Supporting Information:

Photostable Ruthenium(II) Isocyanoborato Luminophores and their Use in Energy Transfer and Photoredox Catalysis

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General Experimental Details

Materials and Methods

[Ru(bpy)$_2$]Cl$_2$ · $x$ H$_2$O, $fac$-[Ir(ppy)$_3$], [Ru(bpy)$_3$]Cl$_2$, K$_2$C$_2$O$_4$, KCN and B(C$_6$F$_5$)$_3$ were obtained from commercial suppliers in high purity and were used without further purification. [Ru(bpy)$_3$][PF$_6$]$_2$ was obtained from the chloride salt after anion exchange with (NH$_4$)$_2$(PF$_6$) in an ethanol/water mixture. [Ru(bpy)$_2$(CN)$_2$] and [Ru(CF$_3$bpy)$_2$(CN)$_2$] were synthesized according to the literature procedure.$^1$

CH$_2$Cl$_2$ for the borylation reaction was dried over 3 Å molecular sieves for 48 hours and degassed by three freeze-pump-thaw cycles and subsequent refill with argon. Glassware was dried at 200 °C overnight and assembled while still hot.

Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. NMR spectra were recorded either on a Bruker Avance III instrument operating at 400 MHz proton frequency or on a Bruker Avance III operating at 500 MHz proton frequency. All chemical shifts are reported in δ values in ppm referred to protons of the residual non-perdeuterated solvent used or its carbon atoms, respectively.$^2$ To describe the signals and their coupling patterns, the following abbreviations are used: s (singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublets of doublets), dt (doublet of triplets), t (triplet), m (multiplet). All coupling constants J are stated in Hertz (Hz).

Elemental Analysis was performed by Ms. Sylvie Mittelheisser (University of Basel, Department of Chemistry), with a Vario Micro Cube instrument from Elementar.

Cyclic voltammetry was performed in an MBraun Glovebox under an Ar-Atmosphere. A glassy carbon disk electrode served as working electrode and two silver wires were used as counter electrode and (pseudo)-reference electrode. To apply and control the voltage, a Versastat3-200 potentiostat from Princeton Applied Research was used.

Preparative photoreductions and triplet-triplet energy transfer reactions were performed either in Schlenk tubes or in flame-sealed NMR tubes. As light source, a Kessil PR160 LED with 440 nm output was used.
All optical spectroscopic experiments were carried out at 293 K. Steady-state absorption and luminescence spectra were recorded using a Cary 5000 spectrophotometer (Varian) and a Fluorolog-3-22 instrument (Horiba Jobin-Yvon), respectively. An LP920-KS apparatus from Edinburgh Instruments was employed for UV-Vis transient absorption and emission spectroscopy. Excitation was performed by a frequency-doubled Nd:YAG laser (Quantel Brilliant b, ca. 10 ns pulse width) or by a frequency-tripled Nd:YAG laser (Quantel Brilliant b, ca. 10 ns pulse width) equipped with an OPO from Opotek. A beam expander (GBE02-A from Thorlabs) was used to ensure homogeneous excitation. Detection of transient absorption spectra occurred on an iCCD camera (Andor), whereas kinetics at a single wavelength were recorded using a photomultiplier tube.

Unless otherwise indicated, the solutions were purged with argon (4.8, PanGas) for at least five minutes before the experiments and sealed under argon (1 atm) using cuvettes with septum caps.

Luminescence lifetime and quenching measurements with \([\text{Ru(bpy)}_2(\text{BCF})_2]\) and \(\text{fac-}[\text{Ir(ppy)}_3]\) were performed on a LifeSpec II spectrometer (time-correlated single photon counting technique) from Edinburgh Instruments using picosecond pulsed diode lasers for excitation at 375 nm. Luminescence lifetime and quenching measurements with \([\text{Ru(bpy)}_3][\text{PF}_6]_2\) and \([\text{Ru(CF}_3\text{bpy})_2(\text{BCF})_2]\) were performed with the abovementioned LP920-KS apparatus from Edinburgh Instruments.

Luminescence quantum yields were determined as described in further detail on page S25.

CD measurements were performed on a JASCO J-1500 CD spectrophotometer at 20 °C in 1115F-QS Hellma cuvettes (10 mm light path).
Synthesis of Complexes

The syntheses of \([\text{Ru(bpy)}_2(\text{BCF})_2]\) and \([\text{Ru(CF}_3\text{bpy)}_2(\text{BCF})_2]\) were conducted on small scales, because no large quantities of these substances were required for our studies.

\[\text{[Ru(bpy)}_2(\text{BCF})_2]\]

\([\text{Ru(bpy)}_2(\text{CN})_2]\) (30.0 mg, 64.45 \(\mu\)mol, 1.0 eq.) and \(\text{B(C}_6\text{F}_5)_3\) (69.3 mg, 135.34 \(\mu\)mol, 2.1 eq.) were dissolved in dry and deaerated \(\text{CH}_2\text{Cl}_2\) (15 mL) under an Ar atmosphere in a 50 mL Schlenk tube, and the resulting yellow solution was heated to 40 °C for 12 h. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (silica, \(\text{CH}_2\text{Cl}_2\)) to yield \([\text{Ru(bpy)}_2(\text{BCF})_2]\) (76.2 mg, 51.1 \(\mu\)mol, 79 %) as a yellow solid.

\(^1\text{H NMR (500 MHz, CD}_2\text{Cl}_2\): } \delta 9.18 (\text{ddd, } J=5.6, 1.6, 0.7 \text{ Hz}, 2\text{H, H1}), 8.21 (\text{m, } 2\text{H, H4}), 8.17 (\text{m, } 2\text{H, H7}), 8.07 (\text{ddd, } J=8.1, 7.8, 1.6 \text{ Hz}, 2\text{H, H3}) 7.95 (\text{ddd, } J=8.2, 7.6, 1.6 \text{ Hz}, 2\text{H, H8}), 7.61 – 7.55 (\text{m, } 4\text{H, H2, H10}), 7.29 (\text{ddd, } J=7.6, 5.6, 1.2 \text{ Hz}, 2\text{H, H9}).

\(^{13}\text{C NMR (126 MHz, CD}_2\text{Cl}_2\): } \delta 156.7, 156.3, 156.2, 153.7, 149.7, 138.9, 138.3, 127.9, 127.2, 123.5, 123.2.

\(^{11}\text{B NMR (160 MHz, CD}_2\text{Cl}_2\): } \delta = -13.80.

\(^{19}\text{F NMR (471 MHz, CD}_2\text{Cl}_2\): } \delta = -134.87 (\text{dd, } J=23.4, 9.1 \text{ Hz}, 12\text{F}), -160.69 (\text{t, } J=20.2 \text{ Hz}, 6\text{F}), -165.88 – -166.48 (\text{m, } 12\text{F}).

Elemental analysis calc. for \(\text{C}_{58}\text{H}_{16}\text{N}_6\text{B}_2\text{F}_{30}\text{Ru}\): C 46.77 %, H 1.08 %, N 5.64 %, found: C 46.67 %, H 1.20 %, N 5.96 %.

ESI-HRMS (m/z): calcd. for \([\text{C}_{58}\text{H}_{16}\text{N}_6\text{B}_2\text{F}_{30}\text{RuNa}]^+ [\text{M+Na}]^+, [\text{C}_{58}\text{H}_{16}\text{B}_2\text{F}_{30}\text{N}_6\text{RuK}]^+ [\text{M+K}]^+: 1513.0085, 1528.9824. found: 1513.0098, 1528.9832.
[[Ru(CF₃bpy)₂(CN)]₂ (10.0 mg, 13.6 μmol, 1.0 eq.) and B(C₆F₅)₃ (14.6 mg, 28.5 μmol, 2.1 eq.) were dissolved in dry and deaerated CH₂Cl₂ (10 mL) under an Ar atmosphere in a 50 mL Schlenk tube, and the resulting orange solution was stirred at room temperature for 10 min. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (silica, CH₃CN). Since the product still contained impurities, it was again subjected to flash column chromatography (silica, CH₂Cl₂) to yield [[Ru(CF₃bpy)₂(BCF)₂] (19.6 mg, 11.1 μmol, 82 %) as a yellow solid.

¹H NMR (500 MHz, CD₃CN) δ = 9.26 (d, J=5.9, 2H, H1), 8.83 (s, 2H, H4), 8.80 (s, 2H, H2), 8.03 – 7.96 (m, 4H, H₂, H₉), 7.69 – 7.64 (m, 2H, H₁₀).

¹³C NMR (126 MHz, CD₃CN) δ 157.6 (s), 157.2 (s), 156.7 (s), 152.8 (s), 152.2 (m), 149.2 (m), 147.3 (m), 140.9 (m), 140.7 – 139.6 (m), 138.9 (m), 138.3 (m), 136.3 (m), 124.6 (m), 124.1 (s), 123.9 (m), 121.8 (m), 121.8 (d), 121.2 (m).

¹¹B NMR (160 MHz, CD₃CN) δ -13.84.

¹⁹F NMR (471 MHz, CD₃CN) δ = -65.46 (s, 6F), -65.50 (s, 6F), -135.78 (dd, J=22.9, 8.3 Hz, 12F), -160.93 (t, J=19.6 Hz, 6F), -166.79 (m, 12F).

Elemental analysis calc. for C₆₂H₁₂₂N₆B₂F₄₂Ru·0.15H₂O·0.5CH₃CN: C 43.05 %, H 1.11 %, N 4.63 %

found: C 42.71 %, H 1.35 %, N 4.92 %.

ESI-HRMS (m/z): calcld. for [C₆₂H₁₂₂N₆B₂F₄₂RuNa]⁺ [M+Na]⁺, [C₆₂H₁₂₂B₂F₄₂N₆RuK]⁺ [M+K]⁺:

1784.9580, 1800.9319; found: 1784.9626, 1800.9345
NMR Spectra of [Ru(bpy)$_2$(BCF)$_2$]

Figure S1: $^1$H NMR spectrum of [Ru(bpy)$_2$(BCF)$_2$] in CD$_2$Cl$_2$ at 293 K.

Figure S2: $^{19}$F NMR spectrum of [Ru(bpy)$_2$(BCF)$_2$] in CD$_2$Cl$_2$ at 293 K.
Figure S3: $^{11}B$ NMR spectrum of [Ru(bpy)$_2$(BCF)$_2$] in CD$_2$Cl$_2$ at 293 K.

Figure S4: $^1$H–$^1$H COSY NMR spectrum of [Ru(bpy)$_2$(BCF)$_2$] in CD$_2$Cl$_2$ at 293 K.
Figure S5: $^1$H-$^1$H NOESY NMR spectrum of [Ru(bpy)$_2$(BCF)$_2$] in CD$_2$Cl$_2$ at 293 K.

Figure S6: $^1$H-$^{13}$C HMQC NMR spectrum of [Ru(bpy)$_2$(BCF)$_2$] in CD$_2$Cl$_2$ at 293 K.
Figure S7: $^1$H-$^1$C HMBC NMR spectrum of [Ru(bpy)$_2$(BCF)$_2$] in CD$_2$Cl$_2$ at 293 K.

Figure S8: $^{13}$C-$^1$H NMR spectrum of [Ru(bpy)$_2$(BCF)$_2$] in CD$_2$Cl$_2$ at 293 K.
NMR Spectra of \([\text{Ru(CF}_3\text{bpy)}_2(\text{BCF})_2]\)

Figure S9: \(^1\text{H}\) NMR spectrum of \([\text{Ru(CF}_3\text{bpy)}_2(\text{BCF})_2]\) in CD\(_3CN\) at 293 K.

Figure S10: \(^{19}\text{F}\) NMR spectrum of \([\text{Ru(CF}_3\text{bpy)}_2(\text{BCF})_2]\) in CD\(_3CN\) at 293 K.
Figure S11: $^{11}$B NMR spectrum of $[\text{Ru(CF}_3\text{bpy)}_2\text{(BCF)}_2]$ in CD$_3$CN at 293 K.

Figure S12: $^{13}$C NMR spectrum of $[\text{Ru(CF}_3\text{bpy)}_2\text{(BCF)}_2]$ in CD$_3$CN at 293 K.
Figure S13: $^1$H-$^1$H NOESY NMR spectrum of [Ru(CF$_3$bpy)$_2$(BCF)$_2$] in CD$_3$CN at 293 K.

Figure S14: $^1$H-$^1$H COSY NMR spectrum of [Ru(CF$_3$bpy)$_2$(BCF)$_2$] in CD$_3$CN at 293 K.
IR Spectra

In the IR spectra of $[\text{Ru(bpy)}_2(\text{BCF})_2]$ (Figure S15) and $[\text{Ru(CF}_3\text{bpy)}_2(\text{BCF})_2]$ (Figure S16), the C≡N stretching frequencies are shifted to higher wavenumbers compared to the same bands in the respective parent complexes $[\text{Ru(bpy)}_2(\text{CN})_2]$ and $[\text{Ru(CF}_3\text{bpy)}_2(\text{CN})_2]$. $[\text{Ru(bpy)}_2(\text{CN})_2]$ exhibits two C≡N stretching bands at 2064 cm$^{-1}$ and 2045 cm$^{-1}$. Upon borylation, these two bands are observed at 2159 cm$^{-1}$ and 2063 cm$^{-1}$. In $[\text{Ru(CF}_3\text{bpy)}_2(\text{BCF})_2]$, the two bands are shifted from 2085 cm$^{-1}$ and 2094 cm$^{-1}$ to 2173 cm$^{-1}$ and 2195 cm$^{-1}$.

Due to the hygroscopic nature of $[\text{Ru(bpy)}_2(\text{CN})_2]$ and $[\text{Ru(CF}_3\text{bpy)}_2(\text{CN})_2]$, strong O-H bands between 2600 cm$^{-1}$ and 3600 cm$^{-1}$ originating from H$_2$O appear in the IR spectra of these two compounds. Furthermore, in the spectra of $[\text{Ru(bpy)}_2(\text{BCF})_2]$ and $[\text{Ru(CF}_3\text{bpy)}_2(\text{BCF})_2]$ C=O bands from ambient CO$_2$ are observed between 2280 cm$^{-1}$ and 2393 cm$^{-1}$.

![Figure S15: IR spectra (neat) of $[\text{Ru(bpy)}_2(\text{BCF})_2]$ (red) and $[\text{Ru(bpy)}_2(\text{CN})_2]$ (green).](image)
Figure S16: IR spectra (neat) of $[\text{Ru(CF}_3\text{bpy)}_2(\text{BCF})_2]$ (red) and $[\text{Ru(CF}_3\text{bpy)}_2(\text{CN})_2]$ (green).
Crystal Structures

[Ru(bpy)$_2$(BCF)$_2$]

CCDC deposition number: 2062751

Single yellow block-shaped crystals of [Ru(bpy)$_2$(BCF)$_2$] were grown from a mixture of CHCl$_3$ and CH$_2$Cl$_2$ by slow evaporation. A suitable crystal (0.22 × 0.18 × 0.16 mm$^3$) was selected and mounted on a Lindemann tube in perfluoroether oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady $T = 130$ K during data collection. The structure was solved with the ShelXT$^3$ structure solution program using the Intrinsic Phasing solution method and by using Olex2$^4$ as the graphical interface. The model was refined with version 2018/3 of ShelXL$^3$ using Least Squares minimisation.
Table S1: Crystallographic data for [Ru(bpy)$_2$(BCF)$_2$].

| Property                          | Value                                      |
|-----------------------------------|--------------------------------------------|
| Formula                          | $\text{C}_2\text{H}_{5.6}\text{Cl}_{5.4}\text{F}_{30}\text{H}_{17.8}\text{N}_6\text{Ru}$ |
| $D_{\text{calc}}$/g cm$^{-3}$     | 1.788                                      |
| $\mu$/mm$^{-1}$                   | 5.347                                      |
| Formula Weight                   | 1704.32                                    |
| Colour                           | yellow                                     |
| Shape                            | block                                      |
| Size/mm$^3$                       | $0.22 \times 0.18 \times 0.16$             |
| $T$/K                            | 130                                        |
| Crystal System                   | monoclinic                                 |
| Space Group                      | $P2_1/c$                                   |
| $a$/Å                            | 12.0356(11)                                |
| $b$/Å                            | 25.201(2)                                  |
| $c$/Å                            | 21.4652(19)                                |
| $\alpha$/°                       | 90                                         |
| $\beta$/°                        | 103.432(3)                                 |
| $\gamma$/°                       | 90                                         |
| $V$/Å$^3$                        | 6332.6(10)                                 |
| $Z$                              | 4                                          |
| $Z'$                             | 1                                          |
| Wavelength/Å                     | 1.541838                                   |
| Radiation type                   | CuK$\alpha$                               |
| $\Theta_{\text{main}}$/°         | 4.098                                      |
| $\Theta_{\text{max}}$/°          | 70.315                                     |
| Measured Refl.                   | 38829                                      |
| Independent Refl.               | 11626                                      |
| Reflections with I > 2(I)        | 11406                                      |
| $R_{\text{int}}$                 | 0.0301                                     |
| Parameters                       | 874                                        |
| Restraints                       | 0                                          |
| Largest Peak                     | 0.901                                      |
| Deepest Hole                     | 0.474                                      |
| GooF                             | 1.019                                      |
| $wR_2$ (all data)                | 0.0749                                     |
| $wr_2$                           | 0.0746                                     |
| $R_1$ (all data)                 | 0.0299                                     |
| $R_1$                            | 0.0295                                     |
Single orange plate crystals of [Ru(CF₃bpy)₂(BCF)₂] were grown from CD₂Cl₂. A suitable crystal with dimensions 0.20 × 0.18 × 0.05 mm³ was selected and mounted on a mylar loop in perfluoroether oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 150 K during data collection. The structure was solved with the ShelXT⁵ solution program using dual methods and by using Olex2⁴ as the graphical interface. The model was refined with ShelXL³ using full matrix least squares minimisation on F².

Table S2: Crystallographic data for [Ru(CF₃bpy)₂(BCF)₂].

| Property                  | Value               |
|---------------------------|---------------------|
| Formula                   | C₆₂H₁₂B₂F₄₂N₆Ru    |
| D calc / g cm⁻³           | 1.934               |
| µ / mm⁻¹                  | 3.776               |
| Formula Weight            | 1761.47             |
| Colour                    | orange              |
| Shape                     | plate               |
| Size / mm³                | 0.20×0.18×0.05      |
| T / K                     | 150                 |
| Crystal System            | monoclinic          |
| Space Group               | C₂/c                |
| a / Å                     | 16.2170(13)         |
| b / Å                     | 16.2866(13)         |
| c / Å                     | 23.0814(18)         |
| α / °                     | 90                  |
| β / °                     | 97.013(3)           |
| γ / °                     | 90                  |
| V / Å³                    | 6050.6(8)           |
| Z                         | 4                   |
| Z'                        | 0.5                 |
| Wavelength / Å            | 1.54178             |
| Radiation type            | Cu Kα               |
| Ψ min / °                 | 3.859               |
| Ψ max / °                 | 70.268              |
| Measured Refl’s.          | 38067               |
| Indep’t Refl’s            | 5637                |
| Refl’s I≥2 σ(1)           | 5493                |
The two compounds $[\text{Ru(bpy)}_2(BCF)_2]$ and $[\text{Ru(CF}_3\text{bpy)}_2(BCF)_2]$ were observed as two different isomers: Whereas $[\text{Ru(bpy)}_2(BCF)_2]$ crystallized as the $\Lambda$-enantiomer, $[\text{Ru(CF}_3\text{bpy)}_2(BCF)_2]$ crystallized as the $\Delta$-enantiomer. The two compounds are shown in Figure S17 without the $(C_6F_5)$ moieties for clarity.

![Molecular structures](image)

**Figure S17:** Molecular structures of $\Lambda$-$[\text{Ru(bpy)}_2(BCF)_2]$ $\Delta$-$[\text{Ru(CF}_3\text{bpy)}_2(BCF)_2]$. The three $(C_6F_5)$ moieties of the BCF ligands, hydrogen atoms and fluorine atoms are not shown for clarity.
Absorption and Emission Spectroscopy

Figure S18: UV-Vis absorption spectra of [Ru(bpy)$_2$(BCF)$_2$] (green) and [Ru(bpy)$_2$(CN)$_2$] (red) in argon-saturated CH$_3$CN at room temperature.

Figure S19: Normalized emission spectra of [Ru(bpy)$_2$(BCF)$_2$] (green) and [Ru(bpy)$_2$(CN)$_2$] (red) in argon-saturated CH$_3$CN at room temperature. Excitation occurred at the respective MLCT-band maxima (390 nm for [Ru(bpy)$_2$(BCF)$_2$] and 490 nm for [Ru(bpy)$_2$(CN)$_2$]).
Figure S20: Luminescence decays of $[\text{Ru(bpy)}_2\text{(CN)}_2]^{-}$ (10^{-5}$ M, red) at 680 nm and $[\text{Ru(CF}_3\text{bpy)}_2\text{(CN)}_2]^{-}$ (10^{-5}$ M, green) at 740 nm in argon-saturated CH$_3$CN at 293 K. Excitation occurred at 532 nm in both cases using laser pulses of ca. 10 ns duration.

Figure S21: UV-Vis absorption spectra of $[\text{Ru(CF}_3\text{bpy)}_2\text{(BCF)}_2]$ (green) and $[\text{Ru(CF}_3\text{bpy)}_2\text{(CN)}_2]$ (red) in argon-saturated CH$_3$CN at room temperature.
Figure S22: Normalized emission spectra of [Ru(CF$_3$bpy)$_2$(BCF)$_2$] (green) and [Ru(CF$_3$bpy)$_2$(CN)$_2$] (red) in argon-saturated CH$_3$CN at 20 °C. Excitation occurred at the respective MLCT absorption band maxima (420 nm for [Ru(CF$_3$bpy)$_2$(BCF)$_2$] and 520 nm for [Ru(CF$_3$bpy)$_2$(CN)$_2$]).
Effect of Different Solvents

Figure S23: UV-Vis absorption spectra of \([\text{Ru(bpy)}_2(\text{BCF})_2]\) recorded in different argon-saturated solvents at 293 K.

Figure S24: Normalized emission spectra of \([\text{Ru(bpy)}_2(\text{BCF})_2]\) in different argon-saturated solvents at 293 K. Excitation occurred at 390 nm in all cases.
Figure S25: Luminescence decay curves of [Ru(bpy)$_2$(BCF)$_2$] ($10^{-5}$ M) at 530 nm in different argon-saturated solvents after 375 nm excitation at 293 K.

Table S3: Excited-state lifetimes of [Ru(bpy)$_2$(BCF)$_2$] in different argon-saturated solvents at 293 K.

| Solvent | $\tau_0$ / ns |
|---------|--------------|
| CH$_3$CN | 8.6          |
| THF     | 13.0         |
| MeOH    | 11.6         |
Circular Dichroism Spectroscopy

CD spectra of [Ru(bpy)$_2$(BCF)$_2$] and [Ru(CF$_3$bpy)$_2$(BCF)$_2$] were measured to explore whether the two complexes were obtained as racemic mixtures of the Δ-isomer and the Λ-isomer or whether formation of one of these two isomers was favored over the other one. The formation of both isomers in a 1:1 ratio was confirmed by the absence of significant signals in the CD spectra shown in Figure S26.

![Figure S26: CD spectra of $10^{-5}$ M [Ru(bpy)$_2$(BCF)$_2$] and $10^{-5}$ M[Ru(CF$_3$bpy)$_2$(BCF)$_2$] in CH$_3$CN at 20 °C.](image)

Photoluminescence Quantum Yields

The photoluminescence quantum yield of [Ru(CF$_3$bpy)$_2$(BCF)$_2$] was determined using an integrating sphere (Hamamatsu absolute photoluminescence quantum yield spectrometer C11347 Quantaurus-QY). Photoluminescence quantum yields of [Ru(bpy)$_2$(BCF)$_2$], [Ru(bpy)$_2$(CN)$_2$] and [Ru(CF$_3$bpy)$_2$(CN)$_2$] were determined by measuring their luminescence spectra in deaerated acetonitrile and comparing the respective spectra to the emission spectrum of [Ru(bpy)$_3$]$^{2+}$ in deaerated acetonitrile recorded under exactly identical conditions and using identical acquisition parameters.$^6$ The literature value for the quantum yield of [Ru(bpy)$_3$]$^{2+}$ in deaerated acetonitrile is 9.5%.$^7$ The emission bands of [Ru(CF$_3$bpy)$_2$(CN)$_2$] and [Ru(bpy)$_2$(CN)$_2$] could not be fully integrated, because their low-energy part is outside of the range of the employed detector. The integrated area was therefore approximated as twice the area of the high-energy part of the emission band, ranging from the onset wavelength to the emission band maximum. Due to the approximative nature of this procedure, we consider the quantum yields indicated for these two complexes in Table 1 of the main paper as upper limits.
**Electrochemistry**

Figure S27: Cyclic voltammogram of 1.0 mM \([\text{Ru(bpy)}_2(\text{CN})_2] \) in dry, deaerated \(\text{CH}_3\text{CN} \) with 0.1 M \(\text{NBu}_4\text{PF}_6 \) as supporting electrolyte at room temperature. The scan rate was 0.1 V/s.

Figure S28: Cyclic voltammogram of 1.0 mM \([\text{Ru(CF}_3\text{bpy)}_2(\text{CN})_2] \) in dry, deaerated \(\text{CH}_3\text{CN} \) with 0.1 M \(\text{NBu}_4\text{PF}_6 \) as supporting electrolyte at room temperature. The scan rate was 0.1 V/s.

Table S4: Electrochemical properties of \([\text{Ru(bpy)}_2(\text{BCF})_2]\) and \([\text{Ru(CF}_3\text{bpy)}_2(\text{BCF})_2]\) and their parent complexes \([\text{Ru(bpy)}_2(\text{CN})_2]\) and \([\text{Ru(CF}_3\text{bpy)}_2(\text{CN})_2].\) All data were measured in dry, deaerated \(\text{CH}_3\text{CN} \) with 0.1 M \(\text{NBu}_4\text{PF}_6 \) as supporting electrolyte at room temperature in an Ar-filled glovebox. The scan rate was 0.1 V/s in all cases.

|          | \(E^{(0/-)}\) / V vs SCE | \(E^{(1/-)}\) / V vs SCE | \(E^{(0/+)}\) / V vs SCE |
|----------|--------------------------|--------------------------|--------------------------|
| \([\text{Ru(bpy)}_2(\text{CN})_2]\) | -1.64                    | -1.89                    | 0.80                     |
| \([\text{Ru(bpy)}_2(\text{BCF})_2]\) | -1.46                    | -1.70                    | 1.63                     |
| \([\text{Ru(CF}_3\text{bpy)}_2(\text{CN})_2]\) | -1.13                    | -1.37                    | 1.14                     |
| \([\text{Ru(CF}_3\text{bpy)}_2(\text{BCF})_2]\) | -0.92                    | -1.13                    | 2.00                     |
Photochemical Synthesis Procedures

General Procedure 1: trans/cis Isomerization of trans-methyl Cinnamate

*Trans*-methyl cinnamate (50 μmol), trimethyl(phenyl)silane (17 μmol, as internal standard) and the respective catalyst (0.5 μmol, 1 mol%) were dissolved in CD$_3$CN (0.6 mL) and the mixture was degassed in an NMR-tube by three freeze-pump-thaw cycles. The NMR-tube was flame-sealed and irradiated for two hours with a blue Kessil LED lamp (440 nm), after which time the ratio of cis/trans (in relation to the internal standard trimethyl(phenyl)silane) was determined by $^1$H NMR spectroscopy.

General Procedure 1a: trans/cis Isomerization of trans-methyl Cinnamate with lower catalyst loading

*Trans*-methyl cinnamate (50 μmol), trimethyl(phenyl)silane (17 μmol, as internal standard) and [Ru(bpy)$_2$(BCF)$_2$] (0.01 μmol, 0.02 mol%) were dissolved in CD$_3$CN (0.6 mL) and the mixture was degassed in an NMR-tube by three freeze-pump-thaw cycles. The NMR-tube was flame-sealed and irradiated for two hours with a blue Kessil LED lamp (440 nm), after which time the ratio of cis/trans (in relation to the internal standard trimethyl(phenyl)silane) was determined by $^1$H NMR spectroscopy.

General Procedure 2: Pinacol Coupling

Benzaldehyde (50 μmol), DiPEA (250 μmol, 5 eq.) and the respective catalyst (0.5 μmol, 1 mol%) were dissolved in CD$_3$CN (0.6 mL) and the mixture was degassed in an NMR-tube by three freeze-pump-thaw cycles. The NMR-tube was sealed and irradiated for two hours with a blue Kessil LED lamp (440 nm).
General Procedure 3: Nickel-catalyzed C-O Coupling

The following procedure was adapted from the literature.\(^8\)

Benzoic acid (98 mg, 0.80 mmol, 2.0 eq.), methyl 4-bromobenzoate (86 mg, 0.40 mmol, 1.0 eq.), NiBr\(_2\)-diglyme (7.0 mg, 0.02 mmol, 5 mol%), 4,4’-di-tert-butyl-2,2’-dipyridyl (5.4 mg, 0.02 mmol, 5 mol%) and photocatalyst (4 \(\mu\)mol, 1 mol%) were dissolved in dry DMF (2 mL) in a 10 mL Schlenk tube and sonicated until no solids remained. N-tert-butyl-isopropylamine (254 \(\mu\)L, 1.6 mmol, 4 eq.) was added, resulting in a suspension that was degassed by bubbling argon through it for 15 min. The reaction mixture was irradiated for 18h with a Kessil LED lamp (440 nm) and was cooled by a fan during the reaction time. Nevertheless, the temperature slightly rose due to the proximity of the lamp. The reaction mixture was subsequently poured into a 20% aq. LiCl solution (5 mL). This solution was extracted with EtOAc (3 \(\times\) 10 mL), the organic phases were combined, washed with aq. sat. K\(_2\)CO\(_3\) solution (1 \(\times\) 20 mL) and with 50% aq. LiCl solution (2 \(\times\) 10 mL). The organic phase was dried over anhydrous MgSO\(_4\), filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, 30% polar solvent mixture with pentane, polar solvent mixture = 1:1 CH\(_2\)Cl\(_2\):EtOAc) to yield the product as a colourless solid.

NMR-data are in agreement with the literature.\(^8\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.24 – 8.17 (m, 2H), 8.16 – 8.10 (m, 2H), 7.69 – 7.62 (m, 1H), 7.56 – 7.49 (m, 2H), 7.35 – 7.28 (m, 2H), 3.93 (s, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 166.5, 164.8, 154.8, 134.0, 131.4, 130.4, 129.3, 128.8, 127.9, 121.9, 52.4.
General Procedure 4: Decarboxylative Addition of Cbz-Proline to Ethyl Maleate

![Chemical Structure](image)

Cbz-proline (5.6 mg, 22.5 µmol, 1.0 eq.), ethyl maleate (4.3 mg, 24.7 µmol, 1.1 eq.), K$_2$HPO$_4$ (4.7 mg, 27.0 µmol, 1.2 eq.) and the respective catalyst (0.225 µmol, 1 mol%) were suspended in CD$_3$CN (0.6 mL). The solution was degassed in an NMR-tube by three freeze-pump-thaw cycles. The NMR-tube was flame-sealed and irradiated for five hours with a blue Kessil LED lamp (440 nm), after which time the ratio of ethyl maleate to the product was determined by $^1$H NMR spectroscopy.

For the preparative-scale experiment with [Ru(CF$_3$bpy)$_2$(BCF)$_2$] as photocatalyst, the following procedure was adapted from the literature.$^9$,10

Cbz-proline (38.0 mg, 0.15 mmol, 1.0 eq.), K$_2$HPO$_4$ (29.2 mg, 0.17 mmol, 1.1 eq.), ethyl maleate (28.9 mg, 0.17 mmol, 1.1 eq.) and [Ru(CF$_3$bpy)$_2$(BCF)$_2$] (2.7 mg, 1 mol%) were suspended in acetonitrile (3 mL) in a 5 mL Schlenk tube under argon atmosphere. The reaction mixture was degassed by three freeze-pump-thaw cycles, backfilled with argon and irradiated for 20 h with a Kessil LED lamp (440 nm). H$_2$O (3 mL) was added and the product was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic phases were dried over Na$_2$SO$_4$ and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (Silica, 20 % EtOAc in pentane) to yield the title compound (47.2 mg, 0.13 mmol, 82 %) as a colourless liquid. For the visualization of the product on TLC plates, iodine and a vanillin stain were used.

NMR data are in agreement with the literature.$^{10}$

$^1$H NMR (400 MHz, Chloroform-$d$) δ = 7.43 – 7.26 (m, 5H), 5.25 – 5.04 (m, 2H), 4.35 – 4.26 (m, 1H), 4.18 – 4.03 (m, 4H), 3.75 – 3.42 (m, 2H), 3.39 – 3.17 (m, 1H), 2.84 – 2.65(m, 1H), 2.56 – 2.22 (m, 1H), 2.06 – 1.71 (m, 4H), 1.27 – 1.18 (m, 6H).
Excited-State Quenching Studies

Methyl Cinnamate

Figure S29, main plot: Decay of [Ru(bpy)$_2$(BCF)$_2$] emission at 530 nm in the absence of trans-methyl cinnamate (blue trace) and in presence of increasing concentrations of trans-methyl cinnamate (other traces) after 375 nm excitation of a $10^{-5}$ M [Ru(bpy)$_2$(BCF)$_2$] solution in argon-saturated CH$_3$CN at 20 °C. Inset: Stern-Volmer plot (with the same color-code for the trans-methyl cinnamate concentration as in the main plot).

Figure S30, main plot: Decay of [Ru(CF$_3$-bpy)$_2$(BCF)$_2$] emission at 525 nm in the absence of trans-methyl cinnamate (blue trace) and in presence of increasing concentrations of trans-methyl cinnamate (other traces) after 425 nm excitation of a $10^{-5}$ M [Ru(CF$_3$-bpy)$_2$(BCF)$_2$] solution in argon-saturated CH$_3$CN at 20 °C. Inset: Stern-Volmer plot (with the same color-code for the trans-methyl cinnamate concentration as in the main plot).
Figure S31, main plot: Emission decay of fac-[Ir(ppy)$_3$] emission at 525 nm in the absence of trans-methyl cinnamate (blue trace) and in the presence of increasing concentrations of trans-methyl cinnamate (other traces) after 375 nm excitation of a 10$^{-5}$ M Ir(ppy)$_3$ solution in argon-saturated CH$_3$CN at 20 °C. Inset: Stern-Volmer plot (with the same color-code for the trans-methyl cinnamate concentration as in the main plot).

Figure S32: Decay of [Ru(bpy)$_3$]$_2^+$ emission at 630 nm in the absence of trans-methyl cinnamate (blue trace) and with 200 mM trans-methyl cinnamate (green trace) after 532 nm excitation of a 10$^{-5}$ M [Ru(bpy)$_3$]$_2$[PF$_6$]$_2$ solution with ~10 ns laser pulses in argon-saturated CH$_3$CN at 20 °C.
Figure S33, main plot: Decay of $[\text{Ru}(bpy)_3]^2+$ emission at 630 nm in the absence of DiPEA (blue trace) and in the presence of increasing concentrations of DiPEA (other traces) after 532 nm excitation of a $10^{-5}$ M $[\text{Ru}(bpy)_3]^2+$ solution with ~10 ns laser pulses in argon-saturated CH$_3$CN at 20 °C. Inset: Stern-Volmer plot (with the same color-code for the DiPEA concentration as in the main plot).

Figure S34, main plot: Decay of $[\text{Ru}(bpy)_2(BCF)_2]$ emission at 530 nm in the absence of DiPEA (blue trace) and in the presence of increasing concentrations of DiPEA (other traces) after 375 nm excitation of a $10^{-5}$ M $[\text{Ru}(bpy)_2(BCF)_2]$ solution in aerated CH$_3$CN at 20 °C. Inset: Stern-Volmer plot (with the same color-code for the DiPEA concentration as in the main plot).
Figure S35: Decay of fac-[Ir(ppy)$_3$] emission at 525 nm without any quencher (green trace) and with 50 mM DiPEA (yellow trace) or 10 mM benzaldehyde (red trace) after 375 nm excitation of a 10$^{-5}$ M fac-[Ir(ppy)$_3$] solution in argon-saturated CH$_3$CN at 20 °C.

Mechanistic Considerations

The mechanism of the photocatalytic pinacol coupling is dependent on the used catalysts and their respective redox potentials. The excited state reduction potential of fac-[Ir(ppy)$_3$] is 0.31 V vs. SCE (see main paper), which is too low to be reductively quenched by DiPEA. The benzaldehyde reduction therefore takes place directly from the excited state, which is strongly reducing (-1.73 V vs. SCE). Regeneration of fac-[Ir(ppy)$_3$] from its one-electron oxidized form subsequently occurs in the electronic ground state; the relevant reduction potential of fac-[Ir(ppy)$_3$]$^+$ is 0.77 V vs. SCE. This mechanism is confirmed by luminescence quenching experiments with fac-[Ir(ppy)$_3$] as the luminophore and DiPEA or benzaldehyde as the quencher (Figure S35). Whereas only very slow excited-state quenching was observed with DiPEA ($k_q < 10^6$ M$^{-1}$s$^{-1}$), reductive quenching by benzaldehyde is nearly two orders of magnitude faster ($k_q = 3.54 \cdot 10^7$ M$^{-1}$s$^{-1}$).

For [Ru(bpy)$_2$(BCF)$_2$], the mechanism differs significantly. Since the excited-state reduction potential is already rather high, $^3$MLCT quenching by DiPEA is much more rapid ($k_q = 1.29 \cdot 10^9$ M$^{-1}$s$^{-1}$) than with fac-[Ir(ppy)$_3$] ($k_q < 10^6$ M$^{-1}$s$^{-1}$). Therefore, the first step in the photocatalytic pinacol coupling with [Ru(bpy)$_2$(BCF)$_2$] is the reductive quenching with DiPEA, followed by the actual benzaldehyde reduction, which takes place with [Ru(bpy)$_2$(BCF)$_2$]$^-$ in the electronic ground state. This species is a much stronger reductant (-1.46 V vs. SCE) than the $^3$MLCT-excited [Ru(bpy)$_2$(BCF)$_2$] (-0.87 V vs. SCE).

With fac-[Ir(ppy)$_3$] as the catalyst, an NMR-yield of 100 % was obtained for the pinacol coupling.
Photostability Measurements

Figure S36: Photostability of [Ru(bpy)2(BCF)2] (a), [Ru(CF3bpy)2(BCF)2] (b), fac-[Ir(ppy)3] (c) and [Ru(bpy)3][PF6]2 (d) upon irradiation with a blue cw laser (447 nm, 1.1 W) in argon-saturated CH3CN at room temperature. Main plots: Loss in luminescence intensity at the respective emission peak wavelength as function of irradiation time. Left insets: Luminescence spectra before (green) and after (red) the irradiation. Right insets: UV-Vis spectra recorded before (green) and after (red) the irradiation.

Photo-Degradation Quantum Yield Calculation

The photo-degradation quantum yield $\Phi_{\text{degr}}$ is defined here as the number of decomposed photosensitizer molecules divided by the number of absorbed photons. In order to avoid systematic errors due to possibly luminescent photo-degradation products, $\Phi_{\text{degr}}$ was determined at $I/I_0 = 0.9$. The number of decomposed photosensitizer molecules at this point was assumed to be 10% of the initial value. The number of photons emitted by the cw laser was calculated by multiplying the power output of the lamp (1.1 W) with the irradiation time and dividing the obtained value by the energy of a photon with 447 nm wavelength (the laser output energy was $4.44 \cdot 10^{-19}$ J). Using the number of photons
emitted by the laser, the number of photons absorbed by the sample was then calculated using the Lambert-Beer law. Since the absorbance at the excitation wavelength was adjusted to 0.1 for all stability measurements, 21 % of the incident photons were absorbed by the four different samples, assuming that the absorbance remains constant during the considered irradiation period. These calculations lead to the values given in Table S5.

Table S5: Input values for the determination of the photo-degradation quantum yield $\Phi_{\text{degr}}$.

| Complex | Time (I/I_0=0.9) | # Abs. Photons | Initial conc. | # Decomposed molecules (I/I_0=0.9) | $\Phi_{\text{degr}}$ |
|---------|------------------|----------------|---------------|-----------------------------------|---------------------|
| [Ru(bpy)$_2$(BCF)$_2$] | 105 min | 5.41 mmol | 149 μM | 44.7 nmol | 0.000826 % |
| [Ru(CF$_3$bpy)$_2$(BCF)$_2$] | 37.4 min | 1.94 mmol | 32 μM | 9.60 nmol | 0.000495 % |
| fac-[Ir(ppy)$_3$] | 12.0 min | 0.621 mmol | 36 μM | 10.8 nmol | 0.00174 % |
| [Ru(bpy)$_3$][PF$_6$]$_2$ | 0.183 min | 9.45 μmol | 8.7 μM | 2.61 nmol | 0.0276 % |

For Figure 7 in the main paper, the change in luminescence intensity was converted to change in concentration ($\Delta c$) by multiplying the normalized luminescence (Figure S36, main plot) with the initial concentration of the respective complex. The initial $\Delta c$-value for each complex was set to 0, because at time = 0 no photo-degradation has occurred yet. Figure 8 in the main paper shows the change in concentration ($\Delta c$) as a function of irradiation time. Since the change in luminescence intensity is directly proportional to the change in concentration, but the initial concentration was different for each complex, the form of presentation shown in the main paper represents the photostability of the complexes better (and in more directly comparable fashion) than the raw data in Figure S36.
DFT Calculations

All DFT calculations were carried out with the Gaussian 09 software package\textsuperscript{11} using the B3LYP functional combined with the LANL2DZ basis set. The geometry optimizations of [Ru(bpy)\textsubscript{2}(BCF)]\textsubscript{2} and derived species were accompanied by frequency analyses. The optimized structures presented in Figure S37 and Figure S38 did not show negative vibrational frequencies, indicating convergence on minimum structures. Characteristic bond lengths and angles of all computed structures are summarized in Table S6. The frontier orbitals of the singlet ground state (Figure S37) are in line with an MLCT-type HOMO-LUMO transition (Ru-centered HOMO, bipyridine-centered LUMO).

![Figure S37: Optimized singlet ground state structure (left) and frontier orbitals (center, HOMO; right, LUMO) of [Ru(bpy)\textsubscript{2}(BCF)]\textsubscript{2} calculated at the B3LYP/LANL2DZ level of theory.]

Starting from the energy-minimized singlet ground state geometry (Figure S37), the corresponding lowest triplet state was optimized (upper structure in Figure S38). In this structure, the central Ru atom has a spin density close to 1, and the remaining spin density is distributed over one bipyridine ligand. Hence, these calculations predict the lowest triplet to be an MLCT state. Additional calculations on starting geometries with much longer Ru-N distances gave another energy-optimized structure (see the central row in Figure S38 for the structure and Table S6 for characteristic bond lengths), which lies higher in energy by about 0.4 kJ/mol compared to the \(^3\)MLCT structure. Spin density calculations provide clear evidence for the metal-centered (MC) character of this slightly higher-lying triplet state (two unpaired electrons at the ruthenium atom). The triplet state energies shown in Figure S38 were determined by comparing their calculated energies to that of the [Ru(bpy)\textsubscript{2}(BCF)]\textsubscript{2} singlet ground state. Comparable calculations on [Ru(CF\textsubscript{3}bpy)\textsubscript{2}(BCF)]\textsubscript{2} were unsuccessful. More specifically, several attempts to obtain the [Ru(CF\textsubscript{3}bpy)\textsubscript{2}(BCF)]\textsubscript{2}-derived \(^3\)MC gave optimized \(^3\)MLCT-like structures, which implies a much higher \(^3\)MC-\(^3\)MLCT energy difference than calculated and experimentally observed for [Ru(bpy)\textsubscript{2}(BCF)]\textsubscript{2} (in an indirect manner through the \(^3\)MLCT lifetime decrease).
Table S6: Selected bond lengths (calculated and determined from the crystal structure) of [Ru(bpy)_2(BCF)_2].

| ligand | bond       | Distance (Å)      | Distance (Å) | Distance (Å) | Distance (Å) | Distance (Å) |
|--------|------------|-------------------|--------------|--------------|--------------|--------------|
|        |            | (Crystal Structure) | (Ground State, DFT) | (\(\text{^1}\)MLCT, DFT) | (\(\text{^3}\)MC, DFT) | (reduced complex, DFT) |
| bpy-1  | Ru-N(1)    | 2.114             | 2.135        | 2.097        | 2.208        | 2.139        |
|        | Ru-N(2)    | 2.069             | 2.105        | 2.028        | 2.351        | 2.111        |
| bpy-2  | Ru-N(3)    | 2.063             | 2.107        | 2.138        | 2.362        | 2.101        |
|        | Ru-N(4)    | 2.112             | 2.137        | 2.134        | 2.221        | 2.128        |
| BArF-1 | Ru-C(21)   | 1.951             | 1.981        | 2.024        | 2.008        | 1.965        |
| BArF-2 | Ru-C(22)   | 1.951             | 1.984        | 2.031        | 2.016        | 1.982        |

| Atoms  | Angle (deg) | Angle (deg) | Distance (Å) | Distance (Å) | Distance (Å) | Distance (Å) |
|--------|-------------|-------------|--------------|--------------|--------------|--------------|
|        | (Crystal Structure) | (Ground State, DFT) | (\(\text{^1}\)MLCT, DFT) | (\(\text{^3}\)MC, DFT) | (reduced complex, DFT) |
| BArF-1 | Ru-C(21)-N(5) | 175.21      | 177.89       | 177.31       | 176.25       | 177.79       |
|        | C(21)-N(5)-B(1) | 176.51      | 174.85       | 175.81       | 177.25       | 175.33       |
| BArF-2 | Ru-C(22)-N(6) | 174.34      | 177.80       | 177.12       | 178.10       | 177.56       |
|        | C(22)-N(6)-B(2) | 172.08      | 176.40       | 175.64       | 178.10       | 178.18       |

Geometry optimizations and spin density calculations of the one-electron reduced [Ru(bpy)_2(BCF)_2] complex show a localized bipyridine radical anion for this reactive species (lower row in Figure S38).
Figure S38: Optimized structures (B3LYP/LANL2DZ) of the open-shell species derived from \([\text{Ru(bpy)}_2(\text{BCF})_2]\) (left), together with the corresponding spin densities (right). Blue color represents positive spin densities, whereas green represents negative spin densities. Pertinent energies and spin densities are given next to the respective structure. See text for details.
XYZ Coordinates for DFT-optimized structures:

_Singlet ground state of [Ru(bpy)₂(BCF)₂] (charge = 0, multiplicity = 1)_

| Atomic | X       | Y       | Z       |
|--------|---------|---------|---------|
| C      | 1.33202100 | 0.92353000 | -0.04408400 |
| C      | -1.49454500 | 0.89607000 | 0.11781100 |
| N      | 2.21152000 | 0.13519500 | -0.09045300 |
| N      | -2.35287500 | 0.08267600 | 0.13305100 |
| C      | 4.76343100 | 0.11192600 | -0.29458400 |
| C      | 4.80427600 | 1.00304000 | -1.38184400 |
| C      | 5.94058600 | 0.09536200 | 0.46882200 |
| C      | 5.88967300 | 1.83121600 | -1.68313200 |
| C      | 7.05322800 | 0.90365100 | 0.20476200 |
| C      | 7.02839200 | 0.08267600 | -0.87736900 |
| C      | 3.33169400 | -1.49743200 | 1.45539200 |
| C      | 3.10875200 | -2.84988600 | 1.74983400 |
| C      | 3.37819300 | -0.67212900 | 2.59467900 |
| C      | 2.96343100 | -3.35375000 | 3.05102000 |
| C      | 3.23295500 | -1.12438500 | 3.90671700 |
| C      | 3.02551500 | -2.48623600 | 4.14022100 |
| C      | 3.37352100 | -1.91291300 | -1.27780500 |
| C      | 4.48710500 | -2.73902700 | -1.51414800 |
| C      | 4.58185300 | -3.66497200 | -2.55368200 |
| C      | 2.32779900 | -2.10651900 | -2.19197800 |
| C      | 5.11794400 | -3.80623300 | -3.44058100 |
| C      | -3.71093500 | -1.57090200 | 1.57693400 |
| C      | -3.94200700 | -2.92480700 | 1.86801800 |
| C      | -3.68810200 | -0.74751300 | 2.71542600 |
| C      | -4.09938100 | -3.43299300 | 3.16317000 |
| C      | -3.83654800 | -1.20710400 | 4.02726300 |
| C      | -4.03941200 | -2.56868900 | 4.25649100 |
| C      | -4.82512800 | -0.13771100 | -0.47372700 |
| C      | -4.73798800 | 0.73338300 | -1.57511300 |
| C      | -6.10617700 | -0.19918100 | 0.09515500 |
| C      | -5.79766200 | 1.50539900 | -2.05658600 |
| C      | -7.20011800 | 0.55297900 | -0.35431100 |
| C      | -7.04559500 | 1.41916300 | -1.43576200 |
| C      | -2.98246500 | -2.11667600 | -0.99276200 |
| C      | -1.71889800 | -2.71137600 | -0.82742300 |
| C      | -3.70001700 | -2.60669500 | -2.09349700 |
| C      | -1.19069400 | -3.68629700 | -1.67655700 |
| C      | -3.20984300 | -3.57885300 | -2.97505500 |
| C      | -1.94237500 | -4.12311900 | -2.76887800 |
| B      | -3.49191800 | -0.95353000 | 0.06129200 |
| B      | 3.41138800 | -0.81773500 | -0.04776100 |
| F      | -3.54467000 | 0.63754900 | 2.57321900 |
| F      | -3.79335200 | -0.32411000 | 5.09649600 |
| F      | -4.18978100 | -3.05119600 | 5.54493900 |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| F       | -4.32182000 | -4.78665000 | 3.36777200  |
| F       | -4.06431400 | -3.86498200 | 0.84056400  |
| F       | -4.99463000 | -2.15323900 | -2.36542000 |
| F       | -3.97865300 | -4.01165400 | -4.04614300 |
| F       | -1.44371200 | -5.08929000 | -3.62520500 |
| F       | 0.06258100  | -4.23119100 | -1.43931500 |
| F       | -0.92564300 | -2.35432600 | 0.26684300  |
| F       | -3.53811600 | 0.83761200  | -2.28417700 |
| F       | -5.62548100 | 2.34705600  | -3.14639400 |
| F       | -8.11211400 | 2.17390600  | -1.89274200 |
| F       | -8.43573400 | 0.44013800  | 0.26623900  |
| F       | -6.37720100 | -1.05800900 | 1.16459000  |
| F       | 1.13241700  | -1.38894700 | -2.09191000 |
| F       | 1.29792000  | -3.15109500 | -4.11621500 |
| F       | 3.57679000  | -4.71692000 | -4.48130800 |
| F       | 5.71656000  | -4.44771600 | -2.70904200 |
| F       | 5.57724100  | -2.67473000 | -0.64143000 |
| F       | 3.01072900  | -3.80443300 | 0.73426400  |
| F       | 2.75081800  | -4.70809600 | 3.26113300  |
| F       | 2.87913000  | -2.96362200 | 5.43131900  |
| F       | 3.29357400  | -0.24123700 | 4.97530300  |
| F       | 3.58819500  | 0.70138200  | 2.43843200  |
| F       | 6.07126500  | -0.76255800 | 1.56202100  |
| F       | 8.18205400  | 0.83503700  | 1.00885800  |
| F       | 8.11760800  | 2.59369200  | -1.15101300 |
| F       | 5.84653900  | 2.69242200  | -2.77007200 |
| F       | 3.71428000  | 1.08412000  | -2.25580200 |
| Ru      | 0.09236300  | 2.29786900  | 0.03755400  |
| N       | -0.42178500 | 2.44648100  | -2.03660700 |
| C       | 0.22227600  | 1.70907700  | -2.98213600 |
| C       | -1.37287800 | 3.36211600  | -2.42594400 |
| C       | -0.04697000 | 1.85245900  | -4.34966000 |
| H       | 0.95523800  | 0.99782800  | -2.62775100 |
| C       | -1.68193500 | 3.54535900  | -3.78587400 |
| C       | -1.01531500 | 2.78638500  | -4.75956900 |
| H       | 0.49188900  | 1.24310500  | -5.06648800 |
| H       | -2.43132600 | 4.26659200  | -4.08713200 |
| H       | -1.24795300 | 2.92001200  | -5.81089500 |
| N       | -1.59999000 | 3.80673300  | -0.06438100 |
| C       | -2.02687900 | 4.11333600  | -1.33311500 |
| C       | -2.14477600 | 4.44786500  | 1.00057700  |
| C       | -3.02626200 | 5.08249400  | -1.54113100 |
| C       | -3.14103600 | 5.42304100  | 0.85505100  |
| H       | -1.77539200 | 4.16883900  | 1.97900500  |
| C       | -3.58943800 | 5.74459800  | -0.43907600 |
| H       | -3.36323600 | 5.32141000  | -2.54201800 |
| H       | -3.54893700 | 5.90966000  | 1.73378600  |
| H       | -4.36095800 | 6.49292600  | -0.58808900 |
| N       | 0.24822600  | 2.46994600  | 2.10930300  |
MLCT triplet state of \([\text{Ru(bpy)}_2(\text{BCF})_2]\) (charge = 0, multiplicity = 3)
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | -4.52607100 | -2.61091500 | 4.16034900 |
| C       | -4.79702300 | -0.01996100 | -0.56478400 |
| C       | -4.60361300 | 0.66208100  | -1.78048100 |
| C       | -6.06658400 | 0.17412000  | -0.00191800 |
| C       | -5.56012500 | 1.47402600  | -2.39087900 |
| C       | -7.06098300 | 0.97646300  | -0.57982600 |
| C       | -6.80736800 | 0.17412000  | -2.00191800 |
| C       | -6.80736800 | 0.17412000  | -2.00191800 |
| C       | -6.80736800 | 0.17412000  | -2.00191800 |
| C       | -6.80736800 | 0.17412000  | -2.00191800 |
| B       | -3.55914400 | -0.88533300 | 0.09482200 |
| B       | -3.43760500 | -0.88132400 | -0.09099100 |
| F       | -3.06438200 | 0.44911700  | 2.80155100  |
| F       | -3.60134600 | -0.65203200 | 5.21040600  |
| F       | -4.81909600 | -3.15458500 | 5.39807400  |
| F       | -5.48312600 | -4.52845200 | 3.06361400  |
| F       | -4.95379900 | -3.45158300 | 0.62986600  |
| F       | -4.95944100 | -2.19128000 | -2.32259000 |
| F       | -3.90399900 | -4.15966900 | -3.85108800 |
| F       | -1.04541000 | -5.24177000 | -3.25926800 |
| F       | -0.01995200 | -4.27673400 | -1.06586500 |
| F       | -1.01234300 | -2.29315800 | 0.48854800  |
| F       | -3.38824100 | -0.52176700 | -2.45503800 |
| F       | -5.29002800 | 2.11397800  | -3.59093100 |
| F       | -7.77451000 | 2.43431000  | -2.36475400 |
| F       | -8.39431100 | 1.12054400  | 0.03735200  |
| F       | -6.22640200 | -0.44381600 | 1.19811400  |
| F       | 1.03012800  | -1.45002600 | -1.97457300 |
| F       | 1.05285400  | -3.22794400 | -3.99313000 |
| F       | 3.30460100  | -4.79152900 | -4.51047900 |
| F       | 5.56086400  | -4.51348100 | -2.89126000 |
| F       | 5.56082200  | -2.73688900 | -0.82302000 |
| F       | 3.07216300  | -3.86316400 | 0.71044800  |
| F       | 2.88589500  | -4.75896200 | 3.24670800  |
| F       | 3.06045800  | -3.00525100 | 5.40565200  |
| F       | 3.44254500  | -0.28315400 | 4.92970300  |
| F       | 3.65438700  | 0.65379000  | 2.37969500  |
| F       | 6.13488900  | -0.80873000 | 1.43658300  |
| F       | 8.26142400  | 0.67507400  | 0.82374800  |
| F       | 8.16865500  | 2.43896300  | -1.33012700 |
| F       | 5.85279600  | 2.58961900  | -2.87948800 |
| F       | 3.70107000  | 1.02660800  | -2.29975000 |
| Ru      | -0.04928900 | 2.32013200  | 0.08947000  |
| N       | -0.40844300 | 2.52023300  | -1.89645600 |
| C       | 0.14302000  | 1.75872800  | -2.90862000 |
| C       | -1.40125800 | 3.50531100  | -2.21977600 |
MC triplet state of [Ru(bpy)$_2$(BCF)$_2$] (charge = 0, multiplicity = 3)
| C  | 7.06142953  | 1.76163614  | -1.09871208  |
| C  | 3.50147127  | -1.52021912 | 1.42850911   |
| C  | 3.29401825  | -2.87292622 | 1.73280813   |
| C  | 3.62072227  | -0.69681406 | 2.56360819   |
| C  | 3.22939125  | -3.37836726 | 3.03966423   |
| C  | 3.55723327  | -1.15123009 | 3.88128729   |
| C  | 3.37193026  | -2.51317819 | 4.12431032   |
| C  | 4.46055934  | -2.76029221 | -1.60871813  |
| C  | 2.27533317  | -2.09326516 | -2.16621916  |
| C  | 4.48720434  | -3.68013328 | -2.65745920  |
| C  | 2.25701317  | -2.9998123  | -3.2351625   |
| C  | 3.36912626  | -3.80088929 | -3.48625627  |
| C  | -3.75345329 | -1.54204912 | 1.64157813   |
| C  | -3.97857930 | -2.88825622 | 1.97025215   |
| C  | -3.67726528 | -0.69375505 | 2.75912621   |
| C  | -4.08352031 | -3.36753326 | 3.28135125   |
| C  | -3.77241129 | -1.12477409 | 4.08565331   |
| C  | -3.97245031 | -2.47990519 | 4.35210133   |
| C  | -4.94399638 | -0.15532601 | -0.3916503   |
| C  | -4.89122038 | 0.72219505  | -1.49328111  |
| C  | -6.21082050 | -0.23574502 | 0.20271102   |
| C  | -5.97094847 | 1.48291411  | -1.94731815  |
| C  | -7.32360654 | 0.50439404  | -0.21886802  |
| C  | -7.20356358 | 1.37729111  | -1.29951510  |
| C  | -3.11252224 | -2.13973016 | -0.94453407  |
| C  | -1.84752614 | -2.73631321 | -0.79480706  |
| C  | -3.84685829 | -2.63065520 | -2.03358016  |
| C  | -1.33094510 | -3.71163429 | -1.65026613  |
| C  | -3.36926826 | -3.60517828 | -2.91977022  |
| C  | -2.09884616 | -4.14914332 | -2.73121921  |
| B  | -3.59781728 | -0.96444107 | 0.10528301   |
| B  | 3.49713027  | -0.83933206 | -0.07423101  |
| F  | -3.52833927 | 0.68684005  | 2.58083319   |
| F  | -3.67854528 | -0.21987202 | 5.13259239   |
| F  | -4.07031831 | -2.93361122 | 5.65567641   |
| F  | -4.30414433 | -4.71475336 | 3.52449827   |
| F  | -4.14847932 | -3.84650729 | 0.96751507   |
| F  | -5.14239139 | -2.17267816 | -2.29003717  |
| F  | -4.15296032 | -4.03874731 | -3.97920631  |
| F  | -1.61243312 | -5.11535039 | -3.59400327  |
| F  | -0.07428401 | -4.25490132 | -1.43026711  |
| F  | -1.03964208 | -2.37598218 | 0.28723002   |
| F  | -3.70744628 | 0.84471506  | -2.22575217  |
| F  | -5.83350246 | 2.33195018  | -3.03593923  |
| F  | -8.28929866 | 2.11980516  | -1.72943813  |
| F  | -8.54356467 | 0.37246703  | 0.42756803   |
| F  | -6.44476748 | -1.10353008 | 1.27302610   |
| F  | 1.10054409  | -1.35556211 | -2.00320115  |
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| F    | 1.13383109 | -3.10835724 | -4.04234431 |
| F    | 3.36584925  | -4.70599536  | -4.53434334  |
| F    | 5.60141744  | -4.47603334  | -2.87837222  |
| F    | 5.59700145  | -2.71218321  | -0.79669906  |
| F    | 3.12919024  | -3.82344729  | 0.72286505   |
| F    | 3.02692023  | -4.73259936  | 3.26029925   |
| F    | 3.36584925  | -4.70599536  | -4.53434334  |
| F    | 5.60141744  | -4.47603334  | -2.87837222  |
| F    | 5.59700145  | -2.71218321  | -0.79669906  |
| F    | 3.12919024  | -3.82344729  | 0.72286505   |
| F    | 3.02692023  | -4.73259936  | 3.26029925   |
| F    | 5.60141744  | -4.47603334  | -2.87837222  |
| F    | 5.59700145  | -2.71218321  | -0.79669906  |
| F    | 3.12919024  | -3.82344729  | 0.72286505   |
| F    | 3.02692023  | -4.73259936  | 3.26029925   |
| F    | 5.60141744  | -4.47603334  | -2.87837222  |
| F    | 5.59700145  | -2.71218321  | -0.79669906  |
| F    | 3.12919024  | -3.82344729  | 0.72286505   |
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| F    | 5.60141744  | -4.47603334  | -2.87837222  |
| F    | 5.59700145  | -2.71218321  | -0.79669906  |
| F    | 3.12919024  | -3.82344729  | 0.72286505   |
| F    | 3.02692023  | -4.73259936  | 3.26029925   |
| F    | 5.60141744  | -4.47603334  | -2.87837222  |
| F    | 5.59700145  | -2.71218321  | -0.79669906  |
| F    | 3.12919024  | -3.82344729  | 0.72286505   |
| F    | 3.02692023  | -4.73259936  | 3.26029925   |
| F    | 5.60141744  | -4.47603334  | -2.87837222  |
| F    | 5.59700145  | -2.71218321  | -0.79669906  |
| F    | 3.12919024  | -3.82344729  | 0.72286505   |
| F    | 3.02692023  | -4.73259936  | 3.26029925   |
| F    | 5.60141744  | -4.47603334  | -2.87837222  |
| F    | 5.59700145  | -2.71218321  | -0.79669906  |
| F    | 3.12919024  | -3.82344729  | 0.72286505   |
| F    | 3.02692023  | -4.73259936  | 3.26029925   |
| F    | 5.60141744  | -4.47603334  | -2.87837222  |
| F    | 5.59700145  | -2.71218321  | -0.79669906  |
| F    | 3.12919024  | -3.82344729  | 0.72286505   |
| F    | 3.02692023  | -4.73259936  | 3.26029925   |
| F    | 5.60141744  | -4.47603334  | -2.87837222  |
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| F    | 3.12919024  | -3.82344729  | 0.72286505   |
| F    | 3.02692023  | -4.73259936  | 3.26029925   |
| F    | 5.60141744  | -4.47603334  | -2.87837222  |
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| F    | 3.02692023  | -4.73259936  | 3.26029925   |
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| F    | 3.02692023  | -4.73259936  | 3.26029925   |
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| F    | 5.59700145  | -2.71218321  | -0.79669906  |
| F    | 3.12919024  | -3.82344729  | 0.72286505   |
| F    | 3.02692023  | -4.73259936  | 3.26029925   |
| F    | 5.60141744  | -4.47603334  | -2.87837222  |
| F    | 5.59700145  | -2.71218321  | -0.79669906  |
| F    | 3.12919024  | -3.82344729  | 0.72286505   |
| F    | 3.02692023  | -4.73259936  | 3.26029925   |
One-electron reduced form of $[\text{Ru}(\text{bpy})_2(\text{BCF})_2]$ (charge = -1, multiplicity = 2)
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| B       | -3.50275300 | -0.98207100 | 0.08534200 |
| B       | 3.43788200  | -0.79932800 | -0.03083100|
| F       | -3.86019900 | 0.99813600  | 2.24483000 |
| F       | -4.22314300 | 0.48550800  | 4.88666900 |
| F       | -4.45831700 | -2.13916600 | 5.80416500 |
| F       | -4.31197200 | -4.24149800 | 3.97912200 |
| F       | -3.93884400 | -3.76937500 | 1.34470000 |
| F       | -4.97162600 | -2.55839900 | -2.13181700|
| F       | -3.91229300 | -4.61110600 | -3.53523100|
| F       | -1.35500300 | -5.56566100 | -2.9659100 |
| F       | 0.11817600  | -4.38741900 | -0.91345800|
| F       | -0.91870500 | -2.32551500 | 0.52462800 |
| F       | -3.40159800 | 0.50174200  | -2.46999500|
| F       | -5.43308500 | 1.86692800  | -3.64585800|
| F       | -7.99488600 | 1.82686000  | -2.54120400|
| F       | -8.45355500 | 0.37444800  | -0.20620800|
| F       | -6.45215000 | -0.98059100 | 1.00167200 |
| F       | 1.10315400  | -1.53256900 | -1.96403700|
| F       | 1.19724600  | -3.48581300 | -3.80673100|
| F       | 3.45642500  | -5.09558300 | -4.08977100|
| F       | 5.65213600  | -4.67380400 | -2.41630300|
| F       | 5.58173700  | -2.71330000 | -0.52247000|
| F       | 3.03752100  | -3.70929300 | 1.01259000 |
| F       | 2.88742600  | -4.39903000 | 3.61485100 |
| F       | 3.15454100  | -2.48815800 | 5.62664200 |
| F       | 3.59458200  | 0.17795300  | 4.93028800 |
| F       | 3.77657200  | 0.90668900  | 2.31321000 |
| F       | 6.17687400  | -0.62390700 | 1.44298800 |
| F       | 8.25050600  | 0.92958600  | 0.67530900 |
| F       | 8.07883100  | 2.52304100  | -1.60397000|
| F       | 5.73669700  | 2.49384600  | -3.12183300|
| F       | 3.64007000  | 0.92598600  | -2.39377200|
| Ru      | -0.09657600 | 2.25302400  | -0.05608200|
| N       | -0.40006500 | 2.37694600  | -2.14125700|
| C       | 0.23867500  | 1.61430900  | -3.07053800|
| C       | -1.32225000 | 3.31134100  | -2.55624100|
| C       | -0.00408000 | 1.74982400  | -4.44380200|
| H       | 0.94908800  | 0.89065700  | -2.69451600|
| C       | -1.60330100 | 3.49010200  | -3.92407300|
| C       | -0.90424900 | 2.70593300  | -4.87963000|
| H       | 0.53033400  | 1.11962100  | -5.14615900|
| H       | -2.32872800 | 4.22795600  | -4.24420800|
| H       | -1.15059100 | 2.83640000  | -5.93621700|
| N       | -1.59794300 | 3.76929900  | -0.20319600|
| C       | -1.98535800 | 4.08197700  | -1.48221400|
| C       | -2.15512900 | 4.42146300  | 0.84780500 |
| C       | -2.96082500 | 5.07130200  | -1.71651200|
| C       | -3.12753200 | 5.41700500  | 0.67686100 |
| H       | -1.80867700 | 4.13022300  | 1.83131400 |
C  -3.53739000  5.74585500  -0.62917800
H  -3.26905800  5.31499100  -2.72578500
H  -3.54642400  5.91511800  1.54421900
H  -4.28941800  6.51000000  -0.79794800
N   0.16489000  2.48913400  2.01573800
C  -0.44083200  1.75791500  2.99520400
C   1.08786100  3.49502300  2.37537100
C  -0.21475400  1.96071900  4.35614700
H  -1.12818900  0.99214800  2.65066300
C   1.34361000  3.73535100  3.76605000
C   0.70695100  2.98601700  4.74484400
H  -0.72981800  1.34949700  5.08934100
H   2.04846100  4.50908500  4.05216000
H   0.90870900  3.17295300  5.79620000
N   1.35728600  3.80604700  -0.00163300
C   1.72007800  4.19705100  1.30142900
C   1.93857700  4.41404500  -1.07050600
C   2.69058500  5.24122600  1.46711600
C   2.88720000  5.43178500  -0.95352500
H   1.62677600  4.06320700  -2.04845200
C   3.26667100  5.85215500  0.36194800
H   2.97752000  5.55221000  2.46624600
H   3.31645500  5.88174900  -1.84217000
H   4.00194900  6.64150100  0.49462100
NMR Spectra Methyl Cinnamate Isomerization

Due to the significant side product formation in the cis/trans isomerization reaction of methyl cinnamate with fac-[Ir(ppy)$_3$] and [Ru(CF$_3$)$_2$ppy)$_2$(BCF)$_2$], we decided to use the internal standard trimethyl(phenyl)silane for the precise determination of the cis/trans product ratio. The concentration of trimethyl(phenyl)silane was chosen to be one third of the methyl cinnamate concentration in order for the methyl resonances of both compounds to have approximately the same integral in the $^1$H NMR spectrum.

Figure S39: Isomerization of methyl cinnamate with fac-[Ir(ppy)$_3$] in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 1. Shown are the $^1$H NMR spectra before the irradiation and after a reaction time of 2h. The integrals for the determination of the cis/trans ratio were normalized with respect to the internal standard trimethyl(phenyl)silane.
Figure S40: Isomerization of methyl cinnamate with \([\text{Ru(bpy)}_2(\text{BCF})_2]\) in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 1a. Shown are the $^1$H NMR spectra before the irradiation and after a reaction time of 8h. The integrals for the determination of the cis/trans ratio were normalized with respect to the internal standard trimethyl(phenyl)silane.

Figure S41: Isomerization of methyl cinnamate with \([\text{Ru(bpy)}_2(\text{BCF})_2]\) in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 1. Shown are the $^1$H NMR spectra before the irradiation and after a reaction time of 2h. The integrals for the determination of the cis/trans ratio were normalized with respect to the internal standard trimethyl(phenyl)silane.
Figure S42: Isomerization of methyl cinnamate with $\text{[Ru(CF}_3\text{bpy)}_2\text{BCF}_3]}_2$ in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 1. Shown are the $^1$H NMR spectra before the irradiation and after a reaction time of 2h. The integrals for the determination of the cis/trans ratio were normalized with respect to the internal standard trimethyl(phenyl)silane.

Figure S43: Isomerization of methyl cinnamate with $\text{[Ru(bpy)}_3]\text{[PF}_6]_2$ in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 1. Shown are the $^1$H NMR spectra before the irradiation and after a reaction time of 2h. The integrals for the determination of the cis/trans ratio were normalized with respect to the internal standard trimethyl(phenyl)silane.
Figure S44: Enlarged region of the $^1$H NMR spectra from Figure S39, Figure S41 and Figure S42, monitoring the isomerization of methyl cinnamate with $\text{[Ru(bpy)$_2$(BCF)$_2$]}$ (top), $\text{[Ru(CF$_3$bpy)$_2$(BCF)$_2$]}$ (middle) and $\text{fac-[Ir(ppy)$_3$]}$ (bottom) after a reaction time of 2 hours in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 1. The integrals for the determination of the cis/trans ratio were normalized with respect to the internal standard trimethyl(phenyl)silane.
NMR Spectra Pinacol Coupling Reaction

Since no significant side product formation was observed in the pinacol coupling reactions, the yields were determined by the ratio of the benzaldehyde resonance at 10.0 ppm to the combined integrals of the meso and dl forms at 4.8 ppm and 4.6 ppm, respectively, of the coupled product.

Figure S45: Pinacol coupling of benzaldehyde with [Ru(bpy)$_2$(BCF)$_2$] in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 2. Shown are the $^1$H NMR spectra before the irradiation and after a reaction time of 2h.
Figure S46: Pinacol coupling of benzaldehyde with fac-[Ir(ppy)$_3$] in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 2. Shown are the $^1$H NMR spectra before the irradiation and after a reaction time of 2h.

Figure S47: Pinacol coupling of benzaldehyde with [Ru(bpy)$_3$]$_2$[PF$_6$]$_2$ in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 2. Shown are the $^1$H NMR spectra before the irradiation and after a reaction time of 2h.
NMR Spectra C-O coupling

Figure S48: $^1$H NMR spectrum of methyl 4-(benzoyloxy)benzoate in CDCl₃ at 293 K.

Figure S49: $^{13}$C-$^1$H-NMR spectrum of methyl 4-(benzoyloxy)benzoate in CDCl₃ at 293 K.
NMR Spectra Decarboxylative Addition of CBz-Proline to Ethyl Maleate

The coupling of Cbz-Proline with ethyl maleate was performed in an NMR tube and reaction progress was monitored by $^1$H NMR spectroscopy, where the integral of the aromatic protons of the Cbz-protecting group (7.43 – 7.22 ppm, 5H) was compared to the integral of the olefinic ethyl maleate protons (6.28 ppm, 2H) after a reaction time of 5 hours. When the reaction was performed in an NMR-tube with [Ru(CF$_3$bpy)$_2$(BCF)$_2$] as the photocatalyst, 88 % of ethyl maleate were consumed after 5 h and product formation could be observed. Since the product and starting material show strongly overlapping $^1$H NMR spectra, the determination of the exact yield is impossible when monitoring the reaction directly in an NMR tube. To circumvent this problem, the reaction was performed on preparative scale and gave a yield of 82 %.

NMR Spectra with [Ru(bpy)$_2$(BCF)$_2$] as photocatalyst

Figure S50: $^1$H NMR spectrum at t=0h of the reaction mixture for the coupling of Cbz-Proline to ethyl maleate with [Ru(bpy)$_2$(BCF)$_2$] in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 4.
Figure S51: $^1$H NMR spectrum at $t=5$ h of the reaction mixture for the coupling of Cbz-Proline to ethyl maleate with $[\text{Ru(bpy)}_2(\text{BCF})_2]$ in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 4.
NMR Spectra with $[\text{Ru}(\text{CF}_3\text{bpy})_2(\text{BCF})_2]$ as Photocatalyst

Figure S52: $^1$H NMR spectrum at t=0h of the reaction mixture for the coupling of Cbz-Proline to ethyl maleate with $[\text{Ru}(\text{CF}_3\text{bpy})_2(\text{BCF})_2]$ in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 4.

Figure S53: $^1$H NMR spectrum at t=5h of the reaction mixture for the coupling of Cbz-Proline to ethyl maleate with $[\text{Ru}(\text{CF}_3\text{bpy})_2(\text{BCF})_2]$ in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 4.
NMR Spectra with [Ru(bpy)$_3$][PF$_6$]$_2$ as Photocatalyst

Figure S54: $^1$H NMR spectrum at t=0h of the reaction mixture for the coupling of Cbz-Proline to ethyl maleate with [Ru(bpy)$_3$][PF$_6$]$_2$ in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 4.

Figure S55: $^1$H NMR spectrum at t=5h of the reaction mixture for the coupling of Cbz-Proline to ethyl maleate with [Ru(bpy)$_3$][PF$_6$]$_2$ in argon-saturated CD$_3$CN upon blue light irradiation applying the conditions described in general procedure 4.
NMR Spectrum diethyl 2-((benzyloxy)carbonyl)pyrrolidin-2-yl)succinate

Pure diethyl 2-((benzyloxy)carbonyl)pyrrolidin-2-yl)succinate could be isolated according to general procedure 4 (preparative scale), the $^1$H NMR spectrum is shown below.

Figure S56: $^1$H NMR spectrum of diethyl 2-((benzyloxy)carbonyl)pyrrolidin-2-yl)succinate in CDCl$_3$ at 293 K.
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