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Supporting Information

CF₃SO₂Na-promoted photocatalytic aerobic oxidations of benzyl

alcohols to aromatic aldehydes and aromatic esters

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1. General information

A. Materials and general procedures

All reagents and solvents were purchased from commercial suppliers Adamas, Bide, TCI, J&K Chemical, Energy Chemical and Meryer, and they were directly used without further purification. CF_3SO_2Na (purity \geq 99%) was purchased from Shandong xiya reagents, PhSO₂Na (purity \geq 99%) and EtSO₂Na (purity \geq 99%) were purchased from Bide. All reactions were conducted in oven-dried reaction vessel under O₂ atmosphere (purity \geq 99.99%) unless otherwise mentioned.

B. Analytical methods

Gas chromatographic-mass spectrometric (GC-MS) analysis was performed on a JEOL JMS-Q1050GC system equipped with a flame-ionization detector. High resolution Gas chromatography and mass spectrometry (Orbitrap Exploris GC, Thermo Fisher, USA). ¹H NMR and ¹³C NMR spectra were recorded on a JEOL ECS-400 or JNM-ECA 600 spectrometers. Chemical shifts were reported in parts per million (ppm), ¹H NMR chemical shifts were internally referenced to tetramethylsilane (TMS) (¹H NMR: TMS references at 0.00 ppm) and residual proton signals of solvents (¹H NMR: CDCl₃ at 7.26 ppm, and DMSO-*d*₆ at 2.50 ppm), and ¹³C NMR chemical shifts were internally referenced to carbon signals of solvents (¹H NMR: CDCl₃ at 7.26 ppm, and DMSO-*d*₆ at 2.50 ppm), and ¹³C NMR chemical shifts were internally referenced to carbon signals of solvents (¹G NMR: CDCl₃ at 77.16 ppm, DMSO-*d*₆ at 39.52 ppm). Coupling constants (*J*) were reported in Hz with the following splitting abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, and br = broad. High resolution mass spectroscopic data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Chromatographic purification of products was accomplished by column chromatography on silica gel (Qingdao Haiyang, 200-300 mesh).

2. Investigations of the reaction conditions

Table S1 Effect of light sources^a

OH 1a	CF ₃ SO ₂ Na (25 mol %) KBr (50 mol %) H ₂ O (20 eq) ACN (1.5 mL), O ₂ (1 atm) hv (10 W, X nm),rt, 24 h	CHO 2a
Entry	Light source (X nm)	Yield (%) ^b
1	400	87
2	dark	nr
3	360	22
4	380	58

^{*a*}Reaction conditions: **1a** (0.2 mmol), CF₃SO₂Na (25 mol%), KBr (50 mol%), H₂O (20 eq), MeCN (ACN) (1.5 mL) under O₂ atmosphere using 10 W blue LEDs at room temperature for 24 h. ^bThe yields were determined by GC-MS using 4-methylacetophenone as the internal standard.

ОН	CF ₃ SO ₂ Na (25 mol %) KBr (50 mol %) H ₂ O (20 eq)	СНО
1a	Solvent (1.5 mL), O ₂ (1 atm) 400 nm (10 W) ,rt, 24 h	2a
Entry	Solvent (1.5 mL)	Yield (%) ^b
1	ACN	87
2	THF	trace`
3	CH ₂ Cl ₂	trace
4	MeCOOEt	34
6	acetone	6
8	DMF	28
9	DMSO	nr

 Table S2 Effect of solvents^a

^{*a*}Reaction conditions: **1a** (0.2 mmol), CF_3SO_2Na (25 mol%), KBr (50 mol %), H₂O (20 eq), solvent (1.5 mL) under O₂ atmosphere using 10 W blue LED at room temperature for 24 h. ^bThe yields were determined by GC-MS using 4-methylacetophenone as the internal standard.

ОН	CF ₃ SO ₂ Na (25 mol %) KBr (50 mol %) H ₂ O (20 eq)	СНО
1a	ACN (X mL), O ₂ (1 atm) 400 nm (10 W) ,rt, 24 h	2a
Entry	Solvent dosage (X mL)	Yield (%) ^b
1	0.5	59
2	1.0	78
3	1.5	87

Table S3 Effect of solvent dosages^a

^aReaction conditions: **1a** (0.2 mmol), CF₃SO₂Na (25 mol%), KBr (50 mol %), H₂O (20 eq), ACN

(X mL) under O_2 atmosphere using 10 W blue LED at room temperature for 24 h. bThe yields were

determined by GC-MS using 4-methylacetophenone as the internal standard.

Table S4	Effect	of	CF ₃ SC)2Na	loadings ^a
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la 1a	CF ₃ SO ₂ Na (X mol %) ←OH ←OH ←CH ←CH ←CF ₃ SO ₂ Na (X mol %) ←CF ₃ SO ₂ Na (X mol %)	CHO 2a
Entry	CF ₃ SO ₂ Na loading (X mol %)	Yield (%) ^b
1°	5	trace
2	10	22
3	25	87
4	50	71
5	75	52
6	100	37

"Reaction conditions: **1a** (0.2 mmol), CF₃SO₂Na (X mol%), KBr (50 mol %), H₂O (20 eq), ACN (1.5 mL) under O₂ atmosphere using 10 W blue LED at room temperature for 24 h. ^bThe yields were determined by GC-MS using 4-methylacetophenone as the internal standard. ^cBenzoic acid is isolated in 57% yield.

 Table S5 Effect of catalysts^a

ОН	Catalyst (25 mol %) KBr (50 mol %) H ₂ O (20 eq)	СНО
1a	ACN (1.5 mL), O ₂ (1 atm) 400 nm (10 W) ,rt, 24 h	2a
Entry	Pre-Cat. (25 mol %)	Yield (%) ^b
1	CF ₃ SO ₂ Na	87
2	CF3SO3Na	nr
3	PhSO ₂ Na	np
4	EtSO ₂ Na	np

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^{*a*}Reaction conditions: **1a** (0.2 mmol), pre-catalyst (25 mol%), KBr (50 mol %), H₂O (20 eq), ACN (1.5 mL) under O₂ atmosphere using 10 W blue LED at room temperature for 24 h. ^bThe yields were determined by GC-MS using 4-methylacetophenone as the internal standard.

OH	CF ₃ SO ₂ Na (25 mol %) KBr (50 mol %) H H ₂ O (X eq)	СНО
1a	ACN (1.5 mL), O ₂ (1 atm) 400 nm (10 W) ,rt, 24 h	2a
Entry	H ₂ O dosage (X eq)	Yield (%) ^b
1	0	trace
2	5	17
3	10	56
4	15	72
5	20	87
6	25	79

Table S6 Effect of H₂O dosages^a

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^{*a*}Reaction conditions: **1a** (0.2 mmol), CF₃SO₂Na (25 mol%), KBr (50 mol %), H₂O (X eq), ACN (1.5 mL) under O₂ atmosphere using 10 W blue LED at room temperature for 24 h. ^bThe yields were determined by GC-MS using 4-methylacetophenone as the internal standard.

Table S7 Effect of KBr dosages^a

OH 1a	CF ₃ SO ₂ Na (25 mol %) KBr (X mol %) H ₂ O (20 eq) ACN (1.5 mL), O ₂ (1 atm) 400 nm (10 W) ,rt, 24 h	CHO 2a
Entry	KBr dosage (X mol %)	Yield (%) ^b
l°	0	trace
2	10	11
3	25	34
4	50	87
6	75	88

^{*a*}Reaction conditions: **1a** (0.2 mmol), CF₃SO₂Na (25 mol%), KBr (X mol %), H₂O (20 eq), ACN (1.5 mL) under O₂ atmosphere using 10 W blue LED at room temperature for 24 h. ^bThe yields were determined by GC-MS using 4-methylacetophenone as the internal standard. ^cBenzoic acid is isolated in 57% yield.

Table S8 Effect of Br sources^a

O⊢ 1a	CF ₃ SO ₂ Na (25 mol %) [Br] (50 mol %) H ₂ O (20 eq) ACN (1.5 mL), O ₂ (1 atm) 400 nm (10 W) ,rt, 24 h	CHO 2a
Entry	Br source (50 mol %)	Yield (%) ^b
1	KBr	87
2	NaBr	82
3	NH ₄ Br	79
5	TBAB	33

^aReaction conditions: **1a** (0.2 mmol), CF₃SO₂Na (25 mol%), [Br] (50 mol %), H₂O (20 eq), ACN (1.5 mL) under O₂ atmosphere using 10 W blue LED at room temperature for 24 h. ^bThe yields were determined by GC-MS using 4-methylacetophenone as the internal standard. **Table S9** Effect of reaction time^a

	CF ₃ SO ₂ Na (25 mol%) DH►	СНО
1a	blue LED (400-405 nm) EA (0.5 mL) O ₂ , rt, time	2a
Entry	Time (h)	Yield (%) ^b
1	8	63
2	16	81
3	24	87
4	32	85

^{*a*}Reaction conditions: **1a** (0.2 mmol), CF₃SO₂Na (25 mol%), KBr (50 mol %), H₂O (20 eq), ACN (1.5 mL) under O₂ atmosphere using 10 W blue LED at room temperature for X h. ^bThe yields were determined by GC-MS using 4-methylacetophenone as the internal standard.

3. General experimental procedures

3.1 Experimental procedures

General procedure A



Aromatic alcohol (1) (0.2 mmol, 1.0 equiv), sodium trifluoromethanesulfinate (25 mol%), KBr (50 mol%), H₂O (20 eq) and MeCN (1.5 mL) were added to an oven-dried reaction tube equipped with magnetic stirring bar, and the reaction tube was irradiated with 10 W blue LED (400-405 nm) for 24 h under O_2 atmosphere (1 atm). After the reaction was completed, the resulting solution was

concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 15:1-10:1) to give the corresponding aromatic aldehyde.

General procedure B

$$\begin{array}{c} \begin{array}{c} CF_{3}SO_{2}Na~(25~mol~\%)\\ \hline \\ R \\ \hline \\ I \end{array} + \begin{array}{c} R'OH~(15~eq)\\ \hline \\ 1 \end{array} & \begin{array}{c} CF_{3}SO_{2}Na~(25~mol~\%)\\ \hline \\ KBr~(50~mol~\%)\\ \hline \\ MeCOOEt~(1.5~mL),~O_{2}~(1~atm)\\ LED~(400~nm,~10~w),~rt,~24~h \end{array} + \begin{array}{c} O\\ \hline \\ R \\ \hline \\ I \end{array} \end{array}$$

Aromatic alcohol (1) (0.2 mmol, 1.0 equiv), sodium trifluoromethanesulfinate (25 mol%), KBr (50 mol%), MeOH (20 equiv) and ethyl acetate (1.5 mL) were added to an oven-dried reaction tube equipped with magnetic stirring bar, and the reaction tube was irradiated with 10 W blue LED (400-405 nm) for 36 h under O_2 atmosphere (1 atm). After the reaction was completed, the resulting solution was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give the corresponding aromatic ester.

3.2 Scale-up reaction for the oxidative esterification



[1,1'-Biphenyl]-4-ylmethanol (1b) (5.0 mmol, 921.2 mg, 1.0 equiv), sodium trifluoromethanesulfinate (25 mol%, 197.6 mg), potassium bromide (50 mol%, 297.5 mg), MeOH (**3a**) (75 mmol, 2.4 g, 15 equiv) and ethyl acetate (7.5 mL) were added to an oven-dried reaction vessel (50 mL) equipped with magnetic stirring bar, and the reaction vessel was irradiated with 10 W LED (400-405 nm) for 48 h under O₂ atmosphere (1 atm). After the reaction was completed, the resulting solution was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give product **4b** in 42% yield.

4. Investigations on the reaction mechanism

4.1 Control experiments

In order to explore the possible mechanism of the present transformation, control experiments were conducted as follows:



Figure S2 Partial enlargement of Figure S1

5. Characterization data of the aldehyde products



Benzaldehyde (2a):¹ Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2a** as a colorless liquid (17.8 mg, 81%). ¹H and ¹³C NMR of **2a** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 10.02 (s, 1H), 7.92 – 7.82 (m, 2H), 7.62 (dd, *J* = 7.3, 3.0 Hz, 1H), 7.53 (dt, *J* = 7.8, 3.9 Hz, 2H).¹³C NMR (100 MHz, Chloroform-*d*) δ 192.6, 136.5, 134.6, 129.9, 129.1.



4-Biphenylcarboxaldehyde (2b):² Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2b** as a white solid (29.5 mg, 81%). ¹H and ¹³C NMR of **2b** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 10.05 (s, 1H), 7.94 (dd, *J* = 5.5, 2.8 Hz, 2H), 7.74 (dd, *J* = 8.3, 1.9 Hz, 2H), 7.69 – 7.58 (m, 2H), 7.55 – 7.34 (m, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.1, 147.3, 139.8, 135.3, 130.4, 129.2, 128.6, 127.8, 127.5.



1-Naphthaldehyde (2c):⁵ Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) to give **2c** as a colorless solid (25.0 mg, 80%). ¹H and ¹³C NMR of **2c** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 10.38 (s, 1H), 9.25 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 8.00 – 7.94 (m, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.68 (ddd, *J* = 8.4, 6.7, 1.4 Hz, 1H), 7.59 (q, *J* = 7.9 Hz, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 193.7, 136.9, 135.4, 133.8, 131.5, 130.6, 129.2, 128.6, 127.1, 125.0. The ¹³C spectral data are consistent with those reported in the literature.⁵



4-Methylbenzaldehyde (2d):¹ Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2d** as a colorless liquid (12.5 mg, 52%). ¹H and ¹³C NMR of **2d** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 8.23 – 7.49 (m, 2H), 7.32 (dd, *J* = 7.9, 4.0 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.2, 145.7, 134.3, 130.0, 129.8, 22.0.



4-(*tert***-Butyl) benzaldehyde (2e):**² Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2e** as a colorless solid (24.0 mg, 74%). ¹H and ¹³C NMR of **2e** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.97 (s, 1H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 1.34 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.2, 158.6, 134.2, 129.8, 126.1, 35.44, 31.2.



2-Methoxybenzaldehyde (2f):¹ Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2f** as a light yellow solid (19.1 mg, 70%). ¹H and ¹³C NMR of **2f** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 10.46 (s, 1H), 7.81 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.54 (ddd, *J* = 8.8, 7.1, 1.8 Hz, 1H), 7.17 – 6.78 (m, 2H), 3.91 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.0, 161.9, 136.1, 128.6, 124.9, 120.8, 111.7, 55.7.



4-Methoxybenzaldehyde (2g):¹ Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2k** as a white solid (20.4 mg, 75%). ¹H and ¹³C NMR of **2k** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.85 (s, 1H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.29 – 6.59 (m,

2H), 3.85 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 191.0, 164.7, 132.1, 130.0, 114.4, 55.7.



3,4-dimethoxybenzaldehyde (2h):² Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 4:1) to give **2g** as a white solid (22.6 mg, 68%). ¹H and ¹³C NMR of **2g** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.83 (s, 1H), 7.46 – 7.40 (m, 1H), 7.38 (d, *J* = 4.5 Hz, 1H), 6.95 (dd, *J* = 8.4, 4.7 Hz, 1H), 3.94 (d, *J* = 4.8 Hz, 3H), 3.91 (d, *J* = 5.4 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 191.0, 154.6, 149.7, 130.2, 127.0, 110.5, 108.9, 56.27, 56.1.



4-Hydroxybenzaldehyde (2i):² Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 1:1) to give **2h** as a white solid (13.7 mg, 56%). ¹H and ¹³C NMR of **2h** is identical with the spectra of the known compound. ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.58 (s, 1H), 9.75 (s, 1H), 8.34 – 7.43 (m, 2H), 7.34 – 6.37 (m, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 191.5 (d, *J* = 17.5 Hz), 163.9, 132.7 (d, *J* = 10.1 Hz), 129.0, 116.4 (d, *J* = 19.0 Hz).



4-Fluorobenzaldehyde (2j):¹ Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2i** as a colorless liquid (19.1 mg, 77%). ¹H and ¹³C NMR of **2i** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.93 (s, 1H), 8.01 – 7.71 (m, 2H), 7.42 – 6.80 (m, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.6, 166.6 (d, *J* = 257.1 Hz), 133.1, 132.3 (d, *J* = 9.7 Hz), 116.4 (d, *J* = 22.3 Hz). ¹⁹F NMR (400 MHz, chloroform-d) δ -102.3.



4-Chlorobenzaldehyde (2k):¹ Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2j** as a

white solid (24.1 mg, 86%). ¹H and ¹³C NMR of **2j** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.97 (s, 1H), 8.10 – 7.66 (m, 2H), 7.49 (dd, *J* = 8.6, 3.4 Hz, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 191.0, 141.0, 134.8, 131.0, 129.6.



2,6-Dichlorobenzaldehyde (21):³ Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) to give **21** as a white solid (29.8 mg, 85%). ¹H and ¹³C NMR of **21** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 10.46 (s, 1H), 7.37 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.9, 136.9, 133.7, 130.4, 129.9.



4-Bromobenzaldehyde (2m):¹ Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2m** as a white solid (30.7 mg, 83%). ¹H and ¹³C NMR of **2m** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.96 (s, 1H), 8.24 – 7.43 (m, 4H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 191.2, 135.2, 132.5, 131.1, 129.9.



3-Methoxybenzaldehyde (2n):¹ Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2n** as a colorless liquid (28.9 mg, 78%). ¹H and ¹³C NMR of **2n** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 7.97 (t, *J* = 2.2 Hz, 1H), 7.78 (dd, *J* = 7.8, 3.1 Hz, 1H), 7.75 – 7.67 (m, 1H), 7.40 (td, *J* = 7.5, 3.2 Hz, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.9, 138.1, 137.4, 132.4, 130.7, 128.5, 123.5.



2-Bromobenzaldehyde (20):¹ Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **20** as a colorless liquid (30.0 mg, 81%). ¹H and ¹³C NMR of **20** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 10.34 (s, 1H), 7.90 (d, *J* = 6.7 Hz, 1H), 7.63 (dd, *J* = 6.8, 2.4 Hz, 1H), 7.42 (dt, *J* = 5.2, 2.5 Hz, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.0, 135.5, 134.0, 133.6, 130.0, 128.0, 127.2.



4-(Trifluoromethyl) benzaldehyde (2p):² Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2p** as a white solid (26.4 mg, 76%). ¹H and ¹³C NMR of **2p** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 10.08 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H) ¹³C NMR (101 MHz, Chloroform-*d*) δ 191.2, 138.7, 135.7 (q, *J* = 32.7 Hz), 130.0, 126.2 (d, *J* = 3.8 Hz), 123.5 (q, *J* = 273.0 Hz). ¹⁹F NMR (400 MHz, chloroform-d) δ -63.3.



4-Cyanobenzaldehyde (2q):³ Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2q** as a white solid (18.6 mg, 71%). ¹H and ¹³C NMR of **2q** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) ¹H NMR (400 MHz, Chloroform-*d*) δ 10.07 (s, 1H), 8.06 – 7.90 (m, 2H), 7.88 – 7.72 (m, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.9, 138.8, 133.0, 130.0, 117.8, 117.7.



4-Nitrobenzaldehyde (2r):¹ Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2r** as a white solid (22.7 mg, 75%). ¹H and ¹³C NMR of **2r** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 10.15 (s, 1H), 8.38 (d, *J* = 8.5 Hz, 2H), 8.07 (d, *J* = 8.6 Hz, 2H). ¹³C

NMR (100 MHz, Chloroform-d) δ 190.4, 151.2, 140.1, 130.6, 124.4.



3-Chloro-4-methoxybenzaldehyde (2s):⁴ Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **2s** as a white solid (25.9 mg, 76%). ¹H and ¹³C NMR of **2s** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.82 (s, 1H), 7.87 (d, *J* = 2.1 Hz, 1H), 7.74 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 3.96 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.9, 159.9, 131.2, 130.7, 130.3, 123.7, 111.8, 56.6.



4,5-Dimethoxy-2-nitrobenzaldehyde (2t):² Prepared according to general procedure A. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **2t** as a white solid (25.7 mg, 61%). ¹H and ¹³C NMR of **2t** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 10.39 (s, 1H), 7.58 (s, 1H), 7.38 (s, 1H), 4.00 (d, *J*=4.6 Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 187.8, 153.3, 152.5, 144.0, 125.6, 109.8, 107.3, 56.9, 56.9.

6. Characterization data of the ester products



Methyl benzoate (4a):⁶ Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **4a** as a colorless oil (18.0 mg, 66%). ¹H and ¹³C NMR of **4a** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 7.95 (m, 2H), 7.66 – 7.51 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 3.92 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 167.2, 133.0, 130.3, 129.7, 128.5, 52.2.



Methyl [1,1'-biphenyl]-4-carboxylate (4b):¹⁰ Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give 4b as a white solid (26.7 mg, 63%). ¹H and ¹³C NMR of 4b is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.64 (dd, *J* = 15.0, 7.9 Hz, 4H), 7.46 (dd, *J* = 8.4, 6.7 Hz, 2H), 7.43 – 7.36 (m, 1H), 3.94 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 167.1, 145.7, 140.1, 130.2, 129.0, 128.9, 128.2, 127.3, 127.1, 52.2.



Methyl 4-methylbenzoate (4c):⁶ Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **4c** as a white solid (15.9 mg, 53%). ¹H and ¹³C NMR of **4c** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 7.65 (m, 2H), 7.22 (dd, *J* = 8.4, 3.4 Hz, 2H), 3.89 (d, *J* = 4.5 Hz, 3H), 2.39 (d, *J* = 3.6 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 167.3, 143.7, 129.7, 129.2, 127.5, 52.0, 21.7.



Methyl 4-(tert-butyl)benzoate (4d):⁷ Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give 4d as a white solid (26.5 mg, 69%). ¹H and ¹³C NMR of 4d is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 7.70 (m, 2H), 7.45 (dd, *J* = 8.6, 3.6 Hz, 2H), 3.90 (d, *J* = 3.8 Hz, 3H), 1.33 (d, *J* = 4.0 Hz, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 167.3, 156.6, 129.5, 127.5, 125.4, 52.1, 35.2, 31.2.



Methyl 4-methoxybenzoate (4e):⁶ Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **4e** as a white solid (21.6 mg, 65%). ¹H and ¹³C NMR of **4e** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 (dd, *J* = 8.6, 3.2 Hz, 2H), 6.90 (dd, *J* = 8.8, 3.5 Hz, 2H), 3.87 (s, 3H), 3.84 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 167.0, 163.4, 131.7, 122.7, 113.7, 55.5, 52.0.



Methyl 4-fluorobenzoate (4f):⁶ Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **4f** as a colorless oil (18.8 mg, 61%). ¹H and ¹³C NMR of **4f** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.04 (ddd, *J* = 9.2, 5.9, 2.9 Hz, 2H), 7.20 – 6.93 (m, 2H), 3.90 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 168.3, 167.1,164.6 (d, *J* = 250 Hz), 132.3, 132.2 (d, *J* = 10 Hz), 126.5, 115.7, 115.5 (d, *J* = 21 Hz), 52.3. ¹⁹F NMR (400 MHz, chloroform-d) δ -105.7.



Methyl 4-chlorobenzoate (4g):⁶ Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give 4g as a white solid (28.0 mg, 82%). ¹H and ¹³C NMR of 4g is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dt, *J* = 8.7, 1.8 Hz, 2H), 7.39 (dt, *J* = 8.7, 1.7 Hz, 2H), 3.89 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.3, 139.5, 131.1, 128.8, 128.7, 52.4.



Methyl 4-bromobenzoate (4h):⁶ Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **4h** as a white solid (30.1 mg, 70%). ¹H and ¹³C NMR of **4h** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 3.90

(s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.5, 131.8, 131.2, 129.1, 128.1, 52.4.



Methyl 3-bromobenzoate (4i):⁸ Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **4i** as a white solid (24.5 mg, 57%). ¹H and ¹³C NMR of **4i** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 2.0 Hz, 1H), 7.95 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.74 – 7.58 (m, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 3.91 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 165.9, 136.0, 132.7, 132.1, 130.1, 128.3, 122.5, 52.5.



Methyl 2-bromobenzoate (4j):⁹ Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **4j** as a white solid (31.0 mg, 72%). ¹H and ¹³C NMR of **4j** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 7.5, 2.1 Hz, 1H), 7.69 – 7.59 (m, 1H), 7.38 – 7.26 (m, 2H), 3.91 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.7, 134.4, 132.7, 132.2, 131.4, 127.3, 121.8, 52.6.



Methyl 4-nitrobenzoate (4k):⁶ Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **4k** as a white solid (25.7 mg, 71%). ¹H and ¹³C NMR of **4k** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.30 – 8.24 (m, 2H), 8.21 – 8.16 (m, 2H), 3.96 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 165.3, 150.6, 135.6, 130.8, 123.64, 52.9.



Methyl 4-cyanobenzoate (41):⁶ Prepared according to general procedure B. The product was

purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **4l** as a white solid (20.6 mg, 64%). ¹H and ¹³C NMR of **4l** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 8.3, 1.9 Hz, 2H), 7.74 (dd, *J* = 8.2, 2.0 Hz, 2H), 3.95 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 165.6, 134.0, 132.3, 130.2, 118.1, 116.5, 52.9.



Methyl 4-(trifluoromethyl)benzoate (4m):⁶ Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give 4m as a white solid (25.3 mg, 62%). ¹H and ¹³C NMR of 4m is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 8.3, 2.8 Hz, 2H), 7.69 (dd, *J* = 8.4, 3.0 Hz, 2H), 3.94 (s, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 166.0, 134.5 (q, J = 30.0 Hz),133.4, 130.1, 125.5, 123.7 (d, J = 272.6 Hz), 52.6. ¹⁹F NMR (400 MHz, chloroform-d) δ -63.1.



Dimethyl terephthalate (4n):⁸ Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **4n** as a white solid (26.0 mg, 67%). ¹H and ¹³C NMR of **4n** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.18 – 8.00 (m, 4H), 3.97 – 3.87 (m, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.4, 134.0, 129.6, 52.5. The ¹³C spectral data are consistent with those reported in the literature.⁸



Methyl 4-(tert-butoxycarbonylamino) benzoate (40):² Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give 40 as a white solid (29.5 mg, 59%). ¹H and ¹³C NMR of 40 is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 8.7, 1.7 Hz, 2H), 7.68 – 7.18 (m, 2H), 6.91 (d, *J* = 30.9 Hz, 1H), 3.86 (s, 3H), 1.49 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.9, 152.4, 142.9, 131.0, 124.4, 117.5, 81.2, 52.0, 28.3.



Ethyl benzoate (4p):¹² Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give 4p as a colorless oil (17.1 mg, 57%). ¹H and ¹³C NMR of 4p is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.7, 132.9, 130.6, 129.6, 128.4, 61.0, 14.4.



Propyl benzoate (4q):¹² Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **4q** as a white solid (8.2 mg, 25%). ¹H and ¹³C NMR of **4q** is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 4.20 (t, *J* = 6.7 Hz, 2H), 1.72 (q, *J* = 7.1 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.7, 132.9, 130.6, 129.6, 128.4, 66.6, 22.2, 10.6.



Isopropyl benzoate (4r):¹² Prepared according to general procedure B. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give 4r as a white solid (14.4 mg, 44%). ¹H and ¹³C NMR of 4r is identical with the spectra of the known compound. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.91 (m, 2H), 7.53 – 7.42 (m, 1H), 7.41 – 7.31 (m, 2H), 5.18 (hept, *J* = 6.3 Hz, 1H), 1.30 (d, *J* = 6.3 Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.2, 132.7, 130.9, 129.6, 128.3, 68.4, 22.0.

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8. NMR spectra of aromatic aldehydes and aromatic esters

O 2a ¹H NMR (400 MHz, Chloroform-*d*)





























50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -24 f1 (ppm)



















¹H NMR (400 MHz, Chloroform-*d*)







4.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -C f1 (ppm)



¹³C NMR (100 MHz, Chloroform-*d*)













¹³C NMR (100 MHz, Chloroform-d)



220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 f1 (ppm)

— 3.92











¹H NMR (400 MHz, Chloroform-*d*)









 $\left\{\begin{array}{c} 7,99\\ 7,97\\ 7,97\\ 7,97\\ 7,97\\ 6,89\\ 6,89\\ 6,89\\ 6,89\\ 6,89\\ 3,87\\ 3,84\\ 3,84\\ 3,84\\ 8,89\\ 6,8$



¹H NMR (400 MHz, Chloroform-*d*)



8.05 8.05 8.05 8.04 8.04 8.03 8.03 8.03 8.03 8.03 8.03 7.12 7.12 7.12 7.10 7.10 7.10 7.07 7.07



















50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -2! f1 (ppm)



MeO₂C









¹H NMR (400 MHz, Chloroform-*d*)







¹H NMR (400 MHz, Chloroform-*d*)



¹³C NMR (100 MHz, Chloroform-*d*)





220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 f1 (ppm)