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Nickel-Catalyzed Decarboxylative C–P Cross-Coupling of Alkenyl Acids with P(O)H Compounds

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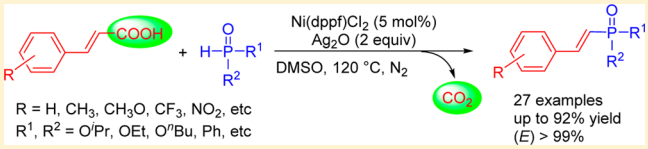
Supporting Information

ABSTRACT: The first nickel-catalyzed decarboxylative C–P coupling of a wide range of alkenyl acids with various P(O)H compounds, especially for H-phosphonates, has been developed, affording a versatile and efficient tool for the preparation of valuable (*E*)-1-alkenylphosphonates, (*E*)-1-alkenylphosphinate oxides, and (*E*)-1-alkenylphosphine oxides with high stereoselectivity and broad substrate applicability. DFT calculation revealed that the phosphine ligand exhibits better catalytic performance than the nitrogen ligand in the reductive elimination step owing to the stronger nucleophilicity and larger size.



INTRODUCTION

Transition-metal-catalyzed cross-coupling reactions for carbon–phosphorus bond formation have become the most straightforward and powerful ways for the preparation of organophosphorus compounds in the past two decades, which have widespread applications in biological, pharmaceutical, material, and catalytic sciences.[1] Among them, alkenylphosphorus compounds are an important class of carbon–phosphorus bond-containing valuable chemicals, which are extensively used as biologically active molecules in medicinal chemistry[2] and as additives or flame-retardants in polymer sciences.[3] Furthermore, they can also serve as useful precursors for asymmetric addition reactions.[4] Efficient methods for the synthesis of alkenylphosphorus compounds mainly include Heck-type coupling of vinylphosphonates with various aryl partners,[5] olefin cross-metathesis,[6] cross-coupling of P(O)H with vinyl halides,[7] and addition of P(O)H to alkynes.[8] However, most of the existing methods are still plagued with problems including lack of stereoselectivity,[8] limited substrate scope,[5,6] relatively drastic conditions not compatible with sensitive functional groups,[7] unsatisfactory yields,[5a,7a,b] the occasional need to use strong bases,[7b,c] and the need for air-sensitive[5] or noble metal catalysts.[6,8a,b,d] In view of these challenges, there is still a strong need to develop more convenient and efficient protocols for the synthesis of alkenylphosphorus compounds with high stereoselectivity from readily available starting materials.

On the other hand, alkenyl acids are one of the most extensively versatile building blocks in transition-metal-catalyzed decarboxylative cross-couplings for the effective construction of C–C,[9] C–N,[10] and C–S[11] bonds due to their commercial availability and structural diversity. Nevertheless, in stark contrast, C–P bond-forming reaction using alkenyl acids as the coupling substrates via decarboxylation is considerably rare, and there is only one reported example. In 2011, the first Cu-mediated decarboxylative coupling of alkenyl acids with secondary phosphine oxides have been reported.[12] This protocol first exemplified that alkenyl acids are potential coupling partners for C–P bond constuction, but this reaction did not work well for the dialkyl H-phosphonate, such as diisoproyl H-phosphonate giving the product in 50% yield. Moreover, alkenyl acids are stable, inexpensive, readily obtainable, and structurally diverse, only CO_2 is generated instead of metal halides, and the configuration of alkenyl acids may ensure high regio- and stereoselectivity. Thus, using alkenyl acids as coupling substrates, the development of efficient and versatile methods to access various alkenylphosphorus compounds via transition-metal-catalyzed decarboxylative coupling is still desirable and attractive in synthetic chemistry.

Although decarboxylative coupling reactions have emerged as fascinating and powerful approaches for regioselective C–C bond formation over the years,[9] the known decarboxylation for the C–P bond formation is scarce.[12,13] Moreover, the commonly employed metal catalysts are limited to the classical Pd, Cu, and Ag metals,[14] and little attention has been paid to use of the metal nickel as a decarboxylative catalyst.[15] Herein, we report the first versatile Ni-catalyzed decarboxylative cross-coupling of various alkenyl acids with P(O)H compounds, especially H-phosphonates, leading to (*E*)-1-alkenylphosphonates, (*E*)-1-alkenylphosphinate oxides, and (*E*)-1-alkenylphosphine oxides in moderate to excellent yields with high stereoselectivity. To the best of our knowledge, the nickel-

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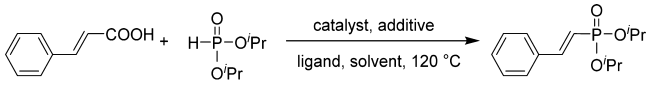
catalyzed decarboxylative coupling of alkenyl acids with P(O)H compounds has never been developed. The protocol reported herein may be used as an efficient complement for the classical Pd-, Cu-, or Ag-catalyzed decarboxylation.

RESULTS AND DISCUSSION

Initially, we optimized the catalytic conditions for the decarboxylative coupling of cinnamic acid **1a** with diisopropyl phosphonate **2a** in the presence of $Ni(OAc)_2$ (5 mol %), Ag_2O (2 equiv), 1,1′-bis(diphenylphosphino)ferrocene (dppf, 7.5 mol %), and DMSO (5 mL) under a nitrogen atmosphere. Gratifyingly, we observed that a 36% yield of the desired product **3a** was obtained after 12 h at 120 °C (Table 1, entry 1). Encouraged by this promising result, the effect of catalysts, ligands, solvents, additives, and temperature on reaction yield was further evaluated, and some representative results are shown in Table 1. Various nickel salts including $Ni(OAc)_2$, $NiBr_2$, $NiCl_2$, and $Ni(acac)_2$ were investigated, with the finding that $NiCl_2$ was the optimal choice for the coupling reaction (entries 1−4). Among the various ligands screened, dppf turned out to be the best ligand and enhanced the decarboxylative coupling to produce **3a** in 64% yield (entry 4). Other ligands and the corresponding yields were as follows: 1,10-phenanthroline (Phen, 8%), 2,2′-bipyridine (bpy, 28%), and dppp (47%) (entries 5−7). Without the ligand, a lower yield of **3a** was observed under similar reaction conditions (entry 8). To advance the process further, $NiCl_2$ coordination complexes such as $Ni(dppf)Cl_2$, $Ni(dppp)Cl_2$, and $Ni(PPh_3)_2Cl_2$ were also evaluated (entries 9−11). Delightedly, $Ni(dppf)Cl_2$ was found to be the best choice and promoted the yield up to 90% (entry 9). Notably, the known Cu-catalyzed decarboxylation of **1a** with **2a** only gave 50% yield,[12] illustrating that nickel catalysts afforded higher reaction efficiency than copper salts using H-phosphonates as substrates. A screening of the additives disclosed Ag_2O as the most favored one to push the reaction forward, affording the desired product **3a** in 90% (entries 9, 12, and 13). The Ag_2O loading was also evaluated, and using 1 equiv of Ag_2O led to a significant yield decrease (35%, entry 14). A subsequent survey on the role of solvents revealed that DMSO was the optimal candidate (entries 15−17). Decreasing the reaction temperature to 100 °C resulted in a lower yield of 76%, and no distinct change was detected by raising the reaction temperature (entry 18). Increasing the loading of ligand dppf did not improve the yield (entry 19). When the reaction time decreased to 6 h, a lower yield of 85% was obtained (entry 20). Note that the decarboxylative coupling did not proceed smoothly in the absence of either $Ni(dppf)Cl_2$ or Ag_2O, disclosing that $Ni(dppf)Cl_2$ and Ag_2O were critical to achieve a high yield.

Table 1. Optimization of the Reaction Conditions[a]



1a **2a** **3a**

entry	catalyst[b]	ligand	additive	solvent	yield[c] (%)
1	$Ni(OAc)_2$	dppf	Ag_2O	DMSO	36
2	$Ni(acac)_2$	dppf	Ag_2O	DMSO	27
3	$NiBr_2$	dppf	Ag_2O	DMSO	54
4	$NiCl_2$	dppf	Ag_2O	DMSO	64
5	$NiCl_2$	Phen	Ag_2O	DMSO	8
6	$NiCl_2$	bpy	Ag_2O	DMSO	26
7	$NiCl_2$	dppp	Ag_2O	DMSO	47
8	$NiCl_2$		Ag_2O	DMSO	20
9	**$Ni(dppf)Cl_2$**		**Ag_2O**	**DMSO**	**90**
10	$Ni(dppp)Cl_2$		Ag_2O	DMSO	50
11	$Ni(PPh_3)Cl_2$		Ag_2O	DMSO	40
12	$Ni(dppf)Cl_2$		Ag_2CO_3	DMSO	trace
13	$Ni(dppf)Cl_2$		AgOAc	DMSO	36
14	$Ni(dppf)Cl_2$		Ag_2O	DMSO	35[d]
15	$Ni(dppf)Cl_2$		Ag_2O	NMP	79
16	$Ni(dppf)Cl_2$		Ag_2O	DMF	86
17	$Ni(dppf)Cl_2$		Ag_2O	toluene	30
18	$Ni(dppf)Cl_2$		Ag_2O	DMSO	76[e]
19	$Ni(dppf)Cl_2$	dppf	Ag_2O	DMSO	89
20	$Ni(dppf)Cl_2$		Ag_2O	DMSO	85[f]

[a]Reaction conditions: **1a** (0.6 mmol), **2a** (0.5 mmol), catalyst (0.025 mmol), ligand (0.03 mmol), additive (1 mmol), solvent (5 mL), 120 °C, 12 h, under nitrogen. [b]Using anhydrous metal salts as catalysts. [c]Yields are based on **2a**. [d]Using 0.5 mmol of Ag_2O. [e]At 100 °C. [f]For 6 h.

With the optimized reaction conditions in hand, the scope and generality of the method were examined by varying the structures of the alkenyl acids. As shown in Table 2, various valuable (*E*)-1-alkenylphosphonates can be conveniently and efficiently obtained in moderate to high yields with high stereoselectivity by this novel Ni-catalyzed decarboxylative coupling reaction, indicating that this method is general and practically useful. Besides the fact that no traces of regio- or stereoisomers were detected by in situ ^{31}P NMR and ^1H NMR analysis in all these decarboxylative couplings, the results demonstrated that this novel Ni-catalyzed decarboxylation exhibited high stereoselectivities with *E*-isomers. In general, both electron-rich and electron-deficient aromatic alkenyl acids were suitable for this method, and a wide range of functional groups, such as methyl, fluoro, chloro, methoxy, trifluoromethyl, carboxyl, nitro, dimethylamino, and phenyl groups were all tolerated under the reaction conditions (**3a−o**). Substituents at the ortho position do not affect the reactivity (entries 4 and 8). Interestingly, (*E*)-2-methyl-3-phenylacrylic acid (**1e**) could also be used in the reaction to afford the expected product **3e** in 50% yield with high stereoselectivity (entry 5). Notably, the alkenyl acid moiety represented a higher chemoselectivity over the fluorine and chlorine as leaving groups, demonstrating the potential of this new method to allow access to highly functionalized targets by stepwise coupling (**3f−h**). Generally, electron-rich substrates showed better reactivity and higher yields than electron-poor ones. For example, cinnamic acid substrates having strong electron-withdrawing groups such as nitro and pentafluoro on the phenyl ring only gave moderate yields of 57% and 53%, respectively (entries 13 and 17). Notably, heteroaromatic alkenyl acids such as **1r** could also be used as suitable substrates to give the corresponding product in moderate yield (entry 18). Unfortunately, aliphatic alkenyl acids such as sorbic acid and crotonic acid only gave a trace amount of the desired products. It is noticeable that (*Z*)-cinnamic acid as the coupling substrate only gave an 87% yield of diisopropyl (*E*)-styrylphosphonate **3a** without the generation of diisopropyl (*Z*)-styrylphosphonate under the similar reaction conditions (entry 19), probably since *Z*-*E* tautomerism occurred in the reaction process under the high-temperature conditions and the *E*-isomer is thermodynamically more stable than the *Z*-isomer.

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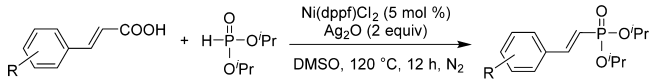
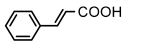
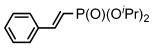
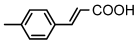
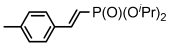
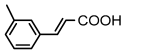
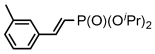
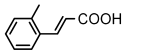
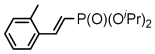
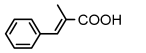
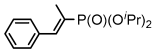
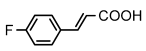
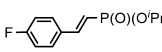
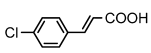
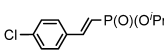
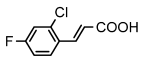
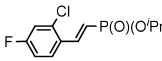
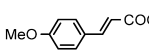
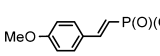
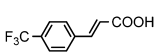
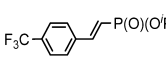
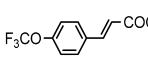
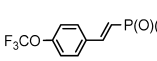
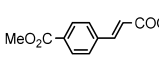
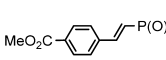
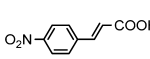
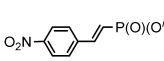
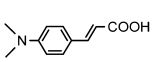
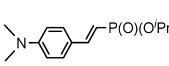
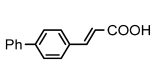
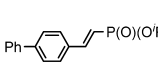
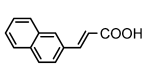
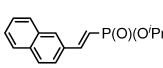
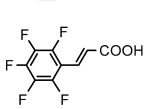
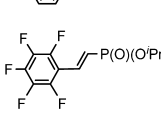
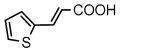
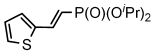
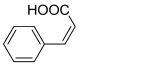
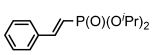
Table 2. Ni-Catalyzed Decarboxylative Coupling of Alkenyl Acids with Diisopropyl Phosphonates[a]



1 **2a** **3a- 3r** (*E*) > 99%

entry	1		products		yield (%)[b]
1		**1a**		**3a**	90
2		**1b**		**3b**	85
3		**1c**		**3c**	82
4		**1d**		**3d**	85
5		**1e**		**3e**	50
6		**1f**		**3f**	83
7		**1g**		**3g**	87
8		**1h**		**3h**	80
9		**1i**		**3i**	84
10		**1j**		**3j**	81
11		**1k**		**3k**	83
12		**1l**		**3l**	80
13		**1m**		**3m**	57
14		**1n**		**3n**	76
15		**1o**		**3o**	66
16		**1p**		**3p**	57
17		**1q**		**3q**	53
18		**1r**		**3r**	58
19		**1s**		**3a**	87

[a]Reaction conditions: **1a** (0.6 mmol), **2a** (0.5 mmol), Ni(dppp)Cl$_2$ (0.025 mmol), Ag$_2$O (1 mmol), DMSO (5 mL), 120 °C, 12 h, under nitrogen. [b]Yields are based on **2a**. No regio- or stereoisomers were detected by ^{31}P NMR and ^{1}H NMR analysis of crude reaction mixtures.

In regard to the H-phosphonates, in addition to **2a**, diethyl (**2b**), and dibutyl (**2c**) phosphonates, as well as 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (**2d**), all could be used as the substrates, affording the desired products **3s**–**u** in 91%, 67%, and 69% yields, respectively (Table 3, entries 1–3). In addition, we note that ethyl phenylphosphinate (**2e**) and diphenylphosphine oxide (**2f**) were also compatible with this reaction, thus affording the corresponding (*E*)-1-alkenylphosphinate oxides (**3v**–**x**) and (*E*)-1-alkenylphosphine oxides (**3y**, **3z**, and **3jf**) products in good to high yields. Obviously, this method with broad substrate applicability and high stereoselectivity provided a general and powerful tool for the preparation of various valuable (*E*)- alkenylphosphorus compounds.

Inspired by the above results, we next briefly turned our attention to extend this method to the synthesis of alkynyl phosphonates starting from alkynyl acids. However, using

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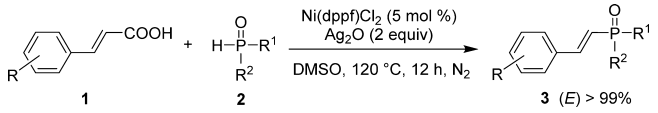
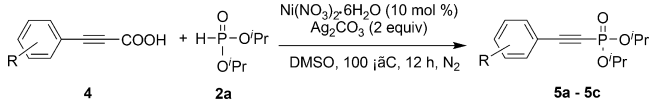
Table 3. Ni-Catalyzed Decarboxylative Coupling of Alkenyl Acids with P(O)H Compounds[a]



entry	1	2	products	yield (%)[b]
1	**1a**	**2b**	**3s**	91
2	**1a**	**2c**	**3t**	67
3	**1a**	**2d**	**3u**	69
4	**1a**	**2e**	**3v**	92
5	**1f**	**2e**	**3w**	73
6	**1j**	**2e**	**3x**	81
7	**1a**	**2f**	**3y**	80
8	**1f**	**2f**	**3z**	78
9	**1j**	**2f**	**3jf**	84

[a]Reaction conditions: **1** (0.6 mmol), **2** (0.5 mmol), Ni(dppp)Cl_2 (0.025 mmol), Ag_2O (1 mmol), DMSO (5 mL), 120 °C, 12 h, under nitrogen. [b]Yields are based on **2**. No regio- or stereoisomers was detected by ^{31}P NMR and ^{1}H NMR analysis of crude reaction mixtures.

Table 4. Ni-Catalyzed Decarboxylative Coupling of Alkynyl Acids with Diisopropyl Phosphonates[a]



entry	4	products	yield (%)[b]
1	**4a**	**5a**	45
2	**4b**	**5b**	36
3	**4c**	**5c**	40

[a]Reaction conditions: **4** (0.3 mmol), **2a** (0.25 mmol), Ni$(NO_3)_2$·$6H_2O$ (0.025 mmol), Ag_2CO_3 (0.5 mmol), DMSO (2 mL), 100 °C, 12 h, under nitrogen. [b]Yields are based on **2a**.

Ni(dppf)Cl_2 as catalyst, the decarboxylative coupling of 3-phenylpropiolic acid **4a** with **2a** only gave a trace amount of the desired product **5a** under the above optimized reaction conditions. After investigation of the reaction conditions, we discovered that the Ni$(NO_3)_2$·$6H_2O$/Ag_2CO_3 catalysis system was the best choice and afforded product **5a** in 45% yield (Table 4, entry 1). In addition to **4a**, alkynyl acid substrates with methoxy and trifluoromethyl groups gave the corresponding coupling products **5b** and **5c** in low yields of 36% and 40%, respectively (Table 4, entries 2 and 3).

Transition-metal-catalyzed decarboxylative coupling reactions for the formation of the C−C bond have been extensively studied both experimentally and theoretically.[16] The results showed the catalytic cycle underwent different steps depending on substrates.[17] To understand the mechanism, radical traps BHT (2,6-di-*tert*-butyl-4-methylphenol) and TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) were added to the reaction system under the optimized reaction conditions, respectively, and a significant yield decrease was not observed (90% and 80% yields, respectively), indicating that this coupling might not be a radical reaction. On the basis of their findings and our

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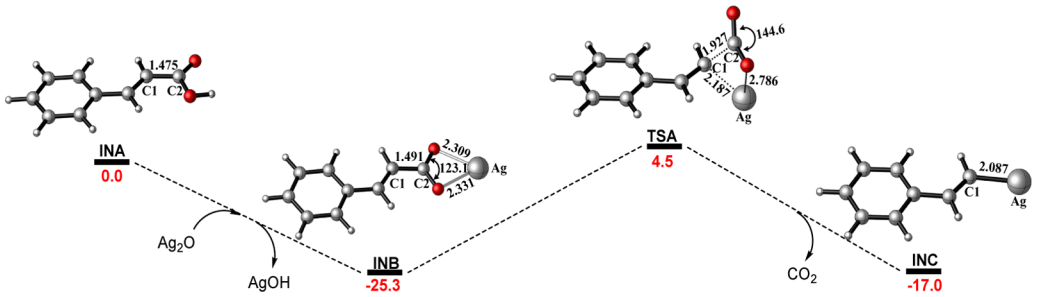
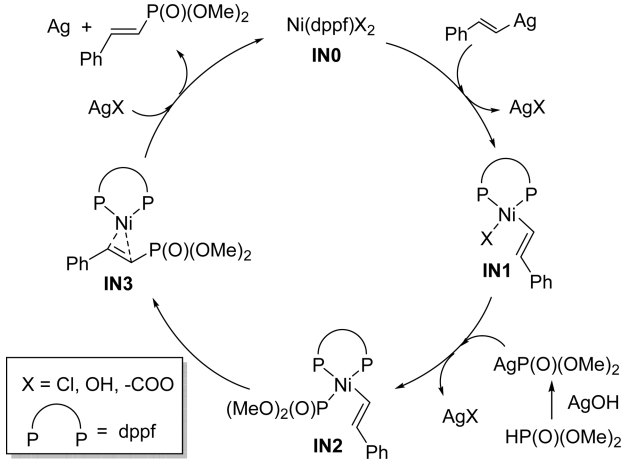


Figure 1. Free energy profile for the decarboxylative step. The energies are given in kcal/mol.

experiences in organophosphorus chemistry,[7d,18] we proposed a mechanism for the intermolecular decarboxylative coupling reactions of alkenyl acids with P(O)H compounds (Figure 1 and Scheme 1). Moreover, density functional theory (DFT)

Scheme 1. Proposed Mechanism

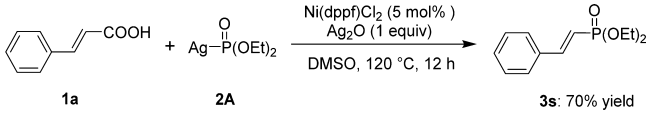


calculations were carried out to investigate the key steps. The model substrates cinnamic acid, dimethyl phosphonate, Ag_2O, and Ni(dppf)Cl_2 were chosen. Relative free energies in solution (DMSO) are employed to analyze the reaction mechanism.

A silver-involved decarboxylative process has been proposed by several groups.[19] Initially, cinnamic acid (**INA**) reacted with Ag_2O to generate cinnamoyloxy silver (**INB**, −25.3 kcal/mol) with the loss of AgOH (Figure 1). Note that the bond length of C1−C2 (1.491 Å) in **INB** is longer than that in **INA** (1.475 Å), indicating the C1−C2 bond is preactivated by silver cation. From **INB**, a four-membered transition state **TSA** (activation energy is 29.8 kcal/mol) is identified, where the O−C2−O angle is increased to 144.6°. Then styrylsilver (**INC**, −17.0 kcal/mol) is formed along with the removal of CO_2.

The approach of **INC** toward catalyst Ni(dppf)X_2 (X = Cl, OH, or −COO) produces an intermediate **IN1** via a ligand-exchange process. Note that dialkyl phosphonate could react with AgOH to form $AgP(O)(OR)_2$,[20] and this process is computed to be exothermic (ΔG = −18.5 kcal/mol, R = Me). We believe that $AgP(O)(OMe)_2$ instead of dimethyl phosphonate may be involved in the next step. To support our hypothesis, a mixture of **1a** (0.48 mmol), $(EtO)_2P(O)Ag$ (**2A**) (0.4 mmol), Ag_2O (0.4 mmol), and Ni(dppf)Cl_2 (0.02 mmol) in DMSO was treated at 120 °C for 12 h, providing the C−P coupling product **3s** in 70% yield (Scheme 2). However, a mixture of **1a**, **2A**, and Ni(dppf)Cl_2 without Ag_2O did not give the corresponding product **3s** under similar conditions. Thus,

Scheme 2. Reaction of Cinnamic Acid with $(EtO)_2P(O)Ag$



the second ligand exchange takes place when $AgP(O)(OR)_2$ reacts with **IN1**, leading to a tetracoordinated Ni(II) complex **IN2**.[21,22] Subsequently, an η^2 Ni (0) complex **IN3** is formed through the reductive elimination (RE) step. Notably, a silver mirror was observed after the reaction was completed. Hence, the catalyst Ni(dppf)X_2 is regenerated by a Ag(I)-mediated oxidation.[23]

It is very interesting to note that nickel catalyst bearing phosphine ligands exhibited an excellent catalytic performance, whereas nitrogen ligands gave only poor yields (Table 1). To understand the origin of the different reactivity between phosphine and nitrogen ligands, the calculations were also carried out using 2,2′-bipyridine as the ligand (Figure 2). Surprisingly, the activation barriers of the RE step are much different. When Ni(dppf)Cl_2 was chosen as model catalyst, the free energy barrier of the RE step is 16.3 kcal/mol lower than that of Ni(bpy)Cl_2 as catalyst, which can be mainly attributed to electronic effect of the ancillary ligand in the corresponding transition state.[24] For instance, in the study of $(R_3P)_2PdMe_2$ species,[25] Ariafard and Yates suggested that for stabilizing the transition state of RE step the suitable ligands should be forming strong bonds with the Pd center and large ligands will lead to a destabilization of the reactant $(R_3P)_2PdMe_2$ complexes but not the transition structures. On the basis of their findings, the phosphine ligand should be a better candidate for the RE step since it is more nucleophilic than the nitrogen ligand.[26] Moreover, the C−P bond length (2.056 Å) in **TS1** is much longer than that (1.971 Å) in **TS1′**, clearly demonstrating that **IN2′** requires more energy to reach **TS1′**.

■ CONCLUSION

In summary, we have successfully developed the first versatile and efficient Ni-catalyzed decarboxylative C−P coupling reaction of various alkenyl acids with a wide range of P(O)H compounds, especially for H-phosphonates, affording valuable (*E*)-1-alkenylphosphonates, (*E*)-1-alkenylphosphinate oxides, and (*E*)-1-alkenylphosphine oxides. Importantly, the present method exhibits good compatibility with various types of P-nucleophiles including H-phosphonates, H-phosphinate esters, and easily oxidized H-phosphine oxides and allows them to be coupled efficiently. In addition, using commercially available, cheap and stable alkenyl acids as the coupling partners only generating CO_2 instead of environmentally unfriendly halides, the remarkable functional group tolerance, the high stereo-

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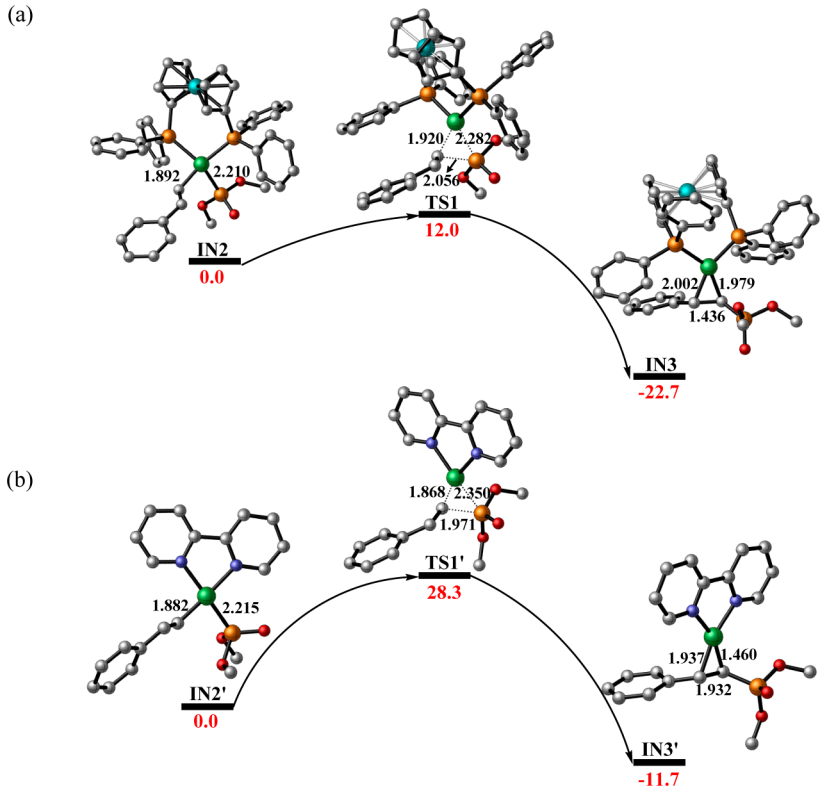

Figure 2. Free energy profile for the reductive elimination step using dppf (a) and bpy (b), respectively. The energies are given in kcal/mol.

selectivity, and moderate to excellent yield mean that this effective method will be attractive for academia and industry. It is foreseeable that this novel Ni-catalyzed decarboxylative C−P coupling system will extend to the nickel-catalyzed decarboxylative cross-coupling for the formation of carbon−carbon and carbon−heteroatom bonds in the future. DFT calculation showed that the phosphine ligand exhibits better catalytic performance than the nitrogen ligand because of the stronger nucleophilicity and larger size. Detailed mechanistic investigations and synthetic applications for this reaction are currently ongoing.

COMPUTATIONAL METHODS

Geometry optimizations for all species studied in this work have been performed via the Gaussian 03 program.[27] A hybrid Becke3LYP (B3LYP) method,[28] which was widely adopted in the previous papers on mechanistic studies of Ni-catalyzed reactions, was used.[7d,29] The D95v(d) basis set was chosen to describe the C, H, N, and O atoms,[30] and the effective core potentials of Hay and Wadt with a valence double-ζ basis set (LanL2DZ) were used for the Ni, Ag, Fe, and P atoms.[31] Polarization functions were also added: Ni(ζ_f) = 3.130, Ag(ζ_f) = 1.611, Fe(ζ_f) = 2.462, and P(ζ_d) = 0.387.[32] For each optimized species, vibrational frequency analyses have been carried out to identify all of the stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency) on the potential energy surfaces. Intrinsic reaction coordinate (IRC) calculations were also performed to confirm that the transition states indeed connect two corresponding minima. Single-point calculations in solution (DMSO) have been calculated (IEF-PCM method with the Bondi radii)[33] with the same method using the SDD[34] pseudopotential for the metal center and the extended 6-311+G(2d,p)[35] basis set for the other atoms using gas-phase geometry. A similar treatment was also used in several recent theoretical studies.[23,29] The free energy correction from frequency calculation was added to the single-point energy to obtain the free energy in solution. All of the solution-phase free energies reported herein correspond to the reference state of 1 mol/L, 298 K. Structures were visualized by the CYLview program.[36]

EXPERIMENTAL SECTION

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. All the reactions were carried out using standard Schlenk techniques. Column chromatography was carried out on silica gel of 300−400 mesh size. ^{31}P, ^{1}H, and $^{13}C\{^{1}H\}$ NMR spectra were measured on 400 or 500 MHz spectrometers. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR were recorded using tetramethylsilane as the internal standard. ^{31}P NMR was recorded using 85% H_3PO_4 as external standard for ^{31}P NMR. Data are represented as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in hertz (Hz), integration. All new compounds were further characterized by elemental analysis.

General Procedure for Ni-Catalyzed Decarboxylative C−P Cross-Coupling of Alkenyl Acids with P(O)H Compounds. Alkenyl acids (0.6 mmol, 1.2 equiv), H-phosphonates (0.5 mmol, 1 equiv), Ni(dppf)Cl_2 (0.025 mmol, 0.05 equiv, 17.1 mg), and Ag_2O (1 mmol, 2 equiv, 231.7 mg) were dissolved in 5 mL of DMSO and stirred at 120 °C for 12 h under an atmosphere of nitrogen. The resulting mixture was concentrated, and the residue was purified by silica gel column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the alkenylphosphorus compounds.

Spectral Data of the Compounds. *Diisopropyl (E)-Styrylphosphonate (**3a**, CAS 78463-00-0).* Colorless oil. 121 mg, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53−7.45 (m, 3H), 7.40−7.36 (m, 3H), 6.31−6.22 (t, J = 17.5 Hz, 1H), 4.76−4.69 (m, 2H), 1.38−1.36 (d, J = 6.2 Hz, 6H), 1.33−1.32 (d, J = 6.2 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 146.8 (d, J_{C-P} = 6.7 Hz), 134.1 (d, J_{C-P} = 22.8 Hz), 129.0, 127.8, 126.6, 114.7 (d, J_{C-P} = 191.5 Hz), 69.5 (d, J_{C-P} = 5.9 Hz), 23.1 (d, J_{C-P} = 4.5 Hz), 23.0 (d, J_{C-P} = 4.5 Hz). ^{31}P NMR ($CDCl_3$, 203 MHz): δ 17.3. ESI-MS: m/z = 269 $[M + H]^+$. Anal. Calcd for $C_{14}H_{21}O_3P$: C, 62.67; H, 7.89. Found: C, 62.45; H, 7.67.

*Diisopropyl (E)-(4-Methylstyryl)phosphonate (**3b**, New Compound).* Light yellow oil; 120 mg, 85% yield. ^{1}H NMR (400 MHz,

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$CDCl_3$): δ 7.50−7.38 (m, 3H), 7.19−7.17 (m, 2H), 6.25−6.16 (t, *J* = 17.6 Hz, 1H), 4.74−4.66 (m, 2H), 2.36 (s, 3H), 1.37−1.36 (d, *J* = 6.2 Hz, 6H), 1.32−1.31 (d, *J* = 6.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.7 (d, J_{C-P} = 6.7 Hz), 139.4, 131.4 (d, J_{C-P} = 23.4 Hz), 128.5, 126.6, 113.6 (d, J_{C-P} = 192.7 Hz), 69.4 (d, J_{C-P} = 5.8 Hz), 23.1 (d, J_{C-P} = 4.5 Hz), 23.0 (d, J_{C-P} = 4.5 Hz), 20.4. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.7. IR (film): 3469, 2978, 2929, 1614, 1411, 1387, 1242, 1176, 1107, 972, 890, 833. ESI-MS: *m*/*z* = 283 $[M + H]^+$. Anal. Calcd for $C_{15}H_{23}O_3P$: C, 63.82; H, 8.21. Found: C, 64.23; H, 8.47.

*Diisopropyl (E)-(3-Methylstyryl)phosphonate (**3c**, New Compound).* Light yellow oil; 115 mg, 82% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.50−7.40 (dd, *J* = 22.4, 17.5 Hz, 1H), 7.30−7.24 (m, 3H), 7.19−7.17 (m, 1H), 6.29−6.21 (t, *J* = 17.5 Hz, 1H), 4.73−4.67 (m, 2H), 1.37−1.36 (d, *J* = 6.2 Hz, 6H), 1.33−1.31 (d, *J* = 6.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.9 (d, J_{C-P} = 7.0 Hz), 134.1 (d, J_{C-P} = 23.0 Hz), 129.8, 127.7, 127.2, 123.9, 114.5 (d, J_{C-P} = 192.0 Hz), 69.4 (d, J_{C-P} = 5.2 Hz), 23.1 (d, J_{C-P} =, 4.3 Hz), 23.0 (d, J_{C-P} = 4.3 Hz), 20.3. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.3. IR (film): 3445, 2976, 2929, 1617, 1381, 1371, 1258, 1102, 982, 888. ESI-MS: *m*/*z* = 283 $[M + H]^+$. Anal. Calcd for $C_{15}H_{23}O_3P$: C, 63.82; H, 8.21; Found: C, 63.65; H, 8.39.

*Diisopropyl (E)-(2-Methylstyryl)phosphonate (**3d**, New Compound).* Light yellow oil; 120 mg, 85% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.79−7.69 (dd, *J* = 22.8, 17.4 Hz, 1H), 7.52−7.50 (m, 1H), 7.28−7.18 (m, 3H), 6.24−6.15 (dd, *J* = 18.3, 17.4 Hz, 1H), 4.78−4.67 (m, 2H), 2.43 (s, 3H), 1.38−1.37 (d, *J* = 6.2 Hz, 6H), 1.34−1.33 (d, *J* = 6.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 145.3 (d, J_{C-P} = 7.3 Hz), 137.1, 134.2 (d, J_{C-P} = 22.8 Hz), 130.7, 129.7, 126.3, 126.0, 117.2 (d, J_{C-P} = 190.9 Hz), 70.4 (d, J_{C-P} = 5.9 Hz), 24.1 (d, *J* = 3.9 Hz), 24.0 (d, J_{C-P} = 3.9 Hz), 19.7. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.1. IR (film): 3420, 2975, 2932, 1610, 1461, 1381, 1371, 1243, 1105, 1007, 982, 891, 837. ESI-MS: *m*/*z* = 283 $[M + H]^+$. Anal. Calcd for $C_{15}H_{23}O_3P$: C, 63.82; H, 8.21. Found: C, 63.51; H, 8.50.

*Diisopropyl (E)-(1-Phenylprop-1-en-2-yl)phosphonate (**3e**, New Compound).* Yellow oil; 70 mg, 50% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.51−7.44 (m, 1H), 7.39−7.38 (m, 4H), 7.34−7.29 (m, 2H), 4.76−4.65 (m, 2H), 2.08−2.04 (dd, *J* = 15.1, 1.6 Hz, 3H), 1.38−1.37 (d, *J* = 6.2 Hz, 6H), 1.32−1.31 (d, *J* = 6.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.9 (d, J_{C-P} = 11.7 Hz), 134.9 (d, J_{C-P} = 24.2 Hz), 128.4, 127.3 127.2, 126.4 (d, J_{C-P} = 179.3 Hz), 69.3 (d, J_{C-P} = 5.9 Hz), 23.1 (d, J_{C-P} = 3.7 Hz), 22.9 (d, J_{C-P} = 3.7 Hz), 13.5 (d, J_{C-P} = 8.7 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 19.8. IR (film): 3465, 2978, 2933, 1622, 1450, 1381, 1242, 1107, 1005, 972, 886. ESI-MS: *m*/*z* = 283 $[M + H]^+$. Anal. Calcd for $C_{15}H_{23}O_3P$: C, 63.82; H, 8.21. Found: C, 63.59; H, 8.18.

*Diisopropyl (E)-(4-Fluorostyryl)phosphonate (**3f**, CAS 1262966-52-8).* Yellow oil; 119 mg, 83% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.50−7.40 (m, 3H), 7.09−7.05 (m, 2H), 6.23−6.14 (t, *J* = 17.3 Hz, 1H), 4.76−4.68 (m, 2H), 1.38−1.36 (d, *J* = 6.3 Hz, 6H), 1.33−1.32 (d, *J* = 6.3 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.8 (d, J_{C-F} = 250.6 Hz), 145.4 (d, J_{C-P} = 7.0 Hz), 134.4 (dd, J_{C-P} = 23.7, J_{C-F} = 3.6 Hz), 128.5 (d, J_{C-F} = 8.3 Hz), 114.9 (d, J_{C-F} = 22.0 Hz), 114.5 (d, J_{C-P} = 193.1 Hz), 69.6 (d, J_{C-P} = 5.4 Hz), 23.2 (d, J_{C-P} = 4.4 Hz), 23.1 (d, J_{C-P} = 4.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.0. ESI-MS: *m*/*z* = 287 $[M + H]^+$. Anal. Calcd for $C_{14}H_{20}FO_3P$: C, 58.74; H, 7.04. Found: C, 58.56; H, 7.25

*Diisopropyl (E)-(4-Chlorostyryl)phosphonate (**3g**, CAS 202747-25-9).* Light orange oil; 131 mg, 87% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48−7.41 (m, 3H), 7.38−7.34 (m, 2H), 6.29−6.20 (t, *J* = 16.9 Hz, 1H), 4.74−4.68 (m, 2H), 1.38−1.36 (d, *J* = 6.1 Hz, 6H), 1.33−1.31 (d, *J* = 6.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 145.2 (d, J_{C-P} = 6.6 Hz), 134.9, 132.6 (d, J_{C-P} = 23.9 Hz), 127.9 (d, J_{C-P} = 25.4 Hz), 115.5 (d, J_{C-P} = 192.2 Hz), 69.6 (d, J_{C-P} = 5.9 Hz), 23.0 (d, J_{C-P} = 4.2 Hz), 22.9 (d, J_{C-P} = 4.2 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 16.6. ESI-MS: *m*/*z* = 304 $[M + H]^+$. Anal. Calcd for $C_{14}H_{20}ClO_3P$: C, 55.54; H, 6.66. Found: C, 55.42; H, 6.87.

*Dipropyl (E)-(2-Chloro-4-fluorostyryl)phosphonate (**3h**, New Compound).* Yellow oil; 128 mg, 80% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.80−7.72 (dd, *J* = 17.5, 22.6 Hz, 1H), 7.60−7.57 (dd, *J* = 6.0, 8.8 Hz, 1H), 7.16−7.14 (dd, *J* = 2.6, 8.4 Hz, 1H), 7.03−6.99 (dt, *J* = 2.6, 4.1 Hz, 1H), 6.29−6.22 (t, *J* = 17.4 Hz, 1H),4.78−4.72 (m, 2H), 1.39−1.34 (dd, *J* = 6.2, 16.1 Hz, 12H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 162.1 (d, J_{C-F} = 253.8 Hz), 140.8 (d, J_{C-P} = 8.1 Hz), 134.4 (d, J_{C-F} = 10.3 Hz), 128.8 (d, J_{C-F} = 20.7 Hz), 127.7 (d, J_{C-F} = 9.0 Hz), 118.0 (d, J_{C-P} = 192.4 Hz), 116.4 (d, J_{C-F} = 24.5 Hz), 113.7 (d, J_{C-F} = 21.5 Hz), 69.8 (d, J_{C-P} = 5.7 Hz), 23.1 (d, J_{C-P} = 3.8 Hz), 23.0 (d, J_{C-P} = 4.9 Hz). ^{31}P NMR ($CDCl_3$, 203 MHz): δ 15.7. IR (film): 3461, 2978, 2938, 1736, 1614, 1601, 1491, 1385, 1242, 1103, 984, 886. ESI-MS: *m*/*z* = 322 $[M + H]^+$. Anal. Calcd for $C_{14}H_{19}ClFO_3P$: C, 52.43; H, 5.97. Found: C, 52.64; H, 6.19.

*Diisopropyl (E)-(4-Methoxystyryl)phosphonate (**3i**, CAS 168025-52-3).* Colorless oil; 125 mg, 84% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48−7.38 (m, 3H), 6.91−6.89 (m, 2H), 6.14−6.06 (t, *J* = 17.4 Hz, 1H), 4.74−4.66 (m, 2H), 3.83 (s, 3H), 1.37−1.36 (d, *J* = 6.2 Hz, 6H), 1.32−1.31 (d, *J* = 6.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.2, 146.4 (d, J_{C-P} = 6.6 Hz), 128.2, 126.9 (d, J_{C-P} = 23.6 Hz), 113.2, 111.8 (d, J_{C-P} = 193.8 Hz), 69.3 (d, J_{C-P} = 5.8 Hz), 23.1 (d, J_{C-P} = 3.7 Hz), 23.0 (d, J_{C-P} = 3.7 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 18.1. ESI-MS: *m*/*z* = 321 $[M + Na]^+$. Anal. Calcd for $C_{15}H_{23}O_4P$: C, 60.39; H, 7.77. Found: C, 60.08; H, 7.67.

*Diisopropyl (E)-(4-(Trifluoromethyl)styryl)phosphonate (**3j**, CAS 1262966-58-4).* Light yellow oil; 136 mg, 81% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.66−7.59 (m, 4H), 7.55−7.45 (dd, *J* = 22.2, 17.4 Hz, 1H), 6.42−6.34 (m, 1H), 4.78−4.70 (m, 2H), 1.39−1.38 (d, *J* = 6.2 Hz, 6H), 1.34−1.33 (d, *J* = 6.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 144.7 (d, J_{C-P} = 6.9 Hz), 137.4 (d, J_{C-P} = 23.5 Hz), 130.6 (q, J_{C-F} = 33.0 Hz), 126.8, 124.8 (q, J_{C-F} = 3.7 Hz), 122.8 (q, J_{C-F} = 272.6 Hz), 118.0 (d, J_{C-P} = 191.4 Hz), 79.8 (d, J_{C-P} = 5.9 Hz), 23.1 (d, J_{C-P} = 4.4 Hz), 23.0 (d, J_{C-P} = 4.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.1. ESI-MS: *m*/*z* = 337 $[M + H]^+$. Anal. Calcd for $C_{15}H_{20}F_3O_3P$: C, 53.57; H, 5.99. Found: C, 53.36; H, 6.18.

*Diisopropyl (E)-(4-(Trifluoromethoxy)styryl)phosphonate (**3k**, New Compound).* Light yellow oil; 146 mg, 83% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.54−7.52 (m, 2H), 7.50−7.42 (dd, *J* = 17.5, 22.4 Hz, 1H), 7.23−7.22 (m, 2H), 6.29−6.22 (dd, *J* = 16.8, 17.3 Hz, 1H), 4.76−4.69 (m, 2H), 1.38−1.37 (d, *J* = 6.2 Hz, 6H), 1.33−1.32 (d, *J* = 6.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 149.3 (q apparent br s), 144.9 (d, J_{C-P} = 6.7 Hz), 132.7 (d, J_{C-P} = 23.7 Hz), 128.1, 120.1, 119.4 (q, J_{C-F} = 257.9 Hz), 116.0 (d, J_{C-P} = 192.1 Hz), 69.7 (d, J_{C-P} = 5.8 Hz), 23.1 (d, J_{C-P} = 4.4 Hz), 23.0 (d, J_{C-P} = 4.4 Hz). ^{31}P NMR ($CDCl_3$, 203 MHz): δ 16.4. IR (film): 3444, 2979, 2929, 2620, 1766, 1708, 1614, 1465, 1385, 1247, 1207, 1287, 1247, 1098, 1058, 981, 888. ESI-MS: *m*/*z* = 375 $[M + Na]^+$. Anal. Calcd for $C_{15}H_{20}F_3O_4P$: C, 51.14; H, 5.72; Found: C, 50.93; H, 5.42.

*Methyl (E)-4-(2-(Dipropoxyphosphoryl)vinyl)benzoate (**3l**, New Compound).* Colorless oil; 130 mg, 80% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 8.01−7.99 (m, 2H), 7.52−7.41 (m, 3H), 6.38−6.31 (dd, *J* = 16.9, 17.3 Hz, 1H), 4.72−4.66 (m, 2H), 3.88 (s, 3H), 1.34−1.33 (d, *J* = 6.2 Hz, 6H), 1.29−1.28 (d, *J* = 6.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.4, 145.2 (d, J_{C-P} = 6.7 Hz), 138.3 (d, J_{C-P} = 23.5 Hz), 130.2, 129.1, 126.5, 117.8 (d, J_{C-P} = 191.4 Hz), 69.7 (d, J_{C-P} = 5.6 Hz), 51.2, 23.1 (d, J_{C-P} = 4.5, Hz), 23.0 (d, J_{C-P} = 4.5, Hz). ^{31}P NMR ($CDCl_3$, 203 MHz): δ 16.0. IR (film): 3415, 3009, 2976, 2925, 1719, 1617, 1519, 1432, 1381, 1276, 1236, 1105, 1000, 887. ESI-MS: *m*/*z* = 349 $[M + Na]^+$. Anal. Calcd for $C_{16}H_{23}O_5P$: C, 58.89; H, 7.10. Found: C, 58.66; H, 7.15.

*Diisopropyl (E)-(4-Nitrostyryl)phosphonate (**3m**, New Compound).* White solid; 89 mg, 57% yield. Mp: 87−88 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.25−8.24 (m, 2H), 7.66−7.64 (m, 2H), 7.55−7.47 (dd, *J* = 22.2, 17.4 Hz, 1H), 6.48−6.42 (dd, *J* = 17.4, 16.0 Hz 1H), 4.80−4.71 (m, 2H), 1.39−1.38 (d, *J* = 6.2 Hz, 6H), 1.35−1.34 (d, *J* = 6.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 147.4, 143.5 (d, J_{C-P} = 6.4 Hz), 140.0 (d, J_{C-P} = 22.8 Hz), 127.3, 123.1, 120.2, (d, J_{C-P} = 190.5 Hz), 70.0 (d, J_{C-P} = 6.0 Hz), 23.1 (t, J_{C-P} = 4.6 Hz). ^{31}P NMR ($CDCl_3$, 203 MHz): δ 14.9. IR (film): 3191, 2917, 2844, 1740, 1597, 1450, 1373, 1258, 1111, 1005. ESI-MS: *m*/*z* = 314 $[M + H]^+$. Anal. Calcd for $C_{14}H_{20}NO_5P$: C, 53.67; H, 6.43; N, 4.47. Found: C, 53.49; H, 6.50; N, 4.40.

*Diisopropyl (E)-(4-(Dimethylamino)styryl)phosphonate (**3n**, CAS 625412-80-8).* Red oil; 118 mg, 76% yield. ^1H NMR (400 MHz,

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$CDCl_3$): δ 7.44−7.34 (m, 3H), 6.68−6.64 (m, 2H), 6.01−5.93 (t, J = 17.6 Hz, 1H), 4.72−4.64 (m, 2H), 3.00 (s, 6H), 1.36−1.35 (d, J = 6.2 Hz, 6H), 1.31−1.30 (d, J = 6.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.6, 147.3, 128.2, 122.1 (d, J_{C-P} = 23.8 Hz), 110.8, 108.1 (d, J_{C-P} = 195.9 Hz), 69.0 (d, J_{C-P} = 5.4 Hz), 23.0 (d, J_{C-P} = 4.2 Hz), 22.9 (d, J_{C-P} = 4.2 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 19.6. ESI-MS: m/z = 312 $[M + H]^+$. Anal. Calcd for $C_{16}H_{26}NO_3P$: C, 61.72; H, 8.42; N, 4.50. Found: C, 61.50; H, 8.58; N, 4.67.

*Diisopropyl (E)-(2-([1,1′-Biphenyl]-4-yl)vinyl)phosphonate (**3o**, New Compound).* Colorless oil; 114 mg, 66% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.61−7.57 (m, 6H), 7.55−7.49 (m, 1H), 7.45−7.42 (m, 2H), 7.45−7.42 (m, 2H), 7.37−7.34 (m, 2H), 6.34−6.27 (t, J = 17.4 Hz, 1H), 4.77−4.70 (m, 2H), 1.39−1.37 (d, J = 6.2 Hz, 6H), 1.34−1.33 (d, J = 6.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 146.2 (d, J_{C-P} = 6.7 Hz), 141.8, 139.2, 133.0 (d, J_{C-P} = 23.6 Hz), 127.9, 127.1, 126.8, 126.5, 126.0, 114.6 (d, J_{C-P} = 192.4 Hz), 69.5 (d, J_{C-P} = 5.6 Hz), 23.1 (d, J_{C-P} = 3.9 Hz), 23.0 (d, J_{C-P} = 4.8 Hz). ^{31}P NMR ($CDCl_3$, 203 MHz): δ 17.3. IR (film): 3465, 3027, 2978, 2933, 1704, 1614, 1487, 1385, 1246, 1107, 988, 886, 825. ESI-MS: m/z = 345 $[M + H]^+$. Anal. Calcd for $C_{20}H_{25}O_3P$: C, 69.75; H, 7.32. Found: C, 69.84; H, 7.63.

*Diisopropyl (E)-(2-(Naphthalen-2-yl)vinyl)phosphonate (**3p**, CAS 1262966-60-8).* Yellow oil; 91 mg, 57% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.89−7.51 (m, 4H), 7.68−7.60 (m, 2H), 7.51−7.49 (m, 2H), 6.42−6.35 (t, J = 17.4, 1H), 4.80−4.72 (m, 2H), 1.40−1.38 (d, J = 6.2 Hz, 6H), 1.35−1.34 (d, J = 6.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 146.7 (d, J_{C-P} = 6.4 Hz), 133.1, 132.3, 131.6 (d, J_{C-P} = 23.6 Hz), 128.2, 127.6, 127.5, 126.7, 126.1, 125.7, 122.3, 114.9 (d, J_{C-P} = 192.3 Hz), 69.5 (d, J_{C-P} = 5.5 Hz), 23.1 (d, J_{C-P} = 3.6 Hz), 23.0 (d, J_{C-P} = 3.6 Hz). ^{31}P NMR ($CDCl_3$, 203 MHz): δ 17.3. ESI-MS: m/z = 319 $[M + H]^+$. Anal. Calcd for $C_{18}H_{23}O_3P$: C, 67.91; H, 7.28. Found: C, 67.70; H, 7.61.

*Diisopropyl (E)-(2-(Perfluorophenyl)vinyl)phosphonate (**3q**, New Compound).* Light brown oil; 95 mg, 53% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44−7.34 (dd, J = 17.9, 24.0 Hz, 1H), 6.68−6.59 (t, J = 17.4 Hz, 1H), 4.77−4.69 (m, 2H), 1.38−1.32 (dd, J = 6.2, 16.8 Hz, 12H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.7, 145.8−143.3 (m), 138.0−135.6 (m), 129.9−129.8 (m), 126.2−124.2 (m), 109.8−109.3 (m), 70.1 (d, J_{C-P} = 5.8 Hz), 23.1 (d, J_{C-P} = 4.4 Hz), 23.0 (d, J_{C-P} = 4.4 Hz). ^{31}P NMR ($CDCl_3$, 203 MHz): δ 14.0. IR (film): 2962, 1728, 1650, 1601, 1524, 1495, 1254, 1103, 1009, 849. ESI-MS: m/z = 359 $[M + H]^+$. Anal. Calcd for $C_{14}H_{16}F_5O_3P$: C, 46.94; H, 4.50. Found: C, 47.32; H, 4.85.

*Diisopropyl (E)-(2-(Thiophene-2-yl)vinyl)phosphonate (**3r**, New Compound).* Yellow oil; 79 mg, 58% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.59−7.52 (dd, J = 17.2, 21.8 Hz, 1H), 7.34−7.44 (m, 1H), 7.19−7.18 (m, 1H), 7.04−7.02 (dd, J = 3.6, 4.8 Hz, 1H), 6.05−5.98 (t, J = 16.8 Hz, 1H), 4.73−4.66 (m, 2H), 1.37−1.35 (d, J = 6.2 Hz, 6H), 1.33−1.31 (d, J = 6.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 139.7 (d, J_{C-P} = 26.5 Hz), 139.1 (d, J_{C-P} = 7.5 Hz), 128.8, 126.9, 126.8, 113.5 (d, J_{C-P} = 194.3 Hz), 69.5 (d, J_{C-P} = 5.5 Hz), 23.1 (d, J_{C-P} = 4.5 Hz), 23.0 (d, J_{C-P} = 4.5 Hz). ^{31}P NMR ($CDCl_3$, 203 MHz): δ 16.7. IR (film): 2954, 2921, 2852, 1454, 1376, 1254, 1005, 976. ESI-MS: m/z = 275 $[M + H]^+$. Anal. Calcd for $C_{12}H_{19}O_3PS$: C, 52.54; H, 6.98. Found: C, 52.67; H, 6.81.

*Diethyl (E)-Styrylphosphonate (**3s**, CAS 20408-33-7).* Colorless oil; 109 mg, 91% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56−7.46 (m, 3H), 7.40−7.36 (m, 3H), 6.30−6.22 (t, J = 17.6 Hz, 1H), 4.18−4.10 (m, 4H), 1.37−1.34 (t, J = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.7 (d, J_{C-P} = 6.2 Hz), 133.9 (d, J_{C-P} = 22.9 Hz), 129.2, 127.8, 126.7, 113.0 (d, J_{C-P} = 191.0 Hz), 60.9 (d, J_{C-P} = 5.2 Hz), 15.4 (d, J_{C-P} = 6.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 19.5. ESI-MS: m/z = 241 $[M + H]^+$. Anal. Calcd for $C_{12}H_{17}O_3P$: C, 60.00; H, 7.13. Found: C, 59.71; H, 7.32.

*Dibutyl (E)-Styrylphosphonate (**3t**, CAS 146896-99-3).* Light yellow oil; 99 mg, 67% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.56−7.45 (m, 3H), 7.40−7.39 (m, 3H), 6.31−6.21 (m, 1H), 7.08−7.05 (m, 4H), 1.69−1.68 (m, 4H), 1.44−1.41 (m, 4H), 0.96−0.92 (m, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 148.6 (d, J_{C-P} = 6.8 Hz), 130.2, 128.8, 127.7, 114.9, 113.0, 65.5 (d, J_{C-P} = 6.7 Hz), 32.5 (d, J_{C-P} = 6.4 Hz), 18.7, 13.6. ^{31}P NMR ($CDCl_3$, 203 MHz): δ 19.5. ESI-MS: m/z = 297 $[M + H]^+$. Anal. Calcd for $C_{16}H_{25}O_3P$: C, 64.85; H, 8.50. Found: C, 64.53; H, 8.37.

*(E)-5,5-Dimethyl-2-styryl-1,3,2-dioxaphosphinane 2-Oxide (**3u**, CAS 1190078-62-6).* Colorless crystal; 87 mg, 69% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.62−7.50 (m, 3H), 7.40−7.38 (m, 3H), 6.35−6.26 (dd, J = 18.8, 17.5 Hz, 1H), 4.26−4.21 (m, 2H), 3.93−3.87 (m, 2H), 1.13 (s, 3H), 1.08 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.1 (d, J_{C-P} = 6.6 Hz), 134.5 (d, J_{C-P} = 23.6 Hz), 130.5, 128.8, 127.7, 111.8 (d, J_{C-P} = 193.2 Hz), 75.4 (d, J_{C-P} = 5.9 Hz), 32.4 (d, J_{C-P} = 5.9 Hz), 21.4 (d, J_{C-P} = 16.9 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 14.9. ESI-MS: m/z = 253 $[M + H]^+$. Anal. Calcd for $C_{13}H_{17}O_3P$: C, 61.90; H, 6.79; Found: C, 61.68; H, 6.87.

*Ethyl (E)-Phenyl(styryl)phosphinate (**3v**, CAS 82943-05-3).* Light yellow oil; 125 mg, 92% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88−7.83 (m, 2H), 7.56−7.46 (m, 6H), 7.37−7.34 (m, 3H), 6.54−6.45 (dd, J = 20.4, 17.5 Hz, 1H), 4.18−4.02 (m, 2H), 1.38−1.35 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.8 (d, J_{C-P} = 5.5 Hz), 134.0 (d, J_{C-P} = 20.1 Hz), 131.1 (d, J_{C-P} = 2.9 Hz), 130.6 (d, J_{C-P} = 138.1 Hz), 130.4 (d, J_{C-P} = 10.0 Hz), 129.1, 127.8, 127.6 (d, J_{C-P} = 13.2 Hz), 126.7, 117.1 (d, J_{C-P} = 139.7 Hz), 69.8 (d, J_{C-P} = 5.9 Hz), 15.5 (d, J_{C-P} = 6.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 31.1. ESI-MS: m/z = 273 $[M + H]^+$. Anal. Calcd for $C_{16}H_{17}O_2P$: C, 70.58; H, 6.29. Found: C, 70.34; H, 6.55.

*Ethyl (E)-(4-Methoxystyryl)(phenyl)phosphinate (**3w**, New Compound).* Light yellow oil; 110 mg, 73% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.85−7.80 (m, 2H), 7.50−7.40 (m, 6H), 6.86−6.84(m, 2H), 6.35−6.26 (dd, J = 20.5, 17.4 Hz, 1H), 4.14−3.98 (m, 2H), 3.77 (s, 3H), 1.35−1.31 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.1, 147.3 (d, J_{C-P} = 5.8 Hz), 131.9 (d, J_{C-P} = 2.2 Hz), 131.6 (d, J_{C-P} = 137.9 Hz), 131.2 (d, J_{C-P} = 10.2 Hz), 129.2, 128.4 (d, J_{C-P} = 12.9 Hz), 127.6 (d, J_{C-P} = 20.5 Hz), 115.4, 114.0, 60.6 (d, J_{C-P} = 5.8 Hz), 55.2, 16.4 (d, J_{C-P} = 6.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 31.7. IR (film): 3421, 2510, 1534, 1448, 1110, 971, 842. ESI-MS: m/z = 325 $[M + Na]^+$. Anal. Calcd for $C_{17}H_{19}O_3P$: C, 67.54; H, 6.34. Found: C, 67.46; H, 6.51.

*Ethyl (E)-Phenyl(4-(trifluoromethyl)styryl)phosphinate (**3x**, New Compound).* Light brown oil; 138 mg, 81% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.87−7.82 (m, 2H), 7.61−7.46 (m, 8H), 6.64−6.55 (dd, J = 19.6, 17.5 Hz, 1H), 4.18−4.01 (m, 2H), 1.37−1.34 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 145.7 (d, J_{C-P} = 5.7 Hz), 138.2 (d, J_{C-P} = 19.9 Hz), 132.3 (d, J = 2.7 Hz), 131.6 (q, J_{C-F} = 12.6 Hz), 131.4 (d, J = 10.2 Hz), 130.2, 128.6 (d, J = 13.1 Hz), 127.8, 125.6 (q, J_{C-F} = 3.7 Hz), 123.7 (q, J_{C-F} = 272.2 Hz), 121.2 (d, J_{C-P} = 137.6 Hz), 60.9 (d, J_{C-P} = 5.8 Hz), 16.4 (d, J_{C-P} = 6.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 30.1. IR (film): 3465, 2980, 1760, 1553, 1256, 1185, 1117, 983. ESI-MS: m/z = 341 $[M + H]^+$. Anal. Calcd for $C_{17}H_{16}F_3O_2P$: C, 60.01; H, 4.74. Found: C, 59.88; H, 4.93.

*(E)-Diphenyl(styryl)phosphine Oxide (**3y**, CAS 3582-82-9).* White solid; 122 mg, 80% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.79−7.73 (m, 3H), 7.56−7.45 (m, 9H), 7.37−7.35 (m, 3H), 6.90−6.80 (dd, J = 22.3, 17.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.5 (d, J_{C-P} = 3.6 Hz), 134.2 (d, J_{C-P} = 17.7 Hz), 132.0 (d, J_{C-P} = 105.8 Hz), 130.8 (d, J_{C-P} = 2.0 Hz), 130.4 (d, J_{C-P} = 10.2 Hz), 129.1, 127.8, 127.6 (d, J_{C-P} = 12.2 Hz), 126.7, 118.8 (d, J_{C-P} = 103.7 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.4. ESI-MS: m/z = 305 $[M + H]^+$. Anal. Calcd for $C_{20}H_{17}OP$: C, 78.93; H, 5.63. Found: C, 78.71; H, 5.90.

*(E)-(4-Methoxystyryl)diphenylphosphine Oxide (**3z**, CAS 59675-60-4).* White solid; 130 mg, 78% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.78−7.74 (m, 4H), 7.54−7.40 (m, 9H), 6.90−6.88 (m, 2H), 6.72−6.64 (dd, J = 22.2, 17.4 Hz, 1H), 3.81 (s, 3H), $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.1, 147.0 (d, J_{C-P} = 3.9 Hz), 133.3 (d, J_{C-P} = 105.7 Hz), 131.6, 131.3 (d, J_{C-P} = 9.9 Hz), 129.3, 128.5 (d, J_{C-P} = 11.9 Hz), 128.0 (d, J_{C-P} = 18.2 Hz), 116.3 (d, J_{C-P} = 106.1 Hz), 114.2, 55.3. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.7. ESI-MS: m/z = 357 $[M + Na]^+$. Anal. Calcd for $C_{21}H_{19}O_2P$: C, 75.44; H, 5.73. Found: C, 75.63; H, 5.99.

*(E)-Diphenyl(4-(trifluoromethyl)styryl)phosphine Oxide (**3jf**, CAS 1429762-73-1).* Light yellow solid; 156 mg, 84% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.78−7.74 (m, 4H), 7.61−7.45 (m, 11H), 7.02−6.94

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(dd, J = 21.9, 17.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 145.5 (d, J_{C-P} = 3.3 Hz), 138.4 (d, J_{C-P} = 17.5 Hz), 132.5 (d, J_{C-P} = 106.4 Hz), 131.9, 131.5 (q, J_{C-F} = 33.5 Hz), 131.2 (d, J_{C-P} = 10.0 Hz), 128.6 (d, J_{C-P} = 12.4 Hz), 127.8, 125.7 (q, J_{C-F} = 3.6 Hz), 123.7 (q, J_{C-F} = 273.6 Hz), 122.6 (d, J_{C-P} = 102.2 Hz). ^{31}P NMR ($CDCl_3$, 203 MHz): δ 22.9. ESI-MS: m/z = 373 $[M + H]^+$. Anal. Calcd for $C_{21}H_{16}F_3OP$: C, 67.74; H, 4.33. Found: C, 68.07; H, 4.45.

*Diisopropyl (Phenylethynyl)phosphonate (**5a**, CAS 204009-80-3).* Colorless oil; 30 mg, 45% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.57−7.55 (m, 2H), 7.47−7.44 (m, 1H), 7.40−7.37 (m, 2H), 4.85−4.80 (m, 2H), 1.43 (d, J = 3.0 Hz, 6H), 1.42 (d, J = 3.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 132.5 (d, J_{C-P} = 2.4 Hz), 130.5, 128.5, 119.8 (d, J_{C-P} = 5.5 Hz), 98.1 (d, J_{C-P} = 52.8 Hz), 72.3 (d, J_{C-P} = 5.5 Hz), 23.9 (d, J_{C-P} = 4.5 Hz), 23.6 (d, J_{C-P} = 4.9 Hz). ^{31}P NMR ($CDCl_3$, 203 MHz): δ −8.5. ESI-MS: m/z = 267 $[M + H]^+$.

*Diisopropyl ((4-Methoxyphenyl)ethynyl)phosphonate (**5b**, CAS 1310329-76-0).* Colorless oil; 27 mg, 36% yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.51−7.50 (m, 2H), 6.90−6.88 (m, 2H), 4.86−4.78 (m, 2H), 3.85 (s, 3H), 1.43−1.42 (d, J = 1.8 Hz, 6H), 1.41−1.40 (d, J = 1.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.3, 134.3 (d, J_{C-P} = 2.4 Hz), 114.2, 111.7 (d, J_{C-P} = 5.6 Hz), 98.8 (d, J_{C-P} = 53.0 Hz), 78.5 (d, J_{C-P} = 298.6 Hz), 72.2 (d, J_{C-P} = 5.4 Hz), 55.4, 23.9 (d, J_{C-P} = 4.7 Hz), 23.6 (d, J_{C-P} = 4.7 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz): δ −8.0; ESI-MS: m/z = 297 $[M + H]^+$.

*Diisopropyl ((4-(Trifluoromethyl)phenyl)ethynyl)phosphonate (**5c**, CAS 1549706-37-7).* Colorless oil; 33 mg, 40% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.69−7.64 (m, 2H), 7.47−7.44 (m, 4H), 4.88−4.81 (m, 2H), 1.44−1.43 (d, J = 3.0 Hz, 6H), 1.43−1.42 (d, J = 2.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 132.8 (d, J_{C-P} = 2.1 Hz), 132.0 (q, J_{C-P} = 33.1 Hz), 125.5 (q, J_{C-P} = 4.7 Hz), 123.5 (d, J_{C-P} = 5.3 Hz), 123.5 (q, J_{C-P} = 269.8 Hz), 95.9 (d, J_{C-P} = 52.0 Hz), 82.1 (d, J_{C-P} = 292.9 Hz), 72.7 (d, J_{C-P} = 5.5 Hz), 23.9 (d, J_{C-P} = 4.7 Hz), 23.6 (d, J_{C-P} = 5.6 Hz); ^{31}P NMR ($CDCl_3$, 203 MHz): δ −9.4. ESI-MS: m/z = 355 $[M + H]^+$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^1H NMR and $^{13}C\{^1H\}$ NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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