# *Supporting Information*

# Intense fluorescence of air-stable sodium diarylformamidinate: effective control with a novel electron-withdrawing 4-cyano-3,5-bis(trifluoromethyl)phenyl group

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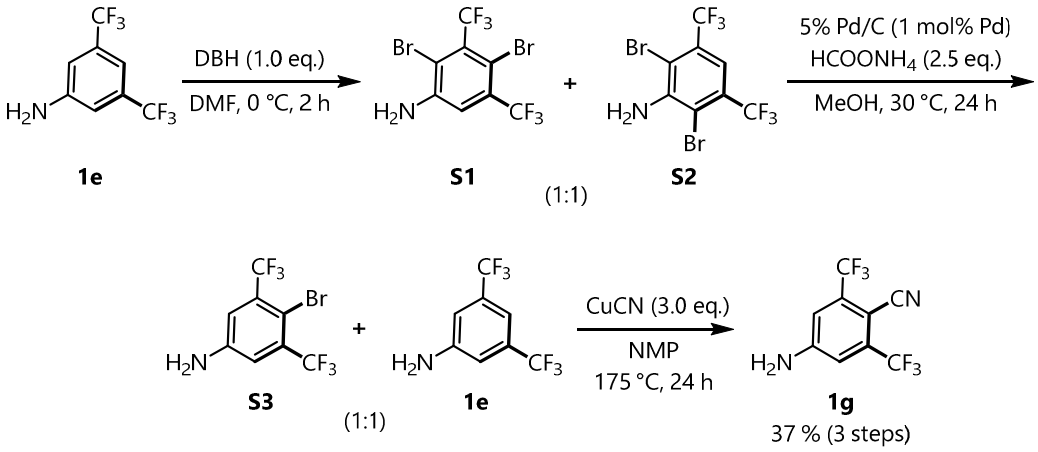
## (A) General

All manipulations were carried out under an atmosphere of $N_2$ or inside $N_2$-filled glove box unless otherwise noted. Column chromatography was performed with Cica silica gel 60N (40–100 μm, spherical, neutral). NMR spectra were recorded on a JEOL ECS-400 spectrometer or a Varian 400-MR FT-NMR spectrometer, operating at 400 MHz ($^1$H), or 101 MHz ($^{13}$C), or 376 MHz ($^{19}$F). Chemical shifts in the internal reference solvents were reported in the following scales: for $^1$H NMR, $CDCl_3$, $CD_3CN$, and DMSO-$d_6$ were relative to C*H*$D_2CN$ (1.94 ppm), and C*H*$D_2SOCD_3$ (2.50 ppm), respectively, and for $^{13}$C NMR, *C*$D_3CN$ (1.32 ppm), and ($C D_3)_2SO$ (39.52 ppm) were reported, respectively. Chemical shifts in each solvent for $^{19}$F NMR were reported in the scale relative to $PhCF_3$ (-65.64 ppm) as an external reference. NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad signal), coupling constant (Hz), and integration. Infrared (IR) spectroscopy was performed using a Jasco FT/IR-4100 spectrometer. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOFII time-of-flight mass spectrometer fitted with an ESI. Melting points (Mp.) were measured on a Yanaco Mp-JS apparatus equipped with a thermometer (30–300 °C). X-ray diffraction data were collected on either a HyPix-6000HE detector equipped in Rigaku XtaLAB Synergy attached with multi-layer mirror monochromate and PhotonJet-S (Cu-K, $\lambda$ = 1.54187 Å) or a Rigaku R-AXIS RAPID diffractometer using multi-layer mirror monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71075 Å). The hydrogen atoms were refined using the riding model. All the calculations and refinement were performed by using SHELXL Version 2022/1. UV-Vis absorption spectra were recorded on a JASCO V-670 spectrometer. Emission spectra were recorded on a JACSO FP-8500 spectrometer and a JASCO FP-6200 spectrofluorometer with a UNISOKU CoolSpeK cryostat. Emission lifetimes were determined using a HORIBA Jobin Yvon FluoroCube lifetime spectrofluorometer equipped with HORIBA NanoLED-455 (excitation wavelength = 455 nm) as an excitation light source and analyzed by a DAS6 FL decay analysis software. Solvents and reagents were obtained from commercial suppliers and used as received. The solvents marked as “SPS” (THF, $Et_2O$, toluene, and hexane) were purified by the solvent purification system GlassContour 4S. The solvents marked as “distilled” were stored in the glove box after purification by distillation using the following drying agents: Na/benzophenone for THF, $Et_2O$, toluene, and hexane; $CaH_2$ for MeCN, $CD_3CN$, and $CH_2Cl_2$. Distilled water was purchased from Nacalai Tesque Inc. and used as received.

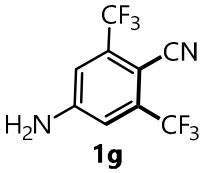
## (B) Materials & Methods

Methyl 4-aminobenzoate (**1a**), 4-aminophenyl methyl sulfone (**1b**), 4-cyanoaniline (**1c**), 4-nitroaniline (**1d**), 3,5-bis(trifluoromethyl)aniline (**1e**), and 4-cyano-3-(trifluoromethyl)aniline (**1f**) were purchased from commercial sources and used as received.

### (B-1) Synthesis of 1g




**4-Amino-2,6-bis(trifluoromethyl)benzonitrile (1g)**[S1]




**1g** was prepared basically according to the known procedures, but modified to increase the selectivity of bromination at 4-position: Under air, 1,3-dibromo-5,5-dimethyl-hydantoin (DBH) (28.6 g, 100 mmol, 1.0 equiv) was added in one portion to the stirred solution of 3,5-bis(trifluoromethyl)aniline (**1e**) (22.9 g, 100 mmol, 1.0 equiv) in DMF (100 mL) and stirred at 0 °C for 4 h. After monitoring the reaction progress by TLC, the mixture was diluted with water (300 mL) and extracted with EtOAc (30 mL, 3 times). The combined organic layer was washed with water (100 mL, 5 times) and brine (30 mL, twice), and dried over $MgSO_4$. After the solids were filtered off, the solvent was removed under reduced pressure and the residue was dried under vacuum. The contents other than **1e**-derived materials including 2,4-dibromo-3,5-bis(trifluoromethyl)aniline (**S1**) 2,6-dibromo-3,5-bis(trifluoromethyl)aniline (**S2**)[S2] in the residue were roughly removed by silica-gel column chromatography (eluent: hexane/EtOAc, 100:0 to 10:1) to afford a mixture containing **S1** and **S2** (*ca*. 1:1) as major products. The obtained red oil was used to the next step without further purification.

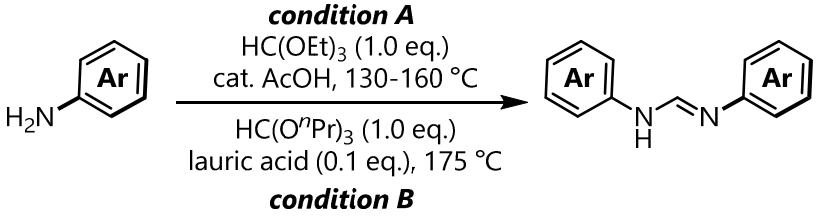
A 500 mL recovery flask was charged with 5 wt% Pd/C (2.13 g, 20.0 mmol, 1 mol% Pd) and dried by heating for 5 min using a heat gun under vacuum. After cooling to ambient temperature, the flask was evacuated and backfilled with nitrogen (three times). A solution of **S1** and **S2** in MeOH (200 mL) was injected to the flask and $HCO_2NH_4$ (15.6 g, 250 mmol, 2.5 equiv) were added subsequently under a gentle stream of nitrogen, and the resulting mixture was stirred at 30 °C for 24 h. After cooling to room temperature, the reaction progress was monitored by TLC. The mixture was filtered through Celite® and all volatiles of the filtrate were removed under reduced pressure. The residual solids were dissolved in water (100 mL) and extracted with EtOAc (100 mL, 3 times). The combined organic layer was washed with water (100 mL, 3 times) and brine (30 mL, twice), and dried over $MgSO_4$. After the solids were filtered off, the solvent was removed under reduced pressure and the residue was dried under vacuum to afford a mixture of 3,5-bis(trifluoromethyl)-4-bromoaniline (**S3**)[S2aNa]nd **1e** (*ca*. 1:1), which was used without further purification.

Under air, to a 200 mL recovery flask containing the above mixture (*ca*. 50 mmol of **S3**) was added CuCN (11.2 g, 125 mmol, 2.5 equiv) and the solids were suspended in NMP (100 mL). The resulting mixture was stirred at 175 °C for 24 h before cooling to room temperature. After monitoring the reaction progress by TLC, the mixture was diluted with EtOAc and water. The precipitates were removed by filtration through Celite® and the filtrate was extracted with EtOAc (5 times).

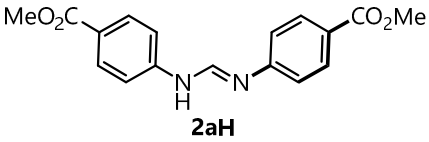
The combined organic layer was washed with water (200 mL, 10 times) and brine (30 mL, 4 times), and dried over $MgSO_4$. The solids were filtered off and the solvent was removed under reduced pressure and the residue was passed through a pad of silica gel (dry charge, eluent: hexane/EtOAc = 1:5), giving a mixture of 4-amino-2,6-bis(trifluoromethyl)benzonitrile (**1g**) and **1e**. After concentration of the filtrate, the residual solids were washed with hexane to afford **1g** (9.40 g, 37 mmol, 37% in 3 steps) as brown solids. If necessary, **1g** can be further purified by silica-gel column chromatography or vacuum sublimation (*ca*. 20 Torr, *ca*. 130 °C), providing pale-yellow solids.

**<u>$^1$H NMR</u>** (400 MHz, $CD_3CN$): $\delta$ 5.67 (br s, 2H), 7.20 (s, 2H) ppm. The spectral data were consistent with the literature.[S1]

### (B-2) Preparation of 1,3-Diarylformamidinates




**1,3-Di(4-methoxycarbonylphenyl)formamidine (2aH)**[S4]

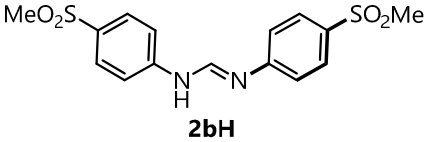


**2aH**

**Condition A**: Under air, to a 50 mL recovery flask were added Methyl 4-aminobenzoate (750 mg, 5.00 mmol, 2.0 equiv), triethyl orthoformate (371 mg, 2.50 mmol, 1.0 equiv), and AcOH (15.0 mg, 0.500 mmol, 0.1 equiv). The resulting mixture was stirred at 130 °C for 24 h before cooling to room temperature. The mixture was washed with toluene (3 mL, 3 times) and the solids were dried under vacuum to afford **2aH** (704.5 mg, 2.25 mmol, 90%) as pale-yellow solids.

**<u>$^1$H NMR</u>** (400 MHz, DMSO-$d_6$): $\delta$ 3.82 (s, 6H), 7.33 (s, 4H), 7.90 (d, $J$ = 8.3 Hz, 4H), 8.45 (s, 1H), 10.4 (s, 1H) ppm. The spectral data were consistent with the literature.

**1,3-Di(4-methanesulfonylphenyl)formamidine (2bH)**[S5]

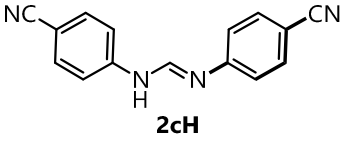


**2bH**

**Condition A**: Under air, to a 50 mL recovery flask were added 4-(methylsulfonyl)aniline (856 mg, 5.00 mmol, 2.0 equiv), triethyl orthoformate (371 mg, 2.50 mmol, 1.0 equiv), and AcOH (15.0 mg, 0.250 mmol, 0.1 equiv). The resulting mixture was suspended in *p*-xylene (4 mL) was stirred at 130 °C for 24 h before cooling to room temperature. The mixture was washed with toluene (3 mL, 3 times) and the solids was dried under vacuum to afford **2bH** (858 mg, 2.43 mmol, 98%) as white solids.

**<u>$^1$H NMR</u>** (400 MHz, DMSO-$d_6$): $\delta$ 3.17 (s, 6H), 7.36-7.61 (br s, 4H), 7.83 (d, $J$ = 8.3 Hz, 4H), 8.48 (br s, 1H), 10.5 (br s, 1H) ppm; **<u>$^{13}$C NMR</u>** (101 MHz, DMSO-$d_6$): $\delta$ 44.0, 119.3, 128.4, 134.3, 149.6 ppm; **<u>IR</u>** (KBr): $\nu$ 3492, 3343, 3013, 2921, 1685, 1585, 1499, 1304, 1145 $cm^{-1}$; **<u>HRMS</u>** (ESI, negative, MeCN): *m/z* calcd. for $C_{15}H_{15}N_2O_4S_2^-$ $[M-H]^-$: 351.0478, found: 351.0463; **<u>Mp.</u>**: 272.2–274.4 °C.

**1,3-Di(4-cyanophenyl)formamidine (2cH)**[S6]

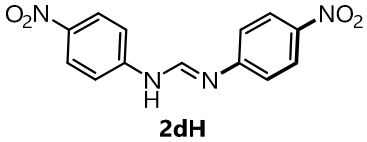


**2cH**

**Condition A**: Under air, to a 50 mL recovery flask were added 4-aminobenzonitrile (1.18 g, 10.0 mmol, 2.0 equiv), triethyl orthoformate (741 mg, 5.00 mmol, 1.0 equiv), and AcOH (30.1 mg, 0.500 mmol, 0.1 equiv). The resulting mixture was stirred at 130 °C for 24 h before cooling to room temperature. The mixture was washed with hexane (3 mL, 3 times) and the solids were dried under vacuum to afford **2cH** (1.21 g, 4.91 mmol, 98%) as yellow solids.

**$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 7.41 (br s, 2H), 7.74 (d, $J$ = 8.4 Hz, 4H), 8.45 (br s, 2H), 10.49 (br s, 1H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$): $\delta$ 104.5, 113.5, 119.4, 119.6, 133.4, 149.5 ppm; **IR** (KBr): $\nu$ 3477, 3326, 3074, 2224, 1667, 1580, 1498, 1314, 1209, 1179 cm$^{-1}$; **HRMS** (ESI, negative, MeCN): *m/z* calcd. for $C_{15}H_9N_4^-$ [M-H]$^-$: 245.0832, found: 245.0793.

**1,3-Di(4-nitrophenyl)formamidine (2dH)**[S4]

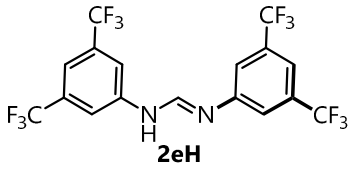


**2dH**

**Condition A**: Under air, to a 50 mL recovery flask were added 4-nitroaniline (1.38 g, 10.0 mmol, 2.0 equiv), triethyl orthoformate (741 mg, 5.00 mmol, 1.0 equiv), and AcOH (30.1 mg, 0.5 mmol, 0.1 equiv). The resulting mixture was suspended in *p*-xylene (4 mL) was stirred at 130 °C for 24 h before cooling to room temperature. The mixture was washed with toluene (3 mL, 3 times) and the solids was dried under vacuum to afford **2dH** (1.29 g, 4.53 mmol, 91 %) as white solids.

**$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 7.49 (s, 4H), 8.21 (d, $J$ = 8.3 Hz, 4H), 8.60 (s, 1H), 10.8 (s, 1H) ppm; **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): δ 119.3 (br) , 125.1, 142.4, 159.8 ppm; **HRMS** (ESI, negative, MeCN): *m/z* calcd. for $C_{13}H_9N_4O_4^-$ [M-H]$^-$: 285.0629, found: 285.0614. The spectral data were consistent with the literature.

**1,3-Di{3,5-bis(trifluoromethyl)phenyl}formamidine (2eH)**[S7]

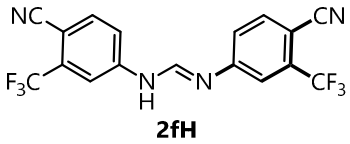


**2eH**

**Condition A**: Under air, to a 100 mL recovery flask were added 3,5-bis(trifluoromethyl)aniline (1.270 g, 5.0 mmol, 2.0 equiv), triethyl orthoformate (371 mg, 2.50 mmol, 1.0 equiv), and AcOH (15 mg, 0.25 mmol, 0.1 equiv). The resulting mixture was stirred at 130 °C for 24 h before cooling to room temperature. The mixture was washed with hexane (3 mL, 3 times) and the solids were dried under vacuum to afford **2eH** (901 mg, 1.92 mmol, 77%) as white solids.

**$^1$H NMR** (400 MHz, Acetone-$d_6$): $\delta$ 7.69 (br s, 4H), 8.01 (br s, 1H), 8.67 (br, s, 1H), 9.66 (br s, 1H) ppm; **HRMS** (ESI, negative, MeCN): *m/z* calcd. for $C_{17}H_7F_{12}N_2^-$ [M–H]$^-$: 467.0423, found: 467.0425. The spectral data were consistent with the literature.

**1,3-Di{4-cyano-3-(trifluoromethyl)phenyl}formamidine (2fH)**

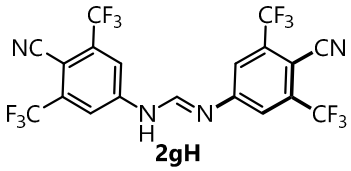


**2fH**

**Condition B**: Under air, to a 100 mL recovery flask were added 4-amino-2-(trifluoromethyl)-benzonitrile (3.70 g, 19.9 mmol, 2.0 equiv), tri-*n*-propyl orthoformate (2.02 g, 10.0 mmol, 1.0 equiv), and lauric acid (200 mg, 1.00 mmol, 0.1 equiv). The resulting mixture was stirred at 170 °C for 24 h before cooling to room temperature. The mixture was washed with toluene and hexane (3 mL, 3 times for each) and the solids were dried under vacuum to afford **2fH** (3.29 g, 8.62 mmol, 86%) as pale-beige solids.

**$^1$H NMR** (400 MHz, $CD_3CN$): $\delta$ 7.62 (br s, 2H), 7.80 (br s, 2H), 7.89 (d, $J$ = 8.8 Hz, 2H), 8.26 (br s, 1H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$): $\delta$ 101.3, 116.1, 117.4, 122.6 (q, $^1J_{CF}$ = 274 Hz), 122.9, 132.1 (1, $^2J_{CF}$ = 31.8 Hz), 136.5, 150.5, 151.3 ppm; **$^{19}$F NMR** (376 MHz, $CD_3CN$): $\delta$ -62.70 (s, 6F) ppm; **IR** (KBr): $\nu$ 3427, 3307, 3076, 2989, 2226, 1665, 1604, 1576, 1435, 1341, 1293, 1185, 1134 cm$^{-1}$; **HRMS** (ESI, negative, MeCN): *m/z* calcd. for $C_{17}H_7F_6N_4^-$ [M-H]$^-$: 381.0580, found: 381.0583. **Mp.**: 268.2–270.0 ℃.

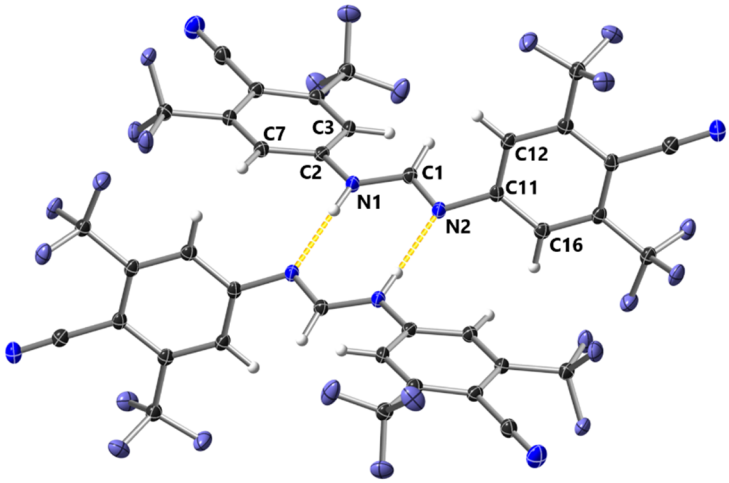
**1,3-Di{4-cyano-3,5-bis(trifluoromethyl)phenyl}formamidine (2gH)**



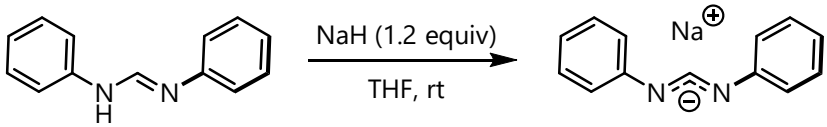
**2gH**

**Condition B**: Under air, to a 100 mL recovery flask were added 4-amino-2,6-bis(trifluoromethyl)benzonitrile (3.57 g, 14.0 mmol, 2.0 equiv), tri-*n*-propyl orthoformate (1.33 g, 7.00 mmol, 1.0 equiv), and lauric acid (140.2 mg, 0.700 mmol, 0.1 equiv). The resulting mixture was stirred at 170 °C for 24 h before cooling to room temperature. The mixture was carefully washed with EtOAc (3 mL, 3 times) and the solids were dried under vacuum to afford **2gH** (2.35 g, 4.58 mmol, 65%) as beige solids.

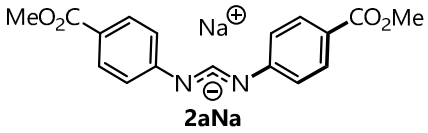
**$^1$H NMR** (400 MHz, $CD_3CN$): $\delta$ 8.02 (br s, 4H), 8.37 (br s, 1H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$): $\delta$ 98.6, 112.6, 121.9 (q, $^1J_{CF}$ = 275 Hz), 134.6 (q, $^2J_{CF}$ = 31.8 Hz), 150.3, 152.9 ppm; **$^{19}$F NMR** (376 MHz, $CD_3CN$): $\delta$ -62.74 (s, 12F) ppm; **IR** (KBr): $\nu$ 3432, 3323, 3088, 2239, 1674, 1605, 1524, 1478, 1372, 1294, 1215, 1188, 1166, 1139 $cm^{-1}$; **HRMS** (ESI, negative, MeCN): *m/z* calcd. for $C_{19}H_5F_{12}N_4^-$ [M-H]$^-$: 517.0328, found: 517.0320; **Mp.**: 244.1–247.4 °C; **X-ray data**: M = 518.28, block, colorless, triclinic, $P\bar{1}$ (#2), $a$ = 8.2148(2) Å, $b$ = 10.0468(3) Å, $c$ = 11.6137(3) Å, $\alpha$ = 90.297(2)°, $\beta$ = 102.341(2)°, $\gamma$ = 93.315(2)°, $V$ = 934.64(4) Å$^3$, $Z$ = 2, $D$calcd = 1.842 g/cm$^3$, $T$ = 100.01(10) K, $R_1$ ($wR_2$) = 0.0306 (0.0822).




**(B-3) Deprotonation of Amidinates**




**Sodium 1,3-Di(4-methoxycarbonylphenyl)formamidinate (2aNa)**

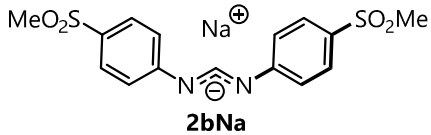


**2aNa**

A 20 mL recovery flask containing **2aH** (312 mg, 1.00 mmol, 1.0 equiv) was taken into the $N_2$-filled glove box and oil-free NaH (pre-washed with hexane, 28.8 mg, 1.20 mmol, 1.2 equiv) was added. The solids were suspended in THF (5 mL) and stirred at room temperature for 24 h. The mixture was filtered through Celite® and the cake was washed with THF. The filtrate was concentrated and dried under reduced pressure to furnish 0.4 THF adduct of **2aNa** (310 mg, 0.854 mmol, 85%) as moisture-sensitive yellow solids.

**$^1$H NMR** (400 MHz, $CD_3CN$): $\delta$ 1.75–1.85 (m, 2H), 3.59–3.68 (m, 2H), 3.79 (s, 6H), 6.99 (d, $J$ = 8.8 Hz, 4H), 7.76 (d, $J$ = 8.8 Hz, 4H), 8.93 (s, 1H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$): $\delta$ 25.2, 51.2, 67.1, 118.4, 119.3, 130.3, 159.5, 159.8, 166.7 ppm; **HRMS** (ESI, negative, MeCN): *m/z* calcd. for $C_{17}H_{15}N_2O_4^-$ [M]$^-$: 311.1037, found: 311.1030.

**Sodium 1,3-Di(4-methansulfonylphenyl)formamidinate (2bNa)**



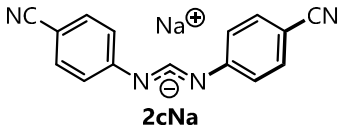
**2bNa**

A 20 mL recovery flask containing **2bH** (352 mg, 1.00 mmol, 1.0 equiv) was taken into the $N_2$-filled glove box and oil-free NaH (pre-washed with hexane, 28.8 mg, 1.20 mmol, 1.2 equiv) was added. The solids were suspended in THF (5 mL)

and stirred at room temperature for 24 h. The mixture was filtered through Celite® and the cake was washed with THF. The filtrate was concentrated and dried under reduced pressure to afford 0.6 THF adduct of **2bNa** (350 mg, 0.838 mmol, 84%) as moisture-sensitive yellow solids.

**$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 1.75–1.85 (m, 2H), 2.98 (s, 6H), 3.59–3.68 (m, 2H), 7.12 (d, $J$ = 8.7 Hz, 4H), 7.63 (d, $J$ = 8.7 Hz, 4H), 8.91 (s, 1H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$): $\delta$ 25.1, 44.4, 67.0, 119.6, 127.9, 128.5, 159.5, 159.7 ppm; **HRMS** (ESI, negative, MeCN): *m/z* calcd. for $C_{15}H_{15}N_2O_4S_2^-$ [M]$^-$: 351.0478, found: 351.0481.

**Sodium 1,3-Di(4-cyanophenyl)formamidinate (2cNa)**

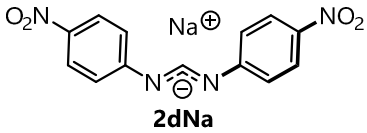


**2cNa**

A 20 mL recovery flask containing **2cH** (98.5 mg, 0.400 mmol, 1.0 equiv) was taken into the $N_2$-filled glove box and oil-free NaH (pre-washed with hexane, 11.5 mg, 0.480 mmol, 1.2 equiv) was added. The solids were suspended in THF (5 mL) and stirred at room temperature for 24 h. The mixture was filtered through Celite® and the cake was washed with THF. The filtrate was concentrated and dried under reduced pressure to afford 0.25 THF adduct of **2cNa** (74.0 mg, 0.258 mmol, 65%) as moisture-sensitive yellow-orange solids.

**$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 1.75–1.80 (m, 1H), 3.58–3.63 (m, 1H), 6.98 (d, $J$ = 8.4 Hz, 4H), 7.41 (d, $J$ = 8.6 Hz, 4H), 8.45 (s, 1H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$): $\delta$ 25.1, 67.0, 98.5, 120.3, 120.9, 132.6, 158.4, 158.9 ppm; **HRMS** (ESI, negative, MeCN): *m/z* calcd. for $C_{15}H_9N_4^-$ [M]$^-$: 245.0832, found: 245.0789.

**Sodium 1,3-Di(4-nitrophenyl)formamidinate (2dNa)**

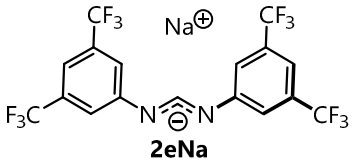


**2dNa**

A 20 mL recovery flask containing **2dH** (286 mg, 1.00 mmol, 1.0 equiv) was taken into the $N_2$-filled glove box and oil-free NaH (pre-washed with hexane, 28.8 mg, 1.20 mmol, 1.2 equiv) was added. The solids were suspended in THF (5 mL) and stirred at room temperature for 24 h. The mixture was filtered through Celite® and the cake was washed with THF. The filtrate was concentrated and dried under reduced pressure to give 0.25 THF adduct of **2dNa** (281 mg, 0.861 mmol, 86%) as purple solids.

**$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 1.70–1.80 (m, 1H), 3.57–3.61 (m, 1H), 7.10 (d, $J$ = 9.0 Hz, 4H), 8.00 (d, $J$ = 9.0 Hz, 4H), 8.69 (s, 1H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$): $\delta$ 25.1, 67.0, 119.7, 125.1, 138.9, 158.4, 160.3 ppm; **IR** (KBr): $\nu$ 3544, 3179, 3103, 1660, 1579, 1523, 1300, 1108 cm$^{-1}$; **HRMS** (ESI, negative, MeCN): *m/z* calcd. for $C_{13}H_9N_4O_4^-$ [M]$^-$: 285.0629, found: 285.0621. **Mp.**: 258.1–259.6 °C.

**Sodium 1,3-Di{3,5-bis(trifluoromethyl)phenyl}formamidinate (2eNa)**

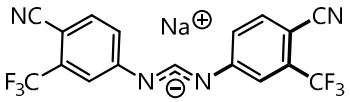


**2eNa**

A 20 mL recovery flask containing **2eH** (187.2 mg, 0.400 mmol, 1.0 equiv) was taken into the $N_2$-filled glove box and oil-free NaH (pre-washed with hexane, 11.5 mg, 0.480 mmol, 1.2 equiv) was added. The solids were suspended in THF (5 mL) and stirred at room temperature for 24 h. The mixture was filtered through Celite® and the cake was washed with THF. The filtrate was concentrated and dried under reduced pressure to give 1.0 THF adduct of **2eNa** (172 mg, 0.306 mmol, 76%) as moisture-sensitive off-white solids.

**$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 1.70–1.81 (m, 4H), 3.57–3.67 (m, 4H), 7.14 (s, 2H), 7.51 (s, 4H), 8.34 (s, 1H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$): $\delta$ 25.1, 67.0, 109.5, 119.9, 124.0 (q, $^1J_{CF}$ = 273 Hz), 130.3 (q, $^2J_{CF}$ = 31.8 Hz), 156.4, 159.1 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$): $\delta$ -61.32 (s, 12F) ppm; **HRMS** (ESI, negative, MeCN): *m/z* calcd. for $C_{17}H_7F_{12}N_2^-$ [M]$^-$: 467.0423, found: 467.0418.

**Sodium 1,3-Di{4-cyano-3-(trifluoromethyl)phenyl}formamidinate (2fNa)**

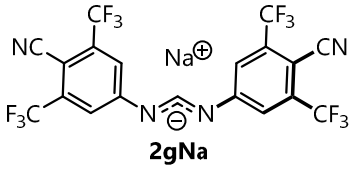


**2fNa**

A 20 mL recovery flask containing **2fH** (765 mg, 2.00 mmol, 1.0 equiv) was taken into the $N_2$-filled glove box and oil-free NaH (pre-washed with hexane, 57.6 mg, 2.40 mmol, 1.2 equiv) was added. The solids were suspended in THF (5 mL) and stirred at room temperature for 24 h. The mixture was filtered through Celite® and the cake was washed with THF. The filtrate was concentrated and dried under reduced pressure to give 0.25 THF adduct of **2fNa** (858 mg, 2.03 mmol, quant.) as moisture-sensitive brown solids.

**$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 1.76–1.85 (m, 1H), 3.60–3.67 (m, 1H), 7.29 (d, $J$ = 8.4 Hz, 2H), 7.33 (s, 2H), 7.69 (d, $J$ = 8.4 Hz, 2H), 8.54 (s, 1H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$): $\delta$ 25.1, 67.0, 94.6, 117.6, 119.1, 123.1 (q, $^1J_{CF}$ = 274 Hz), 122.3, 131.3 (q, $^2J_{CF}$ = 24.7 Hz), 135.5, 159.2, 159.9 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$): $\delta$ -60.95 (s, 6F) ppm; **HRMS** (ESI, negative, MeCN): $m/z$ calcd. for $C_{17}H_7F_6N_4^-$ [M]$^-$: 381.0580, found: 381.0577.

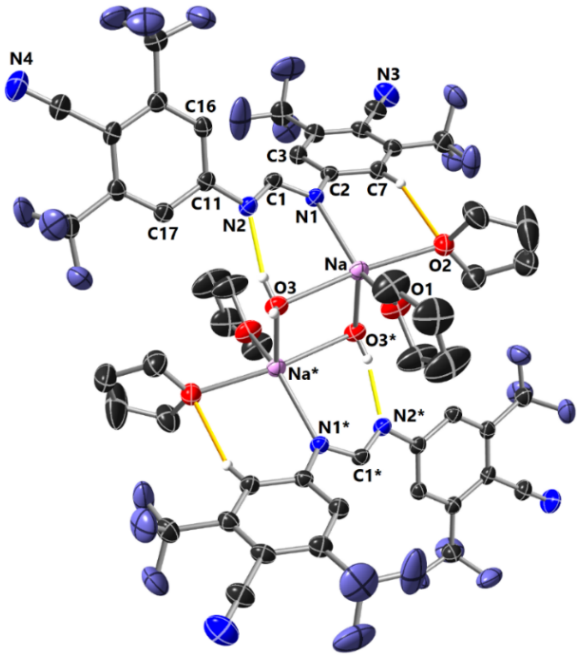
**Sodium 1,3-Di{4-cyano-3,5-bis(trifluoromethyl)phenyl}formamidinate (2gNa)**



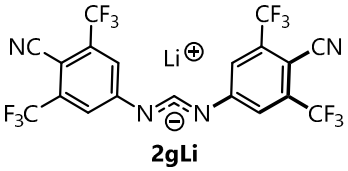
**2gNa**

A 20 mL recovery flask containing **2gH** (1.04 g, 2.00 mmol, 1.0 equiv) was taken into the $N_2$-filled glove box and oil-free NaH (pre-washed with hexane, 57.6 mg, 2.40 mmol, 1.2 equiv) was added. The solids were suspended in THF (5 mL) and stirred at room temperature for 24 h. The mixture was filtered through Celite® and the cake was washed with THF. The filtrate was concentrated and dried under reduced pressure to give **2gNa** (1.08 g, 1.99 mmol, 99%) as yellow solids. Single crystals suitable for X-ray crystallography were prepared by slow diffusion of hexane into a THF solution under air.

**$^1$H NMR** (400 MHz, $CD_3CN$): $\delta$ 7.84 (s, 4H), 8.55 (s, 1H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$): $\delta$ 91.4, 114.0, 121.1 (app. q, $^3J_{CF}$ = 1.5 Hz), 122.5 (q, $^1J_{CF}$ = 275 Hz), 134.0 (q, $^2J_{CF}$ = 31.2 Hz), 159.1, 160.7 ppm; **$^{19}$F NMR** (376 MHz, $CD_3CN$): $\delta$ -62.76 (s, 12F) ppm; **IR** (KBr): $\nu$ 3484, 3372, 3247, 2240, 2230, 1676, 1611, 1513, 14004, 1324, 1289, 1215, 1190, 1131 cm$^{-1}$; **HRMS** (ESI, negative, $CH_3CN$): $m/z$ calcd. for $C_{19}H_5F_{12}N_4^-$ [M]$^-$: 517.0328, found: 517.0304; **Mp.**: >290 °C; **X-ray data**: M = 1404.97, block, yellow, triclinic, $P\bar{1}$ (#2), $a$ = 10.1787(12) Å, $b$ = 11.7677(17) Å, $c$ = 14.651(2) Å, $\alpha$ = 73.314(5)°, $\beta$ = 73.689(5)°, $\gamma$ = 72.357(5)°, $V$ = 1565.4(4) Å$^3$, $Z$ = 1, $D$ = 1.490 g/cm$^3$, $T$ = 293(2) K, $R_1$ ($wR_2$) = 0.0587 (0.1570).



**Lithium 1,3-Di{4-cyano-3,5-bis(trifluoromethyl)phenyl}formamidinate (2gLi)**

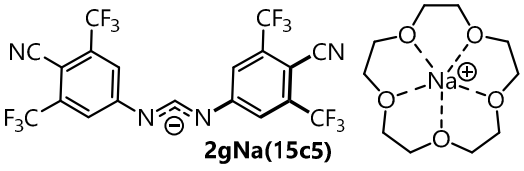


2gLi

A 20 mL recovery flask containing **2gH** (155 mg, 0.300 mmol, 1.0 equiv) was taken into the $N_2$-filled glove box and LiH (2.86 mg, 0.360 mmol, 1.2 equiv) was added. The solids were then suspended in THF (3 mL) and stirred at room temperature for 24 h. The mixture was filtered through Celite® and the cake was washed with THF. The filtrate was concentrated and dried under reduced pressure to give 1.0 THF adduct of **2gLi** (164 mg, 0.275 mmol, 92%) as yellow solids.

**$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 1.72–1.80 (m, 4H), 3.57–3.62 (m, 4H), 7.66 (s, 4H), 8.65 (s, 1H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$): $\delta$ 25.1, 67.0, 91.2, 114.0, 121.0, 122.5 (q, $^1J_{CF}$ = 275 Hz), 133.9 (q, $^2J_{CF}$ = 30.9 Hz), 159.2, 160.5 ppm; **$^{19}$F NMR** (376 MHz, $CD_3CN$): $\delta$ -62.73 (s, 12F) ppm; **IR** (KBr): $\nu$ 3483, 3372, 3247, 2248, 2229, 1675, 1610, 1511, 1403, 1327, 1287, 1215, 1188, 1132 cm$^{-1}$; **HRMS** (ESI, negative, MeCN): *m/z* calcd. for $C_{19}H_5F_{12}N_4^-$ $[M]^-$: 517.0328, found: 517.0317; **Mp.**: 244.2–246.3 °C.

**(1,4,7,10,13-Pentaoxacyclopentadecane)sodium 1,3-Di{4-cyano-3,5-bis(trifluoromethyl)phenyl}formamidinate (2gNa(15c5))**

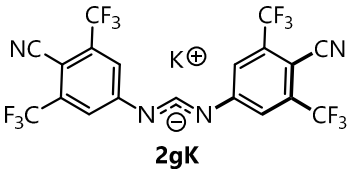


2gNa(15c5)

A 20 mL recovery flask containing **2gNa** (540.2 mg, 1.00 mmol, 1.0 equiv) was taken into the $N_2$-filled glove box and 15-crown-5 (220 mg, 1.00 mmol, 1.00 equiv) was added. The solids were then suspended in THF (4 mL) and stirred at room temperature for 24 h. The mixture was concentrated and dried under reduced pressure to afford **2gNa(15c5)** (757 mg, 0.99 mmol, 99%) as yellow solids.

**$^1$H NMR** (400 MHz, $CD_3CN$): $\delta$ 3.61 (s, 24H), 7.70 (s, 4H), 8.63 (s,1H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$): $\delta$ 69.2, 91.6, 113.9. 120.9, 122.5 (q, $^1J_{CF}$ = 275 Hz), 133.9 (q, $^2J_{CF}$ = 30.8 Hz), 158.7, 160.5 ppm; **$^{19}$F NMR** (376 MHz, $CD_3CN$): $\delta$ -61.14 (s, 12F) ppm; **IR** (KBr): $\nu$ 3440, 3246, 2909, 2222, 1659, 1498, 1355, 1299, 1181, 1136 cm$^{-1}$; **HRMS** (ESI, positive, MeCN): *m/z* calcd. for $C_{10}H_{20}O_5Na^+$ $[M]^+$: 243.1203, found: 243.1199; (ESI, negative, MeCN): *m/z* calcd. for $C_{19}H_5F_{12}N_4^-$ $[M]^-$: 517.0328, found: 517.0300; **Mp.**: 128.2–130.4 °C.

**Potassium 1,3-Di{4-cyano-3,5-bis(trifluoromethyl)phenyl}formamidinate (2gK)**

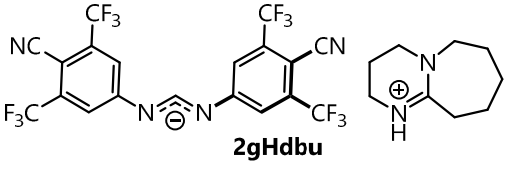


2gK

A 20 mL recovery flask containing **2gH** (77.7 mg, 0.150 mmol, 1.0 equiv) was taken into the $N_2$-filled glove box and KH (7.21 mg, 0.180 mmol, 1.2 equiv) was added. The solids were then suspended in THF (1 mL) and stirred at room temperature for 24 h. The mixture was filtered through Celite® and the cake was washed with THF. The filtrate was concentrated and dried under reduced pressure to give adduct of **2gK** (82.1 mg, 0.148 mmol, 98%) as yellow solids.

**$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 7.68 (s, 4H), 8.67 (s, 1H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$): $\delta$ 91.8, 113.9, 121.0, 122.5 (q, $^1J_{CF}$ = 275 Hz), 134.0 (q, $^2J_{CF}$ = 31.8 Hz), 158.5, 160.1 ppm; **$^{19}$F NMR** (376 MHz, $CD_3CN$): $\delta$ -62.70 (s, 12F) ppm; **IR** (KBr): $\nu$ 3483, 3372, 2227, 1674, 1605, 1509, 1323, 1297, 1216, 1185, 1133 cm$^{-1}$; **HRMS** (ESI, negative, $CH_3CN$): *m/z* calcd. for $C_{19}H_5F_{12}N_4^-$ $[M]^-$: 517.0328, found: 517.0310. **Mp.**: >275 °C (decomp.).

**1,8-Diazabicyclo[5.4.0]undec-7-en-8-ium 1,3-Di{4-cyano-3,5-bis(trifluoromethyl)phenyl}formamidinate (2gHdbu)**



2gHdbu

A 20 mL recovery flask containing **2gH** (518 mg, 1.00 mmol, 1.0 equiv) was taken into the $N_2$-filled glove box and anhydrous DBU (152 mg, 1.00 mmol, 1.0 equiv) was added. The solids were suspended in THF (5 mL) and stirred at room temperature for 24 h. The mixture was concentrated and dried under reduced pressure to give 0.2 THF adduct of **2gHdbu** (565 mg, 0.844 mmol, 84%) as yellow solids.

**$^{1}$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 1.57–1.70 (m, 6H), 1.73–1.78 (m, 0.8H), 1.86–1.91 (m, 2H), 2.57–2.60 (m, 2H), 3.23 (t, $J$ =5.7 Hz, 2H), 3.44 (t, $J$ = 5.7 Hz, 2H), 3.49–3.51 (m, 2H), 3.57–3.61 (m, 0.8H), 7.66 (s, 4H), 8.65 (s, 1H) ppm; **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 19.1, 23.5, 25.1, 26.1, 28.3, 32.1, 38.1, 47.9, 53.3, 67.0, 91.3, 114.0, 121.0, 122.5 (q, $^{1}J_{CF}$ = 272 Hz), 133.9 (q, $^{2}J_{CF}$ = 30.6 Hz), 159.1, 160.5, 164.9 ppm; **$^{19}$F NMR** (376 MHz, $CD_3CN$): $\delta$ -62.67 (s, 12F) ppm; **IR** (KBr): $v$ 3410, 3204, 2942, 2223, 1648, 1516, 1356, 1323, 1283, 1204, 1179, 1130 cm$^{-1}$; **HRMS** (ESI, negative, MeCN): $m/z$ calcd. for $C_{19}H_5F_{12}N_4^-$ [M]$^-$: 517.0328, found: 517.0294; **Mp.**: 118.2–122.5 ℃.

## (C) Cyclic Voltammetry (CV)

**2gNa** exhibited irreversible oxidation upon measurements. The voltammograms suggested decomposition of **2gNa**.

Conditions for the CV measurements using **2gNa**:

| | | |
|---|---|---|
| Reference: $Ag/Ag^+$ ($AgNO_3$) | Electrodes: Pt/C | Solvent: MeCN |
| Electrolyte: $TBAPF_6$ (0.1 M) | Concentration: $1.0 \times 10^{-3}$ M | Range: –1.5~+2.0 V (*vs*. SCE) |

Result:

Resting potential: –0.94 V (*vs*. SCE)

$E_{ox}$ = +0.23 (1$^{st}$ cycle), +0.14 V (2$^{nd}$ and 3$^{rd}$ cycles), +1.15 (1$^{st}$ cycle), +1.10 V (2$^{nd}$ and 3$^{rd}$ cycles) (*vs*. SCE)

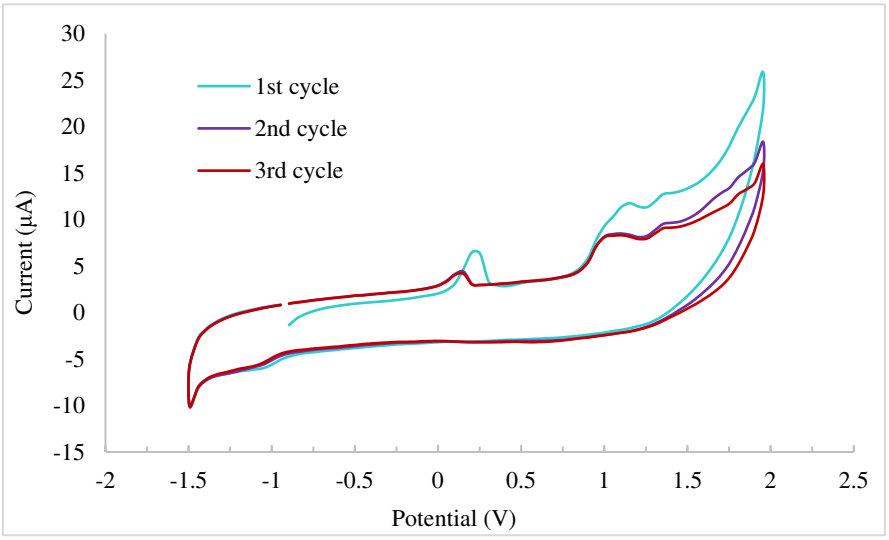



**Figure S1.** Cyclic voltammogram of **2gNa**.

## (D) Absorption & Emission Properties

For **2aH** and **2aNa**:

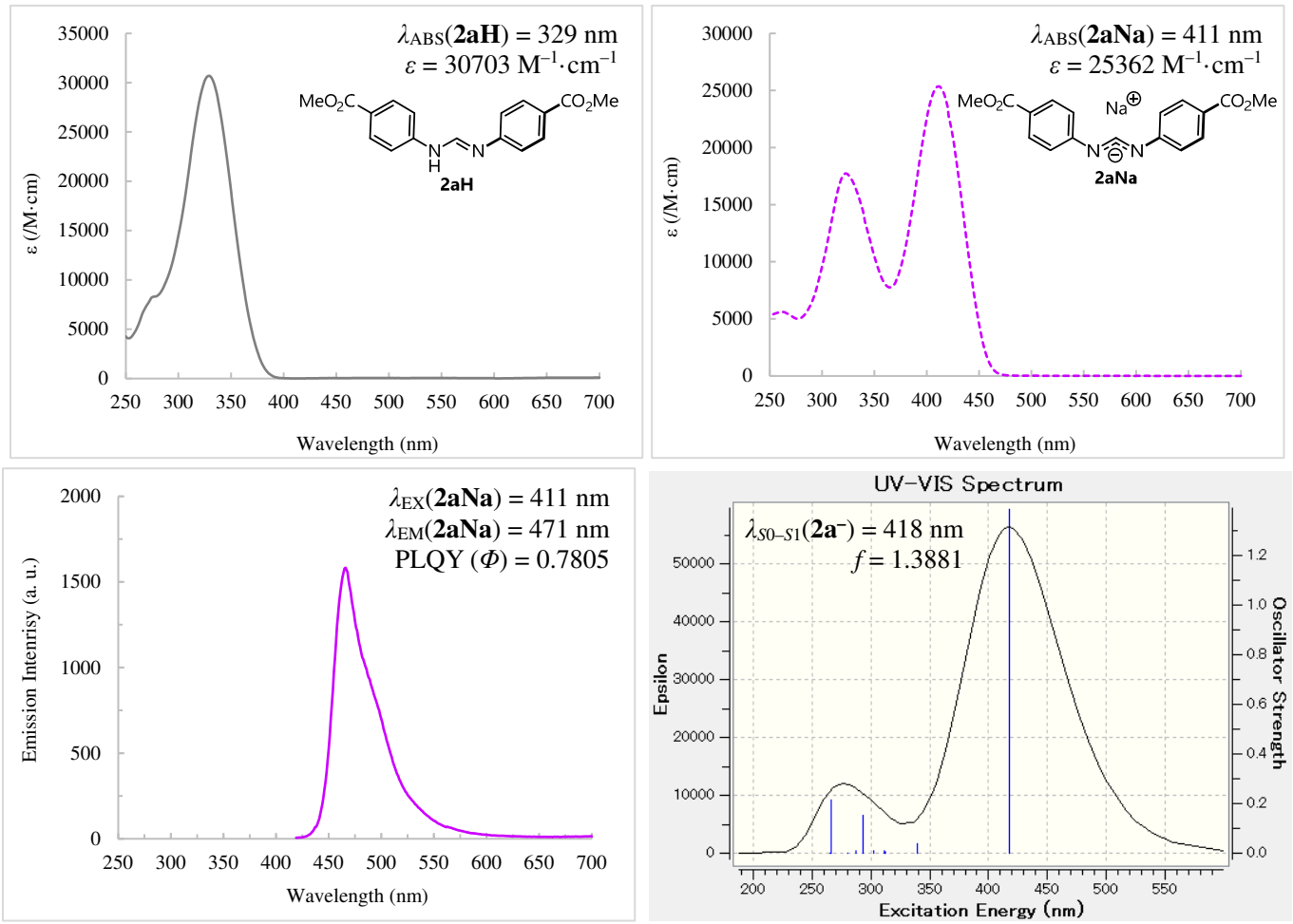



**Figure S2.** (Top, left) UV-Vis absorption spectrum of **2aH** in THF ($1.0 \times 10^{-5}$ M). (Top, right) UV-Vis absorption spectra of **2aNa** in THF ($1.0 \times 10^{-4}$ M). (Bottom, left) emission spectra of **2aNa** in THF ($1.0 \times 10^{-4}$ M). (Bottom, right) DFT-based simulation of UV-Vis spectrum, the excitation energies, and the oscillator strengths for the optimized geometry of **2a**$^{-}$.

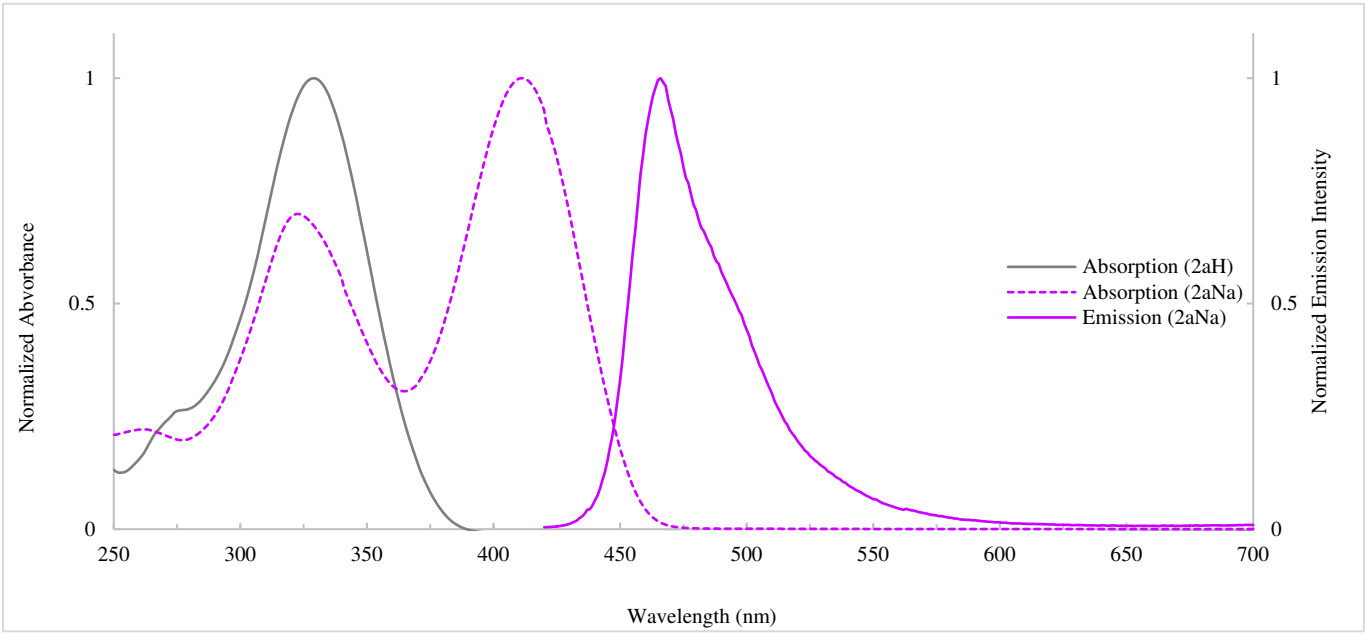



**Figure S3.** Normalized absorption and emission spectra of **2aH** and **2aNa** in THF.

For **2bH** and **2bNa**:

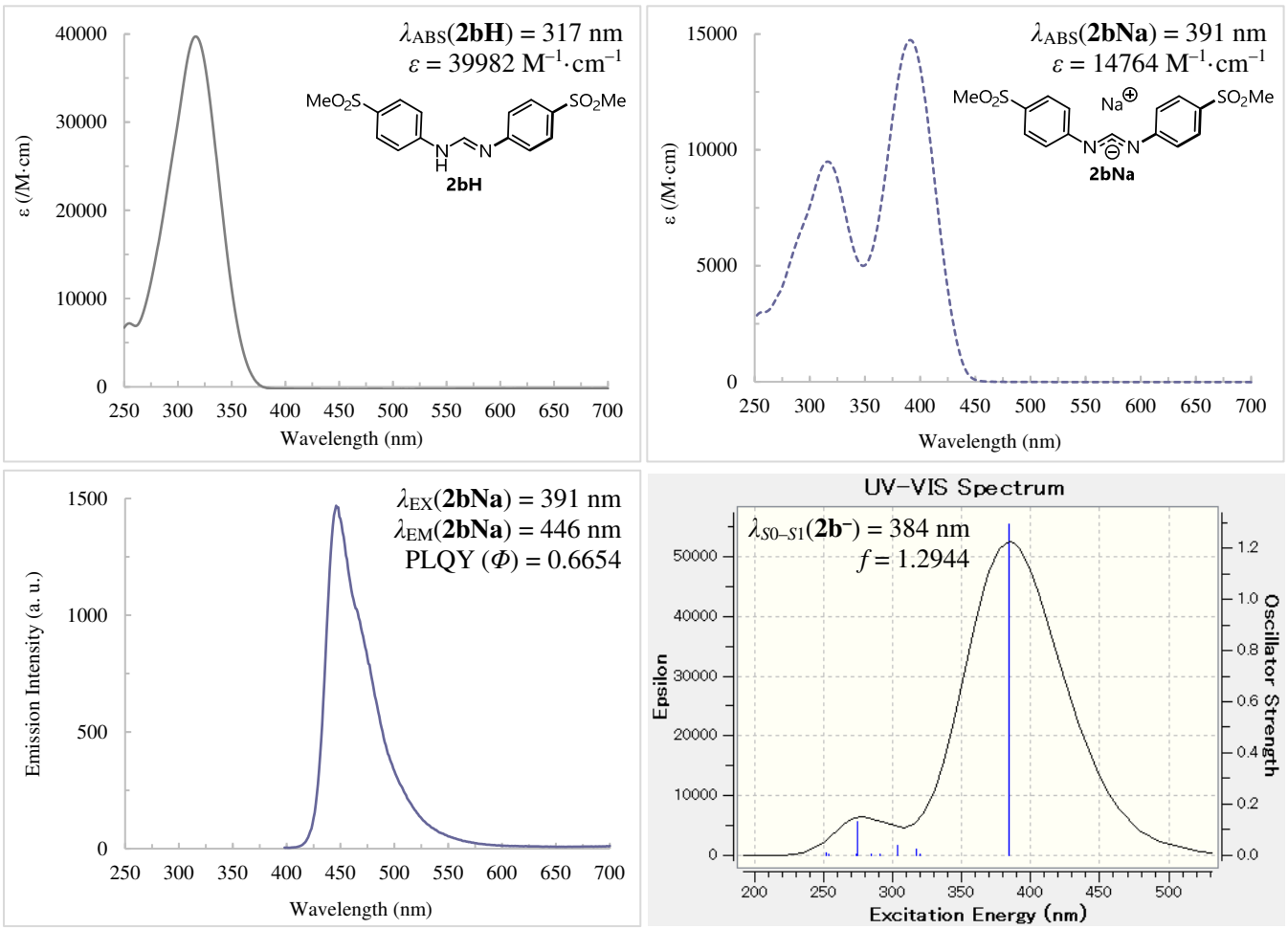



**Figure S4.** (Top, left) UV-Vis absorption spectrum of **2bH** in THF ($1.0 \times 10^{-5}$ M). (Top, right) UV-Vis absorption spectra of **2bNa** in THF ($1.0 \times 10^{-4}$ M). (Bottom, left) emission spectra of **2bNa** in THF ($1.0 \times 10^{-4}$ M). (Bottom, right) DFT-based simulation of UV-Vis spectrum, the excitation energies, and the oscillator strengths for the optimized geometry of **2b**$^{-}$.

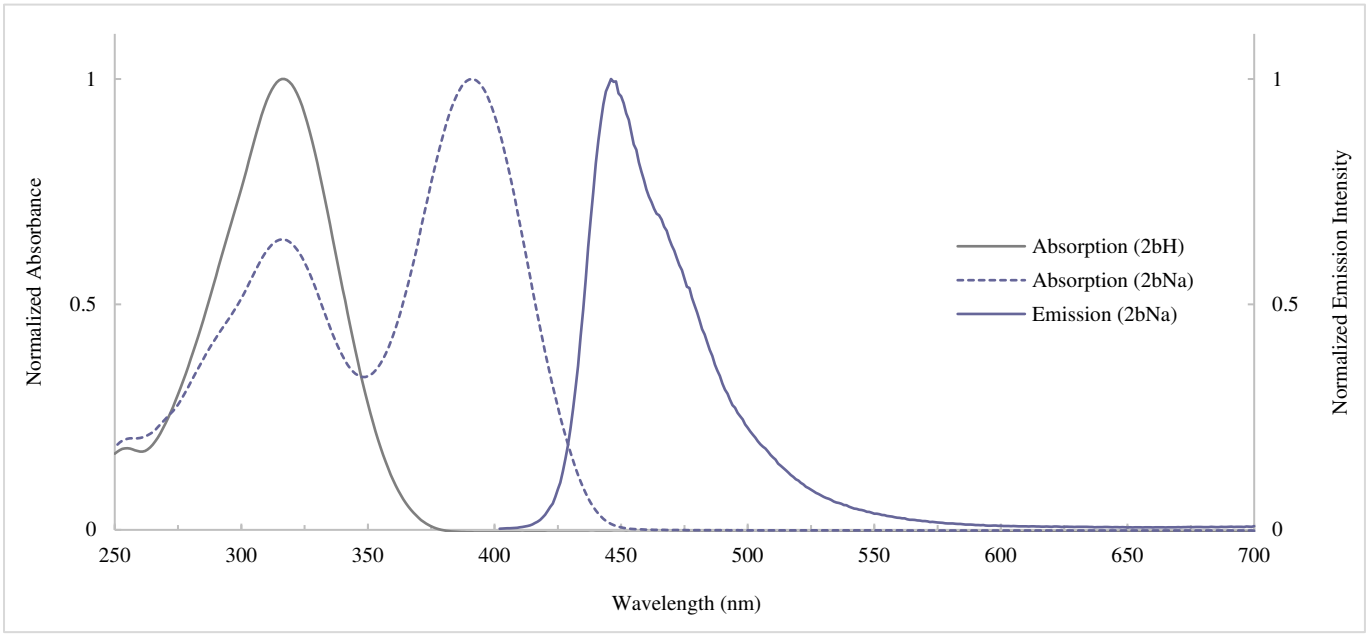



**Figure S5.** Normalized absorption and emission spectra of **2bH** and **2bNa** in THF.

For **2cH** and **2cNa**:

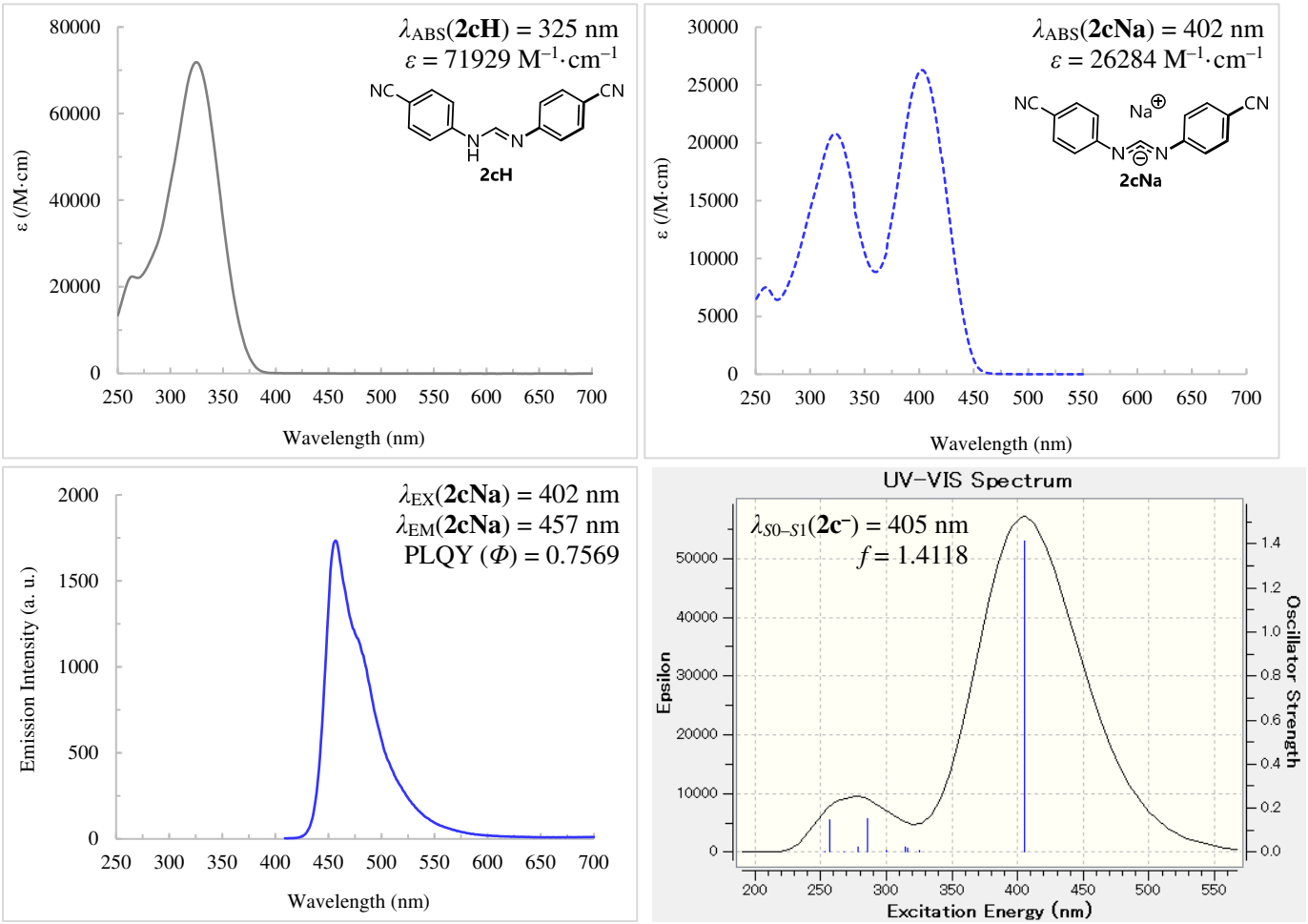



**Figure S6.** (Top, left) UV-Vis absorption spectrum of **2cH** in THF ($1.0 \times 10^{-5}$ M). (Top, right) UV-Vis absorption spectra of **2cNa** in THF ($1.0 \times 10^{-4}$ M). (Bottom, left) emission spectra of **2cNa** in THF ($1.0 \times 10^{-4}$ M). (Bottom, right) DFT-based simulation of UV-Vis spectrum, the excitation energies, and the oscillator strengths for the optimized geometry of **2c**$^{-}$.

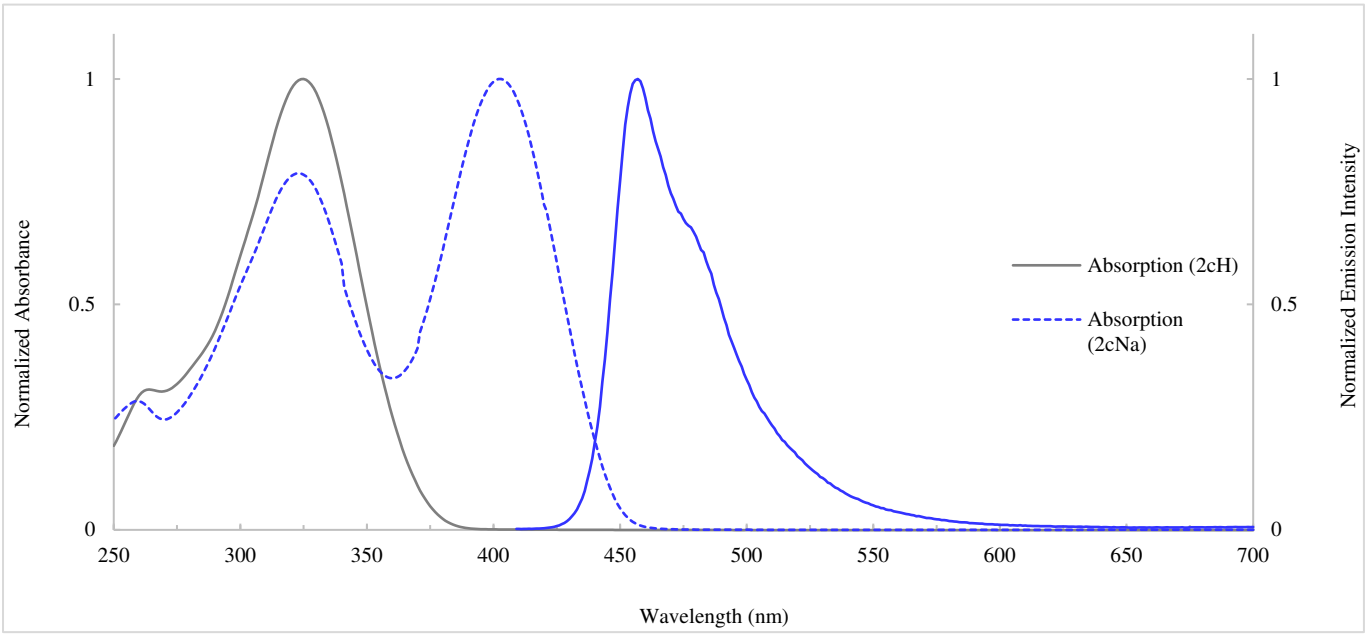



**Figure S7.** Normalized absorption and emission spectra of **2cH** and **2cNa** in THF.

For **2dH** and **2dNa**:

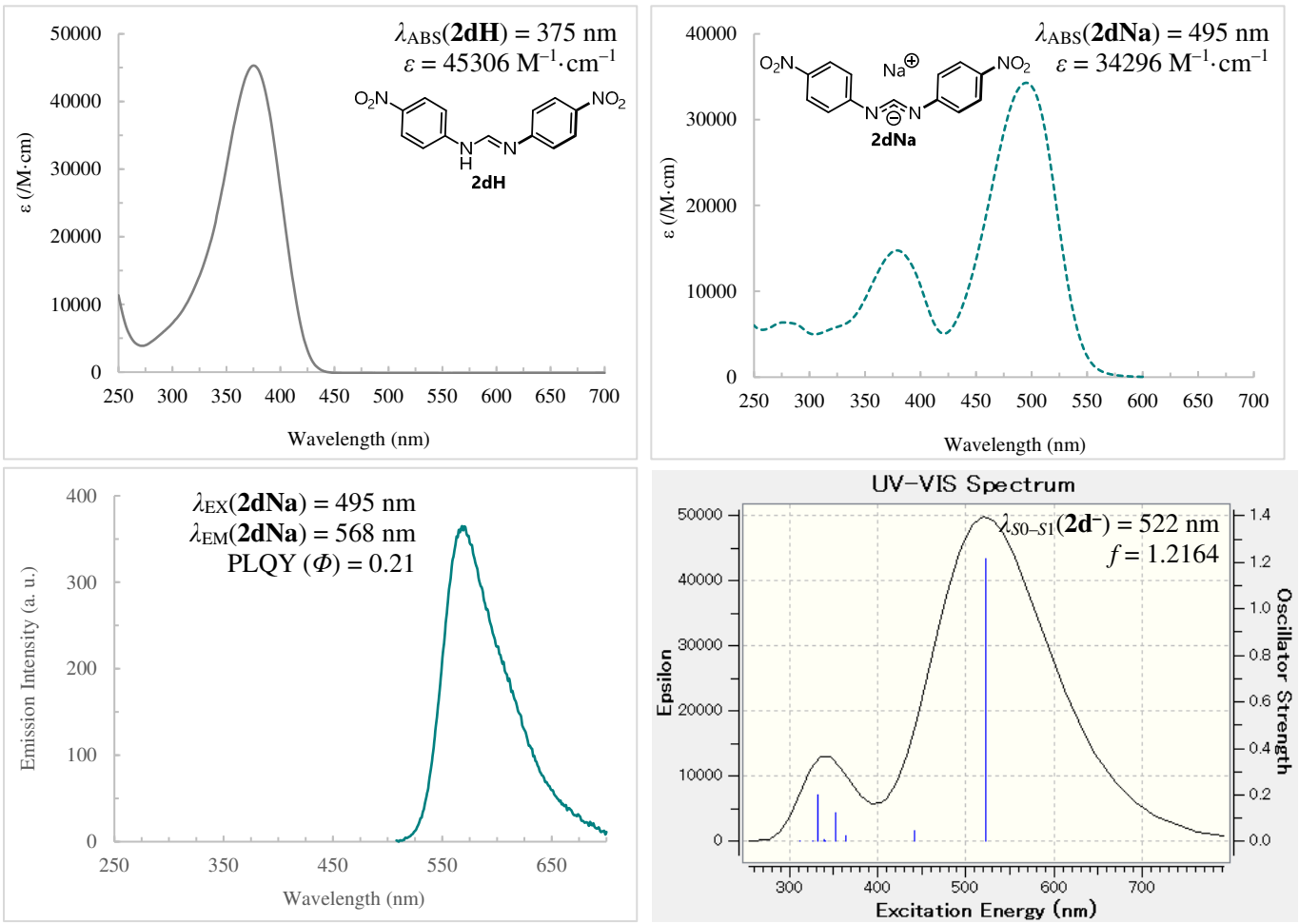



**Figure S8.** (Top, left) UV-Vis absorption spectrum of **2dH** in THF ($1.0 \times 10^{-5}$ M). (Top, right) UV-Vis absorption spectra of **2dNa** in THF ($1.0 \times 10^{-4}$ M). (Bottom, left) emission spectra of **2dNa** in THF ($1.0 \times 10^{-4}$ M). (Bottom, right) DFT-based simulation of UV-Vis spectrum, the excitation energies, and the oscillator strengths for the optimized geometry of **2d**$^{-}$.

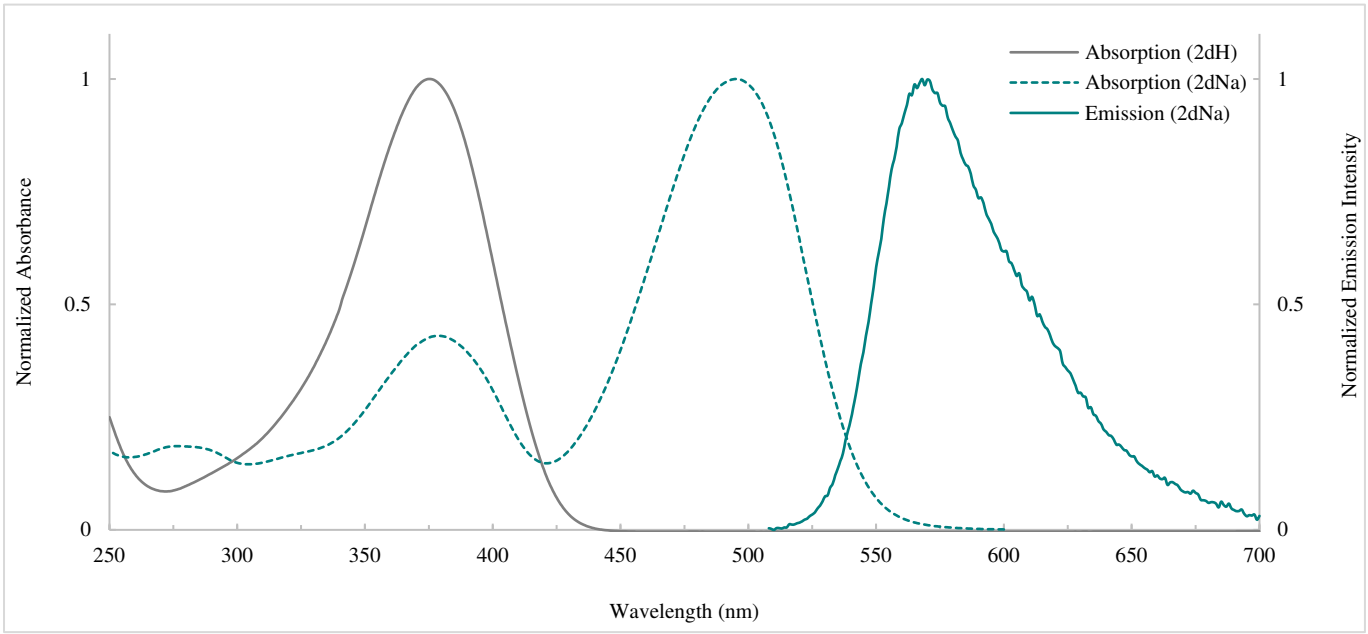



**Figure S9.** Normalized absorption and emission spectra of **2dH** and **2dNa** in THF.

For **2eH** and **2eNa**:

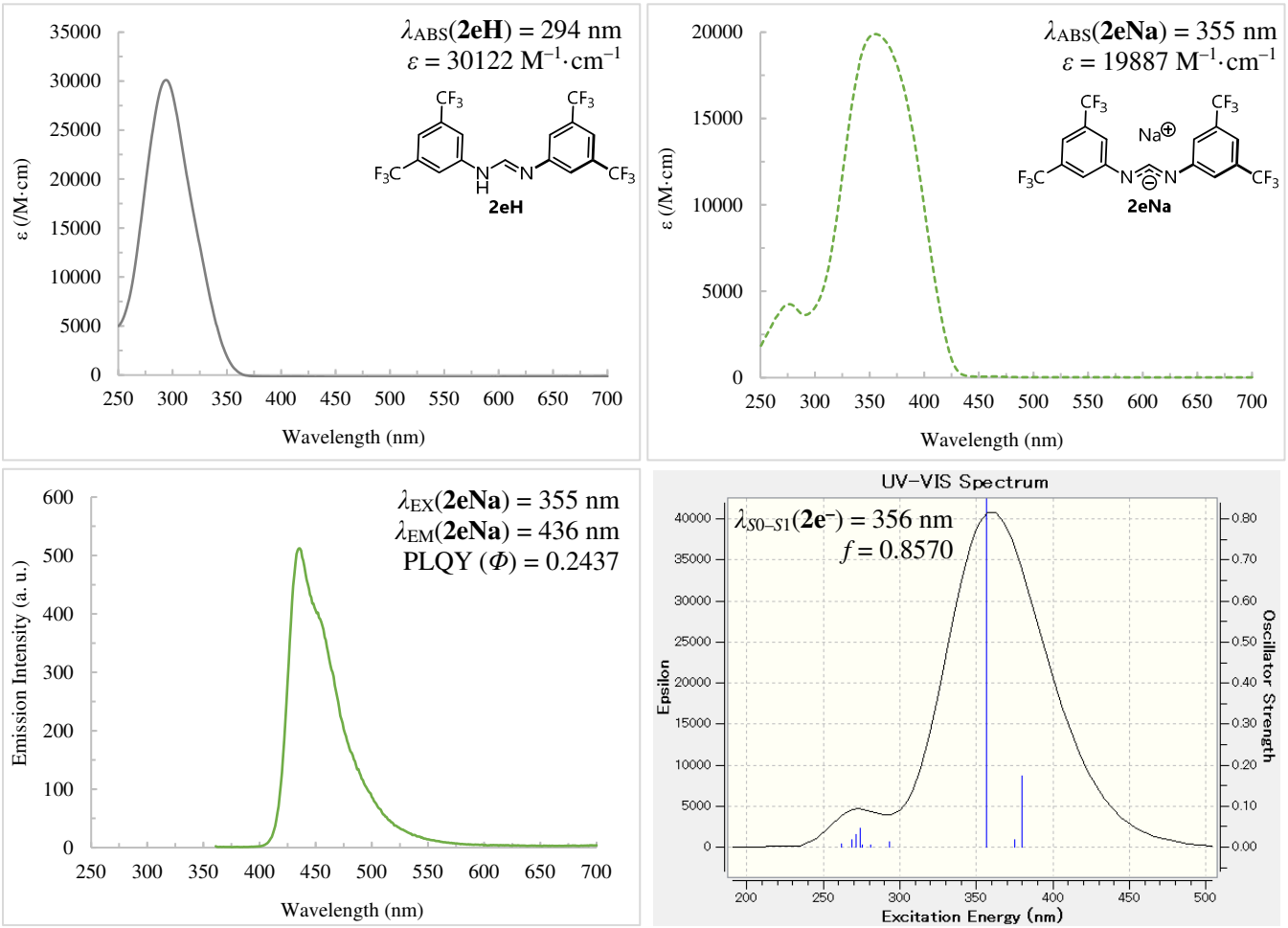



**Figure S10.** (Top, left) UV-Vis absorption spectrum of **2eH** in THF ($1.0 \times 10^{-5}$ M). (Top, right) UV-Vis absorption spectra of **2eNa** in THF ($1.0 \times 10^{-4}$ M). (Bottom, left) emission spectra of **2eNa** in THF ($1.0 \times 10^{-4}$ M). (Bottom, right) DFT-based simulation of UV-Vis spectrum, the excitation energies, and the oscillator strengths for the optimized geometry of **2e**$^-$.

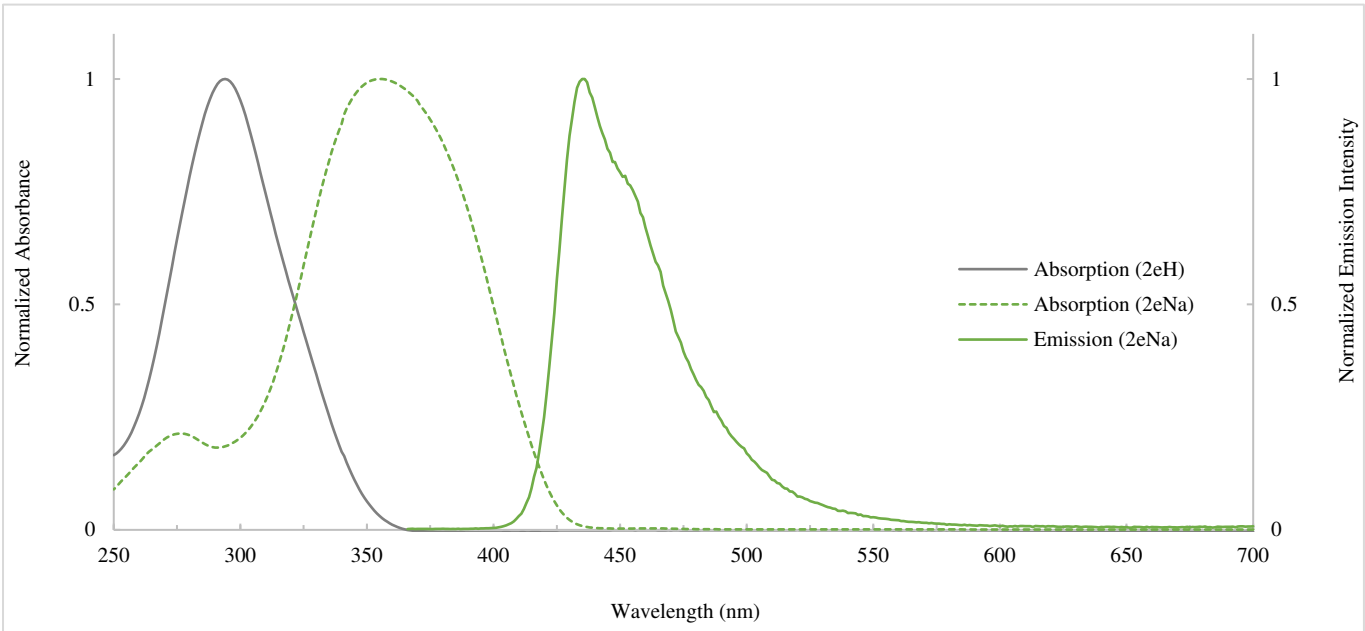



**Figure S11.** Normalized absorption and emission spectra of **2eH** and **2eNa** in THF.

For **2fH** and **2fNa**:

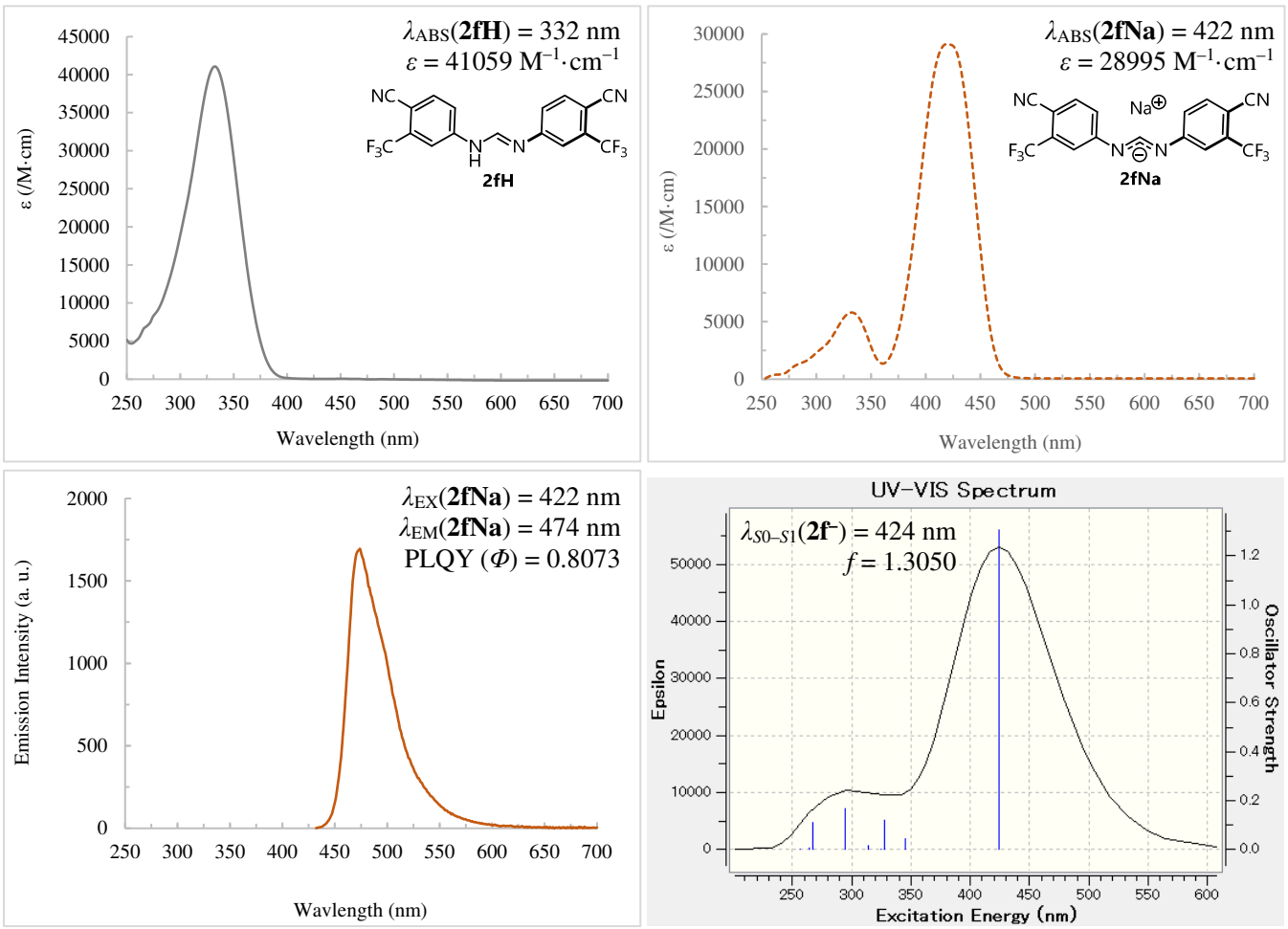



**Figure S12.** (Top, left) UV-Vis absorption spectrum of **2fH** in THF ($1.0 \times 10^{-5}$ M). (Top, right) UV-Vis absorption spectra of **2fNa** in THF ($1.0 \times 10^{-4}$ M). (Bottom, left) emission spectra of **2fNa** in THF ($1.0 \times 10^{-4}$ M). (Bottom, right) DFT-based simulation of UV-Vis spectrum, the excitation energies, and the oscillator strengths for the optimized geometry of **2f**$^{-}$.

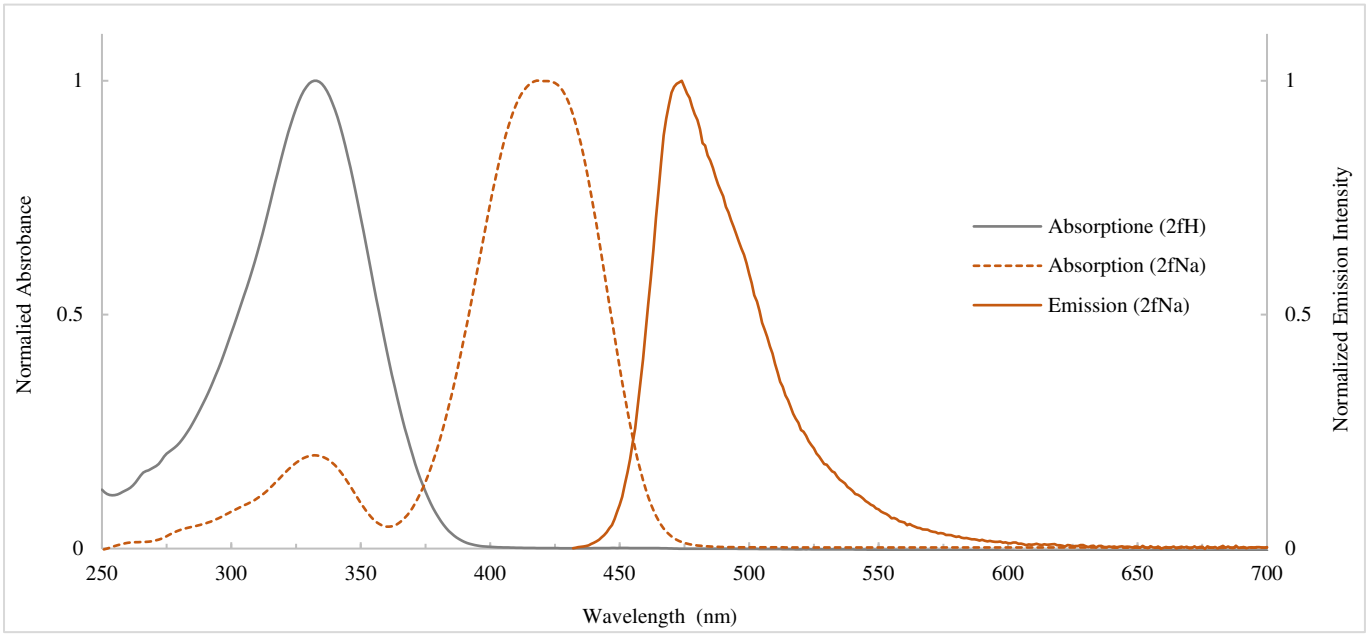



**Figure S13.** Normalized absorption and emission spectra of **2fH** and **2fNa** in THF.

For **2gH** and **2gNa**:

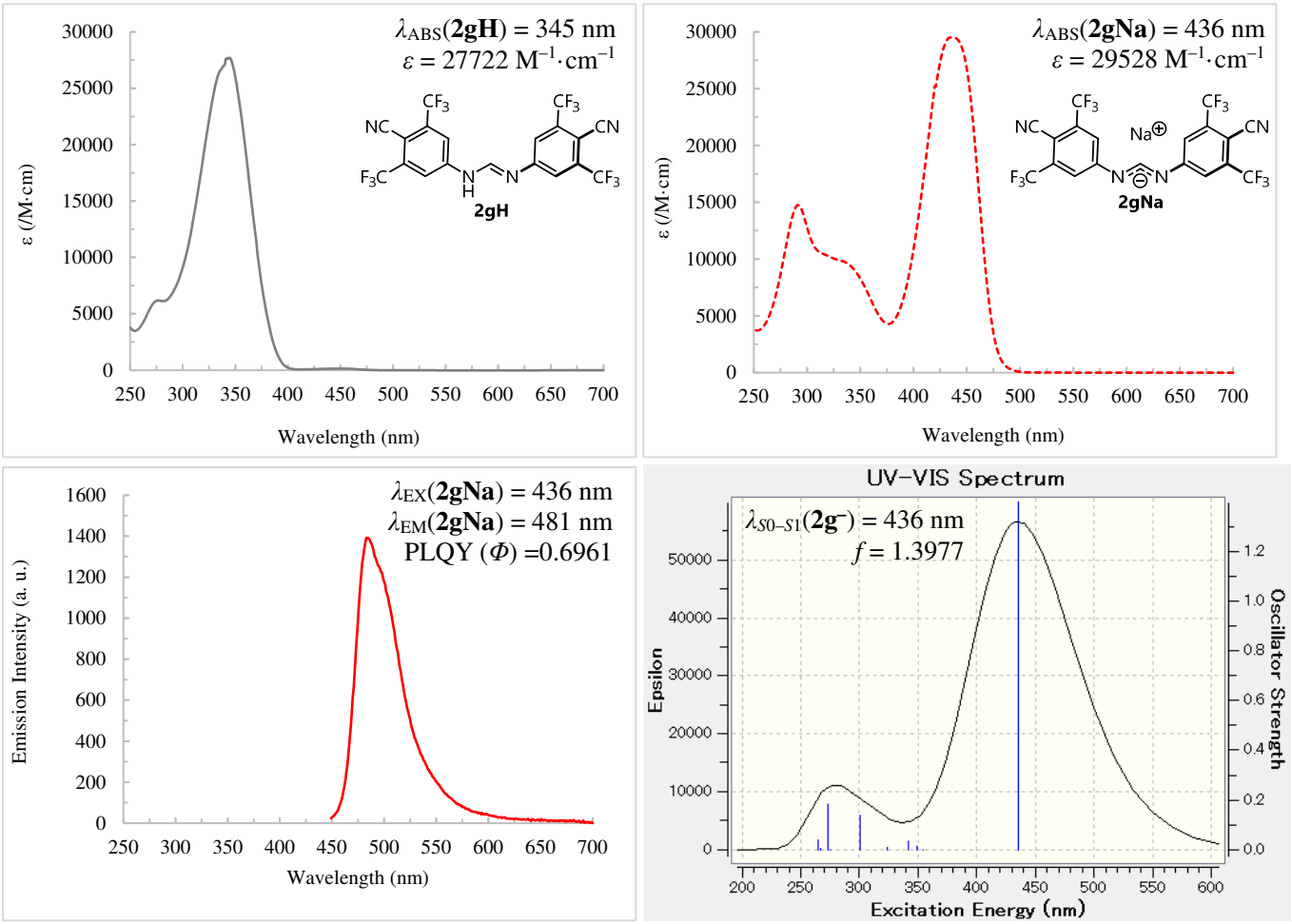



**Figure S14.** (Top, left) UV-Vis absorption spectrum of **2gH** in THF ($1.0 \times 10^{-5}$ M). (Top, right) UV-Vis absorption spectra of **2gNa** in THF ($1.0 \times 10^{-4}$ M). (Bottom, left) emission spectra of **2gNa** in THF ($1.0 \times 10^{-4}$ M). (Bottom, right) DFT-based simulation of UV-Vis spectrum, the excitation energies, and the oscillator strengths for the optimized geometry of **2g**$^{-}$.

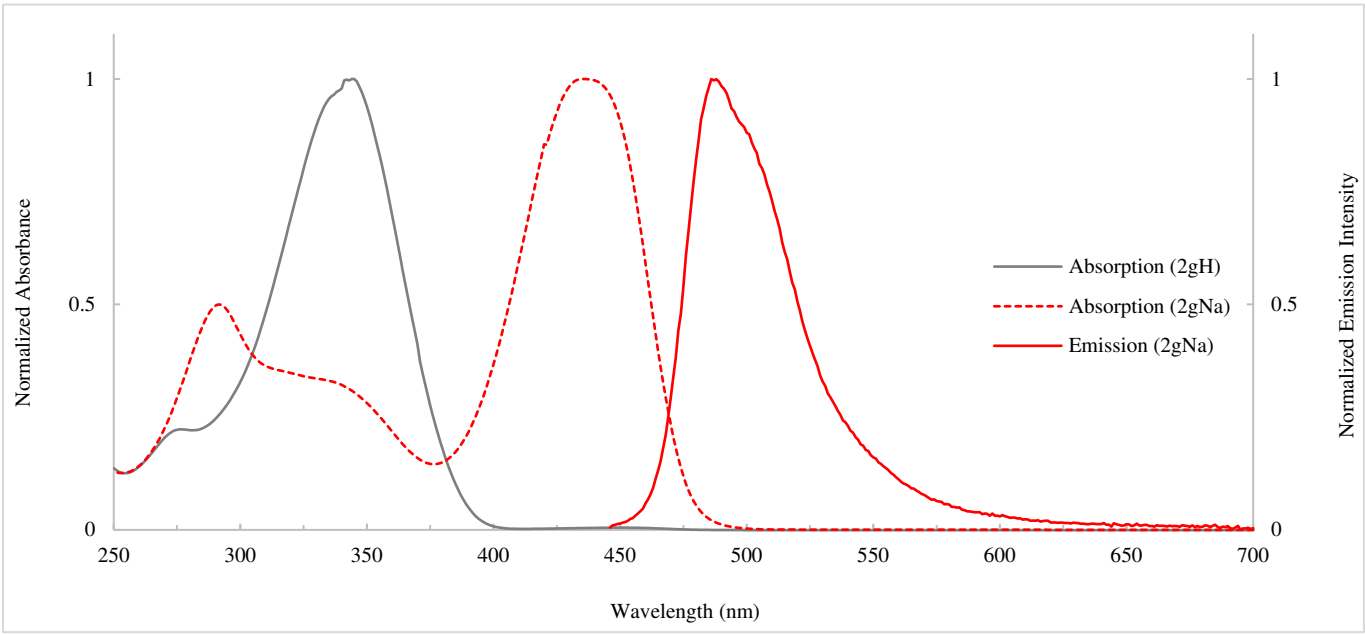



**Figure S15.** Normalized absorption and emission spectra of **2gH** and **2gNa** in THF.

**Table S1.** Summary of Photophysical Properties of **2aH–2gH** and **2aNa–2gNa** in THF.

| amidine | $\varepsilon$ ($M^{-1}\cdot cm^{-1}$) | $\lambda_{ABS}$ (nm) | amidinate | $\varepsilon$ ($M^{-1}\cdot cm^{-1}$) | $\lambda_{ABS}$ (nm) | $\lambda_{EM}$ (nm) | $\Delta\nu$ ($cm^{-1}$) | $\Phi$ (%) |
|---|---|---|---|---|---|---|---|---|
| **2aH** | 30703 | 329 | **2aNa** | 25362 | 411 | 471 | 3099 | 78 |
| **2bH** | 39982 | 317 | **2bNa** | 14764 | 391 | 446 | 3154 | 67 |
| **2cH** | 71929 | 325 | **2cNa** | 26284 | 402 | 457 | 2994 | 76 |
| **2dH** | 45306 | 375 | **2dNa** | 34286 | 495 | 568 | 2596 | 21 |
| **2eH** | 30122 | 294 | **2eNa** | 19887 | 355 | 436 | 5233 | 24 |
| **2fH** | 41059 | 332 | **2fNa** | 28995 | 422 | 474 | 2600 | 81 |
| **2gH** | 27722 | 345 | **2gNa** | 29528 | 436 | 481 | 2146 | 65 |

**2aH–2gH**: $1.0 \times 10^{-5}$ M, **2aNa–2gNa**: $1.0 \times 10^{-4}$ M.

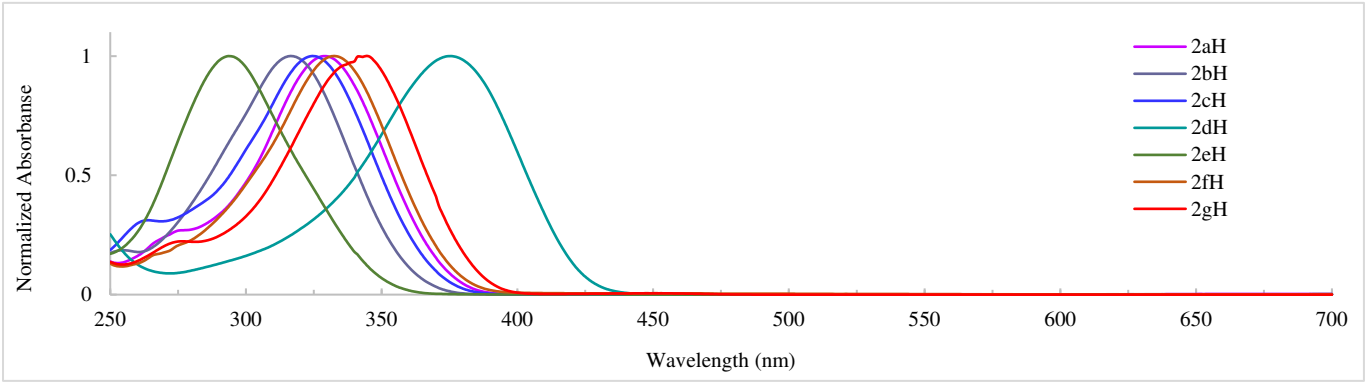



**Figure S16.** Normalized absorption of **2aH–2gH** in THF.

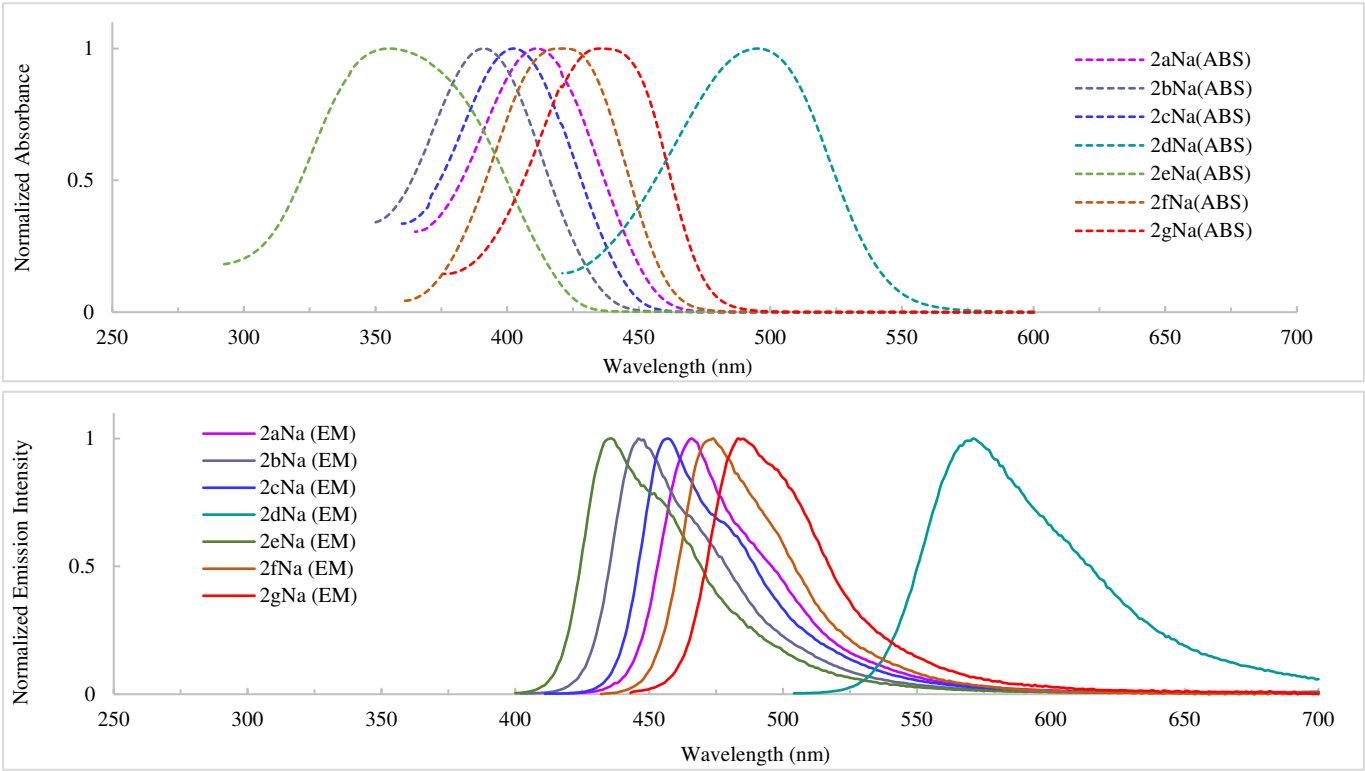



**Figure S17.** (Top) normalized absorption spectra of **2aNa–2gNa** in THF. (Bottom) normalized emission spectra of **2aNa–2gNa**.

## (E) Cation Effects on the Absorption & Emission Spectra

For **2gNa** in THF (1.0 x $10^{-5}$ M):

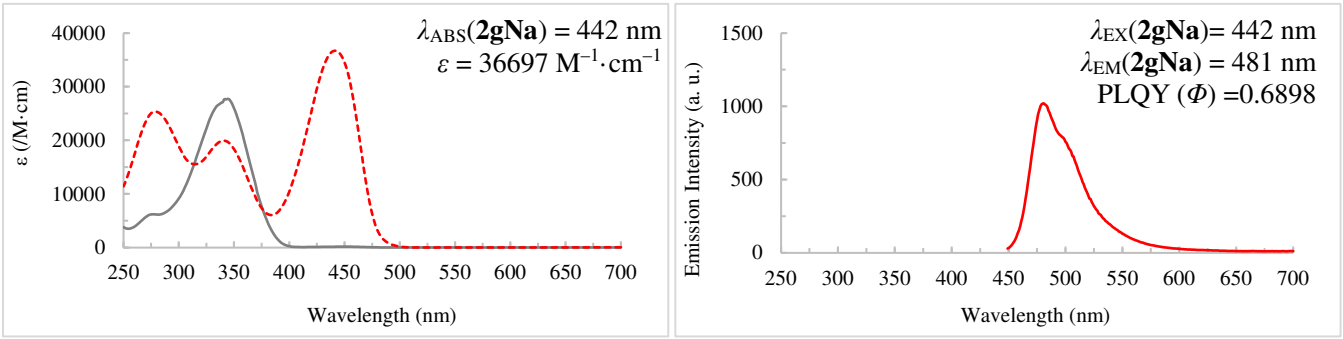



**Figure S18.** (Left) UV-Vis absorption spectrum of **2gH** and **2gNa**. (Right) emission spectrum of **2gNa**.

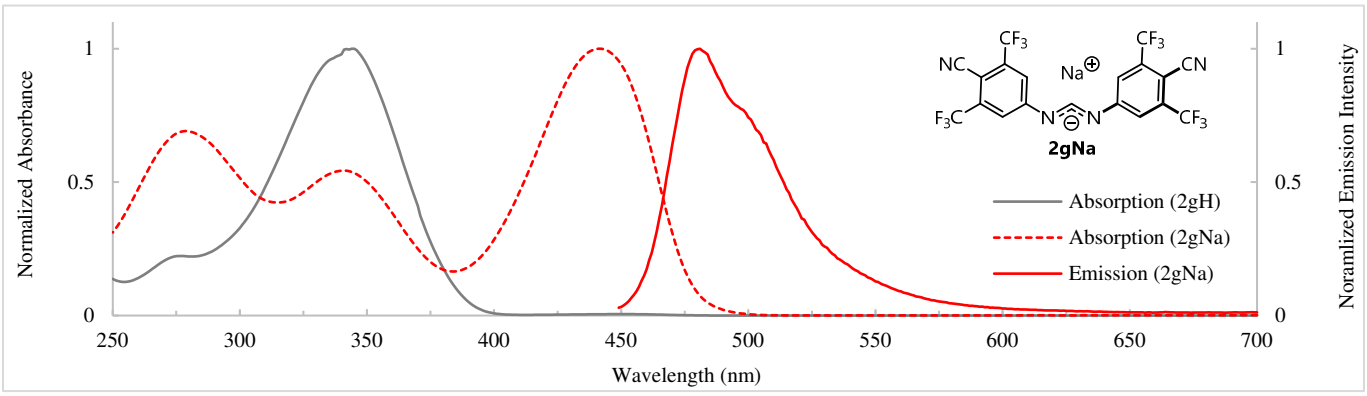



**Figure S19.** Normalized absorption and emission spectra of **2gH** and **2gNa** in THF.

For **2gLi** in THF (1.0 x $10^{-5}$ M):

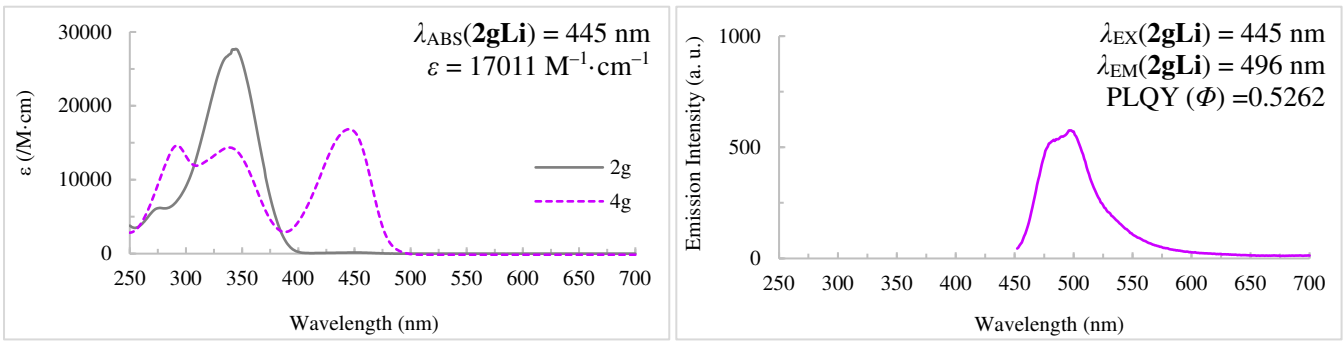



**Figure S20.** (Left) UV-Vis absorption spectrum of **2gH** and **2gLi**. (Right) emission spectrum of **2gLi**.

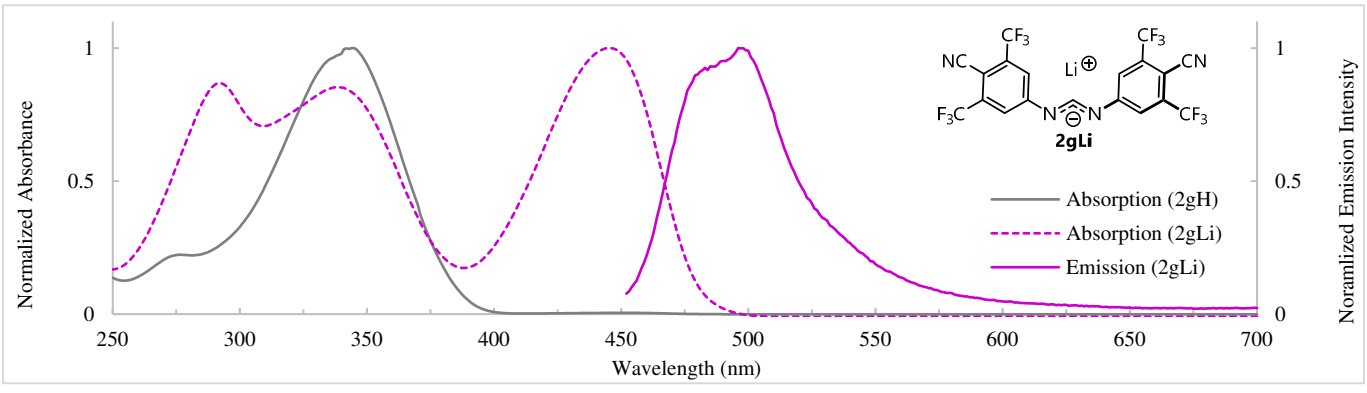



**Figure S21.** Normalized absorption and emission spectra of **2gH** and **2gLi** in THF.

For **2gNa(15c5)** in THF (1.0 x $10^{-5}$ M):

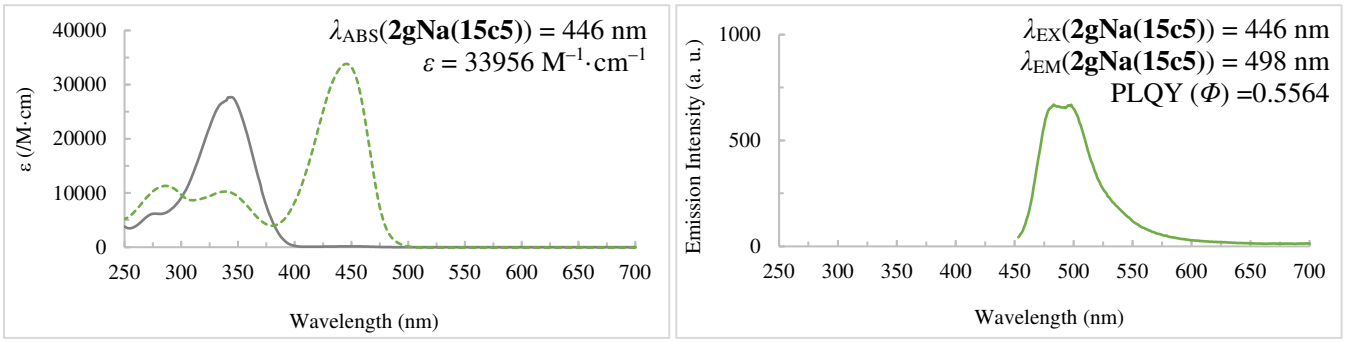



**Figure S22.** (Left) UV-Vis absorption spectrum of **2gH** and **2gNa(15c5)**. (Right) emission spectrum of **2gNa(15c5)**.

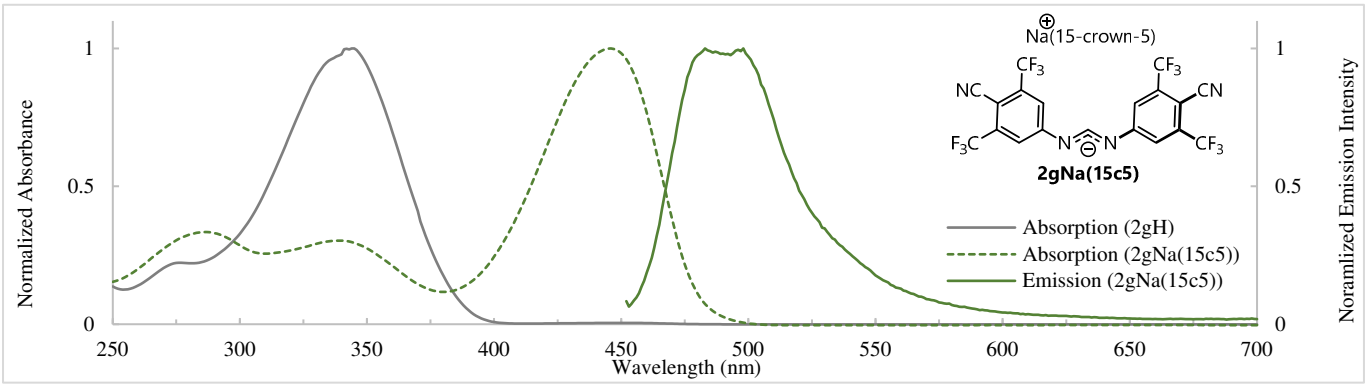



**Figure S23.** Normalized absorption and emission spectra of **2gH** and **2gNa(15c5)** in THF.

For **2gK** in THF (1.0 x $10^{-5}$ M):

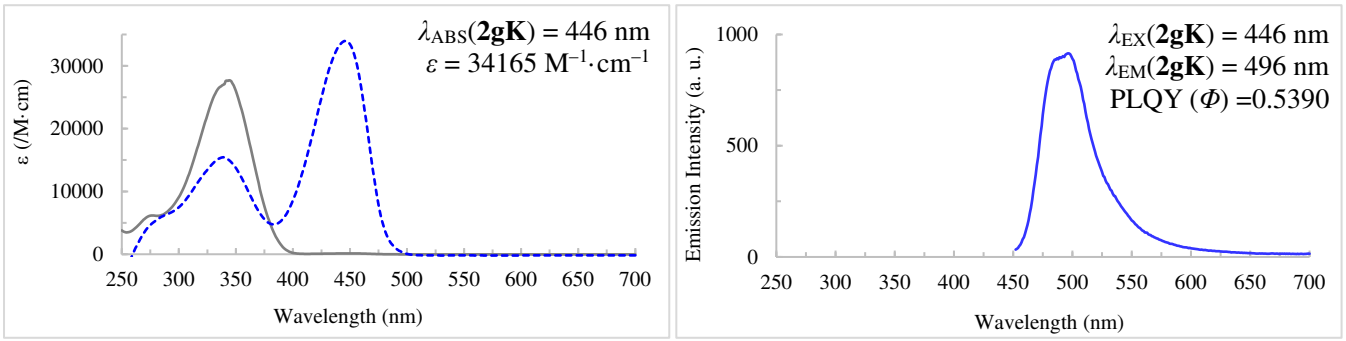



**Figure S24.** (Left) UV-Vis absorption spectrum of **2gH** and **2gK**. (Right) emission spectrum of **2gK**.

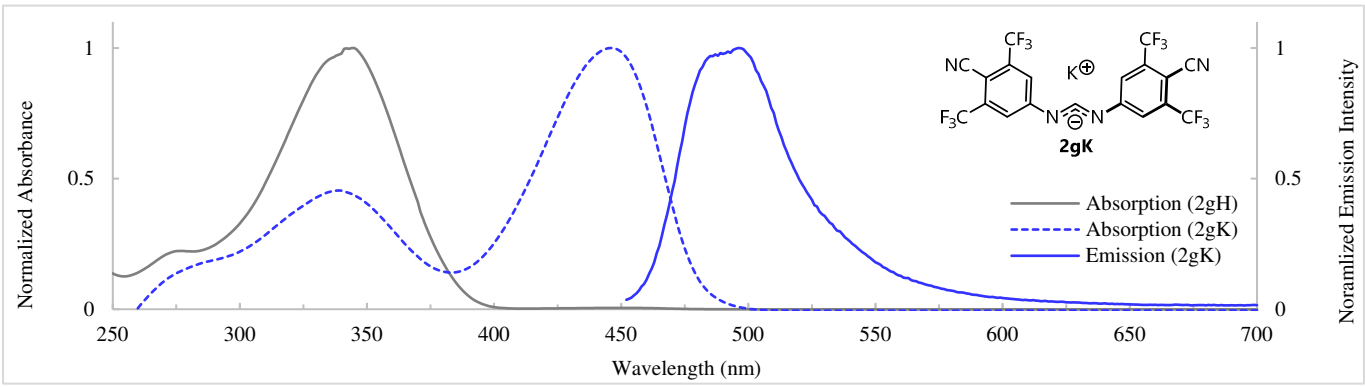



**Figure S25.** Normalized absorption and emission spectra of **2gH** and **2gK** in THF.

For **2gHdbu** in THF (1.0 x $10^{-5}$ M):

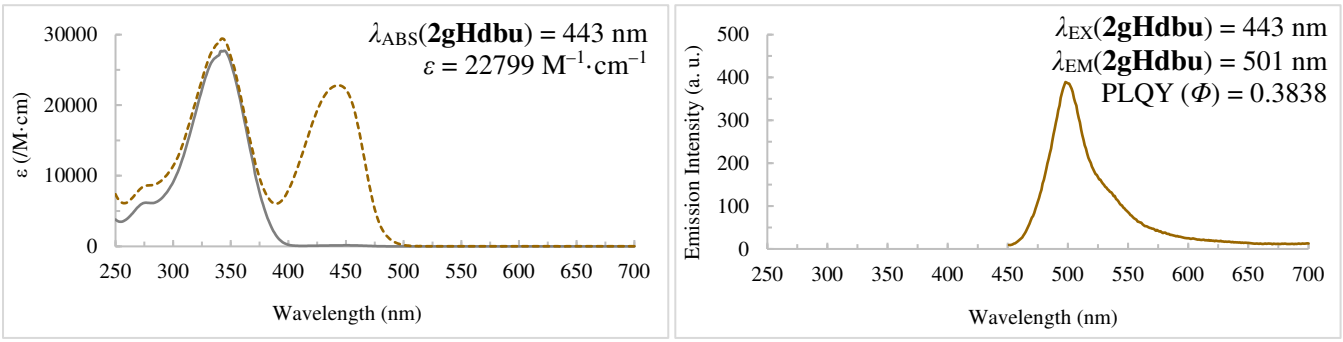



**Figure S26.** (Left) UV-Vis absorption spectrum of **2gH** and **2gHdbu**. (Right) emission spectrum of **2gHdbu**.

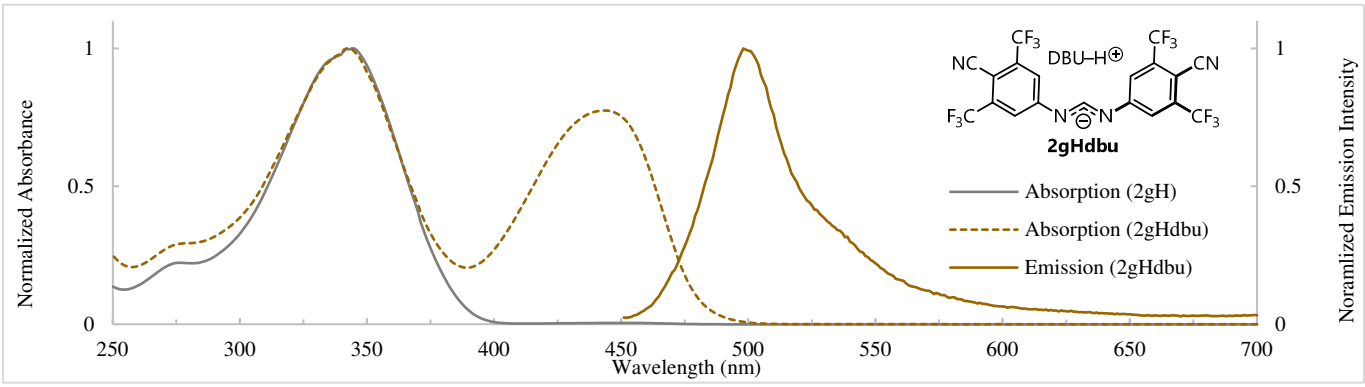



**Figure S27.** Normalized absorption and emission spectra of **2gH** and **2gHdbu** in THF.

**Table S2.** Summary of Photophysical Properties of **2gM** in THF.

| cation | **2gM** | $\varepsilon$ ($M^{-1}\cdot cm^{-1}$) | $\lambda_{ABS}$ (nm) | $\lambda_{EM}$ (nm) | $\Delta\nu$ ($cm^{-1}$) | $\Phi$ (%) |
|---|---|---|---|---|---|---|
| $Li^+$ | **2gLi** | 17011 | 445 | 496 | 2311 | 53 |
| $Na^+$ | **2gNa** | 36697 | 442 | 481 | 1834 | 69 |
| $[Na(15\text{-crown-}5)]^+$ | **2gNa(15c5)** | 33955 | 446 | 498 | 2341 | 56 |
| $K^+$ | **2gK** | 34165 | 446 | 496 | 2260 | 54 |
| DBU-$H^+$ | **2gHdbu** | 22799 | 443 | 498 | 2493 | 38 |

**2gM**: 1.0 × $10^{-5}$ M

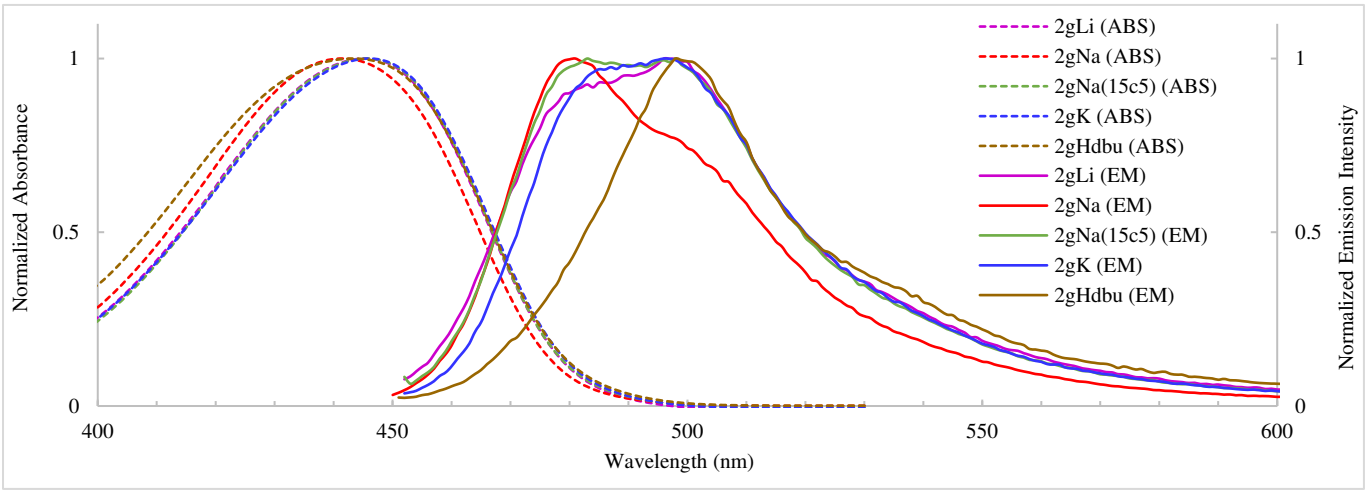



**Figure S28.** Normalized absorption and emission spectra of **2gNa**–**2gHdbu** in THF.

## (F) Solid-State Emission Properties

**Table S3.** Solid-State Emission of **2gNa**–**2gDBUH**.

| cation | **2gM** | $\lambda_{EX}$ (nm) | $\lambda_{EM}$ (nm) | $\Phi$ (%) |
|---|---|---|---|---|
| $Li^+$ | **2gLi** | 445 | 498 | 9 |
| Na | **2gNa** | 442 | 504 | 14 |
| $Na(thf)_2(OH_2)$ | **2gNa(xt)** | 442 | 498 | 14 |
| $[Na(15\text{-crown-5})]^+$ | **2gNa(15c5)** | 446 | 524 | 29 |
| $K^+$ | **2gK** | 446 | 499 | 13 |
| DBU–$H^+$ | **2gHdbu** | 443 | 538 | 14 |

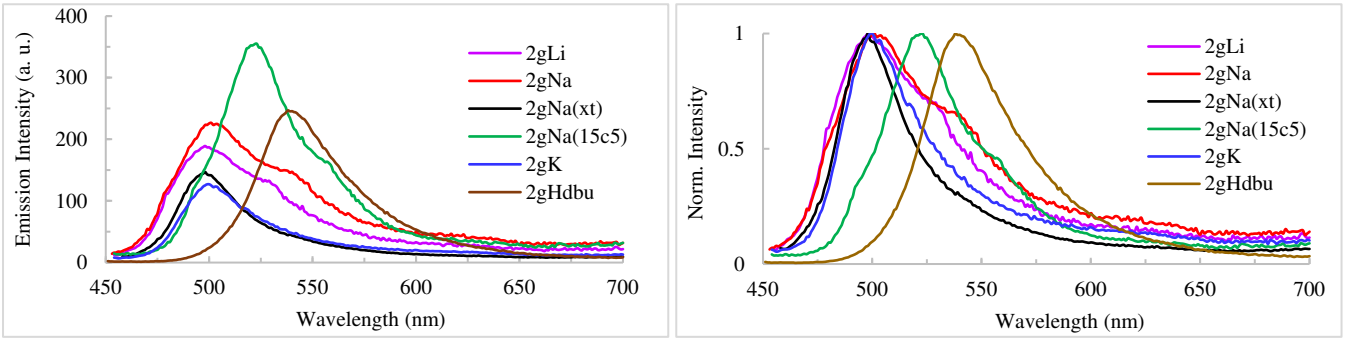



**Figure S29.** (Left) solid-state emission spectra of **2gM**. (Right) normalized spectra.

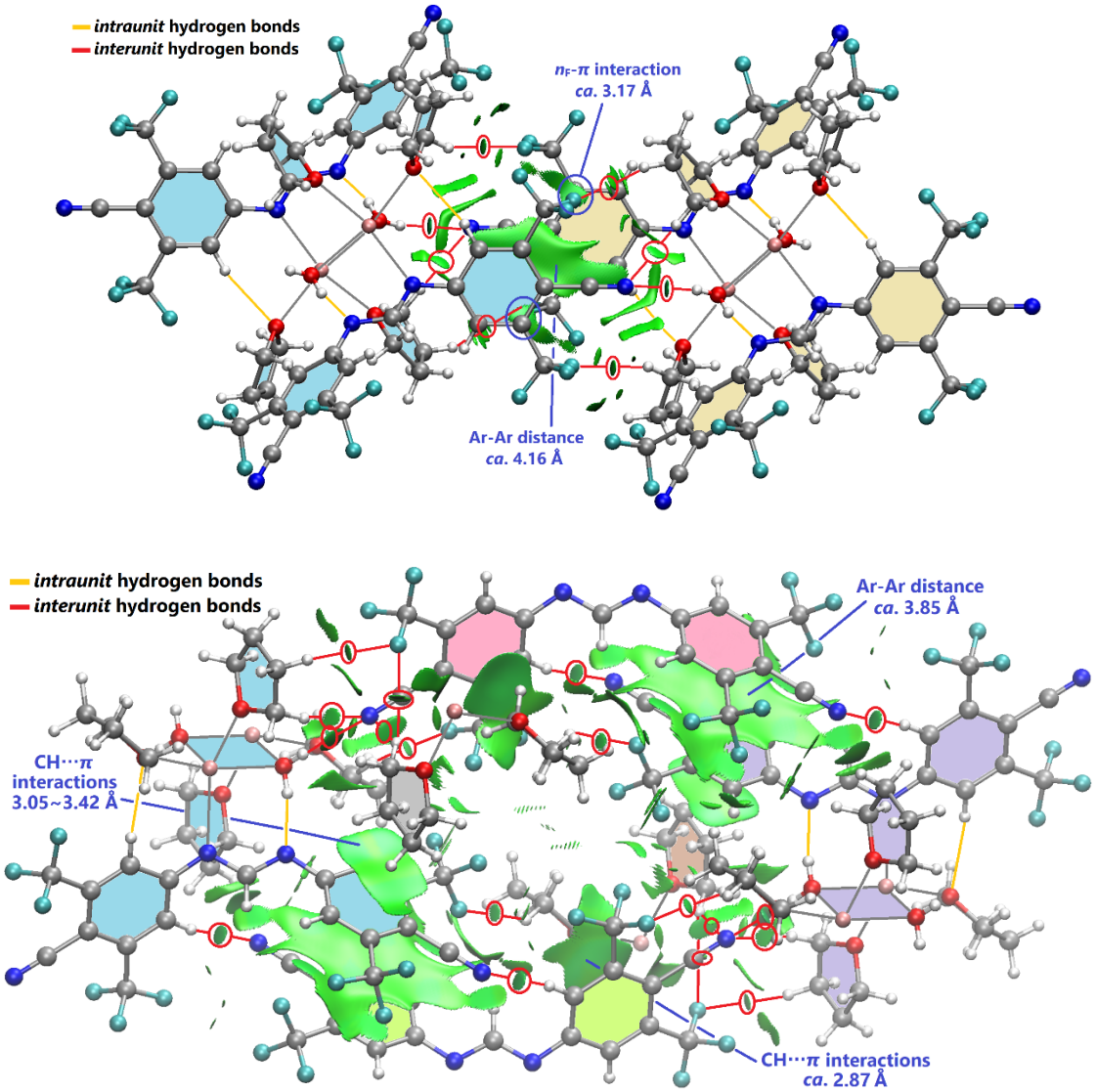



**Figure S30.** Mappings of intra- and intermolecular interactions of $[$**2gNa**$(thf)_2(OH_2)]_2$ in the crystal structures. (Top) Interunit interactions of "X axis". (Bottom) Interunit interactions of "Y and Z axes".

## (G) Solvent Effects on the Absorption & Emission

**Table S4.** Photophysical Properties of **2gNa(15c5)** in Various Solvents.

| solvent | $\varepsilon_r$ | $\varepsilon$ ($M^{-1}\cdot cm^{-1}$) | $\lambda_{ABS}$ (nm) | $\lambda_{EM}$ (nm) | $\Delta\nu$ ($cm^{-1}$) | $\Phi$ (%) | $\tau$ (ns) |
|---|---|---|---|---|---|---|---|
| toluene | 2.38 | 14999 | 432 | 474 | 2078 | 91 | - |
| $CHCl_3$ | 4.81 | 11615 | 430 | 478 | 2362 | 80 | - |
| THF | 7.58 | 33956 | 446 | 498 | 2341 | 56 | 1.54 |
| MeCN | 35.9 | 94224 | 449 | 497 | 2126 | 0.56 | 3.37 |
| DMSO | 46.5 | 59932 | 459 | 509 | 2164 | 4.3 | - |

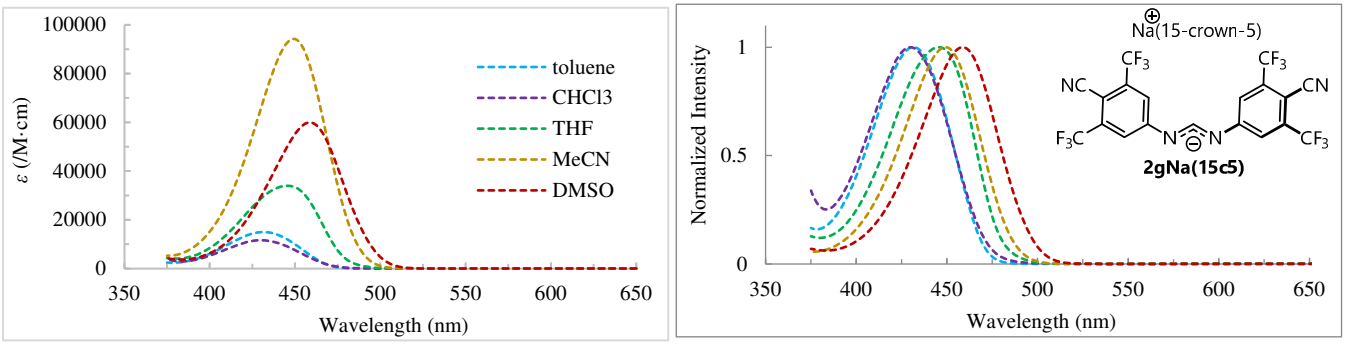



**Figure S31.** (Left) UV-Vis absorption spectra of **2gNa(15c5)** in various solvents ($1.0 \times 10^{-5}$ M). (Right) normalized spectra.

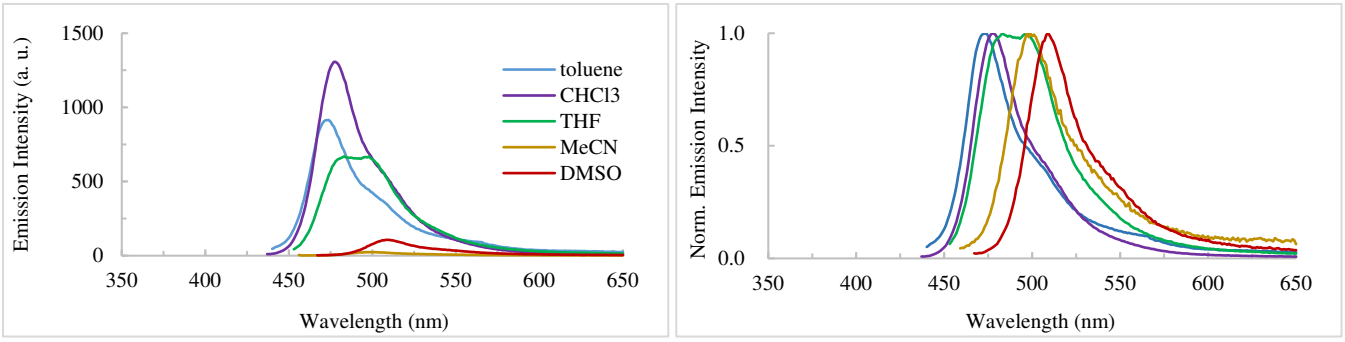
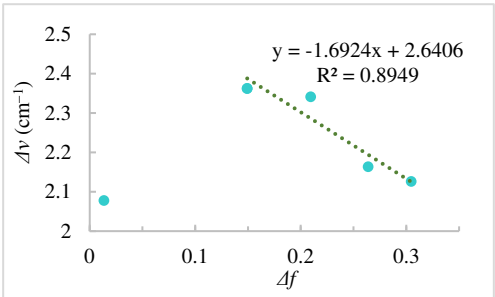



**Figure S32.** (Left) Emission spectra of **2gNa(15c5)** in various solvents ($1.0 \times 10^{-5}$ M). (Right) normalized spectra.

**Table S5.** Lippert-Mataga plot for **2gNa(15c5)**.

| solvent | $\varepsilon_r$ | $n$ | $\Delta f$ | $\lambda_{ABS}$ (nm) | $\nu_{ABS}$ ($cm^{-1}$) | $\lambda_{EM}$ (nm) | $\nu_{EM}$ ($cm^{-1}$) | $\Delta\nu$ ($cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| toluene | 2.38 | 1.496 | 0.013504 | 431.5 | 23175.0 | 474.0 | 21097.0 | 2077.9 |
| $CHCl_3$ | 4.81 | 1.443 | 0.149202 | 429.5 | 23282.9 | 478.0 | 20920.5 | 2362.4 |
| THF | 7.58 | 1.408 | 0.209297 | 446.0 | 22421.5 | 498.0 | 20080.3 | 2341.2 |
| MeCN | 35.9 | 1.344 | 0.304587 | 449.5 | 22246.9 | 497.0 | 20120.7 | 2126.2 |
| DMSO | 46.5 | 1.477 | 0.263734 | 458.5 | 21810.3 | 509.0 | 19646.4 | 2163.9 |




Lippert-Mataga equation:

$$\Delta\nu = \frac{2(\Delta\mu)^2}{hca^3}\Delta f + const. \qquad \text{(eq. 1)}$$

$$\Delta\nu = \nu_{ABS} - \nu_{EM} \qquad \text{(eq. 2)}$$

$$\Delta\mu = \mu_{EX} - \mu_{GR} \qquad \text{(eq. 3)}$$

$$\Delta f = \frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1} \qquad \text{(eq. 4)}$$

($\varepsilon_r$: dielectric constant, $n$: refractive index, $h$: Planck constant ($6.6256\times10^{-27}$), $c$: speed of light ($2.9979\times10^{10}$ cm/s), $a$: Onsager radius (for $\mathbf{2g}^-$: 7.22 Å)[S8], $\mu$: dipole moment (for **2gNa(15c5)** anion: $\mu_{EX}$ = 0.07 Debye, $\mu_{GR}$ = 0.99 Debye).

**Table S6.** Photophysical Properties of **2dNa** in Solvents.

| solvent | $\varepsilon_r$ | $\varepsilon$ ($M^{-1}\cdot cm^{-1}$) | $\lambda_{ABS}$ (nm) | $\lambda_{EM}$ (nm) | $\Delta\nu$ ($cm^{-1}$) | $\Phi$ (%) |
|---|---|---|---|---|---|---|
| THF | 7.58 | 11469 | 469 | 571 | 3809 | 56 |
| MeCN | 35.9 | 8102 | 530 | — | — | <0.1 |
| DMSO | 46.5 | 5346 | 550 | — | — | <0.1 |

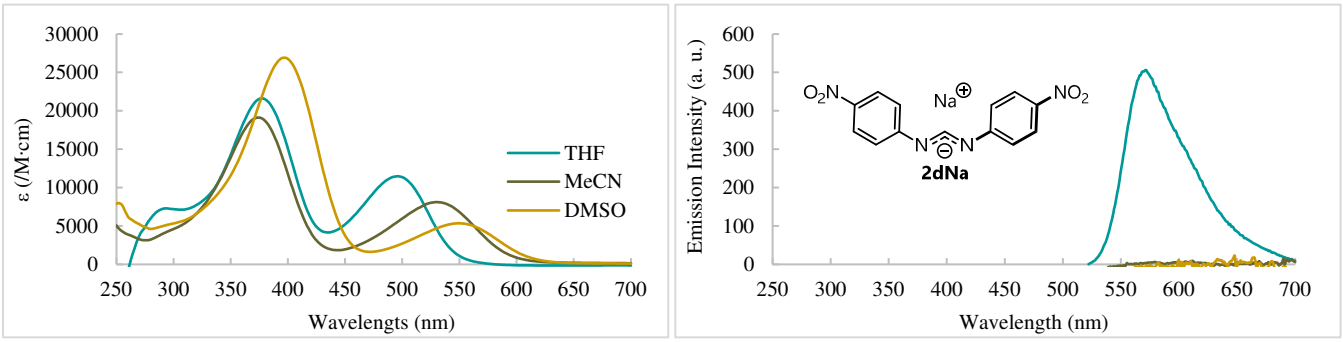
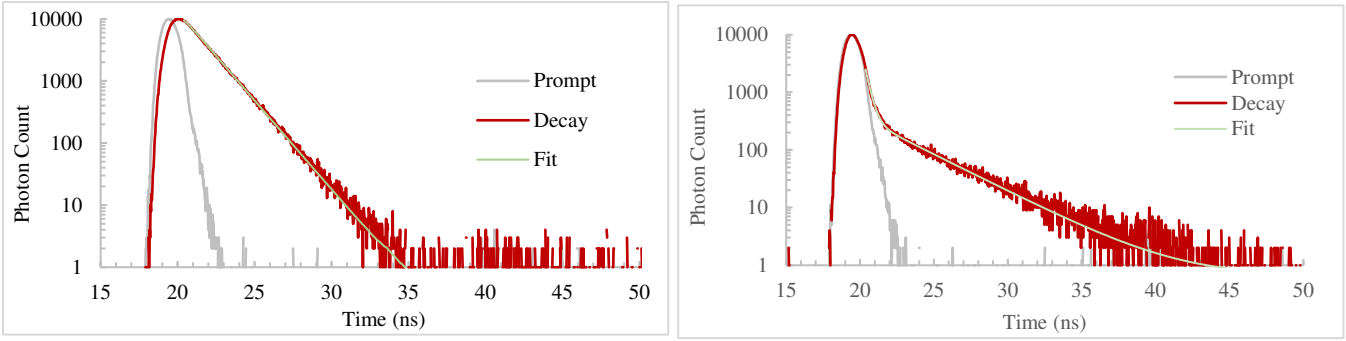



**Figure S33.** (Left) UV-Vis absorption of **2dNa** in solvents ($1.0 \times 10^{-5}$ M). (Right) emission spectra of **2dNa** ($1.0 \times 10^{-4}$ M).

## (H) Emission Lifetimes




$\tau$ = 1.54 ns (100%), $\chi^2$ = 1.096

$\tau_1$ = 0.32 ns (38.7%), $\tau_2$ = 3.37 ns (61.3%), $\chi^2$ = 1.195

**Figure S34.** (Left) emission decay of **2gNa(15c5)** in THF ($1.0 \times 10^{-5}$ M, argon-bubbled). (Right) emission decay of **2gNa(15c5)** in MeCN ($1.0 \times 10^{-5}$ M, argon-bubbled).*

**The emission in MeCN would be a prompt fluorescence (no delayed emission), though it appears to exhibit biexponential decay. The emission was extremely weak in MeCN, thus overlapping to the measurement threshold.*

## (I) Temperature Dependence of Photoluminescence

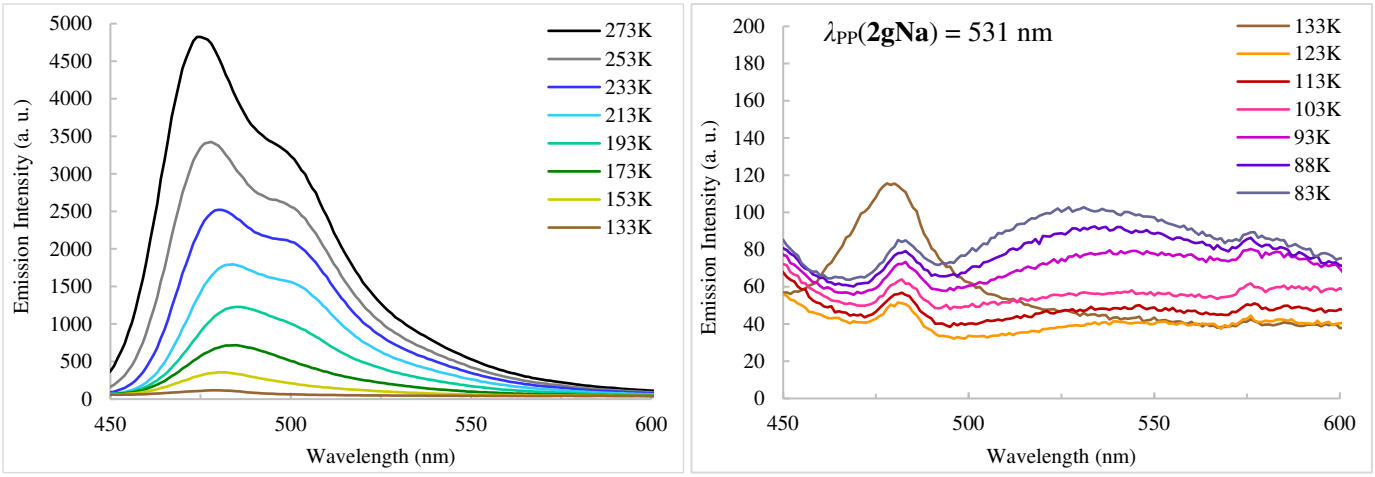



**Figure S35.** Variable-temperature emission spectra of **2gNa** in 2MeTHF ($1.0 \times 10^{-5}$ M) at 273–133 K (left) and 133–83 K (right) under 421 nm photoexcitation.

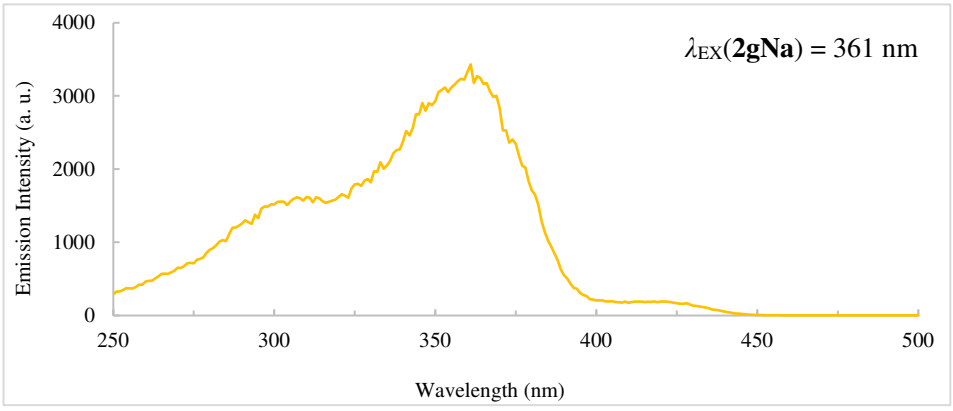



**Figure S36.** Excitation spectrum of **2gNa** in 2MeTHF ($1.0 \times 10^{-5}$ M) at 77 K corresponding to the phosphorescence with the emission maximum at 531 nm.

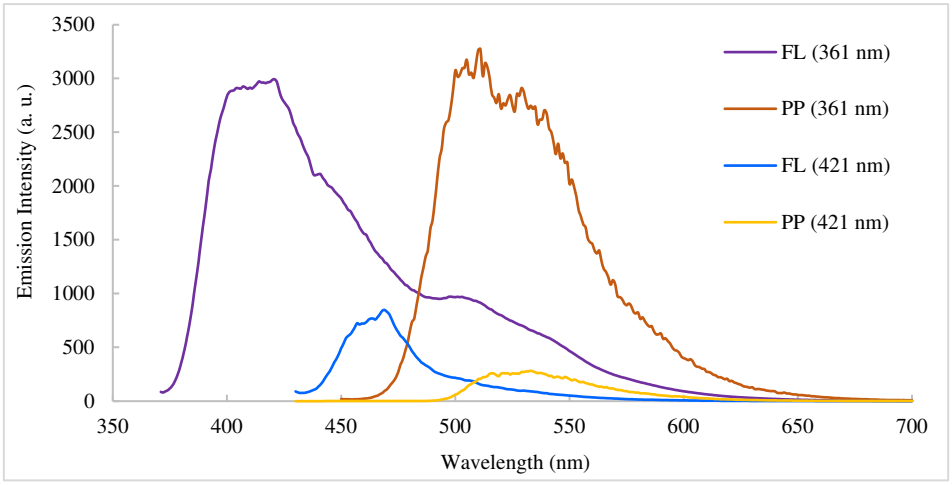



**Figure S37.** Fluorescence (FL) and phosphorescence spectra of **2gNa** in 2MeTHF at 77 K upon 361- and 421-nm irradiation (delay: 10 ms). FL: fluorescence, PP: phosphorescence.

## (J) Computational Details

All quantum chemical calculations were performed using Gaussian 09 program package.[S9] All the optimized geometries, frequencies, and zero-point energies were calculated using B3LYP[S10] functional including a D3 version of Grimme's dispersion with Becke-Johnson damping (D3(BJ)).[S11] The geometry optimizations and frequency calculations were carried out with 6-31+G(d,p) basis set. The geometry optimizations were performed without any symmetry constraint followed by analytical frequency calculations to confirm that a minimum had been reached. A single-point energy calculations were conducted with the polarized valence triple-ζ basis set 6-311++G(2d,p) basis set. Solvent effects (THF; $\varepsilon$ = 7.58) were introduced for all calculations by means of the polarizable continuum models implemented in Gaussian 09. SMD[S12] model was employed for the single-point calculations at the geometries that optimized with IEFPCM[S13] model for all the minima.

The electronic energies and the Gibbs energies at 298.15 K and 1 atm were obtained by adding the thermal energy corrections and the Gibbs energy corrections derived from the analytical frequency calculations to the single-point energies, respectively. The energy levels of the frontier orbitals (HOMO and LUMO(+$x$) orbitals), excitation energies, absorption (or emission) wavelengths, and the oscillator strengths were estimated by the time-dependent (TD) calculation of each optimized ground-state geometries at TD-B3LYP-D3(BJ)/6-311++G(2d,p)/SMD(THF). For the $S_1$ excited states, the same levels of theory were used to estimate the above parameters against each optimized excited-state geometries at TD-B3LYP-D3(BJ)/6-31+G(d,p)/IEFPCM(THF). These calculations involve a certain margin error.

**(J-1) Frontier Orbital Energies, Excitation Parameters, and NBO Analysis of *N*,*N*'-Diarylformamidinate Anions**

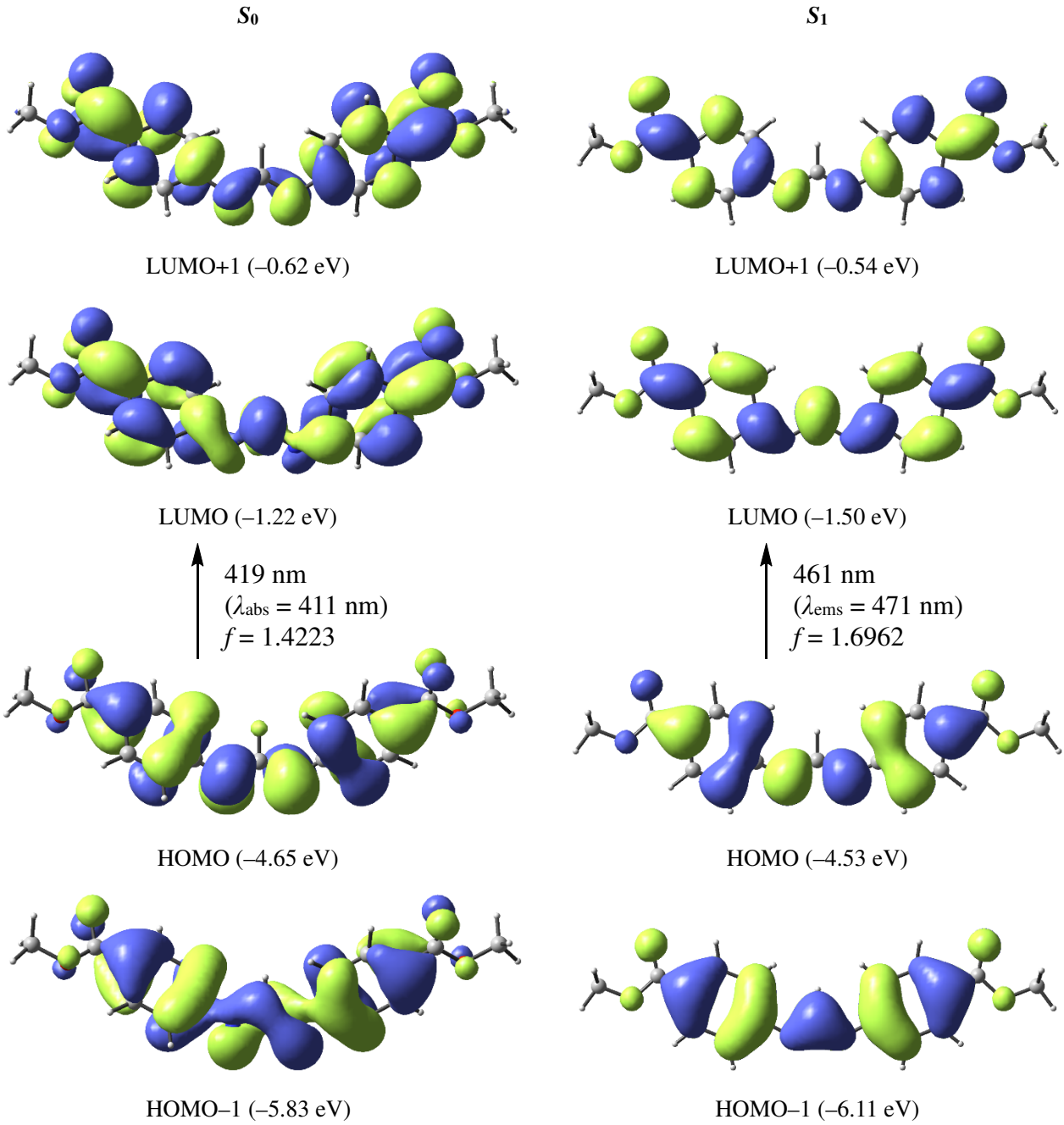



**Figure S38.** $S_0$- and $S_1$-state MOs, orbital energies, excitation energies, and oscillator strengths of **2a**$^-$.

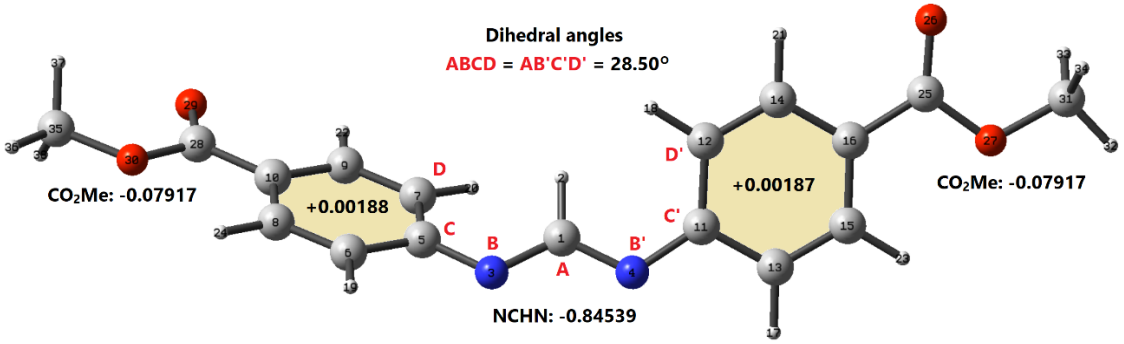



**Figure S39.** Dihedral angles and the sum of natural atomic charges of diazaallyl, aryl, and electron-withdrawing groups of **2a**$^-$ ($S_0$).

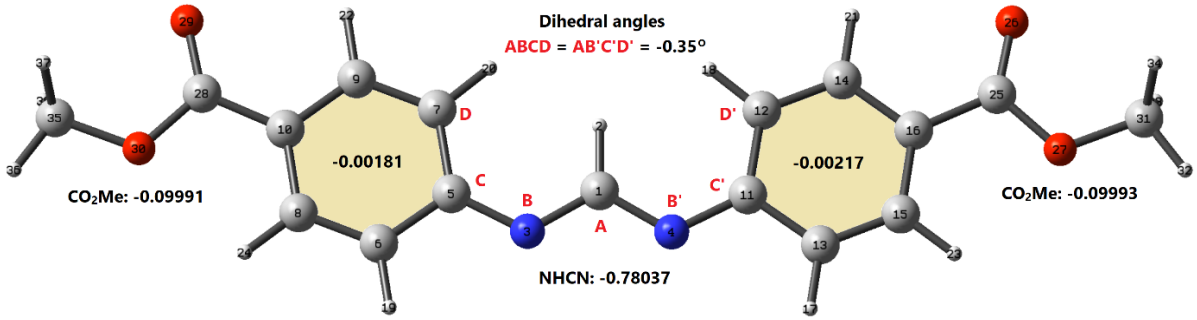



**Figure S40.** Dihedral angles and the sum of natural atomic charges of diazaallyl, aryl, and electron-withdrawing groups of **2a**$^-$ anion ($S_1$).

**Table S7.** Natural atomic charges of **2a**$^-$ at the $S_0$ and $S_1$ states.

| $S_0$ | | | | | | | | | $S_1$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **NCHN** | | NPA ($\delta$) | **Ar1** | | NPA ($\delta$) | **Ar2** | | NPA ($\delta$) | **NCHN** | | NPA ($\delta$) | **Ar1** | | NPA ($\delta$) | **Ar2** | | NPA ($\delta$) |
| C | 1 | 0.30242 | C | 5 | 0.18412 | C | 11 | 0.18412 | C | 1 | 0.41673 | C | 5 | 0.18079 | C | 11 | 0.18080 |
| H | 2 | 0.12598 | C | 6 | -0.24335 | C | 12 | -0.27349 | H | 2 | 0.12652 | C | 6 | -0.24566 | C | 12 | -0.30353 |
| N | 3 | -0.63689 | C | 7 | -0.27349 | C | 13 | -0.24336 | N | 3 | -0.66181 | C | 7 | -0.30354 | C | 13 | -0.24573 |
| N | 4 | -0.63690 | C | 8 | -0.16339 | C | 14 | -0.15211 | N | 4 | -0.66181 | C | 8 | -0.16150 | C | 14 | -0.07839 |
| | | | C | 9 | -0.15211 | C | 15 | -0.16339 | | | | C | 9 | -0.07840 | C | 15 | -0.16160 |
| | | | C | 10 | -0.22617 | C | 16 | -0.22617 | | | | C | 10 | -0.25840 | C | 16 | -0.25844 |
| | | | H | 17 | 0.21453 | H | 19 | 0.21453 | | | | H | 17 | 0.21479 | H | 19 | 0.21477 |
| | | | H | 18 | 0.21612 | H | 20 | 0.21612 | | | | H | 18 | 0.20916 | H | 20 | 0.20915 |
| | | | H | 21 | 0.22321 | H | 22 | 0.22321 | | | | H | 21 | 0.21780 | H | 22 | 0.21780 |
| | | | H | 23 | 0.22241 | H | 24 | 0.22241 | | | | H | 23 | 0.22315 | H | 24 | 0.22300 |
| | | | C | 28 | 0.80590 | C | 25 | 0.80590 | | | | C | 28 | 0.79675 | C | 25 | 0.79676 |
| | | | O | 29 | -0.66638 | O | 26 | -0.66638 | | | | O | 29 | -0.67399 | O | 26 | -0.67399 |
| | | | O | 30 | -0.56894 | O | 27 | -0.56894 | | | | O | 30 | -0.56917 | O | 27 | -0.56917 |
| | | | C | 35 | -0.21239 | C | 31 | -0.21239 | | | | C | 35 | -0.21306 | C | 31 | -0.21305 |
| | | | H | 36 | 0.19010 | H | 32 | 0.19010 | | | | H | 36 | 0.18931 | H | 32 | 0.18931 |
| | | | H | 37 | 0.18632 | H | 33 | 0.18632 | | | | H | 37 | 0.18508 | H | 33 | 0.18508 |
| | | | H | 38 | 0.18622 | H | 34 | 0.18622 | | | | H | 38 | 0.18515 | H | 34 | 0.18515 |
| **sum** | | -0.84539 | **sum** | | -0.07729 | **sum** | | -0.7730 | **sum** | | -0.78037 | **sum** | | -0.10174 | **sum** | | -0.10208 |
| | | | aryl | | -0.00188 | aryl | | -0.00187 | | | | aryl | | -0.00181 | aryl | | -0.00217 |
| | | | EWG | | -0.07917 | EWG | | -0.07917 | | | | EWG | | -0.09993 | EWG | | -0.09991 |

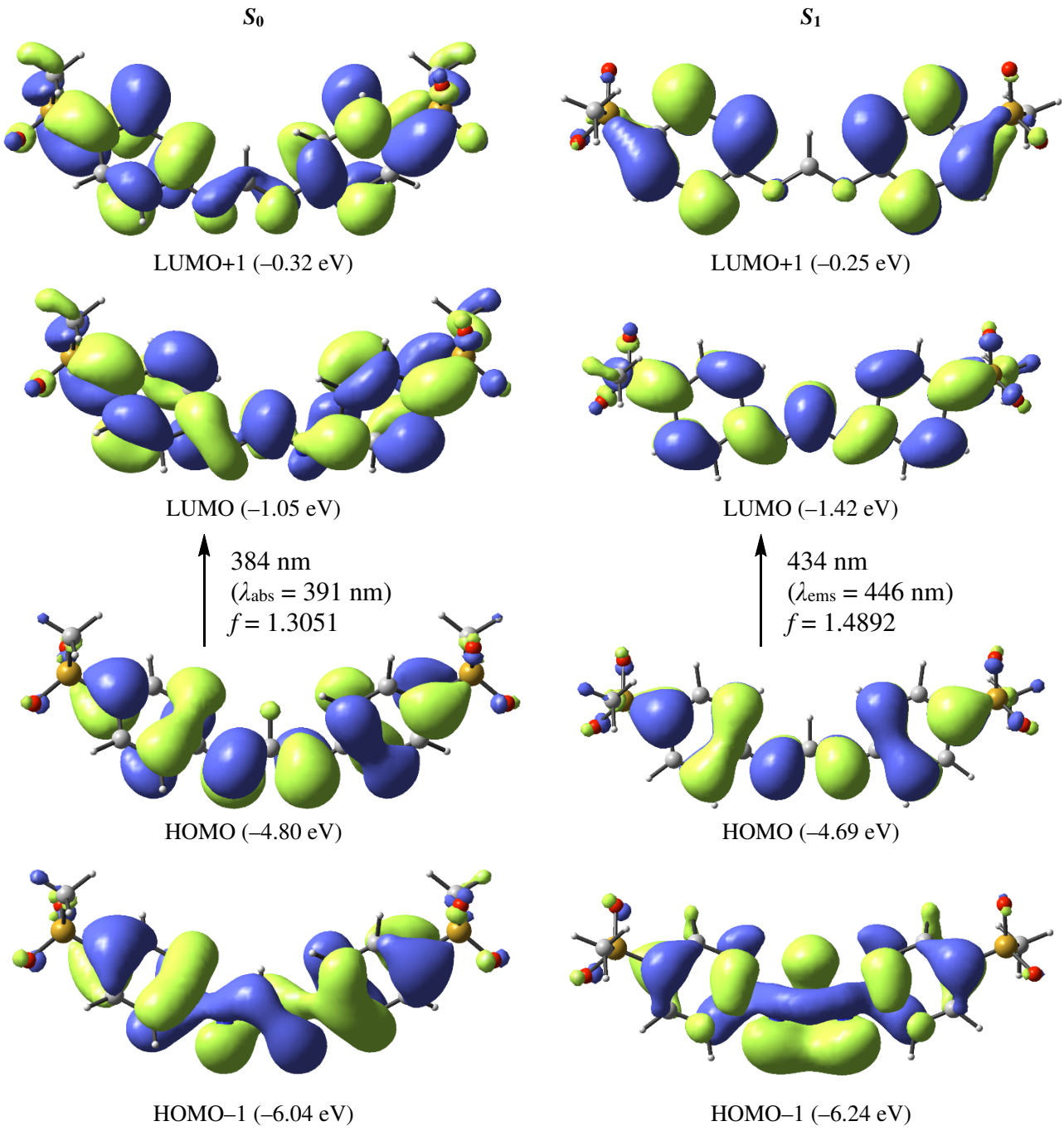



**Figure S41.** $S_0$- and $S_1$-state MOs, orbital energies, excitation energies, and oscillator strengths of **2b**$^-$.

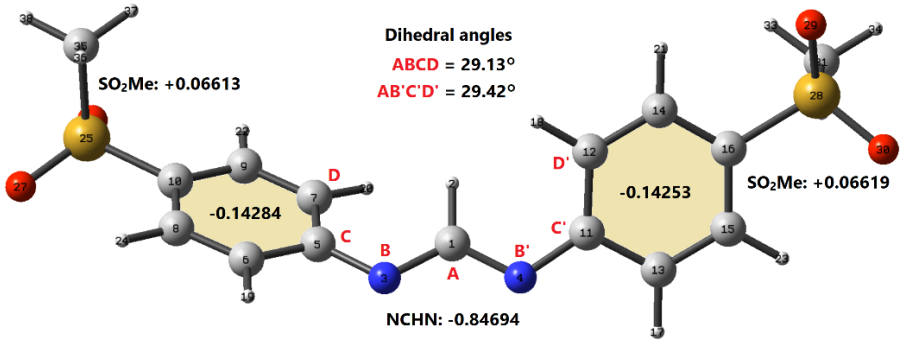



**Figure S42.** Dihedral angles and the sum of natural atomic charges of diazaallyl, aryl, and electron-withdrawing groups of **2b**$^-$ ($S_0$).

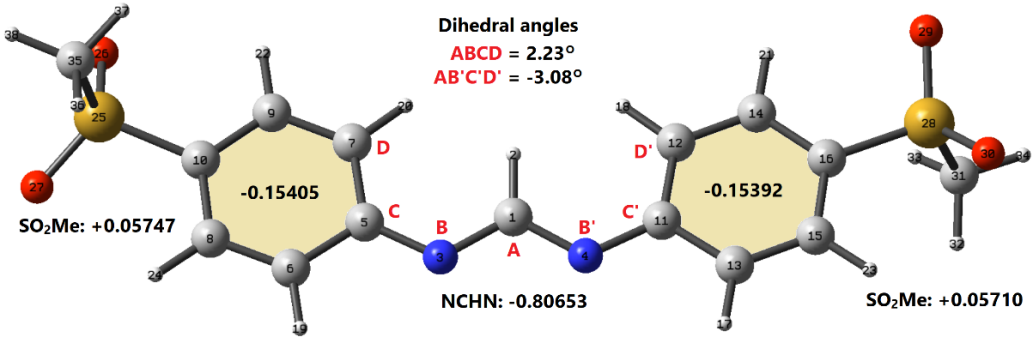



**Figure S43.** Dihedral angles and the sum of natural atomic charges of diazaallyl, aryl, and electron-withdrawing groups of **2b**$^-$ ($S_1$).

**Table S8.** Natural atomic charges of **2b**$^-$ at the $S_0$ and $S_1$ states.

| $S_0$ | | | | | | | | | $S_1$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **NCHN** | | NPA ($\delta$) | **Ar1** | | NPA ($\delta$) | **Ar2** | | NPA ($\delta$) | **NCHN** | | NPA ($\delta$) | **Ar1** | | NPA ($\delta$) | **Ar2** | | NPA ($\delta$) |
| C | 1 | 0.30418 | C | 5 | 0.18376 | C | 11 | 0.18379 | C | 1 | 0.31464 | C | 5 | 0.18642 | C | 11 | 0.18634 |
| H | 2 | 0.12465 | C | 6 | -0.23248 | C | 12 | -0.26494 | H | 2 | 0.13631 | C | 6 | -0.23633 | C | 12 | -0.26302 |
| N | 3 | -0.63802 | C | 7 | -0.26511 | C | 13 | -0.23249 | N | 3 | -0.62885 | C | 7 | -0.26274 | C | 13 | -0.23614 |
| N | 4 | -0.63775 | C | 8 | -0.18681 | C | 14 | -0.18124 | N | 4 | -0.62863 | C | 8 | -0.18148 | C | 14 | -0.18260 |
| | | | C | 9 | -0.18118 | C | 15 | -0.18674 | | | | C | 9 | -0.18282 | C | 15 | -0.18152 |
| | | | C | 10 | -0.36420 | C | 16 | -0.36395 | | | | C | 10 | -0.37626 | C | 16 | -0.37626 |
| | | | H | 17 | 0.21939 | H | 19 | 0.21932 | | | | H | 17 | 0.21950 | H | 19 | 0.21953 |
| | | | H | 18 | 0.21975 | H | 20 | 0.21970 | | | | H | 18 | 0.21440 | H | 20 | 0.21431 |
| | | | H | 21 | 0.23179 | H | 22 | 0.23180 | | | | H | 21 | 0.23346 | H | 22 | 0.23342 |
| | | | H | 23 | 0.23225 | H | 24 | 0.23222 | | | | H | 23 | 0.23180 | H | 24 | 0.23202 |
| | | | S | 28 | 2.10294 | S | 25 | 2.10298 | | | | S | 28 | 2.10069 | S | 25 | 2.10084 |
| | | | O | 29 | -0.98460 | O | 26 | -0.98470 | | | | O | 29 | -0.98667 | O | 26 | -0.98689 |
| | | | O | 30 | -0.98415 | O | 27 | -0.98412 | | | | O | 30 | -0.98633 | O | 27 | -0.98638 |
| | | | C | 35 | -0.78732 | C | 31 | -0.78727 | | | | C | 35 | -0.78538 | C | 31 | -0.78548 |
| | | | H | 36 | 0.23831 | H | 32 | 0.23834 | | | | H | 36 | 0.23663 | H | 32 | 0.23671 |
| | | | H | 37 | 0.23791 | H | 33 | 0.23790 | | | | H | 37 | 0.23652 | H | 33 | 0.23633 |
| | | | H | 38 | 0.24304 | H | 34 | 0.24306 | | | | H | 38 | 0.24201 | H | 34 | 0.24197 |
| **sum** | | -0.84694 | **sum** | | -0.07671 | **sum** | | -0.07634 | **sum** | | -0.80653 | **sum** | | -0.09658 | **sum** | | -0.09682 |
| | | | aryl | | -0.14284 | aryl | | -0.14253 | | | | aryl | | -0.15405 | aryl | | -0.15392 |
| | | | EWG | | 0.06613 | EWG | | 0.06619 | | | | EWG | | 0.05747 | EWG | | 0.05710 |

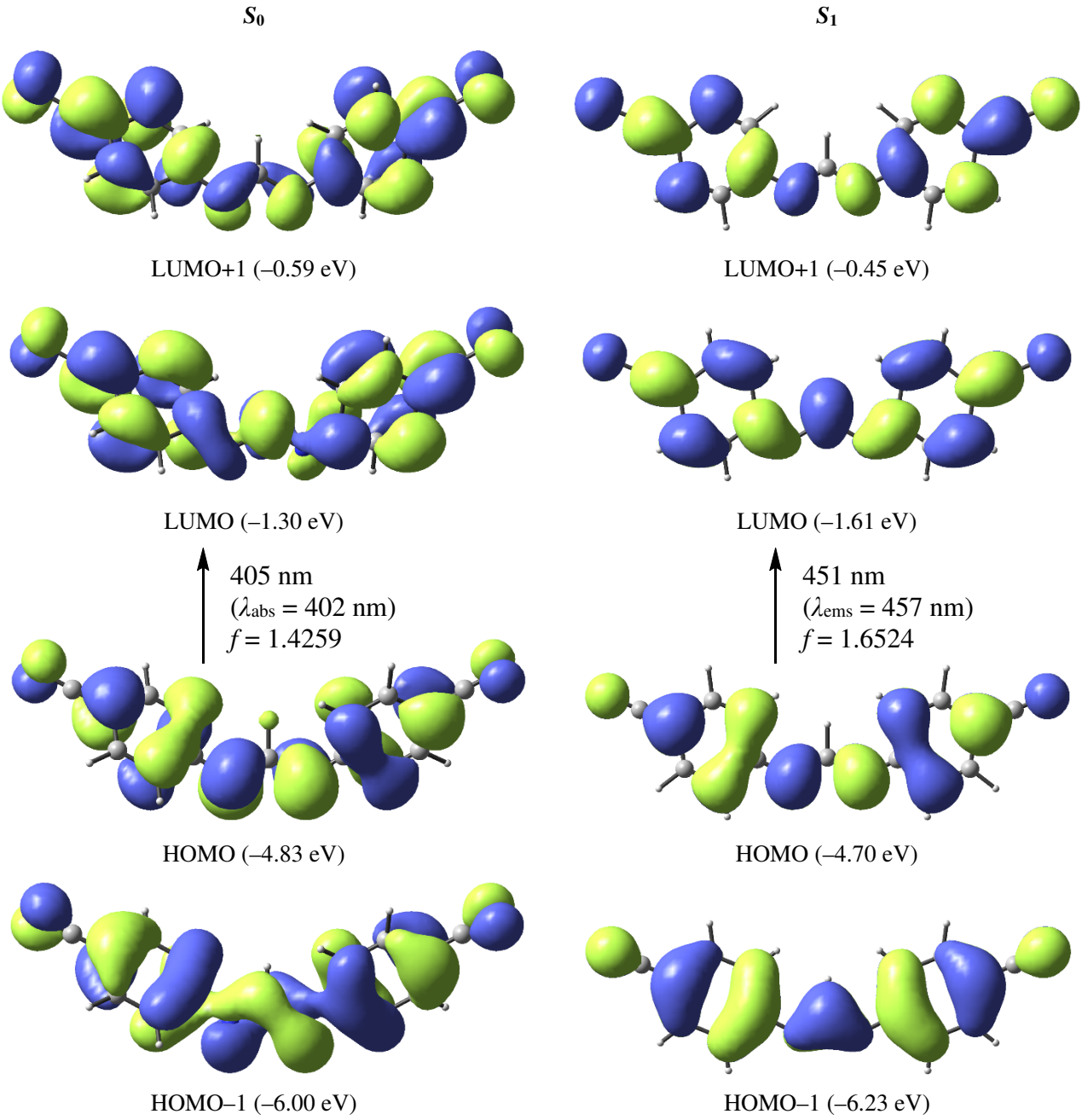



**Figure S44.** $S_0$- and $S_1$-state MOs, orbital energies, excitation energies, and oscillator strengths of **2c**$^-$.

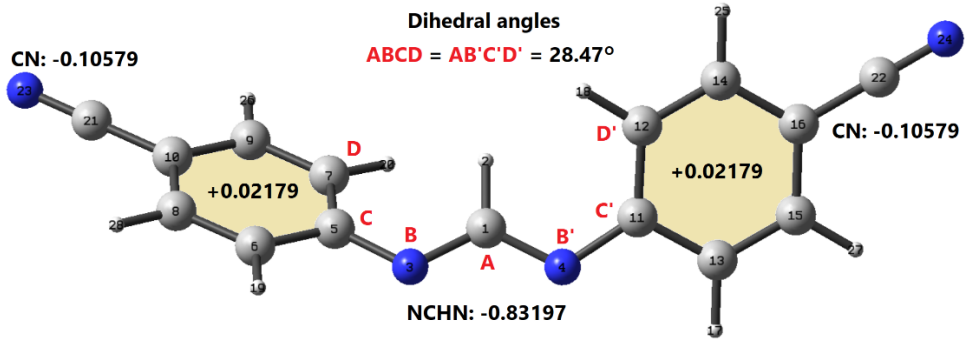



**Figure S45.** Dihedral angles and the sum of natural atomic charges of diazaallyl, aryl, and electron-withdrawing groups of **2c**$^{-}$ ($S_0$).

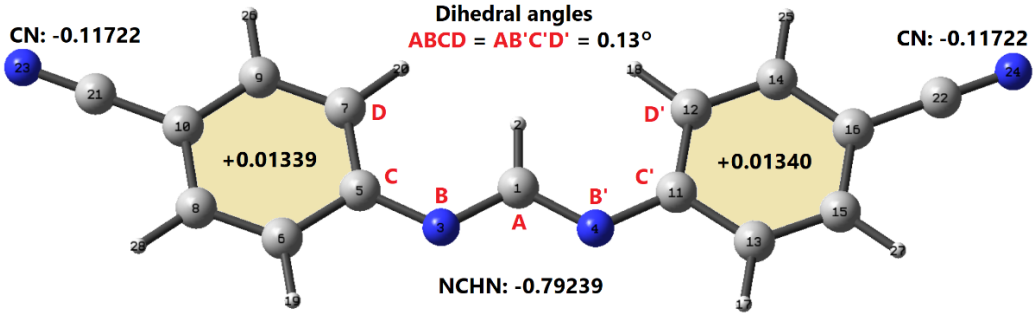



**Figure S46.** Dihedral angles and the sum of natural atomic charges of diazaallyl, aryl, and electron-withdrawing groups of **2c**$^{-}$ ($S_1$).

**Table S9.** Natural atomic charges of **2c**$^{-}$ at the $S_0$ and $S_1$ states.

| $S_0$ | | | | | | | | | $S_1$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **NCHN** | | NPA ($\delta$) | **Ar1** | | NPA ($\delta$) | **Ar2** | | NPA ($\delta$) | **NCHN** | | NPA ($\delta$) | **Ar1** | | NPA ($\delta$) | **Ar2** | | NPA ($\delta$) |
| C | 1 | 0.30516 | C | 5 | 0.18639 | C | 11 | 0.18639 | C | 1 | 0.31500 | C | 5 | 0.18845 | C | 11 | 0.18845 |
| H | 2 | 0.12759 | C | 6 | -0.23413 | C | 12 | -0.26689 | H | 2 | 0.13595 | C | 6 | -0.23790 | C | 12 | -0.26360 |
| N | 3 | -0.63236 | C | 7 | -0.26689 | C | 13 | -0.23413 | N | 3 | -0.62167 | C | 7 | -0.26360 | C | 13 | -0.23790 |
| N | 4 | -0.63236 | C | 8 | -0.15019 | C | 14 | -0.14309 | N | 4 | -0.62167 | C | 8 | -0.14674 | C | 14 | -0.14402 |
| | | | C | 9 | -0.14309 | C | 15 | -0.15019 | | | | C | 9 | -0.14402 | C | 15 | -0.14674 |
| | | | C | 10 | -0.26131 | C | 16 | -0.26131 | | | | C | 10 | -0.26613 | C | 16 | -0.26612 |
| | | | H | 19 | 0.22178 | H | 17 | 0.22178 | | | | H | 19 | 0.22098 | H | 17 | 0.22098 |
| | | | H | 20 | 0.22126 | H | 18 | 0.22126 | | | | H | 20 | 0.21592 | H | 18 | 0.21592 |
| | | | C | 22 | 0.34453 | C | 21 | 0.34453 | | | | C | 22 | 0.34074 | C | 21 | 0.34074 |
| | | | N | 24 | -0.45032 | N | 23 | -0.45032 | | | | N | 24 | -0.45796 | N | 23 | -0.45796 |
| | | | H | 26 | 0.22364 | H | 25 | 0.22364 | | | | H | 26 | 0.22205 | H | 25 | 0.22205 |
| | | | H | 28 | 0.22433 | H | 27 | 0.22433 | | | | H | 28 | 0.22438 | H | 27 | 0.22438 |
| **sum** | | -0.83197 | **sum** | | -0.08400 | **sum** | | -0.08400 | **sum** | | -0.79239 | **sum** | | -0.10383 | **sum** | | -0.10382 |
| | | | aryl | | 0.02179 | aryl | | 0.02179 | | | | aryl | | 0.01339 | aryl | | 0.01340 |
| | | | EWG | | -0.10579 | EWG | | -0.10579 | | | | EWG | | -0.11722 | EWG | | -0.11722 |

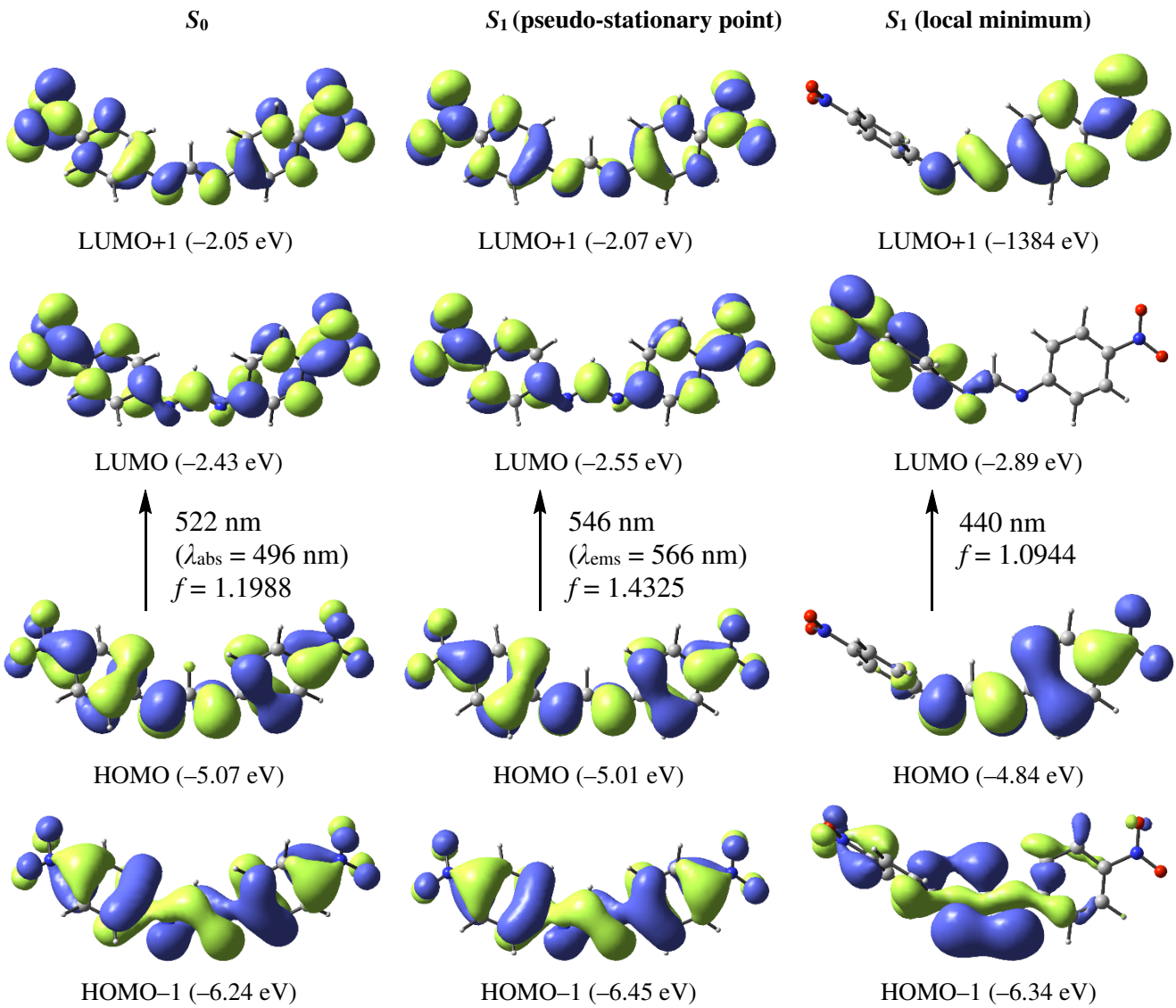



**Figure S47.** $S_0$- and $S_1$-state MOs, orbital energies, excitation energies, and oscillator strengths of **2d**$^-$.

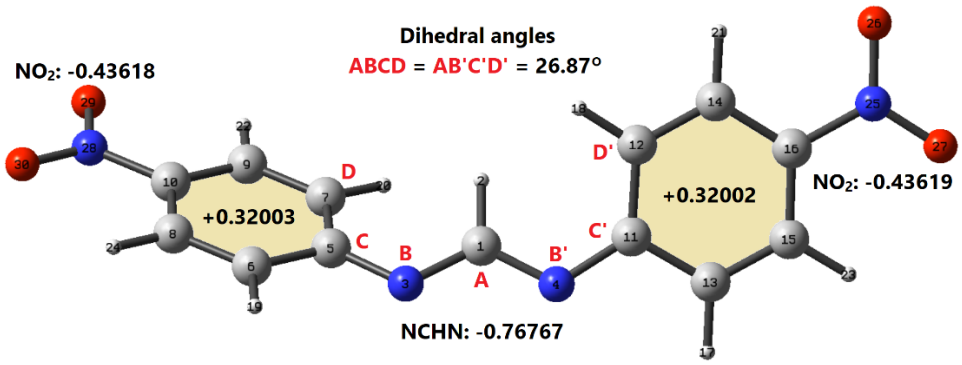



**Figure S48.** Dihedral angles and the sum of natural atomic charges of diazaallyl, aryl, and electron-withdrawing groups of **2d**$^{-}$ ($S_0$).

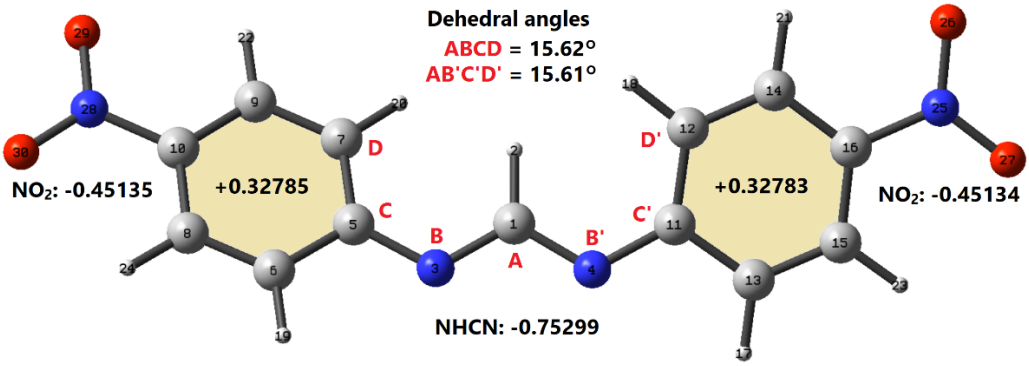



**Figure S49.** Dihedral angles and the sum of natural atomic charges of diazaallyl, aryl, and electron-withdrawing groups of **2d**$^{-}$ (pseudo-stationary point at $S_1$).

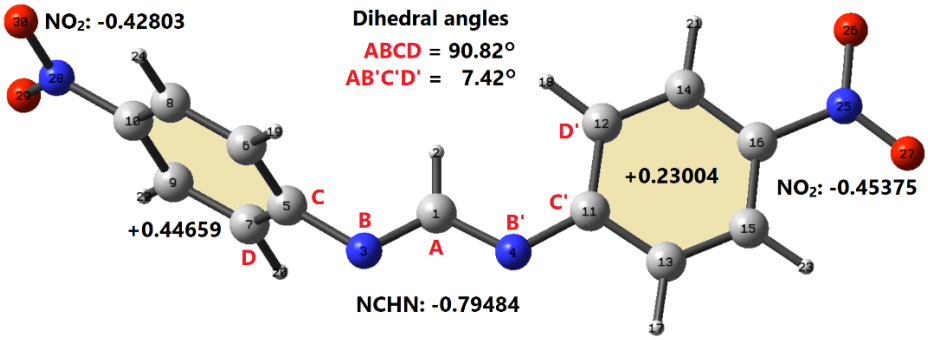


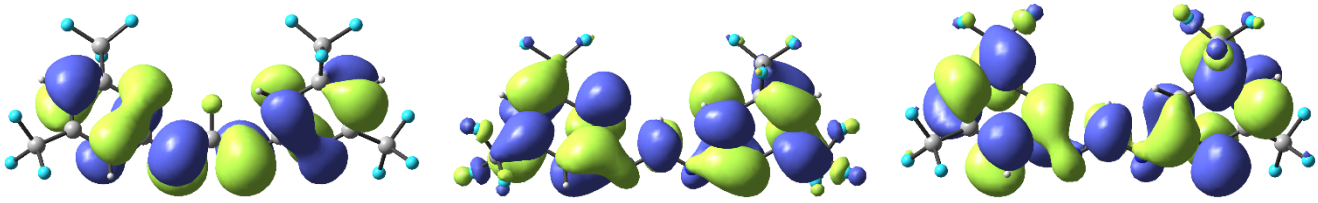

**Figure S50.** Dihedral angles and the sum of natural atomic charges of diazaallyl, aryl, and electron-withdrawing groups of **2d**$^{-}$ (local minimum at $S_1$).

**Table S10.** Natural atomic charges of **2d**$^{-}$ at the $S_0$ and $S_1$ (a pseudo-stationary point and a local minimum) states.

| $S_0$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **NCHN** | | NPA ($\delta$) | **Ar1** | | NPA ($\delta$) | **Ar2** | | NPA ($\delta$) |
| C | 1 | 0.30981 | C | 5 | 0.19839 | C | 11 | 0.19839 |
| H | 2 | 0.13514 | C | 6 | -0.22588 | C | 12 | -0.25843 |
| N | 3 | -0.60631 | C | 7 | -0.25843 | C | 13 | -0.22588 |
| N | 4 | -0.60631 | C | 8 | -0.17585 | C | 14 | -0.16821 |
| | | | C | 9 | -0.16821 | C | 15 | -0.17585 |
| | | | C | 10 | 0.02355 | C | 16 | 0.02355 |
| | | | H | 19 | 0.22402 | H | 17 | 0.22402 |
| | | | H | 20 | 0.22293 | H | 18 | 0.22292 |
| | | | H | 22 | 0.23956 | H | 21 | 0.23956 |
| | | | H | 24 | 0.23995 | H | 23 | 0.23995 |
| | | | N | 28 | 0.47420 | N | 25 | 0.47420 |
| | | | O | 29 | -0.45545 | O | 26 | -0.45545 |
| | | | O | 30 | -0.45494 | O | 27 | -0.45493 |
| **sum** | | -0.76767 | **sum** | | -0.11616 | **sum** | | -0.11616 |
| | | | aryl | | 0.32003 | aryl | | 0.32002 |
| | | | EWG | | -0.43619 | EWG | | -0.43618 |

| $S_1$ (a pseudo-stationary point) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **NCHN** | | NPA ($\delta$) | **Ar1** | | NPA ($\delta$) | **Ar2** | | NPA ($\delta$) |
| C | 1 | 0.31194 | C | 5 | 0.19277 | C | 11 | 0.19277 |
| H | 2 | 0.13774 | C | 6 | -0.22265 | C | 12 | -0.25387 |
| N | 3 | -0.60133 | C | 7 | -0.25387 | C | 13 | -0.22266 |
| N | 4 | -0.60134 | C | 8 | -0.17447 | C | 14 | -0.16775 |
| | | | C | 9 | -0.16774 | C | 15 | -0.17447 |
| | | | C | 10 | 0.02814 | C | 16 | 0.02814 |
| | | | H | 19 | 0.22498 | H | 17 | 0.22498 |
| | | | H | 20 | 0.22053 | H | 18 | 0.22053 |
| | | | H | 22 | 0.23949 | H | 21 | 0.23949 |
| | | | H | 24 | 0.24067 | H | 23 | 0.24067 |
| | | | N | 28 | 0.46527 | N | 25 | 0.46528 |
| | | | O | 29 | -0.45871 | O | 26 | -0.45871 |
| | | | O | 30 | -0.45791 | O | 27 | -0.45791 |
| **sum** | | -0.75299 | **sum** | | -0.12350 | **sum** | | -0.12351 |
| | | | aryl | | 0.32785 | aryl | | 0.32783 |
| | | | EWG | | -0.45135 | EWG | | -0.45134 |

| $S_1$ (a local minimum) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **NCHN** | | NPA ($\delta$) | **Ar1** | | NPA ($\delta$) | **Ar2** | | NPA ($\delta$) |
| C | 1 | 0.30126 | C | 5 | 0.21516 | C | 11 | 0.19728 |
| H | 2 | 0.13743 | C | 6 | -0.23364 | C | 12 | -0.27610 |
| N | 3 | -0.57591 | C | 7 | -0.23384 | C | 13 | -0.23729 |
| N | 4 | -0.65762 | C | 8 | -0.14610 | C | 14 | -0.17874 |
| | | | C | 9 | -0.14598 | C | 15 | -0.18955 |
| | | | C | 10 | 0.03995 | C | 16 | 0.00696 |
| | | | H | 19 | 0.23273 | H | 17 | 0.21907 |
| | | | H | 20 | 0.23284 | H | 18 | 0.21435 |
| | | | H | 22 | 0.24276 | H | 21 | 0.23626 |
| | | | H | 24 | 0.24271 | H | 23 | 0.23780 |
| | | | N | 28 | 0.44543 | N | 25 | 0.48002 |
| | | | O | 29 | -0.43666 | O | 26 | -0.46726 |
| | | | O | 30 | -0.43680 | O | 27 | -0.46651 |
| **sum** | | -0.79484 | **sum** | | 0.01856 | **sum** | | -0.22371 |
| | | | aryl | | 0.44659 | aryl | | 0.23004 |
| | | | EWG | | -0.42803 | EWG | | -0.45375 |



HOMO (-4.85 eV) LUMO (-0.99 eV) LUMO+2 (-0.81 eV)

**Figure S51.** Frontier orbitals for the ground state ($S_0$) of **2e⁻**.

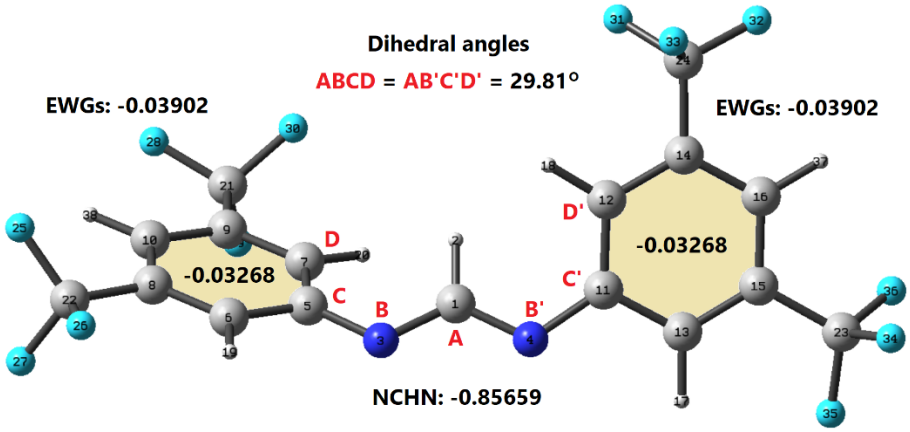



**Figure S52.** Dihedral angles and the sum of natural atomic charges of diazaallyl, aryl, and electron-withdrawing groups of **2e⁻** ($S_0$).

**Table S11.** Natural atomic charges of **2e⁻** at the $S_0$ state.

| | | | $S_0$ | | | | | |
|---|---|---|---|---|---|---|---|---|
| **NCHN** | | NPA ($\delta$) | **Ar1** | | NPA ($\delta$) | **Ar2** | | NPA ($\delta$) |
| C | 1 | 0.30255 | C | 5 | 0.16823 | C | 11 | 0.16823 |
| H | 2 | 0.12508 | C | 6 | -0.17870 | C | 12 | -0.22101 |
| N | 3 | -0.64211 | C | 7 | -0.22101 | C | 13 | -0.17869 |
| N | 4 | -0.64211 | C | 8 | -0.15311 | C | 14 | -0.14664 |
| | | | C | 9 | -0.14664 | C | 15 | -0.15311 |
| | | | C | 10 | -0.20924 | C | 16 | -0.20924 |
| | | | H | 19 | 0.23490 | H | 17 | 0.23490 |
| | | | H | 20 | 0.23155 | H | 18 | 0.23154 |
| | | | C | 21 | 1.09014 | C | 23 | 1.09040 |
| | | | C | 22 | 1.09040 | C | 24 | 1.09014 |
| | | | F | 25 | -0.37099 | F | 31 | -0.36969 |
| | | | F | 26 | -0.36551 | F | 32 | -0.36780 |
| | | | F | 27 | -0.37329 | F | 33 | -0.37228 |
| | | | F | 28 | -0.36781 | F | 34 | -0.37329 |
| | | | F | 29 | -0.37229 | F | 35 | -0.36552 |
| | | | F | 30 | -0.36967 | F | 36 | -0.37098 |
| | | | H | 38 | 0.24134 | H | 37 | 0.24134 |
| **sum** | | -0.85659 | **sum** | | -0.07170 | **sum** | | -0.07170 |
| | | | aryl | | -0.03268 | aryl | | -0.03268 |
| | | | EWG | | -0.03902 | EWG | | -0.03902 |

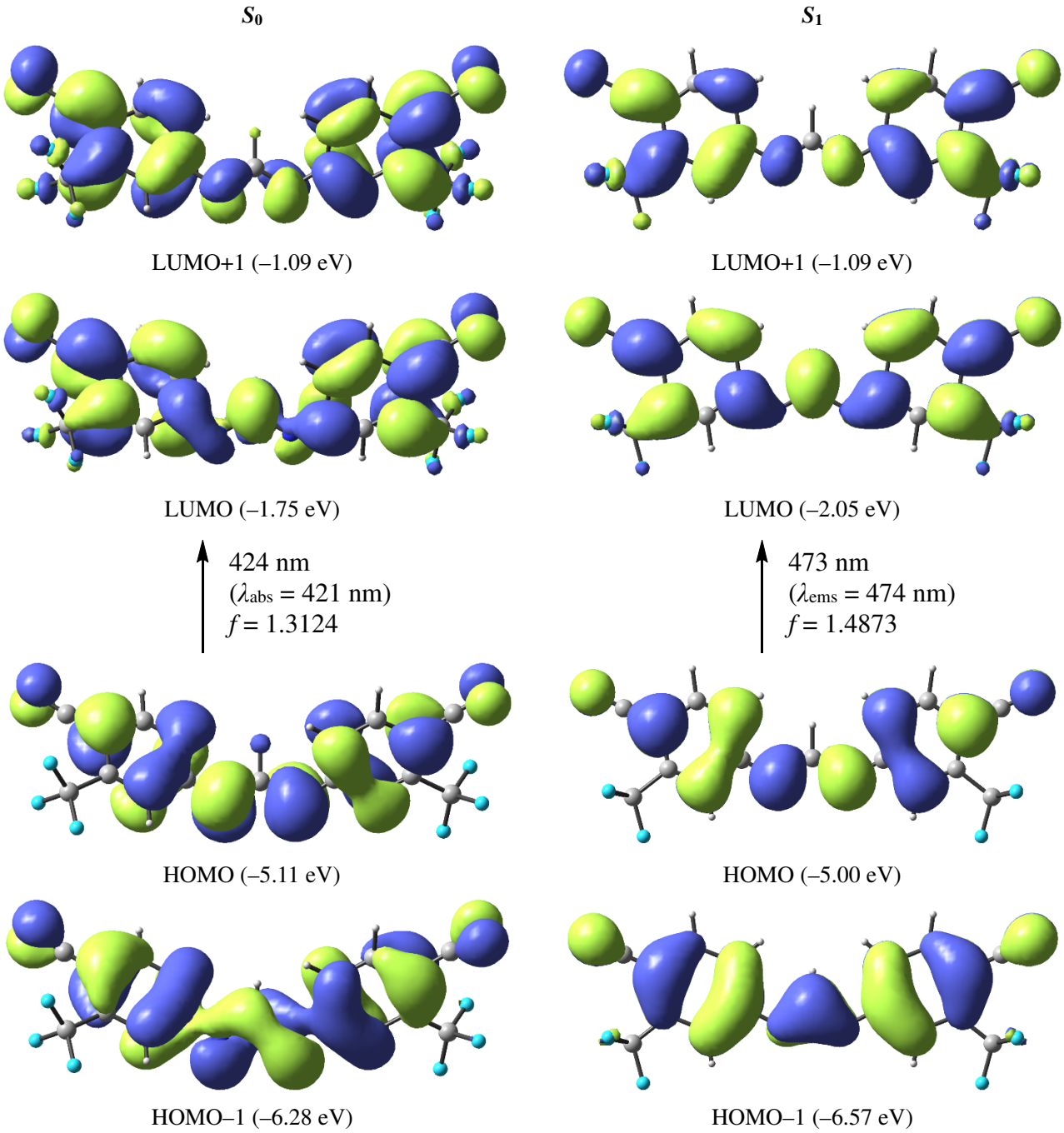



**Figure S53.** $S_0$- and $S_1$-state MOs, orbital energies, excitation energies, and oscillator strengths of **2f**$^{-}$.

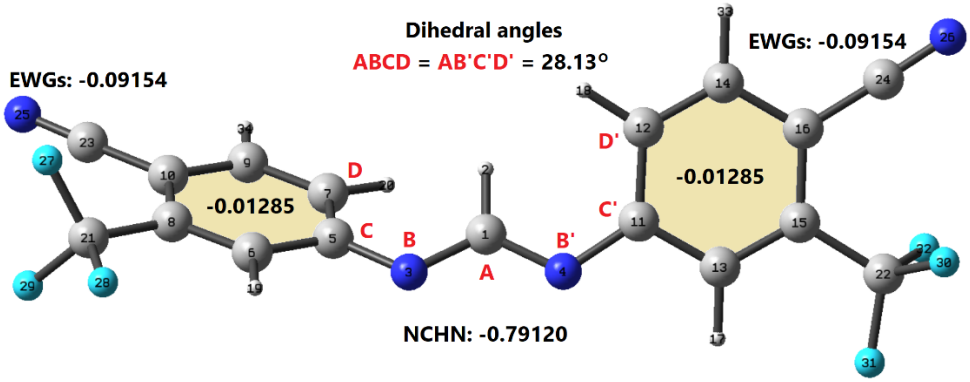



**Figure S54.** Dihedral angles and the sum of natural atomic charges of diazaallyl, aryl, and electron-withdrawing groups of **2f**$^{-}$ ($S_0$).

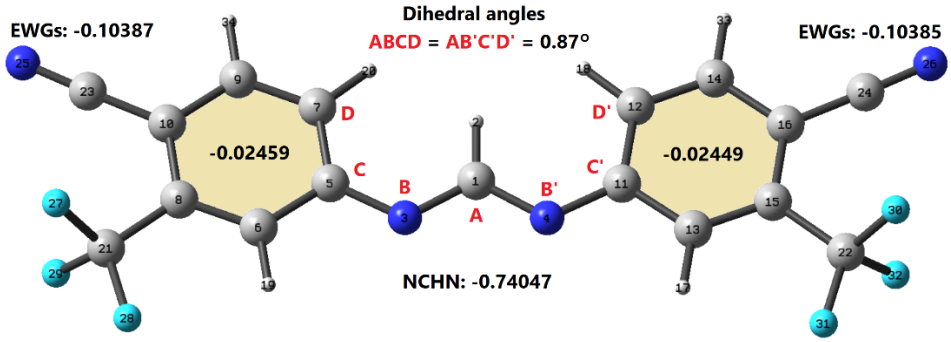



**Figure S55.** Dihedral angles and the sum of natural atomic charges of diazaallyl, aryl, and electron-withdrawing groups of **2f**$^{-}$ ($S_1$).

**Table S12.** Natural atomic charges of **2f**$^{-}$ at the $S_0$ and $S_1$ states.

| $S_0$ | | | | | | | | | $S_1$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **NCHN** | | NPA ($\delta$) | **Ar1** | | NPA ($\delta$) | **Ar2** | | NPA ($\delta$) | **NCHN** | | NPA ($\delta$) | **Ar1** | | NPA ($\delta$) | **Ar2** | | NPA ($\delta$) |
| C | 1 | 0.31055 | C | 5 | 0.19177 | C | 11 | 0.19177 | C | 1 | 0.40670 | C | 5 | 0.18121 | C | 11 | 0.18121 |
| H | 2 | 0.13237 | C | 6 | -0.19014 | C | 12 | -0.24855 | H | 2 | 0.12782 | C | 6 | -0.18479 | C | 12 | -0.24301 |
| N | 3 | -0.61706 | C | 7 | -0.24855 | C | 13 | -0.19014 | N | 3 | -0.63750 | C | 7 | -0.24301 | C | 13 | -0.18476 |
| N | 4 | -0.61706 | C | 8 | -0.10396 | C | 14 | -0.12827 | N | 4 | -0.63749 | C | 8 | -0.10983 | C | 14 | -0.13193 |
| | | | C | 9 | -0.12827 | C | 15 | -0.10396 | | | | C | 9 | -0.13193 | C | 15 | -0.10980 |
| | | | C | 10 | -0.23177 | C | 16 | -0.23177 | | | | C | 10 | -0.23152 | C | 16 | -0.23153 |
| | | | H | 17 | 0.24025 | H | 19 | 0.24025 | | | | H | 17 | 0.24397 | H | 19 | 0.24402 |
| | | | H | 18 | 0.22702 | H | 20 | 0.22702 | | | | H | 18 | 0.22196 | H | 20 | 0.22196 |
| | | | C | 22 | 1.08851 | C | 21 | 1.08851 | | | | C | 22 | 1.08757 | C | 21 | 1.08758 |
| | | | C | 24 | 0.33003 | C | 23 | 0.33003 | | | | C | 24 | 0.32637 | C | 23 | 0.32637 |
| | | | N | 26 | -0.41698 | N | 25 | -0.41698 | | | | N | 26 | -0.42214 | N | 25 | -0.42214 |
| | | | F | 30 | -0.36570 | F | 27 | -0.36612 | | | | F | 30 | -0.36727 | F | 27 | -0.36722 |
| | | | F | 31 | -0.36128 | F | 28 | -0.36128 | | | | F | 31 | -0.36118 | F | 28 | -0.36117 |
| | | | F | 32 | -0.36612 | F | 29 | -0.36570 | | | | F | 32 | -0.36722 | F | 29 | -0.36727 |
| | | | H | 33 | 0.23080 | H | 34 | 0.23080 | | | | H | 33 | 0.22935 | H | 34 | 0.22935 |
| **sum** | | -0.79120 | **sum** | | -0.10439 | **sum** | | -0.10439 | **sum** | | -0.74047 | **sum** | | -0.12846 | **sum** | | -0.12846 |
| | | | aryl | | -0.01285 | aryl | | -0.01285 | | | | aryl | | -0.02459 | aryl | | -0.02459 |
| | | | EWG | | -0.09154 | EWG | | -0.09154 | | | | EWG | | -0.10387 | EWG | | -0.10387 |

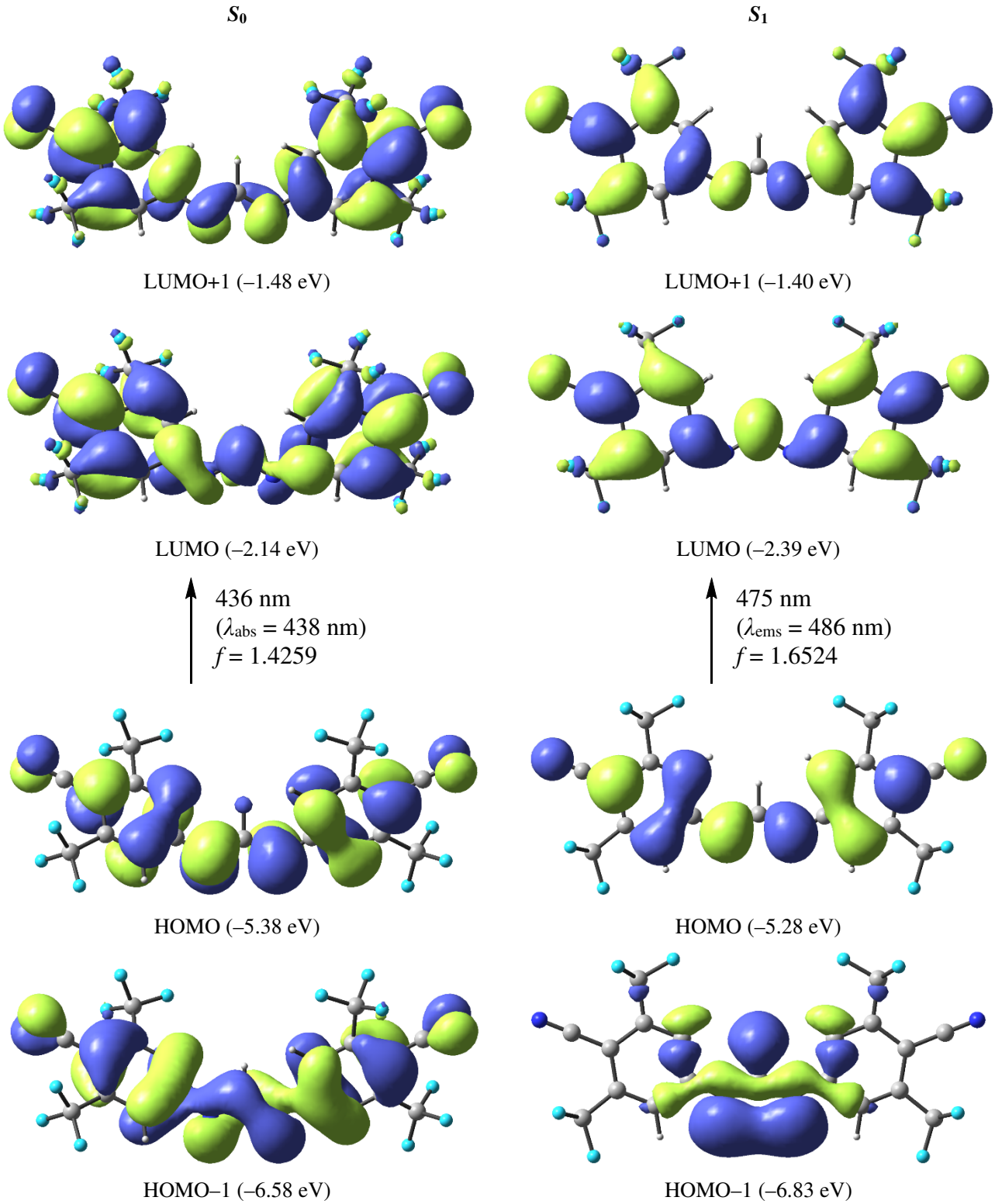



**Figure S56.** $S_0$- and $S_1$-state MOs, orbital energies, excitation energies, and oscillator strengths of **2g**$^-$.

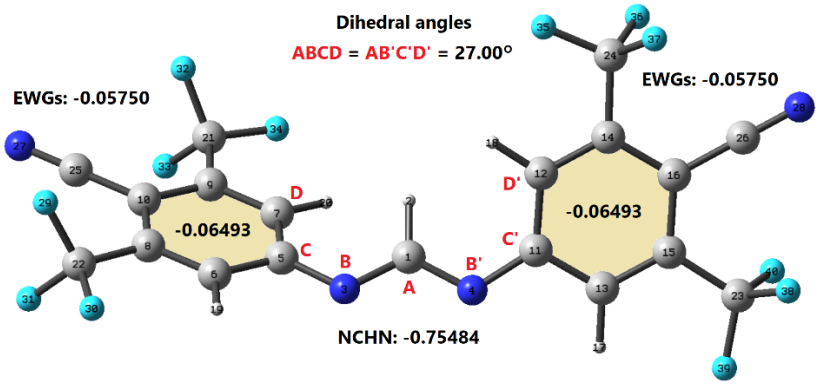



**Figure S57.** Dihedral angles and the sum of natural atomic charges of diazaallyl, aryl, and electron-withdrawing groups of **2g**⁻ ($S_0$).

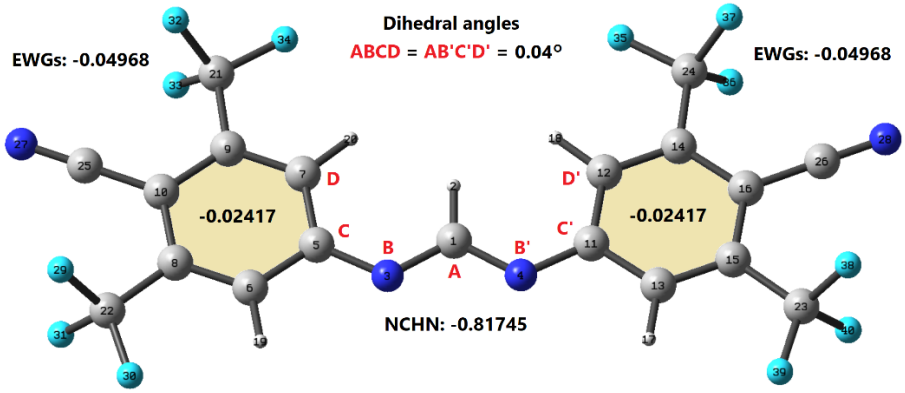



**Figure S58.** Dihedral angles and the sum of natural atomic charges of diazaallyl, aryl, and electron-withdrawing groups of **2g**⁻ ($S_1$).

**Table S13.** Natural atomic charges of **2g**⁻ at the $S_0$ and $S_1$ states.

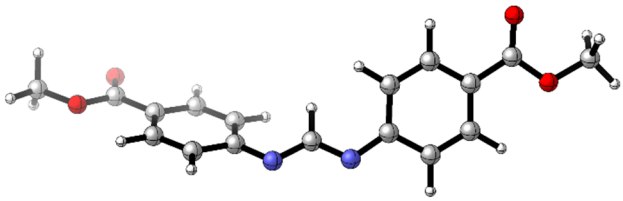
| $S_0$ | | | | | | | | | $S_1$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **NCHN** | | NPA ($\delta$) | **Ar1** | | NPA ($\delta$) | **Ar2** | | NPA ($\delta$) | **NCHN** | | NPA ($\delta$) | **Ar1** | | NPA ($\delta$) | **Ar2** | | NPA ($\delta$) |
| C | 1 | 0.31495 | C | 5 | 0.19850 | C | 11 | 0.19850 | C | 1 | 0.31143 | C | 5 | 0.36967 | C | 11 | 0.37007 |
| H | 2 | 0.13645 | C | 6 | -0.17516 | C | 12 | -0.20749 | H | 2 | 0.14052 | C | 6 | -0.23510 | C | 12 | -0.24758 |
| N | 3 | -0.60312 | C | 7 | -0.20749 | C | 13 | -0.17516 | N | 3 | -0.63472 | C | 7 | -0.24757 | C | 13 | -0.23500 |
| N | 4 | -0.60312 | C | 8 | -0.09190 | C | 14 | -0.08747 | N | 4 | -0.63468 | C | 8 | -0.10979 | C | 14 | -0.09027 |
| | | | C | 9 | -0.08747 | C | 15 | -0.09190 | | | | C | 9 | -0.09047 | C | 15 | -0.10956 |
| | | | C | 10 | -0.19400 | C | 16 | -0.19400 | | | | C | 10 | -0.19829 | C | 16 | -0.19941 |
| | | | H | 19 | 0.24605 | H | 17 | 0.24605 | | | | H | 19 | 0.24998 | H | 17 | 0.24996 |
| | | | H | 20 | 0.24654 | H | 18 | 0.24654 | | | | H | 20 | 0.23740 | H | 18 | 0.23742 |
| | | | C | 21 | 1.08896 | C | 23 | 1.08906 | | | | C | 21 | 1.08820 | C | 23 | 1.12663 |
| | | | C | 22 | 1.08906 | C | 24 | 1.08896 | | | | C | 22 | 1.12662 | C | 24 | 1.08832 |
| | | | C | 25 | 0.30525 | C | 26 | 0.30525 | | | | C | 25 | 0.29998 | C | 26 | 0.30522 |
| | | | N | 27 | -0.37570 | N | 28 | -0.37570 | | | | N | 27 | -0.38013 | N | 28 | -0.38557 |
| | | | F | 29 | -0.36247 | F | 35 | -0.35938 | | | | F | 29 | -0.36827 | F | 35 | -0.36102 |
| | | | F | 30 | -0.35814 | F | 36 | -0.36163 | | | | F | 30 | -0.36337 | F | 36 | -0.36165 |
| | | | F | 31 | -0.36210 | F | 37 | -0.36135 | | | | F | 31 | -0.36828 | F | 37 | -0.36170 |
| | | | F | 32 | -0.36163 | F | 38 | -0.36210 | | | | F | 32 | -0.36167 | F | 38 | -0.36826 |
| | | | F | 33 | -0.36135 | F | 39 | -0.35814 | | | | F | 33 | -0.36172 | F | 39 | -0.36333 |
| | | | F | 34 | -0.35938 | F | 40 | -0.36247 | | | | F | 34 | -0.36104 | F | 40 | -0.36826 |
| **sum** | | -0.75484 | **sum** | | -0.12243 | **sum** | | -0.12243 | **sum** | | -0.81745 | **sum** | | -0.07385 | **sum** | | -0.07399 |
| | | | aryl | | -0.06493 | aryl | | -0.06493 | | | | aryl | | -0.02417 | aryl | | -0.02437 |
| | | | EWG | | -0.05750 | EWG | | -0.05750 | | | | EWG | | -0.04968 | EWG | | -0.04962 |

**Table S14.** Summary of the calculated photoexcitation parameters

| | state | frontier orbitals | $E_{EX}$ (eV) | wavelengths (nm) | | | | oscillator strength $f$ |
|---|---|---|---|---|---|---|---|---|
| | | | | calcd. $\lambda_{S0–S1}$ | $\lambda_{ABS}$ | calcd. $\lambda_{S1–S0}$ | $\lambda_{EM}$ | |
| **2a**$^-$ | $S_0$ | HOMO/LUMO | 2.96 | 419 | 411 | — | — | 1.4223 |
| | $S_1$ | HOMO/LUMO | 2.69 | — | — | 461 | 471 | 1.6962 |
| **2b**$^-$ | $S_0$ | HOMO/LUMO | 3.22 | 385 | 391 | — | — | 1.3051 |
| | $S_1$ | HOMO/LUMO | 2.85 | — | — | 434 | 446 | 1.4892 |
| **2c**$^-$ | $S_0$ | HOMO/LUMO | 3.07 | 403 | 402 | — | — | 1.4259 |
| | $S_1$ | HOMO/LUMO | 2.75 | — | — | 451 | 457 | 1.6524 |
| **2d**$^-$ | $S_0$ | HOMO/LUMO | 2.39 | 519 | 496 | — | — | 1.1988 |
| | $S_1$ | HOMO/LUMO | 2.27 | — | — | 546 | 566 | 1.4325 |
| **2e**$^-$ | $S_0$ | HOMO/LUMO | 3.27 | 379 | — | — | — | 0.1734 |
| | | HOMO/LUMO+2 | 3.48 | 356 | 355 | — | 436 | 0.8568 |
| **2f**$^-$ | $S_0$ | HOMO/LUMO | 2.94 | 424 | 421 | — | — | 1.3124 |
| | $S_1$ | HOMO/LUMO | 2.62 | — | — | 473 | 474 | 1.4873 |
| **2g**$^-$ | $S_0$ | HOMO/LUMO | 2.87 | 436 | 438 | — | — | 1.3913 |
| | $S_1$ | HOMO/LUMO | 2.70 | — | — | 475 | 486 | 1.6759 |

## (J-2) Cartesian Coordinates of DFT-Optimized States

Singlet ground state ($S_0$) of **2a**$^-$



$E_{298}$(B3LYP) = -1067.49364381 Hartree

$E_{298}$(TD-B3LYP) = -1067.38452088 Hartree

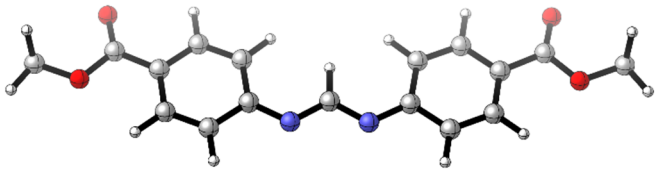
$G_{298}$(B3LYP) = -1067.56759381 Hartree

$G_{298}$(TD-B3LYP) = -1067.45847088 Hartree

-1 1

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.000042 | 1.220719 | -0.000634 | H | -3.790630 | -1.611825 | 1.429885 |
| H | 0.000066 | 0.116603 | -0.000275 | H | 3.790814 | -1.612650 | -1.429214 |
| N | 1.157712 | 1.852775 | 0.128877 | H | -5.559413 | 1.355406 | -1.125707 |
| N | -1.157656 | 1.852645 | -0.130550 | H | 5.559411 | 1.356215 | 1.124613 |
| C | 2.322971 | 1.131197 | 0.016491 | C | -6.091238 | -0.964626 | 0.258756 |
| C | 3.483054 | 1.621847 | 0.674305 | O | -6.257780 | -1.996619 | 0.903746 |
| C | 2.475851 | -0.053545 | -0.759755 | O | -7.102607 | -0.389278 | -0.441129 |
| C | 4.696746 | 0.960126 | 0.600691 | C | 6.091313 | -0.964760 | -0.258251 |
| C | 3.693170 | -0.713401 | -0.829225 | O | 6.257908 | -1.997150 | -0.902591 |
| C | 4.825439 | -0.228521 | -0.148571 | O | 7.102602 | -0.389036 | 0.441441 |
| C | -2.322892 | 1.131107 | -0.017665 | C | -8.374592 | -1.057369 | -0.383657 |
| C | -2.475713 | -0.053153 | 0.759330 | H | -9.043607 | -0.460133 | -1.002224 |
| C | -3.483018 | 1.621325 | -0.675727 | H | -8.292597 | -2.072520 | -0.779140 |
| C | -3.693029 | -0.712961 | 0.829314 | H | -8.740316 | -1.097814 | 0.645114 |
| C | -4.696708 | 0.959656 | -0.601594 | C | 8.374563 | -1.057223 | 0.384570 |
| C | -4.825353 | -0.228501 | 0.148452 | H | 9.043505 | -0.459660 | 1.002898 |
| H | -3.390056 | 2.534285 | -1.255895 | H | 8.292449 | -2.072139 | 0.780630 |
| H | -1.635871 | -0.430072 | 1.333105 | H | 8.740454 | -1.098287 | -0.644118 |
| H | 3.390048 | 2.535179 | 1.253880 | | | | |
| H | 1.636047 | -0.430819 | -1.333354 | | | | |

Singlet excited state ($S_1$) of **2a**$^-$



$E_{298}$(B3LYP) = -1067.49025005 Hartree

$E_{298}$(TD-B3LYP) = -1067.39146512 Hartree

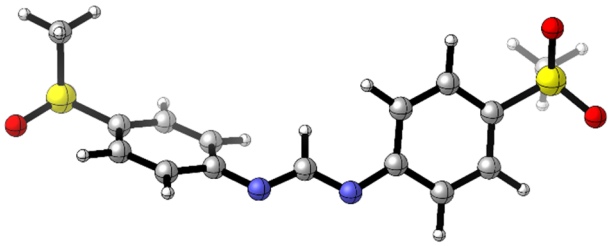
$G_{298}$(B3LYP) = -1067.56074105 Hartree

$G_{298}$(TD-B3LYP) = -1067.46195612 Hartree

-1 1

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.000003 | 0.749196 | -0.000068 | H | 4.023943 | -2.198059 | 0.097586 |
| H | 0.000004 | -0.344069 | 0.000014 | H | -4.023927 | -2.198085 | -0.097382 |
| N | -1.148132 | 1.435631 | -0.034781 | H | 5.650880 | 1.796069 | 0.127222 |
| N | 1.148136 | 1.435640 | 0.034546 | H | -5.649878 | 1.796034 | -0.127464 |
| C | -2.359330 | 0.807542 | -0.064602 | C | 6.330624 | -0.881030 | 0.130054 |
| C | -3.515227 | 1.646817 | -0.088807 | O | 6.569698 | -2.094437 | 0.132308 |
| C | -2.585068 | -0.613123 | -0.070619 | O | 7.335765 | 0.044996 | 0.142881 |
| C | -4.795128 | 1.130215 | -0.111313 | C | -6.330614 | -0.881068 | -0.129983 |
| C | -3.866923 | -1.124302 | -0.093999 | O | -6.569683 | -2.094476 | -0.132107 |
| C | -5.003470 | -0.277533 | -0.112629 | O | -7.335757 | 0.044954 | -0.142892 |
| C | 2.359336 | 0.807559 | 0.064447 | C | 8.672928 | -0.474865 | 0.158134 |
| C | 2.585079 | -0.613105 | 0.070630 | H | 9.325115 | 0.398397 | 0.164794 |
| C | 3.515230 | 1.646841 | 0.088559 | H | 8.841741 | -1.081996 | 1.051388 |
| C | 3.866935 | -1.124276 | 0.094079 | H | 8.861527 | -1.083326 | -0.730276 |
| C | 4.795132 | 1.130245 | 0.111139 | C | -8.672919 | -0.474913 | -0.158046 |
| C | 5.003479 | -0.277502 | 0.112620 | H | -9.325109 | 0.398346 | -0.164792 |
| H | 3.352857 | 2.720626 | 0.086175 | H | -8.841756 | -1.082152 | -1.051221 |
| H | 1.750143 | -1.303743 | 0.056775 | H | -8.861491 | -1.083268 | 0.730443 |
| H | -3.352858 | 2.720603 | -0.086551 | | | | |
| H | -1.750130 | -1.303757 | -0.056692 | | | | |

Singlet ground state ($S_0$) of **2b**$^-$



$E_{298}$(B3LYP) = -1787.63044753 Hartree

$E_{298}$(TD-B3LYP) = -1787.51193383 Hartree

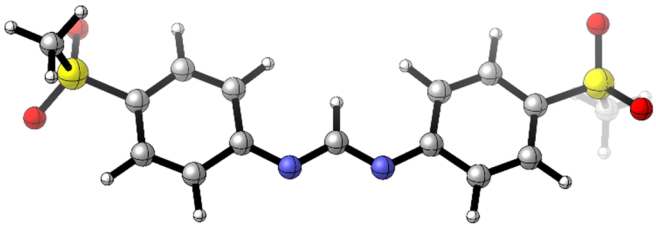
$G_{298}$(B3LYP) = -1787.70787953 Hartree

$G_{298}$(TD-B3LYP) = -1787.58936583 Hartree

-1 1

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.028481 | -0.934253 | -0.543316 | H | 3.729904 | 0.831890 | 2.138480 |
| H | -0.023411 | 0.043745 | -0.029450 | H | -3.762955 | 2.305735 | -0.591711 |
| N | -1.191876 | -1.535877 | -0.742925 | H | 5.555169 | -0.573542 | -1.499567 |
| N | 1.129173 | -1.449143 | -0.930331 | H | -5.616159 | -1.477245 | 0.301884 |
| C | -2.348392 | -0.824430 | -0.529424 | S | -6.337610 | 1.317754 | 0.243763 |
| C | -3.522998 | -1.545808 | -0.184256 | O | -6.350000 | 2.614847 | -0.477617 |
| C | -2.473781 | 0.585808 | -0.684357 | O | -7.459495 | 0.371213 | 0.024192 |
| C | -4.731919 | -0.907035 | 0.038084 | S | 6.297187 | 0.952587 | 0.836777 |
| C | -3.682240 | 1.231872 | -0.459124 | O | 6.319434 | 1.087987 | 2.314646 |
| C | -4.811527 | 0.488217 | -0.094289 | O | 7.411522 | 0.232339 | 0.171835 |
| C | 2.291977 | -0.876977 | -0.471885 | C | 6.258805 | 2.620175 | 0.150601 |
| C | 2.427708 | -0.208752 | 0.778444 | H | 6.169794 | 2.544934 | -0.933684 |
| C | 3.461304 | -1.005040 | -1.269156 | H | 5.407202 | 3.149888 | 0.578628 |
| C | 3.641046 | 0.335963 | 1.177585 | H | 7.198285 | 3.099585 | 0.432506 |
| C | 4.675103 | -0.466116 | -0.874587 | C | -6.295860 | 1.690998 | 2.007742 |
| C | 4.764927 | 0.212083 | 0.351273 | H | -6.217066 | 0.752138 | 2.556845 |
| H | 3.379352 | -1.536951 | -2.211598 | H | -5.437365 | 2.334032 | 2.204185 |
| H | 1.580198 | -0.153806 | 1.452626 | H | -7.230003 | 2.203977 | 2.244602 |
| H | -3.448202 | -2.624386 | -0.091018 | | | | |
| H | -1.622208 | 1.167144 | -1.020122 | | | | |

Singlet excited state ($S_1$) of **2b**$^-$



$E_{298}$(B3LYP) = -1787.62632704 Hartree

$E_{298}$(TD-B3LYP) = -1787.52146094 Hartree

$G_{298}$(B3LYP) = -1787.69941004 Hartree

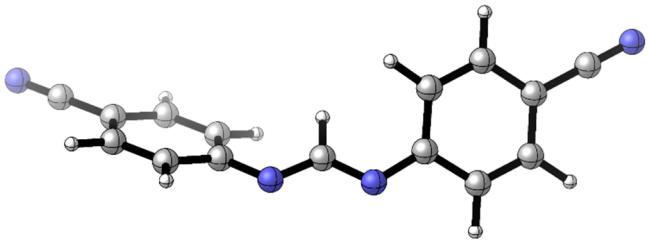
$G_{298}$(TD-B3LYP) = -1787.59454394 Hartree

-1 1

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.011399 | 0.849946 | -0.007706 | H | -1.714361 | -1.207049 | -0.054740 |
| H | 0.016711 | -0.238994 | 0.072550 | H | 3.371682 | 2.818316 | -0.176228 |
| N | 1.158222 | 1.541056 | -0.096221 | H | 1.735419 | -1.201281 | -0.112361 |
| N | -1.141487 | 1.536753 | -0.002157 | H | -3.978362 | -2.128536 | 0.025919 |
| C | 2.364528 | 0.910796 | -0.124723 | H | 4.002788 | -2.116822 | -0.102989 |
| C | 3.526175 | 1.743715 | -0.154810 | H | -5.650196 | 1.854237 | 0.216529 |
| C | 2.575190 | -0.517539 | -0.112499 | H | 5.671117 | 1.871456 | -0.187241 |
| C | 4.804382 | 1.220859 | -0.154747 | S | 6.588523 | -0.874644 | -0.012894 |
| C | 3.853200 | -1.042295 | -0.109943 | O | 6.551142 | -2.286507 | -0.476487 |
| C | 4.973430 | -0.187658 | -0.132032 | O | 7.560491 | 0.059158 | -0.639469 |
| C | -2.345691 | 0.902749 | 0.033143 | S | -6.568051 | -0.891391 | 0.083590 |
| C | -2.553970 | -0.525843 | 0.005357 | O | -6.503031 | -2.310573 | 0.520940 |
| C | -3.507938 | 1.732519 | 0.101427 | O | -7.506261 | 0.030026 | 0.776945 |
| C | -3.830092 | -1.053975 | 0.046436 | C | -7.057071 | -0.906910 | -1.657227 |
| C | -4.783674 | 1.206152 | 0.148057 | H | -7.035450 | 0.118153 | -2.029277 |
| C | -4.949973 | -0.202675 | 0.128156 | H | -6.357685 | -1.538870 | -2.205823 |
| H | -3.355495 | 2.807323 | 0.125390 | H | -8.069213 | -1.315064 | -1.702265 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 6.980109 | -0.920281 | 1.752010 | H | 6.251854 | -1.562890 | 2.248352 |
| H | 6.934863 | 0.097871 | 2.140553 | H | 7.988835 | -1.328255 | 1.847241 |

Singlet ground state ($S_0$) of **2c**$^-$



$E_{298}$(B3LYP) = -796.21197985 Hartree

$E_{298}$(TD-B3LYP) = -796.09943089 Hartree

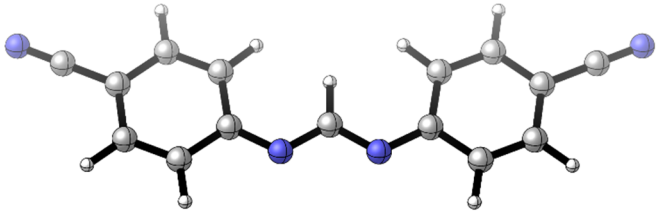
$G_{298}$(B3LYP) = -796.27277885 Hartree

$G_{298}$(TD-B3LYP) = -796.16022989 Hartree

-1 1

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.000011 | -0.912777 | -0.000193 | C | 4.820659 | 0.526624 | 0.046865 |
| H | 0.000002 | 0.191384 | 0.000104 | H | 3.358585 | -2.232446 | -1.326993 |
| N | -1.154052 | -1.545330 | 0.154327 | H | 1.663299 | 0.734926 | 1.299526 |
| N | 1.154015 | -1.545276 | -0.155055 | H | -3.358644 | -2.233080 | 1.325871 |
| C | -2.320889 | -0.825974 | 0.066114 | H | -1.663273 | 0.735654 | -1.299049 |
| C | -3.465322 | -1.320097 | 0.749047 | C | -6.070196 | 1.206536 | -0.099193 |
| C | -2.490036 | 0.358067 | -0.707721 | C | 6.070251 | 1.206289 | 0.099975 |
| C | -4.681359 | -0.663018 | 0.703147 | N | -7.095493 | 1.764810 | -0.139210 |
| C | -3.706363 | 1.021084 | -0.755045 | N | 7.095571 | 1.764497 | 0.140313 |
| C | -4.820631 | 0.526792 | -0.046472 | H | 3.810233 | 1.919040 | 1.356074 |
| C | 2.320871 | -0.825996 | -0.066465 | H | -3.810165 | 1.919881 | -1.354934 |
| C | 2.490053 | 0.357625 | 0.708004 | H | 5.535248 | -1.057205 | -1.244882 |
| C | 3.465288 | -1.319782 | -0.749669 | H | -5.535272 | -1.057721 | 1.244408 |
| C | 3.706403 | 1.020573 | 0.755696 | | | | |
| C | 4.681348 | -0.662769 | -0.703407 | | | | |

Singlet excited state ($S_1$) of **2c**$^-$



$E_{298}$(B3LYP) = -796.20838020 Hartree

$E_{298}$(TD-B3LYP) = -796.10744435 Hartree

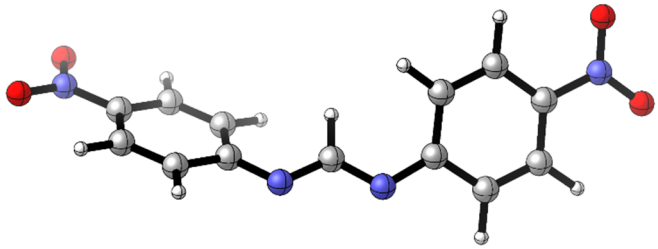
$G_{298}$(B3LYP) = -796.26651320 Hartree

$G_{298}$(TD-B3LYP) = -796.16557735 Hartree

-1 1

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.000001 | -0.637895 | 0.000002 | C | -4.989893 | 0.397989 | 0.064281 |
| H | 0.000001 | 0.454658 | 0.000007 | H | -3.359638 | -2.608422 | 0.063577 |
| N | 1.149814 | -1.326444 | -0.020945 | H | -1.738108 | 1.413756 | 0.012518 |
| N | -1.149813 | -1.326444 | 0.020942 | H | 3.359639 | -2.608422 | -0.063595 |
| C | 2.357074 | -0.698384 | -0.035938 | H | 1.738109 | 1.413756 | -0.012495 |
| C | 3.517207 | -1.534262 | -0.058255 | C | 6.292623 | 0.948101 | -0.076944 |
| C | 2.575628 | 0.727151 | -0.029258 | C | -6.292622 | 0.948101 | 0.076951 |
| C | 4.794486 | -1.016157 | -0.071995 | N | 7.375138 | 1.400747 | -0.088159 |
| C | 3.852216 | 1.248227 | -0.042832 | N | -7.375137 | 1.400747 | 0.087168 |
| C | 4.989895 | 0.397989 | -0.064276 | H | -3.997004 | 2.324199 | 0.036861 |
| C | -2.357073 | -0.698384 | 0.035940 | H | 3.997006 | 2.324198 | -0.036836 |
| C | -2.575626 | 0.727151 | 0.029273 | H | -5.655955 | -1.675306 | 0.088297 |
| C | -3.517206 | -1.534261 | 0.058247 | H | 5.655956 | -1.675306 | -0.088312 |
| C | -3.852214 | 1.248228 | 0.042847 | | | | |
| C | -4.794485 | -1.016157 | 0.071988 | | | | |

Singlet ground state ($S_0$) of **2d**$^-$



$E_{298}$(B3LYP) = -1020.81488623 Hartree

$E_{298}$(TD-B3LYP) = -1020.72768105 Hartree

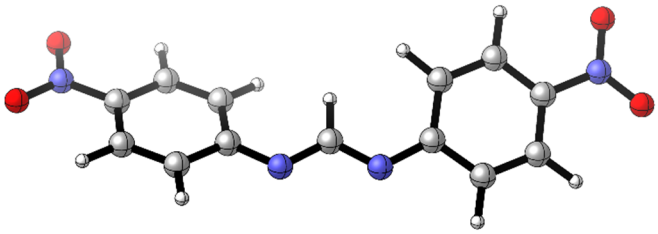
$G_{298}$(B3LYP) = -1020.87972223 Hartree

$G_{298}$(TD-B3LYP) = -1020.79251705 Hartree

-1 1

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.000006 | -1.025977 | -0.000030 | H | 3.345463 | -2.426462 | -1.280991 |
| H | -0.000002 | 0.076281 | 0.000028 | H | 1.676215 | 0.642457 | 1.253128 |
| N | -1.150401 | -1.665612 | 0.154796 | H | -3.345478 | -2.426567 | 1.280797 |
| N | 1.150385 | -1.665605 | -0.154923 | H | -1.676219 | 0.642600 | -1.253015 |
| C | -2.321735 | -0.965894 | 0.068740 | H | 3.854751 | 1.784939 | 1.300468 |
| C | -3.465618 | -1.501300 | 0.727569 | H | -3.854744 | 1.785109 | -1.300219 |
| C | -2.501978 | 0.236519 | -0.680226 | H | 5.547377 | -1.275278 | -1.206436 |
| C | -4.689462 | -0.865995 | 0.688224 | H | -5.547381 | -1.275353 | 1.206382 |
| C | -3.725921 | 0.876395 | -0.725599 | N | 6.087913 | 0.998051 | 0.082375 |
| C | -4.823131 | 0.333673 | -0.035761 | O | 6.190412 | 2.058310 | 0.731770 |
| C | 2.321724 | -0.965906 | -0.068787 | O | 7.053556 | 0.500037 | -0.530409 |
| C | 2.501974 | 0.236427 | 0.680304 | N | -6.087903 | 0.998120 | -0.082187 |
| C | 3.465608 | -1.501254 | -0.727665 | O | -6.190397 | 2.058443 | -0.731478 |
| C | 3.725923 | 0.876287 | 0.725753 | O | -7.053545 | 0.500058 | 0.530561 |
| C | 4.689458 | -0.865966 | -0.688243 | | | | |
| C | 4.823133 | 0.333625 | 0.035868 | | | | |

Stationary point geometry for singlet excited state ($S_1$) of **2d**$^-$



$E_{298}$(B3LYP) = -1020.81310026 Hartree

$E_{298}$(TD-B3LYP) = -1020.72963015 Hartree

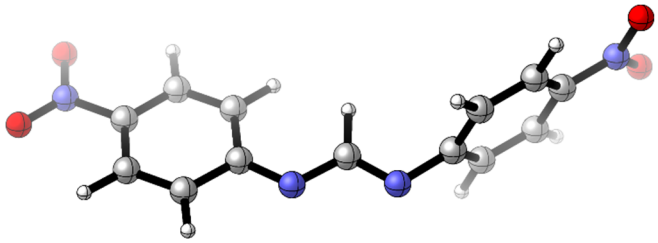
$G_{298}$(B3LYP) = -1020.87681726 Hartree

$G_{298}$(TD-B3LYP) = -1020.79334715 Hartree

-1 1

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.000003 | -0.865657 | 0.000015 | H | -1.715097 | 1.079462 | -0.722313 |
| H | 0.000008 | 0.229940 | -0.000014 | H | 3.349376 | -2.666885 | -0.678548 |
| N | 1.145177 | -1.539045 | -0.054856 | H | 1.715114 | 1.079433 | 0.722410 |
| N | -1.145182 | -1.539037 | 0.054921 | H | -3.965973 | 2.062887 | -0.706064 |
| C | 2.349743 | -0.877174 | -0.018525 | H | 3.965988 | 2.062869 | 0.706111 |
| C | 3.496876 | -1.632780 | -0.386320 | H | -5.630175 | -1.654605 | 0.683342 |
| C | 2.549820 | 0.477016 | 0.384649 | H | 5.630159 | -1.654591 | -0.683413 |
| C | 4.763326 | -1.075968 | -0.392705 | N | -6.227587 | 0.854803 | 0.002896 |
| C | 3.814204 | 1.038583 | 0.390998 | O | -6.351246 | 2.060013 | -0.340309 |
| C | 4.923411 | 0.268257 | -0.006151 | O | -7.210421 | 0.145618 | 0.343013 |
| C | -2.349740 | -0.877167 | 0.018562 | N | 6.227585 | 0.854806 | -0.002943 |
| C | -2.549811 | 0.477033 | -0.384592 | O | 6.351251 | 2.060014 | 0.340282 |
| C | -3.496885 | -1.632782 | 0.386313 | O | 7.210413 | 0.145628 | -0.343100 |
| C | -3.814195 | 1.038595 | -0.390967 | | | | |
| C | -4.763335 | -1.075975 | 0.392668 | | | | |
| C | -4.923411 | 0.268257 | 0.006133 | | | | |
| H | -3.349390 | -2.666892 | 0.678529 | | | | |

Local minimum for singlet excited state ($S_1$) of **2d**$^-$



$E_{298}$(B3LYP) = -1020.79940902 Hartree

$E_{298}$(TD-B3LYP) = -1020.74396349 Hartree

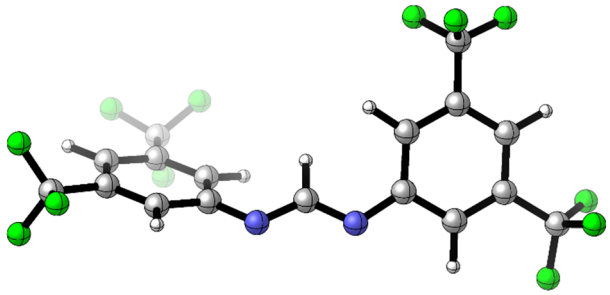
$G_{298}$(B3LYP) = -1020.85677502 Hartree

$G_{298}$(TD-B3LYP) = -1020.80132949 Hartree

-1 1

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.053053 | -0.127528 | -0.906171 | H | -3.413915 | 0.065715 | -2.656634 |
| H | 0.127514 | 0.014926 | 0.178277 | H | 2.396947 | -2.385637 | -0.594091 |
| N | 1.117385 | -0.272461 | -1.622420 | H | 2.604746 | 1.877461 | -1.060762 |
| N | -1.165300 | -0.131654 | -1.529309 | H | -5.655399 | 0.179252 | -1.552552 |
| C | 2.350056 | -0.253867 | -0.891257 | H | 4.777865 | 1.903215 | 0.154836 |
| C | 2.915093 | -1.446733 | -0.424161 | H | -3.760315 | -0.146709 | 2.299113 |
| C | 3.031644 | 0.952049 | -0.686241 | H | 4.572296 | -2.357862 | 0.617989 |
| C | 4.134130 | -1.438368 | 0.252527 | N | -6.113056 | 0.092629 | 1.075226 |
| C | 4.250353 | 0.972795 | -0.009367 | O | -7.116972 | 0.190381 | 0.359634 |
| C | 4.812650 | -0.224967 | 0.468571 | O | -6.153100 | 0.045902 | 2.310431 |
| C | -2.305158 | -0.085563 | -0.810788 | N | 6.044961 | -0.209365 | 1.152680 |
| C | -3.509612 | 0.025076 | -1.578240 | O | 6.643756 | 0.922832 | 1.347828 |
| C | -2.423888 | -0.151525 | 0.618790 | O | 6.551591 | -1.327341 | 1.567316 |
| C | -4.746447 | 0.088406 | -0.973272 | | | | |
| C | -3.661858 | -0.093974 | 1.222964 | | | | |
| C | -4.811312 | 0.029717 | 0.426429 | | | | |
| H | -1.547703 | -0.262151 | 1.242678 | | | | |

Singlet ground state ($S_0$) of **2e**$^-$



$E_{298}$(B3LYP) = -1960.27638370 Hartree

$E_{298}$(TD-B3LYP) = -1960.15629633 Hartree

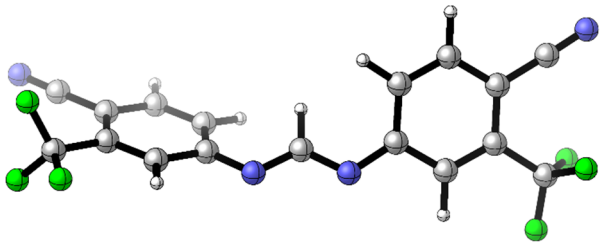
$G_{298}$(B3LYP) = -1960.37011370 Hartree

$G_{298}$(TD-B3LYP) = -1960.25002633 Hartree

-1 1

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.000119 | 1.245267 | -0.000591 | C | -3.795014 | -1.900433 | 1.729837 |
| H | 0.000005 | 0.139422 | 0.000056 | C | -5.893286 | 1.456765 | -1.320437 |
| N | -1.157842 | 1.874506 | -0.129992 | C | 5.893609 | 1.457251 | 1.318821 |
| N | 1.158209 | 1.874421 | 0.128074 | C | 3.794479 | -1.903354 | -1.727189 |
| C | -2.318336 | 1.142381 | -0.014445 | F | -6.596573 | 0.473039 | -1.947609 |
| C | -3.472350 | 1.608505 | -0.694169 | F | -5.601240 | 2.387181 | -2.261249 |
| C | -2.468201 | -0.021189 | 0.779210 | F | -6.772500 | 2.047687 | -0.456967 |
| C | -4.679496 | 0.926914 | -0.613697 | F | -4.920960 | -2.625149 | 1.511571 |
| C | -3.690820 | -0.693940 | 0.841389 | F | -3.806262 | -1.564515 | 3.053644 |
| C | -4.813605 | -0.240612 | 0.151484 | F | -2.745744 | -2.753300 | 1.572888 |
| C | 2.318552 | 1.141924 | 0.013369 | F | 2.745774 | -2.756506 | -1.567890 |
| C | 2.468174 | -0.022624 | -0.778894 | F | 4.920994 | -2.627245 | -1.509169 |
| C | 3.472679 | 1.608637 | 0.692499 | F | 3.804073 | -1.569261 | -3.051463 |
| C | 3.690664 | -0.695688 | -0.840294 | F | 6.772579 | 2.047501 | 0.454639 |
| C | 4.679690 | 0.926715 | 0.612818 | F | 5.601713 | 2.388463 | 2.258897 |
| C | 4.813552 | -0.241761 | -0.150958 | F | 6.597110 | 0.474121 | 1.946674 |
| H | 3.384017 | 2.508877 | 1.288966 | H | 5.757464 | -0.767591 | -0.209092 |
| H | 1.632291 | -0.384119 | -1.366411 | H | -5.757624 | -0.766188 | 0.210226 |
| H | -3.383496 | 2.508007 | -1.291720 | | | | |
| H | -1.632396 | -0.382149 | 1.367162 | | | | |

Singlet ground state ($S_0$) of **2f**$^-$



$E_{298}$(B3LYP) = -1470.51814305 Hartree

$E_{298}$(TD-B3LYP) = -1470.41076136 Hartree

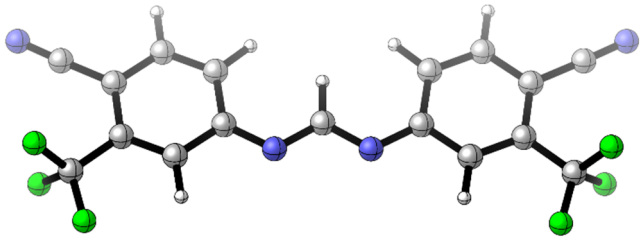
$G_{298}$(B3LYP) = -1470.59770905 Hartree

$G_{298}$(TD-B3LYP) = -1470.49032736 Hartree

-1 1

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.000028 | -0.424459 | -0.000093 | H | -3.487862 | -1.768084 | 0.842052 |
| H | -0.000041 | 0.679369 | -0.000060 | H | -1.484671 | 1.220927 | -1.522778 |
| N | -1.162250 | -1.059950 | -0.003945 | C | -5.995299 | -0.790472 | 0.624891 |
| N | 1.162209 | -1.059923 | 0.003722 | C | 5.995252 | -0.790330 | -0.625092 |
| C | -2.304131 | -0.348931 | -0.260439 | C | -6.000966 | 1.675175 | -0.981550 |
| C | -3.526897 | -0.857798 | 0.256936 | C | 6.000877 | 1.675233 | 0.981477 |
| C | -2.378467 | 0.829746 | -1.050628 | N | -6.976701 | 2.272730 | -1.209064 |
| C | -4.732145 | -0.217030 | 0.041544 | N | 6.976602 | 2.272792 | 1.209024 |
| C | -3.586484 | 1.473962 | -1.265261 | F | -6.612694 | 0.084513 | 1.466653 |
| C | -4.787104 | 0.976099 | -0.724865 | F | -5.782331 | -1.923093 | 1.333626 |
| C | 2.304075 | -0.348896 | 0.260255 | F | -6.908661 | -1.099652 | -0.336836 |
| C | 2.378391 | 0.829742 | 1.050506 | F | 6.908618 | -1.099545 | 0.336621 |
| C | 3.526851 | -0.857715 | -0.257145 | F | 5.782303 | -1.922919 | -1.333885 |
| C | 3.586397 | 1.473967 | 1.265174 | F | 6.612635 | 0.084708 | -1.466807 |
| C | 4.732088 | -0.216938 | -0.041718 | H | 3.618978 | 2.371856 | 1.873328 |
| C | 4.787026 | 0.976152 | 0.724755 | H | -3.619081 | 2.371883 | -1.873367 |
| H | 3.487832 | -1.767971 | -0.842309 | | | | |
| H | 1.484587 | 1.220883 | 1.522674 | | | | |

Singlet Excited state ($S_1$) of **2f**$^-$



$E_{298}$(B3LYP) = -1470.51468198 Hartree

$E_{298}$(TD-B3LYP) = -1470.41842354 Hartree

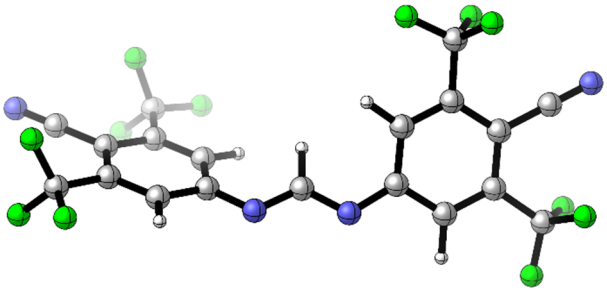
$G_{298}$(B3LYP) = -1470.59113798 Hartree

$G_{298}$(TD-B3LYP) = -1470.49487954 Hartree

-1 1

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.000000 | -0.037099 | -0.000005 | H | -1.726188 | 2.026675 | -0.109498 |
| H | 0.000000 | 1.055220 | -0.000001 | C | -5.960284 | -1.324519 | -0.194677 |
| N | -1.145986 | -0.724249 | -0.045485 | C | 5.960285 | -1.324515 | 0.194679 |
| N | 1.145987 | -0.724249 | 0.045473 | C | -6.263332 | 1.614976 | -0.256610 |
| C | -2.350013 | -0.084599 | -0.095834 | C | 6.263330 | 1.614980 | 0.256618 |
| C | -3.500619 | -0.917808 | -0.122028 | N | -7.309333 | 2.139975 | -0.303372 |
| C | -2.561850 | 1.338764 | -0.124784 | N | 7.309329 | 2.139982 | 0.303385 |
| C | -4.782309 | -0.402734 | -0.171634 | F | -6.804156 | -1.117142 | 0.859638 |
| C | -3.839191 | 1.855385 | -0.176850 | F | -5.610131 | -2.632335 | -0.154822 |
| C | -4.981440 | 1.017635 | -0.201676 | F | -6.726222 | -1.162694 | -1.314477 |
| C | 2.350013 | -0.084598 | 0.095826 | F | 6.726218 | -1.162691 | 1.314482 |
| C | 2.561848 | 1.338766 | 0.124778 | F | 5.610132 | -2.632332 | 0.154821 |
| C | 3.500620 | -0.917806 | 0.122022 | F | 6.804160 | -1.117137 | -0.859632 |
| C | 3.839189 | 1.855387 | 0.176850 | H | 3.985754 | 2.930247 | 0.200150 |
| C | 4.782309 | -0.402731 | 0.171633 | H | -3.985757 | 2.930245 | -0.200147 |
| C | 4.981439 | 1.017638 | 0.201679 | | | | |
| H | 3.342544 | -1.989125 | 0.099982 | | | | |
| H | 1.726186 | 2.026676 | 0.109491 | | | | |
| H | -3.341543 | -1.989127 | -0.099990 | | | | |

Singlet ground state ($S_0$) of **2g**$^-$



$E_{298}$(B3LYP) = -2144.81847078 Hartree

$E_{298}$(TD-B3LYP) = -2144.71389236 Hartree

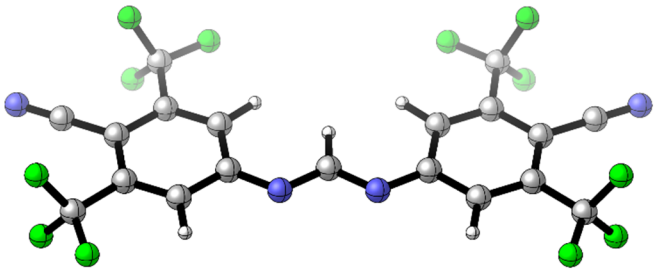
$G_{298}$(B3LYP) = -2144.91645578 Hartree

$G_{298}$(TD-B3LYP) = -2144.81187736 Hartree

-1 1

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.000022 | -1.159376 | 0.000040 | C | 5.946486 | -1.606689 | -0.964767 |
| H | 0.000015 | -0.056160 | 0.000016 | C | -5.946436 | -1.606713 | 0.964870 |
| N | 1.157364 | -1.799430 | -0.070312 | C | -3.746897 | 1.994336 | -1.825237 |
| N | -1.157312 | -1.799441 | 0.070420 | C | 6.099776 | 0.864254 | 0.556290 |
| C | 2.317820 | -1.101613 | 0.105793 | C | -6.099754 | 0.864162 | -0.556295 |
| C | 3.503906 | -1.633206 | -0.462075 | N | 7.127765 | 1.400263 | 0.671702 |
| C | 2.447211 | 0.091199 | 0.867828 | N | -7.127748 | 1.400157 | -0.671731 |
| C | 4.723316 | -0.999435 | -0.322247 | F | 6.518153 | -0.764119 | -1.865648 |
| C | 3.669239 | 0.727953 | 1.005632 | F | 5.671320 | -2.753445 | -1.625501 |
| C | 4.842994 | 0.208158 | 0.411587 | F | 6.906653 | -1.903639 | -0.049451 |
| C | -2.317777 | -1.101645 | -0.105714 | F | 4.187985 | 3.047713 | 1.088164 |
| C | -2.447181 | 0.091133 | -0.867802 | F | 4.600248 | 1.871036 | 2.875322 |
| C | -3.503856 | -1.633225 | 0.462177 | F | 2.548732 | 2.354673 | 2.338786 |
| C | -3.669217 | 0.727867 | -1.005634 | F | -2.548730 | 2.354537 | -2.338864 |
| C | -4.723274 | -0.999475 | 0.322323 | F | -4.187982 | 3.047620 | -1.088264 |
| C | -4.842966 | 0.208085 | -0.411565 | F | -4.600245 | 1.870861 | -2.875369 |
| H | -3.427517 | -2.555003 | 1.024429 | F | -6.906603 | -1.903712 | 0.049569 |
| H | -1.584955 | 0.499483 | -1.377116 | F | -5.671258 | -2.753439 | 1.625652 |
| H | 3.427577 | -2.555008 | -1.024287 | F | -6.518109 | -0.764111 | 1.865716 |
| H | 1.584979 | 0.499562 | 1.377123 | | | | |
| C | 3.746905 | 1.994458 | 1.825181 | | | | |

Singlet excited state ($S_1$) of **2g**$^-$



$E_{298}$(B3LYP) = -2144.81515281 Hartree

$E_{298}$(TD-B3LYP) = -2144.71922541 Hartree

$G_{298}$(B3LYP) = -2144.91128581 Hartree

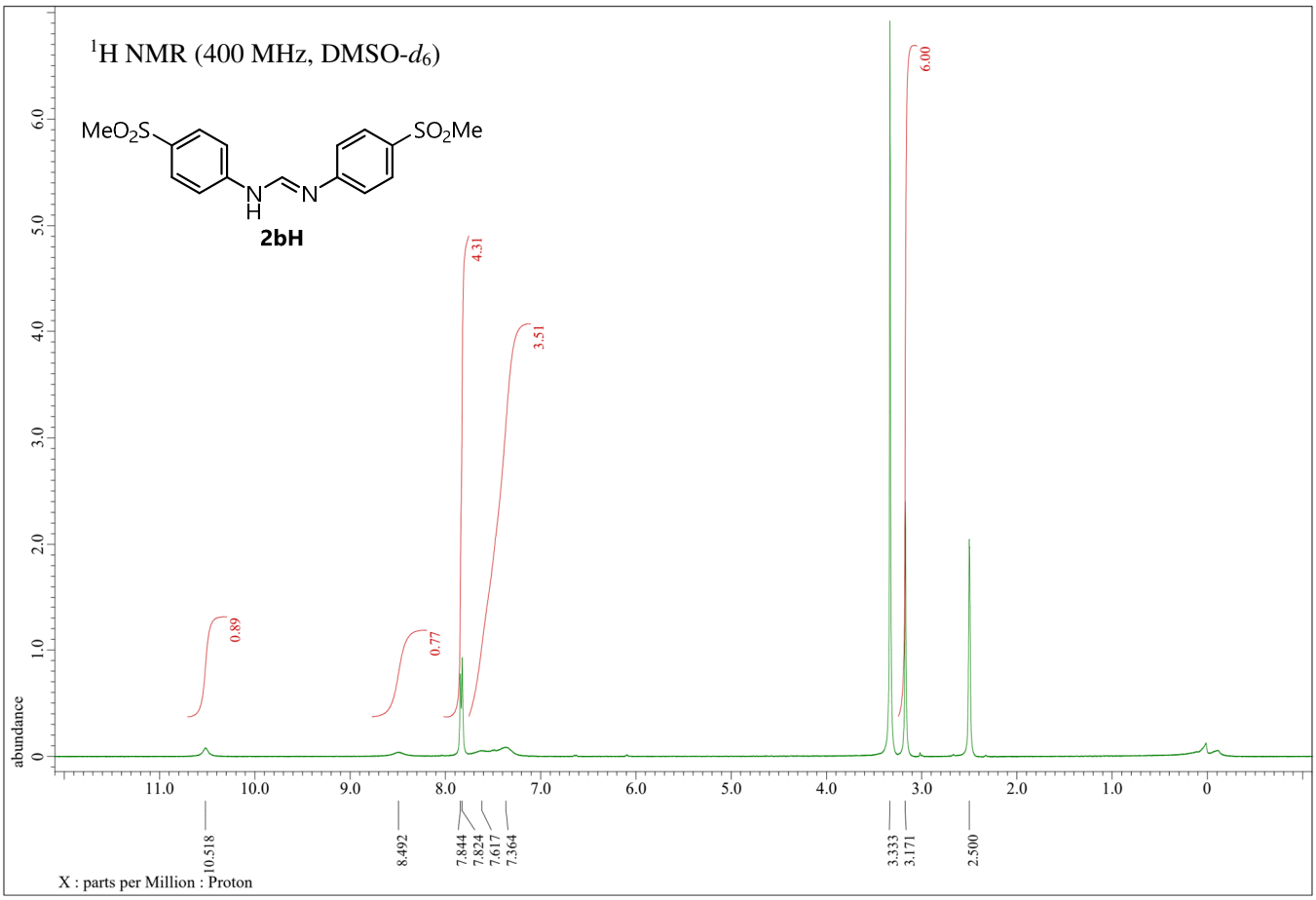
$G_{298}$(TD-B3LYP) = -2144.81535841 Hartree

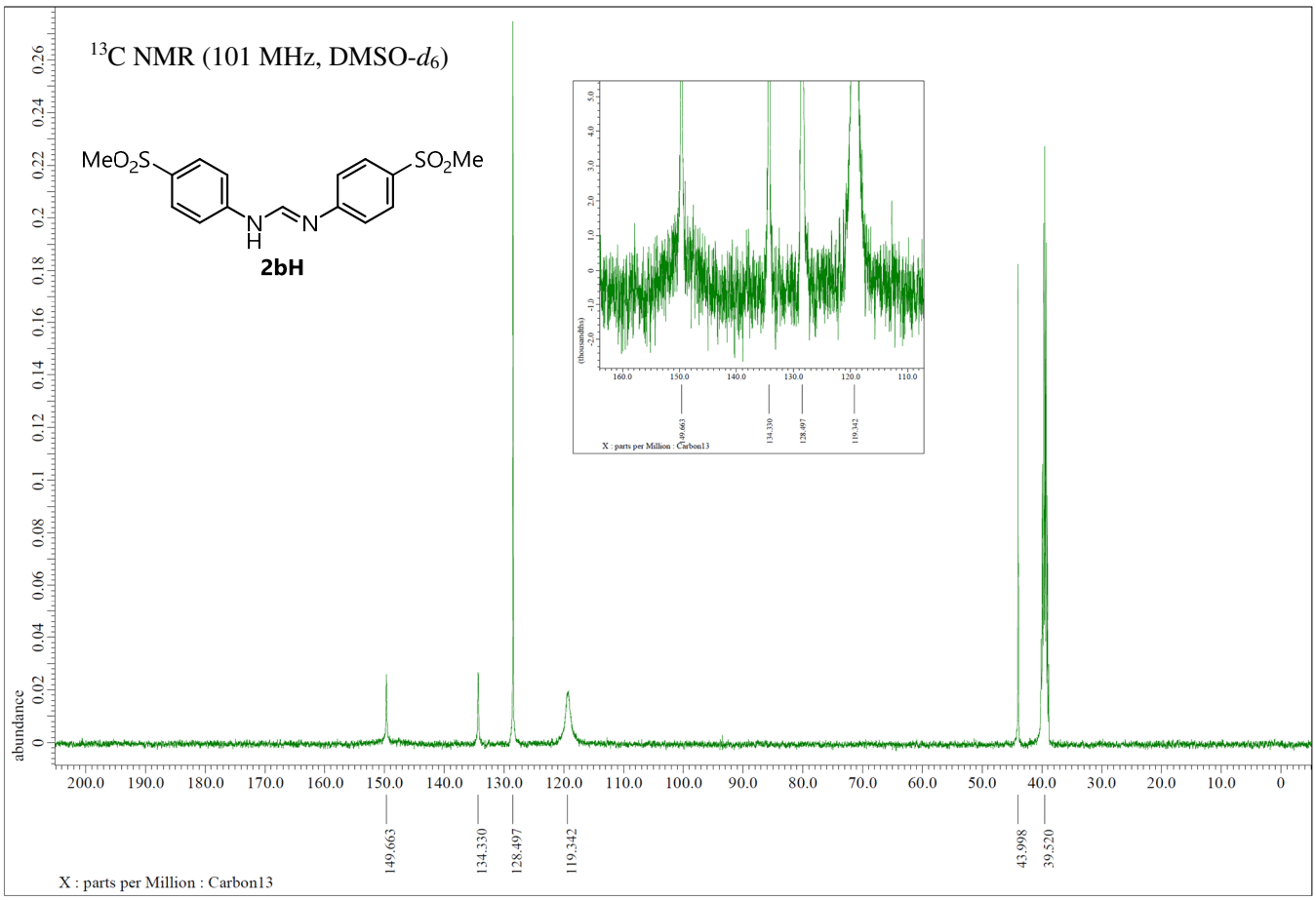
-1 1

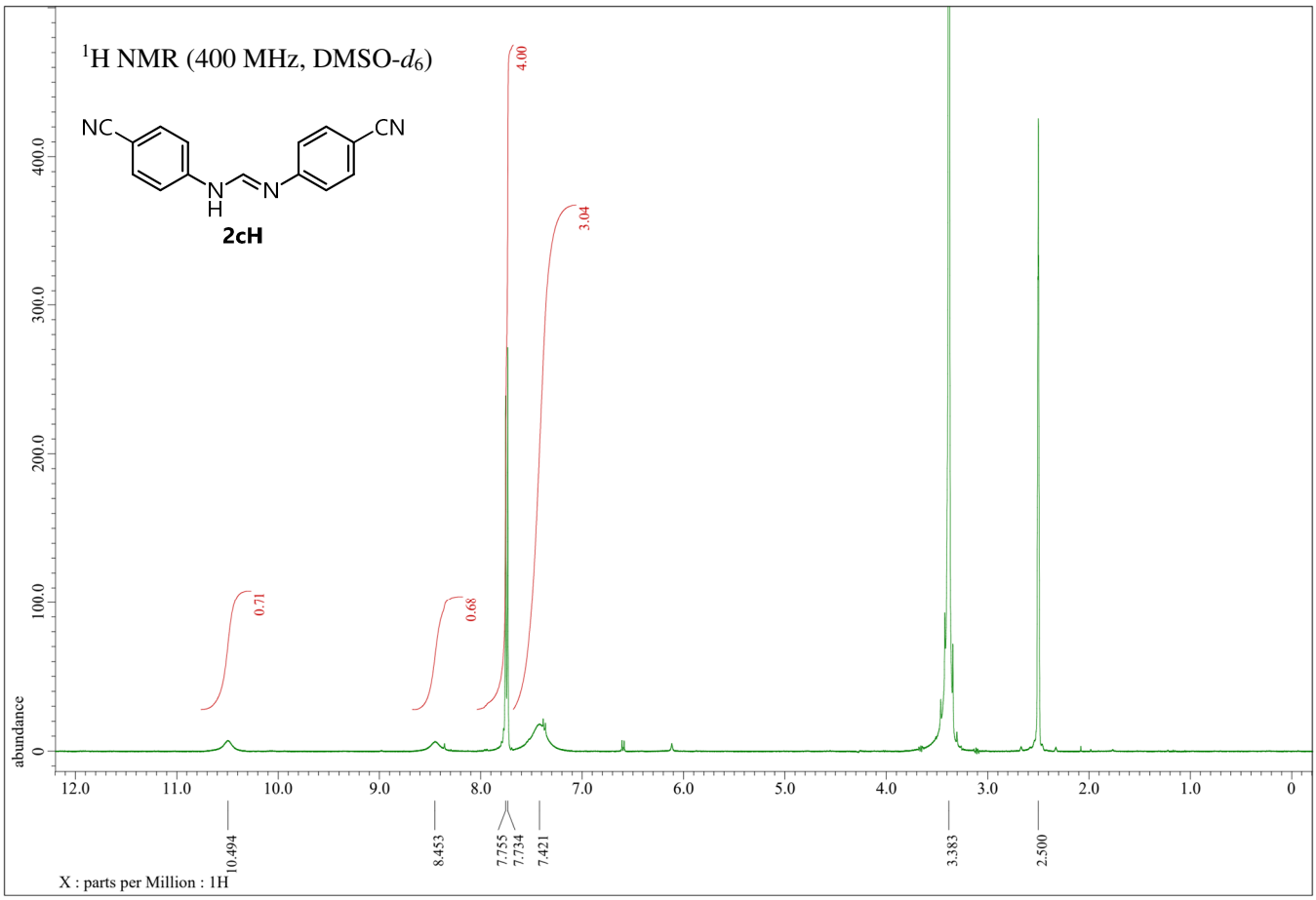
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.000000 | 0.873730 | -0.000031 | C | 5.009969 | -0.136340 | -0.004020 |
| H | 0.000000 | -0.219516 | 0.000049 | H | 3.331059 | 2.855079 | -0.003861 |
| N | -1.143600 | 1.563270 | 0.000874 | H | 1.754079 | -1.166745 | 0.000934 |
| N | 1.143599 | 1.563270 | -0.001015 | H | -3.331059 | 2.855079 | 0.003778 |
| C | -2.356101 | 0.940498 | 0.001588 | H | -1.754079 | -1.166745 | -0.001095 |
| C | -3.498756 | 1.785236 | 0.003343 | C | -4.054510 | -2.482686 | 0.001310 |
| C | -2.584297 | -0.475145 | 0.000648 | C | -5.950432 | 2.221704 | 0.006454 |
| C | -4.781876 | 1.279180 | 0.004549 | C | 5.950432 | 2.221705 | -0.006394 |
| C | -3.864497 | -0.986048 | 0.001830 | C | 4.054510 | -2.482686 | -0.001324 |
| C | -5.009969 | -0.136340 | 0.004057 | C | -6.321066 | -0.668640 | 0.005812 |
| C | 2.356101 | 0.940498 | -0.001689 | C | 6.321066 | -0.668640 | -0.005682 |
| C | 2.584297 | -0.475145 | -0.000746 | N | -7.407726 | -1.102390 | 0.007327 |
| C | 3.498756 | 1.785236 | -0.003406 | N | 7.407726 | -1.102390 | -0.007118 |
| C | 3.864498 | -0.986048 | -0.001861 | F | -6.753205 | 2.049064 | -1.081178 |
| C | 4.781876 | 1.279180 | -0.004541 | F | -5.572917 | 3.521288 | 0.006205 |

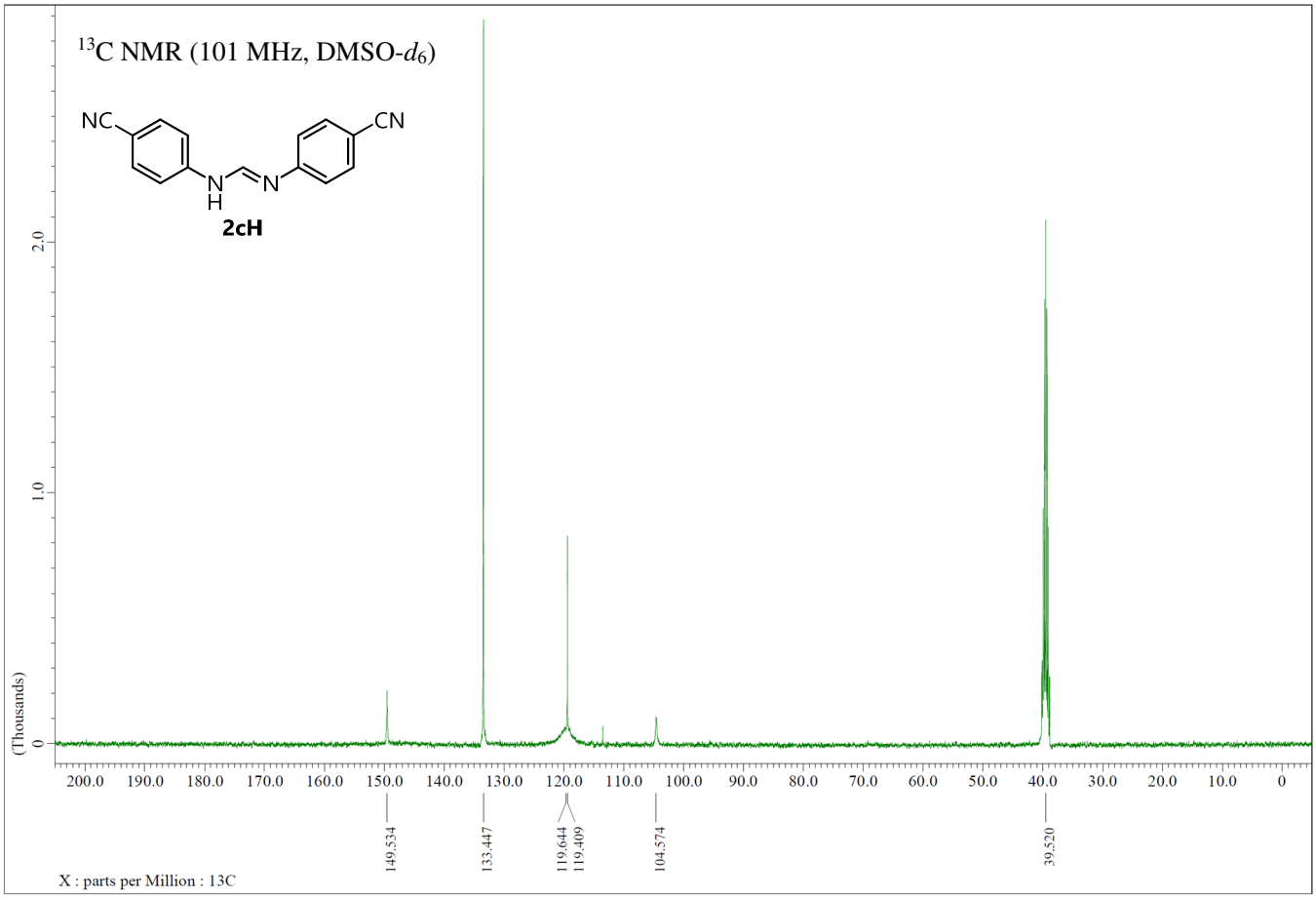
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| F | -6.750045 | 2.048566 | 1.096341 | F | 4.743712 | -2.908849 | -1.092891 |
| F | -4.751792 | -2.907283 | -1.085663 | F | 6.750122 | 2.048532 | -1.096219 |
| F | -4.743550 | -2.908852 | 1.092979 | F | 5.572916 | 3.521289 | -0.006213 |
| F | -2.880914 | -3.156993 | -0.003600 | F | 6.753128 | 2.049099 | 1.081300 |
| F | 2.880914 | -3.156993 | 0.003412 | | | | |
| F | 4.751632 | -2.907285 | 1.085752 | | | | |

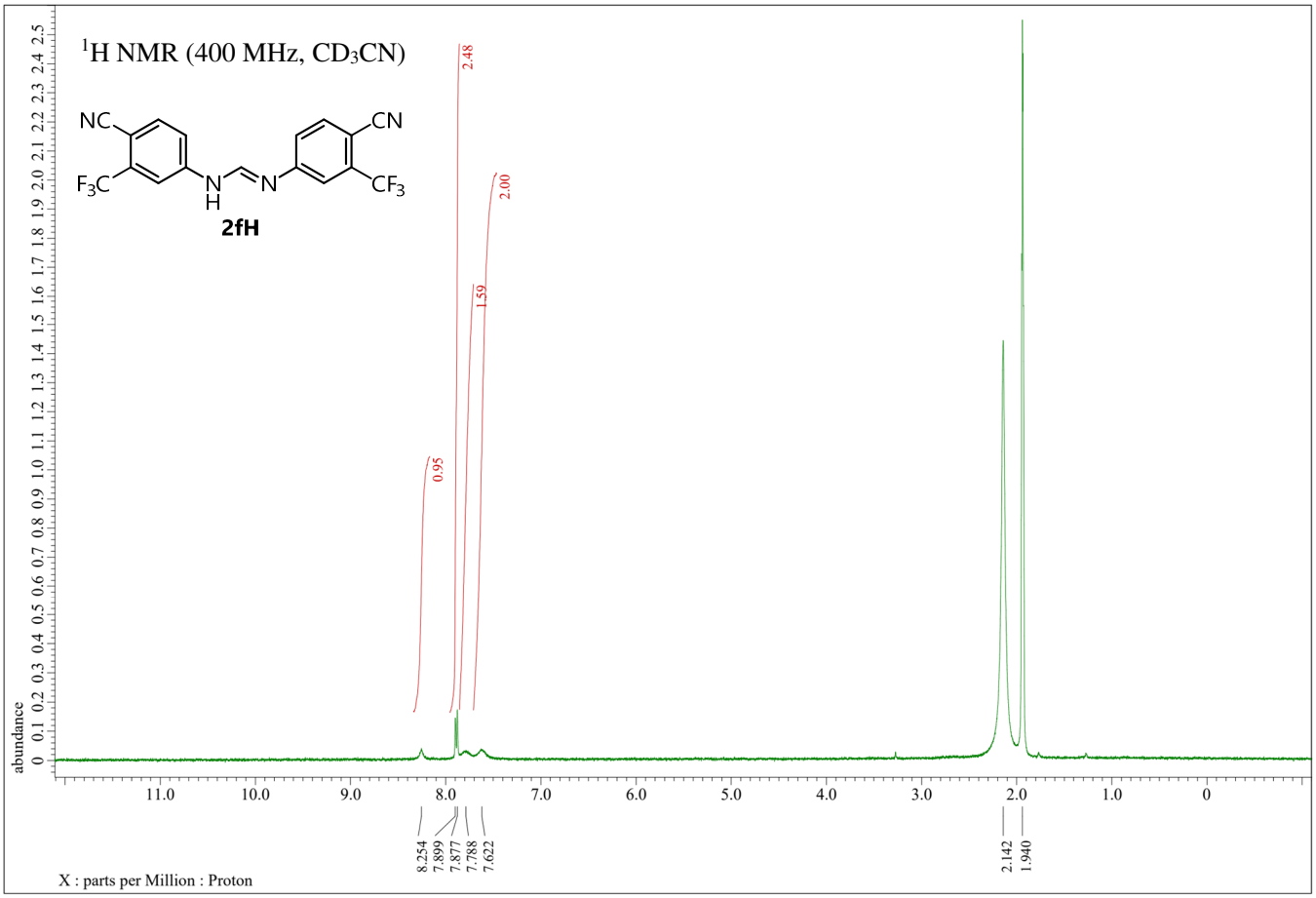
## (K) Copies of NMR Spectra

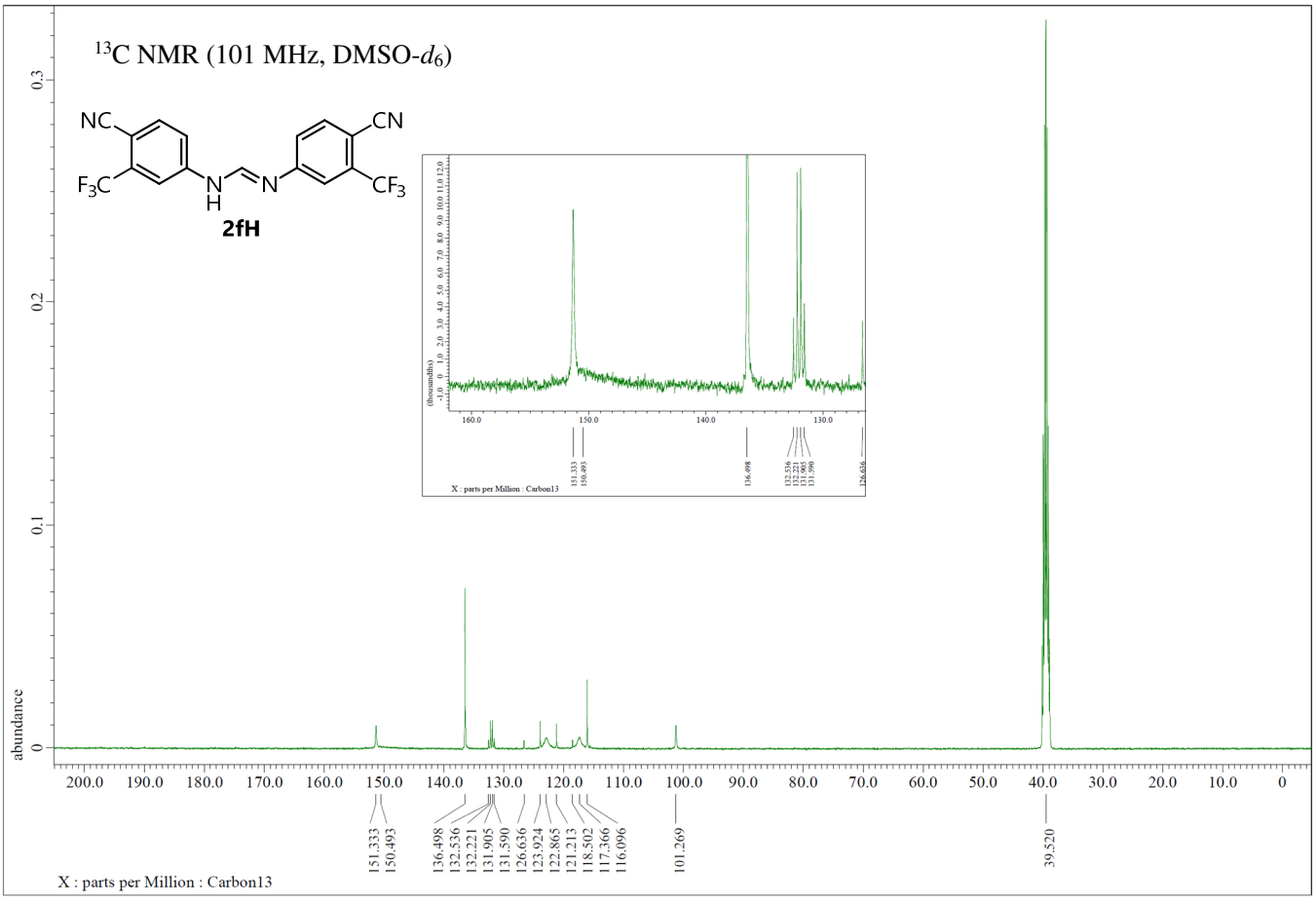


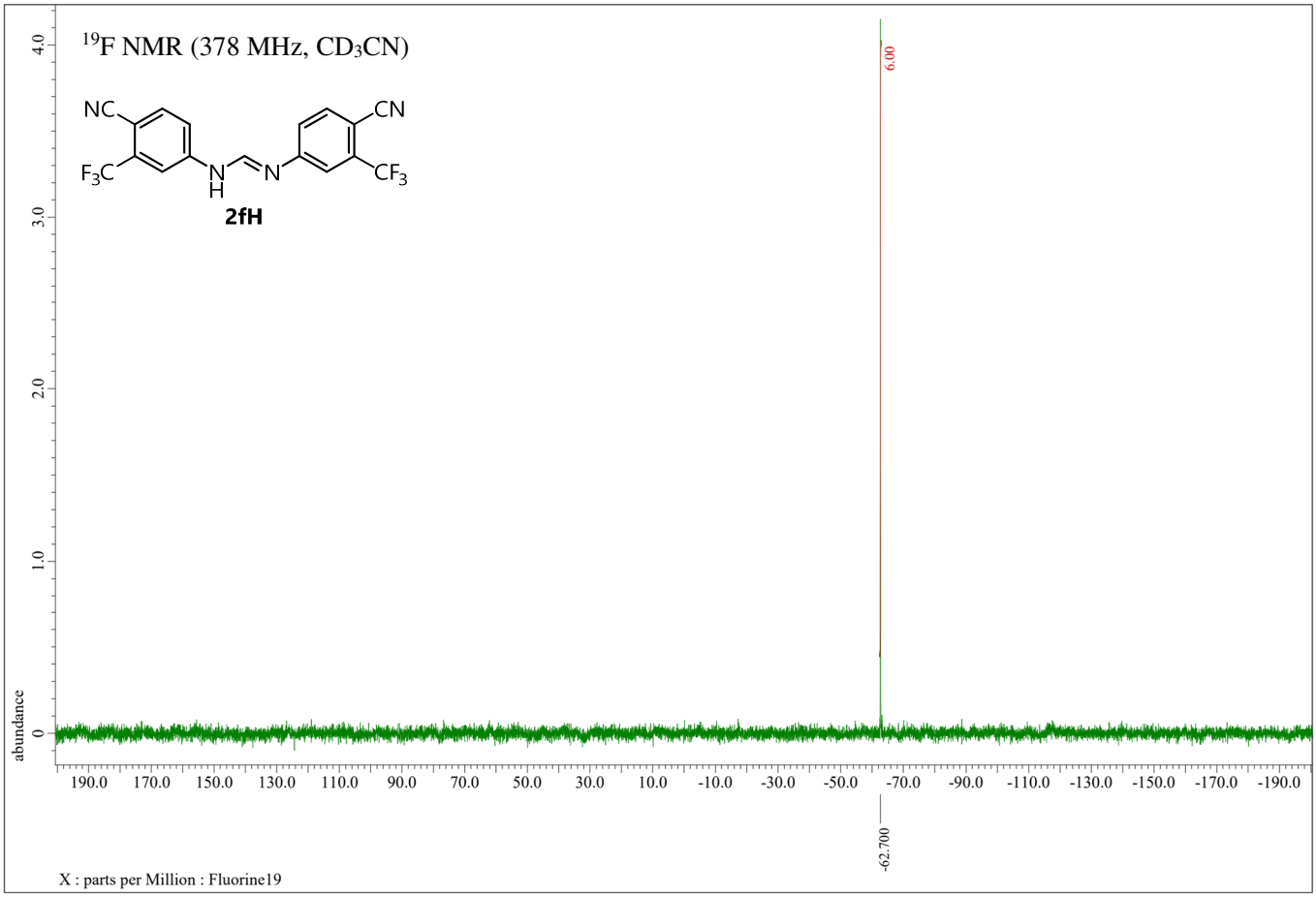



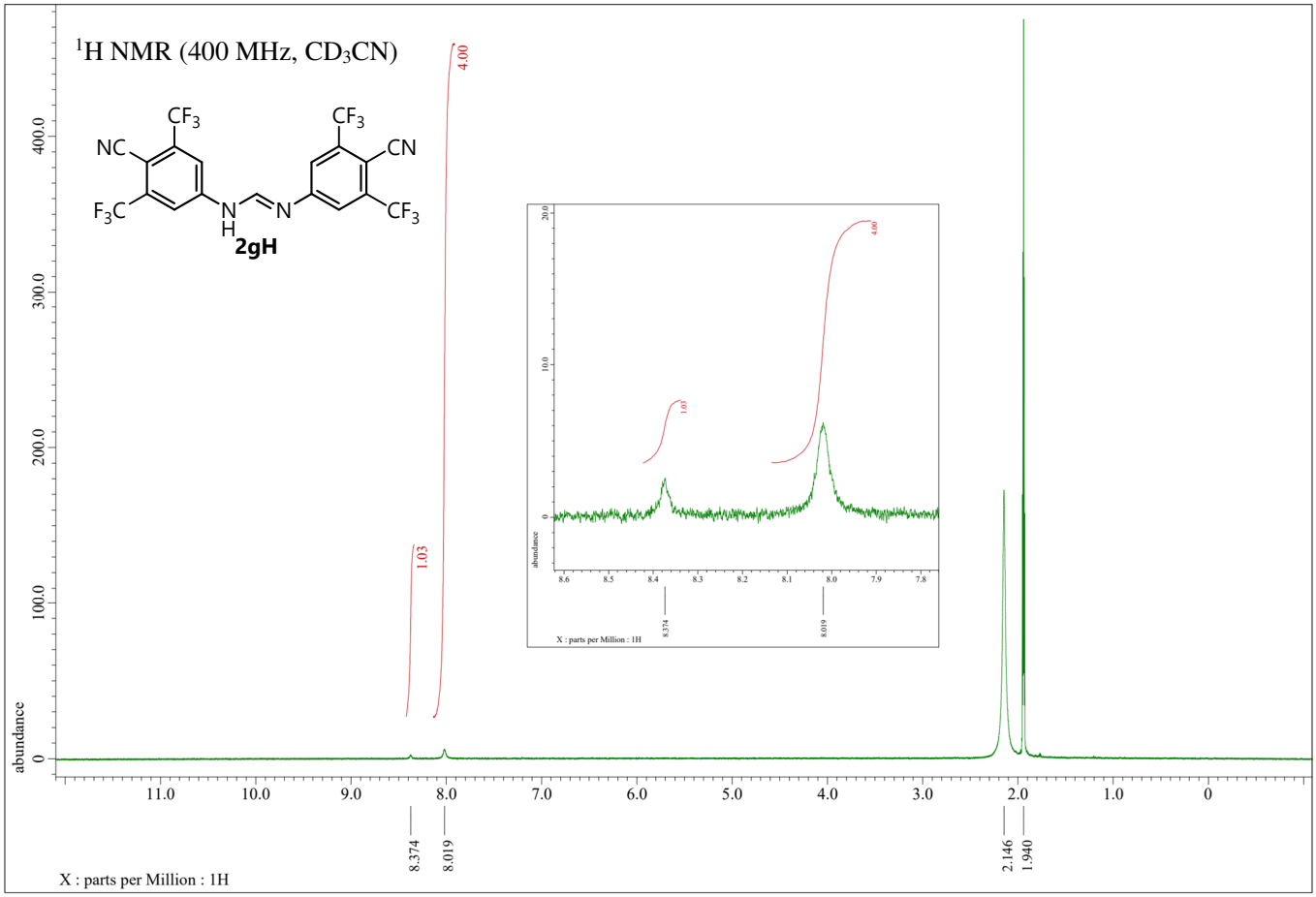

$^{1}$H NMR (400 MHz, DMSO-$d_6$)
NC
CN
N
H
N
2cH
4.00
3.04
0.71
0.68
abundance
400.0
300.0
200.0
100.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.494
8.453
7.755
7.734
7.421
3.383
2.500
X : parts per Million : 1H

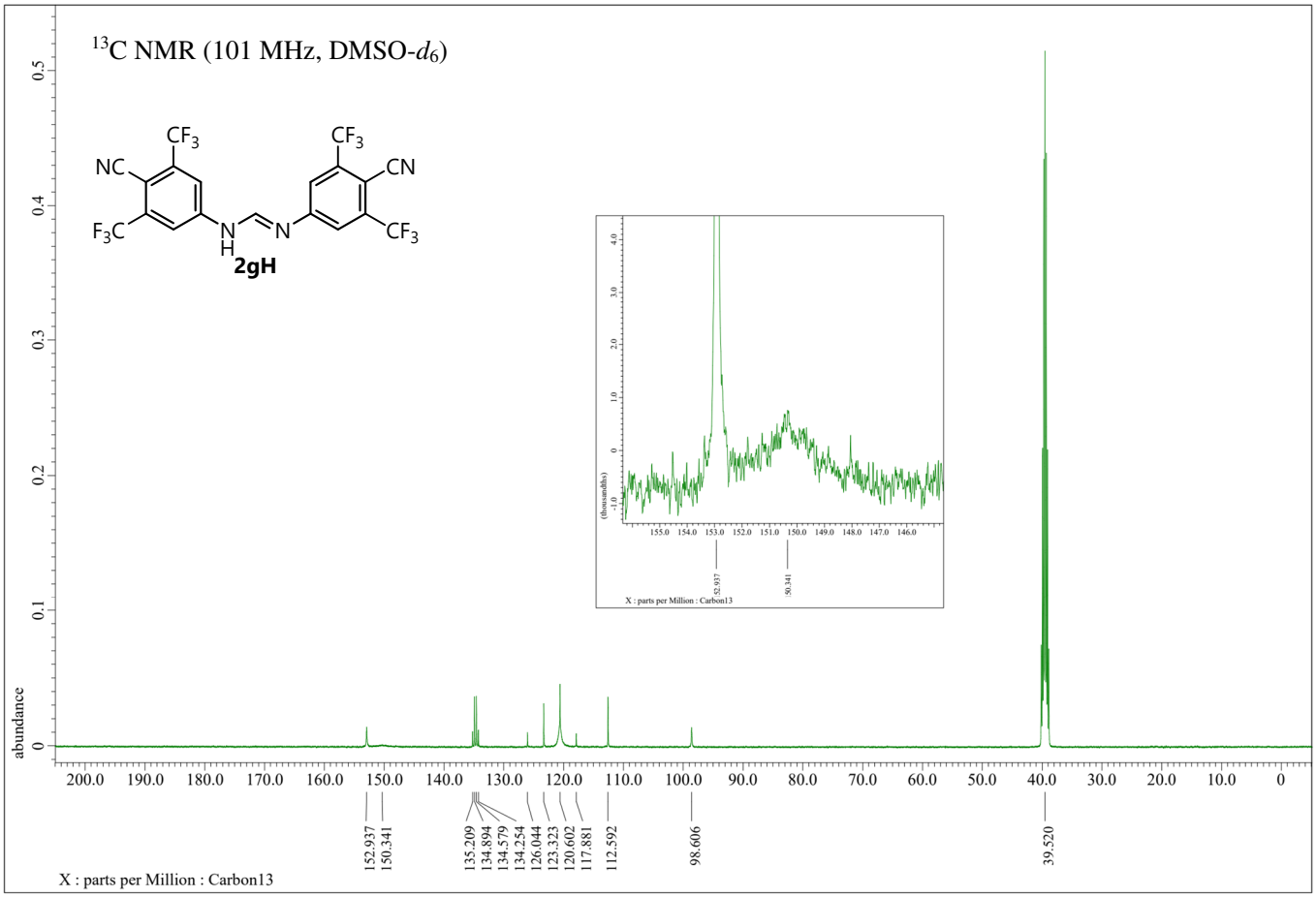

$^{13}$C NMR (101 MHz, DMSO-$d_6$)
NC
CN
N
H
N
2cH
(Thousands)
2.0
1.0
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
149.534
133.447
119.644
119.409
104.574
39.520
X : parts per Million : 13C

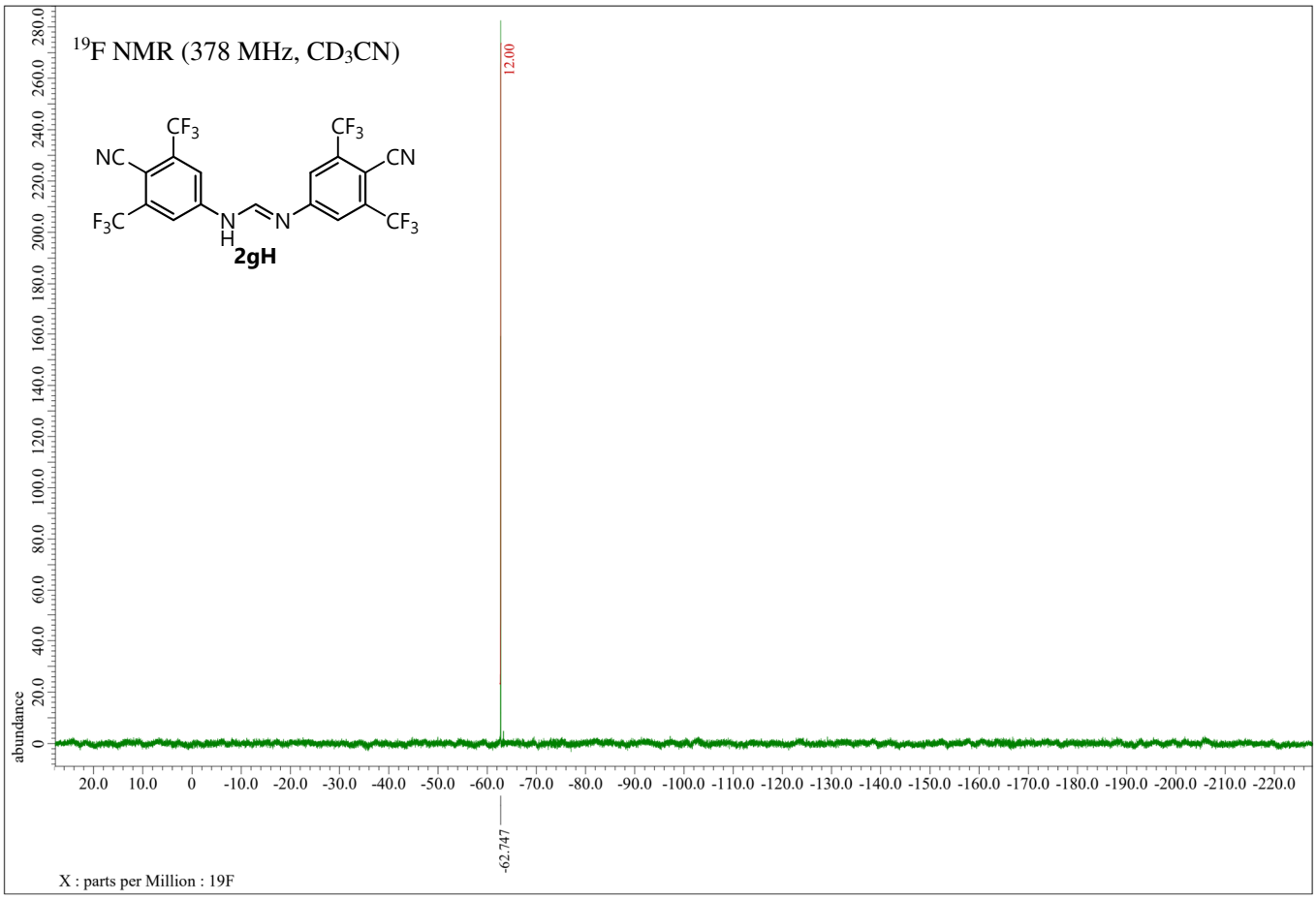

$^1$H NMR (400 MHz, $CD_3CN$)
NC
CN
$F_3C$
$CF_3$
N
H
N
2fH
2.48
2.00
1.59
0.95
abundance
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.254
7.899
7.877
7.788
7.622
2.142
1.940
X : parts per Million : Proton

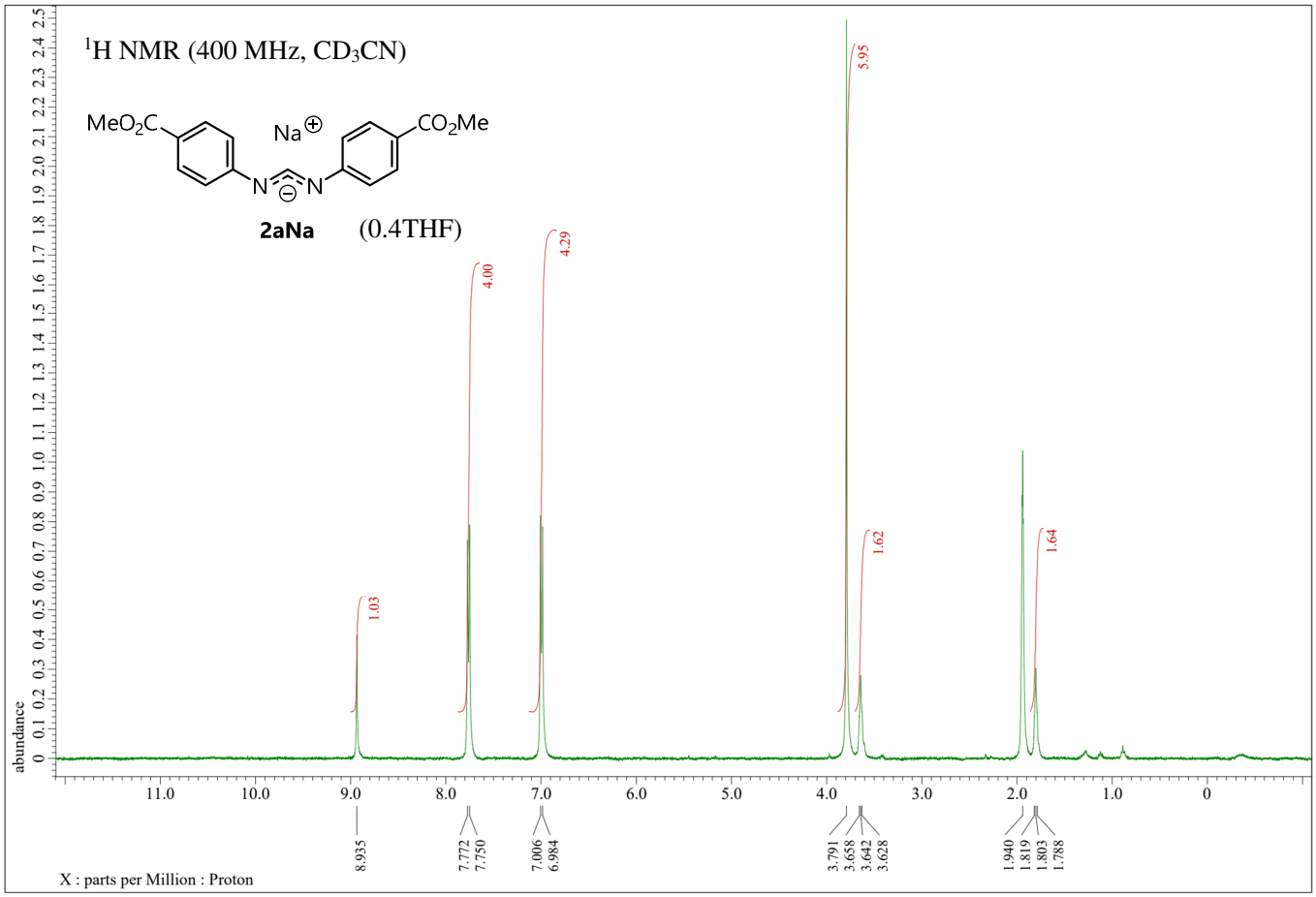

$^{13}$C NMR (101 MHz, DMSO-$d_6$)
NC
CN
$F_3C$
$CF_3$
N
H
N
2fH
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
151.333
150.493
136.498
132.536
132.221
131.905
131.590
126.636
123.924
122.865
121.213
118.502
117.366
116.096
101.269
39.520
X : parts per Million : Carbon13

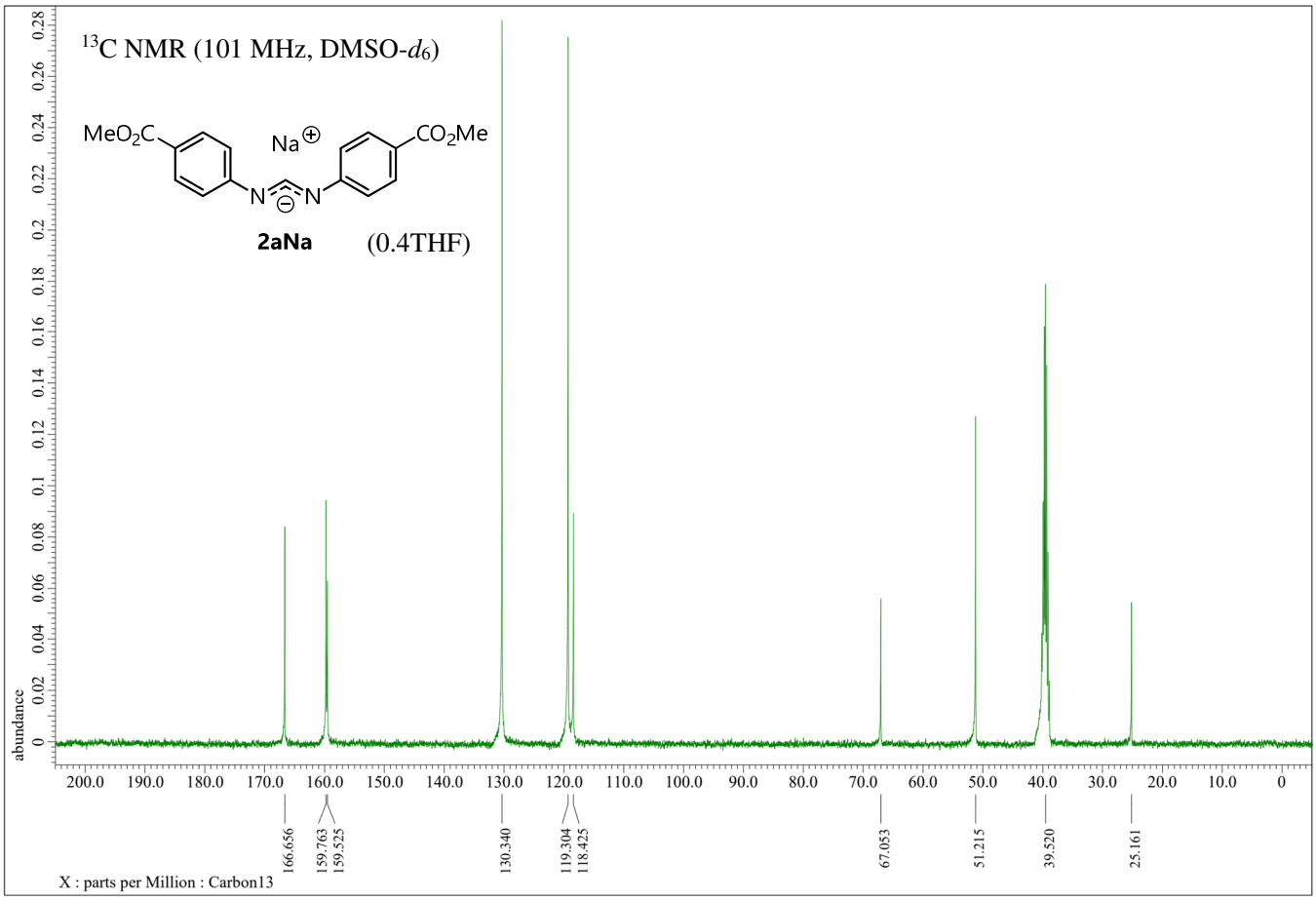

19F NMR (378 MHz, CD3CN)
NC
CN
F3C
CF3
N
H
N
2fH
6.00
abundance
4.0
3.0
2.0
1.0
0
190.0 170.0 150.0 130.0 110.0 90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0
-62.700
X : parts per Million : Fluorine19

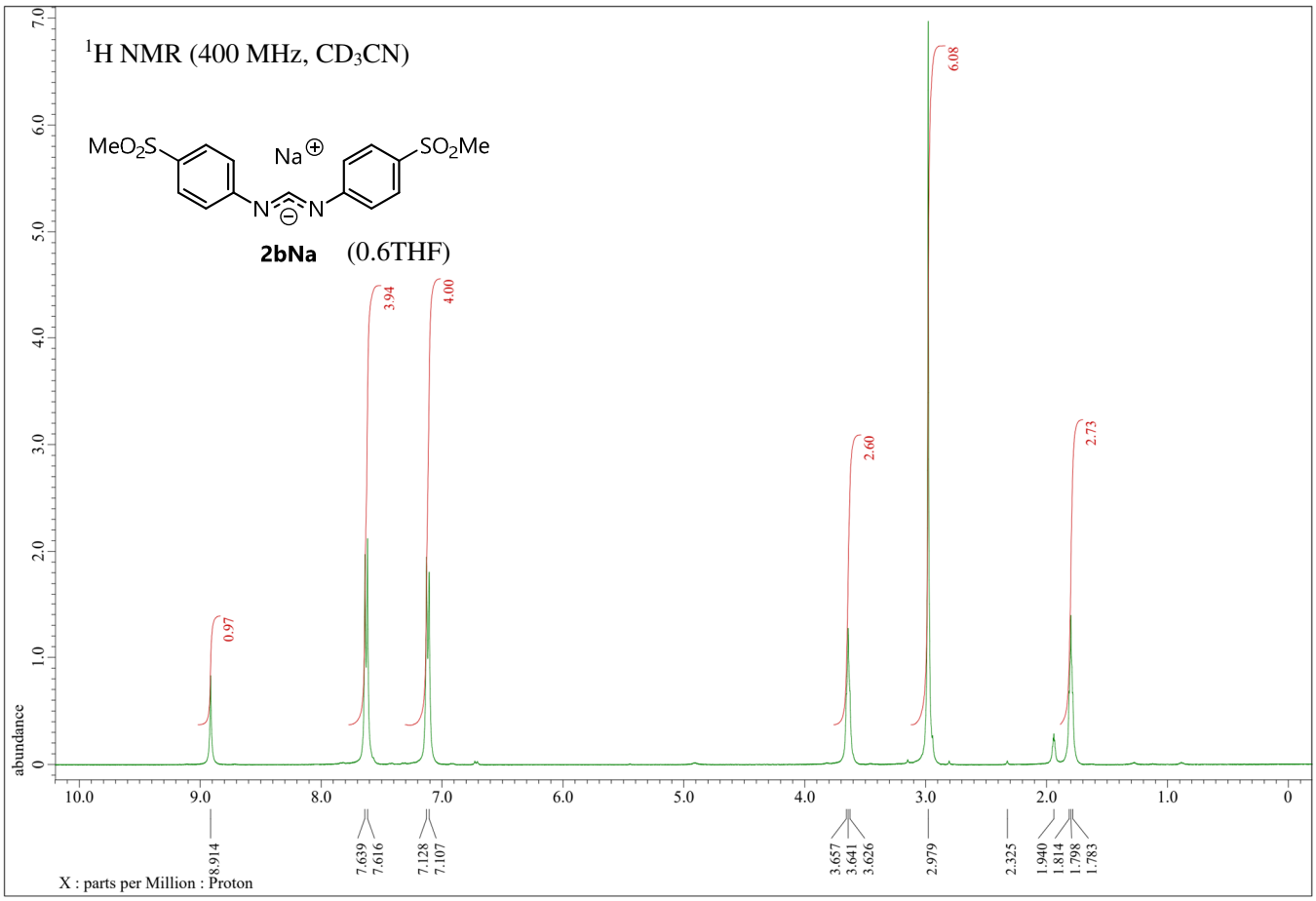

1H NMR (400 MHz, CD3CN)
CF3
NC
CF3
CN
F3C
CF3
N
H
N
2gH
4.00
1.03
abundance
400.0
300.0
200.0
100.0
0
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
8.374
8.019
2.146
1.940
X : parts per Million : 1H

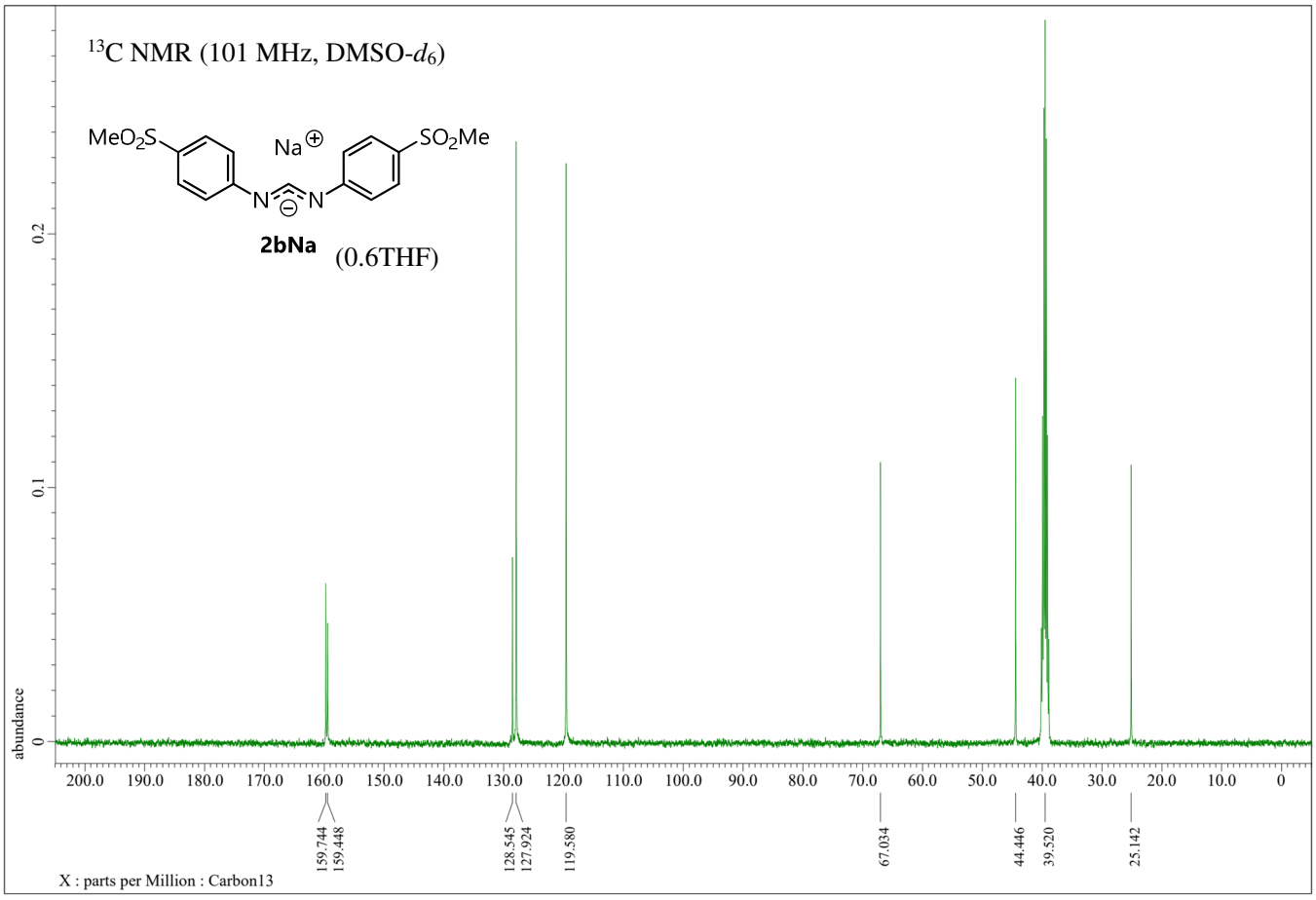

$^{13}$C NMR (101 MHz, DMSO-$d_6$)
CF3
NC
CF3
CN
F3C
N
H
N
CF3
2gH
abundance
X : parts per Million : Carbon13
152.937
150.341
135.209
134.894
134.579
134.254
126.044
123.323
120.602
117.881
112.592
98.606
39.520

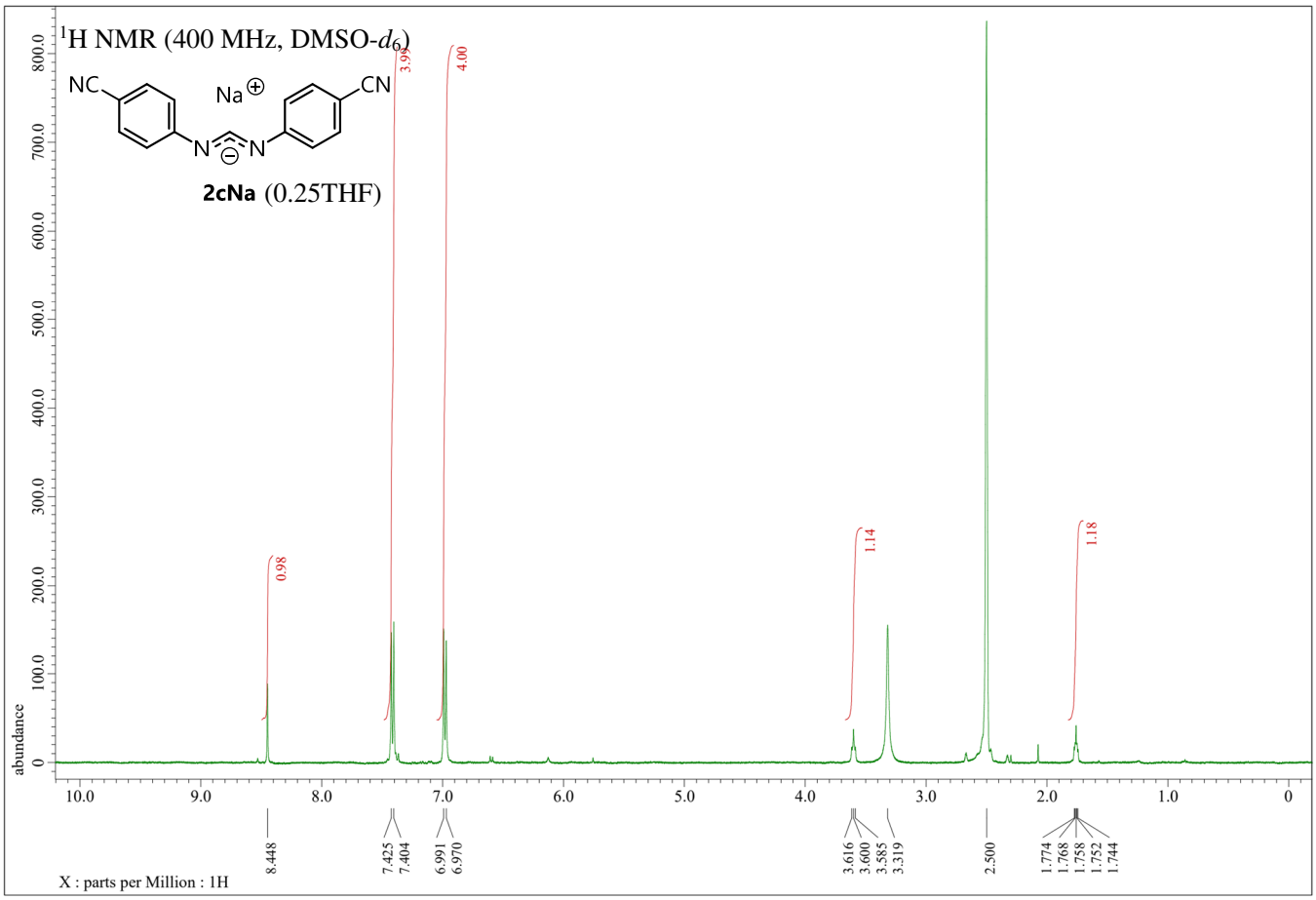

$^{19}$F NMR (378 MHz, $CD_3CN$)
CF3
NC
CF3
CN
F3C
N
H
N
CF3
2gH
12.00
abundance
X : parts per Million : 19F
-62.747

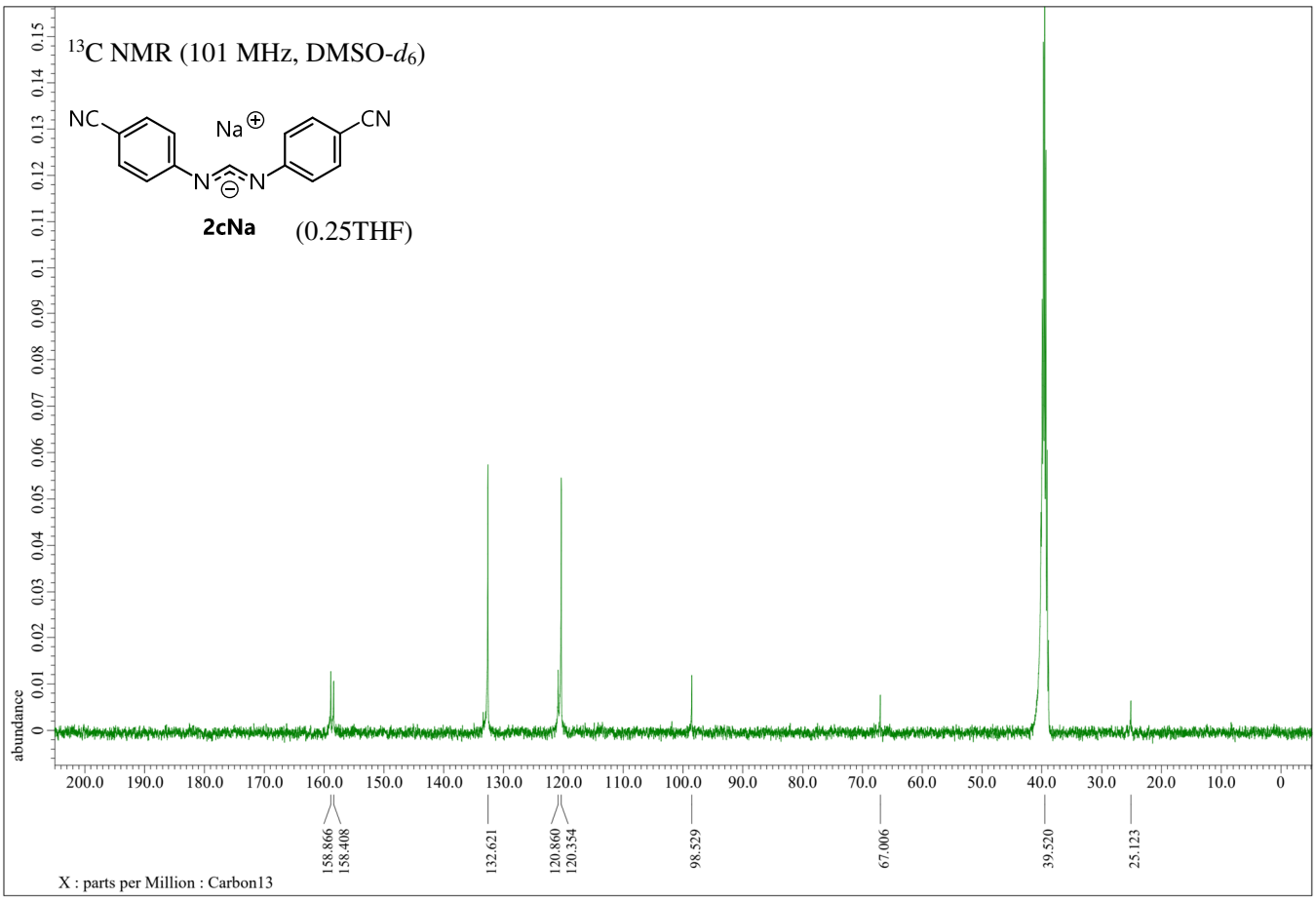

$^1$H NMR (400 MHz, $CD_3CN$)
$MeO_2C$
Na
$CO_2Me$
N
N
2aNa
(0.4THF)
5.95
4.29
4.00
1.62
1.64
1.03
abundance
X : parts per Million : Proton
8.935
7.772
7.750
7.006
6.984
3.791
3.658
3.642
3.628
1.940
1.819
1.803
1.788

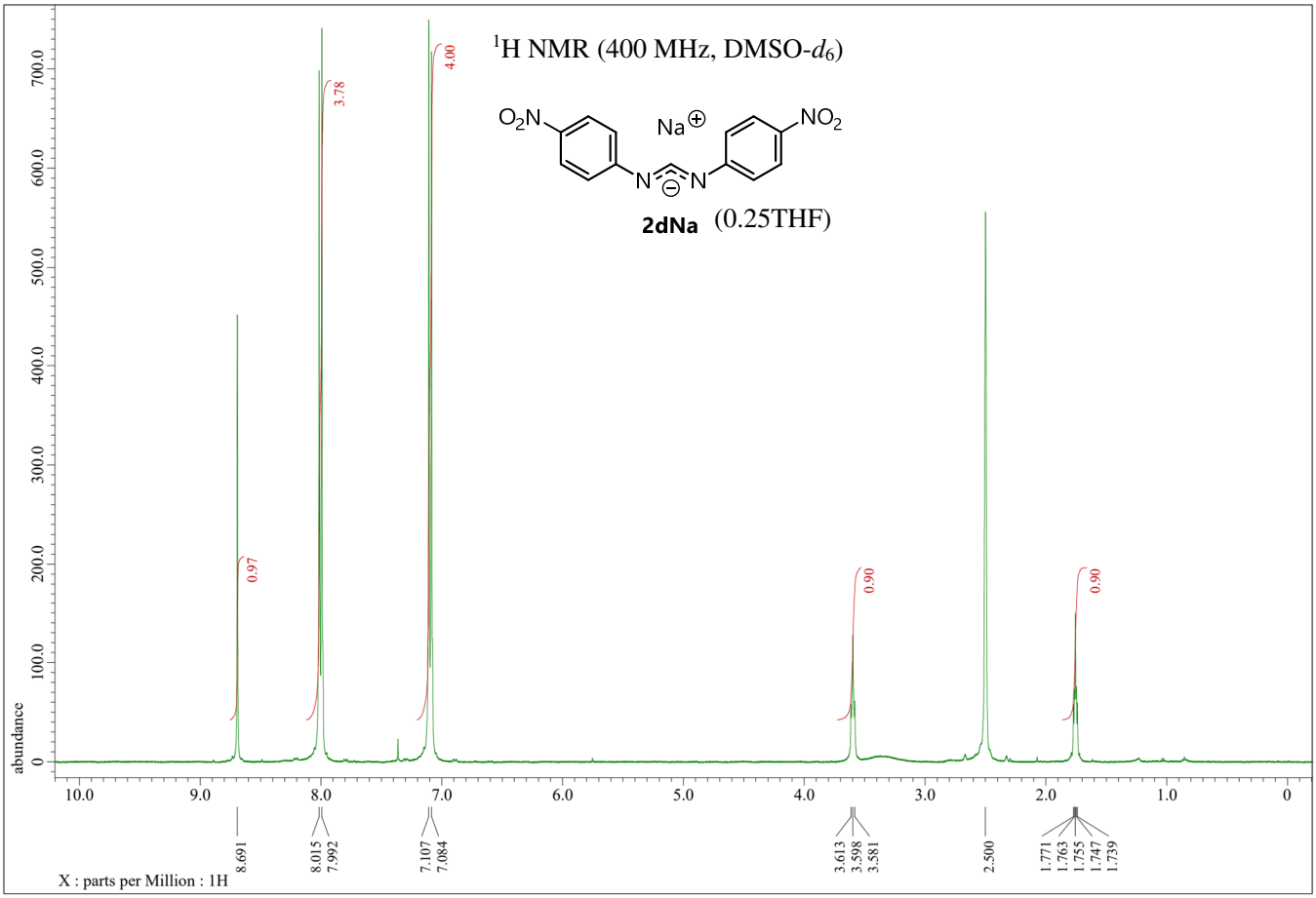

$^{13}$C NMR (101 MHz, DMSO-$d_6$)
$MeO_2C$
Na
$CO_2Me$
N
N
2aNa
(0.4THF)
abundance
X : parts per Million : Carbon13
166.656
159.763
159.525
130.340
119.304
118.425
67.053
51.215
39.520
25.161

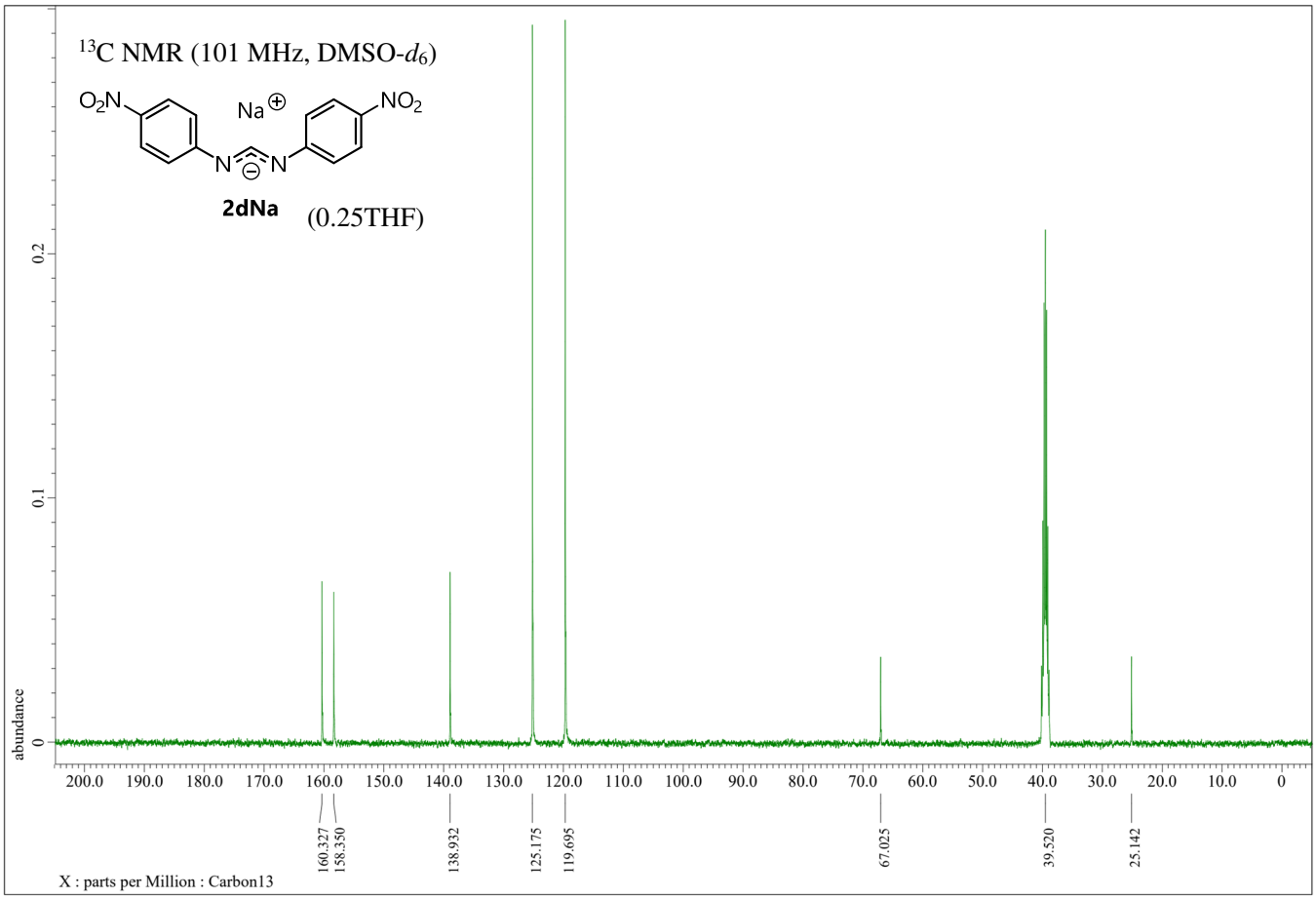

$^1$H NMR (400 MHz, $CD_3CN$)
$MeO_2S$
Na
$SO_2Me$
N
N
2bNa (0.6THF)
6.08
3.94
4.00
2.60
2.73
0.97
abundance
X : parts per Million : Proton
8.914
7.639
7.616
7.128
7.107
3.657
3.641
3.626
2.979
2.325
1.940
1.814
1.798
1.783

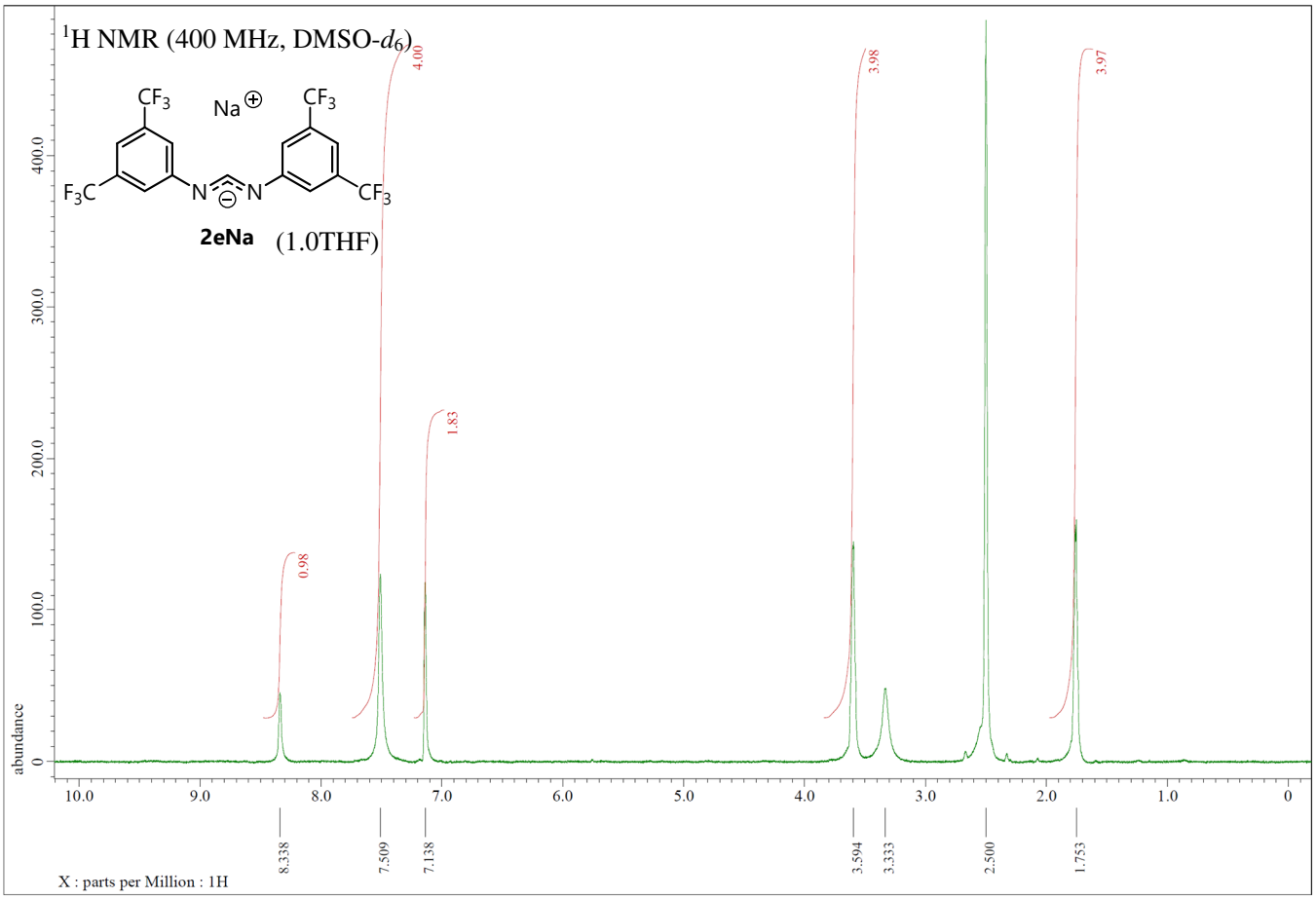

$^{13}$C NMR (101 MHz, DMSO-$d_6$)
$MeO_2S$
Na
$SO_2Me$
N
N
2bNa (0.6THF)
abundance
X : parts per Million : Carbon13
159.744
159.448
128.545
127.924
119.580
67.034
44.446
39.520
25.142

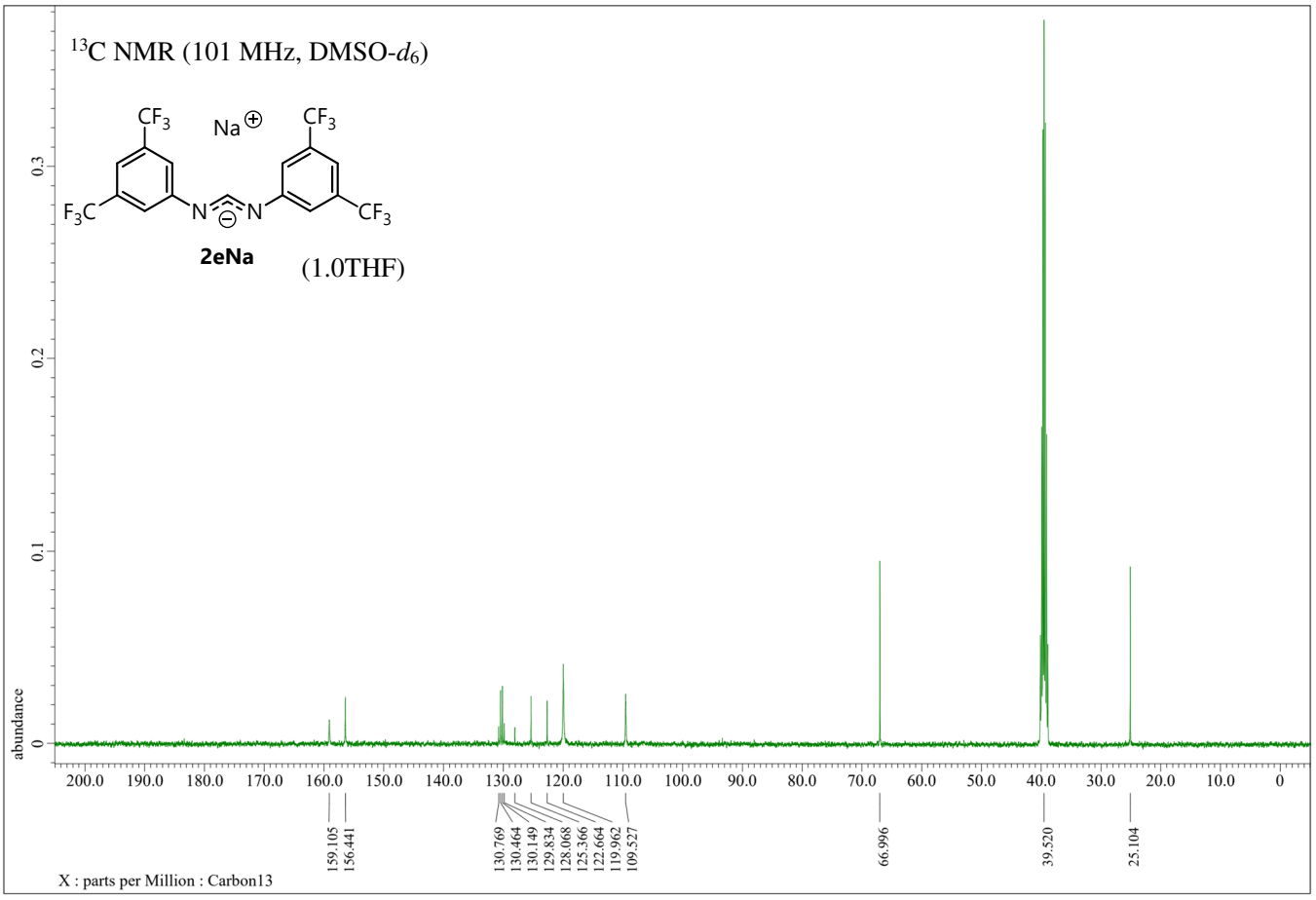

$^1$H NMR (400 MHz, DMSO-$d_6$)
NC
Na
CN
N
N
2cNa (0.25THF)
3.99
4.00
0.98
1.14
1.18
abundance
X : parts per Million : 1H
8.448
7.425
7.404
6.991
6.970
3.616
3.600
3.585
3.319
2.500
1.774
1.768
1.758
1.752
1.744

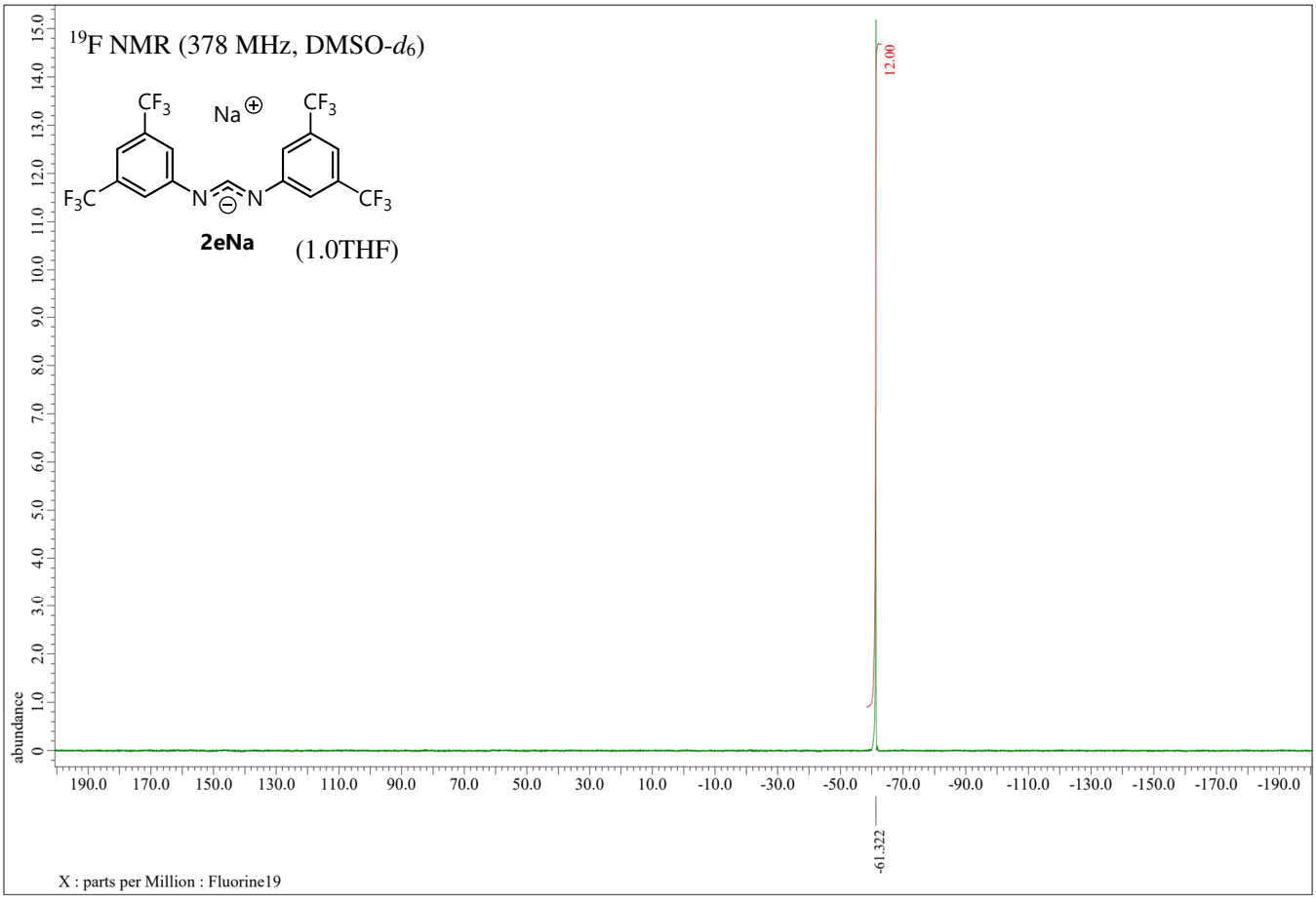

$^{13}$C NMR (101 MHz, DMSO-$d_6$)
NC
Na
CN
N
N
2cNa (0.25THF)
abundance
X : parts per Million : Carbon13
158.866
158.408
132.621
120.860
120.354
98.529
67.006
39.520
25.123

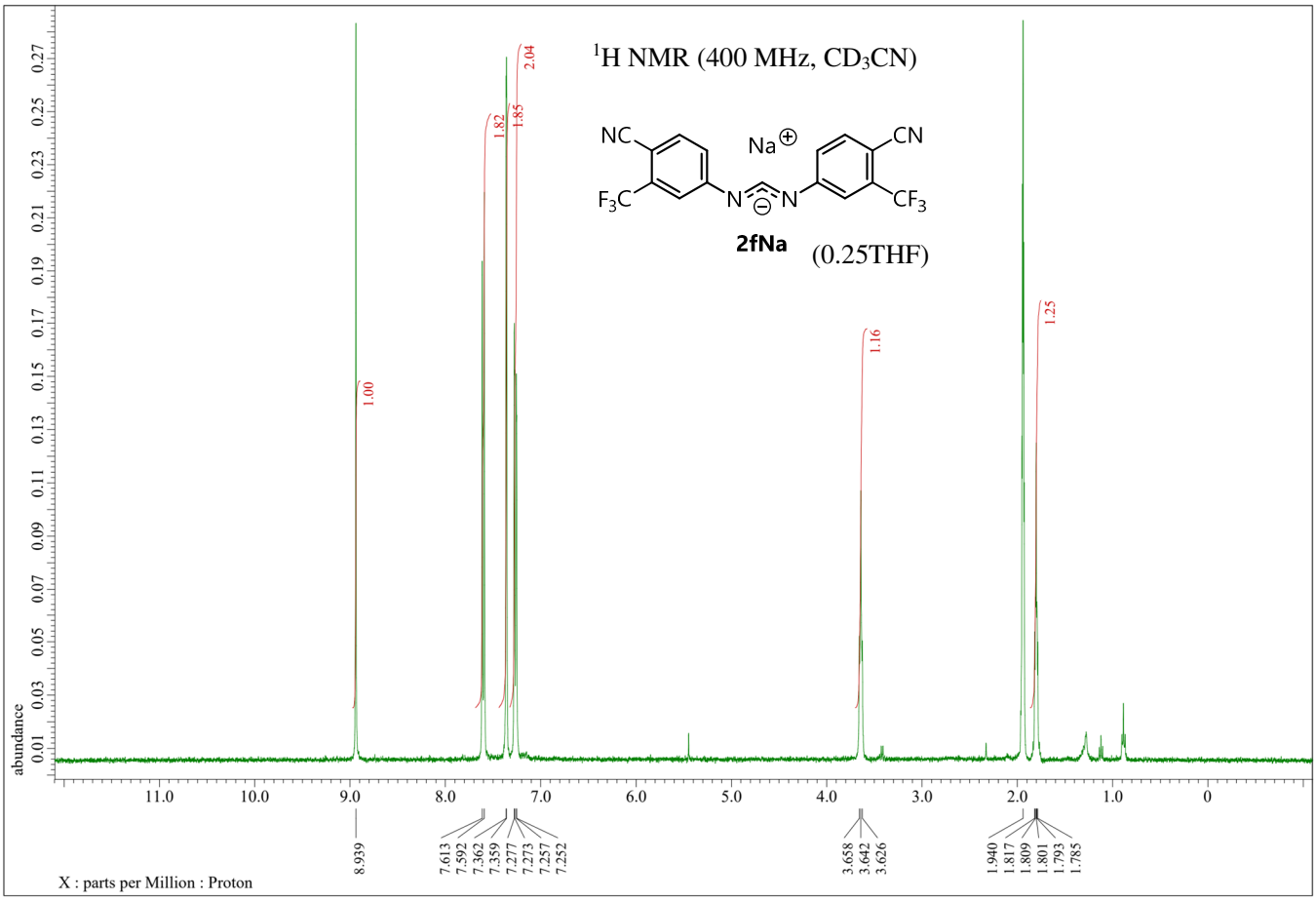

$^1$H NMR (400 MHz, DMSO-$d_6$)
$O_2N$
Na
$NO_2$
N
N
2dNa (0.25THF)
abundance
X : parts per Million : 1H

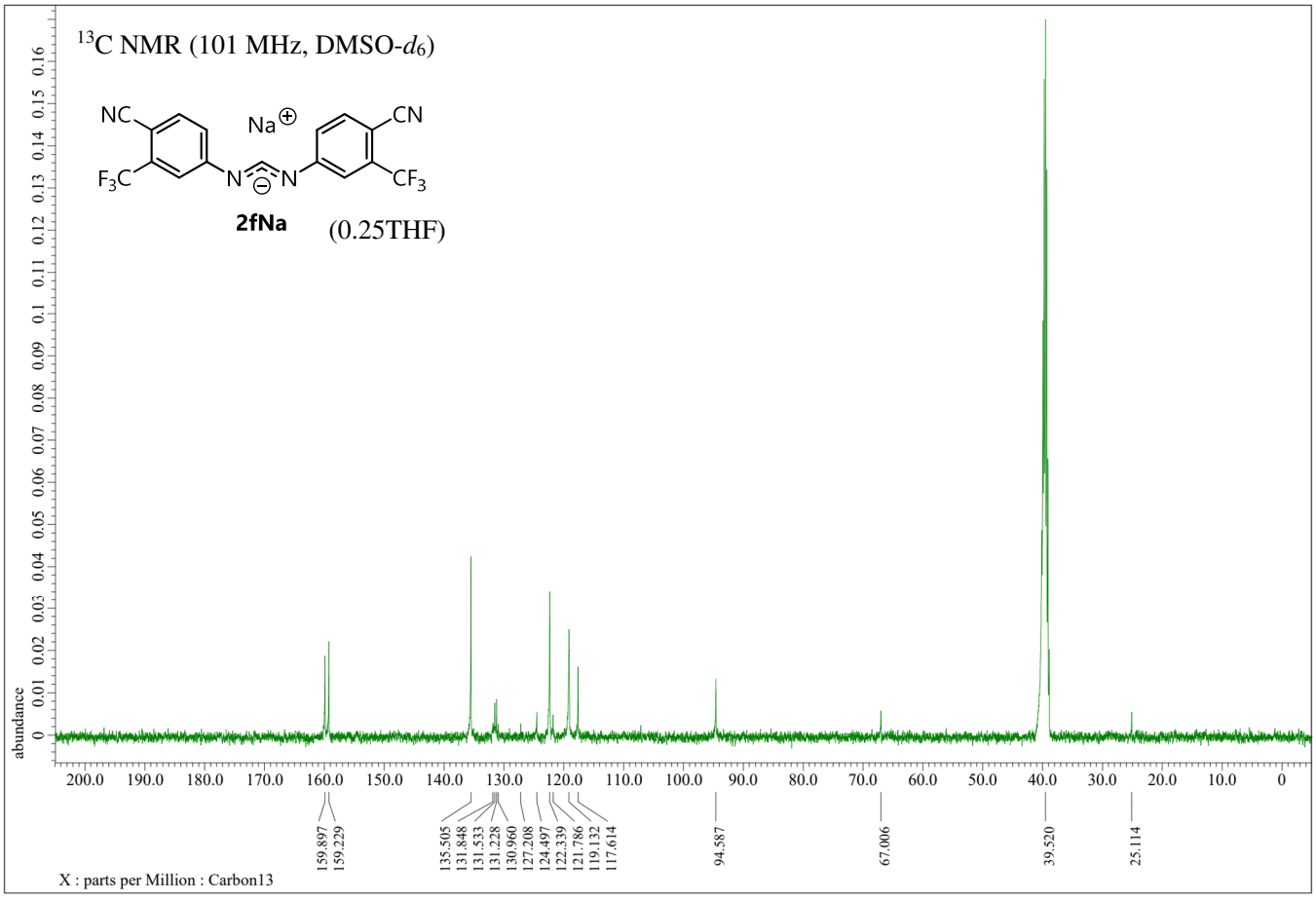

$^{13}$C NMR (101 MHz, DMSO-$d_6$)
$O_2N$
Na
$NO_2$
N
N
2dNa (0.25THF)
abundance
X : parts per Million : Carbon13

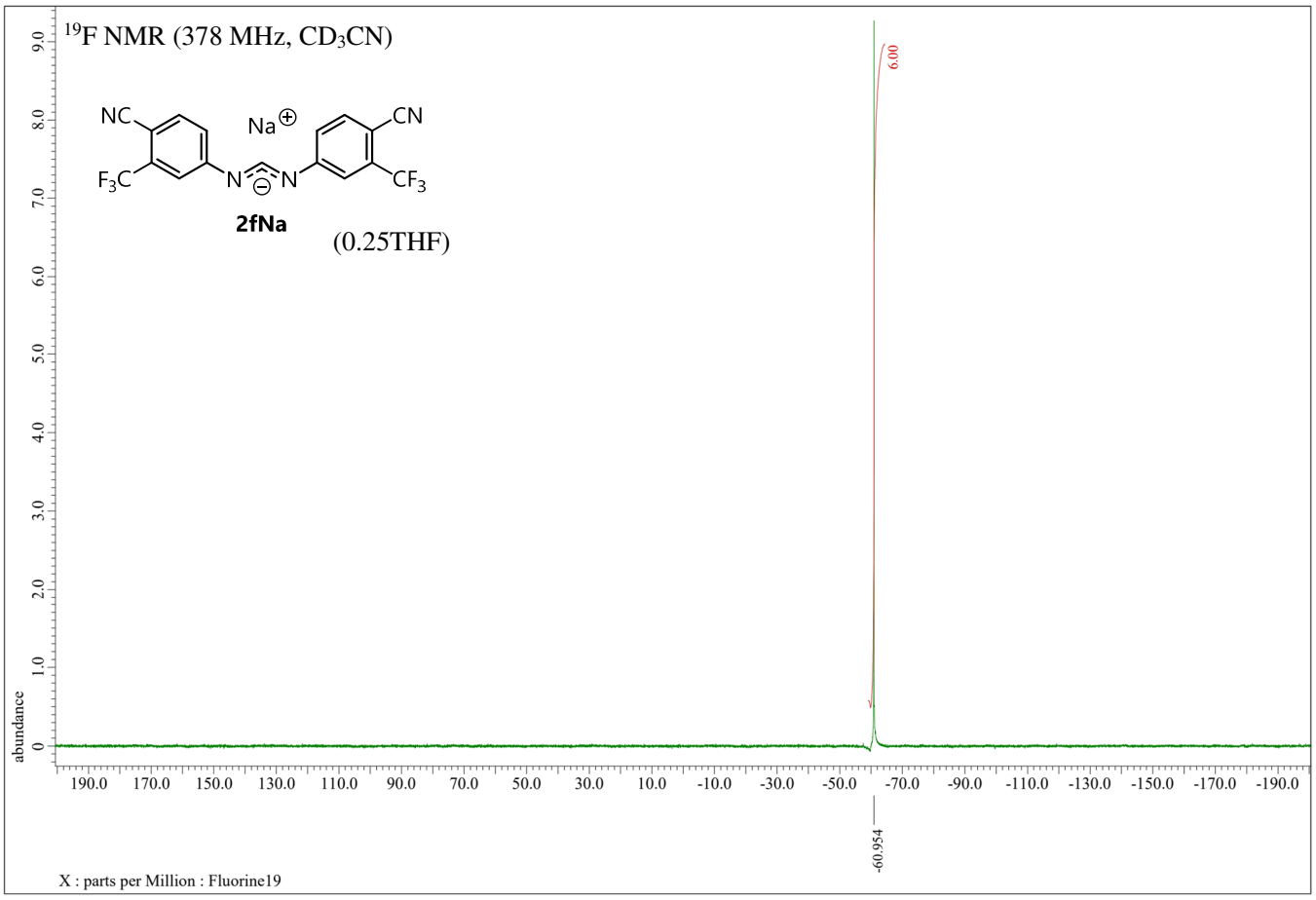

$^1$H NMR (400 MHz, DMSO-$d_6$)
CF3
Na
CF3
F3C
N
N
CF3
2eNa
(1.0THF)
4.00
3.98
3.97
1.83
0.98
abundance
X : parts per Million : 1H
8.338
7.509
7.138
3.594
3.333
2.500
1.753

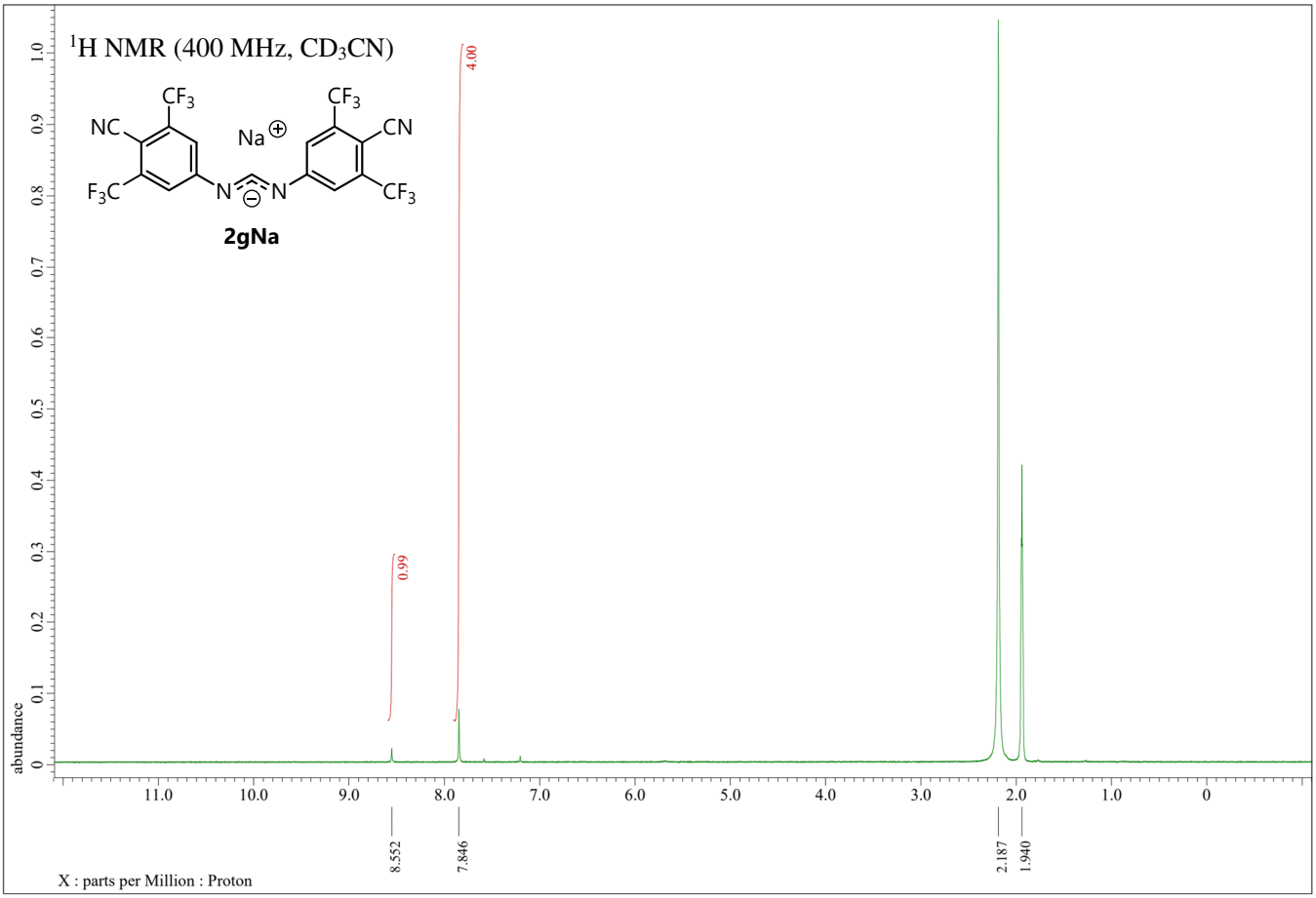

$^{13}$C NMR (101 MHz, DMSO-$d_6$)
CF3
Na
CF3
F3C
N
N
CF3
2eNa
(1.0THF)
abundance
X : parts per Million : Carbon13
159.105
156.441
130.769
130.464
130.149
129.834
128.068
125.366
122.664
119.962
109.527
66.996
39.520
25.104

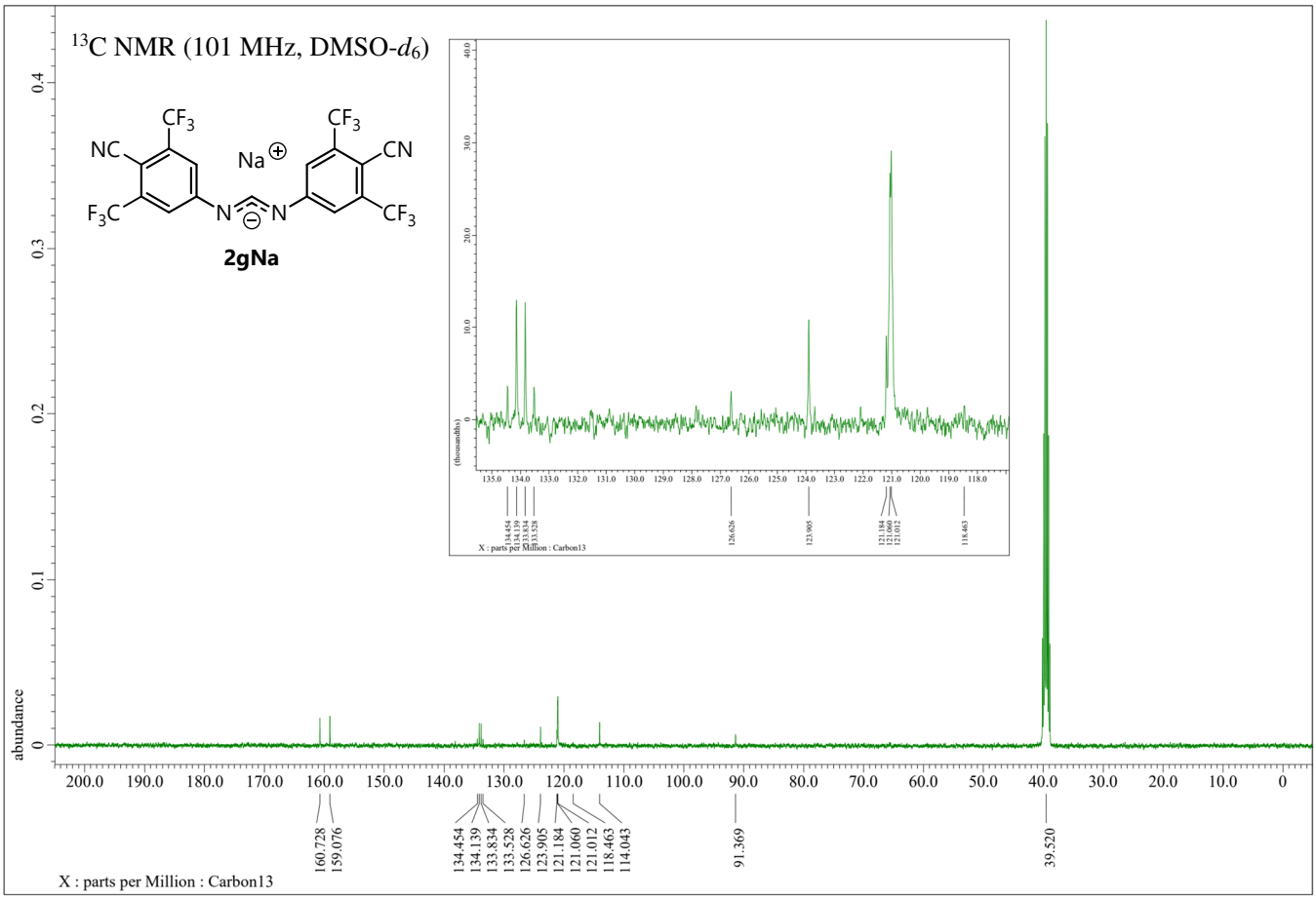

19F NMR (378 MHz, DMSO-d6)
CF3
Na
CF3
F3C
N
N
CF3
2eNa
(1.0THF)
12.00
-61.322
abundance
X : parts per Million : Fluorine19

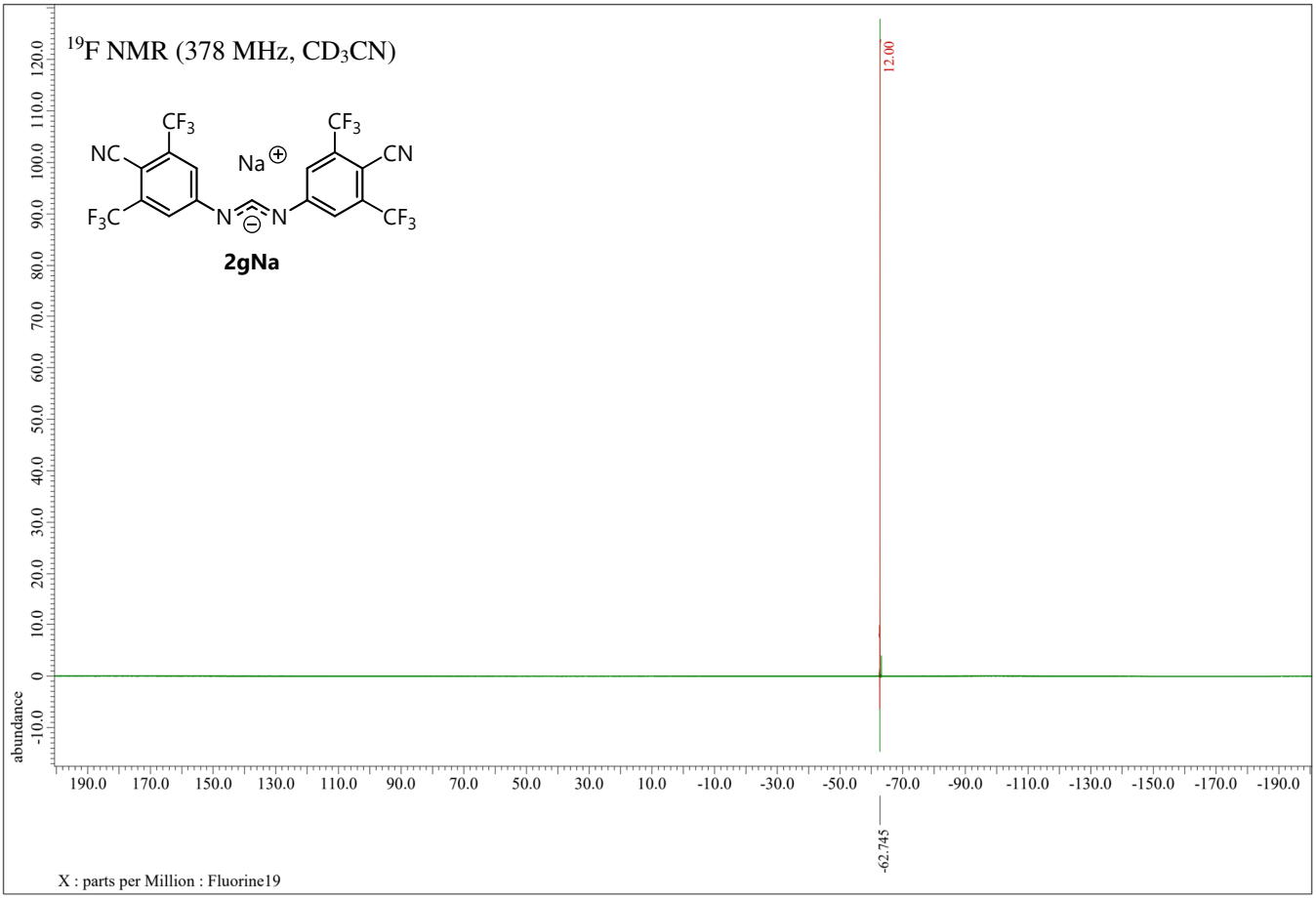

1H NMR (400 MHz, CD3CN)
NC
Na
CN
F3C
N
N
CF3
2fNa
(0.25THF)
1.00
1.82
1.85
2.04
1.16
1.25
8.939
7.613
7.592
7.362
7.359
7.277
7.273
7.257
7.252
3.658
3.642
3.626
1.940
1.817
1.809
1.801
1.793
1.785
abundance
X : parts per Million : Proton

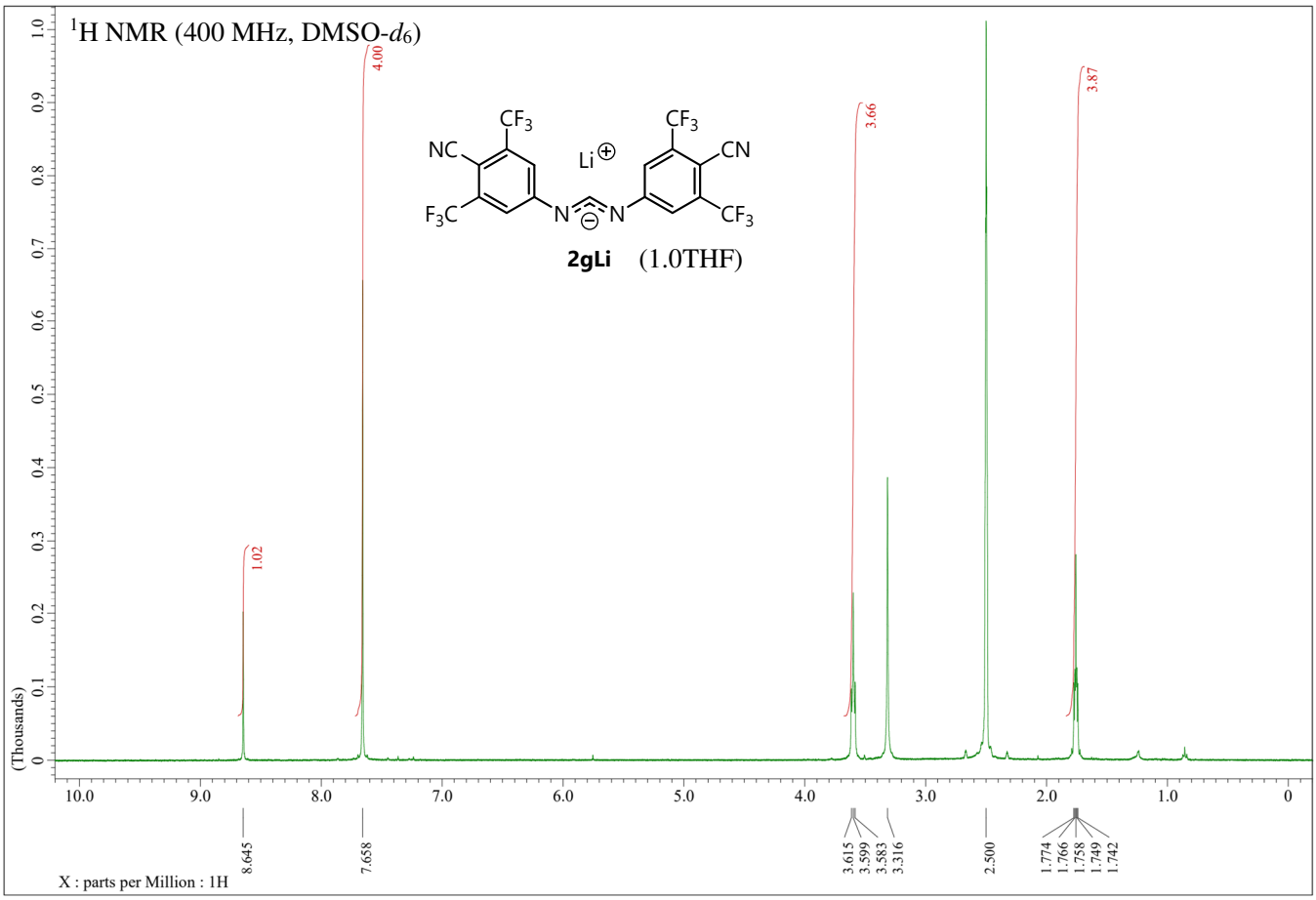

$^{13}$C NMR (101 MHz, DMSO-$d_6$)
NC
Na
CN
$F_3C$
N
N
$CF_3$
2fNa
(0.25THF)
abundance
X : parts per Million : Carbon13
159.897
159.229
135.505
131.848
131.533
131.228
130.960
127.208
124.497
122.339
121.786
119.132
117.614
94.587
67.006
39.520
25.114

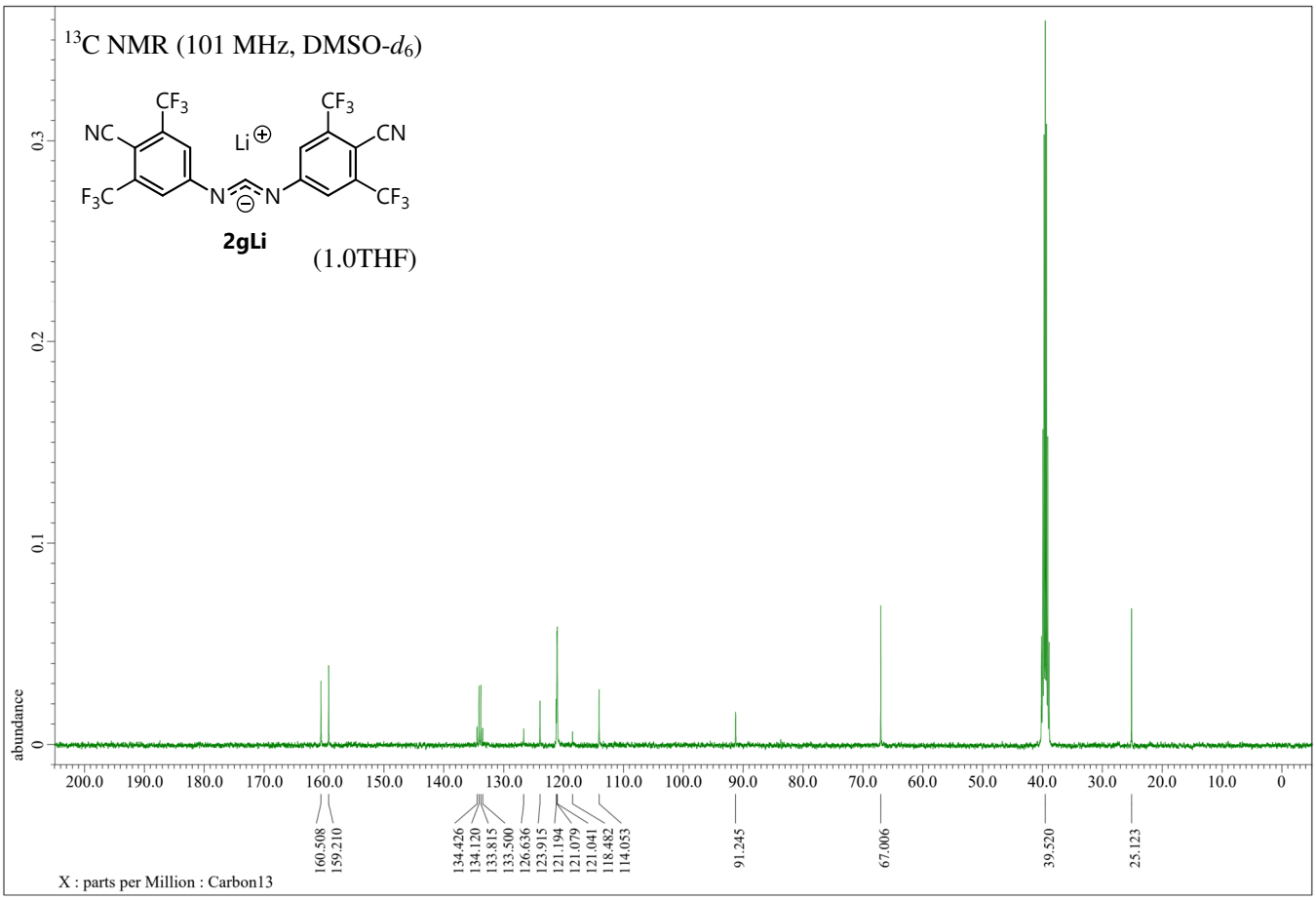

$^{19}$F NMR (378 MHz, $CD_3CN$)
NC
Na
CN
$F_3C$
N
N
$CF_3$
2fNa
(0.25THF)
6.00
abundance
X : parts per Million : Fluorine19
-60.954

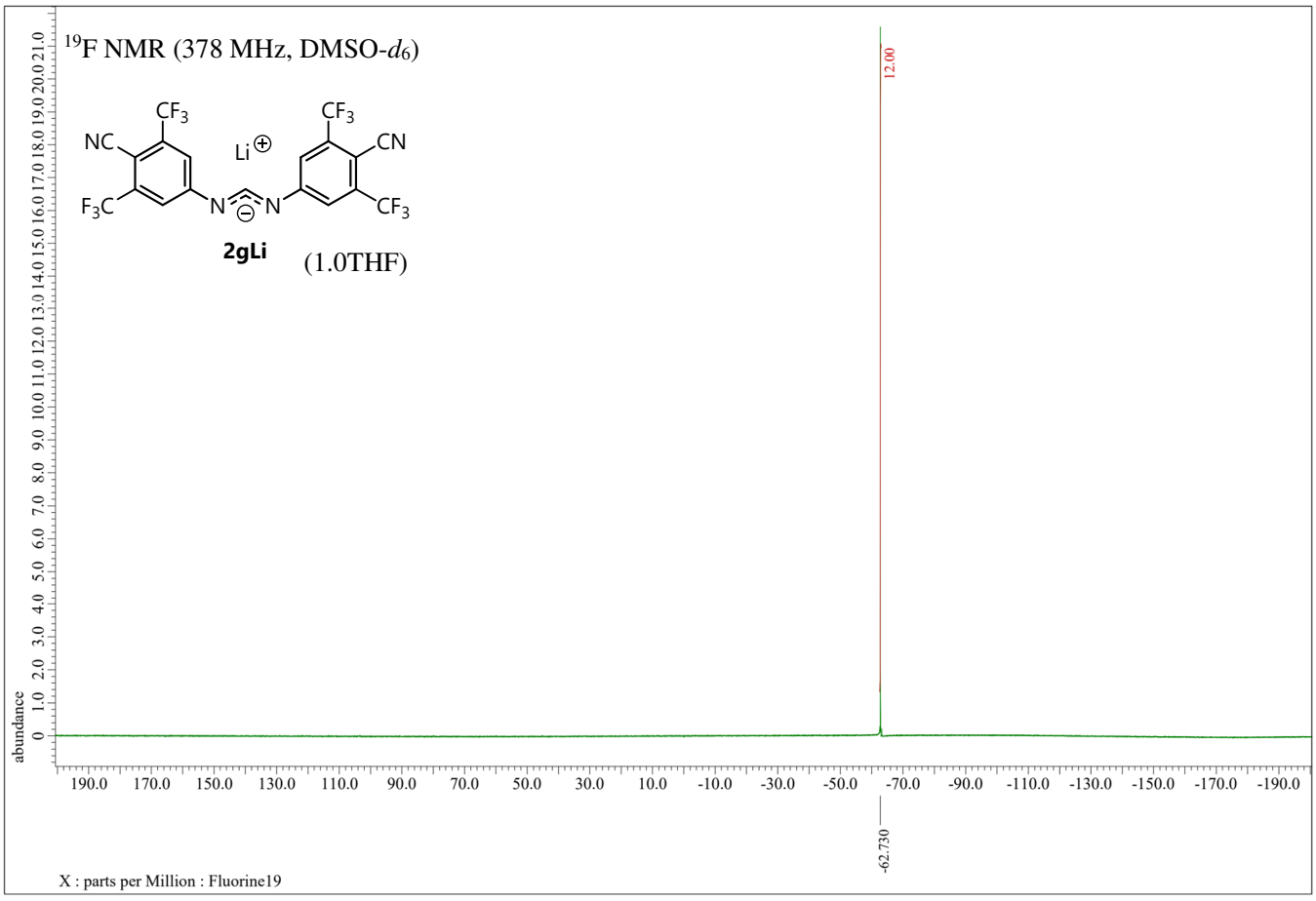

$^1$H NMR (400 MHz, $CD_3CN$)
2gNa
4.00
0.99
abundance
8.552
7.846
2.187
1.940
X : parts per Million : Proton

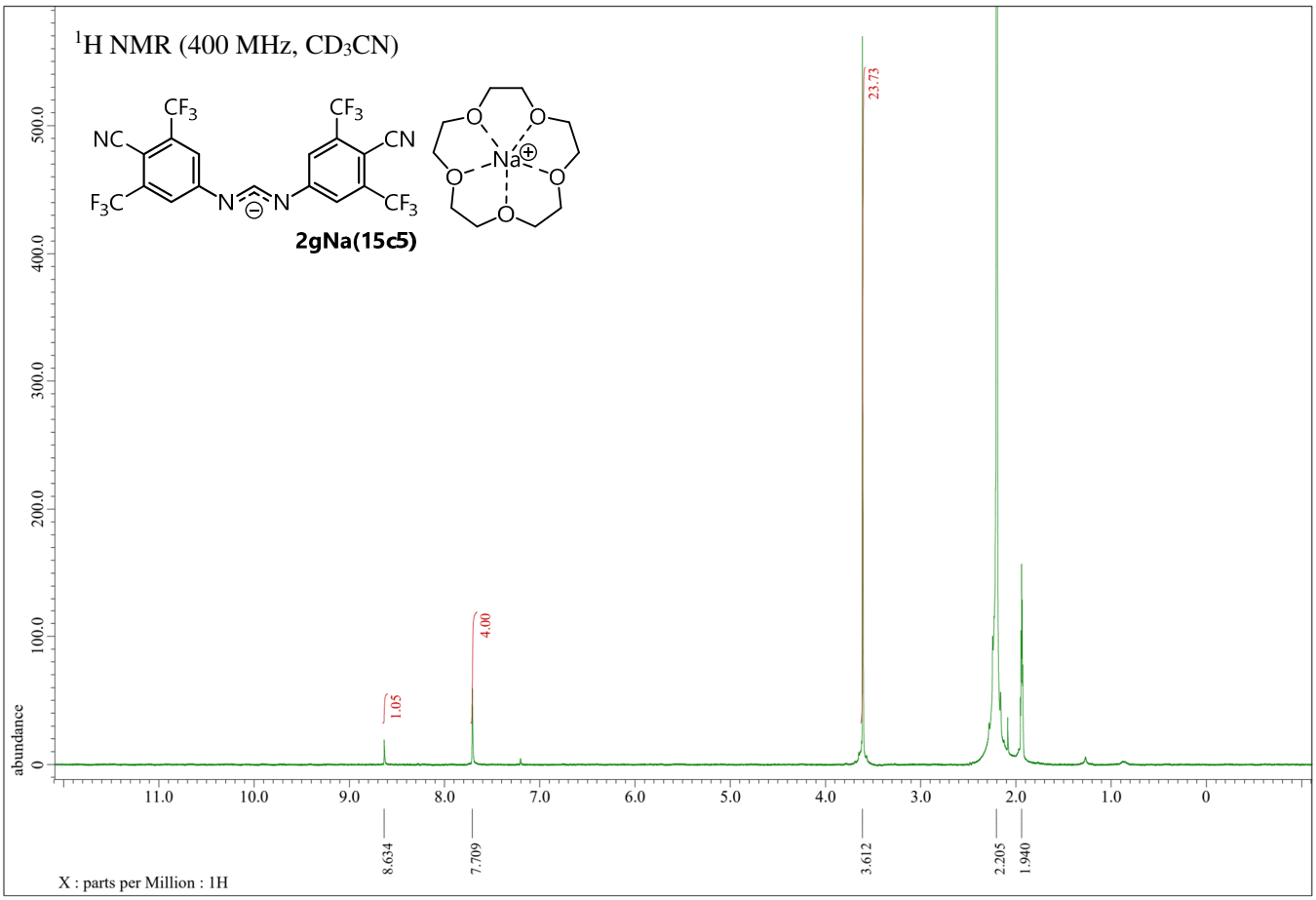

$^{13}$C NMR (101 MHz, DMSO-$d_6$)
2gNa
abundance
160.728
159.076
134.454
134.139
133.834
133.528
126.626
123.905
121.184
121.060
121.012
118.463
114.043
91.369
39.520
X : parts per Million : Carbon13

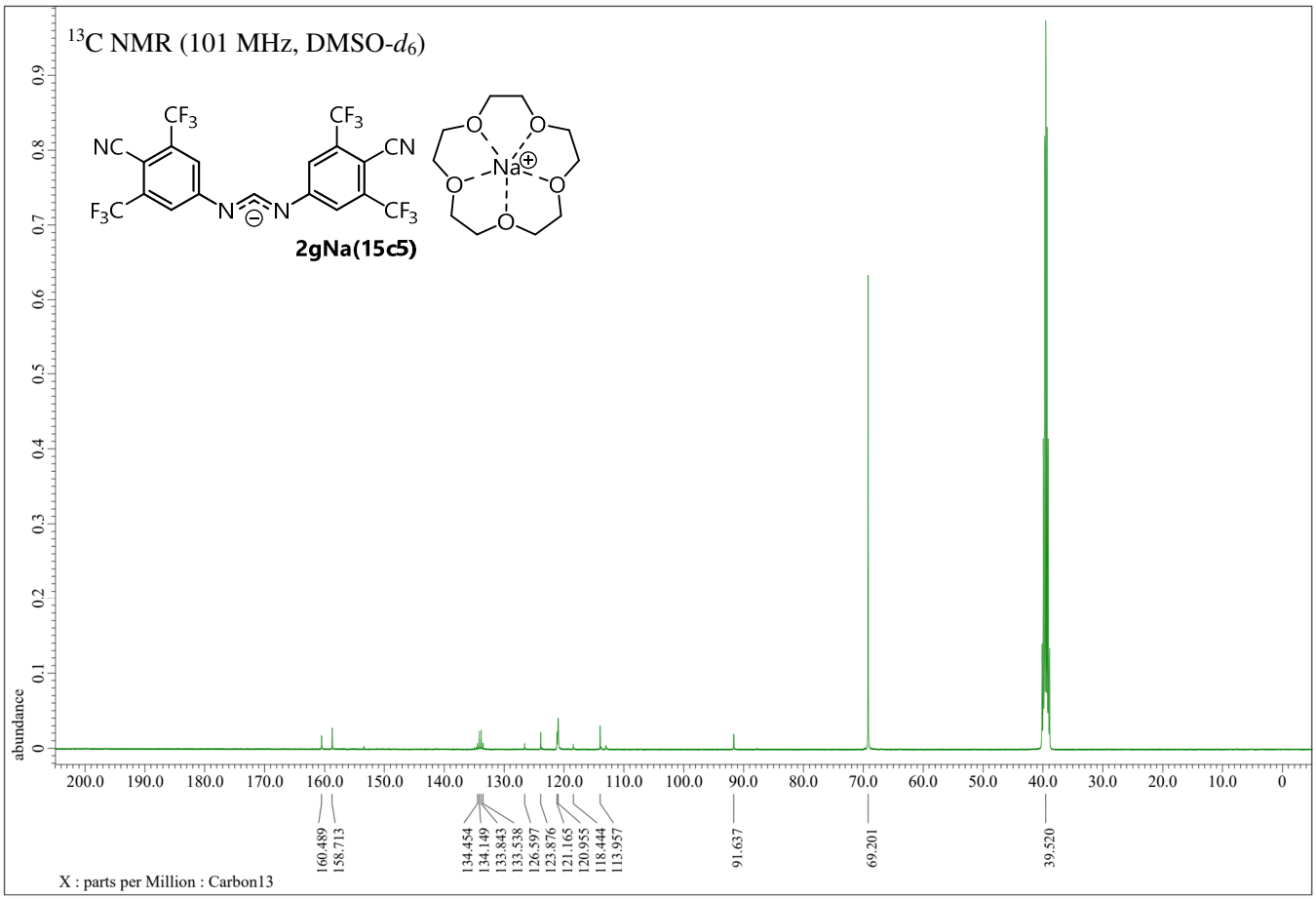

19F NMR (378 MHz, CD3CN)
CF3
NC
Na
CN
F3C
N
N
CF3
2gNa
12.00
abundance
-62.745
X : parts per Million : Fluorine19

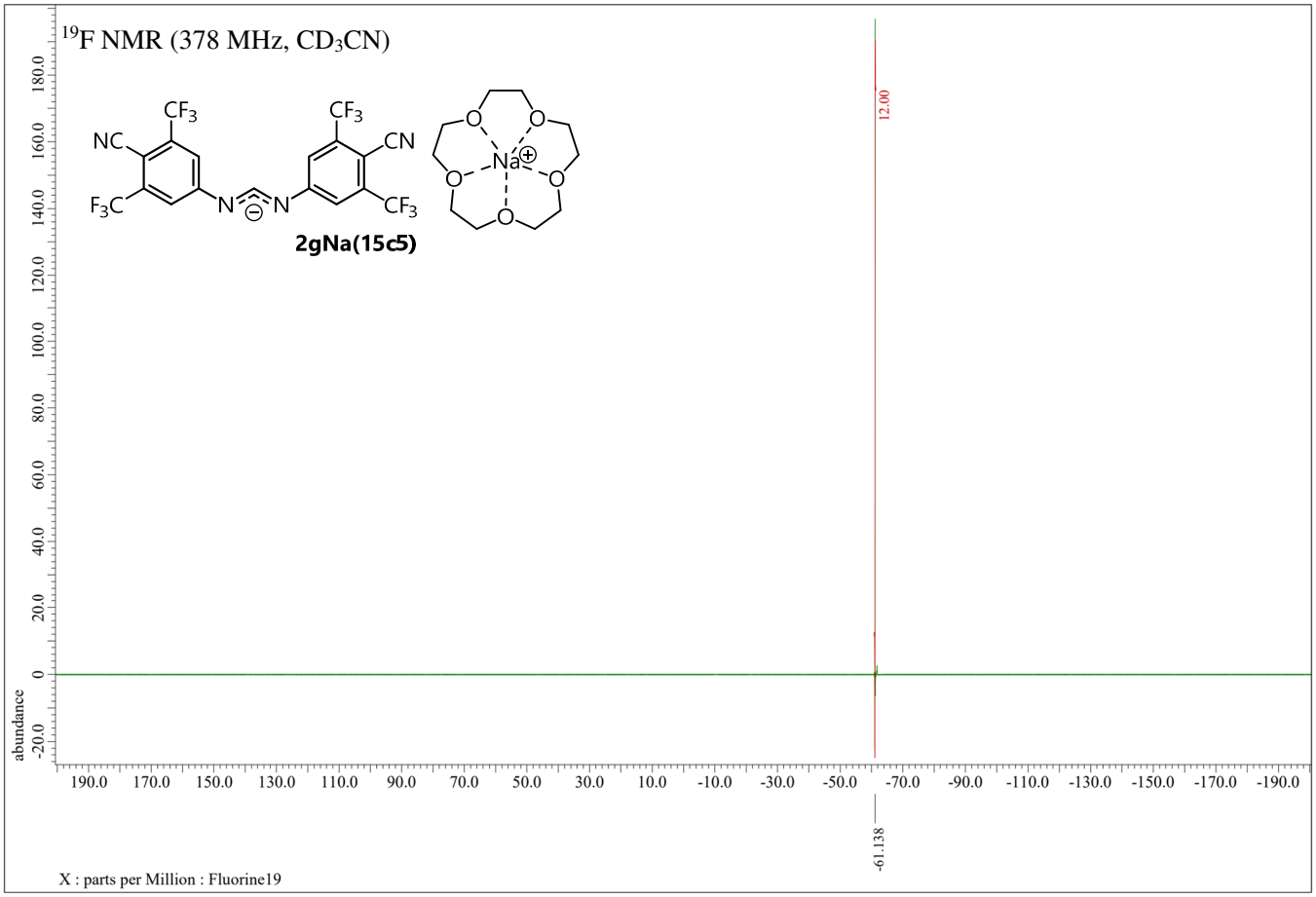

1H NMR (400 MHz, DMSO-d6)
CF3
NC
Li
CN
F3C
N
N
CF3
2gLi (1.0THF)
4.00
3.66
3.87
1.02
(Thousands)
8.645
7.658
3.615
3.599
3.583
3.316
2.500
1.774
1.766
1.758
1.749
1.742
X : parts per Million : 1H

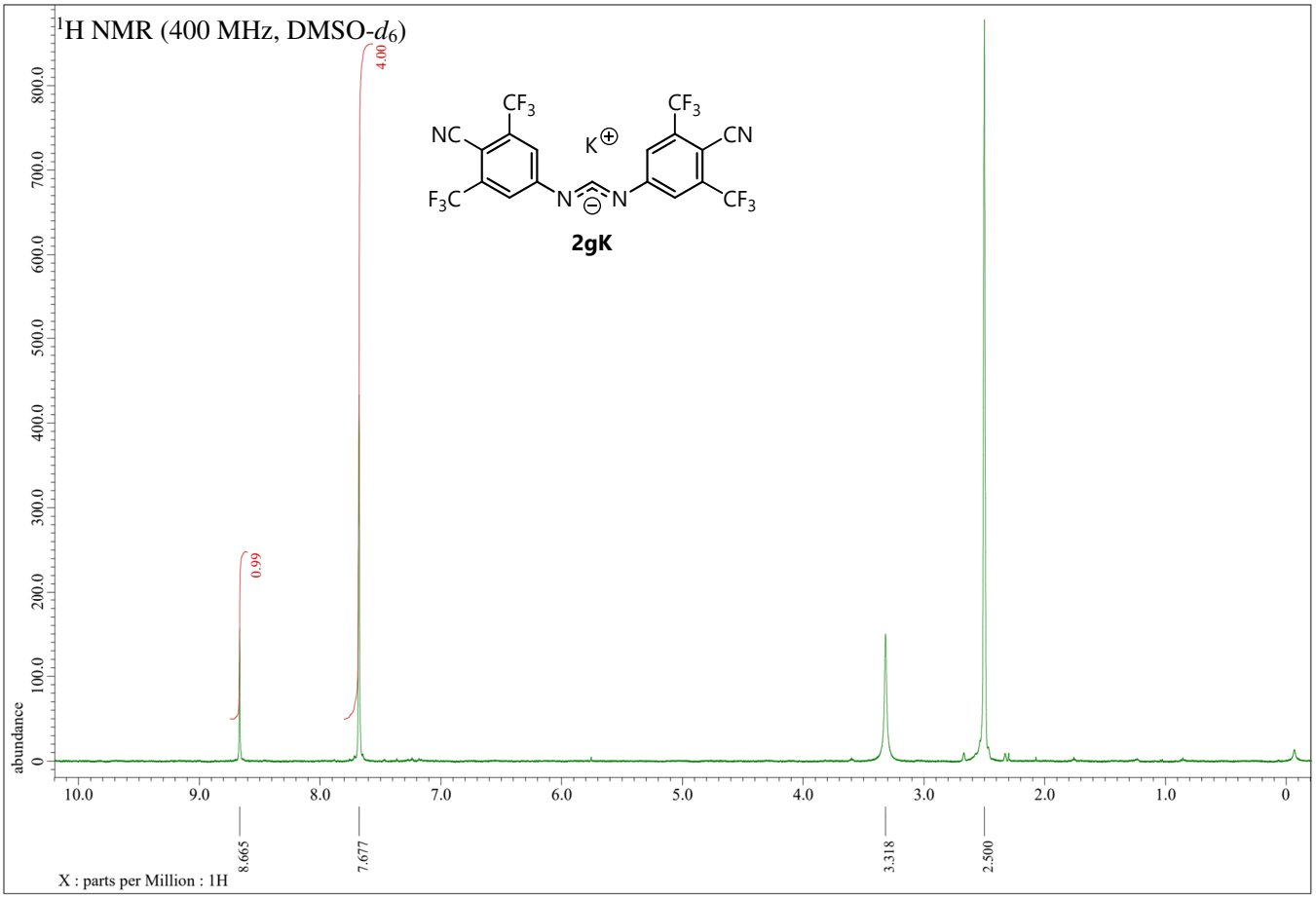

$^{13}$C NMR (101 MHz, DMSO-$d_6$)
2gLi
(1.0THF)
abundance
X : parts per Million : Carbon13
160.508
159.210
134.426
134.120
133.815
133.500
126.636
123.915
121.194
121.079
121.041
118.482
114.053
91.245
67.006
39.520
25.123

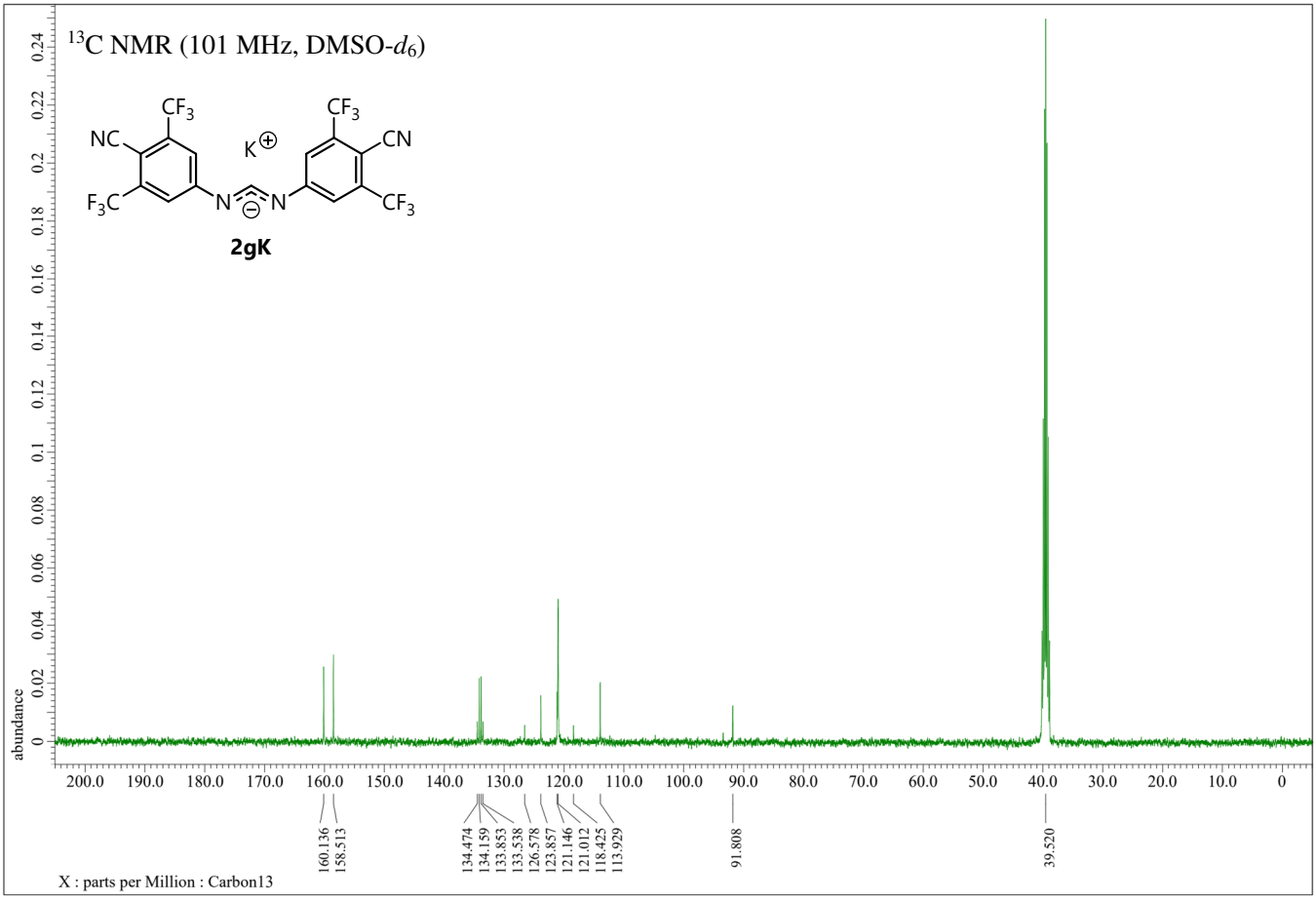

$^{19}$F NMR (378 MHz, DMSO-$d_6$)
2gLi
(1.0THF)
abundance
X : parts per Million : Fluorine19
12.00
-62.730

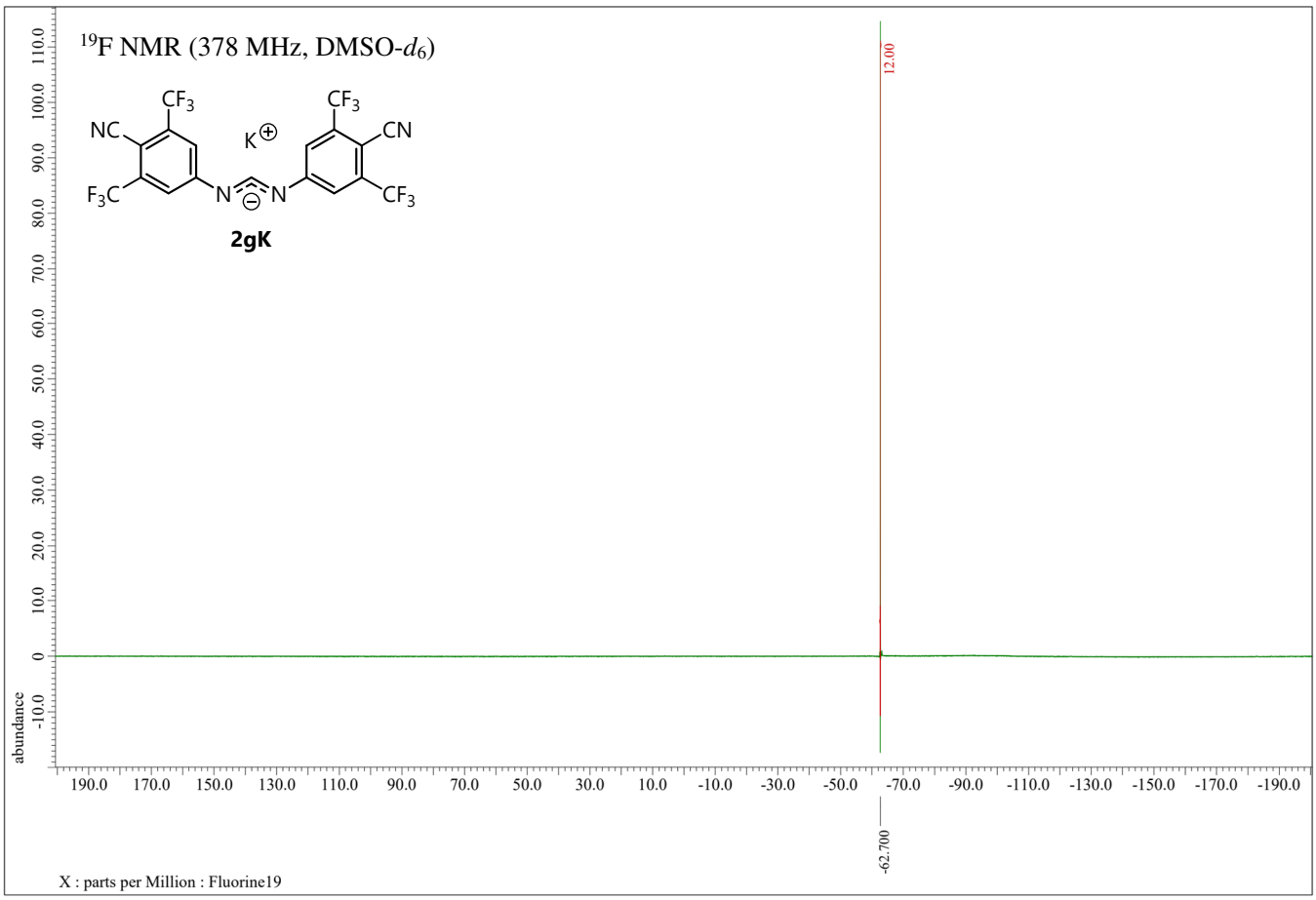

$^1$H NMR (400 MHz, $CD_3CN$)
2gNa(15c5)
abundance
X : parts per Million : 1H
23.73
4.00
1.05
8.634
7.709
3.612
2.205
1.940

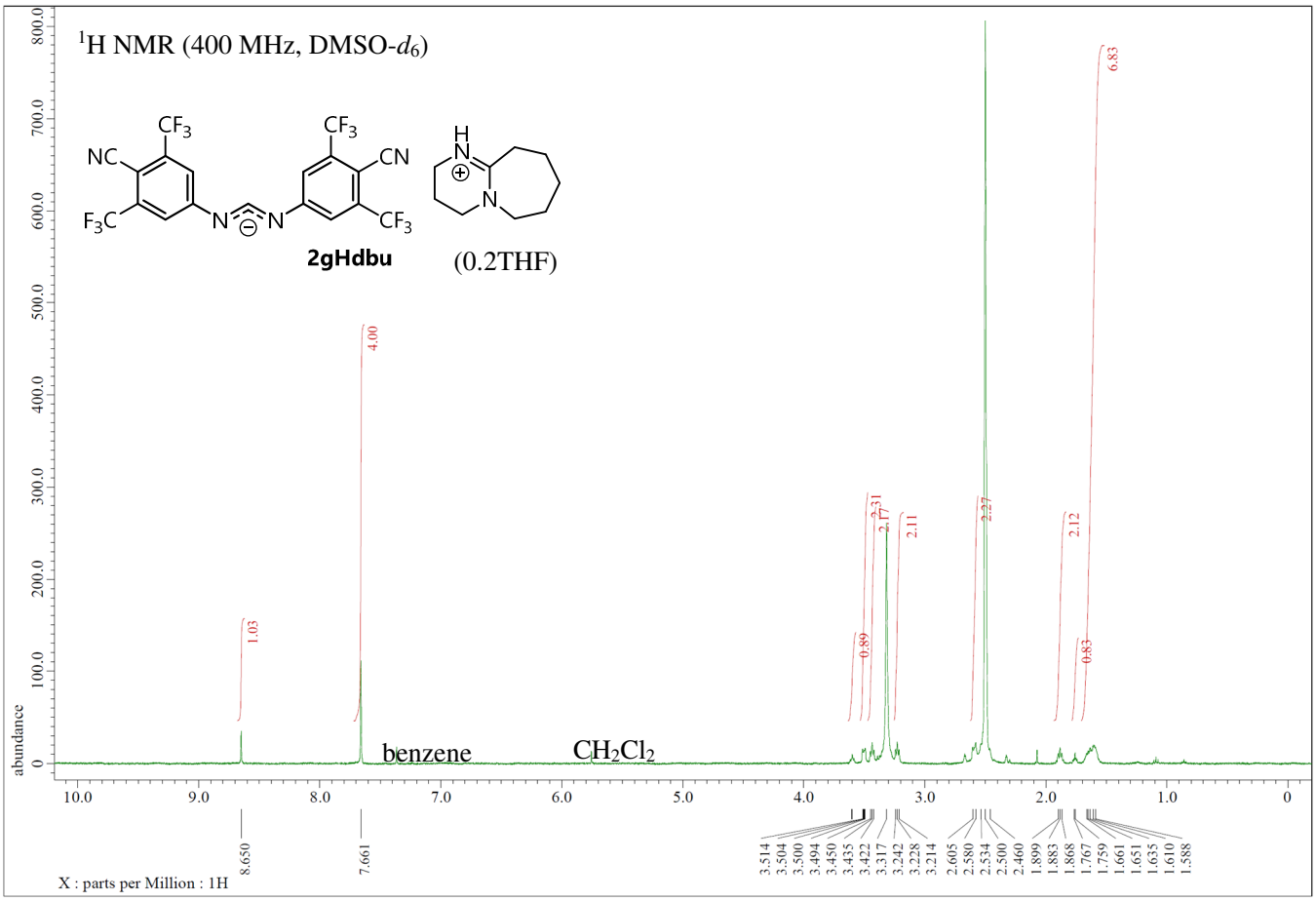

$^{13}$C NMR (101 MHz, DMSO-$d_6$)
2gNa(15c5)
abundance
X : parts per Million : Carbon13
160.489
158.713
134.454
134.149
133.843
133.538
126.597
123.876
121.165
120.955
118.444
113.957
91.637
69.201
39.520

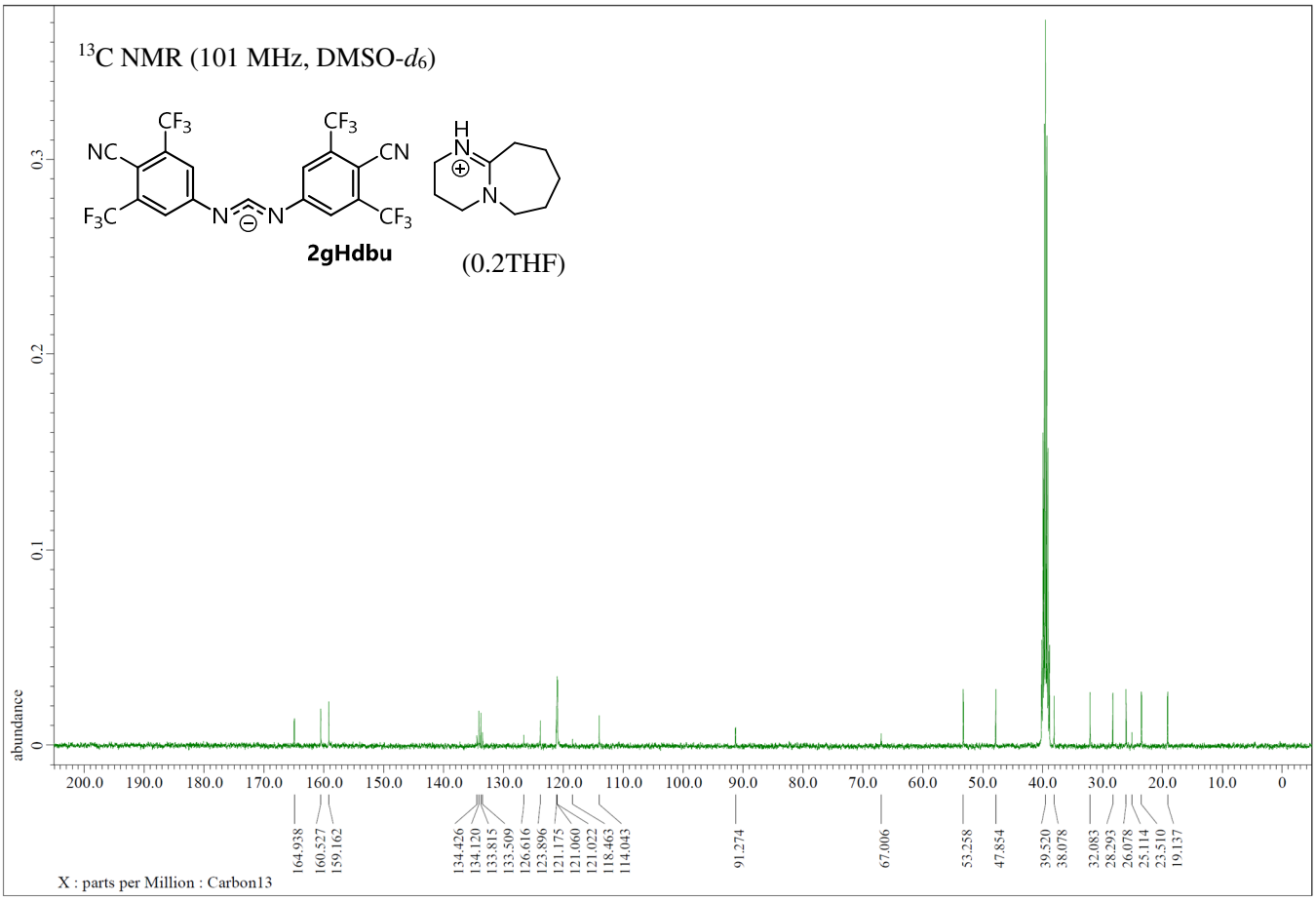

19F NMR (378 MHz, CD3CN)
CF3
NC
CF3
CN
F3C
N
N
CF3
2gNa(15c5)
O
O
Na
O
O
O
12.00
abundance
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0
-20.0
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
30.0
10.0
-10.0
-30.0
-50.0
-70.0
-90.0
-110.0
-130.0
-150.0
-170.0
-190.0
-61.138
X : parts per Million : Fluorine19

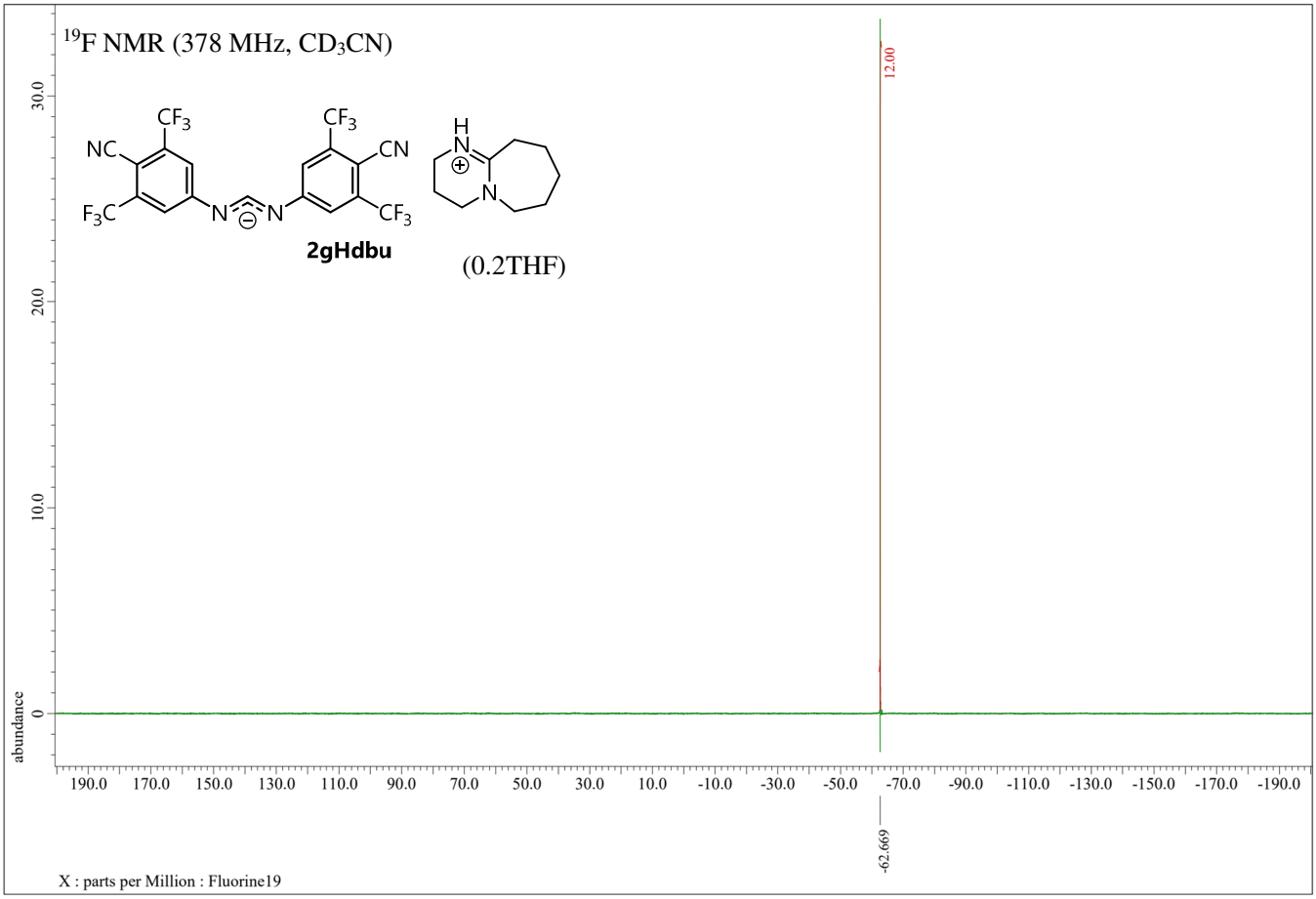

1H NMR (400 MHz, DMSO-d6)
4.00
0.99
CF3
NC
CF3
CN
K
F3C
N
N
CF3
2gK
abundance
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.665
7.677
3.318
2.500
X : parts per Million : 1H


$^{13}$C NMR (101 MHz, DMSO-$d_6$)
CF3
NC
K⊕
CF3
CN
F3C
N
N
CF3
2gK
abundance
X : parts per Million : Carbon13
160.136
158.513
134.474
134.159
133.853
133.538
126.578
123.857
121.146
121.012
118.425
113.929
91.808
39.520


$^{19}$F NMR (378 MHz, DMSO-$d_6$)
CF3
NC
K⊕
CF3
CN
F3C
N
N
CF3
2gK
12.00
-62.700
abundance
X : parts per Million : Fluorine19


$^{1}$H NMR (400 MHz, DMSO-$d_6$)
2gHdbu
(0.2THF)
benzene
$CH_2Cl_2$
X : parts per Million : 1H
abundance


$^{13}$C NMR (101 MHz, DMSO-$d_6$)
2gHdbu
(0.2THF)
X : parts per Million : Carbon13
abundance


19F NMR (378 MHz, CD3CN)
2gHdbu
(0.2THF)
12.00
-62.669
abundance
30.0
20.0
10.0
0
190.0 170.0 150.0 130.0 110.0 90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0
X : parts per Million : Fluorine19

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