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Carboxylation of styrenes with CBr_4 and DMSO *via* cooperative photoredox and cobalt catalysis†

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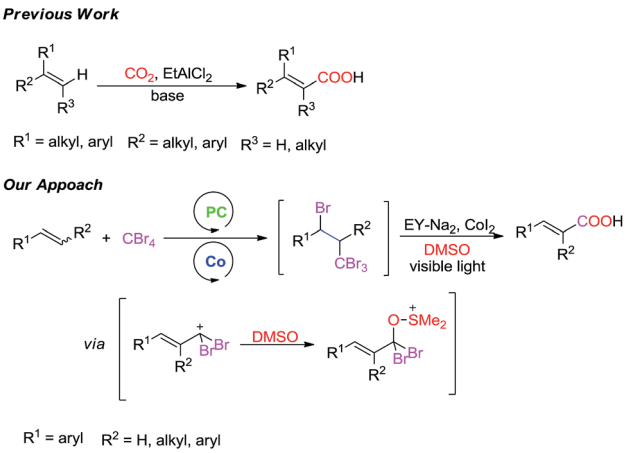
Cooperative photoredox and cobalt catalyzed carboxylation of styrenes with CBr_4 to afford the corresponding α,β-unsaturated carboxylic acids has been realized through radical addition and Kornblum (DMSO) oxidation. DMSO serves as the oxidant, oxygen source and solvent under these photocatalytic conditions.

Introduction

The direct carboxylation of alkenes[1,2] is a formidable challenge despite its high potential as a practical method for the preparation of unsaturated carboxylic acid derivatives. A well-known process for carboxylation of alkenes is the transition-metal-catalyzed C–C bond formation with CO_2, which has become a fundamental synthetic transformation in recent years.[2] Most of those methodologies require the use of rare and expensive metals.[3] More recently, Tanaka's group reported that alkenes underwent carboxylation with CO_2 in the presence of $EtAlCl_2$ and 2,6-dibromopyridine to afford the corresponding α,β- or β,γ-unsaturated carboxylic acids, but the substrate scope was limited to α-arylalkenes and trialkyl-substituted alkenes (Scheme 1).[4] The radical-mediated approach can be a complementary route to the carboxylation of alkenes because radicals have high activity and efficiency.[5] By virtue of this radical carboxylation strategy, several terminal alkenes, which are difficult to carboxylation with CO_2, have been successfully transformed into the corresponding α,β-unsaturated carboxylic acids.

In the last decade, visible-light driven photoredox catalysis has developed into a versatile tool for organic synthesis that is especially attractive as a sustainable chemical process.[6] This is because solar energy (visible light) is clean and renewable. However, most of the reported such reactions often employ ruthenium or iridium polypyridyl complexes which are expensive and potentially toxic. Therefore, the organic dyes, eosin Y,[7] would be an appropriate alternative to transition metal photocatalysts.[8]



Scheme 1 Carboxylation of styrenes.

Traditionally, carboxylation of styrenes[1a–c] was though addition of CX_4 and acid-catalyzedhydrolysis reaction for two steps. In contrast to traditional methods we design a new method for the synthesis of α,β-unsaturated carboxylic acids directly. We herein report the successful development of a carboxylation of styrenes employing CBr_4 and DMSO *via* cooperative photoredox and cobalt catalysis (CoI_2)[9] (Scheme 1).

Results and discussion

At first, the carboxylation of alkene was performed using styrene **1a** and CBr_4 with eosin Y disodium (10 mol%) as a photocatalyst under irradiation from a fluorescent bulb (18 W) and under a nitrogen atmosphere for 15 h in DMSO at 50 °C as the model reaction (Table 1).[10] In contrast, Xia group reported the bromination of styrene in the similar photoredox conditions but for 120 hours.[11] Subsequently, several catalysts were evaluated to give rise to target compound **2a** (entries 1–4), of which eosin Y disodium provided the highest yield of the target product **2a** and the intermediate **3** (entry 1). Atom-transfer radical additions of organic halides to alkenes giving the intermediate **3**

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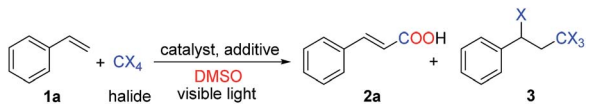
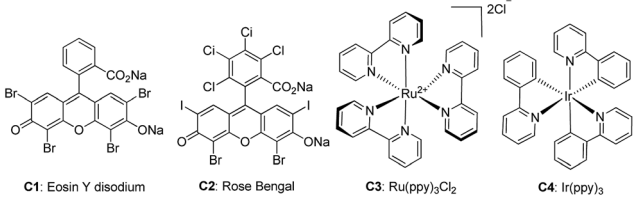
Table 1 Optimization of visible light driven carboxylation of styrene



Entry[a]	Halide	Catalyst	Additive	2a[b] (%)	3[b] (%)
1	CBr_4	C1	None	15	28
2	CBr_4	C3	None	7	19
3	CBr_4	C4	None	11	23
4	CBr_4	C2	None	10	26
5[c]	CBr_4	C1	None	13	17
6[d]	CBr_4	C1	None	8	27
7	$BrCCl_3$	C1	None	13	25
8	CCl_4	C1	None	n.r.	n.r.
9	CBr_4	C1	$Co(acac)_2$	n.r.	n.r.
10	CBr_4	C1	$Co(OAc)_2 \cdot 4H_2O$	Trace	n.d.
11	CBr_4	C1	$CoCO_3$	n.r.	n.r.
12	CBr_4	C1	CoF_2	28	12
13	CBr_4	C1	$CoCl_2$	19	8
14	CBr_4	C1	$CoBr_2$	Trace	n.d.
15	CBr_4	C1	CoI_2	70	19
16	CBr_4	C1	I_2	Trace	34
17[e]	CBr_4	C1	CoI_2	42	19
18[f]	CBr_4	C1	CoI_2	65	15
19[g]	CBr_4	C1	CoI_2	42	24
20[h]	CBr_4	C1	CoI_2	51	39
21[i]	**CBr_4**	**C1**	**CoI_2**	**72**	**9**
22[j]	CBr_4	C1	CoI_2	70	12

[a] Reaction conditions: all reactions were carried out with **1a** (0.50 mmol), halide (1.00 mmol), 10 mol% catalyst and additive (0.50 mmol) in solvent (2.00 mL) at 50 °C for 15 h irradiation by 18 W fluorescent lamp under nitrogen atmosphere unless otherwise stated. [b] Isolated yield; n.r. = no reaction; n.d. = no detected. [c] 5 mol% eosin Y disodium was used. [d] 20 mol% eosin Y disodium was used. [e] The reaction was conducted at rt. [f] The reaction was conducted at 80 °C. [g] CoI_2 (0.50 equiv.) was used. [h] CoI_2 (2.00 equiv.) was used. [i] The reaction was conducted using 1.00 mL DMSO. [j] Green LEDs was used for irradiation.

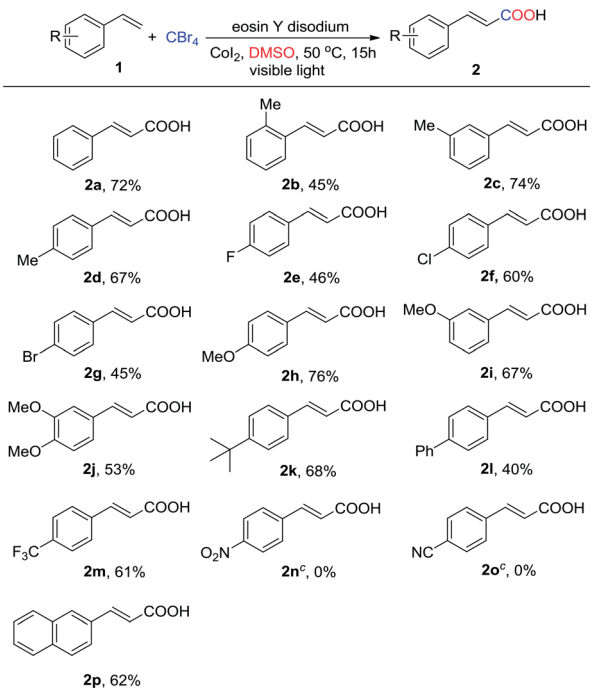


were previously reported by groups of Stephenson,[11a–c] Reiser[11d] and Melchiorre[11e]. Different concentrations of eosin Y disodium were tested. Unfortunately, the yield of **2a** could not be improved (entries 5 and 6). We also investigated $BrCCl_3$ (ref. 11*a* and *b*) but the yield did not increase (entry 7). No conversion could be observed when CCl_4 was used (entry 8).[12] This phenomenon may be attributed to the carbon–chlorine bond more stable (relative to a carbon–bromine bond). Furthermore, we examined different solvent types, such as the protic solvent MeOH; non-polar solvent THF; dipolar solvents CH_3CN, CH_3NO_3 and DMF. However, **2a** was not observed in any of the cases (not shown). Cobalt catalysts in various oxidation states have recently attracted particular attention in the development of applicable transformations due to its economy and low toxicity.[9] Subsequently, different cobalt catalysts were tested, including $Co(acac)_2$, $Co(OAc)_2 \cdot 4H_2O$, $CoCO_3$, CoF_2, $CoCl_2$, $CoBr_2$ and CoI_2 (entries 9–15). These investigations identified CoI_2 as the most efficient catalyst, which provided the desired product **2a** in 70% isolated yield. We also explored the effect of iodide and observed that the addition of I_2 resulted in a low yield (entry 16). However, lower or higher reaction temperature led to lower yields (entries 17–18). Next, we varied the amount of the CoI_2 from 0.50 equiv. to 2.00 equiv. (entries 19–20). These experiments revealed that 1.0 equiv. of CoI_2 gave the best yield (entry 15). In addition, a study of the reaction concentration indicated that increased concentration (*i.e.*, 0.25 mol L^{-1} *vs.* 0.50 mol L^{-1}) slightly improved the yield (entries 15 *vs.* 21). The use of green LEDs (entry 22) was almost effective as white LEDs.

After determining the optimized conditions for the synthesis of **2a**, we examined a diverse range of styrenes (Table 2). Initially, we evaluated the electronic effect of substrates with substituents on the aryl ring. Arylalkenes with methyl substituents at the *m* and *p* positions on the aryl ring furnished the target products in good yields (Table 2, **2c** and **2d**), while the *o*-methyl substituted arylalkene had a low yield of 45% due to the steric effect (Table 2, **2b**). The styrenes bearing the electron-withdrawing groups (F, Cl, and Br) were tolerated and provided moderate yields (Table 2, **2e–2g**). For comparison, the yields were well tolerated when the styrenes contained electron-donating substituents such as methoxy and *tert*-butyl (Table 2, **2h**, **2i** and **2k**). However, when dimethoxy and phenyl groups were introduced to the phenyl ring, the corresponding α,β-unsaturated acid products (Table 2, **2j** and **2l**) were isolated in 53% and 40% yields, respectively. It is noteworthy that 4-(trifluoromethyl)styrene gave the target product in good yield (Table 2, **2m**). Nevertheless, the styrenes bearing the nitro and nitrile groups failed to provide the target products (Table 2, **2n** and **2o**). These result indicated strong electron withdrawing groups impaired the reactivity to give the target products. Moreover, we were delighted to find that 1-naphthylalkene could also afford the corresponding α,β-unsaturated acid **2p** in yield of 62%.

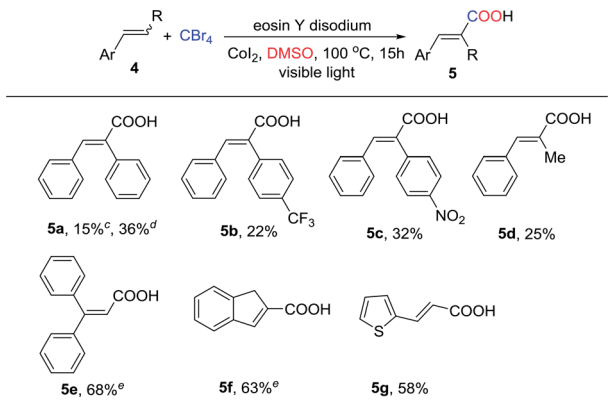
Next, we turned our attention to exam the scope of arylalkenes with various substituents on the α- or β-positions under the optimized conditions (Table 3). Unfortunately, the desired product was not obtained when (*E*)-1,2-diphenylethene was conducted under the optimized reaction conditions. Then we increased the reaction temperature to 100 °C and obtained the target product. In addition, both (*Z*)-and (*E*)-1,2-diphenylethene produced product **5a** in 15% and 36% yields. The reaction of stilbenes **4b** and **4c** bearing substituents such as trifluoromethyl and nitro groups furnished the regioselective products **5b** and **5c**, respectively, in 22% and 32% yields. Moreover, arylalkene with the methyl group on the β-position (**4d**) furnished the corresponding α,β-unsaturated acid product in a low yield (Table 3, **5d**). These results indicated that arylalkenes with various substituents on the β-positions gave low yields which may be because of the steric effect. It is worth mentioning that 1,1-diphenylethylene and indene also proceeded efficiently with yields of 68% and 63% (Table 3, **5e** and

Table 2 Carboxylation of styrenes[a,b]



[a] Alkene (**1a–1p** 0.50 mmol), 10 mol% eosin Y disodium, CBr_4 (1.00 mmol), CoI_2 (0.50 mmol), DMSO (1.00 mL), 50 °C, N_2. [b] Isolated yield. [c] Afforded the intermediate 1-nitro-4-(1,3,3,3-tetrabromopropyl) benzene (**3n**) and 4-(1,3,3,3-tetrabromopropyl)benzonitrile (**3o**) in 25% and 35% yields, respectively.

Table 3 Carboxylation of arylvinyls[a,b]



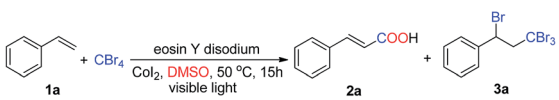
[a] Alkene (**4a–4f** 0.50 mmol), 10 mol% eosin Y disodium, CBr_4 (1.00 mmol), CoI_2 (0.50 mmol), DMSO (1.00 mL), 100 °C, N_2, 18 W white LED. [b] Isolated yield. [c] Using (*Z*)-1,2-diphenylethene. [d] Using (*E*)-1,2-diphenylethene. [e] Reaction run at 50 °C.

5f). Notably, 2-vinylthiophene was also a suitable substrate for the reaction, affording the product 5 g in 58% yield. However, no desired products were observed when other vinyl-substituted heterocycles such as 2-vinylpyrrole, 2-vinylpyridine and 3-vinylindole were used.

Several control experiments were designed to elucidate the plausible reaction mechanism for this carboxylation of styrenes (Scheme 2a). Firstly, the reaction of **1a** and CBr_4 in the absence of eosin Y disodium, visible light or CoI_2 under the standard reaction conditions was investigated. **3a** and **2a** were obtained in moderate yields respectively (Scheme 2a, entries 1 and 2). These results indicated that eosin Y disodium, visible light and CoI_2 were all very important to achieve this reaction. In comparison, 30% yield of **3a** with trace amount of **2a** were detected without eosin Y disodium, which was essential factor in the second step reaction (Scheme 2a, entries 2 *vs.* 3). Moreover, TEMPO (2.00 equiv.), a well-known radical scavenger, was found to inhibit this reaction process (Scheme 2a, entry 4), which suggested that the first step of the reaction may occur through a radical mechanism.

To gain insight into mechanism of the second step reaction, a proposed intermediate **3a** was tested under the standard conditions resulting in target product **2a** in a yield of 76% (Scheme 2b, entry 1), which indicated that **3a** was a possible intermediate for this reaction. Besides, in the absence of eosin Y disodium and light or CoI_2, the reaction generated **2a** in the yields of 53% and 60% respectively (Scheme 2b, entries 2 and 3), showing that eosin Y disodium and CoI_2 all play important roles in this step of the reaction mechanism. **3a** failed to be transformed into **2a** in the presence of eosin Y disodium, visible light and TEMPO. These results suggested that the mechanism may contain a radical process (Scheme 2b, entries 3 *vs.* 4). In comparison, almost the similar yield of **2a** was generated (Scheme 2a, entries 2, 5 and 6). Addition of TEMPO had no obvious effect on the reaction which suggested that this

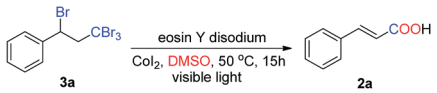
a)



entry[a]	CBr_4	eosin Y disodium	visible light	CoI_2	TEMPO	**2a**[b] (%)	**3a**[b] (%)
1	+	-	-	+	-	47	19
2	+	+	+	-	-	15	28
3	+	-	+	-	-	trace	30
4	+	+	+	+	+	n.r.	n.r.

[a] Reaction conditions: all reactions were carried out with **1a** (0.50 mmol), CBr_4 (1.00 mmol), 10 mol % eosin Y disodium, CoI_2 (0.50 mmol) and TEMPO (1.00 mmol) in DMSO (1.00 mL) at 50 °C for 15 h irradiation by 18 W fluorescent lamp under nitrogen atmosphere unless otherwise stated; [b] Isolated yield; n.r. = no reaction.

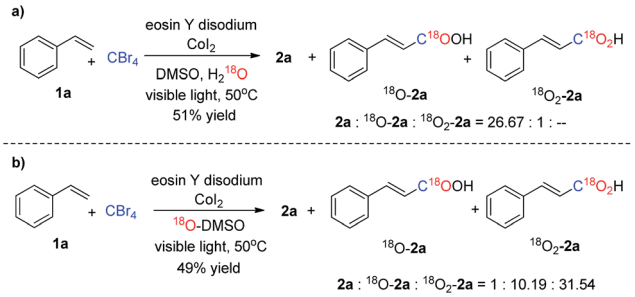
b)



entry[a]	eosin Y disudium	visible light	CoI_2	TEMPO	**2a** (%)[b]
1	+	+	+	-	76
2	-	-	+	-	53
3	+	+	-	-	60
4	+	+	-	+	trace
5	-	-	+	+	51
6	+	+	+	+	47

[a] Reaction conditions: all reactions were carried out with **3a** (0.20 mmol), 10 mol % eosin Y disodium, CoI_2 (0.20 mmol) and TEMPO (0.80 mmol) in DMSO (1.00 mL) at 50 °C for 15 h irradiation by 18 W fluorescent lamp under nitrogen atmosphere unless otherwise stated; [b] Isolated yield.

Scheme 2 Mechanistic studies of cascade reactions.

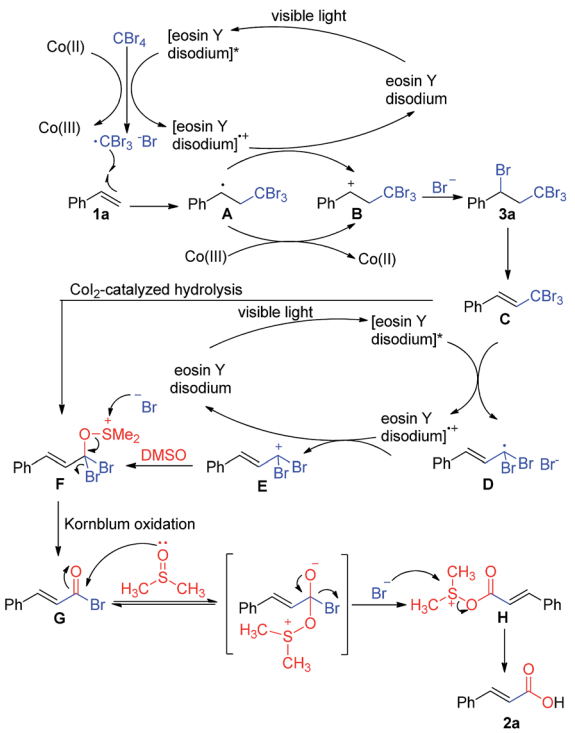


Scheme 3 Labeling studies.

mechanism may contain a CoI_2-catalyzed hydrolysis process (Scheme 2b, entries 5 and 6). The above results strongly suggested that this transformation may be achieved *via* cooperative photoredox and CoI_2.

To further understand the mechanism, ^{18}O-labeled H_2O and DMSO experiments were performed between styrene **1a** and CBr_4 under optimized conditions (Scheme 3). When the reaction of **1a** was conducted in the presence of 10.00 equiv. of $H_2{}^{18}O$ under the standard conditions, only **2a** and ^{18}O-**2a** were obtained in 51% yield with the ratio of 26.67 : 1.00 based on MS analysis. And no $^{18}O_2$-**2a** was observed (Scheme 3a). In contrast, when the reaction was performed with ^{18}O-labeled DMSO, the three products could also be obtained with the ratio 1.00 : 10.19 : 31.54 (Scheme 3b). These experimental results indicated that DMSO served as the source of oxygen in this transformation.

Based on the above results and previous reports, a plausible mechanism for the carboxylation is shown (Scheme 4). The



Scheme 4 Proposed reaction mechanism.

excited [eosin Y disodium]* or Co(II) transfers an electron to the halide, generating a radical[13,14] that adds to the alkene under electronic and steric control. The resulting radical combines with the halide with concurrent electron transfer back to [eosin Y disodium]$^+$ or Co(III), thus, regenerating the catalyst or Co(II).[15] Then, the intermediate **3a** is eliminated, giving compound **C**, which undergoes SET (single electron transfer) reduction to generate the alkyl radical.[16] Oxidation of the alkyl radical by [eosin Y disodium]$^+$ generates carbocation **E**, accompanied by formation of the catalyst. Nucleophilic attack of DMSO to carbocation **E** affords alkoxysulfonium **F**,[17] which also may be obtained from **3a** by CoI_2-catalyzed hydrolysis reaction. Then, a reaction similar to Kornblum (DMSO) oxidation proceeds to give compound **G**. Finally, nucleophilic attack by DMSO leads to the desired product **2a**.

Conclusions

In summary, we have developed a methodology that combines the photoredox/cabolt-catalyzed radical addition of halides onto alkenes and Kornblum (DMSO) oxidation of the dibromo-substituted carbocation, which enabled the transformation of alkenes with a variety of functional groups into the corresponding α,β-unsaturated carboxylic acids. The preliminary mechanistic studies suggested that DMSO as the oxidant, oxygen source and solvent plays a key roles in this reaction.

Experimental

General information

All reactions were carried out under nitrogen and stirred magnetically. DMSO was distilled prior to use. ^1H and ^{13}C NMR spectra were recorded on 500 MHz or 600 MHz spectrometers using $CDCl_3$ with TMS or residual solvent as standard unless otherwise noted. Melting points were determined using a Laboratory Device WRS-3 and are uncorrected/calibrated. TLC analysis was performed using Kangbino glass-backed plates (60 Å, 250 μm) and visualized using UV and phosphomolybdic acid stains. High-resolution mass spectra were obtained using an Agilent 1290 Infinity II-6530B in the ESI mode. Low-resolution mass spectra were obtained using an Agilent 1290 Infinity II-6460 in the ESI mode.

Preparation of substrates (derivatives of styrene)

2-Methylstyrene (1b).[18] 2-Methylbenzaldehyde (1.00 g, 8.30 mmol, 1.00 equiv.) was added to a solution of methyltriphenylphosphonium bromide (3.5 g, 10.00 mmol, 1.20 equiv.) and K_2CO_3 (1.80 g, 13.00 mmol, 1.5 equiv.) in dioxane (7.00 mL). The mixture was refluxed at 110 °C over 10 h. After being cooled to room temperature, excess solvent was removed by rotary evaporation. The residue was diluted with petroleum ether and filtered through celite and concentrated under vacuum. The crude product was purified by flash column chromatography (petroleum ether) to obtain the corresponding product as a colorless oil; 0.50 g, 4.23 mmol; 51% yield. ^1H NMR (500 MHz, $CDCl_3$), δ 7.51–7.47 (m, 1H), 7.21–7.14 (m, 3H), 6.96

(dd, J = 17.4, 11.0 Hz, 1H), 5.65 (dd, J = 17.4, 1.4 Hz, 1H), 5.30 (dd, J = 11.0, 1.4 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$), δ 136.8, 135.4, 134.8, 130.2, 127.6, 126.1, 125.3, 115.1, 19.7.

3-Methylstyrene (1c).[18] *m*-Tolualdehyde (1.00 g, 8.30 mmol, 1.00 equiv.) was added to a solution of methyltriphenylphosphonium bromide (3.57 g, 10.00 mmol, 1.20 equiv.) and K_2CO_3 (1.70 g, 13.00 mmol, 1.5 equiv.) in dioxane (7.00 mL). The mixture was refluxed at 110 °C over 10 h. After being cooled to room temperature, excess solvent was removed by rotary evaporation. The residue was diluted with petroleum ether and filtered through celite and concentrated under vacuum. The crude product was purified by flash column chromatography (petroleum ether) to obtain the corresponding product as a colorless oil; 0.80 g, 6.80 mmol; 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27–7.23 (m, 3H), 7.12–7.10 (m, 1H), 6.73 (dd, J = 17.6, 10.9 Hz, 1H), 5.78 (d, J = 17.6 Hz, 1H), 5.25 (d, J = 10.9 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 137.5, 137.0, 128.6, 128.4, 126.9, 123.4, 113.6, 21.4.

3-Methoxystyrene (1i).[19] 3-Methoxybenzaldehyde (1.00 g, 7.40 mmol, 1.00 equiv.) was added to a solution of methyltriphenylphosphonium bromide (3.20 g, 8.90 mmol, 1.20 equiv.) and K_2CO_3 (1.60 g, 11.80 mmol, 1.60 equiv.) in THF (10.00 mL). The mixture was refluxed at 75 °C over 10 h. After being cooled to room temperature, excess solvent was removed by rotary evaporation. The residue was diluted with petroleum ether and filtered through celite and concentrated under vacuum. The crude product was purified by flash column chromatography (petroleum ether) to obtain the corresponding product as a colorless oil; 0.79 g, 6.00 mmol; 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.27 (t, J = 7.9 Hz, 1H), 7.03 (m, 1H), 6.98 (s, 1H), 6.86–6.83 (m, 1H), 6.72 (dd, J = 17.6, 10.9 Hz, 1H), 5.77 (d, J = 17.6 Hz, 1H), 5.28 (d, J = 10.9 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$), δ 159.8, 139.0, 136.8, 129.5, 118.9, 114.1, 113.4, 111.5, 55.2.

3,4-(Dimethoxy)styrene (1j).[19] 3,4-Dimethoxybenzaldehyde (1.00 g, 6.00 mmol, 1.00 equiv.) was added to a solution of methyltriphenylphosphonium bromide (2.60 g, 7.20 mmol, 1.20 equiv.) and K_2CO_3 (1.20 g, 9.00 mmol, 1.50 equiv.) in THF (10.00 mL). The mixture was refluxed at 75 °C over 10 h. After being cooled to room temperature, excess solvent was removed by rotary evaporation. The residue was diluted with petroleum ether and filtered through celite and concentrated under vacuum. The crude product was purified by flash column chromatography (petroleum ether) to obtain the corresponding product as a colorless oil; 0.83 g, 4.98 mmol; 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$), δ 6.99–6.94 (m, 2H), 6.83 (d, J = 8.2 Hz, 1H), 6.66 (dd, J = 17.5, 10.9 Hz, 1H), 5.62 (d, J = 17.5 Hz, 1H), 5.16 (d, J = 10.9 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$), δ 149.0, 149.0, 136.5, 130.7, 119.4, 1118, 111.0, 108.5, 55.9, 55.8.

4-Phenylstyrene (1l).[18] 4-Biphenylcarboxaldehyde (1.00 g, 5.49 mmol, 1.00 equiv.) was added to a solution of methyltriphenylphosphonium bromide (2.40 g, 6.70 mmol, 1.20 equiv.) and K_2CO_3 (1.20 g, 8.77 mmol, 1.50 equiv.) in THF (7.00 mL). The mixture was refluxed at 75 °C over 10 h. After being cooled to room temperature, excess solvent was removed by rotary evaporation. The residue was diluted with petroleum ether and filtered through celite and concentrated under vacuum. The crude product was purified by flash column chromatography (petroleum ether) to obtain the corresponding product as a white solid; 0.60 g, 3.34 mmol; 61% yield; mp 119–120 °C (Lit. 120–122 °C), ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.63–7.57 (m, 4H), 7.50 (d, J = 8.2 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.5 Hz, 1H), 6.78 (dd, J = 17.6, 10.9 Hz, 1H), 5.81 (d, J = 17.6 Hz, 1H), 5.29 (d, J = 11.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ 140.7, 140.6, 136.6, 136.4, 128.8, 127.3, 127.2, 127.0, 126.6, 113.9.

4-(Trifluoromethyl)styrene (1m).[18] 4-(Trifluoromethyl)benzaldehyde (1.00 g, 5.70 mmol, 1.00 equiv.) was added to a solution of methyltriphenylphosphonium bromide (2.40 g, 6.84 mmol, 1.20 equiv.) and K_2CO_3 (1.18 g, 8.55 mmol, 1.50 equiv.) in THF (8.00 mL). The mixture was refluxed at 75 °C over 10 h. After being cooled to room temperature, excess solvent was removed by rotary evaporation. The residue was diluted with petroleum ether and filtered through celite and concentrated under vacuum. The crude product was purified by flash column chromatography (petroleum ether) to obtain the corresponding product as a colorless oil; 0.66 g, 3.88 mmol; 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.59 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 6.76 (dd, J = 17.6, 10.9 Hz, 1H), 5.86 (d, J = 17.6 Hz, 1H), 5.40 (d, J = 10.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ 140.9, 135.6, 129.8 (q, J = 32.3 Hz), 126.4, 125.5 (q, J = 3.8 Hz), 123.1, 116.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ − 62.5 (s, 3F)

4-Nitrostyrene (1o).[18] 4-Nitrobenzaldehyde (1.00 g, 6.60 mmol, 1.00 equiv.) was added to a solution of methyltriphenylphosphonium bromide (2.80 g, 7.90 mmol, 1.20 equiv.) and K_2CO_3 (1.40 g, 9.90 mmol, 1.50 equiv.) in THF (10.00 mL). The mixture was refluxed at 75 °C over 10 h. After being cooled to room temperature, excess solvent was removed by rotary evaporation. The residue was diluted with petroleum ether and filtered through celite and concentrated under vacuum. The crude product was purified by flash column chromatography (petroleum ether) to obtain the corresponding product as a yellow oil; 0.65 g, 4.36 mmol; 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.16 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.7 Hz, 2H), 6.77 (dd, J = 17.6, 10.9 Hz, 1H), 5.92 (d, J = 17.6 Hz, 1H), 5.49 (d, J = 10.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ 147.1, 143.8, 134.9, 126.8, 123.9, 118.6.

4-Cyanostyrene (1p).[18] 4-Cyanobenzaldehyde (0.50 g, 3.82 mmol, 1.00 equiv.) was added to a solution of methyltriphenylphosphonium bromide (1.60 g, 4.58 mmol, 1.20 equiv.) and K_2CO_3 (0.83 g, 6.04 mmol, 1.50 equiv.) in dioxane (4.00 mL). The mixture was refluxed at 110 °C over 10 h. After being cooled to room temperature, excess solvent was removed by rotary evaporation. The residue was diluted with petroleum ether and filtered through celite and concentrated under vacuum. The crude product was purified by flash column chromatography (petroleum ether) to obtain the corresponding product as a colorless oil; 0.48 g, 3.70 mmol; 98% yield. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.62 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 6.73 (dd, J = 17.6, 10.9 Hz, 1H), 5.88 (d, J = 17.3 Hz, 1H), 5.45 (d, J = 10.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ 141.9, 135.4, 132.4, 126.7, 118.9, 117.7, 111.1.

2-Vinylnaphthalene (1p).[20] 2-Naphthaldehyde (1.00 g, 6.40 mmol, 1.00 equiv.) was added to a solution of methyltriphenylphosphonium bromide (2.70 g, 7.69 mmol, 1.20 equiv.) and K_2CO_3 (1.30 g, 9.60 mmol, 1.50 equiv.) in THF (12.00 mL). The mixture was refluxed at 75 °C over 10 h. After being cooled to room temperature, excess solvent was removed by rotary evaporation. The residue was diluted with petroleum ether and filtered through celite and concentrated under vacuum. The crude product was purified by flash column chromatography (petroleum ether) to obtain the corresponding product as a white solid; 0.96 g, 6.20 mmol; 97% yield; mp 63–64 °C (Lit. 62–66 °C), ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.85–7.80 (m, 3H), 7.77 (s, 1H), 7.69–7.64 (m, 1H), 7.51–7.44 (m, 2H), 6.91 (ddd, J = 17.6, 10.9, 2.0 Hz, 1H), 5.90 (dd, J = 17.6, 2.0 Hz, 1H), 5.36 (dd, J = 10.8, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ 136.9, 135.0, 133.6, 133.2, 128.2, 128.0, 127.7, 126.4, 126.2, 125.2, 123.2, 114.2.

(*E*/*Z*)-1-Styryl-4-(trifluoromethyl)benzene (4b/4b′).[18] A solution of benzyltriphenylphosphonium bromide (1.52 g, 3.50 mmol, 1.20 equiv.) and $LiOH\cdot H_2O$ (0.36 g, 8.60 mmol, 3.00 equiv.) in isopropanol (10.00 mL) was stirred at room temperature for 30 min, and then 4-(trifluoromethyl)benzaldehyde (0.50 g, 2.87 mmol, 1.00 equiv.) was added. The reaction mixture was stirred at 75 °C for 6 h. After being cooled to room temperature, excess solvent was removed by rotary evaporation. The residue was quenched with water and extracted with ethyl acetate and the combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether) to obtain the corresponding product (E/Z = 38/62) as a white solid; 0.64 g, 2.58 mmol; 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$, signals corresponding to (*E*)-isomer) δ 7.60 (s, 4H), 7.46 (d, J = 8.1 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.19 (d, J = 16.2 Hz, 1H), 7.12 (d, J = 16.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, signals corresponding to (*E*)-isomer), δ 140.8, 136.6, 131.2, 129.4, 128.3, 128.8, 127.1, 126.8, 126.6, 125.7 (q, J = 3.8 Hz), 123.3; ^{1}H NMR (600 MHz, $CDCl_3$, representative signals corresponding to (*Z*)-isomer), δ 7.46 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.25–7.21 (m, 5H), 6.72 (d, J = 12.2 Hz, 1H), 6.59 (d, J = 12.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, representative signals corresponding to (*Z*)-isomer) δ 140.9, 136.7, 132.3, 129.2, 128.8, 128.8, 128.4, 127.6, 125.2 (q, J = 3.7 Hz), 123.3, 121.5.

(*E*)-1-Nitro-4-styrylbenzene (4c).[18] A solution of benzyltriphenylphosphonium bromide (5.20 g, 12.01 mmol, 1.20 equiv.) and $LiOH\cdot H_2O$ (1.24 g, 29.76 mmol, 3.00 equiv.) in 2-propanol (40.00 mL) was stirred at room temperature for 30 min, and then 4-nitrobenzaldehyde (1.50 g, 9.93 mmol, 1.00 equiv.) was added. The reaction mixture was stirred at 75 °C for 6 h. After being cooled to room temperature, excess solvent was removed by rotary evaporation. The residue was quenched with water and extracted with ethyl acetate and the combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether) to obtain the corresponding product: (*E*)-isomer; yellow solid; 1.16 g, 5.10 mmol; 52% yield; mp 154–155 °C (Lit. 155–158 °C), ^{1}H NMR (600 MHz, $CDCl_3$), δ 8.22 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.27 (d, J = 16.5 Hz, 1H), 7.15 (d, J = 16.3 Hz, 1H), ^{13}C NMR (150 MHz, $CDCl_3$), 146.8, 143.9, 136.2, 133.3, 128.9, 128.9, 127.0, 126.9, 126.3, 124.2.

(*Z*/*E*)-β-Methylstyrene (4d/4d′).[18] Benzaldehyde (0.50 g, 4.72 mmol, 1.00 equiv.) was added to a solution of ethyltriphenylphosphonium bromide (2.00 g, 5.39 mmol, 1.14 equiv.) and K_2CO_3 (1.00 g, 7.25 mmol, 1.50 equiv.) in dioxane (4.00 mL). The mixture was refluxed at 110 °C over 10 h. After being cooled to room temperature, excess solvent was removed by rotary evaporation. The residue was diluted with petroleum ether and filtered through celite and concentrated under vacuum. The crude product was purified by flash column chromatography (petroleum ether) to obtain the corresponding product (E/Z = 44/56) as a colorless oil; 0.33 g, 3.00 mmol; 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$, signals corresponding to (*Z*)-isomer) δ 7.41–7.27 (m, 4H), 7.27–7.20 (m, 1H), 6.51–6.43 (m, 1H), 5.88–5.81 (m, 1H), 1.95 (dd, J = 7.2, 1.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, signals corresponding to (*Z*)-isomer) δ 137.7, 129.9, 128.9, 128.1, 126.8, 126.4, 14.6; ^{1}H NMR (500 MHz, $CDCl_3$, representative signals corresponding to (*E*)-isomer) δ 7.41–7.27 (m, 4H), 7.27–7.20 (m, 1H), 6.51–6.43 (m, 1H), 6.32–6.25 (m, 1H), 1.93 (dd, J = 6.6, 1.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, representative signals corresponding to (*E*)-isomer) δ 138.0, 131.1, 128.5, 123.8, 125.9, 125.7, 18.5.

2-Vinylthiophene (4g).[21] Thiophene-2-carbaldehyde (1.00 g, 8.92 mmol, 1.00 equiv.) was added to a solution of ethyltriphenylphosphonium bromide (3.80 g, 10.70 mmol, 1.20 equiv.) and K_2CO_3 (1.85 g, 13.38 mmol, 1.50 equiv.) in dioxane (10.00 mL). The mixture was refluxed at 110 °C over 10 h. After being cooled to room temperature, excess solvent was removed by rotary evaporation. The residue was diluted with petroleum ether and filtered through celite and concentrated under vacuum. The crude product was purified by flash column chromatography (petroleum ether) to obtain the corresponding product as a colorless oil; 0.59 g, 5.35 mmol; 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.19 (d, J = 5.0 Hz, 1H), 7.00 (m, 2H), 6.85 (dd, J = 17.5, 11.0 Hz, 1H), 5.60 (d, J = 12.5 Hz, 1H), 5.17 (d, J = 10.5 Hz, 1H), ^{13}C NMR (125 MHz, $CDCl_3$), δ 143.1, 129.9, 127.3, 125.8, 124.3, 113.2.

2-Vinylpyrrole (4h).[21] Pyrrole-2-carbaldehyde (1.00 g, 10.52 mmol, 1.00 equiv.) was added to a solution of ethyltriphenylphosphonium bromide (4.51 g, 12.63 mmol, 1.20 equiv.) and K_2CO_3 (2.18 g, 15.78 mmol, 1.50 equiv.) in dioxane (10.00 mL). The mixture was refluxed at 110 °C over 10 h. After being cooled to room temperature, excess solvent was removed by rotary evaporation. The residue was diluted with 9 : 1 petroleum ether/ethyl acetate and filtered through celite and concentrated under vacuum. The crude product was purified by flash column chromatography (19 : 1 petroleum ether/EtOAc) to obtain the corresponding product as a colorless oil; 0.55 g, 5.79 mmol; 55% yield. ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.24 (s, 1H), 6.78 (s, 1H), 6.61 (dd, J = 18.0, 11.0 Hz, 1H), 6.32–6.23 (m, 2H), 5.31 (d, J = 17.5 Hz, 1H), 5.05 (d, J = 11.5 Hz, 1H), ^{13}C NMR (125 MHz, $CDCl_3$), δ 130.9, 127.2, 118.8, 109.5, 108.5, 108.0.

3-Vinylindole (4j).[22] To a stirred suspension of methyltriphenylphosphonium bromide (2.96 g, 8.30 mmol, 1.2 equiv.) in THF (20 mL), cooled to −50 °C, *n*-BuLi (2.90 mL, 2.4 M in hexanes, 6.90 mmol, 1.00 equiv.) was slowly added. The resulting yellow suspension was stirred and allowed to warm to 0 °C in approximately 45 minutes. After cooling to −30 °C, a premixed solution of an indole 3-carboxaldehyde (6.90 mmol, 1 equiv.) and LiHMDS (6.90 mL, 1.0 M in THF, 6.90 mmol, 1.00 equiv.), in THF (8.00 mL) was added. The resulting suspension was then stirred at room temperature for 1 h, then poured onto H_2O and extracted with EtOAc (2×). The combined organic phases were dried (Na_2SO_4), filtered and evaporated. The crude residue was then purified by a short chromatography on silica gel (petroleum ether/ethyl acetate 9 : 1) to obtain the corresponding product as a white solid; 0.90 g, 6.28 mmol; 91% yield; mp 84–86 °C (Lit. 80–81 °C), ^{1}H NMR (500 MHz, DMSO-d_6), δ 11.19 (s, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.48 (s, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.12 (t, J = 7.0 Hz, 1H), 7.05 (t, J = 8.0 Hz, 1H), 6.86 (dd, J = 18.0, 11.5 Hz, 1H), 5.61 (d, J = 17.5 Hz, 1H), 5.04 (d, J = 11.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6), δ 137.3, 130.7, 125.9, 125.6, 120.0, 119.97, 119.95, 114.3, 112.2, 109.4.

Carboxylation of alkenes

Procedures for the carboxylation of arylvinyls. Styrene (52 mg, 0.50 mmol, 1.00 equiv.), CBr_4 (331 mg, 1.00 mmol, 2.00 equiv.), 10 mol% eosin Y disodium (31 mg, 0.05 mmol) and CoI_2 (156 mg, 0.50 mmol, 1.00 equiv.) and 1 mL DMSO were combined in dried flask. The solution was stirred at 50 °C for 15 h on the condition of visible light (18 W fluorescent lamp) under nitrogen. After cooling to room temperature, the reaction mixture was extracted with ethylacetate (20.00 mL × 3) and then washed with brine (20.00 mL). The organic layer was dried over anhydrous Na_2SO_4 followed by filtration and then condensation. The residue was purified by silica gel column chromatography to afford corresponding product **2a** and intermediate **3a**.

Cinnamic acid (2a).[23] Following the general procedure: white solid; 53 mg, 0.36 mmol; 72% yield; mp 134–136 °C (Lit. 133–135 °C); R_f = 0.51 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (500 MHz, DMSO-d_6), δ 12.39 (brs, 1H), 7.67–7.64 (m, 2H), 7.59 (d, J = 16.0 Hz, 1H), 7.42–7.37 (m, 3H), 6.52 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6), δ 168.1, 144.4, 134.7, 130.7, 129.4, 128.7, 119.7; MS (ESI): m/z (% relative intensity) = 147.0 (100) $(M - H)^-$.

(*E*)-3-(*o*-Tolyl)acrylic acid (2b).[24] Following the general procedure using 2-methylstyrene in place of styrene: white solid; 62 mg, 0.23 mmol; 45% yield; mp 184–185 °C (Lit. 175–176 °C); R_f = 0.46 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, J = 15.6 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.26–7.22 (m, 2H), 6.39 (d, J = 16.2 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.3, 144.7, 138.0, 133.0, 130.9, 130.5, 126.65, 126.5, 118.2, 19.8; MS (ESI): m/z (% relative intensity) = 161.1 (100) $(M - H)^-$.

(*E*)-3-(*m*-Tolyl)acrylic acid (2c).[25] Following the general procedure using 3-methylstyrene in place of styrene: white solid; 102 mg, 0.37 mmol; 74% yield; mp 115–117 °C (Lit. 116–118 °C); R_f = 0.42 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.77 (d, J = 15.6 Hz, 1H), 7.36 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H), 7.23 (d, J = 7.2 Hz, 1H), 6.45 (d, J = 16.2 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$), δ 172.6, 147.3, 138.7, 134.0, 131.6, 129.0, 128.9, 125.6, 117.1, 21.3; MS (ESI): m/z (% relative intensity) = 161.0 (100) $(M - H)^-$.

(*E*)-3-(*p*-Tolyl)acrylic acid (2d).[24] Following the general procedure using 4-methylstyrene in place of styrene: white solid; 92 mg, 0.34 mmol; 67% yield; mp 190–192 °C (Lit. 199–200 °C); R_f = 0.45 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (500 MHz, DMSO-d_6), δ 7.56–7.52 (m, 3H), 7.20 (d, J = 8.0 Hz, 2H), 6.44 (d, J = 16.0 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6), δ 168.1, 144.4, 140.6, 131.9, 129.9, 128.6, 118.5, 21.4; MS (ESI): m/z (% relative intensity) = 161.1 (100) $(M - H)^-$.

(*E*)-3-(4-Fluorophenyl)acrylic acid (2e).[24] Following the general procedure using 4-fluorostyrene in place of styrene: white solid; 38 mg, 0.23 mmol; 46% yield; mp 198–200 °C (Lit. 205–207 °C); R_f = 0.41 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.38 (brs, 1H), 7.78–7.73 (m, 2H), 7.58 (d, J = 16.0 Hz, 1H), 7.24 (t, J = 9.0 Hz, 2H), 6.49 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6), δ 168.0, 163.6 (d, $^2J_{CF}$ = 246.3 Hz), 143.1, 131.3 (d, J = 3.1 Hz), 131.0 (d, J = 8.5 Hz), 119.6 (d, J = 2.4 Hz), 116.3 (d, J = 21.2 Hz); ^{19}F NMR (470 MHz, DMSO-d_6), δ − 110.44 (m, 1F); MS (ESI): m/z (% relative intensity) = 165.0 (100) $(M - H)^-$.

(*E*)-3-(4-Chlorophenyl)acrylic acid (2f).[25] Following the general procedure using 1-chlorostyrene in place of styrene: white solid; 56 mg, 0.30 mmol; 60% yield; mp 241–243 °C (Lit. 247–249 °C); R_f = 0.38 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (500 MHz, DMSO-d_6), δ 12.50 (brs, 1H), 7.76 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 16.0 Hz, 1H), 7.51 (d, J = 8.5 Hz, 2H), 6.59 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6), δ 167.8, 143.0, 135.1, 133.7, 130.4, 129.4, 120.5; MS (ESI): m/z (% relative intensity) = 181.0 (100) $(M - H)^-$.

(*E*)-3-(4-Bromophenyl)acrylic acid (2g).[26] Following the general procedure using 4-bromostyrene in place of styrene: white solid; 56 mg, 0.30 mmol; 60% yield; mp 255–256 °C (Lit. 264–265 °C); R_f = 0.43 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (500 MHz, DMSO-d_6), δ 7.65 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 16.0 Hz, 1H), 6.55 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6), δ 167.8, 143.1, 134.0, 132.3, 130.6, 124.0, 120.6; MS (ESI): m/z (% relative intensity) = 226.9 (100) $(M - H)^-$

(*E*)-3-(4-Methoxyphenyl)acrylic acid (2h).[24] Following the general procedure using 4-methoxy styrene in place of styrene: white solid; 68 mg, 0.38 mmol; 76% yield; mp 170–171 °C (Lit. 175–176 °C); R_f = 0.40 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01), ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.23 (brs, 1H), 7.64 (d, J = 9.0 Hz, 2H), 7.55 (d, J = 16.2 Hz, 1H), 6.97 (d, J = 8.4 Hz, 2H), 6.38 (d, J = 16.2 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6), δ 167.8, 160.9, 143.7, 129.9, 126.8, 116.5, 114.3, 55.3; MS (ESI): m/z (% relative intensity) = 177.0 (100) $(M - H)^-$.

(*E*)-3-(3-Methoxyphenyl)acrylic acid (2i).[25] Following the general procedure using 3-methoxystyrene in place of styrene: white solid; 60 mg, 0.34 mmol; 67% yield; mp 110–112 °C (Lit.

117–119 °C); R_f = 0.43 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.77 (d, J = 16.2 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.15 (d, J = 7.2 Hz, 1H), 7.07 (s, 1H), 6.97 (dd, J = 7.8, 1.8 Hz, 1H), 6.45 (d, J = 15.6 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$), δ 172.3, 159.9, 147.1, 135.4, 130.0, 121.1, 117.6, 116.7, 113.2, 55.4; MS (ESI): m/z (% relative intensity) = 177.0 (100) $(M - H)^-$.

(*E*)-3-(3,4-Dimethoxyphenyl)acrylic acid (2j).[27] Following the general procedure using 3,4-dimethoxytyrene in place of styrene: white solid; 55 mg, 0.27 mmol; 53% yield; mp 189–191 °C (Lit. 191 °C); R_f = 0.34 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.73 (d, J = 16.0 Hz, 1H), 7.15 (dd, J = 8.0, 1.5 Hz, 1H), 7.08 (d, J = 1.5 Hz, 1H), 6.89 (d, J = 8.5 Hz, 1H), 6.33 (d, J = 16.0 Hz, 1H), 3.93 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$), δ 172.2, 151.5, 149.3, 147.0, 127.0, 123.1, 114.8, 111.0, 109.8, 56.0, 55.9; MS (ESI): m/z (% relative intensity) = 206.9 (100) $(M - H)^-$.

(*E*)-3-(4-(*tert*-Butyl)phenyl)acrylic acid (2k).[26] Following the general procedure using 4-(*tert*-butyl)styrene in place of styrene: white solid; 83 mg, 0.34 mmol; 68% yield; mp 202–203 °C (Lit. 202–204 °C); R_f = 0.46 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.79 (d, J = 15.9 Hz, 1H), 7.50 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 6.43 (d, J = 15.9 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$), δ 172.7, 154.4, 147.0, 131.3, 128.3, 126.0, 116.4, 35.0, 31.2; MS (ESI): m/z (% relative intensity) = 203.0 (100) $(M - H)^-$.

(*E*)-3-([1,1′-Biphenyl]-4-yl)acrylic acid (2l). Following the general procedure using 4-phenylstyrene in place of styrene: white solid; 50 mg, 0.20 mmol; 40% yield; mp 215–217 °C; R_f = 0.39 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (500 MHz, DMSO-d_6), δ 7.77 (d, J = 8.0 Hz, 2H), 7.73–7.69 (m, 4H), 7.63 (d, J = 16.0 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 8.0 Hz, 1H), 6.57 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6), δ 168.0, 143.9, 142.2, 139.7, 133.8, 129.5, 129.3, 128.4, 127.5, 127.1, 119.6; MS (ESI): m/z (% relative intensity) = 223.0 (100) $(M - H)^-$, HRMS (ESI): m/z calcd for $C_{15}H_{12}O_2$ $(M - H)^-$ 223.0765, found 223.0764.

(*E*)-3-(4-(Trifluoromethyl)phenyl)acrylic acid (2m).[28] Following the general procedure using 4-trifluoromethylstyrene in place of styrene: white solid; 66 mg, 0.31 mmol; 61% yield; mp 206–208 °C; R_f = 0.43 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (500 MHz, DMSO-d_6), δ 12.59 (brs, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 16.0 Hz, 1H), 6.67 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6), δ 167.6, 142.5, 138.7, 130.3 (q, J = 31.7), 129.3, 126.1 (q, J = 3.7 Hz), 124.5 (d, J = 271.3 Hz), 122.6; ^{19}F NMR (470 MHz, DMSO-d_6), δ − 61.28 (s, 3F); MS (ESI): m/z (% relative intensity) = 215.0 (100) $(M - H)^-$.

(*E*)-3-(Naphthalen-2-yl)acrylic acid (2p). Following the general procedure using 2-vinylnaphthalene in place of styrene: white solid; 61 mg, 0.31 mmol; 62% yield; mp 203–204 °C; R_f = 0.41 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (500 MHz, DMSO-d_6), δ 12.44 (brs, 1H), 8.17 (s, 1H), 7.96–7.91 (m, 3H), 7.88–7.84 (m, 1H), 7.74 (d, J = 16.0 Hz, 1H), 7.58–7.53 (m, 2H), 6.65 (d, J = 15.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6), δ 168.1, 144.4, 134.1, 133.3, 132.3, 130.1, 129.0, 128.9, 128.1, 127.7, 127.2, 124.4, 120.0; MS (ESI): m/z (% relative intensity) = 197.0 (100) $(M - H)^-$; HRMS (ESI): m/z calcd for $C_{13}H_{10}O_2$ $(M - H)^-$ 197.0608, found 197.0605.

(1,3,3,3-Tetrabromopropyl)benzene (3a).[29] Following the general procedure: white solid; 19 mg, 0.05 mmol; 9% yield; mp 55–57 °C; R_f = 0.63 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.53 (d, J = 7.3 Hz, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 5.38 (dd, J = 7.8, 4.0 Hz, 1H), 4.19–4.07 (m, 2H), ^{13}C NMR (125 MHz, $CDCl_3$), δ 140.8, 129.0, 128.9, 128.2, 66.5, 50.2, 35.3. MS (ESI): m/z (% relative intensity) = 437.0 (100) $(M + H)^+$.

1-Nitro-4-(1,3,3,3-tetrabromopropyl)benzene (3n). Following the general procedure: yellow oil; 60 mg, 0.13 mmol; 25% yield; R_f = 0.59 (petroleum ether : ethyl acetate = 9 : 1); ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.24 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 5.38 (dd, J = 8.5, 3.5 Hz, 1H), 4.18–4.02 (m, 2H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 147.5, 129.3, 124.1, 66.0, 47.4, 34.0. MS (ESI): m/z (% relative intensity) = 477.7 (100) $(M + H)^+$; HRMS (ESI): m/z calcd for $C_{13}H_{10}O_2$ $(M + H)^+$ 477.7283, found 477.7282.

4-(1,3,3,3-Tetrabromopropyl)benzonitrile (3o). Following the general procedure: yellow oil; 80 mg, 0.13 mmol; 35% yield; R_f = 0.55 (petroleum ether : ethyl acetate = 9 : 1); ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.67 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H), 5.32 (dd, J = 8.5, 3.5 Hz, 1H), 4.14–3.99 (m, 2H), ^{13}C NMR (126 MHz, $CDCl_3$), δ 145.6, 132.7, 129.0, 118.2, 112.8, 65.9, 47.9, 34.1. MS (ESI): m/z (% relative intensity) = 457.7 (100) $(M + H)^+$; HRMS (ESI): m/z calcd for $C_{13}H_{10}O_2$ $(M + H)^+$ 457.7283, found 457.7385.

Carboxylation of substituted arylvinyls

(*E*)-2,3-Diphenylacrylic acid (5a).[30] Following the general procedure using (*E*)-1,2-diphenylethene in place of styrene. The reaction was stirred at 100 °C for 6 h: white solid; 40 mg, 0.18 mmol; 36% yield; mp 170–171 °C (Lit. 171–172 °C); R_f = 0.41 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.72 (brs, 1H), 7.76 (s, 1H), 7.39–7.34 (m, 3H), 7.24–7.13 (m, 5H), 7.04 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.8, 139.4, 136.8, 134.9, 133.8, 130.6, 129.9, 129.5, 128.9, 128.7, 128.0; MS (ESI): m/z (% relative intensity) = 223.0 (100) $(M - H)^-$.

(*E*)-2,3-Diphenylacrylic acid (5a′). Following the general procedure using (*Z*)-1,2-diphenylethene in place of styrene. The reaction was stirred at 100 °C for 6 h: white solid; 17 mg, 0.08 mmol; 15% yield; mp 170–171 °C (Lit. 171–172 °C); R_f = 0.41 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.71 (brs, 1H), 7.75 (s, 1H), 7.40–7.34 (m, 3H), 7.24–7.14 (m, 5H), 7.04 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.8, 139.4, 136.8, 134.9, 133.8, 130.6, 129.9, 129.5, 128.9, 128.7, 128.0; MS (ESI): m/z (% relative intensity) = 223.0 (100) $(M - H)^-$.

(*E*)-3-Phenyl-2-(4-(trifluoromethyl)phenyl)acrylic acid (5b). Following the general procedure using (*Z*/*E*)-1-styryl-4-(trifluoromethyl)benzene in place of styrene. The reaction was stirred at 100 °C for 6 h: white solid; 32 mg, 0.11 mmol; 22% yield; mp 192–194 °C; R_f = 0.45 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.65 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 143.6, 139.1, 133.7, 130.7, 130.4,

130.1, 129.9, 128.5, 125.6 (d, J = 3.4 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ − 62.61 (s, 3F); MS (ESI): m/z (% relative intensity) = 291.0 (100) $(M - H)^-$; HRMS (ESI): m/z calcd for $C_{16}H_{11}F_3O_2$ $(M - H)^-$ 291.0638, found 291.0638.

(*E*)-2-(4-Nitrophenyl)-3-phenylacrylic acid (5c). Following the general procedure using (*E*)-1-nitro-4-styrylbenzene in place of styrene. The reaction was stirred at 100 °C for 6 h: white solid; 32 mg, 0.11 mmol; 22% yield; mp 220–223 °C; R_f = 0.34 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, J = 8.5 Hz, 2H), 8.08 (s, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 1H), 7.22 (t, J = 8.0 Hz, 2H), 7.06 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 147.6, 144.4, 142.3, 133.3, 131.2, 130.7, 130.3, 129.4, 128.6, 123.9; MS (ESI): m/z (% relative intensity) = 268.0 (100); HRMS (ESI): m/z calcd for $C_{15}H_{11}NO_4$ $(M - H)^-$ 268.0615, found 268.0614.

(*E*)-2-Methyl-3-phenylacrylic acid (5d). Following the general procedure using (*Z*/*E*)-prop-1-en-1-ylbenzene in place of styrene. The reaction was stirred at 100 °C for 6 h: white solid; 20 mg, 0.13 mmol; 25% yield; mp 59–61 °C; R_f = 0.41 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01); ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.52 (brs, 1H), 7.60 (s, 1H), 7.48–7.42 (m, 4H), 7.36 (t, J = 5.5 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 169.3, 137.6, 135.5, 129.6, 128.7, 128.5, 128.4, 13.9; MS (ESI): m/z (% relative intensity) = 161.0 (100) $(M - H)^-$; HRMS (ESI): m/z calcd for $C_{10}H_{10}O_2$ $(M - H)^-$ 161.0680, found 161.0680.

3,3-Diphenylacrylic acid (5e).[31] Following the general procedure using (*Z*/*E*)-prop-1-en-1-ylbenzene in place of styrene: white solid; 68 mg, 0.38 mmol; 76% yield; mp 146–148 °C (Lit. 158 °C); R_f = 0.44 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01). ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.15 (brs, 1H), 7.40–7.33 (m, 6H), 7.27–7.22 (m, 2H), 7.15–7.12 (m, 2H), 6.35 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.2, 154.1, 141.0, 139.3, 129.7, 129.4, 129.0, 128.3, 119.3; MS (ESI): m/z (% relative intensity) = 223.0 (100) $(M - H)^-$.

1*H*-Indene-2-carboxylic acid (5f).[32] Following the general procedure using (*Z*/*E*)-prop-1-en-1-ylbenzene in place of styrene: white solid; 50 mg, 0.32 mmol; 63% yield; mp 233–235 °C; R_f = 0.46 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01). ^{1}H NMR (500 MHz, DMSO-d_6) 7.68 (s, 1H), 7.61–7.56 (m, 1H), 7.55–7.52 (m, 1H), 7.35–7.31 (m, 2H), 3.62 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.1, 145.1, 143.0, 140.6, 138.9, 127.7, 127.2, 124.8, 123.8, 38.6; MS (ESI): m/z (% relative intensity) = 159.0 (100) $(M - H)^-$.

(*E*)-3-(Thiophen-2-yl)acrylic acid (5g).[33] Following the general procedure using 2-vinylthiophene in place of styrene: white solid; 45 mg, 0.29 mmol; 58% yield; mp 143–147 °C (Lit. 140–142 °C); R_f = 0.44 (hexane : ethyl acetate : acetic acid = 2 : 2 : 0.01). ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.43 (brs, 1H), 7.73 (d, J = 16.0 Hz, 1H), 7.68 (d, J = 10.0 Hz, 1H), 7.49 (d, J = 3.0 Hz, 1H), 7.14–7.11 (m, 1H), 6.17 (d, J = 16.0 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.98, 139.18, 137.35, 132.19, 129.96, 129.03, 117.66. MS (ESI): m/z (% relative intensity) = 153.0 (100) $(M - H)^-$.

^{18}O Labeling experiment

^{18}O Labeled H_2O experiment. Styrene (26 mg, 0.25 mmol, 1.00 equiv.), CBr_4 (166 mg, 0.50 mmol, 2.00 equiv.), 10 mol% eosin Y disodium (15 mg, 0.03 mmol), CoI_2 (78 mg, 0.25 mmol, 2.00 equiv.), ^{18}O–H_2O (45 mg, 5.00 mmol, 10.00 equiv.) and 0.50 mL DMSO were combined in dried flask. The solution was stirred at 50 °C for 15 h on the condition of visible light (18 W fluorescent lamp) under nitrogen. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (10.00 mL × 3) and then washed with brine (10.00 mL). The organic layer was dried over anhydrous Na_2SO_4 followed by filtration and then condensation. The residue was purified by silica gel column chromatography to afford the corresponding product. ESI-ms analysis of this product clearly assigned the presence of both compounds **2a** (M^- at 147.0) and ^{18}O-**2a** (M^- at 149.0) in noticeable amount.

Method for preparation of ^{18}O labeled DMSO.[34] Solid dimethylsulfur dibromide (5.00 g, 22.50 mmol, 1.00 equiv.) prepared as per known procedure[35] was added portion wise over 15 min to a vigorously stirred solution of triethylamine (6.30 mL, 45.00 mmol, 2.00 equiv.) freshly distilled from calcium hydride and ^{18}O-labeled water (97 atom% ^{18}O) (0.20 mL, 11.00 mmol, 0.50 equiv.) in 15.00 mL of tetrahydrofuran (freshly distilled from sodium metal). The temperature of the reaction was maintained below 50 °C. The precipitate of triethylamine hydrobromide was removed by centrifugation and washed twice with ether. The combined yellow supernatant and washings were dried on high vacuum pressure pump at room temperature (15 mm) to remove the solvent and was given 0.50 g of a brownish black liquid. Without further purification the reaction was performed styrene (26 mg, 0.25 mmol, 1.00 equiv.), CBr_4 (166 mg, 0.50 mmol, 2.00 equiv.), 10 mol% eosin Y disodium (15 mg, 0.03 mmol), CoI_2 (78 mg, 0.25 mmol, 2.00 equiv.) following the general procedure giving the corresponding product **2a**. ESI-ms analysis of this product clearly assigned the presence of both compounds **2a** (M^- at 147.0), ^{18}O-**2a** (M^- at 149.0) and $^{18}O_2$-**2a** (M^- at 151.0) in noticeable amount.

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