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Palladium-catalysed aminocarbonylation of iodoarenes and iodoalkenes with aminophosphonate as *N*-nucleophile

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ABSTRACT

The high-yielding synthesis of novel *N*-acyl phosphonates with unprecedented structure was carried out by a homogeneous carbonylation reaction under mild reaction conditions. The palladium-catalysed aminocarbonylation of iodoalkenes (1-iodo-cyclohexene, 1-iodo-4-*tert*-butyl-cyclohexene, 1-iodo-2-methyl-cyclohexene and α-iodostyrene) with diethyl α-aminobenzyl-phosphonate as *N*-nucleophile resulted in the exclusive formation of carboxamides. The same reaction with iodoaromatics (iodobenzene, 2-iodothiophene) provided the corresponding carboxamide in high yields and some 2-keto-carboxamides as side products due to single and double carbon monoxide insertion, respectively.

1. Introduction

Alkyl/aryl phosphonates have a wide application in organic and bioorganic chemistry. Due to their biological activity, they are used as bioregulators, herbicides and antimalarial agents.[1] Phosphonate derivatives have gained an important role even in catalysis. Their catalytic application can be divided into two major groups: (i) immobilised silica catalysts are modified by various transition metal phosphonates and (ii) transition metal complexes, used as homogeneous catalysts, contain phosphorus ligands bearing a phosphonate moiety.

As for the heterogeneous catalytic application, a range of heterogeneous metal alkyl phosphonate modified silica catalysts have been developed for oxidations. Vanadyl and cobalt(II) alkyl phosphonate modified silicas were used for the oxidation of sulfides[2] and allylic alcohols.[3,4] Cerium(IV) alkyl phosphonate modified silica proved to be an efficient catalyst for the oxidation of alcohols to ketones or carboxylic acids.[5] Zirconium phosphonate films containing manganese(III) porphyrines are efficient catalysts towards the epoxidation of cyclooctene.[6] Titanium phosphonates supported on palladium[7] and immobilised titanium phosphonates[8] are used as catalysts for the hydrogenation of acetophenone and for the enantioselective addition of diethylzinc to benzaldehyde, respectively. A further interesting application of alkyl phosphonates is the formation of coatings on magnetic nanoparticles.[9]

On the other hand, the coordination chemistry of phosphonated phosphanes (primarily triphenylphosphine derivatives) with palladium(II) and platinum(II) was investigated in detail.[10] These highly water soluble ligands were exploited in rhodium-catalysed hydroformylation[11,12] and in carbonylation of benzyl chloride towards phenylacetic acid.[13] The heterobidentate (hemilabile) phosphonate–phosphane ligands were used successfully in methanol carbonylation.[14,15] Bulky triphenylphosphines possessing the $PO(OEt)_2$ moiety were used as ligands in platinum-catalysed hydroformylation in the presence of tin(II) chloride.[16]

Alkyl phosphonates have been coupled to the *para* position of a pincer-ligand via Suzuki coupling.[17] It was proved that diphenyl methylphosphonate can be formed by reductive elimination from a Pd(II) intermediate possessing methyl and $P(O)(OPh)_2$ moieties.[18]

The replacement of a carboxylic group by an organophosphorus moiety allows the resulting compounds to be bound to enzymes that transfer substrates possessing a carboxylic functionality, and this way may act as 'false' substrates. Phosphonates, acting as farnesyltransferase inhibitors, are promising antimalarial agents.[19] Other type of inhibitors can be found among the phosphonates, e.g., β-carboxamido-phosphonates were found as potent inhibitors of glycerol phosphate dehydratase.[20] The potential biological importance of our target compounds also prompted us to investigate the possibility of their high-yielding synthesis.

The work presented here describes the functionalisation of aminoalkyl phosphonates on their amino functionality, in order to

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synthesise novel *N*-acyl phosphonates with unprecedented structure. From another point of view, palladium-catalysed aminocarbonylation of iodoaromatics and iodoalkenes was applied to the coupling of a phosphonate moiety to an aryl/alkenyl fragment.

2. Results and discussion

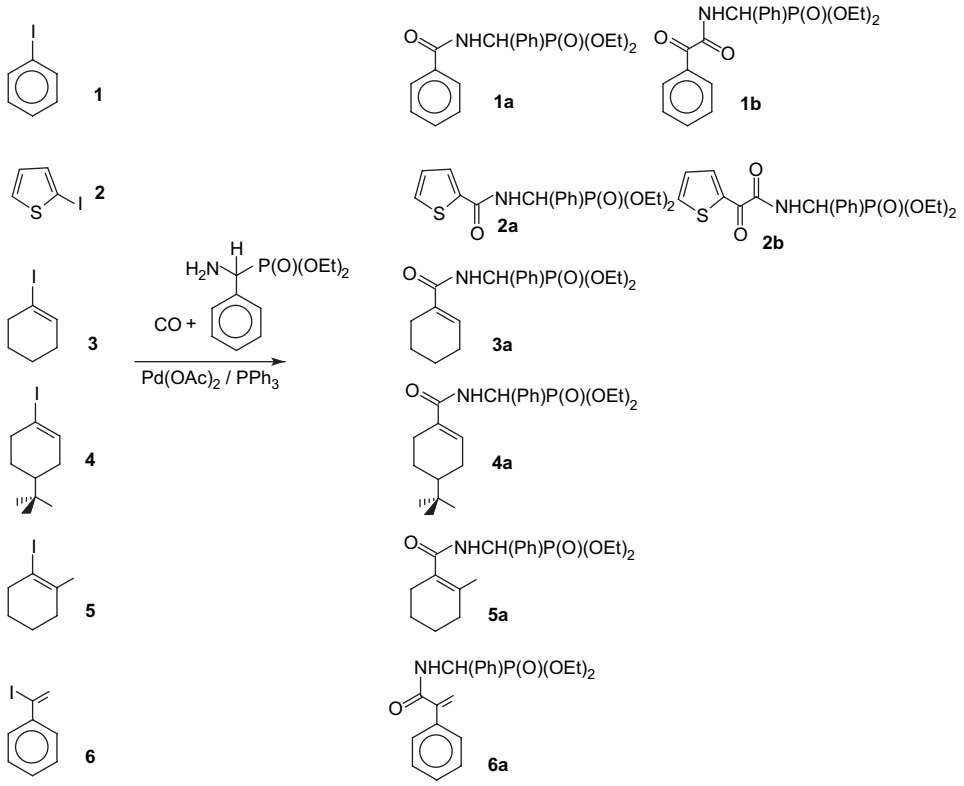
Iodoaromatics and iodoalkenes like iodobenzene (**1**), 2-iodothiophene (**2**), 1-iodo-cyclohexene (**3**), 4-*tert*-butyl-1-iodo-cyclohexene (**4**), 2-methyl-1-iodo-1-cyclohexene (**5**) and 1′-iodostyrene (**6**) were reacted with carbon monoxide and racemic diethyl α-aminobenzyl-phosphonate (Scheme 1). A widely applied palladium(0) catalyst formed in situ from palladium acetate and triphenylphosphine was used also in this case.[21] The corresponding carboxamides (**1a**–**6a**) were formed with high chemoselectivity and isolated in moderate to good yields. Ketocarboxamide formation, due to double carbon monoxide insertion, was observed only with iodoaromatics (iodobenzene (**1**) and iodothiophene (**2**)) as substrate resulting in **1b** and **2b** in traces (less than 5% in all cases) and in 14% yield, respectively. No ketocarboxamides were detected in case of the iodoalkenes (**3**–**6**).

It is known from previous studies that by the aminocarbonylation of iodoaromatics, carried out with simple amines or amines with ester functionality (amino acid esters), the ketocarboxamide formation is highly favoured.[22] Especially under increased carbon monoxide pressure, high selectivities towards double carbon monoxide insertion were observed. Surprisingly, the application of an *N*-nucleophile with a phosphonate functionality (diethyl α-aminobenzyl-phosphonate) resulted in low ketocarboxamide selectivity, which reflects the high influence of the phosphonate group bound to the α-carbon. This fact might be due to the coordination of the phosphonate group to the palladium(0) intermediates, modifying its structure favouring monocarbonylation. Furthermore, from mechanistic aspects (vide infra) it seems to be obvious that the lack of double carbon monoxide insertion is due to the difficulty in forming the corresponding carbamoyl ligand. The insertion of carbon monoxide into the palladium–N bond (i.e., into palladium—sterically highly bulky amido ligand) is unfavoured.

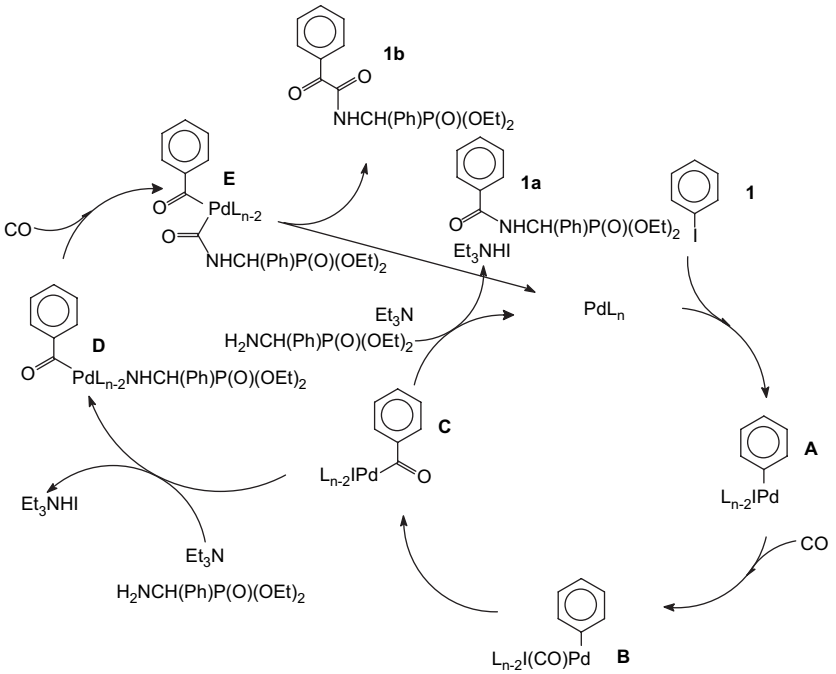
Even the effect of the carbon monoxide pressure on carboxamide (**1a**) yield shows an optimum. Practically no product formation can be detected either at low (less than 10 bar) or high (ca. higher than 55 bar) carbon monoxide pressure (entries 1–5). A similar phenomenon was already observed in the aminocarbonylation of iodoferrocene.[23]

The aminocarbonylation of **3**, **4** and **6** proceeds with excellent conversion and high isolated yields (entries 7, 8 and 10) at atmospheric carbon monoxide pressure. Much lower reactivity was observed with **5**, possessing a methyl group adjacent to the iodo substituents, under the same reaction conditions (entry 9).

The formation of the above products can be rationalised on the basis of the following simplified reaction mechanism (Scheme 2). The oxidative addition of the iodoaryl/iodoalkenyl bond of the substrate to palladium(0) complexes (PdL_n, where L stands for triphenylphosphine and solvent donor ligands), formed in situ from palladium(II)-acetate and triphenylphosphine, resulted in the corresponding palladium-aryl/alkenyl catalytic intermediate (**A**). It is followed by carbon monoxide activation yielding a complex with terminal carbonyl ligand (**B**) and its insertion into palladium-aryl/alkenyl bond results in the corresponding palladium-acyl complex (**C**). This catalytic intermediate could react further in two ways. (i) The aminolysis of **C** by primary or secondary amine affords the corresponding amide as major product. The elimination of the hydrogen iodide by triethylamine provides the 'starting' palladium(0) complex. (ii) The activation of the amine as an amido complex (**D**) is followed by carbon monoxide activation resulting as a carbonyl complex, which undergoes carbon monoxide insertion into the palladium-nitrogen bond resulting in a carbamoyl complex (**E**). The corresponding ketocarboxamides are formed from the latter intermediate by reductive elimination.



Scheme 1. Aminocarbonylation of iodoaromatics and iodoalkenes **1**–**6** with diethyl α-aminobenzyl-phosphonate.



Scheme 2. A simplified reaction mechanism for the aminocarbonylation with diethyl α-aminobenzyl-phosphonate as *N*-nucleophile.

3. Conclusions

The palladium-catalysed aminocarbonylation of various iodoaromatics and iodoalkenes towards the corresponding carboxamides was carried out in high isolated yields. This way, novel substituted phosphonates with *N*-acyl groups were obtained. The highly selective formation of carboxamides to ketocarboxamides can be explained by favoured single carbon monoxide insertion relative to double CO insertion. The reaction tolerates structural variation of the iodo-substrate. The high chemoselectivity and the easy work-up of the reaction mixtures make these reactions of synthetic importance.

4. Experimental

4.1. General procedures

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Inova 400 spectrometer at 400.13 MHz and 100.62 MHz, respectively. Chemical shifts δ are reported in parts per million relative to $CHCl_3$ (7.26 and 77.00 ppm for ^{1}H and ^{13}C, respectively). Elemental analyses were measured on a 1108 Carlo Erba apparatus. Samples of the catalytic reactions were analysed with a Hewlett Packard 5830A gas chromatograph fitted with a capillary column coated with OV-1.

Substrates **1** and **2**, as well as diethyl α-aminobenzyl-phosphonate were purchased from Aldrich and were used as obtained. Substrates **3**–**6** were synthesised in a three-step synthesis according to modified conventional synthetic procedures[22,24,25] by using the corresponding keto derivatives as starting materials.

4.2. Aminocarbonylation experiments carried out at normal pressure

In a typical experiment, a solution of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol), substrates (**3**–**6**) (0.5 mmol) and diethyl α-aminobenzyl-phosphonate (153.7 mg, 0.55 mmol) (see Table 1) was dissolved in 10 mL DMF under argon. Triethylamine (1.0 mL) was added to the homogeneous yellow solution and the atmosphere was changed to carbon monoxide. The colour changed to dark red. The reaction was conducted for 20 h at 50 °C. Some metallic palladium was formed at the end of the reaction, which was filtered. A sample of this solution was immediately analysed by GC–MS. The mixture was then concentrated and evaporated to dryness in vacuo. The residue was dissolved in chloroform (20 mL) and washed with water (20 mL). The organic phase was thoroughly washed twice with 5% HCl (20 mL), saturated $NaHCO_3$ (20 mL), brine (20 mL), dried over Na_2SO_4 and concentrated to a yellow waxy material or a thick oil. Chromatography (silica, EtOAc/$CHCl_3$ or EtOAc/CH_2Cl_2, for exact eluent composition see characterisation) yielded the desired carboxamides (**3a**–**6a**).

Table 1
Aminocarbonylation of iodoaromatics and iodoalkenes with diethyl α-aminobenzyl-phosphonate as amine nucleophile[a]

Entry	Substrate	Retention time [h]	*p*(CO) [bar]	Conversion [%]	Ratio of the carbonylated products,[b] (isolated yields) [%]	
					Carboxamide	Ketocarboxamide
1	**1**	20	10	0	—	—
2	**1**	20	20	55	96 (**1a**), (n.d.)	4 (**1b**)
3	**1**	40	20	60	98 (**1a**), (52)	2 (**1b**)
4	**1**	40	40	85	98 (**1a**), (72)	2 (**1b**)
5	**1**	24	60	3<	n.d.	n.d.
6	**2**	20	40	>98	86 (**2a**), (76)	14 (**2b**)
7	**3**	20	1	>98	100 (**3a**), (82)	0
8	**4**	20	1	>98	100 (**4a**), (80)	0
9	**5**	20	40	50	100 (**5a**), (43)	0
10	**6**	23	1	>98	100 (**6a**), (70)	0

[a] Reaction conditions: 0.025 mmol $Pd(OAc)_2$; 0.05 mmol PPh_3, 10 mL DMF; α-aminobenzyl-phosphonate/substrate=1.1/1; 1 mmol substrate: iodobenzene (**1**), 2-iodothiophene (**2**), 1-iodo-cyclohexene (**3**), 4-*tert*-butyl-1-iodo-cyclohexene (**4**), 2-methyl-1-iodo-1-cyclohexene (**5**), 1′-iodostyrene (**6**), reaction temperature: 50 °C.
[b] Determined by GC–MS.

4.3. Aminocarbonylation experiments carried out at high pressure

The DMF solution of the catalyst precursor and reactants (amounts given in Section 4.2) was transferred under argon into

a 100 mL stainless steel autoclave. The reaction vessel was pressurised to 10–60 bar total pressure with carbon monoxide and the magnetically stirred mixture was heated in an oil bath at 50 °C for 24 h. The work-up procedure is identical with that given above.

4.4. Characterisation of the products

*4.4.1. Diethyl N-benzoyl-α-aminobenzyl-phosphonate (**1a**)*

^{1}H NMR ($CDCl_3$) δ: 7.80–7.84 (m, 2H, Ph-*ortho*), 7.50–7.53 (m, 2H, Ph-*meta*), 7.40–7.43 (m, 1H, Ph-*para*), 7.25–7.36 (m, 5H, Ph), 5.76 (dd, 9.4, 21.2 Hz, 1H, C*H*), 4.02–4.15 (m, 2H, 2×(OCH_aH$_b$)), 3.88–3.97 (m, 1H, OCH$_a$$H_b$), 3.66–3.75 (m, 1H, OCH$_a$$H_b$), 1.25 (t, 7.0 Hz, 3H), 1.05 (t, 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 166.9, 135.3, 134.0, 131.6, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.4, 63.1 (^2J(P,C)=7.0 Hz), 63.3 (^2J(P,C)=7.0 Hz), 51.2 (^1J(P,C)=153.8 Hz), 16.4 (^3J(P,C)=5.9 Hz), 16.1 (^3J(P,C)=5.9 Hz). IR (KBr, (cm^{-1})): 1654 (CON), 1247 (P═O), 1025 (P–O). MS *m*/*z* (rel int. %): 347 (7), 210 (60), 105 (100), 77 (30). Analysis calculated for $C_{18}H_{22}NO_4P$ (347.35): C, 62.24; H, 6.38; N, 4.03. Found: C, 62.10; H, 6.55; N, 3.79. R_f (40% EtOAc/CH_2Cl_2) 0.42; off-white solid, mp 87–90 °C. Yield: 72%.

*4.4.2. Diethyl N-phenylglyoxyloyl-α-aminobenzyl-phosphonate (**1b**)*

MS *m*/*z* (rel int. %): 375 (3), 270 (10), 238 (32), 105 (100), 77 (35).

*4.4.3. Diethyl N-(2-thiophenyl-carbonyl)-α-aminobenzyl-phosphonate (**2a**)*

^{1}H NMR ($CDCl_3$) 7.65 (dd, 3.7, 1.0 Hz, 1H, Thioph), 7.34 (dd, 4.8, 1.0 Hz, 1H, Thioph), 7.20 (br s, 1H, NH), 7.05 (dd, 3.7, 4.8 Hz, 1H, Thioph), 5.66 (dd, 1H, 9.3, 21.2 Hz, C*H*), 4.08–4.20 (m, 2H, 2×(OCH_aH$_b$)), 3.95 (dq, 7.0, 12.0 Hz, OCH$_a$$H_b$), 3.73 (dq, 7.0, 12.0 Hz, OCH$_a$$H_b$), 1.30 (t, 7.0 Hz, 3H), 1.09 (t, 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 161.1, 138.2, 135.1, 133.1, 130.6, 63.4 (^2J(P,C)=6.9 Hz), 63.2 (^2J(P,C)=6.9 Hz), 50.6 (^1J(P,C)=154.4 Hz), 16.3 (^3J(P,C)=5.7 Hz), 16.1 (^3J(P,C)=5.7 Hz). IR (KBr, (cm^{-1})): 1649 (CON), 1228 (P═O), 1029 (P–O). MS *m*/*z* (rel int. %): 353 (2), 277 (6), 216 (43), 111 (100), 83 (5). Analysis calculated for $C_{16}H_{20}NO_4PS$ (353.37): C, 54.38; H, 5.70; N, 3.96. Found: C, 54.26; H, 5.57; N, 3.74. R_f (30% EtOAc/$CHCl_3$) 0.34; off-white solid, mp 122–125 °C. Yield: 76%.

*4.4.4. Diethyl N-(2-thiophenyl-glyoxyloyl)-α-aminobenzyl-phosphonate (**2b**)*

MS *m*/*z* (rel int. %): 381 (4), 265 (8), 244 (35), 132 (15), 111 (100), 91 (24).

*4.4.5. Diethyl N-(cyclohexen-1-yl-carbonyl)-α-aminobenzyl-phosphonate (**3a**)*

^{1}H NMR ($CDCl_3$) δ: 7.42 (d, 7.2 Hz, 2H, Ph-*ortho*), 7.22–7.33 (m, 3H, Ph), 6.78 (br s, 1H, NH), 6.62 (br s, 1H, ═CH), 5.55 (dd, 9.3, 21.0 Hz, 1H, C*H*), 4.02–4.15 (m, 2H, 2×(OCH_aH$_b$)), 3.86–3.95 (m, 1H, OCH$_a$$H_b$), 3.80 (m, 1H, OCH$_a$$H_b$), 2.25 (br s, 2H, CH_2), 2.12 (br s, 2H, CH_2), 1.55–1.65 (m, 4H, 2×CH_2), 1.25 (t, 7.0 Hz, 3H), 1.05 (t, 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 167.7, 135.4, 134.4, 132.9, 128.6, 128.0, 127.9, 63.3 (^2J(P,C)=6.9 Hz), 62.9 (^2J(P,C)=6.9 Hz), 49.1 (^1J(P,C)=152.7 Hz), 25.3, 24.2, 22.0, 21.4, 16.3 (^3J(P,C)=5.7 Hz), 16.1 (^3J(P,C)=5.7 Hz). IR (KBr, (cm^{-1})): 1658 (CON), 1632 (C═C), 1247 (P═O), 1027 (P–O). MS *m*/*z* (rel int. %): 351 (9), 242 (12), 214 (54), 109 (100), 81 (28). Analysis calculated for $C_{18}H_{26}NO_4P$ (351.38): C, 61.53; H, 7.46; N, 3.99. Found: C, 61.40; H, 7.41; N, 3.80. R_f (50% EtOAc/$CHCl_3$) 0.54; off-white solid, mp 92–95 °C. Yield: 82%.

*4.4.6. Diethyl N-(4-tert-butyl-cyclohexen-1-yl)-α-aminobenzyl-phosphonate (**4a**)*

^{1}H NMR ($CDCl_3$) δ: 7.40 (d, 7.2 Hz, 2H, Ph-*ortho*), 7.16–7.26 (m, 3H, Ph), 6.65 (br s, 1H, ═CH), 6.58 (br s, 1H, NH), 5.54 (dd, 9.4, 21.0 Hz, 1H, C*H*), 4.02–4.15 (m, 2H, 2×(OCH_aH$_b$)), 3.86–3.95 (m, 1H, OCH$_a$$H_b$), 3.65–3.73 (m, 1H, OCH$_a$$H_b$), 1.55–2.27 (m, 7H, CH+3×CH_2), 1.25 (t, 7.0 Hz, 3H), 1.06 (t, 7.0 Hz, 3H), 0.88 (s, 9H, ^{t}Bu). ^{13}C NMR ($CDCl_3$) δ: 167.7, 135.4, 134.4, 132.9, 128.6, 128.0, 127.9, 63.1 (^2J(P,C)=6.9 Hz), 62.9 (^2J(P,C)=6.9 Hz), 50.0 (^1J(P,C)=153.1 Hz), 43.3, 39.2, 32.0, 27.0, 25.7, 23.5, 16.3 (^3J(P,C)=5.4 Hz), 16.1 (^3J(P,C)=5.4 Hz). IR (KBr, (cm^{-1})): 1664 (CON), 1637 (C═C), 1245 (P═O), 1028 (P–O). MS *m*/*z* (rel int. %): 407 (7), 270 (53), 165 (100), 106 (16). Analysis calculated for $C_{22}H_{34}NO_4P$ (407.49): C, 64.85; H, 8.41; N, 3.44. Found: C, 64.72; H, 8.23; N, 3.28. R_f (40% EtOAc/$CHCl_3$) 0.61; yellow solid, mp 76–78 °C. Yield: 80%.

*4.4.7. Diethyl N-(2-methyl-cyclohexen-1-yl)-α-aminobenzyl-phosphonate (**5a**)*

^{1}H NMR ($CDCl_3$) δ: 7.42 (d, 7.2 Hz, 2H, Ph-*ortho*), 7.21–7.35 (m, 3H, Ph), 6.50 (br s, 1H, NH), 5.55 (dd, 9.6, 20.8 Hz, 1H, C*H*), 4.05–4.16 (m, 2H, 2×(OCH_aH$_b$)), 3.86–3.95 (m, 1H, OCH$_a$$H_b$), 3.65–3.73 (m, 1H, OCH$_a$$H_b$), 1.73 (s, 3H, ═$CCH_3$), 1.55–2.22 (m, 8H, 4×$CH_2$), 1.25 (t, 7.0 Hz, 3H), 1.06 (t, 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 170.8, 135.7, 135.2, 132.3, 128.6, 128.0, 127.9, 63.1 (^2J(P,C)=7.0 Hz), 62.9 (^2J(P,C)=7.0 Hz), 49.8 (^1J(P,C)=152.7 Hz), 31.4, 26.8, 25.5, 22.1, 20.8, 16.4 (^3J(P,C)=5.6 Hz), 16.1 (^3J(P,C)=5.6 Hz). IR (KBr, (cm^{-1})): 1651 (CON), 1237 (P═O), 1023 (P–O). MS *m*/*z* (rel int. %): 365 (10), 228 (23), 123 (100), 95 (21). Analysis calculated for $C_{19}H_{28}NO_4P$ (365.41): C, 62.45; H, 7.72; N, 3.83. Found: C, 62.32; H, 7.49; N, 3.61. R_f (50% EtOAc/CH_2Cl_2) 0.49; off-white solid, mp 79–83 °C. Yield: 43%.

*4.4.8. Diethyl N-(1-phenyl-ethen-1-yl-carbonyl)-α-aminobenzyl-phosphonate (**6a**)*

^{1}H NMR ($CDCl_3$) δ: 7.20–7.55 (m, 10H, 2×Ph), 6.80 (br s, 1H, NH), 6.05 (s, 1H, ═CH), 5.65 (s, 1H, ═CH), 5.60 (dd, 9.4, 20.6 Hz, 1H, C*H*), 4.00–4.15 (m, 2H, 2×(OCH_aH$_b$)), 3.88–3.96 (m, 1H, OCH$_a$$H_b$), 3.71–3.80 (m, 1H, OCH$_a$$H_b$), 1.26 (t, 7.0 Hz, 3H), 1.07 (t, 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 166.8, 144.3, 136.4, 136.2, 132.0, 131.9, 128.6, 128.5, 128.0, 127.9, 122.0, 63.1 (^2J(P,C)=6.9 Hz), 62.9 (^2J(P,C)=6.9 Hz), 50.4 (^1J(P,C)=152.7 Hz), 16.3 (^3J(P,C)=5.7 Hz), 16.1 (^3J(P,C)=5.7 Hz). MS *m*/*z* (rel int. %): 373 (4), 268 (33), 236 (60), 131 (31), 103 (100), 77 (25). Analysis calculated for $C_{20}H_{24}NO_4P$ (373.39): C, 64.34; H, 6.48; N, 3.75. Found: C, 64.22; H, 6.63; N, 3.48. R_f (30% EtOAc/$CHCl_3$) 0.38; highly viscous oil. Yield: 70%.

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