Supplementary Information

Photocatalytic Direct Borylation of Carboxylic Acids

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Supplementary Methods

1. General Information

All available compounds were purchased from commercial suppliers and were used without further purification unless otherwise noted.

NMR spectra were recorded on Bruker Advance 400 (400 MHz for \(^1\text{H}\); 100 MHz for \(^{13}\text{C}\)) spectrometer. The chemical shifts (\(\delta\)) are given in parts per million relatives to CDCl\(_3\) (7.26 ppm for \(^1\text{H}\)) or TMS (0 ppm for \(^1\text{H}\)), and CDCl\(_3\) (77.0 ppm for \(^{13}\text{C}\)). \(^1\text{H}\), \(^{13}\text{C}\) multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), quartet (q), multiplet (m), and broad resonance (br).

Flash column chromatography and preparative thin-layer chromatography were performed on silica gel;

Ultra-performance liquid chromatography-mass spectrometry (UPLC-MS) was performed on an ACQUITY UPLC H-Class PLUS instrument equipped with a Waters PDA e\(\lambda\) Detector and a Waters Acquity QDA mass spectrometer. High-resolution mass spectroscopy was performed on a Bruker Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. Fluorescence spectra were measured on an F-7000 spectrophotometer. (Hitachi, Japan)

Unless otherwise noted, all reactions were carried out under an air atmosphere in screw-capped vials. A LED (30 W, \(\lambda\) max = 440 nm) may be shared by 14 screw-capped vials for irradiation obtained from Xuzhou Aijia Electronic Technology Co., LTD. In each case, each LED was set up, and the light source was placed ~2 cm from the reaction vessels (Fig. 1). A box was placed over the lights to shield the light. The reaction temperature was measured using a contact thermometer to be 35 °C.
Supplementary Fig. 1 Photographs of the used light source in the reactions under irradiation of blue LED (λ = 440 nm). a reaction equipment with light source, air fans and magnetic stirrers. b Light reaction in progress. c The wavelength range of the light source, which is provided by Xuzhou Aijia Electronic Technology Co., LTD.

2. Procedure for Optimization Studies

A 5 mL vial equipped with a magnetic stir bar was charged with 3-acetyl-carboxylic acid (16.5 mg, 0.1 mmol), photocatalyst, [Co] catalyst, borylated reagent, or other additives; the anhydrous solvent was then into the vial. The reaction mixture was stirred without irradiation for 10 min at ambient temperature, and then a guanidine-based reagent was gradually added to the vial under stirring. The reaction mixture was stirred without irradiation for another 10 min at ambient temperature and then irradiated for 24 h while maintaining the temperature at approximately 35 °C through cooling with a fan. 1,3,5-trimethoxybenzene (HPLC internal standard quantification based on the standard internal 1,3,5-trimethoxybenzene, the peak area and relative correction factor of reaction product) was added then the mixture was analyzed by HPLC.
**Supplementary Table 1. Evaluation of Photosensitizers.**

| Conditions | Result$^a$ |
|------------|------------|
| 1. [Ir(dF(CF<sub>3</sub>)<sub>2</sub>(5,5'-CF<sub>3</sub>-bpy)]PF<sub>6</sub> [Ir-1] (1 mol%) | 56% |
| 2. [Ir(dF(CF<sub>3</sub>)<sub>2</sub>)(dtbbpy)]PF<sub>6</sub> [Ir-2] (1 mol%) | 8% |
| 3. [Ir(dF(CF<sub>3</sub>)<sub>2</sub>)(bpy)]PF<sub>6</sub> [Ir-3] (1 mol%) | 5% |
| 4. [Ir(dF(CF<sub>3</sub>)<sub>2</sub>)(4,4'-CF<sub>3</sub>-bpy)]PF<sub>6</sub> [Ir-4] (1 mol%) | 23% |
| 5. [Ir(dF3(Cppy)<sub>2</sub>)(dtbbpy)]PF<sub>6</sub> [Ir-5] (1 mol%) | trace |
| 6. [Ir(ppy)<sub>2</sub>)(1,10-phenanthroline)]PF<sub>6</sub> [Ir-6] (1 mol%) | trace |
| 7. [Ir(ppy)<sub>2</sub>)(dtbbpy)]PF<sub>6</sub> [Ir-7] (1 mol%) | NR |
| 8. Mes-Acr-MeBF<sub>4</sub> (20 mol%) | NR |
| 9. [Ru(Tris(4,7-diphenyl-1,10-phenanthroline)](PF<sub>6</sub>)<sub>2</sub> (5 mol%) | NR |
| 10. [Ru(bpz)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> (5 mol%) | NR |
| 11. [Ru(Tris(2,2'-bipyridine)](PF<sub>6</sub>)<sub>2</sub> (5 mol%) | NR |

$^a$Yield was determined by HPLC with 1,3,5-trimethoxybenzene as an internal standard.
Supplementary Table 2. Evaluation of Guanidine-based Cocatalysts

| Conditions            | Result<sup>a</sup> |
|-----------------------|---------------------|
| 1. No Guanidine       | NR                  |
| 2. TMG (0.75 equiv.) | 56%                 |
| 3. BTMG (0.75 equiv.)| 32%                 |
| 4. TBD (0.75 equiv.) | 27%                 |
| 5. MTBD (0.75 equiv.)| 21%                 |
| 6. HMPA (0.75 equiv.)| NR                  |
| 7. TMG (0.25 equiv.) | 15%                 |
| 8. TMG (0.5 equiv.)  | 46%                 |
| 9. TMG (0.75 equiv.) | 56%                 |
| 10. TMG (1 equiv.)   | 22%                 |
| 11. TMG (2 equiv.)   | 2%                  |

<sup>a</sup> Yield was determined by HPLC with 1,3,5-trimethoxybenzene as an internal standard.
**Supplementary Table 3. Evaluation of Co Catalyst**

| Conditions | Result<sup>a</sup> |
|------------|-------------------|
| 1. No [Co] | 15%               |
| 2. Co(dmgH)₂Cl₂ | 34%              |
| 3. Co(dmgH)₂pyCl | 56%              |
| 4. Co(dmgH)₂(4-MeO)PyCl | 51%              |
| 5. Co(dmgH)₂(4-diMeN)PyCl | 51%              |
| 6. Co(dmgH)₂(4-tBu)PyCl | 48%              |
| 7. Co(dmgH)₂(3,5-diMe)PyCl | 44%              |
| 8. Co(dmgH)₂(4-CN)PyCl | 32%              |
| 9. Co(dmgH)₂(4-CO₂Et)PyCl | 31%              |
| 10. Co(dmgH)₂(4-Br)pyCl | 22%              |
| 11. Co(dmgH)₂(3-Br)pyCl | 26%              |
| 12. Co(dmgH)₂(4-I)pyCl | 25%              |

<sup>a</sup>Yield was determined by HPLC with 1,3,5-trimethoxybenzene as an internal standard.
Supplementary Table 4. Evaluation of Other Metal Catalyst under Ar or Air conditions

| Conditions                  | Result<sup>a</sup> (Air condition) |
|-----------------------------|------------------------------------|
| 1. No metal catalyst        | Trace                              |
| 2. Ag<sub>2</sub>CO<sub>3</sub> (20%) | 13% (no significant improvement)  |
| 3. AgI (20%)                | 11% (no significant improvement)   |
| 4. AgI (1 eq)               | 15% (no significant improvement)   |
| 5. Cu(MeCN)<sub>4</sub>BF<sub>4</sub> (20%) | 7% (no significant improvement)    |
| 6. FeCl<sub>2</sub> (20%)   | 3% (no significant improvement)    |
| 7. NiCl<sub>2</sub> (20%)   | 10% (no significant improvement)   |
| 8. MnBr<sub>2</sub> (20%)   | 2% (no significant improvement)    |
| 9. Pd(OAc)<sub>2</sub> (20%) | 3% (no significant improvement)    |
| 10. NiBr<sub>2</sub>(DME) (10%) | 8% (no significant improvement)   |
| 11. CoCl<sub>2</sub> (10%)  | 8% (no significant improvement)    |
| 12. Co(dmgH)<sub>2</sub>pyCl (10%) | 9% (56%)                      |
| 13. Co(dmgH)<sub>2</sub>pyCl (100%) | 28%                               |

<sup>a</sup>Yield was determined by HPLC with 1,3,5-trimethoxybenzene as an internal standard.
Supplementary Table 5. Evaluation of Different Oxidants.

| Conditions                          | Resulta |
|------------------------------------|----------|
| 1. conditions under Ar             | 9%       |
| 2. conditions under Air            | 56%      |
| 3. conditions under O₂             | 14%      |
| 4. conditions under Air + MnO₂ (1 equiv.) | 19%    |
| 5. conditions under Air + Na₂S₂O₈ (1 equiv.) | 47%    |
| 6. conditions under Air + p-BQ (1 equiv.) | NR    |
| 7. conditions under Air + H₂O (1 equiv.) | 28%    |

a Yield was determined by HPLC with 1,3,5-trimethoxybenzene as an internal standard.

Supplementary Table 6. Evaluation of Borylated Reagent

| Conditions                           | Resulta |
|--------------------------------------|----------|
| 1. B₂pin₂                            | 56%      |
| 2. Bis(neopentyl glycolato)diboron   | NR       |
| 3. Bis(catecholato)diborane         | NR       |
| 4. Hypodiboric acid                  | NR       |
| 5. HBpin                             | NR       |
| 6. Trimethylamine borane             | NR       |

a Yield was determined by HPLC with 1,3,5-trimethoxybenzene as an internal standard.
### Supplementary Table 7. Evaluation of Solvents

| Conditions          | Result¹ |
|---------------------|---------|
| 1. MeCN             | Trace   |
| 2. DMA              | NR      |
| 3. DMSO             | NR      |
| 5. MeOH             | NR      |
| 6. Dioxane          | Trace   |
| 7. Acetone          | 7%      |
| 8. THF              | Trace   |
| 9. Toluene          | Trace   |
| 10. Benzotrifluoride| <10%    |
| 11. HMPA            | NR      |
| 12. CCl₄            | NR      |
| 13. MeNO₂           | NR      |
| 14. Trifluoroethanol| NR      |
| 15. EA              | 56%     |
| 16. tert-Butyl acetate| 58%    |
| 17. Methyl acetate  | 13%     |
| 18. Cyclohexyl acetate| 43%   |
| 19. Isopropyl acetate| 52%    |
| 20. Propyl acetate  | 43%     |
| 21. 2,2,2-Trifluoroethyl acetate| 18% |
| 22. Ethyl propionate| 30%     |
| 23. Methyl formate  | Trace   |
| 24. Ethyl trifluoroacetate| NR |
| 25. Ethyl bromoacetate| NR     |
| 26. Delta-Valerolactone| NR     |
27. tert-Butyl acetate (2 mL) 70%
28. tert-Butyl acetate (3 mL) 66%

**Supplementary Table 8. Evaluation of TMG Loading**

| Conditions          | Result¹ |
|---------------------|---------|
| 1. TMG (75 mol%)    | 70%     |
| 2. TMG (100 mol%)   | 19%     |
| 3. TMG (50 mol%)    | 75%     |
| 4. TMG (25 mol%)    | 42%     |

¹yield was determined by HPLC with 1,3,5-trimethoxybenzene as an internal standard.

**Supplementary Table 9. Evaluation of Co Catalyst Loading**

| Conditions           | Result¹ |
|----------------------|---------|
| 1. Co(dmgH)₂pyCl (10 mol%) | 70%     |
| 2. Co(dmgH)₂pyCl (5 mol%)    | 36%     |
| 3. Co(dmgH)₂pyCl (15 mol%)   | 72%     |

¹Yield was determined by HPLC with 1,3,5-trimethoxybenzene as an internal standard.
Supplementary Table 10. Evaluation of Catalyst Loading

| Conditions                        | Resulta |
|-----------------------------------|----------|
| 1. [Ir] (3 mol%)                  | 75%      |
| 2. [Ir] (3 mol%), TMG (50 mol%)   | 72%      |
| 3. [Ir] (3 mol%), [Co] (15 mol%), TMG (50 mol%) | 78%      |

aYield was determined by HPLC with 1,3,5-trimethoxybenzene as an internal standard.

3. Procedure for Decarboxylative Borylation.

A 5 mL vial equipped with a magnetic stir bar was charged with 3-acetyl-carboxylic acid (16.5 mg, 0.1 mmol), [Ir(dF(CF₃)ppy)](5,5'-dCF₃-bpy)PF₆ (3.6 mg, 0.003 mmol), Co(dmgH₂pyCl (6 mg, 0.015 mmol), B₂pin₂ (39 mg, 0.15 mmol), AcO'Bu (2 mL) was then into the vial. The reaction mixture was stirred without irradiation for 10 min at ambient temperature, and then TMG (7 μL, 0.05 mmol) was gradually added to the vial under stirring. The reaction mixture was stirred without irradiation for another 10 min at ambient temperature and then irradiated for 24 h while maintaining the temperature at approximately 35 °C through cooling with a fan. The solvent was removed on a rotary evaporator under reduced pressure, and the residue was purified by preparative thin-layer chromatography.
**4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (2a).** The title compound 2a was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.6). It was obtained as white solid (13 mg, 67%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.81 (d, $J = 6.9$ Hz, 1H), 7.46 (t, $J = 7.4$ Hz, 1H), 7.37 (t, $J = 7.4$ Hz, 1H), 1.35 (s, 4H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 134.74, 131.25, 127.71, 83.77, 24.89. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data. $^1$

![Structure of 2a](image)

**2-(3,5-dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b).** The title compound 2b was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.6). It was obtained as white solid (15 mg, 74%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.44 (s, 2H), 7.10 (s, 1H), 2.32 (s, 3H), 2.32 (s, 3H), 1.34 (s, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 137.17, 132.99, 132.39, 83.69, 24.87, 21.15. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data. $^2$

![Structure of 2b](image)

**2-(3,4-dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c).** The title compound 2c was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.6). It was obtained as white solid (15 mg, 68%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.51
(s, 1H), 7.48 (d, J = 7.4 Hz, 1H), 7.08 (d, J = 7.4 Hz, 1H), 2.21 (s, 3H), 2.20 (s, 3H), 1.27 (s, 12H). \(^{13} \text{C NMR} \) (101 MHz, Chloroform-d) \( \delta \) 140.15, 135.93, 135.89, 132.40, 129.17, 83.59, 24.85, 20.03, 19.48. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data\(^4\).

2-(2,4-dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d). The title compound 2d was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.8). It was obtained as white solid (11 mg, 48%). \(^1 \text{H NMR} \) (400 MHz, Chloroform-d) \( \delta \) 7.59 (d, J = 8.1 Hz, 1H), 6.94 – 6.88 (m, 2H), 2.43 (s, 3H), 2.24 (s, 3H), 1.26 (s, 12H). \(^{13} \text{C NMR} \) (101 MHz, Chloroform-d) \( \delta \) 144.94, 140.86, 136.09, 130.72, 125.53, 83.23, 24.89, 22.12, 21.50. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data\(^2\).

2-mesityl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e). The title compound 2e was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.7). It was obtained as white solid (13 mg, 55%). \(^1 \text{H NMR} \) (400 MHz, Chloroform-d) \( \delta \) 6.77 (s, 2H), 2.36 (s, 6H), 2.24 (s, 3H), 1.37 (s, 12H). \(^{13} \text{C NMR} \) (101 MHz, Chloroform-d) \( \delta \) 142.12, 138.92, 127.44, 83.46, 24.96, 22.20, 21.25. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data\(^3\).
4,4,5,5-tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (2f), The title compound 2f was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.6). It was obtained as white solid (11 mg, 51%). $^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 7.70 (d, $J = 7.6$ Hz, 2H), 7.19 (d, $J = 7.6$ Hz, 2H), 2.36 (s, 3H), 1.34 (s, 12H). $^{13}$C NMR (101 MHz, Chloroform-\textit{d}) $\delta$ 141.39, 134.81, 128.53, 83.62, 24.88, 21.74. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data.$^{1}$

2-(4-ethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g), The title compound 2g was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.5). It was obtained as white solid (12 mg, 53%). $^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 7.74 (d, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 7.9$ Hz, 2H), 2.66 (q, $J = 7.6$ Hz, 2H), 1.34 (s, 12H), 1.23 (t, $J = 7.7$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-\textit{d}) $\delta$ 147.74, 134.90, 127.36, 83.62, 29.12, 24.86, 15.49. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data.$^{5}$

2-(4-(tert-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h), The title compound 2h was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.8). It was
obtained as white solid (13 mg, 52%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.76 (d, $J = 8.3$ Hz, 2H), 7.41 (d, $J = 8.3$ Hz, 2H), 1.33 (s, 12H), 1.32 (s, 9H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 154.50, 134.69, 124.71, 83.62, 34.91, 31.21, 24.85. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data.$^1$

2-[(1,1'-biphenyl)-4-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i). The title compound 2i was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.6). it was obtained as light yellow solid (15 mg, 56%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.89 (d, $J = 7.9$ Hz, 2H), 7.64 – 7.59 (m, 4H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.35 (t, $J = 7.3$ Hz, 1H), 1.36 (s, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 143.90, 141.04, 135.27, 128.78, 127.57, 127.25, 126.48, 83.83, 24.91. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data$^1$.

2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j). The title compound 2j was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.4). it was obtained as white solid (17 mg, 77%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.75 (d, $J = 8.6$ Hz, 2H), 6.90 (d, $J = 8.6$ Hz, 2H), 3.83 (s, 3H), 1.33 (s, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 162.14, 136.51, 113.31, 83.55, 55.10, 24.87. The carbon
directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data.\textsuperscript{1}

\ \begin{center}
\includegraphics[width=0.2\textwidth]{figure1}
\end{center}

\textbf{4,4,5,5-tetramethyl-2-(4-phenoxyphenyl)-1,3,2-dioxaborolane (2k)}, The title compound \textit{2k} was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.7). It was obtained as white solid (10 mg, 37\%). \textbf{\textit{\textsuperscript{1}H NMR}} (400 MHz, Chloroform-\textit{d}) $\delta$ 7.78 (d, $J = 8.5$ Hz, 2H), 7.38 – 7.32 (m, 2H), 7.13 (t, $J = 7.4$ Hz, 1H), 7.06 – 7.01 (m, 2H), 6.98 (d, $J = 8.6$ Hz, 2H), 1.34 (s, 12H). \textbf{\textit{\textsuperscript{13}C NMR}} (101 MHz, Chloroform-\textit{d}) $\delta$ 160.18, 156.54, 136.63, 129.80, 123.66, 119.47, 117.67, 83.75, 24.88. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data.\textsuperscript{2}

\ \begin{center}
\includegraphics[width=0.2\textwidth]{figure2}
\end{center}

\textbf{1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2l)}, The title compound \textit{2l} was prepared according to the procedure and was purified by preparative thin-layer chromatography (toluene/EA: 1/20, Rf: 0.6). It was obtained as white solid (15 mg, 48\%). \textbf{\textit{\textsuperscript{1}H NMR}} (400 MHz, Chloroform-\textit{d}) $\delta$ 7.73 (s, 4H), 1.28 (s, 12H). \textbf{\textit{\textsuperscript{13}C NMR}} (101 MHz, Chloroform-\textit{d}) $\delta$ 133.88, 83.84, 24.88. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data.\textsuperscript{2}
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (2m), The title compound 2m was prepared according to the procedure and was purified by preparative thin-layer chromatography (toluene/DCM: 1/1, Rf: 0.5). It was obtained as white solid (9 mg, 41%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 9.98 (s, 1H), 7.89 (d, $J$ = 8.2 Hz, 2H), 7.79 (d, $J$ = 8.2 Hz, 2H), 1.29 (s, 12H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 192.67, 138.11, 135.22, 128.71, 84.34, 24.90. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data.

1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (2n), The title compound 2n was prepared according to the procedure and was purified by preparative thin-layer chromatography (CHCl$_3$/DCM: 1/1, Rf: 0.5). It was obtained as white solid (16 mg, 69%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.29 (s, 1H), 7.99 (d, $J$ = 7.8 Hz, 1H), 7.92 (d, $J$ = 7.3 Hz, 1H), 7.40 (t, $J$ = 7.6 Hz, 1H), 2.57 (s, 3H), 1.29 (s, 12H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 198.42, 139.41, 136.52, 134.81, 130.77, 128.04, 84.16, 26.77, 24.90. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data.

1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (2o),
The title compound 2o was prepared according to the procedure and was purified by preparative thin-layer chromatography (CHCl₃/DCM: 1/1, Rf: 0.5). It was obtained as white solid (11 mg, 46%). \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 7.84 (q, \(J = 8.3\) Hz, 1H), 2.55 (s, 3H), 1.29 (s, 12H). \(^1\)C NMR (101 MHz, Chloroform-d) \(\delta\) 198.46, 139.00, 134.92, 127.28, 84.22, 26.77, 24.88. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data\(^7\).

ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2p). The title compound 2p was prepared according to the procedure and was purified by preparative thin-layer chromatography (CHCl₃/DCM: 1/1, Rf: 0.5). It was obtained as white solid (14 mg, 50%). \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 8.02 (d, \(J = 7.8\) Hz, 2H), 7.87 (d, \(J = 7.8\) Hz, 1H), 4.38 (q, \(J = 7.1\) Hz, 2H), 1.40 (t, \(J = 7.1\) Hz, 3H), 1.36 (s, 12H). \(^1\)C NMR (101 MHz, Chloroform-d) \(\delta\) 166.67, 135.00, 132.82 (q, \(J = 32.1\) Hz), 134.62, 128.55, 84.16, 61.04, 24.89, 14.33. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data\(^2\).

4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (2q), The title compound 2q was prepared according to the procedure and was purified by preparative thin-layer chromatography (toluene/DCM: 1/1, Rf: 0.5). It was obtained as white solid (8 mg, 31%). \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 7.91 (d, \(J = 7.8\) Hz, 2H), 7.61 (d, \(J = 7.8\) Hz, 1H), 1.36 (s, 12H). \(^1\)C NMR (101 MHz, Chloroform-d) \(\delta\) 135.00, 132.82 (q, \(J = 32.1\) Hz), 124.13 (d, \(J = 272.1\) Hz),
124.31 (q, J = 3.6 Hz), 84.27, 77.33, 24.87. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data.

2-(4-(difluoromethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2r), The title compound 2r was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.5). It was obtained as white solid (9 mg, 38%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.82 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 7.7 Hz, 2H), 6.58 (t, J = 56.4 Hz, 1H), 1.28 (s, 12H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 136.79 (t, J = 22.1 Hz), 135.02, 124.72 (t, J = 6.0 Hz), 114.66 (t, J = 238.8 Hz), 84.11, 24.88. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data.

2-(3-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2s), The title compound 2s was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.8). It was obtained as white solid (15 mg, 63%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.78 (s, 1H), 7.66 (d, J = 7.3 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 1.34 (s, 12H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 134.56, 134.03, 132.64, 131.27, 129.19, 84.14, 24.86. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data.
2-(3-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2t), The title compound 2t was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.8). It was obtained as a light yellow solid (9 mg, 32%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.86 (d, $J = 1.5$ Hz, 1H), 7.64 (d, $J = 7.3$ Hz, 1H), 7.53 – 7.49 (m, 1H), 7.17 (t, $J = 8.7$ Hz, 2H), 1.27 (s, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 137.47, 134.19, 133.08, 129.49, 122.45, 84.16, 24.86. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data$^9$.

2-(3-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2u), The title compound 2u was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.7). It was obtained as yellow solid (25 mg, 75%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.07 (t, $J = 1.5$ Hz, 1H), 7.74 – 7.70 (m, 1H), 7.70 – 7.66 (m, 1H), 7.04 (t, $J = 7.6$ Hz, 1H), 1.27 (s, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 143.41, 140.10, 133.64, 129.65, 94.53, 84.15, 24.86. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data$^{10}$.
**4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (2v).** The title compound 2v was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.7). It was obtained as light yellow solid (21 mg, 85%). \[^1H\text{NMR}\] (400 MHz, Chloroform-\(d\)) \(\delta 8.76\) (d, \(J = 8.4\) Hz, 1H), 8.08 (dd, \(J = 6.8, 1.4\) Hz, 1H), 7.93 (d, \(J = 8.2\) Hz, 1H), 7.83 (d, \(J = 8.4\) Hz, 1H), 7.56 – 7.50 (m, 1H), 7.47 (dd, \(J = 8.1, 6.8\) Hz, 2H), 1.42 (s, 12H). \[^{13}\text{C\ NMR}\] (101 MHz, Chloroform-\(d\)) \(\delta 136.92, 135.65, 133.20, 131.61, 128.41, 128.35, 126.34, 125.48, 124.97, 83.74, 24.99.\) The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were consistent with the reported data.\(^3\)

**4,4,5,5-tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (2w).** The title compound 2w was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.7). It was obtained as light yellow solid (13 mg, 50%). \[^1H\text{NMR}\] (400 MHz, Chloroform-\(d\)) \(\delta 8.76\) (d, \(J = 8.3\) Hz, 1H), 8.08 (dd, \(J = 6.9, 1.4\) Hz, 1H), 7.93 (d, \(J = 8.2\) Hz, 1H), 7.83 (d, \(J = 7.8\) Hz, 1H), 7.56 – 7.50 (m, 1H), 7.49 – 7.45 (m, 2H), 1.42 (s, 12H). \[^{13}\text{C\ NMR}\] (101 MHz, Chloroform-\(d\)) \(\delta 136.91, 135.64, 133.20, 131.61, 128.41, 128.34, 126.34, 125.48, 124.97, 83.74, 24.99.\) The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were consistent with the reported data.\(^1\)
4,4,5,5-tetramethyl-2-(4-methylnaphthalen-1-yl)-1,3,2-dioxaborolane (2x).
The title compound 2x was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.8). It was obtained as light yellow solid (9 mg, 33%). $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.75 – 8.69 (m, 1H), 7.96 – 7.92 (m, 1H), 7.90 (d, $J = 7.0$ Hz, 1H), 7.50 – 7.40 (m, 2H), 7.25 (d, $J = 7.0$ Hz, 1H), 2.64 (s, 3H), 1.35 (s, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 138.15, 136.96, 135.62, 132.89, 132.43, 128.99, 125.99, 125.33, 124.18, 83.59, 24.96, 19.95. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data\textsuperscript{11}.

2-(4-fluoronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2y).
The title compound 2y was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.8). It was obtained as light yellow solid (20 mg, 73%). $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.72 (d, $J = 8.4$ Hz, 1H), 8.05 (d, $J = 8.0$ Hz, 1H), 7.96 (dd, $J = 7.5$, 6.4 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.49 – 7.43 (m, 1H), 7.06 (dd, $J = 10.5$, 7.8 Hz, 1H), 1.35 (s, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 161.21 (d, $J = 256.5$ Hz), 138.76 (d, $J = 4.8$ Hz), 136.16 (d, $J = 8.8$ Hz), 128.30 (d, $J = 2.9$ Hz), 127.30, 125.81 (d, $J = 2.1$ Hz), 123.53 (d, $J = 14.9$ Hz), 120.57 (d, $J = 6.3$ Hz), 108.80 (d, $J = 18.9$ Hz), 83.77, 24.97. The carbon directly attached to the boron atom
was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data².

![Boron compound](image)

2-(5-chloronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2z).
The title compound 2z was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.7). It was obtained as light yellow solid (17 mg, 58%).¹H NMR (400 MHz, Chloroform-d) δ 8.30 (s, 1H), 8.16 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.53 (d, J = 7.1 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 1.33 (s, 12H).¹³C NMR (101 MHz, Chloroform-d) δ 136.41, 133.92, 132.31, 131.82, 131.66, 127.87, 127.20, 125.66, 123.43, 84.13, 24.94. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. HRMS (EI): m/z calculated for [C₁₆H₁₈BClO₂] [M+H]⁺: 288.1083, found: 288.1081.

![Boron compound](image)

2-(4-chloronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2aa).
The title compound 2aa was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.8). It was obtained as light yellow solid (19 mg, 57%).¹H NMR (400 MHz, Chloroform-d) δ 8.76 – 8.70 (m, 1H), 8.26 – 8.21 (m, 1H), 7.90 (d, J = 7.5 Hz, 1H), 7.54 – 7.47 (m, 3H), 1.35 (s, 12H).¹³C NMR (101 MHz, Chloroform-d) δ 138.09, 135.75, 135.40, 130.51, 128.81, 127.10, 126.63, 125.48, 124.55, 83.94, 24.96. The carbon directly attached to the boron atom was not detected due to quadrupolar
broadening. **HRMS** (El): m/z calculated for [C_{16}H_{18}BClO_2][M+H]^+: 288.1083, found: 288.1082.

2-(6-bromonaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2ab),

The title compound 2ab was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.8). It was obtained as light yellow solid (17 mg, 50%). **^1H NMR** (400 MHz, Chloroform-d) $\delta$ 8.25 (s, 1H), 7.92 (s, 1H), 7.78 (d, $J = 8.2$ Hz, 1H), 7.66 (dd, $J = 8.4$, 6.1 Hz, 2H), 7.47 (dd, $J = 8.7$, 1.9 Hz, 1H), 1.31 (s, 12H). **^13C NMR** (101 MHz, Chloroform-d) $\delta$ 136.07, 135.99, 131.51, 131.19, 130.28, 129.83, 129.27, 126.07, 121.15, 84.08, 24.94. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. **HRMS** (El): m/z calculated for [C_{16}H_{18}BBrO_2][M+H]^+: 332.0578, found: 332.0574.

2-(5-bromonaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2ac),

The title compound 2ac was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.8). It was obtained as light yellow solid (21 mg, 65%). **^1H NMR** (400 MHz, Chloroform-d) $\delta$ 8.70 (d, $J = 8.5$ Hz, 1H), 8.30 (d, $J = 8.6$ Hz, 1H), 8.05 (dd, $J = 6.8$, 1.3 Hz, 1H), 7.71 (dd, $J = 7.4$, 1.1 Hz, 1H), 7.50 (dd, $J = 8.5$, 6.9 Hz, 1H), 7.29 (dd, $J = 8.5$, 7.4 Hz, 1H), 1.35 (s, 12H). **^13C NMR** (101 MHz, Chloroform-d) $\delta$ 137.19, 135.39, 130.65, 129.53, 128.67, 127.40, 125.54, 125.37, 122.08, 82.93, 23.92.
The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. HRMS (EI): m/z calculated for [C_{16}H_{18}BBrO_{2}] [M+H]^+: 332.0578, found: 332.0574.

2-(5-bromonaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2ad),

The title compound 2ad was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.8). It was obtained as light yellow solid (21 mg, 63%). \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 8.27 (s, 1H), 8.12 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 7.4 Hz, 1H), 7.25 (t, J = 7.8 Hz, 1H), 1.33 (s, 12H). \(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta\) 136.54, 134.03, 133.52, 131.95, 130.94, 128.64, 126.15, 126.11, 122.70, 84.13, 24.94. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. HRMS (EI): m/z calculated for [C_{16}H_{18}BBrO_{2}] [M+H]^+: 332.0578, found: 332.0574.

2-(benzo[b]thiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2ae),

The title compound 2ae was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.5). It was obtained as white solid (14 mg, 53%). \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 8.24 (s, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 5.4 Hz, 1H), 7.28 (d, J = 5.4 Hz, 1H), 1.31 (s, 12H). \(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta\) 142.70, 139.18, 130.73, 129.71, 126.01, 124.13, 121.83, 83.86, 24.92. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data.\(^{12}\)
**4,4,5,5-tetramethyl-2-(4-(thiophen-3-yl)phenyl)-1,3,2-dioxaborolane (2af).**

The title compound **2af** was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.5). It was obtained as white solid (9 mg, 30%). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.84 (d, \(J = 8.2\) Hz, 1H), 7.61 (d, \(J = 8.2\) Hz, 1H), 7.53 – 7.49 (m, 1H), 7.43 (dd, \(J = 5.0, 1.3\) Hz, 1H), 7.39 (dd, \(J = 5.0, 2.9\) Hz, 1H), 1.36 (s, 12H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 142.22, 138.37, 135.33, 129.92, 129.89, 126.33, 126.25, 125.68, 120.93, 83.81, 24.89. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data\(^3\).

**2-(benzofuran-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2ag).** The title compound **2ag** was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.8). It was obtained as white solid (13 mg, 53%). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.11 (s, 1H), 7.75 (dd, \(J = 8.3, 1.3\) Hz, 1H), 7.61 (d, \(J = 2.2\) Hz, 1H), 7.50 (dt, \(J = 8.3, 0.9\) Hz, 1H), 6.77 (dd, \(J = 2.2, 1.0\) Hz, 1H), 1.37 (s, 12H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 157.01, 144.92, 130.74, 128.62, 110.89, 106.65, 99.99, 83.76, 24.91. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were in consistent with the reported data\(^2\).
2-(benzofuran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2ah). The title compound 2ah was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.8). It was obtained as white solid (8 mg, 35%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.71 (dd, $J = 7.1, 1.0$ Hz, 1H), 7.65 (d, $J = 2.1$ Hz, 1H), 7.59 (dt, $J = 8.2, 1.0$ Hz, 1H), 7.29 (dd, $J = 8.2, 7.2$ Hz, 1H), 7.22 (dd, $J = 2.2, 1.0$ Hz, 1H), 1.38 (s, 14H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 154.24, 145.20, 132.60, 130.10, 123.56, 114.04, 108.45, 83.69, 24.99. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were consistent with the reported data$^{13}$.

2-(6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2ai). The title compound 2ai was prepared according to the procedure and was purified by preparative thin-layer chromatography (PE/DCM: 1/1, Rf: 0.9). It was obtained as white solid (15 mg, 32%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.30 (s, 1H), 7.90 (s, 1H), 7.85 (d, $J = 8.5$ Hz, 1H), 7.81 – 7.75 (m, 3H), 7.65 (dd, $J = 8.5, 1.8$ Hz, 1H), 7.53 (d, $J = 2.3$ Hz, 1H), 7.47 (dd, $J = 8.4, 2.3$ Hz, 1H), 6.92 (d, $J = 8.4$ Hz, 1H), 3.83 (s, 3H), 2.11 (d, $J = 2.9$ Hz, 6H), 2.03 (br, 3H), 1.76 – 1.70 (m, 6H), 1.33 (s, 12H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 158.66, 140.01, 138.86, 135.97, 135.40, 133.06, 131.61, 130.74, 129.01, 127.13, 125.96, 125.63, 124.81, 112.07, 83.90,
The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. The NMR data were consistent with the reported data\textsuperscript{1}.

\[(Z)-3-(4-fluorobenzyl)-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)thiazolidine-2,4-dione (2aj)\], The title compound 2aj was prepared according to the procedure and was purified by preparative thin-layer chromatography (DCM/CHCl\textsubscript{3}: 1/1, Rf: 0.4). It was obtained as white solid (13 mg, 30\%).\textsuperscript{1}H NMR (400 MHz, Chloroform-\textit{d}) \(\delta\) 7.91 (s, 1H), 7.88 (d, \(J = 8.1\) Hz, 2H), 7.48 (d, \(J = 8.1\) Hz, 2H), 7.43 (dd, \(J = 8.6, 5.3\) Hz, 2H), 7.01 (t, \(J = 8.7\) Hz, 2H), 4.86 (s, 2H), 1.35 (s, 12H).\textsuperscript{13}C NMR (101 MHz, Chloroform-\textit{d}) \(\delta\) 167.75, 166.03, 162.65 (d, \(J = 246.7\) Hz), 135.42, 134.10, 130.93 (d, \(J = 8.3\) Hz), 129.27, 122.21, 115.66 (d, \(J = 21.6\) Hz), 84.21, 44.52, 24.88. HRMS (ESI): m/z calculated for \([\text{C}_{23}\text{H}_{24}\text{BFNO}_4\text{S}]^{+}\): 440.1498, found: 440.1490.

A 5 mL vial equipped with a magnetic stir bar was charged with 4-acetyl-carboxylic acid (16.5 mg, 0.1 mmol), \([\text{Ir}(\text{dF}(_3\text{ppy}))_{2}(5,5'-\text{dCF}_3\text{bpy})]\text{PF}_6 (3\% \text{mol})\), \(\text{Co(dmgH)}_2\text{pyCl} (15\% \text{mol})\) TMG (50\% mol), tert-Butyl acetate, 440nm LED, Air, 24h → NaBO\textsubscript{3} THF/H\textsubscript{2}O, 1h

\[\text{Ac} \quad 1\text{o} \quad \text{COOH} \quad \text{Ir}[dF(CF}_3_{ppy}]\text{Co(dmgH)}_2\text{pyCl} \quad \text{NaBO}_3 \quad \text{Ac} \quad 3\text{o} \quad \text{OH} \quad \text{Ac} \quad 2\text{aj} \]

The reaction mixture was stirred without irradiation for 10 min at ambient temperature, and then TMG (7 \(\mu\)L, 0.05 mmol) was gradually added to the vial under stirring. The reaction mixture was...
stirred without irradiation for another 10 min at ambient temperature and then irradiated for 24 h while maintaining the temperature at approximately 35 °C through cooling with a fan. The solvent was removed on a rotary evaporator under reduced pressure, then NaBO₃ 4H₂O and 1:1 THF/H₂O (2 mL), and the resulting mixture was stirred at room temperature under air for 1 hour. After 1 hour, the reaction was quenched with saturated NH₄Cl (4 mL), and the contents of the round-bottom flask were transferred to a separatory funnel containing 5 mL brine using Et₂O (5 mL×2). The layers were separated, and the aqueous layer was extracted with additional Et₂O (2 × 5 mL). The combined organics were dried over Na₂SO₄, then purified by preparative thin-layer chromatography (MeOH/DCM: 1/20, Rf: 0.6). 2o' was obtained as light yellow solid (9 mg, 64%).

¹H NMR (600 MHz, Chloroform-d) δ 7.84 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 2.50 (s, 3H). ¹³C NMR (151 MHz, Chloroform-d) δ 197.41, 160.40, 131.04, 130.24, 115.37, 26.36.

When replacing benzoic acid with sodium benzoate, no any product was monitored according to the procedure above.

4. Mechanistic Studies

4.1 Control Experiment

Following the above same condition but only without Co(dmgH)₂pyCl, or
Light, or TMG or Ir[dF(CF<sub>3</sub>)ppy)](5,5'-dCF<sub>3</sub>bpy)PF<sub>6</sub>, the corresponding results are listed in the Table 11.

**Supplementary Table 11.** Control experiment

| Conditions<sup>a</sup> | Result |
|----------------------|--------|
| 1. Conditions        | 77%    |
| 2. No [Co]           | 49%    |
| 3. No Lght           | Trace  |
| 4. No [TMG]          | NR     |
| 5. No [Ir]           | NR     |

<sup>a</sup>Yield was determined by HPLC with 1,3,5-trimethoxybenzene as an internal standard.

4.2 Detection of CO<sub>2</sub>

![Diagram of the reaction process involving Ir[dF(CF<sub>3</sub>)ppy)](5,5'-dCF<sub>3</sub>bpy)PF<sub>6</sub>, B<sub>2</sub>pin<sub>2</sub>, Co(dmgH)<sub>2</sub>Cl<sub>2</sub>, AcO'Bu, and light, resulting in CO<sub>2</sub> production.]

Supplementary Fig. 2. Conditions: 1 (0.1 mmol), B<sub>2</sub>pin<sub>2</sub> (1.5 equiv.), [Ir-1] (3 mol%), Co(dmgH)<sub>2</sub>Cl<sub>2</sub> (15 mol%), AcO'Bu (2 mL), 440nm LED. After 24 hours, a gas sample was taken from the headspace of the sealed reaction vial via a syringe with a valve for measurement. a Gas chromatographic retention time of carbon dioxide. b Mass spectrum of carbon dioxide.

4.3 Stern-Volmer Quenching Experiment

The quenching rate $k_q$ was determined using the Stern-Volmer relationship:

$$I/I_0 = k_q \times [qunker] + 1 \quad (1)$$
Where \( I_0 \) is the fluorescence intensity without the quencher, \( I \) is the fluorescence intensity with the quencher, and \( \tau_0 \) is the lifetime of the photoexcited state of the photocatalyst. The excited-state lifetime of \( \text{Ir}[dF(CF_3)ppy] (5,5'-dCF_3bpy)PF_6 \) in DCM is 279ns.\(^{14}\)

**Evaluation of 3-acetyl-benzoic acid (1n) as potential quencher for photoexcited \( \text{Ir}[dF(CF_3)ppy] (5,5'-dCF_3bpy)PF_6 \)**

Fluorescence quenching studies were carried out using a solution of \( \text{Ir}[dF(CF_3)ppy] (5,5'-dCF_3bpy)PF_6 \) (1×10\(^{-5}\) M), 3-acetyl-benzoic acid with different concentration (0-40 mM) in AcO'Bu. The samples were prepared in 4 mL quartz cuvettes, which were irradiated at 300 nm, and emission was detected at 602 nm. As shown in Fig. 3 the fluorescence intensity gradually decreased with the concentration increase of 3-acetyl-benzoic acid from 0 mM to 40 mM.

**Supplementary Fig. 3.** (A) The fluorescence emission spectra of \( ^{1}\text{Ir}^{(III)} \) with different concentrations of 3-acetyl-benzoic acid (1n). (B) Combined Stern–Volmer emission quenching data. For carboxylate, \( k_q \) (1n) =2.5×10\(^8\) M\(^{-1}\)s\(^{-1}\).

**Evaluation of Co(dmgh)\(_2\)pyCl (Co-1) as potential quencher for photoexcited \( \text{Ir}[dF(CF_3)ppy] (5,5'-dCF_3bpy)PF_6 \)**

Fluorescence quenching studies were carried out using a solution of \( \text{Ir}[dF(CF_3)ppy] (5,5'-dCF_3bpy)PF_6 \) (1×10\(^{-5}\) M), Co(dmgh)\(_2\)pyCl with different concentration (0-88 \( \mu \)M) in AcO'Bu. The samples were prepared in 4 mL quartz cuvettes, which were irradiated at 300 nm, and emission was detected at 602
nm. As shown in Fig. 4, the fluorescence intensity dramatically decreased with the concentration increase of Co(dmgh)_2pyCl from 0 mM to 88 μM.

**Supplementary Fig. 4.** (A) The fluorescence emission spectra of *Ir(III) with different concentration of Co(dmgh)_2pyCl; (B) Combined Stern–Volmer emission quenching data. For Co(dmgh)_2pyCl, k_q (Co-1) =1.2×10^{11} M^{-1}s^{-1}.

**Evaluation of TMG as potential quencher for photoexcited Ir[dF(CF_3)ppy](5,5'-dCF_3bpy)PF_6**

Fluorescence quenching studies were carried out using a solution of Ir[dF(CF_3)ppy](5,5'-dCF_3bpy)PF_6 (1×10^{-5} M), TMG with different concentration (0-60 μM, 0-0.6 mM) in AcO'Bu. The samples were prepared in 4 mL quartz cuvettes, which were irradiated at 300 nm, and emission was detected at 602 nm. As shown in Fig. 5, no quenching was observed.

**Supplementary Fig. 5.** The fluorescence emission spectra of *Ir(III) with different concentrations of TMG; No quenching was observed.
4.4 Synthesis and conversion of the intermediate R-Co(III)

PhCo(dmgH)$_2$py was synthesized according to literature.$^{15}$ $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.71 – 8.66 (m, 2H), 7.68 (tt, $J =$ 7.6, 1.6 Hz, 1H), 7.35 – 7.26 (m, 4H), 6.91 – 6.78 (m, 3H), 3.42 (s, 2H), 1.96 (s, 12H). The $^1$HNMR data were in consistent with the reported data.

A 5 mL vial equipped with a magnetic stir bar was charged with PhCo(dmgH)$_2$py (22 mg, 0.05 mmol), anhydrous AcO'Bu solvent (2 mL), B$_2$pin$_2$ (1.5 equiv.), and different conditions (listed below table) were conducted, no related product 2a was detected, excluding the possible intermediates.

**Supplementary Table 12.** Condition screening on the conversion of the intermediate Ph-Co(III)

| Conditions | Result |
|------------|--------|
| 1. B$_2$pin$_2$ (1.5 equiv.), RT | NR |
| 2. B$_2$pin$_2$ (1.5 equiv.), 40$^\circ$C | NR |
| 3. B$_2$pin$_2$ (1.5 equiv.), TMG (50 mol%), 40$^\circ$C | NR |
| 4. B$_2$pin$_2$ (1.5 equiv.), TMG (50 mol%), [Ir] (3 mol%), Light (440nM LED) | NR |
| 5. B$_2$pin$_2$ (1.5 equiv.), TMG (50 mol%), HOAc (50 mol%), 40$^\circ$C | NR |
| 6. B$_2$pin$_2$ (1.5 equiv.), TMG (50 mol%), HOAc (50 mol%), [Ir] (3 mol%), Light (440nM LED) | NR |
4.5 Radical Trapping or Inhibiting Experiments

Following the standard borylated condition with TEMPO (31 mg, 0.2 mmol), the 2ai’ was acquired with a 10% yield, and no 2n was detected.

Following the above same radical inhibiting experiments without TMG, no 2n and the captured product of TEMPO 2n’ were detected.

4.6 in situ $^1$HNMR Analysis

Condition 1: A 5 mL vial equipped with a magnetic stir bar was charged with 3-acetyl-benzoic acid (5 mg, 0.033 mmol), anhydrous AcO$i^\text{Bu}$ solvent (1 mL); The vial was sealed and shook for 1 minute to make solid dissolved. 0.5 ml of the above were conducted in screw-cap NMR tubes; a Capillary tube containing pure C$_6$D$_6$ was placed in each of the NMR tubes to allow locking and shimming for NMR experiments. The data was shown as curve 1 in Fig. 6.

Condition 2: A 5 mL vial equipped with a magnetic stir bar was charged with TMG (2 $\mu$L, 0.016 mmol), anhydrous AcO$i^\text{Bu}$ solvent (1 mL); The vial was sealed and shook for 1 minute to make solid dissolved. The $^1$H NMR analysis was conducted with the same condition as condition 1 and the data was shown in curve 2 in Fig. 6.

Condition 3: A 5 mL vial equipped with a magnetic stir bar was charged with 3-acetyl-benzoic acid (5 mg, 0.033 mmol), TMG (2 $\mu$L, 0.016 mmol), anhydrous AcO$i^\text{Bu}$ solvent (1 mL); The vial was sealed and shaken for 1 minute to make solid dissolved. The $^1$H NMR analysis was conducted with the same
Condition as condition 1 and the data was shown in curve 3 in Fig. 6.

Condition 4: A 5 mL vial equipped with a magnetic stir bar was charged with 3-acetyl-benzoic acid (5 mg, 0.033 mmol), TMG (4 µL, 0.032 mmol), anhydrous AcO\textsubscript{t}Bu solvent (1 mL); The vial was sealed and shook for 1 minute to make solid dissolved. The \textsuperscript{1}H NMR analysis was conducted with the same condition as condition 1 and the data was shown in curve 4 in Fig. 6.

Condition 5: A 5 mL vial equipped with a magnetic stir bar was charged with 3-acetyl-carboxylic acid (16.5 mg, 0.1 mmol), [Ir(dF(CF\textsubscript{3}ppy)\textsubscript{2})(5,5'-CF\textsubscript{3}-bpy)]PF\textsubscript{6} (3.6 mg, 0.003 mmol), Co(dmgh)\textsubscript{2}pyCl (6 mg, 0.015 mmol), B\textsubscript{2}pin\textsubscript{2} (39 mg, 0.15 mmol), AcO\textsubscript{t}Bu (2 mL) was then into the vial. The reaction mixture was stirred without irradiation for 10 min at ambient temperature, and then TMG (7 µL, 0.05 mmol) was gradually added to the vial under stirring. The reaction mixture was stirred without irradiation for another 10 min at ambient temperature and then irradiated for 5 h while maintaining the temperature at approximately 35 °C through cooling with a fan. The \textsuperscript{1}H NMR analysis was conducted with the same condition as condition 1 and the data was shown in curve 5 in Fig. 6.

Supplementary Fig. 6. \textit{in situ} \textsuperscript{1}HNMR analysis
4.6 in situ $^{11}$BNMR Analysis

Condition 1: A 5 mL vial equipped with a magnetic stir bar was charged with $\text{B}_2\text{pin}_2$ (12.5 mg, 0.1 mmol), anhydrous MeCN solvent (1 mL); The vial was sealed and shook for 1 minute to make solid dissolved. 0.5 ml of the above were conducted in screw-cap NMR tubes; a Capillary tube containing pure C$_6$D$_6$ was placed in each of the NMR tubes to allow locking and shimming for NMR experiments. The data was shown as curve 1 in Fig. 7.

Condition 2: A 5 mL vial equipped with a magnetic stir bar was charged with $\text{B}_2\text{pin}_2$ (12.5 mg, 0.1 mmol), anhydrous Ethyl acetate solvent (1 mL); The $^{11}$B NMR analysis was conducted with the same condition as condition 1 and the data was shown as curve 2 in Fig. 7.

Condition 3: A 5 mL vial equipped with a magnetic stir bar was charged with $\text{B}_2\text{pin}_2$ (12.5 mg, 0.1 mmol), TMG (2 µL, 0.016 mmol), anhydrous AcO'Bu (1 mL); The $^{11}$B NMR analysis was conducted with the same condition with condition 1 and the data was shown as curve 3 in Fig. 7.

Supplementary Fig. 7. in situ $^{11}$B NMR analysis

4.7 Determination of Quantum Yield (standard ferrioxalate actinometry)

4.7.1 Determination of Photon Flux of the Reactor

The photon flux of blue LED was determined by standard ferrioxalate actinometry$^{16-18}$.

1. A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (368.4 mg, 0.750 mmol) in 5.0 mL of 0.20 M aqueous
sulfuric acid. A 0.15 M buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (541 mg, 3.00 mmol) and sodium acetate (1.23 g, 15.0 mmol) in 20 mL of 0.20 M aqueous sulfuric acid.

2. To 4 mL, a quartz cuvette equipped with a magnetic stir bar was added 0.50 mL of the ferrioxalate solution. The quartz cell was sealed and placed 2 cm away from the blue LEDs. After irradiation for different seconds, 1.5 mL of the aqueous sulfuric acid and 2.0 mL of the buffered solution were added to the vial \( V_t = 0.5 + 1.5 + 2 \text{ mL} \). After 1 hour, 45 \( \mu \text{L} \) \( V_2 \) of the above solution was taken as an aliquot and diluted with 3.0 mL \( V_3 \) of 0.20 M aqueous sulfuric acid; then 1mL \( V_4 \) of the resulting solution was taken as an aliquot and diluted with 3.0 mL \( V_5 \) of 0.20 M aqueous sulfuric acid.

3. The absorbance of the resulting solution in a quartz cuvette (\( l = 1.0 \text{ cm} \)) at 510 nm was measured by a UV-Vis spectrometer. A non-irradiated sample and other samples with 5s, 15s, 30s, 45s, 60s, and 90s irradiation time were also prepared, and the absorbance at 510 nm was measured.

The amount of ferrous ion formed was calculated as follows: \( \text{Mol Fe}^{2+} = \frac{V_1 V_3 V_5 \Delta A_{510} / \varepsilon_{510} V_2 V_4}{V_1 V_3 V_5} \) (2)

**Supplementary Table 13.** Raw chemical actinometry data to determine the photon flux

| irradiation time(s) | Absorbance | \( \Delta A \) | Mol Fe\(^{2+}\) (mol) |
|---------------------|------------|--------------|----------------------|
| non-irradiation     | 0.005      |              |                      |
| 5                   | 0.011      | 0.006        | 4.33\times10^{-7}    |
| 15                  | 0.021      | 0.016        | 1.15\times10^{-6}    |
| 30                  | 0.030      | 0.025        | 1.80\times10^{-6}    |
| 45                  | 0.037      | 0.032        | 2.31\times10^{-6}    |
| 60                  | 0.051      | 0.046        | 3.32\times10^{-6}    |
| 90                  | 0.069      | 0.064        | 4.61\times10^{-6}    |
Supplementary Fig. 8. Compiled linear fits for the photon flux

Photon flux may be determined by: \( \text{photon flux} = \frac{\text{Mol Fe}^{2+}}{\Phi \cdot t \cdot f} \) (3)

where \( \Phi \) is the quantum yield for the ferrioxalate actinometer (approximated as 0.845, which was reported for a 0.15 M solution at \( \lambda = 457.9 \) nm)\(^{19} \), \( t \) is the irradiation time, and \( f \) is the fraction of light absorbed at 440 nm (the mean fraction of light absorbed by the ferrioxalate solution approximately equal to 1 at 440 nm at 0.15 M ferrioxalate).

The value of the slope collected is \( 5.32 \times 10^{-8} \); division by the known quantum yield \( \Phi = 0.845 \) yields a photon flux of \( 6.3 \times 10^{-8} \) einsteins s\(^{-1} \).

4.7.2 Determination of the Reaction Quantum Yield

To a 4 mL a quartz cuvette equipped with a magnetic stir bar was charged with 3-acetyl -carboxylic acid (16.5 mg, 0.1 mmol), \([\text{Ir(dF(CF}_3\text{ppy})_2(5,5'\text{-CF}_3\text{-bpy})]PF}_6\) (3.6 mg, 0.003 mmol), \(\text{Co(dmgh)}_2\text{pyCl} \) (6 mg, 0.015mmol), \(\text{B}_2\text{pin}_2 \) (39mg, 0.15 mmol), \(\text{AcO'Bu} \) (2 mL). The reaction mixture was stirred without irradiation for 10 min at ambient temperature and then TMG (7 \( \mu \)L, 0.05 mmol) was gradually added to the vial under stirring. The reaction mixture was stirred without irradiation for another 10 min at ambient temperature, and then placed 2 cm away from the blue LEDs and irradiated for 1 h while maintaining the
temperature at approximately 35 °C through cooling with a fan. 1,3,5-
trimethoxybenzene (HPLC internal standard quantification based on the
internal standard 1,3,5-trimethoxybenzene, the peak area and relative
correction factor of reaction product) was added then the mixture was analyzed
by HPLC. and the 32% yield of product 2n (3.2× 10⁻⁵ mol) was determined.

the absorbance of the solution at 450 nm was 3, f = 1.0000 – 10⁻₈≈ 1 (A =
3.987)

\[ \Phi = \frac{\text{mol product/flux} \times t \times f}{3.2 \times 10^{-5} \text{ mol} / 3600 \text{s} \times 6.3 \times 10^{-8} \text{ Einstein/s}} = 0.14. \]

4.8. Computational Study

All density functional theory (DFT) calculations were carried out with the
Gaussian 16, Revision A.03. The B3LYP functional is mainly used in our
research (CAM-B3LYP, M06, PBE1PBE are also used to check the validity of
the computational method), and the 6-311+g(d,p) basis set was used for
organic molecules, For metal-containing molecules, light elements (C,H,N,O
etc) were treated using the 6-31G* basis set while metal atoms (Co and Ir) were
treated using the LanL2DZ/SDD basis set. For all the calculations, Grimme-D3
correction was utilized for the Empirical Dispersion, [ S. Grimme, J. Antony, S.
Ehrlich and H. Krieg, J. Chem. Phys., 132 (2010) 154104] and the solvent effect
of ethyl-ethanoate was included with Truhlar’s SMD model [A. V. Marenich, C.
J. Cramer, and D. G. Truhlar, J. Phys. Chem. B, 113 (2009) 6378-96].

4.8.1. Calculation of redox potential

The redox potentials were obtained from the computation of oxidation-
reduction half-reactions, according to

\[ \Delta G = -nFE, \]  \hspace{1cm} (4)

\[ E^0 \ (\text{versus SCE}) = - (\Delta G_{\text{red}} / nF) - E(\text{SCE}), \]  \hspace{1cm} (5)
\[ E({\text{SCE}}) = 4.6812\text{V} \]

Where \( \Delta G \) is the free energy change (J/mol), \( n \) is the number of electrons transfer in oxidation-reduction half-reaction, \( F = 96485 \text{ J mol}^{-1}\text{V}^{-1} \) is the Faraday constant, \( E \) is the oxidation-reduction half-reactions’ potential. \( E({\text{SCE}}) \) is the potential of Saturated Calomel Electrode.

The Gibbs free energies were computed through the DFT and TDDFT calculation with frequency analysis.

**Supplementary Table 14.** The computed \( \Delta G \) and \( E_{\text{red}}^0 \) (versus SCE) for the redox half-reactions of different molecules and complexes

|                  | \( \Delta G \) (kcal/mol) | \( E_{\text{red}}^0 \) (versus SCE) (V) |
|------------------|---------------------------|---------------------------------------|
| 1b''/ PhCOOH     | -165.9                    | 2.51                                  |
| PhCOONa''/ PhCOONa | -149.9                    | 1.82                                  |
| PhCOO+/ PhCOO^-   | -120.4                    | 0.54                                  |
| 1b'/ 1a in Oxidation-HAT | -140.0                    | 1.39                                  |
| 1d'/ 1c in PT-Oxidation | -139.2                    | 1.36                                  |
| 1b'-1/ 1a-1 in Oxidation-HAT | -141.7                    | 1.46                                  |
| 1d'-1/ 1c-1 in PT-Oxidation | -140.3                    | 1.40                                  |
| 1b'-2/ 1a-2      | -134.1                    | 1.13                                  |
| 1b'-3/ 1a-3      | -140.4                    | 1.41                                  |
| [Ir-1]^{IV/III}  | -146.9                    | 1.69                                  |
| [Ir-7]^{IV/III}  | -131.0                    | 1.00                                  |
| [Ir-1]^{IV/III*} | -98.4                     | -0.42                                 |
| [Ir-7]^{IV/III*} | -78.8                     | -1.27                                 |
| [Ir-1]^{III/II}  | -82.8                     | -1.09                                 |
| [Ir-7]^{III/II}  | -65.5                     | -1.84                                 |
| [Ir-1]^{III/II*} | -131.3                    | 1.01                                  |
| [Ir-7]^{III/II*} | -113.6                    | 0.25                                  |
| [Co-1]^{III/II}  | -83.3                     | -1.07                                 |
Note: Ir$^{III}$ is computed on Ir$^{III}$’s lowest triplet excited state $T_1$ optimization structure by TDDFT.

Note: 1a-1, 1a-2, 1a-3 are other possible conformers of the complex of benzoic acid and TMG, details are listed in 4.8.6.

**Discussion**

| $E^0$ (V) | Reaction | Note |
|-----------|----------|------|
| 2.51      | PhCOOH$^{+/+}$ PhCOOH | too high to be oxidized |
| 1.69      | [Ir-1]$^{IV/III}$ | give good yield (with light, with Co) |
| 1.39      | 1b'/1a in Oxidation-PT | lower enough to be oxidized by [Ir-1]$^{IV/III}$ |
| 1.36      | 1d'/1c in PT-Oxidation | lower enough to be oxidized by [Ir-1]$^{IV/III}$ |
| 1.01      | [Ir-1]$^{III/II}$ | give poor yield (with light, no Co) |
| 1.00      | [Ir-7]$^{IV/III}$ | cannot oxidize 1a'/1c |
| 0.25      | [Ir-7]$^{III/II}$ | cannot oxidize 1a'/1c |
| 0.0       |            |      |
| -0.42     | [Ir-1]$^{III/II}$ | [Ir-1]$^{III}$ can be oxidized by Co |
| -1.07     | [Co-1]$^{III}$ | cannot oxidize 1a/1c, but can oxidize [Ir-1]$^{III}$, [Ir-7]$^{III}$ |
| -1.09     | [Ir-1]$^{III}$ | cannot oxidize 1a/1c (no light, no Co) |
| -1.27     | [Ir-7]$^{III/II}$ | [Ir-7]$^{III}$ can be oxidized by Co |
| -1.84     | [Ir-7]$^{III}$ | cannot oxidize 1a'/1c |

The computation data above does tell the effects of TMG, which is lowering the redox potential of benzoic acid to 1a/1c for about 1.12V/1.15V, and the effects of photo-inducing by lowering the redox potential of [Ir-1]$^{IV/III}$ to [Ir-1]$^{IV/III}$ for about 2.1V, which drives the [Co-1]$^{III}$ oxidize [Ir-1]$^{III}$ to [Ir-1]$^{V}$ for further reaction.

To check the validity of the computational method, we have utilized other functionals (CAM-B3LYP, M06, PBE1PBE) and bigger basis (SDD), and received similar results (showed in Table 15 below).
### Supplementary Table 15. $E_{\text{red}}^0$ (versus SCE) for the redox half-reactions of [Ir-1], [Ir-7], and [Co-1], utilizing various functionals and LanL2DZ, SDD basis sets for metal elements, 6-31g* for other elements.

| $E_{\text{red}}^0$ (V) | B3LYP | CAM-B3LYP | M06  | PBE1PBE |
|------------------------|-------|-----------|------|---------|
|                        | LanL2DZ | SDD | LanL2DZ | SDD | LanL2DZ | SDD | LanL2DZ | SDD |
| [Ir-1]$^{IV}$/III      | 1.69  | 1.71     | 1.95  | 1.97    | 1.73  | 1.77    | 1.77  | 1.79  |
| [Ir-1]$^{IV}$/Br*      | -0.42 | -0.41    | -0.32 | -0.30   | -0.47 | -0.50   | -0.50 | -0.51 |
| [Ir-1]$^{III}$/II      | -1.09 | -1.07    | -1.15 | -1.15   | -1.10 | -1.10   | -1.08 | -1.08 |
| [Ir-1]$^{III}$/II*     | 1.01  | 1.05     | 1.11  | 1.12    | 1.10  | 1.17    | 1.19  | 1.21  |
| [Ir-7]$^{IV}$/III      | 1.00  | 1.17     | 1.14  | 1.17    | 1.04  | 1.08    | 1.10  | 1.12  |
| [Ir-7]$^{IV}$/Br*      | -1.27 | -1.21    | -1.23 | -1.21   | -1.30 | -1.32   | -1.33 | -1.33 |
| [Ir-7]$^{III}$/II      | -2.02 | -2.06    | -2.07 | -2.06   | -1.95 | -1.94   | -1.95 | -1.94 |
| [Ir-7]$^{III}$/II*     | 0.25  | 0.31     | 0.30  | 0.31    | 0.39  | 0.46    | 0.49  | 0.51  |
| [Co-1]$^{III}$/II      | -1.07 | -1.19    | -1.00 | -1.13   | -1.14 | -1.14   | -1.12 | -1.22 |

### 4.8.2. Calculation of the activation energy of the redox reaction

According to Marcus theory, the energy barrier of the reaction, i.e. the activation energy can be calculated as following:

$$
\Delta G^\dagger = \frac{(\lambda_0 + \Delta G^0)^2}{4 \lambda_0}
$$

Where $\lambda_0$ is the reorganization energy and $\Delta G^0$ is the energy change of reaction. $\lambda_0$ and $\Delta G^0$ can be calculated from adiabatic state energies at the optimized structure of the initial and final states. Because of the complexity to treat the whole redox reaction with the donor-acceptor complex, we computed the two half reactions separately first, and then combined the results to get the approximate result. (showed in Table 16 and 17 below)

### Supplementary Table 16. Reorganization energy $\lambda_0$, energy change $\Delta G^0$, and the activation energy $\Delta G^\dagger$ of the half redox reactions are listed below

|            | Reduction | Oxidization |
|------------|-----------|-------------|
| $[\text{Ir-1}]^{IV}$ | $[\text{Ir-7}]^{IV}$ | PhCOOH | $1a$ | $1c$ |
| $\lambda_0$ (a.u.) | 0.0030    | 0.0033      | 0.0073 | 0.0176 | 0.0218 |
| $\Delta G^0$ (a.u.) | -0.2300   | -0.2047     | 0.2686 | 0.2193 | 0.2262 |
Supplementary Table 17. Reorganization energy $\lambda_0$, energy change $\Delta G^0$, and the activation energy $\Delta G^\ddagger$ of the the combined whole redox reactions are listed below.

|            | [Ir-1]$^\text{IV}$ | [Ir-7]$^\text{IV}$ |
|------------|---------------------|---------------------|
|            | PhCOOH 1a 1c        | PhCOOH 1a 1c        |
| $\lambda_0$(a.u.) | 0.0103 0.0206 0.0248 | 0.0106 0.0209 0.0252 |
| $\Delta G^0$(a.u.) | 0.0387 -0.0106 -0.0038 | 0.0639 0.0146 0.0214 |
| $\Delta G^0$(kcal/mol) | 24.27 -6.66 -2.38 | 40.10 9.16 13.44 |
| $\Delta G^\ddagger$(a.u.) | 0.058 0.001 0.004 | 0.131 0.015 0.022 |
| $\Delta G^\ddagger$(kcal/mol) | 36.50 0.76 2.80 | 81.93 9.46 13.53 |

The computed results shown above once again confirms that TMG group is essential to promote the redox reaction, by lowering both $\Delta G^0$ (thermodynamics) and $\Delta G^\ddagger$ (kinetics). In particular, the $\Delta G^\ddagger$ of the [Ir-1]$^\text{IV}$ 1a/1c redox reaction is much smaller than the ones of [Ir-7]$^\text{IV}$ (0.76/2.80 kcal/mol vs 9.46/13.53 kcal/mol), agreeing well with the big difference of yield between these two catalysts.

Since the rate of proton transfer (1a to 1c) is fast, and the reverse proton transfer (1c to 1a) rate is also fast, at ground state 1a and 1c could reach a Boltzmann distribution first, and then proceed the redox reaction. According to the low activation energy of both redox paths (0.76 kcal/mol for 1a, 2.80 kcal/mol for 1c) and the limitation of computational accuracy, we conclude that Oxidation-HAT process and PT-Oxidation process could both contribute to the TMG-assisted benzoic acid oxidation reaction effectively.

4.8.3. Molecular orbital analyses on radical forming

To further understand the role of TMG to reduce the redox potential, we compare the involved molecular orbitals (MOs) of the benzoic acid and benzoic acid-TMG complex.

From the comparison of the MOs, it is clear that the main difference comes from the Singly-Occupied MOs (SOMOs) for the corresponding radical. For complex 1a and 1c, the SOMO is much delocalized to the TMG molecules, and the orbital energies are decreased comparing to the one of isolated benzoic
Supplementary Table 18. Comparing the orbital of SOMO that one electron excited, and their corresponding electron energy (eV)

|            | SOMO | Orbital energy /eV |
|------------|------|--------------------|
| PhCOOH     |      | -7.72              |
| Complex 1c |      | -6.78              |
| Complex 1a |      | -6.53              |
| TMG        |      | -6.34              |

Supplementary Fig. 9. The energy profile for the activation of benzoic acid by TMG.
Supplementary Fig. 10. Energy profile for complete borylation

Supplementary Table 19. The possible conformers of borylation

|   |   |   |
|---|---|---|
| 1e | complex2 |   |
| 1e-TS-1 | 1e-TS | 1e-TS-2 |
| 1e-TS-3 | 1e-TS-4 |   |
Supplementary Table 20. Other possible conformers and binding energy.

Supplementary Table 21. Binding energy of potential reactants of the decarboxylation reaction

|     | binding energy (kcal/mol) |
|-----|---------------------------|
| 1a  | -3.3                      |
|     |       |
|-----|-------|
|  1c | -13.7 |
|  1b' |  3.4  |
|  1d  |  5.1  |
|  1d' |  8.5  |
|PhCOONa | -39.2 |
|  1a-1 | -4.2  |
|  1c-1 | -14.6 |
|  1a-2 |  6.5  |
|  1a-3 |  3.4  |

According to the data above, complex 1a, 1a-1 are able to form, and then proceed proton transfer to form 1c, 1c-1 respectively. There is only small structure and energy difference between 1a-1, 1c-1 and 1a, 1c, caused by the rotation of the TMG group.

Since the redox potential of 1a, 1c (1.39V, 1.36V) are both lower than those of 1a-1, 1c-1 (1.46V, 1.40V), implying more improvement caused by TMG. We picked 1a, 1c as the representatives of the mechanism in our research.

For complex 1a-2 and 1a-3, they are not easy to form because of their positive binding energy.
Spectra

Supplementary Fig. 11. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2α

Supplementary Fig. 12. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2α
Supplementary Fig. 13. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2b

Supplementary Fig. 14. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2b
Supplementary Fig. 15. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2c

Supplementary Fig. 16. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2c
Supplementary Fig. 17. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2d

Supplementary Fig. 18. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2d
Supplementary Fig. 19. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2e

Supplementary Fig. 20. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2e
Supplementary Fig. 21. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2f

Supplementary Fig. 22. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2f
Supplementary Fig. 23. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2g

Supplementary Fig. 24. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2g
Supplementary Fig. 25. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2h

Supplementary Fig. 26. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2h
Supplementary Fig. 27. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2i

Supplementary Fig. 28. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2i
Supplementary Fig. 29. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2j

Supplementary Fig. 30. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2j
Supplementary Fig. 3. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2k

Supplementary Fig. 32. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2k
Supplementary Fig. 33. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2I

Supplementary Fig. 34. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2I
Supplementary Fig. 3. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2m

Supplementary Fig. 3. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2m
Supplementary Fig. 37. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2n

Supplementary Fig. 38. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2n
Supplementary Fig. 39. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2o

Supplementary Fig. 40. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2o
Supplementary Fig. 4. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2p

Supplementary Fig. 42. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2p
Supplementary Fig. 4. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2q

Supplementary Fig. 44. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2q
Supplementary Fig. 45. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2r

Supplementary Fig. 46. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2r
Supplementary Fig. 47. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2s

Supplementary Fig. 48. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2s
Supplementary Fig. 49. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2t

Supplementary Fig. 50. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2t
Supplementary Fig. 51. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2u

Supplementary Fig. 52. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2u
Supplementary Fig. 53. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2v

Supplementary Fig. 54. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2v
Supplementary Fig. 5. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2w

Supplementary Fig. 56. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2w
Supplementary Fig. 57. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2x

Supplementary Fig. 58. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2x
Supplementary Fig. 59. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2y

Supplementary Fig. 60. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2y
Supplementary Fig. 61. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2z

Supplementary Fig. 62. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2z
Supplementary Fig. 63. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2aa

Supplementary Fig. 64. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2aa
Supplementary Fig. 65. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2ab

Supplementary Fig. 66. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2ab
Supplementary Fig. 67. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2ac

Supplementary Fig. 68. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2ac
Supplementary Fig. 69. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2ad

Supplementary Fig. 70. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2ad
Supplementary Fig. 71. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2ae

Supplementary Fig. 72. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2ae
Supplementary Fig. 73. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2af

Supplementary Fig. 74. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2af
Supplementary Fig. 75. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2ag

Supplementary Fig. 76. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2ag
Supplementary Fig. 7. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2ah

Supplementary Fig. 78. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2ah
Supplementary Fig. 7. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2ai

Supplementary Fig. 8. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2ai
Supplementary Fig. 81. $^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2aj

Supplementary Fig. 82. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2aj
Supplementary Fig. 83. $^1$H NMR (600 MHz, 298 K, CDCl$_3$) of 2o’

Supplementary Fig. 84. $^{13}$C NMR (101 MHz, 298 K, CDCl$_3$) of 2o’
### Supplementary Table 21. Cartesian coordinates of important structures

|     | 1a          | 1b          |
|-----|-------------|-------------|
| C   | -5.72309000 | -0.06967100 | C   | -5.56618000 | -0.05166300 | -0.01781600 |
| C   | -4.97098400 | -0.92563000 | C   | -5.020000   | -0.9118700  | 0.8174700   |
| C   | -3.58112200 | -0.93724800 | C   | -2.85844300 | -0.92198600 | -0.94269900 |
| C   | -2.93257500 | -0.09041300 | C   | -2.85844300 | -0.09260600 | -0.14821900 |
| C   | -3.69266200 | 0.76579400  | C   | -3.59439800 | 0.75657000  | -0.98269900 |
| C   | -5.08193300 | 0.77621500  | C   | -4.98553300 | 0.7770900   | -0.91886600 |
| H   | -6.80483300 | -0.06167500 | H   | -6.73965500 | -0.03592400 | 0.03273400  |
| H   | -5.46707400 | -1.58363500 | H   | -5.44685800 | -1.54700500 | 1.51849200  |
| C   | -1.43673300 | -0.71188000 | C   | -1.35128400 | -0.09121300 | -0.23858000 |
| O   | -0.84963000 | 0.67127700  | O   | -0.77175100 | 0.64608000  | -0.10365900 |
| C   | 2.73742900  | -0.26900000 | C   | 2.67150300  | -0.27294000 | 0.22032200  |
| N   | 1.75884600  | -1.11742700 | N   | 1.71953500  | -1.14727500 | 0.45460700  |
| H   | 0.22535700  | -0.90003100 | H   | 0.40549500  | -0.93691300 | 0.49938400  |
| N   | 3.94734200  | -0.59503400 | N   | 3.85216500  | -0.60354300 | -0.39755000 |
| H   | 2.59367700  | 1.03783000  | H   | 2.50556000  | 1.03136800  | 0.58718800  |
| C   | 3.08161600  | 2.14603400  | C   | 2.98721100  | 2.13813900  | -0.23964100 |
| H   | 3.61857000  | 2.87349400  | H   | 3.61909300  | 2.81464800  | 0.34490500  |
| H   | 3.74673400  | 1.78782300  | H   | 3.55417300  | 1.76892300  | -1.09118300 |
| H   | 2.23520200  | 2.65368800  | H   | 2.13041500  | 2.70419500  | -0.62059000 |
| N   | 1.48225600  | 1.39633000  | N   | 1.45092600  | 1.40019200  | 1.52675700  |
| H   | 0.56024700  | 1.57145700  | H   | 0.50498000  | 1.59177600  | 1.01139000  |
| H   | 1.30574900  | 0.61142400  | H   | 1.30259200  | 0.60737300  | 2.25805200  |
| H   | 1.74560800  | 2.31800100  | H   | 1.75984500  | 2.30861400  | 2.05017300  |
| H   | 2.04703200  | -2.08013100 | H   | 2.01012500  | -2.11218100 | 0.35022600  |
| C   | 5.21157500  | -0.08567100 | C   | 5.13373500  | -0.04201500 | 0.03466300  |
| H   | 5.85447800  | 0.27306700  | H   | 5.68360100  | 0.37023700  | -0.81642700 |
| H   | 5.03617700  | 0.72988600  | H   | 4.98372500  | 0.74350400  | 0.77162400  |
| H   | 5.74057500  | -0.88457400 | H   | 5.74323400  | -0.82898400 | 0.49278000  |
| C   | 4.07589200  | -1.86092000 | C   | 3.96212600  | -1.86558300 | -1.11947400 |
| H   | 4.22284200  | -2.71172000 | H   | 4.18072100  | -2.70991700 | -0.45113300 |
| H   | 3.19550400  | -2.04703300 | H   | 3.04469800  | -2.07340600 | -1.67110300 |
| H   | 4.94506000  | -1.80236000 | H   | 4.77970200  | -1.78197700 | -1.83847000 |
| 1b'   | 1c     |
|-------|--------|
| C     | C      |
| -5.58758400 | -5.71040500 |
| C     | C      |
| -4.98795500 | -5.00930700 |
| C     | C      |
| -3.60326500 | -5.00930700 |
| C     | C      |
| -3.61666300 | -4.98795500 |
| C     | C      |
| -2.81097100 | -3.61666300 |
| C     | C      |
| -2.9069700 | -3.60326500 |
| H     | H      |
| -6.66601700 | -6.79388000 |
| H     | H      |
| -5.59802400 | -5.71040500 |
| H     | H      |
| -5.54829100 | -5.00930700 |
| C     | C      |
| -1.32798100 | -1.32798100 |
| O     | O      |
| -0.61629900 | -0.61629900 |
| C     | C      |
| 2.72534900  | 2.72534900 |
| N     | N      |
| 1.90253800  | 1.90253800 |
| C     | C      |
| 0.14705000  | 0.14705000 |
| H     | H      |
| 1.55074500  | 1.55074500 |
| N     | N      |
| 2.81853300  | 2.81853300 |
| C     | C      |
| 2.62981400  | 2.62981400 |
| H     | H      |
| 2.91223000  | 2.91223000 |
| H     | H      |
| 2.64112800  | 2.64112800 |
| H     | H      |
| 1.25475500  | 1.25475500 |
| C     | C      |
| 1.65074000  | 1.65074000 |
| H     | H      |
| 0.82257100  | 0.82257100 |
| H     | H      |
| 1.34222900  | 1.34222900 |
| C     | C      |
| 2.43736700  | 2.43736700 |
| C     | C      |
| 2.23348300  | 2.23348300 |
| C     | C      |
| 4.96360600  | 4.96360600 |
| H     | H      |
| 5.13244100  | 5.13244100 |
| H     | H      |
| 4.72185800  | 4.72185800 |
| H     | H      |
| 5.88217300  | 5.88217300 |
| C     | C      |
| 4.24943400  | 4.24943400 |
| H     | H      |
| 4.74124900  | 4.74124900 |
| H     | H      |
| 3.43596400  | 3.43596400 |
| H     | H      |
| 5.02956200  | 5.02956200 |
| 1c' | 1d |
|-----|-----|
| C  -5.36241600  0.13143900  -0.36795400 | C  -5.87870700  0.08434500  0.18985000 |
| C  -5.87870700  0.08434500  0.18985000 | C  -5.16466900  -0.91049400  -0.19960000 |
| C  -4.82729300  -1.06484600  0.11279200 | C  -5.16466900  -0.91049400  -0.19960000 |
| C  -3.45069700  -1.20092700  0.26828300 | C  -3.79345600  -1.02900800  -0.87547200 |
| C  -3.79345600  -1.02900800  -0.87547200 | C  -2.60291100  -0.13567500  -0.06037600 |
| C  -2.60291100  -0.13567500  -0.06037600 | C  -3.14232100  1.06235600  -0.54553100 |
| C  -3.14232100  1.06235600  -0.54553100 | C  -3.14200200  -0.14457200  -0.19960000 |
| C  -3.14200200  -0.14457200  -0.19960000 | C  -3.85641900  0.85402400  -0.87547200 |
| H  -6.43522300  0.23469600  -0.48773000 | H  -6.94842200  0.17372100  0.34228800 |
| H  -6.94842200  0.17372100  0.34228800 | H  -5.48246400  -1.89067800  0.36583700 |
| H  -5.48246400  -1.89067800  0.36583700 | H  -5.02794700  -2.12551200  0.64026000 |
| H  -5.02794700  -2.12551200  0.64026000 | C  -1.26216000  -0.27643300  0.09661900 |
| C  -1.26216000  -0.27643300  0.09661900 | C  -2.47987800  1.88073500  -0.79925900 |
| C  -2.47987800  1.88073500  -0.79925900 | C  -3.79345600  -1.02900800  -0.87547200 |
| C  -3.79345600  -1.02900800  -0.87547200 | H  -2.60291100  -0.13567500  -0.06037600 |
| H  -2.60291100  -0.13567500  -0.06037600 | H  -3.14200200  -0.14457200  -0.19960000 |
| H  -3.14200200  -0.14457200  -0.19960000 | H  -3.85641900  0.85402400  -0.87547200 |
| H  -3.85641900  0.85402400  -0.87547200 | H  -4.51918000  1.19489300  -0.69550400 |
| H  -4.51918000  1.19489300  -0.69550400 | H  -5.22726200  0.96489200  -0.67715100 |
| H  -5.22726200  0.96489200  -0.67715100 | H  -6.43522300  0.23469600  -0.48773000 |
| H  -6.43522300  0.23469600  -0.48773000 | H  -5.48246400  -1.89067800  0.36583700 |
| H  -5.48246400  -1.89067800  0.36583700 | H  -5.02794700  -2.12551200  0.64026000 |
| H  -5.02794700  -2.12551200  0.64026000 | C  -1.26216000  -0.27643300  0.09661900 |
| C  -1.26216000  -0.27643300  0.09661900 | C  -2.47987800  1.88073500  -0.79925900 |
| C  -2.47987800  1.88073500  -0.79925900 | C  -3.79345600  -1.02900800  -0.87547200 |
| C  -3.79345600  -1.02900800  -0.87547200 | H  -2.60291100  -0.13567500  -0.06037600 |
| H  -2.60291100  -0.13567500  -0.06037600 | H  -3.14200200  -0.14457200  -0.19960000 |
| H  -3.14200200  -0.14457200  -0.19960000 | H  -3.85641900  0.85402400  -0.87547200 |
| H  -3.85641900  0.85402400  -0.87547200 | H  -4.51918000  1.19489300  -0.69550400 |
| H  -4.51918000  1.19489300  -0.69550400 | H  -5.22726200  0.96489200  -0.67715100 |
| 1d'          | 1d-TS                     |
|--------------|---------------------------|
| C            | -5.29244000               | C            | 0.00000000 |
|              | 0.24481900                | 0.00000000   | -2.56737000|
| C            | -4.82858000               | C            | -0.00248300 |
|              | -1.03253600               | 1.21153800   | -1.87652900|
| C            | -3.47219500               | C            | 0.00000000  |
|              | -1.24709400               | 1.22945200   | -0.47478400|
| C            | -2.57447400               | C            | 0.00000000  |
| -0.17711700  | -0.04190000               | 0.00000000   | 0.14175300  |
| C            | -3.03800100               | C            | 0.00000000  |
| 1.10169000   | -0.38229500               | -1.22945200  | -0.47478400|
| C            | -4.39845800               | C            | 0.00248300  |
| 1.31021800   | -0.58937300               | -1.21153800  | -1.87652900|
| H            | -6.35133800               | H            | 0.00000000  |
| 0.40758000   | -0.64313000               | 0.00000000   | -3.65145800|
| H            | -5.52668100               | H            | 0.00000000  |
| -1.85699700  | -0.05688900               | 0.00000000   | 2.10765700  |
| H            | -3.10031400               | H            | 0.00482700  |
| 2.23020100   | 0.33078400                | 2.15607900   | 0.08226500  |
| H            | -2.33786600               | H            | -0.00482700 |
| 1.92345700   | 0.46831200                | -2.15607900  | 0.08226500  |
| H            | -4.76150500               | H            | 0.00222700  |
| 2.30066400   | -0.83664100               | -2.15328200  | -2.41446300|
| C            | -1.12226700               | C            | 0.00000000  |
| -0.43014500  | 0.20694700                | 0.00000000   | 2.10765700  |
| O            | -0.32983700               | O            | -0.15163400 |
| 0.34951400   | -0.44691700               | -1.14586500  | 2.40246000  |
| O            | -0.72886000               | O            | 0.15163400  |
| -1.32130000  | 0.96286500                | 1.14586500   | 2.40246000  |
| C            | 2.51023100                | C            | 0.00000000  |
| -0.35674300  | 0.18761600                | 0.00000000   | -3.65145800|
| N            | 1.97593600                | H            | 0.96525400  |
| -1.50610700  | 0.57081600                | -1.54622100  | 0.80070900  |
| H            | 0.96525400                | N            | 3.61755400  |
| -0.30523200  | -0.55213800               | 0.55471500   | 0.80479500  |
| N            | 1.83984500                | C            | 1.89156000  |
| 0.80479500   | 0.55471500                | 2.01953200   | -0.25755600|
| C            | 2.61007500                | H            | 2.14397600  |
| 2.73252300   | 0.15513900                | 1.78090400   | -1.28723400|
| H            | 2.14397600                | H            | 0.90013900  |
| 1.78090400   | 0.15513900                | 2.47123500   | -0.23472800|
| C            | 1.37722100                | C            | 0.39365800  |
| 0.99445800   | 1.93365600                | 1.46312600   | 1.91846300  |
| H            | 1.32411200                | H            | 1.32411200  |
| 0.04721400   | 2.46112000                | 0.04721400   | 2.46112000  |
| H            | 2.08006800                | H            | 2.49539500  |
| 1.65930400   | 2.44773000                | -2.36824100  | 0.48795300  |
| H            | 2.49539500                | C            | 4.59414200  |
| -2.36824100  | 0.48795300                | 0.79421000   | -0.48208800|
| H            | 4.60378300                | H            | 4.38331000  |
| 1.35902100   | -1.41558300               | 1.45377400   | 0.35447700  |
| H            | 4.38331000                | H            | 5.57913800  |
| 1.45377400   | 0.35447700                | 0.35117800   | -0.32301700|
| C            | 4.08670400                | C            | 4.70682500  |
| -1.49994500  | -1.26518300               | -2.12674600  | -0.61685600|
| H            | 4.70682500                | H            | 3.24034900  |
| -2.07436600  | -1.63994200               | -2.07436600  | -1.63994200|
| H            | 4.68721800                | H            | -1.16854200 |
| -1.16854200  | -2.11188700               | -1.16854200  | -2.11188700|
| 1e-TS          | 1e-TS-3          |
|---------------|---------------|
| B  0.60942000 | -0.94800200  |
| O  1.37142900 | -0.97177700  |
| O  1.35216400 | -1.19261000  |
| C  2.78120500 | -1.01740600  |
| C  2.69832200 | -1.58950900  |
| B  1.07169700 | -0.70012000  |
| O  -1.84400500| 0.56842400   |
| C  -0.82942600| -0.69808300  |
| C  -0.23111300| -0.24414200  |
| C  -2.33662400| -0.75507500  |
| C  0.07374000 | 1.84035700   |
| C  0.25605200 | 2.49945000   |
| C  0.54934600 | 2.23160400   |
| C  1.00159500 | 3.68667800   |
| H  -0.13748300| 2.12246000   |
| C  1.29297800 | 3.42183800   |
| H  0.37877420 | 1.65159500   |
| C  1.51547400 | 4.13859200   |
| C  1.18229900 | 4.24736200   |
| C  1.69756600 | 3.77831200   |
| H  -0.73867600| 1.27624200   |
| H  -4.38741000| 1.58432200   |
| C  -3.15002800| 1.56695000   |
| H  -2.67347800| 1.80129000   |
| C  -0.40323700| 0.11517200   |
| C  -1.99447000| -0.31258700  |
| H  -5.08249700| 0.15877900   |
| H  -3.63805200| 1.13046500   |
| H  -2.00874000| -0.09469800  |
| H  -0.67533900| -2.54913700  |
| C  -2.80659400| -2.86154200  |
| C  -4.18066800| -0.95160600  |
| H  -0.08428300| -0.53735200  |
| H  2.51160400 | -0.80157900  |
| H  3.98266800 | -2.02224900  |
| C  3.70246200 | -0.99469800  |
| H  4.72502700 | -1.20081000  |
| C  3.56503300 | -1.44509200  |
| C  3.57703000 | 0.08355000   |
| C  3.30511800 | 0.41924700   |
| H  3.14863000 | 0.80974000   |
| H  4.37429900 | 0.45650100   |
| H  2.77334400 | 1.06917500   |
| C  3.53427300 | -1.89464800  |
| H  4.57401000 | 0.2.02053800  |
| H  3.53237600 | -1.41995400  |
| H  3.07660200 | -2.87921100  |
| C  2.73889500 | -3.11821800  |
| H  2.84840000 | -0.43922500  |
| H  3.73229700 | -3.50028200  |
| H  2.01257900 | -3.56111800  |
| 1f | 1f' |
|---|---|
| B | -0.0009500 | 1.9770890 | 0.0001390 | C | -2.1727120 | -0.1055910 | -0.5050990 |
| O | -1.0830820 | 1.2627550 | 0.3837610 | N | -0.9479330 | -0.8375710 | 0.3020150 |
| O | 1.0829790 | 1.2629390 | -0.3837610 | N | -3.0815450 | -0.8375710 | 0.3020150 |
| C | -0.7871030 | -0.1596510 | 0.0431620 | N | -2.1741330 | 1.2782420 | -0.2568490 |
| C | 0.7871090 | -0.1595670 | -0.0432960 | N | -2.1741330 | 1.2782420 | -0.2568490 |
| C | -2.0673070 | 1.7856580 | 1.1155430 | H | -2.5711070 | 2.7556220 | 1.1863000 |
| H | -2.4587160 | -0.9602790 | 1.1301510 | H | -2.5572230 | 1.0921710 | 1.7994940 |
| H | -1.1018430 | -2.0842940 | 0.9632200 | H | -1.0216770 | 1.9040500 | 1.4284250 |
| H | -1.0125530 | -0.7462350 | 2.1252990 | C | -1.5348060 | 2.1290100 | -1.2458930 |
| C | 1.4753420 | -0.4299690 | 1.2924820 | H | -0.4461590 | 2.1991500 | -1.1099360 |
| H | 1.3514100 | -1.4733330 | 1.5918350 | H | -1.7351370 | 1.7505440 | -2.2502110 |
| H | 2.5433530 | -0.2263590 | 1.1894240 | H | -1.9476260 | 3.1411300 | -1.1745540 |
| H | 1.0806420 | 0.2106200 | 2.0838210 | H | -1.0441810 | -1.5472470 | -1.4468270 |
| C | 1.3694860 | -1.0380230 | -1.1378880 | C | -4.8385320 | -0.4391610 | 0.1920870 |
| H | 2.4591010 | -0.9601740 | -1.1296210 | H | -5.0358210 | -0.8052420 | 1.0614070 |
| H | 1.1019620 | -2.0840200 | -0.9638160 | H | -4.5626250 | 0.6464160 | 0.1619690 |
| H | 1.0135910 | -0.7455810 | -2.1255410 | H | -4.9549260 | -0.8472180 | -0.7178190 |
| C | -1.4759560 | -0.4299300 | -1.2925300 | C | -2.9196290 | -2.2825520 | 0.3762350 |
| H | -1.3518220 | -1.4732620 | -1.5919660 | H | -3.1627900 | -2.7877110 | -0.5752690 |
| H | -2.5457200 | -0.2262260 | -1.1892400 | H | -1.8992800 | -2.5428490 | 0.6558270 |
| H | -1.0810250 | 0.2107050 | -2.0839150 | H | -3.5941390 | -2.6715680 | 1.1423190 |
| B | 0.3786370 | -0.4513960 | -0.4373060 | 0.4632050 | -1.1135810 | -0.9919260 |
| O | 0.7481810 | 0.4989760 | 0.5007000 | O | 2.6268490 | -0.7645170 | -0.1849590 |
| C | 2.1996860 | 0.6235480 | 0.4241480 | C | 2.4958960 | 1.8027360 | -0.5057560 |
| H | 2.0010890 | 2.6947800 | -0.1151630 | H | 3.5684220 | 2.0025360 | -0.5636950 |
| H | 2.1202850 | 1.6182800 | -1.5148850 | H | 3.8527520 | -0.7183370 | -1.0861270 |
| C | 4.7239040 | -0.3632550 | -0.5287390 | H | 4.0736480 | -1.7219630 | -1.4583110 |
| H | 3.6958100 | -0.0650630 | -1.9446040 | H | 2.7357920 | 0.9041490 | 1.8208680 |
| C | 3.8292500 | 0.9109690 | 1.8159350 | H | 2.3908230 | 1.8854220 | 2.1566550 |
| H | 2.3927760 | 0.1600990 | 2.5400100 | C | 2.7848030 | -1.8588470 | 0.8741610 |
| H | 2.8833440 | -2.8243420 | 0.3722990 | H | 3.6750050 | -1.6967800 | 1.4863920 |
| H | 1.9125850 | -1.9036750 | 1.5308030 |
| B     | 0.28138400 | 0.49764000 | -0.26634200 |
|-------|------------|------------|-------------|
| O     | 0.46950400 | 1.56204500 | -1.27687800 |
| C     | 0.87192100 | 1.02923000 | 0.97629100  |
| C     | 1.34036900 | 2.56267100 | -0.73705100 |
| C     | 1.09115100 | 2.43123000 | 0.80106800  |
| B     | -1.37615200 | 0.01078600 | -0.21332300 |
| O     | -2.39128600 | 0.71328900 | 0.41861300  |
| O     | -1.88788600 | -1.13442900 | -0.81513400 |
| C     | -3.59581600 | -0.10497700 | 0.43413000  |
| C     | -3.34363800 | -1.08558400 | -0.76506300 |
| N     | 1.21037600 | -0.75996900 | -0.75271200 |
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| N     | 3.08917600 | -2.15502100 | -0.70510200 |
| C     | 2.83191500 | -2.01542700 | 2.17174900  |
| C     | 0.41064000 | -1.87834400 | 1.75745200  |
| C     | 3.50214700 | -3.53128200 | -0.42762800 |
| C     | 3.62637500 | -1.60719400 | -1.94352600 |
| H     | 2.82762200 | -2.98284300 | 2.68377100  |
| H     | 3.79956700 | -1.67288800 | 1.69513000  |
| H     | 2.69643900 | -1.22510600 | 2.91866700  |
| C     | 0.20705300 | -0.90158200 | 2.20541600  |
| H     | 3.96327800 | -2.07768900 | 0.98361500  |
| C     | 0.32890900 | 2.65542900  | 2.52389000  |
| H     | 4.54344200 | -3.56633000 | -0.09354200 |
| C     | 2.86983200 | -3.97397200 | 0.33857500  |
| H     | 3.40974900 | -4.13134900 | -1.33985300 |
| H     | 3.12350900 | -2.01301300 | -2.82876600 |
| H     | 3.53262400 | -0.51702400 | -1.95129200 |
| H     | 4.68720100 | -1.85444500 | -2.00583400 |
| H     | 1.30468400 | -0.78242800 | -1.76039300 |
| H     | 2.79317300 | 2.23739200  | -1.12248000 |
| H     | 3.12403200 | 1.31333100  | -0.64841100 |
| H     | 2.84760400 | 2.10710200  | -2.20677200 |
| H     | 3.48129900 | 3.03984200  | -0.83937300 |
| H     | 0.95575900 | 3.91695900  | -1.33103100 |
| H     | 1.51462400 | 4.72947700  | -0.85569400 |
| H     | 1.18430900 | 3.93008800  | -2.40119700 |
| H     | -0.11131300 | 4.10941800 | -1.21385900 |
| C     | 2.27349500 | 2.85407800  | 1.68125000  |
| H     | 2.59306300 | 3.90107000  | 1.50340000  |
| H     | 2.00952200 | 2.74747000  | 2.73703000  |
| H     | 3.15007900 | 2.23311200  | 1.49098200  |
| C     | -0.17131000 | 3.18342800 | 1.26282200  |
| H     | -0.39479100 | 2.98748400 | 2.29423200  |
| H     | -0.03819700 | 4.26889100 | 1.22917600  |
| H     | -1.02982200 | 2.90519200 | 0.64932400  |
| C     | -3.63192400 | -0.81089000 | 1.79367400  |
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| H     | -4.59945100 | -1.40797800 | 1.91369300  |
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| H     | -5.72766600 | 0.29953900  | 0.20514000  |
| H     | -4.89771900 | 1.44826200  | 1.15969400  |
| H     | -4.72971900 | 1.43005500  | -0.59884100 |
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| H     | -3.43473700 | -1.16654600 | -2.91157800 |
| H     | -4.90646000 | -0.50644800 | -2.17752000 |
| H     | -3.43391800 | 0.48272900  | -2.27403500 |
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| H     | -4.96394100 | -2.48594700 | -0.43562200 |
| H     | -3.64928700 | -3.10570300 | -1.44606100 |
| H     | -3.42815700 | -2.98034000 | 0.30265100  |
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