR and at δ 135.7 ppm (**1a**), δ 137.5 ppm (**2a**) and δ 137.0 ppm (**3a**) in the ¹³C{¹H} NMR spectra. The assignments of the ¹H and ¹³C{¹H} NMR spectra for a representative compound (**3a**) are shown in Fig. 2 and Fig. 3 respectively.

Another interesting feature is the observation of two sets of geminal couplings (²J_{HH} = ca. 14–17 Hz) for the two diastereotopic CH₂ moieties present in **1a** that appeared at (δ 5.15 ppm and δ 5.05 ppm) and (δ 3.26 ppm and δ 3.16 ppm) and the three sets of such geminal couplings (²J_{HH} = ca. 13–16 Hz) for the three diastereotopic CH₂ moieties present in **2a** that appeared at (δ 5.25 ppm and δ 5.18 ppm), (δ 4.20 ppm and δ 4.13 ppm) and (δ 3.58 ppm

and δ 3.28 ppm) and in **3a** at (δ 5.25 ppm and δ 5.17 ppm), (δ 4.22 ppm and δ 4.13 ppm) and (δ 3.51 ppm and δ 3.18 ppm).

Further corroboration of the presence of the [1,2,3]-triazolooxazine ring in (**1–3**)a came from the IR studies that showed strong ν_{C-O} (ether) stretching band at ca. 1080 cm⁻¹ [Supporting Information Table S1]. Additionally, the stretching ν_{C-H} (cm⁻¹) vibration assignable to the CH₂ moieties of the [1,2,3]-triazolooxazine ring appeared at ca. 2900–2800 cm⁻¹, while the two benzyl ring C=C stretching bands were observed at ~ 1600 and 1450 cm⁻¹ with medium to weak intensities. As expected similar IR spectra were observed for all of the respective silver(I) (**1–3**)b, gold(I) (**1–3**)c, palladium(II) (**1–3**)d and (**1–3**)e complexes [Supporting Information Table S1].

Both of the dimethyl [1,2,3]-triazolooxazine and the dihydro [1,2,3]-triazolooxazines were synthesized by using the Cu mediated “Click reaction” involving a [3 + 2] cycloaddition reaction between the corresponding azido alcohol PhCH₂CH(N₃)CR₂OH (*R* = H, Me) and propargyl bromide [27–29].

This new class of chiral bicyclic [1,2,3]-triazolooxazine derived *N*-heterocyclic carbene ligands bearing dimethyl and dihydro substituents at the 6,6 position of the [1,2,3]-triazolooxazine, were characterised in its metal complexes through a variety of metalation studies. In this regard, the following silver complexes, [(*S*)-7-benzyl-6,6-(*R*¹)₂-2-*R*²-[1,2,3]-triazolooxazin-3-ylidene]AgCl [*R*¹ = *R*² = Me (**1b**); *R*¹ = H, *R*² = Me (**2b**); *R*¹ = H, *R*² = Et (**3b**)], were obtained from the reaction of the corresponding [1,2,3]-triazolooxazin-3-ium iodide salts (**1–3**)a with Ag₂O in the presence of one equivalent of NaCl in CH₂Cl₂ at room temperature in ca. 91% (**1b**), ca. 68% (**2b**) and ca. 65% (**3b**) yields respectively (Scheme 2). The ¹H NMR spectra of the silver (**1–3**)b complexes showed the absence of the diagnostic [1,2,3]-triazolooxazin-3-ium (C₂HN₃) resonances appearing at δ 9.38 ppm (**1a**), δ 9.29 ppm (**2a**) and δ 9.30 ppm (**3a**) in the NHC precursors and thereby attesting to the formation of the desired silver (**1–3**)b complexes. Interestingly, the diastereotopic OCH₂ moieties of silver complexes (**1–3**)b appeared at higher frequency region in comparison to its corresponding ligand (**1–3**)a, while for the benzyl CH₂ group the differences were less significant. For example, the OCH₂ resonance appeared upfield shifted at δ (4.99 ppm and 4.88 ppm) from the corresponding value of δ (5.15 ppm and 5.05 ppm) for **1a**, while the diastereotopic benzyl CH₂ resonances of **1b** appeared at δ (3.25 ppm and 3.17 ppm) with respect to that of δ (3.26 ppm and 3.16 ppm) for **1a**. Along the same line of observation, the ¹H NMR spectra of the **2b** and **3b** complexes also showed upfield shifts ($\Delta\delta$) of ca. 0.30 ppm and ca. 0.20 ppm for the OCH₂ moieties as compared to that in **2a** and **3a** respectively.

The molecular structures of the silver complexes (**1b** and **3b**) were determined by the single crystal X-ray crystallography studies [Fig. 4 (**1b**), Fig. 5 (**3b**) and Supporting Information Tables S2 and S4]. The X-ray diffraction studies showed that the chiral bicyclic triazolooxazine derived NHC moiety was bound to the metal center in a linear fashion with a chloride moiety at the opposite end. The geometry at the metal center is consistent with the observation of linear \angle C1 – Ag1 – Cl1 angle of \angle 174.48(17)° in **1b** and of \angle 176.95(11)° in **3b**. The C_{carbene}–Ag bond distances in **1b** [2.075(5) Å] and **3b** [2.063(4) Å], were comparable to the sum of the covalent radii of Ag and C (2.18 Å) [30].

Significantly enough the silver complexes **1b** and **3b** represented the only structurally characterised example of the chiral bicyclic [1,2,3]-triazolooxazine derived *N*-heterocyclic carbene ligands. In this context, the closest structurally characterised examples were those of a handful of silver complexes reported for the family of the [1,2,3]-triazole derived *N*-heterocyclic carbene analogues (Table 1). The C_{carbene}–Ag distances of 2.075(5) Å in **1b** and 2.063(4) Å in **3b** were comparable to 2.064(12) Å in [(4-cobaltoceniumyl-1-ferrocenyl-3-methyltriazolylidene)AgCl]OTf [31],

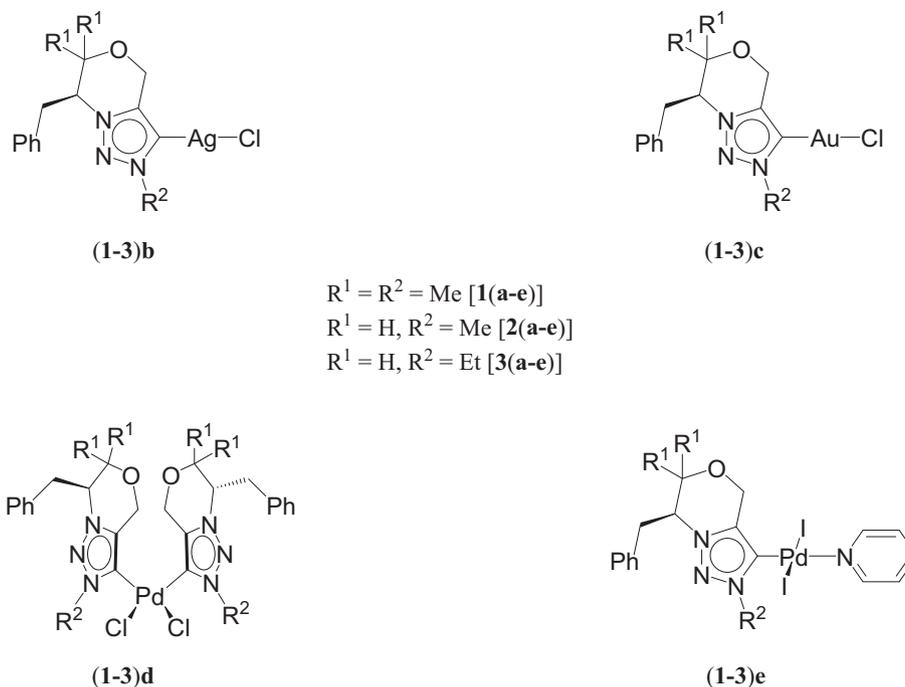
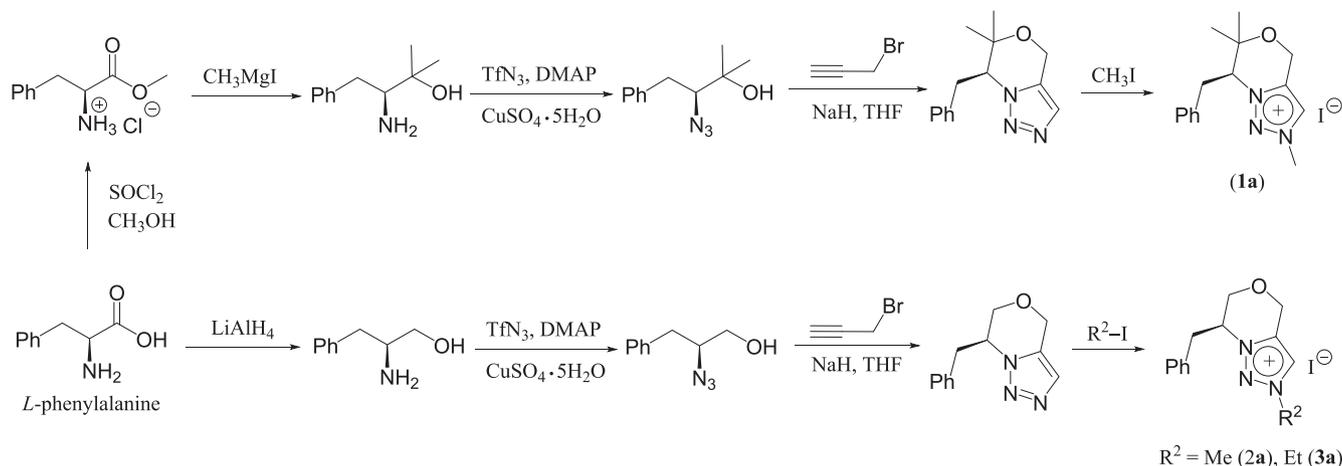


Fig. 1. Pd(II) (1-3)d and (1-3)e, Ag(I) (1-3)b, and Au(I) (1-3)c complexes of the chiral bicyclic triazolooxazine derived *N*-heterocyclic carbene (NHC) ligands.



Scheme 1. Synthetic routes to the chiral bicyclic triazolooxazine derived *N*-heterocyclic carbene (NHC) ligand precursors (1-3)a are shown.

2.075(4) Å in $\{[(1,3-(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)_2\text{-5-CH}_2\text{-4-ylidene})_2\text{NH}]\text{Ag}_2\text{Cl}_2\}$ [32] and 2.084(4) Å in $\{[(1\text{-methyl-2-phenyl-4-tolyl-[1,2,3]-triazol-5-ylidene})]\text{AgCl}\}$ [33].

In the absence of any chiral bicyclic [1,2,3]-triazolooxazoline derived *N*-heterocyclic carbene complexes of silver, a comparison of the $C_{\text{carbene}}\text{-Ag}$ distances in **1b** and **3b** is made with another type of chiral dicationic and tricationic silver complexes of chiral bicyclic [1,2,4]-triazolooxazoline derived *N*-heterocyclic carbene platforms namely, $\{2,2'\text{-[5-R-[1,2,4]-triazolooxazin-3-ylidene]}_2\text{-C}_6\text{H}_4\}_2\text{Ag}_2(\text{X})_2$ and $\{2,2'\text{-[5-R-[1,2,4]-triazolooxazin-3-ylidene]}_2\text{-C}_6\text{H}_4\}_3\text{Ag}_3(\text{X})_3$ ($R = \text{Ph}, \text{CH}_2\text{Ph}, i\text{-Pr}$; $\text{X} = \text{PF}_6, \text{BF}_4, \text{Cl}$) [34]. For example, the $C_{\text{carbene}}\text{-Ag}$ distances of 2.044(12) Å and 2.085(12) Å in representative dicationic $\{2,2'\text{-[5-Ph-[1,2,4]-triazolooxazin-3-ylidene]}_2\text{-C}_6\text{H}_4\}_2\text{Ag}_2(\text{PF}_6)_2$ and of 2.083(5) Å and 2.078(5) Å in representative tricationic $\{2,2'\text{-[5-CH}_2\text{Ph-[1,2,4]-triazolooxazin-3-ylidene]}_2\text{-C}_6\text{H}_4\}_3\text{Ag}_3(\text{PF}_6)_3$ complexes are comparable to that of 2.075(5) Å and 2.063(4) Å in the covalent silver complexes **1b** and **3b** respectively. Other than the above mentioned chiral bicyclic

[1,2,4]-triazolooxazoline derived *N*-heterocyclic carbene complexes of silver, a handful of structurally characterised [1,2,4]-triazolium based *N*-heterocyclic carbene complexes are known, that exhibit bond distances of 2.085(10) Å and 2.086(11) Å in a dimeric $\{[(S)\text{-}(5\text{-}(fluorodiphenylmethyl)\text{-2-phenyl-pyrrolo-[1,2,4]-triazol-3-ylidene})]\text{AgCl}\}_2$ [35] and of 2.079(3) Å in $[1\text{-}(tert\text{-butyl})\text{-3-phenyl-4-(p-tolyl)-[1,2,4]-triazol-2-ylidene}]\text{AgCl}$ [36]. The above examples clearly depict the rarity of the silver complexes of the chiral bicyclic [1,2,3]-triazolooxazine derived *N*-heterocyclic carbene ligands, and for which the complexes **1b** and **3b** represents the only structurally characterised examples known till date.

The silver complexes (1-3)b were conveniently transmetalated with $(\text{SMe}_2)\text{AuCl}$ at room temperature to obtain the following gold complexes, $[(S)\text{-}7\text{-benzyl-6,6-(R}^1)_2\text{-2-R}^2\text{-[1,2,3]-triazolooxazin-3-ylidene}]\text{AuCl}$ [$R^1 = R^2 = \text{Me}$ (**1c**); $R^1 = \text{H}, R^2 = \text{Me}$ (**2c**); $R^1 = \text{H}, R^2 = \text{Et}$ (**3c**)], in ca. 71% (**1c**), ca. 68% (**2c**) and ca. 85% (**3c**) yields respectively (Scheme 2). Quite expectedly, the ^1H NMR spectra of the gold complexes (1-3)c closely resembled the related silver

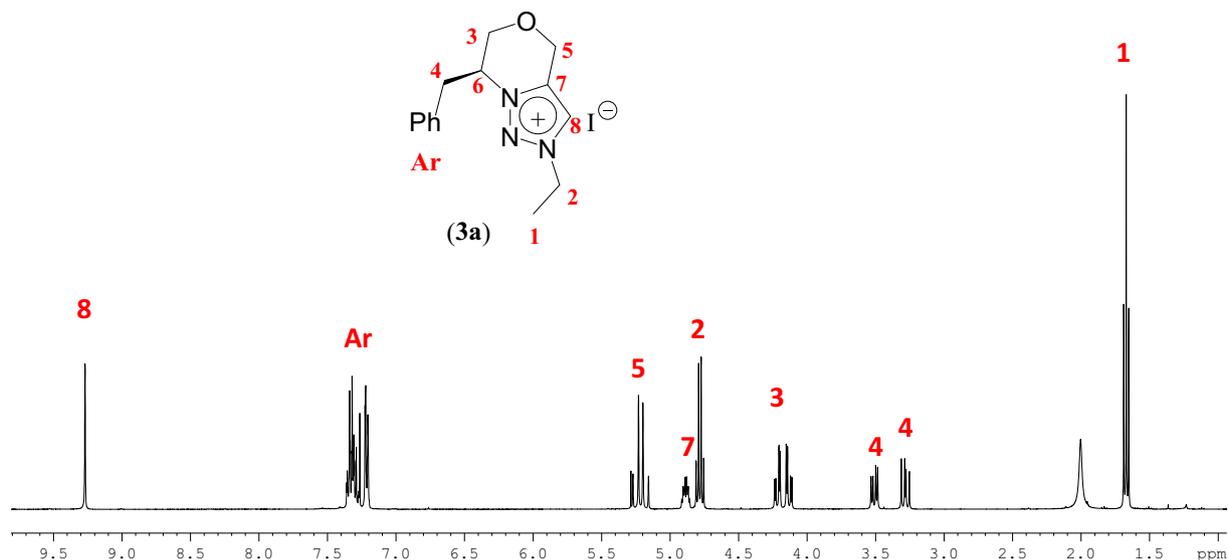


Fig. 2. ^1H NMR assignments of a representative compound **3a**.

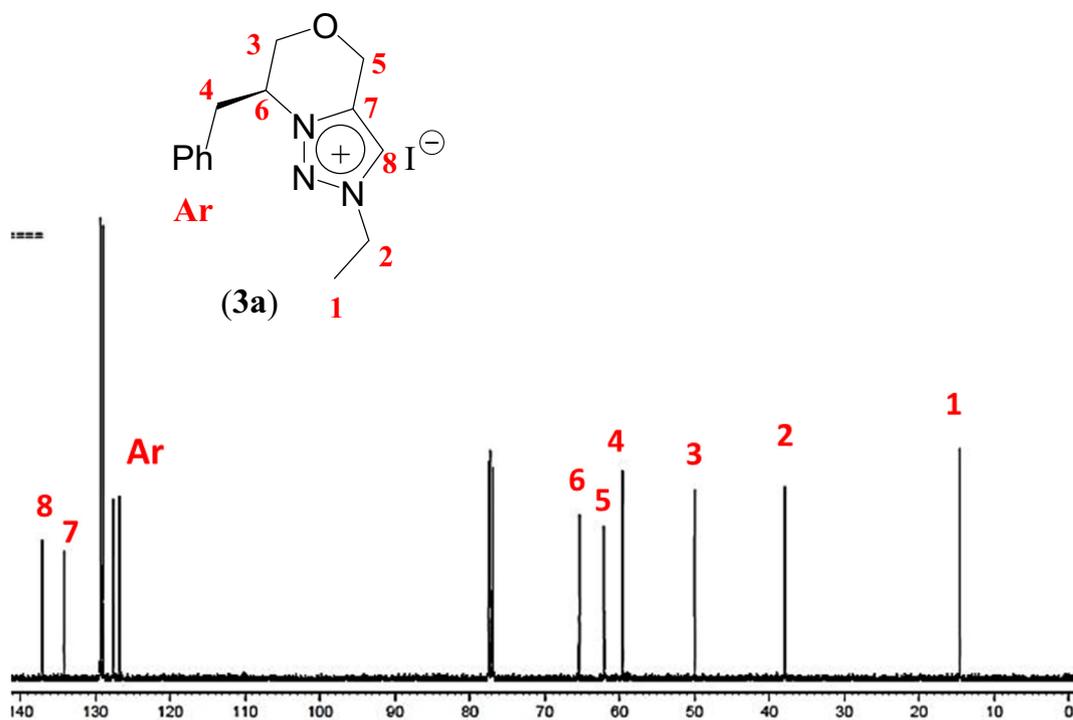
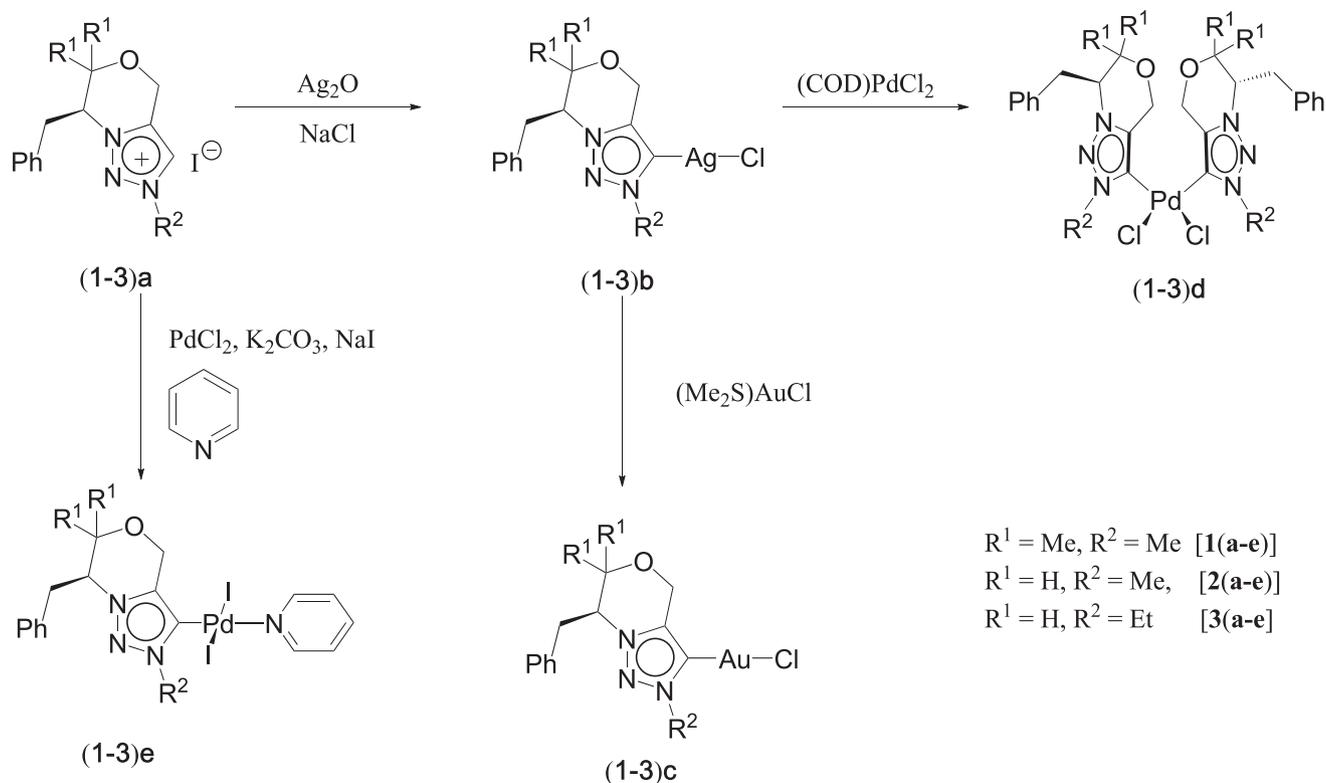


Fig. 3. $^{13}\text{C}\{^1\text{H}\}$ NMR assignments of a representative compound **3a**.

analogues (**1–3**)**b**, indicating their structural homology as an outcome of similar electronic environment prevalent in these metal complexes. For example, the NCH_3 resonance of the gold **1c** complex appeared at δ 3.93 ppm in close agreement with the value of δ 4.03 ppm, observed in case of the silver **1b** complex. Furthermore, for the gold **1c** complex, the two doublets arising out of the diastereotopic OCH_2 protons appeared at δ 4.92 ppm and δ 4.80 ppm and are similar to that of δ 4.99 ppm and δ 4.88 ppm

observed for the silver **1b** complex. In the $^{13}\text{C}\{^1\text{H}\}$ NMR, the diagnostic peak for the $\text{C}_{\text{carbene}}\text{-Au}$ resonance appeared at δ 153.1 ppm for **1c**, δ 154.1 ppm for **2c** and δ 159.1 ppm for **3c** respectively and are similar to the related [1,2,3]-triazole based *N*-heterocyclic carbene gold complexes. For instance, the corresponding $\text{C}_{\text{carbene}}\text{-Au}$ resonances appeared at δ 156.2 ppm for [1,4-bis(ferrocenyl)-3-methyl-[1,2,3]-triazol-5-ylidene]AuCl [37], δ 157.0 ppm for [(1,4-(*n*-Bu) $_2$ -3-methyl-[1,2,3]-triazol-5-yl-



Scheme 2. Synthetic routes to the Pd(II) (**1-3d**) and (**1-3e**), Ag(I) (**1-3b**), and Au(I) (**1-3c**) complexes of the chiral bicyclic triazolooxazine derived *N*-heterocyclic carbene (NHC) ligands are shown.

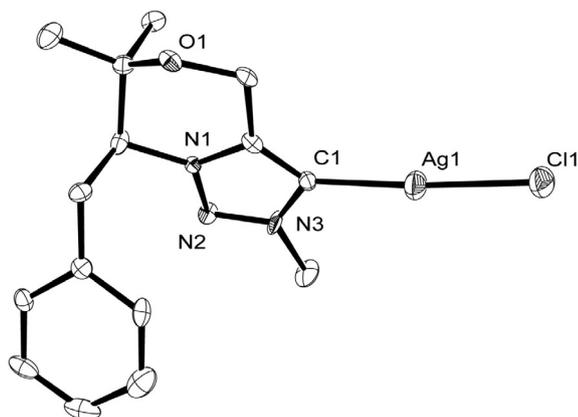


Fig. 4. ORTEP diagram of **1b** with thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Ag1 – C1 2.075(5), Ag1 – Cl1 2.3338(17), N3 – C1 1.377(7), C1 – Ag1 – Cl1 174.48(17), N3 – C1 – Ag1 126.7(4), N1 – N2 – N3 102.2(4), N2 – N3 – C1 115.6(4).

dene)]AuCl [38] and δ 156.6 ppm for [1-(*n*-Bu)-3-methyl-4-(CMe₂-OAc)-[1,2,3]-triazol-5-ylidene)]AuCl [38].

In concurrence with the similar NMR data observed for the silver (**1-3b**) and the gold (**1-3c**) complexes, the single crystal X-ray diffraction study revealed analogous molecular structures for these complexes (Figs. 4–7 and Supporting Information Fig. S1 and Tables S1–S3). All of the silver **1b** and **3b** and the gold (**1-3c**) complexes exhibited a linear geometry at the metal centre consistent with that of the *d*¹⁰ configuration of the metal ion, with the singlet chiral bicyclic [1,2,3]-triazolooxazine-3-ylidene ligand and a chloride moiety occupying the diametrically opposite sites. Furthermore, consistent with a shorter covalent radius (*r*_{cov} / Å) of Au as compared to Ag by 0.09 Å [30], the *C*_{carbene}–Au bond distances in

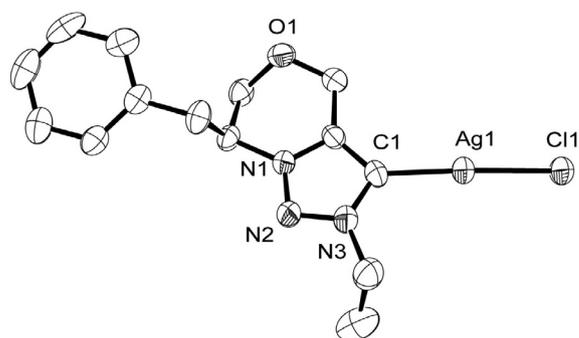


Fig. 5. ORTEP diagram of **3b** with thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Ag1 – C1 2.063(4), Ag1 – Cl1 2.3161(10), N3 – C1 1.354(5), C1 – Ag1 – Cl1 176.95(11), N3 – C1 – Ag1 125.6(3), N3 – N2 – N1 102.3(3), N2 – N3 – C1 115.7(3).

1c [1.985(6) Å], **2c** [2.000(12) Å] and **3c** [1.981(7) Å], are indeed smaller than the corresponding *C*_{carbene}–Ag bond distances in **1b** [2.075(5) Å] and **3b** [2.063(4) Å] by ca. 0.08–0.09 Å. For the comparison purpose the *C*_{carbene}–Au distances in {[1,4-dicobaltoceniumyl-3-methyl-[1,2,3]-triazol-5-ylidene)]AuCl}(PF₆)(OTf) [1.982(4) Å] [31] and [(1,3-(2,6-*i*-Pr₂C₆H₃)₂-4-phenyl-[1,2,3]-triazol-5-ylidene)]AuCl [1.991(6) Å] [39] are also in good agreement with that observed in the gold (**1-3c**) complexes. In this context, it is worth noting that though a related chiral bicyclic [1,2,4]-triazolooxazine derived *N*-heterocyclic carbene complex of gold namely, [(*S*)-8-benzyl-2-mesityl-[1,2,4]-triazolooxazine-3-ylidene]AuCl [40], has been prepared *in situ*, no spectroscopic as well as X-ray crystallography data had been reported for the same.

Further characterization of the [1,2,3]-triazolooxazine derived *N*-heterocyclic carbene ligands (**1-3a**) was carried out, by preparing two types of palladium complexes, *i.e.* the (NHC)₂PdCl₂ type

Table 1

A comparison of the metrical data of the structurally characterised silver complexes of the chiral bicyclic triazolooxazoline derived *N*-heterocyclic carbenes with the closely related [1,2,3]-triazole and [1,2,4]-triazole based *N*-heterocyclic carbene analogues.

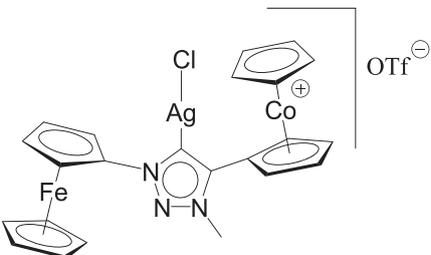
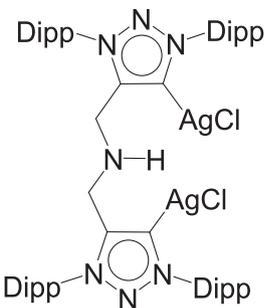
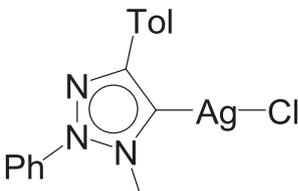
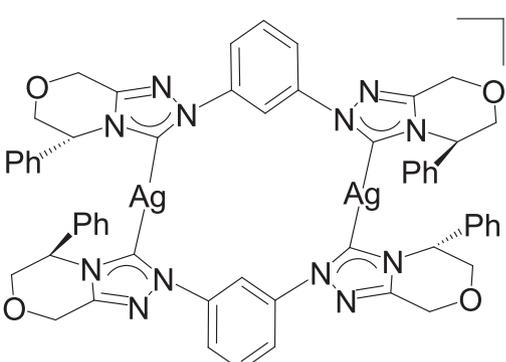
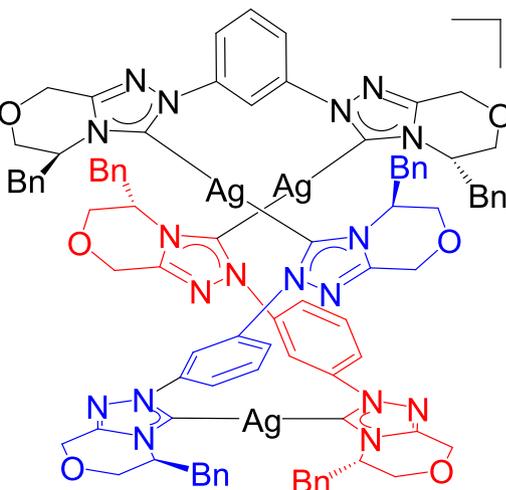
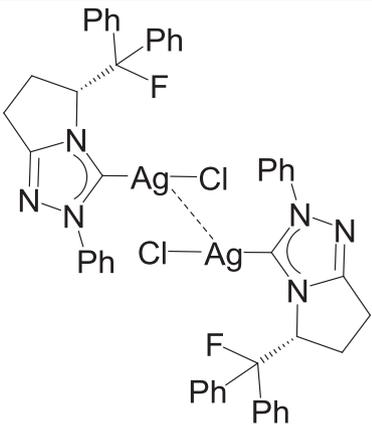
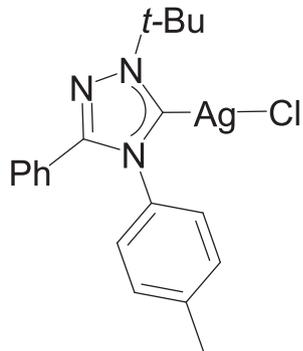
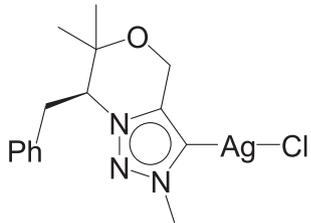
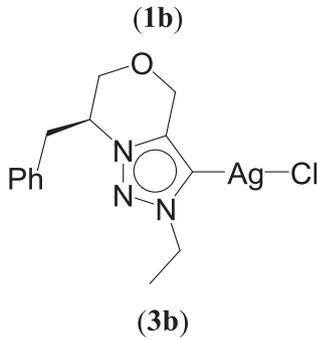
S. No.	complex	$d(\text{C}_{\text{carbene}}-\text{Ag})$ (Å)	$d(\text{Ag}-\text{Cl})$ (Å)	Reference
1		2.064(12)	2.345(3)	<i>Chem. Eur. J.</i> 2018 , 24, 3742–3753
2		2.075(4)	2.324(3)	<i>ChemistrySelect</i> 2018 , 3(38), 10706–10710
3		2.084(4)	2.335(1)	<i>Inorg. Chem.</i> 2013 , 52, 6142–6152
4		2.044(12) and 2.085(12)	N.A	<i>Chem. Sci.</i> , 2012 , 3, 359–363
5		2.083(5) and 2.078(5)	N.A	<i>Chem. Sci.</i> , 2012 , 3, 359–363

Table 1 (continued)

S. No.	complex	$d(\text{C}_{\text{carbene}}-\text{Ag})/(\text{\AA})$	$d(\text{Ag}-\text{Cl})/(\text{\AA})$	Reference
6		2.085(10) and 2.086(11)	2.334(2) and 2.326(3)	<i>Organometallics</i> , 2010 , 29, 20, 4424–4427
7		2.079(3)	2.3601(6)	<i>Dalton Trans.</i> , 2014 , 43, 15465–15474
8		2.075(5)	2.3338(17)	This work
9		2.063(4)	2.3161(10)	This work

(**1–3**)**d** and the PEPSI type $(\text{NHC})\text{PdI}_2(\text{NC}_5\text{H}_5)$ (**1–3**)**e** complexes (NHC = (*S*)-7-benzyl-6,6-(R^1)₂-2- R^2 -[1,2,3]-triazolooxazin-3-ylidene; $\text{R}^1 = \text{H}, \text{Me}$ and $\text{R}^2 = \text{Me}, \text{Et}$). The silver complexes (**1–3**)**b** reacted with $(\text{COD})\text{PdCl}_2$ at room temperature to yield the [(*S*)-7-benzyl-6,6-(R^1)₂-2- R^2 -[1,2,3]-triazolooxazin-3-ylidene]₂ PdCl_2 [$\text{R}^1 = \text{R}^2 = \text{Me}$ (**1d**); $\text{R}^1 = \text{H}, \text{R}^2 = \text{Me}$ (**2d**); $\text{R}^1 = \text{H}, \text{R}^2 = \text{Et}$ (**3d**)] complexes in 28–67% yields (Scheme 2). Quite expectedly, the ¹H NMR spectra of the palladium (**1–3**)**d** complexes, mirrored that of its analogous silver (**1–3**)**b** and gold (**1–3**)**c** complexes, so the analysis of ¹³C{¹H}

NMR spectra can serve as a diagnostic tool for them. The $\text{C}_{\text{carbene}}-\text{Pd}$ resonances appeared at δ 143.9 ppm (**1d**), δ 137.5 ppm (**2d**) and δ 143.6 ppm (**3d**) in the respective ¹³C{¹H} NMR spectra, which were significantly upfield shifted from the related [1,2,3]-triazolooxazine based *trans*-(NHC)₂ PdCl_2 type complexes. For example, the corresponding $\text{C}_{\text{carbene}}-\text{Pd}$ resonances appeared at δ 159.0 ppm for [1-ethyl-3-methyl-4-phenyl-[1,2,3]-triazol-5-ylidene]₂ PdCl_2 [41] and δ 157.1 ppm for [1-(*n*-Bu)-3-methyl-4-(CMe_2OMe)-[1,2,3]-triazol-5-ylidene]₂ PdCl_2 [42].

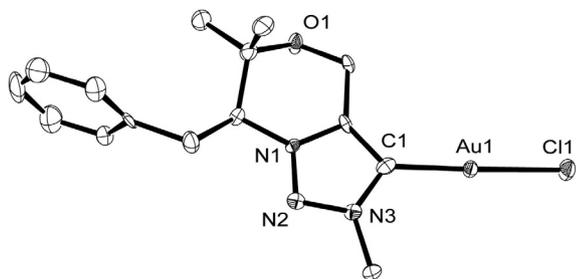


Fig. 6. ORTEP diagram of **1c** with thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Au1 – C1 1.985(6), Au1 – Cl1 2.2936(16), N3 – C1 1.370(6), C1 – Au1 – Cl1 178.4(3), N3 – C1 – Au1 125.1(4), N3 – N2 – N1 103.2(4), N2 – N3 – C1 115.1(5).

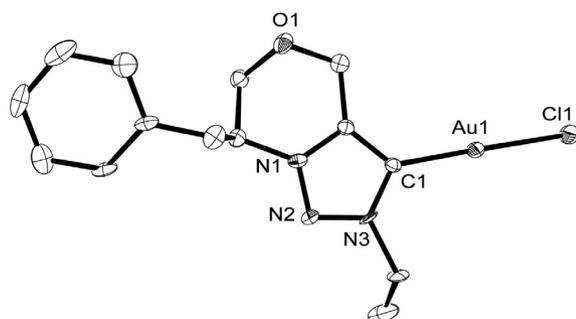


Fig. 7. ORTEP diagram of **3c** with thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Au1 – C1 1.981(7), Au1 – Cl1 2.296(2), N3 – C1 1.350(9), C1 – Au1 – Cl1 178.5(2), N1 – C1 – Au1 126.6(6), N3 – N2 – N1 102.7(6), N2 – N3 – C1 115.3(7).

In contrast to the conventional wisdom of *trans* form being more stable than the *cis* one, the molecular structures of palladium complexes (**1–3d**) [Fig. 8 (**1d**), Supporting information Fig. S2 (**2d**), Fig. 9 (**3d**) and Supporting Information Tables S2–S4] as determined by the single crystal X-ray crystallography, demonstrated that the two chiral bicyclic [1,2,3]-triazolooxazoline derived *N*-heterocyclic carbene ligands were in unusual *cis* disposition around the square planar d^8 palladium metal centre, with the other two sites occupied by the chloride moiety. The observation of the square planar geometry at the metal centre is consistent with the value of $\angle C_{\text{carbene}} - \text{Pd} - C_{\text{carbene}} = 92.0(5)^\circ$ (**1d**), $90.6(4)^\circ$ (**2d**), and $89.75(13)^\circ$ (**3d**) and $\angle \text{Cl1} - \text{Pd} - \text{Cl2} = 94.77(12)^\circ$ (**1d**), $93.58(9)^\circ$ (**2d**) and $93.43(3)^\circ$ (**3d**). In the absence of any structurally characterised example of chiral bicyclic [1,2,3]-triazolooxazoline derived *N*-heterocyclic carbene ligand based palladium complexes, a comparison of the $C_{\text{carbene}} - \text{Pd}$ bond distances in **1d** [1.975(10) Å], **2d** [1.970(10) Å and 1.984(10) Å] and **3d** [1.980(3) Å and 1.984(10) Å] was made with that of the only two structurally characterised racemic bicyclic [1,2,3]-triazolooxazoline derived *N*-heterocyclic carbene based PEPPSI type $(\text{NHC})\text{PdI}_2(\text{NC}_5\text{H}_5)$ complexes, namely [3-(*R*)-5a,6,7,8,9,9a-hexahydro-benzo[1,2,3]-triazolooxazin-4-ylidene] $\text{PdI}_2(\text{NC}_5\text{H}_5)$ [R = Me, $d/ C_{\text{carbene}} - \text{Pd} = 1.989(14)$ Å; R = Et, $d/ C_{\text{carbene}} - \text{Pd} = 1.961(6)$ Å] [43]. The Pd–Cl distances were found to be [2.374(2) Å] in **1d**, [2.396(3) Å and 2.366(3) Å] in **2d** and [2.3902(8) Å and 2.3757(8) Å] in **3d** respectively.

The metallation of the [1,2,3]-triazolooxazin-3-ium iodide salts (**1–3a**) with PdCl_2 in pyridine, using K_2CO_3 as base and KI yielded the PEPPSI type $(\text{NHC})\text{PdI}_2(\text{NC}_5\text{H}_5)$ complexes (**1–3e**) in 32–46% yields (Scheme 2). Notably, the palladium (**1–3e**) complexes were purified by column chromatography in a mixed solvent medium of petroleum ether : EtOAc (4:1 v/v) as the eluent.

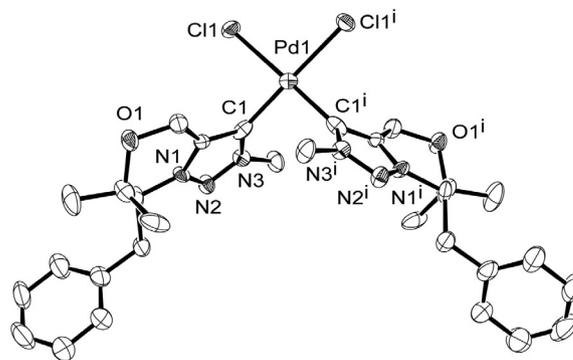


Fig. 8. ORTEP diagram of **1d** with thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Pd1 – C1 1.975(10), Pd1 – Cl1 2.374(2), N1 – C1 – Pd1 126.4(6), C1 – Pd1 – Cl1i 92.0(5), C1 – Pd1 – Cl1 86.6(3), Cl1 – Pd1 – Cl1i 94.77(12), Cl1i – Pd1 – Cl1i 86.6(3), C1 – Pd1 – Cl1i 178.5(3).

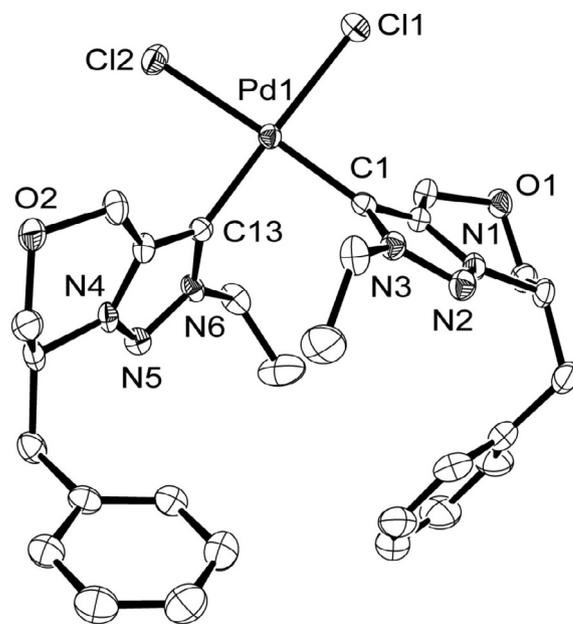


Fig. 9. ORTEP diagram of **3d** with thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Pd1 – C1 1.980(3), Pd1 – Cl1 2.3902(8), Pd1 – Cl2 2.3757(8), N3 – C1 – Pd1 129.7(2), N6 – C13 – Pd1 126.2(2), C1 – Pd1 – C13 89.75(13), C1 – Pd1 – Cl1 88.61(9), C1 – Pd1 – Cl2 177.74(9), C13 – Pd1 – Cl1 178.04(9), C13 – Pd1 – Cl2 88.19(9), Cl2 – Pd1 – Cl1 93.43(3).

The most interesting feature about the PEPPSI (**1–3e**) type complexes is the metal-bound “throwaway” pyridine moiety, which functions as a labile ligand by giving way to the incoming substrate in catalytic cycle. The metal-bound pyridine moiety appeared as distinct resonances in both the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra with regard to that of the free pyridine. For example, the *o*- NC_5H_5 resonances in ^1H NMR appeared at δ 9.03 ppm – 9.01 ppm (**1e**), δ 9.03 ppm – 9.01 ppm (**2e**) and δ 8.99 ppm – 8.97 ppm (**3e**) in comparison to the value of δ 8.58 ppm in free pyridine [44]. Similarly in the $^{13}\text{C}\{^1\text{H}\}$ NMR the *o*- NC_5H_5 resonances appeared significantly downfield shifted at δ 154.1 ppm (**1e**), δ 153.1 ppm (**2e**) and δ 153.8 ppm (**3e**) from the value of δ 149.5 ppm for free pyridine [44]. Furthermore, the characteristic $C_{\text{carbene}} - \text{Pd}$ resonances at δ 137.6 ppm (**1e**), δ 138.5 ppm (**2e**) and δ 137.6 ppm (**3e**) in the respective $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were considerably downfield shifted with respect to the corresponding values, associated with the only two structurally characterised racemic bicyclic [1,2,3]-tri-

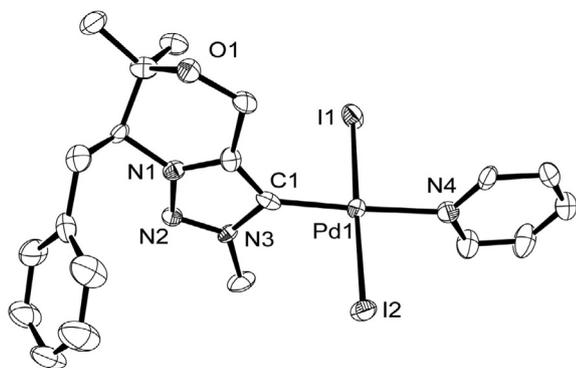


Fig. 10. ORTEP diagram of **1e** with thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Pd1 – C1 1.974(8), Pd1 – N4 2.078(7), Pd1 – I1 2.6038(9), Pd1 – I2 2.6004(10), N3 – C1 – Pd1 125.5(6), C1 – Pd1 – N4 176.7(3), C1 – Pd1 – I1 88.0(2), C1 – Pd1 – I2 93.8(2), N4 – Pd1 – I1 88.64(19), N4 – Pd1 – I2 89.59(19), I2 – Pd1 – I1 177.32(3).

azolooxazine derived *N*-heterocyclic carbene based PEPPSI type (NHC) $\text{PdI}_2(\text{NC}_5\text{H}_5)$ complexes, namely [3-(*R*)-5a,6,7,8,9,9a-hexahydro-benzo-[1,2,3]-triazolooxazin-4-ylidene] $\text{PdI}_2(\text{NC}_5\text{H}_5)$ [*R* = Me (δ 129.0 ppm); *R* = Et (δ 127.4 ppm)] [43].

The molecular structures of the palladium (**1–3e**) complexes as determined by the single crystal X-ray crystallography [Fig. 10 (**1e**), Supporting information Fig. S3 (**2e**), Fig. 11 (**3e**) and Supporting Information Tables S1–S3] were also in corroboration with the presence of a metal coordinated pyridine moiety. The Pd – N_{pyridine} bond distances in **1e** [1.974(8) Å], **2e** [1.974(9) Å] and **3e** [1.968(6) Å] were comparable to the sum of the covalent radii of Pd and N (2.10 Å) [30]. Furthermore, the Pd – N_{pyridine} bond distances in (**1–3e**) were in good agreement with that of the only two structurally characterised racemic bicyclic [1,2,3]-triazolooxazine derived *N*-heterocyclic carbene based PEPPSI type (NHC) $\text{PdI}_2(\text{NC}_5\text{H}_5)$ complexes, namely [3-(*R*)-5a,6,7,8,9,9a-hexahydro-benzo-[1,2,3]-triazolooxazin-4-ylidene] $\text{PdI}_2(\text{NC}_5\text{H}_5)$ [*R* = Me, *d*/ $\text{Pd} - N_{\text{pyridine}}$ = 2.090(11) Å; *R* = Et, *d*/ $\text{Pd} - N_{\text{pyridine}}$ = 2.096(5) Å]. In the same line of comparison the $C_{\text{carbene}} - \text{Pd}$ bond distances in **1e** [1.974(8) Å], **2e** [1.974(9) Å] and **3e** [1.968(6) Å] and Pd – I bond distances in **1e** [2.6038(9) Å and 2.6004(10) Å], **2e** [2.5989(10) Å and 2.6116(10) Å] and **3e** [2.5964(8) Å and 2.6219(8) Å] were in similar range with the aforementioned complexes, [3-

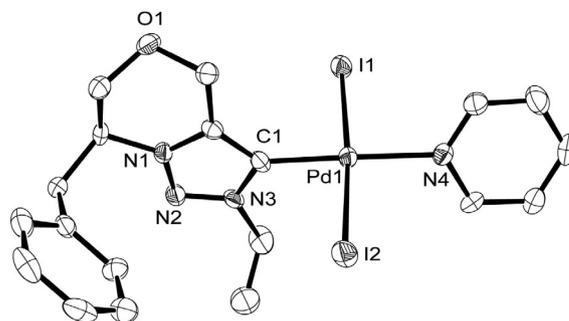
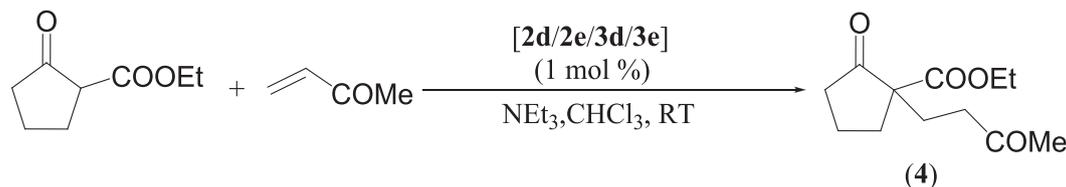


Fig. 11. ORTEP diagram of **3e** with thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Pd1 – C1 1.968(6), Pd1 – N4 2.110(5), Pd1 – I1 2.5964(8), Pd1 – I2 2.6219(8), N3 – C1 – Pd1 124.3(5), C1 – Pd1 – N4 175.1(3), C1 – Pd1 – I1 86.39(19), C1 – Pd1 – I2 89.05(19), N4 – Pd1 – I1 91.75(16), N4 – Pd1 – I2 93.04(16), I1 – Pd1 – I2 174.48(2).

2-oxocyclopentane-1-carboxylate and a Michael acceptor substrate, methyl vinyl ketone, the palladium (**2–3d**) and (**2–3e**) complexes efficiently produced the desired product ethyl-2-oxo-1-(3-oxobutyl)cyclopentane-1-carboxylate (**4**) (Equation 1) under ambient temperature at 1 mol % of catalyst loading and 8 h of reaction time, exhibiting near quantitative yield [85% (**2d**), 91% (**2e**), 88% (**3d**), 89% (**3e**)] with negligible chiral induction [*ee* 1–14%] (Table 2). Among the low enantioselectivities of the palladium (**2–3d**) and (**2–3e**) complexes, the (NHC) $_2\text{PdCl}_2$ type (**3d**) complex showed the maximum enantiomeric excess (*ee*) of 14%.

The observation of low asymmetric induction may be attributed to the far away disposition of the chiral centre from the catalytically active metal centre, partaking the catalysis and, thereby pointed towards subdued asymmetric transfer for this type of the chiral bicyclic [1,2,3]-triazolooxazine derived *N*-heterocyclic carbene ligands, (*S*)-7-benzyl-6,6-(R^1) $_2$ -2- R^2 -[1,2,3]-triazolooxazin-3-ylidene [R^1 = H, Me; R^2 = Me, Et]. Despite the observation of the low *ee* values, all of the palladium (**2–3d**) and (**2–3e**) complexes exhibited near equal yield for the representative substrates, implying the catalytic pocket arising out of the ligand dispositions around the metal centre remaining similar. Furthermore, no variation in product yields were observed between that of the (NHC) $_2\text{PdCl}_2$ type (**2–3d**) and the PEPPSI type (NHC) $\text{PdI}_2(\text{NC}_5\text{H}_5)$ (**2–3e**) complexes.



(*R*)-5a,6,7,8,9,9a-hexahydro-benzo-[1,2,3]-triazolooxazin-4-ylidene] $\text{PdI}_2(\text{NC}_5\text{H}_5)$ [*R* = Me, *d*/ $C_{\text{carbene}} - \text{Pd}$ = 1.989(14) Å, *d*/ $\text{Pd} - \text{I}$ = 2.6187(17) Å and 2.5904(17) Å; *R* = Et, *d*/ $C_{\text{carbene}} - \text{Pd}$ = 1.961(6) Å, *d*/ $\text{Pd} - \text{I}$ = 2.6123(10) Å and 2.6031(10) Å] [43].

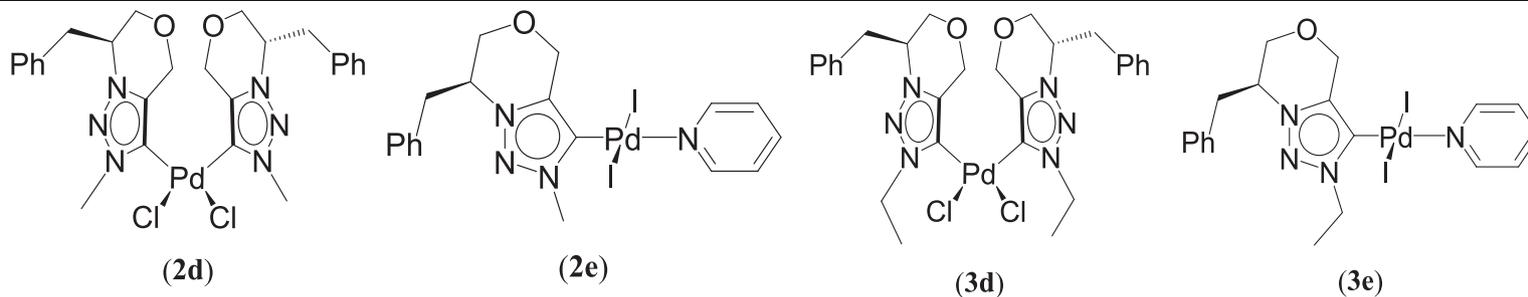
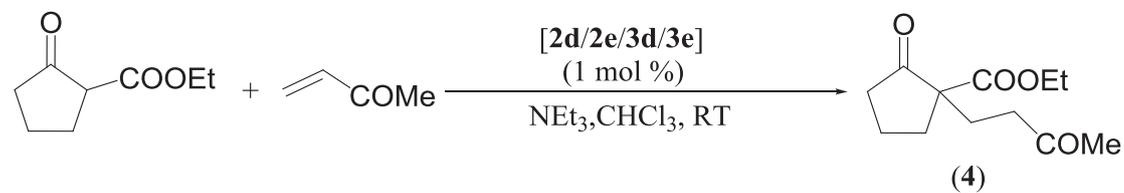
The asymmetric induction ability of the chiral bicyclic [1,2,3]-triazolooxazine derived *N*-heterocyclic carbene ligands, (*S*)-7-benzyl-6,6-(R^1) $_2$ -2- R^2 -[1,2,3]-triazolooxazin-3-ylidene [R^1 = H, Me; R^2 = Me, Et] was probed in asymmetric Michael addition reaction using the archetypal pair of palladium (NHC) $_2\text{PdCl}_2$ type (**2–3d**) and the PEPPSI type (NHC) $\text{PdI}_2(\text{NC}_5\text{H}_5)$ (**2–3e**) complexes. Specifically, for a representative pair of Michael donor substrate, ethyl-

Equation 1. Asymmetric Michael addition of ethyl-2-oxocyclopentane-1-carboxylate with methyl vinyl ketone using chiral Pd complexes (**2d/2e/3d/3e**) of the chiral bicyclic triazolooxazine derived *N*-heterocyclic carbene (NHC) ligands is shown.

In this regard, important is the comparison of the catalytic activities of our palladium (NHC) $_2\text{PdCl}_2$ type (**2–3d**) and the PEPPSI type (NHC) $\text{PdI}_2(\text{NC}_5\text{H}_5)$ (**2–3e**) complexes with that of the other related palladium analogous for the asymmetric Michael addition reaction of similar substrates. For example, the chiral cationic C_2 -symmetric *N*-heterocyclic carbene complex of the type (NHC) $\text{Pd}(\text{OH}_2)_2(\text{OTf})_2$ [NHC = 2,2'-bis(3-*R*-benzo-imidazol-2-ylidene)-1,1'-

Table 2

Selected results for the asymmetric Michael addition of ethyl-2-oxocyclopentane-1-carboxylate with methyl vinyl ketone as catalyzed using Pd – NHC (**2d/2e/3d/3e**) complexes.



	yield ^a	ee ^b						
	85	1	91	1	88	14	89	3

Reaction conditions: 1.00 mmol of Michael donor (ethyl-2-oxocyclopentane-1-carboxylate), 3.00 mmol of Michael acceptor (methyl vinyl ketone), 3.00 mmol of Et_3N , 1 mol % of catalyst (**2d/2e/3d/3e**) in 5 mL of solvent at room temperature for 8 h. (a) isolated yields (b) enantiomeric excess was determined by chiral GC using CP-Chirasil-Dex-CB column.

binaphthalene); R = Me, CH₂Ph], with 5 mol % of catalyst loading together with 4 Å molecular sieves produced the Michael addition adduct, *t*-Bu-2-oxo-1-(3-oxobutyl)cyclopentane-1-carboxylate, in high yield (ca. 98%) and high enantioselectivity (ca. 71% *ee*) at room temperature for the representative substrates, *t*-Bu-2-oxocyclopentane-1-carboxylate and methyl vinyl ketone [45]. Similarly, [Pd{(R)-tol-BINAP}(OH₂)₂](OTf)₂, type complex catalysed the Michael addition reaction at 5 mol % of catalyst loading at -20 °C in ca. 92% yield and ca. 92% enantioselectivity for the representative substrates, *t*-Bu-2-oxocyclopentane-1-carboxylate and methyl vinyl ketone [46]. Significantly enough, despite the above comparisons, the palladium (2-3)d and (2-3)e complexes represents the only examples of structurally characterised molecular catalysts for the asymmetric Michael addition reaction. Furthermore, the palladium (2-3)d and (2-3)e complexes operated at a much lower catalyst loading of 1 mol % as opposed to 5 mol % for the above catalysts, and also exhibited lower reaction time of 8 h as opposed to 24 h for the above mentioned literature examples.

3. Conclusion

In summary, a new class of chiral bicyclic [1,2,3]-triazolooxazine derived *N*-heterocyclic carbene (NHC) ligands (1-3)a was synthesised and characterised by preparing its silver (NHC)AgCl (1-3)b, gold (NHC)AuCl (1-3)c, palladium (NHC)₂PdCl₂ (1-3)d and the PEPPSI type (NHC)PdI₂(NC₅H₅) (1-3)e complexes. Significantly enough, the silver (1b and 3b), gold (1-3)c, and the palladium (1-3)d and (1-3)e complexes represent the only structurally characterized examples known till date of the chiral bicyclic [1,2,3]-triazolooxazine based *N*-heterocyclic carbene ligands. These new class of chiral bicyclic [1,2,3]-triazolooxazine derived *N*-heterocyclic carbene (NHC) ligands successfully stabilised monomeric transition metal complexes as observed from the molecular structures of silver (1b and 3b), gold (1-3)c, and the palladium (1-3)d and (1-3)e complexes. The palladium (2-3)d and (2-3)e complexes efficiently catalysed the asymmetric Michael addition reaction in high yields and low enantioselectivities. The lack of any meaningful asymmetric induction in this catalysis has been attributed to the distant location of the chiral auxiliary from the catalytically active metal centre.

3.1. Experimental section

3.1.1. General procedures

All manipulations were carried out using standard Schlenk techniques. Solvents were purified and degassed by standard procedures. *L*-phenylalanine, triflic anhydride, sodium azide, methyl vinyl ketone were purchased from Spectrochem Chemicals and propargyl bromide, ethyl-2-oxocyclopentane-1-carboxylate were purchased from Sigma Aldrich Chemicals and used without any further purification. ¹H NMR and ¹³C{¹H} NMR spectra were recorded on Bruker 400 MHz and Bruker 500 MHz NMR spectrometer. ¹H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublet (dd), doublet of triplets (dt), triplets of triplets (tt), multiplet (m). The (*S*)-3-amino-2-methyl-4-phenylbutan-2-ol [47] and (*S*)-7-benzyl-6,7-dihydro-4*H*-[1,2,3]-triazolo[5,1-*c*][1,4]oxazine [27-29] were synthesized by modification of procedures reported in literature. High-resolution mass spectrometry measurements were done on a Micromass Q-ToF spectrometer and a Bruker maxis impact spectrometer. Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Elemental Analysis was carried out on Thermo Quest FLASH 1112 SERIES (CHNS) Elemental Analyser. For the catalysis runs, the GCMS analyses were done using Agilent Technologies

7890A GC systems with 5975C inert XL EI/CI MSD Triple-Axis detector and the GC analyses were done using Agilent Technologies 7890A GC systems with CP-Chirasil-Dex CB chiral column. X-ray diffraction data for all compounds were collected on a Rigaku Hg 724 + diffractometer. Crystal data collection and refinement parameters were summarized in Supporting Information Tables S2-S4. CCDC-1011069 (for 1b), CCDC-1012239 (for 1c), CCDC-1021594 (for 1d), CCDC-1024176 (for 1e), CCDC-1011070 (for 2c), CCDC-1059753 (for 2d), CCDC-1024225 (for 2e), CCDC-1023266 (for 3b), CCDC-1024174 (for 3c) and CCDC-1012271 (for 3d), CCDC-1040518 (for 3e) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data centre via www.ccdc.cam.ac.uk/data_request/cif.

3.1.2. Synthesis of *L*-phenylalanine methyl ester hydrochloride [47]

To a suspension of *L*-phenylalanine (5.00 g, 30.3 mmol) in CH₃-OH (ca.75 mL), SOCl₂ (5.20 mL, 43.7 mmol) was added dropwise at 0 °C, over a period of 30 min and the resulting reaction mixture was stirred for overnight at room temperature. Then all the volatiles were removed in vacuo, the crude compound was triturated with Et₂O (ca. 30 mL) followed by filtration and drying under vacuum to give the product as a white solid (3.60 g, 55%). ¹H NMR (D₂O, 500 MHz, 25 °C), δ 7.35-7.29 (m, 3H, (CH₂C₆H₅), 7.20 (d, 2H, ³J_{HH} = 7 Hz, CH₂C₆H₅), 4.34 (t, 1H, ³J_{HH} = 7 Hz, CHNH₂), 3.74 (s, 3H, OCH₃), 3.25 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 5 Hz, CH₂C₆H₅), 3.12 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 7 Hz, CH₂C₆H₅). HRMS (ESI): *m/z* 180.1017, [M + H]⁺, Calcd. 180.1019. Anal. Calcd. for C₁₀H₁₄ClNO₂: C, 55.69; H, 6.54; N, 6.49, Found: C, 55.52; H, 6.40; N, 6.63%.

3.1.3. Synthesis of (*S*)-3-amino-2-methyl-4-phenylbutan-2-ol [47]

L-phenylalanine methyl ester hydrochloride (8.00 g, 37.1 mmol) was added in portions, over a period of 30 min, to a solution of CH₃MgI [prepared by CH₃I (13.8 mL, 223 mmol) and Mg (5.38 g, 223 mmol) in Et₂O (ca. 250 mL)]. The resulting heterogeneous mixture was heated to reflux for 6 h. A saturated aqueous solution of NH₄Cl (ca. 60 mL) was added dropwise at 0 °C with vigorous stirring. The reaction mixture was filtered by celite and the organic layer was separated. The aqueous layer was basified with aqueous NH₃ and extracted with Et₂O (ca. 3 × 30 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to give crude amino alcohol, which was further purified by vacuum distillation at 220 °C, to give amino alcohol as colorless oil (1.99 g, 30%). ¹H NMR (CDCl₃, 500 MHz, 25 °C), δ 7.33 (t, 2H, ³J_{HH} = 7 Hz, CH₂C₆H₅), 7.24 (t, 1H, ³J_{HH} = 7 Hz, CH₂C₆H₅), 7.21 (d, 2H, ³J_{HH} = 7 Hz, CH₂C₆H₅), 3.03 (dd, 1H, ³J_{HH} = 13 Hz, ³J_{HH} = 2 Hz, CHNH₂), 2.82 (dd, 1H, ²J_{HH} = 11 Hz, ³J_{HH} = 2 Hz, CH₂C₆H₅), 2.28 (dd, 1H, ²J_{HH} = 11 Hz, ³J_{HH} = 12 Hz, CH₂C₆H₅), 2.24 (br, 3H, OH and NH₂), 1.31 (s, 3H, CH₃), 1.22 (s, 3H, CH₃).

3.1.4. Synthesis of (*S*)-3-azido-2-methyl-4-phenylbutan-2-ol

A mixture of (*S*)-3-amino-2-methyl-4-phenylbutan-2-ol (1.24 g, 6.91 mmol), 4-dimethylaminopyridine (0.562 g, 4.42 mmol) and CuSO₄·5H₂O (0.077 g, 0.311 mmol) were dissolved in CH₂Cl₂ (ca. 120 mL). The CF₃SO₂N₃ solution in CH₂Cl₂ (ca. 90 mL) [prepared by dropwise addition of triflic anhydride (4.60 mL, 27.3 mmol) in a mixture of NaN₃ (7.48 g, 115 mmol), distilled water (ca. 25 mL) and CH₂Cl₂ (ca. 75 mL) at 0 °C, followed by the extraction of the CH₂Cl₂ layer after stirring 2 h] was added dropwise at room temperature. The reaction mixture was then stirred vigorously for 2 h at room temperature, after which the color changed from blue to green. The organic layer was washed with 10% aqueous citric acid solution (ca. 3 × 50 mL), with saturated aqueous solution of NaHCO₃ (ca. 3 × 60 mL) and saturated aqueous solution of NaCl (ca. 3 × 80 mL), dried over anhydrous Na₂SO₄, filtered and evaporated in vacuo to give as a crude azido alcohol (0.795 g, 56%). ¹H

NMR (CDCl₃, 400 MHz, 25 °C): δ 7.33–7.23 (m, 5H, CH₂C₆H₅), 3.42 (dd, 1H, ³J_{HH} = 11 Hz, ²J_{HH} = 3 Hz, CHN₃), 3.02 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 3 Hz, CH₂C₆H₅), 2.63 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 11 Hz, CH₂C₆H₅), 1.91 (br, 1H, OH), 1.31 (s, 3H, CH₃), 1.28 (s, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): 138.4 (CH₂C₆H₅), 129.3 (CH₂C₆H₅), 128.8 (CH₂C₆H₅), 126.9 (CH₂C₆H₅), 74.1 (CHN₃), 73.3 (CH₂C₆H₅), 36.5 (C(CH₃)₂), 26.6 (CH₃), 25.6 (CH₃).

3.1.5. Synthesis of (S)-7-benzyl-6,6-dimethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazine

NaH (0.224 g, 9.36 mmol) was added to a solution of (S)-3-azido-2-methyl-4-phenylbutan-2-ol (1.28 g, 6.24 mmol) in dry THF (ca. 50 mL), after which propargyl bromide (0.965 g, 8.11 mmol) was added dropwise over a period of 20 min at 0 °C. The reaction mixture was stirred for 24 h at room temperature and then the solvent was removed in *vacuo*. The residue was extracted with EtOAc (ca. 3 × 60 mL), washed with brine, dried over anhydrous Na₂SO₄, filtered and evaporated in *vacuum* to give the product as a yellow oil (1.15 g, 76%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.44 (s, 1H, C₂HN₃ of C₅H₄N₃O), 7.28–7.21 (m, 3H, CH₂C₆H₅), 7.10–7.08 (d, 2H, ³J_{HH} = 7 Hz, CH₂C₆H₅), 4.86 (s, 2H, OCH₂ of C₅H₄N₃O), 4.58 (t, 1H, ³J_{HH} = 6 Hz, CHCH₂C₆H₅), 3.40 (dd, 1H, ²-J_{HH} = 14 Hz, ³J_{HH} = 6 Hz, CH₂C₆H₅), 3.18 (dd, 1H, ²J_{HH} = 14 Hz, ³-J_{HH} = 6 Hz, CH₂C₆H₅), 1.43 (s, 3H, CH₃), 1.21 (s, 3H, CH₃).

3.1.6. Synthesis of ((S)-7-benzyl-2,6,6-trimethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-2-ium iodide) (1a)

A mixture of (S)-7-benzyl-6,6-dimethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazine (1.10 g, 4.52 mmol) and methyl iodide (6.42 g, 45.2 mmol) was stirred at 80 °C in CH₃CN (ca. 100 mL) for 24 h, after which, the volatiles were removed under vacuum. The yellow solid thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluted with MeOH:CHCl₃ (1:9 v/v) to give the product **1a** as a light yellow solid (1.06 g, 61%). ¹H NMR (CDCl₃, 500 MHz, 25 °C): δ 9.38 (s, 1H, C₂HN₃ of C₅H₄N₃O), 7.26–7.19 (m, 3H, CH₂C₆H₅), 7.00–6.98 (m, 2H, CH₂C₆H₅), 5.15 (d, 1H, ²J_{HH} = 17 Hz, OCH₂ of C₅H₄N₃O), 5.05 (d, 1H, ²J_{HH} = 17 Hz, OCH₂ of C₅H₄N₃O), 4.60 (dd, 1H, ³J_{HH} = 9 Hz, ³J_{HH} = 5 Hz, CHCH₂C₆H₅), 4.23 (s, 3H, NCH₃), 3.26 (dd, 1H, ²J_{HH} = 14 Hz, ³-J_{HH} = 5 Hz, CH₂C₆H₅), 3.16 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 9 Hz, CH₂C₆H₅), 1.46 (s, 3H, CH₃), 1.31 (s, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃, 125 MHz, 25 °C): 135.7 (C₂HN₃ of C₅H₄N₃O), 135.4 (C₂HN₃ of C₅H₄N₃O), 129.2 (CH₂C₆H₅), 129.1 (CH₂C₆H₅), 128.6 (CH₂C₆H₅), 127.8 (CH₂C₆H₅), 74.2 (CHCH₂C₆H₅), 68.0 (OCH₂ of C₅H₄N₃O), 57.3 (CH₂C₆H₅), 41.4 (C(CH₃)₂ of C₅H₄N₃O), 36.9 (NCH₃), 24.4 (CH₃), 23.5 (CH₃). IR data (cm⁻¹) KBr pellet: 3159 (w), 3111 (w), 3067 (w), 3037 (w), 2969 (w), 2925 (m), 2850 (w), 1644 (m), 1432 (w), 1329 (m), 1274 (w), 1247 (w), 1210 (w), 1142 (m), 1080 (s), 954 (w), 926 (w), 895 (w), 804 (m), 702 (w), 548 (w), 507 (w), 468 (w). HRMS (ESI): *m/z* 258.1596, [M–I]⁺, Calcd. 258.1601. Anal. Calcd. for C₁₅H₂₀N₃O: C, 46.77; H, 5.23; N, 10.91. Found: C, 46.58; H, 5.34; N, 10.15. [α]_D²⁵ – 52.9 (c 1.00 in CHCl₃).

3.1.7. Synthesis of ((S)-7-benzyl-2,6,6-trimethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene)AgCl (1b)

A mixture of (S)-7-benzyl-2,6,6-trimethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-2-ium iodide (**1a**) (0.200 g, 0.519 mmol), Ag₂O (0.120 g, 0.519 mmol) and NaCl (0.030 g, 0.519 mmol) in CH₂Cl₂ (ca. 50 mL) was stirred overnight at room temperature. The reaction mixture was filtered through a pad of celite and volatiles were removed under vacuum to give the product **1b** as a light brown solid (0.189 g, 91%). ¹H NMR (CDCl₃, 500 MHz, 25 °C): δ 7.30–7.28 (m, 3H, CH₂C₆H₅), 7.02–7.00 (d, 2H, ³-J_{HH} = 7 Hz, CH₂C₆H₅), 4.99 (d, 1H, ²J_{HH} = 17 Hz, OCH₂ of C₅H₃N₃O), 4.88 (d, 1H, ²J_{HH} = 17 Hz, OCH₂ of C₅H₃N₃O), 4.47 (dd, 1H, ³J_{HH} = 9 Hz, ³J_{HH} = 5 Hz, CHCH₂C₆H₅), 4.03 (s, 3H, NCH₃), 3.25 (dd, 1H, ²J_{HH} = 14-

Hz, ³J_{HH} = 5 Hz, CH₂C₆H₅), 3.17 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 9 Hz, CH₂C₆H₅), 1.46 (s, 3H, CH₃), 1.30 (s, 3H, CH₃). IR data (cm⁻¹) KBr pellet: 3016 (w), 2979 (w), 2925 (w), 1632 (m), 1454 (m), 1315 (w), 1269 (w), 1249 (w), 1210 (m), 1146 (w), 1071 (s), 833 (m), 761 (m), 710 (w), 558 (w), 510 (w). HRMS (ESI): *m/z* 364.0581, [M–Cl]⁺, Calcd. 364.0574. Anal. Calcd. for C₁₅H₁₉N₃OAgCl: C, 44.97; H, 4.78; N, 10.49. Found: C, 45.27; H, 3.84; N, 10.18.

3.1.8. Synthesis of ((S)-7-benzyl-2,6,6-trimethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene)AuCl (1c)

A mixture of ((S)-7-benzyl-2,6,6-trimethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene)AgCl (**1b**) (0.179 g, 0.447 mmol) and (Me₂S)AuCl (0.132 g, 0.447 mmol) in CH₃CN (ca. 50 mL) was stirred overnight at room temperature. The reaction mixture was filtered; the filtrate was collected and was dried under vacuum to give the product **1c** as a light yellow solid (0.157 g, 71%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.26–7.19 (m, 3H, CH₂C₆H₅), 6.95 (d, 2H, ³J_{HH} = 7 Hz, CH₂C₆H₅), 4.92 (d, 1H, ²-J_{HH} = 17 Hz, OCH₂ of C₅H₃N₃O), 4.80 (d, 1H, ²J_{HH} = 17 Hz, OCH₂ of C₅H₃N₃O), 4.40 (dd, 1H, ³J_{HH} = 9 Hz, ³J_{HH} = 5 Hz, CHCH₂C₆H₅), 3.93 (s, 3H, CH₃), 3.20 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 5 Hz, CH₂C₆H₅), 3.10 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 9 Hz, CH₂C₆H₅), 1.41 (s, 3H, CH₃), 1.22 (s, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): 153.4 (Au–C), 138.9 (C₂N₃ of C₅H₃N₃O), 136.1 (CH₂C₆H₅), 129.1 (CH₂C₆H₅), 128.9 (CH₂C₆H₅), 127.6 (CH₂C₆H₅), 74.0 (CHCH₂C₆H₅), 66.8 (OCH₂ of C₅H₃N₃O), 58.1 (CH₂C₆H₅), 42.0 (C(CH₃)₂ of C₅H₃N₃O), 37.1 (NCH₃), 24.0 (CH₃), 23.6 (CH₃). IR data (cm⁻¹) KBr pellet: 3032 (w), 2966 (w), 2925 (w), 2857 (w), 1533 (m), 1491 (w), 1454 (m), 1386 (w), 1374 (m), 1312 (m), 1269 (w), 1250 (w), 1213 (m), 1145 (m), 1080 (s), 954 (w), 923 (w), 893 (w), 833 (s), 757 (m), 738 (m), 704 (s), 651 (w), 599 (w), 558 (w), 509 (w). LRMS (ESI): *m/z* 495, [M–Cl + CH₃CN]⁺, Calcd. 495. Anal. Calcd. for C₁₅-H₁₉N₃O₂AuCl·H₂O: C, 35.48; H, 4.17; N, 8.28. Found: C, 34.55; H, 3.16; N, 8.27. [α]_D²⁵ – 90.2 (c 1.00 in CHCl₃).

3.1.9. Synthesis of ((S)-7-benzyl-2,6,6-trimethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene)PdCl₂ (1d)

A mixture of ((S)-7-benzyl-2,6,6-trimethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene)AgCl (**1b**) (0.200 g, 0.499 mmol) and (COD)PdCl₂ (0.071 g, 0.249 mmol) in CH₃CN (ca. 50 mL) was stirred at room temperature, until the formation of an off-white AgCl precipitate was observed. The reaction mixture was filtered and solvent was removed under vacuum to give the product **1d** as light yellow solid (0.187 g, 67%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.28–7.26 (m, 3H, CH₂C₆H₅), 6.95–6.94 (m, 2H, CH₂C₆H₅), 4.90 (d, 1H, ²J_{HH} = 13 Hz, OCH₂ of C₅H₃N₃O), 4.69 (br, 1H, OCH₂ of C₅H₃N₃O), 4.40 (br, 1H, CHCH₂C₆H₅), 4.16 (s, 3H, CH₃), 3.19 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 5 Hz, CH₂C₆H₅), 3.04 (d, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 9 Hz, CH₂C₆H₅), 1.42 (s, 3H, CH₃), 1.24 (s, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): 143.9 (Pd–C), 136.2 (C₂N₃ of C₅H₃N₃O), 135.9 (CH₂C₆H₅), 129.0 (CH₂C₆H₅), 128.9 (CH₂C₆H₅), 127.6 (CH₂C₆H₅), 74.1 (CHCH₂C₆H₅), 66.4 (OCH₂ of C₅H₃N₃O), 58.3 (CH₂C₆H₅), 42.0 (C(CH₃)₂ of C₅H₃N₃O), 37.1 (NCH₃), 23.9 (CH₃), 23.6 (CH₃). IR data (cm⁻¹) KBr pellet: 3650 (w), 3475 (s), 3276 (w), 3052 (w), 3028 (w), 3005 (w), 2974 (w), 2914 (w), 2853 (w), 1649 (s), 1604 (w), 1524 (w), 1497 (w), 1458 (m), 1390 (w), 1374 (w), 1341 (w), 1324 (w), 1286 (w), 1268 (m), 1246 (w), 1214 (w), 1166 (w), 1137 (m), 1087 (s), 1059 (w), 1039 (w), 1005 (w), 905 (w), 879 (w), 831 (m), 797 (w), 744 (m), 708 (m), 696 (m), 650 (w), 562 (w), 542 (w), 510 (w), 487 (w). HRMS (ESI): *m/z* 657.1744 [M–Cl]⁺, calcd. 655.1782. Anal. Calcd. for C₃₀H₃₈N₆O₂PdCl₂·H₂O: C, 50.75; H, 5.68; N, 11.84. Found: C, 50.07; H, 4.93; N, 11.71. [α]_D²⁵ – 97.2 (c 1.00 in CHCl₃).

3.1.10. Synthesis of *trans*-{(S)-7-benzyl-2,6,6-trimethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene)PdCl₂(pyridine) (**1e**)

A mixture of (S)-7-benzyl-2,6,6-trimethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-2-ium iodide (**1a**) (0.438 g, 1.13 mmol), PdCl₂ (0.201 g, 1.13 mmol), K₂CO₃ (1.25 g, 9.10 mmol) and NaI (0.852 g, 5.68 mmol) was refluxed in pyridine (5 mL, 63 mmol) for 16 h. The reaction mixture was cooled to room temperature, diluted with CHCl₃ (ca. 100 mL) and subsequently washed with saturated aqueous CuSO₄ solution (ca. 3 × 50 mL). The organic layer was separated and dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated under vacuum to give a sticky, brown residue. The residue thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluted with EtOAc:petroleum ether (1:4 v/v) to give the product **1e** as a yellow solid (0.256 g, 32%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 9.03–9.01 (m, 2H, NC₅H₅), 7.72 (t, 1H, ³J_{HH} = 8 Hz, NC₅H₅), 7.31–7.21 (m, 5H, CH₂C₆H₅), 7.02 (d, 2H, ³J_{HH} = 8 Hz, NC₅H₅), 5.18 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₃N₃O), 5.08 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₃N₃O), 4.28 (dd, 1H, ³J_{HH} = 8 Hz, ³J_{HH} = 6 Hz, CHCH₂C₆H₅), 4.13 (s, 3H, NCH₃), 3.18 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 6 Hz, CH₂C₆H₅), 3.12 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 8 Hz, CH₂C₆H₅), 1.57 (s, 3H, CH₃), 1.25 (s, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃, 125 MHz, 25 °C): δ 154.1 (NC₅H₅), 137.6 (Pd–C), 136.2 (NC₅H₅), 136.2 (C₂N₃ of C₅H₃N₃O), 129.3 (NC₅H₅), 128.9 (CH₂C₆H₅), 128.3 (CH₂C₆H₅), 127.3 (CH₂C₆H₅), 124.5 (CH₂C₆H₅), 73.9 (CHCH₂C₆H₅), 66.3 (OCH₂ of C₅H₃N₃O), 59.4 (CH₂C₆H₅), 42.7 (C(CH₃)₂ of C₅H₃N₃O), 36.8 (NCH₃), 23.9 (CH₃), 23.6 (CH₃). IR data (cm⁻¹) KBr pellet: 2923 (m), 2853 (w), 1601 (w), 1449 (m), 1264 (w), 1241 (w), 1211 (m), 1142 (w), 1084 (s), 830 (m), 760 (w), 737(w), 696 (s), 666 (w), 539 (w), 509 (w). HRMS (ESI): *m/z* 569.0052, [M–I]⁺, Calcd. 569.0032. Anal. Calcd. for C₂₀H₂₄I₂N₄OPd: C, 34.48; H, 3.47; N, 8.04. Found: C, 34.72; H, 3.00; N, 7.90. [α]_D²⁵ – 110.8 (c 1.00 in CHCl₃).

3.1.11. Synthesis of {(S)-7-benzyl-2-methyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-2-ium iodide} (**2a**)

A mixture of (S)-7-benzyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazine (1.00 g, 4.65 mmol) and methyl iodide (6.60 g, 46.5 mmol) was stirred at 80 °C in CH₃CN (ca. 50 mL) for 24 h, after which, the volatiles were removed under vacuum. The yellow solid thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluted with MeOH:CHCl₃ (1:9 v/v) to give the product **2a** as a light yellow solid (1.20 g, 73%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 9.29 (s, 1H, C₂HN₃ of C₅H₆N₃O), 7.34–7.23 (m, 5H, CH₂C₆H₅), 5.25 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₆N₃O), 5.18 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₆N₃O), 4.92–4.86 (m, 1H, CHCH₂C₆H₅), 4.50 (s, 3H, NCH₃), 4.20 (dd, 1H, ²J_{HH} = 13 Hz, ³J_{HH} = 4 Hz, OCH₂ of C₅H₆N₃O), 4.13 (dd, 1H, ²J_{HH} = 13 Hz, ³J_{HH} = 4 Hz, OCH₂ of C₅H₆N₃O), 3.54 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 5 Hz, CH₂C₆H₅), 3.16 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 10 Hz, CH₂C₆H₅). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): 137.5 (C₂HN₃ of C₅H₆N₃O), 134.1 (C₂HN₃ of C₅H₆N₃O), 129.4 (CH₂C₆H₅), 129.2 (CH₂C₆H₅), 128.3 (CH₂C₆H₅), 127.9 (CH₂C₆H₅), 65.4 (CHCH₂C₆H₅), 62.3 (OCH₂ of C₅H₆N₃O), 59.8 (CH₂C₆H₅), 41.5 (OCH₂ of C₅H₆N₃O), 38.1(NCH₃). IR data (cm⁻¹) KBr pellet: 3153 (w), 3036 (s), 3009 (s), 2911 (s), 2750 (w), 2362 (m), 2343 (m), 2250 (w), 1601 (s), 1489 (w), 1450 (s), 1388 (w), 1334 (m), 1260 (w), 1235 (m), 1200 (w), 1177 (m), 1106 (s), 1087 (s), 1064 (s), 970 (w), 935 (w), 904 (m), 853 (w), 831 (w), 805 (m), 751 (m), 703 (m), 677 (w), 553 (w), 541 (w), 499 (w), 477 (w). LRMS (ESI): *m/z* 230, [M–I]⁺, Calcd. 230.

3.1.12. Synthesis of {(S)-7-benzyl-2-methyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene)AgCl (**2b**)

A mixture of (S)-7-benzyl-2-methyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-2-ium iodide (**2a**) (0.605 g, 1.69 mmol), Ag₂O (0.393 g, 1.69 mmol) and NaCl (0.098 g, 1.69 mmol) in CH₂

Cl₂ (ca. 50 mL) was stirred for overnight at room temperature. The reaction mixture was filtered through a pad of celite and volatiles were removed under vacuum to give the product **2b** as a light brown solid (0.429 g, 68%). ¹H NMR (CDCl₃, 500 MHz, 25 °C): δ 7.38–7.32 (m, 3H, CH₂C₆H₅), 7.21 (d, 2H, ³J_{HH} = 8 Hz, CH₂C₆H₅), 4.95 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₅N₃O), 4.86 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₅N₃O), 4.65–4.61 (m, 1H, CHCH₂C₆H₅), 4.24 (s, 3H, NCH₃), 3.97 (dd, 1H, ²J_{HH} = 13 Hz, ³J_{HH} = 5 Hz, OCH₂ of C₅H₅N₃O), 3.92 (dd, 1H, ²J_{HH} = 13 Hz, ³J_{HH} = 5 Hz, OCH₂ of C₅H₅N₃O), 3.48 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 5 Hz, CH₂C₆H₅), 3.12 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 10 Hz, CH₂C₆H₅). Anal. Calcd. for C₁₃H₁₅AgClN₃O: C, 41.91; H, 4.06; N, 11.28. Found: C, 41.85; H, 3.73; N, 10.96%.

3.1.13. Synthesis of {(S)-7-benzyl-2-methyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene)AuCl (**2c**)

A mixture of {(S)-7-benzyl-2-methyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4] oxazin-3-ylidene)AgCl (**2b**) (0.200 g, 0.539 mmol) and (Me₂S)AuCl (0.159 g, 0.539 mmol) in CH₃CN (ca. 50 mL) was stirred overnight at room temperature. The reaction mixture was filtered; the filtrate was collected and was dried under vacuum to give the product **2c** as a light yellow solid (0.186 g, 75%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.38–7.31 (m, 3H, CH₂C₆H₅), 7.21 (d, 2H, ³J_{HH} = 8 Hz, CH₂C₆H₅), 4.95 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₅N₃O), 4.86 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₅N₃O), 4.66–4.61 (m, 1H, CHCH₂C₆H₅), 4.20 (s, 3H, NCH₃), 3.97 (dd, 1H, ²J_{HH} = 13 Hz, ³J_{HH} = 5 Hz, OCH₂ of C₅H₅N₃O), 3.92 (dd, 1H, ²J_{HH} = 13 Hz, ³J_{HH} = 5 Hz, OCH₂ of C₅H₅N₃O), 3.48 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 5 Hz, CH₂C₆H₅), 3.12 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 10 Hz, CH₂C₆H₅). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): 154.1 (Au–C), 140.3 (C₂N₃ of C₅H₅N₃O), 134.5 (CH₂C₆H₅), 129.4 (CH₂C₆H₅), 129.3 (CH₂C₆H₅), 128.0 (CH₂C₆H₅), 65.9 (CHCH₂C₆H₅), 63.3 (OCH₂ of C₅H₅N₃O), 58.8 (CH₂C₆H₅), 42.3 (OCH₂ of C₅H₅N₃O), 38.4 (NCH₃). IR data (cm⁻¹) KBr pellet: 3542 (w), 3057 (w), 3027 (w), 2928 (m), 2854 (w), 2359 (w), 2318 (w), 2247 (w), 1639 (w), 1603 (w), 1530 (w), 1454 (m), 1440 (m), 1317 (m), 1249 (m), 1224 (m), 1112 (m), 1088 (m), 1061 (m), 1027 (w), 971 (m), 927 (w), 902 (m), 815 (m), 780 (w), 751 (s), 707 (s), 666 (w), 616 (w), 558 (w), 522 (w), 499 (w). Anal. Calcd. for C₁₃H₁₅N₃OAuCl: C, 33.82; H, 3.27; N, 9.10. Found: C, 34.65; H, 3.17; N, 8.24. [α]_D²⁵ 38.1 (c 1.00 in CHCl₃).

3.1.14. Synthesis of {(S)-7-benzyl-2-ethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene)₂PdCl₂ (**2d**)

A mixture of {(S)-7-benzyl-2-ethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4] oxazin-3-ylidene)AgCl (**2b**) (0.496 g, 0.133 mmol) and (COD)PdCl₂ (0.190 g, 0.666 mmol) in CH₃CN (ca. 50 mL) was stirred at room temperature, until the formation of an off-white AgCl precipitate was observed. The reaction mixture was filtered and solvent was removed under vacuum to give the product **2d** as light yellow solid (0.403 g, 47%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.37–7.30 (m, 3H, CH₂C₆H₅), 7.17 (d, 2H, ³J_{HH} = 8 Hz, CH₂C₆H₅), 4.85 (br, 2H, OCH₂ of C₅H₅N₃O), 4.53–4.50 (m, 1H, CHCH₂C₆H₅), 4.37 (s, 3H, NCH₃), 3.90 (dq, 2H, ²J_{HH} = 13 Hz, ³J_{HH} = 5 Hz, OCH₂ of C₅H₅N₃O), 3.44 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 5 Hz, CH₂C₆H₅), 3.06 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 10 Hz, CH₂C₆H₅). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): 137.5 (Pd–C), 134.1 (C₂N₃ of C₅H₅N₃O), 139.5 (CH₂C₆H₅), 129.3 (CH₂C₆H₅), 128.4 (CH₂C₆H₅), 128.0 (CH₂C₆H₅), 65.5 (CHCH₂C₆H₅), 62.3 (OCH₂ of C₅H₅N₃O), 59.8 (CH₂C₆H₅), 41.5 (OCH₂ of C₅H₅N₃O), 38.2 (NCH₃). IR data (cm⁻¹) KBr pellet: 3698 (w), 3023 (w), 2923 (s), 2852 (m), 2363 (s), 2343 (m), 1617 (s), 1450 (m), 1321 (m), 1265 (w), 1221 (m), 1156 (w), 1097 (s), 936 (w), 817 (m), 741 (m), 704 (s), 557 (w). HRMS (ESI): *m/z* 599.1156, [M]⁺, Calcd. 599.1155. Anal. Calcd. for C₂₆H₃₀N₆O₂PdCl₂: C, 44.99; H, 4.47; N, 11.66. Found: C, 44.93; H, 4.08; N, 12.48%. [α]_D²⁵ – 65.9 (c 1.00 in CHCl₃).

3.1.15. Synthesis of *trans*-{(S)-7-benzyl-2-methyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene}Pd₂(pyridine) (**2e**)

A mixture of (S)-7-benzyl-2-methyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-2-ium iodide (**2a**) (0.231 g, 0.649 mmol), PdCl₂ (0.115 g, 0.649 mmol), K₂CO₃ (0.717 g, 5.19 mmol) and KI (0.862 g, 5.19 mmol) was refluxed in pyridine (5 mL, 63 mmol) for 16 h. The reaction mixture was cooled to room temperature, diluted with CHCl₃ (ca. 100 mL) and subsequently washed with saturated aqueous CuSO₄ solution (ca. 3 × 50 mL). The organic layer was separated and dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated under vacuum to give a sticky, brown residue. The residue thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluted with EtOAc:petroleum ether (1:4 v/v) to give the product **2e** as a yellow solid (0.186 g, 43%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 9.03–9.01 (m, 2H, NC₅H₅), 7.72 (t, 1H, ³J_{HH} = 8 Hz, NC₅H₅), 7.31–7.21 (m, 5H, CH₂C₆H₅), 7.02 (d, 2H, ³J_{HH} = 8 Hz, NC₅H₅), 5.18 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₅N₃O), 5.08 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₅N₃O), 4.28 (dd, 1H, ³J_{HH} = 8 Hz, ³J_{HH} = 6 Hz, CHCH₂C₆H₅), 4.13 (s, 3H, NCH₃), 3.97 (dd, 1H, ²J_{HH} = 12 Hz, ³J_{HH} = 4 Hz, OCH₂ of C₅H₅N₃O), 3.92 (dd, 1H, ²J_{HH} = 12 Hz, ³J_{HH} = 4 Hz, OCH₂ of C₅H₅N₃O), 3.18 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 6 Hz, CH₂C₆H₅), 3.12 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 8 Hz, CH₂C₆H₅). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 153.1 (NC₅H₅), 138.5 (Pd–C), 137.4 (NC₅H₅), 135.5 (C₂N₃ of C₅H₅N₃O), 129.5 (NC₅H₅), 128.8 (CH₂C₆H₅), 128.3 (CH₂C₆H₅), 127.3 (CH₂C₆H₅), 125.5 (CH₂C₆H₅), 65.9 (CHCH₂C₆H₅), 63.9 (OCH₂ of C₅H₅N₃O), 57.7 (CH₂C₆H₅), 42.8 (OCH₂ of C₅H₅N₃O), 37.5 (NCH₃). IR data (cm⁻¹) KBr pellet: 2979 (w), 2928 (m), 2847 (w), 2358 (m), 1601 (s), 1446 (s), 1359 (w), 1309 (s), 1241 (w), 1198 (w), 1149 (w), 1091 (s), 1069 (s), 974 (w), 932 (w), 884 (w), 789 (w), 757 (m), 730 (w), 703 (m), 694 (s), 642 (w), 596 (w), 559 (w). LRMS (ESI): *m/z* 540.9717, [M]⁺, Calcd. 540.5187. Anal. Calcd. for C₁₈H₂₀N₄OPd₂: C, 32.34; H, 3.02; N, 8.38. Found: C, 32.14; H, 2.78; N, 7.82%. [α]_D²⁵ 37.2 (c 1.00 in CHCl₃).

3.1.16. Synthesis of {(S)-7-benzyl-2-ethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-2-ium iodide} (**3a**)

A mixture of (S)-7-benzyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazine (0.407 g, 1.90 mmol) and ethyl iodide (2.98 g, 19.2 mmol) was stirred at 80 °C in CH₃CN (ca. 50 mL) for 24 h, after which, the volatiles were removed under vacuum. The yellow solid thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluted with MeOH:CHCl₃ (1:9 v/v) to give the product **3a** as a light yellow solid (0.262 g, 37%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 9.30 (s, 1H, C₂HN₃ of C₅H₆N₃O), 7.35–7.29 (m, 3H, CH₂C₆H₅), 7.22–7.20 (m, 2H, CH₂C₆H₅), 5.25 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₆N₃O), 5.17 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₆N₃O), 4.91–4.85 (m, 1H, CHCH₂C₆H₅), 4.78 (q, 2H, ³J_{HH} = 8 Hz, NCH₂CH₃), 4.22 (dd, 1H, ²J_{HH} = 13 Hz, ³J_{HH} = 4 Hz, OCH₂ of C₅H₆N₃O), 4.13 (dd, 1H, ²J_{HH} = 13 Hz, ³J_{HH} = 4 Hz, OCH₂ of C₅H₆N₃O), 3.51 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 5 Hz, CH₂C₆H₅), 3.16 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 10 Hz, CH₂C₆H₅), 1.67 (t, 3H, ³J_{HH} = 8 Hz, NCH₂CH₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): 137.0 (C₂HN₃ of C₅H₆N₃O), 134.1 (C₂HN₃ of C₅H₆N₃O), 129.3 (CH₂C₆H₅), 128.9 (CH₂C₆H₅), 128.9 (CH₂C₆H₅), 127.5 (CH₂C₆H₅), 65.3 (CHCH₂C₆H₅), 62.0 (OCH₂ of C₅H₆N₃O), 59.5 (CH₂C₆H₅), 50.1 (OCH₂ of C₅H₆N₃O), 37.9 (NCH₂CH₃), 14.5 (NCH₂CH₃). IR data (cm⁻¹) KBr pellet: 3027 (m), 2926 (s), 2873 (m), 2438 (w), 2250 (w), 2118 (w), 1981 (w), 1614 (s), 1453 (s), 1331 (s), 1530 (w), 1227 (m), 1203 (w), 1156 (m), 1104 (s), 1029 (w), 969 (m), 937 (m), 903 (w), 878 (w), 834 (m), 758 (m), 754 (m), 740 (m), 705 (s), 543 (m), 501 (m). HRMS (ESI): *m/z* 244.1448, [M–I]⁺, Calcd. 244.1444. Anal. Calcd. for C₁₄H₁₈N₃IO·H₂O: C, 43.20; H, 5.18; N, 10.80. Found: C, 43.59; H, 3.71; N, 10.41. [α]_D²⁵ 13.8 (c 1.00 in CHCl₃).

3.1.17. Synthesis of {(S)-7-benzyl-2-ethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene}AgCl (**3b**)

A mixture of (S)-7-benzyl-2-ethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-2-ium iodide (**3a**) (1.27 g, 3.44 mmol), Ag₂O (0.799 g, 3.44 mmol) and NaCl (0.201 g, 3.44 mmol) in CH₂Cl₂ (ca. 50 mL) was stirred overnight at room temperature. The reaction mixture was filtered through a pad of celite and volatiles were removed under vacuum to give the product **3b** as a light brown solid (0.869 g, 65%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.37–7.28 (m, 3H, CH₂C₆H₅), 7.20 (d, 2H, ³J_{HH} = 8 Hz, CH₂C₆H₅), 4.93 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₅N₃O), 4.84 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₅N₃O), 4.66–4.61 (m, 1H, CHCH₂C₆H₅), 4.51 (q, 2H, ³J_{HH} = 8 Hz, NCH₂CH₃), 3.97 (dd, 1H, ²J_{HH} = 13 Hz, ³J_{HH} = 4 Hz, OCH₂ of C₅H₅N₃O), 3.93 (dd, 1H, ²J_{HH} = 13 Hz, ³J_{HH} = 4 Hz, OCH₂ of C₅H₅N₃O), 3.47 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 5 Hz, CH₂C₆H₅), 3.14 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 10 Hz, CH₂C₆H₅), 1.59 (t, 3H, ³J_{HH} = 8 Hz, NCH₂CH₃). ¹³C{¹H} NMR (CDCl₃, 125 MHz, 25 °C): 159.1 (Ag–C), 141.4 (C₂N₃ of C₅H₅N₃O), 134.7 (CH₂C₆H₅), 129.3 (CH₂C₆H₅), 129.0 (CH₂C₆H₅), 127.6 (CH₂C₆H₅), 66.0 (CHCH₂C₆H₅), 63.8 (OCH₂ of C₅H₅N₃O), 58.8 (CH₂C₆H₅), 51.7 (OCH₂ of C₅H₅N₃O), 38.3 (NCH₂CH₃), 16.2 (NCH₂CH₃). IR data (cm⁻¹) KBr pellet: 3083 (w), 3055 (w), 2979 (w), 2935 (m), 2875 (w), 1601 (s), 1491 (w), 1452 (s), 1438 (s), 1365 (m), 1320 (m), 1306 (m), 1243 (w), 1218 (w), 1187 (w), 1155 (w), 1109 (s), 1091 (s), 1063 (s), 1028 (w), 969 (m), 936 (w), 902 (m), 831 (w), 797 (m), 747 (m), 702 (s), 610 (w), 555 (w), 499 (m). LRMS (ESI): *m/z* 350, [M–Cl]⁺, Calcd. 350. Anal. Calcd. for C₁₄H₁₇AgClN₃O: C, 43.49; H, 4.43; N, 10.87. Found: C, 43.59; H, 3.71; N, 10.41. [α]_D²⁵ 38.06 (c 1.00 in CHCl₃).

3.1.18. Synthesis of {(S)-7-benzyl-2-ethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene}AuCl (**3c**)

A mixture of (S)-7-benzyl-2-ethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene}AgCl (**3b**) (0.206 g, 0.533 mmol) and (Me₂S)AuCl (0.157 g, 0.533 mmol) in CH₃CN (ca. 50 mL) was stirred overnight at room temperature. The reaction mixture was filtered the filtrate was collected and was dried under vacuum to give the product **3c** as a light yellow solid (0.215 g, 85%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.37–7.26 (m, 3H, CH₂C₆H₅), 7.20 (d, 2H, ³J_{HH} = 8 Hz, CH₂C₆H₅), 4.95 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₅N₃O), 4.85 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₅H₅N₃O), 4.67–4.62 (m, 1H, CHCH₂C₆H₅), 4.54 (q, 2H, ³J_{HH} = 8 Hz, NCH₂CH₃), 3.98 (dd, 1H, ²J_{HH} = 13 Hz, ³J_{HH} = 4 Hz, OCH₂ of C₅H₅N₃O), 3.94 (dd, 1H, ²J_{HH} = 13 Hz, ³J_{HH} = 4 Hz, OCH₂ of C₅H₅N₃O), 3.47 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 5 Hz, CH₂C₆H₅), 3.15 (dd, 1H, ²J_{HH} = 14 Hz, ³J_{HH} = 10 Hz, CH₂C₆H₅), 1.62 (t, 3H, ³J_{HH} = 8 Hz, NCH₂CH₃). ¹³C{¹H} NMR (CDCl₃, 125 MHz, 25 °C): 152.5 (Au–C), 140.1 (C₂N₃ of C₅H₅N₃O), 134.7 (CH₂C₆H₅), 129.4 (CH₂C₆H₅), 129.2 (CH₂C₆H₅), 127.8 (CH₂C₆H₅), 66.0 (CHCH₂C₆H₅), 63.3 (OCH₂ of C₅H₅N₃O), 58.8 (CH₂C₆H₅), 51.0 (OCH₂ of C₅H₅N₃O), 38.3 (NCH₂CH₃), 15.8 (NCH₂CH₃). IR data (cm⁻¹) KBr pellet: 3054 (w), 3022 (w), 2924 (s), 2874 (m), 2853 (m), 2362 (w), 2343 (w), 1961 (w), 1627 (m), 1601 (m), 1527 (w), 1495 (w), 1453 (s), 1438 (s), 1363 (w), 1353 (w), 1306 (s), 1243 (w), 1217 (w), 1192 (w), 1088 (s), 1064 (s), 1028 (w), 970 (m), 923 (w), 902 (m), 880 (w), 837 (w), 797 (m), 779 (w), 747 (s), 702 (s), 613 (w), 599 (w), 549 (w), 540 (w), 498 (m), 433 (w). Anal. Calcd. for C₁₄H₁₇AuClN₃O·H₂O: C, 34.06; H, 3.88; N, 8.51. Found: C, 34.55; H, 3.16; N, 8.27. [α]_D²⁵ 14.96 (c 1.00 in CHCl₃).

3.1.19. Synthesis of {(S)-7-benzyl-2-ethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene}PdCl₂ (**3d**)

A mixture of (S)-7-benzyl-2-ethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene}AgCl (**3b**) (0.276 g, 0.718 mmol) and (COD)PdCl₂ (0.102 g, 0.359 mmol) in CH₃CN (ca. 50 mL) was stirred at room temperature, until the formation of an off-white AgCl precipitate was observed. The reaction mixture was filtered

and solvent was removed under vacuum to give the product **3d** as light yellow solid (0.129 g, 28%). ^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 7.37–7.29 (m, 3H, $\text{CH}_2\text{C}_6\text{H}_5$), 7.19–7.17 (m, 3H, $\text{CH}_2\text{C}_6\text{H}_5$), 5.32 (d, 1H, $^2J_{\text{HH}} = 16$ Hz, OCH_2 of $\text{C}_5\text{H}_5\text{N}_3\text{O}$), 5.19 (d, 1H, $^2J_{\text{HH}} = 16$ Hz, OCH_2 of $\text{C}_5\text{H}_5\text{N}_3\text{O}$), 4.93 (q, 2H, $^3J_{\text{HH}} = 8$ Hz, NCH_2CH_3), 4.52–4.49 (m, 1H, $\text{CHCH}_2\text{C}_6\text{H}_5$), 3.95 (dd, 1H, $^2J_{\text{HH}} = 13$ Hz, $^3J_{\text{HH}} = 4$ Hz, OCH_2 of $\text{C}_5\text{H}_5\text{N}_3\text{O}$), 3.89 (dd, 1H, $^2J_{\text{HH}} = 13$ Hz, $^3J_{\text{HH}} = 4$ Hz, OCH_2 of $\text{C}_5\text{H}_5\text{N}_3\text{O}$), 3.42 (dd, 1H, $^2J_{\text{HH}} = 14$ Hz, $^3J_{\text{HH}} = 5$ Hz, $\text{CH}_2\text{C}_6\text{H}_5$), 3.09 (dd, 1H, $^2J_{\text{HH}} = 14$ Hz, $^3J_{\text{HH}} = 10$ Hz, $\text{CH}_2\text{C}_6\text{H}_5$), 1.82 (t, 3H, $^3J_{\text{HH}} = 8$ Hz, NCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz, 25 °C): 143.6 (Pd–C), 137.5 (C_2N_3 of $\text{C}_5\text{H}_5\text{N}_3\text{O}$), 134.5 ($\text{CH}_2\text{C}_6\text{H}_5$), 129.3 ($\text{CH}_2\text{C}_6\text{H}_5$), 129.0 ($\text{CH}_2\text{C}_6\text{H}_5$), 127.6 ($\text{CH}_2\text{C}_6\text{H}_5$), 65.9 ($\text{CHCH}_2\text{C}_6\text{H}_5$), 63.6 (OCH_2 of $\text{C}_5\text{H}_5\text{N}_3\text{O}$), 58.5 ($\text{CH}_2\text{C}_6\text{H}_5$), 50.6 (OCH_2 of $\text{C}_5\text{H}_5\text{N}_3\text{O}$), 38.1 (NCH_2CH_3), 15.1 (NCH_2CH_3). IR data (cm^{-1}) KBr pellet: 3030 (w), 3976 (w), 2927 (w), 2871 (w), 1636 (m), 1495 (w), 1455 (s), 1381 (w), 1357 (w), 1301 (s), 1261 (w), 1236 (w), 1202 (w), 1180 (w), 1100 (s), 1069 (m), 1031 (w), 1002 (w), 935 (m), 881 (w), 789 (m), 756 (w), 729 (w), 702 (s), 644 (w), 588 (w), 556 (w), 514 (w). Anal. Calcd. for $\text{C}_{28}\text{H}_{34}\text{N}_6\text{O}_2\text{PdCl}_2$: C, 50.65; H, 5.16; N, 12.66. Found: C, 50.23; H, 4.71; N, 11.92. $[\alpha]_{\text{D}}^{25}$ 37.2 (c 1.00 in CHCl_3).

3.1.20. Synthesis of *trans*-{(S)-7-benzyl-2-ethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-3-ylidene}PdI₂(pyridine) (**3e**)

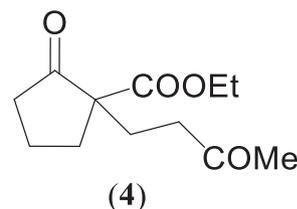
A mixture of (S)-7-benzyl-2-ethyl-6,7-dihydro-4H-[1,2,3]-triazolo[5,1-c][1,4]oxazin-2-ium iodide (**3a**) (0.320 g, 0.862 mmol), PdCl₂ (0.152 g, 0.862 mmol), K₂CO₃ (0.952 g, 6.90 mmol) and KI (1.14 g, 6.90 mmol) was refluxed in pyridine (5 mL, 63 mmol) for 16 h. The reaction mixture was cooled to room temperature, diluted with CHCl_3 (ca. 100 mL) and subsequently washed with saturated aqueous CuSO_4 solution (ca. 3×50 mL). The organic layer was separated and dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under vacuum to give a sticky, brown residue. The residue thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluted with EtOAc:petroleum ether (1:4 v/v) to give the product **3e** as a yellow solid (0.195 g, 46%). ^1H NMR (CDCl_3 , 500 MHz, 25 °C): δ 8.99–8.97 (m, 2H, NC_5H_5), 7.72–7.68 (m, 1H, NC_5H_5), 7.34–7.27 (m, 5H, $\text{CH}_2\text{C}_6\text{H}_5$), 7.16–7.15 (m, 2H, NC_5H_5), 5.14 (d, 1H, $^2J_{\text{HH}} = 16$ Hz, OCH_2 of $\text{C}_5\text{H}_5\text{N}_3\text{O}$), 5.02 (d, 1H, $^2J_{\text{HH}} = 16$ Hz, OCH_2 of $\text{C}_5\text{H}_5\text{N}_3\text{O}$), 4.79 (q, 2H, $^3J_{\text{HH}} = 8$ Hz, NCH_2CH_3), 4.53–4.48 (m, 1H, $\text{CHCH}_2\text{C}_6\text{H}_5$), 3.93 (dd, 1H, $^2J_{\text{HH}} = 13$ Hz, $^3J_{\text{HH}} = 4$ Hz, OCH_2 of $\text{C}_5\text{H}_5\text{N}_3\text{O}$), 3.90 (dd, 1H, $^2J_{\text{HH}} = 13$ Hz, $^3J_{\text{HH}} = 4$ Hz, OCH_2 of $\text{C}_5\text{H}_5\text{N}_3\text{O}$), 3.43 (dd, 1H, $^2J_{\text{HH}} = 14$ Hz, $^3J_{\text{HH}} = 5$ Hz, $\text{CH}_2\text{C}_6\text{H}_5$), 3.11 (dd, 1H, $^2J_{\text{HH}} = 14$ Hz, $^3J_{\text{HH}} = 10$ Hz, $\text{CH}_2\text{C}_6\text{H}_5$), 1.70 (t, 3H, $^3J_{\text{HH}} = 8$ Hz, NCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz, 25 °C): δ 153.8 (NC_5H_5), 137.6 (Pd–C), 136.9 (NC_5H_5), 134.9 (C_2N_3 of $\text{C}_5\text{H}_5\text{N}_3\text{O}$), 129.4 (NC_5H_5), 129.1 ($\text{CH}_2\text{C}_6\text{H}_5$), 127.5 ($\text{CH}_2\text{C}_6\text{H}_5$), 124.4 ($\text{CH}_2\text{C}_6\text{H}_5$), 116.5 ($\text{CH}_2\text{C}_6\text{H}_5$), 65.8 ($\text{CHCH}_2\text{C}_6\text{H}_5$), 64.2 (OCH_2 of $\text{C}_5\text{H}_5\text{N}_3\text{O}$), 58.4 ($\text{CH}_2\text{C}_6\text{H}_5$), 51.4 (OCH_2 of $\text{C}_5\text{H}_5\text{N}_3\text{O}$), 38.1 (NCH_2CH_3), 14.6 (NCH_2CH_3). IR data (cm^{-1}) KBr pellet: 3019 (w), 2979 (w), 2928 (s), 2847 (w), 2368 (w), 1601 (m), 1446 (s), 1359 (w), 1327 (w), 1309 (s), 1288 (m), 1241 (w), 1198 (w), 1149 (w), 1091 (s), 1069 (s), 974 (w), 932 (m), 884 (w), 789 (m), 757 (m), 729 (w), 703 (m), 694 (m), 641 (w), 596 (w), 559 (w), 513 (w). HRMS (ESI): m/z 554.9869, $[\text{M}-\text{I}]^+$, Calcd. 554.9875. Anal. Calcd. for $\text{C}_{19}\text{H}_{22}\text{I}_2\text{N}_4\text{OPd}$: C, 33.43; H, 3.25; N, 8.21. Found: C, 33.48; H, 2.92; N, 7.91. $[\alpha]_{\text{D}}^{25}$ 37.3 (c 1.00 in CHCl_3).

3.1.21. General procedure for asymmetric Michael addition reaction of ethyl-2-oxocyclopentane-1-carboxylate with methyl vinyl ketone (Table 2)

A mixture of catalyst (**2d/2e/3d/3e**) (0.01 mmol, 1 mol %), ethyl-2-oxocyclopentane-1-carboxylate (0.156 g, 1.00 mmol), methyl vinyl ketone (0.210 g, 3.00 mmol) Et₃N (0.304 g, 3.00 mmol) was added in 5 mL CHCl_3 and the resultant solution was stirred for

8 h at room temperature. The volatiles were then removed in *vacuo* and the crude product was purified by column chromatography using silica as a stationary phase and eluting with a mixed medium of petroleum ether:EtOAc (v/v 80:20 to 70:30) to give the product ethyl-2-oxo-1-(3-oxobutyl)cyclopentane-1-carboxylate (**4**) as a colorless liquid. The *ee* was determined by chiral GC with a CP-Chirasil-Dex CB column, GC conditions: injection temperature: 250 °C, detector temperature: 300 °C, column temperature: initial temperature 60 °C, ramp 3 °C/min to 120 °C then hold 5 min, 3 °C/min to 130 °C then hold 20 min.

3.1.22. Synthesis of ethyl-2-oxo-1-(3-oxobutyl)cyclopentane-1-carboxylate (**4**) [48]



Yields: 0.192 g, 85% (**2d**), 0.206 g, 91% (**2e**), 0.198 g, 88% (**3d**), 0.201 g, 89% (**3e**).

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 4.12 (dq, 2H, $^3J_{\text{HH}} = 7$ Hz and 2 Hz, CH_2CH_3), 2.69–2.63 (m, 1H, $\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}$), 2.46–2.23 (m, 4H, $\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}$ and $\text{C}(\text{O})(\text{CH}_2)_3\text{C}$), 2.09 (s, 3H, CH_3CO), 2.08–2.03 (m, 1H, $\text{C}(\text{O})(\text{CH}_2)_3\text{C}$), 2.00–1.81 (m, 4H, $\text{C}(\text{O})(\text{CH}_2)_3\text{C}$), 1.21 (t, 3H, $^3J_{\text{HH}} = 7$ Hz, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz, 25 °C): δ 215.0 (CO), 207.9 (CH_3CO), 171.5 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 61.5 (CH_2CH_3), 59.1 ($\text{C}(\text{O})\text{CC}(\text{O})\text{CH}_2$), 39.0 ($\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{C}$), 38.1 ($\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}$), 34.5 ($\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}$), 30.0 (CH_3CO), 27.1 ($\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{C}$), 19.7 ($\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{C}$), 14.2 (CH_2CH_3). GC–MS (ESI): $m/z = 226$ $[\text{M}]^+ +$. Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{O}_4$: C, 63.70; H, 8.02; Found: C, 63.63; H, 7.59%. GC [CP-Chirasil-Dex CB, column temperature = 60 °C (initial), inject temperature = 250 °C, detector temperature = 300 °C]: $t_{\text{R}} = 40.6$ min, $t_{\text{R}} = 44.1$ min.

CRediT authorship contribution statement

Manoj Kumar Gangwar: Methodology, Investigation, Data curation. **Shreyata Dey:** Methodology, Investigation, Data curation, Writing - original draft. **Prakasham. A. P.:** Visualization, Software. **Prasenjit Ghosh:** Conceptualization, Supervision, Funding acquisition, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

CCDC-1011069 (for **1b**), CCDC-1012239 (for **1c**), CCDC-1021594 (for **1d**), CCDC-1024176 (for **1e**), CCDC-1011070 (for **2c**), CCDC-1059753 (for **2d**), CCDC-1024225 (for **2e**), CCDC-1023266 (for **3b**), CCDC-1024174 (for **3c**) and CCDC-1012271 (for **3d**), CCDC-1040518 (for **3e**) contain the supplementary crystallographic data. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data (^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, IR, HRMS, CHNS) of the compounds (**1–3a**), (**1–3b**), (**1–3c**), (**1–3d**) and (**1–3e**), and (^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, GC and GC–MS) of the catalysis product **4** (PDF) can be found with this article. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2020.115011>.

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