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Complete List of Authors:	Lipshutz, Bruce; University of California, Department of Chemistry Isley, Nicholas; UCSB, Chemistry & Biochemistry Linstadt, Roscoe; UCSB, Chemistry & Biochemistry Slack, Eric; UCSB, Chemistry & Biochemistry

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Copper-Catalyzed Hydrophosphinations of Styrenes in Water at Room Temperature

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Nicholas A. Isley,[a] Roscoe T. H. Linstadt,[a] Eric D. Slack,[a] and Bruce H. Lipshutz[a]†

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Copper-catalyzed hydrophosphinations of styrenyl systems in water, at room temperature is herein reported, enabled by our 'designer' surfactant TPGS-750-M. This is an attractive alternative to the more developed Pd and Pt catalyzed versions.

Dedicated to a great colleague and friend, Bill Kaska, on the occasion of his 80th birthday.

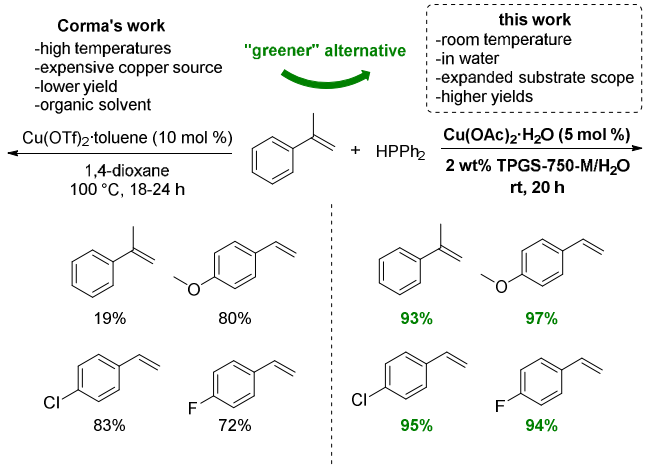
Introduction

Organophosphines are fundamentally important to many aspects of synthetic organic chemistry. Representative applications include ligands for metal-catalyzed transformations,[1] biologically active substances, advanced materials, and building blocks of supramolecular chemistry.[2] Adding the elements of P-H across an olefin is an efficient and direct way of accessing organophosphines in terms of atom-economy, addressing one of the twelve-principles of green chemistry[3] and paving the way for more sustainable methods. Both Pd and Pt (others[4]) have been reported to catalytically activate P-H bonds to facilitate addition across activated olefins, but the catalyst loading is not economically practical for industrial use, as both Pd and Pt are precious metals.[4] Alternatively, calcium- and potassium-catalyzed hydrophosphinations were recently reported.[5] Microwave-assisted, solvent-free, and metal-free have also been reported,[6] but the phosphine source was oxidized prior to the reaction, thus adding an extra step to reduce the phosphine before it becomes of value again, *e.g.,* as a ligand for transition-metal catalysis.

A greener and less costly alternative has been pursued employing micellar catalysis, enabled by our "designer" surfactant TPGS-750-M. This technology allows for reactions to take place in water, and usually at room temperature.[7] Upon dissolution of typically two weight percent of this amphiphile in water, the surfactant spontaneously self-aggregates into nanometer-sized micelles.[8] The reaction occurs within their lipophilic cores, providing an environment for water-insoluble substrates and catalysts.[9] Moreover, due to the high concentration of reactants within these nanoreactors, reaction rates at room temperature are oftentimes comparable to those observed in traditional organic solvents.[10] In addition to these virtues of micellar catalysis, we focused on a base metal as catalyst that is inexpensive, nontoxic, and environmentally friendly: copper. Recently, Corma and co-workers reported the first catalytic use of copper in hydrophosphinations of styrenes.[11] Nonetheless, the scope of the chemistry was limited, as only mono-substituted and activated substrates participated, with only moderate yields. High catalyst loadings of an relatively expensive copper source were needed,[12] and high temperatures were required. One major limitation was that α-substituted styrenes were functionalized in very poor yields.

Herein, we report a very mild, copper-catalyzed strategy for the addition of diphenylphosphine to activated mono-, di-, and tri-substituted olefins containing functionalized aromatic/hetero-aromatic systems (Scheme 1).

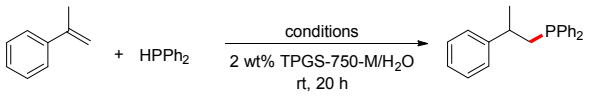
Scheme 1 Comparison between 2 wt % TPGS-750-M/H_2O and organic solvent



Initial optimization was done on α-methyl styrene, as this was a difficult substrate in the published study by Corma[11] (Table 1). A variety of copper sources was screened (see Supporting Information), with $Cu(OAc)_2•H_2O$ giving the best results, considering it is the least expensive and is air-stable. The presence of a ligand was found to be unnecessary for high conversion using copper(II) acetate (entries 1 vs. 2). The loading of both copper and diphenylphosphine was varied to ultimately give complete conversion in under 24 hours. The optimal levels were found to be 5 mol % of copper(II) acetate monohydrate and 1.5 equivalents of diphenylphosphine (entry 6). A control experiment was also conducted (entry 7) to ensure that copper is necessary to facilitate the desired transformation. Another control experiment was

conducted in the absence of TPGS-750-M and only moderate conversion was observed (entry 8).

Table 1 Optimization of Cu-catalyzed hydrophosphinations

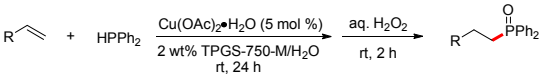


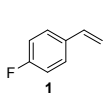
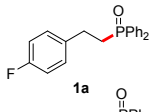
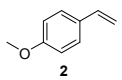
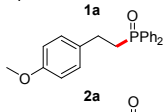
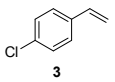
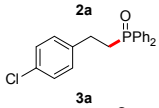
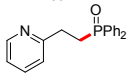
entry	conditions	conversion[a]
1	1.2 equiv $HPPh_2$, $Cu(OAc)_2.H_2O$ (3 mol %), BDP[b] (3 mol %)	65
2	1.2 equiv $HPPh_2$, $Cu(OAc)_2.H_2O$ (3 mol %)	67
3[c]	2.2 equiv $HPPh_2$, $Cu(OAc)_2.H_2O$ (3 mol %)	>99
4	2.0 equiv $HPPh_2$, $Cu(OAc)_2.H_2O$ (3 mol %)	93
5	1.2 equiv $HPPh_2$, $Cu(OAc)_2.H_2O$ (10 mol %)	73
6	**1.5 equiv $HPPh_2$, $Cu(OAc)_2.H_2O$ (5 mol %)**	**95**
7	1.2 equiv $HPPh_2$	3
8	entry 3 and H_2O as solvent	41

[a] Determined by GC or ^{1}H-NMR (crude). [b] 1,2 **b**is(**di**phenyl**p**hosphino)benzene. [c] Reaction time: 40 h.

Several electronically varyied styrenes were evaluated in this hydrophosphination (Table 2). The desired phosphorylated products were oxidized in-situ to their respective phosphine oxides, which are more easily isolated and characterized spectroscopically. Both the *p*-chloro- and fluoro-substituted styrenes afforded the desired products in high yields (entries 1 and 3). Additionally, an electron-rich olefin (entry 2) also led to the hydrophosphinated product in high yield, and the heteroaromatic vinylpyridine, likewise, afforded the desired product in good yield (entry 4).

Table 2 Hydrophosphinations of vinyl-substituted aromatics[a]

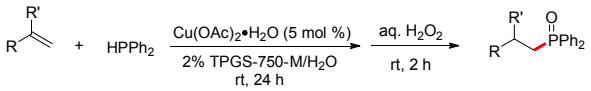


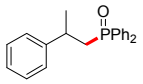
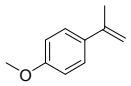
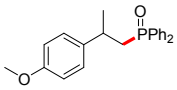
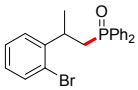
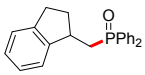
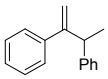
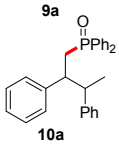
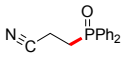
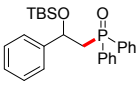
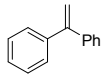
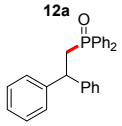
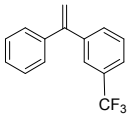
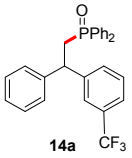
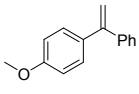
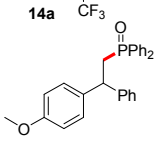
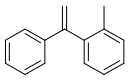
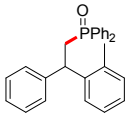
entry	styrene	product	yield (%)[b]
1	 **1**	 **1a**	94
2	 **2**	 **2a**	97
3	 **3**	 **3a**	95
4	 **4**	 **4a**	82

[a] Conditions: 1.5 equiv $HPPh_2$, 5 mol% [Cu], 0.5 mL 2 wt% TPGS-750-M/H_2O, rt, 24 h, 0.25 mmol scale. [b] Isolated, chromatographically purified.

Next, various α-substituted styrenes were studied. Based on our promising initial hydrophosphination of α-methyl styrene, a wide scope of substrate compatibility was anticipated. Simple α-methyl styrene **6** underwent hydrophosphination in high isolated yield (Table 3). An electron-rich version **7** also afforded the desired product in high yield (entry 2).

Table 3 Hydrophosphinations of α-Substituted Styrenes[a]



entry	styrene	product	yield (%)[b]
1	 **6**	 **6a**	93
2	 **7**	 **7a**	91
3	 **8**	 **8a**	trace[c]
4	 **9**	 **9a**	57[c]
5	 **10**	 **10a**	48
6	 **11**	 **11a**	81
7	 **12**	 **12a**	trace
8	 **13**	 **13a**	44 (70[c])
9	 **14**	 **14a**	85
10	 **15**	 **15a**	6[c,d]
11	 **16**	 **16a**	trace[c]

[a] Conditions: 1.5 equiv $HPPh_2$, 5 mol % [Cu], 0.5 mL 2 wt%TPGS-750-M/H_2O, rt, 24 h, 0.25 mmol scale [b] Isolated, chromatographically purified. [c] Conditions: 2.0 equiv $HPPh_2$, 5 mol % [Cu], 0.5 mL 2 wt%TPGS-750-M/H_2O, 50 ℃, 48 h. [d] Conversion: determined by ^{1}H-NMR.

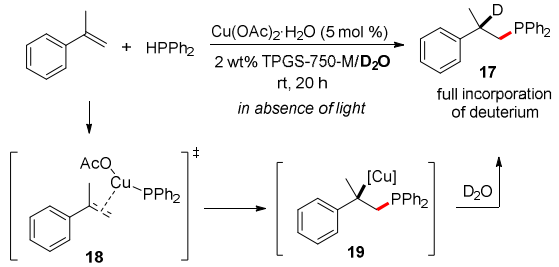
The methyl moiety in substituted styrene **6** could be replaced with a phenethyl residue, as in **10**, or an OTBS group in **12**. While

the former gave product **10a** in modest yield, the latter gave only traces of **12a**, with starting material being recovered. Switching a sterically larger phenyl for methyl group (entry 8) also gave the product in modest yield along with recovered starting material. Heating the mixture increased the yield to 70%. The methylene indanyl array (entry 4) yielded the desired product, but also required mild heating to 50 °C.

α-Aryl substituted styrenes in addition to **13** were also explored. The *m*-CF_3-substituted **14** afforded the desired derivative in very good yield, while the *p*-substituted electron-rich methoxy analog **15** led to **15a** in poor yield. The *o*-tolyl derivative **16** only gave trace amounts of the desired product. Lastly, an electron-poor example without α-substitution, acrylonitrile, was attempted and the desired product was obtained in good yield (entry 6). In the composite, it appears that bulky substituents at or near the α-position severely hinder phosphine addition, and electron-rich styrene systems suppress the extent of conversion. On the other hand, electron-deficient substrates are tolerated with and without α-substitution, suggesting that these educts are functioning as Michael acceptors towards copper.

In order to demonstrate the formation of a carbon-copper bond as a potential intermediate, rigorous exclusion of light in deuterium oxide led to **17**, with full incorporation of deuterium by low-resolution mass spectrometry (Scheme 2). After initial coordination of the olefin with copper (**18**), and under a non-radical pathway, intermediate **19** is likely with the formation of a carbon-copper bond. The nucleophilic carbon-copper bond of **19** then reacts with deuterium oxide. In analogous work involving addition of an H–B bond across styrenyl systems catalysed by copper also demonstrated the likelihood of a carbon-copper bond at the α-position,[17] further supporting intermediate **19**.

Scheme 2 Evidence of non-radical pathway during hydrophosphinations



Lastly, preliminary experiments demonstrate our developed conditions are not amenable to isolated alkenes and alkynes; however, the addition of phosphorous across ynoates and ynones does occur, although further screening is under study to control selectivity and increase the level of conversion.

Conclusions

In conclusion, we have demonstrated the potential of micellar catalysis to be applied to hydrophosphination reactions in water, and in most cases, at room temperature. These compare rather favorably with related conversions performed under traditional conditions using organic solvents. With simpler styrene substrates, the isolated yields are high, and involve mild conditions compared to literature procedures. While this methodology works well for basic styrenes, the substrate scope is limited to electron-poor and sterically unhindered substrates.

Experimental

General

Unless otherwise noted, all reactions were performed under an atmosphere of argon. TPGS-750-M was synthetized by our previously reported procedure[7] and dissolved in HPLC grade water that had been thoroughly purged of oxygen using an argon flow. Diphenylphosphine was used as received by Sigma-Aldrich®. Analytical thin layer chromatography (TLC) was performed using Silica Gel 60 F254 plates (Merck, 0.25 mm thick). Flash chromatography was performed with glass columns using Silica Flash® P60 (SiliCycle, 40-63 μm). For gas chromatography a HP-5 column (30 m x 0.250 mm, 0.25 micron, Agilent Technologies) was employed for conversion analysis. General temperature program: 50 °C for 5 min; heating rate 5 °C/min; 280 °C for 10 min; split-inlet at 200 °C and 8.97 psi (H_2, constant pressure) with 40:1 split ration, FID at 290 °C. ^{1}H and ^{13}C spectra were recorded at 25°C on a Varian UNITY INOVA 400, 500, or 600 MHz instrument. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sep = septet, m = multiplet, br = broad), coupling constant in hertz (Hz), and integration. Chemical shifts of ^{13}C NMR spectra are reported in ppm from the central peak of $CDCl_3$ (77.23 ppm) on the δ scale. Chemical shifts of ^{31}P NMR spectra are reported in ppm and were internally referenced using tetramethylsilane. High resolution mass analyses were obtained using a PE Sciex QStar Pulsar quadrupole/TOF instrument (API) for ESI, or a GCT Premier TOF MS (Waters Corp) for FI. IR analysis was performed on PerkinElmer FI-IR Spectrometer UATR Two and all samples were neat.

Representative experimental procedure:
Unless otherwise noted all reactions were performed on a 0.25 mmol scale in a 5 mL microwave conical vial equipped with a septum and spin vane. First, $Cu(OAc)_2$•H_2O (2.5 mg, 0.0125 mmol) was added to the vial and a septum attached. The vial was purged of any oxygen with an argon flow followed by the addition of 2 wt % TPGS-750-M/H_2O (0.4 mL). Once the copper dissolved, $HPPh_2$ (65 μL, 70 mg, 0.375 mmol) was added. Upon the addition of $HPPh_2$, the solution became colored (red, brown, yellow, and orange). The color dissipated within a few to 10 min and the solution became cloudy and white. After the dissipation of color, the substrate (0.25 mmol) was added via syringe. The sides of the vial were subsequently washed with more 2 wt % TPGS-750-M/H_2O (0.2 mL). The

reaction was vigorously stirred for 24 h. The mixture was quenched with H_2O_2 (0.2 mL, 30% aq.) and stirred at rt for 2 h. *Note:* The reaction mixture with products **4a**, **5a**, **7a, 11a**, and **12a** were cooled to 0 °C in an ice-bath before the addition of hydrogen peroxide and were only stirred for 30 min. Next $Na_2S_2O_3$ (0.3 mL, sat. aq.) was added and the mixture stirred at rt. The mixture was filtered through a pad of silica gel using 10% (v/v) MeOH/DCM. The mixture was then concentrated via rotary evaporation and purified by flash chromatography using MeOH/DCM.

Compounds **7**, **8**, and **9** were synthesized via a Tebbe reaction from their respective ketone precursor by a procedure previously reported.[13] Compound **10** was synthesized from propiophenone through an α-arylation procedure[14] followed by a Tebbe reaction[13] previously published. Compounds **13**, **14**, **15**, and **16** were synthesized by a previously published procedure.[15]

Product's **3a**,[16] **4a**,[6] **6a**,[11] **11a**.[6] ^{1}H NMR spectral data matched that previously reported.

(4-Fluorophenethyl)diphenylphosphine oxide **1a**. White powder; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (dd, J = 7.8, 9 Hz, 4H), 7.56-7.53 (m, 2H), 7.51-7.44 (m, 4H), 7.12 (dd, J = 5.4, 9 Hz, 2H), 6.94 (t, J = 8.4 Hz, 2H), 2.92 (dt, J = 7.8, 12 Hz, 2H), 2.59-2.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.5, 132.1, 132.0, 131.0, 130.9, 129.7, 129.6, 129.0, 128.9, 115.6, 115.5, 32.2 ($^1J_{CP}$ = 277 Hz), 27.0; ^{31}P NMR (160 MHz, $CDCl_3$): δ 31.35; IR (neat): 3378, 3066, 2925, 2854, 1719, 1601, 1510, 1438, 1182, 1124, 826, 696, 552 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{18}FOPNa$ $(M+Na)^+$: 347.0977; found: 347.0961.

(4-Methoxyphenethyl)diphenylphosphine oxide **2a**. White powder; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (dd, J = 7.8, 11.4 Hz, 4H), 7.55-7.52 (m, 2H), 7.50-7.47 (m, 4H), 7.08 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.4 Hz, 2H), 3.77 (s, 3H), 2.88 (dt, J = 7.8, 12.6 Hz, 2H), 2.58-2.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.3, 133.4, 133.3, 132.6, 132.0, 131.0, 130.9, 129.2, 128.9, 128.8, 114.2, 55.4, 32.3 ($^1J_{CP}$ = 277 Hz), 26.8; ^{31}P NMR (160 MHz, $CDCl_3$): δ 31.66; IR (neat): 2944, 2867, 1591, 1513, 1437, 1328, 1246, 1171, 1067, 905, 726, 649, 560, 510 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{21}O_2PNa$ $(M+Na)^+$: 359.1177; found: 359.1162.

(2-(4-Methyoxyphenyl)propyl)diphenylphosphine oxide **7a**. White powder; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77-7.72 (m, 2H), 7.67-7.62 (m, 2H), 7.52-7.44 (m, 4H), 7.41-7.36 (m, 2H) 7.05 (d, J = 15 Hz, 2H), 6.73 (d, J = 15 Hz, 2H), 3.76 (s, 3H), 3.34-3.29 (m, 2H), 2.61-2.57 (m, 1H), 1.36 (d, J = 10 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 131.6, 131.4, 130.8, 130.7, 130.53, 130.47, 128.6, 128.5, 128.4, 128.3, 127.6, 113.8, 55.2, 33.4, 23.6 δ; ^{31}P NMR (160 MHz, $CDCl_3$, unreferenced): δ 30.4; IR (neat): 3054, 2930, 1588, 1516, 1437, 1375, 1244, 1161, 1071, 958, 850, 822, 768 cm^{-1}; HRMS (FI) calcd. for $C_{22}H_{23}O_2P$ (M^+): 350.1436; found 350.1447.

(((2,3-Dihydro-1H-inden-1-yl)methyl)diphenylphosphine oxide) **9a**. White powder; contained an unknown impurity not removable by chromatography (determined to be 95% pure by GC analysis); ^{1}H NMR (500 MHz, $CDCl_3$): 7.85-7.77 (m, 3H), 7.76-7.70 (m, 1H), 7.61-7.55 (m, 7H), 7.53-7.39 (m, 2H), 3.78 (d, J = 11 Hz, 1H), 3.63-3.55 (m, 1H), 2.91-2.84 (m, 1H), 2.81-2.74 (m, 1H), 2.44 (dt, J = 10.5, 15 Hz), 2.30-2.34 (m, 1H), 1.75-1.71 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): unable to clearly assign peaks due to impurity; ^{31}P NMR (160 MHz, $CDCl_3$): δ 30.53; IR (neat): 3053, 3018, 2855, 1715, 1595, 1478, 1438, 1182, 1025, 748, 696, 561 cm^{-1}; HRMS (EI) calcd. for $C_{22}H_{21}OP$ (M^+) 332.1330; found 332.01324.

(2,3-Diphenylbutyl)diphenylphosphine oxide **10a**. White powder; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, J = 7.8 Hz, 3H), 7.82 (dd, J = 7.2, 11.4 Hz, 4H), 7.59-7.52 (m, 5H), 7.51-7.46 (m, 6H), 7.43 (t, J = 7.8 Hz, 2H), 4.16 (br m , J = 15.6 Hz, 2H), 3.71-3.65 (m, 1H), 3.17-3.13 (m, 1H), (d, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.1, 141.8, 133.8, 132.4, 131.4, 131.3, 129.4, 128.9, 128.8, 128.7, 128.1, 127.9, 43.7, 43.3, 32.0 ($^1J_{CP}$ = 281 Hz), 15.5; ^{31}P NMR (160 MHz, $CDCl_3$): δ 31.66; IR (neat): 3052, 2923, 2853, 1676, 1438, 1272, 1185, 1120, 741, 695, 523 cm^{-1}; HRMS (FI) calcd. for $C_{28}H_{27}OP$ (M^+): 410.1800; found: 410.1819.

(2,2-Diphenylethyl)diphenylphosphine oxide **13a**. White powder; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54-7.02 (m, 20H), 4.68 (m, 1H), 3.10 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.9, 143.824, 131.3, 131.3, 130.7, 130.6, 130.4, 130.3, 128.5, 128.4, 128.4, 128.3, 128.3, 127.8, 127.8, 126.8, 126.4, 125.8, 44.4, 36.7, 36.3, 29.7; ^{31}P NMR (160 MHz, $CDCl_3$): δ 28.96; IR (neat): 3710, 2922, 1731, 1436, 1176, 1055, 1033, 884, 742, 524, 508 cm^{-1}; HRMS (FI) calcd. for $C_{26}H_{23}OP$ (M^+): 382.1486; found: 382.1499.

Diphenyl(2-phenyl-2-(3-(trifluoromethyl)phenyl)ethyl)-phosphine oxide **14a**. White powder; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68-7.08 (m, 19H), 4.79 (m, 1H), 3.11 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.4, 143.3, 143.2, 130.6, 130.6, 130.4, 130.4, 128.8, 128.6, 128.5, 128.4, 128.3, 128.3, 127.6, 126.8, 124.5, 124.4, 123.4, 123.4, 44.3, 36.5, 36.0; ^{31}P NMR (160 MHz, $CDCl_3$): δ 28.90; IR (neat): 3072, 2940, 2891, 1592, 1437, 1327, 1175, 1114, 1075, 814, 687, 525 cm^{-1}; HRMS (EI) calcd. for $C_{27}H_{22}F_3OP$ (M^+): 450.1360, found: 450.1369.

Notes and references

[a] Department of Chemistry & Biochemistry, University of California, Santa Barbara, CA 93106, USA
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