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Dual [Fe + Phosphine] Catalysis: Application in Catalytic Wittig Olefination

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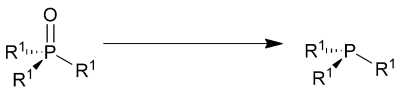
In memory of J. L. A. Roustan

Iron hydride complexes of the general formula $P_2Fe(NO)CO)H$ are highly active catalysts for the hydrosilylation of aldehydes or ketones and phosphine oxides. Depending on the solvent, the in situ reduction of the phosphine oxide can be faster than the corresponding hydrosilylation of a carbonyl group. This unusual activity was used within the context of catalytic Wittig olefination.

Introduction

Although under investigation for decades, metal-catalyzed reductions of carbonyl groups are a continuously developing field in organic chemistry.[1] Since Wilkinson's landmark reports[2] on transition-metal-catalyzed reductions, a large number of new catalysts with sophisticated ligand architectures have been developed and Noyori's Ru-[3] and Rh-based[4] chiral catalysts are the most prominent representatives in this field. In the past 10 years, Fe-based complexes have entered this field. Starting from early reports by the groups of Nishiyama[5] and Beller,[6] the groups of Chirik,[7] Morris,[8] Milstein,[9] and, in particular, Casey[10] developed highly active and selective Fe complexes for selective carbonyl reductions using either H_2 gas or transfer hydrogenation or hydrosilylation conditions. Compared with the field of C=O reductions, the field of deoxygenation of element oxo species such as phosphine oxides has only recently become the focus of organometallic catalysis. Brønsted acids,[11] Cu salts,[12] and titanium alkoxides[13] were shown to be suitable catalysts for the reduction of P=O bonds with silanes as stoichiometric reductants (Scheme 1). To date, no corresponding Fe-catalyzed process has been reported. This is surprising, given that phosphines are used in various fields of organic and organometallic chemistry and that the oxidation of a phosphine to the corresponding phosphine oxide can be unwanted (e.g., phosphine synthesis, phosphine catalysis, and organometallic synthesis) or a desired (e.g., Wittig,[14] Appel,[15] and Mitsunobu[16] reactions) synthetically useful transformation.



conditions	yield	
$Cu(OTf)_2$ [10 mol %] TMDS [3 equiv.] toluene, 100 °C, 18 h	79 %	(1)
$(p\text{-}NO_2C_6H_4O)_2P(=O)OH$ [7.5 mol %] $(EtO)_2MeSiH$ [4 equiv.] toluene, 110 °C, 18 h	73 %	(2)

Scheme 1. Beller's[11,12] organometallic- and organo-catalyzed reduction of phosphine oxides. TMDS = tetramethyldisiloxane.

The latter reactions have found widespread use; however, the fact that stoichiometric amounts of phosphine oxide waste are produced in these transformations limits their application on a large scale. A chemoselective reduction of phosphine oxides to phosphines and hence their in situ recycling can potentially open a new field in method development.[17] Since O'Brien's initial landmark report on phosphine-catalyzed Wittig-type olefination,[18] a number of reports on redox-based phosphine catalysis such as Appel reaction[19] and Mitsunobu reaction[20] have been published. Herein, we report the use of a readily accessible Fe–H complex in the selective hydrosilylation of carbonyl groups and phosphine oxides and its application in a combined $FeH–PPh_3$-catalyzed Wittig olefination reaction.

Results and Discussion

The catalytic Wittig reaction presents certain challenges to a probable catalytic system. The selective reduction of a C=O bond relative to a P=O bond is certainly the most important one. O'Brien showed that phospholanes such as **1** or their derivatives exhibit the important balance between nucleophilicity

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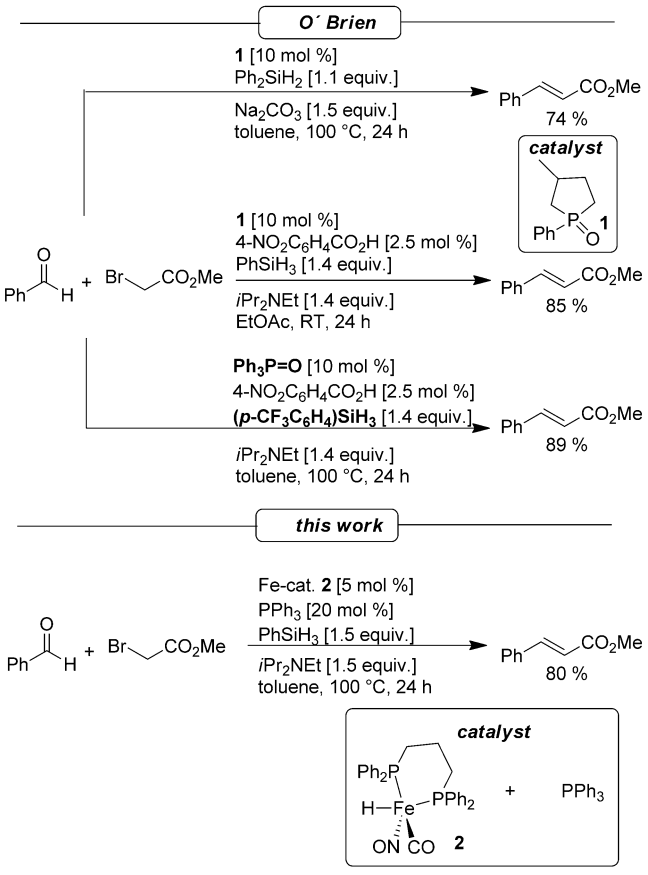
and oxophilicity that allow the nucleophilic substitution of the alkyl halide, subsequent deprotonation of the phosphonium salt, and subsequent 1,2-addition– elimination reaction of the phosphine oxide to be faster than the competing hydrosilylation of the carbonyl-containing starting material. However, in the vast majority of cases, expensive phosphines need to be used; only a couple of examples using inexpensive triphenylphosphine as an organocatalyst were reported.[18b] In the latter case, the highly active trifluorophenylsilane was used as a stoichiometric reductant.

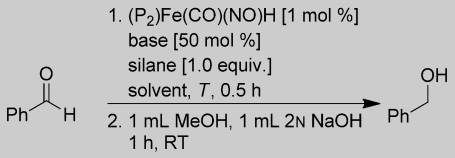
Because of our previous reports on the Fe-catalyzed hydrosilylation of alkynes[21a] or alcohols,[21b] we contemplated whether the Fe–H complexes that were used would be able to reduce P=O bonds and hence suitable for a coupled catalytic transformation, that is, a [Fe + phosphine]-catalyzed Wittig reaction with inexpensive triphenylphosphine as an organocatalyst and simple phenylsilane as a stoichiometric reductant. (Scheme 2).



Scheme 2. O'Brien's catalytic Wittig reactions[18] and our [Fe + phosphine]-catalyzed Wittig reaction.

Therefore, we initiated our study by investigating the interplay between C=O and P=O bond reduction. Various complexes of the general formula $P_2Fe(CO)(NO)H$,[21] solvents, and temperatures were tested in the hydrosilylation of benzaldehyde (Table 1).

Table 1. Development of the Fe–H-catalyzed hydrosilylation of aldehydes.[a]



Entry	Base	Solvent	T [°C]	Catalyst	Conversion [%][b]
1	NEt_3	THF	80	**3** [$P_2 = (PPh_3)_2$]	78
2	NEt_3	toluene	80	**3** [$P_2 = (PPh_3)_2$]	12
3	NEt_3	1,4-dioxane	80	**3** [$P_2 = (PPh_3)_2$]	13
4	NEt_3	MTBE	80	**3** [$P_2 = (PPh_3)_2$]	11
5	iPr_2Net	THF	80	**3** [$P_2 = (PPh_3)_2$]	12
6	NEt_3	THF	60	**3** [$P_2 = (PPh_3)_2$]	38
7	NEt_3	THF	40	**3** [$P_2 = (PPh_3)_2$]	14
8	NEt_3	THF	80	**4** [P_2 = dppe][c]	11
9	NEt_3	THF	80	**2** [P_2 = dppp]	86
10	NEt_3	THF	80	**5** [P_2 = dppf][d]	13

[a] Reactions were performed on a 0.3 mmol scale; [b] Conversion to benzyl alcohol determined by using ^{1}H NMR spectroscopy with mesitylene as an internal standard; [c] dppe = 1,2-Bis(diphenylphosphino)-ethane; [d] dppf = 1,1′-Bis(diphenylphosphino)ferrocene. MTBE = Methyl *tert*-butyl ether.

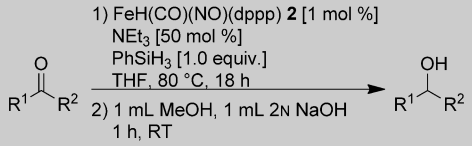
Both the triphenylphosphine complex **3** and the 1,3-bis(diphenylphosphino)propane (dppp) complex **2** showed good activity, giving the desired alcohol within 30 min. To get a deeper insight into the functional group compatibility, various aldehydes and ketones were tested under optimal conditions and the corresponding alcohols were isolated in good to excellent yields (Table 2).

Both ketones and aldehydes proved to be reactive under the given conditions. Ethers, halides, and electron-rich and electron-poor C=C bonds were stable under the given conditions.

We then turned our attention to the corresponding deoxygenation of phosphine oxides. Under similar conditions, but with 5 mol% of the Fe–H catalyst **2**, the P–O bond in triphenylphosphine oxide can be reduced in moderate yields. By choosing toluene as a solvent and iPr_2NEt as a base, the yield could be significantly increased. Different aromatic and aliphatic phosphine oxides were subjected to the reaction conditions and could be reduced in moderate to good yields (Table 3).

With this result in hand, we used the Fe-catalyzed reduction protocol for the catalytic Wittig olefination with various aldehydes or ketones and α-halocarboxylic acid esters and the stoichiometric reductant phenylsilane (Scheme 3). The initial investigation indicated that the addition of α-halocarboxylic acid

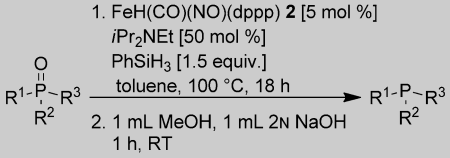
Table 2. Hydrosilylation of aldehydes and ketones.[a]



Entry	R^1	R^2	Product	Yield [%][b]
1	Ph	H	**6a**	87
2	4-MeO-C_6H_4	H	**6b**	98
3	3-Br-C_6H_4	H	**6c**	91
4	C_9H_{19}	H	**6d**	88
5	2-quinoline	H	**6e**	60
6	citronellal		**6f**	98
7	Ph	Me	**6g**	98
8	$(CH_3)_2C{=}CHCH_2CH_2$	Me	**6h**	66

[a] Reactions were performed on a 0.3 mmol scale; [b] Isolated yield.

Table 3. Reduction of phosphine oxides.[a]



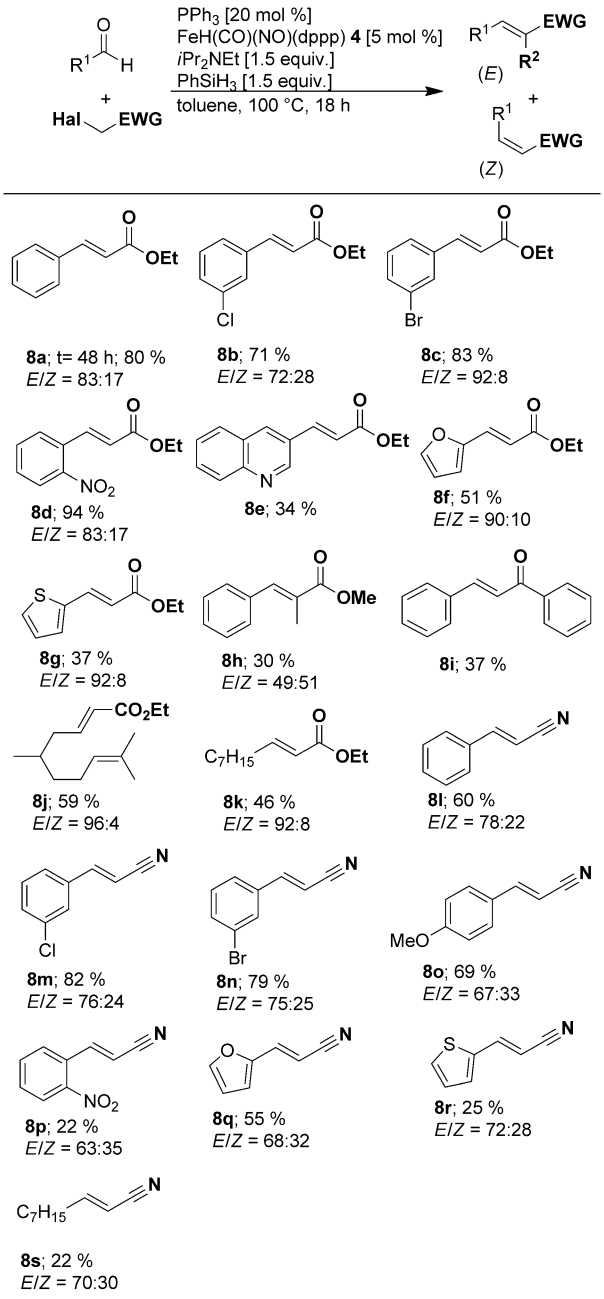
Entry	R^1	R^2	R^3	Product	Yield [%][b]
1	Ph	Ph	Ph	**7a**	65
2	Ph	Ph	Me	**7b**	79
3	Ph	Ph	Cy	**7c**	44
4	Bu	Bu	Bu	**7d**	55
5	4-Me-C_6H_4	4-Me-C_6H_4	4-Me-C_6H_4	**7e**	67
6	4-F-C_6H_4	4-F-C_6H_4	4-F-C_6H_4	**7f**	47

[a] Reactions were performed on a 0.3 mmol scale; [b] Isolated yield.

derivatives to the reaction mixture led to the clean formation of the desired olefination products in moderate to good yields. The reaction proved to be widely applicable. Various aromatic and aliphatic aldehydes were olefinated with catalytic amounts of triphenylphosphine in the presence of α-bromo ethylacetate or α-chloro acetonitrile. Moderate to good yields and *E/Z* selectivities were obtained. Importantly, NMR spectroscopic analysis of the crude product revealed that in none of these cases, the corresponding alcohol, that is, the product of a competing carbonyl reduction, was formed.

Conclusions

Herein, we describe the dual [Fe + phosphine] catalysis. The $[Fe(CO)_3(NO)]$ anion-derived Fe–H complex (dppp)Fe(CO)(NO)H (dppp = 1,3-bis(diphenylphosphino)propane) showed good activity for the hydrosilylation of various aldehydes or ketones. Moreover, phosphine oxides were converted into the corresponding phosphines. Owing to its good activity in the presence of a base, the catalytic system was demonstrated to allow a catalytic Wittig olefination with the organocatalyst triphenylphosphine. Under the given reaction conditions, a selective deoxygenation of phosphine oxides was observed, but no competing reduction of aldehydes was observed. Future work will be directed toward expanding this transformation to other phosphine catalysts.



Scheme 3. Dual [Fe + phosphine] catalysis: Application in catalytic Wittig olefination. Reactions were performed on a 0.3 mmol scale; isolated yields are shown. Hal = Halogen; EWG = Electron-withdrawing group.

Experimental Section

General procedure for the reduction of aldehydes and ketones (GP-I)

A 10 mL Schlenk tube was charged with (dppp)Fe(CO)(NO)H (**2**; 1 mol%, 0.003 mmol), THF (400 μL), and triethylamine (50 mol%, 0.15 mmol). Then, the corresponding aldehyde or ketone (1 equiv., 0.3 mmol) and phenylsilane (1 equiv., 0.3 mmol) were added. The Schlenk tube was sealed and heated to 80 °C for 18 h. After the reaction mixture was cooled to RT, methanol (1 mL) and an aqueous solution of sodium hydroxide (2 N, 1 mL) were added dropwise. The mixture was stirred for 1 h at RT and filtered through a silica gel plug (ethyl acetate). Finally, the sample was purified by using silica gel chromatography, which yielded the corresponding product.

Benzyl alcohol 6a: The product was obtained according to GP-I starting from benzaldehyde (30 μL, 0.3 mmol) after purification (petroleum ether/ethyl acetate 5:1) in 87% yield (27.2 mg, 0.25 mmol) as a colorless oil. Spectroscopic data were identical to those described in the literature.[22] R_f = 0.32 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.33 (m, 4H), 7.33–7.24 (m, 1H), 4.67 (s, 2H), 1.84 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.9, 128.6, 127.7, 127.0, 65.4 ppm; IR (film) $\tilde{\nu}$ = 3324 (br), 3064 (w), 3030 (w), 2928 (w), 2873 (w), 1496 (w), 1454 (m), 1430 (w), 1208 (w), 1133 (m), 1080 (m), 1037 (m), 1014 (s), 912 (w), 803 (w), 734 (s), 697 (s), 595 cm^{-1} (m); GC–MS (ESI): *m/z* (%): 108 (100) [M^+], 91 (15); 79 (72), 51 (14).

4-Methoxybenzyl alcohol 6b: The product was obtained according to GP-I starting from 4-anisaldehyde (41 μL, 0.3 mmol) after purification (petroleum ether/ethyl acetate 1:1) in 98% yield (40.5 mg, 0.29 mmol) as a colorless oil. Spectroscopic data were identical to those described in the literature.[23] R_f = 0.44 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 4.60 (s, 2H), 3.80 (s, 3H), 1.85–1.66 ppm (s (br), 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.2, 133.1, 128.7, 114.0, 65.0, 55.3 ppm; IR (film) $\tilde{\nu}$ = 3348 (br), 3004 (w), 2933 (w), 2836 (w), 1677 (w), 1611 (m), 1586 (w), 1511 (s), 1463 (m), 1441 (m), 1429 (m), 1301 (m), 1244 (s), 1172 (m), 1132 (s), 1108 (s), 1028 (s), 932 (w), 813 (s), 741 (m), 697 (s), 636 (w), 570 (m), 493 cm^{-1} (s); GC–MS (ESI): *m/z* (%): 138 (100) [M^+], 121 (33); 109 (39), 94 (18), 77 (16), 65 (3), 51 (4), 38 (3)..

3-Bromobenzyl alcohol 6c: The product was obtained according to GP-I starting from 3-bromobenzaldehyde (35 μL, 0.3 mmol) after purification (petroleum ether/ethyl acetate 4:1) in 91% yield (50.8 mg, 0.27 mmol) as a colorless oil. Spectroscopic data were identical to those described in the literature.[23] R_f = 0.41 (petroleum ether/ethyl acetate 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.47 (m, 1H), 7.39 (dt, J_1 = 7.2 Hz, J_2 = 1.9 Hz, 1H), 7.26–7.16 (m, 2H), 4.60 (s, 2H), 2.49 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0, 130.6, 130.1, 129.9, 125.3, 122.6, 64.4 ppm; IR (film) $\tilde{\nu}$ = 3313 (br), 2928 (w), 2873 (w), 1597 (w), 1570 (m), 1473 (m), 1427 (s), 1360 (w), 1199 (s), 1091 (w), 1069 (m), 1012 (s), 882 (m), 844 (m), 828 (m), 773 (s), 695 (s), 666 (w), 612 (m), 506 cm^{-1} (m); GC–MS (ESI): *m/z* (%): 186 (100) [M^+], 169 (12); 157 (23), 107 (92), 89 (14), 77 (94), 63 (8), 51 (21).

1-Decanol 6d: The product was obtained according to GP-I starting from 1-decanal (56 μL, 0.3 mmol) after purification (petroleum ether/ethyl acetate 5:1) in 88% yield (41.8 mg, 0.26 mmol) as a colorless oil. Spectroscopic data were identical to those described in the literature.[22] R_f = 0.40 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (t, J = 6.6 Hz, 2H), 1.63–1.50 (m, 2H), 1.40–1.19 (m, 15H), 0.88 ppm (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.1, 32.8, 31.9, 29.6, 29.6, 29.4, 29.3, 25.7, 22.7, 14.1 ppm; IR (film) $\tilde{\nu}$ = 3330 (br), 2922 (s), 2853 (s), 1465 (m), 1378 (w), 1122 (w), 1056 (s), 721 cm^{-1} (m); GC–MS (ESI): *m/z* (%): 157 (1) [M^+], 140 (11); 112 (34), 97 (42), 83 (77), 70 (100), 55 (96), 43 (70).

Quinolin-2-ylmethanol 6e: The product was obtained according to GP-I starting from 2-quinolinecarboxaldehyde (47.2 mg, 0.3 mmol) after purification (petroleum ether/ethyl acetate 2:1) in 60% yield (28.7 mg, 0.18 mmol) as a yellow oil. Spectroscopic data were identical to those described in the literature.[24] R_f = 0.24 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.3 Hz, 1H), 8.07 (d, J = 8.7 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.71 (t, J = 7.8 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 8.8 Hz, 1H), 4.92 (s, 2H), 4.78–4.05 ppm (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1, 146.7, 136.8, 129.8, 128.6, 127.7, 127.6, 126.4, 118.4, 64.2 ppm; IR (film) $\tilde{\nu}$ = 3183 (br), 3042 (m), 2906 (w), 1616 (w), 1599 (m), 1566 (w), 1504 (m), 1467 (w), 1426 (m), 1375 (w), 1314 (m), 1224 (m), 1139 (m), 1117 (m), 1067 (s), 1017 (w), 978 (w), 954 (w), 914 (w), 834 (s), 776 (m), 752 (s), 699 (m), 622 (m), 559 cm^{-1} (w); GC–MS (ESI): *m/z* (%): 159 (100) [M^+], 130 (82); 102 (9), 77 (9), 51 (6).

3,7-Dimethyloct-6-en-1-ol 6f: The product was obtained according to GP-I starting from citronellal (54 μL, 0.3 mmol) after purification (petroleum ether/ethyl acetate 4:1) in 98% yield (45.7 mg, 0.29 mmol) as a colorless oil. Spectroscopic data were identical to those described in the literature.[25] R_f = 0.61 (petroleum ether/ethyl acetate 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.10 (tt, J_1 = 7.2 Hz, J_2 = 1.4 Hz, 1H), 3.75–3.60 (m, 2H), 2.09–1.89 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.65–1.49 (m, 3H), 1.42–1.29 (m, 2H), 1.24–1.10 (m, 1H), 0.90 ppm (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.3, 124.7, 61.1, 39.9, 37.2, 29.2, 25.7, 25.4, 19.5, 17.6 ppm; IR (film) $\tilde{\nu}$ = 3329 (br), 2962 (m), 2914 (s), 2872 (m), 1452 (m), 1377 (m), 1134 (w), 1056 (s), 1010 (m), 963 (w), 910 (w), 830 (m), 739 (m), 698 cm^{-1} (m); GC–MS (ESI): *m/z* (%): 156 (15) [M^+], 138 (13), 123 (31), 109 (22), 95 (46), 82 (50), 69 (100), 55 (46), 41 (71), 29 (9).

1-Phenylethanol 6g: The product was obtained according to GP-I starting from acetophenone (35 μL, 0.3 mmol) after purification (petroleum ether/ethyl acetate 5:1) in 98% yield (36.0 mg, 0.29 mmol) as a colorless oil. Spectroscopic data were identical to those described in the literature.[25] R_f = 0.44 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.21 (m, 5H), 4.85 (q, J = 6.4 Hz, 1H), 2.22 (s, 1H), 1.46 ppm (d, J = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.9, 128.5, 127.5, 125.4, 70.4, 25.2 ppm; IR (film) $\tilde{\nu}$ = 3335 (br), 3062 (w), 3029 (w), 2972 (m), 2927 (w), 2874 (w), 1602 (w), 1493 (m), 1450 (m), 1368 (m), 1284 (m), 1203 (m), 1098 (m), 1075 (s), 1029 (m), 1010 (s), 996 (m), 897 (m), 759 (s), 696 (s), 605 (m), 538 cm^{-1} (s); GC–MS (EI, 70 eV): *m/z* (%): 122 (33) [M^+], 107 (100), 79 (56), 51 (11), 43 (14).

6-Methylhept-5-en-2-ol 6h: The product was obtained according to GP-I starting from 6-methyl-5-hepten-2-one (44 μL, 0.3 mmol) after purification (*n*-pentane/diethyl ether 20:1) in 66% yield (25.2 mg, 0.20 mmol) as a colorless oil. Spectroscopic data were identical to those described in the literature.[26] R_f = 0.51 (*n*-pentane/diethyl ether 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.13 (tt, J_1 = 7.2 Hz, J_2 = 1.5 Hz, 1H), 3.87–3.74 (m, 1H), 2.16–1.98 (m, 2H), 1.69 (s, 3H), 1.63 (s, 3H), 1.53–1.44 (m, 3H), 1.19 ppm (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.1, 124.0, 68.0, 39.2, 25.7, 24.5, 23.5, 17.7 ppm; IR (film) $\tilde{\nu}$ = 3350 (br), 2966 (m), 2923 (m), 2857 (m), 1450 (m), 1376 (m), 1303 (w), 1172 (w), 1115 (m), 1073 (m), 1028 (w), 990 (w), 952 (w), 932 (m), 908 (w), 856 (w), 825 (w), 733

(s), 698 (w), 647 (w), 555 cm^{-1} (w); GC–MS (ESI): *m/z* (%): 128 (15) [M^+], 110 (27), 95 (100), 81 (11), 69 (38), 55 (18), 41 (31).

General procedure for the reduction of phosphine oxides (GP-II)

A 10 mL Schlenk tube was charged with (dppp)Fe(CO)(NO)H (**2**; 5 mol%, 0.015 mmol), toluene (400 μL), and *i*Pr_2NEt (50 mol%, 0.15 mmol). Then, the corresponding phosphine oxide (1 equiv., 0.3 mmol) and phenylsilane (1.5 equiv., 0.45 mmol) were added. The Schlenk tube was sealed and heated to 100 °C for 18 h. Afterward, the reaction mixture was cooled to RT, methanol (1 mL) and an aqueous solution of sodium hydroxide (2 N, 1 mL) were added dropwise. The mixture was stirred for 1 h at RT and filtered through a silica gel plug (ethyl acetate). Finally, the sample was purified by using silica gel chromatography, which yielded the corresponding product.

Triphenylphosphine 7a: The product was obtained according to GP-II starting from triphenylphosphine oxide (83.5 mg, 0.3 mmol) after purification (petroleum ether/ethyl acetate 20:1) in 65% yield (51.2 mg, 0.20 mmol) as a white solid. Spectroscopic data were identical to those described in the literature.[27] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.25 ppm (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.3, 137.1, 133.9, 133.6, 128.7, 128.6, 128.5 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −5.45 ppm.

Methyldiphenylphosphine 7b: The product was obtained according to GP-II starting from methyldiphenylphosphine oxide (64.9 mg, 0.3 mmol) after purification (petroleum ether/ethyl acetate 20:1) in 79% yield (47.5 mg, 0.24 mmol) as a white solid. Spectroscopic data were identical to those described in the literature.[28] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.37 (m, 4H), 7.36–7.27 (m, 6H), 1.66 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.3, 132.3, 132.0, 128.4, 126.9, 12.5 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −26.90 ppm; IR (film) $\tilde{\nu}$ = 3069 (w), 3052 (w), 2967 (w), 2905 (w), 1585 (w), 1579 (m), 1433 (s), 1328 (w), 1305 (w), 1280 (w), 1184 (w), 1156 (w), 1098 (m), 1069 (w), 1026 (w), 999 (w), 909 (w), 877 (s), 736 (s), 691 (s), 503 cm^{-1} (s); GC–MS (EI, 70 eV): *m/z* (%): 200 (100) [M^+], 183 (62).

Cyclohexyldiphenylphosphine 7c: The product was obtained according to GP-II starting from cyclohexyldiphenylphosphine oxide (85.3 mg, 0.3 mmol) after purification (petroleum ether/ethyl acetate 20:1) in 44% yield (35.2 mg, 0.13 mmol) as a white solid. Spectroscopic data were identical to those described in the literature.[11] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.42 (m, 4H), 7.40–7.23 (m, 6H), 2.28–2.21 (m, 1H), 1.85–1.58 (m, 5H), 1.38–1.12 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.2, 133.8, 133.6, 128.6, 128.3, 35.3, 29.7, 29.5, 26.9, 26.8, 26.4 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −3.63 ppm; IR (film) $\tilde{\nu}$ = 3069 (w), 3052 (w), 2922 (s), 2849 (m), 1586 (w), 1495 (w), 1479 (w), 1447 (m), 1433 (m), 1397 (w), 1377 (w), 1344 (w), 1306 (w), 1268 (w), 1173 (m), 1158 (m), 1092 (m), 1069 (w), 1026 (m), 999 (m), 915 (w), 886 (w), 851 (w), 806 (m), 737 (s), 694 (s), 626 (w), 502 cm^{-1} (s); GC–MS (EI, 70 eV): *m/z* (%): 268 (100) [M^+], 213 (33), 186 (56), 108 (52).

Tributylphosphine 7d: The product was obtained according to GP-II starting from tributylphosphine oxide (65.5 mg, 0.3 mmol) after purification (petroleum ether/ethyl acetate 20:1) in 55% yield (33.4 mg, 0.17 mmol) as a white solid. Spectroscopic data were identical to those described in the literature.[29] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.49–1.30 (m, 17H), 0.91 ppm (t, J = 6.3 Hz, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.3, 29.7, 28.4, 26.9, 24.7, 23.9, 13.9, 13.7 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −30.60 ppm; IR (film) $\tilde{\nu}$ = 3403 (w), 2956 (s), 2929 (s), 2871 (m), 1641 (w), 1665 (m), 1408 (w), 1379 (w), 1345 (w), 1308 (w), 1277 (w), 1228 (m), 1148 (s), 1093 (m), 1069 (m), 1002 (m), 1073 (w), 968 (m), 901 (m), 802 (m), 720 (m), 698 (m), 547 (m), 509 cm^{-1} (m); GC–MS (EI, 70 eV): *m/z* (%): 202 (43) [M^+], 173 (74), 160 (13), 146 (26), 131 (24), 118 (33), 104 (37), 89 (10), 76 (100), 62 (45).

Tri(*p*-tolyl)phosphine 7e: The product was obtained according to GP-II starting from tri(*p*-tolyl)phosphine oxide (96.1 mg, 0.3 mmol) after purification (petroleum ether/ethyl acetate 20:1) in 67% yield (61.2 mg, 0.20 mmol) as a white solid. Spectroscopic data were identical to those described in the literature.[12] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27–7.08 (m, 12H), 2.33 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.5, 133.7, 129.3, 21.3 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −7.93 ppm; IR (film) $\tilde{\nu}$ = 3013 (w), 2920 (w), 2861 (w), 1916 (w), 1657 (w), 1594 (w), 1494 (m), 1440 (m), 1393 (m), 1351 (w), 1306 (w), 1271 (w), 1211 (w), 1185 (m), 1116 (m), 1089 (m), 1037 (w), 1018 (m), 846 (w), 808 (s), 710 (m), 658 (w), 640 (w), 622 (m), 604 (m), 526 (s), 514 cm^{-1} (s); GC–MS (EI, 70 eV): *m/z* (%): 304 (100) [M^+], 211 (10), 183 (5), 152 (4), 122 (7), 78 (3).

Tri(4-fluorophenyl)phosphine 7f: The product was obtained according to GP-II starting from tris(4-fluorophenyl)phosphine oxide (99.7 mg, 0.3 mmol) after purification (petroleum ether/ethyl acetate 20:1) in 47% yield (45.0 mg, 0.14 mmol) as a white solid. Spectroscopic data were identical to those described in the literature.[27] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.19 (m, 6H), 7.11–7.00 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.1, 161.8, 135.4, 135.5, 135.4, 135.3, 132.5, 132.4, 116.1, 116.0, 115.8, 115.7 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −9.08 ppm; IR (film) $\tilde{\nu}$ = 3064 (w), 2925 (w), 2853 (w), 1896 (w), 1585 (s), 1492 (s), 1464 (m), 1392 (m), 1299 (w), 1220 (s), 1157 (s), 1116 (w), 1089 (m), 1042 (w), 1013 (m), 941 (w), 821 (s), 738 (w), 711 (w), 663 (w), 604 (w), 515 cm^{-1} (s); GC–MS (EI, 70 eV): *m/z* (%): 316 (100) [M^+], 219 (26), 201 (4), 170 (3), 158 (4), 126 (19).

General procedure for the catalytic Wittig reaction (GP-III)

A 10 mL Schlenk tube was charged with (dppp)Fe(CO)(NO)H (**2**; 5 mol%, 0.015 mmol), toluene (400 μL), *i*Pr_2NEt (1.5 equiv., 0.45 mmol), and triphenylphosphine (20 mol%, 0.06 mmol). Then, the corresponding aldehyde (1 equiv., 0.3 mmol), organohalide (1.3 equiv., 0.39 mmol), and phenylsilane (1.5 equiv., 0.45 mmol) were added. The Schlenk tube was sealed and heated to 100 °C for 20 h. Afterward, the reaction mixture was filtered through a silica gel plug. Conversions were determined by using ^{1}H NMR spectroscopy with mesitylene as an internal standard. Finally, the sample was purified by using silica gel chromatography, which yielded the corresponding product.

(*E*)-Ethyl cinnamate 8a: The product was obtained according to GP-III, but with 48 h reaction time, starting from benzaldehyde (30 μL, 0.3 mmol) and ethyl bromoacetate (43 μL, 0.39 mmol), as a mixture of regioisomers (*E*/*Z* = 83:17). Purification by using silica gel chromatography (petroleum ether/ethyl acetate 20:1) yielded the product as a mixture of regioisomers in 80% (42.2 mg, 0.24 mmol) combined yield as a colorless oil. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 40:1). Spectroscopic data were identical to those described in the literature.[30] R_f = 0.41 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, J = 16.0 Hz, 1H), 7.55–7.49 (m, 2H), 7.41–7.35 (m, 3H), 6.44 (d, J = 16.1 Hz, 1H), 4.26 (q, J = 7.24 Hz, 2H), 1.34 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.1, 144.6, 134.9, 130.2, 128.9, 128.1, 118.3, 60.5, 14.3 ppm; IR (film) $\tilde{\nu}$ = 3061 (w), 2980 (m), 1707 (s), 1637 (s), 1578 (w), 1495 (w), 1449 (m), 1391 (w), 1366 (m), 1309 (s), 1267(m), 1201

(s), 1163 (s), 1094 (m), 1072 (m), 1035 (m), 978 (m), 864 (m), 838 (w), 765 (s), 739 (w), 710 (m), 698 (m), 684 (s), 619 (w), 588 (m), 573 (m), 511 (m), 483 cm^{-1} (m); GC–MS (EI, 70 eV): *m/z* (%): 176 (43) [M^+], 148 (12), 131 (100), 103 (30), 77 (16), 51 (7).

(*E*)-Ethyl 3-(3-chlorophenyl)acrylate 8b: The product was obtained according to GP-III starting from 3-chlorobenzaldehyde (34 μL, 0.3 mmol) and ethyl bromoacetate (43 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z* = 72:28). Purification by using silica gel chromatography (petroleum ether/ethyl acetate 20:1) yielded the product as a mixture of regioisomers in 71% (45.2 mg, 0.21 mmol) combined yield as a colorless oil. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 20:1). Spectroscopic data were identical to those described in the literature.[32] R_f = 0.24 (petroleum ether/ethyl acetate 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 16.2 Hz, 1H), 7.52–7.49 (m, 1H), 7.41–7.26 (m, 3H), 6.43 (d, *J* = 16.2 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6, 142.9, 136.3, 134.9, 130.1, 130.1, 127.8, 126.2, 119.8, 60.7, 14.3 ppm; IR (film) $\tilde{\nu}$ = 3063 (w), 2981 (m), 2938 (w), 2903 (w), 1708 (s), 1639 (s), 1594 (w), 1566 (m), 1475 (m), 1445 (w), 1428 (w), 1392 (w), 1366 (m), 1303 (s), 1311 (s), 1269 (s), 1200 (s), 1175 (s), 1163 (s), 1095 (m), 1078 (m), 1034 (s), 979 (s), 910 (m), 859 (s), 784 (s), 734 (w), 683 (m), 672 (s), 575 (m), 511 (w), 436 (m), 415 cm^{-1} (w); GC–MS (ESI): *m/z* (%): 233 (100) [$M + Na^+$], 165 (96), 137 (20), 102 (6); HRMS (ESI): *m/z*: calcd for $C_{11}H_{11}ClO_2 + Na^+$: 233.0340; found: 233.0338.

(*E*)-Ethyl 3-(3-bromophenyl)acrylate 8c: The product was obtained according to GP-III starting from 3-bromobenzaldehyde (35 μL, 0.3 mmol) and ethyl bromoacetate (43 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z* = 92:8). Purification by using silica gel chromatography (petroleum ether/ethyl acetate 20:1) yielded the product as a mixture of regioisomers in 83% (63.8 mg, 0.25 mmol) combined yield as a colorless oil. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 10:1). Spectroscopic data were identical to those described in the literature.[32] R_f = 0.27 (petroleum ether/ethyl acetate 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (t, *J* = 1.6 Hz, 1H), 7.60 (d, *J* = 16.0 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.28–7.22 (m, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.5, 142.8, 136.6, 133.0, 130.7, 130.4, 126.6, 133.0, 119.8, 60.7, 14.3 ppm; IR (film) $\tilde{\nu}$ = 3062 (w), 2980 (m), 2935 (w), 2903 (w), 1708 (s), 1638 (m), 1592 (w), 1561 (m), 1473 (m), 1445 (w), 1418 (w), 1392 (w), 1366 (m), 1310 (s), 1268 (m), 1196 (s), 1174 (s), 1162 (s), 1113 (w), 1093 (m), 1072 (m), 1033 (m), 978 (m), 892 (w), 858 (m), 782 (s), 756 (w), 725 (m), 668 (s), 578 (m), 540 (w), 510 cm^{-1} (w); GC–MS (ESI): *m/z* (%): 254 (41) [M^+], 226 (18), 209 (100), 183 (14), 131 (10), 102 (58), 75 (10), 51 (9); HRMS (ESI): *m/z*: calcd for $C_{11}H_{11}BrO_2 + Na^+$: 276.9835; found: 276.9826.

(*E*)-Ethyl 3-(2-nitrophenyl)acrylate 8d: The product was obtained according to GP-III starting from 2-nitrobenzaldehyde (45.3 mg, 0.3 mmol) and ethyl bromoacetate (43 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z* = 75:25). Purification by using silica gel chromatography (petroleum ether/ethyl acetate 5:1) yielded the product as a mixture of regioisomers in 64% (42.6 mg, 0.19 mmol) combined yield as a colorless oil. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 5:1). Spectroscopic data were identical to those described in the literature.[31] ***E* isomer:** R_f = 0.42 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 15.9 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.67–7.67 (m, 2H), 7.59–7.51 (m, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.35 ppm (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.8, 148.3, 139.8, 133.5, 130.7, 130.2, 129.1, 124.9, 123.4, 60.9, 14.3 ppm; IR (film) $\tilde{\nu}$ = 2982 (w), 1711 (s), 1639 (m), 1606 (w), 1572 (m), 1521 (s), 1477 (m), 1443 (m), 1392 (w), 1366 (m), 1343 (s), 1289 (s), 1272 (s), 1249 (m), 1199 (m), 1178 (s), 1114 (w), 1031 (s), 973 (s), 911 (w), 886 (w), 856 (m), 833 (w), 785 (m), 755 (s), 731 (s), 715 (m), 686 (m), 664 (m), 586 (m), 524 cm^{-1} (m); GC–MS (ESI): *m/z* (%): 244 (100) [$M + Na^+$], 133 (44), 130 (98); HRMS (ESI): *m/z*: calcd for $C_{11}H_{11}NO_4 + Na^+$: 244.0580; found: 244.0575. ***Z* isomer:** R_f = 0.42 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.6 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.44–7.38 (m, 2H), 6.10 (d, *J* = 11.8 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.11 ppm (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 141.3, 133.0, 131.1, 128.9, 124.4, 121.4, 60.4, 13.9 ppm; IR (film) $\tilde{\nu}$ = 3071 (w), 2983 (w), 2937 (w), 2871 (w), 1715 (s), 1641 (w), 1608 (w), 1572 (w), 1520 (s), 1477 (w), 1443 (w), 1403 (w), 1384 (w), 1342 (s), 1292 (m), 1193 (s), 1157 (s), 1113 (m), 1095 (m), 1079 (m), 1028 (s), 961 (w), 858 (m), 832 (m), 816 (m), 788 (s), 756 (m), 732 (m), 706 (m), 665 (m), 591 cm^{-1} (m); GC–MS (ESI): *m/z* (%): 244 (100) [M^+], 176 (11), 130 (97), 102 (3); HRMS (ESI): *m/z*: calcd for $C_{11}H_{11}NO_4 + Na^+$: 244.0580; found: 244.0570.

(*E*)-Ethyl 3-(quinolin-2-yl)acrylate 8e: The product was obtained according to GP-III starting from 2-quinolinecarboxaldehyde (47.2 mg, 0.3 mmol) and ethyl bromoacetate (43 μL, 0.39 mmol) as a mixture of regioisomers. Purification by using silica gel chromatography (petroleum ether/ethyl acetate 10:1) yielded the product as a mixture of regioisomers in 34% (22.9 mg, 0.10 mmol) combined yield as a colorless oil. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 6:1). Spectroscopic data were identical to those described in the literature.[33] R_f = 0.56 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 16.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.36 ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6, 153.3, 148.3, 144.1, 136.8, 130.1, 129.9, 128.1, 127.5, 127.3, 123.8, 120.2, 60.8, 14.3 ppm; IR (film) $\tilde{\nu}$ = 3058 (w), 2980 (w), 2934 (w), 1708 (s), 1641 (m), 1616 (w), 1593 (m), 1556 (w), 1504 (m), 1463 (w), 1445 (w), 1427 (m), 1391 (m), 1366 (w), 1342 (m), 1291 (s), 1250 (s), 1231 (m), 1211 (m), 1176 (s), 1157 (s), 1117 (m), 1095 (m), 1032 (s), 978 (s), 923 (w), 900 (w), 869 (w), 823 (s), 789 (m), 756 (s), 723 (m), 698 (w), 656 (m), 543 (w), 519 (w), 503 cm^{-1} (s); GC–MS (EI, 70 eV): *m/z* (%): 227 (80) [M^+], 198 (13), 182 (100), 155 (76), 128 (34), 101 (9), 91 (8), 77 (17); HRMS (EI): *m/z*: calcd for $C_{14}H_{13}NO_2^+$: 227.0946; found: 227.0945.

(*E*)-Ethyl 3-(furan-2-yl)acrylate 8f: The product was obtained according to GP-III starting from 2-furfural (25 μL, 0.3 mmol) and ethyl bromoacetate (43 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z* = 90:10). The regioisomers were separated by using silica gel chromatography (petroleum ether/ethyl acetate 20:1), and the regioisomers could be isolated in 51% (25.4 mg, 0.15 mmol) combined yield as colorless oils. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 20:1). Spectroscopic data were identical to those described in the literature.[31] R_f = 0.37 (petroleum ether/ethyl acetate 20:1); ***E* isomer:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 1.5 Hz, 1H), 7.43 (d, *J* = 15.7 Hz, 1H), 6.60 (d, *J* = 3.4 Hz, 1H), 6.46 (q, *J* = 1.5 Hz, 1H), 6.31 (d, *J* = 15.7 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.32 ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.1, 151.0, 144.7, 131.0, 116.0, 114.6, 112.2, 60.4, 14.3 ppm; IR (film) $\tilde{\nu}$ = 3129 (w), 2982 (m), 1703 (s), 1637 (s), 1559 (w), 1478 (w), 1446 (w), 1390 (w), 1366 (m), 1303 (s), 1280 (m), 1259 (s), 1208 (s), 1159 (s), 1094 (m), 1075 (m), 1016

(s), 970 (s), 929 (m), 883 (m), 859 (m), 814 (m), 790 (m), 745 (s), 680 (m), 593 (s), 513 (m), 441 cm^{-1} (w); GC–MS (ESI): *m/z* (%): 189 (47) [$M+Na^+$], 139 (6), 121 (100); HRMS (ESI): *m/z*: calcd for $C_9H_{10}O_3+Na^+$: 189.0522; found: 189.0536. ***Z* isomer:** $R_f=0.41$ (petroleum ether/ethyl acetate 20:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.67$ (d, $J=3.7$ Hz, 1H), 7.48 (d, $J=1.8$ Hz, 1H), 6.79 (d, $J=12.8$ Hz, 1H), 6.52–6.49 (m, 1H), 5.74 (d, $J=12.8$ Hz, 1H), 4.23 (q, $J=7.2$ Hz, 2H), 1.32 ppm (t, $J=7.2$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=166.0$, 150.8, 143.9, 130.4, 117.0, 114.4, 112.6, 60.2, 14.3 ppm; IR ($CDCl_3$) $\tilde{\nu}=3072$ (w), 3052 (w), 3005 (w), 2957 (w), 2924 (m), 2852 (w), 2174 (m), 1714 (m), 1639 (w), 1593 (w), 1463 (w), 1430 (m), 1367 (w), 1304 (w), 1261 (w), 1209 (w), 1127 (s), 1088 (s), 1028 (m), 998 (w), 973 (w), 919 (w), 834 (s), 738 (m), 697 (m), 594 (w), 498 (m), 447 cm^{-1} (w); GC–MS (ESI): *m/z* (%): 169 (60) [M^+], 138 (29), 121 (100), 110 (5), 94 (20), 65 (21), 39 (18); HRMS (ESI): *m/z*: calcd for $C_9H_{10}O_3^+$: 166.0630; found: 166.0631.

(*E*)-Ethyl 3-(thiophen-2-yl)acrylate 8g: The product was obtained according to GP-III starting from 2-thiophenecarboxaldehyde (28 μL, 0.3 mmol) and ethyl bromoacetate (43 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z*=92:8). Purification by using silica gel chromatography (petroleum ether/ethyl acetate 20:1) yielded the product as a mixture of regioisomers in 37% (20.2 mg, 0.11 mmol) combined yield as a colorless oil. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 10:1). Spectroscopic data were identical to those described in the literature.[34] $R_f=0.35$ (petroleum ether/ethyl acetate 20:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.78$ (d, $J=15.8$ Hz, 1H), 7.37 (d, $J=5.0$ Hz, 1H), 7.25 (d, $J=3.4$ Hz, 1H), 7.05 (dd, $J_1=5.0$ Hz, $J_2=3.3$ Hz, 1H), 6.24 (d, $J=15.6$ Hz, 1H), 4.25 (q, $J=7.1$ Hz, 2H), 1.33 ppm (t, $J=7.1$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=166.9$, 139.6, 137.0, 130.8, 128.3, 128.1, 117.0, 60.5, 14.3 ppm; IR (film) $\tilde{\nu}=3106$ (w), 2980 (m), 2934 (w), 2903 (w), 1702 (s), 1624 (s), 1517 (w), 1464 (w), 1444 (w), 1426 (w), 1392 (m), 1304 (s), 1260 (s), 1229 (m), 1202 (s), 1157 (s), 1094 (m), 1032 (s), 968 (s), 845 (s), 829 (m), 778 (w), 701 (s), 595 (m), 571 (w), 487 cm^{-1} (m); GC–MS (ESI): *m/z* (%): 205 (100) [$M+Na^+$], 137 (99), 109 (17); HRMS (ESI): *m/z*: calcd for $C_9H_{10}O_2S+Na^+$: 205.0294; found: 205.0282.

(*E*)-Methyl 2-methyl-3-phenylacrylate 8h: The product was obtained according to GP-III starting from benzaldehyde (30 μL, 0.3 mmol) and methyl 2-bromopropionate (43 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z*=49:51). Purification by using silica gel chromatography (petroleum ether/ethyl acetate 10:1) yielded the product as a mixture of regioisomers in 30% (16.1 mg, 0.09 mmol) combined yield as a colorless oil. Spectroscopic data were identical to those described in the literature.[18a] $R_f=0.58$ (petroleum ether/ethyl acetate 10:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta=$ 7.71–7.68 (m, 1H), 7.39 (d, $J=4.3$ Hz, 4H), 7.36–7.30 (m, 1H), 3.82 (s, 3H), 2.12 ppm (d, $J=2.5$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 169.2, 139.0, 135.9, 129.8, 129.6, 129.0, 128.4, 128.3, 128.0, 127.6, 52.1, 14.1 ppm; IR (film) $\tilde{\nu}=3025$ (w), 2950 (w), 1706 (s), 1636 (m), 1576 (w), 1492 (w), 1434 (m), 1388 (w), 1356 (w), 1312 (m), 1295 (m), 1251 (s), 1201 (s), 1112 (s), 1075 (w), 1031 (w), 1018 (w), 1001 (m), 981 (m), 949 (m), 929 (m), 853 (w), 817 (w), 764 (s), 739 (m), 702 (s), 691 (s), 650 (w), 618 (m), 591 (m), 573 (m), 511 cm^{-1} (s); GC–MS (ESI): *m/z* (%): 199 (100) [$M+Na^+$], 145 (20), 131 (39), 117 (99), 103 (8); HRMS (ESI): *m/z*: calcd for $C_{11}H_{12}O_2+Na^+$: 199.0730; found: 199.0734.

(*E*)-Benzylidenacetophenone 8i: The product was obtained according to GP-III starting from benzaldehyde (30 μL, 0.3 mmol) and 2-bromoacetophenone (77.6 mg, 0.39 mmol) as a mixture of regioisomers. Purification by using silica gel chromatography (petroleum ether/ethyl acetate 20:1) yielded the product as a mixture of regioisomers in 37% (23.4 mg, 0.11 mmol) combined yield as a colorless oil. The regioisomers could not be separated by using semi-preparative HPLC. Spectroscopic data were identical to those described in the literature.[18a] $R_f=0.21$ (petroleum ether/ethyl acetate 40:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta=8.05$–8.00 (m, 2H), 7.82 (d, $J=$ 15.8 Hz, 1H), 7.69–7.61 (m, 2H), 7.61–7.48 (m, 4H), 7.46–7.40 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=190.6$, 144.9, 138.2, 134.9, 132.8, 130.6, 128.9, 128.6, 128.5, 128.5, 122.1 ppm; IR (film) $\tilde{\nu}=$ 3058 (w), 3026 (w), 2924 (w), 2850 (w), 1662 (s), 1602 (s), 1575 (s), 1494 (m), 1448 (s), 1395 (w), 1334 (s), 1305 (m), 1285 (m), 1213 (s), 1176 (m), 1159 (m), 1073 (w), 1034 (m), 1015 (m), 998 (m), 978 (m), 931 (w), 887 (w), 859 (w), 783 (m), 745 (s), 686 (s), 595 (w), 565 cm^{-1} (s); GC–MS (EI, 70 eV): *m/z* (%): 208 (100) [M^+], 179 (15), 169 (6), 131 (31), 105 (25), 77 (42), 51 (9).

(*E*)-Ethyl 5,9-dimethyldeca-2,8-dienoate 8j: The product was obtained according to GP-III starting from citronellal (54 μL, 0.3 mmol) and ethyl bromoacetate (43 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z*=96:4). Purification by using silica gel chromatography (petroleum ether/ethyl acetate 20:1) yielded the product as a mixture of regioisomers in 59% (39.5 mg, 0.18 mmol) combined yield as a colorless oil. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 40:1). Spectroscopic data were identical to those described in the literature.[35] $R_f=0.57$ (petroleum ether/ethyl acetate 20:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.00$–6.88 (m, 1H), 5.81 (dt, $J_1=15.6$ Hz, $J_2=$ 1.3 Hz, 1H), 5.08 (tt, $J_1=7.2$ Hz, $J_2=1.3$ Hz, 1H), 4.18 (q, $J=7.1$ Hz, 2H), 2.27–2.16 (m, 1H), 2.10–1.89 (m, 3H), 1.68 (s, 3H), 1.66–1.58 (m, 1H), 1.60 (s, 3H), 1.42–1.29 (m, 1H), 1.29 (t, $J=7.1$ Hz, 3H), 1.26–1.10 (m, 1H), 0.91 ppm (d, $J=6.7$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=166.7$, 148.2, 131.5, 124.4, 122.4, 60.1, 39.6, 36.7, 32.1, 25.7, 25.5, 19.5, 17.6, 14.3 ppm; IR (film) $\tilde{\nu}=2964$ (m), 2914 (m), 1719 (s), 1653 (m), 1447 (m), 1367 (m), 1310 (m), 1264 (s), 1181 (s), 1156 (s), 1116 (m), 1097 (m), 1045 (s), 982 (s), 889 (w), 835 (w), 741 (w), 704 cm^{-1} (w); GC–MS (ESI): *m/z* (%): 224 (10) [M^+], 181 (14); 150 (19), 136 (47), 109 (43), 95 (46), 81 (35), 69 (100), 55 (32), 41 (65); HRMS (ESI): *m/z*: calcd for $C_{14}H_{24}O_2^+$: 224.1776; found: 224.1774.

(*E*)-Ethyl dec-2-enoate 8k: The product was obtained according to GP-III starting from octanal (47 μL, 0.3 mmol) and ethyl bromoacetate (43 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z*=92:8). Purification by using silica gel chromatography (petroleum ether/ethyl acetate 20:1) yielded the product as a mixture of regioisomers in 46% (27.3 mg, 0.14 mmol) combined yield as a colorless oil. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 20:1). Spectroscopic data were identical to those described in the literature.[31] $R_f=0.42$ (petroleum ether/ethyl acetate 20:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta=6.97$ (dt, $J_1=15.5$ Hz, $J_2=7.0$ Hz, 1H), 5.81 (dt, $J_1=15.4$ Hz, $J_2=1.5$ Hz, 1H), 4.18 (q, $J=7.1$ Hz, 2H), 2.19 (q, $J=7.2$ Hz, 2H), 1.51–1.40 (m, 3H), 1.35–1.23 (m, 10H), 0.88 ppm (t, $J=6.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=166.8$, 149.5, 121.2, 60.1, 32.2, 31.7, 29.1, 28.0, 26.9, 22.6, 14.3, 14.1 ppm; IR (film) $\tilde{\nu}=2956$ (m), 2926 (m), 2856 (m), 1720 (s), 1654 (m), 1464 (w), 1366 (w), 1308 (m), 1269 (s), 1165 (s), 1126 (m), 1096 (w), 1041 (m), 979 (m), 855 (w), 723 (w), 546 cm^{-1} (w); GC–MS (EI, 70 eV): *m/z* (%): 198 (6) [M^+], 153 (100), 141 (8), 127 (25), 115 (31), 110 (56), 101 (94), 84 (50), 73 (59), 69 (46), 55 (99), 43 (61), 29 (41); HRMS (EI): *m/z*: calcd for $C_{12}H_{22}O_2^+$: 198.1620; found: 198.1619.

(*E*)-Cinnamonitrile 8l: The product was obtained according to GP-III starting from benzaldehyde (30 μL, 0.3 mmol) and chloroacetonitrile (25 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z*=78:22). Purification by using silica gel chromatography (petroleum ether/

ethyl acetate 20:1) yielded the product as a mixture of regioisomers in 60% (23.2 mg, 0.18 mmol) combined yield as a colorless oil. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 20:1). Spectroscopic data were identical to those described in the literature.[36] R_f = 0.38 (petroleum ether/ethyl acetate 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.35 (m, 6H), 5.88 ppm (d, J = 16.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.7, 133.6, 131.2, 129.1, 127.4, 118.2, 96.4 ppm; IR (film) $\tilde{\nu}$ = 3054 (w), 2216 (s), 1617 (s), 1576 (m), 1494 (m), 1448 (m), 1338 (w), 1300 (w), 1271 (w), 1180 (m), 1159 (w), 1159 (w), 1075 (w), 1029 (w), 965 (s), 920 (w), 844 (w), 827 (w), 778 (m, 746 (s), 687 (s), 623 (m), 579 (m), 533 (m), 503 (m), 436 cm^{-1} (m); GC–MS (ESI): *m/z* (%): 129 (100) [M^+], 102 (19), 76 (5), 63 (4), 51 (7).

(*E*)-3-(3-Chlorophenyl)acrylonitrile 8m: The product was obtained according to GP-III starting from 3-chlorobenzaldehyde (34 μL, 0.3 mmol) and chloroacetonitrile (25 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z* = 76:24). Purification by using silica gel chromatography (petroleum ether/ethyl acetate 10:1) yielded the product as a mixture of regioisomers in 82% (40.4 mg, 0.25 mmol) combined yield as a colorless oil. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 10:1). Spectroscopic data were identical to those described in the literature.[37] ***E* isomer:** R_f = 0.36 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.30 (m, 5H), 5.90 ppm (d, J = 16.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.0, 135.3, 135.2, 131.1, 130.4, 127.1, 125.6, 117.6, 98.0 ppm; IR (film) $\tilde{\nu}$ = 3064 (w), 2926 (w), 2854 (w), 2218 (s), 1620 (m), 1593 (m), 1565 (s), 1474 (m), 1428 (m), 1416 (m), 1308 (w), 1285 (w), 1259 (w), 1204 (m), 1066 (w), 1133 (w), 1095 (m), 1077 (m), 997 (w), 962 (s), 905 (s), 888 (m), 745 (s), 776 (w), 730 (s), 706 (s), 698 (s), 678 (s), 649 (m), 623 (w), 568 (w), 509 (w), 439 (w), 419 cm^{-1} (m); GC–MS (EI, 70 eV): *m/z* (%): 163 (100) [M^+], 136 (8), 128 (49), 101 (7); HRMS (ESI): *m/z*: calcd for $C_9H_6ClN^+$: 163.0189; found: 166.0185. ***Z* isomer:** R_f = 0.36 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (dt, J_1 = 6.7 Hz, J_2 = 1.8 Hz, 1H), 7.71 (t, J = 1.8 Hz, 1H), 7.45–7.35 (m, 2H), 7.08 (d, J = 12.1 Hz, 1H), 5.52 ppm (d, J = 12.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.1, 135.1, 134.0, 131.0, 130.2, 129.1, 126.7, 116.8, 96.8 ppm; IR (film) $\tilde{\nu}$ = 3066 (w), 2969 (w), 2926 (w), 2854 (w), 2214 (s), 1709 (w), 1612 (m), 1592 (w), 1562 (s), 1478 (m), 1389 (w), 1300 (w), 1283 (w), 1227 (w), 1181 (m), 1001 (m), 1081 (m), 999 (w), 956 (w), 882 (m), 854 (w), 833 (m), 794 (s), 757 (m), 732 (w), 679 (s), 649 (m), 579 (w), 485 (w), 425 cm^{-1} (w); GC–MS (EI, 70 eV): *m/z* (%): 163 (100) [M^+], 136 (8), 128 (48), 101 (8); HRMS (ESI): *m/z*: calcd for $C_9H_6ClN^+$: 163.0189: found: 163.0187.

(*E*)-3-(3-Bromophenyl)acrylonitrile 8n: The product was obtained according to GP-III starting from 3-bromobenzaldehyde (35 μL, 0.3 mmol) and chloroacetonitrile (25 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z* = 75:25). Purification by using silica gel chromatography (petroleum ether/ethyl acetate 10:1) yielded the product as a mixture of regioisomers in 79% (49.2 mg, 0.24 mmol) combined yield as a colorless oil. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 10:1). Spectroscopic data were identical to those described in the literature.[38] ***E* isomer:** R_f = 0.35 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.53 (m, 2H), 7.40–7.35 (m, 1H), 7.31 (d, J = 4.3 Hz, 1H), 7.28 (d, J = 8.7 Hz, 1H), 5.90 ppm (d, J = 16.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.9, 135.5, 134.0, 130.6, 130.1, 126.0, 123.3, 117.5, 98.1 ppm; IR (film) $\tilde{\nu}$ = 3060 (w), 2218 (s), 1620 (m), 1590 (w), 1562 (m), 1472 (m), 1424 (m), 1415 (m), 1283 (w), 1259 (w), 1202 (m), 1170 (w), 1090 (w), 1071 (m), 1032 (w), 994 (m), 961 (s), 887 (m), 873 (m), 826 (w), 775 (s), 732 (w), 680 (s), 623 (w), 561 (w), 508 cm^{-1} (w); GC–MS (EI, 70 eV): *m/z* (%): 207 (100) [M^+], 128 (73), 101 (21), 77 (10), 564 (10), 50 (9); HRMS (ESI): *m/z*: calcd for $C_9H_6BrN + Na^+$: 229.9576: found: 229.9583. ***Z* isomer:** R_f = 0.35 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, J = 9.4 Hz, 2H), 7.58 (d, J = 7.7 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 7.06 (d, J = 12.0 Hz, 1H), 5.52 ppm (d, J = 12.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.0, 135.4, 133.8, 132.1, 130.5, 127.1, 123.0, 116.8, 96.8 ppm; IR (film) $\tilde{\nu}$ = 3064 (w), 2968 (w), 2922 (w), 2851 (w), 2214 (m), 1708 (w), 1611 (w), 1557 (s), 1473 (m), 1424 (m), 1387 (w), 1297 (w), 1284 (w), 1230 (w), 1180 (m), 1093 (w), 1073 (m), 997 (m), 970 (w), 951 (w), 907 (w), 882 (m), 791 (s), 752 (m), 727 (m), 678 (s), 664 (m), 656 (w), 593 (m), 513 cm^{-1} (m); GC–MS (EI, 70 eV): *m/z* (%): 207 (100) [M^+], 128 (92), 101 (24), 75 (13), 50 (11); HRMS (ESI): *m/z*: calcd for $C_9H_6BrN^+$: 209.9756; found: 209.9769.

(*E*)-3-(4-Methoxyphenyl)acrylonitrile 8o: The product was obtained according to GP-III starting from anisaldehyde (41 μL, 0.3 mmol) and chloroacetonitrile (25 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z* = 67:33). Purification by using silica gel chromatography (petroleum ether/ethyl acetate 10:1) yielded the product as a mixture of regioisomers in 69% (26.6 mg, 0.21 mmol) combined yield as a colorless oil. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 10:1). Spectroscopic data were identical to those described in the literature.[37] ***E* isomer:** R_f = 0.29 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 16.7 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 5.71 (d, J = 16.7 Hz, 1H), 3.85 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.1, 150.0, 132.0, 129.1, 126.4, 118.7, 114.5, 99.4, 55.5 ppm; IR (film) $\tilde{\nu}$ = 2936 (w), 2840 (w), 2212 (s), 1682 (m), 1598 (s), 1574 (m), 1510 (s), 1460 (m), 1442 (w), 1423 (m), 1311 (m), 1249 (s), 1215 (m), 1174 (s), 1158 (s), 1111 (w), 1024 (s), 967 (m), 834 (s), 802 (s), 768 (m), 717 (w), 641 (w), 607 (m), 599 (m), 543 (m), 516 (m), 496 (m), 480 cm^{-1} (m); GC–MS (ESI): *m/z* (%): 159 (100) [M^+], 144 (17), 135 (30), 116 (27), 89 (18). ***Z* isomer:** R_f = 0.29 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 12.0 Hz, 1H), 6.95 (d, J = 8.8 Hz, 2H), 5.29 (d, J = 12.0 Hz, 1H), 3.86 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.7, 148.0, 131.0, 126.6, 114.3, 91.9, 55.4 ppm; IR (film) $\tilde{\nu}$ = 3065 (w), 2962 (w), 2839 (w), 2209 (s), 1599 (s), 1569 (m), 1509 (s), 1460 (m), 1442 (w), 1424 (w), 1403 (w), 1327 (w), 1307 (m), 1257 (s), 1172 (s), 1117 (w), 1027 (s), 971 (w), 835 (s), 751 (m), 709 (m), 690 (m), 629 (w), 578 (s), 516 (m), 496 (m), 454 (w), 416 cm^{-1} (w); GC–MS (ESI): *m/z* (%): 159 (100) [M^+], 144 (16), 116 (24), 89 (15), 63 (6).

(*E*)-3-(2-Nitrophenyl)acrylonitrile 8p: The product was obtained according to GP-III starting from 2-nitrobenzaldehyde (45.3 mg, 0.3 mmol) and chloroacetonitrile (25 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z* = 65:25). Purification by using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) yielded the product as a mixture of regioisomers in 22% (11.4 mg, 0.07 mmol) combined yield as a colorless oil. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 5:1). Spectroscopic data were identical to those described in the literature.[39] R_f = 0.36 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.22 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.73 (d, J = 11.7 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 5.72 ppm (d, J = 11.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.6, 134.3, 131.0, 130.7, 129.6, 125.3, 115.9, 100.2 ppm; IR (film) $\tilde{\nu}$ = 3111 (w), 3063 (m), 2918 (m), 2849 (w), 2217 (m), 1602 (w), 1567 (m), 1514 (s), 1437 (m), 1382 (m), 1342 (s), 1305 (m), 1291 (m), 1218 (m), 1178 (w), 1161 (w), 1140 (w), 1076 (w), 997 (m), 945 (w), 884 (m), 856 (m), 809 (s), 787 (s), 763 (s), 742 (m), 710 (s), 687 (m), 662 (m), 587 (w), 550 (w), 523 cm^{-1} (w); GC–MS (EI, 70 eV): *m/z*

(%): 174 (26) [M^+], 157 (45), 146 (21), 128 (30), 119 (78), 116 (100), 101 (90), 92 (98), 89 (94), 77 (53), 75 (62), 63 (29) 51 (51), 39 (17); HRMS (EI): *m/z*: calcd for $C_9H_6N_2O_2^+$: 174.0429; found: 174.0425.

(*E*)-3-(Furan-2-yl)acrylonitrile 8q: The product was obtained according to GP-III starting from 2-furfural (25 μL, 0.3 mmol) and chloroacetonitrile (25 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z* = 68:32). Purification by using silica gel chromatography (petroleum ether/ethyl acetate 10:1) yielded the product as a mixture of regioisomers in 55% (19.5 mg, 0.16 mmol) combined yield as a colorless oil. The regioisomers could not be separated by using semi-preparative HPLC. Spectroscopic data were identical to those described in the literature.[40] R_f = 0.32 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, J = 1.7 Hz, 1H), 7.11 (d, J = 16.3 Hz, 1H), 6.62 (d, J = 3.5 Hz, 1H), 6.50 (dd, J_1 = 3.5 Hz, J_2 = 1.7 Hz, 1H), 5.76 ppm (d, J = 16.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.9, 145.5, 136.1, 115.4, 112.6, 110.6, 93.4 ppm; IR (film) $\tilde{\nu}$ = 3127 (w), 3063 (w), 2924 (w), 2213 (s), 1689 (w), 1627 (s), 1552 (w), 1504 (w), 1473 (m), 1430 (w), 1390 (m), 1269 (m), 1205 (w), 1150 (m), 1073 (w), 1017 (s), 953 (m), 929 (m), 884 (m), 806 (m), 746 (s), 660 (w), 591 (s), 547 (w), 517 (w), 491 (w), 439 (w), 417 cm^{-1} (m); GC–MS (EI, 70 eV): *m/z* (%): 119 (100) [M^+], 90 (28), 64 (19), 39 (6).

(*E*)-3-(Thiophen-2-yl)acrylonitrile 8r: The product was obtained according to GP-III starting from 2-thiophenecarboxaldehyde (28 μL, 0.3 mmol) and chloroacetonitrile (25 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z* = 72:28). Purification by using silica gel chromatography (petroleum ether/ethyl acetate 10:1) yielded the product as a mixture of regioisomers in 25% (10.0 mg, 0.07 mmol) combined yield as a colorless oil. The regioisomers were separated by using semi-preparative HPLC (petroleum ether/ethyl acetate 10:1). Spectroscopic data were identical to those described in the literature.[18b] R_f = 0.26 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, J = 16.3 Hz, 1H), 7.42 (d, J = 5.2 Hz, 1H), 7.25 (d, J = 3.7 Hz, 1H), 7.08 (dd, J_1 = 5.2 Hz, J_2 = 3.7 Hz, 1H), 5.65 ppm (d, J = 16.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.7, 138.4, 131.2, 129.3, 128.4, 118.0, 94.5 ppm; IR (film) $\tilde{\nu}$ = 3107 (w), 3050 (w), 2923 (w), 2213 (s), 1738 (w), 1604 (s), 1516 (w), 1420 (m), 1361 (m), 1274 (w), 1246 (w), 1225 (m), 1207 (m), 1080 (w), 1048 (m), 1954 (s), 857 (m), 802 (m), 755 (w), 710 (s), 631 (w), 600 (w), 580 (w), 533 (w), 490 (w), 447 cm^{-1} (m); GC–MS (EI, 70 eV): *m/z* (%): 135 (100) [M^+], 108 (12), 91 (10), 45 (7); HRMS (EI, 70 eV): *m/z*: calcd for $C_7H_5NS^+$: 135.0143; found: 135.0148.

(*E*)-Dec-2-enenitrile 8s: The product was obtained according to GP-III starting from octanal (47 μL, 0.3 mmol) and chloroacetonitrile (43 μL, 0.39 mmol) as a mixture of regioisomers (*E*/*Z* = 92:8). Purification by using silica gel chromatography (petroleum ether/ethyl acetate 20:1) yielded the product as a mixture of regioisomers in 46% (27.3 mg, 0.14 mmol) combined yield as a colorless oil. The regioisomers could not be separated by using semi-preparative HPLC. Spectroscopic data were identical to those described in the literature.[41] Mixture of regioisomers: R_f = 0.34 (petroleum ether/ethyl acetate 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.97 (dt, J_1 = 15.6 Hz, J_2 = 6.9 Hz, 1H), 6.72 (dt, J_1 = 16.2 Hz, J_2 = 6.9 Hz, 1H), 5.81 (dt, J_1 = 15.4 Hz, J_2 = 1.6 Hz, 1H), 5.32 (dt, J_1 = 16.0 Hz, J_2 = 1.6 Hz, 1H), 2.21 (quintet, J = 7.5 Hz, 4H), 1.52–1.38 (m, 4H), 1.38–1.21 (m, 16H), 0.94–0.82 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.8, 156.2, 149.5, 121.2, 99.6, 60.1, 33.3, 32.2, 31.7, 31.7, 29.1, 29.1, 29.0, 28.0, 27.6, 27.0, 22.6, 22.6, 14.3, 14.1 ppm; IR (film) $\tilde{\nu}$ = 2956 (m), 2926 (s), 2856 (m), 1719 (s), 1654 (m), 1634 (w), 1465 (m), 1367 (m), 1308 (m), 1266 (s), 1178 (s), 1126 (m), 1096 (w), 1042 (m), 978 (m), 922 (w), 856 (w), 723 cm^{-1} (w); GC–MS (EI, 70 eV): *m/z* (%): 150 (14) [$M-H^+$], 136 (28), 122 (87), 108 (31), 83 (58), 69 (71), 54 (47), 43 (100), 29 (20); HRMS (EI): *m/z*: calcd for $C_{10}H_{17}N-H^+$: 150.1283; found: 150.1290.

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