Phospha-Mannich reactions of phosphinous acids R_2P–OH and their derivatives

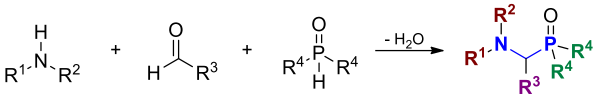
Dmitry V. Moiseev
Akzo Nobel, EMEA, Balashikha, Moscow Region, Russia, 143900

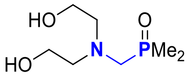
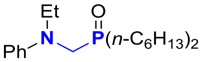
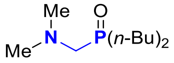
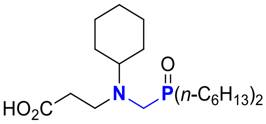
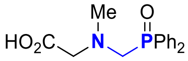
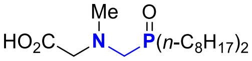
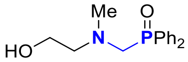
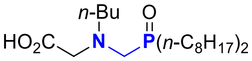
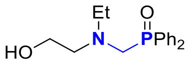
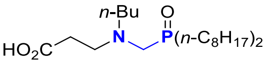
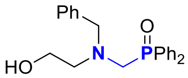
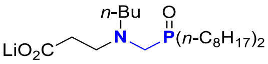
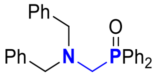
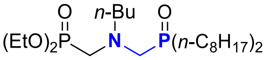
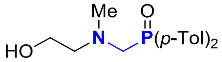
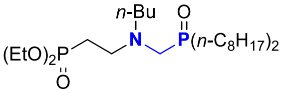
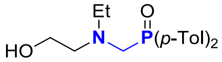
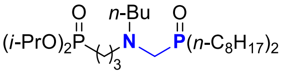
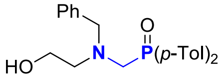
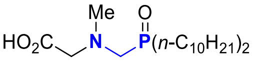
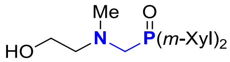
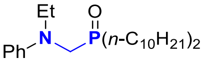
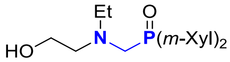
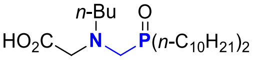
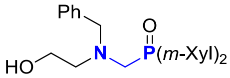
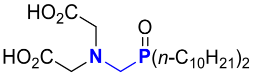
E-mail: Dmitriy.Moiseev@akzonobel.com
ORCID: 0000-0003-0152-5880
Telephone: +7 (495) 795 01 60
Postal address: 143900 Russia, Moscow Region, Balashikha, Severnaya Promzona, Pokrovsky proezd, 9

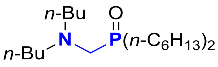
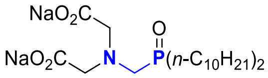
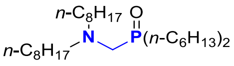
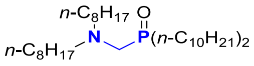
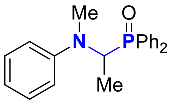
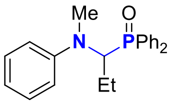
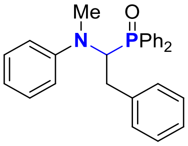
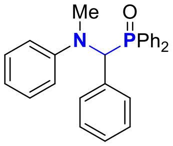
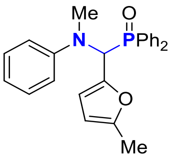
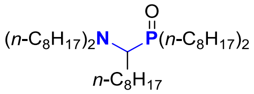
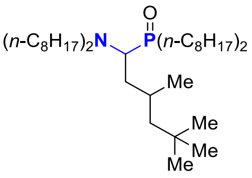
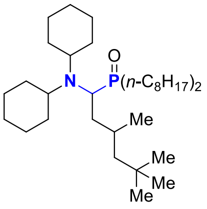
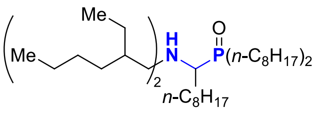
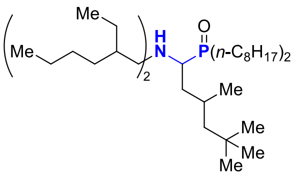
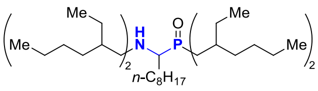
Supplemental Materials

Contents

Table S1. P(O),N-acetals, obtained by 3C-phospha-Mannich reactions between secondary amines, SPOs, and *p*-CH_2O, or other aldehydes.



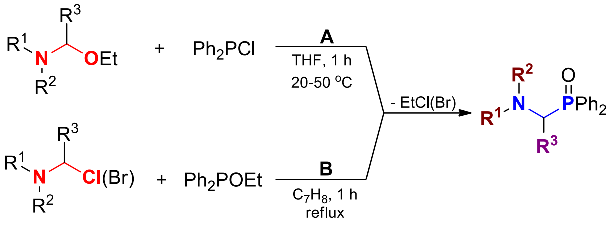
Entry	Product	Assistant	Conditions	Yield,%
1		NaOH	SF, 80 °C, 8 h	(-)*[1]
2		–	MeCN, reflux, 3 h	75[2]
3		–	H_2O, 150 °C, 3 h	62[3]
4		–	MeCN, reflux, 3 h	86[2]
5		–	MeCN, reflux, 4 h	68[4]
6		–	MeCN, reflux	(-)*[5]
7		µW	MeCN, 100 °C, 0.5 h	95[6,7]
8		HCl	MeCN, reflux, 2 h	90[8]
9		µW	MeCN, 100 °C, 0.5 h	95[6,7]
10		–	$CHCl_3$, reflux, 1 h	84[9]
11		µW	MeCN, 100 °C, 0.5 h	90[6,7]
12		–	MeCN, reflux, 3 h	84[2]
13		–	SF, 120 °C, ~ 3 h	37[10]
14		PTSA	C_6H_6, reflux	60[8]
15		µW	MeCN, 100 °C, 0.5 h	96[6,7]
16		PTSA	MeCN, reflux, 3 h	78[11]
17		µW	MeCN, 100 °C, 0.5 h	93[6,7]
18		PTSA	C_6H_6, reflux	40[12]
19		µW	MeCN, 100 °C, 0.5 h	89[6,7]
20		–	MeCN, reflux	(-)*[5]
21		µW	MeCN, 100 °C, 0.5 h	93**[6,7]
22		–	MeCN, reflux, 3 h	54[2]
23		µW	MeCN, 100 °C, 0.5 h	88[6,7]
24		HCl	MeCN, reflux, 2 h	90[8]
25		µW	MeCN, 100 °C, 0.5 h	92[6,7]
26		–	MeCN, reflux, 3 h	86[13]

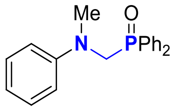
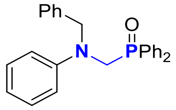
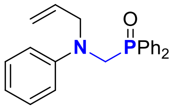
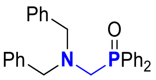
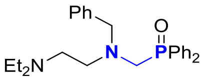
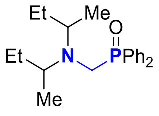
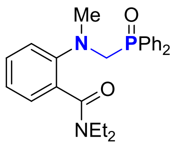
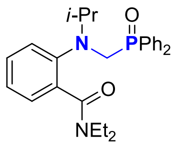
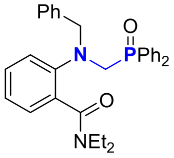
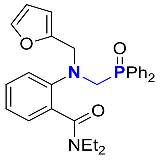
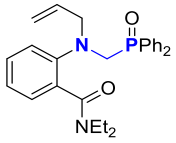
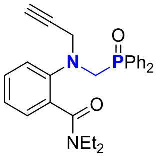
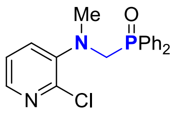
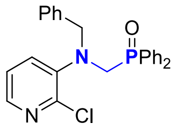
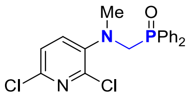
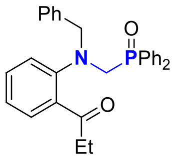
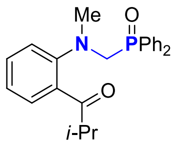
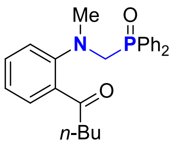
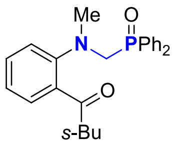
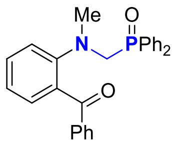
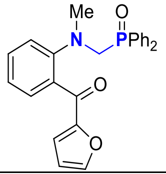
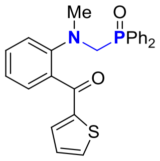
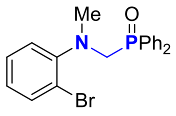
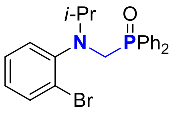
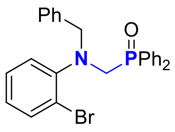
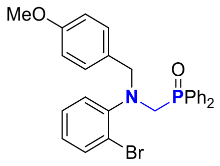
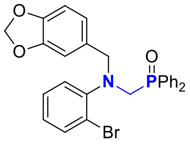
Entry	Product	Assistant	Conditions	Yield,%	Entry	Product	Assistant	Conditions	Yield,%
27		PTSA	C_6H_6, reflux	85[8]	28		–	MeCN, reflux, 3 h	70[2]
29		PTSA	C_6H_6, reflux	80[8]	30		–	MeCN, reflux, 3 h	60[2,14]
31		–	C_7H_8, reflux, 1 h	30[15]	32		–	C_7H_8, reflux, 1 h	50[15]
33		–	C_7H_8, reflux, 1 h	85[15]	34		–	C_7H_8, reflux, 1 h	73[15]
35		–	C_7H_8, reflux, 1 h	84[15]	36		PTSA	C_7H_8, reflux, 24 h	57[16]
37		PTSA	C_7H_8, reflux, 72 h	65[16]	38		PTSA	C_7H_8, reflux, 96 h	24[16]
39		PTSA	C_7H_8, reflux, 24 h	69[16]	40		PTSA	C_7H_8, reflux, 72 h	72[16]
41		PTSA	C_7H_8, reflux, 8 h	27[16]	42				

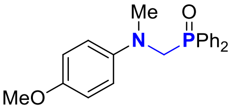
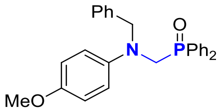
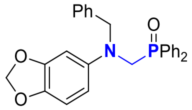
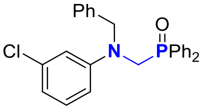
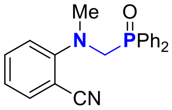
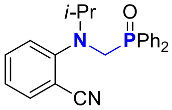
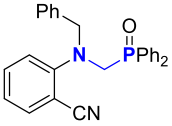
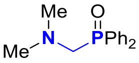
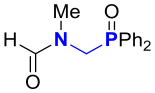
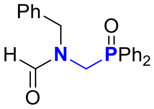
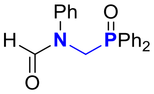
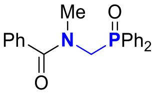
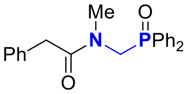
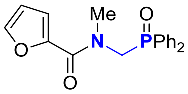
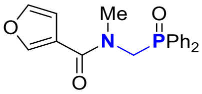
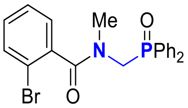
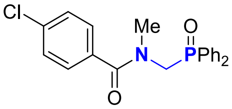
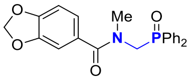
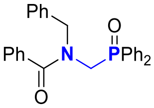
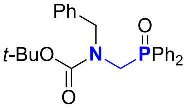
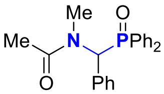
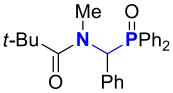
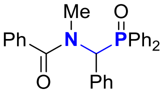
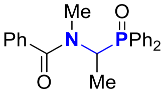
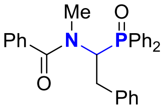
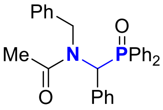
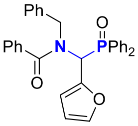
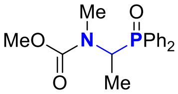
* Not reported

** *m*-Xyl = 3,5-Me_2-C_6H_3

Table S2. P(O),N-acetals, obtained by Mannich-Arbuzov reactions.

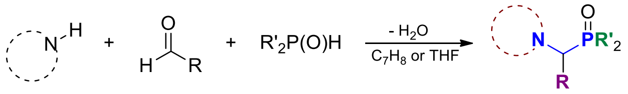


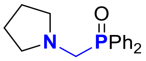
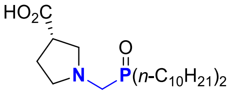
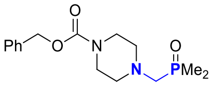
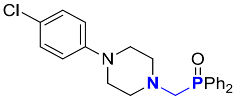
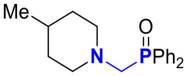
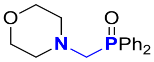
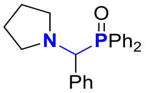
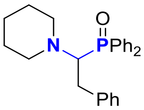
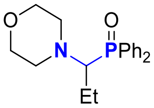
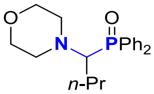
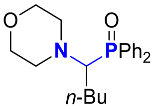
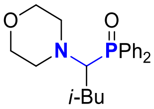
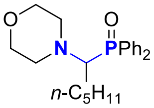
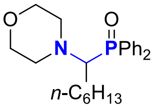
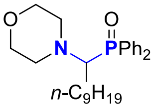
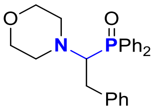
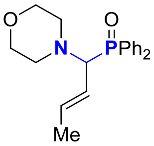
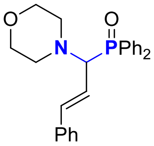
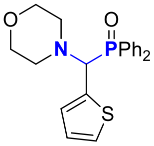
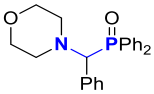
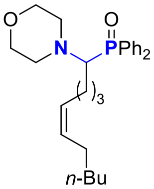
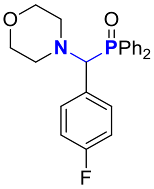
Entry	Product	Path	Yield,%
1		**A**	90,[17,18] 91,[15] 99[19-21]
2		**A**	94[15]
3		**A**	92[17]
4		**A**	74[15]
5		**A**	63[22]
6		**A**	73[23]
7		**A**	76[24]
8		**A**	72[25]
9		**A**	66[24]
10		**A**	64[24]
11		**A**	71[24]
12		**A**	68[25]
13		**A**	86[26]
14		**A**	91[26]
15		**A**	85[26]
16		**A**	45[27]
17		**A**	47,[27] 55[25]
18		**A**	52[25]
19		**A**	43[27]
20		**A**	60[27]
21		**A**	57[27]
22		**A**	55[27]
23		**A**	75[28]
24		**A**	75[28]
25		**A**	72[28]
26		**A**	69[28]
27		**A**	65[28]

Entry	Product	Path	Yield,%
28		**A**	88[17]
29		**A**	82[17]
30		**A**	71[17]
31		**A**	84[17]
32		**A**	78[25]
33		**A**	76[25]
34		**A**	73[25]
35		**B**	78[15]
36		**B**	82[29,30]
37		**B**	80[29,30]
38		**B**	75[29]
39		**B**	81,[31] 91[32]
40		**B**	85[32]
41		**B**	90[33]
42		**B**	86[32]
43		**B**	87[32]
44		**B**	89[32]
45		**B**	90[32]
46		**B**	84,[31] 89[32]
47		**B**	68[29]
48		**B**	85[31]
49		**B**	80[31]
50		**B**	82[31]
51		**B**	85[31]
52		**B**	82[31]
53		**B**	78[31]
54		**B**	72[31]
55		**A**	90*[34]
56			
57			

* in AcOH

Table S3. P(O),N-acetals with cyclic amine arms, obtained by 3C-phospha-Mannich reactions.



Entry	Product	Conditions	Yield,%	Entry	Product	Conditions	Yield,%
1		SF, μW, HCl, 80 °C, 1 h	91[35]	2		MeCN, HCl, reflux, 3 h	93[13]
3		THF, 60 °C, overnight	93[36]	4		SF, μW, HCl, 80 °C, 1 h	73[35]
5		SF, μW, HCl, 80 °C, 1 h	93[35]	6		SF, μW, HCl, 80 °C, 1 h C_7H_8, reflux, aq. HCl, 80 C_7H_8, reflux, 1 h	89[35] 95[37] 80[15]
7		C_7H_8, reflux, 1 h	90[38]	8		C_7H_8, reflux, 1 h	88[15]
9		C_7H_8, reflux, 1 h	86[15]	10		C_7H_8, reflux, 1 h	74[38]
11		C_7H_8, reflux, 1 h	70[38]	12		C_7H_8, reflux, 1 h	83 [15]
13		C_7H_8, reflux, 1 h	73[38]	14		C_7H_8, reflux, 1 h	92[39]
15		C_7H_8, reflux, 1 h	96[15]	16		C_7H_8, reflux, 1 h	78[15]
17		THF, 40 °C, 1 h	80[15]	18		THF, 40 °C, 1 h	82[15]
19		C_7H_8, reflux, 1 h	90[38]	20		C_7H_8, reflux, 1 h	87[15]
21		C_7H_8, reflux, 0.25 h	91[39]	22		C_7H_8, reflux, 1 h	94[38]

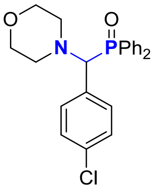
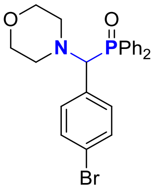
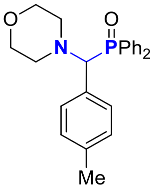
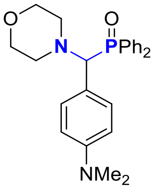
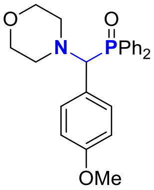
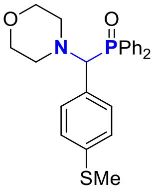
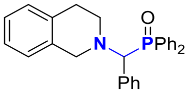
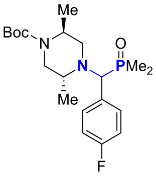
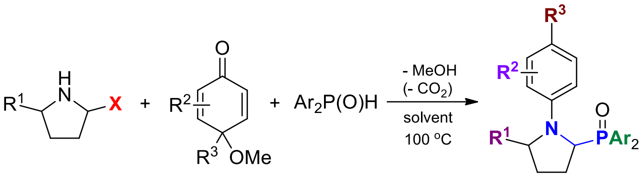
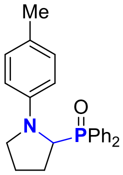
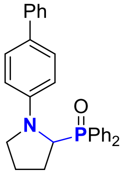
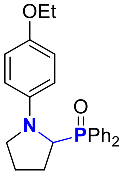
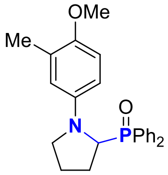
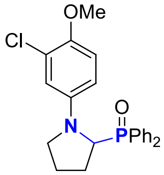
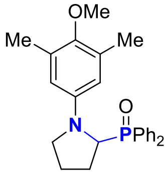
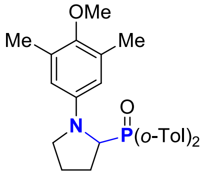
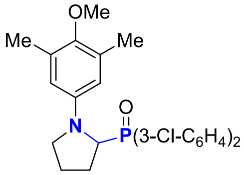
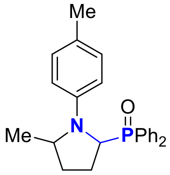
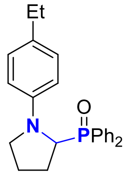
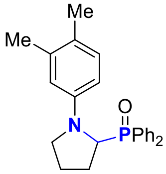
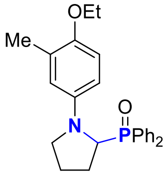
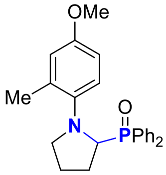
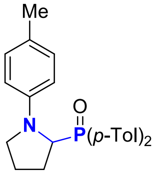
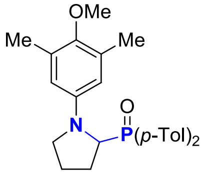
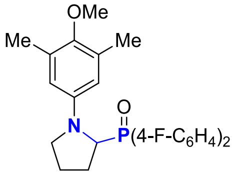
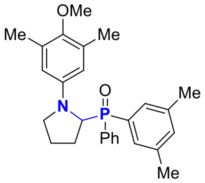
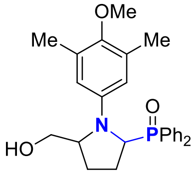
Entry	Product	Conditions	Yield,%
23		C_7H_8, reflux, 1 h	96[38]
24		C_7H_8, reflux, 1 h	79[38]
25		C_7H_8, reflux, 1 h	87[38]
26		C_7H_8, reflux, 1 h	90[38]
27		C_7H_8, reflux, 1 h	76[38]
28		C_7H_8, reflux, 1 h	89[38]
29		DCE, 90 °C, 3 h 4A MS, AgOAc	64[40]
30		C_7H_8, reflux, 16 h	85[41]

Table S4. *N*-Aryl 2-phosphinoyl pyrrolidines, obtained by reactions of SPOs with *p*-quinone monoacetals and pyrrolidine derivatives.



Entry	Product	X	Conditions	Yield,%
1		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	77[42]
		H	C_7H_8, AcOH, 100 °C, 3 h	80[43]
3		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	58[42]
		H	C_7H_8, AcOH, 100 °C, 3 h	60[43]
5		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	74[42]
7		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	80[42]
		H	C_7H_8, AcOH, 100 °C, 5 h	83[43]
9		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	45[42]
11		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	83[42]
		H	C_7H_8, AcOH, 100 °C, 5 h	83[43]
13		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	62[42]
		H	C_7H_8, AcOH, 100 °C, 5 h	57[43]
15		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	76[42]
17		H	C_7H_8, AcOH, 100 °C, 5 h	79[43]
2		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	74[42]
		H	C_7H_8, AcOH, 100 °C, 3 h	70[43]
4		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	77[42]
		H	C_7H_8, AcOH, 100 °C, 3 h	80[43]
6		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	72[42]
8		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	0[42]
10		H	C_7H_8, AcOH, 100 °C, 3 h	85[43]
12		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	80[42]
		H	C_7H_8, AcOH, 100 °C, 5 h	81[43]
14		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	82[42]
		H	C_7H_8, AcOH, 100 °C, 5 h	73[43]
16		CO_2H	MeCN/Et$_3$N, 100 °C, 24 h	80[42]
18		H	C_7H_8, AcOH, 100 °C, 4 h	25[43]

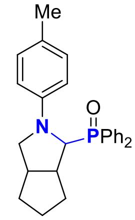
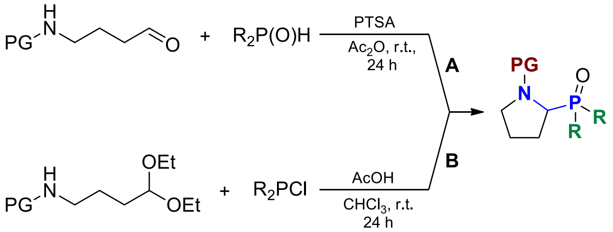
19		H	C_7H_8, AcOH, 100 °C, 10 h	40[43]	20

Table S5. *N*-Protected 2-phosphinoyl pyrrolidines, obtained by reactions of SPOs with 4-aminobutyraldehyde, or reactions of phosphinous chlorides with 4,4-diethoxybutan-1-amines.



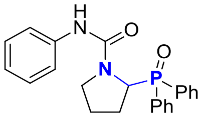
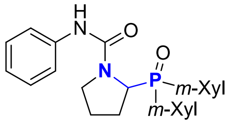
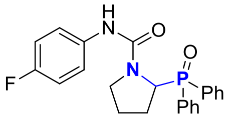
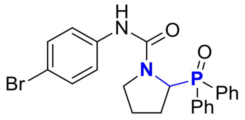
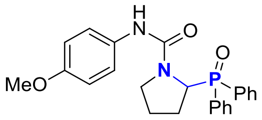
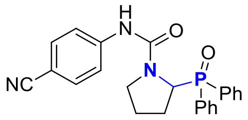
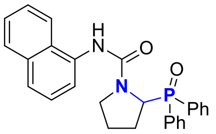
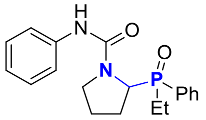
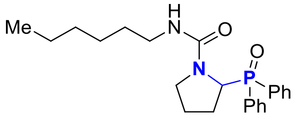
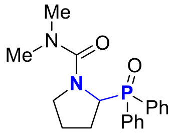
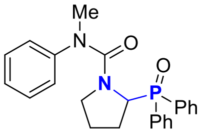
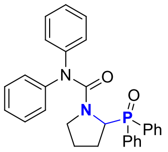
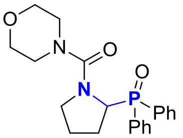
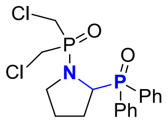
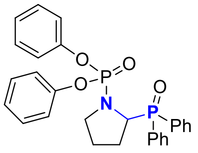
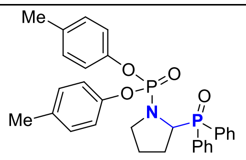
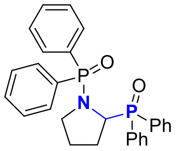
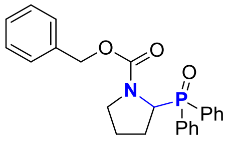
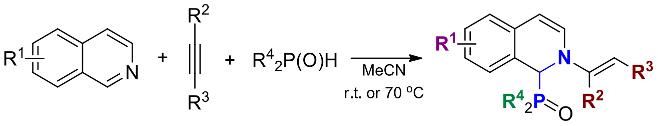
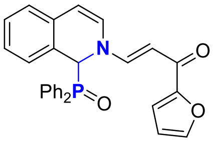
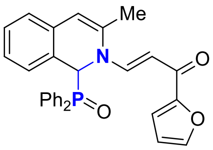
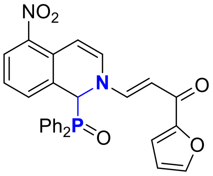
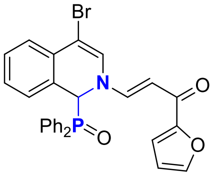
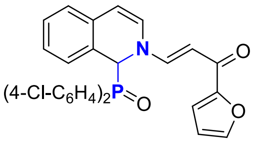
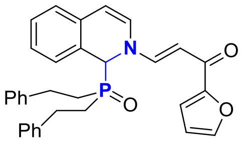
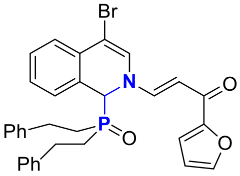
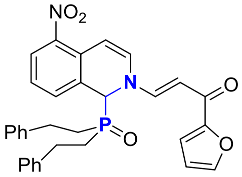
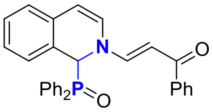
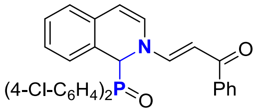
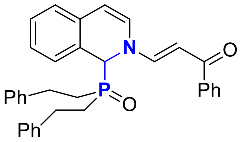
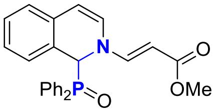
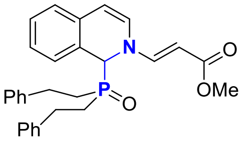
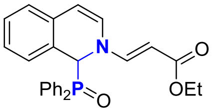
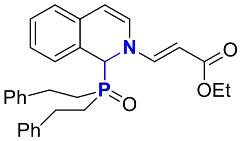
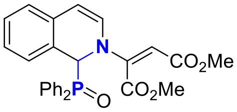
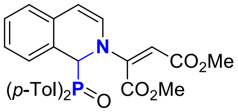
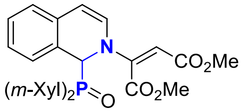
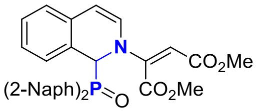
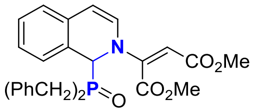
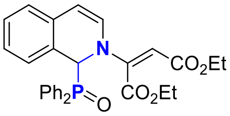
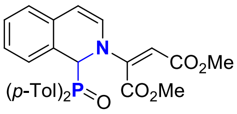
Entry	Product	Path	Yield,%	Entry	Product	Path	Yield,%
1		**B**	69[44]	2		**B**	47[44]
3		**B**	52[44]	4		**B**	55[44]
5		**B**	47[44]	6		**B**	78[44]
7		**B**	82[45]	8		**B**	25[44]
9		**B**	45[44]	10		**B**	46[45]
11		**B**	58[45]	12		**B**	73[44]
13		**B**	73[45]	14		**B**	48[46]
15		**B**	82[46]	16		**B**	67[44]
17		**B**	75[46]	18		**A**	67[47,48]

Table S6. P(O),N-acetals, obtained by reactions of SPOs with isoquinolines in the presence of acetylenes.



Entry	Product	Conditions	Yield,%	Entry	Product	Conditions	Yield,%
1		MeCN, r.t., 5 h	91[49]	2		MeCN, r.t., 4 h	74[49]
3		MeCN, r.t., 7 h	87[49]	4		MeCN, r.t., 8 h	91[49]
5		MeCN, r.t., 10 h	65[49]	6		MeCN, r.t., 8 h	70[49]
7		MeCN, r.t., 10 h	80[49]	8		MeCN, r.t., 12 h	87[49]
9		MeCN, r.t., 3 h	87[49]	10		MeCN, r.t., 7 h	78[49]
11		MeCN, r.t., 6 h	82[49]	12		MeCN, 70 °C, 1.5 h	93[50,51]
13		MeCN, 70 °C, 2.5 h	85[50,51]	14		MeCN, 70 °C, 1.5 h	87[50,51]
15		MeCN, 70 °C, 3 h	87[50,51]	16		MeCN, r.t., 1 h	83[52,53]
17		MeCN, r.t., 1 h	85[52,53]	18		MeCN, r.t., 1 h	83[52,53]
19		MeCN, r.t., 1 h	73[52,53]	20		MeCN, r.t., 1 h	71[52,53]
21		MeCN, r.t., 1 h MeCN, 70 °C, 1.5 h	80[52,53] 60[50,51]	22		MeCN, r.t., 1 h	81[52,53]

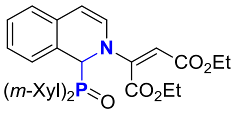
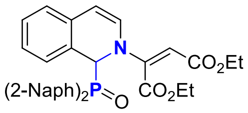
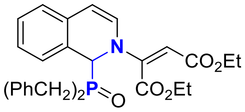
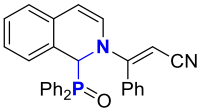
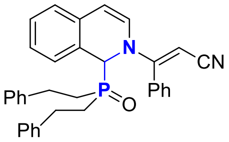
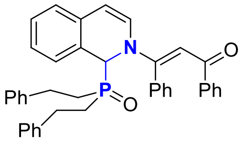
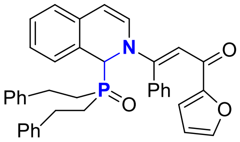
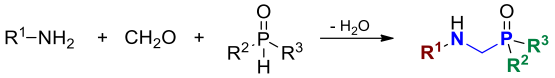
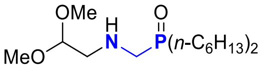
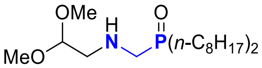
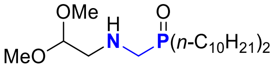
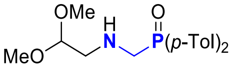
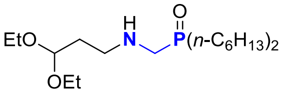
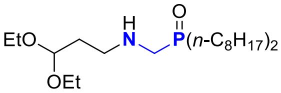
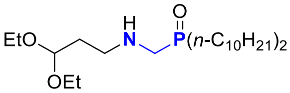
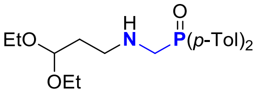
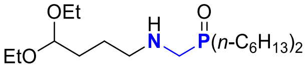
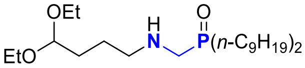
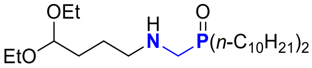
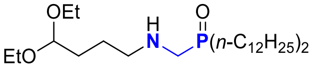
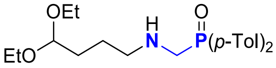
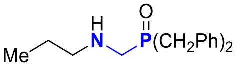
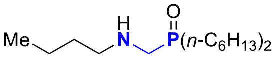
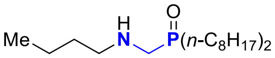
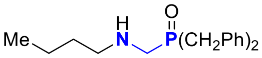
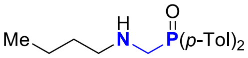
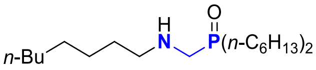
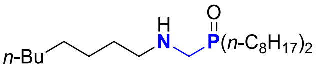
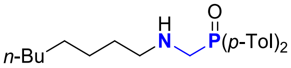
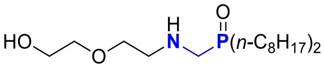
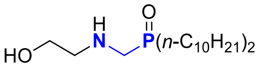
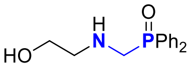
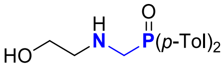
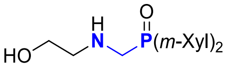
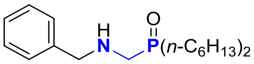
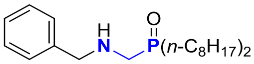
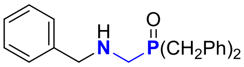
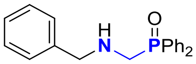
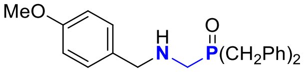
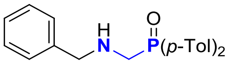
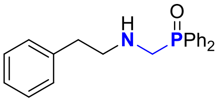
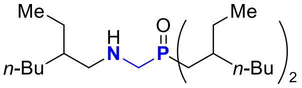
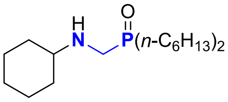
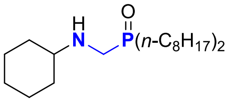
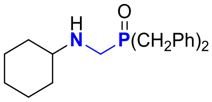
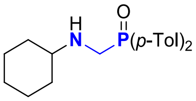
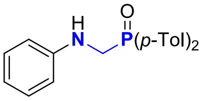
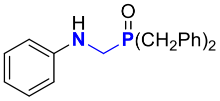
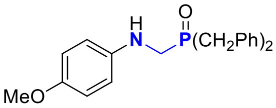
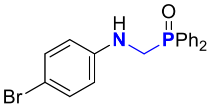
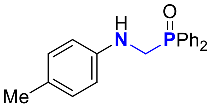
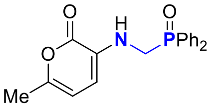
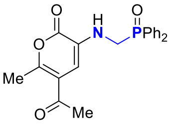
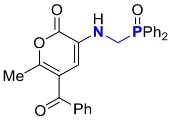
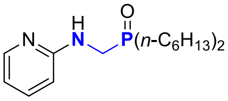
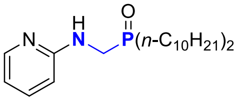
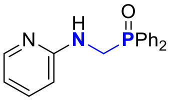
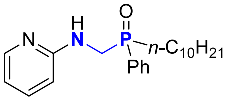
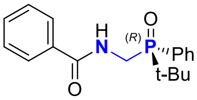
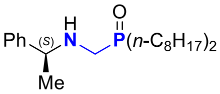
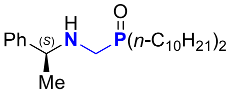
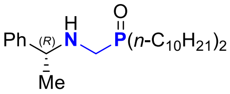
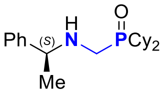
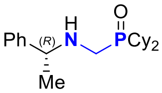
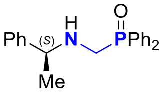
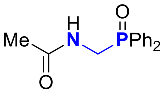
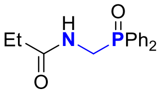
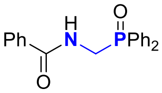
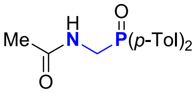
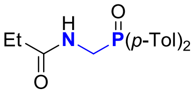
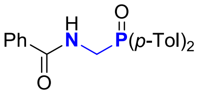
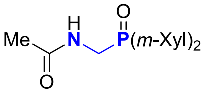
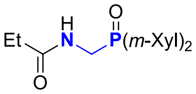
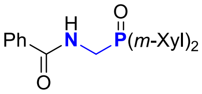
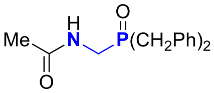
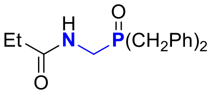
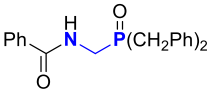
23		MeCN, r.t., 1 h	79[52,53]
24		MeCN, r.t., 1 h	70[52,53]
25		MeCN, r.t., 1 h MeCN, 70 °C, 1.5 h	70[52,53] 74[50,51]
26		MeCN, r.t., 16 h	93[54]
27		MeCN, r.t., 20 h	89[54]
28		MeCN, 70 °C, 72 h	51[49]
29		MeCN, 70 °C, 65 h	65[49]
30			

Table S7. P(O),NH-acetals, obtained by 3C-phospha-Mannich reactions between primary amines, CH_2O, and SPOs.



Entry	Product	Assistant	Conditions	Yield,%	Entry	Product	Assistant	Conditions	Yield,%
1		PTSA	C_6H_6, reflux, 3 h	91[55]	2		PTSA	C_6H_6, reflux, 6 h	93[56]
3		PTSA	C_6H_6, reflux, 6 h	95[56,57]	4		PTSA	C_6H_6, reflux, 7 h	93[57,58]
5		PTSA	C_6H_6, reflux, 4 h	75[59]	6		PTSA	C_6H_6, reflux, 4 h	68[59]
7		PTSA	C_6H_6, reflux, 4 h	82[59]	8		PTSA	C_6H_6, reflux, 7 h	98[57]
9		PTSA	C_6H_6, reflux, 4 h	81[59]	10		PTSA	C_6H_6, reflux	64[60]
11		PTSA	C_6H_6, reflux, 4 h	88[59]	12		PTSA	C_6H_6, reflux	53[60]
13		PTSA	C_6H_6, reflux, 6 h	92[61]	14		µW	MeCN, 100 °C, 1 h	96[62,63]
15		PTSA	C_6H_6, reflux	81[8]	16		PTSA	C_6H_6, reflux	98[8]
17		µW	MeCN, 100 °C, 1 h	98[62-64]	18		µW –	MeCN, 100 °C, 1 h C_6H_6, reflux, 4 h	96,[62,63] 97[64] 92[65]
19		PTSA	C_6H_6, reflux, 3-5 h	70,[12] 85[2]	20		PTSA	C_6H_6, reflux	80,[12] 89[2]
21		PTSA	C_6H_6, reflux	80[8]	22		PTSA	C_6H_6, reflux	73[2,66]
23		PTSA	C_6H_6, reflux	89[2,66]	24		µW	MeCN, 100 °C, 0.5 h	96[6,7]
25		µW	MeCN, 100 °C, 0.5 h	89[6,7]	26		µW	MeCN, 100 °C, 0.5 h	95[6,7]
27		PTSA	C_6H_6, reflux	90[2,66]	28		PTSA	C_6H_6, reflux	94[2,66]
29		µW	MeCN, 100 °C, 1 h	97,[64] 98[62,63]	30		– µW Na_2SO_4	SF, 120 °C, 2 h MeCN, 100 °C, 1 h C_7H_8, reflux, 24 h	45[a][10] 98[63] 62[67]

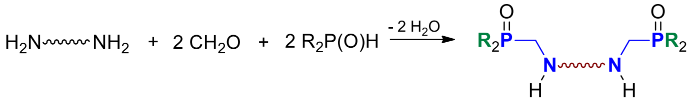
31		µW	MeCN, 100 °C, 1 h	95[62,63]	32		µW	MeCN, 100 °C, 1 h	94,[64] 95[62,63]
33		–	SF, 120 °C, 2 h	39[10]	34		PTSA	C_7H_8, reflux	92[68]
35		PTSA	C_6H_6, reflux	98[8]	36		PTSA	C_6H_6, reflux	82[8]
37		µW	MeCN, 100 °C, 1 h	96[62-64]	38		µW	MeCN, 100 °C, 1 h	98[62-64]
39		µW	MeCN, 100 °C, 1 h	94[62,63]	40		µW – –	MeCN, 100 °C, 1 h SF, 150 °C, 9 h SF, 160–170 °C, 9 h	94[62,63] 73[69] 72[70]
41		µW	MeCN, 100 °C, 1 h	95[62,63]	42		Na_2SO_4	C_7H_8, reflux, 24 h	73[67]
43		Na_2SO_4	C_7H_8, reflux, 24 h	31[67]	44		µW	MeCN, 100 °C, 3 h	98[71,72]
45		µW	MeCN, 100 °C, 2 h	98[71,72]	46		µW	MeCN, 100 °C, 2 h	97[71,72]
47		PTSA	C_6H_6, reflux	70[66]	48		PTSA	MeCN, reflux	~70[8]
49		–	SF, 120 °C, 2 h	26[a][10]	50		PTSA	C_7H_8, reflux, 5 h	88[73,74]
51		–	C_7H_8, reflux, 15 h	66[75]	52		PTSA	C_7H_8, reflux	95[73]
53		PTSA	C_7H_8, reflux	95[73]	54		PTSA	C_7H_8, reflux, 3 h	94[74]
55		PTSA	C_7H_8, reflux	92[73]	56		PTSA	C_7H_8, reflux	93[73]
57		µW	MeCN, 100 °C, 1 h	97[76]	58		µW	SF, 220-240 °C, 3.5 h[b]	72[63,77]

59		μW	SF, 220-240 °C, 3.5 h^b	91[63,77]	60		μW	SF, 220-240 °C, 3.5 h^b	78[63,77]
61		μW	SF, 220-240 °C, 3.5 h^b	85[63,77]	62		μW	SF, 220-240 °C, 3.5 h^b	89[63,77]
63		μW	SF, 220-240 °C, 3.5 h^b	78[63,77]	64		μW	SF, 220-240 °C, 3.5 h^b	75[63,77]
65		μW	SF, 220-240 °C, 3.5 h^b	66[63,77]	66		μW	SF, 220-240 °C, 3.5 h^b	58[63,77]
67		μW	SF, 220-240 °C, 3.5 h^b	93[63,77]	68		μW	SF, 220-240 °C, 3.5 h^b	62[63,77]
69		μW	SF, 220-240 °C, 3.5 h^b	64[63,77]	70				

a Isolated as a hydrochloride

b 10-fold excess of the amide was used

Table S8. 3C-Phospa-Mannich reactions of primary diamines, CH_2O, and SPOs.



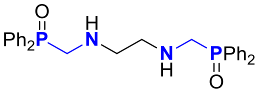
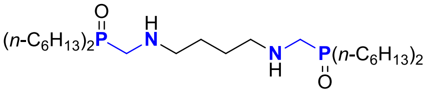
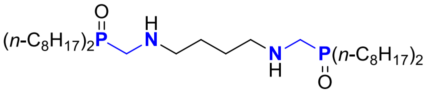
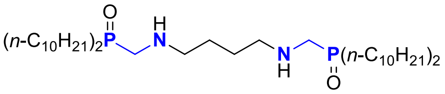
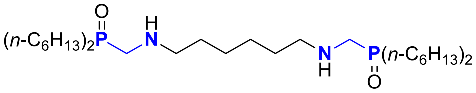
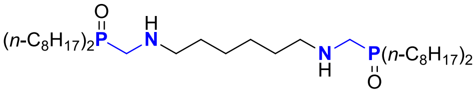
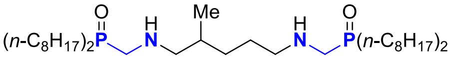
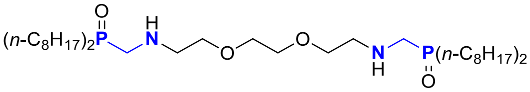
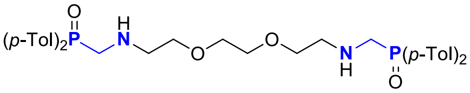
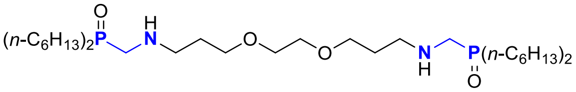
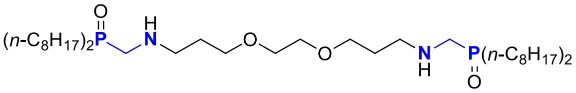
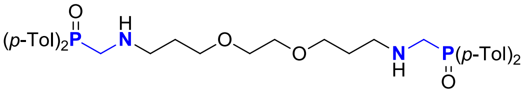
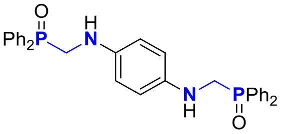
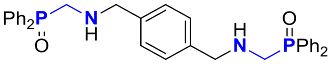
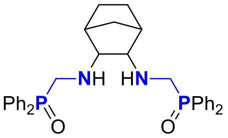
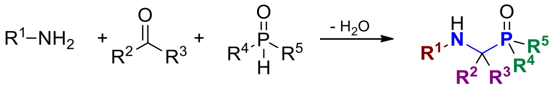
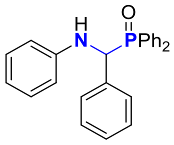
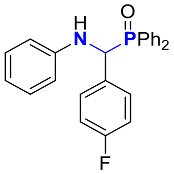
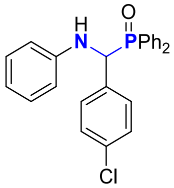
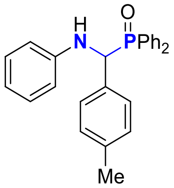
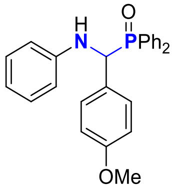
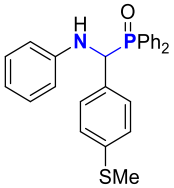
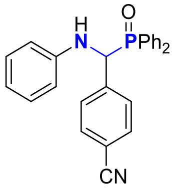
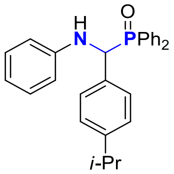
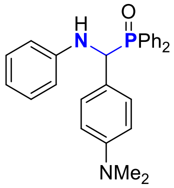
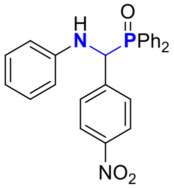
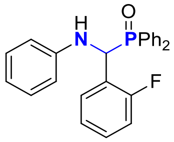
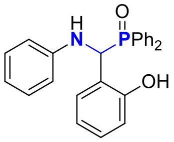
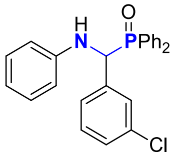
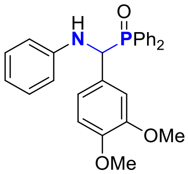
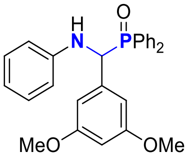
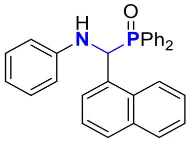
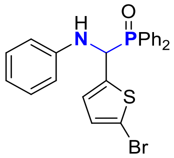
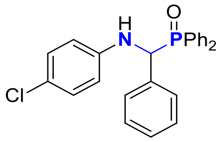
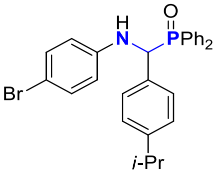
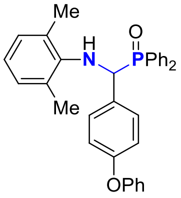
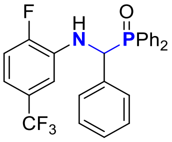
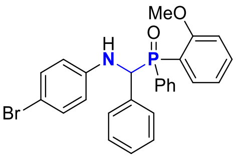
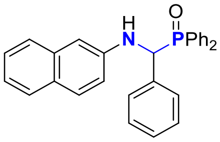
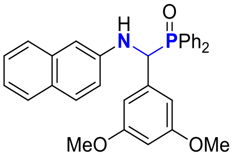
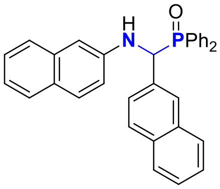
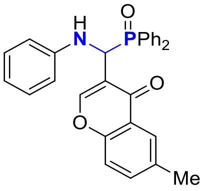
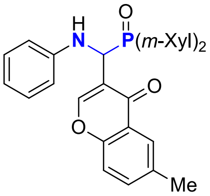
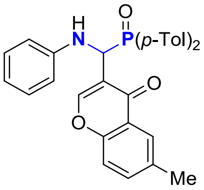
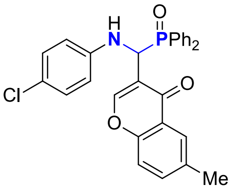
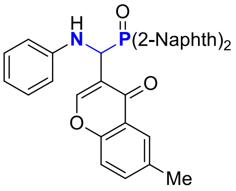
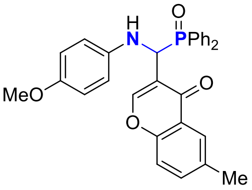
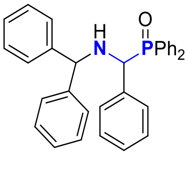
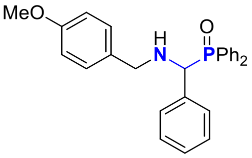
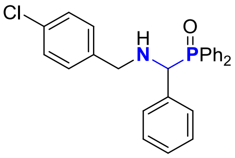
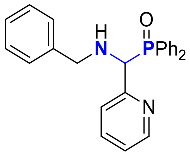
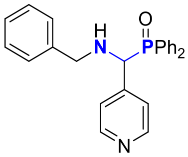
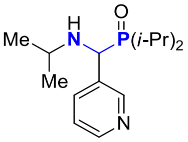
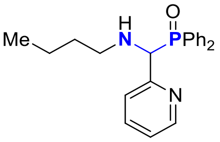
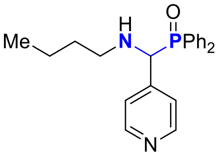
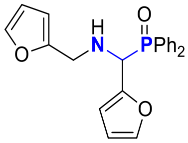
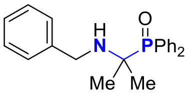
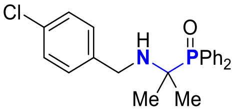
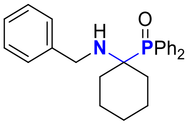
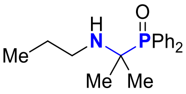
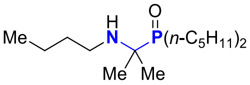
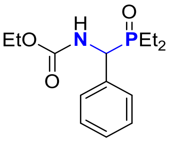
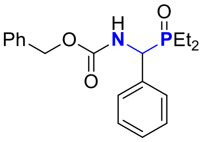
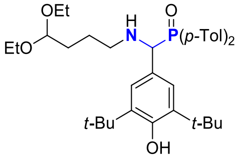
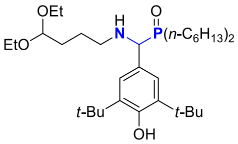
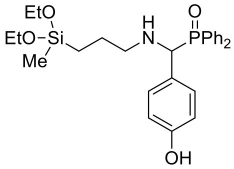
Entry	Product	Assistant	Conditions	Yield, %
1		–	C_6H_6, 140–150 °C, 4 h	69[78]
2		PTSA	C_7H_8, reflux, 4 h	85[66,79,80]
3		PTSA	C_7H_8, reflux, 4 h	72[81]
4		PTSA	C_7H_8, reflux	75[8]
5		PTSA	C_7H_8, reflux, 4 h	85[66]
6		PTSA	C_7H_8, reflux	85[8,80]
7		PTSA	C_7H_8, reflux, 4 h	90[66,80,82]
8		PTSA	C_7H_8, reflux	69[66]
9		PTSA	C_6H_6-Pet. ether, reflux, 4 h	85[83]
10		PTSA	C_7H_8, reflux, 4 h	83[80]
11		PTSA	C_7H_8, reflux, 4 h	79[66,80,82]
12		PTSA	C_7H_8, reflux, 3 h	54[84,85]
13		–	DMF, 70 °C, 8 h	87[86]
14		–	C_6H_6, 140 °C, 4 h	28[78]
15		–	C_6H_6, 120–160 °C, 4.5 h	40[78]

Table S9. P(O),NH-acetals, obtained by 3C-phospha-Mannich reactions of primary amines with SPOs and carbonyl compounds.



Entry	Product	Assistant	Conditions	Yield, %
1		–	EtOH, r.t., 0.5 h	80[87]
		Indium complex	SF, r.t., 6 h	96[88]
		$AgSbF_6$	SF, r.t., 6 h	94[89]
2		Indium complex	SF, r.t., 6 h	94[88]
3		Indium complex	SF, r.t., 6 h	98[88]
		$AgSbF_6$	SF, r.t., 6 h	92[89]
4		Indium complex	SF, r.t., 6 h	96[88]
		$AgSbF_6$	SF, r.t., 6 h	87[89]
5		Indium complex	SF, r.t., 6 h	98[88]
		$AgSbF_6$	SF, r.t., 6 h	94[89]
6		Indium complex	SF, r.t., 6 h	98[88]
7		Indium complex	SF, r.t., 6 h	86[88]
		$AgSbF_6$	SF, r.t., 6 h	92[89]
8		Indium complex	SF, r.t., 6 h	95[88]
9		Indium complex	SF, r.t., 6 h	92[88]
10		Indium complex	SF, r.t., 6 h	96[88]
		$AgSbF_6$	SF, r.t., 6 h	88[89]
11		Indium complex	SF, r.t., 6 h	95[88]
12		–	C_7H_8, r.t., 4 h	90[90]
13		Indium complex	SF, r.t., 6 h	94[88]
		$AgSbF_6$	SF, r.t., 6 h	90[89]
14		In (2 mol%)	SF, r.t., 6 h	94[88]
15		ZrO_2 ball mill	SF, 600 rpm, 4 h	99[91]
16		$AgSbF_6$	SF, r.t., 6 h	80[89]

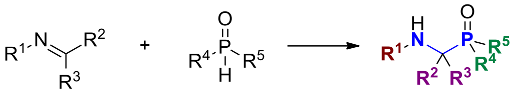
17		$AgSbF_6$	SF, r.t., 6 h	82[89]	18		ZrO_2 ball mill	SF, 600 rpm, 4 h	95[91]
19		Indium complex	SF, r.t., 6 h	97[88]	20		Indium complex	SF, r.t., 6 h	96[88]
21		–	C_7H_8, 100 °C, 8 h	92[92]	22		–	C_7H_8, reflux, 24 h	80[67]
23		ZrO_2 ball mill	SF, 600 rpm, 4 h	93[91]	24		ZrO_2 ball mill	SF, 600 rpm, 4 h	95[91]
25		ZrO_2 ball mill	SF, 600 rpm, 4 h	99[91]	26		–	MeCN, r.t., 1 h	94[53,93]
27		–	MeCN, r.t., 1 h	93[53,93]	28		–	MeCN, r.t., 1 h	95[53,93]
29		–	MeCN, r.t., 1 h	93[53,93]	30		–	MeCN, r.t., 1 h	94[53,93]
31		–	MeCN, r.t., 1 h	94[53,93]	32		Indium complex	SF, r.t., 6 h	95[88]
33		In (2 mol%)	SF, r.t., 6 h	96[88]	34		In (2 mol%)	SF, r.t., 6 h	92[88]

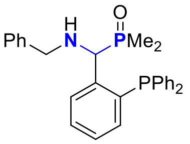
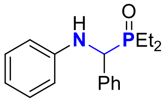
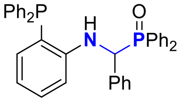
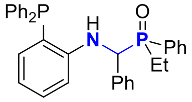
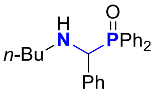
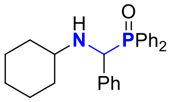
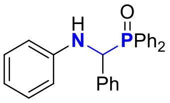
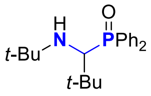
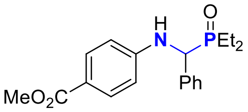
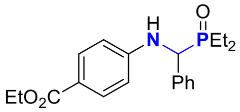
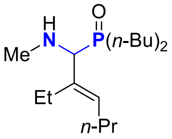
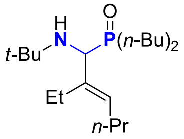
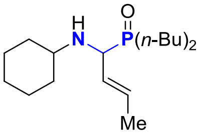
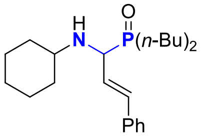
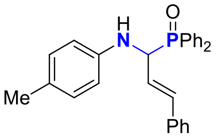
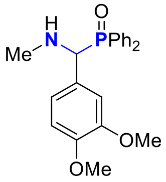
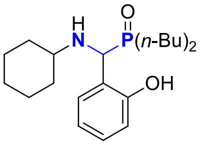
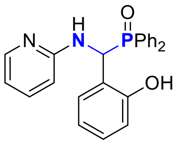
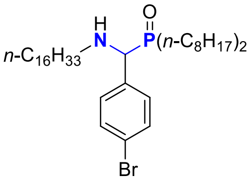
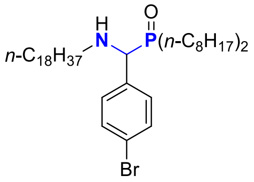
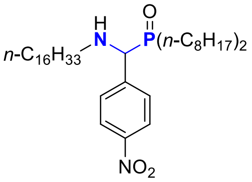
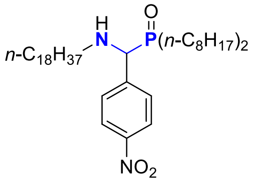
35		–	CH_2Cl_2, r.t., 24 h	88[94]
36		–	CH_2Cl_2, r.t., 24 h	72[94]
37		–	–	–[a] [95]
38		–	CH_2Cl_2, r.t., 24 h	81[94]
39		–	CH_2Cl_2, r.t., 24 h	86[94]
40		–	SF, 50 °C, 24 h	–[b] [96]
41		µW, SiO_2	SF, minutes	68[97,98]
		µW	SF, 100 °C, 0.5 h	80[99]
42		µW, SiO_2	SF, minutes	65[97,98]
43		µW	SF, 100 °C, 0.5 h	80[99]
44		µW, SiO_2	SF, minutes	69[97,98]
45		–	C_6H_6, reflux, 3 h	38[100]
46		CF_3CO_2H	Ac_2O, r.t.	54[101]
47		–	Ac_2O/AcCl, r.t.	67[102]
48		PTSA	C_6H_6, reflux	55[60]
49		PTSA	C_6H_6, reflux	83[60]
50		–	EtOH, 90 °C, 12 h	87[103]

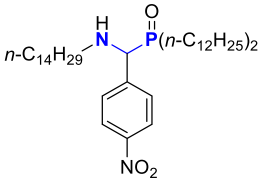
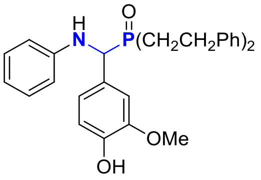
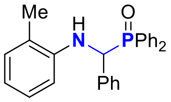
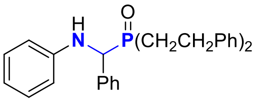
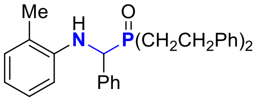
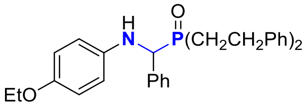
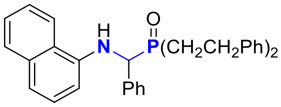
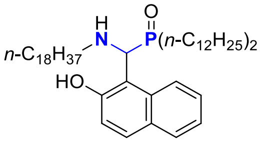
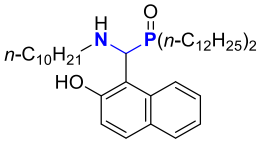
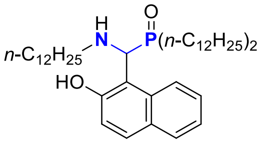
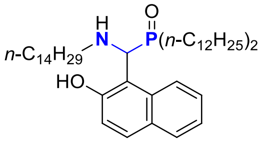
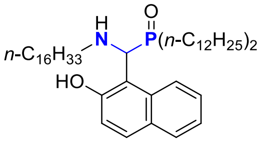
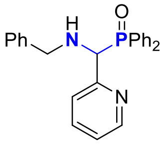
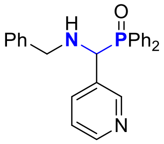
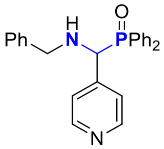
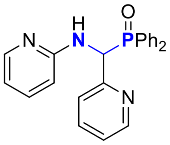
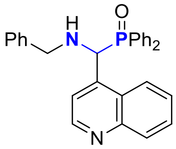
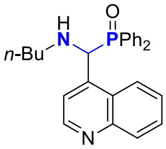
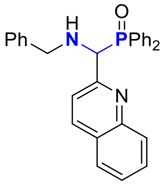
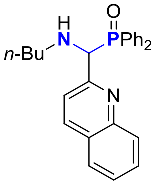
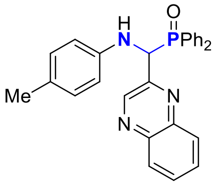
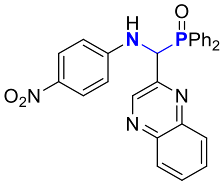
[a] Conditions and yield are not given.

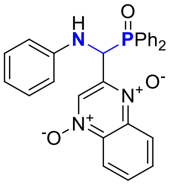
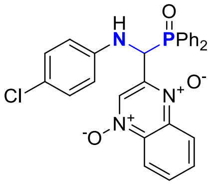
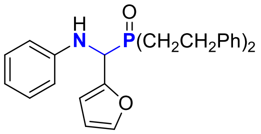
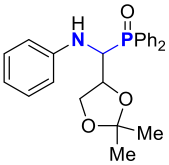
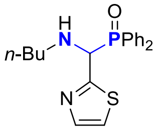
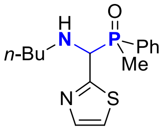
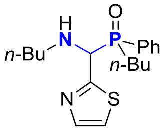
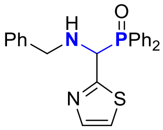
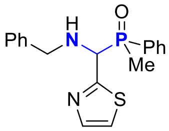
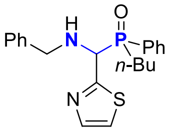
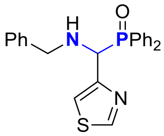
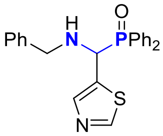
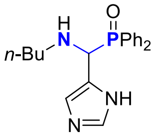
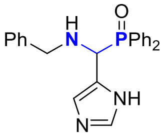
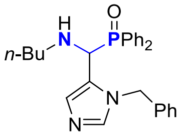
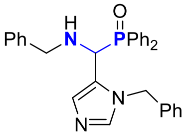
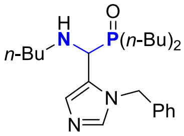
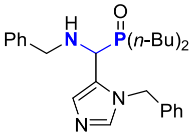
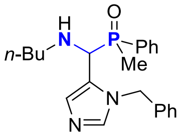
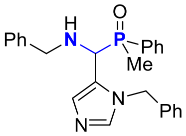
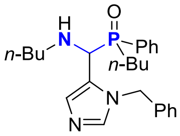
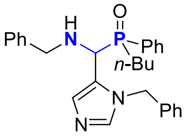
[b] Yield is not reported.

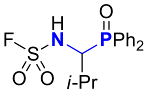
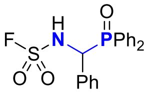
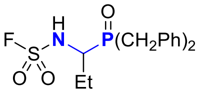
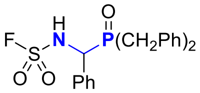
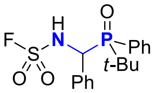
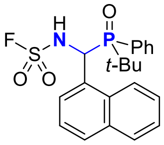
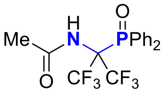
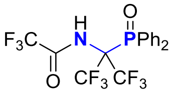
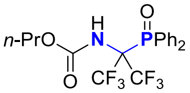
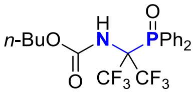
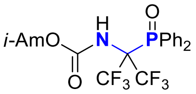
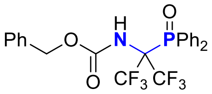
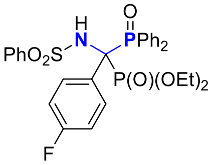
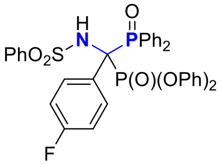
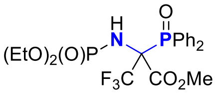
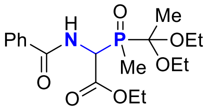
Table S10. P(O),NH-acetals, obtained by 2C-phospha-Mannich reactions between imines and SPOs.



Entry	Product	Assistant	Conditions	Yield,%
1		*t*-BuOK	$(MeOCH_2)_2$, 80 °C, 2 h	68[104,105]
2		–	C_6H_6-$C_5H_5N^+$	20[106]
3		–	C_7H_8, reflux, 2 h	78[107]
4		–	C_7H_8, reflux, 6 h	80[107]
5		µW	SF, 100 °C, 10 min	89[7,108]
6		µW	SF, 100 °C, 10 min	88[7,108]
7		–	SF, 80 °C, 10 min	89[7,108]
		–	C_7H_8, 60 °C, 2.5 h	88[110]
8		CdI_2	C_6H_6, 40 °C, 1.5 h	52[109]
9		–	C_6H_6-$C_5H_5N^+$	25[106]
10		–	C_6H_6-$C_5H_5N^+$	20[106]
11		–	SF, 50 °C, 30 h	88[111]
12		–	SF, 50 °C, 30 h	92[111]
13		–	SF, r.t., 24 h	78[111]
14		–	SF, r.t., 24 h	92[111]
15		–	C_6H_6, 60 °C, 0.5 h	73[112]
16		–	C_7H_8, reflux, 1 h	95[113]
17		–	Et_2O, reflux, 20 h	75[114]
18		–	C_7H_8, 110 °C, 30 min	82[115]
19		–	EtOH, reflux, 16 h	77[116]
20		–	EtOH, reflux, 16 h	81[116]
21		–	EtOH, reflux, 16 h	76[116]
22		–	EtOH, reflux, 16 h	82[116]

23		PTSA	C_6H_6, reflux, 5 h	80**[117]	24		–	SF, 65 °C, 58 h	90[118]
25		–	SF, r.t., 0.25 h	98[118]	26		–	SF, 65 °C, 4.5 h	87[118]
27		–	SF, 65 °C, 20.5 h	60[118]	28		–	SF, 55 °C, 5.5 h	85[118]
29		–	SF, 65 °C, 65.5 h	90[118]	30		–	EtOH, reflux, 25 h	56[119]
31		–	EtOH, reflux, 25 h	62[119]	32		–	EtOH, reflux, 25 h	65[119]
33		–	EtOH, reflux, 25 h	73[119]	34		–	EtOH, reflux, 25 h	52[119]
35		–	$CHCl_3$, r.t., 24 h	88[120]	36		–	$CHCl_3$, r.t., 24 h	94[120]
37		–	$CHCl_3$, r.t., 24 h	91[120]	38		–	C_7H_8, 110 °C, 0.5 h	74[115]
39		–	C_7H_8, reflux, 1 h	65[121]	40		–	C_7H_8, reflux, 1 h	77[121]
41		–	C_7H_8, reflux, 1 h	52[121]	42		–	C_7H_8, reflux, 1 h	57[121]
43		MeONa	EtOH, 0 °C, 0.5 h	83[122,123]	44		MeONa	EtOH, 0 °C, 0.5 h	54[122,123]

45		MeONa	EtOH, 0 °C, 2 h	79[122,123]	46		MeONa	EtOH, 0 °C, 2 h	62[122,123]
47		–	SF, 65 °C, 17 h	98[118]	48		–	C_6H_6, r.t., 2.5 h	67[124,125]
49		–	C_7H_8, reflux, 2 h	65[126]	50		–	C_7H_8, reflux, 2 h	62***[126]
51		–	C_7H_8, reflux, 2 h	67***[126]	52		–	C_7H_8, reflux, 2 h	58[126]
53		–	C_7H_8, reflux, 2 h	57***[126]	54		–	C_7H_8, reflux, 2 h	58***[126]
55		–	C_7H_8, reflux, 2 h	75[127]	56		–	C_7H_8, reflux, 2 h	70[127]
57		–	C_7H_8, reflux, 1 h	48[128]	58		–	C_7H_8, reflux, 1 h	89[128]
59		–	CH_2Cl_2, reflux, 2 h	63[129]	60		–	CH_2Cl_2, reflux, 2 h	55[129]
61		–	CH_2Cl_2, reflux, 2 h	56***[129]	62		–	CH_2Cl_2, reflux, 2 h	52***[129]
63		–	CH_2Cl_2, reflux, 2 h	62***[129]	64		–	CH_2Cl_2, reflux, 2 h	56***[129]
65		–	CH_2Cl_2, reflux, 2 h	65***[129]	66		–	CH_2Cl_2, reflux, 2 h	56***[129]

67		–	Et_2O, r.t., 0.5 h	90[130]	68		–	Et_2O, r.t., 0.5 h	90[130]
69		–	Et_2O, r.t., 0.5 h	90[130]	70		–	Et_2O, r.t., 0.5 h	97[130]
71		–	Et_2O, r.t., 0.5 h	86[130]	72		–	Et_2O, r.t., 0.5 h	91[130]
73		–	Et_2O, r.t., overnight	92[131]	74		–	Et_2O, r.t., 1 h	72[132]
75		–	Et_2O, r.t., 1 h	68[132]	76		–	Et_2O, r.t., 1 h	83[132]
77		–	Et_2O, r.t., 1 h	88[132]	78		–	Et_2O, r.t., 1 h	93[132]
79		–	C_6H_6, r.t., 1 h	64[133]	80		–	C_6H_6, r.t., 1 h	91[134]
81		–	Et_2O, r.t., 1 h	72[135]	82		–	C_7H_8	(–)*[136]

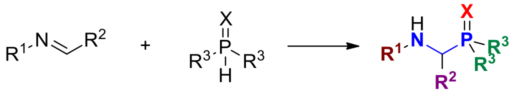
+ $Et_2P(O)H$ was formed in situ by hydrolysis of Et_2PCl in the presence of pyridine.

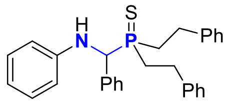
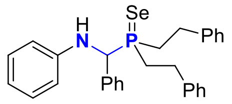
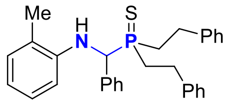
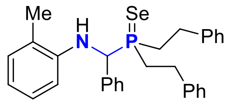
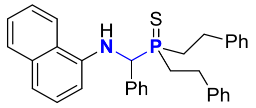
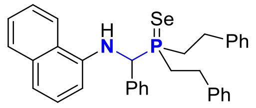
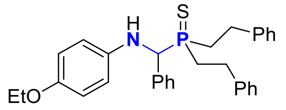
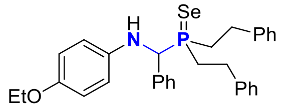
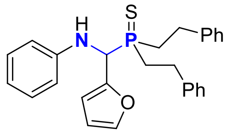
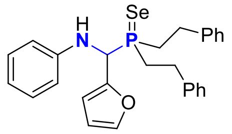
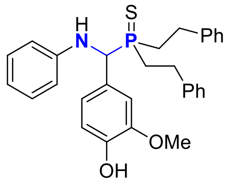
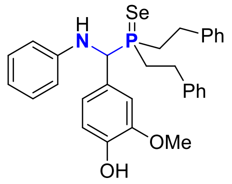
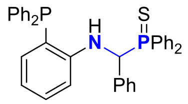
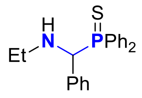
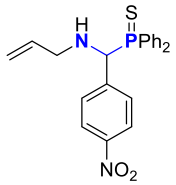
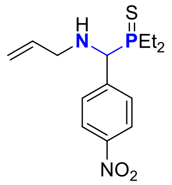
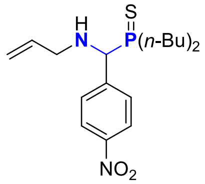
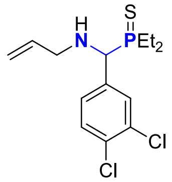
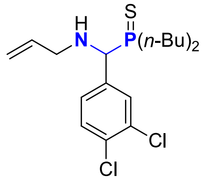
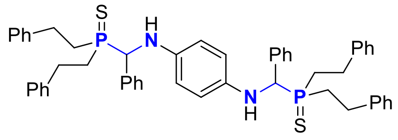
* Not isolated

** Isolated as tosylate

*** Isolated as oxalate

Table S11. P(S),NH- and P(Se),NH-acetals, obtained by reaction of imines with secondary phosphine sulfides and selenides, respectively.



Entry	Product	Conditions	Yield,%	Entry	Product	Conditions	Yield,%
1		SF, r.t., 0.5 h	78[118]	2		SF, 55 °C, 5.5 h	81[118]
3		SF, 65 °C, 5 h	99[118]	4		SF, 65 °C, 5 h	87[118]
5		SF, 65 °C, 16 h	67[118]	6		SF, 55 °C, 6.5 h	70[118]
7		SF, 65 °C, 5 h	76[118]	8		SF, 55 °C, 4 h	86[118]
9		SF, 65 °C, 7 h	82[118]	10		SF, 55 °C, 5 h	93[118]
11		SF, 65 °C, 8.5 h	78[118]	12		SF, 55 °C, 11 h	90[118]
13		C_7H_8, r.t.-reflux	81[107]	14		Et_2O, reflux, 0.5 h	88[137,138]
15		Et_2O, reflux, 0.5 h	89[137,138]	16		Et_2O, reflux, 0.5 h	70[137,138]
17		Et_2O, reflux, 0.5 h	84[137,138]	18		Et_2O, reflux, 0.5 h	66[137,138]
19		Et_2O, reflux, 0.5 h	61[137,138]	20		SF, 65 °C	85[118]

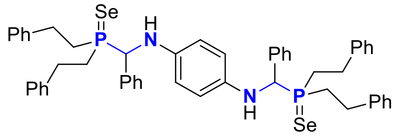
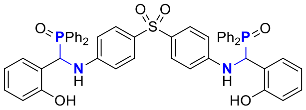
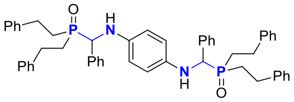
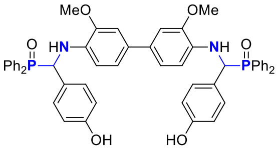
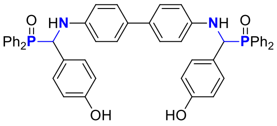
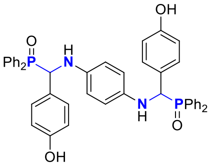
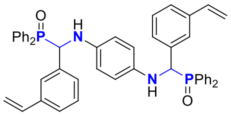
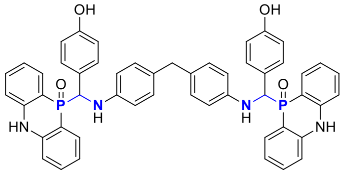
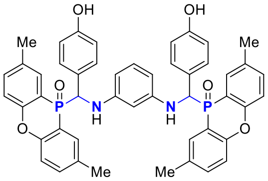
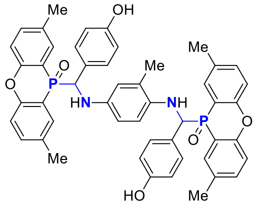
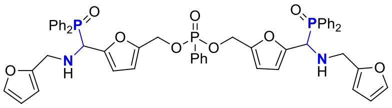
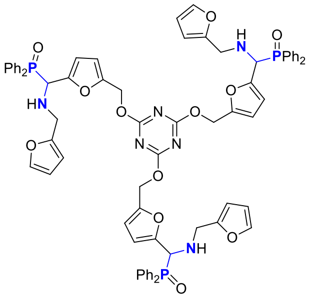
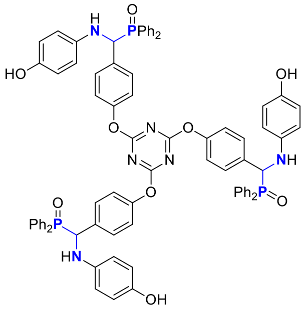
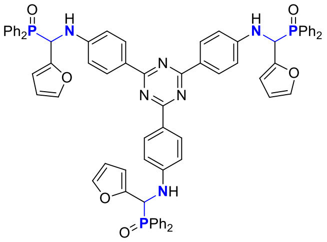
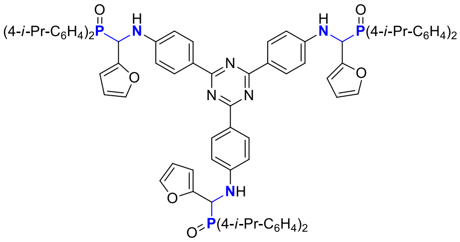
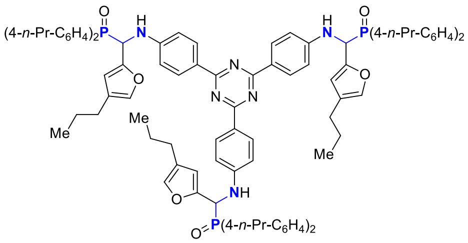
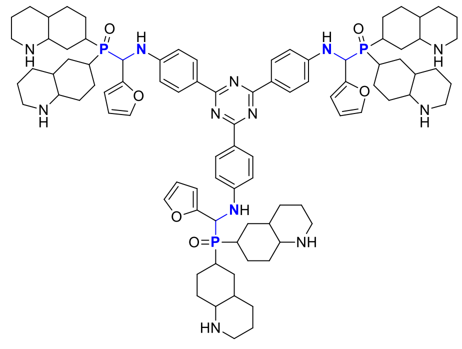
Entry	Product	Conditions	Yield,%	Entry	Product	Conditions	Yield,%
21		SF, 65 °C	77[118]	22			

Table S12. Bis- and tris-P(O),NH-acetals, obtained by reactions of SPOs with bis- and tris-imines, respectively.

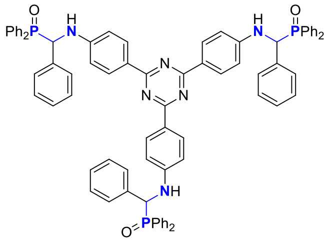
Product	Yield, %	Product	Yield, %
	91[139]		98[118]
	(-)*[140]		(-)*[140]
	(-)*[140]		(-)*[141]
	92[142,143]		(-)*[140]
	(-)*[140]		91[96]
	(-)*[144]		(-)*[145]
	77[146]		63[146]



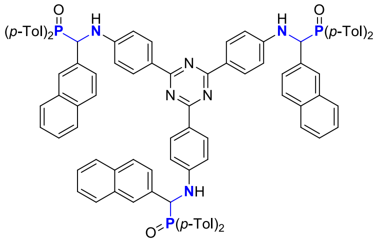
60[146]



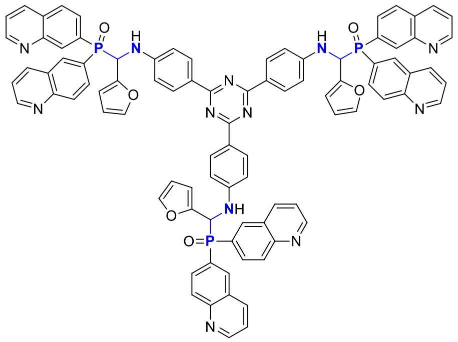
69[146]



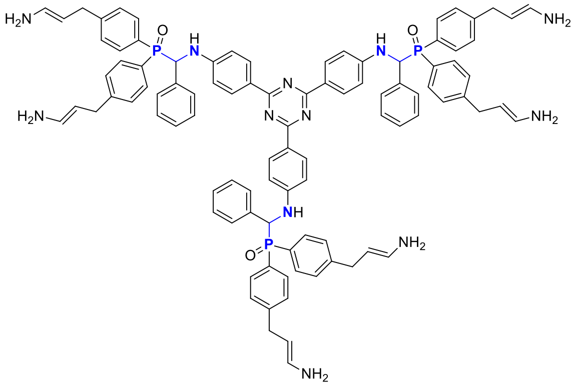
60[146]



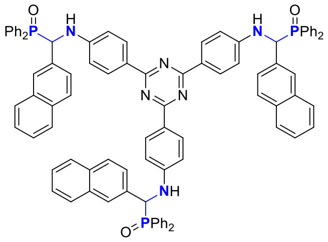
63[146]



58[146]



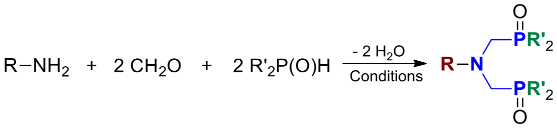
59[146]

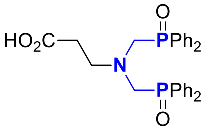
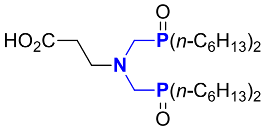
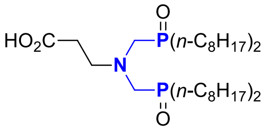
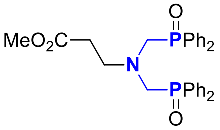
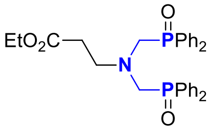
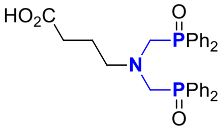
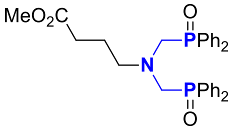
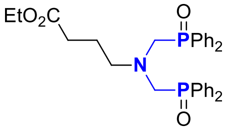
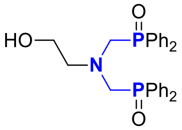
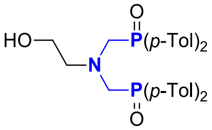
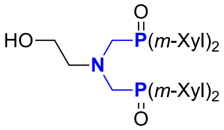
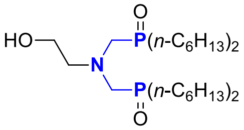
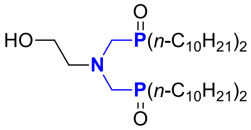
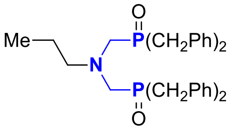
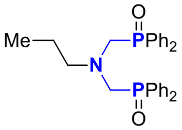
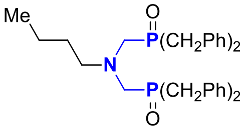
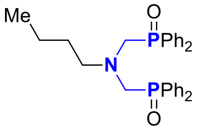
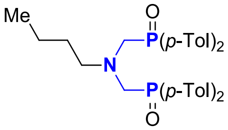
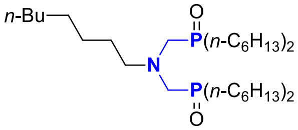
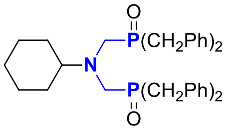
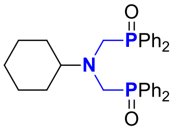
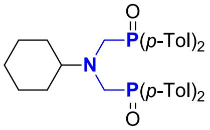
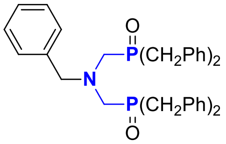
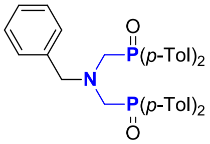
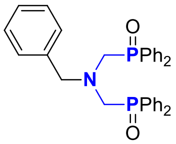
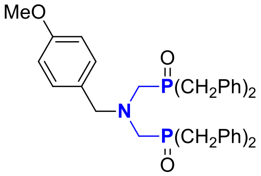


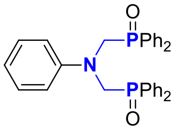
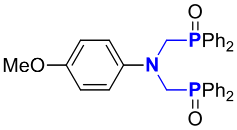
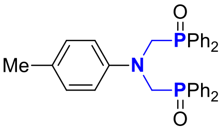
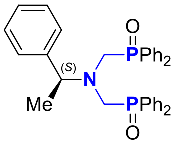
61[146]

* Yield is not reported.

Table S13. [P(O)]$_2$,N-acetals, obtained by 3C-phospha-Mannich reactions of primary amines with 2 equiv. both *p*-CH_2O and SPOs.

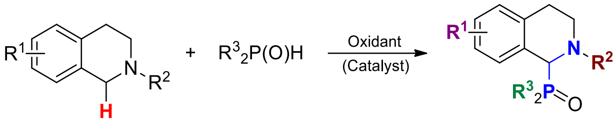


Entry	Product	Assistant	Conditions	Yield,%
1		μW	MeCN, 100 °C, 1 h	61[147]
2		–	MeCN, reflux, 3 h	93[a][148,149]
3		–	$CHCl_3$, reflux, 1 h	93[9]
		–	MeCN, reflux, 3 h	81[13,149,150]
4		μW	MeCN, 100 °C, 1 h	89[147]
5		μW	MeCN, 100 °C, 1 h	85[147]
6		μW	MeCN, 100 °C, 1 h	60[147]
7		μW	MeCN, 100 °C, 1 h	94[147]
8		μW	MeCN, 100 °C, 1 h	80[147]
9		μW	MeCN, 120 °C, 1 h	95[6,7]
10		μW	MeCN, 120 °C, 1 h	93[6,7]
11		μW	MeCN, 120 °C, 1 h	91[6,7]
12		PTSA	MeCN, reflux, 4 h	45[8]
13		PTSA	MeCN, reflux, 4 h	51[2]
14		μW	MeCN, 100 °C, 1 h	95[62,63]
15		μW	SF, 100 °C, 1 h	78[151,152]
16		μW	MeCN, 100 °C, 1 h	96[62,63]
17		μW	SF, 100 °C, 1 h	75[151,152]
18		μW	MeCN, 100 °C, 1 h	98[62,63]
19		PTSA	MeCN, reflux, 4 h	50[2]
20		μW	MeCN, 100 °C, 1 h	95[62,63]
21		μW	MeCN, 100 °C, 2 h	90[72,152,153]
22		μW	MeCN, 100 °C, 1 h	95[62,63]
23		μW	MeCN, 100 °C, 1 h	97[62,63]
24		μW	MeCN, 100 °C, 1 h	94[62,63]
25		μW	MeCN, 100 °C, 1.5 h	95[72,152,154,155]
26		μW	MeCN, 100 °C, 1 h	94[62,63]

27		μW	MeCN, 100 °C, 1.5 h	55[72,152,154]
28		μW	MeCN, 100 °C, 1.5 h	94[72,152,154,155]
29		μW	MeCN, 100 °C, 1.5 h	89[72,152,154]
30		μW	MeCN, 100 °C, 2 h	92[7,76,156]

[a] Isolated as a hydrochloride

Table S14. P(O),N-acetals, obtained by reactions of SPOs with *N*-substituted 1,2,3,4-tetrahydroisoquinolines in the presence of oxidant/activator.



CATALYST ABBRIVIATIONS:

Cobalt catalysts:

Co (**1**) = CoNiFe hydrotalcite

Co (**2**) = $Co(OAc)_2$ + *N*-hydroxyphthalimide

Co (**3**) = chloro(pyridine)cobaloxime, $[Co^{III}(dmgH)(py)Cl]$, dmgH = dimethylglyoximato

Co (**4**) = $H_{14}[(Co(H_2O)_3)_2(C_{10}H_8N_2)_4(P_4W_{30}Nb_6O_{123})]\cdot 4(C_{10}H_8N_2)\cdot 8H_2O$

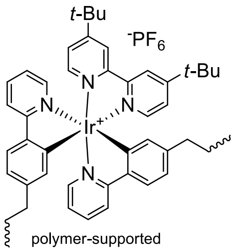
Gold catalysts:

Au (**1**) = $[(phen)AuCl_2]Cl$, phen = 1,10-phenanthroline

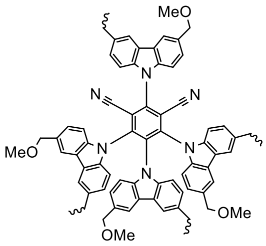
Au (**2**) = $[Au(tpy)Cl]Cl_2$, tpy= 2,6-di(isoquinolin-3-yl)pyridine

Copper catalyst :

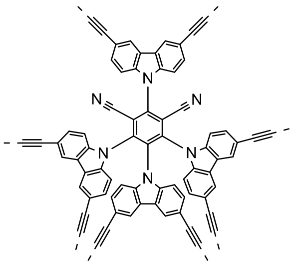
Cu (**1**) = $[Cu(Sal)_2(NCMe)]_2$ + *n*-$Bu_4N^+Cl^-$, Sal = salicylate



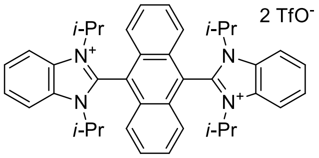
Iridium photocatalyst
Ir (**1**)



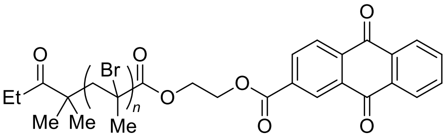
4CzIPN-based photocatalyst
4CzIPN (**1**)



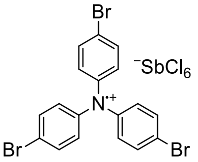
4CzIPN-based photocatalyst
4CzIPN (**2**)



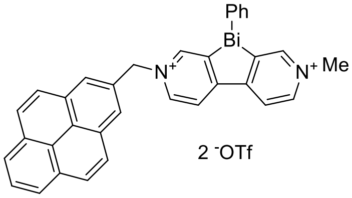
Anthracene-based photocatalyst
Ant (**1**)



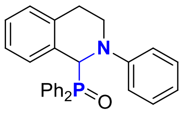
Anthraquinone-basesd photocatalyst
Ant (**2**)

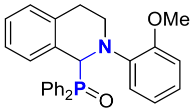
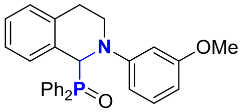
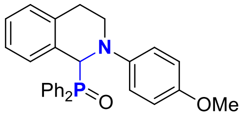
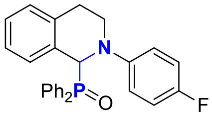
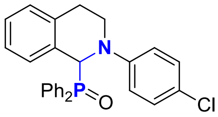
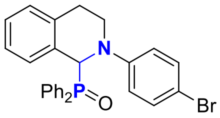


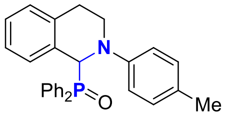
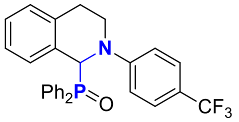
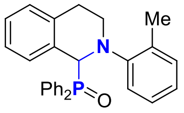
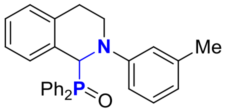
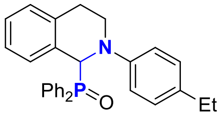
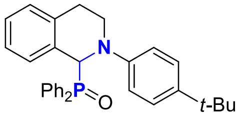
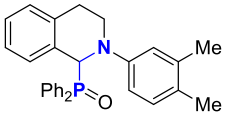
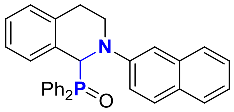
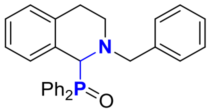
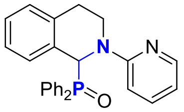
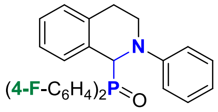
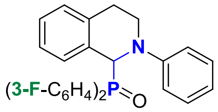
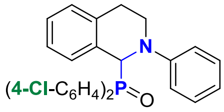
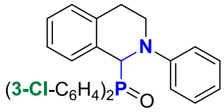
tris(4-bromophenyl)aminium
hexachloro-antimonate
TBPA

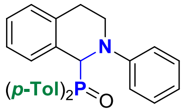
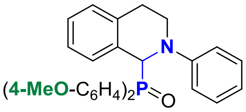
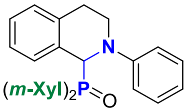
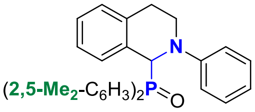
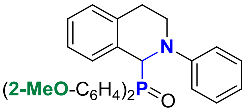
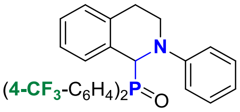
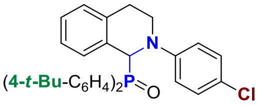
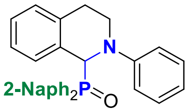
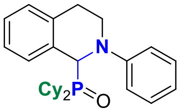
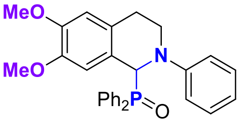
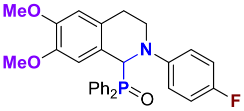
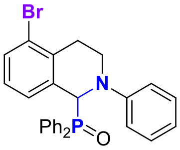


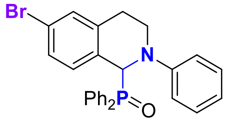
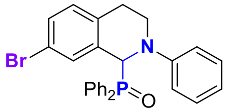
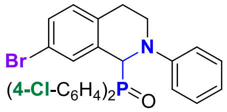
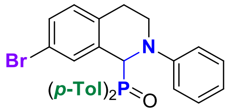
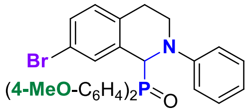
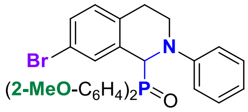
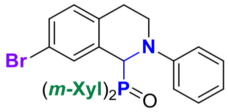
Bi (**1**)

Entry	Product	Catalyst	Oxidant	Conditions	Yield, %
1		–	*t*-BuOOH	MeCN, 80 °C, 24 h	85[157]
		Co (**1**)	O_2	Dioxane, 80 °C, 24 h	61[158]
		Co (**2**)	Air	MeCN, 80 °C, 16 h	85[159]
		Au (**1**)	Air	MeCN, 60 °C, 5 h	85[160]
		TBPA	Air	THF, r.t., 5–8 h	86[161]
		Ir (**1**)	Air	MeOH, 7.1W white LED, r.t., 14 h	92[162]
		Au (**2**)	Air	MeCN, 5W blue LED, r.t., 24 h	87[163]
		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	76[164]
		Ant (**2**)	Air	MeOH, purple LED, r.t., 24 h	86[165]

Entry	Product	Catalyst	Oxidant	Conditions	Yield, %
		–	*N*-ethoxy-2-methylpyridinium BF_4	DMF, $NaHCO_3$, 5W blue LED, r.t., 15 h	91[166]
		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	92[167,168]
		4CzIPN (**2**)	O_2	Ethylene glycol, 3W blue LED, r.t., 6 h	74[169]
		$FeCl_3$	Air	EtOH, 60 °C	40[170]
		Co (**3**)	–	CH_2Cl_2, r.t., 3W blue LED, 24 h	76[171]
		Ant (**1**)	Air	MeCN, white LED, r.t., 12 h	93[172]
		CdSe dots	–	MeCN, blue LED, r.t., 18 h	36[173]
		Bi (**1**)	Air	MeOH, white LED, r.t., 24 h	74[174]
		–	PEC cell* / $BiVO_4$ photoanode / NHPI**	MeCN, blue LED, r.t.	90[175]
		–	EC cell*** / RVC anode	MeCN, r.t.	85[175]
		–	Air	MeOH, r.t., 20W blue LED, 12 h	52[176]
2		Co (**1**)	O_2	Dioxane, 80 °C, 27 h	54[158]
		Au (**1**)	Air	MeCN, 60 °C, 5 h	85[160]
		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	91[164]
		–	PEC cell / $BiVO_4$ photoanode / NHPI	MeCN, blue LED, r.t.	91[175]
		–	EC cell / RVC anode	MeCN, r.t.	84[175]
3		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	71[164]
		–	PEC cell / $BiVO_4$ photoanode / NHPI	MeCN, blue LED, r.t.	86[175]
		–	EC cell / RVC anode	MeCN, r.t.	99[175]
4		Au (**1**)	Air	MeCN, 60 °C, 12 h	90[160]
		Au (**2**)	Air	MeCN, 5W blue LED, r.t., 24 h	85[163]
		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	50[164]
		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	89[167]
		Co (**3**)	–	CH_2Cl_2, r.t., 3W blue LED, 24 h	70[171]
		–	PEC cell / $BiVO_4$ photoanode / NHPI	MeCN, blue LED, r.t.	88[175]
		–	EC cell / RVC anode	MeCN, r.t.	80[175]
5		Co (**1**)	O_2	Dioxane, 80 °C, 26 h	56[158]
		Au (**1**)	Air	MeCN, 60 °C, 7 h	84[160]
		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	88[164]
		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	81[167]
		–	EC cell / RVC anode	MeCN, r.t.	84[175]
6		Co (**1**)	O_2	Dioxane, 80 °C, 26 h	62[158]
		Au (**1**)	Air	MeCN, 60 °C, 5 h	86[160]
		Au (**2**)	Air	MeCN, 5W blue LED, r.t., 24 h	82[163]
		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	81[164]
		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	79[167]
		Co (**3**)	–	CH_2Cl_2, r.t., 3W blue LED, 24 h	55[171]
		–	EC cell / RVC anode	MeCN, r.t.	58[175]
7		Co (**2**)	Air	MeCN, 80 °C, 16 h	71[159]
		Au (**1**)	Air	MeCN, 60 °C, 7 h	88[160]
		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	64[164]
		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	83[167]
		Co (**3**)	–	CH_2Cl_2, r.t., 3W blue LED, 24 h	60[171]
		–	EC cell / RVC anode	MeCN, r.t.	76[175]
8		Au (**1**)	Air	MeCN, 60 °C, 3 h	94[160]
		Au (**2**)	Air	MeCN, 5W blue LED, r.t., 24 h	91[163]
		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	91[167,168]

Entry	Product	Catalyst	Oxidant	Conditions	Yield, %
		–	PEC cell / $BiVO_4$ photoanode / NHPI	MeCN, blue LED, r.t.	90[175]
		–	EC cell / RVC anode	MeCN, r.t.	87[175]
9		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	41[164]
		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	73[167]
		–	PEC cell / $BiVO_4$ photoanode / NHPI	MeCN, blue LED, r.t.	85[175]
		–	EC cell / RVC anode	MeCN, r.t.	95[175]
10		Co (**1**)	O_2	Dioxane, 80 °C, 25 h	55[158]
11		–	EC cell / RVC anode	MeCN, r.t.	99[175]
12		–	EC cell / RVC anode	MeCN, r.t.	84[175]
13		Co (**1**)	O_2	Dioxane, 80 °C, 28 h	36[158]
14		–	EC cell / RVC anode	MeCN, r.t.	90[175]
15		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	68[164]
16		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	41[164]
		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	64[167]
17		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	67[167,168]
18		Au (**1**)	Air	MeCN, 60 °C, 6 h	91[160]
		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	81[167]
		–	PEC cell / $BiVO_4$ photoanode / NHPI	MeCN, blue LED, r.t.	72[175]
		–	EC cell / RVC anode	MeCN, r.t.	78[175]
19		Au (**1**)	Air	MeCN, 60 °C, 6 h	80[160]
20		Ir (**1**)	Air	MeOH, 7.1W white LED, r.t., 14 h	87[162]
		Au (**1**)	Air	MeCN, 60 °C, 6 h	87[160]
		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	79[167]
		–	EC cell / RVC anode	MeCN, r.t.	48[175]
21		Au (**1**)	Air	MeCN, 60 °C, 8 h	84[160]
		Au (**2**)	Air	MeCN, 5W blue LED, r.t., 24 h	92[163]

Entry	Product	Catalyst	Oxidant	Conditions	Yield, %
22		Ir (**1**)	Air	MeOH, 7.1W white LED, r.t., 14 h	85[162]
		Au (**1**)	Air	MeCN, 60 °C, 8 h	68[160]
		Au (**2**)	Air	MeCN, 5W blue LED, r.t., 24 h	83[163]
		Ant (**2**)	Air	MeOH, purple LED, r.t., 24 h	84[165]
		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	90[167]
		$FeCl_3$	Air	EtOH, 60 °C	45[170]
		Bi (**1**)	Air	MeOH, white LED, r.t., 24 h	60[174]
		–	PEC cell / $BiVO_4$ photoanode / NHPI	MeCN, blue LED, r.t.	85[175]
		–	EC cell / RVC anode	MeCN, r.t.	76[175]
23		Ir (**1**)	Air	MeOH, 7.1W white LED, r.t., 14 h	89[162]
		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	77[167]
		–	PEC cell / $BiVO_4$ photoanode / NHPI	MeCN, blue LED, r.t.	80[175]
		–	EC cell / RVC anode	MeCN, r.t.	84[175]
24		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	87[167]
		–	PEC cell / $BiVO_4$ photoanode / NHPI	MeCN, blue LED, r.t.	84[175]
		–	EC cell / RVC anode	MeCN, r.t.	92[175]
25		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	80[167]
26		Cu (**1**)	O_2	MeCN, 60 °C, 48 h	50[177]
27		Ir (**1**)	Air	MeOH, 7.1W white LED, r.t., 14 h	61[162]
28		Co (**3**)	–	CH_2Cl_2, r.t., 3W blue LED, 24 h	68[171]
29		–	PEC cell / $BiVO_4$ photoanode / NHPI	MeCN, blue LED, r.t.	79[175]
30		Ir (**1**)	Air	MeOH, 7.1W white LED, r.t., 14 h	77[162]
31		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	96[164]
32		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	85[167,168]
33		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	75[167]

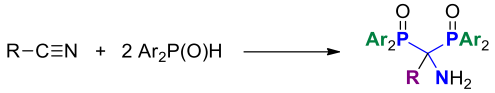
Entry	Product	Catalyst	Oxidant	Conditions	Yield, %
34		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	78[167]
35		4CzIPN (**1**)	Air	H_2O, 7W blue LED, r.t., 12 h	76[167]
		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	97[164]
36		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	76[164]
37		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	76[164]
38		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	77[164]
39		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	68[164]
40		Co (**4**)	O_2	EtOH, 10W white LED, r.t.	88[164]

* PEC cell = photoelectrochemical cell

** NHPI = *N*-hydroxyphthalimide

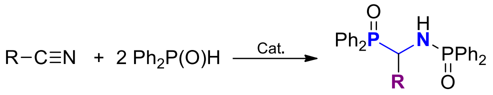
*** EC cell = electrochemical cell

Table S15. P(O),NH$_2$-acetals, obtained by reactions of nitriles and diaryl SPOs.



R	Ar	Cat	Conditions	Yield, %
Me	Ph	La(dmba)$_3$ (10 mol%)	MeCN, r.t., 14 h	90[178,179]
Me	Ph	[(thf)$_4$Ca(PPh$_3$)$_2$] (3 mol%)	THF, r.t., 12 h	87[180]
Me	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	MeCN, r.t., 36 h	56[181]
Me	*p*-Tol	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	MeCN, r.t., 36 h	46[181]
Me	*m*-Xyl	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	MeCN, r.t., 36 h	43[181]
Me	2-Naph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	MeCN, r.t., 36 h	54[181]
cyclo-Pr	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*cyclo*-PrCN, r.t., 36 h	24[181]
Et	Ph	La(dmba)$_3$ (10 mol%)	EtCN, 80 °C, 48 h	84[178,179]
MeOCH$_2$	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	MeOCH$_2$CN, r.t., 36 h	70[181]
MeOCH$_2$CH$_2$	Ph	La(dmba)$_3$ (20 mol%)	Py, 80 °C, 48 h	67[178,179]
Me$_2$NCH$_2$CH$_2$	Ph	La(dmba)$_3$ (20 mol%)	Py, 80 °C, 48 h	70[178,179]
Ph	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	58[181]
4-F-C$_6$H$_4$	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	61[181]
4-Cl-C$_6$H$_4$	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	59[181]
4-Br-C$_6$H$_4$	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	66[181]
4-I-C$_6$H$_4$	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	62[181]
p-Tol	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	50[181]
4-CF$_3$-C$_6$H$_4$	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	70[181]
4-MeO-C$_6$H$_4$	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	30[181]
4-CF$_3$O-C$_6$H$_4$	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	53[181]
4-MeO$_2$C-C$_6$H$_4$	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	58[181]
4-NC-C$_6$H$_4$	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	60[181]
m-Tol	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	52[181]
2-Naph	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	63[181]
3-Py	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	65[181]
4-Py	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	66[181]
2-Thienyl	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	65[181]
2-Furyl	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	81[181]
3-CN-2-Py	Ph	Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%) + DABCO (1 equiv.) + KCl (1 equiv.)	*t*-BuOMe, 40 °C, 36 h	71[181]

Table S16. *N*-phosphinoyl P(O),NH-acetals, formed in reactions of nitriles with SPOs.



R	Catalyst	Conditions	Yield, %
Ph	La(dmba)$_3$ (10 mol%)	PhCN, r.t., 14 h	90[178,179]
Ph	$(Me_3Si)_2NK$ (20 mol%)	SF, 60 °C, 1.5 h	96[182]
Ph	[(thf)$_4$Ca(PPh_3)$_2$] (5 mol%)	THF, r.t., 24 h	83[180]
4-F-C_6H_4	La(dmba)$_3$ (10 mol%)	4-F-C_6H_4CN, r.t., 24 h	88[178,179]
4-Cl-C_6H_4	La(dmba)$_3$ (10 mol%)	Py, r.t., 14 h	90[178,179]
4-Cl-C_6H_4	$(Me_3Si)_2NK$ (20 mol%)	C_7H_8, 60 °C, 1.5 h	92[182]
4-Br-C_6H_4	$(Me_3Si)_2NK$ (20 mol%)	C_7H_8, 60 °C, 1.5 h	91[182]
p-Tol	$(Me_3Si)_2NK$ (20 mol%)	SF, 60 °C, 3 h	86[182]
4-CF_3-C_6H_4	La(dmba)$_3$ (10 mol%)	Py, r.t., 14 h	85[178,179]
4-CF_3-C_6H_4	$(Me_3Si)_2NK$ (20 mol%)	C_7H_8, 60 °C, 1 h	95[182]
4-*t*-Bu-C_6H_4	La(dmba)$_3$ (10 mol%)	Py, r.t., 24 h	80[178,179]
4-*t*-Bu-C_6H_4	$(Me_3Si)_2NK$ (20 mol%)	SF, 60 °C, 3 h	92[182]
4-MeO-C_6H_4	La(dmba)$_3$ (10 mol%)	Py, r.t., 48 h	89[178,179]
4-MeO-C_6H_4	$(Me_3Si)_2NK$ (20 mol%)	SF, 60 °C, 3 h	92[182]
4-MeS-C_6H_4	La(dmba)$_3$ (10 mol%)	Py, r.t., 72 h	63[178,179]
4-MeS-C_6H_4	$(Me_3Si)_2NK$ (20 mol%)	C_7H_8, 60 °C, 6 h	68[182]
4-Me_2N-C_6H_4	La(dmba)$_3$ (10 mol%)	Py, 80 °C, 48 h	71[178,179]
4-Me_2N-C_6H_4	$(Me_3Si)_2NK$ (20 mol%)	C_7H_8, 60 °C, 8 h	53[182]
4-MeO_2C-C_6H_4	$(Me_3Si)_2NK$ (20 mol%)	C_7H_8, 60 °C, 1.5 h	93[182]
2-F-C_6H_4	La(dmba)$_3$ (10 mol%)	2-F-C_6H_4CN, r.t., 48 h	64[178,179]
o-Tol	La(dmba)$_3$ (10 mol%)	2-Me-C_6H_4CN, r.t., 14 h	78[178,179]
3-F-C_6H_4	La(dmba)$_3$ (10 mol%)	Py, r.t., 14 h	88[178,179]
m-Tol	La(dmba)$_3$ (10 mol%)	3-Me-C_6H_4CN, r.t., 14 h	86[178,179]
2-Naph	La(dmba)$_3$ (10 mol%)	Py, 80 °C, 48 h	60[178,179]
2-Py	$(Me_3Si)_2NK$ (20 mol%)	SF, 60 °C, 3 h	96[182]
2-Thienyl	$(Me_3Si)_2NK$ (20 mol%)	SF, 60 °C, 1.5 h	90[182]
Cy	La(dmba)$_3$ (10 mol%)	CyCN, 80 °C, 14 h	72[178,179]
i-Pr	La(dmba)$_3$ (10 mol%)	i-PrCN, r.t., 14 h	85[178,179]
$PhCH_2$	La(dmba)$_3$ (10 mol%)	$PhCH_2CN$, r.t., 14 h	88[178,179]
4-F-C_6H_4-CH_2	$(Me_3Si)_2NK$ (20 mol%)	C_7H_8, 60 °C, 8 h	57[182]
$MeOCH_2CH_2$	La(dmba)$_3$ (20 mol%)	Py, 80 °C, 120 h	38[178,179]
$Me_2NCH_2CH_2$	La(dmba)$_3$ (20 mol%)	Py, 80 °C, 120 h	40[178,179]

Table S17. Papers, describing syntheses of P(O),N-, P(O),NH-, and P(O),NH_2-acetals by oxidation of P,N-acetals.

Year	Reference
2022	Sukhikh, T. S.; Kolybalov, D. S.; Pylova, E. K.; Konchenko, S. N. Luminescent Zn Halide Complexes with 2-(2-Aminophenyl)benzothiazole Derivatives. *Inorganics* **2022**, *10*, id: 138. DOI: 10.3390/inorganics10090138.
2022	Pandey, M. K.; Kote, B. S.; Mondal, D.; Kunchur, H. S.; Radhakrishna, L.; Balakrishna, M. S. Transition Metal Complexes of 2,6-Dibenzhydryl Derived Bisphosphine: Synthesis, Structural Studies and Palladium Complex Promoted Suzuki-Miyaura Reactions. *ChemistrySelect* **2022**, *7*, id: e202201245. DOI: 10.1002/slct.202201245.
2022	Sukhikh, T. S.; Kolybalov, D. S.; Khisamov, R. M.; Konchenko, S. N. Phenyl-2-benzothiazole-Based α-Aminophosphines: Synthesis, Crystal Structure, and Photophysical Properties. *J. Struct. Chem.* **2022**, *63*, 1446-1452. DOI: 10.1134/S0022476622090074.
2022	Mondal, D.; Sardar, G.; Kabra, D.; Balakrishna, M. S. 2,2′-Bipyridine Derived Doubly B ← N Fused Bisphosphine-Chalcogenides, $[C_5H_3N(BF_2)\{NCH_2P(E)Ph_2\}]_2$ (E = O, S, Se): Tuning of Structural Features and Photophysical Studies. *Dalton Trans.* **2022**, *51*, 6884-6898. DOI: 10.1039/d2dt00287f.
2022	Khisamov, R. M.; Ryadun, A. A.; Konchenko, S. N.; Sukhikh, T. S. Molecular Environment Effects That Modulate the Photophysical Properties of Novel 1,3-Phosphinoamines Based on 2,1,3-Benzothiadiazole. *Molecules* **2022**, *27*, id: 3857. DOI: 10.3390/molecules27123857.
2021	Seah, J. W. K.; Lee, J. X. T.; Li, Y.; Pullarkat, S. A.; Tan, N. S.; Leung, P.-H. Chelating Phosphine–N-Heterocyclic Carbene Platinum Complexes *via* Catalytic Asymmetric Hydrophosphination and Their Cytotoxicity Toward MKN74 and MCF7 Cancer Cell Lines. *Inorg. Chem.* **2021**, *60*, 17276-17287. DOI: 10.1021/acs.inorgchem.1c02625.
2021	Seah, J. W. K.; Li, Y.; Pullarkat, S. A.; Leung, P.-H. Access to a Chiral Phosphine–NHC Palladium(II) Complex *via* the Asymmetric Hydrophosphination of Achiral Vinyl Azoles. *Organometallics* **2021**, *40*, 2118-2122. DOI: 10.1021/acs.organomet.1c00262.
2020	Page, S. J.; Rogers-Simmonds, D.; White, A. J. P.; Miller, P. W. Synthesis and Crystallographic Characterisation of a Homologous Series of Bis-Tridentate Phosphine Oxide NP_3O_3 Fe(II), Co(II), Ni(II) and Cu(II) Complexes. *Inorg. Chim. Acta* **2020**, *512*, id: 119870. DOI: 10.1016/j.ica.2020.119870.
2020	Nolla-Saltiel, R.; Geer, A. M.; Taylor, L. J.; Churchill, O.; Davies, E. S.; Lewis, W.; Blake, A. J.; Kays, D. L. Hydrophosphination of Activated Alkenes by a Cobalt(I) Pincer Complex. *Adv. Synth. Catal.* **2020**, *362*, 3148-3157. DOI: 10.1002/adsc.202000514.
2019	Junges, C. H.; Dresch, L. C.; da Costa, M. T.; Tirloni, B.; Casagrande, O. L. Pyrazolyl-Phosphinoyl Nickel(II) Complexes: Synthesis, Characterization and Ethylene Dimerization Studies. *Appl. Organometal. Chem.* **2019**, *33*, id: e4887. DOI: 10.1002/aoc.4887.
2019	Almeida, R. F. M.; Santos, F. C.; Marycz, K.; Alicka, M.; Krasowska, A.; Suchodolski, J.; Panek, J. J.; Jezierska, A.; Starosta, R. New Diphenylphosphane Derivatives of Ketoconazole are Promising Antifungal Agents. *Sci. Rep.* **2019**, *9*, id:16214. DOI: 10.1038/s41598-019-52525-7.
2018	Takata, T.; Nishikawa, D.; Hirano, K.; Miura, M. Synthesis of α-Aminophosphines by Copper-Catalyzed Regioselective Hydroamination of Vinylphosphines. *Chem. Eur. J.* **2018**, *24*, 10975-10978. DOI: 10.1002/chem.201802491.
2018	Komarnicka, U. K.; Kozieł, S.; Starosta, R.; Kyzioł, A. Selective Cu(I) Complex with Phosphine-Peptide (SarGly) Conjugate *contra* Breast Cancer: Synthesis, Spectroscopic Characterization and Insight into Cytotoxic Action. *J. Inorg. Biochem.* **2018**, *186*, 162-175. DOI: 10.1016/j.jinorgbio.2018.06.009.
2016	Altan, O.; Serindağ, O.; Sayın, K.; Karakaş, D. Pd(II) Complexes of Novel Phosphine Ligands: Synthesis, Characterization, and Catalytic Activities on Heck Reaction. *Phosphorus Sulfur Silicon Relat. Elem.* **2016**, *191*, 993-999. DOI: 10.1080/10426507.2015.1119827.
2016	Komarnicka, U. K.; Starosta, R.; Kyzioł, A.; Płotek, M.; Puchalska, M.; Jeżowska-Bojczuk, M. New Copper(I) Complexes Bearing Lomefloxacin Motif: Spectroscopic Properties, *in Vitro* Cytotoxicity and Interactions with DNA and Human Serum Albumin. *J. Inorg. Biochem.* **2016**, *165*, 25-35. DOI: 10.1016/j.jinorgbio.2016.09.015.
2015	Lach, J.; Peulecke, N.; Kindermann, M. K.; Palm, G. J.; Köckerling, M.; Heinicke, J. W. α-Phosphanyl Amino Acids: Synthesis, Structure and Properties of Alkyl and Heterocyclic *N*-Substituted Siphenylphosphanylglycines. *Tetrahedron* **2015**, *71*, 4933-4945. DOI: 10.1016/j.tet.2015.05.101.
2015	Musina, E. I.; Wittmann, T. I.; Strelnik, I. D.; Naumova, O. E.; Karasik, A. A.; Krivolapov, D. B.; Islamov, D. R.; Kataeva, O. N.; Sinyashin, O. G.; Lönnecke, P.et al. Influence of the *rac–meso* Isomerization of Seven-Membered Cyclic Bisphosphines on the Predominant Formation of Chelate Complexes. *Polyhedron* **2015**, *100*, 344-350. DOI: 10.1016/j.poly.2015.08.033.

Year	Reference
2015	Płotek, M.; Starosta, R.; Komarnicka, U. K.; Skórska-Stania, A.; Jeżowska-Bojczuk, M.; Stochel, G.; Kyzioł, A. New Ruthenium(II) Coordination Compounds Possessing Bidentate Aminomethylphosphane Ligands: Synthesis, Characterization and Preliminary Biological Study *in Vitro*. *Dalton Trans.* **2015**, *44*, 13969-13978. DOI: 10.1039/C5DT01119A.
2015	Komarnicka, U. K.; Starosta, R.; Guz-Regner, K.; Bugla-Płoskońska, G.; Kyzioł, A.; Jeżowska-Bojczuk, M. Phosphine Derivatives of Sparfloxacin – Synthesis, Structures and *in Vitro* Activity. *J. Mol. Struct.* **2015**, *1096*, 55-63. DOI: 10.1016/j.molstruc.2015.04.044.
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Table S18. Papers and patents, describing syntheses of P(O),N-, P(O),NH-, and P(O),NH_2-acetals by nucleophilic substitution of α-halo- or α-sulfonato-group within tertiary phosphine oxides by amines or NH_3.

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Table S19. Papers, describing syntheses of P(O),N-, P(O),NH-, and P(O),NH$_2$-acetals by hydroamination of vinylphosphine oxides.

Year	Reference
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2019	de los Santos, J. M.; Rubiales, G.; Sbai, Z. E.; Carramiñana, V.; Ochoa de Retana, A. M.; Palacios, F. Reaction of Phosphinyl Nitrosoalkenes with Electron-Rich Heterocycles. *Phosphorus Sulfur Silicon Relat. Elem.* **2019**, *194*, 545-549. DOI: 10.1080/10426507.2018.1542400.
2018	Takata, T.; Nishikawa, D.; Hirano, K.; Miura, M. Synthesis of α-Aminophosphines by Copper-Catalyzed Regioselective Hydroamination of Vinylphosphines. *Chem. Eur. J.* **2018**, *24*, 10975-10978. DOI: 10.1002/chem.201802491.
2016	Gazizov, M. B.; Tarakanova, A. L.; Ismagilov, R. K.; Shamsutdinova, L. P.; Karimova, R. F.; Burangulova, R. N. Addition of Phthalimide and Acetone to Phosphorylated Methylene Quinones. *Russ. J. Gen. Chem.* **2016**, *86*, 326-330. DOI: 10.1134/S1070363216020213.
2016	Galkina, M. A.; Bodrin, G. V.; Goryunov, E. I.; Goryunova, I. B.; Sherstneva, A. S.; Urmambetova, J. S.; Kolotyrkina, N. G.; Il'in, M. M.; Brel, V. K.; Kochetkov, K. A. Regioselective Aza-Michael Addition of Azoles to 4-(Diphenylphosphoryl)but-3-en-2-one. *Mendeleev Commun.* **2016**, *26*, 75-76. DOI: 10.1016/j.mencom.2016.01.029.
2016	Galkina, M. A.; Bodrin, G. V.; Goryunov, E. I.; Goryunova, I. B.; Ambartsumyan, A. A.; Vasil'eva, T. T.; Protopopova, P. S.; Saifutiarova, A. E.; Uryupin, A. B.; Brel, V. K. et al. Aza-Michael Reaction as an Efficient Method for the Synthesis of First Representatives of β-Azahetaryl-β-Diphenylphosphorylalkanones. *Russ. Chem. Bull.* **2016**, *65*, 1855-1858. DOI: 10.1007/s11172-016-1520-y.
2011	de los Santos, J. M.; Ignacio, R.; Aparicio, D.; Palacios, F. Phosphorated 1,2-Oxazabuta-1,3-dienes as Synthetic Tools for the Preparation of α-Amino Phosphorus Derivatives and Functionalized Nitrogen-Containing Heterocycles. *Phosphorus Sulfur Silicon Relat. Elem.* **2011**, *186*, 735-741. DOI: 10.1080/10426507.2010.522632.
2007	de los Santos, J. M.; Ignacio, R.; Aparicio, D.; Palacios, F. Michael Addition of Amine Derivatives to Conjugate Phosphinyl and Phosphonyl Nitrosoalkenes. Preparation of α-Amino Phosphine Oxide and Phosphonate Derivatives. *J. Org. Chem.* **2007**, *72*, 5202-5206. DOI: 10.1021/jo0705521.
2006	Aparicio, D.; Attanasi, O. A.; Filippone, P.; Ignacio, R.; Lillini, S.; Mantellini, F.; Palacios, F.; de los Santos, J. M. Straightforward Access to Pyrazines, Piperazinones, and Quinoxalines by Reactions of 1,2-Diaza-1,3-butadienes with 1,2-Diamines under Solution, Solvent-Free, or Solid-Phase Conditions. *J. Org. Chem.* **2006**, *71*, 5897-5905. DOI: 10.1021/jo060450v.
2005	Palacios, F.; Aparicio, D.; López, Y.; de los Santos, J. M. Synthesis of Functionalized α-Amino-Phosphine Oxides and -Phosphonates by Addition of Amines and Aminoesters to 4-Phosphinyl- and 4-Phosphonyl-1,2-diaza-1,3-butadienes. *Tetrahedron* **2005**, *61*, 2815-2830. DOI: 10.1016/j.tet.2005.01.081.
2005	Palacios, F.; Aparicio, D.; de los Santos, J. M.; Ignacio, R.; López, Y. An Efficient Synthesis of Functionalized α-Amino-Phosphine Oxides and -Phosphonates by Addition of Aminoalcohols to 4-Phosphorylated-1,2-diaza-1,3-butadienes. *ARKIVOC* **2005**, *VI*, 153-161. DOI: 10.3998/ark.5550190.0006.612.
2004	Palacios, F.; Aparicio, D.; López, Y.; de los Santos, J. M. Addition of Amine Derivatives to Phosphorylated 1,2-Diaza-1,3-butadienes. Synthesis of α-Aminophosphonates. *Tetrahedron Lett.* **2004**, *45*, 4345-4348. DOI: 10.1016/j.tetlet.2004.03.192.
1991	smagilov, R. K.; Moskva, V. V.; Arkhipov, V. P.; Ivantsov, A. E.; Kopylova, L. Y. Synthesis and Properties of Phosphorylated 2,6-Di-*tert*-butyl-4-methylene-2,5-cyclohexadiene-1-ones. *Zh. Obshch. Khim.* **1991**, *61*, 387-391.

Table S20. Papers, describing syntheses of P(O),N-, P(O),NH-, and P(O),NH_2-acetals by cycloaddition reactions of vinylphosphine oxides with diazo compounds.

Year	Reference
1990	Dziwok, K.; Lachmann, J.; Wilkinson, D. L.; Müller, G.; Schmidbaur, H. 1,1’-Bis(diphenylphosphino)bicyclopropyl: Synthesis, Properties, Precursors, Derivatives, and Metal Complexes. *Chem. Ber.* **1990**, *123*, 423-431. DOI: 10.1002/cber.19901230303.
1985	Minami, T.; Hanamoto, T.; Hirao, I. Synthesis of Heterocyclic Compounds Containing Phosphorus Residues by Cycloaddition of 1,3-Dipoles to Cyclobutenylphosphorus Compounds. *J. Org. Chem.* **1985**, *50*, 1278-1281. DOI: 10.1021/jo00208a024.
1980	Heydt, H.; Busch, K.-H.; Regitz, M. Untersuchungen an Diazoverbindungen und Aziden, XXXVI. [3+2]-Cycloaddition von Diazoalkanen an 1-Cyclopropenyl-phosphinoxide; Isomerisierung der Cycloaddukte. *Justus Liebigs Ann. Chem.* **1980**, 590-599. DOI: 10.1002/jlac.198019800411.
1973	Pudovik, A. N.; Gareev, R. D.; Stabrovskaya, L. A.; Evstaf'ev, G. I.; Remizov, A. B. Reactivity of Unsaturated Organophosphorus Compounds in the 1,3-Dipolar Cycloaddition of Diaryldiazomethanes. *Zh. Obshch. Khim.* **1973**, *43*, 1674-1682.
1973	Pudovik, A. N.; Gareev, R. D.; Stabrovskaya, L. A.; Aganov, A. V. 1,3-Dipolar Cycloaddition of 9-Diazofluorene to Unsaturated Organophosphorus Compounds. *Zh. Obshch. Khim.* **1973**, *43*, 1236-1240.
1972	Quin, L. D.; Borleske, S. G. Synthesis of a Phospholecarboxylic Ester. *Tetrahedron Lett.* **1972**, *13*, 299-302. DOI: 10.1016/S0040-4039(01)84306-9.
1971	Pudovik, A. N.; Gareev, R. D.; Aganov, A. V.; Raevskaya, O. E.; Stabrovskaya, L. A. Reaction of Diphenyldiazomethane with Tertiary Vinyl- and Allylphosphine Oxide. *Zh. Obshch. Khim.* **1971**, *41*, 1008-1016.
1965	Campbell, I. G. M.; Cookson, R. C.; Hocking, M. B.; Hughes, A. N. Synthesis and Chemistry of Phospholes. *J. Chem. Soc.* **1965**, 2184-2193. DOI: 10.1039/JR9650002184.

Table S21. Papers and patents, describing syntheses of P(O),N-, P(O),NH-, and P(O),NH_2-acetals by cycloaddition reactions of α-diazo, or α-azido, phosphine oxides with alkenes or alkynes.

Year	Reference
2022	de Juan, A.; Lozano, D.; Heard, A. W.; Jinks, M. A.; Suarez, J. M.; Tizzard, G. J.; Goldup, S. M. A Chiral Interlocking Auxiliary Strategy for the Synthesis of Mechanically Planar Chiral Rotaxanes. *Nat. Chem.* **2022**, *14*, 179-187. DOI: 10.1038/s41557-021-00825-9.
2016	Lewis, J. E. M.; Bordoli, R. J.; Denis, M.; Fletcher, C. J.; Galli, M.; Neal, E. A.; Rochette, E. M.; Goldup, S. M. High Yielding Synthesis of 2,2′-Bipyridine Macrocycles, Versatile Intermediates in the Synthesis of Rotaxanes. *Chem. Sci.* **2016**, *7*, 3154-3161. DOI: 10.1039/C6SC00011H.
2015	Galli, M.; Lewis, J. E. M.; Goldup, S. M. A Stimuli-Responsive Rotaxane–Gold Catalyst: Regulation of Activity and Diastereoselectivity. *Angew. Chem. Int. Ed.* **2015**, *54*, 13545-13549. DOI: 10.1002/anie.201505464.
2010	Gandelman, M.; Schuster, E. M.; Nisnevich, G. Novel Diarylphosphine- and Dialkylphosphine-Containing Compounds, Processes of Preparing Same and Uses Thereof as Tridentate Ligands. U.S. Patent 2010/0292084, Nov 18, **2010**.
2009	Schuster, E. M.; Nisnevich, G.; Botoshansky, M.; Gandelman, M. Synthesis of Novel Bulky, Electron-Rich Propargyl and Azidomethyl Dialkyl Phosphines and Their Use in the Preparation of Pincer Click Ligands. *Organometallics* **2009**, *28*, 5025-5031. DOI: 10.1021/om900545s.
2008	Schuster, E. M.; Botoshansky, M.; Gandelman, M. Pincer Click Ligands. *Angew. Chem. Int. Ed.* **2008**, *47*, 4555-4558. DOI: 10.1002/anie.200800123.
2001	Yamashita, M.; Reddy, P. M.; Kato, Y.; Reddy, V. K.; Suzuki, K.; Oshikawa, T. Synthesis of Novel Deoxy λ^5 Phospha Sugar Nucleosides: 1,3-Dipolar Cycloaddition of an Azidophospholane with Alkynes. *Carbohydr. Res.* **2001**, *336*, 257-270. DOI: 10.1016/S0008-6215(01)00264-6.
1999	Yamashita, M.; Suzuki, K.; Kato, Y.; Iida, A.; Ikai, K.; Reddy, P. M.; Oshikawa, T. Novel Synthesis and Structures of Amines and Triazole-Derived Glycoside and Nucleoside Derivatives of Phosphanyl Sugar Analogs. *J. Carbohydr. Chem.* **1999**, *18*, 915-935. DOI: 10.1080/07328309908544044.
1999	Yamashita, M.; Kato, Y.; Suzuki, K.; Oshikawa, T.; Iida, A.; Reddy, P. M. Synthesis and Structure of Novel Glycoside and Nucleoside Derivatives of Phospha Sugar Analogs. *Phosphorus Sulfur Silicon Relat. Elem.* **1999**, *144*, 641-644. DOI: 10.1080/10426509908546326.
1998	Yamashita, M.; Kato, Y.; Suzuki, K.; Oshikawa, T. A novel preparation and X-ray crystallographic analysis of phospha sugar nucleoside derivatives. *Heterocyclic Commun.* **1998**, *4*, 411-414.
1996	Yamashita, K.; Oshikawa, T.; Suzuki, K. Preparation of Phospha Sugar *N*-Nucleoside Derivatives as Drugs. Jpn. Patent 8-245666, Sep 24, **1996**.
1991	Yamashita, K.; Iumi, K.; Iida, A. Preparation of Phosphorus-Containing Nucleosides. Jpn. Patent 3-11089, Jan 18, **1991**.
1990	Hanaya, T.; Miyoshi, A.; Noguchi, A.; Kawamoto, H.; Armour, M.-A.; Hogg, A. M.; Yamamoto, H. A Convenient Synthesis of (2*R*)-1-Amino-1-Deoxy-1-Phosphinylglycerols. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3590-3594. DOI: 10.1246/bcsj.63.3590.
1989	Regitz, M.; Böhshar, M.; Arenz, S.; Heydt, H. Diazoverbindungen, 70. Intramolekulare Cycloaddition von 5-(Diazomethyl)-5H-benzocycloheptenen – Teilschritt einer neuen Benzosemibullvalen-Synthese. *Chem. Ber.* **1989**, *122*, 565-575. DOI: 10.1002/cber.19891220327.
1987	Heydt, H.; Breiner, H.-W.; Hell, V.; Regitz, M. Diazo Compounds, 65. Isomerization Reactions in the System 4-Diazo-1-butene/2.3-Diazabicyclo[3.1.0]hex-2-ene/1.4-Dihydropyridazine. *Z. Naturforsch. B* **1987**, *42*, 210-216. DOI: 10.1515/znb-1987-0215.
1985	Böhshar, M.; Heydt, H.; Maas, G.; Gümbel, H.; Regitz, M. Intramolekulare [4+3]-Cycloaddition bei 5-Diazomethyl-5H-benzocyloheptenen - Teilschritt einer neuen Benzosemibullvalen-Synthese. *Angew. Chem.* **1985**, *97*, 571-572. DOI: 10.1002/ange.19850970710.
1985	Böhshar, M.; Maas, G.; Heydt, H.; Regitz, M. Untersuchungen an Diazoverbindungen und Aziden LVII. Tri- und Tetracyclen aus 5-(Diazomethyl)-5h-benzocycloheptenen und 4-Phenyl-1,2,4-triazolin-3,5-dion. *Tetrahedron* **1985**, *41*, 825-835. DOI: 10.1016/S0040-4020(01)96463-4.
1981	Capuano, L.; Tammer, T. Cycloreaktionen von α-Acylketenen mit Phosphinyldiazoalkanen und Isonitrilen. *Chem. Ber.* **1981**, *114*, 456-467. DOI: 10.1002/cber.19811140207.

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1979	Regitz, M.; Weber, B.; Eckstein, U. Untersuchungen an Diazoverbindungen und Aziden, XXXII. Substitutionsreaktionen am Diazokohlenstoff von Diazomethylphosphorylverbindungen. *Justus Liebigs Ann. Chem.* **1979**, 1002-1019. DOI: 10.1002/jlac.197919790711.
1971	Seyferth, D.; Hilbert, P. Azidonethyldiphenylphosphine Oxide. *Org. Prep. Proc. Int.* **1971**, *3*, 51-53. DOI: 10.1080/00304947109356035.
1969	Regitz, M.; Anschütz, W. Reaktionen CH-aktiver Verbindungen mit Aziden, XXV. Synthese von Diphenylphosphinyl-diazomethanen durch Diazogruppen-Übertragung. *Chem. Ber.* **1969**, *102*, 2216-2229. DOI: 10.1002/cber.19691020709.

Table S22. Papers, describing syntheses of P(O),N-, P(O),NH-, and P(O),NH_2-acetals by reactions of 2*H*-azirine-2-phosphine oxides with nucleophiles.

Year	Reference
2021	Carramiñana Jiménez, V. Diseño y Evaluación de Nuevos Derivados de Aziridinas Fosforadas como Agentes Antiproliferativos. PhD Dissertation, University of the Basque Country, Vitoria, Spain, **2021**.
2020	Carramiñana, V.; Ochoa de Retana, A. M.; Palacios, F.; de los Santos, J. M. Synthesis of α-Aminophosphonic Acid Derivatives Through the Addition of O- and S-Nucleophiles to 2*H*-Azirines and Their Antiproliferative Effect on A549 Human Lung Adenocarcinoma Cells. *Molecules* **2020**, *25*, id: 3332. DOI: 10.3390/molecules25153332.
2020	Carramiñana, V.; Ochoa de Retana, A. M.; de los Santos, J. M.; Palacios, F. First Synthesis of Merged Hybrids Phosphorylated Azirino[2,1-*b*]benzo[*e*][1,3]oxazine Derivatives as Anticancer Agents. *Eur. J. Med. Chem.* **2020**, *185*, id: 111771. DOI: 10.1016/j.ejmech.2019.111771.
2019	Carramiñana, V.; Ochoa de Retana, A. M.; del Burgo, A. V.; de los Santos, J. M.; Palacios, F. Synthesis and Biological Evaluation of Cyanoaziridine Phosphine Oxides and Phosphonates with Antiproliferative Activity. *Eur. J. Med. Chem.* **2019**, *163*, 736-746. DOI: 10.1016/j.ejmech.2018.12.002.
2016	del Burgo, A. V.; Ochoa de Retana, A. M.; de los Santos, J. M.; Palacios, F. Reaction of 2*H*-Azirine-Phosphine Oxides and -Phosphonates with Enolates Derived from β-Keto Esters. *J. Org. Chem.* **2016**, *81*, 100-108. DOI: 10.1021/acs.joc.5b02347.
2011	Palacios, F.; Ochoa de Retana, A. M.; del Burgo, A. V. Selective Synthesis of Substituted Pyrrole-2-phosphine Oxides and -phosphonates from 2*H*-Azirines and Enolates from Acetyl Acetates and Malonates. *J. Org. Chem.* **2011**, *76*, 9472-9477. DOI: 10.1021/jo201932m.
2009	Lemos, A. Addition and Cycloaddition Reactions of Phosphinyl- and Phosphonyl-2*H*-Azirines, Nitrosoalkenes and Azoalkenes. *Molecules* **2009**, *14*, 4098-4119. DOI: 10.3390/molecules14104098.
2006	Palacios, F.; Ochoa de Retana, A. M.; Alonso, J. M. Regioselective Synthesis of Fluoroalkylated β-Aminophosphorus Derivatives and Aziridines from Phosphorylated Oximes and Nucleophilic Reagents. *J. Org. Chem.* **2006**, *71*, 6141-6148. DOI: 10.1021/jo060865g.
2005	Palacios, F.; Ochoa de Retana, A. M.; Alonso, J. M. Reaction of 2*H*-Azirine Phosphine Oxide and -Phosphonates with Nucleophiles. Stereoselective Synthesis of Functionalized Aziridines and α- and β-Aminophosphorus Derivatives. *J. Org. Chem.* **2005**, *70*, 8895-8901. DOI: 10.1021/jo051404i.
2004	Palacios, F.; Ochoa de Retana, A. M.; Gil, J. I.; Alonso, J. M. Regioselective Synthesis of 4- and 5-Oxazole-Phosphine Oxides and -Phosphonates from 2*H*-Azirines and Acyl Chlorides. *Tetrahedron* **2004**, *60*, 8937-8947. DOI: 10.1016/j.tet.2004.07.013.
2004	Hassner, A.; Usak, D.; Kumareswaran, R.; Friedman, O. Stereoselective Addition of Sulfone Carbanions to C=N: A Critical Dependence on the Stability and Reactivity of the Amide Anions in MIRC Reactions. *Eur. J. Org. Chem.* **2004**, 2421-2426. DOI: 10.1002/ejoc.200300781.
2002	Palacios, F.; Aparicio, D.; Ochoa de Retana, A. M.; de los Santos, J. M.; Gil, J. I.; Alonso, J. M. Asymmetric Synthesis of 2*H*-Azirines Derived from Phosphine Oxides Using Solid-Supported Amines. Ring Opening of Azirines with Carboxylic Acids. *J. Org. Chem.* **2002**, *67*, 7283-7288. DOI: 10.1021/jo025995d.
2002	Palacios, F.; Ochoa de Retana, A. M. a.; Gil, J. I.; Alonso, J. M. a. Synthesis of Optically Active Oxazoles from Phosphorylated 2*H*-Azirines and *N*-Protected Amino Acids or Peptides. *Tetrahedron Asymmetry* **2002**, *13*, 2541-2552. DOI: 10.1016/S0957-4166(02)00686-9.
2000	Palacios, F.; Ochoa de Retana, A. M.; Gil, J. I.; Ezpeleta, J. M. Simple Asymmetric Synthesis of 2*H*-Azirines Derived from Phosphine Oxides. *J. Org. Chem.* **2000**, *65*, 3213-3217. DOI: 10.1021/jo9915426.

Table S23. Papers, describing synthesis of P(O),NH_2-acetals by action of hydrazine on P(O),N-acetals with a phthalimide arm.

Year	Reference
2016	Gazizov, M. B.; Tarakanova, A. L.; Ismagilov, R. K.; Shamsutdinova, L. P.; Karimova, R. F.; Burangulova, R. N. Addition of Phthalimide and Acetone to Phosphorylated Methylene Quinones. *Russ. J. Gen. Chem.* **2016**, *86*, 326-330. DOI: 10.1134/S1070363216020213
2005	Jovic, F.; Louise, L.; Mioskowski, C.; Renard, P.-Y. Immunologically Driven Antibodies Chemical Engineering: Design and Synthesis of a Hapten Aimed at Nerve Agent Hydrolysis. *Tetrahedron Lett.* **2005**, *46*, 6809-6814. DOI: 10.1016/j.tetlet.2005.08.032
2001	Novák, T.; Tatai, J.; Bakó, P.; Czugler, M.; Keglevich, G.; Tóke, L. Asymmetric Michael Addition Catalyzed by D-Glucose-Based Azacrown Ethers. *Synlett.* **2001**, 424-426. DOI: 10.1055/s-2001-11395
2001	Novák, T.; Bakó, P.; Keglevich, G.; Dobó, A.; Vékey, K.; Tóke, L. Synthesis of D-Glucose-Based Azacrown Ethers with Phosphinoxidoalkyl Side Chains and Their Application to an Enantioselective Reaction. *J. Incl. Phenom.* **2001**, *40*, 207-212. DOI: 10.1023/A:1011840831308
2001	Cristau, H.-J.; Brahic, C.; Pirat, J.-L. Synthesis of Bis(hydroxymethyl)phosphorylated Compounds, Analogs of α-Aminophosphonic Acids or Alkylidenebisphosphonic Acids. *Tetrahedron* **2001**, *57*, 9149-9156. DOI: 10.1016/S0040-4020(01)00929-2
1997	Vasil’eva, T. V.; Osipova, M. P.; Kormachev, V. V. Phosphorus-Containing Intermediates and Dyes. XI. Phosphorylated Amino Compounds Prepared by Reactions of Bis(2,5-dimethoxyphenyl)phosphinous Acid with Aromatic Aldehydes. *Zh. Obshch. Khim.* **1997**, *67*, 384-386
1995	Plenat, F.; Cassagne, M.; Cristau, H. J. Synthesis of New Phosphorus 2,4,5-Imidazolidinetriones. *Tetrahedron* **1995**, *51*, 9551-9558. DOI: 10.1016/0040-4020(95)00595-Y
1994	Hägele, G.; Varbanov, S.; Ollig, J.; Kropp, H.-W. Aminomethylphosphine Oxides: Synthesis, Dissociation and Stability Constants, $^{31}P\{^1H\}$-NMR-Controlled Titrations. *Z. Anorg. Allg. Chem.* **1994**, *620*, 914-920. DOI: 10.1002/zaac.19946200526
1988	Varbanov, S.; Borisov, G. New Tertiary Phosphine Oxides and Their Application as Flame Retardants for Polymers. *Acta Polym.* **1988**, *39*, 507-515. DOI: 10.1002/actp.1988.010390909
1987	Varbanov, S.; Agopian, G.; Borisov, G. Polyurethane Foams Based on Dimethylaminomethylphosphine Oxide Adducts with Ethylene and Propylene Oxides. *Eur. Polym. J.* **1987**, *23*, 639-642. DOI: 10.1016/0014-3057(87)90011-5
1984	Eisenbarth, P.; Regitz, M. Untersuchungen an Diazoverbindungen und Aziden, XLIII. 1,2-Dewarpyridazine – Vorstufen zur Erzeugung von Azacyclobutadienen? *Chem. Ber.* **1984**, *117*, 445-454. DOI: 10.1002/cber.19841170204
1971	Regitz, M.; Liedhegener, A.; Eckstein, U.; Martin, M.; Anschütz, W. Quecksilber- und Silber-Derivate von Diphenylphosphinyl- und Diäthylphosphono-diazomethan. *Liebigs Ann. Chem.* **1971**, *748*, 207-210. DOI: 10.1002/jlac.19717480122

Table S24. Papers and patents, describing synthesis of P(O),NH$_2$-acetals by acid hydrolysis of P(O),N- and P(O),NH-acetals.

Year	Reference
2022	Sun, S.; Wei, Y.; Xu, J. Visible-Light-Induced [1+5] Annulation of Phosphoryl Diazomethylarenes and Pyridinium 1,4-Zwitterionic Thiolates. *Org. Lett.* **2022**, *24*, 6024-6030. DOI: 10.1021/acs.orglett.2c02321
2020	Luo, Y.; Fu, Z.; Fu, X.; Du, C.; Xu, J. Microwave-Assisted Periselective Annulation of Triarylphosphenes with Aldehydes and Ketones. *Org. Biomol. Chem.* **2020**, *18*, 9526-9537. DOI: 10.1039/D0OB02011G
2020	Luo, Y.; Xu, J. Annulation of Diaryl(aryl)phosphenes and Cyclic Imines to Access Benzo-δ-phospholactams. *Org. Lett.* **2020**, *22*, 7780-7785. DOI: 10.1021/acs.orglett.0c02346
2020	Łupicka-Słowik, A.; Psurski, M.; Grzywa, R.; Cuprych, M.; Ciekot, J.; Goldeman, W.; Wojaczyńska, E.; Wojaczyński, J.; Oleksyszyn, J.; Sieńczyk, M. Structure-Based Design, Synthesis, and Evaluation of the Biological Activity of Novel Phosphoroorganic Small Molecule IAP Antagonists. *Invest. New Drugs* **2020**, *38*, 1350-1364. DOI: 10.1007/s10637-020-00923-4
2020	Wang, J.; Deng, G.; Liu, C.; Chen, Z.; Yu, K.; Chen, W.; Zhang, H.; Yang, X. Transition Metal-Free Synthesis of α-Aminophosphine Oxides through C(sp^3)–P Coupling of 2-Azaallyls. *Adv. Synth. Catal.* **2020**, *362*, 2268-2273. DOI: 10.1002/adsc.201901553
2019	Sieńczyk, M.; Łupicka-Słowik, A.; Grzywa, R.; Oleksyszyn, J.; Dawidczyk, M.; Psurski, M.; Goldeman, W.; Olszewski, T. Organophosphorus Peptide Derivatives Which are Analogs of *N*-terminal Sequence of the Smac Protein, Method of Their Production and Application. Pol. Patent 233,276, Sep 30, **2019**
2017	Zhang, W.; Gilbertson, S. R. Diastereoselective Synthesis of *N*-Sulfinyl α-Aminophosphine Sulfides and Phosphines. *Tetrahedron Lett.* **2017**, *58*, 2175-2177. DOI: 10.1016/j.tetlet.2017.03.067
2011	Pradhan, B. S. Novel Pyrrole Derivatives and Their Synthesis. U.S. Patent 2011/0263870, Oct 27, **2011**
2011	Ingle, G. K.; Liang, Y.; Mormino, M. G.; Li, G.; Fronczek, F. R.; Antilla, J. C. Chiral Magnesium BINOL Phosphate-Catalyzed Phosphination of Imines: Access to Enantioenriched α-Amino Phosphine Oxides. *Org. Lett.* **2011**, *13*, 2054-2057. DOI: 10.1021/ol200456y
2010	Zhao, D.; Mao, L.; Yang, D.; Wang, R. Zinc-Mediated Asymmetric Additions of Dialkylphosphine Oxides to α,β-Unsaturated Ketones and *N*-Sulfinylimines. *J. Org. Chem.* **2010**, *75*, 6756-6763. DOI: 10.1021/jo1014917
2005	Olszewski, T.; Boduszek, B. Synthesis of New Imidazole Aminophosphine Oxides. *Polish J. Chem.* **2005**, *79*, 553-559
1996	Onys'ko, P. P.; Kim, T. V.; Kiseleva, E. I.; Prokopenko, V. P.; Sinitsa, A. D. Sigmatropic Isomerizations in 2-Azaallyl Systems. XV. Peculiarities of *N*-Benzylarylcarboximidoyl Chloride Reaction with Ethyl Diphenylphosphinite. *Zh. Obshch. Khim.* **1996**, *66*, 1283-1286
1990	Van Es, J. J. G. S.; Jaarsveld, K.; Van der Gen, A. Diphenylphosphinoyl-Substituted Ylides. 1. Thermal 1,3-Dipolar Cycloaddition of a-(Diphenylphosphinoyl)glycine Ester Imines. Dipole Formation as the Rate-Determining Step. *J. Org. Chem.* **1990**, *55*, 4063-4069. DOI: 10.1021/jo00300a022
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1980	Regitz, M.; Eckes, H. Carbene, 22. Phosphene: Abfangreaktionen von (Diphenylmethylen)phenyl-phosphan-oxid durch [2 + 2]-Cycloaddition mit Aldehyden. *Chem. Ber.* **1980**, *113*, 3303-3312. DOI: 10.1002/cber.19801131018
1976	Stec, W. J.; Lesiak, K. A Novel Route to 1-Aminoalkylphosphonic Acid. *J. Org. Chem.* **1976**, *41*, 3757-3759. DOI: 10.1021/jo00885a024
1975	Mukhacheva, O. A.; Nikolaeva, V. G.; Yafarova, R. L.; Shchelkunova, M. A.; Razumov, A. I. Study of Phosphinic and Phosphinous Acid Derivatives XCIII. Synthesis of N-Phosphorylated Alkyluretanes and Ureas by Lossen and Curtius Rearrangements. *Zh. Obshch. Khim.* **1975**, *45*, 526-532
1974	Gross, H.; Costisella, B.; Brennecke, L. Über α-Substituierte Phosphonate XV. Eine C-N-Umlagerung von Phosphorylgruppen. *Phosphorus Relat. Group V Elem.* **1974**, *4*, 241-246
1971	Kreutzkamp, N.; Herberg, K.; Lämmerhirt, K.; Schmidt-Samoa, E. Neue Synthesen tertiärer Aminomethyl-Phosphinoxide. *Arch. Pharmaz.* **1971**, *304*, 896-899. DOI: 10.1002/ardp.19713041205
1968	Hoffmann, H.; Förster, H. Darstellung von α-Aminophosphonsäureestern und Verwandten Verbindungen. *Monatsh. Chem.* **1968**, *99*, 380-388. DOI: 10.1007/BF00908943
1967	Popoff, I. C.; Block, B. P.; Huber, L. K. Aminoalkylphosphinic Acids. U.S. Patent 3,332,987, Jul 25, **1967**

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Table S25. Papers, describing synthesis of P(O),NH_2-acetals by reduction of P(O),NH-acetals.

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2020	Zwillinger-Tripolszky, A. Aminofoszfin-Oxidok, Gyűrűs Aminofoszfonátok és Rokonvegyületeik Szintézise és Felhasználási Lehetőségei. PhD Dissertation, Budapest University of Technology and Economics, Budapest, Hungary, **2020**
2019	Bálint, E.; Tripolszky, A.; Hegedűs, L.; Keglevich, G. Microwave-Sssisted Synthesis of *N*,*N*-Bis(phosphinoylmethyl)amines and *N*,*N*,*N*-Tris(phosphinoylmethyl)amines Bearing Different Substituents on the Phosphorus Atoms. *Beilstein J. Org. Chem.* **2019**, *15*, 469-473. DOI: 10.3762/bjoc.15.40
2018	Sowa, S.; Stankevič, M.; Flis, A.; Pietrusiewicz, K. M. Reduction of Tertiary Phosphine Oxides by BH_3 Assisted by Neighboring Activating Groups. *Synthesis* **2018**, *50*, 2106-2118. DOI: 10.1055/s-0036-1591546
1992	Maier, L.; Spörri, H. Organic Phosphorus Compounds 104. Synthesis and Biological Activity of *N*-Hydroxycarbonylmethyl-Aminomethyl-Di(*n*-propyl)- and -Di(*n*-butyl)phosphine Oxides. *Phosphorus Sulfur Silicon Relat. Elem.* **1992**, *70*, 59-61. DOI: 10.1080/10426509208049151
2002	Hall, R. G.; Riebli, P. The Concept of P-H Protection Extended to Phosphine Oxides: Preparation of Functional, Unsymmetrical Secondary and Tertiary Phosphine Oxides. *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, *177*, 1557-1562. DOI: 10.1080/10426500212269
1990	Afarinkia, K.; Rees, C. W.; Cadogan, J. I. G. Synthesis of Organophosphorus Compounds *via* Silyl Esters of Phosphorous Acids. *Tetrahedron* **1990**, *46*, 7175-7196. DOI: 10.1016/S0040-4020(01)87899-6
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1990	Maier, L. Organic Phosphorus Compounds 91. Synthesis and Properties of 1-Amino-2-Arylethylphosphonic and -phosphinic Acids as well as -phosphine Oxides. *Phosphorus Sulfur Silicon Relat. Elem.* **1990**, *53*, 43-67. DOI: 10.1080/10426509008038012

Table S26. Papers and patents, describing applications of P(O),N-, P(O),NH-, and P(O),NH_2-acetals as ligands.

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2022	Sukhikh, T. S.; Kolybalov, D. S.; Pylova, E. K.; Konchenko, S. N. Luminescent Zn Halide Complexes with 2-(2-Aminophenyl)benzothiazole Derivatives. *Inorganics* **2022**, *10*, id: 138. DOI: 10.3390/inorganics10090138.
2020	Page, S. J.; Rogers-Simmonds, D.; White, A. J. P.; Miller, P. W. Synthesis and Crystallographic Characterisation of a Homologous Series of Bis-Tridentate Phosphine Oxide NP_3O_3 Fe(II), Co(II), Ni(II) and Cu(II) Complexes. *Inorg. Chim. Acta* **2020**, *512*, id: 119870. DOI: 10.1016/j.ica.2020.119870.
2019	Artem'ev, A. V.; Davydova, M. P.; Berezin, A. S.; Brel, V. K.; Morgalyuk, V. P.; Bagryanskaya, I. Yu.; Samsonenko, D. G. Luminescence of the Mn^{2+} Ion in Non-O_h and T_d Coordination Environments: The Missing Case of Square Pyramid. *Dalton Trans.* **2019**, *48*, 16448-16456. DOI: 10.1039/C9DT03283E.
2018	Georgieva, Z. V.; Ugrinov, A. G.; Nikolova, R. P.; Shivachev, B. L.; Zareva, S. Y.; Varbanov, S. G.; Tosheva, T. D.; Gencheva, G. G. Coordination of Bis((dimethylphosphinyl)methyl)amine to Copper(II). Synthesis and Single-Crystal Structure of Its Mononuclear Octahedral Copper(II) Complex. *Bulg. Chem. Commun.* **2018**, *50*, 251-259.
2018	Garifzyanov, A. R.; Davletshina, N. V.; Gaynullin, A. Z.; Ivshin, K. A.; Kataeva, O. N.; Cherkasov, R. A. Synthesis and Structure of a Copper(II) Complex of *N*,*N'*-Bis(di-*para*-tolylphosphinoylmethyl)-1,8-diamino-3,6-dioxaoctane. *Russ. J. Gen. Chem.* **2018**, *88*, 154-157. DOI: 10.1134/s1070363218010280.
2016	Bell, J.; Samb, I.; Toullec, P. Y.; Michelet, V.; Leray, I. Synthesis and Complexing Properties of Molecular Probes Linked with Fluorescent Phosphane Oxide Derivatives. *J. Photochem. Photobiol. A* **2016**, *318*, 25-32. DOI: 10.1016/j.jphotochem.2015.11.017.
2015	Reiss, G. J. Two Structurally Related, Hydrogen-Bonded Polymorphs of the Zwitterionic Complex Trichlorido((dimethylphosphoryl)methanaminium-κ*O*)zinc(II). *Main Group Met. Chem.* **2015**, *38*, 125-131. DOI: 10.1515/mgmc-2015-0024.
2015	Garifzyanov, A. R.; Koshkin, S. A.; Davletshina, N. V.; Chibirev, Y. O.; Islamov, D. R.; Kataeva, O. N.; Cherkasov, R. A. Synthesis and Structure of Complexes of *N*-(Diphenylphosphoryl)methyl-*N*-Methylaminoacetic Acid with Ions of Cooper(II) and Nickel(II). *Russ. J. Org. Chem.* **2015**, *51*, 1659-1661. DOI: 10.1134/S1070428015110238.
2015	Bykowska, A.; Starosta, R.; Jezierska, J.; Jeżowska-Bojczuk, M. Coordination Versatility of Phosphine Derivatives of Fuoroquinolones. New Cu^I and Cu^{II} Complexes and Their Interactions with DNA. *RSC Adv.* **2015**, *5*, 80804-80815. DOI: 10.1039/C5RA07483E.
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2013	Reiss, G. J. Pseudosymmetric *fac*-Diaquatrichlorido-[(dimethylphosphoryl)methanaminium-κ*O*]manganese(II). *Acta Cryst.* **2013**, *E69*, m250-m251. DOI: 10.1107/s1600536813008751.
2013	Reiss, G. J. Bis[(dimethylphosphoryl)methanaminium] Tetrachloridopalladate(II). *Acta Cryst.* **2013**, *E69*, m614-m615. DOI: 10.1107/s1600536813028067.

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2013	Lambertz, C.; Luppa, A.; Reiss, G. J. Crystal Structure of Bis((dimethylphosphoryl)methanaminium)hexachloridostannate(IV), $C_6H_{22}Cl_6N_2O_2P_2Sn$. *Z. Krystallog*. **2013**, *228*, 227-228. DOI: 10.1524/ncrs.2013.0113.
2012	Bogomilova, A.; Günther, M.; Wagner, E.; Hägele, G.; Troev, K. Synthesis and Characterization of New Platinum(II) Phosphinate Complexes. *J. Coord. Chem.* **2012**, *65*, 1093-1106. DOI: 10.1080/00958972.2012.666797.
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2011	Liu, N.; Wang, Z.-X. Kumada Coupling of Aryl, Heteroaryl, and Vinyl Chlorides Catalyzed by Amido Pincer Nickel Complexes. *J. Org. Chem.* **2011**, *76*, 10031-10038. DOI: 10.1021/jo201821g.
2009	Kochel, A. Synthesis and Magnetic Properties of the Copper(II) Complex Derived from Dimethyl Aminomethylphosphine Oxide Ligand. X-Ray Crystal Structure of DMAO and $[Cu(NO_3)_2(POC_3H_{10}N)_2]$. *Inorg. Chim. Acta* **2009**, *362*, 1379-1382. DOI: 10.1016/j.ica.2008.05.025.
2003	Priya, S.; Balakrishna, M. S.; Mague, J. T.; Mobin, S. M. Insertion of Carbon Fragments into P(III)−N Bonds in Aminophosphines and Aminobis(phosphines): Synthesis, Reactivity, and Coordination Chemistry of Resulting Phosphine Oxide Derivatives. Crystal and Molecular Structures of $(Ph_2P(O)CH_2)_2NR$ (R = Me, ^{n}Pr, ^{n}Bu), $Ph_2P(O)CH(OH)^nPr$, and *cis*-$[MoO_2Cl_2\{(Ph_2P(O)CH_2)_2NEt\text{-}\kappa O,\kappa O\}]$. *Inorg. Chem.* **2003**, *42*, 1272-1281. DOI: 10.1021/ic026118t.
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1996	Pasechnik, M. P.; Matveev, S. V.; Tolkachev, D. V.; Matveeva, A. G.; Matrosov, E. I.; Polikarpov, Y. M.; Kabachnik, M. I. Intramolecular Hydrogen Bonds in the Copper(II) Complex with cis,cis-1,3,5-Tri[2-(diphenylphosphoryl)ethylamino]cyclohexane. Russ. Chem. Bull. 1996, 45, 1466-1471. DOI: 10.1007/BF01434234.
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1994	Varbanov, S.; Russeva, E.; Ganchev, A. Zinc Complexes of Dimethyl(phthalimidomethyl)phosphine Oxide. *Z. Naturforsch. B* **1994**, *49*, 258-262. DOI: 10.1515/znb-1994-0218.
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1991	Macíček, J.; Angelova, O.; Dodoff, N. Structure of *cis*-Dichloro[methylphosphinylidenebis(methylamine-N,N')]platinum(II) Hemihydrate. *Acta Cryst*. **1991**, *C47*, 971-973. DOI: 10.1107/S0108270190012689.
1990	Dodoff, N.; Macček, J.; Angelova, O.; Varbanov, S.; Spassovska, N. Chromium(III), Cobalt(II), Nickel(II) and Copper(II) Complexes of (Dimethyl-Phosphinyl)Methanamine. Crystal Structure of *fac*-Tris{(Dimethyl-Phosphinyl)Methanamine-N,O}Nickel(II) Chloride Trihydrate. *J. Coord. Chem.* **1990**, *22*, 219-228. DOI: 10.1080/00958979009408218.

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1988	Yatsimirskii, K. B.; Kabachnik, M. I.; Sinyavskaya, É. I.; Tsymbal, L. V.; Pisareva, S. A.; Medved', T. Y. Complexes of Alkali Metals, Magnesium, and Calcium with Phosphoryl-Containing Pendant Tetraazamacrocyclic Ligand. *Russ. Chem. Bull.* **1988**, *37*, 1874-1879. DOI: 10.1007/BF00962505.
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1987	Stherbakov, B. K.; Pisareva, S. A.; Medved', T. Y.; Kabachnik, M. I. New Cyclopendant Organophosphorus Ligands. *Phosphorus Sulfur Silicon Relat. Elem.* **1987**, *30*, 733-733. DOI: 10.1080/03086648708079227.
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1984	Yatsimirskii, K. B.; Sinyavskaya, E. I.; Tsimbal, L. V.; Medved', T. Y.; Shcherbakov, B. K.; Polikarpov, Y. M.; Kabachnik, M. I. Interaction of Magnesium and Calcium Iodides with Tris(diphenylphosphinylmethyl)-1,4,7-triazacyclononane. *Zh. Neorg. Khim.* **1984**, *29*, 888-893.
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1980	Konstantinovskaya, M. A.; Sinyavskaya, É. I. Complexes of Copper(II) Chloride with Amino-Substituted Derivatives of Phosphine Oxides. *Zh. Neorg. Khim.* **1980**, *25*, 416-422.
1980	Bashkirov, Sh. Sh.; Kuramshin, I. Ya.; Khramov, A. S.; Pudovik, A. N. Effect of Substituents at Phosphorus and Tin Atoms on the Parameters of Moessbauer Spectra of Complexes of Tin Halides with Organophosphorus Ligands. Probability of the Moessbauer Effect. *Koord. Khim.* **1980**, *6*, 537-541.
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1976	Osipenko, N. G.; Petrov, E. S.; Tsvetkov, E. N.; Ranneva, Yu. I.; Shatenshtein, A. I. Effect of the Structure of Phosphoryl-Containing Compounds on Their Ability to Solvate Lithium and Potassium Cations Based on Results of Measuring the H-Function of Solutions of *tert*-Butoxides in *tert*-Butyl Alcohol. *Zh. Obshch. Khim*. **1976**, *46*, 2647-265.
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Table S27. Papers and patents, describing applications of P(O),N-, P(O),NH-, and P(O),NH_2-acetals for metal extraction/separation.

Year	Reference
2022	Kukkonen, E.; Virtanen, E. J.; Moilanen, J. O. α-Aminophosphonates, -Phosphinates, and -Phosphine Oxides as Extraction and Precipitation Agents for Rare Earth Metals, Thorium, and Uranium: A Review. *Molecules* **2022**, *27*, id: 3465. DOI: 10.3390/molecules27113465.
2022	Turanov, A. N.; Karandashev, V. K.; Khvostikov, V. A.; Tcarkova, K. V.; Sharova, E. V.; Artyushin, O. I.; Bondarenko, N. A. Extraction of REE(III), U(VI), and Th(IV) with Modified Carbamoylmethylphosphine Oxides from Nitric Acid Solutions. *Russ. J. Gen. Chem.* **2022**, *92*, 1049-1055. DOI: 10.1134/s1070363222060160.
2020	Huang, M.; Fu, Y.; Lu, Y.; Liao, W.; Li, Z. A Novel Extractant Bis(2-ethylhexyl) ((2-Ethylhexylamino)methyl)phosphine Oxide for Cerium(IV) Extraction and Separation from Sulfate Medium. *J. Rare Earths* **2020**, *38*, 1330-1336. DOI: 10.1016/j.jre.2019.12.009.
2020	Simonescu, C. M.; Lavric, V.; Musina, A.; Antonescu, O. M.; Culita, D. C.; Marinescu, V.; Tardei, C.; Oprea, O.; Pandele, A. M. Experimental and Modeling of Cadmium Ions Removal by Chelating Resins. *J. Mol. Liq.* **2020**, *307*, id: 112973. DOI: 10.1016/j.molliq.2020.112973.
2019	Abdulbur-Alfakhoury, E.; van Zutphen, S.; Leermakers, M. Development of the Diffusive Gradients in Thin Films Technique (DGT) for Platinum (Pt), Palladium (Pd), and Rhodium (Rh) in Natural Waters. *Talanta* **2019**, *203*, 34-48. DOI: 10.1016/j.talanta.2019.05.038.
2019	Cherkasov, R. A.; Garifzyanov, A. R.; Davletshina, N. y. V.; Gaynullin, A. Z.; Kataeva, O. N.; Ivshin, K. A. Synthesis and Membrane-Transport Properties of Phosphorylated Diamines, Azapodands and Their Derivatives. *Phosphorus Sulfur Silicon Relat. Elem.* **2019**, *194*, 560-564. DOI: 10.1080/10426507.2018.1543297.
2018	Musina, A.; van Zutphen, S.; Lavric, V. Late Transition Metal Recovery from a Silver Nitrate Electrolyte Using a Phosphine-Oxide Bearing Scavenger. *New J. Chem.* **2018**, *42*, 7969-7975. DOI: 10.1039/C7NJ04928E.
2018	Garipova, A. R.; Kamkina, A. G.; Urazgalieva, A. A.; Garifzyanov, A. R.; Cherkasov, R. A. Membrane Extraction of Lithium and Sodium Ions with 2-Ethylhexyl Hydrogen [Bis(2-ethylhexyl)amino]methylphosphonate. *Russ. J. Gen. Chem.* **2018**, *88*, 120-123. DOI: 10.1134/S107036321801019X.
2018	Garifzyanov, A. R.; Davletshina, N. V.; Gayneev, A. M.; Gaynullin, A. Z.; Cherkasov, R. A. Synthesis, Transport, and Ionophoric Properties of α,ω-Diphosphorylated Azapodands: XI. Membrane Transport of Metals by Phosphorylated Diazapodands. *Russ. J. Gen. Chem.* **2018**, *88*, 1850-1852. DOI: 10.1134/S1070363218090141.
2017	Ricoux, Q.; Méricq, J. P.; Bouyer, D.; Bocokić, V.; Hernandez-Juarez, L. C.; van Zutphen, S.; Faura, C. A Selective Dynamic Sorption-Filtration Process for Separation of Pd(II) Ions Using an Aminophosphine Oxide Polymer. *Sep. Purif. Technol.* **2017**, *174*, 159-165. DOI: 10.1016/j.seppur.2016.10.025.
2017	Garifzyanov, A. R.; Leont'eva, S. V.; Stoyanov, O. V.; Cherkasov, R. A. Concentration of Metal Ions with Quasi-Liquid Emulsions Based on N,N-Bis(dihexylphosphorylmethyl)octylamine. *Izv. Kazan Tech. Univ.* **2017**, *20*, 27-31.
2016	Koshkin, S. A.; Garifzyanov, A. R.; Davletshina, N. V.; Davletshin, R. R.; Stoyanov, O. V.; Cherkasov, R. A. Synthesis, Structure of New Phosphoryl Methyl Derivative Aminoacids and Their Membrane Transport Properties Related to Alkali Metals: An Engineering Approach with Multidisciplinary Applications. In *Pathways to Modern Physical Chemistry: An Engineering Approach with Multidisciplinary Applications*; Wolf, R., Zaikov, G. E., Haghi, A. K., Eds.; Apple Academic Press: New York, 2016, pp. 341-353.
2016	Petrov, S. N.; Valeeva, L. F.; Garifzyanov, A. R.; Cherkasov, R. A. Synthesis of New Lipophilic Extractants for Liquid Extraction of Metal Ions. *Phosphorus Sulfur Silicon Relat. Elem.* **2016**, *191*, 1570-1571. DOI: 10.1080/10426507.2016.1216116.
2016	Davletshin, R. R.; Davletshina, N. y. V.; Nurgaliev, D. D.; Garifzyanov, A. R.; Cherkasov, R. A.; Ivshin, K. A.; Kataeva, O. N. Synthesis and Membrane Transport Properties of Bis(dihexylphosphorylmethyl)-1,4-diaminebutane. *Phosphorus Sulfur Silicon Relat. Elem.* **2016**, *191*, 1670-1670. DOI: 10.1080/10426507.2016.1227818.
2016	Davletshina, N. y. V.; Davletshin, R. R.; Baturshina, E. A.; Gaynullin, A. Z.; Garifzyanov, A. R.; Cherkasov, R. A. Membrane Extraction of Alkaline Earth Metal by Phosphorylated Azapodands. *Phosphorus Sulfur Silicon Relat. Elem.* **2016**, *191*, 1671-1672. DOI: 10.1080/10426507.2016.1227819.

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2016	Pellet-Rostaing, S.; Leydier, A.; Arrachart, G.; Turgis, R.; Dubois, V. Compounds with Phosphine Oxide and Amine Functions, Useful as Uranium(VI) Ligands, and Uses thereof, in Particular for Extracting Uranium(VI) from Aqueous Solutions of Sulphuric Acid. World Patent 2016/156591, Oct 6, **2016**.
2015	Ricoux, Q.; Bocokić, V.; Méricq, J. P.; Bouyer, D.; van Zutphen, S.; Faur, C. Selective Recovery of Palladium Using an Innovative Functional Polymer Containing Phosphine Oxide. *Chem. Eng. J.* **2015**, *264*, 772-779. DOI: 10.1016/j.cej.2014.11.139.
2015	Koshkin, S. A.; Garifzyanov, A. R.; Davletshina, N. V.; Davletshin, R. R.; Stoyanov, O. V.; Cherkasov, R. A. Synthesis, Structure of New Phosphorylmethyl Derivatives of Amino Acids and Their Membrane-Transport Properties toward Alkali Metals. *Izv. Kazan Tech. Univ.* **2015**, *18*, 7-11.
2015	Davletshina, N. V.; Koshkin, S. A.; Garifzyanov, A. R.; Davletshin, R. R.; Filimonova, M. A.; Cherkasov, R. A. Membrane Transport of Alkali Metals with Phosphorylmethyl Derivatives of Amino Acids. *Russ. J. Gen. Chem.* **2015**, *85*, 1791-1792. DOI: 10.1134/s1070363215070403.
2014	Muşină, A.; Bocokić, V.; Lavric, V.; van Zutphen, S. Phosphorus-Based Polymers for Selective Capture of Platinum Group Metals. *Ind. Eng. Chem. Res.* **2014**, *53*, 13362-13369. DOI: 10.1021/ie502153f.
2014	Davletshina, N. V.; Garifzyanov, A. R.; Stoyanov, O. V.; Cherkasov, R. A. Active Transport of Some Rare-Earth Metal Ions by Aminophosphoryl Membrane Transporters. *Izv. Kazan Tech. Univ.* **2014**, *17*, 31-36.
2014	Garifzyanov, A. R.; Davletshina, N. V.; Valeeva, M. S.; Koshkin, S. A.; Cherkasov, R. A. Preparation and Membrane Transport Properties of Phosphorylated Derivatives of Sarcosine. *Russ. J. Gen. Chem.* **2014**, *84*, 1251-1252. DOI: 10.1134/S1070363214060345.
2014	Garifzyanov, A. R.; Davletshina, N. V.; Garipova, A. R.; Cherkasov, R. A. Sinergetic Membrane Extraction of Lithium Ions with New Organophosphorus Carriers. *Russ. J. Gen. Chem.* **2014**, *84*, 285-288. DOI: 10.1134/S1070363214020224.
2013	Davletshina, N. V.; Garifzyanov, A.; Cherkasov, R. The Active Transport of Ions of Rare-Earth Elements, Alkali Metals, Al(III), and Mg(II) with New Lipophilic *N*,*N*-Bis[(Dihexylphosphoryl)Methyl]Octylamine. *Phosphorus Sulfur Silicon Relat. Elem.* **2013**, *188*, 4-6. DOI: 10.1080/10426507.2012.740691.
2013	Davletshina, N.; Cherkasov, R.; Garifzyanov, A.; Valeeva, M.; Koshkin, S.; Davletshin, R.; Leont'eva, S. Bis(Dialkylphosphinylmethyl)Alkylamines as the Liquid and Membrane Extractants of Rare Earth and Trace Metal Ions. *Phosphorus Sulfur Silicon Relat. Elem.* **2013**, *188*, 13-14. DOI: 10.1080/10426507.2012.740693.
2013	Garifzyanov, A. R.; Leont'eva, S. V.; Davletshina, N. V.; Davletshin, R. R.; Cherkasov, R. A. Synthesis, Transport, and Ionophore Properties of α,ω-Bisphosphorylated Azapodands: IX. Extraction of Metal Ions with Quasiliquid Emulsions on the Basis of *N*,*N*'-Bis(dioctylphosphorylmethyl)-1,8-diamino-3,6-dioxaoctane and Acidic Components. *Russ. J. Gen. Chem.* **2013**, *83*, 2301-2305. DOI: 10.1134/S1070363213120128.
2013	Garifzyanov, A. R.; Leont'ev, S. V.; Davletshina, N. V.; Voloshin, A. V.; Cherkasov, R. A. Synthesis, Transport, and Ionophore Properties of α,ω-Biphosphorylated Azapodands: VIII. Solvent Extraction of the Metal Ions with *N*,*N*'-Bis(dioctylphosphorylmethyl)-1,8-diamino-3,6-dioxaoctane. *Russ. J. Gen. Chem.* **2013**, *83*, 1997-2004. DOI: 10.1134/S1070363213110054.
2013	Garifzyanov, A. R.; Davletshina, N. V.; Myatish, E. Y.; Cherkasov, R. A. Membrane Extraction of Metal Ions by Aminophosphoryl Reagents in the Active Transport Conditions. *Russ. J. Gen. Chem.* **2013**, *83*, 267-273. DOI: 10.1134/S1070363213020060.
2013	Garifzyanov, A. R.; Davletshin, R. R.; Davletshina, N. V.; Cherkasov, R. A. Synthesis, Transport, and Ionophoric Properties of α,ω-Biphosphorylated Azapodands: VI. New Cesium-Selective Electrodes Based on the Phosphorylated Azapodands. *Russ. J. Gen. Chem.* **2013**, *83*, 260-266. DOI: 10.1134/S1070363213020059.
2012	Cherkasov, R. A.; Garifzyanov, A. R.; Bazanova, E. B.; Davletshin, R. R.; Leont'eva, S. V. Liquid Extraction of Some Rare Earth Elements with Aminomethylphosphine Oxides. *Russ. J. Gen. Chem.* **2012**, *82*, 33-42. DOI: 10.1134/S1070363212010069.
2012	Garifzyanov, A. R.; Davletshin, R. R.; Davletshina, N. V.; Cherkasov, R. A. Synthesis, Transport and Ionophore Properties of α,ω-Biphosphorylated Azapodands: V. Acid–Base Properties of New Phosphorylated Azapodands and α,ω-Diamines and Their Participation in the Membrane Transport of I–III Groups Metal Ions. *Russ. J. Gen. Chem.* **2012**, *82*, 1646-1653. DOI: 10.1134/S1070363212100039.

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2012	Turanov, A. N.; Karandashev, V. K.; Baulin, V. E. Extraction of Rare Earth Elements with Phosphoryl-Containing Lariat Crown Ether in the Presence of Ionic Liquids. *Russ. J. Inorg. Chem.* **2012**, *57*, 292-296. DOI: 10.1134/S0036023612020246.
2011	Cherkasov, R. A.; Garifzyanov, A. R.; Bazanova, O. B.; Leont'eva, S. V. Solvent Extraction of Some Trace Metals and Iron with *N*-Octyl-*N*,*N*-bis(dihexylphosphinylmethyl)amine. *Russ. J. Gen. Chem.* **2011**, *81*, 2080-2087. DOI: 10.1134/S1070363211100070.
2011	Cherkasov, R. A.; Garifzjanov, A. R.; Davletshin, R. R. Synthesis of New α-Bisaminophosphinoxides. *Phosphorus Sulfur Silicon Relat. Elem.* **2011**, *186*, 785-786. DOI: 10.1080/10426507.2010.517585.
2011	Cherkasov, R. A.; Garivzyanov, A. R.; Kurnosova, N. V. Synthesis and Membrane Transport Properties of *N*-Functionalized α-Aminophosphine Oxides. *Phosphorus Sulfur Silicon Relat. Elem.* **2011**, *186*, 787-789. DOI: 10.1080/10426507.2010.515954.
2011	Cherkasov, R. A.; Garifzyanov, A. R.; Galeev, R. R.; Kurnosova, N. V.; Davletshin, R. R.; Zakharov, S. V. Membrane Transport of Metal Ions with Lipophilic Aminomethylphosphine Oxides. *Russ. J. Gen. Chem.* **2011**, *81*, 1464-1469. DOI: 10.1134/S1070363211070103.
2010	Cherkasov, R. A.; Garifzyanov, A. R.; Leont'eva, S. V.; Davletshin, R. R.; Koshkin, S. A. New Aminophosphoryl Extractants for Liquid Extraction of Pt(IV) Ions. *Russ. J. Gen. Chem.* **2010**, *80*, 151-152. DOI: 10.1134/S107036321001024X.
2009	Cherkasov, R. A.; Garifzyanov, A. R.; Leont'ev, S. V.; Davletshin, R. R.; Koshkin, S. A. Extraction of Scandium Ions by New Aminophosphinyl Extractants. *Russ. J. Gen. Chem.* **2009**, *79*, 2599-2605. DOI: 10.1134/S107036320912007X.
2008	Cherkasov, R. A.; Vasil'ev, R. I.; Garifzyanov, A. R.; Talan, A. S. Synthesis, Transport, and Ionophoric Properties of α,ω-Diphosphorylated Aza Podands: IV. Induced Membrane Transport of Alkali and Alkaline-Earth Metal Ions. *Russ. J. Gen. Chem.* **2008**, *78*, 1167-1171. DOI: 10.1134/S107036320806011X.
2008	Cherkasov, R. A.; Garifzjanov, A. R.; Krasnova, N. S.; Talan, A. S.; Badretdinova, G. Z.; Burnaeva, L. M.; Ivkova, G. A. Functionalized Phosphoryl Compounds: Synthesis, Extraction, Transport and Ionophore Properties. *Phosphorus Sulfur Silicon Relat. Elem.* **2008**, *183*, 406-409. DOI: 10.1080/10426500701735353.
2006	Cherkasov, R. A.; Nuriazdanova, G. K.; Garifzyanov, A. R. Synthesis, Transport and Ionophore Properties of α,ω-Diphosphorylated Aza Podands: III. Liquid Ion-Selective Electrodes Based on Phosphorylated Aza Podands. *Russ. J. Gen. Chem.* **2006**, *76*, 202-205. DOI: 10.1134/S107036320602006X.
2005	Garifzyanov, A. R.; Vasil'ev, R. I.; Cherkasov, R. A. Synthesis and Ionophoric Properties of α,ω-Diphosphorylated Aza Podands: II. Kabachnik-Fields Reaction as a Method for Design of α,ω-Diphosphorylated Aza Podands and Their Use for Determination of Metal Ions. *Russ. J. Gen. Chem.* **2005**, *75*, 217-224. DOI: 10.1007/s11176-005-0201-6.
2004	Turanov, A. N.; Karandashev, V. K.; Yarkevich, A. N.; Safronova, Z. V. Extraction of Rhenium(VII) from Sulfuric Acid Solutions with Phosphorylated Amines. *Zh. Neorg. Khim.* **2004**, *49*, 1390-1393.
2001	Novák, T.; Bakó, P.; Keglevich, G.; Dobó, A.; Vékey, K.; Tóke, L. Synthesis of D-Glucose-Based Azacrown Ethers with Phosphinoxidoalkyl Side Chains and Their Application to an Enantioselective Reaction. *J. Incl. Phenom.* **2001**, *40*, 207-212. DOI: 10.1023/A:1011840831308.
2000	Kharitonov, A. V.; Jarkevich, A. N.; Safronova, Z. V.; Turanov, A. N. Platinum and Palladium Extraction Separation Process. Rus. Patent 2,151,209, Jun 20, **2000**.
1999	Turanov, A. N.; Kharitonov, A. V.; Yarkevich, A. N.; Safronova, Z. V.; Tsvetkov, E. N. Synthesis of Phosphoryalated Aza-Crown Ethers and Their Extraction Ability with Respect to Palladium. *Zh. Obshch. Khim.* **1999**, *69*, 1097-1101.
1978	Skorovarov, D. I.; Laskorin, B. N.; Savina, L. A.; Chernetsov, O. K.; Stupin, N. P.; Fedorova, L. A.; Shiryaeva, A. K.; Buskina, I. A. Extraction of Ruthenium Nitrosonitrate Complexes by Some Amino-Substituted Phosphoryl-Containing Organic Compounds. *Radiokhimiya* **1978**, *20*, 407-413.
1973	Rusina, M. N.; Polikarpov, Y. M.; Yaroshenko, G. F.; Timakova, L. M. Amino-Substituted Phosphine Oxides as Rare Earth Element Extractants. *Zh. Obshch. Khim.* **1973**, *43*, 238-242.
1970	Laskorin, B. N.; Fedorova, L. A.; Stupin, N. P.; Kabachnik, M. I.; Medved', T. Y.; Polikarpov, Y. M. Extraction Properties of Amino-Substituted Phosphine Oxide and Their Derivatives. *Radiokhimiya* **1970**, *12*, 335-344.
1969	Laskorin, B. N.; Fedorova, L. A.; Stupin, N. P.; Kabachnik, M. I.; Medved', T. Y.; Polikarpov, Y. M.; Savina, L. A. Study of the Extraction Properties of Amino-Substituted Phosphine Oxides and Their *N*-Oxides. *Dokl. Akad. Nauk. SSSR* **1969**, *189*, 1017-1020.

Table S28. Papers, describing applications of P(O),N-, P(O),NH-, and P(O),NH_2-acetals for extraction of organic or inorganic acids.

Year	Reference
2019	avletshina, N. V.; Nasyrov, I. R.; Khabibullina, A. R.; Davletshin, R. R.; Gaynullin, A. Z.; Cherkasov, R. A. Synthesis and Transport and Ionophoric Properties of α,ω-Diphosphorylated Azapodands: XII. Membrane Transport of Organic Acids by Diphosphorylated Diamines and Diazapodands. *Russ. J. Gen. Chem.* **2019**, *89*, 2424-2431. DOI: 10.1134/S1070363219120168.
2018	Garifzyanov, A. R.; Davletshina, N. V.; Akhmadullina, L. I.; Gaynullin, A. Z.; Cherkasov, R. A. Synthesis, Transport, and Ionophoric Properties of α,ω-Biphosphorylated Azapodands: X. Membrane Transport of Organic Acids by Phosphorylated α,ω-Diazapodands. *Russ. J. Gen. Chem.* **2018**, *88*, 1462-1469. DOI: 10.1134/S1070363218070186.
2016	Davletshin, R. R.; Davletshina, N. y. V.; Nurgaliev, D. D.; Garifzyanov, A. R.; Cherkasov, R. A.; Ivshin, K. A.; Kataeva, O. N. Synthesis and Membrane Transport Properties of Bis(dihexylphosphorylmethyl)-1,4-diaminebutane. *Phosphorus Sulfur Silicon Relat. Elem.* **2016**, *191*, 1670-1670. DOI: 10.1080/10426507.2016.1227818.
2016	Cherkasov, R. A.; Koshkin, S. A.; Garifzyanov, A. R.; Davletshina, N. y. V. Synthesis of Lipophilic *N*-Phosphorylmethylated Amino Acids and Their Membrane-Transport Properties towards Some Organic Acids. *Phosphorus Sulfur Silicon Relat. Elem.* **2016**, *191*, 1650-1651. DOI: 10.1080/10426507.2016.1223666.
2014	Garifzyanov, A. R.; Davletshina, N. V.; Valeeva, M. S.; Koshkin, S. A.; Cherkasov, R. A. Preparation and Membrane Transport Properties of Phosphorylated Derivatives of Sarcosine. *Russ. J. Gen. Chem.* **2014**, *84*, 1251-1252. DOI: 10.1134/S1070363214060345.
2014	Koshkin, S. A.; Garifzyanov, A. R.; Davletshina, N. V.; Valeeva, M. S.; Cherkasov, R. A. Membrane Transport of Organic Acids by *N*-Methylphosphorylated Amino Acids. *Russ. J. Gen. Chem.* **2014**, *84*, 2289-2290. DOI: 10.1134/S1070363214110462.
2013	Garifzyanov, A. R.; Davletshin, R. R.; Davletshina, N. V.; Cherkasov, R. A. Synthesis, Transport, and Ionophore Properties of α,ω-Biphosphorylated Azapodands: VII. Membrane Transport of Mineral Acids by Phosphorylated α,ω-Diamines and Azapodands. *Russ. J. Gen. Chem.* **2013**, *83*, 398-399. DOI: 10.1134/S1070363213020278.
2012	Cherkasov, R. A.; Garifzyanov, A. R.; Kurnosova, N. V.; Matveeva, E. V.; Odinets, I. L. Synthesis of the Novel β-Aminophosphoryl Compounds and Their Acid-Base Properties and Membrane-Transport Abilities towards Carboxylic Acids. *Russ. Chem. Bull.* **2012**, *61*, 174-180. DOI: 10.1007/s11172-012-0024-7.
2011	Cherkasov, R. A.; Garifzyanov, A. R.; Koshkin, S. A. Synthesis of Optically Active α-Aminophosphine Oxides and Enantioselective Membrane Transport of Acids with Their Participation. *Russ. J. Gen. Chem.* **2011**, *81*, 773-774. DOI: 10.1134/S107036321104027X.
2011	Cherkasov, R. A.; Garifzyanov, A. R.; Koshkin, S. A. Synthesis of α-Aminophosphine Oxides with Chiral Phosphorus and Carbon Atoms. *Phosphorus Sulfur Silicon Relat. Elem.* **2011**, *186*, 782-784. DOI: 10.1080/10426507.2010.524181.
2009	Cherkasov, R. A.; Garifzyanov, A. R.; Talan, A. S.; Davletshin, R. R.; Kurnosova, N. V. Synthesis of New Liophilic Functionalized Aminomethylphosphine Oxides and Their Acid-Base and Membrane-Transport Properties toward Acidic Substrates. *Russ. J. Gen. Chem.* **2009**, *79*, 1835-1849. DOI: 10.1134/S1070363209090114.
2008	Cherkasov, R. A.; Talan, A. S.; Tarasov, A. V.; Garifzyanov, A. P. Synthesis of Novel Mono- and Bisaminophosphoryl Compounds and Their Membrane Transport Properties for Acidic Substrates. *Russ. J. Gen. Chem.* **2008**, *78*, 1330-1333. DOI: 10.1134/S1070363208070062.
2005	Garifzyanov, A. R.; Shirshova, N. V.; Cherkasov, R. A. Membrane Transport of Inorganic Acids with α-Aminophosphoryl Compounds. *Russ. J. Gen. Chem.* **2005**, *75*, 537-540. DOI: 10.1007/s11176-005-0268-0.

Table S29. Papers, describing applications of P(O),NH_2-acetals as precursors for α-diazo phosphine oxides.

Year	Reference
2022	Sun, S.; Wei, Y.; Xu, J. Visible-Light-Induced [1+5] Annulation of Phosphoryl Diazomethylarenes and Pyridinium 1,4-Zwitterionic Thiolates. *Org. Lett.* **2022**, *24*, 6024-6030. DOI: 10.1021/acs.orglett.2c02321.
2020	Luo, Y.; Fu, Z.; Fu, X.; Du, C.; Xu, J. Microwave-Assisted Periselective Annulation of Triarylphosphenes with Aldehydes and Ketones. *Org. Biomol. Chem.* **2020**, *18*, 9526-9537. DOI: 10.1039/D0OB02011G.
2020	Luo, Y.; Xu, J. Annulation of Diaryl(aryl)phosphenes and Cyclic Imines to Access Benzo-δ-phospholactams. *Org. Lett.* **2020**, *22*, 7780-7785. DOI: 10.1021/acs.orglett.0c02346.
2016	Marinozzi, M.; Pertusati, F.; Serpi, M. λ^5-Phosphorus-Containing α-Diazo Compounds: A Valuable Tool for Accessing Phosphorus-Functionalized Molecules. *Chem. Rev.* **2016**, *116*, 13991-14055. DOI: 10.1021/acs.chemrev.6b00373.
1980	Regitz, M.; Eckes, H. Carbene, 22. Phosphene: Abfangreaktionen von (Diphenylmethylen)phenyl-phosphan-oxid durch [2 + 2]-Cycloaddition mit Aldehyden. *Chem. Ber.* **1980**, *113*, 3303-3312. DOI: 10.1002/cber.19801131018.
1971	Regitz, M.; Liedhegener, A.; Eckstein, U.; Martin, M.; Anschütz, W. Quecksilber- und Silber-Derivate von Diphenylphosphinyl- und Diäthylphosphono-diazomethan. *Liebigs Ann. Chem.* **1971**, *748*, 207-210. DOI: 10.1002/jlac.19717480122.
1965	Kreutzkamp, N.; Schmidt-Samoa, E.; Herberg, K. Diazomethylphosphine Oxides. *Angew. Chem. Int. Ed.* **1965**, *4*, 1078-1078. DOI: 10.1002/anie.196510781.
1961	Horner, L.; Hoffmann, H.; Ertel, H.; Klahre, G. Phosphororganische Verbindungen Darstellung und Eigenschaften α-Substituierter Phosphinoxyde. *Tetrahedron Lett.* **1961**, *2*, 9-11. DOI: 10.1016/S0040-4039(01)99195-6.

Table S30. Papers and patents, describing applications of P(O),N-, P(O),NH-, and P(O),NH_2-acetals as precursors for P,N-ligands.

Year	Reference
2022	Takahashi, K.; Sakurazawa, Y.; Iwai, A.; Iwasawa, N. Catalytic Synthesis of a Methylmalonate Salt from Ethylene and Carbon Dioxide through Photoinduced Activation and Photoredox-Catalyzed Reduction of Nickelalactones. *ACS Catal.* **2022**, *12*, 3776-3781. DOI: 10.1021/acscatal.2c01053.
2022	He, F.; Gourlaouen, C.; Pang, H.; Braunstein, P. Experimental and Theoretical Study of Ni^{II}- and Pd^{II}-Promoted Double Geminal $C(sp^3)$-H Bond Activation Providing Facile Access to NHC Pincer Complexes: Isolated Intermediates and Mechanism. *Chem. Eur. J.* **2022**, *28*, id: e202200507. DOI: 10.1002/chem.202200507.
2021	Popovics-Tóth, N.; Rávai, B.; Tajti, Á.; Varga, B.; Bagi, P.; Perdih, F.; Szabó, P. T.; Hackler, L.; Puskás, L. G.; Bálint, E. Three-Component Synthesis, Utilization and Biological Activity of Phosphinoyl-Functionalized Isoindolinones. *Org. Biomol. Chem.* **2021**, *19*, 8754-8760. DOI: 10.1039/D1OB01610E.
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Table S32. Papers and patents, describing applications of P(O),N-, P(O),NH-, and P(O),NH_2-acetals as flame retardants in polymers.

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Table S33. Papers, describing applications of P(O),N- and P(O),NH-acetals as organocatalysts.

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Table S35. Papers and patents, describing syntheses of Schiff bases from P(O),NH_2-acetals, and their application.

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Table S36. Papers and patents, describing applications of P(O),N-, P(O),NH-, and P(O),NH_2-acetals in pharmacology.

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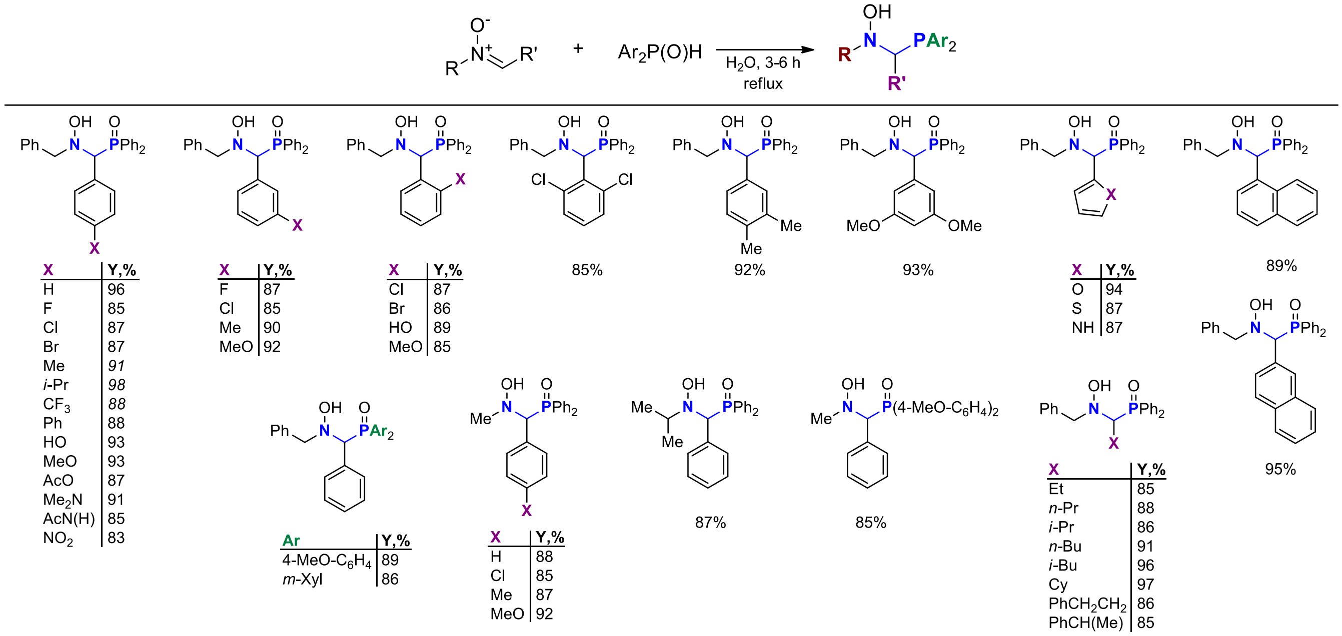
Figure S1. *N*-hydroxy P(O),N-acetals, obtained by reaction of SPOs with nitrones.[183,184]



X	Y,%
H	96
F	85
Cl	87
Br	87
Me	*91*
i-Pr	*98*
CF_3	*88*
Ph	88
HO	93
MeO	93
AcO	87
Me_2N	91
AcN(H)	85
NO_2	83

X	Y,%
F	87
Cl	85
Me	90
MeO	92

X	Y,%
Cl	87
Br	86
HO	89
MeO	85

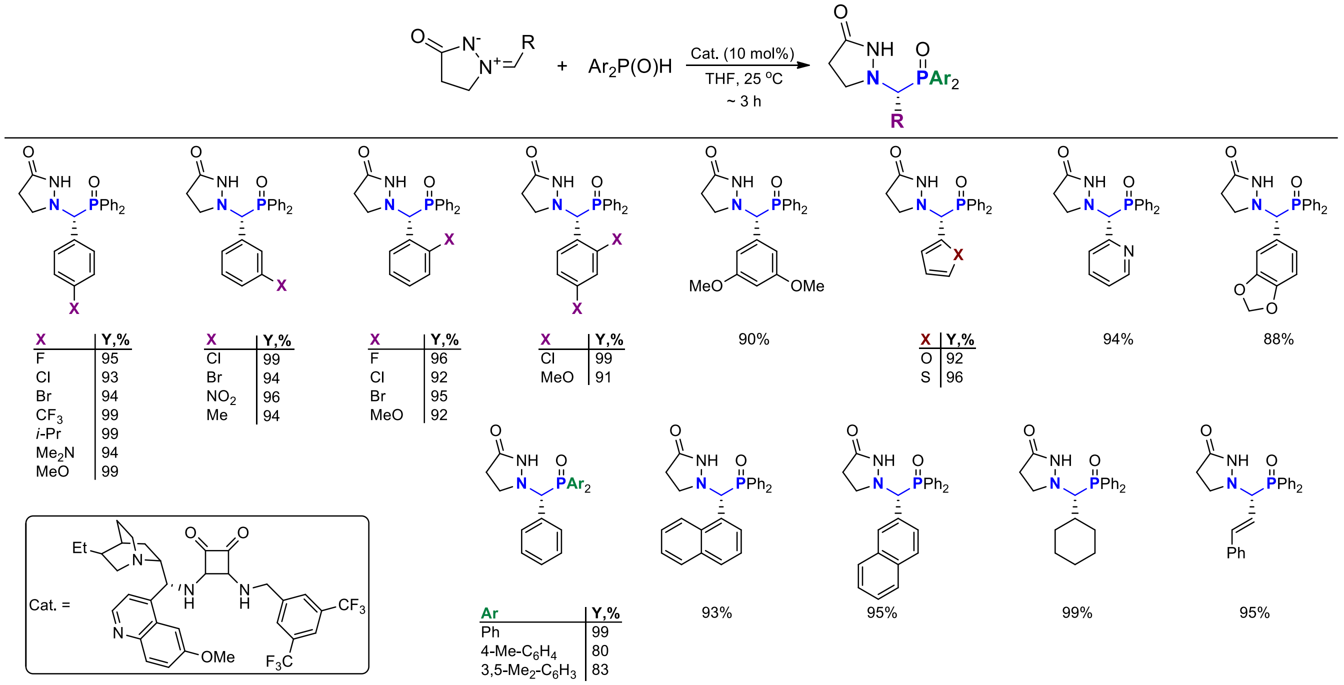
X	Y,%
O	94
S	87
NH	87

Ar	Y,%
4-MeO-C_6H_4	89
m-Xyl	86

X	Y,%
H	88
Cl	85
Me	87
MeO	92

X	Y,%
Et	85
n-Pr	88
i-Pr	86
n-Bu	91
i-Bu	96
Cy	97
$PhCH_2CH_2$	86
PhCH(Me)	85

Figure S2. P(O),N-acetals, obtained by reaction of cyclic azomethine imines with SPOs.[185,186]



X	Y,%
F	95
Cl	93
Br	94
CF_3	99
i-Pr	99
Me_2N	94
MeO	99

X	Y,%
Cl	99
Br	94
NO_2	96
Me	94

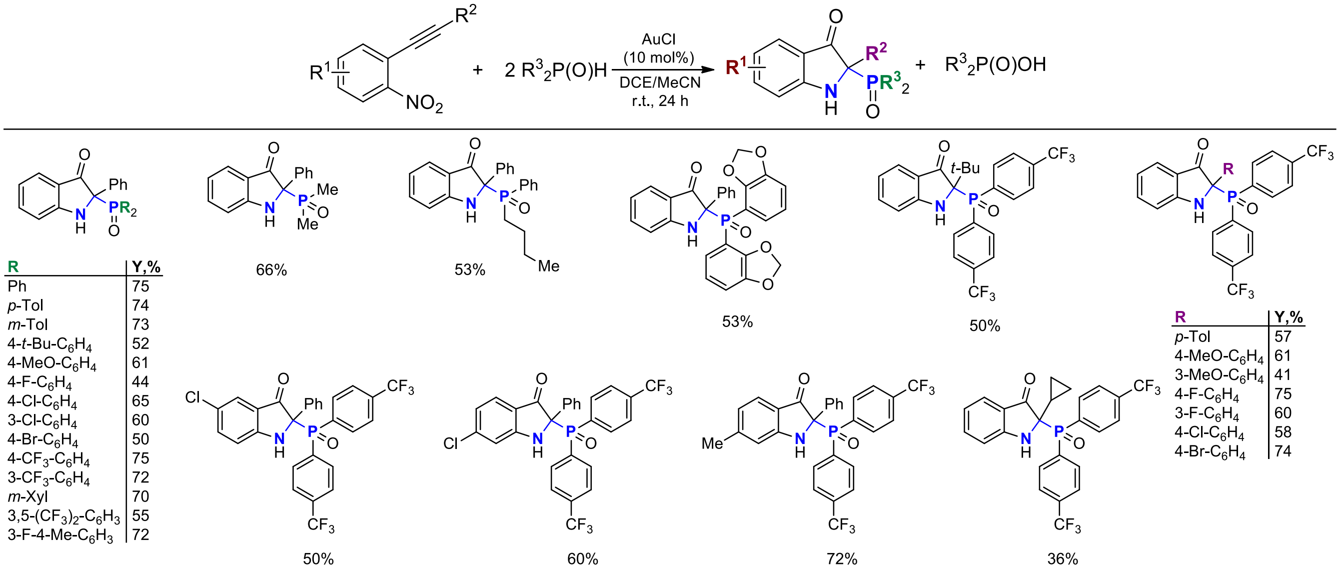
X	Y,%
F	96
Cl	92
Br	95
MeO	92

X	Y,%
Cl	99
MeO	91

X	Y,%
O	92
S	96

Ar	Y,%
Ph	99
4-Me-C_6H_4	80
3,5-Me_2-C_6H_3	83

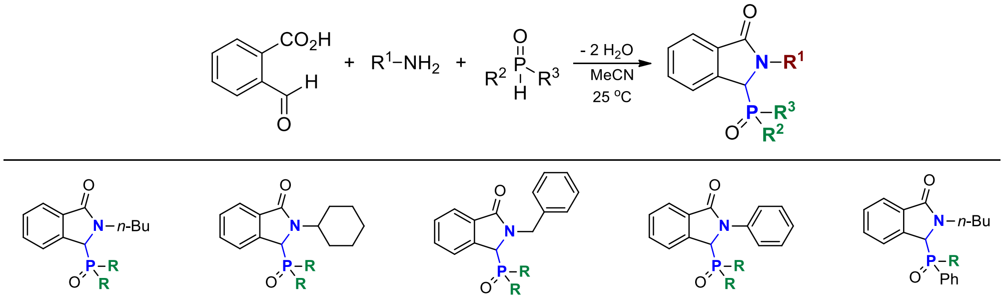
Figure S3. Au(I)-Catalyzed reaction of 1-nitro-2-(arylethynyl)benzenes with SPOs.[187]



R	Y,%
Ph	75
p-Tol	74
m-Tol	73
4-*t*-Bu-C_6H_4	52
4-MeO-C_6H_4	61
4-F-C_6H_4	44
4-Cl-C_6H_4	65
3-Cl-C_6H_4	60
4-Br-C_6H_4	50
4-CF_3-C_6H_4	75
3-CF_3-C_6H_4	72
m-Xyl	70
3,5-$(CF_3)_2$-C_6H_3	55
3-F-4-Me-C_6H_3	72

R	Y,%
p-Tol	57
4-MeO-C_6H_4	61
3-MeO-C_6H_4	41
4-F-C_6H_4	75
3-F-C_6H_4	60
4-Cl-C_6H_4	58
4-Br-C_6H_4	74

Figure S4. 3-Phosphinoyl-1-isoindolinones, obtained by reaction of 2-formylbenzoic acid, primary amines and SPOs.



R	Y,%
Ph	98
p-Tol	99
m-Xyl	97
2-Naph	96
$PhCH_2$	96

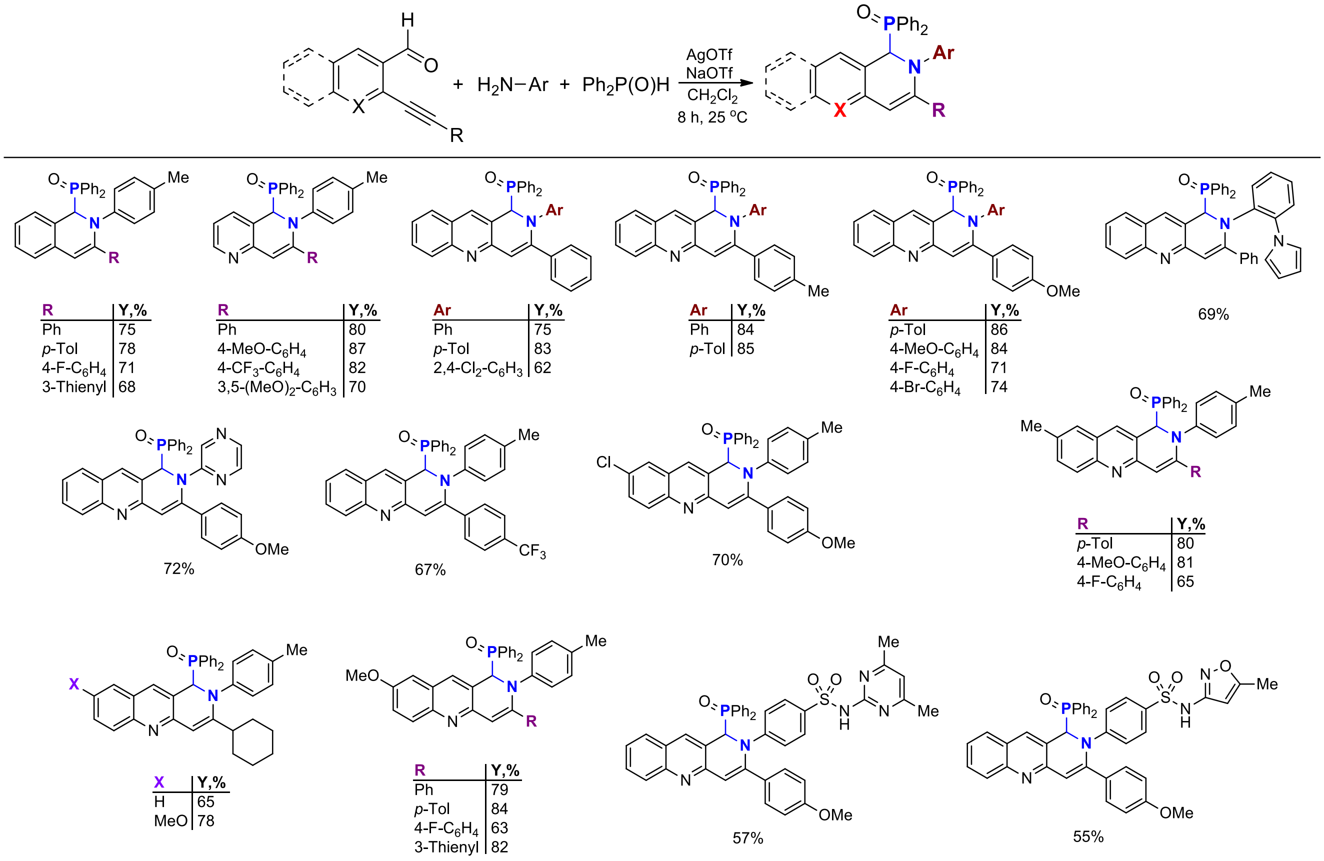
R	Y,%
Ph	94
p-Tol	97
m-Xyl	96
2-Naph	95
$PhCH_2$	94

R	Y,%
Ph	97
p-Tol	98
m-Xyl	97
2-Naph	97
$PhCH_2$	96

R	Y,%
Ph	96
p-Tol	98
m-Xyl	97

R	Y,%
t-Bu	94
o-Tol	96
2-MeO-C_6H_4	95
2-CF_3-C_6H_4	97
3-CF_3-C_6H_4	96
4-CF_3-C_6H_4	98
1-Naph	97
2-Ph-C_6H_4	96

Figure S5. 3C-Reaction of *ortho*-alkynyl aromatic aldehydes with anilines and $Ph_2P(O)H$.[188]



R	Y,%
Ph	75
p-Tol	78
4-F-C_6H_4	71
3-Thienyl	68

R	Y,%
Ph	80
4-MeO-C_6H_4	87
4-CF_3-C_6H_4	82
3,5-$(MeO)_2$-C_6H_3	70

Ar	Y,%
Ph	75
p-Tol	83
2,4-Cl_2-C_6H_3	62

Ar	Y,%
Ph	84
p-Tol	85

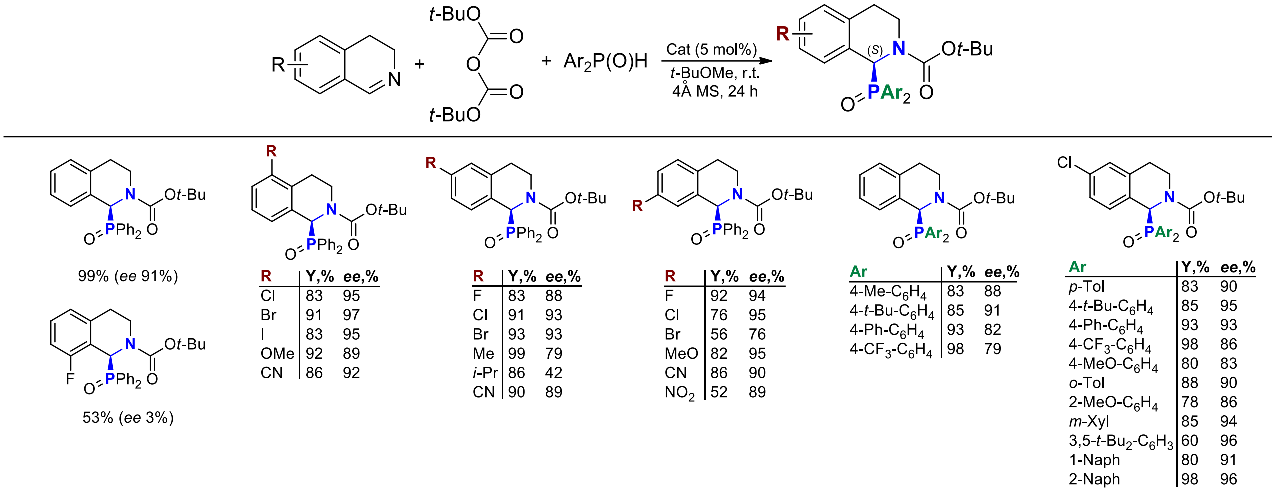
Ar	Y,%
p-Tol	86
4-MeO-C_6H_4	84
4-F-C_6H_4	71
4-Br-C_6H_4	74

R	Y,%
p-Tol	80
4-MeO-C_6H_4	81
4-F-C_6H_4	65

X	Y,%
H	65
MeO	78

R	Y,%
Ph	79
p-Tol	84
4-F-C_6H_4	63
3-Thienyl	82

Figure S6. Reaction of 3,4-dihydroisoquinolines, di-*t*-Bu dicarbonate and SPOs.[189]



99% (*ee* 91%)

53% (*ee* 3%)

R	Y,%	ee,%
Cl	83	95
Br	91	97
I	83	95
OMe	92	89
CN	86	92

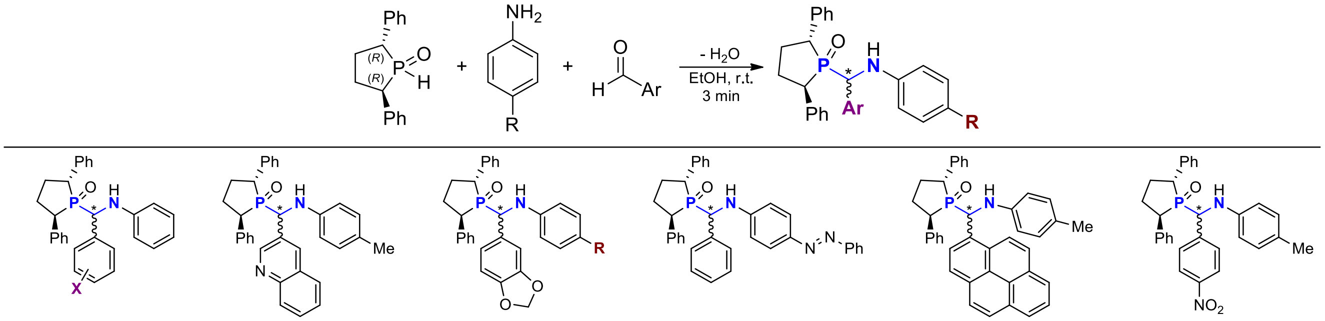
R	Y,%	ee,%
F	83	88
Cl	91	93
Br	93	93
Me	99	79
i-Pr	86	42
CN	90	89

R	Y,%	ee,%
F	92	94
Cl	76	95
Br	56	76
MeO	82	95
CN	86	90
NO_2	52	89

Ar	Y,%	ee,%
4-Me-C_6H_4	83	88
4-*t*-Bu-C_6H_4	85	91
4-Ph-C_6H_4	93	82
4-CF_3-C_6H_4	98	79

Ar	Y,%	ee,%
p-Tol	83	90
4-*t*-Bu-C_6H_4	85	95
4-Ph-C_6H_4	93	93
4-CF_3-C_6H_4	98	86
4-MeO-C_6H_4	80	83
o-Tol	88	90
2-MeO-C_6H_4	78	86
m-Xyl	85	94
3,5-*t*-Bu_2-C_6H_3	60	96
1-Naph	80	91
2-Naph	98	96

Figure S7. P(O),NH-acetals, obtained by reaction of 2,5-diphenylphospholane 1-oxide with anilines and aromatic aldehydes.[87]



X	Y,%	R:S,%
H	98	60:40
2-PhO	97	76:24
2-MeO	96	86:14
4-NO_2	96	58:42

96% (R:S = 73:27)

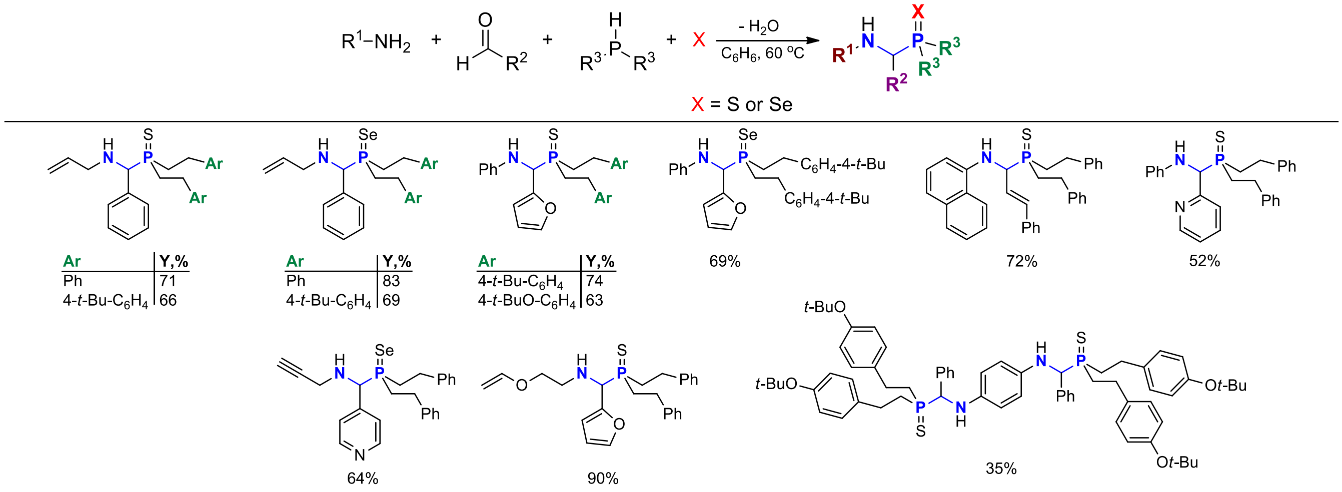
R	Y,%	R:S,%
H	97	73:27
Me	98	62:38

98% (R:S = 79:21)

96% (R:S = 80:20)

97% (R:S = 52:48)

Figure S8. P(S),NH- and P(Se),NH-acetals, obtained by 4C-reaction of primary amines, aldehydes, secondary phosphines and S or Se.[190]

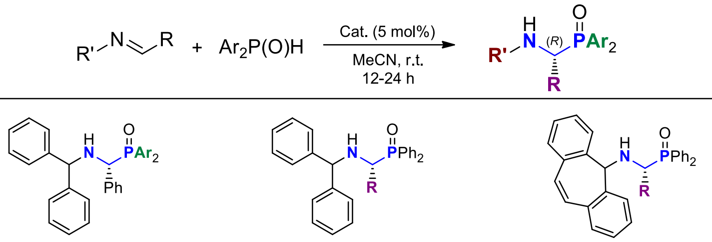


Ar	Y,%
Ph	71
4-*t*-Bu-C_6H_4	66

Ar	Y,%
Ph	83
4-*t*-Bu-C_6H_4	69

Ar	Y,%
4-*t*-Bu-C_6H_4	74
4-*t*-BuO-C_6H_4	63

Figure S9. P(O),NH-acetals, obtained by enantioselective addition of $Ar_2P(O)H$ to imines in the presence of chiral Mg phosphate.[191,192]

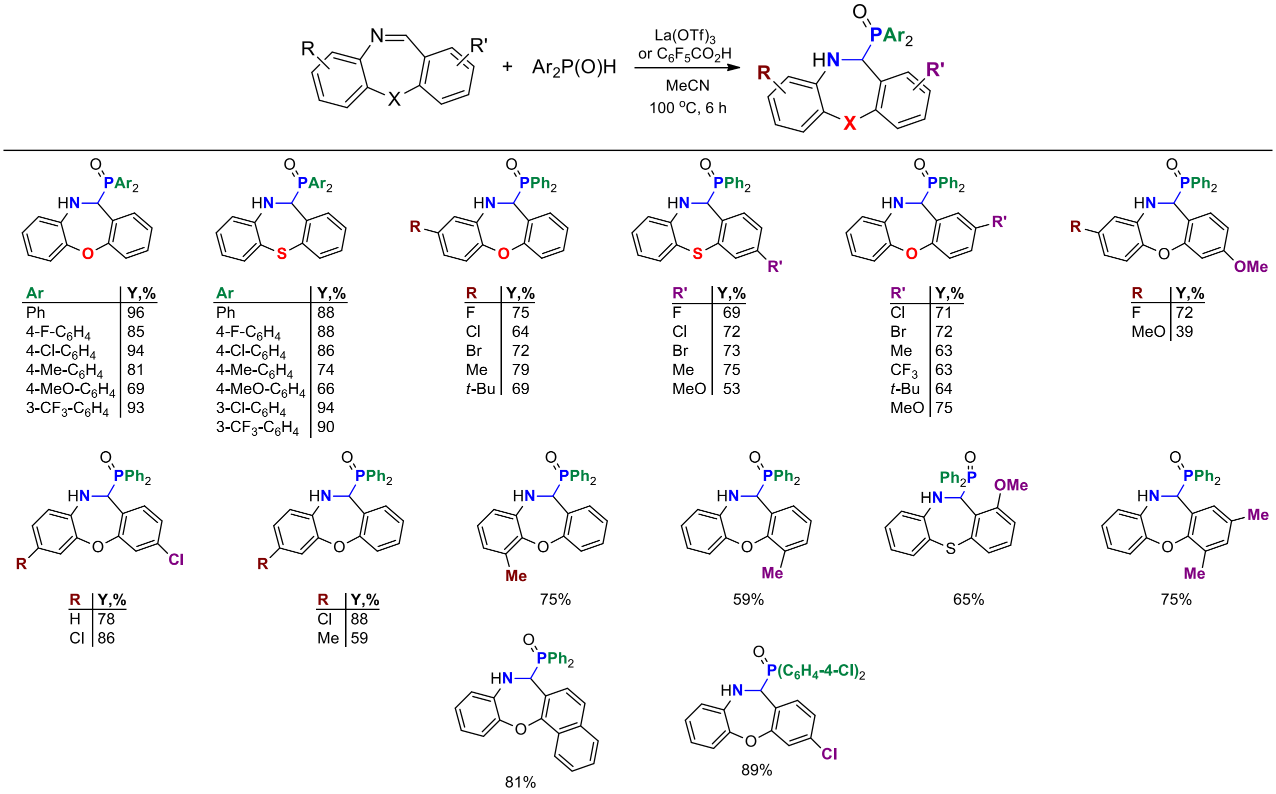


Ar	Y,%	*ee*,%
p-Tol	63	89
4-MeO-C_6H_4	79	87
4-F-C_6H_4	88	84
4-Cl-C_6H_4	93	84

R	Y,%	*ee*,%
Ph	95	93
o-Tol	96	89
m-Tol	95	92
4-MeO-C_6H_4	95	90
4-F-C_6H_4	95	90
4-Br-C_6H_4	97	92
4-NO_2-C_6H_4	97	95
1-Naph	95	96
2-Furyl	93	91
n-Pr	88	62
i-Pr	92	86
n-Bu	65	52
Cy	96	91
$PhCH_2CH_2$	73	48

R	Y,%	*ee*,%
Ph	90	99
o-Tol	92	96
4-MeO-C_6H_4	92	92
4-F-C_6H_4	95	16
2-Furyl	98	87
n-Pr	73	80
i-Pr	72	85
n-Bu	84	74
$PhCH_2CH_2$	86	93

Figure S10. P(O),NH-acetals, obtained by reactions of dibenzo[*b*,*f*][1,4]-oxa- and -thi-azepines with SPOs.[193]



Ar	Y,%
Ph	96
4-F-C_6H_4	85
4-Cl-C_6H_4	94
4-Me-C_6H_4	81
4-MeO-C_6H_4	69
3-CF_3-C_6H_4	93

Ar	Y,%
Ph	88
4-F-C_6H_4	88
4-Cl-C_6H_4	86
4-Me-C_6H_4	74
4-MeO-C_6H_4	66
3-Cl-C_6H_4	94
3-CF_3-C_6H_4	90

R	Y,%
F	75
Cl	64
Br	72
Me	79
t-Bu	69

R'	Y,%
F	69
Cl	72
Br	73
Me	75
MeO	53

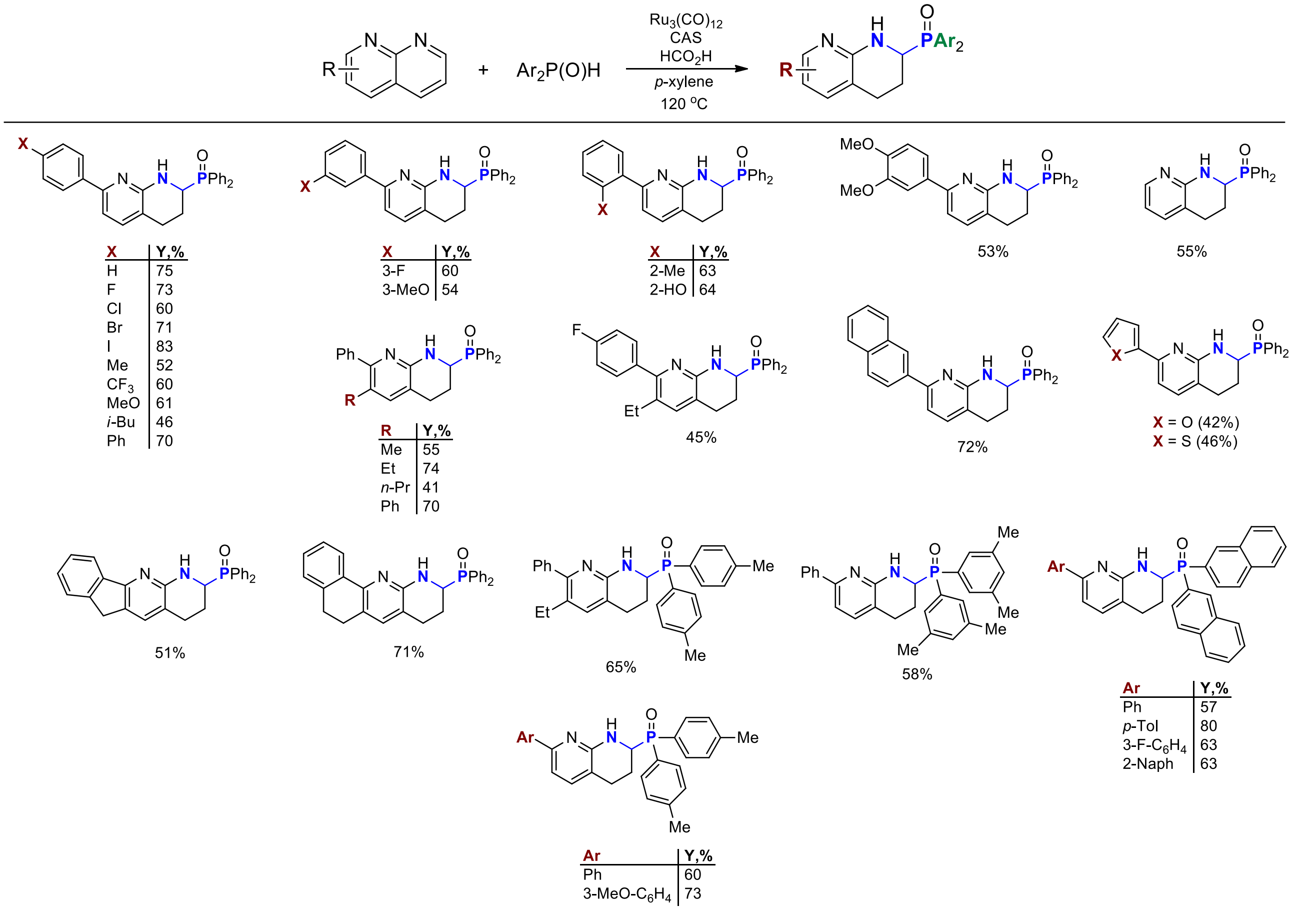
R'	Y,%
Cl	71
Br	72
Me	63
CF_3	63
t-Bu	64
MeO	75

R	Y,%
F	72
MeO	39

R	Y,%
H	78
Cl	86

R	Y,%
Cl	88
Me	59

Figure S11. P(O),NH-acetals, obtained by Ru-catalyzed reaction of 1,8-naphthyridines with SPOs.[194]



X	Y,%
H	75
F	73
Cl	60
Br	71
I	83
Me	52
CF_3	60
MeO	61
i-Bu	46
Ph	70

X	Y,%
3-F	60
3-MeO	54

X	Y,%
2-Me	63
2-HO	64

53%

55%

R	Y,%
Me	55
Et	74
n-Pr	41
Ph	70

45%

72%

X = O (42%)
X = S (46%)

51%

71%

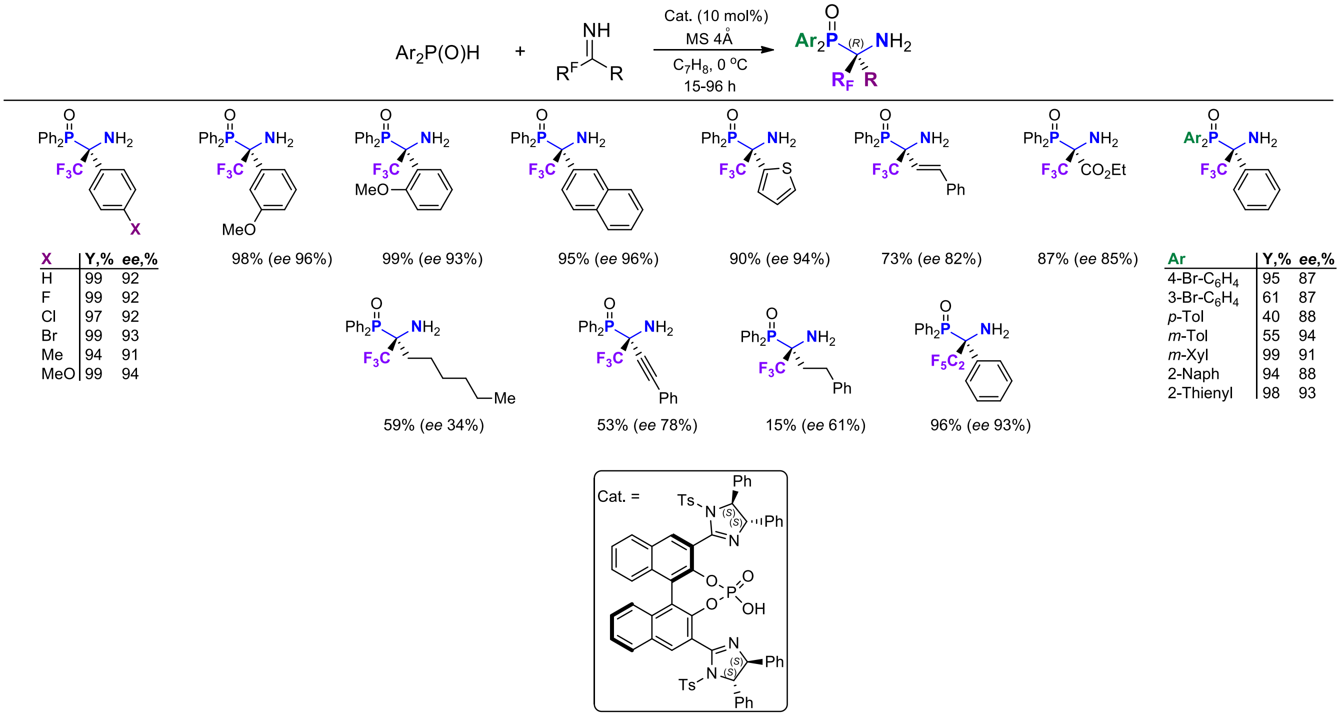
65%

58%

Ar	Y,%
Ph	57
p-Tol	80
3-F-C_6H_4	63
2-Naph	63

Ar	Y,%
Ph	60
3-MeO-C_6H_4	73

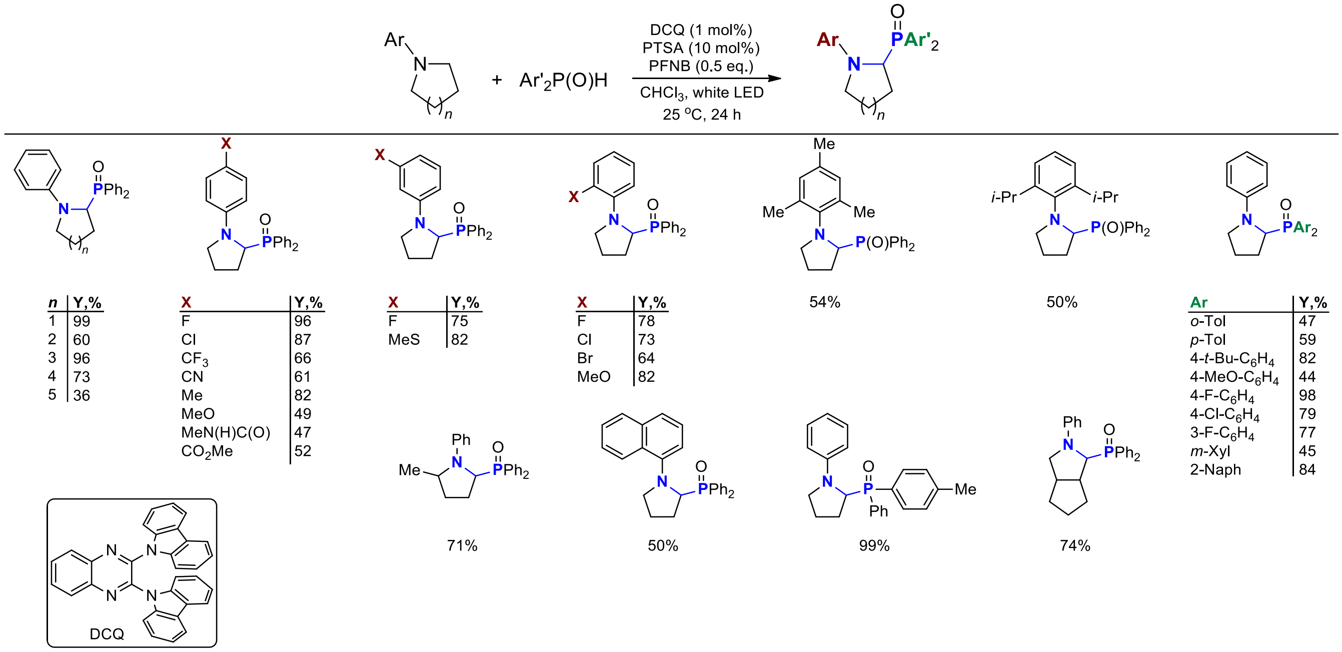
Figure S12. Enantioselective hydrophosphinoylation of ketimines with SPOs.[195]



X	Y,%	ee,%
H	99	92
F	99	92
Cl	97	92
Br	99	93
Me	94	91
MeO	99	94

Ar	Y,%	ee,%
4-Br-C_6H_4	95	87
3-Br-C_6H_4	61	87
p-Tol	40	88
m-Tol	55	94
m-Xyl	99	91
2-Naph	94	88
2-Thienyl	98	93

Figure S13. P(O),N-acetals, obtained by photocatalytic reaction of *N*-aryl heterocycles with SPOs.[196]



n	Y,%
1	99
2	60
3	96
4	73
5	36

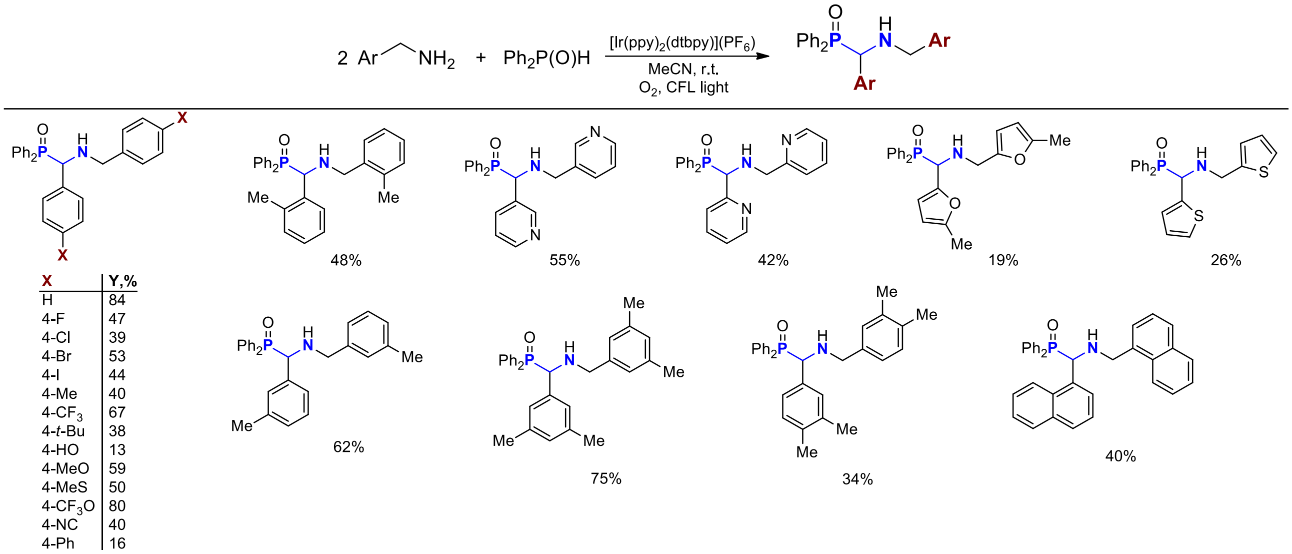
X	Y,%
F	96
Cl	87
CF_3	66
CN	61
Me	82
MeO	49
MeN(H)C(O)	47
CO_2Me	52

X	Y,%
F	75
MeS	82

X	Y,%
F	78
Cl	73
Br	64
MeO	82

Ar	Y,%
o-Tol	47
p-Tol	59
4-*t*-Bu-C_6H_4	82
4-MeO-C_6H_4	44
4-F-C_6H_4	98
4-Cl-C_6H_4	79
3-F-C_6H_4	77
m-Xyl	45
2-Naph	84

Figure S14. P(O),NH-acetals, obtained by visible-light mediated reaction of benzylamines with $Ph_2P(O)H$ in the presence of an Ir complex.[197]



X	Y,%
H	84
4-F	47
4-Cl	39
4-Br	53
4-I	44
4-Me	40
4-CF_3	67
4-*t*-Bu	38
4-HO	13
4-MeO	59
4-MeS	50
4-CF_3O	80
4-NC	40
4-Ph	16

Figure S15. Products of a Cu-catalyzed reaction of α-amino ketones with $Ph_2P(O)H$ and *t*-BuOOH.[198]

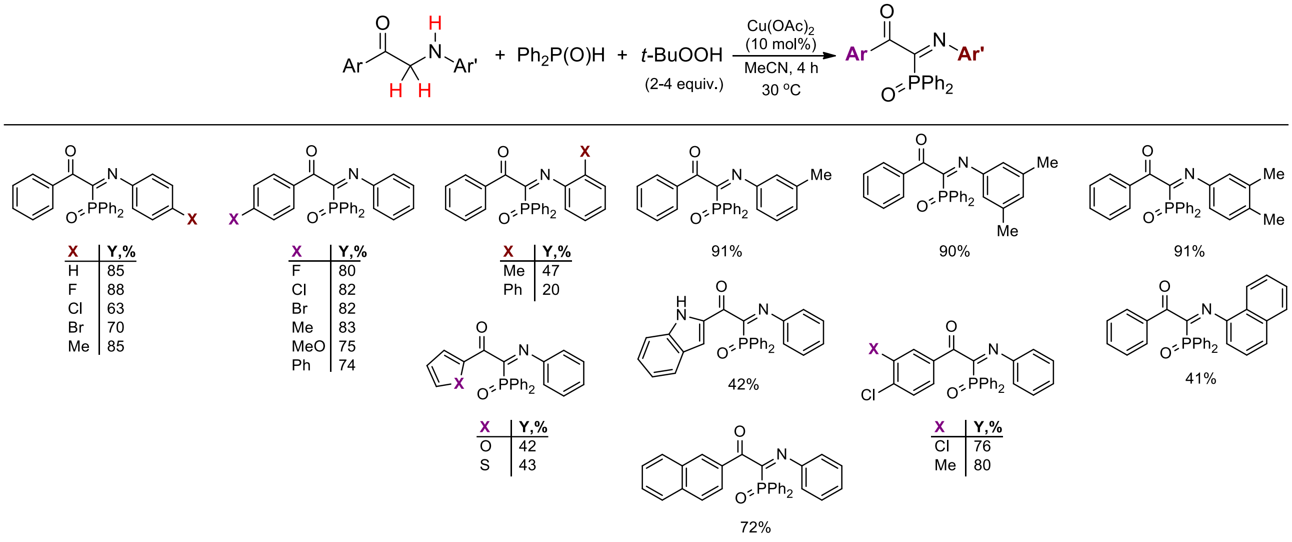
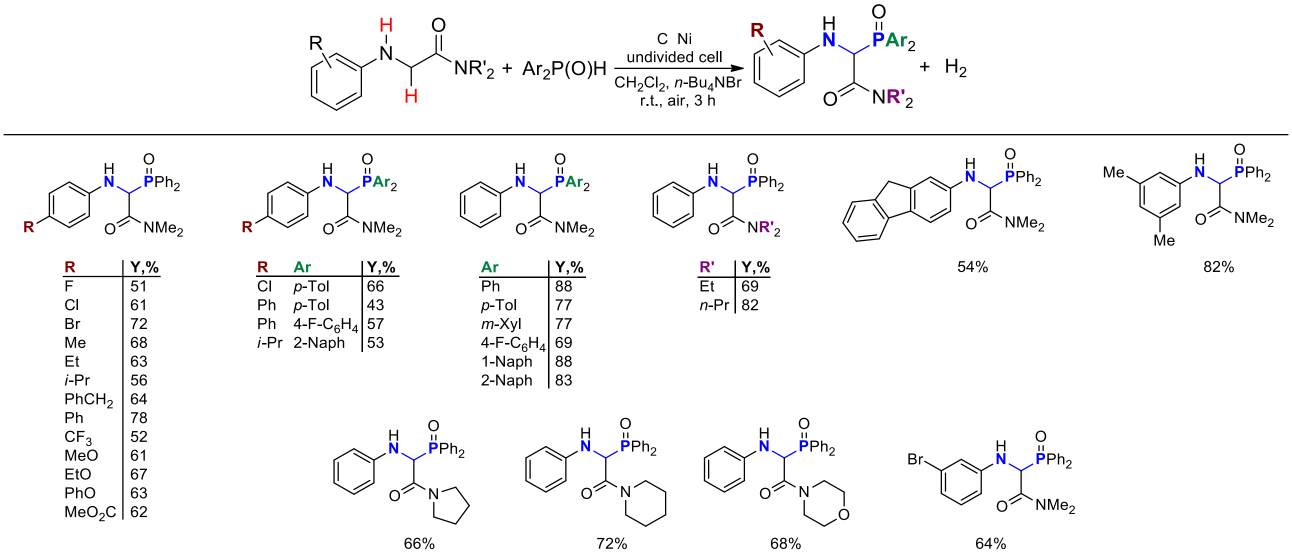


Figure S16. P(O),NH-acetals, obtained by electrochemical reaction of *N*-aryl glycinamides with SPOs.[199]



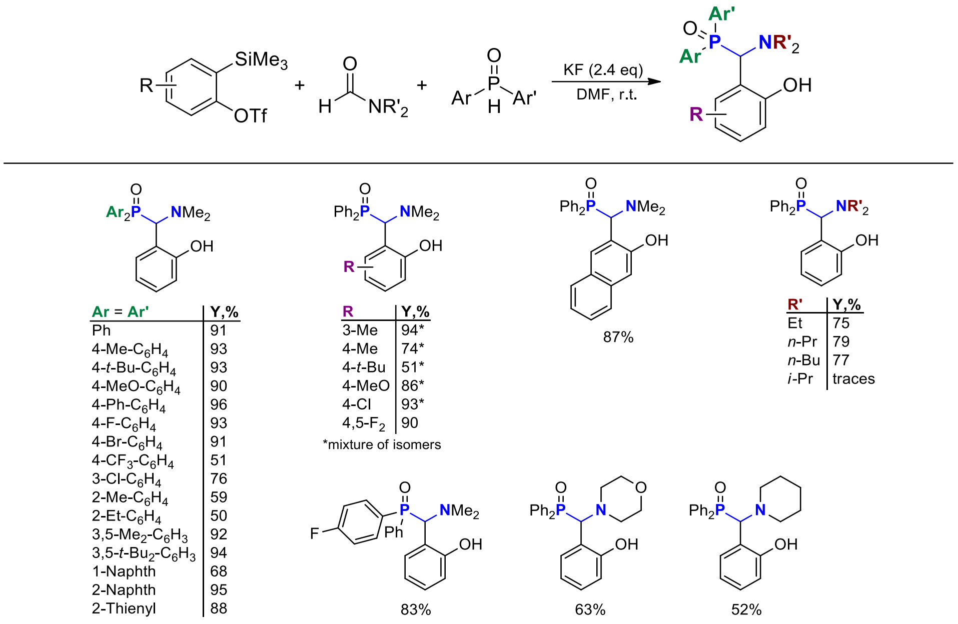
R	Y,%
F	51
Cl	61
Br	72
Me	68
Et	63
i-Pr	56
PhCH$_2$	64
Ph	78
CF$_3$	52
MeO	61
EtO	67
PhO	63
MeO$_2$C	62

R	Ar	Y,%
Cl	*p*-Tol	66
Ph	*p*-Tol	43
Ph	4-F-C$_6$H$_4$	57
i-Pr	2-Naph	53

Ar	Y,%
Ph	88
p-Tol	77
m-Xyl	77
4-F-C$_6$H$_4$	69
1-Naph	88
2-Naph	83

R'	Y,%
Et	69
n-Pr	82

Figure S17. P(O),N-acetals, obtained by reaction of aryne precursors with formamides and SPOs.[200]



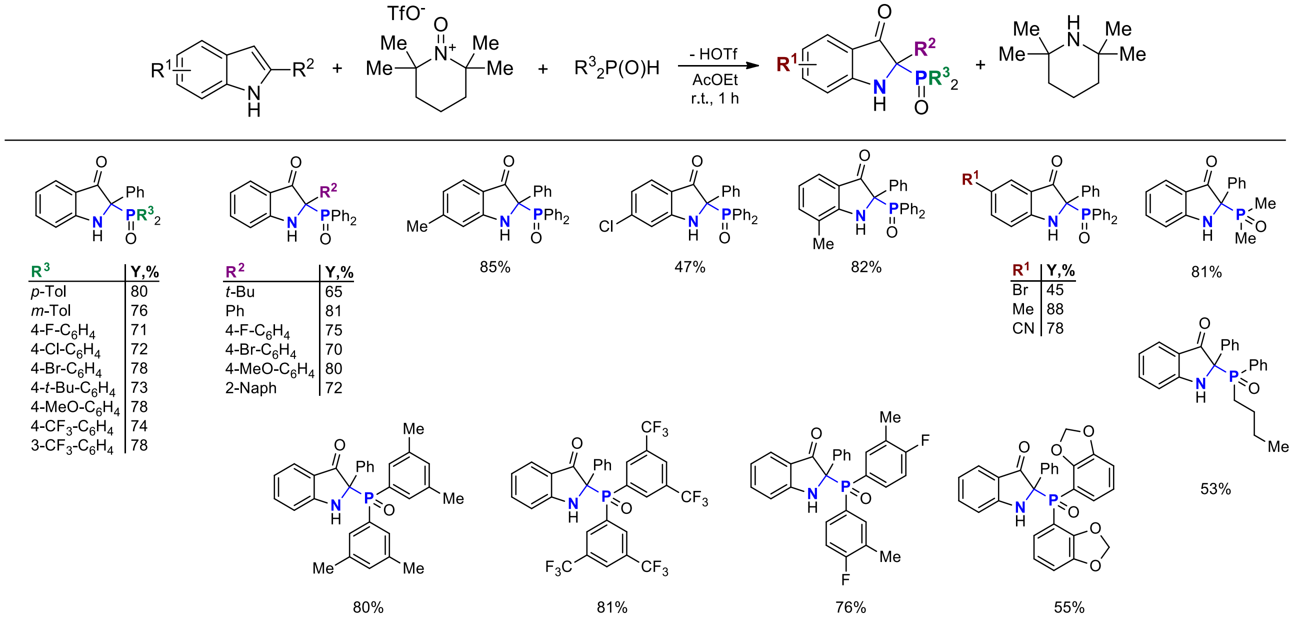
Ar = Ar'	Y,%
Ph	91
4-Me-C_6H_4	93
4-*t*-Bu-C_6H_4	93
4-MeO-C_6H_4	90
4-Ph-C_6H_4	96
4-F-C_6H_4	93
4-Br-C_6H_4	91
4-CF_3-C_6H_4	51
3-Cl-C_6H_4	76
2-Me-C_6H_4	59
2-Et-C_6H_4	50
3,5-Me_2-C_6H_3	92
3,5-*t*-Bu_2-C_6H_3	94
1-Naphth	68
2-Naphth	95
2-Thienyl	88

R	Y,%
3-Me	94*
4-Me	74*
4-*t*-Bu	51*
4-MeO	86*
4-Cl	93*
4,5-F_2	90

*mixture of isomers

R'	Y,%
Et	75
n-Pr	79
n-Bu	77
i-Pr	traces

Figure S18. P(O),NH-acetals, obtained by reaction of 2-substituted indoles with SPOs in the presence of an oxoammonium salt.[201]

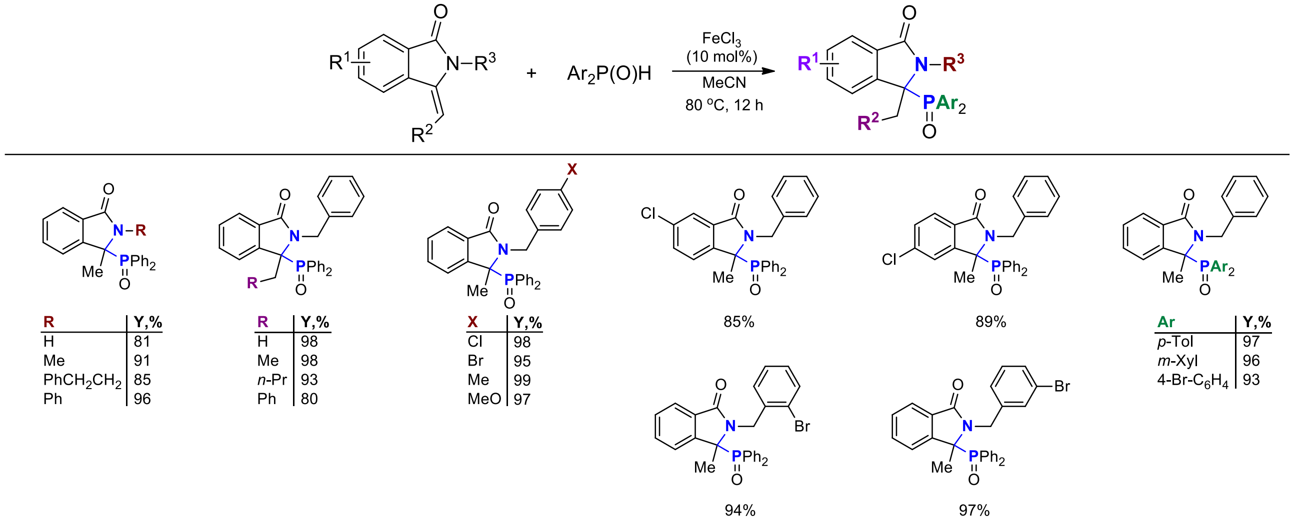


R3	Y,%
p-Tol	80
m-Tol	76
4-F-C_6H_4	71
4-Cl-C_6H_4	72
4-Br-C_6H_4	78
4-t-Bu-C_6H_4	73
4-MeO-C_6H_4	78
4-CF_3-C_6H_4	74
3-CF_3-C_6H_4	78

R2	Y,%
t-Bu	65
Ph	81
4-F-C_6H_4	75
4-Br-C_6H_4	70
4-MeO-C_6H_4	80
2-Naph	72

R1	Y,%
Br	45
Me	88
CN	78

Figure S19. P(O),N-acetals, obtained by reaction of 3-methyleneisoindolin-1-ones with SPOs.[202]



R	Y,%
H	81
Me	91
$PhCH_2CH_2$	85
Ph	96

R	Y,%
H	98
Me	98
n-Pr	93
Ph	80

X	Y,%
Cl	98
Br	95
Me	99
MeO	97

85%

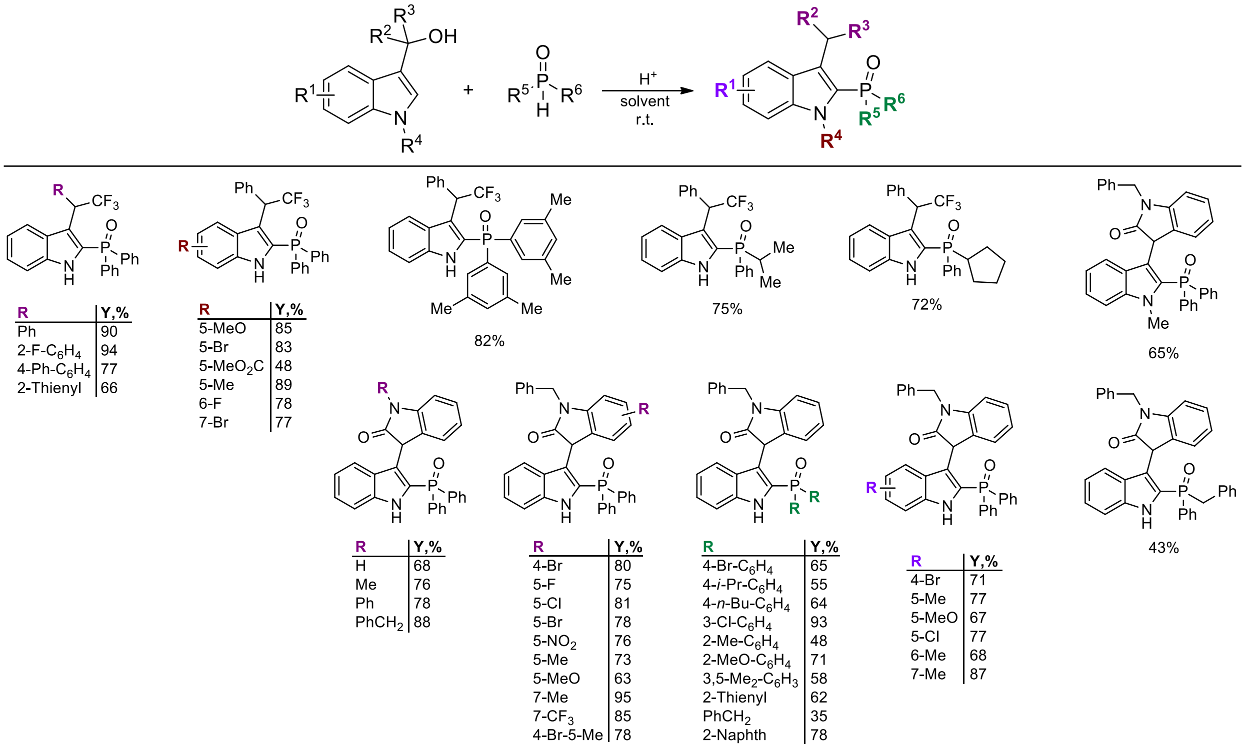
89%

Ar	Y,%
p-Tol	97
m-Xyl	96
4-Br-C_6H_4	93

94%

97%

Figure S20. Products of reaction of SPOs with 3-(α-hydroxyalkyl)indoles.[203-205]



R	Y,%
Ph	90
2-F-C_6H_4	94
4-Ph-C_6H_4	77
2-Thienyl	66

R	Y,%
5-MeO	85
5-Br	83
5-MeO_2C	48
5-Me	89
6-F	78
7-Br	77

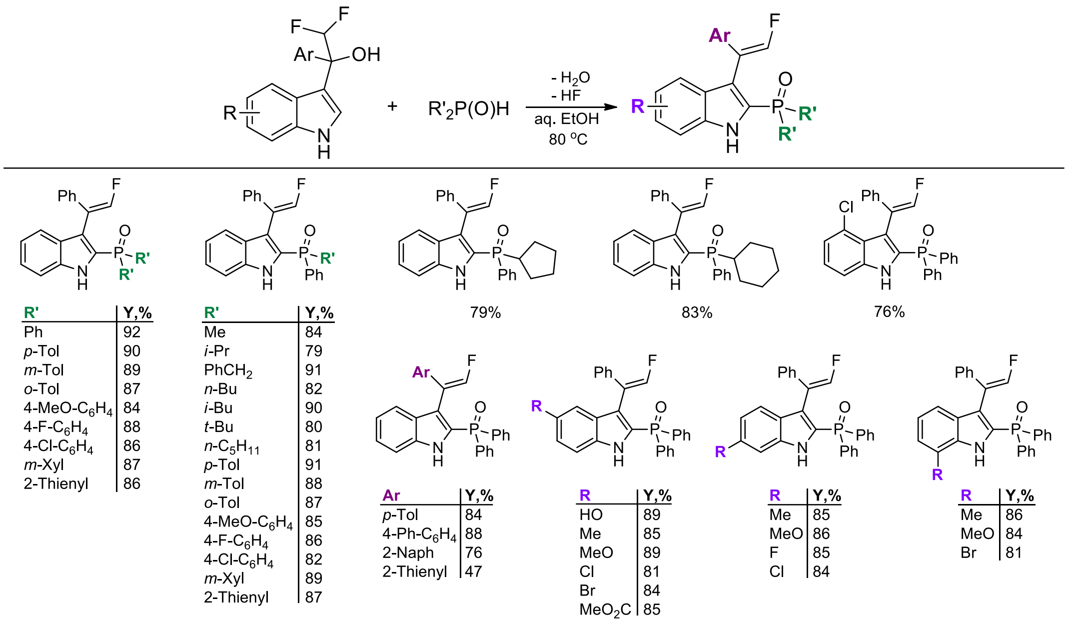
R	Y,%
H	68
Me	76
Ph	78
$PhCH_2$	88

R	Y,%
4-Br	80
5-F	75
5-Cl	81
5-Br	78
5-NO_2	76
5-Me	73
5-MeO	63
7-Me	95
7-CF_3	85
4-Br-5-Me	78

R	Y,%
4-Br-C_6H_4	65
4-*i*-Pr-C_6H_4	55
4-*n*-Bu-C_6H_4	64
3-Cl-C_6H_4	93
2-Me-C_6H_4	48
2-MeO-C_6H_4	71
3,5-Me_2-C_6H_3	58
2-Thienyl	62
$PhCH_2$	35
2-Naphth	78

R	Y,%
4-Br	71
5-Me	77
5-MeO	67
5-Cl	77
6-Me	68
7-Me	87

Figure S21. Products of reaction of $Ph_2P(O)H$ with difluorinated 3-(α-hydroxyalkyl)indoles.[206,207]



R'	Y,%
Ph	92
p-Tol	90
m-Tol	89
o-Tol	87
4-MeO-C_6H_4	84
4-F-C_6H_4	88
4-Cl-C_6H_4	86
m-Xyl	87
2-Thienyl	86

R'	Y,%
Me	84
i-Pr	79
$PhCH_2$	91
n-Bu	82
i-Bu	90
t-Bu	80
n-C_5H_{11}	81
p-Tol	91
m-Tol	88
o-Tol	87
4-MeO-C_6H_4	85
4-F-C_6H_4	86
4-Cl-C_6H_4	82
m-Xyl	89
2-Thienyl	87

79%

83%

76%

Ar	Y,%
p-Tol	84
4-Ph-C_6H_4	88
2-Naph	76
2-Thienyl	47

R	Y,%
HO	89
Me	85
MeO	89
Cl	81
Br	84
MeO_2C	85

R	Y,%
Me	85
MeO	86
F	85
Cl	84

R	Y,%
Me	86
MeO	84
Br	81

Figure S22. Products of 3C-reaction of indoles with SPOs and carbonyl compounds.[208]

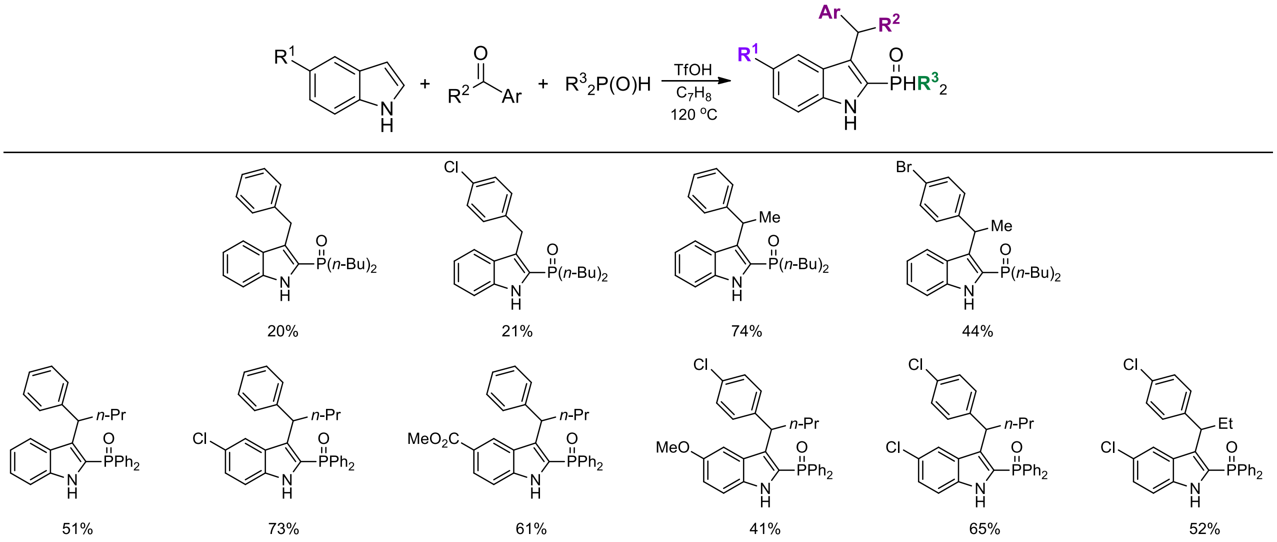
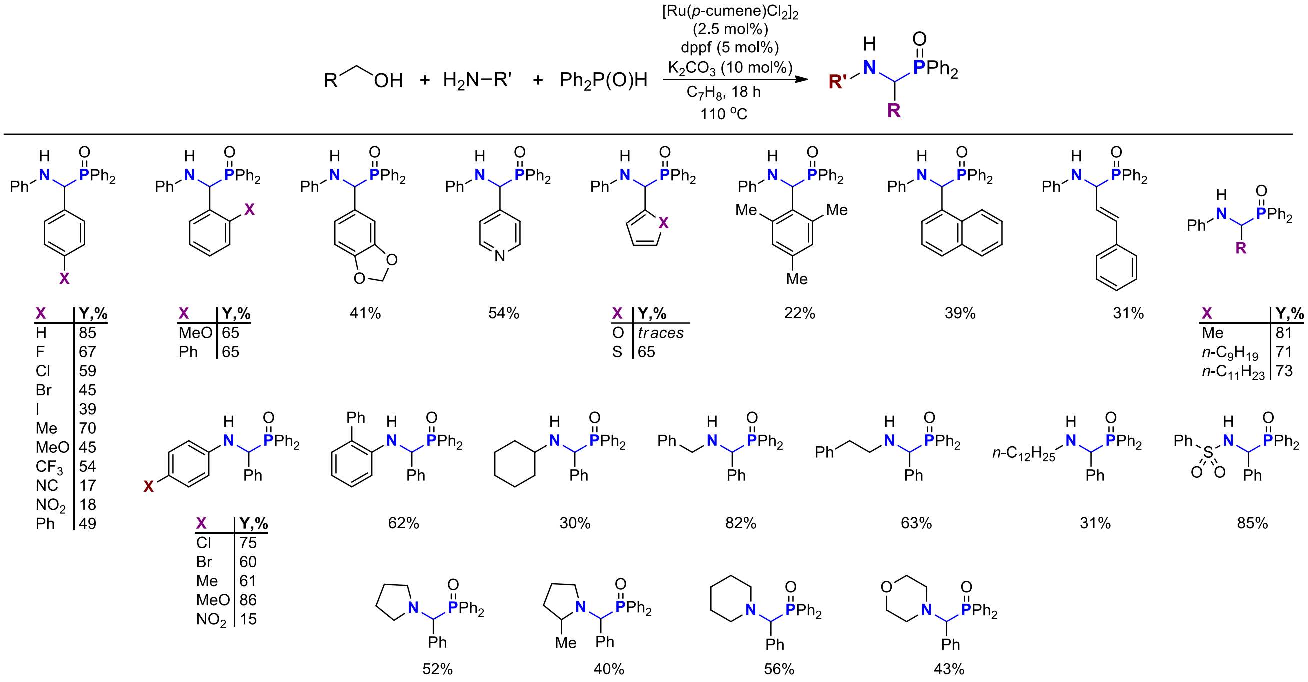


Figure S23. P(O),NH- and P(O),N-acetals, obtained by Ru-catalyzed reaction of primary alcohols with primary amines and $Ph_2P(O)H$.[209]



$$R\frown OH + H_2N{-}R' + Ph_2P(O)H \xrightarrow[C_7H_8,\ 18\ h,\ 110\ ^oC]{[Ru(p\text{-cumene})Cl_2]_2\ (2.5\ mol\%),\ dppf\ (5\ mol\%),\ K_2CO_3\ (10\ mol\%)}$$

X	Y,%
H	85
F	67
Cl	59
Br	45
I	39
Me	70
MeO	45
CF_3	54
NC	17
NO_2	18
Ph	49

X	Y,%
MeO	65
Ph	65

X	Y,%
O	*traces*
S	65

X	Y,%
Me	81
n-C_9H_{19}	71
n-$C_{11}H_{23}$	73

X	Y,%
Cl	75
Br	60
Me	61
MeO	86
NO_2	15

Figure S24. P(O),NH-acetals, obtained by reaction of THF, or other ethers, with primary amines and SPOs.[210]

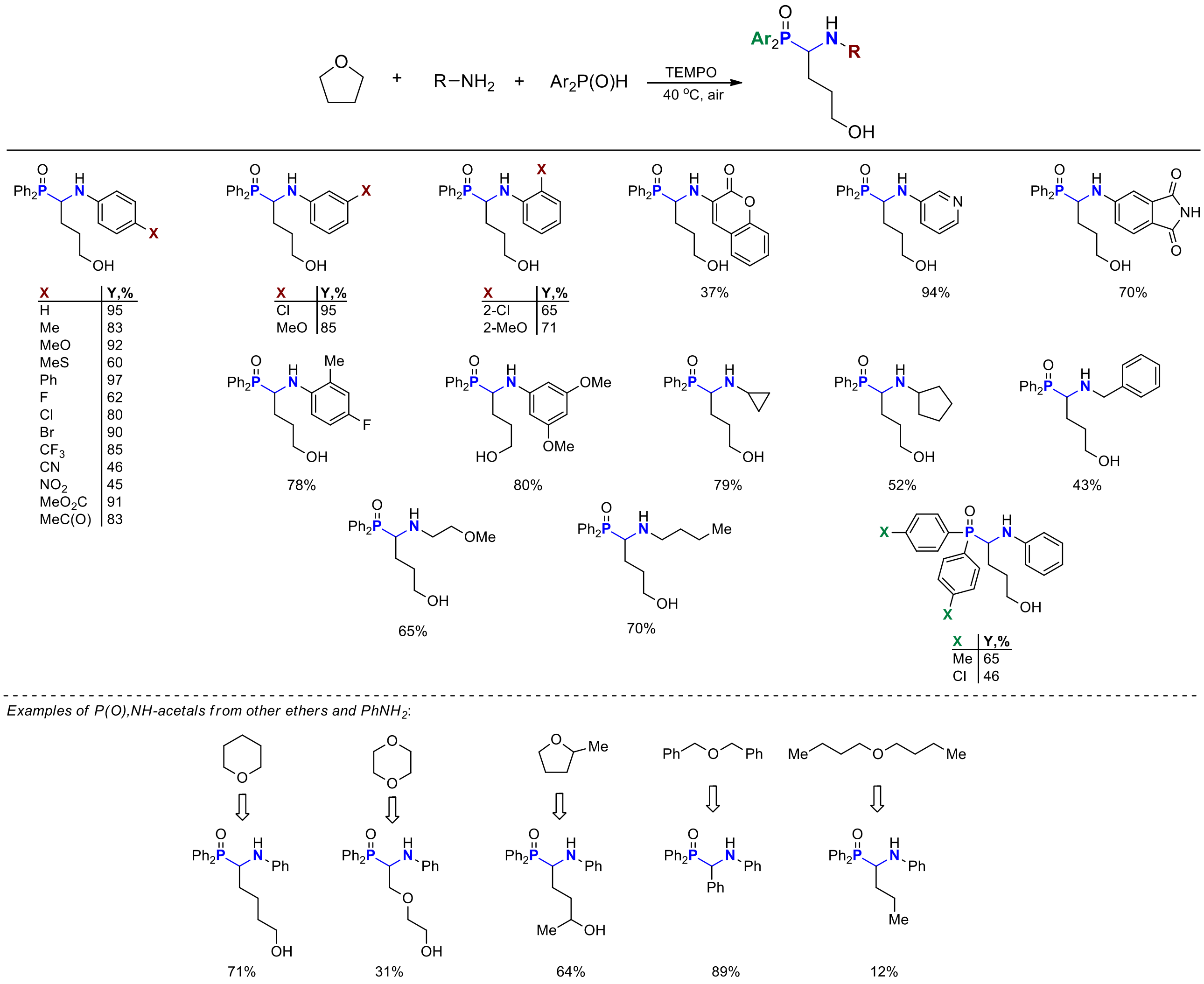
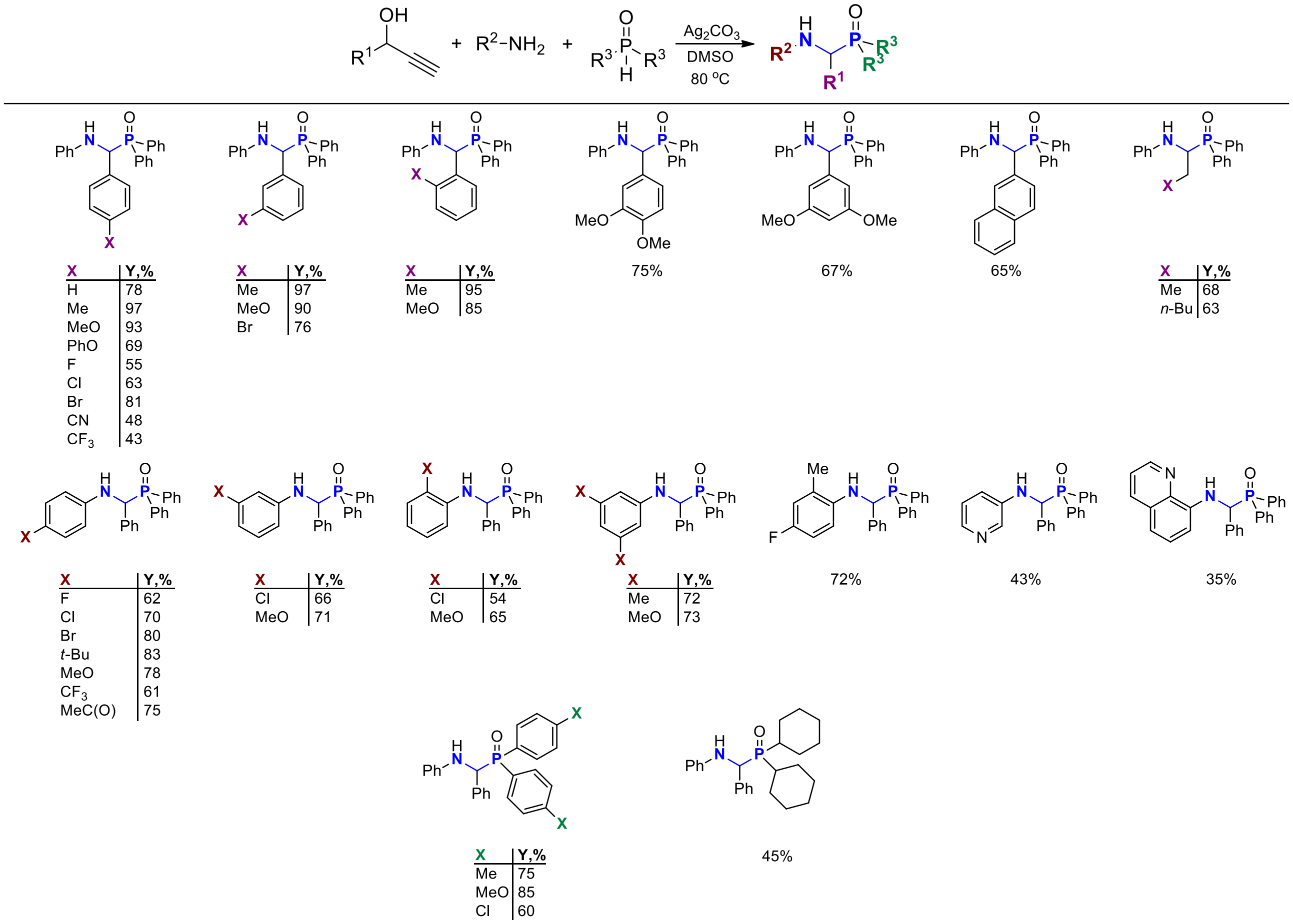


Figure S25. P(O),NH-acetals, obtained by 3C-reaction of propargylic alcohols with aromatic amines and SPOs.[211]



X	Y,%
H	78
Me	97
MeO	93
PhO	69
F	55
Cl	63
Br	81
CN	48
CF_3	43

X	Y,%
Me	97
MeO	90
Br	76

X	Y,%
Me	95
MeO	85

X	Y,%
Me	68
n-Bu	63

X	Y,%
F	62
Cl	70
Br	80
t-Bu	83
MeO	78
CF_3	61
MeC(O)	75

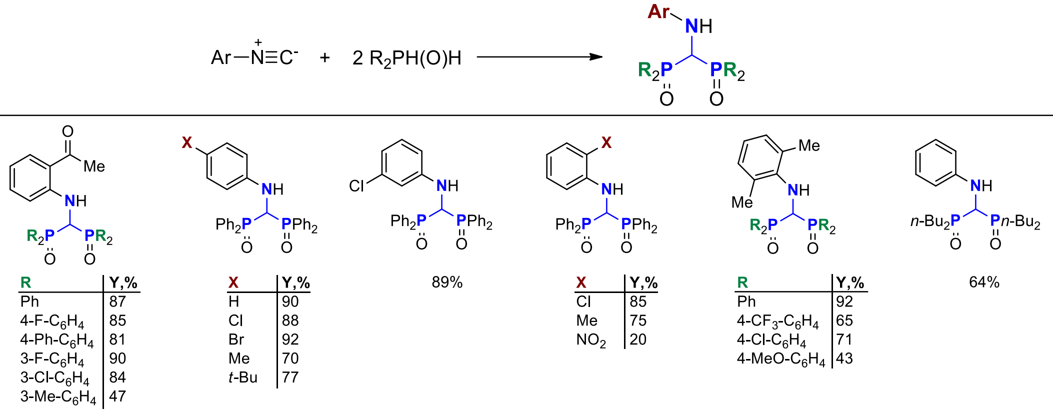
X	Y,%
Cl	66
MeO	71

X	Y,%
Cl	54
MeO	65

X	Y,%
Me	72
MeO	73

X	Y,%
Me	75
MeO	85
Cl	60

Figure S26. P(O),NH-acetals, obtained by double nucleophilic addition of SPOs to aromatic isocyanides.[212-214]



R	Y,%
Ph	87
4-F-C_6H_4	85
4-Ph-C_6H_4	81
3-F-C_6H_4	90
3-Cl-C_6H_4	84
3-Me-C_6H_4	47

X	Y,%
H	90
Cl	88
Br	92
Me	70
t-Bu	77

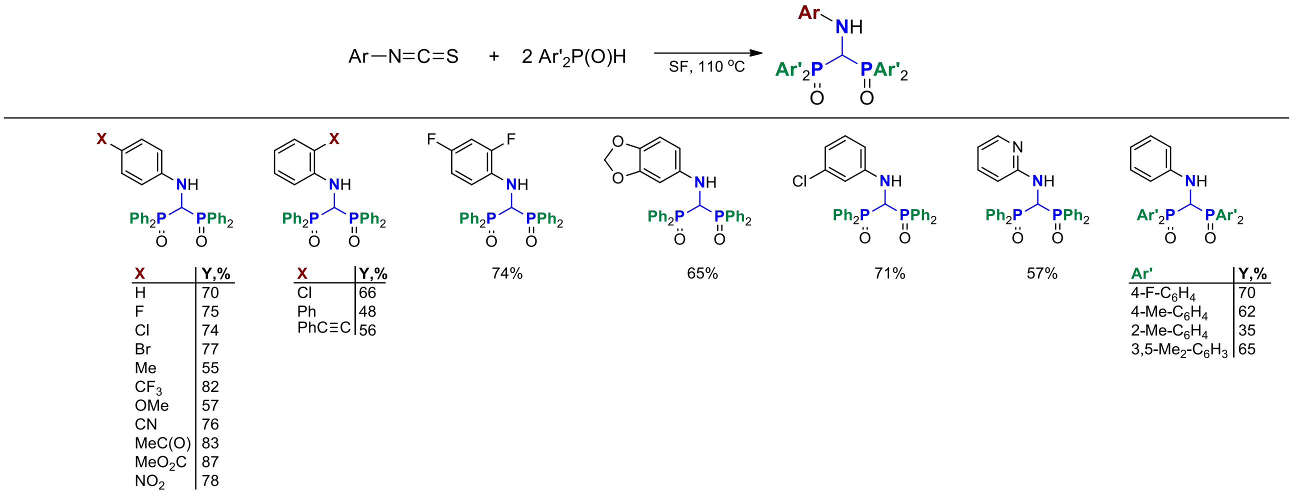
89%

X	Y,%
Cl	85
Me	75
NO_2	20

R	Y,%
Ph	92
4-CF_3-C_6H_4	65
4-Cl-C_6H_4	71
4-MeO-C_6H_4	43

64%

Figure S27. P(O),NH-acetals, obtained by 1:2 reaction of aryl isothiocyanates with SPOs.[215]



X	Y,%
H	70
F	75
Cl	74
Br	77
Me	55
CF_3	82
OMe	57
CN	76
MeC(O)	83
MeO_2C	87
NO_2	78

X	Y,%
Cl	66
Ph	48
PhC≡C	56

Ar'	Y,%
4-F-C_6H_4	70
4-Me-C_6H_4	62
2-Me-C_6H_4	35
3,5-Me_2-C_6H_3	65

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