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OXOFUNCTIONALIZED *TRANS*-2-CARBOXYCINNAMIC ACIDS BY CATALYTIC DOMINO OXIDATION OF NAPHTHOLS AND HYDRONAPHTHOQUINONES

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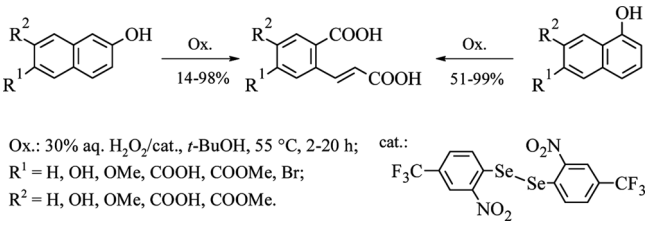
GRAPHICAL ABSTRACT



Abstract *The catalytic oxidation of naphthalenes was investigated. Hydrogen peroxide (30% aqueous) was used as an oxygen source, and 2,2′-dinitro-4,4′-ditrifluoromethyldiphenyl diselenide was the oxygen-transfer catalyst. Unsubstituted naphthols produce trans-2-carboxycinnamic acid in nearly quantitative yields. Both naphthols bearing substituents on the conjugated ring deliver corresponding trans-2-carboxycinnamic acids in good to excellent yields. The 1,7- and 2,6-hydronaphthoquinones, substituted by carboxy and carboxymethyl groups, produce hydroxycinnamic acids in satisfactory to excellent yields. A catalytic domino reaction mechanism is proposed.*

Keywords Catalysis; cinnamic acids; domino reaction; naphthalenes; oxidation; selenium

INTRODUCTION

Oxofunctionalized cinnamic acids conjugated to sugar, amine, and phenol moieties have been found in a large number of natural products with diverse physiological properties.[1–4] Some of them have a broad range of antioxidant, antibacterial, antifungal, antiviral, anti-inflammatory, and anticarcinogenic activities in vitro and in vivo.[3–7] They are important synthetic targets as well as useful building blocks.[3–14] Although various cinnamic acids can be obtained in several different ways, there is a lack of general method for synthesis of free *trans*-2-carboxycinnamic acids oxofunctionalized on remote ring carbon atoms.[9–14]

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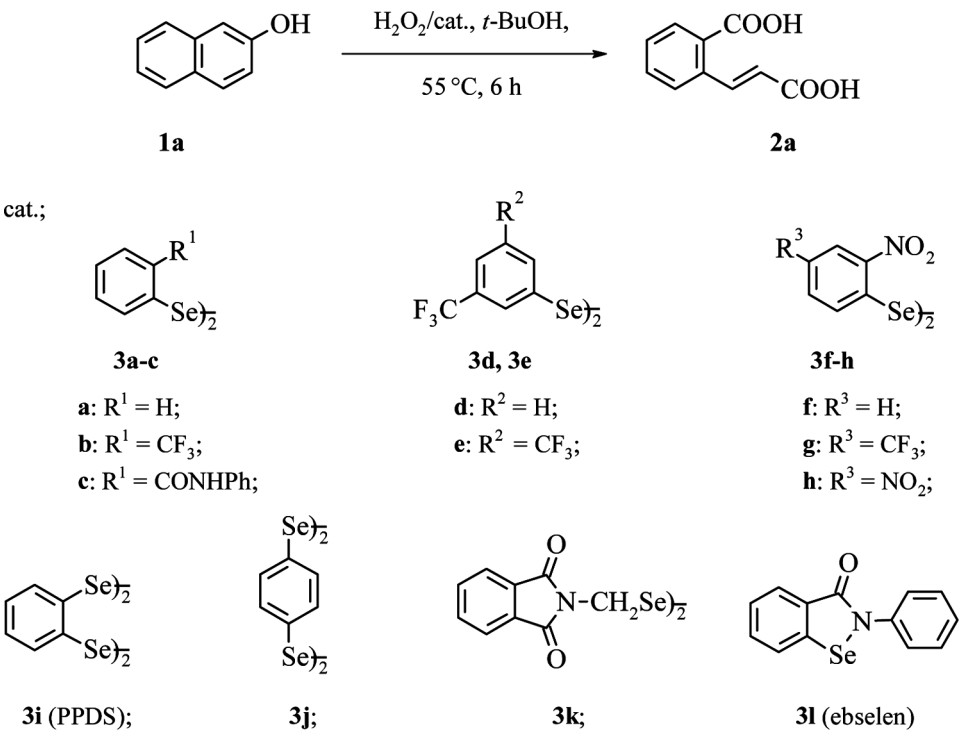
Simple carboxycinnamic acids were obtained in yields greater than 89% via palladium-catalyzed coupling of aryl halides with acrylic acid, but cinnamic acid, with steric hindrance of the carboxy group at the 2 position at the benzene ring, was formed in the lowest yield.[10] Recently, 2-carboxycinnamic acid has been reported as a bioconversion product of *Bacillus thermoleovorans* grown on naphthalene and condensation of Meldrum's acid with 2-carboxybenzaldehyde.[11] Its 5- and 4-methoxy derivatives were prepared in moderate yields by oxidation of 6- and 7-methoxy-2-naphthols with hazardous 93% hydrogen peroxide (H_2O_2) in acetic acid.[12] When safe diluted 6–9% peroxyacetic acid was used, *trans* 5-hydroxy- and 5-methoxy-2-carboxycinnamic acids were obtained in poor yields.[13]

All these methods have issues related to the use of transition metal or to the production of a large amount of inorganic or organic waste. Particularly interesting are one-step naphthol catalytic oxidation methodologies that involve the use of hydrogen peroxide as stoichiometric "green" oxidant, because they generate the water as the only reduction product; the organoselenium compounds which were successfully applied during recent decades as green reagents, and useful oxidation reaction catalysts such as selenium-containing glutathione peroxidase, which catalyzes the reduction of peroxides in living cells.[15]



Scheme 1. Oxidation of 2-naphthol (**1a**).

RESULTS AND DISCUSSION

In this work, we present a versatile general method for synthesis of *trans*-2-carboxycinnamic acids oxofunctionalized on the benzene ring at remote carbons. It is based on catalytic 30% aqueous hydrogen peroxide domino oxidation of naphthols and hydronaphthoquinones with atom economy.[16]

In our previous work, we reported a facile method for preparation of *trans*-2-carboxycinnamic acid by oxidation of both unsubstituted naphthols with H_2O_2 activated by a catalytic amount of poly-1,2-diphenylenediselenide (PPDS).[17] Employment of the selenium catalyst was based on the known fact that diaryl diselenides are oxidized in situ with hydroperoxides to areneseleninic acids, the proper catalysts.[16] They act via areneseleninic anhydride[18] and areneperoxyseleninic acid[19] as highly active electrophilic oxidants.[16,20]

More recently, the reagents aqueous H_2O_2/diaryl diselenides were applied successfully for preparative functional-group transformations,[19–23] 2-aminophenol cyclocondensation to questiomycin A,[24] phenol ring rearrangement to

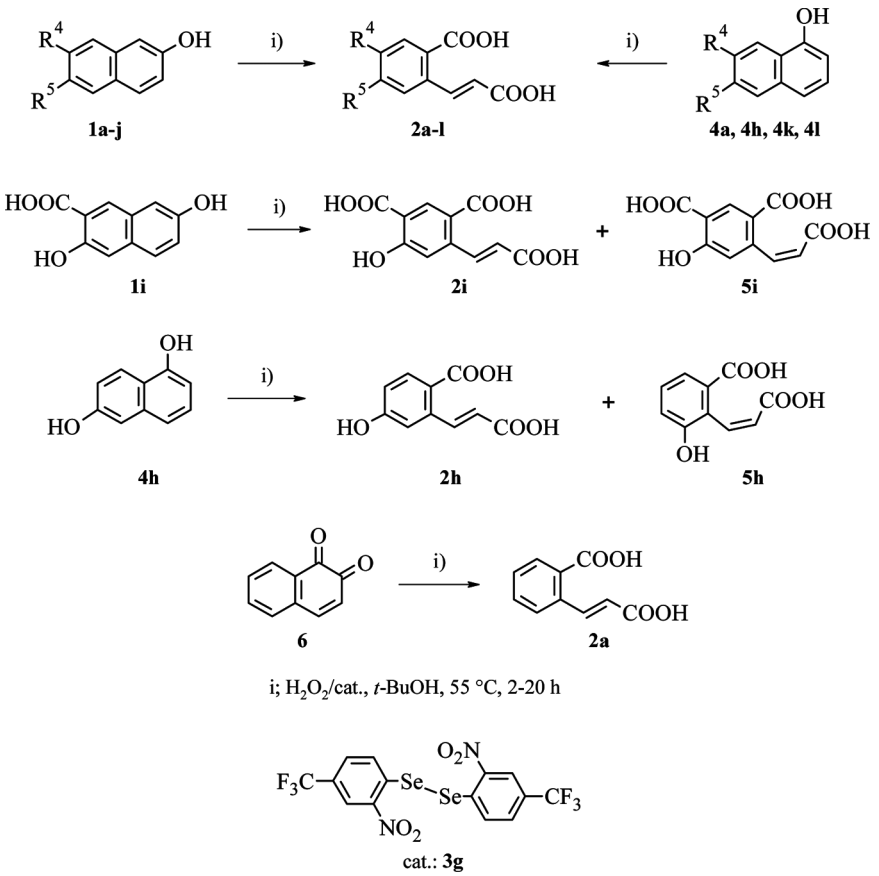
Table 1. Results of oxidative conversion of 2-naphthol (**1a**) into *trans*-2-carboxycinnamic acid (**2a**) with H_2O_2/solvent/catalyst systems

Catalyst	Solvent	Product **2a** yield (%)[a]	Mp (°C)[b]
None	*t*-BuOH	—[c]	—
MTO	*t*-BuOH	(27)	—
$Na_2WO_4 \times 2H_2O$	*t*-BuOH	51	187–190
$(NH_4)_6Mo_7O_{24} \times 4H_2O$	*t*-BuOH	45	187–190
SeO_2	*t*-BuOH	54	197–198
3a	*t*-BuOH	60	191–195
3b	*t*-BuOH	80	208–209
3c	*t*-BuOH	93	191–193
3d	*t*-BuOH	59	187–189
3e	*t*-BuOH	66	196–198
3f	*t*-BuOH	100[d]	196–198
3g	*t*-BuOH	100	202–203
3g	CF_3CH_2OH	92	200–202
3g	AcOH	77	196–198
3g	HCOOH	61	196–198
3g	Acetone	(27)[c]	—
3g	THF	(20)[c]	—
3g	CH_3OH	(4)[c]	—
3g	1,4-Dioxane	(4)[c]	—
3g	CH_3CN	(3)[c]	—
3h	*t*-BuOH	63	195–197
3i	*t*-BuOH	73	205–208
3j	*t*-BuOH	55	198–200
3k	*t*-BuOH	55	191–192
3l	*t*-BuOH	75	199–201

[a]Preparative yield. Data in parantheses refer to the yield determined by ^{1}H NMR.
[b]Ref. [17]: mp 204–205 °C; ref. [46]: mp 170.5–205 °C.
[c]Unreacted substrate **1a** was isolated in 70–95% yield.
[d]Yellow solid was formed.

muconolactones,[25] and 4-phenylcyclohexanone ring contraction to 3-phenylcyclopentanecarboxylic acid, a new inhibitor of steroid-metabolizing enzymes.[26]

We have found that oxidation of 2-hydroxynaphthalene (**1a**) with aqueous H_2O_2 (30%) in *tert*-butanol under mild reaction conditions, in the presence of different catalysts, gave the *trans*-2-carboxycinnamic acid (**2a**). Inorganic sodium tungstate, methyltrioxorhenium(VII) (MTO), ammonium molybdate, selenium(IV) oxide, and 12 different organoselenium compounds [diphenyl diselenides **3a–j**, dimethyl diselenide **3k**, and ebselen (**3l**)] were tested as catalysts (Scheme 1). They were used in 5.0% molar ratio to substrate **1a**. No reaction was observed without a catalyst. Among inorganic catalysts, only selenium(IV) oxide gave pure *trans*-2-carboxycinnamic acid in moderate 54% yield. Preparative yields of the desired **2a** increased when organoselenium compounds **3a–l**, listed in Table 1, were utilized. Diphenyl diselenides **3f** and **3g**, having two nitro groups at the 2 and 2′ positions, exhibited great catalytic activity. When **3g**, which has two different electron-withdrawing substituents at the benzene ring, the nitro and trifluoromethyl groups, was a catalyst, **2a** was produced in pronounced purity. Reactions in media other than *tert*-butanol were sluggish and less selective, with 2,2,2-trifluoroethanol as the single exception (Table 1).



Scheme 2. Oxidative conversion of 2-naphthols **1** and 1-naphthols **4** to *trans*-2-carboxycinnamic acid **2a–l**.

It should be noted that 2,2′-dinitro-4,4′-di(trifluoromethyl)diphenyl diselenide (**3g**) is easily prepared via selenenylation of an inexpensive, commercially available 1-chloro-2-nitro-4-trifluoromethylbenzene with dilithium diselenide[25,27] and was recently utilized in our laboratory as a catalyst for H_2O_2 domino transformations of the aromatic ring in phenols.[25]

In this work, the elaborated reagent H_2O_2/**3g** was successfully applied for preparative oxidations of 13 substituted naphthalenes (**1a–g, 1i, 1j, 4a, 4h, 4k**, and **4l**) to corresponding *trans*-2-carboxycinnamic acids **2a–l**, accompanied by minute amounts of *cis*-cinnamic acids **5i** and **5h** in two cases. Although the results strongly depend on the structure of naphthalenes, the reaction has synthetic value because of good selectivity and moderate to good yields of the desired cinnamic acids. The substrates used were naphthalene, its mono-substituted derivatives, and both naphthols having both electron-donating and electron-withdrawing substituents at remote carbon atoms on conjugated benzene rings.

The reaction conditions were optimized. It was found that precatalyst **3g** could be used in 5.0% molar relation to the substrate. The reaction was faster and the products were less colored when the molar ratio of H_2O_2 to the substrate was 5:1. The reaction was carried out in *tert*-butanol at 55 °C for 2 h to 20 h depending on the substrate used. The results are presented in Scheme 2 and Table 2.

Naphthalene and both naphthoic acids remained resistant toward oxidation with H_2O_2/**3g** in *tert*-butanol at reflux. All 1- and 2-methyl, methoxy, formyl, and acetyl naphthalenes were oxidized to a mixture of naphthoic acids, menadione, 3-carboxymethylbenzofuranone, naphthyl acetates, and cinnamic acids. Interestingly, the electron-donating hydroxyl group on both naphthols **1a** and **4a** activated

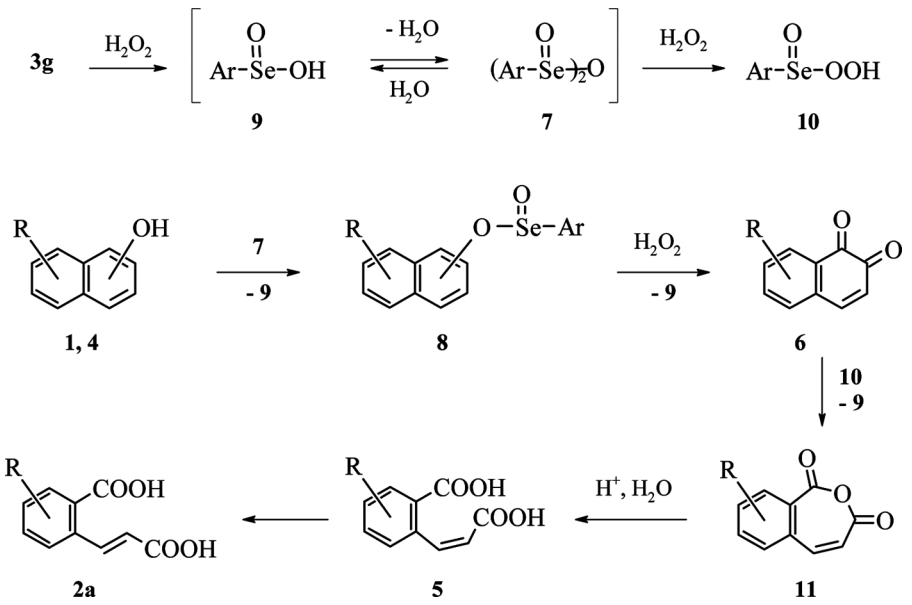
Table 2. Results of catalytic domino oxidation of 2-naphthols **1** and 1-naphthols **4** to *trans*-2-carboxycinnamic acids **2**

Substrate	R^4	R^5	Reaction time (h)	Product	Yield (%)[a]
1a	H	H	2	**2a**	98
1b	OH	H	20	**2b**	86
1c	OCH_3	H	20	**2c**	63
1d	H	OCH_3	20	**2d**	68
1e	H	COOH	20	**2e**	90 (94)
1f	H	$COOCH_3$	20	**2f**	66 (87)
1g	H	Br	20	**2g**	75
1h	H	OH	20	**2h**	—[b]
1i	COOH	OH	20	**2i**	(14)
				5i	(7)
1j	$COOCH_3$	OH	20	**2j**	75
4a	H	H	6	**2a**	99
4h	H	OH	20	**2h**	(51)
				5h	(13)
4k	OH	COOH	20	**2k**	98
4l	OH	$COOCH_3$	20	**2l**	86
6	—	—	4	**2a**	81[c]

[a]Preparative yield. Data in parantheses refer to the yield determined by ^{1}H NMR.
[b]Mixture of polymeric 2,6-naphthoquinone was formed.
[c]1.5 eq. of H_2O_2 was used.

substrates, and the desired *trans*-2-carboxycinnamic acid (**2a**) was formed almost quantitatively. When 2-naphthols **1b–g** with second hydroxyl, methoxy, carboxy, carboxymethyl, or bromine groups at 6 and 7 position were oxidized, 4- and 5-substituted *trans*-2-carboxycinnamic acids **2b–g** were formed in good yields. 2-Carboxy-5-hydroxycinnamic acid **2h** was not formed from dihydroxynaphthalene **1h** but electron-withdrawing carboxy and carboxymethyl substituents, on **1i, 1j**, and **4k, 4l**, stabilized the hydronaphthoquinone molecules, and 5- and 4-hydroxycinnamic acids **2i, 2j**, and **2k, 2l**, were formed in poor to almost quantitative yields, respectively. When 1,6-dihydroxynaphthalene (**4h**), having both nonequivalent hydroxyl groups free, was oxidized to 5- and 6-substituted 2-carboxycinnamic acids **2h** and **5h**, the desired *trans*-2-carboxy-5-hydroxycinnamic acid (**2h**) was a major product. An additional experiment showed that oxidation of the naphthoquinone **6** intermediate gave acid **2a**, the same as obtained from corresponding naphthols **1a** and **4a** (Scheme 2, Table 2).

Taking into consideration our earlier experiments of oxidation of hydroxylated benzene rings,[17,25] the nature the selenium(IV) reagent,[18–20,28] and the results presented in this work, the domino reaction sequence shown in Scheme 3 is proposed. Initially, both naphthols **1** and **4** are *O*-selenenylated, by generated in situ seleninic anhydride **7** produced from diselenide **3g** and H_2O_2. Seleninyl esters **8** undergo 2,3-sigmatropic rearrangement to selenoates, which upon H_2O_2 oxidation yield the key intermediate, 1,2-naphthoquinone (**6**), while seleninic acid **9** is recovered. Peroxyseleninic acid **10** promoted Baeyer–Villiger oxidation of intermediate **6**, and then consecutive ring opening of 2-carboxycinnamic acid anhydride (**11**) and isomerization of **5** finally give the stable *trans*-2-carboxycinnamic acids **2** (Scheme 3).



Scheme 3. Plausible reaction sequence from hydroxylated naphthalenes **1** and **4** to *trans*-2-carboxycinnamic acids **2**.

CONCLUSION

In conclusion, 1- and 2-hydroxynaphthalenes **1** and **4** can be converted by oxidation with 30% aqueous H_2O_2 in the presence of 2,2′-dinitro-4,4′-di(trifluoromethyl)diphenyl diselenide (**3g**) as a catalyst to *trans*-2-carboxycinnamic acids **2** with an atom-economical protocol. It is the first case of the general, regioselective oxidative domino[29] conversion of inexpensive and easily available naphtholic precursors to *trans*-2-carboxycinnamic acids oxofunctionalized on remote ring carbons to carboxy and carboxyethylenyl groups.

EXPERIMENTAL

Melting points were determined on a digital melting-point apparatus, Electrothermal IA 91100. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were measured with a Bruker DRX 300 spectrometer. Infrared (IR) was measured on a Perkin-Elmer 2000 Fourier transform (FT) spectrometer.

Aqueous hydrogen peroxide (30%), selenium(IV) oxide, diphenyl diselenide (**3a**), *tert*-butanol, silica gel (70–230 mesh), and other commercially available reagents and solvents were purchased from Aldrich or Fluka. The catalysts **3b** and **3d–k** were obtained by selenenylation of the corresponding haloarenes or *N*-(chloromethyl) phthalimide.[16,25,30,31] 2,2′-Dicarbamoylphenyldiphenyl diselenide (**3c**) and ebselen (**3l**) were obtained from anthranilic acid and elementary selenium using a modified literature procedure.[32] The methyl esters **1f, 1j**, and **4l** were prepared by refluxing the respective naphthoic acid starting materials **1e, 1i**, and **4k** in dry methanol in the presence of H_2SO_4. The purity of the products was confirmed by comparison of their melting points with data given in the literature for **1f**,[33] **1j**,[34] **1l**,[35] **2a**,[17] **2b**,[36] **2c**,[12] **2d**,[12] **2g**,[14] and **2h**[13] and by measuring their ^{1}H NMR, ^{13}C NMR, and IR spectra. Because some physicochemical data reported in the previous papers are incorrect, we revised them carefully. The desired new compounds **2e, 2f**, and **2i–l** were fully characterized.

Methyl 2-Naphthoates (1f, 1j, 4l)

Preparation. Concentrated H_2SO_4 (0.50 ml) was added dropwise to a magnetically stirred solution of corresponding 2-carboxyhydroxynaphthalene (**1e, 1i, 4k**) (10.0 mmol) in dry methanol (25 ml), and the reaction mixture was gently refluxed for 10 h. The solvent was removed in vacuum, diethyl ether was added (200 ml), and the organic layer was washed with cold water (2×25 ml), several times with 2.5% aqueous $NaHCO_3$ solution, brine, and water. After drying over anhydrous Na_2SO_4, the solvent was distilled off to give the crude product almost quantitatively. The esters were characterized.

Methyl 6-hydroxy-2-naphthoate (1f). Recrystallization from chloroform gave colorless powder (1.47 g, 7.27 mmol, 73%). Mp 173–175 °C (170 °C[33]). ^{1}H NMR ($CDCl_3$)[33]: 8.54 (s, 1H, H-1), 8.01 (dd, $J = 8.6$, 1.5 Hz, 1H, H-3), 7.86 (d, $J = 8.6$ Hz, 1H, H-8), 7.70 (d, $J = 8.6$ Hz, 1H, H-4), 7.19 (s, 1H, H-5), 7.17 (dd, $J =$ 8.6, 2.4 Hz, H-7), 5.60 (s, 1H, OH), 3.97 (s, 3H, OCH_3). IR (KBr): $\gamma = 3419\ cm^{-1}$ (OH), 2953 cm^{-1} (CH_3), 1684 cm^{-1} (C=O), 1206, 1100 cm^{-1} (C–O).

Methyl 3,7-dihydroxy-2-naphthoate (1j). Mp 170–172 °C ($CHCl_3$). ^1H NMR[34] (DMSO-d_6): 9.98 (s, 1H, OH), 9.65 (s, 1H, OH), 8.26 (s, 1H, H-1), 7.63 (d, $J = 8.6$ Hz, 1H, H-5), 7.24 (s, 1H, H-4), 7.17 (s, 1H, H-8), 7.15 (dd, $J = 8.6$, 2.2 Hz, 1H, H-6), 3.93 (s, 3H, OCH_3). IR (KBr): $\gamma = 3340\ cm^{-1}$ (OH), $2954\ cm^{-1}$ (CH_3), $1683\ cm^{-1}$ (C=O), 1266, 1218, $1074\ cm^{-1}$ (C–O).

Methyl 3,5-dihydroxy-2-naphthoate (4l).[35] Recrystallization from methanol–water (12 ml, 2:1) gave green-yellow prisms (2.11 g, 9.67 mmol, 97%). Mp 167–169 °C. ^1H NMR (DMSO-d_6): 10.15 (s, 1H, OH), 10.08 (s, 1H, OH), 8.37 (s, 1H, H-1), 7.50 (s, 1H, H-4), 7.40 (d, $J = 8.3$ Hz, 1H, H-8), 7.16 (dd, $J = 8.3$, 7.4 Hz, 1H, H-7), 6.89 (d, $J = 7.4$ Hz, 1H, H-6), 3.93 (s, 3H, OCH_3). ^{13}C NMR (DMSO-d_6): 168.7, 154.1, 151.5, 128.6, 127.9, 116.1 (C), 131.7, 124.3, 119.6, 110.3, 106.0 (CH), 52.5 (CH_3). IR (KBr): $\gamma = 3510$, $3442\ cm^{-1}$ (OH), $2957\ cm^{-1}$ (CH_3), $1698\ cm^{-1}$ (C=O), 1277, 1181, $1096\ cm^{-1}$ (C–O).

Catalyst Evaluation

A catalyst [MTO, $Na_2WO_4 \times 2H_2O$, $(NH_4)_6Mo_7O_{24} \times 4H_2O$, SeO_2, or selenoorganic compounds **3a–l** (0.250 mmol, 5.00 mol%)] was added to a solution of 2-hydroxynaphthalene (**2a**) (0.721 g, 5.00 mmol) in *tert*-butanol (20 ml) and H_2O_2 (2.5 ml, 25 mmol). The reaction mixture was stirred at 55 °C for 6 h, and then the mixture was treated with a pinch of Pt/C. After 30 min, cold brine (10 ml) and $NaHCO_3$ (1.0 g, 12 mmol) were added during vigorous stirring until the evolution of dioxygen and carbon dioxide ceased. The mixture was washed with diethyl ether (2×100 ml), and the aqueous layer was acidified with concentrated aqueous hydrochloric acid to pH ca. 2. The carboxylic acid was extracted with diethyl ether (3×100 ml and 4×50 ml). The combined extracts were dried with anhydrous Na_2SO_4, the solvent was distilled off, and the residue was dried in a dessicator (20 mmHg, P_2O_5) to give pure, by ^1H NMR, *trans*-2-carboxycinnamic acid (**2a**).[17] In the cases of tungstate and molybdate catalysts, the formed sticky solid was washed with diethyl ether to give pure acid **2a**; see Table 1 for the results.

Preparative Oxidation of Naphthalenes

Powdered 2,2′-dinitro-4,4′-di(trifluoromethyl)diphenyl diselenide (**3g**) (0.270 g, 0.500 mmol, 5.00 mol%) was added to a solution of naphthalene (**1a–j, 4a, 4h, 4k, 4l**) (10.0 mmol) and hydrogen peroxide (5.0 ml, 50 mmol) in *tert*-butanol (40 ml), and the mixture was stirred at 55 °C, for 2 to 20 h; see Table 2. The pure acids **2c, 2d, 2f, 2g**, and **2j** crystallized after adding water (40–100 ml) and cooling the reaction mixture, and they were isolated by filtration. The reaction mixture containing acids **2a, 2b, 2h, 2i, 2k**, and **2l** was treated with a pinch of Pt/C, and the solvent was distilled off. The residue was treated with diethyl ether (30 ml), brine (50 ml), and $NaHCO_3$ added portionwise during vigorous stirring until the evolution of carbon dioxide ceased and the layers separated. The aqueous layer was washed with diethyl ether (30 ml), acidified with aqueous 2.0 M hydrochloric acid to pH ca. 2.5, and extracted with diethyl ether (5×150 and 4×25 ml). The combined extracts were washed with brine and water several times and dried with anhydrous Na_2SO_4. The solvent was

distilled off, and the residue was dried in a dessicator (20 mmHg, P_2O_5) and washed with diethyl ether (2×2 ml) to give pure *trans*-2-carboxycinnamic acids **2a, 2b, 2k**, and **2l**. The crude **2 h** and **2i** were recrystallized from diethyl ether. In the case of **2e**, after the reaction most of the solvent was distilled off. The acid crystallized directly after adding water and cooling, and it was isolated by filtration. See Table 2.

Caution

Waste brine containing residues of selenium can be harmful for the environment because selenium is an essential trace element and supranormal doses are harmful to vegetation and human health and animals,[37] so all manipulations of the waste require special attention. There no evidence that selenoorganic compounds, such as 2,2′-dinitro-4,4′-di(trifluoromethyl)diphenyl diselenide (**3g**), are toxic.[20,38–40] Although the diphenyl diselenide and its derivatives with electron-withdrowing substituents such as nitro and trifluoromethyl groups are intensively tested for drugs[38–41] and ecofriendly oxygen transfer catalysts,[15–26,32,42–45] gloves and glasses should be used in each experiment.

***E*-2-Carboxycinnamic acid (2a).** Colorless powder. Mp 204–205 °C (diethyl ether) (203 °C[14], 204–205 °C[17]). ^{1}H NMR (DMSO-d_6)[17]: 12.8 (s, 2H, COOH), 8.31 (d, $J = 15.9$ Hz, 1H, C*H*=CH–COOH), 7.88 (dd, $J = 7.4$, 1.3 Hz, 1H, H-3 or H-6), 7.81 (dd, $J = 7.6$, 1.3 Hz, 1H, H-3 or H-6), 7.59 (ddd, $J = 7.4$, 7.2, 1.3 Hz, 1H, H-4 or H-5), 7.50 (ddd, $J = 7.6$, 7.2, 1.3 Hz, 1H, H-4 or H-5), 6.41 (d, $J = 15.9$ Hz, C*H*-COOH). ^{13}C NMR (DMSO-d_6): 168.8, 169.1, 135.6, 131.7 (C), 143.3, 132.7, 131.0, 130.2, 128.3, 122.0 (CH). IR[14] (KBr): $\gamma = 2200$–$3300\ cm^{-1}$ (COOH), $1679\ cm^{-1}$ (C=O), $1626\ cm^{-1}$ (C=C).

***E*-2-Carboxy-4-hydroxycinnamic acid (2b).** Colorless solid. Mp 217.5–218.0 °C (diethyl ether) (dec.) (220–222 °C[36]). ^{1}H NMR (DMSO-d_6): 12.71 (s, 2H, COOH), 10.22 (s, 1H, OH), 8.24 (d, $J = 15.9$ Hz, 1H, C*H*=CH–COOH), 7.71 (d, $J = 8.6$ Hz, 1H, H-6), 7.23 (d, $J = 2.5$ Hz, 1H, H-3), 6.96 (dd, $J = 8.6$, 2.5hz, 1H, H-5), 6.27 (d, $J = 15.9$ Hz, 1H, C*H*-COOH). ^{13}C NMR (DMSO-d_6): 168.1, 167.8, 158.7, 132.9, 125.3 (C), 142.2, 129.3, 119.1, 118.1, 116.5 (CH). IR (KBr): $\gamma = 2200$–$3600\ cm^{-1}$ (COOH, OH), $1699\ cm^{-1}$ (C=O), $1604\ cm^{-1}$ (C=C), 1246, $1222\ cm^{-1}$ (C–O).

***E*-2-Carboxy-4-methoxycinnamic acid (2c).** Colorless solid. Mp 208.5–210.5 °C (*t*-butanol–water, 1:1) (195–196 °C[12]). ^{1}H NMR[12] (DMSO-d_6): 12.81 (s, 2H, COOH), 8.25 (d, $J = 15.9$ Hz, 1H, C*H*=CH–COOH), 7.78 (d, $J = 8.7$ Hz, 1H, H-6), 7.34 (d, $J = 2.5$hz, 1H, H-3), 7.13 (dd, $J = 8.7$, 2.5 Hz, 1H, H-5), 6.33 (d, $J = 15.9$ Hz, 1H, C*H*-COOH), 3.81 (s, 3H, OCH_3). ^{13}C NMR (DMSO-d_6): 168.0, 167.7, 160.1, 132.9, 126.8 (C), 141.9, 129.2, 119.1, 117.9, 114.9 (CH), 55.5 (CH_3). IR[12] (KBr): $\gamma = 2300$–$3300\ cm^{-1}$ (COOH), $1683\ cm^{-1}$ (C=O), $1596\ cm^{-1}$ (C=C), 1236, $1075\ cm^{-1}$ (C–O).

***E*-2-Carboxy-5-methoxycinnamic acid (2d).** Cream-colored powder. Mp 201.5–202.5 °C (water) (206–207 °C [12]). ^{1}H NMR (DMSO-d_6): 12.66 (s, 2H, COOH), 8.41 (d, $J = 16.0$ Hz, 1H, C*H*=CH–COOH), 7.89 (d, $J = 8.7$ Hz, 1H, H-3), 7.26 (d, $J = 2.5$hz, 1H, H-6), 7.04 (dd, $J = 8.7$, 2.5 Hz, 1H, H-4), 6.44 (d, $J = 16.0$ Hz,

1H, C*H*-COOH), 3.86 (s, 3H, OCH_3). ^{13}C NMR (DMSO-d_6): 167.52, 167.47, 161.9, 137.7, 122.6 (C), 142.9, 132.9, 121.7, 115.3, 112.5 (CH), 55.6 (CH_3). IR[12] (KBr): $\gamma = 2200–3300\,cm^{-1}$ (COOH), 1702, $1688\,cm^{-1}$ (C=O), 1637, $1603\,cm^{-1}$ (C=C), 1264, 1242, 1208, $1155\,cm^{-1}$ (C–O).

***E*-2,5-Dicarboxycinnamic acid (2e).** Colorless needles. Mp 273–274 °C (*t*-butanol–water, 1:1). ^1H NMR (DMSO-d_6): 13.19 (s, 3H, COOH), 8.26 (d, $J = 15.6$ Hz, 1H, C*H*=CH–COOH), 8.21 (s, 1H, H-6), 7.91–8.06 (m, 2H, H-3, H-4), 6.42 (d, $J = 15.6$ Hz, 1H, C*H*-COOH). ^{13}C NMR (DMSO-d_6): 167.6, 167.2, 166.3, 135.1, 134.6, 133.8 (C), 141.9, 130.6, 130.0, 128.3, 122.3 (CH). IR (KBr): $\gamma = 2200–3300\,cm^{-1}$ (COOH), 1735, 1699, $1670\,cm^{-1}$ (C=O), $1621\,cm^{-1}$ (C=C). Found: C, 56.03; H, 3.34. ($C_{11}H_8O_6$) 236.18 requires C, 55.94; H, 3.41.

***E*-2-Carboxy-5-carboxymethylcinnamic acid (2f).** Colorless needles. Mp 210–212 °C (*t*-butanol–water, 1:1). ^1H NMR (DMSO-d_6): 13.11 (s, 2H, COOH), 8.24 (d, $J = 15.9$ Hz, 1H, C*H*=CH–COOH), 8.21 (d, $J = 1.1$ Hz, 1H, H-6), 8.02 (dd, $J = 8.2$, 1.1 Hz, 1H, H-4), 7.97 (d, $J = 8.2$ Hz, 1H, H-3), 6.44 (d, $J = 15.9$ Hz, 1H, C*H*-COOH), 3.89 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): 167.5, 167.1, 165.2, 135.2, 134.8, 132.5 (C), 141.7, 130.7, 129.8, 128.1, 122.4 (CH), 52.5 (CH_3). IR (KBr): $\gamma = 2200–3300\,cm^{-1}$ (COOH), 1735, $1686\,cm^{-1}$ (C=O), $1626\,cm^{-1}$ (C=C), $1149\,cm^{-1}$ (C–O). Found: C, 57.34; H, 4.14. ($C_{12}H_{10}O_6$) 250.20 requires C, 57.60; H, 4.03.

***E*-5-Bromo-2-carboxycinnamic acid (2g).** Cream-colored powder. Mp 176–178 °C (water) (183–185 °C[14]). ^1H NMR (DMSO-d_6)[14]: 12.97 (s, 2H, COOH), 8.24 (d, $J = 15.9$ Hz, 1H, C*H*=CH–COOH), 7.99 (s, 1H, H-6), 7.80 (d, $J = 8.4$ Hz, 1H, H-3 or H-4), 7.67 (d, $J = 8.4$ Hz, 1H, H-3 or H-4), 6.48 (d, $J = 15.9$ Hz, 1H, C*H*-COOH). ^{13}C NMR (DMSO-d_6): 167.4, 167.2, 137.3, 129.9, 125.9 (C), 141.1, 2×132.4, 130.3, 122.8 (CH). IR[14] (KBr): $\gamma = 2300–3200\,cm^{-1}$ (COOH), $1683\,cm^{-1}$ (C=O), $1633\,cm^{-1}$ (C=C).

***E*-2-Carboxy-5-hydroxycinnamic acid (2h).** Mixture with *Z*-2-carboxy-6-hydroxycinnamic acid (**5h**) (4:1) was formed. Brown yellow powder. Mp 240 °C (water) (250–252 °C[13]). ^1H NMR (DMSO-d_6): 12.68 (s, 2H, COOH), 10.35 (s, 1H, OH), 8.40 (d, $J = 15.9$ Hz, 1H, C*H*=CH–COOH), 7.82 (d, $J = 8.6$ Hz, 1H, H-3), 7.05 (d, $J = 2.4$ Hz, 1H, H-6), 6.87 (dd, $J = 8.6$, 2.4 Hz, 1H, H-4), 6.22 (d, $J = 15.9$ Hz, 1H, C*H*-COOH). ^{13}C NMR (DMSO-d_6): 167.5, 167.3, 160.7, 137.9, 120.9 (C), 143.5, 133.2, 120.9, 116.4, 114.0 (CH). IR (KBr): $\gamma = 2300–3600\,cm^{-1}$ (COOH, OH), $1687\,cm^{-1}$ (C=O), $1624\,cm^{-1}$ (C=C), 1267, $1235\,cm^{-1}$ (C–O).

2,4-Dicarboxy-5-hydroxycinnamic acids (2i) and (5i). Mixture of isomers *trans* and *cis* in a ratio of 2:1. Yellow powder. Mp 250 °C (water). IR (KBr): $\gamma = 2200–3400\,cm^{-1}$ (COOH, OH), $1688\,cm^{-1}$ (C=O), $1639\,cm^{-1}$ (C=C), $1234\,cm^{-1}$ (C–O). ^1H NMR (DMSO-d_6) isomer *trans* **2i**: 11.8 (s, 3H, COOH), 8.39 (s, 1H, H-3), 8.36 (d, $J = 15.9$ Hz, 1H, C*H*=CH–COOH), 7.29 (s, 1H, H-6), 6.43 (d, $J = 15.9$ Hz, 1H, C*H*-COOH), 4.76 (s, 1H, OH). ^1H NMR (DMSO-d_6) isomer *cis* **5i**: 11.8 (s, 3H, COOH), 8.00 (d, $J = 9.6$ Hz, 1H, C*H*=CH–COOH), 7.67 (s, 1H, H-3), 7.27 (s, 1H, H-6), 6.60 (d, $J = 9.6$ Hz, 1H, C*H*-COOH), 4.76 (s, 1H, OH). Found: C, 52.03; H, 3.40. ($C_{11}H_8O_7$) 252.18 requires C, 52.39; H, 3.20.

***E*-2-Carboxy-4-carboxymethyl-5-hydroxycinnamic acid (2j).** Pale yellow powder. Mp 216.5–219.0 °C (*t*-butanol–water, 1:1). ^{1}H NMR (DMSO-d_6): 12.85 (s, 2H, COOH), 10.88 (s, 1H, OH), 8.35 (d, $J = 15.9$ Hz, 1H, C*H*=CH–COOH), 8.35 (s, 1H, H-3), 7.26 (s, 1H, H-6), 6.37 (d, $J = 15.9$ Hz, 1H, C*H*-COOH), 3.90 (s, 1H, OCH_3). ^{13}C NMR (DMSO-d_6): 167.5, 167.1, 166.6, 161.8, 142.4, 121.0, 114.1 (C), 141.9, 133.9, 123.2, 116.5 (CH), 52.6 (CH_3). IR (KBr): $\gamma = 2200$–$3600\,cm^{-1}$ (COOH, OH), $1691\,cm^{-1}$ (C=O), $1629\,cm^{-1}$ (C=C), 1193, 1173, $1119\,cm^{-1}$ (C–O). Found: C, 54.12; H, 3.62. ($C_{12}H_{10}O_7$) 266.20 requires C, 54.14; H, 3.79.

***E*-2,5-Dicarboxy-4-hydroxycinnamic acid (2k).** Pale red-brown powder. Mp 237 °C (dec.) (diethyl ether). ^{1}H NMR (DMSO-d_6): 11.01 (s, 3H, COOH), 8.12 (s, 1H, H-6), 8.11 (d, $J = 15.9$ Hz, 1H, C*H*=CH–COOH), 7.33 (s, 1H, H-3), 6.29 (d, $J = 15.9$ Hz, 1H, C*H*-COOH), 5.00 (s, 1H, OH). ^{13}C NMR (DMSO-d_6): 170.5, 167.5, 167.4, 161.0, 137.4, 125.1, 116.6 (C), 141.5, 129.8, 119.6, 118.6 (CH). IR (KBr): $\gamma = 2200$–$3600\,cm^{-1}$ (COOH, OH), 1691, $1669\,cm^{-1}$ (C=O), $1635\,cm^{-1}$ (C=C), 1222 (C–O). Found: C, 52.35; H, 3.10. ($C_{11}H_8O_7$) 252.18 requires C, 52.39; H, 3.20.

***E*-2-Carboxy-5-carboxymethyl-4-hydroxycinnamic acid (2l).** The conformers in a ratio of 21:1 were observed. Pale brown powder. Mp 215.0–215.5 °C (diethyl ether). IR (KBr): $\gamma = 2200$–$3500\,cm^{-1}$ (COOH, OH), $1684\,cm^{-1}$ (C=O), 1632, $1610\,cm^{-1}$ (C=C), 1261, 1200, 1164, $1110\,cm^{-1}$ (C–O). ^{1}H NMR (DMSO-d_6) major: 12.95 (s, 2H, COOH), 10.76 (s, 1H, OH), 8.13 (d, $J = 15.9$ Hz, 1H, C*H*=CH–COOH), 8.08 (s, 1H, H-6), 7.39 (s, 1H, H-4), 6.30 (d, $J = 15.9$ Hz, 1H, C*H*-COOH), 3.89 (s, 3H, OCH_3), minor: 12.95 (s, 2H, COOH), 10.76 (s, 1H, OH), 8.12 (d, $J = 15.9$ Hz, 1H, C*H*=CH–COOH), 8.11 (s, 1H, H-6), 7.33 (s, 1H, H-4), 6.29 (d, $J = 15.9$ Hz, 1H, C*H*-COOH), 3.89 (s, 3H, OCH_3). ^{13}C NMR (DMSO-d_6) major: 167.4, 167.3, 167.2, 159.3, 136.7, 125.2, 117.6 (C), 114.3, 129.7, 119.6, 118.8 (CH), 52.6 (CH_3). Found: C, 54.44; H, 3.69. ($C_{12}H_{10}O_7$) 266.20 requires C, 54.14, H; 3.79.

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