Supporting Information

Title:

Stereoelectronic control of oxidation potentials of 3,7-bis(diarylamino)phenothiazines

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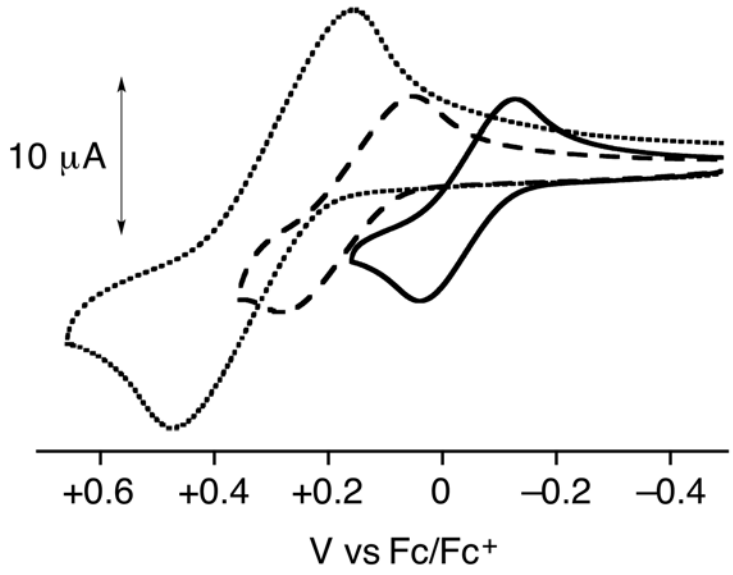

Fig. S1 Cyclic voltammograms of **1d** (solid line), **1e** (dashed line), and **1f** (dotted line) in dichloromethane (2×10^{-4} M). Only first oxidation processes of **1d** and **1e** were shown here.

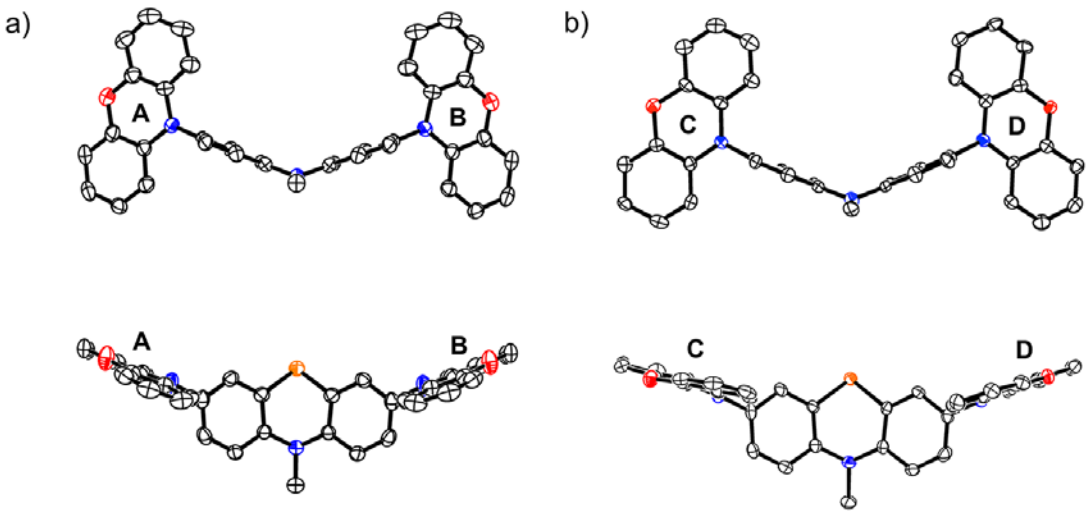

Fig. S2 ORTEP views of **1f** (a) and **1f**$^{\bullet+}$•$GaBr_4^-$ (b) (upper: side view; lower: top view). Compound **1f** has a mirror symmetry along the C–S axis of the central phenothiazine moiety. The dihedral angle of the phenoxazine moiety D defined by two benzene rings (3.2°) is slightly smaller than those of the phenoxazine moieties A (B) and C (7.9 and 8.2°, respectively). In addition, the C–O bond lengths at the phenoxazine moiety D (av. 1.38 Å) are shorter than those at the phenoxazine moieties A (B) and C (1.40–1.41 Å). These results indicate that the phenoxazine moiety D is in the radical cationic states.

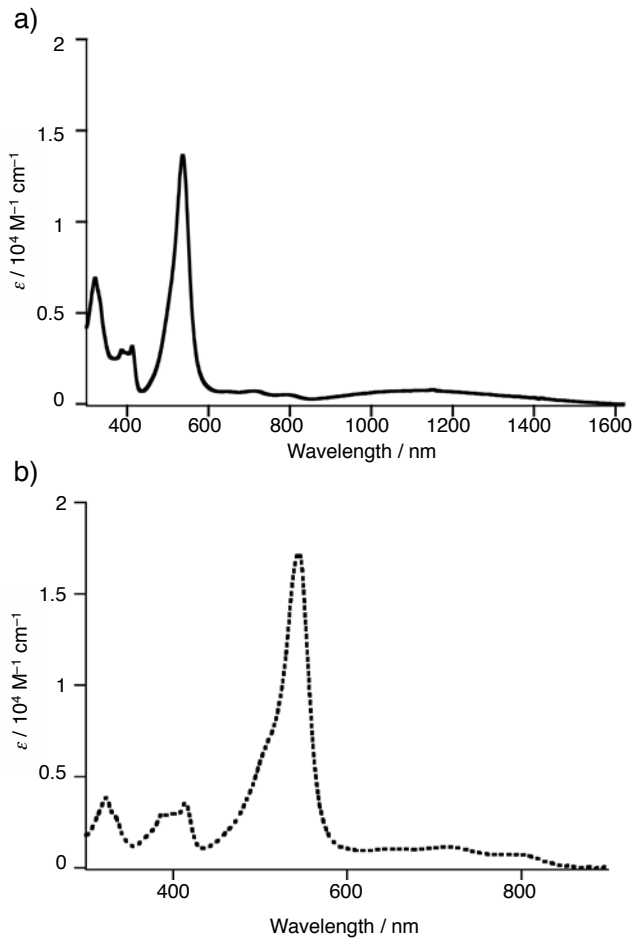

Fig. S3 Absorption spectra of (a) $\mathbf{1f^{\bullet+}{\bullet}GaBr_4^-}$ and (b) $\mathbf{2f^{\bullet+}{\bullet}PF_6^-}$ in CH_2Cl_2.[S1] The absorption around 540 nm of $\mathbf{1f^{\bullet+}{\bullet}GaBr_4^-}$ was assigned to the terminal phenothiazine radical cation.

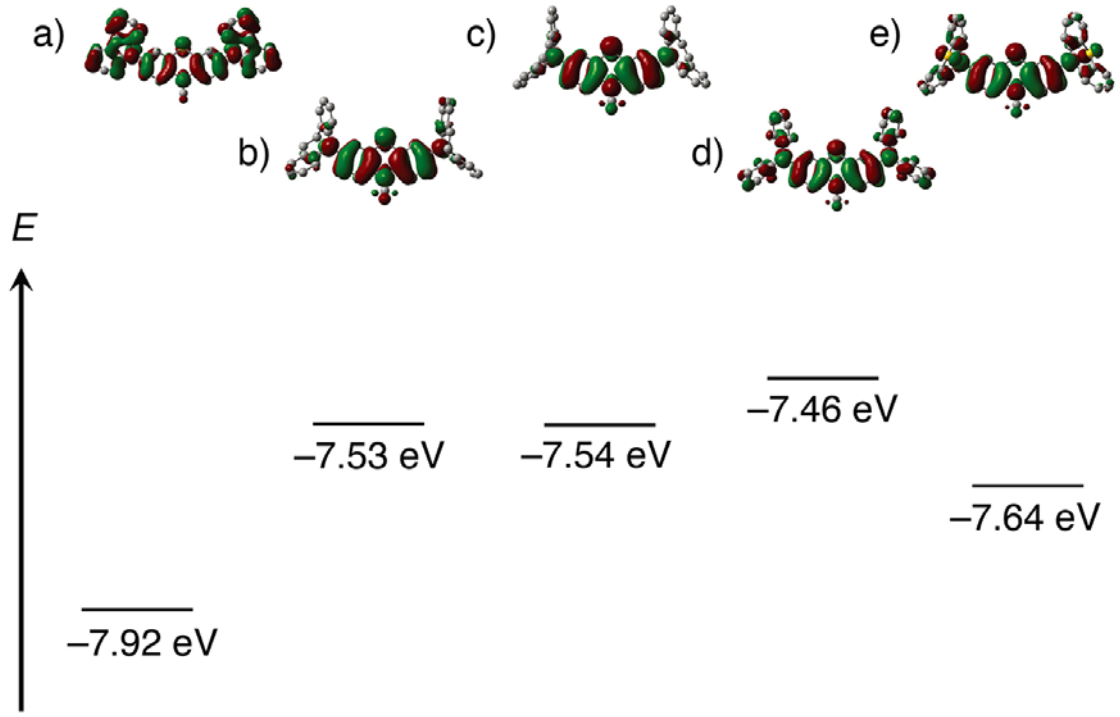

Fig. S4 Energy diagrams and pictures of KS-SOMO for optimized structure calculated by *Gaussian 09* with the UB3LYP/6-31G** level of theory.[S2] (a) **1a**$^{\bullet+}$, (b) **1b**$^{\bullet+}$, (c) **1c**$^{\bullet+}$, (d) **1d**$^{\bullet+}$, and (e) **1e**$^{\bullet+}$. The SOMO orbitals of radical cations generally reflect the HOMO orbitals of neutral species. The SOMO has red colored orbitals on the sulfur and nitrogen atoms and green colored orbitals on the carbon atoms in the thiazine ring in the phenothiazine ring. Thus, the S–C and N–C bonds have anti-bonding character. Removing an electron from HOMO reduces the anti-bonding character in the S–C and N–C bonds; thus, they are shortened in the radical cation states.

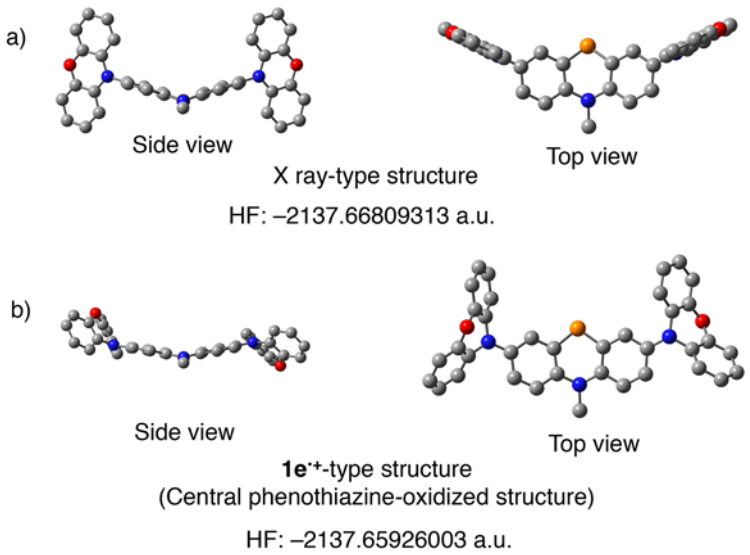

Fig. S5 Optimized structures of **1f**$^{\bullet+}$ and their heat of formations;[S2] (a) X-ray-type structure (optimized from the crystal structure of **1f**$^{\bullet+}$) and (b) **1e**$^{\bullet+}$-type structure (optimization from the structure where the central phenothiazine moiety has planar structure), showing that the optimized structure (a) has a lower energy (HF(structure b) – HF(structure a) = +5.54 kcal mol^{-1}).

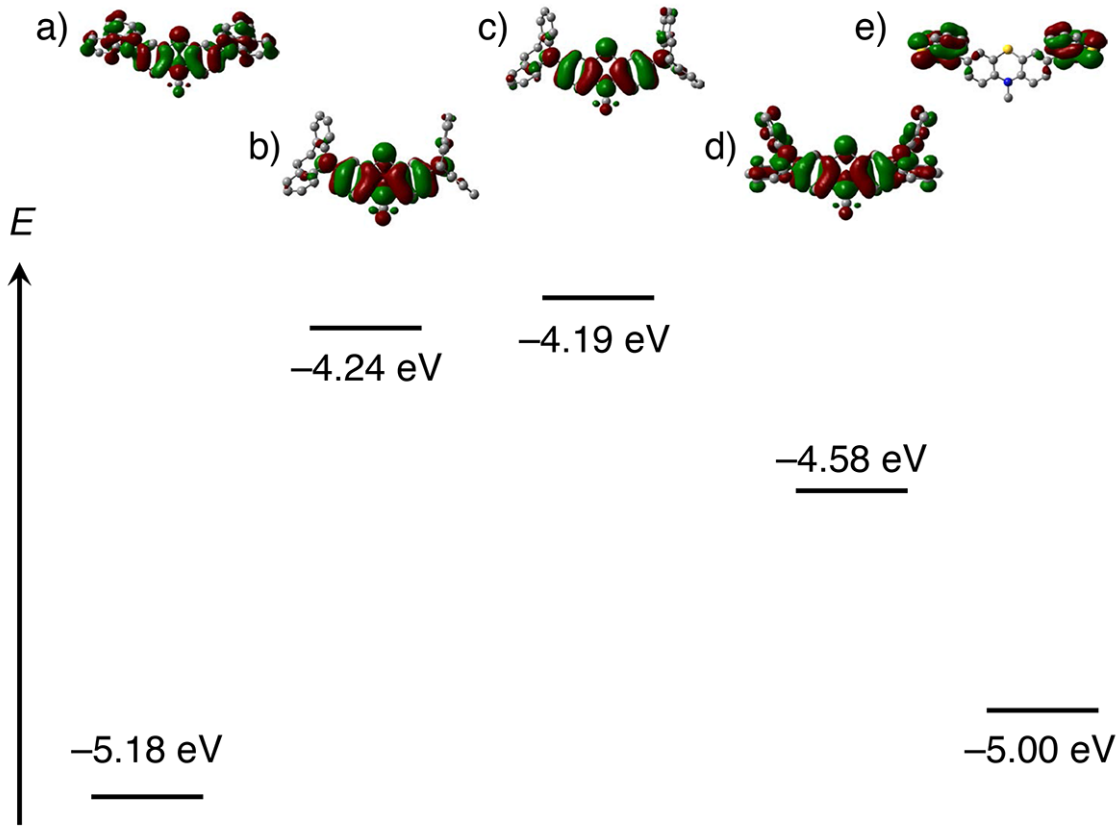

Fig. S6 Energy diagrams and pictures of KS-HOMO for optimized structure calculated by *Gasussian 09* with the B3LYP/6-31G** level of theory.[S2] (a) **1a**, (b) **1b**, (c) **1c**, (d) **1d**, and (e) **1e**.

Table S1-1 Crystallographic data of **1a**, **1b'**, and **1c**.

	1a	**1b'**	**1c**
Formula	$C_{37}H_{25}N_3S$	$C_{47}H_{37}N_3S$	$C_{41}H_{29}N_3S$
Formula weight	543.68	675.89	595.76
Crystal color	colorless	yellow	yellow
morphology	block	block	block
Size / mm^3	0.30 × 0.20 × 0.01	0.10 × 0.05 × 0.05	0.20 × 0.15 × 0.05
Crystal system	monoclinic	monoclinic	moniclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a / Å	13.022(8)	14.182(11)	18.942(16)
b / Å	9.483(6)	13.573(11)	7.309(5)
c / Å	21.773(13)	18.170(15)	23.453(19)
α / degree	90	90	90
β / degree	93.312(7)	96.605(8)	111.966 (10)
γ / degree	90	90	90
V / $Å^3$	2684(3)	3474(5)	3011(4)
Z value	4	4	4
T / K	150(2)	150(2)	150(2)
D_{calc} / g cm^{-3}	1.345	1.292	1.314
F(000)	1136	1424	1248
μ / cm^{-1}	1.54	1.33	1.43
No. of reflections measured	26332	34899	29258
No. of unique reflections	6105	6172	6802
No. of observed reflections	6105	6172	6802
No. of variables	395	497	435
Reflection/ Parameter Ratio	15.46	12.42	15.63
$R1$ [$I > 2.00s(I)$]	0.0502	0.0549	0.0820
R_w	0.0704	0.1427	0.2144
Goodness-of-fit	1.341	1.313	1.839

Table S1-2 Crystallographic data of **1d**, **1e**, and **1f**.

	1d	**1e**	**1f**
Formula	$C_{37}H_{29}N_3S$	$C_{37}H_{25}N_3S_3 \bullet C_7H_8$	$C_{37}H_{25}N_3O_2S \bullet C_4H_8O$
Formula weight	547.72	699.95	647.79
Crystal color	colorless	colorless	colorless
morphology	platelet	block	block
Size / mm^3	0.20 × 0.15 × 0.01	0.20 × 0.20 × 0.15	0.20 × 0.20 × 0.15
Crystal system	orthorhombic	triclinic	orthorhombic
Space group	*Aba*2 (No. 41)	*P*-1 (No. 2)	*Pnma* (No. 62)
a / Å	21.784(11)	10.758(6)	28.24(3)
b / Å	27.581(14)	12.675(7)	20.01(2)
c / Å	9.343(5)	14.281(8)	5.663(6)
α / degree	90	68.315(18)	90
β / degree	90	82.98(3)	90
γ / degree	90	75.22(3)	90
V / $Å^3$	5613(5)	1748.7(17)	3201(6)
Z value	8	2	4
T / K	150(2)	150(2)	150(2)
D_{calc} / g cm^{-3}	1.296	1.329	1.327
F(000)	2304	732	1238
μ / cm^{-1}	1.47	2.49	1.47
No. of reflections measured	28364	17642	30996
No. of unique reflections	6315	7821	3762
No. of observed reflections	6315	7821	3762
No. of variables	399	484	253
Reflection/ Parameter Ratio	15.83	16.16	14.87
*R*1 [$I > 2.00s(I)$]	0.0538	0.0481	0.0937
R_w	0.0646	0.0678	0.2277
Goodness-of-fit	1.080	1.319	1.724

Table S1-3 Crystallographic data of **1a**$^{\bullet+}$•SbF_6^-, **1b**$^{\bullet+}$•SbF_6^-, and **1c**$^{\bullet+}$•$GaBr_4^-$.

	1a$^{\bullet+}$•SbF_6^-	**1b**$^{\bullet+}$•SbF_6^-	**1c**$^{\bullet+}$•$GaBr_4^-$
Formula	$C_{37}H_{25}N_3S$•SbF_6 •CH_3CN•$(C_6H_6)_{0.5}$	$C_{41}H_{35}N_3S$ •SbF_6•$(C_6H_5Cl)_{0.75}$	$C_{41}H_{29}N_3S$•$GaBr_4$ •C_6H_5Cl
Formula weight	863.58	916.44	1097.65
Crystal color	green	green	green
morphology	block	block	block
Size / mm^3	0.20 × 0.05 × 0.05	0.15 × 0.05 × 0.02	0.20 × 0.10 × 0.02
Crystal system	monoclinic	moniclinic	moniclinic
Space group	$P2_1/n$ (No. 14)	$C2/_C$ (No. 15)	$P2_1/c$ (No. 14)
a / Å	13.5112(9)	43.28(2)	18.327(10)
b / Å	7.4584(4)	12.154(5)	10.704(6)
c / Å	35.454(3)	33.650(5)	23.653(13)
α / degree	90	90	90
β / degree	92.068(4)	115.783(8)	92.738(5)
γ / degree	90	90	90
V / $Å^3$	3570(4)	15937(12)	4635(4)
Z value	4	16	4
T / K	150(2)	150(2)	150(2)
D_{calc} / g cm^{-3}	1.599	1.528	1.537
$F(000)$	1728	7400	2164
μ / cm^{-1}	9.00	8.59	41.90
No. of reflections measured	34157	79297	46426
No. of unique reflections	8090	18096	10558
No. of observed reflections	8090	18096	10558
No. of variables	518	1109	548
Reflection/ Parameter Ratio	15.62	16.29	19.26
$R1$ [$I > 2.00s(I)$]	0.0370	0.0754	0.0960
R_w	0.1243	0.1902	0.1555
Goodness-of-fit	0.894	1.669	2.710

Table S1-4 Crystallographic data of **1d$^{\bullet+}$•SbF$_6^-$**, **1e$^{\bullet+}$•SbF$_6^-$**, and **1f$^{\bullet+}$•GaBr$_4^-$**.

	1d$^{\bullet+}$•SbF$_6^-$	**1e$^{\bullet+}$•SbF$_6^-$**	**1f$^{\bullet+}$•GaBr$_4^-$**
Formula	$C_{37}H_{29}N_3S$•SbF_6 •$(CH_2Cl_2)_{0.25}$	$C_{37}H_{25}N_3S_3$•SbF_6 •C_7H_8	$C_{37}H_{25}N_3O_2S$ •$GaBr_4$
Formula weight	804.69	935.70	965.02
Crystal color	green	black	purple
morphology	block	platelet	block
Size / mm^3	0.20 × 0.05 × 0.02	0.20 × 0.20 × 0.01	0.20 × 0.20 × 0.10
Crystal system	moniclinic	monoclinic	monoclinic
Space group	*P*n (No. 7)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a / Å	18.0621(12)	17.920(6)	7.251(4)
b / Å	21.7543(11)	8.445(3)	27.486(13)
c / Å	18.1682(13)	26.392(9)	17.493(8)
α / degree	90	90	90
β / degree	108.862(3)	91.079(4)	93.977(6)
γ / degree	90	90	90
V / Å^3	6755.4(8)	3993(3)	3478(3)
Z value	8	4	4
T / K	150(2)	150(2)	150(2)
D_{calc} / g cm^{-3}	1.582	1.556	1.843
F(000)	3228	1884	1884
μ / cm^{-1}	9.82	9.11	54.99
No. of reflections measured	69130	39213	35148
No. of unique reflections	29250	9025	7918
No. of observed reflections	29250	9025	7918
No. of variables	1860	558	458
Reflection/ Parameter Ratio	15.73	16.17	17.29
*R*1 [$I > 2.00s(I)$]	0.0620	0.0480	0.0622
R_w	0.1491	0.1326	0.0844
Goodness-of-fit	1.218	1.347	1.328

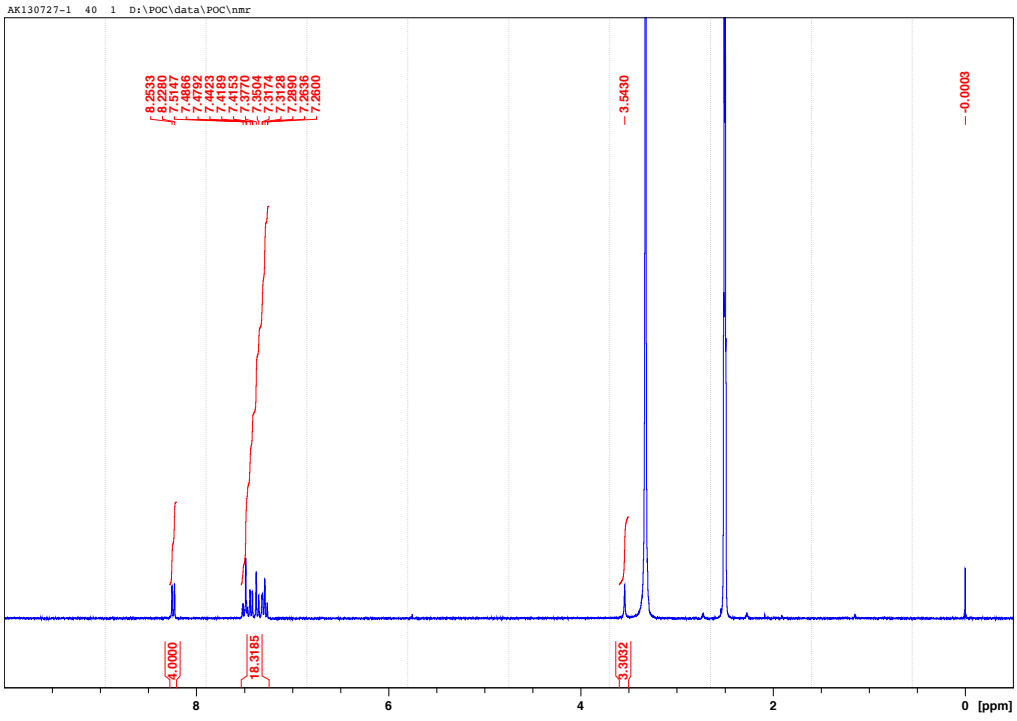

Fig. S7-1 ^{1}H NMR of **1a** (DMSO-d_6).

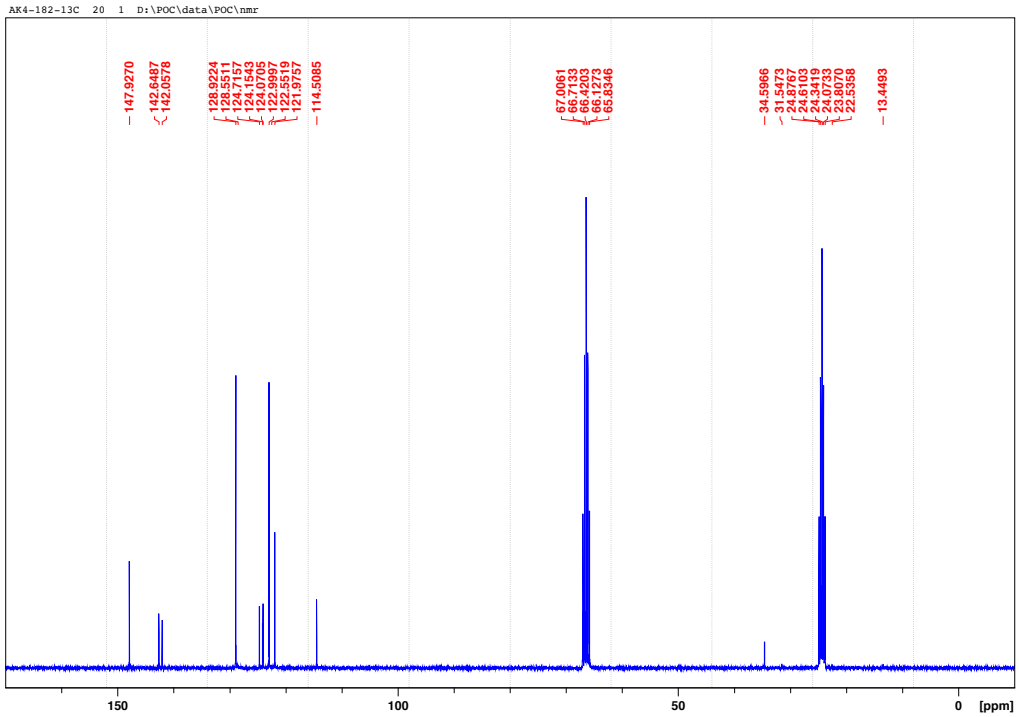

Fig. S7-2 ^{13}C NMR of **1a** (DMSO-d_6).

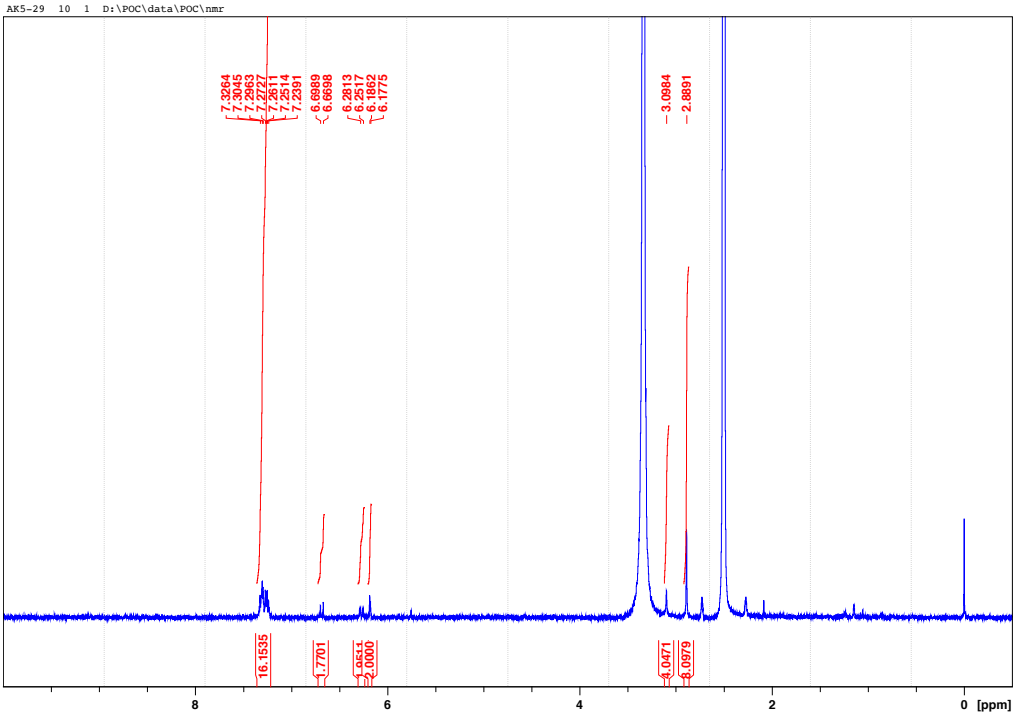

Fig. S8-1 ^{1}H NMR of **1b** (DMSO-d_6).

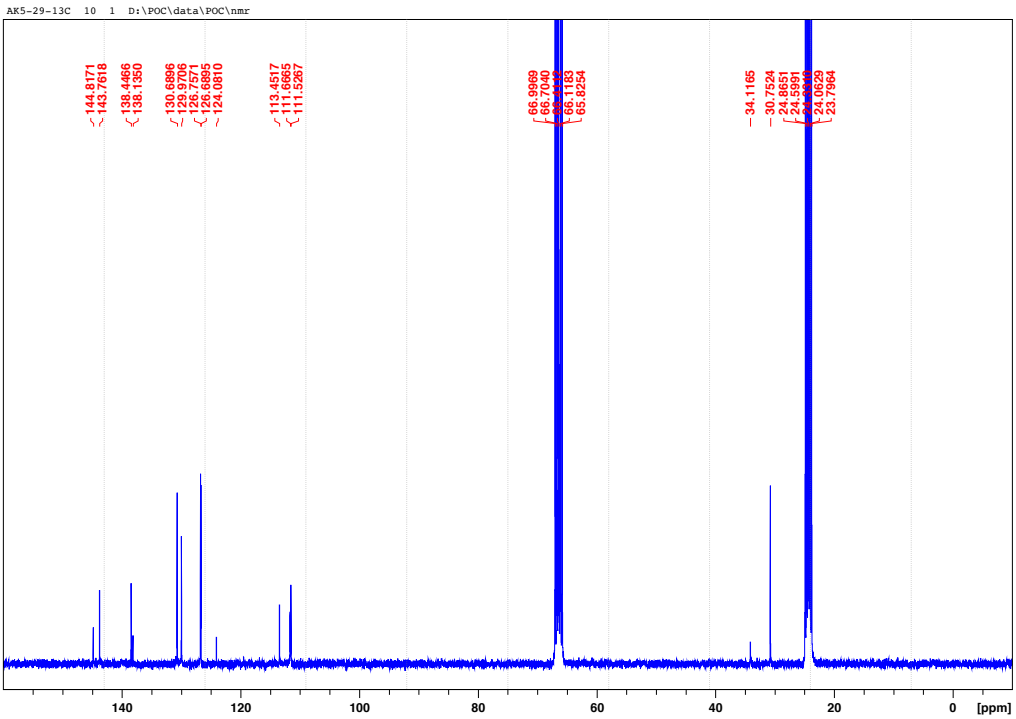

Fig. S8-2 ^{13}C NMR of **1b** (DMSO-d_6).

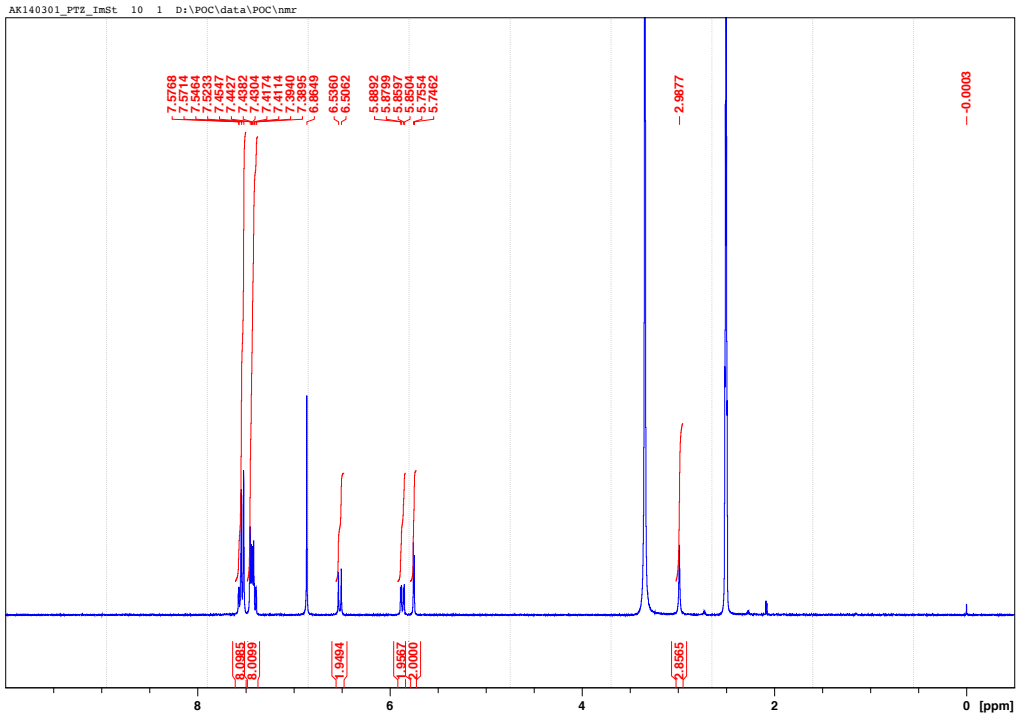

Fig. S9-1 ^{1}H NMR of **1c** (DMSO-d_6).

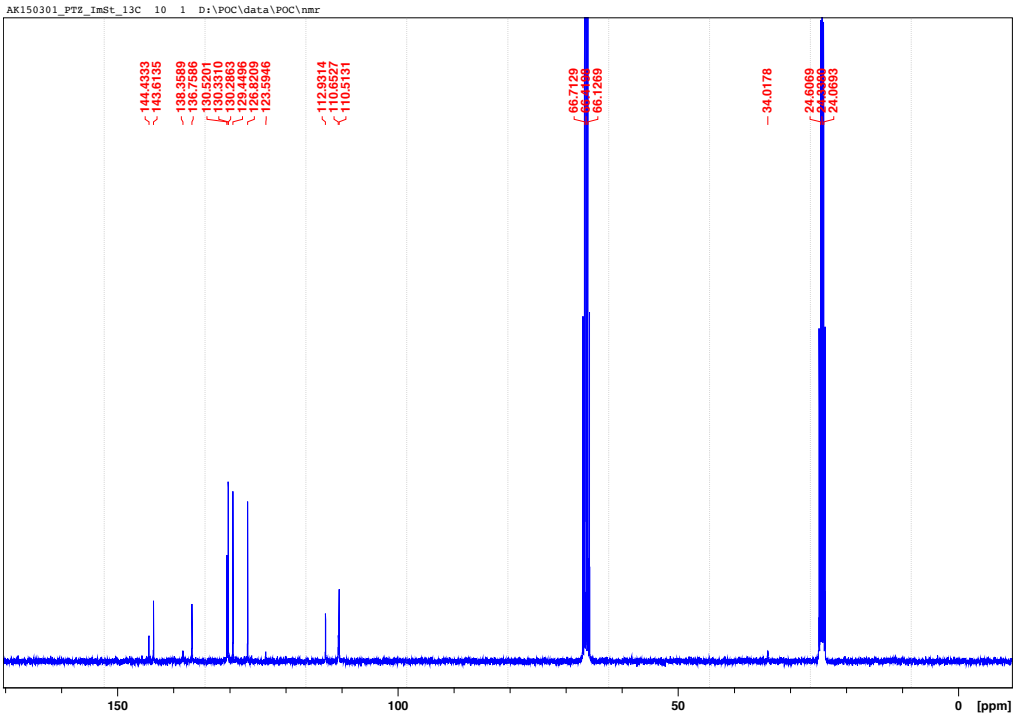

Fig. S9-2 ^{13}C NMR of **1c** (DMSO-d_6).

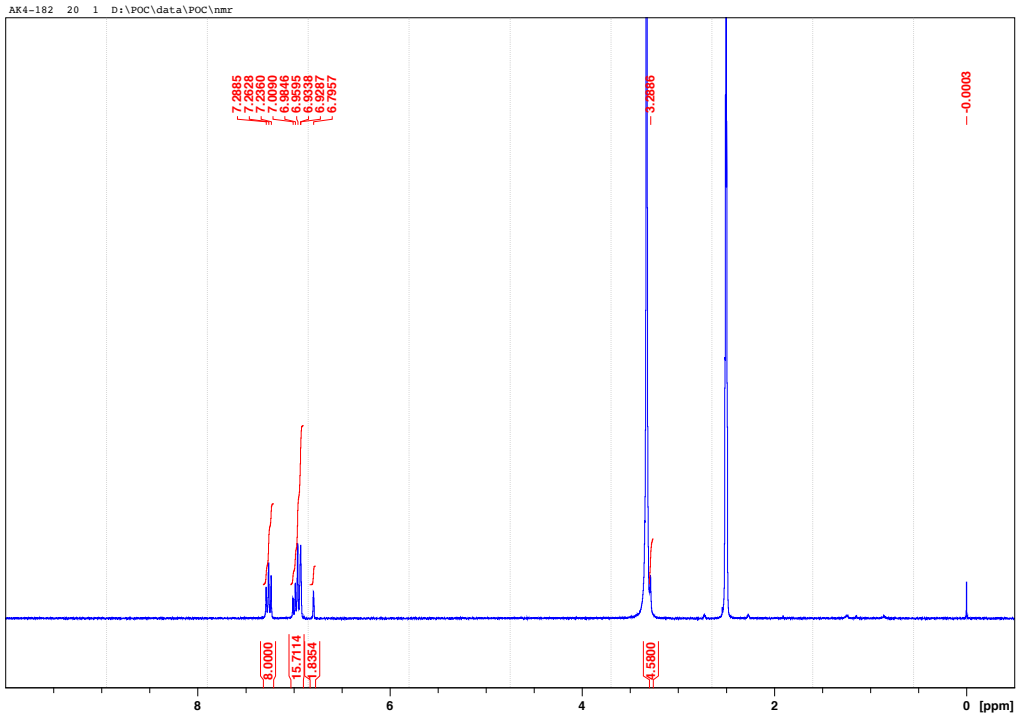

Fig. S10-1 ^{1}H NMR of **1d** (DMSO-d_6).

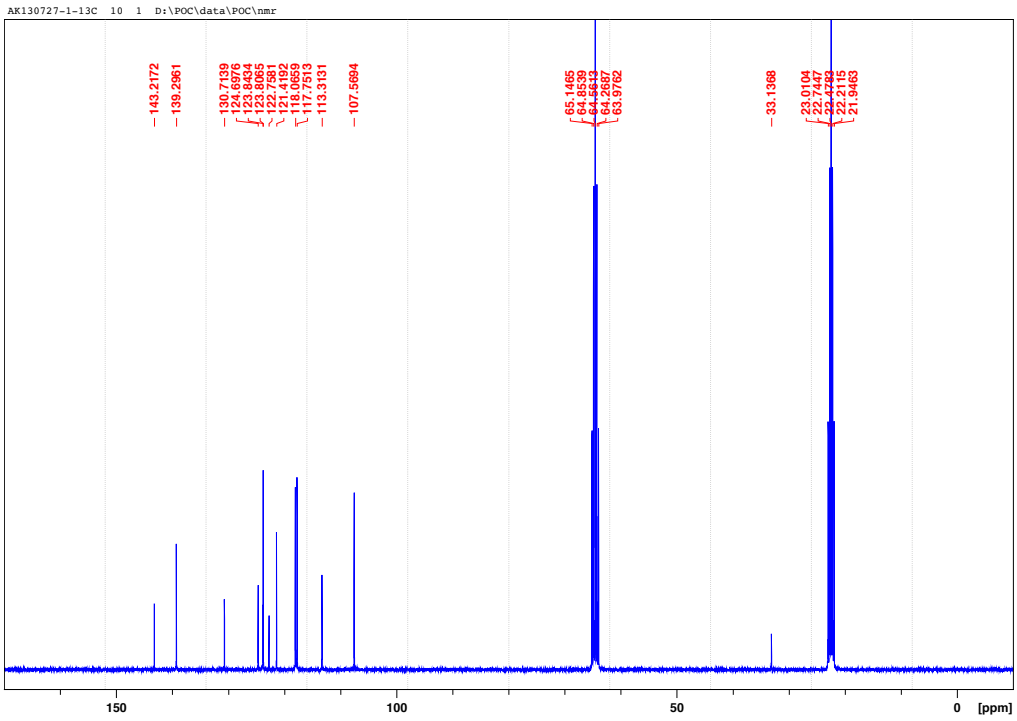

Fig. S10-2 ^{13}C NMR of **1d** (DMSO-d_6).

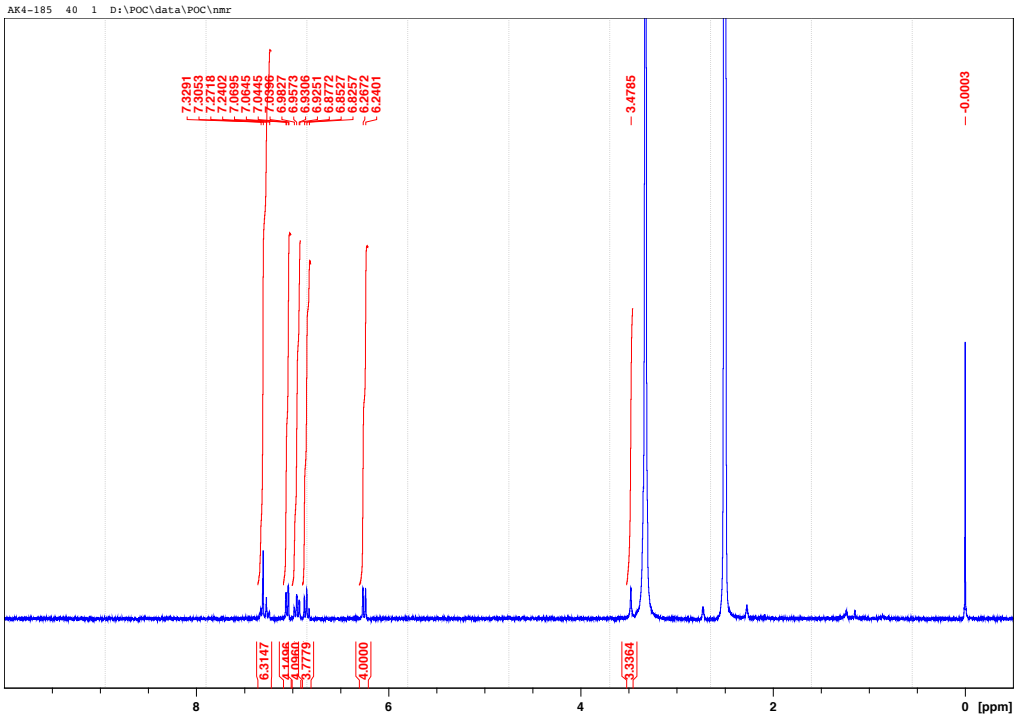

Fig. S11-1 ^{1}H NMR of **1e** (DMSO-d_6).

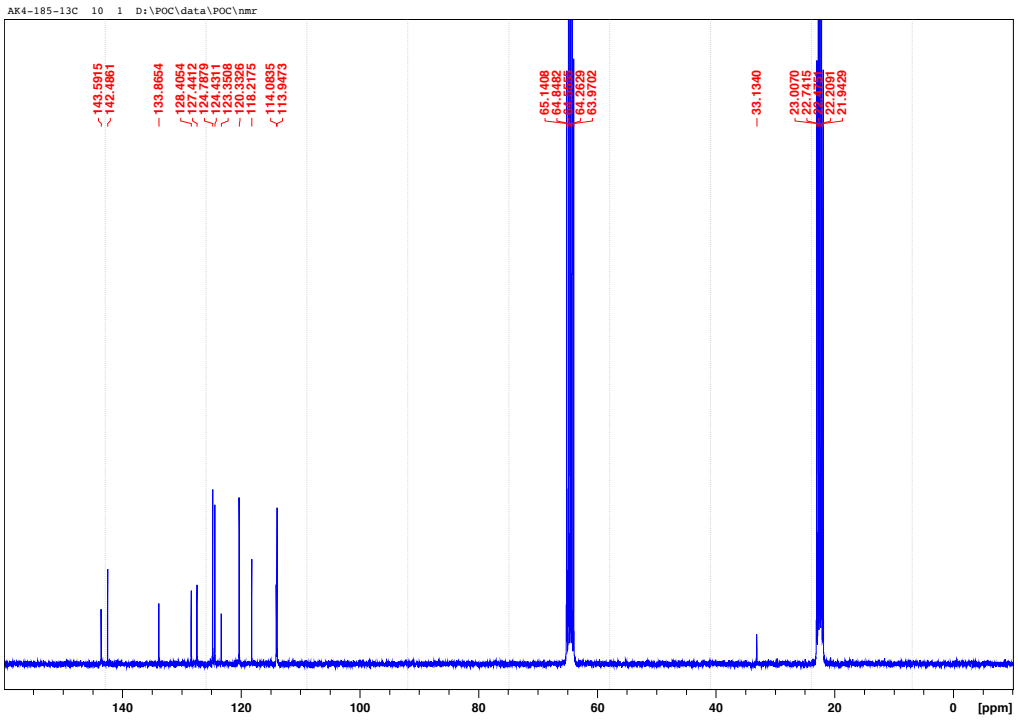

Fig. S11-2 ^{13}C NMR of **1e** (DMSO-d_6).

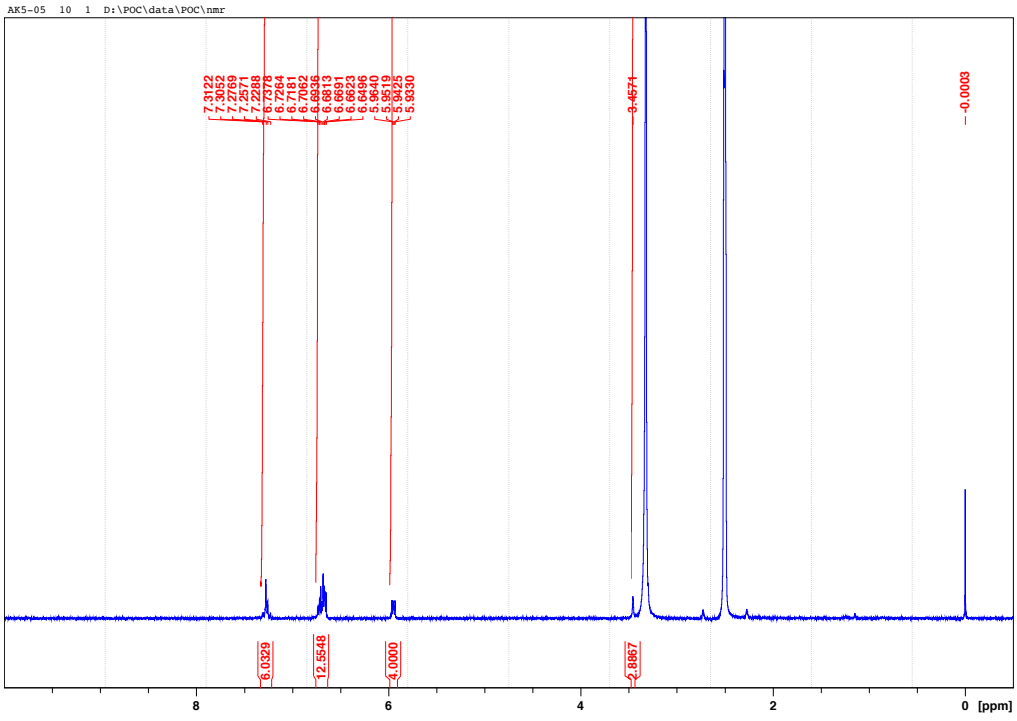

Fig. S12-1 ^{1}H NMR of **1f** (DMSO-d_6).

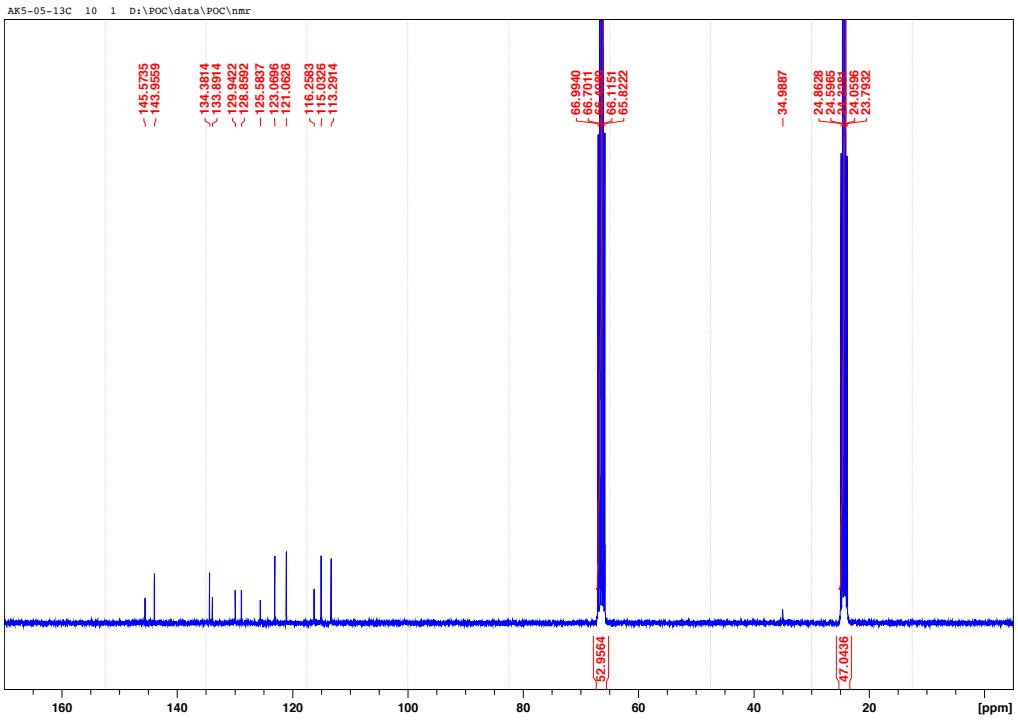

Fig. S12-2 ^{13}C NMR of **1f** (DMSO-d_6).

Table S2-1 Cartesian coordinates of optimized structure of **1a**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.000100	-0.641587	-1.559870
2	7	0	0.000013	-2.706433	0.626724
3	7	0	-4.872493	0.113823	0.057153
4	7	0	4.872420	0.113925	0.056646
5	6	0	-1.348551	-0.971872	-0.442248
6	6	0	-2.543477	-0.271231	-0.580637
7	6	0	-3.651041	-0.593051	0.214079
8	6	0	-3.533227	-1.611268	1.162107
9	6	0	-2.331099	-2.301480	1.312086
10	6	0	-1.219715	-2.003624	0.509609
11	6	0	1.219733	-2.003621	0.509470
12	6	0	2.331228	-2.301480	1.311795
13	6	0	3.533323	-1.611250	1.161703
14	6	0	3.651031	-0.592994	0.213686
15	6	0	2.543366	-0.271201	-0.580905
16	6	0	1.348466	-0.971868	-0.442387
17	6	0	0.000069	-3.970238	1.348380
18	6	0	-6.111287	-0.453816	-0.261307
19	6	0	-6.434584	-1.788448	-0.519911
20	6	0	-7.758877	-2.084449	-0.834938
21	6	0	-8.739915	-1.079968	-0.895687
22	6	0	-8.409318	0.248864	-0.647328
23	6	0	-7.085585	0.574773	-0.329764
24	6	0	-6.403563	1.818810	-0.039030
25	6	0	-6.820474	3.151874	0.052780
26	6	0	-5.888279	4.133295	0.376062
27	6	0	-4.545347	3.793870	0.613729
28	6	0	-4.103173	2.475618	0.528767
29	6	0	-5.041971	1.496483	0.193181
30	6	0	6.111418	-0.453780	-0.260974
31	6	0	6.434936	-1.788486	-0.518939
32	6	0	7.759381	-2.084510	-0.833300
33	6	0	8.740365	-1.079976	-0.894059
34	6	0	8.409556	0.248924	-0.646364
35	6	0	7.085673	0.574843	-0.329436
36	6	0	6.403448	1.818960	-0.039541
37	6	0	6.820274	3.152074	0.051906
38	6	0	5.887919	4.133592	0.374423
39	6	0	4.544913	3.794197	0.611707
40	6	0	4.102824	2.475895	0.527088
41	6	0	5.041778	1.496654	0.192231
42	1	0	-2.625661	0.513070	-1.325653
43	1	0	-4.376974	-1.848751	1.800961
44	1	0	-2.261582	-3.064905	2.077482
45	1	0	2.261826	-3.064938	2.077170
46	1	0	4.377132	-1.848743	1.800467
47	1	0	2.625444	0.513053	-1.325980
48	1	0	0.883523	-4.543266	1.060654
49	1	0	0.000220	-3.854514	2.442639
50	1	0	-0.883498	-4.543211	1.060893
51	1	0	-5.680507	-2.566975	-0.482427
52	1	0	-8.035664	-3.114406	-1.040252
53	1	0	-9.763387	-1.344938	-1.142419
54	1	0	-9.167302	1.025007	-0.703182
55	1	0	-7.859563	3.415237	-0.123172
56	1	0	-6.199501	5.170814	0.448562
57	1	0	-3.834813	4.573752	0.871362
58	1	0	-3.066919	2.219816	0.720647
59	1	0	5.680915	-2.567062	-0.481483
60	1	0	8.036334	-3.114530	-1.038078
61	1	0	9.763949	-1.344961	-1.140302
62	1	0	9.167485	1.025117	-0.702265
63	1	0	7.859429	3.415392	-0.123707
64	1	0	6.199071	5.171153	0.446639
65	1	0	3.834244	4.574144	0.868768
66	1	0	3.066516	2.220145	0.718723

Table S2-2 Cartesian coordinates of optimized structure of **1b**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000013	0.922642	1.138493
2	7	0	-0.000136	-2.035246	1.634520
3	7	0	-4.860029	0.035083	-0.462818
4	7	0	4.860111	0.034776	-0.462291
5	6	0	-1.352723	-0.185987	0.783025
6	6	0	-2.532436	0.327389	0.251264
7	6	0	-3.655081	-0.497445	0.048096
8	6	0	-3.530731	-1.856671	0.379494
9	6	0	-2.329215	-2.370106	0.866363
10	6	0	-1.217714	-1.550335	1.096564
11	6	0	1.217533	-1.550472	1.096702
12	6	0	2.329039	-2.370272	0.866658
13	6	0	3.530631	-1.856891	0.379889
14	6	0	3.655086	-0.497696	0.048431
15	6	0	2.532445	0.327191	0.251486
16	6	0	1.352667	-0.186127	0.783138
17	6	0	-0.000269	-3.348512	2.250795
18	6	0	-5.105188	1.447947	-0.430929
19	6	0	-4.632109	2.279204	-1.448898
20	6	0	-4.884875	3.651156	-1.402929
21	6	0	-5.622037	4.185383	-0.345497
22	6	0	-6.105623	3.349239	0.662457
23	6	0	-5.848932	1.975173	0.636610
24	6	0	-6.384326	1.015971	1.668822
25	6	0	-7.503035	0.119875	1.103738
26	6	0	-7.188539	-0.771148	-0.092670
27	6	0	-8.220588	-1.617379	-0.533654
28	6	0	-8.061150	-2.491513	-1.602559
29	6	0	-6.840836	-2.530244	-2.281648
30	6	0	-5.812659	-1.686165	-1.882146
31	6	0	-5.966076	-0.810657	-0.793094
32	6	0	5.966281	-0.810879	-0.792362
33	6	0	5.812966	-1.686834	-1.881087
34	6	0	6.841349	-2.530707	-2.280470
35	6	0	8.061792	-2.491291	-1.601646
36	6	0	8.221120	-1.616723	-0.533091
37	6	0	7.188846	-0.770720	-0.092173
38	6	0	7.503224	0.120675	1.103996
39	6	0	6.384491	1.017072	1.668549
40	6	0	5.848915	1.975618	0.635826
41	6	0	6.105488	3.349725	0.660813
42	6	0	5.621578	4.185243	-0.347500
43	6	0	4.884205	3.650334	-1.404442
44	6	0	4.631585	2.278332	-1.449587
45	6	0	5.105010	1.447697	-0.431262
46	1	0	-2.578241	1.381478	0.007032
47	1	0	-4.370365	-2.527273	0.246139
48	1	0	-2.273458	-3.432110	1.077021
49	1	0	2.273269	-3.432272	1.077314
50	1	0	4.370244	-2.527549	0.246687
51	1	0	2.578304	1.381282	0.007273
52	1	0	0.884495	-3.445291	2.884200
53	1	0	-0.885012	-3.445091	2.884245
54	1	0	-0.000366	-4.181986	1.529094
55	1	0	-4.069968	1.842229	-2.268344
56	1	0	-4.512984	4.297059	-2.192601
57	1	0	-5.823769	5.251861	-0.306462
58	1	0	-6.684789	3.767505	1.481976
59	1	0	-5.569552	0.391865	2.052922
60	1	0	-6.789612	1.572022	2.520764
61	1	0	-7.873025	-0.522925	1.912902
62	1	0	-8.348803	0.764838	0.828471
63	1	0	-9.171323	-1.589335	-0.005660
64	1	0	-8.881319	-3.135608	-1.905469
65	1	0	-6.698433	-3.199019	-3.125297
66	1	0	-4.862888	-1.684881	-2.407497
67	1	0	4.863115	-1.686051	-2.406290
68	1	0	6.699005	-3.199839	-3.123846
69	1	0	8.882147	-3.135168	-1.904514
70	1	0	9.171951	-1.588140	-0.005304
71	1	0	7.872960	-0.521902	1.913462
72	1	0	8.349131	0.765412	0.828648
73	1	0	5.569740	0.393121	2.052960
74	1	0	6.789705	1.573627	2.520193

75	1	0	6.684787	3.768522	1.479967
76	1	0	5.823225	5.251762	-0.309129
77	1	0	4.512040	4.295750	-2.194383
78	1	0	4.069301	1.840843	-2.268656

Table S2-3 Cartesian coordinates of optimized structure of **1c**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.029909	0.563935	-1.593406
2	7	0	-0.014297	-2.424197	-1.320599
3	7	0	-4.698578	0.127260	0.644430
4	7	0	4.996294	0.085880	-0.375798
5	6	0	-1.319717	-0.413609	-0.841305
6	6	0	-2.458471	0.222682	-0.354595
7	6	0	-3.540726	-0.520093	0.150648
8	6	0	-3.418164	-1.917471	0.174178
9	6	0	-2.256489	-2.542812	-0.278188
10	6	0	-1.187093	-1.813284	-0.811105
11	6	0	1.238845	-1.821766	-1.046124
12	6	0	2.382568	-2.558839	-0.716939
13	6	0	3.615466	-1.943454	-0.502122
14	6	0	3.746635	-0.548194	-0.571833
15	6	0	2.592126	0.203439	-0.855740
16	6	0	1.374935	-0.423682	-1.108741
17	6	0	-0.044142	-3.851835	-1.574549
18	6	0	-4.900773	1.524590	0.416416
19	6	0	-4.331043	2.451440	1.295399
20	6	0	-4.440089	3.819313	1.054710
21	6	0	-5.129145	4.270485	-0.074740
22	6	0	-5.713233	3.354589	-0.942173
23	6	0	-5.629787	1.967797	-0.709657
24	6	0	-6.320532	1.051074	-1.614686
25	6	0	-6.861038	-0.150802	-1.313880
26	6	0	-6.881668	-0.816250	-0.012710
27	6	0	-7.965429	-1.655452	0.312217
28	6	0	-8.064597	-2.260220	1.560001
29	6	0	-7.073818	-2.040890	2.521512
30	6	0	-5.984542	-1.227810	2.215974
31	6	0	-5.869815	-0.631298	0.956030
32	6	0	5.078003	1.507941	-0.251879
33	6	0	5.137592	2.294340	-1.407071
34	6	0	5.136121	3.684765	-1.321437
35	6	0	5.078336	4.300901	-0.067938
36	6	0	5.036500	3.524707	1.084482
37	6	0	5.053179	2.117552	1.022477
38	6	0	5.073823	1.349932	2.266343
39	6	0	5.646737	0.144600	2.480414
40	6	0	6.383033	-0.673043	1.518077
41	6	0	7.431929	-1.494413	1.975917
42	6	0	8.206497	-2.238977	1.093860
43	6	0	7.948434	-2.182025	-0.278927
44	6	0	6.904979	-1.389536	-0.752185
45	6	0	6.110349	-0.652398	0.132070
46	1	0	-2.503950	1.304296	-0.386024
47	1	0	-4.224957	-2.529048	0.558493
48	1	0	-2.197652	-3.623359	-0.212522
49	1	0	2.324453	-3.637290	-0.622037
50	1	0	4.472245	-2.560215	-0.260876
51	1	0	2.637656	1.284906	-0.890916
52	1	0	-0.981732	-4.105713	-2.074583
53	1	0	0.039747	-4.470377	-0.665671
54	1	0	0.780019	-4.112685	-2.242535
55	1	0	-3.781731	2.077872	2.153658
56	1	0	-3.981412	4.528578	1.736929
57	1	0	-5.211421	5.334493	-0.275395
58	1	0	-6.258925	3.706531	-1.813698
59	1	0	-6.500072	1.437820	-2.615935
60	1	0	-7.436754	-0.644054	-2.094680
61	1	0	-8.742634	-1.816597	-0.430292
62	1	0	-8.913301	-2.898868	1.786001
63	1	0	-7.145194	-2.508122	3.499060
64	1	0	-5.192711	-1.060071	2.939061
65	1	0	5.159762	1.794879	-2.370392
66	1	0	5.168956	4.284145	-2.226167
67	1	0	5.067919	5.384056	0.008268
68	1	0	5.002436	4.004490	2.059104
69	1	0	4.663773	1.864094	3.133419
70	1	0	5.657137	-0.223969	3.504344
71	1	0	7.641489	-1.528648	3.041830
72	1	0	9.012610	-2.860111	1.472809
73	1	0	8.550618	-2.758686	-0.974517
74	1	0	6.673558	-1.345889	-1.811681

Table S2-4 Cartesian coordinates of optimized structure of **1d**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.533760	-1.169505	1.485616
2	6	0	2.326826	-1.351746	2.158395
3	6	0	1.218611	-0.532132	1.899129
4	6	0	1.351847	0.452682	0.900340
5	6	0	2.536927	0.594666	0.184951
6	6	0	3.655157	-0.199229	0.484397
7	6	0	-1.351837	0.452693	0.900342
8	6	0	-1.218608	-0.532121	1.899132
9	6	0	-2.326830	-1.351725	2.158402
10	1	0	-2.260542	-2.135995	2.903302
11	6	0	-3.533764	-1.169473	1.485628
12	6	0	-3.655153	-0.199198	0.484407
13	6	0	-2.536917	0.594686	0.184955
14	1	0	4.382663	-1.800248	1.726008
15	1	0	2.260533	-2.136016	2.903293
16	1	0	2.601976	1.340782	-0.599646
17	1	0	-4.382674	-1.800207	1.726021
18	1	0	-2.601964	1.340802	-0.599641
19	16	0	0.000009	1.574665	0.595622
20	6	0	-0.000001	-1.423585	3.841758
21	1	0	-0.884093	-1.157313	4.424678
22	1	0	-0.000005	-2.514416	3.690014
23	1	0	0.884095	-1.157320	4.424677
24	7	0	0.000002	-0.659362	2.605714
25	7	0	4.875676	-0.024233	-0.224511
26	7	0	-4.875672	-0.024192	-0.224496
27	6	0	-5.580320	-1.160409	-0.704609
28	6	0	-6.981382	-1.221012	-0.621558
29	6	0	-4.886273	-2.245786	-1.264202
30	6	0	-7.666502	-2.336621	-1.097949
31	1	0	-7.525616	-0.391005	-0.183963
32	6	0	-5.579969	-3.364357	-1.721021
33	1	0	-3.804838	-2.204855	-1.338040
34	6	0	-6.973133	-3.417426	-1.646249
35	1	0	-8.750069	-2.365095	-1.025359
36	1	0	-5.025728	-4.193477	-2.151806
37	1	0	-7.510439	-4.287796	-2.009870
38	6	0	-5.380820	1.285036	-0.446678
39	6	0	-5.962531	1.627667	-1.678540
40	6	0	-5.299222	2.260784	0.560294
41	6	0	-6.459586	2.912049	-1.888138
42	1	0	-6.021125	0.883316	-2.465345
43	6	0	-5.782819	3.547617	0.333735
44	1	0	-4.856275	2.003870	1.516541
45	6	0	-6.370447	3.882047	-0.887683
46	1	0	-6.905663	3.158622	-2.847488
47	1	0	-5.710559	4.288901	1.124536
48	1	0	-6.751831	4.884009	-1.058056
49	6	0	5.580256	-1.160453	-0.704722
50	6	0	6.981308	-1.221191	-0.621597
51	6	0	4.886147	-2.245705	-1.264483
52	6	0	7.666357	-2.336804	-1.098079
53	1	0	7.525591	-0.391287	-0.183869
54	6	0	5.579772	-3.364281	-1.721398
55	1	0	3.804720	-2.204672	-1.338382
56	6	0	6.972927	-3.417483	-1.646551
57	1	0	8.749918	-2.365383	-1.025427
58	1	0	5.025483	-4.193301	-2.152316
59	1	0	7.510178	-4.287856	-2.010245
60	6	0	5.380889	1.284988	-0.446599
61	6	0	5.962486	1.627724	-1.678487
62	6	0	5.299465	2.260628	0.560491
63	6	0	6.459600	2.912098	-1.887993
64	1	0	6.020943	0.883462	-2.465386
65	6	0	5.783123	3.547455	0.334027
66	1	0	4.856608	2.003635	1.516759
67	6	0	6.370637	3.881987	-0.887417
68	1	0	6.905585	3.158752	-2.847365
69	1	0	5.710998	4.288653	1.124922
70	1	0	6.752068	4.883944	-1.057718

Table S2-5 Cartesian coordinates of optimized structure of **1e**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.000024	-1.404877	0.945985
2	7	0	-0.000002	-2.043230	-1.992083
3	7	0	-4.899937	0.089234	-0.083673
4	6	0	-1.348696	-1.110424	-0.181213
5	6	0	-2.541590	-0.569382	0.292450
6	6	0	-3.650697	-0.440581	-0.554246
7	6	0	-3.532348	-0.830287	-1.886882
8	6	0	-2.327473	-1.336481	-2.374808
9	6	0	-1.219302	-1.499954	-1.530333
10	6	0	0.000026	-2.755576	-3.262080
11	6	0	-6.329374	2.073917	0.118265
12	6	0	-6.483781	3.456037	0.231776
13	6	0	-5.376437	4.301793	0.172082
14	6	0	-4.108356	3.746452	0.020627
15	6	0	-3.941941	2.363309	-0.051515
16	6	0	-5.048123	1.500760	-0.002602
17	6	0	-5.787188	-0.781494	0.605719
18	6	0	-5.360455	-2.017498	1.115646
19	6	0	-6.247846	-2.862603	1.782220
20	6	0	-7.573226	-2.484574	1.981915
21	6	0	-8.008776	-1.254925	1.488508
22	6	0	-7.137817	-0.422806	0.784176
23	1	0	-2.617985	-0.261203	1.330397
24	1	0	-4.386149	-0.720146	-2.546913
25	1	0	-2.256376	-1.599240	-3.423198
26	1	0	0.000000	-2.092714	-4.140233
27	1	0	-0.883484	-3.394760	-3.310062
28	1	0	-7.483380	3.864599	0.345685
29	1	0	-5.507776	5.376850	0.240898
30	1	0	-3.232473	4.386171	-0.031252
31	1	0	-2.945780	1.953249	-0.158133
32	1	0	-4.332063	-2.327393	0.980881
33	1	0	-5.887795	-3.816857	2.154837
34	1	0	-8.262781	-3.134254	2.511207
35	1	0	-9.038307	-0.939030	1.627766
36	7	0	4.899912	0.089230	-0.083625
37	6	0	1.348663	-1.110417	-0.181197
38	6	0	2.541557	-0.569383	0.292484
39	6	0	3.650669	-0.440559	-0.554200
40	6	0	3.532329	-0.830269	-1.886843
41	6	0	2.327463	-1.336461	-2.374780
42	6	0	1.219281	-1.499929	-1.530316
43	6	0	6.329473	2.073822	0.118145
44	6	0	6.483989	3.455931	0.231640
45	6	0	5.376690	4.301754	0.172078
46	6	0	4.108551	3.746500	0.020761
47	6	0	3.942031	2.363371	-0.051356
48	6	0	5.048166	1.500751	-0.002554
49	6	0	5.787101	-0.781484	0.605873
50	6	0	5.360296	-2.017370	1.115953
51	6	0	6.247649	-2.862467	1.782601
52	6	0	7.573078	-2.484536	1.982139
53	6	0	8.008726	-1.255007	1.488500
54	6	0	7.137791	-0.422904	0.784131
55	1	0	2.617939	-0.261235	1.330441
56	1	0	4.386140	-0.720126	-2.546861
57	1	0	2.256378	-1.599229	-3.423169
58	1	0	0.883590	-3.394686	-3.310060
59	1	0	7.483627	3.864431	0.345424
60	1	0	5.508104	5.376803	0.240876
61	1	0	3.232714	4.386289	-0.031023
62	1	0	2.945835	1.953372	-0.157877
63	1	0	4.331862	-2.327181	0.981301
64	1	0	5.887534	-3.816635	2.155377
65	1	0	8.262617	-3.134206	2.511464
66	1	0	9.038305	-0.939210	1.627625
67	16	0	-7.777542	1.044047	0.003219
68	16	0	7.777520	1.043801	0.002902

Table S3-1 Cartesian coordinates of optimized structure of **1a**$^{\bullet+}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.000002	0.006466	-1.215610
2	7	0	0.000001	-2.492553	0.603010
3	7	0	-4.979545	0.078701	0.034205
4	7	0	4.979540	0.078708	0.034212
5	6	0	-1.356872	-0.646679	-0.289363
6	6	0	-2.590026	-0.019906	-0.425790
7	6	0	-3.741468	-0.555809	0.170597
8	6	0	-3.618956	-1.736274	0.930141
9	6	0	-2.391598	-2.356275	1.075879
10	6	0	-1.227861	-1.841422	0.463764
11	6	0	1.227855	-1.841410	0.463776
12	6	0	2.391589	-2.356258	1.075902
13	6	0	3.618947	-1.736257	0.930165
14	6	0	3.741461	-0.555798	0.170610
15	6	0	2.590022	-0.019901	-0.425786
16	6	0	1.356867	-0.646672	-0.289358
17	6	0	0.000012	-3.892127	1.051839
18	6	0	-5.219942	1.466304	0.142332
19	6	0	-4.338054	2.502182	0.460356
20	6	0	-4.858855	3.793545	0.543165
21	6	0	-6.221527	4.045171	0.329934
22	6	0	-7.101778	3.001206	0.044111
23	6	0	-6.602526	1.701498	-0.046211
24	6	0	-7.229246	0.412926	-0.284374
25	6	0	-8.540950	0.027403	-0.562772
26	6	0	-8.815227	-1.321634	-0.790089
27	6	0	-7.788287	-2.275790	-0.760645
28	6	0	-6.469232	-1.912602	-0.489062
29	6	0	-6.208453	-0.564995	-0.228076
30	6	0	5.219944	1.466309	0.142340
31	6	0	4.338058	2.502193	0.460353
32	6	0	4.858867	3.793553	0.543167
33	6	0	6.221541	4.045171	0.329950
34	6	0	7.101789	3.001201	0.044135
35	6	0	6.602530	1.701496	-0.046191
36	6	0	7.229246	0.412919	-0.284339
37	6	0	8.540953	0.027388	-0.562715
38	6	0	8.815226	-1.321652	-0.790021
39	6	0	7.788280	-2.275801	-0.760590
40	6	0	6.469223	-1.912605	-0.489031
41	6	0	6.208447	-0.564996	-0.228053
42	1	0	-2.668828	0.871200	-1.037688
43	1	0	-4.482545	-2.131159	1.451208
44	1	0	-2.329646	-3.227081	1.715296
45	1	0	2.329632	-3.227060	1.715323
46	1	0	4.482534	-2.131136	1.451239
47	1	0	2.668825	0.871201	-1.037691
48	1	0	-0.000016	-3.975834	2.144504
49	1	0	-0.880065	-4.393584	0.652246
50	1	0	0.880129	-4.393551	0.652295
51	1	0	-3.287897	2.322062	0.656403
52	1	0	-4.193584	4.616276	0.784253
53	1	0	-6.596193	5.060945	0.400263
54	1	0	-8.160192	3.196200	-0.096665
55	1	0	-9.334515	0.766308	-0.611928
56	1	0	-9.831241	-1.634973	-1.006069
57	1	0	-8.018410	-3.316934	-0.962114
58	1	0	-5.681997	-2.656880	-0.502904
59	1	0	3.287898	2.322080	0.656390
60	1	0	4.193597	4.616288	0.784245
61	1	0	6.596213	5.060942	0.400286
62	1	0	8.160205	3.196188	-0.096630
63	1	0	9.334522	0.766289	-0.611867
64	1	0	9.831242	-1.634997	-1.005985
65	1	0	8.018401	-3.316948	-0.962049
66	1	0	5.681984	-2.656879	-0.502884

Table S3-2 Cartesian coordinates of optimized structure of **1b**$^{\bullet+}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.006152	0.719635	0.876547
2	7	0	0.007124	-2.379654	0.938126
3	7	0	-5.038506	0.037564	0.277490
4	7	0	4.913281	0.042854	-0.405703
5	6	0	-1.375536	-0.359067	0.669995
6	6	0	-2.618504	0.233173	0.503349
7	6	0	-3.799564	-0.541001	0.438269

8	6	0	-3.655581	-1.953494	0.504080
9	6	0	-2.416981	-2.537060	0.660983
10	6	0	-1.235182	-1.768460	0.766161
11	6	0	1.217121	-1.771107	0.604789
12	6	0	2.379930	-2.540050	0.368775
13	6	0	3.585878	-1.959266	0.040306
14	6	0	3.711816	-0.549038	-0.086372
15	6	0	2.553434	0.226927	0.145531
16	6	0	1.343673	-0.362230	0.481104
17	6	0	0.035507	-3.777771	1.393627
18	6	0	-6.210766	-0.760464	0.008667
19	6	0	-6.891688	-1.403802	1.042623
20	6	0	-8.034970	-2.148699	0.749860
21	6	0	-8.490130	-2.232476	-0.566846
22	6	0	-7.807458	-1.572791	-1.590569
23	6	0	-6.655218	-0.828503	-1.319577
24	6	0	-5.900078	-0.055765	-2.372211
25	6	0	-6.068943	1.468979	-2.223014
26	6	0	-5.704509	2.124760	-0.895942
27	6	0	-5.886383	3.515078	-0.805815
28	6	0	-5.605024	4.228961	0.353849
29	6	0	-5.138782	3.556581	1.485635
30	6	0	-4.960230	2.179691	1.431807
31	6	0	-5.224199	1.467190	0.251631
32	6	0	6.092939	-0.724524	-0.720766
33	6	0	6.074700	-1.498602	-1.891379
34	6	0	7.184534	-2.245766	-2.266697
35	6	0	8.334608	-2.204171	-1.475679
36	6	0	8.355107	-1.417493	-0.329164
37	6	0	7.245297	-0.661531	0.084302
38	6	0	7.412658	0.166696	1.352912
39	6	0	6.229084	1.022489	1.845788
40	6	0	5.736395	1.988503	0.797019
41	6	0	5.938527	3.370144	0.867938
42	6	0	5.500148	4.210603	-0.157036
43	6	0	4.860705	3.678785	-1.277807
44	6	0	4.656877	2.301356	-1.371999
45	6	0	5.086747	1.473710	-0.334182
46	1	0	-2.678573	1.310881	0.419570
47	1	0	-4.528569	-2.586320	0.413908
48	1	0	-2.363951	-3.618097	0.666651
49	1	0	2.337044	-3.620271	0.419360
50	1	0	4.445711	-2.593400	-0.129110
51	1	0	2.606748	1.305097	0.062199
52	1	0	0.946686	-3.947053	1.964619
53	1	0	-0.810493	-3.953263	2.055320
54	1	0	-0.004963	-4.482931	0.556405
55	1	0	-6.529955	-1.313822	2.062194
56	1	0	-8.570672	-2.652618	1.547874
57	1	0	-9.381175	-2.808058	-0.797099
58	1	0	-8.171103	-1.636652	-2.612420
59	1	0	-4.835573	-0.315639	-2.334608
60	1	0	-6.255589	-0.340208	-3.367125
61	1	0	-5.488101	1.959074	-3.014269
62	1	0	-7.117769	1.717232	-2.430359
63	1	0	-6.259146	4.044060	-1.679254
64	1	0	-5.757572	5.303283	0.378322
65	1	0	-4.932481	4.095995	2.404401
66	1	0	-4.622239	1.633153	2.306738
67	1	0	5.178809	-1.496463	-2.504465
68	1	0	7.158008	-2.840230	-3.174225
69	1	0	9.214013	-2.775128	-1.756130
70	1	0	9.257304	-1.382550	0.276220
71	1	0	7.708614	-0.510741	2.163513
72	1	0	8.271611	0.831547	1.195794
73	1	0	5.408739	0.369863	2.166709
74	1	0	6.555367	1.573012	2.733251
75	1	0	6.442677	3.789974	1.733978
76	1	0	5.663659	5.281153	-0.082938
77	1	0	4.529756	4.330140	-2.080279
78	1	0	4.175680	1.866493	-2.242546

Table S3-3 Cartesian coordinates of optimized structure of **1c**$^{\bullet+}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.015684	0.670360	-0.927308
2	7	0	0.002806	-2.421889	-0.710844
3	7	0	-5.034258	0.069425	-0.337241
4	7	0	4.905058	0.085491	0.474023
5	6	0	-1.372703	-0.380088	-0.640740
6	6	0	-2.615135	0.229044	-0.543323
7	6	0	-3.798184	-0.532442	-0.420245
8	6	0	-3.662548	-1.945550	-0.363705
9	6	0	-2.425397	-2.545420	-0.454361

10	6	0	-1.238370	-1.792992	-0.609883
11	6	0	1.211889	-1.790462	-0.420097
12	6	0	2.367582	-2.539544	-0.100366
13	6	0	3.572465	-1.935640	0.186801
14	6	0	3.704171	-0.521055	0.179799
15	6	0	2.553136	0.236305	-0.130607
16	6	0	1.343795	-0.376372	-0.422866
17	6	0	0.028563	-3.855217	-1.039725
18	6	0	-5.175361	1.498264	-0.272574
19	6	0	-5.046894	2.263167	-1.435037
20	6	0	-5.113910	3.652876	-1.366235
21	6	0	-5.308092	4.276869	-0.130016
22	6	0	-5.453155	3.512578	1.022056
23	6	0	-5.414275	2.105131	0.978034
24	6	0	-5.656515	1.339779	2.199944
25	6	0	-6.243708	0.125871	2.303835
26	6	0	-6.769046	-0.700504	1.218189
27	6	0	-7.884613	-1.527780	1.453629
28	6	0	-8.463576	-2.270417	0.430908
29	6	0	-7.937898	-2.210986	-0.863470
30	6	0	-6.820149	-1.419851	-1.118967
31	6	0	-6.229287	-0.688701	-0.085028
32	6	0	5.085213	1.505898	0.348445
33	6	0	4.583748	2.361365	1.333150
34	6	0	4.695105	3.741506	1.180299
35	6	0	5.309293	4.265030	0.038383
36	6	0	5.823957	3.411129	-0.930405
37	6	0	5.746699	2.011619	-0.790043
38	6	0	6.375896	1.151858	-1.791331
39	6	0	6.942556	-0.059752	-1.591263
40	6	0	7.053277	-0.788188	-0.328326
41	6	0	8.169656	-1.616521	-0.100492
42	6	0	8.352935	-2.265580	1.115132
43	6	0	7.417651	-2.107914	2.142654
44	6	0	6.292388	-1.313254	1.936060
45	6	0	6.101347	-0.677035	0.706661
46	1	0	-2.672454	1.310034	-0.560535
47	1	0	-4.539142	-2.564255	-0.224809
48	1	0	-2.376995	-3.622780	-0.362681
49	1	0	2.317610	-3.619244	-0.045767
50	1	0	4.425953	-2.553706	0.431681
51	1	0	2.610729	1.317244	-0.147601
52	1	0	-0.805404	-4.082497	-1.701053
53	1	0	0.949817	-4.081588	-1.573359
54	1	0	-0.036175	-4.482025	-0.143752
55	1	0	-4.880817	1.760296	-2.382560
56	1	0	-5.008893	4.245145	-2.269444
57	1	0	-5.353664	5.359502	-0.068614
58	1	0	-5.622436	4.000466	1.977607
59	1	0	-5.434430	1.864205	3.126583
60	1	0	-6.452132	-0.239961	3.306699
61	1	0	-8.306403	-1.563233	2.453918
62	1	0	-9.329273	-2.891265	0.638296
63	1	0	-8.391511	-2.782608	-1.666637
64	1	0	-6.387659	-1.372261	-2.113396
65	1	0	4.096880	1.935523	2.204865
66	1	0	4.299926	4.404187	1.943386
67	1	0	5.392256	5.339489	-0.090399
68	1	0	6.316536	3.821356	-1.807221
69	1	0	6.490468	1.596449	-2.777343
70	1	0	7.472971	-0.503949	-2.430493
71	1	0	8.907235	-1.727352	-0.890056
72	1	0	9.227834	-2.889529	1.267187
73	1	0	7.560881	-2.606094	3.096027
74	1	0	5.547046	-1.190635	2.715594

Table S3-4 Cartesian coordinates of optimized structure of **1d**$^{+}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.000007	0.374925	-1.101871
2	7	0	0.000010	-2.471451	0.114726
3	7	0	-4.992289	0.144889	0.061909
4	7	0	4.992284	0.144944	0.061973
5	6	0	-1.361120	-0.477220	-0.362129
6	6	0	-2.591981	0.161817	-0.370639
7	6	0	-3.759832	-0.490285	0.078075
8	6	0	-3.625926	-1.814603	0.564588
9	6	0	-2.399441	-2.445547	0.579794
10	6	0	-1.228474	-1.810021	0.107569
11	6	0	1.228452	-1.809917	0.107772
12	6	0	2.399384	-2.445311	0.580338
13	6	0	3.625844	-1.814350	0.565165
14	6	0	3.759772	-0.490166	0.078292

15	6	0	2.591983	0.161861	-0.370634
16	6	0	1.361111	-0.477176	-0.362080
17	6	0	0.000024	-3.934744	0.253838
18	6	0	-5.092345	1.575927	0.048685
19	6	0	-5.887144	2.205962	-0.917316
20	6	0	-6.008399	3.594056	-0.914694
21	6	0	-5.337826	4.359187	0.042059
22	6	0	-4.547262	3.728573	1.005210
23	6	0	-4.426341	2.340108	1.016937
24	6	0	-6.212203	-0.608236	0.037562
25	6	0	-7.232417	-0.303286	0.948089
26	6	0	-8.428791	-1.016021	0.910265
27	6	0	-8.614389	-2.035301	-0.026770
28	6	0	-7.597539	-2.335574	-0.935306
29	6	0	-6.400297	-1.622223	-0.912361
30	6	0	5.092450	1.575953	0.048803
31	6	0	4.426389	2.340191	1.016967
32	6	0	4.547422	3.728647	1.005271
33	6	0	5.338170	4.359216	0.042239
34	6	0	6.008793	3.594029	-0.914434
35	6	0	5.887420	2.205950	-0.917100
36	6	0	6.212108	-0.608340	0.037508
37	6	0	7.232576	-0.303317	0.947736
38	6	0	8.428852	-1.016194	0.909757
39	6	0	8.614121	-2.035666	-0.027146
40	6	0	7.597021	-2.336005	-0.935367
41	6	0	6.399851	-1.622526	-0.912267
42	1	0	-2.657269	1.174210	-0.750613
43	1	0	-4.491404	-2.329514	0.961929
44	1	0	-2.343399	-3.436873	1.010520
45	1	0	2.343245	-3.436539	1.011307
46	1	0	4.491303	-2.329068	0.962810
47	1	0	2.657308	1.174201	-0.750762
48	1	0	-0.879978	-4.339116	-0.243381
49	1	0	0.880329	-4.339065	-0.242883
50	1	0	-0.000285	-4.248771	1.303512
51	1	0	-6.402963	1.607445	-1.660649
52	1	0	-6.623823	4.078310	-1.666210
53	1	0	-5.435048	5.440029	0.040404
54	1	0	-4.035251	4.316567	1.760463
55	1	0	-3.830296	1.844991	1.776763
56	1	0	-7.082394	0.486137	1.676833
57	1	0	-9.215220	-0.778074	1.619446
58	1	0	-9.547824	-2.588168	-0.052170
59	1	0	-7.740971	-3.116179	-1.675831
60	1	0	-5.617861	-1.837250	-1.632971
61	1	0	3.830193	1.845147	1.776717
62	1	0	4.035355	4.316660	1.760473
63	1	0	5.435472	5.440050	0.040603
64	1	0	6.624359	4.078245	-1.665856
65	1	0	6.403259	1.607412	-1.660404
66	1	0	7.082803	0.486268	1.676359
67	1	0	9.215469	-0.778240	1.618725
68	1	0	9.547508	-2.588608	-0.052682
69	1	0	7.740177	-3.116758	-1.675787
70	1	0	5.617214	-1.837628	-1.632642

Table S3-5 Cartesian coordinates of optimized structure of **1e**$^{\bullet+}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.027898	0.609632	-0.908773
2	16	0	6.924807	0.684404	-1.496440
3	16	0	-6.355106	0.896483	2.063535
4	7	0	0.014137	-2.482283	-0.663588
5	7	0	4.901279	0.053377	0.582099
6	7	0	-5.044150	0.012945	-0.450469
7	6	0	1.345434	-0.432120	-0.367231
8	6	0	2.548466	0.185314	-0.056804
9	6	0	3.697681	-0.563476	0.275470
10	6	0	3.571032	-1.977238	0.274089
11	6	0	2.372276	-2.587632	-0.027655
12	6	0	1.216777	-1.845773	-0.359836
13	6	0	-1.228529	-1.852336	-0.592294
14	6	0	-2.416943	-2.601188	-0.439131
15	6	0	-3.656703	-2.000896	-0.389106
16	6	0	-3.796907	-0.591683	-0.490620
17	6	0	-2.611220	0.166522	-0.594005
18	6	0	-1.364786	-0.441720	-0.649245
19	6	0	0.045902	-3.919770	-0.974055
20	6	0	7.146298	-0.504243	-0.183244
21	6	0	8.337327	-1.226118	-0.059945
22	6	0	8.496604	-2.128005	0.990848
23	6	0	7.488067	-2.284199	1.945103

24	6	0	6.304304	-1.556247	1.835721
25	6	0	6.115791	-0.695998	0.749980
26	6	0	5.091702	1.466524	0.409434
27	6	0	4.429684	2.400171	1.212500
28	6	0	4.623573	3.763027	0.993312
29	6	0	5.502198	4.193634	-0.004128
30	6	0	6.209057	3.266054	-0.767583
31	6	0	6.008909	1.897667	-0.561547
32	6	0	-5.781909	1.986993	0.772427
33	6	0	-5.932846	3.372815	0.881792
34	6	0	-5.504368	4.201727	-0.153592
35	6	0	-4.960770	3.652409	-1.317689
36	6	0	-4.820224	2.271024	-1.438399
37	6	0	-5.193845	1.439280	-0.378250
38	6	0	-6.239381	-0.729275	-0.161418
39	6	0	-6.733613	-1.697478	-1.041040
40	6	0	-7.883626	-2.412006	-0.709971
41	6	0	-8.559692	-2.137047	0.481426
42	6	0	-8.104647	-1.131212	1.332395
43	6	0	-6.943666	-0.420775	1.012702
44	1	0	2.599764	1.265502	-0.092101
45	1	0	4.423508	-2.597514	0.513375
46	1	0	2.330961	-3.667865	0.020108
47	1	0	-2.369712	-3.675155	-0.313353
48	1	0	-4.529071	-2.621724	-0.238701
49	1	0	-2.661845	1.247068	-0.620113
50	1	0	-0.784959	-4.158129	-1.635191
51	1	0	0.969490	-4.149882	-1.502340
52	1	0	-0.019398	-4.535053	-0.070217
53	1	0	9.137449	-1.067488	-0.775596
54	1	0	9.422183	-2.687243	1.080963
55	1	0	7.628425	-2.959675	2.782497
56	1	0	5.522156	-1.652221	2.581978
57	1	0	3.766335	2.052751	1.998095
58	1	0	4.101472	4.486453	1.610788
59	1	0	5.660625	5.254485	-0.168758
60	1	0	6.927098	3.597269	-1.510725
61	1	0	-6.399127	3.793276	1.766838
62	1	0	-5.623158	5.276589	-0.063210
63	1	0	-4.661580	4.296882	-2.137663
64	1	0	-4.419639	1.831199	-2.346103
65	1	0	-6.212180	-1.886197	-1.973948
66	1	0	-8.259583	-3.170305	-1.388813
67	1	0	-9.460498	-2.686336	0.735175
68	1	0	-8.653616	-0.883627	2.235090

Summary of results of TD-DFT calculation for **1a**$^{\bullet+}$ using the *Gaussian 09* program at UB3LYP/6-31(d,p) level of theory with the broken symmetry method.

Excitation energies and oscillator strengths:

Excited State 1: 2.010-A 0.6921 eV 1791.52 nm f=0.3945 <S**2>=0.760
141B ->142B 1.02887
141B <-142B -0.25445
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1987.28339312
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.015-A 0.7996 eV 1550.65 nm f=0.0001 <S**2>=0.765
139B ->142B 0.99118
140B ->142B -0.12014

Excited State 3: 2.015-A 0.7996 eV 1550.62 nm f=0.0001 <S**2>=0.765
138B ->142B -0.17707
139B ->142B 0.12177
140B ->142B 0.97525

Excited State 4: 2.008-A 0.9707 eV 1277.23 nm f=0.0203 <S**2>=0.758
135B ->142B 0.10318
138B ->142B 0.97745
140B ->142B 0.17737

Excited State 5: 2.018-A 1.8261 eV 678.97 nm f=0.0106 <S**2>=0.768
135B ->142B -0.44651
137B ->142B 0.88635

Summary of results of TD-DFT calculation for **1b**$^{\bullet+}$ using the *Gaussian 09* program at UB3LYP/6-31(d,p) level of theory with the broken symmetry method.

Excitation energies and oscillator strengths:

Excited State 1: 2.014-A 1.2656 eV 979.68 nm f=0.4211 <S**2>=0.764
157B ->158B 0.99455
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2144.49918447
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.022-A 1.5685 eV 790.45 nm f=0.0033 <S**2>=0.772
149B ->158B 0.14254
154B ->158B 0.13678
156B ->158B 0.96411

Excited State 3: 2.016-A 2.0357 eV 609.05 nm f=0.0039 <S**2>=0.767
154B ->158B -0.39241
155B ->158B 0.89208
156B ->158B 0.16344

Excited State 4: 2.016-A 2.0652 eV 600.35 nm f=0.0029 <S**2>=0.766
154B ->158B 0.89036
155B ->158B 0.42226

Excited State 5: 2.015-A 2.2370 eV 554.25 nm f=0.0002 <S**2>=0.765
152B ->158B -0.51855
153B ->158B 0.84526

Summary of results of TD-DFT calculation for **1c**$^{\bullet+}$ using the *Gaussian 09* program at UB3LYP/6-31(d,p) level of theory with the broken symmetry method.

Excitation energies and oscillator strengths:

Excited State 1: 2.014-A 1.2968 eV 956.08 nm f=0.3420 <S**2>=0.764
155B ->156B 0.99446
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2142.05954141
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.015-A 1.4642 eV 846.76 nm f=0.0027 <S**2>=0.765
152B ->156B 0.23824
154B ->156B 0.96838

Excited State 3: 2.013-A 1.5531 eV 798.32 nm f=0.0584 <S**2>=0.763
153B ->156B 0.99681

Excited State 4: 2.021-A 1.6389 eV 756.50 nm f=0.0010 <S**2>=0.771
149B ->156B -0.12097
152B ->156B 0.95319
154B ->156B -0.24449

Excited State 5: 2.015-A 2.3161 eV 535.32 nm f=0.0008 <S**2>=0.766
151B ->156B 0.99493

Summary of results of TD-DFT calculation for **1d**$^{\bullet+}$ using the *Gaussian 09* program at UB3LYP/6-31(d,p) level of theory with the broken symmetry method.

Excitation energies and oscillator strengths:

Excited State 1: 2.012-A 1.0044 eV 1234.36 nm f=0.4606 <S**2>=0.762
143B ->144B 1.00148
143B <-144B -0.12568
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1989.65309942
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.017-A 1.3877 eV 893.46 nm f=0.0119 <S**2>=0.767
141B ->144B 0.13777
142B ->144B 0.97641

Excited State 3: 2.022-A 2.1272 eV 582.85 nm f=0.0140 <S**2>=0.772
137B ->144B 0.29349
139B ->144B 0.21930
141B ->144B 0.90383
142B ->144B -0.16155

Excited State 4: 2.020-A 2.2902 eV 541.38 nm f=0.0003 <S**2>=0.770
140B ->144B 0.99497

Excited State 5: 2.020-A 2.3573 eV 525.95 nm f=0.0006 <S**2>=0.770
137B ->144B 0.25505
139B ->144B 0.90622
141B ->144B -0.31928

Summary of results of TD-DFT calculation for **1e**$^{\bullet+}$ using the *Gaussian 09* program at UB3LYP/6-31(d,p) level of theory with the broken symmetry method.

Excitation energies and oscillator strengths:

Excited State 1: 2.013-A 1.1213 eV 1105.73 nm f=0.3284 <S**2>=0.763
157B ->158B 0.99728
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2783.60932023
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.014-A 1.2936 eV 958.44 nm f=0.0063 <S**2>=0.764
154B ->158B 0.13740
156B ->158B 0.98650

Excited State 3: 2.014-A 1.5349 eV 807.78 nm f=0.0986 <S**2>=0.764
155B ->158B 0.99531

Excited State 4: 2.020-A 1.6184 eV 766.09 nm f=0.0010 <S**2>=0.770
151B ->158B 0.16432
154B ->158B 0.96496
156B ->158B -0.14894

Excited State 5: 2.020-A 2.3267 eV 532.88 nm f=0.0278 <S**2>=0.770
149B ->158B -0.21838
151B ->158B -0.45621
152B ->158B -0.57731
153B ->158B 0.61499
154B ->158B 0.10766

Table 4 Comparison of near-IR absorption bands and dihedral angles.

Compound	Experimental / nm	TDDFT /nm (assignment)	Dihedral angle[a] (plane A/C) / (plane B/D)
1a$^{\bullet+}$	1200	1550 (SOMO-β to LUMO-β)	43.8° / 43.8°
1b$^{\bullet+}$	950	979 (SOMO-β to LUMO-β)	5.98°/ 6.83°
1c$^{\bullet+}$	918	956 (SOMO-β to LUMO-β)	2.94°/ 2.64°
1d$^{\bullet+}$	1118	1234 (SOMO-β to LUMO-β)	23.1° / 23.1°
1e$^{\bullet+}$	963	1105 (SOMO-β to LUMO-β)	4.73°/ 3.85°

[a] Calculated values from the optimized structures. For naming of planes in **$(Ar_2N)_2$-PTZ**, see Fig. 3.

Reference

[S1] Phenoxazine radical cation $\mathbf{2f^{\bullet+}PF_6^-}$ was prepared from **2f** using tris(4-bromophenyl)aminium hexafluorophosphate as an oxidant.

[S2] *Gaussian 09*, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.