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Towards a sustainable synthesis of aromatic isocyanates : by the palladium diphosphane catalyzed reduction of nitrobenzene; a first step

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Towards a sustainable synthesis of aromatic isocyanates

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The whole is more than the sum of its parts
Aristotle, Metaphysica, 384-322 BC

Seek not to understand that you may believe, but believe that you may understand
Saint Augustine, Civitate Dei, 426 AC

voor mijn ouders,
voor Lauranne

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List of abbreviations

AC	autoclave
ax	axial
Azo	azobenzene
Azoxy	azoxybenzene
bipy	bipyridine
BP	Becke Perdew functional
bpap	1,3–bis(1,3,5,7–tetramethyl–4,6,8–trioxa–2–phospha-amantyl)propane
br	broad (in NMR)
Bu	butyl
cal	Calories (1 cal = 4.184 Joule)
COD	1,4-cyclo-octadiene
COSY	correlation spectroscopy
CPCam	*p*-cresyl phenyl carbamate
CSD	Cambridge Structural Database
d	doublet (in NMR)
dba	dibenzylidene acetone
dd	double doublet (in NMR)
DFT	density functional theory
DMAN	1,8–bis(dimethylamino)naphthalene (Proton Sponge®)
DMC	dimethyl carbonate
DME	dimethyl ether
DMM	dimethoxy methane
DMO	dimethyl oxalate
DMPU	*N,N′*–di(3-methylphenyl) urea
DPC	diphenyl carbonate
DPO	*N,N′*–diphenyl oxalimide
dppb	1,4–bis(diphenylphosphanyl)butane
dppbz	1,2–bis(diphenylphosphanyl)benzene
dppe	1,2–bis(diphenylphosphanyl)ethane
dppe	1,2–bis(diphenylphosphanyl)ethane
dppm	bis(diphenylphosphanyl)methane
dppp	1,3–bis(diphenylphosphanyl)propane
DPU	*N,N′*–diphenyl urea
EA	elemental analysis
eq	equatorial
Eq(s).	Equation(s)
ESI	electron spray ionization
Et	ethyl
Exp.	experiment
F_5–L2	1,2–bis(di–pentafluorophenylphosphanyl)ethane
FID	free inductive decay (NMR) or flame ionization detector (GC)
FT	fourier transform
GLC	gas liquid chromatography
h	hour(s)

HOTs	*p*-toluenesulfonic acid
HPLC	high performance liquid chromatography
i (or *iso*)	iso
IR	infra red
J	coupling constant (in Hertz)
L2	1,2–bis(diphenylphosphanyl)ethane
L3	1,3–bis(diphenylphosphanyl)propane
L3X	2,2–dimethyl–1,3–bis(diphenylphosphanyl)propane
L4	1,4–bis(diphenylphosphanyl)butane
L4X	4,5–bis(diphenylphosphanylmethyl)–2,2–dimethyl–1,3–dioxolane
L5Fc	1,1'-bis(diphenylphosphanyl)ferrocene
LD50	lethal dose, whereby 50% of a given population dies
M	metal
m	multiplet (in NMR)
m	*meta*
MBA	*N*-methylene benzenamine
MDA	4,4'–methylene dianiline
MDI	4,4'–methylene diphenyl diisocyanate
Me	methyl
MEG	mono ethylene glycol
Mes	mesitylene
MF	methyl formate
MMFF	Merck molecular force field
MOF	metal organic framework
MPC	methyl phenylcarbamate
MPPU	3–methylphenyl phenylurea
MS	mass spectrometry
napht	naphtalene
NMR	nuclear magnetic resonance
o	*ortho*
OAc	acetate
oEtO-L2	1,2–bis(di–*o*–ethoxyphenylphosphanyl)ethane
oEtO-L3	1,3–bis(di–*o*–ethoxyphenylphosphanyl)propane
oEtO-L3X^2	2,2–diethyl–1,3–bis(di–*o*–ethoxyphenylphosphanyl)propane
oEtO-L4	1,4–bis(di–*o*–ethoxyphenylphosphanyl)butane
oMe-L3	1,3–bis(di–*o*–methylphenylphosphanyl)propane
oMeO-L2	1,2–bis(di–*o*–methoxyphenylphosphanyl)ethane
oMeO-L3	1,3–bis(di–*o*–methoxyphenylphosphanyl)propane
oMeO-L3X	2,2–dimethyl–1,3–bis(di–*o*–methoxyphenylphosphanyl)propane
oMeO-L3X^2	2,2–diethyl–1,3–bis(di–*o*–methoxyphenylphosphanyl)propane
oMeO-L3X^R	5,5–bis(di–*o*–methoxyphenylphosphanylmethyl)–2–cyclohexyl–1,3–dioxane
oMeO-L4	1,4–bis(di–*o*–methoxyphenylphosphanyl)butane
oMeO-L4X	4,5–bis(di–*o*–methoxyphenylphosphanylmethyl)–2,2–dimethyl–1,3–dioxolane
oMeO-L5Fc	1,1'-bis(di–*o*–methoxyphenylphosphanyl)ferrocene
P	pressure in bar
p	*para*

pbq	parabenzoquinone
Ph	phenyl
phen	1,10–phenanthroline
p*K*a	–log (ionisation constant (*K*a))
pMeO-L3	1,3–bis(di–*p*–methoxyphenylphosphanyl)propane
pMeO-L4	1,4–bis(di–*p*–methoxyphenylphosphanyl)butane
PPA	phenylphosphonic acid
ppm	parts per million
Pr	propyl
rpm	revolutions per minute
s	singlet (in NMR)
Sym.	simulation
t	triplet (in NMR)
TDI	2,4–toluene diisocyanate
tert	*tertiary*
TFE	2,2,2–trifluoroethanol
TLV	threshold limit value (in mg/kg)
TMBA	2,4,6–trimethylbenzoic acid
tmof	Trimethyl orthoformate
TMS	tetramethylsilane
TOF	turn over frequency (moles substrate / moles catalyst × unit of time)
TON	turn over number (moles substrate / moles catalyst)
TPB	*N*,*N*′,*N*″–triphenylbiurea
UHV	ultra high vacuum
UV	ultra violet
ΔH_f°	heat of formation