Supporting Information

Hydroxyl Radical-Mediated Oxidative Cleavage of C=C Band and Further

Esterification Reaction by Heterogeneous Semiconductor Photocatalysis

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Table of Contents

| General Methods | S1 |
|-----------------------|----|
| Experimental Section | S1 |
| Characterization data | S8 |
| <u>NMR Spectra</u> | |

General Methods

All chemicals were commercially available and used without further purification. All reactions were carried out in oven-dried glassware under an atmosphere of oxygen, unless stated otherwise. For quantitative flash chromatography, technical grade solvents were used. Analytical thin-layer chromatography was performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm). The plates were visualized by exposure to ultraviolet light. ¹H NMR spectra were recorded on Bruker DRX (500, 400 or 300 MHz) and ¹³C NMR spectra on Bruker DRX (125, 100 or 75 MHz) spectrometer. Mass spectra were taken on a Finnigan TSQ Quantum-MS instrument in the electrospray ionization (ESI) mode. Elemental analyses were performed on a Yanagimoto MT3CHN recorder.

Experimental Section

1、 Synthesis of TCN:

Tubular carbon nitride (TCN) was synthesized by directly self-assembly of melamine according to Fu's method.^{S1} Typically, 1g (8 mmol) melamine with 1.2g of phosphorous acid was dissolved in 100 mL deionized water (pH=1) with strong stirring for 30 minutes. Then the mixture was transferred into an autoclave with Teflon liner and heated at 180 °C for 10 hours. Then the mixture after hydrothermal reaction was centrifuged, washed with deionized water for more than 10 times until the phosphorus was completely removed. Finally, the resultant solids were heated to 600 °C for 1.5 hours under a flow of nitrogen with a heating rate of 2.5 °C min⁻¹ and TCN was obtained.

2、 Synthesis of g-C₃N₄:

Graphite phase carbon nitride $(g-C_3N_4)$ was synthesized by directly heating melamine. Typically, melamine hydrochloride was contained in a covered crucible and then heated to 500 °C in a muffle furnace for 2 h with a heating rate of 20 °C min⁻¹, followed by a further heat treatment at 520 °C for 2 h.

3、Synthesis of CN620:

The CN620 photocatalyst was synthesized following the reported method.^{S2} 1 g of g-C₃N₄ was put into a crucible, heated to 620 °C at a ramp rate of 5 °C min⁻¹ in a tube furnace under N₂ condition, respectively, and maintained at the corresponding temperature for 2 h. After being cooled down to room temperature, the resultant powders were collected.

4、 Synthesis of metal-doped graphitic carbon nitride :

The Cu/C₃N₄ photocatalyst was synthesized following the reported method.^{S3} Typically, melamine (2g) was uniformly mixed with copper(II) acetate (3 mmol). The resulting mixture was then heated to 550 °C with 2 °C min⁻¹ in a tube furnace under N₂ atmosphere and kept for 2 h. After cooling to room temperature, the final solid product (Cu-doped C₃N₄) was collected without further purification. Similarly, the Fe(NO₃)₃·9H₂O and Co(NO₃)₂·6H₂O were selected as metal salts to prepare metal-doped Fe/C₃N₄, Co/C₃N₄.

5, Preparation of benzaldehyde (1b)



A 25 mL clean and dry Schlenk reaction tube with a magnetic stirring rotor was equipped with styrene **1a** (0.5 mmol), TCN (10 mg), MeCN (1.5 mL) and H₂O (0.5 mL). The mixture was irradiated with a Xe lamp (250 W) and the distance of the reaction vial from the light is about 6 centimeters with an oxygen ball for 10 h (Figure S1). The reaction vial cooled by a electric fan and the temperature of the reaction mixture is about 36 °C. After the reaction, the solvent was removed under reduced pressure. Purification of the crude product was achieved by flash column chromatography using petrol n-hexane/ethyl acetate (8:1~16:1) as eluent, and the collected product was evaporated and concentrated in the oven (60 °C) for further drying and weighing.



Figure S1. The photochemical set 250 W Xe lamp.

6. Optimization of the Esterification reaction conditions

Table S1 Optimization of the Esterification reaction conditions^a

| | + MeOH 1a | 250 W Xe lamp TCN Acid O ₂ (1 atm) | | < |
|-----------------|------------------|--|---------|------------------------|
| Entry | Catalyst | Addition | Solvent | Yield (%) ^b |
| 1 | TCN (10 mg) | $H_2SO_4(98 \text{ wt\%})$ | МеОН | 57 |
| 2 | TCN (10 mg) | HClO ₄ (70 wt%) | МеОН | 46 |
| 3 | TCN (10 mg) | HCl (37 wt%) | МеОН | 69 |
| 4 | TCN (10 mg) | HNO ₃ (68 wt%) | МеОН | 53 |
| 5 ^c | TCN (10 mg) | HCl (37 wt%) | МеОН | 77 |
| 6^d | TCN (10 mg) | HCl (37 wt%) | МеОН | 15 |
| 7 | TCN (5 mg) | HCl (37 wt%) | МеОН | 39 |
| 8 | TCN (20 mg) | HCl (37 wt%) | MeOH | 75 |
| 9 ^e | TCN (10 mg) | HCl (37 wt%) | MeOH | NR |
| 10 ^f | TCN (10 mg) | HCl (37 wt%) | МеОН | NR |
| 11 | without catalyst | HCl (37 wt%) | MeOH | NR |

^{*a*} Reaction conditions: 1a styrene (0.5 mmol), TCN (10 mg), acid (0.5 mL) in MeOH (2 mL) were irradiated with a 250 W Xe lamp under oxygen at room temperature for 10 h; ^{*b*} isolated yield; ^{*c*} HCl (37 wt%, 0.3 mL); ^{*d*} HCl (37 wt%, 0.2 mL); ^{*e*} without light; ^f under nitrogen condition.

7, Preparation of Methyl benzoate (1c)



A 25 mL clean and dry Schlenk reaction tube with a magnetic stirring rotor was equipped with styrene **1a** (0.5 mmol), TCN (10 mg), HCl (0.3 mL, 37 wt% aqueous) in MeOH (2 mL). The mixture was irradiated with a Xe lamp (250 W) with an oxygen ball for 10 h. The temperature of the reaction mixture is about 30 °C and the distance of the reaction vial from the light is about 6 centimeters (Figure S1). After the reaction, the solvent was removed under reduced pressure. Purification of the crude product was achieved by flash column chromatography using petrol n-hexane/ethyl acetate (8:1~16:1) as eluent, and the collected product was evaporated and concentrated in the oven (60 °C) for further drying and weighing.

8、 Determination of the apparent quantum yield of catalysts

Apparent quantum yield (AQY) was measured under a certain wavelength of monochromatic light irradiation obtained by equipping 250 W Xe lamp with monochromatic filters, and the AQY was calculated through the following equation:

$$\eta_{AQY} = \frac{N_e}{N_p} \times 100\% = \frac{n \times M \times N_A}{\frac{W \times S \times t}{h \times v}} \times 100\%$$

where N_e and N_p stand for the amount of electrons involved in the reduction and incident photons, *n* is the number of electrons needed to form a product molecule, *M* is the molar number of products. N_A and *h* represent the Avogadro's constant and Planck constant, respectively. *W*, *S*, *t* and *v* are the light density, irradiation area, time and light frequency, respectively.

| Condition | AQY _(1b) (%) | |
|-------------------------------------|-------------------------|--|
| 250 W Xe lamp (λ=380 nm) | 0.0069 | |
| 250 W Xe lamp (λ=420 nm) | 0.0057 | |
| 250 W Xe lamp (λ=500 nm) | 0.0026 | |
| 23 W White LED (λ =500 nm) | 0.0017 | |
| 5 W Blue LED (λ =450 nm) | 0.0005 | |
| 7 W UV-LED (λ=365 nm) | 0.0044 | |

9、 Reaction under visible-light irradiation ($\lambda > 420$ nm)

| Condition | 1b Yield (%) | 1c Yield (%) |
|-------------------------------|--------------|--------------|
| 250 W Xe lamp (full spectrum) | 80 | 77 |
| 250 W Xe lamp (λ>420 nm) | 63 | 57 |



Figure S2. The photochemical set 250 W Xe lamp with a filter (λ >420 nm).

10、 General procedure for the cleavage of alkenes using Sunlight



Figure S3. The photograph of outdoor equipment of sunlight-driven.

The scaled-up reaction conditions of visible-light promoted oxidative cleavage reaction of alkenes under sunlight: styrene 1a (20 mmol), TCN (300 mg), MeCN (30 mL) and H₂O (10 mL) were irradiated with sunlight under oxygen at ambient temperature (38 °C) for 9 h (from 8 am to 5 pm on August 21, 2020, Wuxi, China). Oxidative esterification reaction conditions: styrene 1a (20 mmol), TCN (300 mg), HCl (6 mL, 37 wt% aqueous) in MeOH (40 mL) were irradiated with sunlight under oxygen at ambient temperature (38 °C) for 9 h (from 8 am to 5 pm on August 21, 2020, Wuxi, China).

11、 Isotope labeling experiment

a) The D₂O isotope experiment



Figure S4. ¹H NMR spectrum.

S1:S2=0.999:0.001

b) The ¹⁸O₂ isotope experiment



Figure S5. GC-MS analysis spectrum.



c) The H_2O^{18} isotope experiment



Figure S6. GC-MS analysis spectrum.

S1:S2= 1520935: 5995011≈0.25:1

d) The ¹⁸O₂ isotope experiment



Figure S7. GC-MS analysis spectrum.

S1:S2= 930160: 76867≈12.10:1

12, Intermediate capture experiment



A 25 mL clean and dry Schlenk reaction tube with a magnetic stirring rotor was equipped with styrene **1a** (0.5 mmol), D-Methionine (1eq, 75 mg), TCN (10 mg), MeCN (1.5 mL) and H_2O (0.5 mL). The mixture was irradiated with a Xe lamp (250 W) with an oxygen ball for 5 h. At the end of the reaction, a small amount of reaction solution was taken, and the product was qualitatively analyzed by mass spectrometry by GC-MS.



Figure S8. GC-MS analysis spectrum of the formation of 1,2-diols 1f.

Characterization of TCN:

The X-ray diffraction (XRD) patterns were obtained on an X-ray diffractometer (Bruker D8 Advance) using Cu Kα radiation. Scanning electron microscopy (SEM) micrographs were taken using a Hitachi S-4800 instrument operating at 15 KV. Fourier transform infrared spectroscopy (FT-IR) was recorded on a Nicolet iS50 Spectrum One spectrometer using KBr pellets. The photoluminescence spectra (PL) were recorded with an Edinburgh FS5 fluorescence spectrophotometer at room temperature. UV-visible absorption spectroscopy was recorded using a UV-visible spectrophotometer (Nicolet UV-2700). Thermo Gravimetric Analysis-Mass Spectroscopy (TG-MS) was performed on a TGA/1100SF, Jupiter Netzsch instrument, equipped with a mass spectrometry (MS) (Aelos QMS 403C) using a standard electron impact ionization detector.



Figure S9. a) FT-IR spectra of the synthesized $g-C_3N_4$ and TCN, b) XRD patterns of assynthesized $g-C_3N_4$ and TCN.



Figure S10. a) Photoluminescence spectra of the synthesized $g-C_3N_4$ and TCN (395 nm excitation at room temperature), b) TG-MS data of TCN.



Figure S11. a) UV-vis light absorption spectra of the synthesized $g-C_3N_4$, TCN and band gap energies (inset), and b) band structure alignments of $g-C_3N_4$ and TCN, respectively.



Figure S12. SEM images of TCN.

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- S3. X. Zou, R. Silva, A. Goswami and T. Asefa, Appl. Surf. Sci., 2015, 357, 221.

NMR data for characteristic compounds



Benzaldehyde (**1b**). Colorless liquid (42mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ 10.01 (s, 1H), 7.93–7.85 (m, 2H), 7.68–7.60 (m, 1H), 7.54 (t, *J* = 7.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 192.39, 136.43, 134.46, 129.73, 129.00. ESI-MS: m/z =107 [M+1]⁺.



4-Methylbenzaldehyde (**2b**). Colorless liquid (45mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ 9.95 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.48–7.11 (m, 2H), 2.42 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 192.02, 145.57, 134.22, 129.85, 129.72, 21.86. ESI-MS: m/z =121 [M+1]⁺.



3-Methylbenzaldehyde (**3b**). Colorless liquid (40mg, 67%). ¹H NMR (400 MHz, CDCl₃) δ 9.98 (s, 1H), 7.70–7.65 (m, 2H), 7.47–7.37 (m, 2H), 2.42 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 192.58, 138.92, 136.51, 135.29, 130.02, 128.88, 127.22, 21.17. ESI-MS: m/z =121 [M+1]⁺.



2-Methylbenzaldehyde (**4b**). Colorless liquid (39mg, 65%). ¹H NMR (400 MHz, CDCl₃) δ 10.26 (s, 1H), 7.80 (dd, *J*=7.6, 1.2 Hz, 1H), 7.48 (td, *J*=7.5, 1.4 Hz, 1H), 7.36 (t, *J*=7.5 Hz, 1H), 7.26 (d, *J*=7.6 Hz, 1H), 2.66 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 192.83, 140.62, 134.17, 133.66, 132.05, 131.78, 126.33, 19.56. ESI-MS: m/z =121 [M+1]⁺.



4-Methoxybenzaldehyde (**5b**). Colorless liquid (49mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 9.89 (s, 1H), 7.89–7.81 (m, 2H), 7.03–6.98 (m, 2H), 3.89 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 190.78, 164.63, 131.97, 129.99, 114.32, 55.57. ESI-MS: m/z =137 [M+1]⁺.



4-Fluorobenzaldehyde (**6b**). Colorless liquid (44mg, 71%). ¹H NMR (400 MHz, CDCl₃) δ 9.97 (s, 1H), 7.94–7.89 (m, 2H), 7.25–7.18 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 190.52, 167.80,



4-Chlorobenzaldehyde (**7b**). Colorless solid (57mg, 81%). ¹H NMR (400 MHz, CDCl₃) δ 10.00 (s, 1H), 7.89–7.76 (m, 2H), 7.60–7.43 (m, 2H). ¹³C NMR (101 MHz, CD₃OD) δ 197.28, 144.57, 140.06, 136.36, 134.55. ESI-MS: m/z =141 [M+1]⁺.



3-Chlorobenzaldehyde (**8b**). Colorless liquid (50mg, 71%). ¹H NMR (400 MHz, CDCl₃) δ 9.98 (s, 1H), 7.85 (t, *J*=1.8 Hz, 1H), 7.77 (dt, *J*=7.6 Hz, 1.3, 1H), 7.60 (ddd, *J*=8.0, 2.2, 1.2 Hz, 1H), 7.49 (t, *J*=7.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 190.80, 137.83, 135.45, 134.36, 130.37, 129.26, 127.96. ESI-MS: m/z =141 [M+1]⁺.



2-Chlorobenzaldehyde (**9b**). Colorless liquid (46mg, 66%). ¹H NMR (400 MHz, CDCl₃) δ 10.48 (s, 1H), 7.92 (dd, *J*=7.7, 1.8 Hz, 1H), 7.53 (ddd, *J*=8.1, 7.2, 1.8 Hz, 1H), 7.47–7.43 (m, 1H), 7.41–7.36 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 189.74, 137.92, 135.10, 132.49, 130.60, 129.37, 127.29. ESI-MS: m/z =141 [M+1]⁺.



4-Bromobenzaldehyde (**10b**). Colorless solid (72mg, 78%). ¹H NMR (400 MHz, CDCl₃) δ 10.00 (s, 1H), 7.81–7.73 (m, 2H), 7.73–7.69 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 190.99, 135.12, 132.44, 130.95, 129.75. ESI-MS: m/z =185 [M+1]⁺.



[1,1'-Biphenyl]-4-carbaldehyde (**11b**). Colorless solid (56mg, 61%). ¹H NMR (400 MHz, CDCl₃) δ 10.08 (s, 1H), 8.02–7.94 (m, 2H), 7.81–7.74 (m, 2H), 7.70–7.62 (m, 2H), 7.60–7.59 (m, 2H), 7.56–7.40 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 191.94, 147.20, 139.73, 135.23, 130.30, 129.06, 128.52, 127.71, 127.40. ESI-MS: m/z =183 [M+1]⁺.



4-Nitrobenzaldehyde (12b). Yellow powder (45mg, 59%). ¹H NMR (400 MHz, CDCl₃) δ 10.18 (s,

1H), 8.58–8.28 (m, 2H), 8.17–7.94 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 190.36, 151.13, 140.08, 130.50, 124.30. ESI-MS: m/z =152 [M+1]⁺.



MeO₂C

Methyl 4-formylbenzoate (**13b**). White solid (59mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 10.10 (s, 1H), 8.22–8.16 (m, 2H), 7.96 – 7.93 (m, 2H), 3.96 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 191.59, 166.02, 139.16, 135.08, 130.16, 129.48, 52.53. ESI-MS: m/z =165 [M+1]⁺.



4-(Tert-butyl)benzaldehyde (**14b**). Faint yellow liquid (54mg, 67%). ¹H NMR (400 MHz, CDCl₃) δ 9.98 (s, 1H), 7.84–7.79 (m, 2H), 7.58–7.52 (m, 2H), 1.35 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 192.05, 158.45, 134.09, 129.70, 125.98, 35.34, 31.06. ESI-MS: m/z =163 [M+1]⁺.



2-Naphthaldehyde (**15b**). Off-white to yellow solid (48mg, 62%). ¹H NMR (400 MHz, CDCl₃) δ 10.12 (s, 1H), 8.28 (s, 1H), 8.01–7.77 (m, 4H), 7.58 (dddd, *J*=22.8, 8.1, 6.9, 1.3 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 192.21, 136.41, 134.50, 134.07, 132.60, 129.49, 129.09, 129.05, 128.04, 127.06, 122.71. ESI-MS: m/z =157 [M+1]⁺.



(4-Formylphenyl)boronic acid (**16b**). White solid (43mg, 57%). ¹H NMR (400 MHz, CD₃OD_SPE) δ 9.99 (s, 1H), 8.08–7.75 (m, 4H), 4.85 (s, 2H). ¹³C NMR (101 MHz, CD₃OD_SPE) δ 193.26, 137.47, 133.96, 133.37, 128.18, 125.52, 124.86. ESI-MS: m/z =151 [M+1]⁺.



4-Hydroxybenzaldehyde (**17b**). Yellow solid (37mg, 60%). ¹H NMR (400 MHz, DMSO) δ 10.63 (s, 1H), 9.81 (s, 1H), 7.81–7.76 (m, 2H), 6.99–6.94 (m, 2H). ¹³C NMR (101 MHz, DMSO) δ 191.36, 163.80, 132.55, 128.90, 116.31. ESI-MS: m/z =123[M+1]⁺.



Picolinaldehyde (18b). Yellow liquid (28mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ 10.01 (d, J=0.8

Hz, 1H), 8.75–8.70 (m, 1H), 7.89 (dt, *J*=7.8, 1.1 Hz, 1H), 7.82 (tdd, *J*=7.8, 1.6, 0.8 Hz, 1H), 7.47 (ddd, *J*=7.5, 4.8, 1.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 193.35, 152.73, 150.16, 137.03, 127.84, 121.64. ESI-MS: m/z =108 [M+1]⁺.



Acetophenone (**21b**). Colorless liquid (48mg, 79%). ¹H NMR (400 MHz, CDCl₃) δ 8.01–7.95 (m, 2H), 7.62–7.55 (m, 1H), 7.52–7.43 (m, 2H), 2.62 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.09, 135.96, 132.01, 129.96, 128.41, 26.63. ESI-MS: m/z =121 [M+1]⁺.



1-(*P*-tolyl)ethan-1-one (**22b**). Colorless liquid (51mg, 76%). ¹H NMR (400 MHz, CDCl₃) δ 7.88– 7.81 (m, 2H), 7.27–7.22 (m, 2H), 2.56 (s, 3H), 2.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.85, 143.87, 134.73, 129.25, 128.44, 26.50, 21.61. ESI-MS: m/z =135 [M+1]⁺.



1-(4-Chlorophenyl)ethan-1-one (**23b**). Colorless liquid (58mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.91–7.86 (m, 2H), 7.45–7.40 (m, 2H), 2.58 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.80, 139.53, 135.43, 129.72, 128.87, 26.52. ESI-MS: m/z =155 [M+1]⁺.



Benzophenone (**24b**). White solid (76mg, 83%). ¹H NMR (400 MHz, CDCl₃) δ 7.83–7.75 (m, 4H), 7.62–7.52 (m, 2H), 7.51–7.42 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 196.71, 137.58, 132.40, 130.03, 128.26. ESI-MS: m/z =183 [M+1]⁺.



Methyl benzoate (1c). Colorless oil (52mg, 77%).¹H NMR (400 MHz, CDCl₃) δ 8.05–7.99 (m, 2H), 7.56–7.47 (m, 1H), 7.40 (t, *J*=7.6 Hz, 2H), 3.88 (d, *J*=1.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.04, 132.89, 130.16, 129.55, 128.34, 52.03. ESI-MS: m/z =137 [M+1]⁺.



Methyl 4-methylbenzoate (**2c**). Colorless oil (50mg, 66%). ¹H NMR (400 MHz, CDCl₃) δ 7.92 (dd, *J*=8.1, 1.4 Hz, 2H), 7.20 (dd, *J*=8.2, 2.1 Hz, 2H), 3.88 (s, 3H), 2.37 (s, 3H). ¹³C NMR (101



Methyl 3-methylbenzoate (**3c**). Colorless oil (40mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ 7.88–7.80 (m, 2H), 7.37–7.25 (m, 2H), 3.89 (s, 3H), 2.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.24, 138.11, 133.66, 130.11, 130.08, 128.25, 126.70, 51.99, 21.22. ESI-MS: m/z =151 [M+1]⁺.



Methyl 2-methylbenzoate (**4c**). Colorless oil (36mg, 48%). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (dd, *J*=8.0, 1.5 Hz, 1H), 7.36 (td, *J*=7.5, 1.5 Hz, 1H), 7.21 (dddd, *J*=7.2, 4.1, 3.0, 1.5 Hz, 2H), 3.86 (s, 3H), 2.59 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.01, 140.19, 131.96, 131.68, 130.58, 129.54, 125.69, 51.75, 21.71. ESI-MS: m/z =151 [M+1]⁺.



Methyl 4-methoxybenzoate (**5c**). White solid (50mg, 60%). ¹H NMR (400 MHz, CDCl₃) δ 7.92–7.83 (m, 2H), 6.91–6.83 (m, 2H), 3.80 (s, 3H), 2.49 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.69, 163.45, 130.52, 130.23, 113.63, 55.38, 26.25. ESI-MS: m/z =167 [M+1]⁺.



Methyl 4-fluorobenzoate (**6c**). White solid (52mg, 67%). ¹H NMR (400 MHz, CDCl₃) δ 8.05 (ddd, *J*=9.0, 4.8, 2.0 Hz, 2H), 7.13–7.06 (m, 2H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.11, 164.47, 132.14, 132.05, 126.40, 126.37, 115.59, 115.37, 52.15. ESI-MS: m/z =155 [M+1]⁺.



Methyl 4-chlorobenzoate (**7c**). White solid (61mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 8.05–7.93 (m, 2H), 7.49–7.35 (m, 2H), 3.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.25, 139.38, 130.98, 128.72, 52.28. ESI-MS: m/z =171 [M+1]⁺.



Methyl 3-chlorobenzoate (**8c**). White solid (51mg, 60%). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (t, J=1.8 Hz, 1H), 7.86 (dt, J=7.8, 1.3 Hz, 1H), 7.46 (ddd, J=8.0, 2.2, 1.1 Hz, 1H), 7.32 (t, J=7.9 Hz, 1H), 3.87 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.77, 134.46, 132.89, 131.83, 129.61, 127.66,

52.33. ESI-MS: m/z =171 [M+1]⁺.



Methyl 2-chlorobenzoate (**9c**). Colorless oil (45mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (dd, J=7.7, 1.6 Hz, 1H), 7.48–7.36 (m, 2H), 7.30 (td, J=7.5, 1.6 Hz, 1H), 3.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.15, 133.66, 132.56, 131.39, 131.06, 130.05, 126.57, 52.42. ESI-MS: m/z =171 [M+1]⁺.



Methyl 4-bromobenzoate (**10c**). White solid (91mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ 7.95–7.86 (m, 2H), 7.63–7.54 (m, 2H), 3.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.38, 131.72, 131.12, 129.04, 128.05, 52.31. ESI-MS: m/z =215 [M+1]⁺.



Methyl [1,1'-biphenyl]-4-carboxylate (**11c**). White solid (56mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ 8.10 (dd, *J*=9.9, 3.2 Hz, 2H), 7.68–7.56 (m, 4H), 7.50–7.35 (m, 3H), 3.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.04, 145.66, 140.02, 130.14, 128.96, 128.91, 128.18, 127.31, 127.08, 52.17. ESI-MS: m/z =213 [M+1]⁺.



Methyl 4-nitrobenzoate (**12c**). Yellow solid (42mg, 46%). ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J*=8.9 Hz, 2H), 8.22 (d, *J*=8.8 Hz, 2H), 3.99 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.15, 150.55, 135.49, 130.69, 123.52, 52.80. ESI-MS: m/z =182 [M+1]⁺.



Dimethyl terephthalate (**13c**). White solid (65mg, 67%). ¹H NMR (400 MHz, CDCl₃) δ 8.11 (s, 4H), 3.95 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 166.29, 133.90, 129.55, 52.44. ESI-MS: m/z =195 [M+1]⁺.



Methyl 4-(tert-butyl)benzoate (14c). White solid (46mg, 48%). ¹H NMR (400 MHz, CDCl₃) δ 8.00–7.92 (m, 2H), 7.49–7.39 (m, 2H), 3.89 (s, 3H), 1.33 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ



Methyl 2-naphthoate (**15c**). White solid (47mg, 51%). ¹H NMR (400 MHz, CDCl₃) δ 8.61 (s, 1H), 8.06 (dd, *J*=8.6, 1.7 Hz, 1H), 7.98–7.92 (m, 1H), 7.87 (dd, *J*=8.6, 1.7 Hz, 2H), 7.56 (dddd, *J*=19.6, 8.2, 6.9, 1.4 Hz, 2H), 3.98 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.28, 135.54, 132.52, 131.08, 129.37, 128.25, 128.17, 127.78, 127.43, 126.65, 125.25, 52.24. ESI-MS: m/z =187 [M+1]⁺.



(HO)₂B²

(4-(Methoxycarbonyl)phenyl)boronic acid (**16c**). White solid (50mg, 55%). ¹H NMR (400 MHz, CD₃OD_SPE) δ 7.96 (d, *J*=7.9 Hz, 2H), 7.83 (d, *J*=7.5 Hz, 2H), 4.88 (s, 2H), 3.90 (s, 3H). ¹³C NMR (101 MHz, CD₃OD_SPE) δ 167.42, 133.46, 133.46, 131.07, 127.98, 127.98, 127.97, 51.26. ESI-MS: m/z =181 [M+1]⁺.



Methyl 4-hydroxybenzoate (**17c**). White solid (41mg, 54%). ¹H NMR (400 MHz, DMSO) δ 10.36 (s, 1H), 8.02–7.51 (m, 2H), 7.16–6.60 (m, 2H), 3.81 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 166.52, 162.44, 131.87, 120.72, 115.77, 52.02. ESI-MS: m/z =153 [M+1]⁺.



Methyl picolinate (**18c**). White solid (32mg, 47%). ¹H NMR (400 MHz, CDCl₃) δ 8.76 (ddd, *J*=4.8, 1.8, 0.9 Hz, 1H), 8.15 (dt, *J*=7.9, 1.1 Hz, 1H), 7.86 (td, *J*=7.8, 1.8 Hz, 1H), 7.50 (ddd, *J*=7.7, 4.7, 1.2 Hz, 1H), 4.02 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.61, 149.74, 147.85, 137.01, 126.92, 125.07, 52.81. ESI-MS: m/z =138 [M+1]⁺.



Ethyl benzoate (1d). Colorless oil (39mg, 52%). ¹H NMR (400 MHz, CDCl₃) δ 8.43–7.79 (m, 2H), 7.59–7.50 (m, 1H), 7.47–7.38 (m, 2H), 4.37 (q, *J*=7.1 Hz, 2H), 1.39 (t, *J*=7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.63, 132.79, 130.52, 129.53, 128.31, 60.94, 14.32. ESI-MS: m/z =151 [M+1]⁺.



Figure. 1b ¹³C NMR spectrum



Figure. 2b ¹³C NMR spectrum



Figure. **3b** ¹³C NMR spectrum



Figure. 4b ¹³C NMR spectrum



Figure. **5b** ¹³C NMR spectrum



Figure. 6b ¹³C NMR spectrum



Figure. 7b ¹³C NMR spectrum



Figure. 8b ¹³C NMR spectrum



Figure. 9b ¹³C NMR spectrum



Figure. 10b ¹³C NMR spectrum



Figure. 11b ¹³C NMR spectrum



Figure. 12b ¹³C NMR spectrum



Figure. 13b ¹³C NMR spectrum



Figure. 14b ¹³C NMR spectrum



Figure. 15b ¹³C NMR spectrum



Figure. 16b ¹³C NMR spectrum



Figure. 17b ¹³C NMR spectrum



Figure. 18b ¹³C NMR spectrum



Figure. 21b ¹³C NMR spectrum



Figure. 22b ¹³C NMR spectrum



Figure. 23b ¹³C NMR spectrum



Figure. 24b ¹³C NMR spectrum



180 175 170 185 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 f1 (ppm)

Figure. 1c ¹³C NMR spectrum



Figure. 2c¹³C NMR spectrum



Figure. **3c** ¹³C NMR spectrum



Figure. 4c ¹³C NMR spectrum



Figure. 5c ¹³C NMR spectrum



Figure. 6c ¹³C NMR spectrum



Figure. 7c¹³C NMR spectrum



Figure. 8c ¹³C NMR spectrum



Figure. 9c ¹³C NMR spectrum



Figure. 10c ¹³C NMR spectrum





Figure. **11c** ¹³C NMR spectrum



Figure. **12c** ¹³C NMR spectrum



Figure. 13c ¹³C NMR spectrum



Figure. 14c ¹³C NMR spectrum



Figure. **15c** ¹³C NMR spectrum



Figure. 16c ¹³C NMR spectrum



Figure. 17c ¹³C NMR spectrum



Figure. 18c ¹³C NMR spectrum



Figure. 1d ¹³C NMR spectrum