Supporting Information:

A Simple, Copper(I) Catalyzed Oxidation of Benzylic/Allylic Alcohols to Carbonyl Compounds: Synthesis of Functionalized Cinnamates in One-pot

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Data and ^1H & ^{13}C NMR spectrums of all compounds

S2-S53

Experimental

General:

IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^1H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in CDCl_3 ; chemical shifts (δ in ppm) and coupling constants (J in Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) ($\delta_{\text{H}} = 0.00$ ppm) or CHCl_3 ($\delta_{\text{H}} = 7.25$ ppm). ^{13}C NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in CDCl_3 ; chemical shifts (δ in ppm) are reported relative to CHCl_3 [$\delta_{\text{C}} = 77.00$ ppm (central line of triplet)]. In the ^{13}C NMR, the nature of carbons (C, CH, CH_2 and CH_3) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^1H -NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed by ^1H , ^{13}C CPD and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF using multimode source. All small scale dry reactions were carried out using Schlenk tube technique. Reactions were monitored by TLC on silica gel using a mixture of petroleum ether and ethyl acetate as eluents. Reactions were generally run under an argon or nitrogen atmosphere. Solvents- petroleum ether with a boiling range of 60 to 80 °C, ethyl acetate, dichloromethane and diethyl ether- were distilled prior use. Diethyl ether and 1,4-dioxane were dried over benzophenone/sodium and DMF was dried over calcium hydride. 1,10-phenanthroline and aromatic aldehydes were purchased from local sources and used as received. CuI and K_3PO_4 were purchased from sigma-Aldrich. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

General Procedure-1 [For the inert oxidation of alcohols to carbonyl compounds; GP-1(method A)]:

In an oven dried Schlenk tube, were added alcohol **1** (69.0–199.5 mg, 0.5 mmol), CuI (10 mol%) and 1,10-Phenanthroline (20 mol%) and K_3PO_4 (2 mmol) followed by the addition of dioxane (2 mL) at room temperature under a nitrogen atmosphere. The stirred reaction mixture was heated in an oil bath at 80 °C for 24–48 h. Progress of the reaction was monitored by TLC till the reaction is completed. Then, the reaction mixture was cooled to room temperature, quenched with aqueous NH_4Cl solution and then extracted with CH_2Cl_2 (3×10 mL). The organic layer was washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the aldehyde/ketone **2** (58–92%).

General Procedure-2 [For the open air oxidation of alcohols to carbonyl compounds; GP-2 (method B)]:

In an oven dried Schlenk tube, were added alcohol **1** (69.0–199.5 mg, 0.5 mmol), CuI (10 mol%) and 1,10-Phenanthroline (20 mol%) and K₃PO₄ (2 mmol) followed by the addition of dioxane (2 mL) at room temperature under open air atmosphere. The stirred reaction mixture was heated in an oil bath at 80 °C for 7–48 h. Progress of the reaction was monitored by TLC till the reaction is completed. Then, the reaction mixture was cooled to room temperature, quenched with aqueous NH₄Cl solution and then extracted with CH₂Cl₂ (3 × 10 mL). The organic layer was washed with saturated NaCl solution, dried (Na₂SO₄), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the aldehyde/ketone **2** (61–97%).

Primary alcohols **1a–1n**, **1z**, **1aa** & **1ac** and secondary alcohols **1x**, **1y** & **1ab** were used as starting materials for copper(I) mediated oxidations were synthesized by reduction reaction on corresponding benzaldehydes and ketones using NaBH₄. The secondary alcohols **1o–1w**, were obtained using standard methyl/phenyl Grignard addition on corresponding benzaldehyde precursors.

Compounds **1a** & **2a**, **1c** & **2c**,^[1] **1b** & **2b**,^[2] **1d** & **2d**,^[3] **1e** & **2e**,^[4] **1f–n**,^[5] & **2f**,^[6] **2g**,^[7] **2h**,^[8] **2i**,^[9] **2j**,^[10] **2k**,^[11] **2l**,^[12] **2m**,^[13] **2n**,^[14] **1o** & **2o**, **1z** & **2z**, **1ad**, **2p**, **2q**, **2s**,^[15] **1r** & **2r**,^[16] **1t–**

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1v & **2t–2v**,^[17] **1w** & **2w**,^[18] **1z** & **2z**,^[19] **1ab** & **2ab**,^[20] **1ac** & **2ac**,^[21] **1ad** & **2ad**,^[22] **1af**^[23] and **2af**^[24] are known in literature.

The esters **3b**, **3e**, **3l**, **3o**, **3q**, and **3r** are known in literature^[25]

[5-(benzyloxy)-2-bromo-4-methoxyphenyl](phenyl)methanol (1y**):**

To the cooled reaction mixture of O-benzyl(*ortho*-bromo)isovanillin (500 mg, 1.56 mmol), at 0 °C, was added phenyl magnesium bromide [4.67 mmol, (prepared from magnesium (112.1 mg, 4.67 mmol) and bromobenzene (1.11 g, 7.00 mmol) in dry THF (5 mL)] in THF (10 mL) under nitrogen atmosphere. Then the reaction mixture was allowed to attain room temperature, stirred for 3 h and monitored by TLC. Then, the mixture was cooled to 0 °C, quenched with aqueous NH₄Cl solution and then extracted with ethyl acetate (3 × 15 mL). The organic layer was washed with saturated NaCl solution, dried (Na₂SO₄), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 85:15 to 80:20) furnished the alcohol **1y** (529.1 mg, 85%). [TLC control (petroleum ether/ethyl acetate 80:20), *R_f*[O-benzyl(*ortho*-bromo)isovanillin]=0.50, *R_f*(**1y**)=0.30, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v*_{max}=3552, 2939, 1499, 1379, 1257, 1152, 1027, 809, 735, 697 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=7.45–7.15 (m, 10H, Ar-H), 7.07 (s, 1H, Ar-H), 6.97 (s, 1H, Ar-H), 6.03 [s, 1H, Ar-CH(OH)], 5.08 (d, 1H, *J*=12.2 Hz, PhCH_aH_bO), 5.06 (d, 1H, *J*=12.2 Hz, PhCH_aH_bO), 3.81 (s, 3H, Ar-OCH₃), 2.60 (br. s, 1H, OH) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=149.4 (s, Ar-C), 147.4 (s, Ar-C), 142.3 (s, Ar-C), 136.4 (s, Ar-C), 134.5 (s, Ar-C), 128.5 (d, 2C, Ar-CH), 128.3 (d, 2C, Ar-CH), 127.8 (d, Ar-CH), 127.5 (d, Ar-CH), 127.4 (d, 2C, Ar-CH), 126.6 (d, 2C, Ar-CH), 115.6 (d, Ar-CH), 113.6 (d, Ar-CH), 113.0

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(s, Ar-C), 74.2 [d, Ar-CH(OH)], 70.8 (t, PhCH₂O), 56.1 (q, Ar-OCH₃) ppm. HR-MS (APCI+) m/z calculated for [C₂₁H₁₈BrO₂]⁺=[(M+H)-H₂O]⁺: 381.0485; found 381.0471.

2n

2-bromo-5-nitrobenzaldehyde (2n): GP-1 was followed to the alcohol **1n** (115 mg, 0.50 mmol) with CuI (9.5 mg, 10 mol%), 1,10-phenanthroline (18 mg, 20 mol%) and K₃PO₄ (212 mg, 1 mmol) in dioxane (2 mL) at room temperature under a nitrogen atmosphere. Then, the reaction mixture was heated in an oil bath at 80 °C for 48 h and monitored by TLC. The reaction mixture was cooled to room temperature, quenched with aqueous NH₄Cl solution and then extracted with CH₂Cl₂ (3 × 10 mL). The organic layer was washed with saturated NaCl solution, dried (Na₂SO₄), and filtered. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 80:20) furnished the aldehyde **2n** (52.3 mg, 74%) as pale yellow solid, recrystallized from petroleum ether and dichloromethane (melting point was checked with literature)^{5b} with the recovery of the starting material **1n** (45 mg, 39%). [TLC control (petroleum ether/ethyl acetate 80:20), R_f(**1n**)=0.35, R_f(**2n**)=0.50, UV detection].

2o

1-phenylethanone (2o): GP-1 was followed to the alcohol **1o** (60 mg, 0.50 mmol) with CuI (9.5 mg, 10 mol%), 1,10-phenanthroline (18 mg, 20 mol%) and K₃PO₄ (212 mg, 1 mmol) in dioxane (2 mL) at room temperature under a nitrogen atmosphere. Then, the reaction mixture was heated in an oil bath at 80 °C for 48 h and monitored by TLC. The reaction mixture was cooled to room temperature, quenched with aqueous NH₄Cl solution and then extracted with CH₂Cl₂ (3 × 10 mL). The organic layer was washed with saturated NaCl solution, dried (Na₂SO₄), and filtered. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 90:10) furnished the ketone **2o** (27.6 mg, 64%) as a colorless viscous oil with the recovery of the starting material **1o** (18 mg, 30%). [TLC control (petroleum ether/ethyl acetate 90:10), R_f(**1o**)=0.35, R_f(**2o**)=0.55, UV detection].

2r

1-(3,4-dimethoxyphenyl)ethanone (2r): GP-1 was followed to the alcohol **1r** (90 mg, 0.50 mmol) with CuI (9.5 mg, 10 mol%), 1,10-phenanthroline (18 mg, 20 mol%) and K₃PO₄ (212 mg, 1 mmol) in dioxane (2 mL) at room temperature under a nitrogen atmosphere. Then, the reaction mixture was heated in an oil bath at 80 °C for 48 h and monitored by TLC. The reaction mixture was cooled to room temperature, quenched with aqueous NH₄Cl solution and then extracted with CH₂Cl₂ (3 × 10 mL). The organic layer was washed with saturated NaCl solution, dried (Na₂SO₄), and filtered. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 90:10 to 80:20) furnished the ketone **2r** (40.9 mg, 61%) as pale

brown solid, recrystallized from petroleum ether and dichloromethane (m.p. 47–52 °C; cross checked with commercial sample) with the recovery of the starting material **1r** (22 mg, 24%). [TLC control (petroleum ether/ethyl acetate 70:30), $R_f(\mathbf{1r})=0.40$, $R_f(\mathbf{2r})=0.60$, UV detection].

1-(2-bromo-5-methoxyphenyl)ethanone (2t): GP-1 was followed to the alcohol **1t** (114.5 mg, 0.50 mmol) with CuI (9.5 mg, 10 mol%), 1,10-phenanthroline (18 mg, 20 mol%) and K_3PO_4 (212 mg, 1 mmol) in dioxane (2 mL) at room temperature under a nitrogen atmosphere. Then, the reaction mixture was heated in an oil bath at 80 °C for 48 h and monitored by TLC. The reaction mixture was cooled to room temperature, quenched with aqueous NH_4Cl solution and then extracted with CH_2Cl_2 (3×10 mL). The organic layer was washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 80:20) furnished the ketone **2t** (58.5 mg, 62%) as pale yellow viscous liquid with the recovery of the starting material **1t** (21 mg, 18%). [TLC control (petroleum ether/ethyl acetate 85:15), $R_f(\mathbf{1t})=0.40$, $R_f(\mathbf{2t})=0.65$, UV detection].

1-[5-(benzyloxy)-2-bromo-4-methoxyphenyl]ethanone (2u): GP-1 was followed to the alcohol **1u** (167.5 mg, 0.50 mmol) with CuI (9.5 mg, 10 mol%), 1,10-phenanthroline (18 mg, 20 mol%) and K_3PO_4 (212 mg, 1 mmol) in dioxane (2 mL) at room temperature under a nitrogen atmosphere. Then, the reaction mixture was heated in an oil bath at 80 °C for 48 h and monitored by TLC. The reaction mixture was cooled to room temperature, quenched with aqueous NH_4Cl solution and then extracted with CH_2Cl_2 (3×10 mL). The organic layer was washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 80:20) furnished the ketone **2u** (89.5 mg, 68%) as pale brown solid, recrystallized from petroleum ether and dichloromethane (melting point was checked with literature report)^{8a} with the recovery of the starting material **1u** (36.5 mg, 22%). [TLC control (petroleum ether/ethyl acetate 75:25), $R_f(\mathbf{1u})=0.40$, $R_f(\mathbf{2u})=0.55$, UV detection].

1-(6-bromo-1,3-benzodioxol-5-yl)ethanone (2v): GP-1 was followed to the alcohol **1v** (121.5 mg, 0.50 mmol) with CuI (9.5 mg, 10 mol%), 1,10-phenanthroline (18 mg, 20 mol%) and K_3PO_4

(212 mg, 1 mmol) in dioxane (2 mL) at room temperature under a nitrogen atmosphere. Then, the reaction mixture was heated in an oil bath at 80 °C for 48 h and monitored by TLC. The reaction mixture was cooled to room temperature, quenched with aqueous NH₄Cl solution and then extracted with CH₂Cl₂ (3 × 10 mL). The organic layer was washed with saturated NaCl solution, dried (Na₂SO₄), and filtered. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 80:20) furnished the ketone **2v** (59.2 mg, 62%) as pale yellow solid, recrystallized from petroleum ether and dichloromethane (melting point was checked with literature report^{8b}) with the recovery of the starting material **1v** (26.8 mg, 22%). [TLC control (petroleum ether/ethyl acetate 80:20), *R_f*(**1v**)=0.40, *R_f*(**2v**)=0.55, UV detection].

1-(2-bromo-4,5-dimethoxyphenyl)ethanone (2w): GP-1 was followed to the alcohol **1w** (115 mg, 0.50 mmol) with CuI (9.5 mg, 10 mol%), 1,10-phenanthroline (18 mg, 20 mol%) and K₃PO₄ (212 mg, 1 mmol) in dioxane (2 mL) at room temperature under a nitrogen atmosphere. Then, the reaction mixture was heated in an oil bath at 80 °C for 48 h and monitored by TLC. The reaction mixture was cooled to room temperature, quenched with aqueous NH₄Cl solution and then extracted with CH₂Cl₂ (3 × 10 mL). The organic layer was washed with saturated NaCl solution, dried (Na₂SO₄), and filtered. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 80:20) furnished the ketone **2w** (67.8 mg, 65%) as brown viscous liquid with the recovery of the starting material **1w** (26 mg, 20%). [TLC control (petroleum ether/ethyl acetate 70:30), *R_f*(**1w**)=0.40, *R_f*(**2w**)=0.58, UV detection].

(2E)-3-phenylacrylaldehyde (1ac): GP-1 was followed to the alcohol **1ac** (68 mg, 0.50 mmol) with CuI (9.5 mg, 10 mol%), 1,10-phenanthroline (18 mg, 20 mol%) and K₃PO₄ (212 mg, 1 mmol) in dioxane (2 mL) at room temperature under a nitrogen atmosphere. Then, the reaction mixture was heated in an oil bath at 80 °C for 24 h and monitored by TLC. The reaction mixture was cooled to room temperature, quenched with aqueous NH₄Cl solution and then extracted with CH₂Cl₂ (3 × 10 mL). The organic layer was washed with saturated NaCl solution, dried (Na₂SO₄), and filtered. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 80:20) furnished the aldehyde **2ac** (34.6 mg, 64%) as viscous oil with the recovery of the starting material **1ac** (15 mg, 22%). [TLC control (petroleum ether/ethyl acetate 90:10), *R_f*(**1ac**)=0.40, *R_f*(**2ac**)=0.65, UV detection].

[5-(benzyloxy)-2-bromo-4-methoxyphenyl](phenyl)methanone (2y**):**

GP-2 was followed to the alcohol **1y** (199.5 mg, 0.50 mmol) with CuI (9.5 mg, 10 mol%), 1,10-Phenanthroline (18 mg, 20 mol%) and K₃PO₄ (212 mg, 1 mmol) in dioxane (2 mL) at room temperature under a nitrogen atmosphere. Then, the reaction mixture was heated in an oil bath at 80 °C for 48 h and monitored by TLC. The reaction mixture was cooled to room temperature, quenched with aqueous NH₄Cl solution and then extracted with CH₂Cl₂ (3 × 10 mL). The organic layer was washed with saturated NaCl solution, dried (Na₂SO₄), and filtered. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 75:25) furnished the ketone **2y** (166.7 mg, 84%) as a colorless viscous oil. [TLC control (petroleum ether/ethyl acetate 70:30), *R_f*(**1y**)=0.46, *R_f*(**2y**)=0.54, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} =2924, 1664, 1595, 1502, 1447, 1374, 1330, 1259, 1208, 1173, 1145, 1025, 852, 808, 717, 697, 627 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.81 (dd, 2H, *J*=8.3 and 1.5 Hz, Ar-H), 7.59 (t, 1H, *J*=7.3 Hz, Ar-H), 7.52–7.42 (m, 4H, Ar-H), 7.40 (dd, 2H, *J*=7.8 and 7.3 Hz, Ar-H), 7.34 (t, 1H, *J*=7.3 Hz, Ar-H), 7.13 (s, 1H, Ar-H), 6.90 (s, 1H, Ar-H), 5.17 (s, 2H, PhCH₂O), 3.83 (s, 3H, Ar-OCH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =195.6 (s, C=O), 150.0 (s, Ar-C), 148.7 (s, Ar-C), 136.5 (s, Ar-C), 135.8 (s, Ar-C), 133.4 (d, Ar-CH), 132.7 (s, Ar-C), 130.2 (d, 2C, Ar-CH), 128.7 (d, 2C, Ar-CH), 128.5 (d, 2C, Ar-CH), 128.2 (d, Ar-CH), 127.4 (d, 2C, Ar-CH), 117.8 (d, Ar-CH), 112.6 (d, Ar-CH), 110.7 (s, Ar-C), 71.2 (t, PhCH₂O), 56.2 (q, Ar-OCH₃) ppm. HR-MS (APCI+) *m/z* calculated for [C₂₁H₁₆⁸¹BrO₂]⁺=[(M+2)+H]–H₂O]⁺: 381.0313; found 381.0315.

Ethyl (2E)-3-(3-methoxyphenyl)but-2-enoate (3p**):**

GP-3 was followed to the alcohol **1p** (76 mg, 0.5 mmol) with CuI (9.5 mg, 10 mol%), 1,10-phenanthroline (18 mg, 20 mol%) and K₃PO₄ (212 mg, 1 mmol) in toluene (2 mL) at 80 °C for 24 h. Progress of the oxidation was monitored by TLC till the reaction is completed. To the cooled reaction mixture at 0 °C, under nitrogen atmosphere, was added ylide [2.5 mmol, generated from 60% NaH (100.2 mg, 2.5 mmol) and TEPA (0.5 mL, 2.5 mmol) in THF (1.5 mL)] in THF (1.5 mL) under nitrogen atmosphere. Then the reaction mixture was refluxed at 65 °C for 12 h and monitored by TLC. Then, the reaction mixture was quenched with aqueous NH₄Cl solution and then extracted with CH₂Cl₂ (3 × 15 mL). The organic layer was washed with saturated NaCl solution, dried (Na₂SO₄), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the cinnamate **3p** (73.8 mg, 67%) as colorless viscous oil. [TLC control *R_f*(**1p**)=0.40, *R_f*(**3p**)=0.70 (petroleum ether/ethyl acetate 80:20, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} =2979, 2936, 1712, 1568, 1465, 1338, 1217, 1159, 1040, 871, 805, 602 cm⁻¹. ¹H NMR (CDCl₃ 400 MHz): δ =7.27 (dd, 1H, *J*=8.3 and 8.0 Hz, ArH), 7.05 (dd, 1H, *J*=8.0 and 2.0 Hz, Ar-H), 6.98 (dd, 1H, *J*=2.4 and 2.0 Hz, Ar-H), 6.89 (dd, 1H, *J*=8.3 and 2.4 Hz, Ar-H), 6.12 [q, 1H, *J*=1.5 Hz, C(Me)=CHCO₂Et], 4.20 (q, 2H, *J*=7.3 Hz, OCH₂CH₃), 3.82 (s, 3H, Ar-OCH₃), 2.55 [d, 3H, *J*=1.5 Hz, Ar-C(CH₃)=CHCO₂Et], 1.31 (t, 3H,

$J=7.3$ Hz, OCH_2CH_3) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=166.8$ (s, $\text{O}=\text{C}-\text{O}$), 159.6 [s, $\text{C}(\text{Me})=\text{CHCO}_2\text{Et}$], 155.4 (s, Ar-C), 143.8 (s, Ar-C), 129.5 [d, Ar-C(Me)=CHCO₂Et], 118.8 (d, Ar-CH), 117.3 (d, Ar-CH), 114.3 (d, Ar-CH), 112.1 (d, Ar-CH), 59.8 (t, OCH_2CH_3), 55.3 (q, Ar-OCH₃), 18.0 [q, Ar-C(CH₃)=CHCO₂Et], 14.3 (q, OCH_2CH_3) ppm.

Ethyl (2E)-3-(3,4,5-trimethoxyphenyl)but-2-enoate (3s):

GP-3 was followed to the alcohol **1s** (98 mg, 0.50 mmol) with CuI (9.5 mg, 10 mol%), 1,10-phenanthroline (18 mg, 20 mol%) and K_3PO_4 (212 mg, 1 mmol) in toluene (2 mL) at 80 °C for 24 h. Progress of the oxidation was monitored by TLC till the reaction is completed. To the cooled reaction mixture at 0 °C, under nitrogen atmosphere, was added ylide [2.5 mmol, generated from 60% NaH (100.2 mg, 2.5 mmol) and TEPA (0.5 mL, 2.5 mmol) in THF (1.5 mL)] in THF (1.5 mL) under nitrogen atmosphere. Then the reaction mixture was refluxed at 65 °C for 12 h and monitored by TLC. Then, the reaction mixture was quenched with aqueous NH_4Cl solution and then extracted with CH_2Cl_2 (3×15 mL). The organic layer was washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 80:20) furnished the cinnamate **3s** (88.2 mg, 63%) as pale yellow viscous oil. [TLC control $R_f(\mathbf{1s})=0.35$, $R_f(\mathbf{3s})=0.65$ (petroleum ether/ethyl acetate 75:25, UV detection)]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2973$, 1702, 1622, 1571, 1428, 1283, 1212, 1156, 1037, 850, 776, 695 cm^{-1} . ^1H NMR (CDCl_3 400 MHz): $\delta=6.66$ (s, 2H, Ar-H), 6.08 [q, 1H, $J=1.5$ Hz, Ar-C(Me)=CHCO₂Et], 4.20 (q, 2H, $J=7.3$ Hz, OCH_2CH_3), 3.87 (s, 6H, $2 \times$ Ar-OCH₃), 3.85 (s, 3H, Ar-OCH₃), 2.54 [d, 3H, $J=1.5$ Hz, $\text{C}(\text{CH}_3)=\text{CHCO}_2\text{Et}$], 1.30 (t, 3H, $J=7.3$ Hz, OCH_2CH_3) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=166.7$ (s, $\text{O}=\text{C}-\text{O}$), 155.4 [s, $\text{C}(\text{Me})=\text{CHCO}_2\text{Et}$], 153.0 (s, 3C, Ar-C), 137.9 [d, Ar-C(Me)=CHCO₂Et], 116.7 (d, Ar-CH), 103.7 (d, Ar-CH), 60.9 (q, Ar-OCH₃), 59.8 (t, OCH_2CH_3), 56.2 (q, $2 \times$ Ar-OCH₃), 18.1 [q, Ar-C(CH₃)=CHCO₂Et], 14.3 (q, OCH_2CH_3) ppm.

Ethyl (2E)-3-(2-bromo-5-methoxyphenyl)but-2-enoate (3t):

GP-3 was followed to the alcohol **1t** (115 mg, 0.50 mmol) with CuI (9.5 mg, 10 mol%), 1,10-phenanthroline (18 mg, 20 mol%) and K_3PO_4 (212 mg, 1 mmol) in toluene (2 mL) at 80 °C for 24 h. Progress of the oxidation was monitored by TLC till the reaction is completed. To the cooled reaction mixture at 0 °C, under nitrogen atmosphere, was added ylide [2.5 mmol, generated from 60% NaH (100.2 mg, 2.5 mmol) and TEPA (0.5 mL, 2.5 mmol) in THF (1.5 mL)] in THF (1.5 mL) under nitrogen atmosphere. Then the reaction mixture was refluxed at 65 °C for 12 h and monitored by TLC. Then, the reaction mixture was quenched with aqueous NH_4Cl solution and then extracted with CH_2Cl_2 (3×15 mL). The organic layer was washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent under reduced

pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 90:10) furnished the cinnamate **3t** (95.6 mg, 64%) as colorless viscous oil. [TLC control $R_f(\mathbf{1t})=0.35$, $R_f(\mathbf{3t})=0.65$ (petroleum ether/ethyl acetate 85:15, UV detection)]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2978$, 1708, 1626, 1577, 1429, 1289, 1215, 1154, 1038, 851, 779, 691 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=7.42$ (d, 1H, $J=8.8$ Hz, Ar-H), 6.71 (dd, 1H, $J=8.8$ and 2.9 Hz, Ar-H), 6.69 (d, 1H, $J=2.9$ Hz, Ar-H), 5.79 [q, 1H, $J=1.5$ Hz, $\text{C}(\text{Me})=\text{CHCO}_2\text{Et}$], 4.21 (q, 2H, $J=7.3$ Hz, OCH_2CH_3), 3.77 (s, 3H, Ar- OCH_3), 2.45 [d, 3H, $J=1.5$ Hz, $\text{C}(\text{CH}_3)=\text{CHCO}_2\text{Et}$], 1.30 (t, 3H, $J=7.3$ Hz, OCH_2CH_3) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=166.3$ (s, $\text{O}=\text{C}-\text{O}$), 158.8 [s, $\text{C}(\text{Me})=\text{CHCO}_2\text{Et}$], 156.9 (s, Ar-C), 145.5 (s, Ar-C), 133.7 (d, Ar-C($\text{Me})=\text{CHCO}_2\text{Et}$), 120.4 (d, Ar-CH), 114.9 (d, Ar-CH), 114.5 [d, Ar-CH], 110.9 (s, Ar-C), 60.0 (t, OCH_2CH_3), 55.5 (q, Ar- OCH_3), 20.2 [q, Ar-C(CH_3)= CHCO_2Et], 14.3 (q, OCH_2CH_3) ppm.

Ethyl (2E)-3-(2-bromo-4,5-dimethoxyphenyl)but-2-enoate (3w):

GP-3 was followed to the alcohol **1w** (131 mg, 0.50 mmol) with CuI (9.5 mg, 10 mol%), 1,10-phenanthroline (18 mg, 20 mol%) and K_3PO_4 (212 mg, 1 mmol) in toluene (2 mL) at 80 °C for 24 h. Progress of the oxidation was monitored by TLC till the reaction is completed. To the cooled reaction mixture at 0 °C, under nitrogen atmosphere, was added ylide [2.5 mmol, generated from 60% NaH (100.2 mg, 2.5 mmol) and TEPA (0.5 mL, 2.5 mmol) in THF (1.5 mL)] in THF (1.5 mL) under nitrogen atmosphere. Then the reaction mixture was refluxed at 65 °C for 12 h and monitored by TLC. Then, the reaction mixture was quenched with aqueous NH_4Cl solution and then extracted with CH_2Cl_2 (3 $\times$ 15 mL). The organic layer was washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 90:10 to 85:15) furnished the cinnamate **3w** (116.6 mg, 71%) as pale yellow viscous oil. [TLC control $R_f(\mathbf{1w})=0.40$, $R_f(\mathbf{3w})=0.65$ (petroleum ether/ethyl acetate 70:30, UV detection)]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2978$, 1712, 1640, 1598, 1500, 1439, 1260, 1233, 1159, 1033, 789 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=7.00$ (s, 1H, Ar-H), 6.64 (s, 1H, Ar-H), 5.79 (q, 1H, $J=1.0$ Hz, $\text{C}(\text{Me})=\text{CHCOOEt}$), 4.20 (q, 2H, $J=7.3$ Hz, OCH_2CH_3), 3.86 (s, 3H, Ar- OCH_3), 3.84 (s, 3H, Ar- OCH_3), 2.45 [d, 3H, $J=1.0$ Hz, $\text{C}(\text{CH}_3)=\text{CHCOOEt}$], 1.29 (t, 3H, $J=7.3$ Hz, OCH_2CH_3) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=166.4$ (s, $\text{O}=\text{C}-\text{O}$), 156.9 [s, $\text{C}(\text{CH}_3)=\text{CHCOOEt}$], 149.0 (s, Ar-C), 148.2 (s, Ar-C), 136.8 (s, Ar-C), 120.6 [d, $\text{C}(\text{CH}_3)=\text{CHCOOEt}$], 115.7 (d, Ar-CH), 111.7 (d, Ar-CH), 110.7 (s, Ar-C), 59.9 (t, OCH_2CH_3), 56.2 (q, Ar- OCH_3), 56.1 (q, Ar- OCH_3), 20.5 [q, $\text{C}(\text{CH}_3)=\text{CHCOOEt}$], 14.3 (q, OCH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[\text{C}_{14}\text{H}_{17}\text{BrNaO}_4]^+=[\text{M}+\text{Na}]^+$: 351.0202; found 351.0196.

¹³C NMR (100 MHz) spectrum of **1y** in CDCl₃

^1H NMR (400 MHz) spectrum of **2b** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2b** in CDCl_3

^1H NMR (400 MHz) spectrum of **2c** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2c** in CDCl_3

¹³C NMR (100 MHz) spectrum of **2d** in CDCl₃

^1H NMR (400 MHz) spectrum of **2e** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2e** in CDCl_3

¹H NMR (400 MHz) spectrum of **2f** in CDCl₃

¹³C NMR (100 MHz) spectrum of **2f** in CDCl₃

^1H NMR (400 MHz) spectrum of **2h** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2h** in CDCl_3

¹H NMR (400 MHz) spectrum of **2i** in CDCl₃

¹³C NMR (100 MHz) spectrum of **2i** in CDCl₃

¹H NMR (400 MHz) spectrum of **2j** in CDCl₃

¹³C NMR (100 MHz) spectrum of **2j** in CDCl₃

¹³C NMR (100 MHz) spectrum of **2l** in CDCl₃

^1H NMR (400 MHz) spectrum of **2m** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2m** in CDCl_3

¹H NMR (400 MHz) spectrum of **2n** in CDCl₃

¹³C NMR (100 MHz) spectrum of **2n** in CDCl₃

¹H NMR (400 MHz) spectrum of **2o** in CDCl₃

¹³C NMR (100 MHz) spectrum of **2o** in CDCl₃

^1H NMR (400 MHz) spectrum of **2p** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2p** in CDCl_3

^1H NMR (400 MHz) spectrum of **2q** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2q** in CDCl_3

^1H NMR (400 MHz) spectrum of **2r** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2r** in CDCl_3

^1H NMR (400 MHz) spectrum of **2s** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2s** in CDCl_3

^1H NMR (400 MHz) spectrum of **2t** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2t** in CDCl_3

^1H NMR (400 MHz) spectrum of **2u** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2u** in CDCl_3

^1H NMR (400 MHz) spectrum of **2v** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2v** in CDCl_3

¹H NMR (400 MHz) spectrum of **2w** in CDCl₃

¹³C NMR (100 MHz) spectrum of **2w** in CDCl₃

^1H NMR (400 MHz) spectrum of **2x** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2x** in CDCl_3

^1H NMR (400 MHz) spectrum of **2y** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2y** in CDCl_3

^1H NMR (400 MHz) spectrum of **2ac** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2ac** in CDCl_3

^1H NMR (400 MHz) spectrum of **2ad** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2ad** in CDCl_3

^1H NMR (400 MHz) spectrum of **2af** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **2af** in CDCl_3

¹H NMR (400 MHz) spectrum of **3e** in CDCl₃

¹³C NMR (100 MHz) spectrum of **3e** in CDCl₃

^1H NMR (400 MHz) spectrum of **3o** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **3o** in CDCl_3

^1H NMR (400 MHz) spectrum of **3p** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **3p** in CDCl_3

^1H NMR (400 MHz) spectrum of **3q** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **3q** in CDCl_3

¹H NMR (400 MHz) spectrum of **3r** in CDCl₃

¹³C NMR (100 MHz) spectrum of **3r** in CDCl₃

^1H NMR (400 MHz) spectrum of **3t** in CDCl_3

^{13}C NMR (100 MHz) spectrum of **3t** in CDCl_3

¹H NMR (400 MHz) spectrum of **3w** in CDCl₃

¹³C NMR (100 MHz) spectrum of **3w** in CDCl₃