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Electronic Supplementary Information

Synthesis of sterically congested unsymmetrical 1,2-dicarbonyl radicals through a stepwise approach

Yuna Song,[ab‡] Hayoung Song,[b‡] Yunseop Choi,[b]
Jongcheol Seo*[b] and Eunsung Lee*[ab]

[a] *Department of Chemistry, Seoul National University. Seoul, 08826, Republic of Korea.*

[b] *Department of Chemistry, Pohang University of Science and Technology. Pohang, 37673, Republic of Korea.*

E-mail: eunsung@snu.ac.kr, jongcheol.seo@postech.ac.kr

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Materials and Methods

1. General methods

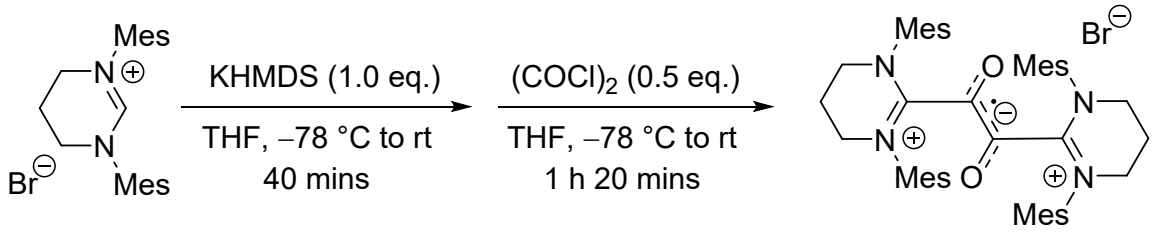
All air- and moisture-insensitive reactions were carried out under an ambient atmosphere, magnetically stirred. All air- and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen. Elemental analyses were performed at Kyungpook National University (KNU) Instrumental Analysis Center with a ThermoFisher Flash 2000. High-resolution mass spectrometry was performed at the Korea Basic Science Institute with a JEOL JMS 700 high-resolution mass spectrometer.

2. Reagents

1,3-Bis(2,4,6-trimethylphenyl)imidazolylidene (*I*Pr), 1,3-bis-(2,4,6-trimethylphenyl)imidazole-ylidene (*I*Mes), 1,3-bis[2,6-bis(1-methylethyl)phenyl]tetrahydro-2(1*H*)-pyrimidinylidene (6-Dipp), 1,3-bis[2,6-bis(1-methylethyl)phenyl]hexahydro-2*H*-1,3-diazepin-2-ylidene (7-Dipp) and 1,3,4,5-tetramethylimidazol-2-ylidene (*I*Me$_4$) was prepared according to the literatures.[1-4] Oxalyl chloride ((COCl)$_2$), 2-mesitylmagnesium bromide (2-MesMgBr), and all other chemicals were purchased from commercial sources and used as received unless otherwise specified. 3Å molecular sieves were activated at 240 ℃ under a dynamic vacuum overnight prior to use. Toluene, pentane, diethyl ether (Et_2O), and tetrahydrofuran (THF) were distilled from deep purple sodium benzophenone ketyl and stored over activated 3Å molecular sieves. Dichloromethane (DCM) was distilled from calcium hydride and stored over activated 3Å molecular sieves. All deuterated solvents were purchased from Aldrich and Cambridge Isotope Laboratories. Acetonitrile-d_3 (CD_3CN) and benzene-d_6 were dried using activated 3Å molecular sieves.

Experimental Details

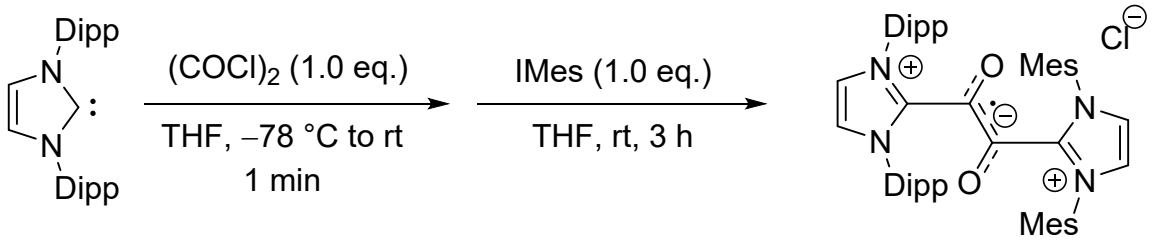
Synthesis of $[(6\text{-Mes})_2C_2O_2]Br$ ([1c]Br)



[**1c**]Br (42% yield)

In a N_2 atmosphere glovebox, dry THF, [(6-Mes)H]Br (50.0 mg, 0.13 mmol, 1.0 eq.), potassium hexamethyldisilazane (KHMDS, 24.9 mg, 0.13 mmol, 1.0 eq.) and oxalyl chloride ($(COCl)_2$, 5.34 μL, 0.062 mmol, 0.5 eq.) were placed in each 20 mL vial at –78 ºC for 30 mins. THF solution (1 mL) of KHMDS was added to the stirred THF solution (5 mL) of [(6-Mes)H]Br and the reaction mixture was warmed to room temperature. After 40 mins, THF solution (0.5 mL) of oxalyl chloride was slowly added to the reaction mixture and stirred. After 1 h 20 mins, dry pentane (10 mL) was added, and the resulting precipitate was washed with cold THF (2 × 1 mL) and dried in vacuo. The residual solid was dissolved in dichloromethane (2.5 mL) and filtered through a pad of Celite. the resulting filtrate was layered with dry pentane for recrystallization and dried in vacuo to afford [**1c**]Br as a purple solid (20.1 mg, 42% yield). The single crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into the dichloromethane solution at room temperature. Data for [**1c**]Br: Anal. Calcd for $[C_{46}H_{56}BrN_4O_2]\bullet(H_2O)_3$: C, 66.49; H, 7.52; N, 6.74. Found: C, 67.06; H, 7.34; N, 7.02. There is also a possibility that chloride anion exists as a counteranion but due to the elemental analysis data (elemental analysis data replacing bromide anion with chloride anion: Anal. Calcd for $[C_{46}H_{56}ClN_4O_2]\bullet(H_2O)_3$: C, 70.25; H, 7.95; N, 7.12. Found: C, 67.06; H, 7.34; N, 7.02), we presumably assigned bromide as a counteranion. Nevertheless, we could not completely rule out chloride as a counter anion in the structure. HRMS (FAB): m/z calcd for $[C_{46}H_{56}N_4O_2$ (M)+] 696.4403, found 696.4401. EPR (microwave frequency = 9.4293 GHz) g_{iso} = 2.0062 (Figure S9).

Synthesis of $[IPrC_2O_2IMes]Cl$ ([2a]Cl)

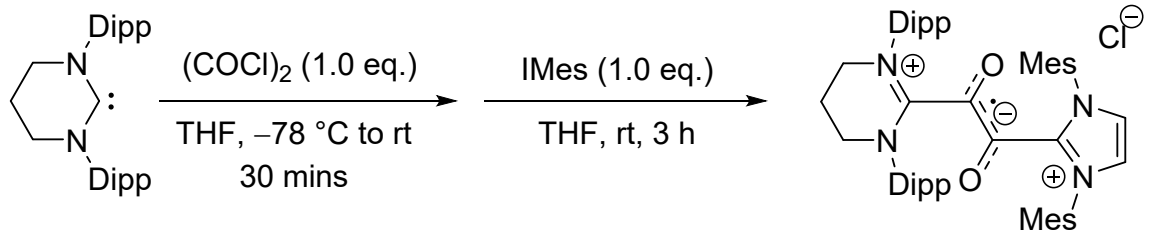


[**2a**]Cl (26% yield)

In a N_2 atmosphere glovebox, dry THF, 1,3-bis-(2,6-diisopropylphenyl)imidazolylidene (*I*Pr, 100

mg, 0.26 mmol, 1.0 eq.) and oxalyl chloride ($(COCl)_2$, 22 µL, 0.26 mmol, 1.0 eq.) were placed in each 20 mL vial at –78 ºC for 30 mins. THF solution (4 mL) of *I*Pr was slowly added to the stirred THF (1 mL) solution of $(COCl)_2$ and the reaction mixture was warmed to room temperature. After 1 min, the solution of 1,3-bis-(2,4,6- trimethylphenyl)imidazolylidene (*I*Mes, 78.2 mg, 0.26 mmol, 1.0 eq.) in THF (4 mL) was added to the reaction mixture. After 3 hours, the reaction mixture was centrifuged, decanted, and washed with dry THF (2 × 2 mL) and distilled water (3 × 3 mL) to obtain a reddish-purple solid ([**2a**]Cl, 53.1 g, 26% yield). The single crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into the dichloromethane solution at room temperature. Data for [**2a**]Cl: Anal. Calcd for $[C_{50}H_{60}ClN_4O_2]\bullet(H_2O)_3$: C, 71.62; H, 7.93; N, 6.68. Found: C, 71.85; H, 7.18; N, 6.83. HRMS (FAB): m/z calcd for $[C_{50}H_{60}N_4O_2$ (M)+] 748.4716, found 748.4720. EPR (microwave frequency = 9.4244 GHz) g_{iso} = 2.00583; hyperfine coupling constants: a(^{14}N) = 2.88, 2.88, 2.72, 2.72 MHz (Figure S9).

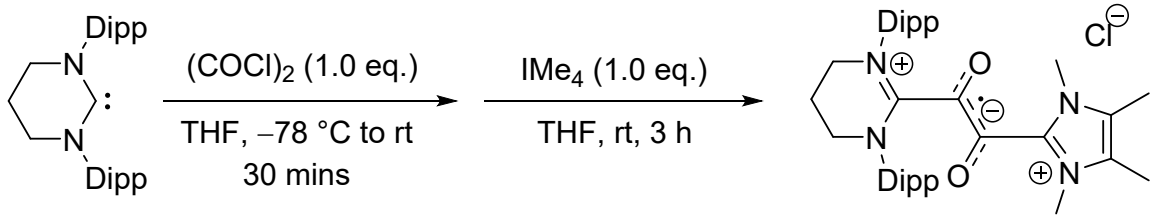
Synthesis of [(6-Dipp)C_2O_2IMes]Cl ([2b]Cl)



(1.02 eq.) [**2b**]Cl (74% yield)

In a N_2 atmosphere glovebox, dry THF, 1,3-Bis[2,6-bis(1-methylethyl)phenyl]tetrahydro-2(1*H*)-pyrimidinylidene (6-Dipp, 169.3 mg, 0.42 mmol, 1.02 eq.) and oxalyl chloride ($(COCl)_2$, 35.2 µL, 0.41 mmol, 1.0 eq.) were placed in each 20 mL vial at –78 ºC for 30 mins. THF solution (7 mL) of 6-Dipp was slowly added to the stirred THF (1 mL) solution of $(COCl)_2$ and the reaction mixture was warmed to room temperature. After 30 mins, the solution of 1,3-bis-(2,4,6-trimethylphenyl)imidazolylidene (*I*Mes, 125.0 mg, 0.41 mmol, 1.0 eq.) in THF (5 mL) was added to the reaction mixture. After 3 hours, the reaction mixture was centrifuged and filtered through a pad of Celite. The resulting filtrate was dried *in vacuo* and washed with distilled water (4 × 2 mL) to obtain a purple solid ([**2b**]Cl, 243.5 g, 74% yield). The single crystals suitable for X-ray analysis were obtained from slow evaporation of THF solution. Data for [**2b**]Cl: Anal. Calcd for $[C_{51}H_{64}ClN_4O_2]\bullet(H_2O)_2$: C, 73.22; H, 8.19; N, 6.70. Found: C, 73.60; H, 8.06; N, 6.43. HRMS (FAB): m/z calcd for $[C_{51}H_{64}N_4O_2$ (M)+] 764.5029, found 764.5026. EPR (microwave frequency = 9.4281 GHz) g_{iso} = 2.00627; hyperfine coupling constants: a(^{14}N) = 2.90, 2.90, 2.56, 2.56 MHz; Gaussian line width = 0.002 mT; Lorentzian line width = 0.04 mT.

Synthesis of [(6-Dipp)$C_2O_2IMe_4$]Cl ([2c]Cl)



(1.02 eq.) [**2c**]Cl (56% yield)

In a N_2 atmosphere glovebox, dry THF, 1,3-Bis[2,6-bis(1-methylethyl)phenyl]tetrahydro-2(1*H*)-pyrimidinylidene (6-Dipp, 200.0 mg, 0.49 mmol, 1.02 eq.) and oxalyl chloride ($(COCl)_2$, 41.6 µL, 0.48 mmol, 1.0 eq.) were placed in each 20 mL vial at –78 ºC for 30 mins. THF solution (7 mL) of 6-Dipp was slowly added to the stirred THF (1 mL) solution of $(COCl)_2$ and the reaction mixture was warmed to room temperature. After 30 mins, the solution of 1,3,4,5-Tetramethylimidazol-2-ylidene (*I*Me_4, 60.2 mg, 0.48 mmol, 1.0 eq.) in dry THF (5 mL) was added to the reaction mixture. After 3 hours, the reaction mixture was centrifuged, decanted, and dried *in vacuo*. The residual solid was dissolved in dry dichloromethane (2.8 mL) and filtered through a pad of Celite. the resulting filtrate was layered with dry pentane for recrystallization and dried in vacuo. the remaining solid was washed with dry cold THF (2 × 2 mL) and toluene (2 × 2 mL) and dried in vacuo. to obtain a reddish brown solid ([**2c**]Cl, 168 mg, 56% yield). The single crystals suitable for X-ray analysis were obtained from a toluene solution. Data for [**2c**]Cl: Desired elemental analysis data were not obtained even from multiple attempts possibly due to residual impurities. HRMS (FAB): m/z calcd for [C37H52N4O2 (M)+] 584.4090, found 584.4093. EPR (microwave frequency = 9.4113 GHz) g_{iso} = 2.0062; hyperfine coupling constants: a(^{14}N) = 3.27, 3.27, 2.93, 2.93 MHz; Gaussian line width = 0.05 mT; Lorentzian line width = 0.007 mT.

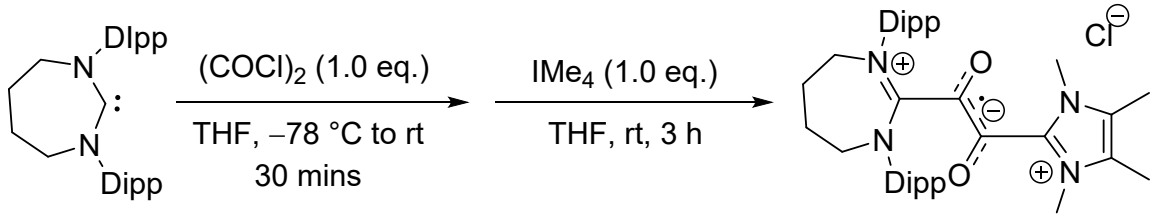
Synthesis of [(7-Dipp)C_2O_2IMes]Cl ([2d]Cl)

(1.02 eq.) [**2d**]Cl (68% yield)

In a N_2 atmosphere glovebox, dry THF, 1,3-bis[2,6-bis(1-methylethyl)phenyl]hexahydro-2*H*-1,3-diazepin-2-ylidene (7-Dipp, 200 mg, 0.48 mmol, 1.02 eq.) and oxalyl chloride ($(COCl)_2$, 40.2 µL, 0.47 mmol, 1.0 eq.) were placed in each 20 mL vial at –78 ºC for 30 mins. THF solution (7 mL) of 7-Dipp was slowly added to the stirred THF (1 mL) solution of $(COCl)_2$ and the reaction mixture was warmed to room temperature. After 30 mins, the solution of 1,3-bis-(2,4,6-trimethylphenyl)imidazolylidene (*I*Mes, 143 mg, 0.47 mmol, 1.0 eq.) in THF (5 mL) was added to the reaction mixture. After 3 hours, the reaction mixture was centrifuged and filtered through a pad of Celite. The resulting filtrate was layered with dry pentane (16 mL) to precipitate the solids. After

decanting the solvent, solids were dried in vacuo and washed with dry cold THF (3 × 2 mL) and diethyl ether (3 × 3 mL) to obtain blue solid ([**2d**]Cl, 259 mg, 68% yield). Data for [**2d**]Cl: Anal. Calcd for $[C_{52}H_{66}ClN_4O_2]\bullet(H_2O)_4$: C, 70.44; H, 8.41; N, 6.32. Found: C, 70.37; H, 7.82; N, 6.34. HRMS (FAB): m/z calcd for $[C_{52}H_{66}N_4O_2$ (M)+] 778.5186, found 778.5184. EPR (microwave frequency = 9.4255 GHz) g_{iso} = 2.00589; hyperfine coupling constants: a(^{14}N) = 2.93, 2.93, 2.61, 2.61 MHz (Figure S9).

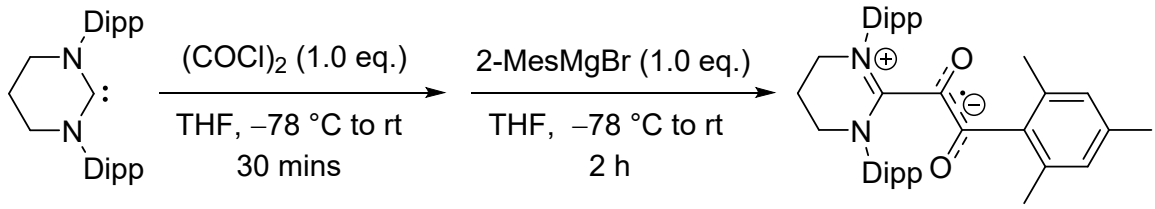
Synthesis of [(7-Dipp)$C_2O_2IMe_4$]Cl ([2e]Cl)



(1.02 eq.) [**2e**]Cl (84% yield)

In a N_2 atmosphere glovebox, dry THF, 1,3-bis[2,6-bis(1-methylethyl)phenyl]hexahydro-2*H*-1,3-diazepin-2-ylidene (7-Dipp, 200 mg, 0.48 mmol, 1.02 eq.) and oxalyl chloride ($(COCl)_2$, 40.2 µL, 0.48 mmol, 1.0 eq.) were placed in each 20 or 40 mL vial at –78 ºC for 30 mins. THF solution (7 mL) of 7-Dipp was slowly added to the stirred THF (1 mL) solution of $(COCl)_2$ and the reaction mixture was warmed to room temperature. After 30 mins, the solution of 1,3,4,5-Tetramethylimidazol-2-ylidene (*I*Me_4, 58.2 mg, 0.47 mmol, 1.0 eq.) in THF (5 mL) was added to the reaction mixture. After 3 hours, dry pentane (10 mL) was added, and the resulting precipitate was washed with cold THF (2 × 1 mL) and dried in vacuo to obtain a reddish brown solid ([**2e**]Cl, 250 mg, 84% yield). The single crystals suitable for X-ray analysis were obtained by storing the concentrated THF, toluene mixture solution at −20 ºC. Data for [**2e**]Cl: Anal. Calcd for $[C_{38}H_{54}ClN_4O_2]\bullet(H_2O)_4$: C, 64.61; H, 8.85; N, 7.93. Found: C, 64.89; H, 8.33; N, 8.51. HRMS (FAB): m/z calcd for [C38H54N4O2 (M)+] 598.4247, found 598.4249. EPR (microwave frequency = 9.4280 GHz) g_{iso} = 2.00627; hyperfine coupling constants: a(^{14}N) = 3.39, 3.39, 2.85, 2.85 MHz (Figure S9).

Synthesis of (6-Dipp)C_2O_2Mes (2f)



2f
Not isolated

In a N_2 atmosphere glovebox, dry THF, 1,3-bis[2,6-bis(1-methylethyl)phenyl]tetrahydro-2(1*H*)-pyrimidinylidene (6-Dipp, 10.0 mg, 0.025 mmol, 1.0 eq.), oxalyl chloride ($(COCl)_2$, 2.12 µL, 0.025

mmol, 1.0 eq.) and 2-mesitylmagnesium bromide (2-MesMgBr, 24.7 μL, 0.025 mmol, 1.0 eq.) were placed in each 4 mL vial at –78 ºC for 30 mins. THF solution (1 mL) of 6-Dipp was slowly added to the stirred THF (0.5 mL) solution of $(COCl)_2$ and the reaction mixture was warmed to room temperature. After 30 mins, a dry THF solution (0.2 mL) of 2-MesMgBr was added to the reaction mixture. After 2 hours, the reaction mixture was centrifuged and filtered through a pad of Celite to obtain dark brown solution. Data for **2f**: EPR (microwave frequency = 9.4277 GHz) g_{iso} = 2.00558; hyperfine coupling constants: a(^{14}N) = 5.42, 5.42 MHz (Figure S9).

X-ray Crystallographic Analysis

CCDC deposition numbers 2350847, 2350848, 2350849, 2350850, and 2350851 contain the supplementary crystallographic data for [**1c**]Br, [**2a**]Cl, [**2b**]Cl, [**2c**]Cl and [**2e**]Cl, respectively. These data can be obtained free of charge *via* https://www.ccdc.cam.ac.uk/

General information

A suitable crystal was coated with paratone-*N* oil and the diffraction data was measured with synchrotron radiation on a 2D beamline or 11C beamline (λ = 0.700 Å) at the Pohang Accelerator Laboratory, Korea. Using Olex2,[5] The structure was solved by ShelXT[6] using intrinsic phasing and refined by ShelXL[7] using least squares minimization. All the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added to their geometrically ideal positions. Solvent mask[8] was used to exclude solvent and some anion molecules during the refinement of [**2b**]Cl and [**2c**]Cl (Grid = 0.25 Å, Solvent R = 1.2 Å).

Table S1. Crystal data and structure refinement for [1c]Br.

Identification code	C2c
Empirical formula	$C_{48}H_{60}BrCl_4N_4O_2$
Formula weight	946.71
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	12.433(3)
b/Å	20.341(4)
c/Å	18.392(4)
α/°	90
β/°	90.85(3)
γ/°	90
Volume/Å^3	4650.8(16)
Z	4
ρ_{calc}g/cm^3	1.352

μ/mm^{-1}	1.156
F(000)	1980.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	synchrotron (λ = 0.700000)
2Θ range for data collection/°	3.84 to 56.346
Index ranges	-16 ≤ h ≤ 16, -25 ≤ k ≤ 26, -24 ≤ l ≤ 24
Reflections collected	9220
Independent reflections	5223 [R_{int} = 0.0491, R_{sigma} = 0.0687]
Data/restraints/parameters	5223/0/283
Goodness-of-fit on F^2	1.143
Final R indexes [I>=2σ (I)]	R_1 = 0.0873, wR_2 = 0.2480
Final R indexes [all data]	R_1 = 0.1160, wR_2 = 0.2850
Largest diff. peak/hole / e Å^{-3}	1.96/-1.20

Table S2. Crystal data and structure refinement for [2a]Cl.

Identification code	p21n
Empirical formula	$C_{51}H_{62}Cl_3N_4O_2$
Formula weight	869.39
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.837(2)
b/Å	21.536(4)
c/Å	22.074(4)
α/°	90
β/°	97.33(3)
γ/°	90
Volume/Å^3	5109.7(18)
Z	4
ρ_{calc}g/cm^3	1.130
μ/mm^{-1}	0.219
F(000)	1852.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	synchrotron (λ = 0.70000)
2Θ range for data collection/°	2.652 to 56.402
Index ranges	-13 ≤ h ≤ 13, -28 ≤ k ≤ 28, -28 ≤ l ≤ 28
Reflections collected	20010

Independent reflections	10632 [R_{int} = 0.0300, R_{sigma} = 0.0545]
Data/restraints/parameters	10632/9/593
Goodness-of-fit on F^2	1.140
Final R indexes [I>=2σ (I)]	R_1 = 0.0999, wR_2 = 0.2906
Final R indexes [all data]	R_1 = 0.1447, wR_2 = 0.3294
Largest diff. peak/hole / e Å^{-3}	1.02/-0.92

Table S3. Crystal data and structure refinement for [2b]Cl.

Identification code	Monoclinic-C2c
Empirical formula	$C_{51}H_{66}ClN_4O_3$
Formula weight	818.52
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/Å	24.135(5)
b/Å	22.011(4)
c/Å	21.701(4)
α/°	90
β/°	122.41(3)
γ/°	90
Volume/Å^3	9733(4)
Z	8
ρ_{calc}g/cm^3	1.117
μ/mm^{-1}	0.122
F(000)	3528.0
Crystal size/mm^3	0.3 × 0.15 × 0.05
Radiation	synchrotron (λ = 0.700000)
2Θ range for data collection/°	3.7 to 57.028
Index ranges	-28 ≤ h ≤ 29, -27 ≤ k ≤ 25, -28 ≤ l ≤ 28
Reflections collected	24582
Independent reflections	8888 [R_{int} = 0.0838, R_{sigma} = 0.0923]
Data/restraints/parameters	8888/0/549
Goodness-of-fit on F^2	0.950
Final R indexes [I>=2σ (I)]	R_1 = 0.0597, wR_2 = 0.1462
Final R indexes [all data]	R_1 = 0.1132, wR_2 = 0.1668
Largest diff. peak/hole / e Å^{-3}	0.63/-0.33

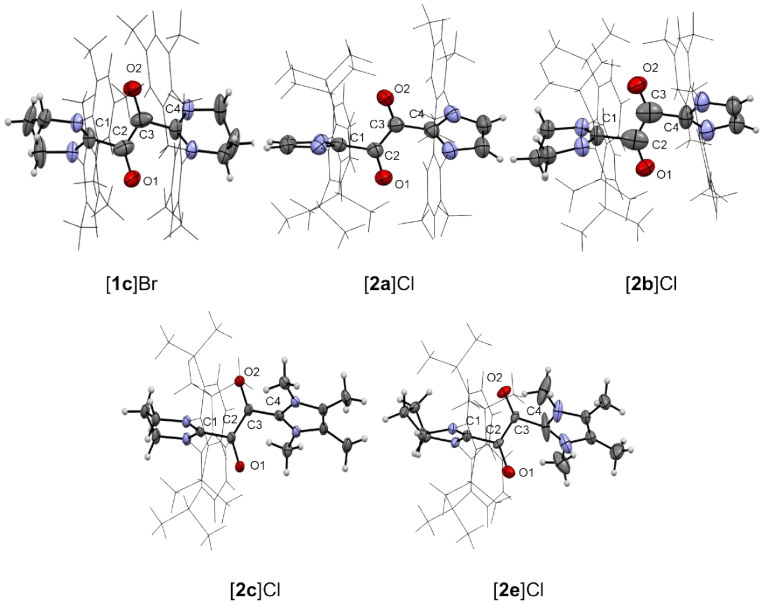
Table S4. Crystal data and structure refinement for [2c]Cl.

Identification code	P-1
Empirical formula	$C_{37}H_{54}ClN_4O_3$
Formula weight	638.29
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	11.704(2)
b/Å	16.986(3)
c/Å	19.521(4)
α/°	87.59(3)
β/°	88.68(3)
γ/°	81.55(3)
Volume/Å^3	3834.8(14)
Z	4
ρ_{calc}g/cm^3	1.106
μ/mm^{-1}	0.137
F(000)	1380.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	synchrotron (λ = 0.700000)
2Θ range for data collection/°	3.262 to 60.688
Index ranges	-16 ≤ h ≤ 16, -24 ≤ k ≤ 24, -27 ≤ l ≤ 27
Reflections collected	36993
Independent reflections	21048 [R_{int} = 0.0572, R_{sigma} = 0.0974]
Data/restraints/parameters	21048/0/859
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0733, wR_2 = 0.1830
Final R indexes [all data]	R_1 = 0.1329, wR_2 = 0.2081
Largest diff. peak/hole / e Å^{-3}	1.05/-0.81

Table S5. Crystal data and structure refinement for [2e]Cl.

Identification code	P21n
Empirical formula	$C_{38}H_{56}ClN_4O_3$
Formula weight	652.31
Temperature/K	100

Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.588(2)
b/Å	18.520(4)
c/Å	17.078(3)
α/°	90
β/°	92.11(3)
γ/°	90
Volume/Å^3	3662.6(13)
Z	4
ρ_{calc}g/cm^3	1.183
μ/mm^{-1}	0.145
F(000)	1412.0
Crystal size/mm^3	0.3 × 0.1 × 0.05
Radiation	synchrotron (λ = 0.700000)
2Θ range for data collection/°	3.246 to 65.848
Index ranges	$-17 \leq h \leq 17$, $-28 \leq k \leq 28$, $-26 \leq l \leq 26$
Reflections collected	23249
Independent reflections	12437 [R_{int} = 0.0789, R_{sigma} = 0.1647]
Data/restraints/parameters	12437/0/448
Goodness-of-fit on F^2	0.884
Final R indexes [I>=2σ (I)]	R_1 = 0.0740, wR_2 = 0.1675
Final R indexes [all data]	R_1 = 0.1920, wR_2 = 0.1976
Largest diff. peak/hole / e Å^{-3}	0.66/-0.45



Structural data

Figure S1. Crystal structures of unsymmetrical 1,2-dicarbonyl radical cations. The displacement ellipsoids are set at a 50% probability level. Dipp groups are simplified, and anions, solvents, and disorders were omitted for clarity. For [**1c**]Br, although we assigned bromide as a counter anion, we could not completely rule out chloride as a counter anion in the structure.

Table S6. Selected bond lengths (Å) and angles (°).

Bond length (Å)	**C1–C2**	**C2–C3**	**C3–C4**	**O1-C2**	**O2-C3**
[**1c**]Br	1.595(9)	1.35(1)	1.595(9)	1.262(7)	1.262(7)
[**2a**]Cl	1.499(5)	1.412(4)	1.478(4)	1.262(4)	1.262(4)
[**2b**]Cl	1.622(6)	1.312(7)	1.580(6)	1.268(5)	1.278(5)
[**2c**]Cl	1.517(3)	1.420(3)	1.493(3)	1.258(3)	1.262(3)
Bond angle (°)	**C1–C2-O1**	**O1–C2–C3**	**C1–C2-C3**	**C2–C3–O2**	**C2-C3-C4**	**O2-C3-C4**
[**1c**]Br	122.6(5)	124.0(6)	112.8(5)	124.0(6)	112.8(5)	122.6(5)
[**2a**]Cl	115.2(3)	127.0(3)	117.7(3)	123.1(3)	117.9(3)	118.9(3)
[**2b**]Cl	117.0(3)	130.6(4)	112.3(4)	127.5(4)	111.8(4)	120.3(4)
[**2c**]Cl	118.4(2)	125.6(2)	116.0(2)	124.3(2)	116.6(2)	119.1(2)

Torsion angle (°)	NHC-C1-C2-O1	O1-C2-C3-O2	O2-C3-C4-NHC2
[**1c**]Br	43.1(7)	170.9(6)	43.1(7)
[**2a**]Cl	79.9(4)	179.0(3)	42.2(5)
[**2b**]Cl	68.7(4)	176.7(4)	41.5(5)
[**2c**]Cl	69.7(3)	179.7(2)	51.3(3)

Table S7. Metric comparison between DFT optimized and X-ray determined structures.

Bond length (Å)	C1–C2	C2–C3	C3–C4	O1-C2	O2-C3
[**1c**]Br (X-ray)	1.595(9)	1.35(1)	1.595(9)	1.262(7)	1.262(7)
[**1c**]Br (DFT)	1.503	1.441	1.534	1.255	1.233
[**2a**]Cl (X-ray)	1.499(5)	1.412(4)	1.478(4)	1.262(4)	1.262(4)
[**2a**]Cl (DFT)	1.505	1.432	1.484	1.242	1.255
[**2b**]Cl (X-ray)	1.622(6)	1.312(7)	1.580(6)	1.268(5)	1.278(5)
[**2b**]Cl (DFT)	1.532	1.436	1.481	1.235	1.257
[**2c**]Cl (X-ray)	1.517(3)	1.420(3)	1.493(3)	1.258(3)	1.262(3)
[**2c**]Cl (DFT)	1.521	1.433	1.479	1.239	1.254

Bond angle (°)	C1–C2-O1	O1–C2–C3	C1–C2-C3	C2–C3–O2	C2-C3-C4	O2-C3-C4
[**1c**]Br (X-ray)	122.6(5)	124.0(6)	112.8(5)	124.0(6)	112.8(5)	122.6(5)
[**1c**]Br (DFT)	118.7	121.4	119.7	128.1	114.2	117.4
[**2a**]Cl (X-ray)	115.2(3)	127.0(3)	117.7(3)	123.1(3)	117.9(3)	118.9(3)
[**2a**]Cl (DFT)	117.2	128.0	114.7	123.4	117.2	119.3
[**2b**]Cl (X-ray)	117.0(3)	130.6(4)	112.3(4)	127.5(4)	111.8(4)	120.3(4)
[**2b**]Cl (DFT)	116.1	128.4	115.4	121.8	118.7	119.4
[**2c**]Cl (X-ray)	118.4(2)	125.6(2)	116.0(2)	124.3(2)	116.6(2)	119.1(2)
[**2c**]Cl (DFT)	116.8	127.2	116.0	123.7	116.8	119.4

Torsion angle (°)	NHC-C1-C2-O1	O1-C2-C3-O2	O2-C3-C4-NHC2
[**1c**]Br (X-ray)	43.1(7)	170.9(6)	43.1(7)
[**1c**]Br (DFT)	42.1	176.5	69.2
[**2a**]Cl (X-ray)	79.9(4)	179.0(3)	42.2(5)
[**2a**]Cl (DFT)	80.6	176.6	46.3
[**2b**]Cl (X-ray)	68.7(4)	176.7(4)	41.5(5)
[**2b**]Cl (DFT)	84.7	176.7	37.6
[**2c**]Cl (X-ray)	69.7(3)	179.7(2)	51.3(3)
[**2c**]Cl (DFT)	73.1	175.5	42.9

DFT calculations at M06/Def2-SVP.

* Due to a disorder, there is no structural data for [**2e**]Cl.

DFT Calculation

General information

Density functional theory (DFT) calculations were performed using Gaussian16.[9] Geometry optimizations were carried out using the atomic coordinates of the structures generated by Chem3D (CambridgeSoft Corp., MA). The nature of all stationary points calculated from full optimizations was confirmed via frequency analysis. All geometry optimizations and NBO calculations[10] were performed using the M06[11] with Def2-SVP basis set,[12] followed by frequency calculations on each optimized structure. Wiberg bond indices (WBIs) were calculated from the optimized geometry with the Löwdin orthogonalization method using Multiwfn.[13]

Coordinates of Optimized Structures

The optimized geometries were displayed in Cartesian coordinates (atomic unit). E° represents 'total electronic energy' and G° represents 'standard Gibbs free energy' in the Hartree unit.

Coordinates of Optimized Structures of [**1c**]Br

E° = -2152.79525; G° = -2151.959378

Charge = 1; Multiplicity = 2;

O 5.3844603434 10.3359342164 12.2885403081
N 3.2928823708 11.1197111243 14.0643699618
N 3.8631392121 9.1812306154 15.2079543791
C 4.1625020794 6.9875357266 14.1910100128
C 4.1786266386 13.3915752345 14.053172597
C 4.4795358811 7.8791474555 15.2323290608
C 3.6170628714 12.3248657202 13.3359809353
C 3.4327970552 7.4432672976 12.9638740019
H 2.5354114231 8.0420876938 13.2021238006
H 3.1059989062 6.5849145382 12.3592782336
H 4.0728202199 8.0757754995 12.321486076
C 3.9398609412 14.7820264363 12.0598320444
C 3.1996362572 12.4539373505 12.005215319
C 4.3198425922 14.61240924 13.3936131713
H 4.7311542008 15.4658564223 13.9463122919
C 4.1656183133 10.1343896382 14.3184453794
C 5.1661154541 7.4671744466 16.3829662646
C 4.5399308924 5.6545564395 14.3396707582
H 4.27800315 4.9433148581 13.5478714501
C 4.57687866 13.2446906601 15.4903879798
H 3.6963815477 13.1388565454 16.1486934287
H 5.1303951953 14.1293245437 15.8366356039
H 5.2252897476 12.3662477366 15.6653510097
C 4.1340420936 16.1046819034 11.3862688101
H 5.2034694934 16.3760818844 11.3423014952
H 3.6279830506 16.9137958831 11.9376167094
H 3.7476748832 16.1041840361 10.3569015609
C 5.2229503078 5.1998458238 15.4710876339
C 2.6505849483 9.2154998814 16.039374807
H 2.9223345789 8.845267485 17.0397450928
H 1.9332559537 8.4841247463 15.6197375974
C 3.3902809483 13.6908443042 11.384257148
H 3.0811206962 13.8074153647 10.3392901063

C 5.5483256146 6.1253742487 16.4618957262
H 6.0907060569 5.7884285902 17.3540884926
C 2.5745294804 11.310813911 11.2718235337
H 3.275431397 10.4609991233 11.2331758193
H 2.3112933706 11.5954476931 10.2433693196
H 1.6495328535 10.9599262221 11.7608198738
C 1.9601528088 11.1143562533 14.6842251722
H 1.2765758519 10.4853023708 14.0817827384
H 1.5769510972 12.1441443291 14.642120741
C 5.4523202854 8.3772667609 17.537329647
H 6.5028931279 8.2738445646 17.851616566
H 4.8316222822 8.1110094966 18.4112539011
H 5.2971668502 9.4364297782 17.2931320932
C 2.0499941046 10.5910946433 16.0960326101
H 1.0566535776 10.5513693757 16.5670439259
H 2.678473768 11.2615003099 16.7070854139
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H 4.8066251883 3.2409257653 16.2604814232
H 6.530852608 3.6186245878 16.1503456961
H 5.6010998226 3.2206799503 14.6779607018
C 5.4384415862 10.1022841056 13.5203601426
O 6.8987381007 9.7182087748 15.3953355024
N 8.6993434812 11.0751915547 13.3919270544
N 8.2583322292 8.9933205786 12.4720420052
C 8.0036919949 6.761379344 13.4303955556
C 7.7190462157 13.3015886103 13.5323338491
C 7.6180259039 7.6996971726 12.4569489904
C 8.3571426879 12.234538818 14.1844839126
C 8.8097755819 7.1539610752 14.6292342295
H 9.6459672041 7.8301438256 14.3774005536
H 9.2328477936 6.2694043516 15.1266675768
H 8.1842861908 7.690118344 15.3654241563
C 7.9688747839 14.6162638347 15.5749150129
C 8.831185152 12.3304213823 15.5003404852
C 7.5452751986 14.4842899296 14.2496776625
H 7.0673022355 15.3347013265 13.74958616
C 7.9247515436 9.9975049686 13.2766327035
C 6.8592650856 7.3408972198 11.3308370659
C 7.6173087917 5.4345147409 13.2386939659
H 7.9352501201 4.6853747413 13.9733031594
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H 6.7246840929 14.089754577 11.796540054
H 6.5953112178 12.3225928085 11.9550615302
C 7.7734672106 15.9068956341 16.3075885108
H 6.793185284 16.35765216 16.0813239462
H 8.536102578 16.6482582017 16.0141255348
H 7.8484412096 15.7762071421 17.3971581863
C 6.8683223722 5.0322930215 12.1306529874
C 9.4434508325 9.0444888646 11.6022476671
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H 10.2583339739 8.4745993937 12.0883552396
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H 8.9443161256 13.6176677236 17.2180883538
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H 5.8893720105 5.7060054789 10.3304184192
C 9.5851366058 11.2120350076 16.1480805058
H 8.9921730449 10.2842939585 16.1435936107
H 9.8352816387 11.4578199353 17.1896736674
H 10.5364825218 11.006600745 15.6270218471
C 9.9600780109 11.190151069 12.6442184267
H 10.7826252874 10.7735645471 13.2563609328
H 10.1660833934 12.2627478165 12.5141942906
C 6.5242367111 8.3104816207 10.238352971
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H 7.1508288263 8.1295167751 9.34662854
H 6.6356078757 9.3576451363 10.5506711921
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H 10.8034651769 10.4947751744 10.7827271069
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C 6.4861463777 3.5994843855 11.9270893154
H 6.6326419825 3.2893174299 10.8805972115
H 5.4182254048 3.430900948 12.1552095848
H 7.0717858114 2.9227086232 12.5672799614
C 6.6972605028 9.8951328621 14.191427718

Coordinates of Optimized Structures of [**2a**]Cl

E° = -2307.3875423; G° = -2306.489227
Charge = 1; Multiplicity = 2;

O 2.8082096961 10.5561651626 7.3875293514
O 2.33944252 11.7888141763 4.1160023133
N -0.1863029367 10.4988060171 5.5619069599
N 1.0849545141 8.894800189 4.8574544567
N 4.3524914119 13.0942953628 7.3298924655
N 5.1458078246 12.3486811779 5.4520090738
C 1.0767681797 10.1710860368 5.2582886144
C 3.0351320729 11.2187775646 6.3462700004
C 2.2286375044 11.1346785851 5.1655873797
C 4.1445913438 12.2049095941 6.3409100663
C 5.4659395961 11.4908059631 4.340447899
C -1.0023671701 9.4056097938 5.3392634832
H -2.0736294659 9.4513173089 5.5236210466
C 6.0140310586 10.2331902485 4.6292875545
C 3.4595147685 13.4087544709 8.4139438829
C -0.6109345325 11.7586542073 6.1216370981
C 2.2512314032 8.1807235819 4.4025131124
C -0.2042931575 8.3980778653 4.8962981517
H -0.4278428894 7.376113177 4.5971037487
C 6.3137390316 9.9004799088 2.2307164312

C 2.4106670681 14.2991122479 8.1571809858
C 2.573802611 8.261911605 3.0387971658
C 5.3335073396 11.9889909692 3.0387368691
C -0.9002905711 12.8184338856 5.246539254
C 6.4256366941 9.4528222273 3.5495055991
H 6.8671225957 8.4698791218 3.7493769911
C -0.7347512144 11.8395534017 7.5199877371
C 3.7171458559 12.8665075284 9.6789820928
C 5.7622708845 11.1627237625 1.9988612264
H 5.6594654025 11.52142486 0.9677544637
C 5.4973876415 13.8180344114 7.0591081577
H 5.8360705511 14.6055076107 7.7294124641
C -0.8017891558 12.6874323009 3.7414171962
H -0.2152781831 11.7801042255 3.5125166475
C 5.9967190552 13.3486571366 5.8876137937
H 6.8893913142 13.6113653926 5.3238265176
C 6.1845824971 9.7656884141 6.0411375546
H 6.7626286042 10.4888727131 6.6442450004
H 6.714894338 8.803276224 6.079361504
H 5.215001277 9.6313614792 6.55130731
C -0.474117327 10.659434702 8.4332244298
H 0.0785351594 9.894570674 7.8582209828
C 2.9732873598 7.4222056357 5.3403621363
C 2.1401056737 14.8079192499 6.7748970685
H 1.4669220102 15.6770442201 6.7954543341
H 1.6500662056 14.032926679 6.1549503342
H 3.0607122276 15.1074657389 6.2454253474
C 6.8017332182 9.0616632454 1.0915239186
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H 7.8285761856 9.3451856095 0.8037417131
H 6.1747760374 9.1889040767 0.1949290182
C 1.607309691 14.6638652016 9.2395857694
H 0.7778655181 15.3601719379 9.0689164849
C 1.8332259055 14.1684266022 10.5256115907
C -1.3458428117 14.0088892064 5.8272563689
H -1.5946373067 14.8584306225 5.1839276153
C 4.7655564086 13.3464298748 2.7695195707
H 5.4761083207 14.1499899045 3.0310314706
H 3.8425086395 13.508218697 3.348295494
H 4.5255423956 13.4638236534 1.7028037577
C 2.8856319493 13.2683826999 10.7230529175
H 3.0572701145 12.8541179303 11.7231832072
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H -2.8175625817 13.4092507415 3.3269582404
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H 4.8791469145 11.5499640017 10.9250354039
H 5.786705362 12.2246234144 9.5533070582
H 4.5742754563 10.954110502 9.268642322
C -1.7979803636 10.0511582915 8.8919381908
H -2.3734104313 10.7735446179 9.4958806433
H -1.6231926348 9.1603371345 9.5165504918
H -2.438268805 9.7517870704 8.0457397942
C 4.4329775829 6.7793763418 3.5112409937
H 5.296981831 6.2100649263 3.1542722065
C 4.0824126241 6.7239221536 4.8568917161
H 4.6706018437 6.1083235882 5.5443358646
C 1.6866438082 5.9885728271 6.9091859627
H 2.3052491592 5.1018745117 6.6875306577
H 0.8287548098 5.9685877938 6.2170726431
H 1.296752157 5.8779031287 7.9338726414
C -0.056420554 13.8533706345 3.1054541416
H -0.6065616814 14.8038158488 3.2100598249
H 0.0755562814 13.6749256385 2.0262461401
H 0.9452249345 13.974610434 3.5481897917
C 0.9681433672 14.5898331532 11.6715166355
H 1.4105616662 15.445673528 12.2094914019
H 0.8462116352 13.7790237508 12.4063572176
H -0.0314711115 14.9046255566 11.3338598622
C 1.0019323023 8.0471077574 1.1157559082
H 0.3364851659 8.5867289555 0.4229011159
H 0.3912635254 7.3228910822 1.6803351069
H 1.7175785433 7.4698506927 0.506073592
C 2.5333282587 10.0474902565 1.2562128147
H 3.3207989188 9.5679733259 0.648794388
H 3.0070370942 10.7751666442 1.9347571864
H 1.8773630103 10.5987671715 0.5627991752
C 3.6461523173 7.2781297283 7.7888727836
H 3.235910857 7.215034556 8.8091955751
H 4.2348265026 8.2062845268 7.7301027214
H 4.3267606348 6.4188455535 7.6642988838

Coordinates of Optimized Structures of [**2b**]Cl

E° = -2347.8457975; G° = -2346.895281

Charge = 1; Multiplicity = 2;

O 13.5568322786 7.0869056591 3.9106637796
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N 13.1041345808 10.0981330988 3.2558570597
N 12.5251054783 9.6243993044 5.4502480041
N 16.5412979867 6.1164098048 3.8844948853
N 17.1994024118 6.8372712386 5.825155646
C 15.01297028 10.5820549758 1.7993249395
C 13.8478121898 9.8339533876 2.0450847311
C 12.1350588547 11.199877506 3.1853104297
H 11.846673054 11.3125151669 2.1293549196
H 12.6342189024 12.1400598914 3.4887333538
C 10.9537276144 10.9033640997 4.0741120128
H 10.4055100684 10.0215656135 3.695277304
H 10.2504632757 11.7488357979 4.0781376653
C 13.2798215448 8.9608448545 1.095827532
C 13.2472014914 9.3759903443 4.361359353
C 12.7175154361 8.9261069088 6.7022132269
C 15.5208323032 11.6494621 2.7503334298
H 14.9783760724 11.5435266608 3.7076076834
C 15.6399148171 10.3981684348 0.5622579304
H 16.544615416 10.9696043237 0.3298191702
C 11.4672810291 10.6462185907 5.4665458957
H 11.8692522275 11.573396838 5.9137785367
H 10.6777163549 10.2802945629 6.1414601974
C 13.9431973842 8.8268486336 -0.1241758316
H 13.5238361262 8.1684586121 -0.892092162
C 11.9485850019 8.2673393863 1.3108761168
H 11.6689209843 8.38708788 2.3724421151
C 13.482350825 9.5586938914 7.7013271366
C 15.1100923736 9.5354639878 -0.3886938682
H 15.6036030828 9.4264066544 -1.3595667464
C 10.8650468104 8.9235396932 0.4563686485
H 11.076974746 8.7932722421 -0.6184713169
H 10.7801580105 10.0080536634 0.6392677971
H 9.8809063369 8.4688142527 0.6558458014
C 12.0080800984 6.7686521369 1.0497613076
H 11.023423799 6.3118106267 1.2422971131
H 12.7472925286 6.286107621 1.7064230724
H 12.2709882102 6.5422150823 0.001448347
C 16.1174543107 6.0614035989 2.5082755015
C 17.0023589754 11.5186687692 3.0787046622
H 17.2025368466 10.5931824723 3.6400998569
H 17.3219441061 12.3600622006 3.7144789863
H 17.6337722639 11.5392625297 2.1740119629
C 12.0042035584 7.7322164647 6.92570805
C 16.7987779008 6.8786592788 1.5963173501
C 15.2194869839 13.0321419236 2.1715616517
H 15.8008765915 13.2080979088 1.2504929573
H 15.488798426 13.8248197484 2.8883642634
H 14.1553837286 13.1541223587 1.9086949111
C 16.3508232178 7.0899838432 4.8027724045
C 17.5107248377 5.2414523981 4.3421582785
H 17.8314375652 4.3970790403 3.7356124893
C 15.2050572179 5.074360634 2.1177814918
C 17.2703863443 7.4746730045 7.1140336595
C 13.5596048712 8.9245641305 8.9446120966
H 14.148941642 9.385482291 9.7442832404
C 15.6032734589 5.7396017204 -0.1999004062
C 17.9199658842 5.6914140151 5.5525479942
H 18.6490851891 5.3069165321 6.2630643784
C 12.1111542666 7.1505164822 8.1916559435
H 11.5685639838 6.2237207901 8.4031926592
C 11.0910444032 7.1086706136 5.8890707857
H 11.3041398561 7.5796143841 4.9139410155
C 16.4418625 6.9740286991 8.1252521251
C 14.1155041947 10.9238877351 7.5177870438
H 14.0866939499 11.1726152286 6.4409143367
C 16.521171704 6.6946847381 0.2421740875
H 17.0516452435 7.3119975354 -0.4914588201
C 12.8813574187 7.7370634095 9.1890483927
H 12.9438092655 7.2669767635 10.1755198237
C 16.6078887093 7.5044973735 9.404985371
H 15.980184887 7.1255184555 10.2205247141
C 17.5617030963 8.4897489418 9.6764621851
C 14.9549628228 4.9476296358 0.7509568689
H 14.2292271571 4.1960539414 0.4174557743
C 13.3162545148 11.9758393425 8.2882259804
H 12.2434345802 11.9711894446 8.0331532548
H 13.7110254587 12.9865194847 8.0940172999
H 13.3863108557 11.7988309158 9.3749867837
C 18.2400271797 8.4591132104 7.3311567592
C 14.1153588484 8.1149970792 4.3056865514
C 17.8015349848 7.8891505948 2.0584395367
H 17.3189670608 8.7173697985 2.6067263785
H 18.3396843551 8.3319587494 1.2078767794
H 18.5528828017 7.4490734832 2.7385527452
C 15.4257366533 5.9148148403 7.8305223526
H 14.6284397755 6.294931472 7.1635035791
H 14.9386819084 5.5627013777 8.7507689662
H 15.8711932518 5.0363966325 7.3319981845
C 18.36412473 8.953190567 8.6298719458
H 19.1150982791 9.7258318372 8.8303148512
C 15.331210124 5.548466155 -1.6591963416
H 14.2622435082 5.3597607898 -1.8486425707
H 15.8813030935 4.6783321019 -2.0561184494
H 15.638308814 6.4236263393 -2.2522781688
C 9.626444635 7.3676103209 6.2367166565
H 9.3601418843 6.9041872497 7.2019465748
H 8.9617037396 6.9391498131 5.4689960428
H 9.3963333457 8.4432450679 6.3186536961
C 15.4684390937 8.2780809328 4.7586110245
C 11.3479421687 5.6171286073 5.7142528084
H 12.4118103221 5.4166268629 5.5137621667
H 10.7677790831 5.2275200474 4.8619698175
H 11.0436020329 5.0392395221 6.6033500808
C 14.5443415608 4.178441357 3.1162529506

H 15.2314696953 3.3930036265 3.4773743617
H 13.6770304327 3.668469562 2.6716587062
H 14.1971781282 4.7497121559 3.9906987015
C 15.5780314349 10.9661577471 7.935020299
H 15.7016367544 10.7805064293 9.0161957504
H 15.9995788358 11.9639998578 7.7309347752
H 16.169520474 10.2246483497 7.3797176837
C 19.073951213 8.9735139642 6.202895325
H 18.4228710394 9.4350903387 5.4396091802
H 19.6438380669 8.1695477742 5.7058227755
H 19.7937616401 9.7284045304 6.5482877789
C 17.6919547593 9.0574665577 11.054840545
H 16.9441557548 9.8525648573 11.2249702328
H 18.682503015 9.5054032647 11.2221595132
H 17.5248053615 8.2914082196 11.8273949656

Coordinates of Optimized Structures of [**2c**]Cl

E° = -1807.9114645; G° = -1807.162380

Charge = 1; Multiplicity = 2;

O 5.8829754951 2.2789595693 6.0327544121
O 5.5612582343 5.1665595572 8.0213321162
N 7.0335307969 5.1709650468 5.1292610013
N 4.8626494522 4.649939095 4.4690418905
N 6.0962934626 3.0140048727 9.9685280842
N 4.6476735476 1.8592003963 8.8369700975
C 8.14387589 4.9940205078 6.0399915143
C 5.8905364365 4.5180580631 5.3024679975
C 8.9402697691 3.8397298108 5.9167991578
C 3.6293844604 3.9270299305 4.6869862172
C 9.4830762693 5.8039841811 7.853901789
H 9.7232036939 6.5725850581 8.5951105333
C 9.9907391118 3.6836328219 6.8263813151
H 10.6277486928 2.7966070548 6.7603981344
C 8.7708100583 2.8370350988 4.7925765104
H 7.7728758013 2.9808529495 4.3400172383
C 8.4090638238 6.0077090751 6.9834115146
C 5.9312390423 6.6323948081 3.515637622
H 5.5783351237 7.3337381379 4.2935016593
H 6.0659936594 7.212207595 2.5909720922
C 10.2567720011 4.6500647399 7.7883889634
H 11.0921313257 4.5136299524 8.4812014041
C 7.2385122796 6.0097126781 3.943513322
H 7.6634286131 5.3801645487 3.1372522209
H 7.9951364123 6.7652994924 4.1955221895
C 4.9137488682 5.5383569383 3.3014295125
H 3.8996931315 5.9392827964 3.1492918048
H 5.1595214626 4.937199992 2.4057029852
C 4.796588648 1.2262365039 10.0645568466
C 7.6486819299 7.318421071 7.03150097
H 6.7114645124 7.1846510166 6.4613455119
C 5.7068522049 1.9584663683 10.7804136113
C 2.8600462442 5.8136385213 6.2531403892
H 3.9392587128 6.0497816145 6.2624302122
C 2.6643756127 4.4858870337 5.5476065994
C 3.4263468861 2.7220801703 3.9922609552
C 5.5750786296 3.9491099025 7.7219076669
C 5.4504913677 2.9363890731 8.7921400624
C 7.2545256565 7.7361139907 8.4431571304
H 6.6665866508 6.9513686783 8.9382161415
H 6.640032615 8.650055767 8.4064730348
H 8.137072839 7.9755898363 9.0603239945
C 1.4616370938 3.7890013915 5.6984657983
H 0.6844008975 4.1982220744 6.351058468
C 5.7799944598 3.4611192962 6.3903467624
C 6.2459916362 1.7564205664 12.1446390893
H 6.0758817883 2.6363900808 12.786190741
H 7.330139748 1.5537442767 12.1363267655
H 5.7573986276 0.8986665282 12.6253137101
C 2.1317304533 6.9269312019 5.5016882864
H 2.4677981816 7.0200926737 4.4555918811
H 2.2904968806 7.8998829953 5.9943119121
H 1.0447176122 6.7382574409 5.4777672666
C 2.4155951158 5.7785312671 7.7102345488
H 1.3204662482 5.6888076351 7.8074131742
H 2.7113393367 6.7106619857 8.2169301063
H 2.8837663021 4.9471320037 8.261402854
C 3.7299423289 1.4447234944 7.7902992814
H 2.8744915725 0.9299018027 8.2456070249
H 4.2350484159 0.788792993 7.0666961933
H 3.3622171384 2.330992152 7.2524638717
C 1.2321062805 2.5949013524 5.0233427064
H 0.2796735302 2.0722578046 5.1494818378
C 8.8335479242 1.3908837639 5.2651939645
H 8.6045897906 0.7100029667 4.4295967679
H 8.1020998445 1.1995411081 6.0647190486
H 9.8389993034 1.1205794359 5.6295244115
C 4.4452744063 2.1426792714 3.0334241785
H 5.3820452041 2.7204482241 3.1410715282
C 2.2048570194 2.0685848461 4.1818127937
H 2.0108558756 1.1310975804 3.6513214353
C 8.473796426 8.4318594904 6.383061438
H 9.3893636896 8.6253623812 6.9675446258
H 7.9008297885 9.3728094522 6.3489703846
H 8.7982055654 8.1952097465 5.3563027828
C 4.0525946672 -0.0028246103 10.4224564738
H 4.3786010054 -0.3759506825 11.4022933365
H 4.219168512 -0.8078356017 9.6883186418

H 2.9652936357 0.1725293371 10.4836778737
C 7.0738042555 4.0328277162 10.3089642478
H 6.5778074706 4.9410978809 10.6806708363
H 7.6619983405 4.2973290378 9.4180961411
H 7.7494038337 3.6374149151 11.0774028255
C 4.7811856757 0.6913192475 3.353403747
H 3.912026561 0.0287825436 3.2039583269
H 5.1302100602 0.588535498 4.3917206416
H 5.5785237455 0.3277270479 2.6850807452
C 3.9603676755 2.2846980754 1.5918983958
H 4.7235504125 1.9228714465 0.8839612916
H 3.7183552179 3.3287490827 1.3316092961
H 3.0467268596 1.689755266 1.4235137268
C 9.8198537329 3.1024280626 3.7130709101
H 10.8377624446 2.9421976892 4.1075335794
H 9.6835906609 2.4208065278 2.8577465624
H 9.7778793222 4.1382479211 3.3365703357

Coordinates of Optimized Structures of [**2d**]Cl

E° = -2387.080753; G° = -2386.102336

Charge = 1; Multiplicity = 2;

O 13.6438788895 7.2331136307 3.742320529
O 15.8876900691 9.3494058962 5.429218059
N 12.9744568376 10.064868243 3.1882521826
N 12.633078338 9.7758390193 5.4957120238
N 16.5570283298 6.1993582218 3.8794425933
N 17.0993445553 6.7485378291 5.9085109879
C 14.9789826597 10.6458912317 1.8819426473
C 13.8159734697 9.8649011885 2.0244178247
C 13.3547256053 8.9971499525 1.0104720878
C 13.2427233144 9.4657774916 4.3514076839
C 12.7407332815 8.9342260944 6.6733607717
C 15.3969269753 11.7197011934 2.8692973296
H 14.7603700064 11.6316396591 3.7676846661
C 15.7053943562 10.5068937909 0.6932051076
H 16.608328826 11.1085359145 0.5456563434
C 14.1125170659 8.9138778557 -0.1571114364
H 13.7764204937 8.2572867176 -0.9664816758
C 12.0456394957 8.2339944926 1.0976428628
H 11.6476638614 8.3543731045 2.1202398983
C 13.4646999171 9.4235948244 7.7823691228
C 15.2762035375 9.6578378546 -0.3161430293
H 15.8463654599 9.5845939724 -1.247454279
C 11.0254896394 8.7927601828 0.1056619651
H 11.3527696122 8.6204142541 -0.9335871595
H 10.8640722837 9.8777264967 0.2150556406
H 10.0508331245 8.2929542579 0.2276326303
C 12.2161318404 6.7367967047 0.8767274882
H 11.2423986379 6.2283782639 0.9704995076
H 12.9067105282 6.3068850424 1.6154271879
H 12.602510826 6.5145066777 -0.1334507966
C 16.2427549676 6.2431296452 2.4731439222
C 16.8410653037 11.5961110463 3.3395335756
H 16.9977292101 10.677896283 3.9252247408
H 17.0961885114 12.4453763242 3.994035124
H 17.5519132099 11.6142967536 2.495744761
C 11.9635733558 7.7610450991 6.7330560332
C 17.0055216664 7.1068255855 1.6757356705
C 15.1640608678 13.0997449268 2.251951196
H 15.8900539733 13.2970600626 1.4449736933
H 15.2889515296 13.8942344288 3.0064500785
H 14.1600882446 13.1981040141 1.8068156314
C 16.3149826644 7.0978307852 4.8618035985
C 17.4918904529 5.2791214024 4.3205932989
H 17.8449585297 4.4860544373 3.6648303168
C 15.383086665 5.2736510736 1.9435847268
C 17.1164310943 7.2594714473 7.2542875519
C 13.4304018121 8.664247975 8.9537080264
H 13.9856745813 9.0133205676 9.8306915137
C 16.0056517227 6.0559848885 -0.2862342066
C 17.8279268466 5.6213676606 5.585928008
H 18.5089332298 5.1715160809 6.3057239723
C 11.9648124968 7.0473373217 7.9358263481
H 11.366533863 6.1343388925 8.0164352727
C 11.0662153212 7.2963885021 5.603330228
H 11.3387952802 7.8475511956 4.6870346852
C 16.2341196801 6.6769193566 8.1715812427
C 14.1898601223 10.7572658167 7.7877618005
H 14.2268258665 11.1253964713 6.7478789984
C 16.8646194588 6.9920305067 0.2933742008
H 17.459479699 7.648698035 -0.3515963966
C 12.6892190314 7.4911809267 9.0338283009
H 12.6658856328 6.9229923921 9.9690099904
C 16.3613507596 7.0584492068 9.507615671
H 15.6873189732 6.6155758172 10.2508109463
C 17.3351706772 7.970859815 9.9236447817
C 15.2727807448 5.2146855062 0.5538639866
H 14.5921773015 4.4765804523 0.1128090253
C 13.4572029059 11.7797979749 8.65875632
H 12.400519675 11.9285100636 8.3819656482
H 13.9574988199 12.7604571272 8.6031245353
H 13.4678543527 11.468123417 9.717036036
C 18.1101361443 8.1748228462 7.6172625013
C 14.1452879133 8.2231169172 4.2876624421
C 17.9552846418 8.0903058206 2.2843375575
H 17.421748782 8.8791166041 2.842657407
H 18.5583506815 8.5889830006 1.5117975697
H 18.6525442269 7.6102828013 2.9946897059
C 15.2153087927 5.6754052237 7.7244106406

H 14.4856363969 6.1216282337 7.0226463345
H 14.6469834342 5.2776689304 8.5768821083
H 15.6787860061 4.8181081676 7.2054185736
C 18.1981870558 8.5142477021 8.9674323975
H 18.9649087997 9.2315356567 9.2819617373
C 15.8874170883 5.9386507306 -1.7736169017
H 14.8631154473 5.6716259194 -2.0788620839
H 16.5516576213 5.1491543291 -2.1648257476
H 16.1672876245 6.8747618913 -2.281386866
C 9.6063573829 7.6120434552 5.9229131405
H 9.2701899682 7.0631027678 6.8189196049
H 8.9497456586 7.31731485 5.0880077265
H 9.4459415579 8.685018796 6.1216887543
C 15.4579768667 8.3130910912 4.8688730171
C 11.2466051638 5.8168031989 5.2878627251
H 12.3080758469 5.5682962802 5.1338886421
H 10.703173395 5.5534029878 4.3658016628
H 10.8496715201 5.1736970841 6.0914784185
C 14.6255956164 4.3322504249 2.8249819715
H 15.2878096702 3.5910286899 3.3054380124
H 13.8777647451 3.7703242702 2.2467709619
H 14.1057433648 4.8829895887 3.6250342292
C 15.6336575517 10.6443447064 8.2569815486
H 15.6978757156 10.3259849456 9.3121504326
H 16.1290077184 11.6266758092 8.1864822092
H 16.1968289706 9.9325004171 7.6390631806
C 19.0031716774 8.7829010476 6.5844830292
H 18.3962958699 9.3360582617 5.8453159654
H 19.5785964665 8.0211821529 6.0303884346
H 19.7223024411 9.4797505406 7.0369001345
C 17.4216109988 8.3846848356 11.3589993576
H 16.7141433365 9.2058298971 11.5735349619
H 18.4259114634 8.7488620249 11.6211751066
H 17.1660978325 7.5568933343 12.0378854267
C 11.7759335012 12.2486701201 3.5568634052
H 12.4752557454 12.8984684955 3.0072844672
H 10.7737375625 12.6861736393 3.4079824556
C 12.1341937219 12.2085657799 5.0368944469
H 11.664406859 13.0498502968 5.571608675
H 13.221332891 12.3392409925 5.1840887984
C 11.7107891658 10.9221663263 5.7093526929
H 11.6813679514 11.0582433738 6.7961466282
H 10.6847586854 10.623052937 5.4293178753
C 11.7539530104 10.8645397697 2.9508078296
H 10.8928208513 10.2781806659 3.3155146444
H 11.6359976611 10.9255440275 1.8608914314

Coordinates of Optimized Structures of [**2e**]Cl

E° = -1847.1534707; G° = -1846.377151

Charge = 1; Multiplicity = 2;

O 5.9852601205 8.5275010084 14.1019751432
O 5.6409064167 5.9523661149 11.7328764894
N 4.3082719919 5.7505156203 14.6085355234
N 6.590411747 5.1362510576 14.5633857875
C 5.5360236462 5.8023967183 14.0971362927
C 3.2699875063 6.5997204427 14.0468728403
C 7.7965212449 5.0479534126 13.7594925579
N 5.7163806735 10.0160427917 11.5814858138
C 2.936643983 7.7979781385 14.7081991772
C 8.8426787744 5.9617049573 13.9933103314
N 7.0265472741 8.5219572245 10.704152523
C 7.8980863951 3.9974882585 12.8297634904
C 6.6843495257 4.4394194304 15.8669250645
H 7.759879902 4.4201011128 16.0956712238
H 6.3845202299 3.3811365853 15.7482795337
C 2.6039695732 6.1656533226 12.8821270889
C 3.495912471 8.1788170044 16.0633188201
H 4.4012093248 7.5712250599 16.2358392185
C 3.8894270146 4.69515119 15.5536638453
H 4.1858140844 3.7254109913 15.1134486707
H 2.7892753769 4.7021998385 15.5544916437
C 8.7553478178 7.0725899089 15.021304884
H 7.6985024549 7.1806034672 15.3216756451
C 1.6400936397 7.0181928426 12.3373085005
H 1.1115420322 6.7157422103 11.4286536042
C 1.9561654221 8.6039965407 14.1214180119
H 1.6684180157 9.5386693145 14.613174027
C 4.432011123 4.8393607967 16.9608516679
H 4.2168089678 3.8937228006 17.4879871222
H 3.8869281312 5.6225332928 17.5107514406
C 5.9267538965 5.128828202 16.9800375889
H 6.359799406 4.8175793464 17.9439061055
H 6.1184133661 6.2152522183 16.9066866817
C 3.9164831151 9.6385038584 16.172023253
H 4.683906453 9.8824552469 15.4234302328
H 4.3420276715 9.8328271855 17.1697773989
H 3.0603103588 10.324936901 16.0571371482
C 9.5835853309 6.7375477796 16.260671227
H 9.2735577602 5.7932209706 16.7379839976
H 9.4958113201 7.5372440849 17.0138551325
H 10.6525999517 6.6370436624 16.0065637392
C 6.1727306018 10.5409830956 10.3820349675
C 1.3271910384 8.2300258585 12.9400634873
H 0.5636904962 8.8771749909 12.4989253335
C 6.9942239277 9.5969735186 9.8253040727
C 10.0155970457 5.7975796157 13.2500654136
H 10.851570583 6.4853825848 13.4118295415
C 6.8104336954 2.9628581052 12.6281796455

H 5.9080904771 3.3031050821 13.1687403765
C 9.1820325824 8.4230910314 14.4560607575
H 10.2622289096 8.4561256566 14.2346461761
H 8.9739533376 9.2205389817 15.1868274331
H 8.6313027805 8.6749006394 13.5354199807
C 1.7294799877 3.838970697 12.7155333935
H 1.6747912547 3.7478518491 13.8126229715
H 1.8969426853 2.8318258245 12.299912897
H 0.7400024215 4.1817674097 12.3677960016
C 2.8257170754 4.8015768337 12.2582742856
H 3.7979108111 4.4119801716 12.6095053965
C 2.4630362301 7.8447999179 17.1408682666
H 1.5781415216 8.4974202782 17.0484132145
H 2.8815959862 7.9971953014 18.1499505784
H 2.1001083111 6.8053095949 17.0709543461
C 9.091212216 3.8874798571 12.1091293176
H 9.2036218991 3.078438932 11.3806064349
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Coordinates of Optimized Structures of **2f**

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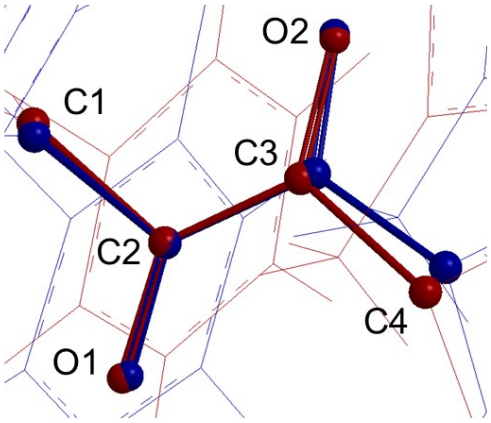


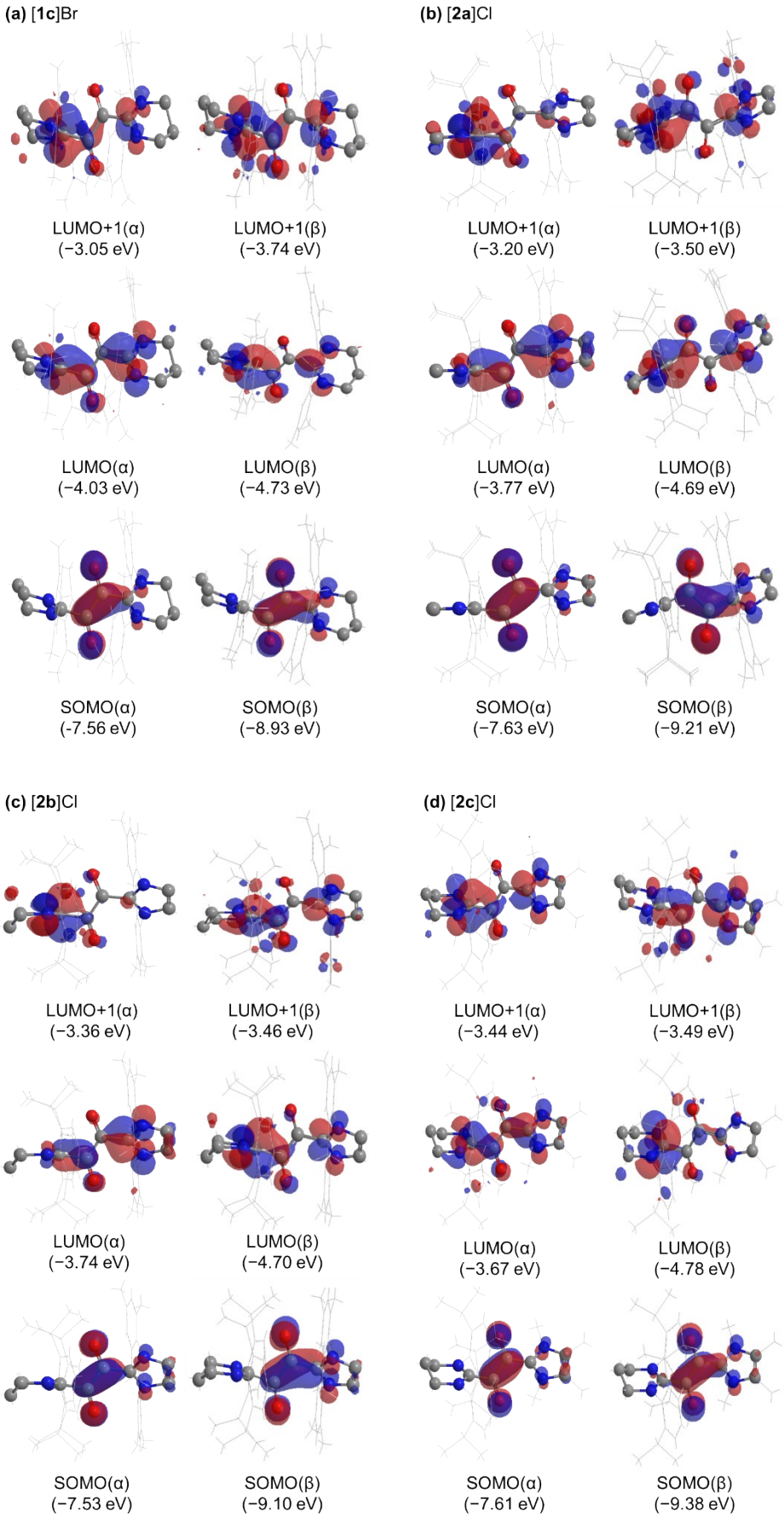
d (Å)	C1–C2	C2–C3	C3–C4	C2–O1	C3–O2
X-ray	1.622(6)	1.321(7)	1.580(6)	1.268(5)	1.278(5)
DFT	1.532	1.436	1.481	1.235	1.257

WBI	C1–C2	C2–C3	C3–C4	C2–O1	C3–O2
X-ray	0.873	1.380	0.944	1.875	1.807
DFT	0.937	1.205	1.061	1.977	1.826

q_{NBO}	O1	C2	C3	O2	2NHC	C_2O_2
X-ray	-0.623	0.353	0.288	-0.621	1.602	-0.602
DFT	-0.617	0.390	0.273	-0.635	1.588	-0.588

Deviations between the solid-state structure and the DFT-optimized structure

Figure S2. Overlaid structures (red: solid state, blue: DFT-optimized) and parameters of Wiberg bond indices and NBO charge of [**2b**]Cl.



Frontier molecular orbitals

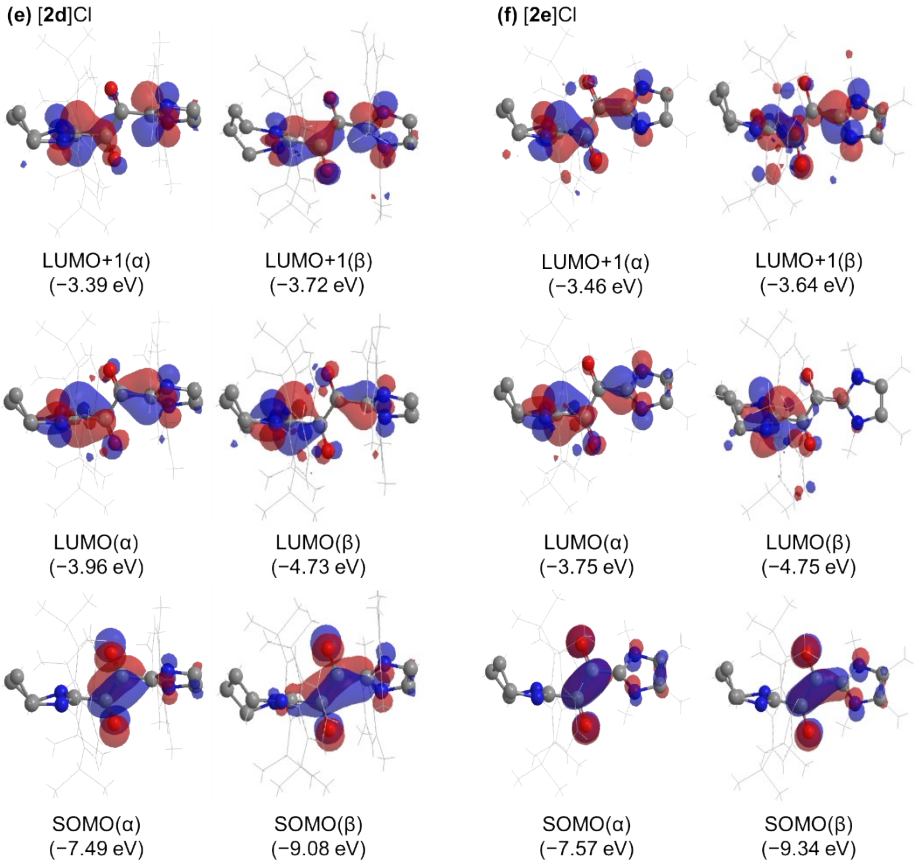
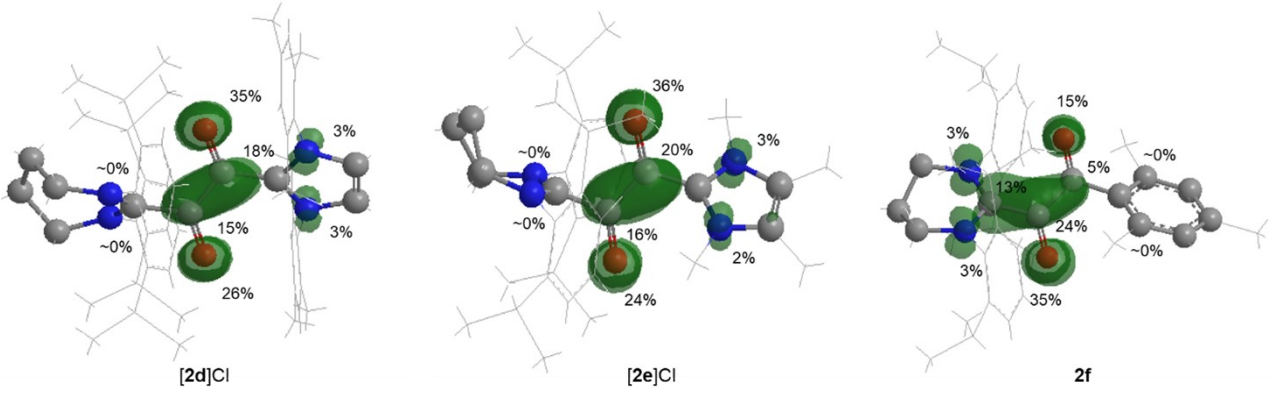
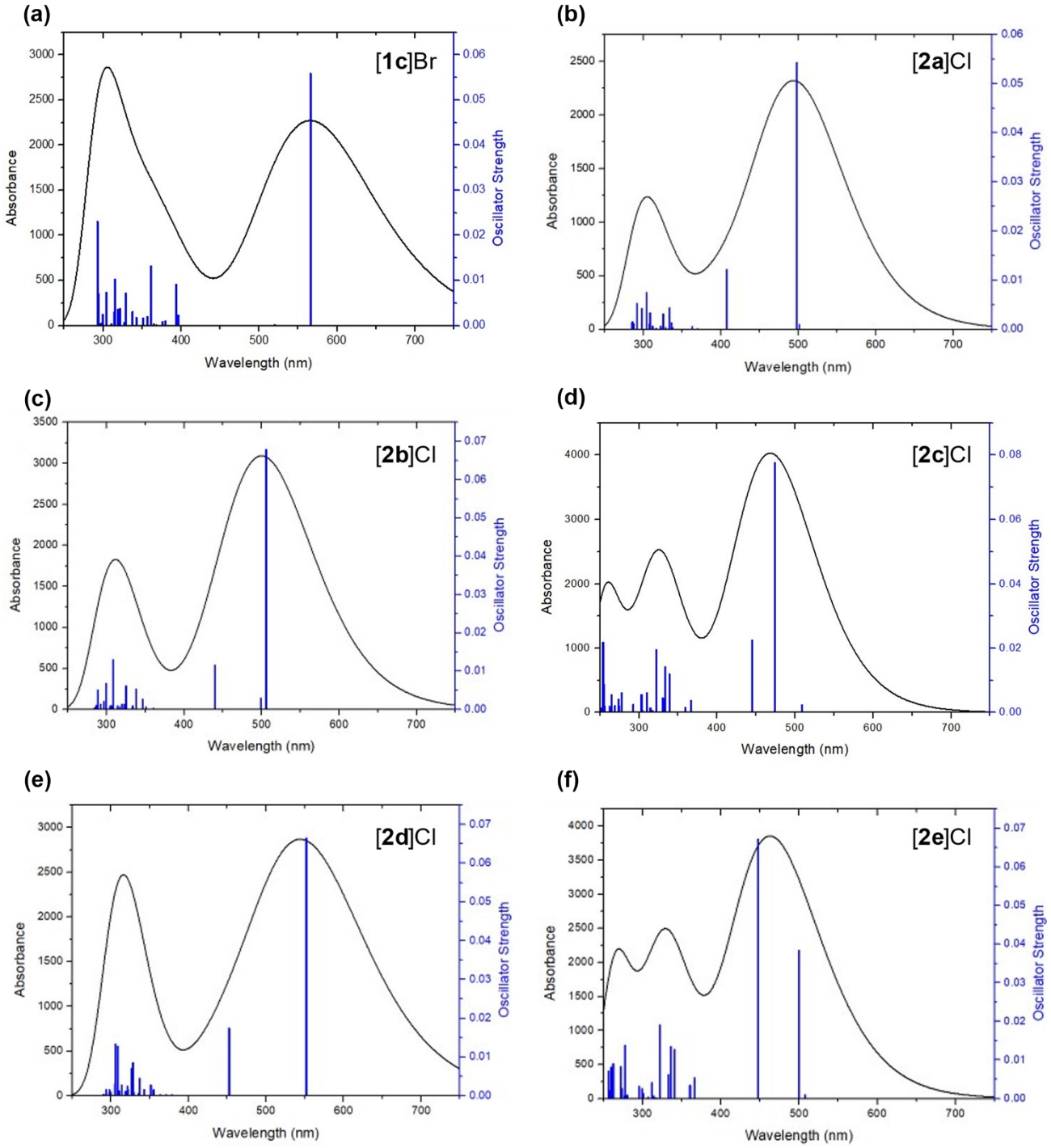


Figure S3. Selected frontier molecular orbitals of [**1c**]Br and [**2a-2e**]Cl.



Spin Density

Figure S4. Spin densities and the visualization of [**2d-2e**]Cl and **2f**.



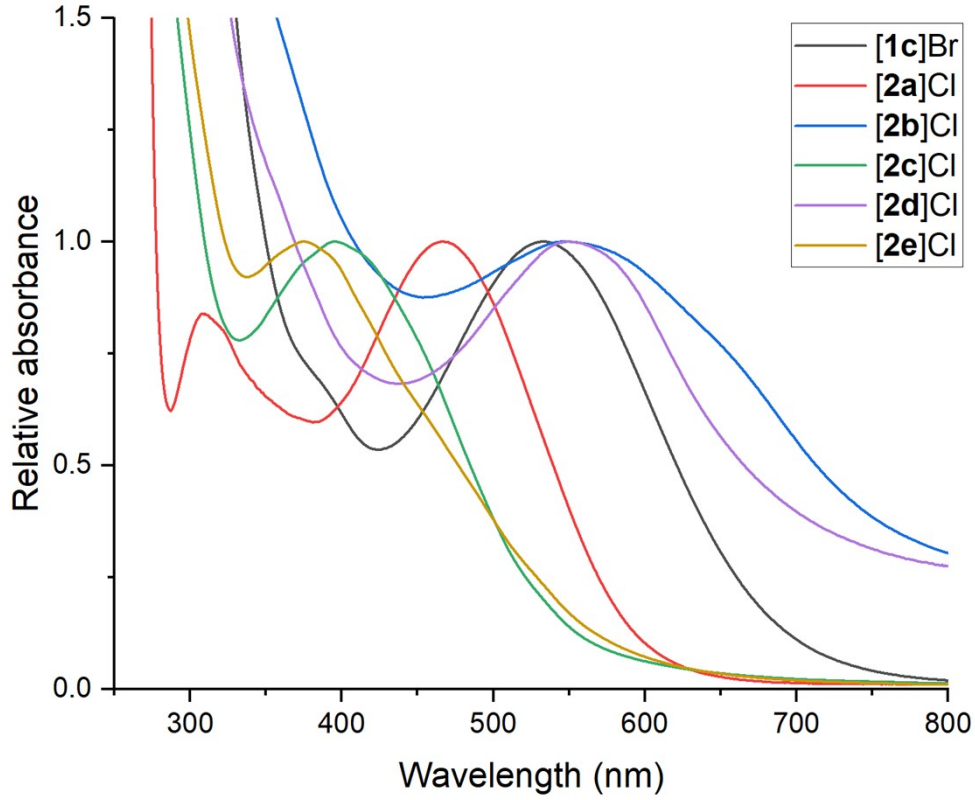
TD-DFT

Figure S5. Simultated UV-Vis spectra and oscillator strengths of [**1c**]Br and [**2a-2e**]Cl.

UV-Vis Spectroscopy

General information

The UV-vis spectra were recorded at room temperature with Cary 6000i UV-Vis-NIR (Agilent Technologies) with quartz UV cell.



UV-Vis spectra

Figure S6. UV-vis absorption of each radical in distilled water (path length = 10 mm); [**1c**]Br: λmax = 533 nm, [**2a**]Cl: λmax = 467 nm, [**2b**]Cl: λmax = 550 nm, [**2c**]Cl: λmax = 395 nm, [**2d**]Cl: λmax = 550 nm, [**2e**]Cl: λmax = 375 nm.

Stability

The water stability of each radical was measured with saturated solution except [**2a**]Cl, [**2c**]Cl and [**2e**]Cl. [**2a**]Cl, [**2c**]Cl and [**2e**]Cl were measured with 10 times diluted solution due to their high solubility.

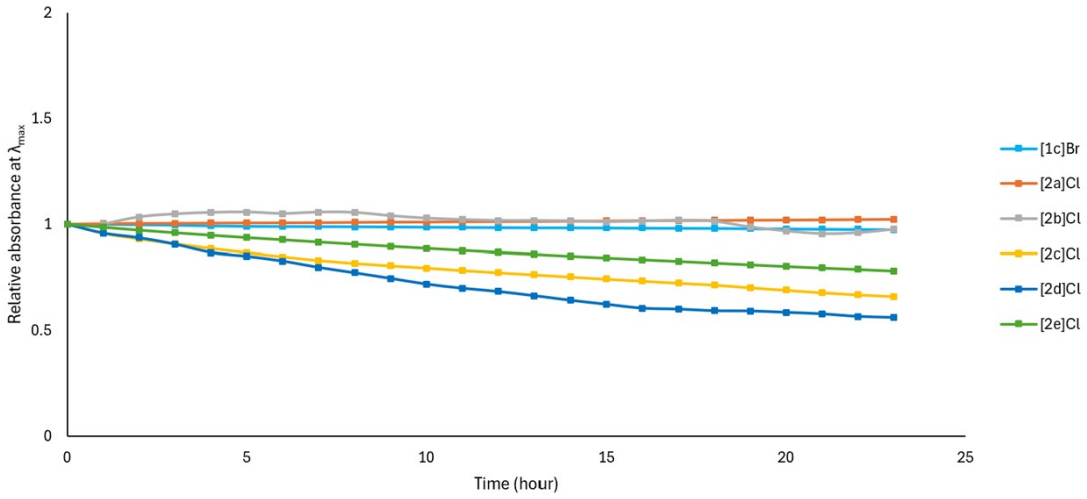
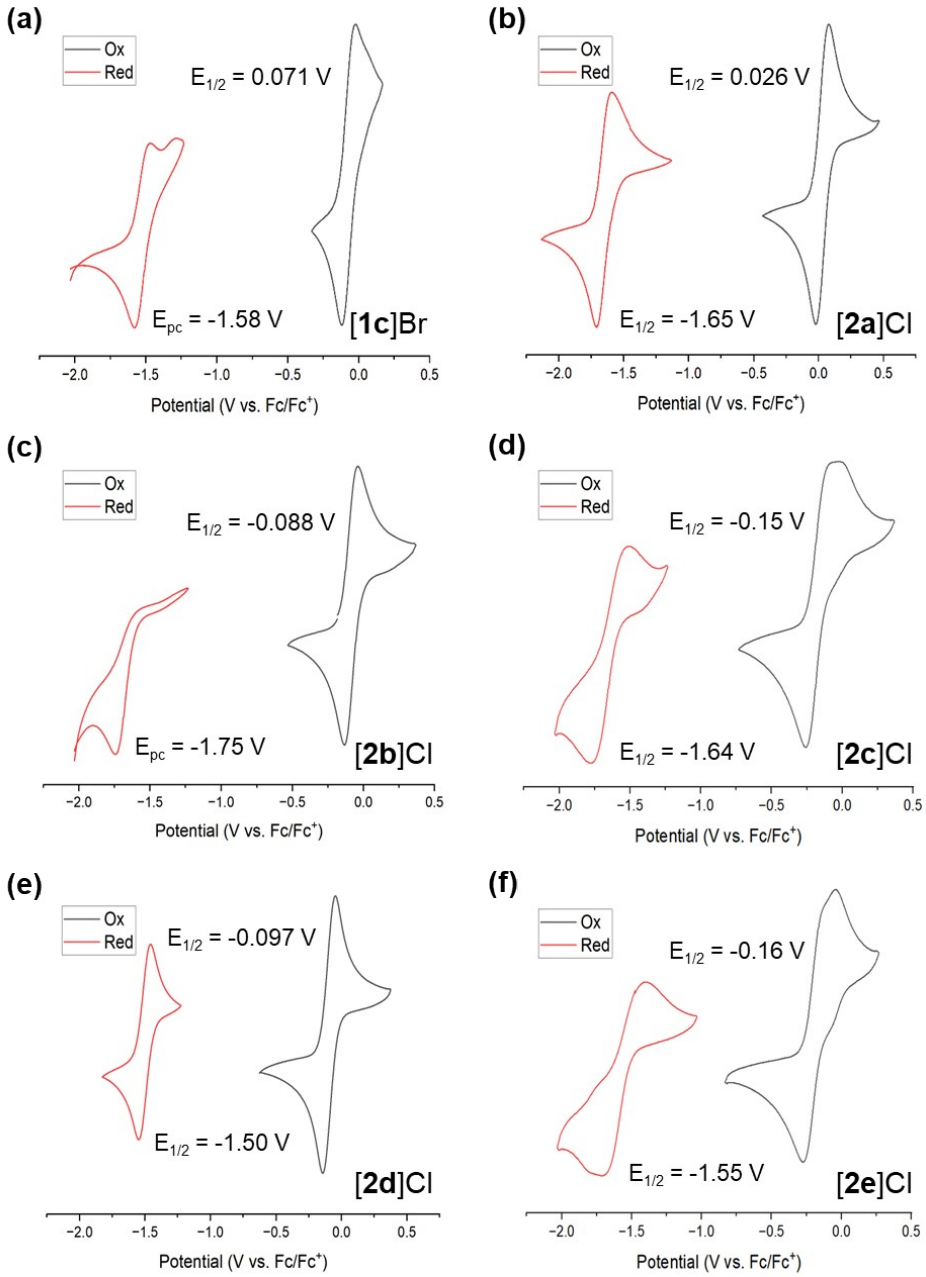


Figure S7. Decay of radicals monitored by UV-vis. Half-life was calculated by assuming 1st order kinetics except [**1c**]Br and [**2a**]Cl. [**1c**]Br and [**2a**]Cl did not exhibit detactable decomposition within a 24-hour time scale due to their high stability; [**1c**]Br (peak height at λ_{max} = 533 nm, $[A]_t = [A]_0\, e^{-(0.001)t}$, $R^2 = 0.9645$), [**2a**]Cl (peak height at λ_{max} = 467 nm, $[A]_t = [A]_0\, e^{(0.001)t}$, $R^2 = 0.9966$), [**2b**]Cl **(**peak height at λ_{max} = 550 nm, $[A]_t = [A]_0\, e^{-(0.009)t}$, $R^2 = 0.9178$, $t_{1/2}$ = 77 h), [**2c**]Cl **(**peak height at λ_{max} = 395 nm, $[A]_t = [A]_0\, e^{-(0.016)t}$, $R^2 = 0.9811$, $t_{1/2}$ = 43 h)**,** [**2d**]Cl **(**peak height at λ_{max} = 550 nm, $[A]_t = [A]_0\, e^{-(0.026)t}$, $R^2 = 0.9733$, $t_{1/2}$ = 27 h), [**2e**]Cl (peak height at λ_{max} = 375 nm, $[A]_t = [A]_0\, e^{-(0.011)t}$, $R^2 = 0.9968$, $t_{1/2}$ = 63 h).

Cyclic Voltammetry

General information

Cyclic voltammograms were recorded at room temperature with either a Gamry Interface 1010E potentiostat or Princeton Applied Research (PAR) VersaSTAT 3 potentiostat. The working electrode was a glassy carbon disk (area = 0.02 cm^2), the reference electrode was Ag/AgCl (saturated), and the counter electrode was a platinum wire.



Cyclic voltammograms

Figure S8. Cyclic voltammogram of [**1c**]Br and [**2a-2e**]Cl in dry and degassed acetonitrile (0.1 M

$[Bu_4N]PF_6$; scan rate = 0.1 V/s). Potential versus vs. Fc/Fc^+.

Electron paramagnetic resonance

General information

EPR spectra were recorded on a Bruker X-band A200 spectrometer. Spectra processing and simulation were performed with Bruker WIN-EPR and EasySpin.[14]

EPR Spectra

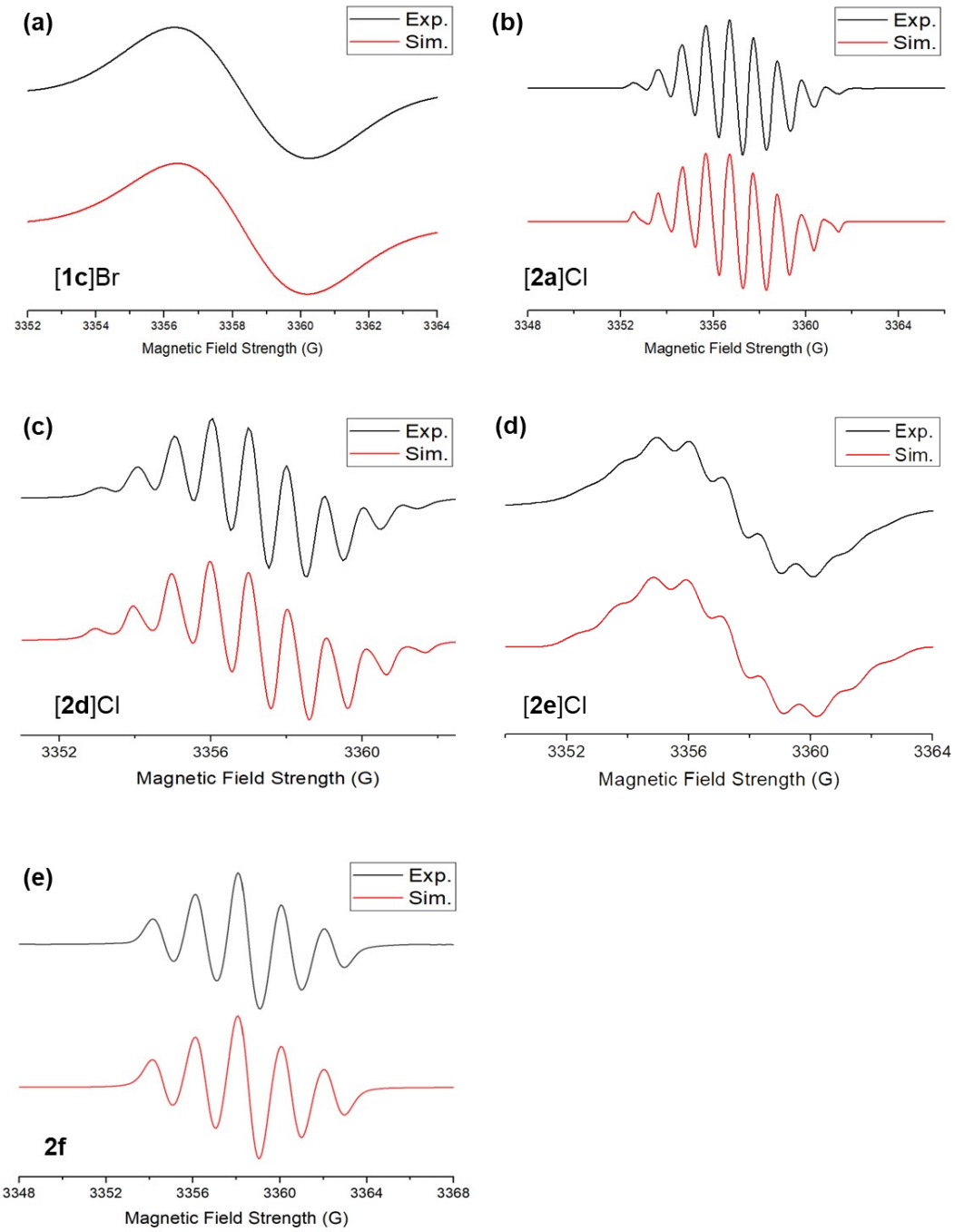


Figure S9. (a) Experimental (top, black) and simulated (bottom, red) EPR spectra of [**1c**]Cl at microwave frequency = 9.4293 GHz. Simulated with the following parameters: g_{iso} = 2.0062; Gaussian line width = 0.17 mT; Lorentzian line width = 0.06 mT. (b) Experimental (top, black) and simulated (bottom, red) EPR spectra of [**2a**]Cl at microwave frequency = 9.4244 GHz. Simulated with the following parameters: g_{iso} = 2.00583; hyperfine coupling constants: a(^{14}N) = 2.88, 2.88, 2.72, 2.72 MHz; Gaussian line width = 0.03 mT; Lorentzian line width = 0.002 mT. (c) Experimental (top, black) and simulated (bottom, red) EPR spectra of [**2d**]Cl at microwave frequency = 9.4255 GHz. Simulated with the following parameters: g_{iso} = 2.00589; hyperfine coupling constants: a(^{14}N) = 2.93, 2.93, 2.61, and 2.61 MHz; Gaussian line width = 0.01 mT;

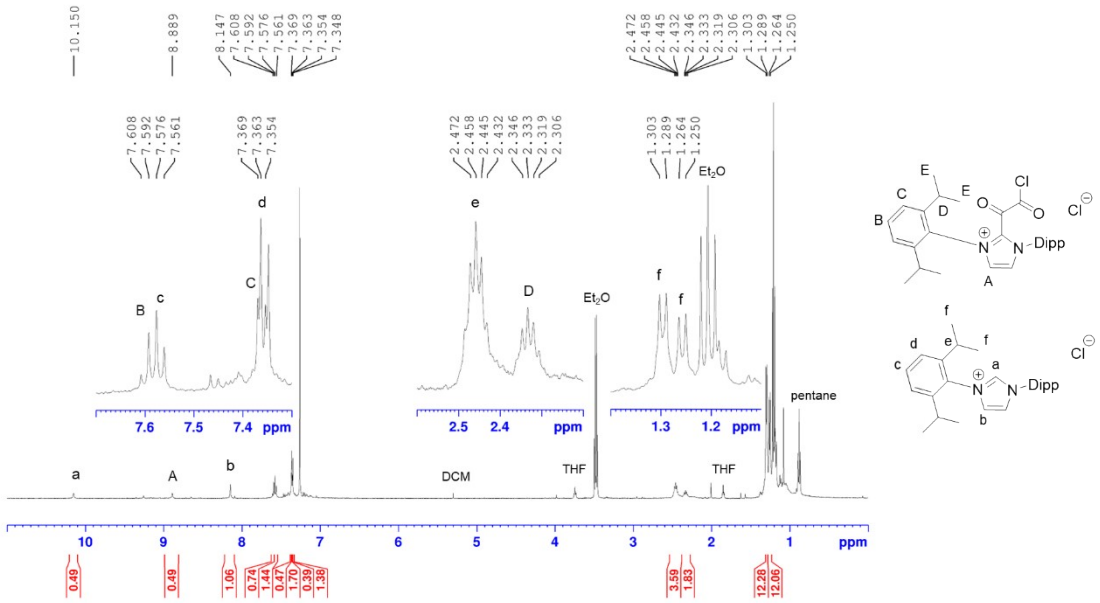
Lorentzian line width = 0.02 mT. (d) Experimental (top, black) and simulated (bottom, red) EPR spectra of [**2e**]Cl at microwave frequency = 9.4280 GHz. Simulated with the following parameters: g_{iso} = 2.00627; hyperfine coupling constants: a(^{14}N) = 3.39, 3.39, 2.85, and 2.85 MHz; Gaussian line width = 0.06 mT; Lorentzian line width = 0.05 mT. (e) Experimental (top, black) and simulated (bottom, red) EPR spectra of **2f** at microwave frequency = 9.4277 GHz. Simulated with the following parameters: g_{iso} = 2.00558; hyperfine coupling constants: a(^{14}N) = 5.42, 5.42 MHz; Gaussian line width = 0.06 mT; Lorentzian line width = 0.03 mT.

NMR Spectroscopic Analysis

General information

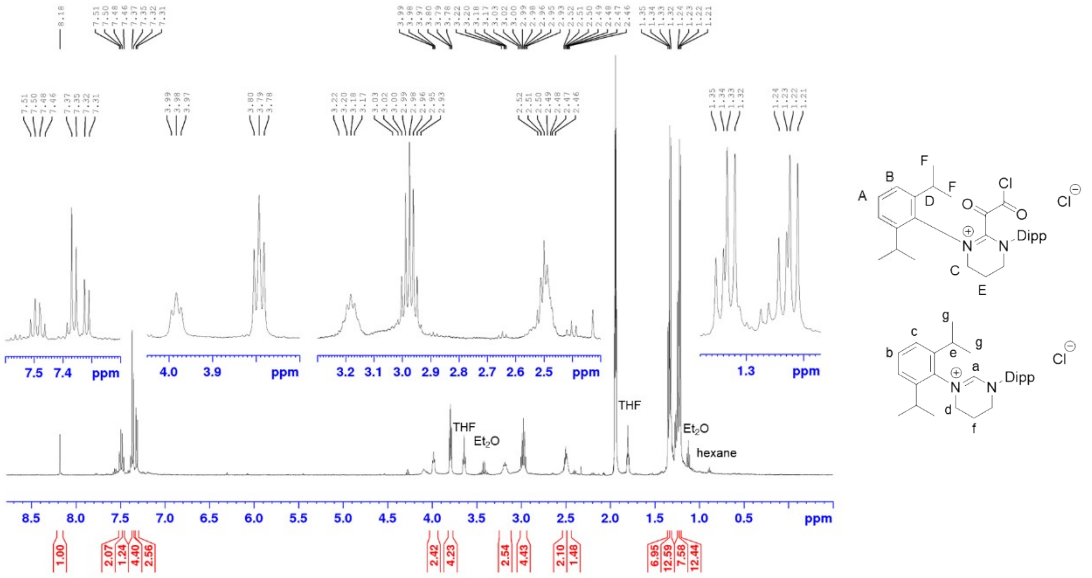
^{1}H NMR spectra were recorded using either a Bruker DRX 500 spectrometer or Bruker AVANCE III 300 spectrometer. Chemical shifts of ^{1}H were referenced to the residual solvent peaks (^{1}H: $CDCl_3$, δ = 7.26 ppm; CD_3CN, δ = 1.94 ppm).[15]

NMR Spectra



^{1}H spectra of [*I*Pr–C_2O_2Cl]Cl

Figure S10. ^{1}H NMR spectrum and assignment of the signals for the mixture of **[*I*Pr–C_2O_2Cl]Cl** and [*I*PrH]Cl. The proton located at the E position of **[*I*Pr–C_2O_2Cl]Cl** could not be assigned due to the overlap with other peaks.



^{1}H spectra of [6-Dipp–C_2O_2Cl]Cl

Figure S11. ^{1}H NMR spectrum and assignment of the signals for the mixture of **[6-Dipp–C_2O_2Cl]Cl** and [6-DippH]Cl.

Electrospray Ionization Mass Spectroscopy

General information

Electrospray ionization mass spectroscopy (ESI-MS) was performed using a 6560 IM-Q-TOF (Agilent Technologies).

ESI-MS spectrum

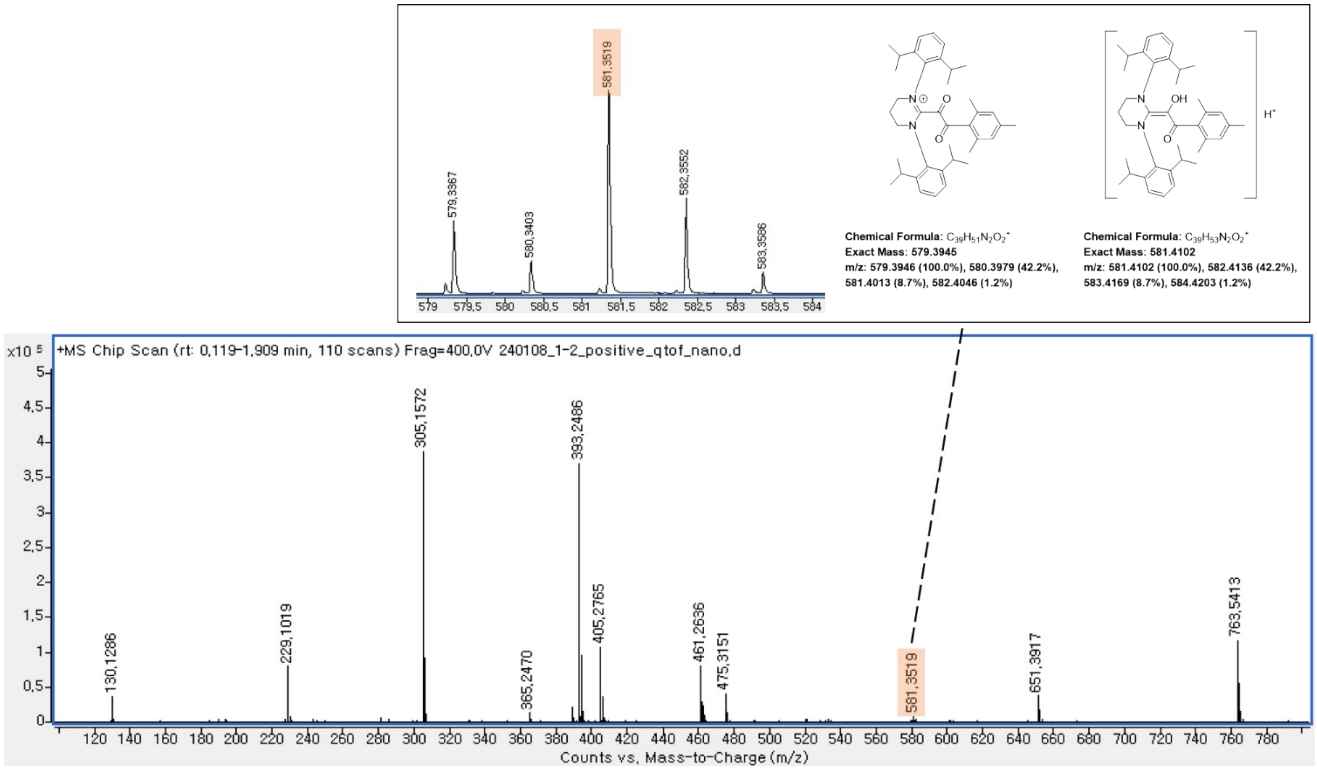


Figure S12. ESI-MS spectrum of **2f**.

Reference

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