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Asymmetric synthesis of optically active vinyltetrahydrofurans via palladium-catalysed cyclisation of bis(hydroxymethyl)allylic carbonates

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ABSTRACT

Optically active 3-alkyl-3-hydroxymethyl-5-vinyltetrahydrofurans were synthesised from the corresponding methyl or isobutyl carbonates of ω,ω-bis(hydroxymethyl)-α,β-unsaturated alcohols via palladium-catalysed cyclisation. The use of chiral ligands gave the corresponding tetrahydrofuran derivatives, which had er values that ranged from moderate to good.

1. Introduction

The Pd^0-catalysed intramolecular allylation of oxygen nucleophiles is a very useful method for the asymmetric synthesis of optically active oxygen heterocycles.[1] This type of transformation frequently occurs under mild conditions, tolerates a broad array of functional groups and proceeds with high stereoselectivity.[2]

Several years ago, we presented results for the Pd^0- and Pd^{II}-catalysed cyclisation reaction of ω,ω-bis(hydroxymethyl)-α,β-unsaturated alcohols as well as the corresponding methyl allylic carbonates and preliminary results concerning the asymmetric Pd^0-catalysed cyclisation of allylic carbonates.[3]

By extending our previous work on the use of methyl allylic carbonates in the synthesis of O-heterocycles,[3b] we herein report the influence of the allylic carbonate (methyl or isobutyl) on heterocyclisation reactions as well as the impact of chiral ligands, both commercially available and new derivatives of carbohydrates received in our group.

2. Results and discussion

New isobutyl carbonates **1b**, **1d**, **1f** and **1h** were prepared according to the procedure described for methyl carbonates **1a**, **1c**, **1e** and **1g**, that is, by palladium-catalysed alkylation of substituted dimethyl malonates with the monoacetate of but-1,4-diol, followed by protection of the hydroxyl function with a *tert*-butyldimethylsilyl group, then reduction of the diester, deprotection of the *tert*-butyldimethyl ether and finally condensation with isobutyl chloroformate.[3b] The cyclisation was first studied with bis(hydroxymethyl) allylic carbonate **1a** as the substrate (Scheme 1).

The ring-closure of methyl carbonate **1a** occurred readily in THF at room temperature in the presence of a catalytic amount of $Pd_2(dba)_3$, associated with dppb, which provided exclusively THF derivatives **2a** and **3a** as a 15:85 mixture and in 92% overall yield (Table 1, entry 1). The configurational assignment of compounds **2a** and **3a** was based on NOESY experiments.[3b]

Isobutyl carbonate **1b** was more reactive under the same conditions (Table 1, entry 2) and gave products **2a** and **3a** with the highest yield (99%) and diastereoselectivity (11:89). The Pd^0-catalysed cyclisation was extended to other allylic carbonates **1c–h** bearing different substituents. In all cases, the corresponding THFs **2b–d** and **3b–d** were obtained in quite high yields (94–96%) after 1–2 h (Table 1, entries 2–8). However, it should be noted that in all cases, the isobutyl carbonate was more reactive and led to cyclic products with higher stereoselectivity. Only methyl and isobutyl carbonate with the 2-naphthylmethyl substituents **1g** and **1h** gave the corresponding THFs with the same yield and selectivity.

Our results led us to conclude that the rest of the carbonate influences the course of cyclisation. The reaction mechanism (Scheme 2) showed that the alkoxide ion generated in situ carries the nucleophile into an ionic active form. This is why the more alkaline ion $i\text{-BuO}^-$ plays a central role in the activation of the nucleophile and, hence, increases the yield and selectivity of the process.

Previous studies on the Pd^0-catalysed asymmetric cyclisation of methyl carbonates containing two enantiotopic hydroxymethyl groups have shown that the use of chiral ligands in association with Pd affords the corresponding THF stereoisomers with low to moderate er values.[3b] The best results were obtained in the presence of (*R*,*S*)-Josiphos as the ligand at 55 °C, when the minor diastereoisomer **2a** was obtained with an enantiomeric ratio (er) of 15:85, while the major diastereoisomer **3a** exhibited an er of 64:36 (Table 2, entry 1).[3b]

Under the same conditions isobutyl carbonate **1b** gave products **2a** and **3a** with a similar yield as well as diastereo- and

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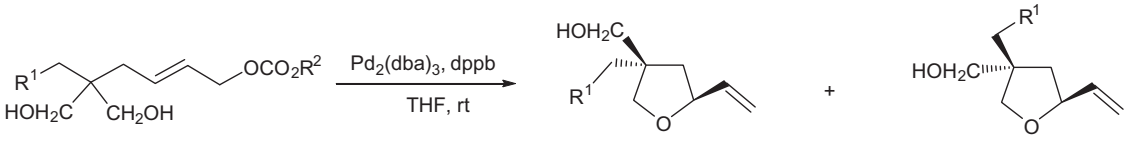


1a: $R^1 = C_6H_5$, R^2 = Me
1b: $R^1 = C_6H_5$, R^2 = *i*-Bu
1c: R^1 = 2-$CH_3C_6H_4$, R^2 = Me
1d: R^1 = 2-$CH_3C_6H_4$, R^2 = *i*-Bu
1e: R^1 = 4-$CH_3C_6H_4$, R^2 = Me
1f: R^1 = 4-$CH_3C_6H_4$, R^2 = *i*-Bu
1g: R^1 = 2-$C_{10}H_7$, R^2 = Me
1h: R^1 = 2-$C_{10}H_7$, R^2 = *i*-Bu

2a: $R^1 = C_6H_5$
2b: R^1 = 2-$CH_3C_6H_4$
2c: R^1 = 4-$CH_3C_6H_4$
2d: R^1 = 2-$C_{10}H_7$

3a: $R^1 = C_6H_5$
3b: R^1 = 2-$CH_3C_6H_4$
3c: R^1 = 4-$CH_3C_6H_4$
3d: R^1 = 2-$C_{10}H_7$

Scheme 1. Pd^0-catalysed synthesis of tetrahydrofurans **2** and **3**.

Table 1
Pd^0-catalysed allylic cyclisation of substrates **1a–h** according to Scheme 1[a]

Entry	Carbonate	Yield (**2**+**3**)[b] (%)	**2**/**3**[c] (%)
1	**1a**	92	15:85
2	**1b**	99	11:89
3	**1c**	94	15:85
4	**1d**	96	10:90
5	**1e**	95	17:83
6	**1f**	96	13:87
7	**1g**	94	13:87
8	**1h**	95	13:87

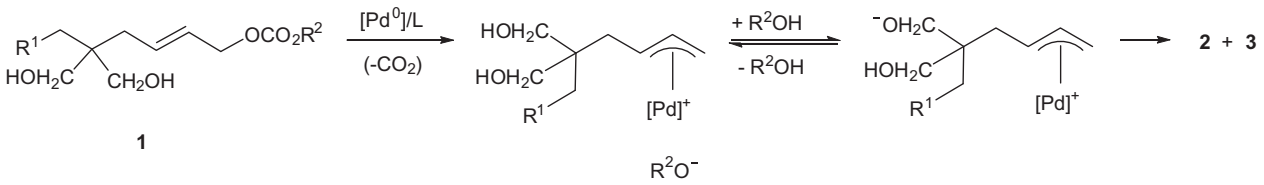
[a] [**1**]/[$Pd_2(dba)_3$]/[dppb] = 40:1:2.2, THF, rt, 1–2 h.
[b] Yield refers to isolated pure products after column chromatography.
[c] Determined by ^{1}H NMR spectroscopy.

enantioselectivity (Table 2, entry 2). Ring-closure of the methyl carbonate **1a** occurred quickly (1 h) at room temperature in the presence of the (*R*,*R*)-Trost ligand and quantitatively provided THFs **2a** and **3a** as a 20:80 mixture of diastereoisomers in favour of stereoisomer **2a**. The major diastereoisomer **3a** was obtained with an er of 59:41, while the minor diastereoisomer **2a** showed an er of 43:57 (Table 2, entry 3).

The use of isobutyl carbonate **1b** under the same conditions afforded an identical yield (99%) and diastereoselectivity (**2a**/**3a** 20:80), although the minor isomer **2a** showed the opposite ratio (er values of 67:33). The major isomer **3a** was obtained with higher selectivity (er 71:29) in comparison with methyl carbonate **1a** (59:41) (Table 2, entry 4).

Asymmetric cyclisation of isobutyl carbonate **1b** was performed in the presence of the phosphorus amidite ligand **L1** (Fig. 1). Cyclisation of **1b** at room temperature afforded a 19:81 mixture of diastereoisomers **2a** and **3a** in 99% yield after 20 h (Table 2, entry 5). The minor isomer was obtained with an er of 20:80 while the major isomer exhibited an er of 76:24. Cyclisation of compound **1b** was also carried out in the presence of the carbohydrate ligand **L2**, prepared according to the procedure described by Sinou.[4] This cyclisation required a longer reaction time and gave products **2a** and **3a** in a good yield of 98% after 72 h with 22:78 diastereoselectivity in favour of stereoisomer **2a** (Table 2, entry 6). The minor isomer was obtained with a higher er of 89:11, while the major isomer had an er of 27:73. The results obtained for the Pd^0-catalysed cyclisation of methyl carbonate **1c** and isobutyl carbonate **1d** bearing the *o*-tolyl substituent in the presence of Trost's ligand again showed a higher efficiency of the isobutyl carbonate (Table 2, entries 7–8). Both carbonates **1c** and **1d** gave cyclisation products with the same diastereoselectivity (**2b**/**3b** 15:85), but the er was better for isobutyl carbonate **1d** (er of **2b** 64:36 and er of **3b** 69:31). Additionally, the minor steroisomer **2b** was obtained with a reversal of configuration going from **1c** (42:58) to **1d** (64:36). The use of (*R*,*S*)-Josiphos as the chiral ligand gave very good diastereoselectivity (**2b**/**3b** 5:95) in excellent yield (98%) after 20 h at 55 °C (Table 2, entry 9). The er value of the major isomer was very low (58:42) while that of the minor isomer was 21:79. Conversely, the phosphorus amidite ligand **L1** showed good selectivity only for the major isomer **3b** (er 70:30) (Table 2, entry 10). Cyclisation of isobutyl carbonate **1d** in the presence of carbohydrate ligands **L2**–**L4** was successful only with the phosphine-amide ligand **L2** (Table 2, entries 11–14). When the reaction was performed at 25 °C, we observed the best selectivity after 72 h: the minor diastereoisomer **2b** was obtained with an enantiomeric ratio of 86:14 and the major diastereoisomer **3b** showed an er of 19:81 (Table 2, entry 11). Increasing the temperature to 55 °C gave the cyclised products in 98% yield in less time (20 h), but resulted in a decrease in enantioselectivity (Table 2, entry 12). The same reaction in the presence of carbohydrate urea ligand **L3** derived from cellobiose and phosphine-imine ligand **L4** derived from glucosamine,[5] afforded practically a 1:1 mixture of enantiomers of both diastereoisomers **2b** and **3b** (Table 2, entries 13, 14).

When we compared the reactivity of the methyl and isobutyl carbonate with a *p*-tolyl substituent in the presence of (*R*,*R*)-Trost's ligand, we again obtained better results for the isobutyl carbonate **1f** (Table 2, entries 15–16). The reaction performed at room temperature gave cyclised products in 93% yields after 1 h with 7:93 diastereoselectivity in favour of diastereoisomer **2c**. Both isomers,

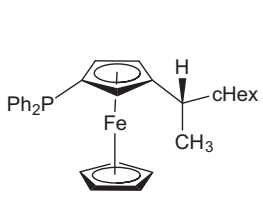


Scheme 2. Mechanism of the Pd^0-catalysed cyclisation.

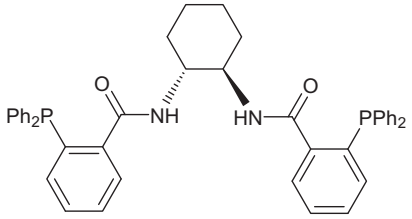
Table 2
Effect of carbonates and ligands on the Pd^0-catalysed asymmetric allylic alkylation[a]

Entry	Carbonate	Ligand	Time (h)	Temp (°C)	Yield **2**+**3**[b]	**2**/**3**[c]	er of **2**[d]	er of **3**[d]
1	**1a**	(*R*,*S*)-Josiphos	20	55	83	18:82	15:85	64:36
2	**1b**	(*R*,*S*)-Josiphos	20	55	83	20:80	18:82	60:40
3	**1a**	(*R*,*R*)-Trost	1	25	99	20:80	43:57	59:41
4	**1b**	(*R*,*R*)-Trost	1	25	99	20:80	67:33	71:29
5	**1b**	**L1**	20	25	99	19:81	20:80	76:24
6	**1b**	**L2**	72	25	98	22:78	89:11	27:73
7	**1c**	(*R*,*R*)-Trost	1	25	92	15:85	42:58	60:40
8	**1d**	(*R*,*R*)-Trost	1	25	95	15:85	64:36	69:31
9	**1d**	(*R*,*S*)-Josiphos	20	55	98	5:95	21:79	58:42
10	**1d**	**L1**	20	25	96	10:90	43:57	70:30
11	**1d**	**L2**	72	25	97	25:75	86:14	19:81
12	**1d**	**L2**	20	55	98	20:80	77:23	33:67
13	**1d**	**L3**	72	25	74	15:85	45:55	48:52
14	**1d**	**L4**	96	25	68	12:88	56:44	50:50
15	**1e**	(*R*,*R*)-Trost	1	25	95	17:83	48:52	62:38
16	**1f**	(*R*,*R*)-Trost	1	25	93	7:93	63:37	70:30
17	**1f**	(*R*,*S*)-Josiphos	20	55	92	25:75	22:78	59:41
18	**1f**	**L1**	20	25	94	20:80	18:82	75:25
19	**1h**	(*R*,*S*)-Josiphos	72	55	98	14:86	18:82	60:40
20	**1h**	**L1**	20	25	95	13:87	79:21	15:85
21	**1h**	**L2**	72	25	98	13:87	88:12	20:80

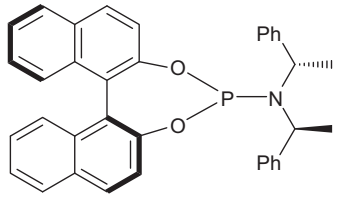
[a] [**1**]/[$Pd_2(dba)_3$]/[ligand] = 40:1:2.2 (4.4), THF.
[b] Yield refers to isolated pure products after column chromatography.
[c] Determined by ^{1}H NMR spectroscopy.
[d] Enantioselectivity (er) was measured by chiral stationary phase HPLC on a Chiralpak AD column (25 cm × 4.6 mm); flow rate = 0.5 ml min^{-1}; hexane/*i*-propanol (90:10), t_R = 18.7 min and t_R = 22.8 min for **2a** and t_R = 17.2 min and t_R = 18.7 min for **3a**; hexane/*i*-propanol (85:15), t_R = 12.3 min and t_R = 16.8 min for **2b** and t_R = 12.2 min and t_R = 14.6 min for **3b**; hexane/*i*-propanol (95:5), t_R = 24.7 min and t_R = 33.3 min for **2c** and t_R = 23.2 min and t_R = 25.1 min for **3c**; hexane/*i*-propanol (95:5), t_R = 42.4 min and t_R = 44.7 min for **2d** and hexane/*i*-propanol (98:2), t_R = 84.6 min and t_R = 88.6 min for **3d**; the first value corresponds to the enantiomer being eluted first.



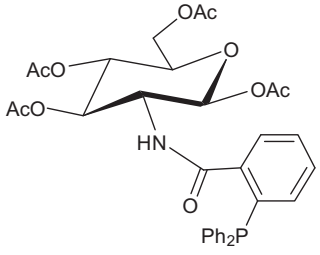
(*R*,*S*)-Josiphos



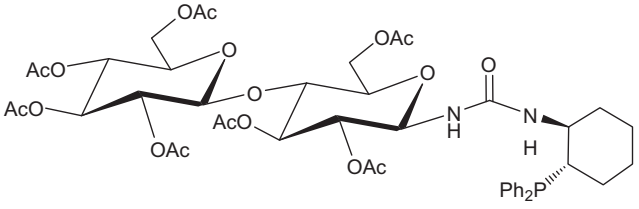
(*R*,*R*)-Trost's ligand



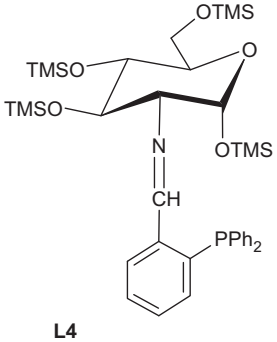
L1 (*S*,*S*,a*S*)



L2



L3



L4

Figure 1. Ligands used herein.

minor **2c** and major **3c,** were obtained with similar enantioselectivity, 63:37 and 70:30 for **2c** and **3c**, respectively (Table 2, entry 16). Cyclisation of isobutyl carbonate **1f** in the presence of (*R*,*S*)-Josiphos as the chiral ligand afforded good selectivity only for the minor isomer **2c** (er 22:78) (Table 2, entry 17). The best results were obtained for the reaction carried out in the presence of the phosphorus amidite ligand **L1** (er 18:82 for **2c** and er 75:25 for **3c**) (Table 2, entry 18).

Finally, the asymmetric cyclisation of the isobutyl carbonate with a 2-naphthylmethyl substituent **1h** was performed in the presence (*R*,*S*)-Josiphos as the chiral ligand (Table 2, entry 19). Cyclisation at 55 °C afforded a 14:86 mixture of stereoisomers. Good er

values for the two stereoisomers **2d** and **3d** were obtained: 18:82 and 60:40 for **2d** and **3d,** respectively. Ligand **L1** gave better selectivity (79:21 for **2d** and 15:85 for **3d**) (Table 2, entry 20), but the best results were obtained for carbohydrate ligand **L2**. The reaction required a longer reaction time but afforded **2d** and **3d** in very good yield (98%) after 72 h with good selectivity (**2d**/**3d** 13:87) and high er values, 88:12 for **2d** and 20:80 for **3d** (Table 2, entry 21).

3. Conclusion

In conclusion, we have developed a simple and efficient methodology for the synthesis of substituted tetrahydrofurans via the Pd^0-catalysed cyclisation of allylic carbonates. The reactions afforded a mixture of stereoisomers with excellent yields and good diastereoselectivities and enantioselectivities. Using as a starting material isobutyl carbonates, we observed significantly higher reactivities and selectivities in comparison with methyl carbonates. The best results were obtained in the asymmetric cyclisation in the presence of a catalytic amount of $Pd_2(dba)_3$ associated with phosphorus amidite ligand **L1** and phosphine-amide ligand **L2** derived from D-glucosamine (er values up to 89:11).

4. Experimental

4.1. General

All solvents and reagents were purchased from Sigma–Aldrich and used as supplied, without additional purification. NMR spectra were recorded in $CDCl_3$ on Brucer Avance III (600 MHz for ^1H NMR, 150 MHz for ^{13}C NMR), coupling constants are reported in Hz. Chromatographic purification of compounds was achieved with 230–400 mesh size silica gel. The progress of the reactions was monitored by silica gel thin layer chromatography plates (Merck TLC Silicagel 60 F_{254}). The enantiomeric ratio was determined by HPLC (ProStar Varian) employing a Chiralpak AD column (25 cm × 4.6 mm).

4.2. Typical procedure for the synthesis of isobutyl carbonates 1b, 1d, 1f, 1h

A solution of the corresponding triol[3b] (2.5 mmol) in CH_2Cl_2 (50 mL) cooled to 0 °C was treated with pyridine (0.4 mL, 5.0 mmol) and isobutyl chloroformate (0.32 mL, 2.5 mmol). After 2–4 h at room temperature, the reaction mixture was quenched with water (10 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The combined organic phases were dried (Na_2SO_4) and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel to give allylic carbonates **1b**, **1d**, **1f** and **1h.**

4.2.1. (*E*)-5-Benzyl-6-hydroxy-5-(hydroxymethyl)hex-2-en-1-yl isobutyl carbonate 1b

Colourless oil, 378 mg, 45% yield. R_f = 0.71 (ethyl acetate/petroleum ether, 4:1). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.98 (d, 6H, J = 6.7, $CH(CH_3)_2$), 1.98–2.02 (m, 1H, $CH(CH_3)_2$), 2.10 (d, 2H, J = 7.3, CH_2–CH=), 2.26 (s, 2H, 2OH), 2.70 (s, 2H, $PhCH_2$), 3.59 (d, 4H, J = 5.5, $2CH_2OH$), 3.95 (d, 2H, J = 6.7, $CH_2CH(CH_3)_2$), 4.62 (d, 2H, J = 6.4, CH_2O), 5.72 (dt, 1H, J = 15.3, 6.4, CH=), 5.94 (dt, 1H, J = 15.3, 7.6, CH=), 7.2–7.35 (m, 5H, C_6H_5). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 18.9 ($CH(CH_3)_2$), 27.8 ($CH(CH_3)_2$), 35.0 (CH_2–CH=), 38.0 ($PhCH_2$), 43.1 ($C(CH_2OH)_2$), 67.7 (CH_2OH), 68.1 (CH_2O), 74.1 ($CH_2CH(CH_3)_2$), 126.4, 127.1, 128.2, 130.5, 132.1, 137.4 (C_6H_5, CH=CH), 155.3 (CO). $C_{19}H_{28}O_5$ (336.19): calcd. C 67.83, H 8.39; found C 67.54, H 8.51.

4.2.2. (*E*)-5-(2-Methylbenzyl-6-hydroxy-5-(hydroxymethyl)hex-2-en-1-yl isobutyl carbonate 1d

Colourless oil, 473 mg, 54% yield. R_f = 0.51 (ethyl acetate/petroleum ether, 1:1). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.87 (d, 6H, J = 6.7, $CH(CH_3)_2$), 1.85–1.95 (m, 1H, $CH(CH_3)_2$), 2.12 (d, 2H, J = 7.5, CH_2–CH=), 2.26 (s, 3H, CH_3Ph), 2.30 (s, 2H, 2OH), 2.63 (s, 2H, $PhCH_2$), 3.54 (s, 4H, $2CH_2OH$), 3.83 (d, 2H, J = 6.5, $CH_2CH(CH_3)_2$), 4.49 (dd, 2H, J = 6.4, 0.7, CH_2O), 5.60 (dtt, 1H, J = 15.2, 6.5, 1.3, CH=), 5.81 (dtt, 1H, J = 15.2, 7.5, 1.2, CH=), 7.05–7.20 (m, 4H, C_6H_4). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 19.1 ($CH(CH_3)_2$), 20.5 (CH_3), 27.0 ($CH(CH_3)_2$), 35.1 (CH_2–CH=), 36.0 ($PhCH_2$), 44.3 ($C(CH_2OH)_2$), 67.0 (CH_2OH), 68.3 (CH_2O), 74.3 ($CH_2CH(CH_3)_2$), 125.8, 126.6, 127.1, 130.9, 131.4, 132.6, 136.2. 137.3 (C_6H_4, CH=CH), 155.5 (CO). $C_{20}H_{30}O_5$ (350.21): calcd C 68.54, H 8.63; found C 68.32, H 8.45.

4.2.3. (*E*)-5-(4-Methylbenzyl-6-hydroxy-5-(hydroxymethyl)hex-2-en-1-yl isobutyl carbonate 1f

Colourless oil, 779 mg, 89% yield. R_f = 0.82 (ethyl acetate/petroleum ether, 4:1). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.89 (d, 6H, J = 6.8, $CH(CH_3)_2$), 1.50 (s, 2H, 2OH), 1.85–2.00 (m, 1H, $CH(CH_3)_2$), 2.02 (d, 2H, J = 7.8, CH_2–CH=), 2.25 (s, 3H, CH_3Ph), 2.55 (s, 2H, $PhCH_2$), 3.50 (s, 4H, $2CH_2OH$), 3.85 (d, 2H, J = 6.4, $CH_2CH(CH_3)_2$), 4.52 (dd, 2H, J = 6.4, 1.1, CH_2O), 5.63 (dtt, 1H, J = 15.4, 6.4, 1.2, CH=), 5.85 (dtt, 1H, J = 15.4, 7.5, 1.1, CH=), 7.15–7.25 (m, 4H, C_6H_4). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 18.9 ($CH(CH_3)_2$), 21.0 (CH_3), 27.8 ($CH(CH_3)_2$), 35.0 (CH_2–CH=), 37.6 ($PhCH_2$), 43.1 ($C(CH_2OH)_2$), 67.8 (CH_2OH), 68.1 (CH_2O), 74.1 ($CH_2CH(CH_3)_2$), 127.0, 128.9, 130.4, 131.2, 134.2, 135.9 (C_6H_4, CH=CH), 155.3 (CO). $C_{20}H_{30}O_5$ (350.21): calcd C 68.54, H 8.63; found C 68.34, H 8.42.

4.2.4. (*E*)-5-(2-Naphthylmethyl-6-hydroxy-5-(hydroxymethyl)-hex-2-en-1-yl isobutyl carbonate 1h

Colourless oil, 560 mg, 58% yield. R_f = 0.63 (ethyl acetate/petroleum ether, 3:1). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.87 (d, 6H, J = 6.7, $CH(CH_3)_2$), 1.89–2.00 (m, 1H, $CH(CH_3)_2$), 2.02 (d, 2H, J = 7.5, CH_2–CH=), 2.38 (s, 2H, 2OH), 2.76 (s, 2H, $CH_2C_{10}H_7$), 3.53 (s, 4H, $2CH_2OH$), 3.85 (d, 2H, J = 6.7, $CH_2CH(CH_3)_2$), 4.53 (d, 2H, J = 6.4, CH_2O), 5.62 (dt, 1H, J = 15.2, 6.4, CH=), 5.88 (dt, 1H, J = 15.2, 7.5, CH=), 7.28–7.273 (m, 7H, $C_{10}H_7$). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 19.1 ($CH(CH_3)_2$), 28.0 ($CH(CH_3)_2$), 35.2 (CH_2–CH=), 38.2 ($CH_2C_{10}H_7$), 44.6 ($C(CH_2OH)_2$), 67.1 (CH_2OH), 68.2 (CH_2O), 74.3 ($CH_2CH(CH_3)_2$), 125.6, 126.1, 127.3, 127.7, 127.8, 129.2, 129.3, 131.3, 132.4, 133.6, 135.1, 135.3 ($C_{10}H_7$, CH=CH), 155.5 (CO). $C_{23}H_{30}O_5$ (386.21): calcd C 71.48, H 7.82; found C 70.99, H 7.53.

4.3. Synthesis of *N*-[(1*S*,2*S*)-2-(Diphenylphosphino)cyclohexyl]-*N*′-(2,3,6,2′,3′,4′,6-hexa-*O*-acetyl-β-D-cellobiose)urea L3

To a solution of 2,3,6,2′,3′,4′,6-hexa-*O*-acetyl-β-D-azidocellobiose[6] (669 mg, 1 mmol) in methylene chloride (8 mL), triphenylphosphine (865 mg, 3.3 mmol) was added. The mixture was stirred at room temperature for 30 min and then flushed with CO_2. Next, (1*S*,2*S*)-2-(diphenylphosphino)cyclohexylamine (283 mg, 1 mmol) was added. The mixture was then stirred and flushed with CO_2 at room temperature 24 h. The solution was next evaporated to dryness and the solid residue was purified by flash chromatography on silica gel, eluting with a ethyl acetate/hexane, 9:1 (R_f = 0.80). White solid, 897 mg, 95% yield, mp 109–110.5 °C; $[\alpha]_D^{20} = -24.8$ (c 0.5, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$): δ = 0.92–1.02 (m, 1H, H-5″b), 1.28–1.35 (m, 3H, H-6″b, H-4″b, H-3″b), 1.60–1.86 (m, 3H, H-5″a, H-4″a, H-3″a), 1.97, 1.99, 2.00, 2.00, 2.02, 2.08, 2.09 (7s, 21H, $7CH_3$, Ac), 2.14–2.22 (m, 2H, H-1″, H-6″a), 3.48–3.58 (m, 1H, H-2″), 3.64 (ddd, 1H, $J_{5',4'}$ = 9.6, $J_{5'6'a}$ = 4.4, $J_{5',6'b}$ = 2.4, H-5′), 3.74 (ddd, 1H, $J_{5,4}$ = 9.2, $J_{5,6a}$ = 1.8,

$J_{5,6b}$ = 4.8, H-5, $J_{6'b,5'}$), 3.80 (t, 1H, $J_{4,3}$ = 9.3, $J_{4,5}$ = 9.2, H-4), 4.05 (dd, 1H, $J_{6'b,6'a}$ = 12.0, $J_{6'b,5'}$ = 2.4, H-6′b), 4.19 (dd, 1H, $J_{6b,6a}$ = 12.0, $J_{6b,5}$ = 4.8, H-6b), 4.37 (dd, 1H, $J_{6'a,6'b}$ = 12.0, $J_{6'a,5'}$ = 4.4, H-6′a), 4.45 (dd, 1H, $J_{6a,6b}$ = 12.0, $J_{6a,5}$ = 1.8, H-6a), 4.53 (d, 1H, $J_{1',2'}$ = 7.9, H-1'), 4.69 (d, 1H, $J_{NH,2''}$ = 8.0, NH), 4.82 (t, 1H, $J_{2,1}$ = 9.3, $J_{2,3}$ = 9.3, H-2), 4.94 (dd, 1H, $J_{2',3'}$ = 9.3, $J_{2',1'}$ = 7.9, H-2′), 4.99 (d,1H, $J_{NH,1}$ = 9.3, NH), 5.09 (t, 1H, $J_{4',3'}$ = 9.6, $J_{4',5'}$ = 9.6, H-4'), 5.16 (t, 1H, $J_{3',2'}$ = 9.3, $J_{3',4'}$ = 9.6, H-3′,), 5.19 (t, 1H, $J_{1,NH}$ = 9.3, $J_{1,2}$ = 9.3, H-1), 5.29 (t, 1H, $J_{3,2}$ = 9.3, $J_{3,4}$ = 9.3, H-3), 7.31–7.46 (m, 10H, $2C_6H_5$). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.5, 20.6, 20.8, 20.9 (CH_3, Ac), 24.4 (C-3″), 25.4 (C-4″), 27.3 (C-5″), 34.2 (C-6″), 41.1 (d, J_{C-P} = 11.8, C-1″), 51.1 (d, J_{C-P} = 16.5, C-2″), 61.6 (C-6′), 62.1 (C-6), 67.9 (C-4), 71.0 (C-2), 71.6 (C-2′), 72.0 (C-5′), 72.6 (C-3), 73.0 (C-3′), 74.3 (C-5), 76.3 (C-4), 80.1 (C-1), 100.6 (C-1'), 128.1, 128.2, 128.3, 128.5, 128.6, 129.00 (C_6H_5), 132.4 (d, J = 17.6, C_6H_5), 134.5 (d, J = 20.5, C_6H_5), 135.2 (d, J = 17.0, C_6H_5), 136.9 (d, J = 13.0, C_6H_5), 155.1 (CO, Urea), 169.0, 169.3, 169.4, 170.2, 170.3, 170.5, 171.3 (CO, Ac). $C_{45}H_{57}N_2O_{18}P$ (944.91): calcd C 57.20, H 6.08, N 2.96; found C 57.14, H 6.09, N 2.98.

4.4. Synthesis of 1,3,4,6-tetra-*O*-trimethylsilyl-2-deoxy-2-{[2-(diphenylphosphino)benzoyl]imino}-α-D-glucopyranose L4

In a Schlenk tube under nitrogen, 2-amino-2-deoxy-1,3,3,6-tetra-*O*-trimethylsilyl-α-D-glucopyranose[7] (1 g, 2.1 mmol) and 2-(diphenylphosphino)benzaldehyde (621 mg, 2.1 mmol) were stirred in toluene (40 mL) at 60 °C for 12 h. After concentration, the residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/hexane, 5:1 (R_f = 0.82). Yellow oil, 1.2 g, 77% yield, $[\alpha]_D^{20} = +41.6$ (c 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.10, 0.18, 0.25, 0.31 (4s, 36H, 4OSi(CH_3)$_3$), 3.25 (dd, 1H, J = 9.4, 3.2, H-2), 3.71 (dd, 1H, J = 9.6, 8.6, H-4), 3.84–3.90 (m, 2H, H-6, H-6′), 3.99 (ddd, 1H, J = 9.6, 3.7, 2.8, H-5), 4.41 (dd, 1H, J = 9.4, 8.6, H-3), 4.80 (d, 1H, J = 3.2, H-1), 7.35–7.52 (m, 13H, C_6H_5), 8.34–8.36 (m, 1H, C_6H_5), 9.19 (d, 1H, J = 6.1, NC*H*). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.0, 0.2, 1.1, 1.5 (4OSi(CH_3)$_3$), 62.5 (C-6), 72.5, 72.8 (C-4, C-5), 74.6 (C-2), 77.0 (C-3), 95.4 (C-1), 127.3 (d, J = 4.4, C_6H_5), 128.4, 128.7, 128.8, 129.0, 129.1, 130.6, 133,7, 133.9, 134.0, 134.1, 134.2, 134.3, (C_6H_5), 136.2 (d, J = 5,6, C_6H_5), 136.7 (d, J = 9.9, C_6H_5), 138.0 (d, J = 18.8, C_6H_5), 139.7 (d, J = 17.8, C_6H_5), 161.1 (d, J = 27.5, NCH). $C_{37}H_{58}NO_5PSi_4$ (740.18): calcd C 60.04, H 7.90, N 1.89; found C 60.01, H 7.86, N 1.96.

4.5. General procedure for the Pd^0-catalysed reaction

The catalytic system was prepared by stirring $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol) and dppb (23.5 mg, 0.055 mmol) or the chiral ligand (0.055 mmol or 0.11 mmol) in THF (3 mL) for 0.5 h. This solution was then added under argon to a Schlenk tube containing the allylic carbonate **1a**–**h** (1 mmol) dissolved in anhydrous THF (3 mL). The solution was stirred at 25 °C (or 55 °C). After being stirred for the indicated time, the solvent was evaporated, and the residue was purified by column chromatography on silica gel.

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