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Wittig reaction with ion-supported Ph_3P

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ABSTRACT

Ion-supported Ph_3P, 4-(diphenylphosphino)benzyltrimethylammonium bromide **A** and *N*-methyl-*N*-[4-(diphenylphosphino)benzyl]pyrrolidinium bromide **B**, were used for the Wittig reaction. Ion-supported phosphonium salts **A1** and **B1**, which were prepared from the reactions of ion-supported Ph_3P **A** and **B** with ethyl bromoacetate, respectively, reacted with aromatic and aliphatic aldehydes in the presence of K_2CO_3 to give the corresponding α,β-unsaturated ethyl esters in good yields with high purity by simple filtration of the reaction mixture and subsequent removal of the solvent from the filtrate. Similarly, ion-supported phosphonium salts **A2** and **B2**, which were prepared from the reactions of ion-supported Ph_3P **A** and **B** with *p*-methylbenzyl bromide, respectively, reacted with aromatic and aliphatic aldehydes in the presence of NaH to provide the corresponding *p*-methylstyrene derivatives in good yields with high purity by simple filtration of the reaction mixture and the subsequent removal of the solvent from the filtrate. In both reactions, the co-product, ion-supported Ph_3PO, could be obtained quantitatively by simple filtration, and was converted into the corresponding ion-supported Ph_3P **A** and **B** again in high yields using dimethyl sulfate, followed by the reduction with $LiAlH_4$. Recovered and regenerated ion-supported Ph_3P **A** and **B** could be reused for the same Wittig reaction while maintaining good yields of ethyl (*E*)-3-(4′-chlorophenyl)-2-propenoate and 1-(4′-chlorophenyl)-2-(4″-methylphenyl)ethene with high purity by simple filtration and removal of the solvent from the filtrate.

1. Introduction

Triphenylphosphine (Ph_3P) is one of the most important reagents, because it can be used for various types of reactions, such as the bromination, iodination, and chlorination of alcohols with carbon tetrabromide (CBr_4), molecular iodine–imidazole (I_2/imidazole), and carbon tetrachloride (CCl_4) (the Appel reaction), respectively, and the esterification of carboxylic acids with alcohols in the presence of diethyl azodicarboxylate (DEAD) (the Mitsunobu reaction).[1,2] The Wittig reaction also requires triphenylphosphine to form carbon–carbon double bonds through the formation of phosphonium ylides and the subsequent reaction with aldehydes or ketones.[3] Moreover, it can be used as a ligand for Pd-catalyzed C–C bond formation (the Mizoroki–Heck reaction,[4a,b] the Sonogashira reaction,[4c] the Stille reaction,[4d,e] and the Suzuki–Miyaura reaction[4f,g]). However, in the halogenation of alcohols with Ph_3P/CBr_4, Ph_3P/I_2/imidazole, or Ph_3P/CCl_4, the esterification and amidation of carboxylic acids with Ph_3P/DEAD or Ph_3P/di(2-pyridyl) disulfide, and the Wittig reaction, a stoichiometric amount of Ph_3PO is formed as a co-product and it must be removed carefully by troublesome column chromatography to obtain the product in the pure state. This is the major drawback of using triphenylphosphine. To solve this problem, we recently reported the first preparation of ion-supported Ph_3P, 4-(diphenylphosphino)benzyltrimethylammonium bromide **A**, and *N*-methyl-*N*-[4-(diphenylphosphino)benzyl]pyrrolidinium bromide **B**, and their synthetic utility in the halogenation of alcohols and the esterification of carboxylic acids as an equivalent required reagent, and the Mizoroki–Heck reaction and the Sonogashira reaction as a catalytic amount of ligand with $Pd(OAc)_2$ or $PdCl_2$.[5]

Here, as part of our study of the synthetic use of ion-supported Ph_3P, we would like to report the Wittig reaction of aromatic and aliphatic aldehydes with ion-supported phosphonium ylides derived from ion-supported Ph_3P, 4-(diphenylphosphino)benzyl-trimethylammonium bromide **A**, and *N*-methyl-*N*-[4-(diphenylphosphino)benzyl]pyrrolidinium bromide **B**.

2. Results and discussion

Ion-supported Ph_3P **A** and **B** were prepared easily in 74% yield (three steps) and 54% yield (four steps), respectively, from commercially available chlorodiphenylphosphine using our previous method.[5] First, ion-supported phosphonium salts **A1** and **B1**, which are the precursors of stabilized ylides, were prepared from the reaction of ethyl bromoacetate with ion-supported Ph_3P **A** and **B** in

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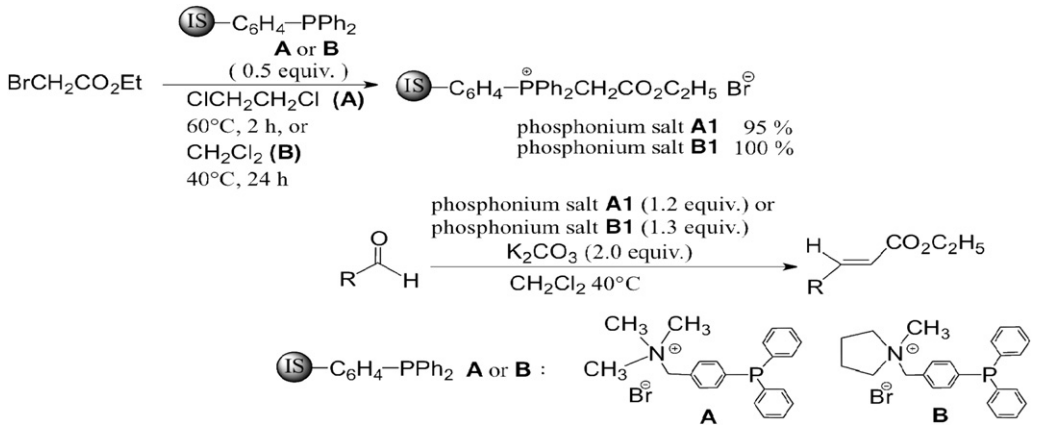
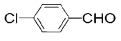
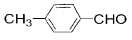
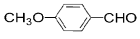
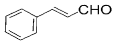
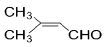
95% yield and 100% yield, respectively. Then, both phosphonium salts **A1** and **B1** were treated with aromatic and aliphatic aldehydes in the presence of potassium carbonate in dichloromethane to provide the corresponding α,β-unsaturated ethyl esters in good yields with high (*E*)-selectivity, as shown in Table 1. Here, after the reaction, the reaction mixture was filtered. α,β-Unsaturated ethyl esters were obtained in high yields with high purity (>90%) after simple removal of the solvent from the filtrate (entries 1, 5–9, 12, 15, 16, and 18). Thus, it is very easy to purify the α,β-unsaturated ethyl esters. Moreover, ion-supported Ph_3PO, the co-product of both reactions with ion-supported phosphonium salts **A1** and **B1**, was recovered by the above filtration in 92–100% yields. The recovered ion-supported Ph_3PO was treated with dimethyl sulfate, followed by the reduction with $LiAlH_4$ to regenerate ion-supported Ph_3P **A** and **B** in high yields.[6] Once ion-supported Ph_3P **A** and **B** were regenerated, ion-supported phosphonium salts **A1** and **B1** could be prepared in high yields again, and they could be reused for the same reaction with *p*-chlorobenzaldehyde to provide ethyl *p*-chlorocinnamate in good yields while keeping a high purity until the second reuse (entries 2, 3 and 13, 14). On the other hand, when Ph_3P was used under the same conditions, α,β-unsaturated ethyl ester was obtained in good yield, however, the purity was approximately 43% and Ph_3PO was recovered in only 50% yield (entry 4). Although phosphonium salts **A1** and **B1** reacted with α,α,α-trifluoroacetophenone in good yields with high purity (entries 10 and 20), they did not react with acetophenone at all (entries 11 and 21), as that of phosphonium salt derived from Ph_3P did not react with ketones.

Then, ion-supported phosphonium salts **A2** and **B2**, which are the precursors of semistabilized ylides, were prepared from the

Table 1
Witting reaction with ion-supported Ph_3P



Substrate	A					B				
	Entry	Time (h)	Yield[a] (%)	Purity[b] (%)	*E*/*Z*	Entry	Time (h)	Yield[a] (%)	Purity[b] (%)	*E*/*Z*
	1	8	94	97	96:4	12	8	98	98	94:6
	2[c]	8	95	97	96:4	13[c]	8	95	90	96:4
	3[d]	8	92	97	96:4	14[d]	8	91	90	96:4
	4[e]	8	99	43	96:4					
	5	10	95	98	97:3	15	8	96	90	96:4
	6	50	98	97	96:4	16	24	91	90	95:5
$CH_3(CH_2)_6CHO$	7	24	100	97	97:3	17	20	90	86	93:7
	8	24	93	89	90:10	18	20	92	95	92:8
	9	24	92	90	95:5	19	16	88	80	94:6
	10	24	92	90	88:12	20	24	95	97	88:12
	11	24	0	—		21	48	0	—	—

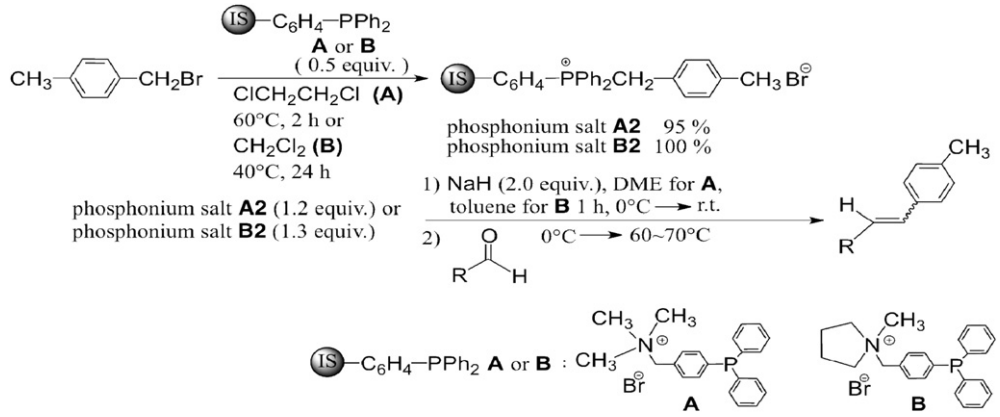
[a] Isolated yield of *E* and *Z* alkenes. Ion-supported Ph_3PO was recovered in 92~100% yields.
[b] Purity of product after removal of solvent from the extracts.
[c] The first regenerated ion-supported Ph_3P **A** or **B** was used.
[d] The second regenerated ion-supported Ph_3P **A** or **B** was used.
[e] Ph_3P was used instead of ion-supported Ph_3P **A** or **B**, and Ph_3PO was recovered in 50% yield.

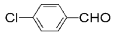
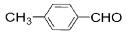
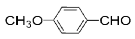
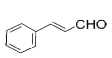
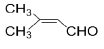
reaction of *p*-methylbenzyl bromide with ion-supported Ph_3P **A** and **B** in 95% yield and 100% yield, respectively. Both phosphonium salts **A2** and **B2** were treated with aromatic and aliphatic aldehydes in the presence of sodium hydride in 1,2-dimethoxyethane or toluene at warming conditions. To a 1,2-dimethoxyethane solution of ion-supported phosphonium salt **A2** or a toluene solution of ion-supported phosphonium salt **B2** was added sodium hydride at 0 °C. After the mixture was stirred for 1 h at room temperature, aromatic or aliphatic aldehyde was added to the mixture at 0 °C and the whole mixture was warmed at 60–70 °C to give *p*-methylstyrene derivative in good yield, as shown in Table 2. Then, after the reaction, the reaction mixture was filtered. *p*-Methylstyrene derivatives were obtained in high yields with high purity (>90%) and moderate (*E*)-selectivity after simple removal of the solvent from the filtrate (entries 1, 5–8, 12, 15, 16, and 18). This is again proof that it is very easy to obtain pure *p*-methylstyrene derivatives. Moreover, ion-supported Ph_3PO, the co-product of both reactions with ion-supported phosphonium salts **A2** and **B2** was recovered by the above filtration in 93–100% yields. The recovered ion-supported Ph_3PO was treated with dimethyl sulfate, followed by reduction with $LiAlH_4$ to regenerate ion-supported Ph_3P **A** and **B** in high yields. Ion-supported phosphonium salts **A2** and **B2** derived from the reaction of regenerated ion-supported Ph_3P **A** and **B** with *p*-methylbenzyl bromide were prepared in high yields again and could be reused for the same reaction with *p*-chlorobenzaldehyde to provide 1-(4′-chlorophenyl)-2-(4″-methylphenyl)ethene in good yields while keeping a high purity until the second reuse (entries 2, 3, and 13, 14).

When Ph_3P was used under the same conditions, 1-(4′-chlorophenyl)-2-(4″-methylphenyl)ethene was obtained in good yield. However, the purity was approximately 46% and Ph_3PO was recovered in only 46% yield (entry 4).

Finally, ion-supported phosphonium salts **A3** and **B3**, which are the precursors of unstabilized ylides, were prepared in 95% and 100% yields, respectively, from the reaction of ion-supported Ph_3P **A** and **B** with *n*-butyl bromide at 100 °C for 50 h. Then, they were

Table 2
Witting reaction with ion-supported Ph_3P



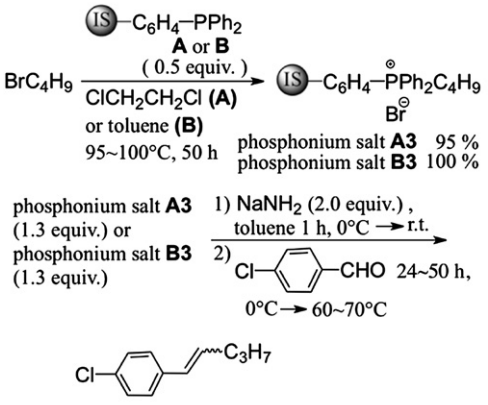
Substrate	A					B				
	Entry	Time (h)	Yield[a] (%)	Purity[b] (%)	*E*/*Z*	Entry	Time (h)	Yield[a] (%)	Purity[b] (%)	*E*/*Z*
	1	8	95	95	75:25	12	9	91	90	75:25
	2[c]	8	94	95	75:25	13[c]	9	90	85	75:25
	3[d]	8	92	95	75:25	14[d]	9	90	81	75:25
	4[e]	9	90	46	50:50					
	5	10	95	95	75:25	15	9	100	90	78:28
	6	50	91	96	79:21	16	24	90	95	81:19
$CH_3(CH_2)_6CHO$	7[f]	24	86	91	71:29	17[f]	24	77	70	74:26
	8[f]	24	91	94	90:10	18	24	82	90	84:16
	9	24	71	64	78:22	19[f]	24	85	56	74:29
	10	50	79	67	91:9	20[f]	24	65	90	68:32
	11	50	Trace	—	—	21[f]	24	Trace	—	—

[a] Isolated yield of *E* and *Z* alkenes. Ion-supported Ph_3PO was recovered in 93~100% yields.
[b] Purity of product after removal of solvent from the extracts.
[c] The first regenerated ion-supported Ph_3P **A** or **B** was used.
[d] The second regenerated ion-supported Ph_3P **A** or **B** was used.
[e] Ph_3P was used instead of ion-supported Ph_3P **A** or **B**, and Ph_3PO was recovered in 46% yield.
[f] $NaNH_2$ was used instead of NaH.

treated with *p*-chlorobenzaldehyde in the presence of sodium amide under the same procedure and conditions shown in Table 2, to give 1-(4′-chlorophenyl)-1-pentene in good yields with high purity after simple filtration of the reaction mixture and removal of the solvent. In both reactions, ion-supported Ph_3PO was recovered in high yields and ion-supported Ph_3P **A** and **B** could be regenerated by the reaction of ion-supported Ph_3PO with dimethyl sulfate and $LiAlH_4$ using the same procedure as that mentioned above. Phosphonium salts **A3** and **B3** could be reused for the same reaction with *p*-chlorobenzaldehyde. Although the yield and purity of 1-(4′-chlorophenyl)-1-pentene were gradually decreased as shown in Scheme 1, ion-supported Ph_3PO from both reactions was recovered by the above filtration in 94–100% yields. The reason may be the fact that the formation of phosphonium salts **A3** and **B3** requires a high temperature and a long reaction time, and the Wittig reaction with them is not very efficient. Thus, the present ion-supported Ph_3P **A** and **B** are not very efficient reagents for the Wittig reaction with alkylphosphonium salts, such as **A3** and **B3**, which are derived from the reaction of ion-supported Ph_3P **A** and **B** with alkyl halides. When Ph_3P was used with *n*-butyl bromide and then *p*-chlorobenzaldehyde in the presence of sodium amide under the same procedure and conditions, 1-(4′-chlorophenyl)-1-pentene was obtained in 80% yield with 40% purity, and Ph_3PO was recovered in only 20% yield.

3. Conclusion

Ion-supported phosphonium salts **A1** and **B1**, which were prepared from the reactions of ion-supported Ph_3P **A** and **B** with ethyl bromoacetate, respectively, and are the precursors of stabilized ylides, reacted with aromatic and aliphatic aldehydes in the presence of K_2CO_3 to give the corresponding α,β-unsaturated ethyl esters in good yields with high purity by simple filtration of the reaction mixture and subsequent removal of the solvent from the filtrate. Similarly, ion-supported phosphonium salts **A2** and **B2**, which were prepared from the reactions of ion-supported Ph_3P **A** and **B** with *p*-methylbenzyl bromide, respectively, and are the precursors of semistabilized ylides, reacted with aromatic and aliphatic aldehydes in the presence of NaH to provide the corresponding *p*-methylstyrene derivatives in good yields with high purity by simple filtration of the reaction mixture and subsequent removal of the solvent from the filtrate. In both reactions, the co-product, ion-supported Ph_3PO, could be obtained quantitatively by simple filtration and was converted into the corresponding ion-supported Ph_3P **A** and **B** again in high yields using dimethyl sulfate, followed by the reaction with $LiAlH_4$. Recovered and regenerated ion-supported Ph_3P **A** and **B** could be reused for the same Wittig reaction while maintaining good yields of α,β-unsaturated ethyl esters and *p*-methylstyrene derivatives, respectively, with high purity by simple filtration and removal of the solvent from the filtrate.



	Yield[a] (%)	Purity[b] (%)	*E*:*Z*
A3	75	74	27:73
	71[c]	73	27:73
	65[d]	60	27:73
$Ph_3PC_4H_9Br$	80[e]	40	19:81
B3	80	80	35:65
	71[c]	70	35:65
	69[d]	55	35:65

[a] Isolated yield of *E* and *Z* alkenes. Ion-supported Ph_3PO was recovered in 94%~100% yields.
[b] Purity of product after removal of solvent from the extracts.
[c] The first regenerated ion-supported Ph_3P **A** or **B** was used.
[d] The second regenerated ion-supported Ph_3P **A** or **B** was used.
[e] Ph_3P was used instead of ion-supported Ph_3P **A** or **B**, and Ph_3PO was recovered in 20% yield.

Scheme 1. Witting reaction with ion-supported phosphonium salts **A3** and **B3**.

4. Experimental section

4.1. General

^1H NMR and ^{13}C NMR spectra were obtained with JEOL-JNM-ECX400, JEOL-JNM-ECS400, and JEOL-JNM-ECA500 spectrometers. Chemical shifts are expressed in parts per million downfield from TMS in δ units. Mass spectra were recorded on JMS-T100GCV, JMS-HX110, and Thermo LTQ Orbitrap spectrometers. IR spectra were measured with a JASCO FT/IR-4100 spectrometer. Melting points were determined with a Yamato Melting Point Apparatus Model MP-21. Silica gel 60 (Kanto Kagaku Co.) was used for column chromatography and Wakogel B-5F was used for preparative *p*-TLC.

4.2. Typical procedure for the Wittig reaction with ion-supported Ph_3P A1

To a solution of ethyl bromoacetate (1.51 g, 9.0 mmol) in 1,2-dichloroethane (30 mL) was added 4-(diphenylphosphino)benzyltrimethylammonium bromide **A** (1.88 g, 4.5 mmol). The obtained mixture was stirred for 2 h at 60 °C. After the reaction, ether was added and the mixture was stirred for 10 min at room temperature. Then, the mixture was filtered and washed with ether. Removal of the solvent from the filtrate gave phosphonium salt **A1** in 95% yield. The obtained phosphonium salt **A1** (358 mg, 0.6 mmol) was dried by a vacuum pump for 2 h at 70 °C. To the flask containing phosphonium salt **A1** was added a solution of *p*-chlorobenzaldehyde (70 mg, 0.5 mmol) in dichloromethane (4 mL) and K_2CO_3 (138 mg, 1.0 mmol). The obtained mixture was stirred for 8 h at 40 °C under an argon atmosphere. After the reaction, ether (5 mL) was added and the obtained mixture was filtered and washed with ether. Removal of the solvent from the filtrate gave ethyl 3-(4′-chlorophenyl)propenoate (*E*/*Z*=96:4) in the crude state. The purity was estimated by ^1H NMR and was 97%. Pure ethyl 3-(4′-chlorophenyl) propenoate was obtained in 94% yield by short flash column chromatography on silica gel (hexane/AcOEt=5:2). The co-product, 4-(diphenylphosphono)benzyltrimethylammonium bromide, was recovered by the above filtration in 98% yield.

4.3. Typical procedure for the Wittig reaction with ion-supported Ph_3P A2

To a solution of 4-methylbenzyl bromide (1.67 g, 9.0 mmol) in 1,2-dichloroethane (30 mL) was added 4-(diphenylphosphino)benzyltrimethylammonium bromide **A** (1.88 g, 4.5 mmol). The obtained

mixture was stirred for 2 h at 60 °C. After the reaction, ether was added and the mixture was stirred for 10 min at room temperature. Then, the mixture was filtered and washed with ether. Removal of the solvent from the filtrate gave phosphonium salt **A2** in 95% yield. The obtained phosphonium salt **A2** (360 mg, 0.6 mmol) was dried by a vacuum pump for 2 h at 70 °C. To the flask containing phosphonium salt **A2** were added NaH (44 mg, 1.0 mmol) and 1,2-dimethoxyethane (2 mL). The obtained mixture was stirred for 1 h at 0 °C under an argon atmosphere. After the reaction, *p*-chlorobenzaldehyde (70 mg, 0.5 mmol) and 1,2-dimethoxyethane (2 mL) were added and the obtained mixture was stirred for 8 h at 60 °C under an argon atmosphere. After the reaction, acetic acid (5 mL) was added and the obtained mixture was filtered and washed with acetic acid. Removal of the solvent from the filtrate gave 1-(4′-chlorophenyl)-2-(4″-methylphenyl)ethene (*E*/*Z*=75:25) in the crude state. The purity was estimated by ^{1}H NMR and was 95%. Pure 1-(4′-chlorophenyl)-2-(4″-methylphenyl)ethene was obtained in 95% yield by short flash column chromatography on silica gel (hexane/$CHCl_3$=1:4). The co-product, 4-(diphenylphosphono)benzyltrimethylammonium bromide, was recovered by the above filtration in 97% yield.

4.4. Typical procedure for the Wittig reaction with ion-supported Ph_3P A3

To a solution of 1-bromobutane (1.90 g, 14 mmol) in 1,2-dichloroethane (4.0 mL) was added 4-(diphenylphosphino)benzyltrimethylammonium bromide (**A**) (1.90 g, 4.5 mmol). The obtained mixture was stirred for 50 h at 95 °C. After the reaction, ether was added and the mixture was stirred for 10 min at room temperature. Then, the mixture was filtered and washed with ether. Removal of the solvent from the filtrate gave phosphonium salt **A3** in 95% yield. The obtained phosphonium salt **A3** (358 mg, 0.65 mmol) was dried by a vacuum pump for 2 h at 70 °C. To the flask containing phosphonium salt **A3** were added $NaNH_2$ (43 mg, 1.0 mmol) and 1,2-Dimethoxyethane (2 mL). The obtained mixture was stirred for 2 h at 0 °C under an argon atmosphere. After the reaction, *p*-chlorobenzaldehyde (70 mg, 0.5 mmol) in 1,2-Dimethoxyethane (2 mL) was added to the mixture at room temperature and the obtained mixture was stirred for 50 h at 60 °C under an argon atmosphere. After the reaction, acetic acid (5 mL) was added and the obtained mixture was filtered and washed with acetic acid. Removal of the solvent from the filtrate gave 1-(4-chlorophenyl)-1-pentene (*E*/*Z*=27:73) in the crude state. The purity was estimated by ^{1}H NMR and was 74%. Pure 1-(4-chlorophenyl)-1-pentene was obtained in 75% yield by column chromatography on silica gel (hexane/$CHCl_3$=1:4). The co-product, 4-(diphenylphosphono)benzyltrimethylammonium bromide, was recovered by the above filtration in 98% yield.

*4.4.1. Phosphonium salt **A1**.* Mp 174–178 °C; IR (neat): 1721, 1492, 1297, 1144, 1113, 759, 723,690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.10 (t, *J*=6.9 Hz, 3H), 3.43 (s, 9H), 4.08 (q, *J*=6.9 Hz, 2H), 5.32 (d, *J*=13.8 Hz, 2H), 5.40 (s, 2H), 7.71–7.73 (m, 4H), 7.87–7.91 (m, 8H), 8.16–8.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.12 (p), 30.43 (s), 52.56 (p), 62.93 (s), 66.44 (s), 118.10 (q), 118.81 (q), 120.63 (q), 121.33 (q), 130.62 (t), 130.72 (t), 134.37 (t), 134.45 (t) 134.63 (t), 134.70 (t), 134.74 (t), 134.78 (t), 165.15 (q); HRMS (ESI) calcd for $C_{26}H_{32}Br_2NO_2P$ [M^+]: 579.0532. Found: 579.0506.

*4.4.2. Phosphonium salt **A2**.* Mp 175–180 °C; IR (neat): 3374, 1411, 1113, 822, 753, 741, 721, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.27 (s, 3H), 3.45 (s, 9H), 5.10 (d, *J*=14.4 Hz, 2H), 5.44 (s, 2H), 7.64–7.72 (m, 8H), 7.77–7.84 (m, 4H), 8.22–8.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.21 (p), 28.47 (s), 52.56 (p), 66.50 (s), 117.85 (q), 118.52 (q), 120.34 (q), 121.01 (q), 129.85 (t), 130.60 (t), 130.70 (t), 131.35 (t), 131.39 (t), 134.58 (t), 134.70 (t), 134.77 (t), 134.97 (t), 135.04 (t), 138.26 (q),138.29 (q); HRMS (ESI) calcd for $C_{30}H_{34}Br_2NP$ [M^+]: 597.0801. Found: 597.0756.

*4.4.3. Phosphonium salt **A3**.* Mp 162–165 °C; IR (Nujol): 1438, 1297, 1411, 1114, 996, 824, 750, 724, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.84–0.97 (m, 3H), 1.56–1.68 (m, 4H), 3.46 (s, 9H), 3.53–3.62 (m, 2H), 5.45 (s, 2H), 7.71–7.74 (m, 4H), 7.79–7.86 (m, 8H), 8.26–8.31 (m, 2H); ^{13}C NMR (100 MHz, DMSO): δ=13.8 (p), 20.8 (s), 23.6 (s), 24.3 (s), 52.6 (p), 66.8 (s), 118.4 (q), 119.3 (q), 120.8 (q), 121.6 (q), 130.7 (t), 130.9 (t), 134.2 (t), 134.3 (t), 134.6 (t), 134.7 (t), 134.8 (t), 134.9 (t); HRMS (ESI) calcd for $C_{26}H_{34}Br_2NP$ [M^+]: 549.0796. Found: 547.0770.

4.5. Typical procedure for the Wittig reaction with ion-supported Ph_3P B1

Ethyl bromoacetate (1.67 g, 10.0 mmol) or 4-methylbenzyl bromide (1.85 g, 10.0 mmol) was added to a flask containing 1-methyl-3-[4′-(diphenylphosphino)benzyl]pyrrolidinium bromide (2.20 g, 5.0 mmol) in 1,2-dichloromethane (8 mL) at 0 °C. The obtained mixture was stirred for 24 h at 40 °C under an argon atmosphere. After the reaction, ether (20 mL) was added and the obtained mixture was stirred for 30 min at 0 °C. Then, the mixture was filtered and washed with ether. Removal of the solvent from the filtrates gave phosphonium salt **B1** or **B2**, in 100% yield. A mixture of phosphonium salt **B1** and K_2CO_3 (277 mg, 2.0 mmol) in a flask was dried by a vacuum pump for 2 h at 70 °C. To the flask containing phosphonium salt **B1** and K_2CO_3 was added a solution of 4-chlorobenzaldehyde (141 mg, 1.0 mmol) in dichloromethane (5 mL). The obtained mixture was stirred for 8 h at 40 °C under an argon atmosphere. After the reaction, ether (10 mL) was added and the obtained mixture was stirred for 10 min at 0 °C. Then, the mixture was filtered and washed with ether. Removal of the solvent from the filtrate gave ethyl 3-(4-chlorophenyl)acrylate (*E*/*Z*=94:6) in 98% purity, which was estimated by ^{1}H NMR. Pure ethyl 3-(4-chlorophenyl)acrylate was obtained in 98% yield by short flash column chromatography on silica gel (AcOEt/hexane=10:1). The co-product, *N*-methyl-*N*-[4-(diphenylphosphono)benzyl]pyrrolidinium bromide, was recovered by the above filtration in 98% yield.

4.6. Typical procedure for the Wittig reaction with ion-supported Ph_3P B2

Phosphonium salt **B2** (939 mg, 1.5 mmol) was dried by a vacuum pump for 2 h at 70 °C. To the flask containing phosphonium salt **B2** were added NaH (80 mg, 2.0 mmol) and toluene (5 mL). The obtained mixture was stirred for 1 h at 0 °C initially to room temperature under an argon atmosphere. Then, 4-chlorobenzaldehyde (141 mg, 1.0 mmol) was added to the solution at 0 °C and the obtained mixture was stirred for 9 h at 0 °C initially to 60 °C. After the reaction, ether (10 mL) was added and the obtained mixture was stirred for 10 min at room temperature. Then, the mixture was filtered and washed with ether. Removal of the solvent from the filtrate gave 1-(4′-chlorophenyl)-2-(4″-methylphenyl)ethene (*E*:*Z*=75:25) in 90% purity, which was estimated by ^{1}H NMR. Pure 1-(4′-chlorophenyl)-2-(4″-methylphenyl)ethene was obtained in 91% yield by short flash column chromatography on silica gel ($CHCl_3$/hexane=10:1). The co-product, *N*-methyl-*N*-[4-(diphenylphosphono)benzyl]pyrrolidinium bromide, was recovered by the above filtration in 98% yield.

4.7. Typical regeneration of ion-supported Ph_3P A or B

Me_2SO_4 (1.1 mmol) was added to a flask containing 1-methyl-3-[4′-(diphenylphosphono)benzyl]pyrrolidinium bromide **B** (1.0 mmol) in chloroform (6 mL) at 0 °C. The obtained mixture was

stirred for 24 h at 60 °C under an argon atmosphere. After the reaction, the mixture was concentrated by a vacuum pump. Then, 1,2-dimethoxyethane (10 mL) and $LiAlH_4$ (3.0 mmol) were added to the reaction mixture at 0 °C, and the obtained mixture was stirred for 2 h at room temperature under an argon atmosphere. The reaction mixture was quenched with ice at first. Then, 1 N aq HBr (5 mL) was added to the aqueous solution, and the obtained solution was washed with ether twice. The aqueous solution was extracted with CH_2Cl_2 (10 mL×3), and the combined organic layer was dried over Na_2SO_4. After removal of the solvent, 1-methyl-3-[4′-(diphenylphosphino)benzyl]pyrrolidinium bromide **B** was obtained in 95% yield. Then, ethyl bromoacetate (334 mg, 2.0 mmol) or 4-methylbenzyl bromide (371 mg, 2.0 mmol) was added to a flask containing 1-methyl-3-[4′-(diphenylphosphino)benzyl]pyrrolidinium bromide **B** (441 mg, 1.0 mmol) in 1,2-dichloromethane (5 mL) at 0 °C. The obtained mixture was stirred for 24 h at 40 °C under an argon atmosphere. After the reaction, ether (10 mL) was added and the obtained mixture was stirred for 30 min at 0 °C. Then, the mixture was filtered and washed with ether. Removal of the solvent from the filtrate gave phosphonium salt **B1** or **B2** in 100% yield.

*4.7.1. Phosphonium salt **B1**.* Mp 145–147 °C; IR (Nujol): 3382, 2726, 1720, 1586, 1305, 1155, 1109, 722, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.03 (t, J=7.2 Hz, 3H), 2.08–2.20 (m, 2H), 2.22–2.36 (m, 2H), 3.23 (s, 3H), 3.70–3.80 (m, 2H), 3.98–4.10 (m, 4H), 5.41 (s, 2H), 5.47 (d, J=13.8 Hz, 2H), 7.65–7.98 (m, 12H), 8.14–8.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.60 (p), 20.88 (s), 21.71 (s), 32.53 (s), 32.98 (s), 47.56 (p), 62.78 (s), 63.23 (s), 63.78 (s), 116.76 (q), 117.46 (q), 119.82 (q), 120.52 (q), 130.15 (t), 130.25 (t), 133.92 (t), 134.01 (t), 134.18 (t), 134.29 (t), 134.40 (t), 134.49 (t), 164.17 (q); HRMS (ESI) calcd for $C_{28}H_{34}Br_2NO_2P$ [M^+]: 605.0669. Found: 605.0688.

*4.7.2. Phosphonium salt **B2**.* Mp 135–137 °C; IR (Nujol): 3408, 1601, 1587, 1514, 1439, 1112, 822, 743, 719, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.02–2.18 (m, 2H), 2.22–2.38 (m, 2H), 2.26 (s, 3H), 3.23 (s, 3H), 3.67–3.81 (m, 2H), 4.01–4.15 (m, 2H), 5.11 (d, J=14.2 Hz, 2H), 5.39 (s, 2H), 6.93 (s, 4H), 7.58–7.72 (m, 8H), 7.72–7.84 (m, 4H), 8.14–8.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=20.36 (s), 20.42 (p), 29.35 (s), 29.74 (s), 47.15 (p), 62.77 (s), 63.08 (s), 63.47 (s), 115.95 (q), 116.63 (q), 119.12 (q), 119.79 (q), 128.81 (t), 129.45 (t), 129.55 (t), 129.63 (t), 129.74 (t), 130.41 (t), 132.32 (t), 132.41 (t), 133.70 (t), 134.45 (t), 135.36 (q), 137.64 (q); HRMS (ESI) calcd for $C_{32}H_{36}Br_2NP$ [M^+]: 623.0923. Found: 623.0958.

*4.7.3. Phosphonium salt **B3**.* Mp 210–215 °C; IR (Nujol): 3402, 1602, 1586, 1458, 1439, 1219, 1112, 937, 752, 721, 659, 628 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=0.85–0.95 (m, 3H), 1.15–1.25 (m, 2H), 1.50–1.70 (m, 2H), 2.10–2.20 (m, 2H), 2.21–2.28 (m, 2H), 3.29 (s, 3H), 3.55–3.86 (m, 4H), 4.04–4.18 (m, 2H), 5.46 (s, 2H), 7.68–7.78 (m, 4H), 7.79–7.88 (m, 8H), 8.24–8.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.64 (p), 21.03 (s), 22.60 (s), 22.99 (s), 23.70 (s), 23.83 (s), 24.53 (s), 47.81 (p), 63.46 (s), 63.99 (s), 117.14 (q), 117.82 (q), 120.28 (q), 130.56 (t), 130.66 (t), 133.70 (t), 133.77 (t), 134.02 (t), 134.11 (t), 134.71 (t), 134.80 (t), 136.21 (q); HRMS (ESI) calcd for $C_{28}H_{35}Br_2NP$ [$M-H]^+$: 574.0885. Found: 574.0879.

4.7.4. Ethyl (E)-3-(4′-chlorophenyl)-2-propenoate. Oil; IR (neat): 1714, 1638, 1269, 981 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.34 (t, J=7.3 Hz, 3H), 4.27 (q, J=7.1 Hz, 2H), 6.41 (d, J=16.0 Hz, 1H), 7.36 (d, J=8.6 Hz, 2H), 7.45 (d, J=8.6 Hz, 2H), 7.63 (d, J=16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.29 (p), 60.61 (s), 118.85 (t), 129.15 (t), 129.17 (t), 132.93 (q), 136.09 (q), 143.09 (t), 166.72 (q); HRMS (ESI) calcd for $C_{11}H_{12}O_2Cl$ [$M+H]^+$: 211.0520. Found: 211.0524.

4.7.5. Ethyl (E)-3-(4′-methylphenyl)-2-propenoate. Oil; IR (neat): 1713, 1636, 1268, 1173, 984 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.34 (t, J=7.1 Hz, 3H), 2.37 (s, 3H), 4.26 (q, J=7.2 Hz, 2H), 6.39 (d, J=16.0 Hz, 1H), 7.19 (d, J=8.2 Hz, 2H), 7.42 (d, J=8.2 Hz, 2H), 7.66 (d, J=16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.33 (p), 21.44 (p), 60.39 (s), 117.15 (t), 128.02 (t), 129.59 (t), 131.71 (q), 140.60 (q), 144.57 (t), 167.19 (q); HRMS (ESI) calcd for $C_{12}H_{15}O_2$ [$M+H]^+$: 191.1066. Found: 191.1066.

4.7.6. Ethyl (E)-3-(4′-methoxyphenyl)-2-propenoate. Oil; IR (neat): 1711, 1634, 1604, 1254, 1171, 983 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.33 (t, J=7.1 Hz, 3H), 3.84 (s, 3H), 4.25 (q, J=7.3 Hz, 2H), 6.31 (d, J=16.0 Hz, 1H), 6.90 (d, J=8.9 Hz, 2H), 7.48 (d, J=8.9 Hz, 2H), 7.64 (d, J=16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.34 (p), 55.36 (p), 60.31 (s), 114.29 (t), 115.73 (t), 127.18 (q), 129.66 (t), 144.23 (t), 161.30 (q), 167.33 (q); HRMS (ESI) calcd for $C_{12}H_{15}O_3$ [$M+H]^+$: 207.1015. Found: 207.1017.

4.7.7. Ethyl (2E,4E)-5-phenyl-2,4-pentadienoate. Oil; IR (neat): 1706, 1626, 999, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.32 (t, J=7.1 Hz, 3H), 4.23 (q, J=7.3 Hz, 2H), 5.99 (d, J=15.1 Hz, 1H), 6.83–6.93 (m, 2H), 7.26–7.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.32 (p), 60.33 (s), 121.32 (t), 126.23 (t), 127.16 (t), 128.79 (t), 129.00 (t), 136.02 (q), 140.34 (t), 144.52 (t), 167.05 (q); HRMS (ESI) calcd for $C_{13}H_{15}O_2$ [$M+H]^+$: 203.1066. Found: 203.1066.

4.7.8. Ethyl (E)-2-decenoate. Oil; IR (neat): 1724, 1655, 1265, 1189, 980 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=0.88 (t, J=6.9 Hz, 3H), 1.29 (t, J=7.2 Hz, 11H), 1.39–1.51 (m, 2H), 2.19 (q, J=7.6 Hz, 2H), 4.18 (q, J=7.5 Hz, 2H), 5.81 (dt, J=1.4, 16.3 Hz, 1H), 6.96 (dt, J=7.0, 16.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.01 (p), 14.23 (p), 22.58 (s), 27.98 (s), 29.01 (s), 29.06 (s), 31.69 (s), 32.15 (s), 60.05 (s), 121.18 (t), 149.42 (t), 166.75 (q); HRMS (ESI) calcd for $C_{12}H_{23}O_2$ [$M+H]^+$: 199.1692. Found: 199.1690.

4.7.9. Ethyl (E)-5-methyl-2,4-hexadienoate. Oil; IR (neat): 1713, 1638, 1276, 1139, 992 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.30 (t, J=7.2 Hz, 3H), 1.88 (s, 3H), 1.90 (s, 3H), 4.20 (q, J=6.8 Hz, 2H), 5.76 (d, J=15.2 Hz, 1H), 5.99 (d, J=11.2 Hz, 1H), 7.56 (dd, J=11.2, 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.33 (p), 18.94 (p), 26.55 (p), 60.11 (s), 118.53 (t), 123.69 (t), 141.00 (t), 146.28 (q), 167.75 (q); HRMS (ESI) calcd for $C_9H_{15}O_2$ [$M+H]^+$: 155.1066. Found: 155.1067.

4.7.10. Ethyl (E)-4,4,4-trifluoro-3-phenylbut-2-enoate. Oil (lit.[7]); IR (neat): 2986, 1736, 1655, 1446, 1028, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.04 (t, J=7.2 Hz, 3H), 4.03 (q, J=7.2 Hz, 2H), 6.60 (q, J=1.4 Hz, 1H), 7.26–7.31 (m, 2H), 7.36–7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.64 (p), 61.03 (s), 122.49 (q), 124.54 (t), 128.13 (t), 128.60 (t), 129.26 (t), 131.02 (q), 142.29 (q), 164.11 (q); ^{19}F NMR (400 MHz, $CDCl_3$): δ=−67.59; HRMS (ESI) calcd for $C_{12}H_{12}F_3O_2$ [$M+H]^+$: 245.0780. Found: 245.0784.

4.7.11. (E)-1-Chloro-4-(4′-methylstyryl)benzene. Mp 185–190 °C (lit.[8] mp 200–204 °C); IR (Nujol): 1511, 1488, 1092, 1014, 971, 824, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.36 (s, 3H), 6.99 (d, J=16.5 Hz, 1H), 7.06 (d, J=16.5 Hz, 1H), 7.17 (d, J=8.5 Hz, 2H), 7.31 (d, J=9.0 Hz, 2H), 7.40 (d, J=9.0 Hz, 2H), 7.42 (d, J=8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.26 (p), 126.34 (t), 126.46 (t), 127.52 (t), 128.78 (t), 129.23 (t), 129.43 (t), 132.89 (q), 134.19 (q), 136.02 (q), 137.80 (q); HRMS (APPI) calcd for $C_{15}H_{13}Cl$ [M^+]: 228.0700. Found: 228.0698.

4.7.12. (E)-1,2-Bis(4′-methylphenyl)ethene. Mp 165–167 °C (lit.[8] mp 180 °C); IR (Nujol): 1515, 971, 822, 717 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.35 (s, 6H), 7.03 (s, 2H), 7.15 (d, J=8.2 Hz, 4H), 7.39 (d, J=8.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.22 (p), 126.28 (t), 127.61 (t), 129.35 (t), 134.72 (q), 137.24 (q); HRMS (ESI) calcd for $C_{16}H_{17}$ [$M+H]^+$: 209.1325. Found: 209.1326.

4.7.13. (E)-1-Methoxy-4-(4′-methylstyryl)benzene. Mp 153–155 °C (lit.[9] mp 160–162 °C); IR (Nujol): 1605, 1515, 1253, 1177, 1031, 968, 824, 722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.34 (s, 3H), 3.81 (s, 3H), 6.88 (d, J=8.7 Hz, 2H), 6.94 (d, J=16.7 Hz, 1H), 7.01 (d, J=16.7 Hz, 1H), 7.14 (d, J=8.0 Hz, 2H), 7.38 (d, J=8.0 Hz, 2H), 7.43 (d, J=8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.19 (p), 55.27 (p), 114.08 (t), 126.13 (t), 126.52 (t), 127.18 (t), 127.55 (t), 129.33 (t), 130.30 (q), 134.83 (q), 137.01 (q), 159.10 (q); HRMS (ESI) calcd for $C_{16}H_{17}O$ $[M+H]^+$: 225.1274. Found: 225.1274.

4.7.14. (E,E)-1-(4′-Methylphenyl)-4-phenyl-1,3-butadiene. Mp 142–145 °C (lit.[10] mp 152–153 °C); IR (Nujol): 993, 973, 822, 804, 747, 720, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.35 (s, 3H), 6.62–6.71 (m, 2H), 6.88–6.98 (m, 2H), 7.14 (d, J=7.8 Hz, 2H), 7.22 (t, J=8.9 Hz, 1H), 7.27–7.36 (m, 4H), 7.43 (d, J=7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.26 (p), 126.30 (t), 127.42 (t), 128.31 (t), 128.63 (t), 128.98 (t), 129.37 (t), 129.42 (t), 132.23 (t), 132.83 (t), 134.57 (q), 137.46 (q), 137.49 (q); HRMS (ESI) calcd for $C_{17}H_{17}$ $[M+H]^+$: 221.1325. Found: 221.1323.

4.7.15. (E)-1-(4′-Methylphenyl)-1-nonene. Oil; IR (neat): 1457, 1038, 964, 792, 722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=0.88 (t, J=7.2 Hz, 3H), 1.20–1.38 (m, 8H), 1.40–1.48 (m, 2H), 2.18 (q, J=7.5 Hz, 2H), 2.32 (s, 3H), 6.16 (dt, J=6.9, 16.0 Hz, 1H), 6.34 (d, J=16.0 Hz, 1H), 7.09 (d, J=8.0 Hz, 2H), 7.23 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.09 (p), 21.10 (p), 22.67 (s), 29.19 (s), 29.45 (s), 30.02 (s), 31.85 (s), 33.04 (s), 125.77 (t), 129.13 (t), 129.47 (t), 130.20 (t), 135.17 (q), 136.37 (q); HRMS (ESI) calcd for $C_{16}H_{25}$ $[M+H]^+$: 217.1951. Found: 217.1953.

4.7.16. (E,E)-4-Methyl-1-(4′-methylphenyl)-1,3-pentadiene. Oil; IR (neat): 3021, 2965, 2920, 1512, 971, 957, 822, 797 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.84 (s, 3H), 1.85 (s, 3H), 2.33 (s, 3H), 5.99 (d, J=10.6 Hz, 1H), 6.40 (d, J=15.5 Hz, 1H), 6.94 (dd, J=10.6, 15.5 Hz, 1H), 7.10 (d, J=8.0 Hz, 2H), 7.29 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=18.53 (p), 21.18 (p), 26.21 (p), 124.79 (t), 125.54 (t), 125.96 (t), 129.24 (t), 129.47 (t), 135.31 (q), 135.90 (q), 136.68 (q); HRMS (ESI) calcd for $C_{13}H_{17}$ $[M+H]^+$: 173.1325. Found: 173.1326.

4.7.17. (E)-1-(4′-Methylphenyl)-2-phenyl-3,3,3-trifluoropropene. Oil (lit.[7]); IR (neat): 3026, 1650, 1514, 1444, 1381, 1272, 1153, 1116, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.26 (s, 3H), 6.89 (d, J=8.0 Hz, 2H), 6.96 (d, J=8.0 Hz, 2H), 7.18 (s, 1H), 7.28–7.36 (m, 2H), 7.37–7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.22 (p), 123.88 (q), 128.67 (t), 128.93 (t), 128.99 (t), 129.25 (q), 129.90 (t), 130.01 (t), 130.66 (q), 132.97 (q), 133.04 (t), 139.09 (q); ^{19}F NMR (400 MHz, $CDCl_3$): δ=−65.59; HRMS (ESI) calcd for $C_{16}H_{13}F_3$ $[M^+]$: 262.0964. Found: 262.0962.

4.7.18. (Z)-1-(4-Chlorophenyl)-1-pentene. Oil; IR (neat): 1652, 1491, 1092, 839 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=0.93 (t, J=7.5 Hz, 3H), 1.43–1.50 (m, 2H), 2.26 (dq, J=1.9, 7.4 Hz, 2H), 5.68 (td, J=7.2, 11.7 Hz, 1H), 6.35 (d, J=11.7 Hz, 1H), 7.19 (d, J=8.5 Hz, 2H), 7.28 (d, J=8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.80 (p), 23.03 (s), 30.62 (s), 127.69 (t), 128.22 (t), 130.00 (t), 132.09 (q), 133.71 (t), 136.21 (q); HRMS (ESI) calcd for $C_{11}H_{13}Cl$ $[M^+]$: 262.0964. Found: 262.0962.

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