

Supporting Information

Visible-Light-Induced Regioselective *N*-oxazolidinone radical addition to indoles and arenes *via* EDA complex formation

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1 General methods

All reactions were carried out under a positive pressure of nitrogen (5 cm of mercury, or with a spring-loaded silicon oil bubbler set to 100 mbar) and dry solvents. If not otherwise stated, reagents were purchased at the highest commercial quality, the solvents were purchased with Across seal and they were used without further purifications. The starting materials, whenever necessary, were synthesized according to the literature procedures. 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) was synthesized according to a reported protocol.

Reactions were monitored by thin layer chromatography (TLC) on Macherey-Nagel pre-coated silica gel plates (0.25 mm) and visualized by UV light. Flash chromatography was performed on standard flash column chromatography on Merck silica gel (60, particle size: 0.040–0.063 mm) using petroleum ether or hexane, ethyl acetate (EtOAc), dichloromethane (DCM), methanol (MeOH) as standard solvents.

^1H NMR ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker Avance spectrometers (300 MHz, 75 MHz, 282 MHz, 121 MHz) or (400 MHz, 101 MHz, 376 MHz, 162 MHz) in CDCl_3 , $\text{DMSO-}d_6$, $\text{MeOH-}d_4$ and $\text{ACN-}d_3$ solutions with internal solvent signals (for ^1H and ^{13}C) as reference (7.26 and 77.2 for CDCl_3 , 2.50 and 39.5 for $\text{DMSO-}d_6$, 3.31 and 49.0 for $\text{MeOH-}d_4$, 1.94 and 1.32 for $\text{ACN-}d_3$). ^1H NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, br. s. = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, hept = heptet, dd = doublet of doublets, ddd = doublet of doublets of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz), and numbers of protons. ^{19}F data are reported as follows: chemical shift (ppm), multiplicity (wherever applicable, s = singlet, d = doublet, t = triplet, q = quartet), coupling constants (Hz), and numbers of fluorine atoms (wherever applicable). Data for ^{13}C NMR are reported in terms of chemical shift, and no special nomenclature is used for equivalent carbons.

High resolution mass spectra (HRMS) were acquired using a Q-TOF Synapt G2-Si/HDMS 8K instrument available at the MS facility of the Unitech COSPECT at the University of Milan.

Chiral HPLC was measured on an Agilent 1100 or 1200 Serie and they are reported according to the IUPAC recommendations 2013.

Gas chromatography-mass spectrometry (GC-MS) was performed on GC Agilent 6890N, inlet: EPC splitsplitless; column: Agilent 19091S-433 HP-5MS 5% phenyl methyl siloxane; MS: quadrupole G2589A EI; Autosampler: Agilent 7683; gas carrier: helium.

3D-printed photoreactors were 3D-printed with Formlabs "FORM 3" 3D-printer, using Clear V4 or Draft V2 resins.

A Fusion 100-X syringe pump, bought from CHEMYX, has been used to feed reagents in home-made flow setups.

All fluidic connections were made by $\frac{1}{4}$ -28-bore finger tight ferules and adapters (connectors, Y- and T-shape) and were purchased by Cole-Parmer seller.

f-Reactor (Mixer) was purchased from Asynt (internal volume 1.75 mL in absence of stirrer and 1.6 mL in presence of the stirrer).

UV-Vis measurements were recorded recorded using a Nicolet Evolution 500 (a ThermoFisher spectrophotometer) and quartz cuvettes with path length of 1 mm in ACN at the appropriate concentrations.

Cyclic voltammetry analyses were carried out under an argon atmosphere by using a Metrohm Autolab Series Potentiostat/Galvanostat Electrochemical System, using a glassy carbon as

working electrode, a platinum foil as counter electrode and a silver wire as pseudo reference electrode. The measurements were carried out under static argon atmosphere, in dry acetonitrile, using tetrabutylammonium tetrafluoroborate (0.1 M) as supporting electrolyte. The scan rate was $100 \text{ mV}\cdot\text{s}^{-1}$. The potentials were determined versus Ag/AgCl (LiCl 2 M in EtOH).

The geometry of the pyridinium ions **1a-c** was calculated with (wB97xD/6-31G(d,p)/IEFPCM(acetonitrile)//wB97xD/6-311+G(d,p)/IEFPCM(acetonitrile)).

2 Description of the Photoredox equipment

The Photoredox reactions were performed with three different reaction set-ups in batch and two different set-ups in flow.

2.1 Photoreactor PR-1 (batch set-up)

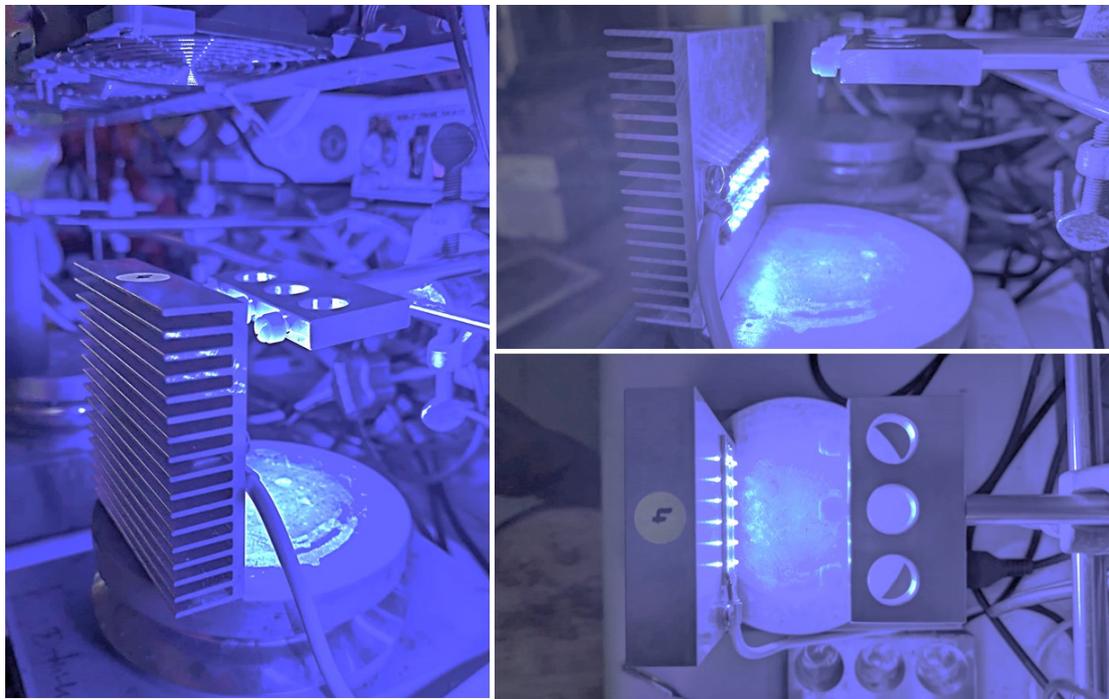


Figure S1 Image of the photoreactor.

The reaction vials for 0.2-0.1 mmol scale reactions (5/10 mL crimp cap vials) were illuminated from the side with LEDs (λ) of 455 ± 10 nm (Figure S1). The irradiation intensity was carefully maintained at ~ 600 mW to ensure optimal conditions for the photochemical reactions. The photoreactor was equipped with a cooling system which includes a solid aluminium heatsinks, a linear heat-conductive adhesive pads, and an air vent. These elements collectively facilitated effective heat dissipation and temperature regulation during the photoreaction, crucial for maintaining stable reaction conditions, particularly given the potential exothermic nature of photochemical reactions.

2.1 Kessil Lamp (batch set-up) PR-2



Figure S2 Image of the cylinder reactor used in this study.

The reaction vial was positioned 4 cm from the Kessil lamp (390 nm, 427 nm and 456 nm) 100 % of light intensity with an estimated power of 350 mW/cm².

2.2 Syrris ASIA System PR-3 (Flow set-up)

Syrris ASIA Premium System was employed. The whole continuous-flow systems can be purchased in a modular fashion (Syrris, Asia Ltd) (*Figure S3*).



Figure S3 *Syrris ASIA Premium System.*

The liquid feed solution was prepared and stored under inert atmosphere and directly pumped from the volumetric flask using a *Syrris ASIA Syringe Pump*. The solution is pumped in a *Syrris ASIA Tube Reactor*: this system is placed inside a *Syrris ASIA Photochemistry Module*, which is equipped with four 450nm LEDs lamps operating at the maximum possible emitting power. A *Syrris ASIA Heater* allows the controlled heating of the coil reactor at the desired temperature (20 °C). After reaching a steady state, a known amount of the output was collected and analysed.

3 Flow equipment: Specifications of the Coil Reactors

All fluidic connections were made by ¼-28-bore finger tight ferules and adapters (connectors, Y- and T-shape) and were purchased by Cole-Parmer seller.

The coil reactor is made from standard HPLC-Tubing, employing PFA (Perfluoroalkoxyalkane) as material of construction.

Reactor Volume = 981 μ L

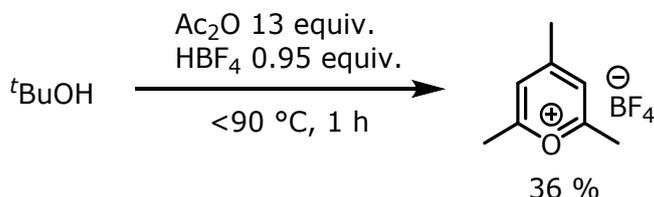
Internal diameter = 0.5 mm

Reaction Length = 80 cm

4 Synthesis and Characterization of the Substrates

4.1 Synthesis of the pyrylium ions

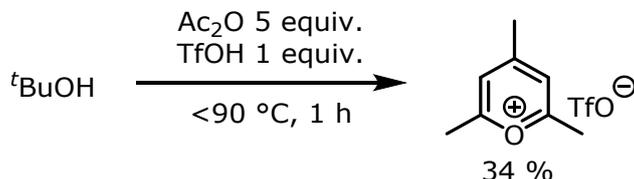
2,4,6-trimethylpyrylium tetrafluoroborate



A 250 ml two-necked flask was charged with acetic anhydride (591 mmol, 13 equiv.) and *tert*-butanol (47 mmol, 1 equiv.), providing a colorless solution. HBF_4 (44 mmol, 0.95 equiv.) was introduced dropwise with a dropping funnel: the addition was exothermic, the solution turned yellow at first, and then reddish. After completion of the addition, the reaction mixture has been cooled by dipping the flask in an ice bath: the formation of a white precipitate has been observed. The reaction was quenched by the addition of 10 ml of cold Et_2O . The white precipitate has been recovered by filtration under vacuum, washed with cold Et_2O and dried. The desired product was recovered as a white solid in 36% yield. All the analytical data are in agreement with the literature.¹

$^1\text{H NMR}$ (300 MHz, MeOD) δ 7.88 (s, 2H), 2.88 (s, 8H). $^{19}\text{F NMR}$ (282 MHz, MeOD) δ -154.88.

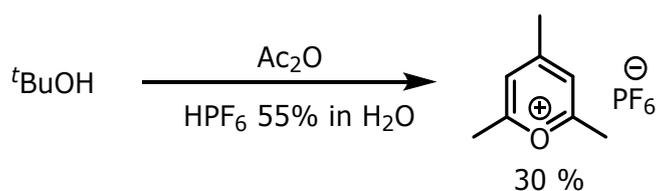
2,4,6-trimethylpyrylium triflate



Into a 100 ml round bottom two-necked flask, the acetic anhydride (65 ml, 688 mmol, 5 equiv.) and the *t*BuOH (13 ml, 136 mmol, 1 equiv.) were introduced. The addition of the TfOH (11.7 ml, 136 mmol, 1 equiv.) was performed with a drip funnel under vigorous stirring controlling with a thermometer that the reaction temperature must be under 90 °C. After the addition, the reaction mixture was slowly cooled down to room temperature, then to 0°C with an ice bath. Et_2O was added and the precipitate was filtered on a Buckner. The desired product was obtained in 45% yield (16.3 g) as a white solid. All the analytical data are in agreement with the literature.²

$^1\text{H NMR}$ (400 MHz, DMSO) δ 7.81 (s, 2H), 2.66 (s, 6H), 2.34 (s, 3H) ppm. $^{19}\text{F NMR}$ (377 MHz, DMSO) δ -77.33 ppm. $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 177.81, 173.98, 123.33, 122.73, 119.53, 23.36, 21.35 ppm. **HRMS (ESI +)** $\text{C}_8\text{H}_{11}\text{O}$: 123.0805 (Calc. Mass 123.0804), **HRMS (ESI -)** $\text{CF}_3\text{O}_3\text{S}$: 148.9529 (Calc. Mass 148.9526).

2,4,6-trimethylpyrylium hexafluorophosphates

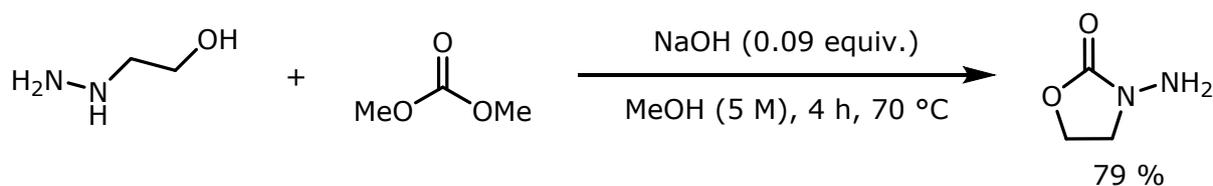


Into a 100 ml round bottom 1 neck flask, the acetic anhydride (25 ml, 264 mmol, 8.4 equiv.) and the $t\text{BuOH}$ (3 ml, 31.1 mmol, 1 equiv.) were introduced. The addition of the HPF_6 (5 ml, 31.1 mmol, 1 equiv.) must be done slowly in order to keep the reaction temperature under 90°C , controlled with a thermometer. After the addition, the reaction mixture was slowly cooled down to room temperature and the precipitate was filtered on a Buckner and washed with Et_2O . The desired product was obtained in 30 % yield (2.5 g) as a light brown solid. All the analytical data are in agreement with the literature. ²

$^1\text{H NMR}$ (400 MHz, DMSO) δ 7.80 (s, 2H), 2.66 (s, 6H), 2.34 (s, 3H) ppm. **$^{19}\text{F NMR}$** (377 MHz, DMSO) δ -68.76, -70.64 ppm. **$^{13}\text{C NMR}$** (101 MHz, DMSO) δ 177.81, 123.32, 27.37, 23.37, 21.34 ppm. **HRMS (ESI +)** $\text{C}_8\text{H}_{11}\text{O}$: 123.0805 (Calc. Mass 123.0804), **HRMS (ESI -)** PF_6^- : 144.9649 (Calc. Mass 144.9647).

4.2 Synthesis of the pyridinium ions

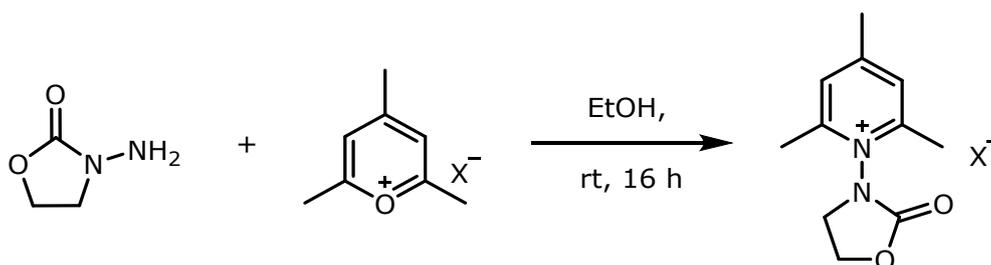
3-aminoxazolidin-2-one



Following a literature procedure,³ under nitrogen atmosphere 2-hydroxyethylhydrazine (2.3 mL, 33 mmol, 1 equiv.) was dissolved in dimethyl carbonate (4.4 mL, 53 mmol, 1.6 equiv.) at room temperature, then a solution of NaOH (119 mg, 3 mmol, 0.09 equiv.) in 0.6 mL of dry methanol was added. The resulting mixture was then stirred at 70°C using an oil bath. After 4 h, the reaction mixture was allowed to cool down to room temperature and the unreacted dimethyl carbonate was removed under reduced pressure. The resulting crude, a colourless oil which solidifies upon standing as yellowish solid, was purified by flash column chromatography on silica gel (CH_2Cl_2 : MeOH = 97:3). The desired product was recovered as a white solid in 79 % yield (2.65 g, 26 mmol). All the analytical data are in agreement with the literature.⁵

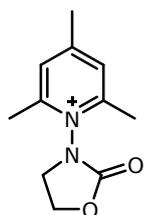
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 4.25 (t, J = 7.5 Hz, 2H), 4.01 (br s, 2H), 3.72 – 3.59 (t, J = 7.5 Hz, 2H).

General procedure A: Synthesis of the pyridinium ions



According to a literature procedure,¹ 3-amino-2-oxazolidinone (4.6 g, 45.3 mmol, 1 equiv.) was dissolved in 150 mL of EtOH (0.3 M) and the pyrylium ion (45.3 mmol, 1 equiv.) was added. The reaction mixture was stirred for 16 h at room temperature. Then, the system was cooled to 0 °C with an ice bath, Et₂O (70 mL) was added and the formation of a white precipitate was observed. The salt was filtered on a Buckner, washed with chilled Et₂O and dried. In analogy to a literature procedure,⁴ the crude was purified by crystallization from a CH₂Cl₂-EtOH solution (2:1 v/v ratio), and then completely precipitated via dropwise addition of Et₂O. The resulting solid was filtered on a Buckner.

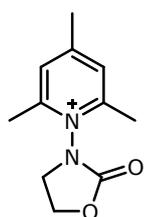
2,4,6-trimethyl-1-(2-oxooxazolidin-3-yl)pyridinium tetrafluoroborate 1a



Prepared according to the general procedure A on 11.4 mmol scale. The desired product was obtained as a white solid in 78 % of yield (2.62 g). All the analytical data are in agreement with the literature.⁵

¹H NMR (400 MHz, CD₃CN) δ 7.72 (s, 2H), 4.76 (td, *J* = 7.9, 1.7 Hz, 2H), 4.15 (td, *J* = 7.9, 1.2 Hz, 2H), 2.70 (s, 6H), 2.59 (s, 3H). ¹⁹F NMR (376 MHz, CD₃CN) δ -151.69, -151.70, -151.71, -151.74, -151.75, -151.76. ¹³C NMR (75 MHz, CD₃CN) δ 164.0, 158.8, 154.2, 129.9, 64.9, 45.9, 22.4, 19.4. HRMS (QTOF) C₁₁H₁₅N₂O₂: 207.1130 (Calc Mass 207.1128).

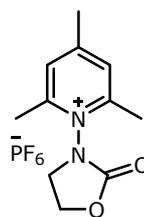
2,4,6-trimethyl-1-(2-oxooxazolidin-3-yl)pyridinium trifluoromethanesulfonate 1b



Prepared according to the general procedure A. The desired product was obtained as a white solid in 71 % of yield (11.5 g). All the analytical data are in agreement with the literature.⁵

¹H NMR (400 MHz, CD₃CN) δ 7.73 (s, 2H), 4.76 (td, *J* = 7.9, 1.7 Hz, 2H), 4.15 (td, *J* = 7.9, 1.7 Hz, 2H), 2.70 (s, 6H), 2.59 (s, 3H). ¹⁹F NMR (376 MHz, CD₃CN) δ -79.23. ¹³C NMR (75 MHz, CD₃CN) δ 164.0, 158.8, 154.2, 129.9, 64.9, 45.9, 22.4, 19.4. HRMS (QTOF) C₁₁H₁₅N₂O₂: 207.1131 (Calc. Mass 207.1128).

2,4,6-trimethyl-1-(2-oxooxazolidin-3-yl)pyridinium hexafluorophosphate

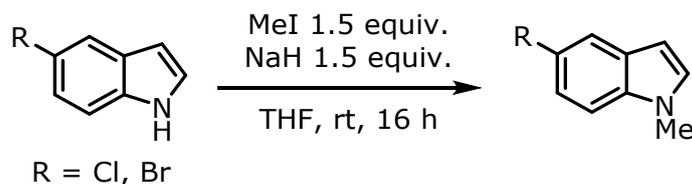


Prepared according to the general procedure A on 4.9 mmol scale. The desired product was obtained as a white solid in 71 % of yield (11.5 g).

¹H NMR (300 MHz, CD₃CN) δ 7.51 (s, 2H), 4.60 – 4.49 (m, 2H), 3.99 – 3.88 (m, 2H), 2.49 (s, 6H), 2.38 (s, 3H). ¹³C NMR (75 MHz, CD₃CN) δ 164.04, 158.77, 154.21, 129.91, 64.88, 45.81, 22.39, 19.35. ¹⁹F NMR (282 MHz, CD₃CN) δ -71.58, -74.09. ³¹P NMR (121 MHz, MeOD) δ -127.22, -133.03, -138.85, -144.68, -150.50, -156.33, -162.15. HRMS (ESI+) C₁₁H₁₅N₂O₂: 207.1134 (Calc. Mass 207.1128). HRMS (ESI-) PF₆: 144.9642 (Calc. Mass 144.9642).

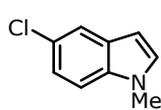
4.3 Synthesis of the Heteroarenes starting materials

General procedure B: Synthesis of 1-methyl-5-substituted indoles



Into a Schlenk 50 ml flask, 300 mg of NaH 60 % in mineral oil (8 mmol, 1.5 equiv.) was washed with 5 ml of pentane (3 times). Then, 18 mL of dry THF (0.3 M) were added and 1 g of 5-substituted indole (1 equiv.) was introduced. The mixture was cool down to 0 °C for 30 minutes and then 500 μ L of methyl iodide (8 mmol, 1.5 equiv.) were added through syringe. The reaction mixture was stirred overnight with the ice bath slowly warming up. After this time, the crude was diluted with 10 mL of H₂O and the aqueous phase was extracted with Et₂O (2 x 15 mL). The combined organic phases were dried with Na₂SO₄, and the solvent was removed under reduced pressure. The reaction crude was purified by column chromatography on silica gel.

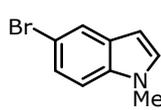
5-Chloro-1-methyl-1H-indole **2b**



Prepared according to the general procedure B on 6.6 mmol scale. The desired product was obtained as a yellow oil in 90 % yield (983 mg) after purification by flash column chromatography (Hexane-AcOEt 98:2 -> 95:5). All the analytical data are in agreement with the literature.⁶

¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 1.9 Hz, 1H), 7.23 (d, J = 8.6 Hz, 1H), 7.18 (dd, J = 8.7, 2.0 Hz, 1H), 7.07 (d, J = 3.1 Hz, 1H), 6.44 (d, J = 3.1 Hz, 1H), 3.78 (s, 3H). R_f = 0.3 (Hexane-EtOAc 9:1)

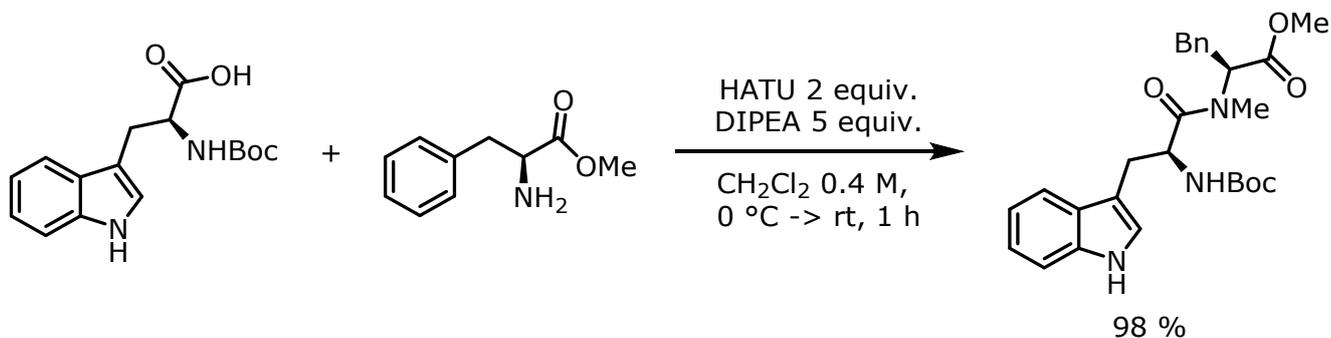
5-Bromo-1-methyl-1H-indole **2c**



Prepared according to the general procedure B on 5.1 mmol scale. The desired product was obtained as a yellow oil in 90 % yield (964 mg) after purification by flash column chromatography (Hexane-AcOEt 98:2 -> 95:5). All the analytical data are in agreement with the literature.⁶

¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 1.9 Hz, 1H), 7.31 (dd, J = 8.6, 1.9 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.05 (d, J = 3.1 Hz, 1H), 6.43 (dd, J = 3.1, 0.9 Hz, 1H), 3.77 (s, 3H). R_f = 0.25 (Hexane-AcOEt 9:1).

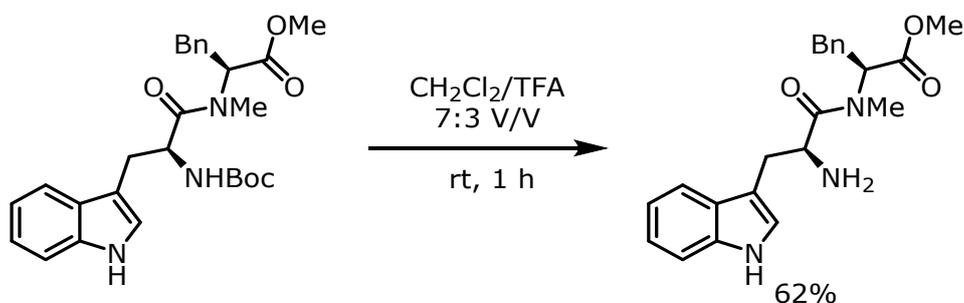
Boc-Trp-Phe-OMe **2m**



Into a Schlenk 25 ml flask, 1.5 g of Boc-L Tryptophan (5 mmol, 1 equiv.) and 1.3 g of *L*-Phenylalanine-OMe (6 mmol, 1.2 equiv.) were dissolved in 12.5 mL of dry CH₂Cl₂ (0.4 M). The mixture was cooled down to 0 °C and HATU (3.8 g, 10 mmol, 2 equiv.) was added. After 10 minutes, DIPEA (4.1 mL, 25 mmol, 5 equiv.) was introduced through syringe. The reaction mixture was stirred for 1 h with the ice bath slowly warming up to room temperature. After this time, the crude was diluted with 10 ml of H₂O and the aqueous phase was extracted with CH₂Cl₂ (2 x 15 ml). The combined organic phases were dried with Na₂SO₄, and the solvent was removed under reduced pressure and the crude was purified by column chromatography on silica gel (Hexane-AcOEt 7:3 → 1:1) to afford the desired product as a white solid in 98 % yield (2.58 g). All analytical data are in agreement with the literature.⁷

¹H NMR (300 MHz, CDCl₃) δ 8.70 (bs, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.08 (m, 5H), 7.02 (s, 1H), 6.81 (dd, *J* = 7.6, 1.9 Hz, 2H), 6.31 (d, *J* = 7.6 Hz, 1H), 5.17 (bs, 1H), 4.81 – 4.68 (m, 1H), 4.44 (m, 1H), 3.61 (s, 3H), 3.29 (m, 1H), 3.14 (dd, *J* = 14.4, 6.8 Hz, 1H), 2.94 (d, *J* = 5.9 Hz, 2H), 1.42 (s, 9H).

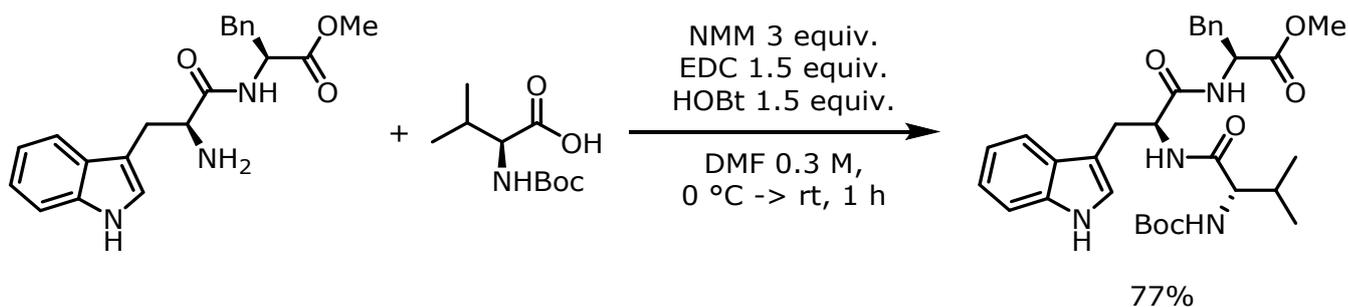
NH₂-Trp-Phe-OMe



Into a 25 mL flask, the dipeptide Boc-Trp-Phe-OMe (665 mg, 1.43 mmol, 1 equiv.) was dissolved in 10 mL of CH₂Cl₂. Then, 4 mL of TFA were added and the reaction mixture was stirred at room temperature for 1 hour. After this time, the volatiles were removed under reduced pressure. The residue was recovered with AcOEt and washed with a s.s. solution of NaHCO₃, water and brine. The combined organic phases were dried over Na₂SO₄ and dried under reduced pressure. The desired product was obtained in 62% yield (323 mg) without any further purification. All analytical data are in agreement with the literature.⁸

¹H NMR (300 MHz, CDCl₃) δ 8.03 (bs, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.23 – 7.08 (m, 5H), 7.01 (d, *J* = 2.3 Hz, 1H), 6.96 (dd, *J* = 6.5, 3.0 Hz, 2H), 4.96 – 4.83 (m, 1H), 3.73 – 3.68 (m, 4H), 3.26 (dd, *J* = 14.5, 4.2 Hz, 1H), 3.04 (dd, *J* = 6.1, 2.8 Hz, 2H), 2.89 (dd, *J* = 14.4, 8.5 Hz, 1H).

Boc-Val-Trp-Phe-OMe 2n

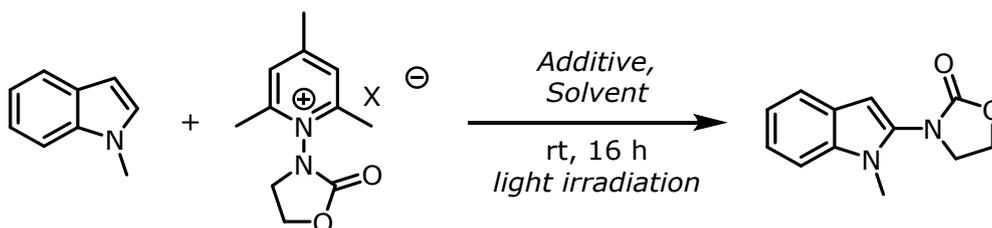


Into a Schlenk 10 mL flask, the *N*-Boc Valine (190 mg, 0.88 mmol, 1 equiv.) was dissolved in 1.5 mL of dry DMF (0.3 M) and the resulted solution was cooled down to 0 °C with an ice bath. Then, the *N*-methylmorpholine (NMM, 290 µL, 2.64 mmol, 3 equiv.), EDC·HCl (250 mg, 1.32 mmol, 1.5 equiv.) and HOBT (180 mg, 1.32 mmol, 1.5 equiv.) were added and the reaction mixture was stirred at 0 °C for 5 minutes. The dipeptide NH₂-Trp-Phe-OMe (323 mg, 0.88 mmol, 1 equiv.) was dissolved in 1.5 mL of dry DMF and transferred to the mixture. The reaction mixture was heat up at 50 °C overnight with an oil bath. After this time, the DMF was removed under high vacuum overnight. Then, the reaction crude was dissolved in 10 mL of AcOEt and the organic phase was washed with water (10 mL X 3). The organic phase was dried over Na₂SO₄ and the volatiles were removed under reduce pressure. The reaction crude was purified by column chromatography on silica gel (CH₂Cl₂-Acetone 9:1 -> 8:2) to afford the desired product as an orange solid in 77 % yield (385 mg).

¹H NMR (300 MHz, CDCl₃) δ 8.18 (s, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.21 – 7.08 (m, 5H), 7.04 (d, *J* = 2.1 Hz, 1H), 6.78 (d, *J* = 7.0 Hz, 2H), 6.65 (d, *J* = 7.7 Hz, 1H), 6.14 (d, *J* = 7.7 Hz, 1H), 4.98 (d, *J* = 8.5 Hz, 1H), 4.74 – 4.62 (m, 2H), 3.98 – 3.87 (m, 1H), 3.61 (s, 3H), 3.36 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.07 (dd, *J* = 14.5, 8.0 Hz, 1H), 2.89 (d, *J* = 5.9 Hz, 2H), 2.06 (dq, *J* = 13.3, 6.7 Hz, 1H), 1.43 (s, 9H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 171.50, 171.31, 170.65, 155.96, 136.41, 135.71, 129.22, 128.60, 127.50, 127.13, 123.68, 122.52, 120.06, 119.03, 111.42, 110.53, 80.11, 60.17, 53.85, 53.45, 52.30, 37.91, 30.93, 28.43, 19.32, 17.45, 0.12. **HRMS (ESI +)** C₃₁H₄₀N₄O₆Na: 587.2842 (Calc. Mass 587.2846). **R_f** = 0.8 (CH₂Cl₂-Acetone 1:1).

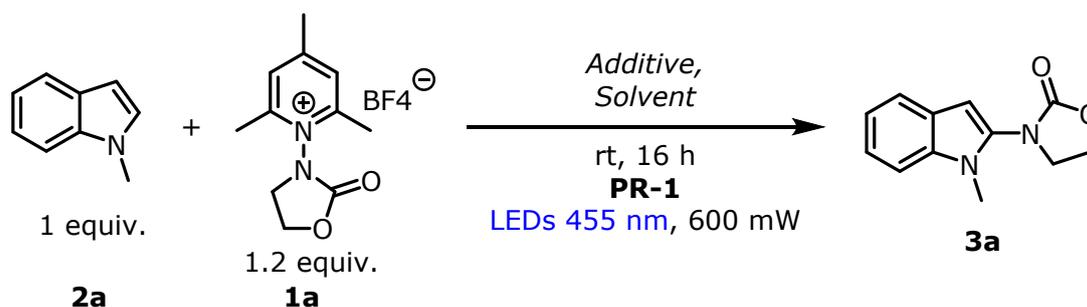
5 Screening of the reaction conditions

General Procedure C



Into a 7 mL vial, the nitrogen radical precursor **1a-c** (1 equiv., 0.2 mmol or 1.2 equiv. 0.24 mmol), the 1-methylindole **2a** (2 equiv., 0.4 mmol, 50 μ L or 1 equiv. 0.2 mmol, 25 μ L) and the additive (5 equiv., 1 mmol or 1 equiv. 0.2 mmol) were introduced. The vial was sealed with a septum cap and three nitrogen-vacuum cycles were done. The previously degassed solvent was added and the reaction mixture was irradiated with **PR-1** or **PR-2** for the appropriate time. After that, the volatiles were removed under reduced pressure and the crude was purified with flash column chromatography Hexane-AcOEt 7:3.

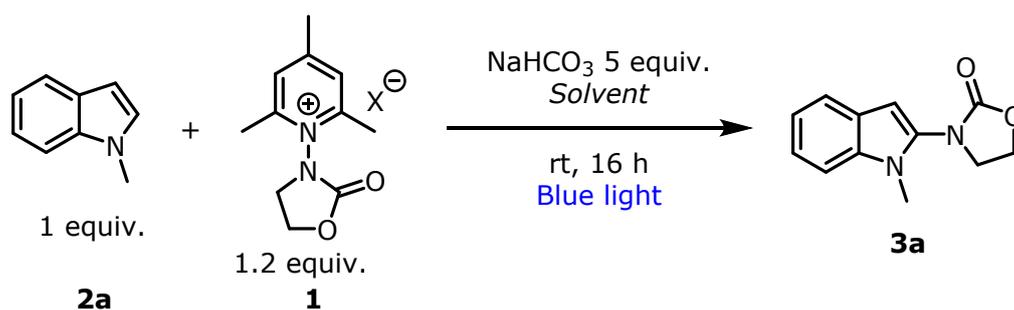
- Screening of the additives



Entry	Additive (equiv.)	Solvent (M)	3a Yield (%)
1	(0.1)	DMSO (0.1)	19
2	(1)	ACN (0.1)	0
3	NaHCO ₃ (5)	ACN (0.1)	38
4	NaHCO ₃ (5)	ACN (0.05)	60
5	Na ₂ CO ₃ (5)	ACN (0.05)	22
6	Na ₂ HPO ₄ (5)	ACN (0.05)	32
7	KHCO ₃ (5)	ACN (0.05)	8
8	K ₂ CO ₃ (5)	ACN (0.05)	0
9	K ₂ HPO ₄ (5)	ACN (0.05)	12
10	Cs ₂ CO ₃ (5)	ACN (0.05)	0

Table 1 Additive screening.

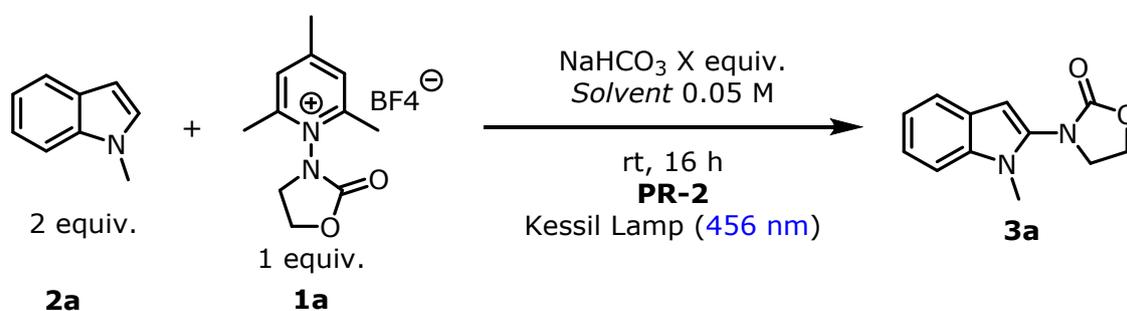
- Nitrogen radical precursor screening and solvent screening



Entry	Set-Up	Counterion X	Solvent (M)	3a Yield (%)
1	PR-1	TfO ⁻	ACN (0.05)	36
2	PR-1	BF ₄ ⁻	ACN (0.05)	60
3	PR-2	BF ₄ ⁻	ACN (0.05)	61
4	PR-2	BF ₄ ⁻	DMSO (0.1)	65
5	PR-2	BF ₄ ⁻	H ₂ O (0.05)	20
6	PR-2	TfO ⁻	H ₂ O (0.05)	43
7	PR-2	BF ₄ ⁻	H ₂ O/ACN 8/2 (0.05)	63
8	PR-2	TfO ⁻	H ₂ O/ACN 8/2 (0.05)	18

Table 2 Nitrogen radical precursor and solvent screening

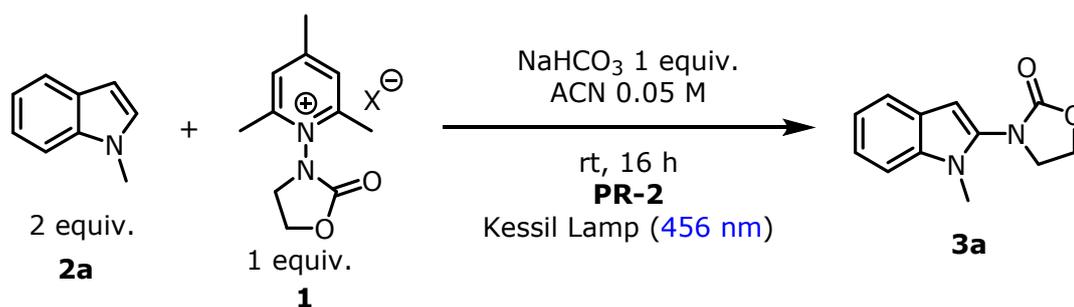
- Stoichiometry screening



Entry	NaHCO ₃ (equiv.)	Solvent	3a Yield (%)
1	3	H ₂ O/ACN 8/2	67
2	1	H ₂ O/ACN 8/2	70
3	1	ACN	78
4	1	DMSO	65
5	0.2	H ₂ O/ACN 8/2	14

Table 3 stoichiometry screening

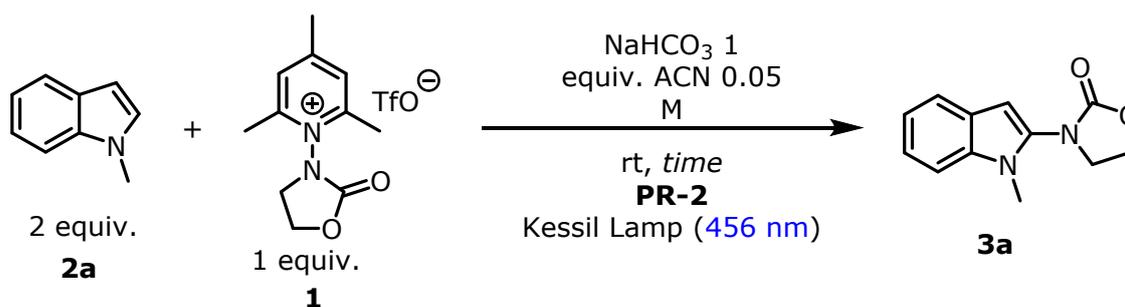
- Counterion screening on the optimized conditions



Entr y	Counterion	3a Yield (%)
1	BF ₄ ⁻	78
2	PF ₆ ⁻	51
3	TfO ⁻	81

Table 4 Counterion screening

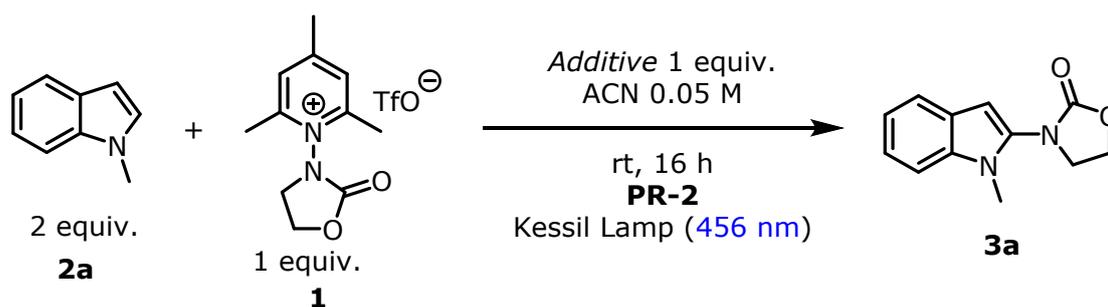
- Time



Entr y	Time (h)	3a Yield (%)
1	2	47
2	4	43
3	8	61
4	16	81

Table 5 Reaction Time screening

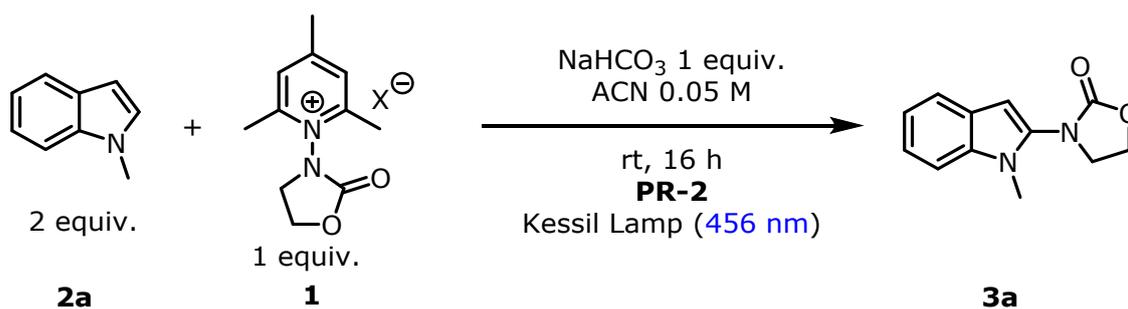
- Another additives screening on the optimized conditions



Entr y	Additiv e	3a Yield (%)
1	Li ₂ CO ₃	66
2	LiCl	66
3	NaCl	70
4	KCl	65

Table 6 screening of other salts as additives

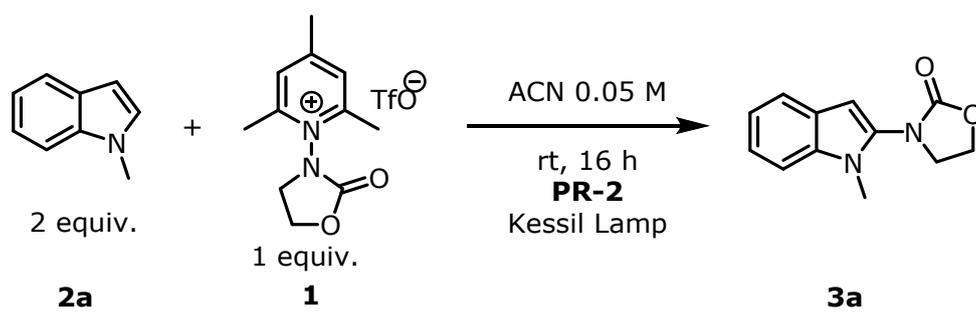
- -Control experiments



Entr y	Precurso r	Notes	3a Yield (%)
1	1b	no light	< 1
2	1b	no light, 70 °C	< 1
3	1b	no NaHCO ₃	66
4	1a	no light	< 1
5	1a	no light, 70 °C	< 1
6	1a	no NaHCO ₃	< 1
7	1c	no NaHCO ₃	< 1

Table 7 Control experiments

- Wavelength screening

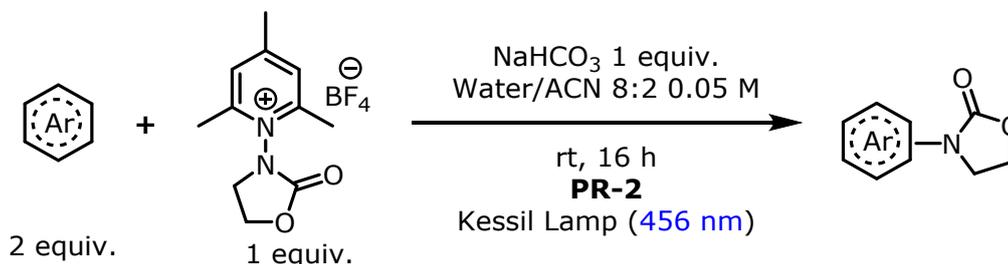


Entry	λ (nm)	Isolated Yield (%)
1	427	55
2	390	50
3	456	66

Table 8 Wavelength screening

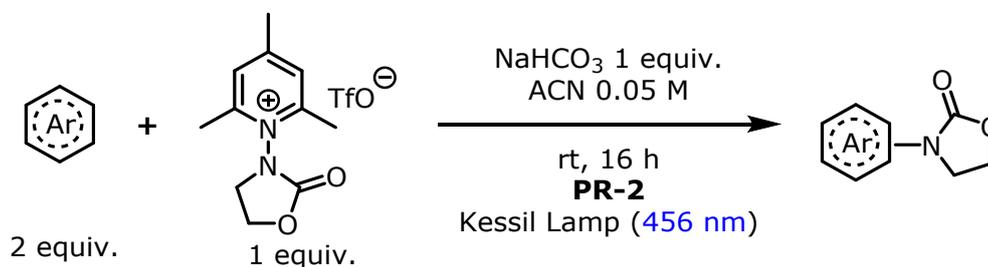
6 Substrate scope

General Procedure D: Photochemical addition of oxazolidinones radicals to heteroarenes and arenes with NaHCO₃ in water/ACN



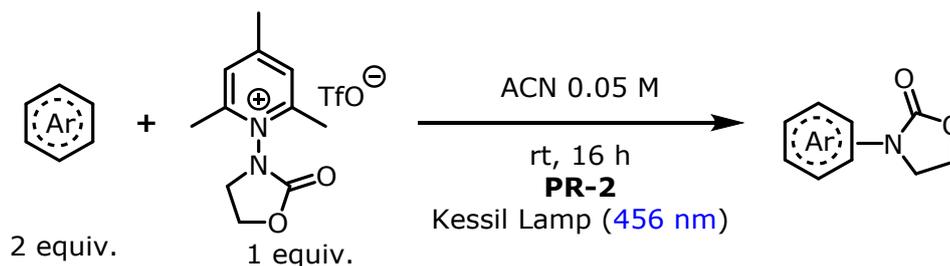
Into a 7 ml vial, the nitrogen radical precursor **1a** (59 mg, 1 equiv., 0.2 mmol), the heteroarenes **2** (2 equiv., 0.4 mmol) and NaHCO₃ (1 equiv., 0.2 mmol) were introduced. The vial was sealed with a septum cap and three nitrogen-vacuum cycles were done. 3.2 ml of previously degassed water and 0.8 mL of previously degassed ACN were added. The reaction mixture was irradiated for 16 hours with **PR-2** (Blue Kessil Lamp 100% Power, 456 nm, the vial was positioned 4 cm from the light source) and the system was cool down with a fan. After that time, the liquids were removed under reduced pressure and the crude was purified with flash column chromatography.

General Procedure E: Photochemical addition of oxazolidinones radicals to heteroarenes and arenes with NaHCO₃ in ACN



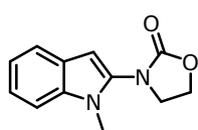
Into a 7 ml vial, the nitrogen radical precursor **1b** (71 mg, 1 equiv., 0.2 mmol), the heteroarenes **2** (2 equiv., 0.4 mmol) and NaHCO₃ (1 equiv., 0.2 mmol) were introduced. The vial was sealed with a septum cap and three nitrogen-vacuum cycles were done. 4 ml of dry and previously degassed ACN were added. The reaction mixture was irradiated for 16 hours with **PR-2** (Blue Kessil Lamp 100% Power, 456 nm, the vial was positioned 4 cm from the light source) and the system was cool down with a fan. After that time, the ACN was removed under reduced pressure and the crude was purified with flash column chromatography.

General Procedure F: Photochemical addition of oxazolidinones radicals to heteroarenes and arenes



Into a 7 ml vial, the nitrogen radical precursor **1b** (71 mg, 1 equiv., 0.2 mmol) and the heteroarenes **2** (2 equiv., 0.4 mmol). The vial was sealed with a septum cap and three nitrogen-vacuum cycles were done. 4 ml of dry and previously degassed ACN were added. The reaction mixture was irradiated for 16 hours with **PR-2** (Blue Kessil Lamp 100% Power, 456 nm, the vial was positioned 4 cm from the light source) and the system was cool down with a fan. After that time, the ACN was removed under reduced pressure and the crude was purified with flash column chromatography.

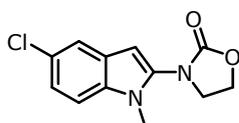
3-(1-methyl-1H-indol-2-yl)oxazolidin-2-one **3a**



Starting from the commercially available 1-methyl-1H-indole (55 μL , 2 equiv., 0.4 mmol), 3-(1-methyl-1H-indol-2-yl)oxazolidin-2-one was prepared according to General Procedure D, E and F. The crude mixture was purified by flash column chromatography on silica gel (Hexane-AcOEt 7:3 \rightarrow 6:4) afford the desired product as yellowish solid in 70% yield with Procedure D (30 mg), in 81% yield with Procedure E (35 mg), in 66% yield with Procedure F (28.5 mg). All the analytical data are in agreement with the literature.⁵

¹H NMR (300 MHz, CDCl_3) δ 7.61 (d, $J = 7.8$ Hz, 1H), 7.38 – 7.27 (m, 2H), 7.16 (ddd, $J = 8.0, 6.9, 1.2$ Hz, 1H), 6.43 (s, 1H), 4.61 (dd, $J = 8.7, 7.0$ Hz, 2H), 4.07 (dd, $J = 8.7, 7.1$ Hz, 2H), 3.72 (s, 3H).

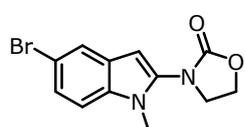
3-(5-chloro-1-methyl-1H-indol-2-yl)oxazolidin-2-one **3b**



Starting from the synthesized 5-chloro-1-methyl-1H-indole (66 mg, 2 equiv., 0.4 mmol), 3-(5-chloro-1-methyl-1H-indol-2-yl) oxazolidin-2-one was prepared according to General Procedure D. The crude mixture was purified by flash column chromatography on silica gel (Hexane-AcOEt 8:2 \rightarrow 1:1) afford the desired product as a white solid in 56% yield (28.1 mg). All the analytical data are in agreement with the literature.⁵

¹H NMR (300 MHz, CDCl_3) δ 7.53 (d, $J = 1.5$ Hz, 1H), 7.24 – 7.17 (m, 2H), 6.33 (s, 1H), 4.60 (dd, $J = 8.7, 7.0$ Hz, 2H), 4.06 (dd, $J = 8.7, 7.0$ Hz, 2H), 3.67 (s, 3H).

3-(5-bromo-1-methyl-1H-indol-2-yl)oxazolidin-2-one **3c**

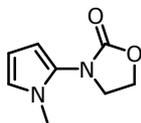


Starting from the synthesized 5-bromo-1-methyl-1H-indole (84 mg, 2 equiv., 0.4 mmol), 3-(5-bromo-1-methyl-1H-indol-2-yl) oxazolidin-2-one was prepared according to General Procedure D, E and F. The crude mixture was purified by flash column chromatography on silica gel (Hexane-AcOEt 7:3 \rightarrow 6:4) afford the desired product as a yellowish oil in 57% yield with Procedure D (33.6 mg),

in 75% yield with Procedure E (44 mg), in 78% yield with Procedure F (46 mg). All the analytical data are in agreement with the literature.⁵

¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 1.6 Hz, 1H), 7.32 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.18 (d, *J* = 8.7 Hz, 1H), 6.32 (d, *J* = 0.8 Hz, 1H), 4.64 – 4.55 (m, 2H), 4.11 – 4.00 (m, 2H), 3.67 (s, 3H).

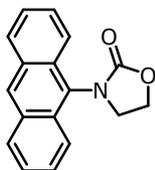
3-(1-methyl-1*H*-pyrrol-2-yl)oxazolidin-2-one **3d**



Starting from the commercially available 1-methylpyrrole (36 μL, 2 equiv., 0.4 mmol), 3-(1-methyl-1*H*-pyrrol-2-yl)oxazolidin-2-one was prepared according to General Procedure D, E and F. The crude mixture was purified by flash column chromatography on silica gel (Hexane-AcOEt 8:2 -> 1:1) afford the desired product as a yellow oil in 48% yield with Procedure D (16 mg), in 10% yield with Procedure E (3 mg), in 15% yield with Procedure F (4 mg). All the analytical data are in agreement with the literature.⁵

¹H NMR (400 MHz, CDCl₃) δ 6.54 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.09 (dd, *J* = 3.8, 3.0 Hz, 1H), 6.03 (dd, *J* = 3.8, 1.9 Hz, 1H), 4.55 – 4.42 (m, 2H), 3.94 – 3.84 (m, 2H), 3.53 (s, 3H).

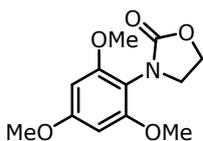
3-(anthracen-9-yl)oxazolidin-2-one **3e**



Starting from the commercially available anthracene (71 mg, 2 equiv., 0.4 mmol), 3-(anthracen-9-yl)oxazolidin-2-one was prepared according to General Procedure E and F. The crude mixture was purified by flash column chromatography on silica gel (Hexane-Toluene 1:1 -> Hexane-AcOEt 6:4 -> 4:6) afford the desired product as a white solid in 44% yield with Procedure E (23 mg), in 23% yield with Procedure F (12.2 mg). All the analytical data are in agreement with the literature.⁵

¹H NMR (400 MHz, CDCl₃) δ 8.52 (s, 1H), 8.11 – 8.04 (m, 2H), 8.00 (dq, *J* = 8.8, 1.0 Hz, 2H), 7.59 (ddd, *J* = 8.8, 6.6, 1.3 Hz, 2H), 7.51 (ddd, *J* = 7.9, 6.6, 1.2 Hz, 2H), 4.87 – 4.77 (m, 2H), 4.21 – 4.10 (m, 2H).

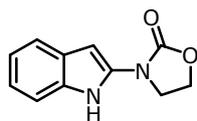
3-(2,4,6-trimethoxyphenyl)oxazolidin-2-one **3f**



Starting from the commercially available 1,3,5-trimethoxybenzene (67 mg, 2 equiv., 0.4 mmol), 3-(2,4,6-trimethoxyphenyl)oxazolidin-2-one was prepared according to General Procedure D, and E. The crude mixture was purified by flash column chromatography on silica gel (Hexane-AcOEt 1:1 -> 4:6) afford the desired product as a white solid in 6% yield with Procedure D (3 mg), in 20% yield with Procedure E (7 mg). All the analytical data are in agreement with the literature.⁵

¹H NMR (300 MHz, CDCl₃) δ 6.13 (s, 2H), 4.47 (dd, *J* = 9.0, 7.2 Hz, 2H), 3.80 (d, *J* = 3.7 Hz, 11H).

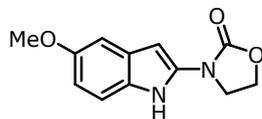
3-(1*H*-indol-2-yl)oxazolidin-2-one **3g**



Starting from the commercially available 1*H*-indole (47 mg, 2 equiv., 0.4 mmol), 3-(1*H*-indol-2-yl)oxazolidin-2-one was prepared according to General Procedure D, E and F. The crude mixture was purified by flash column chromatography on silica gel (Hexane-AcOEt 7:3 -> 6:4) afford the desired product as yellowish solid in 53% yield with Procedure D (21 mg), in 30% yield with Procedure E (12.2 mg), in 12% yield with Procedure F (5 mg). All the analytical data are in agreement with the literature.⁵

¹H NMR (300 MHz, CDCl₃) δ 9.94 (bs, 1H), 7.50 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.12 (dtd, *J* = 14.1, 7.2, 1.4 Hz, 2H), 5.78 (d, *J* = 1.3 Hz, 1H), 4.68 – 4.57 (m, 3H), 4.20 – 4.02 (m, 3H).

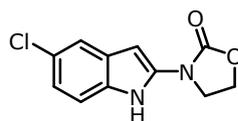
3-(5-methoxy-1*H*-indol-2-yl)oxazolidin-2-one **3h**



Starting from the commercially available 5-Methoxyindole (59 mg, 2 equiv., 0.4 mmol), 3-(5-methoxy-1*H*-indol-2-yl)oxazolidin-2-one was prepared according to General Procedure D and F. The crude mixture was purified by flash column chromatography on silica gel (Hexane-AcOEt 7:3 -> 6:4) afford the desired product as yellowish solid in 18% yield (8.4 mg) with procedure D and 31% yield (14.4 mg) with procedure F.

¹H NMR (300 MHz, CD₃CN) δ 9.95 (s, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 6.98 (d, *J* = 2.5 Hz, 1H), 6.70 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.80 (dd, *J* = 2.2, 0.9 Hz, 1H), 4.58 – 4.45 (m, 3H), 4.09 – 3.97 (m, 2H), 3.78 (s, 4H). **¹³C NMR** (75 MHz, CD₃CN) δ 155.37, 154.48, 135.86, 129.37, 128.25, 128.16, 111.57, 109.70, 101.52, 85.26, 63.09, 55.18, 44.43. **HRMS (ESI+)** C₁₂H₁₂N₂O₃Na: 255.0745 (Calc. Mass 255.0746).

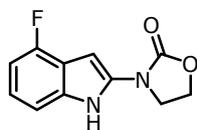
3-(5-chloro-1*H*-indol-2-yl)oxazolidin-2-one **3i**



Starting from the commercially available 5-Chloroindole (61 mg, 2 equiv., 0.4 mmol), 3-(5-chloro-1*H*-indol-2-yl)oxazolidin-2-one was prepared according to General Procedure D and F. The crude mixture was purified by flash column chromatography on silica gel (Hexane-AcOEt 7:3 -> 6:4) afford the desired product as yellowish solid in 33% yield (15.6 mg) with procedure D and in 18% yield (8.7 mg) with procedure F.

¹H NMR (300 MHz, Acetone) δ 10.69 (s, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.42 (s, 1H), 7.02 (dd, *J* = 8.6, 1.8 Hz, 1H), 5.90 (s, 1H), 4.65 (td, *J* = 8.1, 1.7 Hz, 2H), 4.18 (td, *J* = 8.1, 1.7 Hz, 2H). **¹³C NMR** (75 MHz, CDCl₃) δ 155.23, 135.50, 131.43, 128.25, 125.92, 121.31, 118.71, 111.70, 84.90, 62.81, 44.24. **HRMS (ESI+)** C₁₁H₁₀N₂O₂Cl: 237.0424 (Calc. Mass 237.0431).

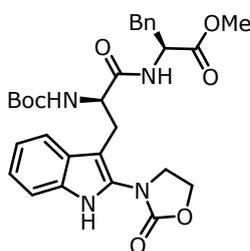
3-(4-fluoro-1*H*-indol-2-yl)oxazolidin-2-one **3l**



Starting from the commercially available 4-fluoroindole (54 mg, 2 equiv., 0.4 mmol), 3-(4-fluoro-1*H*-indol-2-yl)oxazolidin-2-one was prepared according to General Procedure D and F. The crude mixture was purified by flash column chromatography on silica gel (Hexane-AcOEt 7:3 -> 6:4) afford the desired product as yellowish solid in 37 % yield (16.3 mg) with procedure D and in 7% yield (3 mg) with procedure F.

¹H NMR (300 MHz, MeOD) δ 7.17 (d, *J* = 8.1 Hz, 1H), 6.98 (td, *J* = 8.0, 5.1 Hz, 1H), 6.69 (dd, *J* = 10.5, 7.8 Hz, 1H), 6.01 (s, 1H), 4.65 – 4.54 (m, 2H), 4.19 – 4.08 (m, 3H). **¹⁹F NMR** (282 MHz, CDCl₃) δ -124.04. **¹³C NMR** (75 MHz, MeOD) 151.36, 141.16, 120.48 (d, *J* = 7.7 Hz), 117.56, 110.38, 106.78, 103.97 (d, *J* = 18.9 Hz), 100.01, 81.51, 63.03, 44.73. **HRMS (ESI-)** C₁₁H₈N₂O₂F: 219.0569 (Calc. Mass 219.0570).

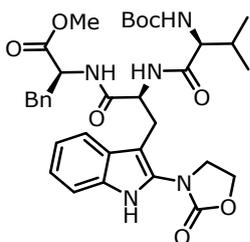
methyl ((R)-2-((tert-butoxycarbonyl)amino)-3-(2-(2-oxooxazolidin-3-yl)-1H-indol-3-yl)propanoyl)-L-phenylalaninate **3m**



Starting from the synthesized dipeptide Boc-Trp-Phe-OMe (186 mg, 2 equiv., 0.4 mmol), methyl ((R)-2-((tert-butoxycarbonyl)amino)-3-(2-(2-oxooxazolidin-3-yl)-1H-indol-3-yl)propanoyl)-L-phenylalaninate was prepared according to General Procedure E. The crude mixture was purified by flash column chromatography on silica gel (CH₂Cl₂-Acetone 1:1) afford the desired product as a white solid in 48% yield (52.8 mg)

¹H NMR (300 MHz, CDCl₃) δ 9.48 (bs, 1H), 7.58 – 7.49 (m, 1H), 7.21 – 7.12 (m, 3H), 7.05 (d, *J* = 4.2 Hz, 3H), 6.96 – 6.88 (m, 2H), 6.44 (bs, 1H), 5.78 (bs, 1H), 4.66 – 4.57 (m, 1H), 4.58 – 4.45 (m, 3H), 4.15 (t, *J* = 7.2 Hz, 2H), 3.55 (s, 3H), 3.18 – 3.10 (m, 2H), 3.00 (d, *J* = 12.9 Hz, 1H), 2.91 (d, *J* = 6.3 Hz, 1H), 2.80 (s, 2H), 1.36 (s, 9H). **¹³C NMR** (75 MHz, CDCl₃) δ 171.35, 171.23, 157.59, 155.65, 135.81, 133.25, 130.98, 129.46, 129.28, 128.89, 128.56, 127.06, 122.50, 121.33, 120.13, 118.48, 111.12, 100.69, 80.06, 68.26, 63.27, 52.24, 46.66, 38.70, 38.12, 28.34, 27.48. **HRMS (ESI+)** C₂₉H₃₄N₄O₇Na: 573.2321 (Calc. Mass 573.2325).

methyl ((S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-methylbutanamido)-3-(2-(2-oxooxazolidin-3-yl)-1H-indol-3-yl)propanoyl)-L-phenylalaninate **3n**

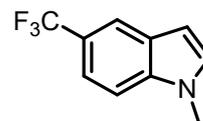
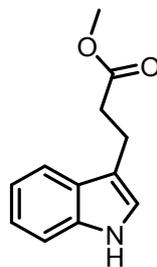
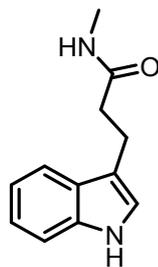
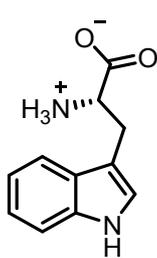
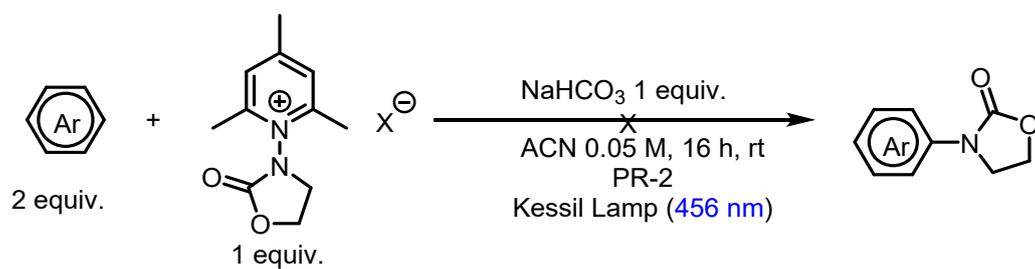


Starting from the synthesized tripeptide Boc-Val-Trp-Phe-OMe (133 mg, 2 equiv., 0.23 mmol), methyl ((S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-methylbutanamido)-3-(2-(2-oxooxazolidin-3-yl)-1H-indol-3-yl)propanoyl)-L-phenylalaninate was prepared according to General Procedure E irradiating at 390 nm instead of 456 nm. The crude mixture was purified by flash column chromatography on silica gel (CH₂Cl₂-Acetone 1:1) afford

the desired product as a white solid in 62% yield (48.5 mg).

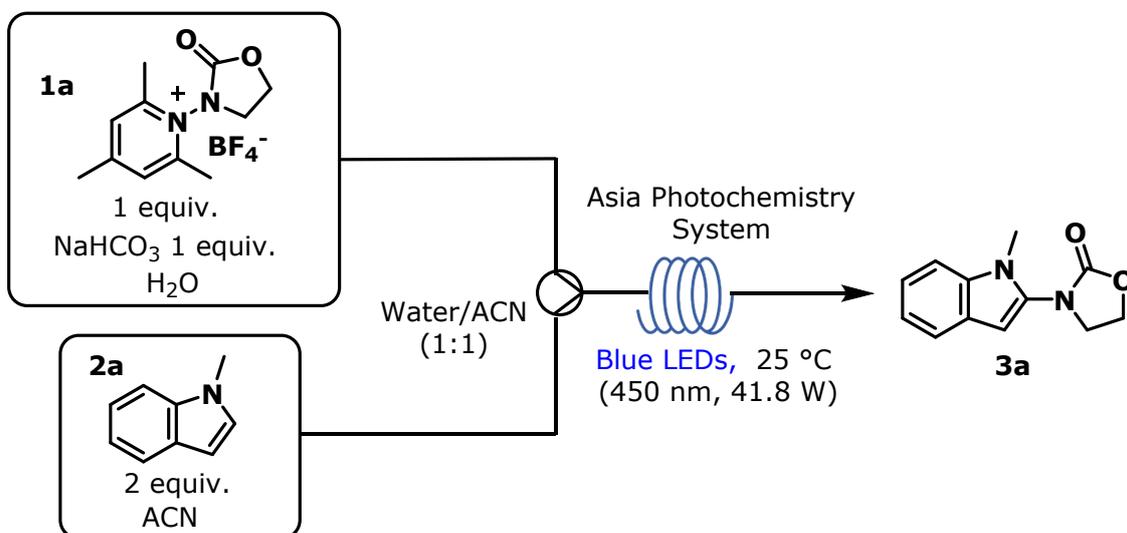
¹H NMR (300 MHz, CDCl₃) δ 9.66 (s, 1H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.37 (d, *J* = 6.9 Hz, 1H), 7.24 – 7.04 (m, 5H), 6.92 (d, *J* = 7.7 Hz, 2H), 6.58 (d, *J* = 7.0 Hz, 1H), 5.05 (d, *J* = 8.3 Hz, 1H), 4.74 (q, *J* = 7.6 Hz, 1H), 4.57 (q, *J* = 6.3 Hz, 1H), 4.50 (t, *J* = 8.2 Hz, 2H), 4.13 (p, *J* = 8.4 Hz, 2H), 3.97 – 3.93 (m, 1H), 3.53 (s, 3H), 3.16 (t, *J* = 7.7 Hz, 2H), 3.01 – 2.81 (m, 2H), 1.95 (td, *J* = 6.8, 5.2 Hz, 1H), 1.40 (s, 9H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.62 (d, *J* = 6.9 Hz, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 172.16, 171.09, 170.84, 157.57, 157.41, 155.97, 135.83, 133.36, 129.64, 129.24, 128.59, 127.05, 122.63, 121.39, 120.31, 118.65, 111.21, 100.97, 79.89, 63.32, 59.91, 53.74, 53.43, 52.24, 46.78, 38.02, 31.13, 28.39, 26.80, 24.22, 19.25, 17.08. **HRMS (ESI+)** C₃₄H₄₃N₅O₈Na: 672.3003 (Calc. Mass 672.3009).

7 Unsuccessful results



8 N -oxazolidinone addition to 1-methylindole in flow conditions

General Procedure G: tests with precursor **1a**



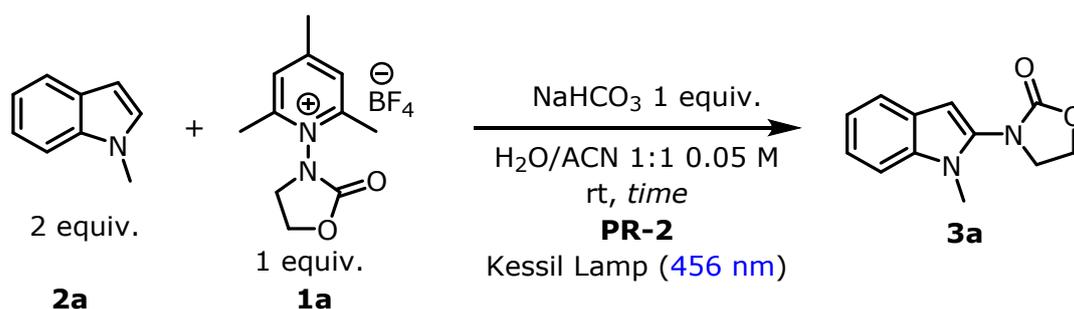
Coil Reactor: 80 cm x 0.05'' in PFA, 981 μ L of volume

Into a 10 mL hart shape flask, 112 mg of the nitrogen radical precursor **1a** (1 equiv., 0.4 mmol), 33.6 mg (1 equiv., 0.4 mmol) of NaHCO₃ were dissolved into 4 mL of previously degassed H₂O. Into another 10 mL hart shape flask, 100 μ L of 1-methylindole **2a** (2 equiv. 0.8 mmol) were dissolved into 4 mL 0.05 M or 2 mL 0.1 M of previously degassed ACN. The two solutions are stored under inert atmosphere and directly pumped from the flask using *Syrris ASIA Syringe Pumps*. The whole coil reactor is filled with the reaction mixture mixture and irradiated with LEDs 456 nm. The first reactor volume is discharged, then 4000 μ L (for 0.05 M) or 2000 μ L (for 0.1 M) are collected, the volatiles are removed under reduced pressure and the reaction crude was purified with flash column chromatography on silica gel (Hexane-AcOEt 7:3 -> 6:4).

Entr y	Concentration (M)	Residence Time (min)	3a Yield (%)
1	0.05	15	23
2	0.05	30	28
3	0.05	45	40
4	0.05	60	43
5	0.1	45	40

Table 9 results of the photo-flow reaction

General Procedure H: Batch Comparison

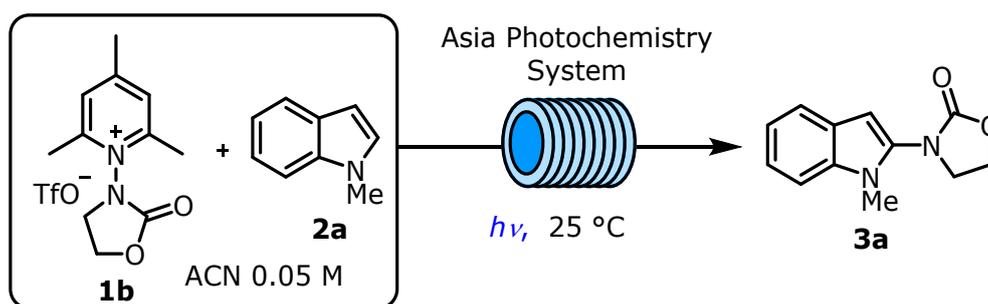


Into a 7 ml vial, the nitrogen radical precursor **1a** (59 mg, 1 equiv., 0.2 mmol), the 1-methylindole **2a** (50 μL , 2 equiv., 0.4 mmol) and NaHCO_3 (1 equiv., 0.2 mmol) were introduced. The vial was sealed with a septum cap and three nitrogen-vacuum cycles were done. 2 ml of previously degassed water and 2 mL of previously degassed ACN were added. The reaction mixture was irradiated with **PR-2** (Blue Kessil Lamp 100% Power, 456 nm, the vial was positioned 4 cm from the light source) and the system was cool down with a fan. After that time, the liquids were removed under reduced pressure and the crude was purified with flash column chromatography on silica gel (Hexane-AcOEt 7:3 \rightarrow 6:4).

Entry	Time (h)	3a Yield (%)
1	2	30
2	4	39
3	8	31
4	16	57

Table 10 Time screening for the flow comparison.

General Procedure I: tests with precursor **1b**



Coil Reactor: 80 cm x 0.05" in PFA, 981 μL of volume

Into a 10 mL hart shape flask, 143 mg of the nitrogen radical precursor **1b** (1 equiv., 0.4 mmol) and 100 μL of 1-methylindole (2 equiv., 0.8mmol) were dissolved into 4 mL of previously degassed ACN. The solution is stored under inert atmosphere and directly pumped from the flask using a *Syrris ASIA Syringe Pump*. The whole coil reactor is filled with the reaction mixture and irradiated with LEDs (456 or 405 nm). The first reactor volume is discharged, then 4000 μL are collected, the volatiles are removed under reduced pressure and the reaction crude was purified with flash column chromatography on silica gel (Hexane-AcOEt 7:3 \rightarrow 6:4).

Irradiation at 456 nm

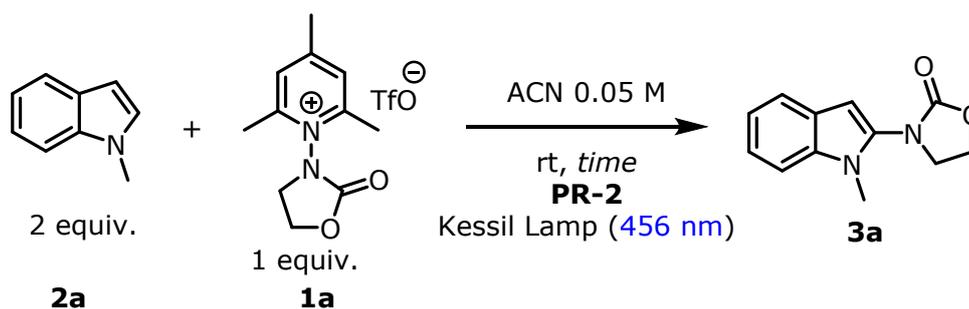
Entr y	Residence Time (min)	3a Yield (%)
1	15	26
2	30	43
3	45	50
4	60	51

Irradiation at 405 nm

Entr y	Residence Time (min)	3a Yield (%)
1	15	42
2	30	53
3	45	65
4	60	63

Table 11 Irradiation at 456 nm and 405 nm.

Batch Comparison



Prepared according to General Procedure F. The crude mixture was purified by flash column chromatography on silica gel (Hexane-AcOEt 7:3 -> 6:4) afford the desired product as yellowish solid.

Entr y	Time (h)	Isolated Yield (%)
1	2	20
2	4	30
3	8	50
4	16	66

Table 12 Time screening for the flow comparison.

8.1 Productivity and Space Time Yield Calculations

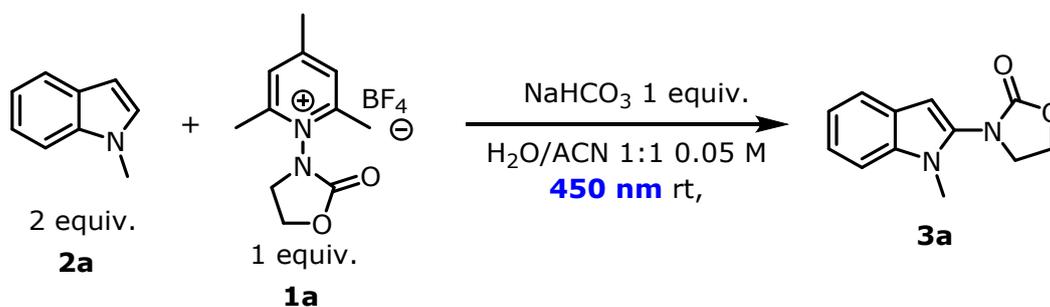
The performances of the experiments under continuous conditions were evaluated in terms of productivity and space-time yield and compared to the same values calculated for the batch reactions. Productivity is defined as the mmol of product per hour provided by the system:

$$\text{Productivity} = \frac{\text{mmol limiting reagent} \cdot \text{yield}}{\text{time (h)}}$$

The space-time yield (STY) instead, is defined as the mmol of product per hour, per unit of volume:

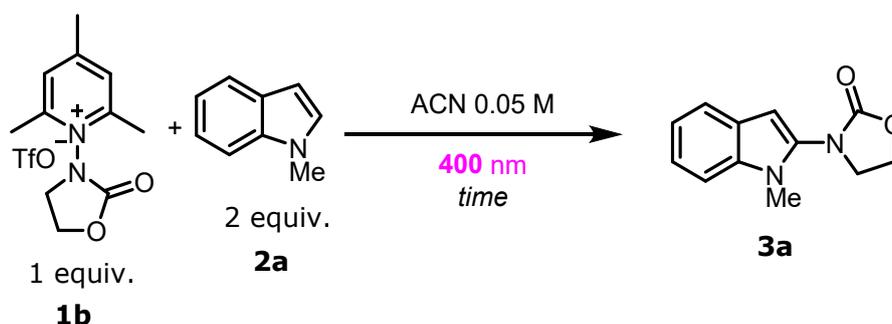
$$\text{STY} = \frac{\text{mmol limiting reagent} \cdot \text{yield}}{\text{time (h)} \cdot \text{volume (ml)}}$$

Time in batch condition: reaction time. Time in flow condition: time to pass the same mmol of limiting agent.



Entry	3a Yield (%)	Productivity (mmolh ⁻¹)	Rel. factor	STY (mmolh ⁻¹ ml ⁻¹)	Rel. factor
Batch 1	70	0.0088	-	0.0350	-
Batch 2	57	0.0071	1	0.0285	1
Flow 981 μL	40	0.06061	8.5	0.0855	8.5

Table 13 Batch 1: optimized batch conditions (General procedure D; H₂O/ACN 8/2 0.05 M, 2 equivalents 1-methylindole **2a**). Batch 2: batch procedure performed with the optimized flow conditions (General procedure H, H₂O/ACN 1/1 0.05 M, 2 equivalents 1-methylindole **2a**). Flow 981 μL: entry 5 table 9



Entry	3a Yield (%)	Productivity (mmolh ⁻¹)	Rel. factor	STY (mmolh ⁻¹ ml ⁻¹)	Rel. factor
Batch 1	66	0.0083	-	0.0330	-
Batch 2	50	0.0063	1	0.025	1
Flow 981 μL	65	0.0985	16	0.0695	3

Table 14 Batch 1: optimized batch conditions (General procedure F; ACN 0.05 M, 2 equivalents 1-methylindole **2a**, λ = 456 nm). Batch 2: batch procedure performed with the optimized flow conditions (ACN 0.05 M, 2 equivalents 1-methylindole **2a**, λ = 390 nm) entry 2 table 8. Flow 981 μL: entry 3 table 11.

9 Mechanistic Studies

9.1 UV Spectra Studies

UV-Vis absorption spectroscopy was employed to gain insight into the photochemical reaction mechanism in the presence of NaHCO_3 , aiming to elucidate the role of this inorganic base as an external electron donor, capable of promoting the formation of an anion- π complex with the nitrogen radical precursor.

The experiments were conducted to assess the appearance or shift of absorption bands in the visible region, indicative of new molecular orbital formation upon mixing. Specifically, UV-Vis absorption spectra were recorded in acetonitrile (0.05 M), using 1 mm quartz cuvettes for the individual components – pyridinium tetrafluoroborate **1a** (A) and sodium bicarbonate (B) – as well as for their binary mixture (A + B) (**Figure S4 A**).

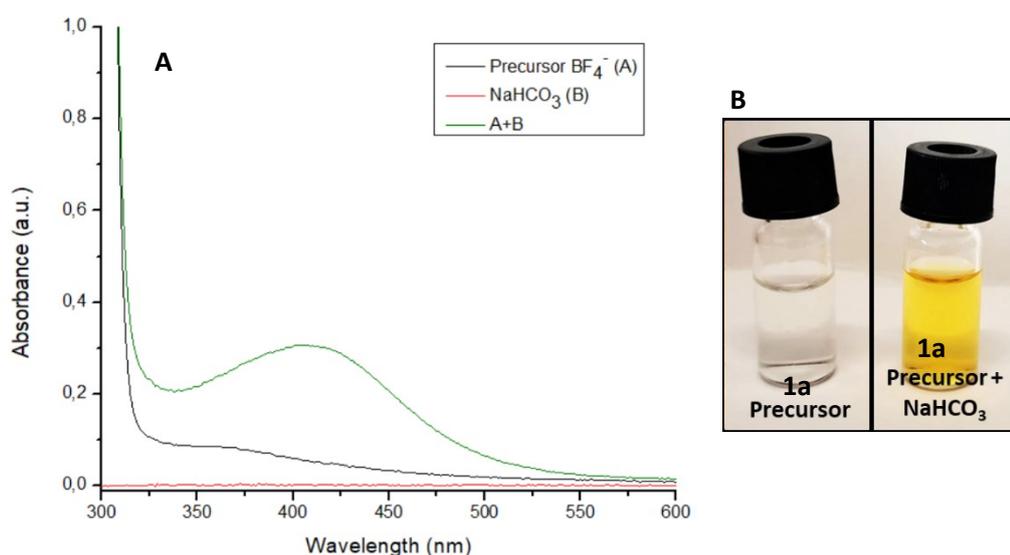


Figure S4 A) UV-Vis absorption spectra in ACN (0.05 M) in the selected range 300-600 nm of: pyridinium salt **1a** (A), NaHCO_3 (B), and their binary combination (A+B). **B)** Colourless solution of **1a** (left) and yellow solution when **1a** is combined with 1 equiv. of NaHCO_3 (right) in ACN 0.1M.

Interestingly, the combination of pyridinium salt **1a** and NaHCO_3 (A+B, green line) led to the appearance of a distinct new absorption band at approximately 410 nm, indicating that the inorganic base actively participates in the formation of a ground-state interaction with the pyridinium salt, which acts as the electron-accepting species. The appearance of this charge-transfer band, together with the observed colour change from colourless to yellow upon addition of sodium bicarbonate as an external donor (**Figure S4 B**), supports the formation of an electron donor-acceptor (EDA) complex as the operative mechanism.

Then, we recorded the UV-spectra of by 1-methylindole **2a** and the mixture of 1-methylindole **2a** and the nitrogen radical precursors tetrafluoroborate **1a** and triflate **1b** respectively (**Figure S5**).

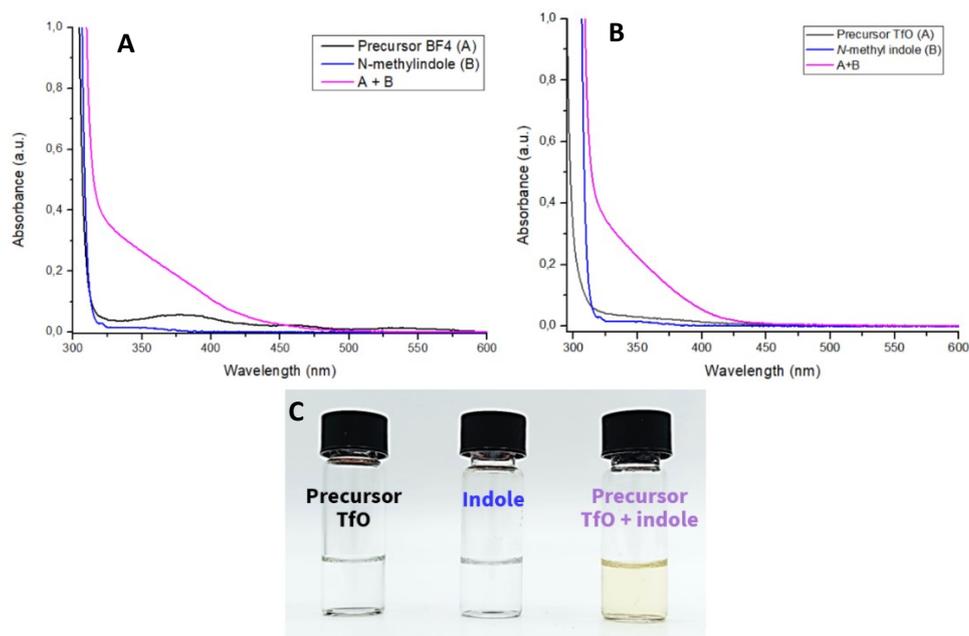


Figure S5 UV-Vis spectra in ACN 0.1 M in the selected range of wavelength 300-600 nm of A) precursor **1a**, 1-methylindole **2a** and their binary mixture (A+B). B) precursor **1b**, 1-methylindole **2a** and their binary mixture. C) Colourless solutions of pyridinium triflate **1b** and 1-methylindole **2a** dissolved in ACN 0.1M; yellowish solution derived from their combination in ACN 0.1M.

Some differences between the two salts were observed recording UV-Vis absorption spectra. In the spectrum of pyridinium ion **1a** two peaks at 370 and 450 nm are present suggesting a possible aggregation of the precursor in solution⁹, while the UV-vis spectrum of pyridinium **1b** has not appreciable peaks. Then, when the precursors **1a** and **1b** are mixed together a new absorption band at ca. 350 nm was observed in both cases due to the interaction of the pyridinium salts **1a** and **1b** with 1-methylindole **2a** (**Figure S5**).

9.2 Cyclic Voltammetry Studies

Cyclic Voltammetry analyses were carried out with a Metrohm Series Potentiostat/Galvanostat Electrochemical System Autolab at room temperature. Glassy carbon was employed as working electrode, a platinum foil as counter electrode and a silver wire as reference electrode. Glassy carbon electrode and platinum foil were purchased by IKA. The surface in solution of the glassy carbon plate and platinum foil has been calculate to be 0.4 cm². Tetrabutylammonium tetrafluoroborate (TBATFB) was selected as a supporting electrolyte at 0.1 M to avoid any possible interferences with other anions. Dry ACN was used as solvent to replicate the reaction conditions. Prior to each measurement, which was recorded three times, the solution was degassed with argon and all the experiments are performed under argon atmosphere. Cyclic voltammetry analyses were scanned from:

- an initial potential of 0 V to 3 V, then from 3 V to -2.8 V (oxidation)
- or an initial potential of 0 V to -2.8 V, then from -2.8 V to 3 V (reduction)

The scan rate was 100 mV·s⁻¹. The solution of LiCl (2 M in ethanol) for the reference electrode in the inner jacket was freshly prepared.

Cyclic voltammetry analysis of pyridinium salts **1a** and **1b** were recorded and the irreversible reduction potential was determined to be -1.35 and -1.26 V vs Ag/AgCl (LiCl 2 M in EtOH), respectively (**Figure S6**).

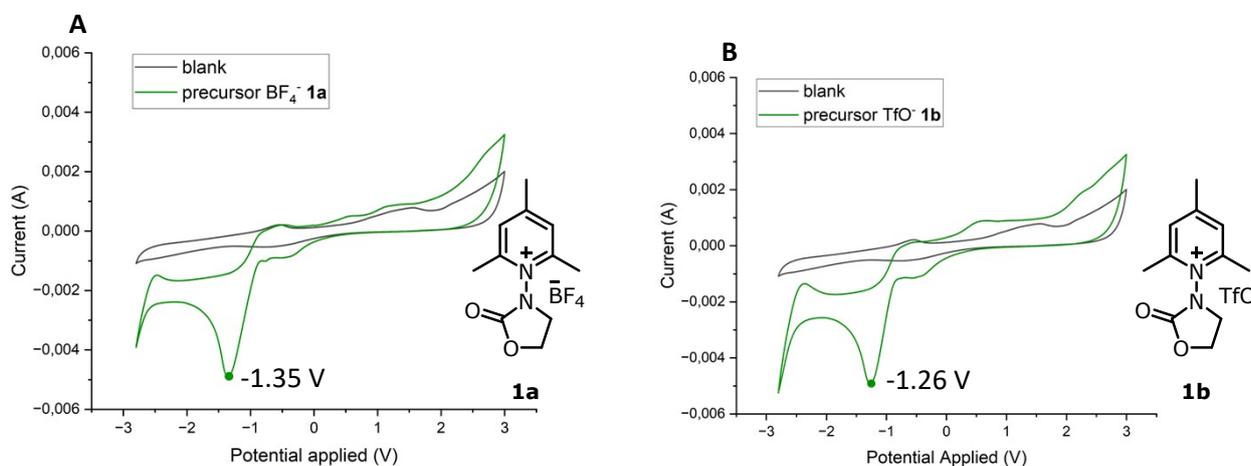


Figure S6 Cyclic voltammogram for compound **1a** (A) and **1b** (B) versus Ag/AgCl (LiCl 2 M in EtOH) with TBATFB 0.1 M in dry ACN at 100 mV/s^{-1} from 0 V to +3 V and from +3 V to -2.8 V at room temperature. Glassy carbon was employed as working electrode, a platinum foil as counter electrode and a silver wire as reference electrode.

Cyclic voltammetry analyses were recorded for the radical precursors **1a** and **1b**, 1-methylindole **2a**, the corresponding binary mixtures (precursor **1a** + 1-methylindole **2a**; precursor **1b** + 1-methylindole **2a**) and product **3a** in ACN (**Figure S7**).

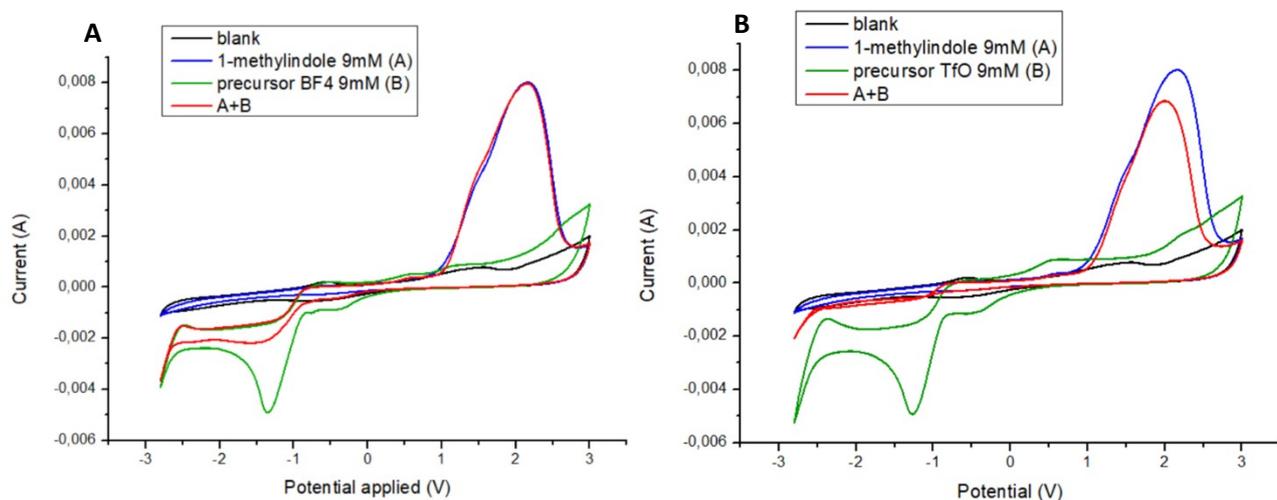


Figure S7 Cyclic voltammetry analyses (oxidative direction) of (A) precursor **1a** (green line), 1-methylindole **2a** (blue line), and their binary mixture (red line) and (B) precursor **1b** (green line), 1-methylindole **2a** (blue line), and their binary mixture (red line). Cyclic voltammogram was recorded versus Ag/AgCl (LiCl 2 M in EtOH) with TBATFB 0.1 M in dry ACN at 100 mV/s^{-1} from 0 V to +3 V and from +3 V to -2.8 V at room temperature. Glassy carbon was employed as working electrode, a platinum foil as counter electrode and a silver wire as reference electrode.

As expected, a reduction peak was observed in the voltammograms for precursors **1a** and **1b** (green lines) and an oxidative peak was observed for 1-methylindole **2a** (blue lines). The direction of the initial scan is oxidative. When a cyclic voltammetry analysis of the binary mixtures was recorded, the consumption of the precursors together with the presence of an oxidative potential was observed (red lines) (**Figure S7A** and **Figure S7B**).

From the voltammograms, a clear difference between the two pyridinium salts can be observed: while tetrafluoroborate precursor **1a** was not completely consumed during the second cycle of the analysis, the triflate precursor **1b** undergoes irreversible reduction of the pyridinium salt. In addition, 1-methylindole **2a** is also partially consumed in the latter case. The incomplete consumption of compound **1a** may represent an evidence of the distinct behaviour of the precursors in the presence of 1-methylindole **2a**.

In the end, the cyclic voltammetry analysis of product **3a** was recorded, resulting in an oxidative potential similar to that of 1-methylindole **2a** as expected (**Figure S8**). However, no product formation was observed by TLC or ^1H NMR analysis, likely due either to the distance between the electrodes – where the redox process occurs – or to the analysis conditions, which may not be optimal for the photochemical reaction.

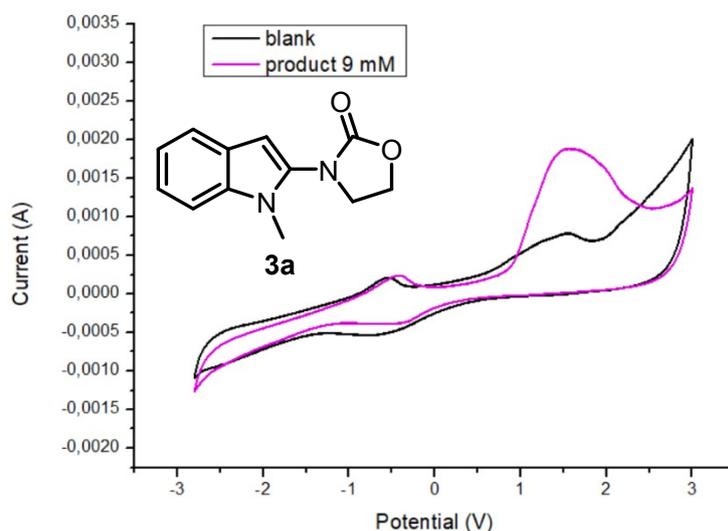


Figure S8 Cyclic voltammetry analyses (oxidative direction) of product **3a** versus Ag/AgCl (LiCl 2 M in EtOH) with TBATFB 0.1 M in dry ACN at 100 mV/s^{-1} from 0 V to +3 V and from +3 V to - 2.8 V at room temperature. Glassy carbon was employed as working electrode, a platinum foil as counter electrode and a silver wire as reference electrode.

9.3 DFT Calculations

Complexation analysis

The optimized geometry of the pyridinium ions **1a-c** was first calculated. Then, 1-methylindole **2a** was added to the optimized structure. The energy difference (ΔG , kcal/mol) between the separated species and the corresponding mixed complexes was then evaluated. The resulting energetic profile indicates that the complexation between 1-methylindole **2a** and the various pyridinium ions **1a-c** is slightly endoergonic, with ΔG values of up to 9 kcal/mol. We therefore assume the establishment of an equilibrium between the pyridinium counterion (X^-) and the electron-donor molecule.

Subsequently, NaHCO_3 was added to the optimized structure of the pyridinium ions **1a-c**. A markedly different situation is observed when NaHCO_3 is mixed with the tetrafluoroborate pyridinium ion **1a**, resulting in a substantial energy decrease of nearly 150 kcal/mol. This suggests that NaHCO_3 can rapidly exchange with the BF_4^- counterion in solution, leading to the formation of pyridinium bicarbonate. An equilibrium is expected between pyridinium bicarbonate and pyridinium salts bearing other counterions.

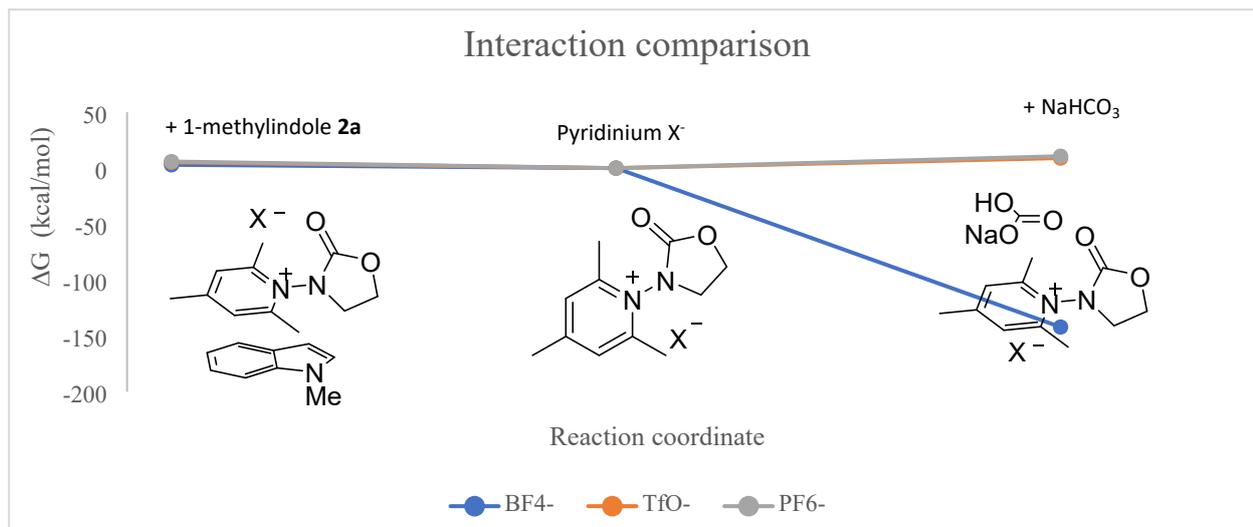
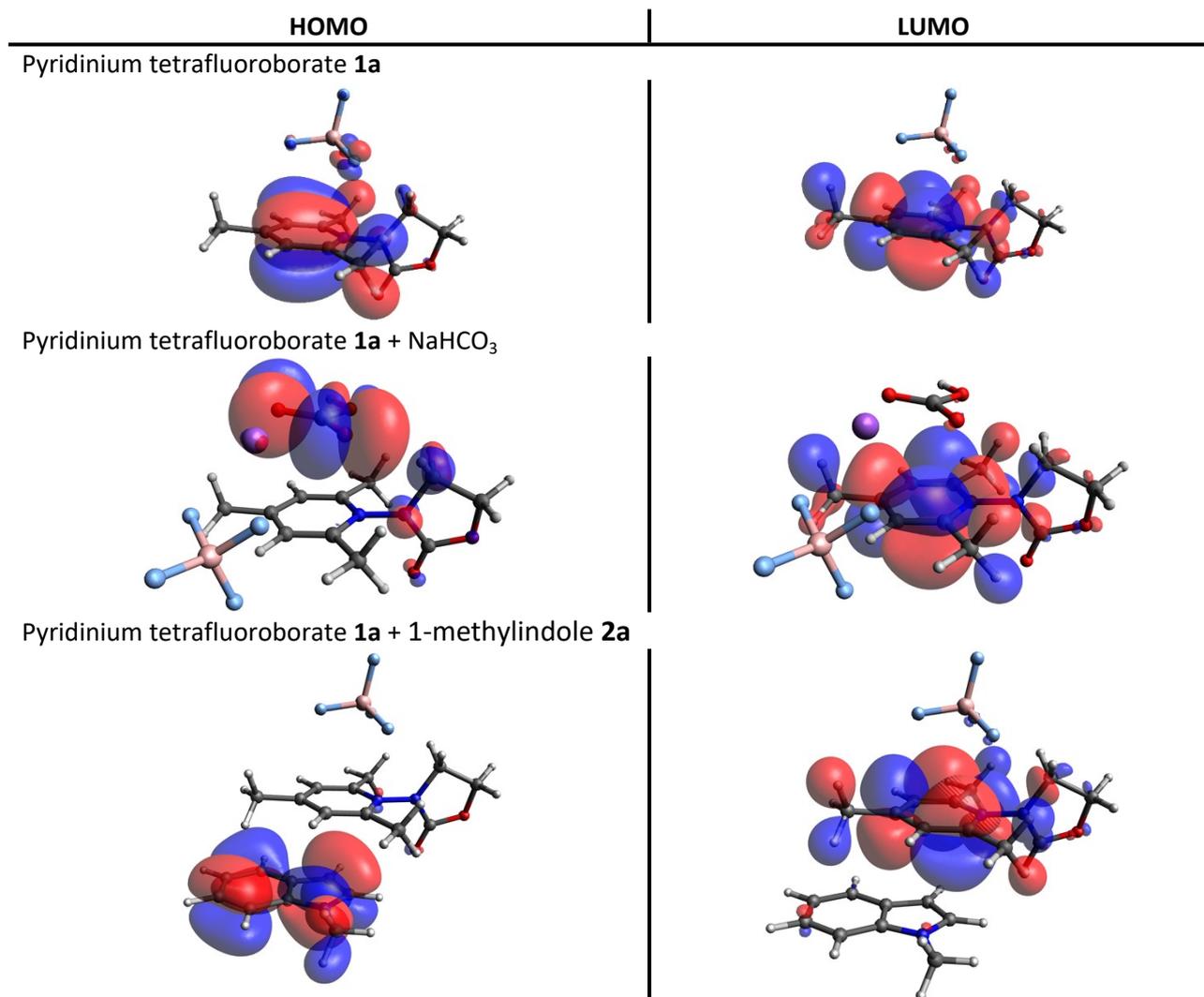


Figure S9

HOMO-LUMO analysis

When NaHCO_3 is added to precursor **1a**, the HOMO is located on NaHCO_3 , while the LUMO is located on the pyridinium moiety. In analogy, when 1-methylindole **2a** is added to precursor **1a**, the HOMO is located on 1-methylindole **2a**, while the LUMO is located on the pyridinium moiety. The same considerations can be done with precursor **1c**.

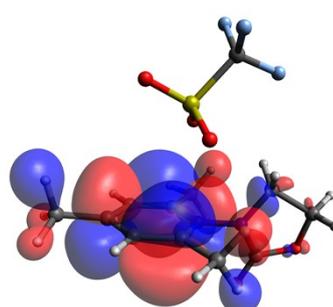
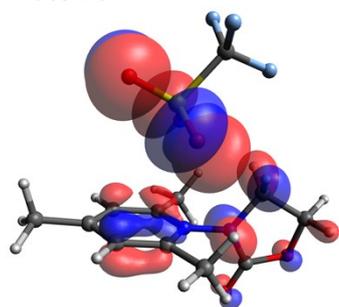
In contrast, a different situation is observed with precursor **1b**, bearing TfO^- as a counterion: the HOMO is located on the pyridinium ion and partially on the counterion TfO^- , indicating a stronger interaction of the TfO^- with the pyridinium.



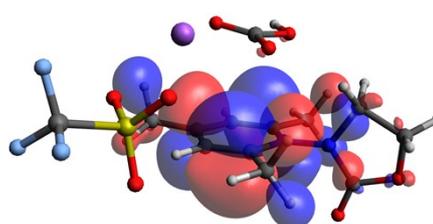
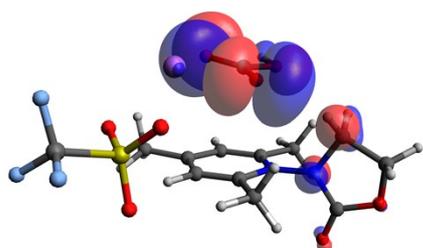
HOMO

LUMO

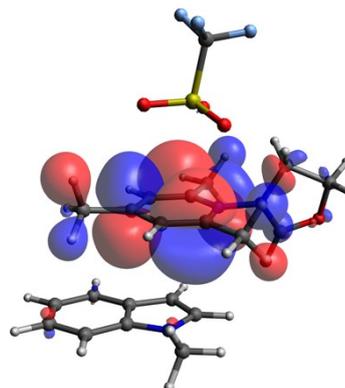
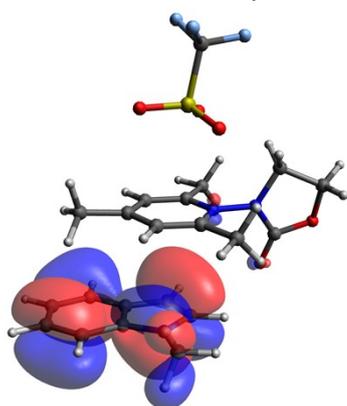
Pyridinium triflate **1b**



Pyridinium triflate **1b** + NaHCO₃



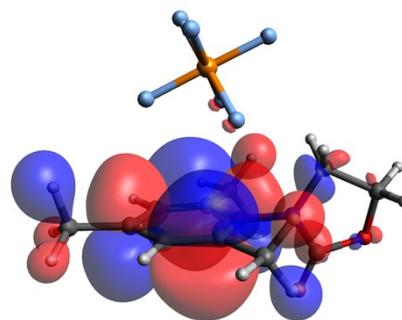
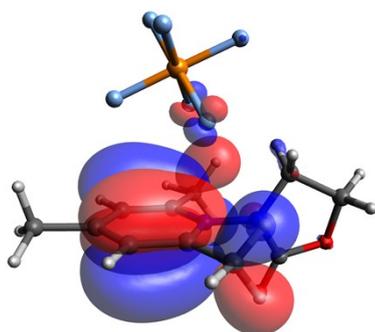
Pyridinium triflate **1b** + 1-methylindole **2a**



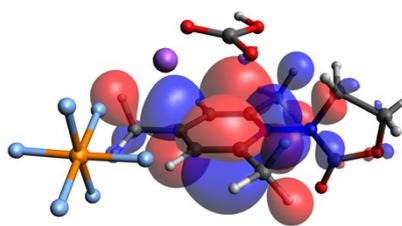
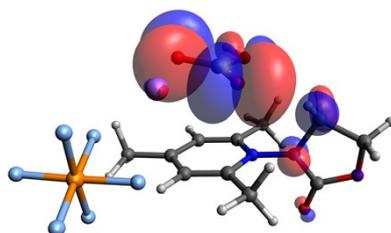
HOMO

LUMO

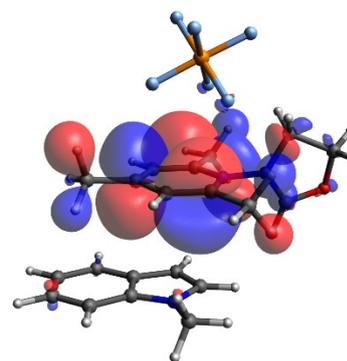
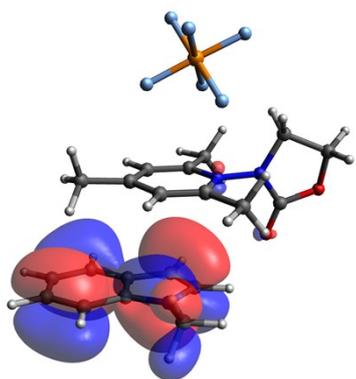
Pyridinium hexafluorophosphate **1c**



Pyridinium hexafluorophosphate **1c** + NaHCO₃



Pyridinium hexafluorophosphate **1c** + 1-methylindole **2a**



BF₄⁻

E = -698181.2850157 kcal/mol

C	-1.87532700	-2.06673000	0.06607700
C	-1.28245700	-1.64285700	1.25349100
C	-0.09827700	-0.94506700	1.24716000
N	0.48417500	-0.67813500	0.04091800
C	-0.03842500	-1.08725200	-1.15274500
C	-1.22021200	-1.78916200	-1.13215800
C	0.69036800	-0.75956200	-2.41039300
C	-3.19391700	-2.76848500	0.07473900
C	0.57898900	-0.47331100	2.48744700
N	1.66326400	0.03105700	0.04874800
C	1.76975100	1.47910400	-0.08652400
C	3.27126000	1.62195900	0.18193100
O	3.83425800	0.30815200	-0.05887700
C	2.87380700	-0.61774900	-0.03085900
O	3.05366000	-1.80588800	-0.07406100
B	-1.94996400	1.91860300	-0.08435400
F	-2.49770700	3.20997100	-0.19461900
F	-1.11687800	1.66364300	-1.19834100
F	-1.17586100	1.83577500	1.09816500
F	-2.98106700	0.96310300	-0.03817900
H	-1.75191600	-1.84832900	2.20634900
H	-1.64072200	-2.11266500	-2.07509400
H	0.15163400	-1.17923100	-3.25708700
H	0.75532900	0.32088800	-2.54529700
H	1.69980100	-1.17538000	-2.39993200
H	-3.98707900	-2.01679900	0.01049900
H	-3.29500400	-3.43699300	-0.78054200
H	-3.33928700	-3.33101400	0.99725900
H	-0.00156500	-0.78320000	3.35380700
H	1.58350700	-0.89343500	2.56820800
H	0.65560800	0.61500400	2.49043100
H	1.47950000	1.80716900	-1.08472900
H	1.15579700	1.99185500	0.65015700
H	3.76185700	2.32119500	-0.48856500
H	3.47721600	1.88159500	1.21992700

PF₆⁻

E = -1022069.732906 kcal/mol

C	0.26855400	2.91416600	0.03498800
C	-0.11587000	2.31652000	1.23366500
C	-0.88505500	1.17748000	1.24557800
N	-1.26678700	0.64629000	0.04656600
C	-0.94595100	1.20490500	-1.15790100

C	-0.17897100	2.34574900	-1.15606000
C	-1.44187000	0.56385400	-2.40836300
C	1.16258400	4.11062400	0.02706500
C	-1.32348800	0.50186600	2.49909800
N	-2.01896400	-0.50632700	0.07358500
C	-1.47540100	-1.85682800	-0.00908600
C	-2.77476200	-2.64016300	0.20699700
O	-3.84373900	-1.70931800	-0.09306700
C	-3.38730400	-0.45633200	-0.07160100
O	-4.06491100	0.53171300	-0.16924100
H	0.19586200	2.73503500	2.18138200
H	0.08295000	2.78815900	-2.10801400
H	-1.08982600	1.13289800	-3.26589700
H	-1.06950700	-0.45725100	-2.49802800
H	-2.53339800	0.54314000	-2.42949200
H	2.20194100	3.76714400	0.02693900
H	1.00920000	4.71729200	-0.86542600
H	1.01343200	4.72384600	0.91609500
H	-0.93298000	1.04643900	3.35609900
H	-2.41306300	0.47485100	2.56510600
H	-0.95087000	-0.52260500	2.53881300
H	-1.01796200	-2.04489600	-0.98060200
H	-0.74196500	-2.04061600	0.77259500
H	-2.87741600	-3.49055500	-0.46042000
H	-2.89357900	-2.95341400	1.24358500
P	2.39595300	-0.91411400	-0.03529200
F	3.57462800	-1.10590600	1.07439600
F	2.13967600	-2.52620900	-0.05077000
F	3.48680600	-1.06896300	-1.23649500
F	2.63194500	0.69988500	-0.01792600
F	1.20280100	-0.72310500	-1.14283900
F	1.28998000	-0.75989000	1.16560900

TfO⁻

E = -1649.609475 kcal/mol

C	-1.34937400	2.98002800	0.00295600
C	-1.40652300	2.28055300	1.20718100
C	-1.54783900	0.91263400	1.22964600
N	-1.62824400	0.25512800	0.03538000
C	-1.58848000	0.88710000	-1.17437800
C	-1.45611900	2.25626100	-1.18287600
C	-1.69148200	0.07537400	-2.41894600
C	-1.14910800	4.46120900	-0.01583800
C	-1.62075400	0.12041600	2.48865900
N	-1.75624200	-1.11474600	0.07272500

C	-0.64549400	-2.05841500	0.01757700
C	-1.43404800	-3.35229500	0.24409800
O	-2.80957700	-3.03061600	-0.07995500
C	-2.98817200	-1.70834700	-0.07848500
O	-4.04744300	-1.15138000	-0.19565700
H	-1.33729300	2.80425600	2.15138000
H	-1.42418400	2.76100300	-2.13924600
H	-1.66829800	0.73805800	-3.28136700
H	-0.84886000	-0.61356100	-2.49107800
H	-2.62241000	-0.49430300	-2.44337500
H	-0.07501000	4.67241700	-0.01546500
H	-1.57798400	4.90863100	-0.91261200
H	-1.58128100	4.93015500	0.86844100
H	-1.58357000	0.79599400	3.34070900
H	-2.54579400	-0.45720000	2.53567300
H	-0.77473900	-0.56598700	2.55033900
H	-0.14306600	-2.02302800	-0.94916800
H	0.07899200	-1.86195900	0.80477500
H	-1.12108000	-4.16386800	-0.40601100
H	-1.40825800	-3.66883200	1.28633300
C	3.41250500	-0.78415400	-0.06027000
F	4.23306500	-0.68127700	0.98752400
F	2.89188800	-2.01488700	-0.05868600
F	4.13884700	-0.64407000	-1.17131700
S	2.06383100	0.49842100	0.02025800
O	2.78788200	1.76915400	0.01525700
O	1.38057700	0.17807800	1.27830000
O	1.27831900	0.22485600	-1.18717600

$\text{BF}_4^- + \text{NaHCO}_3$

E = -966016.8203266 kcal/mol

C	0.25919600	-0.40890700	-0.81134100
C	-0.71903200	0.40865100	-1.33660100
C	-0.46399200	1.75232400	-1.60541600
C	0.83268300	2.23243900	-1.40196100
C	1.82273100	1.41914300	-0.89790000
N	1.49849200	0.12527400	-0.59706200
C	0.01680000	-1.83689000	-0.46035700
C	-1.55916500	2.66264800	-2.06084100
C	3.21883500	1.88459100	-0.65490100
N	2.45084900	-0.68891200	-0.02927300
C	2.73581400	-0.77507300	1.39848700
C	3.63019900	-2.01726200	1.36412500
O	4.14371000	-2.08158100	0.01034900
C	3.35467000	-1.37583700	-0.81027900

O	3.43695300	-1.35135200	-2.01370500
B	-3.85499000	-1.22001600	-0.27885300
F	-5.16522400	-1.66298700	-0.26413000
F	-3.16502800	-1.66979400	0.88012500
F	-3.17710900	-1.66620100	-1.42029400
F	-3.81554000	0.20487500	-0.24641500
Na	-2.54350300	0.44018100	1.74255500
O	-0.17992600	0.19363600	2.14071400
C	-0.07245700	1.42994600	1.96430700
O	-0.98471500	2.24862200	1.70510600
O	1.20904100	1.92533300	2.05848500
H	-1.70180000	-0.01635200	-1.49811200
H	1.07923200	3.26313300	-1.62612300
H	-1.01375300	-2.08706600	-0.70656900
H	0.69420000	-2.49637100	-1.00828700
H	0.16848200	-1.98535000	0.61132000
H	-1.18316800	3.43956700	-2.72895600
H	-2.35867300	2.10938600	-2.55522000
H	-1.98302900	3.15380100	-1.17818000
H	3.32386800	2.90916100	-1.00881000
H	3.44816800	1.86365000	0.41300900
H	3.93879100	1.25673500	-1.18465300
H	3.26164700	0.11566400	1.75014000
H	1.81670400	-0.89241700	1.97282300
H	4.47980200	-1.95542200	2.04003500
H	3.06457600	-2.93266800	1.54965700
H	1.14096200	2.87316900	1.89335300

PF₆⁻ + NaHCO₃

E = -1289903.303484 kcal/mol

C	0.94220000	-0.48027100	-0.73650500
C	-0.11869100	0.27483600	-1.18796500
C	0.03133400	1.62957300	-1.47812100
C	1.30201500	2.19568300	-1.34111800
C	2.37221900	1.44806500	-0.90295200
N	2.15588600	0.13164700	-0.60134200
C	0.81933800	-1.92432600	-0.38813500
C	-1.14292200	2.45620700	-1.89544700
C	3.74557300	2.00622100	-0.73727200
N	3.20217700	-0.63131900	-0.13613300
C	3.61532300	-0.73791500	1.25898900
C	4.59226000	-1.90662100	1.10413100
O	4.99127900	-1.89051400	-0.28886300
C	4.08599200	-1.22158400	-1.01416800
O	4.06421000	-1.15169200	-2.21835100

Na	-1.72928000	0.02367500	2.07813500
O	0.67192400	-0.08237000	2.25950800
C	0.69059800	1.16670500	2.14709500
O	-0.28797800	1.93904500	2.03415900
O	1.94503900	1.73480500	2.13665900
H	-1.08501500	-0.19969300	-1.28318600
H	1.46572700	3.24109900	-1.57293900
H	-0.21326600	-2.23566700	-0.53679100
H	1.47385300	-2.53767100	-1.01213100
H	1.08049700	-2.07653100	0.66109400
H	-0.86112600	3.18517800	-2.65790900
H	-1.95636400	1.82935000	-2.26003500
H	-1.51044200	3.00723800	-1.02381100
H	3.75474100	3.04456500	-1.06549700
H	4.04746900	1.97348300	0.31205300
H	4.47056900	1.44628100	-1.33242100
H	4.10254900	0.17890300	1.59823600
H	2.76088200	-0.94408600	1.90394500
H	5.48972300	-1.80047600	1.70900200
H	4.11416500	-2.86800400	1.30230900
H	1.80676300	2.68450500	2.04087500
P	-3.85257000	-0.56276200	-0.22902700
F	-4.29175800	-0.66153300	1.34275300
F	-3.01400500	0.81051700	0.13481000
F	-2.49089900	-1.42675500	0.14593000
F	-3.33564600	-0.44746400	-1.76545300
F	-4.63166000	-1.93712900	-0.55924100
F	-5.16089300	0.31976300	-0.56553400

TfO⁻ + NaHCO₃

E = -1302979.919103 kcal/mol

C	1.06095000	-0.37458500	-0.81960100
C	0.21746500	0.56344200	-1.37498400
C	0.66919000	1.84656700	-1.68039800
C	2.02270300	2.13317400	-1.48424300
C	2.87968900	1.19720900	-0.94984700
N	2.36512200	-0.02370900	-0.61163300
C	0.61041000	-1.73983700	-0.42672800
C	-0.27839100	2.89538000	-2.16719100
C	4.33050000	1.45482700	-0.71794000
N	3.18339600	-0.95246900	-0.01157500
C	3.43684900	-1.04167600	1.42188900
C	4.15919200	-2.39200800	1.42917500
O	4.66980900	-2.56139800	0.08352100
C	3.99378600	-1.77515900	-0.76379600

O	4.09174500	-1.79129700	-1.96616100
Na	-1.57612700	1.13731300	1.78638300
O	0.71243100	0.44330700	2.10908100
C	1.04717900	1.63180000	1.89548400
O	0.30394000	2.59822600	1.60593500
O	2.39845900	1.88524600	1.98486400
H	-0.81896700	0.29144900	-1.53188600
H	2.42059500	3.10830300	-1.73725900
H	-0.43547500	-1.86321100	-0.70737800
H	1.20868100	-2.51039100	-0.91822500
H	0.69908500	-1.86107500	0.65568500
H	0.21512100	3.60381100	-2.83474400
H	-0.64600900	3.45078900	-1.29748300
H	4.58306900	2.44859500	-1.08497800
H	4.56251000	1.41158800	0.34857200
H	4.94560300	0.72169700	-1.24489500
H	4.06829800	-0.21824500	1.76300100
H	2.50422200	-1.02454400	1.98562700
H	5.00445000	-2.42403100	2.11255900
H	3.47640400	-3.21928900	1.63258100
H	2.50545600	2.82510100	1.79649200
C	-5.02184700	-0.68660200	-0.08064200
F	-5.50227100	-0.01355600	0.96614100
F	-5.37411200	-1.96643100	0.03891900
F	-5.57167800	-0.19421900	-1.19056300
O	-2.79876500	-1.30190600	-1.33933300
O	-2.72473500	-1.08293600	1.13678100
O	-2.95773100	0.92596100	-0.25690700
S	-3.18446800	-0.53124800	-0.15209700
H	-1.13848500	2.45326800	-2.67166000

$\text{BF}_4^- + \text{NaHCO}_3 \text{ S}^1$

E = -965923.6765655 kcal/mol

C	0.03708100	-0.74366300	-0.79556500
C	-0.91179100	0.10117100	-1.28285100
C	-0.62334600	1.44736800	-1.64949800
C	0.74091200	1.82411600	-1.62876800
C	1.72758000	1.01033200	-1.15728800
N	1.36224300	-0.27436500	-0.69231500
C	-0.20717800	-2.17492400	-0.44021600
C	-1.70083800	2.39054400	-2.08952400
C	3.18459300	1.34391000	-1.16885500
N	2.24827900	-0.99684300	0.05607500
C	2.44643100	-0.82435100	1.48733600
C	3.45591400	-1.95113800	1.74562400

O 3.97430300 -2.31105300 0.44843700
 C 3.19097000 -1.80555500 -0.52327400
 O 3.33458700 -2.04683500 -1.69935500
 B -3.97769600 -1.23415000 0.20977900
 F -5.20290900 -1.65962700 0.69178500
 F -2.99116200 -1.31648700 1.23621900
 F -3.56707400 -1.98255900 -0.89244500
 F -4.04780700 0.14387900 -0.15944700
 Na -2.26613900 0.89734100 1.17496400
 O 0.15807600 1.34020300 1.54983000
 C 0.63096200 2.50237400 1.40709200
 O -0.20187200 3.33050100 1.01121300
 O 1.88901900 2.72614800 1.68331200
 H -1.91720100 -0.29121100 -1.39769600
 H 1.03339300 2.80213300 -1.99970000
 H -1.25956500 -2.40656400 -0.60094200
 H 0.41066300 -2.84024800 -1.05263700
 H 0.03111400 -2.38183500 0.60846600
 H -1.32813100 3.11449600 -2.82078700
 H -2.54158800 1.85496500 -2.54076200
 H -2.10567500 2.97182800 -1.24668200
 H 3.32521400 2.34093400 -1.58839700
 H 3.61812200 1.34073500 -0.16277100
 H 3.74935000 0.62880100 -1.77555100
 H 2.84382300 0.16910200 1.71778100
 H 1.51478400 -0.97535600 2.03615400
 H 4.29292400 -1.64387700 2.36990600
 H 2.97921100 -2.83458600 2.17461500
 H 2.11582800 3.64947000 1.50139700

Excited state	Electronic transition (nm)	Oscillator strength	HOMO-LUMO contribution
S1	400	0.0005	50%

TfO⁻ + NaHCO₃ S¹

E = -1302887.033875 kcal/mol

C 0.89135800 -0.45200500 -1.08888000
 C 0.24132300 0.64229100 -1.57094000
 C 0.85552000 1.92574600 -1.65301500
 C 2.23944600 1.97712200 -1.35633300
 C 2.93456300 0.90771100 -0.87680100
 N 2.23568600 -0.30669900 -0.69020200
 C 0.32099800 -1.83284500 -1.03464600

C	0.10080300	3.13695200	-2.11026700
C	4.40540300	0.89707500	-0.61054800
N	2.79874600	-1.29947200	0.06058200
C	2.75090900	-1.35658600	1.51372300
C	3.42577900	-2.71599000	1.74013300
O	4.09705700	-3.02529900	0.50089400
C	3.63930200	-2.23317400	-0.48706500
O	3.94768800	-2.35707900	-1.64967900
Na	-1.37141300	1.46272000	0.72278200
O	0.97862100	1.26627900	1.57502300
C	1.72865000	2.27394000	1.70345700
O	1.21090800	3.33212100	1.31858000
O	2.92436300	2.12778500	2.21226600
H	-0.78242600	0.51231000	-1.91113900
H	2.78757000	2.90126900	-1.51432800
H	-0.70107700	-1.82655200	-1.41416200
H	0.92030800	-2.52371700	-1.63697900
H	0.29384600	-2.22394900	-0.01258300
H	0.73235900	3.80371900	-2.70598200
H	-0.27545200	3.73198100	-1.26454300
H	4.82157700	1.88069100	-0.83201700
H	4.63583300	0.66368100	0.43459300
H	4.91394700	0.15611600	-1.23564600
H	3.30187900	-0.52443200	1.96254900
H	1.72082400	-1.34219100	1.87577400
H	4.17175500	-2.69903400	2.53253400
H	2.69723700	-3.50549300	1.93412500
H	3.39284000	2.97481800	2.22232900
C	-4.95854600	-0.52506000	0.45272200
F	-5.01891100	0.45770300	1.35446000
F	-5.21800900	-1.67922400	1.06681000
F	-5.89673000	-0.31219500	-0.46953200
O	-3.35484000	-1.67222600	-1.28632100
O	-2.37720500	-0.77765100	0.82196300
O	-3.13844700	0.77904100	-0.91123600
S	-3.28602500	-0.57114400	-0.32534000
H	-0.76545200	2.86096200	-2.71915900

Excited state	Electronic transition (nm)	Oscillator strength	HOMO-LUMO contribution
S1	404	0.0004	49%

BF₄⁻ + 1-methylindole **2a**

E = -951138.4043677 kcal/mol

C	-0.79244100	1.56246100	-0.32760200
C	-0.47625400	0.94141700	0.87914000
C	0.44909800	-0.07043700	0.93737400
N	1.06643900	-0.44792800	-0.22221300
C	0.77322600	0.10135000	-1.43615900
C	-0.16664400	1.10362400	-1.48316100
C	1.47558500	-0.40776700	-2.64758700
C	-1.76352500	2.69512700	-0.36117400
C	0.81950200	-0.76516200	2.20271400
N	2.04711700	-1.41086600	-0.13551800
C	3.46489900	-1.11644100	0.04397800
C	3.97787900	-2.54912500	0.20566800
O	2.95642000	-3.39020100	-0.38370000
C	1.80508100	-2.72055700	-0.48348700
O	0.75747900	-3.20115000	-0.82478500
B	2.97364800	2.56191800	0.41269000
F	4.13164100	3.34403000	0.58759000
F	3.07881800	1.83109600	-0.79286300
F	2.85288100	1.65635500	1.49431500
F	1.83985700	3.39251800	0.36572300
H	-0.95621500	1.25459500	1.79694000
H	-0.39993600	1.54174600	-2.44437600
H	1.13767100	0.14845200	-3.51926900
H	2.55505600	-0.28003900	-2.55585700
H	1.25865200	-1.46658800	-2.80467400
H	-1.32952300	3.55469900	0.15754200
H	-2.00727800	2.98644400	-1.38188600
H	-2.68416600	2.41932100	0.15827900
H	0.18789300	-0.40209700	3.01119800
H	0.69345300	-1.84550100	2.11256400
H	1.86043700	-0.56102700	2.45989700
H	3.87689400	-0.60797300	-0.82809900
H	3.63290200	-0.50153100	0.92500300
H	4.90788600	-2.73472600	-0.32348600
H	4.07369300	-2.83283900	1.25348800
C	-3.61194200	-0.44622000	0.52496600
C	-3.28993600	-0.56848800	-0.84828200
C	-2.29075500	-1.59020100	-0.94604800
C	-2.05859300	-2.03121100	0.32540400
N	-2.84906000	-1.35060200	1.22123700
H	-1.79249800	-1.94222000	-1.83549200
H	-1.37239400	-2.79024500	0.66923100
C	-2.87825200	-1.53726400	2.65584600

H	-2.15063400	-2.29984300	2.92952800
H	-2.62481800	-0.60709600	3.17104800
H	-3.86820200	-1.86298200	2.98430300
C	-3.93865000	0.26208700	-1.77342600
H	-3.70369100	0.19438200	-2.83038600
C	-4.87912300	1.16813500	-1.31801200
H	-5.38654600	1.81669100	-2.02344600
C	-5.18617000	1.27116100	0.05219900
H	-5.92538900	1.99413800	0.37854000
C	-4.55794700	0.47102300	0.99104000
H	-4.79315000	0.55417800	2.04608700

PF₆⁻ + 1-methylindole **2a**

E = -1275026.46885 kcal/mol

C	0.90367700	-1.47352900	-0.43627500
C	0.70387500	-0.84637300	0.79334600
C	0.04343300	0.35650300	0.88047200
N	-0.42154000	0.92194200	-0.27316100
C	-0.21315300	0.37985000	-1.50828800
C	0.45932400	-0.81851300	-1.58420900
C	-0.71683300	1.10646200	-2.70932200
C	1.55354400	-2.81635800	-0.50566700
C	-0.19318900	1.06762900	2.17048200
N	-1.17056700	2.07180700	-0.15521400
C	-2.62635800	2.09299900	-0.05504500
C	-2.80564400	3.58525300	0.23314800
O	-1.60869100	4.21848500	-0.27823500
C	-0.62874600	3.31567300	-0.40458200
O	0.51530600	3.57041900	-0.69290300
H	1.06196300	-1.30661800	1.70600600
H	0.62373100	-1.25373600	-2.56205300
H	-0.44504700	0.55101600	-3.60561800
H	-1.80437000	1.20066600	-2.68200400
H	-0.27642100	2.10453100	-2.77103800
H	0.83150200	-3.57018300	-0.17515300
H	1.87210600	-3.05677100	-1.52009400
H	2.42122200	-2.85816300	0.15700200
H	0.29623100	0.52300600	2.97710200
H	0.20468900	2.08428200	2.13914500
H	-1.26122400	1.12199200	2.39025500
H	-3.09441600	1.77822300	-0.98971800
H	-2.97980200	1.44995400	0.74788800
H	-3.65981900	4.02280500	-0.27816800
H	-2.85999400	3.78988100	1.30406600
C	4.02703800	-0.18351200	0.59207600

C	3.79092500	0.08163300	-0.77988700
C	3.06817000	1.31759600	-0.84126400
C	2.90425900	1.73881800	0.44853400
N	3.48364200	0.84659900	1.32258100
H	2.70302700	1.82573800	-1.72098400
H	2.40842500	2.62452200	0.81924000
C	3.47716200	0.93264100	2.76614500
H	3.00406400	1.86817300	3.06465400
H	2.91922100	0.09889900	3.20456300
H	4.49733000	0.91559500	3.15899700
C	4.24970000	-0.83835600	-1.73616400
H	4.07512700	-0.66257800	-2.79349200
C	4.92396900	-1.97053900	-1.31103300
H	5.28311100	-2.68855300	-2.04149100
C	5.14864400	-2.21324600	0.05892500
H	5.67824600	-3.11128800	0.36053400
C	4.70233300	-1.32890800	1.02824200
H	4.87294400	-1.51771300	2.08328600
P	-3.30300200	-1.69192800	0.23061200
F	-1.95108800	-2.59069300	0.11731900
F	-2.55211400	-0.72066100	1.31975000
F	-2.75533100	-0.73498700	-0.98162900
F	-4.63022400	-0.75766200	0.34468300
F	-4.04385900	-2.64164100	-0.85676600
F	-3.83996800	-2.62799600	1.44328200

TfO⁻ + 1-methylindole **2a**

E = -1288102.446291 kcal/mol

C	0.94648300	-1.49568500	-0.43807800
C	0.80496000	-0.86319800	0.79739200
C	0.27694900	0.40358800	0.89409600
N	-0.11923200	1.02674400	-0.25664000
C	0.02793800	0.47272700	-1.49603100
C	0.57188900	-0.78937600	-1.58054000
C	-0.41030600	1.24907200	-2.69090100
C	1.45307200	-2.89815400	-0.51845900
C	0.08450300	1.10884800	2.19370600
N	-0.72343600	2.25819600	-0.13242300
C	-2.16428800	2.45074900	-0.00386500
C	-2.16523600	3.96071600	0.25045900
O	-0.90771000	4.43992800	-0.28246900
C	-0.04367000	3.42563400	-0.40975000
O	1.11706400	3.54124500	-0.72089200
H	1.10796300	-1.36677400	1.70723100
H	0.68781000	-1.23308600	-2.56149100

H	-0.20633100	0.66934700	-3.58990300
H	-1.48343800	1.44643200	-2.64605300
H	0.12721500	2.19775000	-2.75895700
H	0.64646100	-3.57551800	-0.21893400
H	1.76825700	-3.15358100	-1.53029500
H	2.29551400	-3.04313400	0.16188300
H	0.55995700	0.53511700	2.98841800
H	0.51191800	2.11306700	2.17486500
H	-0.98267600	1.18450500	2.41678300
H	-2.68472300	2.16316300	-0.91955200
H	-2.56816600	1.86904900	0.82386100
H	-2.96737000	4.48298400	-0.26587700
H	-2.18667600	4.19562600	1.31635500
C	4.18760300	-0.55594400	0.61308600
C	3.98547700	-0.25841600	-0.75778600
C	3.39626800	1.04679200	-0.81261700
C	3.27305900	1.47449500	0.47957900
N	3.75252200	0.52056700	1.34905800
H	3.08791300	1.59584100	-1.68942300
H	2.87092100	2.40422600	0.85563700
C	3.75948200	0.60187700	2.79288300
H	3.36093800	1.56995800	3.09649800
H	3.13994500	-0.18755200	3.22997900
H	4.77665500	0.50400100	3.18206700
C	4.34831900	-1.21526500	-1.71906400
H	4.19696400	-1.01518000	-2.77566800
C	4.89764000	-2.41514900	-1.29982200
H	5.18159500	-3.16225000	-2.03419200
C	5.09026400	-2.68934600	0.06906900
H	5.52078700	-3.64036900	0.36604800
C	4.73681900	-1.76909100	1.04315000
H	4.88330300	-1.98177200	2.09729700
O	-2.26359200	-2.53847700	0.08124200
O	-2.64984500	-0.44549000	1.35498300
O	-2.81365100	-0.43637800	-1.11866400
C	-4.70480200	-1.60667500	0.24449200
S	-2.90567300	-1.21812100	0.12589800
F	-4.96420600	-2.32263600	1.34223200
F	-5.42628800	-0.48310300	0.29957900
F	-5.10901600	-2.30940500	-0.81742100

BF₄⁻ + 1-methylindole **2a** S¹

E = -950823.7108093 kcal/mol

C	-0.78832600	1.75925000	-0.54912100
C	-0.26174100	1.34562100	0.70250000

C	0.40238900	0.17327600	0.87142900
N	0.53523400	-0.70373000	-0.23054600
C	0.09253000	-0.29578100	-1.51748000
C	-0.54986200	0.90103000	-1.63988900
C	0.30810000	-1.25684100	-2.64159300
C	-1.41595700	3.11026200	-0.71227200
C	1.00017600	-0.28101400	2.16296500
N	1.58370800	-1.59560500	-0.17499800
C	2.96924000	-1.26335400	-0.48788700
C	3.62259200	-2.60404000	-0.15140300
O	2.55040400	-3.57316000	-0.19482600
C	1.36527500	-2.94179600	-0.11478500
O	0.30659400	-3.52707300	-0.00975100
B	3.28898200	2.35839000	0.17815100
F	4.48727500	3.00360000	-0.17212300
F	2.76876900	1.69759500	-0.94503900
F	3.56651800	1.40718200	1.19329800
F	2.36861800	3.29963500	0.65727600
H	-0.37608000	1.98854300	1.56950700
H	-0.91825300	1.17219200	-2.62501400
H	-0.19875100	-0.88992600	-3.53530600
H	1.36697800	-1.38725500	-2.89069600
H	-0.08981500	-2.24988300	-2.40343300
H	-0.66364000	3.90939800	-0.71368000
H	-1.97511000	3.17788800	-1.64970600
H	-2.11245200	3.32801300	0.10553900
H	0.66885200	0.37601700	2.96895000
H	0.71088300	-1.30916600	2.40818900
H	2.09157200	-0.23309400	2.12666000
H	3.07544400	-0.98542700	-1.54091800
H	3.32290400	-0.43847200	0.12873300
H	4.38208800	-2.91186800	-0.86767100
H	4.03978700	-2.61256300	0.85824100
C	-3.27777300	-0.09836300	0.72355200
C	-3.20542300	-0.70938300	-0.54982900
C	-2.41350700	-1.86181000	-0.40473400
C	-2.04170800	-1.93488100	0.96563500
N	-2.54874500	-0.90566900	1.62543500
H	-2.12962500	-2.58440200	-1.15165000
H	-1.42623800	-2.68293500	1.43959600
C	-2.38053400	-0.60333000	3.03489900
H	-1.77645900	-1.38267400	3.49462000
H	-1.87745100	0.35996700	3.13528000
H	-3.35743600	-0.56167500	3.51845900
C	-3.80747100	-0.08399100	-1.65338900

H	-3.74754300	-0.53031900	-2.63881400
C	-4.47548100	1.11521100	-1.44369500
H	-4.94954800	1.62091800	-2.27600500
C	-4.54070800	1.68523400	-0.16906100
H	-5.06767600	2.62246100	-0.03383700
C	-3.93809800	1.08300700	0.94949800
H	-3.98760500	1.54725300	1.92682100

TfO⁻ + 1-methylindole **2a** S¹

E = -1287755.394572 kcal/mol

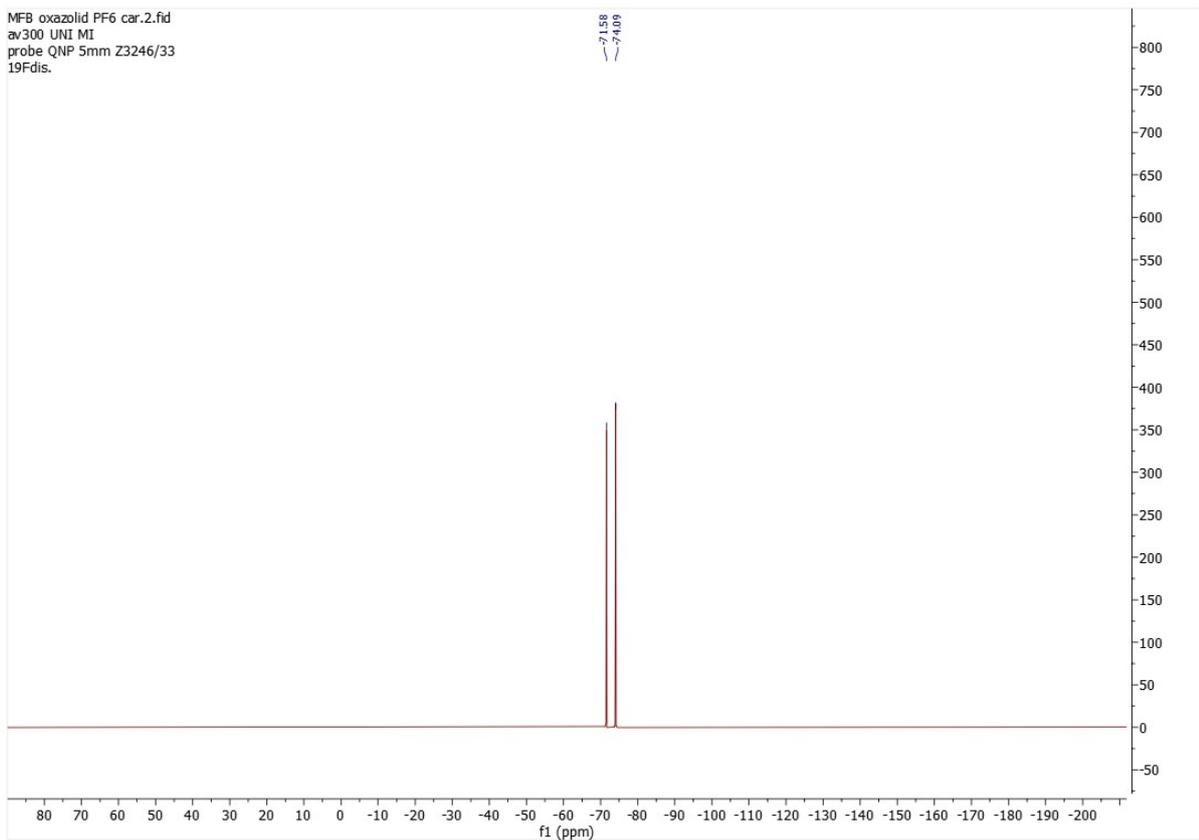
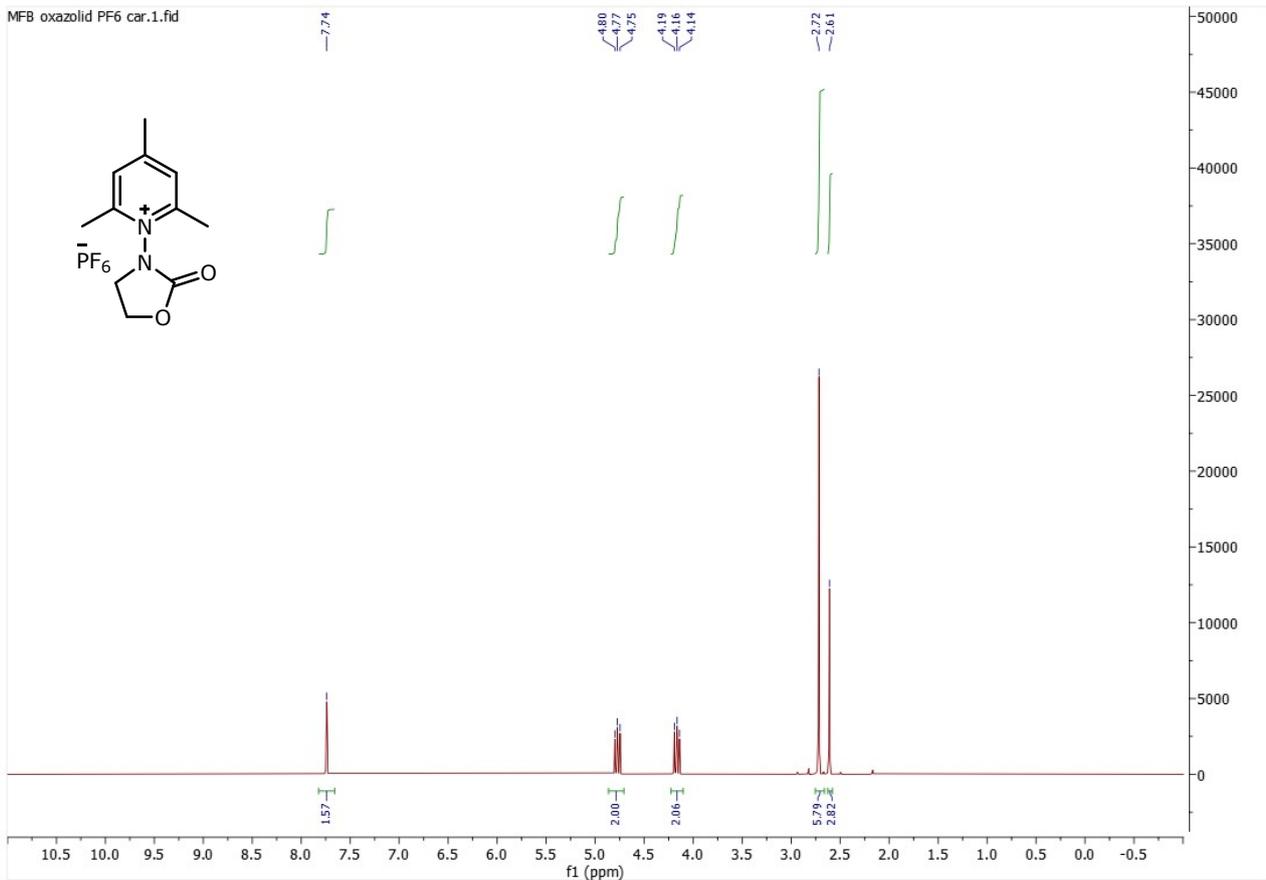
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C	0.51651700	-1.17515900	0.65543600
C	0.35508600	0.16157700	0.84064000
N	0.58565100	1.03634200	-0.24778000
C	0.86854000	0.50729800	-1.53592500
C	1.00103300	-0.84377600	-1.67468900
C	1.06194100	1.49393500	-2.64189500
C	0.93846600	-3.22887200	-0.77853300
C	-0.02205100	0.80034600	2.13773200
N	-0.05829100	2.25276000	-0.19189100
C	-1.46151600	2.45757400	-0.52967600
C	-1.58441500	3.93963200	-0.16924200
O	-0.22995000	4.44611700	-0.16623600
C	0.63852700	3.42231300	-0.08642500
O	1.83486900	3.57191800	0.05373400
H	0.36702200	-1.82367600	1.51298600
H	1.25747500	-1.22254000	-2.65960700
H	1.42548500	0.97684100	-3.53097600
H	0.13583600	2.01177400	-2.91461600
H	1.79120000	2.26450700	-2.36841900
H	-0.05914100	-3.68591700	-0.78172300
H	1.42793000	-3.49058500	-1.72058600
H	1.50430100	-3.70165000	0.03246400
H	-0.00545400	0.05291800	2.93258500
H	0.66617200	1.61117500	2.40317800
H	-1.03234400	1.21738300	2.09774900
H	-1.64335300	2.25739700	-1.59043200
H	-2.10918300	1.81384000	0.06739500
H	-2.15714300	4.51819400	-0.89147200
H	-1.99675900	4.08224600	0.83211500
C	3.85682100	-0.96080900	0.74462500
C	4.04277100	-0.33836400	-0.51175000
C	3.75177300	1.02550500	-0.33825200
C	3.41476600	1.20274500	1.03197700
N	3.48050200	0.04237400	1.66566600

H	3.78031500	1.82022300	-1.06508000
H	3.12520200	2.11826300	1.52355000
C	3.18800900	-0.20907600	3.06499400
H	2.91013800	0.72759100	3.54352400
H	2.36034900	-0.91730100	3.13387000
H	4.07044300	-0.62428300	3.55362700
C	4.37683300	-1.12108200	-1.62913700
H	4.50734500	-0.66291400	-2.60219400
C	4.53188900	-2.48912000	-1.44894700
H	4.78887600	-3.11794300	-2.29256000
C	4.35581400	-3.07052600	-0.18993100
H	4.48297500	-4.14080900	-0.07760900
C	4.01264700	-2.30965900	0.94176600
H	3.86721800	-2.77918800	1.90698400
O	-2.86188700	-2.21418200	0.63320700
O	-3.21452600	0.16901400	1.22959700
O	-2.87218200	-0.47529100	-1.14130300
C	-5.13204000	-1.09534600	0.00003400
S	-3.30958800	-0.88259800	0.20142800
F	-5.70100400	-1.46764300	1.15158400
F	-5.70452800	0.04803200	-0.39249600
F	-5.40441500	-2.02946900	-0.91756100

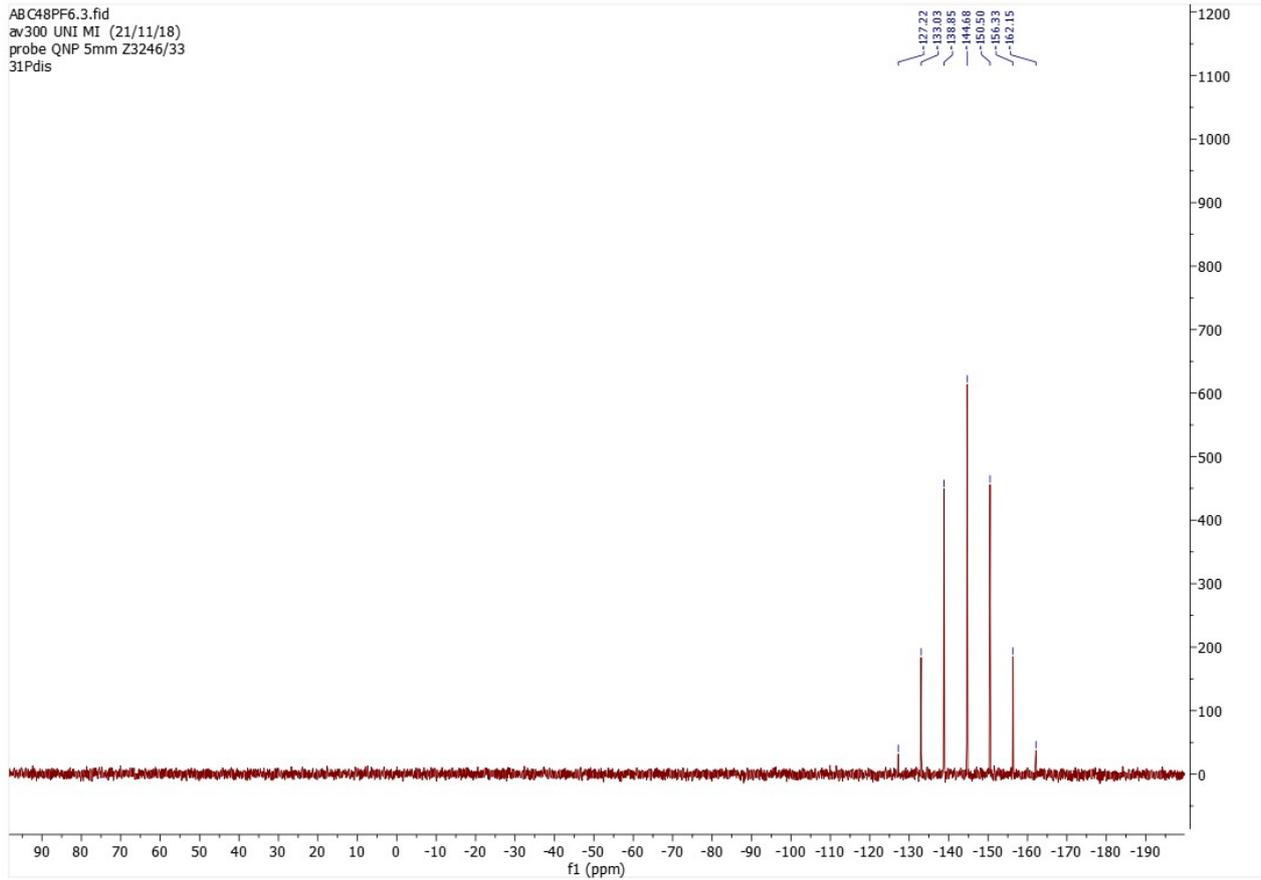
Excited state	Electronic transition (nm)	Oscillator strength	HOMO-LUMO contribution
S1	517	0.0004	50%

10 NMR Spectra

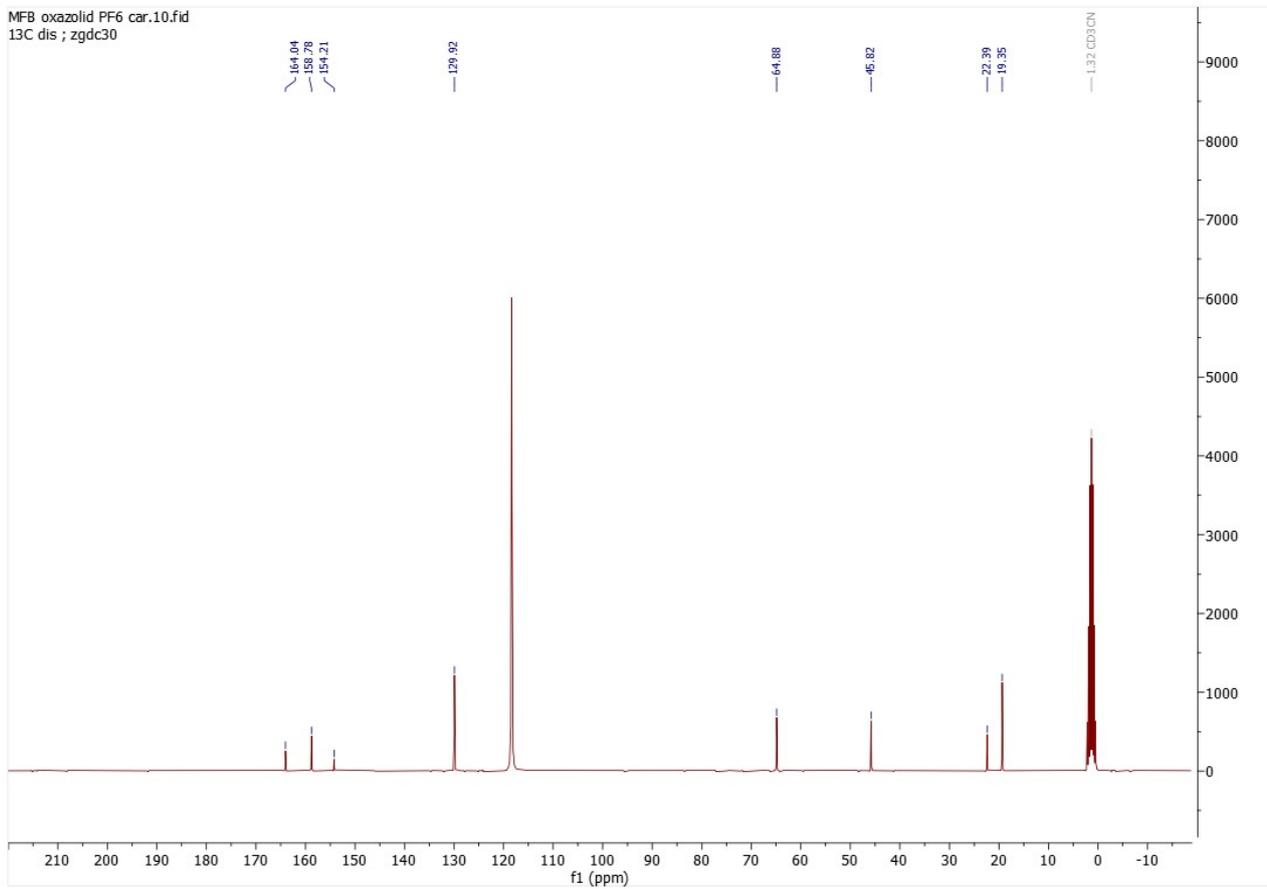
2,4,6-trimethyl-1-(2-oxooxazolidin-3-yl)pyridinium hexafluorophosphates



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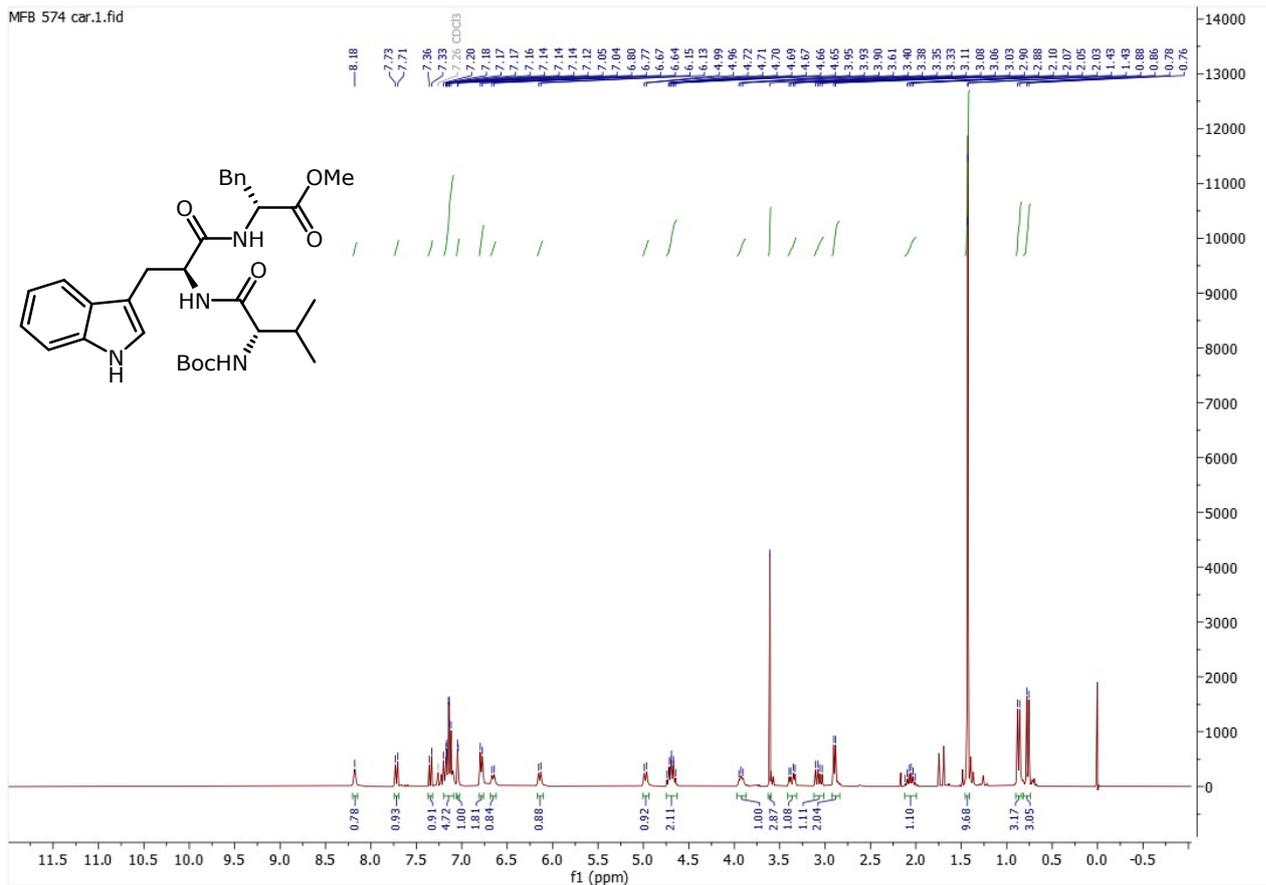


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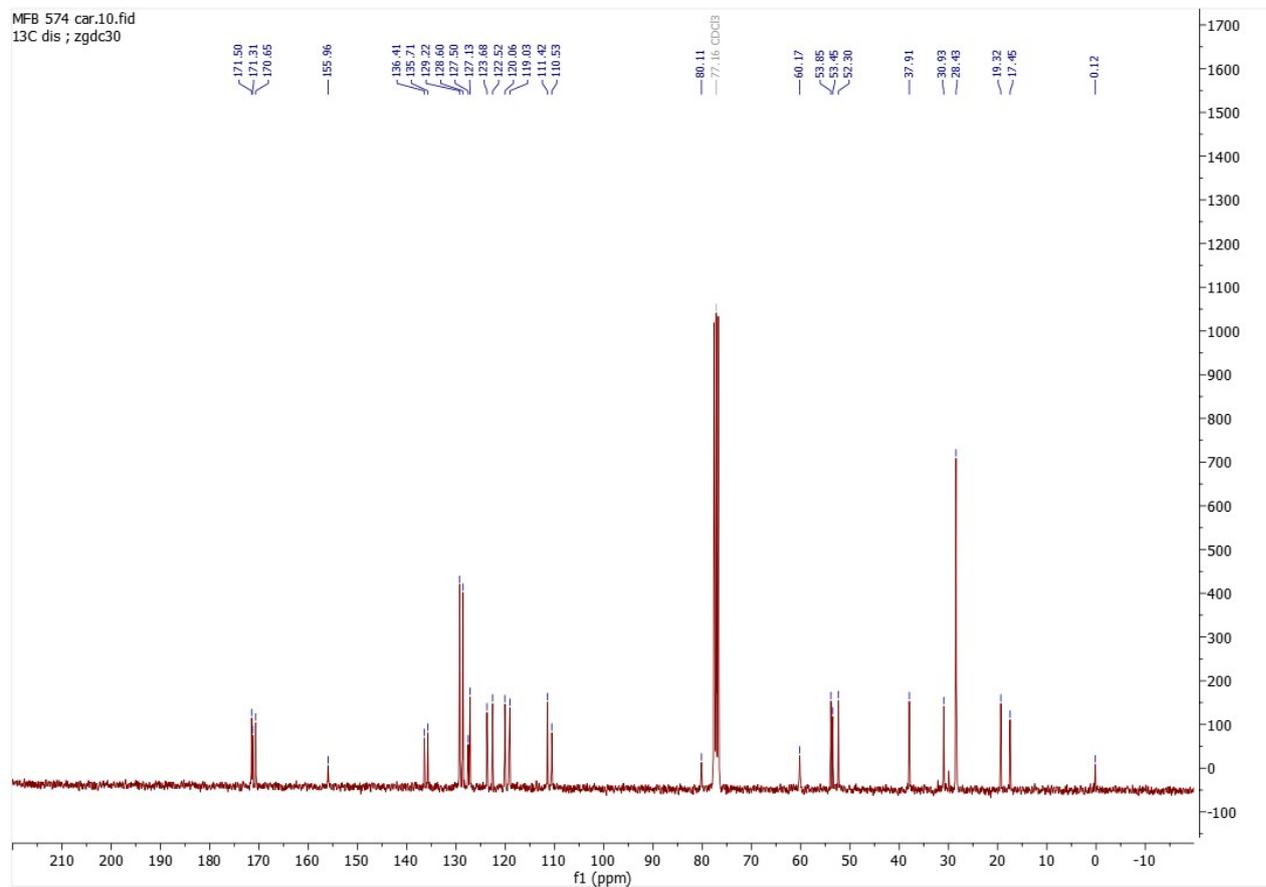


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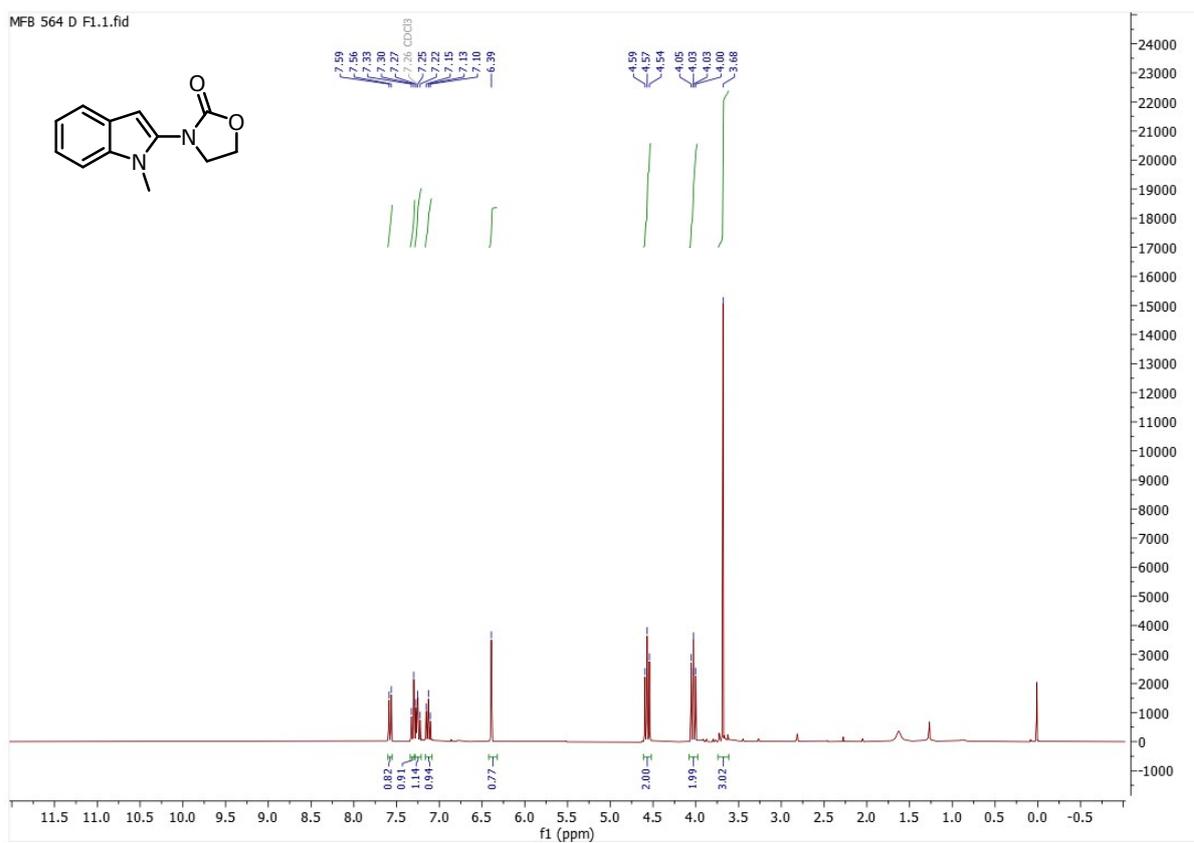
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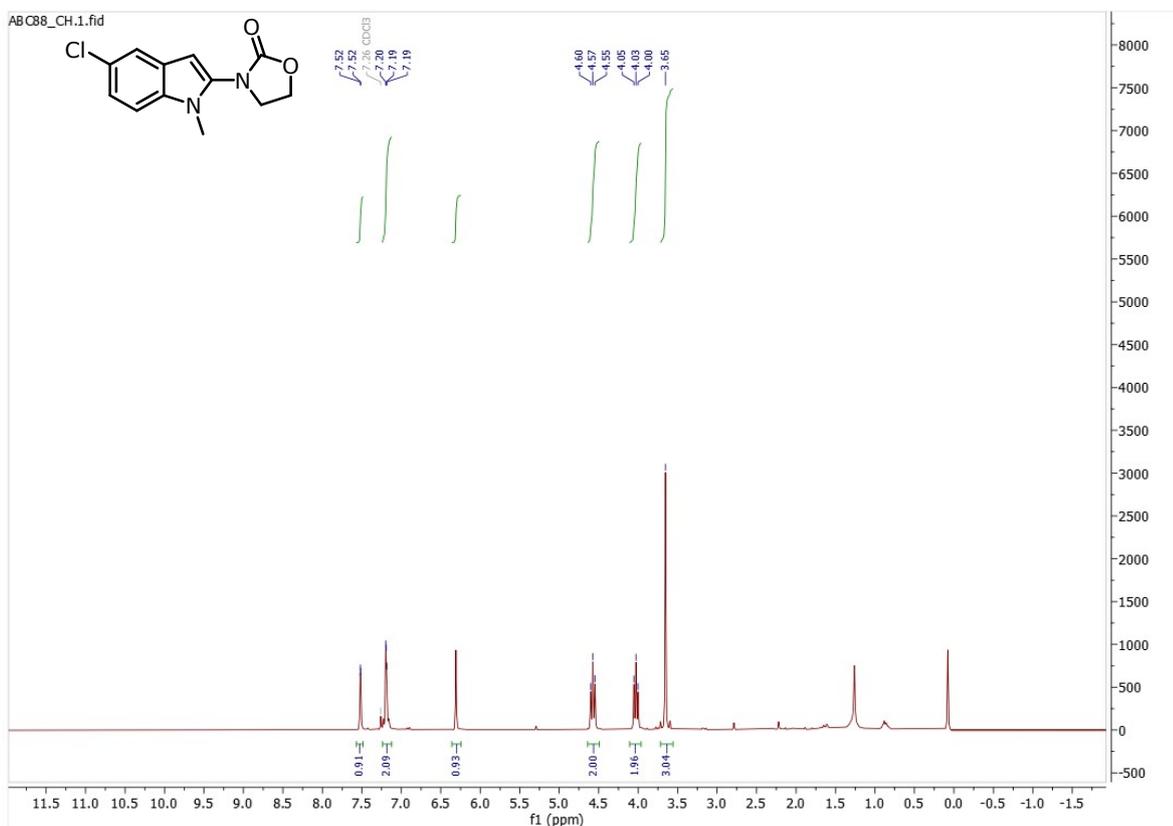
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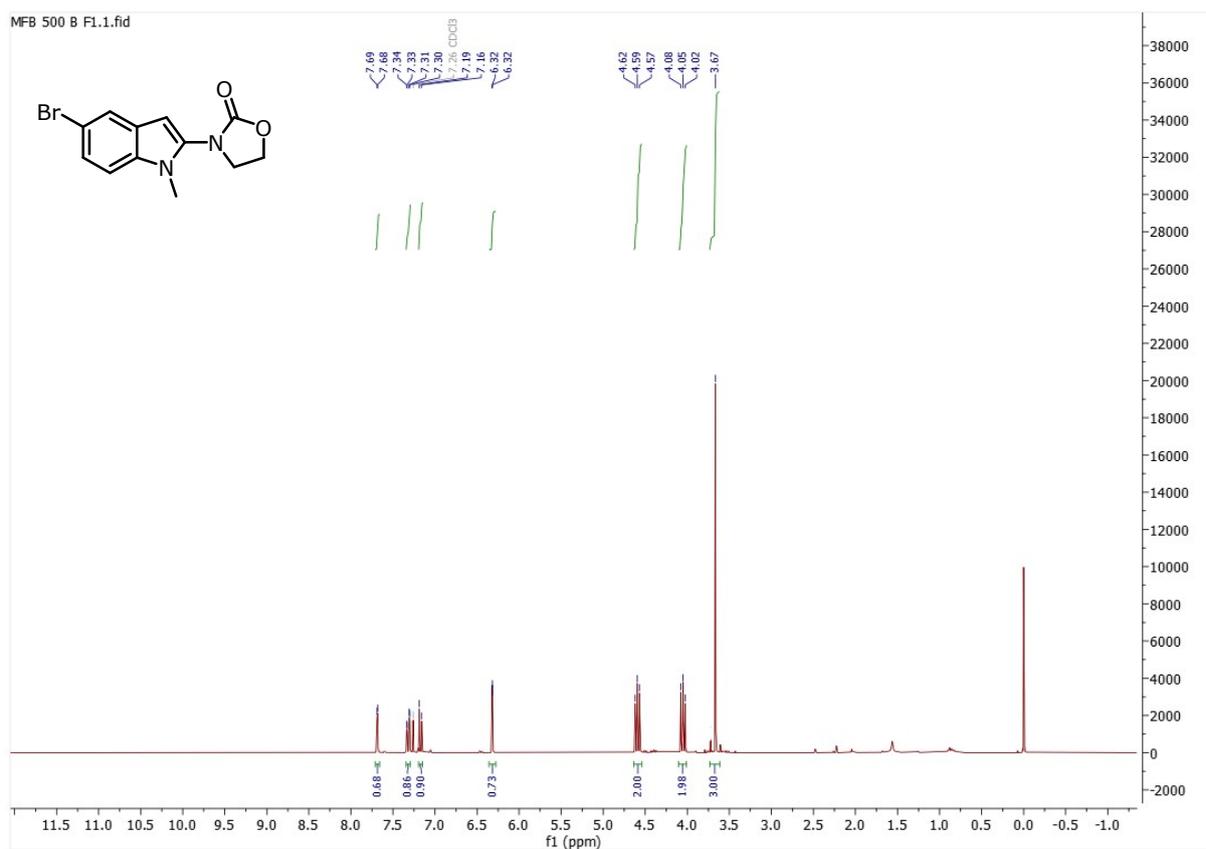
3-(1-methyl-1H-indol-2-yl)oxazolidin-2-one **3a**



3-(5-chloro-1-methyl-1H-indol-2-yl)oxazolidin-2-one **3b**

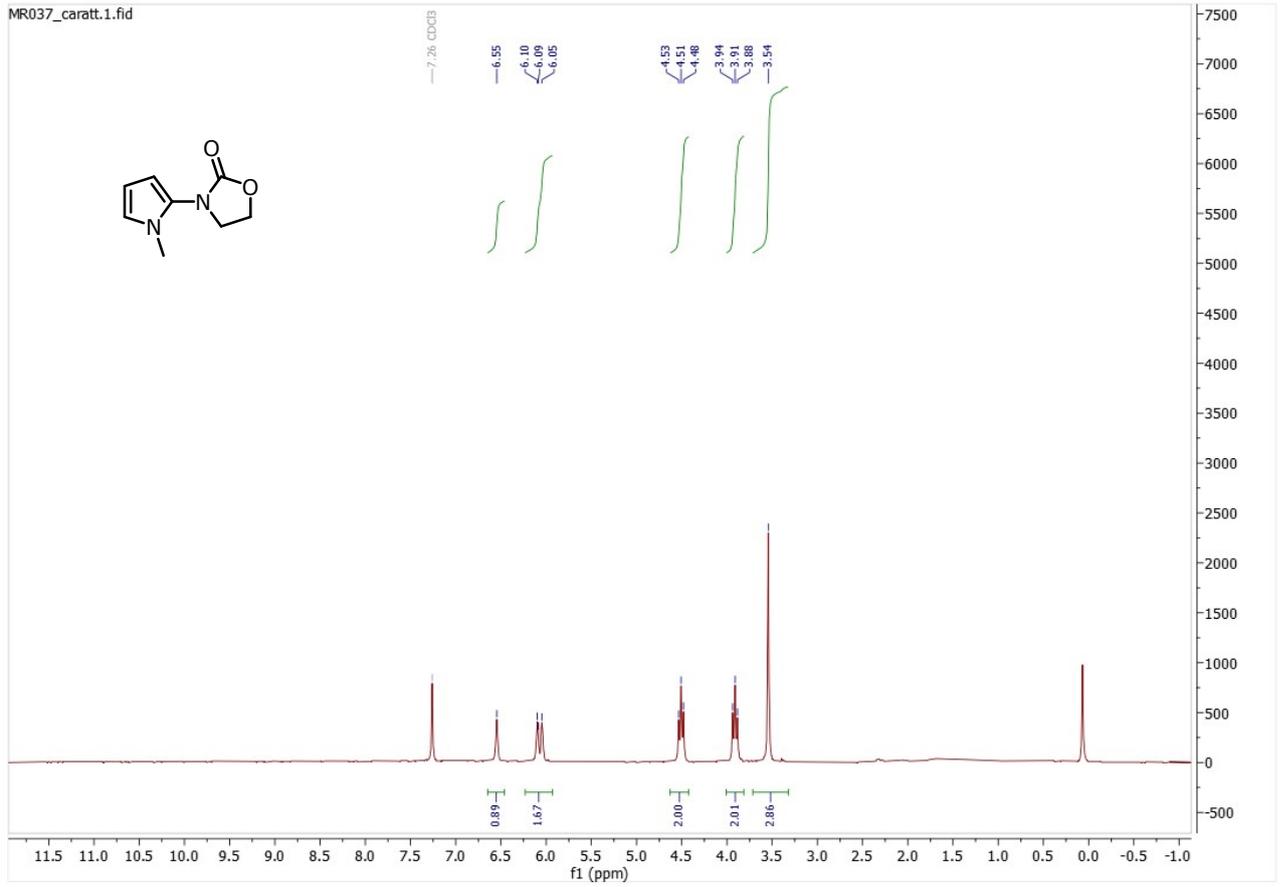


3-(5-bromo-1-methyl-1H-indol-2-yl)oxazolidin-2-one 3c

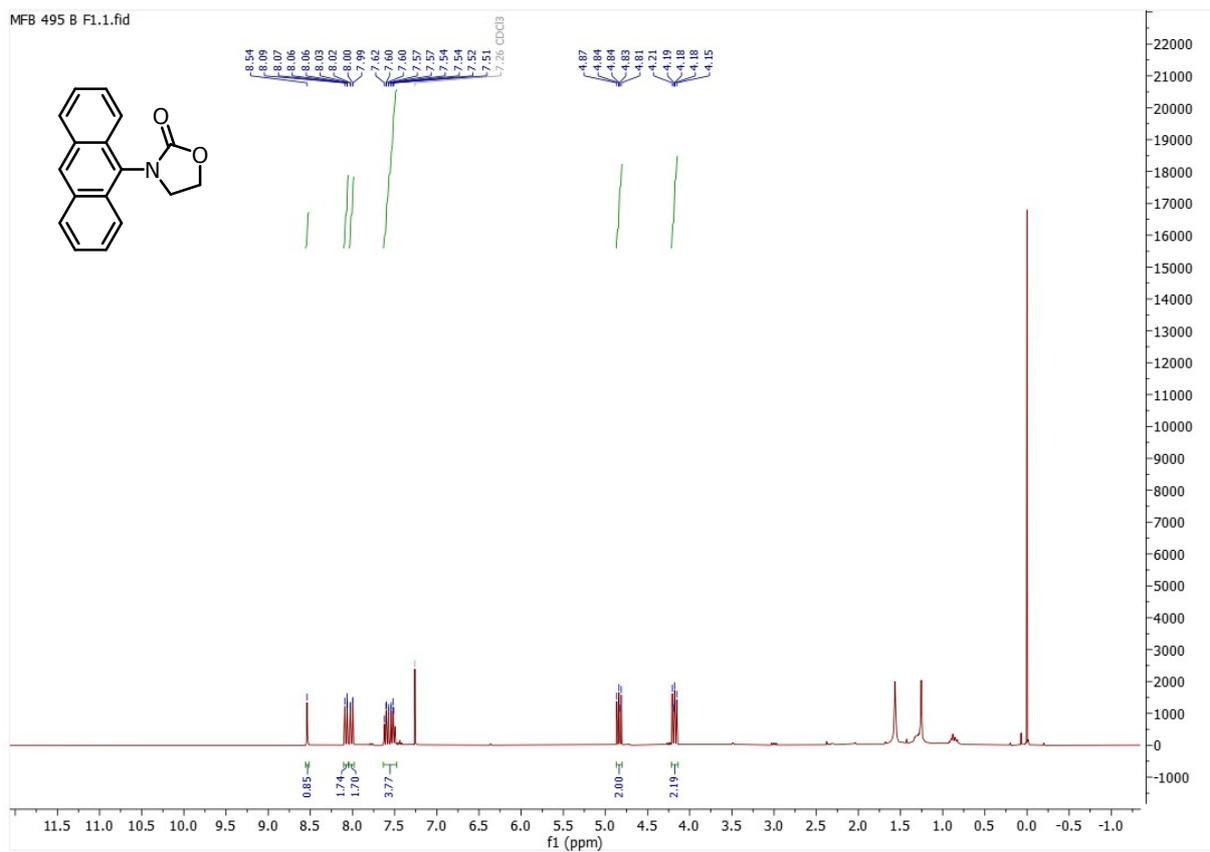


3-(1-methyl-1H-pyrrol-2-yl)oxazolidin-2-one 3d

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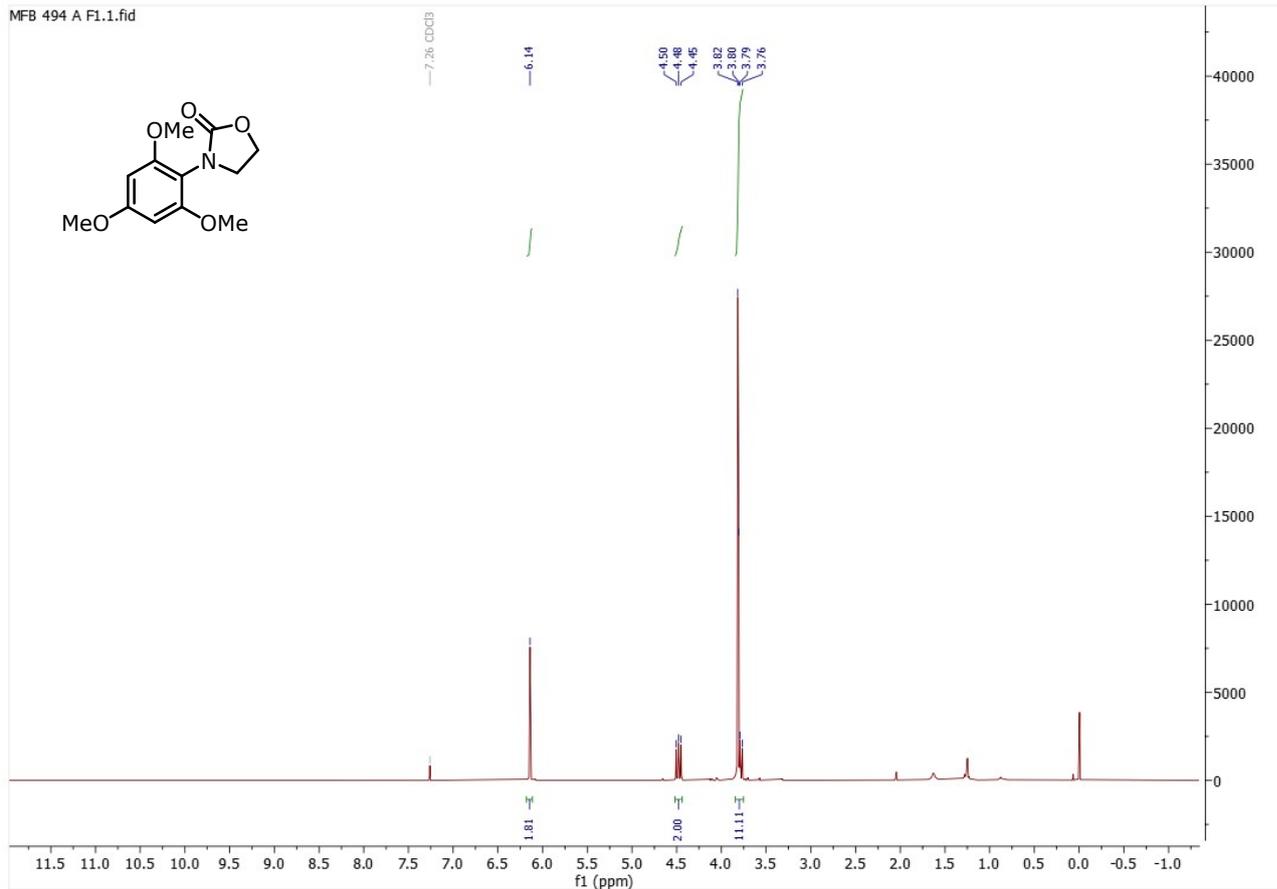


3-(anthracen-9-yl)oxazolidin-2-one **3e**

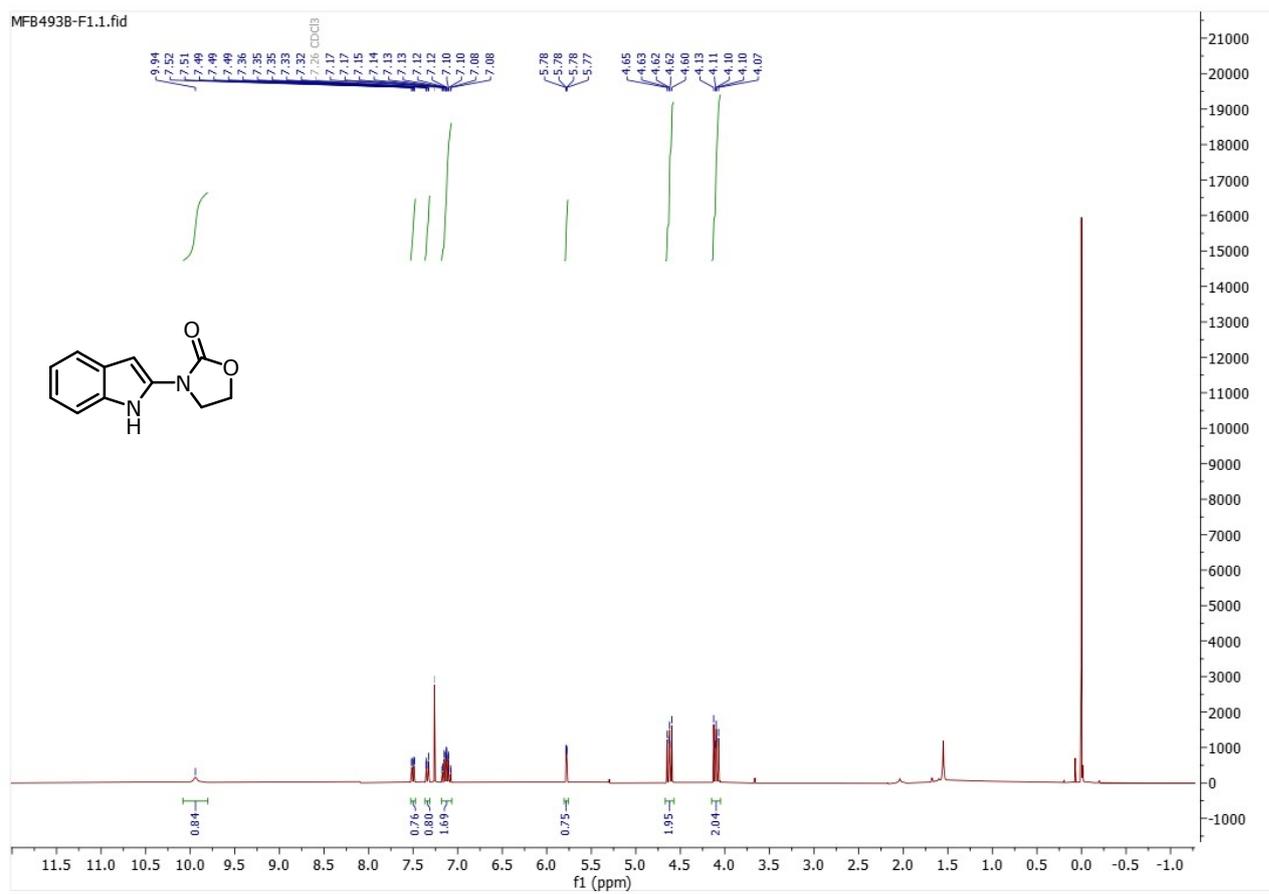


3-(2,4,6-trimethoxyphenyl)oxazolidin-2-one **3f**

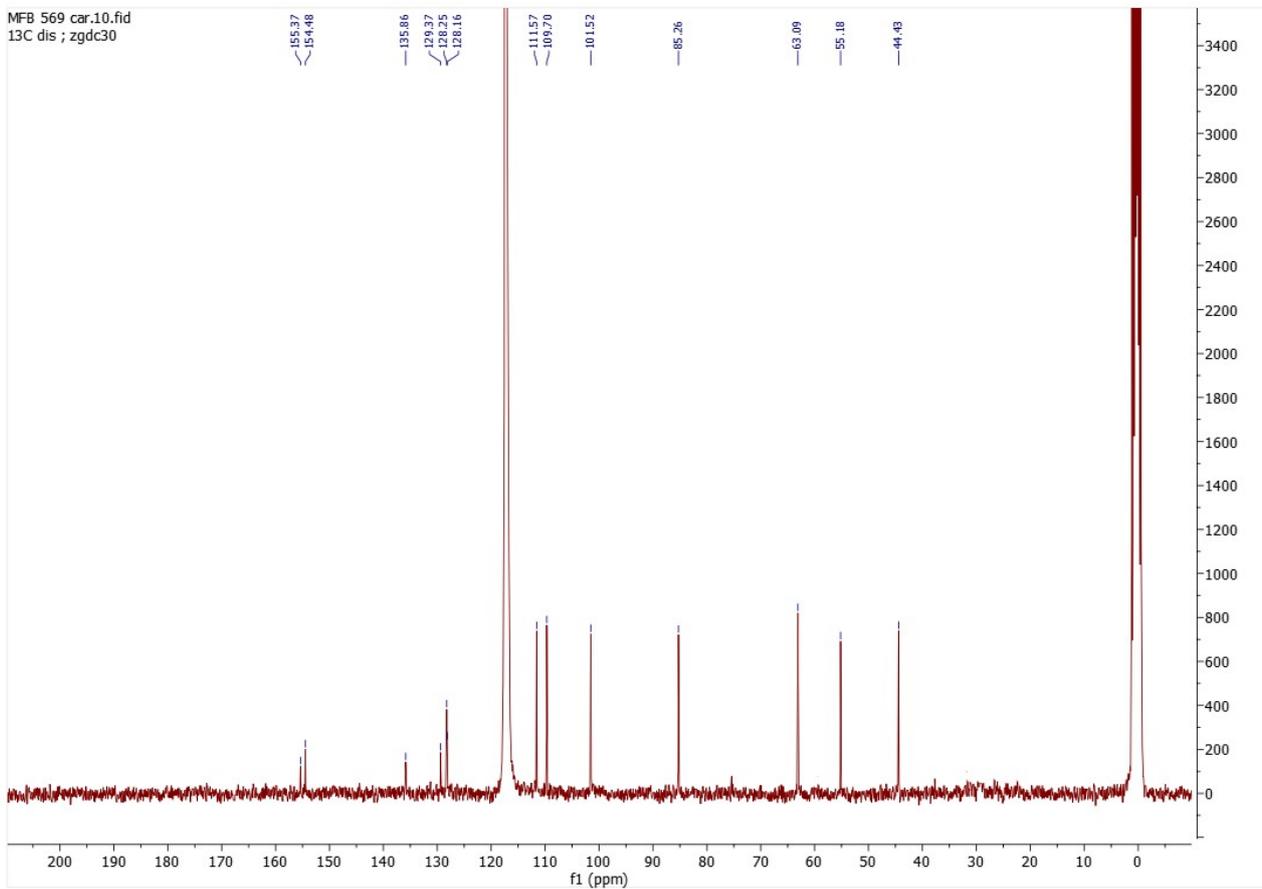
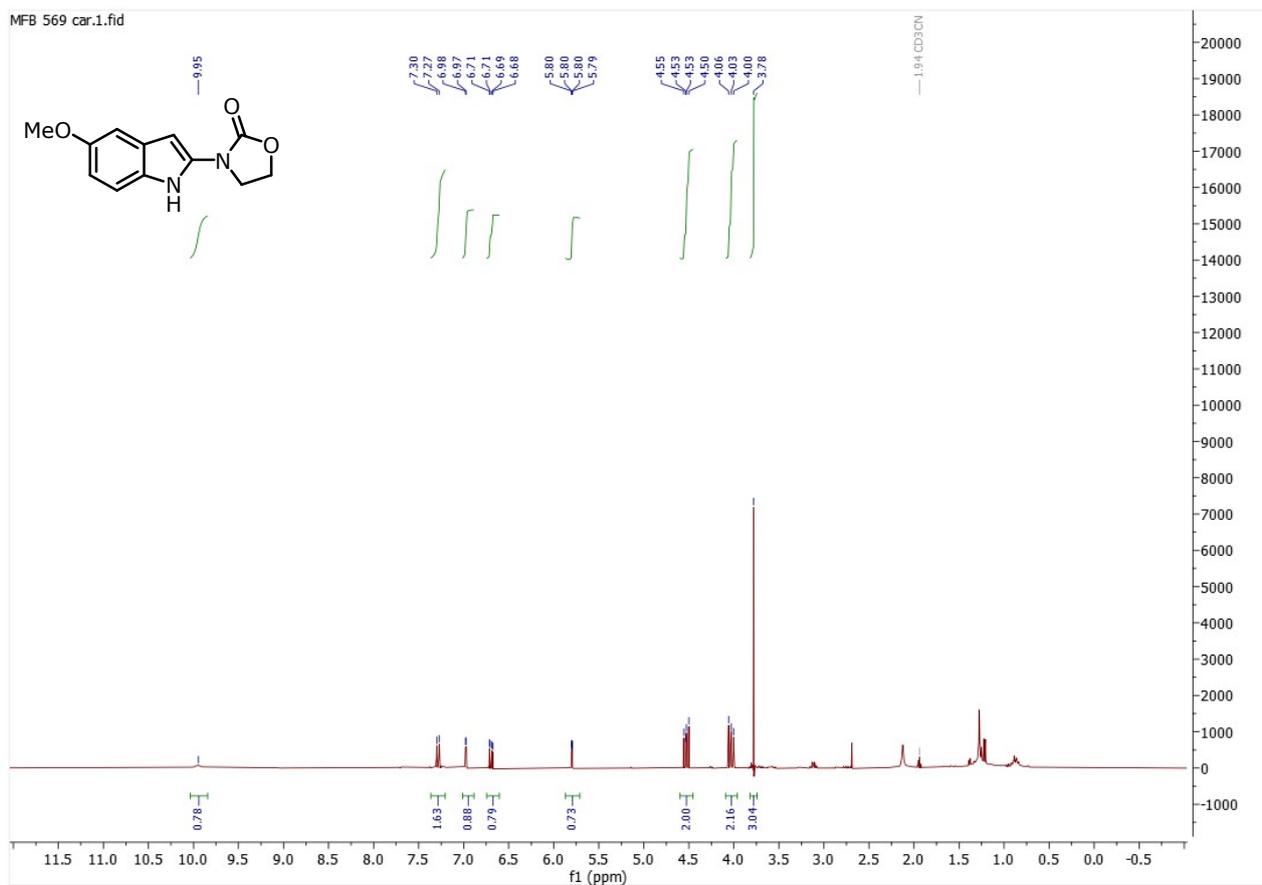
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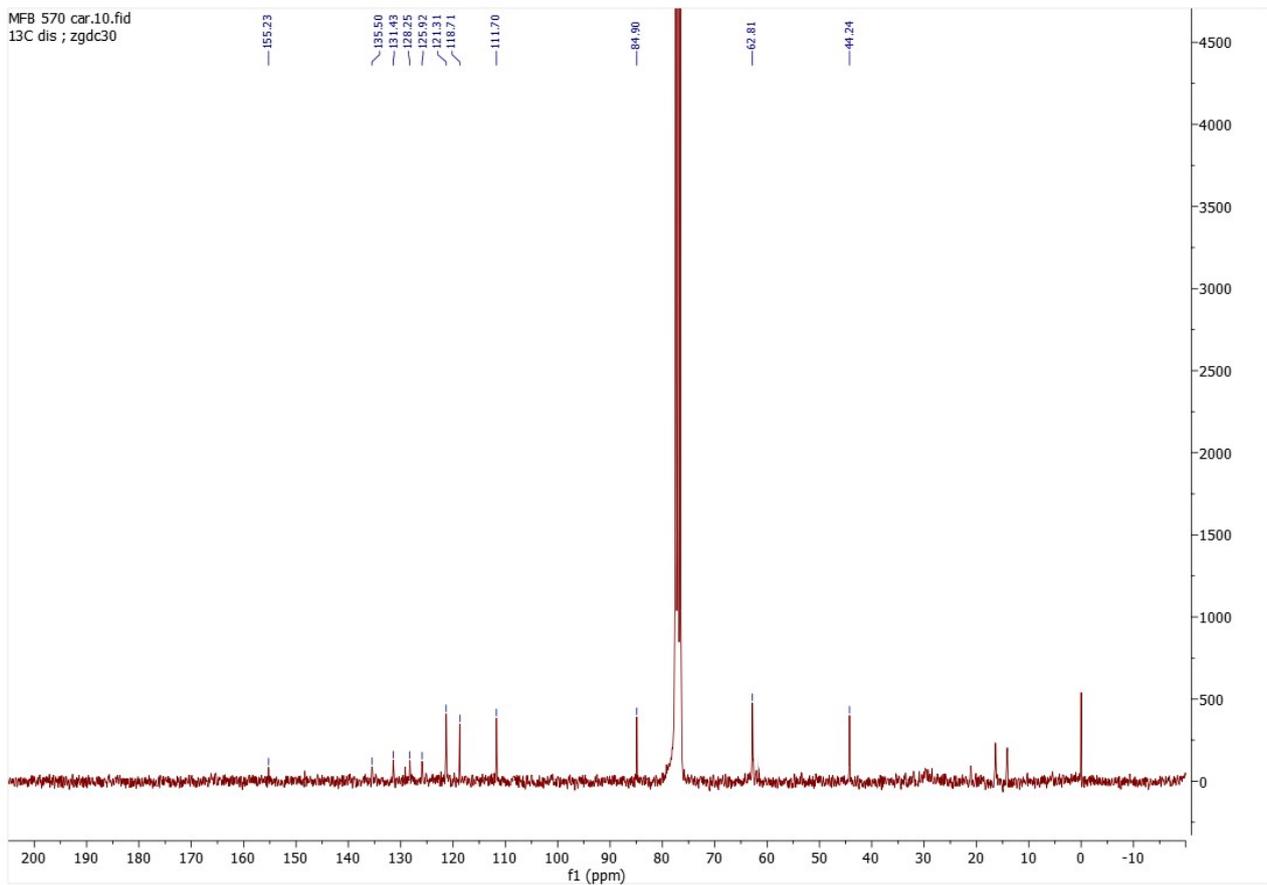
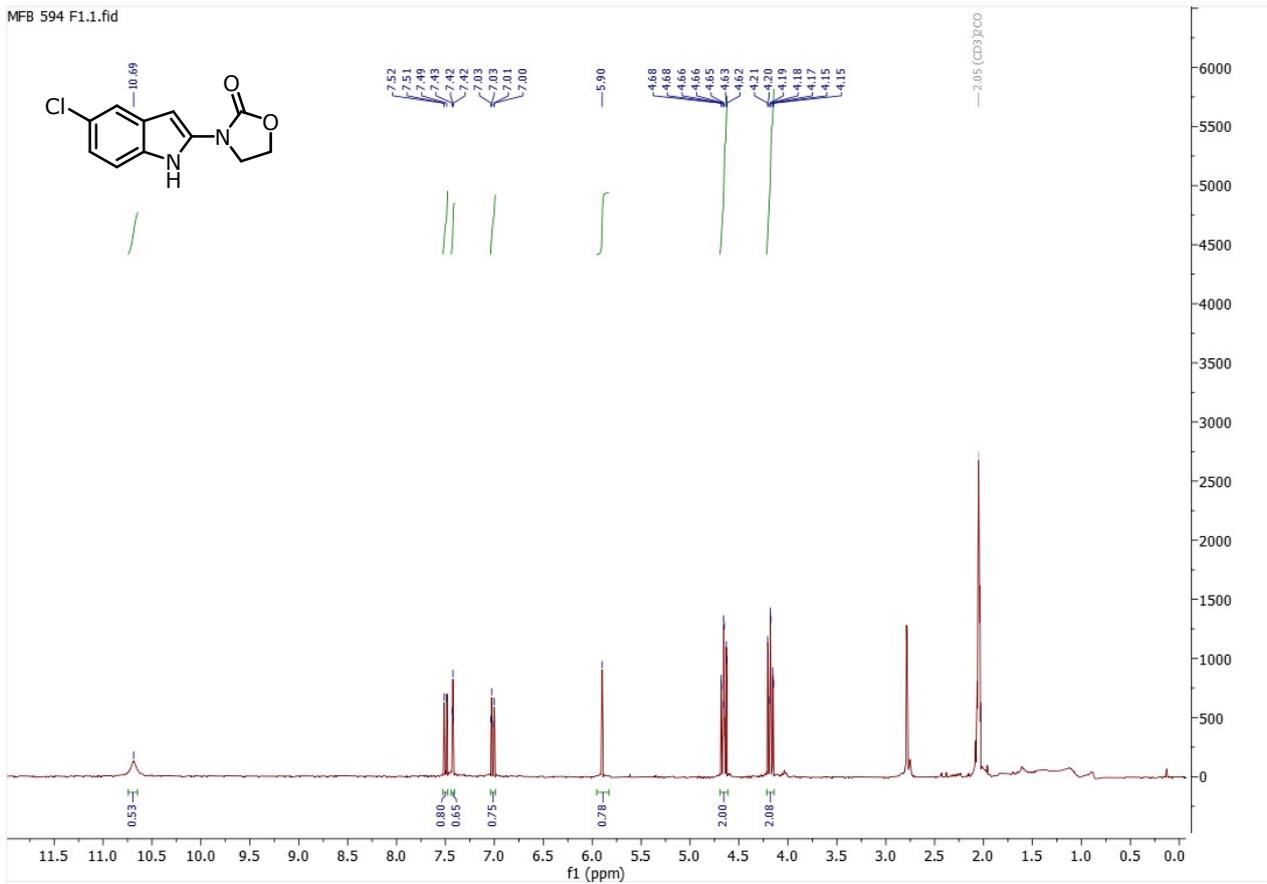
3-(1*H*-indol-2-yl)oxazolidin-2-one **3h**



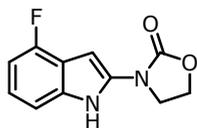
3-(5-methoxy-1H-indol-2-yl)oxazolidin-2-one **3i**

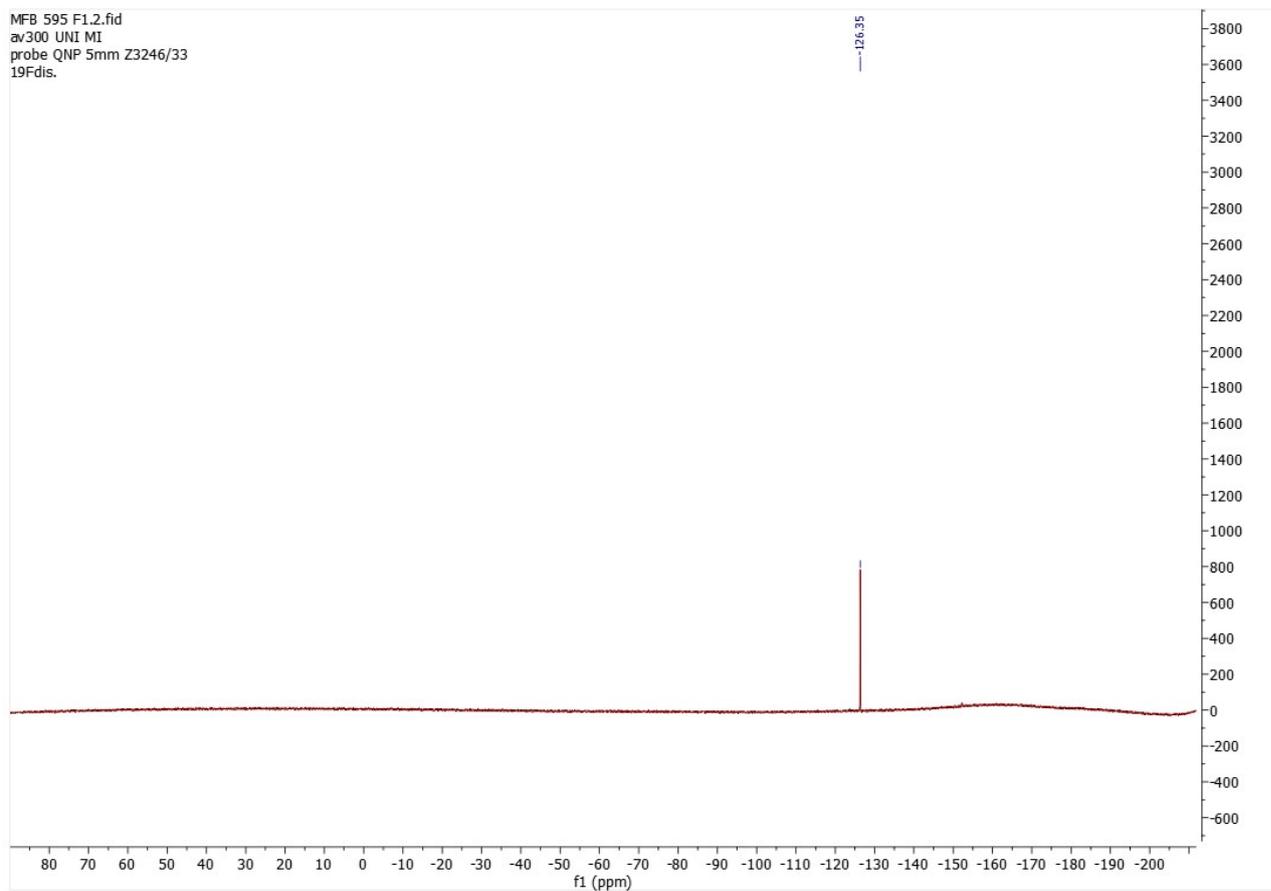
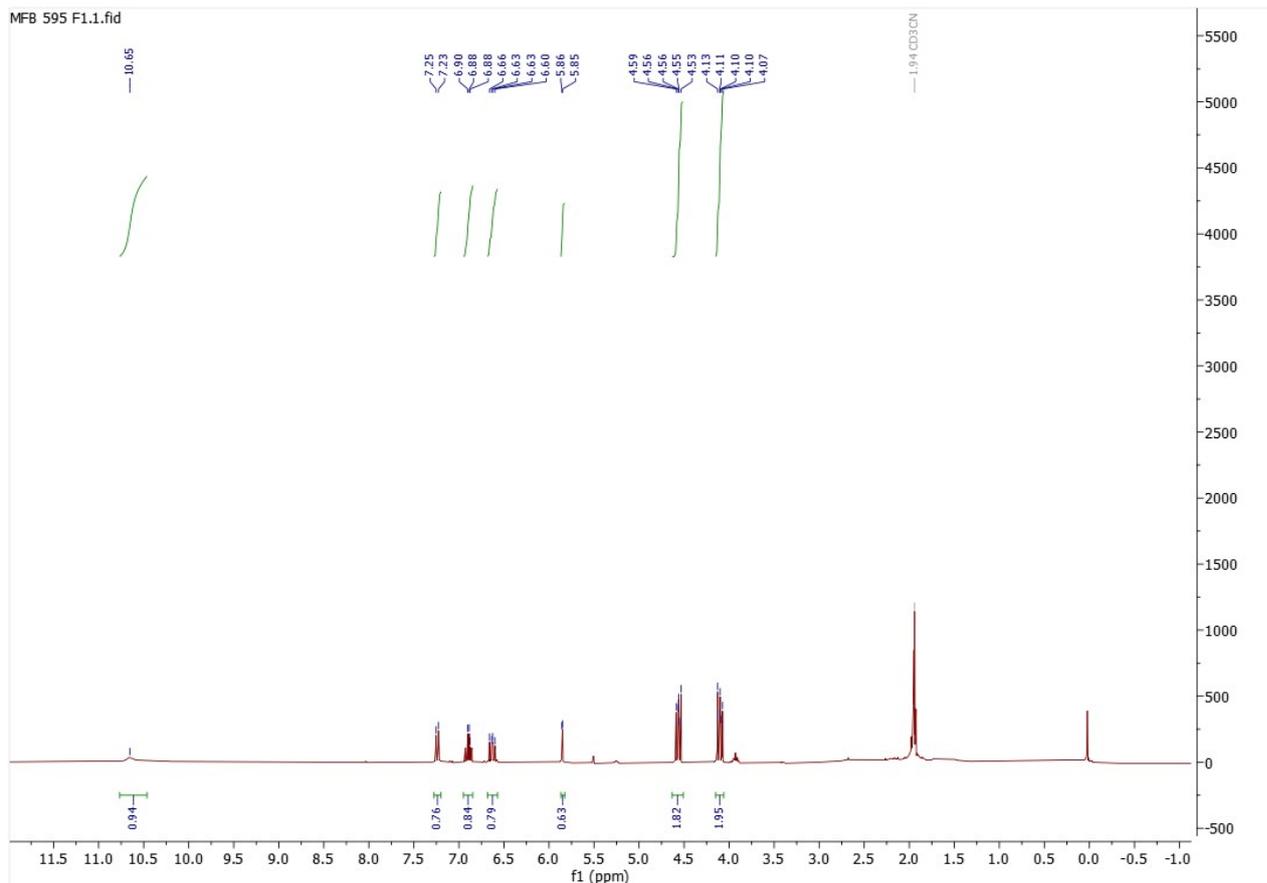


3-(5-chloro-1H-indol-2-yl)oxazolidin-2-one **3j**

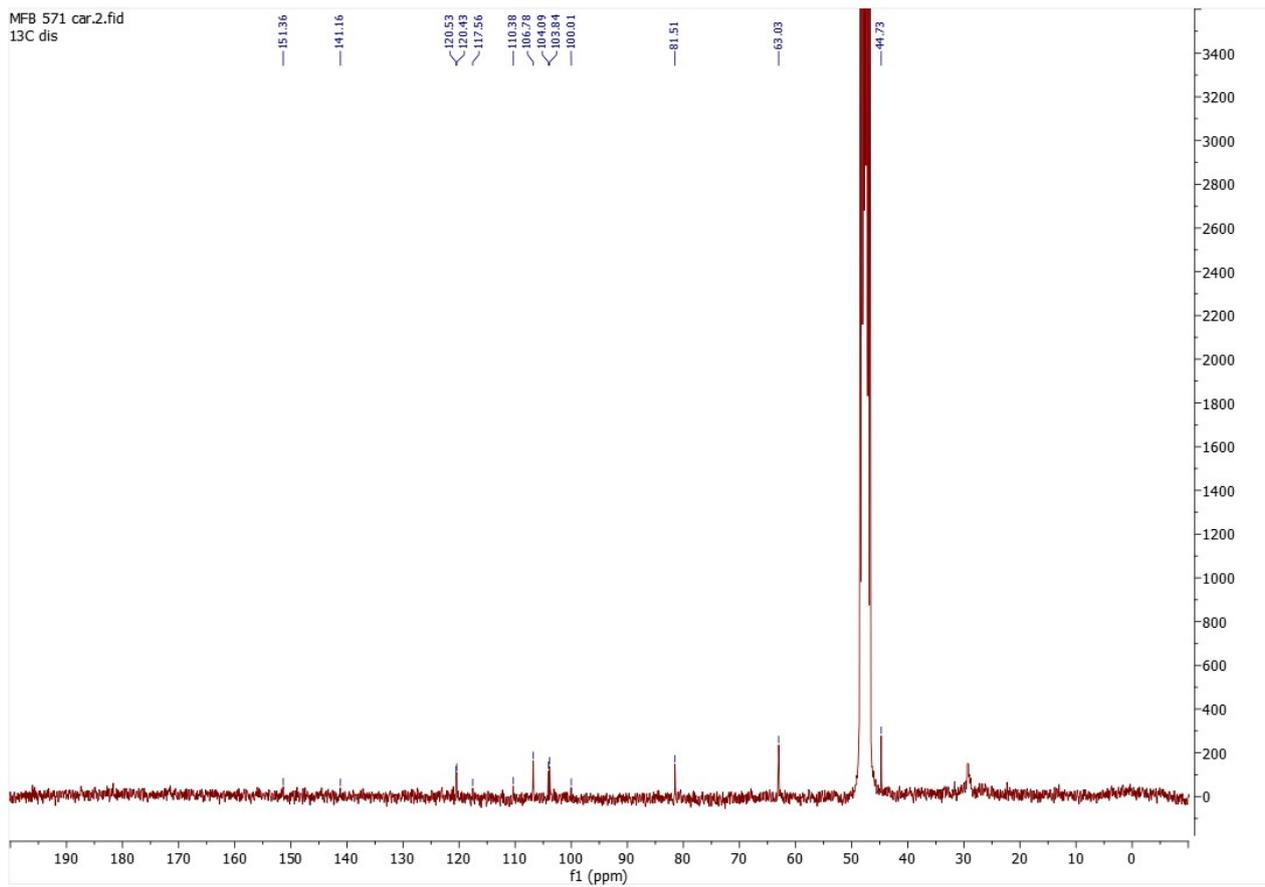


3-(4-fluoro-1*H*-indol-2-yl)oxazolidin-2-one 3k

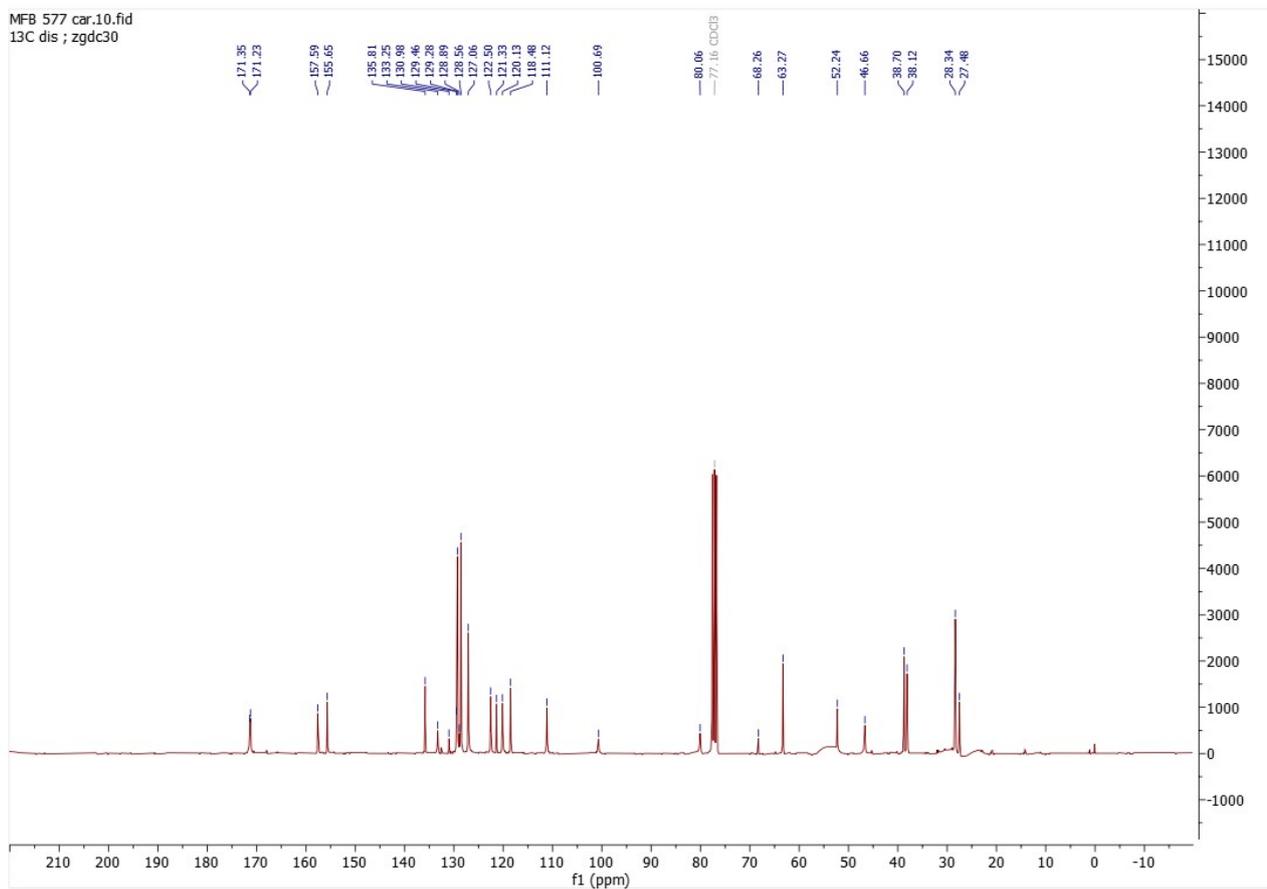
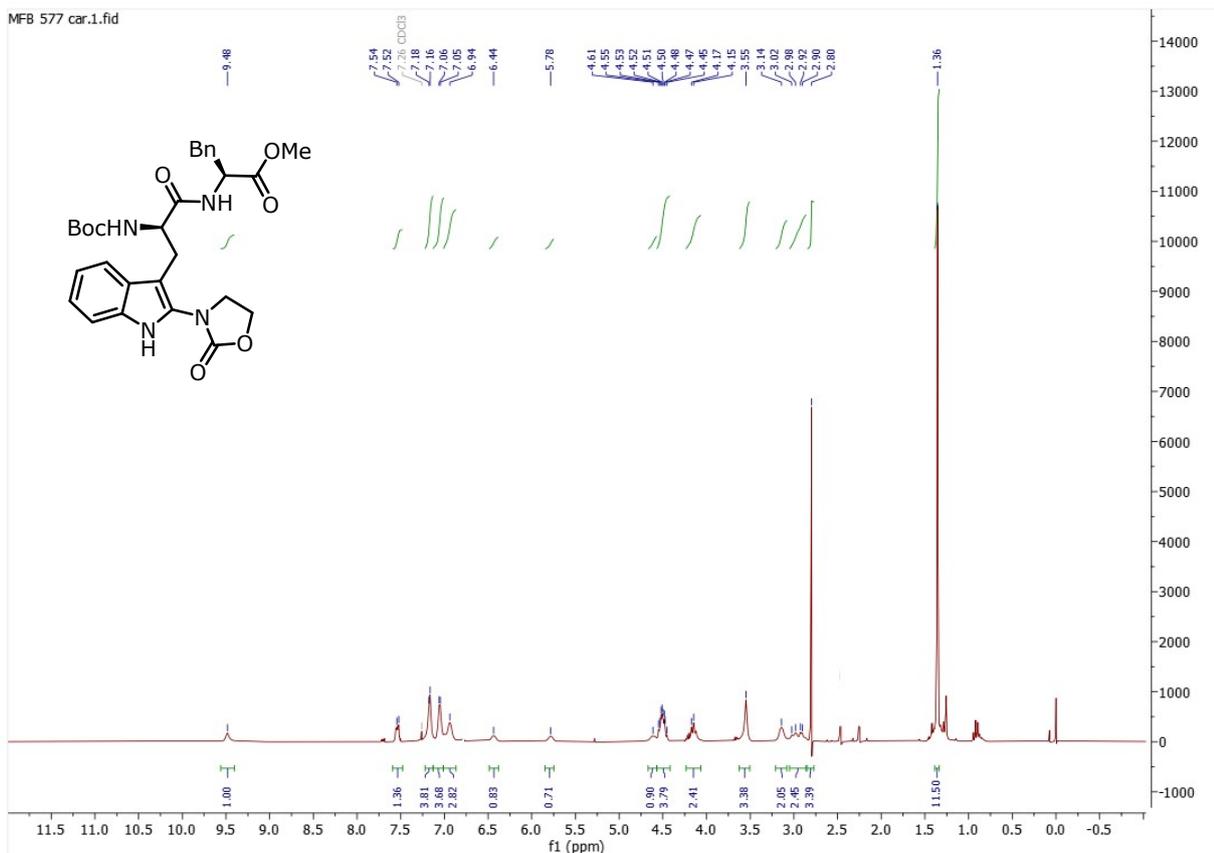




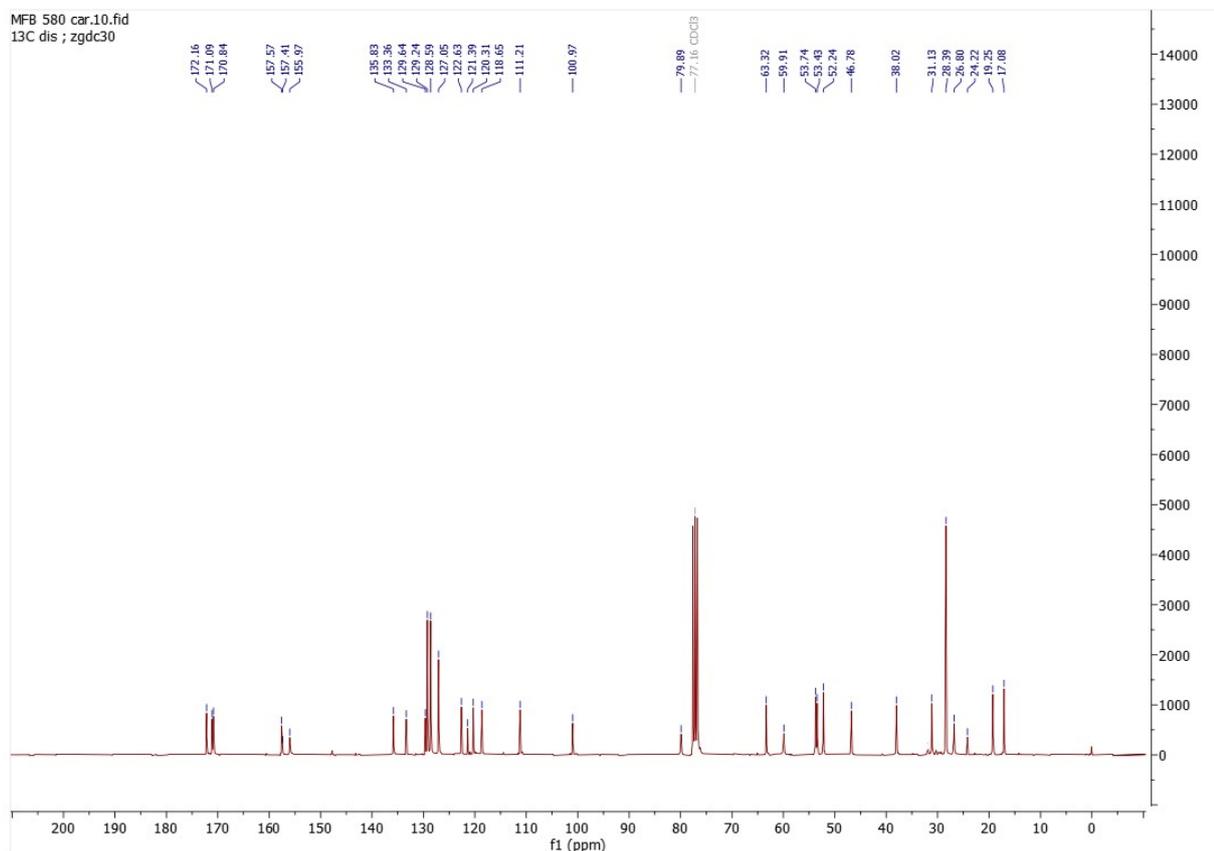
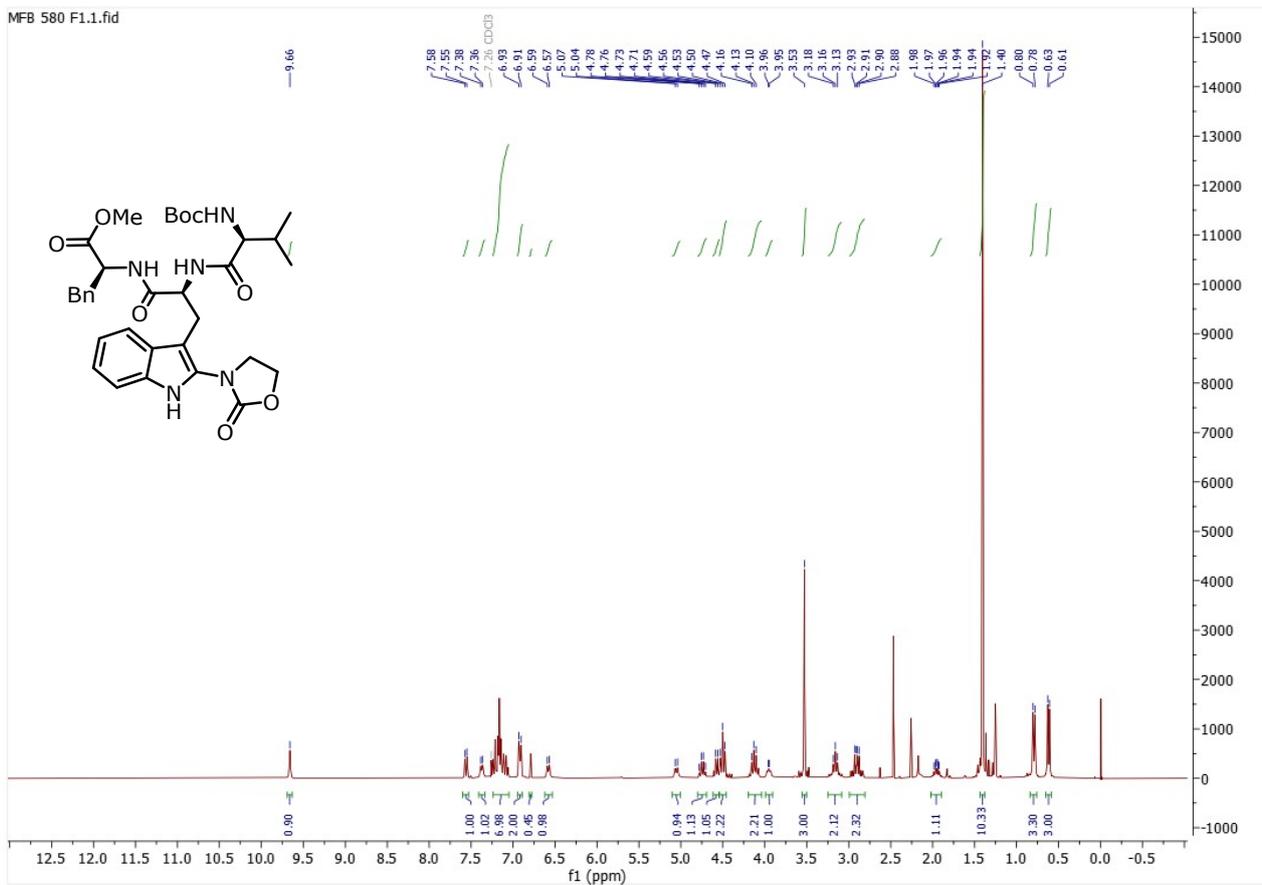
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13C dis



methyl ((R)-2-((tert-butoxycarbonyl)amino)-3-(2-(2-oxooxazolidin-3-yl)-1H-indol-3-yl)propanoyl)-L-phenylalaninate **3I**



methyl ((S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-methylbutanamido)-3-(2-(2-oxooxazolidin-3-yl)-1H-indol-3-yl)propanoyl)-L-phenylalaninate **3m**



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