Iron(III) and Ruthenium(II) Porphyrin Complex-Catalyzed Selective Olefination of Aldehydes with Ethyl Diazoacetate

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Abstract: The commercially available Fe(III) and Ru(II) porphyrin complexes Fe(TPP)Cl and Ru(TPP)(CO) are efficient catalysts for selective olefination of a variety of aldehydes with ethyl diazoacetate in the presence of triphenylphosphine. The reactions were carried out under mild conditions in a one-pot fashion with the use of a stoichiometrical amount of EDA, which proceeded with excellent yields and high (*E*)-selectivity. Air atmosphere, low catalyst loadings, and functional group tolerance were also demonstrated.

The Wittig reaction and its many variants remain the methods of choice for constructing carbon−carbon double bonds in organic synthesis for a variety of applications.[1] To avoid the basic conditions required for the generation of phosphorane precursors, there is growing interest in developing alternative protocols that can directly use easily accessible diazo compounds[2] for the transformation under neutral conditions. Several metal complexes were shown to catalyze the olefination of aldehydes with suitable diazo compounds in the presence of tertiary phosphines.[3] Although metalloporphyrins have been well-known for many years to catalyze carbene-type transformations with diazo reagents such as cyclopropanation of alkenes[4] and C−H insertion of alkanes,[5] it was only demonstrated very recently that an iron(II) porphyrin complex, iron(II) *meso*-tetra(*p*-tolyl)porphyrin Fe(TTP), can catalyze the olefination of a selection of aldehydes with ethyl diazoacetate (EDA) in the presence of triphenylphoshphine.[6] This represents the first example of a metalloporphyrin system that is effective for the catalytic olefination process.

As a part of our program of metalloporphyrin-based catalysis, we are interested in developing practical catalytic processes for carbon−carbon bond formation including olefination of aldehydes. Different from the use of iron(II) porphyrin complex,[6] which is air and moisture sensitive, we would like to identify alternative stable metalloporphyrins, ideally available from commercial sources, as efficient catalysts for olefination of aldehydes. We also hoped to simplify the reaction procedure by eliminating the slow EDA addition step and to further improve it by decreasing the amounts of EDA and solvent used in the iron(II) system.[6] Other improvements desired for practical applications would be high yields and selectivity with good catalyst turnover numbers, enhanced reaction rates, and wide substrate scope. Herein, we report our finding that the commercially available iron(III) and ruthenium(II) porphyrin complexes Fe(TPP)Cl and Ru(TPP)(CO) (Figure 1) are general and efficient catalysts for selective olefination of a variety of aldehydes with EDA in the presence of triphenylphosphine (eq 1). Due to their stability, the reactions catalyzed by Fe(TPP)Cl and Ru(TPP)(CO) can be carried out with standard synthetic techniques (without the need of a glovebox) under either nitrogen or air.

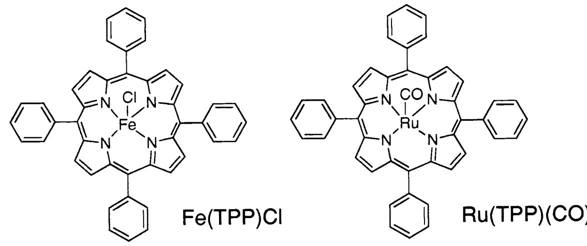

FIGURE 1. Structures of Fe(TPP)Cl and Ru(TPP)(CO).

$$\mathrm{RCHO} + \mathrm{N_2CHCO_2Et} \xrightarrow[\mathrm{Ph_3P}]{[\mathrm{M(TPP)}]} \mathrm{RCH{=}CHCO_2Et} \qquad (1)$$

We first evaluated the catalytic activities of a series of commercially available metal complexes of *meso*-tet-

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TABLE 1. Olefination of Benzaldehyde with EDA Catalyzed by Metal Complexes of *meso*-Tetraphenylporphyrin (TPP)[a]

entry	[M(TPP]	azine (yield, %)[b]	olefin (yield, %)[c]	E:Z[d]
1	V(TPP)(O)	65	0	
2	Cr(TPP)Cl	73	0	
3	Mn(TPP)Cl	66	0	
4	Fe(TPP)Cl	0	96	96:4
5	Co(TPP)	17	62	93:7
6	Ni(TPP)	65	0	
7	Cu(TPP)	67	0	
8	Zn(TPP)	74	0	
9	Ru(TPP)(CO)	0	97	96:4
10	−	68	0	

[a] Reactions were carried out at 80 °C in toluene for 2 h under N_2 with 1.0 equiv of benzaldehyde, 1.2 equiv of EDA, 1.2 equiv of Ph_3P, and 2 mol % of [M(TPP)]. Concentration: 2 mL of toluene/0.5 mmol of benzaldehyde. [b] Yields were determined by GC. [c] Yields represent isolated yields of >95% purity as determined by GC and ^{1}H NMR. [d] The ratio of E:Z isomers was determined by GC or ^{1}H NMR.

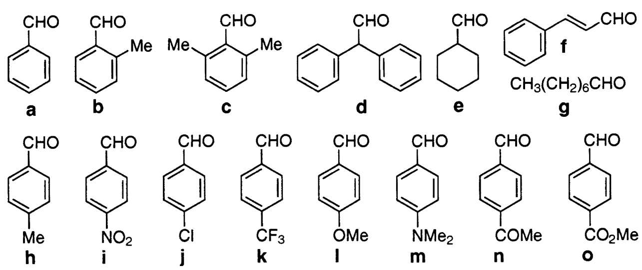


FIGURE 2. Structures of aldehyde substrates.

raphenylporphyrin [M(TPP)] using benzaldehyde as a model substrate (Table 1). The metalloporphyrins include V(TPP)(O), Cr(TPP)Cl, Mn(TPP)Cl, Fe(TPP)Cl, Co(TPP), Ni(TPP), Cu(TPP), Zn(TPP), and Ru(TPP)(CO). The reactions were typically carried out in toluene at 80 °C for 2 h with 1.2 equiv of EDA, using 2 mol % [M(TPP)] in the presence of 1.2 equiv of Ph_3P per benzaldehyde at a concentration of 0.25 M (2 mL of solvent/0.50 mmol of aldehyde). The reaction can be performed in a one-pot fashion without the need for slow addition of the EDA. Among the metalloporphyrins investigated under the above conditions (Table 1), the iron(III) (Table 1, entry 4) and ruthenium(II) (Table 1, entry 9) complexes (Figure 1) exhibited the highest catalytic reactivity, producing the desired ethyl cinnamate ($PhCH{=}CHCO_2Et$) in excellent yields (Fe(TPP)Cl, 96%; Ru(TPP)(CO), 97%) and high (E)-selectivity (Fe(TPP)Cl, 96%; Ru(TPP)(CO), 96%). The cobalt(II) complex [Co(TPP)] (Table 1, entry 5) showed a modest catalytic activity under such conditions, yielding azine ($PhCH{=}N{-}N{=}CHCO_2Et$, ~17%), as well as ethyl cinnamate (62%). The use of all other metalloporphyrins (Table 1, entries 1−3 and 6−8) only resulted in the formation of the azine product with similar yields (65−74%). The similar yield of azine (68%) was also observed in the absence of a catalyst (Table 1, entry 10), indicating no catalytic activities of the other metalloporphyrins.

Considering its low cost and high catalytic activity, the scope of the olefination reactions by Fe(TPP)Cl was further explored for a variety of aldehydes (Figure 2), the results of which are summarized in Table 2. Under the aforementioned general reaction conditions, with the use of 0.7−2.0 mol % Fe(TPP)Cl, both electron-neutral (Table 2, entries 1 and 9) and electron-poor (Table 2, entries 10, 13, and 14) benzaldehydes can be olefinated in high yields and high (E)-selectivity at 80 °C within 1 h. Similar conditions can also be effective for less-reactive electron-rich benzaldehydes. For example, 4-methoxybenzaldehyde can be coupled with EDA to form the desired olefin in 93% yield and 93% (E)-selectivity (Table 2, entry 15). With longer reaction time (24 h), even electron-rich 4-dimethylaminobenzaldehyde (Table 2, entries 16−18) was selectively converted to the corresponding (E)-olefin in high yield. Sterically demanding benzaldehydes are also suitable substrates for the olefination reaction, including both 2-monosubstituted and 2,6-disubstituted benzaldehydes (Table 2, entries 21 and 22). When 4-acetylbenzaldehyde and methyl 4-formylbenzoate (Table 2, entries 19 and 20) were used, the formyl groups were chemoselectively olefinated with EDA without affecting the acetyl and acetoxy functional groups. Excellent yields were also obtained for the olefination reactions of non-aromatic aldehydes such as α,β-unsaturated (Table 2, entry 28), benzyl (Table 2, entry 23), cyclic (Table 2, entries 26 and 27), and aliphatic aldehydes (Table 2, entry 29).

TABLE 2. Olefination of Aldehydes with EDA Catalyzed by Fe(TPP)Cl[a]

entry	RCHO	[Fe] (mol %)	temp (°C)	time (h)[b]	yield (%)[c]	E:Z[d]
1	**a**	2.0	80	1.0	96	96:4
2[e]	**a**	2.0	80	1.0	99	95:5
3[f]	**a**	2.0	68	1.0	95	94:6
4	**a**	2.0	50	1.0	92	94:6
5	**a**	2.0	23	1.0	68	93:7
6	**a**	0.6	80	1.0	98	93:7
7	**a**	0.3	80	1.0	97	93:7
8	**a**	0.01	80	0.5	89	92:8
9	**h**	0.7	80	0.5	97	95:5
10	**i**	2.0	80	0.3	89	95:5
11[e]	**i**	2.0	80	0.3	79	92:8
12	**i**	2.0	23	2.0	90	94:6
13	**j**	1.0	80	0.3	81	94:6
14	**k**	1.5	80	1.0	86	96:4
15	**l**	1.5	80	2.0	93	93:7
16	**m**	1.5	80	2.0	25[g]	95:5
17	**m**	1.5	80	12.0	68[g]	97:3
18	**m**	1.5	80	24.0	81	96:4
19	**n**	1.5	80	1.0	91	94:6
20	**o**	1.5	80	1.0	84	94:6
21	**b**	1.5	80	1.0	95	91:9
22	**c**	1.5	80	4.0	84	91:9
23	**d**	1.5	80	0.5	86	94:6
24[e]	**d**	1.5	80	0.5	92	94:6
25	**d**	1.5	23	11.0	86	97:3
26	**e**	1.5	80	1.0	66	95:5
27	**e**	1.5	80	2.0	88	98:2
28	**f**	1.5	80	1.0	99	93:7
29	**g**	1.5	80	1.0	84	95:5

[a] Reactions were carried out in toluene under N_2 with 1.0 equiv of RCHO, 1.2 equiv of EDA, 1.2 equiv of Ph_3P, and cat. Fe(TPP)Cl. Concentration: 2 mL of toluene/0.5 mmol of RCHO. [b] Reaction times have not been optimized. [c] Yields represent isolated yields of >95% purity as determined by GC and ^{1}H NMR. [d] The ratio of E:Z isomers was determined by GC or ^{1}H NMR. [e] The reaction was carried out in the air. [f] The reaction was carried out in THF. [g] Yields were determined by GC.

Although most of the reactions were carried out in toluene, other common solvents can also be used without affecting the yield and selectivity as illustrated by the reaction of benzaldehyde in THF (Table 2, entry 3). The use of elevated temperature (80 °C) allowed most of

TABLE 3. Olefination of Aldehydes with EDA Catalyzed by Ru(TPP)(CO)[a]

entry	RCHO	[Ru] (mol %)	temp (°C)	time (h)[b]	yield (%)[c]	E:Z[d]
1	**a**	0.7	80	2.0	95	93:7
2	**c**	0.7	80	4.0	95	94:6
3	**e**	0.7	80	2.0	93	93:7
4	**f**	1.5	80	1.0	94	92:8
5	**g**	0.7	80	1.0	90	93:7
6	**i**	0.7	80	0.3	91	93:7
7	**k**	0.7	80	1.0	94	94:6
8	**l**	0.7	80	1.0	95	93:7
9	**m**	1.5	80	24.0	81	92:8
10	**o**	1.5	80	1.0	97	94:6

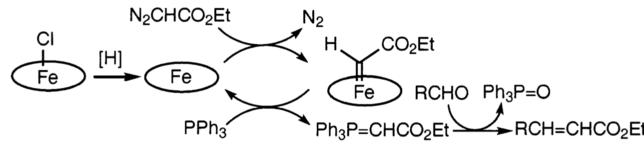
[a] Reactions were carried out in toluene under N_2 with 1.0 equiv of RCHO, 1.2 equiv of EDA, 1.2 equiv of Ph_3P, and cat. Ru(TPP)(CO). Concentration: 2 mL of toluene/0.5 mmol of RCHO. [b] Reaction times have not been optimized. [c] Yields represent isolated yields of >95% purity as determined by GC and ^{1}H NMR. [d] The ratio of E:Z isomers was determined by GC or ^{1}H NMR.

reactions to complete in ≤1 h. However, olefinations can be performed at lower temperature (Table 2, entries 3 and 4) or even at room temperature (Table 2, entries 5, 12, and 25). The high stability of Fe(TPP)Cl permits effective olefination with low catalyst loading (Table 2, entries 6−8). For example, the olefination of benzaldehyde can be effectively performed at 80 °C in 30 min with as low as 0.01 mol % Fe(TPP)Cl (Table 2, entry 8: TON = 8900; TOF = 17 800/h), the lowest catalyst loading reported thus far for the catalytic olefination of aldehydes with diazo compounds.[3,6] The potential practicality of this methodology is further enhanced with our later discovery that the use of a nitrogen atmosphere is not necessary for certain substrates. For example, similar yield and selectivity were achieved when reactions were carried out in the air (Table 2, entries 2, 11, and 24).

Although Ru(TPP)(CO) is relatively more expensive than Fe(TPP)Cl, we found Ru(TPP)(CO) is also an efficient and general catalyst for the aldehyde olefination (Table 3). Under the typical reaction conditions, Ru(TPP)(CO) is effective for the olefination of a variety of aldehydes with high yields and high (E)-selectivity. Examples include electron-neutral (Table 3, entry 1), electron-poor (Table 3, entries 6 and 7), electron-rich (Table 3, entries 8 and 9), sterically demanding (Table 3, entry 2), and functionalized (Table 3, entry 10) aromatic aldehydes as well as α,β-unsaturated (Table 2, entry 4), cyclic (Table 3, entry 3), and aliphatic (Table 3, entry 5) nonaromatic aldehydes. From all the examples examined, the catalytic efficiency of Ru(TPP)(CO) equals that of Fe(TPP)Cl. This is the first demonstration that a ruthenium porphyrin complex can catalyze the olefination of carbonyl compounds with diazo reagents.

We presume that the current olefination reactions proceed in a mechanism that is similar to the one proposed for the iron(II) porphyrin complex[6] and other metal complex systems,[3] involving a metal−carbene active intermediate. While it is a reasonable presumption for the Ru(II) complex Ru(TPP)(CO), which is known to form carbene complexes and to mediate cyclopropanation of alkenes,[7] this requires that the Fe(III) center of Fe(TPP)Cl can be in situ reduced to Fe(II), presumably by

SCHEME 1. Proposed Olefination Mechanism by Fe(TPP)Cl



EDA (Scheme 1).[4i,8] Alternative mechanisms, however, warrant consideration, in view of the facts that certain reactions can take place efficiently at room temperature or in the air.[4i] More studies are obviously needed for the full understanding of the current catalytic systems.

In summary, we have developed two general and efficient catalytic systems, based on the commercially available Fe(TPP)Cl and Ru(TPP)(CO), respectively, for highly selective olefination of a wide variety of aldehydes under mild conditions. This represents the first report that a ruthenium−porphyrin complex can catalyze this type of reaction. In combination with the excellent stability of the catalysts and the simplicity of the one-pot protocol, the new methodologies should find practical applications in organic synthesis for constructing carbon−carbon double bonds. We are currently working to expand the scope of these methodologies to other types of carbonyl substrates and to apply it with the use of different carbene sources.

Experimental Section

General Considerations. All reactions were carried out in oven-dried glassware under standard Schlenk techniques. Toluene and tetrahydrofuran were distilled under nitrogen from sodium benzophenone ketyl. Triphenylphosphine, EDA, and Fe(TPP)Cl were supplied by Strem Chemical Co. Ru(TPP)(CO) was obtained from Aldrich Chemical Co. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Varian Mercury 300 spectrometer and referenced with respect to residual solvent or internal TMS standard. GC/GC-MS spectroscopy was carried out on a Hewlett-Packard G1800B GCD system. High-resolution mass spectroscopy was performed by the Mass Spectrometry Center located in the Chemistry Department of the University of Tennessee on a VG Analytical hybrid high-performance ZAB-EQ (B-E-Q geometry) instrument, using the electron impact (EI) ionization technique with a 70-eV electron beam. Thin-layer chromatography was carried out on E. Merck Silica Gel 60 F-254 TLC plates.

General Procedures for Olefination Reaction. A certain mol % of Fe(TPP)Cl or Ru(TPP)(CO) and 1.2 equiv of triphenylphosphine were placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screwcap, evacuated, and backfilled with nitrogen. The screwcap was replaced with a rubber septum, and 1.0 equiv of aldehyde (0.5 mmol) was added via syringe, followed by solvent (2 mL) and 1.2 equiv of EDA. The tube was purged with nitrogen for 2 min and its contents were stirred at constant temperature in an oil bath. After the reaction finished, the resulting mixture was cooled to room temperature and concentrated. The residue was purified by flash silica gel chromatography to give the product.

Ethyl (*E*)-3-phenyl-2-propenoate[9] was synthesized from benzaldehyde (**a**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, 1H, J = 16.2 Hz), 7.50 (m, 2H), 7.35(m, 3H), 6.44 (d, 1H, J = 16.2 Hz), 4.26 (q, 2H, J = 7.1 Hz), 1.33 (t, 3H, J = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9, 144.5, 134.3, 130.1, 128.8, 127.9, 118.1, 60.4, 14.2. HRMS-EI ([M]$^+$): calcd for $C_{11}H_{12}O_2$ 176.0837, found

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176.0838, with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-3-(2-methylphenyl)-2-propenoate[10] was synthesized from 2-methylbenzaldehyde (**b**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, 1H, J = 15.6 Hz), 7.53 (d, 1H, J = 7.2 Hz), 7.20 (m, 3H), 6.35 (d, 1H, J = 15.6 Hz), 4.26 (q, 2H, J = 7.2 Hz), 2.42 (s, 3H), 1.33 (t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 142.5, 137.8, 133.7, 131.0, 130.2, 126.6, 126.5, 119.5, 60.7, 20.0, 14.6. HRMS-EI ([M]$^+$): calcd for $C_{12}H_{14}O_2$ 190.0994, found 190.0990, with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-3-(2,6-dimethylphenyl)-2-propenoate[11] was synthesized from 2,6-dimethylbenzaldehyde (**c**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, 1H, J = 16.2 Hz), 7.06 (m, 3H), 6.06 (d, 1H, J = 16.2 Hz), 4.27 (q, 2H, J = 7.2 Hz), 2.34 (s, 6H), 1.34 (t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 143.2, 126.5, 133.9, 128.2, 128.1, 123.8, 60.4, 21.0, 14.2. HRMS-EI ([M]$^+$): calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1152, with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-3,3-diphenylacrylate[12] was synthesized from diphenylacetaldehyde (**d**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (dd, 1H, J = 15.6, 7.2 Hz), 7.23 (m, 10H), 5.73 (d, 1H, J = 15.6 Hz), 4.86 (d, 1H, J = 7.2 Hz), 4.17 (q, 2H, J = 7.2 Hz), 1.24 (t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 149.8, 141.4, 128.6, 128.5, 126.8, 122.9, 60.3, 53.3, 14.1. HRMS-EI ([M]$^+$): calcd for $C_{18}H_{18}O_2$ 266.1307, found 266.1300, with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-3-cyclohexyl-2-propenoate[13] was synthesized from cyclohexanecarboxaldehyde (**e**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92 (dd, 1H, J = 15.9, 7.2 Hz), 5.76 (d, 1H, J = 15.9 Hz), 4.18 (q, 2H, J = 7.2 Hz), 2.14 (m, 1H), 1.75 (m, 5H), 1.29 (t, 3H, J = 7.2 Hz), 1.16 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.1, 154.2, 118.8, 60.1, 40.3, 31.6, 25.9, 25.7, 14.2. HRMS-EI ([M]$^+$): calcd for $C_{11}H_{18}O_2$ 182.1307, found 182.1307, with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*,*E*)-5-phenylpenta-2,4-dienoate[9] was synthesized from *trans*-cinnamaldehyde (**f**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.5−6.8 (m, 8H), 5.99 (d, 1H, J = 15.0 Hz), 4.22 (q, 2H, J = 7.2 Hz), 1.31 (t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.0, 144.5, 140.3, 135.9, 128.9, 128.7, 127.1, 126.1, 121.2, 60.2, 14.2. HRMS-EI ([M]$^+$): calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0991, with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-2-decenoate[14] was synthesized from octylaldehyde (**g**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.97 (dt, 1H, J = 15.6, 7.2 Hz), 5.81 (d, 1H, J = 15.6 Hz), 4.18 (q, 2H, J = 7.2 Hz), 2.19 (m, 2H), 1.45 (m, 2H), 1.29 (m, 11H), 0.89 (t, 3H, J = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 149.4, 121.1, 60.0, 32.1, 31.7, 29.0, 28.0, 22.6, 14.2, 14.0. HRMS-EI ([M − OC_2H_5]$^+$): calcd for $C_{10}H_{17}O$ 153.1279, found 153.1282, with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-3-(4-methylphenyl)-2-propenoate[9] was synthesized from 4-methylbenzaldehyde (**h**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, 1H, J = 15.6 Hz), 7.40 (d, 2H, J = 7.8 Hz), 7.17 (d, 2H, J = 7.8 Hz), 6.39 (d, 1H, J = 15.6 Hz), 4.25 (q, 2H, J = 7.1 Hz), 2.35 (s, 3H), 1.32 (t, 3H, J = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.0, 144.5, 140.5, 131.6, 129.5, 127.9, 117.0, 60.3, 21.3, 14.2. HRMS-EI ([M]$^+$): calcd for $C_{12}H_{14}O_2$ 190.0994, found 190.0990, with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-3-(4-nitrophenyl)-2-propenoate[15] was synthesized from 4-nitrobenzaldehyde (**i**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (d, 2H, J = 8.7 Hz), 7.71 (d, 1H, J = 16.2 Hz), 7.69 (d, 2H, J = 8.7 Hz), 6.57 (d, 1H, J = 16.2 Hz), 4.30 (q, 2H, J = 7.2 Hz), 1.35 (t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9, 148.3, 141.5, 140.5, 128.5, 124.0, 122.5, 60.9, 14.1. HRMS-EI ([M]$^+$): calcd for $C_{11}H_{11}NO_4$ 221.0688, found 221.0687, with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-3-(4-chlorophenyl)-2-propenoate[9] was synthesized from 4-chlorobenzaldehyde (**j**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (d, 1H, J = 16.2 Hz), 7.44 (d, 2H, J = 8.4 Hz), 7.34 (d, 2H, J = 8.4 Hz), 6.40 (d, 1H, J = 16.2 Hz), 4.26 (q, 2H, J = 7.2 Hz), 1.33 (t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6, 143.0, 136.0, 132.8, 129.1, 128.6, 118.7, 60.5, 14.2. HRMS-EI ([M]$^+$): calcd for $C_{11}H_{11}ClO_2$ 210.0448, found 210.0448, with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-3-(4-trifluoromethylphenyl)-2-propenoate[9] was synthesized from 4-trifluorotolualdehyde (**k**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, 1H, J = 16.2 Hz), 7.62 (s, 4H), 6.51 (d, 1H, J = 16.2 Hz), 4.28 (q, 2H, J = 6.9 Hz), 1.34 (t, 3H, J = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 142.6, 137.8, 132.0, 129.6, 128.1, 125.7, 120.8, 60.7, 14.2. HRMS-EI ([M]$^+$): calcd for $C_{12}H_{11}O_2F_3$ 244.0711, found 244.0718, with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-3-(4-methoxyphenyl)-2-propenoate[9] was synthesized from 4-methoxybenzaldehyde (**l**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, 1H, J = 15.9 Hz), 7.46 (d, 2H, J = 9.0 Hz), 6.88 (d, 2H, J = 9.0 Hz), 6.30 (d, 1H, J = 15.9 Hz), 4.24 (q, 2H, J = 7.2 Hz), 3.81 (s, 3H), 1.32 (t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2, 161.2, 144.1, 129.5, 127.0, 115.6, 114.1, 60.2, 55.2, 14.2. HRMS-EI ([M]$^+$): calcd for $C_{12}H_{14}O_3$ 206.0943, found 206.0950, with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-3-(4-dimethyaminophenyl)-2-propenoate[16] was synthesized from 4-dimethylaminobenzaldehyde (**m**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (d, 1H, J = 15.6 Hz), 7.40 (d, 2H, J = 9.0 Hz), 6.64 (d, 2H, J = 9.0 Hz), 6.21 (d, 1H, J = 15.6 Hz), 4.23 (q, 2H, J = 6.9 Hz), 2.98 (s, 6H), 1.32 (t, 3H, J = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.8, 151.6, 145.0, 129.6, 122.1, 112.4, 111.6, 59.9, 40.0, 14.3. HRMS-EI ([M]$^+$): calcd for $C_{13}H_{17}NO_2$ 219.1259, found 219.1255, with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-3-(4-acetylphenyl)-2-propenoate[16] was synthesized from 4-acetylbenzaldehyde (**n**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, 2H, J = 7.8 Hz), 7.69 (d, 1H, J = 16.2 Hz), 7.6 (d, 2H, J = 7.8 Hz), 6.52 (d, 1H, J = 16.2 Hz), 4.28 (q, 2H, J = 7.2 Hz), 2.61 (s, 3H), 1.35 (t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.1, 166.3, 142.8, 138.6, 137.8, 128.7, 128.0, 120.6, 60.6, 26.5, 14.1. HRMS-EI ([M]$^+$): calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0943, with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-3-(4-acetoxyphenyl)-2-propenoate[17] was synthesized from methyl 4-formylbenzoate (**o**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, 2H, J = 8.1 Hz), 7.69 (d, 1H, J = 15.9 Hz), 7.57 (d, 2H, J = 8.1 Hz), 6.51 (d, 1H, J = 15.9 Hz), 4.28 (q, 2H, J = 7.1 Hz), 3.92 (s, 3H), 1.34 (t, 3H, J = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 166.3, 143.0, 138.6, 131.2, 130.0, 127.8, 120.6, 60.6, 52.1, 14.2. HRMS-EI ([M]$^+$): calcd for $C_{13}H_{14}O_4$ 234.0892, found 234.0890, with an isotope distribution pattern that is the same as the calculated one.

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