## Electronic Supplementary Information for:

# Stealth Fast Photoswitching of Negative Photochromic Naphthalene-Bridged Phenoxyl-Imidazolyl Radical Complexes

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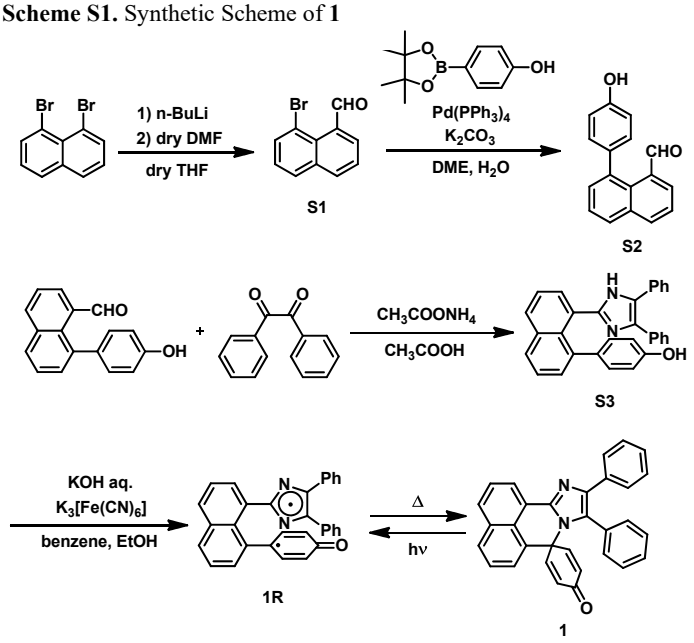
**CONTENTS**

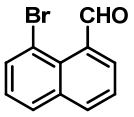
## 1. Syntheses

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 (Wakogel® C-300). $^1$H NMR spectra were recorded at 400 MHz on a Bruker AVANCE III 400 NanoBay. DMSO-$d_6$, $CD_2Cl_2$ and $CDCl_3$ were used as deuterated solvent. ESI–TOF–MS spectra were recorded on a Bruker micrOTOF II-AGA1. All glassware was washed with distilled water and dried. Unless otherwise noted, all reagents and reaction solvents were purchased from TCI, Wako Co. Ltd., Aldrich Chemical Co., Inc., Kanto Chemical Co., Inc. and ACROS Organics and were used without further purification.

**Scheme S1.** Synthetic Scheme of **1**



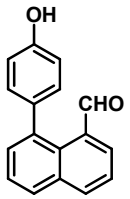

**8-bromo-1-naphthaldehyde (S1)**



S1

12.1 mL (19.36 mmol) of n-butyl lithium solution (1.6 M in hexane) was added into a solution of 3.7 g (12.94 mmol) of 1,8-dibromonaphthalene in 36 mL of anhydrous THF at −78 °C under $N_2$ atmosphere. The resulting reaction mixture was stirred at −78 °C for 20 minutes, treated with 1.9 mL (24.54 mmol) of anhydrous DMF, and then kept stirred at −78 °C for 15 minutes. The reaction mixture was slowly warmed to room temperature, and stirred for 30 minutes at room temperature. After the quenching with water, the reaction mixture was extracted with $CH_2Cl_2$. The organic extract was washed with water and brine, and dried over $Na_2SO_4$. After removal of the solvents, the crude product was purified by silica gel column chromatography ($CH_2Cl_2$/hexane = 2/3), to give desired product as a white solid (1.75 g, 57 %). $^1$H NMR (400 MHz, $CDCl_3$) δ: 11.44 (s, 1H), 8.01 (d, $J$ = 8.2 Hz, 1H), 7.94–7.88 (m, 3H), 7.57 (t, $J$ = 7.8 Hz, 1H), 7.40 (t, $J$ = 7.8 Hz, 1H).

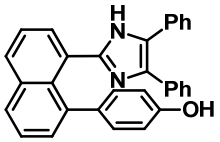
**8-(4-hydroxyphenyl)-1-naphthaldehyde (S2)**



S2

$K_2CO_3$ (163 mg, 1.18 mmol), 1-bromo-8-naphthaldehyde (400 mg, 1.70 mmol), and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (450 mg, 2.05 mmol) were added to DME (8 mL) and water (4.8 mL) and the mixture was purged with $N_2$ gas. $Pd(PPh_3)_4$ (56 mg, 0.048 mmol) was added to the solution and the solution was refluxed for 12 hours. The reaction mixture was extracted with $CH_2Cl_2$, and the organic extract was washed with water and brine, and dried over $Na_2SO_4$. After removal of the solvents, the crude product was purified by silica gel column chromatography ($CH_2Cl_2$/AcOEt = 25/1), to give desired product as a yellow solid (328 mg, 78 %). $^1$H NMR (400 MHz, DMSO-$d_6$) δ: 9.76 (br, 1H), 9.46 (s, 1H), 8.23 (d, $J$ = 8.4 Hz, 1H), 8.03 (d, $J$ = 8.2 Hz, 1H), 7.80 (d, $J$ = 7.4 Hz, 1H), 7.67–7.62 (m, 2H), 7.52 (d, $J$ = 7.4 Hz, 1H), 7.20 (d, $J$ = 8.4 Hz, 2H), 6.87 (d, $J$ = 8.4 Hz, 2H).

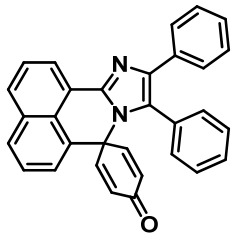
**4-(8-(4,5-diphenyl-1*H*-imidazol-2-yl)naphthalen-1-yl)phenol (S3)**



S3

8-(4-hydroxyphenyl)-1-naphthaldehyde (98 mg, 0.395 mmol), benzil (153 mg, 0.728 mmol) and ammonium acetate (225 mg, 2.92 mmol) were dissolved in acetic acid 5 mL. The mixture was stirred at 110 °C for 25 hours. After cooling to room temperature, the reaction mixture was neutralized with aqueous $NH_3$, and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was washed with water and brine, dried with $Na_2SO_4$, and evaporated. The product was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/AcOEt = 5/1) to give desired product as a pale brown solid (140 mg, 81 %). $^1$H NMR (400 MHz, DMSO-$d_6$) δ: 11.75 (s, 1H), 9.04 (s, 1H), 8.11 (d, $J$ = 8.2 Hz, 1H), 8.00 (d, $J$ = 8.2 Hz, 1H), 7.72 (d, $J$ = 7.0 Hz, 1H), 7.66–7.59 (m, 2H), 7.39 (d, $J$ = 7.0 Hz, 1H), 7.34–7.14 (m, 10H), 6.93 (d, $J$ = 8.3 Hz, 2H), 6.39 (d, $J$ = 8.3 Hz, 2H); HRMS (ESI-TOF) calculated for $C_{31}H_{22}N_2O$ $[M+H]^+$: 439.1805, found: 489.1798.

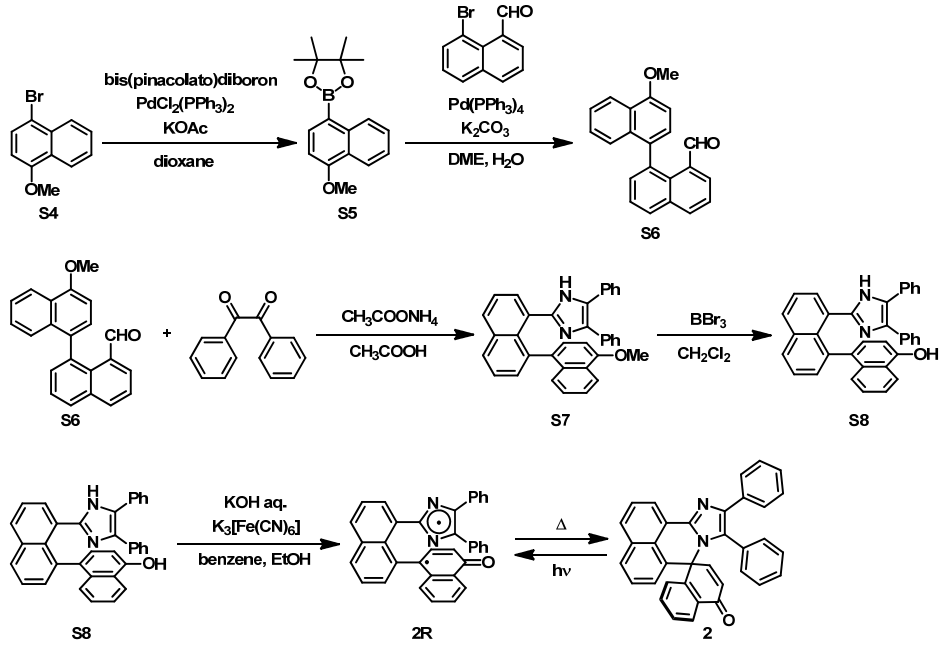
**naphthalene bridged phenoxyl-imidazolyl radical complex (1)**



1

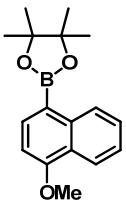
To a solution of 8-(4-hydroxyphenyl)-1-naphthaldehyde (98 mg, 0.395 mmol) (150 mg, 0.342 mmol) in benzene 60 mL and ethanol 1.8 mL was added KOH (2.1 g, 37.4 mmol) and $K_3[Fe(CN)_6]$ (1.5 g, 4.56 mmol) in water 60 mL. The mixture was vigorously stirred for 1.5 hours at room temperature. The reaction mixture was washed with water and the solvent was removed by evaporation. The crude product was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/AcOEt = 5/1) to give desired product as a pale yellow powder. The product was recrystallized from $CHCl_3$ and hexane to give pale yellow crystals (52 mg, 35 %). $^1$H NMR (400 MHz, $CD_2Cl_2$) δ: 8.54 (d, $J$ = 7.2 Hz, 1H), 7.92 (d, $J$ = 8.3 Hz, 1H), 7.88 (d, $J$ = 8.3 Hz, 1H), 7.70 (t, $J$ = 7.6 Hz, 1H), 7.55 (d, $J$ = 7.6 Hz, 2H), 7.50–7.42 (m, 2H), 7.38–7.31 (m, 5H), 7.22–7.14 (m, 3H), 6.94 (d, $J$ = 9.8 Hz, 2H), 5.84 (d, $J$ = 9.8 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 184.65, 149.29, 141.25, 140.25, 134.70, 133.87, 133.27, 131.23, 130.34, 130.16, 129.05, 128.90, 128.76, 128.48, 127.52, 127.31, 127.08, 127.03, 126.67, 126.41, 125.91, 124.94, 123.27, 121.43, 62.93. HRMS (ESI-TOF) calculated for $C_{31}H_{20}N_2O$ $[M+H]^+$: 437.1648, found: 437.1667.

**Scheme S2.** Synthetic Scheme of **2**




**1-bromo-4-methoxynaphthalene (S4)** was synthesized according to a literature procedure[S1].

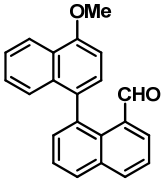
**2-(4-methoxynaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S5)**



S5

KOAc (4.02 g, 51.44 mmol), 1-bromo-4-methoxynaphthalene (2.61 g, 11.01 mmol) and bis(pinacolato)diboron (3.5 g, 13.78 mmol) were added to dioxane (50 mL), and the mixture was purged with $N_2$ gas. $PdCl_2(PPh_3)_2$ (400 mg, 0.570 mmol) was added to the solution and the solution was stirred at 80 °C for 12 hours. The reaction mixture was cooled to room temperature and filtered. The mixture was added water and extracted with $CH_2Cl_2$. The organic extract was washed with water and brine, and dried over $Na_2SO_4$. After removal of the solvents, the crude product was purified by silica gel column chromatography (hexane/$CH_2Cl_2$ = 2/1), to give desired product as a white solid (1.74 g, 56 %). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 8.5 Hz, 1H), 8.28 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H).

**4'-methoxy-[1,1'-binaphthalene]-8-carbaldehyde (S6)**

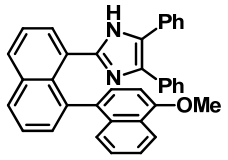


S6

$K_2CO_3$ (242 mg, 1.75 mmol), 1-bromo-8-naphthaldehyde (403 mg, 1.71 mmol) and 2-(4-methoxynaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (580 mg, 2.04 mmol) were added to DME 8 mL and water 4.8 mL, and the mixture was purged with $N_2$ gas. $Pd(PPh_3)_4$ (60 mg, 0.0519 mmol) was added to the solution and the solution was stirred at 90 °C for 21 hours. The reaction mixture was added water and extracted with $CH_2Cl_2$. The organic extract was washed with water and brine, and dried over $Na_2SO_4$. After removal of the solvents, the crude product was purified by silica gel column chromatography (hexane/$CH_2Cl_2$ = 1/1), to give desired product as a yellow solid (460 mg, 86 %). $^1$H NMR (400 MHz, $CDCl_3$) δ: 9.22 (s, 1H),

8.37 (d, $J$ = 8.4 Hz, 1H), 8.13 (d, $J$ = 8.2 Hz, 1H), 8.00 (d, $J$ = 8.0 Hz, 1H), 7.84 (d, $J$ = 7.2 Hz, 1H), 7.66–7.48 (m, 5H), 7.39 (t, $J$ = 7.8 Hz, 1H), 7.32 (d, $J$ = 7.8 Hz, 1H), 6.87 (d, $J$ = 7.8 Hz, 1H), 4.07 (s, 3H).

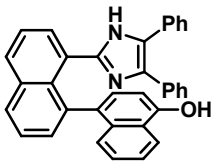
**2-(4'-methoxy-[1,1'-binaphthalen]-8-yl)-4,5-diphenyl-1*H*-imidazole (S7)**



S7

4'-methoxy-[1,1'-binaphthalene]-8-carbaldehyde (100 mg, 0.320 mmol), benzil (100 mg, 0.476 mmol) and ammonium acetate (350 mg, 4.54 mmol) were dissolved in acetic acid 4 mL. The mixture was stirred at 110 °C for 23 hours. After cooling to room temperature, the reaction mixture was neutralized with aqueous $NH_3$, and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was washed with water and brine, dried with $Na_2SO_4$, and evaporated. The product was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/AcOEt = 10/1) to give desired product as a white solid (145 mg, 90 %). $^1$H NMR (400 MHz, DMSO-$d_6$, 333 K) δ: 11.38 (br, 1H), 8.17 (d, $J$ = 8.2 Hz, 1H), 8.11 (d, $J$ = 8.2 Hz, 1H), 7.92 (d, $J$ = 8.2 Hz, 1H), 7.66 (d, $J$ = 8.0 Hz, 1H), 7.62 (d, $J$ = 8.0 Hz, 1H), 7.55 (d, $J$ = 7.2 Hz, 1H), 7.51 (d, $J$ = 8.2 Hz, 1H), 7.41 (d, $J$ = 7.2 Hz, 1H), 7.33 (t, $J$ = 7.8 Hz, 1H), 7.27 (t, $J$ = 7.8 Hz, 1H), 7.20–7.14 (m, 3H), 7.10–7.06 (m, 3H), 7.00 (d, $J$ = 7.8 Hz, 1H), 6.85 (br, 4H), 6.44 (d, $J$ = 8.0 Hz, 1H), 3.60 (s, 3H); HRMS (ESI-TOF) calculated for $C_{36}H_{26}N_2O$ $[M+H]^+$: 503.2118, found: 503.2094.

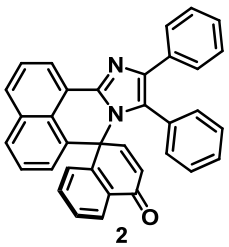
**8'-(4,5-diphenyl-1*H*-imidazol-2-yl)-[1,1'-binaphthalen]-4-ol (S8)**



S8

2-(4'-methoxy-[1,1'-binaphthalen]-8-yl)-4,5-diphenyl-1*H*-imidazole (150 mg, 0.298 mmol) was dissolved in dry $CH_2Cl_2$ 8.5 mL. $BBr_3$ (990 μL, 0.952 mmol) was dropwised into the solution at 0 °C and stirred at room temperature for 10 hours. The reaction mixture was neutralized with aqueous $NaHCO_3$, and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was washed with water and brine, dried with anhydrous $Na_2SO_4$, and evaporated to give gray solid 122 mg (84 %). $^1$H NMR (400 MHz, DMSO-$d_6$, 333 K) δ: 11.36 (br, 1H), 9.48 (s, 1H), 8.16 (d, $J$ = 8.0 Hz, 1H), 8.08 (d, $J$ = 8.2 Hz, 1H), 7.93 (d, $J$ = 8.2 Hz, 1H), 7.66–7.61 (m, 2H), 7.56 (d, $J$ = 7.2 Hz, 1H), 7.51 (d, $J$ = 8.2 Hz, 1H), 7.39 (d, $J$ = 7.0 Hz, 1H), 7.28 (t, $J$ = 7.0 Hz, 1H), 7.24 (d, $J$ = 7.8 Hz, 1H), 7.21–7.18 (br, 3H), 7.05 (br, 3H), 6.89–6.84 (m, 5H), 6.46 (d, $J$ = 7.8 Hz, 1H); HRMS (ESI-TOF) calculated for $C_{35}H_{24}N_2O$ $[M+H]^+$: 489.1961, found: 489.1966.

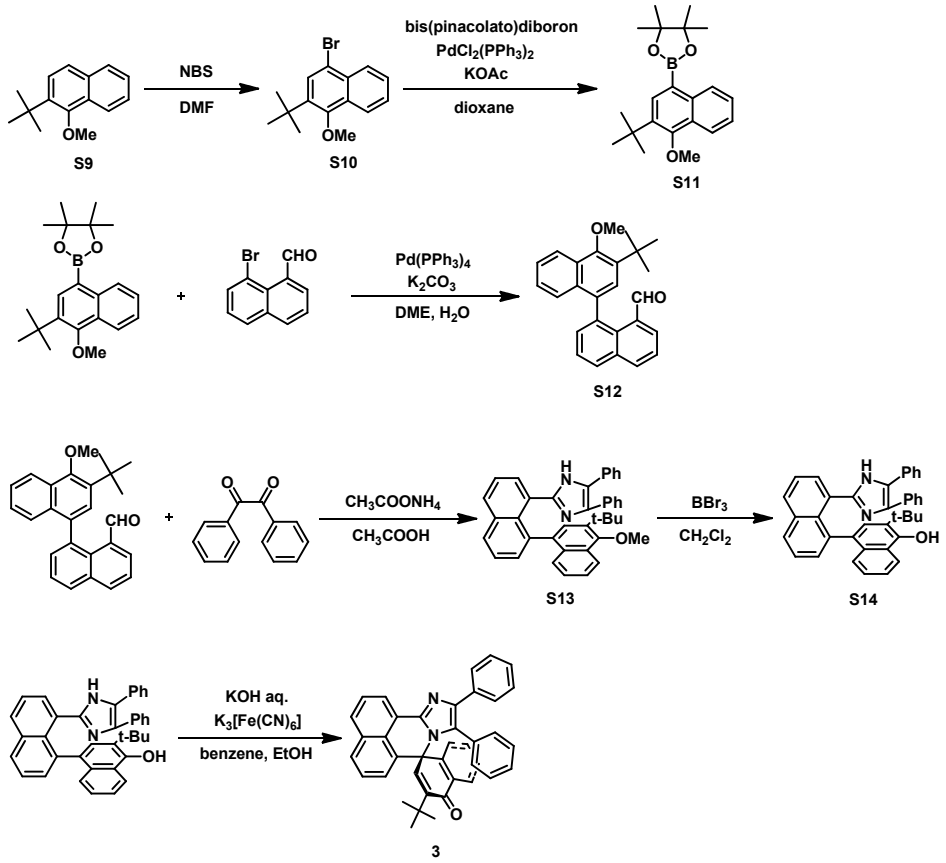
**naphthalene bridged naphthoxyl-imidazolyl radical complex (2)**



2

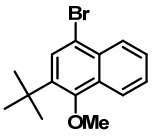
To a solution of 8'-(4,5-diphenyl-1*H*-imidazol-2-yl)-[1,1'-binaphthalen]-4-ol (109 mg, 0.223 mmol) in benzene 100 mL and ethanol 0.2 mL was added KOH (2.57 g, 45.80 mmol) and $K_3[Fe(CN)_6]$ (2.5 g, 7.59 mmol) in water 80 mL. The mixture was vigorously stirred for 1.5 hours at room temperature. The reaction mixture was washed with water and the solvent was removed by evaporation. Then the crude product was separated by $SiO_2$ column chromatography using $CH_2Cl_2$ as the eluent to give desired product as a yellow solid 27 mg. The yellow solid was recrystallized from $CH_2Cl_2$/hexane, to give pale yellow crystal 18 mg (17 %). $^1$H NMR (400 MHz, DMSO-$d_6$) δ: 8.53 (d, $J$ = 7.2 Hz, 1H), 8.06 (d, $J$ = 8.4 Hz, 1H), 7.94 (d, $J$ = 8.0 Hz, 1H), 7.81 (t, $J$ = 7.6 Hz, 2H), 7.53–7.37 (m, 7H), 7.34–7.26 (m, 2H), 7.20–7.11 (m, 3H), 7.02 (d, $J$ = 7.6 Hz, 2H), 6.84 (t, $J$ = 7.6 Hz, 1H), 6.05 (d, $J$ = 10.0 Hz, 1H), 5.89 (d, $J$ = 7.6 Hz, 1H); HRMS (ESI-TOF) calculated for $C_{35}H_{22}N_2O$ $[M+H]^+$: 487.1805, found: 487.1786.

**Scheme S3.** Synthetic Scheme of **3**



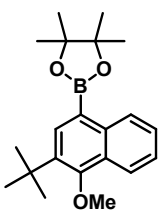

**2-(*tert*-butyl)-1-methoxynaphthalene (S9)** was synthesized according to a literature procedure[S2].

**4-bromo-2-(tert-butyl)-1-methoxynaphthalene (S10)**


S10

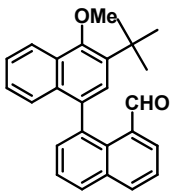
2-(*tert*-butyl)-1-methoxynaphthalene (202 mg, 0.942 mmol) was dissolved in DMF 2.2 mL, and the solution was cooled to 0 °C. *N*-bromosuccinimide (213 mg, 1.20 mmol) was added to the solution and the solution was stirred for 4 hours at room temperature. After quenching with water, the reaction mixture was extracted with $CH_2Cl_2$. The organic extract was washed with water and brine, and dried over $MgSO_4$. After removal of the solvents, the crude product was purified by silica gel column chromatography ($CH_2Cl_2$/hexane = 1/4), to give desired product as transparent oil 252 mg (91 %). $^1$H NMR (400 MHz, $CDCl_3$): δ: 8.16–8.13 (m, 1H), 8.08–8.05 (m, 1H), 7.80 (s, 1H), 7.56–7.50 (m, 1H), 3.95 (s, 3H), 1.49 (s, 9H).

**2-(3-(*tert*-butyl)-4-methoxynaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S11)**


S11

KOAc (333 mg, 3.39 mmol), 2-(*tert*-butyl)-1-methoxynaphthalene (250 mg, 0.853 mmol) and bis(pinacolato)diboron (265 mg, 1.04 mmol) were added to dioxane (3 mL), and the mixture was purged with $N_2$ gas. $PdCl_2(PPh_3)_2$ (30 mg, 0.0427 mmol) was added to the solution and the solution was stirred at 80 °C for 11 hours. The reaction mixture was added water and extracted with $CH_2Cl_2$. The organic extract was washed with water and brine, and dried over $Na_2SO_4$. After removal of the solvents, the crude product was purified by silica gel column chromatography (hexane/$CH_2Cl_2$ = 3/1), to give desired product as transparent oil (202 mg, 70 %). $^1$H NMR (400 MHz, $CDCl_3$): δ: 8.75–8.72 (m, 1H), 8.12 (s, 1H), 8.09–8.05 (m, 1H), 7.49–7.44 (m, 1H), 3.96 (s, 3H), 1.51 (s, 9H), 1.41 (s, 12H).

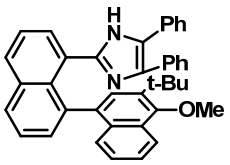
**3'-(*tert*-butyl)-4'-methoxy-[1,1'-binaphthalene]-8-carbaldehyde (S12)**



S12

$K_2CO_3$ (54 mg, 0.391 mmol), 1-bromo-8-naphthaldehyde (86 mg, 0.366 mmol) and 2-(3-(*tert*-butyl)-4-methoxynaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (150 mg, 0.441 mmol) were added to DME 1.7 mL and water 1 mL, and the mixture was purged with $N_2$ gas. $Pd(PPh_3)_4$ (13 mg, 0.0113 mmol) was added to the solution and the solution was stirred at 90 °C for 17 hours. The reaction mixture was added water and extracted with $CH_2Cl_2$. The organic extract was washed with water and brine, and dried over $Na_2SO_4$. After removal of the solvents, the crude product was purified by silica gel column chromatography (hexane/$CH_2Cl_2$ = 1/1), to give desired product as a yellow amorphous (115 mg, 85 %). $^1$H NMR (400 MHz, $CDCl_3$) δ: 9.05 (s, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 8.02 (dd, *J* = 7.2 Hz, *J* = 2.4 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.68–7.49 (m, 5H), 7.44 (s, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 4.05 (s, 3H), 1.47 (s, 9H).

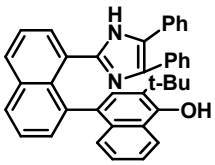
**2-(3'-(*tert*-butyl)-4'-methoxy-[1,1'-binaphthalen]-8-yl)-4,5-diphenyl-1*H*-imidazole (S13)**



S13

3'-(*tert*-butyl)-4'-methoxy-[1,1'-binaphthalene]-8-carbaldehyde (78 mg, 0.212 mmol), benzil (68 mg, 0.323 mmol) and ammonium acetate (167 mg, 2.17 mmol) were dissolved in acetic acid 2 mL. The mixture was stirred at 110 °C for 42 hours. After cooling to room temperature, the reaction mixture was neutralized with aqueous $NH_3$, and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was washed with water and brine, dried with $Na_2SO_4$, and evaporated. The product was purified by $SiO_2$ column chromatography ($CH_2Cl_2$/AcOEt = 10/1) to give a orange amorphous (80 mg, 68 %). The desired product included a few percent of the by-product or the diastereomer which cannot be isolated by the $SiO_2$ column chromatography. $^1$H NMR (400 MHz, DMSO-$d_6$, 333 K) δ: 11.49 (br, 1H), 8.17 (t, *J* = 5.2 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.68–7.63 (m, 3H), 7.51–7.37 (m, 4H), 7.05–7.03 (m, 4H), 6.89–6.78 (m, 3H), 3.60 (s, 3H), 1.07 (s, 9H); HRMS (ESI-TOF) calculated for $C_{40}H_{34}N_2O$ $[M+H]^+$: 559.2744, found: 559.2716.

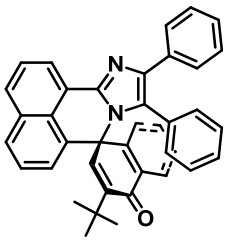
**3-(*tert*-butyl)-8'-(4,5-diphenyl-1*H*-imidazol-2-yl)-[1,1'-binaphthalen]-4-ol (S14)**



S14

2-(3'-(*tert*-butyl)-4'-methoxy-[1,1'-binaphthalen]-8-yl)-4,5-diphenyl-1*H*-imidazole (40 mg, 0.0717 mmol) was dissolved in dry $CH_2Cl_2$ 1.5 mL. $BBr_3$ (180 μL, 0.180 mmol) was dropwised into the solution at 0 °C and stirred at room temperature for 12 hours. The reaction mixture was neutralized with aqueous $NaHCO_3$, and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was washed with water and brine, dried with anhydrous $Na_2SO_4$, and evaporated to give gray solid 35 mg (87 %). $^1$H NMR (400 MHz, DMSO-$d_6$, 333 K) δ: 11.30 (br, 1H), 8.55 (s, 1H), 8.16–8.06 (m, 3H), 7.83–7.81 (m, 1H), 7.65–7.61 (m, 3H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.34–7.31 (m, 2H), 7.12–7.10 (m, 3H), 7.04–7.02 (m, 3H), 6.95 (s, 1H), 6.91 (br, 2H), 6.75 (br, 2H), 1.08 (s, 9H); HRMS (ESI-TOF) calculated for $C_{39}H_{32}N_2O$ $[M+H]^+$: 545.2587, found: 545.2575.

**Compound 3**

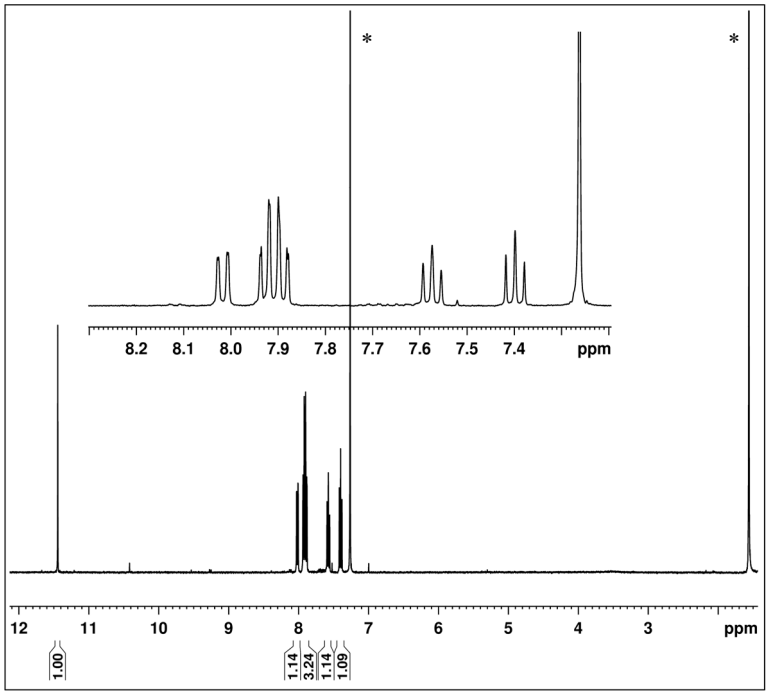


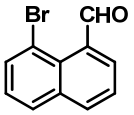
**3**

To a solution of 3-(*tert*-butyl)-8'-(4,5-diphenyl-1*H*-imidazol-2-yl)-[1,1'-binaphthalen]-4-ol (10 mg, 0.0184 mmol) in benzene 5 mL and ethanol 0.4 mL was added KOH (135 mg, 2.41 mmol) and $K_3[Fe(CN)_6]$ (250 mg, 0.759 mmol) in water 4 mL. The mixture was vigorously stirred for 1 hour at room temperature. The reaction mixture was washed with water and the solvent was removed by evaporation. Then the crude product was separated by $SiO_2$ column chromatography using $CH_2Cl_2$ as the eluent to give desired product as a pale yellow solid 6 mg (60 %). $^1$H NMR (400 MHz, DMSO-$d_6$) δ: 8.53 (d, $J$ = 7.2 Hz, 1H), 8.04 (d, $J$ = 8.4 Hz, 1H), 7.91 (d, $J$ = 8.0 Hz, 1H), 7.85 (d, $J$ = 7.6 Hz, 1H), 7.79 (t, $J$ = 7.6 Hz, 1H), 7.52–7.44 (m, 3H), 7.34–7.25 (m, 5H), 7.18–7.10 (m, 4H), 6.96 (d, $J$ = 7.6 Hz, 1H), 6.89–6.83 (m, 2H), 5.80 (d, $J$ = 7.6 Hz, 1H), 1.09 (s, 9H); HRMS (ESI-TOF) calculated for $C_{39}H_{30}N_2O$ $[M+H]^+$: 543.2431, found: 543.2429.

## 2. NMR Spectra

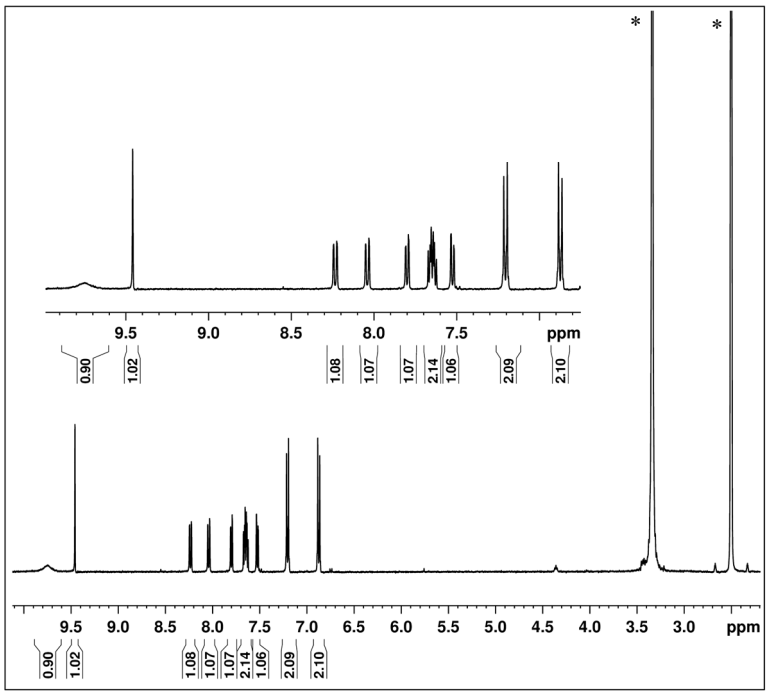
### $^1$H NMR Spectra

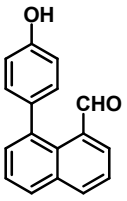



S1

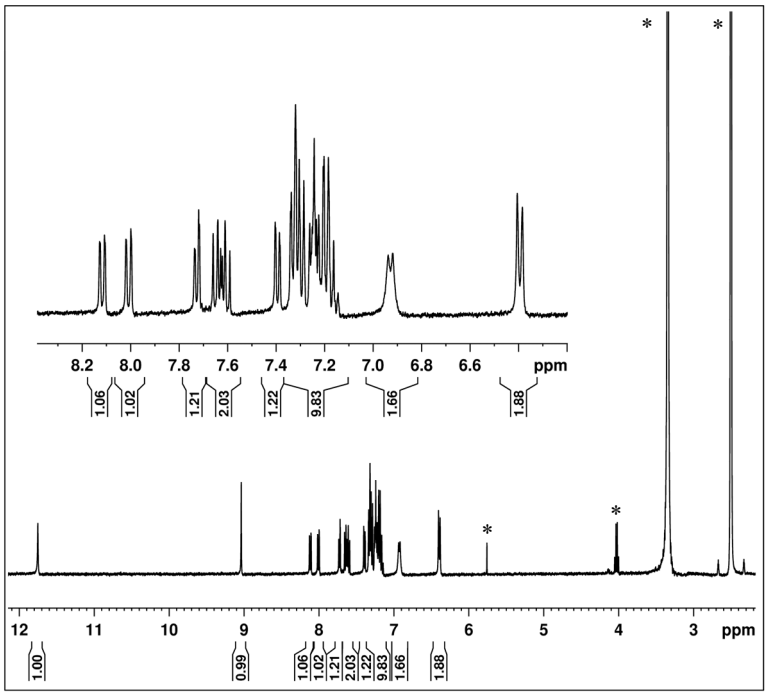
**Figure S1.** $^1$H NMR spectrum of **8-bromo-1-naphthaldehyde (S1)** in $CDCl_3$ (* solvent peaks).

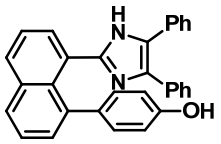



S2

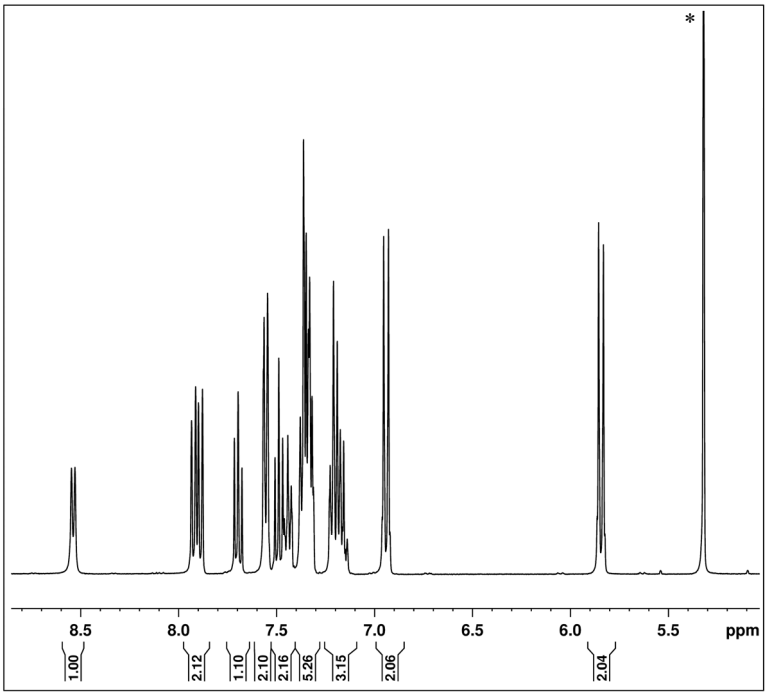
**Figure S2.** $^1$H NMR spectrum of **8-(4-hydroxyphenyl)-1-naphthaldehyde (S2)** in DMSO-$d_6$ (* solvent peaks).

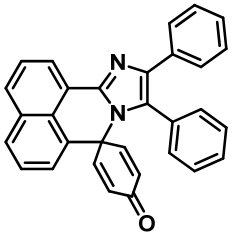



S3

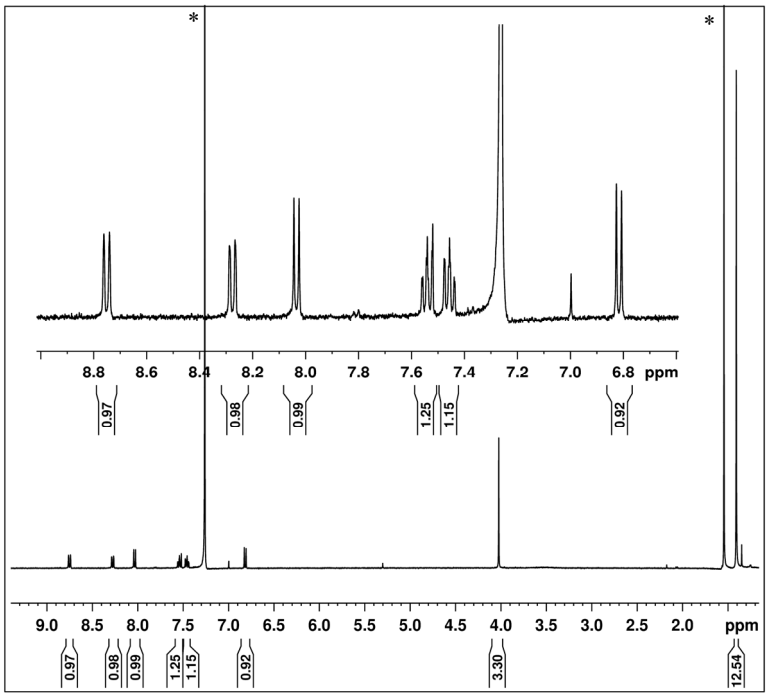
**Figure S3.** $^{1}$H NMR spectrum of **4-(8-(4,5-diphenyl-1*H*-imidazol-2-yl)naphthalen-1-yl)phenol (S3)** in DMSO-$d_6$ (* solvent peaks).




1

**Figure S4.** $^{1}$H NMR spectrum of **1** in $CD_2Cl_2$ (* solvent peaks).



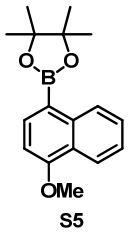
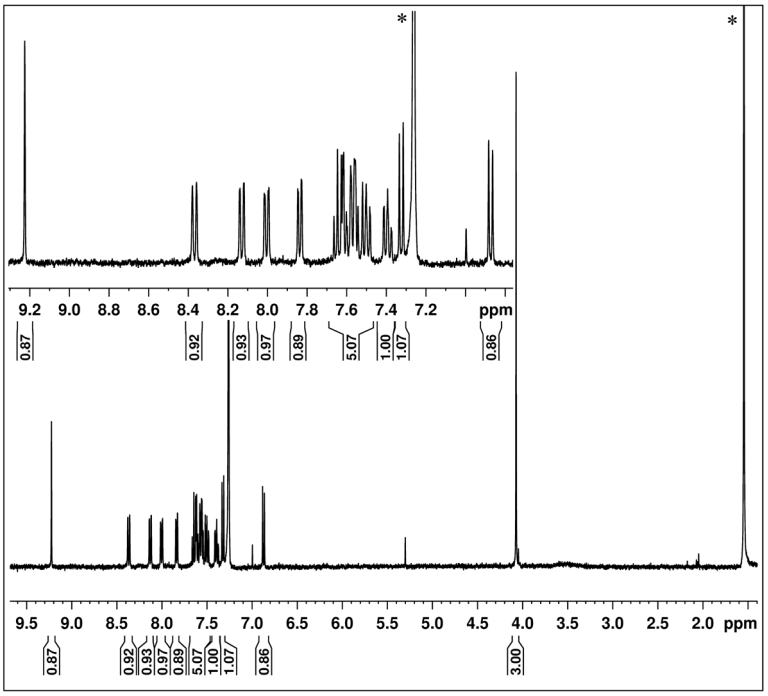




**Figure S5.** $^{1}$H NMR spectrum of **2-(4-methoxynaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S5)** in $CDCl_3$ (* solvent peaks).



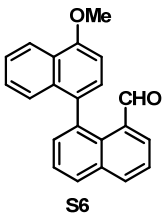
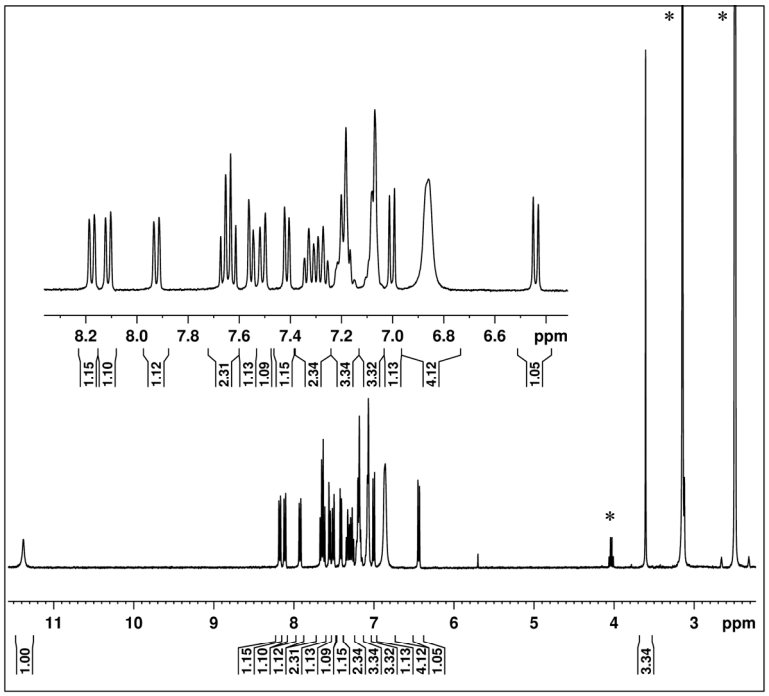
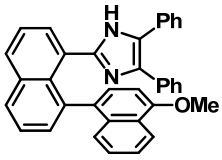



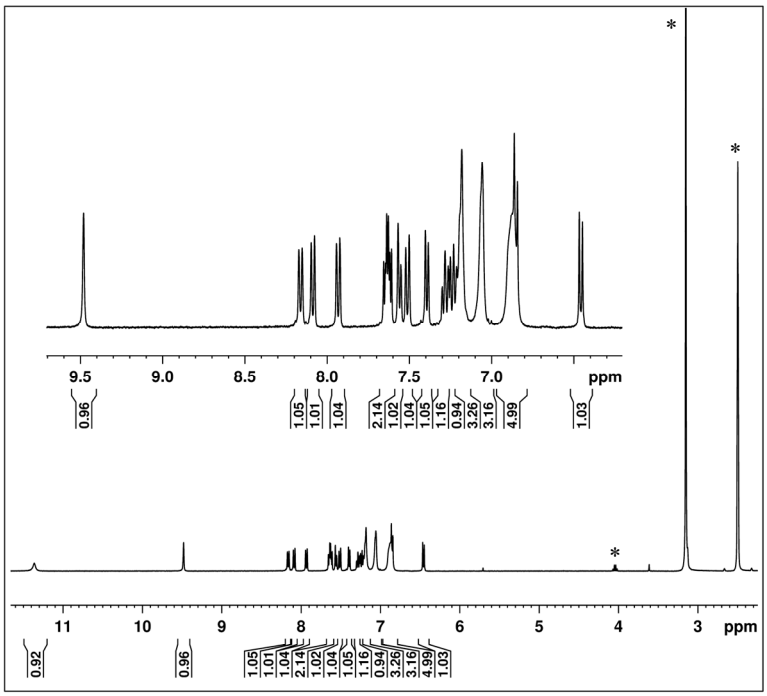

**Figure S6.** $^{1}$H NMR spectrum of **4'-methoxy-[1,1'-binaphthalene]-8-carbaldehyde (S6)** in $CDCl_3$ (* solvent peaks).

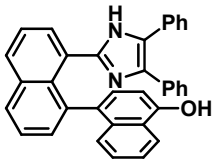



S7

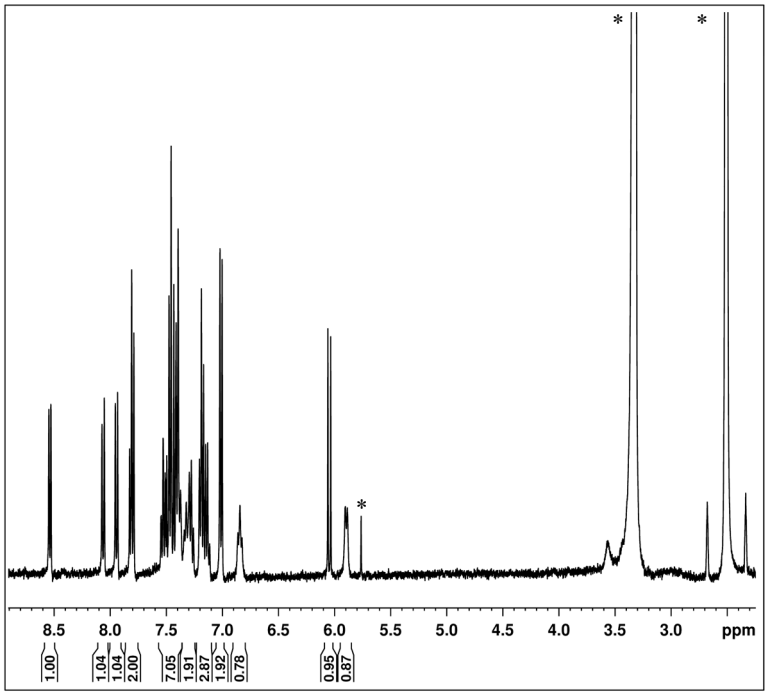
**Figure S7.** [1]H NMR spectrum of **2-(4'-methoxy-[1,1'-binaphthalen]-8-yl)-4,5-diphenyl-1*H*-imidazole (S7)** in DMSO-*d*$_6$ at 333 K (* solvent peaks).




S8

**Figure S8.** [1]H NMR spectrum of **8'-(4,5-diphenyl-1*H*-imidazol-2-yl)-[1,1'-binaphthalen]-4-ol (S8)** in DMSO-*d*$_6$ at 333 K (* solvent peaks).



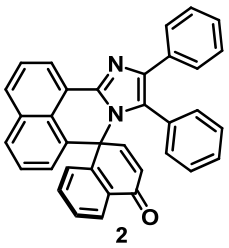




**Figure S9.** $^{1}$H NMR spectrum of **2** in DMSO-$d_6$ (* solvent peaks).

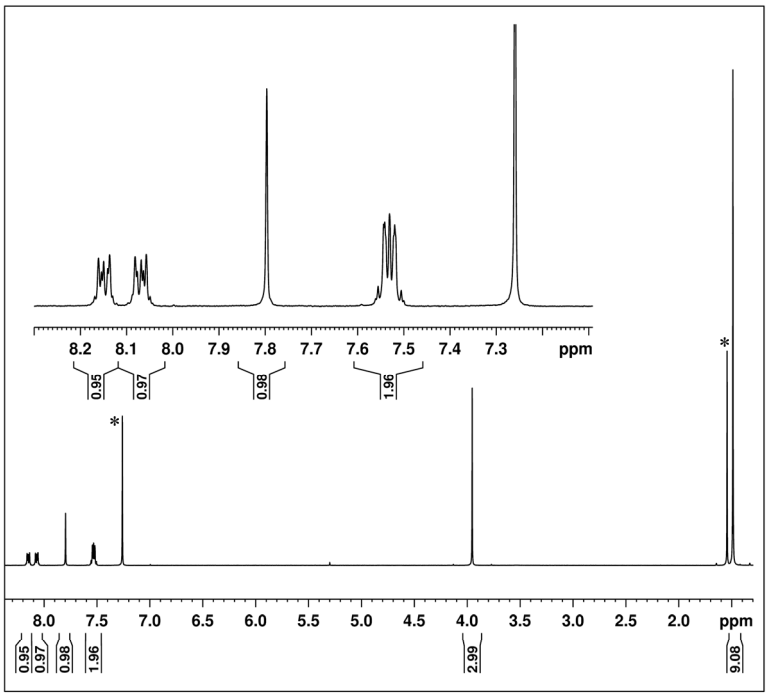



**Figure S10.** $^{1}$H NMR spectrum of **4-bromo-2-(tert-butyl)-1-methoxynaphthalene (S10)** in $CDCl_3$ (* solvent peaks).

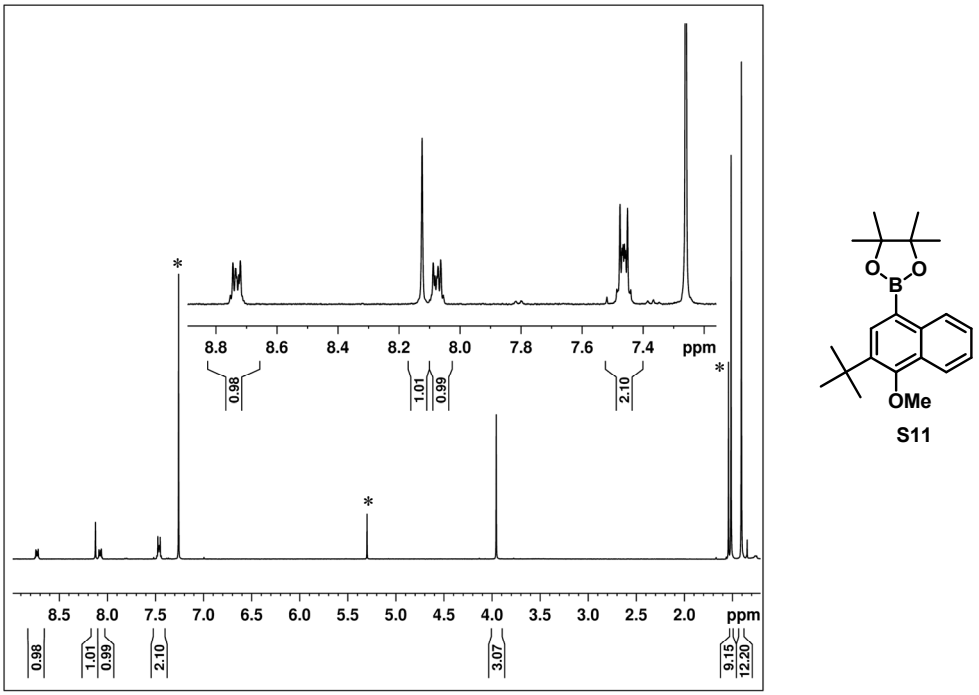



**Figure S11.** $^{1}$H NMR spectrum of **2-(3-(*tert*-butyl)-4-methoxynaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S11)** in $CDCl_3$ (* solvent peaks).

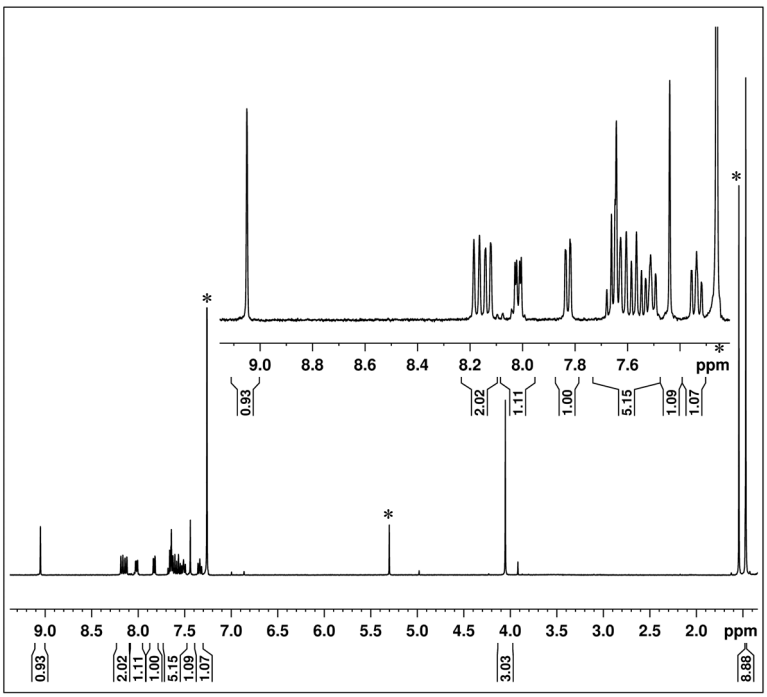



**Figure S12.** $^{1}$H NMR spectrum of **3'-(*tert*-butyl)-4'-methoxy-[1,1'-binaphthalene]-8-carbaldehyde (S12)** in $CDCl_3$ (* solvent peaks).

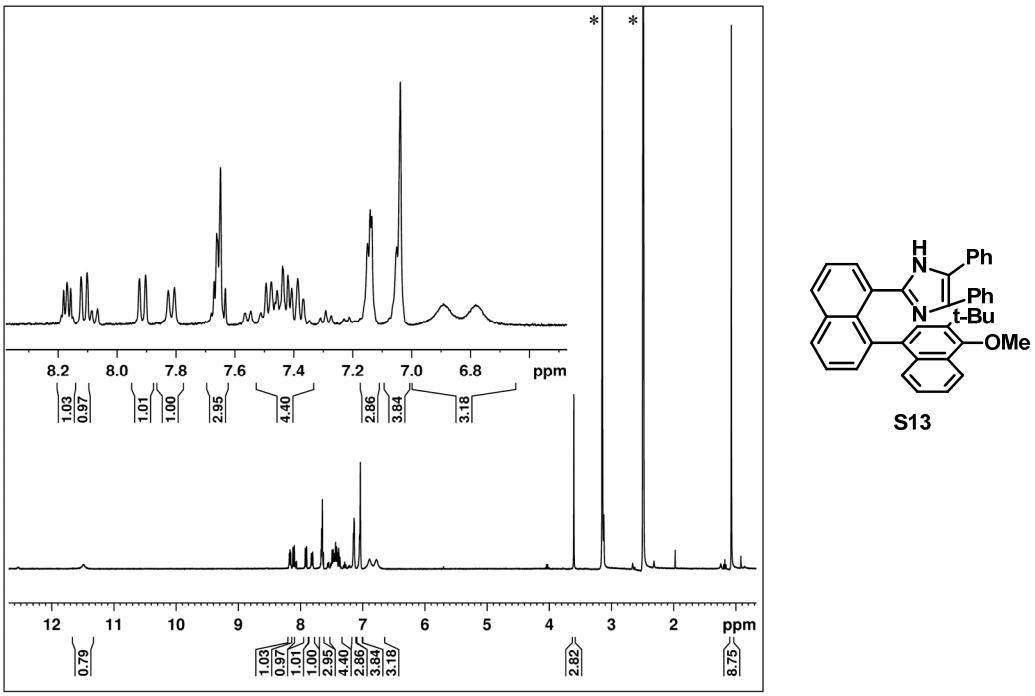



**Figure S13.** $^{1}$H NMR spectrum of **2-(3'-(*tert*-butyl)-4'-methoxy-[1,1'-binaphthalen]-8-yl)-4,5-diphenyl-1*H*-imidazole (S13)** in DMSO-$d_6$ at 333 K (* solvent peaks).

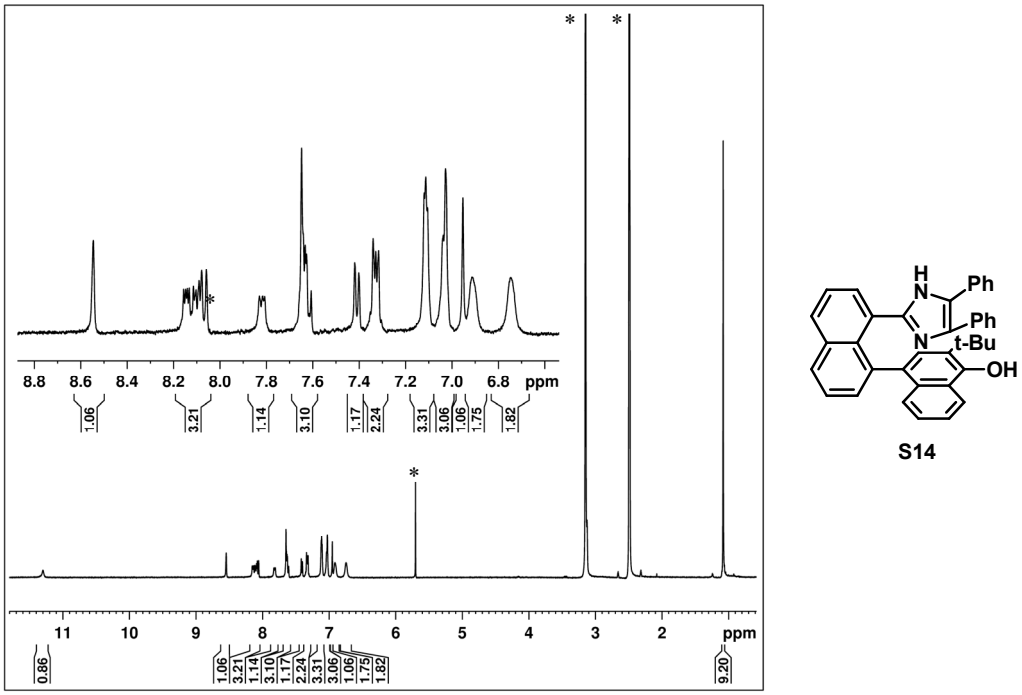



**Figure S14.** [1]H NMR spectrum of **3-(*tert*-butyl)-8'-(4,5-diphenyl-1*H*-imidazol-2-yl)-[1,1'-binaphthalen]-4-ol (S14)** in DMSO-$d_6$ at 333 K (* solvent peaks).

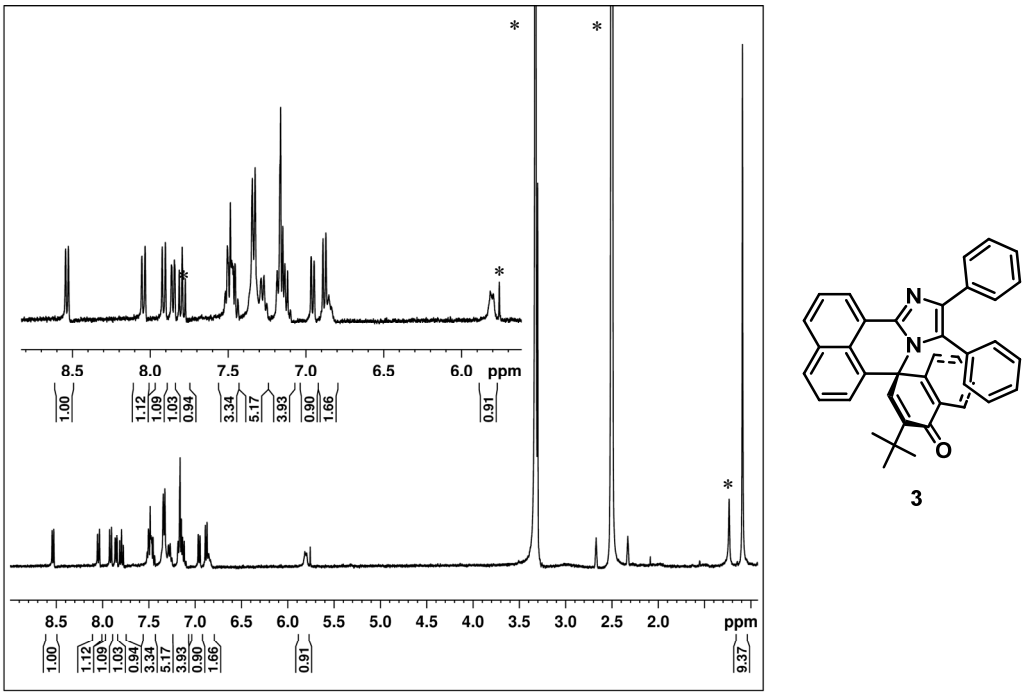
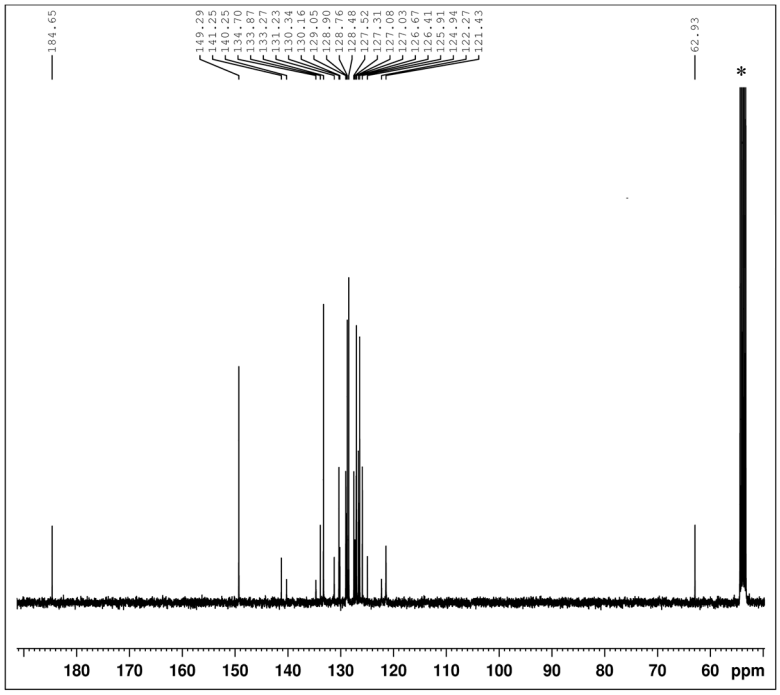
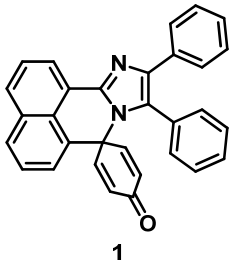



**Figure S15.** [1]H NMR spectrum of **3** in DMSO-$d_6$ (* solvent peaks).

## $^{13}$C NMR Spectra




**1**

**Figure S16.** $^{13}$C NMR spectrum of **1** in $CD_2Cl_2$ (* solvent peaks).

## 3. HR-ESI-TOF MS Spectra

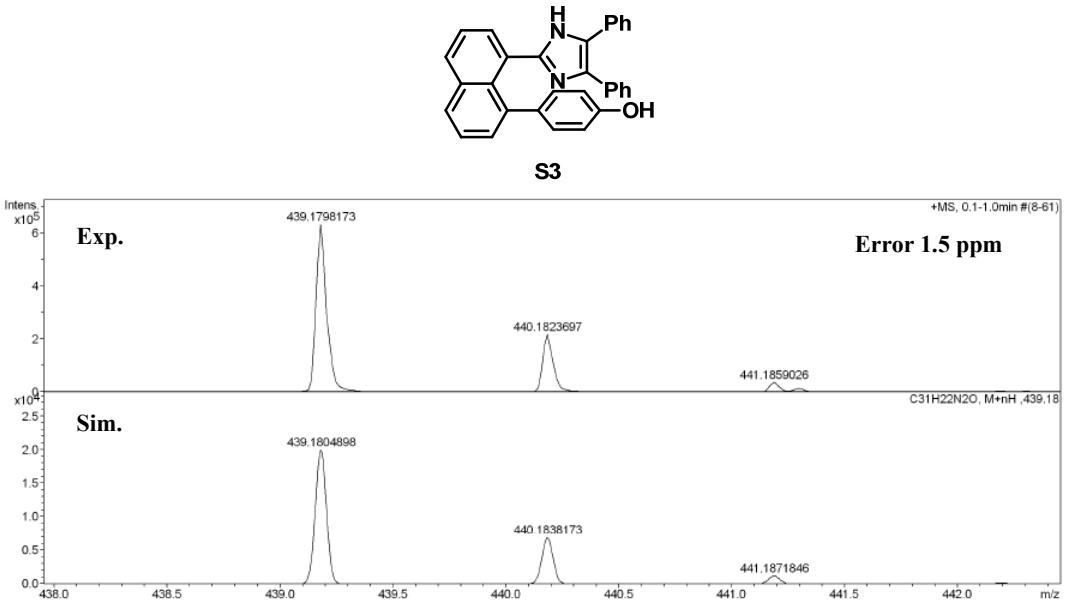



**Figure S17.** HR-ESI-TOF MS spectra of **4-(8-(4,5-diphenyl-1*H*-imidazol-2-yl)naphthalen-1-yl)phenol (S3)**.

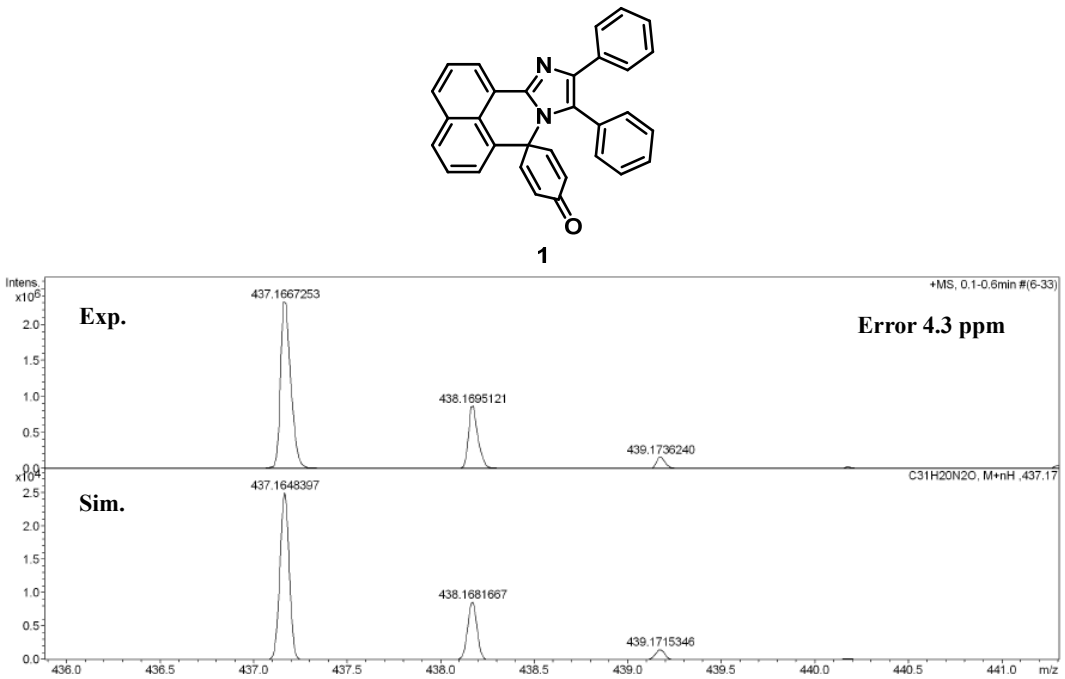



**Figure S18.** HR-ESI-TOF MS spectra of **1**.

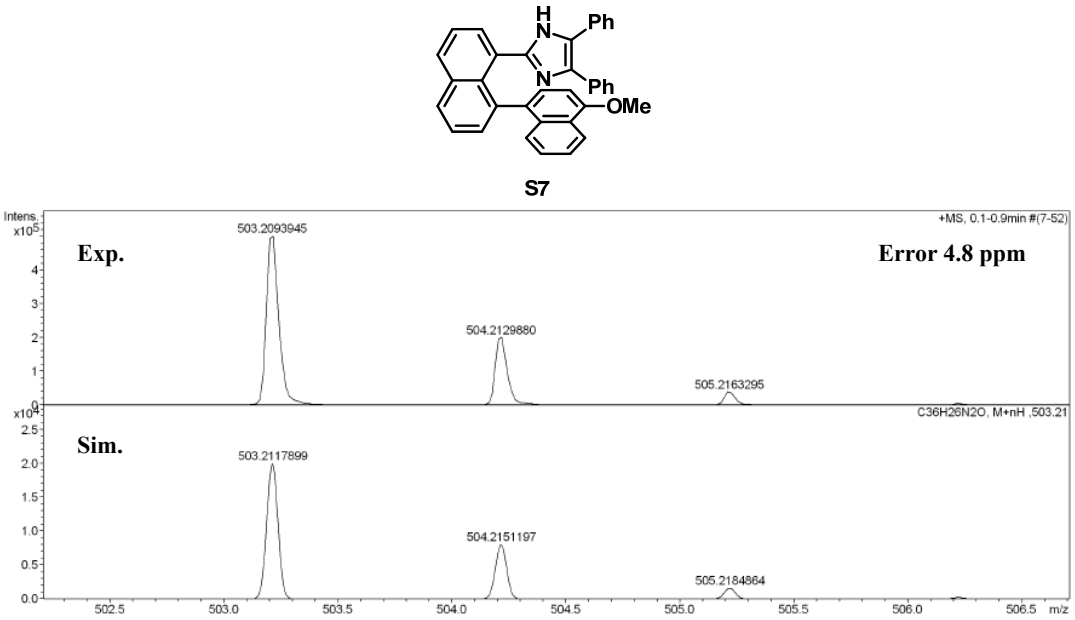



**Figure S19.** HR-ESI-TOF MS spectra of **2-(4'-methoxy-[1,1'-binaphthalen]-8-yl)-4,5-diphenyl-1*H*-imidazole (S7)**.

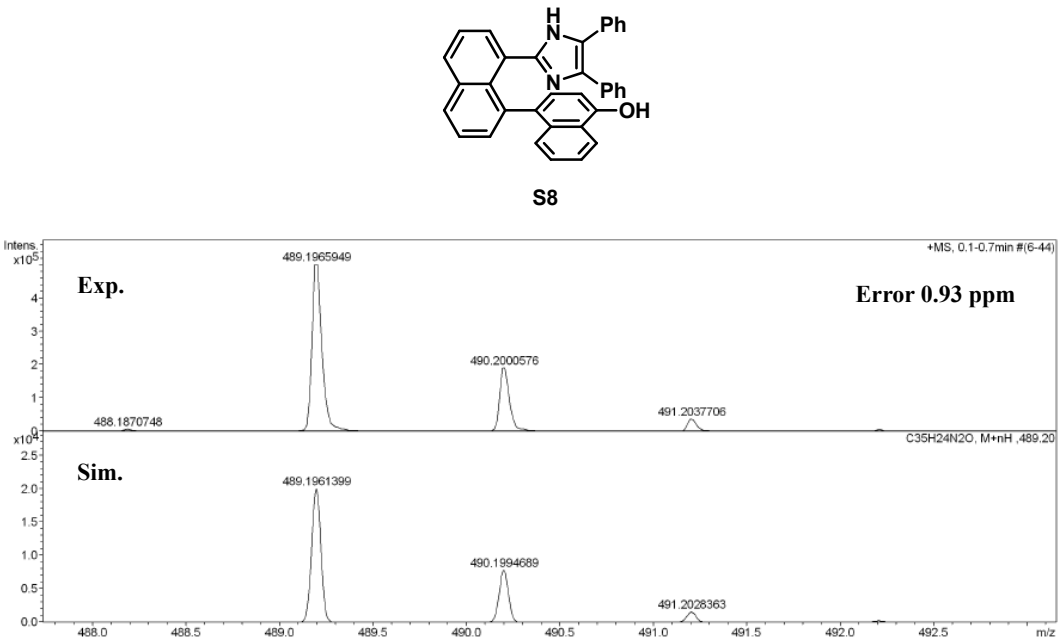
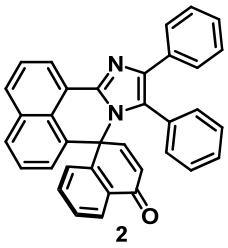



**Figure S20.** HR-ESI-TOF MS spectra of **8'-(4,5-diphenyl-1*H*-imidazol-2-yl)-[1,1'-binaphthalen]-4-ol (S8)**.




**2**

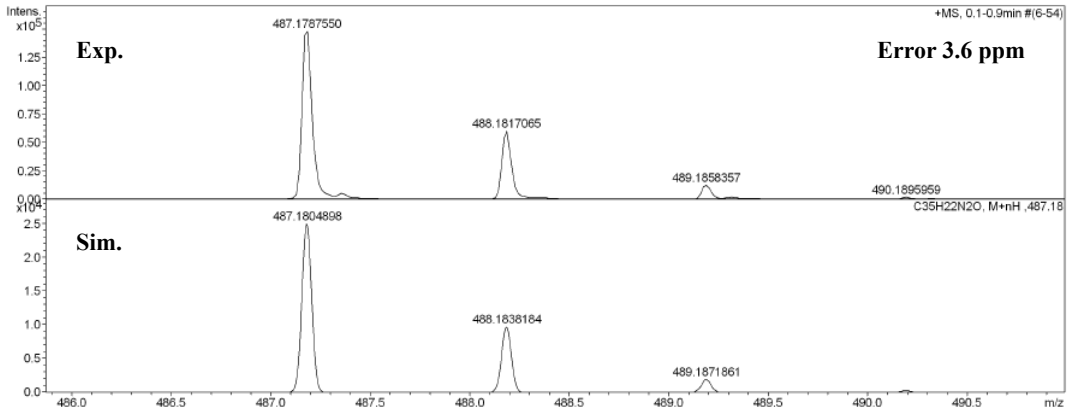
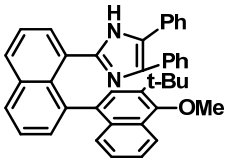



**Figure S21.** HR-ESI-TOF MS spectra of **2**.




**S13**

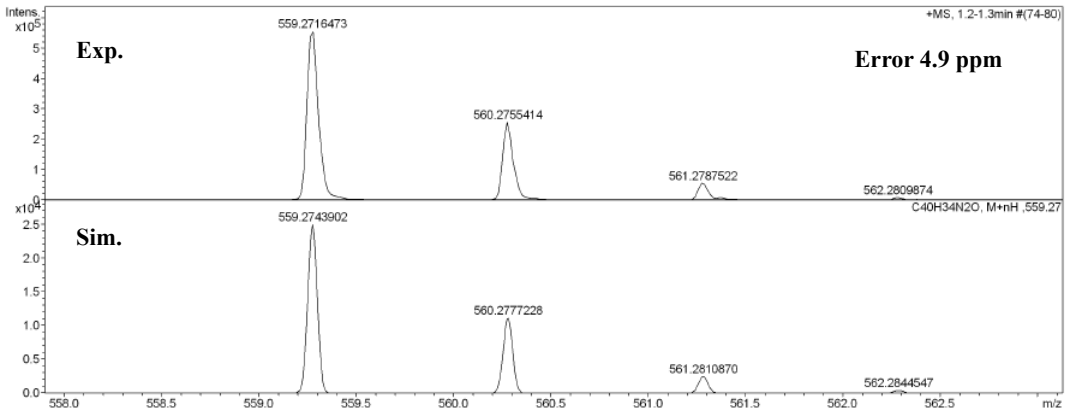



**Figure S22**. HR-ESI-TOF MS spectra of **2-(3'-(*tert*-butyl)-4'-methoxy-[1,1'-binaphthalen]-8-yl)-4,5-diphenyl-1*H*-imidazole (S13)**.

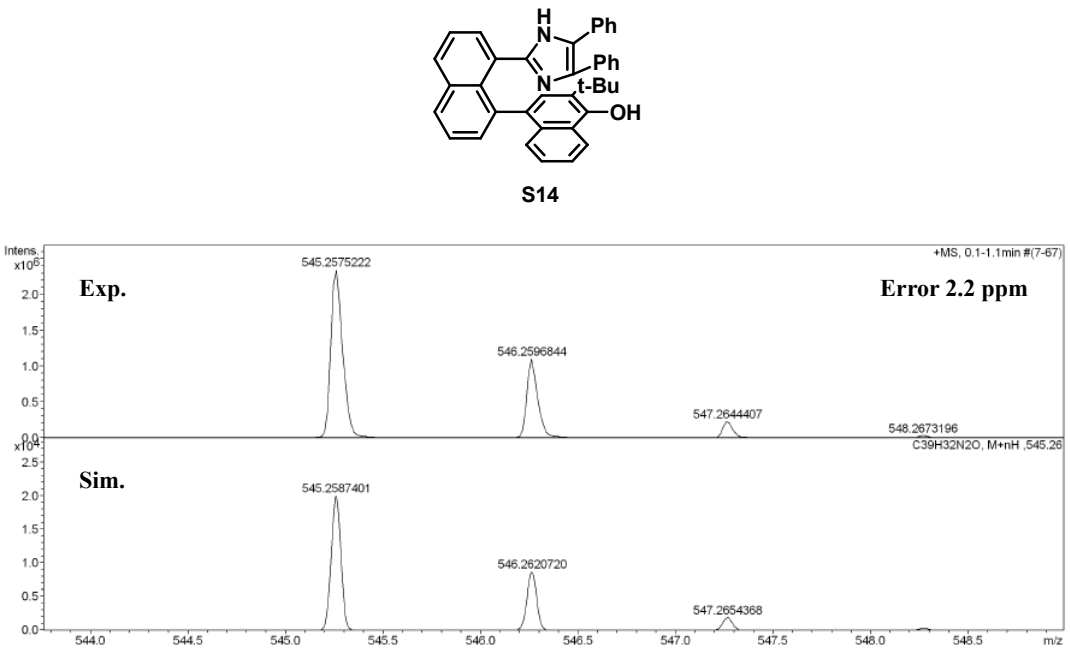



**Figure S23.** HR-ESI-TOF MS spectra of **3-(*tert*-butyl)-8'-(4,5-diphenyl-1*H*-imidazol-2-yl)-[1,1'-binaphthalen]-4-ol (S14)**.

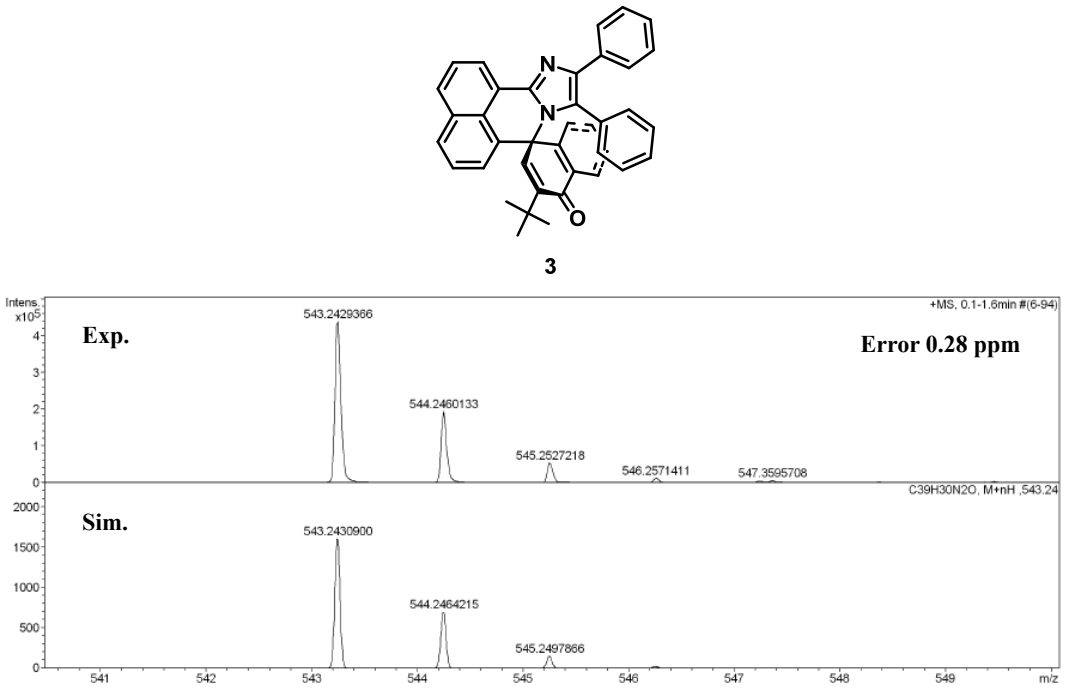



**Figure S24.** HR-ESI-TOF MS spectra of **3**.

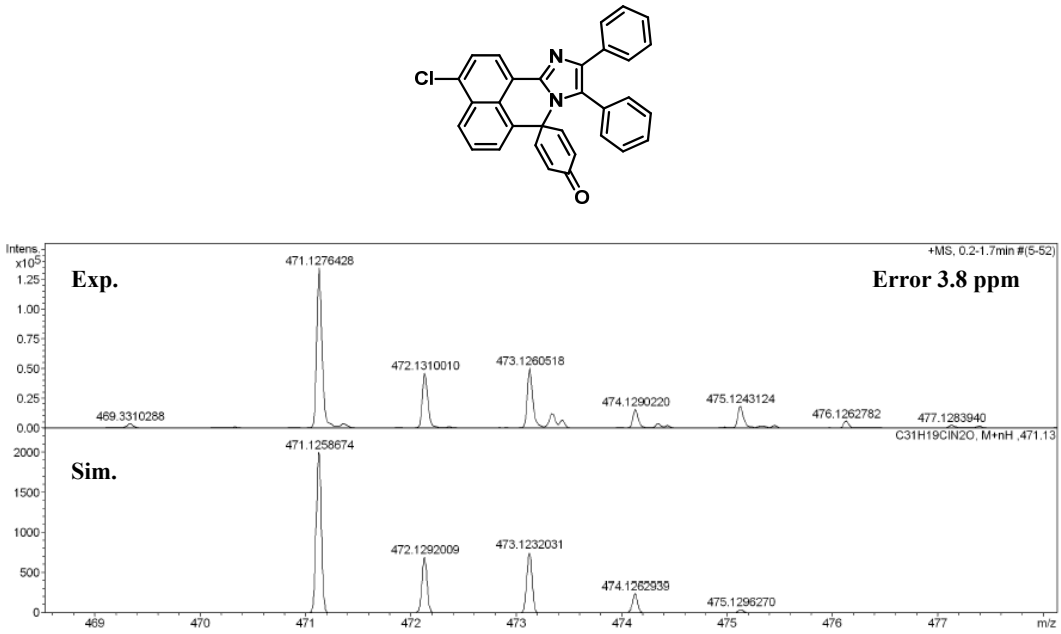



**Figure S25.** HR-ESI-TOF MS spectra of **by-product 2**.

## 4. HPLC Chromatograms

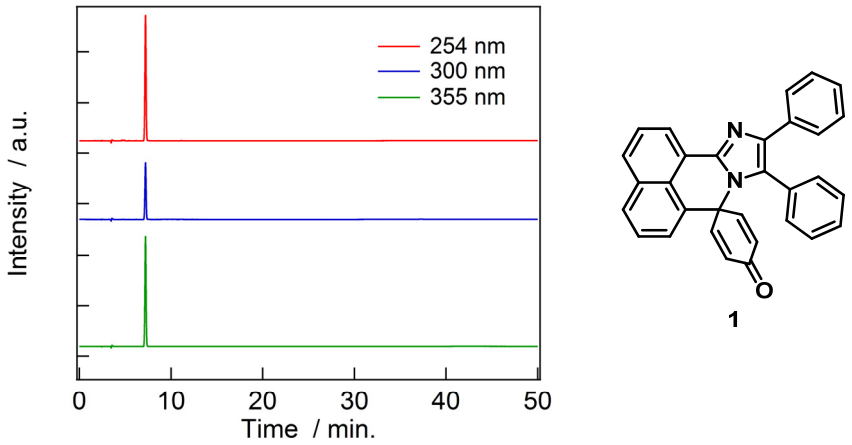



**Figure S26.** HPLC chromatograms of **1**; 99 % purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25cm×4.6mm, 5μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was $CH_3CN/H_2O$ = 9/2 with a flow rate of 1.0 mL/min (detection wavelength; 254, 300 and 355 nm).

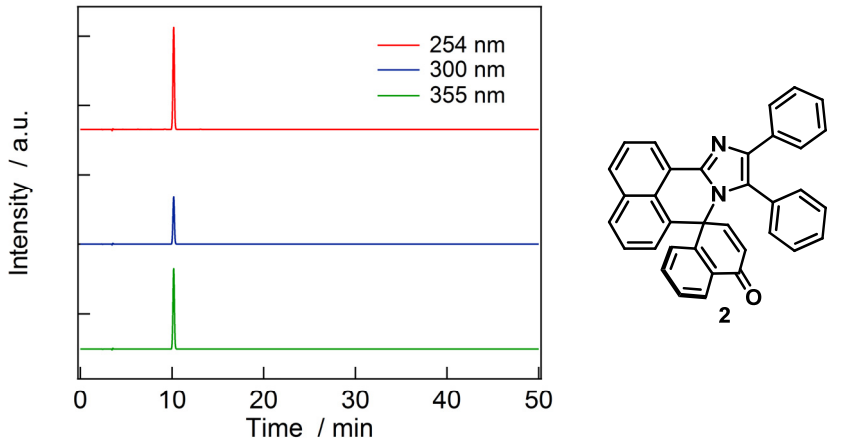
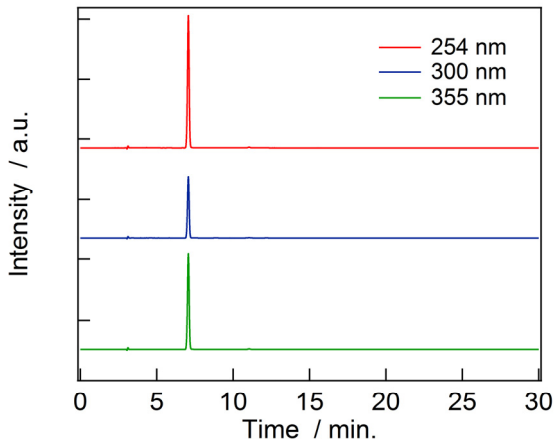
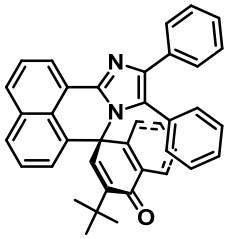


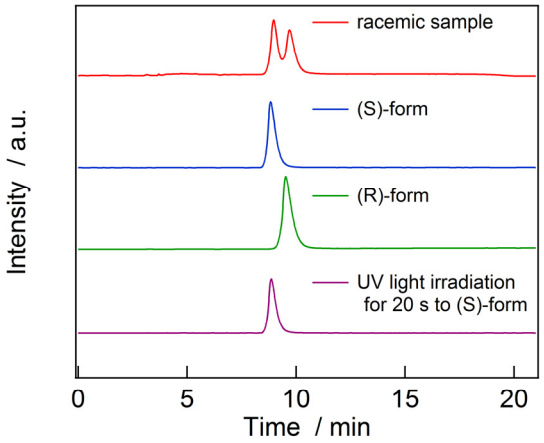

**Figure S27.** HPLC chromatograms of **2**; 99 % purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25cm×4.6mm, 5μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was $CH_3CN/H_2O$ = 9/2 with a flow rate of 1.0 mL/min (detection wavelength; 254, 300 and 355 nm).

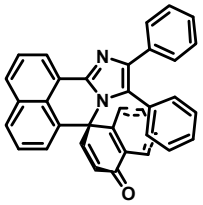


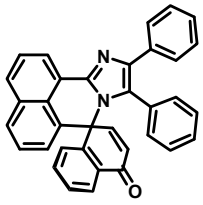

**3**

**Figure S28.** HPLC chromatograms of **3**; 99 % purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25cm×4.6mm, 5μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was $CH_3CN$ with a flow rate of 1.0 mL/min (detection wavelength; 254, 300 and 355 nm).




**S**

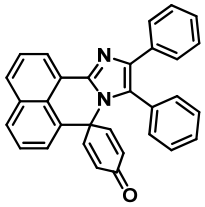



**R**

**Figure S29.** Chiral HPLC chromatograms of **2**; (S)-form 99 %ee and (R)-form 99 %ee. HPLC analysis was performed using a silica gel substituted Cellulose tris(3,5-dichlorophenylcarbamate) column (CHIRALPAK IC, Daicel Corporation), equipped with a UV detector; the mobile phase was $CH_2Cl_2$:hexane=1:1 (0.1 % diethylamine) with a flow rate of 6.0 mL/min (detection wavelength; 254 nm).

## 5. X-ray Crystallographic Analyses

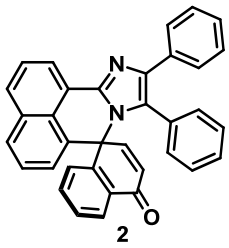
The diffraction data of the single crystals were collected on the Bruker APEX II CCD area detector (Mo Kα, λ = 0.71073 nm). The data refinement was carried out by the Bruker APEXII software package with SHELXT program.[S3] All non-hydrogen atoms were anisotropically refined.




**1**

**Table S1.** Crystallographic Parameters of **1**

| | | |
|---|---|---|
| Empirical formula | $C_{31}H_{20}N_2O$ | |
| Formula weight | 436.49 | |
| Temperature | 90 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | monoclinic | |
| Space group | P 1 21/c 1 | |
| Unit cell dimensions | a = 15.6295(14) Å | α = 90° |
| | b = 11.7772(10) Å | β = 100.3750(10)° |
| | c = 23.646(2) Å | γ = 90° |
| Volume | 4281.4(7) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.354 $g/m^3$ | |
| Absorption coefficient | 0.082 $mm^{-1}$ | |
| F(000) | 1824 | |
| Theta range for data collection | 1.45 to 26.39° | |
| Index ranges | -17<=h<=19, -8<=k<=14, -29<=l<=28 | |
| Reflections collected | 22198 | |
| Independent reflections | 8756 [R(int) = 0.0187] | |
| Absorption correction | Empirical | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 8756 / 0 / 613 | |
| Goodness-of-fit on $F^2$ | 0.989 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0369, wR2 = 0.0874 | |
| R indices (all data) | R1 = 0.0475, wR2 = 0.0932 | |
| Largest diff. peak and hole | 0.262 and -0.217 $eÅ^{-3}$ | |




**2**

**Table S2.** Crystallographic Parameters of **2**

| | | |
|---|---|---|
| Empirical formula | $C_{35}H_{22}N_2O$ | |
| Formula weight | 486.54 | |
| Temperature | 90 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | monoclinic | |
| Space group | P 1 21 1 | |
| Unit cell dimensions | a = 10.417(3) Å | α = 90° |
| | b = 7.846(3) Å | β = 109.024(4)° |
| | c = 15.614(5) Å | γ = 90° |
| Volume | 1206.5(7) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.339 $Mg/m^3$ | |
| Absorption coefficient | 0.081 $mm^{-1}$ | |
| F(000) | 508 | |
| Theta range for data collection | 1.38 to 26.55° | |
| Index ranges | -13<=h<=9, -9<=k<=9, -19<=l<=17 | |
| Reflections collected | 6504 | |
| Independent reflections | 4678 [R(int) = 0.0145] | |
| Absorption correction | Empirical | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4678 / 1 / 343 | |
| Goodness-of-fit on $F^2$ | 1.029 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0323, wR2 = 0.0705 | |
| R indices (all data) | R1 = 0.0371, wR2 = 0.0728 | |
| Largest diff. peak and hole | 0.157 and -0.187 $eÅ^{-3}$ | |

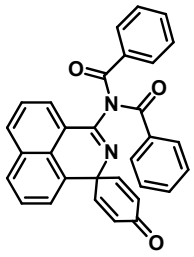


**Table S3.** Crystallographic Parameters of **by-product 1**

| | | |
|---|---|---|
| Empirical formula | $C_{31}H_{20}N_2O_3$ | |
| Formula weight | 468.49 | |
| Temperature | 90 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | monoclinic | |
| Space group | P 1 21/n 1 | |
| Unit cell dimensions | a = 10.4123(13) Å | α = 90° |
| | b = 10.6141(13) Å | β = 101.1402(17)° |
| | c = 22.372(5) Å | γ = 90° |
| Volume | 2425.9(5) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.283 $Mg/m^3$ | |
| Absorption coefficient | 0.083 $mm^{-1}$ | |
| F(000) | 976 | |
| Theta range for data collection | 1.86 to 25.40° | |
| Index ranges | -12<=h<=12, -12<=k<=12, -26<=l<=18 | |
| Reflections collected | 11645 | |
| Independent reflections | 4436 [R(int) = 0.0208] | |
| Absorption correction | Empirical | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4436 / 0 / 405 | |
| Goodness-of-fit on $F^2$ | 0.997 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0341, wR2 = 0.0748 | |
| R indices (all data) | R1 = 0.0454, wR2 = 0.0800 | |
| Largest diff. peak and hole | 0.221 and -0.195 $eÅ^{-3}$ | |

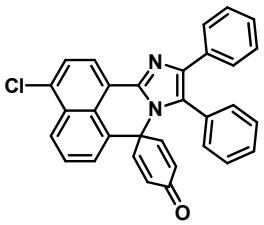



**Table S4.** Crystallographic Parameters of **by-product 2**

| | | |
|---|---|---|
| Empirical formula | $C_{31}H_{19.46}Cl_{0.08}N_2O$ | |
| Formula weight | 438.91 | |
| Temperature | 90 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | monoclinic | |
| Space group | P 1 21/n 1 | |
| Unit cell dimensions | a = 15.6018(16) Å | α = 90° |
| | b = 11.8059(12) Å | β = 100.4922(12)° |
| | c = 23.666(2) Å | γ = 90° |
| Volume | 4286.2(8) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.360 $Mg/m^3$ | |
| Absorption coefficient | 0.093 $mm^{-1}$ | |
| F(000) | 1831 | |
| Theta range for data collection | 1.45 to 26.50° | |
| Index ranges | -11<=h<=19, -14<=k<=14, -29<=l<=29 | |
| Reflections collected | 22553 | |
| Independent reflections | 8842 [R(int) = 0.0256] | |
| Absorption correction | Empirical | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 8842 / 12 / 636 | |
| Goodness-of-fit on $F^2$ | 1.068 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0415, wR2 = 0.1010 | |
| R indices (all data) | R1 = 0.0577, wR2 = 0.1098 | |
| Largest diff. peak and hole | 0.426 and -0.244 $eÅ^{-3}$ | |

## 6. Steady-state UV–vis absorption spectra

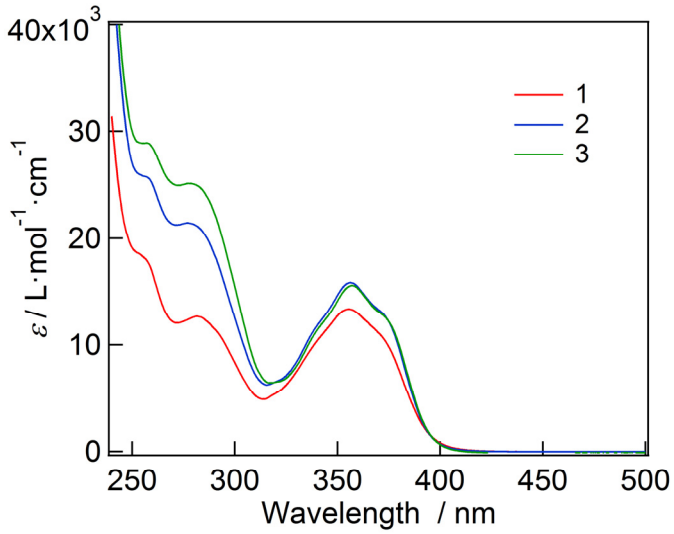



**Figure S30.** Steady-state absorption spectra of **1**, **2** and **3** in 2-methyl THF at 298 K.

## 7. Time profiles of the transient absorbance excited at 355 nm

The laser flash photolysis experiments were carried out with a TSP-1000 time resolved spectrophotometer (Unisoku). A 10 Hz Q-switched Nd:YAG laser (Continuum Minilite II) with the third harmonic at 355 nm (pulse width, 5 ns) was employed for the excitation light. A halogen lamp (OSRAM HLX64623) was used as the probe beam arranged in an orientation perpendicular to the exciting laser beam. The probe beam was monitored with a photomultiplier tube (Hamamatsu R2949) through a spectrometer (Unisoku MD200) for the time profile for the thermal isomerization. Optical grade solvents were used for all measurements.

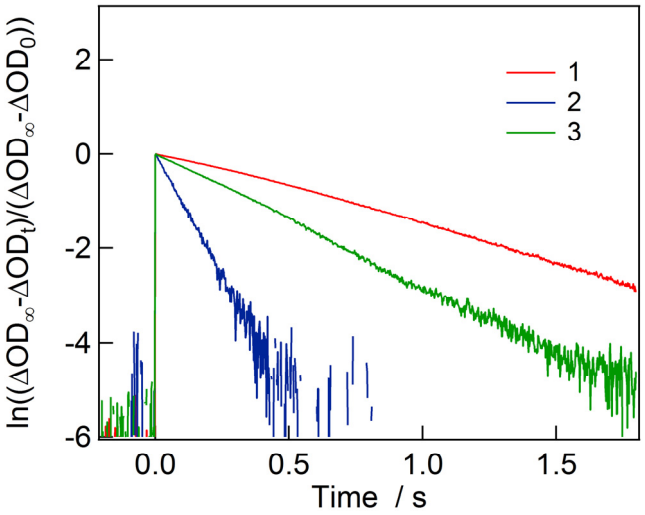



**Figure S31.** First-order plots for the time profiles of the transient absorbance at 380 nm (**1**: $7.4\times10^{-5}$ M, **2**: $5.9\times10^{-5}$ M, **3**: $4.9\times10^{-5}$ M) in Ar-saturated benzene excited by 355-nm laser pulse (5 ns, 7 mJ) at 298 K.

## 8. Durability against the repetitive laser pulse excitation

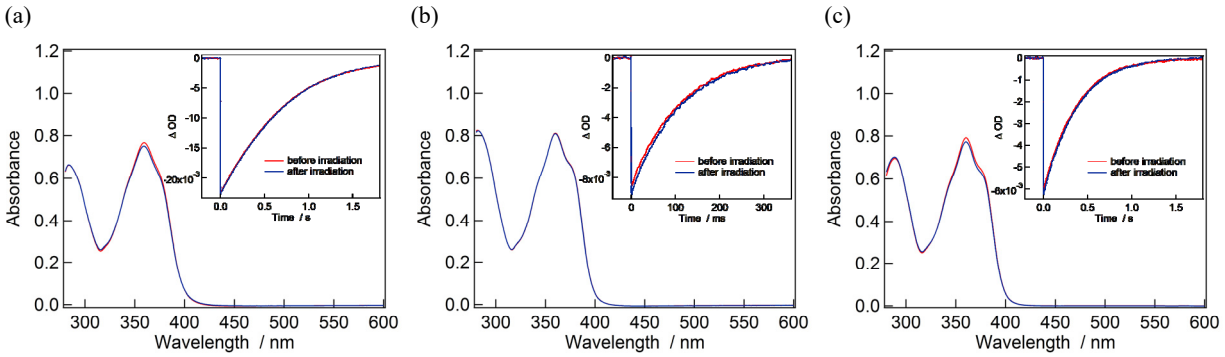



**Figure S32.** Durability of (a) **1**, (b) **2**, and (c) **3** against the repetitive 355-nm laser pulse excitation (5 mJ, 10,000 shots, 10 Hz) in Ar-saturated benzene at 298 K.

## 9. TDDFT calculations for the UV–vis absorption spectrum

All calculations were 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) level of the theory for the optimized structures.

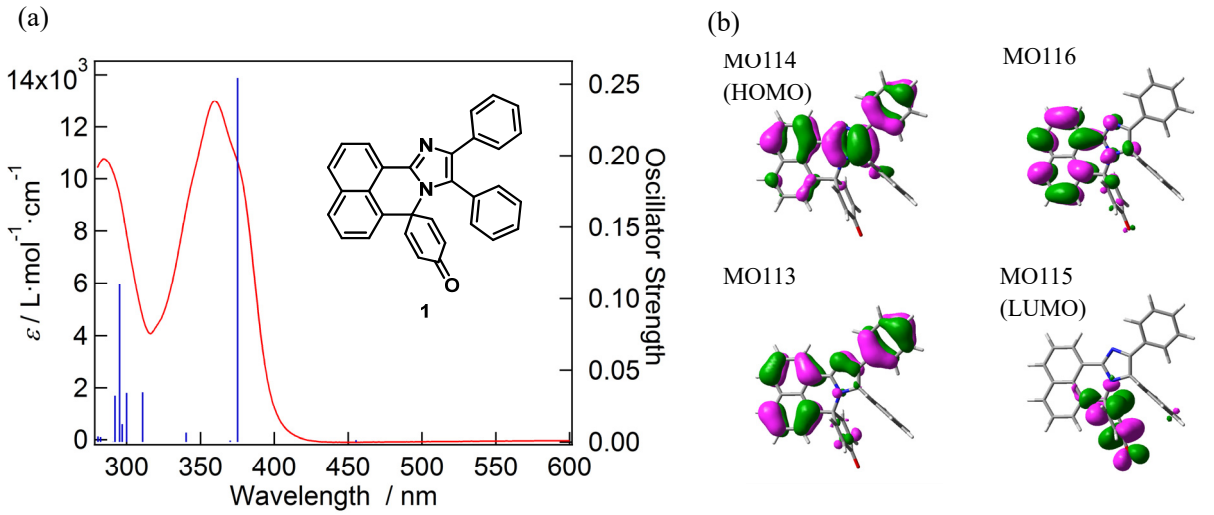



**Figure S33.** UV−Vis absorption spectrum of **1** in benzene. The calculated spectra (MPW1PW91/6-31+G(d)//MPW1PW91/6-31G(d) level of the theory) are shown by the blue perpendicular lines. (b) The relevant molecular orbitals of **1**.

**Table S5.** Standard Orientation of the Optimized Geometry for **1**

| Tag | Symbol | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | C | -3.7891600 | 0.9722590 | -0.3639520 |
| 2 | C | -5.0921270 | 0.4511100 | -0.4668320 |
| 3 | C | -5.3113160 | -0.8994670 | -0.3586480 |
| 4 | C | -4.2290810 | -1.7854470 | -0.1549550 |
| 5 | C | -2.9072140 | -1.2550770 | -0.0647710 |
| 6 | C | -2.7038510 | 0.1452620 | -0.1656030 |
| 7 | C | -4.4168100 | -3.1847920 | -0.0370600 |
| 8 | C | -3.3454520 | -4.0238440 | 0.1527620 |
| 9 | C | -2.0385190 | -3.5091760 | 0.2213100 |
| 10 | C | -1.8192080 | -2.1519400 | 0.1110240 |
| 11 | C | -1.3083350 | 0.7831360 | 0.0391680 |
| 12 | C | -0.4832940 | -1.6006930 | 0.1213010 |
| 13 | C | -1.0649420 | 1.7606720 | -1.0817730 |
| 14 | C | -1.0900760 | 3.0865170 | -0.9155020 |
| 15 | C | -1.2654570 | 3.7055030 | 0.4130490 |
| 16 | C | -1.3752830 | 2.7778600 | 1.5563340 |
| 17 | C | -1.3568160 | 1.4515180 | 1.3937710 |
| 18 | O | -1.3086760 | 4.9169260 | 0.5606520 |
| 19 | N | -0.2626360 | -0.2529330 | 0.0351510 |
| 20 | C | 1.1168050 | -0.0736960 | 0.0278980 |
| 21 | C | 1.6473820 | -1.3531540 | 0.1060870 |
| 22 | N | 0.6400440 | -2.2777070 | 0.1614700 |
| 23 | C | 3.0486350 | -1.7969720 | 0.1112230 |
| 24 | C | 1.7880340 | 1.2303250 | -0.1408820 |
| 25 | C | 4.1179570 | -0.9483150 | 0.4251380 |
| 26 | C | 5.4246450 | -1.4235750 | 0.4142940 |
| 27 | C | 5.6902990 | -2.7524720 | 0.0975950 |
| 28 | C | 4.6329630 | -3.6072120 | -0.2041550 |
| 29 | C | 3.3268630 | -3.1358150 | -0.1964810 |
| 30 | C | 1.9458290 | 2.1187840 | 0.9280930 |
| 31 | C | 2.5924550 | 3.3365620 | 0.7445980 |
| 32 | C | 3.1060980 | 3.6742210 | -0.5049080 |
| 33 | C | 2.9807420 | 2.7845090 | -1.5683470 |
| 34 | C | 2.3272210 | 1.5708630 | -1.3876290 |
| 35 | H | -3.6429670 | 2.0443480 | -0.4356320 |
| 36 | H | -5.9225110 | 1.1308280 | -0.6258180 |
| 37 | H | -6.3162850 | -1.3045930 | -0.4284310 |
| 38 | H | -5.4253070 | -3.5818330 | -0.1010370 |
| 39 | H | -3.5016410 | -5.0937410 | 0.2430870 |
| 40 | H | -1.1853540 | -4.1651990 | 0.3505830 |
| 41 | H | -0.9214170 | 1.3147410 | -2.0618300 |
| 42 | H | -0.9558530 | 3.7684790 | -1.7483020 |
| 43 | H | -1.4619820 | 3.2332570 | 2.5374560 |
| 44 | H | -1.4336340 | 0.7720650 | 2.2386000 |
| 45 | H | 3.9311840 | 0.0851360 | 0.6909780 |
| 46 | H | 6.2390540 | -0.7500690 | 0.6628870 |

| | | | | |
|---|---|---|---|---|
| 47 | H | 6.7116180 | -3.1200660 | 0.0908480 |
| 48 | H | 4.8264300 | -4.6473950 | -0.4479660 |
| 49 | H | 2.4983210 | -3.7961000 | -0.4255620 |
| 50 | H | 1.5606230 | 1.8505360 | 1.9053940 |
| 51 | H | 2.6991890 | 4.0211120 | 1.5797470 |
| 52 | H | 3.6104350 | 4.6246570 | -0.6461850 |
| 53 | H | 3.3921330 | 3.0358840 | -2.5406970 |
| 54 | H | 2.2315670 | 0.8722890 | -2.2125740 |

SCF Done: E(RmPW1PW91) = -1377.76630388 A.U.

Zero-point correction = 0.428202 (Hartree/Particle)
Thermal correction to Energy = 0.453011
Thermal correction to Enthalpy = 0.453955
Thermal correction to Gibbs Free Energy = 0.372129
Sum of electronic and zero-point Energies = -1377.338102
Sum of electronic and thermal Energies = -1377.313293
Sum of electronic and thermal Enthalpies = -1377.312349
Sum of electronic and thermal Free Energies = -1377.394175

Low frequencies --- -8.0629 -6.2552 -2.9355 -0.0006 -0.0005 -0.0003
Low frequencies --- 18.8566 28.7595 30.9589

The Result for the TDDFT calculation

Excited State 1: Singlet-A 2.7230 eV 455.32 nm f=0.0013 <S**2>=0.000
114 ->115 0.70395
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1377.70148825
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.3056 eV 375.07 nm f=0.2543 <S**2>=0.000
114 ->116 0.69914

Excited State 3: Singlet-A 3.3494 eV 370.17 nm f=0.0011 <S**2>=0.000
107 ->115 -0.17871
108 ->115 0.30722
109 ->115 0.57967

Excited State 4: Singlet-A 3.6437 eV 340.27 nm f=0.0063 <S**2>=0.000
113 ->115 0.68460

Excited State 5: Singlet-A 3.9893 eV 310.79 nm f=0.0348 <S**2>=0.000
114 ->117 0.67889

Excited State 6: Singlet-A 4.1330 eV 299.99 nm f=0.0344 <S**2>=0.000
110 ->116 0.19277
113 ->116 0.29508
114 ->118 0.56829

Excited State 7: Singlet-A 4.1760 eV 296.90 nm f=0.0122 <S**2>=0.000
111 ->115 0.49161
112 ->115 -0.47691

| | | | | | |
|---|---|---|---|---|---|
| Excited State 8: | Singlet-A | 4.2007 eV | 295.15 nm | f=0.1102 | <S**2>=0.000 |
| 113 ->116 | 0.60729 | | | | |
| 114 ->118 | -0.27638 | | | | |
| 114 ->119 | 0.14749 | | | | |
| Excited State 9: | Singlet-A | 4.2457 eV | 292.02 nm | f=0.0325 | <S**2>=0.000 |
| 110 ->115 | -0.13538 | | | | |
| 110 ->116 | 0.16075 | | | | |
| 112 ->115 | -0.10061 | | | | |
| 113 ->116 | -0.15376 | | | | |
| 114 ->119 | 0.61081 | | | | |
| 114 ->121 | 0.10166 | | | | |
| Excited State 10: | Singlet-A | 4.2641 eV | 290.76 nm | f=0.0002 | <S**2>=0.000 |
| 108 ->115 | -0.22967 | | | | |
| 110 ->115 | 0.16129 | | | | |
| 111 ->115 | 0.43093 | | | | |
| 112 ->115 | 0.45284 | | | | |
| 114 ->119 | 0.10892 | | | | |
| Excited State 11: | Singlet-A | 4.3908 eV | 282.37 nm | f=0.0033 | <S**2>=0.000 |
| 108 ->115 | -0.35267 | | | | |
| 109 ->115 | 0.27917 | | | | |
| 110 ->115 | 0.44496 | | | | |
| 111 ->115 | -0.19249 | | | | |
| 112 ->115 | -0.20907 | | | | |
| Excited State 12: | Singlet-A | 4.4190 eV | 280.57 nm | f=0.0037 | <S**2>=0.000 |
| 107 ->115 | -0.17840 | | | | |
| 108 ->115 | 0.41415 | | | | |
| 109 ->115 | -0.21666 | | | | |
| 110 ->115 | 0.46345 | | | | |
| 114 ->119 | 0.10962 | | | | |
| Excited State 13: | Singlet-A | 4.5008 eV | 275.47 nm | f=0.0278 | <S**2>=0.000 |
| 114 ->120 | 0.67522 | | | | |
| 114 ->121 | -0.11655 | | | | |
| Excited State 14: | Singlet-A | 4.5141 eV | 274.66 nm | f=0.0127 | <S**2>=0.000 |
| 105 ->115 | -0.11893 | | | | |
| 107 ->115 | 0.61511 | | | | |
| 108 ->115 | 0.20149 | | | | |
| 109 ->115 | 0.11258 | | | | |
| 110 ->115 | 0.12431 | | | | |
| Excited State 15: | Singlet-A | 4.6370 eV | 267.38 nm | f=0.0485 | <S**2>=0.000 |
| 110 ->116 | -0.17020 | | | | |
| 112 ->116 | 0.47882 | | | | |
| 114 ->118 | 0.10743 | | | | |
| 114 ->121 | 0.42028 | | | | |
| Excited State 16: | Singlet-A | 4.6703 eV | 265.48 nm | f=0.0969 | <S**2>=0.000 |
| 110 ->116 | 0.16488 | | | | |
| 111 ->116 | -0.12260 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 112 ->116 | 0.48499 | | | | |
| 113 ->118 | -0.10407 | | | | |
| 114 ->118 | -0.17213 | | | | |
| 114 ->120 | -0.11978 | | | | |
| 114 ->121 | -0.37196 | | | | |
| Excited State 17: | Singlet-A | 4.7636 eV | 260.27 nm | f=0.0102 | <S**2>=0.000 |
| 106 ->116 | 0.10538 | | | | |
| 111 ->116 | 0.63578 | | | | |
| 112 ->116 | 0.14748 | | | | |
| Excited State 18: | Singlet-A | 4.7981 eV | 258.40 nm | f=0.0532 | <S**2>=0.000 |
| 107 ->116 | 0.15750 | | | | |
| 110 ->116 | 0.28047 | | | | |
| 111 ->116 | 0.15831 | | | | |
| 113 ->117 | 0.32950 | | | | |
| 113 ->118 | -0.20080 | | | | |
| 113 ->119 | -0.11585 | | | | |
| 114 ->118 | -0.13435 | | | | |
| 114 ->119 | -0.20699 | | | | |
| 114 ->121 | 0.29353 | | | | |
| Excited State 19: | Singlet-A | 4.8510 eV | 255.59 nm | f=0.0054 | <S**2>=0.000 |
| 105 ->115 | 0.47870 | | | | |
| 106 ->115 | -0.45701 | | | | |
| 107 ->115 | 0.15574 | | | | |
| Excited State 20: | Singlet-A | 4.9108 eV | 252.47 nm | f=0.0034 | <S**2>=0.000 |
| 107 ->116 | -0.12887 | | | | |
| 109 ->116 | -0.11191 | | | | |
| 112 ->118 | -0.15742 | | | | |
| 112 ->121 | -0.18227 | | | | |
| 113 ->123 | 0.11268 | | | | |
| 114 ->122 | -0.34687 | | | | |
| 114 ->123 | 0.44696 | | | | |
| Excited State 21: | Singlet-A | 4.9327 eV | 251.35 nm | f=0.0087 | <S**2>=0.000 |
| 107 ->116 | 0.36506 | | | | |
| 109 ->116 | 0.46002 | | | | |
| 110 ->116 | -0.24984 | | | | |
| 114 ->122 | -0.11009 | | | | |
| 114 ->123 | 0.10638 | | | | |
| Excited State 22: | Singlet-A | 4.9975 eV | 248.09 nm | f=0.0358 | <S**2>=0.000 |
| 109 ->116 | -0.15300 | | | | |
| 113 ->117 | 0.38289 | | | | |
| 113 ->118 | 0.18396 | | | | |
| 114 ->121 | -0.12064 | | | | |
| 114 ->122 | 0.39827 | | | | |
| 114 ->123 | 0.13000 | | | | |
| 114 ->125 | -0.12315 | | | | |
| Excited State 23: | Singlet-A | 5.0138 eV | 247.28 nm | f=0.0039 | <S**2>=0.000 |
| 107 ->116 | -0.33082 | | | | |
| 108 ->116 | 0.26666 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 109 ->116 | 0.36691 | | | | |
| 109 ->117 | -0.10101 | | | | |
| 114 ->122 | 0.29882 | | | | |
| 114 ->123 | 0.16875 | | | | |
| Excited State 24: | Singlet-A | 5.0284 eV | 246.57 nm | f=0.0227 | <S**2>=0.000 |
| 105 ->115 | -0.13520 | | | | |
| 106 ->115 | -0.12949 | | | | |
| 107 ->116 | -0.26843 | | | | |
| 108 ->116 | 0.20434 | | | | |
| 109 ->116 | 0.12344 | | | | |
| 113 ->117 | 0.31833 | | | | |
| 113 ->118 | 0.15075 | | | | |
| 114 ->122 | -0.28331 | | | | |
| 114 ->123 | -0.25326 | | | | |
| Excited State 25: | Singlet-A | 5.0919 eV | 243.49 nm | f=0.0037 | <S**2>=0.000 |
| 107 ->116 | 0.20689 | | | | |
| 108 ->116 | 0.55490 | | | | |
| 109 ->116 | -0.23187 | | | | |
| 110 ->116 | -0.19892 | | | | |
| Excited State 26: | Singlet-A | 5.1586 eV | 240.35 nm | f=0.1112 | <S**2>=0.000 |
| 104 ->115 | -0.10995 | | | | |
| 105 ->115 | 0.41101 | | | | |
| 106 ->115 | 0.45025 | | | | |
| 106 ->116 | -0.10405 | | | | |
| 107 ->116 | -0.14243 | | | | |
| 113 ->117 | 0.17028 | | | | |
| 114 ->125 | -0.10741 | | | | |
| Excited State 27: | Singlet-A | 5.2448 eV | 236.39 nm | f=0.0647 | <S**2>=0.000 |
| 104 ->115 | -0.12563 | | | | |
| 113 ->117 | 0.14170 | | | | |
| 113 ->118 | 0.14196 | | | | |
| 114 ->123 | 0.21415 | | | | |
| 114 ->124 | 0.26351 | | | | |
| 114 ->125 | 0.50939 | | | | |
| Excited State 28: | Singlet-A | 5.2718 eV | 235.18 nm | f=0.0271 | <S**2>=0.000 |
| 105 ->116 | 0.19556 | | | | |
| 106 ->116 | 0.44011 | | | | |
| 111 ->116 | -0.11661 | | | | |
| 111 ->117 | 0.20456 | | | | |
| 113 ->118 | 0.23503 | | | | |
| 113 ->119 | -0.23270 | | | | |
| Excited State 29: | Singlet-A | 5.2945 eV | 234.17 nm | f=0.0900 | <S**2>=0.000 |
| 105 ->116 | 0.10685 | | | | |
| 106 ->116 | 0.36982 | | | | |
| 113 ->118 | -0.35529 | | | | |
| 113 ->119 | 0.37885 | | | | |
| Excited State 30: | Singlet-A | 5.3481 eV | 231.83 nm | f=0.0106 | <S**2>=0.000 |
| 114 ->124 | 0.59181 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 114 ->125 | -0.31055 | | | | |
| | | | | | |
| Excited State 31: | Singlet-A | 5.3839 eV | 230.29 nm | f=0.0254 | <S**2>=0.000 |
| 106 ->116 | -0.19954 | | | | |
| 108 ->118 | 0.13413 | | | | |
| 108 ->119 | -0.22177 | | | | |
| 111 ->117 | 0.28003 | | | | |
| 111 ->119 | 0.10073 | | | | |
| 111 ->120 | -0.22969 | | | | |
| 112 ->117 | -0.16725 | | | | |
| 112 ->118 | -0.12620 | | | | |
| 112 ->120 | 0.12813 | | | | |
| 113 ->118 | -0.17767 | | | | |
| 113 ->120 | -0.10592 | | | | |
| | | | | | |
| Excited State 32: | Singlet-A | 5.4558 eV | 227.25 nm | f=0.0063 | <S**2>=0.000 |
| 104 ->115 | 0.19300 | | | | |
| 105 ->116 | 0.32829 | | | | |
| 109 ->117 | -0.12512 | | | | |
| 111 ->117 | -0.14950 | | | | |
| 112 ->117 | 0.19434 | | | | |
| 114 ->125 | 0.15039 | | | | |
| 114 ->126 | 0.42283 | | | | |
| | | | | | |
| Excited State 33: | Singlet-A | 5.4659 eV | 226.83 nm | f=0.0357 | <S**2>=0.000 |
| 105 ->116 | -0.26131 | | | | |
| 106 ->116 | 0.14071 | | | | |
| 109 ->117 | -0.11451 | | | | |
| 111 ->117 | -0.17194 | | | | |
| 112 ->117 | 0.31324 | | | | |
| 112 ->118 | -0.18713 | | | | |
| 112 ->119 | 0.16064 | | | | |
| 113 ->120 | -0.21725 | | | | |
| 114 ->123 | -0.19282 | | | | |
| 114 ->126 | -0.18792 | | | | |
| | | | | | |
| Excited State 34: | Singlet-A | 5.4825 eV | 226.15 nm | f=0.0099 | <S**2>=0.000 |
| 105 ->116 | -0.33908 | | | | |
| 108 ->117 | 0.10517 | | | | |
| 109 ->117 | 0.21485 | | | | |
| 114 ->126 | 0.46978 | | | | |
| | | | | | |
| Excited State 35: | Singlet-A | 5.5071 eV | 225.14 nm | f=0.0308 | <S**2>=0.000 |
| 104 ->115 | 0.21567 | | | | |
| 105 ->116 | 0.16118 | | | | |
| 107 ->117 | -0.12946 | | | | |
| 108 ->117 | 0.19643 | | | | |
| 109 ->116 | 0.13660 | | | | |
| 109 ->117 | 0.46701 | | | | |
| 109 ->118 | 0.11734 | | | | |
| 112 ->117 | 0.21481 | | | | |
| 114 ->126 | -0.14950 | | | | |
| | | | | | |
| Excited State 36: | Singlet-A | 5.5257 eV | 224.38 nm | f=0.0083 | <S**2>=0.000 |
| 105 ->116 | -0.12740 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 111 ->117 | 0.12024 | | | | |
| 111 ->120 | -0.13733 | | | | |
| 112 ->117 | 0.39767 | | | | |
| 112 ->118 | 0.22411 | | | | |
| 113 ->120 | 0.24097 | | | | |
| 113 ->121 | 0.11843 | | | | |
| 114 ->123 | 0.16308 | | | | |
| 114 ->125 | -0.12284 | | | | |
| 114 ->128 | -0.17093 | | | | |
| Excited State 37: | Singlet-A | 5.5340 eV | 224.04 nm | f=0.1805 | <S**2>=0.000 |
| 103 ->115 | -0.30303 | | | | |
| 110 ->116 | 0.17892 | | | | |
| 112 ->117 | -0.11378 | | | | |
| 113 ->118 | 0.20539 | | | | |
| 113 ->119 | 0.33647 | | | | |
| 113 ->121 | 0.25822 | | | | |
| 114 ->127 | -0.21399 | | | | |
| Excited State 38: | Singlet-A | 5.5405 eV | 223.78 nm | f=0.0376 | <S**2>=0.000 |
| 103 ->115 | 0.43355 | | | | |
| 104 ->115 | -0.30030 | | | | |
| 105 ->116 | 0.14721 | | | | |
| 112 ->117 | 0.13524 | | | | |
| 113 ->119 | 0.11996 | | | | |
| 113 ->121 | 0.11424 | | | | |
| 114 ->127 | -0.28690 | | | | |
| Excited State 39: | Singlet-A | 5.5451 eV | 223.59 nm | f=0.0837 | <S**2>=0.000 |
| 103 ->115 | 0.12566 | | | | |
| 104 ->115 | -0.12942 | | | | |
| 113 ->119 | 0.19232 | | | | |
| 113 ->121 | 0.16228 | | | | |
| 114 ->127 | 0.56075 | | | | |
| 114 ->129 | -0.10331 | | | | |
| Excited State 40: | Singlet-A | 5.5636 eV | 222.85 nm | f=0.0033 | <S**2>=0.000 |
| 111 ->117 | 0.10813 | | | | |
| 113 ->120 | 0.11775 | | | | |
| 114 ->122 | -0.13866 | | | | |
| 114 ->128 | 0.61057 | | | | |

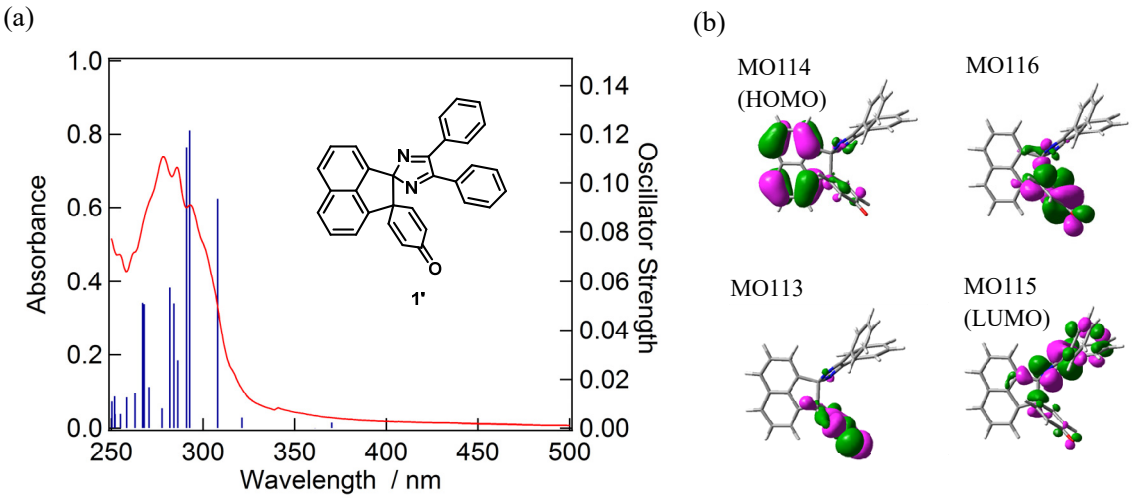



**Figure S34.** UV−Vis absorption spectrum for the solution of **1** at photostationary state after 365-nm UV light irradiation in 2-methyl THF at 153 K. The calculated spectra for **1'** (MPW1PW91/6-31+G(d)//MPW1PW91/6-31G(d) level of the theory) are shown by the blue perpendicular lines. (b) The relevant molecular orbitals of **1'**.

**Table S6.** Standard Orientation of the Optimized Geometry for **1'**

| Tag | Symbol | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | C | -4.2893690 | 0.3625950 | 0.9732200 |
| 2 | C | -5.3993560 | -0.4393260 | 0.5984210 |
| 3 | C | -5.3065530 | -1.4338850 | -0.3526630 |
| 4 | C | -4.0654290 | -1.7040660 | -0.9839330 |
| 5 | C | -2.9753150 | -0.9149470 | -0.5689400 |
| 6 | C | -3.0791320 | 0.1148350 | 0.3785770 |
| 7 | C | -3.7887310 | -2.6692440 | -1.9844020 |
| 8 | C | -2.5126390 | -2.7965330 | -2.4948500 |
| 9 | C | -1.4284090 | -2.0032620 | -2.0398750 |
| 10 | C | -1.6752640 | -1.0691630 | -1.0676920 |
| 11 | C | -1.7398870 | 0.8542330 | 0.4715220 |
| 12 | C | -1.8726930 | 2.1171560 | -0.3343100 |
| 13 | C | -1.7217660 | 3.3416880 | 0.1836740 |
| 14 | C | -1.3596810 | 3.5512430 | 1.5952910 |
| 15 | C | -1.1836110 | 2.3306990 | 2.4050120 |
| 16 | C | -1.3408260 | 1.1045440 | 1.8925600 |
| 17 | O | -1.2144180 | 4.6684460 | 2.0714790 |
| 18 | H | -4.4115740 | 1.1553770 | 1.7041680 |
| 19 | H | -6.3576380 | -0.2493770 | 1.0716000 |
| 20 | H | -6.1849390 | -2.0130890 | -0.6210680 |
| 21 | H | -4.5866470 | -3.3069240 | -2.3530040 |
| 22 | H | -2.3248650 | -3.5361340 | -3.2668840 |
| 23 | H | -0.4366800 | -2.1465040 | -2.4556940 |
| 24 | H | -2.1315400 | 1.9839290 | -1.3804020 |

| | | | | |
|---|---|---|---|---|
| 25 | H | -1.8531030 | 4.2354230 | -0.4177280 |
| 26 | H | -0.9190570 | 2.4829400 | 3.4465940 |
| 27 | H | -1.2083380 | 0.2207220 | 2.5076600 |
| 28 | C | -0.7393100 | -0.1545880 | -0.2858010 |
| 29 | N | 0.2030190 | 0.5419140 | -1.1292980 |
| 30 | N | -0.0019190 | -0.9512690 | 0.6823930 |
| 31 | C | 1.3747080 | 0.1908950 | -0.7316920 |
| 32 | C | 1.2438560 | -0.7501900 | 0.4345740 |
| 33 | C | 2.5935230 | 0.6698010 | -1.4036680 |
| 34 | C | 2.6160800 | 1.9710840 | -1.9201500 |
| 35 | C | 3.7027170 | -0.1621060 | -1.5943790 |
| 36 | C | 3.7345830 | 2.4361190 | -2.5986200 |
| 37 | H | 1.7474130 | 2.6042580 | -1.7775520 |
| 38 | C | 4.8153940 | 0.3034580 | -2.2865140 |
| 39 | H | 3.6904200 | -1.1779900 | -1.2151530 |
| 40 | C | 4.8365820 | 1.6034080 | -2.7835590 |
| 41 | H | 3.7468950 | 3.4496410 | -2.9860270 |
| 42 | H | 5.6667630 | -0.3520890 | -2.4378520 |
| 43 | H | 5.7095380 | 1.9672680 | -3.3159620 |
| 44 | C | 2.3025530 | -1.3647220 | 1.2519770 |
| 45 | C | 2.0950410 | -2.6422230 | 1.7867120 |
| 46 | C | 3.4787970 | -0.6745410 | 1.5667480 |
| 47 | C | 3.0539760 | -3.2243950 | 2.6046810 |
| 48 | H | 1.1732170 | -3.1629460 | 1.5519700 |
| 49 | C | 4.4309070 | -1.2565800 | 2.3966230 |
| 50 | H | 3.6415580 | 0.3248150 | 1.1790550 |
| 51 | C | 4.2246330 | -2.5331340 | 2.9112530 |
| 52 | H | 2.8872520 | -4.2181870 | 3.0074640 |
| 53 | H | 5.3343960 | -0.7085970 | 2.6432340 |
| 54 | H | 4.9723150 | -2.9877370 | 3.5532840 |

SCF Done: E(RmPW1PW91) = -1377.73280797 A.U.

Zero-point correction = 0.427209 (Hartree/Particle)
Thermal correction to Energy = 0.452133
Thermal correction to Enthalpy = 0.453077
Thermal correction to Gibbs Free Energy = 0.370663
Sum of electronic and zero-point Energies = -1377.305599
Sum of electronic and thermal Energies = -1377.280675
Sum of electronic and thermal Enthalpies = -1377.279731
Sum of electronic and thermal Free Energies = -1377.362144

Low frequencies --- -0.9499 -0.0002 0.0002 0.0005 2.5505 8.2441
Low frequencies --- 21.3402 24.9211 32.1880

The Result for the TDDFT calculation

Excited State 1: Singlet-A 3.3487 eV 370.25 nm f=0.0022 <S**2>=0.000
114 ->115 0.69497
This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1377.64725433
Copying the excited state density for this state as the 1-particle RhoCI density.

| | | | | | | |
|---|---|---|---|---|---|---|
| Excited State | 2: | Singlet-A | 3.4332 eV | 361.14 nm | f=0.0001 | <S**2>=0.000 |
| 113 ->115 | | 0.26390 | | | | |
| 113 ->116 | | 0.62510 | | | | |
| 114 ->115 | | 0.10442 | | | | |
| Excited State | 3: | Singlet-A | 3.8599 eV | 321.21 nm | f=0.0042 | <S**2>=0.000 |
| 114 ->116 | | 0.69298 | | | | |
| Excited State | 4: | Singlet-A | 4.0257 eV | 307.98 nm | f=0.0936 | <S**2>=0.000 |
| 105 ->115 | | -0.32482 | | | | |
| 106 ->115 | | -0.13315 | | | | |
| 109 ->115 | | -0.17997 | | | | |
| 112 ->115 | | 0.46310 | | | | |
| 113 ->115 | | -0.29143 | | | | |
| 113 ->116 | | 0.11283 | | | | |
| Excited State | 5: | Singlet-A | 4.2355 eV | 292.72 nm | f=0.1216 | <S**2>=0.000 |
| 112 ->115 | | 0.28373 | | | | |
| 113 ->115 | | 0.46721 | | | | |
| 113 ->116 | | -0.19931 | | | | |
| 114 ->117 | | 0.38259 | | | | |
| Excited State | 6: | Singlet-A | 4.2605 eV | 291.01 nm | f=0.1147 | <S**2>=0.000 |
| 105 ->115 | | 0.11416 | | | | |
| 112 ->115 | | -0.16792 | | | | |
| 113 ->115 | | -0.30972 | | | | |
| 113 ->116 | | 0.13718 | | | | |
| 114 ->117 | | 0.56008 | | | | |
| Excited State | 7: | Singlet-A | 4.3319 eV | 286.21 nm | f=0.0277 | <S**2>=0.000 |
| 110 ->115 | | -0.24729 | | | | |
| 111 ->115 | | 0.64810 | | | | |
| Excited State | 8: | Singlet-A | 4.3641 eV | 284.10 nm | f=0.0510 | <S**2>=0.000 |
| 103 ->115 | | 0.10985 | | | | |
| 110 ->115 | | 0.63357 | | | | |
| 111 ->115 | | 0.25451 | | | | |
| Excited State | 9: | Singlet-A | 4.3980 eV | 281.91 nm | f=0.0575 | <S**2>=0.000 |
| 105 ->115 | | 0.19181 | | | | |
| 106 ->115 | | 0.12615 | | | | |
| 109 ->115 | | 0.52938 | | | | |
| 112 ->115 | | 0.31549 | | | | |
| 113 ->115 | | -0.10605 | | | | |
| 114 ->117 | | -0.10250 | | | | |
| 114 ->118 | | -0.11418 | | | | |
| Excited State | 10: | Singlet-A | 4.4660 eV | 277.62 nm | f=0.0080 | <S**2>=0.000 |
| 109 ->115 | | -0.10474 | | | | |
| 111 ->117 | | -0.40060 | | | | |
| 112 ->117 | | 0.15937 | | | | |
| 114 ->118 | | -0.19723 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 114 ->119 | -0.11221 | | | | |
| 114 ->120 | 0.47212 | | | | |
| Excited State 11: | Singlet-A | 4.5822 eV | 270.57 nm | f=0.0168 | <S**2>=0.000 |
| 105 ->115 | 0.35731 | | | | |
| 106 ->115 | 0.32080 | | | | |
| 109 ->115 | -0.35562 | | | | |
| 112 ->115 | 0.15425 | | | | |
| 114 ->118 | -0.25714 | | | | |
| Excited State 12: | Singlet-A | 4.6280 eV | 267.90 nm | f=0.0507 | <S**2>=0.000 |
| 106 ->115 | -0.14106 | | | | |
| 107 ->115 | -0.15456 | | | | |
| 108 ->115 | 0.56899 | | | | |
| 112 ->115 | -0.11147 | | | | |
| 114 ->118 | -0.25875 | | | | |
| Excited State 13: | Singlet-A | 4.6422 eV | 267.08 nm | f=0.0512 | <S**2>=0.000 |
| 105 ->115 | 0.12834 | | | | |
| 106 ->115 | 0.14983 | | | | |
| 107 ->115 | -0.15688 | | | | |
| 108 ->115 | 0.27302 | | | | |
| 114 ->118 | 0.54415 | | | | |
| 114 ->120 | 0.11369 | | | | |
| Excited State 14: | Singlet-A | 4.7156 eV | 262.92 nm | f=0.0143 | <S**2>=0.000 |
| 107 ->115 | 0.63406 | | | | |
| 108 ->115 | 0.22021 | | | | |
| Excited State 15: | Singlet-A | 4.7987 eV | 258.37 nm | f=0.0125 | <S**2>=0.000 |
| 105 ->115 | -0.31424 | | | | |
| 106 ->115 | 0.47921 | | | | |
| 110 ->116 | -0.17090 | | | | |
| 112 ->116 | -0.26255 | | | | |
| Excited State 16: | Singlet-A | 4.8626 eV | 254.97 nm | f=0.0057 | <S**2>=0.000 |
| 105 ->115 | 0.17268 | | | | |
| 106 ->115 | -0.20817 | | | | |
| 111 ->116 | 0.53097 | | | | |
| 112 ->116 | -0.33284 | | | | |
| Excited State 17: | Singlet-A | 4.9201 eV | 251.99 nm | f=0.0056 | <S**2>=0.000 |
| 110 ->116 | -0.15519 | | | | |
| 111 ->116 | -0.22603 | | | | |
| 112 ->116 | -0.19844 | | | | |
| 113 ->117 | 0.56651 | | | | |
| 113 ->118 | -0.12439 | | | | |
| Excited State 18: | Singlet-A | 4.9241 eV | 251.79 nm | f=0.0129 | <S**2>=0.000 |
| 105 ->115 | -0.12333 | | | | |
| 106 ->115 | 0.11939 | | | | |
| 106 ->116 | -0.12211 | | | | |
| 110 ->116 | 0.19526 | | | | |
| 111 ->116 | 0.35998 | | | | |
| 112 ->116 | 0.34117 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 113 ->117 | 0.35706 | | | | |
| | | | | | |
| Excited State 19: | Singlet-A | 4.9521 eV | 250.37 nm | f=0.0109 | <S**2>=0.000 |
| 106 ->116 | -0.10009 | | | | |
| 110 ->116 | 0.57027 | | | | |
| 112 ->116 | -0.33973 | | | | |
| | | | | | |
| Excited State 20: | Singlet-A | 5.0781 eV | 244.15 nm | f=0.0182 | <S**2>=0.000 |
| 102 ->115 | 0.10706 | | | | |
| 103 ->115 | 0.42222 | | | | |
| 104 ->115 | 0.10899 | | | | |
| 108 ->115 | -0.11946 | | | | |
| 111 ->117 | -0.15337 | | | | |
| 112 ->117 | -0.39441 | | | | |
| 112 ->118 | -0.10504 | | | | |
| 113 ->118 | 0.13305 | | | | |
| | | | | | |
| Excited State 21: | Singlet-A | 5.1192 eV | 242.19 nm | f=0.0017 | <S**2>=0.000 |
| 103 ->115 | 0.37805 | | | | |
| 104 ->115 | 0.10203 | | | | |
| 106 ->116 | -0.11149 | | | | |
| 111 ->117 | 0.14782 | | | | |
| 112 ->117 | 0.48590 | | | | |
| | | | | | |
| Excited State 22: | Singlet-A | 5.1402 eV | 241.21 nm | f=0.0006 | <S**2>=0.000 |
| 114 ->119 | 0.67369 | | | | |
| 114 ->120 | 0.13112 | | | | |
| | | | | | |
| Excited State 23: | Singlet-A | 5.2031 eV | 238.29 nm | f=0.0081 | <S**2>=0.000 |
| 103 ->115 | 0.13691 | | | | |
| 106 ->116 | 0.35555 | | | | |
| 107 ->116 | -0.10015 | | | | |
| 108 ->116 | -0.28541 | | | | |
| 109 ->116 | 0.40289 | | | | |
| 110 ->116 | 0.19215 | | | | |
| 112 ->116 | 0.10212 | | | | |
| | | | | | |
| Excited State 24: | Singlet-A | 5.2372 eV | 236.74 nm | f=0.0345 | <S**2>=0.000 |
| 104 ->115 | -0.11898 | | | | |
| 110 ->117 | 0.39973 | | | | |
| 112 ->118 | -0.18922 | | | | |
| 113 ->117 | 0.12222 | | | | |
| 113 ->118 | 0.46018 | | | | |
| | | | | | |
| Excited State 25: | Singlet-A | 5.2572 eV | 235.84 nm | f=0.0235 | <S**2>=0.000 |
| 109 ->116 | 0.18236 | | | | |
| 109 ->118 | -0.10692 | | | | |
| 110 ->117 | 0.45201 | | | | |
| 113 ->117 | -0.11158 | | | | |
| 113 ->118 | -0.40251 | | | | |
| | | | | | |
| Excited State 26: | Singlet-A | 5.2707 eV | 235.23 nm | f=0.0009 | <S**2>=0.000 |
| 104 ->115 | 0.12007 | | | | |
| 106 ->116 | -0.15463 | | | | |
| 107 ->115 | 0.13087 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 107 ->116 | 0.11371 | | | | |
| 108 ->116 | 0.12649 | | | | |
| 109 ->116 | 0.22298 | | | | |
| 109 ->117 | 0.23864 | | | | |
| 109 ->118 | 0.38685 | | | | |
| 110 ->121 | 0.14109 | | | | |
| 112 ->118 | 0.15214 | | | | |
| 112 ->119 | 0.21988 | | | | |
| Excited State 27: | Singlet-A | 5.2989 eV | 233.98 nm | f=0.0075 | <S**2>=0.000 |
| 106 ->116 | -0.27476 | | | | |
| 108 ->116 | 0.21655 | | | | |
| 109 ->116 | 0.43933 | | | | |
| 109 ->117 | -0.10082 | | | | |
| 109 ->118 | -0.19693 | | | | |
| 110 ->117 | -0.23600 | | | | |
| 112 ->119 | -0.10808 | | | | |
| Excited State 28: | Singlet-A | 5.3342 eV | 232.43 nm | f=0.0697 | <S**2>=0.000 |
| 104 ->115 | 0.29663 | | | | |
| 109 ->118 | -0.16195 | | | | |
| 110 ->117 | 0.10595 | | | | |
| 111 ->118 | 0.13554 | | | | |
| 112 ->118 | 0.49008 | | | | |
| 112 ->119 | -0.10613 | | | | |
| 113 ->118 | 0.18716 | | | | |
| Excited State 29: | Singlet-A | 5.3564 eV | 231.47 nm | f=0.0080 | <S**2>=0.000 |
| 103 ->115 | -0.17062 | | | | |
| 104 ->115 | 0.56524 | | | | |
| 108 ->117 | 0.11217 | | | | |
| 112 ->118 | -0.28835 | | | | |
| Excited State 30: | Singlet-A | 5.4211 eV | 228.71 nm | f=0.0532 | <S**2>=0.000 |
| 107 ->118 | 0.28908 | | | | |
| 108 ->117 | -0.22792 | | | | |
| 108 ->118 | -0.18742 | | | | |
| 109 ->116 | -0.10686 | | | | |
| 109 ->122 | 0.10150 | | | | |
| 110 ->118 | 0.33373 | | | | |
| 110 ->119 | -0.25049 | | | | |
| 112 ->121 | -0.16955 | | | | |
| 114 ->119 | 0.11075 | | | | |
| Excited State 31: | Singlet-A | 5.4258 eV | 228.51 nm | f=0.0005 | <S**2>=0.000 |
| 106 ->116 | 0.14998 | | | | |
| 106 ->117 | 0.10117 | | | | |
| 107 ->117 | -0.13483 | | | | |
| 108 ->116 | 0.10943 | | | | |
| 108 ->117 | -0.20639 | | | | |
| 112 ->118 | -0.14631 | | | | |
| 114 ->121 | 0.13301 | | | | |
| 114 ->122 | 0.34057 | | | | |
| 114 ->123 | 0.38705 | | | | |
| 114 ->124 | 0.12613 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Excited State 32: | Singlet-A | 5.4697 eV | 226.67 nm | f=0.0528 | <S**2>=0.000 |
| 106 ->116 | 0.29936 | | | | |
| 106 ->117 | -0.28340 | | | | |
| 107 ->116 | 0.12979 | | | | |
| 107 ->117 | 0.16280 | | | | |
| 108 ->116 | 0.26669 | | | | |
| 108 ->117 | 0.23092 | | | | |
| 108 ->118 | -0.11424 | | | | |
| 109 ->117 | -0.17920 | | | | |
| 110 ->117 | -0.13340 | | | | |
| Excited State 33: | Singlet-A | 5.5120 eV | 224.93 nm | f=0.0155 | <S**2>=0.000 |
| 106 ->116 | -0.14430 | | | | |
| 107 ->116 | 0.42371 | | | | |
| 107 ->117 | 0.13671 | | | | |
| 108 ->116 | -0.36061 | | | | |
| 108 ->117 | 0.17357 | | | | |
| 109 ->117 | -0.20668 | | | | |
| 114 ->121 | 0.10985 | | | | |
| 114 ->122 | 0.11783 | | | | |
| 114 ->123 | 0.12011 | | | | |
| Excited State 34: | Singlet-A | 5.5219 eV | 224.53 nm | f=0.0408 | <S**2>=0.000 |
| 106 ->117 | -0.25765 | | | | |
| 107 ->116 | 0.37997 | | | | |
| 107 ->117 | -0.21022 | | | | |
| 108 ->117 | -0.36443 | | | | |
| 114 ->121 | -0.10909 | | | | |
| 114 ->122 | -0.13289 | | | | |
| 114 ->123 | -0.14199 | | | | |
| Excited State 35: | Singlet-A | 5.5423 eV | 223.71 nm | f=0.1978 | <S**2>=0.000 |
| 107 ->117 | -0.10617 | | | | |
| 107 ->118 | -0.19689 | | | | |
| 108 ->118 | 0.15161 | | | | |
| 110 ->118 | 0.54307 | | | | |
| 110 ->119 | 0.18108 | | | | |
| 111 ->118 | 0.15292 | | | | |
| 112 ->121 | 0.10173 | | | | |
| Excited State 36: | Singlet-A | 5.5514 eV | 223.34 nm | f=0.0514 | <S**2>=0.000 |
| 107 ->116 | 0.10798 | | | | |
| 109 ->117 | 0.15601 | | | | |
| 110 ->118 | -0.13151 | | | | |
| 111 ->117 | 0.19982 | | | | |
| 111 ->118 | 0.52485 | | | | |
| 112 ->118 | -0.14859 | | | | |
| 114 ->120 | 0.11599 | | | | |
| 114 ->121 | -0.21933 | | | | |
| Excited State 37: | Singlet-A | 5.5643 eV | 222.82 nm | f=0.0140 | <S**2>=0.000 |
| 107 ->116 | 0.18955 | | | | |
| 108 ->117 | 0.14681 | | | | |
| 109 ->117 | 0.38666 | | | | |

111 ->118 -0.30382
112 ->118 0.10607
114 ->121 -0.35996

Excited State 38: Singlet-A 5.5878 eV 221.89 nm f=0.0196 <S**2>=0.000
107 ->116 0.11999
109 ->117 0.33316
109 ->118 -0.17618
112 ->119 -0.13248
114 ->121 0.49833
114 ->122 -0.11284
114 ->123 -0.10650

Excited State 39: Singlet-A 5.6413 eV 219.78 nm f=0.0105 <S**2>=0.000
105 ->116 0.63095
106 ->117 0.18029
109 ->116 -0.11390

Excited State 40: Singlet-A 5.6728 eV 218.56 nm f=0.2216 <S**2>=0.000
105 ->116 -0.19843
106 ->116 0.13786
106 ->117 0.48001
106 ->118 0.10223
107 ->116 0.14185
108 ->116 0.19530
109 ->117 -0.13051
111 ->117 -0.10743
114 ->120 -0.11215
114 ->122 -0.11628

## 10. Eyring Analysis for the Thermal Back Reaction

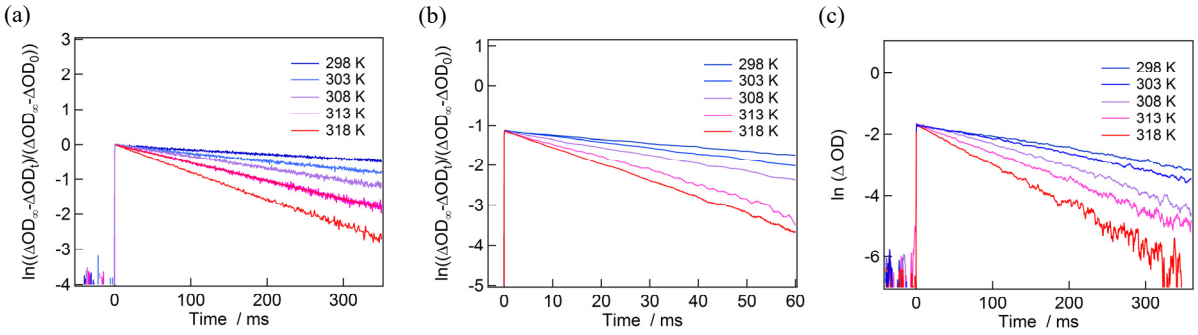



**Figure S35.** First-order plots for the time profiles of the transient absorbance at 380 nm of (a) **1**, (b) **2**, and (c) **3** in Ar-saturated benzene excited by 355-nm laser pulse (5 ns, 7 mJ) at 298 K.

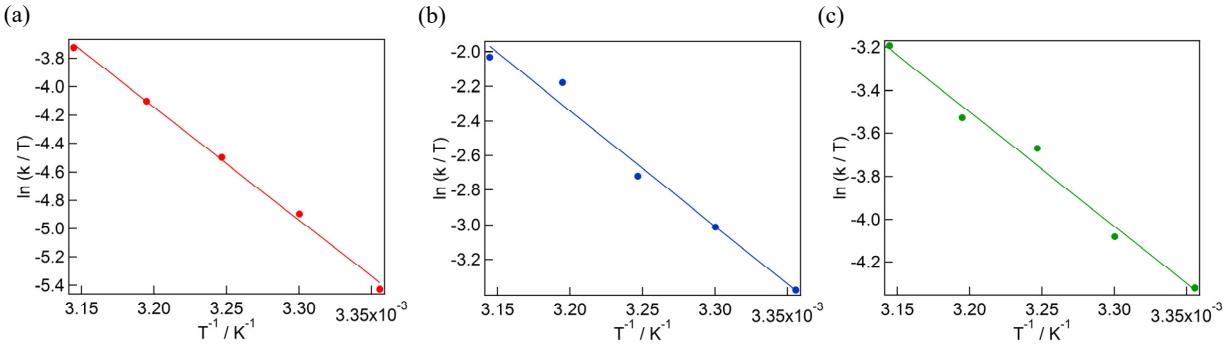



**Figure S36.** Eyring plots for the time profiles of the transient absorbance at 380 nm of (a) **1**, (b) **2**, and (c) **3** in Ar-saturated benzene excited by 355-nm laser pulse (5 ns, 7 mJ) at 298 K.

**Table S7.** Activation Parameters for the Thermal Back Reactions

| | $\Delta H^{\ddagger}$ [kJ·mol$^{-1}$] | $\Delta S^{\ddagger}$ [J·mol$^{-1}$·K$^{-1}$] | $\Delta G^{\ddagger}$ [kJ·mol$^{-1}$] |
|---|---|---|---|
| **1** | 66.2 | −20.2 | 72.2 |
| **2** | 55.6 | −39.0 | 67.3 |
| **3** | 44.2 | −85.2 | 69.6 |

## 11. VT-NMR spectroscopy under UV light irradiation

$^1$H NMR spectra for the solution of **1** at 200 K were recorded at 400 MHz on a Bruker AVANCE III 400 NanoBay. The excitation UV light (365 nm, 4 mW) was guided with an optical fiber into the NMR spectrometer (15 m, $\varphi$: 4 mm). THF-$d_8$ was used as deuterated solvent.

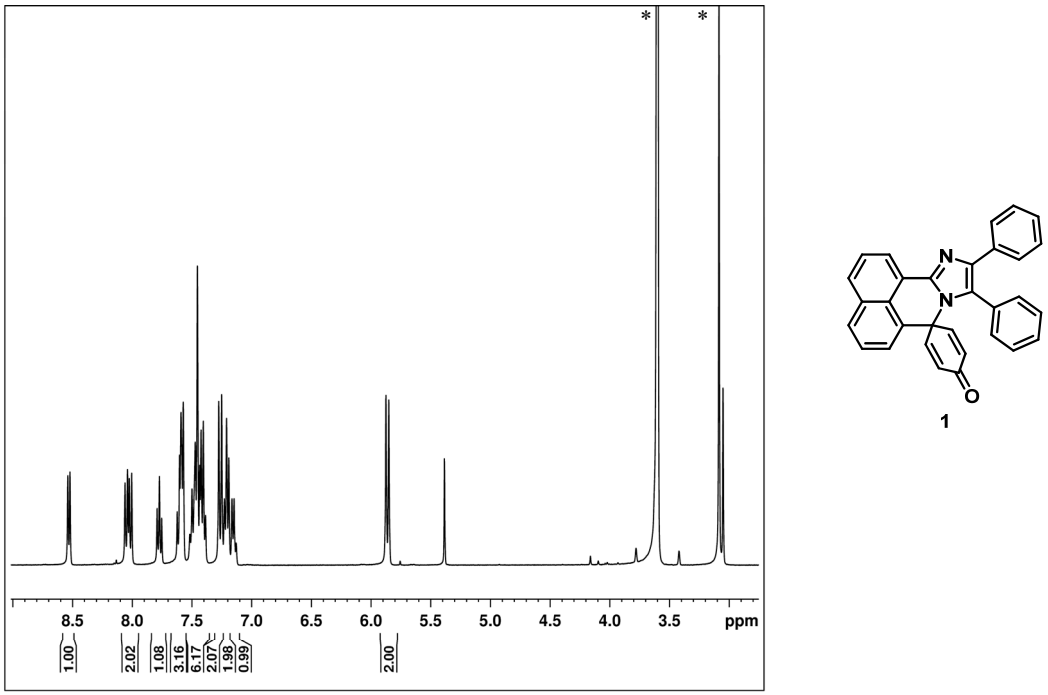



**Figure S37.** $^1$H NMR spectrum of **1** in THF-$d_8$ at 200 K (* solvent peaks).

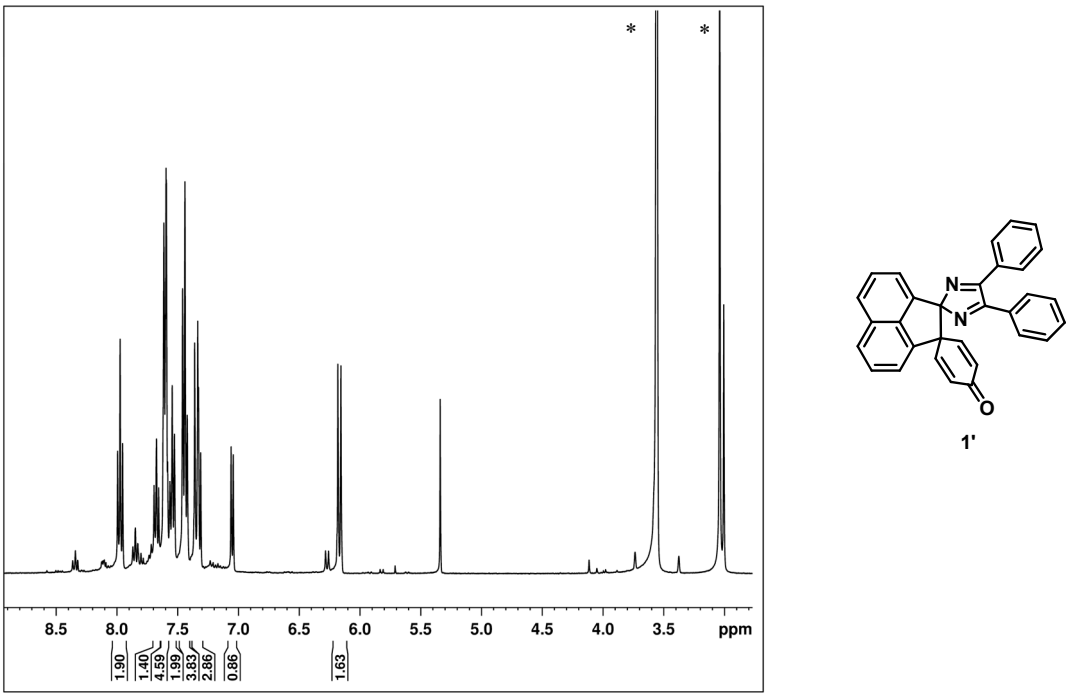



**Figure S38.** $^1$H NMR spectrum for the solution of **1** at PSS after 365-nm UV light irradiation in THF-$d_8$ at 200 K (* solvent peaks).

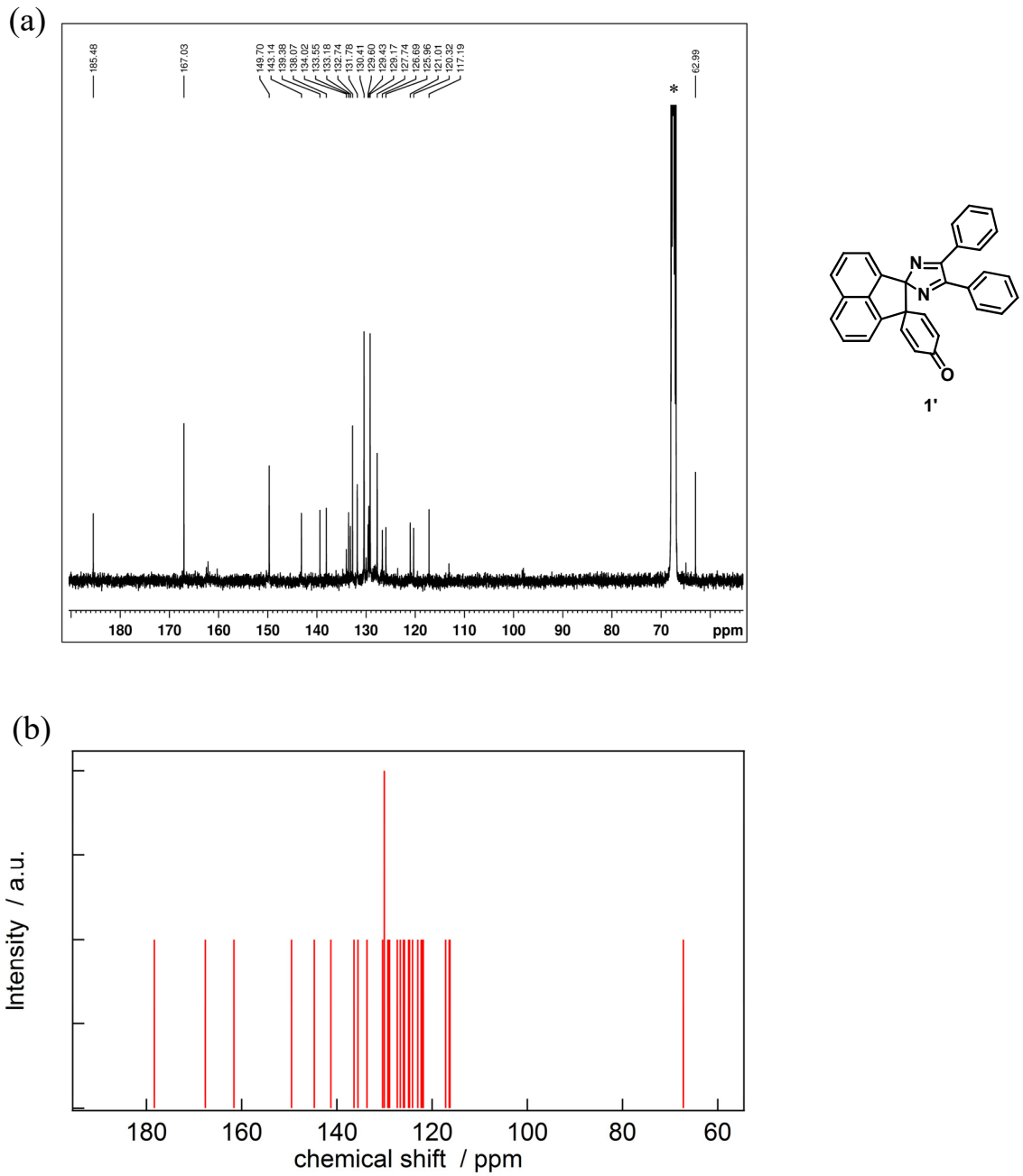



**Figure S39.** (a) $^{13}$C NMR spectrum for the solution of **1** at PSS after 365-nm UV light irradiation in THF-$d_8$ at 200 K (* solvent peaks), (b) Theoretical $^{13}$C NMR spectrum for **1'** by the GIAO-DFT (MPW1PW91/6-31+G(d,p)//MPW1PW91/6-31G(d) level of the theory).

## 12. Time-resolved FT-IR measurement

The time-resolved FT-IR spectra for **1** were recorded on a Bruker VERTEX 70 spectrometer (rapid scan mode, 160 kHz). The FT-IR spectra of the $CD_2Cl_2$ solution of **1** were measured with a 200-μm $CaF_2$ liquid cell. A Q-switched Nd:YAG laser (Continuum Surelite II Q-switched Nd:YAG) with the third harmonic at 355 nm (pulse width, 5 ns) was employed for the excitation light (2 mJ/pulse). The calculations for the IR spectra were 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. The IR spectrum for **1** can be well described by the DFT calculation (MPW1PW91/6-31G(d)). The strong absorption at 1670 $cm^{-1}$ can be assigned to the C=O stretching vibration of the cyclohexadienone ring and that at 1265 $cm^{-1}$ can be assigned to the C–N stretching vibration between the imidazole ring and the cyclohexadienone ring. The absorption band at 1670 $cm^{-1}$ was shifted to 1664 $cm^{-1}$ upon UV light excitation, indicating the photo-isomerization of **1** accompanied with the change of the binding mode between the imidazole ring and the cyclohexadienone ring as well as the result of the NMR spectroscopy. Moreover, the characteristic band at 1557 $cm^{-1}$ in the transient IR spectrum can be ascribed to the C–N stretching vibration on the imidazole ring of the 2,4-isomer.

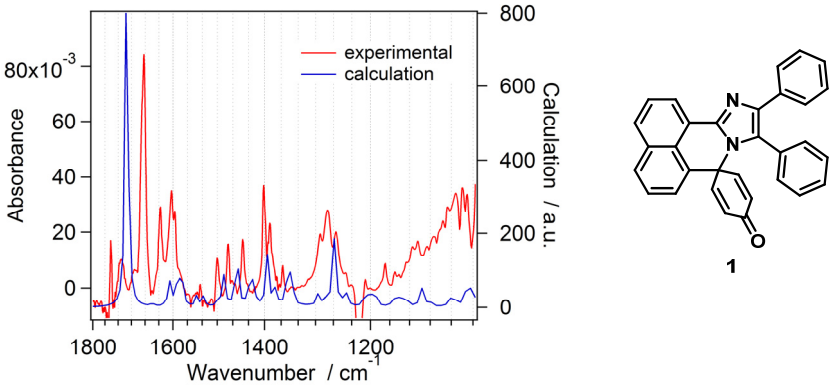



**Figure S40.** Experimental and calculated FT-IR spectra of **1** (MPW1PW91/6-31G(d) level of the theory, frequency scaling factor 0.9499[S5]).

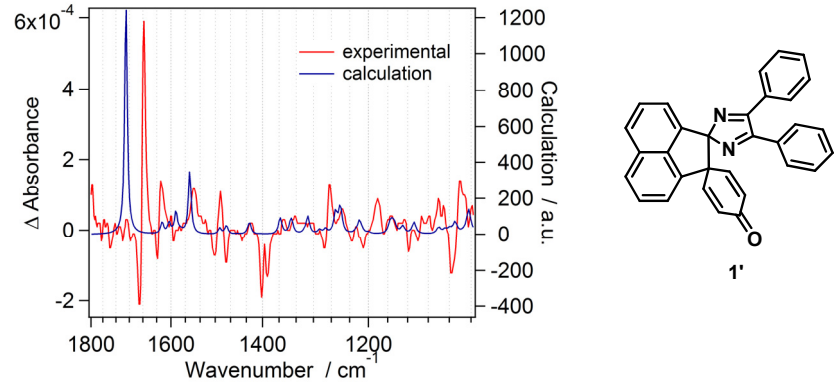



**Figure S41.** Experimental transient FT-IR spectrum of **1** upon UV light excitation at 355 nm (5 ns, 2 mJ) and calculated FT-IR spectrum of **1'** (MPW1PW91/6-31G(d) level of the theory, frequency scaling factor 0.9499[S5]).

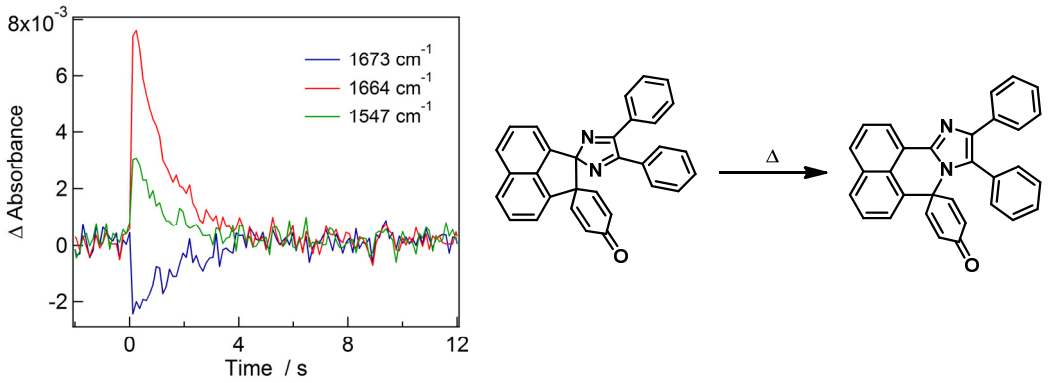



**Figure S42.** Time profiles for the transient absorbance upon UV light excitation at 355 nm (5 ns, 2 mJ) at 293 K.

## 13. Conversion Efficiency

The conversion efficiency from the 1,4-isomer to the 2,4-isomer can be estimated by the laser actinometry. We used the quantum yield of the triplet state of benzophenone as the standard. The conversion efficiency $\Phi_N$ can be defined as follows,

$$\Delta OD_{(BPh)} = \frac{\phi_{BPh}\varepsilon_{BPh}}{\phi_N \varepsilon_i (1-\frac{\varepsilon_f}{\varepsilon_i})} \left|\Delta OD_{(N)}\right|$$

where $\Delta OD_{(BPh)}$ is the magnitude of the triplet absorption at 530 nm of benzophenone after laser pulse excitation, $\Delta OD_{(N)}$ (N=1, 2, and 3) is the absorption change at 380 nm with the negative photochromic reaction of **1**, **2**, and **3**, $\Phi_{BPh}$ is the quantum yield of the intersystem crossing of benzophenone ($\Phi_{BPh}$ = 1), $\Phi_N$ is the conversion efficiency from the initial 1,4-isomer to the transient 2,4-isomer, $\varepsilon_{BPh}$ is the extinction coefficient of the triplet state of benzophenone (7220 $M^{-1}cm^{-1}$ at 530 nm),[S6] $\varepsilon_f/\varepsilon_i$ is the ratio of the extinction coefficient of the 1,4-isomer ($\varepsilon_i$) and that the 2,4-isomer ($\varepsilon_f$) at 380 nm. Because the 1,4-isomer almost isomerize into the 2,4-isomer at photostationary state at 153 K and the absorption at 380 nm is not be much affected by the polarity of solvent, $\varepsilon_f/\varepsilon_i$ is estimated from the ratio of the absorbance in Me-THF at 153 K and the absorbance at PSS after 365-nm UV light irradiation (25 mW) in Me-THF at 153 K (Fig. 2a, $\varepsilon_f/\varepsilon_i$(**1**) = 0.03, $\varepsilon_f/\varepsilon_i$(**2**) = 0.04, $\varepsilon_f/\varepsilon_i$(**3**) = 0.13).

The solutions of benzophenone, **1**, **2** and **3** in benzene matched absorbance at 355 nm (Abs. = 0.54) are irradiated with various laser energies ($\lambda_{ex.}$ = 355 nm) at 298 K. The solution of benzophenone was degassed with Ar-bubbling. The $\Delta OD_{(BPh)}$ and $\Delta OD_{(N)}$ for benzophenone, **1**, **2** and **3** were estimated just after laser excitation (Fig. S44 and S45). The $\Delta OD_{(BPh)}$ values are plotted against the $\Delta OD_{(N)}$ values. It gives excellent straight line. $\Phi_N$ of **1**, **2**, and **3** were estimated from the slope of the fit of the data and were estimated to be 0.18, 0.06, and 0.04, respectively (Fig. S46).

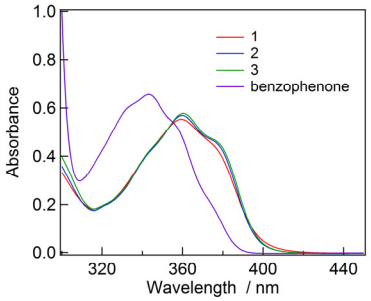



**Figure S43.** Absorption spectra of **1**, **2**, **3**, and benzophenone in benzene.

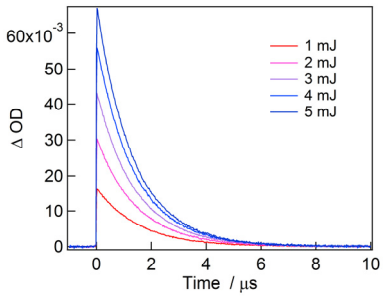



**Figure S44.** Transient absorbance of benzophenone excited by the 355-nm laser pulse in benzene at 298 K ($\lambda_{obs.}$ = 530 nm).

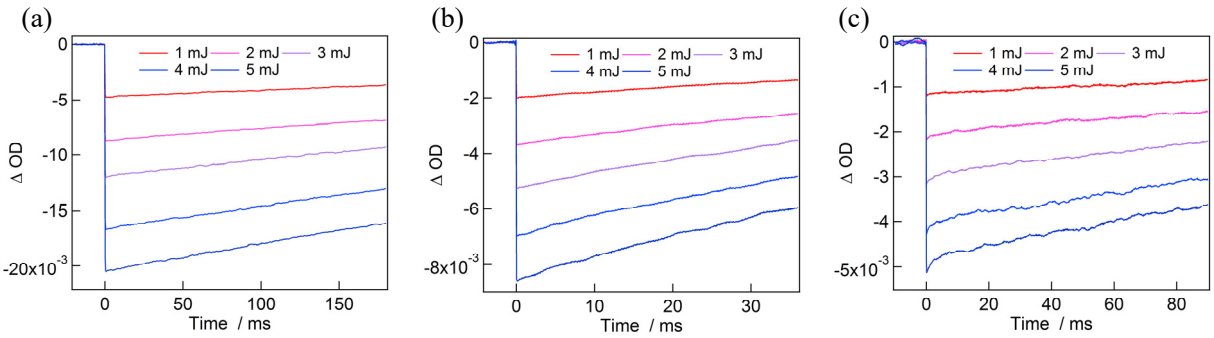



**Figure S45.** Transient absorbance of (a) **1**, (b) **2**, and (c) **3** excited by the 355-nm laser pulse in benzene at 298 K($\lambda_{obs.}$ = 380 nm).

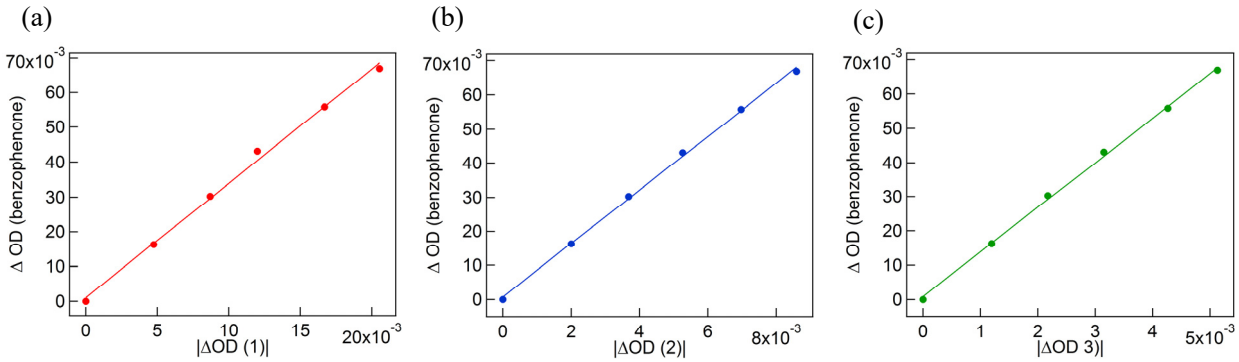



**Figure S46.** $\Delta OD_{(BPh)}$ vs $\Delta OD_{(N)}$ plots of (a) **1**, (b) **2**, and (c) **3** at various laser intensity (1, 2, 3, 4, and 5 mJ).

## 14. CD spectra

Circular dichroism (CD) spectra were recorded on a JASCO J-820 spectropolarimeter. The CD spectra of the solution of the enantiomers **2** were measured with a 10-mm quartz cell. The CD spectra of the solution of the enantiomers **2** at photostationary state were measured after UV light irradiation (365 nm, 10 mW) with a 5-mm quartz cell at 153 K using a CRYL-416 liquid nitrogen-cooled cryostat (JASCO) equipped with a TC-22HK temperature controller.

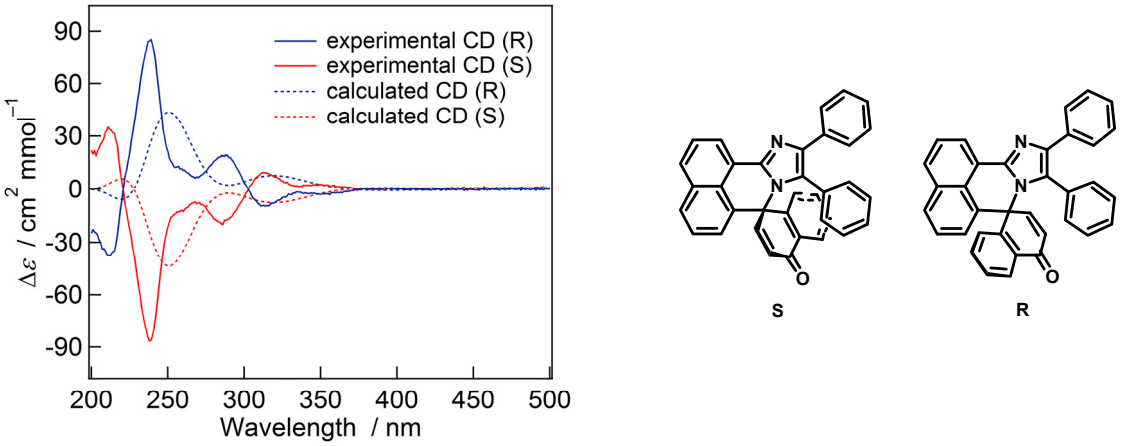
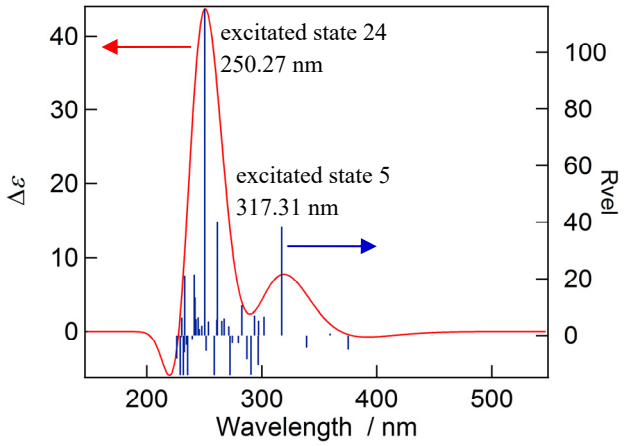



**Figure S47.** Experimental CD spectra in acetonitrile and calculated CD spectra of the enantiomers of **2** (MPW1PW91/6-31+G(d)//MPW1PW91/6-31G(d) level of the theory).




excited state 5

| | |
|---|---|
| MO127→MO130 | 0.68907 |

excited state 24

| | |
|---|---|
| MO120→MO129 | 0.19201 |
| MO121→MO129 | -0.26643 |
| MO122→MO129 | -0.19960 |
| MO123→MO129 | -0.12762 |
| MO126→MO130 | 0.41042 |
| MO126→MO131 | -0.20036 |
| MO126→MO132 | 0.10085 |
| MO126→MO133 | -0.10801 |
| MO127→MO135 | -0.17113 |
| MO127→MO136 | -0.11496 |
| MO127→MO137 | 0.11504 |

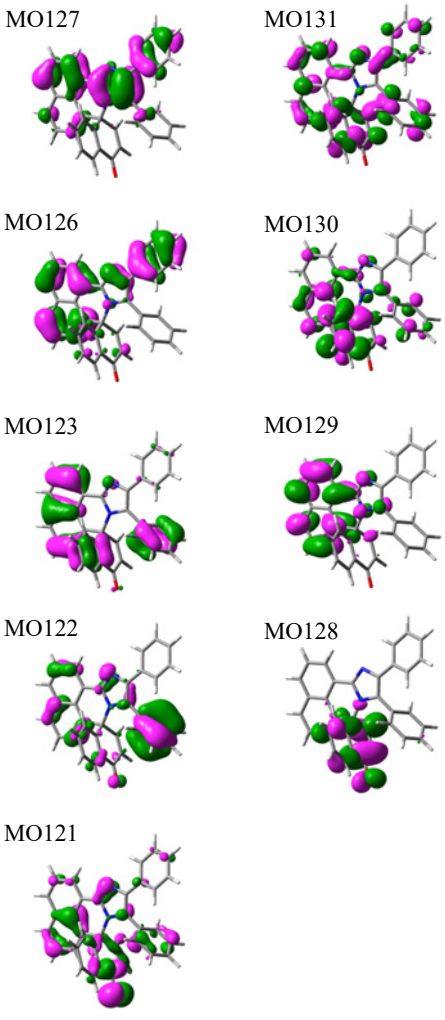



**Figure S48.** The calculated spectrum for the (R)-form of **2** (MPW1PW91/6-31+G(d)//MPW1PW91/6-31G(d) level of the theory) and the relevant molecular orbitals.

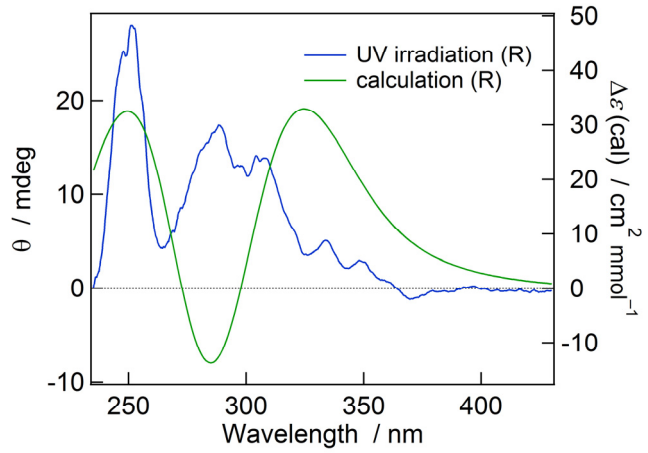
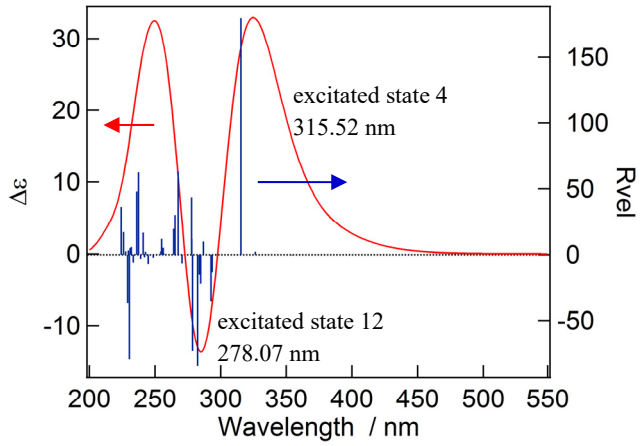



**Figure S49.** CD spectrum for the Me-THF solution of the (R)-form of **2** at PSS at 153 K and calculated CD spectrum of the (R)-form of **2'** (MPW1PW91/6-31+G(d)//MPW1PW91/6-31G(d) level of the theory).




excited state 4

| | |
|---|---|
| MO117→MO128 | 0.27896 |
| MO120→MO128 | -0.12856 |
| MO126→MO128 | 0.60500 |

excited state 12

| | |
|---|---|
| MO120→MO128 | -0.22924 |
| MO122→MO129 | 0.13567 |
| MO124→MO128 | 0.23982 |
| MO125→MO129 | 0.16952 |
| MO126→MO129 | 0.53764 |

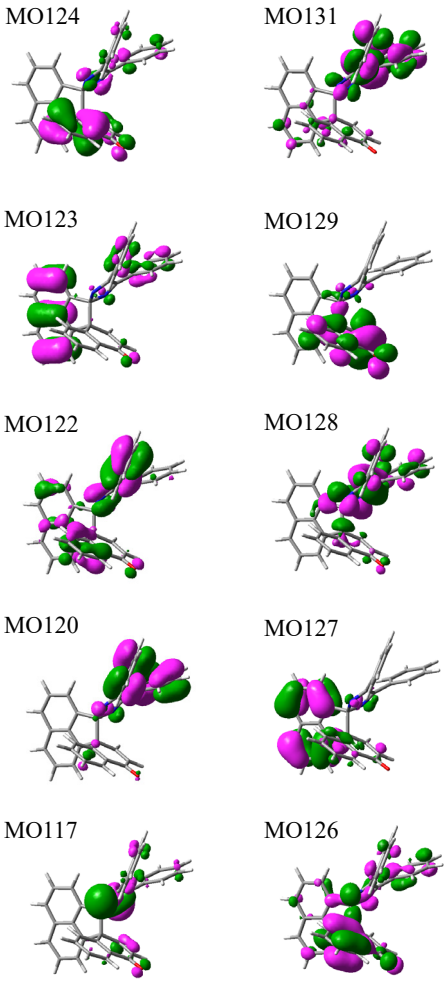



**Figure S50.** The calculated spectrum for the (R)-form of **2'** (MPW1PW91/6-31+G(d)//MPW1PW91/6-31G(d) level of the theory) and the relevant molecular orbitals.

**Table S8.** Standard Orientation of the Optimized Geometry for the (R)-form of **2**

| Tag | Symbol | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | C | 1.8020340 | -1.1995880 | -0.4661840 |
| 2 | C | 2.4055530 | -1.4653130 | -1.7018290 |
| 3 | C | -3.6632970 | -0.1530860 | -0.8928810 |
| 4 | C | -4.8807950 | 0.5466070 | -0.9781780 |
| 5 | C | -4.9262480 | 1.8957030 | -0.7305020 |
| 6 | C | -3.7475840 | 2.6001090 | -0.3962440 |
| 7 | C | -2.5125650 | 1.8887650 | -0.3191600 |
| 8 | C | -2.4897330 | 0.4915760 | -0.5636730 |
| 9 | C | -3.7548270 | 3.9930930 | -0.1371610 |
| 10 | C | -2.5932220 | 4.6561390 | 0.1772050 |
| 11 | C | -1.3704210 | 3.9643660 | 0.2383050 |
| 12 | C | -1.3266660 | 2.6077160 | -0.0072040 |
| 13 | C | -0.0783330 | 1.8794420 | 0.0025940 |
| 14 | N | -0.0353510 | 0.5298820 | -0.2179570 |
| 15 | C | 1.3040150 | 0.1611110 | -0.1843020 |
| 16 | C | 1.9962420 | 1.3381950 | 0.0616680 |
| 17 | N | 1.1215680 | 2.3847430 | 0.1716060 |
| 18 | C | 3.4412580 | 1.5739540 | 0.1900560 |
| 19 | C | 4.3577160 | 0.5545880 | 0.4786530 |
| 20 | C | 5.7148750 | 0.8350280 | 0.5921030 |
| 21 | C | 6.1835920 | 2.1349960 | 0.4267740 |
| 22 | C | 5.2788960 | 3.1574760 | 0.1516500 |
| 23 | C | 3.9229890 | 2.8809840 | 0.0355380 |
| 24 | C | 2.9069450 | -2.7296970 | -1.9877000 |
| 25 | C | 2.8135520 | -3.7467840 | -1.0413070 |
| 26 | C | 2.2317020 | -3.4888150 | 0.1969540 |
| 27 | C | 1.7351860 | -2.2218720 | 0.4871320 |
| 28 | O | -1.8659660 | -4.4665040 | -0.7850070 |
| 29 | C | -1.6334030 | -2.6157260 | 0.6804090 |
| 30 | C | -1.3862680 | -1.2446610 | 0.8186120 |
| 31 | C | -1.2002280 | -0.3485440 | -0.4043530 |
| 32 | C | -1.0209390 | -1.1268530 | -1.6831970 |
| 33 | C | -1.2530240 | -2.4373380 | -1.8013600 |
| 34 | C | -1.6144060 | -3.2786580 | -0.6504360 |
| 35 | C | -1.3647240 | -0.6810790 | 2.0947130 |
| 36 | C | -1.5791700 | -1.4722970 | 3.2161550 |
| 37 | C | -1.8313710 | -2.8382470 | 3.0780890 |
| 38 | C | -1.8584980 | -3.4032710 | 1.8135460 |
| 39 | H | 2.4807950 | -0.6679830 | -2.4341060 |
| 40 | H | -3.6576940 | -1.2203690 | -1.0841280 |
| 41 | H | -5.7843430 | 0.0056750 | -1.2386100 |
| 42 | H | -5.8646040 | 2.4387260 | -0.7899960 |
| 43 | H | -4.6980510 | 4.5279660 | -0.1933230 |
| 44 | H | -2.6118350 | 5.7230230 | 0.3740150 |
| 45 | H | -0.4459690 | 4.4814990 | 0.4685330 |
| 46 | H | 4.0105220 | -0.4607090 | 0.6281440 |

| | | | | |
|---|---|---|---|---|
| 47 | H | 6.4083700 | 0.0310960 | 0.8189840 |
| 48 | H | 7.2437270 | 2.3502100 | 0.5166900 |
| 49 | H | 5.6314280 | 4.1766350 | 0.0255220 |
| 50 | H | 3.2122420 | 3.6723960 | -0.1731950 |
| 51 | H | 3.3702150 | -2.9213840 | -2.9502650 |
| 52 | H | 3.1994730 | -4.7361340 | -1.2649490 |
| 53 | H | 2.1663660 | -4.2749680 | 0.9420850 |
| 54 | H | 1.2973850 | -2.0194710 | 1.4583500 |
| 55 | H | -0.7469960 | -0.5247140 | -2.5449710 |
| 56 | H | -1.1668360 | -2.9462530 | -2.7553550 |
| 57 | H | -1.1743990 | 0.3811440 | 2.2112740 |
| 58 | H | -1.5521530 | -1.0206180 | 4.2025770 |
| 59 | H | -2.0030780 | -3.4527120 | 3.9556680 |
| 60 | H | -2.0433560 | -4.4615340 | 1.6646510 |

SCF Done: E(RmPW1PW91) = -1531.39395856 A.U.

Zero-point correction = 0.476159 (Hartree/Particle)
Thermal correction to Energy = 0.503524
Thermal correction to Enthalpy = 0.504469
Thermal correction to Gibbs Free Energy = 0.417421
Sum of electronic and zero-point Energies = -1530.917800
Sum of electronic and thermal Energies = -1530.890434
Sum of electronic and thermal Enthalpies = -1530.889490
Sum of electronic and thermal Free Energies = -1530.976538

Low frequencies --- -6.8513 -6.2662 -0.0006 0.0003 0.0009 5.8679
Low frequencies --- 21.9868 27.5900 30.5899

The Result for the TDDFT calculation

<0|del|b> * <b|rxdel|0> + <0|del|b> * <b|delr+rdel|0>
Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)

| state | XX | YY | ZZ | R(velocity) | E-M Angle |
|---|---|---|---|---|---|
| 1 | -0.7178 | -0.9126 | 2.1960 | 0.1885 | 90.00 |
| 2 | -74.0824 | 13.6946 | 44.9575 | -5.1434 | 90.69 |
| 3 | 1.5594 | -0.3906 | 1.1429 | 0.7706 | 72.04 |
| 4 | 1.9045 | -6.6274 | -8.5657 | -4.4295 | 105.94 |
| 5 | 33.4088 | 70.0001 | 11.5655 | 38.3248 | 67.97 |
| 6 | -16.2181 | 5.7712 | 30.3338 | 6.6290 | 67.14 |
| 7 | 36.2761 | -37.9438 | 17.5206 | 5.2843 | 82.95 |
| 8 | -7.7742 | 5.6748 | -29.7356 | -10.6117 | 101.32 |
| 9 | 1.2842 | -10.3897 | 30.2846 | 7.0597 | 77.42 |
| 10 | -27.8584 | -19.2887 | 5.6568 | -13.8301 | 114.17 |
| 11 | -18.3652 | -0.9755 | -6.2803 | -8.5403 | 95.93 |
| 12 | 27.9224 | -12.5636 | 16.7606 | 10.7065 | 76.31 |
| 13 | 6.1872 | 16.3301 | -31.0760 | -2.8529 | 98.52 |
| 14 | -37.2214 | -13.1333 | 42.0521 | -2.7675 | 101.10 |

| | | | | | |
|---|---|---|---|---|---|
| 15 | -30.5605 | -39.1022 | -9.5938 | -26.4188 | 102.95 |
| 16 | -7.8032 | 1.8847 | 15.8386 | 3.3067 | 81.31 |
| 17 | -6.7984 | 5.9650 | 18.8908 | 6.0191 | 87.12 |
| 18 | -12.1928 | 10.3462 | 17.4949 | 5.2161 | 79.64 |
| 19 | -15.5005 | 100.8691 | 35.2620 | 40.2102 | 66.11 |
| 20 | -9.2929 | 12.7273 | 13.4801 | 5.6382 | 74.02 |
| 21 | 34.1671 | -106.5037 | -29.6431 | -33.9933 | 114.23 |
| 22 | 25.6428 | -7.2213 | -3.4067 | 5.0049 | 72.07 |
| 23 | -1.4517 | -8.4078 | -6.7840 | -5.5478 | 101.59 |
| 24 | 18.7579 | 179.5407 | 147.8413 | 115.3800 | 76.30 |
| 25 | 3.2962 | 8.2696 | -1.1489 | 3.4723 | 51.68 |
| 26 | 3.6222 | 0.2454 | 3.1912 | 2.3529 | 61.83 |
| 27 | 5.4057 | 8.9240 | 4.9278 | 6.4192 | 45.15 |
| 28 | -5.1212 | 16.1565 | 6.5045 | 5.8466 | 63.67 |
| 29 | -27.1995 | 39.8888 | 27.3815 | 13.3569 | 82.93 |
| 30 | -34.7128 | -21.3171 | 120.6307 | 21.5336 | 83.98 |
| 31 | -2.9038 | 57.6003 | -58.5998 | -1.3011 | 91.58 |
| 32 | 2.2527 | -31.9762 | -14.5611 | -14.7616 | 119.07 |
| 33 | -52.9326 | -26.8786 | 69.5826 | -3.4095 | 91.56 |
| 34 | 50.6194 | 9.0209 | 4.0751 | 21.2385 | 56.54 |
| 35 | -9.8638 | -14.3704 | 5.9758 | -6.0861 | 108.94 |
| 36 | 0.9458 | -75.9741 | -13.6581 | -29.5622 | 160.08 |
| 37 | 13.2509 | 27.7251 | -21.8919 | 6.3614 | 54.84 |
| 38 | -4.9820 | 0.7346 | 2.7175 | -0.5100 | 95.83 |
| 39 | -5.9574 | -13.1239 | -28.5994 | -15.8936 | 98.24 |
| 40 | -0.5836 | 3.2831 | -27.5480 | -8.2828 | 112.83 |

1/2[<0|r|b>*<b|rxdel|0> + (<0|rxdel|b>*<b|r|0>)*]

Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)

| state | XX | YY | ZZ | R(length) |
|---|---|---|---|---|
| 1 | 2.6450 | 1.4927 | -3.2939 | 0.2813 |
| 2 | 83.5476 | -39.8133 | -57.1845 | -4.4834 |
| 3 | 0.9327 | 0.9458 | 0.1198 | 0.6661 |
| 4 | -10.1157 | -6.6828 | 2.1928 | -4.8686 |
| 5 | 54.3271 | -1.8055 | 59.8721 | 37.4646 |
| 6 | 11.4802 | 8.4297 | -0.0088 | 6.6337 |
| 7 | 45.0560 | -12.6550 | -16.8917 | 5.1697 |
| 8 | -8.8080 | -32.6471 | 10.3802 | -10.3583 |
| 9 | -1.2579 | 36.3927 | -14.6122 | 6.8408 |
| 10 | 11.3040 | 7.1872 | -59.4752 | -13.6614 |
| 11 | -9.1980 | -20.3681 | 9.4725 | -6.6979 |
| 12 | 42.5340 | 8.1953 | -15.7459 | 11.6611 |
| 13 | -7.7201 | -0.9799 | 1.1664 | -2.5112 |
| 14 | 7.6249 | 0.6950 | -15.6890 | -2.4564 |
| 15 | -28.3462 | -9.1897 | -39.1122 | -25.5494 |
| 16 | 13.5290 | 3.2357 | -4.4842 | 4.0935 |

| | | | | |
|---|---|---|---|---|
| 17 | 23.1363 | -24.5681 | 19.9334 | 6.1672 |
| 18 | 24.4736 | -7.1363 | -0.1697 | 5.7225 |
| 19 | 110.7387 | -14.7175 | 30.2309 | 42.0840 |
| 20 | 18.7748 | -1.7463 | 0.3098 | 5.7794 |
| 21 | -95.8133 | 50.9696 | -60.6176 | -35.1538 |
| 22 | -14.1431 | 0.1080 | 32.6427 | 6.2025 |
| 23 | -12.9615 | 1.9208 | -6.4462 | -5.8290 |
| 24 | 218.8058 | 36.8728 | 112.5210 | 122.7332 |
| 25 | -0.5967 | 1.6583 | 10.3519 | 3.8045 |
| 26 | 1.3955 | 6.7400 | -0.5032 | 2.5441 |
| 27 | 9.0800 | -1.5259 | 11.4257 | 6.3266 |
| 28 | 23.2205 | -7.8528 | 1.0070 | 5.4582 |
| 29 | 68.8966 | -50.7349 | 19.5590 | 12.5736 |
| 30 | 160.4682 | 0.5829 | -92.4922 | 22.8530 |
| 31 | -32.8745 | -10.4444 | 32.5732 | -3.5819 |
| 32 | -56.5923 | 13.9077 | -5.1712 | -15.9519 |
| 33 | 127.9956 | -22.4702 | -105.8741 | -0.1162 |
| 34 | -17.2899 | 92.1971 | -8.9353 | 21.9907 |
| 35 | -6.6358 | 0.9849 | -10.6247 | -5.4252 |
| 36 | -44.0543 | 1.9051 | -53.8569 | -32.0021 |
| 37 | -5.0318 | 2.5702 | 20.9060 | 6.1481 |
| 38 | 1.9405 | -1.0774 | -1.7963 | -0.3111 |
| 39 | -44.1449 | 2.4268 | -4.3834 | -15.3672 |
| 40 | -16.6725 | 1.2990 | -8.9233 | -8.0990 |

1/2[<0|del|b>*<b|r|0> + (<0|r|b>*<b|del|0>)*] (Au)

| state | X | Y | Z | Dip. S. | Osc. (frdel) |
|---|---|---|---|---|---|
| 1 | 0.0000 | -0.0011 | -0.0001 | 0.0012 | 0.0008 |
| 2 | -0.3059 | -0.0854 | -0.0008 | 0.3921 | 0.2614 |
| 3 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 4 | -0.0001 | -0.0011 | -0.0004 | 0.0016 | 0.0010 |
| 5 | -0.0201 | -0.0001 | -0.0009 | 0.0210 | 0.0140 |
| 6 | -0.0596 | -0.0120 | 0.0000 | 0.0716 | 0.0477 |
| 7 | -0.1157 | -0.0186 | -0.0030 | 0.1373 | 0.0916 |
| 8 | -0.0422 | -0.0062 | -0.0003 | 0.0487 | 0.0324 |
| 9 | -0.0002 | -0.0292 | -0.0009 | 0.0303 | 0.0202 |
| 10 | -0.0002 | -0.0011 | -0.0090 | 0.0104 | 0.0069 |
| 11 | -0.0033 | -0.0235 | 0.0000 | 0.0268 | 0.0179 |
| 12 | -0.0019 | -0.0004 | -0.0162 | 0.0185 | 0.0123 |
| 13 | -0.0210 | 0.0000 | -0.0057 | 0.0267 | 0.0178 |
| 14 | -0.0016 | -0.0171 | -0.0123 | 0.0310 | 0.0207 |
| 15 | -0.0500 | -0.0073 | -0.0008 | 0.0581 | 0.0387 |
| 16 | -0.0061 | -0.0062 | -0.0001 | 0.0124 | 0.0083 |
| 17 | -0.0992 | -0.0093 | -0.0004 | 0.1089 | 0.0726 |
| 18 | -0.0796 | -0.0006 | -0.0001 | 0.0803 | 0.0535 |
| 19 | -0.0065 | -0.0007 | -0.0335 | 0.0407 | 0.0271 |

| | | | | | |
|---|---|---|---|---|---|
| 20 | -0.0009 | -0.0092 | 0.0000 | 0.0101 | 0.0067 |
| 21 | -0.0132 | -0.0182 | -0.0411 | 0.0725 | 0.0484 |
| 22 | -0.0023 | 0.0000 | -0.0016 | 0.0039 | 0.0026 |
| 23 | -0.0029 | -0.0176 | -0.0001 | 0.0205 | 0.0137 |
| 24 | -0.0477 | -0.1262 | -0.0010 | 0.1749 | 0.1166 |
| 25 | 0.0000 | -0.0001 | -0.0021 | 0.0022 | 0.0015 |
| 26 | -0.0006 | -0.0008 | 0.0000 | 0.0014 | 0.0010 |
| 27 | -0.0019 | -0.0006 | -0.0007 | 0.0031 | 0.0021 |
| 28 | -0.0037 | -0.0049 | -0.0006 | 0.0092 | 0.0061 |
| 29 | -0.0159 | -0.0961 | -0.0006 | 0.1126 | 0.0751 |
| 30 | -0.1235 | 0.0000 | -0.0028 | 0.1263 | 0.0842 |
| 31 | -0.0143 | -0.0222 | -0.0026 | 0.0391 | 0.0260 |
| 32 | -0.0133 | -0.0044 | 0.0000 | 0.0178 | 0.0118 |
| 33 | -0.0359 | -0.0484 | -0.0113 | 0.0956 | 0.0638 |
| 34 | -0.0059 | -0.0337 | -0.0015 | 0.0411 | 0.0274 |
| 35 | -0.0014 | -0.0060 | -0.0004 | 0.0077 | 0.0051 |
| 36 | -0.0056 | -0.0004 | -0.0064 | 0.0124 | 0.0082 |
| 37 | -0.0071 | -0.0005 | -0.0122 | 0.0198 | 0.0132 |
| 38 | 0.0000 | -0.0028 | -0.0007 | 0.0036 | 0.0024 |
| 39 | -0.0774 | -0.0015 | 0.0000 | 0.0790 | 0.0527 |
| 40 | -0.0236 | -0.0089 | -0.0008 | 0.0332 | 0.0221 |

Excited State 1: Singlet-A 2.7668 eV 448.11 nm f=0.0009 <S**2>=0.000
127 ->128 0.70420
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1531.33015760
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.3052 eV 375.12 nm f=0.2610 <S**2>=0.000
127 ->129 0.70071

Excited State 3: Singlet-A 3.4504 eV 359.34 nm f=0.0000 <S**2>=0.000
119 ->128 0.11870
120 ->128 0.38943
121 ->128 0.53717
122 ->128 0.13569

Excited State 4: Singlet-A 3.6579 eV 338.95 nm f=0.0012 <S**2>=0.000
126 ->128 0.68713

Excited State 5: Singlet-A 3.9073 eV 317.31 nm f=0.0145 <S**2>=0.000
127 ->130 0.68907

Excited State 6: Singlet-A 4.1071 eV 301.88 nm f=0.0508 <S**2>=0.000
123 ->129 -0.13852
126 ->129 -0.28130
127 ->131 0.60259

Excited State 7: Singlet-A 4.1730 eV 297.11 nm f=0.0893 <S**2>=0.000
124 ->128 0.11499
126 ->129 0.60536

127 ->131 0.27698

Excited State 8: Singlet-A 4.1777 eV 296.77 nm f=0.0326 <S**2>=0.000
119 ->128 0.10886
124 ->128 0.53387
125 ->128 -0.38103
126 ->129 -0.11627

Excited State 9: Singlet-A 4.2216 eV 293.69 nm f=0.0198 <S**2>=0.000
123 ->129 0.21460
126 ->129 -0.13347
127 ->132 0.46545
127 ->133 -0.37440

Excited State 10: Singlet-A 4.2669 eV 290.57 nm f=0.0070 <S**2>=0.000
121 ->128 0.10461
122 ->128 -0.22476
123 ->128 -0.33420
124 ->128 0.30149
125 ->128 0.46906

Excited State 11: Singlet-A 4.3203 eV 286.98 nm f=0.0177 <S**2>=0.000
127 ->131 0.10615
127 ->132 0.40509
127 ->133 0.51621
127 ->134 -0.17435

Excited State 12: Singlet-A 4.3859 eV 282.69 nm f=0.0129 <S**2>=0.000
122 ->128 0.24970
123 ->128 0.49693
124 ->128 0.25411
125 ->128 0.32861

Excited State 13: Singlet-A 4.4344 eV 279.60 nm f=0.0179 <S**2>=0.000
119 ->128 0.14886
120 ->128 -0.15683
122 ->128 0.57165
123 ->128 -0.29714

Excited State 14: Singlet-A 4.5198 eV 274.32 nm f=0.0199 <S**2>=0.000
119 ->128 0.58121
120 ->128 -0.20763
122 ->128 -0.15158
123 ->128 0.17445

Excited State 15: Singlet-A 4.5527 eV 272.33 nm f=0.0380 <S**2>=0.000
119 ->128 0.13293
120 ->128 0.10685
121 ->128 -0.11154
127 ->133 0.10769
127 ->134 0.53797
127 ->135 -0.33873

Excited State 16: Singlet-A 4.5693 eV 271.34 nm f=0.0084 <S**2>=0.000
118 ->128 -0.13386

| | | | | | |
|---|---|---|---|---|---|
| 119 ->128 | 0.17252 | | | | |
| 120 ->128 | 0.46896 | | | | |
| 121 ->128 | -0.41021 | | | | |
| 127 ->134 | -0.17061 | | | | |
| Excited State 17: | Singlet-A | 4.6380 eV | 267.32 nm | f=0.0744 | <S**2>=0.000 |
| 121 ->129 | -0.10117 | | | | |
| 123 ->129 | -0.21239 | | | | |
| 125 ->129 | -0.29083 | | | | |
| 126 ->132 | 0.10175 | | | | |
| 127 ->132 | 0.17979 | | | | |
| 127 ->134 | 0.22626 | | | | |
| 127 ->135 | 0.44043 | | | | |
| Excited State 18: | Singlet-A | 4.6747 eV | 265.23 nm | f=0.0548 | <S**2>=0.000 |
| 124 ->129 | -0.18987 | | | | |
| 125 ->129 | 0.58820 | | | | |
| 127 ->132 | 0.13762 | | | | |
| 127 ->134 | 0.19058 | | | | |
| 127 ->135 | 0.12443 | | | | |
| Excited State 19: | Singlet-A | 4.7433 eV | 261.39 nm | f=0.0281 | <S**2>=0.000 |
| 117 ->128 | -0.19993 | | | | |
| 118 ->128 | 0.51171 | | | | |
| 120 ->128 | 0.12230 | | | | |
| 123 ->129 | 0.10923 | | | | |
| 124 ->129 | -0.25865 | | | | |
| 126 ->130 | 0.17833 | | | | |
| Excited State 20: | Singlet-A | 4.7537 eV | 260.82 nm | f=0.0070 | <S**2>=0.000 |
| 118 ->128 | 0.14717 | | | | |
| 124 ->129 | 0.55638 | | | | |
| 125 ->129 | 0.20538 | | | | |
| 126 ->130 | 0.20218 | | | | |
| 127 ->135 | 0.12499 | | | | |
| Excited State 21: | Singlet-A | 4.7926 eV | 258.70 nm | f=0.0506 | <S**2>=0.000 |
| 118 ->128 | -0.31130 | | | | |
| 119 ->128 | -0.10142 | | | | |
| 120 ->129 | -0.10125 | | | | |
| 123 ->129 | 0.17286 | | | | |
| 124 ->129 | -0.18493 | | | | |
| 126 ->130 | 0.35119 | | | | |
| 126 ->132 | -0.13850 | | | | |
| 127 ->132 | -0.12770 | | | | |
| 127 ->133 | 0.13609 | | | | |
| 127 ->134 | 0.14483 | | | | |
| 127 ->135 | 0.24183 | | | | |
| Excited State 22: | Singlet-A | 4.8897 eV | 253.56 nm | f=0.0028 | <S**2>=0.000 |
| 120 ->129 | -0.15298 | | | | |
| 121 ->129 | 0.14406 | | | | |
| 122 ->129 | 0.10008 | | | | |
| 123 ->129 | -0.11604 | | | | |
| 125 ->131 | 0.13448 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 125 ->133 | -0.10926 | | | | |
| 125 ->134 | -0.16147 | | | | |
| 127 ->136 | -0.32734 | | | | |
| 127 ->137 | 0.43341 | | | | |
| 127 ->138 | -0.13077 | | | | |
| Excited State 23: | Singlet-A | 4.9303 eV | 251.47 nm | f=0.0143 | <S**2>=0.000 |
| 120 ->129 | -0.25522 | | | | |
| 121 ->129 | 0.30431 | | | | |
| 122 ->129 | 0.24069 | | | | |
| 123 ->129 | -0.27948 | | | | |
| 126 ->130 | 0.20782 | | | | |
| 126 ->131 | -0.17670 | | | | |
| 127 ->135 | -0.13445 | | | | |
| 127 ->138 | 0.16150 | | | | |
| Excited State 24: | Singlet-A | 4.9540 eV | 250.27 nm | f=0.1200 | <S**2>=0.000 |
| 120 ->129 | 0.19201 | | | | |
| 121 ->129 | -0.26643 | | | | |
| 122 ->129 | -0.19960 | | | | |
| 123 ->129 | -0.12762 | | | | |
| 126 ->130 | 0.41042 | | | | |
| 126 ->131 | -0.20036 | | | | |
| 126 ->132 | 0.10085 | | | | |
| 126 ->133 | -0.10801 | | | | |
| 127 ->135 | -0.17113 | | | | |
| 127 ->136 | -0.11496 | | | | |
| 127 ->137 | 0.11504 | | | | |
| Excited State 25: | Singlet-A | 5.0036 eV | 247.79 nm | f=0.0014 | <S**2>=0.000 |
| 118 ->129 | 0.15017 | | | | |
| 119 ->129 | -0.19453 | | | | |
| 120 ->129 | 0.27438 | | | | |
| 122 ->129 | 0.44936 | | | | |
| 123 ->129 | 0.30532 | | | | |
| 126 ->131 | -0.16182 | | | | |
| Excited State 26: | Singlet-A | 5.0487 eV | 245.58 nm | f=0.0010 | <S**2>=0.000 |
| 127 ->136 | 0.54673 | | | | |
| 127 ->137 | 0.35131 | | | | |
| 127 ->140 | 0.10215 | | | | |
| 127 ->141 | -0.15285 | | | | |
| Excited State 27: | Singlet-A | 5.0685 eV | 244.62 nm | f=0.0021 | <S**2>=0.000 |
| 119 ->129 | -0.19327 | | | | |
| 120 ->129 | 0.41449 | | | | |
| 121 ->129 | 0.43740 | | | | |
| 122 ->129 | -0.22149 | | | | |
| 123 ->129 | -0.11553 | | | | |
| Excited State 28: | Singlet-A | 5.1072 eV | 242.76 nm | f=0.0060 | <S**2>=0.000 |
| 117 ->129 | -0.11501 | | | | |
| 119 ->129 | 0.54787 | | | | |
| 120 ->129 | 0.17486 | | | | |
| 121 ->129 | 0.17534 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 122 ->129 | 0.16948 | | | | |
| 126 ->131 | 0.14225 | | | | |
| 126 ->132 | 0.16740 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Excited State 29: | Singlet-A | 5.1268 eV | 241.84 nm | f=0.0765 | <S**2>=0.000 |
| 117 ->128 | 0.34706 | | | | |
| 117 ->129 | 0.10577 | | | | |
| 119 ->129 | -0.18976 | | | | |
| 121 ->129 | -0.10539 | | | | |
| 126 ->130 | 0.16193 | | | | |
| 126 ->131 | 0.34610 | | | | |
| 126 ->132 | 0.27734 | | | | |
| 127 ->137 | -0.10143 | | | | |
| 127 ->138 | -0.17581 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Excited State 30: | Singlet-A | 5.1410 eV | 241.17 nm | f=0.0886 | <S**2>=0.000 |
| 117 ->128 | 0.28481 | | | | |
| 118 ->128 | 0.11737 | | | | |
| 126 ->131 | 0.11308 | | | | |
| 127 ->136 | -0.10390 | | | | |
| 127 ->137 | 0.23930 | | | | |
| 127 ->138 | 0.46616 | | | | |
| 127 ->139 | 0.11109 | | | | |
| 127 ->140 | -0.10162 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Excited State 31: | Singlet-A | 5.1754 eV | 239.57 nm | f=0.0273 | <S**2>=0.000 |
| 117 ->128 | 0.44508 | | | | |
| 118 ->128 | 0.16311 | | | | |
| 119 ->129 | 0.11275 | | | | |
| 126 ->131 | -0.36599 | | | | |
| 126 ->132 | -0.13668 | | | | |
| 127 ->138 | -0.16024 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Excited State 32: | Singlet-A | 5.2638 eV | 235.54 nm | f=0.0121 | <S**2>=0.000 |
| 117 ->129 | 0.24678 | | | | |
| 118 ->129 | 0.27030 | | | | |
| 119 ->129 | 0.16527 | | | | |
| 122 ->131 | -0.12893 | | | | |
| 122 ->133 | 0.12112 | | | | |
| 124 ->130 | 0.32161 | | | | |
| 126 ->132 | -0.15831 | | | | |
| 126 ->133 | -0.25280 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Excited State 33: | Singlet-A | 5.2881 eV | 234.46 nm | f=0.0654 | <S**2>=0.000 |
| 116 ->128 | -0.17655 | | | | |
| 117 ->129 | 0.25857 | | | | |
| 118 ->129 | 0.28210 | | | | |
| 122 ->129 | -0.15024 | | | | |
| 126 ->131 | -0.14469 | | | | |
| 126 ->132 | 0.21143 | | | | |
| 126 ->133 | 0.40302 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Excited State 34: | Singlet-A | 5.3245 eV | 232.85 nm | f=0.0285 | <S**2>=0.000 |
| 116 ->128 | 0.46614 | | | | |
| 117 ->129 | 0.38562 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 118 ->129 | -0.11446 | | | | |
| | | | | | |
| Excited State 35: | Singlet-A | 5.3290 eV | 232.66 nm | f=0.0051 | <S**2>=0.000 |
| 127 ->138 | -0.23514 | | | | |
| 127 ->139 | 0.59373 | | | | |
| 127 ->140 | -0.13980 | | | | |
| | | | | | |
| Excited State 36: | Singlet-A | 5.3516 eV | 231.68 nm | f=0.0087 | <S**2>=0.000 |
| 116 ->128 | 0.30044 | | | | |
| 117 ->129 | -0.23270 | | | | |
| 124 ->130 | 0.25157 | | | | |
| 125 ->130 | -0.24212 | | | | |
| 126 ->132 | 0.17460 | | | | |
| 126 ->133 | 0.26278 | | | | |
| 127 ->139 | -0.12379 | | | | |
| | | | | | |
| Excited State 37: | Singlet-A | 5.3798 eV | 230.46 nm | f=0.0128 | <S**2>=0.000 |
| 116 ->128 | 0.24323 | | | | |
| 117 ->129 | -0.25098 | | | | |
| 118 ->129 | 0.51240 | | | | |
| 124 ->130 | -0.18047 | | | | |
| | | | | | |
| Excited State 38: | Singlet-A | 5.3943 eV | 229.84 nm | f=0.0024 | <S**2>=0.000 |
| 127 ->138 | 0.12767 | | | | |
| 127 ->139 | 0.21210 | | | | |
| 127 ->140 | 0.61640 | | | | |
| | | | | | |
| Excited State 39: | Singlet-A | 5.4136 eV | 229.02 nm | f=0.0541 | <S**2>=0.000 |
| 121 ->130 | 0.10261 | | | | |
| 123 ->130 | -0.14695 | | | | |
| 125 ->130 | 0.50650 | | | | |
| 125 ->131 | 0.15224 | | | | |
| 125 ->133 | -0.15033 | | | | |
| 126 ->133 | 0.12971 | | | | |
| 126 ->134 | 0.10351 | | | | |
| 127 ->137 | -0.11712 | | | | |
| 127 ->140 | -0.13288 | | | | |
| | | | | | |
| Excited State 40: | Singlet-A | 5.4861 eV | 226.00 nm | f=0.0221 | <S**2>=0.000 |
| 121 ->130 | -0.14197 | | | | |
| 122 ->130 | -0.10132 | | | | |
| 124 ->130 | 0.24021 | | | | |
| 125 ->130 | 0.31245 | | | | |
| 125 ->131 | -0.27508 | | | | |
| 126 ->134 | -0.26696 | | | | |
| 127 ->137 | 0.15178 | | | | |
| 127 ->138 | -0.13871 | | | | |
| 127 ->141 | 0.19577 | | | | |

**Table S9.** Standard Orientation of the Optimized Geometry for the (R)-form of **2'**

| Tag | Symbol | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | C | -4.0058310 | -0.8849470 | 1.1806860 |
| 2 | C | -4.9840980 | -1.7890540 | 0.6918490 |
| 3 | C | -4.7729480 | -2.5791040 | -0.4190340 |
| 4 | C | -3.5362470 | -2.5207120 | -1.1097900 |
| 5 | C | -2.5736860 | -1.6362360 | -0.5837460 |
| 6 | C | -2.8006090 | -0.8123640 | 0.5292210 |
| 7 | C | -3.1540790 | -3.2379090 | -2.2713710 |
| 8 | C | -1.9041220 | -3.0506900 | -2.8254600 |
| 9 | C | -0.9474680 | -2.1672650 | -2.2628040 |
| 10 | C | -1.2955310 | -1.4716090 | -1.1344440 |
| 11 | H | -4.2243800 | -0.2616480 | 2.0418030 |
| 12 | H | -5.9370880 | -1.8487270 | 1.2081990 |
| 13 | H | -5.5546940 | -3.2467490 | -0.7685990 |
| 14 | H | -3.8524340 | -3.9318440 | -2.7296110 |
| 15 | H | -1.6357690 | -3.6028360 | -3.7207150 |
| 16 | H | 0.0299140 | -2.0585280 | -2.7209650 |
| 17 | C | -0.4823700 | -0.5554400 | -0.2274800 |
| 18 | N | 0.2854940 | 0.4226500 | -0.9564260 |
| 19 | N | 0.4335270 | -1.3849240 | 0.5457630 |
| 20 | C | 1.5213020 | 0.1979940 | -0.6799780 |
| 21 | C | 1.6151360 | -0.9466010 | 0.2909940 |
| 22 | C | 2.6016210 | 0.9816350 | -1.3007860 |
| 23 | C | 2.3778200 | 2.3352920 | -1.5816790 |
| 24 | C | 3.8166660 | 0.3961950 | -1.6743410 |
| 25 | C | 3.3596180 | 3.0919420 | -2.2069010 |
| 26 | H | 1.4273300 | 2.7761890 | -1.3021850 |
| 27 | C | 4.7917800 | 1.1551270 | -2.3125820 |
| 28 | H | 3.9943320 | -0.6557720 | -1.4802560 |
| 29 | C | 4.5687490 | 2.5039490 | -2.5735470 |
| 30 | H | 3.1812030 | 4.1426910 | -2.4108570 |
| 31 | H | 5.7270450 | 0.6901150 | -2.6068050 |
| 32 | H | 5.3347040 | 3.0961800 | -3.0640310 |
| 33 | C | 2.8075220 | -1.5285910 | 0.9285630 |
| 34 | C | 2.8308890 | -2.9022570 | 1.1994560 |
| 35 | C | 3.8873640 | -0.7338850 | 1.3300970 |
| 36 | C | 3.9215350 | -3.4720650 | 1.8423920 |
| 37 | H | 1.9825800 | -3.5075830 | 0.8995120 |
| 38 | C | 4.9719170 | -1.3068470 | 1.9854810 |
| 39 | H | 3.8719950 | 0.3344890 | 1.1460890 |
| 40 | C | 4.9950510 | -2.6756540 | 2.2365810 |
| 41 | H | 3.9338450 | -4.5390800 | 2.0399040 |
| 42 | H | 5.7991900 | -0.6802720 | 2.3023810 |
| 43 | H | 5.8460580 | -3.1212000 | 2.7417540 |
| 44 | C | -1.5957600 | 0.1029350 | 0.7542110 |

| | | | | |
|---|---|---|---|---|
| 45 | C | -1.9393320 | 1.5227080 | 0.3217000 |
| 46 | C | -1.1354300 | 0.0128640 | 2.1787110 |
| 47 | C | -2.4914760 | 1.7606160 | -0.9408350 |
| 48 | C | -1.7253390 | 2.6161540 | 1.1723640 |
| 49 | C | -0.9533210 | 1.0633260 | 2.9860390 |
| 50 | H | -0.9477140 | -0.9930000 | 2.5378880 |
| 51 | C | -2.8081660 | 3.0479070 | -1.3487310 |
| 52 | H | -2.6648560 | 0.9300390 | -1.6156300 |
| 53 | C | -2.0464780 | 3.9127370 | 0.7546390 |
| 54 | C | -1.1834860 | 2.4431680 | 2.5441410 |
| 55 | H | -0.6188600 | 0.9397900 | 4.0109620 |
| 56 | C | -2.5843100 | 4.1339420 | -0.5006850 |
| 57 | H | -3.2327020 | 3.2058230 | -2.3351880 |
| 58 | H | -1.8637940 | 4.7243890 | 1.4503940 |
| 59 | H | -2.8350410 | 5.1400660 | -0.8210490 |
| 60 | O | -0.9594130 | 3.3949770 | 3.2792580 |

SCF Done: E(RmPW1PW91) = -1531.35539268 A.U.

Zero-point correction = 0.474843 (Hartree/Particle)
Thermal correction to Energy = 0.502424
Thermal correction to Enthalpy = 0.503368
Thermal correction to Gibbs Free Energy = 0.414629
Sum of electronic and zero-point Energies = -1530.880550
Sum of electronic and thermal Energies = -1530.852969
Sum of electronic and thermal Enthalpies = -1530.852025
Sum of electronic and thermal Free Energies = -1530.940763

Low frequencies --- -5.8489 0.0005 0.0005 0.0007 1.6650 3.7998
Low frequencies --- 14.8508 17.0213 30.5828

The Result for the TDDFT calculation

<0|del|b> * <b|rxdel|0> + <0|del|b> * <b|delr+rdel|0>
Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)

| state | XX | YY | ZZ | R(velocity) | E-M Angle |
|---|---|---|---|---|---|
| 1 | 8.2255 | 32.8048 | 7.1389 | 16.0564 | 46.27 |
| 2 | -0.7534 | -3.1858 | 2.6653 | -0.4247 | 95.70 |
| 3 | 0.3994 | 5.2610 | 0.4856 | 2.0487 | 81.58 |
| 4 | -3.7795 | 182.1229 | 361.7622 | 180.0352 | 21.42 |
| 5 | 14.1154 | -111.5974 | 58.2824 | -13.0665 | 97.19 |
| 6 | -67.3502 | -2.4137 | -36.8884 | -35.5507 | 133.77 |
| 7 | -45.4202 | 42.3708 | 32.6399 | 9.8635 | 76.66 |
| 8 | 5.5853 | -51.7243 | -20.8836 | -22.3409 | 135.10 |
| 9 | 5.2399 | -73.1901 | 23.2075 | -14.9143 | 126.93 |
| 10 | -74.4673 | -148.4902 | -31.3382 | -84.7652 | 157.61 |
| 11 | -177.5864 | -15.1184 | -27.5383 | -73.4144 | 171.58 |
| 12 | 46.7913 | -9.7023 | -1.5909 | 11.8327 | 73.42 |

| | | | | | |
|---|---|---|---|---|---|
| 13 | 64.6596 | 48.8366 | 17.6923 | 43.7295 | 24.77 |
| 14 | -10.7426 | -43.0143 | 34.4248 | -6.4440 | 144.33 |
| 15 | 82.0061 | -66.6554 | 173.4926 | 62.9477 | 63.81 |
| 16 | 33.5442 | 39.3006 | 18.0382 | 30.2944 | 20.54 |
| 17 | -54.6422 | 74.7349 | 38.4532 | 19.5153 | 85.27 |
| 18 | 2.6755 | -10.0993 | 9.9762 | 0.8508 | 88.24 |
| 19 | 2.4310 | 4.6325 | 8.4913 | 5.1850 | 61.80 |
| 20 | 33.5557 | 12.9343 | -10.7917 | 11.8994 | 60.71 |
| 21 | -6.8678 | 13.9692 | -0.0973 | 2.3347 | 67.40 |
| 22 | 44.4985 | -47.1190 | -3.9561 | -2.1922 | 98.76 |
| 23 | -10.4129 | -5.2557 | -5.2186 | -6.9624 | 151.58 |
| 24 | 56.3799 | 2.4189 | -52.8586 | 1.9801 | 86.06 |
| 25 | -0.8859 | -4.9842 | -0.0004 | -1.9568 | 118.89 |
| 26 | -9.5709 | 15.5730 | 43.6570 | 16.5530 | 40.51 |
| 27 | 8.3456 | 4.1032 | -11.4762 | 0.3242 | 88.46 |
| 28 | -70.9389 | 100.2493 | -38.7500 | -3.1465 | 93.03 |
| 29 | 111.5332 | 41.4228 | 34.5324 | 62.4961 | 52.61 |
| 30 | 105.0791 | 62.0704 | -23.4622 | 47.8958 | 42.51 |
| 31 | -4.4806 | -9.2633 | 14.5377 | 0.2646 | 88.78 |
| 32 | -29.6120 | -58.7597 | 70.6458 | -5.9086 | 94.86 |
| 33 | 0.5879 | 9.5201 | 7.0449 | 5.7176 | 39.74 |
| 34 | 25.6984 | 1.1332 | -11.8698 | 4.9873 | 78.69 |
| 35 | -48.2344 | 12.0025 | -202.7109 | -79.6476 | 159.11 |
| 36 | -12.2584 | 1.8571 | 19.4643 | 3.0210 | 73.40 |
| 37 | -199.9948 | -18.6654 | 107.8176 | -36.9475 | 100.24 |
| 38 | -4.4429 | -84.7548 | 96.2500 | 2.3508 | 84.39 |
| 39 | -13.6035 | 69.2882 | -4.3256 | 17.1197 | 34.47 |
| 40 | 60.8964 | 32.5918 | 16.1037 | 36.5306 | 59.95 |

1/2[<0|r|b>*<b|rxdel|0> + (<0|rxdel|b>*<b|r|0>)*]

Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)

| state | XX | YY | ZZ | R(length) |
|---|---|---|---|---|
| 1 | 13.8143 | -4.1537 | 38.3130 | 15.9912 |
| 2 | -0.8306 | 4.7120 | -3.8914 | -0.0033 |
| 3 | 8.3968 | -6.2023 | 3.5310 | 1.9085 |
| 4 | 562.7653 | -7.0026 | -2.8541 | 184.3028 |
| 5 | -31.4833 | 61.3173 | -67.9895 | -12.7185 |
| 6 | -99.3870 | 2.5398 | -5.6664 | -34.1712 |
| 7 | 78.3388 | -14.6643 | -33.6009 | 10.0245 |
| 8 | -78.5982 | 7.3565 | 4.6692 | -22.1908 |
| 9 | -49.9460 | 3.5124 | 0.8109 | -15.2075 |
| 10 | -192.7906 | 7.5496 | -75.6713 | -86.9708 |
| 11 | 0.2256 | -28.0400 | -192.4786 | -73.4310 |
| 12 | -1.6355 | 57.2174 | -21.0570 | 11.5083 |
| 13 | 52.8246 | 72.7992 | 5.2765 | 43.6335 |
| 14 | -16.7618 | 1.4137 | -4.5473 | -6.6318 |

| | | | | |
|---|---|---|---|---|
| 15 | 82.5433 | 123.9923 | -12.2095 | 64.7754 |
| 16 | 0.8141 | 8.4682 | 80.3582 | 29.8802 |
| 17 | 265.7683 | -172.4869 | -24.4335 | 22.9493 |
| 18 | -2.1751 | 5.7150 | 4.2678 | 2.6026 |
| 19 | 9.9876 | 2.4343 | 3.9401 | 5.4540 |
| 20 | -6.0399 | 15.3530 | 27.5350 | 12.2827 |
| 21 | 0.5103 | 1.0157 | 8.3508 | 3.2923 |
| 22 | -9.9864 | 15.8977 | -13.1333 | -2.4074 |
| 23 | 0.0686 | -8.2576 | -13.1657 | -7.1183 |
| 24 | 4.8031 | -5.4199 | 13.3724 | 4.2518 |
| 25 | -3.8618 | -1.8510 | -0.0720 | -1.9283 |
| 26 | 56.4992 | 1.7263 | -6.8068 | 17.1395 |
| 27 | -15.4025 | 5.1801 | 11.1463 | 0.3079 |
| 28 | 37.0882 | -44.6930 | -2.2815 | -3.2954 |
| 29 | 32.9417 | 110.2131 | 46.1744 | 63.1097 |
| 30 | 34.8390 | 47.7313 | 64.3470 | 48.9724 |
| 31 | 6.8890 | 1.3036 | -8.4774 | -0.0949 |
| 32 | 43.0756 | -9.9021 | -52.7452 | -6.5239 |
| 33 | 9.1160 | 8.8014 | -1.6289 | 5.4295 |
| 34 | -0.5545 | 38.7218 | -29.1604 | 3.0023 |
| 35 | -132.7795 | -116.7335 | 1.9811 | -82.5107 |
| 36 | 18.6041 | 0.6595 | -9.9591 | 3.1015 |
| 37 | 45.0024 | 152.1291 | -295.1308 | -32.6664 |
| 38 | 6.4767 | -3.0886 | 3.8590 | 2.4157 |
| 39 | 35.2336 | -2.1969 | 19.0637 | 17.3668 |
| 40 | 37.1080 | 89.1605 | -18.9854 | 35.7610 |

1/2[<0|del|b>*<b|r|0> + (<0|r|b>*<b|del|0>)*] (Au)

| state | X | Y | Z | Dip. S. | Osc. (frdel) |
|---|---|---|---|---|---|
| 1 | -0.0057 | -0.0005 | -0.0035 | 0.0097 | 0.0065 |
| 2 | 0.0000 | 0.0000 | 0.0000 | 0.0001 | 0.0000 |
| 3 | 0.0000 | -0.0008 | -0.0004 | 0.0012 | 0.0008 |
| 4 | -0.1009 | -0.0025 | 0.0000 | 0.1034 | 0.0689 |
| 5 | -0.1827 | -0.1377 | -0.0186 | 0.3390 | 0.2260 |
| 6 | -0.0135 | -0.0005 | -0.0144 | 0.0284 | 0.0189 |
| 7 | -0.0379 | -0.0044 | -0.0095 | 0.0518 | 0.0346 |
| 8 | -0.0248 | -0.0054 | -0.0008 | 0.0311 | 0.0207 |
| 9 | -0.0428 | -0.0003 | 0.0000 | 0.0432 | 0.0288 |
| 10 | -0.0503 | -0.0008 | -0.0138 | 0.0649 | 0.0433 |
| 11 | -0.0002 | -0.0030 | -0.0302 | 0.0335 | 0.0223 |
| 12 | -0.0002 | -0.0403 | -0.0017 | 0.0422 | 0.0281 |
| 13 | -0.0324 | -0.0179 | -0.0026 | 0.0529 | 0.0353 |
| 14 | -0.0385 | -0.0013 | -0.0040 | 0.0439 | 0.0292 |
| 15 | -0.1128 | -0.0234 | -0.0002 | 0.1365 | 0.0910 |
| 16 | 0.0000 | -0.0018 | -0.0090 | 0.0108 | 0.0072 |
| 17 | -0.0143 | -0.0280 | -0.0463 | 0.0886 | 0.0591 |

| | | | | | |
|---|---|---|---|---|---|
| 18 | -0.0237 | -0.0002 | 0.0000 | 0.0239 | 0.0159 |
| 19 | -0.0064 | 0.0000 | -0.0005 | 0.0069 | 0.0046 |
| 20 | -0.0064 | -0.0010 | -0.0101 | 0.0175 | 0.0116 |
| 21 | -0.0001 | 0.0000 | -0.0042 | 0.0042 | 0.0028 |
| 22 | -0.0016 | -0.0048 | -0.0085 | 0.0149 | 0.0100 |
| 23 | 0.0000 | -0.0007 | -0.0031 | 0.0038 | 0.0025 |
| 24 | -0.0020 | -0.0329 | -0.0005 | 0.0354 | 0.0236 |
| 25 | -0.0015 | -0.0001 | 0.0000 | 0.0016 | 0.0011 |
| 26 | -0.0137 | -0.0018 | -0.0007 | 0.0162 | 0.0108 |
| 27 | -0.0025 | -0.0009 | -0.0058 | 0.0092 | 0.0061 |
| 28 | -0.0030 | -0.0103 | -0.0380 | 0.0513 | 0.0342 |
| 29 | -0.0007 | -0.0341 | -0.0036 | 0.0384 | 0.0256 |
| 30 | -0.0432 | -0.0350 | -0.0119 | 0.0901 | 0.0601 |
| 31 | -0.0054 | -0.0001 | -0.0003 | 0.0058 | 0.0039 |
| 32 | -0.0498 | -0.0011 | -0.0039 | 0.0548 | 0.0365 |
| 33 | -0.0023 | -0.0036 | -0.0002 | 0.0062 | 0.0041 |
| 34 | -0.0002 | -0.0115 | -0.0023 | 0.0140 | 0.0093 |
| 35 | -0.0215 | -0.0234 | -0.0050 | 0.0498 | 0.0332 |
| 36 | -0.0029 | -0.0012 | -0.0032 | 0.0073 | 0.0049 |
| 37 | -0.0009 | -0.0175 | -0.0738 | 0.0922 | 0.0614 |
| 38 | -0.0597 | -0.0002 | -0.0005 | 0.0605 | 0.0403 |
| 39 | -0.0620 | -0.0022 | -0.0120 | 0.0762 | 0.0508 |
| 40 | -0.0097 | -0.0089 | -0.0262 | 0.0448 | 0.0299 |

Excited State 1: Singlet-A 3.3486 eV 370.26 nm f=0.0063 <S**2>=0.000
127 ->128 0.70082
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1531.27217677
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.4982 eV 354.43 nm f=0.0001 <S**2>=0.000
125 ->128 0.20891
125 ->129 0.61738
126 ->129 -0.20005

Excited State 3: Singlet-A 3.7981 eV 326.44 nm f=0.0010 <S**2>=0.000
127 ->129 0.69362

Excited State 4: Singlet-A 3.9296 eV 315.52 nm f=0.0711 <S**2>=0.000
117 ->128 0.27896
120 ->128 -0.12856
126 ->128 0.60500

Excited State 5: Singlet-A 4.2237 eV 293.55 nm f=0.2238 <S**2>=0.000
122 ->128 -0.17216
125 ->128 -0.16122
127 ->130 0.63574

Excited State 6: Singlet-A 4.2359 eV 292.70 nm f=0.0179 <S**2>=0.000
117 ->128 -0.18430
118 ->128 0.13056

| | | | | | | |
|---|---|---|---|---|---|---|
| 120 ->128 | 0.14584 | | | | | |
| 122 ->128 | 0.22898 | | | | | |
| 123 ->128 | 0.12069 | | | | | |
| 125 ->128 | 0.49245 | | | | | |
| 125 ->129 | -0.12901 | | | | | |
| 126 ->128 | 0.10041 | | | | | |
| 127 ->130 | 0.23714 | | | | | |
| Excited State 7: | Singlet-A | 4.3206 eV | 286.96 nm | f=0.0352 | <S**2>=0.000 | |
| 122 ->128 | 0.36474 | | | | | |
| 123 ->128 | 0.17835 | | | | | |
| 124 ->128 | 0.41486 | | | | | |
| 125 ->128 | -0.31766 | | | | | |
| 126 ->128 | 0.10647 | | | | | |
| 126 ->129 | -0.16727 | | | | | |
| Excited State 8: | Singlet-A | 4.3526 eV | 284.85 nm | f=0.0206 | <S**2>=0.000 | |
| 117 ->128 | 0.15828 | | | | | |
| 118 ->128 | -0.10795 | | | | | |
| 120 ->128 | -0.20811 | | | | | |
| 122 ->128 | -0.28072 | | | | | |
| 123 ->128 | 0.39671 | | | | | |
| 124 ->128 | 0.24610 | | | | | |
| 125 ->128 | 0.19296 | | | | | |
| 125 ->129 | -0.12798 | | | | | |
| 126 ->128 | -0.15261 | | | | | |
| 126 ->129 | -0.14621 | | | | | |
| Excited State 9: | Singlet-A | 4.3673 eV | 283.89 nm | f=0.0294 | <S**2>=0.000 | |
| 123 ->128 | 0.49559 | | | | | |
| 124 ->128 | -0.40507 | | | | | |
| 125 ->128 | -0.14193 | | | | | |
| 125 ->129 | 0.11689 | | | | | |
| 126 ->129 | 0.10359 | | | | | |
| Excited State 10: | Singlet-A | 4.3880 eV | 282.55 nm | f=0.0443 | <S**2>=0.000 | |
| 117 ->128 | 0.20829 | | | | | |
| 118 ->128 | -0.10433 | | | | | |
| 120 ->128 | -0.36547 | | | | | |
| 122 ->128 | 0.37810 | | | | | |
| 123 ->128 | -0.10094 | | | | | |
| 124 ->128 | -0.15662 | | | | | |
| 125 ->128 | 0.10983 | | | | | |
| 126 ->128 | -0.18361 | | | | | |
| 126 ->129 | -0.11184 | | | | | |
| 127 ->131 | 0.11377 | | | | | |
| 127 ->133 | 0.11952 | | | | | |
| Excited State 11: | Singlet-A | 4.4502 eV | 278.60 nm | f=0.0224 | <S**2>=0.000 | |
| 121 ->128 | 0.47263 | | | | | |
| 122 ->128 | 0.14550 | | | | | |
| 122 ->130 | 0.10308 | | | | | |
| 123 ->130 | -0.25069 | | | | | |
| 127 ->131 | -0.17628 | | | | | |
| 127 ->132 | -0.15336 | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 127 ->133 | -0.27343 | | | | |
| | | | | | |
| Excited State 12: | Singlet-A | 4.4588 eV | 278.07 nm | f=0.0276 | <S**2>=0.000 |
| 120 ->128 | -0.22924 | | | | |
| 122 ->129 | 0.13567 | | | | |
| 124 ->128 | 0.23982 | | | | |
| 125 ->129 | 0.16952 | | | | |
| 126 ->129 | 0.53764 | | | | |
| | | | | | |
| Excited State 13: | Singlet-A | 4.4631 eV | 277.80 nm | f=0.0353 | <S**2>=0.000 |
| 121 ->128 | 0.48024 | | | | |
| 123 ->128 | 0.13221 | | | | |
| 123 ->130 | 0.24631 | | | | |
| 127 ->131 | 0.16101 | | | | |
| 127 ->132 | 0.17852 | | | | |
| 127 ->133 | 0.27813 | | | | |
| | | | | | |
| Excited State 14: | Singlet-A | 4.5811 eV | 270.64 nm | f=0.0305 | <S**2>=0.000 |
| 117 ->128 | 0.28671 | | | | |
| 118 ->128 | -0.35795 | | | | |
| 120 ->128 | 0.40686 | | | | |
| 127 ->131 | 0.21202 | | | | |
| | | | | | |
| Excited State 15: | Singlet-A | 4.6332 eV | 267.60 nm | f=0.0949 | <S**2>=0.000 |
| 117 ->128 | -0.11148 | | | | |
| 118 ->128 | 0.17398 | | | | |
| 123 ->130 | -0.11979 | | | | |
| 127 ->131 | 0.60366 | | | | |
| 127 ->133 | -0.13382 | | | | |
| | | | | | |
| Excited State 16: | Singlet-A | 4.6744 eV | 265.24 nm | f=0.0070 | <S**2>=0.000 |
| 119 ->128 | 0.65131 | | | | |
| | | | | | |
| Excited State 17: | Singlet-A | 4.6909 eV | 264.31 nm | f=0.0608 | <S**2>=0.000 |
| 118 ->129 | -0.14007 | | | | |
| 124 ->129 | 0.64627 | | | | |
| | | | | | |
| Excited State 18: | Singlet-A | 4.8265 eV | 256.88 nm | f=0.0166 | <S**2>=0.000 |
| 115 ->128 | 0.13406 | | | | |
| 117 ->128 | 0.39909 | | | | |
| 118 ->128 | 0.47646 | | | | |
| 120 ->128 | 0.10130 | | | | |
| 123 ->129 | 0.16092 | | | | |
| 126 ->128 | -0.10027 | | | | |
| | | | | | |
| Excited State 19: | Singlet-A | 4.8386 eV | 256.24 nm | f=0.0047 | <S**2>=0.000 |
| 118 ->128 | -0.10187 | | | | |
| 122 ->129 | -0.36641 | | | | |
| 123 ->129 | 0.56948 | | | | |
| | | | | | |
| Excited State 20: | Singlet-A | 4.8610 eV | 255.06 nm | f=0.0118 | <S**2>=0.000 |
| 122 ->129 | 0.40080 | | | | |
| 123 ->129 | 0.23511 | | | | |
| 126 ->129 | -0.15053 | | | | |
| 126 ->130 | 0.44339 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Excited State 21: | Singlet-A | 4.8722 eV | 254.47 nm | f=0.0031 | <S**2>=0.000 |
| 122 ->129 | -0.36139 | | | | |
| 123 ->129 | -0.26609 | | | | |
| 126 ->129 | 0.12445 | | | | |
| 126 ->130 | 0.47892 | | | | |
| Excited State 22: | Singlet-A | 4.9837 eV | 248.78 nm | f=0.0104 | <S**2>=0.000 |
| 120 ->129 | -0.16690 | | | | |
| 121 ->129 | 0.63570 | | | | |
| 122 ->129 | 0.11845 | | | | |
| Excited State 23: | Singlet-A | 5.0617 eV | 244.94 nm | f=0.0028 | <S**2>=0.000 |
| 125 ->130 | 0.66460 | | | | |
| 126 ->130 | -0.13525 | | | | |
| Excited State 24: | Singlet-A | 5.1046 eV | 242.89 nm | f=0.0227 | <S**2>=0.000 |
| 114 ->128 | -0.12898 | | | | |
| 115 ->128 | 0.49312 | | | | |
| 116 ->128 | -0.18918 | | | | |
| 117 ->131 | 0.11577 | | | | |
| 118 ->128 | -0.16969 | | | | |
| 122 ->129 | 0.10041 | | | | |
| 126 ->131 | 0.24279 | | | | |
| Excited State 25: | Singlet-A | 5.1197 eV | 242.17 nm | f=0.0011 | <S**2>=0.000 |
| 120 ->129 | -0.19169 | | | | |
| 124 ->130 | 0.10472 | | | | |
| 127 ->132 | 0.56132 | | | | |
| 127 ->133 | -0.29381 | | | | |
| Excited State 26: | Singlet-A | 5.1439 eV | 241.03 nm | f=0.0114 | <S**2>=0.000 |
| 120 ->129 | -0.21218 | | | | |
| 124 ->130 | 0.60613 | | | | |
| 127 ->132 | -0.16591 | | | | |
| Excited State 27: | Singlet-A | 5.1592 eV | 240.32 nm | f=0.0062 | <S**2>=0.000 |
| 117 ->129 | -0.10256 | | | | |
| 120 ->129 | 0.56129 | | | | |
| 121 ->129 | 0.14575 | | | | |
| 124 ->130 | 0.28155 | | | | |
| 127 ->132 | 0.14843 | | | | |
| Excited State 28: | Singlet-A | 5.1843 eV | 239.15 nm | f=0.0343 | <S**2>=0.000 |
| 115 ->128 | 0.20672 | | | | |
| 116 ->128 | -0.10871 | | | | |
| 122 ->130 | 0.41547 | | | | |
| 123 ->130 | 0.20406 | | | | |
| 126 ->131 | -0.30723 | | | | |
| 127 ->134 | -0.24125 | | | | |
| Excited State 29: | Singlet-A | 5.2198 eV | 237.53 nm | f=0.0262 | <S**2>=0.000 |
| 122 ->130 | 0.27385 | | | | |
| 124 ->130 | -0.10837 | | | | |
| 127 ->133 | 0.12502 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 127 ->134 | 0.58097 | | | | |
| 127 ->135 | 0.12373 | | | | |
| Excited State 30: | Singlet-A | 5.2500 eV | 236.16 nm | f=0.0618 | <S**2>=0.000 |
| 115 ->128 | -0.13090 | | | | |
| 121 ->130 | 0.19368 | | | | |
| 122 ->130 | 0.36842 | | | | |
| 123 ->130 | 0.14287 | | | | |
| 126 ->131 | 0.45721 | | | | |
| Excited State 31: | Singlet-A | 5.2767 eV | 234.96 nm | f=0.0040 | <S**2>=0.000 |
| 119 ->128 | 0.17352 | | | | |
| 120 ->130 | 0.22839 | | | | |
| 120 ->131 | 0.37780 | | | | |
| 121 ->130 | 0.22270 | | | | |
| 121 ->131 | 0.19552 | | | | |
| 122 ->132 | -0.14670 | | | | |
| 122 ->135 | 0.10928 | | | | |
| 123 ->131 | -0.10099 | | | | |
| 123 ->132 | -0.10532 | | | | |
| 126 ->132 | 0.15017 | | | | |
| Excited State 32: | Singlet-A | 5.3091 eV | 233.53 nm | f=0.0372 | <S**2>=0.000 |
| 116 ->128 | -0.23361 | | | | |
| 120 ->130 | -0.21830 | | | | |
| 121 ->130 | 0.51398 | | | | |
| 123 ->130 | -0.14369 | | | | |
| 126 ->131 | -0.20094 | | | | |
| Excited State 33: | Singlet-A | 5.3434 eV | 232.03 nm | f=0.0040 | <S**2>=0.000 |
| 125 ->130 | 0.12230 | | | | |
| 125 ->131 | 0.64690 | | | | |
| 125 ->136 | -0.14300 | | | | |
| Excited State 34: | Singlet-A | 5.3645 eV | 231.12 nm | f=0.0096 | <S**2>=0.000 |
| 115 ->128 | 0.19808 | | | | |
| 116 ->128 | 0.57311 | | | | |
| 118 ->129 | -0.10761 | | | | |
| 120 ->130 | -0.10006 | | | | |
| 121 ->130 | 0.13033 | | | | |
| 126 ->131 | -0.11859 | | | | |
| 127 ->136 | -0.13981 | | | | |
| Excited State 35: | Singlet-A | 5.3784 eV | 230.52 nm | f=0.0344 | <S**2>=0.000 |
| 115 ->128 | 0.13041 | | | | |
| 116 ->128 | 0.12745 | | | | |
| 117 ->129 | -0.19692 | | | | |
| 118 ->129 | 0.47842 | | | | |
| 127 ->136 | 0.30382 | | | | |
| Excited State 36: | Singlet-A | 5.3951 eV | 229.81 nm | f=0.0051 | <S**2>=0.000 |
| 118 ->129 | 0.11110 | | | | |
| 119 ->129 | 0.54294 | | | | |
| 119 ->130 | 0.12045 | | | | |
| 119 ->131 | 0.21043 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 121 ->131 | -0.11145 | | | | |
| 122 ->131 | -0.10641 | | | | |
| | | | | | |
| Excited State 37: | Singlet-A | 5.4082 eV | 229.25 nm | f=0.0645 | <S**2>=0.000 |
| 117 ->129 | 0.12984 | | | | |
| 118 ->129 | -0.24299 | | | | |
| 119 ->129 | 0.12823 | | | | |
| 122 ->131 | 0.20643 | | | | |
| 123 ->131 | 0.13058 | | | | |
| 124 ->131 | -0.22716 | | | | |
| 124 ->134 | -0.15990 | | | | |
| 126 ->136 | -0.11263 | | | | |
| 127 ->136 | 0.38004 | | | | |
| | | | | | |
| Excited State 38: | Singlet-A | 5.4438 eV | 227.75 nm | f=0.0411 | <S**2>=0.000 |
| 119 ->129 | 0.35794 | | | | |
| 119 ->130 | -0.14503 | | | | |
| 119 ->131 | -0.21723 | | | | |
| 121 ->130 | -0.12017 | | | | |
| 121 ->131 | 0.10304 | | | | |
| 122 ->131 | 0.31553 | | | | |
| 124 ->131 | 0.20164 | | | | |
| 127 ->136 | -0.15013 | | | | |
| | | | | | |
| Excited State 39: | Singlet-A | 5.4819 eV | 226.17 nm | f=0.0518 | <S**2>=0.000 |
| 118 ->130 | 0.16495 | | | | |
| 119 ->129 | -0.16510 | | | | |
| 119 ->130 | 0.12247 | | | | |
| 119 ->131 | 0.19201 | | | | |
| 121 ->131 | -0.12884 | | | | |
| 121 ->132 | 0.10432 | | | | |
| 122 ->131 | 0.37136 | | | | |
| 123 ->131 | 0.25220 | | | | |
| 124 ->131 | 0.11090 | | | | |
| 127 ->135 | -0.12575 | | | | |
| 127 ->136 | -0.18406 | | | | |
| | | | | | |
| Excited State 40: | Singlet-A | 5.5294 eV | 224.23 nm | f=0.0301 | <S**2>=0.000 |
| 117 ->130 | -0.14898 | | | | |
| 118 ->130 | 0.27615 | | | | |
| 120 ->130 | 0.38100 | | | | |
| 120 ->131 | -0.13995 | | | | |
| 121 ->130 | 0.11571 | | | | |
| 123 ->130 | -0.18090 | | | | |
| 123 ->131 | -0.11344 | | | | |
| 127 ->133 | 0.11750 | | | | |
| 127 ->134 | -0.11509 | | | | |
| 127 ->135 | 0.28970 | | | | |

## 15. DFT calculations for the transition states

The DFT calculations were carried out to understand the thermodynamics and the reaction kinetics for the negative photochromism of **1** and **2**. All calculations was carried out using the Gaussian 09 program (Revision D.01).[S4] The molecular structures were fully optimized at the (U)M05-2X/6-31G(d,p) level of theory. The stationary nature of the structures was confirmed by harmonic vibrational frequency calculations; that is, equilibrium species possess all real frequencies, whereas transition states possess only one imaginary frequency. The calculated energy diagrams for **1** and **2** are shown in Figure S45. The experimental observation for the thermal stability of each transient species can be qualitatively explained by the DFT calculations. The biradical species is extremely unstable and the activation free energy barrier for the relaxation path is small. That is why we could not observe the transient absorbance attributable to the biradical species by the nanosecond laser flash photolysis. The large steric repulsion between the imidazolyl radical and the phenoxyl (or naphthoxyl) radical will destabilize the biradical species. The activation free energy barrier for the thermal recombination reaction from the biradical species into the 2,4-isomer (TS2) is smaller than that into the 1,4-isomer (TS1). This result supports that the 2,4-isomer is kinetically generated through the thermal recombination reaction of the photogenerated biradical species upon UV light irradiation. On the other hand, the 2,4-isomer is thermodynamically unstable, compared with the 1,4-isomer, leading to the isomerization reaction from the 2,4-isomer into the 1,4-isomer through the biradical species by the thermodynamic controlled reaction. The thermal back reaction from the 2,4-isomer into the 1,4-isomer of **2** was accelerated as compared with that of **1** by replacing the phenoxyl unit to the naphthoxyl unit. However, the reason for the acceleration of the thermal back reaction of **2** cannot be explained by the calculated activation free energy between the reactions of **1** and **2**. While the calculated activation free energy barrier of TS1 of **2** is smaller than that of **1**, the energy of TS2 of **2** increases according to the calculation. This calculated result suggests the reduction of the rate for the thermal isomerization reaction from the 2,4-isomer of **2**, which conflicts with the experimental results. Presumably, considerations of some solvent effects and more suitable calculations for the open-shell biradical species are required to quantitatively discuss about the activation free energy for the thermal back reactions.

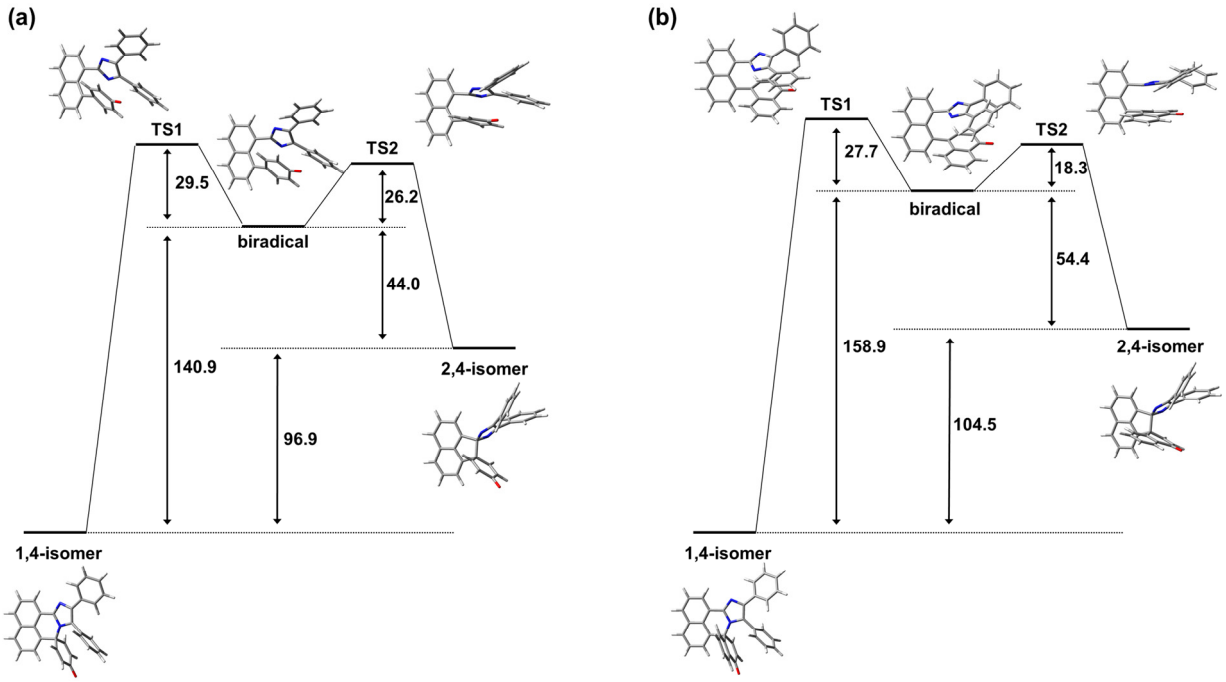



**Figure S51.** Energy diagrams for the thermal back reactions and the optimized molecular structures of (a) **1** and (b) **2** calculated by the DFT method (M05-2X/6-31G(d,p) level of the theory). The Gibbs free energies at 298.15 K are given in the unit of kJ $mol^{-1}$.

**Table S10.** Standard Orientation of the Optimized Geometry for the 1,4-isomer of **1**

| Tag | Symbol | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | C | 3.7511130 | 0.9834800 | 0.3970250 |
| 2 | C | 5.0606020 | 0.4735620 | 0.5147380 |
| 3 | C | 5.2932970 | -0.8725440 | 0.4028360 |
| 4 | C | 4.2200800 | -1.7678410 | 0.1801880 |
| 5 | C | 2.8997230 | -1.2529240 | 0.0773130 |
| 6 | C | 2.6810980 | 0.1459420 | 0.1838820 |
| 7 | C | 4.4260500 | -3.1659820 | 0.0552390 |
| 8 | C | 3.3683160 | -4.0140250 | -0.1531920 |
| 9 | C | 2.0532620 | -3.5112330 | -0.2335660 |
| 10 | C | 1.8238550 | -2.1608930 | -0.1172610 |
| 11 | C | 1.2881310 | 0.7693870 | -0.0506530 |
| 12 | C | 0.4768370 | -1.6188850 | -0.1338790 |
| 13 | C | 1.0118050 | 1.7636090 | 1.0501880 |
| 14 | C | 0.9995740 | 3.0830580 | 0.8579810 |
| 15 | C | 1.1694510 | 3.6739890 | -0.4884600 |
| 16 | C | 1.3367600 | 2.7254520 | -1.6137860 |
| 17 | C | 1.3487400 | 1.4065480 | -1.4204440 |
| 18 | O | 1.1618220 | 4.8785280 | -0.6664670 |
| 19 | N | 0.2527240 | -0.2751060 | -0.0425990 |
| 20 | C | -1.1252360 | -0.0994010 | -0.0387880 |
| 21 | C | -1.6524680 | -1.3750710 | -0.1193060 |
| 22 | N | -0.6425010 | -2.3001950 | -0.1775520 |
| 23 | C | -3.0605510 | -1.8068260 | -0.1205610 |
| 24 | C | -1.7734970 | 1.2156260 | 0.1498620 |
| 25 | C | -4.1145900 | -0.9359280 | -0.4167300 |
| 26 | C | -5.4277790 | -1.3929400 | -0.4010300 |
| 27 | C | -5.7084790 | -2.7217660 | -0.0986760 |
| 28 | C | -4.6626750 | -3.5960700 | 0.1850240 |
| 29 | C | -3.3496090 | -3.1437280 | 0.1739450 |
| 30 | C | -1.8815410 | 2.1315270 | -0.8986710 |
| 31 | C | -2.4310000 | 3.3895090 | -0.6751230 |
| 32 | C | -2.9021390 | 3.7297700 | 0.5904480 |
| 33 | C | -2.8429900 | 2.8028850 | 1.6277850 |
| 34 | C | -2.2810470 | 1.5507090 | 1.4086720 |
| 35 | H | 3.5885410 | 2.0517230 | 0.4662680 |
| 36 | H | 5.8807360 | 1.1585040 | 0.6865200 |
| 37 | H | 6.2982070 | -1.2698220 | 0.4822780 |
| 38 | H | 5.4365190 | -3.5498660 | 0.1287730 |
| 39 | H | 3.5370260 | -5.0789550 | -0.2488030 |
| 40 | H | 1.2072130 | -4.1706230 | -0.3752690 |
| 41 | H | 0.8628640 | 1.3307850 | 2.0332920 |
| 42 | H | 0.8283990 | 3.7803560 | 1.6679520 |
| 43 | H | 1.4274560 | 3.1651240 | -2.5991220 |
| 44 | H | 1.4576510 | 0.7068890 | -2.2428100 |

| | | | | |
|---|---|---|---|---|
| 45 | H | -3.9105290 | 0.0954620 | -0.6706250 |
| 46 | H | -6.2334210 | -0.7076850 | -0.6340630 |
| 47 | H | -6.7323720 | -3.0742400 | -0.0891820 |
| 48 | H | -4.8704530 | -4.6335140 | 0.4168220 |
| 49 | H | -2.5281870 | -3.8137670 | 0.3891330 |
| 50 | H | -1.5213150 | 1.8584080 | -1.8815480 |
| 51 | H | -2.4906860 | 4.1039290 | -1.4863410 |
| 52 | H | -3.3256440 | 4.7111000 | 0.7633410 |
| 53 | H | -3.2279220 | 3.0579730 | 2.6070720 |
| 54 | H | -2.2207710 | 0.8231200 | 2.2091160 |

SCF Done: E(RM052X) = -1378.00369160 A.U.

Zero-point correction = 0.431185 (Hartree/Particle)
Thermal correction to Energy = 0.455839
Thermal correction to Enthalpy = 0.456783
Thermal correction to Gibbs Free Energy = 0.374496
Sum of electronic and zero-point Energies = -1377.572506
Sum of electronic and thermal Energies = -1377.547853
Sum of electronic and thermal Enthalpies = -1377.546909
Sum of electronic and thermal Free Energies = -1377.629196

Low frequencies --- -13.7992 -6.8227 -4.7060 -0.0004 -0.0002 0.0005
Low frequencies --- 12.4850 26.4166 32.1655

**Table S11.** Standard Orientation of the Optimized Geometry for the Biradical Species of **1**

| Tag | Symbol | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | C | -4.0100150 | -1.6950790 | 0.7876750 |
| 2 | C | -5.3404480 | -1.4173770 | 0.4138870 |
| 3 | C | -5.6458130 | -0.2137560 | -0.1607760 |
| 4 | C | -4.6259240 | 0.7292020 | -0.4469240 |
| 5 | C | -3.2677400 | 0.4145280 | -0.1625080 |
| 6 | C | -2.9871400 | -0.8007910 | 0.5452990 |
| 7 | C | -4.9572710 | 1.9918510 | -1.0031940 |
| 8 | C | -3.9864970 | 2.9199030 | -1.2695530 |
| 9 | C | -2.6322920 | 2.5896090 | -1.0661610 |
| 10 | C | -2.2665650 | 1.3522260 | -0.5773850 |
| 11 | C | -1.6632880 | -1.0949050 | 1.1326030 |
| 12 | C | -0.8382520 | 1.0286900 | -0.5957180 |
| 13 | C | -1.0142450 | -0.1422830 | 1.9558860 |
| 14 | C | 0.2262170 | -0.3975210 | 2.4736830 |
| 15 | C | 0.8914010 | -1.6661590 | 2.2377490 |
| 16 | C | 0.1647510 | -2.6502510 | 1.4502440 |
| 17 | C | -1.0627060 | -2.3658050 | 0.9284710 |
| 18 | O | 2.0358170 | -1.8960840 | 2.6709750 |
| 19 | N | -0.3666710 | -0.1651320 | -1.0728920 |
| 20 | C | 0.9381380 | -0.0925240 | -0.8883950 |
| 21 | C | 1.2484770 | 1.2454360 | -0.3380080 |

| | | | | |
|---|---|---|---|---|
| 22 | N | 0.1020610 | 1.9044190 | -0.1797620 |
| 23 | C | 2.5283090 | 1.8776860 | -0.0426580 |
| 24 | C | 1.8052570 | -1.2345690 | -1.1870700 |
| 25 | C | 3.7086720 | 1.5252340 | -0.7117900 |
| 26 | C | 4.8969010 | 2.1836370 | -0.4217880 |
| 27 | C | 4.9227410 | 3.1935220 | 0.5361280 |
| 28 | C | 3.7497420 | 3.5594400 | 1.1950180 |
| 29 | C | 2.5579670 | 2.9145060 | 0.9021830 |
| 30 | C | 1.4297960 | -2.1045910 | -2.2193270 |
| 31 | C | 2.1819440 | -3.2396690 | -2.4839580 |
| 32 | C | 3.3040540 | -3.5304990 | -1.7090700 |
| 33 | C | 3.6683940 | -2.6827430 | -0.6668510 |
| 34 | C | 2.9280480 | -1.5357010 | -0.4058720 |
| 35 | H | -3.7880650 | -2.6055360 | 1.3310170 |
| 36 | H | -6.1181830 | -2.1395300 | 0.6261840 |
| 37 | H | -6.6703040 | 0.0411690 | -0.4051140 |
| 38 | H | -6.0005070 | 2.2103140 | -1.1991180 |
| 39 | H | -4.2480260 | 3.8899830 | -1.6717020 |
| 40 | H | -1.8491330 | 3.2854330 | -1.3377100 |
| 41 | H | -1.5007650 | 0.8076660 | 2.1393980 |
| 42 | H | 0.7534650 | 0.3267900 | 3.0809130 |
| 43 | H | 0.6668140 | -3.5903470 | 1.2624630 |
| 44 | H | -1.5709070 | -3.0782490 | 0.2908250 |
| 45 | H | 3.6887840 | 0.7532490 | -1.4690790 |
| 46 | H | 5.8027680 | 1.9105050 | -0.9476070 |
| 47 | H | 5.8526220 | 3.6988050 | 0.7647920 |
| 48 | H | 3.7674410 | 4.3490970 | 1.9354760 |
| 49 | H | 1.6341940 | 3.1901410 | 1.3929290 |
| 50 | H | 0.5428870 | -1.8732100 | -2.7942620 |
| 51 | H | 1.8920480 | -3.9019830 | -3.2899610 |
| 52 | H | 3.8854520 | -4.4214830 | -1.9112150 |
| 53 | H | 4.5199000 | -2.9203530 | -0.0424490 |
| 54 | H | 3.1895750 | -0.9062900 | 0.4340680 |

SCF Done: E(UM052X) = -1377.94575346 A.U.

Zero-point correction = 0.426821 (Hartree/Particle)
Thermal correction to Energy = 0.452172
Thermal correction to Enthalpy = 0.453117
Thermal correction to Gibbs Free Energy = 0.370208
Sum of electronic and zero-point Energies = -1377.518933
Sum of electronic and thermal Energies = -1377.493581
Sum of electronic and thermal Enthalpies = -1377.492637
Sum of electronic and thermal Free Energies = -1377.575545

Low frequencies --- -10.4816 -6.3781 -0.0003 -0.0001 0.0007 3.5914
Low frequencies --- 16.6091 30.6819 33.4261

**Table S12.** Standard Orientation of the Optimized Geometry for the 2,4-isomer of **1**

| Tag | Symbol | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | C | -4.2515310 | 0.3092360 | 1.0621970 |
| 2 | C | -5.3691360 | -0.4870520 | 0.6846440 |
| 3 | C | -5.2997520 | -1.4358870 | -0.3110740 |
| 4 | C | -4.0745770 | -1.6677920 | -0.9920640 |
| 5 | C | -2.9822600 | -0.8940770 | -0.5740510 |
| 6 | C | -3.0625520 | 0.0936660 | 0.4219300 |
| 7 | C | -3.8209430 | -2.5827200 | -2.0473420 |
| 8 | C | -2.5615850 | -2.6732720 | -2.6002270 |
| 9 | C | -1.4665110 | -1.8933070 | -2.1382450 |
| 10 | C | -1.6943760 | -1.0129750 | -1.1170400 |
| 11 | C | -1.7283860 | 0.8446240 | 0.4887220 |
| 12 | C | -1.8995070 | 2.1087200 | -0.3113040 |
| 13 | C | -1.7489850 | 3.3306270 | 0.2039290 |
| 14 | C | -1.3495170 | 3.5330790 | 1.6107480 |
| 15 | C | -1.1354420 | 2.3098000 | 2.4155400 |
| 16 | C | -1.2921980 | 1.0877790 | 1.9014290 |
| 17 | O | -1.2038590 | 4.6459940 | 2.0880500 |
| 18 | H | -4.3529800 | 1.0710970 | 1.8256690 |
| 19 | H | -6.3120880 | -0.3259480 | 1.1922470 |
| 20 | H | -6.1800740 | -2.0076970 | -0.5793550 |
| 21 | H | -4.6237470 | -3.2067680 | -2.4215270 |
| 22 | H | -2.3928960 | -3.3715200 | -3.4106870 |
| 23 | H | -0.4860050 | -2.0054810 | -2.5840750 |
| 24 | H | -2.1817630 | 1.9689840 | -1.3490560 |
| 25 | H | -1.9044390 | 4.2264610 | -0.3838630 |
| 26 | H | -0.8447410 | 2.4658850 | 3.4469550 |
| 27 | H | -1.1352440 | 0.2014330 | 2.5035450 |
| 28 | C | -0.7471540 | -0.1377000 | -0.3051190 |
| 29 | N | 0.2092740 | 0.5812450 | -1.1187580 |
| 30 | N | -0.0184310 | -0.9821340 | 0.6353170 |
| 31 | C | 1.3707700 | 0.2105490 | -0.7248240 |
| 32 | C | 1.2251100 | -0.7775600 | 0.4056230 |
| 33 | C | 2.6060040 | 0.7093250 | -1.3583820 |
| 34 | C | 2.6376640 | 2.0295400 | -1.8164740 |
| 35 | C | 3.7099980 | -0.1230820 | -1.5608990 |
| 36 | C | 3.7705410 | 2.5165940 | -2.4550670 |
| 37 | H | 1.7676550 | 2.6548560 | -1.6610040 |
| 38 | C | 4.8374610 | 0.3665080 | -2.2109940 |
| 39 | H | 3.6830060 | -1.1505590 | -1.2211900 |
| 40 | C | 4.8713550 | 1.6860190 | -2.6525330 |
| 41 | H | 3.7953160 | 3.5424020 | -2.8000980 |
| 42 | H | 5.6880010 | -0.2832430 | -2.3734310 |
| 43 | H | 5.7536850 | 2.0665040 | -3.1516800 |
| 44 | C | 2.2855520 | -1.4267390 | 1.2001120 |
| 45 | C | 2.0814310 | -2.7301640 | 1.6617340 |

| | | | | |
|---|---|---|---|---|
| 46 | C | 3.4514780 | -0.7410290 | 1.5524590 |
| 47 | C | 3.0427350 | -3.3476660 | 2.4511350 |
| 48 | H | 1.1644960 | -3.2395550 | 1.3950690 |
| 49 | C | 4.4059030 | -1.3602850 | 2.3519360 |
| 50 | H | 3.6045600 | 0.2761130 | 1.2158220 |
| 51 | C | 4.2067550 | -2.6642130 | 2.7957420 |
| 52 | H | 2.8839240 | -4.3600220 | 2.8002670 |
| 53 | H | 5.3033050 | -0.8223750 | 2.6296080 |
| 54 | H | 4.9549310 | -3.1455690 | 3.4130270 |

SCF Done: E(RM052X) = -1377.96603945 A.U.

Zero-point correction = 0.430194 (Hartree/Particle)
Thermal correction to Energy = 0.454951
Thermal correction to Enthalpy = 0.455895
Thermal correction to Gibbs Free Energy = 0.373710
Sum of electronic and zero-point Energies = -1377.535846
Sum of electronic and thermal Energies = -1377.511088
Sum of electronic and thermal Enthalpies = -1377.510144
Sum of electronic and thermal Free Energies = -1377.592329

Low frequencies --- -4.8332 -0.0007 -0.0006 -0.0005 3.8120 5.8650
Low frequencies --- 21.7368 24.3175 31.5776

**Table S13.** Standard Orientation of the Transition State Between the Biradical and the 1,4-isomer of **1**

| Tag | Symbol | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | C | -3.8540140 | -1.7797300 | 0.6029080 |
| 2 | C | -5.2088350 | -1.5297710 | 0.2888290 |
| 3 | C | -5.5936180 | -0.3050070 | -0.1868690 |
| 4 | C | -4.6330190 | 0.7144780 | -0.4175110 |
| 5 | C | -3.2647820 | 0.4405480 | -0.1703030 |
| 6 | C | -2.8942630 | -0.8131200 | 0.4022920 |
| 7 | C | -5.0053530 | 2.0035980 | -0.8786860 |
| 8 | C | -4.0586200 | 2.9729980 | -1.0876130 |
| 9 | C | -2.6898210 | 2.6836600 | -0.9059850 |
| 10 | C | -2.2926020 | 1.4334430 | -0.4885730 |
| 11 | C | -1.5142040 | -1.0312350 | 0.8911620 |
| 12 | C | -0.8694900 | 1.0950360 | -0.4374800 |
| 13 | C | -0.9895180 | -0.1448480 | 1.8951770 |
| 14 | C | 0.2201180 | -0.3872810 | 2.4570780 |
| 15 | C | 0.9263720 | -1.6514260 | 2.2203200 |
| 16 | C | 0.2494000 | -2.6366600 | 1.3572330 |
| 17 | C | -0.9071170 | -2.3388520 | 0.7376480 |
| 18 | O | 2.0212820 | -1.8891290 | 2.7224760 |
| 19 | N | -0.4273520 | -0.1683320 | -0.8382910 |
| 20 | C | 0.8972460 | -0.1162270 | -0.6836240 |
| 21 | C | 1.2331410 | 1.2075060 | -0.2400180 |
| 22 | N | 0.0850910 | 1.9352120 | -0.0950790 |

| | | | | |
|---|---|---|---|---|
| 23 | C | 2.5232210 | 1.8715470 | -0.0669290 |
| 24 | C | 1.7397450 | -1.2747090 | -1.0331930 |
| 25 | C | 3.6754840 | 1.4692810 | -0.7555190 |
| 26 | C | 4.8692030 | 2.1567480 | -0.5799540 |
| 27 | C | 4.9316460 | 3.2466630 | 0.2845530 |
| 28 | C | 3.7861870 | 3.6628270 | 0.9601010 |
| 29 | C | 2.5871200 | 2.9899290 | 0.7773480 |
| 30 | C | 1.3163030 | -2.1251550 | -2.0608660 |
| 31 | C | 2.0460420 | -3.2643230 | -2.3766740 |
| 32 | C | 3.2066110 | -3.5708930 | -1.6699130 |
| 33 | C | 3.6308490 | -2.7313950 | -0.6434550 |
| 34 | C | 2.9044930 | -1.5898730 | -0.3247050 |
| 35 | H | -3.5759410 | -2.7239600 | 1.0545380 |
| 36 | H | -5.9444490 | -2.3051600 | 0.4596030 |
| 37 | H | -6.6360860 | -0.0949600 | -0.3947890 |
| 38 | H | -6.0547150 | 2.2096440 | -1.0533810 |
| 39 | H | -4.3541970 | 3.9578060 | -1.4256810 |
| 40 | H | -1.9309160 | 3.4224950 | -1.1278180 |
| 41 | H | -1.5445980 | 0.7548850 | 2.1264910 |
| 42 | H | 0.6755730 | 0.2966440 | 3.1614630 |
| 43 | H | 0.7627410 | -3.5775660 | 1.2063110 |
| 44 | H | -1.3686590 | -3.0278440 | 0.0414460 |
| 45 | H | 3.6291120 | 0.6345630 | -1.4410410 |
| 46 | H | 5.7518110 | 1.8431700 | -1.1228700 |
| 47 | H | 5.8664560 | 3.7748580 | 0.4243580 |
| 48 | H | 3.8283360 | 4.5160470 | 1.6252780 |
| 49 | H | 1.6838420 | 3.3109870 | 1.2783500 |
| 50 | H | 0.4071440 | -1.8818140 | -2.5952920 |
| 51 | H | 1.7101120 | -3.9130390 | -3.1762110 |
| 52 | H | 3.7735790 | -4.4604950 | -1.9142320 |
| 53 | H | 4.5202410 | -2.9719420 | -0.0750910 |
| 54 | H | 3.2186340 | -0.9659820 | 0.5016630 |

SCF Done: E(UM052X) = -1377.93714693 A.U.

Zero-point correction = 0.427376 (Hartree/Particle)
Thermal correction to Energy = 0.451884
Thermal correction to Enthalpy = 0.452828
Thermal correction to Gibbs Free Energy = 0.372846
Sum of electronic and zero-point Energies = -1377.509771
Sum of electronic and thermal Energies = -1377.485263
Sum of electronic and thermal Enthalpies = -1377.484319
Sum of electronic and thermal Free Energies = -1377.564301

Low frequencies --- -631.7548 -8.8125 -5.7833 -0.0009 -0.0007 -0.0004
Low frequencies --- 8.0626 21.8419 39.0813
****** 1 imaginary frequencies (negative Signs) ******

**Table S14.** Standard Orientation of the Transition State Between the Biradical and the 2,4-isomer of **1**

| Tag | Symbol | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | C | 3.9385630 | 0.2564920 | 2.0116690 |
| 2 | C | 5.2846340 | 0.4776870 | 1.6306610 |
| 3 | C | 5.6619920 | 0.4007240 | 0.3150560 |
| 4 | C | 4.6991440 | 0.1483070 | -0.6963210 |
| 5 | C | 3.3453990 | -0.0005780 | -0.3151180 |
| 6 | C | 2.9817570 | 0.0056860 | 1.0584590 |
| 7 | C | 5.0286890 | 0.0317080 | -2.0708230 |
| 8 | C | 4.0527160 | -0.2133360 | -3.0029000 |
| 9 | C | 2.6926600 | -0.2992170 | -2.6216970 |
| 10 | C | 2.3394870 | -0.1731040 | -1.3007960 |
| 11 | C | 1.5950800 | -0.4035290 | 1.4110090 |
| 12 | C | 0.9215570 | -0.0706980 | -0.8822140 |
| 13 | C | 1.3336240 | -1.8204510 | 1.5207720 |
| 14 | C | 0.1477160 | -2.2837070 | 1.9756620 |
| 15 | C | -0.9315120 | -1.3552030 | 2.3244820 |
| 16 | C | -0.5890620 | 0.0715470 | 2.3119470 |
| 17 | C | 0.6523500 | 0.5055680 | 1.9530030 |
| 18 | O | -2.0651090 | -1.7445790 | 2.6085640 |
| 19 | N | 0.3552190 | 1.1805090 | -0.7080290 |
| 20 | C | -0.9267580 | 0.9370270 | -0.5793550 |
| 21 | C | -1.1477700 | -0.5223920 | -0.7690610 |
| 22 | N | 0.0249170 | -1.0910490 | -0.9832080 |
| 23 | C | -2.3995000 | -1.2724450 | -0.8683980 |
| 24 | C | -1.8882360 | 1.9966800 | -0.2554620 |
| 25 | C | -3.5573580 | -0.6890310 | -1.4001850 |
| 26 | C | -4.7136230 | -1.4436780 | -1.5490470 |
| 27 | C | -4.7292230 | -2.7821210 | -1.1647560 |
| 28 | C | -3.5791710 | -3.3708830 | -0.6439780 |
| 29 | C | -2.4187220 | -2.6239990 | -0.5015730 |
| 30 | C | -1.6240830 | 3.3029550 | -0.6830730 |
| 31 | C | -2.4961940 | 4.3341580 | -0.3590630 |
| 32 | C | -3.6311340 | 4.0755330 | 0.4062460 |
| 33 | C | -3.8891900 | 2.7810580 | 0.8515190 |
| 34 | C | -3.0250750 | 1.7432820 | 0.5237490 |
| 35 | H | 3.6686130 | 0.2513280 | 3.0605490 |
| 36 | H | 6.0234330 | 0.6777950 | 2.3960000 |
| 37 | H | 6.6988730 | 0.5328270 | 0.0299860 |
| 38 | H | 6.0647980 | 0.1322130 | -2.3714560 |
| 39 | H | 4.3153190 | -0.3142010 | -4.0480620 |
| 40 | H | 1.9247640 | -0.4343630 | -3.3722840 |
| 41 | H | 2.1142800 | -2.5001560 | 1.2019800 |
| 42 | H | -0.0680840 | -3.3408740 | 2.0583460 |
| 43 | H | -1.3561310 | 0.7563820 | 2.6482190 |
| 44 | H | 0.8911610 | 1.5609460 | 1.9483100 |
| 45 | H | -3.5431760 | 0.3449950 | -1.7177450 |

| | | | | |
|---|---|---|---|---|
| 46 | H | -5.6007310 | -0.9880900 | -1.9696840 |
| 47 | H | -5.6348290 | -3.3655720 | -1.2732340 |
| 48 | H | -3.5894770 | -4.4107240 | -0.3439330 |
| 49 | H | -1.5153180 | -3.0662780 | -0.1048300 |
| 50 | H | -0.7316210 | 3.4880100 | -1.2660420 |
| 51 | H | -2.2898820 | 5.3403710 | -0.7009540 |
| 52 | H | -4.3087720 | 4.8808000 | 0.6601790 |
| 53 | H | -4.7604650 | 2.5787160 | 1.4611860 |
| 54 | H | -3.2153790 | 0.7420380 | 0.8911430 |

SCF Done: E(UM052X) = -1377.90452448 A.U.

Zero-point correction = 0.428200 (Hartree/Particle)
Thermal correction to Energy = 0.452834
Thermal correction to Enthalpy = 0.453778
Thermal correction to Gibbs Free Energy = 0.372716
Sum of electronic and zero-point Energies = -1377.476325
Sum of electronic and thermal Energies = -1377.451690
Sum of electronic and thermal Enthalpies = -1377.450746
Sum of electronic and thermal Free Energies = -1377.531809

Low frequencies --- -408.5235 -8.8708 -4.2988 -0.0004 -0.0002 0.0003
Low frequencies --- 6.7952 11.8141 37.2919
****** 1 imaginary frequencies (negative Signs) ******

**Table S15.** Standard Orientation of the Optimized Geometry for the 1,4-isomer of **2**

| Tag | Symbol | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | C | 1.7898470 | -1.1649870 | -0.4620410 |
| 2 | C | 2.3845850 | -1.4283570 | -1.6999840 |
| 3 | C | -3.6490530 | -0.2220770 | -0.8826740 |
| 4 | C | -4.8859170 | 0.4496730 | -0.9623650 |
| 5 | C | -4.9609430 | 1.7963970 | -0.7185930 |
| 6 | C | -3.7947850 | 2.5289990 | -0.3932060 |
| 7 | C | -2.5479340 | 1.8506580 | -0.3220010 |
| 8 | C | -2.4935010 | 0.4530300 | -0.5647450 |
| 9 | C | -3.8360440 | 3.9239930 | -0.1371190 |
| 10 | C | -2.6916320 | 4.6148490 | 0.1690940 |
| 11 | C | -1.4488310 | 3.9510030 | 0.2255650 |
| 12 | C | -1.3784740 | 2.5998140 | -0.0171690 |
| 13 | C | -0.1088200 | 1.8959470 | -0.0080490 |
| 14 | N | -0.0450930 | 0.5501890 | -0.2260670 |
| 15 | C | 1.2966560 | 0.1997000 | -0.1791520 |
| 16 | C | 1.9705010 | 1.3831290 | 0.0620860 |
| 17 | N | 1.0808020 | 2.4208160 | 0.1645910 |
| 18 | C | 3.4179330 | 1.6252790 | 0.1865660 |
| 19 | C | 4.3280580 | 0.6034600 | 0.4772790 |
| 20 | C | 5.6860650 | 0.8826630 | 0.5832450 |

| | | | | |
|---|---|---|---|---|
| 21 | C | 6.1544170 | 2.1814190 | 0.4090240 |
| 22 | C | 5.2518360 | 3.2045950 | 0.1315360 |
| 23 | C | 3.8946930 | 2.9302490 | 0.0218030 |
| 24 | C | 2.8214870 | -2.7101730 | -2.0108190 |
| 25 | C | 2.6666540 | -3.7406950 | -1.0868630 |
| 26 | C | 2.1027920 | -3.4789720 | 0.1587540 |
| 27 | C | 1.6764210 | -2.1933080 | 0.4769550 |
| 28 | O | -1.6534580 | -4.4986930 | -0.7323620 |
| 29 | C | -1.5207240 | -2.6208270 | 0.7066070 |
| 30 | C | -1.3406260 | -1.2418910 | 0.8232350 |
| 31 | C | -1.1880840 | -0.3548320 | -0.4076820 |
| 32 | C | -0.9826630 | -1.1380350 | -1.6824990 |
| 33 | C | -1.1482660 | -2.4569850 | -1.7863200 |
| 34 | C | -1.4670570 | -3.3003490 | -0.6178160 |
| 35 | C | -1.3299900 | -0.6556720 | 2.0881490 |
| 36 | C | -1.4846020 | -1.4425180 | 3.2218720 |
| 37 | C | -1.6652550 | -2.8221340 | 3.1053400 |
| 38 | C | -1.6847700 | -3.4069400 | 1.8492950 |
| 39 | H | 2.4928190 | -0.6188490 | -2.4117370 |
| 40 | H | -3.6139650 | -1.2885410 | -1.0670360 |
| 41 | H | -5.7764460 | -0.1115740 | -1.2138860 |
| 42 | H | -5.9091450 | 2.3178430 | -0.7726270 |
| 43 | H | -4.7913590 | 4.4324710 | -0.1898080 |
| 44 | H | -2.7350130 | 5.6788610 | 0.3633340 |
| 45 | H | -0.5354440 | 4.4858520 | 0.4496590 |
| 46 | H | 3.9754580 | -0.4071870 | 0.6325570 |
| 47 | H | 6.3787640 | 0.0818470 | 0.8109530 |
| 48 | H | 7.2126250 | 2.3950950 | 0.4940170 |
| 49 | H | 5.6060910 | 4.2195340 | -0.0007590 |
| 50 | H | 3.1829710 | 3.7171640 | -0.1889540 |
| 51 | H | 3.2756980 | -2.9069610 | -2.9737780 |
| 52 | H | 2.9933210 | -4.7431780 | -1.3328300 |
| 53 | H | 1.9914910 | -4.2755590 | 0.8835830 |
| 54 | H | 1.2458980 | -1.9852730 | 1.4484460 |
| 55 | H | -0.7328870 | -0.5316650 | -2.5465080 |
| 56 | H | -1.0332240 | -2.9759110 | -2.7291100 |
| 57 | H | -1.1893470 | 0.4151380 | 2.1819840 |
| 58 | H | -1.4648860 | -0.9795150 | 4.2004190 |
| 59 | H | -1.7865690 | -3.4304370 | 3.9924870 |
| 60 | H | -1.8130070 | -4.4732800 | 1.7149630 |

SCF Done: E(RM052X) = -1531.66204600 A.U.

Zero-point correction = 0.479608 (Hartree/Particle)
Thermal correction to Energy = 0.506739
Thermal correction to Enthalpy = 0.507683
Thermal correction to Gibbs Free Energy = 0.421193
Sum of electronic and zero-point Energies = -1531.182438
Sum of electronic and thermal Energies = -1531.155307
Sum of electronic and thermal Enthalpies = -1531.154363

Sum of electronic and thermal Free Energies = -1531.240853

Low frequencies --- -10.2677 -2.1523 -0.0002 0.0007 0.0008 5.9820
Low frequencies --- 21.3646 28.3038 34.9806

**Table S16.** Standard Orientation of the Optimized Geometry for the Biradical Species of **2**

| Tag | Symbol | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | C | -0.0774420 | 4.4720350 | -0.4878010 |
| 2 | C | -0.7771790 | 3.4965330 | -1.1784880 |
| 3 | C | 1.1803030 | 4.1744450 | 0.0486600 |
| 4 | C | 1.7435870 | 2.9227330 | -0.1303460 |
| 5 | C | -1.9503540 | 0.7400990 | 1.4596250 |
| 6 | C | -1.4627600 | 2.0237930 | 1.7442840 |
| 7 | C | 4.0457160 | 1.0091700 | -1.1174070 |
| 8 | C | 5.3832310 | 0.6734940 | -0.8259000 |
| 9 | C | 5.6541630 | -0.4351460 | -0.0719750 |
| 10 | C | 4.6030790 | -1.2351710 | 0.4417320 |
| 11 | C | 3.2471710 | -0.8689750 | 0.2052280 |
| 12 | C | 2.9886090 | 0.2662970 | -0.6315760 |
| 13 | C | 4.9025440 | -2.4165730 | 1.1682940 |
| 14 | C | 3.9024730 | -3.2272800 | 1.6308880 |
| 15 | C | 2.5574640 | -2.8569080 | 1.4328480 |
| 16 | C | 2.2242980 | -1.6895890 | 0.7806100 |
| 17 | C | 0.7943690 | -1.3512290 | 0.7294980 |
| 18 | N | 0.2882070 | -0.1697530 | 1.1860270 |
| 19 | C | -1.0137390 | -0.2684160 | 0.9644440 |
| 20 | C | -1.2671230 | -1.5800440 | 0.3280970 |
| 21 | N | -0.1148950 | -2.2432690 | 0.2682990 |
| 22 | C | -2.4958300 | -2.1524750 | -0.2172760 |
| 23 | C | -2.6808760 | -3.5402070 | -0.1559710 |
| 24 | C | -3.8194220 | -4.1161860 | -0.7013290 |
| 25 | C | -4.7694290 | -3.3176150 | -1.3359980 |
| 26 | C | -4.5747970 | -1.9416870 | -1.4284900 |
| 27 | C | -3.4462240 | -1.3542180 | -0.8700890 |
| 28 | C | -2.3069270 | 2.9962070 | 2.2582180 |
| 29 | C | -3.6444760 | 2.6992490 | 2.5138190 |
| 30 | C | -4.1300790 | 1.4197970 | 2.2604140 |
| 31 | C | -3.2915260 | 0.4428820 | 1.7382580 |
| 32 | O | -2.1886470 | 1.4166290 | -2.4076640 |
| 33 | C | -0.3895760 | -0.0888530 | -2.2591080 |
| 34 | C | 0.8973380 | -0.3299950 | -1.8394900 |
| 35 | C | 1.6227280 | 0.6118580 | -1.0901980 |
| 36 | C | 1.0682800 | 1.9324580 | -0.8702600 |
| 37 | C | -0.2182340 | 2.2323570 | -1.3684150 |
| 38 | C | -1.0275200 | 1.1959660 | -2.0475330 |
| 39 | H | -0.5102880 | 5.4540720 | -0.3442710 |
| 40 | H | -1.7696890 | 3.6726180 | -1.5716330 |

| | | | | |
|---|---|---|---|---|
| 41 | H | 1.7171460 | 4.9244010 | 0.6160780 |
| 42 | H | 2.7034990 | 2.6951240 | 0.3112470 |
| 43 | H | -0.4198590 | 2.2374860 | 1.5513590 |
| 44 | H | 3.8357830 | 1.8513940 | -1.7654750 |
| 45 | H | 6.1860930 | 1.2792380 | -1.2256310 |
| 46 | H | 6.6762970 | -0.7286710 | 0.1362760 |
| 47 | H | 5.9432380 | -2.6719290 | 1.3297040 |
| 48 | H | 4.1349690 | -4.1401140 | 2.1635840 |
| 49 | H | 1.7581910 | -3.4752040 | 1.8201890 |
| 50 | H | -1.9215340 | -4.1441490 | 0.3229810 |
| 51 | H | -3.9654000 | -5.1871380 | -0.6380770 |
| 52 | H | -5.6544550 | -3.7688750 | -1.7668760 |
| 53 | H | -5.2968650 | -1.3227490 | -1.9452640 |
| 54 | H | -3.2829380 | -0.2887680 | -0.9756840 |
| 55 | H | -1.9204360 | 3.9880810 | 2.4572450 |
| 56 | H | -4.3030400 | 3.4593970 | 2.9153160 |
| 57 | H | -5.1631130 | 1.1779810 | 2.4760660 |
| 58 | H | -3.6719810 | -0.5544400 | 1.5680180 |
| 59 | H | -0.9630970 | -0.8384650 | -2.7878540 |
| 60 | H | 1.3524250 | -1.2939900 | -2.0298900 |

SCF Done: E(UM052X) = -1531.59788757 A.U.

Zero-point correction = 0.475685 (Hartree/Particle)
Thermal correction to Energy = 0.503375
Thermal correction to Enthalpy = 0.504319
Thermal correction to Gibbs Free Energy = 0.417554
Sum of electronic and zero-point Energies = -1531.122203
Sum of electronic and thermal Energies = -1531.094513
Sum of electronic and thermal Enthalpies = -1531.093568
Sum of electronic and thermal Free Energies = -1531.180333

Low frequencies --- -9.0736 -7.2587 -4.6517 -0.0007 -0.0006 0.0001
Low frequencies --- 21.4203 30.6512 44.5760

**Table S17.** Standard Orientation of the Optimized Geometry for the 2,4-isomer of **2**

| Tag | Symbol | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | C | -3.9353650 | -0.7925770 | 1.5067060 |
| 2 | C | -5.0132440 | -1.6072330 | 1.0621000 |
| 3 | C | -4.9823410 | -2.2867920 | -0.1354840 |
| 4 | C | -3.8347250 | -2.2099590 | -0.9688430 |
| 5 | C | -2.7713300 | -1.4350400 | -0.4833300 |
| 6 | C | -2.8175290 | -0.7109240 | 0.7211800 |
| 7 | C | -3.6386820 | -2.8105810 | -2.2411380 |
| 8 | C | -2.4599990 | -2.6145080 | -2.9271950 |
| 9 | C | -1.3890780 | -1.8415720 | -2.4000570 |
| 10 | C | -1.5594420 | -1.2658830 | -1.1723730 |
| 11 | H | -4.0166900 | -0.2399110 | 2.4348370 |

| | | | | |
|---|---|---|---|---|
| 12 | H | -5.8972240 | -1.6778880 | 1.6839470 |
| 13 | H | -5.8346470 | -2.8786670 | -0.4473100 |
| 14 | H | -4.4248530 | -3.4169940 | -2.6749750 |
| 15 | H | -2.3364900 | -3.0722120 | -3.9009620 |
| 16 | H | -0.4690730 | -1.7238540 | -2.9587570 |
| 17 | C | -0.5955370 | -0.5162740 | -0.2662530 |
| 18 | N | 0.2254100 | 0.4667110 | -0.9294690 |
| 19 | N | 0.2771940 | -1.4972450 | 0.3780420 |
| 20 | C | 1.4428760 | 0.1414670 | -0.6952490 |
| 21 | C | 1.4755630 | -1.1090310 | 0.1458500 |
| 22 | C | 2.5727210 | 0.9248530 | -1.2290420 |
| 23 | C | 2.4319520 | 2.3122570 | -1.3291970 |
| 24 | C | 3.7430000 | 0.3094950 | -1.6810260 |
| 25 | C | 3.4615550 | 3.0770730 | -1.8615260 |
| 26 | H | 1.5128690 | 2.7696000 | -0.9838990 |
| 27 | C | 4.7656820 | 1.0796750 | -2.2237440 |
| 28 | H | 3.8490020 | -0.7660480 | -1.6176390 |
| 29 | C | 4.6287460 | 2.4621150 | -2.3088700 |
| 30 | H | 3.3537610 | 4.1522300 | -1.9282930 |
| 31 | H | 5.6680720 | 0.5996920 | -2.5804170 |
| 32 | H | 5.4301930 | 3.0599570 | -2.7246780 |
| 33 | C | 2.6493810 | -1.8207800 | 0.6863770 |
| 34 | C | 2.6124800 | -3.2150190 | 0.7760800 |
| 35 | C | 3.7623220 | -1.1237590 | 1.1646930 |
| 36 | C | 3.6882000 | -3.9059460 | 1.3183520 |
| 37 | H | 1.7342080 | -3.7368460 | 0.4184040 |
| 38 | C | 4.8316450 | -1.8198510 | 1.7173590 |
| 39 | H | 3.7853320 | -0.0425930 | 1.1158740 |
| 40 | C | 4.7993360 | -3.2094810 | 1.7883380 |
| 41 | H | 3.6595660 | -4.9866370 | 1.3780250 |
| 42 | H | 5.6883690 | -1.2759390 | 2.0942930 |
| 43 | H | 5.6368820 | -3.7489090 | 2.2128210 |
| 44 | C | -1.5639190 | 0.1477830 | 0.8466730 |
| 45 | C | -1.8603990 | 1.5904160 | 0.4549430 |
| 46 | C | -0.9168890 | 0.0236860 | 2.1952790 |
| 47 | C | -2.6898450 | 1.8778150 | -0.6309500 |
| 48 | C | -1.2627100 | 2.6542220 | 1.1390340 |
| 49 | C | -0.3739380 | 1.0456240 | 2.8601820 |
| 50 | H | -0.8607370 | -0.9827850 | 2.5907470 |
| 51 | C | -2.9018320 | 3.1906950 | -1.0295610 |
| 52 | H | -3.1669630 | 1.0718200 | -1.1726220 |
| 53 | C | -1.4771640 | 3.9738140 | 0.7342390 |
| 54 | C | -0.4191480 | 2.4243630 | 2.3423860 |
| 55 | H | 0.1262340 | 0.9104410 | 3.8108420 |
| 56 | C | -2.2922670 | 4.2461400 | -0.3517820 |
| 57 | H | -3.5479630 | 3.3914880 | -1.8752060 |
| 58 | H | -0.9946700 | 4.7598240 | 1.3007960 |
| 59 | H | -2.4616410 | 5.2679490 | -0.6667460 |
| 60 | O | 0.1734720 | 3.3327900 | 2.9007500 |

| | | | |
|---|---|---|---|
| SCF Done: E(RM052X) | = | -1531.61840083 | A.U. |

| | | |
|---|---|---|
| Zero-point correction | = | 0.478261 (Hartree/Particle) |
| Thermal correction to Energy | = | 0.505672 |
| Thermal correction to Enthalpy | = | 0.506616 |
| Thermal correction to Gibbs Free Energy | = | 0.417345 |
| Sum of electronic and zero-point Energies | = | -1531.140140 |
| Sum of electronic and thermal Energies | = | -1531.112729 |
| Sum of electronic and thermal Enthalpies | = | -1531.111785 |
| Sum of electronic and thermal Free Energies | = | -1531.201056 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Low frequencies --- | -8.0179 | -2.3913 | -0.0008 | -0.0004 | 0.0004 | 4.0778 |
| Low frequencies --- | 8.7344 | 19.6277 | 29.3377 | | | |

**Table S18.** Standard Orientation of the Transition State Between the Biradical and the 1,4-isomer of **2**

| Tag | Symbol | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | C | -0.3993760 | 4.3854180 | -0.4065300 |
| 2 | C | -1.0503160 | 3.3653210 | -1.0864140 |
| 3 | C | 0.8692230 | 4.1616830 | 0.1265170 |
| 4 | C | 1.4933990 | 2.9314900 | -0.0300730 |
| 5 | C | -1.7690020 | 0.8827240 | 1.2273370 |
| 6 | C | -1.1838060 | 1.8355370 | 2.0749290 |
| 7 | C | 3.8738970 | 1.1905960 | -1.0496990 |
| 8 | C | 5.2416920 | 0.9069990 | -0.8434690 |
| 9 | C | 5.6197810 | -0.2378070 | -0.1947800 |
| 10 | C | 4.6457730 | -1.1471430 | 0.2911710 |
| 11 | C | 3.2702350 | -0.8424920 | 0.1265500 |
| 12 | C | 2.8957610 | 0.3421450 | -0.5780650 |
| 13 | C | 5.0150050 | -2.3682350 | 0.9129290 |
| 14 | C | 4.0595130 | -3.2541740 | 1.3351490 |
| 15 | C | 2.6895050 | -2.9427010 | 1.1981950 |
| 16 | C | 2.2969670 | -1.7509060 | 0.6367950 |
| 17 | C | 0.8706540 | -1.4107270 | 0.5600440 |
| 18 | N | 0.4079250 | -0.1706330 | 0.9564190 |
| 19 | C | -0.9098630 | -0.2170680 | 0.7398110 |
| 20 | C | -1.2078620 | -1.5231320 | 0.1961160 |
| 21 | N | -0.0626220 | -2.2635930 | 0.1692820 |
| 22 | C | -2.4755850 | -2.2123430 | -0.1098900 |
| 23 | C | -2.6808970 | -3.4716800 | 0.4670980 |
| 24 | C | -3.8443870 | -4.1835970 | 0.2064120 |
| 25 | C | -4.8033580 | -3.6610220 | -0.6573320 |
| 26 | C | -4.5874170 | -2.4279950 | -1.2655700 |
| 27 | C | -3.4314740 | -1.7032480 | -0.9960550 |
| 28 | C | -1.9233950 | 2.9022480 | 2.5628670 |
| 29 | C | -3.2671230 | 3.0412280 | 2.2217270 |
| 30 | C | -3.8585780 | 2.0963490 | 1.3921200 |

| | | | | |
|---|---|---|---|---|
| 31 | C | -3.1197950 | 1.0252630 | 0.8978720 |
| 32 | O | -2.3464620 | 1.1920180 | -2.2695390 |
| 33 | C | -0.4702590 | -0.2273040 | -2.1219000 |
| 34 | C | 0.8500030 | -0.3547400 | -1.7954760 |
| 35 | C | 1.4698040 | 0.5791000 | -0.9220610 |
| 36 | C | 0.8657210 | 1.9081040 | -0.7499830 |
| 37 | C | -0.4244100 | 2.1350280 | -1.2576130 |
| 38 | C | -1.1853020 | 1.0375140 | -1.9105410 |
| 39 | H | -0.8860250 | 5.3422040 | -0.2673390 |
| 40 | H | -2.0545270 | 3.4832670 | -1.4709120 |
| 41 | H | 1.3683340 | 4.9449450 | 0.6831210 |
| 42 | H | 2.4583320 | 2.7550000 | 0.4238290 |
| 43 | H | -0.1401880 | 1.7242150 | 2.3351310 |
| 44 | H | 3.5895400 | 2.0705470 | -1.6126040 |
| 45 | H | 5.9877360 | 1.5930850 | -1.2232540 |
| 46 | H | 6.6679200 | -0.4720260 | -0.0512800 |
| 47 | H | 6.0685240 | -2.5930210 | 1.0295480 |
| 48 | H | 4.3494910 | -4.1919650 | 1.7912780 |
| 49 | H | 1.9292420 | -3.6264770 | 1.5520850 |
| 50 | H | -1.9189090 | -3.8759730 | 1.1201740 |
| 51 | H | -3.9999980 | -5.1488070 | 0.6717770 |
| 52 | H | -5.7087320 | -4.2176120 | -0.8649140 |
| 53 | H | -5.3160080 | -2.0289490 | -1.9600430 |
| 54 | H | -3.2573930 | -0.7617240 | -1.5031930 |
| 55 | H | -1.4494740 | 3.6273450 | 3.2134890 |
| 56 | H | -3.8460660 | 3.8734600 | 2.6027040 |
| 57 | H | -4.9028920 | 2.1881490 | 1.1206810 |
| 58 | H | -3.6050650 | 0.3069720 | 0.2575780 |
| 59 | H | -0.9863670 | -0.9833460 | -2.6996970 |
| 60 | H | 1.3987560 | -1.2484420 | -2.0608850 |

SCF Done: E(UM052X) = -1531.59159573 A.U.

Zero-point correction = 0.477137 (Hartree/Particle)
Thermal correction to Energy = 0.503682
Thermal correction to Enthalpy = 0.504626
Thermal correction to Gibbs Free Energy = 0.421826
Sum of electronic and zero-point Energies = -1531.114459
Sum of electronic and thermal Energies = -1531.087914
Sum of electronic and thermal Enthalpies = -1531.086970
Sum of electronic and thermal Free Energies = -1531.169770

Low frequencies --- -167.0667 -7.2100 -6.1901 -0.0007 0.0002 0.0005
Low frequencies --- 9.6182 33.3842 50.3451
****** 1 imaginary frequencies (negative Signs) ******

**Table S19.** Standard Orientation of the Transition State Between the Biradical and the 2,4-isomer of **2**

| Tag | Symbol | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | C | 0.4542530 | 4.4382030 | -0.4926970 |
| 2 | C | -0.4555080 | 3.5479450 | -1.0488590 |
| 3 | C | 1.7169160 | 3.9858710 | -0.1078590 |
| 4 | C | 2.0778450 | 2.6575260 | -0.2918940 |
| 5 | C | -2.1800930 | 0.8560330 | 1.2712960 |
| 6 | C | -1.8043500 | 2.1693390 | 1.5879670 |
| 7 | C | 3.9569680 | 0.3311870 | -1.7201970 |
| 8 | C | 5.2966200 | -0.0365180 | -1.4551210 |
| 9 | C | 5.6083440 | -0.7827400 | -0.3483860 |
| 10 | C | 4.5915450 | -1.2108430 | 0.5418370 |
| 11 | C | 3.2480830 | -0.8539270 | 0.2650980 |
| 12 | C | 2.9445660 | -0.0683430 | -0.8793540 |
| 13 | C | 4.8645640 | -1.9876670 | 1.6963350 |
| 14 | C | 3.8461400 | -2.3907800 | 2.5201230 |
| 15 | C | 2.5052190 | -2.0475600 | 2.2289220 |
| 16 | C | 2.2063980 | -1.2864790 | 1.1262770 |
| 17 | C | 0.7974690 | -0.9889820 | 0.7719170 |
| 18 | N | 0.1274270 | 0.1248660 | 1.2046560 |
| 19 | C | -1.1286070 | -0.0855210 | 0.8606050 |
| 20 | C | -1.2057980 | -1.4311230 | 0.2323200 |
| 21 | N | -0.0024330 | -1.9799610 | 0.2809560 |
| 22 | C | -2.3578670 | -2.1857190 | -0.2866100 |
| 23 | C | -2.3621950 | -3.5766070 | -0.1352220 |
| 24 | C | -3.4172590 | -4.3314880 | -0.6323310 |
| 25 | C | -4.4684510 | -3.7080380 | -1.2990700 |
| 26 | C | -4.4578220 | -2.3255750 | -1.4730990 |
| 27 | C | -3.4110210 | -1.5627290 | -0.9703950 |
| 28 | C | -2.7494710 | 3.0842920 | 2.0264160 |
| 29 | C | -4.0802630 | 2.6997160 | 2.1768300 |
| 30 | C | -4.4543650 | 1.3890960 | 1.9005060 |
| 31 | C | -3.5123490 | 0.4695540 | 1.4529760 |
| 32 | O | -2.2690800 | 1.6195340 | -1.9936870 |
| 33 | C | -0.6447000 | -0.0862850 | -2.0523330 |
| 34 | C | 0.6652500 | -0.4498660 | -1.8680000 |
| 35 | C | 1.5352570 | 0.3511310 | -1.1105550 |
| 36 | C | 1.1783060 | 1.7549280 | -0.8722670 |
| 37 | C | -0.1011700 | 2.2151840 | -1.2327050 |
| 38 | C | -1.1134770 | 1.2742600 | -1.7753170 |
| 39 | H | 0.1818360 | 5.4759670 | -0.3478150 |
| 40 | H | -1.4557020 | 3.8497690 | -1.3312710 |
| 41 | H | 2.4240910 | 4.6728670 | 0.3398080 |
| 42 | H | 3.0564820 | 2.3141480 | 0.0150440 |
| 43 | H | -0.7643760 | 2.4490040 | 1.4885710 |
| 44 | H | 3.7246800 | 0.9401100 | -2.5855790 |
| 45 | H | 6.0771370 | 0.2840570 | -2.1331870 |
| 46 | H | 6.6357760 | -1.0562990 | -0.1387290 |

| | | | | |
|---|---|---|---|---|
| 47 | H | 5.8908630 | -2.2611480 | 1.9116090 |
| 48 | H | 4.0616460 | -2.9861370 | 3.3981850 |
| 49 | H | 1.7053460 | -2.3911940 | 2.8721400 |
| 50 | H | -1.5292510 | -4.0449840 | 0.3720240 |
| 51 | H | -3.4175210 | -5.4064090 | -0.5022490 |
| 52 | H | -5.2891930 | -4.2969960 | -1.6891980 |
| 53 | H | -5.2626680 | -1.8387920 | -2.0092380 |
| 54 | H | -3.3918760 | -0.4909970 | -1.1355060 |
| 55 | H | -2.4466500 | 4.0986500 | 2.2552020 |
| 56 | H | -4.8183690 | 3.4147690 | 2.5185500 |
| 57 | H | -5.4814010 | 1.0758770 | 2.0390220 |
| 58 | H | -3.8113470 | -0.5523790 | 1.2700800 |
| 59 | H | -1.3412370 | -0.7428180 | -2.5557730 |
| 60 | H | 0.9955540 | -1.4425080 | -2.1443740 |

SCF Done: E(UM052X) = -1531.59472206 A.U.

Zero-point correction = 0.477231 (Hartree/Particle)
Thermal correction to Energy = 0.503816
Thermal correction to Enthalpy = 0.504760
Thermal correction to Gibbs Free Energy = 0.421350
Sum of electronic and zero-point Energies = -1531.117492
Sum of electronic and thermal Energies = -1531.090906
Sum of electronic and thermal Enthalpies = -1531.089962
Sum of electronic and thermal Free Energies = -1531.173372

Low frequencies --- -61.4628 -6.1745 -4.8056 -0.0002 0.0000 0.0003
Low frequencies --- 6.5184 25.6403 39.6834
****** 1 imaginary frequencies (negative Signs) ******

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