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# Access to fused π-extended acridone derivatives through a regioselective oxidative demethylation

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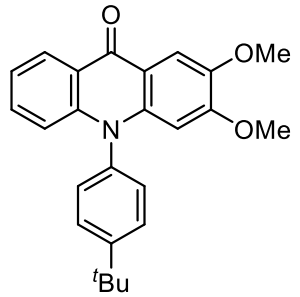
## 1. General remarks

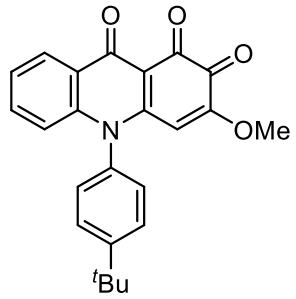
All reagents and solvents were commercially available and were used without further purification unless otherwise noted. For thin layer chromatography Silica gel 60 F254 plates from Merck were used and examined under UV-light irradiation (254 nm and 365 nm). Flash column chromatography was performed on silica gel (particle size: 200-300 mesh). Melting points were measured with a MPA100 OptiMelt. IR-Spectra were recorded as KBr-pellets on a Bruker VERTEX 80V spectrometer. NMR spectra were taken on Bruker AVANCE III HD (600 MHz). Chemical shifts ($\delta$) are reported in parts per million (ppm) relative to traces of $CHCl_3$ and DMSO in the corresponding deuterated solvents. HRMS experiments were carried out on a ThermoFisher LTQ Orbitrap XL. Absorption spectra were recorded on a Shimadzu UV2600. Emission spectra, absolute quantum yields, as well as fluorescence lifetimes were measured on FluoroMax-4 spectrometer equipped with an integral sphere and a time-correlated single photon counting system with a NanoLED laser. Crystal structure analysis was accomplished with a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. Cyclic voltammagrams were obtained using a glassy carbon working electrode, a platinum counter electrode, and a Ag reference electrode tested on CHI660E station. 2,3-dimethoxyacridone was synthesized according to the reported method. [S1]

## 2. Experimental section



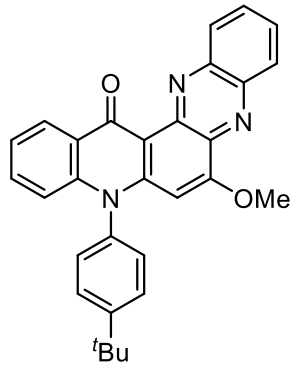

***N*-(4-*tert*-butylphenyl)-2,3-dimethoxyacridone 2**

A 120 mL screw capped glass vial was charged with 2,3-dimethoxyacridone (1.13 g, 4.43 mmol), 4-*tert*-butyl-1-bromobenzene (1.22 g, 5,76 mmol), CuI (83 mg, 0.44 mmol), 2,2,6,6-tetramethylheptane-3,5-dione (170 mg, 0.89 mmol), $K_2CO_3$ (0.92 g, 6.65 mmol) and dry DMF (9 mL). The mixture was heated in an oil bath at 160 ºC for 48 hours. After cooling down to room temperature, the mixture was diluted with dichloromethane (200 mL) and washed with water (6×200 mL) and dried over $Na_2SO_4$. The solvent was removed by rotatory evaporation and the crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate 10:1) to give the product as light yellow solid (1.10 g, 64%). m. p. : 262-264 ºC.$^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) = 8.59 (dd, $J$ = 8.0, 1.3 Hz, 1H), 7.96 (s, 1H), 7.70 (d, $J$ = 8.4 Hz, 2H), 7.47 (ddd, $J$ = 8.5, 7.1, 1.5 Hz, 1H), 7.33 - 7.22 (m, 3H), 6.78 (d, $J$ = 8.6 Hz, 1H), 6.13 (s, 1H), 4.02 (s, 3H), 3.65 (s, 3H), 1.45 (s, 9H).$^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) = 176.7, 154.5, 153.1, 145.7, 142.9, 139.7, 136.4, 132.5, 129.5, 128.0, 127.1, 121.5, 121.4, 116.9, 115.8, 106.5, 98.6, 56.4, 55.8, 35.2, 31.5. IR (KBr) $\tilde{\nu}$ ($cm^{-1}$) = 2955, 1632, 1598, 1510, 1490, 1472, 1430, 1364, 1305, 1278, 1247, 1213, 1157, 1131, 1110, 1020, 899, 860, 824, 782, 755, 611.HRMS(ESI) (*m/z*): $[M+H]^+$calcd. for $C_{25}H_{26}NO_3$, 388.1913, found, 388.1902.




***N*-(4-*tert*-butylphenyl)-3-methoxyacridine-1,2,9-trione 3**

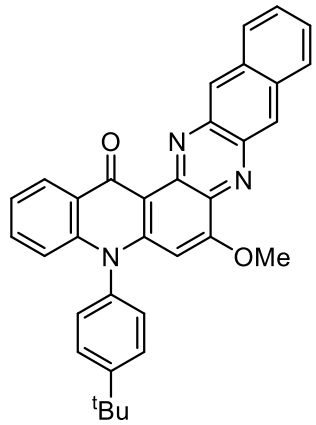
Compound **2** (1.10 g, 2.84 mmol) was dissolved in dichloromethane (14 mL), acetonitrile (70 mL) and water (14 mL). Ceric ammonium nitrate (6.03 g, 11 mmol) was added to the above solution and the reaction was stirred at room temperature for 15 minutes. The reaction solution was diluted with dichloromethane (200 mL) and washed with water (3×200 mL) and dried over $Na_2SO_4$. The solvent was removed by rotatory evaporation and the crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate 4:1) to give the product as red solid (0.70 g, 64%). m.p.: 318-320 ℃ (dec.)**.** $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ (ppm) = 8.26 (dd, $J$ = 7.9, 1.2 Hz, 1H), 7.79 (d, $J$ = 8.5 Hz, 2H), 7.65 - 7.60 (m, 1H), 7.56 (d, $J$ = 8.4 Hz, 2H), 7.48 (t, $J$ = 7.5 Hz, 1H), 6.71 (d, $J$ = 8.5 Hz, 1H), 3.41 (s, 3H), 1.40 (s, 9H).$^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$ (ppm) = 174.6, 173.6, 172.3, 154.8, 154.0, 153.5, 141.2, 134.6, 133.0, 128.7, 127.6 (2C), 126.0, 125.9, 119.4, 110.0, 103.5, 55.4, 34.9, 31.0. IR (KBr) $\tilde{\nu}$ (cm$^{-1}$) = 3059, 2960, 2868, 2360, 2341, 1703, 1676, 1630, 1605, 1509, 1476, 1459, 1446, 1426, 1367, 1334, 1299, 1252, 1198, 1118, 1092, 765. HRMS(ESI) (*m/z*): $[M+H]^+$calcd. for $C_{24}H_{22}NO_4$, 388.1549, found, 388.1551.




**5-(4-*tert*-butylphenyl)-7-methoxyquinonelino[3,2-a]phenazin-14-one 5**

A 120 mL screw capped glass vial was charged with compound **3** (190 mg, 0.5 mmol), chloroform (10 mL), acetic acid (5 mL) and phenylene-1,2-diamine (72 mg, 0.66 mmol). The vial was screw-capped and the vial was heated in an oil bath at 80 ºC for 40 hours. After cooling down to room temperature, the mixture was diluted with dichloromethane (100 mL) and washed with water (3×200 mL) and dried over $Na_2SO_4$. The solvent was removed by rotatory evaporation and the crude product was suspended in methanol (10 mL) and filtered off to give the product as pale brown solid (160 mg, 70%). m.p.: 360-361 ℃ (dec.)**.** $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) = 8.78 (dd, $J$ = 8.0, 1.5 Hz, 1H), 8.56 (d, $J$ = 8.5 Hz, 1H), 8.33 (d, $J$ = 8.4 Hz, 1H), 7.90 (ddd, $J$ = 8.4, 6.6, 1.4 Hz, 1H), 7.82 (ddd, $J$ = 8.3, 6.6, 1.4 Hz, 1H), 7.78 (dt, $J$ = 8.4, 2.1 Hz, 2H), 7.50 (ddd, $J$ = 8.6, 6.9, 1.7 Hz, 1H), 7.45-7.38 (m, 3H), 6.82 (d, $J$ = 8.4 Hz, 1H), 6.43 (s, 1H), 3.85 (s, 3H), 1.49 (s, 9H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) = 175.7, 157.7, 153.6, 147.7, 144.5, 144.0, 141.4, 140.2, 136.1, 133.9, 132.0, 130.9, 130.4, 129.8, 129.5, 129.2, 128.1, 127.4, 126.0, 123.5, 117.4, 108.8, 99.4, 56.1, 35.1, 31.4. IR (KBr) $\tilde{\nu}$ (cm$^{-1}$)

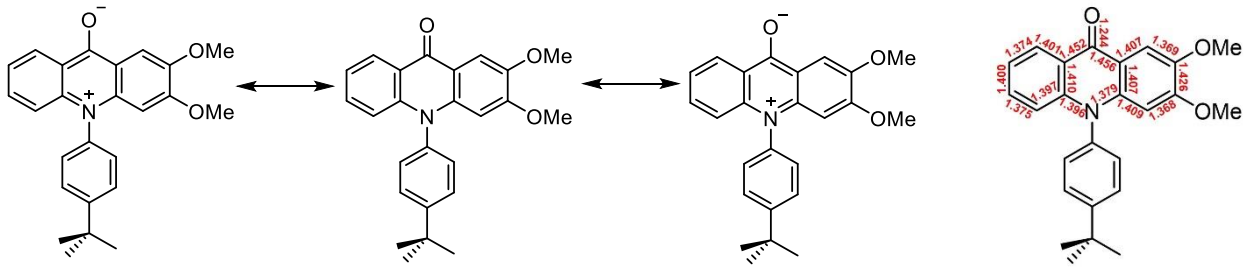
= 2947, 1642, 1601, 1548, 1511, 1477, 1446, 1425, 1363, 1399, 1309, 1259, 1227, 1198, 1156, 1118, 1054, 1025, 864, 827, 752, 616, 578. HRMS(ESI) (*m/z*): $[M+H]^+$calcd. for $C_{30}H_{26}N_3O_2$, 460.2025, found, 460.2017.



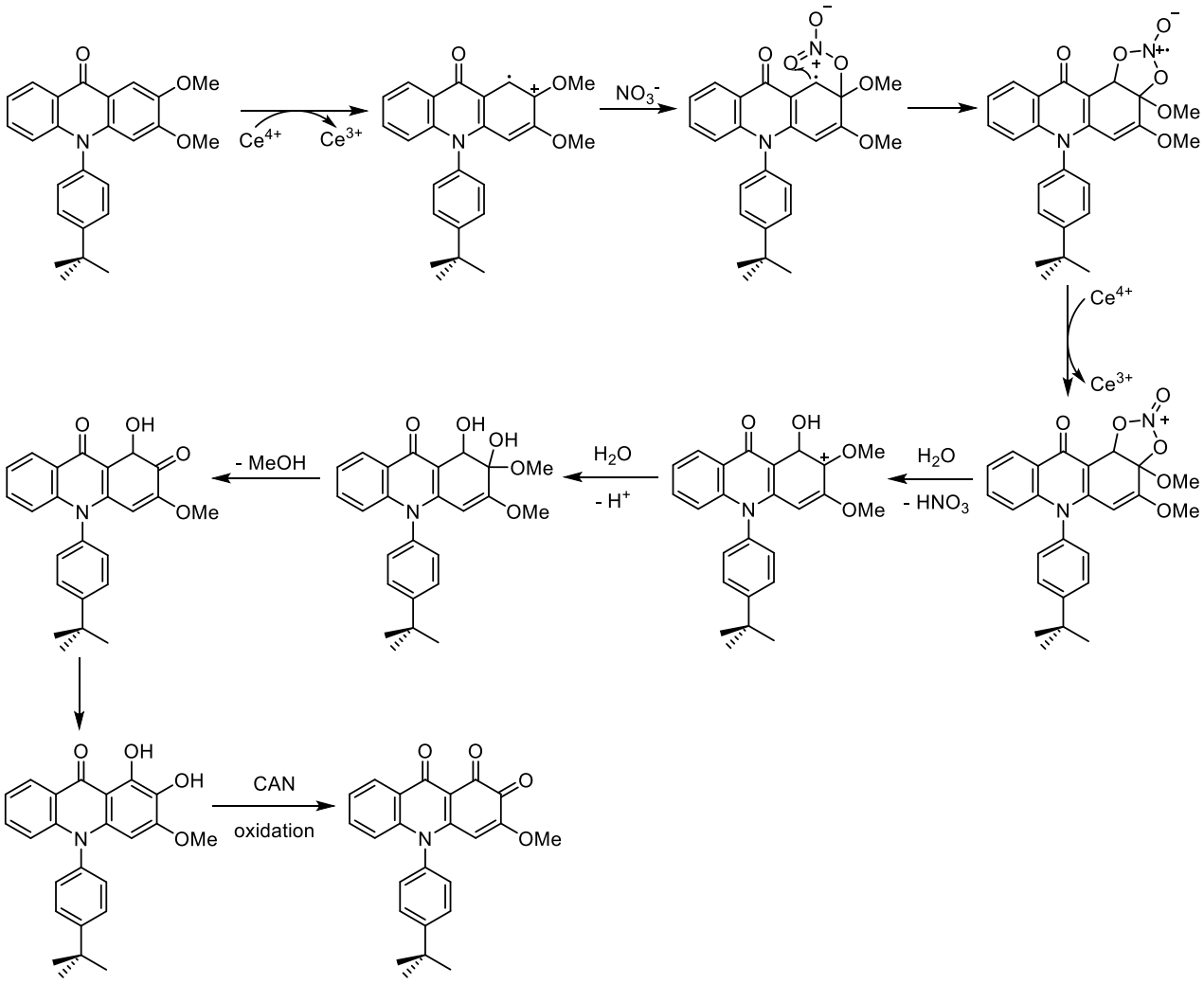

**5-(4-*tert*-butylphenyl)-7-methoxybenzo[i]quinonelino[3,2-a]phenazin-16-one 6**

A 120 mL screw capped glass vial was charged with compound **3** (180 mg, 0.46 mmol), chloroform (14 mL), acetic acid (7 mL) and naphthalene-2,3-diamine (95 mg, 0.60 mmol). The vial was screw-capped and the vial was heated in an oil bath at 80 ºC for 40 hours. After cooling down to room temperature, the mixture was diluted with dichloromethane (100 mL) and washed with water (3×200 mL) and dried over $Na_2SO_4$. The solvent was removed by rotatory evaporation and the crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate 10:1) to give the product as red solid (90 mg, 38%). m.p.: 364-366 ℃ (dec.)**.** $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) = 9.20 (s, 1H), 8.98 (s, 1H), 8.81 (dd, $J$ = 8.0, 1.6 Hz, 1H), 8.20 (d, $J$ = 8.3 Hz, 1H), 8.14 (d, $J$ = 8.2 Hz, 1H), 7.79 (d, $J$ = 8.4 Hz, 2H), 7.59-7.53 (m, 2H), 7.53-7.50 (m, 1H), 7.45-7.43 (m, 3H), 6.83 (d, $J$ = 8.4 Hz, 1H), 6.38 (s, 1H), 3.87 (s, 3H), 1.50 (s, 9H). Record of $^{13}$C NMR spectrum was not successful due to the poor solubility. IR (KBr) $\tilde{\nu}$ ($cm^{-1}$) = 2963, 2284, 1638, 1610, 1508, 1482, 1444, 1430, 1399, 1311, 1249, 1226, 1154, 1119, 1056, 877, 828, 749, 616, 562, 485.HRMS(ESI) (*m/z*): $[M+H]^+$calcd. for $C_{34}H_{28}N_3O_2$, 510.2182, found, 510.2184.

## 3. Reaction mechanism



**Scheme S1**. The resonance structures of **2** and its bond lengths in the crystal.



**Scheme S2**. Proposed mechanism for the oxidative demethylation

## 4. NMR Spectra

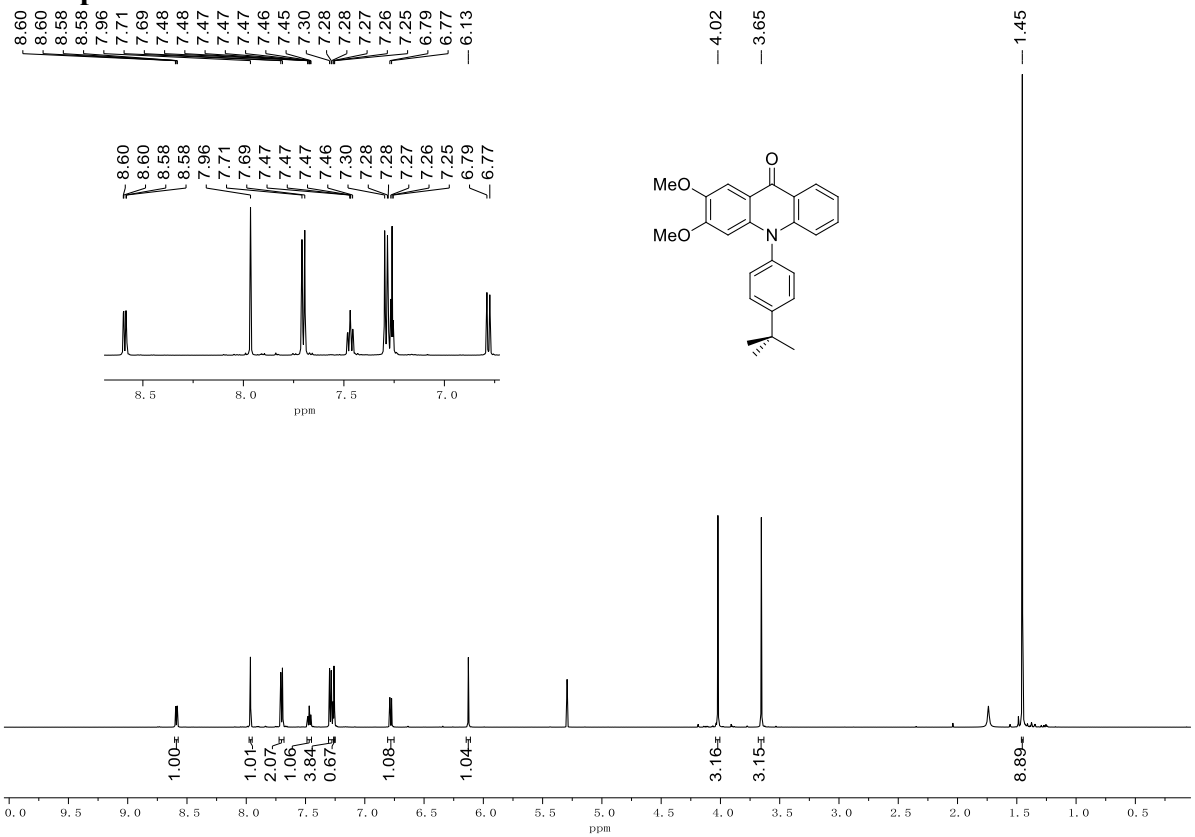



**Figure S1**. $^{1}H$ NMR spectrum ($CDCl_3$, 600 MHz) of **2**

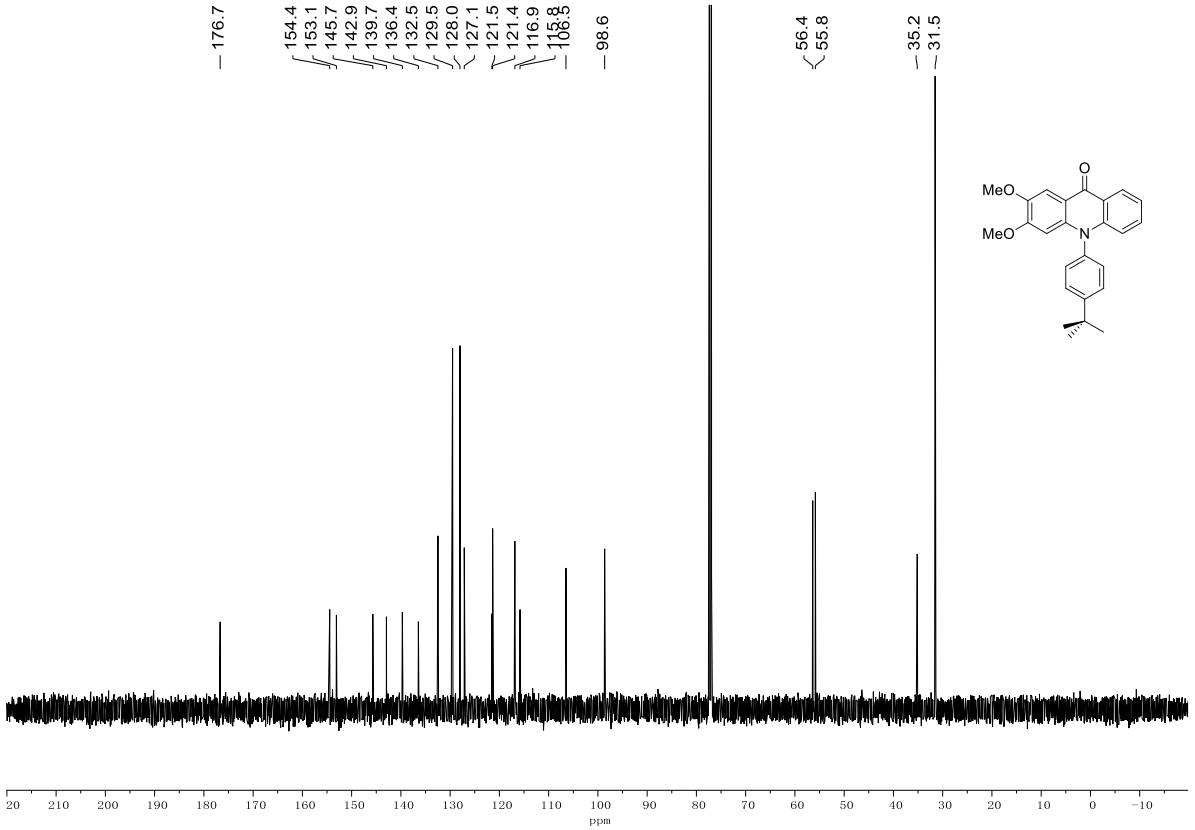



**Figure S2**. $^{13}C$ NMR spectrum ($CDCl_3$, 150 MHz) of **2**

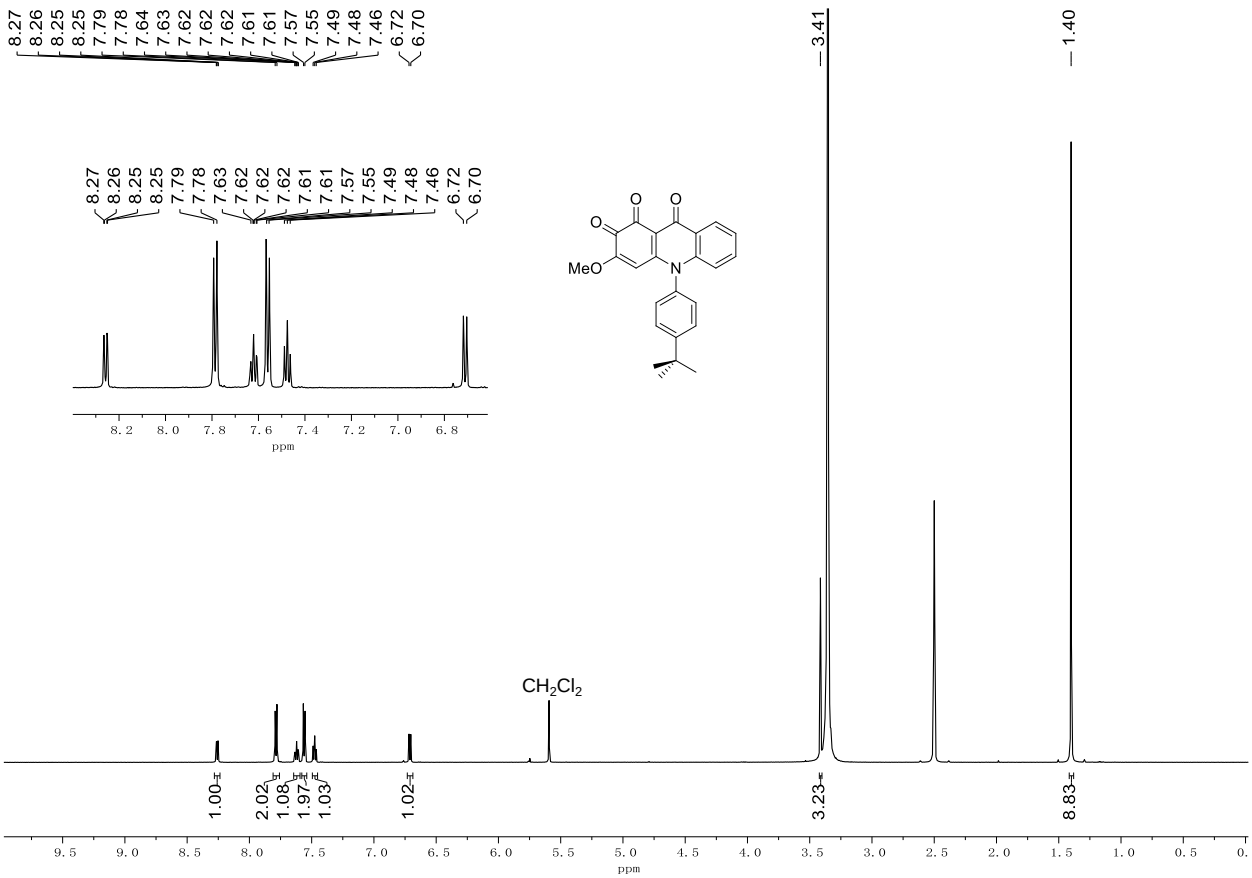



**Figure S3**. $^{1}$H NMR spectrum (DMSO-$d_6$, 600 MHz) of **4**

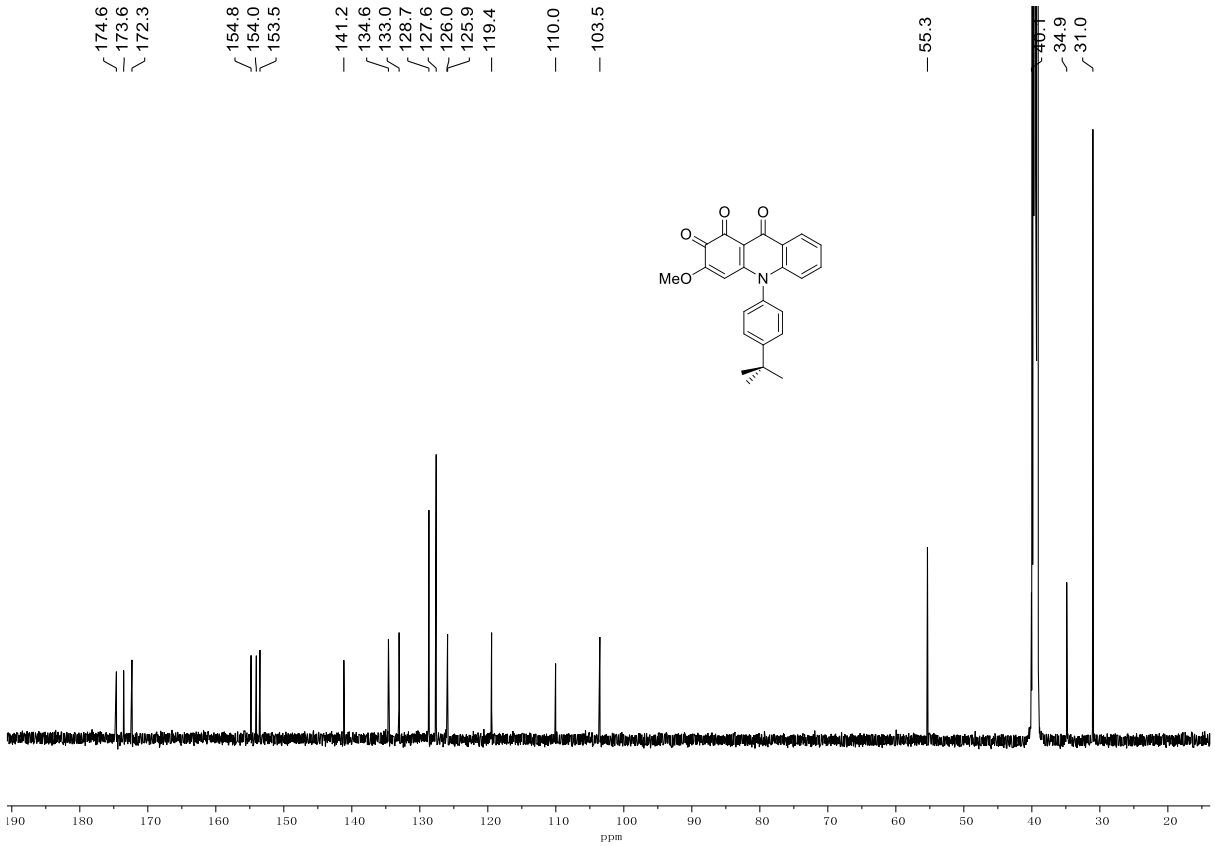



**Figure S4**. $^{13}$C NMR spectrum (DMSO-$d_6$, 150 MHz) of **4**

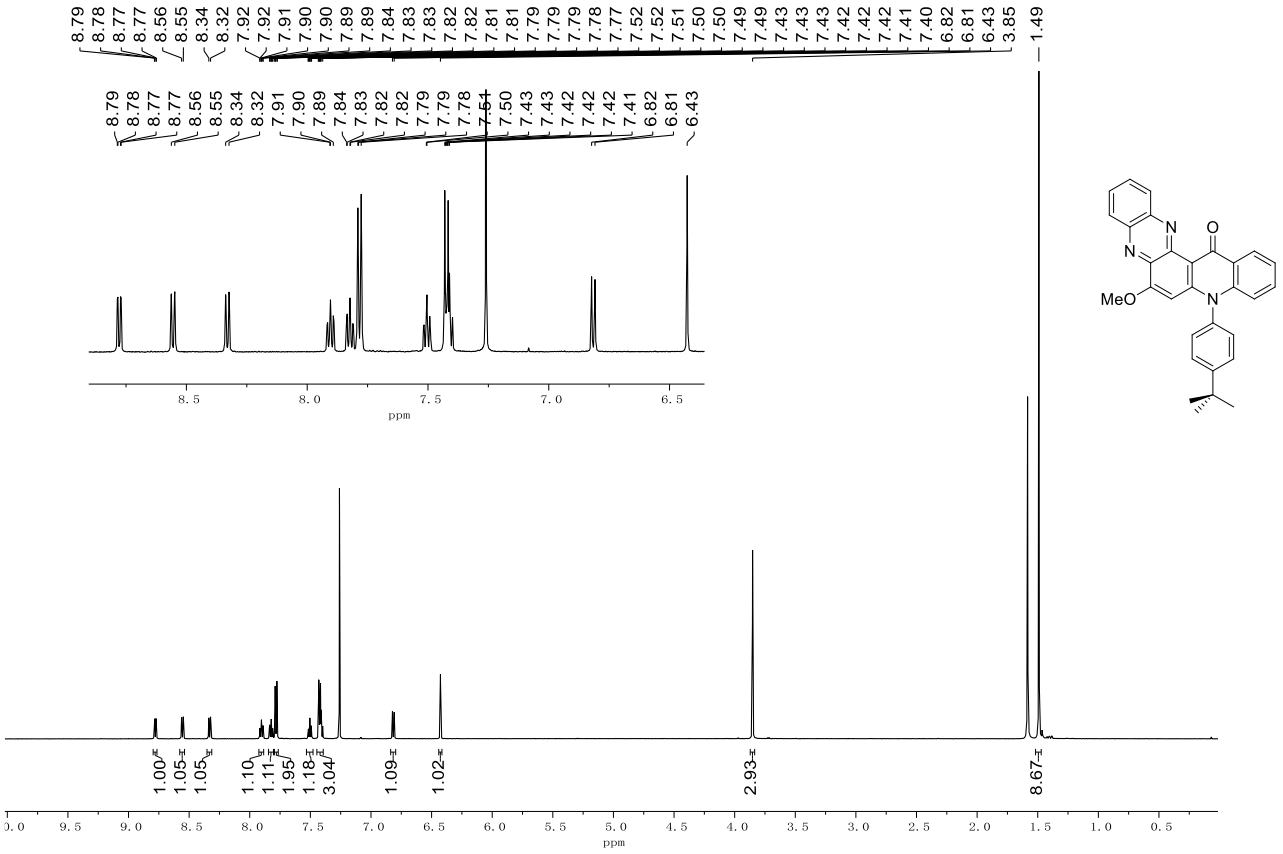



**Figure S5**. $^{1}H$ NMR spectrum ($CDCl_3$, 600 MHz) of **5**

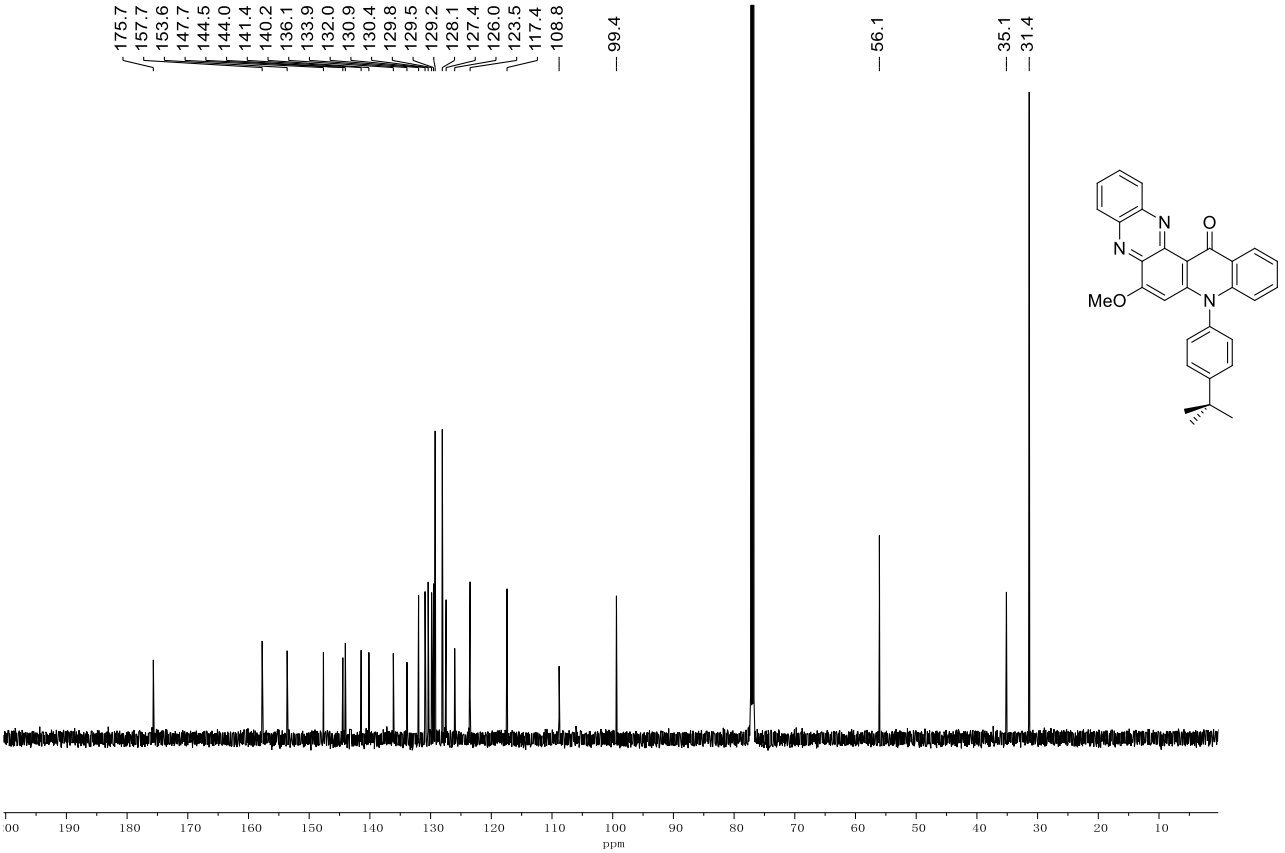



**Figure S6**. $^{13}C$ NMR spectrum ($CDCl_3$, 150 MHz) of **5**

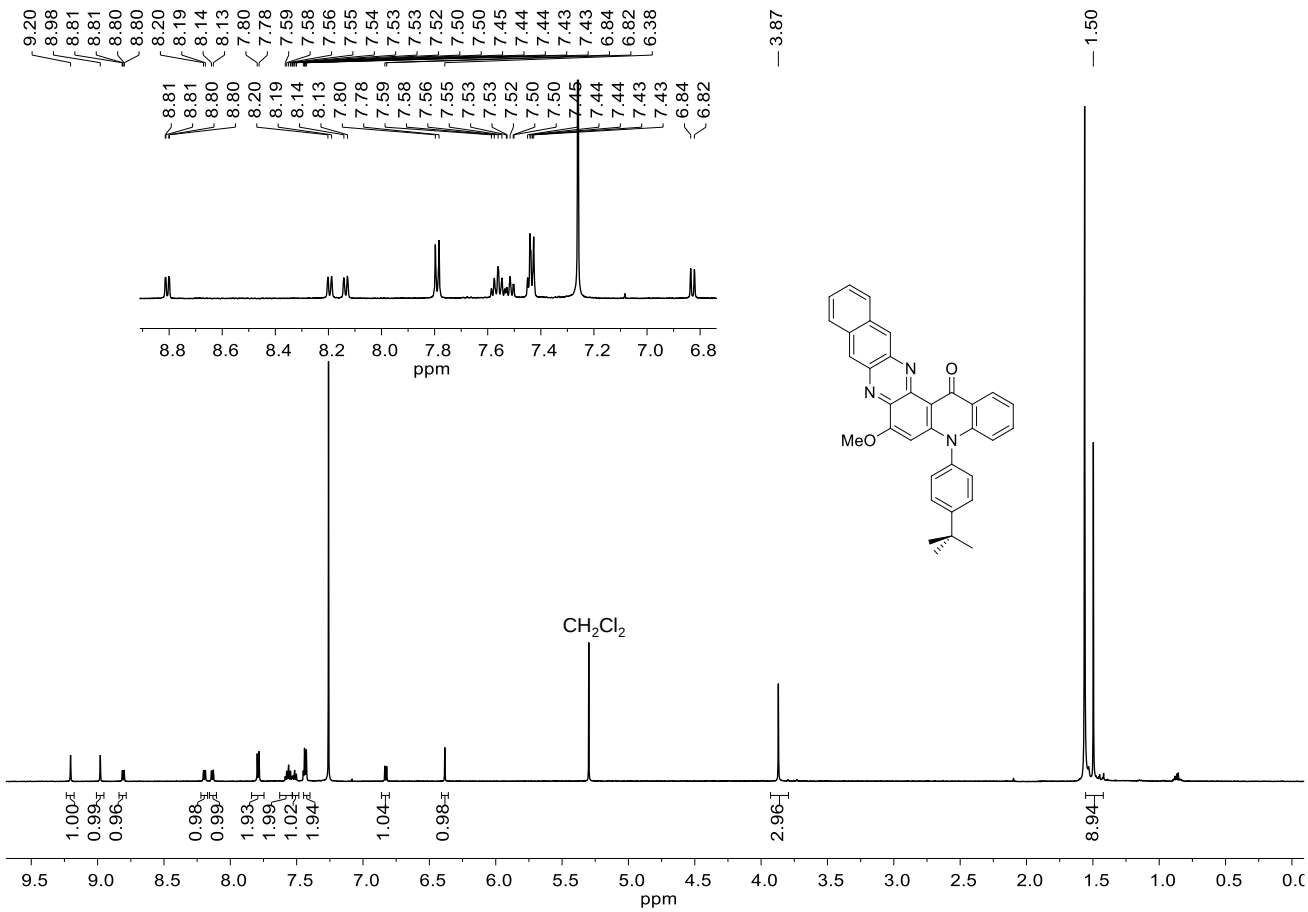



**Figure S7**. $^{1}H$ NMR spectrum ($CDCl_3$, 600 MHz) of **6**

**5. Fluorescence decay curves**

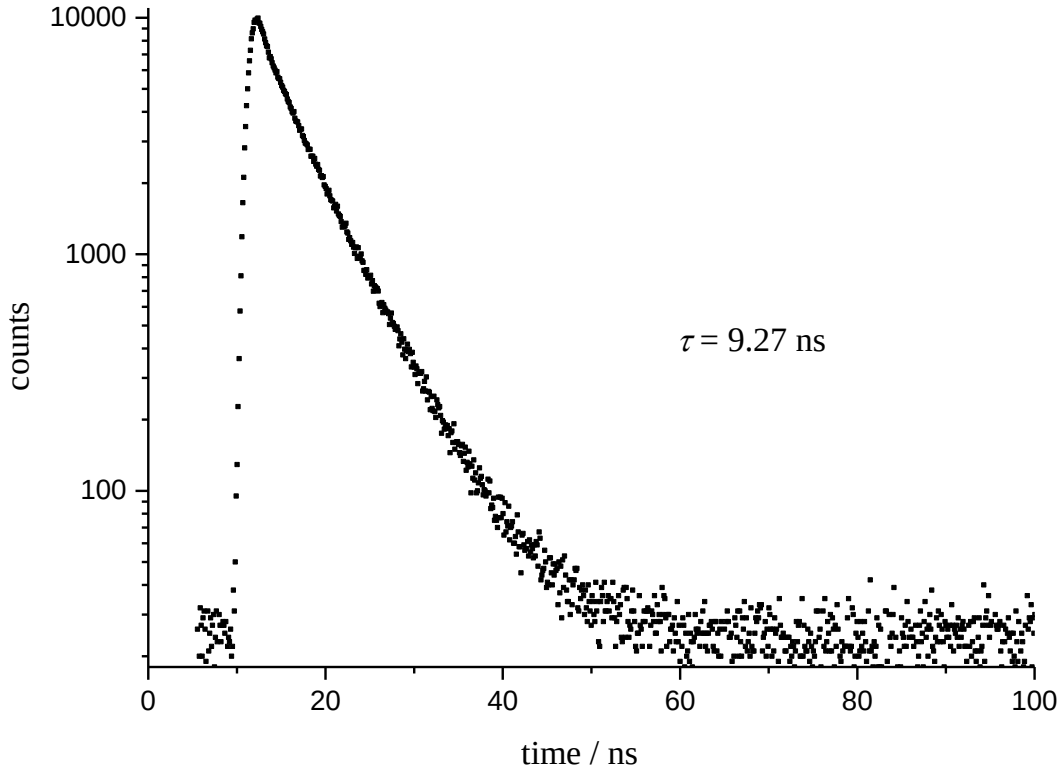



**Figure S8**. Fluorescence decay curve of **5** in dichloromethane at room temperature.

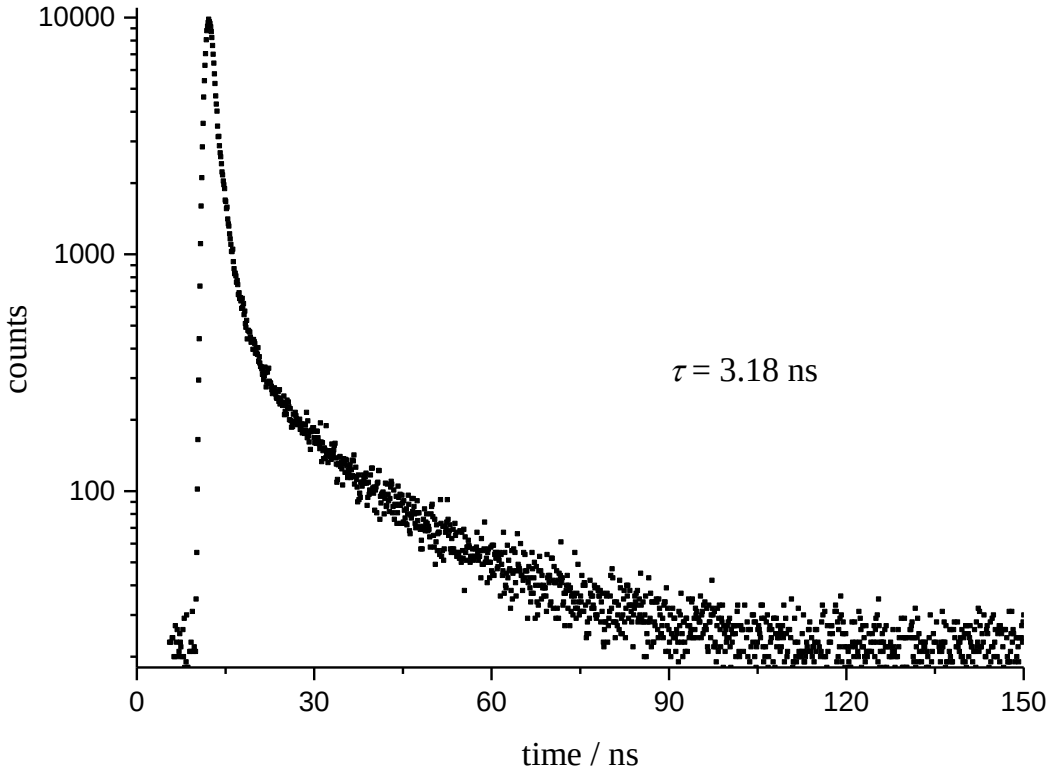



**Figure S9**. Fluorescence decay curve of **6** in solid state at room temperature.

**6. CV and DPV curves**

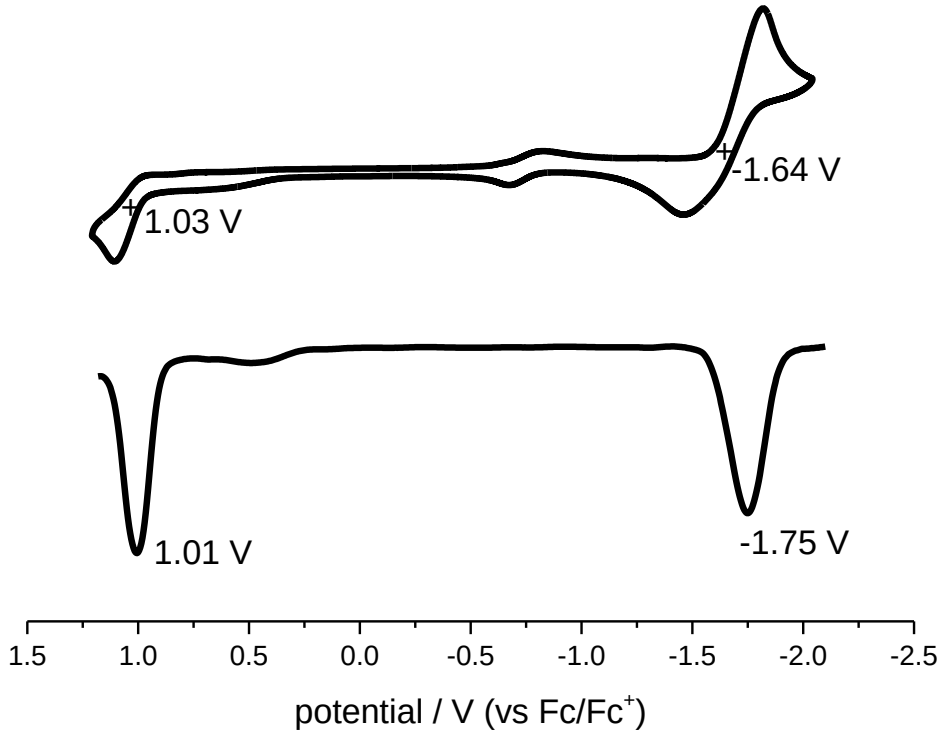



**Figure S10.** CV and DPV curves of **5**

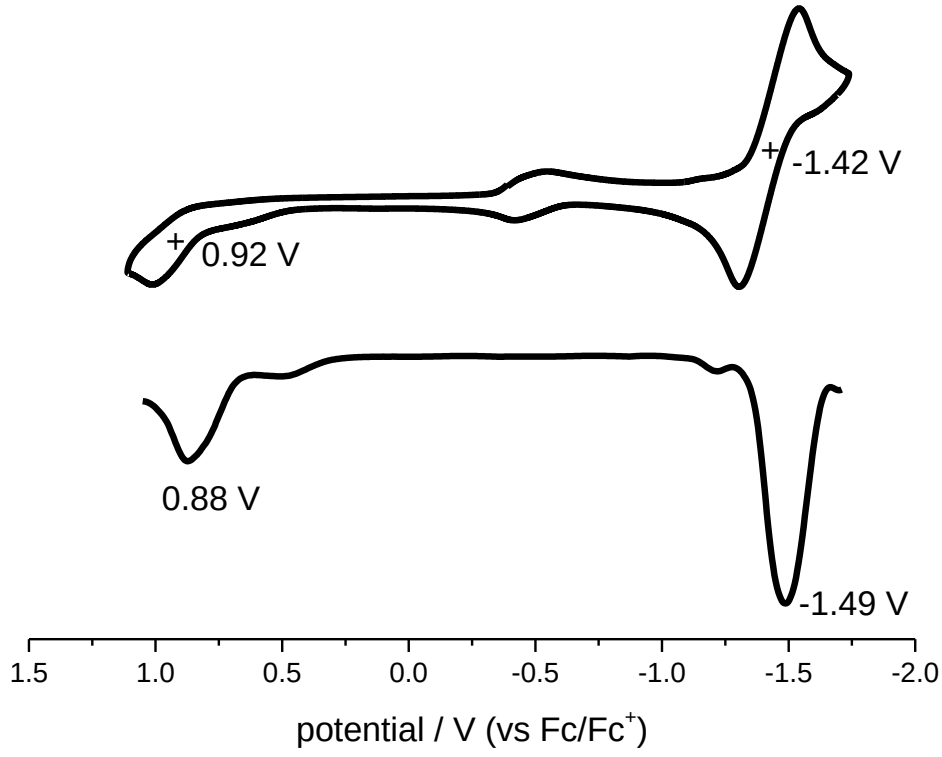



**Figure S11.** CV and DPV curves of **6**

## 7. X-ray crystallographic structure determination

**Table S1.** Crystal data and structure refinement for **2**

| | |
|---|---|
| Empirical formula | $C_{25}H_{25}NO_3$ |
| Formula weight | 387.46 |
| Temperature/K | 150.00(10) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 8.6227(10) |
| b/Å | 11.3588(12) |
| c/Å | 11.8411(17) |
| α/° | 117.309(13) |
| β/° | 91.977(11) |
| γ/° | 96.236(10) |
| Volume/Å$^3$ | 1019.7(2) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.262 |
| μ/mm$^{-1}$ | 0.657 |
| F(000) | 412.0 |
| Radiation | Cu Kα ($\lambda$ = 1.54184) |
| 2Θ range for data collection/° | 8.442 to 133.194 |
| Index ranges | $-10 \le h \le 6$, $-13 \le k \le 13$, $-14 \le l \le 13$ |
| Reflections collected | 6322 |
| Independent reflections | 3591 [$R_{int}$ = 0.0587, $R_{sigma}$ = 0.0541] |
| Data/restraints/parameters | 3591/0/267 |
| Goodness-of-fit on F$^2$ | 1.089 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0936, $wR_2$ = 0.2981 |
| Final R indexes [all data] | $R_1$ = 0.1154, $wR_2$ = 0.3188 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.43/-0.41 |

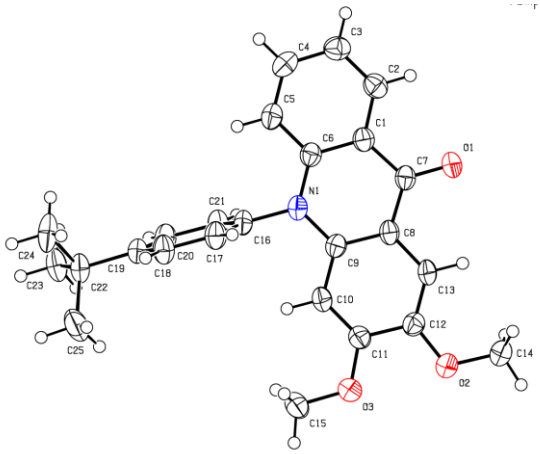



**Figure S12.** Crystal structure of **2** with an ellipsoid contour at the 50% probability level.

**Table S2.** Crystal data and structure refinement for **5**

| | |
|---|---|
| Empirical formula | $C_{32}H_{27}Cl_6N_3O_2$ |
| Formula weight | 698.26 |
| Temperature/K | 149.99(10) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 11.7193(8) |
| b/Å | 25.313(2) |
| c/Å | 11.1041(10) |
| α/° | 90 |
| β/° | 105.097(9) |
| γ/° | 90 |
| Volume/Å$^3$ | 3180.4(5) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.458 |
| μ/mm$^{-1}$ | 0.576 |
| F(000) | 1432.0 |
| Radiation | Mo Kα ($\lambda$ = 0.71073) |
| 2Θ range for data collection/° | 3.942 to 49.998 |
| Index ranges | $-13 \le h \le 11$, $-30 \le k \le 23$, $-13 \le l \le 13$ |
| Reflections collected | 13938 |
| Independent reflections | 5599 [$R_{int}$ = 0.0412, $R_{sigma}$ = 0.0598] |
| Data/restraints/parameters | 5599/0/392 |
| Goodness-of-fit on F$^2$ | 1.038 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0668, $wR_2$ = 0.1583 |
| Final R indexes [all data] | $R_1$ = 0.0916, $wR_2$ = 0.1756 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.74/-0.66 |

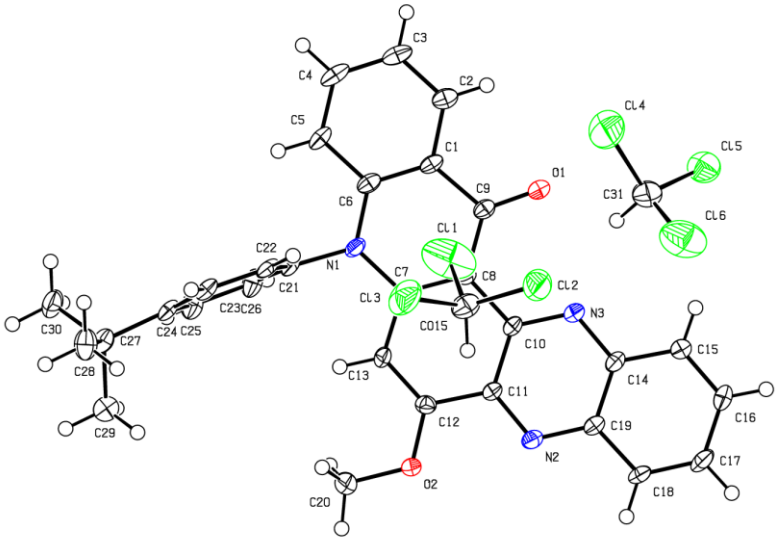



**Figure S13.** Crystal structure of **5** with an ellipsoid contour at the 50% probability level.

**Table S3.** Crystal data and structure refinement for **6**

| | |
|---|---|
| Empirical formula | $C_{36}H_{29}Cl_6N_3O_2$ |
| Formula weight | 748.32 |
| Temperature/K | 149.99(10) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 11.5804(4) |
| b/Å | 12.1813(6) |
| c/Å | 12.9925(5) |
| α/° | 101.203(4) |
| β/° | 101.376(3) |
| γ/° | 103.039(3) |
| Volume/Å$^3$ | 1694.85(13) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.466 |
| μ/mm$^{-1}$ | 4.935 |
| F(000) | 768.0 |
| Radiation | Cu Kα ($\lambda$ = 1.54184) |
| 2Θ range for data collection/° | 7.168 to 147.926 |
| Index ranges | $-14 \leq h \leq 11$, $-14 \leq k \leq 15$, $-16 \leq l \leq 14$ |
| Reflections collected | 11542 |
| Independent reflections | 6648 [$R_{int}$ = 0.0314, $R_{sigma}$ = 0.0450] |
| Data/restraints/parameters | 6648/0/428 |
| Goodness-of-fit on F$^2$ | 1.038 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0465, $wR_2$ = 0.1186 |
| Final R indexes [all data] | $R_1$ = 0.0564, $wR_2$ = 0.1267 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.59/-0.68 |

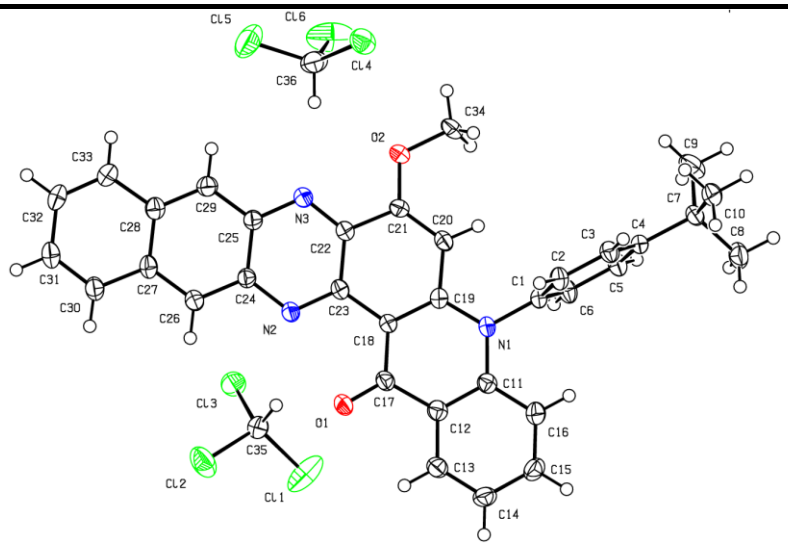



**Figure S14**. Crystal structure of **6** with an ellipsoid contour at the 50% probability level.

## 8. Theoretical calculations

All the theoretical calculations were carried out using a *Gaussian 16* software.[S2] All the calculations were based on the optimized geometries at B3LYP/6-31G(d,p) level of theory. The frontier molecular orbitals are calculated at the B3LYP/6-311+G(d,p) level of theory. The calculation of excited state properties was performed using time-depended DFT methods at B3LYP/6-311G+(d,p) level of theory in the solvent dichloromethane. The nucleus-independent chemical shift (NICS) calculation was done at GIAO-B3LYP/6-311+G(d,p) level of theory. Bq atoms were inserted at the calculated positions and the Bq positions that are at the 1 Å away above the molecule were fixed with the assistant of Multiwfn 3.8 software, as well as the generation of isotropic chemical shielding surfaces (ICSS) and related quantities.[S3] The hole transfer integral was calculated by $t_h$ = 1/2 ($E_{HOMO} - E_{HOMO-1}$) and the electron transfer integral was calculated by $t_e$ = 1/2($E_{LUMO+1} - E_{LUMO}$). To calculate the reorganization energy $\lambda$, the geometry of the molecule was first optimized at the ground state and the single point energy was then calculated with the charge of 0, +1 and -1. The energies were denoted as $E_{G0}$, $E_{G+1}$ and $E_{G-1}$, respectively. Then the geometry of the molecule was optimized with the charge of +1 (Cation) and -1 (Anion) and the single point energy was calculated with the charge of 0, +1 and 0, -1, respectively. The energies were denoted as $E_{C0}$, $E_{C+1}$, $E_{A0}$ and $E_{A-1}$, respectively. The hole reorganization energy was calculated by $\lambda_h = (E_{C0} - E_{G0}) + (E_{G+1} - E_{C+1})$ and the electron reorganization energy was calculated by $\lambda_e = (E_{A0} - E_{G0}) + (E_{G-1} - E_{A-1})$.

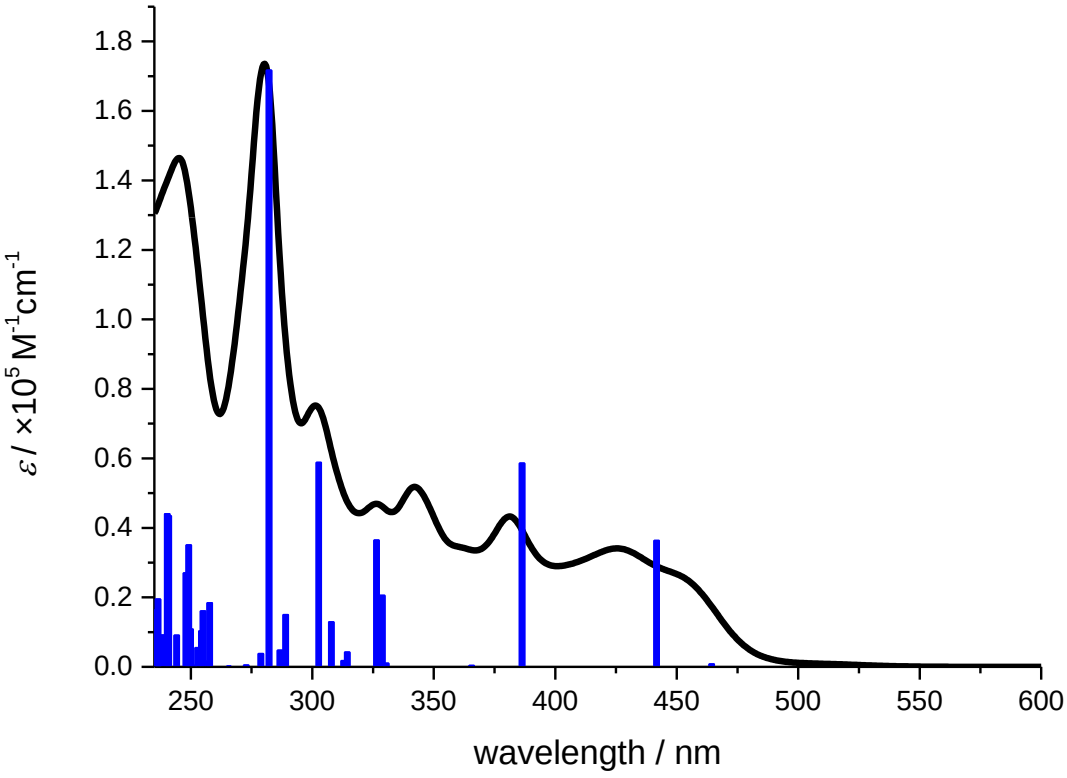



**Figure S15**. UV/Vis absorption spectrum of compound **5** and TD-DFT calculated oscillator strength (blue column) in dichloromethane solvent at B3LYP/6-311G+(d,p) level.

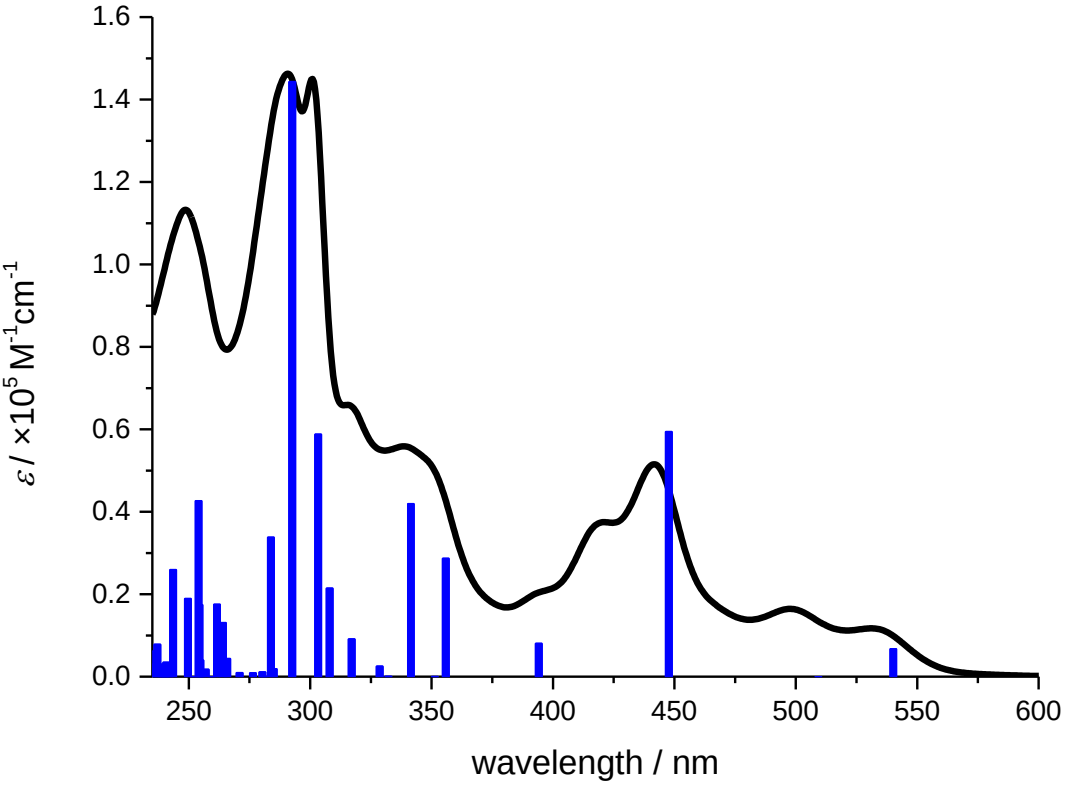



**Figure S16**. UV/Vis absorption spectrum of compound **6** and TD-DFT calculated oscillator strength (blue column) in dichloromethane solvent at B3LYP/6-311G+(d,p) level.

**Table S4**. TD-DFT calculated first-ten electron transitions of **5** in dichloromethane at B3LYP / 6-311+G(d,p) level

| | | | | | |
|---|---|---|---|---|---|
| Excited State 1: | Singlet-A | 2.6698 eV | 464.39 nm | f=0.0025 | <S**2>=0.000 |
| 114 ->122 | 0.12233 | | | | |
| 120 ->122 | 0.68178 | | | | |
| 121 ->122 | -0.12800 | | | | |
| Excited State 2: | Singlet-A | 2.8065 eV | 441.78 nm | f=0.1708 | <S**2>=0.000 |
| 120 ->122 | 0.12488 | | | | |
| 121 ->122 | 0.68419 | | | | |
| Excited State 3: | Singlet-A | 3.2090 eV | 386.37 nm | f=0.2761 | <S**2>=0.000 |
| 119 ->122 | 0.68222 | | | | |
| 121 ->123 | -0.12388 | | | | |
| Excited State 4: | Singlet-A | 3.3912 eV | 365.61 nm | f=0.0005 | <S**2>=0.000 |
| 114 ->122 | 0.11155 | | | | |
| 114 ->123 | -0.10102 | | | | |
| 120 ->123 | 0.67492 | | | | |
| Excited State 5: | Singlet-A | 3.7516 eV | 330.48 nm | f=0.0035 | <S**2>=0.000 |
| 114 ->122 | 0.66957 | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 120 ->122 | | -0.11964 | | | | |
| 120 ->123 | | -0.10516 | | | | |
| Excited State | 6: | Singlet-A | 3.7704 eV | 328.84 nm | f=0.0961 | <S**2>=0.000 |
| 115 ->122 | | -0.16335 | | | | |
| 118 ->122 | | 0.54960 | | | | |
| 121 ->123 | | -0.37074 | | | | |
| Excited State | 7: | Singlet-A | 3.7976 eV | 326.48 nm | f=0.1712 | <S**2>=0.000 |
| 116 ->122 | | 0.11441 | | | | |
| 118 ->122 | | 0.36713 | | | | |
| 119 ->123 | | 0.10258 | | | | |
| 121 ->123 | | 0.55264 | | | | |
| Excited State | 8: | Singlet-A | 3.9426 eV | 314.47 nm | f=0.0187 | <S**2>=0.000 |
| 115 ->122 | | 0.41163 | | | | |
| 116 ->122 | | -0.33650 | | | | |
| 117 ->122 | | 0.23631 | | | | |
| 118 ->122 | | 0.20234 | | | | |
| 119 ->123 | | -0.25402 | | | | |
| 119 ->124 | | 0.11472 | | | | |
| 121 ->124 | | -0.13923 | | | | |
| Excited State | 9: | Singlet-A | 3.9617 eV | 312.96 nm | f=0.0070 | <S**2>=0.000 |
| 115 ->122 | | -0.16054 | | | | |
| 116 ->122 | | 0.14213 | | | | |
| 117 ->122 | | 0.65833 | | | | |
| Excited State | 10: | Singlet-A | 4.0271 eV | 307.87 nm | f=0.0599 | <S**2>=0.000 |
| 115 ->122 | | 0.39637 | | | | |
| 116 ->122 | | 0.53827 | | | | |
| 121 ->123 | | -0.10553 | | | | |
| 121 ->124 | | -0.11490 | | | | |

HOMO: 121, LUMO: 122

**Table S5**. TD-DFT calculated first-ten electron transitions of **6** in dichloromethane at B3LYP / 6-311+G(d,p) level

| | | | | | | |
|---|---|---|---|---|---|---|
| Excited State | 1: | Singlet-A | 2.2957 eV | 540.08 nm | f=0.0511 | <S**2>=0.000 |
| 134 -> 135 | | 0.70377 | | | | |
| Excited State | 2: | Singlet-A | 2.4348 eV | 509.22 nm | f=0.0004 | <S**2>=0.000 |
| 127 -> 135 | | -0.11945 | | | | |
| 132 -> 135 | | 0.69381 | | | | |
| Excited State | 3: | Singlet-A | 2.7694 eV | 447.69 nm | f=0.4460 | <S**2>=0.000 |
| 131 -> 135 | | 0.10076 | | | | |
| 133 -> 135 | | 0.69081 | | | | |
| Excited State | 4: | Singlet-A | 3.1458 eV | 394.13 nm | f=0.0610 | <S**2>=0.000 |
| 131 -> 135 | | 0.68069 | | | | |
| 134 -> 136 | | 0.11049 | | | | |
| Excited State | 5: | Singlet-A | 3.3746 eV | 367.41 nm | f=0.0000 | <S**2>=0.000 |

| | | | | | |
|---|---|---|---|---|---|
| 127 -> 135 | 0.11448 | | | | |
| 127 -> 136 | 0.10673 | | | | |
| 132 -> 136 | 0.67516 | | | | |
| Excited State 6: | Singlet-A | 3.4846 eV | 355.81 nm | f=0.2156 | <S**2>=0.000 |
| 129 -> 135 | 0.11091 | | | | |
| 130 -> 135 | 0.29571 | | | | |
| 131 -> 135 | -0.13396 | | | | |
| 134 -> 136 | 0.58599 | | | | |
| 134 -> 138 | 0.11309 | | | | |
| Excited State 7: | Singlet-A | 3.5288 eV | 351.35 nm | f=0.0008 | <S**2>=0.000 |
| 127 -> 135 | 0.67644 | | | | |
| 132 -> 135 | 0.11635 | | | | |
| 132 -> 136 | -0.11334 | | | | |
| Excited State 8: | Singlet-A | 3.6310 eV | 341.46 nm | f=0.3150 | <S**2>=0.000 |
| 129 -> 135 | 0.17915 | | | | |
| 130 -> 135 | 0.49436 | | | | |
| 133 -> 136 | 0.10565 | | | | |
| 134 -> 136 | -0.36215 | | | | |
| 134 -> 137 | -0.12722 | | | | |
| 134 -> 138 | 0.19527 | | | | |
| Excited State 9: | Singlet-A | 3.7324 eV | 332.18 nm | f=0.0009 | <S**2>=0.000 |
| 129 -> 135 | 0.64914 | | | | |
| 130 -> 135 | -0.25533 | | | | |
| Excited State 10: | Singlet-A | 3.7733 eV | 328.58 nm | f=0.0196 | <S**2>=0.000 |
| 128 -> 135 | 0.66626 | | | | |
| 133 -> 136 | -0.16440 | | | | |

HOMO: 177, LUMO: 178

**Cartesian coordinates for theoretically optimized structures**

**5** opt B3LYP/6-31G(d,p) Imaginary Frequency 0

| | | | |
|---|---|---|---|
| C | 1.24491900 | -1.93393300 | -0.01548900 |
| C | 0.15345300 | -1.11054900 | -0.01807600 |
| C | 0.28996100 | 0.31820200 | -0.01233900 |
| C | 1.55340200 | 0.93150400 | -0.00459000 |
| C | 2.72430200 | 0.07084200 | -0.00155800 |
| C | 2.57927100 | -1.37083000 | -0.00687500 |
| C | 0.37036400 | 3.13433300 | -0.00186300 |
| C | -0.86667300 | 2.46545700 | -0.00913500 |
| C | -2.06131200 | 3.21505200 | -0.01041100 |
| H | -3.02019100 | 2.71326400 | -0.01610600 |
| C | -2.00816800 | 4.60131500 | -0.00456500 |
| C | -0.77854800 | 5.27490400 | 0.00249100 |
| C | 0.39405000 | 4.53795800 | 0.00372300 |
| H | -0.83920000 | -1.53157800 | -0.02496600 |

| | | | |
|---|---|---|---|
| H | -2.93734600 | 5.16398800 | -0.00559800 |
| H | -0.74816200 | 6.35994000 | 0.00692900 |
| H | 1.37177500 | 5.00741600 | 0.00906700 |
| C | -2.16895400 | 0.40013200 | -0.01853300 |
| C | -2.79925800 | 0.08288700 | 1.18741000 |
| C | -2.79771100 | 0.09078700 | -1.22297200 |
| C | -4.04297000 | -0.54235100 | 1.17676100 |
| H | -2.31148300 | 0.32861000 | 2.12553300 |
| C | -4.04568000 | -0.53651000 | -1.22066500 |
| H | -2.31005500 | 0.34198700 | -2.15973700 |
| C | -4.69794500 | -0.86768300 | -0.02466500 |
| H | -4.51038300 | -0.77781300 | 2.12773200 |
| H | -4.50662900 | -0.76296300 | -2.17459200 |
| C | 1.66498800 | 2.40386000 | 0.00027700 |
| O | 2.71955500 | 3.03529300 | 0.00584500 |
| C | -0.08449500 | -3.90646000 | -0.02886700 |
| H | 0.11084200 | -4.97903200 | -0.03129200 |
| H | -0.66593200 | -3.64268600 | 0.86314000 |
| H | -0.65687200 | -3.63701800 | -0.92504400 |
| O | 1.19157600 | -3.28090100 | -0.02047200 |
| C | 5.00656200 | -0.22948400 | 0.00953100 |
| C | 6.32402900 | 0.31700800 | 0.01833200 |
| C | 4.84496200 | -1.65655700 | 0.00402100 |
| C | 7.41244200 | -0.51851400 | 0.02139200 |
| H | 6.41940400 | 1.39764500 | 0.02236200 |
| C | 5.99647900 | -2.49518200 | 0.00738700 |
| C | 7.24892400 | -1.93475400 | 0.01588200 |
| H | 8.41560100 | -0.10222600 | 0.02809200 |
| H | 5.84239400 | -3.56940000 | 0.00307000 |
| H | 8.12946800 | -2.57040400 | 0.01849200 |
| N | -0.88733800 | 1.06256500 | -0.01504900 |
| N | 3.61500700 | -2.20444500 | -0.00416100 |
| N | 3.95023800 | 0.60236100 | 0.00663100 |
| C | -6.07408700 | -1.55695300 | 0.01413600 |
| C | -6.63121400 | -1.83065000 | -1.39542600 |
| C | -5.94945700 | -2.90918300 | 0.75583500 |
| C | -7.07990800 | -0.65134900 | 0.76414200 |
| H | -6.77251400 | -0.90671000 | -1.96550000 |
| H | -5.97781500 | -2.49355900 | -1.97201600 |
| H | -7.60696500 | -2.31971600 | -1.31576800 |
| H | -5.59788900 | -2.78103700 | 1.78374700 |
| H | -6.92293700 | -3.40958400 | 0.79796400 |
| H | -5.24844000 | -3.57539400 | 0.24240000 |
| H | -8.06401600 | -1.13072600 | 0.80451400 |

| | | | |
|---|---|---|---|
| H | -6.76461400 | -0.45409800 | 1.79284500 |
| H | -7.19281100 | 0.31280500 | 0.25805800 |

**6** opt B3LYP/6-31G(d,p) Imaginary Frequency 0

| | | | |
|---|---|---|---|
| C | 0.46148800 | -1.76622600 | -0.01242600 |
| C | -0.68102000 | -1.01912000 | -0.01396900 |
| C | -0.64236100 | 0.41901300 | -0.01004600 |
| C | 0.57329300 | 1.11892000 | -0.00452700 |
| C | 1.80600600 | 0.34380500 | -0.00341100 |
| C | 1.75929200 | -1.11465600 | -0.00719100 |
| C | -0.76167600 | 3.23241500 | -0.00098000 |
| C | -1.94836900 | 2.47812800 | -0.00690000 |
| C | -3.19319100 | 3.14081400 | -0.00769500 |
| H | -4.11412200 | 2.57239900 | -0.01243700 |
| C | -3.23831900 | 4.52740300 | -0.00257800 |
| C | -2.05929700 | 5.28605300 | 0.00324400 |
| C | -0.83730800 | 4.63408300 | 0.00393300 |
| H | -1.64316800 | -1.50577400 | -0.01833800 |
| H | -4.20490500 | 5.02302500 | -0.00321600 |
| H | -2.10574400 | 6.37053500 | 0.00712100 |
| H | 0.10477900 | 5.17150700 | 0.00825800 |
| C | -3.10145400 | 0.32630100 | -0.01634400 |
| C | -3.71023500 | -0.03224600 | 1.18900100 |
| C | -3.70598100 | -0.02548200 | -1.22148200 |
| C | -4.90902900 | -0.73986500 | 1.17702100 |
| H | -3.24154200 | 0.24646900 | 2.12762100 |
| C | -4.90879900 | -0.73545000 | -1.22041200 |
| H | -3.23519900 | 0.25777100 | -2.15772500 |
| C | -5.53917400 | -1.10881900 | -0.02508800 |
| H | -5.36082000 | -1.00573400 | 2.12751500 |
| H | -5.35204700 | -0.99299400 | -2.17482100 |
| C | 0.58132700 | 2.59462200 | 0.00017500 |
| O | 1.58865300 | 3.29915100 | 0.00512900 |
| C | -0.73000300 | -3.82429600 | -0.02092700 |
| H | -0.46209200 | -4.88104400 | -0.02263400 |
| H | -1.32624100 | -3.59932600 | 0.87192500 |
| H | -1.32080500 | -3.59504300 | -0.91629600 |
| O | 0.50058100 | -3.11314200 | -0.01554000 |
| N | -1.86894700 | 1.07677800 | -0.01191700 |
| N | 2.84004200 | -1.87425800 | -0.00622900 |
| N | 2.98353600 | 0.95669500 | 0.00098200 |
| C | 4.10614900 | 0.19803000 | 0.00192700 |
| C | 5.36222500 | 0.82840300 | 0.00645100 |
| C | 4.04175300 | -1.24382700 | -0.00162300 |

| | | | |
|---|---|---|---|
| C | 6.54131400 | 0.08093800 | 0.00757400 |
| H | 5.38551400 | 1.91369200 | 0.00903300 |
| C | 5.22598600 | -1.99776000 | -0.00044000 |
| C | 7.83243600 | 0.70214200 | 0.01210500 |
| C | 6.47281900 | -1.37004400 | 0.00406600 |
| H | 5.14563100 | -3.08068100 | -0.00317900 |
| C | 8.97563000 | -0.04858500 | 0.01312500 |
| H | 7.88180300 | 1.78744500 | 0.01471100 |
| C | 7.69754000 | -2.11298400 | 0.00531800 |
| C | 8.90766600 | -1.47579900 | 0.00969000 |
| H | 9.94680000 | 0.43745000 | 0.01656500 |
| H | 7.64261800 | -3.19820800 | 0.00269000 |
| H | 9.82795100 | -2.05237700 | 0.01057800 |
| C | -6.86707300 | -1.88711800 | 0.01206500 |
| C | -7.40157500 | -2.19949300 | -1.39822300 |
| C | -6.65643400 | -3.22684900 | 0.75691100 |
| C | -7.93179800 | -1.04753200 | 0.75768200 |
| H | -7.60200900 | -1.28797500 | -1.97055100 |
| H | -6.70460300 | -2.81910300 | -1.97195600 |
| H | -8.34324000 | -2.75150400 | -1.31978600 |
| H | -6.31660700 | -3.07431100 | 1.78543900 |
| H | -7.59547200 | -3.78930800 | 0.79762400 |
| H | -5.91241600 | -3.84714000 | 0.24646800 |
| H | -8.88276800 | -1.58980300 | 0.79635900 |
| H | -7.63282300 | -0.82844600 | 1.78683200 |
| H | -8.10571900 | -0.09362800 | 0.24948000 |

## 9. References

[S1] M. Orda-Zgadzaj, W. Abraham, *Synthesis* **2007**, 3345-3356.
[S2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 16, Revision A.03*, Gaussian, Inc., Wallingford CT, **2016**.
[S3] (a) T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580-592. (b) H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Org. Lett.* **2006**, *8*, 863-866. (c) S. Klod, E. Kleinpeter, *J. Chem. Soc., Perkin Trans. 2* **2001**, 1893-1898. (d) Z. Liu, T. Lu, Q. Chen, *Carbon* **2020**, *165*, 468-475.