Substituted Pyridylamide Ligands in Microwave-Accelerated Mo(0)-Catalysed Allylic Alkylations

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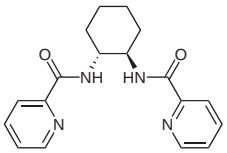
Abstract: Novel 4- and 6-substituted bis-pyridylamides were prepared by microwave accelerated nucleophilic substitution of the 4- and 6-halo substituted derivatives of the parent ligand **1a**. The ligands were used in the asymmetric allylation of cinnamyl carbonate catalysed by Mo(0) in which the 4-chloro- and 4-pyrrolidyl substituted ligand derivatives exhibited high regioselectivity (74:1 and 88:1, respectively) and enantioselectivity (96% ee), whereas 6-substituted ligands afforded no product under the same conditions. Other allylic substrates were used to explore the generality of the procedure.

Key words: molybdenum, allylations, asymmetric catalysis, pyridylamides, microwaves

Allylic alkylations catalysed by Mo(0) complexes have become of great interest since they afford selectively the more substituted product when non-symmetrical allylic substrates are used, as opposed to most Pd(0)-catalysed allylations.[1] After Trost's findings that pyridylamide **1a** (Figure 1) served as an efficient ligand in asymmetric allylations catalysed by Mo(0),[2] a number of other ligands have been developed including bis(dihydrooxazoles),[3] bipyridines[4] and C_1-symmetric pyridylamides.[5]

As part of our work on microwave accelerated highly selective transition metal catalysed reactions,[6] we explored the allylation catalysed by Mo(0) and developed a convenient and robust reaction procedure for the microwave accelerated reaction of cinnamyl carbonate with sodium dimethyl malonate using $Mo(CO)_6$, ligand **1a** and *N*,*O*-bis(trimethylsilyl)acetamide (BSA) under air, that afforded the product with high regio- and enantioselectivity.[7] Due to our interest in pyridylamides,[8] we decided to prepare derivatives of **1a** and study the influence of subtituents in the pyridine rings on the outcome of the catalytic reaction.[9] Our results showed that electronic effects were important. Thus, an electron-withdrawing subtituent (4-nitro) in the pyridine rings resulted in a less selective catalyst. On the other hand, a higher regio- and enantioselectivity was obtained by using a ligand with an electron-donating group (4-methoxy) in the pyridine rings. Steric effects were also important and a ligand with a methyl group in the 6 position of the pyridine rings afforded a catalyst exhibiting poor activity and selectivity.



1a

Figure 1 The structure of the bis-pyridylamide **1a**

We wanted to study the generality of our findings and explore whether a more selective catalyst could be prepared by further modification of the electronic properties of the pyridine nitrogen atoms of the ligand. Moreover, since this kind of ligands can be used in other asymmetric catalysed processes[10] we wanted to develop a facile synthesis for derivatives of **1a**.

The strategy that we previously employed for the synthesis of the different bis(pyridylamide) ligands was based either on the reaction of the corresponding substituted pyridine-2-carboxylic acid with a coupling reagent or, alternatively, on making the acid chloride to activate the carboxylic function, followed by condensation with the chiral diamine. This route requires first the preparation of the substituted pyridine-2-carboxylic acid, which is accessible from a multistep synthesis and a tedious workup procedure for the isolation of the amphoteric picolinic acid derivative. Since the ability of α- and γ-halopyridines to undergo nucleophilic substitution is well known,[11] we thought that the corresponding 4- or 6-halosubstituted ligand derivatives would constitute versatile building blocks giving access to a series of other substituted ligands by direct nucleophilic substitution. Thus, we prepared **1b** by treating 4-chloropyridine-2-carboxylic acid as its sulfuric/hydrobromic acid salt with *N*,*N*′-carbonyldiimidazole (CDI)[12] in THF at 50 °C in the presence of K_2CO_3 and then adding the diamine at once to give the ligand derivative. The analogue **1c** was prepared in a similar fashion but using commercially available 6-bromopyridine-2-carboxylic acid (Scheme 1).

Then, direct nucleophilic substitution was accomplished in a few minutes by heating the substrate **1b** or **1c** with the appropriate nucleophile in a microwave cavity to afford the corresponding derivatives in essentially quantitative isolated yield after workup and removal of the volatiles under vacuum (Scheme 2).

We also synthesised the ligand **1f** with 3-hydroxy substituted pyridine rings, to explore the effect of substituents in

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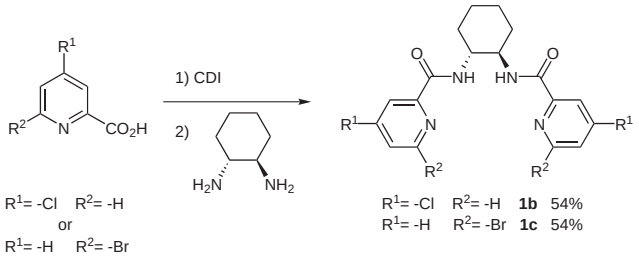
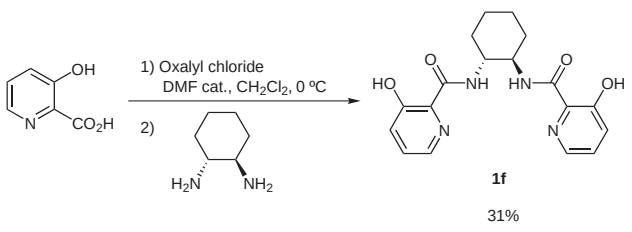


Scheme 1



Scheme 3

other positions, from commercially available 3-hydroxypyridine-2-carboxylic acid by preparation of the acid chloride using oxalyl chloride and its subsequent reaction with (1*R*,2*R*)-1,2-diaminocyclohexane (Scheme 3). We attempted to make the 3-methoxy substituted derivative by methylation of **1f**, but to our surprise no product could be obtained using different methods and conditions.

With these new ligands in hand, we performed the microwave accelerated Mo(0)-catalysed allylation of 3-phenylprop-2-enyl carbonate (**2a**) using sodium dimethyl malonate as the nucleophile (Table 1). As previously observed, when a ligand containing electron-donating substitutents in the 4-position of the pyridine rings was used, a catalyst exhibiting higher regioselectivity was produced. Thus, ligands **1b** and **1d** afforded the product with an excellent branched to linear ratio (74:1 and 88:1, respectively) although the enantioselectivity was slightly lower than for the parent ligand. It can also be noted that the ligand **1d** afforded a catalyst with lower activity, all starting material being consumed only after 12 minutes of reaction at 170 °C. On the other hand, when ligands **1c**, **1e** and **1f** were used, no reaction occurred. We have already shown,[9] that a ligand bearing a methyl group in the 6 position of the pyridine rings afforded a less reactive and less selective catalyst, and it can thus be concluded that ligands with 6-substituted pyridine rings give rise to catalysts with low activity. Whether this is due to steric or electronic factors is not clear. In the case of **1f**, the introduction of an additional donor atom in the ligand might result in an inactive catalyst. Representative examples of temperature profile of the microwave accelerated alkylations (Figure 2) favour a temperature of 160–170 °C for the reaction, which is then generally used.

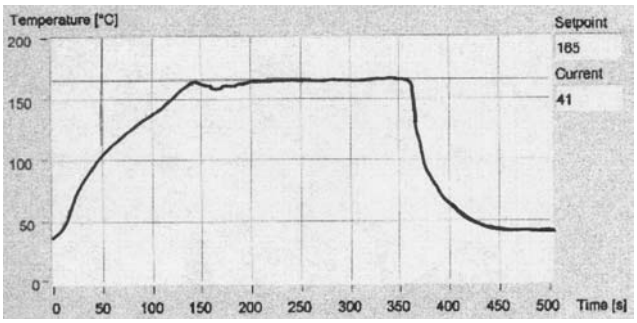
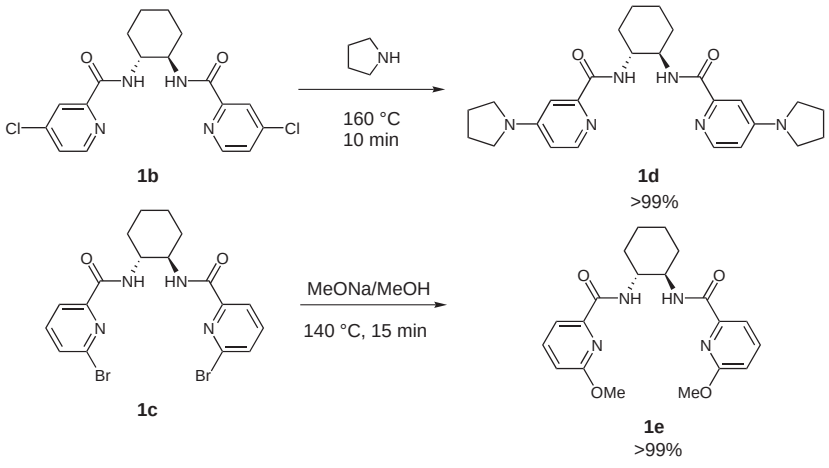


Figure 2 Representative examples of temperature profile of the microwave accelerated alkylations.

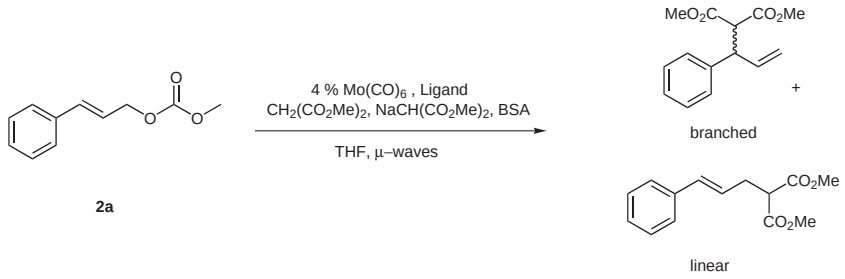
Having found easily available **1b** as a highly regioselective ligand for the allylation of 3-phenylprop-2-enyl carbonate using sodium dimethyl malonate as nucleophile, we decided to explore the reaction of other allylic carbonates.

First we studied the reaction of 4-substituted cinnamyl substrates **2a**–**d** (Table 2). Again, we found that the ligand **1b** afforded the corresponding branched product with higher regioselectivity than **1a**. It can also be noted that the substituents on the phenyl ring in the substrate have an



Scheme 2

Table 1 Allylation of **2a** Using Ligands **1a–f**

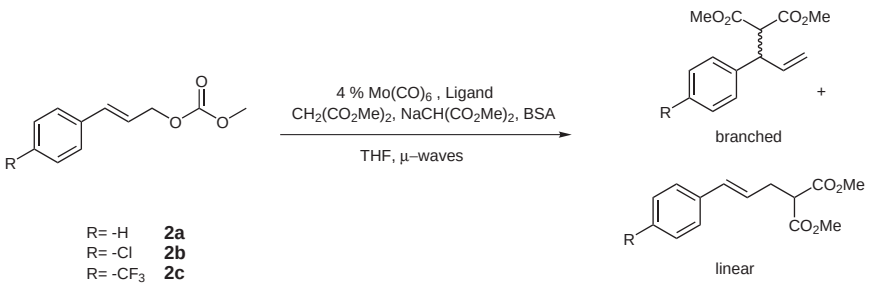


2a

Ligand	Temp (°C)	Time (min)	Yield (%)[a]	Regioselectiviy[b]	ee (%)[c]
1a	160	6	80	19:1	98
1b	165	6	89	74:1	96
1c	160	6	0	–	–
1d	170	12	91	88:1	96
1e	160	6	0	–	–
1f	160	6	0	–	–

[a] Isolated yield.
[b] Determined by GC-MS.
[c] Determined by chiral HPLC using a Daicel OD-H (0.46 cm Ø × 25 cm) column.

Table 2 Allylation of **2a–d** Using Ligands **1a** and **1b**



R= -H **2a**
R= -Cl **2b**
R= -CF_3 **2c**
R= -OMe **2d**

R	Ligand	Temp (°C)	Time (min)	Yield (%)[a]	Regioselectivity[b]	ee (%)[c]
H	**1a**	160	5	80	19:1	98
H	**1b**	165	6	89	74:1	96
Cl	**1a**	165	6	51	32:1	96
Cl	**1b**	165	6	86	47:1	90
CF_3	**1a**	165	6	50	11:1	99
CF_3	**1b**	165	6	66	22:1	96
MeO	**1°**	165	6	59	51:1	98
MeO	**1b**	165	6	79	57:1	94

[a] Isolated yield.
[b] Determined by GC-MS.
[c] Determined by chiral HPLC using a Daicel OD-H (0.46 cm ∅ × 25 cm) column.

effect on the selectivity of the nucleophilic attack. Thus, an electron-donating group in the phenyl ring afforded the product with a higher branched to linear ratio whereas the opposite was found for an electron-withdrawing group. As seen before for the model substrate **2a**, the enantioselectivity of the product obtained when using ligand **1b** was slightly lower than when using the parent ligand.

We also compared ligands **1a** and **1b** using different racemic 4-phenyl substituted methyl carbonate derivatives of 1-arylprop-2-en-1-ols **3a–c** (Table 3). Unfortunately, we were not able to include the 4-methoxy substituted derivative in this reaction series due to its thermal instability. The results show once more that **1b** affords the corresponding branched product with higher regioselectivity than **1a**. Furthermore, in analogy to what has been shown previously,[2a] the ratio between branched and linear products obtained for substrates **2a–d** differs slightly when using the isomeric carbonates **3a–c** as substrates in the reaction. Enantioselectivities using ligand **1b** for substrates **3a–c** were moderate to good, varying from 74 to 90% ee depending on the substrate. It has recently been shown[13] that a kinetic resolution takes place when using this kind of substrates. In THF, a significant memory effect is operating with the slowly reacting enantiomer providing the product with lower ee than the fast reacting enantiomer. This results in lower product ee when the reactions are run to completion.

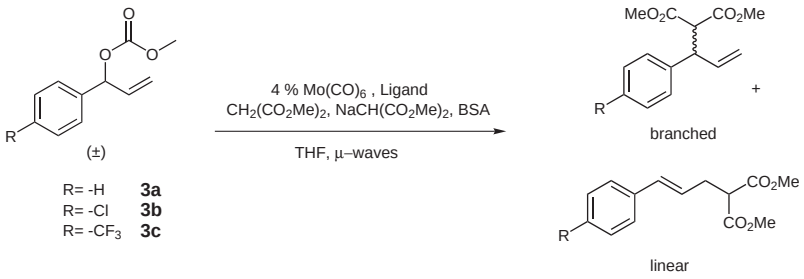
In summary, we have developed a simple route towards 4- and 6-substituted pyridylamide ligands. The ligands were used in the microwave accelerated allylation of cinnamyl carbonates catalysed by Mo(0) in which the 4-chloro and 4-pyrrolidyl substituted ligands afforded the products with considerably higher regioselectivity than the parent ligand and with 96% ee. Furthermore, when using other allylic carbonates in the reaction, the catalyst derived from the 4-chloro substituted ligand yielded the product with higher regioselectivity than the catalyst derived from the parent ligand, which is of interest for synthetic purposes.

Allylic carbonates **2a–d** and **3a–c** were prepared according to previously published procedures.[14] THF was distilled over Na/benzophenone and CH_2Cl_2 over CaH_2. The microwave heating was performed with a Smith Creator™ single mode cavity from Personal Chemistry AB, Uppsala, Sweden. Unless otherwise noted, all ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 500 and 125.7 MHz, respectively. Chemical shifts are reported in ppm relative to the solvent as internal standard.

4-Chloropyridine-2-carboxylic Acid Mixed Salt

Into a flame dried 250 mL flask a mixture of pyridine-2-carboxylic acid (10 g, 0.08 mol) and anhyd NaBr[15] (17 g, 0.16 mol) was refluxed in $SOCl_2$ (50 mL) for 22 h. The initially dark green mixture changed to a dark red colour. Excess $SOCl_2$ was removed by rotatory evaporation and the residue was dissolved in CH_2Cl_2 (200 mL) and filtered through Celite to remove any insoluble material. The resulting red solution was transferred into a three-necked 1 L flask equipped with a thermometer, a mechanical stirrer and an addition funnel. The solution was cooled to –5 °C and H_2O (200 mL) was added dropwise while stirring vigorously, keeping the temperature between –5 and 2 °C. The solution changed to orange in colour with formation of a white precipitate. The mixture was further stirred at r.t. for 25 h and then concentrated under rotatory evaporation. Complete removal of H_2O was achieved by successively adding toluene to the wet solid and evaporating under reduced pressure. The solid was recrystallised from a minimum amount of EtOH to give 9.6 g

Table 3 Allylation of **3a–c** Using Ligands **1a** and **1b**



R	Ligand	Temp (°C)	Time (min)	Yield (%)[a]	Regioselectivity	ee (%)[c]
H	**1a**	165	6	76	13:1	96
H	**1b**	165	6	89	69:1	86
Cl	**1a**	165	6	78	26:1	96
Cl	**1b**	165	6	70	34:1	74
CF_3	**1a**	165	6	48	10:1	98
CF_3	**1b**	165	6	52	20:1	90

[a] Isolated yield.
[b] Determined by GC-MS.
[c] Determined by chiral HPLC using a Daicel OD-H (0.46 cm ∅ × 25 cm) column.

(48%) of a yellow product consisting of a 0.57:0.43 mixture of the sulphuric and hydrobromic acid salts (according to elemental analysis).

^{1}H NMR (DMSO-d_6): δ = 12.17 (2 H, br s), 8.70 (1 H, d, *J* = 4.9 Hz), 8.08 (1 H, d, *J* = 1.6 Hz), 7.83 (1 H, dd, *J* = 4.9, 1.6 Hz).

^{13}C NMR (DMSO-d_6): δ = 165.8, 151.6, 150.7, 145.3, 128.0, 125.7.

Anal. Calcd for $C_6H_{5.57}Br_{0.43}ClNO_{4.28}S_{0.57}$: C, 29.02; H, 2.24; Br, 13.84; Cl, 14.28; N, 5.64; O, 27.58; S, 7.35. Found: C, 28.59; H, 2.16; Br, 13.92; Cl, 14.50; N, 5.52; O, 27.18; S, 7.06.

(1*R*,2*R*)-1,2-Bis[(4-chloropyridine)-2-carboxyamido]cyclohexane (1b)

A suspension of 4-chloropyridine-2-carboxylic acid mixed salt (1.0 g, 4.03 mmol), 1,1′-carbonyldiimidazol (649 mg, 4.0 mmol) and K_2CO_3 (553 mg, 4.0 mmol) in THF (5 mL) was heated at 50 °C under N_2 for 1 h. Then (1*R*,2*R*)-1,2-diaminocyclohexane (223 mg, 1.96 mmol) was added at once and the reaction mixture was stirred at 50 °C for a further 1 h. H_2O (20 mL) was added to the cold mixture and the resulting suspension was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried (Na_2SO_4) and the solvent evaporated. The crude product was purified by column chromatography on silica gel (eluent: 20% EtOAc–hexanes) to yield 408 mg (54%) of the pure product; $[\alpha]_D^{20}$ –12.1 (*c* = 0.24, $CHCl_3$).

^{1}H NMR: δ = 8.43 (1 H, d, *J* = 5.9 Hz), 8.17 (1 H, br s), 8.07 (1 H, d, *J* = 1.8 Hz), 7.37 (1 H, dd, *J* = 5.9, 1.8 Hz), 4.06 (1 H, br s), 2.20 (1 H, br s), 1.86 (1 H, br s), 1.47 (2 H, br s).

^{13}C NMR: δ = 163.8, 151.6, 149.5, 146.0, 126.5, 123.1, 53.9, 32.9, 25.2.

Anal. Calcd for $C_{18}H_{18}Cl_2N_4O_2$: C, 54.97; H, 4.61; N, 14.25. Found: C, 54.85; H, 4.77; N, 14.16.

(1*R*,2*R*)-1,2-Bis[(6-bromopyridine)-2-carboxyamido]cyclohexane (1c)

A suspension of 6-bromopyridine-2-carboxylic acid (200 mg, 1 mmol) and 1,1′-carbonyldiimidazol (195 mg, 1.2 mmol) in THF (1 mL) was heated at 50 °C under N_2 for 1 h. Then (1*R*,2*R*)-1,2-diaminocyclohexane (57 mg, 0.5 mmol) was added at once and the reaction mixture was stirred at 50 °C as described for **1b**. The crude product was recrystallized from EtOH to yield 130 mg (54%) of the pure product as white needles; $[\alpha]_D^{20}$ –193.8 (*c* = 1.1, $CHCl_3$).

^{1}H NMR: δ= 8.07 (1 H, d, *J* = 7.3 Hz), 8.02 (1 H, d, *J* = 6.1 Hz), 7.61 (1 H, dd, *J* = 7.3 Hz), 7.52 (1 H, d, *J* = 7.3 Hz), 4.02 (1 H, br s), 2.20 (1 H, br d, *J* = 11.0 Hz), 1.83 (1 H, br s), 1.46 (2 H, br s).

^{13}C NMR: δ = 163.6, 151.3, 140.6, 139.8, 131.0, 121.7, 54.1, 32.8, 25.2.

Anal. Calcd for $C_{18}H_{18}Br_2N_4O_2$: C, 44.84; H, 3.76; N, 11.62. Found: C, 44.71; H, 3.82; N, 11.59.

(1*R*-2*R*)-1,2-Bis[(4-*N*-pyrrolidylpyridine)-2-carboxyamido]cyclohexane (1d)

A solution of **1b** (100 mg, 0.25 mmol) in pyrrolidine (2.5 mL) was heated in the microwave cavity at 160 °C for 10 min. The reaction mixture was concentrated under vacuum and the residue was dissolved in $CHCl_3$ (5 mL). The organic solution was washed with aq 20% K_2CO_3 solution (2 × 5 mL) and dried (Na_2SO_4). Evaporation of the solvent afforded a yellowish solid. Further evaporation of pyrrolidine in a desiccator under vacuum afforded the pure product; yield: 116 mg (>99%); $[\alpha]_D^{20}$ +70.1 (*c* = 0.16, $CHCl_3$).

^{1}H NMR: δ = 8.24 (1 H, br d, *J* = 6.1 Hz), 8.07 (1 H, d, *J* = 6.1 Hz), 7.21 (1 H, d, *J* = 2.4 Hz), 6.32 (1 H, dd, *J* = 6.1, 2.4 Hz), 4.00 (1 H, br s), 3.29 (4 H, br s), 2.19 (1 H, br s), 1.98 (4 H, br s), 1.79 (1 H, br s), 1.43 (2 H, br s).

^{13}C NMR: δ= 165.9, 152.9, 150.3, 148.5, 108.6, 106.0, 53.4, 47.6, 33.1, 25.7, 25.2.

(1*R*,2*R*)-1,2-Bis[(6-methoxypyridine)-2-carboxyamido]cyclohexane (1e)

A suspension of **1c** (50 mg, 0.1 mmol) and solid MeONa (54 mg, 1.0 mmol) in MeOH (2 mL) was heated in the microwave cavity at 140 °C for 15 min. H_2O (4 mL) was added to the resulting solution and the turbid mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were dried (Na_2SO_4) and the solvent evaporated to afford 38 mg (>99%) of the pure product; $[\alpha]_D^{20}$ –101.3 (*c* = 1.07, $CHCl_3$).

^{1}H NMR: δ = 8.12 (1 H, br d, *J* = 6.1 Hz), 7.62 (2 H, m), 6.80 (1 H, d, *J* = 8.54 Hz), 4.01 (3 H, s), 4.00 (1 H, br s), 2.24 (1 H, br s), 1.82 (1 H, br s), 1.44 (2 H, br s).

^{13}C NMR: δ = 165.1, 163.2, 147.5, 139.8, 115.7, 114.6, 54.1, 54.0, 32.9, 25.2.

Anal. Calcd for $C_{20}H_{24}N_4O_4$: C, 62,49; H, 6,29; N, 14,57. Found: C, 62,28; H, 6,39; N, 14,45.

(1*R*,2*R*)-1,2-Bis[(3-hydroxypyridine)-2-carboxyamido]cyclohexane (1f)

Oxalyl chloride (0.5 mL, 5.9 mmol) was added to a suspension of 3-hydroxypyridine-2-carboxylic acid (0.72 g, 5.2 mmol) and a catalytic amount of DMF in anhyd CH_2Cl_2 (5 mL) at 0 °C. The resulting suspension was stirred at 0 °C for 1 h. The mixture was concentrated under vacuum to give an almost colourless solid that was immediately suspended in anhyd CH_2Cl_2 (5 mL). To the resulting suspension, a solution of (1*R*,2*R*)-1,2-diaminocyclohexane (294 mg, 2.6 mmol) and ethyldiisopropylamine (2.7 mL, 15.6 mmol) in CH_2Cl_2 (5 mL) was added at 0 °C and the mixture was stirred for 14 h. Evaporation of the solvent afforded the crude product. Purification by liquid chromatography on silica gel (eluent: hexanes–EtOAc, 5:1) yielded 284 mg (31%) of the pure product; $[\alpha]_D^{20}$ –91.4 (*c* = 0.14, $CHCl_3$).

^{1}H NMR: δ = 12.06 (1 H, s), 8.33 (1 H, br s), 8.09 (1 H, d, *J* = 4.9 Hz), 7.33 (1 H, dd, *J* = 8.5, 4.9 Hz), 7.26 (1 H, d, *J* = 8.5 Hz), 4.06 (1 H, br s), 2.27 (1 H, br s), 1.92 (1 H, br s), 1.52 (2 H, br s).

^{13}C NMR: δ = 169.5, 158.1, 140.0, 131.6, 129.0, 126.3, 53.5, 32.7, 25.1.

Microwave-Assisted Allylic Alkylations; General Procedure

Two different stock solutions were prepared: *Solution-N*, containing the nucleophile, sodium dimethyl malonate in THF, was made by adding dimethyl malonate (880 μL, 7.7 mmol) to a suspension of 60% NaH in mineral oil (27 mg, 0.68 mmol) in THF (10 mL). *Solution-S*, containing the corresponding allylic substrate, was prepared by dissolving the allylic carbonate **2** or **3** (7.1 mmol) in THF (10 mL). The appropriate ligand **1** (0.034 mmol) and $Mo(CO)_6$ (6.9 mg, 0.026 mmol) were transferred to a SmithProcess Vial™. *Solution-N* (1 mL, 0.77 mmol of the nucleophile), *Solution-S* (1 mL, 0.71 mmol of the substrate) and BSA (208 μL) were added in this order and the sample was microwave heated to the appropriate temperature for the indicated time. Directly after reaction, the reaction mixture (dark coloured) was diluted with Et_2O to a total volume of 10 mL (a precipitate appeared). The yellow-orange solution was filtered and analysed by GC-MS. Purification of the crude product was achieved by column chromatography on silica gel (eluent: EtOAc–hexanes). The structures of all products were confirmed by comparison with published spectroscopic data[14,16] and GC-MS analyses.

Acknowledgements

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