SUPPORTING INFORMATION

D•–A Radicals Fabricated from Polychlorinated Trityl and Pyridinium Featuring a SOMO–LUMO Electronic Transition

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Content

1. Materials and instrumentation

All reactions were performed using standard Schlenk and glovebox (Vigor) techniques under a nitrogen atmosphere. All chemicals were purchased from Energy Chemical Inc. If no other special reagents were indicated, other reagents and solvents were used as commercially available without further purification. THF and Toluene were distilled from sodium/benzophenone before use, and other chemicals were used as commercially available without further purification. Column chromatographic purification of products was accomplished using 200-300 mesh silica gel. **HTTM-Bpin** was prepared according to the literature procedure.[1] **6-Br-Phen** was prepared according to the literature procedure.[2]

NMR spectra were measured on a Bruker Avance-400 spectrometer or JOEL 400 MHz NMR spectrometer in the solvents indicated; chemical shifts are reported in units (ppm) by assigning the TMS resonance in the ^{1}H spectrum as 0.00 ppm, the $CDCl_3$ resonance in the ^{13}C spectrum as 77.16 ppm. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet).

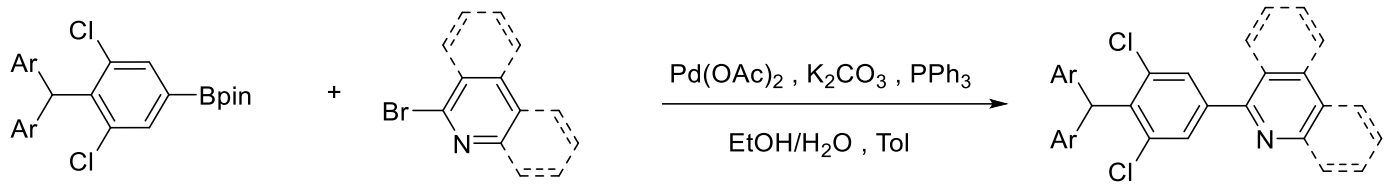
UV–Visible spectra were recorded using a PE Lambda950. The fluorescence experiments were performed on an Edinburgh FLS980. The experimental quantum yields were determined by recording the emission signals within an integrating light sphere on an FLS980. Photoluminescence Spectrometer (Edinburgh Instruments) equipped with an ozone-free Xenon Arc Lamp (450 W), photomultiplier, R928P and double grating excitation and emission monochromators (Czerny-Turner type).

EPR experiments were measured using a CIQTEK EPR200 spectrometer at room temperature in dry-degassed solvent. The samples were placed in 4-mm EPR sample tubes. DPPH (2,2-Diphenyl-1-picrylhydrazyl) powder (g = 2.0037) was utilized as a g-value reference.

High-resolution mass spectra (HRMS) were collected on a WATERS I-Class VION IMS QTof mass spectrometer in an APCI positive mode.

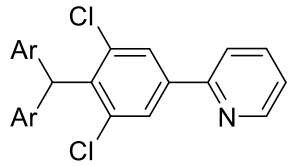
2. Synthesis

Synthesis of radical precursors H-1a/H-1b/H-1c



HTTM-Bpin **2-Br-Py/1-Br-*i*Qu/6-Br-Phen** **H-1a/H-1b/H-1c**

General method for Suzuki–Miyaura cross-coupling reaction between **HTTM-Bpin** and aryl bromides (**2-Br-Py**/**1-Br-*i*Qu/6-Br-Phen**): A vessel was charged with aryl bromides (0.25 mmol, 1.0 equiv.), and ethanol (0.5 mL), water (1.0 mL), toluene (2.0 mL), **HTTM-Bpin** (161.5 mg, 0.25 mmol, 1.0 equiv.), potassium carbonate (K_2CO_3, 138.2 mg, 1.0 mmol, 4.0 equiv.), triphenylphosphine (PPh_3, 10.0 mg, 0.0375 mmol, 15.0 mol%), and palladium acetate ($Pd(OAc)_2$, 3.0 mg, 0.0125 mmol, 5.0 mol%) under nitrogen atmosphere. The reaction mixture was heated at 95 °C for 10 hours. After cooling to room temperature, the solution was extracted with dichloromethane (3 x 10.0 mL) and the combined organic layers were washed with saturated aqueous sodium chloride (10.0 mL) and water (10.0 mL). The organic phase was dried over sodium sulfate and filtered. The crude product was further purified through short column chromatography on silica gel, giving the coupling product **H-1a/H-1b/H-1c**, respectively.



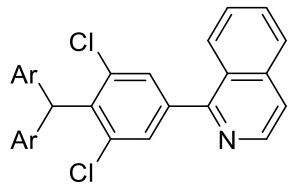
H-1a

According to the general method with **2-Br-Py** (2-bromopyridine, 39.5 mg, 0.25 mmol, 1.0 equiv.), **H-1a** was obtained in 79% yield (117.5 mg) as white solid (eluent: petrol ether/ethyl acetate = 70/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 8.69 (d, *J* = 4.4 Hz, 1H), 8.01 (d, *J* = 1.6 Hz, 1H), 7.87 (d, *J* = 1.6 Hz, 1H), 7.80 – 7.71 (m, 2H), 7.37 – 7.36 (m, 2H), 7.30 – 7.28 (m, 1H), 7.24 (dd, *J* = 4.8, 2.0 Hz, 2H), 6.78 (s, 1H).

^{13}C{H} NMR (100 MHz, $CDCl_3$) δ/ppm 154.15, 150.04, 140.16, 138.27, 138.09, 137.97, 137.34, 137.28, 137.19, 135.44, 134.39, 134.36, 133.77, 133.75, 130.10, 130.07, 128.53, 128.49, 128.40, 126.76, 123.35, 120.61, 50.29.

HRMS (APCI$^+$) m/z: $[M]^+$ calcd for $C_{24}H_{11}Cl_8N^+$: 592.8400; found 592.8385



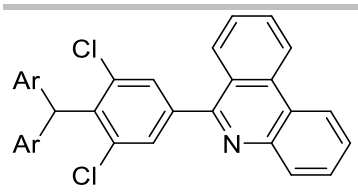
H-1b

According to the general method with **1-Br-*i*Qu** (1-bromoisoquinoline, 52.0 mg, 0.25 mmol, 1.0 equiv.), **H-1b** was obtained in 86% yield (140.0 mg) as white solid (eluent: petrol ether/ethyl acetate = 30/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 8.62 (d, *J* = 5.6 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.75 – 7.69 (m, 3H), 7.64 – 7.58 (m, 2H), 7.40 – 7.38 (m, 2H), 7.28 – 7.26 (m, 2H), 6.85 (s, 1H).

^{13}C{H} NMR (100 MHz, $CDCl_3$) δ/ppm 157.24, 142.29, 140.47, 138.30, 138.13, 137.56, 137.44, 137.34, 137.04, 136.85, 135.37, 134.36, 133.82, 131.57, 130.56, 130.17, 130.11, 129.91, 128.57, 128.54, 128.06, 127.43, 126.75, 126.48, 121.05, 50.34.

HRMS (APCI$^+$) m/z: $[M]^+$ calcd for $C_{28}H_{13}Cl_8N^+$: 642.8556; found 642.8536



H-1c

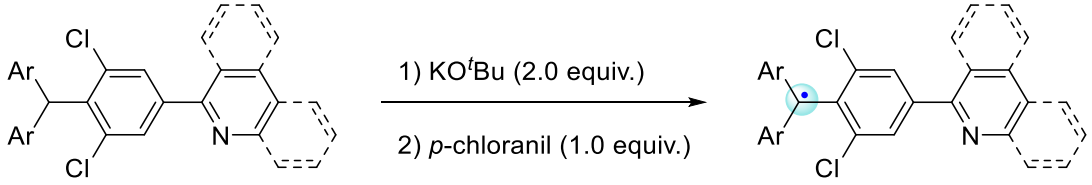
According to the general method with **6-Br-Phen** (6-bromophenanthridine, 64.5 mg, 0.25 mmol, 1.0 equiv.), **H-1c** was obtained in 80% yield (140.1 mg) as white solid (eluent: petrol ether/ dichloromethane = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 8.72 (d, *J* = 8.3 Hz, 1H), 8.63 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.24 (d, *J* = 7.3 Hz, 1H), 8.05 – 7.99 (m, 1H), 7.92 – 7.88 (m, 1H), 7.83 – 7.66 (m, 4H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.41 (dd, *J* = 5.7, 2.2 Hz, 2H), 7.29 (dd, *J* = 10.3, 2.2 Hz, 2H), 6.88 (s, 1H).

^{13}C{H} NMR (100 MHz, $CDCl_3$) δ/ppm 157.78, 143.63, 140.62, 138.30, 138.14, 137.59, 137.48, 137.38, 136.87, 135.46, 134.41, 134.34, 133.84, 133.67, 131.52, 131.09, 130.47, 130.18, 130.12, 129.86, 129.27, 128.57, 128.13, 127.74, 127.69, 124.71, 124.02, 122.60, 122.18, 50.34.

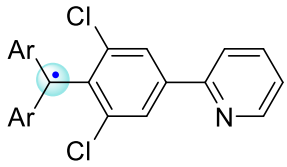
HRMS (APCI$^+$) m/z: $[M]^+$ calcd for $C_{32}H_{15}Cl_8N^+$: 692.8713; found 692.8695

Synthesis of radical precursors 1a/1b/1c



H-1a/H-1b/H-1c **1a/1b/1c**

The α-H compound **H-1a/H-1b/H-1c** (0.5 mmol, 1.0 equiv.) was dissolved in anhydrous tetrahydrofuran (THF, 5.0 mL, 0.1 M) under an inert gas atmosphere. Then potassium tert-butoxide (KO^{t}Bu, 112.2 mg, 1.0 mmol, 2.0 equiv.). was added, and the reaction mixture was stirred for 10.0 h in the dark at room temperature. *p*-Chloranil (122.9 mg, 0.5 mmol, 1.0 equiv.) was then added, and the reaction mixture was stirred for a further 4.0 h in the dark. The solution was extracted with dichloromethane (3 x 10.0 mL) and the combined organic layers were washed with saturated aqueous sodium chloride (10.0 mL) and water (10.0 mL). The organic phase was dried over sodium sulfate and concentrated under a vacuum. The crude product was further purified through short column chromatography on silica gel, giving the product **1a/1b/1c**, respectively.



1a

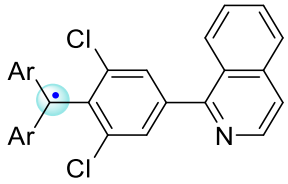
According to the general method with **H-1a** (298.5 mg, 0.5 mmol, 1.0 equiv.), **1a** was obtained in 87% yield (258.8 mg) as a red solid. (eluent: petrol ether/ethyl acetate = 70/1).

UV-Vis: (dichloromethane, λ (nm), ε (M^{-1} cm^{-1})): 377(22250), 606(499).

Crystals: Single crystals of **1a** were grown by slow evaporation from a mixture of methanol and dichloromethane.

EPR (dichloromethane, T = 298 K): *g* = 2.0033

HRMS (APCI$^+$) m/z: $[M]^+$ calcd for $C_{24}H_{10}Cl_8N^+$: 591.8321; found 591.8316.



1b

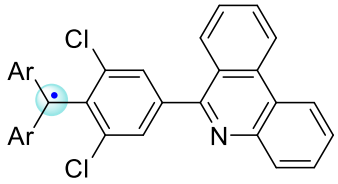
According to the general method with **H-1b** (323.9 mg, 0.5 mmol, 1.0 equiv.), **1b** was obtained in 80% yield (258.4 mg) as a red solid. (eluent: petrol ether/ethyl acetate = 30/1).

UV-Vis: (dichloromethane, λ (nm), ε (M^{-1} cm^{-1})): 375(31931), 547(967).

Crystals: Single crystals of **1b** were grown by slow evaporation from a mixture of methanol and dichloromethane.

EPR (dichloromethane, T = 298 K): *g* = 2.0034

HRMS (APCI$^+$) m/z: $[M]^+$ calcd for $C_{28}H_{12}Cl_8N^+$: 641.8478; found 641.8469.



1c

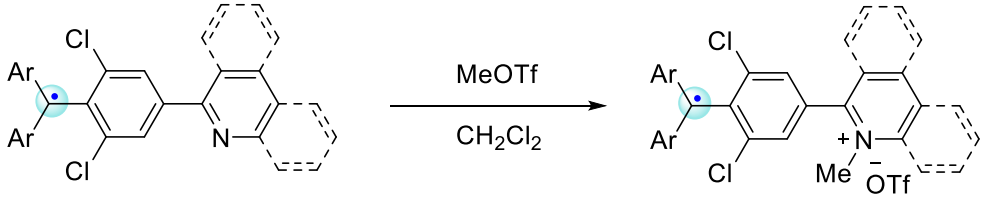
According to the general method with **H-1c** (348.9 mg, 0.5 mmol, 1.0 equiv.), **1c** was obtained in 82% yield (285.3 mg) as a red solid. (eluent: petrol ether/ dichloromethane = 2/1).

UV-Vis: (dichloromethane, λ (nm), ε (M^{-1} cm^{-1})): 375(40257), 547(1195).

EPR (dichloromethane, T = 298 K): *g* = 2.0035

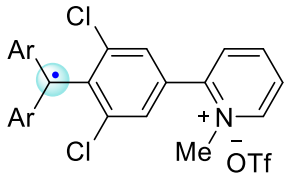
HRMS (APCI$^+$) m/z: $[M]^+$ calcd for $C_{32}H_{14}Cl_8N^+$: 691.8634; found 691.8631.

Synthesis of radical precursors 2a/2b/2c



1a/1b/1c **2a/2b/2c**

General method for the synthesis of radicals **2a/2b/2c**: To a solution of **1a/1b/1c** (0.2 mmol, 1.0 equiv.) in dichloromethane (2.0 mL), methyl trifluoromethanesulfonate (65.6 mg, 0.4 mmol, 2.0 equiv.) was added dropwise at 0 °C. The solution was allowed to warm to room temperature and stirred for 12 h. The crude product was purified through short column chromatography on silica gel (eluent: dichloromethane/methanol = 20/1), giving the product **2a/2b/2c**, respectively.



2a

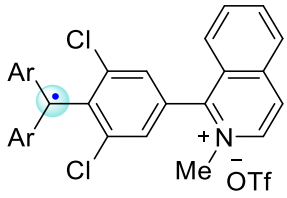
According to the general method with **1a** (119.2 mg, 0.2 mmol, 1.0 equiv.), **2a** was obtained in 91% yield (138.1 mg) as a red solid.

UV-Vis: (dichloromethane, λ (nm), ε (M^{-1} cm^{-1})): 375(22709), 544(925).

Crystals: Single crystals of **2a** were grown by slow evaporation from a mixture of toluene and dichloromethane.

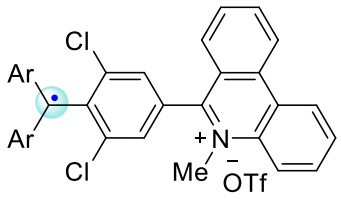
EPR (dichloromethane, T = 298 K): *g* = 2.0035.

HRMS (APCI$^+$) m/z: $[M\text{-}OTf]^+$ calcd for $C_{25}H_{13}Cl_8N^+$: 606.8551; found 606.8549.



2b

According to the general method with **1b** (129.2 mg, 0.2 mmol, 1.0 equiv.), **2b** was obtained in 89% yield (144.2 mg) as a red solid.
UV-Vis: (dichloromethane, λ (nm), ε (M^{-1} cm^{-1})): 375(29415), 556(881).
EPR (dichloromethane, T = 298 K): *g* = 2.0035.
HRMS (APCI$^+$) m/z: [M-OTf]$^+$ calcd for $C_{29}H_{15}Cl_8N^+$: 656.8707; found 656.8703.



2c

According to the general method with **1c** (139.6 mg, 0.2 mmol, 1.0 equiv.), **2c** was obtained in 82% yield (141.0 mg) as a red solid.
UV-Vis: (dichloromethane, λ (nm), ε (M^{-1} cm^{-1})): 377(28219), 550(1014).
Crystals: Single crystals of **2c** were grown by slow evaporation from a mixture of toluene and dichloromethane.
EPR (dichloromethane, T = 298 K): *g* = 2.0036.
HRMS (APCI$^+$) m/z: [M-OTf]$^+$ calcd for $C_{33}H_{17}Cl_8N^+$: 706.8864; found 706.8859.

3. Crystallographic data

X-ray data collection and structural refinement. Intensity data for compounds **1a**, **1b**, **2a**, and **2c** were collected using a Bruker APEX II diffractometer. Using Olex2 [a], the structure was solved with Olex2.solve [b] structure solution program using Charge Flipping and refined with the SHELXL [c] refinement package using Least Squares minimisation. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC 2529636-2529639 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif. [a] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341; [b] Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75; [c] Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Table S1. X-ray data.

Compound Formula	**1a**(2529636) $C_{24}H_{10}Cl_8N$	**1b**(2529637) $C_{28}H_{12}Cl_8N$	**2a•0.5H$_2$O**(2529638) $C_{26}H_{14}Cl_8F_3NO_{3.5}S$	**2c•CH$_2$Cl$_2$**(2529639) $C_{35}H_{19}Cl_{10}F_3NO_3S$
Fw	595.974	645.99	769.04	945.07
T, K	150.00	150.00	150.00	150.00
Cryst syst	triclinic	monoclinic	triclinic	triclinic
Space size	P-1	$P2_1/c$	P-1	P-1
a, Å	8.0726(9)	12.3163(4)	8.1074(3)	8.2874(4)
b, Å	11.5152(13)	13.5475(4)	16.1060(7)	8.3231(4)
c, Å	13.8359(16)	15.9782(5)	24.0635(10)	28.0291(14)
α, deg	77.165(5)	90	80.449(2)	92.261(3)
β, deg	86.376(4)	101.319(2)	87.704(2)	96.458(3)
γ, deg	71.324(4)	90	84.824(2)	96.987(3)
V, A^3	1187.9(2)	2614.19(14)	3085.0(2)	1904.06(16)
Z	2	4	2	2
d_{calcd} g.cm^{-3}	1.666	1.641	1.656	1.648
μ, mm^{-1}	8.799	8.051	7.775	7.679
Size (mm^3)	0.98 × 0.101 × 0.089	0.049 × 0.042 × 0.031	0.062 × 0.056 × 0.043	0.052 × 0.044 × 0.032
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
Refl collected	40429	22742	42875	38981
T_{min}/T_{max}	0.543/0.753	0.575/0.753	0.601/0.753	0.491/0.753
N_{easd}	4028	3565	9257	4790
[R_{int}]	0.0521	0.0781	0.0676	0.1494
GOF	1.034	1.080	1.108	1.051
R [I>2sigma(I)]	0.0264	0.0482	0.0915	0.1079
R_w[I>2sigma(I)]	0.0679	0.1124	0.2283	0.2717
Largest diff peak/hole[e.Å^{-3}]	0.42/-0.47	0.80/-0.59	2.24/-0.76	0.77/-1.21

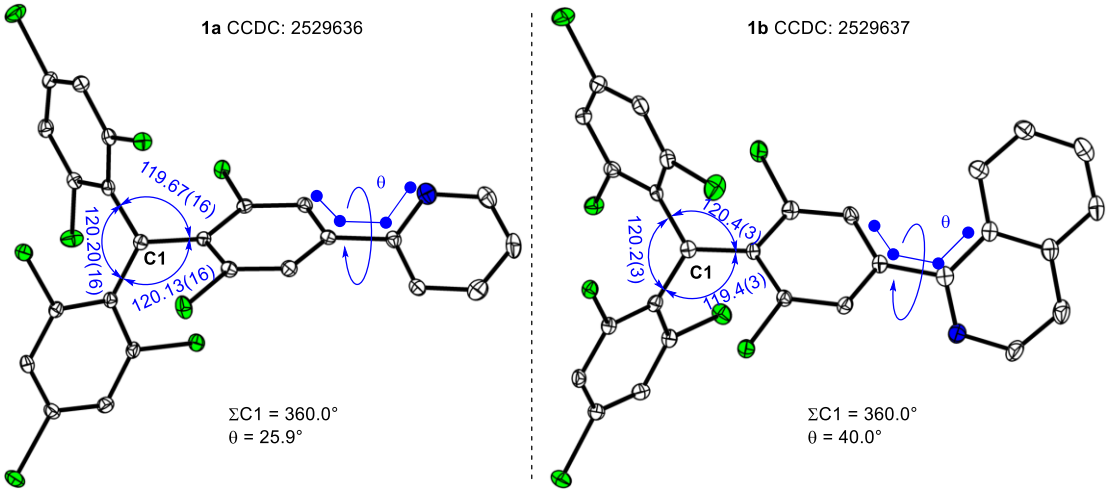


Fig. S1. Single crystal structures of **1a** and **1b**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids at 30% probability level are shown in the crystal structure.

4. EPR measurement

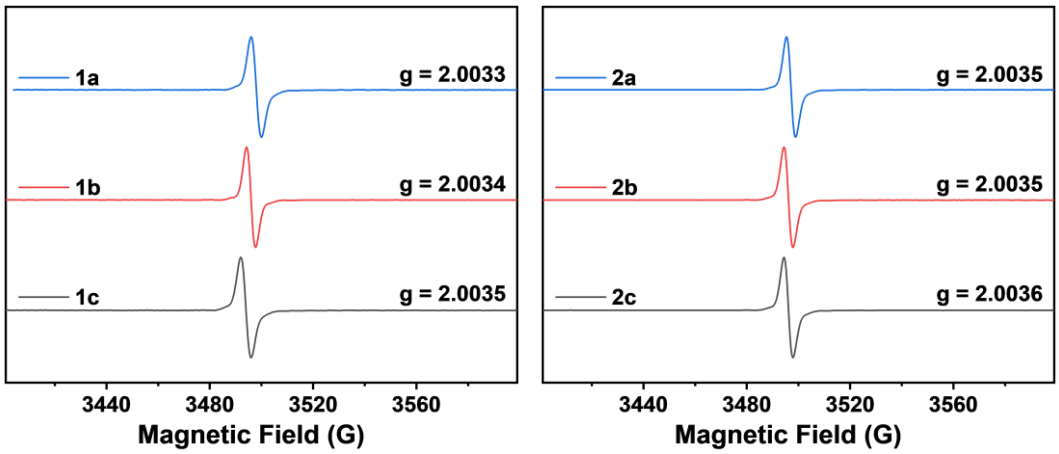


Fig. S2. EPR spectra of **1a**–**1c** and **2a**–**2c** in 1.0 mM dichloromethane at 298 K.

5. Photophysical measurements

5.1. UV-Vis and PL spectra.

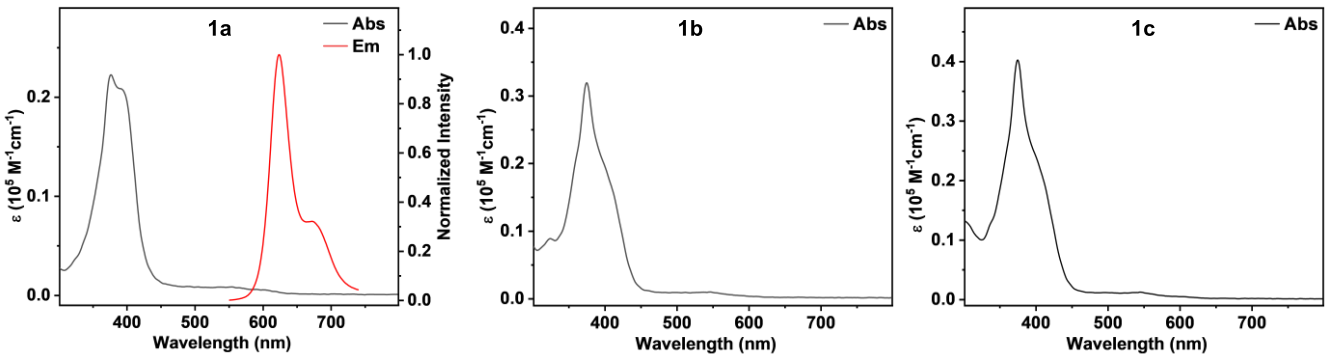


Fig. S3. The UV-Vis absorption of **1a**–**1c** and photoluminescence spectra following 375 nm excitation of **1a** radicals in 0.01 mM dichloromethane solution.

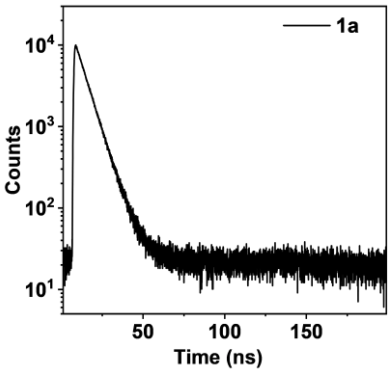


Fig. S4. Photoluminescence decay spectra of **1a** in 0.01 mM dichloromethane solution.

5.2. Natural light stability monitored by UV-Vis.

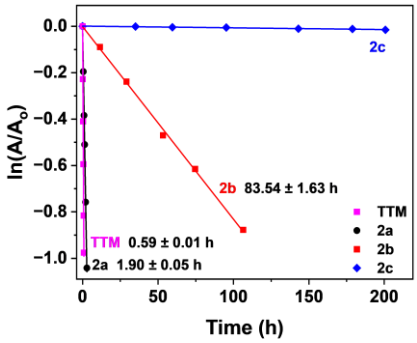


Fig. S5. The decay of the absorption intensities for **TTM** and **2a**–**2c** under natural light.

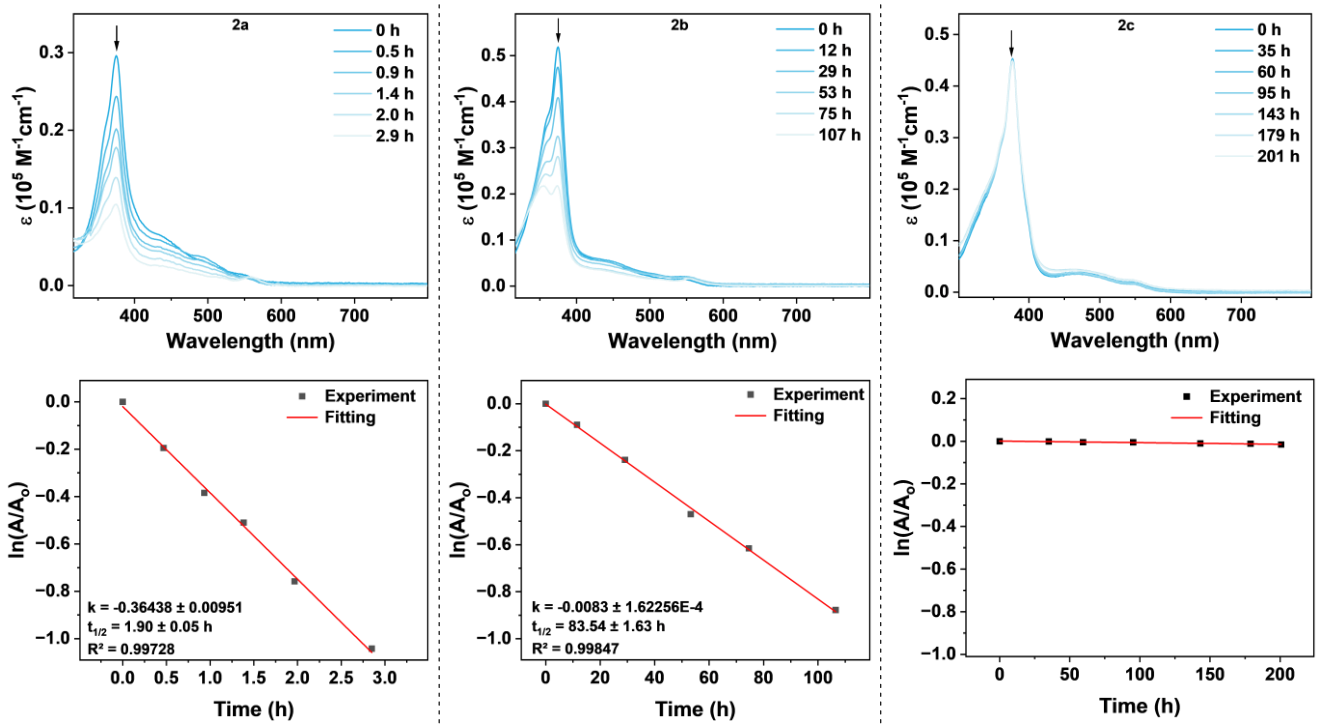


Fig. S6. The absorption decay of **2a**–**2c** in dichloromethane under natural light.

5.3. Protonation–deprotonation properties.

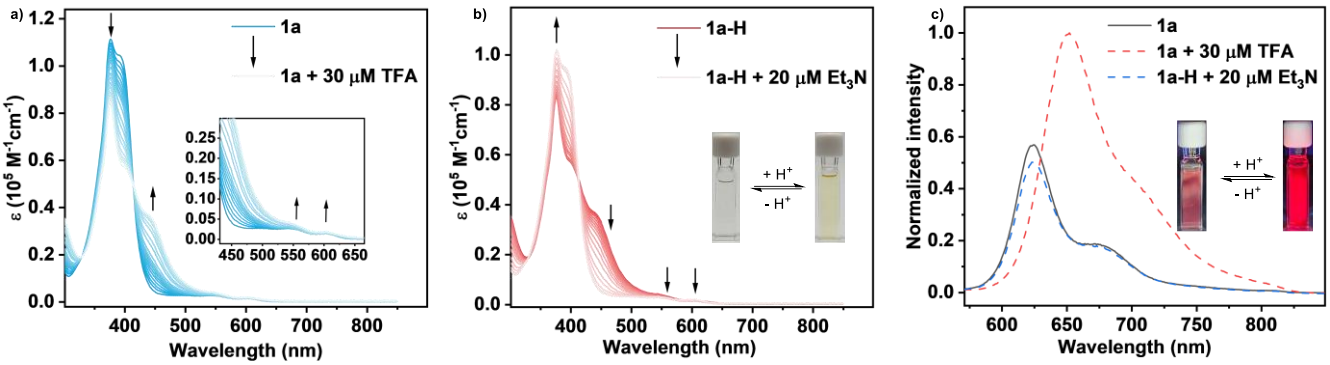


Fig. S7. Changes in UV-Vis absorption and photoluminescence spectra upon addition of TFA (acid) to a dichloromethane solution of **1a**, and recovery of the spectra following addition of Et_3N (base).

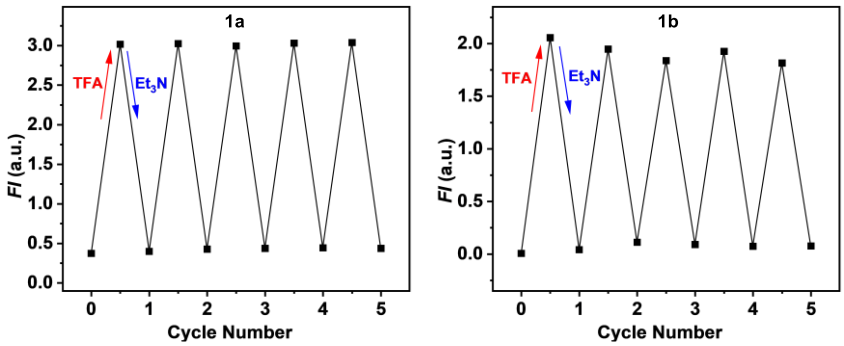


Fig. S8. Acid-base cycle experiments of **1a** and **1b**.

Table S2. Absorption and luminescence of **1a**–**1c** and **2a**–**2c** radicals in dichloromethane solution.

	λ_{abs} (nm)	λ_{em} (nm)	τ (ns)	ϕ (%)	k_r (s^{-1})[a]	k_{nr} (s^{-1})[a]
1a	375, 606	624	6.67	0.45	6.75×10^5	1.49×10^8
1b	375, 547	/	/	/	/	/
1c	375, 547	/	/	/	/	/
2a	375, 544	649	22.87	12.87	5.63×10^6	3.81×10^7
2b	375, 556	709	3.62	3.49	9.64×10^6	2.67×10^8
2c	375, 550	799	2.77	2.86	1.03×10^7	3.51×10^8

[a] Calculated from the equation: $\phi = k_r/(k_r + k_{nr})$; $\tau = 1/(k_r + k_{nr})$.

6. Theoretical study

All the computational calculations reported in this work were performed using the Gaussian 09 code.[3] The geometries for the ground state of these compounds were optimized at the (U)B3LYP hybrid functional and 6-31G(d) basis set for all atoms. It should be pointed out that the structures of all stationary points were fully optimized, and frequency calculations were performed at the same level. The frequency calculations confirmed the nature of all revealed equilibrium geometries: there were no imaginary frequencies. The simulated UV-Vis spectra for optimized molecules were performed at the time-dependent density functional theory (TD-DFT) at the ground-state equilibrium geometries, which were determined using the (U)B3LYP, in association with the 6-311G(d,p) basis set. The analysis of simulated UV-Vis spectra and molecular orbitals (MOs) and spin density was performed using a multifunctional wave-function analyser (Multiwfn)[4] and VMD.[5]

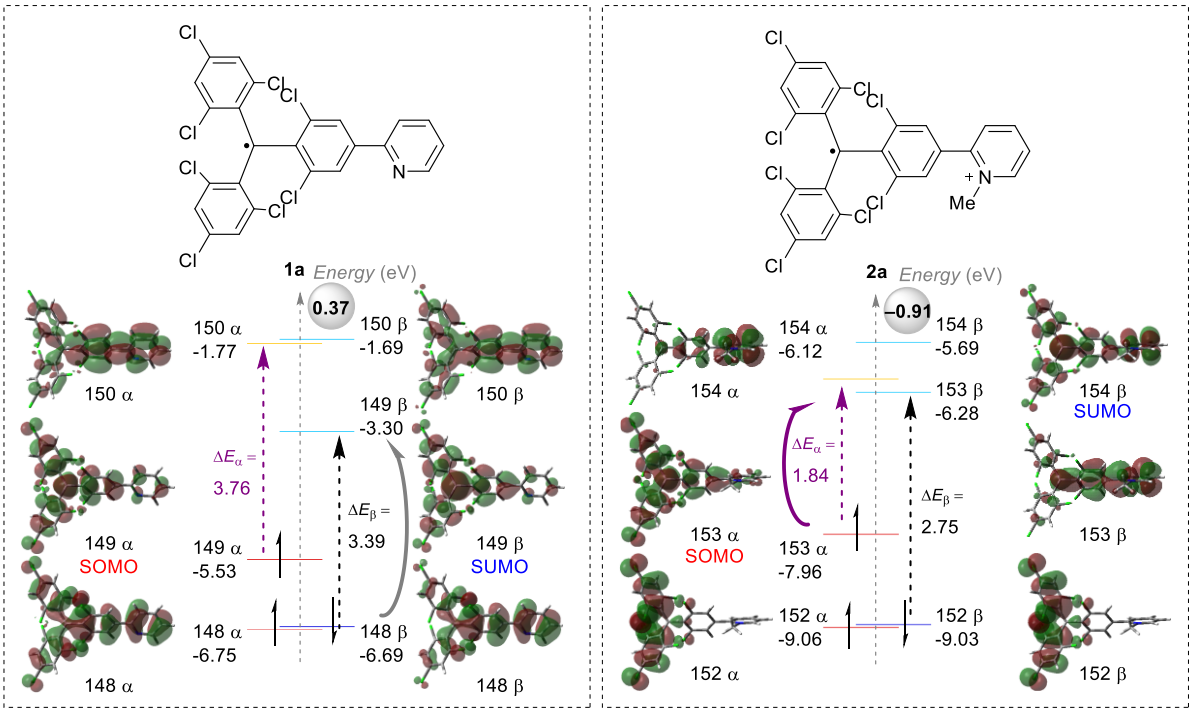


Fig. S9. Plots of the frontier molecular orbitals of **1a**, **2a** (Isovalue 0.02).

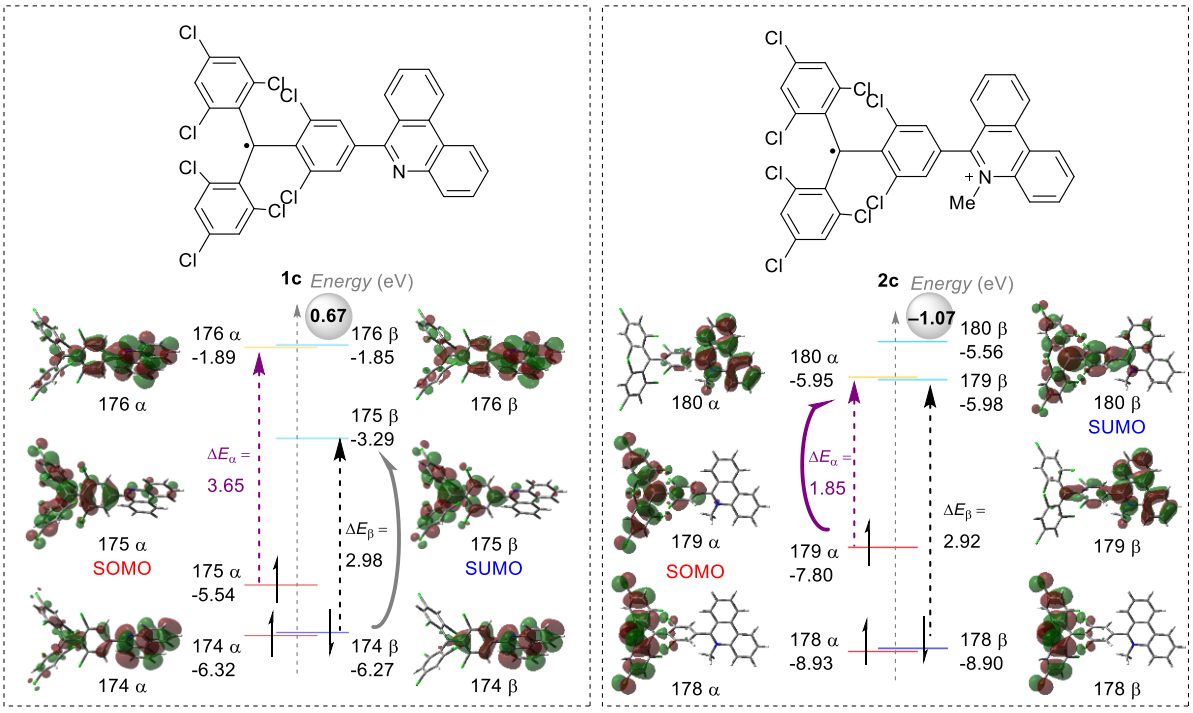


Fig. S10. Plots of the frontier molecular orbitals of **1c**, **2c** (Isovalue 0.02).

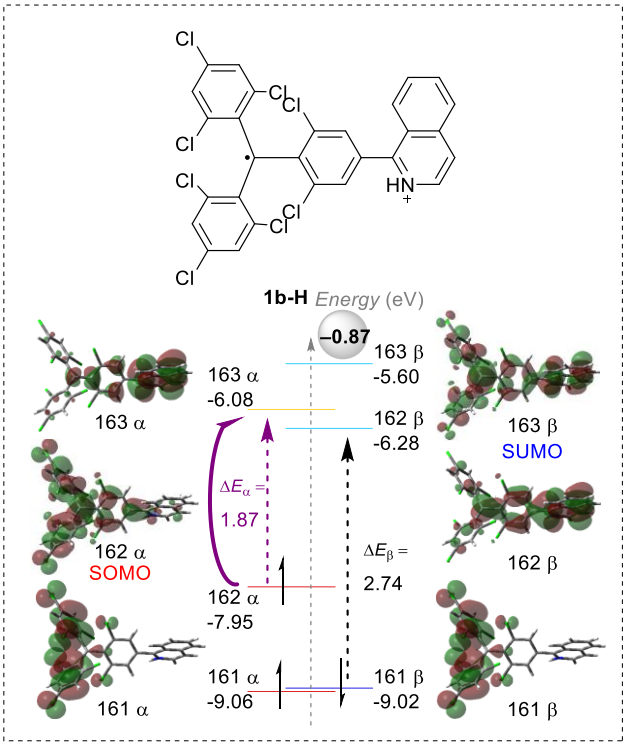


Fig. S11. Plots of the frontier molecular orbitals of **1b-H** (Isovalue 0.02).

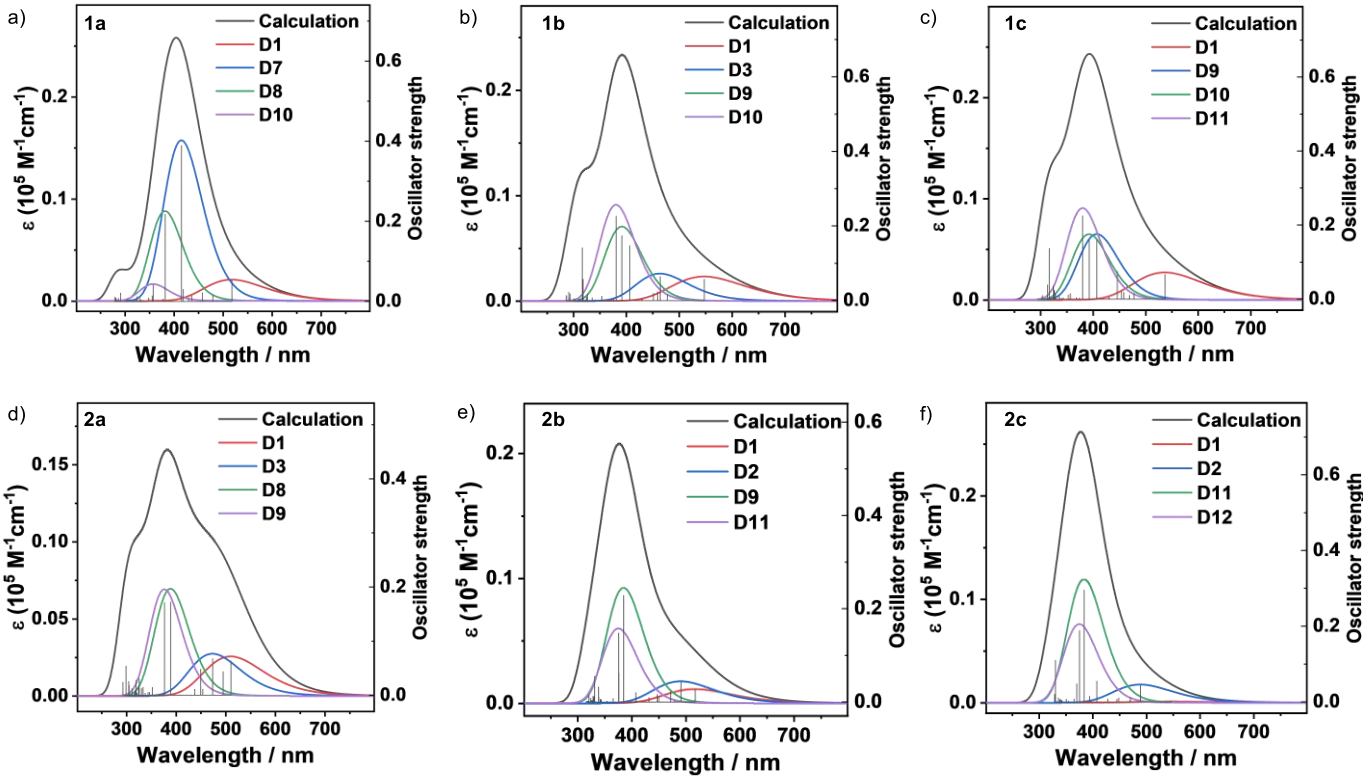
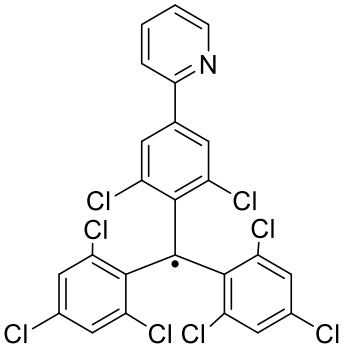


Fig. S12. Calculated UV-Vis absorption spectra of **1a**–**1c, and 2a**–**2c** radicals in dichloromethane.

Table S3. Calculated UV-Vis absorption spectra parameters of **1a**–**1c, and 2a**–**2c**

	Energy (eV)	Wavelength (nm)	Oscillator strength (*f*)	Contribution
1a	2.3950 (Excited State 1)	517.68	0.0514	148β→149β (77%) 149α→150α (12%)
	2.9864 (Excited State 7)	415.16	0.3892	149α→150α (60%) 148β→149β (16%) 145β→149β (10%)
	3.2476 (Excited State 8)	381.77	0.2176	149α→151α (68%) 146β→149β (10%)
	3.4680 (Excited State 10)	357.51	0.0407	148β→150β (25%) 148α→150α (21%) 149α→150α (8%)
1b	2.2652 (Excited State 1)	547.34	0.0571	161β→162β (75%)
	2.6730 (Excited State 3)	463.84	0.0639	161β→163β (25%) 161α→163α (24%) 159β→162β (17%)
	3.1663 (Excited State 9)	391.57	0.1744	162α→163α (25%) 153α→162β (25%) 156α→162β (15%)
	3.2580 (Excited State 10)	317.98	0.0568	162α→164α (67%)
1c	2.3106 (Excited State 1)	536.59	0.0668	174β→175β (74%)
	3.0452 (Excited State 9)	407.15	0.1609	175α→176α (27%) 166β→175β (20%) 165β→175β (12%)
	3.1599 (Excited State 10)	392.37	0.1607	175α→176α (22%) 166β→175β (17%) 165β→175β (14%) 168β→175β (14%)
	3.2625 (Excited State 11)	380.03	0.2245	175α→177α (67%)
2a	2.4302 (Excited State 1)	510.18	0.0632	153α→154α (83%)
	2.6183 (Excited State 3)	473.53	0.0675	151β→153β (70%) 149β→153β (15%)
	3.1885 (Excited State 8)	388.85	0.1719	153α→155α (61%) 147β→153β (15%)
	3.2933 (Excited State 9)	376.47	0.1710	153α→156α (53%)
2b	2.3985 (Excited State 1)	516.92	0.0277	166α→167α (95%)
	2.5275 (Excited State 2)	490.54	0.0433	165β→166β (85%)
	3.2214 (Excited State 9)	384.88	0.2283	166α→169α (47%) 162β→166β (23%)
	3.3030 (Excited State 11)	375.37	0.1480	166α→170α (43%) 160β→166β (14%) 165β→166β (5%)
2c	2.2715 (Excited State 1)	545.83	0.0027	179α→180α (99%)
	2.5364 (Excited State 2)	488.82	0.0432	178β→179β (77%)
	3.2306 (Excited State 11)	383.78	0.2951	179α→182α (46%) 171β→179β (26%)
	3.3061 (Excited State 12)	375.02	0.1878	179α→183α (58%)



1a

Zero-point correction= 0.268841 (Hartree/Particle)
Thermal correction to Energy= 0.298546
Thermal correction to Enthalpy= 0.299490
Thermal correction to Gibbs Free Energy= 0.203234
Sum of electronic and zero-point Energies= -4656.578447
Sum of electronic and thermal Energies= -4656.548743
Sum of electronic and thermal Enthalpies= -4656.547799
Sum of electronic and thermal Free Energies= -4656.644055

C	-2.95861400	-0.85988400	0.91320400
C	-1.57087800	-0.83706300	0.89757800
C	-0.81648300	-0.01192400	0.02295400
C	-1.60632900	0.80177500	-0.83419100
C	-2.99212600	0.79357600	-0.82567000
C	-3.69756400	-0.04692400	0.04503500
Cl	-0.77924600	-1.82560100	2.11804500
Cl	-0.85577100	1.81706500	-2.05749600
C	0.65400000	-0.00045100	0.00731000
C	1.40244500	-1.27125700	-0.02316200
C	1.38492700	1.28057500	0.02117600
C	-5.18383300	-0.04573100	0.02423500
C	-5.94581100	-1.04390900	0.65355700
C	-7.33504900	-0.97366700	0.59690100
C	-7.93239900	0.08171100	-0.08945300
C	-7.09605500	1.01951700	-0.69832100
N	-5.76466300	0.96629300	-0.64849300
C	2.47712700	-1.55068000	0.86038300
C	3.19338600	-2.74296900	0.83846900
C	2.84533400	-3.72046700	-0.08745700
C	1.80138600	-3.51511100	-0.98297200
C	1.10582800	-2.31098500	-0.94255200
C	1.09436100	2.31605900	0.94707800
C	1.77321500	3.53003200	0.97166600
C	2.79375400	3.74978100	0.05287200
C	3.13491700	2.77694900	-0.88057200
C	2.43548900	1.57460200	-0.88625200
Cl	3.73282700	-5.22825600	-0.12618200
Cl	3.66038300	5.26992000	0.07156100
Cl	-0.12284300	-2.10716300	-2.17718600
Cl	2.92440900	-0.42459600	2.12871300
Cl	-0.10349100	2.09500500	2.20867100
Cl	2.86976500	0.45433400	-2.16423700
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H	-3.54455800	1.42646100	-1.50811300
H	-5.46766700	-1.87243300	1.16423100
H	-7.94005000	-1.73763600	1.07744000
H	-9.01155700	0.17602800	-0.15943900
H	-7.51758500	1.85617300	-1.25329500
H	3.99471200	-2.90937300	1.54740800
H	1.54260600	-4.26818200	-1.71675200
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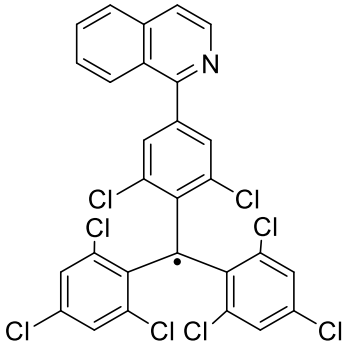

1b

Zero-point correction= 0.315792 (Hartree/Particle)
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Thermal correction to Enthalpy= 0.349028
Thermal correction to Gibbs Free Energy= 0.247391
Sum of electronic and zero-point Energies= -4810.169475
Sum of electronic and thermal Energies= -4810.137184
Sum of electronic and thermal Enthalpies= -4810.136240
Sum of electronic and thermal Free Energies= 4810.237877

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C	-1.09227100	0.80787400	-0.54302300
C	-0.22332100	0.01603000	0.25006800
C	-0.88191600	-0.76445000	1.23882500
C	-2.25774600	-0.76810200	1.40952700
C	-3.08175200	0.00648300	0.58390400
Cl	-0.47487400	1.79388000	-1.86171000
Cl	0.03591000	-1.71960800	2.39387000
C	1.23791100	0.00383800	0.06733800
C	1.98285700	1.27226200	-0.03638700
C	1.95968800	-1.28012500	-0.01102700
C	-4.55337000	0.00872800	0.82423200
C	-5.51937400	-0.01546500	-0.24274500
C	-6.90060900	0.09668100	0.12255600
C	-7.22523700	0.16884300	1.49971200
C	-6.21505100	0.10037700	2.42868600
N	-4.90173400	0.03050100	2.10309800
C	2.92989900	1.52400800	-1.06262100
C	3.64358500	2.71328400	-1.16809100
C	3.42285100	3.71607100	-0.23006200
C	2.50621700	3.53925800	0.80072300
C	1.81046600	2.33760400	0.88565700
C	1.54459000	-2.34086600	-0.85747200
C	2.21218400	-3.55843800	-0.93956100
C	3.34863400	-3.75705400	-0.16298600
C	3.81497400	-2.75944000	0.68619900
C	3.12422300	-1.55379900	0.75255200
Cl	4.30954700	5.22004400	-0.34887500
Cl	4.20282600	-5.28140000	-0.25600500
Cl	0.75344200	2.17214000	2.27403900
Cl	3.20190200	0.36360700	-2.35018700
Cl	0.18600900	-2.15114000	-1.95141800
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C	-6.18393800	-0.19960000	-2.57773600
C	-7.54248000	-0.03586400	-2.21612400
C	-7.89353100	0.10017100	-0.89325300
Cl	3.73171500	-0.40047800	1.92609400
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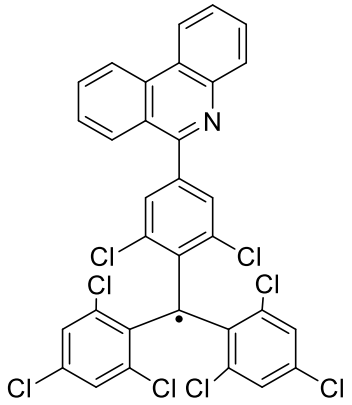
H	-2.70255600	-1.35457700	2.20380700
H	-8.26292400	0.25518000	1.81027300
H	-6.43202300	0.11616400	3.49440400
H	4.34298700	2.85764600	-1.98199700
H	2.34654800	4.31316300	1.54101000
H	1.85932700	-4.32792900	-1.61470500
H	4.68920000	-2.91989100	1.30458000
H	-4.16543300	-0.34825200	-1.90932400
H	-5.91908900	-0.34137700	-3.62166000
H	-8.30836800	-0.03689200	-2.98678900
H	-8.93657600	0.19835000	-0.60335900



1c

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Thermal correction to Enthalpy= 0.398570
Thermal correction to Gibbs Free Energy= 0.290689
Sum of electronic and zero-point Energies= -4963.770618
Sum of electronic and thermal Energies= -4963.735580
Sum of electronic and thermal Enthalpies= -4963.734636
Sum of electronic and thermal Free Energies= -4963.842517

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C	-0.40644800	-0.74213900	0.87832200
C	-1.79625900	-0.71776600	0.89677000
C	-2.50622700	0.06317400	-0.02170700
Cl	0.38921300	1.65948600	-2.26658800
Cl	0.35408500	-1.69253000	2.14746700
C	1.84258500	-0.01187200	-0.04749600
C	2.59129700	1.25758600	-0.10880800
C	2.57208900	-1.29202700	0.01210500
C	-3.99829100	0.07353800	-0.08269900
C	-4.82525600	0.19124900	1.10885000
C	-6.23821200	0.07209200	0.95667000
C	-6.77732200	-0.10626200	-0.37841000
C	-5.85755600	-0.10899800	-1.46321500
N	-4.49539200	-0.02947000	-1.28850600
C	3.65468700	1.47786500	-1.02246300
C	4.37026600	2.66895300	-1.08825800
C	4.03355700	3.70563300	-0.22460600
C	3.00112200	3.56007700	0.69570100
C	2.30644200	2.35592800	0.74335700
C	2.26824700	-2.38562100	-0.84016700
C	2.94714000	-3.59902400	-0.79495300
C	3.98041800	-3.75937500	0.12189700
C	4.33397000	-2.72841500	0.98582100
C	3.63455300	-1.52773000	0.92278500
Cl	4.92098200	5.21210500	-0.29572900
Cl	4.84748000	-5.27794100	0.18930300
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Cl	4.08702700	0.27008500	-2.21838900
Cl	1.05205700	-2.24573200	-2.09472800
Cl	4.08573500	-0.32702500	2.11973200
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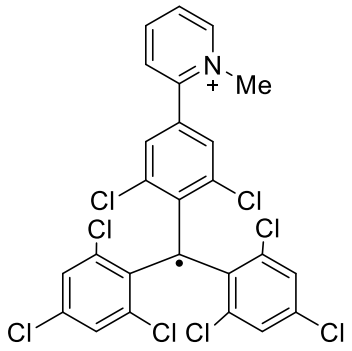
C	-5.11443000	0.57211500	3.49657900
C	-6.50352000	0.40503100	3.35459100
C	-7.05229200	0.17027200	2.10829700
C	-8.15323500	-0.24620200	-0.66877000
C	-8.59719900	-0.36709400	-1.97343700
C	-7.68206700	-0.35389900	-3.04449500
C	-6.33105000	-0.22913900	-2.79015900
H	-2.30968000	1.36246600	-1.72259200
H	-2.31833600	-1.32402900	1.62709300
H	5.16224100	2.78801500	-1.81699600
H	2.75085200	4.35998200	1.38124600
H	2.68353000	-4.39507200	-1.48003200
H	5.12634200	-2.85914700	1.71211300
H	-3.22658100	0.62754700	2.50271000
H	-4.68790500	0.78932700	4.47157500
H	-7.15088100	0.47969600	4.22403900
H	-8.12875300	0.07585900	2.01646200
H	-8.88066100	-0.25815300	0.13626300
H	-9.66026200	-0.47246200	-2.17166300
H	-8.04054700	-0.44754100	-4.06573000
H	-5.59451400	-0.22695600	-3.58740400



2a

Zero-point correction= 0.310566 (Hartree/Particle)
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Thermal correction to Enthalpy= 0.342843
Thermal correction to Gibbs Free Energy= 0.243528
Sum of electronic and zero-point Energies= -4696.222067
Sum of electronic and thermal Energies= -4696.190733
Sum of electronic and thermal Enthalpies= -4696.189789
Sum of electronic and thermal Free Energies= -4696.289105

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C	1.40312300	-0.76747100	-0.99392900
C	0.65516500	0.01874400	-0.07149100
C	1.44140100	0.81726500	0.80774000
C	2.82965800	0.81886000	0.78638100
C	3.52543700	0.01838200	-0.13108800
Cl	0.61607500	-1.72813700	-2.22067700
Cl	0.70756800	1.79366900	2.05673700
C	-0.81286300	0.00569300	-0.03018900
C	-1.53422800	-1.27810900	-0.04007200
C	-1.56106400	1.27247100	0.02045700
C	4.99518600	0.04532800	-0.23797200
C	5.61564400	0.26547600	-1.47612000
C	6.99628800	0.33949900	-1.58844700
C	7.78305900	0.19390400	-0.43954500
C	7.15554500	-0.04785100	0.76193400
N	5.79987500	-0.13639100	0.86006100
C	-2.62855200	-1.53384700	-0.90971500
C	-3.32682300	-2.73616100	-0.91317300
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C	-1.87894500	-3.56035900	0.84411100
C	-1.19765900	-2.35005200	0.82711600
C	-1.29664100	2.35090400	-0.86411800
C	-2.00800300	3.54391900	-0.84440300
C	-3.03146500	3.70325900	0.08710300
C	-3.33875900	2.68767000	0.98890000
C	-2.61236300	1.50306300	0.94818100
Cl	-3.81264200	-5.25518900	-0.02478200
Cl	-3.93441000	5.19163900	0.12547600
Cl	0.06722900	-2.17672900	2.03575800
Cl	-3.11211200	-0.37035000	-2.12440300
Cl	-0.09175400	2.20647000	-2.13345300
C	5.24277400	-0.49369100	2.19066000
Cl	-2.99970000	0.33021400	2.18889200
H	3.29514000	-1.38651600	-1.76463300
H	3.35448300	1.46855300	1.47695200
H	4.97939600	0.41387900	-2.34064600
H	7.45725600	0.52502300	-2.55341200
H	8.86450500	0.25713700	-0.47282100
H	7.70439700	-0.19148200	1.68464400
H	-4.14411200	-2.88760900	-1.60738400

H	-1.59627300	-4.33732800	1.54344400
H	-1.78156000	4.32668200	-1.55763700
H	-4.12075800	2.82051700	1.72623000
H	5.97275900	-1.11465100	2.70979000
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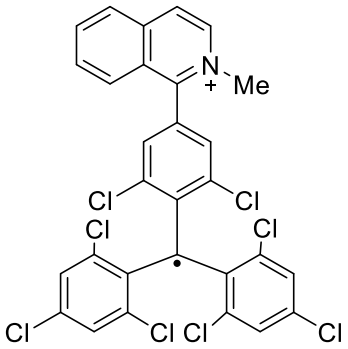
H	4.31777000	-1.05101400	2.05628700

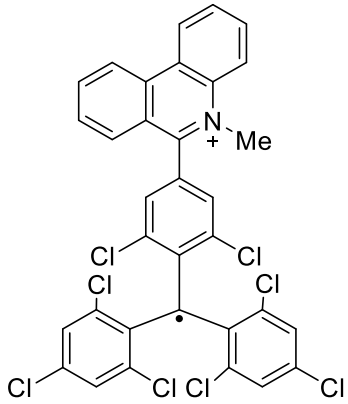


2b

Zero-point correction= 0.357261 (Hartree/Particle)
Thermal correction to Energy= 0.391402
Thermal correction to Enthalpy= 0.392346
Thermal correction to Gibbs Free Energy= 0.286530
Sum of electronic and zero-point Energies= -4849.825141
Sum of electronic and thermal Energies= -4849.791001
Sum of electronic and thermal Enthalpies= -4849.790057
Sum of electronic and thermal Free Energies= -4849.895872

C	2.23979500	0.41331500	1.32247300
C	0.85948500	0.52671300	1.19542400
C	0.12907600	-0.08994900	0.14236500
C	0.91839700	-0.81922800	-0.78851700
C	2.30060600	-0.93649600	-0.67780100
C	2.97145700	-0.32750200	0.38825300
Cl	0.05318100	1.40213200	2.47352400
Cl	0.20917900	-1.55168300	-2.20632000
C	-1.33562000	0.01288700	0.02766600
C	-1.99292600	1.32559800	0.13677300
C	-2.13632000	-1.20320700	-0.19448600
C	4.44595200	-0.45658200	0.51168600
C	5.33374200	0.18567700	-0.39649000
C	6.75045800	0.02302700	-0.23098400
C	7.20706500	-0.76069900	0.85936800
C	6.31362100	-1.34519100	1.70392900
N	4.95332400	-1.20355800	1.52002200
C	-3.12244500	1.54824300	0.96964800
C	-3.75878700	2.78046200	1.06950500
C	-3.27590600	3.85548900	0.32826300
C	-2.16904600	3.70677600	-0.50404300
C	-1.55265500	2.46458500	-0.58665600
C	-1.97064700	-2.38196900	0.57818800
C	-2.72549000	-3.53251200	0.38804000
C	-3.69765700	-3.54308700	-0.60943400
C	-3.91059600	-2.42243800	-1.40738900
C	-3.13982100	-1.28434900	-1.19704300
Cl	-4.06293500	5.40527600	0.44331000
Cl	-4.65572200	-4.97604100	-0.86075700
Cl	-0.23040600	2.35085600	-1.73906200
Cl	-3.73699800	0.28911500	2.01970800
Cl	-0.84376700	-2.43269300	1.92792400
C	4.07056300	-1.92974000	2.46824000
C	4.85386800	1.00533200	-1.45640900
C	5.74224500	1.60389800	-2.32117000
C	7.13767800	1.42229100	-2.16580100
C	7.63546400	0.65086400	-1.13687800
Cl	-3.40824900	0.03258400	-2.31894200
H	2.73222500	0.90839800	2.15240700
H	2.84464500	-1.49954000	-1.42804900
H	8.26914200	-0.90210500	1.02911200
H	6.61154400	-1.95257600	2.54824500
H	-4.60767600	2.90149200	1.73100800

H	-1.80600400	4.53758800	-1.09615800
H	-2.57391000	-4.39702400	1.02223200
H	-4.65301400	-2.43743900	-2.19569300
H	3.17647000	-2.26871200	1.94892100
H	4.61871200	-2.78924400	2.85311200
H	3.78797400	-1.27380100	3.29455100
H	3.78830000	1.16028100	-1.57440900
H	5.37082100	2.22788400	-3.12775500
H	7.81976300	1.90418200	-2.85956900
H	8.70560700	0.51999600	-1.00795700



2c

Zero-point correction= 0.404681 (Hartree/Particle)
Thermal correction to Energy= 0.441342
Thermal correction to Enthalpy= 0.442286
Thermal correction to Gibbs Free Energy= 0.330612
Sum of electronic and zero-point Energies= -5003.424237
Sum of electronic and thermal Energies= -5003.387576
Sum of electronic and thermal Enthalpies= -5003.386632
Sum of electronic and thermal Free Energies= -5003.498306

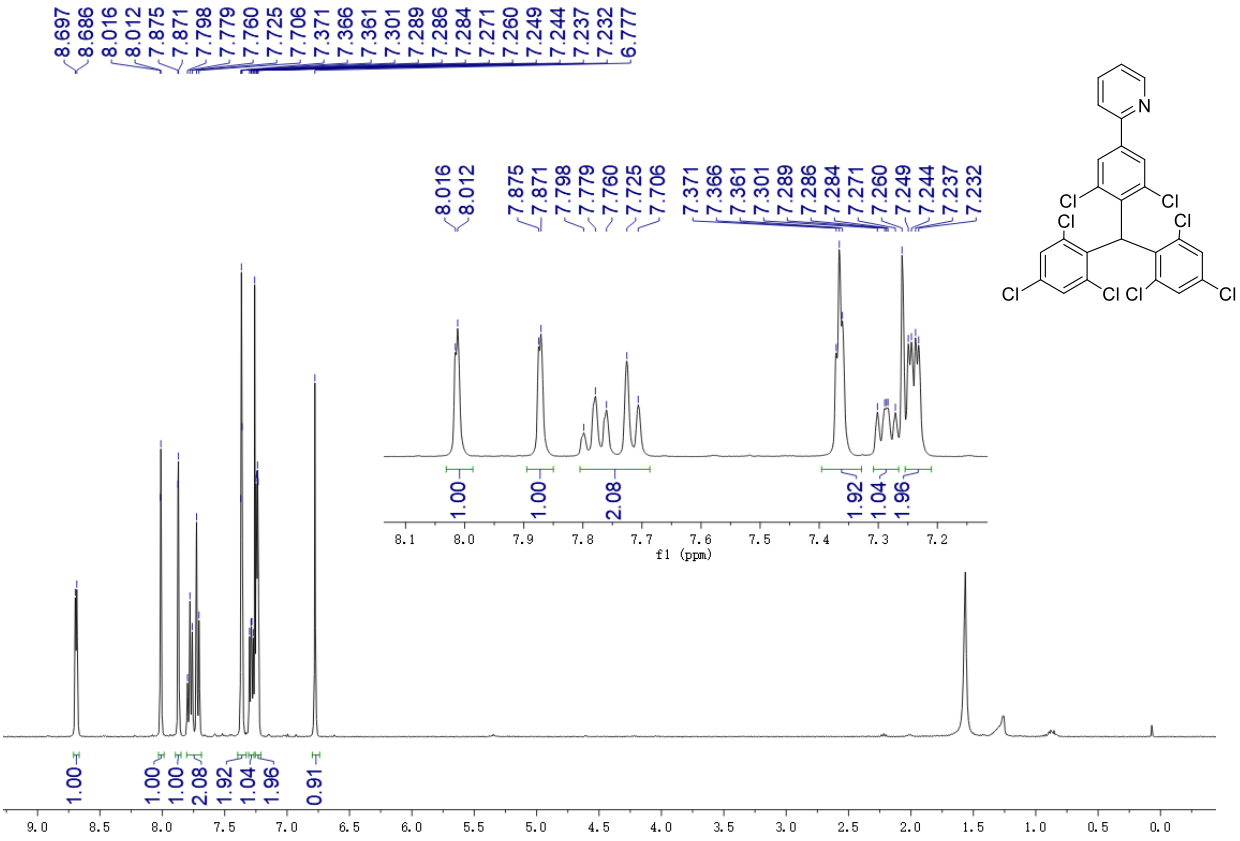
C	-1.93929900	-0.03946900	-0.01574100
C	-0.46579100	-0.04409700	-0.02788500
C	-2.67216000	-1.30602900	0.15062700
C	-2.67009600	1.22937100	-0.16996000
C	0.30352300	-0.71954900	0.95855300
C	1.69432300	-0.74321800	0.94515800
C	2.39482000	-0.06596700	-0.05836200
C	1.68434300	0.63131100	-1.03987500
C	0.29246000	0.62522000	-1.02621200
C	-2.37424700	-2.46906200	-0.60603100
C	-3.06291500	-3.66769200	-0.46814200
C	-4.10067800	-3.74555100	0.45754900
C	-4.44357400	-2.64390000	1.23631500
C	-3.73687900	-1.45662100	1.07919900
C	-3.75186400	1.38263900	-1.07831000
C	-4.45812500	2.57171500	-1.22244600
C	-4.09735400	3.67265000	-0.45068600
C	-3.04207200	3.59238200	0.45471900
C	-2.35392900	2.39205300	0.58016900
Cl	-0.48036000	1.42247100	-2.37404200
Cl	-0.45329800	-1.49860600	2.32617300
Cl	-1.15132700	-2.44075600	-1.86977400
Cl	-4.17202400	-0.16323200	2.17611600
Cl	-4.97716200	-5.24007000	0.64282500
Cl	-1.10584100	2.36127200	1.81809300
Cl	-4.21116600	0.09027100	-2.16680600
Cl	-4.97335900	5.16935000	-0.61967600
C	6.01927900	1.12098100	0.35328200
C	4.59169000	1.11205400	0.36347500
C	3.88456800	-0.05598100	-0.05674200
N	4.55023100	-1.15580100	-0.44347800
C	5.95953200	-1.23249400	-0.41047800
C	6.71267100	-0.09092800	-0.02926600
C	6.68271700	2.30391500	0.73887500
C	5.96880600	3.42103000	1.13429900
C	4.56078900	3.40284500	1.17085200
C	3.88050700	2.26572300	0.79426700

C	6.61360600	-2.43305500	-0.75574500
C	7.99507200	-2.50020000	-0.73581200
C	8.75508500	-1.37648600	-0.37468900
C	8.12174500	-0.19967000	-0.02688000
C	3.82142900	-2.33173700	-0.97842600
H	2.22036500	-1.26147200	1.73954300
H	2.20248800	1.15534900	-1.83529600
H	-2.80949400	-4.51826600	-1.08854300
H	-5.23755100	-2.71015700	1.96983800
H	-5.26573600	2.64001300	-1.94072900
H	-2.77410200	4.44268400	1.06936100
H	7.76460200	2.35081100	0.73296100

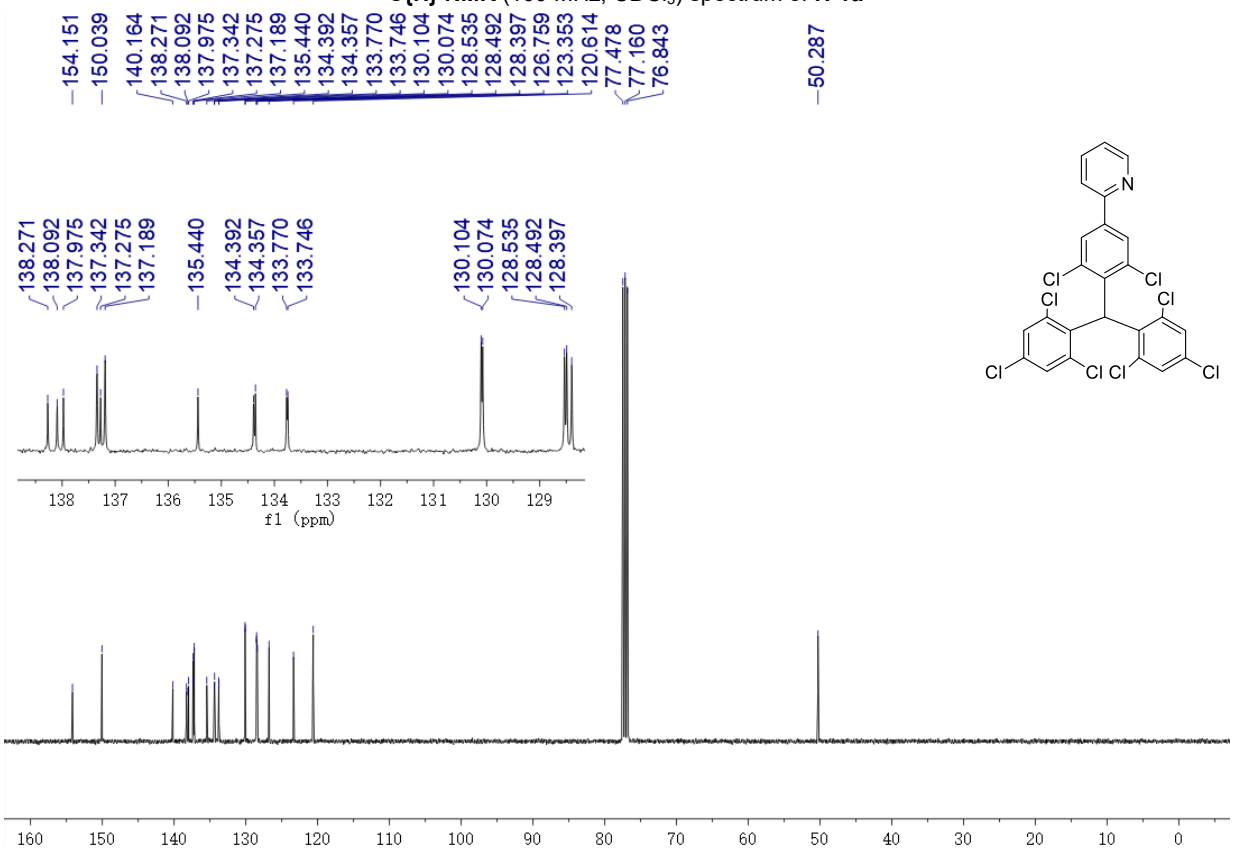
H	6.50313800	4.31963300	1.42775400
H	4.01353600	4.28099900	1.49751100
H	2.79835400	2.24577900	0.82687100
H	6.05467400	-3.31726500	-1.02856100
H	8.48717900	-3.43081000	-0.99940600
H	9.83873900	-1.43271800	-0.36251200
H	8.72358000	0.65379800	0.25972400
H	2.77055800	-2.08908700	-1.08935700
H	4.23846800	-2.58710200	-1.95360800
H	3.92884400	-3.17660600	-0.29457100

7. NMR Spectra

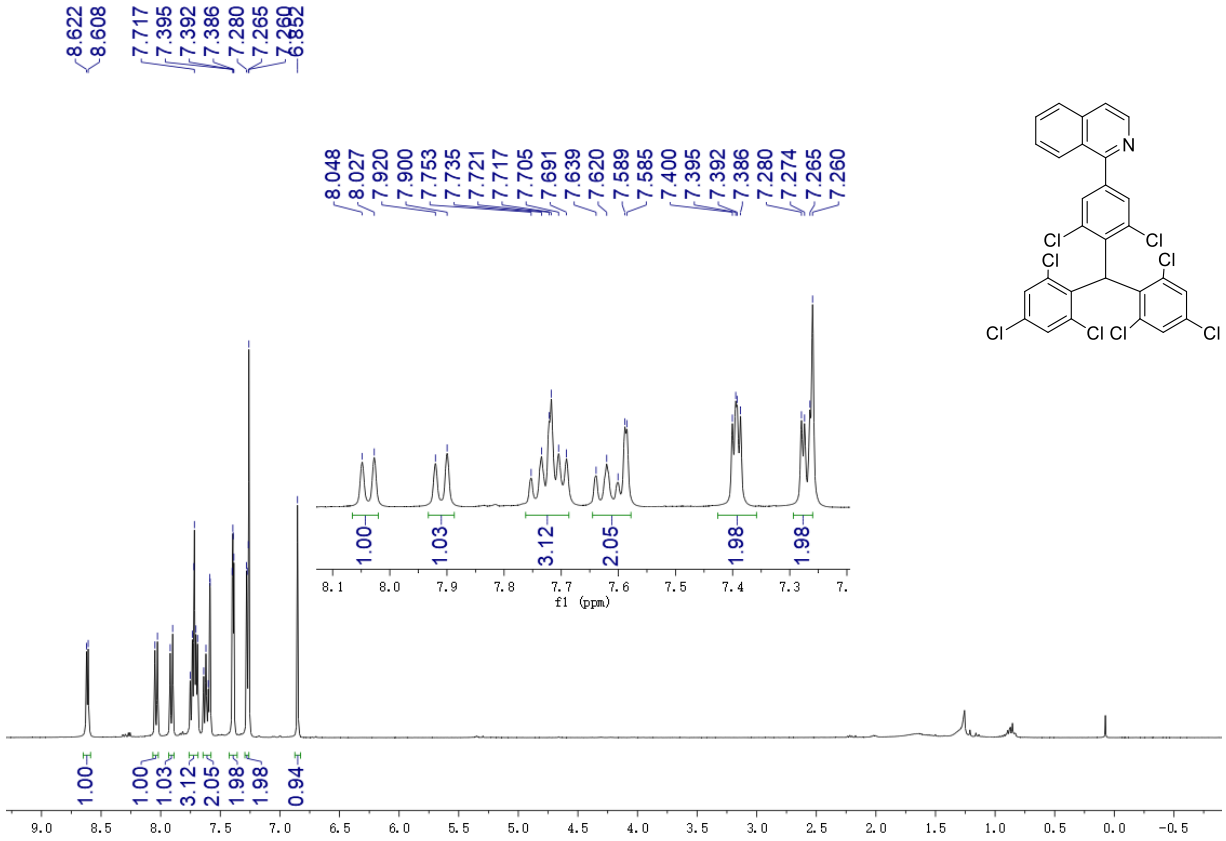
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **H-1a**



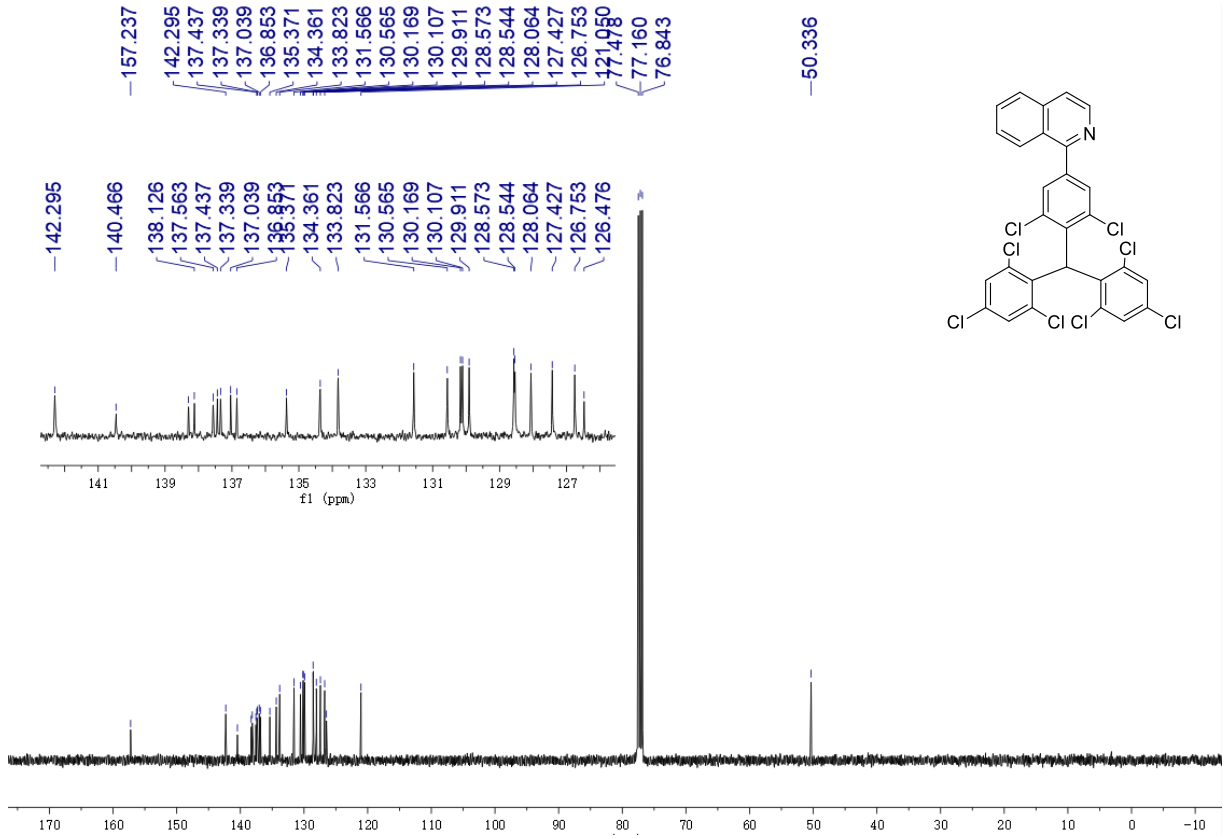
^{13}C{H} NMR (100 MHz, $CDCl_3$) spectrum of **H-1a**



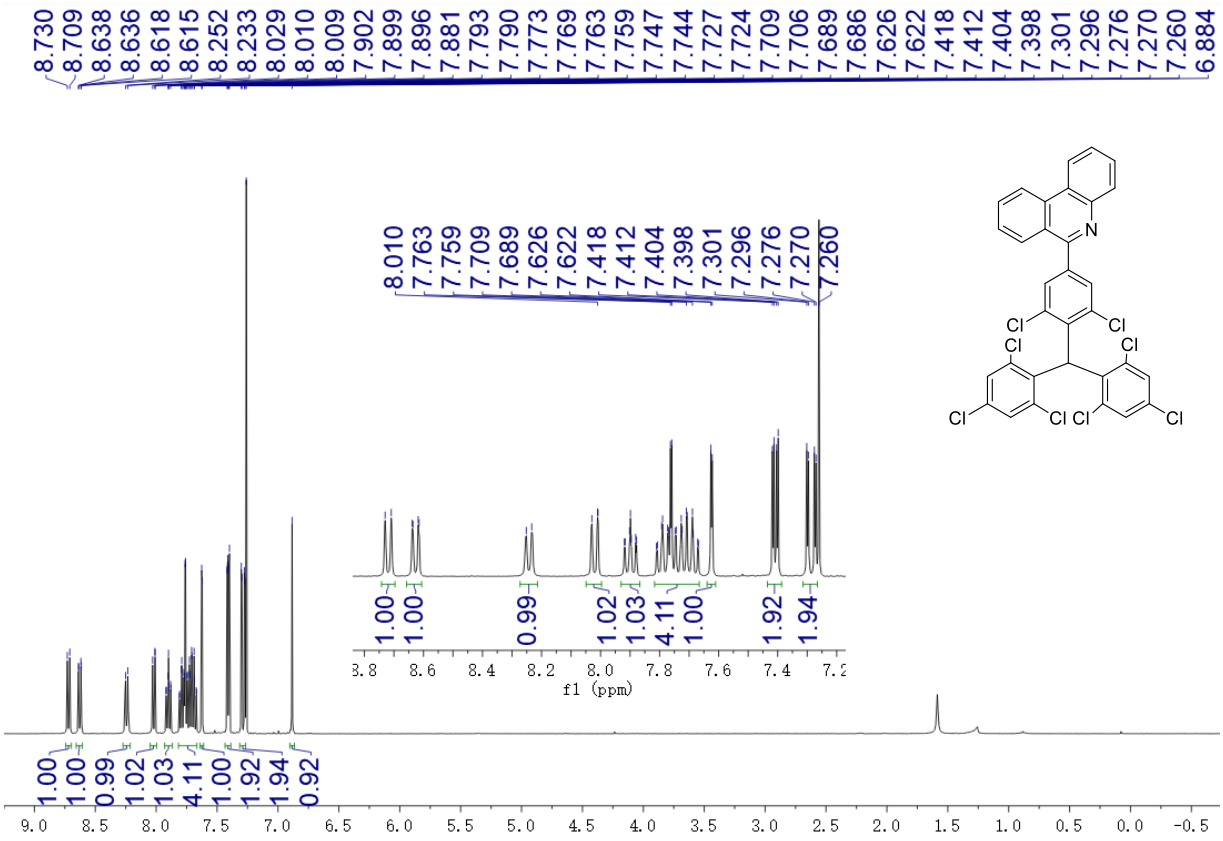
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **H-1b**



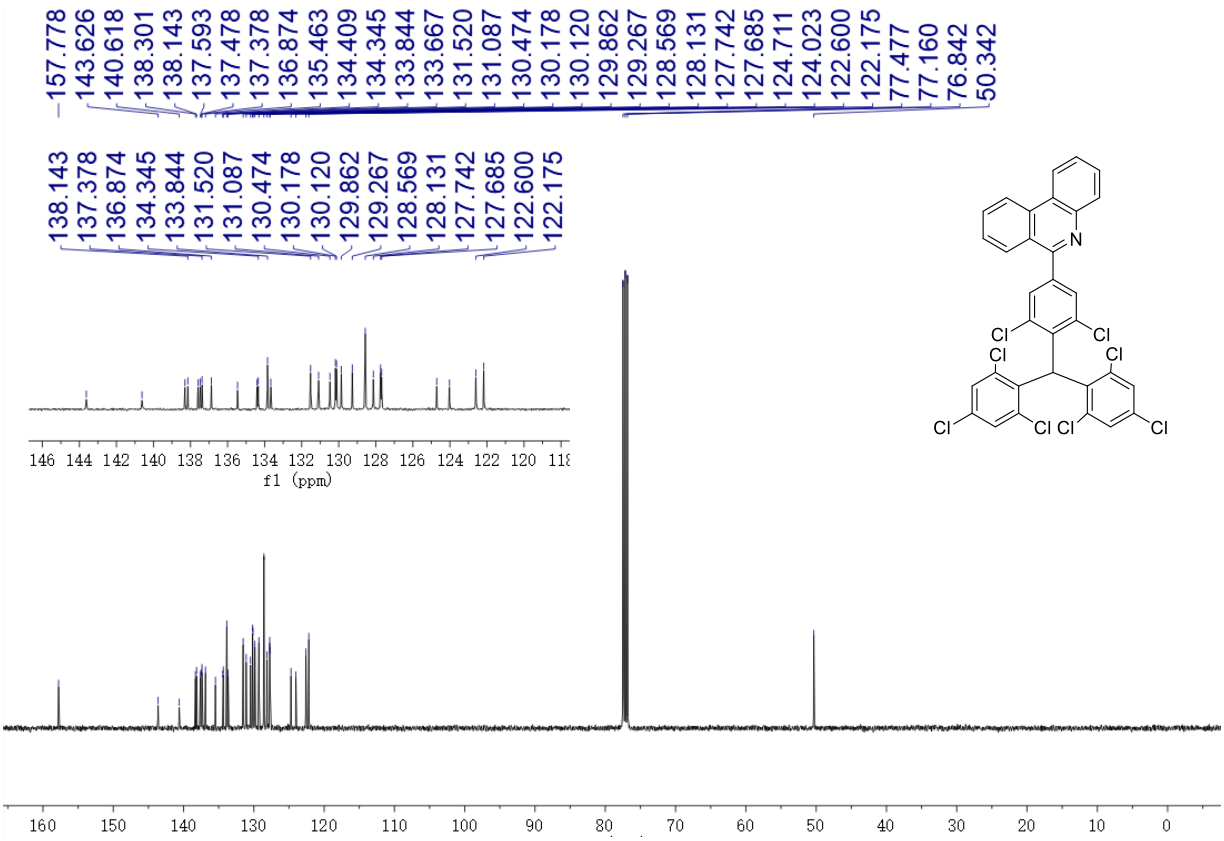
^{13}C{H} NMR (100 MHz, $CDCl_3$) spectrum of **H-1b**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **H-1c**



^{13}C{H} NMR (100 MHz, $CDCl_3$) spectrum of **H-1c**



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