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Catalyst-free alcoholysis of phosphane-boranes: a smooth, cheap, and efficient deprotection procedure

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ABSTRACT

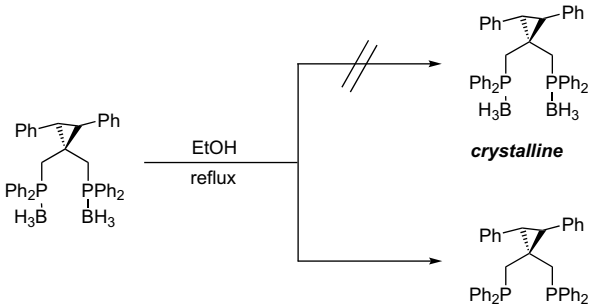
Catalyst-free alcoholytic deprotection of borane-protected phosphorus compounds offers a smooth, efficient, and clean alternative to existing deprotection methods. In this paper we report our results on the general applicability of deprotecting phosphane- and phosphite-borane adducts by means of simple alcoholysis without the use of molecular sieves as a catalyst. Phosphane-boranes bearing at least one aromatic substituent are readily deprotected in high yields. Borane complexes of trialkylphosphanes or phosphites, however, cannot be deprotected in this way. The main merit of our method is its simplicity: apart from evaporation of the solvent, no further work-up or purification is needed.

1. Introduction

The main drawback in handling most trivalent phosphorus compounds is their sensitivity toward oxygen and air. Although oxidation of these compounds can efficiently and reliably be suppressed during their synthesis, their purification is much more challenging, often affording complex mixtures due to oxidation. To circumvent this problem, such compounds are first protected (mostly as oxides, sulfides, or borane adducts), purified, and then deprotected again. Although two extra steps are needed, this often results in higher yields.

Borane complexes of trivalent phosphorus compounds have attracted a lot of interest as stable, easy to handle precursors of the free phosphorus compounds. Their properties and use have been extensively reviewed.[1–3] Deprotection is usually accomplished with an excess of an amine, such as diethylamine, DABCO or TMEDA.[4–7] More inert P–B bonds can be cleaved with a strong acid, for example, $HBF_4{\cdot}OEt_2$.[8,9] Direct use of the phosphane-boranes, whereby the P–B bond is cleaved in situ, has been reported.[5,10,11] Nevertheless, one often needs the isolated phosphorus compounds and then it is clear that the feasibility of the final purification plays a decisive role in the choice of the deprotection method. Finally, a polymer-supported deprotection method has also been reported, thereby eliminating the final purification step.[12]

In our lab one of the authors accidentally discovered an alternative deprotection method when trying to recrystallize an in-house made phosphane-borane in EtOH (Scheme 1). The free



Scheme 1. Unexpected alcoholytic deprotection.

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phosphane was obtained instead of the recrystallized adduct. To the best of our knowledge only one article has been devoted to the BH_3-decomplexation by means of alcoholysis.[13] However, it is suggested in that paper that the use of molecular sieves is required to catalyze the deprotection.

In this paper we wish to present our results on the general applicability of deprotecting phosphane- and phosphite-borane adducts by means of simple alcoholysis without the use of molecular sieves.

2. Results and discussion

The substrates tested are presented in Figure 1. Stirring commercially available phosphanes, diphosphanes, and two phosphites with an excess of $BH_3 \cdot SMe_2$ quantitatively afforded the borane adducts **1a**–**13a**. Phosphane-boranes **14a**–**16a** were synthesized by reducing their corresponding chlorodiarylphosphanes ($ClPAr_2$) according to the literature procedure.[14] The synthesis of the chlorodiarylphosphanes ($ClPAr_2$) has been described elsewhere.[15,16]

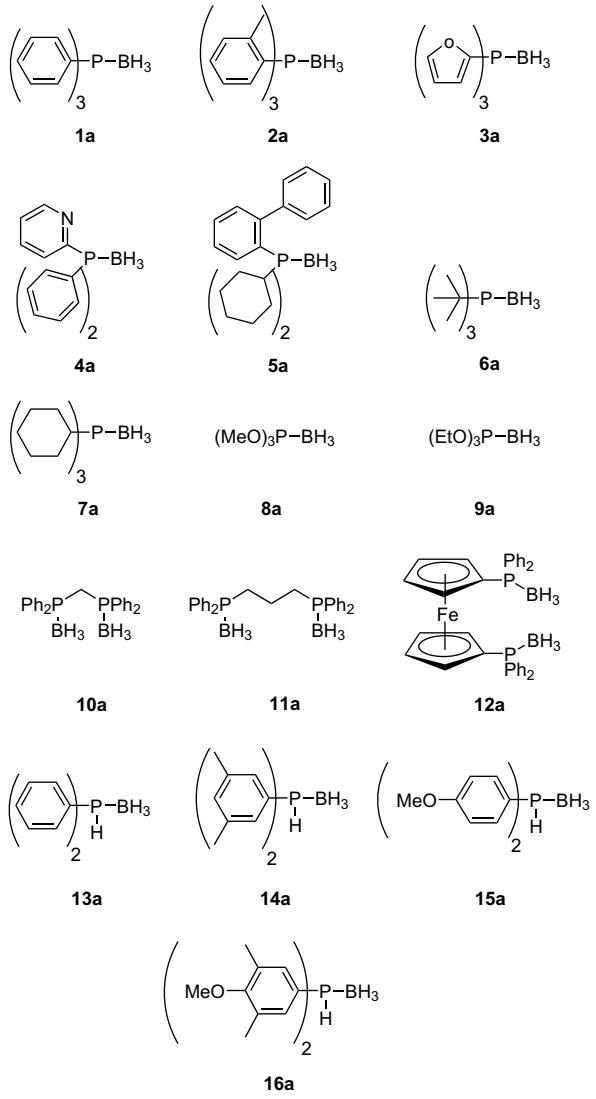
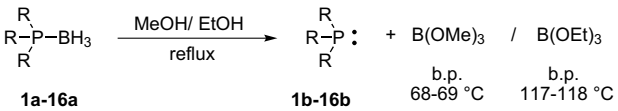


Figure 1. Substrates tested in alcoholytic deprotection.

We opted for methanol or ethanol as the solvents of choice for performing the alcoholysis (Scheme 2). In this way, the relatively volatile borates, trimethyl borate, and triethyl borate, respectively, can be removed by evaporation, thus making any further purification obsolete.



Scheme 2. General scheme for alcoholytic deprotection.

2.1. Deprotection in neat alcohol at reflux temperature

The substrates were mixed with either methanol or ethanol and then heated to reflux temperature, affording in most cases a homogenous solution. When TLC analysis revealed completion of the reactions, the mixtures were concentrated. A thorough removal of residual alcohol and borate by applying high vacuum at elevated temperature yielded the free phosphorus compounds, as confirmed by ^1H and ^{31}P NMR spectroscopy. The results of the deprotection reactions in ethanol are presented in Table 1.

Table 1
Deprotection in ethanol at reflux

Entry	Substrate	Reaction time	Conversion[a] (%)	Yield (%)
1	**1a**	24 h	100	95
2	**2a**	1 h	100	96
3	**3a**	15 min	100	100
4	**4a**	4 h	100	97
5	**5a**	72 h	100	52
6	**6a**	72 h	0	0
7	**7a**	72 h	7	—
8	**8a**	72 h	0	0
9	**9a**	72 h	0	0
10	**10a**	24 h	100	91[c]
11	**11a**	36 h	100	94
12	**12a**	24 h	100	89[c]
13	**13a**	1.5 h	100	75[b]
14	**14a**	30 min	100	71[b]
15	**15a**	1 h	100	81[b]
16	**16a**	30 min	100	73[b]

[a] When the substrates were not fully converted, the conversions and the yields were estimated on the basis of the ^{31}P NMR spectra of the mixtures.
[b] Due to the extreme oxygen sensitivity of the secondary phosphanes, the yields were strongly dependent on the scale of the reactions (50 mg scale: yield<20%; 300 mg scale: yield>70%).
[c] The precipitated products were isolated from the reaction mixture by filtration.

The deboronation in methanol, as compared to ethanol, is slightly slower, which can be merely ascribed to a lower reaction temperature (results in methanol not shown). The trends were, however, the same. Secondly, the influence of the phosphorus substituents on the deprotection rate seems to be electronic in nature. If it were predominantly influenced by sterical hindrance, adduct **2a** would react more sluggishly than **1a**. Also, one would expect the non-hindered phosphite-boranes **8a** and **9a** to be very good substrates. In both cases the reverse was observed: substrate **2a** reacts faster than **1a** (compare entries 1 and 2 in Table 1) while the phosphite-boranes **8a** and **9a** are inert (entries 8 and 9). In striking contrast to aromatic substituents on phosphorus, aliphatic ones have a detrimental effect on the rate. The decrease in rate follows the number of aliphatic substituents (compare entries 1 with 10 or 11, then with 5 and finally with 6 or 7). Substrates with three aliphatic groups on phosphorus are inert (entries 6 and 7). Triaryl phosphanes on the other hand react rapidly with excellent yields (entries 1–4). Finally, the secondary diarylphosphane-boranes **13a**–**16a** are among the best substrates (entries 13–16). The reactions proceeded so smoothly that hydrogen gas evolution could be observed. An attempt at ambient temperature was unsuccessful, however (results not shown). Due to the extended reaction times for deprotection of substrates **5a** and **10a**–**12a**, oxygen trickling in

the reaction vessel could not always be prevented. As a result, these products were contaminated with some P-oxides. However, the scarce solubility of some of these products could be used as an advantage, allowing isolation of the pure product by simple filtration from the reaction medium (entries 10 and 12 in Table 1).

Thus, in methanol or ethanol at reflux temperature, deprotection of phosphane-boranes, containing at least two aromatic substituents, proceeds with excellent yields in a moderate to high rate.

2.2. Deprotection at more elevated temperatures

We attempted to accelerate the deprotection of substrates **5a**–**8a** and **10a**–**12a** by increasing the reaction temperature. For this purpose, we chose toluene as a co-solvent, not only for its higher boiling point but also for its excellent dissolving properties. As a consequence, homogenous reaction mixtures were obtained. Moreover, it is the solvent of choice for deprotection by amine displacement.[5] The results, summarized in Table 2, reveal that substrate **5a** is now within the scope of this deprotection method (entry 1). Substrates **10a**–**12a** were converted at much more acceptable rates (compare entries 5–7 of Table 2 with entries 10–12 of Table 1). Finally, substrates **6a**, **7a**, and **8a** remained quasi-inert (entries 2, 3, and 4).

Table 2
Deprotection in MeOH/toluene (1:1) ratio at 100 °C

Entry	Substrate	Reaction time (h)	Conversion[a] (%)	Yield (%)
1	**5a**	22	100	97
2	**6a**	72	7	[b]
3	**7a**	72	6	[b]
4	**8a**	72	0	0
5	**10a**	3	100	100
6	**11a**	4	100	98
7	**12a**	4	100	99

[a] When the substrates were not fully converted, the conversions were estimated on the basis of the ^{31}P NMR spectra of the mixtures.
[b] Not determined.

2.3. Deprotection at more elevated temperatures under microwave irradiation

A dramatic rate acceleration was observed under microwave irradiation (Table 3).[17] Phosphane-boranes, bearing at least one aromatic substituent, were deprotected tremendously fast (entries 1–3 and 7–8). Even otherwise sluggishly reacting substrates **5a**, **11a**, and **12a** were converted in less than 10–15 min (entries 3, 7, and 8). On the other hand, trialkylphosphane-boranes remained inert under the conditions used (entries 4 and 5). Also, triethyl phosphite (**9a**) could not be deprotected in this way (entry 6).

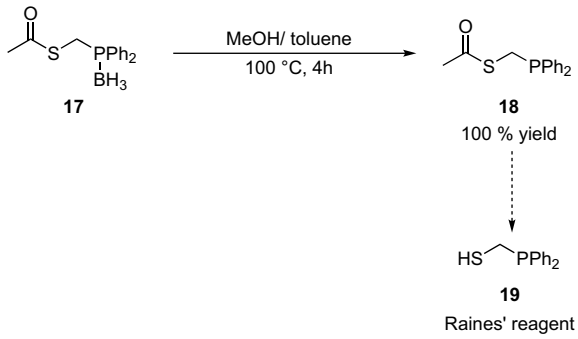
Table 3
Deprotection under microwave irradiation in MeOH (300 W, 120 °C)

Entry	Substrate	Irradiation time (min)	Conversion[a] (%)	Yield[b] (%)
1	**1a**	10	100	99
2	**4a**	10	100	100
3	**5a**	15	87	86
4	**6a**	30	5	0
5	**7a**	25	2	0
6	**9a**	25	0	0
7	**11a**	10	100	98
8	**12a**	10	100	98

[a] Estimated on the basis of ^{31}P NMR of the crude reaction mixtures.
[b] Isolated yields.

2.4. Application of the method

As an example, commercially available precursor **17** of Raines' reagent was successfully deboronated using elevated temperature as described in Section 2.2, nicely demonstrating the usefulness of this method (Scheme 3). Further deacetylation of intermediate **18** yields phosphanethiol **19**, the actual reagent used in traceless Staudinger ligation.[18]



Scheme 3. Deboronation of Raines' reagent precursor **17**.

3. Conclusion and future perspectives

Catalyst-free alcoholytic deprotection of borane-protected phosphorus compounds offers a smooth, efficient, and clean alternative to existing deprotection methods. The most remarkable aspect is its simplicity in setting up the reaction as well as in the subsequent work-up/purification. Basically, the substrate is dissolved in the proper alcoholic solvent and the reaction mixture is heated to reflux. Work-up simply consists of the removal of the solvent under reduced pressure, along with the volatile borate esters formed, affording in most cases nearly pure product. Free phosphanes with a low solubility in methanol or ethanol can be obtained in a pure state from the reaction mixture by simple filtration, without any further purification.

In pure methanol or ethanol at reflux, the scope is restricted to borane adducts of tertiary and secondary phosphanes with at least two aromatic substituents. However, the method is readily extended to tertiary phosphanes with at least one aromatic substituent by performing the reaction in a mixture of toluene and methanol at more elevated temperatures. Borane-protected phosphites as well as phosphanes with three aliphatic substituents fall outside the scope of this procedure.

Finally, microwave irradiation dramatically accelerates the deboronation reaction of phosphane-boranes bearing at least one aromatic substituent. Borane-protected trialkylphosphanes, however, remained nearly inert, even under microwave conditions.

4. Experimental part

4.1. General

All reactions were carried out at an argon/vacuum manifold using Schlenk techniques. HPLC-grade methanol and ethanol were degassed by three freeze-pump-thaw cycles; drying has no influence on the conversion or yield. Toluene was freshly distilled over sodium, and CH_2Cl_2 over CaH_2. Other commercially available solvents and reagents were used as purchased. Silica gel of the type LC60A (60–200 μm) was used for flash chromatography. Analytical TLC was performed using Macherey-Nagel SIL G-25 UV_{254} plates. Melting points were measured with a Kofler melting point apparatus. NMR spectra were recorded with a Bruker 300 Avance Ultrashield in $CDCl_3$. Chemical shifts (δ) are expressed in parts per million (for ^{1}H and ^{13}C relative to TMS, for ^{31}P relative to 85% aqueous phosphoric acid), coupling constants (J) in hertz. The ^{13}C NMR spectra were obtained by means of the attached proton test (APT) and the ^{31}P spectra with ^{1}H decoupling. Infrared spectra were measured using a Perkin Elmer FTIR Spectrum 1000 spectrometer.

Low resolution electrospray and atmospheric pressure chemical ionization mass spectra, ESI-MS, and APCI-MS, respectively, were recorded with an Agilent HP 1100 series spectrometer. On the same machine, which is also equipped with a DAD-detector, LC–MS analyses were run in order to confirm the purity of the substrates **1a**–**16a**. Low resolution electron impact ionization mass spectra, EIMS, were obtained with a Hewlett–Packard 5988A spectrometer. Accurate, high-resolution mass spectra, HRMS-ESI were acquired on a quadrupole/orthogonal-acceleration time-of-flight (Q/oaTOF) tandem mass spectrometer (qTof 2, Micromass, Manchester, UK) equipped with a standard electrospray ionization (ESI) interface. Samples (about 10 pmol/μL) were infused in a acetonitrile/water (1:1) mixture at 3 μL/min. Accurate mass measurements were performed using the lock mass of the protonated peptide YGGFL (m/z=556.2771), which was added to the sample (10 pmol/μL).

For the microwave irradiation experiments a multimode Milestone MicroSYNTH reactor (Laboratory Microwave Systems) was used in the standard configuration as delivered, including proprietary software. All the experiments were carried out in sealed microwave process vials (15 mL) under argon. The temperature control was performed using both external infrared and internal fiber optic sensors.

4.2. Synthesis of the substrates 1a–13a

To a solution of the free phosphorus compound (1 mmol) in CH_2Cl_2 (2 mL), $BH_3{\cdot}SMe_2$ (94% in SMe_2, 10 mmol; 20 mmol for diphosphanes) was added. After stirring for 24 h at ambient temperature a saturated aqueous NH_4Cl solution (5 mL) was gently added. The mixture was left for 1 h, then poured into water (50 mL), and extracted with CH_2Cl_2 (3×50 mL). The combined organic phase was washed with a saturated aqueous $NaHCO_3$ solution (50 mL), dried over $MgSO_4$, filtered, and concentrated. Filtration over silica gel and eluting with CH_2Cl_2 (100 mL) yielded the borane adducts in nearly quantitative yields after evaporation and high vacuum removal of the solvents. The purity was confirmed by LC–MS.

4.2.1. Triphenylphosphane-borane(1:1) (**1a**)[19]

White crystalline solid; yield 95%; mp 182–183 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.20 (m, 15H, Ph-*H*), 2.05–0.10 (br, 3H, B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.2 (d, J=9.7 Hz, CH), 131.3 (d, J=2.3 Hz, CH), 129.2 (d, J=56.8 Hz, C), 128.8 (d, J=10.2 Hz, CH); ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.8 (br). IR (KBr, cm^{-1}) 3054, 2372 (BH_3), 2340 (BH_3), 1969, 1899, 1827, 1752, 1680, 1597, 1481, 1460, 1434, 1310, 1130, 1103, 1056, 1000, 745, 734, 704, 692. ESI-MS m/z (rel intensity) 292 (28), 275 (100, $[M-H]^+$), 263 (14, $[M-BH_3+H]^+$), 185 (5, $[PPh_2]^+$); EIMS m/z (rel intensity) 273 (11, $[M-3H]^+$), 262 (100, $[M-BH_3]^+$), 194 (7), 185 (18, $[PPh_2]^+$), 184 (18), 183 (78), 165 (12), 152 (13), 133 (5), 115 (7), 108 (36, $[PPh]^+$), 107 (30), 89 (23), 78 (15), 77 (18, $[Ph]^+$), 63 (15), 51 (16). Anal. Calcd for $C_{18}H_{18}BP$: C, 78.30; H, 6.57. Found: C, 78.48; H, 6.59.

4.2.2. Tri(2-tolyl)phosphane-borane(1:1) (**2a**)

White crystalline solid; yield 99%; mp 153 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (m, 3H, Ar-*H*), 7.33 (m, 3H, Ar-*H*), 7.14 (m, 3H, Ar-*H*), 6.98 (m, 3H, Ar-*H*), 2.46 (s, 9H, ArC*H*$_3$), 2.06–0.76 (br, 3H, B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9 (d, J=11.3 Hz, C), 133.5 (d, J=7.4 Hz, CH), 132.2 (d, J=9.0 Hz, CH), 131.4 (d, J=2.2 Hz, CH), 127.1 (d, J=53.4 Hz, C), 126.0 (d, J=9.0 Hz, CH), 23.1 (d, J=4.0 Hz, CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.9 (br). IR (KBr, cm^{-1}) 3054, 2975, 2749, 2394 (BH_3), 2289 (BH_3), 2144, 1946, 1819, 1685, 1589, 1449, 1285, 1264, 1199, 1154, 1074, 1065, 972, 884, 812, 752, 716. ESI-MS m/z (rel intensity) 321 (7, $[Ar_3P(O)+H]^+$), 305 (100, $[M-BH_3+H]^+$); EIMS m/z (rel intensity) 304 (62, $[M-BH_3]^+$), 289 (100, $[M-BH_3-CH_3]^+$), 211 (19), 197 (31), 196 (31), 179 (22), 165 (41), 152 (9), 133 (10), 121 (14), 107 (6), 103 (6), 91 (55, $[C_7H_7]^+$), 78 (33), 77 (31), 65 (46), 49 (29). Anal. Calcd for $C_{21}H_{24}BP$: C, 79.27; H, 7.60. Found: C, 79.08; H, 7.63.

4.2.3. Tri(2-furyl)phosphane-borane(1:1) (**3a**)

White crystalline solid; yield 97%; mp 60 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (m, app. s, 3H, Ar-*H*5), 7.09 (m, 3H, Ar-*H*4), 6.44 (m, 3H, Ar-*H*3), 1.15 (br q, J=96.4 Hz, 3H, B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4 (d, J=5.6 Hz, CH), 142.1 (d, J=85.9 Hz, C), 123.7 (d, J=22.0 Hz, CH), 111.3 (d, J=8.5 Hz, CH); ^{31}P NMR (121 MHz, $CDCl_3$) δ −25.0 (br). IR (KBr, cm^{-1}) 3144, 3132, 2415 (BH_3), 2317 (BH_3), 2248 (BH_3), 1734, 1553, 1456, 1365, 1219, 1168, 1153, 1132, 1088, 1065, 1052, 1014, 990, 910, 758, 656. ESI-MS m/z (rel intensity) 249 (10, $[Ar_3P(O)+H]^+$), 233 (100, $[M-BH_3+H]^+$); EIMS m/z (rel intensity) 232 (100, $[M-BH_3]^+$), 204 (11), 185 (6), 175 (5), 165 (35, $[PAr_2]^+$), 152 (32), 134 (33), 129 (21), 128 (21), 109 (53), 98 (29, $[PAr_2]^+$), 89 (12), 78 (36), 70 (72), 51 (47), 41 (5). Anal. Calcd for $C_{12}H_{12}BO_3P$: C, 58.59; H, 4.92. Found: C, 58.53; H, 4.90.

4.2.4. Diphenyl(2-pyridyl)phosphane(P–B)borane(1:1) (**4a**)

Following the general procedure in Section 4.2, the product was further purified by flash chromatography on silica gel (eluted with *n*-hexane/EtOAc 9:1). White crystalline solid; yield 83%; mp 135 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (m, 1H, Py-*H*), 8.08 (m, 1H, Py-*H*), 7.83–7.67 (m, 5H, Ar-*H*), 7.54–7.33 (m, 7H, Ar-*H*), 1.97–0.72 (br, 3H, B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4 (d, J=76.3 Hz, C), 150.7 (d, J=12.9 Hz, CH), 136.2 (d, J=9.9 Hz, CH), 133.4 (d, J=9.6 Hz, CH), 131.3 (d, J=2.2 Hz, CH), 130.0 (d, J=26.5 Hz, CH), 128.7 (d, J=59.2 Hz, C), 128.6 (d, J=10.4 Hz, CH), 124.9 (d, J=2.3 Hz, CH); ^{31}P NMR (121 MHz, $CDCl_3$) δ 18.7 (br). IR (KBr, cm^{-1}) 3070, 2387 (BH_3), 2360 (BH_3), 2338 (BH_3), 1946, 1812, 1734, 1646, 1551, 1436, 1405, 1290, 1227, 1199, 1058, 978, 882, 760, 701. ESI-MS m/z (rel intensity) 276 (44, $[M-H]^+$), 264 (100, $[M-BH_3+H]^+$), 186 (8, $[PPh_2+H]^+$); EIMS m/z (rel intensity) 274 (16, $[M-3H]^+$), 263 (100, $[M-BH_3]^+$), 262 (78, $[M-BH_4]^+$), 197 (20), 186 (25), 185 (63, $[PPh_2]^+$), 184 (20), 183 (38), 166 (22), 157 (12), 152 (12), 139 (6), 131 (6), 107 (36), 92 (54), 78 (57, $[Py]^+$), 77 (30, $[Ph]^+$), 51 (65). Anal. Calcd for $C_{17}H_{17}BNP$: C, 73.68; H, 6.18. Found: C, 73.83; H, 6.21.

4.2.5. (2-Biphenylyl)dicyclohexylphosphane-borane(1:1) (**5a**)

White foam; yield 100%; mp 115 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (m, 1H, Ar-*H*), 7.51–7.38 (m, 4H, Ar-*H*), 7.28–7.14 (m, 4H, Ar-*H*), 1.76–1.41 (m, 12H, Cy-*H*), 1.39–0.88 (m, 10H, Cy-*H*), 1.39–(−0.25) (br, 3H, B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8 (s, C), 142.0 (d, J=1.9 Hz, C), 137.5 (d, J=15.9 Hz, CH), 131.4 (d, J=6.2 Hz, CH), 130.4 (d, J=2.1 Hz, CH), 128.9 (s, CH), 128.1 (d, J=4.6 Hz, CH), 128.0 (s, CH), 127.4 (d, J=11.9 Hz, CH), 125.6 (d, J=45.8 Hz, C), 34.0 (d, J=32.3 Hz, CH), 28.3 (d, J=60.3 Hz, CH_2), 26.8 (d, J=12.3 Hz, CH_2), 26.6 (d, J=11.9 Hz, CH_2); ^{31}P NMR (121 MHz, $CDCl_3$) δ 35.9 (br). IR (KBr, cm^{-1}) 3054, 2930, 2851, 2378 (BH_3), 2351 (BH_3), 2264 (BH_3), 1871, 1747, 1587, 1446, 1328, 1303, 1171, 1062, 1044, 1024, 1006, 964, 915, 853, 822, 764, 747, 737, 706, 654, 628. ESI-MS m/z (rel intensity) 361 (100, $[M-3H]^+$); APCI-MS m/z (rel intensity) 351 (100, $[M-BH_3+H]^+$); EIMS m/z (rel intensity) 361 (5, $[M-3H]^+$), 350 (50, $[M-BH_3]^+$), 349 (54, $[M-BH_4]^+$), 295 (2), 268 (5), 267 (24, $[M-BH_3-Cy]^+$), 199 (6), 198 (6), 197 (7, $[PCy_2]^+$), 185 (25), 184 (21, $[PAr]^+$), 183 (64), 163 (18), 152 (10), 137 (5), 115 (6), 83 (29), 67 (19), 55 (100), 41 (55). Anal. Calcd for $C_{24}H_{34}BP$: C, 79.12; H, 9.41. Found: C, 78.94; H, 9.38.

4.2.6. Tri(tert-butyl)phosphane-borane(1:1) (**6a**)

White foam; yield 100%; mp>250 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.42 (d, J=12.0 Hz, 27H, C(C*H*$_3$)$_3$), 0.40 (br q, J=96.0 Hz, 3H, B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.8 (d, J=10.7 Hz, C), 30.3 (s, CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 57.9 (q, J=62.8 Hz). IR (KBr, cm^{-1}) 2997, 2974, 2910, 2367 (BH_3), 2346 (BH_3), 2155, 2026, 1899, 1819, 1736, 1682, 1484, 1473, 1390, 1371, 1177, 1093, 1078, 907,

812, 750, 665, 641. ESI-MS *m*/*z* (rel intensity) 256 (90), 232 (100), 215 (82, $[M-H]^+$); EIMS *m*/*z* (rel intensity) 215 (2, $[M-H]^+$), 202 (29, $[M-BH_3]^+$), 172 (2), 157 (4), 146 (28, $[M-BH_3-C_4H_8]^+$), 116 (3), 101 (4), 91 (16), 90 (16), 57 (100, $[C_4H_9]^+$), 41 (50). Anal. Calcd for $C_{12}H_{30}BP$: C, 66.68; H, 13.99. Found: C, 66.49; H, 14.05.

4.2.7. Tricyclohexylphosphane-borane(1:1) (**7a**)

White solid; yield 62%; mp 179 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.05–1.55 (m, 18H, Cy-*H*), 1.50–1.10 (m, 15H, Cy-*H*), 0.90–(−0.35) (br, 3H, B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.9 (d, *J*=30.5 Hz, CH), 27.8 (d, *J*=1.7 Hz, CH_2), 27.3 (d, *J*=10.3 Hz, CH_2), 26.1 (d, *J*=0.8 Hz, CH_2); ^{31}P NMR (121 MHz, $CDCl_3$) δ 28.0 (br). IR (KBr, cm^{-1}) 2924, 2851, 2361 (BH_3), 2338 (BH_3), 1445, 1406. ESI-MS *m*/*z* (rel intensity) 611 (8, $[2M+Na]^+$), 332 (13), 317 (8, $[M+Na]^+$), 310 (42), 297 (4, $[Cy_3P(O)+H]^+$), 291 (100, $[M-3H]^+$); EIMS *m*/*z* (rel intensity) 280 (29, $[M-BH_3]^+$), 209 (4), 199 (22), 198 (53), 143 (4), 117 (41), 116 (12), 115 (18), 83 (39, $[Cy]^+$), 81 (26), 69 (17), 55 (100), 53 (14), 41 (51). Anal. Calcd for $C_{18}H_{36}BP$: C, 73.47; H, 12.33. Found: C, 73.31; H, 12.29.

4.2.8. Trimethyl phosphite-borane(1:1) (**8a**)[20]

Colorless, clear oil; yield 100%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.73 (d, *J*=11.1 Hz, 9H, C*H*$_3$), 0.43 (br q, *J*=96.3 Hz, 3H, B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.2 (d, *J*=3.8 Hz, CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 119.3 (q, *J*=100.0 Hz). IR (KBr, cm^{-1}) 2360 (BH_3). APCI-MS *m*/*z* (rel intensity) 125 (100, $[M-BH_3+H]^+$), 93 (5, $[M-BH_3-CH_3OH+H]^+$); EIMS *m*/*z* (rel intensity) 124 (87, $[M-BH_3]^+$), 121 (11), 93 (100, $[M-BH_3-OCH_3]^+$), 82 (28), 79 (18), 59 (18), 58 (12).

4.2.9. Triethyl phosphite-borane(1:1) (**9a**)[21]

Colorless, clear oil; yield 100%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.07 (m, 6H, C*H*$_2$), 1.32 (t, *J*=7.0 Hz, 9H, C*H*$_3$), 0.40 (br q, *J*=93.0 Hz, 3H, B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 62.6 (d, *J*=3.3 Hz, CH_2), 16. 2 (d, *J*=5.6 Hz, CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 114.0 (q, *J*=101.6 Hz). IR (KBr, cm^{-1}) 2982, 2943, 2909, 2396 (BH_3), 1456, 1392, 1162, 1130, 1102, 1016, 974, 953, 914, 884, 796. APCI-MS *m*/*z* (rel intensity) 167 (100, $[M-BH_3+H]^+$), 139 (97), 121 (25, $[M-BH_3-EtOH+H]^+$), 111 (40), 93 (11), 83 (89); EIMS *m*/*z* (rel intensity) 166 (20, $[M-BH_3]^+$), 149 (26), 139 (20), 128 (19), 107 (23), 93 (71), 86 (100), 69 (43), 57 (88), 48 (48).

4.2.10. Methylenebis(diphenylphosphane)-borane(1:2) (**10a**)[22]

White crystalline solid; yield 94%; mp 213 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (m, 8H, Ph-*H*3 and *H*5), 7.43 (m, 4H, Ph-*H*4), 7.34 (m, 8H, Ph-*H*2 and *H*6), 3.24 (t, *J*=10.9 Hz, 2H, C*H*$_2$), 1.40–0.40 (br, 6H, B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.7 (d, *J*=9.9 Hz, CH), 131.6 (d, *J*=2.3 Hz, CH), 128.8 (d, *J*=10.3 Hz, CH), 128.4 (dd, *J*=56.4, 2.4 Hz, C), 23.8 (t, *J*=24.8 Hz, CH_2); ^{31}P NMR (121 MHz, $CDCl_3$) δ 14.6 (br). IR (KBr, cm^{-1}) 2409 (BH_3), 2359 (BH_3), 2343 (BH_3), 1485, 1437, 1366, 1312, 1167, 1104, 1056, 1027, 999, 808, 798, 767, 751, 742, 712, 694. APCI-MS *m*/*z* (rel intensity) 471 (8), 455 (7), 417 (35, $[Ph_2P(O)CH_2P(O)Ph_2+H]^+$), 401 (100, $[Ph_2P(O)CH_2PPh_2+H]^+$), 385 (53, $[M-2BH_3+H]^+$); EIMS *m*/*z* (rel intensity) 409 (1, $[M-3H]^+$), 398 (1, $[M-BH_3]^+$), 384 (4, $[M-2BH_3]^+$), 320 (3), 308 (12), 262 (22), 232 (1), 199 (18), 186 (10), 185 (10, $[PPh_2]^+$), 183 (31), 165 (14), 152 (7), 133 (3), 121 (47), 109 (6), 108 (23, $[PPh]^+$), 107 (18), 85 (43), 84 (62), 78 (11), 77 (16, $[Ph]^+$), 51 (46), 49 (100), 48 (15), 47 (23). Anal. Calcd for $C_{25}H_{28}B_2P_2$: C, 72.87; H, 6.85. Found: C, 72.61; H, 6.88.

4.2.11. Propane-1,3-diyl-bis(diphenylphosphane)-borane(1:2) (**11a**)[23]

White foam; yield 92%; mp 155 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (m, 8H, Ph-*H*3), 7.51–7.36 (m, 12H, Ph-*H*2 and *H*4), 2.33 (m, 4H, *H*1 and *H*3), 1.72 (m, 2H, *H*2), 1.52–0.25 (br, 6H, B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.1 (d, *J*=9.1 Hz, CH), 131.3 (d, *J*=2.3 Hz, CH), 129.0 (d, *J*=55.2 Hz, C), 128.9 (d, *J*=9.9 Hz, CH), 26.7 (dd, *J*=36.3, 11.1 Hz, CH_2), 17.4 (s, CH_2); ^{31}P NMR (121 MHz, $CDCl_3$) δ 15.8 (br). IR (KBr, cm^{-1}) 3077, 3057, 2941, 2931, 2904, 2382 (BH_3), 2261 (BH_3), 2119, 1972, 1897, 1814, 1669, 1559, 1485, 1456, 1414, 1331, 1312, 1265, 1185, 1161, 1132, 1110, 1061, 1028, 999, 964, 827, 737, 702, 694. ESI-MS *m*/*z* (rel intensity) 463 (37, $[M+Na]^+$), 458 (100, $[M+NH_4]^+$), 441 (28, $[M+H]^+$), 439 (45, $[M-H]^+$), 427 (23, $[M-BH_3+H]^+$), 413 (18, $[M-2BH_3+H]^+$); EIMS *m*/*z* (rel intensity) 439 (1, $[M-H]^+$), 425 (61, $[M-BH_4]^+$), 412 (6, $[M-2BH_3]^+$), 335 (32), 315 (3), 294 (5), 289 (4), 259 (6), 237 (10), 227 (8), 199 (18), 186 (17), 185 (28, $[PPh_2]^+$), 183 (100), 165 (27), 152 (17), 133 (12), 121 (33), 109 (49), 108 (51, $[PPh]^+$), 91 (21, $[C_7H_7]^+$), 89 (33), 78 (24), 77 (20), 51 (18), 41 (5). Anal. Calcd for $C_{27}H_{32}B_2P_2$: C, 73.68; H, 7.33. Found: C, 73.92; H, 7.36.

4.2.12. 1,1′-Bis(diphenylphosphanyl)ferrocene-borane(1:2) (**12a**)[24]

Orange solid; yield 100%; mp 191 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.30 (m, 20H, Ph-*H*), 4.53 (m, 4H, Cp-*H*), 4.25 (m, 4H, Cp-*H*), 2.45–0.50 (br, 6H, B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.5 (d, *J*=9.6 Hz, CH), 131.1 (d, *J*=2.3 Hz, CH), 130.7 (d, *J*=59.4 Hz, C), 128.5 (d, *J*=10.2 Hz, CH), 74.6 (d, *J*=7.5 Hz, CH), 73.9 (d, *J*=9.7 Hz, CH), 70.4 (d, *J*=66.9 Hz, C); ^{31}P NMR (121 MHz, $CDCl_3$) δ 15.7 (br). IR (KBr, cm^{-1}) 3070, 2889, 2377 (BH_3), 2248 (BH_3), 2047, 1685, 1594, 1571, 1437, 1310, 1173, 1104, 1057, 897, 835, 737, 703. ESI-MS *m*/*z* (rel intensity) 605 (26, $[M+Na]^+$), 600 (100, $[M+NH_4]^+$), 581 (36, $[M-H]^+$), 569 (5, $[M-BH_3+H]^+$); EIMS *m*/*z* (rel intensity) 554 (26, $[M-2BH_3]^+$), 477 (9, $[M-2BH_3-Ph]^+$), 370 (20), 293 (4), 263 (4), 250 (4), 226 (11), 186 (21), 185 (20, $[PPh_2]^+$), 171 (38), 170 (38), 149 (16), 120 (20), 115 (21), 108 (32, $[PPh]^+$), 107 (26), 84 (100), 77 (32, $[Ph]^+$), 40 (25). Anal. Calcd for $C_{34}H_{34}B_2FeP_2$: C, 70.16; H, 5.89. Found: C, 70.02; H, 5.91.

4.2.13. Diphenylphosphane-borane(1:1) (**13a**)[25]

White crystalline solid; yield 97%; mp 40 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82–7.34 (m, 10H, Ph-*H*), 6.30 (dq, *J*=379, 6.9 Hz, 1H, P-*H*), 1.07 (br q, *J*=90.9 Hz, 3H, B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.0 (d, *J*=9.4 Hz, CH), 131.7 (d, *J*=2.5 Hz, CH), 129.1 (d, *J*=10.3 Hz, CH), 126.3 (d, *J*=57.2 Hz, C); ^{31}P NMR (121 MHz, $CDCl_3$) δ 1.4 (br). IR (KBr, cm^{-1}) 3200, 3053, 2394 (BH_3), 1970, 1886, 1666, 1584, 1441, 1117, 1057, 900, 810, 753, 699. ESI-MS *m*/*z* (rel intensity) 427 (6, $[2HP(O)Ph_2+Na]^+$), 405 (13, $[2HP(O)Ph_2+H]^+$), 225 (7, $[HP(O)Ph_2+Na]^+$), 203 (100, $[HP(O)Ph_2+H]^+$); EIMS *m*/*z* (rel intensity) 197 (19, $[M-3H]^+$), 186 (100, $[M-BH_3]^+$), 170 (3), 165 (11), 152 (10), 139 (6), 119 (13), 109 (64, $[HPPh]^+$), 108 (96, $[PPh]^+$), 107 (67), 89 (51), 78 (26), 77 (30, $[Ph]^+$), 63 (28), 51 (54). Anal. Calcd for $C_{12}H_{14}BP$: C, 72.06; H, 7.05. Found: C, 72.02; H, 7.08.

4.3. Synthesis of the substrates 14a–16a

To a solution of the chlorodiarylphosphane (66 mmol) in THF (30 mL), a solution of borane–THF in THF (1 M; 100 mL) was added at 0 °C. After stirring for 2 h, $LiAlH_4$ (82 mmol) was added in small portions. The reaction was stirred for another 2 h at 0 °C, upon which it was carefully quenched into a mixture of concentrated HCl (37% aq; 50 mL) and ice. The product was extracted with toluene (3×100 mL) and the combined organic phase dried (Na_2SO_4) and concentrated. Purification by flash chromatography yielded the isolated secondary phosphane-boranes **14a**–**16a**.

4.3.1. Di(3,5-dimethylphenyl)phosphane-borane(1:1) (**14a**)

Purified by flash chromatography on silica gel (eluent: *n*-pentane/toluene 8:2); white crystalline solid; yield 65%; mp 106 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J*=12.1 Hz, 4H, Ar-*H*2 and *H*6), 7.15 (s, 2H, Ar-*H*4), 6.19 (dq, *J*=377, 6.9 Hz, 1H, P-*H*), 2.36 (s, 12H, ArC*H*$_3$), 1.77–0.41 (br, 3H, B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8 (d, *J*=10.6 Hz, C), 133.4 (d, *J*=2.3 Hz, CH), 130.5 (d, *J*=9.8 Hz, CH), 126.2

(d, J=79.2 Hz, C), 21.3 (s, CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 1.8 (br). IR (KBr, cm^{-1}) 3027, 2949, 2917, 2860, 2732, 2578, 2388 (BH_3), 2345 (BH_3), 2245, 1799, 1752, 1602, 1508, 1458, 1377, 1309, 1270, 1170, 1134, 1058, 994, 947, 915, 847, 733, 691, 598. ESI-MS m/z (rel intensity) 517 (14, $[2HP(O)Ar_2+H]^+$), 296 (13), 272 (43, $[M-2H+NH_4]^+$), 259 (100, $[HP(O)Ar_2+H]^+$), 255 (60, $[M-H]^+$), 243 (19, $[M-BH_3+H]^+$); APCI-MS m/z (rel intensity) 275 (13, $[HOP(O)Ar_2+H]^+$), 259 (71, $[HP(O)Ar_2+H]^+$), 243 (100, $[M-BH_3+H]^+$); EIMS m/z (rel intensity) 256 (10, $[M]^+$), 255 (20, $[M-H]^+$), 254 (13, $[M-2H]^+$), 253 (23, M−3H), 242 (100, $[M-BH_3]^+$), 221 (10), 211 (5), 193 (5), 178 (4), 165 (3), 136 (98, $[PAr]^+$), 133 (16), 105 (20, $[C_7H_7CH_3]^+$), 92 (43), 91 (56, $[C_7H_7]^+$), 77 (31, $[Ph]^+$), 65 (13), 51 (15). Anal. Calcd for $C_{16}H_{22}BP$: C, 75.03; H, 8.66. Found: C, 74.88; H, 8.63.

*4.3.2. Di(4-methoxyphenyl)phosphane-borane(1:1) (**15a**)*

Purified by flash chromatography on silica gel (eluted with n-hexane/CH_2Cl_2 7:3); white crystalline solid; yield 50%; mp 76 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (m, 4H, Ar-*H*2), 6.96 (m, 4H, Ar-*H*3), 6.31 (dq, J=377.8, 6.8 Hz, 1H, P-*H*), 3.83 (s, 6H, OCH_3), 1.71–0.31 (br, 3H, BH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3 (d, J=2.1 Hz, C), 134.6 (d, J=10.8 Hz, CH), 117.3 (d, J=62.3 Hz, C), 114.7 (d, J=11.3 Hz, CH), 55.4 (s, CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ −2.6 (br). IR (KBr, cm^{-1}) 3061, 3028, 2995, 2963, 2839, 2380 (BH_3), 2346 (BH_3), 2044, 1893, 1773, 1617, 1596, 1570, 1501, 1462, 1294, 1250, 1180, 1114, 1064, 1026, 910, 829, 669. ESI-MS m/z (rel intensity) 547 (23, $[2HP(O)Ar_2+Na]^+$), 525 (13, $[2HP(O)Ar_2+H]^+$), 285 (27, $[HP(O)Ar_2+Na]^+$), 276 (45, $[M-2H+NH_4]^+$), 263 (100, $[HP(O)Ar_2+H]^+$), 259 (87, $[M-H]^+$), 139 (12, $[PAr+H]^+$), 85 (63); APCI-MS m/z (rel intensity) 263 (6, $[HP(O)Ar_2+H]^+$), 247 (100, $[M-BH_3+H]+$); EIMS m/z (rel intensity) 259 (7, $[M-H]^+$), 246 (50, $[M-BH_3]^+$), 225 (3), 170 (4), 150 (4), 138 (100, $[PAr]^+$), 119 (12), 109 (12), 108 (20), 107 (14), 95 (16), 91 (13, $[C_7H_7]^+$), 78 (11), 77 (12), 51 (8), 50 (8), 43 (7). Anal. Calcd for $C_{14}H_{18}BO_2P$: C, 64.65; H, 6.98. Found: C, 64.45; H, 7.01.

*4.3.3. Di(3,5-dimethyl-4-methoxyphenyl)phosphane-borane(1:1) (**16a**)*

Purified by flash chromatography on silica gel (eluted with n-hexane/CH_2Cl_2 7:3); white crystalline solid; yield 35%; mp 81 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, J=11.7 Hz, 4H, Ar-*H*2), 6.19 (dq, J=377.8, 6.8 Hz, 1H, P-*H*), 3.72 (s, 6H, OCH_3), 2.28 (s, 12H, ArCH_3), 1.79–0.17 (br, 3H, BH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9 (d, J=2.7 Hz, C), 133.5 (d, J=10.2 Hz, CH), 132.1 (d, J=11.5 Hz, C), 121.1 (d, J=59.1 Hz, C), 59.7 (s, CH_3), 16.1 (s, CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ −0.5 (br). IR (KBr, cm^{-1}) 2928, 2848, 2388 (BH_3), 2349 (BH_3), 1589, 1480, 1454, 1280, 1224, 1120, 1092, 1060, 1036, 1011, 914, 872, 766, 639. ESI-MS m/z (rel intensity) 637 (7, $[2HP(O)Ar_2+H]^+$), 332 (58, $[M-2H+NH_4]^+$), 319 (31, $[HP(O)Ar_2+H]^+$), 315 (100, $[M-H]^+$); APCI-MS m/z (rel intensity) 319 (8, $[HOP(O)Ar_2+H]^+$), 303 (100, $[HP(O)Ar_2+H]^+$); EIMS m/z (rel intensity) 315 (11, $[M-H]^+$), 302 (64, $[M-BH_3]^+$), 281 (3), 179 (3), 168 (5), 167 (31), 166 (100, $[PAr]^+$), 151 (21), 143 (17), 121 (19), 91 (24, $[C_7H_7]^+$), 77 (16), 65 (9), 43 (6). Anal. Calcd for $C_{18}H_{26}BO_2P$: C, 68.38; H, 8.29. Found: C, 68.26; H, 8.26.

4.4. General procedure for deprotection in methanol or ethanol at reflux temperature

Using Schlenk techniques, a solution of the borane-protected phosphorus compound (0.1 M) was brought to reflux in MeOH or EtOH. When TLC analysis indicated the absence of starting material, the solvent was evaporated at the rotary evaporator followed by high-vacuum removal of residual solvent and borate at slightly elevated temperature (40 °C).

4.5. General procedure for deprotection in methanol/toluene

Using Schlenk techniques, the borane-protected phosphorus compound was dissolved in a 1:1 MeOH/toluene mixture (0.1 M). The solution was heated to 100 °C. The remaining steps of the procedure are identical to those described in Section 4.4.

4.6. Procedure for the deprotection under microwave irradiation

Applying a 15 mL microwave vial, the borane-protected phosphorus compound was dissolved in MeOH (0.1 M). The reaction vial was flushed with argon, sealed, and irradiated in the microwave reactor at a ceiling temperature of 120 °C at 300 W maximum power for the stipulated time (Table 3). After completion of the reaction the mixture was cooled with an air flow for 15 min before opening. The remaining steps of the procedure are identical to the general procedure.

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