Supplementary Information for

Studies on the Enantioselective Iminium Ion Trapping of Radicals Triggered by an Electron-Relay Mechanism

Ana Bahamonde,† John J. Murphy,† Marika Savarese,‡ Eric Bremond,‡ Andrea Cavalli,‡ and Paolo Melchiorre*,†,§

†ICIQ - Institute of Chemical Research of Catalonia – the Barcelona Institute of Science and Technology, Avinguda Països Catalans 16, 43007 Tarragona, Spain
‡IIT - Istituto Italiano di Tecnologia, via Morego 30, 16163 Genova, Italy.
§ICREA - Catalan Institution for Research and Advanced Studies, Passeig Lluís Companys 23, 08010 Barcelona, Spain.

*Correspondence to: pmelchiorre@iciq.es

1ICIQ - Institute of Chemical Research of Catalonia – the Barcelona Institute of Science and Technology, Avinguda Països Catalans 16, 43007 Tarragona, Spain
2IIT - Istituto Italiano di Tecnologia, via Morego 30, 16163 Genova, Italy.
3ICREA - Catalan Institution for Research and Advanced Studies, Passeig Lluís Companys 23, 08010 Barcelona, Spain.

*Correspondence to: pmelchiorre@iciq.es
# Table of Contents

A. General Information S3  
B. Catalyst Synthesis S4  
   B1. Synthesis of Carbazoles S4  
   B2. Synthesis of Catalysts 4 S5  
C. General Procedures for the Enantioselective Iminium Ion Radical Trap S8  
D. Kinetic Studies S9  
E. Spectroscopic Studies on the Equilibrium of Iminium Ion Formation S18  
   D1. Characterization of the Intermediates involved in Iminium Ion Formation S19  
F. Optical Absorption Spectra S22  
   F1. Mixtures of TBADT and 2a S22  
   F2. Reaction Mixture S23  
   F3. Preparation and Characterisation of the Shelf-Stable Carbazoliumyl Radical Cation Salt 7 S24  
G. Computational Studies S25  
   G1. Computational Details S25  
   G2. Optimized Cartesian Coordinates of Intermediate D-1 S25  
   G3. Computed Absorption Spectrum of Intermediate D-1 S28  
   G4. Computed Absorption Spectrum of the Shelf-Stable Carbazoliumyl Radical Cation Salt 7 S28  
H. Cyclic Voltammetry S30  
I. References S31  
J. NMR Spectra S32
A. General Information

The NMR spectra were recorded at 400 MHz or 500 MHz for $^1$H and at 100 MHz or 125 MHz for $^{13}$C, respectively. The chemical shifts (δ) for $^1$H and $^{13}$C are given in ppm and are internally referenced to residual protio solvent signals (for CDCl$_3$ @ 7.26 ppm and 77.0 ppm, respectively; for CD$_3$CN @ 1.96 ppm $^1$H NMR, 118.26 ppm and 1.79 ppm $^{13}$C NMR). Coupling constants are given in Hz. When necessary, $^1$H and $^{13}$C signals were assigned by means of g-COSY 2D-NMR sequence. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; m, multiplet; bs, broad signal. Optical rotations are reported as follows: [α]$_D$ (c in g per 100 mL, solvent).

UV-Vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with photomultiplier detector, double beam optics and D$_2$ and W light sources. Cyclic voltammetry studies were carried out on a Princeton Applied Research PARSTAT 2273 potentiostat offering compliance voltage up to ±100 V (available at the counter electrode), ±10 V scan range and ±2 A current range.

General Procedures. All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques, unless otherwise stated. Synthesis grade solvents were used as purchased, anhydrous solvents were taken from a commercial SPS solvent dispenser. Chromatographic purification of products was accomplished using force-flow chromatography (FC) on silica gel (35-70 mesh). Deactivated silica was prepared by adding triethylamine (12.5 g, 2.5 w/w%) to silica gel (35-70 mesh, 500 g) in a 2 L round-bottomed flask and spinning on a rotary evaporator for 12 hours to homogenize the mixture. For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF254, 0.25 mm) were employed, UV light as the visualizing agent and an acidic mixture of para-anisaldehyde or basic aqueous potassium permanganate (KMnO$_4$) stain solutions, and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotatory evaporator.

Determination of Enantiomeric Purity: HPLC analysis on chiral stationary phase was performed on a Waters ACQUITY® UPC$^2$ instrument, using Trefoil AMY1, CEL1, and CEL2 and Daicel Chiralpak IC-3 as the chiral columns. The exact conditions for the analyses are specified within the characterization section. HPLC traces were compared to racemic samples prepared performing the reaction in the presence of racemic carbazole-derived primary amine catalyst 4b.

Materials. Reagents were purchased at the highest commercial quality from Sigma Aldrich, Fluka, and Alfa Aesar and used as received, without further purification, unless otherwise stated. The inorganic photocatalyst tetrabutylammonium decatungstate (TBADT) was prepared following a literature procedure (1). 2-methylbenzo[d][1,3]dioxole 2b was prepared following a literature procedure (2). β-Methyl cyclohexenone 1a and benzodioxole 2a are commercially available. Catalysts 4a, 4c, and 4d were prepared according to literature procedure (3). Full details for the synthesis of other aminocatalysts 4 used within this study are provided in the following Section B; the 1-nitrocyclohexene employed for catalyst preparation is commercially available or can be prepared from cyclohexanone (3).
B. Catalyst Synthesis

B.1. Synthesis of Carbazoles

3,6-Di-tert-butyl-9H-carbazole was prepared according to literature (4). To an oven-dried three neck flask fitted with a dropping funnel, inert gas inlet, and gas outlet connected with an aqueous NaOH trap, was added carbazole (10 g, 60 mmol, 1 equiv), anhydrous aluminium trichloride (8 g, 60 mmol, 1 equiv) and anhydrous methylene chloride (200 mL). Once a flow of argon through the base trap was established, the reaction was cooled to 0 ºC and a solution of tert-butyl chloride (13.2 mL, 120 mmol, 2 equiv) in methylene chloride (40 mL) was added dropwise via the addition funnel. After the addition was complete, the reaction was allowed to warm up to room temperature and stirred for 12 hours. Copious amounts of HCl gas are produced during this reaction. The reaction was then poured into iced water (400 mL) and extracted with methylene chloride (3 x 100 mL), the organics were subsequently washed with water and brine and dried over magnesium sulfate. Concentration yielded a grey solid which could be crystallised from boiling ethanol to give a colourless solid, 11.8 g (70% yield).

\[ \text{H NMR: (400 MHz, CDCl}_3\] \( \delta 8.08 (d, J = 1.85 \text{ Hz}, 2 \text{ H}), 7.84 (bs, 1 \text{ H}), 7.47 (dd, J = 8.45 \text{ Hz}, 1.45 \text{ Hz}, 2 \text{ H}), 7.33 (d, J = 8.45 \text{ Hz}, 2 \text{ H}), 1.46 (s, 18 \text{ H}). \]

\[ \text{C NMR: (101 MHz, CDCl}_3\] \( \delta 142.2, 138.0, 123.5, 123.3, 116.2, 110.0, 34.7, 32.0. \]

3,6-diaryl-9H-carbazoles were prepared by the following sequence of reactions.

3,6-Dibromo-9H-carbazole was prepared according to literature (5). To a stirred suspension of carbazole (6.5 g, 38.9 mmol, 1 equiv) in toluene (35 mL) at 0 ºC was added dropwise N-bromosuccinimide (NBS, 15 g, 84.2 mmol, 2.16 equiv) dissolved in DMF (100 mL) over 1 hour. The reaction was then allowed to stir at ambient temperature for 30 minutes before pouring the reaction mixture into ice-water (500 mL). The product was isolated by filtration and washed with cold methanol (20 mL). The solid product was then collected and crystallized from boiling ethanol giving an off-white solid (5.44 g, 43% yield).

\[ \text{H NMR: (300 MHz, CDCl}_3\] \( \delta 10.34 (bs, 1 \text{ H}), 8.14 (d, J = 1.85 \text{ Hz}, 2 \text{ H}), 7.53 (dd, J = 8.56 \text{ Hz}, 1.85 \text{ Hz}, 2 \text{ H}), 7.31 (d, J = 8.56 \text{ Hz}, 2 \text{ H}). \]

\[ \text{C NMR: (75 MHz, CDCl}_3\] \( \delta 138.3, 129.3, 124.1, 123.3, 112.3, 116.2, 110.0, 34.7, 32.0. \]

3,6-diaryl-9H-carbazole was prepared according to a modified literature procedure (6). To a sealed tube was added 3,6-dibromo-9H-carbazole (2.11 g, 5 mmol, 1 equiv), the aryl boronic acid (15 mmol, 3 equiv), powdered anhydrous caesium carbonate (4.98 g, 15 mmol, 3 equiv), tetrakis(triphenylphosphine)palladium (289 mg, 0.75 mmol, 5 mol%), toluene (18 mL), ethanol (12 mL) and water (12 mL). The biphasic suspension was stirred rapidly at 100 ºC for 16 hours. The reaction was allowed to cool and the organic phase was separated. The aqueous phase was extracted with ethyl acetate (2 x 20 mL). The combined organic phases were washed with water, then brine and dried over MgSO\(_4\) before being concentrated. The pure carbazoles were obtained after flash chromatography (hexane:ethyl acetate 5:1) as white solids.

The yields obtained for the different aromatic groups of the isolated compounds were: 46% for Ar = Ph; 59% for Ar = p-OMeC\(_6\)H\(_4\); 75% for Ar = p-CIC\(_6\)H\(_4\); and 50% for Ar = p-CF\(_3\)C\(_6\)H\(_4\).
B.2. Synthesis of Catalysts 4

All the enantiopure chiral aminocatalysts 4 were synthesized according to the general scheme below.

![Scheme S2. Preparation of the enantiopure chiral carbazole-based primary amine catalysts.](image)

**General procedure for the aza-Michael addition.**
To an oven dried, argon purged 2-neck round bottomed flask fitted with an argon inlet and septum was added the requisite carbazole (1 equiv) and anhydrous THF (0.05 M). The reaction mixture was brought to 0 °C and n-butyllithium (1.05 equiv) was added dropwise. The reaction was stirred at 0 °C for 30 minutes. The mixture was cooled to -78 °C. 1-Nitrocyclohex-1-ene (1.1 equiv) was added to the cold solution. The solution was allowed to reach -20 °C and stirred until full consumption of the carbazole, as inferred by TLC analysis (hexane : ethyl acetate 20:1). The reaction was subsequently quenched with saturated aqueous NH₄Cl solution and extracted with EtOAc. The organic phase was washed with water and brine, dried over magnesium sulphate and concentrated. The crude material (syn nitroalkane) was continued to the next step without further purification.

**General procedure for the syn to anti epimerization of the aza-Michael addition adducts.**
To the crude syn nitroalkane (1 equiv) in a round bottomed flask was added ethyl acetate (0.1 M), methanol (2 equiv) and triethylamine (2 equiv). The reaction mixture was stirred at 40 ºC until epimerization was complete as determined by ¹H NMR analysis of the epimeric protons. The reaction mixture was then concentrated to dryness. The crude material containing the anti nitroalkane was continued to the next step immediately.

**General procedure for the reduction of the nitroalkane.**
To the crude anti nitroalkane (1 equiv) suspended in a solution of EtOAc/nBuOH (1:3) in a Parr hydrogenation flask was added Raney Nickel (commercial slurry in water, 2 tps per mmol of nitroalkane). The flask was then charged with a hydrogen atmosphere (3-3.5 bar) and shook for 12-24 hours. The reaction mixture was filtered through celite and rinsed with ethyl acetate (CAUTION: Raney nickel oxidizes exothermically, the filter cake must not be allowed to become dry) and concentrated. The residue was purified by flash chromatography (1-3% MeOH in DCM, deactivated silica) to obtain the racemic aminocatalyst as a white-yellow solid (70-89% yield over 3 steps).

**General procedure for the resolution of the racemic catalyst.**
To an oven dried, argon purged, round-bottomed flask was added rac-4 (3.56 mmol, 1 equiv) and anhydrous tetrahydrofuran (40 mL). The solution was cooled to 0 °C and anhydrous pyridine (401 µL, 4.98 mmol, 1.4 equiv) was added followed by dropwise addition of (1R)-(−)-menthyl chloroformate (0.916 mL, 4.27 mmol). The reaction was then stirred for 12 hours at room temperature. The reaction was diluted with methylene chloride and washed with 2 M HCl solution, water and then brine solution. The organic phase was then dried over MgSO₄, and concentrated to an off-white solid. The residue containing both menthyl carbamates of (S,S)-4 and (R,R)-4 was separated by flash chromatography (pentane:DCM 1:1) to afford both of the enantiopure menthyl carbamates of (R,R)-4 (first fraction) and (S,S)-4 (second fraction).
General procedure for the hydrolysis of enantiopure (-)-menthyl carbamate to give enantiopure catalysts 4.

To an oven dried, argon purged, two neck flask fitted with a condenser/argon inlet and septum was added the enantiopure (-)-menthyl carbamate (1 equiv) and it was diluted with anhydrous methylene chloride (0.1 M). To this mixture was sequentially added trifluoroacetic acid (10 equiv) and trifluoromethanesulfonic acid (3 equiv). The green reaction mixture was heated to reflux for exactly 2 hours, then cautiously quenched with a saturated solution of NaHCO₃, and extracted with methylene chloride (2 x 20 mL). The organic phases were combined, washed with water, brine and dried over MgSO₄ before being concentrated. The enantiopure catalyst 4 was obtained after flash chromatography (1-2% MeOH in DCM, deactivated silica) as a white solid: 50-60% yields for (R,R)-4 and 55-70% yields for (S,S)-4 over 2 steps.

General Procedure for the determination of enantiomeric excess of the aminocatalysts 4.
The catalyst 4 (2 mg) was added to a small sample vial and dissolved in methylene chloride (200 uL), followed by the addition of one drop of triethylamine and one drop of 1-fluoro-2,4-dinitrobenzene (Sanger’s reagent). The crude material was then filtered through a pipette filled with silica gel using a solution of hexane:EtOAc (9:1). Only the brightly colored portion of the filtrate was collected, and diluted for injection in the HPLC equipped with a chiral stationary phase column.

\[(1S,2S)-2(3,6-di-tert-butyl-9H-carbazol-9-vl)cyclohexan-1-amine 4b\]

\[\text{H} \quad \text{NMR}\] (500 MHz, CDCl₃) δ 8.12 (d, J = 8.9 Hz, 2H), 7.60-7.37 (m, 4H), 4.14 (ddd, J = 12.4 Hz, 10.2 Hz, 3.9 Hz, 1H), 3.72 (td, J = 10.6 Hz, 4.1 Hz, 1H), 2.39 (qd, J = 12.6 Hz, 3.7 Hz, 1H), 2.25-2.12 (m, 1H), 1.94 (t, J = 13.3 Hz, 3H), 1.67-1.52 (m, 2H), 1.48 (s, 18H), 1.45-1.34 (m, 1H).

\[\text{C} \quad \text{NMR}\] (126 MHz, CDCl₃) δ 141.6, 140.2 137.0, 124.0, 123.5, 122.9, 122.5, 116.4, 116.0, 111.0, 108.4, 63.2, 52.1, 35.4, 34.6, 32.01, 29.5, 26.2, 25.2.

The enantiomeric excess of the catalyst, derived with Sanger’s reagent, was determined to be 99% by HPLC analysis on a Daicel Chiralpak IC-3 column: 70/30 hexane/isopropanol, flow rate 0.8 mL/min, \(\lambda = 350 \text{ nm}\): \(\tau_{\text{Major}} = 12.34 \text{ min}\), \(\tau_{\text{Minor}} = 8.33\). \([\alpha]_{D}^{26} = -65.4 \ (c = 0.06, \text{CHCl}_3)\). Characterization data in agreement with the literature (3).

\[(1S,2S)-2(3,6-diphenyl-9H-carbazol-9-vl)cyclohexan-1-amine 4e\]

\[\text{H} \quad \text{NMR}\] (400 MHz, CDCl₃) δ 8.47 (d, J = 10.7 Hz, 2H), 7.85 – 7.78 (d, J = 7.6 Hz, 4H), 7.70 (d, J = 8.4 Hz, 2H), 7.64 (bs, J = 8.8 Hz, 2H), 7.55 (bs, J = 7.7 Hz, 4H), 7.46 – 7.38 (m, 2H), 4.29 (ddd, J = 12.6, 10.5, 3.7 Hz, 1H), 3.82 (bs, J = 10.5, 4.1 Hz, 1H), 2.48 (tq, J = 11.4, 3.7 Hz, 1H), 2.32 – 2.18 (bs, 1H), 2.09 – 1.95 (m, 3H), 1.67 – 1.34 (m, 3H).

\[\text{C} \quad \text{NMR}\] (101 MHz, CDCl₃) δ 141.9, 141.8, 141.62, 138.40, 132.74, 132.63, 128.87, 127.31, 126.62, 125.65, 125.04, 124.87, 123.40, 119.07, 118.70, 111.96, 109.63, 109.78, 106.0, 104.2, 70.09, 34.9, 29.5, 26.1, 25.1.

HRMS calculated for C₃₈H₃₂N₂ 417.2325, found 417.2343.
The enantiomeric excess of the catalyst, derived with Sanger’s reagent, was determined to be 99% by UPC³ analysis using the following conditions: Daicel Chiralpak IC-3 column with a gradient (100% CO₂ to 60/40 CO₂/MeOH over 4 minutes, curve 6), flow rate 3 mL/min, \(\lambda = 260 \text{ nm}\): \(\tau_{\text{Major}} = 7.72 \text{ min}\), \(\tau_{\text{Minor}} = 6.70 \text{ min}\). \([\alpha]_{D}^{25} = -25 \pm 2 \ (c = 0.10, \text{CHCl}_3)\).
(1S,2S)-2-(3,6-bis(4-methoxyphenyl)-9H-carbazol-9-yl)cyclohexan-1-amine 4f

$^1$H NMR: (400 MHz, CDCl$_3$) δ 8.29 (d, $J = 8.8$ Hz, 2H), 7.77 – 7.58 (m, 6H), 7.58 – 7.41 (m, 2H), 7.02 (d, $J = 8.3$ Hz, 4H), 4.42 – 4.24 (m, 1H), 3.88 (s, 6H), 3.69 (td, $J = 10.8$, 10.0, 4.0 Hz, 1H), 2.45 – 2.25 (m, 1H), 2.22 – 2.08 (m, 1H), 2.02 – 1.75 (m, 3H), 1.65 – 1.42 (m, 3H).

$^{13}$C NMR: (101 MHz, CDCl$_3$) δ 158.67, 141.13, 137.90, 134.46, 134.32, 132.39, 132.23, 128.94, 128.18, 125.28, 124.63, 123.33, 118.49, 118.06, 114.27, 111.74, 109.66, 62.00, 55.38, 52.05, 34.15, 29.37, 25.83, 24.92.

HRMS calculated for C$_{33}$H$_{27}$N$_2$O$_2$ 477.2537, found 477.2554.

The enantiomeric excess of the catalyst, derived with Sanger’s reagent, was determined to be 99% by UPC$^2$ analysis using the following conditions: Daicel Chiralpak IC-3 column with a gradient (100% CO$_2$ to 60/40 CO$_2$/MeOH over 4 minutes, curve 6), flow rate 3 mL/min, λ = 260 nm: $\tau_{\text{Major}} = 7.43$ min, $\tau_{\text{Minor}} = 6.57$ min.

$[\alpha]_0^{25} = -19 \pm 2$ (c = 0.06, CHCl$_3$).

(1S,2S)-2-(3,6-bis(4-(trifluoromethyl)phenyl)-9H-carbazol-9-yl)cyclohexan-1-amine 4g

$^1$H NMR: (400 MHz, CDCl$_3$) δ 8.32 (d, $J = 7.5$ Hz, 2H), 7.78 – 7.56 (m, 8H), 7.54 – 7.35 (m, 4H), 4.32 (ddd, $J = 12.5$, 10.4, 3.9 Hz, 1H), 3.74 (td, $J = 9.6$, 4.2 Hz, 1H), 2.38 (td, $J = 12.8$, 9.0 Hz, 1H), 2.26 – 2.12 (m, 1H), 2.04 – 1.81 (m, 3H), 1.65 – 1.39 (m, 3H).

$^{13}$C NMR: (101 MHz, CDCl$_3$) δ 141.84, 140.31, 138.63, 132.66, 131.43, 128.99, 128.49, 127.33, 125.51, 124.89, 123.35, 118.59, 118.91, 112.17, 109.77, 63.44, 52.11, 35.33, 29.60, 26.18, 25.20.

HRMS calculated for C$_{36}$H$_{25}$Cl$_3$N$_2$ 485.1546, found 485.1563.

The enantiomeric excess of the catalyst, derived with Sanger’s reagent, was determined to be 99% by UPC$^2$ analysis using the following conditions: Daicel Chiralpak IC-3 column with a gradient (100% CO$_2$ to 60/40 CO$_2$/EtOH over 4 minutes, curve 6), flow rate 3 mL/min, λ = 260 nm: $\tau_{\text{Major}} = 6.89$ min, $\tau_{\text{Minor}} = 6.22$ min.

$[\alpha]_0^{25} = -33 \pm 2$ (c = 0.09, CHCl$_3$).

(1S,2S)-2-(3,6-bis(4-methoxyphenyl)-9H-carbazol-9-yl)cyclohexan-1-amine 4h

$^1$H NMR: (400 MHz, CDCl$_3$) δ 8.43 (d, $J = 8.0$ Hz, 2H), 7.85 (d, $J = 8.2$ Hz, 4H), 7.81 – 7.69 (m, 8H), 4.38 – 4.23 (m, 1H), 3.82 (s, 6H), 2.45 (tt, $J = 12.3$, 6.5 Hz, 1H), 2.24 (d, $J = 12.3$ Hz, 1H), 2.07 – 1.86 (m, 2H), 1.71 – 1.44 (m, 3H), 1.41 – 1.22 (m, 1H).

$^{13}$C NMR: (101 MHz, CDCl$_3$) δ 145.27, 145.19, 142.12, 138.93, 131.31, 131.21, 128.54, 127.38, 125.84, 125.79, 125.75, 125.72, 125.16, 124.81, 123.34, 123.14, 119.28, 118.94, 112.26, 109.93, 63.23, 52.03, 35.08, 29.55, 26.03, 25.07.

$^{19}$F NMR: (376 MHz, CDCl$_3$) δ -61.89.

HRMS calculated for C$_{32}$H$_{27}$F$_6$N$_2$ 553.2073, found 553.2100.

The enantiomeric excess of the catalyst, derived with Sanger’s reagent, was determined to be 99% by UPC$^2$ analysis using the following conditions: Daicel Chiralpak IC-3 column with a gradient (100% CO$_2$ to 60/40 CO$_2$/MeOH over 4 minutes, curve 6), flow rate 3 mL/min, λ = 260 nm: $\tau_{\text{Major}} = 4.58$ min, $\tau_{\text{Minor}} = 4.26$ min.

$[\alpha]_0^{25} = -19 \pm 2$ (c = 0.12, CHCl$_3$).
C. General Procedures for the Enantioselective Iminium Ion Radical Trap

A 5 mL argon-purged glass vial was charged with the tetrabutylammonium decatungstate photocatalyst (TBADT, 0.01 mmol, 5 mol%), the chiral carbazole-derived primary amine catalyst (S,S)-4 (0.04 mmol, 20 mol%), benzoic acid (0.04 mmol, 20 mol%), and tetrabutylammonium tetrafluoroborate (0.2 mmol, 100 mol%). To the vial was then added anhydrous acetonitrile (400 µL), β-methyl cyclohexenone 1a (0.2 mmol, 1 equiv) and 2-methyl benzodioxole 2b (0.6 mmol, 3 equiv). The vial was further flushed with argon, closed with a Teflon-coated cap, and sealed with Parafilm, and then placed into a 3D-printed plastic support mounted on an aluminium block fitted with a 365 nm high-power single LED (λ = 365 nm, irradiance = 60±2 mW/cm², as controlled by an external power supply and measured using a photodiode light detector at the start of each reaction; the set-up is detailed in Figure S1). This set-up secured a reliable irradiation while keeping a constant distance of 1.5 cm between the reaction vessel and the light source. No stirring was applied and the irradiation was maintained for the indicated time. The reaction was then diluted with methylene chloride (5 mL) and passed through a pad of silica. The volatiles were removed in vacuum and the residue was purified by column chromatography to give product 3b in the stated yield and optical purity.

Figure S1. Reaction set-up and the illumination system. The light source for illuminating the reaction vessel consisted in a 365 nm high-power single black LED (λ_{max} = 365 nm) commercialized under the name of 365nm UV LED Gen 2 Emitter LZ1-00UV00. It was purchase from LED Engin. The LZ1-00UV00 365nm UV LED Gen 2 Emitter is a single LED which provides 2.7 W power centered at 365 nm.
Purification of compound 3b by flash column chromatography on silica gel: gradient eluent from pure hexane to 9:1 hexane: diethyl ether.

The enantiomeric excess of 3b was determined by UPC\textsuperscript{2} analysis using the following conditions: Daicel Chiralpak IC-3 column with a gradient (100% CO\textsubscript{2} to 60/40 CO\textsubscript{2}/EtOH over 4 minutes, curve 6), flow rate 3 mL/min, λ = 283 nm: t\textsubscript{Major} = 2.21 min, t\textsubscript{Minor} = 2.27 min.

Catalyst 4b and 4e afforded the compound with an enantiomeric excess of 88%. Catalyst 4f, 4g and 4h afforded the compound with an enantiomeric excess of 87%.

Products 3a and 3b were fully characterized and the data are in agreement with literature (3).

D. Kinetic Studies

All kinetic experiments were conducted using the set-up detailed in Section C and depicted in Figure S1, and an illumination system (HP black LED, λ\textsubscript{max} = 365 nm) with an irradiance of 60±2 mW/cm\textsuperscript{2}. This ensured the reactions not to be light limited.

The reaction between β-methyl cyclohexenone 1a and 2-methyl benzodioxole 2b to afford the radical conjugate addition product 3b was chosen as the model for the kinetic studies (Scheme S1). We applied the method of initial-rate kinetics, monitoring the progress of the reactions by \textsuperscript{1}H NMR analysis and following the conversion until 15%. The initial rates were plotted against concentration to obtain straight lines. Our initial-rate kinetic studies required an independent reaction to be performed for every data-point at different times.

Two independent series of kinetic investigations were performed using both carbazole-based aminocatalysts 4b and 4e, which provided similar and reproducible kinetic profiles.

![Scheme S1: The model reaction for the kinetic studies.](image)

Procedure for the initial-rate kinetics: Three sets of reactions with equivalent concentrations of each reactant, except for the component whose order is being measured, were carried out in three identical 5 mL glass vials. The vials containing the reaction mixtures were positioned 1.5 cm away from the light source. Each one was irradiated from the bottom with a HP LED centered at 365 nm irradiating with 450 μA (irradiance of 60±2 mW/cm\textsuperscript{2}) without stirring. This procedure was repeated 4 times quenching the reactions at different time intervals and the whole experiment was repeated twice.

The model reaction was set up utilizing a stock solution containing 105 mg of the aminocatalyst (4b or 4e) (0.28 mmol, 20 mol%), 34 mg of benzoic acid (0.28 mmol, 20 mol%), 464 mg of NBu\textsubscript{4}BF\textsubscript{4} (1.4 mmol, 1 equiv), 231 mg of TBADT (0.07 mmol, 5 mol%) dissolved in 2.8 mL of anhydrous acetonitrile. To this solution (0.1 M in 4), 158 μL of 3-methyl-2-cyclohexenone 1a (1.4 mmol, 1 equiv) and 560 μL of 3-methylbenzodioxole 2b (4.2 mmol, 3 equiv) were sequentially added. After irradiating for the indicated time, the conversion of both substrates (3-methyl-2-cyclohexenone 1a and 3-methylbenzodioxole 2b) into the final product 3b was determined by \textsuperscript{1}H NMR analysis of the crude reaction mixture. The reaction is clean and nor byproducts or substrate decomposition has been observed.

These conditions account for the following concentrations: [4] = 0.1 M, [1a] = 0.5 M, [2b] = 1.5 M, [TBADT] = 0.025 M, [NBu\textsubscript{4}BF\textsubscript{4}] = 0.5 M and [benzoic acid] = 0.1 M.
To measure the order with respect to each component, we varied the concentration of the reagent under study in the following ranges:

- [benzoic acid] from 0.05 M to 0.3 M.
- [4] from 0.05 M to 0.2 M.
- [1a] from 0.25 M to 1 M.
- [2b] from 0.75 M to 3 M.
- [TBADT] from 0.006 to 0.05 M.

**Rate dependence on the light intensity:**

As shown in Figure S2, the rate of the model reaction catalyzed by 4b was found to linearly correlate with the light intensity to then reach a standstill for irradiances higher than 40 mW/cm². All the following kinetic studies were performed using the set-up discussed in Figure S1 and an illumination system (HP black LED, λ_max = 365 nm) with an irradiance of 60±2 mW/cm². This ensured the reactions not to be light limited.
Rate dependence on [benzoic acid]

As shown in Figure S3, a 0.1 M (20 mol%) concentration of benzoic acid provided for the highest reaction rate. All other kinetic experiments were conducted using a 1:1 catalyst 4:benzoic acid ratio (20 mol%).

Figure S3: Reaction profiles of initial-rate measurements at different initial concentrations of benzoic acid: [benzoic acid]₀ = 0.05 M (blue line); [benzoic acid]₀ = 0.1 M (red line); [benzoic acid]₀ = 0.2 M (green line); [benzoic acid]₀ = 0.3 M (purple line). Rate constants calculated from the slope of the plots.
Rate dependence on the electronic properties of different aminocatalysts

As shown in Figure S4, a correlation is observed between the reaction rate and the electronic properties of the carbazole moiety contained in the aminocatalysts 4. The larger the reduction potential of (and the more electron poor) the carbazole tethered to the aminocatalyst, the faster the reaction proceeds.
Order dependence in catalyst 4

Figure S5. Reaction profiles at different initial concentrations of catalyst 4b/4e showing a first-order dependence in [4]. Rate constants calculated from the slope of the plots. [4b]₀ = [BA]₀ = 0.05 M (blue line); [4b]₀ = [BA]₀ = 0.1 M (red line); [4b]₀ = [BA]₀ = 0.2 M (green line) (up left); [4e]₀ = [BA]₀ = 0.05 M (blue line); [4e]₀ = [BA]₀ = 0.1 M (red line); [4e]₀ = [BA]₀ = 0.2 M (green line) (up right). Rates determined while varying: [4b]₀ (down left) and [4e]₀ (down right). BA = benzoic acid; the error bars represent the standard deviation.

As shown in Figure S5, a first-order dependence in [4] was determined.
Order dependence in enone 1a

Figure S6. Reaction profiles of initial-rate measurements at different initial concentrations of 1a showing a saturation kinetic profile. Rate constants calculated from the slope of the plots. \([1a]_0 = 1.0\) M (green line), \([1a]_0 = 0.5\) M (red line) and \([1a]_0 = 0.25\) M (blue line) (up). Lineweaver-Burk plot for the rates determined while varying \([1a]_0\) (down panels). Both data obtained employing catalyst 4b (plots in the left panel), and catalyst 4e (plots in the right) show saturation kinetics. BA = benzoic acid.

As shown in Figure S6, a saturation kinetics profile with respect to \([1a]\) was observed for both catalysts 4b and 4e. It was confirmed by Lineweaver-Burk plot.
Order dependence in benzodioxole 2b

As shown in Figure S7, a zeroth-order dependence in [2b] was determined.
Order dependence in water

Figure S8. Reaction profiles of initial-rate measurements at different initial concentrations of water showing a zeroth-order dependence. Rate constants calculated from the slope of the plots. $[\text{H}_2\text{O}]_0 = 0$ (blue line); $[\text{H}_2\text{O}]_0 = 0.5$ M (red line); $[\text{H}_2\text{O}]_0 = 2.5$ M (green line) (upper panels). Rates determined while varying $[\text{H}_2\text{O}]_0$ (down panels). Both data obtained employing catalyst 4b (plots in the left panel), and catalyst 4e (plots in the right panel) show zeroth order kinetics. BA = benzoic acid, the error bars represent the standard deviation.

As shown in Figure S8, a zeroth-order dependence in [water] was determined.
Order dependence in the photocatalyst (TBADT)

Figure S9. Reaction profiles of initial-rate measurements at different initial concentrations of TBADT showing a saturation kinetic profile. Rate constants calculated from the slope of the plots. [TBADT]₀ = 0.006 M (purple line); [TBADT]₀ = 0.0125 M (blue line); [TBADT]₀ = 0.025 M (red line); [TBADT]₀ = 0.05 M (green line) (upper panels). Lineweaver-Burk plot for the rates determined while varying [TBADT]₀ (down panels). Both data obtained employing catalyst 4b (plots in the left panel), and catalyst 4e (plots in the right panel) show a saturation kinetics profiles. BA = benzoic acid, the error bars represent the standard deviation.

As shown in Figure S9, when doubling the amount of photocatalyst (from 5 to 10 mol%), no change in the reaction rate was observed. However, lowering the amount of TBADT to 2.5 or 1.25 mol% decreased the rate of the model reaction, indicating a saturation kinetic profile in [TBADT]. This profile was confirmed by the Lineweaver-Burk plot.
E. Spectroscopic Studies on the Equilibrium of Iminium Ion Formation

A series of $^1$H NMR spectroscopic experiments were carried out to study the equilibrium of iminium ion formation under the conditions used in the kinetic experiments. The $^1$H NMR spectrum of a solution containing the aminocatalyst 4b (18.8 mg, 0.05 mmol, 20 mol%), benzoic acid (6 mg, 0.05 mmol, 20 mol%), 3-methyl-2-cyclohexen-1-one 1a (28 μL, 0.25 mmol, 1 equiv), benzodioxole 2b (86 μL, 0.75 mmol, 3 equiv), TBADT (41.3 mg, 0.0125 mmol, 5 mol%), and tetrabutylammonium tetrafluoroborate (82.2 mg, 0.25 mmol, 1 equiv) in 0.5 mL of CD$_3$CN was recorded (Figure S10).

The protonated free catalyst 4b·PhCO$_2$H, the imine F-1, and the iminium ion A-1 were detected in a ratio of 1:0.3:1.3, respectively (Figure S10). These spectroscopic studies are consonant with the notion that a definitive resting state for catalyst 4b cannot be identified, with the catalyst concentration shared between different closed-shell intermediates. Interestingly, the non-protonated free catalyst 4b was not detected.

The assignment of the different species was made on the basis of diagnostic NMR peaks extrapolated by the characterization data of authentic samples (see following Section E.1), as discussed below:
- Protonated aminocatalyst 4b·PhCO₂H: one of the protons contained in the multiplet 4.81 – 4.55 (2H) and triplet of doublets at 4.04 ppm ($J = 10.5, 3.2$ Hz, 1H).
- Imine F-1: triplet of doublets at 5.12 ppm ($J = 10.5, 4.7$ Hz, 1H) and triplet of doublets at 4.75 ppm ($J = 10.5, 4.8$ Hz, 1H).
- Iminium A-1: singlet at 5.17 ppm (1H), triplet of doublets at 4.99 ppm ($J = 11.8, 4.5$ Hz, 1H), one of the protons contained in the multiplet 4.81 – 4.55 (2H).

E.1 Characterization of the Intermediates involved in Iminium Ion Formation

2-(3,6-di-tert-butyl-9H-carbazol-9-yl)cyclohexan-1-aminium benzoate (4b·PhCO₂H):

An authentic sample of the protonated catalyst 4b was synthesized as follows: to an oven-dried, argon purged 5 mL glass vial sealed with a Teflon septum was added (rac)-2-(3,6-di-tert-butyl-9H-carbazol-9-yl)cyclohexan-1-amine 4b (15.2 mg, 0.04 mmol, 1 equiv) and benzoic acid (4.9 mg, 0.04 mmol, 1 equiv). The vial was then charged with anhydrous acetonitrile (0.5 mL). The mixture was heated to 70 °C until the precipitate was dissolved. The mixture was allowed to cool; a white crystalline solid formed. The solid was collected by filtration and washed with cold anhydrous acetonitrile to give white crystalline solid, 10.1 mg (51%).

$^1$H NMR: (400 MHz, CDCl₃) $\delta$ 8.11 (d, $J = 13.9$ Hz, 2H), 8.07 – 8.02 (m, 1H), 7.61 – 7.39 (m, 6H), 4.26 (ddd, $J = 12.3, 10.3, 3.9$ Hz, 1H), 3.80 (td, $J = 10.4, 4.5$ Hz, 1H), 3.72 (s, 3H), 2.40 (qd, $J = 13.4, 12.6, 4.8$ Hz, 1H), 2.34 – 2.18 (m, 1H), 2.00 – 1.87 (m, 3H), 1.67 – 1.50 (m, 2H), 1.47 (s, 19H).

$^{13}$C NMR: (101 MHz, CDCl₃) $\delta$ 170.45, 141.78, 140.07, 136.85, 132.40, 132.19, 129.77, 128.10, 124.14, 123.57, 122.99, 122.61, 116.47, 115.99, 110.97, 108.41, 62.22, 52.04, 34.61, 34.36, 32.00, 29.42, 26.00, 25.10.

HRMS: Calculated for C₂₆H₃₇N₂ 377.2951, found 377.2958.
(Z)-N-(2-(3,6-di-tert-butyl-9H-carbazol-9-yl)cyclohexyl)-3-methylcyclohex-2-en-1-imine (F-1):
An authentic sample of the imine intermediate F-1 was synthetized according to the literature (3).

\[
\begin{align*}
1^H \text{NMR:} & (400 \, \text{MHz, CDCl}_3) \delta 8.00 (d, J = 1.72 \, \text{Hz}, 1 \, \text{H}), 7.91 (d, J = 1.72 \, \text{Hz}, 1 \, \text{H}), 7.69 (d, J = 8.77 \, \text{Hz}, 1 \, \text{H}), 7.58 (d, J = 8.58 \, \text{Hz}, 1 \, \text{H}), 7.51 (td, J = 8.77 \, \text{Hz}, 1.80 \, \text{Hz}, 2 \, \text{H}), 4.92-5.07 (m, 2 \, \text{H}), 4.30-4.34 (m, 1 \, \text{H}), 2.72 (qd, J = 12.75 \, \text{Hz}, 3.74 \, \text{Hz}, 1 \, \text{H}), 2.14-2.50 (m, 6 \, \text{H}), 1.95-2.13 (m, 3 \, \text{H}), 1.69-1.88 (m, 2 \, \text{H}), 1.35-1.60 (m, 19 \, \text{H}), 1.23-1.33 (m, 1 \, \text{H}), 1.09 (s, 3 \, \text{H}). \\
13^C \text{NMR:} & (101 \, \text{MHz, CDCl}_3) \delta 175.8, 171.7, 142.7, 142.0, 139.6, 137.2, 124.6, 124.5, 123.2, 121.8, 116.6, 115.0, 114.8, 110.5, 109.3, 57.2, 57.1, 34.6, 34.6, 32.0, 29.6, 29.3, 29.2, 25.2, 24.8, 24.2, 19.7. \\
\text{HRMS:} & \text{Calculated for C}_{33}\text{H}_{45}\text{N}_2 \text{469.3577, found 469.3575.}
\end{align*}
\]

(Z)-2-(3,6-di-tert-butyl-9H-carbazol-9-yl)-N-(3-methylcyclohex-2-en-1-ylidene)cyclohexan-1-aminium tetrafluoroborate (A-1):
An authentic sample of the iminium ion A-1 was synthetized according to the literature (3).

\[
\begin{align*}
1^H \text{NMR:} & (400 \, \text{MHz, CDCl}_3) \delta 10.01 (bs, 1 \, \text{H}), 8.02 (d, J = 1.79 \, \text{Hz}, 1 \, \text{H}), 7.91 (d, J = 0.89 \, \text{Hz}), 7.49-7.62 (m, 4 \, \text{H}), 5.03 (s, 1 \, \text{H}), 4.61-4.72 (m, 1 \, \text{H}), 4.34-4.46 (m, 1 \, \text{H}), 2.74 (qd, J = 13.06 \, \text{Hz}, 3.73 \, \text{Hz}, 1 \, \text{H}), 2.21-2.40 (m, 4 \, \text{H}), 2.02-2.15 (m, 2 \, \text{H}), 1.83-2.01 (m, 2 \, \text{H}), 1.68-1.83 (m, 1 \, \text{H}), 1.53-1.61 (m, 2 \, \text{H}), 1.47-1.53 (m, 1 \, \text{H}), 1.38-1.47 (m, 18 \, \text{H}), 1.27-1.37 (m, 1 \, \text{H}), 1.14 (m, 3 \, \text{H}). \\
13^C \text{NMR:} & (101 \, \text{MHz, CDCl}_3) \delta 177.2, 175.2, 143.4, 142.4, 139.3, 137.0, 125.0, 124.5, 123.4, 121.9, 116.7, 115.1, 114.7, 110.4, 108.8, 57.3, 34.7, 34.6, 32.0, 32.0, 31.1, 30.4, 29.5, 29.3, 25.5, 24.7, 24.1, 19.7. \\
\text{HRMS:} & \text{Calculated for C}_{33}\text{H}_{45}\text{N}_2 \text{469.3577, found 469.3573.}
\end{align*}
\]

The structure of the carbazole-based iminium ion A-1 was confirmed by X-ray analysis: CCDC1437991.
F. Optical Absorption Spectra

All the spectra were recorded in acetonitrile, using the same concentration as in the reaction conditions, in a 1 mm Hellma Quartz SUPRASIL® cuvette. Due to the high concentration of the solutions, short path cuvettes were employed in order to avoid signal saturation.

The absorption spectra recorded after irradiation with a high power LED centered at 365 nm was performed in the same vessel used for the irradiation of the sample, a 1 mm Hellma Quartz SUPRASIL® cuvette closed with a Teflon cap.

F1. Mixtures of TBADT and 2b

\[
\begin{align*}
\text{Me-O} & \quad + \quad [\text{W}_{10}\text{O}_{32}]^{6-} \\
\text{TBADT} & \quad \text{5 mol%} \\
\text{CH}_{3}\text{CN} & \quad [2a]_{0} = 0.03 \text{ M} \\
& \quad \rightarrow \\
\text{Me-O} & \quad + \quad [\text{HW}_{10}\text{O}_{32}]^{6-} \\
\text{TBADT-H} & \quad \text{1/2[H}_{2}\text{W}_{10}\text{O}_{32}]^{4+} + \text{1/2[H}_{2}\text{O}]^{2+} \\
& \quad \text{1 mm Hellma Quartz SUPRASIL® cuvette} \\
& \quad \text{closed with a Teflon cap}.
\end{align*}
\]

Figure S11. Optical absorption spectrum, recorded in CH$_3$CN, of a mixture containing [2b] = 0.09 M (12.5 μL, 0.09 mmol, 3 equiv), [TBABF$_4$] = 0.03 M (9.9 mg, 0.03 mmol, 1 equiv) and [TBADT] = 0.0015 M (5 mg, 0.0015 mmol, 5 mol%) dissolved in 1 mL of CH$_3$CN. Blue spectrum recorded after mixing the reagents; red spectrum recorded after irradiating the mixture for 30 minutes with a high power LED centered at 365 nm (irradiance = 60±2 mW/cm$^2$).

The solution containing a mixture of benzodioxole 2b and photocatalyst (TBADT) did not shown any color (blue line in Figure S11). Upon irradiation with a high power LED centred at 365 nm, an intense blue color developed, as evinced by the appearance of characteristic peaks clearly observable in the absorption spectrum, with maxima at 630 nm and 980 nm (red spectrum in Figure S11). It is know that the reduced photocatalyst TBADT-H and its disproportionated byproduct [H$_2$W$_{10}$O$_{32}$]$^4$ are blue in solution (7).
F2. Reaction Mixture

Figure S12. Optical absorption spectra, recorded in CH$_3$CN. Blue spectrum: mixture containing [1a] = 0.03 M (3.4 μL, 0.03 mmol, 1 equiv), [4b] = 0.006 M (2.3 mg, 0.006 mmol, 20 mol%), [benzoic acid] = 0.006 M (0.7 mg, 0.006 mmol, 20 mol%), [2b] = 0.09 M (12.5 μL, 0.09 mmol, 3 equiv), [TBABF$_4$] = 0.03 M (9.9 mg, 0.03 mmol, 1 equiv) and [TBADT] = 0.0015 M (5 mg, 0.0015 mmol, 5 mol%) dissolved in 1 mL of CH$_3$CN, recorded after mixing the reagents but without illumination. Red spectrum: same mixture as for the blue spectrum but recorded after irradiating for 30 minutes with a high power LED centred at 365 nm (irradiance = 60±2 mW/cm$^2$). Green spectrum: mixture containing [2b] = 0.09 M (12.5 μL, 0.09 mmol, 3 equiv), [TBABF$_4$] = 0.03 M (9.9 mg, 0.03 mmol, 1 equiv) and [TBADT] = 0.0015 M dissolved in 1 mL of CH$_3$CN; the spectrum was recorded after irradiating for 30 minutes with a high power LED centred at 365 nm (irradiance = 60±2 mW/cm$^2$). Purple spectrum: same mixture as for the blue and red spectra, excluding the enone 1a; the spectrum was recorded after irradiating for 30 minutes with a high power LED centred at 365 nm (irradiance = 60±2 mW/cm$^2$). The fact that, in the absence of 1a, the spectrum does not show the characteristic new band at ≈800 nm (observable in the red spectrum instead) further corroborates that the carbazoliumyl radical cation (which can be generated only in the presence of enone 1a) is responsible for the appearance of this peak.

A series of model reactions were performed in CH$_3$CN under the standard conditions but in quartz cuvettes and their absorption spectra were acquired. The mixture containing all the reaction components, without illumination, did not absorb in the visible region (blue spectrum in Figure S12). Upon irradiation (using a high power black LED, $\lambda$$_{max}$ = 365 nm, with an irradiance of 60±2 mW/cm$^2$), also after an irradiation time as short as 10 minutes, the absorption spectra of the overall reaction displayed three maxima in the visible region at 630, 800, and 900 nm (red spectrum in Figure S12). As a control experiment, the absorption spectrum of an identically irradiated solution containing a mixture of the TBADT photoredox catalyst and the radical precursor 2b was recorded (same experiment as discussed in Figure S11). The green spectrum in Figure S12 displays characteristic peaks with maxima at 630 and 980 nm, but it lacks the newly formed band at ≈800 nm, which can be clearly observed in the red spectrum instead.

The purple spectrum in Figure S12 displays the absorption of an irradiated mixture of all the components of the reaction mixture excluding the enone 1a. The fact that, in the absence of 1a, the spectrum does not show the characteristic new band at ≈800 nm (observable in the red spectrum instead) further corroborates that the carbazoliumyl radical cation (which can be generated only in the presence of enone 1a upon radical conjugate addition to the iminium ion) is responsible for the appearance of this peak.

The absorption spectra of irradiated solutions of the reaction mixture and solutions containing only TBADT and 2b were acquired 8 times recording the absorption spectra after different times of irradiation (10, 20, 30, 37, 45 and 60 minutes) – these experiments provided identical results.
F.3 Preparation and Characterisation of the Shelf-Stable Carbazoliumyl Radical Cation Salt 7

3,6-di-tert-butyl-9-cyclohexyl-9H-carbazole was prepared according to (3). To an oven-dried, argon purged vial was added lithium tert-butoxide (152 mg, 1.9 mmol, 1.9 eq.), 3,6-di-tert-butyl-9H-carbazole (279 mg, 1 mmol, 1 equiv) and copper(I) iodide (19.5 mg, 10 mol%). The flask was evacuated and back-filled with argon three times before acetonitrile (4 mL) and cyclohexyliodide (250 µL, 1.9 mmol, 1.9 eq) was added. The reaction was placed in an ice-bath and irradiated with a 100 W Hg-Lamp positioned directly above the vessel for 12 hours. The mixture was then diluted with methylene chloride and filtered through Celite before concentration to give a brown residue. The product was purified by flash chromatography (1% Et<sub>2</sub>O in hexanes) to give the product as a white solid, 286 mg (79%).

<sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>) δ 8.10-8.13 (m, 2 H), 7.44-7.51 (m, 4 H), 4.44 (tt, J = 12.00 Hz, 4.05 Hz, 1 H), 2.73 (qd, J = 12.53 Hz, 3.18 Hz, 2 H), 1.92-2.04 (m, 4 H), 1.81-1.89 (m, 1 H), 1.49-1.60 (m, 2 H), 1.47 (s, 18 H), 1.34-1.44 (m, 1 H).

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>) δ 141.2, 138.2, 123.1, 122.9, 116.2, 109.6, 53.4, 34.6, 32.0, 30.9, 26.6, 25.8.

HRMS: Calculated for C<sub>26</sub>H<sub>36</sub>N 362.2842, found 362.2842.

3,6-di-tert-butyl-9-cyclohexyl-9H-carbazoliumyl hexachloroantimonate was prepared according to (3). To an oven-dried, argon purged vial was added 3,6-di-tert-butyl-9-cyclohexyl-9H-carbazole (36.2 mg, 0.1 mmol, 1 equiv) and anhydrous methylene chloride (1 mL). The solution was then cooled to 0 °C before antimony(V) pentachloride (158 µL, 0.158 mmol, 1 M in DCM, 1.58 eq.) was added. An instantaneous reaction took place causing the solution to turn dark green. The reaction was allowed to stir at 0 °C for 20 minutes before it was diluted with anhydrous hexanes and stirred until precipitation of the product had completed. The green suspension was filtered in an inert atmosphere and washed with anhydrous hexane before drying under high vacuum to give the title compound as a dark green solid, 51 mg (73% yield). This compound was stable for months if stored in a desiccator. The UV-Vis spectrum of 7 is shown in Figure S13.

Figure S13. UV-Vis Spectrum of 3,6-di-tert-butyl-9-cyclohexyl-9H-carbazoliumyl hexachloroantimonate 7 [0.4 mM] in CH<sub>3</sub>CN. λ<sub>max</sub> = 800 nm.
G. Computational Studies

G1. Computational Details
All the computations performed in this study were carried out with Density Functional Theory (DFT, 8) and its Time Dependent variant (TDDFT, 9-12). All the minimum energy structures of the potential energy surface were fully optimized using the global hybrid functional B3LYP (I3-I5) and the 6-31G(d) basis set, and confirmed by harmonic frequency computations. Solvent effects (acetonitrile) were taken into account by the means of the polarizable continuum model (PCM) in the linear response formalism (16-18).

TDDFT computations were performed at the B3LYP/6-31G(d)/PCM level of theory on minimum energy structures. In order to confirm the nature of transitions, calculations employing a range separated functional (CAM-B3LYP, 19) on B3LYP same geometries were performed. All computations were carried out using the Gaussian 09 Rev C.01 suite of programs (20).

G2. Computed Minimum Energy Structure of Intermediate D-1

*Optimized Cartesian Coordinates of Intermediate D-1*

|    |    |    |    |
|----|----|----|----|
| H  |  1.476 | -3.367 |  5.277 |
| H  |  2.585 | -1.514 |  3.986 |
| H  |  7.267 |  1.997 | -0.276 |
| H  |  2.465 | -3.993 |  3.961 |
| H  |  0.055 |  5.095 |  3.023 |
| C  |  1.552 | -3.424 |  4.186 |
| H  |  7.595 |  0.390 | -0.950 |
| H  |  8.069 |  1.838 | -1.850 |
| C  |  1.678 | -2.004 |  3.617 |
| C  |  7.295 |  1.412 | -1.202 |
| H  | -0.719 |  6.238 |  1.908 |
| C  | -0.198 |  5.277 |  1.973 |
| H  |  0.829 | -1.404 |  3.957 |
| H  |  0.737 |  5.367 |  1.409 |
| H  | -2.245 |  3.964 |  3.292 |
| H  |  5.584 |  3.569 | -1.420 |
| H  |  2.633 | -2.607 |  1.794 |
| H  |  0.274 | -5.170 |  3.991 |
| C  |  1.736 | -2.053 |  2.077 |
| C  |  0.335 | -4.149 |  3.596 |
| H  |  4.197 | -2.149 |  0.531 |
| Element | X-coord | Y-coord | Z-coord |
|---------|---------|---------|---------|
| H       | 5.837   | -1.080  | -0.921  |
| C       | 4.061   | -1.115  | 0.238   |
| C       | 4.985   | -0.498  | -0.590  |
| N       | 1.905   | -0.713  | 1.485   |
| C       | 2.956   | -0.356  | 0.665   |
| C       | 1.036   | 0.375   | 1.611   |
| H       | -0.600  | -0.313  | 2.876   |
| C       | 4.856   | 0.848   | -1.015  |
| C       | 5.927   | 1.457   | -1.928  |
| C       | -0.172  | 0.499   | 2.304   |
| H       | 6.417   | 3.298   | -2.954  |
| C       | 2.796   | 0.996   | 0.252   |
| H       | -0.585  | -3.635  | 3.909   |
| C       | 1.553   | 1.464   | 0.860   |
| C       | -0.849  | 1.721   | 2.236   |
| C       | 5.623   | 2.920   | -2.302  |
| C       | 3.732   | 1.589   | -0.574  |
| H       | -1.785  | 1.804   | 2.773   |
| C       | -0.364  | 2.815   | 1.502   |
| C       | -2.421  | 4.148   | 2.226   |
| H       | -2.903  | 5.127   | 2.136   |
| C       | 0.868   | 2.661   | 0.808   |
| C       | -1.109  | 4.152   | 1.419   |
| H       | 1.271   | 3.484   | 0.228   |
| H       | 3.600   | 2.619   | -0.881  |
| H       | 1.268   | -4.801  | 1.748   |
| C       | 0.407   | -4.197  | 2.065   |
| H       | -3.128  | 3.397   | 1.856   |
| H       | 4.676   | 3.016   | -2.846  |
| C       | 0.540   | -2.799  | 1.422   |
| H       | 6.279   | -0.417  | -3.044  |
| C       | 6.011   | 0.627   | -3.235  |
|     |       |       |       |
|-----|-------|-------|-------|
| H   | 6.777 | 1.054 | -3.892|
| H   | -0.377| -2.230| 1.622 |
| C   | -1.450| 4.450 | -0.064|
| H   | -0.555| 4.513 | -0.690|
| H   | -1.974| 5.410 | -0.135|
| H   | -0.486| -4.679| 1.648 |
| H   | 5.056 | 0.641 | -3.772|
| N   | 0.836 | -2.952| 0.005 |
| H   | -2.103| 3.674 | -0.479|
| H   | 0.343 | -1.208| -3.202|
| C   | -0.066| -2.920| -0.903|
| C   | -1.560| -2.687| -0.736|
| H   | -1.741| 0.555 | -2.029|
| H   | 1.448 | -3.262| -2.376|
| H   | -0.368| -0.287| -1.302|
| C   | -2.085| -1.581| -1.702|
| C   | -0.189| -2.158| -3.330|
| H   | -2.059| -1.176| -3.841|
| C   | 0.357 | -3.197| -2.333|
| C   | -1.459| -0.225| -1.315|
| C   | -1.702| -1.954| -3.157|
| H   | 0.019 | -2.493| -4.352|
| H   | -0.042| -4.186| -2.607|
| H   | -1.779| 0.085 | -0.317|
| H   | -2.206| -2.886| -3.443|
| H   | -1.827| -2.434| 0.292 |
| H   | -2.052| -3.641| -0.968|
| C   | -3.634| -1.471| -1.564|
| C   | -4.699| 0.022 | -0.215|
| C   | -4.779| 0.495 | -1.524|
| C   | -5.290| 0.690 | 0.841 |
| C   | -5.452| 1.661 | -1.840|
C  -5.981  1.879  0.536
H  -5.222  0.312  1.856
C  -6.060  2.353 -0.774
H  -5.507  2.022 -2.861
H  -6.462  2.430  1.339
H  -6.600  3.271 -0.983
O  -3.960 -1.133 -0.183
O  -4.097 -0.345 -2.366
C  -4.466 -2.688 -1.952
H  -4.342 -2.929 -3.010
H  -4.200 -3.562 -1.353
H  -5.520 -2.457 -1.773

G3. Computed Absorption Spectrum of Intermediate D-1

We used TDDFT methods to compute the absorption spectrum of intermediate D-1, which confirms the intense absorption peak in the red portion of the UV-Vis spectrum (Figure S14). The modeled band, centered at 758 nm, compares well with the experimentally observed band (purple line), providing further support for the carbazoliumyl radical cation intermediate D-1 being responsible for the peak experimentally observed at ≈800 nm.

Figure S14. Experimental (purple line) and computed (dotted line) absorption spectra of intermediate D-1. The modeled band spectrum in CH$_3$CN solvent was obtained by a Gaussian convolution (full width at half maximum of 0.2 eV) of vertical transitions computed at TD-B3LYP/6-31G(d)/PCM level of theory.

G4. Computed Absorption Spectrum of the Shelf-Stable Carbazoliumyl Radical Cation Salt 7

To verify whether the level of theory adopted was adequate for the molecular systems under investigation, trial simulations of the absorption spectrum of the carbazoliumyl radical cation 7 were generated (see Section F3 for the absorption spectrum of the authentic sample of 7). To confirm the nature of transitions, further calculations were carried out using a range separated functional (CAM-B3LYP), which fully confirmed the previous computational results.

For 7, we computed a vertical transition centered at 759 nm (Figure S15). The good outcomes of these simulations confirmed the suitability of the global hybrid functional (B3LYP) used for simulating the absorption spectrum of intermediate D-1, reported in the previous section G3.
Figure S15. Experimental (full purple line) and computed (dotted purple line) absorption spectra of 7. The simulated spectrum is obtained assigning a Gaussian band shape to compute vertical transitions, setting a full width half maximum of 0.2 eV. The intense vertical transition corresponds to a one-electron excitation involving orbitals HOMO-1 and LUMO mainly centered on the carbazole. These data represent the theoretical reference for the 3,6-tert-butyl carbazole radical cation unit.
H. Cyclic Voltammetry

Figure S16. Cyclic voltammogram of aminocatalyst 4b [0.02 M] in [0.1 M] TBAPF$_6$ in CH$_3$CN. Sweep rate: 50 mV/s. Pt electrode working electrode, Ag/AgCl (KCl 3 M) reference electrode, Pt wire auxiliary electrode. 4b: $E_{1/2} = 1.16$ V.

Figure S17. Cyclic voltammograms of aminocatalysts 4 [0.02 M] in [0.1 M] TBAPF$_6$ in CH$_3$CN. Sweep rate: 50 mV/s. Pt electrode working electrode, Ag/AgCl (KCl 3 M) reference electrode, Pt wire auxiliary electrode. 4e: $E_{1/2} = 1.10$ V (top left), 4f: $E_{1/2} = 1.02$ V (top right), 4g: $E_{1/2} = 1.17$ V (bottom left) and 4h: $E_{1/2} = 1.25$ V (bottom right).

In all voltammograms, a first reversible oxidation, corresponding to the oxidation of the carbazole moiety to give the carbazole radical cation, is followed by an additional irreversible oxidation at about +1.4 V, which is due to the oxidation of the primary amine moiety within the aminocatalyst 4, are observed. In addition, in the voltammogram of 4f an extra oxidation, corresponding to further oxidation of the carbazole radical cation, is observed.

The electrochemical characterization of catalysts 4a, 4c, and 4d is detailed in (3).
I. References

1. Yamase, T.; Usami, T. *J. Chem. Soc., Dalton Trans.* 1988, 1, 183–190.
2. Nichols, D. E.; Kostuba, L. *J. J. Med. Chem.* 1979, 22, 1264–1267.
3. Murphy, J. J.; Bastida, D.; Paria, S.; Fagnoni, M.; Melchiorre, P. *Nature* 2016 532, 218-222.
4. Lv, J.; Liu, Q.; Tang, J.; Perdih, F.; Kranjc, K. A. *Tetrahedron Lett.* 2012, 53, 5248–5252.
5. Ku, C.-H.; Kuo, C.-H.; Chen, C.-Y.; Leung, M.-K.; Hsieh, K.-H. *J. Mat. Chem.* 2008, 18, 1296–1301.
6. Nesvadba, P.; Wenderborn, F.; Schäfer, T.; Schmidhalter, B.; Ricci, A.; Murer, P.; Chebotareva, N. WO2010046259, 2010
7. Yamase, T.; Takabayashi, N.; Kaji, M. *J. Chem. Soc., Dalton Trans.* 1984, 5, 793-799.
8. Parr, R. G. *Density functional theory of atoms and molecules*; Springer Netherlands, 1980.
9. Runge, E.; Gross, E. K. U. *Phys. Rev. Lett.* 1984, 52, 997–1000.
10. Stratmann, R. E.; Scuseria, G.E.; Frisch, M. *J. J. Chem. Phys.* 1998, 109, 8218–8224.
11. Perdew, J. P.; Ruzsinszky, A.; Tao, J.; Staroverov, V. N.; Scuseria, G. E.; Csonka, G. I. *J. Chem. Phys.* 2005, 123, 6220–6229.
12. Dreuw, A.; Head-Gordon, M. *Chem. Rev.* 2005, 105, 4009–4037.
13. Becke, A. *D. J. Chem. Phys.* 1993, 98, 5648–5652.
14. Barone, V.; Orlandini, L.; Adamo, C. *Chem. Phys. Lett.* 1994, 231, 295–300.
15. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* 1994, 98, 11623–11627.
16. Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* 2005, 105, 2999–3094.
17. Corni, S.; Cammi, R.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* 2005, 123, 134512–10.
18. Scalmani, G.; Frisch, M. J.; Mennucci, B.; Tomasi, J.; Cammi, R.; Barone, V. *J. Chem. Phys.* 2006, 126, 94107–15.
19. Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* 2004, 393, 51–57.
20. Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparrini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.