Supplementary Information

Fluorescent-state switching of a 10-hydroxybezo[*h*]quinoline skeleton through electronic nature of substituents

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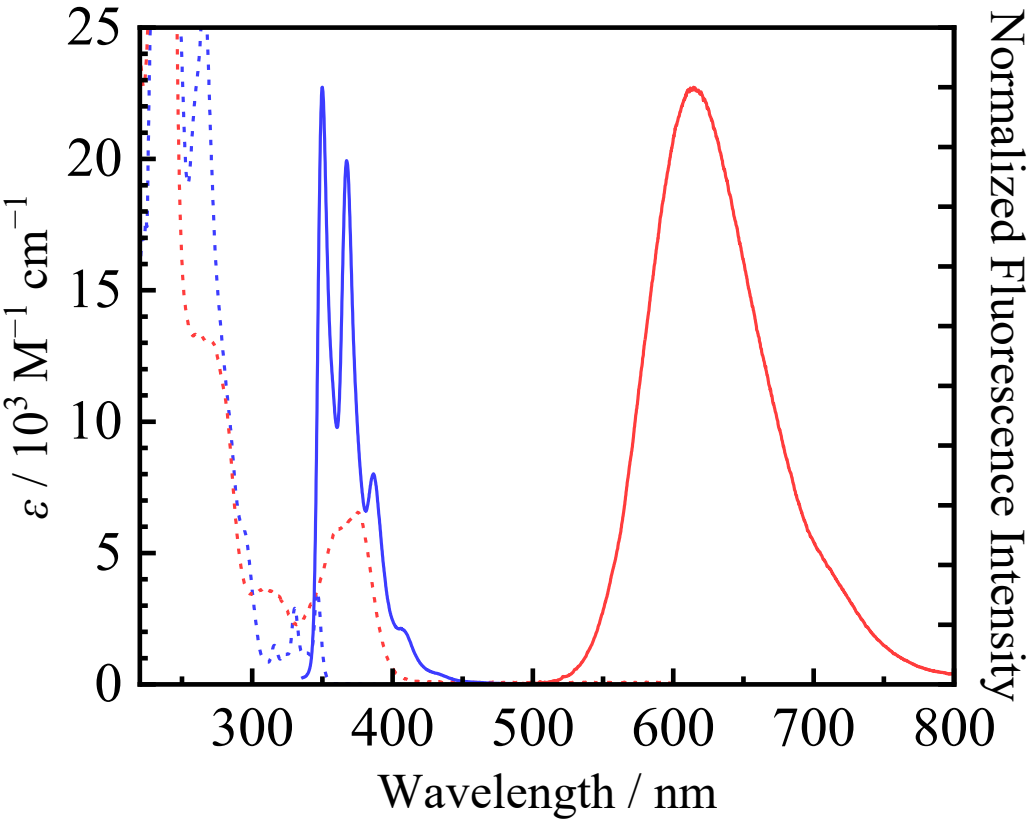

Fig. S1 Absorption (broken curves) and fluorescence spectra (solid curves) of HBq (red) and benzo[*h*]quinoline (blue) in THF.

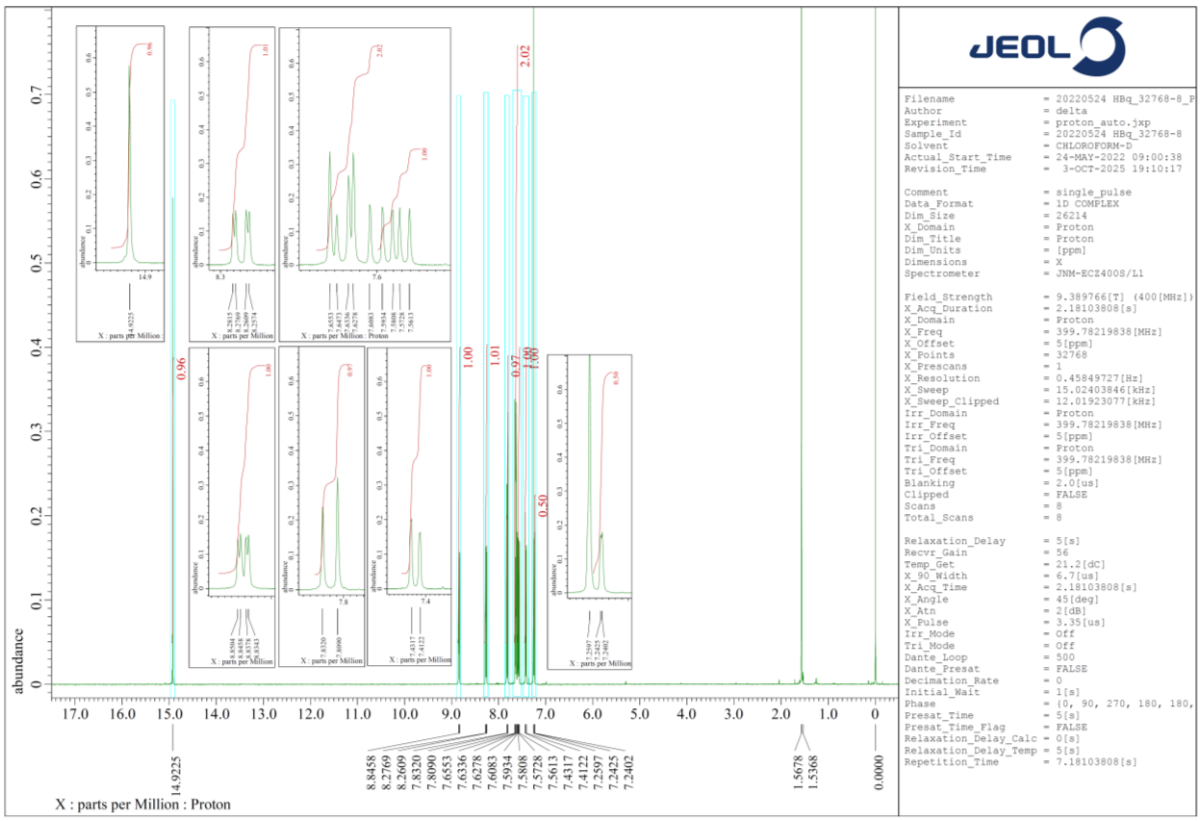

Fig. S2 ^{1}H-NMR spectrum of **HBq** in $CDCl_3$.

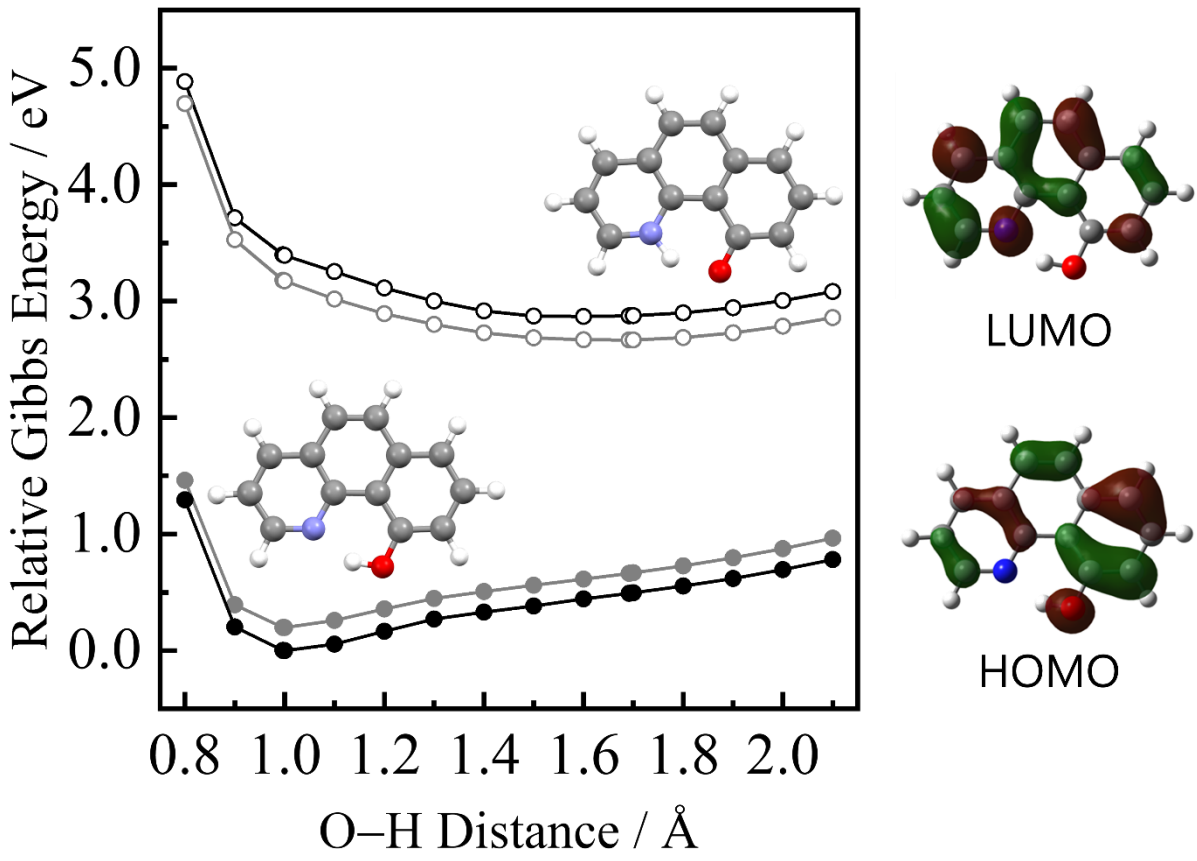

Fig. S3 Results of (TD-)DFT calculations for HBq in vacuum (B3LYP/6-31G(d,p) level): dependences of the O–H distances on the relative Gibbs energies of ground (close circles) and S_1 states (open circles) in the ground- (black) and S_1-state-optimized geometries (gray) with Kohn–Sham orbitals in the ground-state-optimized geometries.

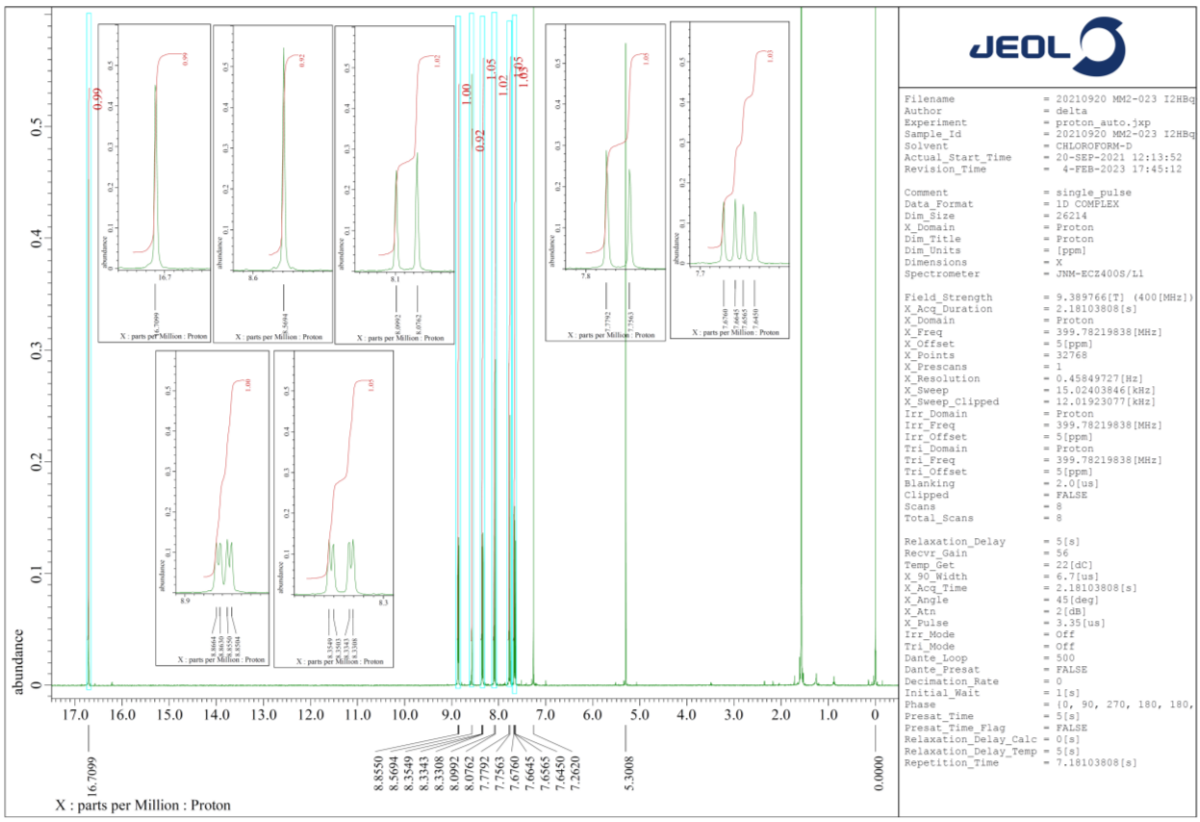

Fig. S4 ^{1}H-NMR spectrum of **HBqI$_2$** in $CDCl_3$.

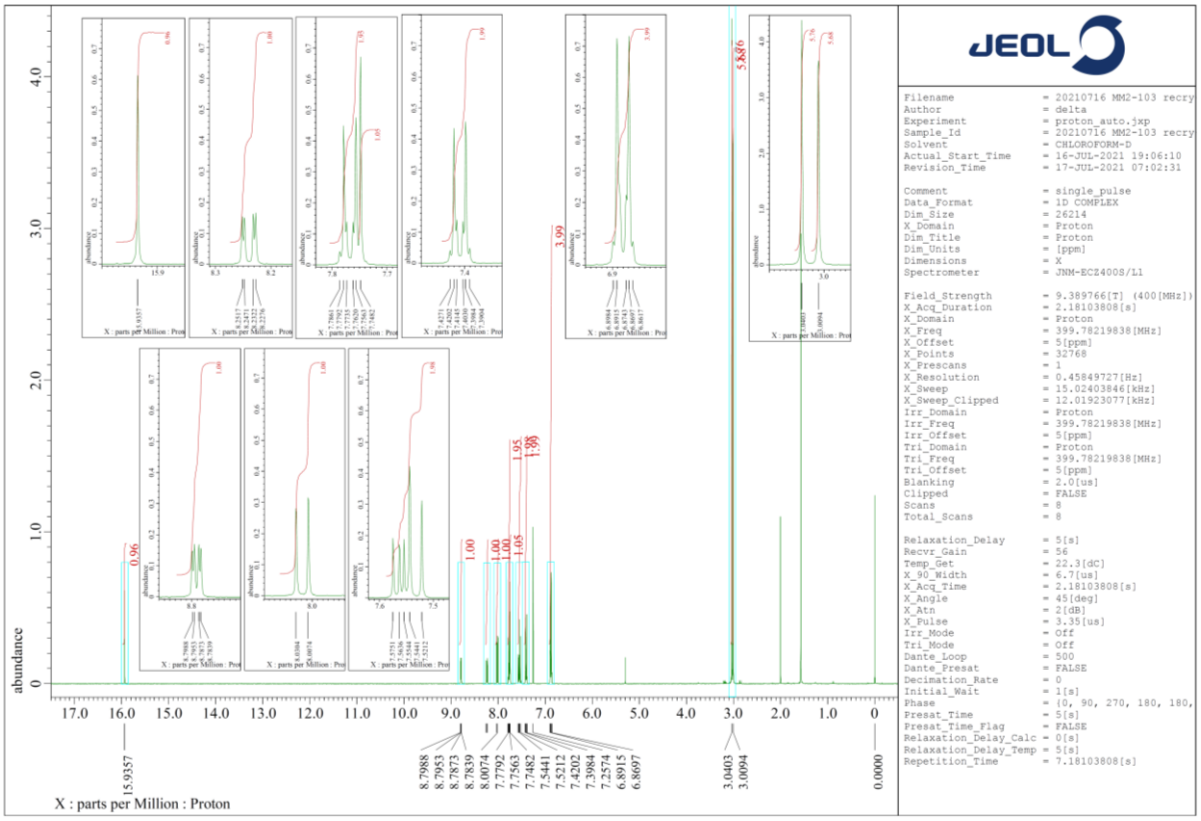

Fig. S5 ^{1}H-NMR spectrum of **1NMe$_2$** in $CDCl_3$.

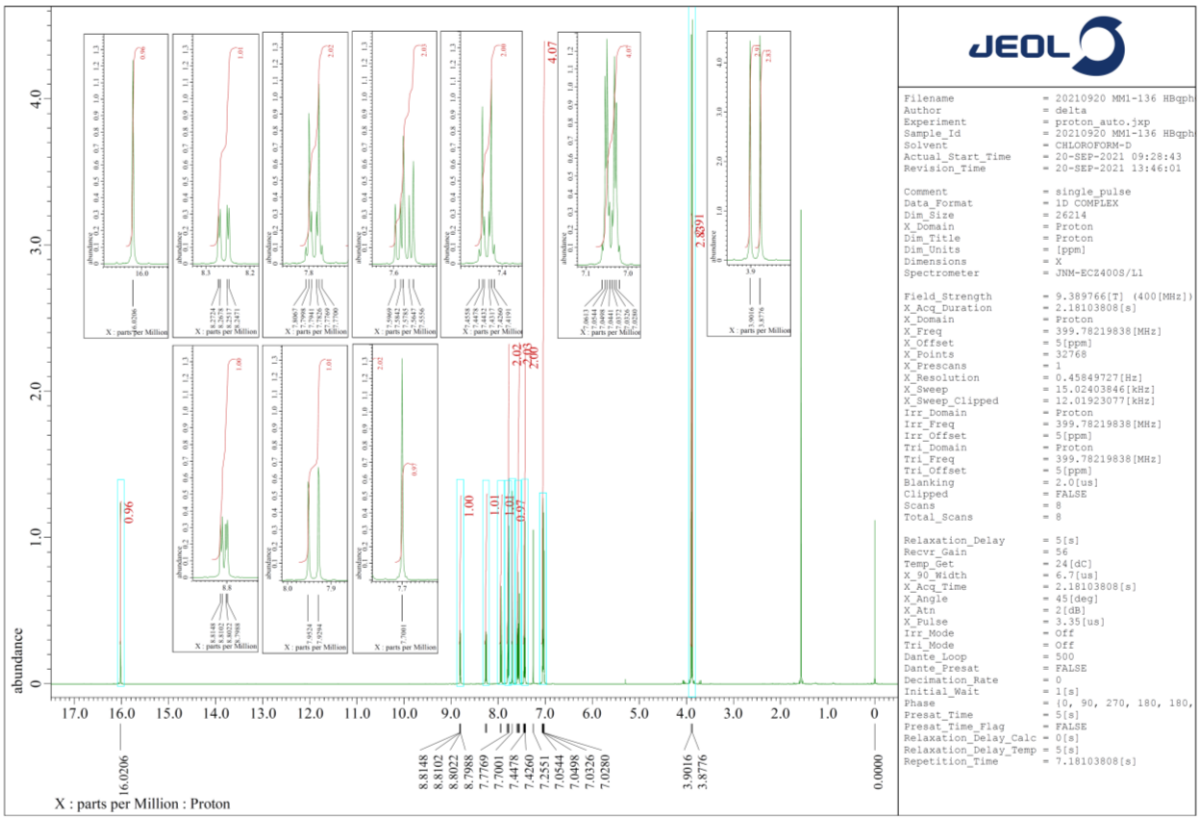

Fig. S6 ^{1}H-NMR spectrum of **1OMe** in $CDCl_3$.

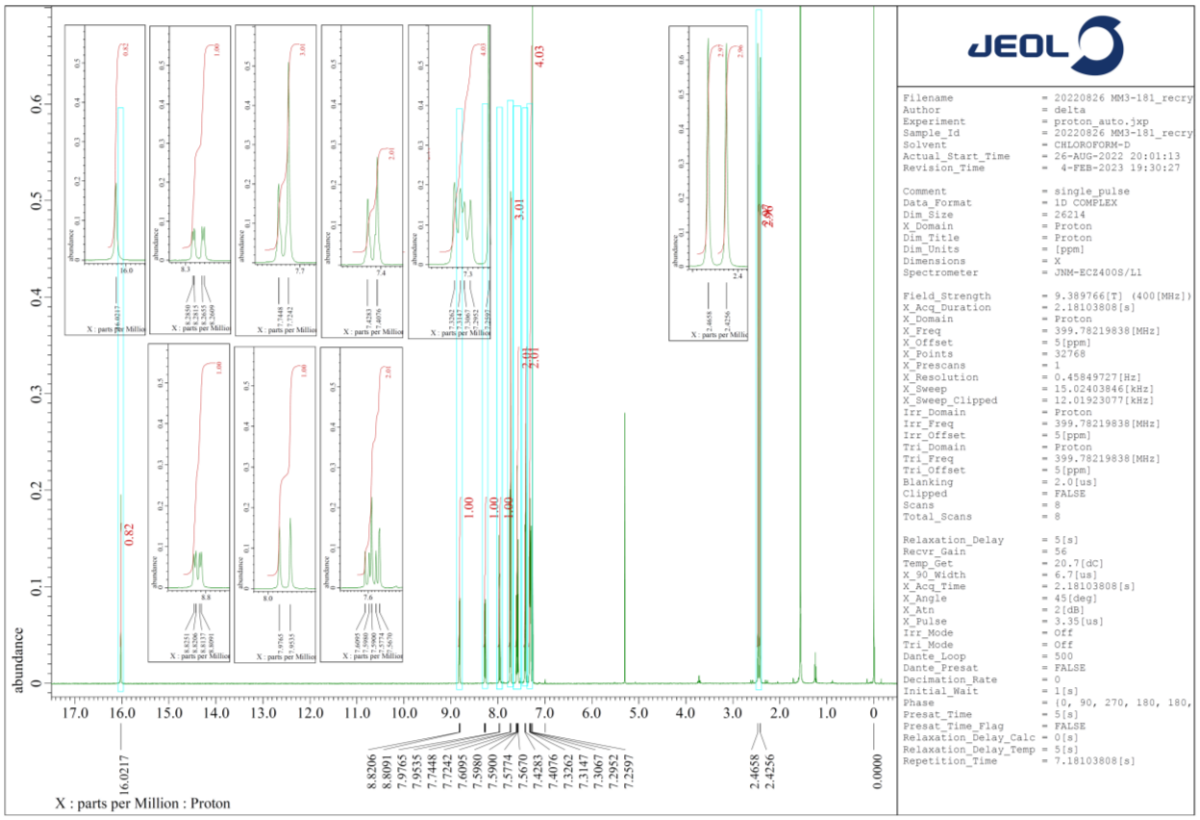

Fig. S7 ^{1}H-NMR spectrum of **1Me** in $CDCl_3$.

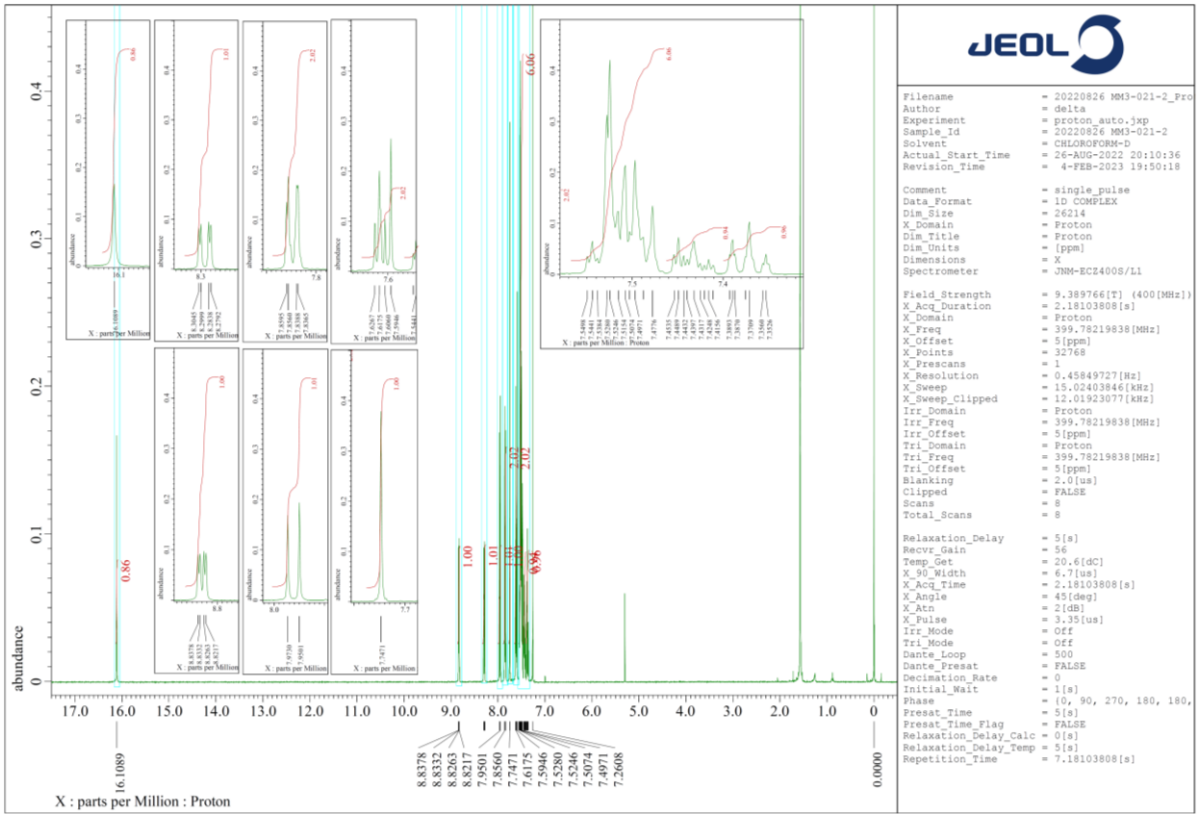

Fig. S8 ^{1}H-NMR spectrum of **1H** in $CDCl_3$.

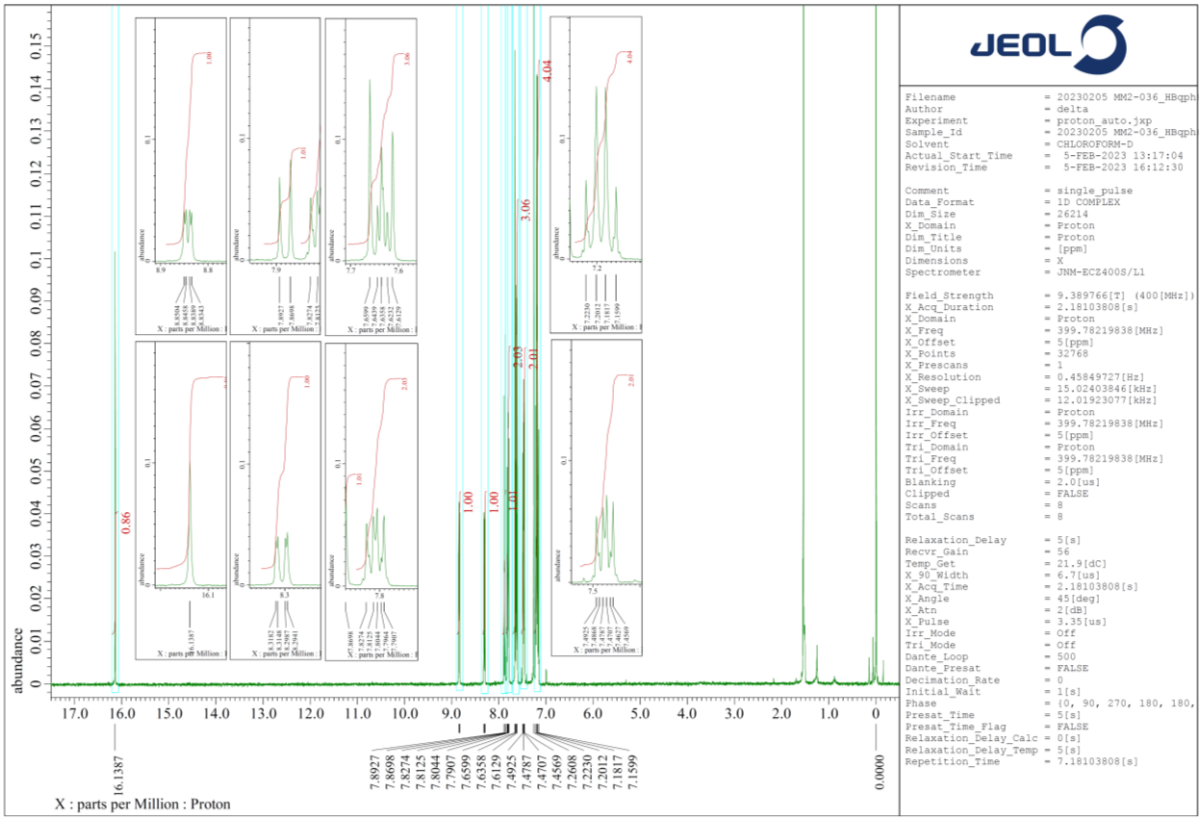

Fig. S9 ^{1}H-NMR spectrum of **1F** in $CDCl_3$.

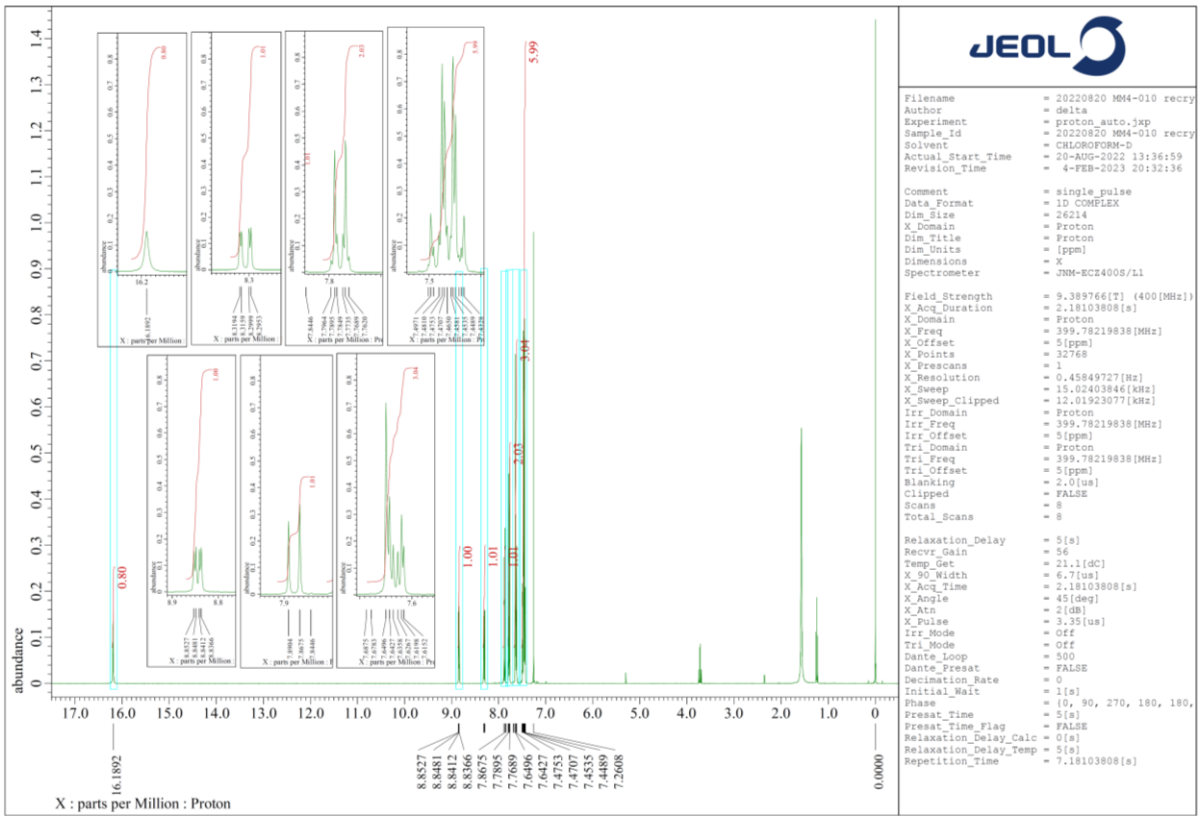

Fig. S10 ^{1}H-NMR spectrum of **1Cl** in $CDCl_3$.

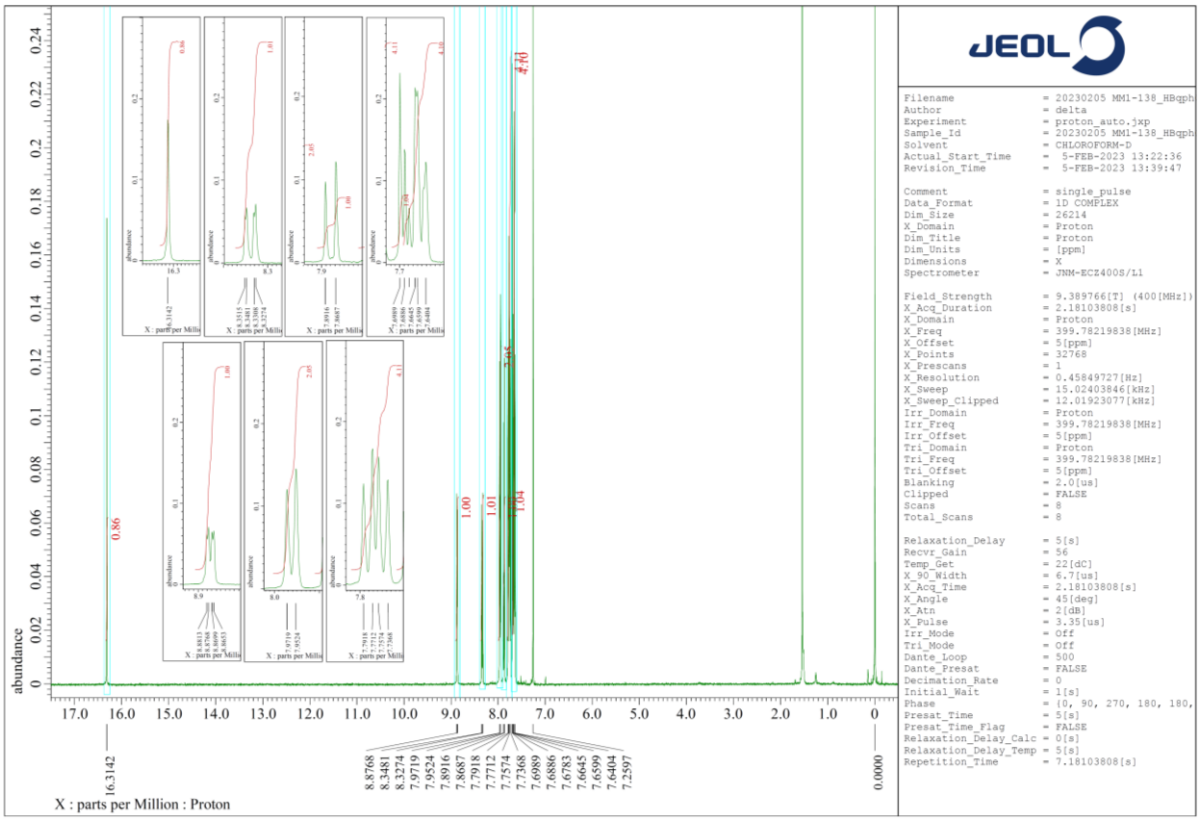

Fig. S11 ^{1}H-NMR spectrum of **1CF$_3$** in $CDCl_3$.

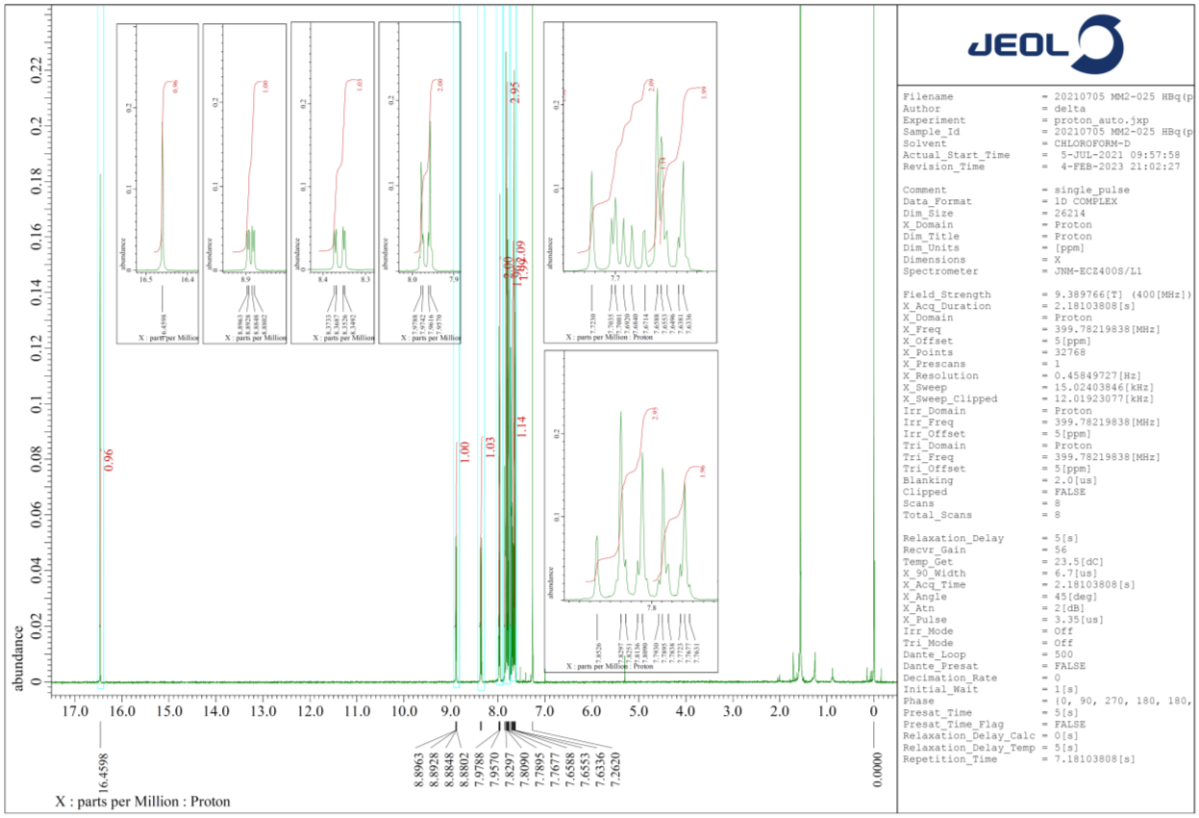

Fig. S12 ^{1}H-NMR spectrum of **1CN** in $CDCl_3$.

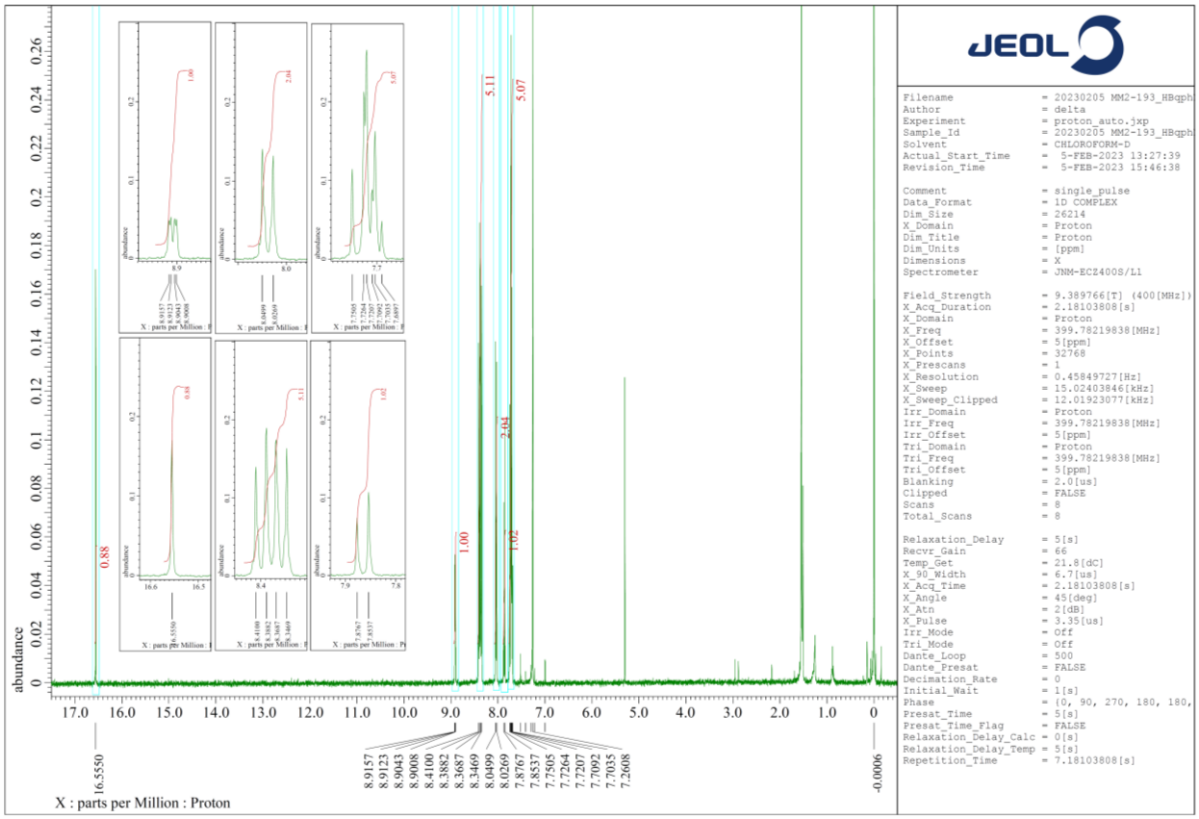

Fig. S13 ^{1}H-NMR spectrum of **1NO$_2$** in $CDCl_3$.

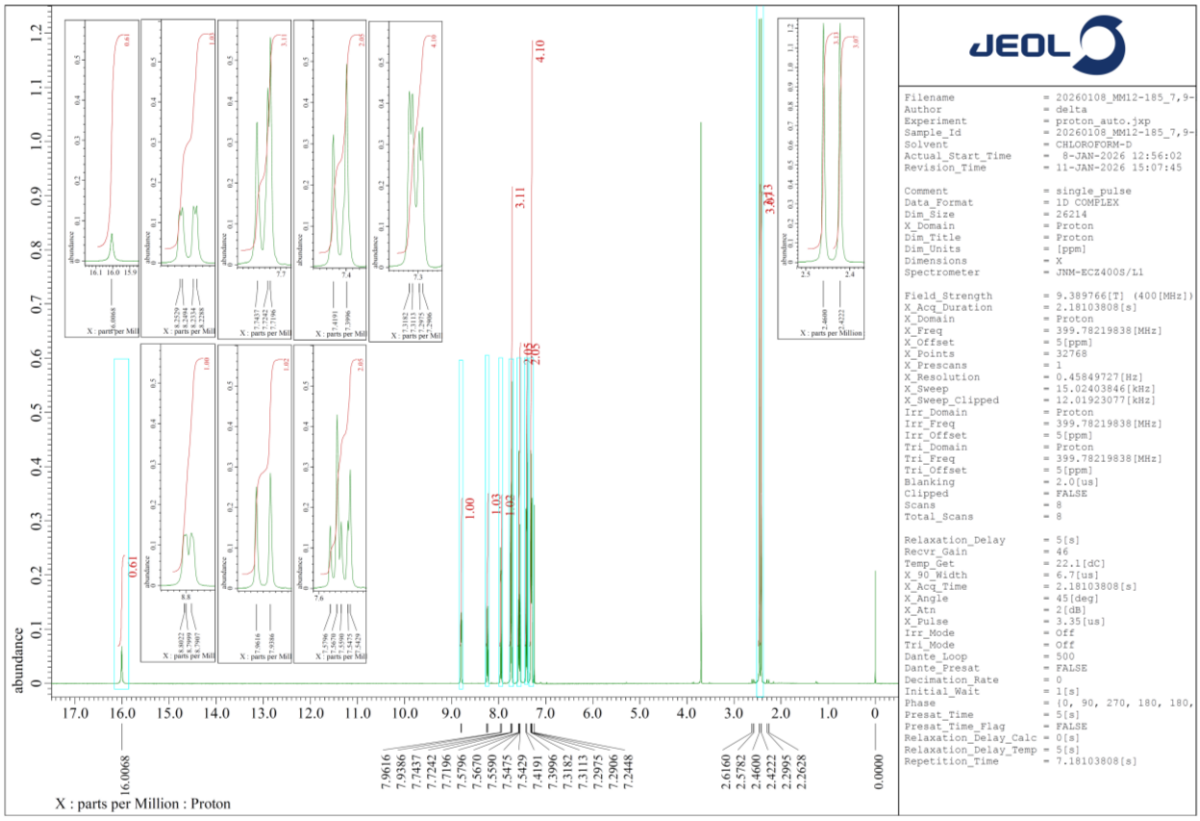

Fig. S14 ^{1}H-NMR spectrum of deuterated **1Me** in $CDCl_3$.

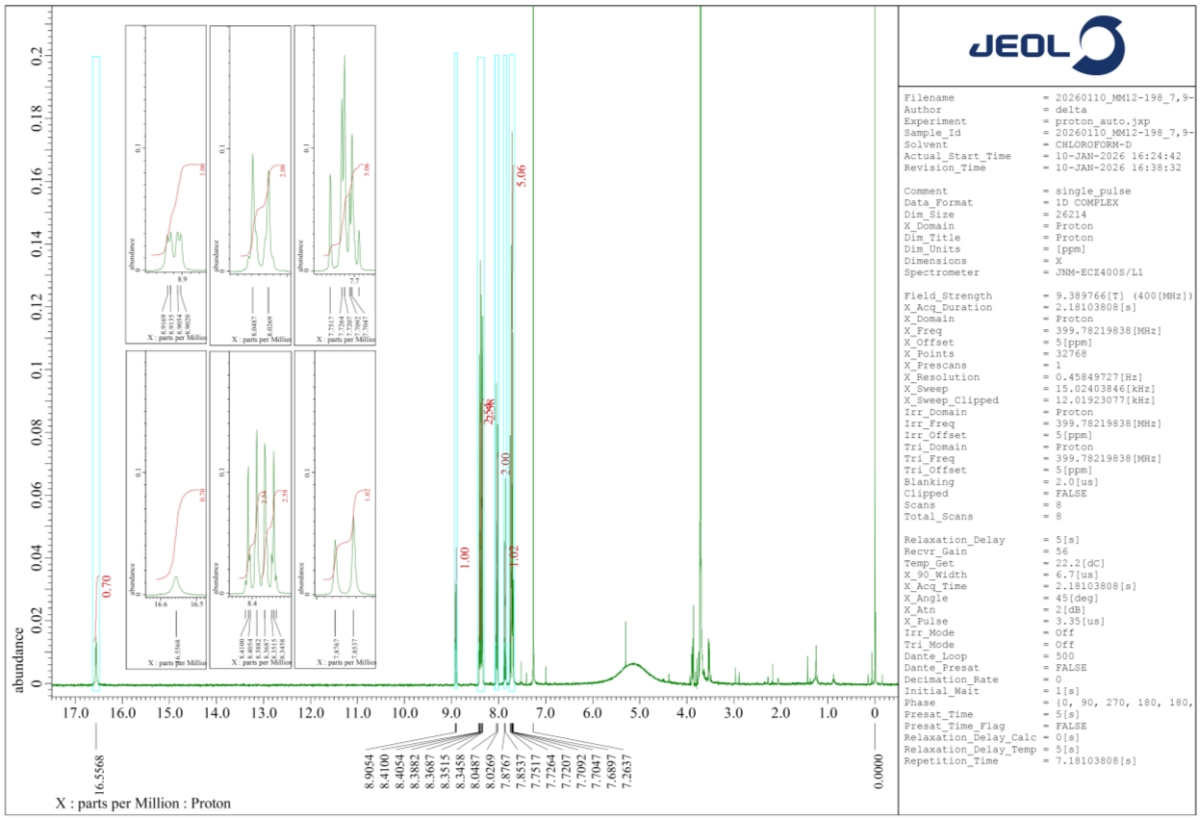

Fig. S15 ^{1}H-NMR spectrum of deuterated **1NO$_2$** in $CDCl_3$.

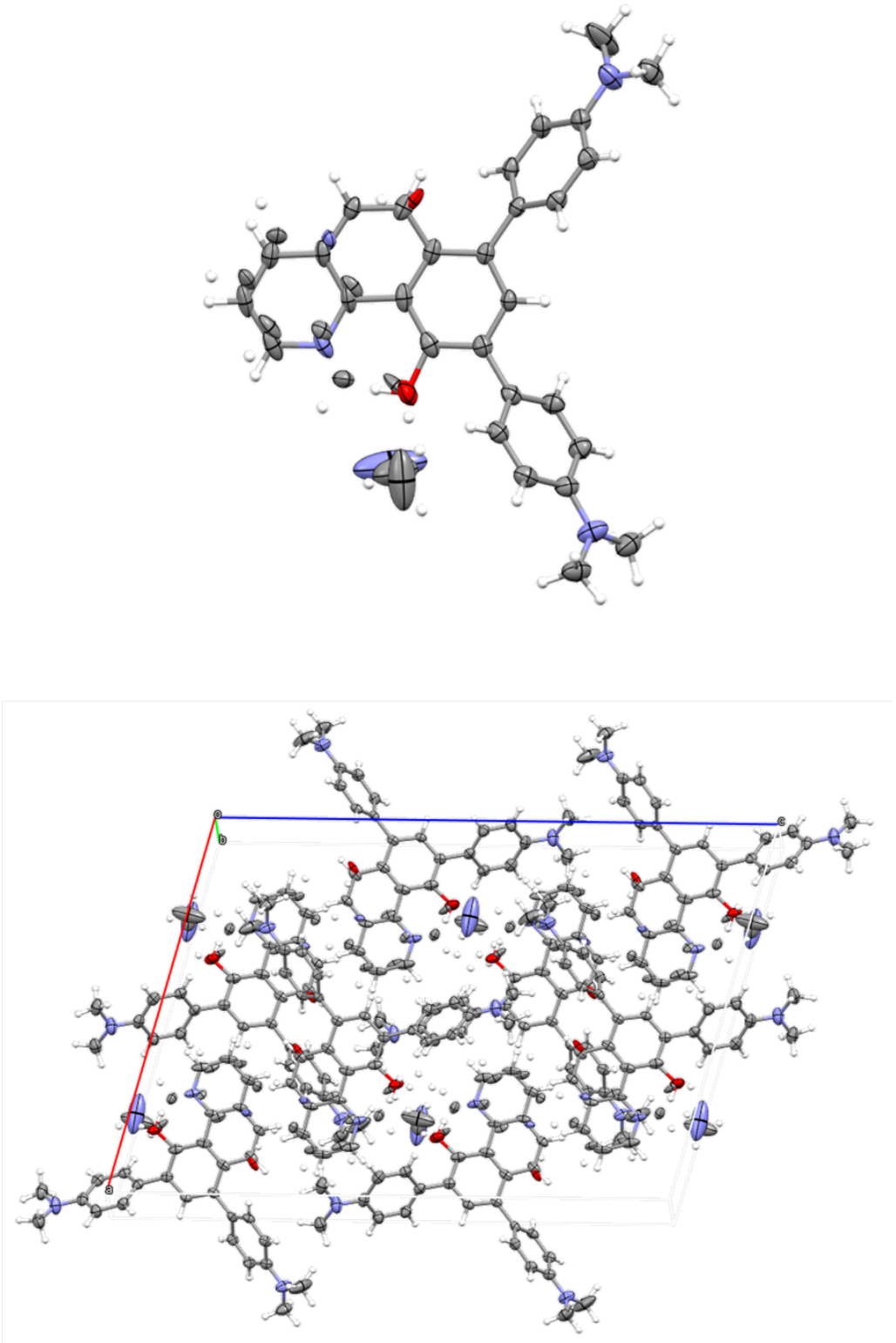

Fig. S16 Crystal structure of **1NMe$_2$**.

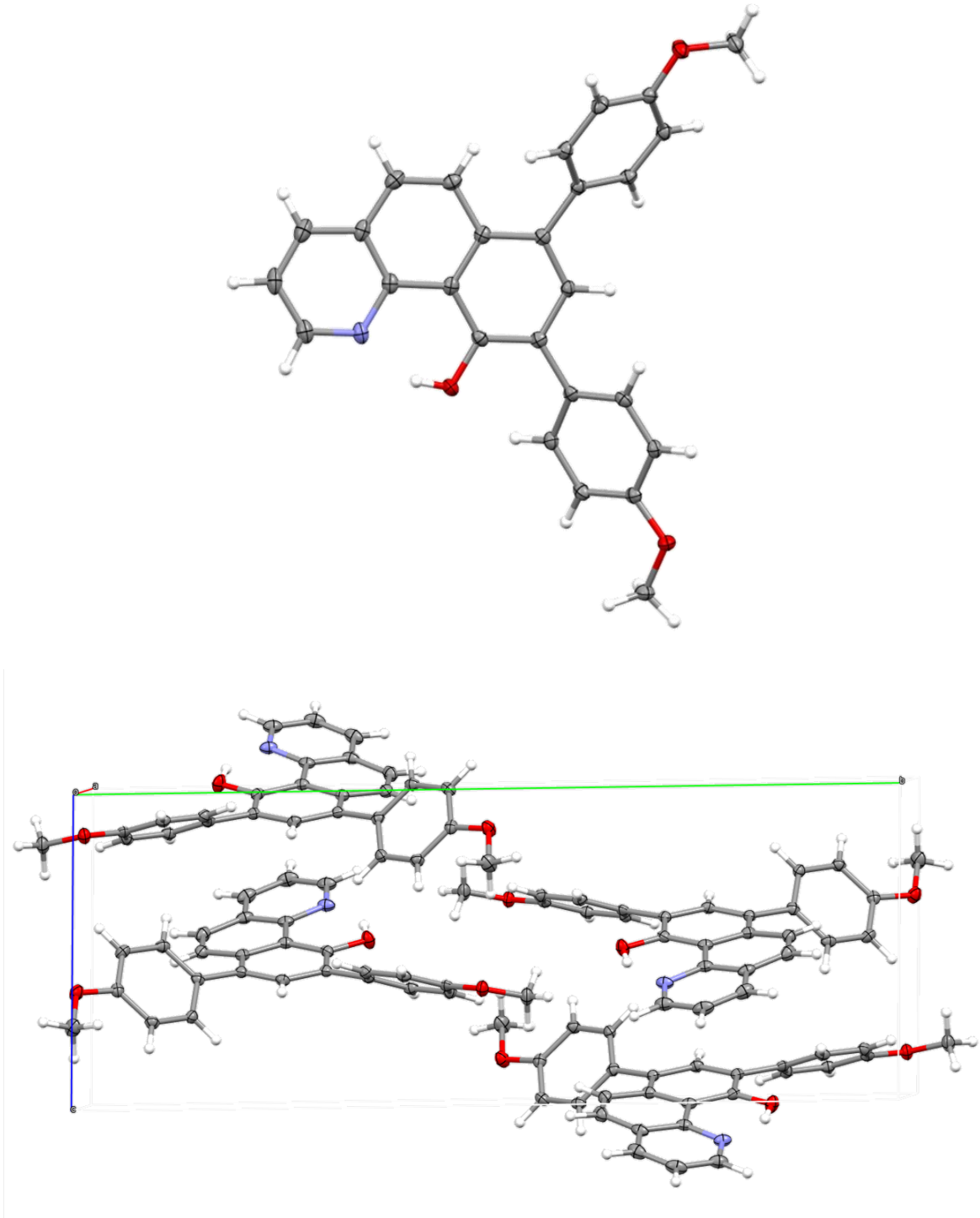

Fig. S17 Crystal structure of **1OMe**.

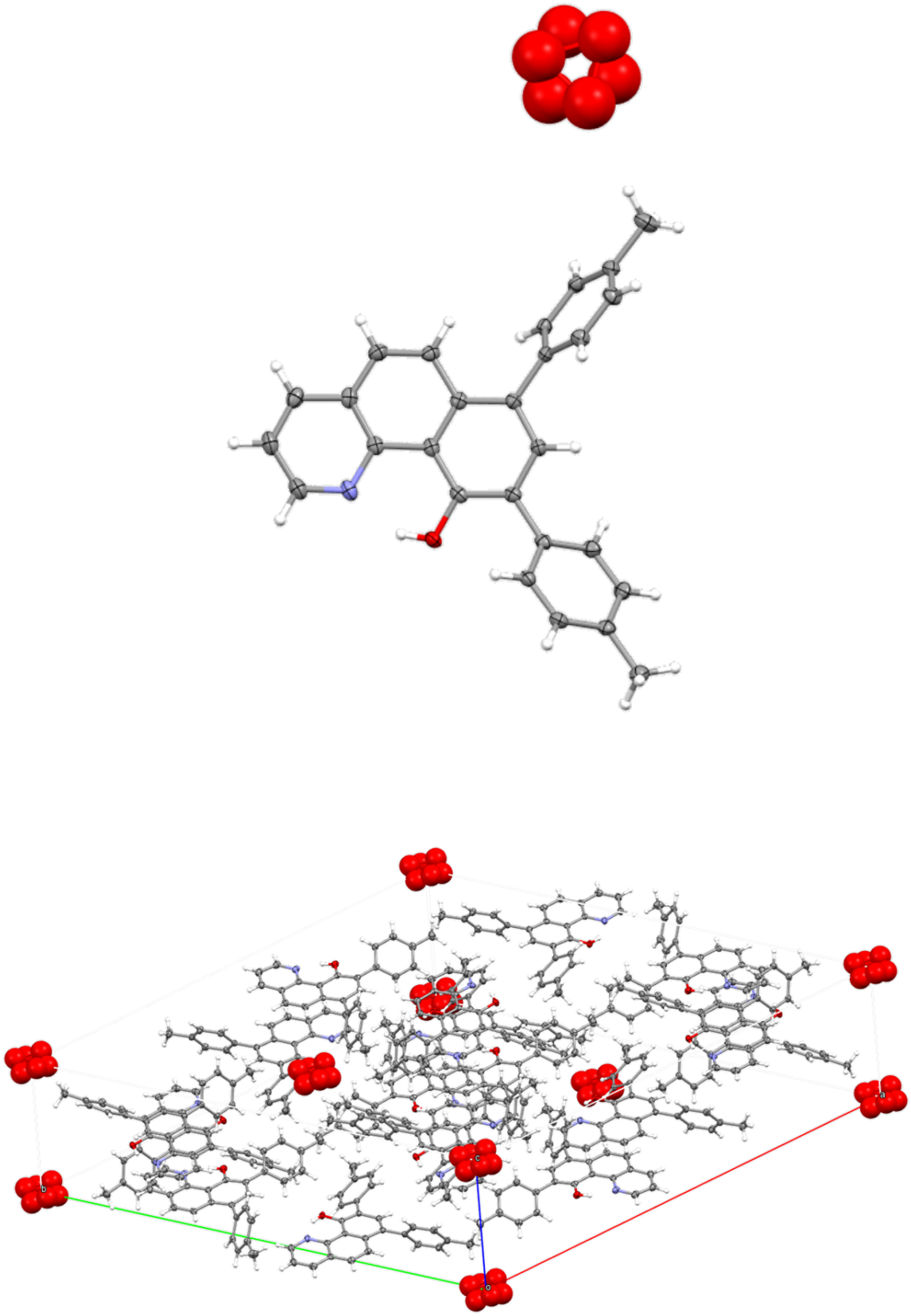

Fig. S18 Crystal structure of **1Me**.

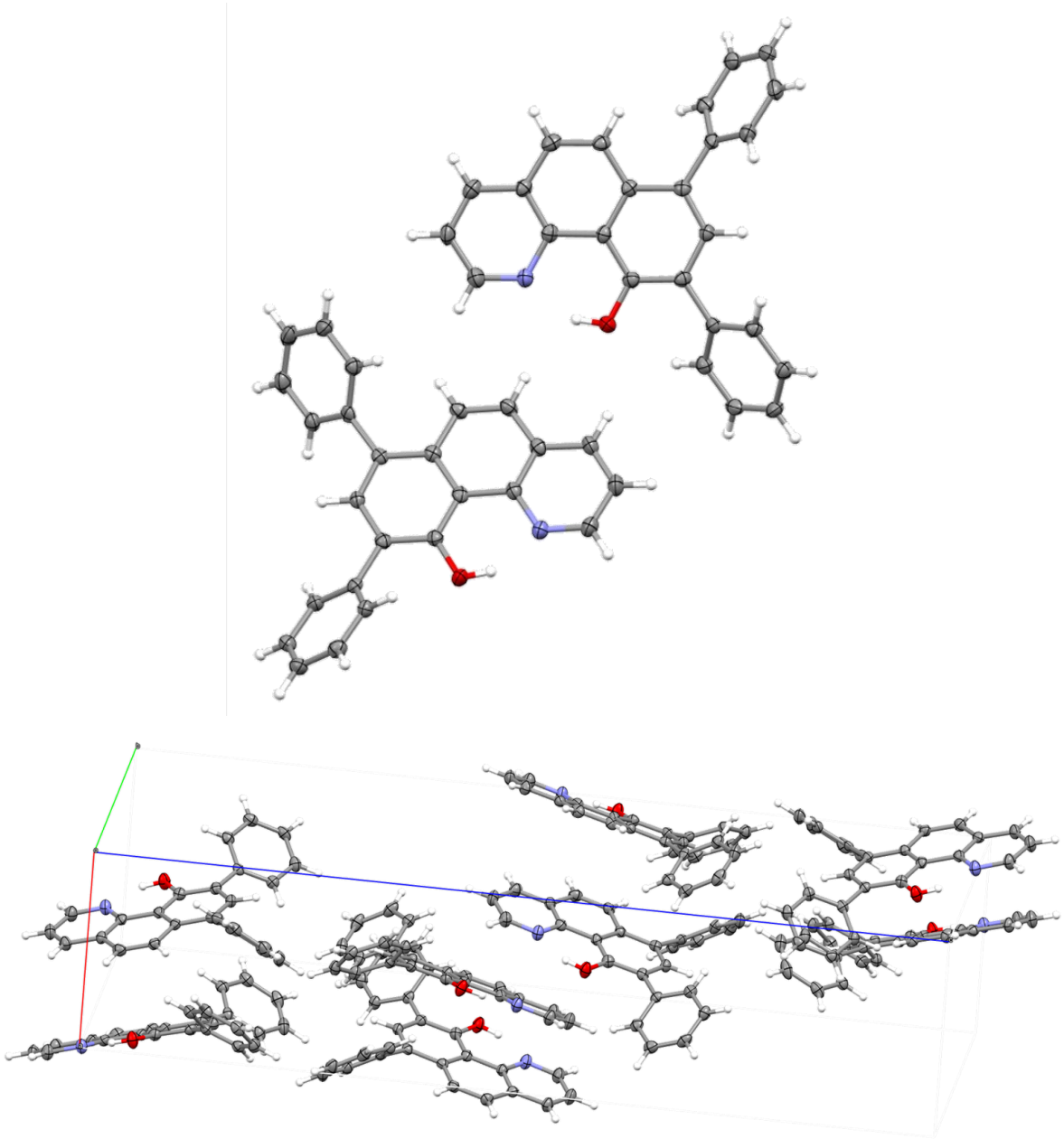

Fig. S19 Crystal structure of **1H**.

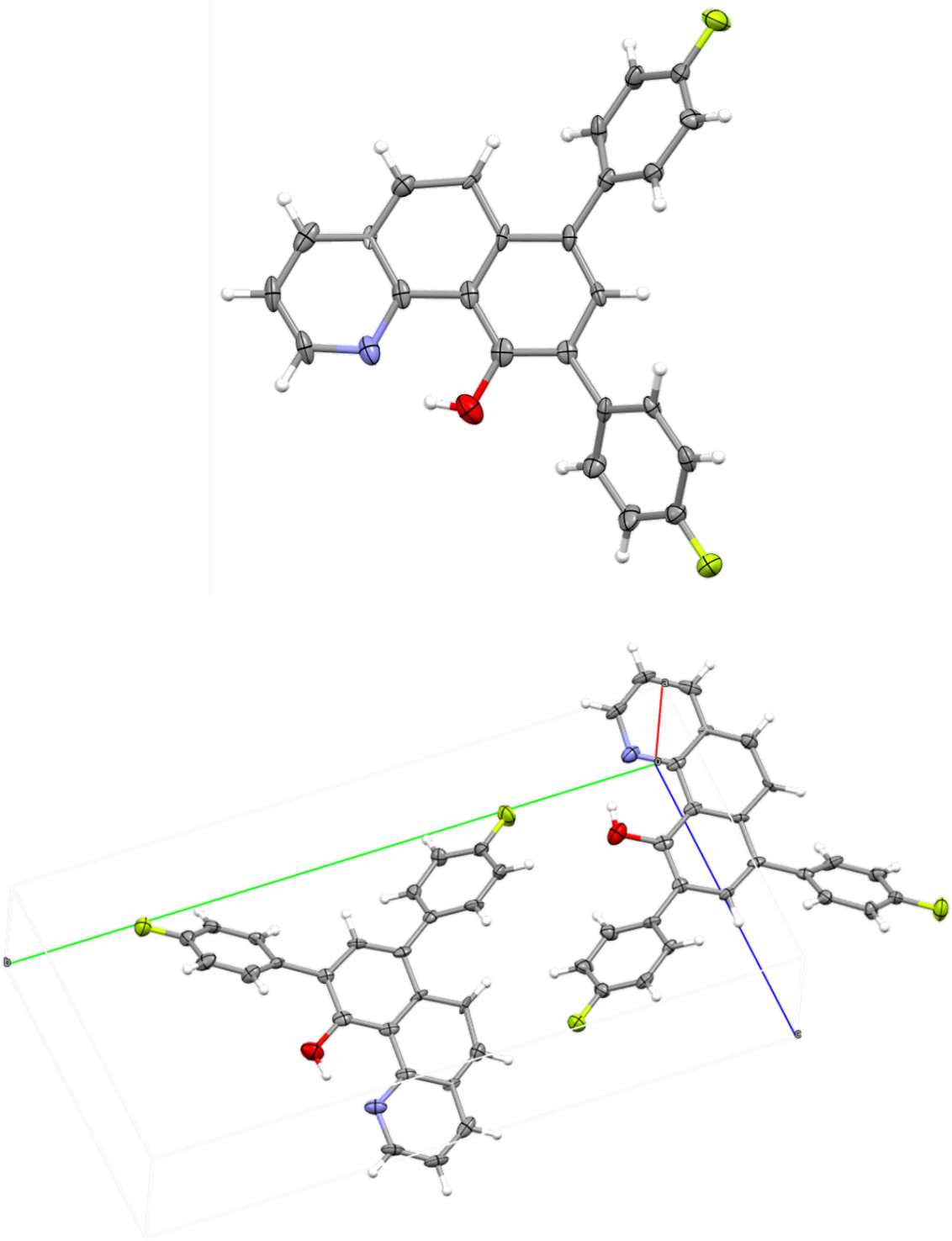

Fig. S20 Crystal structure of **1F**.

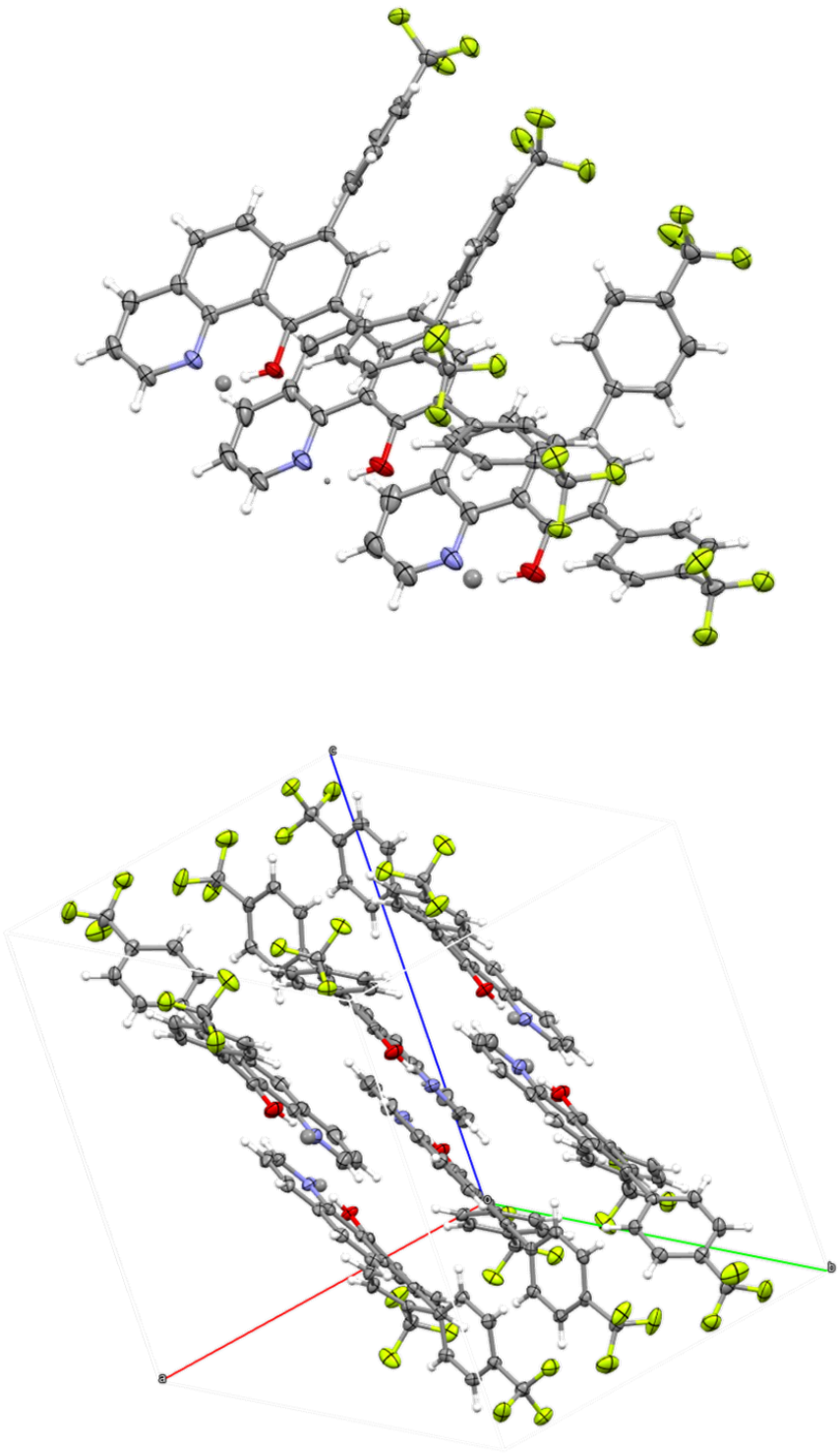

Fig. S21 Crystal structure of **1CF$_3$**.

Table S1 Crystallographic parameters of **1NMe$_2$**, **1OMe** and **1Me**.

	1NMe$_2$	**1OMe**	**1Me**
Empirical formula	$C_{29.5}H_{27.75}N_{3.25}O$	$C_{27}H_{21}NO_3$	$C_{27}H_{21}NO_{1.17}$
Formula weight	443.80	407.45	378.11
Crystal system	monoclinic	monoclinic	trigonal
Space group	$I2/a$	$P2_1/c$	$R\bar{3}$
a / Å	18.9713(7)	8.7730(4)	31.2623(8)
b / Å	9.4358(3)	24.1239(8)	31.2623(8)
c / Å	27.1606(11)	9.6591(4)	10.4233(3)
α / deg	90	90	90
β / deg	105.179(4)	108.576(4)	90
γ / deg	90	90	120
Volume / Å^3	4692.4(3)	1937.74(14)	8822.2(5)
Z	8	4	18
Z'	1	1	1
ρ_{calc} / g cm^{-3}	1.256	1.397	1.281
μ / mm^{-1}	0.077	0.091	0.078
$F(000)$	1884.0	856.0	3588.0
Crystal size / mm^3	0.552 × 0.27 × 0.213	0.964 × 0.147 × 0.102	0.62 × 0.17 × 0.129
2θ range / deg	4.714– 52.74	4.758–52.738	4.188–52.73
Index ranges	$-22 \le h \le 23$ $-11 \le k \le 8$ $-33 \le l \le 33$	$-9 \le h \le 10$ $-30 \le k \le 30$ $11 \le l \le 12$	$-29 \le h \le 39$ $-38 \le k \le 39$ $-12 \le l \le 12$
Reflections collected	13150	11936	12446
Independent reflections	4765	3954	3995
Goodness-of-fit on F_2	1.026	1.030	1.018
Final R indexes[a] ($I \ge 2\sigma(I)$)	$R_1 = 0.0466$ w$R_2 = 0.1129$	$R_1 = 0.0366$ w$R_2 = 0.0944$	$R_1 = 0.0471$ w$R_2 = 0.1244$

a) $R_1 = \sum\left||F_o| - |F_c|\right| / \sum|F_o|$, $wR_2 = \left\{\sum w\left(F_o^2 - F_c^2\right)^2 / \sum w\left(F_o^2\right)^2\right\}^{1/2}$.

Table S2 Crystallographic parameters of **1H**, **1F** and **1CF$_3$**.

	1H	**1F**	**1CF$_3$**
Empirical formula	$C_{25}H_{17}NO$	$C_{25}H_{15}F_2NO$	$C_{27}H_{15}F_6NO$
Formula weight	347.39	383.38	483.40
Crystal system	orthorhombic	monoclinic	triclinic
Space group	$Pna2_1$	$P2_1$	$P\bar{1}$
a / Å	7.7291(5)	3.8336(2)	14.0330(3)
b / Å	13.5968(9)	20.9976(9)	14.9961(3)
c / Å	32.5171(19)	10.5840(4)	15.6184(3)
α / deg	90	90	106.652(2)
β / deg	90	92.115(4)	94.045(2)
γ / deg	90	90	99.828(2)
Volume / Å^3	3417.3(4)	851.39(7)	3077.75(11)
Z	8	2	6
Z'	2	1	3
ρ_{calc} / g cm^{-3}	1.350	1.495	1.565
μ / mm^{-1}	0.082	0.106	0.133
$F(000)$	1456.0	396.0	1476.0
Crystal size / mm^3	0.954 × 0.107 × 0.057	0.887 × 0.158 × 0.142	0.86 × 0.085 × 0.067
2θ range / deg	4.806–52.73	4.312–52.736	3.708–52.744
Index ranges	$-9 \le h \le 6$ $-16 \le k \le 15$ $-31 \le l \le 40$	$-3 \le h \le 4$ $-25 \le k \le 26$ $-13 \le l \le 12$	$-17 \le h \le 17$ $-18 \le k \le 18$ $-19 \le l \le 19$
Reflections collected	14274	4865	37387
Independent reflections	6378	3141	12595
Goodness-of-fit on F_2	1.049	1.082	1.022
Final R indexes[a] ($I \ge 2\sigma(I)$)	$R_1 = 0.0399$ w$R_2 = 0.1025$	$R_1 = 0.0544$ w$R_2 = 0.1434$	$R_1 = 0.0694$ w$R_2 = 0.1856$

a) $R_1 = \sum\left||F_o| - |F_c|\right| / \sum|F_o|$, $wR_2 = \left\{\sum w\left(F_o^2 - F_c^2\right)^2 / \sum w\left(F_o^2\right)^2\right\}^{1/2}$.

Table S3 Selected bond lengths and dihedral angles of **1R** in crystalline phases.

Derivative	$C_{(10)}$–O	$C_{(8)}$–$C_{(7)}$–$C_{(1')}$– $C_{(2')}$	$C_{(8)}$–$C_{(9)}$–$C_{(1'')}$– $C_{(2'')}$
1NMe$_2$	1.404(3) Å	−47.9(2)°	−46.6(2)°
1OMe	1.354(2) Å	+42.1(2)°	+29.4(2)°
1Me	1.355(2) Å	−57.5(2)°	−34.9(2)°
1H	1.351(3) Å	−51.7(4)°	+43.2(4)°
	1.359(3) Å	−50.9(4)°	+41.7(4)°
1F	1.409(7) Å	−40.5(6)°	+43.6(6)°
	1.359(3) Å	−44.0(3)°	−23.2(3)°
1CF$_3$	1.363(4) Å	−49.7(3)°	−39.5(4)°
	1.368(4) Å	+49.4(4)°	−28.9(4)°

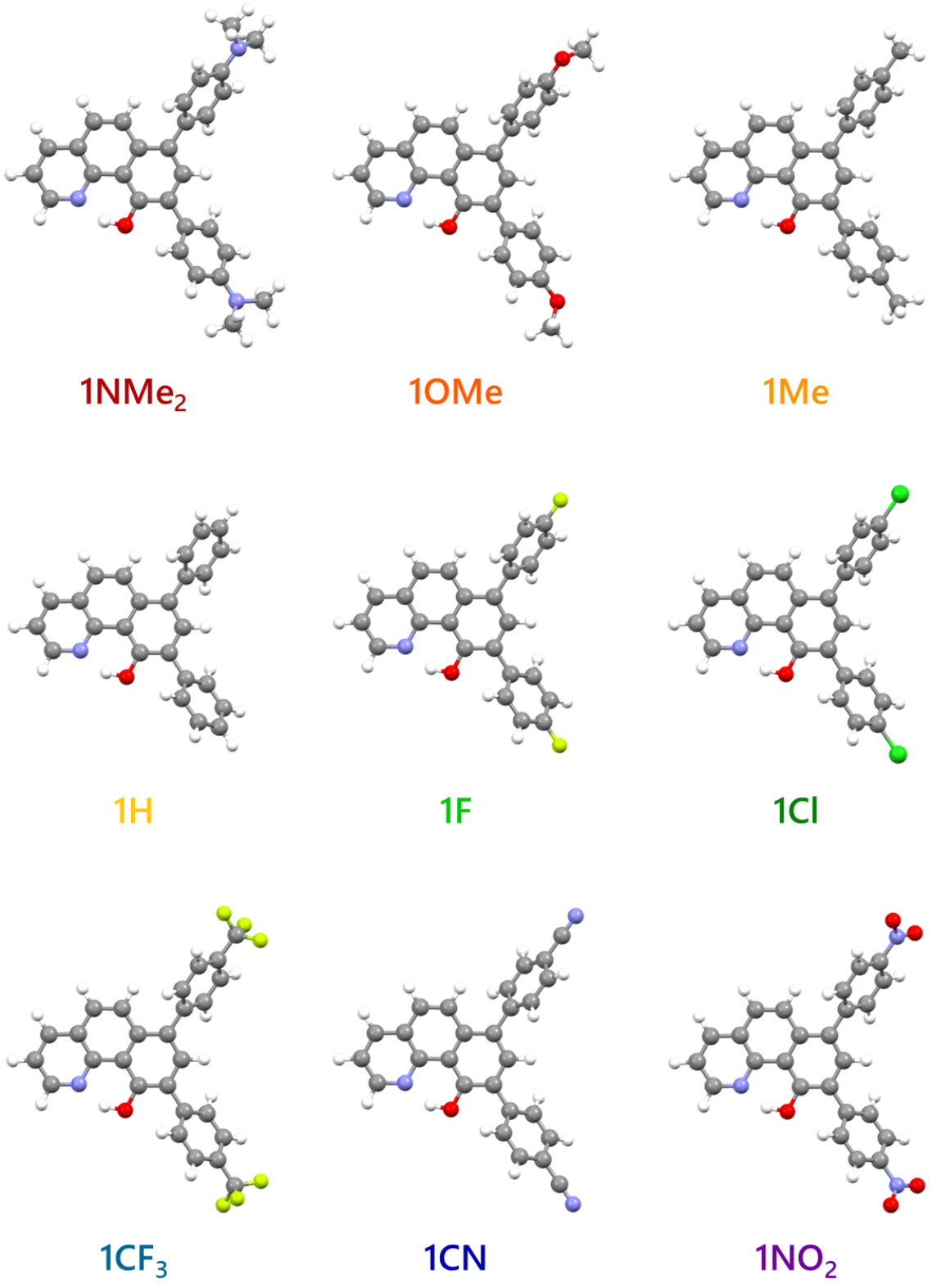

Fig. S22 Optimized geometries of **1R** in the ground states in dichloromethane.

Table S4 Selected lengths and dihedral angles of optimized **1R** in dichloromethane.

Derivative	State	$C_{(10)}$–O	O–H (O···H)	H–$N_{(1)}$ (H···$N_{(1)}$)	$C_{(8)}$–$C_{(7)}$–$C_{(1')}$– $C_{(2')}$ $C_{(8)}$–$C_{(9)}$–$C_{(1'')}$– $C_{(2'')}$
1NMe$_2$	GS	1.3508 Å	1.0025 Å	1.6331 Å	+57.06° −42.12°
	S_1	1.2769 Å	1.6710 Å	1.0379 Å	+43.61° −27.91°
1OMe	GS	1.3501Å	1.0035 Å	1.6322 Å	+58.58° −44.55°
	S_1	1.2716 Å	1.7033 Å	1.0327 Å	+44.53° −29.39°
1Me	GS	1.3487Å	1.0031 Å	1.6318 Å	+58.64° −45.01°
	S_1	1.2702 Å	1.7145 Å	1.0313 Å	+45.07° −30.74°
1H	GS	1.3477 Å	1.0038 Å	1.6314 Å	+58.38° −46.34°
	S_1	1.2698 Å	1.7221 Å	1.0311 Å	+45.74° −31.95°
1F	GS	1.3484 Å	1.0040 Å	1.6300 Å	+59.44° −45.28°
	S_1	1.2694 Å	1.7229 Å	1.0304 Å	+45.74° −31.10°
1Cl	GS	1.3461 Å	1.0052 Å	1.6277 Å	+58.67° −44.79°
	S_1	1.2678 Å	1.7311 Å	1.0286 Å	+45.49° −30.57°
1CF$_3$	GS	1.3445 Å	1.0062 Å	1.6242 Å	+57.55° −44.64°
	S_1	1.2660 Å	1.7388 Å	1.0278 Å	+46.02° −31.19°
1CN	GS	1.3442 Å	1.0067 Å	1.6211 Å	−55.68° −43.10°
	S_1	1.2635 Å	1.7476 Å	1.0268 Å	−44.87° −28.30°
1NO$_2$	GS	1.3417 Å	1.0088 Å	1.6140 Å	+54.42° −42.41°
	S_1	1.3039 Å	1.0711 Å	1.4718 Å	−89.76° −38.33°

Table S5 Calculated excited states of **1NMe$_2$** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO115 → MO116	2.7829 eV (445.52 nm)	0.2988
S_2	MO114 → MO116	3.0257 eV (409.77 nm)	0.0866
S_3	MO115 → MO117	3.2209 eV (384.94 nm)	0.0592
S_4	MO114 → MO117	3.4918 eV (355.07 nm)	0.0878
S_5	MO113 → MO116 (86%) MO114 → MO117 (14%)	3.6680 eV (338.02 nm)	0.1376
S_6	MO115 → MO118	3.9205 eV (316.25 nm)	0.3222
S_7	MO112 → MO116 (28%) MO113 → MO117 (54%) MO115 → MO119 (18%)	4.0700 eV (304.63 nm)	0.0130
S_8	MO114 → MO118 (14%) MO114 → MO120 (12%) MO115 → MO119 (50%) MO115 → MO120 (24%)	4.1225 eV (300.75 nm)	0.0075
S_9	MO114 → MO119 (19%) MO114 → MO120 (18%) MO115 → MO120 (63%)	4.1450 eV (299.12 nm)	0.0473
S_{10}	MO114 → MO118 (66%) MO114 → MO119 (14%) MO115 → MO120 (20%)	4.1787 eV (296.71 nm)	0.1994
S_{11}	MO112 → MO116	4.3140 eV (287.40 nm)	0.1227
S_{12}	MO112 → MO116 (16%) MO114 → MO119 (29%) MO115 → MO119 (22%) MO115 → MO121 (33%)	4.3784 eV (283.17 nm)	0.1980
S_{13}	MO115 → MO121	4.3983 eV (281.89 nm)	0.2380
S_{14}	MO111 → MO116 (21%) MO115 → MO122 (79%)	4.4950 eV (275.83 nm)	0.0181
S_{15}	MO114 → MO120 (70%) MO115 → MO122 (30%)	4.5269 eV (273.88 nm)	0.0112
S_{16}	MO108 → MO116 (31%) MO111 → MO116 (37%) MO114 → MO120 (32%)	4.5571 eV (272.07 nm)	0.0228
S_{17}	MO114 → MO120 (11%) MO114 → MO121 (27%) MO115 → MO121 (11%) MO115 → MO122 (12%) MO115 → MO123 (39%)	4.5839 eV (270.48 nm)	0.0376
S_{18}	MO110 → MO116 (38%) MO111 → MO116 (15%) MO112 → MO117 (25%) MO113 → MO118 (9%) MO114 → MO121 (13%)	4.6058 eV (269.19 nm)	0.1380
S_{19}	MO109 → MO116 (26%) MO110 → MO116 (55%) MO111 → MO116 (19%)	4.6402 eV (267.19 nm)	0.2436

S_{20}	MO108 → MO116 (72%) MO110 → MO116 (28%)	4.6791 eV (264.98 nm)	0.0553
S_{21}	MO109 → MO116 (18%) MO114 → MO121 (51%) MO114 → MO122 (17%) MO115 → MO124 (14%)	4.7093 eV (263.27 nm)	0.1746
S_{22}	MO115 → MO124	4.7793 eV (259.42 nm)	0.0386
S_{23}	MO109 → MO116 (21%) MO113 → MO118 (79%)	4.7891 eV (258.89 nm)	0.0383
S_{24}	MO109 → MO116 (37%) MO113 → MO118 (17%) MO115 → MO125 (46%)	4.8829 eV (253.91 nm)	0.0199
S_{25}	MO109 → MO116 (17%) MO114 → MO122 (19%) MO114 → MO123 (10%) MO115 → MO122 (8%) MO115 → MO123 (13%) MO115 → MO124 (12%) MO115 → MO125 (21%)	4.9264 eV (251.67 nm)	0.0882
S_{26}	MO109 → MO116 (10%) MO112 → MO117 (8%) MO113 → MO119 (18%) MO114 → MO123 (25%) MO114 → MO124 (8%) MO115 → MO124 (17%) MO115 → MO126 (14%)	4.9817 eV (248.88 nm)	0.0596
S_{27}	MO109 → MO116 (16%) MO112 → MO117 (17%) MO113 → MO119 (52%) MO114 → MO122 (15%)	4.9986 eV (248.04 nm)	0.1256
S_{28}	MO108 → MO117 (30%) MO111 → MO117 (70%)	5.0136 eV (247.30 nm)	0.0087
S_{29}	MO115 → MO126 (65%) MO115 → MO127 (35%)	5.0471 eV (245.66 nm)	0.0042
S_{30}	MO113 → MO118 (17%) MO113 → MO119 (39%) MO114 → MO123 (19%) MO115 → MO125 (25%)	5.0689 eV (244.60 nm)	0.2562

HOMO: MO115, LUMO: MO116

Table S6 Calculated excited states of **1OMe** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO107 → MO108	3.0683 eV (404.08 nm)	0.3267
S_2	MO107 → MO109	3.4868 eV (355.58 nm)	0.0388
S_3	MO106 → MO108 (79%) MO107 → MO109 (21%)	3.7464 eV (330.94 nm)	0.1532
S_4	MO104 → MO109 (15%) MO105 → MO108 (73%) MO107 → MO109 (12%)	4.0579 eV (305.54 nm)	0.0469
S_5	MO105 → MO108 (21%) MO106 → MO109 (23%) MO107 → MO110 (56%)	4.1615 eV (297.93 nm)	0.0776
S_6	MO106 → MO109	4.2227 eV (293.62 nm)	0.3329
S_7	MO105 → MO109 (12%) MO107 → MO111 (76%) MO107 → MO112 (12%)	4.3546 eV (284.72 nm)	0.0280
S_8	MO104 → MO108 (63%) MO106 → MO109 (14%) MO107 → MO111 (23%)	4.3732 eV (283.51 nm)	0.0297
S_9	MO103 → MO108 (16%) MO104 → MO108 (18%) MO107 → MO112 (66%)	4.3930 eV (282.23 nm)	0.0232
S_{10}	MO104 → MO108 (14%) MO105 → MO109 (23%) MO107 → MO113 (63%)	4.5070 eV (275.10 nm)	0.2288
S_{11}	MO100 → MO108 (48%) MO103 → MO108 (29%) MO107 → MO113 (23%)	4.5901 eV (270.11 nm)	0.1265
S_{12}	MO100 → MO108 (32%) MO103 → MO108 (19%) MO104 → MO108 (14%) MO105 → MO109 (35%)	4.6011 eV (269.47 nm)	0.1177
S_{13}	MO100 → MO108 (22%) MO102 → MO108 (51%) MO104 → MO109 (15%) MO107 → MO112 (12%)	4.7316 eV (262.04 nm)	0.0077
S_{14}	MO102 → MO108 (31%) MO103 → MO108 (36%) MO104 → MO109 (33%)	4.7385 eV (261.65 nm)	0.0785
S_{15}	MO101 → MO108 (28%) MO102 → MO108 (43%) MO103 → MO108 (15%) MO107 → MO115 (14%)	4.7676 eV (260.06 nm)	0.1747
S_{16}	MO101 → MO108 (21%) MO106 → MO110 (79%)	4.8311 eV (256.64 nm)	0.1458
S_{17}	MO107 → MO114 (87%) MO107 → MO119 (13%)	4.9165 eV (252.18 nm)	0.0013
S_{18}	MO106 → MO111 (85%) MO107 → MO111 (15%)	4.9659 eV (249.67 nm)	0.0796

S_{19}	MO103 → MO110 (16%) MO105 → MO112 (17%) MO106 → MO112 (67%)	5.0223 eV (246.87 nm)	0.0060
S_{20}	MO102 → MO109 (13%) MO104 → MO110 (20%) MO106 → MO110 (21%) MO107 → MO115 (46%)	5.0599 eV (245.03 nm)	0.2088
S_{21}	MO100 → MO109 (49%) MO103 → MO109 (31%) MO106 → MO112 (20%)	5.0897 eV (243.60 nm)	0.0070
S_{22}	MO101 → MO108 (16%) MO104 → MO109 (20%) MO105 → MO110 (21%) MO106 → MO113 (11%) MO107 → MO115 (32%)	5.1251 eV (241.92 nm)	0.3734
S_{23}	MO102 → MO109 (32%) MO105 → MO110 (37%) MO105 → MO111 (12%) MO106 → MO111 (19%)	5.2026 eV (238.31 nm)	0.0783
S_{24}	MO103 → MO109 (22%) MO105 → MO110 (23%) MO107 → MO116 (45%) MO107 → MO117 (10%)	5.2083 eV (238.05 nm)	0.0442
S_{25}	MO100 → MO109 (34%) MO107 → MO116 (46%) MO107 → MO117 (20%)	5.2114 eV (237.91 nm)	0.0293
S_{26}	MO101 → MO108 (13%) MO102 → MO109 (37%) MO103 → MO109 (27%) MO107 → MO116 (23%)	5.2293 eV (237.10 nm)	0.0709
S_{27}	MO107 → MO117	5.2551 eV (235.93 nm)	0.0058
S_{28}	MO105 → MO111 (28%) MO106 → MO113 (54%) MO107 → MO117 (18%)	5.2765 eV (234.97 nm)	0.0153
S_{29}	MO102 → MO113 (12%) MO104 → MO109 (13%) MO105 → MO111 (55%) MO106 → MO111 (20%)	5.3354 eV (232.38 nm)	0.0170
S_{30}	MO105 → MO111 (28%) MO107 → MO118 (72%)	5.3758 eV (230.64 nm)	0.0325

HOMO: MO107, LUMO: MO108

Table S7 Calculated excited states of **1Me** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO099 → MO100	3.1478 eV (393.88 nm)	0.3394
S_2	MO098 → MO100 (22%) MO099 → MO101 (78%)	3.5688 eV (347.41 nm)	0.0465
S_3	MO098 → MO100	3.9981 eV (310.10 nm)	0.1821
S_4	MO098 → MO100 (15%) MO098 → MO101 (14%) MO099 → MO102 (71%)	4.1945 eV (295.59 nm)	0.1713
S_5	MO095 → MO101 (14%) MO097 → MO100 (72%) MO099 → MO102 (14%)	4.3611 eV (284.30 nm)	0.0675
S_6	MO095 → MO100 (17%) MO099 → MO102 (15%) MO099 → MO103 (68%)	4.4000 eV (281.78 nm)	0.2499
S_7	MO097 → MO100 (19%) MO098 → MO101 (46%) MO099 → MO103 (35%)	4.4394 eV (279.28 nm)	0.2430
S_8	MO095 → MO100 (18%) MO099 → MO104 (82%)	4.4691 eV (277.43 nm)	0.0030
S_9	MO092 → MO100 (12%) MO096 → MO100 (31%) MO099 → MO104 (33%) MO099 → MO105 (24%)	4.4978 eV (275.66 nm)	0.0190
S_{10}	MO092 → MO100 (12%) MO095 → MO100 (41%) MO096 → MO100 (14%) MO098 → MO101 (33%)	4.5669 eV (271.48 nm)	0.2296
S_{11}	MO095 → MO100 (32%) MO099 → MO105 (68%)	4.5883 eV (270.22 nm)	0.0108
S_{12}	MO094 → MO100 (75%) MO099 → MO105 (25%)	4.6323 eV (267.65 nm)	0.0189
S_{13}	MO092 → MO100 (69%) MO099 → MO105 (31%)	4.6815 eV (264.84 nm)	0.0083
S_{14}	MO095 → MO100 (19%) MO097 → MO100 (18%) MO097 → MO101 (63%)	4.8377 eV (256.29 nm)	0.1105
S_{15}	MO093 → MO100 (25%) MO095 → MO101 (20%) MO097 → MO101 (46%) MO098 → MO102 (9%)	4.8555 eV (255.35 nm)	0.0913
S_{16}	MO092 → MO101 (23%) MO096 → MO101 (64%) MO099 → MO107 (13%)	4.9831 eV (248.81 nm)	0.0234
S_{17}	MO093 → MO100 (19%) MO096 → MO101 (25%) MO098 → MO102 (56%)	4.9949 eV (248.22 nm)	0.0625
S_{18}	MO099 → MO107	5.0203 eV (246.96 nm)	0.0021

S_{19}	MO094 → MO101 (61%) MO094 → MO103 (12%) MO097 → MO104 (14%) MO099 → MO107 (13%)	5.0591 eV (245.07 nm)	0.0159
S_{20}	MO094 → MO101 (22%) MO098 → MO102 (16%) MO099 → MO106 (52%) MO099 → MO107 (10%)	5.0828 eV (243.93 nm)	0.1248
S_{21}	MO092 → MO101	5.1456 eV (240.95 nm)	0.0056
S_{22}	MO093 → MO100 (80%) MO099 → MO106 (20%)	5.2086 eV (238.04 nm)	0.6087
S_{23}	MO092 → MO101 (12%) MO094 → MO103 (11%) MO096 → MO102 (28%) MO096 → MO106 (12%) MO098 → MO105 (37%)	5.2490 eV (236.21 nm)	0.0040
S_{24}	MO093 → MO100 (9%) MO094 → MO101 (14%) MO096 → MO102 (14%) MO097 → MO103 (12%) MO098 → MO104 (27%) MO098 → MO105 (24%)	5.2738 eV (235.09 nm)	0.0425
S_{25}	MO098 → MO103	5.3238 eV (232.88 nm)	0.0382
S_{26}	MO099 → MO108 (83%) MO099 → MO112 (17%)	5.3465 eV (231.90 nm)	0.0008
S_{27}	MO099 → MO109	5.3864 eV (230.18 nm)	0.0100
S_{28}	MO097 → MO102 (20%) MO099 → MO110 (80%)	5.4356 eV (228.10 nm)	0.0848
S_{29}	MO093 → MO101 (25%) MO097 → MO102 (47%) MO097 → MO104 (9%) MO098 → MO104 (19%)	5.4656 eV (226.84 nm)	0.0007
S_{30}	MO094 → MO103 (19%) MO097 → MO104 (37%) MO098 → MO104 (44%)	5.5112 eV (224.97 nm)	0.0336

HOMO: MO099, LUMO: MO100

Table S8 Calculated excited states of **1H** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO091 → MO092	3.1959 eV (387.95 nm)	0.3325
S_2	MO090 → MO092 (24%) MO091 → MO093 (76%)	3.6175 eV (342.73 nm)	0.0481
S_3	MO090 → MO092	4.1006 eV (302.35 nm)	0.1300
S_4	MO090 → MO092 (28%) MO091 → MO094 (72%)	4.2210 eV (293.74 nm)	0.2221
S_5	MO091 → MO095	4.3682 eV (283.83 nm)	0.1873
S_6	MO086 → MO092 (16%) MO088 → MO092 (22%) MO090 → MO093 (36%) MO091 → MO094 (9%) MO091 → MO096 (17%)	4.4889 eV (276.20 nm)	0.2486
S_7	MO091 → MO096	4.5171 eV (274.48 nm)	0.0512
S_8	MO084 → MO092 (15%) MO088 → MO092 (10%) MO089 → MO092 (27%) MO090 → MO093 (7%) MO091 → MO096 (22%) MO091 → MO097 (19%)	4.5311 eV (273.63 nm)	0.0293
S_9	MO087 → MO092 (61%) MO089 → MO092 (13%) MO091 → MO096 (12%) MO091 → MO097 (14%)	4.5774 eV (270.86 nm)	0.0184
S_{10}	MO085 → MO092 (19%) MO091 → MO097 (81%)	4.6146 eV (268.68 nm)	0.0141
S_{11}	MO088 → MO092	4.6525 eV (266.49 nm)	0.1878
S_{12}	MO086 → MO092 (25%) MO088 → MO092 (23%) MO089 → MO092 (52%)	4.6981 eV (263.90 nm)	0.0224
S_{13}	MO084 → MO092 (26%) MO086 → MO092 (58%) MO091 → MO098 (16%)	4.7312 eV (262.05 nm)	0.1645
S_{14}	MO084 → MO092 (8%) MO085 → MO092 (29%) MO086 → MO092 (7%) MO086 → MO093 (11%) MO088 → MO093 (16%) MO090 → MO094 (12%) MO091 → MO098 (17%)	4.9321 eV (251.38 nm)	0.0327
S_{15}	MO084 → MO093 (30%) MO089 → MO093 (59%) MO090 → MO094 (11%)	5.0094 eV (247.50 nm)	0.0043
S_{16}	MO085 → MO092 (13%) MO086 → MO093 (11%) MO087 → MO093 (45%) MO089 → MO093 (12%) MO090 → MO094 (19%)	5.0381 eV (246.10 nm)	0.0408

S_{17}	MO090 → MO094 (22%) MO091 → MO099 (78%)	5.0720 eV (244.45 nm)	0.0052
S_{18}	MO087 → MO093 (15%) MO088 → MO093 (46%) MO091 → MO099 (39%)	5.0820 eV (243.97 nm)	0.0152
S_{19}	MO086 → MO093 (79%) MO089 → MO093 (21%)	5.1124 eV (242.52 nm)	0.0887
S_{20}	MO085 → MO093 (12%) MO086 → MO093 (16%) MO087 → MO093 (14%) MO089 → MO093 (16%) MO090 → MO093 (9%) MO091 → MO098 (33%)	5.1185 eV (242.23 nm)	0.1752
S_{21}	MO084 → MO093 (54%) MO086 → MO093 (26%) MO087 → MO093 (20%)	5.1669 eV (239.96 nm)	0.0490
S_{22}	MO085 → MO092 (56%) MO087 → MO093 (18%) MO090 → MO095 (26%)	5.2693 eV (235.30 nm)	0.3812
S_{23}	MO086 → MO097 (11%) MO089 → MO094 (38%) MO090 → MO095 (11%) MO090 → MO097 (40%)	5.3273 eV (232.73 nm)	0.0109
S_{24}	MO088 → MO095 (16%) MO090 → MO095 (84%)	5.3444 eV (231.99 nm)	0.0859
S_{25}	MO086 → MO095 (22%) MO088 → MO093 (14%) MO090 → MO095 (24%) MO090 → MO096 (40%)	5.3766 eV (230.60 nm)	0.0296
S_{26}	MO091 → MO100	5.4166 eV (228.90 nm)	0.0016
S_{27}	MO091 → MO100 (17%) MO091 → MO101 (71%) MO091 → MO102 (12%)	5.4587 eV (227.13 nm)	0.0169
S_{28}	MO088 → MO094 (21%) MO091 → MO102 (79%)	5.4914 eV (225.78 nm)	0.0738
S_{29}	MO086 → MO096 (10%) MO087 → MO096 (23%) MO088 → MO095 (19%) MO090 → MO096 (48%)	5.5645 eV (222.81 nm)	0.0201
S_{30}	MO083 → MO092 (18%) MO085 → MO093 (37%) MO090 → MO094 (11%) MO091 → MO102 (34%)	5.6139 eV (220.85 nm)	0.1155

HOMO: MO091, LUMO: MO092

Table S9 Calculated excited states of **1F** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO099 → MO100	3.2056 eV (386.77 nm)	0.3313
S_2	MO098 → MO100 (24%) MO099 → MO101 (76%)	3.6265 eV (341.88 nm)	0.0459
S_3	MO098 → MO100 (75%) MO099 → MO102 (25%)	4.0961 eV (302.69 nm)	0.1439
S_4	MO099 → MO102	4.2364 eV (292.66 nm)	0.1826
S_5	MO099 → MO103	4.3179 eV (287.14 nm)	0.0216
S_6	MO099 → MO104	4.3861 eV (282.68 nm)	0.0061
S_7	MO098 → MO101 (14%) MO099 → MO105 (86%)	4.4424 eV (279.10 nm)	0.1779
S_8	MO096 → MO100 (34%) MO096 → MO101 (11%) MO098 → MO101 (42%) MO099 → MO102 (13%)	4.4871 eV (276.31 nm)	0.2517
S_9	MO092 → MO100 (10%) MO096 → MO100 (20%) MO097 → MO100 (51%) MO098 → MO101 (19%)	4.5363 eV (273.31 nm)	0.0781
S_{10}	MO092 → MO100 (62%) MO095 → MO100 (26%) MO098 → MO101 (12%)	4.6099 eV (268.95 nm)	0.0273
S_{11}	MO092 → MO100 (16%) MO096 → MO100 (63%) MO099 → MO106 (21%)	4.6898 eV (264.37 nm)	0.3445
S_{12}	MO095 → MO100	4.8638 eV (254.91 nm)	0.0059
S_{13}	MO094 → MO100 (60%) MO096 → MO101 (27%) MO098 → MO102 (13%)	4.9072 eV (252.66 nm)	0.0051
S_{14}	MO093 → MO100 (37%) MO094 → MO100 (48%) MO099 → MO106 (15%)	4.9377 eV (251.10 nm)	0.0329
S_{15}	MO092 → MO101 (18%) MO097 → MO101 (82%)	4.9966 eV (248.14 nm)	0.0958
S_{16}	MO092 → MO101 (33%) MO095 → MO101 (16%) MO098 → MO102 (51%)	5.0664 eV (244.72 nm)	0.0209
S_{17}	MO099 → MO107	5.1001 eV (243.10 nm)	0.0013
S_{18}	MO092 → MO101 (50%) MO095 → MO101 (27%) MO096 → MO101 (23%)	5.1074 eV (242.75 nm)	0.0064
S_{19}	MO096 → MO101 (11%) MO097 → MO101 (19%) MO098 → MO101 (12%) MO099 → MO106 (58%)	5.1291 eV (241.73 nm)	0.1838

S_{20}	MO093 → MO100 (12%) MO094 → MO101 (11%) MO096 → MO101 (12%) MO098 → MO102 (18%) MO098 → MO103 (37%) MO099 → MO106 (10%)	5.1910 eV (238.84 nm)	0.1232
S_{21}	MO095 → MO100 (17%) MO095 → MO101 (22%) MO095 → MO106 (11%) MO098 → MO104 (50%)	5.2142 eV (237.78 nm)	0.0080
S_{22}	MO093 → MO100 (28%) MO094 → MO105 (10%) MO096 → MO101 (22%) MO097 → MO103 (16%) MO098 → MO102 (24%)	5.2804 eV (234.80 nm)	0.3357
S_{23}	MO094 → MO105 (13%) MO097 → MO102 (14%) MO097 → MO103 (27%) MO098 → MO103 (46%)	5.3407 eV (232.15 nm)	0.0668
S_{24}	MO095 → MO101	5.3592 eV (231.35 nm)	0.0059
S_{25}	MO093 → MO101 (19%) MO098 → MO105 (81%)	5.3874 eV (230.14 nm)	0.0463
S_{26}	MO093 → MO101 (22%) MO096 → MO102 (12%) MO099 → MO108 (50%) MO099 → MO110 (16%)	5.4637 eV (226.92 nm)	0.0277
S_{27}	MO097 → MO103 (11%) MO098 → MO105 (16%) MO099 → MO108 (55%) MO099 → MO109 (18%)	5.4761 eV (226.41 nm)	0.0557
S_{28}	MO093 → MO101 (12%) MO094 → MO101 (19%) MO094 → MO105 (12%) MO097 → MO102 (11%) MO097 → MO103 (16%) MO098 → MO103 (7%) MO098 → MO105 (8%) MO099 → MO108 (6%) MO099 → MO110 (9%)	5.4862 eV (225.99 nm)	0.0148
S_{29}	MO093 → MO101 (10%) MO099 → MO108 (13%) MO099 → MO109 (42%) MO099 → MO110 (35%)	5.5260 eV (224.37 nm)	0.0072
S_{30}	MO091 → MO100 (15%) MO093 → MO101 (36%) MO096 → MO102 (11%) MO097 → MO103 (18%) MO098 → MO102 (10%) MO099 → MO109 (10%)	5.5977 eV (221.49 nm)	0.0862

HOMO: MO099, LUMO: MO100

Table S10 Calculated excited states of **1Cl** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO107 → MO108	3.2028 eV (387.11 nm)	0.3669
S_2	MO106 → MO108 (24%) MO107 → MO109 (76%)	3.6302 eV (341.54 nm)	0.0541
S_3	MO106 → MO108	4.0747 eV (304.27 nm)	0.1038
S_4	MO106 → MO108 (35%) MO107 → MO110 (65%)	4.1638 eV (297.77 nm)	0.4090
S_5	MO107 → MO110 (17%) MO107 → MO111 (83%)	4.2360 eV (292.69 nm)	0.1399
S_6	MO107 → MO112	4.3248 eV (286.68 nm)	0.0076
S_7	MO107 → MO113	4.3952 eV (282.09 nm)	0.0084
S_8	MO104 → MO108 (23%) MO104 → MO109 (10%) MO105 → MO108 (33%) MO106 → MO109 (34%)	4.4522 eV (278.48 nm)	0.1940
S_9	MO105 → MO108	4.4916 eV (276.04 nm)	0.1167
S_{10}	MO100 → MO108 (59%) MO103 → MO108 (26%) MO106 → MO109 (15%)	4.6012 eV (269.46 nm)	0.0428
S_{11}	MO100 → MO108 (28%) MO104 → MO108 (72%)	4.6481 eV (266.74 nm)	0.2478
S_{12}	MO103 → MO108 (66%) MO106 → MO113 (19%) MO107 → MO113 (15%)	4.8367 eV (256.34 nm)	0.0113
S_{13}	MO100 → MO108 (20%) MO101 → MO108 (55%) MO106 → MO110 (25%)	4.8570 eV (255.27 nm)	0.0246
S_{14}	MO101 → MO108 (28%) MO102 → MO108 (72%)	4.9093 eV (252.55 nm)	0.0286
S_{15}	MO105 → MO109	4.9471 eV (250.62 nm)	0.0917
S_{16}	MO104 → MO109 (40%) MO105 → MO109 (13%) MO106 → MO110 (47%)	5.0118 eV (247.39 nm)	0.0404
S_{17}	MO101 → MO108 (12%) MO101 → MO109 (8%) MO104 → MO108 (10%) MO105 → MO109 (14%) MO106 → MO111 (13%) MO107 → MO114 (35%) MO107 → MO115 (8%)	5.0459 eV (245.71 nm)	0.2197
S_{18}	MO107 → MO115	5.0763 eV (244.24 nm)	0.0062
S_{19}	MO100 → MO109 (56%) MO103 → MO109 (31%) MO105 → MO109 (13%)	5.0870 eV (243.73 nm)	0.0219

S_{20}	MO102 → MO108 (7%) MO102 → MO109 (16%) MO102 → MO111 (17%) MO105 → MO112 (19%) MO106 → MO111 (9%) MO106 → MO112 (32%)	5.1480 eV (240.84 nm)	0.0531
S_{21}	MO100 → MO109 (12%) MO101 → MO108 (9%) MO104 → MO109 (19%) MO106 → MO111 (41%) MO106 → MO113 (19%)	5.1642 eV (240.08 nm)	0.0158
S_{22}	MO100 → MO109 (23%) MO106 → MO110 (15%) MO106 → MO113 (62%)	5.1834 eV (239.19 nm)	0.0089
S_{23}	MO101 → MO108 (60%) MO104 → MO109 (40%)	5.2197 eV (237.53 nm)	0.5407
S_{24}	MO106 → MO112	5.3273 eV (232.73 nm)	0.0109
S_{25}	MO103 → MO109 (70%) MO106 → MO113 (30%)	5.3371 eV (232.31 nm)	0.0042
S_{26}	MO107 → MO116	5.3873 eV (230.14 nm)	0.0030
S_{27}	MO104 → MO110 (11%) MO107 → MO116 (35%) MO107 → MO117 (43%) MO107 → MO119 (11%)	5.3977 eV (229.70 nm)	0.0417
S_{28}	MO102 → MO109 (50%) MO105 → MO110 (18%) MO106 → MO112 (16%) MO107 → MO118 (16%)	5.4331 eV (228.20 nm)	0.0029
S_{29}	MO104 → MO110 (18%) MO107 → MO118 (55%) MO107 → MO119 (27%)	5.4704 eV (226.64 nm)	0.0280
S_{30}	MO105 → MO110 (72%) MO105 → MO111 (28%)	5.5106 eV (224.99 nm)	0.0319

HOMO: MO107, LUMO: MO108

Table S11 Calculated excited states of **1CF$_3$** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO123 → MO124	3.2370 eV (383.02 nm)	0.3880
S_2	MO122 → MO124 (26%) MO123 → MO125 (74%)	3.6695 eV (337.88 nm)	0.0765
S_3	MO123 → MO126	3.9368 eV (314.93 nm)	0.1946
S_4	MO123 → MO125 (21%) MO123 → MO126 (13%) MO123 → MO127 (66%)	4.0331 eV (307.42 nm)	0.0507
S_5	MO122 → MO124 (72%) MO123 → MO127 (28%)	4.2078 eV (294.65 nm)	0.3526
S_6	MO123 → MO128	4.3651 eV (284.03 nm)	0.0031
S_7	MO123 → MO129	4.4509 eV (278.56 nm)	0.0016
S_8	MO122 → MO125 (76%) MO123 → MO130 (24%)	4.5172 eV (274.47 nm)	0.3001
S_9	MO117 → MO124 (54%) MO118 → MO124 (13%) MO120 → MO124 (23%) MO122 → MO125 (10%)	4.5910 eV (270.06 nm)	0.0243
S_{10}	MO119 → MO124 (8%) MO121 → MO124 (35%) MO122 → MO125 (22%) MO122 → MO127 (24%) MO123 → MO130 (11%)	4.7242 eV (262.44 nm)	0.1730
S_{11}	MO118 → MO124 (44%) MO119 → MO124 (39%) MO122 → MO127 (17%)	4.8164 eV (257.42 nm)	0.0565
S_{12}	MO118 → MO124 (15%) MO119 → MO124 (22%) MO120 → MO124 (42%) MO122 → MO127 (9%) MO123 → MO129 (12%)	4.8505 eV (255.61 nm)	0.0289
S_{13}	MO122 → MO126	4.9057 eV (252.74 nm)	0.1111
S_{14}	MO119 → MO124	4.9235 eV (251.82 nm)	0.0082
S_{15}	MO116 → MO124 (17%) MO119 → MO124 (19%) MO122 → MO126 (22%) MO123 → MO130 (42%)	4.9482 eV (250.57 nm)	0.0535
S_{16}	MO117 → MO124 (9%) MO117 → MO125 (41%) MO118 → MO125 (12%) MO120 → MO125 (19%) MO121 → MO125 (19%)	5.0506 eV (245.49 nm)	0.0011
S_{17}	MO116 → MO125 (13%) MO122 → MO127 (58%) MO123 → MO130 (29%)	5.1095 eV (242.65 nm)	0.5175

S_{18}	MO116 → MO124 (24%) MO118 → MO124 (12%) MO121 → MO125 (51%) MO122 → MO127 (13%)	5.1286 eV (241.75 nm)	0.0144
S_{19}	MO118 → MO124 (15%) MO118 → MO126 (20%) MO119 → MO125 (28%) MO123 → MO131 (37%)	5.2008 eV (238.40 nm)	0.0338
S_{20}	MO118 → MO125 (14%) MO122 → MO128 (16%) MO123 → MO131 (70%)	5.2172 eV (237.65 nm)	0.0009
S_{21}	MO120 → MO125 (48%) MO120 → MO126 (26%) MO120 → MO127 (14%) MO121 → MO129 (12%)	5.2439 eV (236.44 nm)	0.0214
S_{22}	MO116 → MO124 (52%) MO119 → MO125 (24%) MO120 → MO125 (11%) MO122 → MO127 (13%)	5.2876 eV (234.48 nm)	0.1224
S_{23}	MO118 → MO125 (27%) MO119 → MO125 (36%) MO120 → MO126 (20%) MO122 → MO128 (17%)	5.3384 eV (232.25 nm)	0.0875
S_{24}	MO118 → MO125 (23%) MO119 → MO125 (31%) MO120 → MO125 (28%) MO122 → MO129 (18%)	5.3600 eV (231.32 nm)	0.0733
S_{25}	MO119 → MO125 (19%) MO122 → MO128 (81%)	5.3732 eV (230.74 nm)	0.0073
S_{26}	MO118 → MO127 (13%) MO118 → MO128 (9%) MO119 → MO125 (18%) MO119 → MO126 (9%) MO119 → MO128 (9%) MO121 → MO126 (33%) MO123 → MO133 (9%)	5.4861 eV (226.00 nm)	0.0298
S_{27}	MO118 → MO125 (16%) MO118 → MO126 (16%) MO121 → MO126 (15%) MO123 → MO133 (53%)	5.5183 eV (224.68 nm)	0.0474
S_{28}	MO118 → MO125 (10%) MO118 → MO126 (20%) MO119 → MO127 (14%) MO121 → MO126 (46%) MO123 → MO132 (10%)	5.5482 eV (223.47 nm)	0.0053
S_{29}	MO123 → MO132 (56%) MO123 → MO133 (24%) MO123 → MO134 (10%) MO123 → MO135 (10%)	5.5779 eV (222.28 nm)	0.0013

S_{30}	MO116 → MO129 (7%) MO117 → MO126 (7%) MO117 → MO127 (10%) MO120 → MO126 (21%) MO120 → MO127 (9%) MO121 → MO127 (8%) MO121 → MO129 (9%) MO122 → MO129 (29%)	5.6090 eV (221.05 nm)	0.0232

HOMO: MO123, LUMO: MO124

Table S12 Calculated excited states of **1CN** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO103 → MO104	3.1737 eV (390.66 nm)	0.4744
S_2	MO102 → MO104 (15%) MO103 → MO105 (85%)	3.5272 eV (351.51 nm)	0.2189
S_3	MO103 → MO106 (81%) MO103 → MO107 (19%)	3.6901 eV (335.99 nm)	0.1145
S_4	MO103 → MO105 (15%) MO103 → MO107 (85%)	3.8159 eV (324.92 nm)	0.0025
S_5	MO102 → MO104 (70%) MO103 → MO107 (30%)	4.1321 eV (300.05 nm)	0.5646
S_6	MO103 → MO108	4.3281 eV (286.46 nm)	0.0091
S_7	MO099 → MO104 (24%) MO103 → MO109 (76%)	4.4054 eV (281.44 nm)	0.0007
S_8	MO101 → MO104 (23%) MO102 → MO105 (77%)	4.4188 eV (280.59 nm)	0.1544
S_9	MO101 → MO104	4.5455 eV (272.77 nm)	0.0138
S_{10}	MO097 → MO104 (37%) MO097 → MO106 (12%) MO099 → MO104 (18%) MO100 → MO104 (33%)	4.5718 eV (271.20 nm)	0.0332
S_{11}	MO100 → MO104 (18%) MO101 → MO104 (11%) MO102 → MO105 (13%) MO102 → MO106 (58%)	4.5987 eV (269.61 nm)	0.1355
S_{12}	MO097 → MO104 (24%) MO099 → MO104 (14%) MO101 → MO104 (37%) MO102 → MO107 (10%) MO103 → MO110 (15%)	4.6541 eV (266.40 nm)	0.0580
S_{13}	MO099 → MO104 (64%) MO101 → MO109 (15%) MO102 → MO109 (21%)	4.7795 eV (259.41 nm)	0.0311
S_{14}	MO099 → MO104 (15%) MO100 → MO104 (28%) MO102 → MO107 (13%) MO103 → MO110 (44%)	4.7970 eV (258.46 nm)	0.0379
S_{15}	MO098 → MO104 (42%) MO098 → MO105 (14%) MO100 → MO104 (11%) MO100 → MO105 (10%) MO100 → MO108 (11%) MO101 → MO105 (12%)	4.8778 eV (254.18 nm)	0.0168
S_{16}	MO100 → MO104 (24%) MO101 → MO105 (76%)	4.9345 eV (251.26 nm)	0.0872

S_{17}	MO096 → MO104 (9%) MO097 → MO105 (13%) MO099 → MO105 (9%) MO100 → MO104 (14%) MO101 → MO104 (9%) MO101 → MO106 (11%) MO102 → MO107 (35%)	4.9788 eV (249.02 nm)	0.4082
S_{18}	MO097 → MO104 (13%) MO097 → MO105 (30%) MO098 → MO105 (12%) MO099 → MO105 (18%) MO100 → MO105 (27%)	5.0169 eV (247.14 nm)	0.2593
S_{19}	MO096 → MO104 (15%) MO097 → MO107 (8%) MO098 → MO105 (31%) MO100 → MO105 (9%) MO100 → MO108 (12%) MO101 → MO106 (12%) MO102 → MO107 (13%)	5.0545 eV (245.30 nm)	0.0444
S_{20}	MO097 → MO106 (15%) MO097 → MO107 (15%) MO100 → MO105 (70%)	5.0986 eV (243.17 nm)	0.3000
S_{21}	MO096 → MO104 (44%) MO100 → MO105 (29%) MO101 → MO107 (15%) MO103 → MO110 (12%)	5.1512 eV (240.69 nm)	0.0994
S_{22}	MO100 → MO106 (19%) MO101 → MO105 (12%) MO101 → MO106 (51%) MO102 → MO109 (18%)	5.1928 eV (238.76 nm)	0.0473
S_{23}	MO099 → MO104 (19%) MO099 → MO106 (38%) MO100 → MO106 (13%) MO101 → MO106 (30%)	5.2098 eV (237.98 nm)	0.0151
S_{24}	MO099 → MO105 (14%) MO103 → MO111 (74%) MO103 → MO118 (12%)	5.2322 eV (236.96 nm)	0.0055
S_{25}	MO097 → MO107 (12%) MO099 → MO105 (71%) MO099 → MO106 (17%)	5.2400 eV (236.61 nm)	0.0046
S_{26}	MO098 → MO105 (19%) MO100 → MO108 (11%) MO102 → MO108 (70%)	5.3203 eV (233.04 nm)	0.0207
S_{27}	MO100 → MO106 (61%) MO101 → MO107 (39%)	5.3526 eV (231.63 nm)	0.0257
S_{28}	MO101 → MO107	5.4058 eV (229.36 nm)	0.0931
S_{29}	MO100 → MO107 (26%) MO102 → MO110 (20%) MO103 → MO113 (54%)	5.4430 eV (227.79 nm)	0.0521

S_{30}	MO097 → MO104 (14%) MO097 → MO107 (35%) MO097 → MO110 (9%) MO098 → MO106 (11%) MO099 → MO107 (18%) MO101 → MO107 (13%)	5.4657 eV (226.84 nm)	0.0288

HOMO: MO103, LUMO: MO104

Table S13 Calculated excited states of **1NO$_2$** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO113 → MO114 (69%) MO113 → MO115 (31%)	2.5492 eV (486.37 nm)	0.2502
S_2	MO113 → MO115	2.6025 eV (476.40 nm)	0.2570
S_3	MO112 → MO115 (20%) MO112 → MO117 (13%) MO113 → MO116 (67%)	3.3702 eV (367.89 nm)	0.1311
S_4	MO112 → MO115 (84%) MO113 → MO117 (16%)	3.4781 eV (356.47 nm)	0.3003
S_5	MO112 → MO114 (57%) MO112 → MO115 (28%) MO113 → MO116 (15%)	3.4952 eV (354.73 nm)	0.0176
S_6	MO105 → MO114 (12%) MO105 → MO115 (53%) MO113 → MO117 (35%)	3.7711 eV (328.78 nm)	0.0298
S_7	MO104 → MO114	3.7869 eV (327.40 nm)	0.0002
S_8	MO113 → MO117	3.7872 eV (327.38 nm)	0.1054
S_9	MO110 → MO114 (16%) MO110 → MO115 (70%) MO111 → MO115 (14%)	3.9133 eV (316.83 nm)	0.0184
S_{10}	MO108 → MO114 (68%) MO109 → MO114 (32%)	3.9596 eV (313.12 nm)	0.0177
S_{11}	MO108 → MO114 (22%) MO111 → MO114 (39%) MO111 → MO115 (39%)	4.0788 eV (303.97 nm)	0.1142
S_{12}	MO111 → MO115	4.0806 eV (303.84 nm)	0.0159
S_{13}	MO109 → MO114	4.2469 eV (291.94 nm)	0.4008
S_{14}	MO110 → MO114	4.2673 eV (290.54 nm)	0.0004
S_{15}	MO109 → MO114 (27%) MO112 → MO116 (54%) MO113 → MO117 (19%)	4.3105 eV (287.63 nm)	0.0211
S_{16}	MO107 → MO115 (49%) MO108 → MO115 (37%) MO110 → MO114 (14%)	4.3325 eV (286.17 nm)	0.0121
S_{17}	MO107 → MO115 (14%) MO109 → MO114 (14%) MO109 → MO115 (31%) MO112 → MO116 (11%) MO113 → MO118 (30%)	4.3572 eV (284.55 nm)	0.0646
S_{18}	MO112 → MO116 (22%) MO113 → MO117 (11%) MO113 → MO118 (47%) MO113 → MO119 (20%)	4.3723 eV (283.57 nm)	0.0050
S_{19}	MO102 → MO114 (15%) MO102 → MO115 (63%) MO108 → MO115 (22%)	4.3888 eV (282.50 nm)	0.0025
S_{20}	MO099 → MO114 (26%) MO100 → MO114 (74%)	4.3925 eV (282.27 nm)	0.0004

S_{21}	MO108 → MO114 (16%) MO108 → MO115 (64%) MO113 → MO119 (20%)	4.4148 eV (280.84 nm)	0.0014
S_{22}	MO113 → MO119 (55%) MO113 → MO120 (45%)	4.4587 eV (278.07 nm)	0.0121
S_{23}	MO107 → MO114 (17%) MO112 → MO117 (16%) MO113 → MO120 (67%)	4.4711 eV (277.30 nm)	0.0123
S_{24}	MO107 → MO114 (87%) MO108 → MO114 (13%)	4.4885 eV (276.23 nm)	0.0020
S_{25}	MO106 → MO114 (19%) MO106 → MO115 (63%) MO112 → MO117 (18%)	4.6574 eV (266.21 nm)	0.1739
S_{26}	MO106 → MO114 (9%) MO107 → MO116 (12%) MO108 → MO116 (6%) MO111 → MO116 (22%) MO111 → MO117 (8%) MO112 → MO117 (23%) MO113 → MO119 (13%) MO113 → MO121 (7%)	4.6793 eV (264.96 nm)	0.1185
S_{27}	MO106 → MO114	4.6933 eV (264.17 nm)	0.0803
S_{28}	MO106 → MO115 (10%) MO107 → MO115 (13%) MO107 → MO116 (38%) MO107 → MO117 (9%) MO108 → MO116 (10%) MO110 → MO116 (20%)	4.7140 eV (263.01 nm)	0.0277
S_{29}	MO113 → MO121	4.7799 eV (259.39 nm)	0.0767
S_{30}	MO111 → MO116 (80%) MO113 → MO121 (20%)	4.9353 eV (251.22 nm)	0.5087

HOMO: MO113, LUMO: MO114

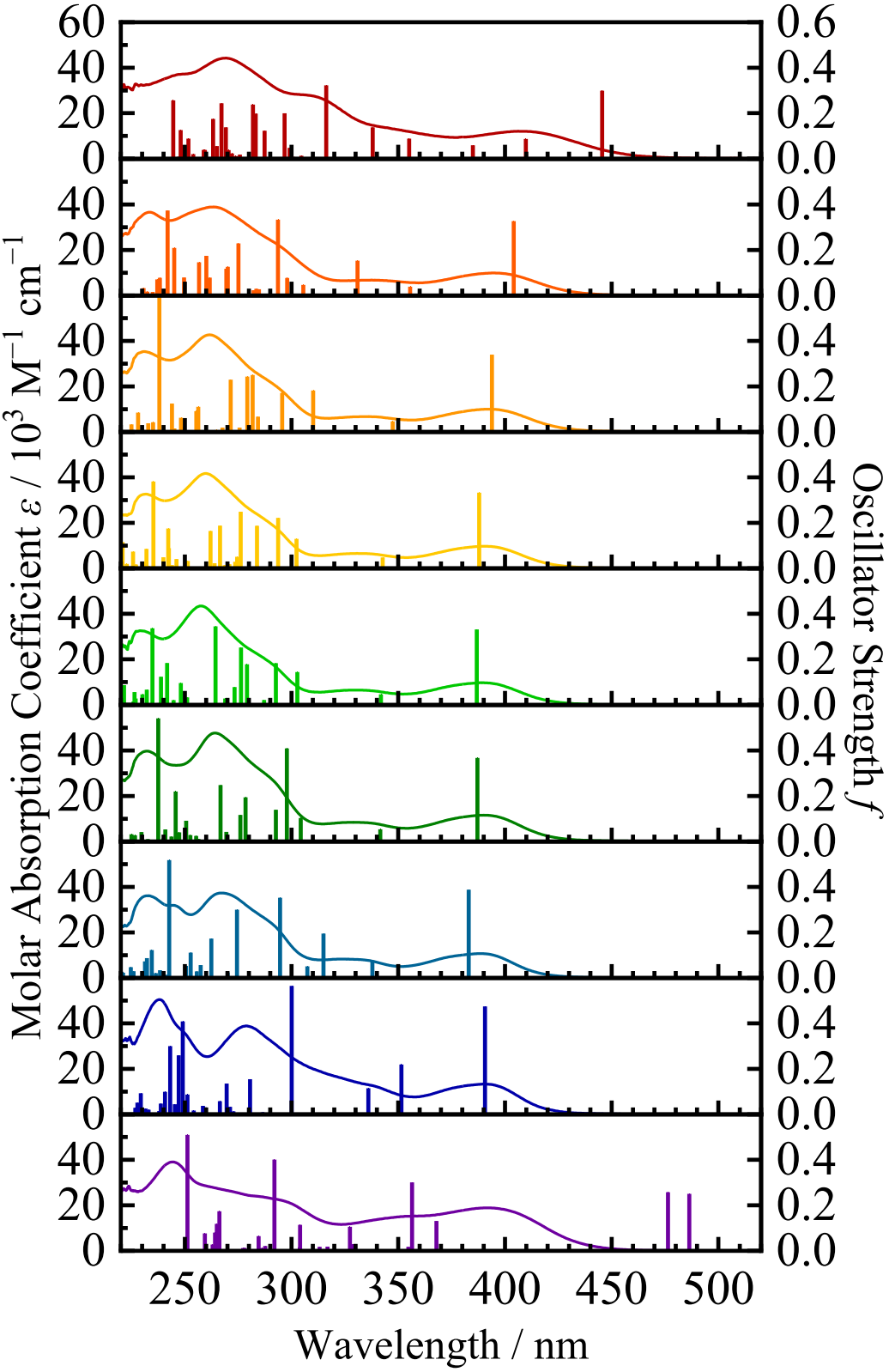

Fig. S23 Comparisons of the absorption spectra and oscillator strengths calculated by TD-DFT (perpendicular bars) of **1R** in dichloromethane. The colors correspond to those indicated in Fig. 1.

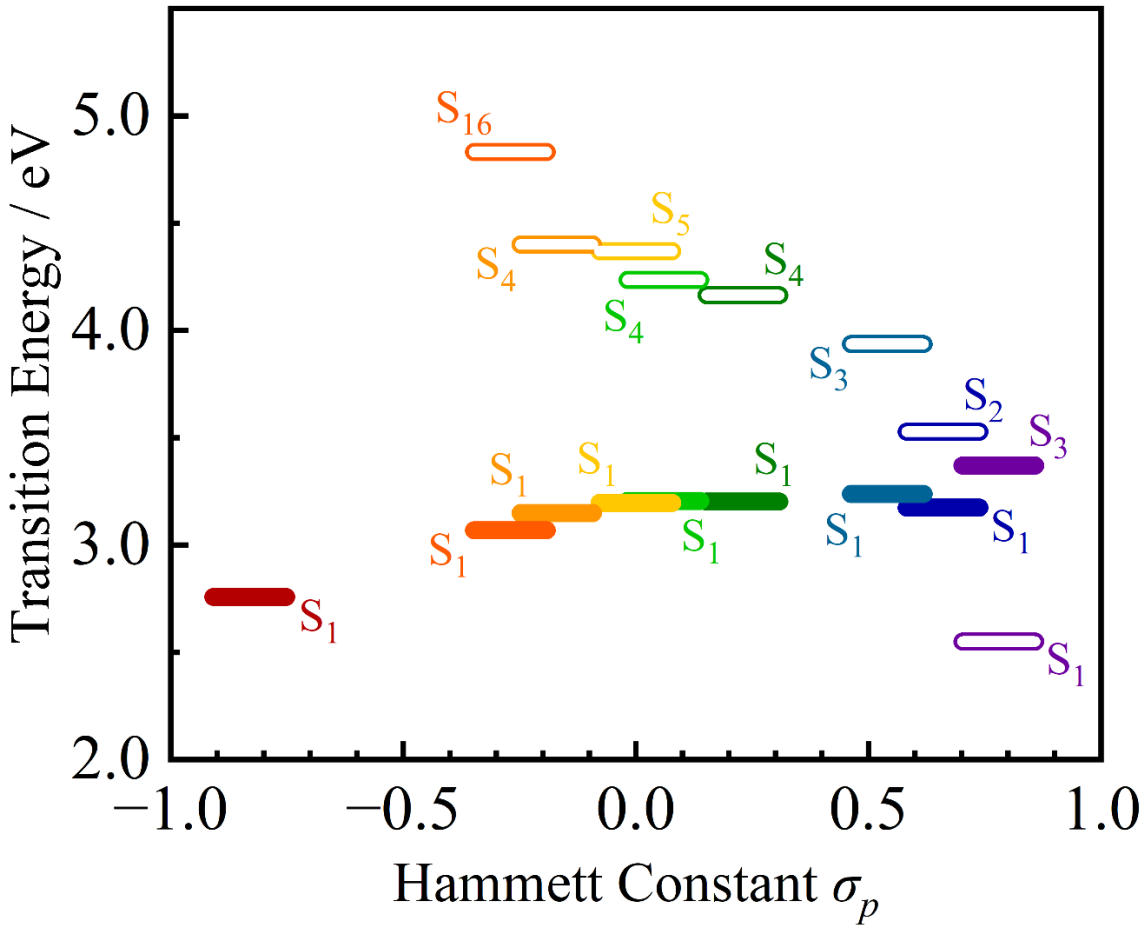

Fig. S24 Transition energies of the charge-transfer excited state in the HBq moiety (closed) and excited state ascribed to the charge-transfer transition from the HBq moiety to the 4-Rphenyl group at 7-position (open) against the σ_p value of the substituent R.

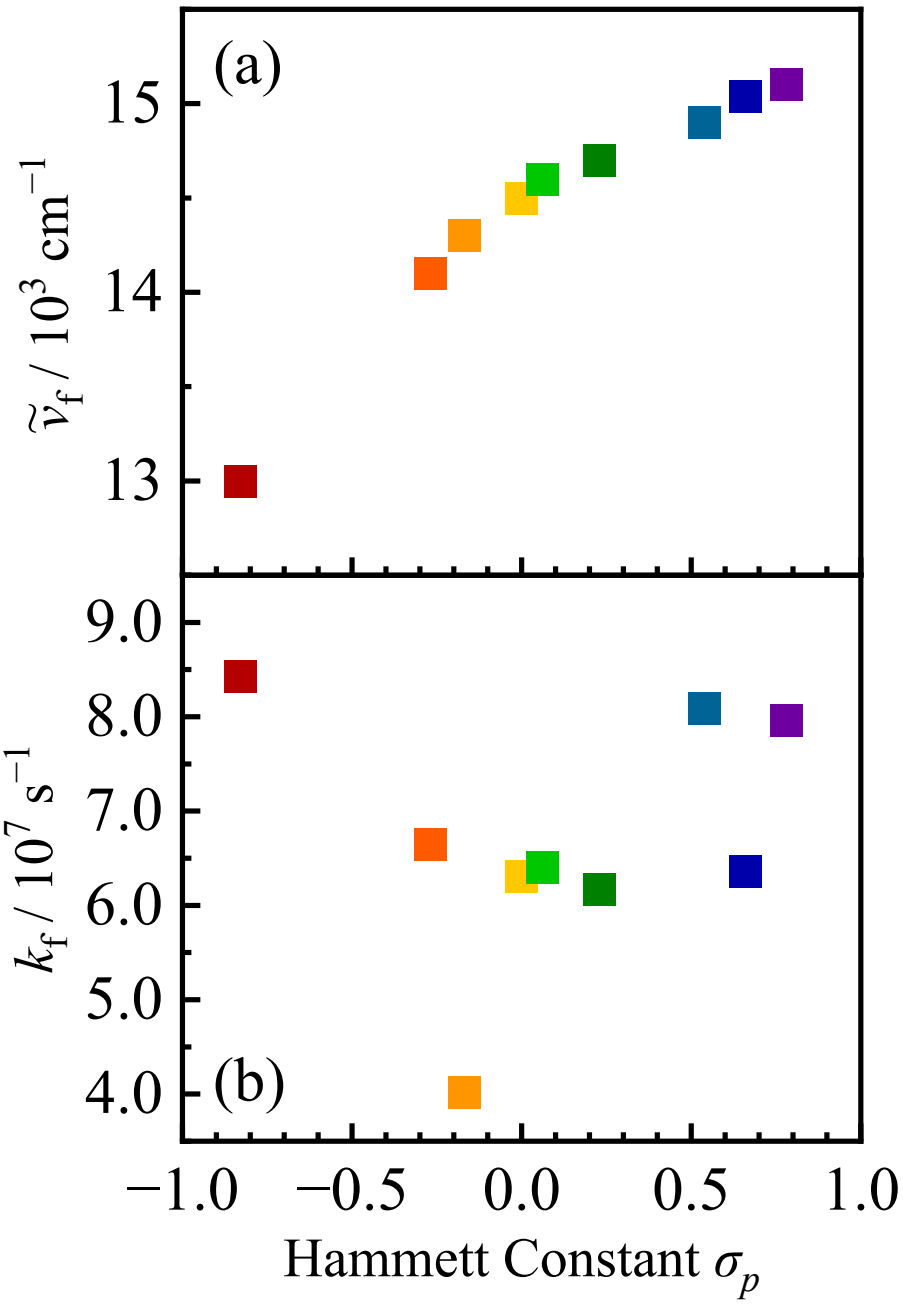

Fig. S25 Dependences of σ_p on the fluorescence maximum wavenumber (a) and fluorescence rate constant (b) of **1R** in dichloromethane.

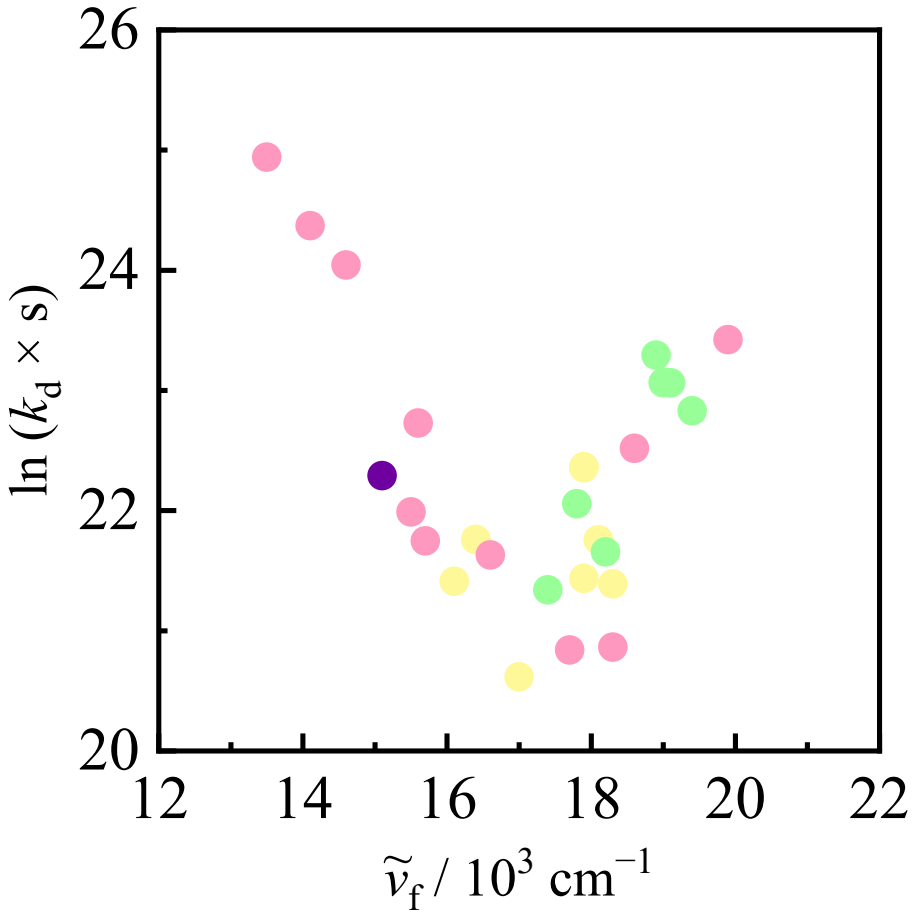

Fig. S26 Energy gap plots for **1NO2** in dichloromethane (purple) with solvent dependences of 1-methoxy-4-(4-nitrophenyl)naphthalene (pink), 1-(4-nitrophenyl)naphthalene (yellow) and 4-methoxy-4′-nitrobiphenyl (green). Data of the reference derivatives were compiled from reference 48 in the main text.

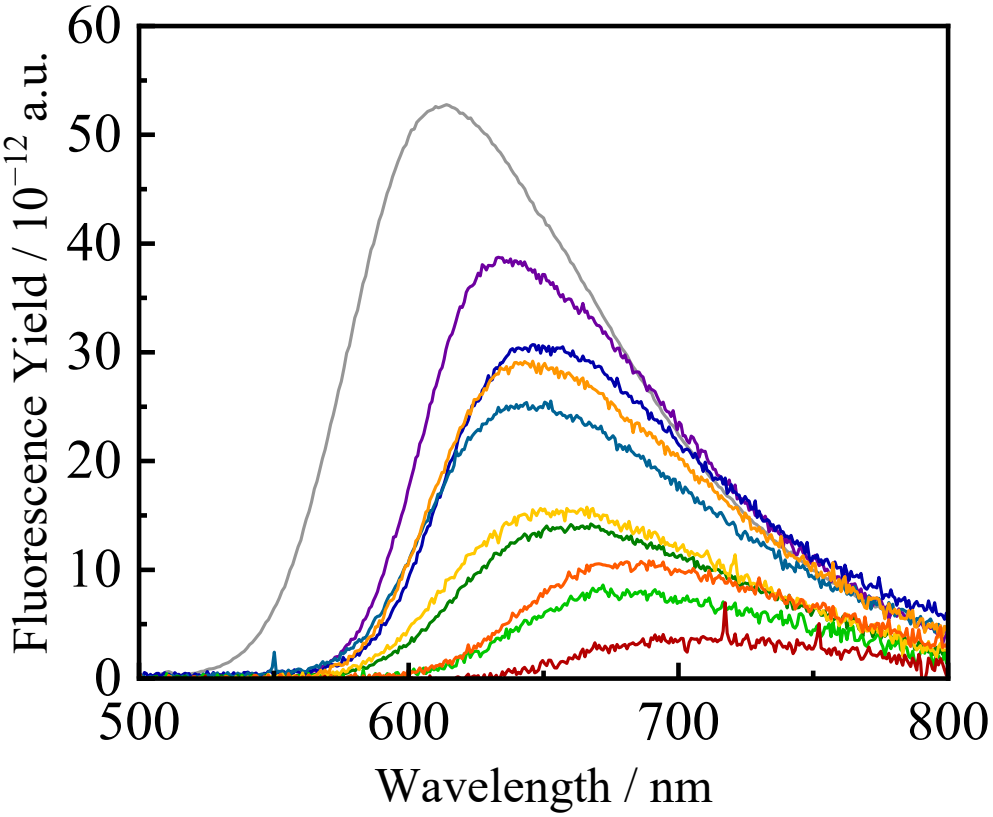

Fig. S27 Fluorescence spectra of **1R** and HBq in crystalline phase. The colors correspond to those indicated in Fig. 1.

Table S14 Photophysical properties of **1R** in crystalline phase.

Derivative	$\Phi_f{}^a$	$\tau_f{}^a$ / ns	$k_f{}^b$ / 10^7 s^{-1}	$k_d{}^b$ / 10^9 s^{-1}	$k_{d,dcm}/k_{d,cryst}{}^c$
1NMe$_2$	0.0041	0.13	3.2	7.7	2.8
1OMe	0.014	0.28	5.0	3.6	2.8
1Me	0.037	0.070 (44%) 0.72 (56%)	5.5	1.4	4.1
1H	0.020	0.53	3.9	1.9	3.1
1F	0.010	0.28	3.6	3.5	1.6
1Cl	0.018	0.38 (39%) 0.65 (61%)	3.2	1.7	3.1
1CF$_3$	0.034	0.73	4.7	1.3	2.6
1CN	0.042	0.80	5.2	1.2	2.2
1NO$_2$	0.047	0.76 (43%) 1.7 (57%)	3.2	0.66	7.2

a) λ_{ex} = 395 nm *b*) $\Phi_f = k_f\langle\tau_f\rangle = k_f / (k_f + k_d)$ and $\langle\tau_f\rangle = \Sigma(A_i\tau_i^2)/\Sigma(A_i\tau_i)$

c) ratio of k_d in dichloromethane to that in crystalline phase.

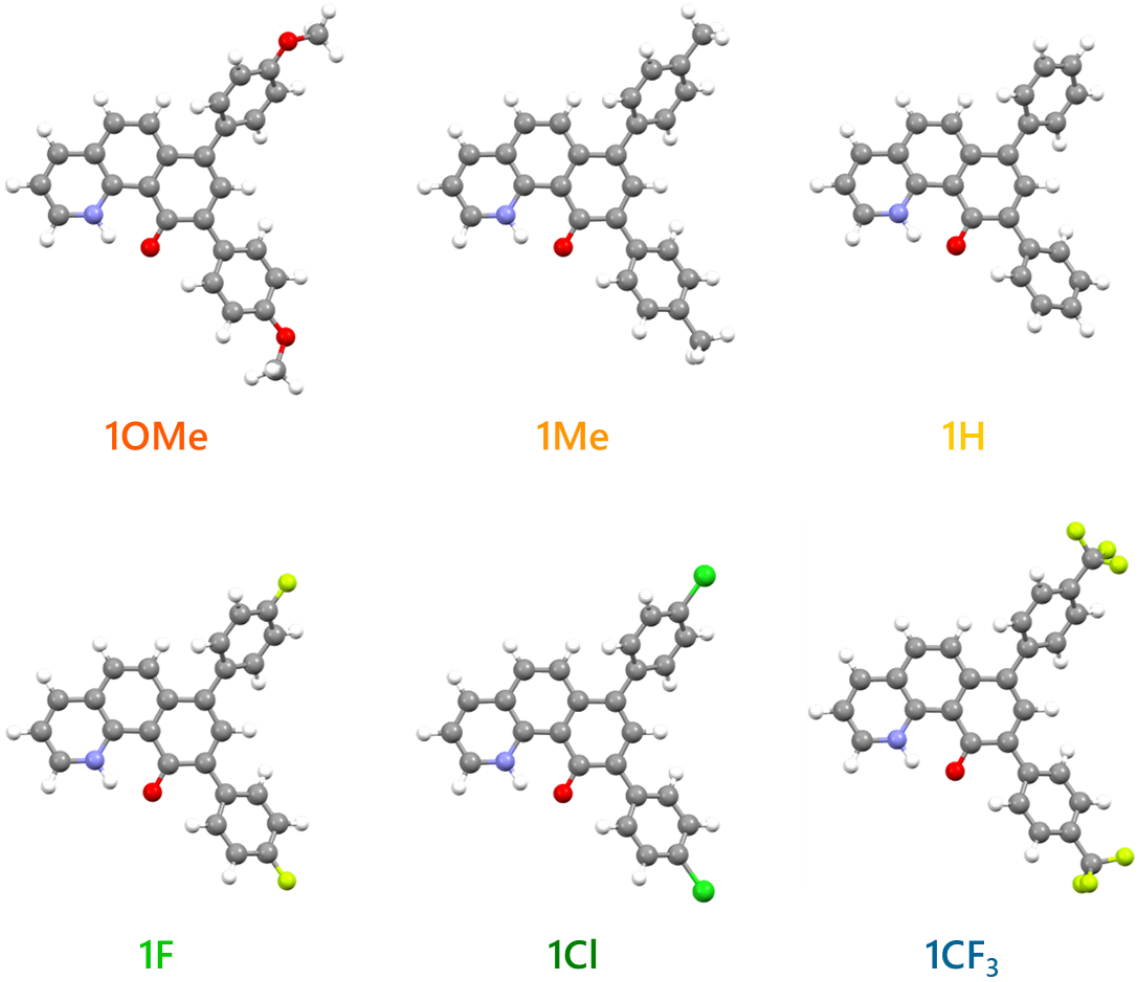

Fig. S28 Optimized geometries of **1R** in the S_1 states in dichloromethane.

Table S15 Calculated excited states of S_1-optimized geometry of **1NMe$_2$** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO113 → MO116 (16%) MO115 → MO116 (84%)	1.0967 eV (1130.51 nm)	0.0000
S_1	MO115 → MO116	1.7490 eV (708.88 nm)	0.3440
T_2	MO111 → MO116 (13%) MO114 → MO116 (72%) MO115 → MO118 (15%)	2.1372 eV (580.11 nm)	0.0000
T_3	MO113 → MO117 (13%) MO114 → MO116 (28%) MO115 → MO117 (59%)	2.1819 eV (568.23 nm)	0.0000
S_2	MO114 → MO116	2.2711 eV (545.93 nm)	0.1022
S_3	MO115 → MO117	2.5677 eV (482.85 nm)	0.0293

HOMO: MO115, LUMO: MO116

Table S16 Calculated excited states of S_1-optimized geometry of **1OMe** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO107 → MO108	1.2132 eV (1022.00 nm)	0.0000
S_1	MO107 → MO108	1.9079 eV (649.84 nm)	0.3271
T_2	MO103 → MO108 (12%) MO107 → MO109 (71%) MO107 → MO110 (17%)	2.2590 eV (548.85 nm)	0.0000
T_3	MO106 → MO108 (75%) MO107 → MO109 (25%)	2.6108 eV (474.90 nm)	0.0000
S_2	MO107 → MO109	2.7179 eV (456.18 nm)	0.0121
S_3	MO106 → MO108 (81%) MO107 → MO109 (19%)	2.9018 eV (427.27 nm)	0.1138

HOMO: MO107, LUMO: MO108

Table S17 Calculated excited states of S_1-optimized geometry of **1Me** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO099 → MO100	1.2544 eV (988.37 nm)	0.0000
S_1	MO099 → MO100	1.9587 eV (632.98 nm)	0.3246
T_2	MO099 → MO101	2.2921 eV (540.93 nm)	0.0000
T_3	MO096 → MO100 (15%) MO099 → MO101 (24%) MO099 → MO102 (61%)	2.6924 eV (460.49 nm)	0.0000
S_2	MO098 → MO100 (14%) MO099 → MO101 (86%)	2.7805 eV (445.91 nm)	0.0220
S_3	MO097 → MO100 (18%) MO098 → MO100 (70%) MO099 → MO102 (12%)	3.1297 eV (396.15 nm)	0.0734

HOMO: MO099, LUMO: MO100

Table S18 Calculated excited states of S_1-optimized geometry of **1H** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO91 → MO92	1.2937 eV (958.37 nm)	0.0000
S_1	MO91 → MO92	1.9961 eV (621.13 nm)	0.3128
T_2	MO91 → MO93	2.3208 eV (534.23 nm)	0.0000
T_3	MO91 → MO93 (27%) MO91 → MO94 (73%)	2.7386 eV (452.73 nm)	0.0000
S_2	MO90 → MO92 (14%) MO91 → MO93 (86%)	2.8269 eV (438.58 nm)	0.0246
S_3	MO88 → MO92 (13%) MO89 → MO92 (53%) MO90 → MO92 (34%)	3.1921 eV (388.41 nm)	0.0117

HOMO: MO91, LUMO: MO92

Table S19 Calculated excited states of S_1-optimized geometry of **1F** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO099 → MO100	1.3040 eV (950.80 nm)	0.0000
S_1	MO099 → MO100	2.0012 eV (619.56 nm)	0.3103
T_2	MO099 → MO101 (81%) MO099 → MO102 (19%)	2.3239 eV (533.52 nm)	0.0000
T_3	MO092 → MO100 (10%) MO098 → MO100 (33%) MO098 → MO102 (9%) MO099 → MO102 (48%)	2.7356 eV (453.22 nm)	0.0000
S_2	MO098 → MO100 (14%) MO099 → MO101 (86%)	2.8289 eV (438.27 nm)	0.0238
S_3	MO097 → MO100 (48%) MO098 → MO100 (52%)	3.2126 eV (385.94 nm)	0.0299

HOMO: MO099, LUMO: MO100

Table S20 Calculated excited states of S_1-optimized geometry of **1Cl** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO107 → MO108	1.3200 eV (939.30 nm)	0.0000
S_1	MO107 → MO108	2.0041 eV (618.64 nm)	0.3336
T_2	MO107 → MO109	2.3315 eV (531.79 nm)	0.0000
T_3	MO107 → MO109 (26%) MO107 → MO110 (74%)	2.7111 eV (457.32 nm)	0.0000
S_2	MO106 → MO108 (14%) MO107 → MO109 (86%)	2.8477 eV (435.39 nm)	0.0259
S_3	MO105 → MO108 (40%) MO106 → MO108 (47%) MO107 → MO110 (13%)	3.2081 eV (386.47 nm)	0.0272

HOMO: MO107, LUMO: MO108

Table S21 Calculated excited states of S_1-optimized geometry of **1CF$_3$** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO123 → MO124	1.3870 eV (893.87 nm)	0.0000
S_1	MO123 → MO124	2.0556 eV (603.15 nm)	0.3341
T_2	MO123 → MO125 (75%) MO123 → MO126 (13%) MO123 → MO127 (12%)	2.3677 eV (523.66 nm)	0.0000
T_3	MO123 → MO126	2.7154 eV (456.59 nm)	0.0000
S_2	MO123 → MO125	2.9208 eV (424.49 nm)	0.0337
S_3	MO121 → MO124 (33%) MO122 → MO124 (32%) MO123 → MO126 (35%)	3.2305 eV (383.80 nm)	0.0716

HOMO: MO123, LUMO: MO124

Table S22 Calculated excited states of S_1-optimized geometry of **1CN** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO103 → MO104	1.4129 eV (877.49 nm)	0.0000
S_1	MO103 → MO104	2.0527 eV (604.00 nm)	0.3848
T_2	MO103 → MO105	2.3358 eV (530.81 nm)	0.0000
T_3	MO102 → MO104 (12%) MO102 → MO106 (10%) MO103 → MO105 (34%) MO103 → MO106 (44%)	2.5387 eV (488.38 nm)	0.0000
S_2	MO103 → MO105 (81%) MO103 → MO106 (19%)	2.9243 eV (423.98 nm)	0.3183
S_3	MO103 → MO106 (58%) MO103 → MO107 (42%)	2.9824 eV (415.72 nm)	0.1591

HOMO: MO103, LUMO: MO104

Table S23 Calculated excited states of S_1-optimized geometry of **1NO₂** in dichloromethane.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO113 → MO114	1.7545 eV (706.68 nm)	0.0000
S_1	MO113 → MO114	1.7623 eV (703.52 nm)	0.0004
T_2	MO113 → MO115 (74%) MO113 → MO116 (26%)	2.0320 eV (610.17 nm)	0.0000
S_2	MO113 → MO115	2.4380 eV (508.54 nm)	0.3602
T_3	MO111 → MO115 (13%) MO111 → MO116 (14%) MO112 → MO116 (11%) MO113 → MO116 (62%)	2.5164 eV (492.70 nm)	0.0000
S_3	MO112 → MO114	2.9235 eV (424.10 nm)	0.0006

HOMO: MO113, LUMO: MO114

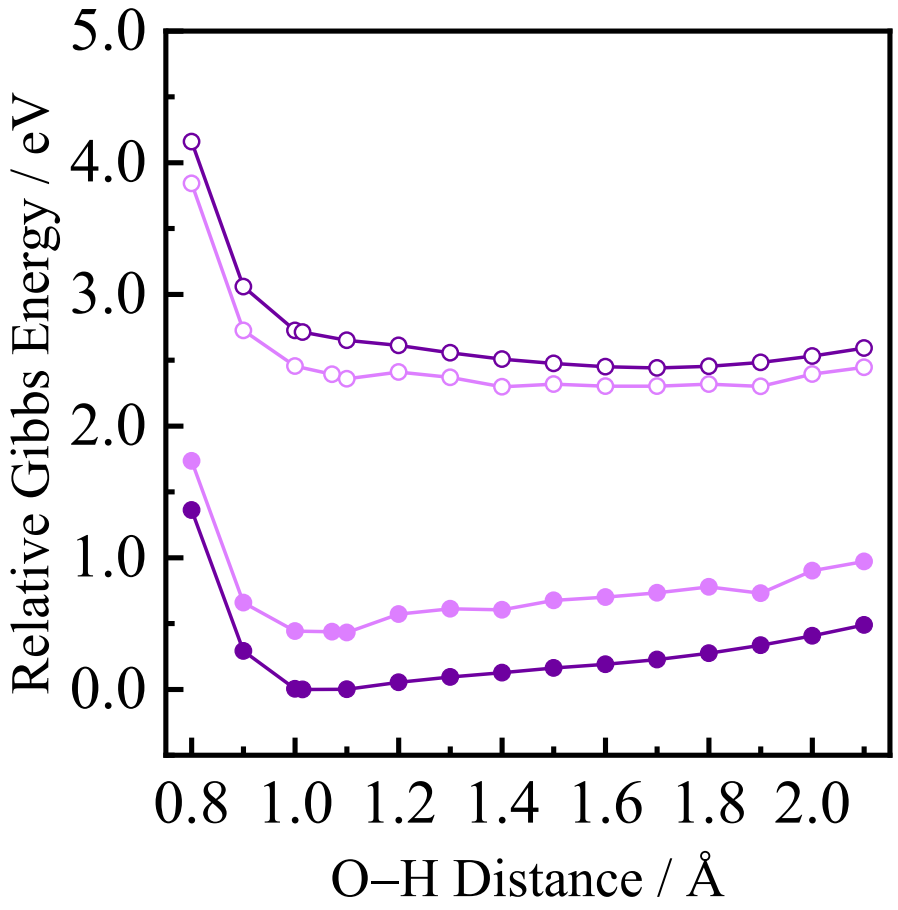

Fig. S29 Dependences of the O–H distances on the relative Gibbs energies of ground (close circles) and S_1 states (open circles) of the ground- (deep color) and S_1-state-optimized (pale color) **1NO₂** in dichloromethane by the (TD-)DFT calculations (B3LYP/6-31G(d,p) level).

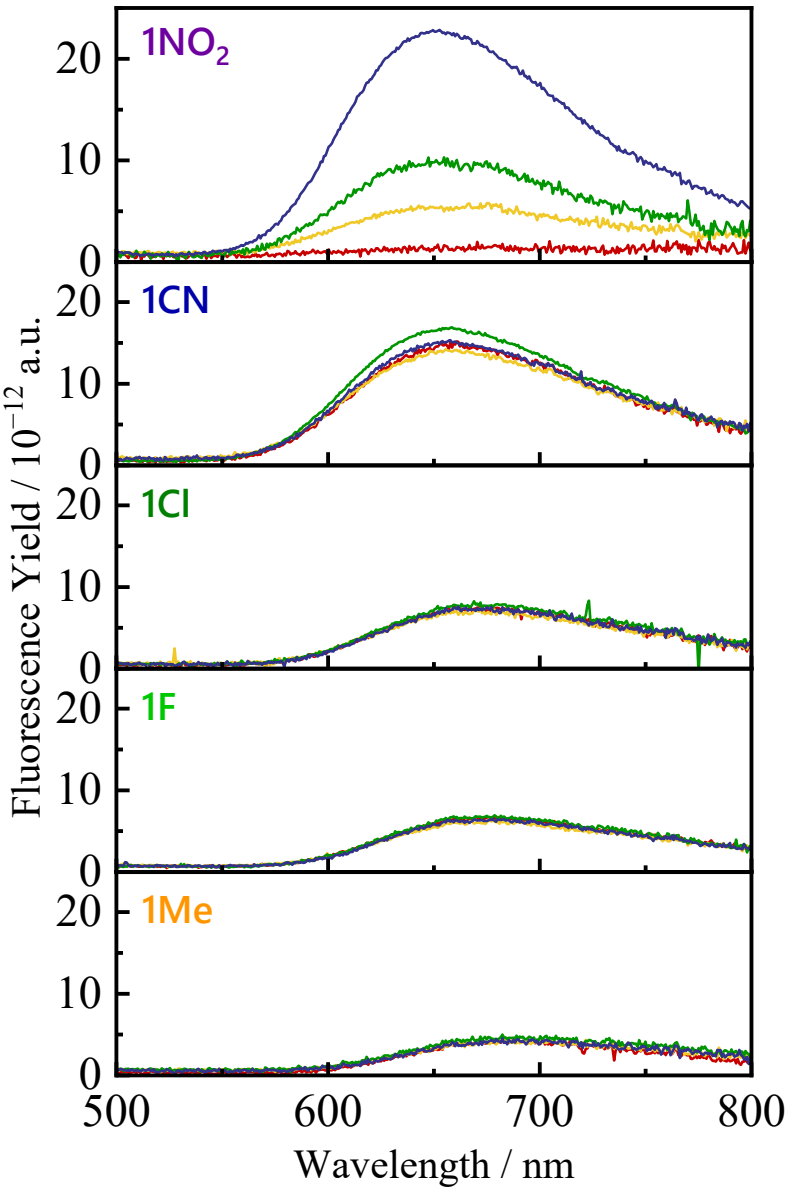

Fig. S30 Fluorescence spectra of several **1R** in ethyl acetate (dark blue), dichloromethane (green), acetone (yellow) and DMF (red).

Table S24 Solvent dependences of Φ_f of **1R**.

Derivative	Ethyl Acetate	Acetone	DMF
1Me	0.006	0.006	0.006
1F	0.01	0.01	0.01
1Cl	0.01	0.01	0.01
1CN	0.02	0.02	0.02
1NO2	0.04	0.01	0.004

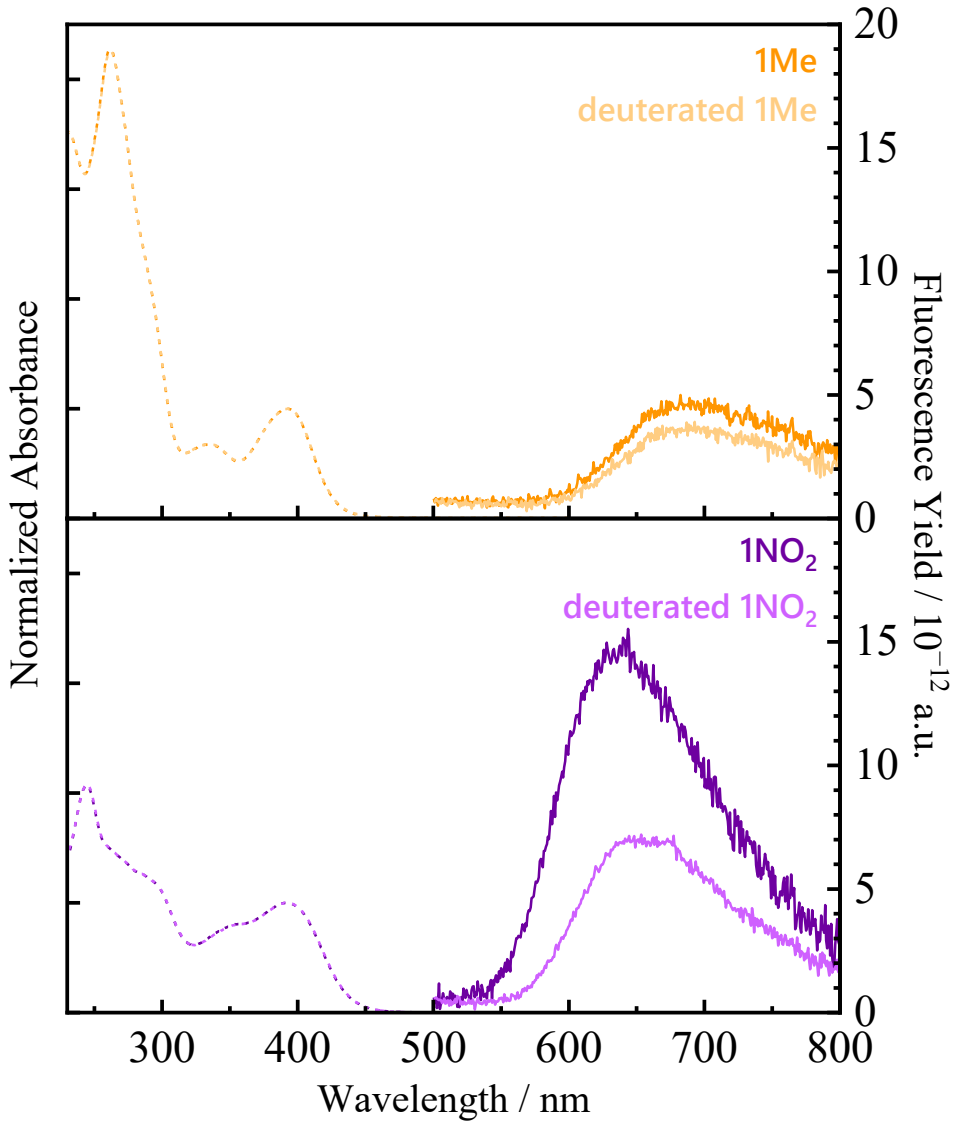

Fig. S31 Absorption (broken curves) and fluorescence spectra (solid curves, λ_{ex} = 390 or 400 nm) of **1Me** (top, λ_{ex} = 390 nm) and **1NO2** (bottom, λ_{ex} = 400 nm) before/after deuteration in dichloromethane at room temperature.

Table S25 Photophysical properties of **1Me** and **1NO2** before/after deuteration in dichloromethane at room temperature.

Derivative	Φ_f	τ_f^c / ns	k_f^d / 10^7 s^{-1}	k_d^d / 10^9 s^{-1}
1Me	0.007[a]	0.17	4.0	5.8
deuterated **1Me**	0.007[a]	0.12	5.4	8.1
1NO2	0.02[b]	0.21	8.0	4.8
deuterated **1NO2**	0.01[b]	0.16	6.9	6.3

a) λ_{ex} = 390 nm *b*) λ_{ex} = 400 nm *c*) λ_{ex} = 395 nm *d*) $\Phi_f = k_f\tau_f = k_f / (k_f + k_d)$

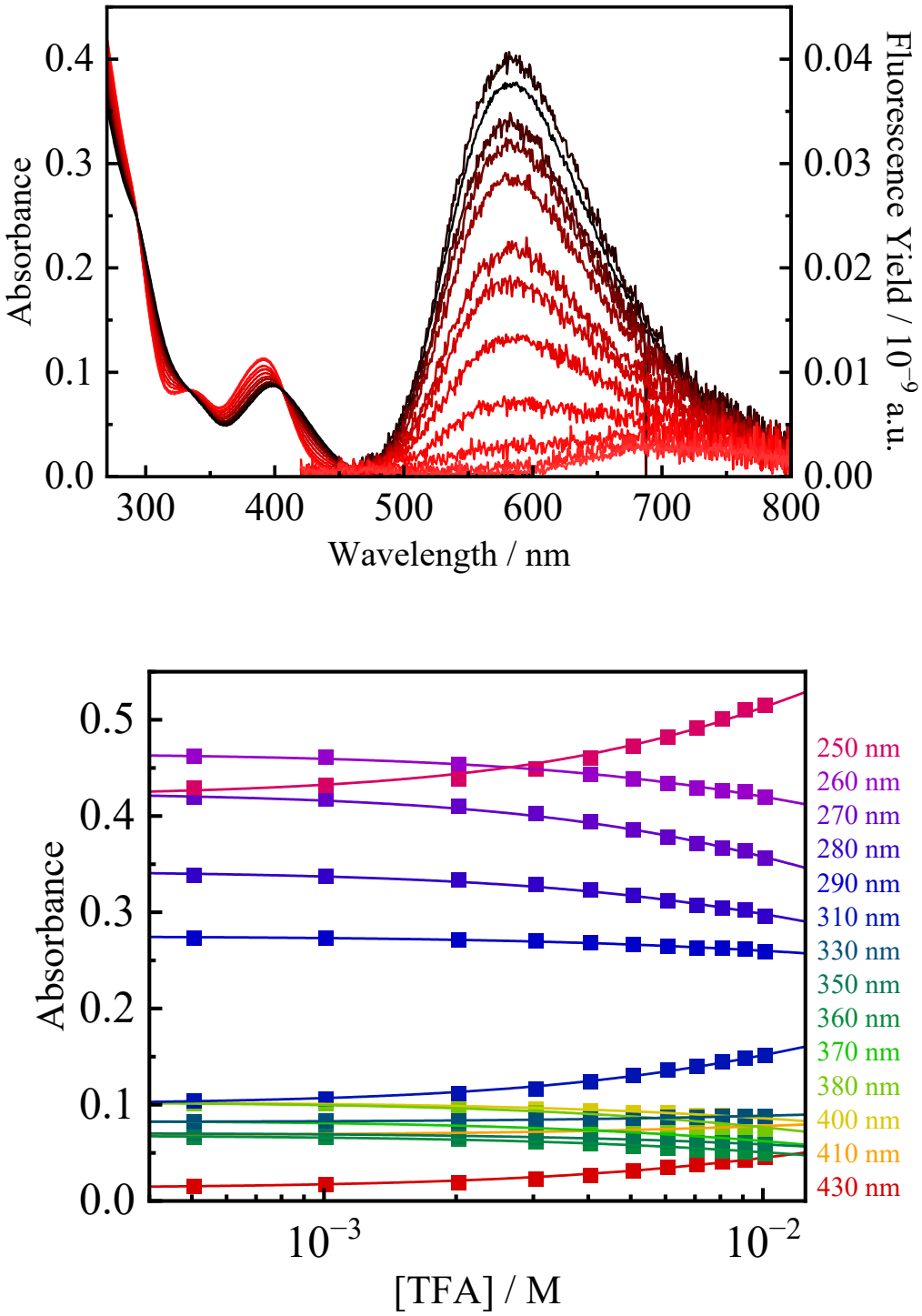

Fig. S32 TFA-concentration dependences of absorption/fluorescence spectra (top, λ_{ex} = 410 nm) and TFA titrations of the absorbances (bottom) of **1OMe** in acetonitrile ([**1OMe**] = 1.06 × 10^{-5} M, red → black: [TFA] = 0–10 mM). The curves represent global fits using equation (1) and pK_b = −1.54 ± 0.09.

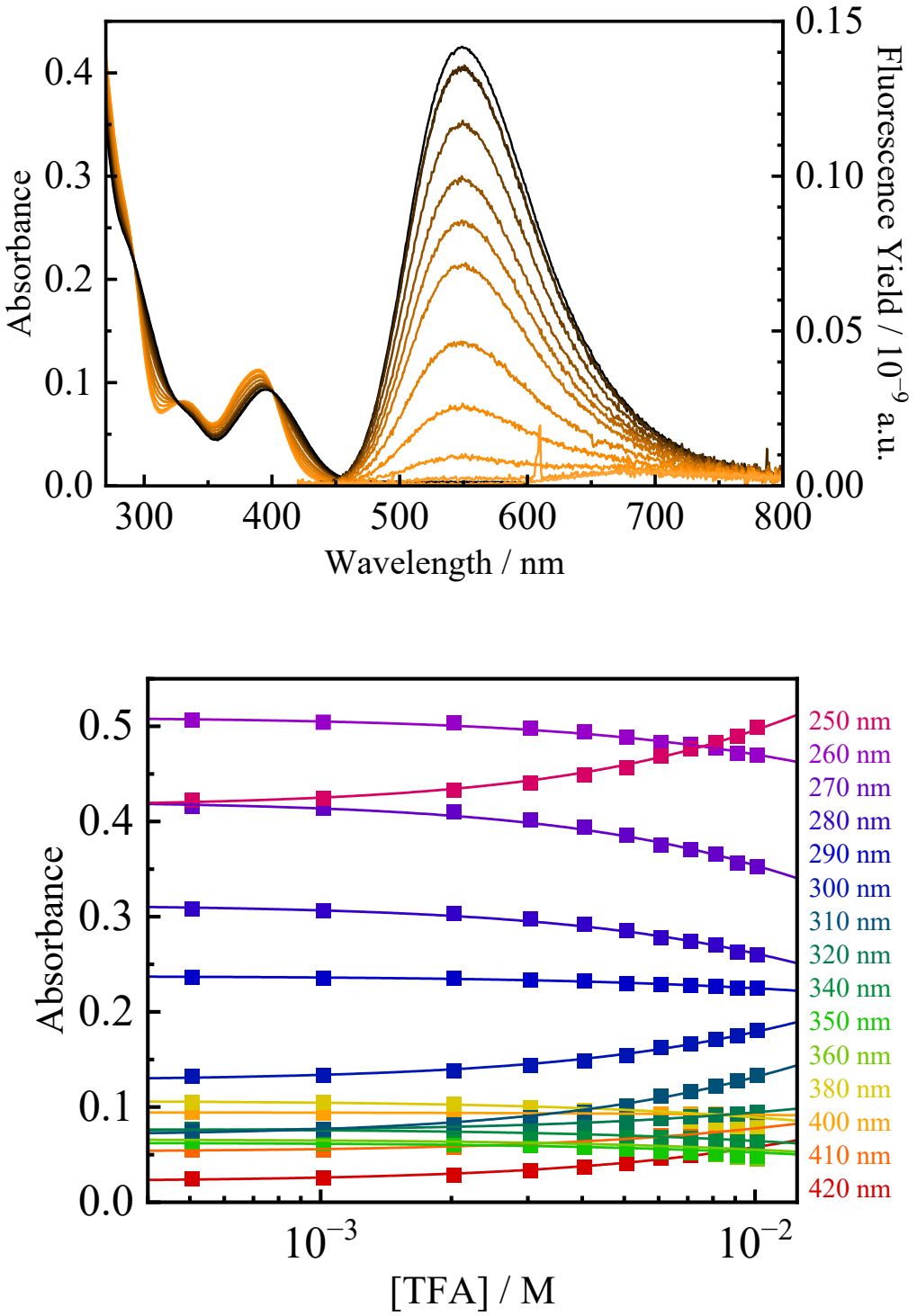

Fig. S33 TFA-concentration dependences of absorption/fluorescence spectra (top, λ_{ex} = 400 nm) and TFA titrations of the absorbances (bottom) of **1Me** in acetonitrile ([**1Me**] = 1.06 × 10^{-5} M, orange → black: [TFA] = 0–10 mM). The curves represent global fits using equation (1) and pK_b = −1.29 ± 0.16.

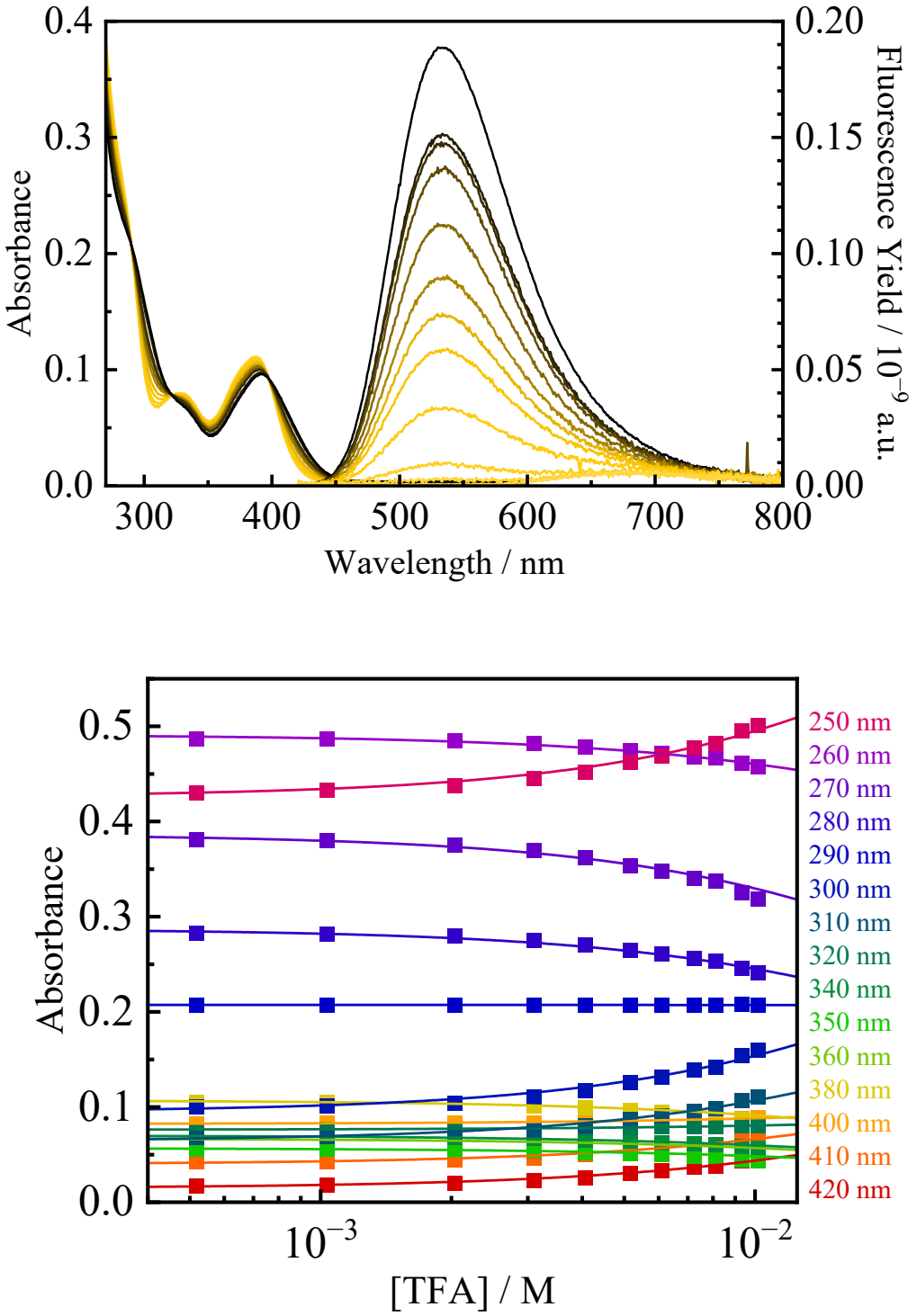

Fig. S34 TFA-concentration dependences of absorption/fluorescence spectra (top, λ_{ex} = 400 nm) and TFA titrations of the absorbances (bottom) of **1H** in acetonitrile ([**1H**] = 1.04 × 10^{-5} M, yellow → black: [TFA] = 0–10 mM). The curves represent global fits using equation (1) and pK_b = −1.24 ± 0.17.

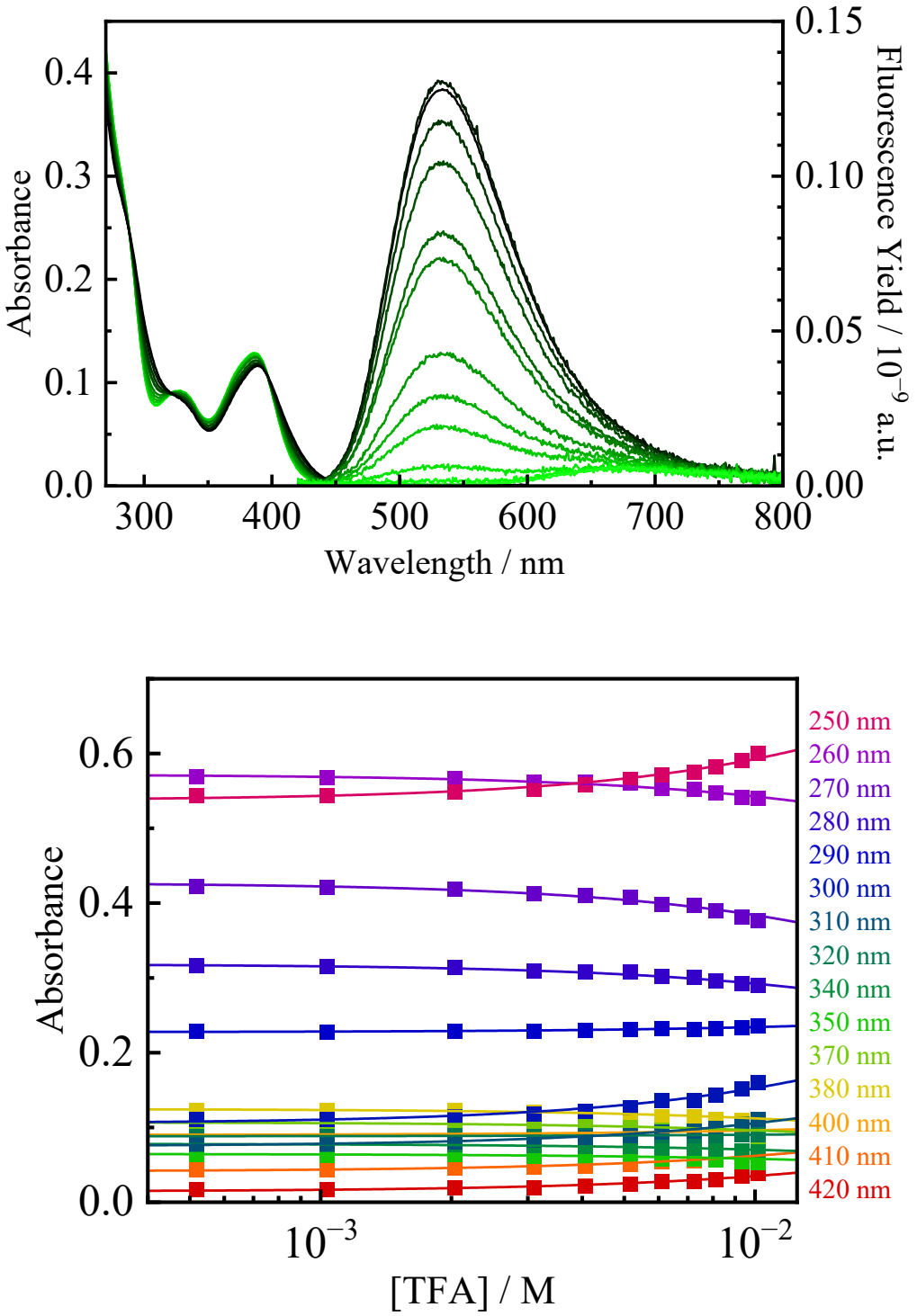

Fig. S35 TFA-concentration dependences of absorption/fluorescence spectra (top, λ_{ex} = 400 nm) and TFA titrations of the absorbances (bottom) of **1F** in acetonitrile ([**1F**] = 1.03 × 10^{-5} M, light green → black: [TFA] = 0–10 mM). The curves represent global fits using equation (1) and pK_b = −1.05 ± 0.33.

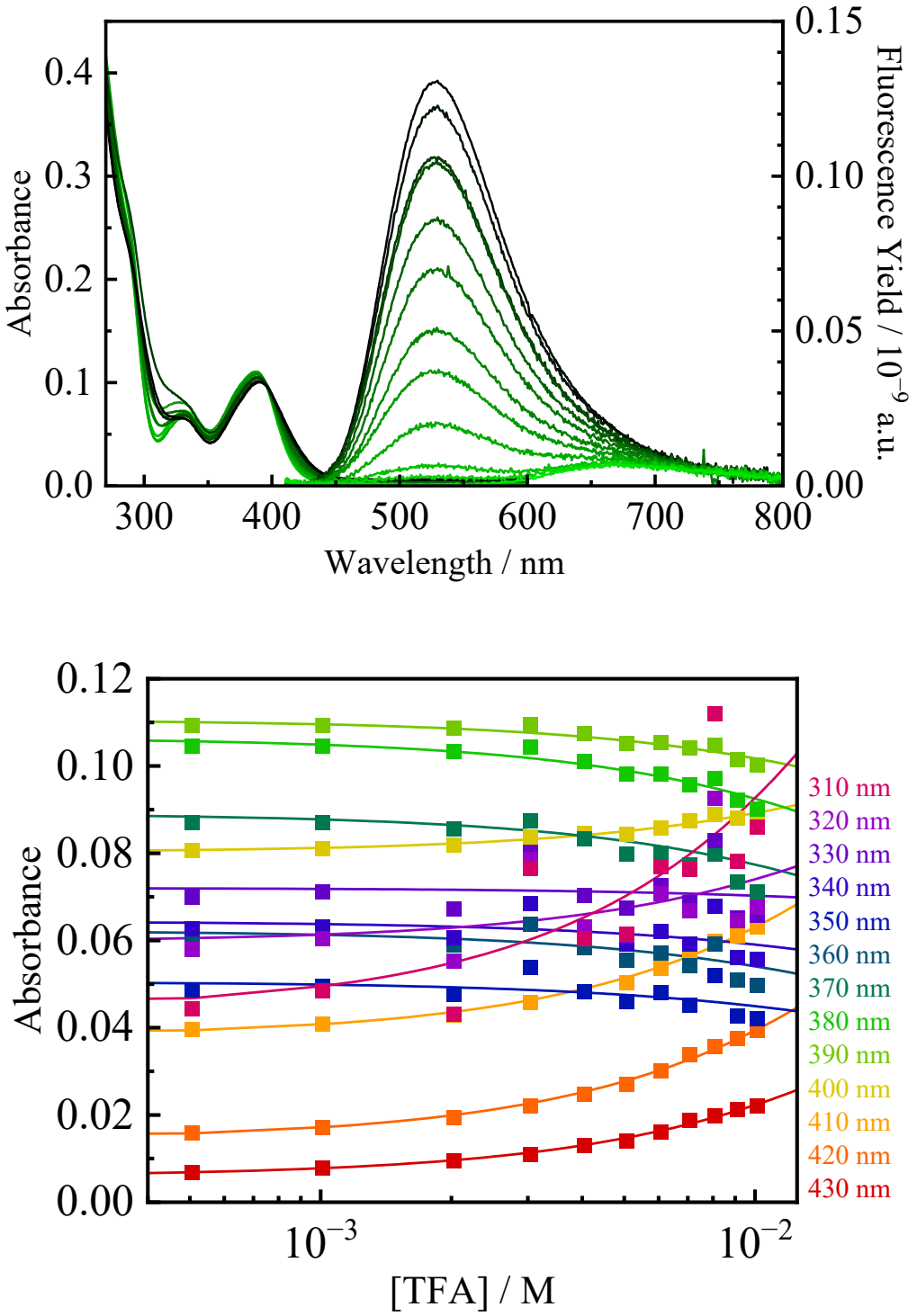

Fig. S36 TFA-concentration dependences of absorption/fluorescence spectra (top, λ_{ex} = 395 nm) and TFA titrations of the absorbances (bottom) of **1Cl** in acetonitrile ([**1Cl**] = 1.00 × 10^{-5} M, green → black: [TFA] = 0–10 mM). The curves represent global fits using equation (1) and pK_b = −1.18 ± 0.78.

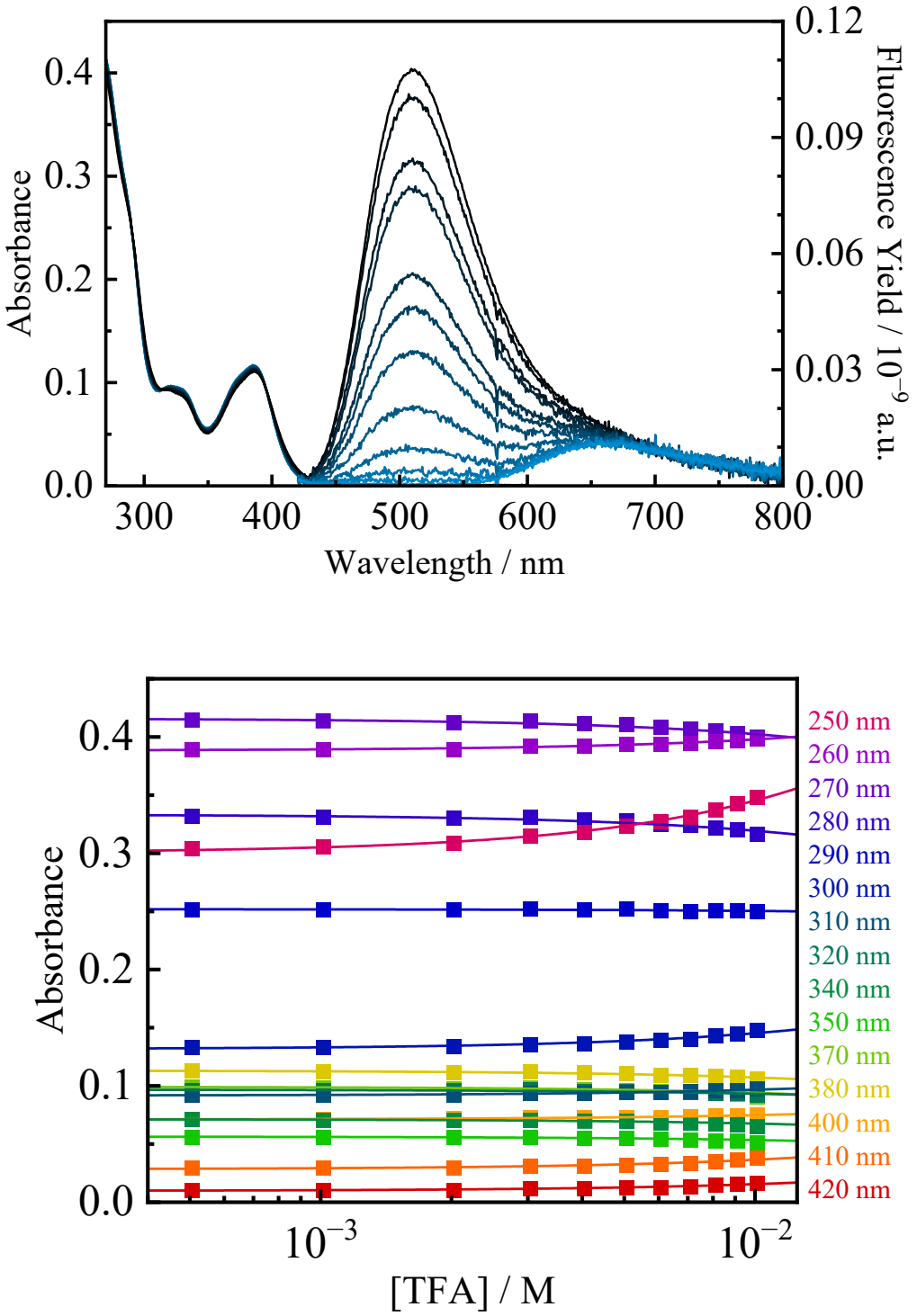

Fig. S37 TFA-concentration dependences of absorption/fluorescence spectra (top, λ_{ex} = 400 nm) and TFA titrations of the absorbances (bottom) of **1CF$_3$** in acetonitrile ([**1CF$_3$**] = 1.03 × 10^{-5} M, light blue → black: [TFA] = 0–10 mM). The curves represent global fits using equation (1) and pK_b = −0.743 ± 0.487.

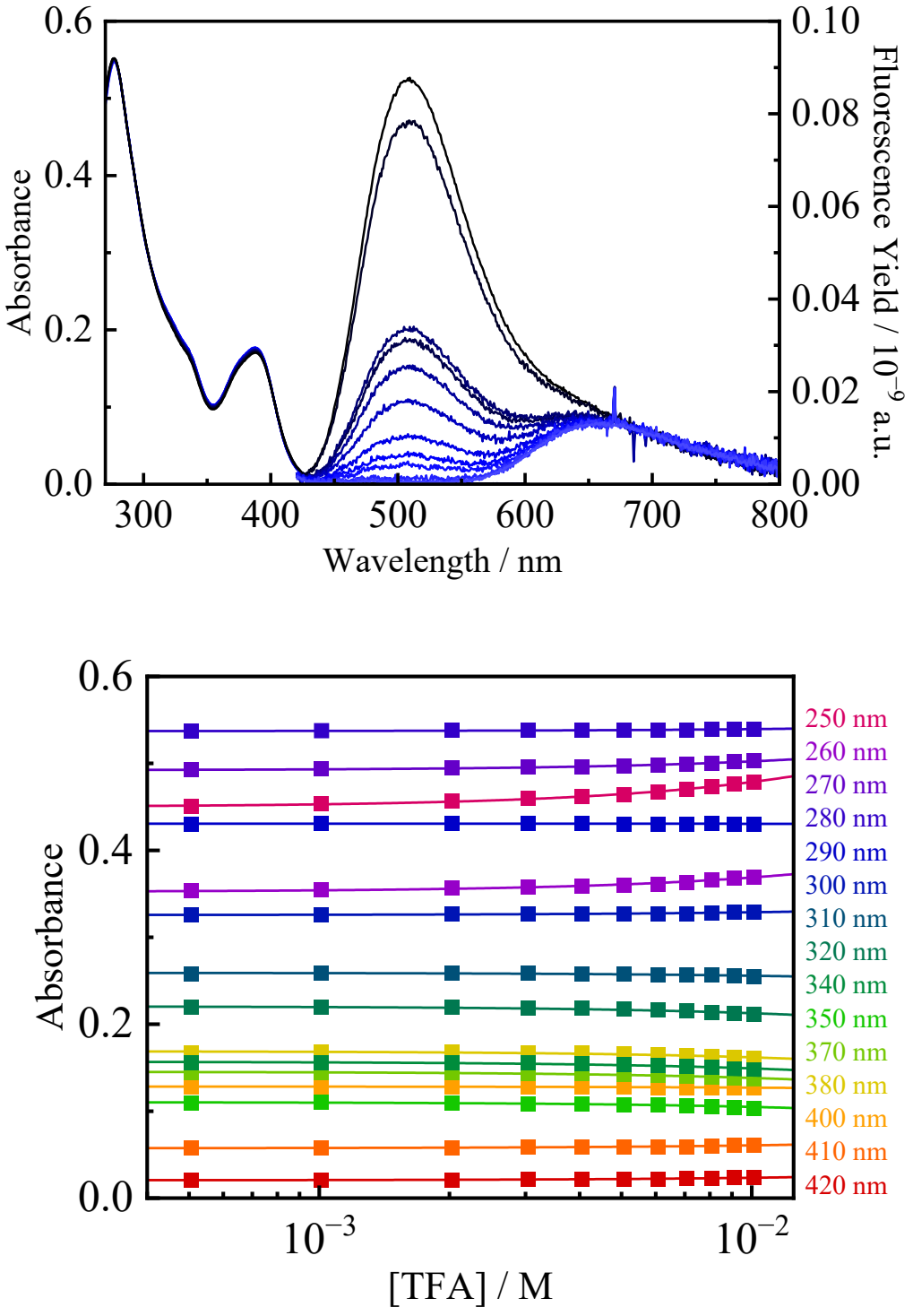

Fig. S38 TFA-concentration dependences of absorption/fluorescence spectra (top, λ_{ex} = 400 nm) and TFA titrations of the absorbances (bottom) of **1CN** in acetonitrile ([**1CN**] = 1.04 × 10^{-5} M, blue → black: [TFA] = 0–10 mM). The curves represent global fits using equation (1) and pK_b = −0.715 ± 0.507.

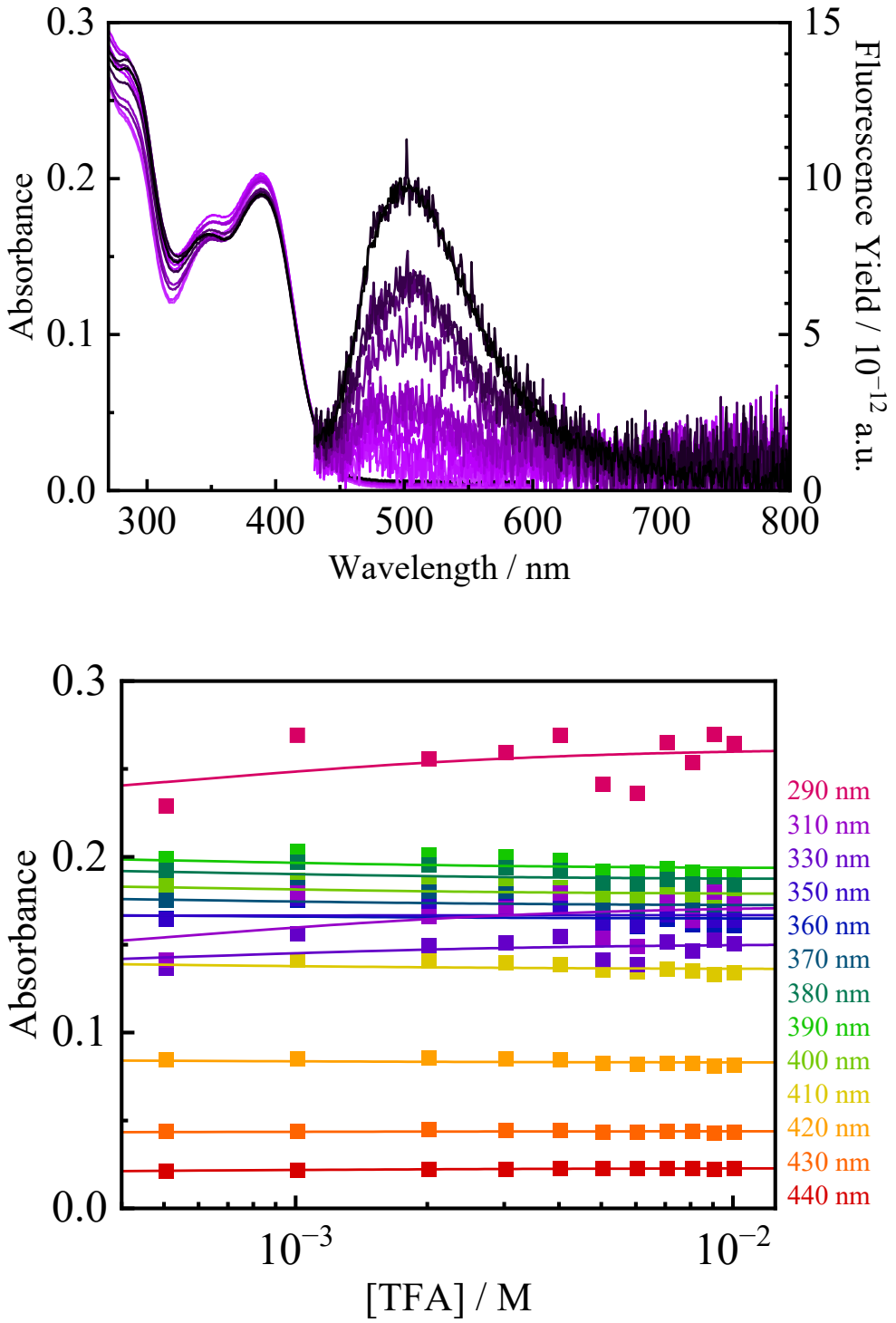

Fig. S39 TFA-concentration dependences of absorption/fluorescence spectra (top, λ_{ex} = 415 nm) and TFA titrations of the absorbances (bottom) of **1NO₂** in acetonitrile ([**1NO₂**] = 1.00 × 10^{-5} M, purple → black: [TFA] = 0–10 mM). The curves represent global fits using equation (1) and pK_b = −3.21 ± 0.21.

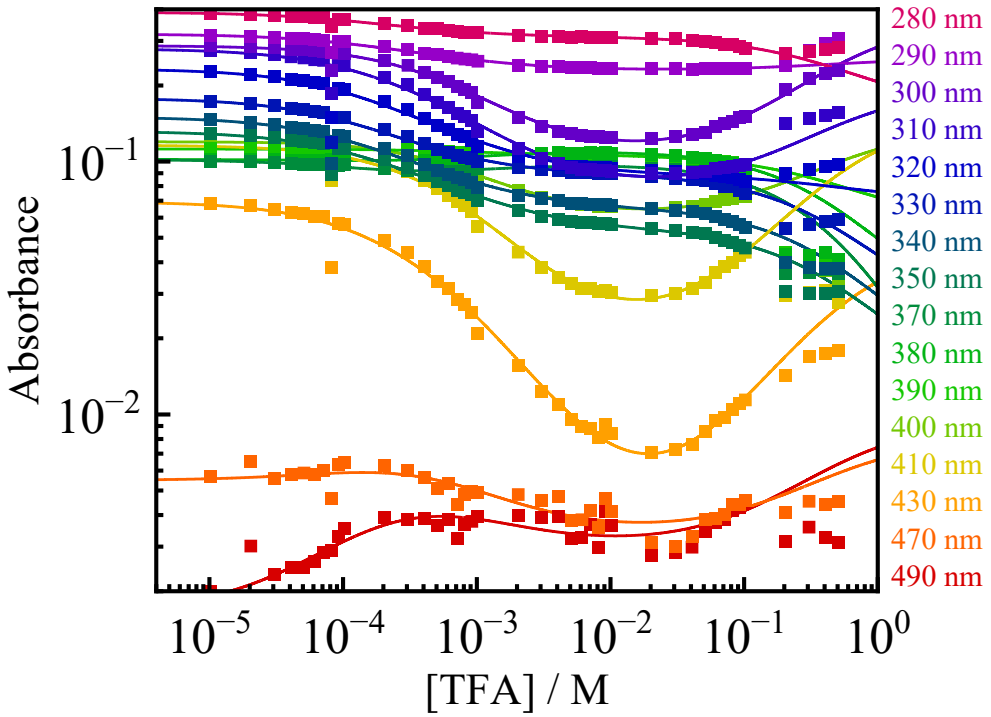

Fig. S40 TFA-concentration dependences of the absorbances of **1NMe$_2$** ([**1NMe$_2$**] = 1.02 × 10^{-5} M) in acetonitrile. The curves represent a global fit using equation (2) and pK_{b1} = −3.89 ± 0.07, pK_{b2} = −3.04 ± 0.06, pK_{b3} = −0.323 ± 0.622.

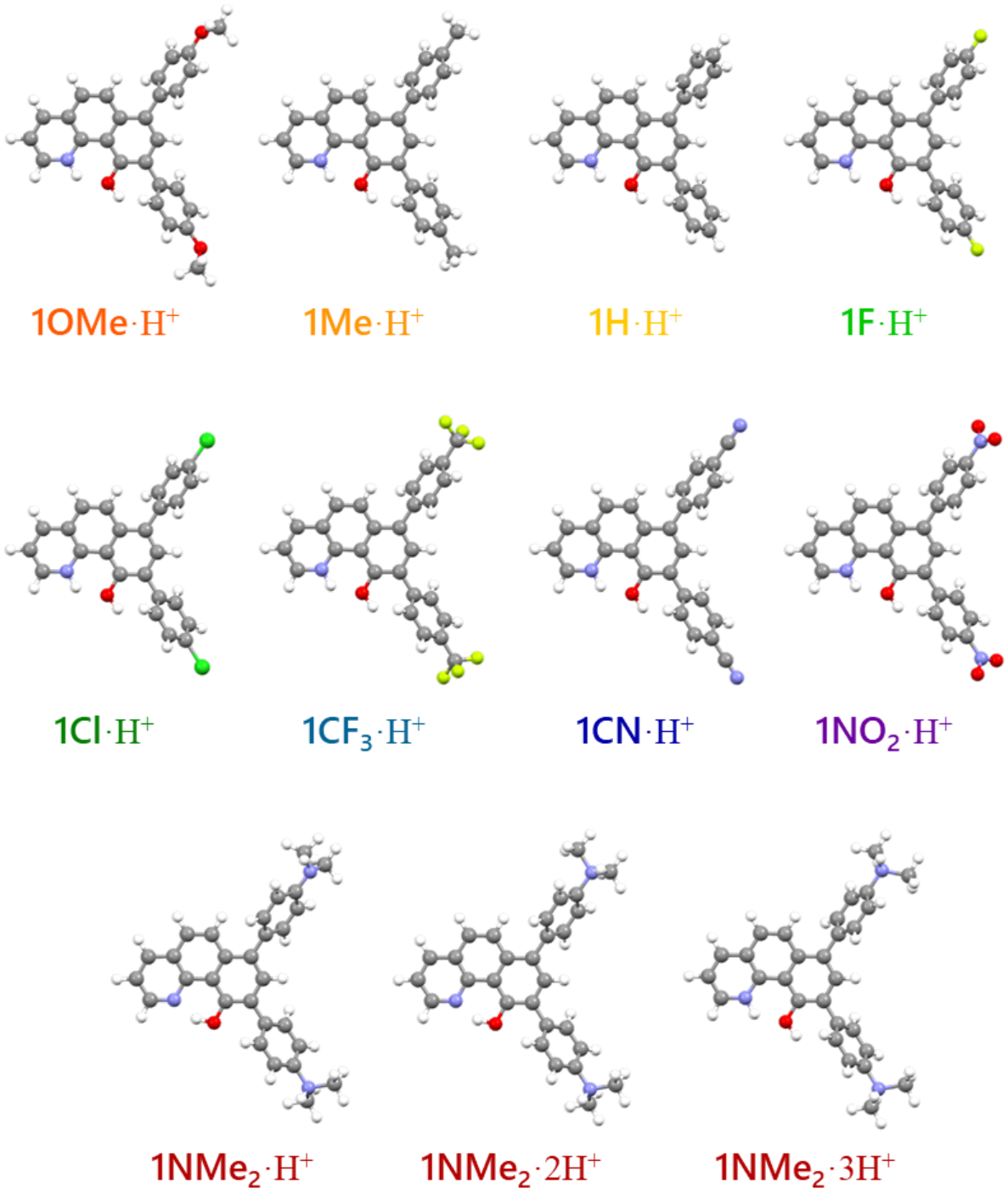

Fig. S41 Optimized geometries of **1R**·H^+ in the ground states in acetonitrile.

Table S26 Thermodynamic parameters of **1R** and its protonated forms in acetonitrile at 298.15 K.

Compound	G_{tot}[a] / a.u.	ΔG_{tot}[b] / a.u.	K_b	pK_b
$HBqNO_2$	−1502.044554	+0.006238	0.001351	2.869
$HBqNO_2 \cdot H^+$	−1502.465088			
HBqCN	−1277.453456	+0.004946	0.005309	2.275
$HBqCN \cdot H^+$	−1277.875282			
$HBqCF_3$	−1767.208804	+0.003674	0.02042	1.690
$HBqCF_3 \cdot H^+$	−1767.631902			
HBqCl	−2012.171437	+0.002396	0.07905	1.102
$HBqCl \cdot H^+$	−2012.595813			
HBqF	−1291.459088	+0.001839	0.1426	0.8459
$HBqF \cdot H^+$	−1291.884021			
HBqH	−1092.901199	+0.000891	0.389	0.410
$HBqH \cdot H^+$	−1093.327080			
HBqMe	−1171.508753	+0.000097	0.90	0.0045
$HBqMe \cdot H^+$	−1171.935428			
HBqOMe	−1321.960675	−0.000263	1.32	−0.121
$HBqOMe \cdot H^+$	−1322.387710			
$HBqNMe_2$	−1360.778667	−0.000264	1.32	−0.121
$HBqNMe \cdot H^+$	−1361.205703	+0.002139	0.1038	0.9839
$HBqNMe \cdot 2H^+$	−1361.630336	+0.008456	0.0001290	3.889
$HBqNMe \cdot 3H^+$	−1362.048652			

[a] G_{tot}: sum of total electronic energy (E_0) and thermal correction to Gibbs free energy (G_{corr}).

[b] calculated using $G_{tot}(CF_3COOH) = -526.966398$ a.u. and $G_{tot}(CF_3COO^-) = -526.539626$ a.u.

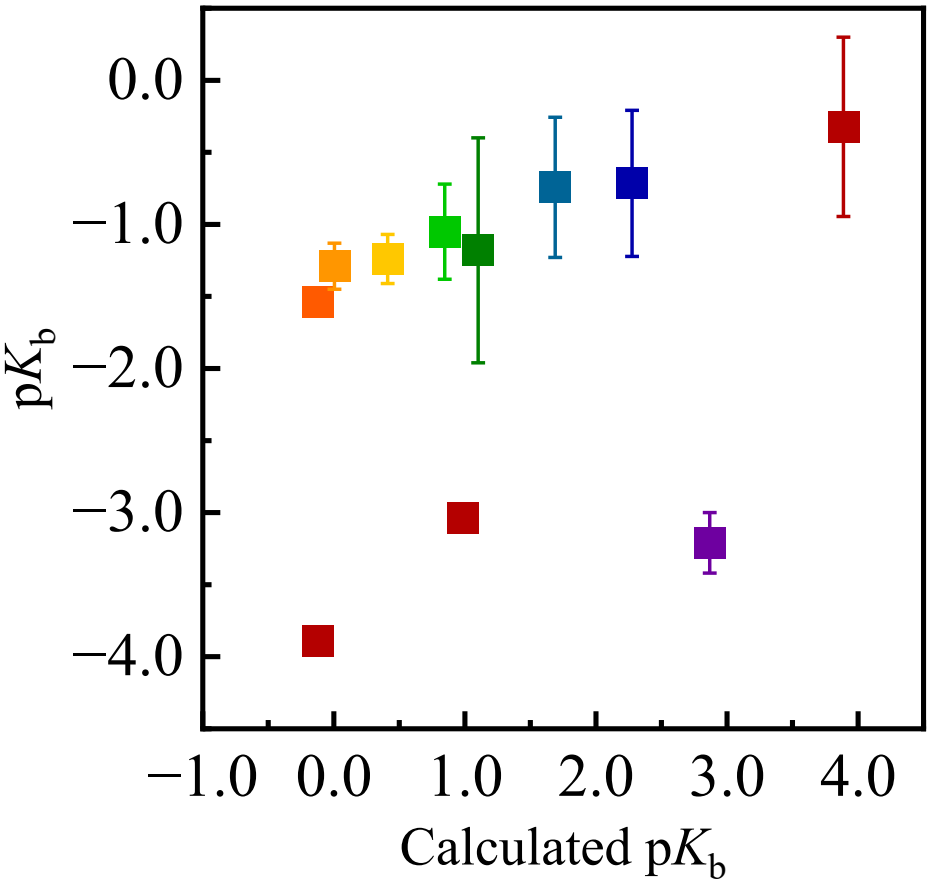

Fig. S42 Plot for comparison between calculated and experimentally-determined pK_b of **1R** in acetonitrile. The colors correspond to those indicated in Fig. 1.

Table S27 Calculated excited states of **1NMe$_2$** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO115 → MO116	2.8013 eV (442.60 nm)	0.2757
S_2	MO114 → MO116	3.0265 eV (409.66 nm)	0.0886
S_3	MO115 → MO117	3.2320 eV (383.61 nm)	0.0585
S_4	MO113 → MO116 (14%) MO114 → MO117 (86%)	3.4834 eV (355.93 nm)	0.0829
S_5	MO112 → MO117 (17%) MO113 → MO116 (83%)	3.6770 eV (337.19 nm)	0.1372
S_6	MO115 → MO118	3.9352 eV (315.07 nm)	0.2933
S_7	MO113 → MO117	4.0718 eV (304.49 nm)	0.0121
S_8	MO113 → MO117 (12%) MO114 → MO118 (9%) MO114 → MO120 (13%) MO115 → MO119 (39%) MO115 → MO120 (27%)	4.1222 eV (300.77 nm)	0.0044
S_9	MO114 → MO119 (26%) MO114 → MO120 (16%) MO115 → MO120 (58%)	4.1422 eV (299.32 nm)	0.0514
S_{10}	MO114 → MO118 (67%) MO114 → MO119 (15%) MO115 → MO120 (18%)	4.1764 eV (296.87 nm)	0.1999
S_{11}	MO112 → MO116 (66%) MO113 → MO117 (34%)	4.3292 eV (286.39 nm)	0.1200
S_{12}	MO112 → MO116 (15%) MO113 → MO117 (11%) MO114 → MO119 (30%) MO115 → MO119 (21%) MO115 → MO121 (23%)	4.3898 eV (282.43 nm)	0.1405
S_{13}	MO115 → MO121	4.4108 eV (281.09 nm)	0.2976
S_{14}	MO114 → MO120 (83%) MO114 → MO123 (17%)	4.4957 eV (275.79 nm)	0.0166
S_{15}	MO114 → MO120 (39%) MO115 → MO122 (61%)	4.5205 eV (274.27 nm)	0.0185
S_{16}	MO108 → MO116 (35%) MO111 → MO116 (41%) MO112 → MO117 (10%) MO114 → MO120 (14%)	4.5690 eV (271.36 nm)	0.0183
S_{17}	MO114 → MO121 (30%) MO115 → MO121 (13%) MO115 → MO122 (11%) MO115 → MO123 (46%)	4.5985 eV (269.62 nm)	0.0334
S_{18}	MO108 → MO116 (13%) MO110 → MO116 (43%) MO111 → MO116 (20%) MO113 → MO118 (10%) MO114 → MO121 (14%)	4.6148 eV (268.67 nm)	0.1153

S_{19}	MO109 → MO116 (19%) MO110 → MO116 (37%) MO111 → MO116 (12%) MO112 → MO117 (32%)	4.6475 eV (266.78 nm)	0.2573
S_{20}	MO108 → MO116 (78%) MO110 → MO116 (22%)	4.6957 eV (264.04 nm)	0.0472
S_{21}	MO109 → MO116 (16%) MO112 → MO117 (14%) MO114 → MO121 (51%) MO114 → MO122 (19%)	4.7150 eV (262.95 nm)	0.1755
S_{22}	MO109 → MO116 (9%) MO113 → MO118 (41%) MO114 → MO121 (14%) MO114 → MO122 (12%) MO114 → MO123 (11%) MO115 → MO123 (13%)	4.7901 eV (258.83 nm)	0.0569
S_{23}	MO109 → MO116 (12%) MO113 → MO118 (33%) MO115 → MO124 (44%) MO115 → MO128 (11%)	4.7991 eV (258.35 nm)	0.0076
S_{24}	MO109 → MO116 (33%) MO109 → MO117 (13%) MO113 → MO118 (16%) MO115 → MO125 (38%)	4.8922 eV (253.43 nm)	0.0243
S_{25}	MO109 → MO116 (14%) MO114 → MO122 (22%) MO114 → MO123 (9%) MO115 → MO122 (6%) MO115 → MO123 (15%) MO115 → MO124 (15%) MO115 → MO125 (19%)	4.9414 eV (250.91 nm)	0.0530
S_{26}	MO109 → MO116 (9%) MO113 → MO119 (17%) MO114 → MO123 (25%) MO114 → MO124 (11%) MO115 → MO124 (17%) MO115 → MO126 (13%) MO115 → MO129 (8%)	4.9936 eV (248.29 nm)	0.0561
S_{27}	MO109 → MO116 (20%) MO113 → MO119 (62%) MO114 → MO122 (18%)	5.0034 eV (247.80 nm)	0.1312
S_{28}	MO108 → MO117 (33%) MO111 → MO117 (67%)	5.0300 eV (246.49 nm)	0.0053
S_{29}	MO109 → MO116 (17%) MO114 → MO124 (65%) MO114 → MO127 (18%)	5.0622 eV (244.92 nm)	0.0515

S_{30}	MO110 → MO117 (26%) MO111 → MO117 (8%) MO112 → MO117 (14%) MO113 → MO118 (9%) MO113 → MO119 (16%) MO114 → MO124 (14%) MO115 → MO125 (13%)	5.0765 eV (244.23 nm)	0.1180

HOMO: MO115, LUMO: MO116

Table S28 Calculated excited states of **1NMe$_2$**·H$^+$ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO115 → MO116	2.7790 eV (446.15 nm)	0.1270
S_2	MO115 → MO117 (86%) MO115 → MO118 (14%)	3.2883 eV (377.04 nm)	0.0601
S_3	MO114 → MO116	3.4348 eV (360.97 nm)	0.2656
S_4	MO115 → MO118	3.5758 eV (346.73 nm)	0.0527
S_5	MO115 → MO119	3.7937 eV (326.82 nm)	0.0005
S_6	MO113 → MO116 (31%) MO114 → MO117 (59%) MO114 → MO118 (10%)	3.8743 eV (320.01 nm)	0.0422
S_7	MO115 → MO120 (54%) MO115 → MO121 (46%)	4.1525 eV (298.58 nm)	0.0284
S_8	MO113 → MO116 (29%) MO114 → MO118 (48%) MO115 → MO118 (9%) MO115 → MO120 (14%)	4.1684 eV (297.44 nm)	0.0027
S_9	MO113 → MO116 (70%) MO115 → MO121 (30%)	4.2798 eV (289.70 nm)	0.4667
S_{10}	MO114 → MO118 (24%) MO115 → MO121 (76%)	4.3329 eV (286.15 nm)	0.2463
S_{11}	MO114 → MO119 (84%) MO115 → MO119 (16%)	4.3899 eV (282.43 nm)	0.0100
S_{12}	MO112 → MO116 (87%) MO115 → MO123 (13%)	4.4775 eV (276.90 nm)	0.0163
S_{13}	MO111 → MO116 (16%) MO115 → MO122 (20%) MO115 → MO123 (46%) MO115 → MO124 (18%)	4.5208 eV (274.25 nm)	0.2713
S_{14}	MO109 → MO116 (11%) MO110 → MO116 (11%) MO113 → MO117 (20%) MO115 → MO120 (6%) MO115 → MO122 (12%) MO115 → MO123 (10%) MO115 → MO124 (22%) MO115 → MO125 (8%)	4.5907 eV (270.08 nm)	0.1977
S_{15}	MO109 → MO116 (47%) MO110 → MO116 (53%)	4.6203 eV (268.34 nm)	0.0843
S_{16}	MO113 → MO117 (27%) MO115 → MO123 (73%)	4.6761 eV (265.15 nm)	0.1841
S_{17}	MO113 → MO118 (19%) MO115 → MO122 (81%)	4.7596 eV (260.49 nm)	0.0299
S_{18}	MO108 → MO116 (13%) MO111 → MO117 (15%) MO113 → MO118 (54%) MO115 → MO124 (18%)	4.7716 eV (259.84 nm)	0.1809

S_{19}	MO114 → MO120 (45%) MO114 → MO121 (32%) MO115 → MO122 (10%) MO115 → MO125 (13%)	4.8814 eV (253.99 nm)	0.0064
S_{20}	MO111 → MO116 (18%) MO113 → MO118 (21%) MO114 → MO120 (40%) MO115 → MO124 (21%)	4.9462 eV (250.67 nm)	0.0335
S_{21}	MO111 → MO116 (18%) MO113 → MO118 (22%) MO114 → MO124 (12%) MO115 → MO125 (48%)	4.9677 eV (249.58 nm)	0.0840
S_{22}	MO109 → MO116 (10%) MO111 → MO116 (11%) MO112 → MO117 (66%) MO112 → MO118 (13%)	4.9937 eV (248.28 nm)	0.0091
S_{23}	MO109 → MO116 (34%) MO110 → MO118 (15%) MO113 → MO119 (51%)	5.0046 eV (247.74 nm)	0.0030
S_{24}	MO111 → MO116 (17%) MO113 → MO117 (12%) MO113 → MO118 (21%) MO114 → MO121 (15%) MO114 → MO123 (9%) MO115 → MO126 (26%)	5.0775 eV (244.18 nm)	0.1784
S_{25}	MO109 → MO117 (39%) MO110 → MO117 (40%) MO110 → MO118 (10%) MO113 → MO119 (11%)	5.1014 eV (243.04 nm)	0.0036
S_{26}	MO114 → MO120 (12%) MO115 → MO126 (52%) MO115 → MO128 (13%) MO115 → MO130 (23%)	5.1123 eV (242.52 nm)	0.0986
S_{27}	MO107 → MO116 (7%) MO108 → MO116 (30%) MO109 → MO116 (13%) MO109 → MO117 (10%) MO110 → MO117 (13%) MO111 → MO117 (27%)	5.1627 eV (240.15 nm)	0.1005
S_{28}	MO110 → MO116 (10%) MO111 → MO117 (8%) MO113 → MO119 (14%) MO114 → MO125 (10%) MO115 → MO126 (8%) MO115 → MO127 (39%) MO115 → MO128 (11%)	5.2277 eV (237.17 nm)	0.0084
S_{29}	MO108 → MO116 (19%) MO110 → MO116 (34%) MO113 → MO119 (47%)	5.2309 eV (237.02 nm)	0.0161

S_{30}	MO108 → MO116 (15%) MO114 → MO122 (22%) MO114 → MO123 (63%)	5.2521 eV (236.07 nm)	0.1904

HOMO: MO115, LUMO: MO116

Table S29 Calculated excited states of **1NMe$_2$**·2H$^+$ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO114 → MO117 (15%) MO115 → MO116 (85%)	3.2785 eV (378.18 nm)	0.3820
S_2	MO115 → MO117	3.7124 eV (333.97 nm)	0.0696
S_3	MO115 → MO118 (83%) MO115 → MO119 (17%)	3.9781 eV (311.67 nm)	0.1861
S_4	MO114 → MO116 (21%) MO115 → MO117 (19%) MO115 → MO119 (60%)	4.0745 eV (304.29 nm)	0.0459
S_5	MO115 → MO120	4.1701 eV (297.32 nm)	0.0172
S_6	MO115 → MO121	4.2432 eV (292.19 nm)	0.0079
S_7	MO114 → MO116 (65%) MO115 → MO117 (21%) MO115 → MO120 (14%)	4.2579 eV (291.19 nm)	0.3340
S_8	MO113 → MO116 (41%) MO114 → MO117 (59%)	4.5428 eV (272.92 nm)	0.2882
S_9	MO109 → MO116	4.6024 eV (269.39 nm)	0.0306
S_{10}	MO113 → MO116 (62%) MO114 → MO118 (22%) MO115 → MO122 (16%)	4.7499 eV (261.03 nm)	0.1979
S_{11}	MO114 → MO118	4.9150 eV (252.26 nm)	0.1082
S_{12}	MO111 → MO116 (31%) MO113 → MO116 (12%) MO113 → MO117 (9%) MO114 → MO118 (32%) MO114 → MO119 (16%)	4.9450 eV (250.73 nm)	0.0461
S_{13}	MO109 → MO116 (15%) MO112 → MO116 (23%) MO113 → MO121 (7%) MO114 → MO118 (8%) MO114 → MO119 (13%) MO114 → MO121 (18%) MO115 → MO122 (16%)	4.9868 eV (248.62 nm)	0.0174
S_{14}	MO114 → MO117 (22%) MO114 → MO119 (20%) MO115 → MO122 (58%)	5.0073 eV (247.60 nm)	0.0540
S_{15}	MO109 → MO116 (17%) MO109 → MO117 (59%) MO113 → MO117 (24%)	5.0623 eV (244.92 nm)	0.0003
S_{16}	MO111 → MO116 (38%) MO114 → MO120 (62%)	5.1067 eV (242.79 nm)	0.1008
S_{17}	MO109 → MO116 (18%) MO110 → MO116 (35%) MO114 → MO120 (47%)	5.1415 eV (241.14 nm)	0.0163

S_{18}	MO111 → MO120 (11%) MO113 → MO116 (24%) MO113 → MO117 (12%) MO114 → MO119 (40%) MO114 → MO120 (13%)	5.1666 eV (239.97 nm)	0.4054
S_{19}	MO112 → MO117 (12%) MO113 → MO117 (59%) MO115 → MO122 (14%) MO115 → MO123 (15%)	5.1835 eV (239.19 nm)	0.1112
S_{20}	MO114 → MO119 (11%) MO115 → MO123 (55%) MO115 → MO125 (34%)	5.1972 eV (238.56 nm)	0.0372
S_{21}	MO110 → MO116 (20%) MO114 → MO121 (80%)	5.2448 eV (236.40 nm)	0.0075
S_{22}	MO108 → MO116 (29%) MO110 → MO117 (16%) MO110 → MO118 (12%) MO110 → MO119 (10%) MO113 → MO117 (12%) MO113 → MO119 (11%) MO114 → MO120 (10%)	5.3305 eV (232.59 nm)	0.0147
S_{23}	MO108 → MO116 (18%) MO110 → MO117 (10%) MO115 → MO123 (16%) MO115 → MO124 (56%)	5.3390 eV (232.22 nm)	0.0015
S_{24}	MO108 → MO116 (43%) MO111 → MO117 (18%) MO111 → MO120 (27%) MO113 → MO117 (12%)	5.3959 eV (229.78 nm)	0.0476
S_{25}	MO115 → MO124 (18%) MO115 → MO125 (82%)	5.4328 eV (228.21 nm)	0.0005
S_{26}	MO111 → MO117	5.4628 eV (226.96 nm)	0.1626
S_{27}	MO109 → MO117 (30%) MO111 → MO117 (15%) MO112 → MO117 (39%) MO113 → MO121 (16%)	5.5222 eV (224.52 nm)	0.0117
S_{28}	MO113 → MO118 (63%) MO113 → MO119 (13%) MO115 → MO126 (24%)	5.5475 eV (223.50 nm)	0.0387
S_{29}	MO107 → MO116 (14%) MO108 → MO116 (18%) MO115 → MO126 (68%)	5.5634 eV (222.86 nm)	0.0281
S_{30}	MO108 → MO121 (8%) MO109 → MO116 (10%) MO109 → MO117 (12%) MO109 → MO119 (8%) MO112 → MO117 (18%) MO112 → MO118 (34%) MO114 → MO121 (10%)	5.6144 eV (220.83 nm)	0.0047

HOMO: MO115, LUMO: MO116

Table S30 Calculated excited states of **1NMe$_2$**·3H$^+$ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO114 → MO117 (14%) MO115 → MO116 (86%)	3.1134 eV (398.22 nm)	0.2147
S_2	MO115 → MO117	3.7160 eV (333.65 nm)	0.0289
S_3	MO114 → MO116 (55%) MO115 → MO117 (35%) MO115 → MO118 (10%)	4.0164 eV (308.70 nm)	0.2817
S_4	MO112 → MO116 (25%) MO115 → MO118 (75%)	4.2636 eV (290.80 nm)	0.0425
S_5	MO112 → MO116	4.3780 eV (283.20 nm)	0.0155
S_6	MO112 → MO116 (31%) MO113 → MO116 (69%)	4.4037 eV (281.54 nm)	0.0399
S_7	MO110 → MO116 (29%) MO115 → MO119 (45%) MO115 → MO121 (14%) MO115 → MO122 (12%)	4.5020 eV (275.40 nm)	0.1142
S_8	MO114 → MO117 (21%) MO115 → MO119 (79%)	4.5213 eV (274.23 nm)	0.1362
S_9	MO111 → MO116	4.5621 eV (271.77 nm)	0.0163
S_{10}	MO110 → MO116 (16%) MO111 → MO116 (16%) MO114 → MO117 (11%) MO115 → MO119 (15%) MO115 → MO120 (42%)	4.6137 eV (268.73 nm)	0.0287
S_{11}	MO115 → MO120 (39%) MO115 → MO121 (43%) MO115 → MO122 (18%)	4.6391 eV (267.26 nm)	0.2432
S_{12}	MO114 → MO117 (35%) MO115 → MO121 (65%)	4.7406 eV (261.54 nm)	0.1887
S_{13}	MO109 → MO116 (45%) MO110 → MO117 (9%) MO113 → MO117 (11%) MO114 → MO117 (9%) MO114 → MO118 (13%) MO115 → MO122 (13%)	4.9201 eV (252.00 nm)	0.1019
S_{14}	MO109 → MO116 (31%) MO112 → MO117 (69%)	4.9763 eV (249.15 nm)	0.0603
S_{15}	MO112 → MO117 (18%) MO113 → MO117 (70%) MO115 → MO121 (12%)	5.0135 eV (247.30 nm)	0.0074
S_{16}	MO112 → MO117 (32%) MO114 → MO117 (21%) MO115 → MO122 (47%)	5.1096 eV (242.65 nm)	0.5153
S_{17}	MO110 → MO120 (8%) MO111 → MO117 (38%) MO111 → MO118 (13%) MO114 → MO118 (12%) MO114 → MO119 (9%) MO114 → MO120 (11%) MO115 → MO122 (9%)	5.1230 eV (242.02 nm)	0.0548

S_{18}	MO110 → MO117 (76%) MO111 → MO117 (24%)	5.2091 eV (238.01 nm)	0.0134
S_{19}	MO110 → MO117 (47%) MO114 → MO118 (53%)	5.3084 eV (233.56 nm)	0.4864
S_{20}	MO111 → MO117 (75%) MO111 → MO121 (25%)	5.3664 eV (231.04 nm)	0.0206
S_{21}	MO112 → MO118 (13%) MO112 → MO121 (31%) MO113 → MO117 (13%) MO113 → MO119 (43%)	5.4030 eV (229.47 nm)	0.0101
S_{22}	MO109 → MO117 (23%) MO114 → MO119 (77%)	5.4893 eV (225.87 nm)	0.0175
S_{23}	MO109 → MO117 (66%) MO115 → MO124 (34%)	5.5801 eV (222.19 nm)	0.0630
S_{24}	MO109 → MO117 (22%) MO112 → MO118 (45%) MO115 → MO123 (33%)	5.6430 eV (219.71 nm)	0.0428
S_{25}	MO115 → MO123 (67%) MO115 → MO124 (33%)	5.6621 eV (218.97 nm)	0.0053
S_{26}	MO108 → MO116 (9%) MO112 → MO118 (9%) MO112 → MO120 (9%) MO113 → MO118 (16%) MO114 → MO120 (32%) MO115 → MO123 (9%) MO115 → MO124 (16%)	5.6699 eV (218.67 nm)	0.0150
S_{27}	MO108 → MO116 (15%) MO111 → MO118 (13%) MO113 → MO118 (60%) MO113 → MO119 (12%)	5.6866 eV (218.03 nm)	0.0128
S_{28}	MO108 → MO116 (16%) MO110 → MO118 (16%) MO112 → MO118 (8%) MO112 → MO121 (9%) MO114 → MO121 (34%) MO115 → MO124 (17%)	5.7140 eV (216.98 nm)	0.1040
S_{29}	MO108 → MO116 (28%) MO111 → MO118 (17%) MO112 → MO118 (33%) MO115 → MO124 (22%)	5.7194 eV (216.78 nm)	0.0115
S_{30}	MO108 → MO116 (19%) MO110 → MO118 (50%) MO114 → MO122 (31%)	5.8336 eV (212.53 nm)	0.0233

HOMO: MO115, LUMO: MO116

Table S31 Calculated excited states of **1OMe** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO107 → MO108	3.1083 eV (398.88 nm)	0.3148
S_2	MO105 → MO108 (13%) MO107 → MO109 (87%)	3.5177 eV (352.46 nm)	0.0355
S_3	MO106 → MO108 (77%) MO107 → MO109 (23%)	3.7226 eV (333.05 nm)	0.1496
S_4	MO105 → MO108 (64%) MO106 → MO109 (36%)	4.0907 eV (303.09 nm)	0.0444
S_5	MO106 → MO109	4.1750 eV (296.97 nm)	0.0290
S_6	MO106 → MO109 (39%) MO107 → MO110 (61%)	4.2074 eV (294.68 nm)	0.3333
S_7	MO107 → MO111	4.3614 eV (284.28 nm)	0.0062
S_8	MO104 → MO108 (69%) MO105 → MO109 (31%)	4.3834 eV (282.85 nm)	0.0080
S_9	MO103 → MO108 (12%) MO107 → MO111 (25%) MO107 → MO112 (63%)	4.4148 eV (280.84 nm)	0.0419
S_{10}	MO104 → MO108 (18%) MO107 → MO113 (82%)	4.5608 eV (271.85 nm)	0.2299
S_{11}	MO100 → MO108 (57%) MO102 → MO108 (13%) MO103 → MO108 (30%)	4.6095 eV (268.97 nm)	0.0074
S_{12}	MO105 → MO109 (62%) MO107 → MO113 (38%)	4.6511 eV (266.57 nm)	0.2901
S_{13}	MO100 → MO108 (18%) MO102 → MO108 (82%)	4.7391 eV (261.62 nm)	0.0362
S_{14}	MO100 → MO108 (27%) MO101 → MO108 (31%) MO104 → MO109 (42%)	4.7664 eV (260.12 nm)	0.0926
S_{15}	MO101 → MO108 (16%) MO102 → MO108 (41%) MO103 → MO108 (18%) MO104 → MO109 (25%)	4.7730 eV (259.76 nm)	0.1065
S_{16}	MO101 → MO108 (19%) MO106 → MO110 (81%)	4.7983 eV (258.39 nm)	0.1443
S_{17}	MO102 → MO108 (13%) MO102 → MO113 (17%) MO105 → MO111 (14%) MO106 → MO111 (56%)	4.9382 eV (251.07 nm)	0.0606
S_{18}	MO106 → MO111 (38%) MO107 → MO114 (62%)	4.9454 eV (250.71 nm)	0.0283
S_{19}	MO106 → MO112	4.9946 eV (248.23 nm)	0.0103
S_{20}	MO101 → MO108 (37%) MO101 → MO109 (13%) MO107 → MO115 (50%)	5.0483 eV (245.60 nm)	0.0790

S_{21}	MO100 → MO109 (48%) MO102 → MO109 (12%) MO103 → MO109 (30%) MO106 → MO112 (10%)	5.0938 eV (243.40 nm)	0.0494
S_{22}	MO100 → MO109 (13%) MO104 → MO109 (22%) MO105 → MO110 (19%) MO106 → MO110 (9%) MO106 → MO113 (10%) MO107 → MO115 (27%)	5.1106 eV (242.60 nm)	0.4621
S_{23}	MO102 → MO109	5.2106 eV (237.95 nm)	0.0051
S_{24}	MO100 → MO109 (26%) MO101 → MO108 (19%) MO105 → MO110 (42%) MO107 → MO117 (13%)	5.2322 eV (236.97 nm)	0.0789
S_{25}	MO101 → MO108 (12%) MO102 → MO109 (23%) MO103 → MO109 (23%) MO105 → MO110 (29%) MO107 → MO116 (13%)	5.2447 eV (236.40 nm)	0.1257
S_{26}	MO100 → MO109 (19%) MO106 → MO114 (17%) MO107 → MO116 (64%)	5.2512 eV (236.11 nm)	0.0208
S_{27}	MO101 → MO109 (15%) MO105 → MO111 (23%) MO107 → MO117 (62%)	5.2897 eV (234.39 nm)	0.0020
S_{28}	MO106 → MO113 (43%) MO107 → MO116 (17%) MO107 → MO117 (40%)	5.2946 eV (234.17 nm)	0.0148
S_{29}	MO102 → MO113 (9%) MO105 → MO111 (41%) MO105 → MO112 (11%) MO106 → MO113 (19%) MO107 → MO118 (20%)	5.3786 eV (230.51 nm)	0.0107
S_{30}	MO101 → MO109 (35%) MO104 → MO110 (24%) MO107 → MO118 (41%)	5.4030 eV (229.47 nm)	0.0305

HOMO: MO107, LUMO: MO108

Table S32 Calculated excited states of **1OMe**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO107 → MO108	2.7226 eV (455.40 nm)	0.1378
S_2	MO106 → MO108	3.0478 eV (406.79 nm)	0.0263
S_3	MO105 → MO108 (22%) MO107 → MO109 (78%)	3.4013 eV (364.52 nm)	0.0604
S_4	MO105 → MO108	3.5581 eV (348.46 nm)	0.1254
S_5	MO102 → MO108 (17%) MO105 → MO108 (13%) MO106 → MO109 (70%)	3.7563 eV (330.07 nm)	0.0897
S_6	MO104 → MO108	3.9353 eV (315.06 nm)	0.0413
S_7	MO102 → MO108 (53%) MO104 → MO108 (21%) MO105 → MO109 (17%) MO107 → MO109 (9%)	3.9819 eV (311.37 nm)	0.1246
S_8	MO103 → MO108	4.1117 eV (301.54 nm)	0.0018
S_9	MO102 → MO109 (17%) MO107 → MO110 (83%)	4.1969 eV (295.42 nm)	0.0898
S_{10}	MO101 → MO108 (13%) MO105 → MO109 (70%) MO107 → MO110 (17%)	4.2972 eV (288.53 nm)	0.0680
S_{11}	MO106 → MO110 (86%) MO107 → MO111 (14%)	4.5368 eV (273.28 nm)	0.1816
S_{12}	MO104 → MO109	4.6047 eV (269.26 nm)	0.0050
S_{13}	MO101 → MO108 (13%) MO102 → MO109 (13%) MO104 → MO109 (21%) MO107 → MO111 (53%)	4.6362 eV (267.43 nm)	0.0199
S_{14}	MO101 → MO108 (43%) MO102 → MO109 (39%) MO106 → MO110 (18%)	4.6789 eV (264.99 nm)	0.2030
S_{15}	MO104 → MO109 (22%) MO106 → MO112 (11%) MO107 → MO112 (53%) MO107 → MO113 (14%)	4.7566 eV (260.66 nm)	0.0467
S_{16}	MO101 → MO108 (17%) MO103 → MO109 (33%) MO105 → MO110 (8%) MO106 → MO111 (13%) MO107 → MO111 (17%) MO107 → MO113 (12%)	4.8056 eV (258.00 nm)	0.2385
S_{17}	MO101 → MO108 (45%) MO105 → MO110 (22%) MO107 → MO113 (33%)	4.8307 eV (256.66 nm)	0.3914
S_{18}	MO102 → MO109 (14%) MO106 → MO111 (40%) MO107 → MO111 (15%) MO107 → MO113 (31%)	4.9310 eV (251.44 nm)	0.1525

S_{19}	MO102 → MO109 (16%) MO103 → MO109 (23%) MO107 → MO113 (61%)	4.9598 eV (249.98 nm)	0.1053
S_{20}	MO102 → MO109 (17%) MO105 → MO110 (35%) MO107 → MO113 (13%) MO107 → MO114 (35%)	5.0715 eV (244.47 nm)	0.2357
S_{21}	MO102 → MO109 (14%) MO105 → MO110 (13%) MO105 → MO112 (16%) MO106 → MO112 (57%)	5.1503 eV (240.73 nm)	0.1044
S_{22}	MO106 → MO112 (22%) MO106 → MO113 (29%) MO107 → MO114 (49%)	5.2355 eV (236.81 nm)	0.3168
S_{23}	MO106 → MO112 (27%) MO107 → MO115 (73%)	5.2840 eV (234.64 nm)	0.0311
S_{24}	MO105 → MO110 (11%) MO106 → MO113 (42%) MO107 → MO115 (47%)	5.3058 eV (233.68 nm)	0.0308
S_{25}	MO100 → MO108 (29%) MO101 → MO109 (31%) MO104 → MO110 (40%)	5.4406 eV (227.89 nm)	0.0049
S_{26}	MO104 → MO110 (62%) MO105 → MO111 (16%) MO106 → MO114 (22%)	5.4542 eV (227.32 nm)	0.0582
S_{27}	MO105 → MO111 (65%) MO106 → MO111 (21%) MO106 → MO114 (14%)	5.4723 eV (226.57 nm)	0.0106
S_{28}	MO100 → MO108 (20%) MO102 → MO110 (27%) MO105 → MO111 (16%) MO107 → MO116 (37%)	5.5066 eV (225.15 nm)	0.0157
S_{29}	MO102 → MO110 (15%) MO104 → MO110 (17%) MO106 → MO117 (14%) MO107 → MO117 (54%)	5.5434 eV (223.66 nm)	0.0359
S_{30}	MO100 → MO108 (17%) MO103 → MO111 (13%) MO106 → MO114 (39%) MO107 → MO117 (31%)	5.5651 eV (222.79 nm)	0.0278

HOMO: MO107, LUMO: MO108

Table S33 Calculated excited states of **1Me** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO099 → MO100	3.1719 eV (390.88 nm)	0.3245
S_2	MO098 → MO100 (22%) MO099 → MO101 (78%)	3.5860 eV (345.74 nm)	0.0470
S_3	MO098 → MO100	4.0200 eV (308.42 nm)	0.1713
S_4	MO098 → MO100 (17%) MO098 → MO101 (14%) MO099 → MO102 (69%)	4.2056 eV (294.80 nm)	0.1644
S_5	MO097 → MO100 (82%) MO099 → MO102 (18%)	4.3677 eV (283.86 nm)	0.0703
S_6	MO099 → MO102 (17%) MO099 → MO103 (83%)	4.4161 eV (280.76 nm)	0.2349
S_7	MO096 → MO100 (29%) MO097 → MO100 (14%) MO098 → MO101 (33%) MO099 → MO103 (24%)	4.4551 eV (278.30 nm)	0.2379
S_8	MO095 → MO100 (28%) MO096 → MO100 (13%) MO099 → MO104 (59%)	4.4774 eV (276.91 nm)	0.0034
S_9	MO092 → MO100 (14%) MO099 → MO104 (44%) MO099 → MO105 (42%)	4.5116 eV (274.81 nm)	0.0172
S_{10}	MO096 → MO100 (52%) MO097 → MO101 (14%) MO099 → MO105 (20%) MO099 → MO106 (14%)	4.5800 eV (270.71 nm)	0.2105
S_{11}	MO092 → MO100 (62%) MO094 → MO100 (38%)	4.5936 eV (269.90 nm)	0.0161
S_{12}	MO094 → MO100 (50%) MO095 → MO100 (18%) MO096 → MO100 (9%) MO098 → MO101 (10%) MO099 → MO105 (13%)	4.6409 eV (267.16 nm)	0.0204
S_{13}	MO092 → MO100 (41%) MO095 → MO100 (23%) MO096 → MO100 (19%) MO099 → MO105 (17%)	4.6960 eV (264.02 nm)	0.0082
S_{14}	MO096 → MO101 (33%) MO097 → MO101 (67%)	4.8455 eV (255.87 nm)	0.1390
S_{15}	MO093 → MO100 (32%) MO095 → MO101 (16%) MO097 → MO101 (41%) MO098 → MO102 (11%)	4.8599 eV (255.11 nm)	0.0623
S_{16}	MO093 → MO100 (15%) MO095 → MO101 (13%) MO096 → MO101 (37%) MO098 → MO102 (35%)	4.9985 eV (248.04 nm)	0.0519

S_{17}	MO095 → MO101 (78%) MO096 → MO101 (22%)	5.0084 eV (247.55 nm)	0.0248
S_{18}	MO095 → MO101 (15%) MO099 → MO107 (73%) MO099 → MO111 (12%)	5.0283 eV (246.57 nm)	0.0015
S_{19}	MO094 → MO101 (56%) MO096 → MO101 (13%) MO097 → MO104 (12%) MO099 → MO107 (19%)	5.0603 eV (245.01 nm)	0.0125
S_{20}	MO094 → MO101 (17%) MO096 → MO101 (17%) MO098 → MO102 (16%) MO099 → MO106 (50%)	5.0885 eV (243.66 nm)	0.1452
S_{21}	MO092 → MO101 (69%) MO095 → MO101 (18%) MO096 → MO101 (13%)	5.1517 eV (240.66 nm)	0.0041
S_{22}	MO093 → MO100 (54%) MO096 → MO101 (31%) MO099 → MO106 (15%)	5.2251 eV (237.29 nm)	0.5622
S_{23}	MO092 → MO101 (18%) MO095 → MO101 (18%) MO096 → MO101 (16%) MO098 → MO105 (48%)	5.2530 eV (236.03 nm)	0.0108
S_{24}	MO093 → MO100 (10%) MO094 → MO101 (14%) MO096 → MO101 (11%) MO097 → MO103 (13%) MO098 → MO104 (28%) MO098 → MO105 (24%)	5.2803 eV (234.80 nm)	0.0423
S_{25}	MO098 → MO103	5.3367 eV (232.32 nm)	0.0531
S_{26}	MO099 → MO108 (82%) MO099 → MO112 (18%)	5.3680 eV (230.97 nm)	0.0005
S_{27}	MO099 → MO109	5.4136 eV (229.03 nm)	0.0108
S_{28}	MO096 → MO102 (21%) MO097 → MO102 (13%) MO099 → MO110 (66%)	5.4440 eV (227.74 nm)	0.0808
S_{29}	MO093 → MO101 (27%) MO097 → MO102 (55%) MO098 → MO104 (18%)	5.4663 eV (226.81 nm)	0.0004
S_{30}	MO094 → MO103 (16%) MO097 → MO104 (33%) MO098 → MO104 (40%) MO098 → MO105 (11%)	5.5207 eV (224.58 nm)	0.0299

HOMO: MO099, LUMO: MO100

Table S34 Calculated excited states of **1Me**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO099 → MO100	2.8701 eV (431.98 nm)	0.1789
S_2	MO098 → MO100 (76%) MO099 → MO101 (24%)	3.4203 eV (362.50 nm)	0.0137
S_3	MO096 → MO100 (16%) MO097 → MO100 (13%) MO099 → MO101 (71%)	3.5549 eV (348.77 nm)	0.0856
S_4	MO097 → MO100	3.8048 eV (325.86 nm)	0.0542
S_5	MO096 → MO100 (83%) MO098 → MO101 (17%)	3.8876 eV (318.92 nm)	0.0982
S_6	MO095 → MO100	3.9923 eV (310.56 nm)	0.0085
S_7	MO094 → MO100 (66%) MO096 → MO100 (11%) MO099 → MO101 (11%) MO099 → MO102 (12%)	4.0463 eV (306.41 nm)	0.0496
S_8	MO094 → MO100 (30%) MO098 → MO101 (70%)	4.1371 eV (299.69 nm)	0.1357
S_9	MO094 → MO101 (14%) MO098 → MO101 (24%) MO099 → MO102 (62%)	4.3183 eV (287.11 nm)	0.1630
S_{10}	MO097 → MO101 (87%) MO099 → MO102 (13%)	4.4738 eV (277.14 nm)	0.0310
S_{11}	MO093 → MO100 (13%) MO096 → MO101 (74%) MO099 → MO102 (13%)	4.5819 eV (270.59 nm)	0.1471
S_{12}	MO095 → MO101 (87%) MO095 → MO102 (13%)	4.6725 eV (265.35 nm)	0.0081
S_{13}	MO093 → MO100 (49%) MO094 → MO101 (31%) MO098 → MO102 (9%) MO099 → MO104 (11%)	4.7193 eV (262.72 nm)	0.0429
S_{14}	MO093 → MO100 (16%) MO095 → MO101 (14%) MO098 → MO102 (17%) MO099 → MO103 (53%)	4.8244 eV (256.99 nm)	0.2081
S_{15}	MO094 → MO101 (20%) MO095 → MO101 (16%) MO099 → MO103 (25%) MO099 → MO104 (39%)	4.8468 eV (255.81 nm)	0.1257
S_{16}	MO098 → MO102 (60%) MO099 → MO104 (40%)	4.9306 eV (251.46 nm)	0.4629
S_{17}	MO094 → MO101 (37%) MO097 → MO103 (14%) MO098 → MO105 (12%) MO099 → MO106 (37%)	4.9471 eV (250.62 nm)	0.2696
S_{18}	MO094 → MO101 (25%) MO098 → MO102 (21%) MO099 → MO105 (54%)	4.9862 eV (248.66 nm)	0.1181

S_{19}	MO096 → MO102 (16%) MO097 → MO102 (19%) MO099 → MO104 (10%) MO099 → MO105 (18%) MO099 → MO106 (37%)	5.1587 eV (240.34 nm)	0.1628
S_{20}	MO095 → MO102 (55%) MO099 → MO103 (25%) MO099 → MO104 (20%)	5.1971 eV (238.56 nm)	0.0113
S_{21}	MO097 → MO102	5.2858 eV (234.56 nm)	0.0433
S_{22}	MO094 → MO101 (13%) MO096 → MO102 (38%) MO097 → MO102 (15%) MO097 → MO104 (11%) MO098 → MO103 (14%) MO098 → MO106 (9%)	5.3380 eV (232.27 nm)	0.2246
S_{23}	MO096 → MO102 (21%) MO097 → MO103 (11%) MO098 → MO105 (16%) MO099 → MO107 (52%)	5.4198 eV (228.76 nm)	0.0496
S_{24}	MO093 → MO101 (11%) MO096 → MO105 (10%) MO097 → MO104 (15%) MO098 → MO106 (13%) MO099 → MO106 (17%) MO099 → MO107 (34%)	5.4640 eV (226.91 nm)	0.0249
S_{25}	MO092 → MO100 (21%) MO093 → MO101 (62%) MO098 → MO103 (17%)	5.4934 eV (225.70 nm)	0.0023
S_{26}	MO095 → MO102 (31%) MO098 → MO103 (52%) MO099 → MO108 (17%)	5.5310 eV (224.16 nm)	0.0736
S_{27}	MO092 → MO100 (22%) MO094 → MO102 (19%) MO095 → MO102 (11%) MO096 → MO102 (8%) MO098 → MO103 (8%) MO098 → MO105 (7%) MO099 → MO108 (25%)	5.5650 eV (222.79 nm)	0.0066
S_{28}	MO095 → MO102 (36%) MO095 → MO105 (11%) MO095 → MO106 (10%) MO098 → MO104 (33%) MO098 → MO106 (10%)	5.6046 eV (221.22 nm)	0.0529
S_{29}	MO093 → MO101 (11%) MO094 → MO102 (33%) MO098 → MO105 (27%) MO098 → MO106 (29%)	5.7087 eV (217.18 nm)	0.1897

S_{30}	MO092 → MO100 (10%) MO094 → MO102 (28%) MO095 → MO103 (16%) MO095 → MO104 (11%) MO096 → MO103 (19%) MO097 → MO103 (16%)	5.7824 eV (214.42 nm)	0.1250

HOMO: MO099, LUMO: MO100

Table S35 Calculated excited states of **1H** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO091 → MO092	3.2194 eV (385.12 nm)	0.3188
S_2	MO090 → MO092 (24%) MO091 → MO093 (76%)	3.6350 eV (341.08 nm)	0.0473
S_3	MO090 → MO092 (68%) MO091 → MO094 (32%)	4.1186 eV (301.03 nm)	0.1083
S_4	MO091 → MO094	4.2310 eV (293.04 nm)	0.2329
S_5	MO091 → MO095	4.3834 eV (282.85 nm)	0.1746
S_6	MO086 → MO092 (14%) MO088 → MO092 (19%) MO089 → MO092 (19%) MO090 → MO093 (30%) MO091 → MO096 (18%)	4.5003 eV (275.50 nm)	0.2253
S_7	MO089 → MO092 (23%) MO091 → MO096 (77%)	4.5251 eV (273.99 nm)	0.0549
S_8	MO084 → MO092 (20%) MO088 → MO092 (13%) MO091 → MO096 (34%) MO091 → MO097 (33%)	4.5441 eV (272.85 nm)	0.0176
S_9	MO087 → MO092 (66%) MO091 → MO096 (14%) MO091 → MO097 (20%)	4.5874 eV (270.27 nm)	0.0370
S_{10}	MO085 → MO092 (18%) MO089 → MO092 (29%) MO091 → MO097 (53%)	4.6167 eV (268.56 nm)	0.0094
S_{11}	MO088 → MO092 (74%) MO089 → MO092 (26%)	4.6608 eV (266.02 nm)	0.1723
S_{12}	MO084 → MO092 (26%) MO087 → MO092 (15%) MO089 → MO092 (30%) MO090 → MO093 (8%) MO091 → MO097 (21%)	4.7157 eV (262.92 nm)	0.0181
S_{13}	MO084 → MO092 (17%) MO086 → MO092 (41%) MO087 → MO093 (9%) MO089 → MO092 (11%) MO090 → MO094 (9%) MO091 → MO098 (13%)	4.7455 eV (261.27 nm)	0.1784
S_{14}	MO084 → MO092 (11%) MO085 → MO092 (28%) MO086 → MO092 (7%) MO086 → MO093 (12%) MO088 → MO093 (13%) MO089 → MO093 (11%) MO091 → MO098 (18%)	4.9448 eV (250.73 nm)	0.0380
S_{15}	MO085 → MO093 (13%) MO087 → MO093 (31%) MO089 → MO093 (56%)	5.0258 eV (246.70 nm)	0.0021

S_{16}	MO085 → MO092 (17%) MO087 → MO093 (56%) MO088 → MO093 (27%)	5.0442 eV (245.79 nm)	0.0382
S_{17}	MO088 → MO093 (68%) MO090 → MO094 (32%)	5.0778 eV (244.17 nm)	0.0070
S_{18}	MO088 → MO093 (30%) MO090 → MO094 (24%) MO091 → MO099 (46%)	5.0894 eV (243.61 nm)	0.0086
S_{19}	MO086 → MO093 (62%) MO090 → MO094 (38%)	5.1196 eV (242.18 nm)	0.0834
S_{20}	MO085 → MO093 (15%) MO086 → MO093 (18%) MO087 → MO093 (18%) MO090 → MO093 (12%) MO091 → MO098 (37%)	5.1299 eV (241.69 nm)	0.1790
S_{21}	MO084 → MO093 (38%) MO086 → MO093 (15%) MO087 → MO093 (17%) MO089 → MO093 (14%) MO090 → MO094 (8%) MO091 → MO098 (8%)	5.1745 eV (239.61 nm)	0.0500
S_{22}	MO084 → MO092 (9%) MO085 → MO092 (30%) MO087 → MO093 (12%) MO090 → MO094 (30%) MO090 → MO095 (19%)	5.2792 eV (234.85 nm)	0.3233
S_{23}	MO086 → MO097 (9%) MO089 → MO092 (7%) MO089 → MO093 (11%) MO089 → MO094 (26%) MO089 → MO095 (9%) MO089 → MO098 (9%) MO090 → MO097 (29%)	5.3323 eV (232.51 nm)	0.0087
S_{24}	MO086 → MO093 (11%) MO087 → MO096 (13%) MO088 → MO095 (17%) MO090 → MO095 (59%)	5.3551 eV (231.53 nm)	0.1081
S_{25}	MO086 → MO095 (19%) MO088 → MO093 (12%) MO090 → MO095 (27%) MO090 → MO096 (32%) MO090 → MO097 (10%)	5.3844 eV (230.26 nm)	0.0477
S_{26}	MO091 → MO100	5.4369 eV (228.04 nm)	0.0006
S_{27}	MO091 → MO101 (74%) MO091 → MO102 (26%)	5.4832 eV (226.12 nm)	0.0324
S_{28}	MO091 → MO102	5.5000 eV (225.43 nm)	0.0510
S_{29}	MO087 → MO094 (9%) MO087 → MO096 (23%) MO088 → MO095 (19%) MO090 → MO096 (49%)	5.5702 eV (222.59 nm)	0.0168

S_{30}	MO083 → MO092 (11%) MO084 → MO093 (7%) MO085 → MO093 (22%) MO086 → MO094 (7%) MO087 → MO094 (19%) MO088 → MO094 (13%) MO091 → MO102 (21%)	5.6230 eV (220.50 nm)	0.1103

HOMO: MO091, LUMO: MO092

Table S36 Calculated excited states of **1H**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO091 → MO092	2.9416 eV (421.48 nm)	0.1851
S_2	MO090 → MO092 (37%) MO091 → MO093 (63%)	3.5757 eV (346.74 nm)	0.0194
S_3	MO087 → MO092 (15%) MO090 → MO092 (85%)	3.7679 eV (329.06 nm)	0.1253
S_4	MO089 → MO092 (87%) MO090 → MO092 (13%)	3.8635 eV (320.91 nm)	0.0140
S_5	MO088 → MO092	4.0022 eV (309.79 nm)	0.1224
S_6	MO087 → MO092 (50%) MO088 → MO092 (50%)	4.0429 eV (306.67 nm)	0.0144
S_7	MO086 → MO092	4.1818 eV (296.49 nm)	0.0280
S_8	MO090 → MO093 (41%) MO091 → MO094 (59%)	4.2946 eV (288.70 nm)	0.0094
S_9	MO087 → MO093 (16%) MO089 → MO093 (18%) MO090 → MO093 (66%)	4.5024 eV (275.37 nm)	0.3602
S_{10}	MO089 → MO093	4.5301 eV (273.69 nm)	0.0376
S_{11}	MO085 → MO092 (20%) MO088 → MO093 (80%)	4.6825 eV (264.78 nm)	0.2228
S_{12}	MO087 → MO093 (44%) MO088 → MO093 (43%) MO091 → MO095 (13%)	4.7174 eV (262.82 nm)	0.0348
S_{13}	MO085 → MO092 (59%) MO086 → MO093 (28%) MO091 → MO094 (13%)	4.7651 eV (260.19 nm)	0.0330
S_{14}	MO091 → MO095	4.8369 eV (256.33 nm)	0.2032
S_{15}	MO087 → MO093 (12%) MO088 → MO093 (16%) MO091 → MO096 (72%)	4.9020 eV (252.92 nm)	0.0165
S_{16}	MO086 → MO093 (44%) MO091 → MO097 (56%)	4.9566 eV (250.14 nm)	0.1623
S_{17}	MO086 → MO093 (68%) MO089 → MO095 (32%)	5.0212 eV (246.92 nm)	0.2276
S_{18}	MO090 → MO094 (77%) MO091 → MO097 (23%)	5.2145 eV (237.77 nm)	0.2461
S_{19}	MO086 → MO093 (24%) MO087 → MO094 (13%) MO090 → MO094 (19%) MO091 → MO098 (44%)	5.2360 eV (236.79 nm)	0.2780
S_{20}	MO086 → MO096 (10%) MO087 → MO094 (15%) MO088 → MO094 (34%) MO088 → MO097 (8%) MO090 → MO096 (20%) MO091 → MO096 (13%)	5.3026 eV (233.82 nm)	0.0061
S_{21}	MO089 → MO094 (81%) MO091 → MO098 (19%)	5.3302 eV (232.61 nm)	0.0247

S_{22}	MO087 → MO094 (36%) MO089 → MO095 (24%) MO091 → MO097 (12%) MO091 → MO098 (12%) MO091 → MO099 (16%)	5.4252 eV (228.53 nm)	0.1373
S_{23}	MO085 → MO093 (10%) MO088 → MO094 (13%) MO089 → MO095 (12%) MO090 → MO095 (9%) MO091 → MO099 (46%) MO091 → MO100 (10%)	5.4912 eV (225.79 nm)	0.0426
S_{24}	MO084 → MO092 (27%) MO085 → MO093 (59%) MO086 → MO094 (14%)	5.5244 eV (224.43 nm)	0.0271
S_{25}	MO085 → MO093 (8%) MO086 → MO094 (8%) MO087 → MO094 (14%) MO087 → MO097 (9%) MO087 → MO098 (9%) MO090 → MO097 (12%) MO090 → MO098 (9%) MO091 → MO099 (31%)	5.5305 eV (224.18 nm)	0.0398
S_{26}	MO084 → MO092 (42%) MO087 → MO094 (14%) MO090 → MO097 (10%) MO091 → MO100 (34%)	5.6240 eV (220.45 nm)	0.0219
S_{27}	MO086 → MO094 (8%) MO087 → MO094 (15%) MO087 → MO096 (9%) MO088 → MO094 (23%) MO088 → MO098 (8%) MO090 → MO095 (37%)	5.6846 eV (218.11 nm)	0.0319
S_{28}	MO084 → MO092 (10%) MO086 → MO094 (21%) MO088 → MO097 (11%) MO090 → MO095 (27%) MO090 → MO096 (31%)	5.7320 eV (216.30 nm)	0.0036
S_{29}	MO086 → MO094 (41%) MO088 → MO095 (15%) MO090 → MO098 (15%) MO091 → MO100 (29%)	5.7881 eV (214.20 nm)	0.2507
S_{30}	MO084 → MO092 (47%) MO086 → MO094 (14%) MO087 → MO095 (39%)	5.8800 eV (210.86 nm)	0.0301

HOMO: MO091, LUMO: MO092

Table S37 Calculated excited states of **1F** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO098 → MO101 (14%) MO099 → MO100 (86%)	3.2372 eV (383.00 nm)	0.3162
S_2	MO099 → MO101	3.6512 eV (339.57 nm)	0.0451
S_3	MO098 → MO100 (73%) MO099 → MO101 (27%)	4.1075 eV (301.85 nm)	0.1509
S_4	MO098 → MO100 (26%) MO099 → MO102 (74%)	4.2417 eV (292.30 nm)	0.1486
S_5	MO099 → MO103	4.3269 eV (286.54 nm)	0.0165
S_6	MO099 → MO104	4.3801 eV (283.06 nm)	0.0116
S_7	MO099 → MO105	4.4802 eV (276.74 nm)	0.2067
S_8	MO092 → MO100 (16%) MO097 → MO100 (68%) MO099 → MO105 (16%)	4.5017 eV (275.42 nm)	0.0227
S_9	MO096 → MO100 (29%) MO098 → MO101 (30%) MO099 → MO105 (41%)	4.5370 eV (273.27 nm)	0.2845
S_{10}	MO092 → MO100 (71%) MO095 → MO100 (29%)	4.6293 eV (267.82 nm)	0.0063
S_{11}	MO096 → MO100 (66%) MO098 → MO102 (15%) MO099 → MO106 (19%)	4.6992 eV (263.84 nm)	0.2329
S_{12}	MO094 → MO100 (14%) MO095 → MO100 (65%) MO098 → MO104 (21%)	4.8896 eV (253.57 nm)	0.0072
S_{13}	MO092 → MO100 (11%) MO094 → MO100 (45%) MO096 → MO100 (8%) MO097 → MO101 (16%) MO099 → MO106 (20%)	4.9270 eV (251.64 nm)	0.0010
S_{14}	MO096 → MO100 (18%) MO096 → MO101 (11%) MO097 → MO101 (43%) MO099 → MO106 (28%)	4.9332 eV (251.33 nm)	0.0804
S_{15}	MO092 → MO101 (9%) MO093 → MO100 (31%) MO097 → MO101 (30%) MO098 → MO102 (30%)	4.9885 eV (248.54 nm)	0.1452
S_{16}	MO096 → MO100 (11%) MO096 → MO101 (44%) MO098 → MO102 (33%) MO099 → MO107 (12%)	5.0950 eV (243.34 nm)	0.0745
S_{17}	MO092 → MO101 (58%) MO095 → MO101 (29%) MO099 → MO107 (13%)	5.1035 eV (242.94 nm)	0.0096
S_{18}	MO097 → MO101 (17%) MO099 → MO107 (83%)	5.1160 eV (242.35 nm)	0.0223

S_{19}	MO092 → MO101 (7%) MO093 → MO100 (7%) MO096 → MO101 (14%) MO098 → MO101 (8%) MO098 → MO102 (11%) MO098 → MO103 (9%) MO099 → MO106 (21%) MO099 → MO107 (23%)	5.1320 eV (241.59 nm)	0.1860
S_{20}	MO093 → MO100 (12%) MO094 → MO100 (10%) MO096 → MO101 (10%) MO097 → MO101 (11%) MO097 → MO103 (10%) MO098 → MO103 (47%)	5.1784 eV (239.42 nm)	0.0988
S_{21}	MO095 → MO101 (23%) MO095 → MO106 (14%) MO098 → MO104 (63%)	5.2015 eV (238.36 nm)	0.0044
S_{22}	MO093 → MO100 (43%) MO094 → MO101 (15%) MO096 → MO101 (30%) MO097 → MO101 (12%)	5.2897 eV (234.39 nm)	0.3768
S_{23}	MO094 → MO101 (39%) MO094 → MO105 (9%) MO096 → MO103 (10%) MO097 → MO102 (11%) MO098 → MO103 (31%)	5.3500 eV (231.75 nm)	0.0136
S_{24}	MO095 → MO101	5.3814 eV (230.39 nm)	0.0071
S_{25}	MO094 → MO101 (35%) MO097 → MO103 (16%) MO098 → MO105 (49%)	5.4271 eV (228.46 nm)	0.0314
S_{26}	MO093 → MO101 (19%) MO094 → MO101 (10%) MO098 → MO105 (11%) MO099 → MO108 (25%) MO099 → MO109 (35%)	5.4650 eV (226.87 nm)	0.0577
S_{27}	MO094 → MO105 (10%) MO097 → MO102 (15%) MO098 → MO105 (23%) MO099 → MO108 (42%) MO099 → MO110 (10%)	5.4965 eV (225.57 nm)	0.0110
S_{28}	MO094 → MO101 (23%) MO094 → MO102 (12%) MO097 → MO103 (28%) MO099 → MO108 (37%)	5.5152 eV (224.80 nm)	0.0080
S_{29}	MO096 → MO102 (13%) MO099 → MO109 (37%) MO099 → MO110 (50%)	5.5705 eV (222.57 nm)	0.0313

S_{30}	MO093 → MO100 (10%) MO093 → MO101 (25%) MO097 → MO102 (37%) MO097 → MO103 (16%) MO099 → MO110 (12%)	5.5913 eV (221.75 nm)	0.0027

HOMO: MO099, LUMO: MO100

Table S38 Calculated excited states of **1F**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO099 → MO100	2.9671 eV (417.86 nm)	0.1856
S_2	MO098 → MO100	3.5755 eV (346.76 nm)	0.0069
S_3	MO097 → MO100 (14%) MO098 → MO100 (45%) MO099 → MO101 (41%)	3.6954 eV (335.51 nm)	0.0974
S_4	MO097 → MO100	4.0073 eV (309.40 nm)	0.1918
S_5	MO095 → MO100 (45%) MO096 → MO100 (55%)	4.1222 eV (300.77 nm)	0.0113
S_6	MO094 → MO100 (32%) MO096 → MO100 (68%)	4.1491 eV (298.82 nm)	0.0131
S_7	MO097 → MO100 (20%) MO098 → MO101 (80%)	4.2778 eV (289.83 nm)	0.0385
S_8	MO094 → MO100 (54%) MO095 → MO100 (33%) MO098 → MO101 (13%)	4.2985 eV (288.43 nm)	0.0068
S_9	MO095 → MO101 (9%) MO097 → MO101 (15%) MO098 → MO101 (35%) MO099 → MO102 (41%)	4.4288 eV (279.95 nm)	0.2192
S_{10}	MO093 → MO100 (16%) MO097 → MO101 (84%)	4.6832 eV (264.75 nm)	0.2638
S_{11}	MO097 → MO101 (22%) MO099 → MO103 (78%)	4.7029 eV (263.64 nm)	0.0152
S_{12}	MO093 → MO100 (54%) MO094 → MO101 (17%) MO099 → MO102 (15%) MO099 → MO104 (14%)	4.7621 eV (260.35 nm)	0.0222
S_{13}	MO096 → MO101 (69%) MO099 → MO104 (31%)	4.7780 eV (259.49 nm)	0.0474
S_{14}	MO097 → MO101 (25%) MO099 → MO104 (75%)	4.8455 eV (255.88 nm)	0.0550
S_{15}	MO093 → MO100 (25%) MO095 → MO101 (40%) MO098 → MO102 (12%) MO099 → MO106 (23%)	4.9418 eV (250.89 nm)	0.3346
S_{16}	MO094 → MO101 (39%) MO095 → MO101 (29%) MO098 → MO103 (10%) MO099 → MO103 (10%) MO099 → MO105 (12%)	4.9659 eV (249.67 nm)	0.0129
S_{17}	MO093 → MO100 (10%) MO095 → MO101 (12%) MO098 → MO102 (9%) MO099 → MO104 (9%) MO099 → MO105 (44%) MO099 → MO106 (16%)	5.0162 eV (247.17 nm)	0.2272

S_{18}	MO094 → MO101 (16%) MO098 → MO102 (84%)	5.1153 eV (242.38 nm)	0.2261
S_{19}	MO094 → MO101 (19%) MO097 → MO102 (18%) MO099 → MO106 (63%)	5.2107 eV (237.94 nm)	0.3310
S_{20}	MO094 → MO105 (11%) MO094 → MO106 (14%) MO095 → MO106 (11%) MO098 → MO103 (53%) MO099 → MO103 (11%)	5.2563 eV (235.88 nm)	0.0139
S_{21}	MO097 → MO104 (32%) MO098 → MO104 (55%) MO099 → MO105 (13%)	5.3814 eV (230.39 nm)	0.0572
S_{22}	MO097 → MO102 (85%) MO098 → MO104 (15%)	5.4634 eV (226.94 nm)	0.1674
S_{23}	MO093 → MO101 (64%) MO094 → MO102 (17%) MO099 → MO108 (19%)	5.5248 eV (224.42 nm)	0.0289
S_{24}	MO099 → MO107	5.5308 eV (224.17 nm)	0.0015
S_{25}	MO095 → MO102 (25%) MO096 → MO102 (58%) MO097 → MO104 (17%)	5.5988 eV (221.45 nm)	0.0027
S_{26}	MO092 → MO100 (23%) MO094 → MO102 (10%) MO096 → MO102 (38%) MO098 → MO104 (16%) MO099 → MO108 (13%)	5.6369 eV (219.95 nm)	0.0254
S_{27}	MO094 → MO102 (10%) MO095 → MO102 (16%) MO097 → MO103 (8%) MO098 → MO103 (20%) MO098 → MO104 (19%) MO098 → MO105 (27%)	5.6778 eV (218.36 nm)	0.0229
S_{28}	MO092 → MO100 (10%) MO095 → MO102 (28%) MO097 → MO103 (10%) MO098 → MO103 (16%) MO098 → MO106 (17%) MO099 → MO108 (19%)	5.7430 eV (215.89 nm)	0.1244
S_{29}	MO094 → MO102 (44%) MO097 → MO103 (23%) MO097 → MO104 (17%) MO098 → MO103 (16%)	5.7685 eV (214.93 nm)	0.1520
S_{30}	MO092 → MO100 (20%) MO093 → MO101 (9%) MO096 → MO104 (9%) MO097 → MO104 (27%) MO098 → MO105 (25%) MO098 → MO106 (10%)	5.8495 eV (211.96 nm)	0.0189

HOMO: MO099, LUMO: MO100

Table S39 Calculated excited states of **1Cl** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO107 → MO108	3.2250 eV (384.45 nm)	0.3516
S_2	MO106 → MO108 (25%) MO107 → MO109 (75%)	3.6462 eV (340.04 nm)	0.0544
S_3	MO106 → MO108 (57%) MO107 → MO110 (43%)	4.0908 eV (303.08 nm)	0.0631
S_4	MO107 → MO110 (79%) MO107 → MO111 (21%)	4.1739 eV (297.05 nm)	0.4402
S_5	MO107 → MO111	4.2455 eV (292.04 nm)	0.1264
S_6	MO107 → MO112	4.3311 eV (286.26 nm)	0.0048
S_7	MO107 → MO112 (14%) MO107 → MO113 (86%)	4.3821 eV (282.93 nm)	0.0092
S_8	MO104 → MO108 (23%) MO104 → MO109 (10%) MO105 → MO108 (34%) MO106 → MO109 (33%)	4.4644 eV (277.71 nm)	0.1802
S_9	MO105 → MO108	4.5095 eV (274.94 nm)	0.1268
S_{10}	MO100 → MO108 (61%) MO103 → MO108 (26%) MO106 → MO109 (13%)	4.6119 eV (268.84 nm)	0.0306
S_{11}	MO100 → MO108 (21%) MO104 → MO108 (65%) MO106 → MO110 (14%)	4.6668 eV (265.67 nm)	0.2440
S_{12}	MO101 → MO108 (20%) MO103 → MO108 (52%) MO106 → MO113 (17%) MO107 → MO113 (11%)	4.8599 eV (255.12 nm)	0.0175
S_{13}	MO100 → MO108 (37%) MO101 → MO108 (63%)	4.8722 eV (254.47 nm)	0.0252
S_{14}	MO101 → MO108 (28%) MO102 → MO108 (72%)	4.9168 eV (252.16 nm)	0.0268
S_{15}	MO105 → MO109 (81%) MO106 → MO110 (19%)	4.9561 eV (250.16 nm)	0.0758
S_{16}	MO100 → MO109 (20%) MO106 → MO110 (80%)	5.0209 eV (246.94 nm)	0.0447
S_{17}	MO101 → MO108 (13%) MO101 → MO109 (9%) MO104 → MO108 (10%) MO105 → MO109 (15%) MO106 → MO111 (13%) MO107 → MO114 (32%) MO107 → MO115 (8%)	5.0555 eV (245.25 nm)	0.2155
S_{18}	MO107 → MO115	5.0818 eV (243.98 nm)	0.0073
S_{19}	MO100 → MO109 (51%) MO102 → MO109 (9%) MO103 → MO109 (27%) MO105 → MO109 (13%)	5.0938 eV (243.40 nm)	0.0269

S_{20}	MO102 → MO108 (8%) MO102 → MO109 (17%) MO102 → MO111 (17%) MO105 → MO112 (19%) MO106 → MO111 (7%) MO106 → MO112 (32%)	5.1558 eV (240.47 nm)	0.0481
S_{21}	MO100 → MO109 (9%) MO101 → MO108 (8%) MO104 → MO109 (17%) MO106 → MO110 (16%) MO106 → MO111 (35%) MO106 → MO113 (15%)	5.1678 eV (239.92 nm)	0.0193
S_{22}	MO100 → MO109 (18%) MO103 → MO110 (25%) MO106 → MO113 (57%)	5.1870 eV (239.03 nm)	0.0114
S_{23}	MO101 → MO108 (45%) MO104 → MO109 (30%) MO106 → MO110 (25%)	5.2383 eV (236.69 nm)	0.5165
S_{24}	MO106 → MO112 (81%) MO106 → MO113 (19%)	5.3323 eV (232.51 nm)	0.0097
S_{25}	MO103 → MO109 (73%) MO106 → MO113 (27%)	5.3611 eV (231.27 nm)	0.0038
S_{26}	MO107 → MO116	5.3882 eV (230.10 nm)	0.0020
S_{27}	MO107 → MO116 (22%) MO107 → MO117 (58%) MO107 → MO120 (20%)	5.4054 eV (229.37 nm)	0.0373
S_{28}	MO102 → MO109 (64%) MO106 → MO112 (19%) MO107 → MO118 (17%)	5.4405 eV (227.89 nm)	0.0025
S_{29}	MO107 → MO118 (39%) MO107 → MO119 (34%) MO107 → MO120 (27%)	5.4830 eV (226.12 nm)	0.0269
S_{30}	MO101 → MO109 (28%) MO105 → MO110 (49%) MO107 → MO119 (13%) MO107 → MO120 (10%)	5.5155 eV (224.79 nm)	0.0248

HOMO: MO107, LUMO: MO108

Table S40 Calculated excited states of **1Cl**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO107 → MO108	2.9715 eV (417.24 nm)	0.1950
S_2	MO106 → MO108 (59%) MO107 → MO109 (41%)	3.5610 eV (348.17 nm)	0.0081
S_3	MO105 → MO108 (25%) MO107 → MO109 (75%)	3.6671 eV (338.10 nm)	0.1003
S_4	MO105 → MO108 (85%) MO106 → MO109 (15%)	3.9596 eV (313.13 nm)	0.1757
S_5	MO102 → MO108 (14%) MO103 → MO108 (62%) MO105 → MO108 (12%) MO107 → MO109 (12%)	4.0953 eV (302.75 nm)	0.0666
S_6	MO104 → MO108	4.1310 eV (300.13 nm)	0.0039
S_7	MO103 → MO108 (11%) MO106 → MO109 (52%) MO107 → MO110 (37%)	4.2409 eV (292.35 nm)	0.0527
S_8	MO102 → MO108	4.2926 eV (288.83 nm)	0.0021
S_9	MO105 → MO109 (20%) MO107 → MO110 (80%)	4.3563 eV (284.61 nm)	0.2746
S_{10}	MO105 → MO109	4.6142 eV (268.70 nm)	0.2231
S_{11}	MO103 → MO109 (13%) MO105 → MO109 (22%) MO107 → MO111 (65%)	4.6798 eV (264.93 nm)	0.0482
S_{12}	MO101 → MO108	4.7136 eV (263.04 nm)	0.0060
S_{13}	MO101 → MO108 (21%) MO104 → MO109 (35%) MO105 → MO109 (8%) MO107 → MO112 (15%) MO107 → MO113 (10%) MO107 → MO114 (11%)	4.7456 eV (261.26 nm)	0.0547
S_{14}	MO101 → MO108 (25%) MO105 → MO109 (14%) MO107 → MO112 (61%)	4.7754 eV (259.63 nm)	0.2158
S_{15}	MO101 → MO108 (19%) MO106 → MO110 (15%) MO107 → MO113 (66%)	4.8521 eV (255.53 nm)	0.0382
S_{16}	MO101 → MO108 (28%) MO103 → MO109 (38%) MO104 → MO109 (15%) MO106 → MO110 (19%)	4.9005 eV (253.00 nm)	0.3091
S_{17}	MO102 → MO109 (66%) MO106 → MO110 (16%) MO107 → MO111 (18%)	4.9389 eV (251.04 nm)	0.0054
S_{18}	MO106 → MO110 (79%) MO107 → MO114 (21%)	5.0160 eV (247.18 nm)	0.2679

S_{19}	MO102 → MO109 (10%) MO103 → MO109 (27%) MO105 → MO110 (22%) MO107 → MO114 (41%)	5.1308 eV (241.65 nm)	0.4515
S_{20}	MO102 → MO109 (21%) MO102 → MO110 (20%) MO102 → MO113 (11%) MO105 → MO111 (14%) MO106 → MO111 (34%)	5.1809 eV (239.31 nm)	0.0105
S_{21}	MO104 → MO110 (10%) MO104 → MO111 (7%) MO104 → MO112 (10%) MO105 → MO110 (12%) MO106 → MO111 (7%) MO106 → MO112 (12%) MO106 → MO113 (17%) MO106 → MO114 (9%) MO107 → MO113 (7%) MO107 → MO114 (9%)	5.2911 eV (234.33 nm)	0.0663
S_{22}	MO105 → MO110 (83%) MO107 → MO116 (17%)	5.3737 eV (230.72 nm)	0.2048
S_{23}	MO101 → MO109 (56%) MO106 → MO112 (24%) MO107 → MO116 (20%)	5.4710 eV (226.62 nm)	0.0081
S_{24}	MO098 → MO108 (19%) MO104 → MO110 (17%) MO106 → MO111 (25%) MO106 → MO112 (39%)	5.5102 eV (225.01 nm)	0.0440
S_{25}	MO106 → MO111 (12%) MO106 → MO112 (14%) MO107 → MO115 (74%)	5.5135 eV (224.87 nm)	0.0064
S_{26}	MO101 → MO109 (27%) MO103 → MO110 (53%) MO106 → MO112 (20%)	5.5433 eV (223.66 nm)	0.0016
S_{27}	MO104 → MO110	5.5576 eV (223.09 nm)	0.0283
S_{28}	MO100 → MO108 (53%) MO101 → MO109 (10%) MO103 → MO110 (12%) MO104 → MO110 (25%)	5.5633 eV (222.86 nm)	0.0147
S_{29}	MO099 → MO108	5.6316 eV (220.16 nm)	0.0106
S_{30}	MO098 → MO108 (22%) MO099 → MO108 (10%) MO103 → MO110 (22%) MO106 → MO114 (25%) MO107 → MO116 (21%)	5.6486 eV (219.49 nm)	0.1348

HOMO: MO107, LUMO: MO108

Table S41 Calculated excited states of **1CF$_3$** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO123 → MO124	3.2547 eV (380.94 nm)	0.3731
S_2	MO122 → MO124 (27%) MO123 → MO125 (73%)	3.6811 eV (336.81 nm)	0.0758
S_3	MO123 → MO126	3.9336 eV (315.19 nm)	0.1862
S_4	MO123 → MO125 (21%) MO123 → MO126 (12%) MO123 → MO127 (67%)	4.0364 eV (307.17 nm)	0.0487
S_5	MO122 → MO124 (72%) MO123 → MO127 (28%)	4.2243 eV (293.50 nm)	0.3410
S_6	MO123 → MO128	4.3718 eV (283.60 nm)	0.0041
S_7	MO120 → MO124 (17%) MO123 → MO129 (83%)	4.4353 eV (279.54 nm)	0.0016
S_8	MO122 → MO125 (75%) MO123 → MO130 (25%)	4.5253 eV (273.98 nm)	0.2866
S_9	MO117 → MO124 (70%) MO118 → MO124 (17%) MO122 → MO125 (13%)	4.5996 eV (269.56 nm)	0.0236
S_{10}	MO121 → MO124 (35%) MO122 → MO125 (22%) MO122 → MO126 (8%) MO122 → MO127 (25%) MO123 → MO130 (10%)	4.7278 eV (262.25 nm)	0.1568
S_{11}	MO118 → MO124 (33%) MO119 → MO124 (24%) MO120 → MO124 (21%) MO122 → MO126 (12%) MO122 → MO127 (10%)	4.8313 eV (256.63 nm)	0.0655
S_{12}	MO117 → MO124 (25%) MO120 → MO124 (51%) MO122 → MO129 (12%) MO123 → MO130 (12%)	4.8697 eV (254.60 nm)	0.0276
S_{13}	MO122 → MO126	4.8971 eV (253.18 nm)	0.0758
S_{14}	MO119 → MO124	4.9290 eV (251.54 nm)	0.0089
S_{15}	MO116 → MO124 (17%) MO119 → MO124 (19%) MO122 → MO126 (18%) MO123 → MO130 (46%)	4.9519 eV (250.38 nm)	0.0630
S_{16}	MO117 → MO124 (12%) MO117 → MO125 (52%) MO118 → MO125 (14%) MO121 → MO125 (22%)	5.0549 eV (245.28 nm)	0.0010
S_{17}	MO116 → MO125 (14%) MO122 → MO127 (57%) MO123 → MO130 (29%)	5.1243 eV (241.95 nm)	0.4883

S_{18}	MO116 → MO124 (18%) MO118 → MO124 (9%) MO120 → MO125 (11%) MO121 → MO125 (45%) MO122 → MO127 (17%)	5.1345 eV (241.47 nm)	0.0628
S_{19}	MO118 → MO124 (16%) MO118 → MO126 (19%) MO119 → MO125 (31%) MO123 → MO131 (34%)	5.2040 eV (238.25 nm)	0.0434
S_{20}	MO118 → MO125 (13%) MO122 → MO128 (15%) MO123 → MO131 (72%)	5.2216 eV (237.44 nm)	0.0008
S_{21}	MO117 → MO125 (14%) MO118 → MO125 (8%) MO120 → MO125 (27%) MO120 → MO126 (19%) MO120 → MO127 (8%) MO122 → MO129 (24%)	5.2566 eV (235.86 nm)	0.0160
S_{22}	MO116 → MO124 (60%) MO119 → MO125 (26%) MO122 → MO127 (14%)	5.2989 eV (233.98 nm)	0.0940
S_{23}	MO118 → MO125 (29%) MO119 → MO125 (34%) MO120 → MO125 (22%) MO122 → MO128 (15%)	5.3472 eV (231.87 nm)	0.1346
S_{24}	MO116 → MO124 (11%) MO117 → MO125 (24%) MO120 → MO125 (37%) MO122 → MO128 (28%)	5.3723 eV (230.79 nm)	0.0328
S_{25}	MO119 → MO125 (22%) MO120 → MO126 (13%) MO122 → MO128 (47%) MO122 → MO129 (18%)	5.3772 eV (230.57 nm)	0.0143
S_{26}	MO118 → MO127 (14%) MO118 → MO128 (11%) MO119 → MO125 (25%) MO121 → MO126 (50%)	5.4850 eV (226.04 nm)	0.0273
S_{27}	MO118 → MO125 (18%) MO118 → MO126 (19%) MO121 → MO126 (24%) MO123 → MO133 (39%)	5.5256 eV (224.38 nm)	0.0438
S_{28}	MO116 → MO125 (14%) MO118 → MO126 (15%) MO119 → MO127 (13%) MO121 → MO126 (34%) MO122 → MO129 (10%) MO123 → MO132 (14%)	5.5444 eV (223.62 nm)	0.0055
S_{29}	MO123 → MO132 (61%) MO123 → MO133 (28%) MO123 → MO135 (11%)	5.5868 eV (221.92 nm)	0.0016

S_{30}	MO116 → MO129 (12%) MO117 → MO126 (11%) MO117 → MO127 (14%) MO121 → MO129 (16%) MO122 → MO129 (47%)	5.5970 eV (221.52 nm)	0.0233

HOMO: MO123, LUMO: MO124

Table S42 Calculated excited states of **1CF$_3$**·H$^+$ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO123 → MO124	3.0545 eV (405.91 nm)	0.2112
S_2	MO119 → MO124 (10%) MO122 → MO124 (32%) MO123 → MO125 (58%)	3.6625 eV (338.52 nm)	0.0332
S_3	MO122 → MO124	3.9417 eV (314.54 nm)	0.2516
S_4	MO121 → MO124	4.1737 eV (297.06 nm)	0.0060
S_5	MO122 → MO124 (15%) MO122 → MO125 (20%) MO123 → MO126 (65%)	4.1932 eV (295.68 nm)	0.0568
S_6	MO119 → MO124 (47%) MO120 → MO124 (22%) MO123 → MO126 (31%)	4.2902 eV (289.00 nm)	0.0593
S_7	MO120 → MO124	4.3407 eV (285.63 nm)	0.0008
S_8	MO118 → MO124 (63%) MO119 → MO124 (15%) MO123 → MO126 (22%)	4.4293 eV (279.92 nm)	0.0970
S_9	MO123 → MO127	4.4848 eV (276.46 nm)	0.1831
S_{10}	MO118 → MO124 (20%) MO122 → MO125 (41%) MO123 → MO127 (27%) MO123 → MO128 (12%)	4.5686 eV (271.39 nm)	0.4026
S_{11}	MO120 → MO125 (18%) MO120 → MO126 (11%) MO123 → MO128 (58%) MO123 → MO129 (13%)	4.7363 eV (261.77 nm)	0.0170
S_{12}	MO121 → MO125 (69%) MO121 → MO127 (12%) MO123 → MO130 (19%)	4.7649 eV (260.20 nm)	0.0214
S_{13}	MO118 → MO125 (13%) MO121 → MO125 (18%) MO122 → MO125 (23%) MO123 → MO129 (46%)	4.8319 eV (256.59 nm)	0.0668
S_{14}	MO117 → MO124 (78%) MO123 → MO129 (22%)	4.8957 eV (253.25 nm)	0.0950
S_{15}	MO119 → MO125 (36%) MO120 → MO125 (18%) MO121 → MO125 (20%) MO123 → MO129 (26%)	4.9208 eV (251.96 nm)	0.1024
S_{16}	MO120 → MO125	4.9515 eV (250.40 nm)	0.0078
S_{17}	MO117 → MO124 (8%) MO117 → MO125 (8%) MO118 → MO125 (13%) MO119 → MO125 (15%) MO121 → MO127 (6%) MO122 → MO125 (9%) MO123 → MO129 (12%) MO123 → MO130 (29%)	5.0788 eV (244.12 nm)	0.2880

S_{18}	MO122 → MO126 (81%) MO123 → MO129 (19%)	5.1271 eV (241.82 nm)	0.1126
S_{19}	MO117 → MO124 (20%) MO118 → MO125 (38%) MO122 → MO126 (42%)	5.2607 eV (235.68 nm)	0.6173
S_{20}	MO120 → MO126	5.2866 eV (234.53 nm)	0.0071
S_{21}	MO119 → MO129 (14%) MO121 → MO126 (27%) MO121 → MO127 (36%) MO122 → MO127 (11%) MO122 → MO130 (12%)	5.3345 eV (232.42 nm)	0.0169
S_{22}	MO117 → MO125 (23%) MO122 → MO127 (77%)	5.4306 eV (228.31 nm)	0.0099
S_{23}	MO119 → MO126 (17%) MO121 → MO126 (56%) MO122 → MO127 (27%)	5.4744 eV (226.48 nm)	0.0125
S_{24}	MO119 → MO126 (49%) MO120 → MO126 (20%) MO121 → MO127 (12%) MO123 → MO131 (19%)	5.5516 eV (223.33 nm)	0.0688
S_{25}	MO116 → MO124 (16%) MO117 → MO125 (58%) MO123 → MO131 (26%)	5.5599 eV (223.00 nm)	0.0417
S_{26}	MO123 → MO131 (38%) MO123 → MO132 (62%)	5.6341 eV (220.06 nm)	0.0041
S_{27}	MO116 → MO124 (34%) MO117 → MO125 (10%) MO118 → MO126 (15%) MO119 → MO126 (14%) MO123 → MO132 (27%)	5.6708 eV (218.64 nm)	0.0713
S_{28}	MO118 → MO126 (42%) MO120 → MO126 (11%) MO122 → MO128 (29%) MO123 → MO131 (18%)	5.7037 eV (217.38 nm)	0.0011
S_{29}	MO120 → MO126 (26%) MO120 → MO127 (11%) MO122 → MO128 (37%) MO122 → MO129 (26%)	5.7810 eV (214.47 nm)	0.0255
S_{30}	MO116 → MO124 (24%) MO119 → MO127 (42%) MO120 → MO127 (21%) MO122 → MO130 (13%)	5.8555 eV (211.74 nm)	0.0393

HOMO: MO123, LUMO: MO124

Table S43 Calculated excited states of **1CN** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO103 → MO104	3.1806 eV (389.81 nm)	0.4577
S_2	MO102 → MO104 (15%) MO103 → MO105 (85%)	3.5247 eV (351.76 nm)	0.2204
S_3	MO102 → MO104 (18%) MO103 → MO106 (82%)	3.6814 eV (336.78 nm)	0.1011
S_4	MO103 → MO106 (22%) MO103 → MO107 (78%)	3.8218 eV (324.41 nm)	0.0010
S_5	MO102 → MO104 (68%) MO103 → MO107 (32%)	4.1405 eV (299.44 nm)	0.5622
S_6	MO103 → MO108	4.3356 eV (285.97 nm)	0.0096
S_7	MO099 → MO104 (20%) MO099 → MO106 (11%) MO103 → MO109 (69%)	4.3909 eV (282.37 nm)	0.0003
S_8	MO101 → MO104 (17%) MO102 → MO105 (61%) MO102 → MO106 (22%)	4.4198 eV (280.52 nm)	0.1285
S_9	MO101 → MO104 (73%) MO102 → MO106 (27%)	4.5465 eV (272.70 nm)	0.0279
S_{10}	MO097 → MO104 (31%) MO099 → MO104 (17%) MO100 → MO104 (19%) MO102 → MO106 (33%)	4.5714 eV (271.22 nm)	0.0815
S_{11}	MO102 → MO106 (58%) MO102 → MO107 (28%) MO103 → MO110 (14%)	4.5818 eV (270.60 nm)	0.0578
S_{12}	MO097 → MO104 (24%) MO099 → MO104 (14%) MO101 → MO104 (37%) MO102 → MO107 (10%) MO103 → MO110 (15%)	4.6640 eV (265.83 nm)	0.0610
S_{13}	MO099 → MO104 (52%) MO099 → MO106 (17%) MO101 → MO109 (13%) MO102 → MO109 (18%)	4.7862 eV (259.05 nm)	0.0304
S_{14}	MO099 → MO104 (15%) MO100 → MO104 (28%) MO102 → MO107 (13%) MO103 → MO110 (44%)	4.8027 eV (258.16 nm)	0.0346
S_{15}	MO098 → MO104 (42%) MO098 → MO105 (14%) MO100 → MO104 (11%) MO100 → MO105 (10%) MO100 → MO108 (11%) MO101 → MO105 (12%)	4.8733 eV (254.41 nm)	0.0170
S_{16}	MO100 → MO104 (21%) MO101 → MO105 (66%) MO102 → MO107 (13%)	4.9337 eV (251.30 nm)	0.0790

S_{17}	MO097 → MO104 (10%) MO097 → MO105 (15%) MO097 → MO106 (13%) MO099 → MO105 (10%) MO100 → MO104 (10%) MO100 → MO106 (8%) MO101 → MO104 (8%) MO102 → MO107 (26%)	4.9886 eV (248.53 nm)	0.2668
S_{18}	MO097 → MO104 (8%) MO097 → MO105 (18%) MO097 → MO106 (13%) MO098 → MO105 (15%) MO099 → MO105 (11%) MO100 → MO105 (20%) MO100 → MO108 (8%) MO103 → MO110 (7%)	5.0178 eV (247.09 nm)	0.3287
S_{19}	MO096 → MO104 (20%) MO097 → MO107 (10%) MO098 → MO105 (35%) MO100 → MO108 (13%) MO102 → MO107 (22%)	5.0563 eV (245.21 nm)	0.1109
S_{20}	MO097 → MO107 (14%) MO100 → MO105 (69%) MO100 → MO106 (17%)	5.1055 eV (242.85 nm)	0.3396
S_{21}	MO096 → MO104 (40%) MO100 → MO105 (20%) MO101 → MO106 (17%) MO101 → MO107 (13%) MO103 → MO110 (10%)	5.1594 eV (240.31 nm)	0.0803
S_{22}	MO098 → MO105 (16%) MO100 → MO106 (25%) MO101 → MO106 (59%)	5.1817 eV (239.27 nm)	0.0579
S_{23}	MO097 → MO104 (11%) MO099 → MO106 (47%) MO101 → MO109 (11%) MO102 → MO109 (31%)	5.2225 eV (237.41 nm)	0.0020
S_{24}	MO099 → MO106 (10%) MO103 → MO111 (66%) MO103 → MO114 (13%) MO103 → MO117 (11%)	5.2349 eV (236.84 nm)	0.0050
S_{25}	MO097 → MO107 (14%) MO099 → MO105 (86%)	5.2543 eV (235.97 nm)	0.0017
S_{26}	MO098 → MO105 (20%) MO102 → MO108 (80%)	5.3243 eV (232.86 nm)	0.0176
S_{27}	MO096 → MO104 (25%) MO100 → MO106 (62%) MO100 → MO107 (13%)	5.3470 eV (231.88 nm)	0.0109
S_{28}	MO100 → MO106 (42%) MO101 → MO107 (58%)	5.4142 eV (229.00 nm)	0.0711

S_{29}	MO096 → MO105 (17%) MO097 → MO106 (14%) MO097 → MO107 (16%) MO101 → MO107 (11%) MO103 → MO113 (42%)	5.4468 eV (227.63 nm)	0.0714
S_{30}	MO097 → MO104 (10%) MO097 → MO106 (21%) MO097 → MO107 (25%) MO099 → MO106 (8%) MO099 → MO107 (12%) MO101 → MO107 (16%) MO102 → MO110 (8%)	5.4543 eV (227.32 nm)	0.0482

HOMO: MO103, LUMO: MO104

Table S44 Calculated excited states of **1CN**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO103 → MO104	3.0586 eV (405.36 nm)	0.2351
S_2	MO102 → MO104 (30%) MO103 → MO105 (70%)	3.6338 eV (341.20 nm)	0.0757
S_3	MO102 → MO104	3.8640 eV (320.87 nm)	0.1695
S_4	MO102 → MO104 (35%) MO103 → MO106 (65%)	4.0048 eV (309.59 nm)	0.2206
S_5	MO102 → MO104 (15%) MO103 → MO107 (85%)	4.1115 eV (301.56 nm)	0.1603
S_6	MO098 → MO104 (11%) MO100 → MO104 (11%) MO101 → MO104 (44%) MO103 → MO106 (13%) MO103 → MO107 (21%)	4.2210 eV (293.73 nm)	0.0528
S_7	MO098 → MO104 (19%) MO100 → MO104 (69%) MO103 → MO107 (12%)	4.2500 eV (291.72 nm)	0.0101
S_8	MO098 → MO104 (58%) MO102 → MO105 (42%)	4.3412 eV (285.60 nm)	0.1422
S_9	MO098 → MO104 (20%) MO099 → MO104 (56%) MO102 → MO105 (24%)	4.4068 eV (281.35 nm)	0.0657
S_{10}	MO100 → MO104 (15%) MO102 → MO105 (66%) MO103 → MO109 (19%)	4.4338 eV (279.63 nm)	0.2874
S_{11}	MO099 → MO105 (18%) MO102 → MO105 (20%) MO103 → MO108 (51%) MO103 → MO109 (11%)	4.6551 eV (266.34 nm)	0.0951
S_{12}	MO098 → MO105 (13%) MO099 → MO105 (10%) MO099 → MO106 (10%) MO101 → MO105 (28%) MO103 → MO109 (39%)	4.6989 eV (263.86 nm)	0.0315
S_{13}	MO098 → MO105 (13%) MO100 → MO105 (44%) MO103 → MO109 (19%) MO103 → MO110 (24%)	4.7539 eV (260.81 nm)	0.0402
S_{14}	MO097 → MO104 (26%) MO100 → MO105 (25%) MO101 → MO105 (31%) MO102 → MO106 (18%)	4.7915 eV (258.76 nm)	0.2169
S_{15}	MO101 → MO105 (43%) MO103 → MO108 (31%) MO103 → MO110 (26%)	4.8781 eV (254.16 nm)	0.0531
S_{16}	MO098 → MO105 (45%) MO102 → MO106 (55%)	4.9038 eV (252.83 nm)	0.0487

S_{17}	MO098 → MO105 (16%) MO099 → MO105 (65%) MO103 → MO110 (19%)	4.9065 eV (252.70 nm)	0.0275
S_{18}	MO097 → MO104 (17%) MO098 → MO105 (22%) MO100 → MO107 (13%) MO103 → MO109 (12%) MO103 → MO110 (36%)	4.9714 eV (249.39 nm)	0.1216
S_{19}	MO101 → MO107 (14%) MO102 → MO107 (86%)	5.0305 eV (246.47 nm)	0.1917
S_{20}	MO097 → MO104 (14%) MO098 → MO105 (31%) MO100 → MO105 (15%) MO101 → MO107 (28%) MO103 → MO108 (12%)	5.1150 eV (242.39 nm)	0.5182
S_{21}	MO098 → MO105 (17%) MO100 → MO107 (43%) MO101 → MO106 (26%) MO102 → MO110 (14%)	5.1824 eV (239.24 nm)	0.0128
S_{22}	MO098 → MO106 (29%) MO098 → MO108 (14%) MO099 → MO106 (57%)	5.1896 eV (238.91 nm)	0.0111
S_{23}	MO098 → MO106 (12%) MO100 → MO106 (13%) MO101 → MO106 (63%) MO103 → MO110 (12%)	5.2343 eV (236.87 nm)	0.1586
S_{24}	MO100 → MO106	5.2907 eV (234.34 nm)	0.0731
S_{25}	MO098 → MO106 (53%) MO100 → MO107 (20%) MO101 → MO107 (27%)	5.4130 eV (229.05 nm)	0.2269
S_{26}	MO097 → MO105 (38%) MO100 → MO107 (28%) MO101 → MO107 (34%)	5.4291 eV (228.37 nm)	0.0667
S_{27}	MO097 → MO105 (25%) MO098 → MO105 (10%) MO098 → MO106 (26%) MO102 → MO108 (20%) MO103 → MO111 (19%)	5.4827 eV (226.14 nm)	0.0020
S_{28}	MO098 → MO107	5.5711 eV (222.55 nm)	0.0851
S_{29}	MO096 → MO104 (26%) MO101 → MO107 (12%) MO102 → MO108 (27%) MO103 → MO111 (35%)	5.6004 eV (221.38 nm)	0.0016
S_{30}	MO098 → MO107 (46%) MO099 → MO107 (54%)	5.6235 eV (220.47 nm)	0.0006

HOMO: MO103, LUMO: MO104

Table S45 Calculated excited states of **1NO$_2$** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO113 → MO114	2.5049 eV (494.96 nm)	0.2538
S_2	MO113 → MO115	2.5611 eV (484.11 nm)	0.2283
S_3	MO112 → MO115 (38%) MO112 → MO117 (9%) MO113 → MO116 (43%) MO113 → MO117 (10%)	3.3640 eV (368.57 nm)	0.0926
S_4	MO112 → MO114 (55%) MO112 → MO115 (45%)	3.4303 eV (361.44 nm)	0.2586
S_5	MO112 → MO114 (49%) MO113 → MO116 (51%)	3.4598 eV (358.36 nm)	0.0960
S_6	MO105 → MO114 (46%) MO105 → MO115 (54%)	3.7748 eV (328.45 nm)	0.0106
S_7	MO104 → MO114	3.7883 eV (327.29 nm)	0.0004
S_8	MO105 → MO114 (17%) MO105 → MO115 (20%) MO113 → MO117 (63%)	3.7949 eV (326.72 nm)	0.1087
S_9	MO110 → MO114 (41%) MO110 → MO115 (49%) MO111 → MO115 (10%)	3.8804 eV (319.51 nm)	0.0176
S_{10}	MO108 → MO114 (64%) MO111 → MO115 (36%)	3.9193 eV (316.35 nm)	0.0179
S_{11}	MO108 → MO114 (12%) MO111 → MO114 (48%) MO111 → MO115 (40%)	4.0220 eV (308.27 nm)	0.1183
S_{12}	MO108 → MO115 (34%) MO111 → MO115 (66%)	4.0355 eV (307.23 nm)	0.0031
S_{13}	MO109 → MO114	4.2243 eV (293.51 nm)	0.3828
S_{14}	MO110 → MO114	4.2466 eV (291.96 nm)	0.0005
S_{15}	MO107 → MO114 (16%) MO107 → MO115 (31%) MO108 → MO114 (14%) MO108 → MO115 (20%) MO110 → MO114 (19%)	4.2828 eV (289.50 nm)	0.0166
S_{16}	MO107 → MO114 (7%) MO107 → MO115 (12%) MO108 → MO115 (15%) MO109 → MO114 (27%) MO109 → MO115 (20%) MO112 → MO116 (19%)	4.3058 eV (287.95 nm)	0.0729
S_{17}	MO112 → MO116 (72%) MO113 → MO117 (28%)	4.3199 eV (287.01 nm)	0.0077
S_{18}	MO108 → MO114 (43%) MO108 → MO115 (57%)	4.3557 eV (284.65 nm)	0.0022

S_{19}	MO108 → MO114 (10%) MO112 → MO116 (22%) MO113 → MO117 (10%) MO113 → MO118 (44%) MO113 → MO119 (14%)	4.3719 eV (283.59 nm)	0.0123
S_{20}	MO101 → MO114 (46%) MO101 → MO115 (54%)	4.4009 eV (281.73 nm)	0.0019
S_{21}	MO099 → MO114 (68%) MO100 → MO115 (32%)	4.4052 eV (281.45 nm)	0.0003
S_{22}	MO107 → MO114 (43%) MO113 → MO119 (19%) MO113 → MO120 (38%)	4.4388 eV (279.32 nm)	0.0021
S_{23}	MO107 → MO115 (18%) MO113 → MO119 (33%) MO113 → MO120 (49%)	4.4418 eV (279.13 nm)	0.0066
S_{24}	MO113 → MO119	4.4620 eV (277.87 nm)	0.0263
S_{25}	MO106 → MO114 (44%) MO106 → MO115 (45%) MO112 → MO117 (11%)	4.6168 eV (268.55 nm)	0.1327
S_{26}	MO106 → MO115	4.6651 eV (265.77 nm)	0.0253
S_{27}	MO107 → MO116 (16%) MO110 → MO116 (9%) MO111 → MO116 (23%) MO111 → MO117 (7%) MO112 → MO117 (26%) MO113 → MO119 (12%) MO113 → MO121 (7%)	4.6841 eV (264.69 nm)	0.1653
S_{28}	MO107 → MO115 (13%) MO107 → MO116 (43%) MO107 → MO117 (9%) MO108 → MO116 (9%) MO110 → MO116 (26%)	4.7107 eV (263.20 nm)	0.0640
S_{29}	MO113 → MO121	4.7701 eV (259.92 nm)	0.0690
S_{30}	MO111 → MO116 (69%) MO111 → MO117 (15%) MO113 → MO121 (16%)	4.9446 eV (250.75 nm)	0.4937

HOMO: MO113, LUMO: MO114

Table S46 Calculated excited states of $\mathbf{1NO_2}\cdot H^+$ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
S_1	MO113 → MO114	2.9572 eV (419.27 nm)	0.2574
S_2	MO113 → MO115	3.0872 eV (401.61 nm)	0.1925
S_3	MO113 → MO114 (16%) MO113 → MO116 (84%)	3.1618 eV (392.13 nm)	0.0403
S_4	MO112 → MO114 (44%) MO113 → MO117 (56%)	3.7197 eV (333.32 nm)	0.0314
S_5	MO105 → MO114 (56%) MO105 → MO116 (18%) MO106 → MO114 (14%) MO113 → MO117 (12%)	3.7798 eV (328.02 nm)	0.0098
S_6	MO106 → MO114 (18%) MO106 → MO115 (54%) MO107 → MO115 (28%)	3.7926 eV (326.91 nm)	0.0002
S_7	MO105 → MO114 (16%) MO112 → MO114 (60%) MO112 → MO116 (24%)	3.8730 eV (320.13 nm)	0.3339
S_8	MO111 → MO114 (20%) MO111 → MO115 (45%) MO112 → MO115 (35%)	3.9583 eV (313.23 nm)	0.0204
S_9	MO112 → MO115	4.0094 eV (309.23 nm)	0.1661
S_{10}	MO109 → MO114 (17%) MO110 → MO114 (69%) MO110 → MO116 (14%)	4.0259 eV (307.96 nm)	0.0162
S_{11}	MO112 → MO115 (25%) MO112 → MO116 (47%) MO113 → MO117 (28%)	4.0520 eV (305.98 nm)	0.1530
S_{12}	MO111 → MO114	4.2229 eV (293.60 nm)	0.0087
S_{13}	MO109 → MO114 (74%) MO109 → MO115 (13%) MO113 → MO118 (13%)	4.3126 eV (287.49 nm)	0.0972
S_{14}	MO102 → MO114 (75%) MO102 → MO116 (25%)	4.3760 eV (283.33 nm)	0.0011
S_{15}	MO104 → MO114 (24%) MO104 → MO115 (76%)	4.3885 eV (282.52 nm)	0.0624
S_{16}	MO108 → MO116 (13%) MO111 → MO114 (20%) MO111 → MO116 (67%)	4.3960 eV (282.04 nm)	0.0069
S_{17}	MO104 → MO114 (9%) MO104 → MO115 (28%) MO109 → MO115 (44%) MO109 → MO116 (19%)	4.4018 eV (281.67 nm)	0.1871
S_{18}	MO108 → MO114 (38%) MO111 → MO116 (21%) MO112 → MO117 (23%) MO113 → MO118 (18%)	4.4236 eV (280.28 nm)	0.0450
S_{19}	MO110 → MO116	4.4944 eV (275.86 nm)	0.0003

S_{20}	MO109 → MO114 (26%) MO109 → MO116 (74%)	4.5011 eV (275.45 nm)	0.0078
S_{21}	MO112 → MO117 (30%) MO113 → MO118 (70%)	4.5127 eV (274.75 nm)	0.0703
S_{22}	MO109 → MO115 (10%) MO109 → MO116 (17%) MO110 → MO115 (38%) MO110 → MO116 (35%)	4.5174 eV (274.46 nm)	0.0141
S_{23}	MO108 → MO114 (10%) MO108 → MO115 (56%) MO108 → MO116 (34%)	4.5967 eV (269.73 nm)	0.0124
S_{24}	MO108 → MO116 (51%) MO109 → MO116 (20%) MO113 → MO118 (29%)	4.6281 eV (267.90 nm)	0.0286
S_{25}	MO113 → MO119	4.7358 eV (261.80 nm)	0.0103
S_{26}	MO105 → MO114 (14%) MO107 → MO114 (43%) MO108 → MO114 (11%) MO113 → MO118 (18%) MO113 → MO120 (14%)	4.8609 eV (255.07 nm)	0.4879
S_{27}	MO106 → MO114 (18%) MO113 → MO118 (24%) MO113 → MO120 (58%)	4.8825 eV (253.94 nm)	0.0356
S_{28}	MO107 → MO114 (19%) MO112 → MO117 (24%) MO113 → MO119 (11%) MO113 → MO120 (46%)	4.9110 eV (252.46 nm)	0.1490
S_{29}	MO107 → MO116 (26%) MO111 → MO117 (74%)	5.0031 eV (247.81 nm)	0.0138
S_{30}	MO105 → MO116 (16%) MO107 → MO116 (66%) MO108 → MO117 (18%)	5.0351 eV (246.24 nm)	0.0304

HOMO: MO113, LUMO: MO114

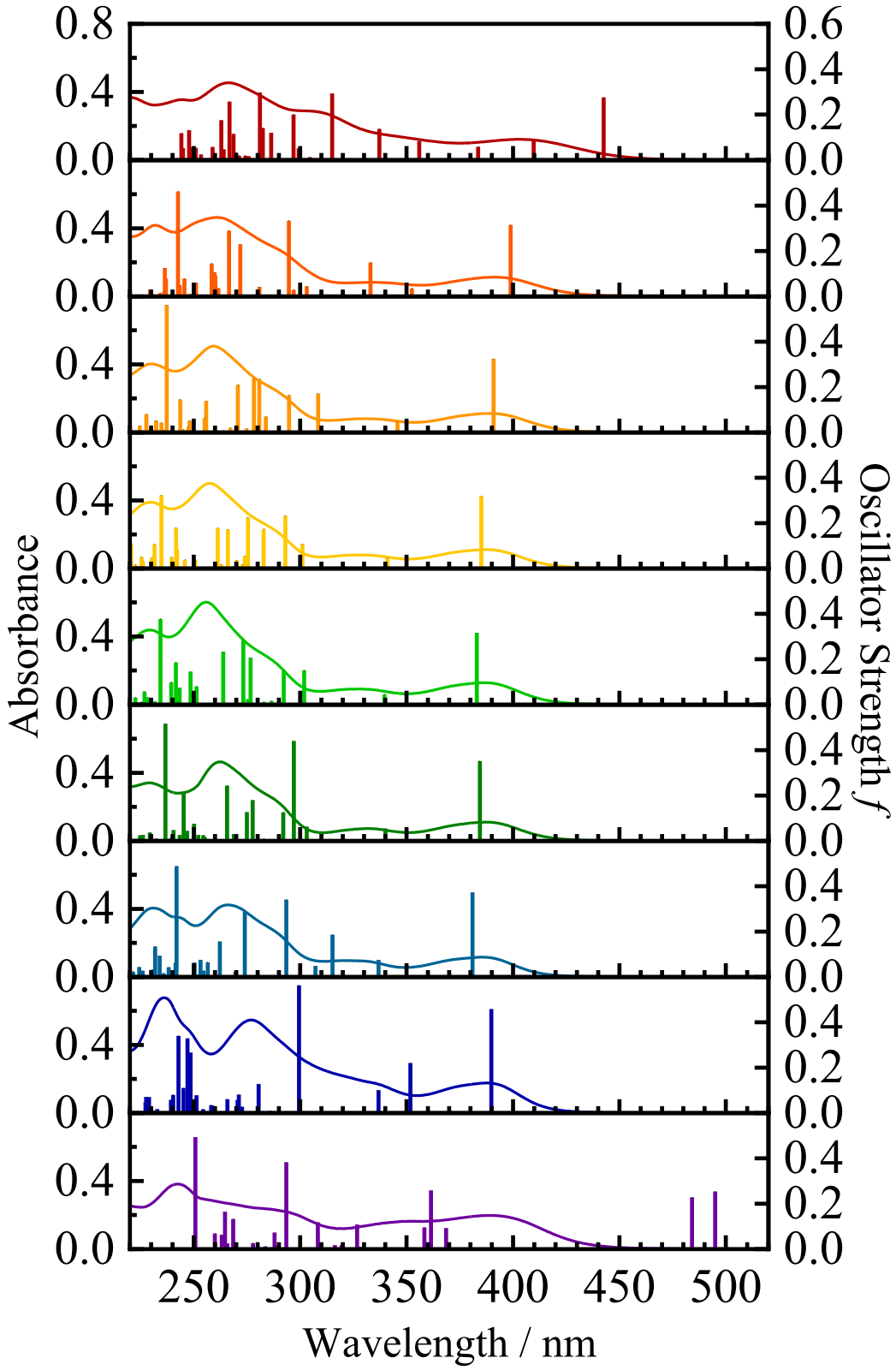

Fig. S43 Comparisons of the absorption spectra and oscillator strengths calculated by TD-DFT (perpendicular bars) of **1R** in acetonitrile. The colors correspond to those indicated in Fig. 1.

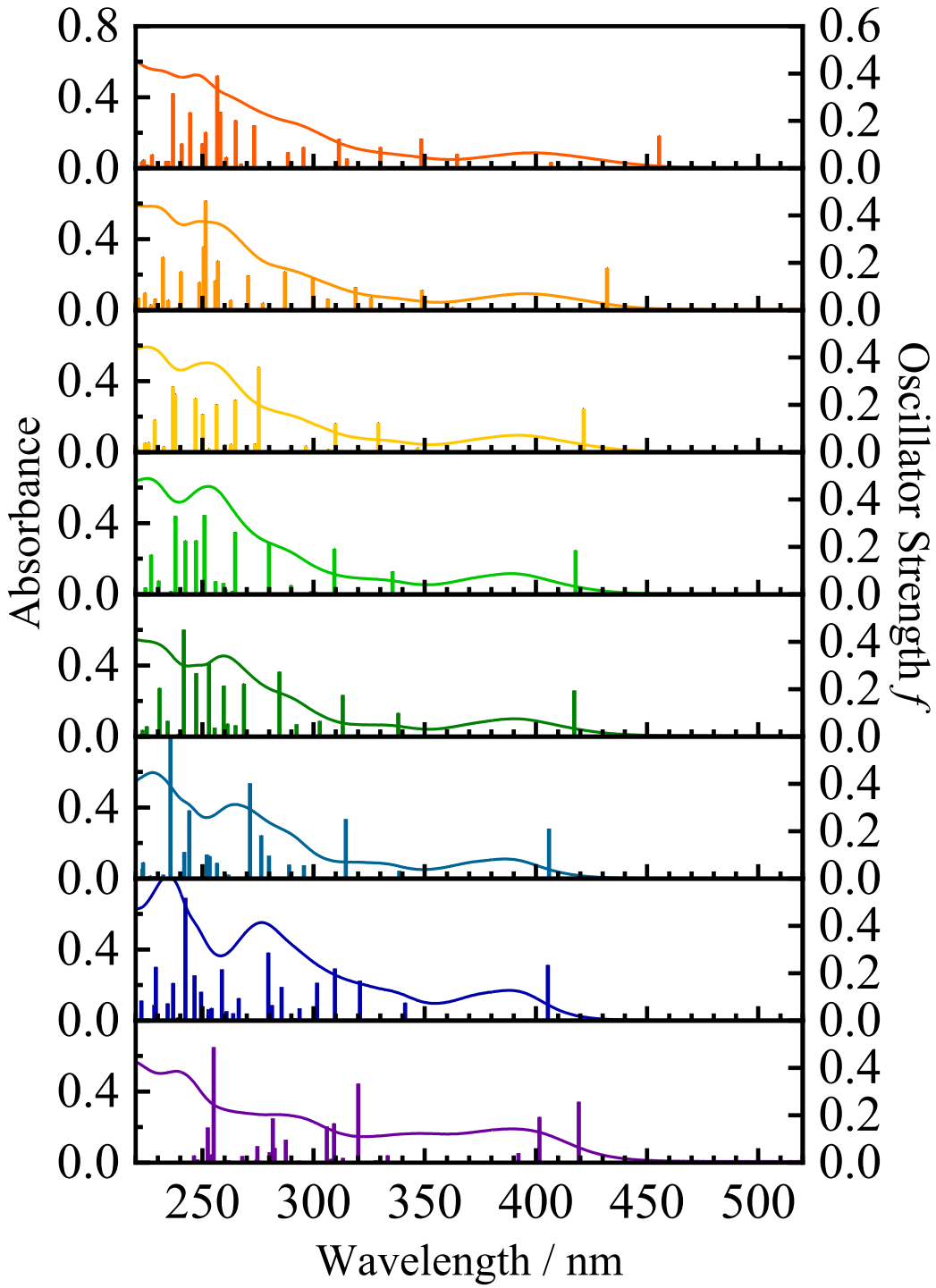

Fig. S44 Comparisons of the absorption spectra ([TFA] = 10 mM) and oscillator strengths calculated by TD-DFT (perpendicular bars) of **1R**·H^+ in acetonitrile. The colors correspond to those indicated in Fig. 1.

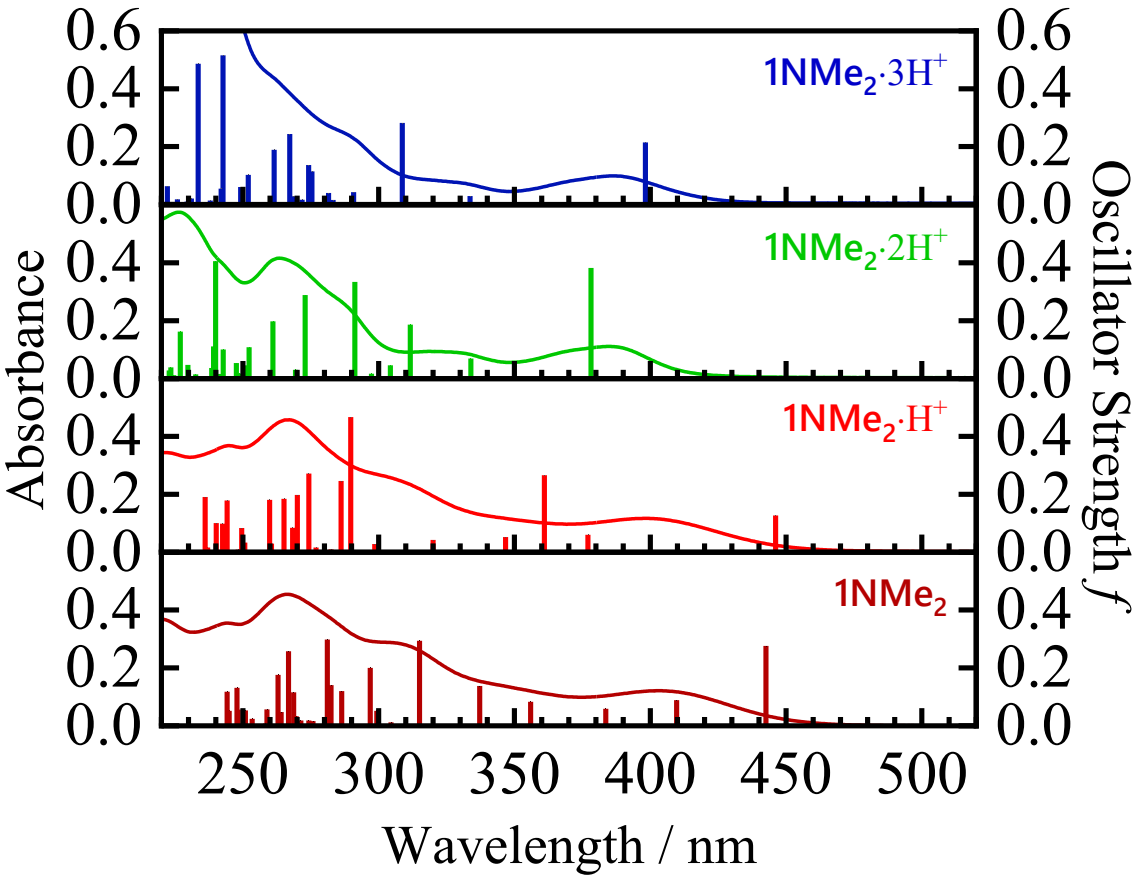

Fig. S45 Comparisons of the absorption spectra ([TFA] = 0, 0.1, 10, 100 mM) and oscillator strengths calculated by TD-DFT (perpendicular bars) of **1NMe$_2$**·H$^+$ in acetonitrile.

Table S47 Calculated excited states of S_1-optimized geometry of **1NMe$_2$** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO115 → MO116	1.1328 eV (1094.50 nm)	0.0000
S_1	MO115 → MO116	1.7810 eV (696.16 nm)	0.3308
T_2	MO111 → MO116 (14%) MO114 → MO116 (70%) MO115 → MO118 (16%)	2.1502 eV (576.61 nm)	0.0000
T_3	MO114 → MO116 (38%) MO115 → MO117 (62%)	2.1932 eV (565.30 nm)	0.0000
S_2	MO114 → MO116	2.2847 eV (542.68 nm)	0.0997
S_3	MO115 → MO117	2.5918 eV (478.37 nm)	0.0306

HOMO: MO115, LUMO: MO116

Table S48 Calculated excited states of S_1-optimized geometry of **1NMe$_2$**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO115 → MO116	1.2383 eV (1001.21 nm)	0.0000
S_1	MO115 → MO116	1.7993 eV (689.07 nm)	0.2584
T_2	MO113 → MO116 (13%) MO115 → MO117 (72%) MO115 → MO120 (15%)	2.2105 eV (560.88 nm)	0.0000
T_3	MO114 → MO116 (68%) MO115 → MO116 (18%) MO115 → MO117 (14%)	2.4193 eV (512.48 nm)	0.0000
S_2	MO114 → MO116 (82%) MO115 → MO118 (18%)	2.6488 eV (468.08 nm)	0.0571
S_3	MO114 → MO116 (43%) MO115 → MO117 (57%)	2.6926 eV (460.45 nm)	0.1179

HOMO: MO115, LUMO: MO116

Table S49 Calculated excited states of S_1-optimized geometry of **1NMe$_2$**·$2H^+$ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO115 → MO116	1.4636 eV (847.14 nm)	0.0000
S_1	MO115 → MO116	2.1288 eV (582.42 nm)	0.3329
T_2	MO115 → MO117	2.3992 eV (516.78 nm)	0.0000
T_3	MO112 → MO116 (10%) MO114 → MO116 (12%) MO115 → MO117 (11%) MO115 → MO118 (57%) MO115 → MO119 (10%)	2.7444 eV (451.77 nm)	0.0000
S_2	MO115 → MO117 (81%) MO115 → MO119 (19%)	2.9854 eV (415.30 nm)	0.0371
S_3	MO115 → MO118	3.2568 eV (380.70 nm)	0.2588

HOMO: MO115, LUMO: MO116

Table S50 Calculated excited states of S_1-optimized geometry of **1NMe$_2$**·$3H^+$ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO115 → MO116	2.0018 eV (619.37 nm)	0.0000
T_2	MO115 → MO116 (25%) MO115 → MO117 (75%)	2.3988 eV (516.87 nm)	0.0000
S_1	MO115 → MO116	2.6281 eV (471.76 nm)	0.2286
T_3	MO114 → MO116 (75%) MO115 → MO117 (25%)	3.0466 eV (406.96 nm)	0.0000
S_2	MO115 → MO117	3.3647 eV (368.49 nm)	0.1341
S_3	MO114 → MO116 (72%) MO115 → MO117 (28%)	3.6585 eV (338.90 nm)	0.1874

HOMO: MO115, LUMO: MO116

Table S51 Calculated excited states of S_1-optimized geometry of **1OMe** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO107 → MO108	1.2608 eV (983.35 nm)	0.0000
S_1	MO107 → MO108	1.9547 eV (634.28 nm)	0.3134
T_2	MO107 → MO109 (80%) MO107 → MO110 (20%)	2.2755 eV (544.88 nm)	0.0000
T_3	MO103 → MO108 (15%) MO106 → MO108 (63%) MO107 → MO109 (22%)	2.6431 eV (469.09 nm)	0.0000
S_2	MO107 → MO109	2.7623 eV (448.85 nm)	0.0111
S_3	MO106 → MO108 (80%) MO107 → MO109 (20%)	2.9332 eV (422.69 nm)	0.1092

HOMO: MO107, LUMO: MO108

Table S52 Calculated excited states of S_1-optimized geometry of **1OMe**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO107 → MO108	1.7498 eV (708.58 nm)	0.0000
S_1	MO107 → MO108	2.1987 eV (563.90 nm)	0.1514
T_2	MO102 → MO108 (20%) MO107 → MO109 (80%)	2.2923 eV (540.88 nm)	0.0000
T_3	MO106 → MO108 (77%) MO107 → MO109 (23%)	2.6313 eV (471.18 nm)	0.0000
S_2	MO106 → MO108	2.7717 eV (447.32 nm)	0.0414
S_3	MO107 → MO109	3.0690 eV (403.99 nm)	0.1783

HOMO: MO107, LUMO: MO108

Table S53 Calculated excited states of S_1-optimized geometry of **1Me** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO099 → MO100	1.3028 eV (951.69 nm)	0.0000
S_1	MO099 → MO100	2.0050 eV (618.37 nm)	0.3153
T_2	MO099 → MO101 (81%) MO099 → MO102 (19%)	2.3070 eV (537.42 nm)	0.0000
T_3	MO096 → MO100 (19%) MO099 → MO102 (81%)	2.7183 eV (456.11 nm)	0.0000
S_2	MO099 → MO101	2.8186 eV (439.87 nm)	0.0212
S_3	MO097 → MO100 (15%) MO098 → MO100 (61%) MO099 → MO101 (11%) MO099 → MO102 (13%)	3.1813 eV (389.73 nm)	0.0640

HOMO: MO099, LUMO: MO100

Table S54 Calculated excited states of S_1-optimized geometry of **1Me**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO099 → MO100	1.8275 eV (678.45 nm)	0.0000
T_2	MO099 → MO101	2.3213 eV (534.12 nm)	0.0000
S_1	MO099 → MO100	2.3553 eV (526.41 nm)	0.1827
T_3	MO098 → MO100	2.8671 eV (432.44 nm)	0.0000
S_2	MO098 → MO100 (70%) MO099 → MO101 (30%)	3.1057 eV (399.21 nm)	0.0232
S_3	MO099 → MO101	3.2290 eV (383.97 nm)	0.2010

HOMO: MO099, LUMO: MO100

Table S55 Calculated excited states of S_1-optimized geometry of **1H** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO091 → MO092	1.3441 eV (922.41 nm)	0.0000
S_1	MO091 → MO092	2.0446 eV (606.41 nm)	0.3041
T_2	MO087 → MO092 (12%) MO091 → MO093 (72%) MO091 → MO094 (16%)	2.3367 eV (530.60 nm)	0.0000
T_3	MO091 → MO094	2.7630 eV (448.73 nm)	0.0000
S_2	MO091 → MO093	2.8673 eV (432.41 nm)	0.0233
S_3	MO088 → MO092 (11%) MO089 → MO092 (53%) MO090 → MO092 (36%)	3.2487 eV (381.65 nm)	0.0114

HOMO: MO091, LUMO: MO092

Table S56 Calculated excited states of S_1-optimized geometry of **1H**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO087 → MO092 (13%) MO091 → MO092 (87%)	1.8700 eV (663.01 nm)	0.0000
T_2	MO091 → MO092 (16%) MO091 → MO093 (84%)	2.3379 eV (530.32 nm)	0.0000
S_1	MO091 → MO092	2.4212 eV (512.07 nm)	0.1819
T_3	MO086 → MO092 (33%) MO090 → MO092 (49%) MO091 → MO093 (18%)	2.9579 eV (419.16 nm)	0.0000
S_2	MO091 → MO093	3.2292 eV (383.95 nm)	0.0767
S_3	MO090 → MO092 (66%) MO091 → MO093 (34%)	3.4004 eV (364.61 nm)	0.1678

HOMO: MO091, LUMO: MO092

Table S57 Calculated excited states of S_1-optimized geometry of **1F** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO099 → MO100	1.3522 eV (916.91 nm)	0.0000
S_1	MO099 → MO100	2.0491 eV (605.06 nm)	0.2985
T_2	MO096 → MO100 (12%) MO099 → MO101 (71%) MO099 → MO102 (17%)	2.3411 eV (529.60 nm)	0.0000
T_3	MO096 → MO100 (14%) MO098 → MO102 (14%) MO099 → MO102 (72%)	2.7630 eV (448.74 nm)	0.0000
S_2	MO099 → MO101	2.8750 eV (431.25 nm)	0.0234
S_3	MO098 → MO100 (80%) MO099 → MO102 (20%)	3.2606 eV (380.25 nm)	0.0331

HOMO: MO099, LUMO: MO100

Table S58 Calculated excited states of S_1-optimized geometry of **1F**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO099 → MO100	1.8859 eV (657.44 nm)	0.0000
T_2	MO098 → MO100 (14%) MO099 → MO101 (86%)	2.3462 eV (528.44 nm)	0.0000
S_1	MO099 → MO100	2.4352 eV (509.12 nm)	0.1842
T_3	MO098 → MO100	2.9432 eV (421.25 nm)	0.0000
S_2	MO098 → MO100 (48%) MO099 → MO101 (52%)	3.2255 eV (384.38 nm)	0.0404
S_3	MO098 → MO100	3.3400 eV (371.21 nm)	0.1802

HOMO: MO099, LUMO: MO100

Table S59 Calculated excited states of S_1-optimized geometry of **1Cl** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO107 → MO108	1.3681 eV (906.26 nm)	0.0000
S_1	MO107 → MO108	2.0522 eV (604.17 nm)	0.3253
T_2	MO107 → MO109	2.3464 eV (528.41 nm)	0.0000
T_3	MO107 → MO109 (25%) MO107 → MO110 (75%)	2.7316 eV (453.90 nm)	0.0000
S_2	MO106 → MO108 (15%) MO107 → MO109 (85%)	2.8870 eV (429.46 nm)	0.0254
S_3	MO105 → MO108 (32%) MO106 → MO108 (47%) MO107 → MO110 (21%)	3.2582 eV (380.53 nm)	0.0204

HOMO: MO107, LUMO: MO108

Table S60 Calculated excited states of S_1-optimized geometry of **1Cl**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO107 → MO108 (86%) MO107 → MO109 (14%)	1.9017 eV (651.95 nm)	0.0000
T_2	MO107 → MO109	2.3422 eV (529.36 nm)	0.0000
S_1	MO107 → MO108	2.4558 eV (504.87 nm)	0.1990
T_3	MO106 → MO108	2.9425 eV (421.36 nm)	0.0000
S_2	MO106 → MO108 (52%) MO107 → MO109 (48%)	3.2222 eV (384.78 nm)	0.0433
S_3	MO107 → MO109	3.3234 eV (373.07 nm)	0.2117

HOMO: MO107, LUMO: MO108

Table S61 Calculated excited states of S_1-optimized geometry of **1CF₃** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO123 → MO124	1.4344 eV (864.39 nm)	0.0000
S_1	MO123 → MO124	2.1035 eV (589.42 nm)	0.3281
T_2	MO123 → MO125 (87%) MO123 → MO134 (13%)	2.3813 eV (520.67 nm)	0.0000
T_3	MO123 → MO126	2.7231 eV (455.31 nm)	0.0000
S_2	MO123 → MO125	2.9597 eV (418.90 nm)	0.0334
S_3	MO122 → MO124 (20%) MO123 → MO126 (80%)	3.2333 eV (383.46 nm)	0.2354

HOMO: MO123, LUMO: MO124

Table S62 Calculated excited states of S_1-optimized geometry of **1CF₃**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO123 → MO124 (82%) MO123 → MO125 (18%)	1.9692 eV (629.60 nm)	0.0000
T_2	MO122 → MO124 (14%) MO123 → MO125 (74%) MO123 → MO132 (12%)	2.3790 eV (521.16 nm)	0.0000
S_1	MO123 → MO124	2.5727 eV (481.93 nm)	0.2158
T_3	MO122 → MO124	3.0237 eV (410.04 nm)	0.0000
S_2	MO122 → MO124 (27%) MO123 → MO125 (73%)	3.3326 eV (372.03 nm)	0.1224
S_3	MO122 → MO124	3.5915 eV (345.22 nm)	0.1846

HOMO: MO123, LUMO: MO124

Table S63 Calculated excited states of S_1-optimized geometry of **1CN** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO103 → MO104	1.4596 eV (849.43 nm)	0.0000
S_1	MO103 → MO104	2.1001 eV (590.38 nm)	0.3819
T_2	MO102 → MO104 (14%) MO103 → MO106 (65%) MO103 → MO107 (21%)	2.3436 eV (529.03 nm)	0.0000
T_3	MO102 → MO104 (11%) MO102 → MO106 (10%) MO103 → MO105 (43%) MO103 → MO106 (36%)	2.5253 eV (490.98 nm)	0.0000
S_2	MO103 → MO105 (74%) MO103 → MO106 (26%)	2.9279 eV (423.46 nm)	0.4492
S_3	MO103 → MO106 (52%) MO103 → MO107 (48%)	3.0007 eV (413.19 nm)	0.0260

HOMO: MO103, LUMO: MO104

Table S64 Calculated excited states of S_1-optimized geometry of **1CN**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO103 → MO104	1.9744 eV (627.94 nm)	0.0000
T_2	MO100 → MO104 (11%) MO103 → MO104 (22%) MO103 → MO105 (67%)	2.3512 eV (527.33 nm)	0.0000
S_1	MO103 → MO104	2.5877 eV (479.13 nm)	0.2521
T_3	MO102 → MO104 (63%) MO103 → MO105 (15%) MO103 → MO107 (22%)	2.9880 eV (414.95 nm)	0.0000
S_2	MO103 → MO105	3.2669 eV (379.52 nm)	0.1977
S_3	MO102 → MO104 (50%) MO103 → MO105 (14%) MO103 → MO106 (27%) MO103 → MO107 (9%)	3.5238 eV (351.85 nm)	0.0611

HOMO: MO103, LUMO: MO104

Table S65 Calculated excited states of S_1-optimized geometry of **1NO₂** in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO113 → MO114	1.7108 eV (724.71 nm)	0.0000
S_1	MO113 → MO114	1.9272 eV (643.34 nm)	0.1767
T_2	MO113 → MO115 (82%) MO113 → MO117 (18%)	2.0417 eV (607.25 nm)	0.0000
T_3	MO110 → MO114	2.3578 eV (525.84 nm)	0.0000
S_2	MO113 → MO115	2.4148 eV (513.44 nm)	0.3363
S_3	MO105 → MO114 (15%) MO112 → MO114 (85%)	3.0821 eV (402.27 nm)	0.1708

HOMO: MO113, LUMO: MO114

Table S66 Calculated excited states of S_1-optimized geometry of **1NO₂**·H^+ in acetonitrile.

Excited State	Transition	Energy (Wavelength)	Oscillator Strength
T_1	MO112 → MO114 (12%) MO113 → MO114 (60%) MO113 → MO115 (28%)	1.9435 eV (637.94 nm)	0.0000
T_2	MO108 → MO114 (11%) MO113 → MO115 (47%) MO113 → MO116 (42%)	2.3215 eV (534.06 nm)	0.0000
S_1	MO113 → MO114	2.3639 eV (524.50 nm)	0.2377
T_3	MO113 → MO114 (19%) MO113 → MO116 (55%) MO113 → MO117 (26%)	2.3741 eV (522.23 nm)	0.0000
S_2	MO113 → MO115 (83%) MO113 → MO116 (17%)	2.7869 eV (444.88 nm)	0.3750
S_3	MO113 → MO116	2.9205 eV (424.53 nm)	0.1182

HOMO: MO113, LUMO: MO114

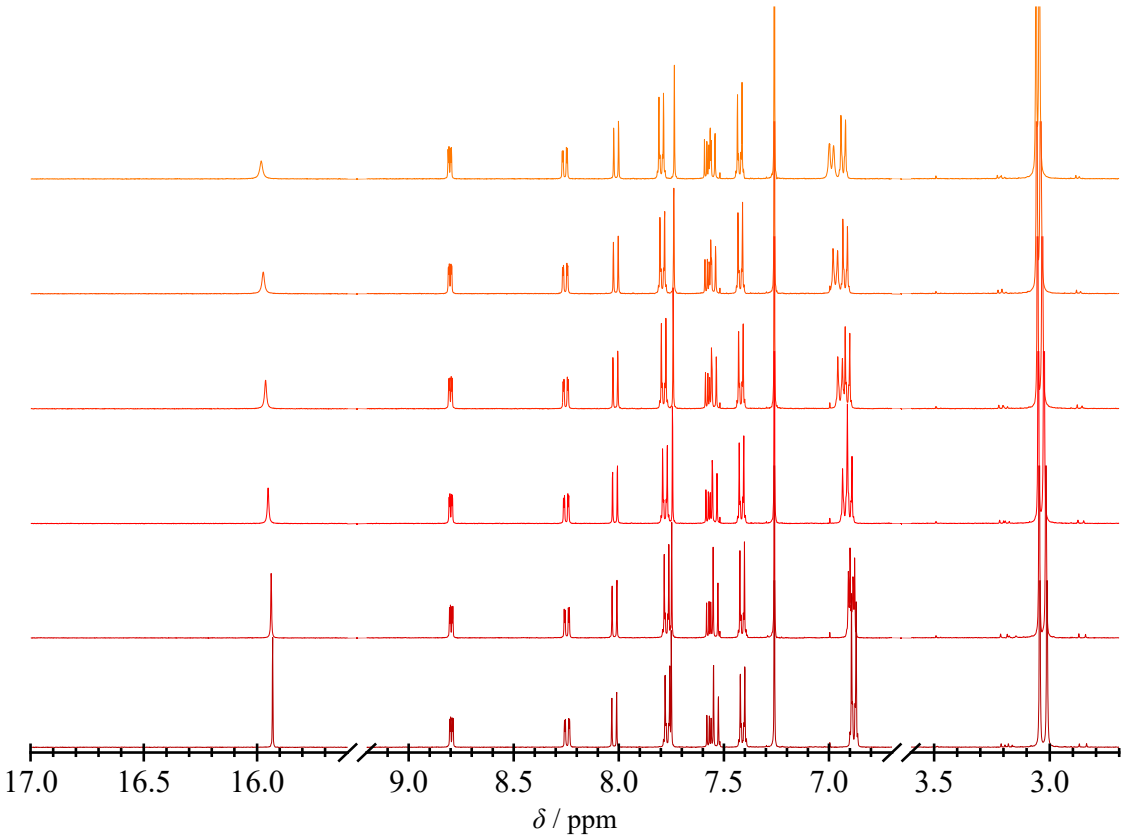

Fig. S46 ^{1}H-NMR spectra of **1NMe$_2$** in $CDCl_3$ ([**1NMe$_2$**]$_0$ = 5.0 mM) upon an addition of 0, 0.040, 0.080, 0.12, 0.16 and 0.20 equivalents of TFA (dark red → orange).

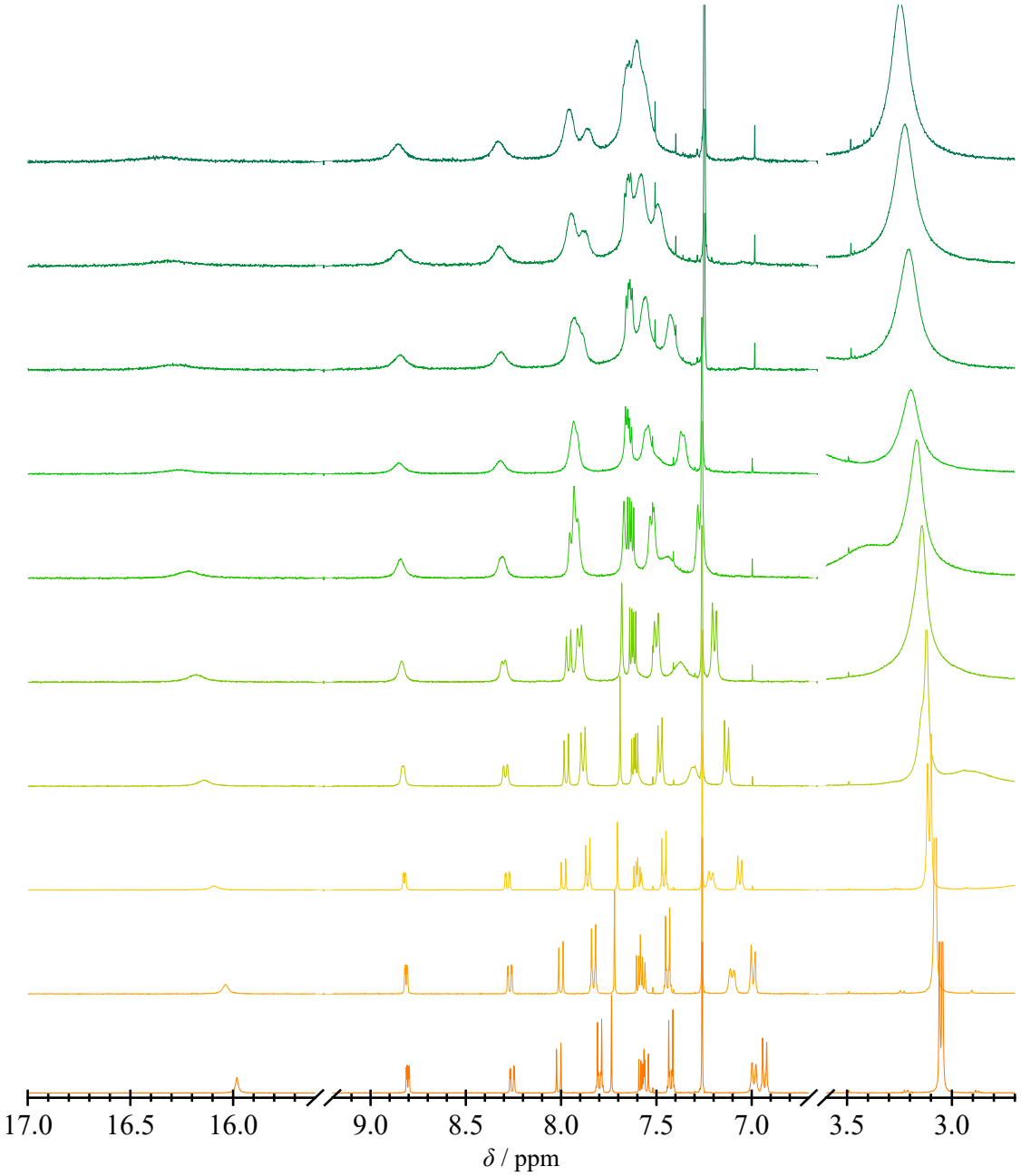

Fig. S47 ^{1}H-NMR spectra of **1NMe$_2$** in $CDCl_3$ ([**1NMe$_2$**]$_0$ = 5.0 mM) upon an addition of 0.20, 0.40, 0.60, 0.80, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 equivalents of TFA (orange → dark green).

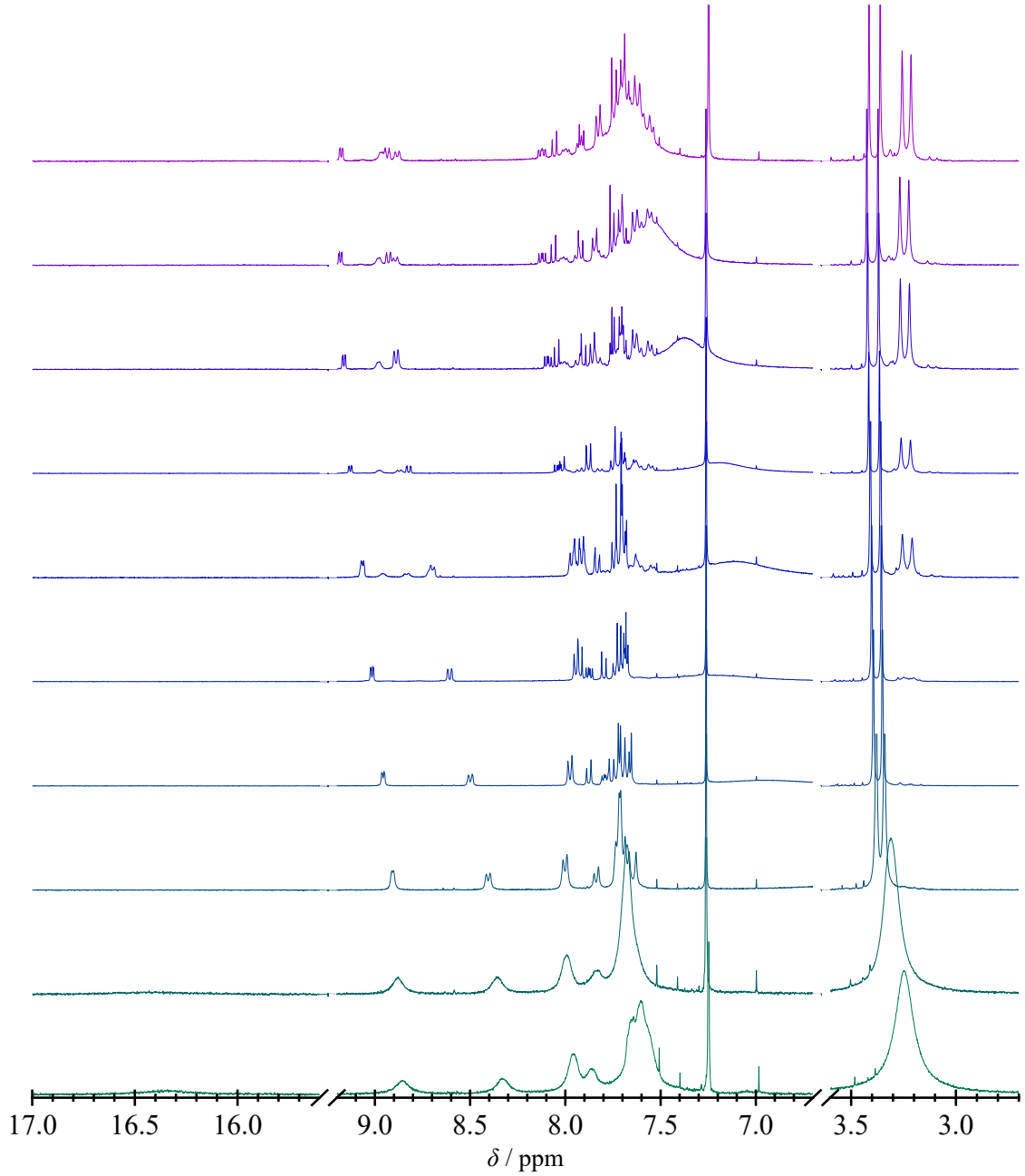

Fig. S48 ^{1}H-NMR spectra of **1NMe$_2$** in $CDCl_3$ ([**1NMe$_2$**]$_0$ = 5.0 mM) upon an addition of 2.0, 4.0, 6.0, 8.0, 10, 12, 14, 16, 18 and 20 equivalents of TFA (dark green → purple).

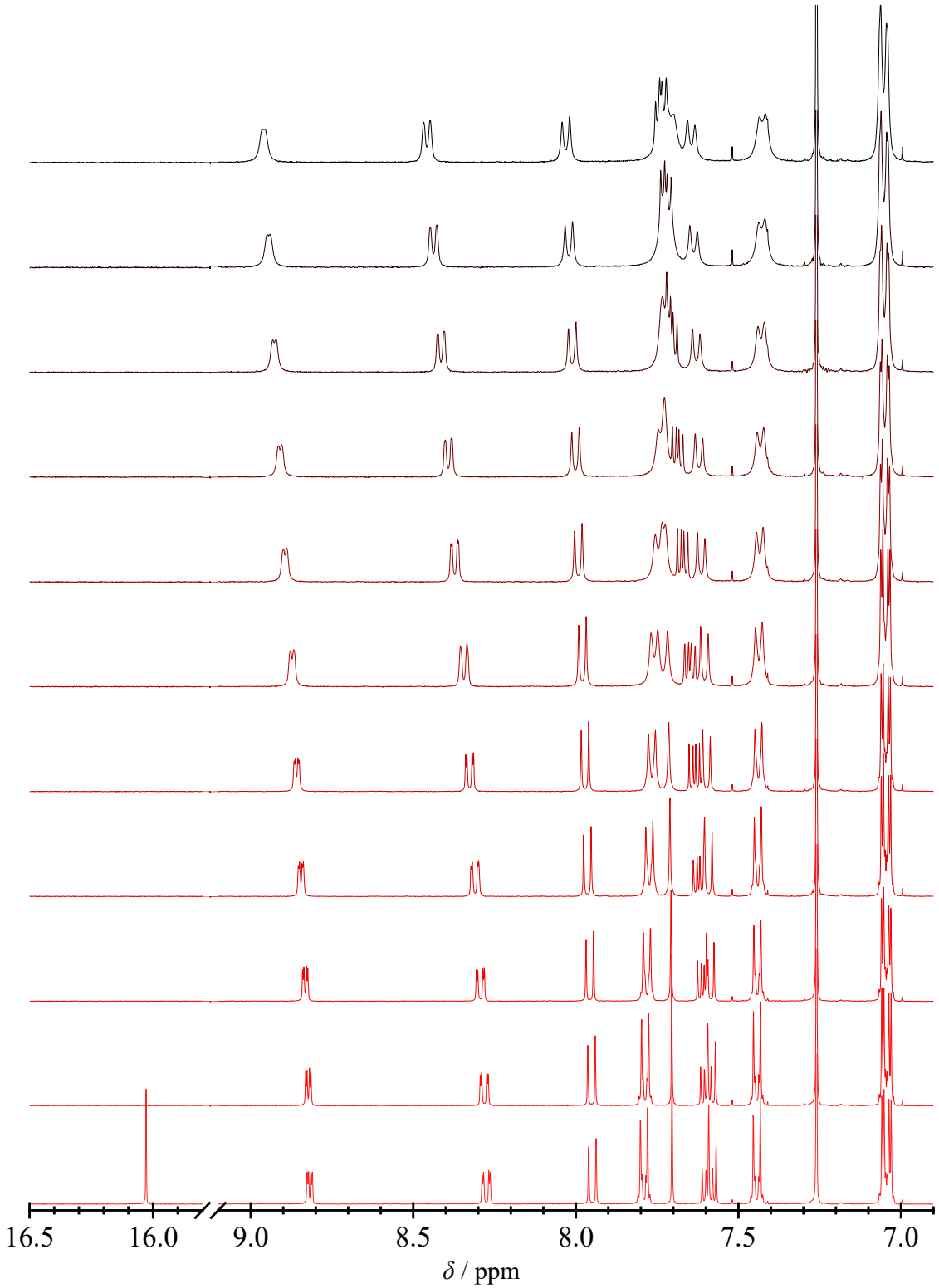

Fig. S49 ^{1}H-NMR spectra of **1OMe** in $CDCl_3$ ([**1OMe**]$_0$ = 5.0 mM) upon an addition of 0, 0.20, 0.40, 0.60, 0.80, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 equivalents of TFA (red → black).

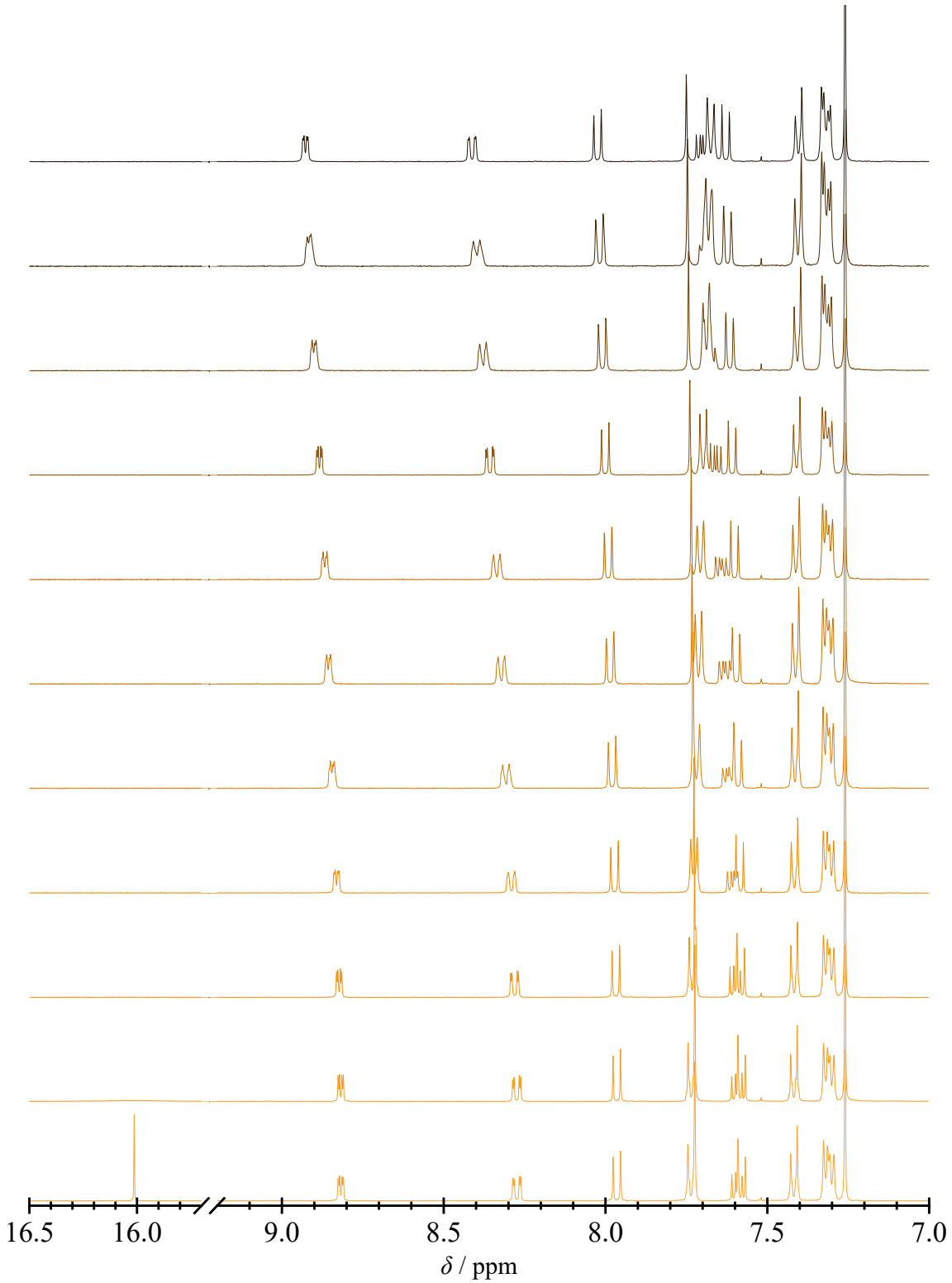

Fig. S50 ^{1}H-NMR spectra of **1Me** in $CDCl_3$ ([**1Me**]$_0$ = 5.3 mM) upon an addition of 0, 0.20, 0.40, 0.60, 0.80, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 equivalents of TFA (orange → black).

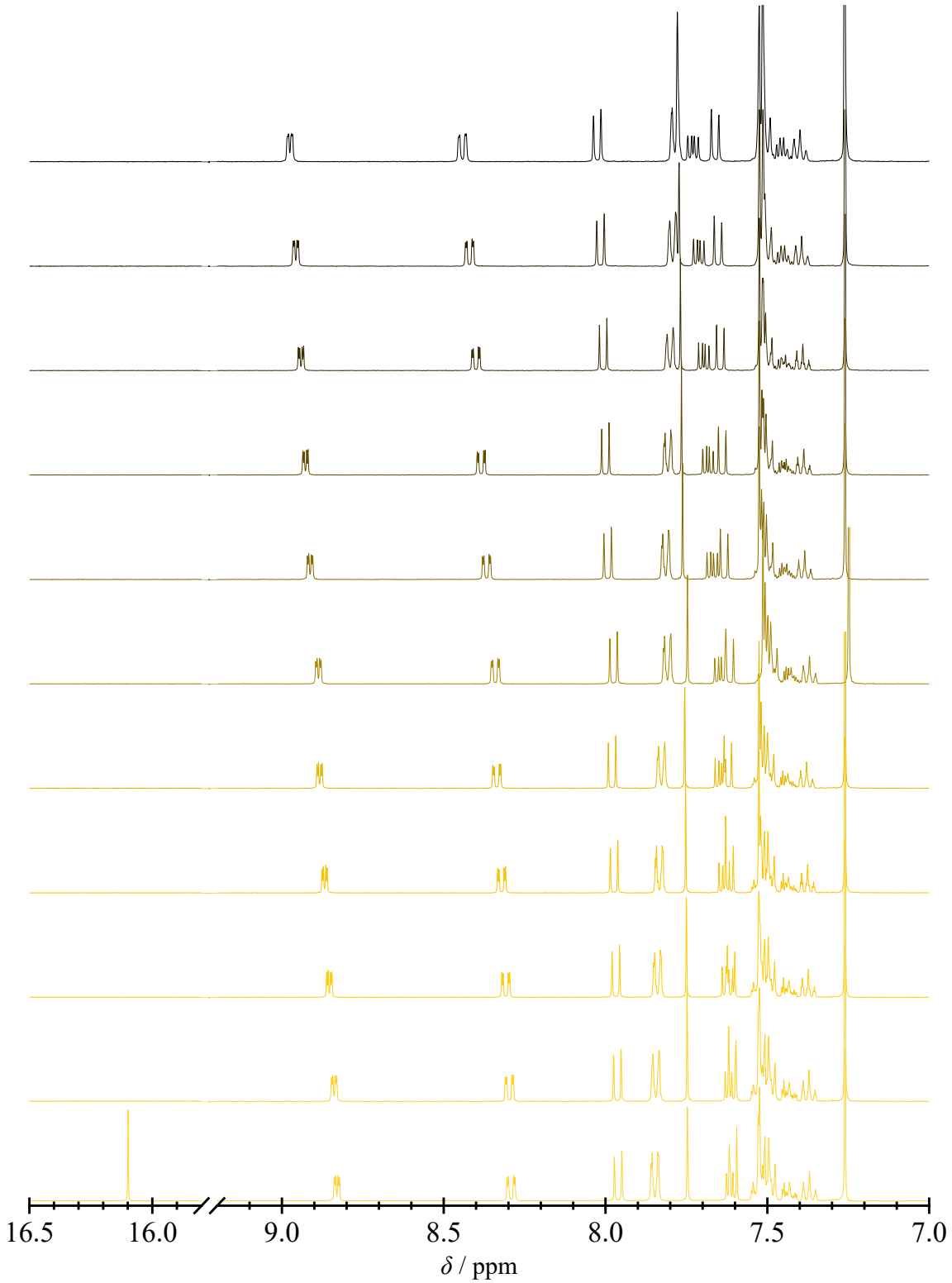

Fig. S51 ^{1}H-NMR spectra of **1H** in $CDCl_3$ ($[\mathbf{1H}]_0$ = 5.4 mM) upon an addition of 0, 0.20, 0.40, 0.60, 0.80, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 equivalents of TFA (yellow → black).

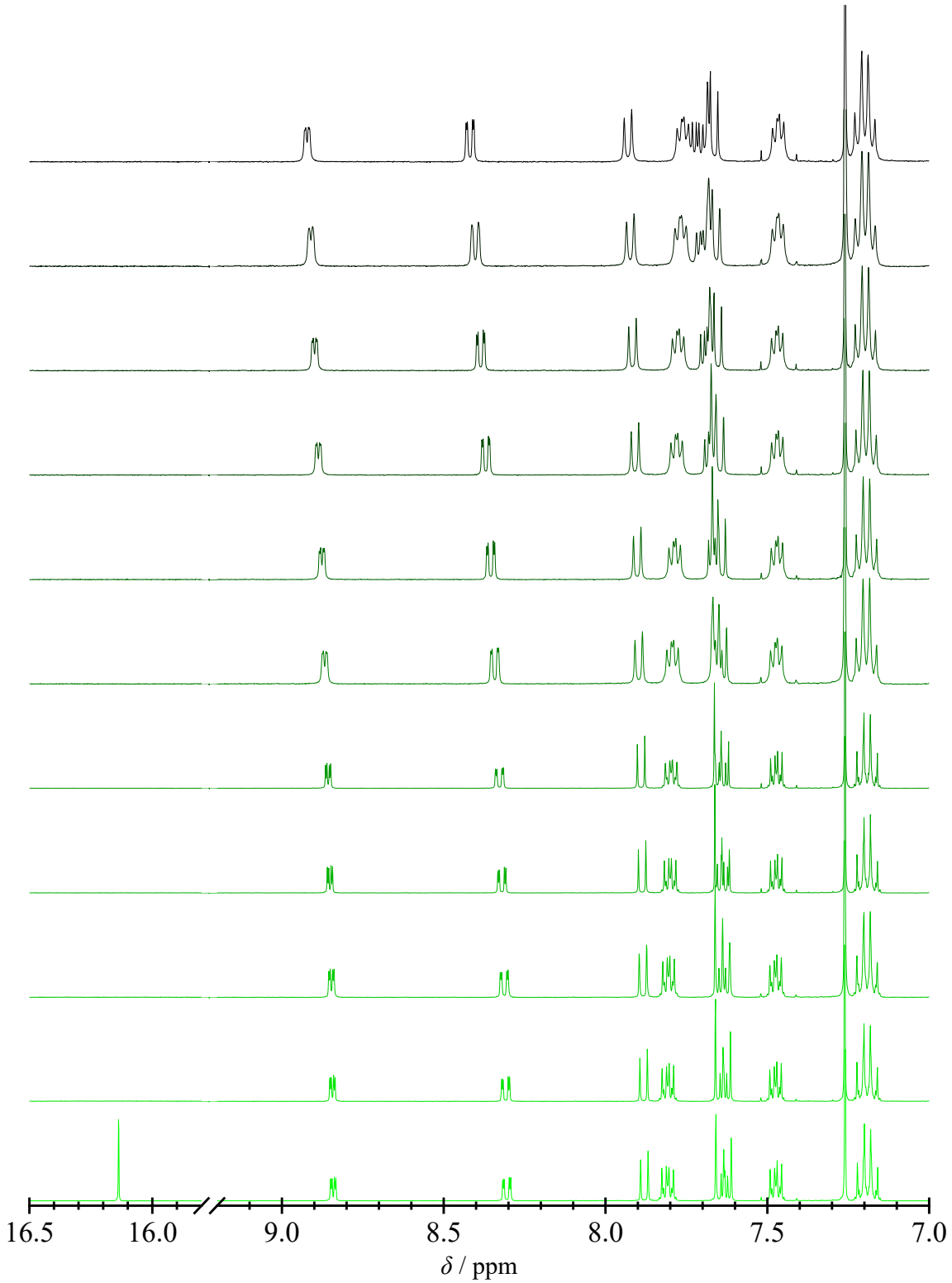

Fig. S52 ^{1}H-NMR spectra of **1F** in $CDCl_3$ ([**1F**]$_0$ = 5.0 mM) upon an addition of 0, 0.20, 0.40, 0.60, 0.80, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 equivalents of TFA (light green → black).

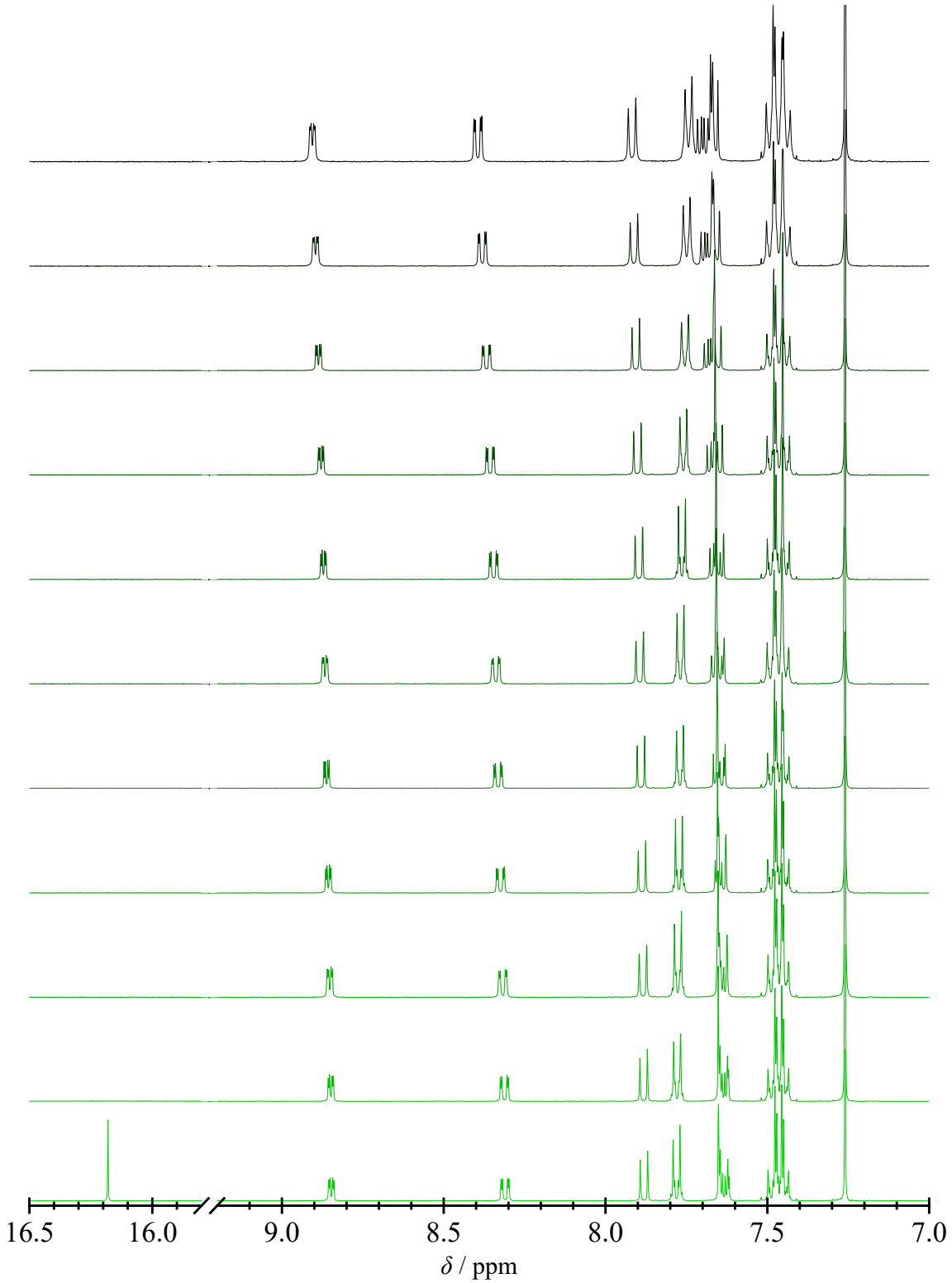

Fig. S53 ^{1}H-NMR spectra of **1Cl** in $CDCl_3$ ([**1Cl**]$_0$ = 4.8 mM) upon an addition of 0, 0.20, 0.40, 0.60, 0.80, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 equivalents of TFA (green → black).

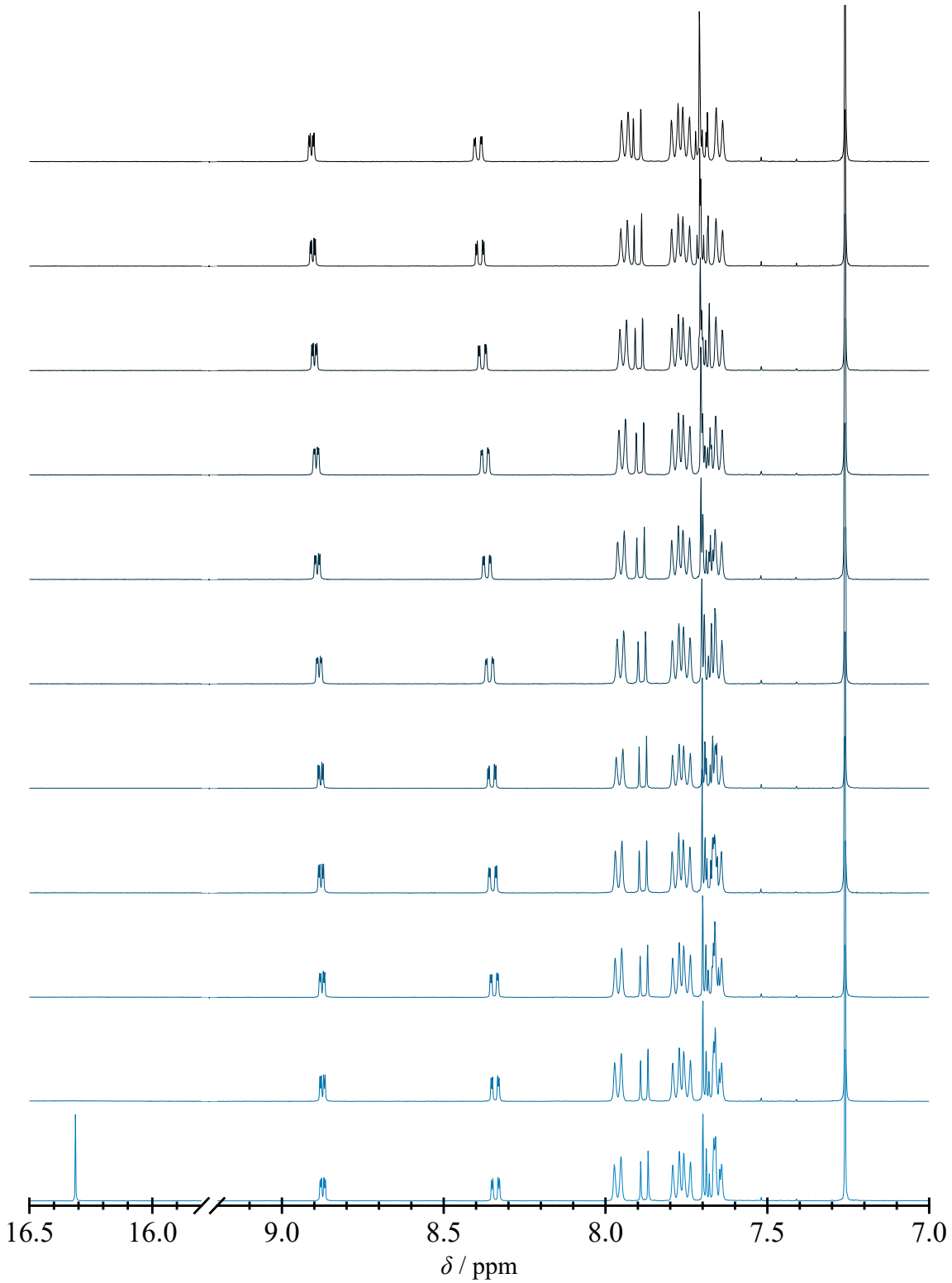

Fig. S54 ^{1}H-NMR spectra of **1CF$_3$** in $CDCl_3$ ([**1CF$_3$**]$_0$ = 5.1 mM) upon an addition of 0, 0.20, 0.40, 0.60, 0.80, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 equivalents of TFA (light blue → black).

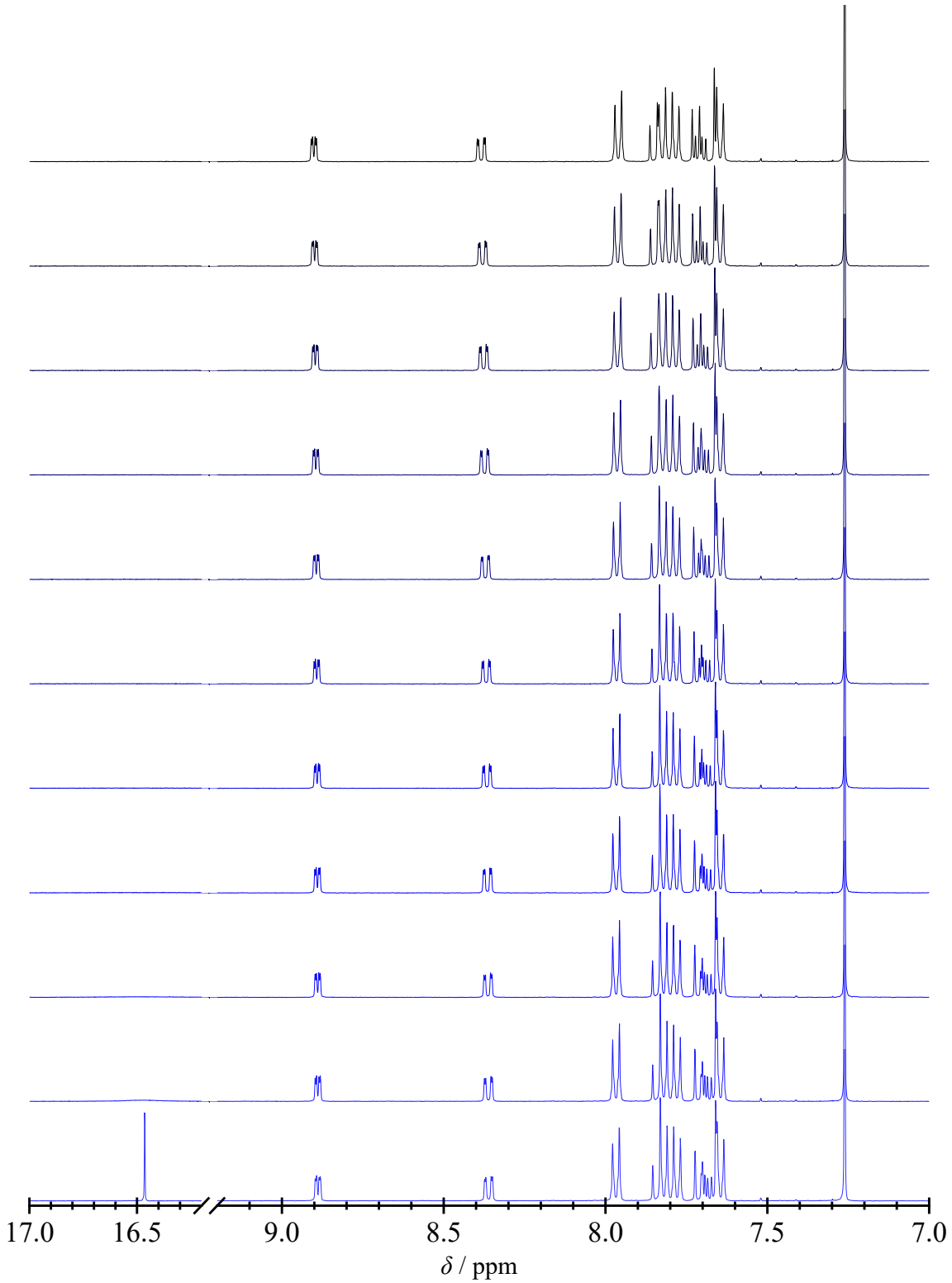

Fig. S55 ^{1}H-NMR spectra of **1CN** in $CDCl_3$ ([**1CN**]$_0$ = 5.1 mM) upon an addition of 0, 0.20, 0.40, 0.60, 0.80, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 equivalents of TFA (blue → black).

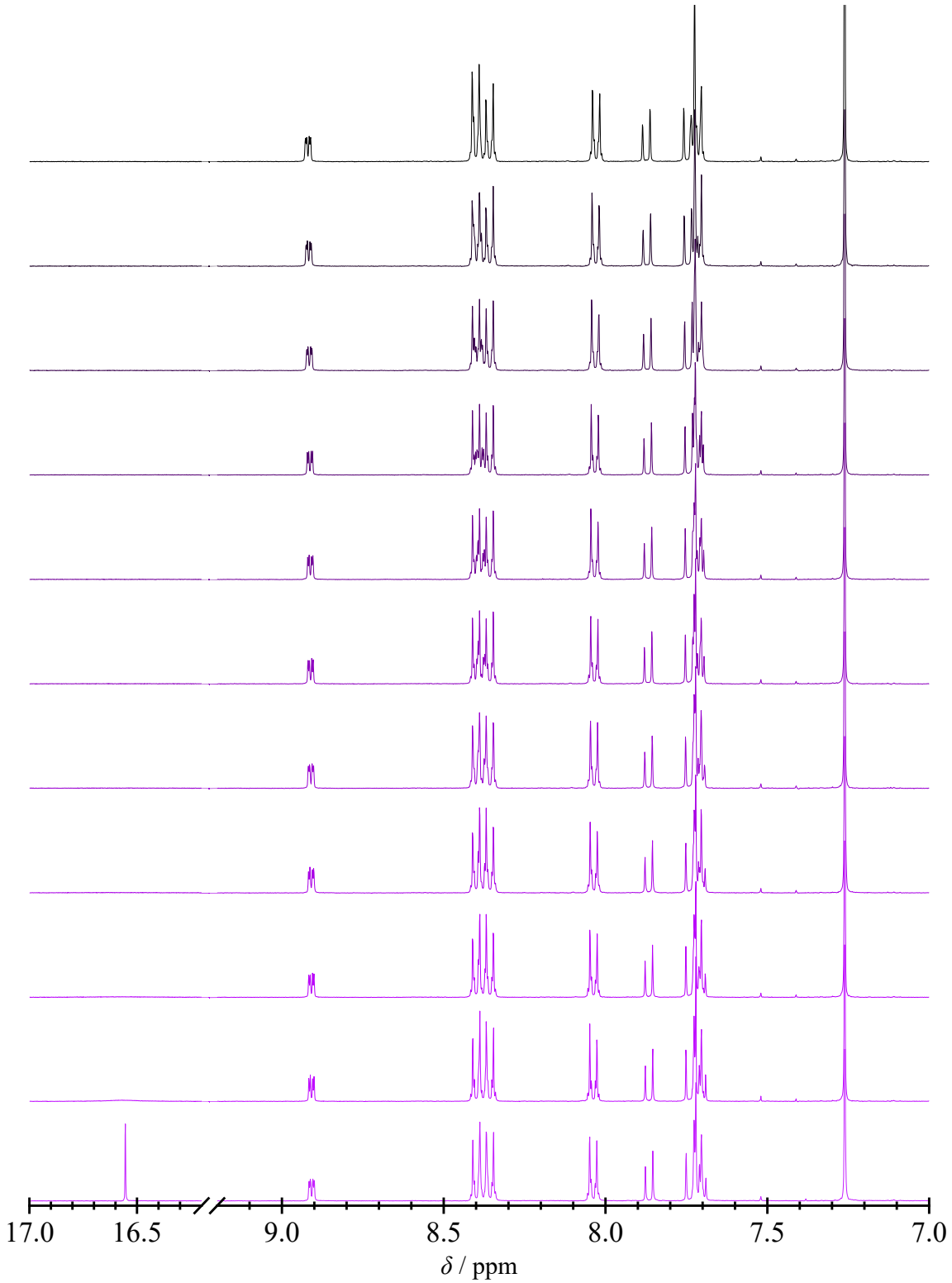

Fig. S56 ^{1}H-NMR spectra of **1NO$_2$** in $CDCl_3$ ([**1NO$_2$**]$_0$ = 4.3 mM) upon an addition of 0, 0.20, 0.40, 0.60, 0.80, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 equivalents of TFA (purple → black).

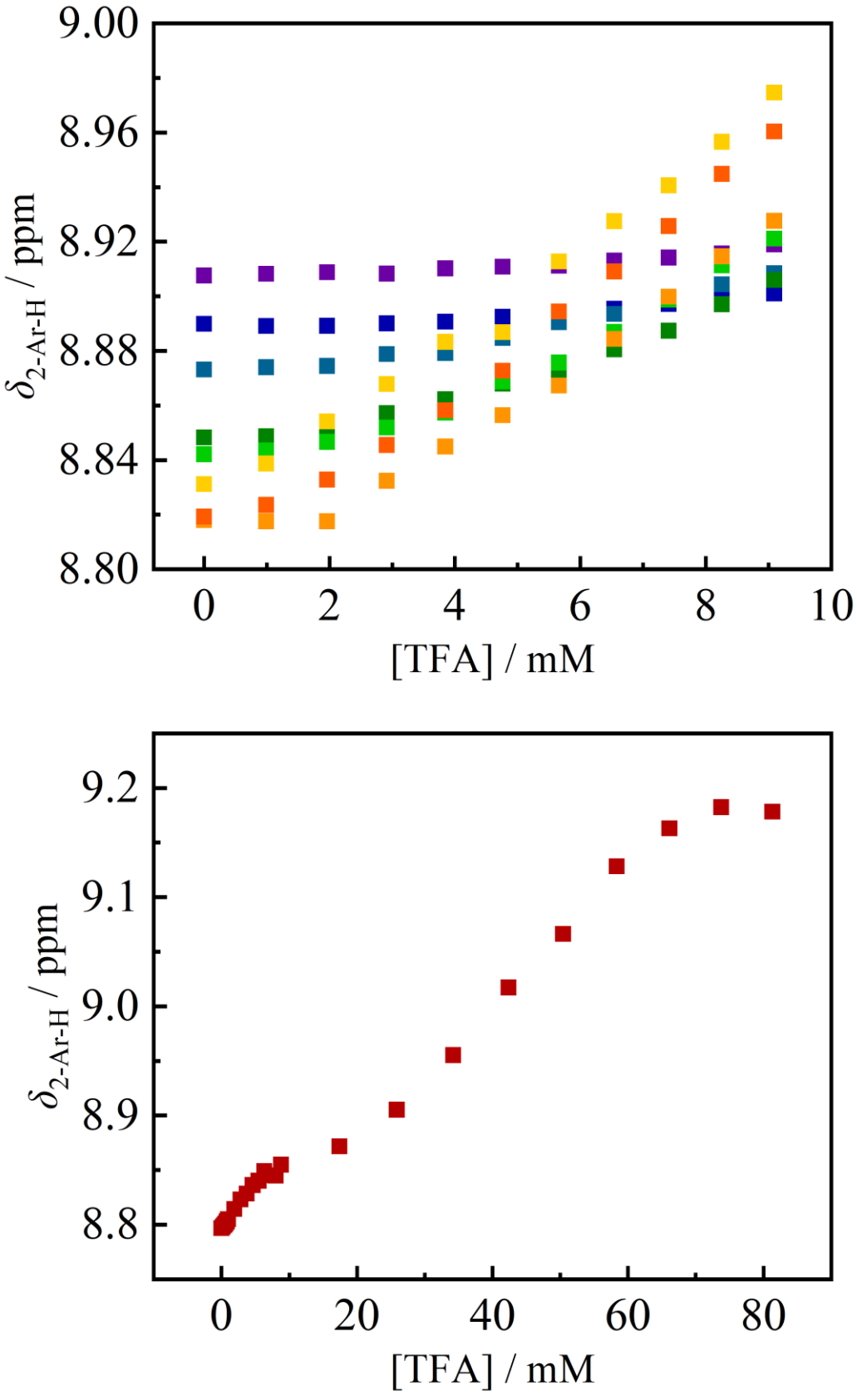

Fig. S57 TFA titrations of the chemical shift of 2-Ar-H signal of **1R** in $CDCl_3$. The colors correspond to those indicated in Fig. 1.