Supporting Information

Visible Light-induced Decarboxylative Iodination of Aromatic Carboxylic Acids

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1. General procedures

All reactions were carried out in dry solvents under argon atmosphere. The solvents used were distilled over standard drying agents and were stored with molecular sieves. The reagents were purchased and used without further purification. Blue LEDs (5 W, $\lambda_{\text{max}} = 455$ nm) were used for blue light irradiation, the light source was placed ~ 3 cm from the reaction tube, six light source was placed around the reaction tube. The reaction tube was placed in a oil bath with a thermocouple (see Figure S1). The reaction progress was monitored by thin layer chromatography (TLC), and the products were obtained by column chromatography on silica gel or preparative thin layer chromatography (pTLC). Electron-impact mass spectra were recorded on a JEOL JMS-Q1050GC Master Quad GC/MS. NMR spectra were recorded on JOEL JNM-ECA 600, JNM-ECS 400 and JNM-ECA 300 for proton and carbon magnetic resonance spectra ($^1$H NMR and $^{13}$C NMR) using tetramethylsilane (TMS) and remained CHCl$_3$ in the solvent of CDCl$_3$ as the internal standards ($^1$H NMR: TMS at 0.00 ppm, CHCl$_3$ at 7.26 ppm; $^{13}$C NMR: CDCl$_3$ at 77.16 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Melting points were recorded on a Beijing Tech X-4 melting point apparatus.

![Figure S1](image)

**Figure S1** Photographs of the used light source in the reactions under irradiation of blue LED.

2. General procedures for the iodination of aromatic carboxylic acids

**General procedure A.** To a 15 mL test tube with septum Cs$_2$CO$_3$ (0.6 mmol, 195 mg), aromatic carboxylic acid (I) (0.3 mmol), [Ir(dF(CF$_3$)ppy)$_2$dtbbpy]PF$_6$ (D) (6 $\mu$mmol, 6.7 mg), N-iodosuccinimide (NIS) (0.9 mmol, 202.5 mg) and I$_2$ (15 $\mu$mol, 5 mol%) were added. The tube was
evacuated and backfilled with argon for three times, and then 3 mL of dry 1,2-dichloroethane (DCE) was added through a syringe under argon. The tube was sealed with Parafilm M® and placed in an oil bath with a contact thermometer, and the reaction was carried out at 50 °C under irradiation with 6 × 5 W blue LEDs (λ_{max} = 455 nm). After 24 or 36 h, the resulting mixture was filtered through a 2 cm thick pad of silica, and the silica was washed with dichloromethane (DCM) (50 mL). The filtrate was collected and the solvent was removed in vacuo. The crude residue was purified by silica gel flash column chromatography to provide the target product (2). *(Note: The reaction was very sensitive to moisture, and the yields sharply decreased to less than 5% when 0.01 equivalent of H₂O was added to the reaction system).*

**General procedure B.** To a 15 mL test tube with septum Cs₂CO₃ (0.6 mmol, 195 mg), aromatic carboxylic acid (1) (0.3 mmol), [Ir(dF(CF₃)ppy)₂dtbbpy]PF₆ (D) (6 μmmol, 6.7 mg), NIS (1.5 mmol, 337.5 mg) and I₂ (60 μmol, 20 mol%) were added. The tube was evacuated and backfilled with argon for three times, and then 3 mL of dry DCE was added through a syringe under argon. The tube was sealed with Parafilm M® and placed in an oil bath with a contact thermometer, and the reaction was carried out at 50 °C under irradiation with 6 × 5 W blue LEDs (λ_{max} = 455 nm). After 24 h or 36 h, the resulting mixture was filtered through a 2 cm thick pad of silica, and the silica was washed with DCM) (50 mL). The filtrate was collected and the solvent was removed in vacuo. The crude residue was purified by silica gel flash column chromatography to provide the target product (2). *(Note: The reaction was very sensitive to moisture, and the yields sharply decreased to less than 5% when 0.01 equivalent of H₂O was added to the reaction system).*

**General procedure C.** To a 15 mL test tube with septum Cs₂CO₃ (0.6 mmol, 195 mg), aromatic carboxylic acid (1) (0.3 mmol), [Ir(dF(CF₃)ppy)₂dtbbpy]PF₆ (D) (6 μmmol, 6.7 mg), NIS (1.5 mmol, 337.5 mg) and I₂ (60 μmol, 20 mol%) were added. The tube was evacuated and backfilled with argon for three times, and then 3 mL of dry CH₃CN was added through a syringe under argon. The tube was sealed with Parafilm M® and placed in an oil bath with a contact thermometer, and the reaction was carried out at 50 °C under irradiation with 6 × 5 W blue LEDs (λ_{max} = 455 nm). After 24 h, the resulting mixture was filtered through a 2 cm thick pad of silica, and the silica was washed with DCM) (50 mL). The filtrate was collected and the solvent was removed in vacuo. The crude residue was purified by silica gel flash column chromatography to provide the target product (2). *(Note: The reaction was very sensitive to moisture, and the yields sharply decreased to less than 5% when 0.01 equivalent of H₂O was added to the reaction system).*
3. Fluorescence quenching experiments

Fluorescence quenching studies were carried out using a solution of [Ir(dF(CF₃)ppy)₂(dtbbpy)](PF₆) (D) (1×10⁻⁶ M), 4-methoxybenzoic acid with different concentration (0-40 mM), Cs₂CO₃ (0-120 mM), and tetrabutylammonium iodide (0-40 mM) in degassed DCE under Ar atmosphere. The samples were prepared in 1.4 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with Parafilm M® inside an argon filled glove-box. As shown in Figure S2-A, the fluorescence intensity dramatically decreased with concentration increase of 4-methoxybenzoic acid from 0 mM to 40 mM. Correspondingly, fluorescence quenching studies were performed using a solution of [Ir(dF(CF₃)ppy)₂(dtbbpy)](PF₆) (D) (1×10⁻⁶ M), NIS with different concentration (0-40 mM), I₂ (0-4 mM), Cs₂CO₃ (0-120 mM), and tetrabutylammonium iodide (0-40 mM) under the similar conditions. As shown in Figure S2-B, the fluorescence intensity almost did not change with concentration increase of NIS from 0 mM to 40 mM. The results indicated that a single electron transfer (SET) occurred from 4-methoxybenzoic acid.
acid (rather than NIS) to photocatalyst [Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbbpy)](PF<sub>6</sub>) (D), which was coincident with Glorius’s work.<sup>1</sup>

4. Variation of reactant and product with time

![Graph showing variation of reactant and product with time with the reaction of 4-methoxybenzoic acid as the example.](image)

**Figure S3.** Variation of reactant and product with time with the reaction of 4-methoxybenzoic acid as the example.

Here, reaction of 4-methoxybenzoic acid under the standard conditions was used as the example.

The five reaction mixtures were placed in five tubes, respectively, and the reactions were performed under the standard conditions. The reaction in one of the tubes was quenched for every 6 h, and 4-methoxybenzoic acid (reactant) and 4-iodoanisole (product) in the resulting mixture were isolated by silica gel flash column chromatography. As shown in Figure S3, the results showed that the reaction could not occur without irradiation of visible light, which indicated that the visible light-induced decarboxylative iodination of aromatic carboxylic acids was not a radical chain process.

Subsequently, to explore further the mechanism of the visible light-induced decarboxylative iodination of aromatic carboxylic acids, a light on-off experiment on reaction of 4-methoxybenzoic acid (1f) with NIS was carried out as follows: 4-methoxybenzoic acid (1f) (0.2 mmol), N-iodosuccinimide (NIS) (0.6 mmol), Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbbpy)(PF<sub>6</sub>) (D) (4 μmol), Cs<sub>2</sub>CO<sub>3</sub> (0.4 mmol), DCE (2 mL), I<sub>2</sub> (10 μmol, 5 mol %) and phenyl methyl ether (0.05 mmol) as the internal standard for NMR determination were placed in a glass tube, and the tube was filled with argon and sealed. A continuous switch experiment of 3 h-on-2 h off was performed, and the sample in the tube was analyzed by NMR spectroscopy. The results showed that the iodination reaction occurred under irradiation of visible light and stopped under dark, which indicated that
iodination of 4-methoxybenzoic acid (1f) was not a radical chain process (Figure S4).

Figure S4 Conversion yields by NMR determination on light on-off experiment for the decarboxylative iodination of 4-methoxybenzoic acid (1f).

5. Electron paramagnetic resonance (EPR) experiments

The radical trapping experiments were carried on a JES FA200 (JEOL Co.) by using DMPO (5,5-dimethylpyrroline N-oxide) as the radical trapping agent. DMPO (100 mM) was added to the following mixtures, respectively: a) NIS (50 mM), Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)(PF$_6$) (D) (1 mM), Cs$_2$CO$_3$ (100 mM) in DCE; b) 4-methoxybenzoic acid (50 mM), Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)(PF$_6$) (D) (1 mM), Cs$_2$CO$_3$ (100 mM) in DCE. The mixtures were degassed, and then 50 μL of them was transferred to a capillary for everyone. The capillary was transferred to a EPR tube, and the tube was irradiated with visible light (440-460 nm) for 10 min. Measurement conditions are as follows: frequency 9.439 GHz, center field 336.7 mT, sweep width 10 mT, power 1 mW, modulation width 0.1 mT, sweep time 2 min, time constant 0.1 s, amplitude 800. As shown in Figure S5-a, no radical signal was observed in the absence of 4-methoxybenzoic acid. When 4-methoxybenzoic acid was added to the system in the absence of NIS, an oxygen-centered radical was found, with a $g$ value of 2.003, $A_N = 1.43$ mT, $A_H = 1.39$ mT, which was assumed to be a benzoic radical (see Figure S5-b). 2
Figure S5 EPR spectra under different conditions: a) mixture of DMPO (100 mM), NIS (50 mM), Ir(dF(CF3)ppy)2(dtbbpy)(PF6) (D) (1 mM), Cs2CO3 (100 mM) in DCE under irradiation of visible light (440-460 nm) for 10 min; b) mixture of DMPO (100 mM), 4-methoxylbenzoic acid (50 mM), Ir(dF(CF3)ppy)2(dtbbpy)(PF6) (D) (1 mM), Cs2CO3 (100 mM) in DCE under irradiation of visible light (440-460 nm) for 10 min.

6. In-situ experiment of benzoyl hypoiodite.

4-Methoxyl benzoic acid (0.3 mmol) was dissolved in degassed dry DCE (3 mL), and then t-butyl hypoiodite (4) (1 equiv) was added to the solution through syringer. After the mixture was stirred for 8 h, Ir(dF(CF3)ppy)2(dtbbpy)(PF6) (D) (2%) and iodine (10%) were added to the solution under Ar, and the mixture was irradiated with six 5 w blue LEDs (λ_{max} = 455 nm) for 24 h. The resulting solution was quenched with an aqueous solution of sodium thiosulfate (5 mL, 1M). The solution was extracted with DCM, and the organic phase was dried and concentrated. The residue was purified by column chromatography to provide desired product 2g in 47% yield.
7. Characterization data of compounds 2a-ad and 3

**Iodobenzene (2a).** Eluent: pentane, the solvent was removed at 0 °C under reduced pressure. Yield: 28.7 mg (47%) followed in general procedure A. Yellow oil. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.72 (d, $J = 8.24$ Hz, 2H), 7.34 (t, $J = 7.33$ Hz, 1H), 7.12 (t, $J = 7.33$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 137.6, 130.4, 127.6, 94.6. EI-MS: M+ m/z 204.

**1-Iodo-2-methylbenzene (2b).** Eluent: pentane, the solvent was removed at 0 °C under reduced pressure. Yield: 34 mg (52%) followed in general procedure A. Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.79 (d, $J = 8.24$ Hz, 1H), 7.24-7.22 (m, 2H), 6.85 (t, $J = 8.70$ Hz, 1H), 2.42 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 141.5, 139.1, 129.9, 128.3, 127.5, 101.3, 28.3. EI-MS: M+ m/z 218.

**1-Iodo-4-methylbenzene (2c).** Eluent: pentane, the solvent was removed under reduced pressure. Yield: 43.8 mg (67%) followed in general procedure A. Colorless solid, mp. 34-35 °C. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.58 (d, $J = 8.24$ Hz, 2H), 6.94 (d, $J = 8.24$ Hz, 2H), 2.28 (s, 6H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 137.5, 137.3, 131.3, 90.4, 21.2. EI-MS: M+ m/z 218.

**1-Iodo-3,5-dimethylbenzene (2d).** Eluent: pentane, the solvent was removed under reduced pressure. Yield: 40.4 mg (58%) followed in general procedure A. Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.37 (s, 2H), 6.96 (s, 1H), 2.28 (s, 6H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 140.0, 135.2, 129.5, 94.4, 21.0. EI-MS: M+ m/z 232.

**2e**
1-Iodo-2-methoxybenzene (2e).\textsuperscript{4} Eluent: pentane/diethyl ether 50:1, the solvent was removed at 0 \degree C under reduced pressure. Yield: 50.5 mg (72\%) followed in general procedure A. Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.78 (d, $J = 7.79$ Hz, 1H), 7.31 (t, $J = 8.24$ Hz, 1H), 6.83 (d, $J = 8.24$ Hz, 1H), 6.72 (t, $J = 8.24$ Hz, 1H), 3.88 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 158.1, 139.6, 129.6, 122.6, 110.1, 86.1, 56.4. EI-MS: M$^+$ m/z 234.

![Image](image.png)

1-Iodo-3-methoxybenzene (2f).\textsuperscript{3} Eluent: pentane/diethyl ether 50:1, the solvent was removed under reduced pressure. Yield: 52.7 mg (75\%) followed in general procedure A. Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.29 (d, $J = 8.24$ Hz, 1H), 7.26 (s, 1H), 7.0 (t, $J = 8.24$ Hz, 1H), 6.87 (d, $J = 8.70$ Hz, 1H), 3.78 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 160.2, 130.9, 129.9, 123.1, 113.8, 94.5, 55.5. EI-MS: M$^+$ m/z 234.

![Image](image.png)

1-Iodo-4-methoxybenzene (2g).\textsuperscript{4} Eluent: pentane/diethyl ether 50:1, the solvent was removed under reduced pressure. Yield: 54.8 mg (78\%) followed in general procedure A. Colorless solid, mp. 50-52\degree C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.56 (d, $J = 8.24$ Hz, 2H), 6.68 (d, $J = 8.24$ Hz, 2H), 3.78 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 159.6, 138.3, 116.5, 82.8, 55.5. EI-MS: M$^+$ m/z 234.

![Image](image.png)

Iodobenzene (2h).\textsuperscript{5} Eluent: pentane, the solvent was removed at 0 \degree C under reduced pressure. Yield: 42.6 mg (64\%) followed in general procedure A. Yellow oil. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.75 (t, $J = 7.79$ Hz, 1H), 7.31 (q, $J = 6.41$ Hz, 1H), 7.07 (t, $J = 8.24$ Hz, 1H), 6.90 (t, $J = 7.79$ Hz, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 163.1 ($J_{F-C} = 245.37$ Hz), 139.6, 130.2, 125.9, 115.9 ($J_{F-C} = 23.00$ Hz), 81.4 ($J_{F-C} = 26.84$ Hz). $^{19}$F NMR (CDCl$_3$, 376.5 MHz) 114.25. EI-MS: M$^+$ m/z 222.

![Image](image.png)

1-Chloro-2-iodobenzene (2i).\textsuperscript{6} Eluent: pentane, the solvent was removed at 0 \degree C under reduced
pressure. Yield: 50.7 mg (72%) followed in general procedure A. Colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta 7.85 \text{ (d, } J = 7.79 \text{ Hz, 1H)}, 7.44 \text{ (d, } J = 7.79 \text{ Hz, 1H)}, 7.28 \text{ (t, } J = 7.33 \text{ Hz, 1H)}, 6.94 \text{ (t, } J = 7.79 \text{ Hz, 1H)}. \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta 140.4, 138.6, 129.3, 128.0, 98.3.\) EI-MS: M\(^+\) m/z 238.0.

1-Chloro-3-iodobenzene (2j).\(^3\) Eluent: pentane, the solvent was removed at 0 \(^\circ\)C under reduced pressure. Yield: 55.7 mg (78%) followed general procedure A; 60.0 mg (84%) followed general procedure B. Colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta 7.72 \text{ (s, 1H)}, 7.59 \text{ (d, } J = 8.24 \text{ Hz, 1H)}, 7.32 \text{ (d, } J = 8.24 \text{ Hz, 1H)}, 7.02 \text{ (t, } J = 8.24 \text{ Hz, 1H)}. \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta 137.3, 135.8, 135.2, 131.1, 128.1, 94.3.\) EI-MS: M\(^+\) m/z 238.0.

1-Chloro-4-iodobenzene (2k).\(^6\) Eluent: pentane, the solvent was removed under reduced pressure. Yield: 59.3 mg (83%) followed general procedure A. White solid, mp. 52-53\(^\circ\)C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta 7.57 \text{ (d, } J = 8.24 \text{ Hz, 2H)}, 7.42 \text{ (d, } J = 8.24 \text{ Hz, 2H)}. \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta 138.6, 134.1, 130.4, 91.2.\) EI-MS: M\(^+\) m/z 238.0.

1-Bromo-2-iodobenzene (2l).\(^3\) Eluent: pentane, the solvent was removed at 0 \(^\circ\)C under reduced pressure. Yield: 60.9 mg (72%) followed in general procedure A. Colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta 7.87 \text{ (d, } J = 7.79 \text{ Hz, 1H)}, 7.63 \text{ (d, } J = 7.79 \text{ Hz, 1H)}, 7.21 \text{ (t, } J = 7.79 \text{ Hz, 1H)}, 7.00 \text{ (t, } J = 7.79 \text{ Hz, 1H)}. \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta 140.5, 132.9, 129.8, 129.6, 128.5, 101.3.\) EI-MS: M\(^+\) m/z 282.

1-Bromo-3-iodobenzene (2m).\(^7\) Eluent: pentane, the solvent was removed under reduced pressure. Yield: 65.4 mg (77%) followed in general procedure A; 67.9 mg (80%) followed in general procedure B. Colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta 7.87 \text{ (s, 1H)}, 7.63 \text{ (d, } J = 7.79 \text{ Hz, 1H),}

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7.47 (d, J = 8.24 Hz, 1H), 6.97 (t, J = 7.79 Hz, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 139.9, 136.2, 131.5, 131.0, 123.2, 94.7. EI-MS: M$^+$ m/z 238.0.

**1-Bromo-4-iodobenzene (2n).** Eluent: pentane, the solvent was removed under reduced pressure. Yield: 64.3 mg (76%) followed in general procedure A; 71.9 mg (85%) followed in general procedure B. White solid, mp. 89-90 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.54 (d, J = 8.24 Hz, 2H), 7.23 (d, J = 8.24 Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 139.2, 133.6, 122.3, 92.2. EI-MS: M$^+$ m/z 238.0.

**1,4-Diiodobenzene (2o).** Eluent: pentane, the solvent was removed under reduced pressure. Yield: 66.3 mg (67%) followed in general procedure A. Colorless solid, mp. 131-132 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.49 (s, 4H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 131.2, 94.5. EI-MS: M$^+$ m/z 330.

**N-(4-Iodophenyl)-N-methylacetamide (2p).** Eluent: pentane/ethyl acetate 20:1, the solvent was removed under reduced pressure. Yield: 26.5 mg (32%) followed in general procedure A. White solid, mp. 143-145 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.65 (d, J = 8.24 Hz, 2H), 6.68 (d, J = 8.24 Hz, 2H), 3.54 (s, 3H), 2.10 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 171.5, 139.8, 136.9, 120.6, 88.1, 37.2, 22.4. EI-MS: M$^+$ m/z 275.

**Methyl 2-iodobenzoate (2q).** Eluent: pentane/diethyl ether 50:1, the solvent was removed under reduced pressure. Yield: 51.1 mg (65%) followed in general procedure B. Yellow oil. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.95 (d, J = 6.87 Hz, 1H), 7.76 (d, J = 6.87 Hz, 1H), 7.36 (t, J = 6.87 Hz, 1H), 7.10 (t, J = 6.87 Hz, 1H), 3.89 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 166.9, 141.3, 135.1, 132.7,
Methyl 3-iodobenzoate (2r). Eluent: pentane/diethyl ether 50:1, the solvent was removed under reduced pressure. Yield: 59.0 mg (75%) followed in general procedure B. Colorless solid, mp. 54-55 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.34 (s, 1H), 7.93-7.85 (m, 2H), 7.14 (t, \(J = 8.24\) Hz, 1H), 3.95 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 165.7, 141.8, 138.6, 132.1, 130.2, 128.8, 93.9, 52.5. EI-MS: M\(^+ \) m/z 262.

Methyl 4-iodobenzoate (2s). Eluent: pentane/diethyl ether 50:1, the solvent was removed under reduced pressure. Yield: 59.7 mg (76%) followed in general procedure B. White solid, mp. 113-115 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.79 (d, \(J = 8.24\) Hz, 2H), 7.64 (d, \(J = 8.24\) Hz, 2H), 3.95 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 167.0, 137.2, 130.6, 129.2, 100.4, 52.2. EI-MS: M\(^+ \) m/z 262.

1-Iodo-2-nitrobenzene (2t). Eluent: pentane/diethyl ether 100:1, the solvent was removed under reduced pressure. Yield: 48.6 mg (65%) followed in general procedure B. Yellow solid, mp. 49-50 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.04 (d, \(J = 7.79\) Hz, 1H), 7.85 (d, \(J = 8.24\) Hz, 1H), 7.49 (t, \(J = 7.79\) Hz, 1H), 7.27 (t, \(J = 8.24\) Hz, 1H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 153.1, 142.0, 133.5, 129.2, 125.5, 86.3. EI-MS: M\(^+ \) m/z 249.

1-Iodo-3-nitrobenzene (2u). Eluent: pentane/diethyl ether 100:1, the solvent was removed under reduced pressure. Yield: 58.3 mg (78%) followed in general procedure B. Yellow solid, mp. 35-37 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.56 (s, 1H), 8.20 (d, \(J = 8.24\) Hz, 1H), 8.03 (d, \(J = 7.79\) Hz, 1H), 7.29 (t, \(J = 7.79\) Hz, 1H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 148.6, 143.5, 132.5, 130.8, 122.8, 93.6. EI-MS: M\(^+ \) m/z 249.
1-Iodo-4-nitrobenzene (2v).\textsuperscript{10} Eluent: pentane/diethyl ether 100:1, the solvent was removed under reduced pressure. Yield: 56.0 mg (75%) followed in general procedure B. Yellow solid, mp. 171-172 °C. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) δ 7.94 (d, J = 8.24, 2H), 7.90 (d, J = 8.24 Hz, 2H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) δ 147.9, 138.8, 125.0, 102.8. EI-MS: M⁺ m/z 249.

2-Iodobenzonitrile (2w).\textsuperscript{11} Eluent: pentane/diethyl ether 20:1, the solvent was removed under reduced pressure. Yield: 48.1 mg (70%) followed in general procedure B. Yellow solid, mp. 52-53 °C. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) δ 7.91 (d, J = 7.79 Hz, 1H), 7.63 (d, J = 8.24 Hz, 1H), 7.49 (t, J = 7.79 Hz, 1H), 7.27 (t, J = 8.24 Hz, 1H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) δ 138.3, 132.3, 131.0, 127.1, 119.5, 116.7, 103.4. EI-MS: M⁺ m/z 229.

4-Iodobenzonitrile (2x).\textsuperscript{4} Eluent: pentane/diethyl ether 20:1, the solvent was removed under reduced pressure. Yield: 58.4 mg (85%) followed in general procedure B. Yellow solid, mp. 124-126 °C. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) δ 7.85 (d, J = 8.24 Hz, 2H), 7.34 (d, J = 8.24 Hz, 2H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) δ 138.6, 133.3, 118.3, 111.9, 100.4. EI-MS: M⁺ m/z 249.

1-Iodo-4-(trifluoromethyl)benzene (2y).\textsuperscript{4} Eluent: pentane, the solvent was removed at 0 °C under reduced pressure. Yield: 66.9 mg (82%) followed in general procedure B. Yellow oil. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) δ 7.83 (d, J = 7.79 Hz, 2H), 7.34 (d, J = 7.79 Hz, 2H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) δ 138.1, 130.3 (J\textsubscript{F-C} = 32.59 Hz), 126.9 (J\textsubscript{F-C} = 3.83 Hz), 124.1 (J\textsubscript{F-C} = 272.20 Hz), 98.7. EI-MS: M⁺ m/z 272.

2-Iodonaphthalene (2z).\textsuperscript{4} Eluent: pentane, the solvent was removed under reduced pressure. Yield:
57.1 mg (75%) followed in general procedure A; 61 mg (80%) followed in general procedure B. White solid, mp. 52-53 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.03 (s, 1H), 7.84-7.81 (m, 1H), 7.77-7.71 m, 2H), 7.59-7.49 (m, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 134.6, 131.9, 130.0, 129.7, 129.3, 127.9, 127.1, 127.0, 126.4, 91.9. EI-MS: M$^+$ m/z 254.

2-Iodobiphenyl (2aa).$^{12}$ Eluent: pentane, the solvent was removed under reduced pressure. Yield: 47.9 mg (57%) followed in general procedure A. Light yellow solid, mp. 55-56 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.00 (d, $J = 8.24$ Hz, 1H), 7.49-7.34 (m, 7H), 7.07 (t, $J = 7.33$ Hz, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 146.7, 144.3, 139.6, 130.2, 129.4, 128.9, 128.2, 120.1, 127.7, 98.8. EI-MS: M$^+$ m/z 280.

3-Iodopyridine (2ab).$^{4}$ Eluent: pentane/diethyl ether 5:1, the solvent was removed at 0 °C under reduced pressure. Yield: 45.5 mg (65%) followed in general procedure C. Yellow oil. $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.86 (s, 1H), 8.79 (d, $J = 5.04$ Hz, 1H), 7.94 (d, $J = 8.24$ Hz, 1H), 7.42 (t, $J = 6.87$ Hz, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 146.7, 144.3, 139.6, 130.2, 129.4, 128.9, 128.2, 120.1, 127.7, 98.8. EI-MS: M$^+$ m/z 205.

2-Iodothiophene (2ac).$^{13}$ Eluent: pentane/diethyl ether 40:1, the solvent was removed at 0 °C under reduced pressure. Yield: 35.9 mg (57%) followed in general procedure C. Yellow oil. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.33 (d, $J = 5.50$ Hz, 1H), 7.60 (t, $J = 7.19$ Hz, 1H), 7.48-7.36 (m, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 137.0, 131.6, 129.0, 73.3. EI-MS: M$^+$ m/z 210.

(2-Iodophenyl)(phenyl)methanone (2ab).$^{14}$ Eluent: pentane/diethyl ether 40:1, the solvent was removed under reduced pressure. Yield: 31.4 mg (34%) followed in general procedure A. Yellow
solid, mp. 31-32 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.82 (d, J = 6.87 Hz, 2H), 7.60 (d, J = 7.19 Hz, 1H), 7.48-7.36 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ 197.9, 144.7, 139.4, 137.6, 132.4, 130.2, 129.2, 128.7, 126.8, 105.5. El-MS: M⁺ m/z 308.

9H-Fluoren-9-one (3).¹⁵ Eluent: pentane/diethyl ether 40:1, the solvent was removed under reduced pressure. Yield: 22.1 mg (41%) followed in general procedure A. Yellow solid, mp. 80-82 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.65 (d, J = 7.33 Hz, 2H), 7.52-7.45 (m, 4H), 7.28 (t, J = 7.33 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 194.0, 144.5, 134.8, 134.3, 129.2, 124.4, 120.4. El-MS: M⁺ m/z 180.
8. References


9. NMR spectra of compounds 2a-ad and 3
2r

X: parts per million: 1H

2r

X: parts per million: 13C