Electronic Supplementary Information for:

Photochromic Carbazolyl-Imidazolyl Radical Complex

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CONTENTS

1. Syntheses

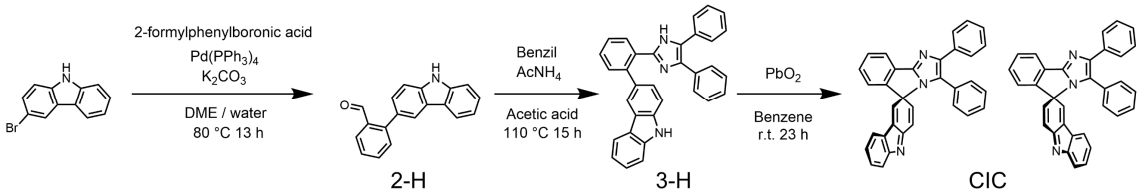
Materials and Reagents

All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (silica gel 60N, Kanto Chemical Co., Inc.). All reagents were purchased from Tokyo Chemical Industry Co. (TCI), FUJIFILM Wako Pure Chemical Co , Sigma-Aldrich Co., and Kanto Chemical Co. and were used without further purification.

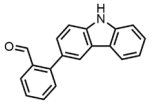
Setups for Material Characterization

Proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were recorded at 400 MHz by JNM-ECS 400 MHz (JEOL). High resolution (HR) ESI–TOF–MS spectra were recorded on a Bruker micrOTOF II-AGA1 (Bruker). High performance liquid chromatography (HPLC) was conducted with Chromaster (Hitachi High-Technologies) equipped with a reverse phase analytical column (Mightysil RP-18GP II, 25 cm × 4.6 mm, 5 μm particle, Kanto Chemical Co.) and a linear photodiode array (PDA) detector. Gel permeation chromatography (GPC) was conducted with a recycling preparative HPLC series (Japan Analytical Industry Co., Ltd.) equipped with two GPC columns (JAIGEL-1H-A and JAIGEL-2H-A) and a UV detector. $CHCl_3$ was used as an eluent with the flow rate of 3.5 mL/min.

Scheme S1. Synthesis of **CIC**.

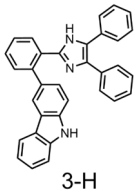


2-(9*H*-carbazol-3-yl)benzaldehyde (2-H).



A Schlenk flask was charged with 3-bromo-*9H*-carbazole (300 mg, 1.22 mmol), 2-formylphenylboronic acid (236 mg, 1.62 mmol), potassium carbonate (252 mg, 1.83 mmol), and tetrakis(triphenylphosphine)palladium(0) (70 mg, 0.061 mmol) in the solvent pair (3 mL of H_2O/20 mL of ethylene glycol dimethyl ether (DME)). The solution was stirred at 80 °C for 13 h. After Celite filtration, the filtrate was transferred to a separation funnel and extracted with ethyl acetate. The organic layer was collected, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and passed through a phase separator paper. After removal of the solvent in vacuo, the crude mixture was purified by silica gel column chromatography (ethyl acetate/hexane = 1/5) to give 2-H as a white solid (281 mg, 85%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.46 (s, 1H), 9.95 (d, J = 1.2 Hz, 1H), 8.23−8.19 (m, 2H), 7.94 (dd, J = 7.6, 1.2 Hz, 1H), 7.77 (ddd, J = 7.6, 7.6, 1.6 Hz, 1H), 7.66−7.52 (m, 4H), 7.46-7.40 (m, 2H), 7.21-7.17 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 193.45 147.10, 140.10, 139.32, 133.97, 133.66, 131.41, 128.91, 128.15, 127.63, 127.32, 126.51, 123.53, 123.00, 122.05, 120.56, 119.91, 111.01, 110.62,; HRMS (ESI-TOF): calcd for $C_{19}H_{13}NO$ [M + Na]$^+$, 294.0889; found, 294.0901.

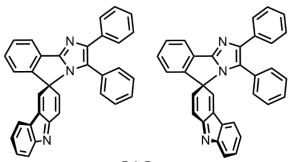
3-(2-(4,5-diphenyl-1*H*-imidazol-2-yl)phenyl)-9*H*-carbazole (3-H).



A sealed tube was charged with 2-H (100 mg, 0.369 mmol), benzil (120 mg, 0.751 mmol), and ammonium acetate (300 mg, 3.90 mmol) in 5 mL of acetic acid. The solution was stirred at 110 °C for 15 h. After cooling to room temperature, the reaction mixture was neutralized with aqueous NH_3. After addition of ethyl acetate, the solution composed of the organic and water layers was transferred to a separation funnel and extracted with ethyl acetate. The organic layer was collected, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and passed through a phase separator paper. After removal of the solvent in vacuo, the crude mixture was

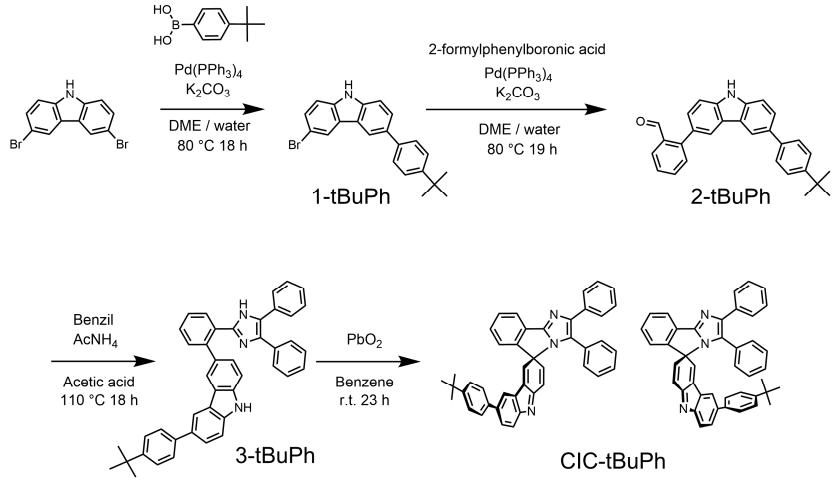
purified by silica gel column chromatography (ethyl acetate/hexane = 2/5) to give 3-H as a white solid (160 mg, 94%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.80 (s, 1H), 11.21 (s, 1H), 8.13 (d, J = 1.2 Hz, 1H), 8.01 (d, J = 7.2 Hz, 1H), 7.72 (dd, J = 8.0, 1.2 Hz, 1H), 7.59−7.51 (m, 2H), 7.47−7.43 (m, 2H), 7.39−7.31 (m, 4H), 7.22−7.08 (m, 10H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 146.69, 142.31, 140.60.139,35, 136.72, 135.93, 131.71, 131.40, 131.25, 131.03, 130.72, 129.53, 128.99, 128.58, 128.43,127.91, 127.71, 127.50, 127.45, 127.06, 126.77, 126.04, 123.13, 122.77, 121.47, 120.52, 119.08, 111.57, 110.58; HRMS (ESI-TOF): calcd for $C_{33}H_{23}N_3$ $[M + H]^+$, 426.1965; found, 462.1952.

2',3'-diphenylspiro[carbazole-3,5'-imidazo[2,1-a]isoindole] (CIC).

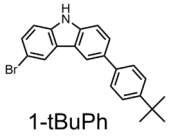

CIC

All manipulations were carried out with the exclusion of light. Under nitrogen, a two-necked round-bottom flask was charged with 3-H (100 mg, 0.212 mmol) and lead (IV) oxide (300 mg, 1.26 mmol) in 50 mL of benzene over 23 h while stirring. The reaction mixture was passed through a phase filter paper. After removal of the solvent in vacuo, the crude mixture was purified by silica gel column chromatography (ethyl acetate/hexane = 1/1) and purified by GPC to give the racemic mixture of enantiomers of CIC as a yellow solid (15 mg, 15%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.95 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.59 (ddd, J = 7.8, 7.8, 0.8 Hz, 1H), 7.51−7.36 (m, 6H), 7.31−7.12 (m, 10H), 6.88 (d, J = 10 Hz, 1H), 6.59 (dd, J = 9.6, 2.4 Hz, 1H), ^{13}C NMR (400 MHz, $CDCl_3$): δ161.08, 157.57, 151.95, 143.10, 141.43, 139.73, 137.84, 134.49, 133.62, 130.70, 130.26,130.16, 129.44, 129.18, 128.76, 128.43,128.33, 127.91, 127.10, 126.97, 126.62, 126.24, 125.41, 123.40, 121.37, 121.32, 121.20, 66.74; HRMS (ESI-TOF): calcd for $C_{33}H_{21}N_3$ $[M + H]^+$, 460.1808; found, 460.1791.

Scheme S2. Synthesis of **CIC-tBuPh**.

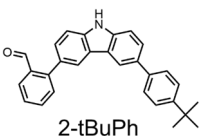


3-bromo-6-(4-(*tert*-butyl)phenyl)-9*H*-carbazole (1-tBuPh).



A Schlenk flask was charged with 3,6-dibromo-*9H*-carbazole (404 mg, 1.25 mmol), 4-*tert*-butylphenylboronic acid (223 mg, 1.25 mmol), potassium carbonate (300 mg, 2.17 mmol), and tetrakis(triphenylphosphine)palladium(0) (80 mg, 0.069 mmol) in the solvent pair (10 mL of H_2O and 40 mL of ethylene glycol dimethyl ether DME). The mixture was stirred at 80 °C for 20 h. After Celite filtration, the filtrate was transferred to a separation funnel and extracted with ethyl acetate. The organic layer was collected, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and passed through a phase separator paper. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1/3) and purified by GPC to give 1-tBuPh as a white solid (130 mg, 28%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.49 (s, 1H), 8.47 (dd, J = 16.8, 1.2 Hz, 2H), 7.74−7.67 (m, 3H), 7.56 (d, J = 8.8 Hz, 1H), 7.52−7.45 (m, 4H), 1.34 (s, 9H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 149.80, 139.18, 138.93, 138.55, 133.35, 128.75, 127.03, 126.23, 125.96, 125.34, 123.23, 122.94, 118.82, 112.42, 112.27, 111.12, 34.67, 31.58; HRMS (ESI-TOF): calcd for $C_{22}H_{20}BrN$ $[M + K]^+$, 416.0411; found, 416.0397.

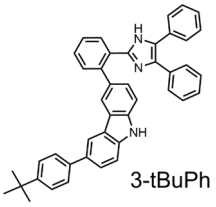
2-(6-(4-(*tert*-butyl)phenyl)-9*H*-carbazol-3-yl)benzaldehyde (2-tBuPh).



A Schlenk flask was charged with 1-tBuPh (190 mg, 0.504 mmol), 2-formylphenylboronic acid (220 mg, 1.47 mmol), potassium carbonate (240 mg, 1.73 mmol), and tetrakis(triphenylphosphine)palladium(0) (28 mg, 0.024 mmol) in the solvent pair (5 mL of H_2O/20 mL of DME). The solution was stirred at

80 °C for 15 h. After Celite filtration, the filtrate was transferred to a separation funnel and extracted with ethyl acetate. The organic layer was collected, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and passed through a phase separator paper. After removal of the solvent in vacuo, the crude mixture was purified by silica gel column chromatography (ethyl acetate/hexane = 1/6) to give 2-tBuPh as a white solid (79 mg, 39%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.53 (s, 1H), 9.97 (d, J = 0.8 Hz, 1H), 8.53 (d, J = 1.6 Hz, 1H), 8.33 (d, J = 2.0 Hz, 1H), 7.95 (dd, J = 8.0, 1.2 Hz, 1H), 7.78 (ddd, J = 7.6, 7.6, 1.6 Hz, 1H), 7.75−7.66 (m, 4H), 7.63−7.5 (m, 3H), 7.49−7.46 (m, 3H), 1.33 (s, 9H). ^{13}C NMR (400 MHz, $CDCl_3$): δ193.32, 149.69, 147.02, 139.76, 139.41, 139.00, 134.03, 133.64, 133.36, 131.42, 129.12, 128.34, 127.68, 127.37, 127.00, 126.08, 125.89, 123.76, 123.60, 122.13, 118.87, 111.16, 110.74, 34.62, 31.53; HRMS (ESI-TOF): calcd for $C_{29}H_{25}NO$ $[M + Na]^+$, 426.1828; found, 426.1808.

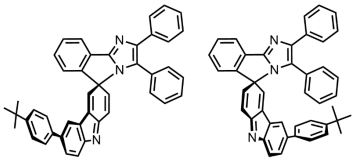
3-(4-(*tert*-butyl)phenyl)-6-(2-(4,5-diphenyl-1*H*-imidazol-2-yl)phenyl)-9*H*-carbazole (3-tBuPh).



3-tBuPh

A sealed tube was charged with 2-tBuPh (100 mg, 0.248 mmol), benzil (78 mg, 0.37 mmol), and ammonium acetate (190 mg, 2.47 mmol) in 5 mL of acetic acid. The solution was stirred at 110 °C for 18 h. After cooling to room temperature, the reaction mixture was neutralized with aqueous NH_3. After addition of ethyl acetate, the solution composed of the organic and water layers was transferred to a separation funnel and extracted with ethyl acetate. The organic layer was collected, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and passed through a phase separator paper. After removal of the solvent in vacuo, the crude mixture was purified by silica gel column chromatography (ethyl acetate/hexane = 1/3) to give 3-tBuPh as an orange solid (141 mg, 96%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.96 (s, 1H), 11.31 (s, 1H), 8.26 (d, J = 1.6 Hz, 1H), 8.15 (d, J = 1.6 Hz, 1H), 7.75 (dd, J = 7.6, 1.2 Hz, 1H), 7.66 (dd, J = 8.8, 1.2 Hz, 2H), 7.61−7.41 (m, 10H), 7.30 (dd, J = 8.8, 2.0 Hz, 1H), 7.21−7.14 (m, 8H), 1.34 (s, 9H). ^{13}C NMR (400 MHz, DMSO-d_6): δ149.18, 146.80, 142.22, 140.03, 139.84, 138.88, 136.76, 135.95, 131.70, 131.45, 131.29, 131.20, 131.02, 130.80, 129.70, 129.00, 128.64, 128.41, 127.86, 127.72, 127.52, 127.05, 126.71, 126.15, 125.01, 123.78, 122.96, 121.47, 118.27, 111.93, 110.87, 34.69, 31.72; HRMS (ESI-TOF): calcd for $C_{43}H_{35}N_3$ $[M + H]^+$, 594.2904; found, 594.2894.

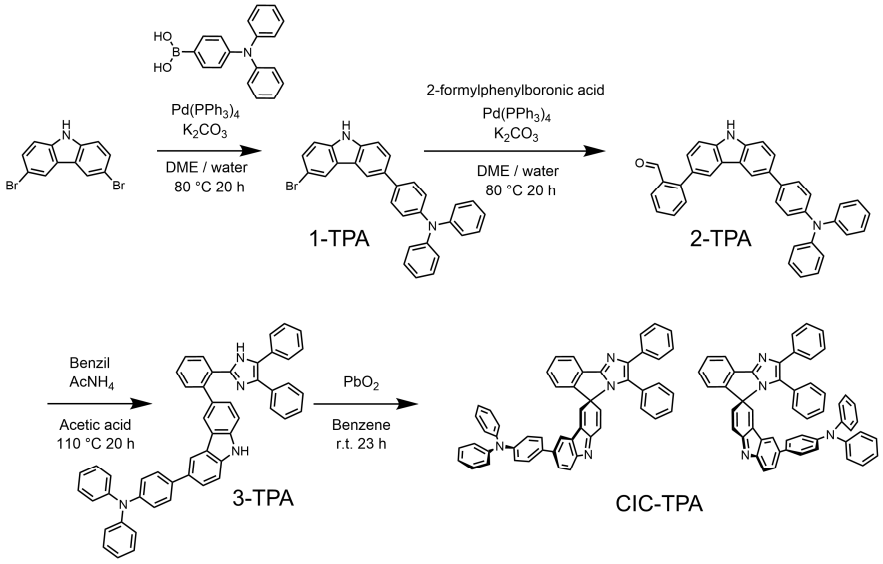
6-(4-(*tert*-butyl)phenyl)-2',3'-diphenylspiro[carbazole-3,5'-imidazo[2,1-*a*]isoindole] (CIC-tBuPh).



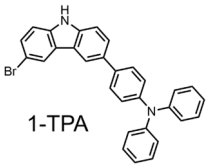
CIC-tBuPh

All manipulations were carried out with the exclusion of light. Under nitrogen, a two-necked round-bottom flask was charged with 3-tBuPh (100 mg, 0.169 mmol) and lead (IV) oxide (300 mg, 1.26 mmol) in 50 mL of benzene over 23 h while stirring. The reaction mixture was passed through a phase filter paper. After removal of the solvent in vacuo, the crude mixture was purified by silica gel column chromatography (ethyl acetate/hexane = 1/1) and purified by GPC to give the racemic mixture of enantiomers of CIC-tBuPh as an orange solid (21 mg, 21%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.00 (d, J = 1.2 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.67 (dd, J = 8.0, 1.6 Hz, 1H), 7.62−7.57 (m, 3H), 7.55−7.46 (m, 6H), 7.39 (ddd, J = 7.8, 7.8, 0.8 Hz, 1H), 7.32−7.30 (m, 2H), 7.27−7.13 (m, 7H), 6.90 (d, J = 9.6 Hz, 1H), 6.61 (dd, J = 9.6, 2.0 Hz, 1H), 1.30 (s, 9H). ^{13}C NMR (400 MHz, $CDCl_3$): δ161.00, 156.49, 151.80, 150.62, 142.91, 141.33,139.47, 139.26, 137.79, 137.60, 134.43, 133.56, 130.70, 130.12, 130.01, 129.30,129.27, 129.06, 128.64, 128.29, 128.21, 127,78, 127.12, 126.95, 126.82, 126.58, 125.87, 125.25, 123.28, 121.24, 121.06, 119.12, 34.57, 31.32; HRMS (ESI-TOF): calcd for $C_{43}H_{33}N_3$ [M + H]$^+$, 592.2747.2468; found, 592.2740.

Scheme S2. Synthesis of **CIC-TPA**.

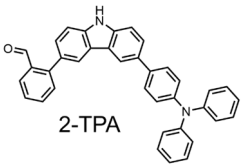


4-(6-bromo-9*H*-carbazol-3-yl)-*N*,*N*-diphenylaniline (1-TPA).



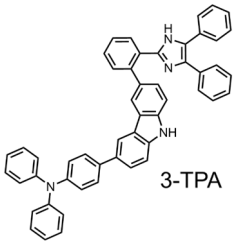
A Schlenk flask was charged with 3,6-dibromo-*9H*-carbazole (1011 mg, 3.140 mmol), 4- (diphenylamino)phenylboronic acid (907 mg, 3.14 mmol), potassium carbonate (649 mg, 4.71 mmol) and tetrakis(triphenylphosphine)palladium(0) (180 mg, 0.156 mmol) in the solvent pair (12.5 mL of H_2O and 50 mL of DME). The reaction was stirred at 80 °C for 20 h. After Celite filtration, the filtrate was transferred to a separation funnel and extracted with ethyl acetate. The organic layer was collected, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and passed through a phase separator paper. After removal of the solvent in vacuo, the crude mixture was purified by silica gel column chromatography (ethyl acetate/hexane = 1/6) and purified by GPC to give to give 1-TPA as a white solid (610 mg, 40%). ^{1}H NMR (400 MHz, DMSO-d_6): δ11.49 (s, 1H), 8.49 (d, J = 1.2 Hz, 1H), 8.43 (d, J = 2.0 Hz, 1H),7.73−7.69 (m, 3H), 7.56−7.45 (m, 3H), 7.35−7.31 (m, 4H), 7.11−7.04 (m, 8H), ^{13}C NMR (400 MHz, $CDCl_3$): 147.94, 146.76, 139.10, 138.57, 136.05, 133.00, 129.51, 128.78, 128.07, 125.96, 125.31, 124.56, 124.43, 123.26, 122.98, 118.51, 112.45, 112.35, 111.24; HRMS (ESI-TOF): calcd for $C_{30}H_{21}BrN_2$ $[M]^+$, 488.0883; found, 488.0863.

2-(6-(4-(diphenylamino)phenyl)-9*H*-carbazol-3-yl)benzaldehyde (2-TPA).



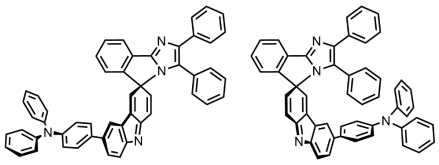
A Schlenk flask was charged with 1-TPA (190 mg, 0.389 mmol), 2-formylphenylboronic acid (174 mg, 1.17 mmol), potassium carbonate (187 mg, 1.36 mmol) and tetrakis(triphenylphosphine)palladium(0) (22 mg, 0.019 mmol) in the solvent pair (5 mL of H_2O and 20 mL of DME). The reaction was stirred at 80 °C for 20 h. After Celite filtration, the filtrate was transferred to a separation funnel and extracted with ethyl acetate. The organic layer was collected, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and passed through a phase separator paper. After removal of the solvent in vacuo, the crude mixture was purified by silica gel column chromatography (ethyl acetate/hexane = 1/5) to give 2-TPA as a yellow solid (50 mg, 25%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.51 (s, 1H), 9.97 (s, 1H), 8.54 (d, J = 1.2 Hz, 1H), 8.33 (d, J = 1.6 Hz, 1H), 7.95 (dd, J = 8.0, 1.2 Hz, 1H), 7.80−7.70 (m, 4H), 7.67−7.56 (m, 4H), 7.47 (dd, J = 7.2, 2.4 Hz, 1H), 7.34−7.30 (m, 4H), 7.10−7.03 (m, 8H). ^{13}C NMR (400 MHz, $CDCl_3$):193.27, 147.88, 146.97, 14.67, 139.76, 139.30, 136.16, 134.02, 133.64, 133.40, 131.40, 129.36, 129.14, 128.35, 128.02, 127.69, 127.38, 125.80, 124.52, 124.31, 123.74, 123.64, 122.84, 122.17, 118.60, 111.20, 110.76; HRMS (ESI-TOF): calcd for $C_{37}H_{26}N_2O$ $[M]^+$, 514.2040; found, 514.2026.

4-(6-(2-(4,5-diphenyl-1H-imidazol-2-yl)phenyl)-9*H*-carbazol-3-yl)-*N*,*N*-diphenylaniline (3-TPA).



A sealed tube was charged with 2-TPA (50 mg, 0.097 mmol), benzil (30 mg, 0.14 mmol) and ammonium acetate (75 mg, 0.97 mmol) in 2 mL of acetic acid. The reaction was stirred at 110 °C for 20 h. After cooling to room temperature, the reaction mixture was neutralized with aqueous NH_3. After addition of ethyl acetate, the solution composed of the organic and water layers was transferred to a separation funnel and extracted with ethyl acetate. The organic layer was collected, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and passed through a phase separator paper. After removal of the solvent in vacuo, the crude mixture was purified by silica gel column chromatography (ethyl acetate/hexane = 1/2) to give 3-TPA as a yellow solid (52 mg, 76%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.00 (s, 1H), 11.31 (s, 1H), 8.24 (s, 1H), 8.12 (s, 1H), 7.73 (dd, J = 7.6, 1.6 Hz, 1H), 7.68−7.65 (m, 2H), 7.61−7.42 (m, 8H), 7.37−7.31 (m, 5H), 7.21−7.00 (m, 16H). ^{13}C NMR (400 MHz, DMSO-d_6): 147.77, 146.81, 146.23, 141.19, 139.95, 139.85, 136.13, 131.23, 131.00, 130.93, 130.81, 130.62, 130.08, 129.71, 129. 01, 128.95, 128.84, 128.58,128.40, 127.91, 127.57, 127.00, 124.79, 124.51, 124.37, 123.83, 123.50, 122.95, 121.40, 117.94, 111.95, 110.93; HRMS (ESI-TOF): calcd for $C_{51}H_{36}N_4$ $[M + H]^+$, 705.3013; found, 705.3011.

4-(2',3'-diphenylspiro[carbazole-3,5'-imidazo[2,1-*a*]isoindol]-6-yl)-*N*,*N*-diphenylaniline (CIC-TPA).



All manipulations were carried out with the exclusion of light. Under nitrogen, a two-necked round-bottom flask was charged with 3-TPA (50 mg, 0.071 mmol) and lead (IV) oxide (170 mg, 0.711 mmol) in 50 mL of benzene over 23 h while stirring. The reaction mixture was passed through a phase filter paper. After removal of the solvent in vacuo, the crude mixture was purified by silica gel column chromatography (ethyl acetate/hexane = 1/1) and purified by GPC to give the racemic mixture of enantiomers of CIC-TPA as a red solid (3 mg, 6%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.00 (d, J = 2.0 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.66 (dd, J = 8.0, 1.6 Hz, 1H), 7.61−7.58 (m, 3H), 7.53−7.49 (m, 3H), 7.44 (d, J = 2.4 Hz, 1H), 7.39 (ddd, J = 7.4, 7.4, 0.8 Hz, 1H), 7.33−7.29 (m, 6H), 7.26-7.14 (m, 7H), 7.07−7.02 (m, 8H), 6.90 (d, J = 9.6 Hz, 1H), 6.60 (dd, J = 10.0, 2.4 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ160.90, 156.29, 151.79, 147.49, 147.39, 142.91, 141.33, 139.37, 138.89, 137.78, 134.43, 134,20, 133.61, 130.69, 130.11, 130.00, 129.30, 129.05, 128.81, 128.63, 128.28, 128.20, 127.77, 127.56, 127.18, 126.95, 126.82, 125.26, 124.49, 123.71, 123.26, 123.07, 121.27, 121.04, 119.55, 66.66; HRMS (ESI-TOF): calcd for $C_{51}H_{34}N_4$ $[M + H]^+$, 703.2856; found, 703.2824.

2. Experimental Setups

X-ray crystallography

Details of the crystal data and a summary of the intensity data collection parameters for ClC-tBuPh are listed in Table S1. A suitable crystal obtained by slow evaporation of the MeOH solution of ClC-tBuPh was mounted with mineral oil on a MiTeGen MicroMounts and transferred to the goniometer of the kappa goniometer of a RIGAKU XtaLAB Synergy-S system with 1.2 kW MicroMax-007HF microfocus rotating anode (Graphite-monochromated Mo Kα radiation (λ = 0.71073 Å)) and HyPix-6000HE hybrid photon-counting detector. Cell parameters were determined and refined, and raw frame data were integrated using CrysAlis^{Pro} (Agilent Technologies, 2010). The structures were solved by direct methods with SHELXT[S1] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2018/3)[S2] by using Olex2 software package.[S3] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions or refined isotropically in the difference Fourier maps. CCDC 2150990 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Steady-State Spectroscopic Measurements

Absorption spectra were measured on a UV3600 spectrophotometer (Shimazu). Fluorescence spectra were measured on a FP-6500 fluorescence spectrophotometer (Jasco). The measurements were performed in benzene and acetonitrile solutions placed in a 10-mm quartz cell at room temperature.

Nanosecond-to-Microsecond Transient Absorption Measurements

For visible transient absorption measurements shown in the main text, the experiments were conducted using a TSP–2000 time resolved spectrophotometer (Unisoku). A 10 Hz Q–switched Nd:YAG (Continuum Minilite II) laser with the third harmonic at 355 nm (ca. 1-2 mJ per 5 ns pulse) was used as the excitation light. For visible to near infrared transient absorption measurements shown in the ESI, the experiments were conducted by the randomly-interleaved-pulse-train (RIPT) method.[38] A picosecond laser, PL2210A (EKSPLA, 1 kHz, 25 ps, 3.4 mJ/pulse for 355 nm), and a supercontinuum (SC) radiation source (SC-450, Fianium, 20 MHz, pulse width: 50–100 ps depending on the wavelength, 450–2000 nm), were employed as the pump–pulse and probe sources, respectively. The

wavelength of the excitation pulse was set to 355 nm. The measurements were performed in benzene and acetonitrile solutions placed in a 2-mm quartz cell under argon condition with stirring at room temperature.

Femtosecond to Nanosecond Transient Absorption Measurements

Transient absorption measurements on the femtosecond to nanosecond time scale were conducted by a homemade pump-probe system. An amplified femtosecond laser, Spirit One 1040-8 (Spectra-Physics, 1040 nm, the pulse width: ~270 fs), was split into two beams with a ratio of 1:9. The stronger beam was directed to a noncollinear optical parametric amplifier (NOPA), Spirit-NOPA-3H (Spectra-Physics) to generate the 390-, and ~600-nm femtosecond laser pulse for the pump beam. The pump beam was chopped prior to the sample at 500 Hz for signal differencing. The other weaker beam was focused to a deuterated water placed in a 10-mm quartz cuvette to generate the white light continuum for the probe beam. Both pump and probe beams were focused to the sample solution placed in the 2-mm quartz cuvette. The polarization between the pump and probe pulses was set at magic angle. The transmitted probe beam was detected with multichannel detection system, PK120-C-RK (UNISOKU), composed of a CMOS linear image sensor and a polychromator. The obtained spectra were calibrated for group velocity dispersion using the data obtained by the optical Kerr signal of CH_2Cl_2 between the pump pulse and the white-light continuum. The instrumental response function was shorter than approximately 100 fs. The sample solutions were stirred with a stirrer during the experiments. The measurements were performed at room temperature.

3. ^{1}H NMR Spectra

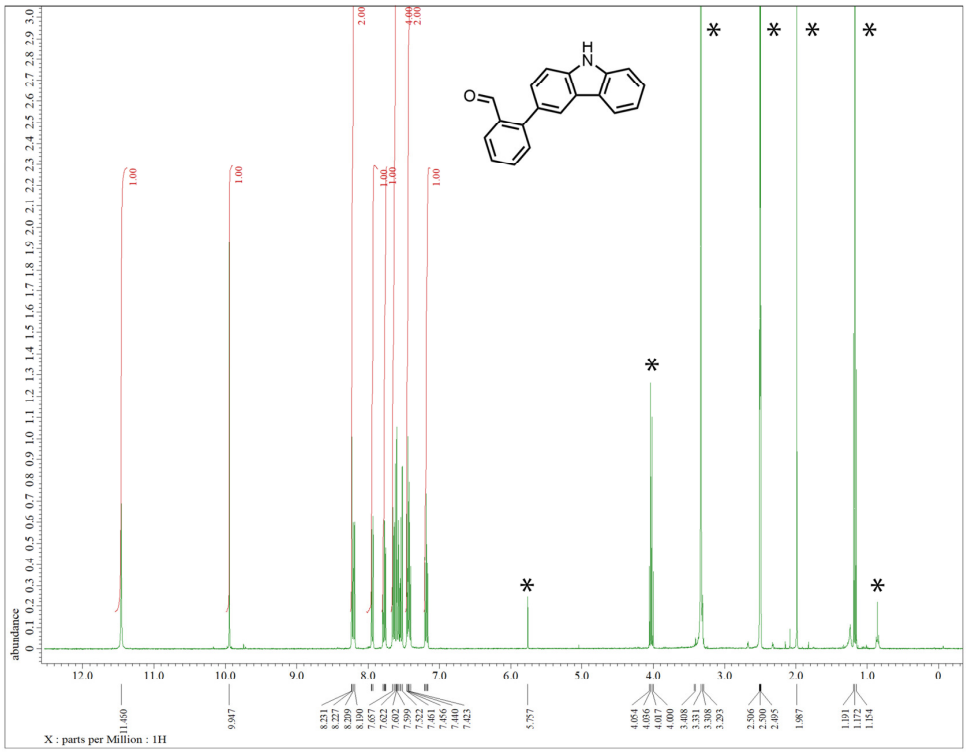


Fig. S1. ^{1}H NMR spectrum of 2-H in DMSO-*d*$_6$ (* solvent peaks).

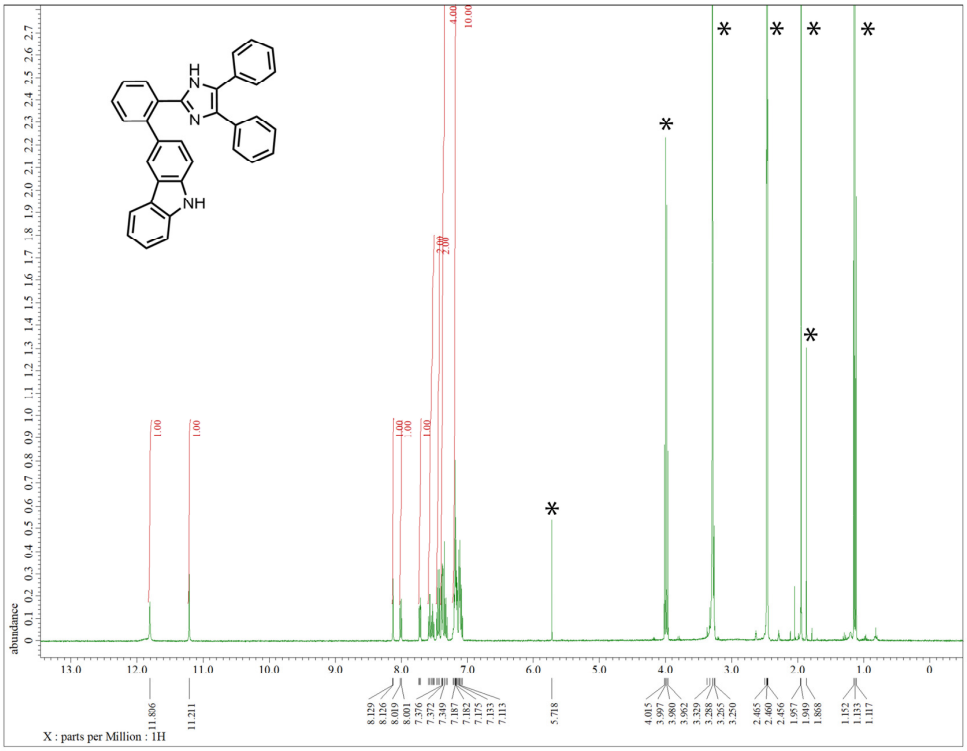


Fig. S2. ^{1}H NMR spectrum of 3-H in DMSO-*d*$_6$ (* solvent peaks).

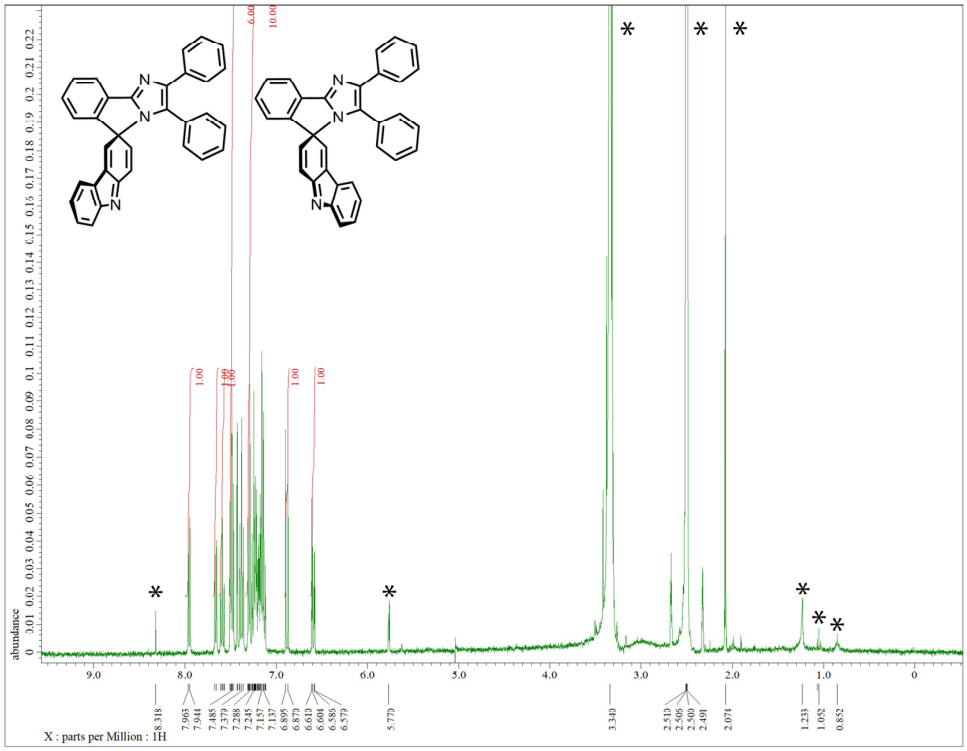


Fig. S3. ^{1}H NMR spectrum of CIC in DMSO-*d*$_6$ (* solvent peaks).

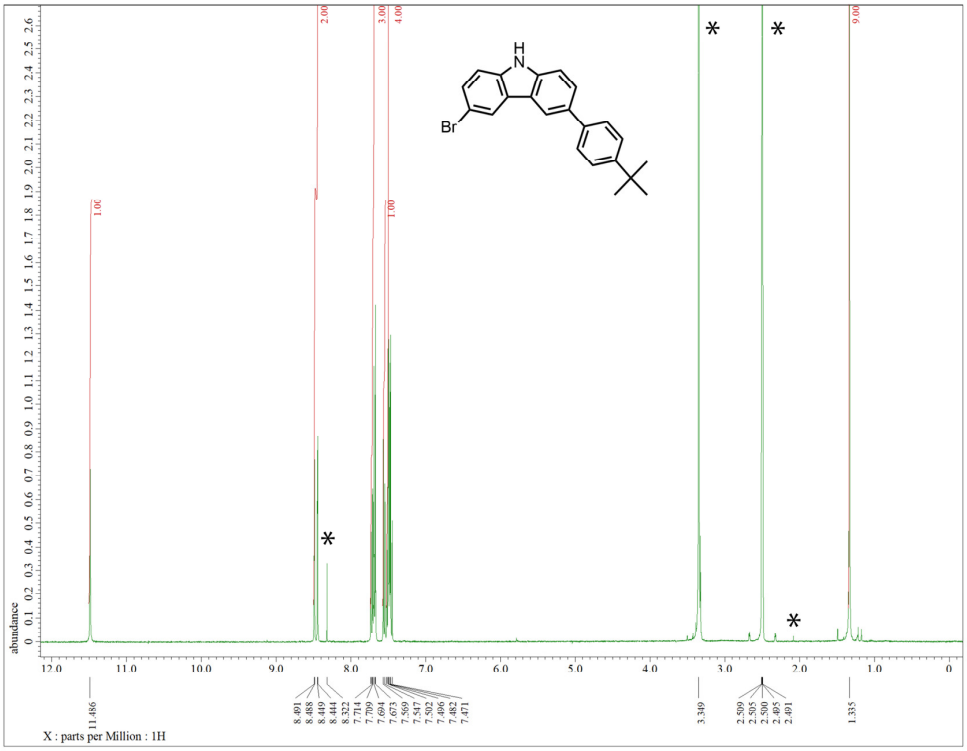


Fig. S4. ^{1}H NMR spectrum of 1-tBuPh in DMSO-*d*$_6$ (* solvent peaks).

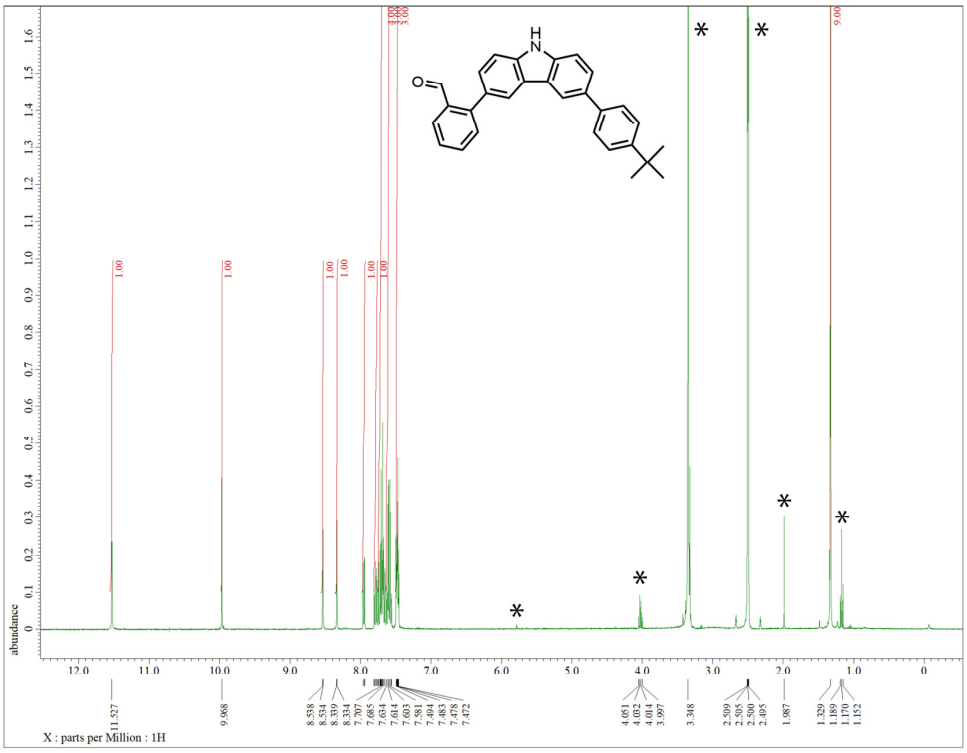


Fig. S5. ^{1}H NMR spectrum of 2-tBuPh in DMSO-d_6 (* solvent peaks).

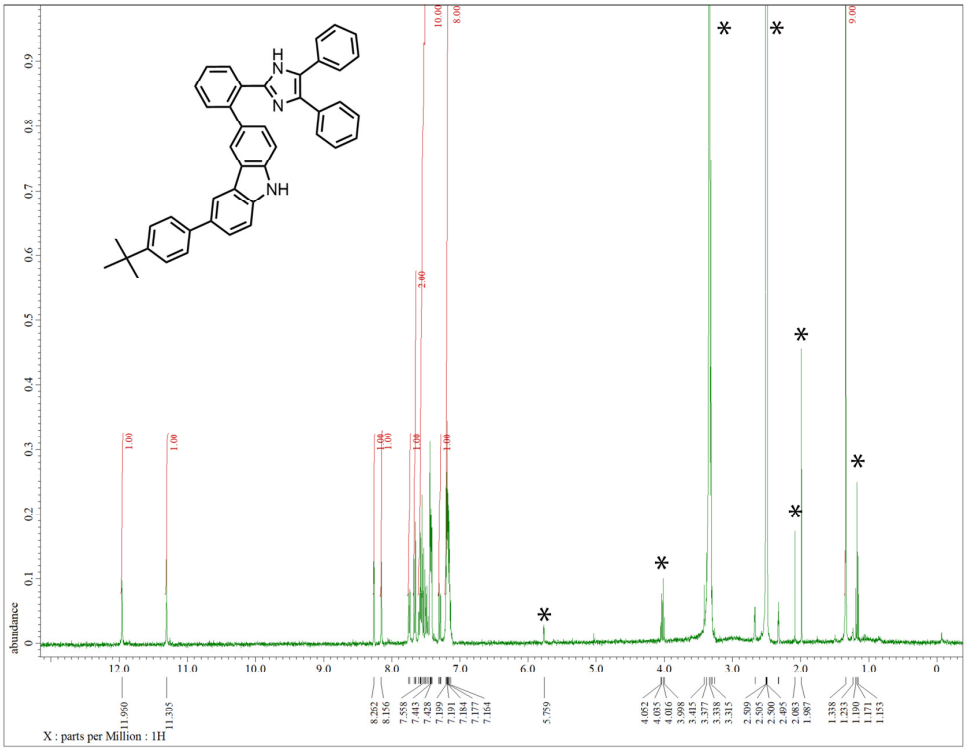


Fig. S6. ^{1}H NMR spectrum of 3-tBuPh in DMSO-d_6 (* solvent peaks).

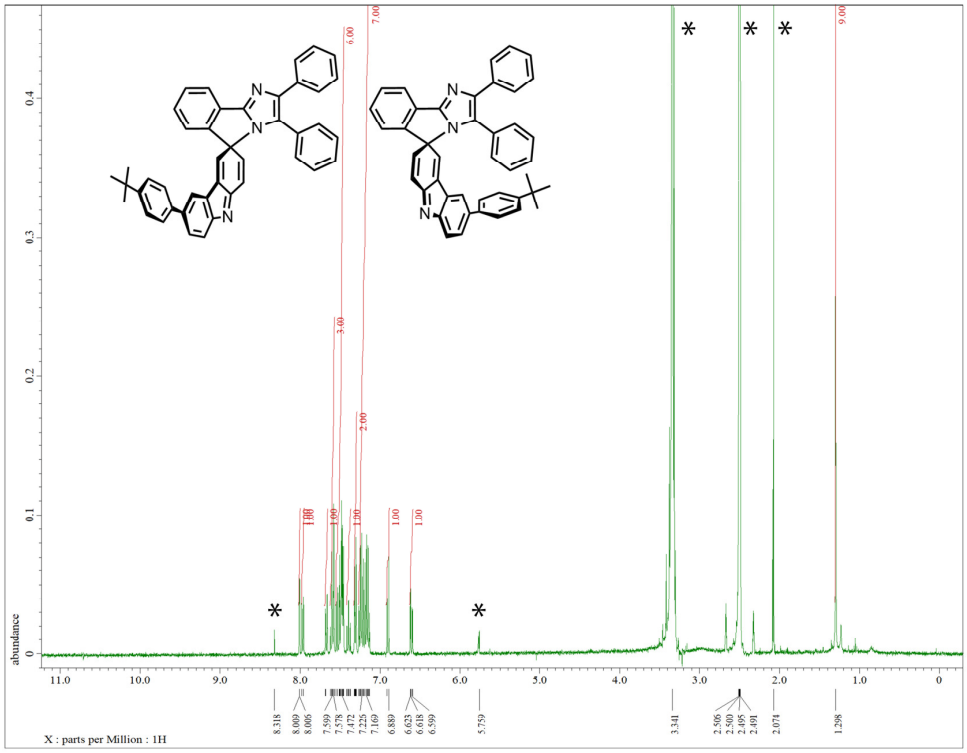


Fig. S7 ^{1}H NMR spectrum of ClC-tBuPh in DMSO-*d*$_6$ (* solvent peaks).

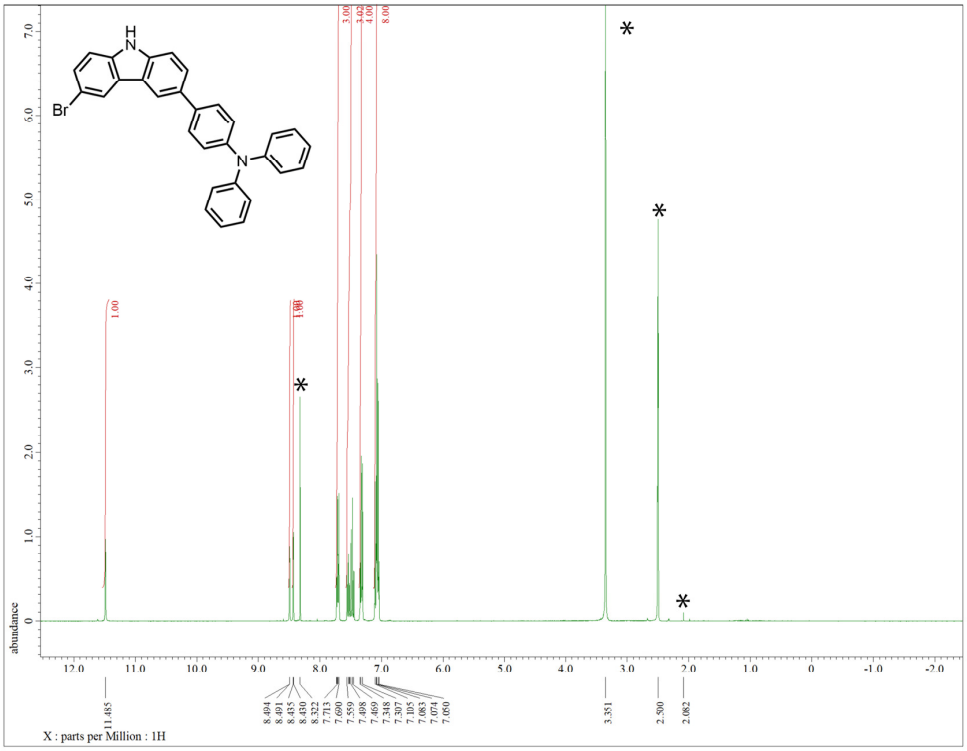


Fig. S8. ^{1}H NMR spectrum of 1-TPA in DMSO-*d*$_6$ (* solvent peaks).

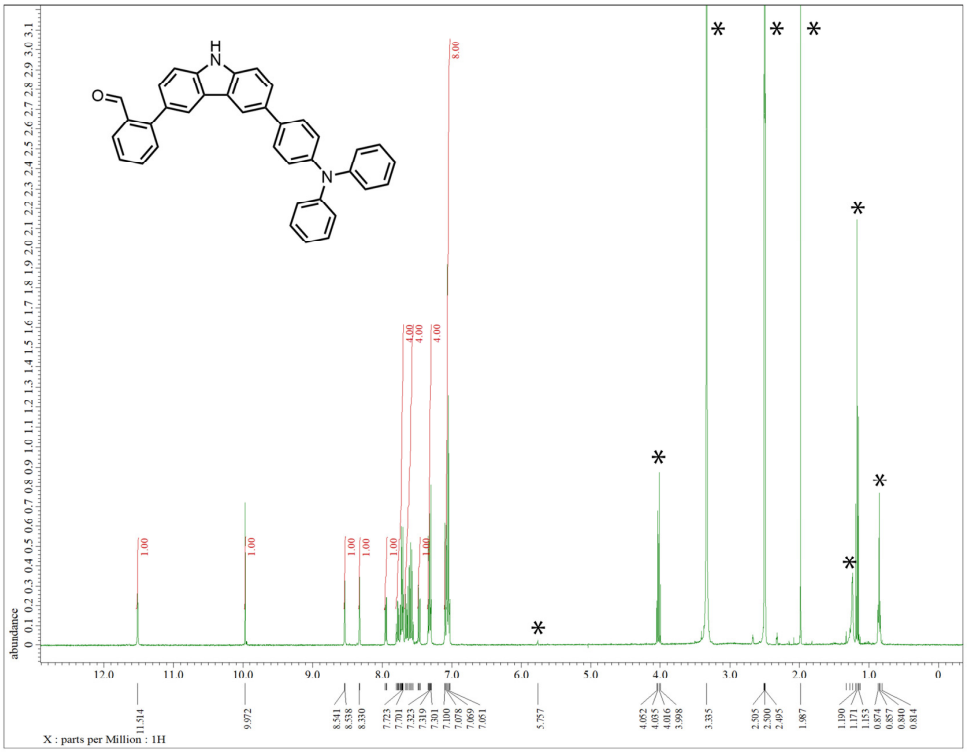


Fig. S9 ^{1}H NMR spectrum of 2-TPA in DMSO-*d*$_6$ (* solvent peaks).

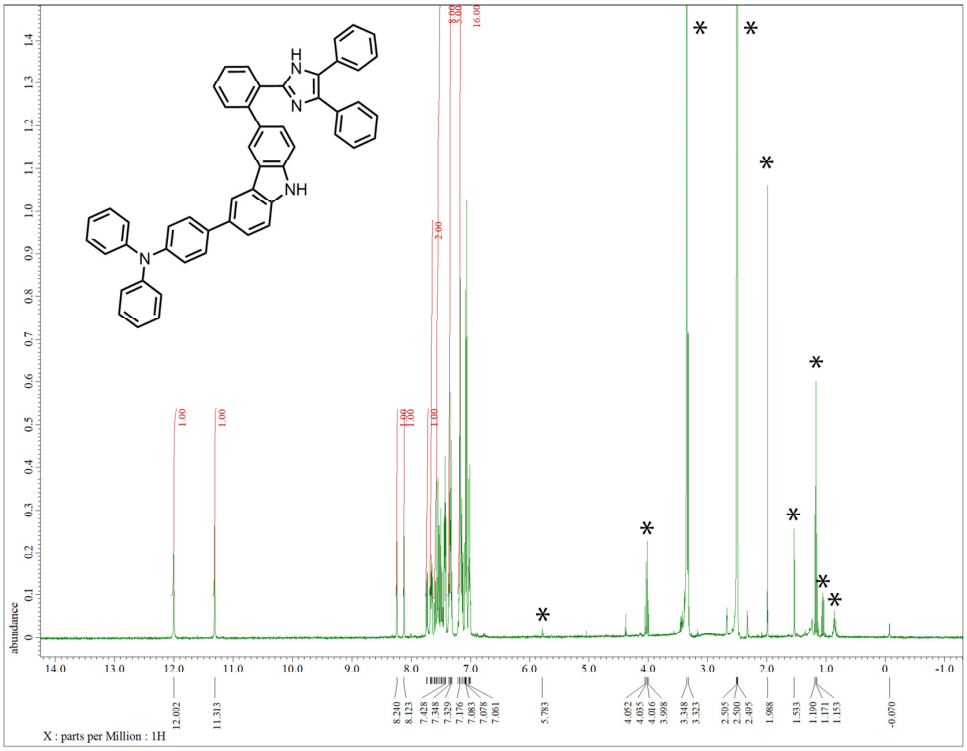


Fig. S10. ^{1}H NMR spectrum of 3-TPA in DMSO-*d*$_6$ (* solvent peaks).

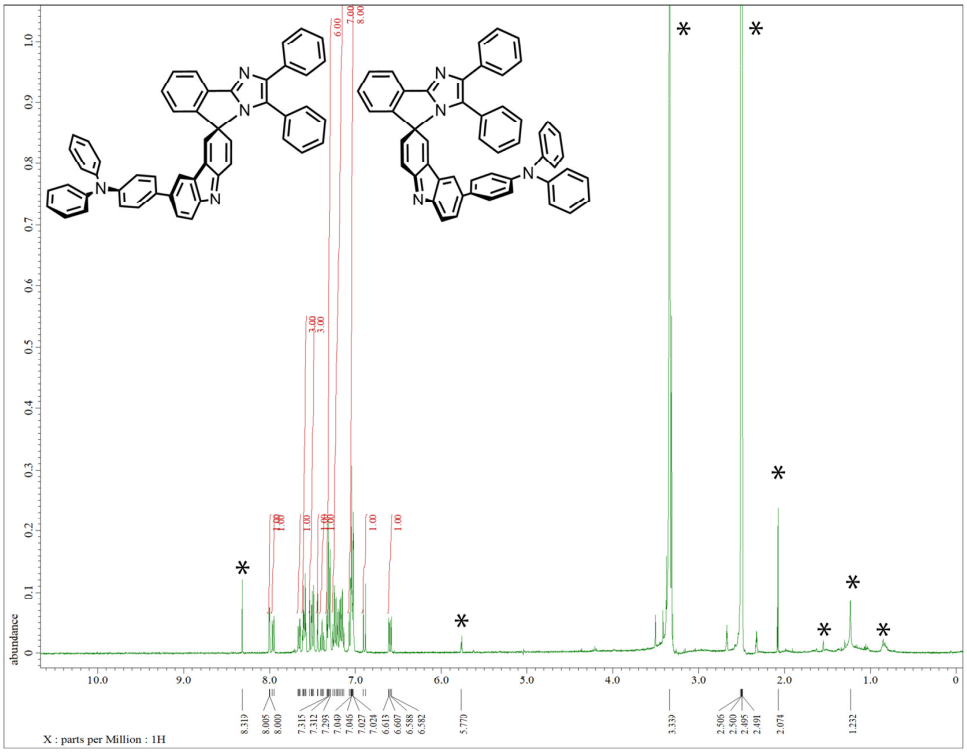


Fig. S11 ^{1}H NMR spectrum of ClC-TPA in DMSO-*d*$_6$ (* solvent peaks).

4. ^{13}C NMR Spectra

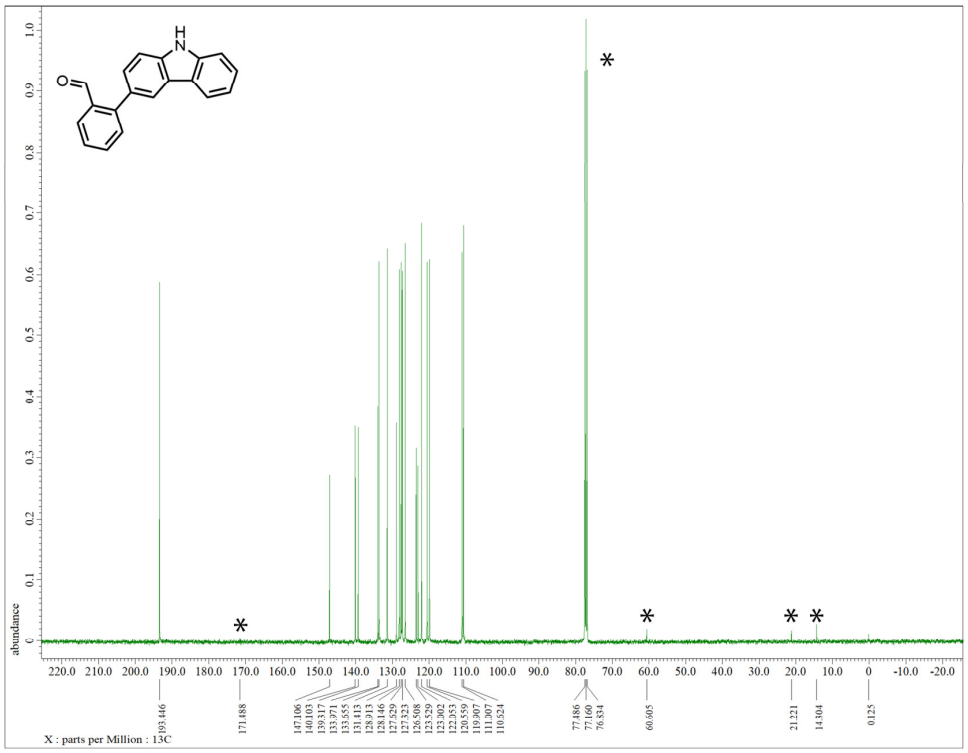


Fig. S12. ^{13}C NMR spectrum of 2-H in $CDCl_3$ (* solvent peaks).

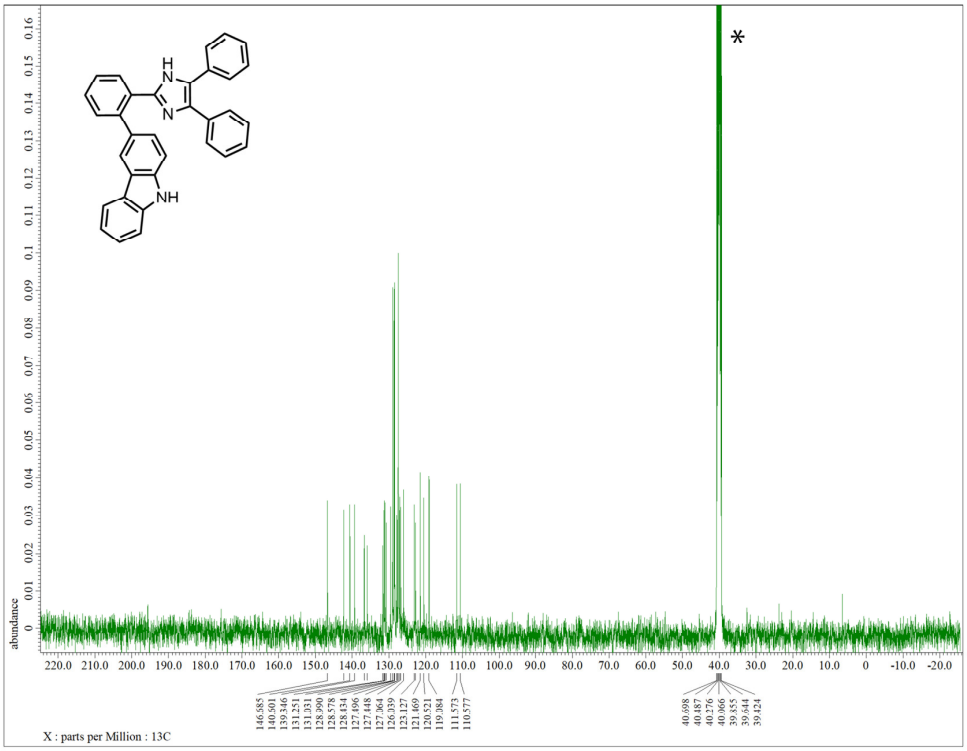


Fig. S13. ^{13}C NMR spectrum of 3-H in DMSO-d_6 (* solvent peaks).

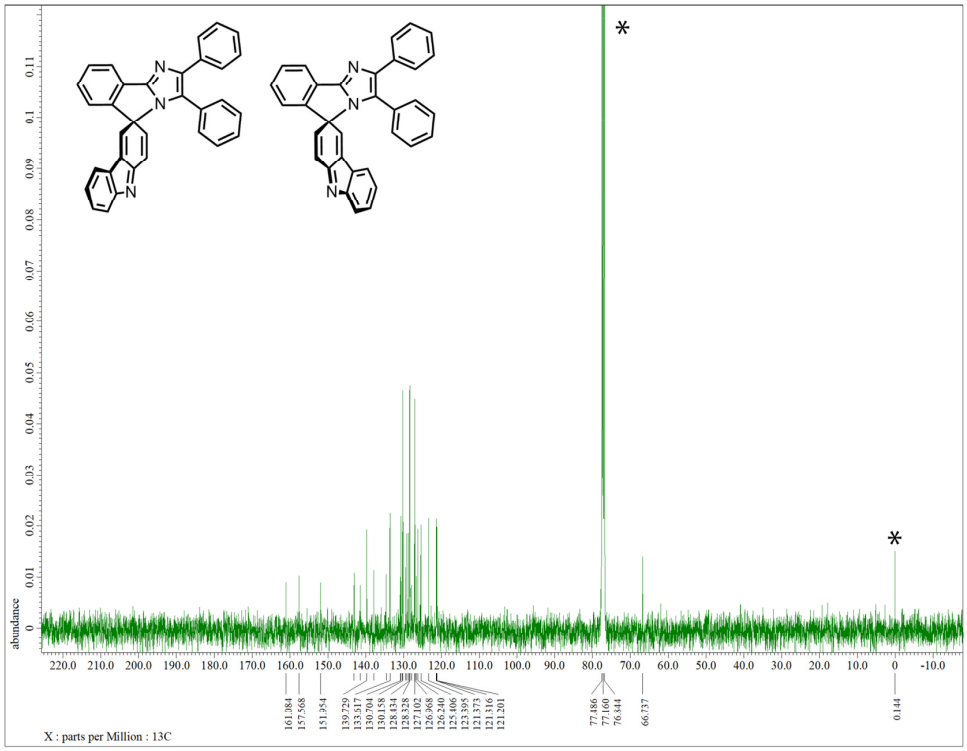


Fig. S14. ^{13}C NMR spectrum of **ClC** in CDC_3 (* solvent peaks).

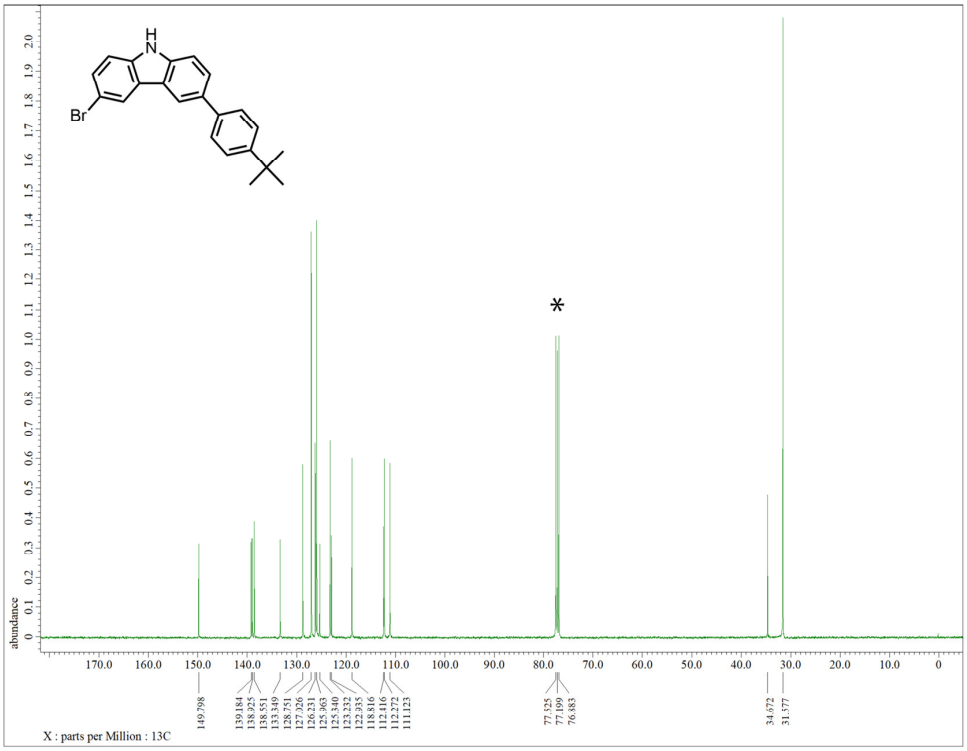


Fig. S15. ^{13}C NMR spectrum of **1-tBuPh** in $CDCl_3$ (* solvent peaks).

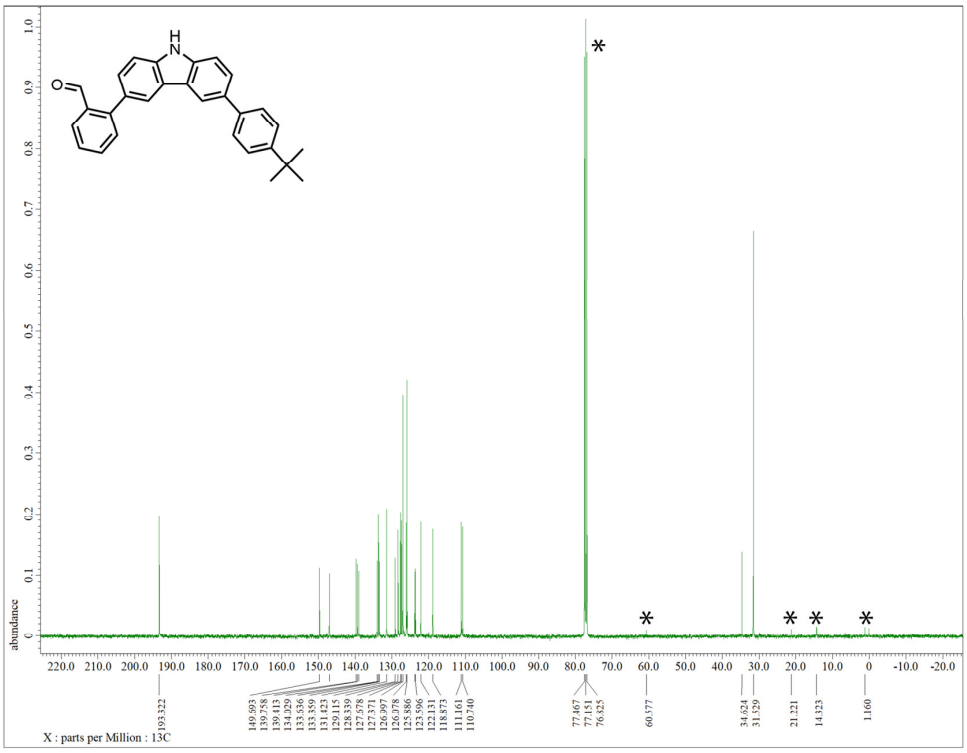


Fig. S16. ^{13}C NMR spectrum of 2-tBuPh in $CDCl_3$ (* solvent peaks).

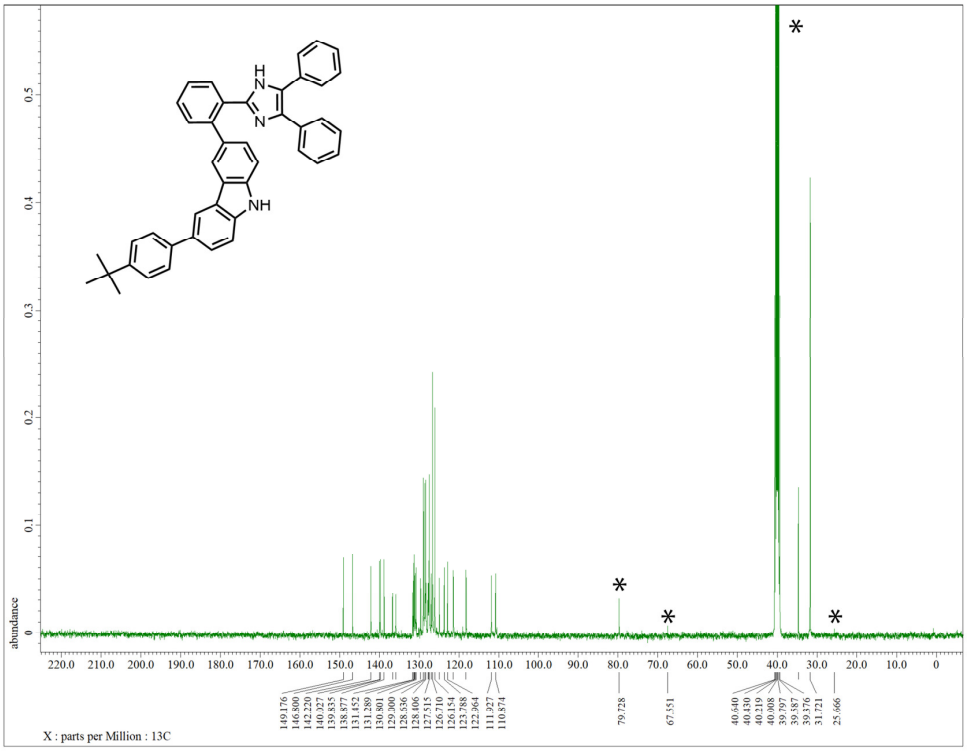


Fig. S17. ^{13}C NMR spectrum of 3-tBuPh in DMSO-d_6 (* solvent peaks).

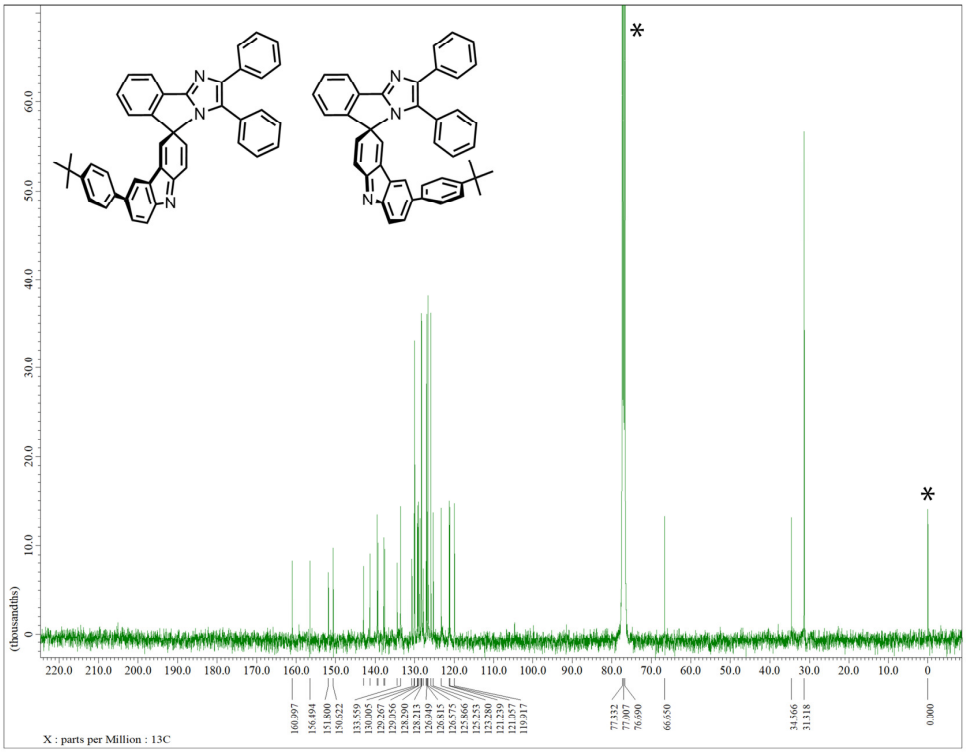


Fig. S18 ^{13}C NMR spectrum of ClC-tBuPh in $CDCl_3$ (* solvent peaks).

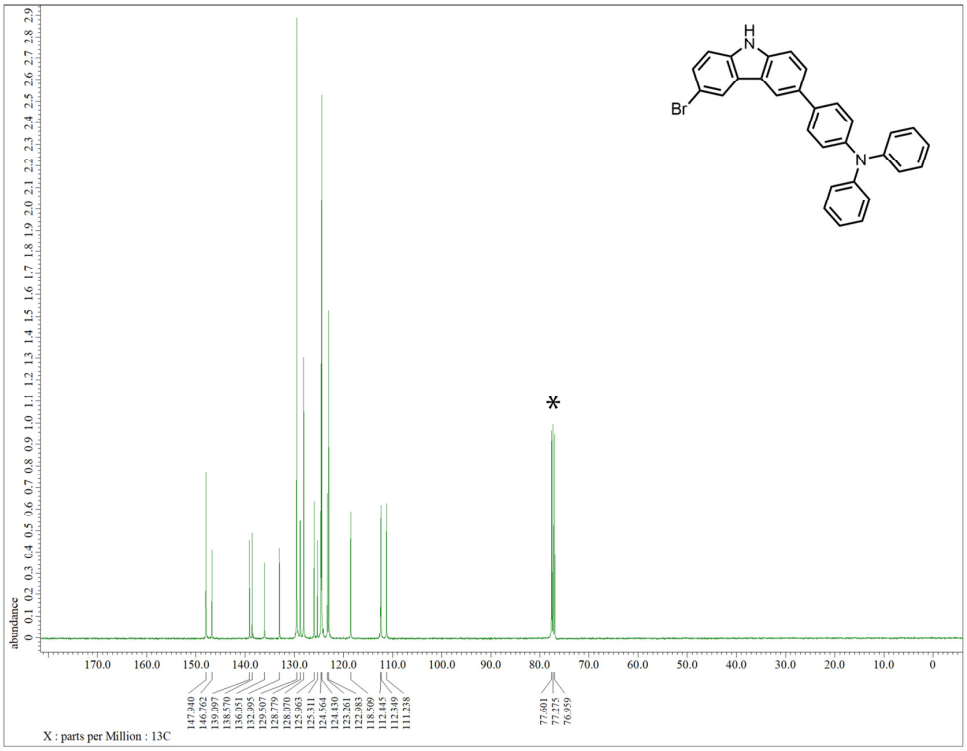


Fig. S19. ^{13}C NMR spectrum of 1-TPA in $CDCl_3$ (* solvent peaks).

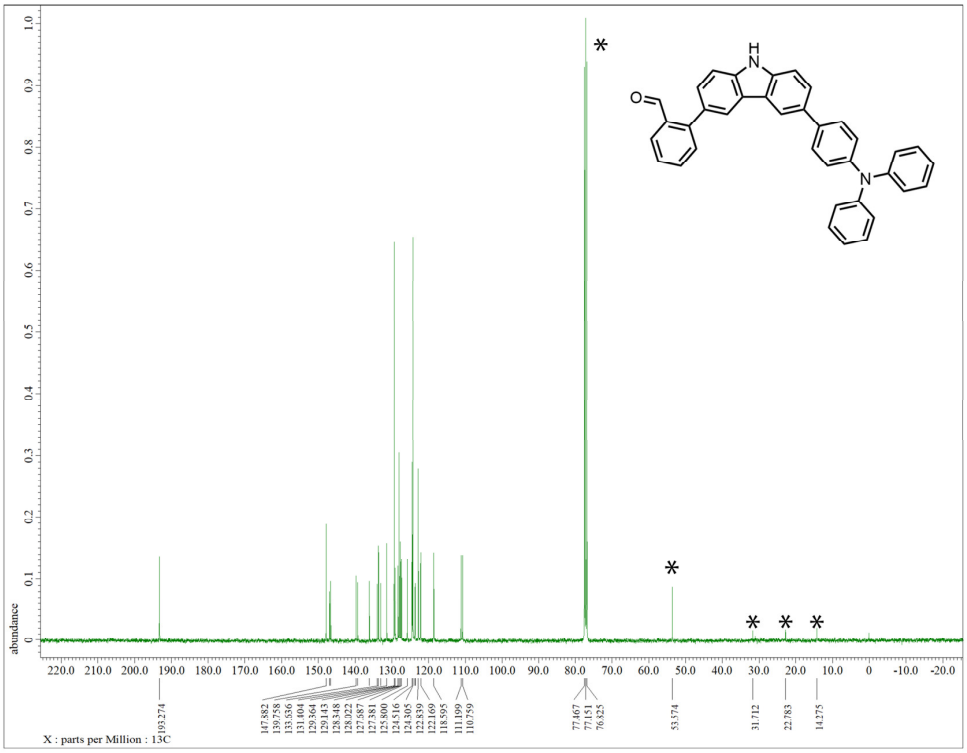


Fig. S20 ^{13}C NMR spectrum of 2-TPA in $CDCl_3$ (* solvent peaks).

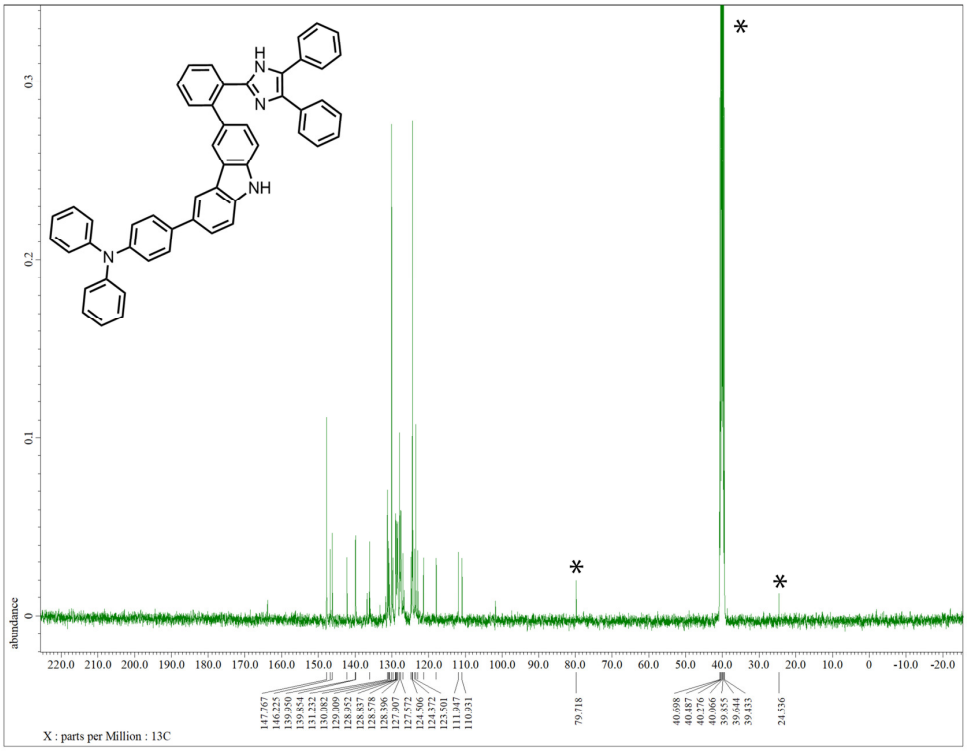


Fig. S21. ^{13}C NMR spectrum of 3-TPA in DMSO-d_6 (* solvent peaks).

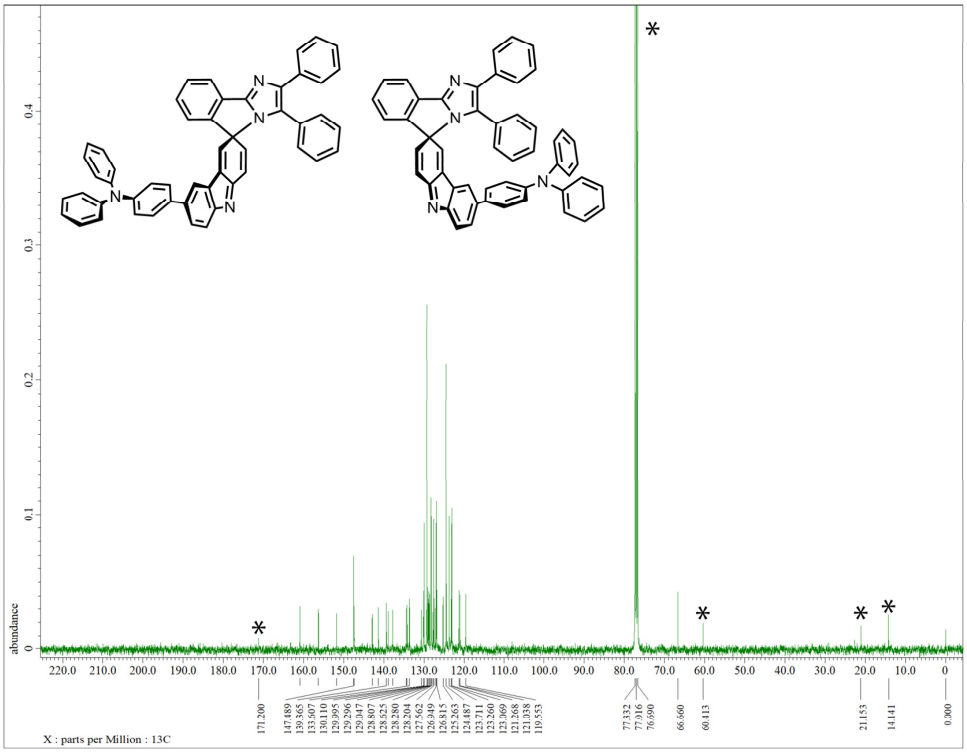


Fig. S22 ^{13}C NMR spectrum of ClC-TPA in $CDCl_3$ (* solvent peaks).

5. HR-ESI-TOF-MS Spectra

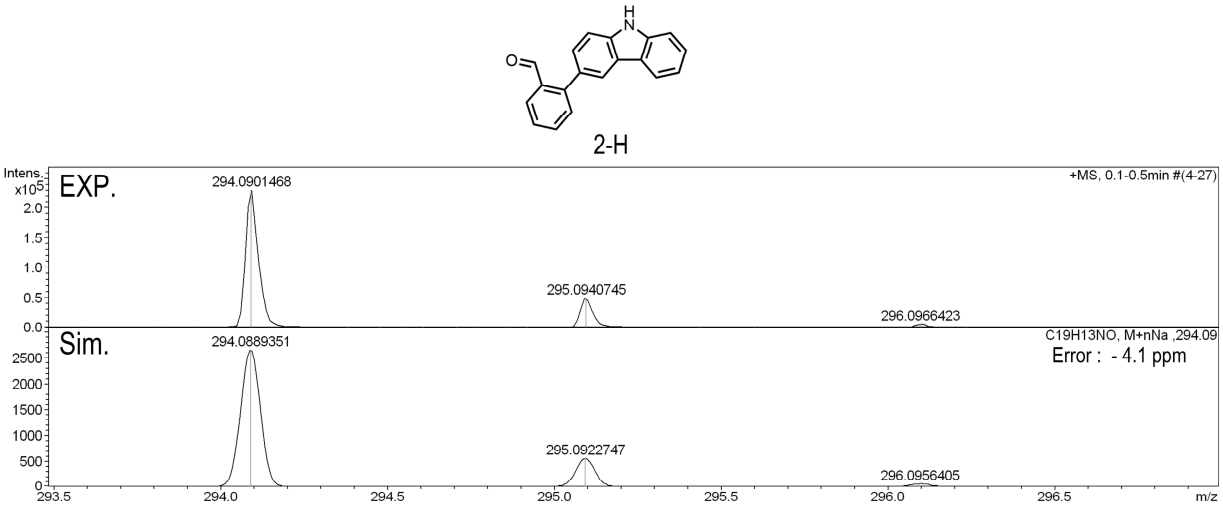


Fig. S23. HR-ESI-TOF-MS of 2-H.

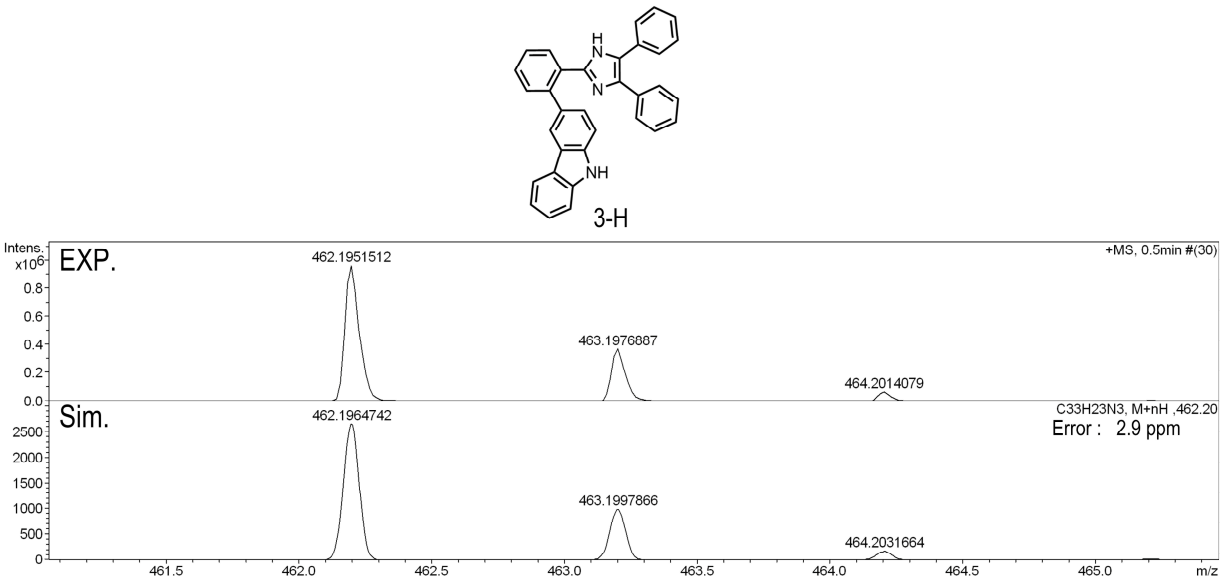


Fig. S24. HR-ESI-TOF-MS of 3-H.

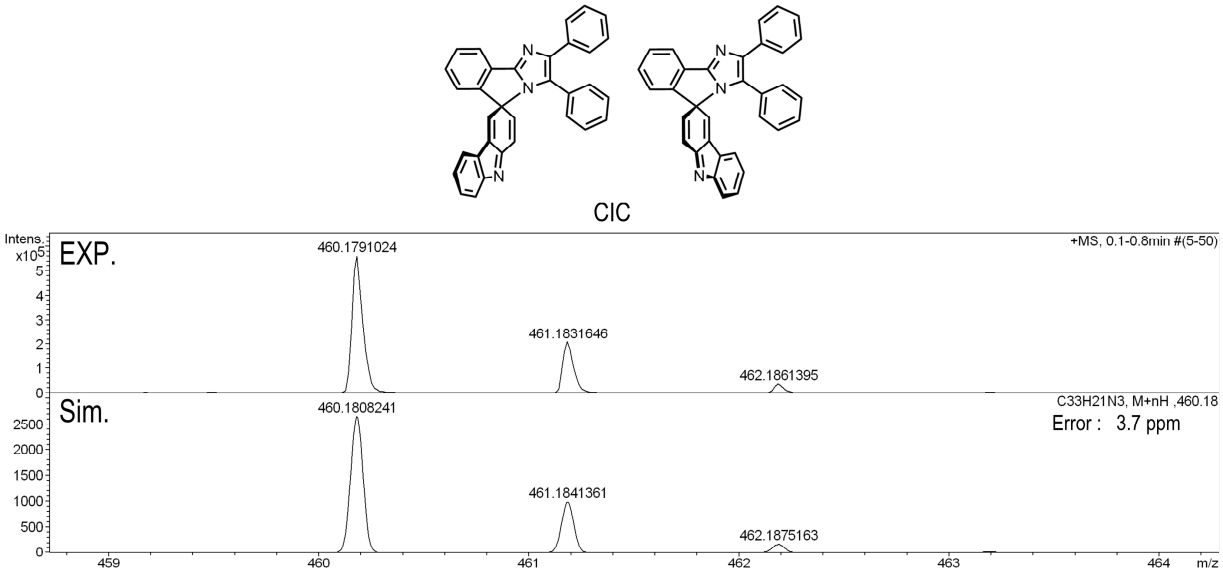


Fig. S25. HR-ESI-TOF-MS of CIC.

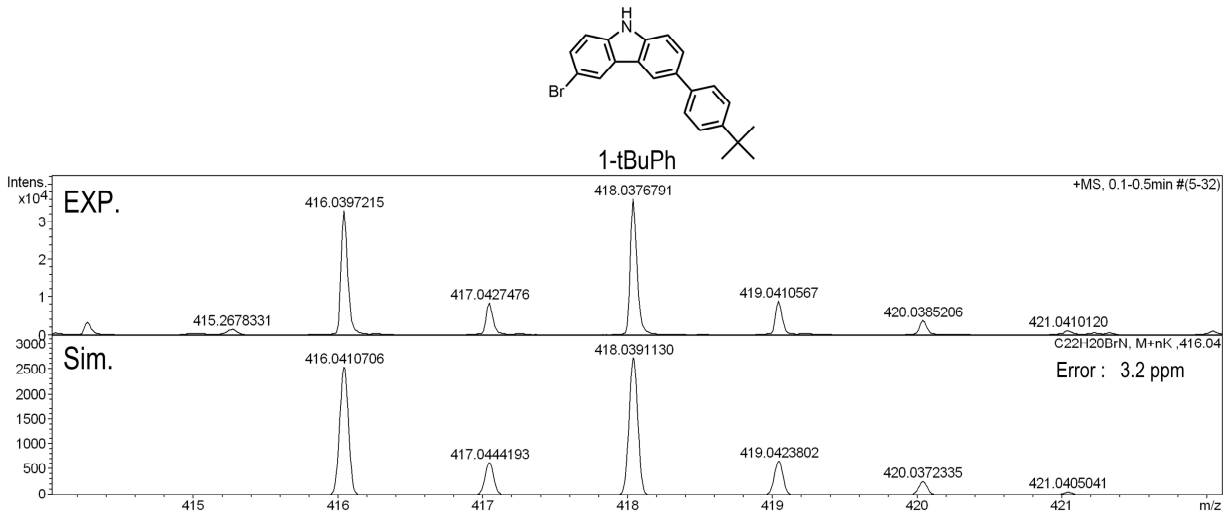


Fig. S26. HR-ESI-TOF-MS of 1-tBuPh.

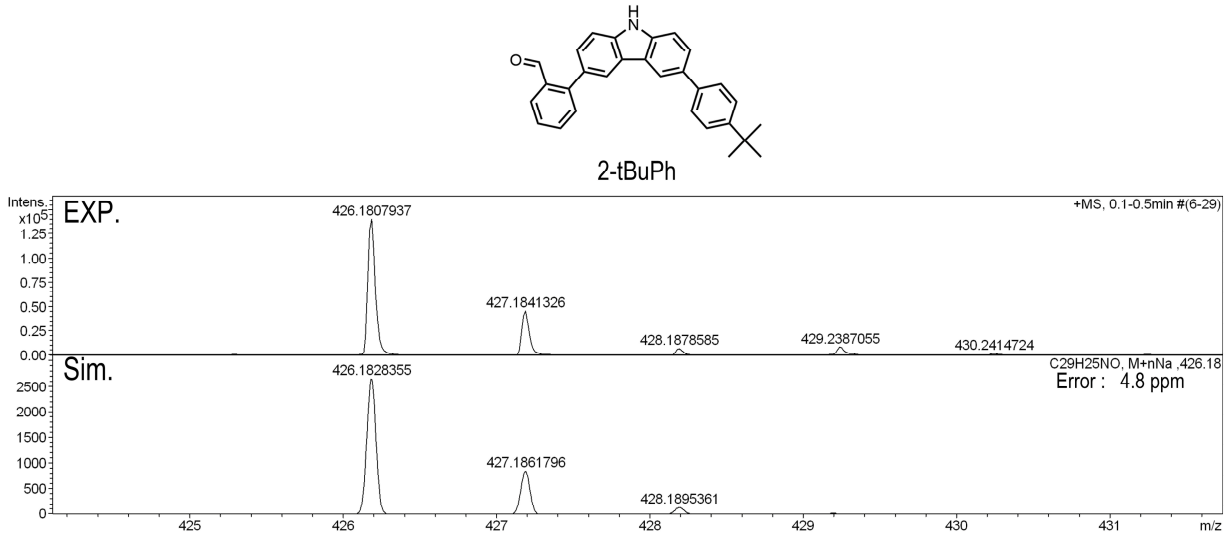


Fig. S27. HR-ESI-TOF-MS of 2-tBuPh.

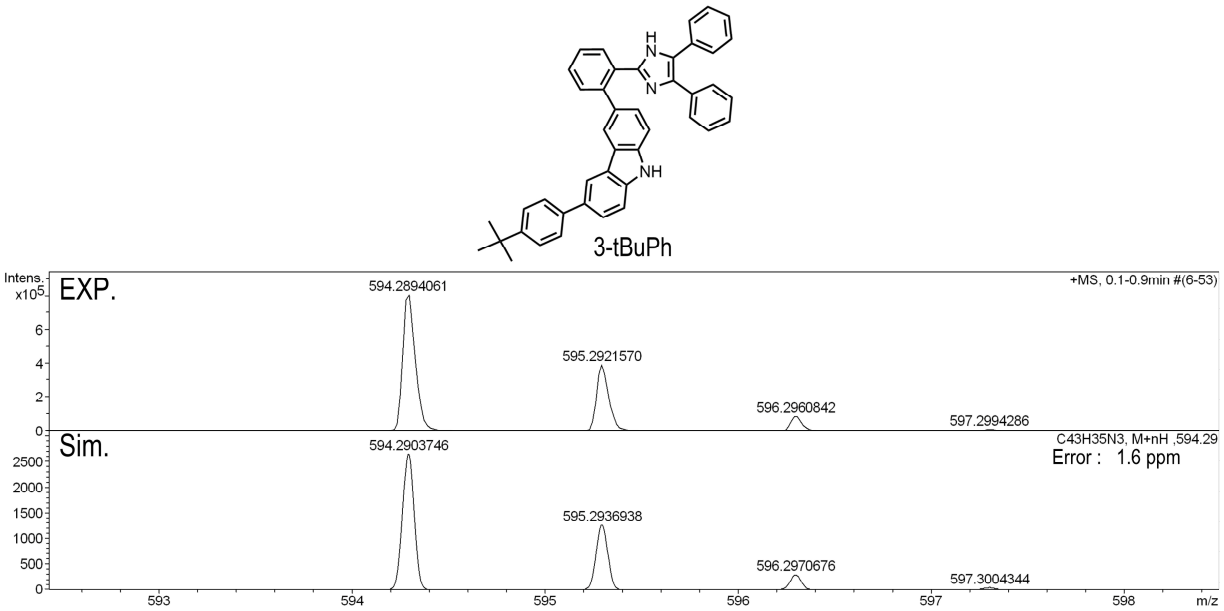


Fig. S28. HR-ESI-TOF-MS of 3-tBuPh.

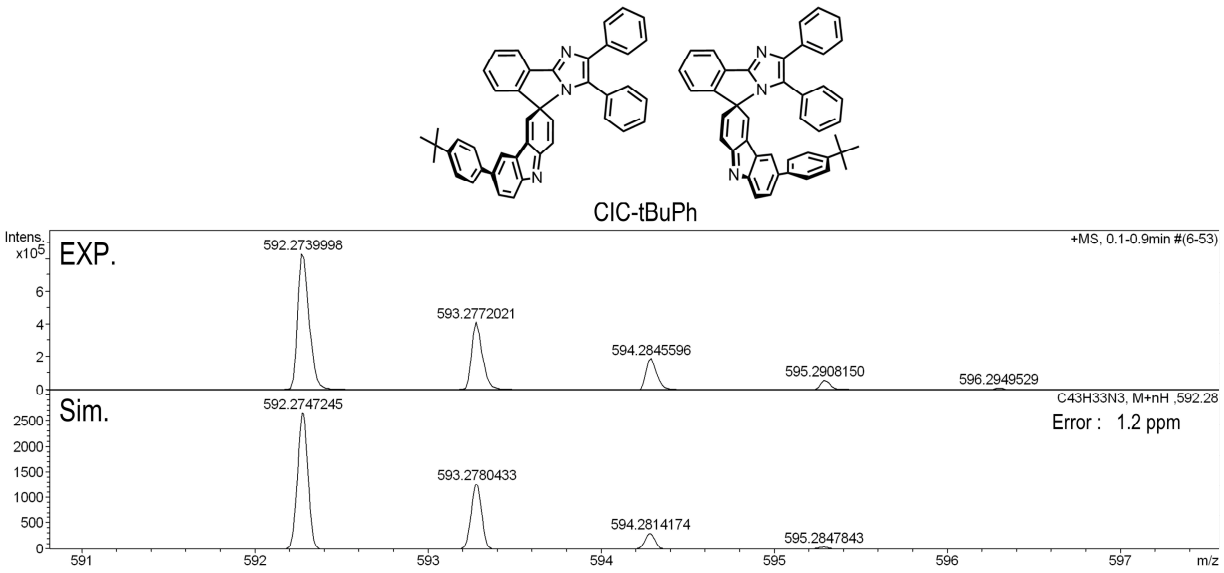


Fig. S29. HR-ESI-TOF-MS of ClC-tBuPh.

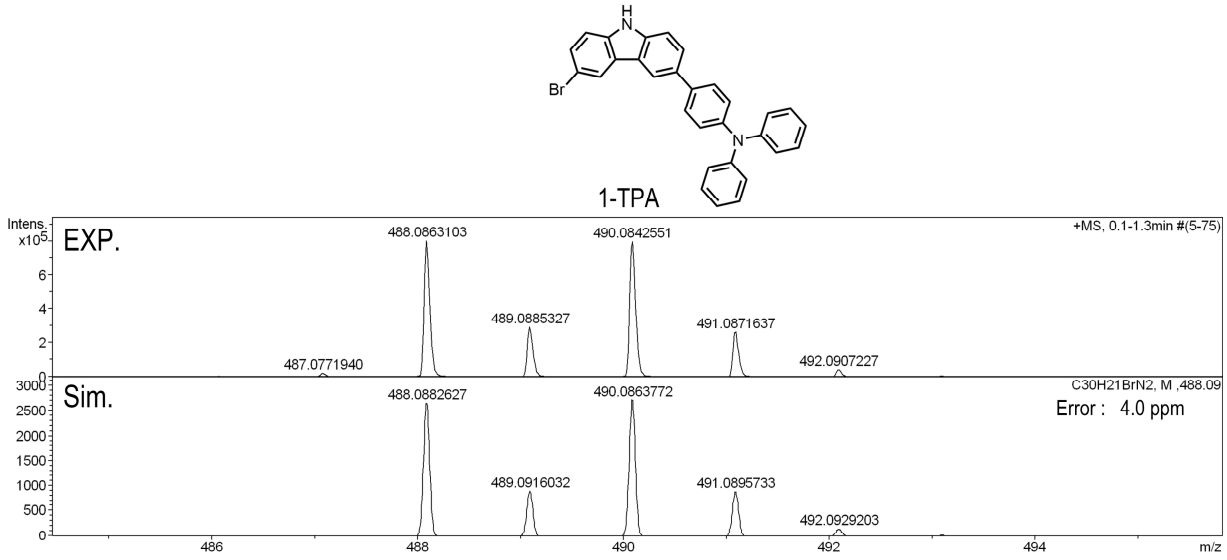


Fig. S30. HR-ESI-TOF-MS of 1-TPA.

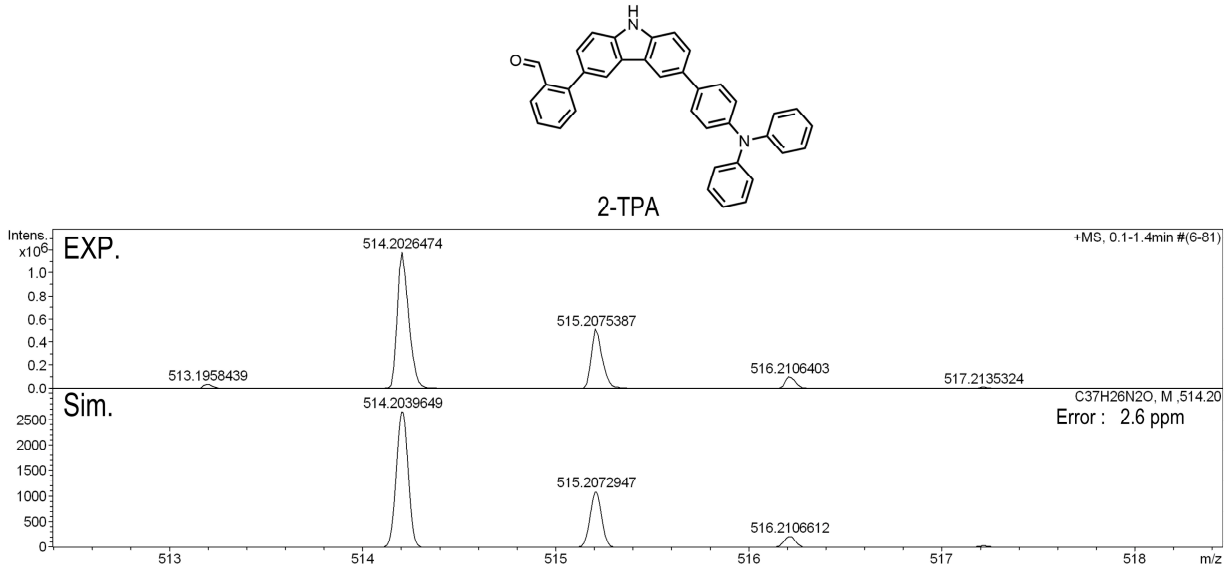


Fig. S31. HR-ESI-TOF-MS of 2-TPA.

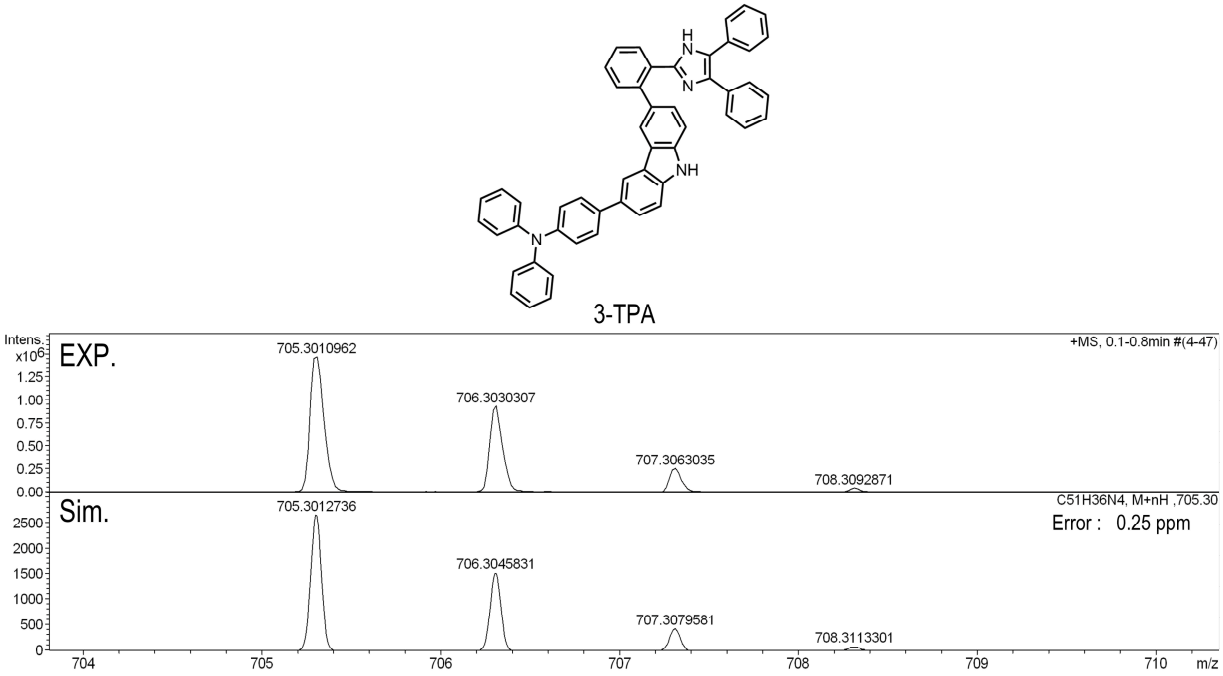


Fig. S32. HR-ESI-TOF-MS of 3-TPA.

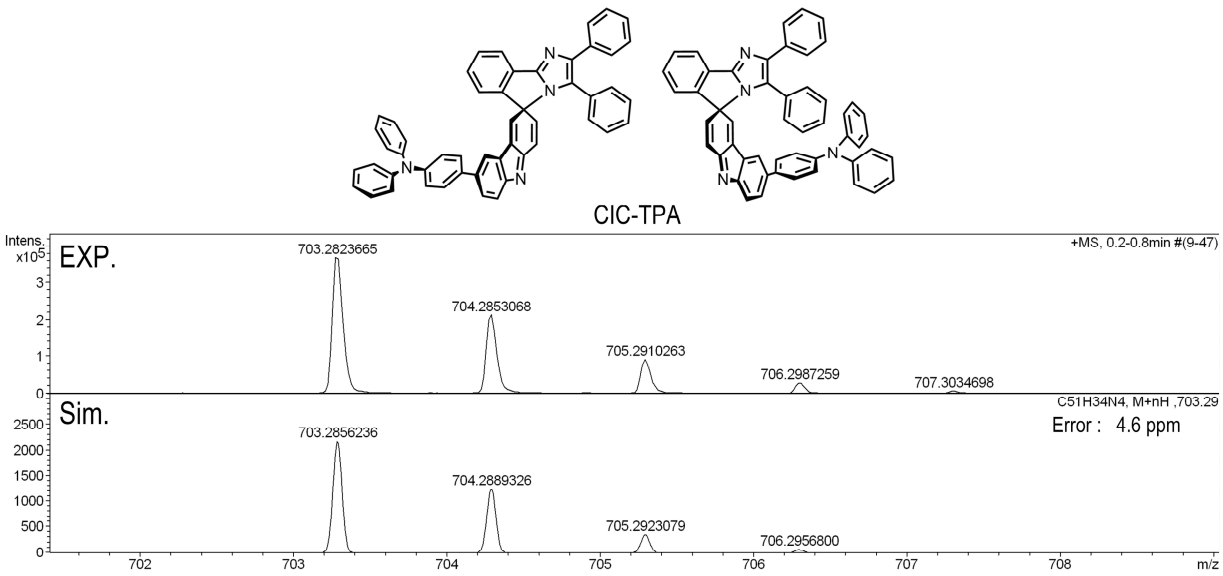


Fig. S33. HR-ESI-TOF-MS of CIC-TPA.

6. HPLC Chromatograms

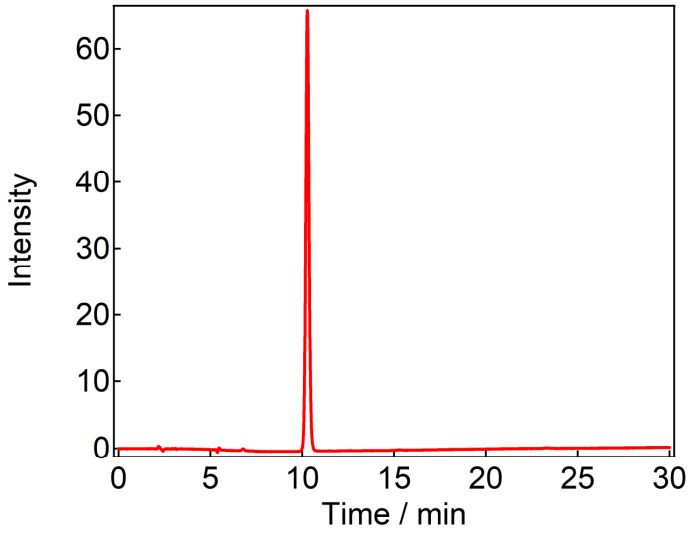


Fig. S34. HPLC chromatogram of CIC; 98% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18GP II, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a photodiode array (PDA) detector; the mobile phase was CH_3CN/H_2O = 2/1 with a flow rate of 1.0 mL/min (detection wavelength; 365 nm). It is noted that peaks below 5 min are due to the injection solvent.

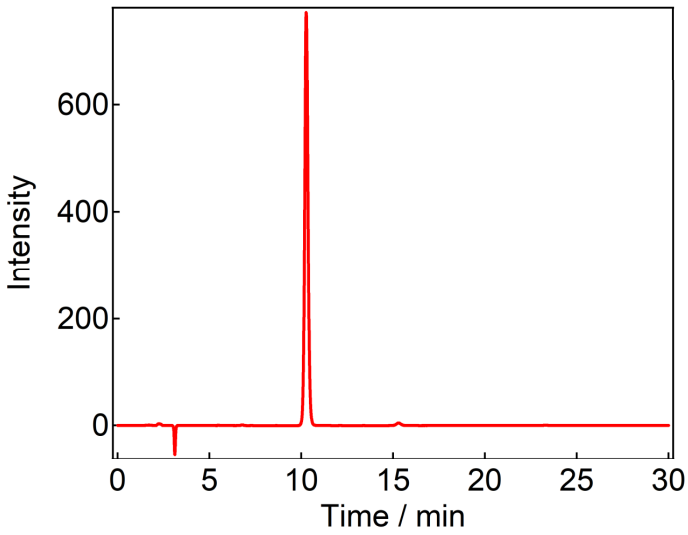


Fig. S35. HPLC chromatogram of CIC; 98% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18GP II, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a PDA detector; the mobile phase was CH_3CN/H_2O = 2/1 with a flow rate of 1.0 mL/min (detection wavelength; 254 nm). It is noted that peaks below 5 min are due to the injection solvent.

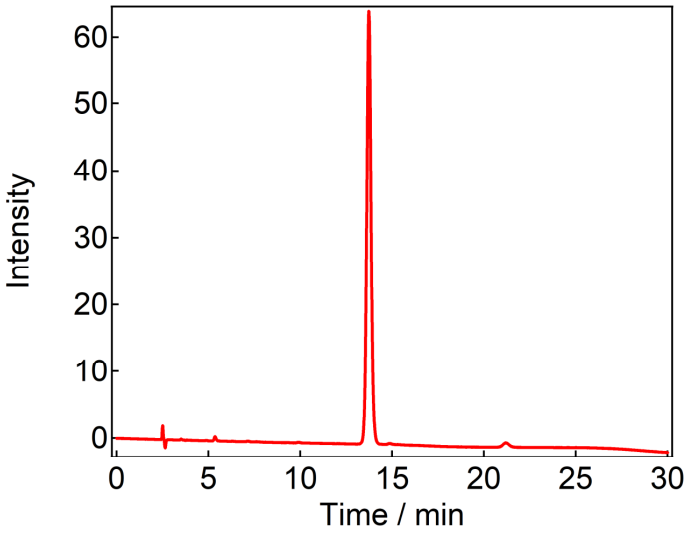


Fig. S36. HPLC chromatogram of CIC-tBuPh; 98% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18GP II, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a PDA detector; the mobile phase was CH_3CN/H_2O = 6/1 with a flow rate of 1.0 mL/min (detection wavelength; 365 nm). It is noted that peaks below 5 min are due to the injection solvent.

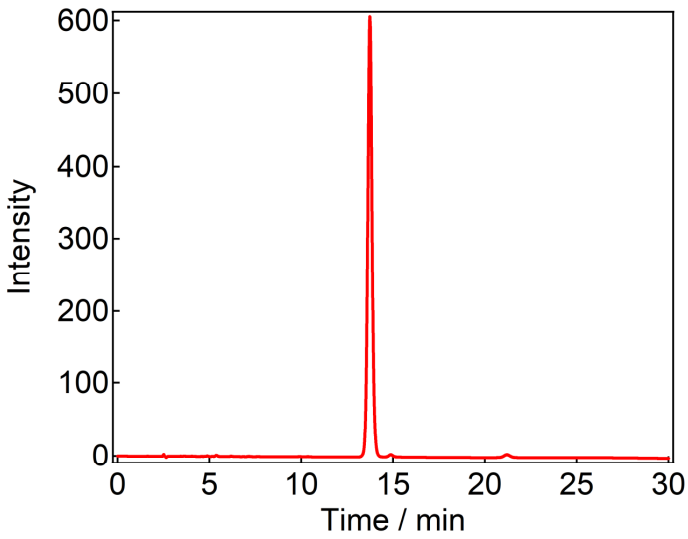


Fig. S37. HPLC chromatogram of ClC-tBuPh; 98% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18GP II, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a PDA detector; the mobile phase was CH_3CN/H_2O = 6/1 with a flow rate of 1.0 mL/min (detection wavelength; 254 nm). It is noted that peaks below 5 min are due to the injection solvent.

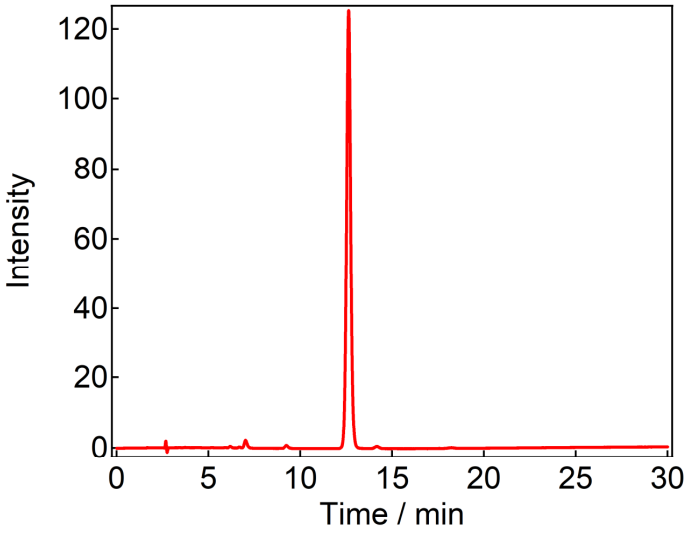


Fig. S38. HPLC chromatogram of CIC-TPA; 98% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18GP II, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a PDA detector; the mobile phase was CH_3CN/H_2O = 9/1 with a flow rate of 1.0 mL/min (detection wavelength; 365 nm). It is noted that peaks below 5 min are due to the injection solvent.

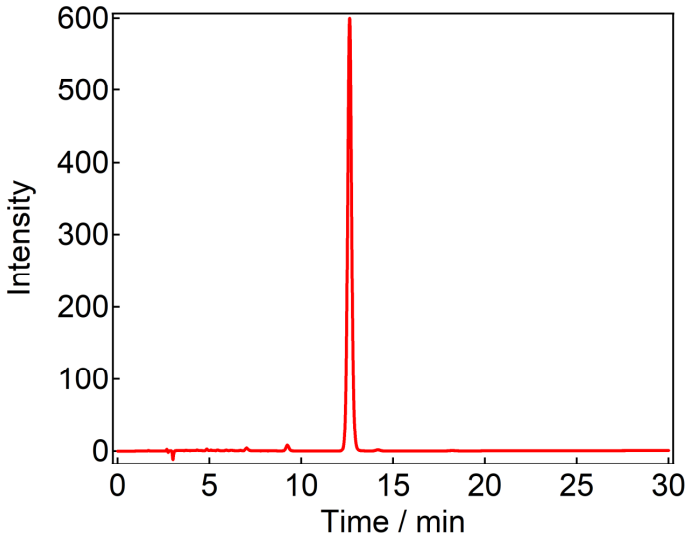


Fig. S39. HPLC chromatogram of CIC-TPA; 98% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18GP II, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a PDA detector; the mobile phase was CH_3CN/H_2O = 9/1 with a flow rate of 1.0 mL/min (detection wavelength; 254 nm). It is noted that peaks below 5 min are due to the injection solvent.

7. X-ray crystallographic Analyses

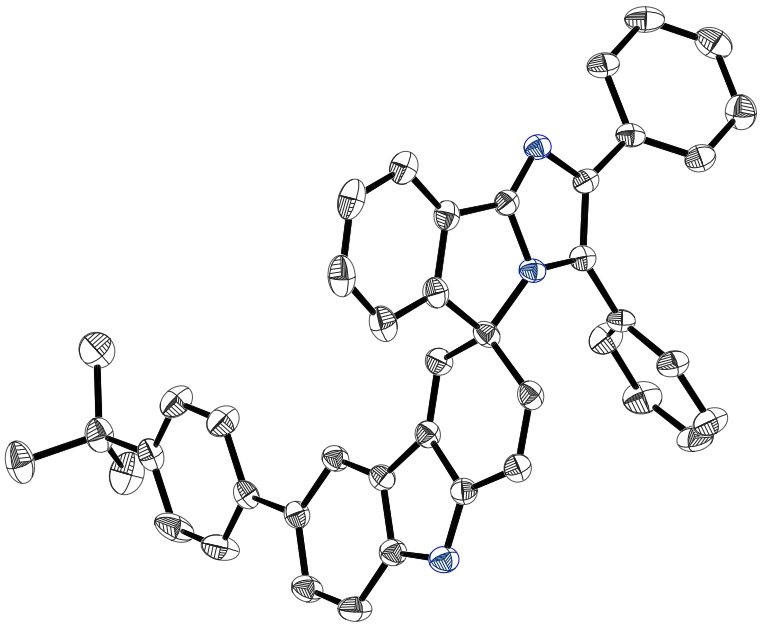


Fig. S40. ORTEP (Oak Ridge Thermal-Ellipsoid Plot) of ClC-tBuPh with 50% thermal probabilities. Solvent molecules are omitted for clarity.

Table S1. Crystallographic data and structure refinement details of ClC-tBuPh.

	ClC-tBuPh
CCDC No.	2150990
formula	$C_{44}H_{37}N_3O$
fw	623.76
T (K)	113(2)
λ (Å)	0.71073
cryst syst	triclinic
space group	P-1
a (Å)	9.8537(6)
b (Å)	11.6155(3)
c (Å)	15.5263(8)
α (deg)	89.445(4)
β (deg)	77.255(5)
γ (deg)	70.765(4)
V (Å^3)	1632.70(15)
Z	2
D_{calc} (g·cm^{-3})	1.269
μ (mm^{-1})	0.076
F(000)	660.0
cryst size (mm^3)	0.15 × 0.15 × 0.05
2θ range (deg)	5.392–62.81
reflns collected	26911
indep reflns/R_{int}	8933/0.0590
params	441
GOF on F^2	1.038
R_1, wR_2 [$I>2\sigma(I)$]	0.0607, 0.1498
R_1, wR_2 (all data)	0.0954, 0.1683

8. Steady-State Absorption Spectra

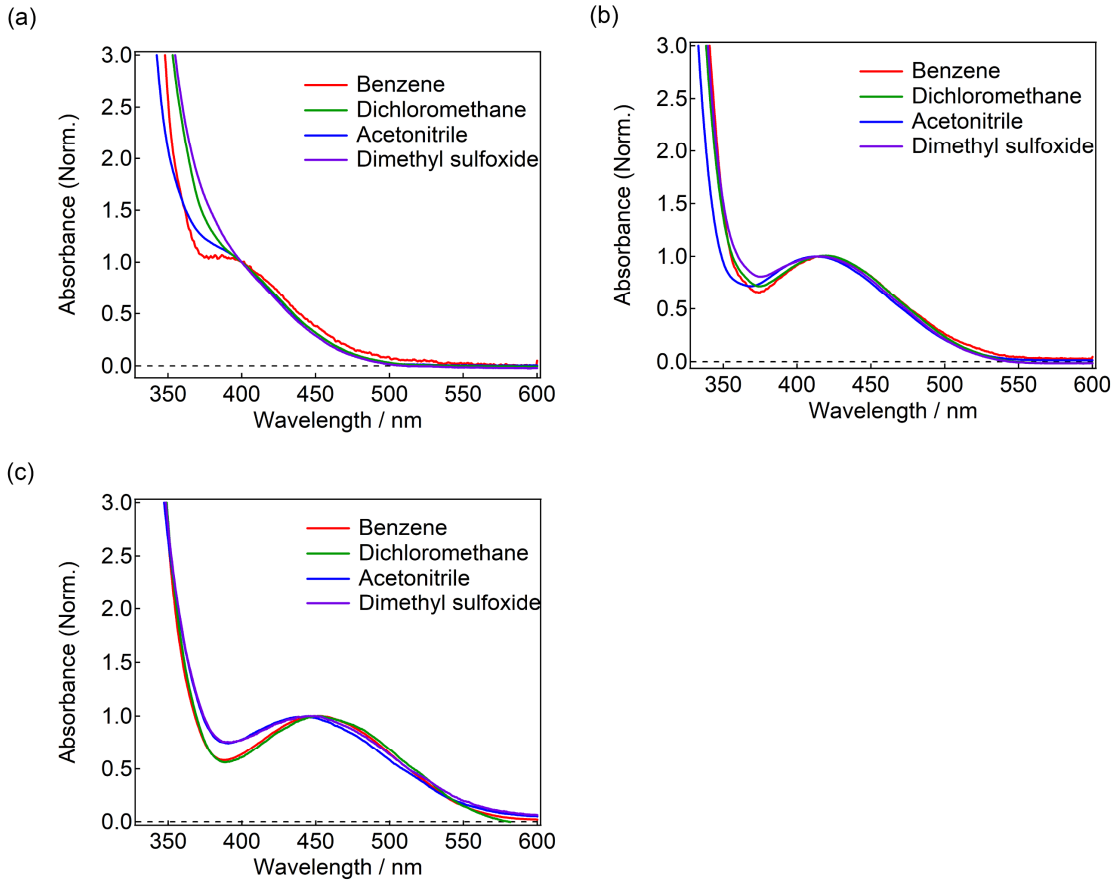


Fig. S41. Normalized steady-state absorption spectra of (a) CIC, (b) CIC-tBuPh and (c) CIC-TPA in different solvents.

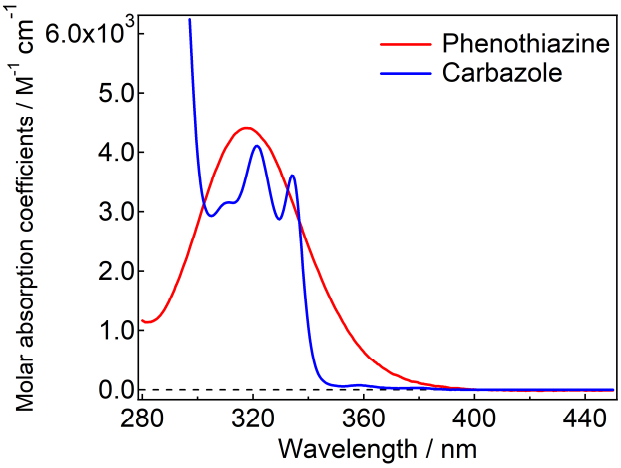


Fig. S42. Steady-state absorption spectra of phenothiazine and carbazole in benzene.

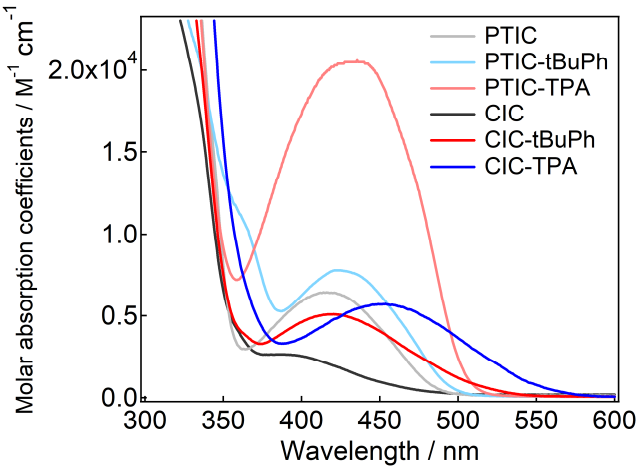


Fig. S43. Steady-state absorption spectra of PTIC and CIC derivatives in benzene.

9. Nanosecond to Microsecond Transient Absorption Measurements

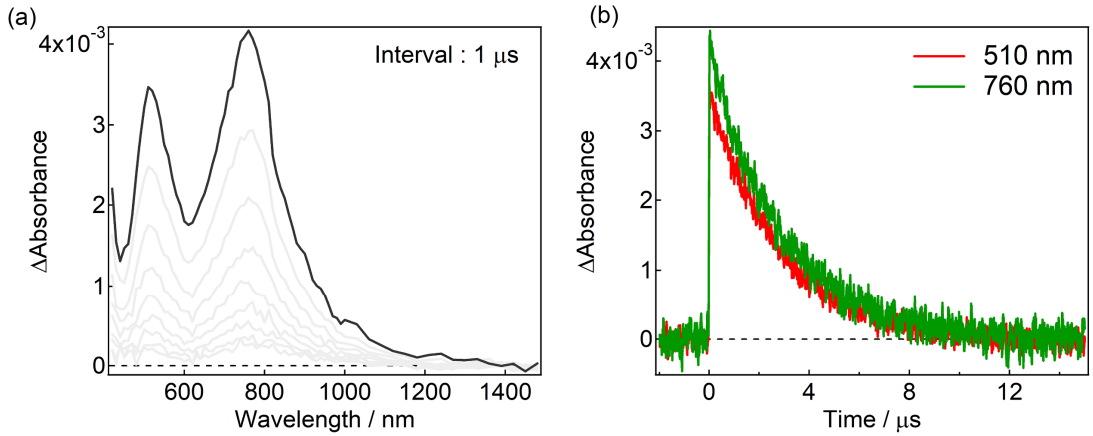


Fig. S44. Nanosecond to microsecond transient absorption spectra and dynamics of CIC in benzene (7.6×10^{-4} M) excited with a 355 nm picosecond laser pulse (2 μJ pulse^{-1}) under argon atmosphere at room temperature.

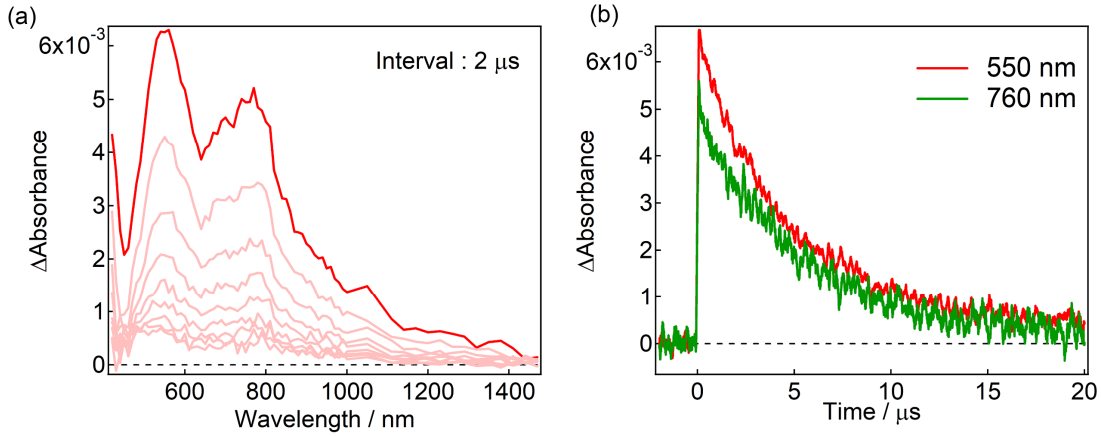


Fig. S45. Nanosecond to microsecond transient absorption spectra and dynamics of CIC-tBuPh in benzene (5.9×10^{-4} M) excited with a 355 nm picosecond laser pulse (5 μJ pulse^{-1}) under argon atmosphere at room temperature.

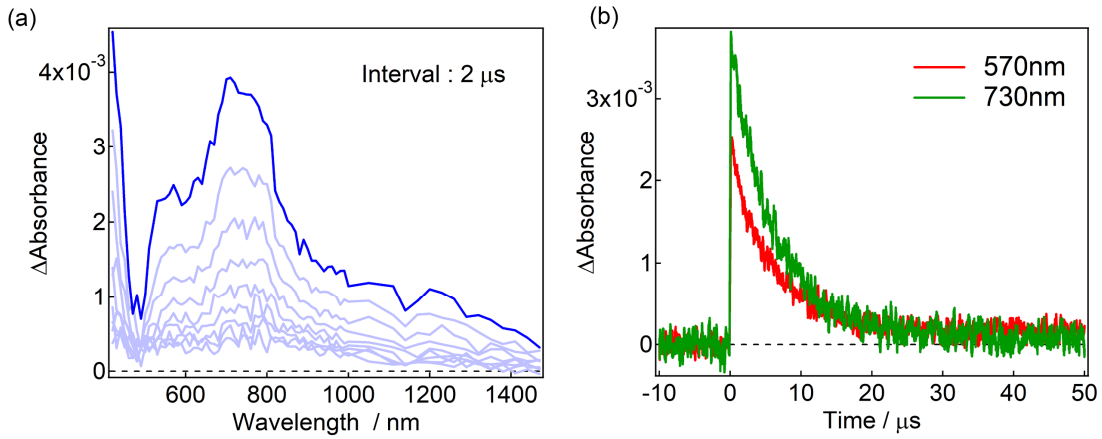


Fig. S46. Nanosecond to microsecond transient absorption spectra and dynamics of CIC-TPA in benzene (5.1×10^{-4} M) excited with a 355 nm picosecond laser pulse (5 μJ $pulse^{-1}$) under argon atmosphere at room temperature.

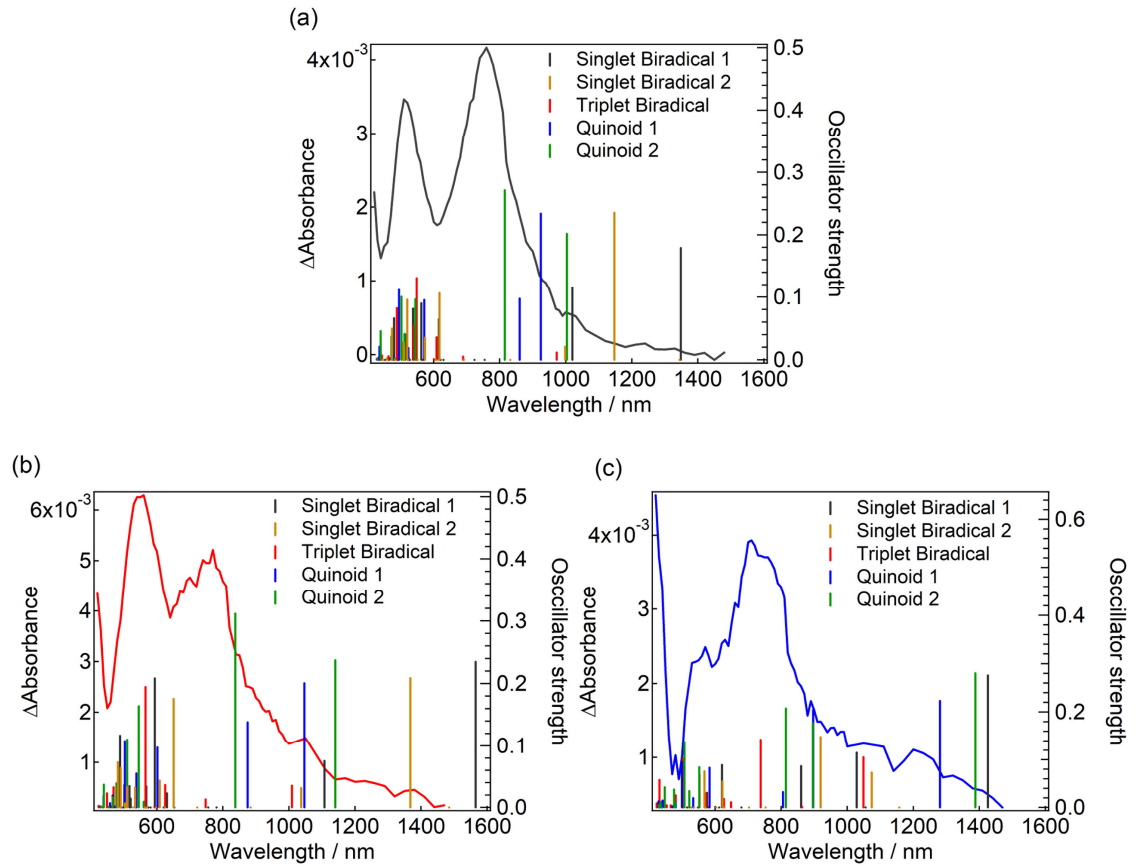


Fig. S47. Nanosecond to microsecond transient absorption spectra of (a) CIC, (b) CIC-tBuPh and (c) CIC-TPA in benzene excited with a 355 nm picosecond laser pulse under argon atmosphere at room temperature. Vertical lines indicate the theoretical spectra of singlet and triplet biradical (U)MPW1PW91/6-31+G(d,p)//UMPW1PW91/6-31G(d) level of theory. The simulation suggests that the triplet biradical of the ring-opening form does not have absorption in the near infrared light region (except CIC-TPA), suggesting that the contribution of the singlet biradical and the quinoidal forms are larger than the triplet biradical form. It is noted that the absorption band is different in different rotational isomers of the carbazole moiety (1 and 2 shown in Fig. S48).

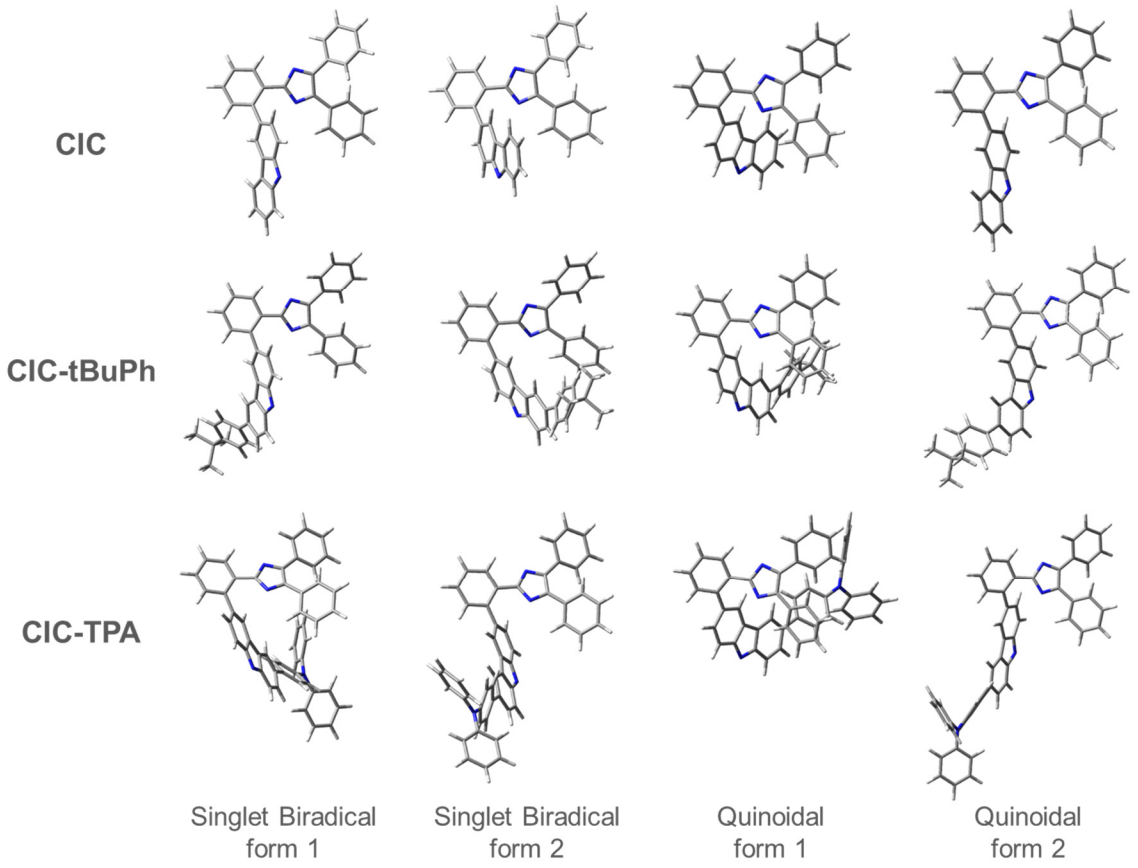


Fig. S48. Optimized structures of the rotational isomers (1 and 2) of the singlet biradical and quinoidal forms of CIC, CIC-tBuPh, and CIC-TPA at (U)MPW1PW91/6-31+G(d,p)//UMPW1PW91/6-31G(d) level of theory.

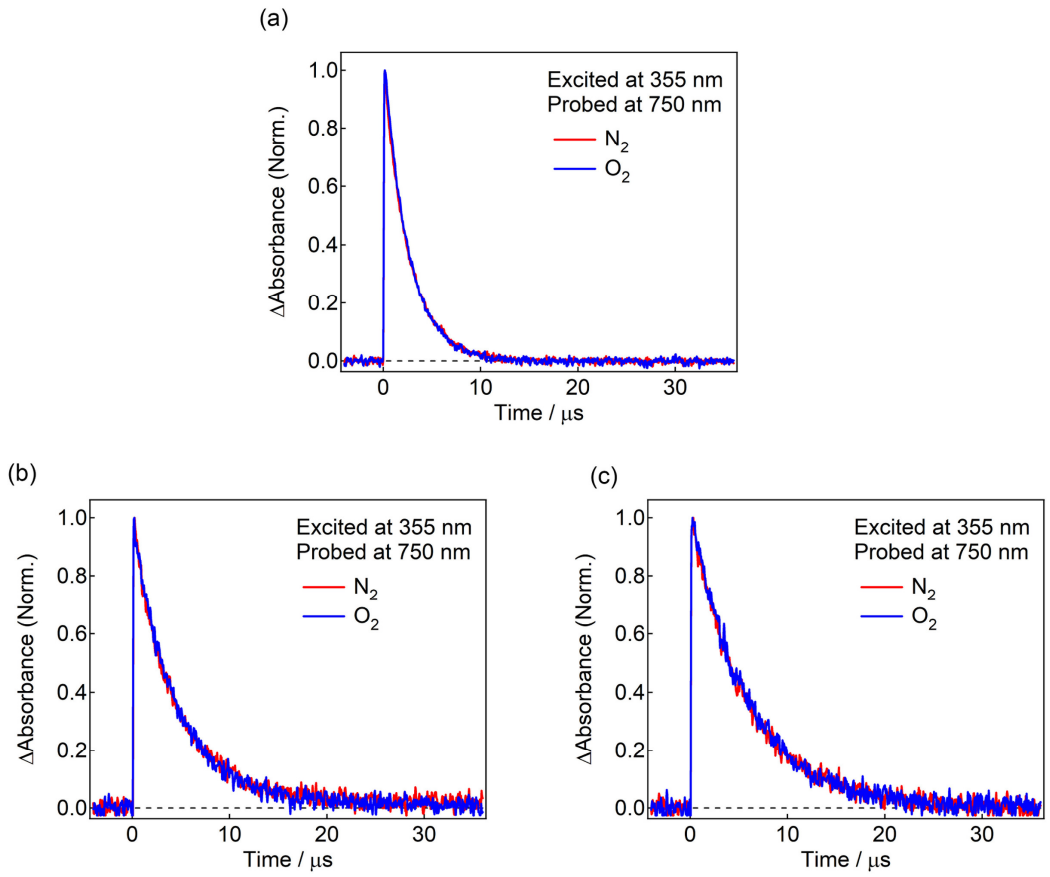


Fig. S49. Nanosecond to microsecond transient absorption dynamics of (a) CIC, (b) CIC-tBuPh and (c) CIC-TPA in benzene excited with a 355 nm picosecond laser pulse under nitrogen or oxygen atmosphere at room temperature.

10. Femtosecond to Nanosecond Transient Absorption Measurements

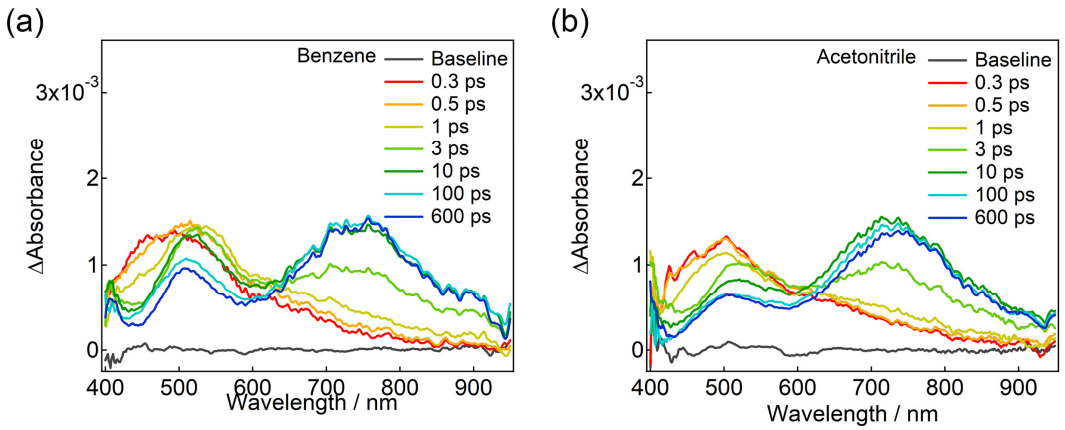


Fig. S50. Time evolutions of the femtosecond to nanosecond transient absorption spectra of CIC in (a) benzene (1.7×10^{-3} M) and (b) acetonitrile (2.2×10^{-3} M) excited with a 390-nm femtosecond laser pulse (36 nJ pulse^{-1}).

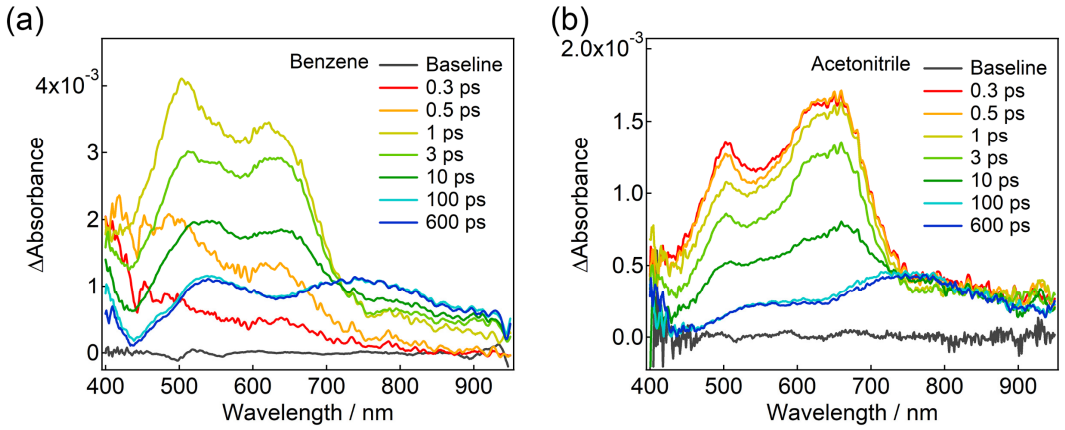


Fig. S51. Time evolutions of the femtosecond to nanosecond transient absorption spectra of CIC-tBuPh in (a) benzene (8.7×10^{-4} M) and (b) acetonitrile (1.1×10^{-3} M) excited with a 390-nm femtosecond laser pulse (36 nJ pulse^{-1}).

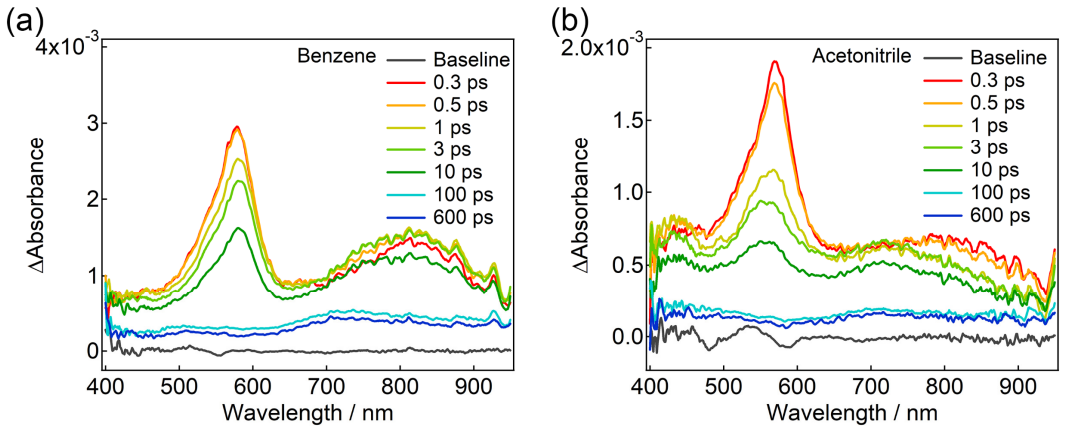


Fig. S52. Time evolutions of femtosecond to nanosecond transient absorption spectra of CIC-TPA in (a) benzene (8.4×10^{-4} M) and (b) acetonitrile (5.3×10^{-4} M) excited with a 390-nm femtosecond laser pulse (36 nJ pulse^{-1}).

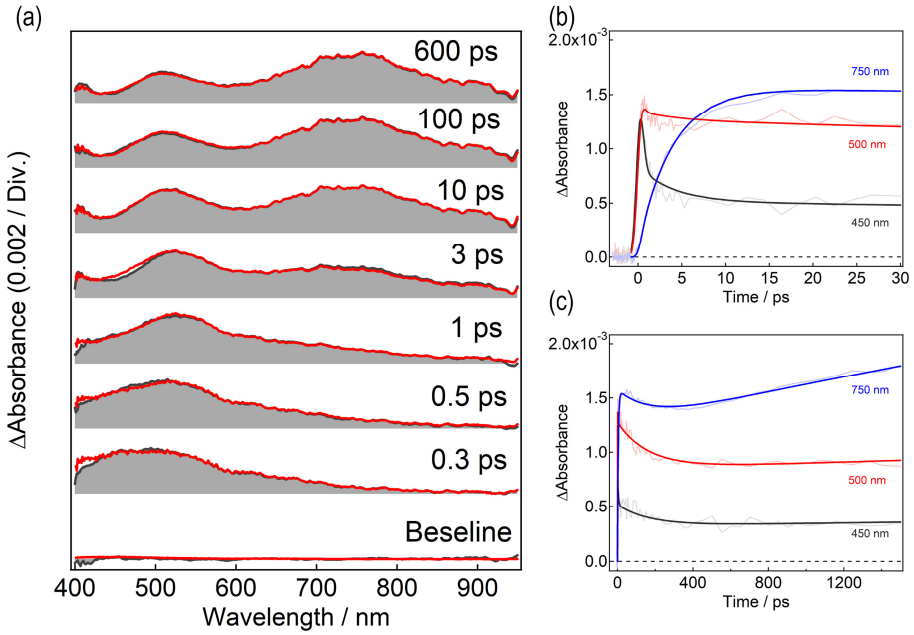


Fig. S53. Time evolutions of femtosecond to nanosecond transient absorption spectra of CIC in benzene (1.7×10^{-3} M) excited with a 390-nm femtosecond laser pulse (36 nJ pulse^{-1}). Thick red, blue and black lines show the fitting lines by SVD global analyses using a five-state sequential kinetic model.

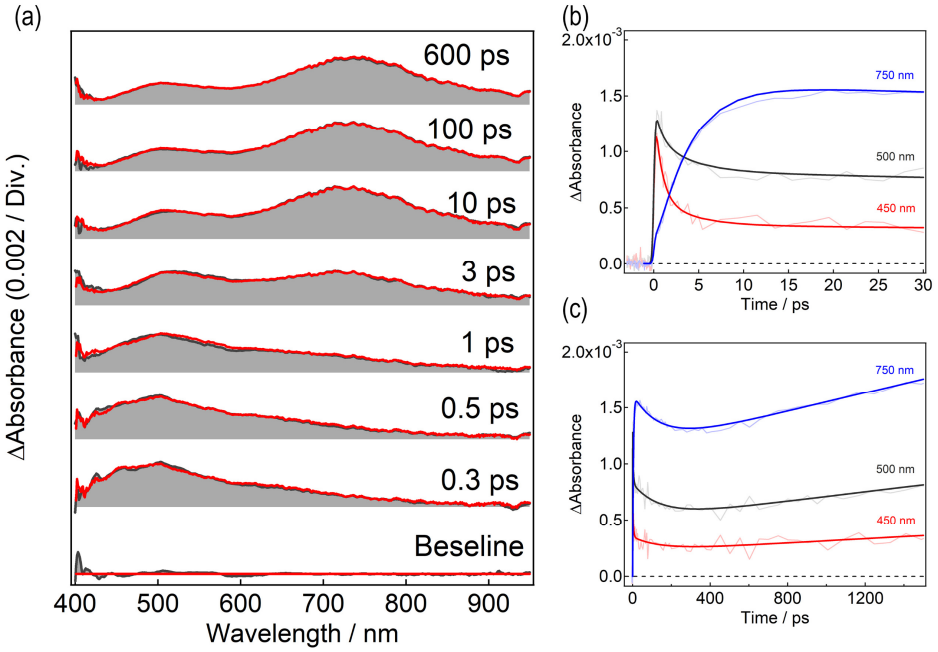


Fig. S54. Time evolutions of femtosecond to nanosecond transient absorption spectra of CIC in acetonitrile (2.2×10^{-3} M) excited with a 390-nm femtosecond laser pulse (36 nJ pulse^{-1}). Thick red, blue and black lines show the fitting lines by SVD global analyses using a five-state sequential kinetic model.

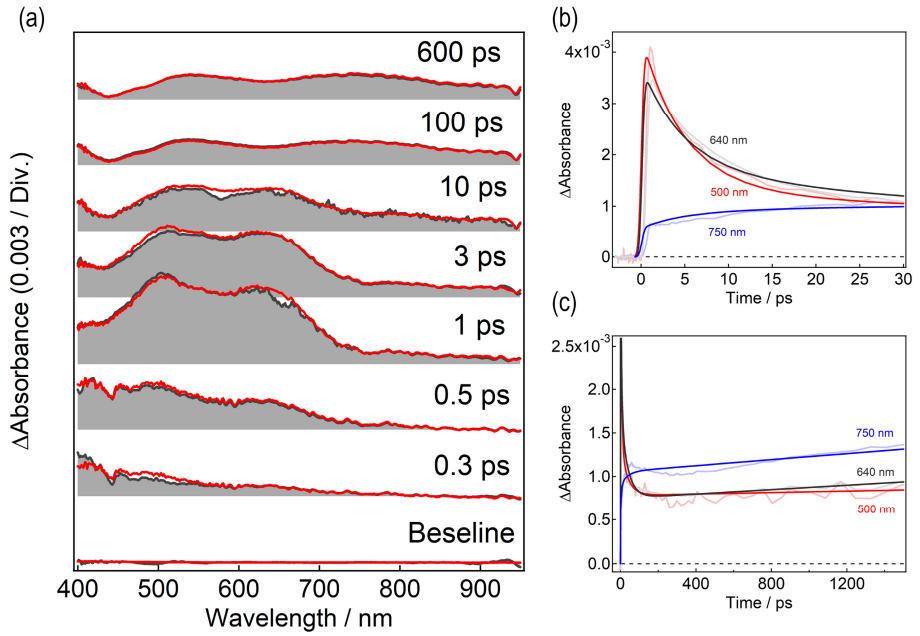


Fig. S55. Time evolutions of femtosecond to nanosecond transient absorption spectra of CIC-tBuPh in benzene (8.7×10^{-4} M) excited with a 390-nm femtosecond laser pulse (36 nJ pulse^{-1}). Thick red, blue and black lines show the fitting lines by SVD global analyses using a five-state sequential kinetic model.

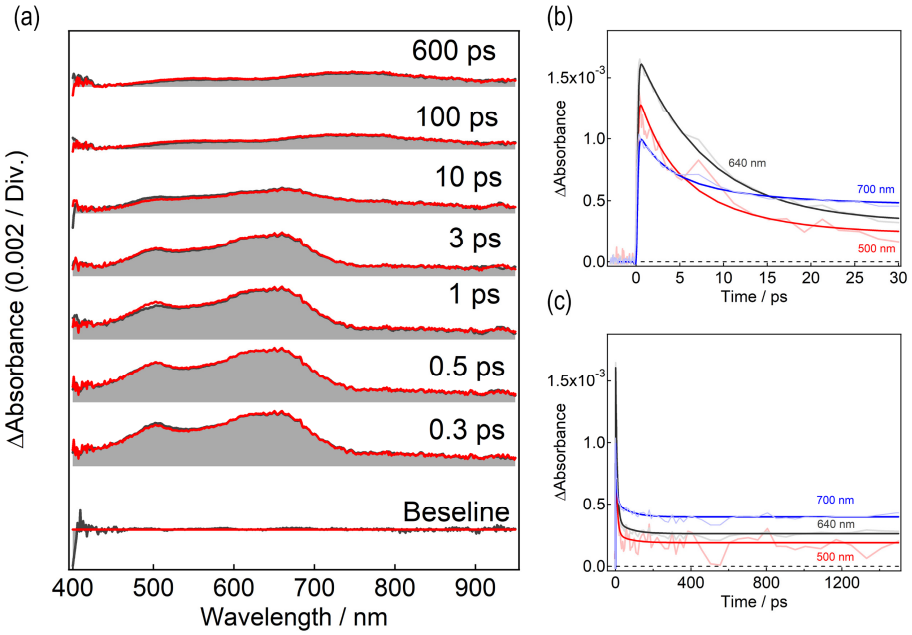


Fig. S56. Time evolutions of femtosecond to nanosecond transient absorption spectra of CIC-tBuPh in acetonitrile (1.1×10^{-3} M) excited with a 390-nm femtosecond laser pulse (36 nJ pulse^{-1}). Thick red, blue and black lines show the fitting lines by SVD global analyses using a five-state sequential kinetic model.

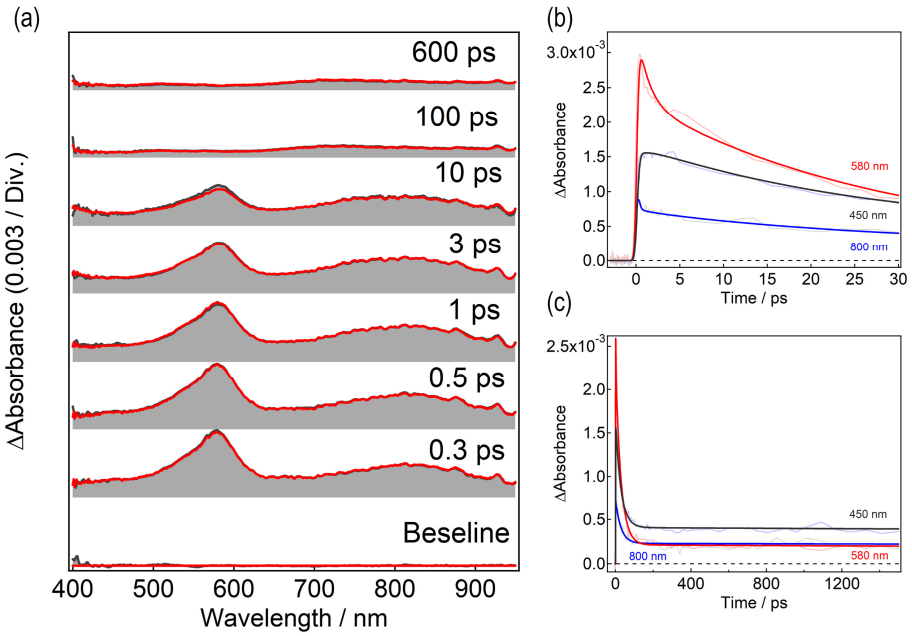


Fig. S57. Time evolutions of femtosecond to nanosecond transient absorption spectra of CIC-TPA in benzene (8.4×10^{-4} M) excited with a 390-nm femtosecond laser pulse (36 nJ pulse^{-1}). Thick red, blue and black lines show the fitting lines by SVD global analyses using a four-state sequential kinetic model.

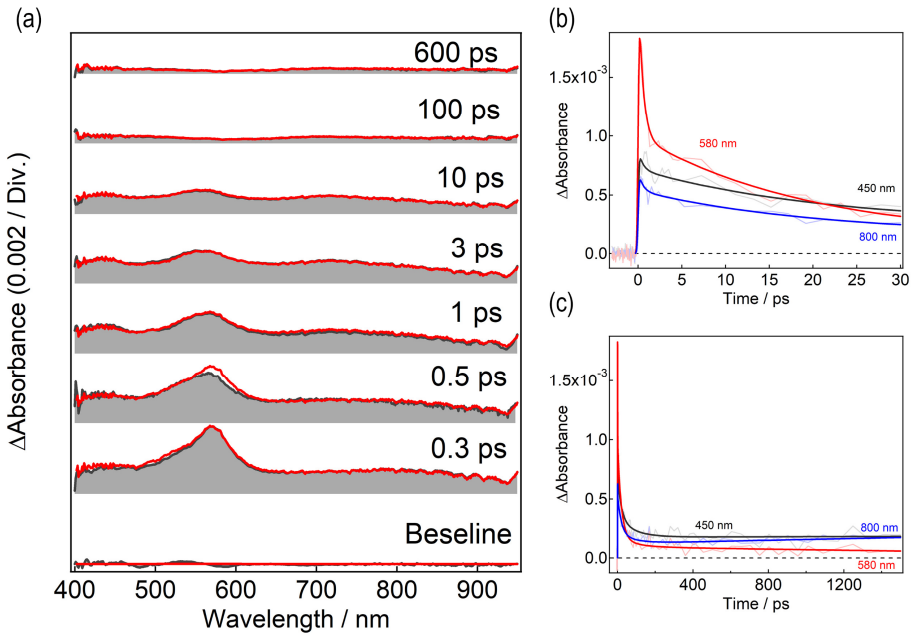


Fig. S58. Time evolutions of femtosecond to nanosecond transient absorption spectra of CIC-TPA in acetonitrile (5.3×10^{-4} M) excited with a 390-nm femtosecond laser pulse (36 nJ pulse^{-1}). Thick red, blue and black lines show the fitting lines by SVD global analyses using a five-state sequential kinetic model.

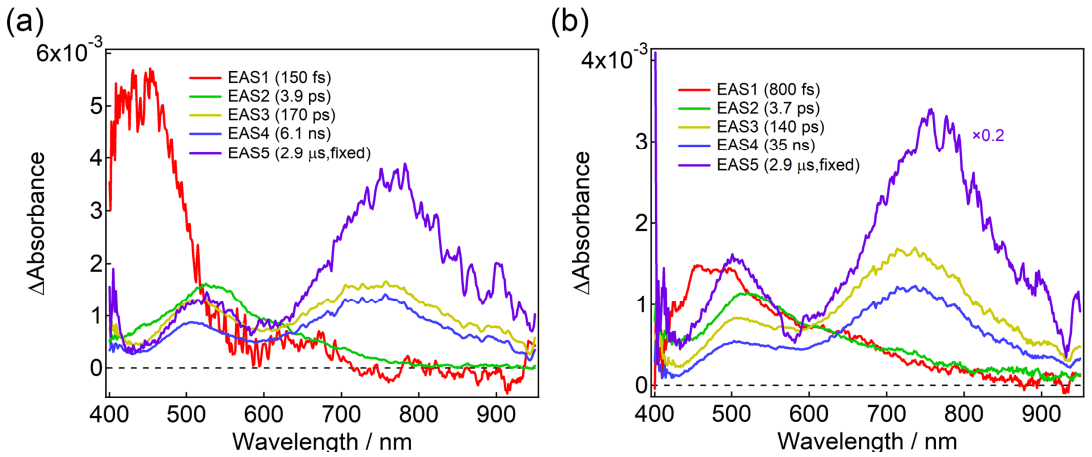


Fig. S59. EAS of the transient absorption spectra of CIC in (a) benzene and (b) acetonitrile excited with a 390-nm femtosecond laser pulse. The first EAS (EAS1) appears to be different from the S1 state of the closed form because the band appears ~400 nm. Because it was reported that the decay of the S1 state is accelerated in polar solvent, EAS1 is not ascribable to the S1 state of the closed form. The time constant of EAS1 is decelerated with the increase in the solvent polarity. However, the maximum of the transient absorption band is different from the simulated absorption band of the cation of the carbazole substructure. The spectral shape of EAS2 is consistent with the simulated absorption spectrum of the cation of the carbazole substructure. However, the time constant of EAS2 does not depend on the solvent polarity. Moreover, the difference in the Gibbs free energy between the S_1 state of the closed form and the CT state is positive. These results suggest that the photoinduced homolysis occurs in CIC.

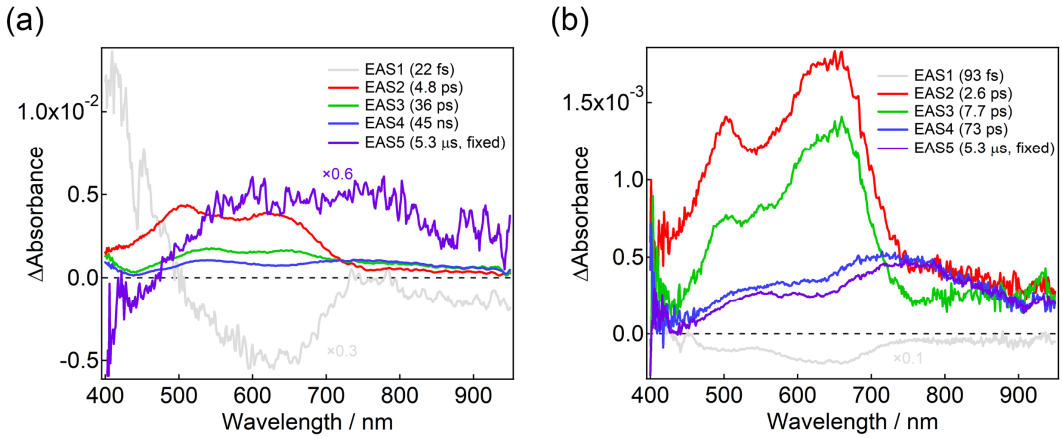


Fig. S60. EAS of the transient absorption spectra of CIC-tBuPh in (a) benzene and (b) acetonitrile excited with a 390-nm femtosecond laser pulse.

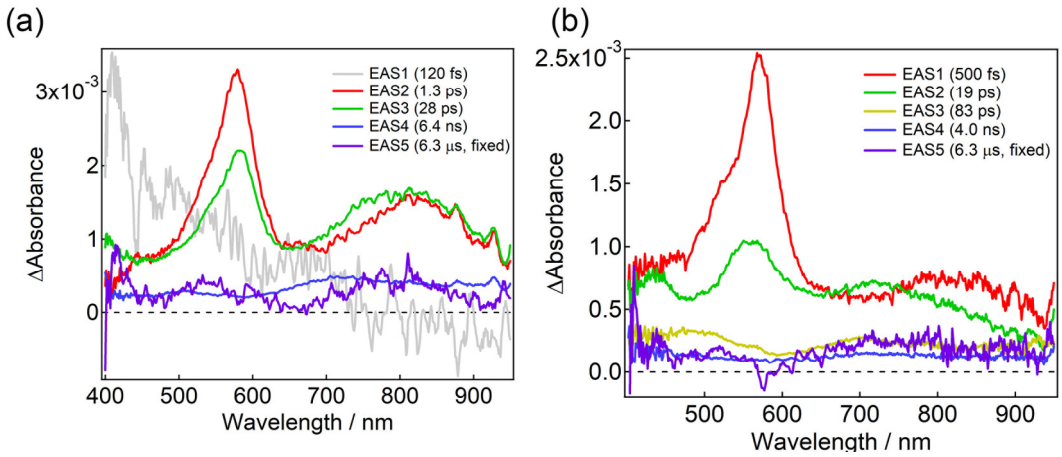


Fig. S61. EAS of the transient absorption spectra of CIC-TPA in (a) benzene and (b) acetonitrile excited with a 390-nm femtosecond laser pulse. In CIC-TPA in benzene, sharp and broad absorption bands are observed instantaneously after the excitation (0.2 ps in Fig. 5b). These bands decay with the time constants of 1.3 and 28 ps, and a small amount of the transient absorption bands ascribable to the ring-opening form is generated. In acetonitrile, the initial decay of the transient absorption bands is accelerated (500 fs and 19 ps), and the amplitude of the generated ring-opening form decreases relative to that in benzene (Fig. S59). Although the acceleration of the decay of the subpicosecond transient species in polar solvents is an opposite behaviour to the CT state of CIC, A possibility that the electron transfer to revert to the ground state is the Marcus inverted region cannot be excluded. Moreover, the substitution of the TPA group would stabilize both the S_1 and CT states. Therefore, it is difficult to assign the initial transient species from these results.

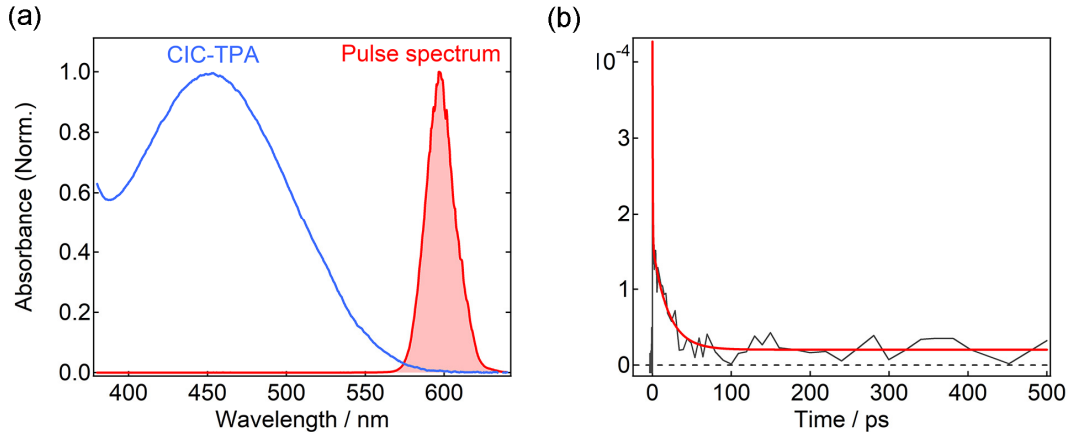


Fig. S62. (a) Absorption spectrum of CIC-TPA in benzene and an excitation pulse spectrum. (b) Picosecond transient absorption dynamics of CIC-TPA in benzene (1.8×10^{-3} M) excited with the pulse shown in Fig. S62a at room temperature. The excitation intensity was 40 nJ pulse^{-1} and the probed wavelength is 750 nm.

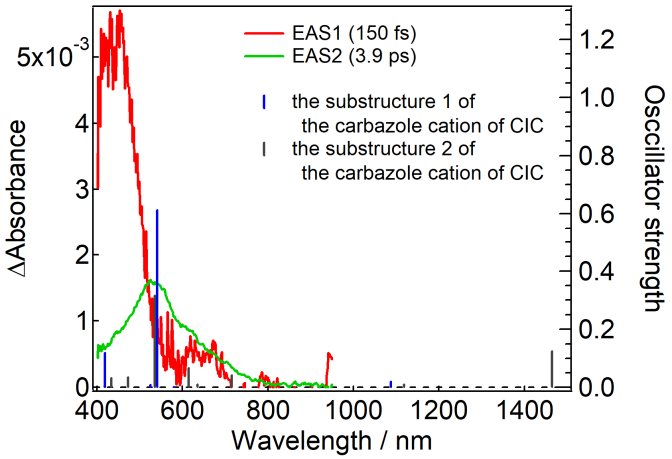


Fig. S63. The first and second EADS (150 fs and 3.9 ps) of the transient absorption spectra of CIC in benzene excited with a 390-nm femtosecond laser pulse. Vertical lines indicate the theoretical spectra of the substructure 1 and 2 of the carbazole cation at MPW1PW91/6-31+G(d,p)//MPW1PW91/6-31+G(d) level of theory. Molecular structures of the substructure 1 and 2 of the carbazole cation are shown in Figs. S67X and S68.

11. DFT calculations

All calculations was carried out using the Gaussian 09 program (Revision D.01).[S4] The molecular structure was fully optimized at the MPW1PW91/6-31G(d) level of theory, and analytical second derivative was computed using vibrational analysis to confirm each stationary point to be a minimum. TDDFT calculations were performed at the MPW1PW91/6-31+G(d,p) level of the theory for the optimized structures.

Table S2. Standard orientation of the optimized geometry for the closed form of CIC.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	1.575133	2.033673	-0.03414
2	C	0.725692	3.204055	-0.09879
3	C	-0.58043	2.785036	0.190939
4	C	-0.61297	1.272516	0.502617
5	N	0.809852	0.956165	0.312912
6	C	1.618072	-0.16007	0.259078
7	C	2.872443	0.347883	-0.08716
8	N	2.819481	1.711815	-0.2735
9	C	0.99269	4.535524	-0.39825
10	C	-0.06988	5.435414	-0.39967
11	C	-1.36905	5.015211	-0.10862
12	C	-1.63621	3.678775	0.193172
13	C	-1.47223	0.561433	-0.5067
14	C	-2.62572	-0.01446	-0.14147
15	C	-3.05377	-0.04953	1.270729
16	C	-2.20988	0.527342	2.288577
17	C	-1.05047	1.104687	1.936658
18	C	-3.69891	-0.70945	-0.84179
19	C	-4.61384	-1.06431	0.175943
20	N	-4.19144	-0.64901	1.454938
21	C	-3.94961	-1.03544	-2.1657
22	C	-5.12672	-1.72417	-2.46596
23	C	-6.02738	-2.07425	-1.45857
24	C	-5.78228	-1.74883	-0.1235
25	C	4.149021	-0.36008	-0.2476
26	C	1.124548	-1.53434	0.425495

27	C	5.144996	0.211757	-1.05048
28	C	6.370019	-0.42071	-1.21927
29	C	6.626727	-1.6352	-0.58761
30	C	5.649129	-2.20475	0.22362
31	C	4.423256	-1.57284	0.397625
32	C	0.446937	-1.94186	1.580579
33	C	-0.02888	-3.24338	1.699699
34	C	0.177246	-4.1611	0.674237
35	C	0.86281	-3.77038	-0.4736
36	C	1.328901	-2.46786	-0.60009
37	H	2.003862	4.854631	-0.62435
38	H	0.114643	6.479446	-0.63075
39	H	-2.18136	5.734201	-0.11694
40	H	-2.64517	3.349994	0.421124
41	H	-1.12369	0.590932	-1.53501
42	H	-2.52488	0.462646	3.324506
43	H	-0.38599	1.544187	2.673934
44	H	-3.25356	-0.76679	-2.95448
45	H	-5.34374	-1.99022	-3.4952
46	H	-6.93506	-2.60932	-1.71895
47	H	-6.47701	-2.0182	0.664169
48	H	4.940797	1.161616	-1.53167
49	H	7.128243	0.03676	-1.84744
50	H	7.583889	-2.12979	-0.71983
51	H	5.844294	-3.14258	0.734521
52	H	3.680431	-2.01657	1.050633
53	H	0.298183	-1.23709	2.390684
54	H	-0.55724	-3.54124	2.599602
55	H	-0.19341	-5.17661	0.769139
56	H	1.028082	-4.48032	-1.27769
57	H	1.857075	-2.16033	-1.49641

SCF Done: E(RmPW1PW91) = -1434.09263582 A.U.

Zero-point correction = 0.452743 (Hartree/Particle)
Thermal correction to Energy = 0.478575

Thermal correction to Enthalpy = 0.479519
Thermal correction to Gibbs Free Energy = 0.394993
Sum of electronic and zero-point Energies = -1433.641078
Sum of electronic and thermal Energies = -1433.615246
Sum of electronic and thermal Enthalpies = -1433.614302
Sum of electronic and thermal Free Energies = -1433.698828

Low frequencies --- -4.9763 -2.3795 -0.0000 0.0002 0.0003 2.0508
Low frequencies --- 17.7507 20.0138 32.9537

The Result for the TDDFT calculation

Excited State 1: Singlet-A 2.4542 eV 505.18 nm f=0.0028 <S**2>=0.000
120 ->121 0.70301
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1434.07171106
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.0690 eV 403.99 nm f=0.0503 <S**2>=0.000
119 ->121 0.69650

Excited State 3: Singlet-A 3.6725 eV 337.60 nm f=0.0994 <S**2>=0.000
120 ->122 0.69094

Excited State 4: Singlet-A 3.7456 eV 331.01 nm f=0.1209 <S**2>=0.000
116 ->121 0.14860
117 ->121 0.60810
118 ->121 -0.17178
119 ->122 0.18200
119 ->123 -0.11231

Excited State 5: Singlet-A 3.8413 eV 322.77 nm f=0.0016 <S**2>=0.000
112 ->121 0.35492
113 ->121 0.17007
116 ->121 0.42454
118 ->121 0.39014

Excited State	6:	Singlet-A	3.9461 eV	314.20 nm	f=0.0010	<S**2>=0.000
112 ->121		0.53305				
113 ->121		0.16923				
116 ->121		-0.16790				
118 ->121		-0.36147				
Excited State	7:	Singlet-A	3.9871 eV	310.97 nm	f=0.0464	<S**2>=0.000
112 ->121		-0.12914				
114 ->121		-0.17965				
115 ->121		-0.13620				
116 ->121		0.42791				
117 ->121		-0.16657				
118 ->121		-0.30910				
120 ->123		0.34080				
Excited State	8:	Singlet-A	3.9951 eV	310.34 nm	f=0.1464	<S**2>=0.000
114 ->121		0.11707				
116 ->121		-0.20800				
117 ->121		0.15979				
118 ->121		0.22363				
120 ->123		0.58079				
Excited State	9:	Singlet-A	4.0916 eV	303.02 nm	f=0.3459	<S**2>=0.000
115 ->121		-0.10292				
120 ->124		0.67576				
Excited State	10:	Singlet-A	4.1227 eV	300.74 nm	f=0.0103	<S**2>=0.000
114 ->121		-0.32292				
115 ->121		0.60156				
Excited State	11:	Singlet-A	4.1977 eV	295.36 nm	f=0.0026	<S**2>=0.000
114 ->121		0.57579				
115 ->121		0.30595				
116 ->121		0.13939				
118 ->121		-0.17724				

Excited State 12:	Singlet-A	4.3210 eV	286.93 nm	f=0.0078	<S**2>=0.000
112 ->121	-0.21938				
113 ->121	0.63630				
114 ->121	-0.11617				
119 ->122	0.11624				
Excited State 13:	Singlet-A	4.3978 eV	281.92 nm	f=0.0111	<S**2>=0.000
120 ->125	0.34185				
120 ->126	0.59246				
Excited State 14:	Singlet-A	4.4890 eV	276.19 nm	f=0.0048	<S**2>=0.000
120 ->125	0.57540				
120 ->126	-0.34302				
Excited State 15:	Singlet-A	4.5213 eV	274.22 nm	f=0.3211	<S**2>=0.000
108 ->121	0.13273				
113 ->121	-0.11302				
117 ->121	-0.15108				
119 ->122	0.63313				
Excited State 16:	Singlet-A	4.7589 eV	260.53 nm	f=0.0289	<S**2>=0.000
110 ->121	-0.17157				
111 ->121	-0.38116				
119 ->122	0.10476				
119 ->123	0.50711				
Excited State 17:	Singlet-A	4.8004 eV	258.28 nm	f=0.1780	<S**2>=0.000
110 ->121	0.12716				
111 ->121	0.50190				
119 ->123	0.38776				
120 ->127	0.18857				
Excited State 18:	Singlet-A	4.8564 eV	255.30 nm	f=0.0246	<S**2>=0.000
111 ->121	-0.10061				
118 ->124	-0.16212				

119 ->123	-0.13846					
120 ->127	0.44649					
120 ->128	-0.10649					
120 ->129	-0.40226					
Excited State 19:	Singlet-A	4.8937 eV	253.35 nm	f=0.0119	<S**2>=0.000	
117 ->122	-0.14361					
118 ->122	0.15635					
118 ->124	0.22394					
120 ->127	0.42567					
120 ->128	0.11794					
120 ->129	0.36444					
Excited State 20:	Singlet-A	4.9530 eV	250.32 nm	f=0.1008	<S**2>=0.000	
110 ->121	0.16135					
111 ->121	-0.12276					
117 ->122	0.55205					
118 ->122	-0.20873					
119 ->123	0.10039					
120 ->127	0.15651					
120 ->129	0.10950					

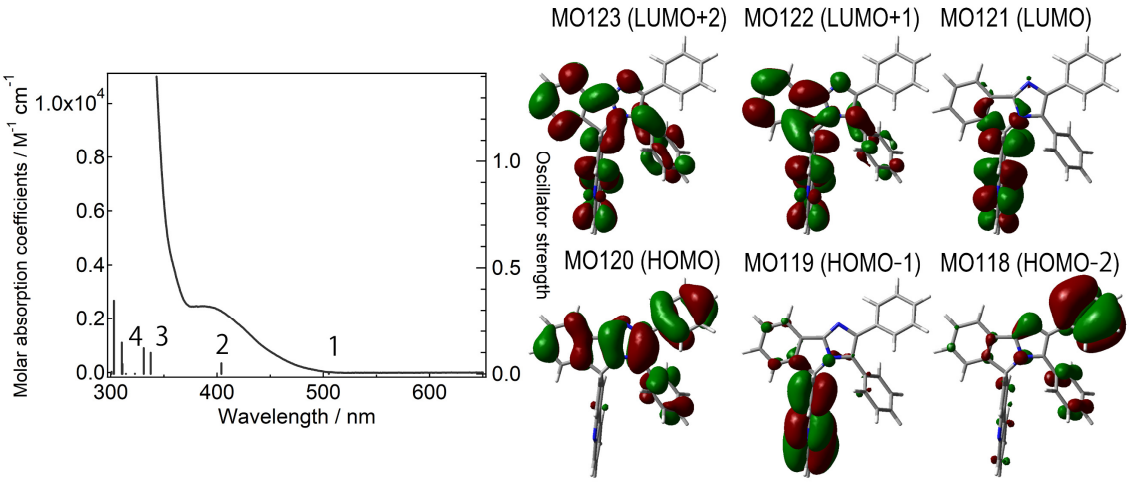


Fig. S64. UV-vis absorption spectrum of CIC in benzene at room temperature. The calculated absorption spectrum MPW1PW91/6-31+G(d,p)//MPW1PW91/6-31G(d) level of the theory) is shown by the red vertical lines. The relevant molecular orbitals of the CIC calculated at the MPW1PW91/6-31G(d) level of the theory.

Table S3. Selected calculated electronic transition of CIC at the MPW1PW91/6-31G(d) level.

No.	Wavelength (nm)	Coefficients	Electronic Transition			*f*
1	505.18	0.70301	120 HOMO	→	121 LUMO	0.0028
2	403.99	0.69650	119 HOMO-1	→	121 LUMO	0.0503
3	337.60	0.69094	120 HOMO	→	122 LUMO+1	0.5726
4	331.01	0.14860	116 HOMO-4	→	121 LUMO	0.1209
		0.60810	117 HOMO-3	→	121 LUMO	
		-0.17178	118 HOMO-2	→	121 LUMO	
		0.18200	119 HOMO-1	→	122 LUMO+1	
		-0.11231	119 HOMO-1	→	123 LUMO+2	

Table S4. Standard orientation of the optimized geometry for the singlet biradical form 1 of the ring-opening form of CIC.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	1.401214	1.532754	-0.154225
2	C	0.633064	2.759917	-0.195757
3	C	-0.779861	2.812429	-0.053134
4	C	-1.607196	1.688902	0.427121
5	N	2.761252	1.555236	-0.022446
6	C	3.115083	0.279341	-0.052868
7	C	1.896244	-0.528967	-0.275516
8	N	0.859066	0.294802	-0.309322
9	C	1.33628	3.944144	-0.491298
10	C	0.675086	5.138755	-0.708743
11	C	-0.717985	5.178067	-0.635632
12	C	-1.425598	4.029012	-0.308711
13	C	-2.790786	1.350008	-0.26841
14	C	-3.595145	0.346479	0.220264
15	C	-3.257185	-0.328511	1.436944
16	C	-2.094592	0.025665	2.14169
17	C	-1.283368	1.020699	1.626133
18	C	-4.838977	-0.283608	-0.213385
19	C	-5.111395	-1.258777	0.788118
20	N	-4.156001	-1.285079	1.784365
21	C	-5.694511	-0.125571	-1.28568
22	C	-6.832164	-0.945389	-1.360372
23	C	-7.100794	-1.899951	-0.379547
24	C	-6.242736	-2.068693	0.708172
25	C	1.720559	-1.955708	-0.515724
26	C	4.498606	-0.120668	0.175542
27	C	2.712532	-2.746727	-1.117313
28	C	2.479882	-4.092375	-1.371931
29	C	1.260098	-4.670653	-1.02912
30	C	0.262739	-3.89102	-0.443647
31	C	0.484663	-2.5448	-0.197247
32	C	5.529485	0.769721	-0.168389

33	C	6.854759	0.440822	0.071929
34	C	7.177091	-0.773976	0.676625
35	C	6.162962	-1.654873	1.043545
36	C	4.833954	-1.335011	0.794933
37	H	2.415073	3.879999	-0.570267
38	H	1.237485	6.0358	-0.945604
39	H	-1.250294	6.107786	-0.808775
40	H	-2.503745	4.077233	-0.193497
41	H	-3.026776	1.864004	-1.195317
42	H	-1.854109	-0.475285	3.073004
43	H	-0.385872	1.314628	2.158697
44	H	-5.502119	0.610419	-2.06045
45	H	-7.513194	-0.833077	-2.197793
46	H	-7.988285	-2.518311	-0.464846
47	H	-6.438437	-2.806117	1.478874
48	H	3.655528	-2.299377	-1.409767
49	H	3.251304	-4.689552	-1.847363
50	H	1.083609	-5.723623	-1.224374
51	H	-0.69218	-4.334919	-0.181629
52	H	-0.286407	-1.924567	0.245616
53	H	5.263936	1.715857	-0.625649
54	H	7.64148	1.133345	-0.209658
55	H	8.214676	-1.028767	0.867428
56	H	6.406375	-2.592512	1.532607
57	H	4.04967	-2.016291	1.104372

SCF Done: E(UmPW1PW91)	=	-1434.06739257	A.U.
Zero-point correction	=	0.449160 (Hartree/Particle)	
Thermal correction to Energy	=	0.475660	
Thermal correction to Enthalpy	=	0.476605	
Thermal correction to Gibbs Free Energy	=	0.389763	
Sum of electronic and zero-point Energies	=	-1433.619195	
Sum of electronic and thermal Energies	=	-1433.592694	
Sum of electronic and thermal Enthalpies	=	-1433.591750	
Sum of electronic and thermal Free Energies	=	-1433.678591	

Low frequencies --- -3.7164 0.0004 0.0005 0.0008 2.0884 6.7250

Low frequencies --- 12.7945 16.3057 33.1996

The Result for the TDDFT calculation

Excited State 1: 3.000-A -0.6501 eV -1907.16 nm f=-0.0000 <S**2>=2.000

120A ->121A 0.74262

120B ->121B -0.74262

120A <-121A -0.23927

120B <-121B 0.23927

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1434.14219771

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 3.000-A 0.7659 eV 1618.88 nm f=0.0000 <S**2>=2.000

119A ->121A 0.70724

119B ->121B -0.70724

119A <-121A 0.10418

119B <-121B -0.10418

Excited State 3: 1.000-A 0.9195 eV 1348.38 nm f=0.1789 <S**2>=0.000

119A ->121A -0.31816

120A ->121A 0.71089

119B ->121B -0.31816

120B ->121B 0.71089

120A <-121A -0.34192

120B <-121B -0.34192

Excited State 4: 1.000-A 1.2156 eV 1019.97 nm f=0.1154 <S**2>=0.000

119A ->121A 0.62864

120A ->121A 0.37477

119B ->121B 0.62864

120B ->121B 0.37477

120A <-121A -0.20001

120B <-121B -0.20001

Excited State 5: 3.000-A 1.6434 eV 754.43 nm f=0.0000 <S**2>=2.000

118A ->121A 0.68053

118B ->121B -0.68053

Excited State 6: 3.000-A 1.7134 eV 723.61 nm f=0.0000 <S**2>=2.000

117A ->121A 0.68640

117B ->121B -0.68640

Excited State 7: 3.000-A 1.9692 eV 629.61 nm f=0.0000 <S**2>=2.000

113A ->121A -0.42689

115A ->121A -0.29664

116A ->121A 0.44133

113B ->121B 0.42689

115B ->121B 0.29664

116B ->121B -0.44133

Excited State 8: 3.000-A 1.9963 eV 621.07 nm f=0.0000 <S**2>=2.000

112A ->121A -0.14261

113A ->121A 0.54768

115A ->121A -0.20474

116A ->121A 0.34445

112B ->121B 0.14261

113B ->121B -0.54768

115B ->121B 0.20474

116B ->121B -0.34445

Excited State 9: 1.000-A 2.0144 eV 615.49 nm f=0.0644 <S**2>=0.000

118A ->121A 0.68874

118B ->121B 0.68874

Excited State 10: 3.000-A 2.1852 eV 567.38 nm f=0.0000 <S**2>=2.000

111A ->121A -0.26105

112A ->121A -0.26437

115A ->121A 0.53121

116A ->121A 0.23989

111B ->121B 0.26105
112B ->121B 0.26437
115B ->121B -0.53121
116B ->121B -0.23989

Excited State 11: 1.000-A 2.2046 eV 562.38 nm f=0.0900 <S**2>=0.000
111A ->121A -0.21563
112A ->121A -0.28037
115A ->121A -0.12103
116A ->121A 0.57826
111B ->121B -0.21563
112B ->121B -0.28037
115B ->121B -0.12103
116B ->121B 0.57826

Excited State 12: 1.000-A 2.3056 eV 537.76 nm f=0.0814 <S**2>=0.000
112A ->121A 0.13313
115A ->121A -0.15189
117A ->121A 0.65151
112B ->121B 0.13313
115B ->121B -0.15189
117B ->121B 0.65151

Excited State 13: 3.000-A 2.3469 eV 528.30 nm f=0.0000 <S**2>=2.000
112A ->121A 0.56273
114A ->121A -0.16256
115A ->121A 0.19832
116A ->121A 0.29735
112B ->121B -0.56273
114B ->121B 0.16256
115B ->121B -0.19832
116B ->121B -0.29735

Excited State 14: 3.000-A 2.3547 eV 526.55 nm f=0.0000 <S**2>=2.000
111A ->121A 0.61960
112A ->121A -0.21710

115A ->121A 0.14747
116A ->121A 0.12750
111B ->121B -0.61960
112B ->121B 0.21710
115B ->121B -0.14747
116B ->121B -0.12750

Excited State 15: 1.000-A 2.3629 eV 524.72 nm f=0.0035 <S**2>=0.000
113A ->121A 0.69418
115A ->121A 0.10726
113B ->121B 0.69418
115B ->121B 0.10726

Excited State 16: 1.000-A 2.4145 eV 513.50 nm f=0.0408 <S**2>=0.000
111A ->121A 0.10791
112A ->121A 0.12378
114A ->121A -0.13083
115A ->121A 0.61428
116A ->121A 0.21816
117A ->121A 0.12672
111B ->121B 0.10791
112B ->121B 0.12378
114B ->121B -0.13083
115B ->121B 0.61428
116B ->121B 0.21816
117B ->121B 0.12672

Excited State 17: 3.000-A 2.5199 eV 492.02 nm f=0.0000 <S**2>=2.000
112A ->121A 0.10925
114A ->121A 0.67260
112B ->121B -0.10925
114B ->121B -0.67260

Excited State 18: 1.000-A 2.5839 eV 479.83 nm f=0.0660 <S**2>=0.000
112A ->121A 0.56360
114A ->121A -0.16139

115A ->121A -0.20723
116A ->121A 0.27263
117A ->121A -0.12750
112B ->121B 0.56360
114B ->121B -0.16139
115B ->121B -0.20723
116B ->121B 0.27263
117B ->121B -0.12750

Excited State 19: 1.000-A 2.6645 eV 465.32 nm f=0.0028 <S**2>=0.000
112A ->121A 0.16931
114A ->121A 0.67259
112B ->121B 0.16931
114B ->121B 0.67259

Excited State 20: 3.000-A 2.7403 eV 452.46 nm f=0.0000 <S**2>=2.000
109A ->121A -0.17822
110A ->121A 0.62572
120A ->122A -0.17538
120A ->124A 0.11241
109B ->121B 0.17822
110B ->121B -0.62572
120B ->122B 0.17538
120B ->124B -0.11241

Table S5. Standard orientation of the optimized geometry for the singlet biradical form 2 of the ring-opening form of CIC.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	1.088770	1.735856	-0.096808
2	C	0.406184	3.008502	-0.004679
3	C	-0.974830	3.185887	-0.294181
4	C	-1.938672	2.080552	-0.437905
5	N	2.337231	1.562851	0.431644
6	C	2.649919	0.311022	0.133075
7	C	1.544833	-0.259704	-0.666936

8	N	0.592468	0.656395	-0.761286
9	C	1.195312	4.137546	0.292492
10	C	0.670549	5.415152	0.242689
11	C	-0.668626	5.596717	-0.108038
12	C	-1.471529	4.494622	-0.365965
13	C	-2.001098	1.055839	0.540564
14	C	-2.976461	0.095714	0.443299
15	C	-3.915087	0.110398	-0.639873
16	C	-3.853027	1.122024	-1.609705
17	C	-2.875580	2.098831	-1.487979
18	C	-3.358241	-1.066612	1.238490
19	C	-4.473774	-1.621399	0.547305
20	N	-4.809212	-0.910346	-0.585755
21	C	-2.886139	-1.655670	2.395286
22	C	-3.532469	-2.806840	2.869639
23	C	-4.626189	-3.352683	2.194866
24	C	-5.110284	-2.767782	1.025504
25	C	1.421644	-1.535974	-1.360496
26	C	3.879508	-0.293998	0.631369
27	C	2.534871	-2.232189	-1.858091
28	C	2.365429	-3.418637	-2.560362
29	C	1.088032	-3.930995	-2.774099
30	C	-0.025408	-3.241092	-2.295135
31	C	0.136523	-2.050399	-1.603447
32	C	4.985781	0.531056	0.894716
33	C	6.157710	-0.003536	1.407625
34	C	6.243542	-1.367756	1.684861
35	C	5.146111	-2.192145	1.449916
36	C	3.972935	-1.663391	0.926130
37	H	2.238533	3.970441	0.533005
38	H	1.300156	6.270346	0.464732
39	H	-1.092605	6.594595	-0.154675
40	H	-2.526651	4.636689	-0.575815
41	H	-1.294089	1.065117	1.363363
42	H	-4.559149	1.126931	-2.432715
43	H	-2.802440	2.880629	-2.236636

44	H	-2.036301	-1.246207	2.932833
45	H	-3.174876	-3.280784	3.778074
46	H	-5.104709	-4.243899	2.587470
47	H	-5.958483	-3.180884	0.490688
48	H	3.530668	-1.827539	-1.718132
49	H	3.233770	-3.940430	-2.949525
50	H	0.959359	-4.861144	-3.318410
51	H	-1.023222	-3.632622	-2.464216
52	H	-0.721299	-1.498577	-1.236565
53	H	4.900840	1.591284	0.686178
54	H	7.008469	0.643629	1.595228
55	H	7.160505	-1.784523	2.089083
56	H	5.200540	-3.250811	1.682040
57	H	3.116149	-2.308016	0.767000

SCF Done: E(UmPW1PW91) = -1434.06570041 A.U.

Zero-point correction = 0.449298 (Hartree/Particle)
Thermal correction to Energy = 0.475780
Thermal correction to Enthalpy = 0.476724
Thermal correction to Gibbs Free Energy = 0.389775
Sum of electronic and zero-point Energies = -1433.619914
Sum of electronic and thermal Energies = -1433.593433
Sum of electronic and thermal Enthalpies = -1433.592488
Sum of electronic and thermal Free Energies = -1433.679438

Low frequencies --- -6.2468 -0.0006 -0.0005 -0.0004 3.9208 4.4249
Low frequencies --- 11.1209 17.8673 28.6616

The Result for the TDDFT calculation

Excited State 1: 3.000-A -0.6903 eV -1795.99 nm f=-0.0000 <S**2>=2.000
120A ->121A 0.72605
120B ->121B -0.72605
120A <-121A -0.18291
120B <-121B 0.18291

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1434.14733821

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 3.000-A 0.9223 eV 1344.24 nm f=0.0000 <S**2>=2.000

119A ->121A 0.70451

119B ->121B -0.70451

Excited State 3: 1.000-A 1.0810 eV 1146.92 nm f=0.2352 <S**2>=0.000

119A ->121A 0.13856

120A ->121A 0.76432

119B ->121B 0.13856

120B ->121B 0.76432

120A <-121A -0.34398

120B <-121B -0.34398

Excited State 4: 1.000-A 1.2424 eV 997.96 nm f=0.0210 <S**2>=0.000

119A ->121A 0.68810

120A ->121A -0.16345

119B ->121B 0.68810

120B ->121B -0.16345

Excited State 5: 3.000-A 1.4908 eV 831.65 nm f=0.0000 <S**2>=2.000

117A ->121A -0.13267

118A ->121A 0.67671

117B ->121B 0.13267

118B ->121B -0.67671

Excited State 6: 3.000-A 1.7918 eV 691.95 nm f=0.0000 <S**2>=2.000

115A ->121A -0.10855

117A ->121A 0.66302

118A ->121A 0.12722

115B ->121B 0.10855

117B ->121B -0.66302

118B ->121B -0.12722

Excited State 7:	1.000-A	2.0072 eV	617.70 nm	f=0.1062	<S**2>=0.000
117A ->121A	0.20527				
118A ->121A	0.65985				
117B ->121B	0.20527				
118B ->121B	0.65985				
Excited State 8:	3.000-A	2.0139 eV	615.64 nm	f=0.0000	<S**2>=2.000
113A ->121A	-0.14499				
115A ->121A	-0.31213				
116A ->121A	0.59148				
113B ->121B	0.14499				
115B ->121B	0.31213				
116B ->121B	-0.59148				
Excited State 9:	3.000-A	2.0462 eV	605.91 nm	f=0.0000	<S**2>=2.000
112A ->121A	0.61283				
113A ->121A	0.32605				
112B ->121B	-0.61283				
113B ->121B	-0.32605				
Excited State 10:	1.000-A	2.1618 eV	573.52 nm	f=0.0352	<S**2>=0.000
111A ->121A	0.16789				
113A ->121A	-0.15004				
115A ->121A	-0.14183				
116A ->121A	0.41023				
117A ->121A	0.47814				
118A ->121A	-0.11692				
111B ->121B	0.16789				
113B ->121B	-0.15004				
115B ->121B	-0.14183				
116B ->121B	0.41023				
117B ->121B	0.47814				
118B ->121B	-0.11692				
Excited State 11:	3.000-A	2.2487 eV	551.37 nm	f=0.0000	<S**2>=2.000
111A ->121A	0.15546				

112A ->121A 0.13546
113A ->121A -0.21716
115A ->121A 0.57603
116A ->121A 0.24206
111B ->121B -0.15546
112B ->121B -0.13546
113B ->121B 0.21716
115B ->121B -0.57603
116B ->121B -0.24206

Excited State 12: 3.000-A 2.3735 eV 522.37 nm f=0.0000 <S**2>=2.000
112A ->121A -0.29048
113A ->121A 0.53371
114A ->121A -0.11221
115A ->121A 0.17010
116A ->121A 0.23821
112B ->121B 0.29048
113B ->121B -0.53371
114B ->121B 0.11221
115B ->121B -0.17010
116B ->121B -0.23821

Excited State 13: 1.000-A 2.3830 eV 520.29 nm f=0.0961 <S**2>=0.000
111A ->121A 0.10930
113A ->121A -0.23262
115A ->121A 0.11366
116A ->121A 0.44823
117A ->121A -0.41500
118A ->121A 0.14258
120A ->122A -0.11331
111B ->121B 0.10930
113B ->121B -0.23262
115B ->121B 0.11366
116B ->121B 0.44823
117B ->121B -0.41500
118B ->121B 0.14258

120B ->122B -0.11331

Excited State 14: 1.000-A 2.4298 eV 510.27 nm f=0.0203 <S**2>=0.000
112A ->121A 0.29670
113A ->121A 0.25251
114A ->121A -0.10837
115A ->121A 0.54369
116A ->121A 0.13239
117A ->121A 0.10923
112B ->121B 0.29670
113B ->121B 0.25251
114B ->121B -0.10837
115B ->121B 0.54369
116B ->121B 0.13239
117B ->121B 0.10923

Excited State 15: 1.000-A 2.4365 eV 508.86 nm f=0.0277 <S**2>=0.000
112A ->121A 0.54053
113A ->121A 0.22621
115A ->121A -0.34774
117A ->121A -0.13282
112B ->121B 0.54053
113B ->121B 0.22621
115B ->121B -0.34774
117B ->121B -0.13282

Excited State 16: 3.000-A 2.4440 eV 507.30 nm f=0.0000 <S**2>=2.000
111A ->121A 0.63201
114A ->121A 0.21412
116A ->121A -0.10151
111B ->121B -0.63201
114B ->121B -0.21412
116B ->121B 0.10151

Excited State 17: 3.000-A 2.5674 eV 482.91 nm f=0.0000 <S**2>=2.000
111A ->121A -0.19692

114A ->121A 0.65281
111B ->121B 0.19692
114B ->121B -0.65281

Excited State 18: 1.000-A 2.6163 eV 473.90 nm f=0.0496 <S**2>=0.000
111A ->121A -0.10624
112A ->121A -0.30692
113A ->121A 0.49461
114A ->121A -0.16141
115A ->121A -0.16732
116A ->121A 0.28498
111B ->121B -0.10624
112B ->121B -0.30692
113B ->121B 0.49461
114B ->121B -0.16141
115B ->121B -0.16732
116B ->121B 0.28498

Excited State 19: 1.000-A 2.7067 eV 458.07 nm f=0.0023 <S**2>=0.000
113A ->121A 0.16825
114A ->121A 0.67048
113B ->121B 0.16825
114B ->121B 0.67048

Excited State 20: 3.000-A 2.7810 eV 445.83 nm f=0.0000 <S**2>=2.000
109A ->121A 0.20213
110A ->121A 0.57614
120A ->122A -0.26850
120A ->124A 0.11365
109B ->121B -0.20213
110B ->121B -0.57614
120B ->122B 0.26850
120B ->124B -0.11365

Table S6. Standard orientation of the optimized geometry for the triplet biradical form of the ring-opening form of CIC.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	1.4107	1.533554	-0.149301
2	C	0.671527	2.782699	-0.193069
3	C	-0.731037	2.875263	-0.005117
4	C	-1.584229	1.758202	0.468826
5	N	2.774457	1.524713	-0.070225
6	C	3.095688	0.239456	-0.080555
7	C	1.84882	-0.542532	-0.230827
8	N	0.831286	0.308314	-0.242901
9	C	1.396923	3.945419	-0.511344
10	C	0.764135	5.163502	-0.692613
11	C	-0.61976	5.245196	-0.557664
12	C	-1.348548	4.111379	-0.212799
13	C	-2.707018	1.368168	-0.290586
14	C	-3.535214	0.379043	0.194518
15	C	-3.2728	-0.229946	1.458527
16	C	-2.167788	0.169726	2.221226
17	C	-1.335327	1.157692	1.715007
18	C	-4.742235	-0.285643	-0.288495
19	C	-5.072315	-1.217603	0.739394
20	N	-4.189232	-1.186674	1.793125
21	C	-5.525534	-0.190158	-1.421257
22	C	-6.647576	-1.027566	-1.53142
23	C	-6.973713	-1.939446	-0.526131
24	C	-6.189926	-2.046049	0.621984
25	C	1.625116	-1.968895	-0.422955
26	C	4.476593	-0.188281	0.109222
27	C	2.574939	-2.807498	-1.028799
28	C	2.294854	-4.152162	-1.235933
29	C	1.068894	-4.682341	-0.841052
30	C	0.112555	-3.855493	-0.251524
31	C	0.381401	-2.510167	-0.052506
32	C	5.514799	0.668179	-0.294079
33	C	6.839866	0.314192	-0.091507
34	C	7.155787	-0.891662	0.534224

35	C	6.135473	-1.738208	0.960047
36	C	4.806121	-1.393518	0.749342
37	H	2.469696	3.850942	-0.631344
38	H	1.344535	6.044278	-0.946598
39	H	-1.13128	6.19134	-0.702442
40	H	-2.421023	4.185973	-0.062666
41	H	-2.885804	1.837427	-1.253313
42	H	-1.981565	-0.287797	3.186745
43	H	-0.47675	1.486641	2.290286
44	H	-5.289192	0.510491	-2.216274
45	H	-7.271976	-0.963346	-2.41675
46	H	-7.847662	-2.57189	-0.641854
47	H	-6.428948	-2.749184	1.41228
48	H	3.521582	-2.39809	-1.362049
49	H	3.033602	-4.786429	-1.715192
50	H	0.855227	-5.73457	-0.999774
51	H	-0.847406	-4.261844	0.050023
52	H	-0.358046	-1.853088	0.391054
53	H	5.254791	1.60825	-0.766731
54	H	7.631654	0.9803	-0.418926
55	H	8.193412	-1.165808	0.695701
56	H	6.374579	-2.668025	1.465894
57	H	4.017973	-2.04706	1.105251

SCF Done: E(UmPW1PW91) = -1434.06560736 A.U.

Zero-point correction	=	0.449118 (Hartree/Particle)
Thermal correction to Energy	=	0.475651
Thermal correction to Enthalpy	=	0.476595
Thermal correction to Gibbs Free Energy	=	0.388470
Sum of electronic and zero-point Energies	=	-1433.617924
Sum of electronic and thermal Energies	=	-1433.591392
Sum of electronic and thermal Enthalpies	=	-1433.590448
Sum of electronic and thermal Free Energies	=	-1433.678572

Low frequencies --- -2.1502 -0.0004 -0.0002 0.0005 4.2442 6.8437

Low frequencies --- 11.9092 15.5650 32.6063

The Result for the TDDFT calculation

Excited State 1: 3.079-A 1.2749 eV 972.52 nm f=0.0116 <S**2>=2.121
118B ->121B 0.10338
119B ->120B 0.62830
119B ->121B 0.75271
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1434.08846280
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 3.060-A 1.7991 eV 689.16 nm f=0.0053 <S**2>=2.091
111B ->120B -0.15020
117B ->120B -0.25326
117B ->121B 0.10997
118B ->120B -0.34390
118B ->121B 0.11121
119B ->120B 0.64723
119B ->121B -0.54226

Excited State 3: 3.074-A 2.0378 eV 608.42 nm f=0.0360 <S**2>=2.112
121A ->122A -0.10475
108B ->120B 0.16034
111B ->120B -0.19534
116B ->120B 0.10138
117B ->120B 0.56931
117B ->121B -0.22873
118B ->120B 0.49868
118B ->121B -0.19638
119B ->120B 0.33500
119B ->121B -0.26759

Excited State 4: 3.053-A 2.0599 eV 601.89 nm f=0.0004 <S**2>=2.080
112B ->120B 0.54648
112B ->121B 0.80608

Excited State 5:	3.086-A	2.2607 eV	548.44 nm	f=0.1305	<S**2>=2.131	
121A ->123A	-0.11671					
111B ->120B	-0.30544					
111B ->121B	0.10314					
114B ->120B	0.11514					
115B ->120B	0.18109					
116B ->120B	0.58704					
116B ->121B	-0.26986					
117B ->120B	-0.36733					
117B ->121B	-0.21083					
118B ->120B	0.28040					
118B ->121B	0.25883					
119B ->120B	-0.13693					

Excited State 6:	3.059-A	2.2971 eV	539.74 nm	f=0.0546	<S**2>=2.089	
111B ->120B	0.29824					
111B ->121B	-0.17798					
114B ->120B	-0.12379					
115B ->120B	-0.17850					
116B ->120B	-0.36932					
117B ->120B	-0.38841					
117B ->121B	-0.34464					
118B ->120B	0.47735					
118B ->121B	0.29120					
119B ->120B	0.14731					
119B ->121B	-0.14738					

Excited State 7:	3.109-A	2.5386 eV	488.39 nm	f=0.0823	<S**2>=2.166	
121A ->123A	0.14823					
111B ->120B	-0.39585					
114B ->121B	-0.15021					
115B ->120B	0.46746					
115B ->121B	-0.14327					
116B ->120B	-0.45878					
117B ->121B	-0.32450					

118B ->120B -0.19343
118B ->121B 0.27339
119B ->120B -0.10823

Excited State 8: 3.074-A 2.6219 eV 472.87 nm f=0.0087 <S**2>=2.112
114B ->120B 0.41006
115B ->120B 0.46996
115B ->121B -0.15471
116B ->120B -0.20524
117B ->120B -0.30233
117B ->121B 0.38101
118B ->120B 0.34526
118B ->121B -0.36361

Excited State 9: 3.086-A 2.6763 eV 463.26 nm f=0.0057 <S**2>=2.131
111B ->120B 0.47886
111B ->121B -0.18110
114B ->120B -0.43614
114B ->121B 0.13823
115B ->120B 0.60612
115B ->121B -0.17772
116B ->120B 0.20243
117B ->120B 0.13452

Excited State 10: 3.091-A 2.7965 eV 443.35 nm f=0.0069 <S**2>=2.138
108B ->120B -0.25929
108B ->121B 0.12097
111B ->120B -0.15297
113B ->120B 0.62025
113B ->121B -0.21759
114B ->120B -0.41049
117B ->120B -0.22878
118B ->121B -0.40401

Excited State 11: 3.084-A 2.8242 eV 439.01 nm f=0.0072 <S**2>=2.127
110B ->121B -0.11367

111B ->120B 0.18555
113B ->120B 0.57692
113B ->121B -0.19437
114B ->120B 0.27119
114B ->121B 0.11656
116B ->121B 0.11320
117B ->120B 0.20630
117B ->121B 0.29286
118B ->120B 0.11623
118B ->121B 0.50981

Excited State 12: 3.077-A 2.8655 eV 432.67 nm f=0.0033 <S**2>=2.117
108B ->120B -0.37669
108B ->121B 0.19309
110B ->120B -0.12864
111B ->120B -0.26664
111B ->121B 0.15606
113B ->120B -0.32682
113B ->121B 0.12055
114B ->120B -0.41213
114B ->121B 0.10948
116B ->121B 0.11692
117B ->121B 0.43696
118B ->120B 0.32233
118B ->121B 0.21096

Excited State 13: 3.090-A 3.0067 eV 412.36 nm f=0.0017 <S**2>=2.137
108B ->120B 0.53234
108B ->121B -0.18037
110B ->120B 0.23802
110B ->121B 0.15295
111B ->120B -0.20450
111B ->121B -0.16952
113B ->120B 0.11362
114B ->120B -0.25511
114B ->121B -0.21672

115B ->121B 0.11426
116B ->120B 0.15577
116B ->121B 0.43984
117B ->121B 0.26948
118B ->121B 0.15095

Excited State 14: 3.118-A 3.0432 eV 407.42 nm f=0.0093 <S**2>=2.181
108B ->120B -0.42660
108B ->121B 0.15696
110B ->120B 0.17762
110B ->121B 0.22170
111B ->121B -0.13950
114B ->120B 0.22049
116B ->120B 0.20801
116B ->121B 0.64407
117B ->121B -0.27891

Excited State 15: 3.129-A 3.1049 eV 399.32 nm f=0.0079 <S**2>=2.197
120A ->124A -0.11591
108B ->120B 0.23195
108B ->121B -0.11698
109B ->120B 0.31824
110B ->120B -0.16186
110B ->121B -0.35829
111B ->121B 0.31363
114B ->120B -0.14749
114B ->121B 0.40936
115B ->121B -0.23166
116B ->121B 0.33778
117B ->120B -0.22762
117B ->121B -0.16376
118B ->121B -0.12551

Excited State 16: 3.232-A 3.1431 eV 394.46 nm f=0.0223 <S**2>=2.361
121A ->122A 0.11875
121A ->123A -0.24226

109B ->120B 0.29144
109B ->121B -0.27181
110B ->120B 0.41197
110B ->121B 0.17879
111B ->120B -0.13629
114B ->121B 0.42400
114B ->126B 0.11061
115B ->121B 0.13314
116B ->120B -0.21898
116B ->121B -0.30485
116B ->123B -0.10071

Excited State 17: 3.219-A 3.2127 eV 385.92 nm f=0.0193 <S**2>=2.341
121A ->123A 0.29269
121A ->124A 0.15226
108B ->120B 0.11555
108B ->121B -0.10235
109B ->120B -0.43714
110B ->121B 0.23902
114B ->121B 0.61687
115B ->121B 0.12386
117B ->120B -0.11201

Excited State 18: 3.087-A 3.2317 eV 383.65 nm f=0.0028 <S**2>=2.132
121A ->122A -0.12964
109B ->120B 0.13705
109B ->121B 0.10164
110B ->120B -0.20499
110B ->121B -0.27496
113B ->121B -0.19286
115B ->120B 0.26193
115B ->121B 0.80682

Excited State 19: 3.387-A 3.2710 eV 379.04 nm f=0.0755 <S**2>=2.618
114A ->127A 0.13143
115A ->126A -0.11558

118A ->128A 0.10100
120A ->122A -0.25690
121A ->122A 0.66038
121A ->123A 0.21946
121A ->124A -0.10001
106B ->120B -0.16536
107B ->120B 0.21756
107B ->121B -0.11657
110B ->120B -0.11789
113B ->127B -0.13034
115B ->125B 0.12983
116B ->122B -0.14804
118B ->121B -0.10331

Excited State 20: 3.766-A 3.3576 eV 369.27 nm f=0.0045 <S**2>=3.296
117A ->124A 0.14627
119A ->122A 0.23762
119A ->123A -0.19782
119A ->124A 0.41379
120A ->128A -0.10166
121A ->124A 0.27922
110B ->120B 0.10527
111B ->120B 0.13570
111B ->121B 0.31572
113B ->121B -0.10214
114B ->121B -0.24236
115B ->121B 0.19281
117B ->124B -0.13511
118B ->124B 0.15693
119B ->122B -0.14103
119B ->123B 0.13465
119B ->124B 0.32121

Table S7. Standard orientation of the optimized geometry for the quinoidal forms 1 of the ring-opening form of CIC.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	-0.974244	5.575085	0.173112
2	C	-1.70626	4.46167	0.502808
3	C	-1.186734	3.155216	0.310908
4	C	0.19186	3.037859	-0.078968
5	C	0.898886	4.202498	-0.478755
6	C	0.332074	5.442846	-0.351227
7	C	0.922074	1.829045	0.065147
8	C	-2.067231	2.026495	0.39731
9	N	0.50527	0.773126	0.834055
10	C	1.473245	-0.11651	0.731207
11	C	2.514041	0.437724	-0.154031
12	N	2.155883	1.660854	-0.505777
13	C	-1.934094	0.934411	-0.524809
14	C	-2.83754	-0.084993	-0.496317
15	C	-3.915298	-0.095873	0.475102
16	C	-4.046259	0.986491	1.388245
17	C	-3.159677	2.026243	1.319543
18	C	-3.046747	-1.301054	-1.265632
19	C	-4.195542	-1.897515	-0.676898
20	N	-4.712417	-1.148647	0.372487
21	C	-2.401141	-1.915065	-2.326116
22	C	-2.909973	-3.127944	-2.804596
23	C	-4.039133	-3.7126	-2.227282
24	C	-4.694884	-3.105593	-1.156546
25	C	3.747447	-0.157678	-0.656528
26	C	1.436733	-1.355693	1.505246
27	C	4.821063	0.679984	-1.000686
28	C	5.990598	0.148859	-1.522969
29	C	6.106467	-1.226122	-1.725587
30	C	5.041718	-2.065088	-1.406522
31	C	3.871153	-1.538757	-0.874831
32	C	2.597081	-1.94959	2.024955

33	C	2.512094	-3.097838	2.802397
34	C	1.272616	-3.673634	3.070573
35	C	0.113031	-3.086719	2.566648
36	C	0.191644	-1.935278	1.796747
37	H	-1.416772	6.560472	0.275445
38	H	-2.738872	4.573347	0.813276
39	H	1.916895	4.074769	-0.826879
40	H	0.892026	6.32879	-0.631894
41	H	-1.153845	0.978214	-1.27594
42	H	-4.8407	0.965696	2.126232
43	H	-3.233457	2.839444	2.032634
44	H	-1.521208	-1.473141	-2.783895
45	H	-2.419145	-3.620415	-3.63775
46	H	-4.411043	-4.65403	-2.618701
47	H	-5.571317	-3.551974	-0.699616
48	H	4.713511	1.747613	-0.847124
49	H	6.816187	0.806718	-1.774984
50	H	7.02174	-1.640641	-2.135979
51	H	5.119981	-3.13372	-1.578413
52	H	3.039495	-2.19567	-0.647233
53	H	3.564061	-1.495197	1.840887
54	H	3.417044	-3.539783	3.206964
55	H	1.209853	-4.574314	3.672983
56	H	-0.855985	-3.529571	2.772901
57	H	-0.704016	-1.469232	1.401833

SCF Done: E(RmPW1PW91) = -1434.05640297 A.U.

Zero-point correction	=	0.450765 (Hartree/Particle)
Thermal correction to Energy	=	0.477080
Thermal correction to Enthalpy	=	0.478024
Thermal correction to Gibbs Free Energy	=	0.391911
Sum of electronic and zero-point Energies	=	-1433.607340
Sum of electronic and thermal Energies	=	-1433.581024
Sum of electronic and thermal Enthalpies	=	-1433.580080
Sum of electronic and thermal Free Energies	=	-1433.666194

Low frequencies --- -1.3753 0.0007 0.0008 0.0010 2.6122 4.9330

Low frequencies --- 13.5328 18.4629 31.5650

The Result for the TDDFT calculation

Excited State 1: Singlet-A 1.3415 eV 924.24 nm f=0.2341 <S**2>=0.000

119 ->121 -0.32435

120 ->121 0.65159

120 <-121 -0.21189

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1434.07761777

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.4411 eV 860.35 nm f=0.0973 <S**2>=0.000

119 ->121 0.62068

120 ->121 0.34942

120 <-121 -0.12250

Excited State 3: Singlet-A 2.1684 eV 571.77 nm f=0.0951 <S**2>=0.000

117 ->121 0.19037

118 ->121 0.65809

Excited State 4: Singlet-A 2.3675 eV 523.70 nm f=0.0188 <S**2>=0.000

111 ->121 0.13041

112 ->121 -0.18169

115 ->121 -0.34397

116 ->121 0.33308

117 ->121 0.44880

Excited State 5: Singlet-A 2.5045 eV 495.04 nm f=0.1115 <S**2>=0.000

112 ->121 0.17733

115 ->121 0.21044

116 ->121 -0.33935

117 ->121 0.47504

118 ->121 -0.16436

120 ->122 0.18145

Excited State 6: Singlet-A 2.6016 eV 476.56 nm f=0.0072 <S**2>=0.000
113 ->121 0.42226
115 ->121 -0.37611
116 ->121 -0.40291

Excited State 7: Singlet-A 2.6084 eV 475.33 nm f=0.0071 <S**2>=0.000
113 ->121 0.55725
115 ->121 0.31122
116 ->121 0.27180

Excited State 8: Singlet-A 2.8445 eV 435.88 nm f=0.0208 <S**2>=0.000
112 ->121 0.54217
114 ->121 0.31612
115 ->121 -0.25261
116 ->121 0.11984

Excited State 9: Singlet-A 2.8958 eV 428.15 nm f=0.0016 <S**2>=0.000
112 ->121 -0.30947
114 ->121 0.61855
116 ->121 -0.10858

Excited State 10: Singlet-A 3.1159 eV 397.91 nm f=0.0292 <S**2>=0.000
109 ->121 -0.15405
110 ->121 -0.20930
111 ->121 0.55498
112 ->121 0.11955
120 ->122 0.28492

Excited State 11: Singlet-A 3.3079 eV 374.81 nm f=0.0924 <S**2>=0.000
108 ->121 0.12393
109 ->121 0.29709
110 ->121 0.54182
111 ->121 0.17063
112 ->121 0.10591

117 ->121 -0.10601
120 ->122 0.17916

Excited State 12: Singlet-A 3.3852 eV 366.25 nm f=0.2530 <S**2>=0.000
108 ->121 0.20016
109 ->121 0.19613
110 ->121 -0.23309
111 ->121 -0.24986
115 ->121 -0.12772
120 ->122 0.46533
120 ->124 -0.14438

Excited State 13: Singlet-A 3.5218 eV 352.04 nm f=0.0805 <S**2>=0.000
109 ->121 0.56544
110 ->121 -0.27281
111 ->121 0.17177
120 ->122 -0.23035

Excited State 14: Singlet-A 3.7092 eV 334.26 nm f=0.0722 <S**2>=0.000
107 ->121 -0.11315
108 ->121 -0.11844
120 ->123 0.67473

Excited State 15: Singlet-A 3.8254 eV 324.11 nm f=0.0599 <S**2>=0.000
107 ->121 0.29939
108 ->121 0.44154
110 ->121 -0.10720
120 ->123 0.15162
120 ->124 0.37944

Excited State 16: Singlet-A 3.8755 eV 319.92 nm f=0.0704 <S**2>=0.000
107 ->121 -0.22281
108 ->121 -0.21698
109 ->121 0.11290
119 ->122 -0.26158
120 ->122 0.11670

120 ->124	0.52893				
Excited State 17:	Singlet-A	3.9087 eV	317.20 nm	f=0.0166	<S**2>=0.000
107 ->121	0.46452				
108 ->121	-0.31318				
120 ->125	0.39413				
Excited State 18:	Singlet-A	3.9636 eV	312.81 nm	f=0.0937	<S**2>=0.000
107 ->121	-0.31640				
108 ->121	0.21881				
120 ->125	0.56155				
Excited State 19:	Singlet-A	4.1370 eV	299.69 nm	f=0.3676	<S**2>=0.000
106 ->121	-0.12579				
108 ->121	-0.12912				
119 ->122	0.62228				
120 ->122	0.11997				
120 ->124	0.15872				
Excited State 20:	Singlet-A	4.3071 eV	287.86 nm	f=0.0329	<S**2>=0.000
120 ->126	0.68848				

Table S8. Standard orientation of the optimized geometry for the quinoidal form 2 of the ring-opening form of CIC.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	0.831874	5.046325	-0.873664
2	C	1.512722	3.877212	-0.648387
3	C	0.844459	2.706129	-0.199891
4	C	-0.595075	2.737880	-0.167710
5	C	-1.263363	3.981530	-0.332372
6	C	-0.568713	5.107734	-0.681682
7	C	-1.379994	1.558839	-0.143787
8	C	1.617162	1.611462	0.305739
9	N	-0.886384	0.310399	-0.413960
10	C	-1.932811	-0.486848	-0.332315

11	C	-3.110538	0.333745	0.017901
12	N	-2.733807	1.597195	0.079429
13	C	2.899884	1.325017	-0.260148
14	C	3.650640	0.307757	0.248375
15	C	3.197799	-0.447216	1.413065
16	C	1.947929	-0.115318	2.013761
17	C	1.182620	0.864026	1.454997
18	C	4.929779	-0.294367	-0.087237
19	C	5.110260	-1.305869	0.892015
20	N	4.044982	-1.382524	1.793269
21	C	5.884923	-0.080042	-1.066994
22	C	7.032130	-0.883200	-1.068372
23	C	7.208638	-1.874578	-0.104571
24	C	6.249670	-2.098255	0.888702
25	C	-4.488395	-0.055205	0.301718
26	C	-1.817726	-1.905739	-0.659692
27	C	-5.522171	0.861090	0.048617
28	C	-6.837901	0.539864	0.346127
29	C	-7.145874	-0.695263	0.915698
30	C	-6.127320	-1.604386	1.189988
31	C	-4.808553	-1.290771	0.885292
32	C	-2.861170	-2.624670	-1.262856
33	C	-2.688007	-3.958992	-1.608608
34	C	-1.476177	-4.597630	-1.356985
35	C	-0.429602	-3.890026	-0.767237
36	C	-0.594452	-2.555469	-0.426969
37	H	1.376616	5.940854	-1.157062
38	H	2.595483	3.874081	-0.701310
39	H	-2.342460	3.984940	-0.235834
40	H	-1.092807	6.045103	-0.836042
41	H	3.223722	1.870555	-1.140504
42	H	1.635252	-0.637311	2.911157
43	H	0.243005	1.143489	1.915423
44	H	5.755302	0.688430	-1.823446
45	H	7.790598	-0.731939	-1.829308
46	H	8.106522	-2.484031	-0.125198

47	H	6.382626	-2.867118	1.641810
48	H	-5.267421	1.821177	-0.385361
49	H	-7.628097	1.253309	0.135310
50	H	-8.175794	-0.945130	1.149771
51	H	-6.359078	-2.559673	1.649690
52	H	-4.019188	-1.995649	1.120013
53	H	-3.799329	-2.129171	-1.485105
54	H	-3.500098	-4.499455	-2.084281
55	H	-1.345785	-5.641784	-1.622987
56	H	0.518094	-4.381148	-0.571475
57	H	0.213416	-1.993597	0.028484

SCF Done: E(RmPW1PW91) = -1434.04889105 A.U.

Zero-point correction= 0.450724 (Hartree/Particle)
Thermal correction to Energy= 0.477054
Thermal correction to Enthalpy= 0.477998
Thermal correction to Gibbs Free Energy= 0.391889
Sum of electronic and zero-point Energies= -1433.605178
Sum of electronic and thermal Energies= -1433.578848
Sum of electronic and thermal Enthalpies= -1433.577904
Sum of electronic and thermal Free Energies= -1433.664013

Low frequencies --- -4.2883 -0.0008 0.0001 0.0010 2.2192 4.4654
Low frequencies --- 14.7686 17.6906 34.5831

The Result for the TDDFT calculation

Excited State 1: Singlet-A 1.2353 eV 1003.65 nm f=0.2018 <S**2>=0.000
119 ->121 -0.41572
120 ->121 0.59300
120 <-121 -0.18605
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1434.07900713
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State	2:	Singlet-A	1.5206 eV	815.35 nm	f=0.2712	<S**2>=0.000
119 ->121		0.56722				
120 ->121		0.44538				
120 <-121		-0.16768				
Excited State	3:	Singlet-A	2.2757 eV	544.82 nm	f=0.0963	<S**2>=0.000
117 ->121		-0.39380				
118 ->121		0.56679				
Excited State	4:	Singlet-A	2.4226 eV	511.77 nm	f=0.0411	<S**2>=0.000
112 ->121		0.30117				
115 ->121		0.21467				
116 ->121		-0.31226				
117 ->121		0.42697				
118 ->121		0.22153				
120 ->122		0.14562				
Excited State	5:	Singlet-A	2.4673 eV	502.52 nm	f=0.1005	<S**2>=0.000
112 ->121		0.18813				
115 ->121		0.35335				
116 ->121		-0.31174				
117 ->121		-0.35162				
118 ->121		-0.30606				
Excited State	6:	Singlet-A	2.5705 eV	482.33 nm	f=0.0024	<S**2>=0.000
113 ->121		0.69000				
Excited State	7:	Singlet-A	2.6257 eV	472.20 nm	f=0.0372	<S**2>=0.000
112 ->121		0.11799				
113 ->121		0.10230				
115 ->121		0.44686				
116 ->121		0.50564				
Excited State	8:	Singlet-A	2.8206 eV	439.57 nm	f=0.0457	<S**2>=0.000
111 ->121		0.14201				
112 ->121		0.53353				

114 ->121 0.19956
115 ->121 -0.30182
116 ->121 0.14905
120 ->122 -0.15204

Excited State 9: Singlet-A 2.8907 eV 428.91 nm f=0.0007 <S**2>=0.000
112 ->121 -0.18495
114 ->121 0.66787
116 ->121 -0.11069

Excited State 10: Singlet-A 3.0591 eV 405.30 nm f=0.0158 <S**2>=0.000
111 ->121 0.64231
112 ->121 -0.10621
120 ->122 0.21832

Excited State 11: Singlet-A 3.2521 eV 381.25 nm f=0.0173 <S**2>=0.000
109 ->121 0.14896
110 ->121 0.66689

Excited State 12: Singlet-A 3.4032 eV 364.32 nm f=0.2064 <S**2>=0.000
108 ->121 0.13011
109 ->121 0.30232
111 ->121 -0.11566
112 ->121 0.11659
117 ->121 -0.12908
120 ->122 0.51998
120 ->124 0.17815

Excited State 13: Singlet-A 3.5970 eV 344.69 nm f=0.1105 <S**2>=0.000
108 ->121 -0.22922
109 ->121 0.57469
110 ->121 -0.13111
111 ->121 0.14088
115 ->121 0.10150
120 ->122 -0.21486

Excited State 14:	Singlet-A	3.6751 eV	337.36 nm	f=0.0817	<S**2>=0.000
108 ->121	-0.16968				
120 ->123	-0.44891				
120 ->124	0.48088				
Excited State 15:	Singlet-A	3.7218 eV	333.13 nm	f=0.1039	<S**2>=0.000
120 ->123	0.52535				
120 ->124	0.44595				
Excited State 16:	Singlet-A	3.8695 eV	320.41 nm	f=0.1271	<S**2>=0.000
107 ->121	0.14230				
108 ->121	0.56276				
110 ->121	-0.10743				
111 ->121	0.10136				
119 ->122	0.23522				
120 ->122	-0.19533				
120 ->124	0.13088				
Excited State 17:	Singlet-A	3.9365 eV	314.96 nm	f=0.0188	<S**2>=0.000
107 ->121	0.65997				
108 ->121	-0.14581				
Excited State 18:	Singlet-A	4.0197 eV	308.44 nm	f=0.0359	<S**2>=0.000
119 ->122	0.17284				
120 ->125	0.65905				
Excited State 19:	Singlet-A	4.1423 eV	299.31 nm	f=0.2463	<S**2>=0.000
106 ->121	-0.11002				
108 ->121	-0.17717				
119 ->122	0.61244				
120 ->122	0.10666				
120 ->125	-0.18517				
Excited State 20:	Singlet-A	4.3043 eV	288.05 nm	f=0.0233	<S**2>=0.000
120 ->126	0.68913				

Table S9. Standard orientation of the optimized geometry for the closed form of ClC-tBuPh.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	-3.923981	-2.613601	-3.408946
2	C	-3.346658	-3.82439	-3.782724
3	C	-2.388599	-4.443373	-2.977681
4	C	-1.984794	-3.863085	-1.774049
5	C	-2.556624	-2.65867	-1.405259
6	C	-3.520545	-2.035644	-2.210314
7	C	-2.289448	-1.829388	-0.130423
8	N	-3.205225	-0.705612	-0.37697
9	C	-3.895323	-0.801796	-1.552502
10	C	-3.494841	0.525069	0.173377
11	C	-4.407149	1.089173	-0.721133
12	N	-4.633917	0.250439	-1.790358
13	C	-5.107438	2.377761	-0.645748
14	C	-2.83776	1.054829	1.376909
15	C	-2.134452	2.264928	1.303227
16	C	-1.49754	2.781518	2.424654
17	C	-1.544989	2.095164	3.635794
18	C	-2.242172	0.893852	3.720625
19	C	-2.889532	0.379774	2.602068
20	C	-5.583031	2.959383	-1.828637
21	C	-6.257771	4.173064	-1.801052
22	C	-6.474426	4.829327	-0.591837
23	C	-6.018418	4.253142	0.590591
24	C	-5.345772	3.036763	0.567197
25	C	-0.857215	-1.369041	-0.111874
26	C	-0.004462	-1.818001	0.818835
27	C	-0.451255	-2.713069	1.903985
28	C	-1.837569	-3.101752	1.984786
29	C	-2.703974	-2.65533	1.061784
30	C	1.416149	-1.631824	1.092241
31	C	1.656987	-2.407173	2.249049
32	N	0.49935	-3.051967	2.723203
33	C	2.438093	-0.929147	0.47951

34	C	3.732974	-0.988547	1.022867
35	C	3.952244	-1.761535	2.175121
36	C	2.92937	-2.474558	2.796322
37	C	4.846129	-0.250884	0.389092
38	C	6.130463	-0.796192	0.313336
39	C	7.176831	-0.101321	-0.284707
40	C	6.991516	1.168259	-0.836985
41	C	5.701447	1.710031	-0.759175
42	C	4.654848	1.022559	-0.16288
43	C	8.119078	1.961838	-1.500772
44	C	9.447643	1.199464	-1.492462
45	C	7.743977	2.258636	-2.962664
46	C	8.321551	3.287787	-0.747574
47	H	-4.667836	-2.126689	-4.029445
48	H	-3.645811	-4.293923	-4.714107
49	H	-1.951417	-5.38586	-3.289897
50	H	-1.240648	-4.34285	-1.146263
51	H	-2.093965	2.795052	0.357546
52	H	-0.956007	3.719164	2.350747
53	H	-1.04136	2.495689	4.509629
54	H	-2.288152	0.355895	4.661999
55	H	-3.445921	-0.547374	2.67901
56	H	-5.417836	2.438207	-2.764853
57	H	-6.616194	4.609073	-2.728542
58	H	-7.001118	5.778207	-0.570169
59	H	-6.196161	4.747223	1.540828
60	H	-5.016928	2.589585	1.4983
61	H	-0.56079	-0.699812	-0.914367
62	H	-2.154273	-3.734436	2.806943
63	H	-3.755908	-2.921325	1.092429
64	H	2.260047	-0.35669	-0.425751
65	H	4.947551	-1.781019	2.607319
66	H	3.112972	-3.060432	3.690052
67	H	6.311933	-1.793214	0.703278
68	H	8.150816	-0.575223	-0.323295
69	H	5.505941	2.698612	-1.164047

70	H	3.678081	1.492598	-0.098154
71	H	10.221583	1.803716	-1.975812
72	H	9.786559	0.983277	-0.474289
73	H	9.378078	0.253888	-2.039663
74	H	8.538381	2.834796	-3.449648
75	H	6.819803	2.839122	-3.03558
76	H	7.601104	1.331336	-3.526102
77	H	8.594142	3.106465	0.296668
78	H	9.123729	3.870597	-1.213367
79	H	7.416766	3.902305	-0.75435

SCF Done: E(RmPW1PW91) = -1822.32025535 A.U.

Zero-point correction= 0.648339 (Hartree/Particle)
Thermal correction to Energy= 0.684446
Thermal correction to Enthalpy= 0.685390
Thermal correction to Gibbs Free Energy= 0.577409
Sum of electronic and zero-point Energies= -1821.673421
Sum of electronic and thermal Energies= -1821.637314
Sum of electronic and thermal Enthalpies= -1821.636370
Sum of electronic and thermal Free Energies= -1821.744351

Low frequencies --- -5.3907 -0.4374 -0.0010 -0.0007 0.0007 2.8592
Low frequencies --- 11.5757 11.8730 22.5747

The Result for the TDDFT calculation

Excited State 1: Singlet-A 2.4540 eV 505.24 nm f=0.0020 <S**2>=0.000
156 -> 157 0.70187
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1822.32293672
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.7949 eV 443.60 nm f=0.1552 <S**2>=0.000
155 -> 157 0.69172

Excited State	3:	Singlet-A	3.6606 eV	338.70 nm	f=0.0474	<S**2>=0.000
153 -> 157		0.56876				
154 -> 157		0.14156				
155 -> 158		0.16690				
156 -> 158		0.30528				
Excited State	4:	Singlet-A	3.6827 eV	336.67 nm	f=0.1352	<S**2>=0.000
153 -> 157		-0.28126				
156 -> 158		0.62447				
Excited State	5:	Singlet-A	3.8331 eV	323.46 nm	f=0.0052	<S**2>=0.000
146 -> 157		0.33203				
147 -> 157		0.17912				
152 -> 157		0.41932				
154 -> 157		-0.40319				
Excited State	6:	Singlet-A	3.9388 eV	314.77 nm	f=0.0032	<S**2>=0.000
146 -> 157		0.52084				
147 -> 157		0.21704				
150 -> 157		-0.11984				
152 -> 157		-0.17067				
154 -> 157		0.30630				
Excited State	7:	Singlet-A	3.9655 eV	312.66 nm	f=0.0700	<S**2>=0.000
150 -> 157		-0.19286				
151 -> 157		0.48883				
154 -> 157		-0.25854				
155 -> 158		0.29374				
155 -> 159		0.10569				
Excited State	8:	Singlet-A	3.9877 eV	310.92 nm	f=0.0855	<S**2>=0.000
146 -> 157		0.11242				
149 -> 157		0.14866				
151 -> 157		-0.13342				
152 -> 157		-0.32600				
154 -> 157		-0.18803				

155 -> 158 -0.14300
156 -> 159 0.49950

Excited State 9: Singlet-A 3.9957 eV 310.30 nm f=0.0993 <S**2>=0.000
148 -> 157 0.12410
151 -> 157 0.12155
152 -> 157 0.36170
153 -> 157 -0.15446
154 -> 157 0.28107
156 -> 159 0.44671
156 -> 160 0.10439

Excited State 10: Singlet-A 4.0912 eV 303.05 nm f=0.4005 <S**2>=0.000
149 -> 157 0.17689
151 -> 157 -0.12749
155 -> 158 0.10564
156 -> 160 0.63228

Excited State 11: Singlet-A 4.1372 eV 299.68 nm f=0.0343 <S**2>=0.000
148 -> 157 0.33626
149 -> 157 0.47540
150 -> 157 0.18217
155 -> 158 0.21679
156 -> 160 -0.23595

Excited State 12: Singlet-A 4.1671 eV 297.53 nm f=0.0226 <S**2>=0.000
150 -> 157 0.58430
151 -> 157 0.33286
155 -> 158 -0.14077

Excited State 13: Singlet-A 4.2011 eV 295.12 nm f=0.0359 <S**2>=0.000
148 -> 157 0.49906
149 -> 157 -0.40972
152 -> 157 -0.14546
154 -> 157 -0.17215
155 -> 158 0.11940

Excited State 14:	Singlet-A	4.2647 eV	290.72 nm	f=0.3910	<S**2>=0.000
148 -> 157	-0.29459				
149 -> 157	-0.16027				
150 -> 157	0.22202				
151 -> 157	-0.22756				
153 -> 157	-0.12491				
155 -> 158	0.47683				
Excited State 15:	Singlet-A	4.3468 eV	285.23 nm	f=0.0011	<S**2>=0.000
146 -> 157	-0.25624				
147 -> 157	0.62980				
Excited State 16:	Singlet-A	4.3925 eV	282.27 nm	f=0.0367	<S**2>=0.000
155 -> 159	-0.13007				
156 -> 161	-0.27562				
156 -> 162	0.59652				
156 -> 163	0.13446				
Excited State 17:	Singlet-A	4.4469 eV	278.81 nm	f=0.0505	<S**2>=0.000
155 -> 159	0.37230				
156 -> 161	0.38574				
156 -> 162	0.18971				
156 -> 163	0.36232				
Excited State 18:	Singlet-A	4.4605 eV	277.96 nm	f=0.1672	<S**2>=0.000
155 -> 159	0.51976				
156 -> 161	-0.35744				
156 -> 163	-0.16889				
Excited State 19:	Singlet-A	4.7074 eV	263.38 nm	f=0.0271	<S**2>=0.000
155 -> 159	-0.12718				
155 -> 160	0.65532				
155 -> 161	-0.18158				
Excited State 20:	Singlet-A	4.7508 eV	260.98 nm	f=0.0614	<S**2>=0.000

142 -> 157	-0.16082
155 -> 160	-0.16425
155 -> 161	-0.37503
156 -> 161	-0.25515
156 -> 162	-0.20747
156 -> 163	0.38695

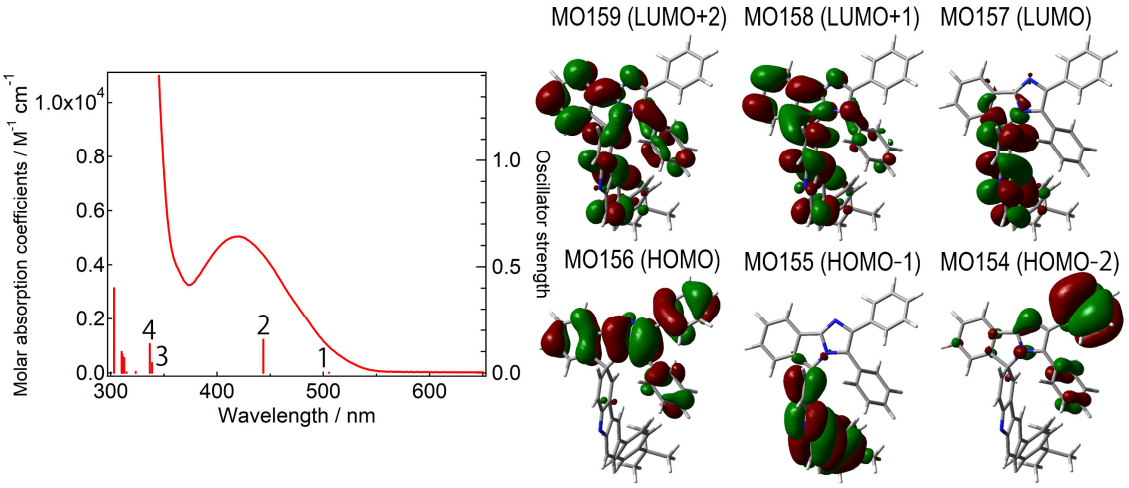


Fig. S65. UV-vis absorption spectrum of CIC-tBuPh in benzene at room temperature. The calculated absorption spectrum MPW1PW91/6-31+G(d,p)//MPW1PW91/6-31G(d) level of the theory) is shown by the red vertical lines. The relevant molecular orbitals of the CIC-tBuPh calculated at the MPW1PW91/6-31G(d) level of the theory.

Table S10. Selected calculated electronic transition of ClC-tBuPh at the MPW1PW91/6-31G(d) level.

No.	Wavelength (nm)	Coefficients	Electronic Transition			*f*
1	505.24	0.70187	156 HOMO	→	157 LUMO	0.0020
2	443.60	0.69172	155 HOMO-1	→	157 LUMO	0.1552
3	338.70	0.56876	153 HOMO-3	→	157 LUMO	0.0474
		0.14156	154 HOMO-2	→	157 LUMO	
		0.16690	155 HOMO-1	→	158 LUMO+1	
		0.30528	156 HOMO	→	158 LUMO+1	
4	336.67	-0.28126	153 HOMO-3	→	157 LUMO	0.1352
		0.62447	156 HOMO	→	158 LUMO+1	

Table S11. Standard orientation of the optimized geometry for the singlet biradical form 1 of the ring-opening form of ClC-tBuPh.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	1.714725	5.194753	0.22979
2	C	1.118423	4.040013	0.718707
3	C	1.777911	2.804047	0.710019
4	C	3.074831	2.741798	0.131154
5	C	3.676377	3.930465	-0.329054
6	C	3.011219	5.141649	-0.282257
7	C	3.800235	1.510484	-0.111954
8	C	1.097747	1.673509	1.375441
9	N	3.238284	0.273883	-0.079906
10	C	4.227222	-0.551085	-0.396199
11	C	5.429914	0.264227	-0.675194
12	N	5.120999	1.53377	-0.468386
13	C	6.753346	-0.111039	-1.163336
14	C	4.028055	-1.994164	-0.371944
15	C	-0.249983	1.393428	1.056178
16	C	-0.907286	0.389219	1.730719
17	C	-0.24722	-0.346268	2.762279
18	C	1.082989	-0.054989	3.094547
19	C	1.738954	0.944234	2.394775

20	C	-2.24865	-0.185025	1.673661
21	C	-2.241963	-1.200886	2.675334
22	N	-1.042131	-1.29755	3.332705
23	C	-3.373282	0.047269	0.914912
24	C	-4.532855	-0.733952	1.132869
25	C	-4.512163	-1.732621	2.122622
26	C	-3.383012	-1.975341	2.896391
27	C	5.069134	-2.894689	-0.094164
28	C	4.819692	-4.259781	-0.028367
29	C	3.533184	-4.749044	-0.23968
30	C	2.488293	-3.862416	-0.500308
31	C	2.728906	-2.498624	-0.557018
32	C	7.853735	0.692455	-0.822342
33	C	9.120427	0.393439	-1.300973
34	C	9.310935	-0.700363	-2.144759
35	C	8.223589	-1.490065	-2.50945
36	C	6.954297	-1.202146	-2.022693
37	C	-5.746131	-0.499732	0.328568
38	C	-6.116147	0.788083	-0.072618
39	C	-7.262602	1.00919	-0.828033
40	C	-8.092742	-0.042999	-1.22296
41	C	-7.716662	-1.33209	-0.820524
42	C	-6.577134	-1.558631	-0.064758
43	C	-9.359046	0.160976	-2.057209
44	C	-9.603201	1.635796	-2.390469
45	C	-9.229283	-0.615078	-3.379223
46	C	-10.576145	-0.363041	-1.27605
47	H	1.17772	6.137047	0.268952
48	H	0.132503	4.095383	1.169042
49	H	4.671038	3.856015	-0.752207
50	H	3.492767	6.040263	-0.653374
51	H	-0.735448	1.955295	0.263652
52	H	1.576128	-0.607202	3.886749
53	H	2.76631	1.187042	2.641399
54	H	-3.375382	0.797999	0.130546
55	H	-5.414874	-2.305712	2.305858

56	H	-3.379689	-2.739856	3.66561
57	H	6.068279	-2.521726	0.098604
58	H	5.631842	-4.942977	0.198281
59	H	3.34219	-5.816317	-0.190933
60	H	1.481761	-4.238006	-0.653069
61	H	1.923819	-1.796491	-0.740052
62	H	7.688952	1.547395	-0.176621
63	H	9.963715	1.015657	-1.018838
64	H	10.302087	-0.93126	-2.521862
65	H	8.361886	-2.330354	-3.182112
66	H	6.109732	-1.808311	-2.330051
67	H	-5.516194	1.638279	0.23709
68	H	-7.508327	2.028871	-1.101032
69	H	-8.32166	-2.185773	-1.110812
70	H	-6.308152	-2.576398	0.200203
71	H	-10.51584	1.731408	-2.986907
72	H	-9.734564	2.240906	-1.487735
73	H	-8.781483	2.062526	-2.974404
74	H	-10.132102	-0.484219	-3.985673
75	H	-9.094315	-1.687164	-3.210157
76	H	-8.373647	-0.257952	-3.960579
77	H	-10.698979	0.1786	-0.333074
78	H	-11.490082	-0.232653	-1.86578
79	H	-10.481855	-1.426823	-1.040188

SCF Done: E(UmPW1PW91) = -1822.29313386 A.U.

Zero-point correction	=	0.644776 (Hartree/Particle)
Thermal correction to Energy	=	0.681555
Thermal correction to Enthalpy	=	0.682500
Thermal correction to Gibbs Free Energy	=	0.572100
Sum of electronic and zero-point Energies	=	-1821.651627
Sum of electronic and thermal Energies	=	-1821.614847
Sum of electronic and thermal Enthalpies	=	-1821.613903
Sum of electronic and thermal Free Energies	=	-1821.724302

Low frequencies --- -2.1180 -1.5536 -0.0021 0.0008 0.0015 4.4169

Low frequencies --- 8.5222 10.7272 21.4269

The Result for the TDDFT calculation

Excited State 1: 3.000-A -0.5911 eV -2097.43 nm f=-0.0000 <S**2>=2.000

156A -> 157A 0.75829

156B -> 157B -0.75829

156A <- 157A -0.29353

156B <- 157B 0.29353

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1822.38998210

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 3.000-A 0.6774 eV 1830.31 nm f=0.0000 <S**2>=2.000

155A -> 157A 0.69843

155B -> 157B -0.69843

155A <- 157A 0.10883

155B <- 157B -0.10883

Excited State 3: 1.000-A 0.7922 eV 1565.15 nm f=0.2347 <S**2>=0.000

155A -> 157A 0.25506

156A -> 157A 0.75640

155B -> 157B 0.25506

156B -> 157B 0.75640

156A <- 157A -0.38678

156B <- 157B -0.38678

Excited State 4: 1.000-A 1.1194 eV 1107.59 nm f=0.0752 <S**2>=0.000

154A -> 157A 0.11563

155A -> 157A 0.64241

156A -> 157A -0.32539

154B -> 157B 0.11563

155B -> 157B 0.64241

156B -> 157B -0.32539

156A <- 157A 0.19256

156B <- 157B 0.19256

Excited State 5: 3.000-A 1.5875 eV 781.01 nm f=0.0000 <S**2>=2.000
149A -> 157A 0.11250
152A -> 157A 0.10769
153A -> 157A -0.10534
154A -> 157A 0.65524
149B -> 157B -0.11250
152B -> 157B -0.10769
153B -> 157B 0.10534
154B -> 157B -0.65524

Excited State 6: 3.000-A 1.6415 eV 755.31 nm f=0.0000 <S**2>=2.000
152A -> 157A 0.21043
153A -> 157A 0.64901
152B -> 157B -0.21043
153B -> 157B -0.64901

Excited State 7: 3.000-A 1.8999 eV 652.58 nm f=0.0000 <S**2>=2.000
147A -> 157A -0.13207
152A -> 157A 0.63029
153A -> 157A -0.18162
154A -> 157A -0.10532
147B -> 157B 0.13207
152B -> 157B -0.63029
153B -> 157B 0.18162
154B -> 157B 0.10532

Excited State 8: 1.000-A 1.9655 eV 630.82 nm f=0.0229 <S**2>=0.000
153A -> 157A 0.50711
154A -> 157A -0.47695
153B -> 157B 0.50711
154B -> 157B -0.47695

Excited State 9: 3.000-A 1.9976 eV 620.67 nm f=0.0000 <S**2>=2.000
146A -> 157A 0.66799

147A -> 157A -0.17148
146B -> 157B -0.66799
147B -> 157B 0.17148

Excited State 10: 1.000-A 2.0888 eV 593.57 nm f=0.2083 <S**2>=0.000
153A -> 157A 0.47089
154A -> 157A 0.48795
155A -> 157A -0.13724
153B -> 157B 0.47089
154B -> 157B 0.48795
155B -> 157B -0.13724

Excited State 11: 3.000-A 2.1361 eV 580.42 nm f=0.0000 <S**2>=2.000
146A -> 157A -0.12167
147A -> 157A -0.24489
149A -> 157A 0.50187
151A -> 157A -0.35991
146B -> 157B 0.12167
147B -> 157B 0.24489
149B -> 157B -0.50187
151B -> 157B 0.35991

Excited State 12: 3.000-A 2.1603 eV 573.92 nm f=0.0000 <S**2>=2.000
147A -> 157A 0.35055
149A -> 157A 0.42376
151A -> 157A 0.38563
147B -> 157B -0.35055
149B -> 157B -0.42376
151B -> 157B -0.38563

Excited State 13: 1.000-A 2.1817 eV 568.30 nm f=0.0339 <S**2>=0.000
147A -> 157A -0.39555
151A -> 157A -0.30919
152A -> 157A 0.46493
147B -> 157B -0.39555
151B -> 157B -0.30919

152B -> 157B 0.46493

Excited State 14: 3.000-A 2.3132 eV 535.98 nm f=0.0000 <S**2>=2.000
146A -> 157A 0.10187
147A -> 157A 0.47891
148A -> 157A 0.23606
151A -> 157A -0.42679
146B -> 157B -0.10187
147B -> 157B -0.47891
148B -> 157B -0.23606
151B -> 157B 0.42679

Excited State 15: 1.000-A 2.3820 eV 520.52 nm f=0.0144 <S**2>=0.000
146A -> 157A 0.64471
147A -> 157A -0.13099
150A -> 157A -0.11176
151A -> 157A -0.18571
152A -> 157A -0.12017
146B -> 157B 0.64471
147B -> 157B -0.13099
150B -> 157B -0.11176
151B -> 157B -0.18571
152B -> 157B -0.12017

Excited State 16: 1.000-A 2.3979 eV 517.04 nm f=0.0346 <S**2>=0.000
146A -> 157A 0.18203
147A -> 157A -0.18276
148A -> 157A -0.15288
151A -> 157A 0.58485
152A -> 157A 0.24494
146B -> 157B 0.18203
147B -> 157B -0.18276
148B -> 157B -0.15288
151B -> 157B 0.58485
152B -> 157B 0.24494

Excited State 17:	1.000-A	2.4709 eV	501.77 nm	f=0.0365	<S**2>=0.000
145A -> 157A	0.17445				
149A -> 157A	0.65755				
145B -> 157B	0.17445				
149B -> 157B	0.65755				
Excited State 18:	3.000-A	2.4914 eV	497.65 nm	f=0.0000	<S**2>=2.000
145A -> 157A	-0.17309				
147A -> 157A	-0.15187				
148A -> 157A	0.62539				
151A -> 157A	0.16702				
145B -> 157B	0.17309				
147B -> 157B	0.15187				
148B -> 157B	-0.62539				
151B -> 157B	-0.16702				
Excited State 19:	3.000-A	2.5174 eV	492.50 nm	f=0.0000	<S**2>=2.000
145A -> 157A	0.20467				
148A -> 157A	0.13985				
150A -> 157A	0.64665				
145B -> 157B	-0.20467				
148B -> 157B	-0.13985				
150B -> 157B	-0.64665				
Excited State 20:	1.000-A	2.5369 eV	488.72 nm	f=0.1167	<S**2>=0.000
146A -> 157A	0.14274				
147A -> 157A	0.46859				
148A -> 157A	0.21169				
150A -> 157A	-0.13561				
152A -> 157A	0.40413				
156A -> 158A	-0.13784				
146B -> 157B	0.14274				
147B -> 157B	0.46859				
148B -> 157B	0.21169				
150B -> 157B	-0.13561				
152B -> 157B	0.40413				

156B -> 158B -0.13784

Table S12. Standard orientation of the optimized geometry for the singlet biradical form 2 of the ring-opening form of ClC-tBuPh.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	5.224937	-2.914064	-3.406164
2	C	4.345041	-3.303982	-2.405935
3	C	3.687718	-2.372682	-1.590508
4	C	3.983948	-0.993613	-1.778504
5	C	4.856386	-0.616693	-2.820272
6	C	5.469437	-1.557816	-3.625418
7	C	3.525244	0.065153	-0.902967
8	C	2.683496	-2.896515	-0.643451
9	N	2.951178	-0.140356	0.311386
10	C	2.723155	1.076736	0.786325
11	C	3.243064	2.052736	-0.196015
12	N	3.712191	1.379964	-1.233754
13	C	3.356661	3.507074	-0.137871
14	C	2.017539	1.260382	2.047833
15	C	1.363939	-2.381828	-0.634986
16	C	0.425655	-2.959064	0.183931
17	C	0.769673	-4.057267	1.033194
18	C	2.072806	-4.566560	1.029743
19	C	3.008893	-3.986759	0.182030
20	C	-0.988725	-2.722437	0.453631
21	C	-1.334213	-3.704490	1.429959
22	N	-0.280524	-4.505561	1.781099
23	C	-1.929408	-1.831771	-0.012028
24	C	-3.252298	-1.895825	0.482767
25	C	-3.581090	-2.871120	1.443313
26	C	-2.641104	-3.773541	1.923003
27	C	1.239851	2.397488	2.320277
28	C	0.542212	2.502561	3.517092
29	C	0.608388	1.479844	4.459883
30	C	1.364282	0.338342	4.192756

31	C	2.054889	0.223439	2.996612
32	C	3.350705	4.235987	-1.338386
33	C	3.498918	5.614814	-1.326759
34	C	3.675350	6.290970	-0.119933
35	C	3.707701	5.576488	1.074697
36	C	3.548061	4.196062	1.069583
37	C	-4.271000	-0.948327	-0.004748
38	C	-3.941008	0.373686	-0.321620
39	C	-4.900652	1.267925	-0.783247
40	C	-6.234408	0.887809	-0.952663
41	C	-6.560696	-0.437440	-0.632419
42	C	-5.609189	-1.333372	-0.170722
43	C	-7.316189	1.842619	-1.461467
44	C	-6.761750	3.237218	-1.767253
45	C	-7.931283	1.276900	-2.753244
46	C	-8.414698	1.984288	-0.393822
47	H	5.701356	-3.665479	-4.027629
48	H	4.114425	-4.356127	-2.274725
49	H	5.054684	0.440779	-2.947357
50	H	6.144196	-1.241441	-4.413885
51	H	1.112190	-1.554860	-1.290038
52	H	2.334233	-5.394604	1.679450
53	H	4.027886	-4.359775	0.174128
54	H	-1.678322	-1.100598	-0.774079
55	H	-4.590080	-2.893909	1.841343
56	H	-2.900033	-4.513721	2.672210
57	H	1.161040	3.186877	1.581847
58	H	-0.062955	3.382557	3.709703
59	H	0.064577	1.566073	5.395129
60	H	1.408252	-0.466724	4.918961
61	H	2.631010	-0.665494	2.767401
62	H	3.226373	3.696253	-2.270183
63	H	3.480146	6.166551	-2.261174
64	H	3.794911	7.369652	-0.112449
65	H	3.865678	6.094346	2.015180
66	H	3.598325	3.645076	2.001773

67	H	-2.922758	0.720933	-0.176195
68	H	-4.591135	2.282720	-1.004824
69	H	-7.581602	-0.786483	-0.754722
70	H	-5.900325	-2.358603	0.035378
71	H	-7.567430	3.881718	-2.132294
72	H	-6.338183	3.711657	-0.876296
73	H	-5.988371	3.205987	-2.541345
74	H	-8.712949	1.947665	-3.126301
75	H	-8.385342	0.294967	-2.592631
76	H	-7.172384	1.170194	-3.534454
77	H	-8.006513	2.394758	0.534971
78	H	-9.202951	2.657948	-0.747223
79	H	-8.879305	1.022635	-0.158143

SCF Done: E(UmPW1PW91) = -1822.29703735 A.U.

Zero-point correction= 0.644930 (Hartree/Particle)
Thermal correction to Energy= 0.681686
Thermal correction to Enthalpy= 0.682630
Thermal correction to Gibbs Free Energy= 0.572194
Sum of electronic and zero-point Energies= -1821.652528
Sum of electronic and thermal Energies= -1821.615772
Sum of electronic and thermal Enthalpies= -1821.614828
Sum of electronic and thermal Free Energies= -1821.725264

Low frequencies --- -2.5160 -0.0008 0.0005 0.0006 2.5289 4.0293
Low frequencies --- 7.3850 11.7970 17.1205

The Result for the TDDFT calculation

Excited State 1: 3.000-A -0.6260 eV -1980.57 nm f=-0.0000 <S**2>=2.000
156A -> 157A 0.73798
156B -> 157B -0.73798
156A <- 157A -0.23341
156B <- 157B 0.23341
This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1822.39533341

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 3.000-A 0.8351 eV 1484.74 nm f=0.0000 <S**2>=2.000

155A -> 157A 0.69821

155B -> 157B -0.69821

Excited State 3: 1.000-A 0.9068 eV 1367.34 nm f=0.2087 <S**2>=0.000

155A -> 157A 0.10957

156A -> 157A 0.78068

155B -> 157B 0.10957

156B -> 157B 0.78068

156A <- 157A -0.36975

156B <- 157B -0.36975

Excited State 4: 1.000-A 1.1954 eV 1037.21 nm f=0.0314 <S**2>=0.000

154A -> 157A 0.16672

155A -> 157A 0.66902

156A -> 157A -0.14846

154B -> 157B 0.16672

155B -> 157B 0.66902

156B -> 157B -0.14846

Excited State 5: 3.000-A 1.4028 eV 883.83 nm f=0.0000 <S**2>=2.000

152A -> 157A -0.12104

154A -> 157A 0.67927

152B -> 157B 0.12104

154B -> 157B -0.67927

Excited State 6: 3.000-A 1.7169 eV 722.14 nm f=0.0000 <S**2>=2.000

153A -> 157A 0.67951

153B -> 157B -0.67951

Excited State 7: 1.000-A 1.9057 eV 650.61 nm f=0.1755 <S**2>=0.000

153A -> 157A 0.12889

154A -> 157A 0.65430

155A -> 157A -0.14964
153B -> 157B 0.12889
154B -> 157B 0.65430
155B -> 157B -0.14964

Excited State 8: 3.000-A 1.9866 eV 624.09 nm f=0.0000 <S**2>=2.000
145A -> 157A -0.12634
152A -> 157A 0.65582
154A -> 157A 0.10574
145B -> 157B 0.12634
152B -> 157B -0.65582
154B -> 157B -0.10574

Excited State 9: 1.000-A 2.0366 eV 608.77 nm f=0.0436 <S**2>=0.000
147A -> 157A 0.15113
153A -> 157A 0.66005
147B -> 157B 0.15113
153B -> 157B 0.66005

Excited State 10: 3.000-A 2.0739 eV 597.84 nm f=0.0000 <S**2>=2.000
146A -> 157A 0.68522
146B -> 157B -0.68522

Excited State 11: 3.000-A 2.1744 eV 570.21 nm f=0.0000 <S**2>=2.000
147A -> 157A -0.14318
149A -> 157A 0.56168
150A -> 157A -0.14388
151A -> 157A -0.30089
147B -> 157B 0.14318
149B -> 157B -0.56168
150B -> 157B 0.14388
151B -> 157B 0.30089

Excited State 12: 3.000-A 2.1993 eV 563.75 nm f=0.0000 <S**2>=2.000
147A -> 157A 0.41985
149A -> 157A 0.31341

151A -> 157A 0.44636
147B -> 157B -0.41985
149B -> 157B -0.31341
151B -> 157B -0.44636

Excited State 13: 1.000-A 2.3210 eV 534.17 nm f=0.0322 <S**2>=0.000
147A -> 157A 0.28482
149A -> 157A 0.21228
151A -> 157A 0.39691
152A -> 157A 0.40238
153A -> 157A -0.13767
154A -> 157A 0.11302
147B -> 157B 0.28482
149B -> 157B 0.21228
151B -> 157B 0.39691
152B -> 157B 0.40238
153B -> 157B -0.13767
154B -> 157B 0.11302

Excited State 14: 3.000-A 2.3493 eV 527.75 nm f=0.0000 <S**2>=2.000
147A -> 157A 0.49557
148A -> 157A 0.22676
151A -> 157A -0.41853
147B -> 157B -0.49557
148B -> 157B -0.22676
151B -> 157B 0.41853

Excited State 15: 1.000-A 2.4298 eV 510.26 nm f=0.0330 <S**2>=0.000
146A -> 157A 0.13652
147A -> 157A -0.14996
148A -> 157A -0.15329
151A -> 157A 0.54215
152A -> 157A -0.34942
146B -> 157B 0.13652
147B -> 157B -0.14996
148B -> 157B -0.15329

151B -> 157B 0.54215
152B -> 157B -0.34942

Excited State 16: 1.000-A 2.4610 eV 503.79 nm f=0.0066 <S**2>=0.000
146A -> 157A 0.64246
149A -> 157A 0.24640
151A -> 157A -0.10394
146B -> 157B 0.64246
149B -> 157B 0.24640
151B -> 157B -0.10394

Excited State 17: 3.000-A 2.5226 eV 491.49 nm f=0.0000 <S**2>=2.000
145A -> 157A 0.16726
148A -> 157A -0.22330
149A -> 157A 0.14253
150A -> 157A 0.61905
145B -> 157B -0.16726
148B -> 157B 0.22330
149B -> 157B -0.14253
150B -> 157B -0.61905

Excited State 18: 1.000-A 2.5278 eV 490.49 nm f=0.0641 <S**2>=0.000
145A -> 157A 0.12637
146A -> 157A -0.17444
149A -> 157A 0.53355
150A -> 157A -0.29658
152A -> 157A -0.24224
145B -> 157B 0.12637
146B -> 157B -0.17444
149B -> 157B 0.53355
150B -> 157B -0.29658
152B -> 157B -0.24224

Excited State 19: 3.000-A 2.5377 eV 488.58 nm f=0.0000 <S**2>=2.000
145A -> 157A -0.16017
147A -> 157A -0.16687

148A -> 157A	0.58015				
150A -> 157A	0.26272				
151A -> 157A	0.13951				
145B -> 157B	0.16017				
147B -> 157B	0.16687				
148B -> 157B	-0.58015				
150B -> 157B	-0.26272				
151B -> 157B	-0.13951				

Excited State 20:	1.000-A	2.5720 eV	482.06 nm	f=0.0732	<S**2>=0.000
147A -> 157A	0.51827				
148A -> 157A	0.23536				
152A -> 157A	-0.34167				
156A -> 158A	0.13995				
147B -> 157B	0.51827				
148B -> 157B	0.23536				
152B -> 157B	-0.34167				
156B -> 158B	0.13995				

Table S13. Standard orientation of the optimized geometry for the triplet biradical form of the ring-opening form of ClC-tBuPh.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	1.883722	5.295867	0.453262
2	C	1.283715	4.164391	0.995932
3	C	1.866418	2.897765	0.8965
4	C	3.091194	2.774911	0.189365
5	C	3.692684	3.934306	-0.338509
6	C	3.103158	5.179577	-0.209417
7	C	3.749422	1.511784	-0.093026
8	C	1.159035	1.782709	1.577145
9	N	3.209713	0.293754	0.158185
10	C	4.121693	-0.572914	-0.265862
11	C	5.243575	0.1968	-0.847026
12	N	4.979635	1.48358	-0.694105
13	C	6.443086	-0.240478	-1.554284

14	C	3.940807	-2.00131	-0.050626
15	C	-0.163169	1.476761	1.196453
16	C	-0.846737	0.489824	1.875469
17	C	-0.233835	-0.200097	2.961304
18	C	1.071478	0.117014	3.35226
19	C	1.752852	1.103904	2.65303
20	C	-2.17876	-0.098265	1.772688
21	C	-2.213501	-1.082751	2.807288
22	N	-1.051736	-1.146133	3.524958
23	C	-3.266361	0.098453	0.952959
24	C	-4.429265	-0.686365	1.138982
25	C	-4.449969	-1.654945	2.160025
26	C	-3.35982	-1.86211	2.995271
27	C	5.021631	-2.889299	0.078176
28	C	4.799067	-4.23517	0.339505
29	C	3.499879	-4.718063	0.476207
30	C	2.419332	-3.842295	0.36817
31	C	2.634954	-2.496585	0.116718
32	C	7.589932	0.569055	-1.512814
33	C	8.733619	0.207318	-2.208771
34	C	8.749405	-0.958105	-2.974557
35	C	7.610439	-1.756141	-3.04305
36	C	6.465672	-1.404059	-2.338572
37	C	-5.603322	-0.486208	0.270679
38	C	-5.956142	0.78565	-0.192719
39	C	-7.066091	0.976484	-1.008154
40	C	-7.875387	-0.091483	-1.404167
41	C	-7.516388	-1.364567	-0.939823
42	C	-6.413417	-1.560972	-0.123782
43	C	-9.102842	0.080198	-2.301119
44	C	-9.333223	1.54225	-2.695137
45	C	-8.913434	-0.741116	-3.588175
46	C	-10.352978	-0.41972	-1.557051
47	H	1.404494	6.263891	0.559048
48	H	0.349501	4.259753	1.5403
49	H	4.627905	3.813487	-0.871835

50	H	3.586196	6.054833	-0.63106
51	H	-0.613078	2.009689	0.363997
52	H	1.53091	-0.405391	4.184029
53	H	2.767437	1.360982	2.936193
54	H	-3.23587	0.823983	0.145858
55	H	-5.356345	-2.230102	2.316543
56	H	-3.388329	-2.60196	3.787776
57	H	6.036992	-2.518287	0.002865
58	H	5.644146	-4.907476	0.447019
59	H	3.329189	-5.770849	0.677387
60	H	1.405899	-4.21112	0.488081
61	H	1.806728	-1.800777	0.050188
62	H	7.559585	1.478707	-0.924057
63	H	9.616861	0.83592	-2.157504
64	H	9.644075	-1.238421	-3.521275
65	H	7.609672	-2.653236	-3.653708
66	H	5.575631	-2.018217	-2.416079
67	H	-5.372958	1.648156	0.114755
68	H	-7.300197	1.985196	-1.327876
69	H	-8.106186	-2.229524	-1.227875
70	H	-6.155824	-2.56805	0.188872
71	H	-10.219408	1.616181	-3.333013
72	H	-9.503339	2.177398	-1.819902
73	H	-8.487239	1.950409	-3.2573
74	H	-9.787477	-0.632805	-4.239628
75	H	-8.786716	-1.806602	-3.376128
76	H	-8.03206	-0.403437	-4.142053
77	H	-10.516408	0.151754	-0.638157
78	H	-11.240465	-0.309153	-2.189672
79	H	-10.269356	-1.475372	-1.283536

SCF Done: E(UmPW1PW91) = -1822.29303015 A.U.

Zero-point correction = 0.644805 (Hartree/Particle)
Thermal correction to Energy = 0.681606
Thermal correction to Enthalpy = 0.682550

Thermal correction to Gibbs Free Energy = 0.570814
Sum of electronic and zero-point Energies = -1821.650688
Sum of electronic and thermal Energies = -1821.613886
Sum of electronic and thermal Enthalpies = -1821.612942
Sum of electronic and thermal Free Energies = -1821.724679

Low frequencies --- -0.0015 -0.0007 0.0002 0.9419 2.5594 5.8260
Low frequencies --- 7.0209 10.4020 19.1453

The Result for the TDDFT calculation

Excited State 1: 3.075-A 1.2289 eV 1008.92 nm f=0.0354 <S**2>=2.114
154B -> 157B -0.15343
155B -> 156B -0.49775
155B -> 157B 0.82837
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1822.34177046
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 3.051-A 1.6582 eV 747.71 nm f=0.0131 <S**2>=2.077
145B -> 156B 0.16124
152B -> 156B 0.14130
153B -> 156B -0.17060
154B -> 156B -0.10844
155B -> 156B 0.80263
155B -> 157B 0.47924

Excited State 3: 3.085-A 1.9838 eV 624.97 nm f=0.0364 <S**2>=2.130
141B -> 156B 0.13850
142B -> 156B -0.14432
152B -> 156B 0.24069
153B -> 156B 0.82555
153B -> 157B 0.23873
154B -> 156B 0.23017
155B -> 156B 0.14950

Excited State 4:	3.055-A	2.0924 eV	592.54 nm	f=0.0009	<S**2>=2.083
145B -> 157B	-0.10711				
146B -> 156B	-0.38596				
146B -> 157B	0.85857				
147B -> 157B	-0.19042				
Excited State 5:	3.080-A	2.1920 eV	565.62 nm	f=0.1945	<S**2>=2.122
151B -> 157B	0.11660				
152B -> 156B	-0.16457				
153B -> 156B	0.17642				
154B -> 156B	-0.52626				
154B -> 157B	0.73783				
155B -> 157B	0.15337				
Excited State 6:	3.067-A	2.3116 eV	536.36 nm	f=0.0229	<S**2>=2.102
144B -> 156B	-0.17641				
145B -> 156B	0.46484				
145B -> 157B	0.13706				
147B -> 156B	-0.23151				
149B -> 156B	-0.32654				
149B -> 157B	-0.10027				
151B -> 156B	-0.20218				
152B -> 156B	0.58886				
153B -> 156B	-0.13531				
154B -> 156B	-0.14943				
155B -> 156B	-0.24334				
Excited State 7:	3.102-A	2.4640 eV	503.17 nm	f=0.0597	<S**2>=2.156
156A -> 159A	-0.10556				
157A -> 159A	-0.12199				
145B -> 156B	-0.29309				
145B -> 157B	-0.10055				
147B -> 156B	0.23555				
149B -> 156B	0.20445				
151B -> 156B	-0.22978				
152B -> 156B	0.40627				

153B -> 156B -0.22414
154B -> 156B 0.46167
154B -> 157B 0.45920

Excited State 8: 3.085-A 2.5286 eV 490.33 nm f=0.0613 <S**2>=2.129
144B -> 156B -0.15356
145B -> 156B 0.23005
147B -> 156B -0.16457
149B -> 156B -0.31783
151B -> 156B 0.44133
151B -> 157B 0.16997
152B -> 156B -0.20648
153B -> 156B -0.13759
153B -> 157B -0.10151
154B -> 156B 0.56898
154B -> 157B 0.30867

Excited State 9: 3.096-A 2.6439 eV 468.94 nm f=0.0326 <S**2>=2.146
145B -> 156B 0.10230
147B -> 156B 0.21727
147B -> 157B 0.11402
148B -> 156B 0.20604
149B -> 156B 0.28251
151B -> 156B 0.69430
152B -> 156B 0.34955
152B -> 157B -0.23252
153B -> 157B 0.12711
154B -> 156B -0.19103

Excited State 10: 3.086-A 2.6850 eV 461.76 nm f=0.0017 <S**2>=2.131
144B -> 156B -0.12371
145B -> 156B 0.34575
147B -> 156B -0.39422
147B -> 157B -0.10899
149B -> 156B 0.74735
149B -> 157B 0.17950

150B -> 156B -0.10618
152B -> 157B 0.10290
154B -> 156B 0.12077

Excited State 11: 3.117-A 2.7609 eV 449.07 nm f=0.0229 <S**2>=2.179
156A -> 161A 0.10048
147B -> 156B 0.29868
148B -> 156B 0.31684
151B -> 156B 0.11689
151B -> 157B 0.33390
152B -> 157B 0.64113
153B -> 157B -0.31857
154B -> 157B -0.20363

Excited State 12: 3.086-A 2.8378 eV 436.90 nm f=0.0005 <S**2>=2.131
142B -> 156B -0.21414
144B -> 156B -0.10601
145B -> 156B -0.18959
147B -> 156B -0.39810
148B -> 156B 0.77350
148B -> 157B 0.19249
149B -> 156B -0.11251
152B -> 157B -0.10873

Excited State 13: 3.086-A 2.9269 eV 423.60 nm f=0.0027 <S**2>=2.130
142B -> 156B -0.28652
144B -> 156B -0.16352
144B -> 157B -0.12687
145B -> 156B 0.16281
147B -> 156B 0.22459
148B -> 157B -0.13989
151B -> 156B -0.12885
151B -> 157B 0.25706
152B -> 156B -0.13311
153B -> 156B -0.26611
153B -> 157B 0.72205

Excited State 14:	3.090-A	2.9640 eV	418.29 nm	f=0.0024	<S**2>=2.136
140B -> 156B	-0.14399				
142B -> 156B	0.60635				
142B -> 157B	0.20118				
144B -> 156B	0.44654				
147B -> 156B	-0.23925				
147B -> 157B	-0.10397				
148B -> 156B	0.13671				
151B -> 157B	0.22089				
152B -> 156B	0.10456				
152B -> 157B	0.14534				
153B -> 157B	0.35195				
Excited State 15:	3.085-A	3.0489 eV	406.65 nm	f=0.0003	<S**2>=2.129
144B -> 157B	0.13042				
145B -> 157B	0.11165				
150B -> 156B	-0.63261				
150B -> 157B	0.68641				
153B -> 157B	0.13228				
Excited State 16:	3.121-A	3.1021 eV	399.68 nm	f=0.0022	<S**2>=2.186
156A -> 160A	0.15969				
157A -> 159A	-0.11080				
157A -> 160A	-0.17974				
142B -> 157B	-0.16085				
144B -> 156B	-0.23558				
144B -> 157B	0.43475				
145B -> 156B	-0.30177				
145B -> 157B	0.45710				
147B -> 156B	-0.13012				
148B -> 156B	-0.13672				
148B -> 157B	0.14020				
150B -> 156B	0.19603				
150B -> 157B	-0.19034				
152B -> 157B	0.21593				

153B -> 157B 0.24748

Excited State 17: 3.085-A 3.1279 eV 396.38 nm f=0.0006 <S**2>=2.130
144B -> 156B -0.10157
144B -> 157B 0.18919
145B -> 157B 0.10044
151B -> 156B -0.16399
151B -> 157B 0.71669
152B -> 156B 0.13271
152B -> 157B -0.52265
153B -> 157B -0.16174

Excited State 18: 3.316-A 3.1667 eV 391.53 nm f=0.0271 <S**2>=2.499
149A -> 163A -0.12668
152A -> 159A 0.12121
153A -> 158A 0.13357
156A -> 166A -0.10217
157A -> 159A -0.23030
157A -> 166A -0.10063
142B -> 156B 0.11958
143B -> 156B 0.44092
144B -> 157B 0.16608
145B -> 156B 0.12393
147B -> 156B 0.14407
147B -> 157B -0.36177
148B -> 156B 0.12382
148B -> 157B -0.29147
149B -> 157B -0.22704
151B -> 157B -0.24710
152B -> 156B -0.16049
152B -> 159B -0.11349

Excited State 19: 3.319-A 3.1988 eV 387.59 nm f=0.0319 <S**2>=2.505
152A -> 159A 0.11093
153A -> 158A 0.10674
155A -> 160A -0.12315

156A -> 159A -0.11005
156A -> 161A 0.13225
157A -> 159A -0.17392
157A -> 160A 0.22496
157A -> 166A -0.10328
142B -> 156B -0.23750
143B -> 156B 0.37469
143B -> 157B 0.11564
144B -> 157B -0.24852
145B -> 156B -0.25192
146B -> 156B -0.12615
147B -> 156B -0.26815
147B -> 157B 0.11608
148B -> 156B -0.24300
151B -> 156B 0.15298
151B -> 157B 0.18296
152B -> 156B 0.10026
152B -> 157B 0.12968
154B -> 160B -0.12449

Excited State 20: 3.231-A 3.2621 eV 380.08 nm f=0.0288 <S**2>=2.360
155A -> 158A -0.11940
156A -> 158A -0.26700
156A -> 160A 0.10108
157A -> 158A -0.31342
157A -> 159A -0.10680
141B -> 156B -0.18889
143B -> 156B 0.14203
145B -> 156B 0.17016
147B -> 157B 0.21327
148B -> 157B 0.32322
149B -> 156B -0.11396
149B -> 157B 0.55067
150B -> 156B 0.14387
152B -> 156B -0.15429

Table S14. Standard orientation of the optimized geometry for the quinoidal form 1 of the ring-opening form of ClC-tBuPh.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	-5.824043	-1.750194	-3.435888
2	C	-5.142947	-2.358373	-2.409582
3	C	-4.162402	-1.659312	-1.661647
4	C	-4.019291	-0.251095	-1.901572
5	C	-4.684151	0.332065	-3.011166
6	C	-5.570497	-0.398541	-3.758863
7	C	-3.361118	0.613084	-0.984555
8	C	-3.284654	-2.389727	-0.789902
9	N	-3.080295	0.273026	0.313219
10	C	-2.521275	1.352277	0.826819
11	C	-2.457069	2.380816	-0.22599
12	N	-3.029251	1.898186	-1.317393
13	C	-1.869958	3.716275	-0.216307
14	C	-2.174711	1.411977	2.245583
15	C	-1.893601	-2.044715	-0.717206
16	C	-1.050095	-2.808339	0.033012
17	C	-1.544957	-3.943538	0.783736
18	C	-2.920576	-4.283927	0.712105
19	C	-3.751338	-3.536659	-0.081741
20	C	0.377447	-2.796396	0.314859
21	C	0.571429	-3.901673	1.190278
22	N	-0.597878	-4.586383	1.459925
23	C	1.439768	-2.001704	-0.067133
24	C	2.732883	-2.296588	0.41265
25	C	2.907964	-3.391551	1.27883
26	C	1.845682	-4.196195	1.673367
27	C	-2.28404	2.593816	2.994346
28	C	-1.996629	2.595559	4.353579
29	C	-1.593575	1.422655	4.987282
30	C	-1.491556	0.240844	4.255257
31	C	-1.784946	0.232045	2.899216
32	C	-2.377113	4.691367	-1.091149

33	C	-1.813091	5.957021	-1.140768
34	C	-0.723623	6.271088	-0.328731
35	C	-0.199731	5.307399	0.529362
36	C	-0.766169	4.040225	0.588175
37	C	3.884721	-1.471512	0.003401
38	C	3.76291	-0.091982	-0.193409
39	C	4.850776	0.682224	-0.582681
40	C	6.111684	0.119106	-0.795312
41	C	6.229069	-1.26345	-0.596406
42	C	5.14893	-2.040251	-0.208305
43	C	7.329588	0.937379	-1.228814
44	C	7.001038	2.423991	-1.396855
45	C	8.436831	0.806099	-0.168864
46	C	7.848955	0.405565	-2.57575
47	H	-6.529357	-2.32331	-4.02867
48	H	-5.277568	-3.419519	-2.23243
49	H	-4.509937	1.384114	-3.202975
50	H	-6.095474	0.065226	-4.587457
51	H	-1.527093	-1.22113	-1.319185
52	H	-3.292087	-5.123382	1.289631
53	H	-4.808974	-3.771998	-0.11865
54	H	1.300024	-1.175407	-0.757465
55	H	3.898835	-3.593794	1.671968
56	H	1.992239	-5.031083	2.349913
57	H	-2.620155	3.506233	2.514811
58	H	-2.096224	3.515051	4.921534
59	H	-1.363819	1.428174	6.048045
60	H	-1.179961	-0.677124	4.743058
61	H	-1.711909	-0.682501	2.321602
62	H	-3.217918	4.430639	-1.723608
63	H	-2.221676	6.703437	-1.814449
64	H	-0.282062	7.261737	-0.369025
65	H	0.658271	5.540825	1.151532
66	H	-0.34059	3.289668	1.244318
67	H	2.808675	0.392818	-0.01126
68	H	4.701447	1.747825	-0.712316

69	H	7.18474	-1.752647	-0.758498
70	H	5.277932	-3.112322	-0.097356
71	H	7.899095	2.965403	-1.710362
72	H	6.234262	2.587819	-2.160727
73	H	6.655488	2.873619	-0.460488
74	H	9.320385	1.379956	-0.469271
75	H	8.746684	-0.233764	-0.031101
76	H	8.097583	1.184783	0.800235
77	H	7.081927	0.489362	-3.351774
78	H	8.724587	0.97978	-2.897695
79	H	8.145497	-0.645225	-2.511717

SCF Done: E(RmPW1PW91) = -1822.28518977 A.U.

Zero-point correction = 0.646289 (Hartree/Particle)
Thermal correction to Energy = 0.682874
Thermal correction to Enthalpy = 0.683819
Thermal correction to Gibbs Free Energy = 0.574491
Sum of electronic and zero-point Energies = -1821.640750
Sum of electronic and thermal Energies = -1821.604165
Sum of electronic and thermal Enthalpies = -1821.603220
Sum of electronic and thermal Free Energies = -1821.712548

Low frequencies --- -0.0008 0.0007 0.0007 1.6425 3.4167 5.3085
Low frequencies --- 9.3932 11.2260 19.7711

The Result for the TDDFT calculation

Excited State 1: Singlet-A 1.1847 eV 1046.56 nm f=0.2006 <S**2>=0.000
154 -> 157 0.11465
155 -> 157 -0.34903
156 -> 157 0.63016
156 <- 157 -0.19191
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1822.33556410
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State	2:	Singlet-A	1.4170 eV	874.96 nm	f=0.1381	<S**2>=0.000
153 -> 157		0.10491				
154 -> 157		-0.12821				
155 -> 157		0.58255				
156 -> 157		0.38907				
156 <- 157		-0.14991				
Excited State	3:	Singlet-A	2.0606 eV	601.68 nm	f=0.0972	<S**2>=0.000
153 -> 157		0.10855				
154 -> 157		0.66484				
155 -> 157		0.14423				
Excited State	4:	Singlet-A	2.3035 eV	538.24 nm	f=0.0549	<S**2>=0.000
146 -> 157		-0.13949				
149 -> 157		-0.22467				
150 -> 157		0.20830				
153 -> 157		0.59503				
Excited State	5:	Singlet-A	2.4652 eV	502.94 nm	f=0.1079	<S**2>=0.000
146 -> 157		-0.23402				
149 -> 157		-0.24574				
150 -> 157		0.44930				
151 -> 157		0.10076				
152 -> 157		0.19646				
153 -> 157		-0.28104				
154 -> 157		0.11660				
156 -> 158		-0.12603				
Excited State	6:	Singlet-A	2.5799 eV	480.59 nm	f=0.0194	<S**2>=0.000
147 -> 157		0.13353				
149 -> 157		-0.25467				
150 -> 157		-0.41295				
151 -> 157		0.11769				
152 -> 157		0.45219				
156 -> 158		-0.10515				

Excited State 7:	Singlet-A	2.6209 eV	473.06 nm	f=0.0014	<S**2>=0.000
147 -> 157	0.63903				
149 -> 157	0.17960				
151 -> 157	0.18919				
Excited State 8:	Singlet-A	2.6613 eV	465.88 nm	f=0.0194	<S**2>=0.000
149 -> 157	0.39641				
150 -> 157	0.19796				
151 -> 157	-0.21717				
152 -> 157	0.44118				
153 -> 157	0.16100				
156 -> 158	-0.11466				
Excited State 9:	Singlet-A	2.7057 eV	458.24 nm	f=0.0070	<S**2>=0.000
147 -> 157	-0.24056				
149 -> 157	0.21366				
151 -> 157	0.61843				
Excited State 10:	Singlet-A	2.8274 eV	438.52 nm	f=0.0183	<S**2>=0.000
146 -> 157	0.56661				
148 -> 157	0.27122				
149 -> 157	-0.25413				
150 -> 157	0.12733				
Excited State 11:	Singlet-A	2.8900 eV	429.01 nm	f=0.0016	<S**2>=0.000
146 -> 157	-0.26796				
148 -> 157	0.63964				
Excited State 12:	Singlet-A	3.1451 eV	394.21 nm	f=0.0298	<S**2>=0.000
144 -> 157	-0.33994				
145 -> 157	0.49322				
156 -> 158	-0.30753				
Excited State 13:	Singlet-A	3.3011 eV	375.58 nm	f=0.2291	<S**2>=0.000
142 -> 157	0.20766				

143 -> 157 0.17945
144 -> 157 -0.37341
152 -> 157 0.14382
156 -> 158 0.45972
156 -> 159 -0.10580

Excited State 14: Singlet-A 3.3710 eV 367.80 nm f=0.1278 <S**2>=0.000
144 -> 157 0.42292
145 -> 157 0.45022
149 -> 157 -0.10501
156 -> 158 0.24892

Excited State 15: Singlet-A 3.5277 eV 351.46 nm f=0.0586 <S**2>=0.000
143 -> 157 0.61932
144 -> 157 0.17981
156 -> 158 -0.14614
156 -> 160 0.15417

Excited State 16: Singlet-A 3.6502 eV 339.66 nm f=0.1045 <S**2>=0.000
142 -> 157 0.11810
156 -> 159 0.66823

Excited State 17: Singlet-A 3.7448 eV 331.09 nm f=0.0548 <S**2>=0.000
142 -> 157 -0.13780
143 -> 157 -0.12841
156 -> 160 0.64997

Excited State 18: Singlet-A 3.7935 eV 326.84 nm f=0.0717 <S**2>=0.000
141 -> 157 -0.26896
142 -> 157 0.51605
143 -> 157 -0.18279
155 -> 158 0.23495
156 -> 158 -0.12248
156 -> 160 0.10009

Excited State 19: Singlet-A 3.8723 eV 320.19 nm f=0.0169 <S**2>=0.000

141 -> 157	-0.34824					
142 -> 157	-0.13998					
155 -> 158	0.11505					
156 -> 161	0.56469					
Excited State 20:	Singlet-A	3.9210 eV	316.20 nm	f=0.0551	<S**2>=0.000	
141 -> 157	0.51135					
142 -> 157	0.22978					
155 -> 158	0.17845					
156 -> 161	0.33773					

Table S15. Standard orientation of the optimized geometry for the quinoidal form 2 of the ring-opening form of ClC-tBuPh.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	-1.575434	5.085334	-0.343121
2	C	-0.962143	3.931469	0.075433
3	C	-1.705183	2.747895	0.328245
4	C	-3.096534	2.748885	-0.040592
5	C	-3.715906	3.976499	-0.399362
6	C	-2.973909	5.116637	-0.552229
7	C	-3.838297	1.553810	-0.218837
8	C	-1.079998	1.669330	1.036651
9	N	-3.268615	0.314390	-0.332475
10	C	-4.284415	-0.502546	-0.530811
11	C	-5.526645	0.296652	-0.520185
12	N	-5.201974	1.567642	-0.371264
13	C	-6.923341	-0.116945	-0.609561
14	C	-4.059591	-1.920353	-0.800496
15	C	0.313020	1.404902	0.842898
16	C	0.913896	0.403145	1.544839
17	C	0.175363	-0.355988	2.545898
18	C	-1.194121	-0.046372	2.782322
19	C	-1.796330	0.918546	2.029070
20	C	2.248384	-0.175685	1.576573
21	C	2.168913	-1.184860	2.571908

22	N	0.905350	-1.278195	3.148319
23	C	3.423924	0.054804	0.889957
24	C	4.561940	-0.726277	1.182998
25	C	4.466720	-1.717872	2.171009
26	C	3.283819	-1.957620	2.870177
27	C	-4.886998	-2.664109	-1.655981
28	C	-4.602972	-3.997001	-1.925907
29	C	-3.494150	-4.609588	-1.347122
30	C	-2.659439	-3.877023	-0.504306
31	C	-2.933894	-2.543839	-0.237466
32	C	-7.869883	0.781278	-1.128911
33	C	-9.211821	0.436787	-1.185812
34	C	-9.637531	-0.804057	-0.712380
35	C	-8.711336	-1.695564	-0.177191
36	C	-7.364516	-1.358384	-0.125859
37	C	5.826199	-0.503391	0.454537
38	C	6.240821	0.781400	0.090785
39	C	7.430534	0.990053	-0.599155
40	C	8.263078	-0.072211	-0.959842
41	C	7.843957	-1.358112	-0.591848
42	C	6.659378	-1.572086	0.095792
43	C	9.574570	0.116891	-1.725198
44	C	9.863984	1.590398	-2.026621
45	C	10.740086	-0.440995	-0.890728
46	C	9.496965	-0.639916	-3.062329
47	H	-0.990669	5.990242	-0.471351
48	H	0.092114	3.951007	0.327439
49	H	-4.778857	3.956708	-0.607948
50	H	-3.452572	6.041397	-0.856982
51	H	0.854808	1.954076	0.079672
52	H	-1.730577	-0.572624	3.563926
53	H	-2.831336	1.178821	2.213784
54	H	3.476933	0.804392	0.105972
55	H	5.351156	-2.296924	2.416477
56	H	3.230637	-2.721345	3.638287
57	H	-5.738081	-2.189155	-2.130606

58	H	-5.245689	-4.556869	-2.597713
59	H	-3.278347	-5.652727	-1.555263
60	H	-1.791940	-4.347655	-0.053061
61	H	-2.289807	-1.962585	0.412928
62	H	-7.526457	1.746068	-1.484212
63	H	-9.931151	1.136573	-1.599075
64	H	-10.688425	-1.071840	-0.755714
65	H	-9.039377	-2.655032	0.209399
66	H	-6.652335	-2.048712	0.311382
67	H	5.638783	1.638628	0.376907
68	H	7.708290	2.007975	-0.847257
69	H	8.449622	-2.219518	-0.857229
70	H	6.357632	-2.587500	0.333618
71	H	10.808020	1.674575	-2.574002
72	H	9.082138	2.040010	-2.647050
73	H	9.959597	2.182414	-1.110805
74	H	11.685620	-0.321496	-1.430935
75	H	10.613079	-1.505579	-0.674644
76	H	10.824558	0.085714	0.064860
77	H	8.678255	-0.258669	-3.680412
78	H	10.431348	-0.519702	-3.621496
79	H	9.332738	-1.711033	-2.914388

SCF Done: E(RmPW1PW91) = -1822.27905122 A.U.

Zero-point correction= 0.646191 (Hartree/Particle)
Thermal correction to Energy= 0.682814
Thermal correction to Enthalpy= 0.683758
Thermal correction to Gibbs Free Energy= 0.574127
Sum of electronic and zero-point Energies= -1821.638131
Sum of electronic and thermal Energies= -1821.601508
Sum of electronic and thermal Enthalpies= -1821.600564
Sum of electronic and thermal Free Energies= -1821.710195

Low frequencies --- -2.1144 -0.0015 0.0011 0.0018 1.3364 5.9211
Low frequencies --- 9.7779 11.6318 21.7462

The Result for the TDDFT calculation

Excited State 1: Singlet-A 1.0874 eV 1140.22 nm f=0.2372 <S**2>=0.000
155 -> 157 0.39221
156 -> 157 0.60053
156 <- 157 -0.17500
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1822.33603444
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.4811 eV 837.11 nm f=0.3117 <S**2>=0.000
154 -> 157 -0.11308
155 -> 157 0.56786
156 -> 157 -0.43722
156 <- 157 0.17905

Excited State 3: Singlet-A 2.2137 eV 560.06 nm f=0.0093 <S**2>=0.000
153 -> 157 0.23348
154 -> 157 0.63762
155 -> 157 0.13201

Excited State 4: Singlet-A 2.2750 eV 544.98 nm f=0.1638 <S**2>=0.000
153 -> 157 0.63741
154 -> 157 -0.22028

Excited State 5: Singlet-A 2.4317 eV 509.88 nm f=0.1102 <S**2>=0.000
146 -> 157 -0.31891
149 -> 157 -0.34182
150 -> 157 0.46678
152 -> 157 -0.16096

Excited State 6: Singlet-A 2.5758 eV 481.35 nm f=0.0146 <S**2>=0.000
147 -> 157 0.58915
150 -> 157 -0.20217
151 -> 157 0.19591

152 -> 157 -0.23175

Excited State 7: Singlet-A 2.5971 eV 477.40 nm f=0.0391 <S**2>=0.000
147 -> 157 0.34605
149 -> 157 0.14720
150 -> 157 0.30256
152 -> 157 0.46449
156 -> 158 -0.14719

Excited State 8: Singlet-A 2.6610 eV 465.93 nm f=0.0165 <S**2>=0.000
146 -> 157 0.11775
149 -> 157 0.47266
150 -> 157 0.32001
152 -> 157 -0.34418
156 -> 158 0.11834

Excited State 9: Singlet-A 2.7263 eV 454.76 nm f=0.0013 <S**2>=0.000
147 -> 157 -0.13929
151 -> 157 0.66508
152 -> 157 0.14750

Excited State 10: Singlet-A 2.8219 eV 439.36 nm f=0.0368 <S**2>=0.000
146 -> 157 0.53214
148 -> 157 -0.25856
149 -> 157 -0.31065
150 -> 157 0.12960

Excited State 11: Singlet-A 2.8813 eV 430.30 nm f=0.0018 <S**2>=0.000
146 -> 157 0.24598
148 -> 157 0.64509
150 -> 157 0.11875

Excited State 12: Singlet-A 3.1411 eV 394.72 nm f=0.0218 <S**2>=0.000
144 -> 157 -0.24734
145 -> 157 0.56828
156 -> 158 -0.26238

Excited State 13:	Singlet-A	3.2679 eV	379.40 nm	f=0.0241	<S**2>=0.000
144 -> 157	0.63260				
145 -> 157	0.21994				
156 -> 158	-0.11866				
Excited State 14:	Singlet-A	3.3519 eV	369.89 nm	f=0.1791	<S**2>=0.000
142 -> 157	-0.10715				
143 -> 157	-0.20984				
145 -> 157	0.26232				
152 -> 157	0.13447				
156 -> 158	0.51375				
156 -> 160	-0.20064				
Excited State 15:	Singlet-A	3.5616 eV	348.11 nm	f=0.1897	<S**2>=0.000
142 -> 157	-0.20984				
143 -> 157	0.49551				
145 -> 157	0.12668				
155 -> 158	0.11025				
156 -> 158	0.19282				
156 -> 159	-0.21966				
156 -> 160	0.25381				

Table S16. Standard orientation of the optimized geometry for the closed form of CIC-TPA.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	5.383916	-0.583191	4.207363
2	C	4.920602	-1.585047	5.056408
3	C	4.118741	-2.621888	4.575859
4	C	3.76131	-2.681324	3.227831
5	C	4.219929	-1.684325	2.385952
6	C	5.026591	-0.642246	2.864735
7	C	3.972042	-1.532278	0.869227
8	N	4.727497	-0.295432	0.624547
9	C	5.312155	0.227753	1.743197
10	C	4.919709	0.603964	-0.402578

11	C	5.671896	1.626423	0.179864
12	N	5.896076	1.375336	1.516032
13	C	6.217387	2.843336	-0.434855
14	C	4.320254	0.455579	-1.73675
15	C	3.464303	1.452342	-2.224656
16	C	2.877447	1.328297	-3.477891
17	C	3.129273	0.20464	-4.261348
18	C	3.981006	-0.789042	-3.788469
19	C	4.578094	-0.662294	-2.538721
20	C	6.505891	3.944291	0.382685
21	C	7.030226	5.111199	-0.158114
22	C	7.280227	5.201991	-1.525265
23	C	7.010289	4.108948	-2.344115
24	C	6.488708	2.938174	-1.805837
25	C	2.502636	-1.331672	0.615051
26	C	1.787574	-2.253984	-0.042908
27	C	2.425338	-3.4542	-0.617927
28	C	3.849274	-3.639406	-0.487162
29	C	4.578081	-2.723469	0.16999
30	C	0.380889	-2.411732	-0.395516
31	C	0.331715	-3.630211	-1.1102
32	N	1.592545	-4.243082	-1.229569
33	C	-0.763723	-1.666624	-0.176831
34	C	-1.993242	-2.133947	-0.673953
35	C	-2.021323	-3.347192	-1.382895
36	C	-0.87282	-4.101481	-1.610385
37	C	-3.234433	-1.367108	-0.448771
38	C	-4.23465	-1.293086	-1.427673
39	C	-5.403225	-0.577499	-1.219119
40	C	-5.626476	0.084647	-0.004771
41	C	-4.634909	0.016482	0.982263
42	C	-3.462853	-0.688631	0.755948
43	N	-6.820721	0.798062	0.216844
44	C	-6.804978	2.006186	0.951755
45	C	-8.048597	0.295131	-0.274092
46	C	-8.349647	-1.068153	-0.17452

47	C	-9.554971	-1.556236	-0.664401
48	C	-10.485276	-0.696115	-1.242214
49	C	-10.191742	0.662075	-1.332999
50	C	-8.981393	1.156877	-0.862647
51	C	-7.803377	2.273261	1.895865
52	C	-7.792692	3.466527	2.6077
53	C	-6.781832	4.402721	2.406505
54	C	-5.782947	4.135225	1.473742
55	C	-5.795249	2.9531	0.743339
56	H	6.006004	0.22538	4.574301
57	H	5.1867	-1.55919	6.108074
58	H	3.768452	-3.390581	5.25652
59	H	3.138465	-3.486305	2.850921
60	H	3.264888	2.324009	-1.610319
61	H	2.214731	2.107647	-3.840168
62	H	2.664518	0.104956	-5.236914
63	H	4.187187	-1.664433	-4.395841
64	H	5.255496	-1.430657	-2.183791
65	H	6.316285	3.862974	1.447061
66	H	7.24459	5.954523	0.491262
67	H	7.689383	6.114239	-1.947923
68	H	7.216569	4.162135	-3.408661
69	H	6.305677	2.087557	-2.45241
70	H	2.064921	-0.430855	1.035447
71	H	4.304666	-4.512374	-0.942275
72	H	5.652438	-2.826644	0.28543
73	H	-0.72101	-0.716899	0.34764
74	H	-2.976161	-3.720591	-1.738823
75	H	-0.913315	-5.03966	-2.152544
76	H	-4.076817	-1.772297	-2.388917
77	H	-6.150044	-0.519003	-2.003174
78	H	-4.795944	0.508472	1.935111
79	H	-2.727698	-0.752095	1.552354
80	H	-7.633868	-1.738802	0.288271
81	H	-9.772953	-2.616199	-0.578825
82	H	-11.428229	-1.079821	-1.617113

83	H	-10.9041	1.34403	-1.78669
84	H	-8.75046	2.213233	-0.946789
85	H	-8.584793	1.540666	2.066117
86	H	-8.574628	3.657522	3.336034
87	H	-6.77272	5.330178	2.969218
88	H	-4.992909	4.858984	1.299345
89	H	-5.023995	2.755015	0.00693

SCF Done: E(RmPW1PW91) = -2182.43313763 A.U.

Zero-point correction = 0.714198 (Hartree/Particle)
Thermal correction to Energy = 0.755386
Thermal correction to Enthalpy = 0.756331
Thermal correction to Gibbs Free Energy = 0.634315
Sum of electronic and zero-point Energies = -2181.720720
Sum of electronic and thermal Energies = -2181.679532
Sum of electronic and thermal Enthalpies = -2181.678587
Sum of electronic and thermal Free Energies = -2181.800603

Low frequencies --- -3.2303 -0.0016 0.0013 0.0016 2.2587 3.8755
Low frequencies --- 8.9801 10.1762 13.9271

The Result for the TDDFT calculation

Excited State 1: Singlet-A 2.3660 eV 524.02 nm f=0.1682 <S**2>=0.000
182 -> 185 0.13923
183 -> 185 -0.14705
184 -> 185 0.67491
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2182.45360025
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.4684 eV 502.29 nm f=0.0238 <S**2>=0.000
183 -> 185 0.68799
184 -> 185 0.14846

Excited State	3:	Singlet-A	3.0920 eV	400.98 nm	f=0.0220	<S**2>=0.000
182 -> 185		0.67577				
184 -> 185		-0.14188				
Excited State	4:	Singlet-A	3.5371 eV	350.52 nm	f=0.2600	<S**2>=0.000
180 -> 185		-0.18052				
182 -> 186		0.11067				
183 -> 186		-0.10087				
184 -> 186		0.60156				
184 -> 187		-0.20680				
184 -> 189		-0.14807				
Excited State	5:	Singlet-A	3.6865 eV	336.32 nm	f=0.1002	<S**2>=0.000
183 -> 186		0.68084				
Excited State	6:	Singlet-A	3.7177 eV	333.50 nm	f=0.4321	<S**2>=0.000
179 -> 185		0.10499				
180 -> 185		0.55890				
181 -> 185		0.15911				
182 -> 186		-0.10780				
184 -> 186		0.11893				
184 -> 189		-0.27658				
Excited State	7:	Singlet-A	3.7428 eV	331.26 nm	f=0.0204	<S**2>=0.000
184 -> 190		0.68492				
Excited State	8:	Singlet-A	3.8391 eV	322.95 nm	f=0.0029	<S**2>=0.000
170 -> 185		0.33929				
171 -> 185		0.15538				
179 -> 185		0.41910				
181 -> 185		-0.37305				
184 -> 187		0.10714				
Excited State	9:	Singlet-A	3.8482 eV	322.19 nm	f=0.1230	<S**2>=0.000
180 -> 185		0.12990				
181 -> 185		0.10955				

184 -> 186 0.30346
184 -> 187 0.48321
184 -> 188 -0.10930
184 -> 189 0.29733

Excited State 10: Singlet-A 3.9419 eV 314.53 nm f=0.0005 <S**2>=0.000
170 -> 185 0.52294
171 -> 185 0.16637
179 -> 185 -0.17401
181 -> 185 0.36092

Excited State 11: Singlet-A 3.9859 eV 311.06 nm f=0.0957 <S**2>=0.000
175 -> 185 0.10018
179 -> 185 -0.18275
181 -> 185 -0.14931
183 -> 187 -0.12540
184 -> 187 0.16907
184 -> 189 -0.21793
184 -> 191 0.56670

Excited State 12: Singlet-A 3.9879 eV 310.90 nm f=0.0516 <S**2>=0.000
170 -> 185 -0.10850
175 -> 185 -0.21120
179 -> 185 0.42706
180 -> 185 -0.17648
181 -> 185 0.32370
183 -> 187 0.19372
184 -> 191 0.26173

Excited State 13: Singlet-A 4.0007 eV 309.91 nm f=0.1931 <S**2>=0.000
179 -> 185 -0.14345
180 -> 185 0.13948
181 -> 185 -0.14860
183 -> 187 0.61007
183 -> 189 -0.12617

Excited State 14:	Singlet-A	4.0075 eV	309.38 nm	f=0.0836	<S**2>=0.000
176 -> 185	-0.10386				
180 -> 185	0.13084				
183 -> 187	-0.11238				
184 -> 187	-0.38591				
184 -> 189	0.41540				
184 -> 191	0.28146				
184 -> 192	0.12518				
Excited State 15:	Singlet-A	4.1007 eV	302.35 nm	f=0.1204	<S**2>=0.000
176 -> 185	0.58410				
178 -> 185	0.17236				
183 -> 187	-0.10020				
183 -> 188	-0.26258				
184 -> 189	0.10457				
Excited State 16:	Singlet-A	4.1019 eV	302.26 nm	f=0.2124	<S**2>=0.000
175 -> 185	0.10353				
176 -> 185	0.24643				
178 -> 185	0.10200				
183 -> 188	0.59724				
183 -> 189	0.11543				
184 -> 188	-0.13560				
Excited State 17:	Singlet-A	4.1737 eV	297.06 nm	f=0.0063	<S**2>=0.000
183 -> 188	0.13444				
184 -> 188	0.66529				
184 -> 189	0.13583				
Excited State 18:	Singlet-A	4.1892 eV	295.96 nm	f=0.0066	<S**2>=0.000
175 -> 185	0.62216				
176 -> 185	-0.15132				
179 -> 185	0.13152				
181 -> 185	0.17617				
Excited State 19:	Singlet-A	4.2388 eV	292.50 nm	f=0.0026	<S**2>=0.000

173 -> 185	0.14229					
174 -> 185	0.14707					
177 -> 185	0.64601					
184 -> 195	-0.11242					

Excited State 20:	Singlet-A	4.2710 eV	290.29 nm	f=0.0231	<S**2>=0.000	
170 -> 185	-0.14475					
171 -> 185	0.16876					
173 -> 185	0.36934					
174 -> 185	-0.30226					
175 -> 185	-0.14338					
176 -> 185	-0.11539					
178 -> 185	0.30352					
182 -> 186	-0.23481					

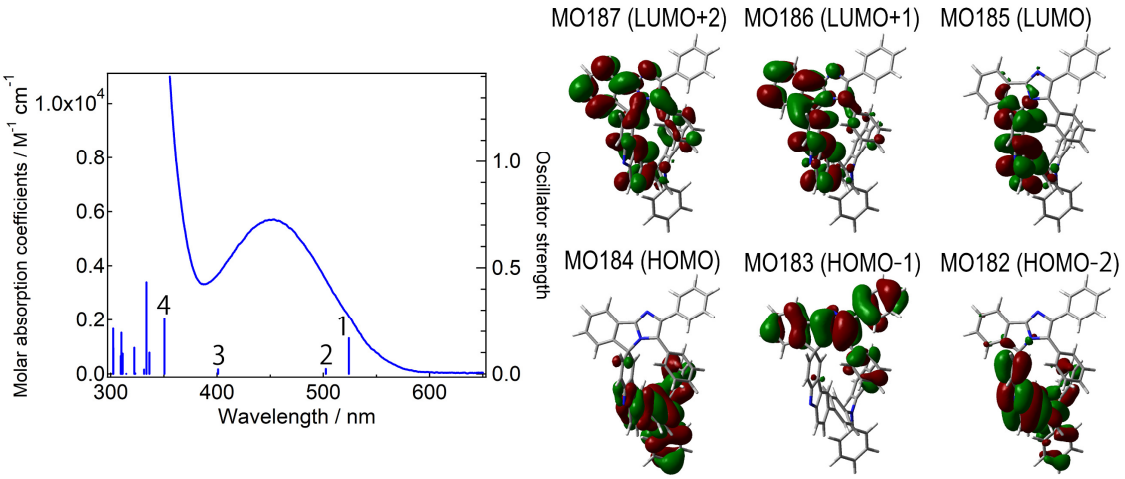


Fig. S66. UV-vis absorption spectrum of CIC-TPA in benzene at room temperature. The calculated absorption spectrum MPW1PW91/6-31+G(d,p)//MPW1PW91/6-31G(d) level of the theory) is shown by the blue vertical lines. The relevant molecular orbitals of the CIC-TPA calculated at the MPW1PW91/6-31G(d) level of the theory.

Table S17. Selected calculated electronic transition of CIC-TPA at the MPW1PW91/6-31G(d) level.

No.	Wavelength (nm)	Coefficients	Electronic Transition			*f*
1	524.02	0.13923	182 HOMO-2	→	185 LUMO	0.1682
		-0.14705	183 HOMO-1	→	185 LUMO	
		0.67491	184 HOMO	→	185 LUMO	
2	502.29	0.68799	183 HOMO-1	→	185 LUMO	0.0238
		0.14846	184 HOMO	→	185 LUMO	
3	400.98	0.67577	182 HOMO-2	→	185 LUMO	0.0220
		-0.14188	184 HOMO	→	186 LUMO+1	
4	328.08	-0.18052	180 HOMO-4	→	185 LUMO	0.2600
		0.11067	182 HOMO-2	→	186 LUMO+1	
		-0.10087	183 HOMO-1	→	186 LUMO+1	
		0.60156	184 HOMO	→	186 LUMO+1	
		-0.20680	184 HOMO	→	187 LUMO+2	
		-0.14807	184 HOMO	→	189 LUMO+3	

Table S18. Standard orientation of the singlet biradical form 1 of the ring-opening form of CIC-TPA.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	-6.572266	0.21834	-4.125188
2	C	-6.631623	-1.173866	-4.208449
3	C	-5.972434	-1.951683	-3.266585
4	C	-5.246703	-1.379665	-2.213193
5	C	-5.245621	0.037009	-2.092518
6	C	-5.887677	0.810116	-3.080491
7	C	-4.707116	0.747434	-0.951867
8	C	-4.465449	-2.284461	-1.349385
9	C	-3.084811	-2.051225	-1.136542
10	C	-2.355364	-2.96134	-0.410475
11	C	-2.97883	-4.123634	0.143449
12	C	-4.342262	-4.356896	-0.066027
13	C	-5.064125	-3.441036	-0.820816
14	N	-4.434515	0.163542	0.24676
15	C	-4.038318	1.162309	1.021991
16	C	-4.04855	2.39987	0.213189
17	N	-4.505079	2.098995	-0.992879
18	C	-0.95629	-3.076449	-0.010843
19	C	-0.902786	-4.285735	0.748412
20	N	-2.111775	-4.915775	0.84065
21	C	0.174847	-2.31604	-0.203574
22	C	1.403131	-2.738397	0.358034
23	C	1.440315	-3.931638	1.108012
24	C	0.308257	-4.707074	1.309508
25	C	2.624038	-1.944879	0.155812
26	C	2.848928	-1.239873	-1.036827
27	C	4.008073	-0.511065	-1.244221
28	C	4.993011	-0.438107	-0.248889
29	C	4.772815	-1.123924	0.954639
30	C	3.619139	-1.865749	1.142682
31	N	6.170981	0.301261	-0.450328
32	C	7.399208	-0.150511	0.089388

33	C	6.147965	1.493215	-1.213476
34	C	8.27957	0.75426	0.693165
35	C	9.49154	0.311939	1.209414
36	C	9.837487	-1.035558	1.148676
37	C	8.959325	-1.938297	0.554466
38	C	7.753289	-1.502728	0.018976
39	C	7.155446	1.750829	-2.14985
40	C	7.139205	2.927601	-2.888592
41	C	6.114255	3.854976	-2.720261
42	C	5.106873	3.596743	-1.79404
43	C	5.124388	2.431293	-1.037371
44	C	-3.60818	3.753318	0.532037
45	C	-3.756774	0.940653	2.434996
46	C	-4.190506	4.836042	-0.147705
47	C	-3.769771	6.133556	0.101346
48	C	-2.74796	6.375108	1.019367
49	C	-2.146743	5.308267	1.682315
50	C	-2.571989	4.007097	1.444418
51	C	-3.971581	1.928135	3.409749
52	C	-3.737138	1.654548	4.751358
53	C	-3.282908	0.397145	5.141828
54	C	-3.079373	-0.595338	4.183378
55	C	-3.322348	-0.331892	2.843966
56	H	-7.068385	0.834075	-4.86807
57	H	-7.16907	-1.652056	-5.02105
58	H	-5.968916	-3.031973	-3.369216
59	H	-5.850278	1.887946	-2.975986
60	H	-2.621812	-1.171383	-1.571193
61	H	-4.813904	-5.236138	0.358846
62	H	-6.125822	-3.597199	-0.981375
63	H	0.131555	-1.380828	-0.753184
64	H	2.391262	-4.268892	1.506482
65	H	0.35012	-5.630461	1.876875
66	H	2.123231	-1.304846	-1.841224
67	H	4.165596	-0.003953	-2.189491
68	H	5.510173	-1.060868	1.747031

69	H	3.464734	-2.359543	2.096716
70	H	8.006775	1.802262	0.753056
71	H	10.163461	1.026262	1.674711
72	H	10.781374	-1.378335	1.559141
73	H	9.219517	-2.990244	0.491635
74	H	7.07879	-2.205942	-0.457348
75	H	7.947628	1.024006	-2.293063
76	H	7.927655	3.11247	-3.611359
77	H	6.100671	4.769294	-3.30399
78	H	4.30588	4.314238	-1.646274
79	H	4.346473	2.239541	-0.306268
80	H	-4.9751	4.632369	-0.867251
81	H	-4.237	6.961595	-0.422036
82	H	-2.417779	7.390985	1.211624
83	H	-1.338303	5.488599	2.383459
84	H	-2.084557	3.180581	1.948651
85	H	-4.348986	2.901272	3.117412
86	H	-3.918076	2.423687	5.49532
87	H	-3.095398	0.188134	6.190267
88	H	-2.732321	-1.578962	4.482725
89	H	-3.180136	-1.098315	2.090701

SCF Done: E(UmPW1PW91) = -2182.41188001 A.U.

Zero-point correction = 0.710727 (Hartree/Particle)
Thermal correction to Energy = 0.752570
Thermal correction to Enthalpy = 0.753514
Thermal correction to Gibbs Free Energy = 0.628971
Sum of electronic and zero-point Energies = -2181.701153
Sum of electronic and thermal Energies = -2181.659310
Sum of electronic and thermal Enthalpies = -2181.658366
Sum of electronic and thermal Free Energies = -2181.782909

Low frequencies --- -4.7927 -1.0327 -0.0011 0.0007 0.0013 3.2245
Low frequencies --- 6.5450 8.0856 10.4699

The Result for the TDDFT calculation

Excited State 1: 3.000-A -0.6342 eV -1954.99 nm f=-0.0000 <S**2>=2.000

183A -> 185A -0.24663

184A -> 185A 0.69148

183B -> 185B 0.24663

184B -> 185B -0.69148

184A <- 185A -0.21103

184B <- 185B 0.21103

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2182.52613671

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 3.000-A 0.7132 eV 1738.48 nm f=0.0000 <S**2>=2.000

182A -> 185A -0.30104

183A -> 185A 0.60068

184A -> 185A 0.23548

182B -> 185B 0.30104

183B -> 185B -0.60068

184B -> 185B -0.23548

Excited State 3: 1.000-A 0.8696 eV 1425.80 nm f=0.2759 <S**2>=0.000

182A -> 185A -0.10449

183A -> 185A 0.18225

184A -> 185A 0.73708

182B -> 185B -0.10449

183B -> 185B 0.18225

184B -> 185B 0.73708

184A <- 185A -0.30481

184B <- 185B -0.30481

Excited State 4: 3.000-A 1.1748 eV 1055.35 nm f=0.0000 <S**2>=2.000

182A -> 185A 0.62699

183A -> 185A 0.26811

184A -> 185A 0.10022

182B -> 185B -0.62699

183B -> 185B -0.26811
184B -> 185B -0.10022

Excited State 5: 1.000-A 1.2056 eV 1028.36 nm f=0.1147 <S**2>=0.000
182A -> 185A -0.35452
183A -> 185A 0.57477
184A -> 185A -0.26475
182B -> 185B -0.35452
183B -> 185B 0.57477
184B -> 185B -0.26475
184A <- 185A 0.16537
184B <- 185B 0.16537

Excited State 6: 1.000-A 1.4409 eV 860.47 nm f=0.0868 <S**2>=0.000
181A -> 185A 0.11613
182A -> 185A 0.58490
183A -> 185A 0.37523
181B -> 185B 0.11613
182B -> 185B 0.58490
183B -> 185B 0.37523

Excited State 7: 3.000-A 1.5479 eV 800.98 nm f=0.0000 <S**2>=2.000
181A -> 185A 0.67196
181B -> 185B -0.67196

Excited State 8: 3.000-A 1.8246 eV 679.52 nm f=0.0000 <S**2>=2.000
180A -> 185A 0.66357
181A -> 185A -0.10306
180B -> 185B -0.66357
181B -> 185B 0.10306

Excited State 9: 1.000-A 1.9981 eV 620.50 nm f=0.0889 <S**2>=0.000
180A -> 185A -0.16921
181A -> 185A 0.66724
180B -> 185B -0.16921
181B -> 185B 0.66724

Excited State 10:	3.000-A	2.0250 eV	612.27 nm	f=0.0000	<S**2>=2.000
173A -> 185A	-0.13929				
179A -> 185A	0.66864				
173B -> 185B	0.13929				
179B -> 185B	-0.66864				
Excited State 11:	3.000-A	2.1309 eV	581.83 nm	f=0.0000	<S**2>=2.000
171A -> 185A	-0.41639				
172A -> 185A	0.52981				
173A -> 185A	0.13970				
171B -> 185B	0.41639				
172B -> 185B	-0.52981				
173B -> 185B	-0.13970				
Excited State 12:	1.000-A	2.1533 eV	575.80 nm	f=0.0306	<S**2>=0.000
173A -> 185A	-0.22362				
179A -> 185A	0.40311				
180A -> 185A	0.50055				
173B -> 185B	-0.22362				
179B -> 185B	0.40311				
180B -> 185B	0.50055				
Excited State 13:	3.000-A	2.2626 eV	547.98 nm	f=0.0000	<S**2>=2.000
173A -> 185A	0.26369				
174A -> 185A	-0.10858				
178A -> 185A	0.61760				
173B -> 185B	-0.26369				
174B -> 185B	0.10858				
178B -> 185B	-0.61760				
Excited State 14:	3.000-A	2.3754 eV	521.96 nm	f=0.0000	<S**2>=2.000
169A -> 185A	0.15002				
173A -> 185A	-0.12596				
174A -> 185A	0.56703				
177A -> 185A	-0.25853				

178A -> 185A 0.16532
169B -> 185B -0.15002
173B -> 185B 0.12596
174B -> 185B -0.56703
177B -> 185B 0.25853
178B -> 185B -0.16532

Excited State 15: 3.000-A 2.4064 eV 515.23 nm f=0.0000 <S**2>=2.000
169A -> 185A 0.17759
173A -> 185A 0.49124
175A -> 185A -0.21479
177A -> 185A -0.21425
178A -> 185A -0.23428
179A -> 185A 0.14653
180A -> 185A 0.10750
169B -> 185B -0.17759
173B -> 185B -0.49124
175B -> 185B 0.21479
177B -> 185B 0.21425
178B -> 185B 0.23428
179B -> 185B -0.14653
180B -> 185B -0.10750

Table S19. Standard orientation of the singlet biradical form 2 of the ring-opening form of CIC-TPA.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	4.671311	4.990749	-1.199617
2	C	3.437998	4.866666	-1.840149
3	C	2.883602	3.608155	-2.034156
4	C	3.524875	2.443042	-1.595519
5	C	4.747474	2.578039	-0.884331
6	C	5.312458	3.859356	-0.729854
7	C	5.414614	1.481094	-0.213185
8	C	2.919185	1.149424	-1.972601
9	C	1.549058	0.922672	-1.717914

10	C	0.973302	-0.257160	-2.134164
11	C	1.739642	-1.230433	-2.844443
12	C	3.093985	-0.997061	-3.117616
13	C	3.667334	0.183997	-2.672849
14	N	4.814199	0.297257	0.082867
15	C	5.734817	-0.386468	0.746568
16	C	6.959383	0.440406	0.811962
17	N	6.700105	1.603943	0.235097
18	C	-0.358682	-0.845683	-2.033132
19	C	-0.243990	-2.100427	-2.706004
20	N	1.012546	-2.334834	-3.191792
21	C	-1.554403	-0.450021	-1.480336
22	C	-2.685465	-1.296418	-1.583374
23	C	-2.558816	-2.529185	-2.253078
24	C	-1.357011	-2.940432	-2.813302
25	C	-3.970733	-0.889873	-0.997083
26	C	-4.028912	-0.127537	0.180155
27	C	-5.236154	0.246057	0.746282
28	C	-6.449244	-0.114692	0.142821
29	C	-6.405251	-0.866570	-1.040244
30	C	-5.192479	-1.249664	-1.587324
31	N	-7.677907	0.267309	0.708580
32	C	-8.793424	-0.601623	0.647727
33	C	-7.808809	1.521868	1.351064
34	C	-10.065549	-0.098137	0.353720
35	C	-11.161855	-0.950822	0.309439
36	C	-11.007202	-2.315617	0.538628
37	C	-9.740693	-2.819225	0.824072
38	C	-8.641309	-1.971816	0.889088
39	C	-8.503218	1.626560	2.561369
40	C	-8.643359	2.861786	3.182308
41	C	-8.081496	4.004924	2.619682
42	C	-7.383579	3.901067	1.419173
43	C	-7.253801	2.673404	0.781161
44	C	8.290556	0.138094	1.325226
45	C	5.420215	-1.687712	1.323210

46	C	9.103446	1.193957	1.770410
47	C	10.388869	0.949550	2.228897
48	C	10.895710	-0.349820	2.234852
49	C	10.108310	-1.401787	1.773928
50	C	8.815586	-1.163822	1.323825
51	C	6.025662	-2.159128	2.499058
52	C	5.655371	-3.385001	3.037554
53	C	4.681159	-4.160095	2.412996
54	C	4.063721	-3.695290	1.251956
55	C	4.420788	-2.467571	0.715800
56	H	5.121464	5.967991	-1.059867
57	H	2.920643	5.746312	-2.209501
58	H	1.953100	3.510055	-2.584280
59	H	6.257376	3.930304	-0.204302
60	H	0.980343	1.667916	-1.169793
61	H	3.669339	-1.730616	-3.671798
62	H	4.712429	0.385508	-2.880476
63	H	-1.652144	0.515445	-0.993570
64	H	-3.417700	-3.190204	-2.299936
65	H	-1.267631	-3.897143	-3.316297
66	H	-3.109108	0.136761	0.692028
67	H	-5.247723	0.809549	1.672526
68	H	-7.331288	-1.136336	-1.535559
69	H	-5.191779	-1.801388	-2.521828
70	H	-10.186783	0.962449	0.162257
71	H	-12.141995	-0.544732	0.080052
72	H	-11.864268	-2.979337	0.496216
73	H	-9.606210	-3.879456	1.013953
74	H	-7.659103	-2.364604	1.128361
75	H	-8.930903	0.735588	3.007950
76	H	-9.184711	2.926534	4.120891
77	H	-8.187066	4.966401	3.110905
78	H	-6.947912	4.785098	0.964290
79	H	-6.723707	2.598236	-0.162071
80	H	8.701064	2.200156	1.748046
81	H	11.001404	1.773441	2.580855

82	H	11.903289	-0.539660	2.590798
83	H	10.504620	-2.411900	1.757188
84	H	8.217603	-1.985145	0.945939
85	H	6.766938	-1.551049	3.004672
86	H	6.123689	-3.732281	3.952903
87	H	4.397947	-5.119838	2.833414
88	H	3.298772	-4.291801	0.765490
89	H	3.939435	-2.088633	-0.178668

SCF Done: E(UmPW1PW91) = -2182.03047883 A.U.

Zero-point correction= 0.710584 (Hartree/Particle)
Thermal correction to Energy= 0.752474
Thermal correction to Enthalpy= 0.753418
Thermal correction to Gibbs Free Energy= 0.628385
Sum of electronic and zero-point Energies= -2181.700429
Sum of electronic and thermal Energies= -2181.658539
Sum of electronic and thermal Enthalpies= -2181.657595
Sum of electronic and thermal Free Energies= -2181.782628

Low frequencies --- -4.7683 -1.1625 -0.0018 0.0008 0.0016 1.9052
Low frequencies --- 5.6064 8.8222 10.0424

The Result for the TDDFT calculation

Excited State 1: 3.000-A -0.5857 eV -2116.80 nm f=-0.0000 <S**2>=2.000
183A -> 185A -0.25212
184A -> 185A 0.71923
183B -> 185B 0.25212
184B -> 185B -0.71923
184A <- 185A -0.29229
184B <- 185B 0.29229
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2182.51976530
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 3.000-A 0.6113 eV 2028.34 nm f=0.0000 <S**2>=2.000

182A -> 185A	-0.37956
183A -> 185A	0.56110
184A -> 185A	0.23949
182B -> 185B	0.37956
183B -> 185B	-0.56110
184B -> 185B	-0.23949

Excited State 3: 1.000-A 0.7227 eV 1715.45 nm f=0.3161 <S**2>=0.000

182A -> 185A	-0.17859
183A -> 185A	0.16548
184A -> 185A	0.74918
182B -> 185B	-0.17859
183B -> 185B	0.16548
184B -> 185B	0.74918
184A <- 185A	-0.35366
184B <- 185B	-0.35366

Excited State 4: 3.000-A 1.0711 eV 1157.49 nm f=0.0000 <S**2>=2.000

182A -> 185A	0.58648
183A -> 185A	0.34713
184A -> 185A	0.12480
182B -> 185B	-0.58648
183B -> 185B	-0.34713
184B -> 185B	-0.12480

Excited State 5: 1.000-A 1.1545 eV 1073.94 nm f=0.0730 <S**2>=0.000

182A -> 185A	-0.34098
183A -> 185A	0.57821
184A -> 185A	-0.31596
182B -> 185B	-0.34098
183B -> 185B	0.57821
184B -> 185B	-0.31596
183A <- 185A	-0.10603
184A <- 185A	0.21441
183B <- 185B	-0.10603

184B <- 185B 0.21441

Excited State 6: 1.000-A 1.3485 eV 919.41 nm f=0.1481 <S**2>=0.000
182A -> 185A 0.58386
183A -> 185A 0.38617
182B -> 185B 0.58386
183B -> 185B 0.38617

Excited State 7: 3.000-A 1.6475 eV 752.55 nm f=0.0000 <S**2>=2.000
181A -> 185A 0.67838
181B -> 185B -0.67838

Excited State 8: 3.000-A 1.7649 eV 702.52 nm f=0.0000 <S**2>=2.000
177A -> 185A 0.12587
180A -> 185A 0.66618
177B -> 185B -0.12587
180B -> 185B -0.66618

Excited State 9: 3.000-A 1.9729 eV 628.43 nm f=0.0000 <S**2>=2.000
173A -> 185A -0.17799
179A -> 185A 0.64549
173B -> 185B 0.17799
179B -> 185B -0.64549

Excited State 10: 1.000-A 1.9924 eV 622.30 nm f=0.0543 <S**2>=0.000
181A -> 185A 0.69136
181B -> 185B 0.69136

Excited State 11: 3.000-A 2.0549 eV 603.37 nm f=0.0000 <S**2>=2.000
171A -> 185A -0.23836
172A -> 185A 0.64492
171B -> 185B 0.23836
172B -> 185B -0.64492

Excited State 12: 3.000-A 2.1752 eV 569.98 nm f=0.0000 <S**2>=2.000
169A -> 185A 0.11191

173A -> 185A -0.29920
174A -> 185A -0.19052
178A -> 185A 0.57631
169B -> 185B -0.11191
173B -> 185B 0.29920
174B -> 185B 0.19052
178B -> 185B -0.57631

Excited State 13: 1.000-A 2.1835 eV 567.81 nm f=0.0758 <S**2>=0.000
173A -> 185A -0.32954
174A -> 185A -0.12777
178A -> 185A 0.14754
179A -> 185A 0.56409
173B -> 185B -0.32954
174B -> 185B -0.12777
178B -> 185B 0.14754
179B -> 185B 0.56409

Excited State 14: 3.000-A 2.3135 eV 535.92 nm f=0.0000 <S**2>=2.000
169A -> 185A -0.17463
173A -> 185A -0.18336
174A -> 185A 0.50061
177A -> 185A 0.34539
178A -> 185A 0.15830
169B -> 185B 0.17463
173B -> 185B 0.18336
174B -> 185B -0.50061
177B -> 185B -0.34539
178B -> 185B -0.15830

Excited State 15: 3.000-A 2.3476 eV 528.14 nm f=0.0000 <S**2>=2.000
173A -> 185A 0.54878
175A -> 185A -0.18220
178A -> 185A 0.32631
179A -> 185A 0.19420
173B -> 185B -0.54878

175B -> 185B	0.18220
178B -> 185B	-0.32631
179B -> 185B	-0.19420

Table S20. Standard orientation of the triplet biradical form of the ring-opening form of CIC-TPA.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	-6.421183	0.001287	-4.284903
2	C	-6.333242	-1.383762	-4.403827
3	C	-5.661238	-2.119279	-3.433033
4	C	-5.074228	-1.510358	-2.320306
5	C	-5.207038	-0.104671	-2.17617
6	C	-5.863283	0.627359	-3.183605
7	C	-4.770467	0.635274	-1.005805
8	C	-4.29285	-2.376585	-1.40433
9	C	-2.920061	-2.125641	-1.188685
10	C	-2.195721	-2.993519	-0.403497
11	C	-2.819318	-4.128911	0.195315
12	C	-4.174432	-4.382126	-0.02055
13	C	-4.893311	-3.504251	-0.828092
14	N	-4.452791	0.058745	0.181487
15	C	-4.179779	1.078388	0.985848
16	C	-4.308945	2.325037	0.200497
17	N	-4.709682	2.00155	-1.0192
18	C	-0.803706	-3.074694	0.026869
19	C	-0.752777	-4.245681	0.847899
20	N	-1.952367	-4.881027	0.951211
21	C	0.322912	-2.313595	-0.183215
22	C	1.545035	-2.69259	0.422866
23	C	1.580693	-3.847027	1.233529
24	C	0.45446	-4.624176	1.451998
25	C	2.758176	-1.892843	0.205873
26	C	2.990516	-1.232678	-1.011159
27	C	4.139185	-0.491634	-1.22994
28	C	5.106202	-0.358526	-0.2227
29	C	4.880026	-1.001926	1.003245

30	C	3.737322	-1.757356	1.202965
31	N	6.268717	0.400028	-0.435921
32	C	7.495956	0.019282	0.157742
33	C	6.228281	1.555833	-1.253481
34	C	8.334047	0.986622	0.723439
35	C	9.547146	0.615661	1.290589
36	C	9.935883	-0.721142	1.319107
37	C	9.099564	-1.685874	0.763215
38	C	7.892969	-1.322755	0.177212
39	C	7.236903	1.788798	-2.194642
40	C	7.20385	2.930331	-2.986372
41	C	6.161107	3.845253	-2.86522
42	C	5.152698	3.611107	-1.933772
43	C	5.186583	2.481325	-1.125268
44	C	-4.013708	3.710424	0.548844
45	C	-3.896651	0.854358	2.396648
46	C	-4.697811	4.739838	-0.118793
47	C	-4.415573	6.068987	0.157481
48	C	-3.432837	6.397809	1.090877
49	C	-2.731041	5.386454	1.741808
50	C	-3.01758	4.052953	1.476557
51	C	-4.203459	1.800046	3.388794
52	C	-3.960848	1.518458	4.727148
53	C	-3.407444	0.295096	5.097728
54	C	-3.112131	-0.657102	4.122085
55	C	-3.362533	-0.386871	2.785763
56	H	-6.929565	0.587431	-5.043299
57	H	-6.769895	-1.891094	-5.258148
58	H	-5.552828	-3.192834	-3.549889
59	H	-5.936221	1.700933	-3.056576
60	H	-2.458058	-1.259743	-1.652203
61	H	-4.646576	-5.24534	0.435501
62	H	-5.950864	-3.676658	-0.999773
63	H	0.280057	-1.40726	-0.779193
64	H	2.527436	-4.152227	1.666287
65	H	0.495231	-5.51789	2.065141

66	H	2.279428	-1.343049	-1.823537
67	H	4.302311	-0.020406	-2.192633
68	H	5.602566	-0.893322	1.804226
69	H	3.577224	-2.215352	2.173775
70	H	8.027687	2.026959	0.713317
71	H	10.185988	1.378034	1.725178
72	H	10.88053	-1.00803	1.768783
73	H	9.393565	-2.730749	0.770028
74	H	7.251786	-2.074892	-0.269438
75	H	8.043102	1.070798	-2.299163
76	H	7.993175	3.097106	-3.712535
77	H	6.134659	4.731923	-3.48975
78	H	4.338201	4.319992	-1.82309
79	H	4.407744	2.308007	-0.390502
80	H	-5.450357	4.470065	-0.850723
81	H	-4.960752	6.853888	-0.356921
82	H	-3.210938	7.438579	1.304243
83	H	-1.951604	5.635985	2.454491
84	H	-2.451135	3.271788	1.970498
85	H	-4.658285	2.744242	3.112427
86	H	-4.213304	2.253816	5.484291
87	H	-3.21485	0.08018	6.144053
88	H	-2.688615	-1.615054	4.405801
89	H	-3.151893	-1.123343	2.018838

SCF Done: E(UmPW1PW91) = -2182.41026134 A.U.

Zero-point correction	=	0.710621 (Hartree/Particle)
Thermal correction to Energy	=	0.752503
Thermal correction to Enthalpy	=	0.753447
Thermal correction to Gibbs Free Energy	=	0.627880
Sum of electronic and zero-point Energies	=	-2181.699641
Sum of electronic and thermal Energies	=	-2181.657758
Sum of electronic and thermal Enthalpies	=	-2181.656814
Sum of electronic and thermal Free Energies	=	-2181.782381

Low frequencies --- -4.0987 -0.8595 -0.0016 -0.0006 0.0012 2.9869

Low frequencies --- 5.6177 9.3561 12.2000

The Result for the TDDFT calculation

Excited State 1: 3.061-A 1.1821 eV 1048.85 nm f=0.1051 <S**2>=2.093

182B -> 184B -0.39294

182B -> 185B -0.37548

183B -> 184B 0.73628

183B -> 185B 0.37432

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2182.47275871

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 3.059-A 1.4360 eV 863.41 nm f=0.0012 <S**2>=2.090

181B -> 184B -0.12236

182B -> 184B 0.30040

182B -> 185B 0.48816

183B -> 184B 0.65893

183B -> 185B -0.45366

Excited State 3: 3.076-A 1.6809 eV 737.60 nm f=0.1425 <S**2>=2.115

181B -> 185B -0.14185

182B -> 184B 0.54039

182B -> 185B 0.26355

183B -> 185B 0.76221

Excited State 4: 3.075-A 1.9127 eV 648.20 nm f=0.0110 <S**2>=2.114

184A -> 186A -0.10430

166B -> 184B 0.13855

180B -> 184B 0.57345

180B -> 185B -0.24473

181B -> 184B 0.68657

181B -> 185B -0.10356

Excited State 5: 3.056-A 1.9782 eV 626.77 nm f=0.0179 <S**2>=2.085

180B -> 184B 0.17932
181B -> 185B -0.17358
182B -> 184B -0.64597
182B -> 185B 0.65042
183B -> 185B 0.19383

Excited State 6: 3.056-A 2.1325 eV 581.40 nm f=0.0018 <S**2>=2.085
172B -> 184B -0.18856
172B -> 185B -0.25681
173B -> 184B 0.50685
173B -> 185B 0.73868

Excited State 7: 3.060-A 2.1667 eV 572.24 nm f=0.0297 <S**2>=2.090
169B -> 184B -0.22321
169B -> 185B 0.14335
172B -> 184B -0.30765
172B -> 185B 0.12204
173B -> 184B -0.14834
177B -> 184B -0.12730
178B -> 184B 0.19603
179B -> 184B 0.29442
180B -> 184B 0.54274
180B -> 185B -0.10780
181B -> 184B -0.44782
181B -> 185B -0.10611
182B -> 184B 0.12086
182B -> 185B -0.22839

Excited State 8: 3.080-A 2.2432 eV 552.71 nm f=0.0681 <S**2>=2.122
184A -> 187A 0.10112
169B -> 184B -0.20138
172B -> 184B -0.19376
177B -> 184B -0.15593
179B -> 184B 0.55030
179B -> 185B -0.15777
180B -> 184B -0.15985

181B -> 184B 0.33742
181B -> 185B 0.54206
182B -> 185B 0.17392
183B -> 185B 0.10970

Excited State 9: 3.100-A 2.4658 eV 502.81 nm f=0.1025 <S**2>=2.153
183A -> 187A 0.10567
184A -> 187A -0.14269
169B -> 184B -0.13502
178B -> 184B 0.13614
179B -> 184B -0.57282
179B -> 185B 0.14435
180B -> 184B 0.14692
180B -> 185B -0.18778
181B -> 184B -0.17574
181B -> 185B 0.62409

Excited State 10: 3.081-A 2.5799 eV 480.59 nm f=0.0254 <S**2>=2.124
169B -> 184B 0.15024
172B -> 184B 0.31265
175B -> 184B -0.25098
177B -> 184B 0.65917
177B -> 185B -0.19503
179B -> 184B 0.26299
180B -> 184B 0.21503
181B -> 184B -0.23649
181B -> 185B 0.29550

Excited State 11: 3.084-A 2.6624 eV 465.69 nm f=0.0043 <S**2>=2.127
169B -> 184B -0.18988
172B -> 184B -0.46022
172B -> 185B 0.14659
173B -> 184B -0.12640
174B -> 184B 0.20491
175B -> 184B 0.32293
177B -> 184B 0.51621

177B -> 185B -0.12189
178B -> 184B -0.44035
180B -> 184B -0.11351

Excited State 12: 3.097-A 2.7328 eV 453.70 nm f=0.0046 <S**2>=2.148
166B -> 184B -0.21117
166B -> 185B 0.10149
169B -> 184B -0.34121
169B -> 185B 0.11423
174B -> 184B 0.31508
175B -> 184B -0.43911
177B -> 184B 0.28166
178B -> 184B 0.47227
180B -> 184B -0.20906
181B -> 184B 0.17788
181B -> 185B -0.21076

Excited State 13: 3.176-A 2.8392 eV 436.69 nm f=0.0114 <S**2>=2.271
185A -> 188A 0.14528
185A -> 189A -0.14423
166B -> 184B -0.15038
172B -> 184B 0.22104
173B -> 184B 0.18756
174B -> 184B 0.75884
174B -> 185B -0.23196
177B -> 184B -0.15015
178B -> 184B -0.17755
178B -> 185B -0.11515
180B -> 185B 0.11027
183B -> 187B 0.11567

Excited State 14: 3.746-A 2.8717 eV 431.75 nm f=0.0577 <S**2>=3.258
177A -> 190A -0.10427
184A -> 189A 0.13564
185A -> 187A -0.22730
185A -> 188A 0.41863

185A -> 189A -0.35566
166B -> 184B -0.11558
169B -> 184B -0.19085
172B -> 185B 0.10235
174B -> 184B -0.30745
178B -> 185B -0.12792
180B -> 185B 0.13929
183B -> 186B -0.10464
183B -> 187B 0.32069
183B -> 188B 0.15673
183B -> 189B -0.11322
183B -> 190B -0.15601

Excited State 15: 3.169-A 2.9298 eV 423.18 nm f=0.0087 <S**2>=2.261
185A -> 188A -0.13032
185A -> 189A 0.11547
166B -> 184B -0.45134
166B -> 185B 0.18277
169B -> 184B -0.12932
169B -> 185B 0.11046
174B -> 184B -0.12839
179B -> 185B 0.15180
180B -> 184B 0.32214
180B -> 185B 0.64104
181B -> 184B 0.11621
181B -> 185B 0.13933
183B -> 187B -0.12195

Table S21. Standard orientation of the quinoidal form 1 of the ring-opening form of CIC-TPA.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	6.730801	0.887266	3.807361
2	C	7.151797	-0.459965	3.781036
3	C	6.595473	-1.343034	2.886909
4	C	5.582127	-0.936463	1.984134
5	C	5.263911	0.461221	1.923412
6	C	5.804215	1.335153	2.901381
7	C	4.545881	1.035401	0.836728
8	C	4.844498	-1.934634	1.256333
9	C	3.428049	-1.794538	1.080400
10	C	2.723891	-2.793003	0.474751
11	C	3.390889	-3.978044	-0.018331
12	C	4.789662	-4.118176	0.158850
13	C	5.482248	-3.126604	0.806940
14	N	4.048220	2.308062	0.897010
15	C	3.466442	2.487279	-0.279000
16	C	3.696085	1.286772	-1.099121
17	N	4.361170	0.410909	-0.368410
18	C	1.321903	-3.021253	0.157034
19	C	1.311915	-4.288913	-0.493322
20	N	2.563852	-4.856959	-0.582886
21	C	0.155631	-2.304015	0.325697
22	C	-1.062723	-2.836706	-0.149391
23	C	-1.055713	-4.092447	-0.788235
24	C	0.111828	-4.822143	-0.965867
25	C	-2.317190	-2.088211	0.018021
26	C	-2.544783	-1.279273	1.142293
27	C	-3.729914	-0.582879	1.310293
28	C	-4.741387	-0.651785	0.341760
29	C	-4.522402	-1.447114	-0.792331
30	C	-3.340570	-2.152694	-0.940713
31	N	-5.944761	0.057438	0.501732
32	C	-7.165812	-0.502459	0.055409
33	C	-5.950372	1.329090	1.122363

34	C	-8.100579	0.289670	-0.620619
35	C	-9.303956	-0.259319	-1.046490
36	C	-9.587379	-1.604149	-0.822165
37	C	-8.655262	-2.395299	-0.155476
38	C	-7.456865	-1.851117	0.290261
39	C	-6.952779	1.662036	2.040685
40	C	-6.964783	2.916362	2.638401
41	C	-5.973142	3.849323	2.346742
42	C	-4.970651	3.516876	1.439026
43	C	-4.960626	2.272070	0.821606
44	C	3.399880	1.014568	-2.504349
45	C	2.725946	3.710589	-0.568472
46	C	3.187803	-0.313839	-2.906627
47	C	2.946831	-0.618013	-4.238610
48	C	2.924782	0.394519	-5.196392
49	C	3.151321	1.713924	-4.812127
50	C	3.386099	2.024640	-3.478509
51	C	3.081364	4.896894	0.094700
52	C	2.371803	6.067888	-0.124063
53	C	1.285207	6.076079	-0.998305
54	C	0.910637	4.902030	-1.646959
55	C	1.622859	3.727898	-1.436485
56	H	7.157505	1.571845	4.533031
57	H	7.887594	-0.810059	4.497572
58	H	6.858775	-2.393600	2.937760
59	H	5.500922	2.374724	2.865467
60	H	2.933503	-0.923204	1.494191
61	H	5.290016	-5.000089	-0.226018
62	H	6.557281	-3.212081	0.918923
63	H	0.167440	-1.321408	0.787333
64	H	-1.997857	-4.514949	-1.121416
65	H	0.101649	-5.791691	-1.451831
66	H	-1.796662	-1.232583	1.927175
67	H	-3.886424	0.010382	2.204144
68	H	-5.282167	-1.495649	-1.564377
69	H	-3.187189	-2.731453	-1.845816

70	H	-7.876401	1.334193	-0.807564
71	H	-10.018643	0.367789	-1.570108
72	H	-10.524975	-2.030861	-1.162378
73	H	-8.866521	-3.442914	0.034466
74	H	-6.739290	-2.465343	0.823307
75	H	-7.718643	0.932497	2.280219
76	H	-7.748733	3.159018	3.348865
77	H	-5.981305	4.824796	2.821377
78	H	-4.195214	4.236510	1.196106
79	H	-4.187331	2.021668	0.103605
80	H	3.209648	-1.093892	-2.154090
81	H	2.773181	-1.648652	-4.530850
82	H	2.735943	0.155589	-6.238191
83	H	3.154091	2.504833	-5.555423
84	H	3.585421	3.051343	-3.192949
85	H	3.922269	4.874096	0.778279
86	H	2.664528	6.979294	0.387478
87	H	0.730361	6.993214	-1.168871
88	H	0.055711	4.898017	-2.315482
89	H	1.312789	2.813714	-1.929470

SCF Done: E(RmPW1PW91) = -2182.38377262 A.U.

Zero-point correction= 0.711998 (Hartree/Particle)
Thermal correction to Energy= 0.753713
Thermal correction to Enthalpy= 0.754658
Thermal correction to Gibbs Free Energy= 0.630459
Sum of electronic and zero-point Energies= -2181.688742
Sum of electronic and thermal Energies= -2181.647027
Sum of electronic and thermal Enthalpies= -2181.646083
Sum of electronic and thermal Free Energies= -2181.770281

Low frequencies --- -2.9427 -0.0012 0.0006 0.0014 1.0251 3.0275
Low frequencies --- 6.4367 8.3257 9.5889

The Result for the TDDFT calculation

Excited State 1: Singlet-A 0.9681 eV 1280.67 nm f=0.2231 <S**2>=0.000

182 -> 185 -0.13263

183 -> 185 -0.23192

184 -> 185 0.66960

184 <- 185 -0.15195

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2182.47148590

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.3824 eV 896.90 nm f=0.2046 <S**2>=0.000

182 -> 185 0.23976

183 -> 185 0.61507

184 -> 185 0.30179

183 <- 185 -0.12568

184 <- 185 -0.15395

Excited State 3: Singlet-A 1.5397 eV 805.23 nm f=0.0322 <S**2>=0.000

181 -> 185 0.13937

182 -> 185 0.63034

183 -> 185 -0.27640

Excited State 4: Singlet-A 2.1270 eV 582.91 nm f=0.0832 <S**2>=0.000

180 -> 185 0.15507

181 -> 185 0.66259

182 -> 185 -0.11065

Excited State 5: Singlet-A 2.3243 eV 533.43 nm f=0.0197 <S**2>=0.000

170 -> 185 0.19685

176 -> 185 -0.16672

178 -> 185 0.16236

179 -> 185 -0.37831

180 -> 185 0.47576

Excited State 6: Singlet-A 2.4829 eV 499.36 nm f=0.0953 <S**2>=0.000

170 -> 185 -0.16817

178 -> 185 -0.11943
179 -> 185 0.40570
180 -> 185 0.45730
181 -> 185 -0.13268
184 -> 186 -0.15046

Excited State 7: Singlet-A 2.5798 eV 480.60 nm f=0.0099 <S**2>=0.000
176 -> 185 -0.22436
178 -> 185 0.54261
179 -> 185 0.34483

Excited State 8: Singlet-A 2.6358 eV 470.39 nm f=0.0025 <S**2>=0.000
170 -> 185 0.21549
171 -> 185 0.64129
173 -> 185 -0.15569

Excited State 9: Singlet-A 2.8125 eV 440.83 nm f=0.0144 <S**2>=0.000
170 -> 185 0.51769
171 -> 185 -0.16255
174 -> 185 0.18395
175 -> 185 0.27010
177 -> 185 -0.15788
178 -> 185 -0.15448
179 -> 185 0.17288

Excited State 10: Singlet-A 2.8375 eV 436.95 nm f=0.0002 <S**2>=0.000
170 -> 185 0.12123
173 -> 185 0.14207
176 -> 185 0.20933
177 -> 185 0.63395

Excited State 11: Singlet-A 2.8701 eV 431.98 nm f=0.0077 <S**2>=0.000
170 -> 185 -0.17807
174 -> 185 -0.24012
175 -> 185 0.50996
176 -> 185 -0.28079

178 -> 185	-0.19888				
Excited State 12:	Singlet-A	2.8929 eV	428.57 nm	f=0.0128	<S**2>=0.000
170 -> 185	-0.18411				
174 -> 185	0.19824				
175 -> 185	0.37917				
176 -> 185	0.39212				
177 -> 185	-0.12636				
178 -> 185	0.25719				
179 -> 185	-0.13015				
Excited State 13:	Singlet-A	3.0263 eV	409.69 nm	f=0.0207	<S**2>=0.000
169 -> 185	0.20593				
170 -> 185	-0.11389				
174 -> 185	0.50802				
176 -> 185	-0.33768				
177 -> 185	0.12107				
184 -> 186	0.16098				
Excited State 14:	Singlet-A	3.1659 eV	391.62 nm	f=0.0886	<S**2>=0.000
168 -> 185	0.35590				
169 -> 185	0.30228				
173 -> 185	0.14325				
174 -> 185	-0.25629				
184 -> 186	0.37993				
Excited State 15:	Singlet-A	3.2030 eV	387.09 nm	f=0.0152	<S**2>=0.000
171 -> 185	0.13138				
173 -> 185	0.65389				
176 -> 185	-0.12204				
177 -> 185	-0.12631				
184 -> 186	-0.10141				

Table S22. Standard orientation of the quinoidal form 2 of the ring-opening form of CIC-TPA.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	-4.574072	4.996487	1.026845
2	C	-3.194791	4.857352	1.304395
3	C	-2.626422	3.610764	1.387782
4	C	-3.399029	2.43209	1.217057
5	C	-4.760613	2.590705	0.780117
6	C	-5.338378	3.888372	0.77586
7	C	-5.50385	1.529779	0.20143
8	C	-2.838108	1.168014	1.600864
9	C	-1.438306	0.929339	1.42517
10	C	-0.899066	-0.254383	1.832574
11	C	-1.713269	-1.253201	2.50999
12	C	-3.092703	-0.98837	2.735693
13	C	-3.630152	0.17716	2.270699
14	N	-6.855384	1.628608	-0.011527
15	C	-7.183743	0.474486	-0.563439
16	C	-5.951909	-0.316159	-0.755336
17	N	-4.940991	0.3705	-0.258771
18	C	0.424934	-0.857093	1.776629
19	C	0.267316	-2.109084	2.428878
20	N	-1.033803	-2.332933	2.861495
21	C	1.650653	-0.463444	1.280104
22	C	2.765703	-1.318435	1.424535
23	C	2.591924	-2.551984	2.072623
24	C	1.357762	-2.957712	2.577447
25	C	4.084556	-0.91688	0.906335
26	C	4.210673	-0.173197	-0.276359
27	C	5.449718	0.195446	-0.775196
28	C	6.624237	-0.153537	-0.095093
29	C	6.511597	-0.886676	1.094126
30	C	5.268271	-1.263775	1.574439
31	N	7.88626	0.221753	-0.593175
32	C	8.988674	-0.656506	-0.470582
33	C	8.060074	1.475715	-1.22405
34	C	10.247472	-0.165396	-0.10567

35	C	11.330405	-1.029217	0.003683
36	C	11.174945	-2.393225	-0.229742
37	C	9.92154	-2.884594	-0.585711
38	C	8.836653	-2.026169	-0.715919
39	C	8.834931	1.582416	-2.384809
40	C	9.01379	2.817743	-2.995348
41	C	8.412833	3.960097	-2.472959
42	C	7.635583	3.854611	-1.322356
43	C	7.465433	2.626936	-0.694143
44	C	-5.725743	-1.583953	-1.444417
45	C	-8.577195	0.146687	-0.847714
46	C	-4.636972	-2.381108	-1.054622
47	C	-4.360445	-3.568707	-1.715871
48	C	-5.155883	-3.977663	-2.785442
49	C	-6.227449	-3.18667	-3.192394
50	C	-6.513287	-1.999953	-2.529058
51	C	-9.483931	1.185762	-1.113626
52	C	-10.823664	0.911425	-1.343515
53	C	-11.287922	-0.402851	-1.298238
54	C	-10.402537	-1.439865	-1.01581
55	C	-9.057808	-1.17088	-0.793176
56	H	-5.019585	5.985111	0.989976
57	H	-2.591503	5.738452	1.496721
58	H	-1.59238	3.518137	1.700329
59	H	-6.384347	3.968211	0.504815
60	H	-0.837721	1.665232	0.900341
61	H	-3.689617	-1.708072	3.284634
62	H	-4.673523	0.400664	2.456441
63	H	1.777196	0.505369	0.806063
64	H	3.440486	-3.223374	2.155055
65	H	1.240321	-3.917428	3.068667
66	H	3.321454	0.081476	-0.844629
67	H	5.516537	0.745817	-1.70709
68	H	7.407535	-1.147305	1.64655
69	H	5.210914	-1.80206	2.515193
70	H	10.368718	0.894395	0.090272

71	H	12.299935	-0.632434	0.288039
72	H	12.021106	-3.06563	-0.135974
73	H	9.786853	-3.944129	-0.779426
74	H	7.865341	-2.409723	-1.008626
75	H	9.293953	0.692665	-2.80169
76	H	9.61725	2.88307	-3.895278
77	H	8.549266	4.921594	-2.9565
78	H	7.168226	4.737736	-0.898072
79	H	6.872559	2.551252	0.210885
80	H	-4.022823	-2.050599	-0.224369
81	H	-3.52206	-4.179007	-1.395889
82	H	-4.938399	-4.90718	-3.301914
83	H	-6.838979	-3.490156	-4.036106
84	H	-7.333831	-1.378658	-2.869446
85	H	-9.111616	2.203558	-1.135933
86	H	-11.511131	1.723396	-1.558088
87	H	-12.337021	-0.616165	-1.476692
88	H	-10.761247	-2.462609	-0.96102
89	H	-8.379004	-1.981304	-0.55346

SCF Done: E(RmPW1PW91) = -2182.02931854 A.U.

Zero-point correction = 0.711979 (Hartree/Particle)
Thermal correction to Energy = 0.753694
Thermal correction to Enthalpy = 0.754638
Thermal correction to Gibbs Free Energy = 0.630799
Sum of electronic and zero-point Energies = -2181.685922
Sum of electronic and thermal Energies = -2181.644207
Sum of electronic and thermal Enthalpies = -2181.643263
Sum of electronic and thermal Free Energies = -2181.767102

Low frequencies --- -2.6773 -0.0022 -0.0009 0.0020 2.4037 3.7118
Low frequencies --- 8.5027 9.4533 11.4136

The Result for the TDDFT calculation

Excited State 1: Singlet-A 0.8933 eV 1387.93 nm f=0.2802 <S**2>=0.000

182 -> 185 -0.18260

183 -> 185 0.20505

184 -> 185 0.66382

184 <- 185 -0.13256

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2182.47108441

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.3836 eV 896.13 nm f=0.1772 <S**2>=0.000

182 -> 185 0.11314

183 -> 185 0.68622

184 -> 185 -0.21398

183 <- 185 -0.13074

184 <- 185 0.14830

Excited State 3: Singlet-A 1.5227 eV 814.24 nm f=0.2072 <S**2>=0.000

182 -> 185 0.66146

184 -> 185 0.22805

Excited State 4: Singlet-A 2.2447 eV 552.33 nm f=0.0844 <S**2>=0.000

180 -> 185 -0.24019

181 -> 185 0.64930

Excited State 5: Singlet-A 2.3771 eV 521.59 nm f=0.0343 <S**2>=0.000

170 -> 185 -0.23863

174 -> 185 -0.10709

176 -> 185 -0.10035

177 -> 185 0.14555

178 -> 185 0.22130

180 -> 185 0.50779

181 -> 185 0.22180

184 -> 186 0.11025

Excited State 6: Singlet-A 2.4449 eV 507.12 nm f=0.1380 <S**2>=0.000

170 -> 185 0.20771

174 -> 185 0.15100
175 -> 185 0.10155
176 -> 185 0.31105
177 -> 185 -0.22949
178 -> 185 -0.32531
180 -> 185 0.36315

Excited State 7: Singlet-A 2.5868 eV 479.30 nm f=0.0100 <S**2>=0.000
171 -> 185 0.64009
173 -> 185 0.13156
174 -> 185 -0.10194
176 -> 185 -0.10822
177 -> 185 -0.14713
179 -> 185 -0.12240

Excited State 8: Singlet-A 2.6078 eV 475.43 nm f=0.0375 <S**2>=0.000
171 -> 185 0.22354
174 -> 185 0.13276
176 -> 185 0.31587
177 -> 185 0.22731
178 -> 185 0.33506
179 -> 185 0.38082

Excited State 9: Singlet-A 2.7720 eV 447.28 nm f=0.0424 <S**2>=0.000
170 -> 185 0.39600
174 -> 185 0.31159
177 -> 185 0.18080
178 -> 185 0.18193
179 -> 185 -0.33492
183 -> 186 -0.10609
184 -> 186 0.16749

Excited State 10: Singlet-A 2.8280 eV 438.41 nm f=0.0001 <S**2>=0.000
171 -> 185 0.10286
173 -> 185 -0.13540
177 -> 185 0.54594

178 -> 185 -0.41256

Excited State 11: Singlet-A 2.8517 eV 434.77 nm f=0.0105 <S**2>=0.000
169 -> 185 -0.10011
170 -> 185 -0.25799
175 -> 185 0.52077
176 -> 185 0.26574
179 -> 185 -0.23100

Excited State 12: Singlet-A 2.8823 eV 430.15 nm f=0.0047 <S**2>=0.000
170 -> 185 -0.33900
174 -> 185 0.37151
175 -> 185 -0.35513
176 -> 185 0.22384
179 -> 185 -0.21967

Excited State 13: Singlet-A 2.9843 eV 415.46 nm f=0.0058 <S**2>=0.000
169 -> 185 -0.19714
170 -> 185 -0.18696
174 -> 185 0.35936
175 -> 185 0.22444
176 -> 185 -0.35619
179 -> 185 0.29851

Excited State 14: Singlet-A 3.1804 eV 389.83 nm f=0.0158 <S**2>=0.000
168 -> 185 0.29094
169 -> 185 -0.21243
171 -> 185 -0.10730
173 -> 185 0.52254
174 -> 185 -0.11918
184 -> 186 0.18918

Excited State 15: Singlet-A 3.1860 eV 389.15 nm f=0.0386 <S**2>=0.000
168 -> 185 -0.38381
169 -> 185 0.24488
173 -> 185 0.42955

174 -> 185	0.10651
184 -> 186	-0.22685

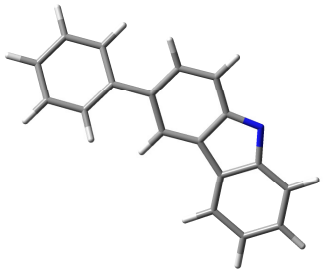


Fig. S67 Molecular structure of the substructure 1 of the carbazole cation of CIC.

Table S23. Standard orientation of the optimized geometry of the substructure of the carbazole cation of CIC.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	5.065794	0.331611	0.504981
2	C	3.769093	0.810186	0.454940
3	C	2.713436	-0.009857	-0.012244
4	C	3.022743	-1.324863	-0.436362
5	C	4.326585	-1.787105	-0.411655
6	C	5.350669	-0.964554	0.065398
7	C	1.354958	0.485828	-0.058954
8	C	0.251633	-0.442824	0.007369
9	C	-1.019539	0.034908	-0.017785
10	C	-1.263096	1.459653	-0.130834
11	C	-0.182862	2.377127	-0.208455
12	C	1.097207	1.883236	-0.164301
13	C	-2.366475	-0.549750	0.054340
14	C	-3.238645	0.568683	-0.030657
15	N	-2.551094	1.764282	-0.141220
16	C	-2.878339	-1.817360	0.169927
17	C	-4.291770	-1.966646	0.201439
18	C	-5.140541	-0.874146	0.117449
19	C	-4.620451	0.427275	-0.001856
20	H	5.859744	0.962063	0.889907

21	H	3.560637	1.806286	0.827997
22	H	2.246726	-1.966305	-0.838089
23	H	4.552513	-2.786769	-0.766117
24	H	6.370548	-1.333707	0.095960
25	H	0.452261	-1.501017	0.126095
26	H	-0.384205	3.438115	-0.311146
27	H	1.930815	2.567323	-0.259478
28	H	-2.243351	-2.694768	0.238575
29	H	-4.710311	-2.963107	0.294392
30	H	-6.214121	-1.022674	0.144148
31	H	-5.265993	1.296175	-0.070154

SCF Done: E(RmPW1PW91) = -747.458643905 A.U.

Zero-point correction= 0.247870 (Hartree/Particle)
Thermal correction to Energy= 0.261271
Thermal correction to Enthalpy= 0.262215
Thermal correction to Gibbs Free Energy= 0.207147
Sum of electronic and zero-point Energies= -747.223262
Sum of electronic and thermal Energies= -747.209861
Sum of electronic and thermal Enthalpies= -747.208917
Sum of electronic and thermal Free Energies= -747.263984

Low frequencies --- -1.1991 0.0007 0.0009 0.0011 3.0100 4.3968
Low frequencies --- 45.1618 58.9585 89.2438

The Result for the TDDFT calculation

Excited State 1: Singlet-A 1.1396 eV 1087.99 nm f=0.0198 <S**2>=0.000
62 -> 64 -0.32128
63 -> 64 0.63081
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -747.447117572
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.1376 eV 580.01 nm f=0.0021 <S**2>=0.000

61 -> 64 0.70089

Excited State 3: Singlet-A 2.2928 eV 540.76 nm f=0.6130 <S**2>=0.000
62 -> 64 0.61620
63 -> 64 0.31928

Excited State 4: Singlet-A 2.3618 eV 524.96 nm f=0.0097 <S**2>=0.000
59 -> 64 0.69773

Excited State 5: Singlet-A 2.9582 eV 419.12 nm f=0.1197 <S**2>=0.000
58 -> 64 0.15349
60 -> 64 0.67317

Excited State 6: Singlet-A 3.3428 eV 370.90 nm f=0.0141 <S**2>=0.000
58 -> 64 0.68500
60 -> 64 -0.14598

Excited State 7: Singlet-A 4.1557 eV 298.35 nm f=0.0050 <S**2>=0.000
51 -> 64 -0.10064
53 -> 64 -0.13091
54 -> 64 0.10616
56 -> 64 0.58069
57 -> 64 -0.32952

Excited State 8: Singlet-A 4.3504 eV 285.00 nm f=0.0226 <S**2>=0.000
54 -> 64 0.28586
55 -> 64 0.54648
57 -> 64 0.21301
63 -> 65 0.24031

Excited State 9: Singlet-A 4.3769 eV 283.27 nm f=0.1750 <S**2>=0.000
55 -> 64 -0.29385
56 -> 64 0.23863
57 -> 64 0.27138
63 -> 65 0.49865

Excited State	10:	Singlet-A	4.5466 eV	272.69 nm	f=0.2989	<S**2>=0.000
53 -> 64	-0.14848					
56 -> 64	0.18304					
57 -> 64	0.46825					
62 -> 65	-0.11710					
63 -> 65	-0.39330					
Excited State	11:	Singlet-A	4.6195 eV	268.39 nm	f=0.0093	<S**2>=0.000
53 -> 64	0.46870					
54 -> 64	-0.41949					
55 -> 64	0.15954					
56 -> 64	0.21454					
Excited State	12:	Singlet-A	4.6687 eV	265.57 nm	f=0.0017	<S**2>=0.000
52 -> 64	-0.11397					
53 -> 64	0.45061					
54 -> 64	0.45190					
55 -> 64	-0.25707					
Excited State	13:	Singlet-A	4.9229 eV	251.85 nm	f=0.0191	<S**2>=0.000
52 -> 64	0.40994					
62 -> 65	0.37688					
63 -> 66	-0.38524					
Excited State	14:	Singlet-A	4.9935 eV	248.29 nm	f=0.0571	<S**2>=0.000
51 -> 64	0.25922					
52 -> 64	0.44500					
63 -> 66	0.43450					
Excited State	15:	Singlet-A	5.0279 eV	246.59 nm	f=0.0135	<S**2>=0.000
51 -> 64	0.63244					
52 -> 64	-0.19293					
53 -> 64	-0.10700					
63 -> 66	-0.16110					
Excited State	16:	Singlet-A	5.1578 eV	240.38 nm	f=0.0047	<S**2>=0.000

61 -> 65 0.53399
61 -> 66 0.21269
62 -> 65 -0.15094
62 -> 66 -0.20290
62 -> 67 0.13771
63 -> 67 0.24652

Excited State 17: Singlet-A 5.3086 eV 233.55 nm f=0.3518 <S**2>=0.000
50 -> 64 -0.13975
52 -> 64 -0.20334
61 -> 66 0.17205
61 -> 67 -0.11616
62 -> 65 0.50067
62 -> 66 -0.12547
63 -> 66 0.30228

Excited State 18: Singlet-A 5.3519 eV 231.66 nm f=0.0887 <S**2>=0.000
61 -> 65 0.18843
61 -> 66 0.10421
62 -> 66 0.62497
63 -> 69 -0.11831

Excited State 19: Singlet-A 5.5353 eV 223.99 nm f=0.0077 <S**2>=0.000
61 -> 65 -0.38089
61 -> 66 0.48812
61 -> 68 0.10695
63 -> 67 0.25164

Excited State 20: Singlet-A 5.6394 eV 219.86 nm f=0.0221 <S**2>=0.000
49 -> 64 0.54060
50 -> 64 -0.37749
60 -> 65 0.13009

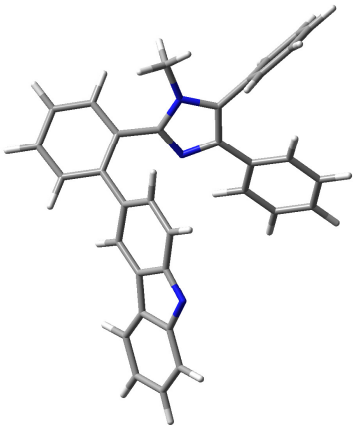


Fig. S68 Molecular structure of the substructure 2 of the carbazole cation of CIC.

Table S24. Standard orientation of the optimized geometry for the substructure 2 of the carbazole cation of CIC.

Tag	Symbol	Coordinates		
		X	Y	Z
1	C	1.101232	4.094967	-0.791542
2	C	-0.917178	2.842546	-0.259124
3	C	-1.678242	3.975052	-0.614303
4	C	-1.063183	5.153334	-0.994486
5	C	0.332870	5.214646	-1.072863
6	C	-1.601584	1.704720	0.330127
7	C	-2.868632	1.300856	-0.209178
8	C	-3.528846	0.259115	0.366257
9	C	-2.988521	-0.390005	1.551497
10	C	-1.760612	0.052921	2.119754
11	C	-1.085612	1.068028	1.500497
12	C	-4.771114	-0.467230	0.097755
13	C	-4.841804	-1.437872	1.129550
14	N	-3.751898	-1.369686	1.995526
15	C	-5.763057	-0.384541	-0.852535
16	C	-6.846135	-1.292490	-0.767760
17	C	-6.912568	-2.239842	0.242677
18	C	-5.900577	-2.327105	1.217654
19	H	2.171863	4.137803	-0.952167
20	H	-2.757757	3.945242	-0.509031

21	H	-1.661292	6.028898	-1.222238
22	H	0.817698	6.130921	-1.392994
23	H	-3.241065	1.789848	-1.103176
24	H	-1.393545	-0.411298	3.028471
25	H	-0.157411	1.435995	1.921115
26	H	-5.732481	0.347810	-1.653271
27	H	-7.635753	-1.242691	-1.509789
28	H	-7.754087	-2.922657	0.284415
29	H	-5.941780	-3.061163	2.014948
30	C	1.244310	1.644768	-0.325992
31	C	2.833015	0.151570	0.023049
32	C	1.700503	-0.449070	-0.557996
33	C	0.499767	2.889962	-0.401546
34	N	0.749545	0.492135	-0.760032
35	N	2.523874	1.480973	0.154199
36	C	3.403174	2.496449	0.713403
37	H	4.070043	2.033456	1.438437
38	H	4.011133	2.956032	-0.070150
39	H	2.808649	3.260865	1.213166
40	C	1.491069	-1.842448	-0.957228
41	C	0.528081	-2.129283	-1.937574
42	C	2.204073	-2.902797	-0.377477
43	C	0.294153	-3.439276	-2.334386
44	H	-0.025069	-1.310911	-2.385588
45	C	1.962417	-4.213397	-0.774655
46	H	2.937565	-2.708355	0.396730
47	C	1.010974	-4.487120	-1.755281
48	H	-0.445847	-3.645954	-3.101207
49	H	2.516907	-5.024092	-0.312935
50	H	0.827967	-5.510646	-2.066365
51	C	4.146882	-0.401557	0.391114
52	C	4.524346	-0.532294	1.734362
53	C	5.029593	-0.818343	-0.613031
54	C	5.766865	-1.065100	2.065577
55	H	3.834195	-0.239462	2.521047
56	C	6.271178	-1.349661	-0.276858

57	H	4.737615	-0.729799	-1.654837
58	C	6.642379	-1.472258	1.060659
59	H	6.047459	-1.169144	3.108738
60	H	6.948870	-1.669216	-1.061826
61	H	7.610191	-1.888913	1.319938

SCF Done: E(RmPW1PW91) = -1473.79252215 A.U.

Zero-point correction= 0.491263 (Hartree/Particle)
Thermal correction to Energy= 0.519757
Thermal correction to Enthalpy= 0.520701
Thermal correction to Gibbs Free Energy= 0.429179
Sum of electronic and zero-point Energies= -1473.301359
Sum of electronic and thermal Energies= -1473.272865
Sum of electronic and thermal Enthalpies= -1473.271921
Sum of electronic and thermal Free Energies= -1473.363443

Low frequencies --- -7.9299 -2.6237 -0.0060 -0.0034 -0.0030 2.7652
Low frequencies --- 13.8798 16.7175 25.2331

The Result for the TDDFT calculation

Excited State 1: Singlet-A 0.8465 eV 1464.60 nm f=0.1246 <S**2>=0.000
124 ->125 0.73238
124 <-125 -0.21533
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1473.79682878
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.1082 eV 1118.82 nm f=0.0111 <S**2>=0.000
119 ->125 -0.18068
121 ->125 -0.17753
122 ->125 0.57750
123 ->125 0.30915

Excited State	3:	Singlet-A	1.3787 eV	899.27 nm	f=0.0034	<S**2>=0.000
122 ->125		-0.32176				
123 ->125		0.62704				
Excited State	4:	Singlet-A	1.7325 eV	715.64 nm	f=0.0419	<S**2>=0.000
121 ->125		0.66735				
122 ->125		0.17710				
Excited State	5:	Singlet-A	1.9531 eV	634.79 nm	f=0.0103	<S**2>=0.000
120 ->125		0.69454				
Excited State	6:	Singlet-A	2.0159 eV	615.02 nm	f=0.0669	<S**2>=0.000
118 ->125		0.19025				
119 ->125		0.64509				
120 ->125		0.10326				
121 ->125		-0.12282				
122 ->125		0.10858				
Excited State	7:	Singlet-A	2.3175 eV	534.99 nm	f=0.3154	<S**2>=0.000
118 ->125		0.65704				
119 ->125		-0.17531				
122 ->125		-0.11556				
Excited State	8:	Singlet-A	2.3621 eV	524.89 nm	f=0.0017	<S**2>=0.000
114 ->125		0.68973				
115 ->125		-0.11220				
Excited State	9:	Singlet-A	2.6240 eV	472.50 nm	f=0.0357	<S**2>=0.000
113 ->125		0.13438				
116 ->125		-0.25421				
117 ->125		0.62647				
Excited State	10:	Singlet-A	2.8616 eV	433.27 nm	f=0.0324	<S**2>=0.000
112 ->125		0.11257				
113 ->125		0.10941				
116 ->125		0.63700				

117 ->125 0.23409

Excited State 11: Singlet-A 2.9690 eV 417.60 nm f=0.0044 <S**2>=0.000
113 ->125 0.16641
115 ->125 0.67057

Excited State 12: Singlet-A 3.1208 eV 397.28 nm f=0.0197 <S**2>=0.000
113 ->125 0.64613
115 ->125 -0.15551
117 ->125 -0.15362
124 ->126 0.13433

Excited State 13: Singlet-A 3.4053 eV 364.09 nm f=0.0214 <S**2>=0.000
112 ->125 0.67687
124 ->126 0.10524

Excited State 14: Singlet-A 3.5507 eV 349.18 nm f=0.1512 <S**2>=0.000
113 ->125 -0.11321
124 ->126 0.66763

Excited State 15: Singlet-A 3.8231 eV 324.30 nm f=0.0829 <S**2>=0.000
124 ->127 0.69102

Excited State 16: Singlet-A 3.8276 eV 323.92 nm f=0.0009 <S**2>=0.000
111 ->125 0.70391

Excited State 17: Singlet-A 4.0508 eV 306.07 nm f=0.0021 <S**2>=0.000
110 ->125 0.70301

Excited State 18: Singlet-A 4.0936 eV 302.88 nm f=0.0517 <S**2>=0.000
124 ->128 0.69502

Excited State 19: Singlet-A 4.2832 eV 289.46 nm f=0.0910 <S**2>=0.000
107 ->125 0.17471
108 ->125 -0.19133
122 ->126 0.50911

122 ->127	-0.13750					
123 ->126	0.33902					
Excited State 20:	Singlet-A	4.4081 eV	281.26 nm	f=0.0140	<S**2>=0.000	
104 ->125	-0.16819					
105 ->125	0.56657					
108 ->125	0.23159					
109 ->125	0.13194					
123 ->126	0.20028					

Table S25. Energy difference between closed form and singlet biradical of CIC and PTIC derivatives. The energy level of the CIC and PTIC derivatives calculated at the MPW1PW91/6-31G(d) and UMPW1PW91/6-31G(d) level of the theory.

	CIC	CIC-tBuPh	CIC-TPA	PTIC	PTIC-tBuPh	PTIC-TPA
Time constant / μs	2.9	5.2	6.2	0.58	0.70	0.51
ΔE / kJ mol^{-1}	53.1	52.6	46.5	66.6	65.8	64.5

11. References

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