Electronic Supplementary Material (ESI) for RSC Mechanochemistry.

Supplementary Information

Diverse Metastable Diarylacetonitrile Radicals Generated by Polymer Mechanochemistry

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1. General Information

All reagents and solvents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Tokyo Chemical Industry, or Kanto Chemical and used as received, unless otherwise noted. CuBr was washed with acetic acid and then washed with ethanol and dried at 70 °C. Styrene was filtrated by aluminum oxide 90 active basic. ^{1}H NMR spectra were obtained using a 500 MHz Bruker AVANCE III HD500 spectrometer. ^{13}C NMR spectra were obtained using a 400 MHz JEOL JNM-ECZ400S/L1 spectrometer. Gel permeation chromatography (GPC) measurements were performed in THF at 40 °C on TOSOH HLC-8320 GPC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), a differential refractive index detector, and UV-vis detector at a flow rate of 0.6 mL/min. The GPC was calibrated with monodisperse polystyrene standards (M_n = 4430–324200 g/mol; M_w/M_n = 1.03–1.08), and all molecular weight data are reported as polystyrene equivalents.

2. Experimental Procedure

2.1. Ball-milling Tests

Grinding tests were performed using mixer mill machine (Retsch MM 400). The mechanical energy was controlled by the frequency of the screw-top grinding jars. The powdered sample was placed in a 10 mL stainless steel screw cap jar containing one 5 mm stainless steel ball. The jar was sealed and locked into the ball-mill machine. The samples were ground for 10 min at 30 Hz. All experiments were conducted at room temperature.

2.2. EPR Spectroscopy

Ground samples were transferred into an EPR glass capillary and weighed, and the capillary was sealed after being degassed. EPR measurements were carried out on a JEOL JES-X320 X-band EPR spectrometer. The spectra of the ground samples were measured using a microwave power of 0.1 mW and a field modulation of 0.1 mT with a time constant of 0.03 s and a sweep rate of 0.50 mTs^{-1} at room temperature. The amount of DAAN radicals were determined by comparing the area of the observed integral spectrum with a 0.05 mM solution of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL) in the benzene under the same experimental conditions. The Mn^{2+} signal was used as an auxiliary standard. The g value was calculated according to the following equation:

$$g = h\nu/\beta H$$

where h is the Planck constant, ν is the microwave frequency, β is the Bohr magneton, and H is the magnetic field.

2.3. Fluorescence Spectroscopy

Fluorescence measurements were carried out using a spectrofluorometer (JASCO FP-8550) with ISF-834 60 mm diameter integrating sphere unit between 350 and 750 nm. Absolute quantum efficiency calculations were carried out using the JASCO Yield Software FWQE-880 Quantum Yield Calculation Program. The external quantum yield (EQY) and internal quantum yield (IQY) were calculated by the following procedure.

1) Measuring incident light

   The spectrum of incident light was measured using an empty cell. The obtained peak area is defined as the area from incident light, S_0 (equivalent number of photons in the incident light).

2) Measuring sample

   The sample was placed on the sample holder, and the scattering and emission spectra of the sample were measured. The obtained excitation wavelength peak area is defined as the area scattered from the sample, S_1 (equivalent number of photons that were not absorbed), and peak area is defined as the area emitted from the sample, S_2.

3) Calculating quantum yield

   The external quantum yield (EQY) and internal quantum yield (IQY) were calculated according to the following equations.

$$\text{EQY [\%]} = \frac{S_2}{S_0} \times 100$$

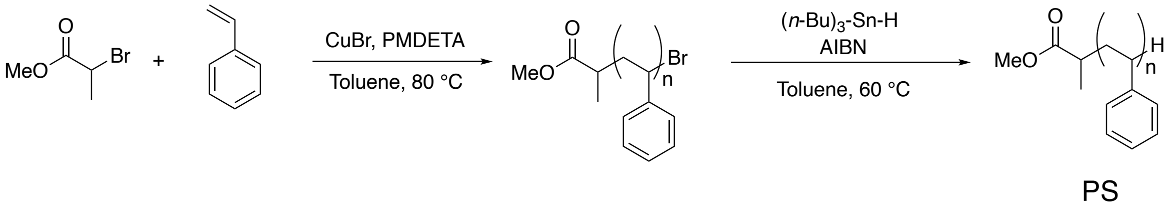
$$\text{IQY [\%]} = \frac{S_2}{S_0 - S_1} \times 100$$

3. Computational details

DFT calculations were executed using the Gaussian16 program package. The geometries of the compounds were optimized without symmetry constraints. Calculations were performed using the unrestricted M06-2X, CAM-B3LYP, or ωB97X-D with the 6-311+G(d,p) basis set. Frequency calculations were carried out to ensure that the optimized geometries were minima on the potential energy surface, in which no imaginary frequencies were observed in any of the compounds. TD-DFT calculations were performed using the unrestricted M06-2X, CAM-B3LYP, or ωB97X-D with the 6-311+G(d,p) to calculate the first 15 doublet transitions.

4. Synthesis Procedure

4.1. Synthesis of PS



PS (M_n = 66.0 kg mol^{-1} ; M_w/M_n = 1.46) was prepared according to literature.[1]

Table S1. M_n and M_w/M_n of polystyrene before and after ball milling (10 min, 30 Hz)

	M_n	M_w/M_n
Before ball milling	66,000	1.46
After ball milling	59,000	1.50

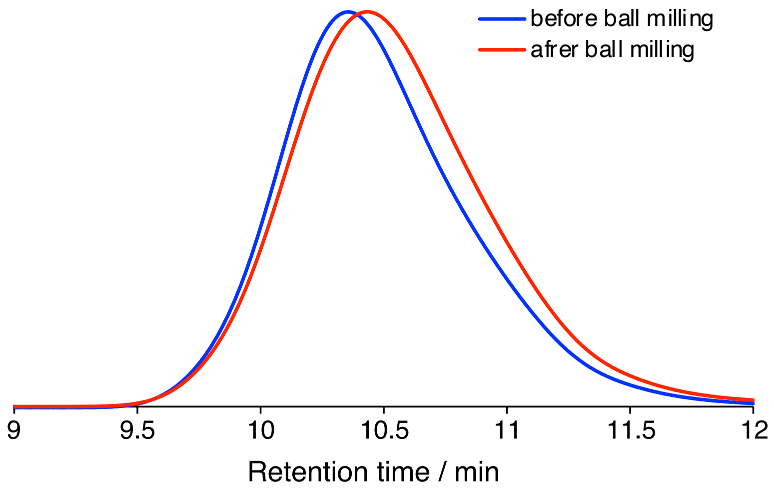
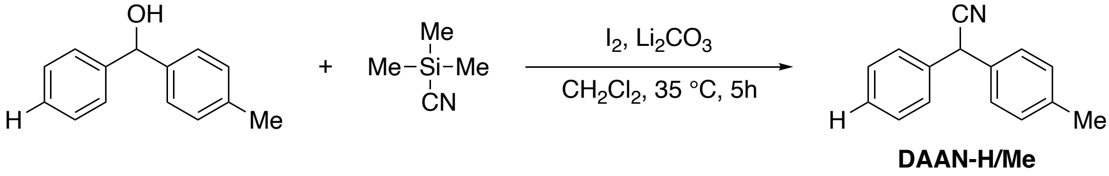


Figure S1. GPC curves of the polystyrene before and after ball milling (30 Hz, 10 min) (THF, RI).

4.2. Synthesis of **DAAN-H/Me**



DAAN-H/Me was synthesized according to the reported procedure.[2] Under a nitrogen atmosphere, 4-methylbenzhydrol (2.97 g, 15.0 mmol), Li_2CO_3 (222 mg, 3.00 mmol), and I_2 (1.76 g, 27.0 mmol) was dissolved in dry CH_2Cl_2 (250 mL). With stirring, trimethylsilyl cyanide (8.37 mL, 67.5 mmol) was added dropwise. Then the resulting mixture was stirred under closed conditions at 35 °C (water bath temperature) for 5 h. The reaction was quenched with saturated solution of $Na_2S_2O_3$. The organic phase was separated, and the aqueous layer was extracted with CH_2Cl_2. All the organic layers were collected, dried over $MgSO_4$, and concentrated *in vacuo* to yield the crude product. The crude product was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1/4, v/v) and dried in vacuo. After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo to give **DAAN-H/Me** as a white powder (2.95 g, 95% yield).

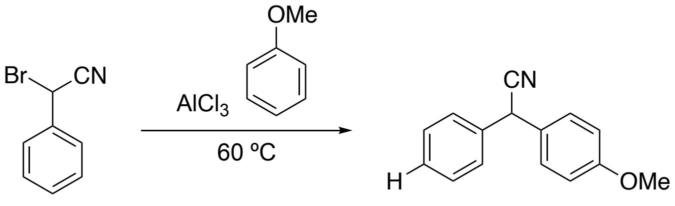
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.38–7.31 (m, 5H, aromatic), 7.23–7.22 (m, 2H, aromatic), 7.17 (d, J = 9.0 Hz, 2H, aromatic), 5.10 (s, 1H, –C*H*(CN)–), 2.34 (s, 3H, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 138.21, 136.27, 133.09, 129.97, 128.27, 127.78, 127.72, 119.97, 42.37, 21.21.

FT-IR (KBr, cm^{-1}): 3028, 2909, 2361, 2244, 1906, 1804, 1600, 1495, 1449, 1377, 1324, 1180, 1110, 1075, 1033, 974, 940, 909, 857, 802, 722, 690, 579, 526, 464.

EI-MS (m/z): $[M]^+$ calcd for $C_{15}H_{13}N$, 207.1048; found, 207.1053.

4.3. Synthesis of **DAAN-H/OMe**



DAAN-H/OMe

DAAN-H/OMe was synthesized according to the reported procedure.[3] Under a nitrogen atmosphere, aluminum chloride (3.57 mg, 26.8 mmol) and 2-bromo-2-phenylacetonitrile (5.00 g, 25.5 mmol) was dissolved in anisole (15 mL) at room temperature. The reaction mixture was heated to 60 ºC for 1.5 h, then cooled to room temperature and poured into the solution of hydrochloric acid (20 mL) in ice water (100 mL). The organic phase was separated, and the water phase was extracted with toluene (3 ×100 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed. The residue was recrystallized from acetone/methanol to give **DAAN-H/OMe** as a white solid (3.70 g, 65% yield).

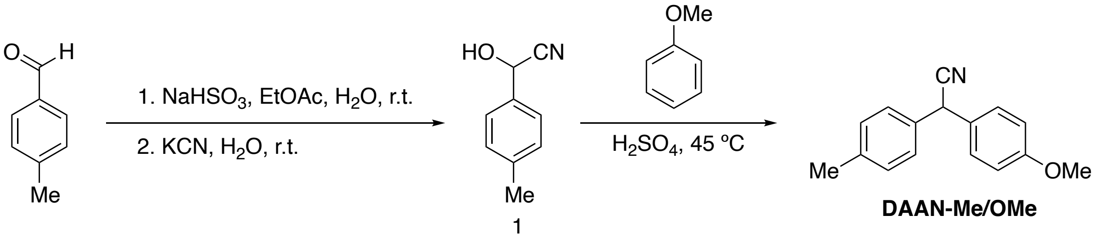
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.38–7.30 (m, 5H, aromatic), 7.26–7.24 (d, J = 8.3 Hz, 2H, aromatic), 6.90–6.88 (d, J = 8.5 Hz, 2H, aromatic), 5.09 (s, 1H, –C*H*(CN)–), 3.79 (s, 3H, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 159.53, 136.32, 129.24, 129.00, 128.24, 128.05, 127.72, 120.00, 114.63, 55.45, 41.93.

FT-IR (KBr, cm^{-1}): 2960, 2904, 2364, 2245, 1610, 1585, 1512, 1494, 1451, 1305, 1260, 1179, 1111, 1030, 825, 779, 723, 692, 649, 591, 545, 478, 447, 418.

EI-MS (m/z): $[M]^+$ calcd for $C_{15}H_{13}NO$, 223.0997; found, 223.0995.

4.4. Synthesis of **DAAN-Me/OMe**



【First step】

In a two-neck round bottom flask, a solution of 4-tolualdehyde (7.07 mL, 60.0 mmol) in ethyl acetate (120 mL) was formed. With stirring, a solution of sodium bisulfite (12.5 g, 120 mmol) in water (60.0 mL) was added at room temperature. The mixture was allowed to stir at room temperature for 1 h, and then a solution of KCN (7.81 g, 120 mmol) in water (120 mL) was added dropwise at 0°C. Once the additional was complete, the mixture was allowed to stir for 16 h as it warmed to room temperature. The reaction mixture was extracted with ethyl acetate, then the combined organic extracts were washed with brine and were dried over Na_2SO_4. After filtration, evaporation, and recrystallization from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo to give compound **1** as a white crystal (7.56 g, 86% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.46-7.41 (m, 2H, aromatic), 7.26–7.25 (m, 2H, aromatic), 5.51 (d, *J* = 7.2 Hz, 1H, –*CH*(CN)OH), 2.56 (d, *J* = 7.2 Hz, 1H, –*OH*), 2.39 (s, 3H, –CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 139.94, 132.26, 129.84, 126.74, 119.13, 63.30, 21.28.

【Second step】

In a two-neck round bottom flask, 4-methylmandelonitrile (compound **1**) (501 mg, 3.0 mmol) was dissolved in anisole (2.5 mL, 23 mmol). With stirring, 96% sulfuric acid (80 μL) was added, and the mixture was allowed to stir at 45 °C for 48 h. After cooling to room temperature, the liquid was decanted and the remaining solid was dissolved in ethyl acetate. The solution was washed with water and brine, and then dried over $NaSO_4$. After filtration and evaporation, and recrystallization from mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo. After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo to give **DAAN-Me/OMe** as a white powder (360 mg, 72% yield).

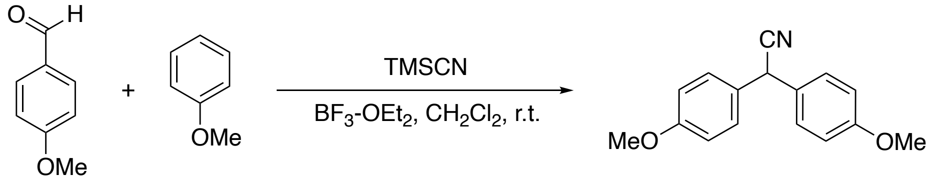
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.25–7.22 (m, 4H, aromatic), 7.16 (d, *J* = 7.8 Hz, 2H, aromatic), 6.88 (d, *J* = 8.4 Hz, 2H, aromatic), 5.05 (s, 1H, –C*H*(CN)–), 3.79 (s, 3H, OCH_3), 2.33 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 159.50, 138.08, 133.45, 129.93, 128.95, 128.35, 127.62, 120.24, 114.62, 55.45, 41.57, 21.19.

FT-IR (KBr, cm^{-1}): 2961, 2932, 2841, 2243, 1889, 1657, 1610, 1581, 1511, 1452, 1300, 1265, 1179, 1112, 1028, 975, 870, 843, 813, 761, 698, 634, 598, 532, 505, 422.

EI-MS (m/z): $[M]^+$ calcd for $C_{16}H_{15}NO$, 237.1155; found, 237.1154.

4.5. Synthesis of **DAAN-OMe/OMe**



DAAN-OMe/OMe

DAAN-OMe/OMe was synthesized according to the reported procedure.[4] To a stirred solution of 4-methoxybenzaldehyde (4.80 mL, 39.5 mmol), anisole (5.12 mL, 47.4 mmol, 1.2 equiv), and trimethylsilyl cyanide (7.34 mL, 59.2 mmol, 1.5 equiv) in CH_2Cl_2 (200 mL) at 0 °C was added BF_3-OEt_2 (5.95 mL, 47.4 mmol, 1.2 equiv). After being stirred at room temperature for 5.5 h, the reaction mixture was diluted with CH_2Cl_2, washed with aq. $NaHCO_3$ and water. All the organic layers were collected, dried over $MgSO_4$. After filtration, evaporation, and recrystallization from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo to give **DAAN-OMe/OMe** as a white crystal (8.22 g, 82% yield).

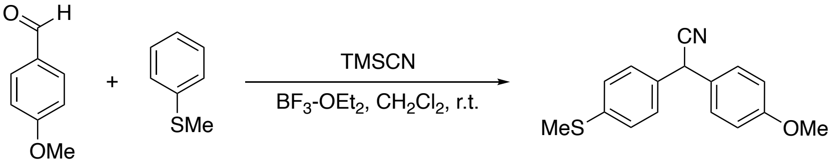
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.23 (d, *J* = 8.6 Hz, 4H, aromatic), 6.89 (d, *J* = 8.5 Hz, 4H, aromatic), 5.04 (s, 1H, –C*H*(CN)–), 3.79 (s, 6H, OC*H*3)

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 159.45, 128.89, 128.37, 120.23, 114.57, 55.45, 41.15.

FT-IR (NaBr, cm^{-1}): 3052, 3005, 2964, 2934, 2899, 2838, 2243, 1889.9, 1609, 1582, 1446, 1334, 1177 , 1115, 970, 865, 812, 808, 768, 632, 595, 542, 512.

EI-MS (m/z): $[M]^+$ calcd for $C_{16}H_{15}NO_2$, 253.1103; found, 253.1102.

4.6. Synthesis of **DAAN-SMe/OMe**



DAAN-SMe/OMe

To a stirred solution of 4-methoxybenzaldehyde (4.51 mL, 37.1 mmol), thioanisole (5.22 mL, 44.6 mmol, 1.2 equiv), and trimethylsilyl cyanide (6.91 mL, 55.7 mmol, 1.5 equiv) in CH_2Cl_2 (160 mL) at 0 °C was added BF_3-OEt_2 (5.60 mL, 44.6 mmol, 1.2 equiv). After being stirred at room temperature for 3.5 h, the reaction mixture was diluted with CH_2Cl_2, washed with aq. $NaHCO_3$ and water. All the organic layers were collected, dried over $MgSO_4$, and concentrated *in vacuo* to yield the crude product. After that, the crude product was poured into the methanol, and corresponding products was precipitated out. The precipitate was purified by recrystallization from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried *in vacuo* to give **DAAN-SMe/OMe** as a white powder (7.24 g, 72% yield).

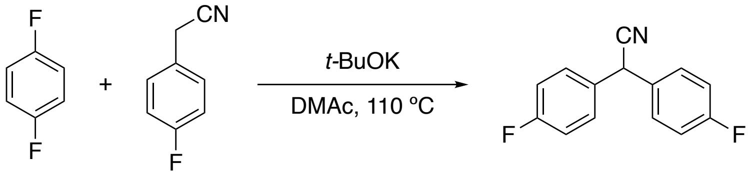
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.26–7.22 (m, 6H, aromatic), 6.89 (d, *J* = 8.7 Hz, 2H, aromatic), 5.05 (s, 1H, –C*H*(CN)–), 3.80 (s, 3H, OC*H*3), 2.47 (s, 3H, SC*H*3)

^{13}C NMR (100 MHz, CDCl$_3$): δ/ppm 159.56, 139.04, 132.94, 128.96, 128.06, 126.98, 119.92, 114.66, 55.47, 41.42, 15.71.

FT-IR (NaBr, cm^{-1}): 3854, 3819, 3748, 3651, 3417, 2960, 2365, 2241, 1607, 1510, 1433, 1303, 1256, 1178, 1092, 1027, 842, 815, 798, 766, 682, 629, 581, 541, 514.

EI-MS (m/z): [M]$^+$ calcd for $C_{16}H_{15}NOS$, 269.0874; found, 269.0872.

4.7. Synthesis of **DAAN-F/F**



DAAN-F/F

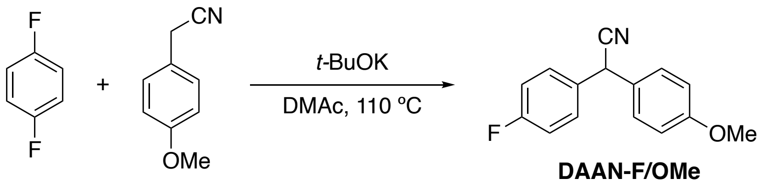
Under a nitrogen atmosphere, *t*-BuOK (19.6 g, 175 mmol) was dissolved in dry DMAc (150 mL) at 110 °C. After 15 min, 4-fluorobenzyl cyanide (5.17 mL, 43.6 mmol) and 1,4-difluorobenzene (5.18 mL, 65.4 mmol) were added. The reaction mixture was stirred for 3 h at 110 °C. The reaction mixture was cooled to r.t., and poured into water. The mixture was neutralized to pH 7 using HCl aq., extracted with toluene, washed with water and brine, dried over anhydrous Na_2SO_4. After filtration and evaporation, the crude product was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1/4, v/v) and dried in vacuo to give. After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo to give **DAAN-F/F** as a white solid (5.22 g, 52% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ/ppm 7.31–7.29 (m, 4H, aromatic), 7.09–7.06 (m, 4H, aromatic), 5.11 (s, 1H, –C*H*(CN)–).

^{13}C NMR (100 MHz, CDCl$_3$): δ/ppm 162.62 (d, J = 247 Hz) 131.63, 129.53 (d, J = 8 Hz), 116.38 (d, J = 22 Hz), 41.22.

FT-IR (KBr, cm^{-1}): 3740, 3081, 2364, 2245, 1887, 1766, 1607, 1419, 1301, 1238, 1165, 1100, 1017, 973, 858, 824, 772, 582, 542, 499, 415.

EI-MS (m/z): [M]$^+$ calcd for $C_{14}H_9F_2O$, 229.0703; found, 229.0697.

4.8. Synthesis of **DAAN-F/OMe**



DAAN-F/OMe

Under a nitrogen atmosphere, *t*-BuOK (18.6 g, 166 mmol) was dissolved in dry DMAc (180 mL) at 110 °C. After 15 min, 4-methoxyphenylacetonitrile (5.60 mL, 41.5 mmol) and 1,4-difluorobenzene (4.93 mL, 62.2 mmol) were added. The reaction mixture was stirred for 4 h at 110 ºC. The reaction mixture was cooled to r.t., and poured into water. The mixture was neutralized to pH 7 using HCl aq., extracted with toluene, washed with water and brine, dried over anhydrous Na_2SO_4. After filtration, evaporation and recrystallization from a mixed solvent of chloroform and methanol, the precipitate collected by filtration was dried in vacuo. After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo to give **DAAN-F/OMe** as a white crystal (5.88 g, 59% yield).

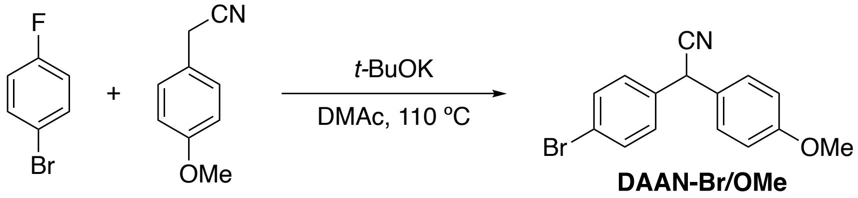
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.31–7.29 (m, 2H, aromatic), 7.23 (d, *J* = 8.4 Hz, 2H, aromatic), 7.07–7.04 (m, 2H, aromatic), 6.90 (d, *J* = 8.3 Hz, 2H, aromatic), 5.07 (s, 1H, –C*H*(CN)–), 3.80 (s, 3H, OC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 162.48 (d, *J* = 249 Hz) , 159.64, 132.19, 129.51 (d, *J* = 8 Hz), 128.94, 127.76, 119.82, 116.09 (d, *J* = 22 Hz), 114.72, 55.46, 41.20.

FT-IR (KBr, cm^{-1}): 3741, 2906, 2363, 2245, 1606, 1508, 1456, 1303, 1256, 1232, 1179, 1110, 1028, 822, 783, 592, 542, 505.

EI-MS (m/z): $[M]^+$ calcd for $C_{15}H_{12}FNO$, 241.0903; found, 241.0906.

4.9. Synthesis of **DAAN-Br/OMe**



In a two-neck round bottom flask, *t*-BuOK (11.1 g, 99.3 mmol) was dissolved in DMAc (100 mL) at 110 °C. After 10 min, 4-methoxyphenylacetonitrile (4.47 mL, 33.1 mmol) and 4-bromofluorobenzene (6.52 mL, 59.6 mmol) were added. The reaction mixture was stirred for 3 h at 110 ºC. The reaction mixture was cooled to r.t., and poured into water. The mixture was neutralized to pH 7 using HCl aq., extracted with toluene, washed with water and brine, dried over anhydrous Na_2SO_4. After filtration, evaporation and recrystallization from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo. After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo to give **DAAN-Br/OMe** as a white crystal (8.82 g, 88% yield).

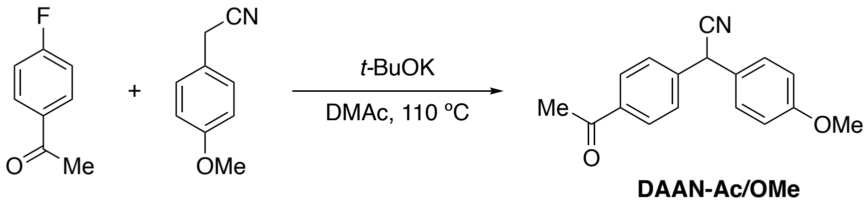
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.50 (d, *J* = 8.3, 2H, aromatic), 7.23–7.20 (m, 4H, aromatic), 6.90 (d, *J* = 8.4 Hz, 2H, aromatic), 5.05 (s, 1H, –C*H*(CN)–), 3.80 (s, 3H, OC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 159.70, 135.40, 132.38, 129.39, 128.94, 127.36, 122.39, 119.46, 114.73, 55.48, 41.43.

FT-IR (KBr, cm^{-1}): 3741, 3674, 3445, 2963, 2896, 2840, 2363, 2246, 1610, 1512, 1486, 1455, 1412, 1303, 1259, 1180, 1117, 1071, 1030, 823, 797, 764, 674, 594, 539, 512, 423.

EI-MS (m/z): $[M]^+$ calcd for $C_{15}H_{12}BrNO$, 301.0102; found, 301.0101.

4.10. Synthesis of **DAAN-Ac/OMe**



Under a nitrogen atmosphere, *t*-BuOK (16.9 g, 151 mmol) was dissolved in dry DMAc (150 mL) at 110 °C. After 15 min, 4-methoxyphenylacetonitrile (5.09 mL, 37.7 mmol) and 4-fluoroacetophenone (6.62 mL, 56.5 mmol) were added. The reaction mixture was stirred for 4 h at 110 ºC. The reaction mixture was cooled to rte., and poured into water. The mixture was neutralized to pH 7 using HCl aq., extracted with toluene, washed with water and brine, dried over anhydrous Na_2SO_4. After filtration, evaporation and recrystallization from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo. After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo to give **DAAN-Ac/OMe** as a white crystal (7.83 g, 78% yield).

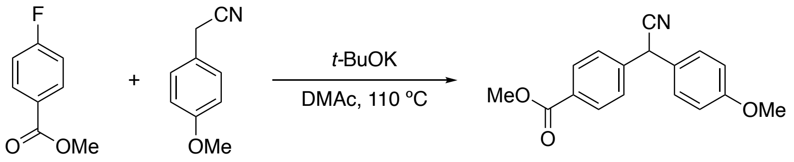
^1H NMR (500 MHz, $CDCl_3$): δ/ppm 7.96 (d, *J* = 8.1, 2H, aromatic), 7.45 (d, *J* = 8.1, 2H, aromatic), 7.24 (d, *J* = 8.8, 2H, aromatic), 6.90 (d, *J* = 8.8 Hz, 2H, aromatic), 5.14 (s, 1H, –C*H*(CN)–), 3.80 (s, 3H, OCH_3), 2.59 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 197.32, 159.74, 141.27, 136.88, 129.24, 129.00, 127.96, 127.22, 119.40, 114.82, 55.46, 41.79, 26.77.

FT-IR (KBr, cm^{-1}): 3741, 2962, 2364, 2247, 1685, 1607, 1512, 1456, 1419, 1360, 1302, 1265, 1180, 1116, 1026, 958, 827, 804, 768, 731, 693, 601, 519.

EI-MS (m/z): $[M]^+$ calcd for $C_{17}H_{15}NO_2$, 265.1103; found, 265.1103.

4.11. Synthesis of **DAAN-COOMe/OMe**



DAAN-COOMe/OMe

Under a nitrogen atmosphere, *t*-BuOK (16.0 g, 142 mmol) was dissolved in dry DMAc (150 mL) at 110 °C. After 15 min, 4-methoxyphenylacetonitrile (4.80 mL, 35.6 mmol) and methyl 4-fluorobenzoate (6.85 mL, 53.3 mmol) were added. The reaction mixture was stirred for 3 h at 110 °C. The reaction mixture was cooled to r.t., and poured into water. The mixture was neutralized to pH 7 using HCl aq., extracted with toluene, washed with water and brine, dried over anhydrous Na_2SO_4. After filtration and evaporation, the crude product was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (3/7, v/v) and dried in vacuo. After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo to give **DAAN-COOMe/OMe** as a white solid (6.35 g, 64% yield).

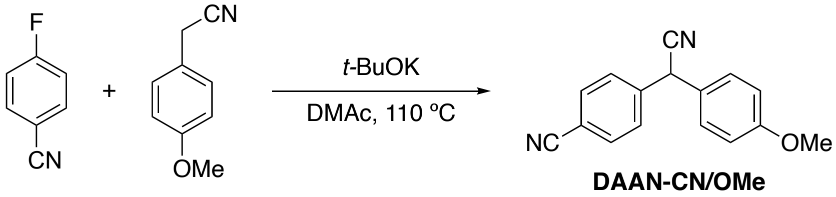
^1H NMR (500 MHz, $CDCl_3$): δ/ppm 8.04 (d, *J* = 8.1, 2H, aromatic), 7.42 (d, *J* = 8.1, 2H, aromatic), 7.23 (d, *J* = 8.4, 2H, aromatic), 6.90 (d, *J* = 8.4 Hz, 2H, aromatic), 5.14 (s, 1H, –C*H*(CN)–), 3.91 (s, 3H, $COOCH_3$), 3.80 (s, 3H, OCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 166.41, 159.72, 141.11, 130.49, 130.15, 129.01, 127.76, 127.26, 119.42, 114.79, 55.45, 52.37, 41.83.

FT-IR (KBr, cm^{-1}): 3859, 3741, 3674, 3651, 3614, 3565, 3003, 2960, 2839, 2362, 2245, 1719, 1651, 1611, 1539, 1512, 1437, 1285, 1254, 1176, 1111, 1025, 867, 829, 776, 736, 696, 592, 543, 491, 468, 416.

EI-MS (m/z): $[M]^+$ calcd for $C_{17}H_{15}NO_2$, 281.1052; found, 281.1053.

4.12. Synthesis of **DAAN-CN/OMe**



Under a nitrogen atmosphere, *t*-BuOK (18.1 g, 161 mmol) was dissolved in dry DMAc (140 mL) at 110 °C. After 15 min, 4-methoxyphenylacetonitrile (5.44 mL, 40.3 mmol) and 4-fluorobenzonitrile (7.32 mg, 60.4 mmol) were added. The reaction mixture was stirred for 4 h at 110 ºC. The reaction mixture was cooled to r.t., and poured into water. The mixture was neutralized to pH 7 using HCl aq., extracted with toluene, washed with water and brine, dried over anhydrous Na_2SO_4. After filtration, evaporation and recrystallization from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo. After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo to give **DAAN-CN/OMe** as a white crystal (6.40 g, 64% yield).

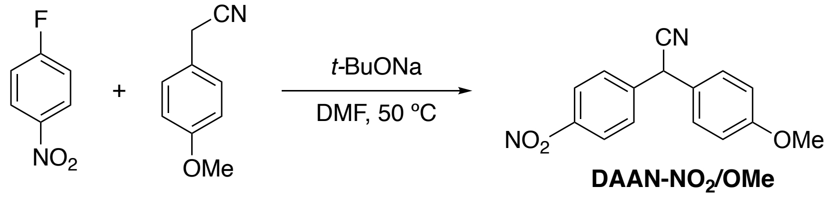
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.67 (d, *J* = 8.1, 2H, aromatic), 7.47 (d, *J* = 8.0, 2H, aromatic), 7.22 (d, *J* = 8.4, 2H, aromatic), 6.91 (d, *J* = 8.4 Hz, 2H, aromatic), 5.14 (s, 1H, –C*H*(CN)–), 3.81 (s, 3H, OC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 159.92, 141.47, 133.03, 129.06, 128.52, 126.60, 118.98, 118.26, 114.97, 112.37, 55.51, 41.84.

FT-IR (KBr, cm^{-1}): 3741, 2962, 2914, 2363, 2236, 1609, 1509, 1452, 1415, 1297, 1262, 1179, 1116, 1025, 870, 830, 806, 768, 695, 596, 568, 544, 517.

EI-MS (m/z): $[M]^+$ calcd for $C_{16}H_{12}N_2O$, 248.0950; found, 248.0945.

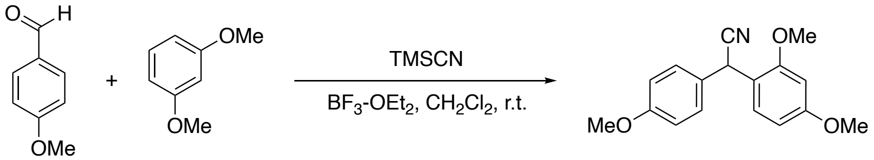
4.13. Synthesis of **DAAN-NO$_2$/OMe**



DAAN-NO$_2$/OMe was synthesized according to the reported procedure.[5] Under a nitrogen atmosphere, *t*-BuONa (5.78 g, 60.0 mmol) was dissolved in dry DMF (60 mL) at 50 °C. After 10 min, 4-methoxyphenylacetonitrile (2.70 mL, 20 mmol) and 4-fluoronitrobenzene (3.53 mL, 30.0 mmol) were added dropwise. The reaction mixture was stirred for 2 h and then poured into water and extracted with toluene. The organic phase was washed with water and brine, dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude product was purified by column chromatography on silica gel with chloroform/hexane (1/2, v/v) and dried in vacuo. After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo to give **DAAN-NO$_2$/OMe** as a yellow solid (3.20 g, 60% yeild).

^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 8.23 (d, *J* = 8.5, 2H, aromatic), 7.54 (d, *J* = 8.4, 2H, aromatic), 7.24 (d, *J* = 8.4, 2H, aromatic), 6.91 (d, *J* = 8.3 Hz, 2H, aromatic), 5.19 (s, 1H, –C*H*(CN)–), 3.81 (s, 3H, OC*H*3).
^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 159.96, 147.71, 143.35, 129.07, 128.73, 126.53, 124.44, 118.98, 115.01, 55.51, 41.61.
FT-IR (KBr, cm^{-1}): 3740, 3110, 2937, 2841, 2362, 1608, 1513, 1345, 1254, 1181, 1109, 1028, 869, 828, 797, 736, 691, 584, 539.
EI-MS (m/z): [M]$^+$ calcd for $C_{15}H_{12}N_2O_3$, 268.0848; found, 268.0853.

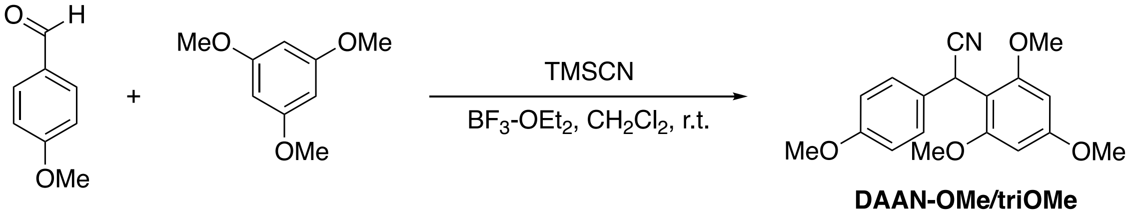
4.14. Synthesis of **DAAN-OMe/diOMe**



DAAN-OMe/diOMe

DAAN-OMe/diOMe was synthesized according to the reported procedure.[4] To a stirred solution of 4-methoxybenzaldehyde (4.29 mL, 35.3 mmol), 1,3-dimethoxybenzene (5.47 mL, 42.4 mmol, 1.2 equiv), and trimethylsilyl cyanide (6.57 mL, 52.9 mmol, 1.5 equiv) in CH_2Cl_2 (180 mL) at 0 °C was added BF_3-OEt_2 (5.32 mL, 42.4 mmol, 1.2 equiv). After being stirred at room temperature for 6 h, the reaction mixture was diluted with CH_2Cl_2, washed with aq. $NaHCO_3$ and water. All the organic layers were collected, dried over $MgSO_4$, and concentrated *in vacuo* to yield crude product. The crude product was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (3/7, v/v) and dried in vacuo. After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo to give **DAAN-OMe/diOMe** as a white powder (7.40 g, 74% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.26 (d, *J* = 8.7 Hz, 2H, aromatic), 7.18 (d, *J* = 8.2 Hz, 1H, aromatic), 6.86 (d, *J* = 8.8 Hz, 2H, aromatic), 6.48–6.46 (m, 2H, aromatic), 5.40 (s, 1H, –C*H*(CN)–), 3.83 (s, 3H, OC*H*3), 3.79 (s, 6H, OC*H*3).
^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 161.07, 159.22, 157.22, 129.41, 128.87, 128.11, 120.56, 117.45, 114.32, 104.86, 98.98, 55.74, 55.54, 55.40, 35.24.
FT-IR (KBr, cm^{-1}): 3001, 2939, 2833, 2365, 2243, 1610, 1508, 1462, 1344, 1299, 1258, 1209, 1179, 1157, 1128, 1035, 927, 837, 799, 770, 637, 607, 526, 472.
EI-MS (m/z): [M]$^+$ calcd for $C_{17}H_{17}NO_3$, 283.1208; found, 283.1206.

4.15. Synthesis of **DAAN-OMe/triOMe**



DAAN-OMe/triOMe

DAAN-OMe/triOMe was synthesized according to the reported procedure.[4] To a stirred solution of 4-methoxybenzaldehyde (3.88 mL, 31.9 mmol), 1,3,5-trimethoxybenzene (6.44 g, 38.3 mmol, 1.2 equiv), and trimethylsilyl cyanide (5.94 mL, 47.9 mmol, 1.5 equiv) in CH_2Cl_2 (190 mL) at 0 °C was added BF_3-OEt_2 (4.81 mL, 38.3 mmol, 1.2 equiv). After being stirred at room temperature for 7.5 h, the reaction mixture was diluted with CH_2Cl_2, washed with aq. $NaHCO_3$ and water. All the organic layers were collected, dried over $MgSO_4$, and concentrated *in vacuo* to yield crude product. The crude product was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (3/7, v/v) and dried in vacuo. After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried *in vacuo* to give **DAAN-OMe/triOMe** as a white powder (6.96 g, 70% yield).

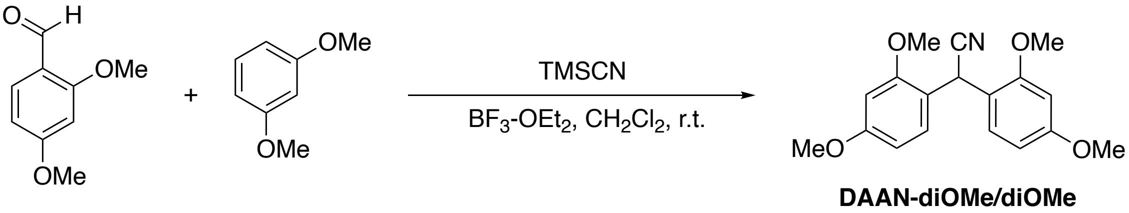
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.29 (d, *J* = 8.7 Hz, 2H, aromatic), 6.81 (d, *J* = 8.7 Hz, 2H, aromatic), 6.13 (s, 2H, aromatic), 5.69 (s, 1H, –C*H*(CN)–), 3.82 (s, 6H, OC*H*3), 3.80 (s, 3H, OC*H*3), 3.77 (s, 3H, OC*H*3).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 161.56, 158.74, 158.36, 128.53, 128.25, 120.30, 113.84, 105.61, 91.21, 56.03, 55.50, 55.34, 29.90.

FT-IR (KBr, cm^{-1}): 3004, 2944, 2839, 2363, 2237, 1591, 1508, 1463, 1418, 1326, 1247, 1224, 1179, 1155, 1115, 1057, 1034, 948, 843, 810, 638, 588, 557, 526.

EI-MS (m/z): $[M]^+$ calcd for $C_{18}H_{19}NO_4$, 313.1314; found, 313.1311.

4.16. Synthesis of **DAAN-diOMe/diOMe**



DAAN-diOMe/diOMe was synthesized according to the reported procedure.[4] To a stirred solution of 2,4-dimethoxybenzaldehyde (5.30 g, 31.9 mmol), 1,3-dimethoxybenzene (4.95 mL, 38.3 mmol, 1.2 equiv), and trimethylsilyl cyanide (5.94 mL, 47.9 mmol, 1.5 equiv) in CH_2Cl_2 (200 mL) at 0 °C was added BF_3-OEt_2 (4.81 mL, 38.3 mmol, 1.2 equiv). After being stirred at room temperature for 6 h, the reaction mixture was diluted with CH_2Cl_2, washed with aq. $NaHCO_3$ and water. All the organic layers were collected, dried over $MgSO_4$, and concentrated *in vacuo* to yield crude product. The crude product was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (2/8, v/v) and dried *in vacuo.* After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried *in vacuo* to give **DAAN-diOMe/diOMe** as a white powder (7.32 g, 73% yield).

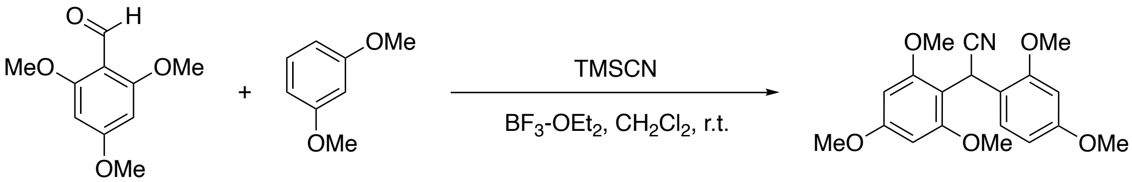
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.15 (d, *J* = 9.2 Hz, 2H, aromatic), 6.46–6.44 (m, 4H, aromatic), 5.51 (s, 1H, –C*H*(CN)–), 3.80–3.79 (m, 12H, OC*H*3).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 160.87, 157.62, 129.70, 120.57, 116.37, 104.36, 98.93, 55.74, 30.35.

FT-IR (KBr, cm^{-1}): 3009, 2936, 2837, 2365, 2242, 1614, 1589, 1504, 1462, 1335, 1292, 1269, 1211, 1163, 1117, 1033, 920, 834, 799, 636, 584, 510, 481.

EI-MS (m/z): $[M]^+$ calcd for $C_{18}H_{19}NO_4$, 313.1314; found, 313.1308.

4.17. Synthesis of **DAAN-diOMe/triOMe**



DAAN-diOMe/triOMe

To a stirred solution of 2,4,6-trimethoxybenzaldehyde (5.71 g, 29.1 mmol), 1,3-dimethoxybenzene (4.51 mL, 35.0 mmol, 1.2 equiv), and trimethylsilyl cyanide (5.42 mL, 43.7 mmol, 1.5 equiv) in CH_2Cl_2 (200 mL) at 0 °C was added BF_3-OEt_2 (4.39 mL, 35.0 mmol, 1.2 equiv). After being stirred at room temperature for 10 h, the reaction mixture was diluted with CH_2Cl_2, washed with aq. $NaHCO_3$ and water. All the organic layers were collected, dried over $MgSO_4$, and concentrated *in vacuo* to yield crude product. The crude product was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (2/8, v/v) and dried *in vacuo.* After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried *in vacuo* to give **DAAN-diOMe/triOMe** as a white powder (6.64 g, 66% yield).

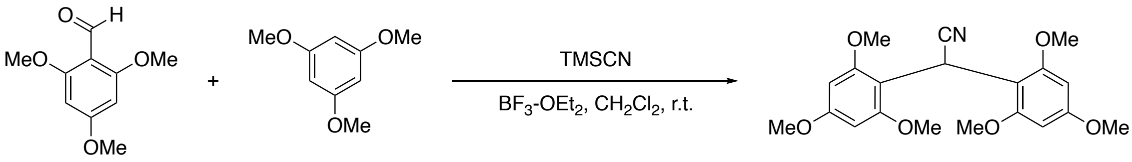
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.06 (d, *J* = 8.5 Hz, 1H, aromatic), 6.43 (d, *J* = 2.4 Hz, 1H, aromatic), 6.37 (m, 1H, aromatic), 6.16 (s, 2H, aromatic), 5.80 (s, 1H, –C*H*(CN)–), 3.84 (s, 3H, OC*H*$_3$), 3.82 (s, 3H, OC*H*$_3$), 3.81 (s, 6H, OC*H*$_3$), 3.77 (s, 3H, OC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 161.46, 160.50, 158.94, 157.89, 129.57, 120.54, 115.97, 104.12, 104.06, 98.54, 91.21, 56.00, 55.74, 55.45, 25.14.

FT-IR (KBr, cm^{-1}): 3001, 2933, 2840, 2365, 2238, 1602, 1503, 1459, 1419, 1336, 1294, 1271, 1209, 1182, 1153, 1119, 1039, 947, 920, 815, 778, 636, 583, 477.

EI-MS (m/z): [M]$^+$ calcd for $C_{19}H_{21}NO_5$, 343.1420; found, 343.1411.

4.18. Synthesis of **DAAN-triOMe/triOMe**



DAAN-triOMe/triOMe

To a stirred solution of 2,4,6-trimethoxybenzaldehyde (5.25 g, 26.8 mmol), 1,3,5-trimethoxybenzene (5.41 g, 32.1 mmol, 1.2 equiv), and trimethylsilyl cyanide (4.98 mL, 40.2 mmol, 1.5 equiv) in CH_2Cl_2 (200 mL) at 0 °C was added BF_3-OEt_2 (4.04 mL, 32.1 mmol, 1.2 equiv). After being stirred at room temperature for 13 h, the reaction mixture was diluted with CH_2Cl_2, washed with aq. $NaHCO_3$ and water. All the organic layers were collected, dried over $MgSO_4$, and concentrated *in vacuo* to yield crude product. The crude product was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (2/8, v/v) and dried *in vacuo.* After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried *in vacuo* to give **DAAN-triOMe/triOMe** as a white powder (6.11 g, 61% yield).

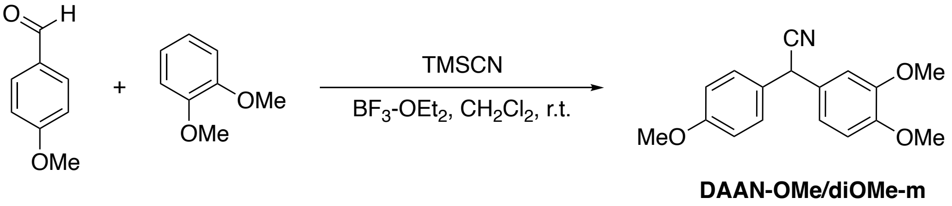
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 6.08 (s, 2H, aromatic), 5.88 (s, 1H, –C*H*(CN)–), 3.78 (s, 6H, OC*H*3), 3.76 (s, 6H, OC*H*3).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 160.55, 158.96, 121.05, 106.08, 91.13, 56.08, 55.34, 21.46.

FT-IR (KBr, cm^{-1}): 3003, 2941, 2840, 2363, 2232, 1599, 1496, 1464, 1420, 1334, 1230, 1206, 1153, 1130, 1059, 1037, 949, 816, 676, 638, 561, 473.

EI-MS (m/z): $[M]^+$ calcd for $C_{20}H_{23}NO_6$, 373.1525; found, 373.1517.

4.19. Synthesis of **DAAN-OMe/diOMe-m**



To a stirred solution of 4-methoxybenzaldehyde (4.29 mL, 35.3 mmol), 1,2-dimethoxybenzene (5.42 mL, 42.4 mmol, 1.2 equiv), and trimethylsilyl cyanide (6.57 mL, 47.9 mmol, 1.5 equiv) in CH_2Cl_2 (200 mL) at 0 °C was added BF_3-OEt_2 (5.32 mL, 42.4 mmol, 1.2 equiv). After being stirred at room temperature for 14 h, the reaction mixture was diluted with CH_2Cl_2, washed with aq. $NaHCO_3$ and water. All the organic layers were collected, dried over $MgSO_4$, and concentrated *in vacuo* to yield crude product. The crude product was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (3/7, v/v) and dried in vacuo. After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo to give **DAAN-diOMe/diOMe-m** as a white powder (5.34 g, 53% yield).

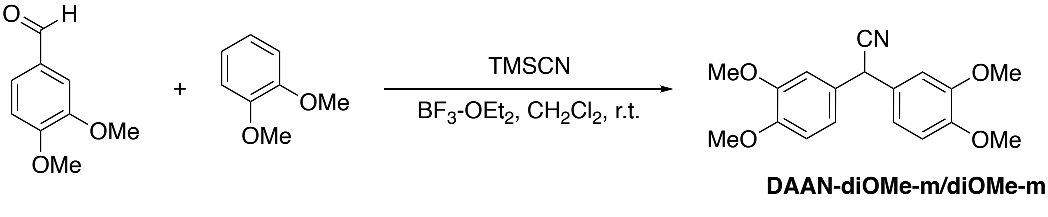
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.24 (d, *J* = 8.7 Hz, 2H), 6.89–6.82 (m, 4H, aromatic), 6.79 (d, *J* = 2.0 Hz, 1H, aromatic), 5.05 (s, 1H, –C*H*(CN)–), 3.85 (s, 3H, OC*H*3), 3.83 (s, 3H, OC*H*3), 3.78 (s, 3H, OC*H*3).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 159.48, 149.50, 148.98, 128.87, 128.67, 128.21, 120.23, 120.13, 114.56, 111.45, 110.76, 56.05, 55.42, 41.11.

FT-IR (KBr, cm^{-1}): 3043, 3003, 2964, 2935, 2902, 2842, 2602, 2241, 2037, 1887, 1844, 1593, 1512, 1455, 1420, 1348, 1302, 1247, 1177, 1149, 1022, 846, 817, 772, 743, 695, 642, 578, 513.

EI-MS (m/z): $[M]^+$ calcd for $C_{17}H_{17}NO_3$, 283.1208; found, 283.1207.

4.20. Synthesis of **DAAN-diOMe-m/diOMe-m**



To a stirred solution of 3,4-dimethoxybenzaldehyde (5.30 g, 31.9 mmol), 1,2-dimethoxybenzene (4.90 mL, 38.3 mmol, 1.2 equiv), and trimethylsilyl cyanide (5.94 mL, 47.9 mmol, 1.5 equiv) in CH_2Cl_2 (200 mL) at 0 °C was added BF_3-OEt_2 (4.81 mL, 38.3 mmol, 1.2 equiv). After being stirred at room temperature for 14 h, the reaction mixture was diluted with CH_2Cl_2, washed with aq. $NaHCO_3$ and water. All the organic layers were collected, dried over $MgSO_4$, and concentrated *in vacuo* to yield crude product. The crude product was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (3/7, v/v) and dried in vacuo. After that, obtained product was recrystallized from a mixed solvent of chloroform and hexane, the precipitate collected by filtration was dried in vacuo to give **DAAN-diOMe-m/diOMe-m** as a white powder (5.34 g, 53% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 6.90–6.84 (m, 4H, aromatic), 6.80 (d, *J* = 2.0 Hz, 2H, aromatic), 5.06 (s, 1H, –C*H*(CN)–), 3.87 (s, 6H, OCH_3), 3.85 (s, 6H, OCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 149.49, 149.03, 128.42, 120.16, 111.40, 110.74, 56.08, 56.05, 41.80.

FT-IR (KBr, cm^{-1}): 3074, 3012, 2956, 2936, 2836, 2597, 2235, 2043, 1841, 1594, 1517, 1463, 1420, 1340, 1258, 1210, 1181, 1146, 1024, 956, 902, 857, 785, 763, 740, 647, 630, 571.

EI-MS (m/z): $[M]^+$ calcd for $C_{18}H_{19}NO_4$, 313.1314; found, 313.1317.

5. *^{1}H NMR and ^{13}C NMR Spectra*

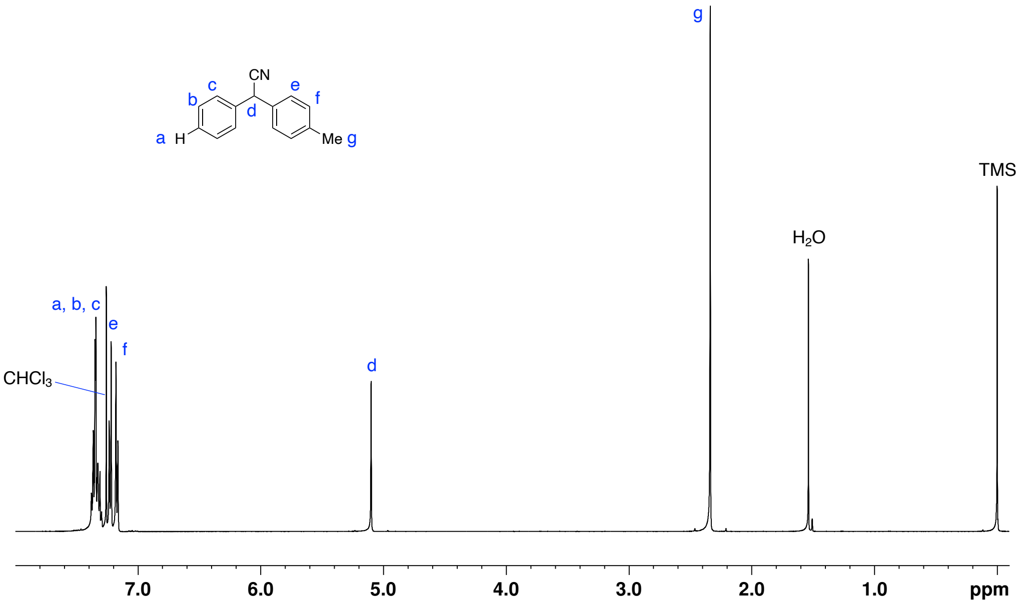


Figure S2. ^{1}H NMR spectrum of **DAAN-H/Me** (CDCl$_3$, 500 MHz).

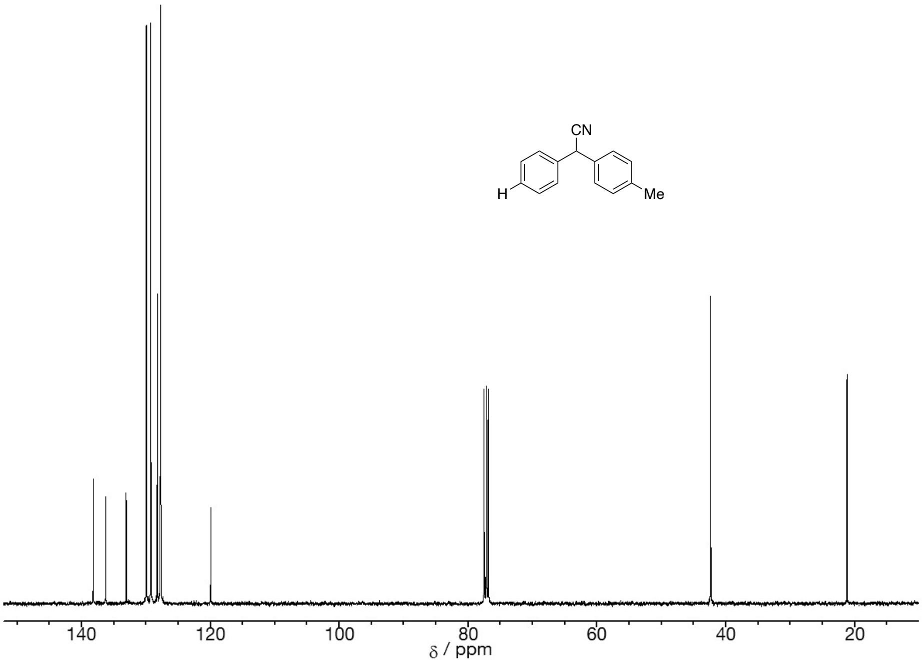


Figure S3. ^{13}C NMR spectrum of **DAAN-H/Me** (CDCl$_3$, 100 MHz).

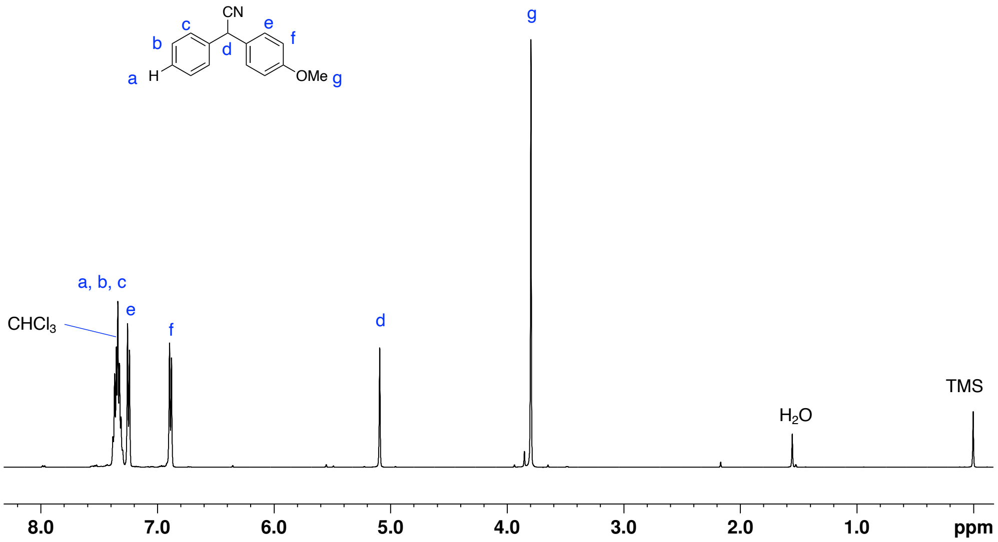


Figure S4. ^{1}H NMR spectrum of **DAAN-H/OMe** ($CDCl_3$, 500 MHz).

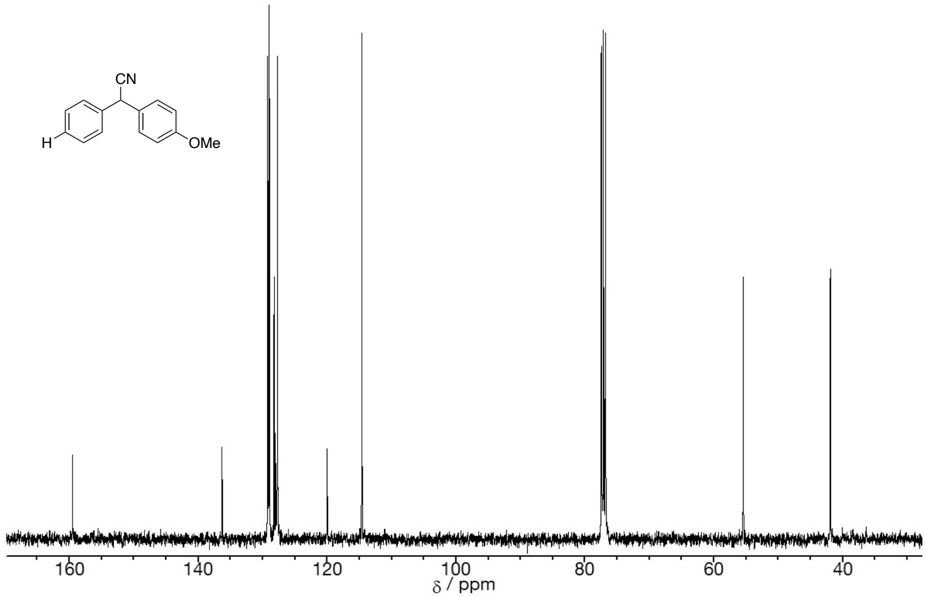


Figure S5. ^{13}C NMR spectrum of **DAAN-H/OMe** ($CDCl_3$, 100 MHz).

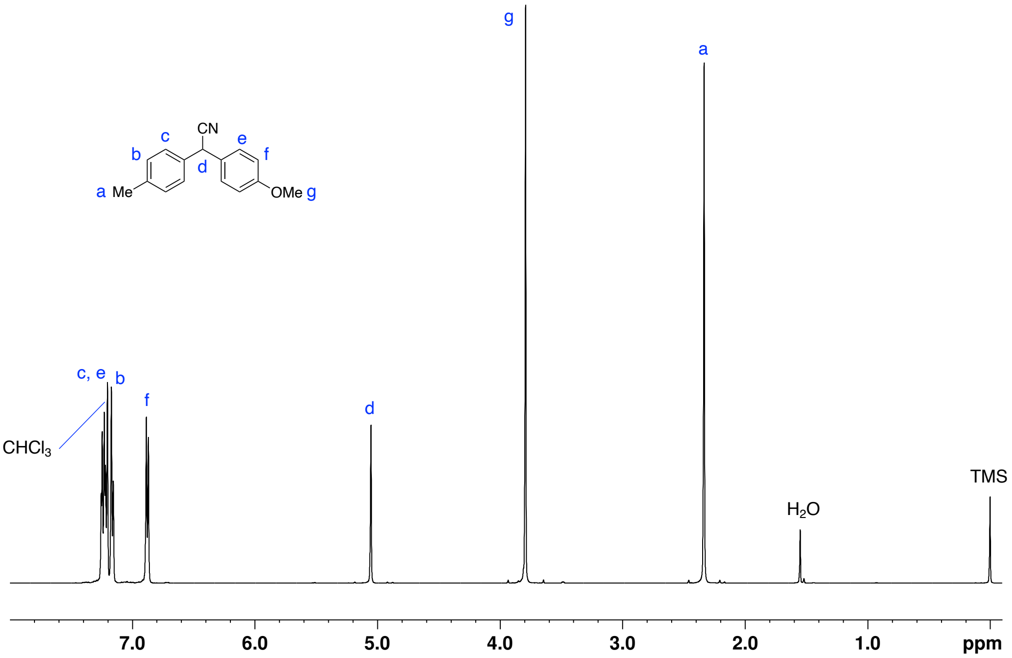


Figure S6. ^{1}H NMR spectrum of **DAAN-Me/OMe** (CDCl$_3$, 500 MHz).

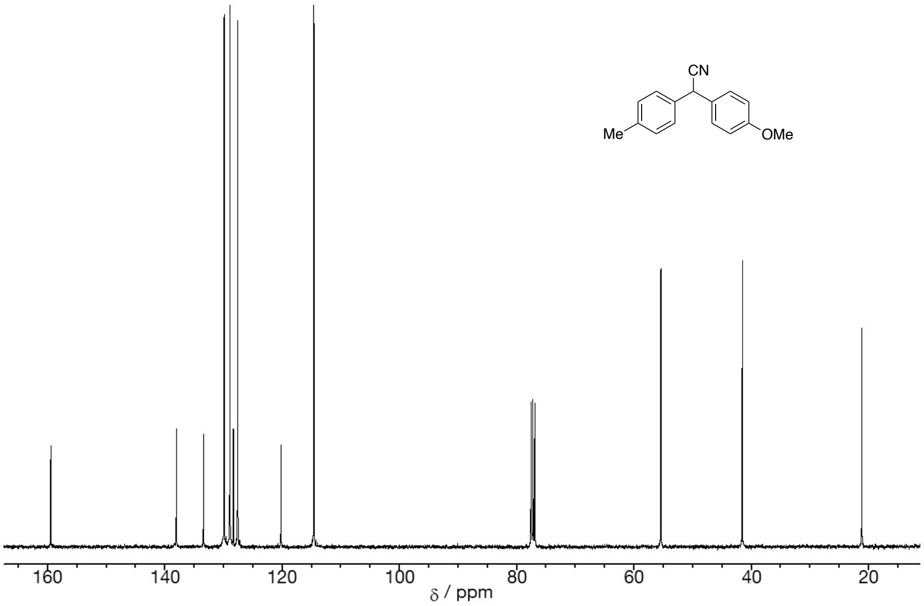


Figure S7. ^{13}C NMR spectrum of **DAAN-Me/OMe** (CDCl$_3$, 100 MHz).

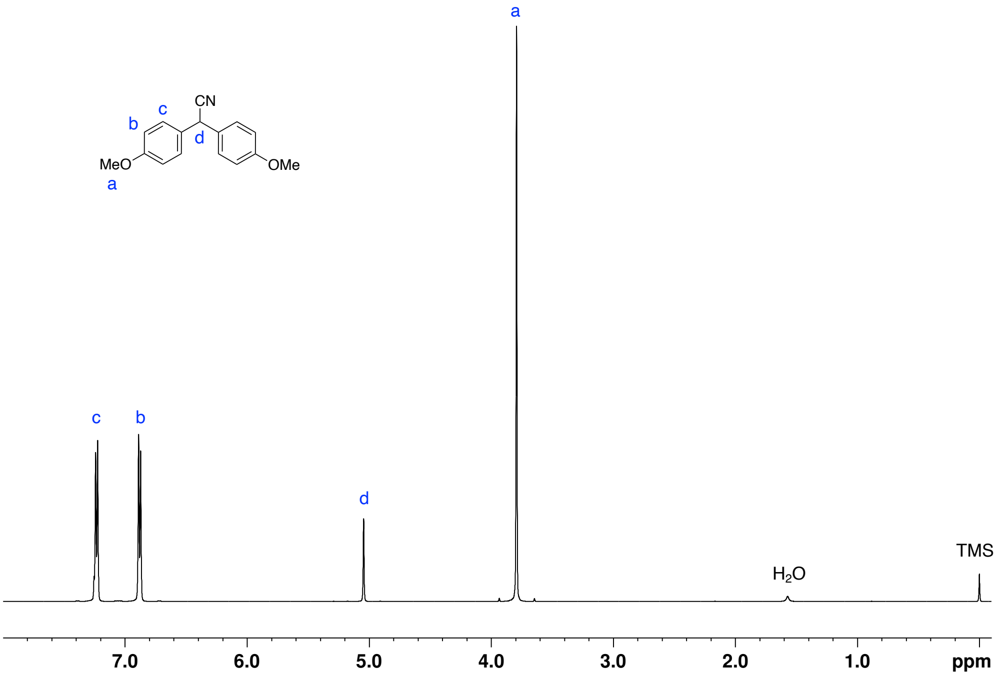


Figure S8. ^{1}H NMR spectrum of **DAAN-OMe/OMe** ($CDCl_3$, 500 MHz).

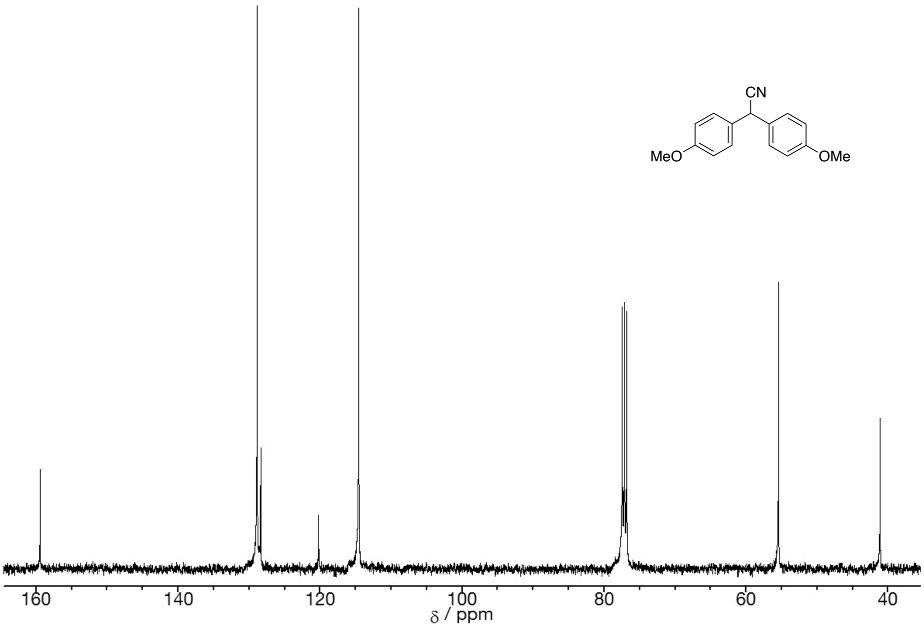


Figure S9. ^{13}C NMR spectrum of **DAAN-OMe/OMe** ($CDCl_3$, 100 MHz).

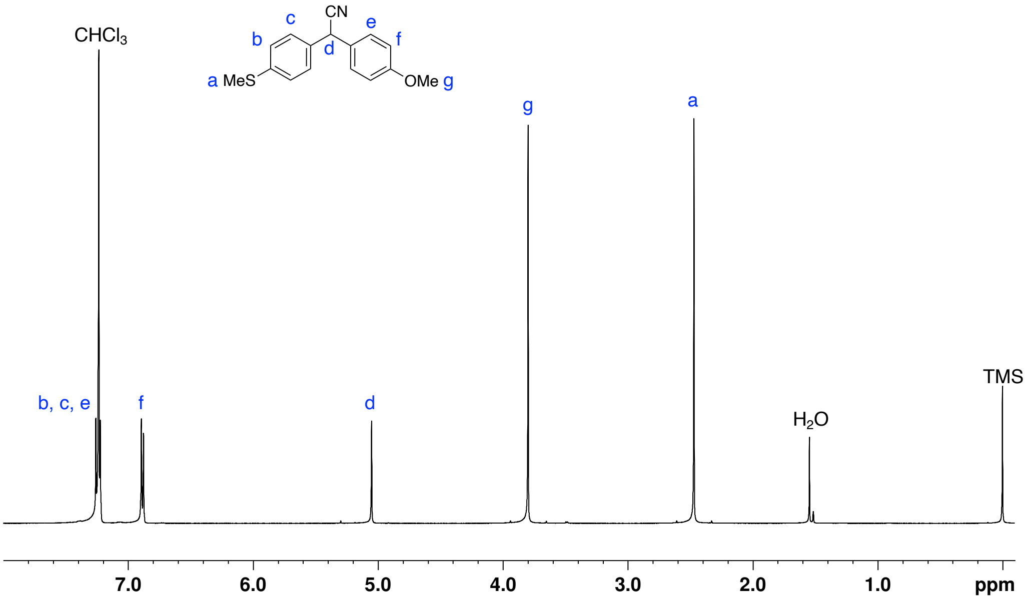


Figure S10. ^{1}H NMR spectrum of **DAAN-SMe/OMe** ($CDCl_3$, 500 MHz).

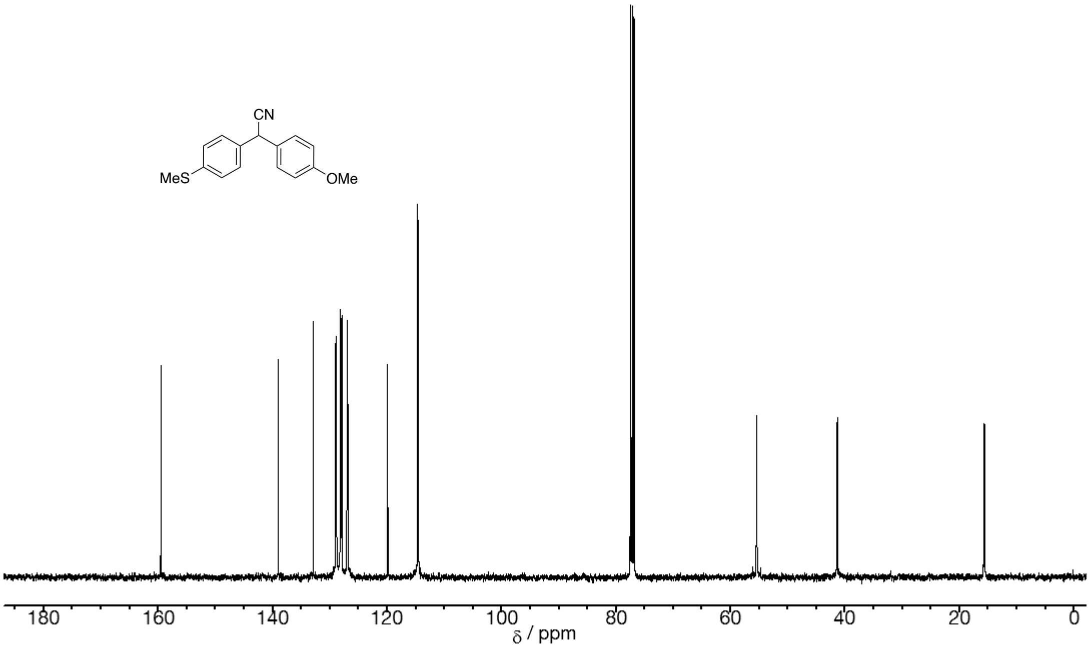


Figure S11. ^{13}C NMR spectrum of **DAAN-SMe/OMe** ($CDCl_3$, 100 MHz).

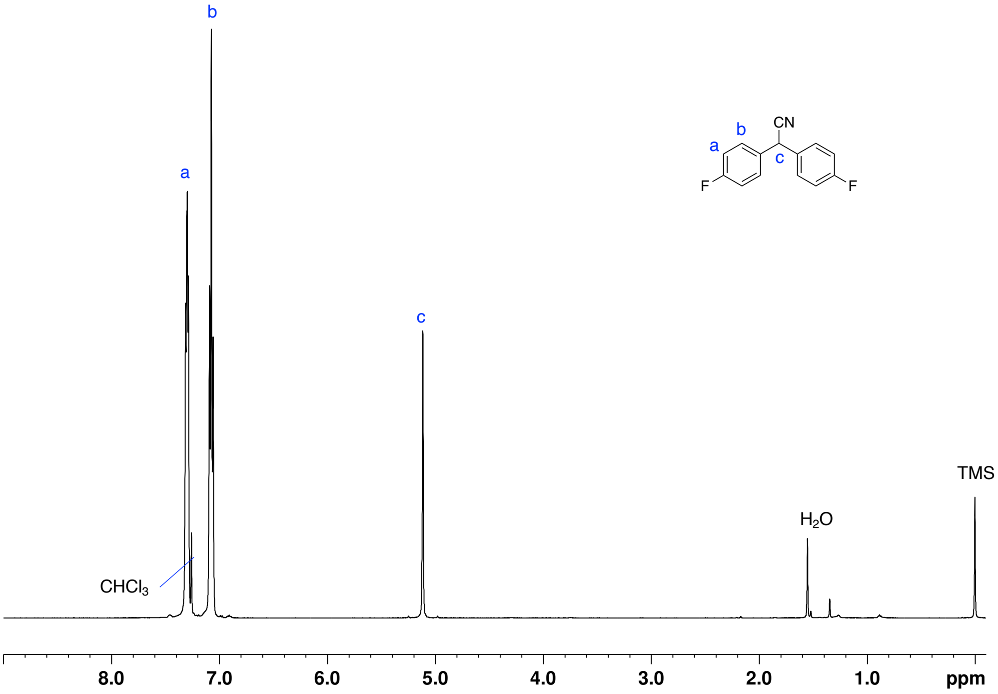


Figure S12. ^{1}H NMR spectrum of **DAAN-F/F** ($CDCl_3$, 500 MHz).

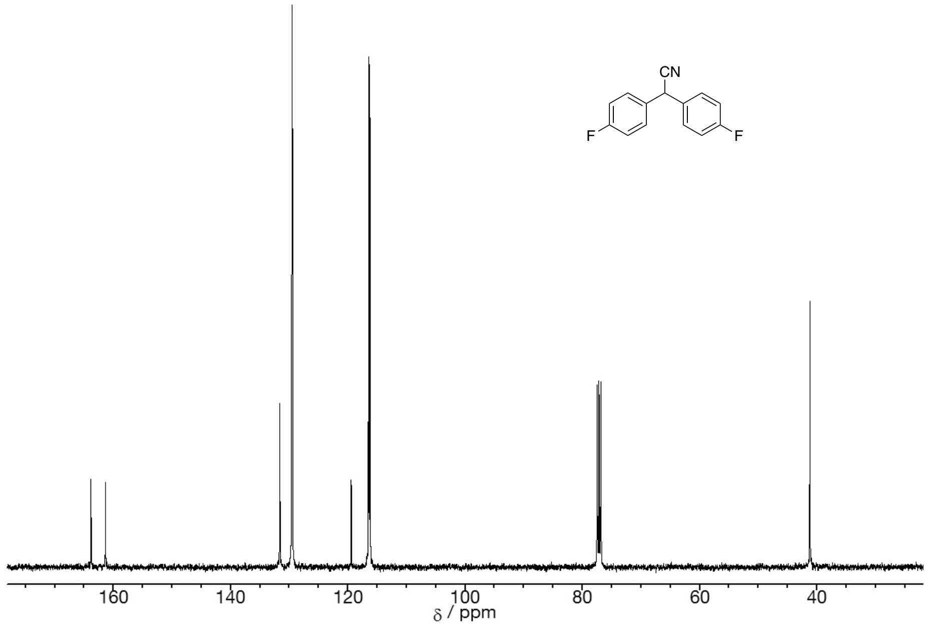


Figure S13. ^{13}C NMR spectrum of **DAAN-F/F** ($CDCl_3$, 100 MHz).

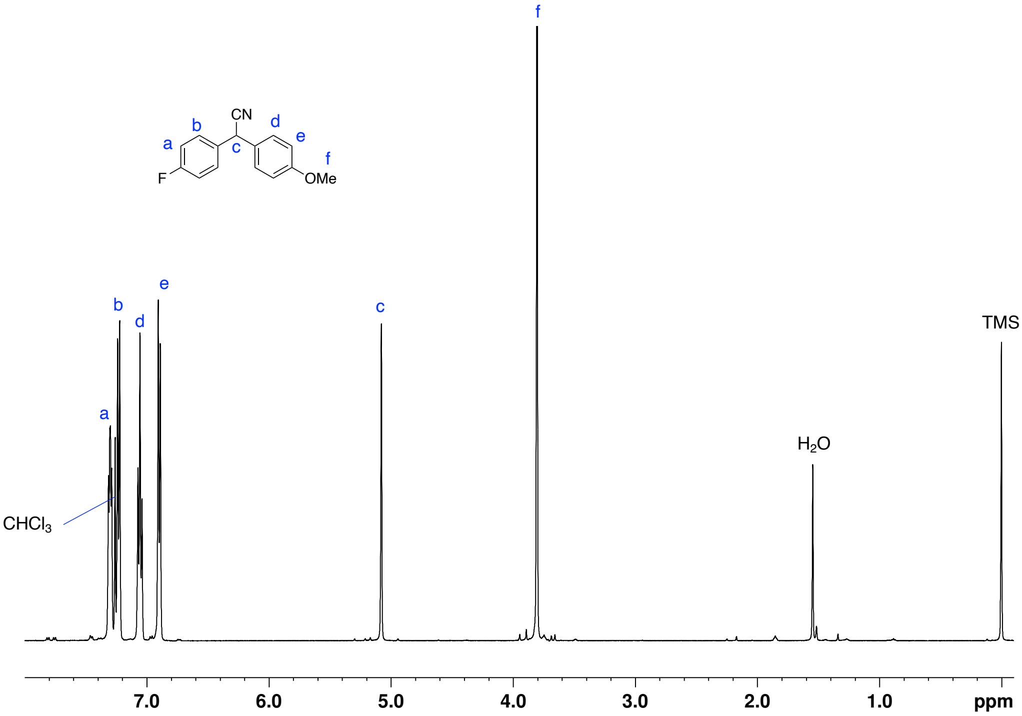


Figure S14. ^{1}H NMR spectrum of **DAAN-F/OMe** ($CDCl_3$, 500 MHz).

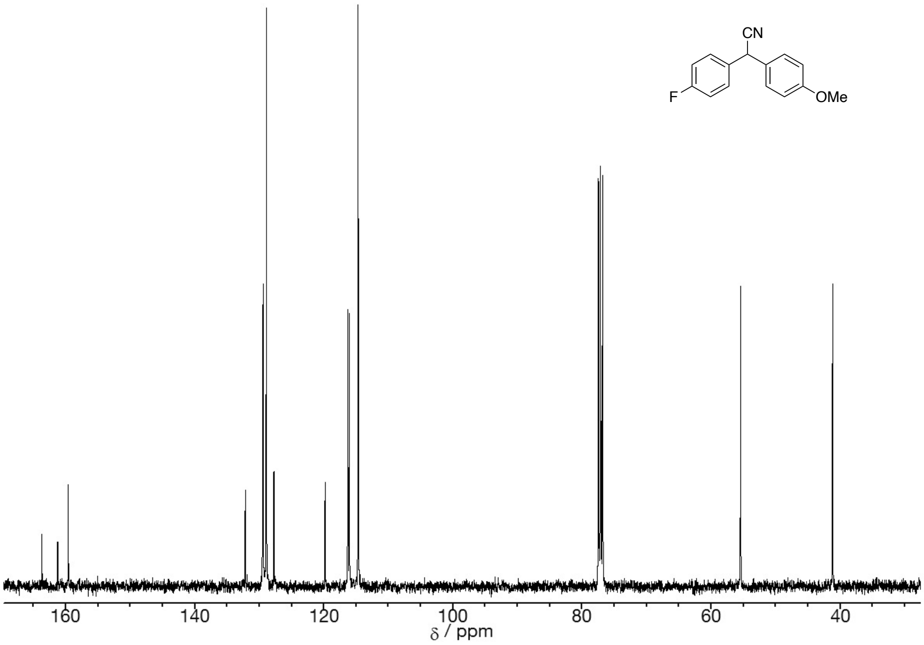


Figure S15. ^{13}C NMR spectrum of **DAAN-F/OMe** ($CDCl_3$, 100 MHz).

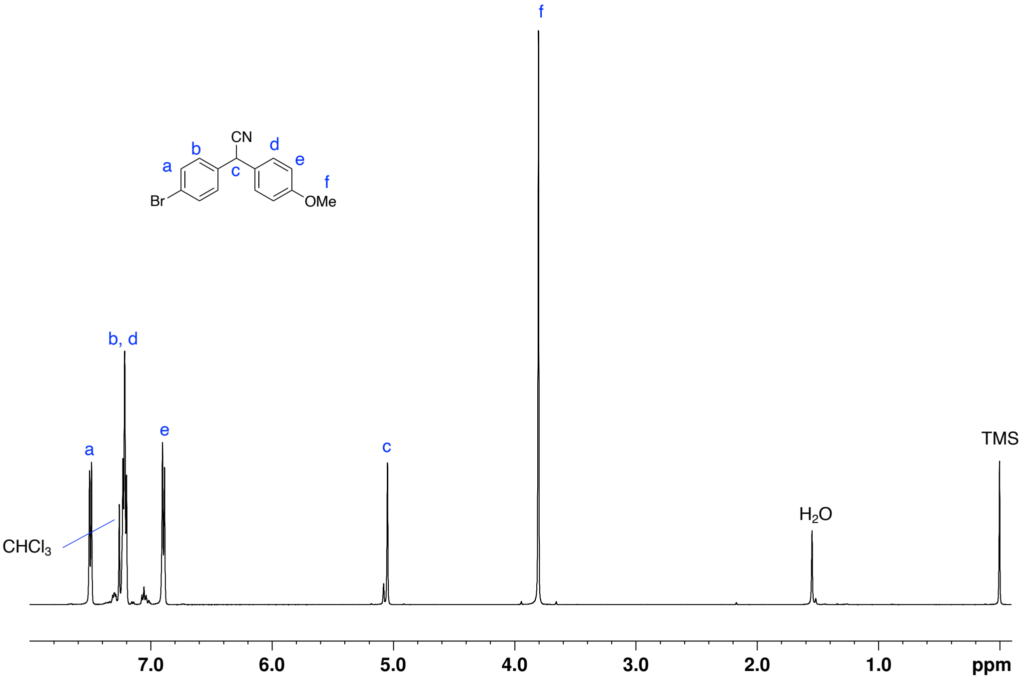


Figure S16. ^{1}H NMR spectrum of **DAAN-Br/OMe** (CDCl$_3$, 500 MHz).

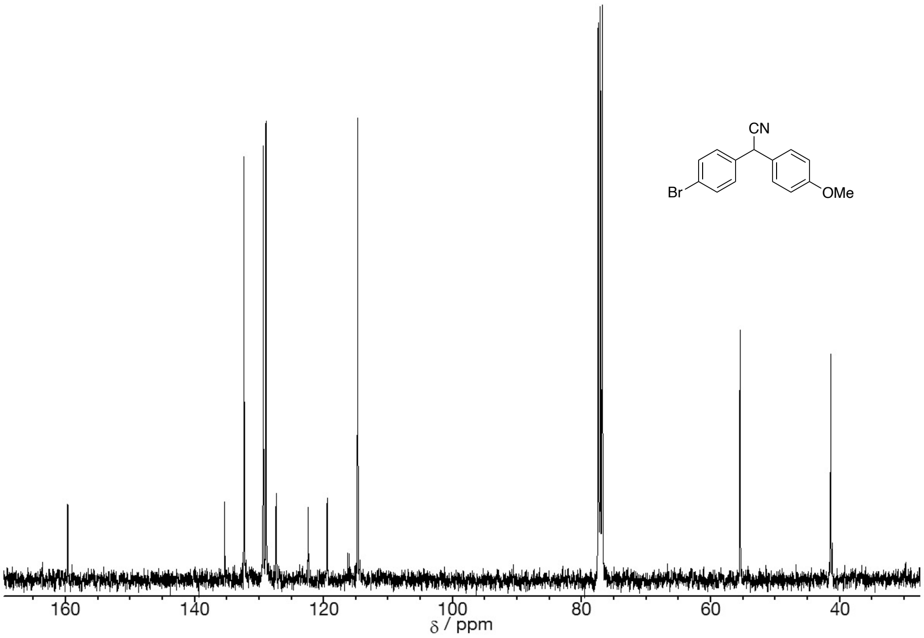


Figure S17. ^{13}C NMR spectrum of **DAAN-Br/OMe** (CDCl$_3$, 100 MHz).

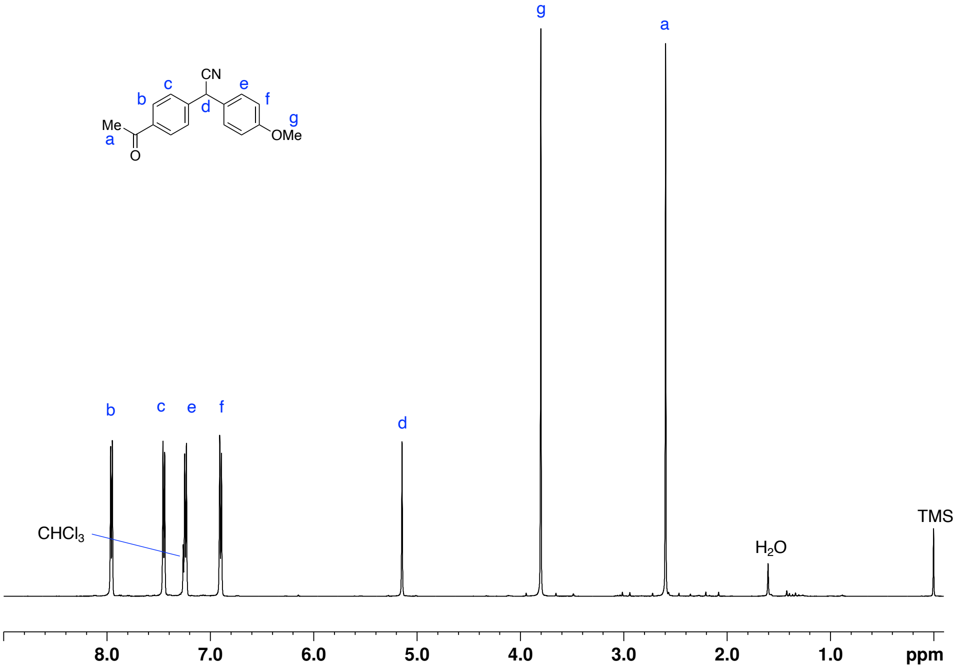


Figure S18. ^{1}H NMR spectrum of **DAAN-Ac/OMe** ($CDCl_3$, 500 MHz).

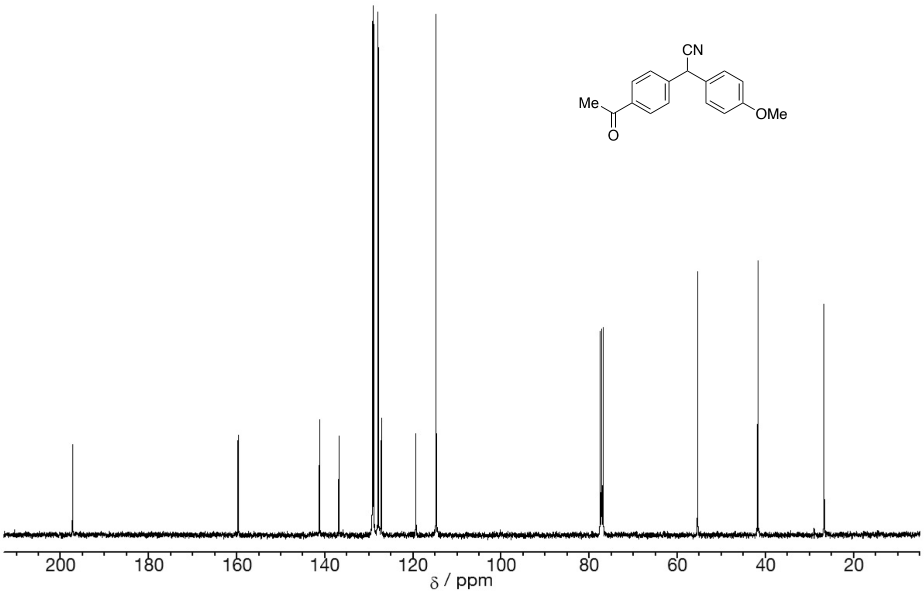


Figure S19. ^{13}C NMR spectrum of **DAAN-Ac/OMe** ($CDCl_3$, 100 MHz).

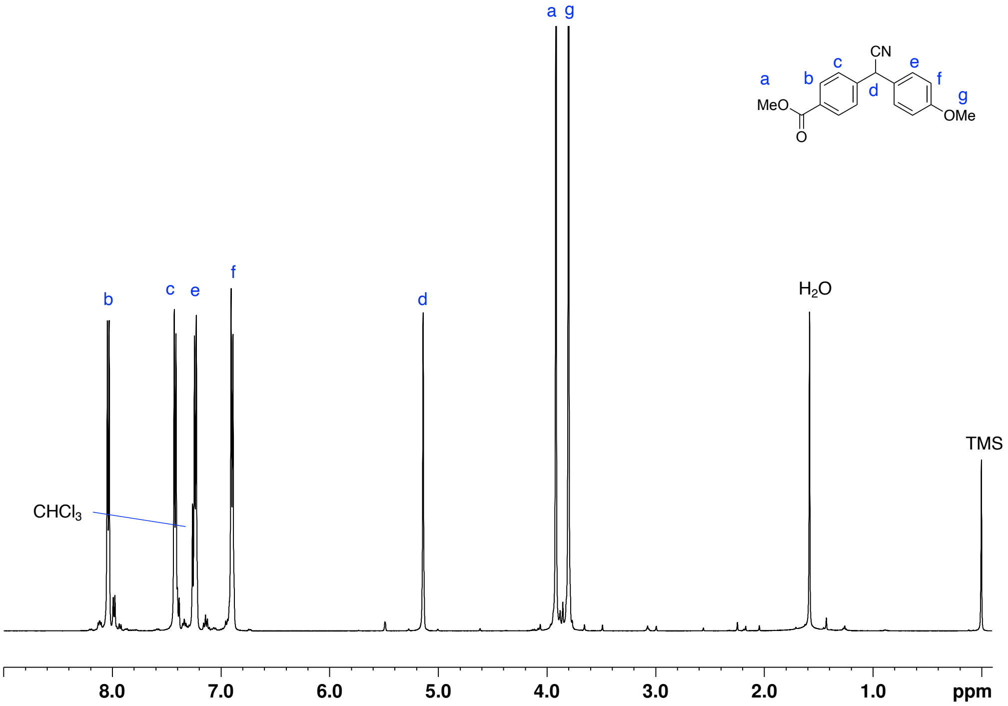


Figure S20. ^{1}H NMR spectrum of **DAAN-COOMe/OMe** ($CDCl_3$, 500 MHz).

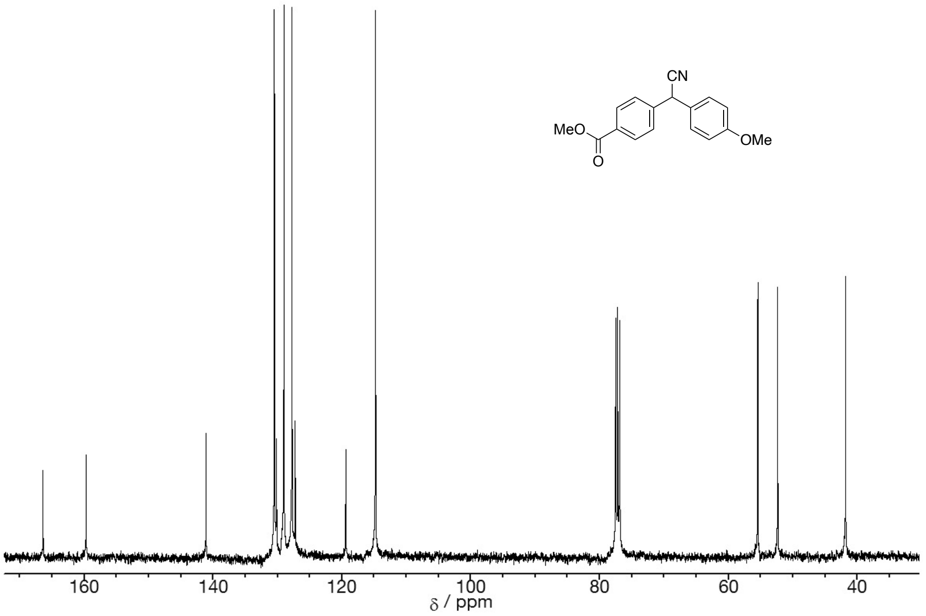


Figure S21. ^{13}C NMR spectrum of **DAAN-COOMe/OMe** ($CDCl_3$, 100 MHz).

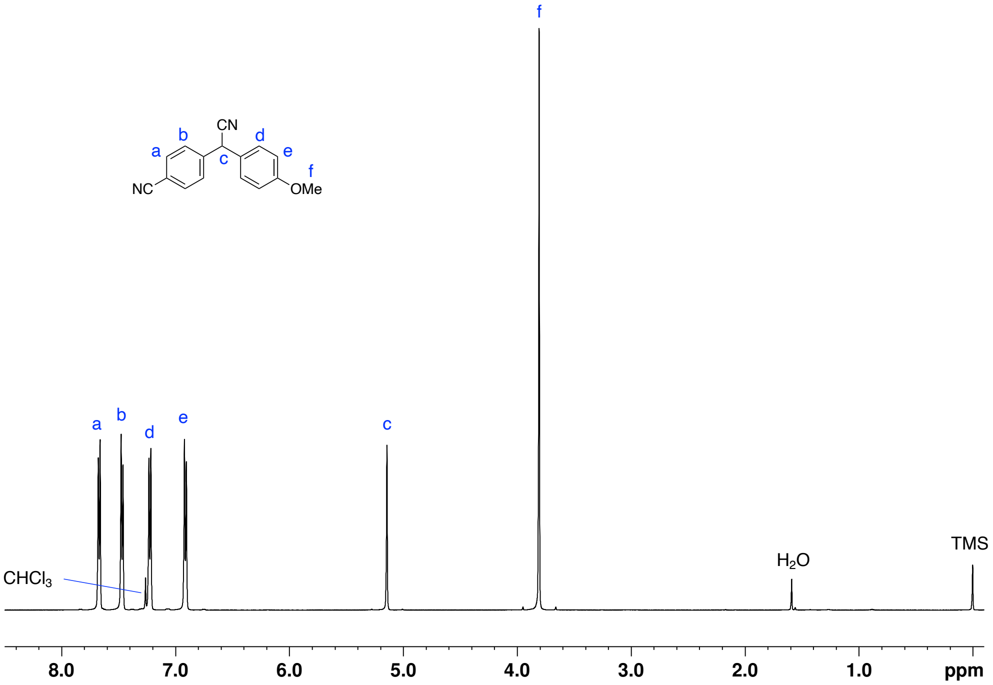


Figure S22. ^{1}H NMR spectrum of **DAAN-CN/OMe** ($CDCl_3$, 500 MHz).

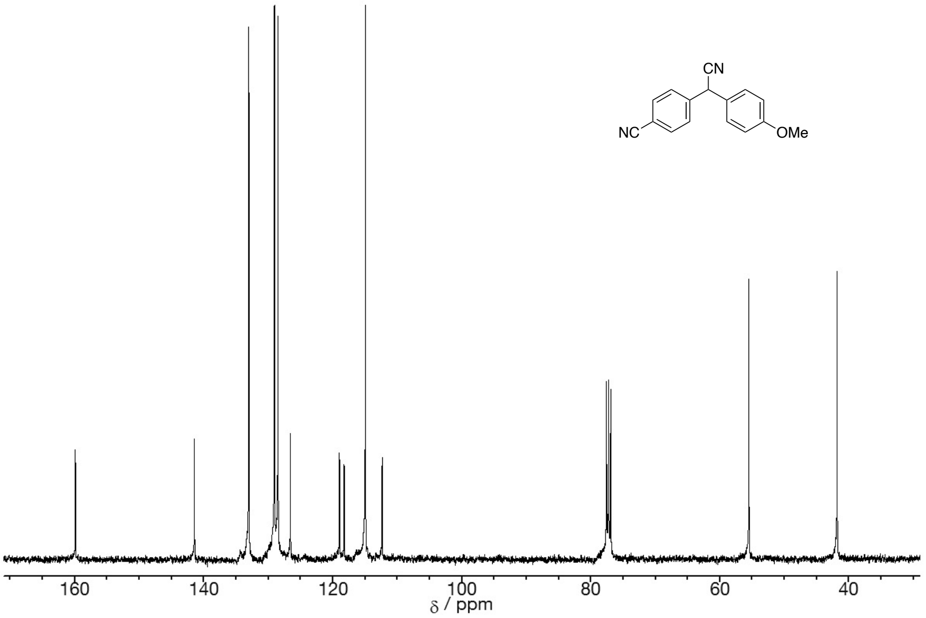


Figure S23. ^{13}C NMR spectrum of **DAAN-CN/OMe** ($CDCl_3$, 100 MHz).

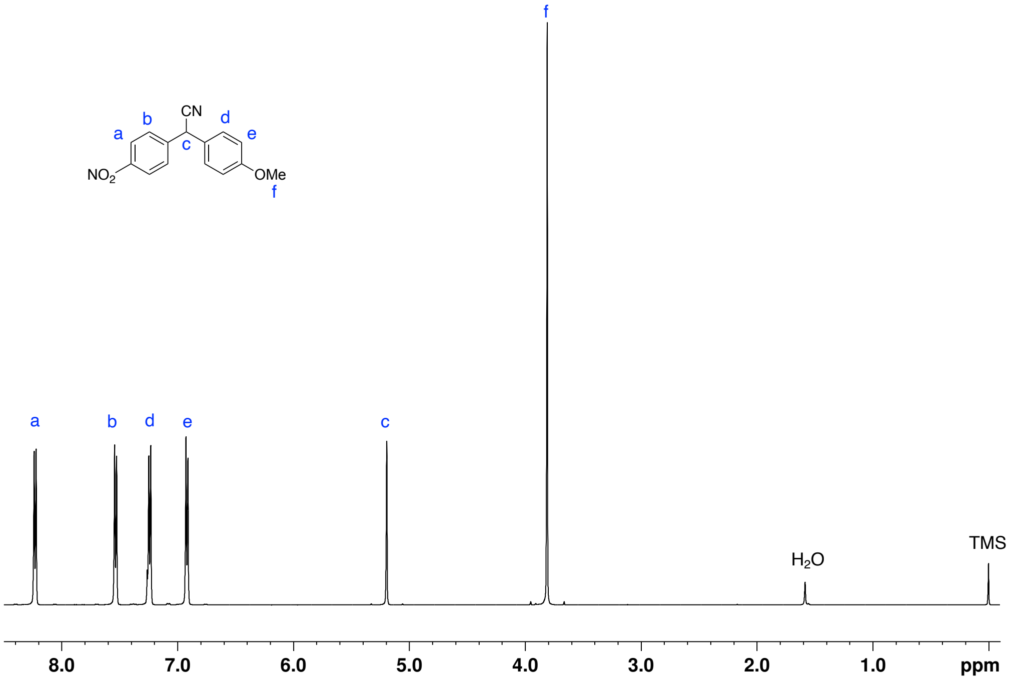


Figure S24. ^{1}H NMR spectrum of **DAAN-NO$_2$/OMe** (CDCl$_3$, 500 MHz).

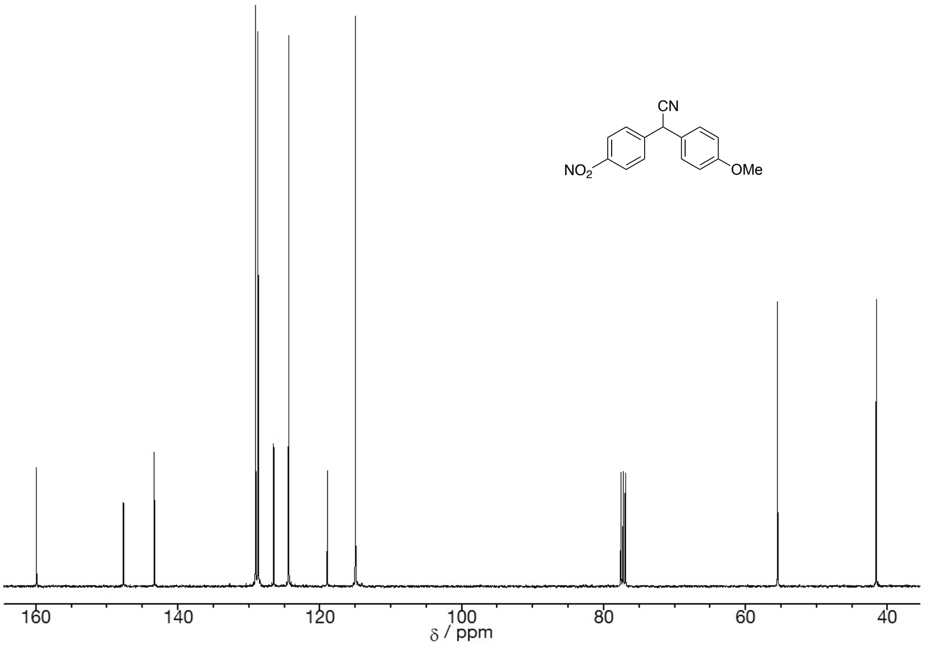


Figure S25. ^{13}C NMR spectrum of **DAAN-NO$_2$/OMe** (CDCl$_3$, 100 MHz).

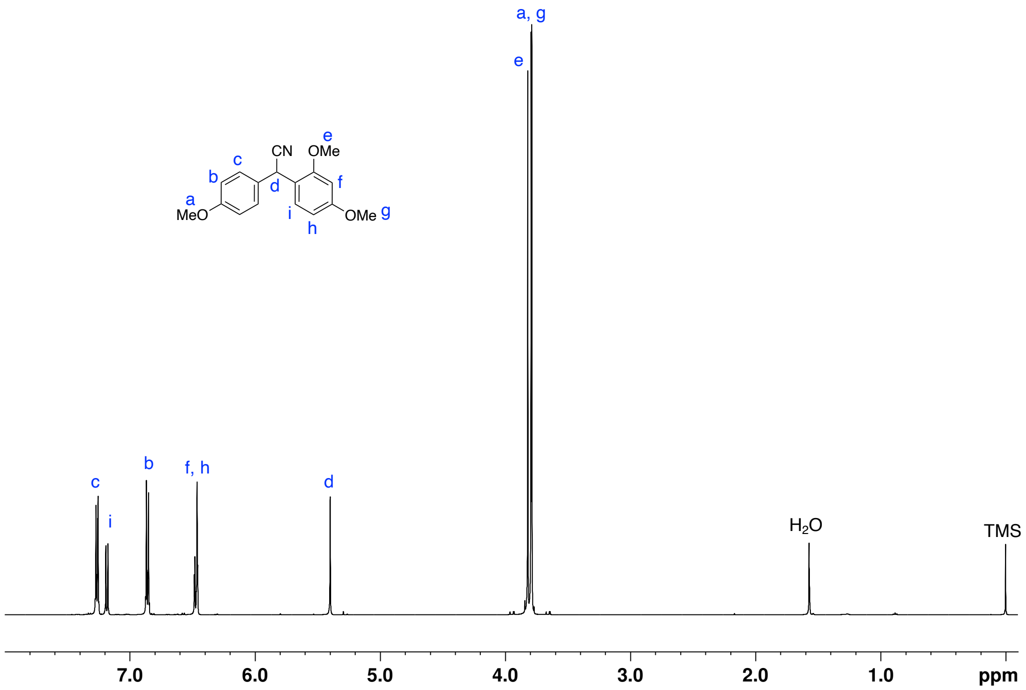


Figure S26. ^{1}H NMR spectrum of **DAAN-OMe/diOMe** (CDCl$_3$, 500 MHz).

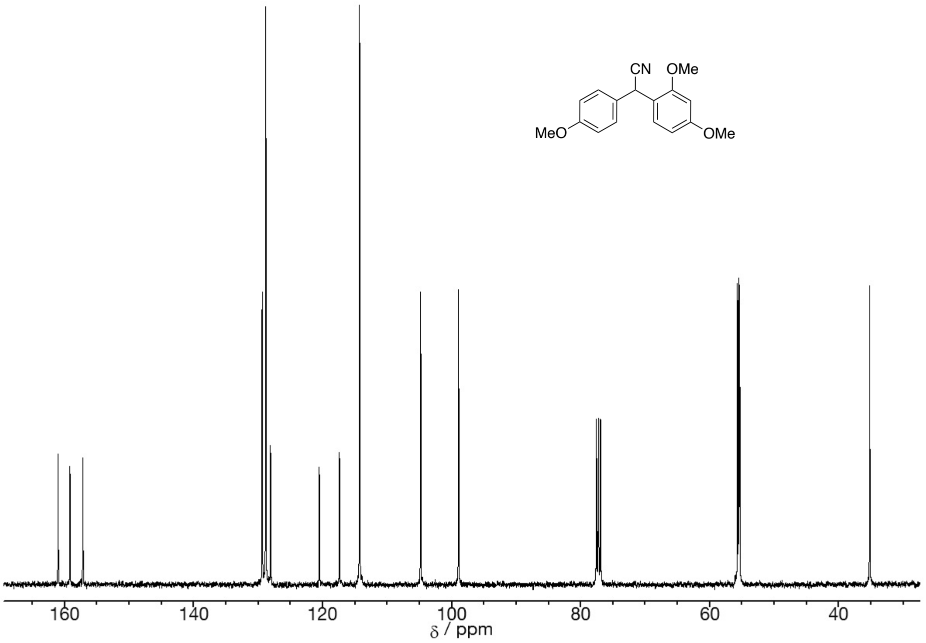


Figure S27. ^{13}C NMR spectrum of **DAAN-OMe/diOMe** (CDCl$_3$, 100 MHz).

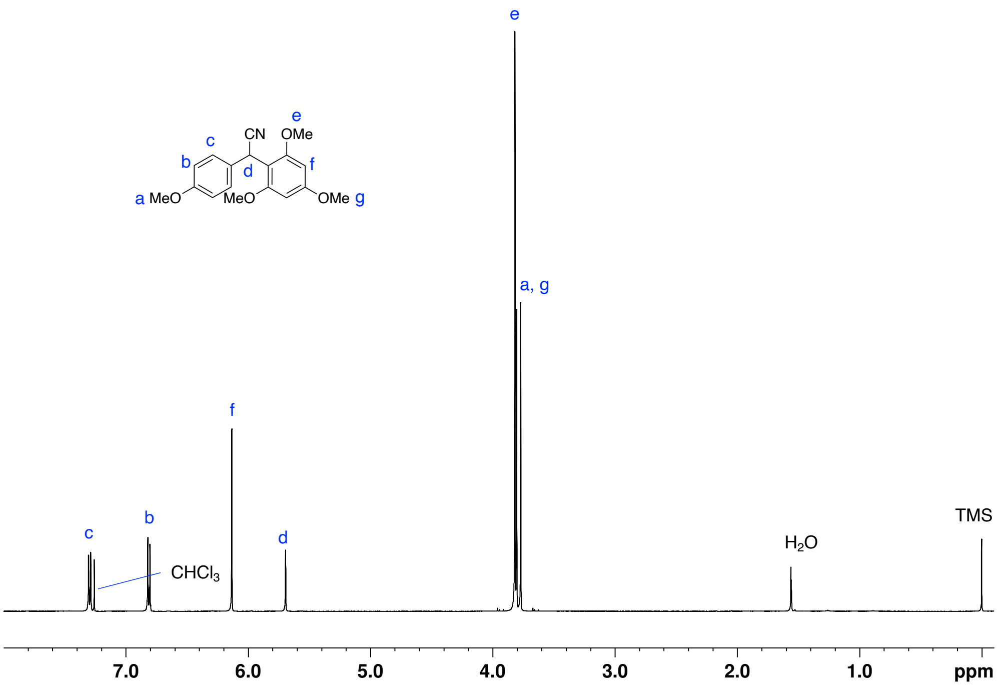


Figure S28. ^{1}H NMR spectrum of **DAAN-OMe/triOMe** (CDCl$_3$, 500 MHz).

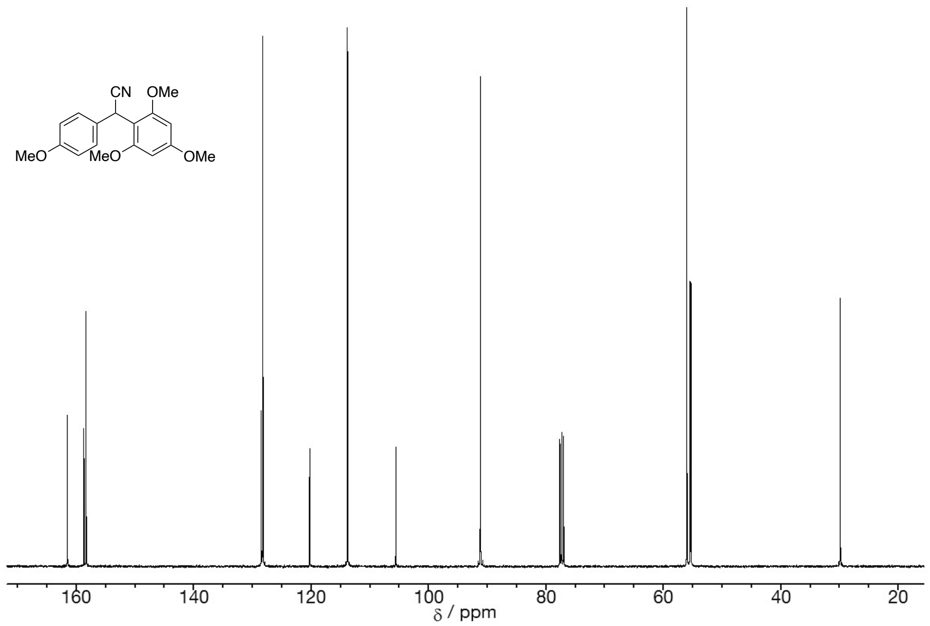


Figure S29. ^{13}C NMR spectrum of **DAAN-OMe/triOMe** (CDCl$_3$, 100 MHz).

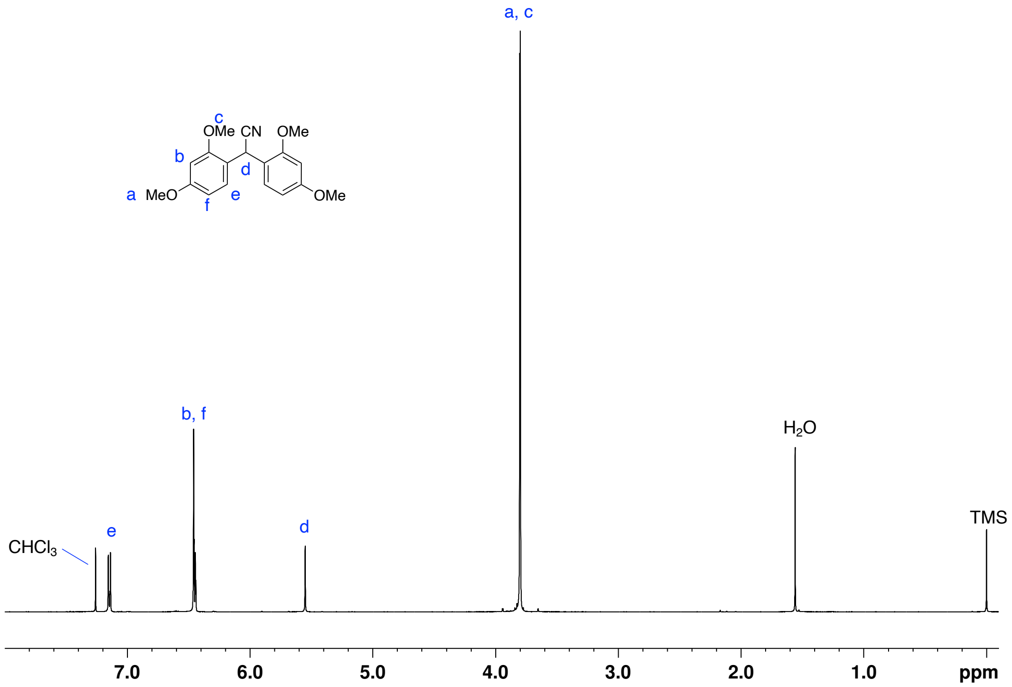


Figure S30. ^{1}H NMR spectrum of **DAAN-diOMe/diOMe** ($CDCl_3$, 500 MHz).

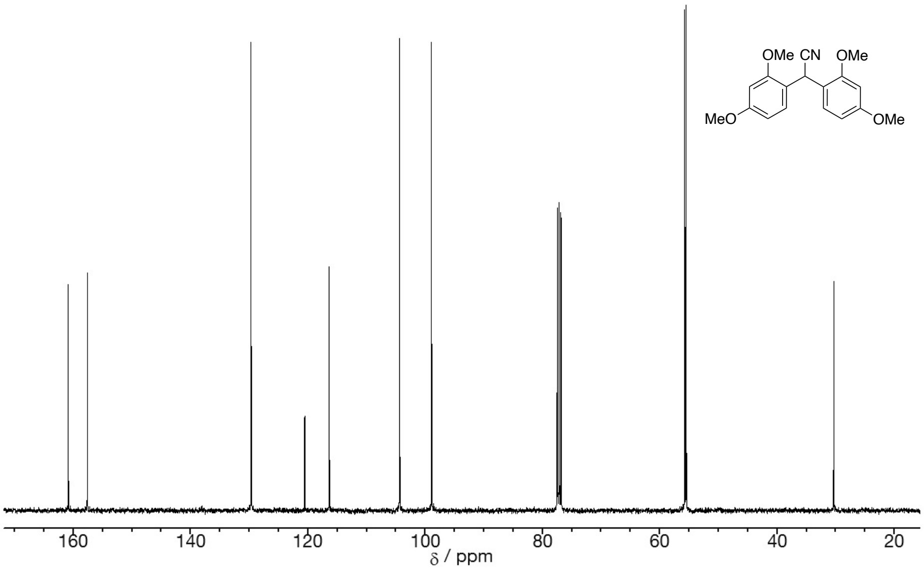


Figure S31. ^{13}C NMR spectrum of **DAAN-diOMe/diOMe** ($CDCl_3$, 100 MHz).

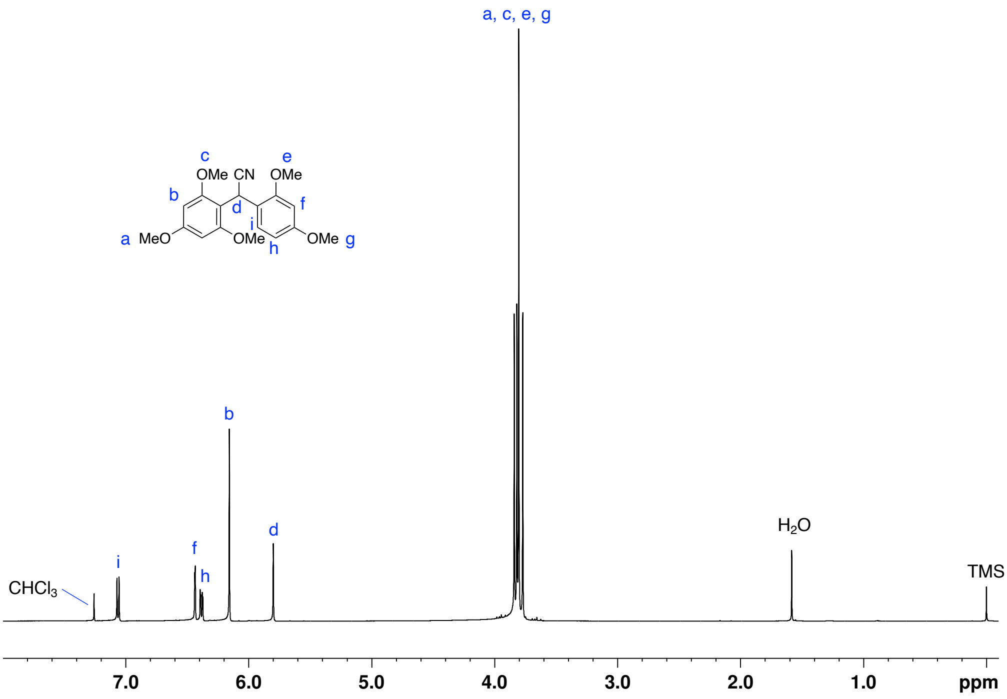


Figure S32. ^{1}H NMR spectrum of **DAAN-diOMe/triOMe** ($CDCl_3$, 500 MHz).

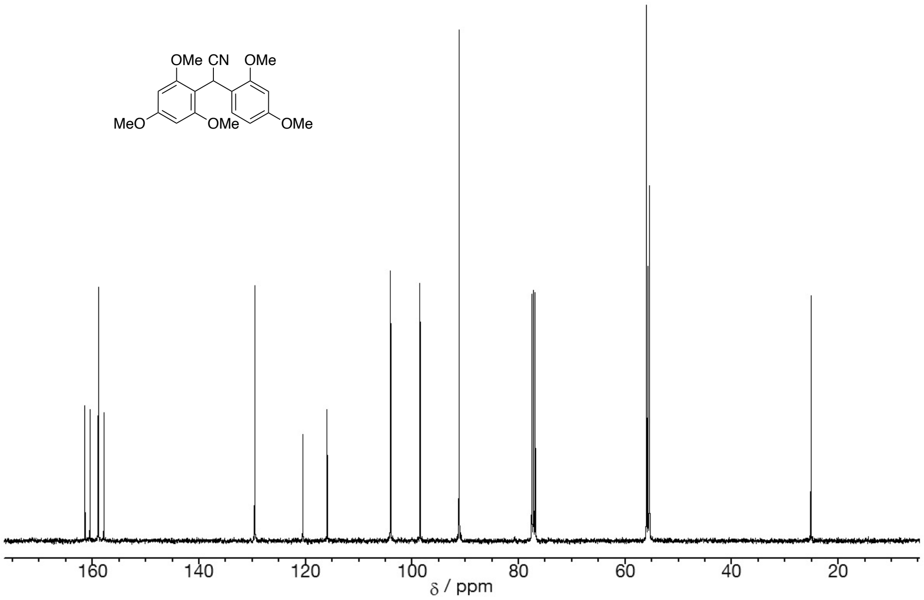


Figure S33. ^{13}C NMR spectrum of **DAAN-diOMe/triOMe** ($CDCl_3$, 100 MHz).

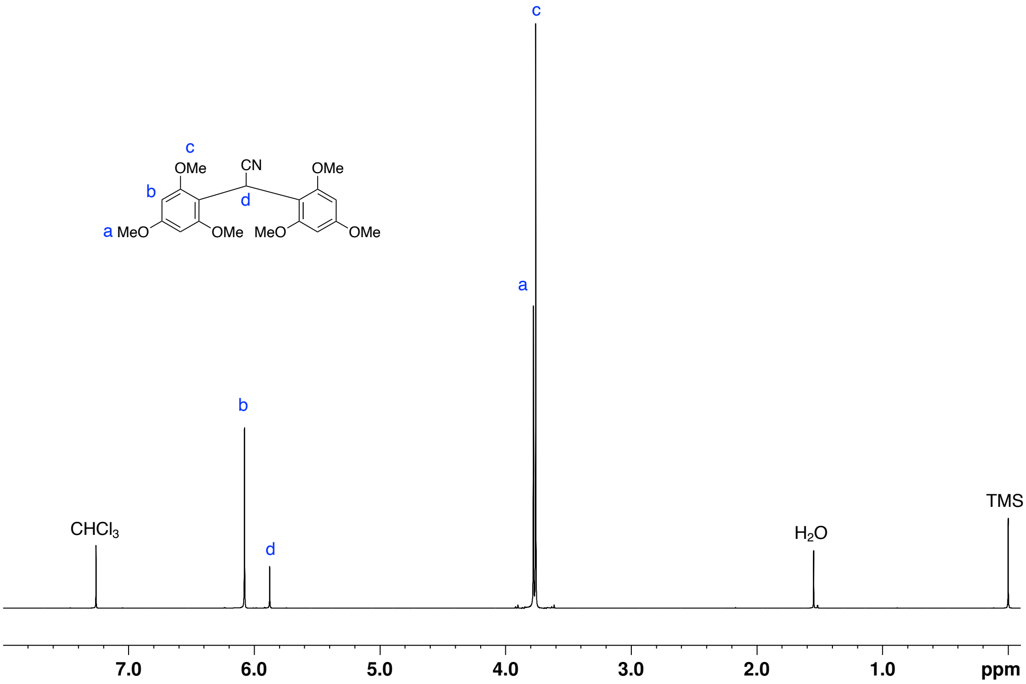


Figure S34. ^{1}H NMR spectrum of **DAAN-triOMe/triOMe** ($CDCl_3$, 500 MHz).

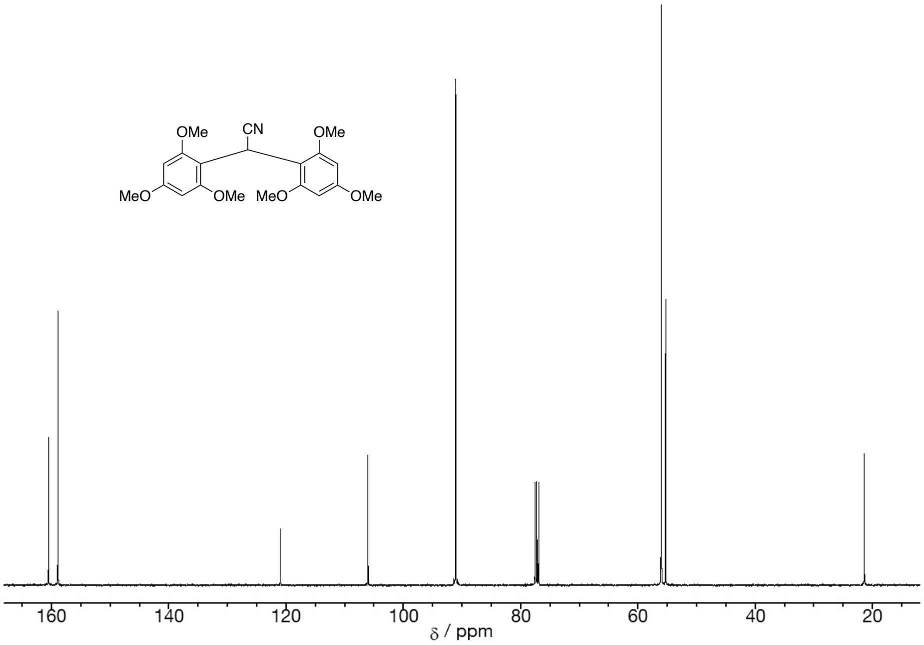


Figure S35. ^{13}C NMR spectrum of **DAAN-triOMe/triOMe** ($CDCl_3$, 100 MHz).

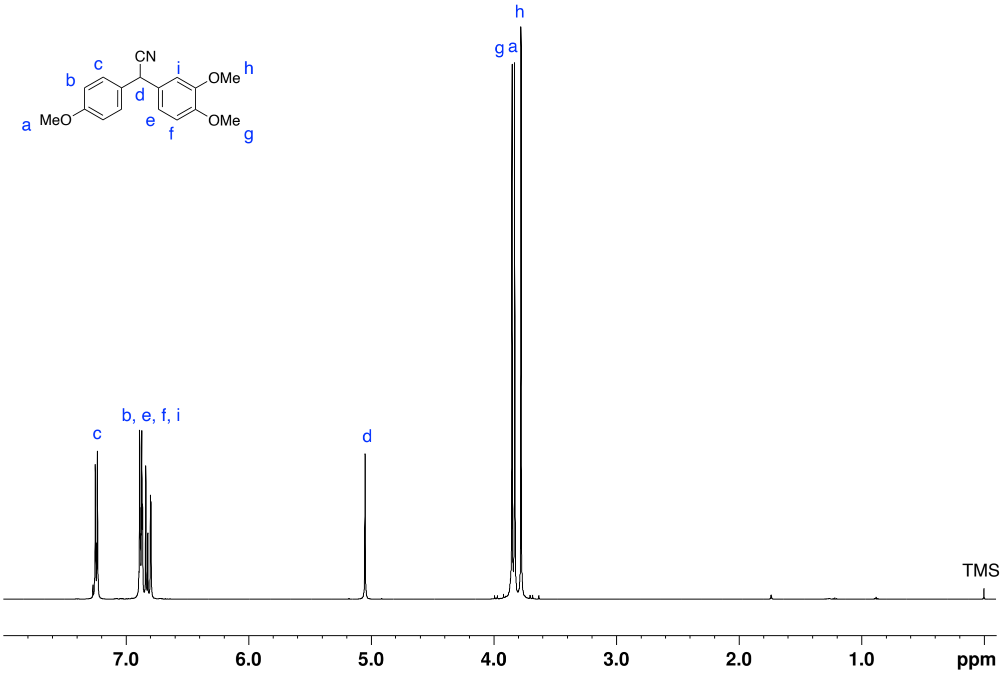


Figure S36. ^{1}H NMR spectrum of **DAAN-OMe**/d**iOMe-m** (CDCl$_3$, 500 MHz).

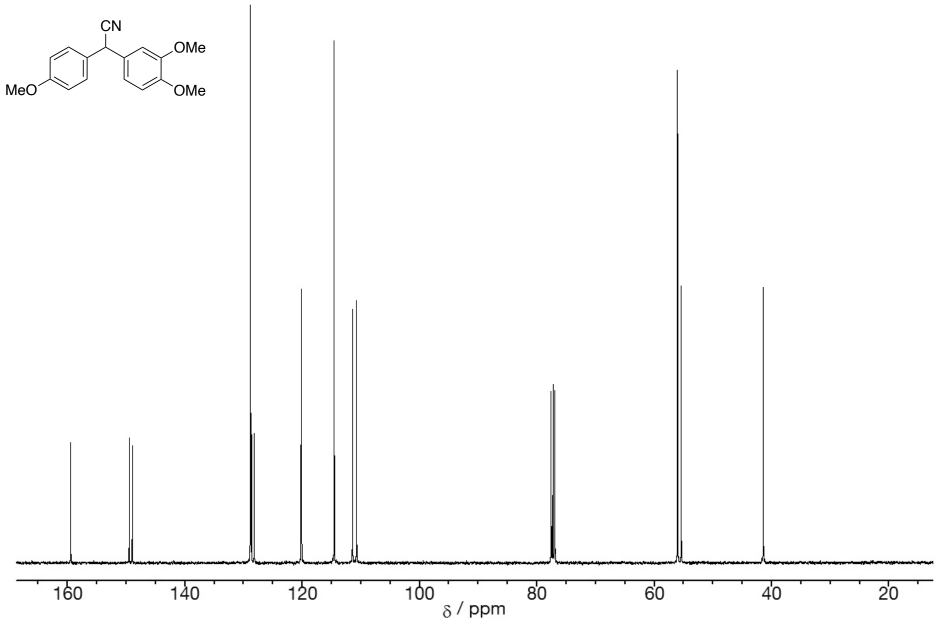


Figure S37. ^{13}C NMR spectrum of **DAAN-OMe/diOMe-m** (CDCl$_3$, 100 MHz)**.**

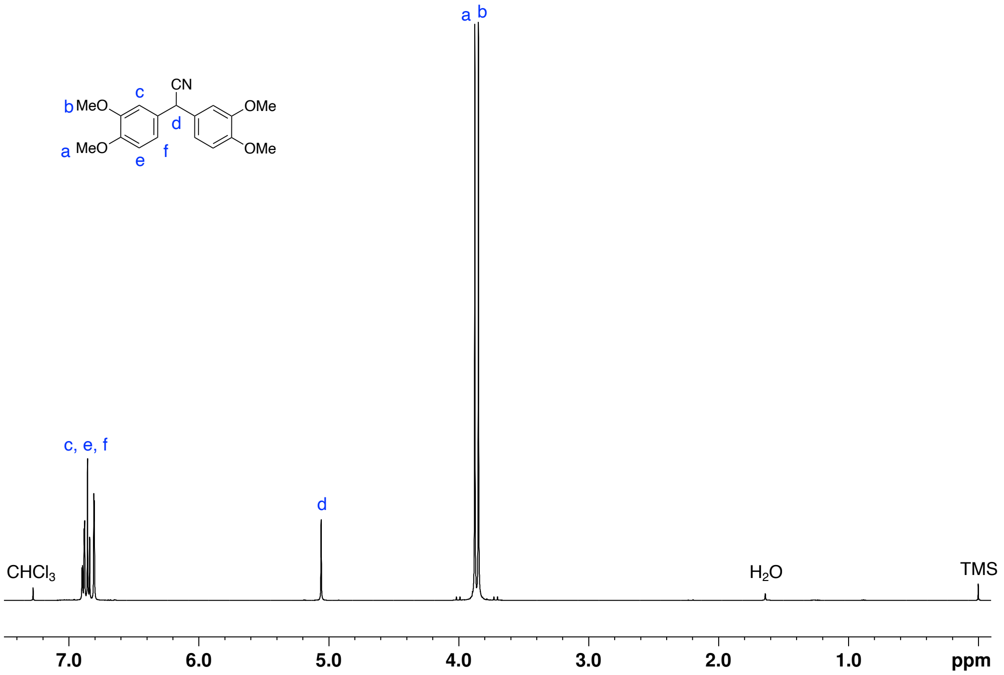


Figure S38. ^{1}H NMR spectrum of **DAAN-diOMe-m/diOMe-m** (CDCl$_3$, 500 MHz).

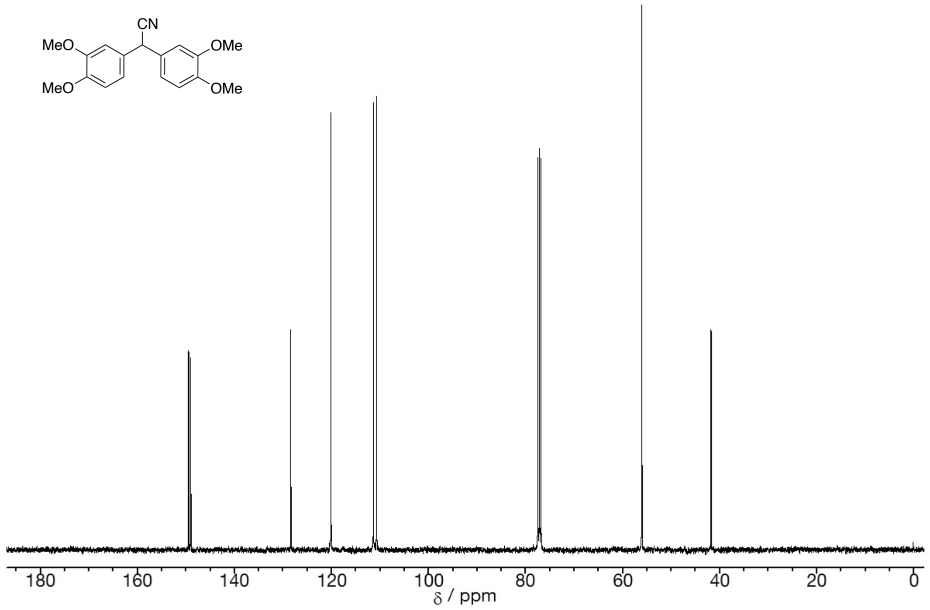


Figure S39. ^{13}C NMR spectrum of **DAAN-diOMe-m/diOMe-m** (CDCl$_3$, 100 MHz).

6. *Supplementary Tables and Figures*

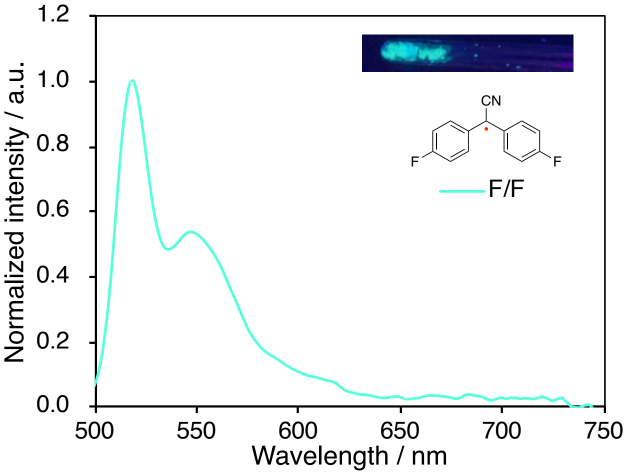


Figure S40. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-F/F** after ball milling.

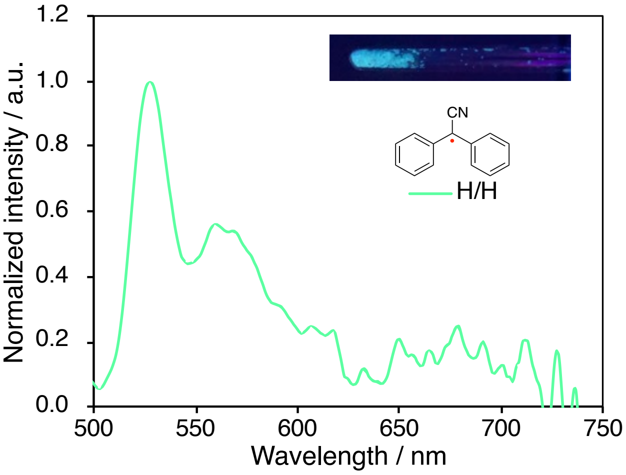


Figure S41. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-H/H** after ball milling.

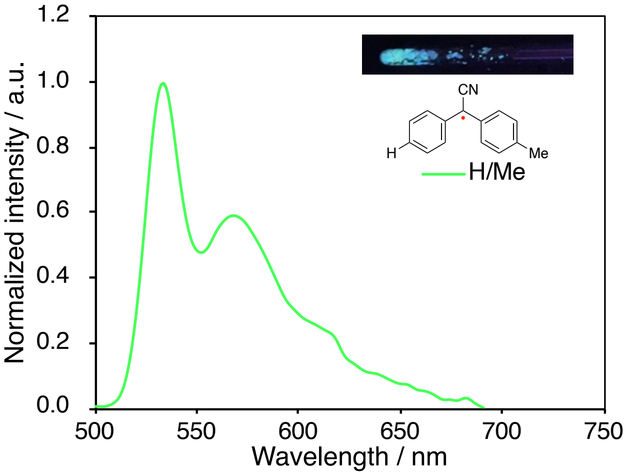


Figure S42. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-H/Me** after ball milling.

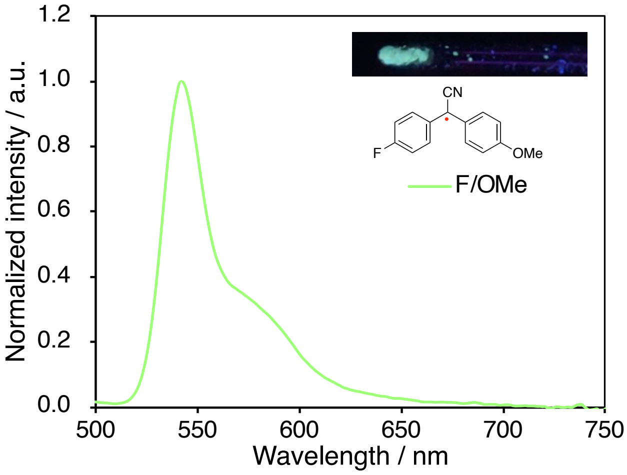


Figure S43. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-F/OMe** after ball milling.

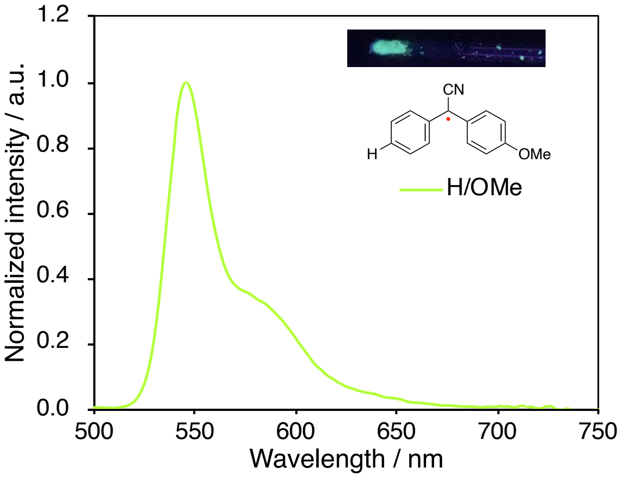


Figure S44. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-H/OMe** after ball milling.

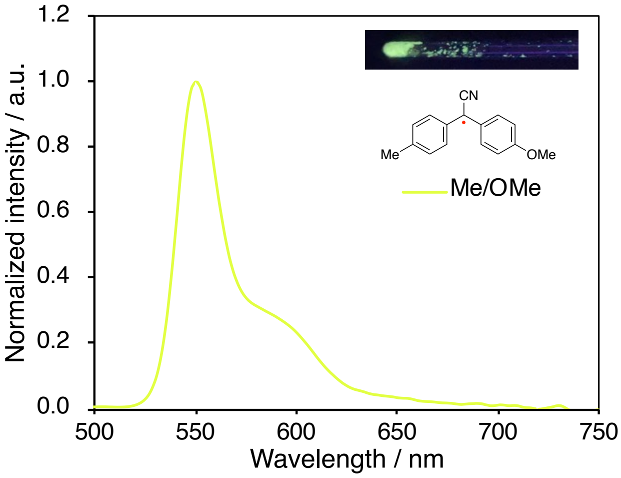


Figure S45. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-Me/OMe** after ball milling.

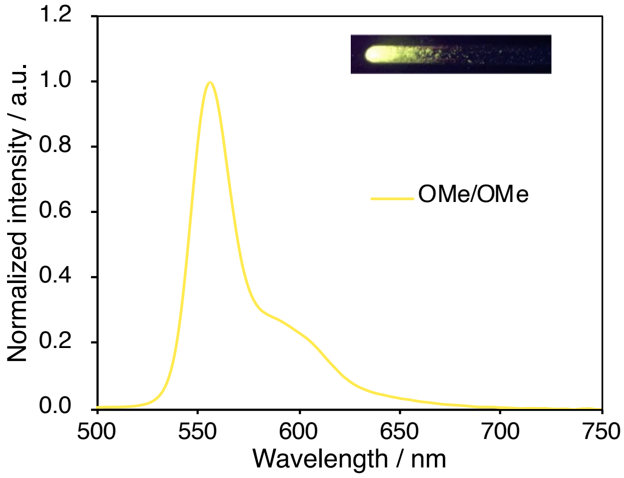


Figure S46. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-OMe/OMe** after ball milling.

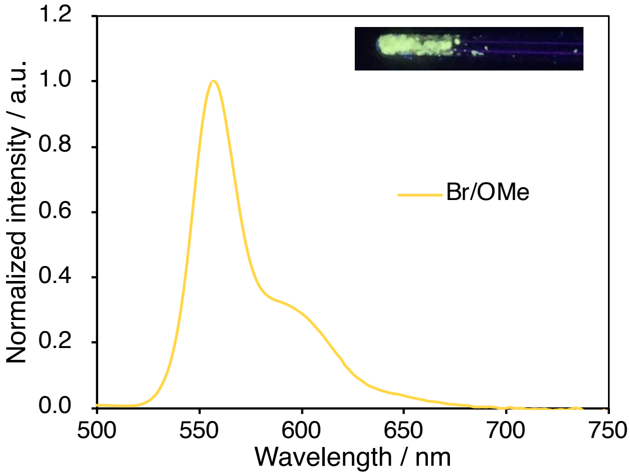


Figure S47. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-Br/OMe** after ball milling.

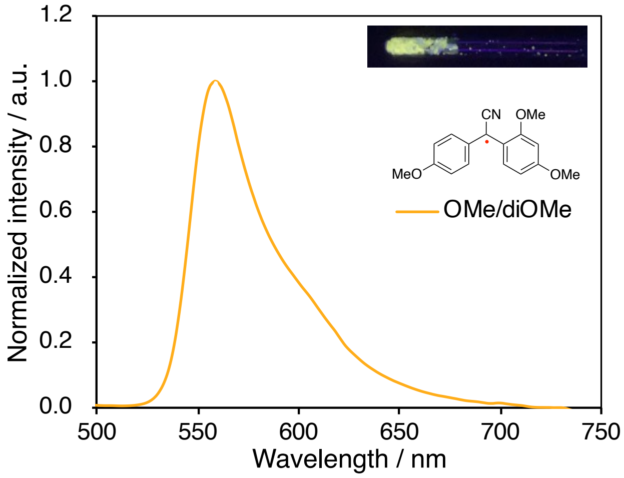


Figure S48. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-OMe/diOMe** after ball milling.

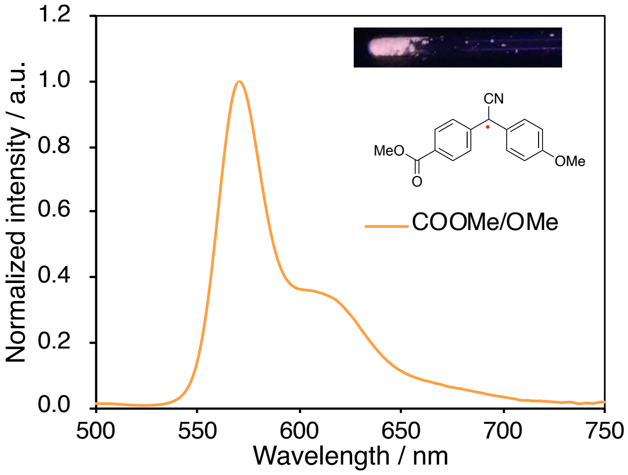


Figure S49. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-COOMe/OMe** after ball milling.

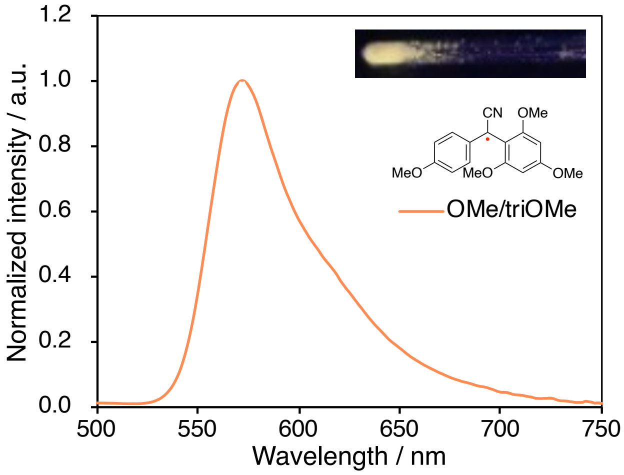


Figure S50. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-OMe/triOMe** after ball milling.

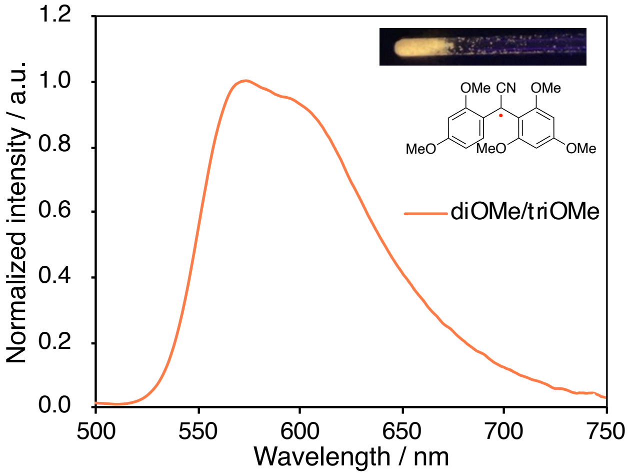


Figure S51. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-diOMe/triOMe** after ball milling.

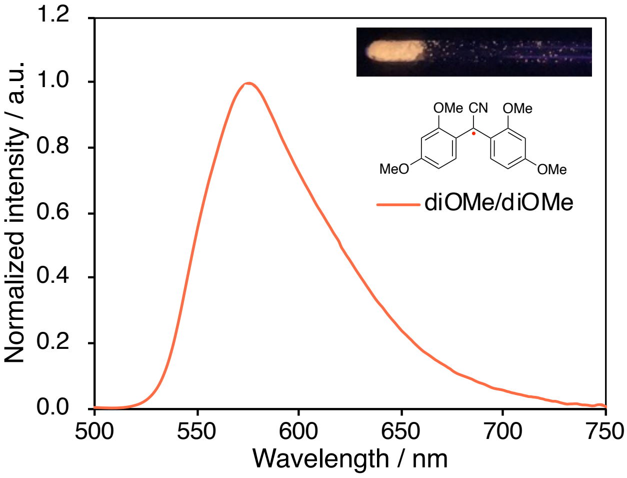


Figure S52. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-diOMe/diOMe** after ball milling.

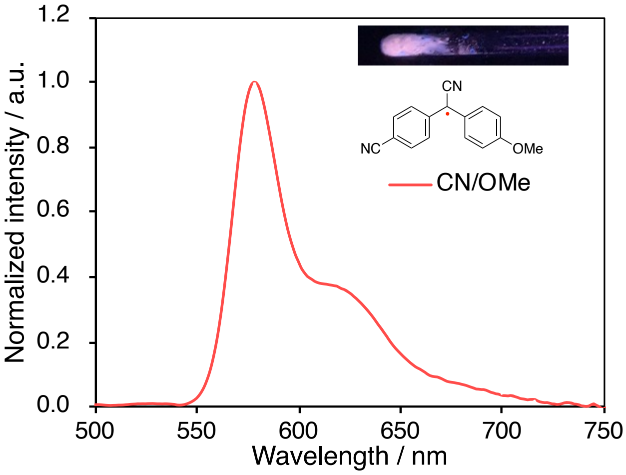


Figure S53. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-CN/OMe** after ball milling.

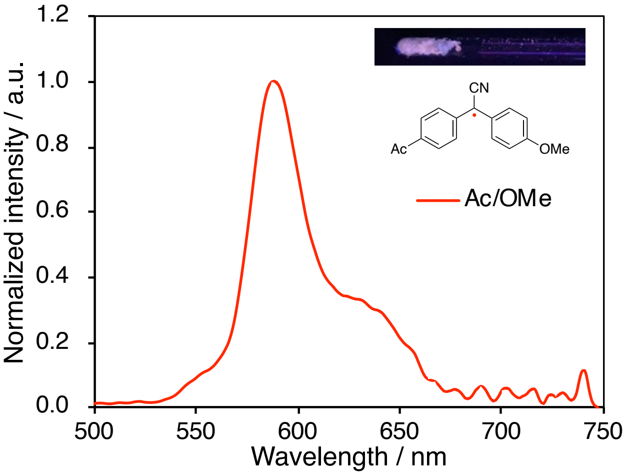


Figure S54. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-Ac/OMe** after ball milling.

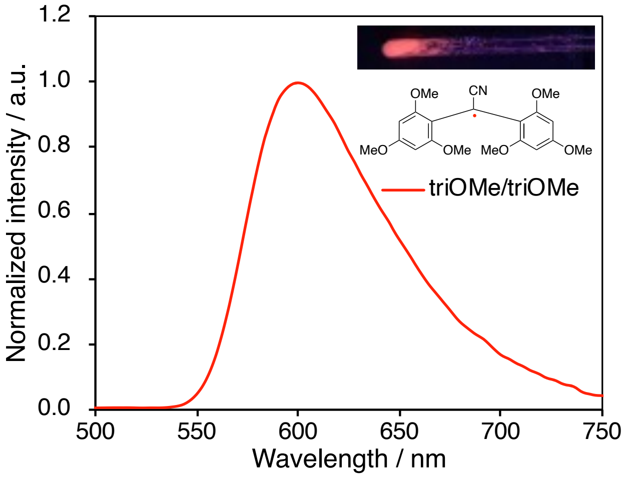


Figure S55. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-triOMe/triOMe** after ball milling.

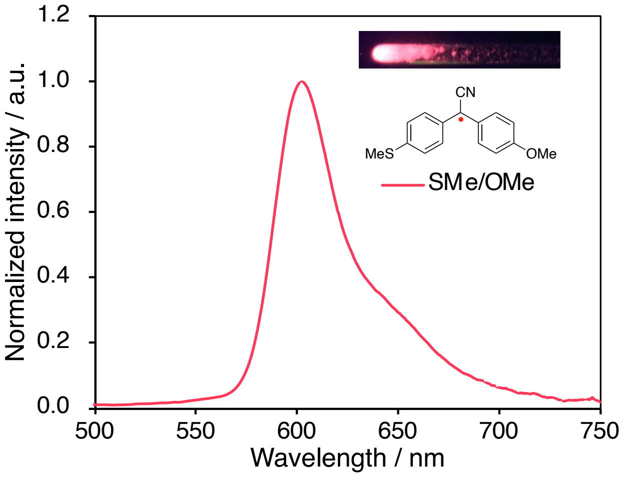


Figure S56. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-SMe/OMe** after ball milling.

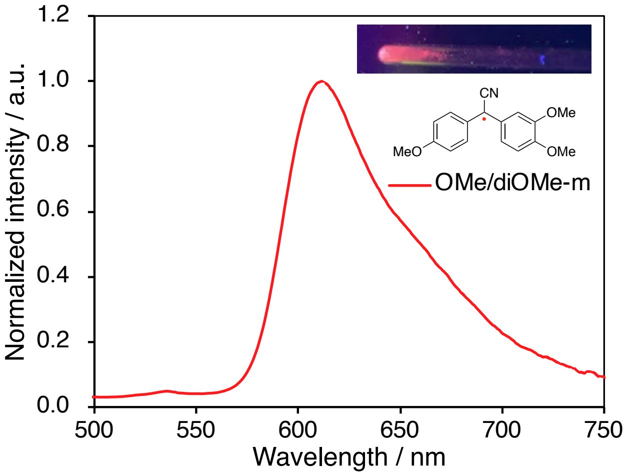


Figure S57. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-OMe/diOMe-m** after ball milling.

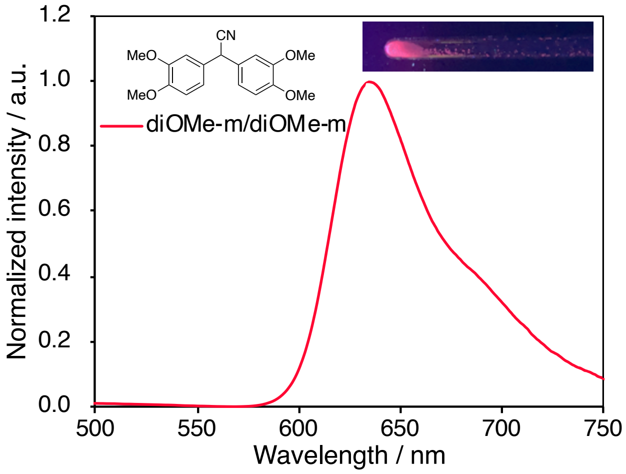


Figure S58. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-diOMe-m/diOMe-m** after ball milling.

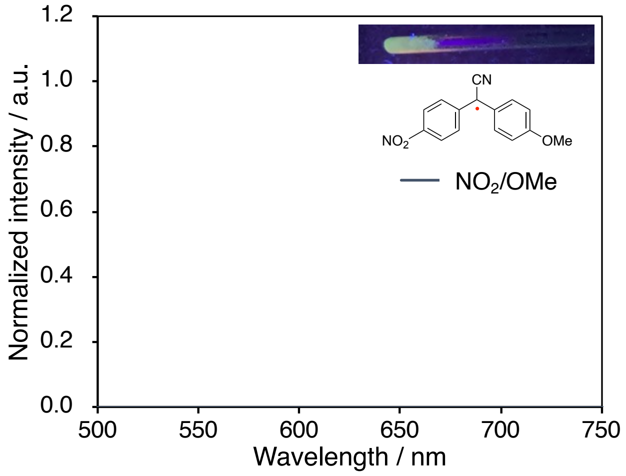


Figure S59. Fluorescence spectrum (λ_{ex} = 365 nm) of a mixture of polystyrene and **DAAN-NO_2/OMe** after ball milling. (No fluorescence was observed.)

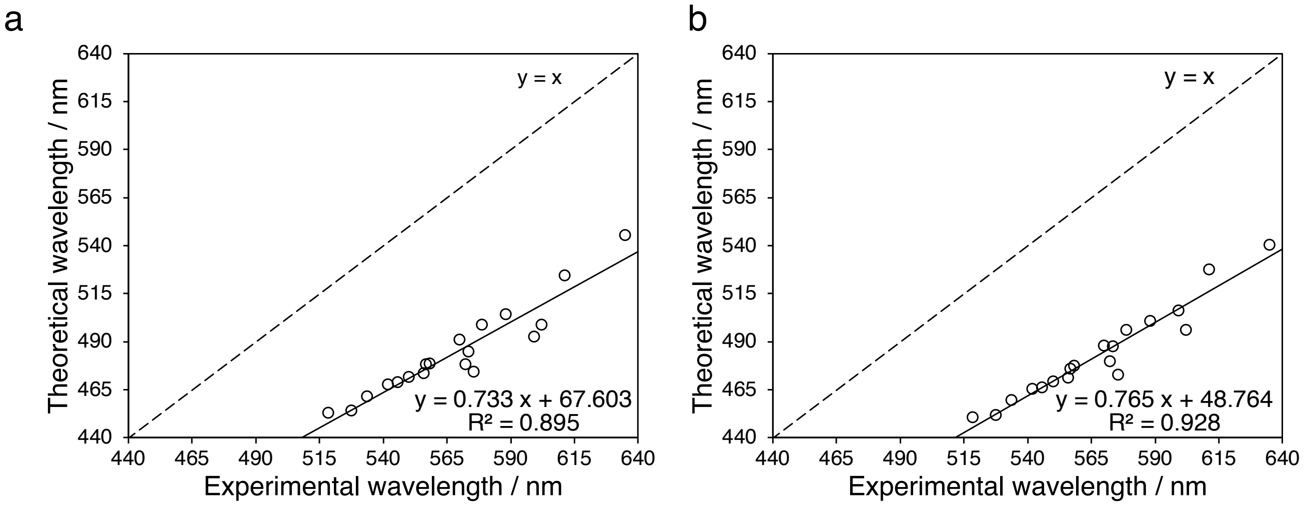


Figure S60. Relationship between theoretical wavelength and experimental wavelength. (a) UCAM-B3LYP/6-311+G(d,p). (b) UωB97X-D /6-311+G(d,p).

Table S2. The relative orbital excitation contributions are indicated (‘up’ = A, and ‘down’ = B)

	α-SOMO	Orbital excitation contribution	Oscillator strength (*f*)
H/H	51A	50B → 51B (72%) 51A → 52A (18%)	0.055
H/Me	55A	54B → 55B (75%) 55A → 56A (15%)	0.073
H/OMe	59A	58B → 59B (81%) 59A → 60A (16%)	0.116
Me/OMe	63A	62B → 63B (81%) 63A → 64A (14%)	0.126
OMe/OMe	67A	66B → 67B (83%)	0.155
SMe/OMe	71A	70B → 71B (81%)	0.190
F/OMe	63A	62B → 63B (81%)	0.121
Br/OMe	76A	75B → 76B (80%) 76A → 77A (7%)	0.142
F/F	59A	58B → 59B (75%) 59A → 60A (4%)	0.069
Ac/OMe	70A	69B → 70B (75%) 70A → 71A (13%)	0.095
CN/OMe	65A	64B → 65B (80%) 65A → 66A (10%)	0.124
COOMe/OMe	74A	73B → 74B (79%) 74A → 75A (10%)	0.113
NO_2/OMe	70A	65B → 71B (34%) 64A → 71A (32%)	0.000
OMe/diOMe	75A	74B → 75B (86%)	0.141
diOMe/diOMe	83A	82B → 83B (86%)	0.129
OMe/triOMe	83A	82B → 83B (86%)	0.137
diOMe/triOMe	91A	90B → 91B (79%)	0.120
triOMe/triOMe	99A	98B → 99B (90%)	0.126
OMe/diOMe-m	75A	74B → 75B (84%)	0.131
diOMe-m/diOMe-m	83A	82B → 83B (86%)	0.128

Table S3. The relative orbital emission contributions are indicated ('up' = A, and 'down' = B)

	α-SOMO	Orbital emission contribution	Oscillator strength (*f*)
H/H	51A	50B ← 51B (71%) 51A ← 52A (24%)	0.046
H/Me	55A	54B ← 55B (72%) 55A ← 56A (22%)	0.058
H/OMe	59A	58B ← 59B (79%) 59A ← 60A (15%)	0.101
Me/OMe	63A	62B ← 63B (78%) 63A ← 64A (16%)	0.106
OMe/OMe	67A	66B ← 67B (79%) 67A ← 68A (16%)	0.130
SMe/OMe	71A	70B ← 71B (80%) 71A ← 72A (14%)	0.1683
F/OMe	63A	62B ← 63B (79%) 63A ← 64A (13%)	0.102
Br/OMe	76A	75B ← 76B (79%) 76A ← 77A (14%)	0.126
F/F	59A	58B ← 59B (71%) 59A ← 60A (22%)	0.052
Ac/OMe	70A	69B ← 70B (66%) 70A ← 71A (24%)	0.054
CN/OMe	65A	64B ← 65B (78%) 65A ← 66A (14%)	0.112
COOMe/OMe	74A	73B ← 74B (76%) 74A ← 75A (16%)	0.094
NO_2/OMe	70A	66A ← 71A (23%) 65A ← 71A (19%)	0.000
OMe/diOMe	75A	74B ← 75B (85%)	0.132
diOMe/diOMe	83A	82B ← 83B (83%)	0.113
OMe/triOMe	83A	82B ← 83B (88%)	0.133
diOMe/triOMe	91A	90B ← 91B (87%)	0.117
triOMe/triOMe	99A	98B ← 99B (91%)	0.101
OMe/diOMe-m	75A	74B ← 75B (76%) 75A ← 76A (16%)	0.146
diOMe-m/diOMe-m	83A	82B ← 83B (87%) 83A ← 84A (7%)	0.165

Table S4. $\Delta E_{\mathrm{SOMO-HOMO}}$ and $\Delta E_{\mathrm{LUMO-SOMO}}$ of DAAN radicals in D_0 and D_1 states

	D_0 state		D_1 state	
	$\Delta E_{\mathrm{SOMO-HOMO}}$ / eV	$\Delta E_{\mathrm{LUMO-SOMO}}$ / eV	$\Delta E_{\mathrm{SOMO-HOMO}}$ / eV	$\Delta E_{\mathrm{LUMO-SOMO}}$ / eV
H/H	5.89	6.43	5.43	5.98
F/F	5.78	6.31	5.40	6.00
H/Me	5.75	6.35	5.33	5.91
F/OMe	5.45	6.18	5.17	6.00
H/OMe	5.47	6.28	5.17	6.01
Me/OMe	5.42	6.21	5.12	5.91
diOMe/diOMe	5.30	5.86	5.07	5.64
OMe/triOMe	5.36	6.03	5.07	5.76
diOMe/triOMe	5.40	5.83	5.07	5.61
triOMe/triOMe	5.32	5.65	5.05	5.49
NO_2/OMe	5.23	5.14	5.05	3.93
OMe/OMe	5.29	6.10	5.04	5.95
OMe/diOMe	5.26	6.00	5.02	5.79
Br/OMe	5.30	6.16	4.99	5.88
COOMe/OMe	5.32	5.76	4.94	5.53
Ac/OMe	5.28	5.57	4.90	5.29
CN/OMe	5.25	5.79	4.86	5.60
SMe/OMe	4.84	6.08	4.67	5.77
OMe/diOMe-m	5.10	6.24	4.71	6.01
diOMe-m/diOMe-m	5.00	6.32	4.54	5.96

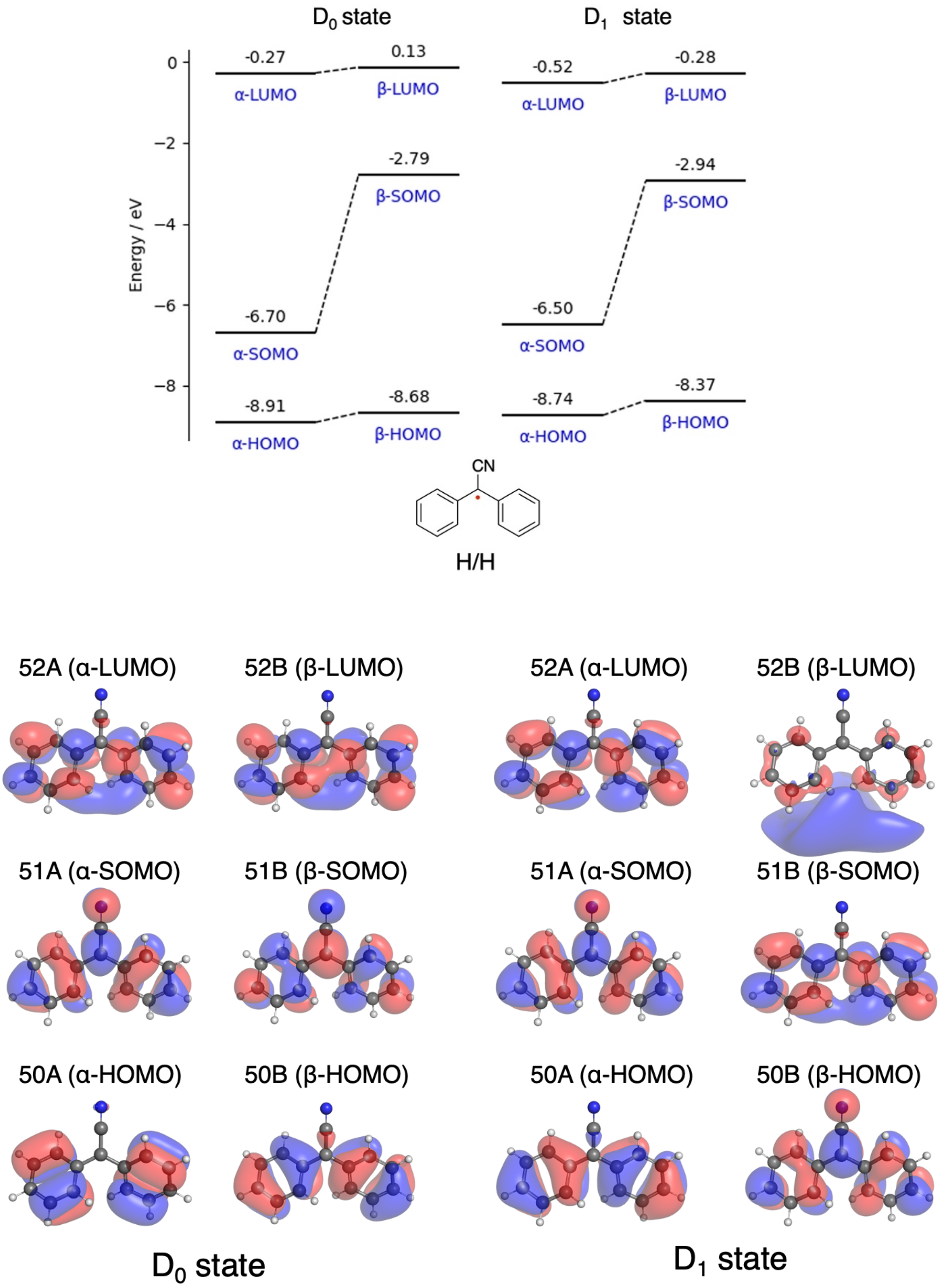


Figure S61. Molecular orbital diagrams for **DAAN-H/H.**

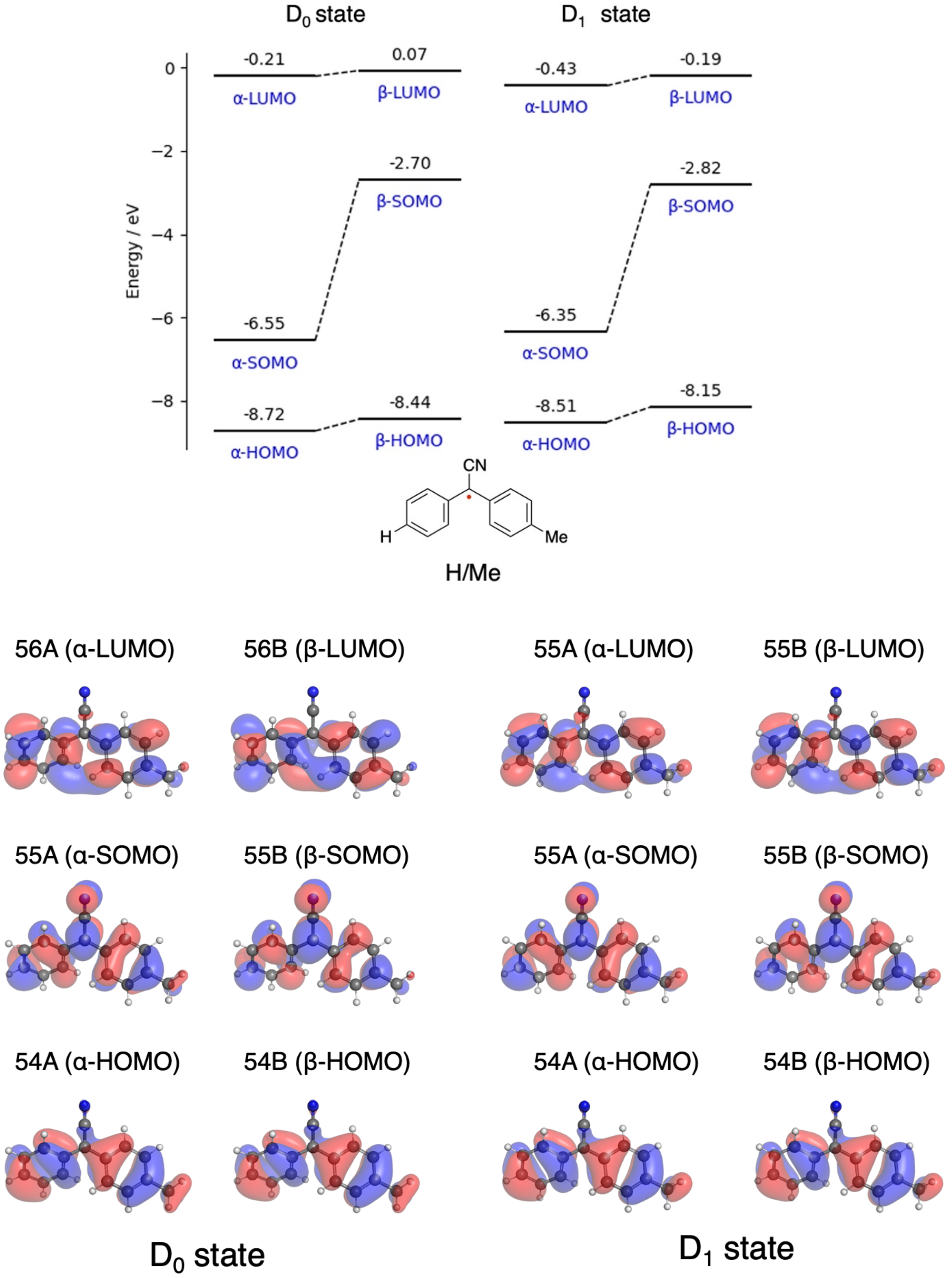


Figure S62. Molecular orbital diagrams for **DAAN-H/Me.**

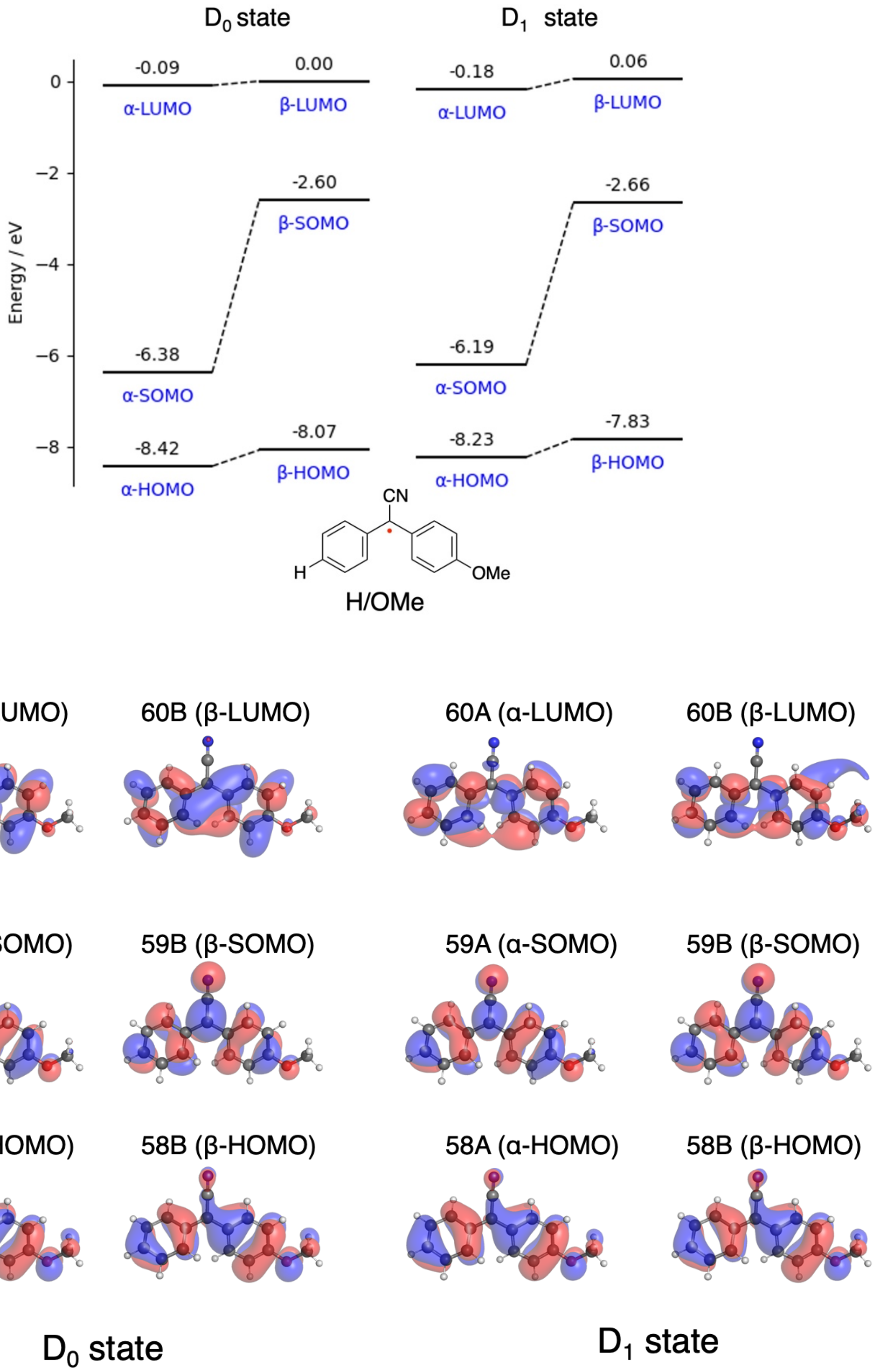


Figure S63. Molecular orbital diagrams for **DAAN-H/OMe.**

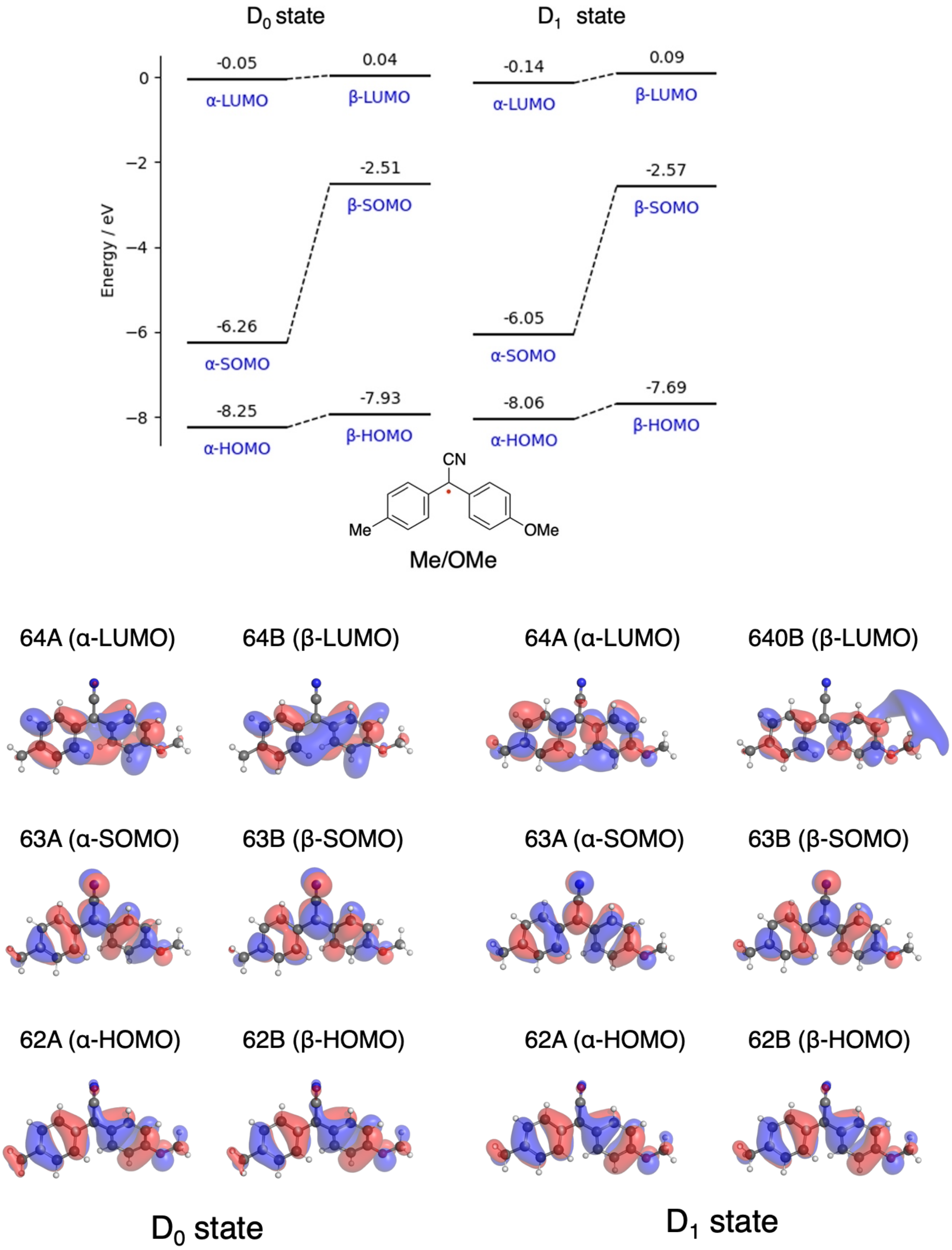


Figure S64. Molecular orbital diagrams for **DAAN-Me/OMe.**

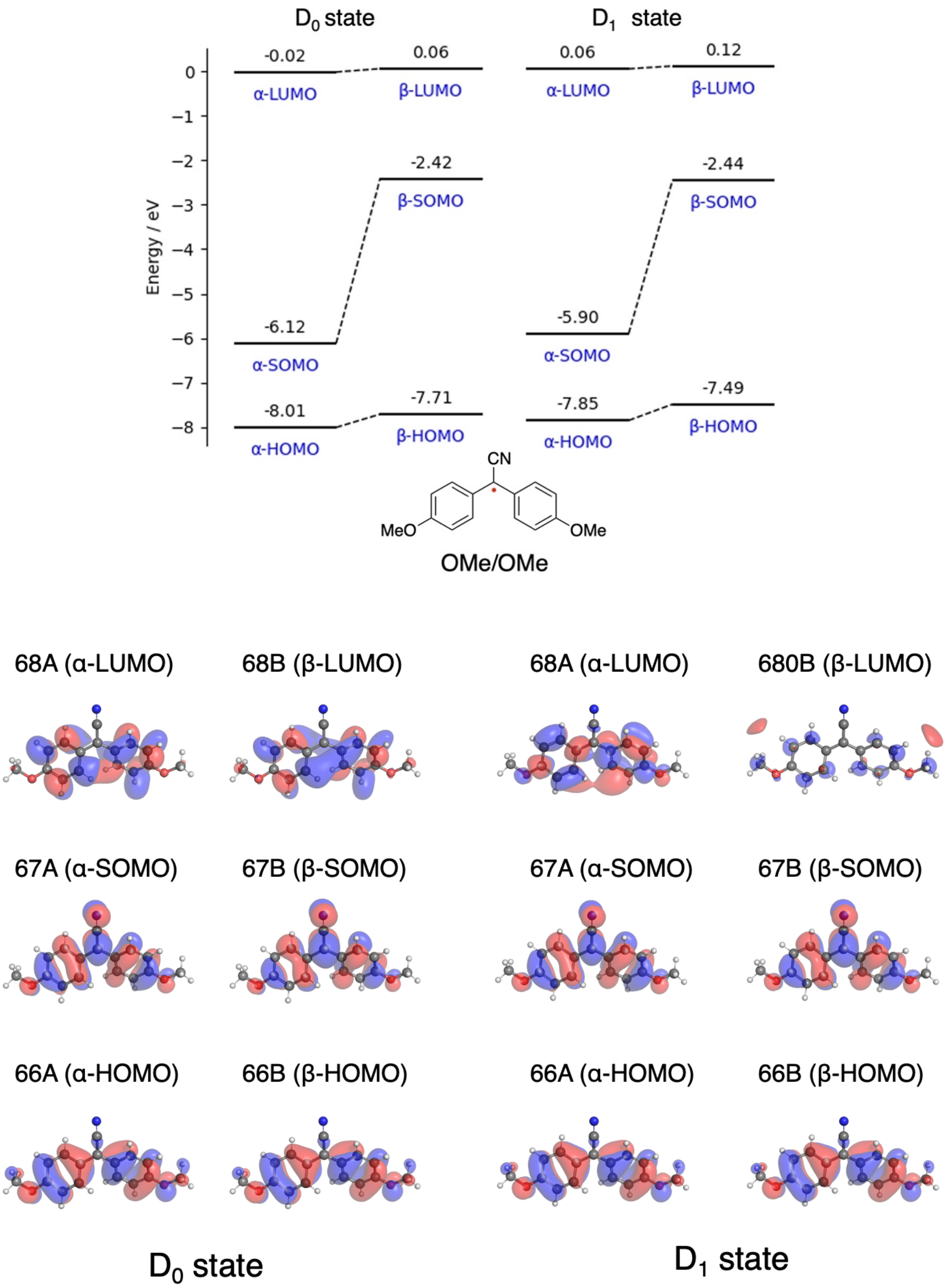


Figure S65. Molecular orbital diagrams for **DAAN-OMe/OMe.**

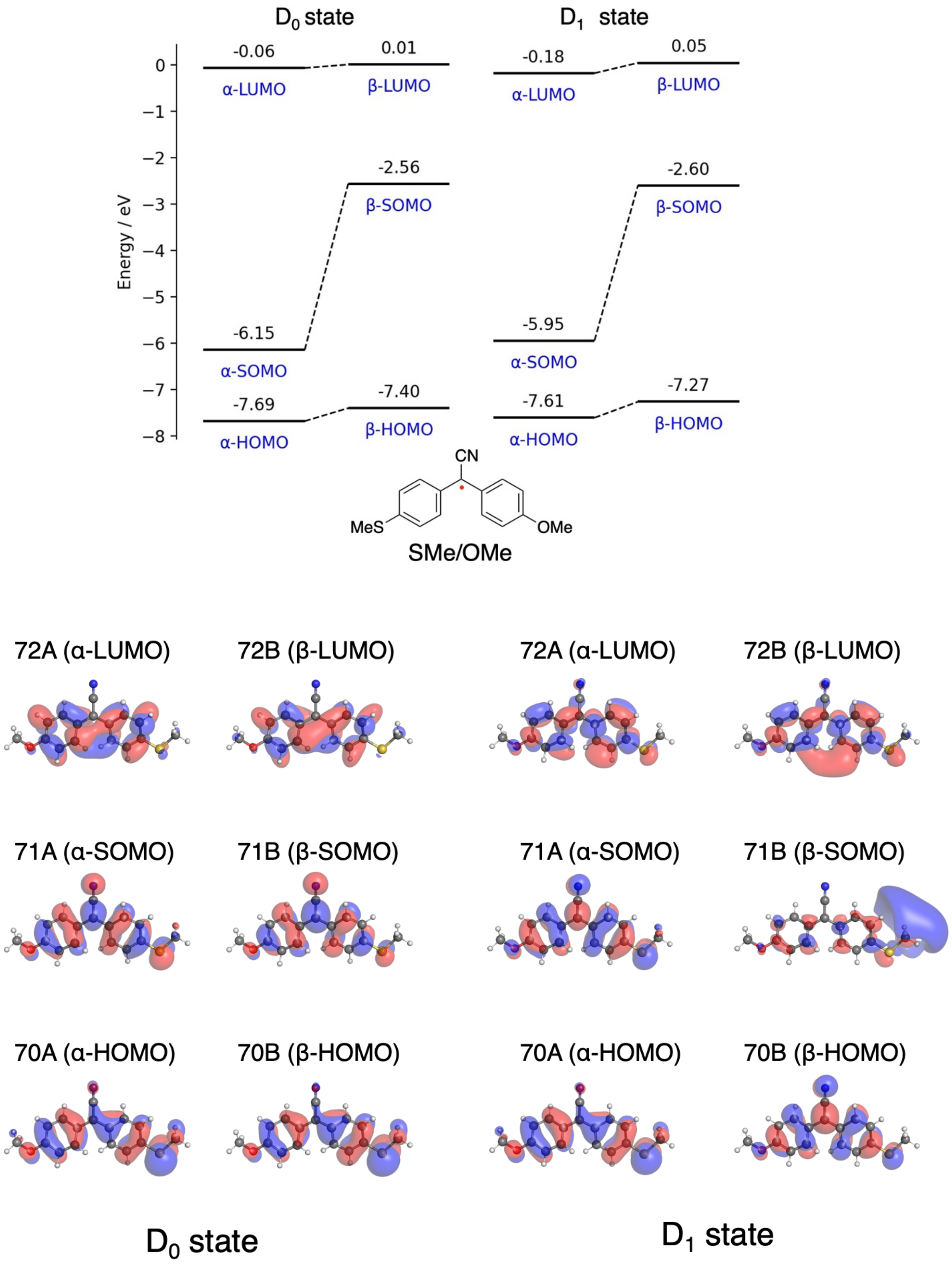


Figure S66. Molecular orbital diagrams for **DAAN-SMe/OMe**.

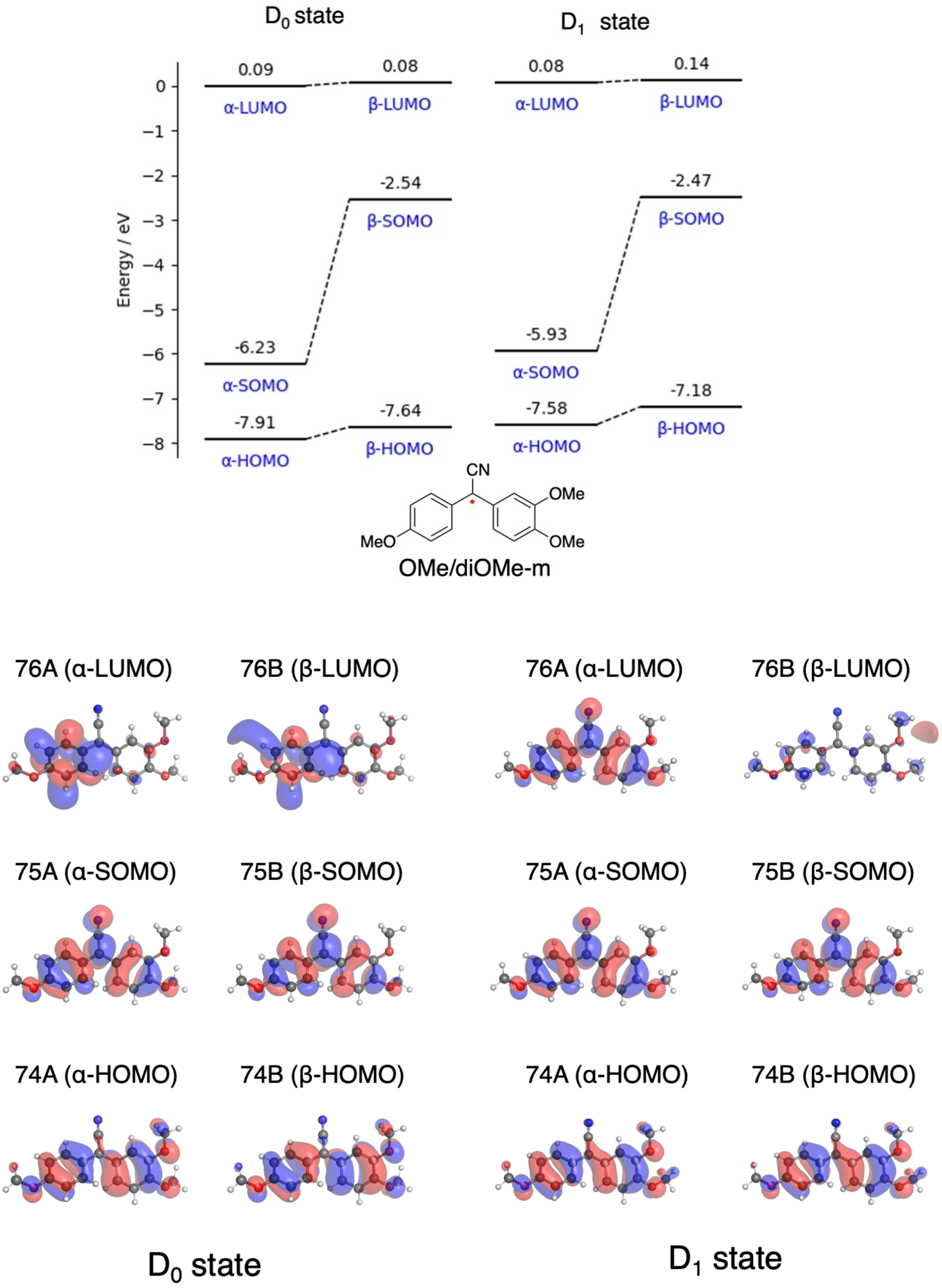


Figure S67. Molecular orbital diagrams for **DAAN-OMe/diOMe-m**.

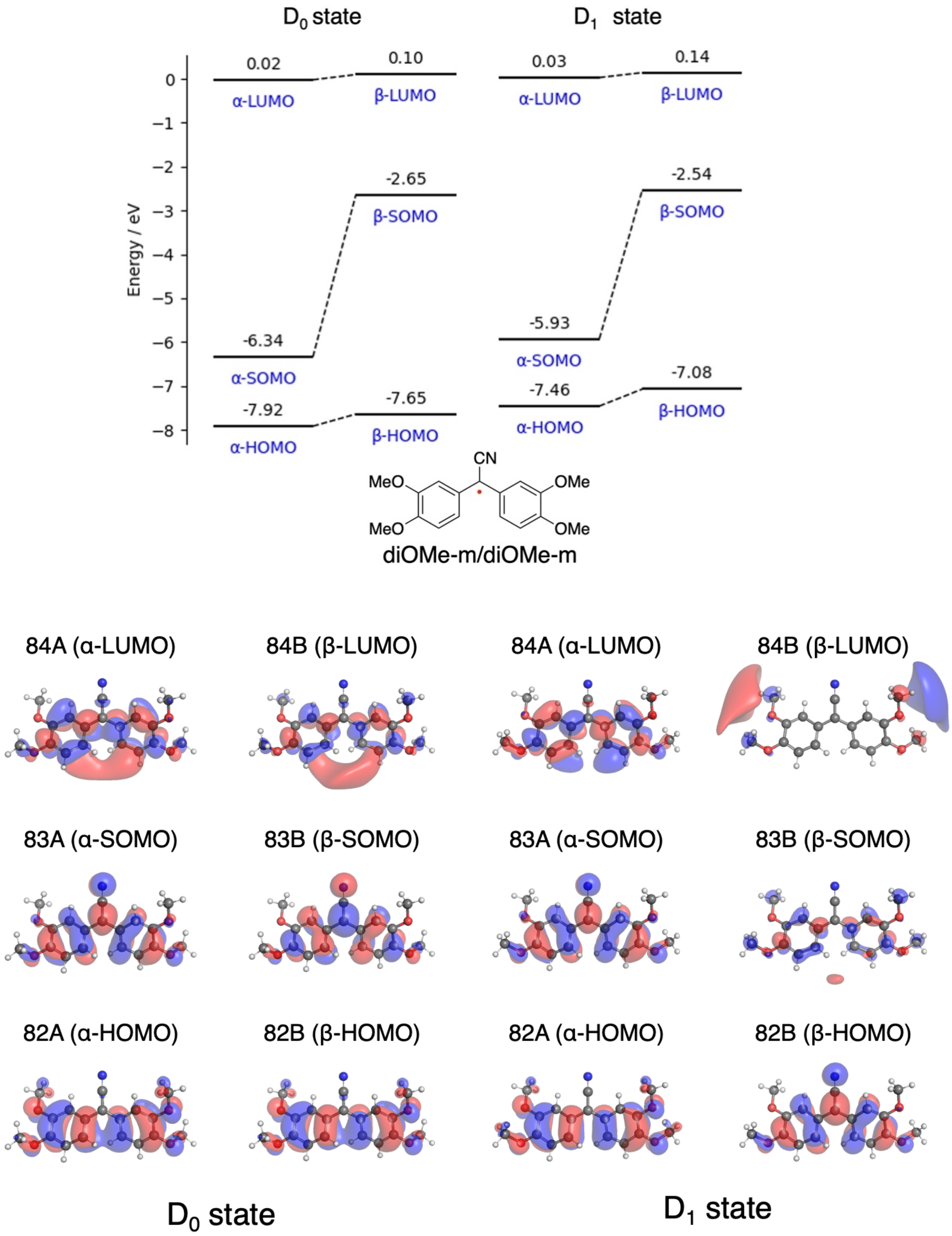
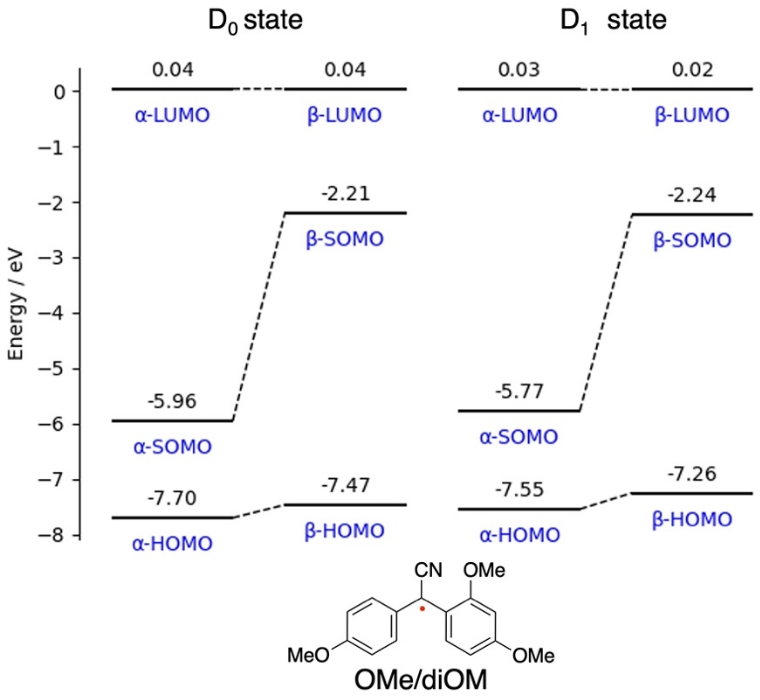


Figure S68. Molecular orbital diagrams for **DAAN-diOMe-m/diOMe-m**.



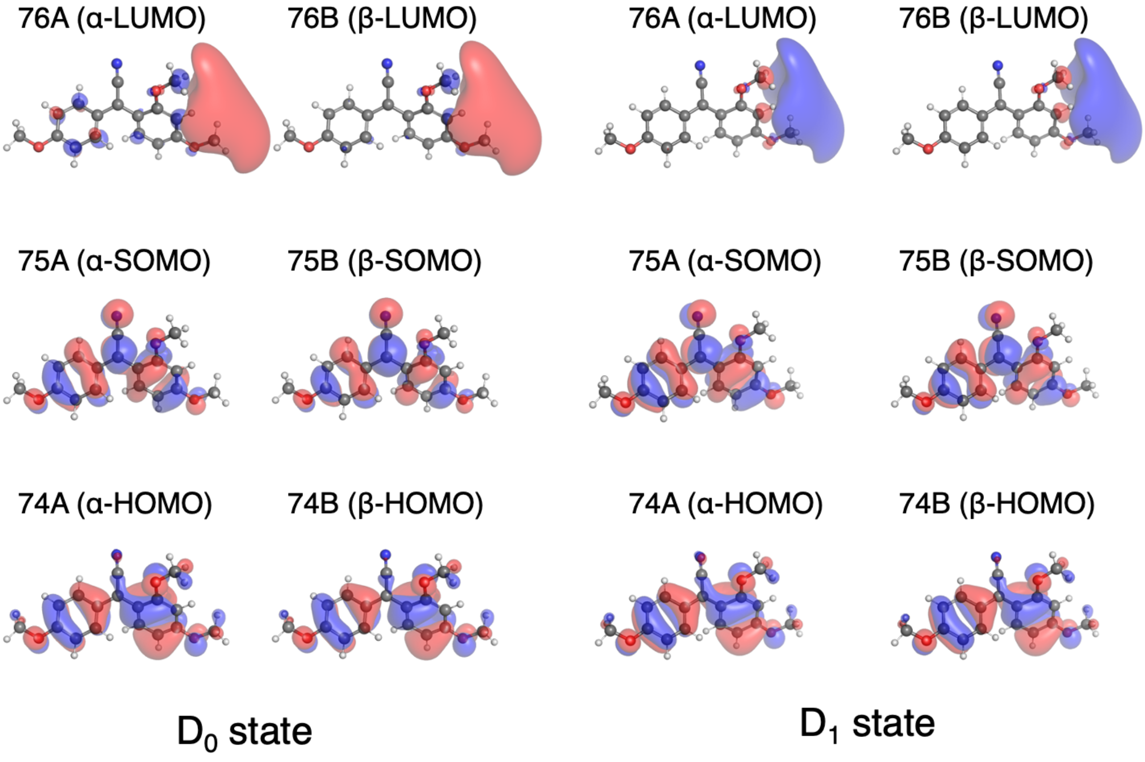
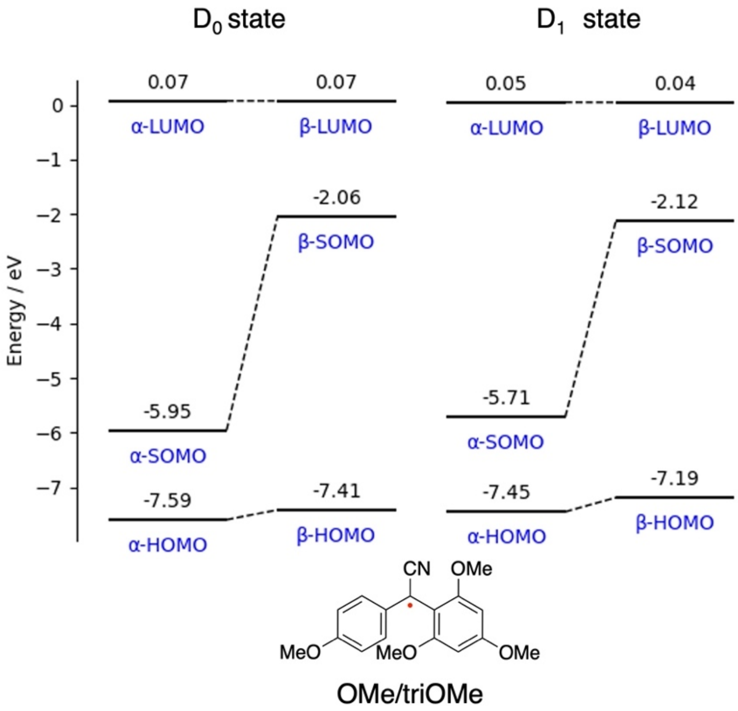


Figure S69. Molecular orbital diagrams for **DAAN-OMe/diOMe**.



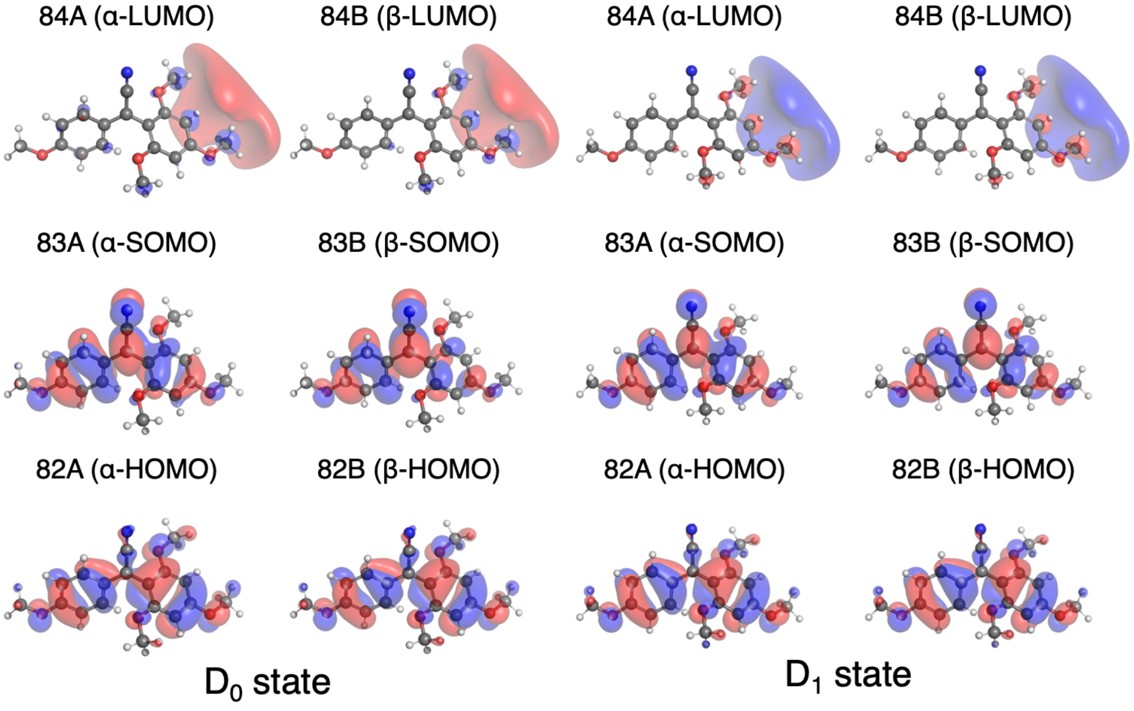


Figure S70. Molecular orbital diagrams for **DAAN-OMe/triOMe**.

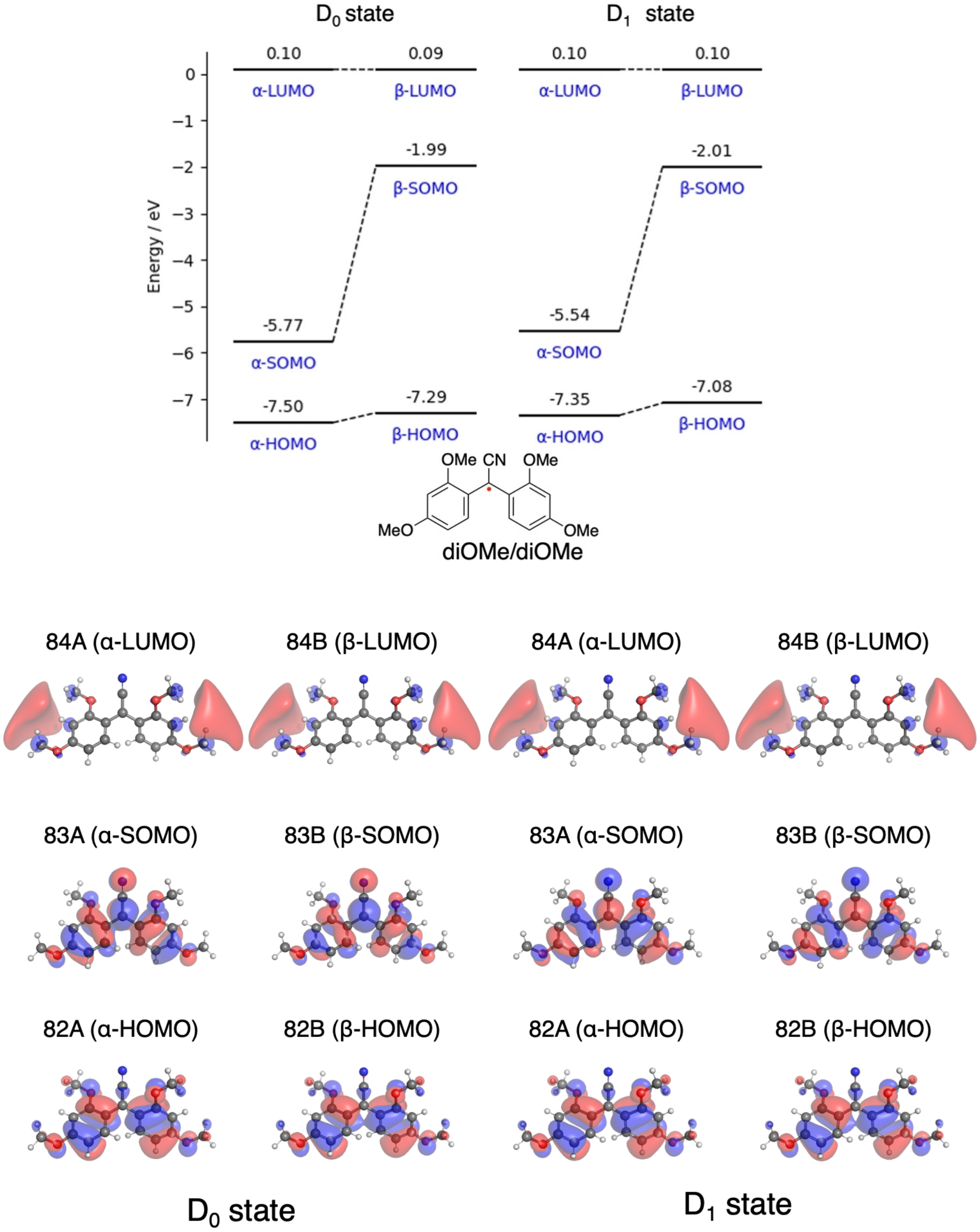


Figure S71. Molecular orbital diagrams for **DAAN-diOMe/diOMe**.

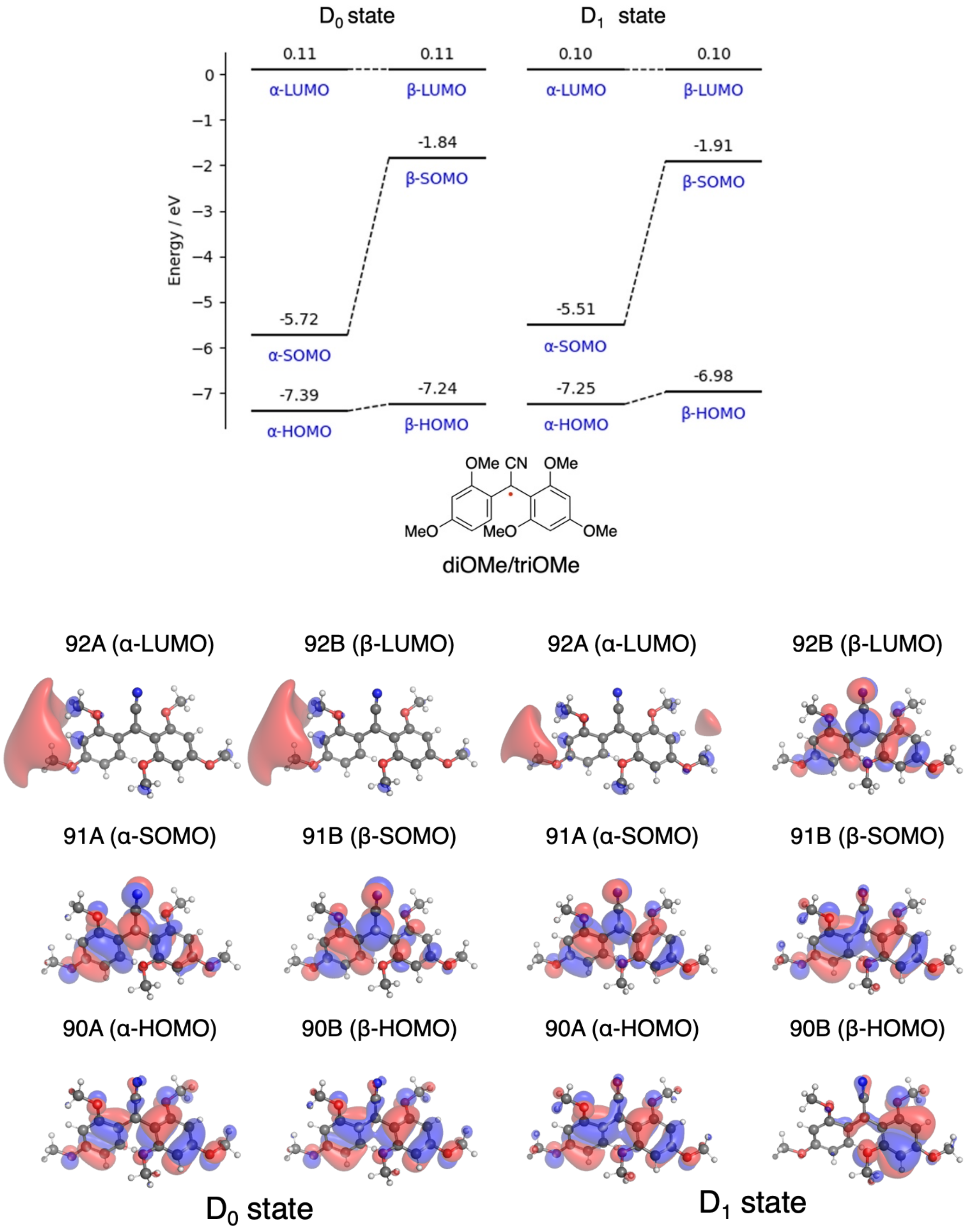


Figure S72. Molecular orbital diagrams for **DAAN-diOMe/triOMe**.

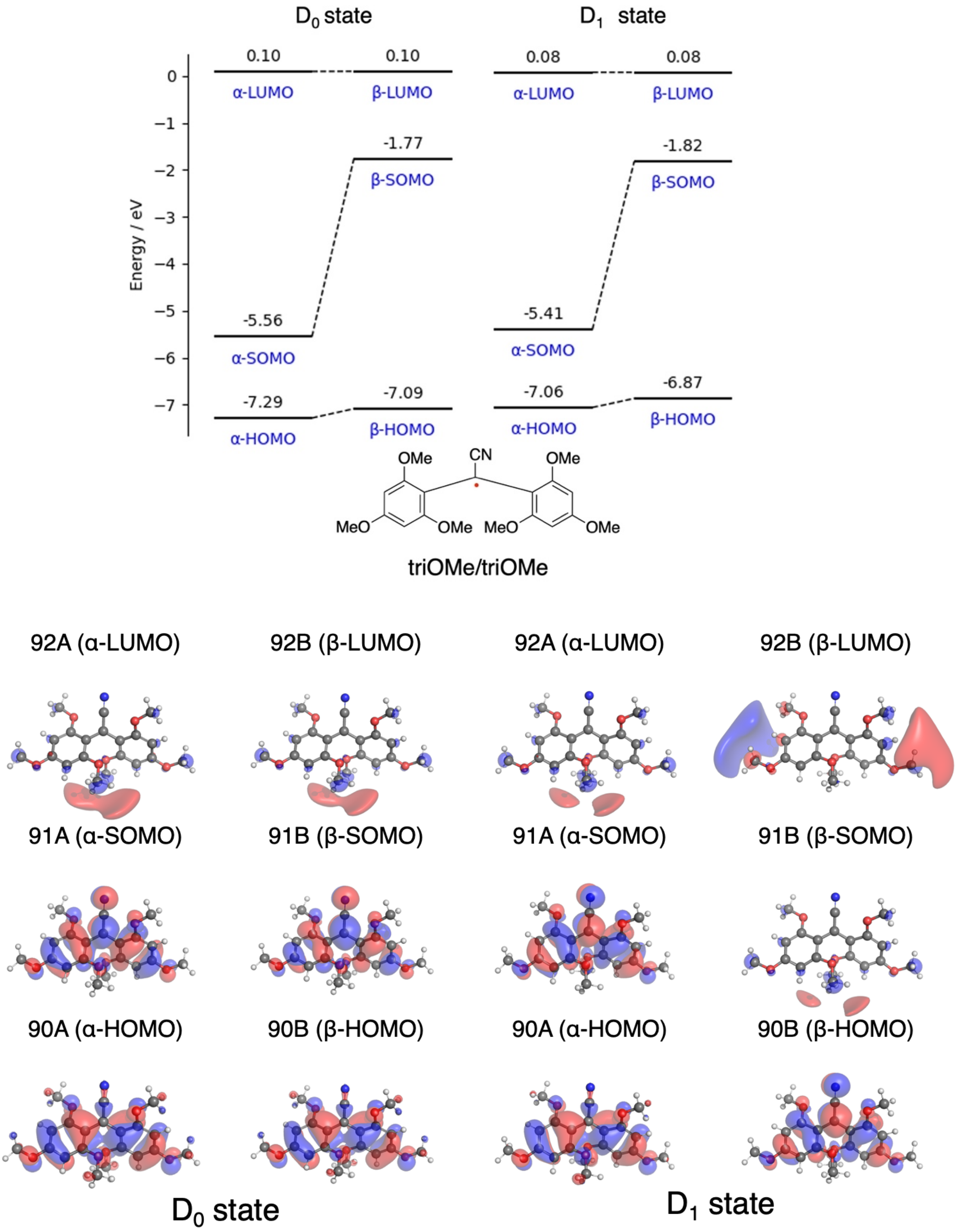


Figure S73. Molecular orbital diagrams for **DAAN-triOMe/triOMe**.

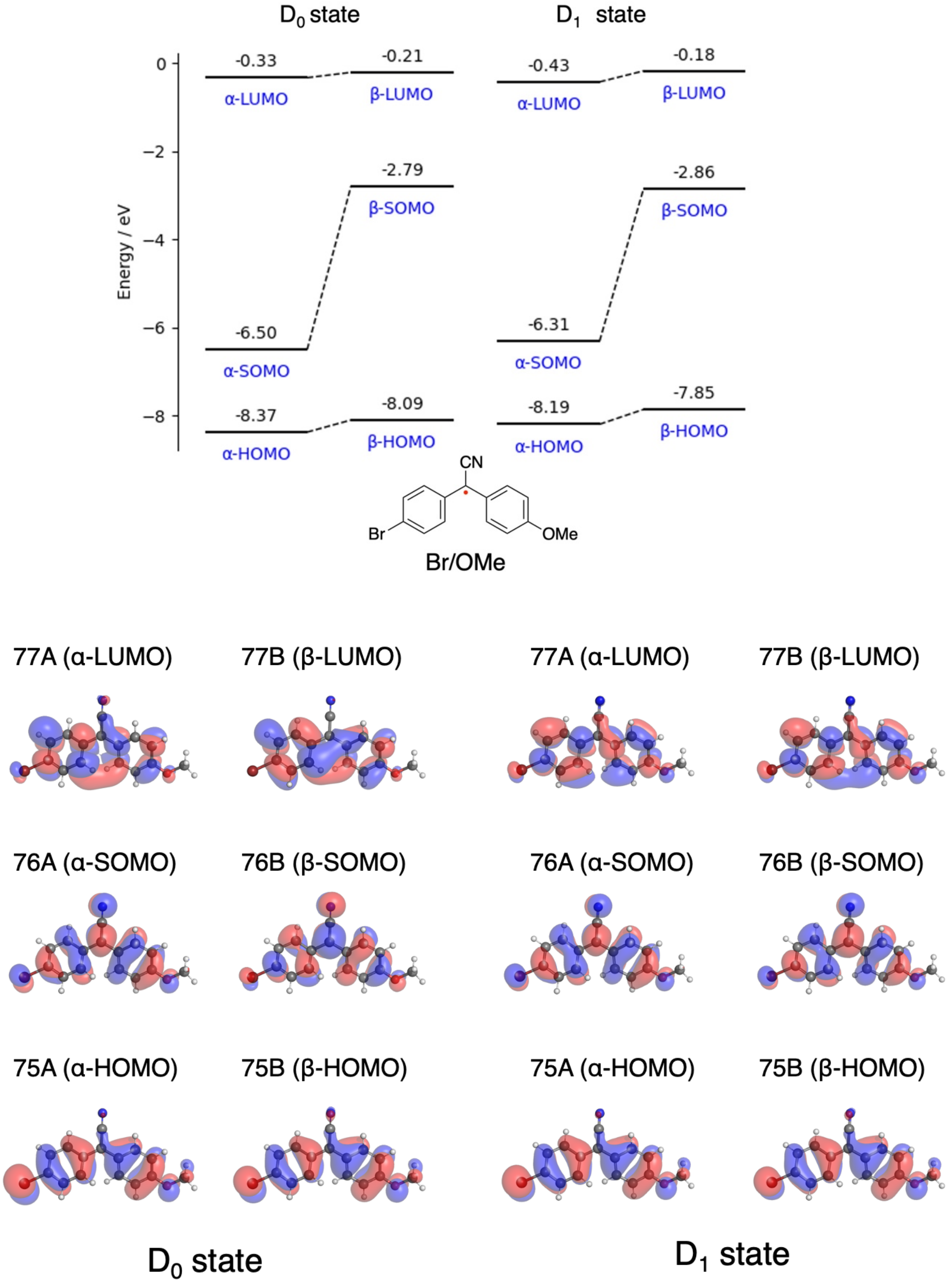


Figure S74. Molecular orbital diagrams for **DAAN-Br/OMe**.

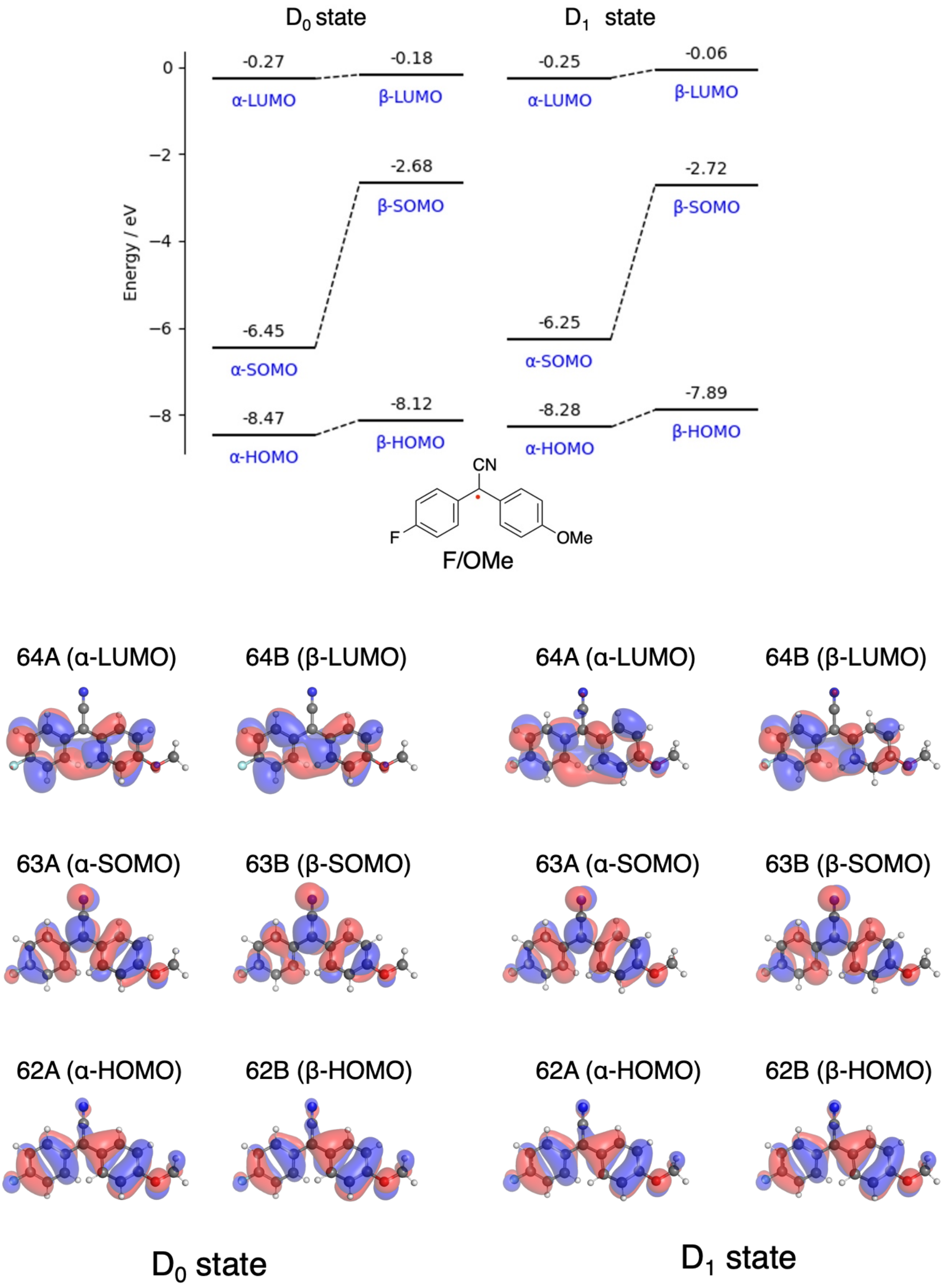


Figure S75. Molecular orbital diagrams for **DAAN-F/OMe**.

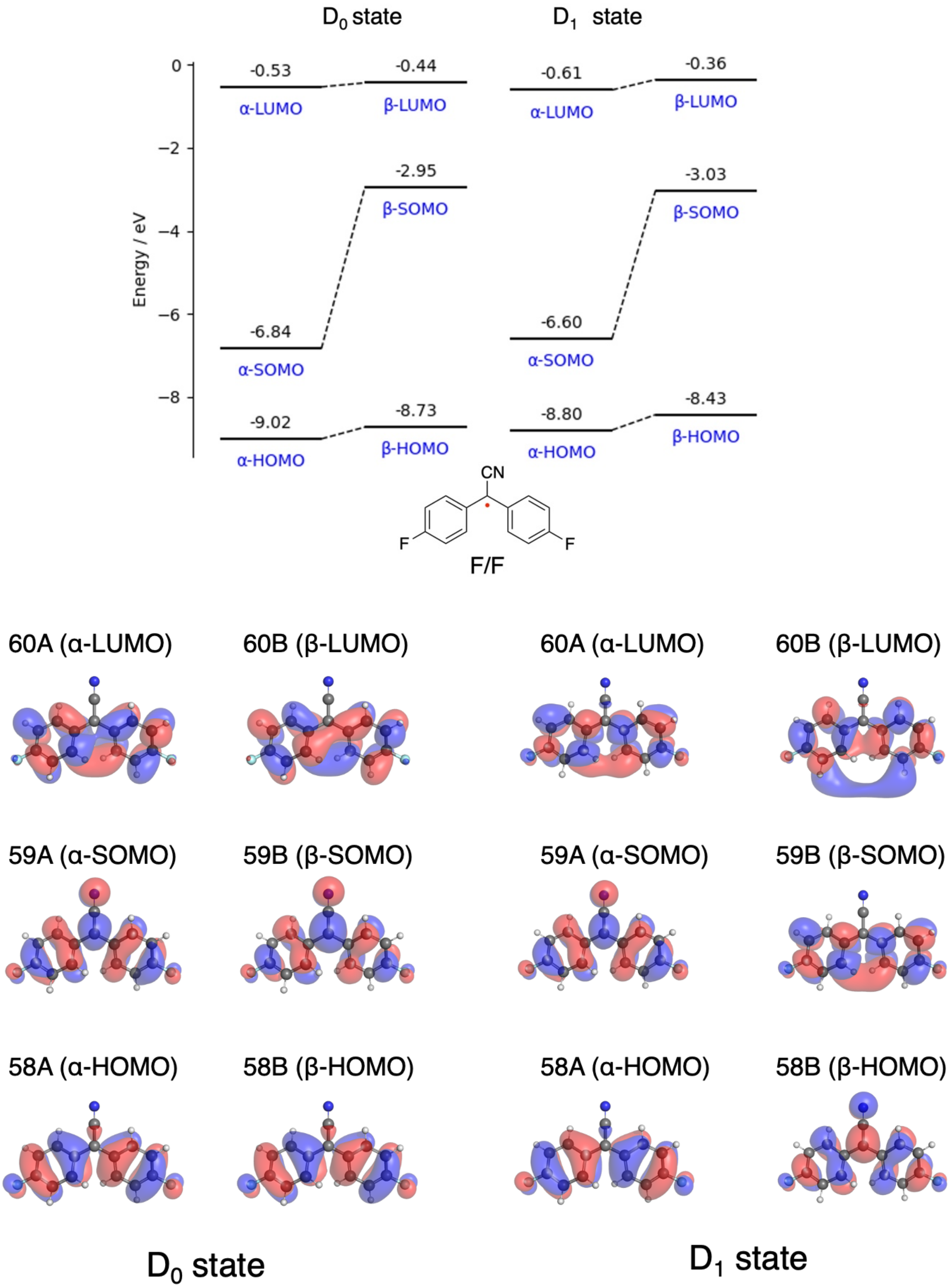


Figure S76. Molecular orbital diagrams for **DAAN-F/F**.

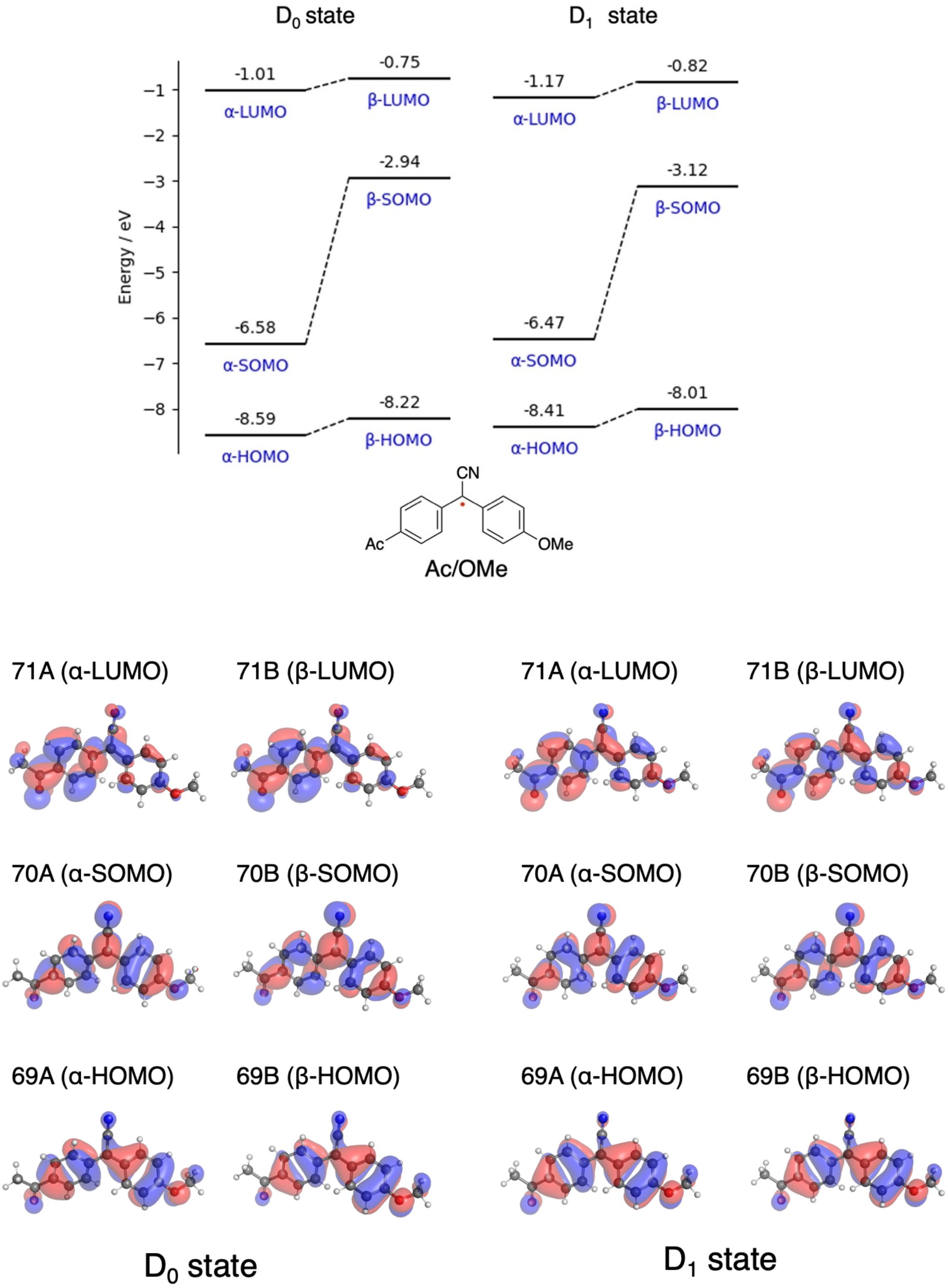


Figure S77. Molecular orbital diagrams for **DAAN-Ac/OMe**.

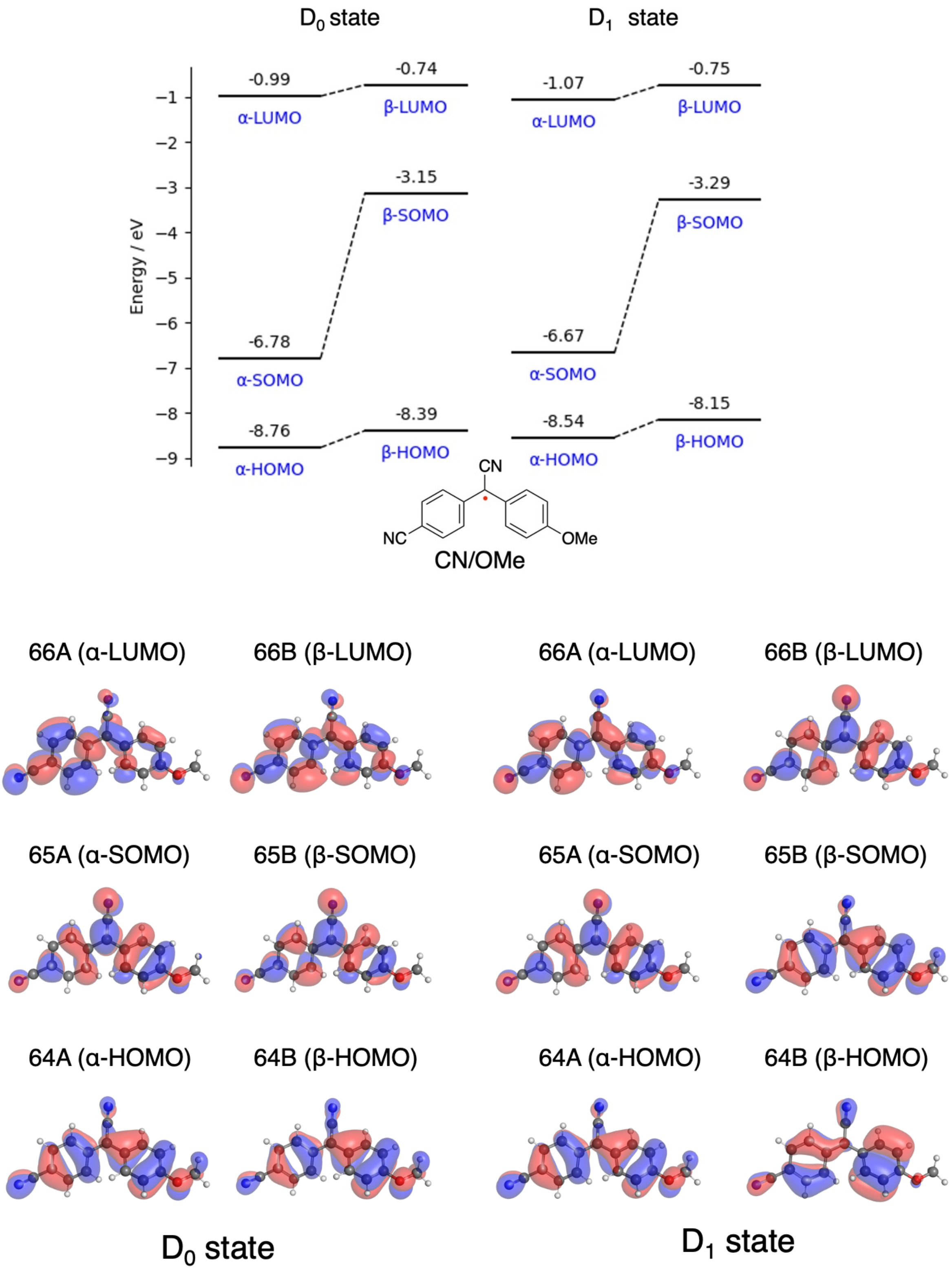


Figure S78. Molecular orbital diagrams for **DAAN-CN/OMe**.

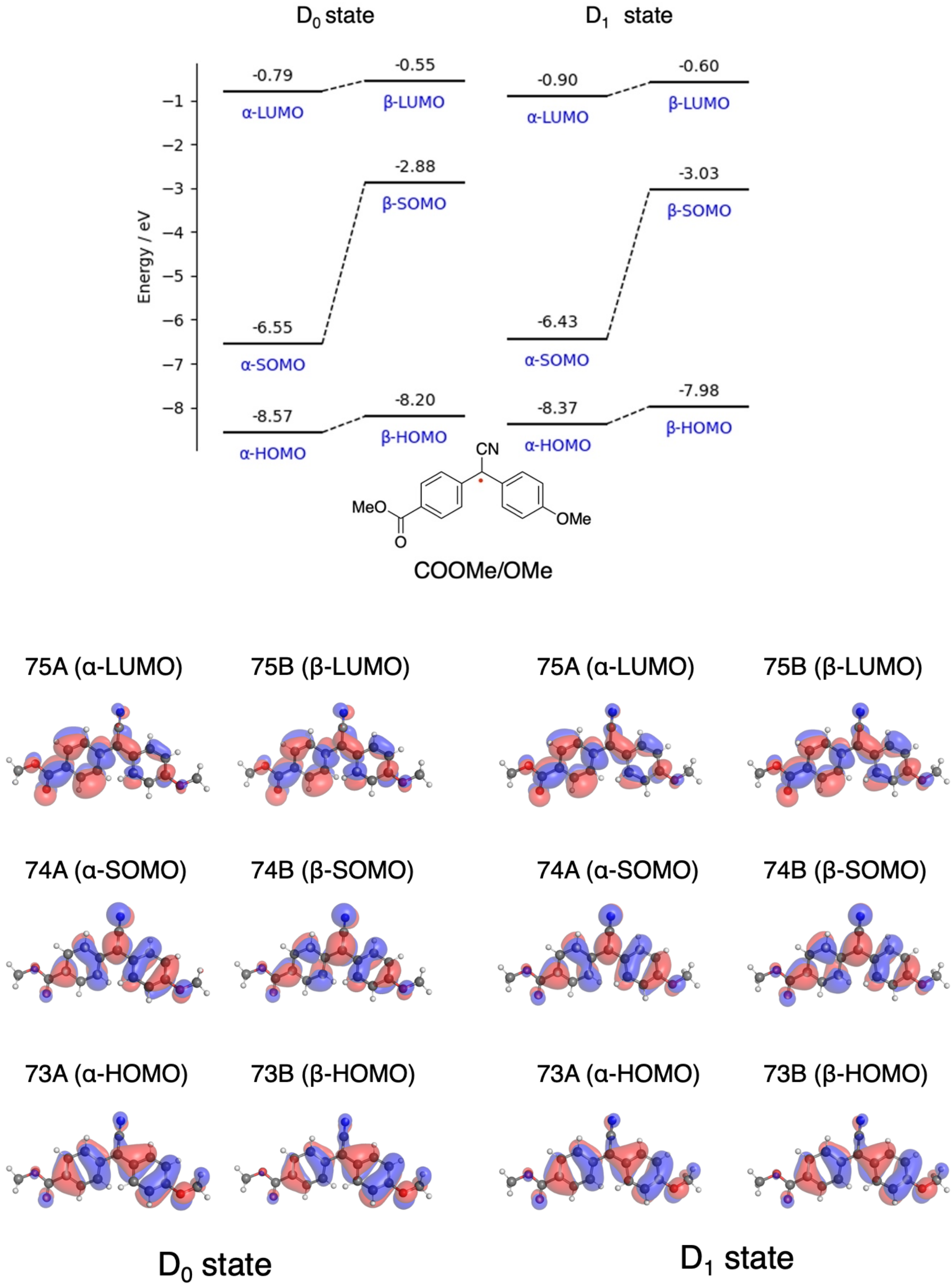


Figure S79. Molecular orbital diagrams for **DAAN-COOMe/OMe**.

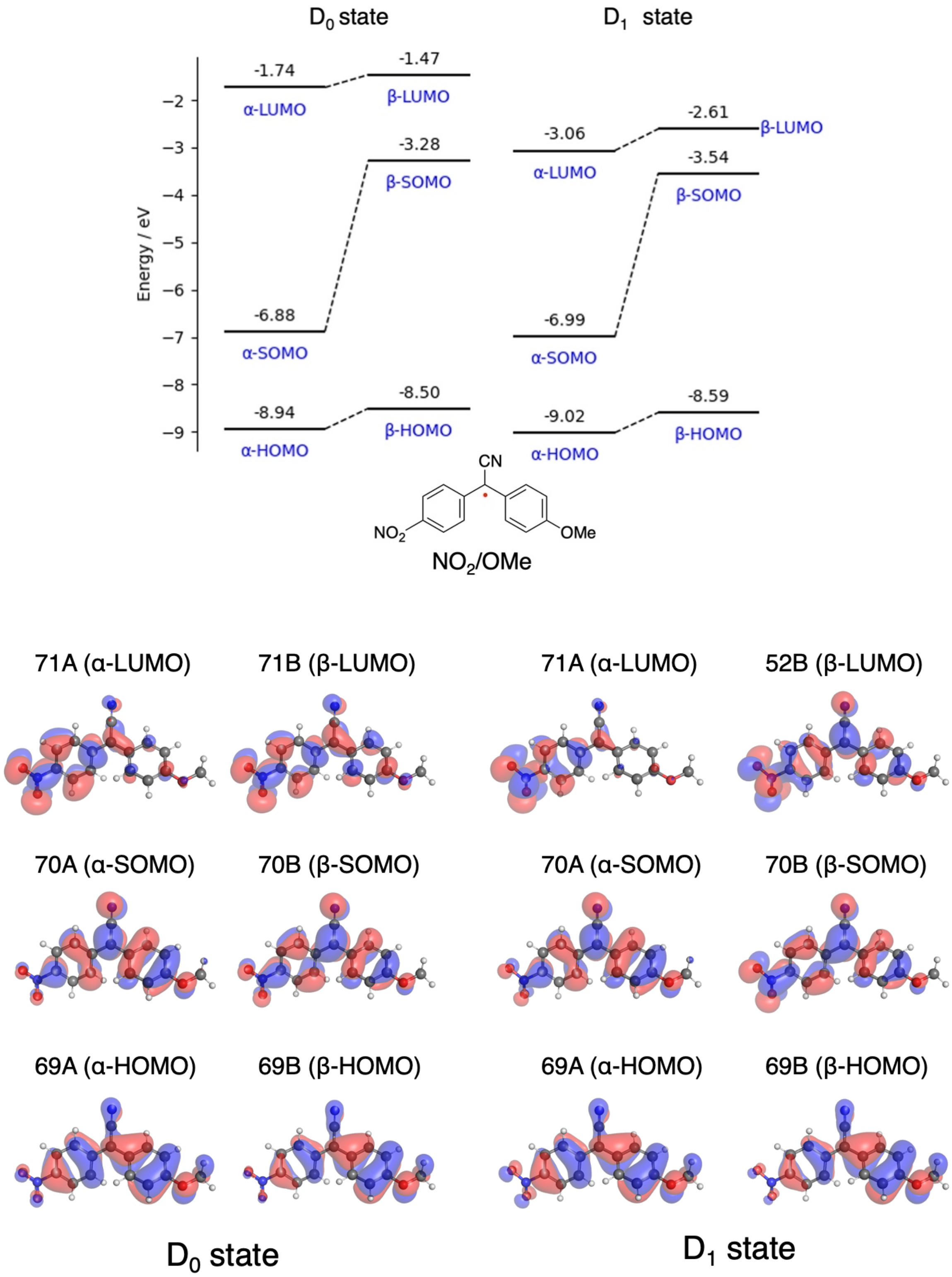


Figure S80. Molecular orbital diagrams for **DAAN-NO$_2$/OMe**.

Table S5. Bond lengths of DAAN radicals in ground (D_0) and excited (D_1) states

	Bond length / Å									
	H/H		**H/Me**		**H/OMe**		**Me/OMe**		**OMe/OMe**	
State	D_0	D_1	D_0	D_1	D_0	D_1	D_0	D_1	D_0	D_1
C1-C2	1.39	1.42	1.39	1.41	1.39	1.41	1.40	1.42	1.40	1.41
C1-C3	1.39	1.41	1.39	1.40	1.39	1.40	1.40	1.41	1.40	1.42
C2-C4	1.39	1.37	1.39	1.37	1.39	1.37	1.38	1.37	1.39	1.37
C3-C5	1.39	1.37	1.39	1.37	1.39	1.38	1.39	1.38	1.38	1.37
C4-C6	1.41	1.45	1.41	1.44	1.41	1.43	1.41	1.44	1.40	1.44
C5-C6	1.41	1.45	1.41	1.44	1.41	1.43	1.41	1.44	1.41	1.44
C6-C7	1.45	1.42	1.46	1.43	1.46	1.43	1.45	1.42	1.45	1.43
C7-C8	1.45	1.42	1.45	1.42	1.45	1.43	1.45	1.43	1.45	1.43
C8-C9	1.41	1.45	1.41	1.45	1.41	1.44	1.41	1.45	1.40	1.44
C8-C10	1.41	1.45	1.41	1.45	1.41	1.45	1.41	1.44	1.41	1.44
C9-C11	1.39	1.37	1.38	1.36	1.39	1.37	1.39	1.37	1.39	1.37
C10-C12	1.39	1.37	1.39	1.36	1.38	1.36	1.38	1.36	1.38	1.37
C11-C13	1.39	1.42	1.40	1.43	1.40	1.42	1.40	1.41	1.40	1.41
C12-C13	1.39	1.41	1.40	1.42	1.40	1.43	1.40	1.42	1.40	1.42

	Bond length / Å									
	SMe/OMe		**F/OMe**		**Br/OMe**		**F/F**		**Ac/OMe**	
State	D_0	D_1	D_0	D_1	D_0	D_1	D_0	D_1	D_0	D_1
C1-C2	1.40	1.42	1.39	1.40	1.39	1.41	1.39	1.41	1.40	1.43
C1-C3	1.40	1.43	1.39	1.39	1.39	1.40	1.39	1.40	1.40	1.43
C2-C4	1.38	1.36	1.38	1.37	1.38	1.37	1.38	1.36	1.38	1.36
C3-C5	1.38	1.36	1.39	1.38	1.39	1.37	1.38	1.37	1.38	1.36
C4-C6	1.41	1.45	1.41	1.43	1.41	1.44	1.41	1.45	1.41	1.45
C5-C6	1.41	1.44	1.41	1.43	1.41	1.44	1.41	1.45	1.41	1.36
C6-C7	1.44	1.42	1.46	1.43	1.45	1.42	1.45	1.42	1.45	1.41
C7-C8	1.45	1.44	1.45	1.43	1.45	1.43	1.45	1.42	1.45	1.43
C8-C9	1.40	1.42	1.41	1.45	1.41	1.44	1.41	1.45	1.41	1.43
C8-C10	1.41	1.43	1.41	1.44	1.41	1.44	1.41	1.45	1.41	1.43
C9-C11	1.39	1.38	1.38	1.37	1.39	1.37	1.38	1.36	1.38	1.37
C10-C12	1.38	1.37	1.39	1.36	1.38	1.36	1.38	1.37	1.39	1.37
C11-C13	1.40	1.40	1.40	1.42	1.40	1.41	1.39	1.41	1.40	1.41
C12-C13	1.40	1.41	1.40	1.43	1.40	1.42	1.39	1.40	1.40	1.42

	Bond length / Å									
	CN/OMe		**COOMe/OMe**		**NO_2/OMe**		**OMe/diOMe**		**diOMe/diOMe**	
State	D_0	D_1	D_0	D_1	D_0	D_1	D_0	D_1	D_0	D_1
C1-C2	1.40	1.42	1.40	1.42	1.40	1.39	1.40	1.40	1.39	1.40
C1-C3	1.40	1.42	1.40	1.41	1.40	1.39	1.40	1.41	1.40	1.42
C2-C4	1.38	1.36	1.38	1.36	1.38	1.39	1.39	1.38	1.40	1.39
C3-C5	1.38	1.37	1.38	1.37	1.38	1.39	1.38	1.37	1.38	1.37
C4-C6	1.41	1.44	1.41	1.44	1.41	1.40	1.41	1.43	1.41	1.45
C5-C6	1.41	1.44	1.41	1.44	1.42	1.40	1.41	1.43	1.41	1.42
C6-C7	1.45	1.41	1.45	1.41	1.44	1.46	1.45	1.43	1.45	1.43
C7-C8	1.45	1.44	1.45	1.44	1.45	1.45	1.46	1.43	1.45	1.43
C8-C9	1.41	1.44	1.41	1.44	1.41	1.41	1.41	1.46	1.41	1.45
C8-C10	1.41	1.43	1.41	1.44	1.41	1.41	1.41	1.42	1.41	1.42
C9-C11	1.39	1.37	1.39	1.37	1.38	1.39	1.40	1.39	1.40	1.39
C10-C12	1.38	1.36	1.38	1.36	1.38	1.38	1.38	1.37	1.38	1.37
C11-C13	1.40	1.41	1.40	1.41	1.39	1.40	1.40	1.39	1.39	1.40
C12-C13	1.40	1.42	1.40	1.42	1.39	1.40	1.40	1.42	1.40	1.42

	Bond length / Å									
	OMe/triOMe		**diOMe/triOMe**		**triOMe/triOMe**		**OMe/diOMe-m**		**diOMe-m/diOMe-m**	
State	D_0	D_1	D_0	D_1	D_0	D_1	D_0	D_1	D_0	D_1
C1-C2	1.40	1.41	1.40	1.39	1.39	1.40	1.40	1.40	1.41	1.44
C1-C3	1.40	1.41	1.40	1.42	1.40	1.40	1.40	1.40	1.39	1.40
C2-C4	1.39	1.37	1.39	1.39	1.40	1.39	1.39	1.38	1.38	1.38
C3-C5	1.37	1.37	1.37	1.37	1.39	1.38	1.38	1.37	1.39	1.37
C4-C6	1.41	1.43	1.42	1.46	1.41	1.44	1.40	1.42	1.41	1.42
C5-C6	1.42	1.44	1.41	1.42	1.42	1.44	1.41	1.42	1.40	1.44
C6-C7	1.44	1.43	1.43	1.44	1.46	1.44	1.45	1.44	1.45	1.43
C7-C8	1.47	1.44	1.48	1.44	1.46	1.44	1.45	1.43	1.45	1.43
C8-C9	1.41	1.44	1.41	1.43	1.41	1.44	1.40	1.46	1.41	1.42
C8-C10	1.40	1.44	1.40	1.43	1.42	1.44	1.41	1.42	1.40	1.44
C9-C11	1.40	1.39	1.40	1.39	1.40	1.39	1.38	1.38	1.38	1.38
C10-C12	1.39	1.38	1.39	1.38	1.39	1.38	1.39	1.36	1.39	1.37
C11-C13	1.39	1.40	1.39	1.40	1.39	1.40	1.41	1.45	1.41	1.44
C12-C13	1.40	1.41	1.40	1.40	1.40	1.40	1.39	1.41	1.39	1.40

Table S6. Dihedral angles of DAAN radicals in ground (D_0) and excited (D_1) states

Sample	State	Dihedral angle / °	Sample	State	Dihedral angle / °
H/H	D_0	45.8	**CN/OMe**	D_0	44.2
	D_1	36.4		D_1	38.3
H/Me	D_0	45.3	**COOMe/OMe**	D_0	44.3
	D_1	36.7		D_1	37.8
H/OMe	D_0	45.0	**NO_2/OMe**	D_0	44.2
	D_1	38.7		D_1	46.2
Me/OMe	D_0	44.5	**OMe/diOMe**	D_0	50.2
	D_1	37.1		D_1	44.1
OMe/OMe	D_0	44.3	**diOMe/diOMe**	D_0	58.8
	D_1	37.4		D_1	51.9
SMe/OMe	D_0	44.0	**OMe/triOMe**	D_0	54.5
	D_1	37.5		D_1	48.5
F/OMe	D_0	44.9	**diOMe/triOMe**	D_0	59.3
	D_1	38.8		D_1	58.3
Br/OMe	D_0	44.6	**triOMe/triOMe**	D_0	62.8
	D_1	37.5		D_1	59.2
F/F	D_0	45.7	**OMe/diOMe-m**	D_0	44.4
	D_1	36.9		D_1	36.5
Ac/OMe	D_0	44.0	**diOMe-m/diOMe-m**	D_0	44.3
	D_1	37.7		D_1	32.9

Table S7. μ_{01} and fluorescence quantum yield of DAAN radicals (EQY = external quantum yield, IQY = internal quantum yield)

	μ_{01} / D	EQY / %	IQY / %
H/H	2.14	0.28	0.52
H/Me	2.43	0.52	2.06
H/OMe	3.24	1.42	3.94
Me/OMe	3.33	1.22	4.15
OMe/OMe	3.71	3.32	8.97
SMe/OMe	4.35	2.24	6.74
F/OMe	3.25	2.46	7.69
Br/OMe	3.66	1.72	5.63
F/F	2.28	1.75	4.10
Ac/OMe	2.47	0.52	0.83
CN/OMe	3.52	2.80	8.87
COOMe/OMe	3.20	3.87	11.80
NO_2/OMe	0.14	–[a]	–[a]
OMe/diOMe	3.75	1.52	5.35
diOMe/diOMe	3.46	3.97	11.49
OMe/triOMe	3.77	3.40	10.50
diOMe/triOMe	3.57	3.90	13.06
triOMe/triOMe	3.39	2.36	7.45
OMe/diOMe-m	4.11	2.66	8.47
diOMe-m/diOMe-m	4.47	6.40	17.05

a. No fluorescence was observed.

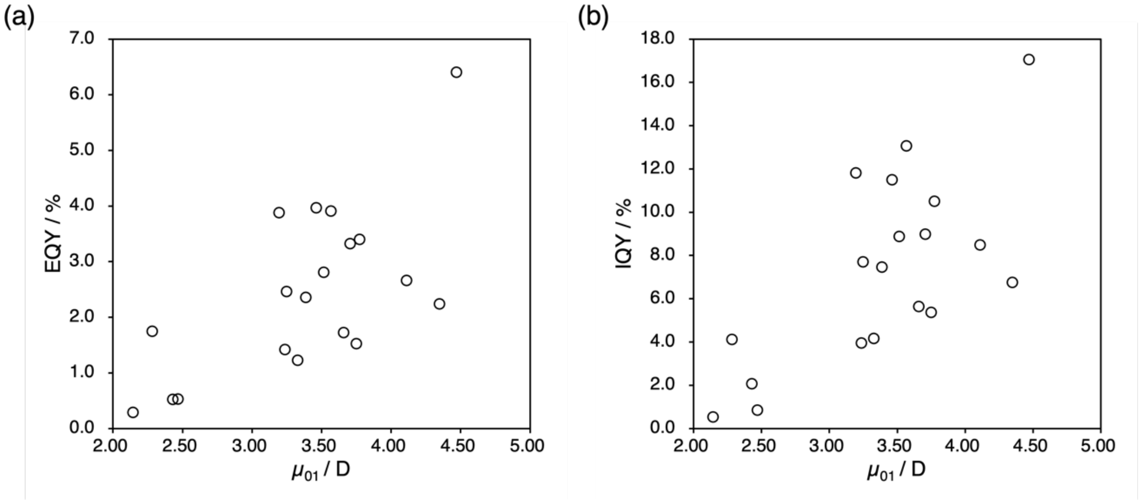


Figure S81. (a) EQY plotted against transition dipole moment (μ_{01}). (b) IQY plotted against transition dipole moment (μ_{01}).

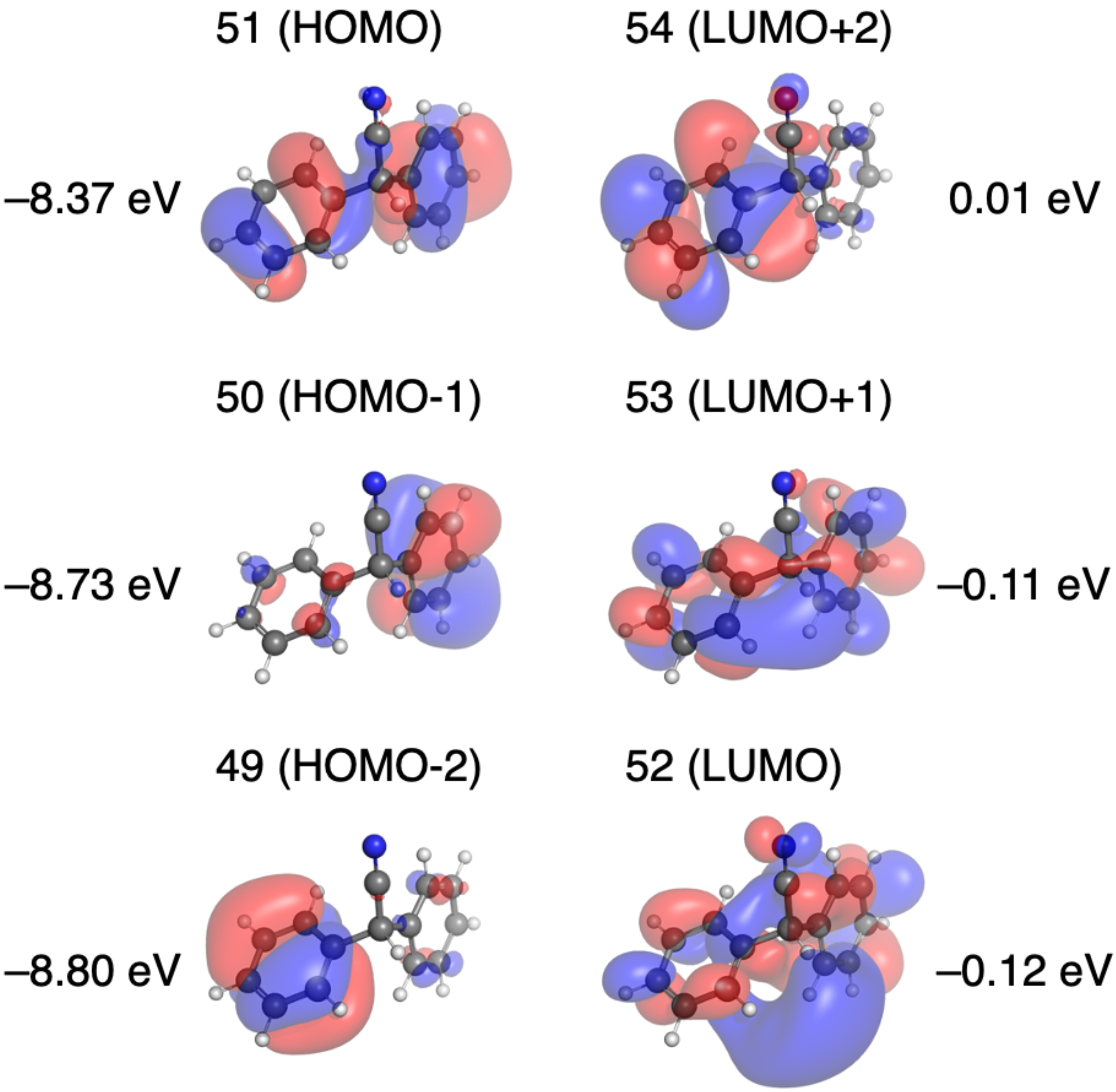


Figure S82. Molecular orbitals for **DAAN-H/H**.

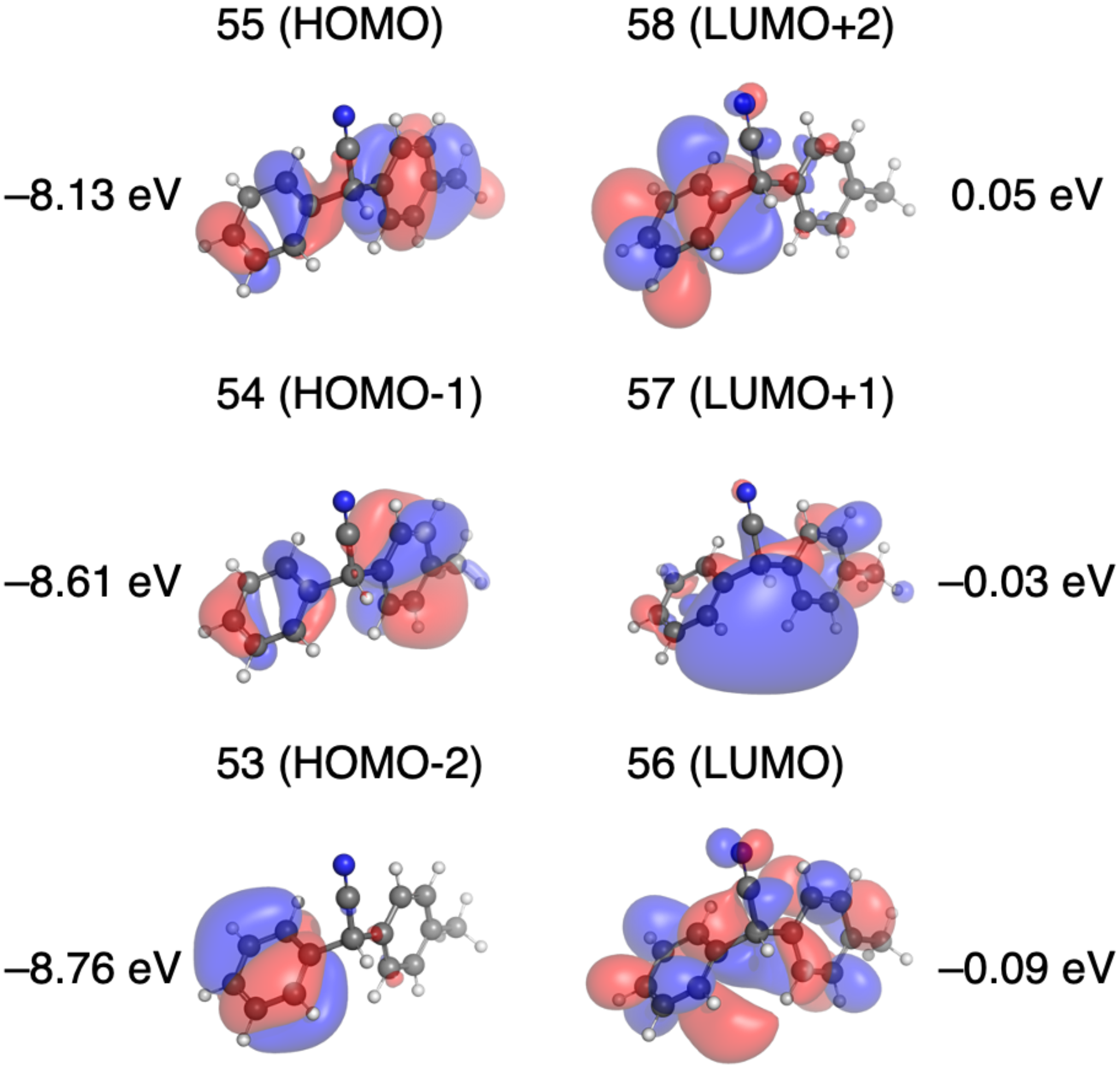


Figure S83. Molecular orbitals for **DAAN-H/Me**.

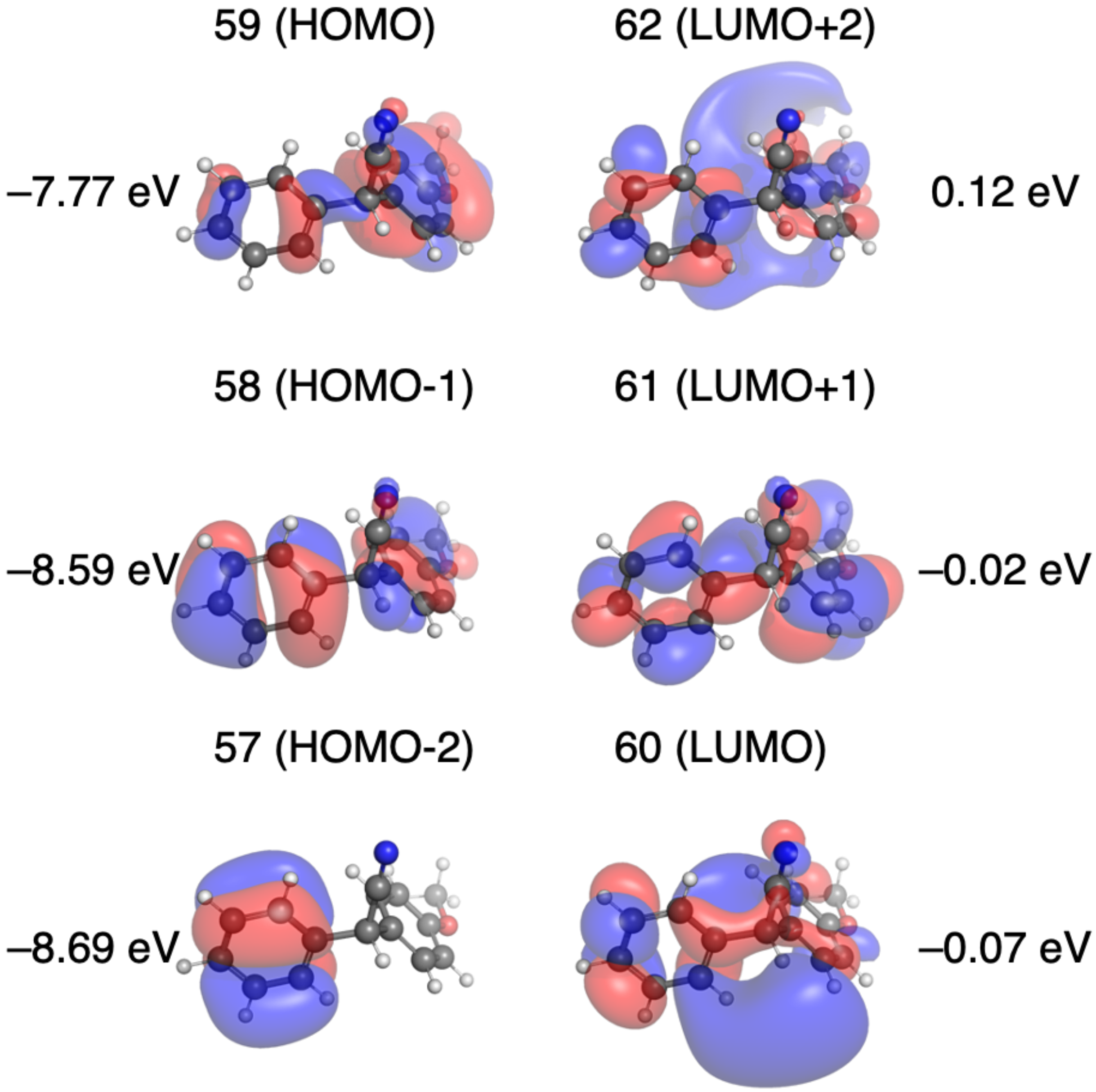


Figure S84. Molecular orbitals for **DAAN-H/OMe**.

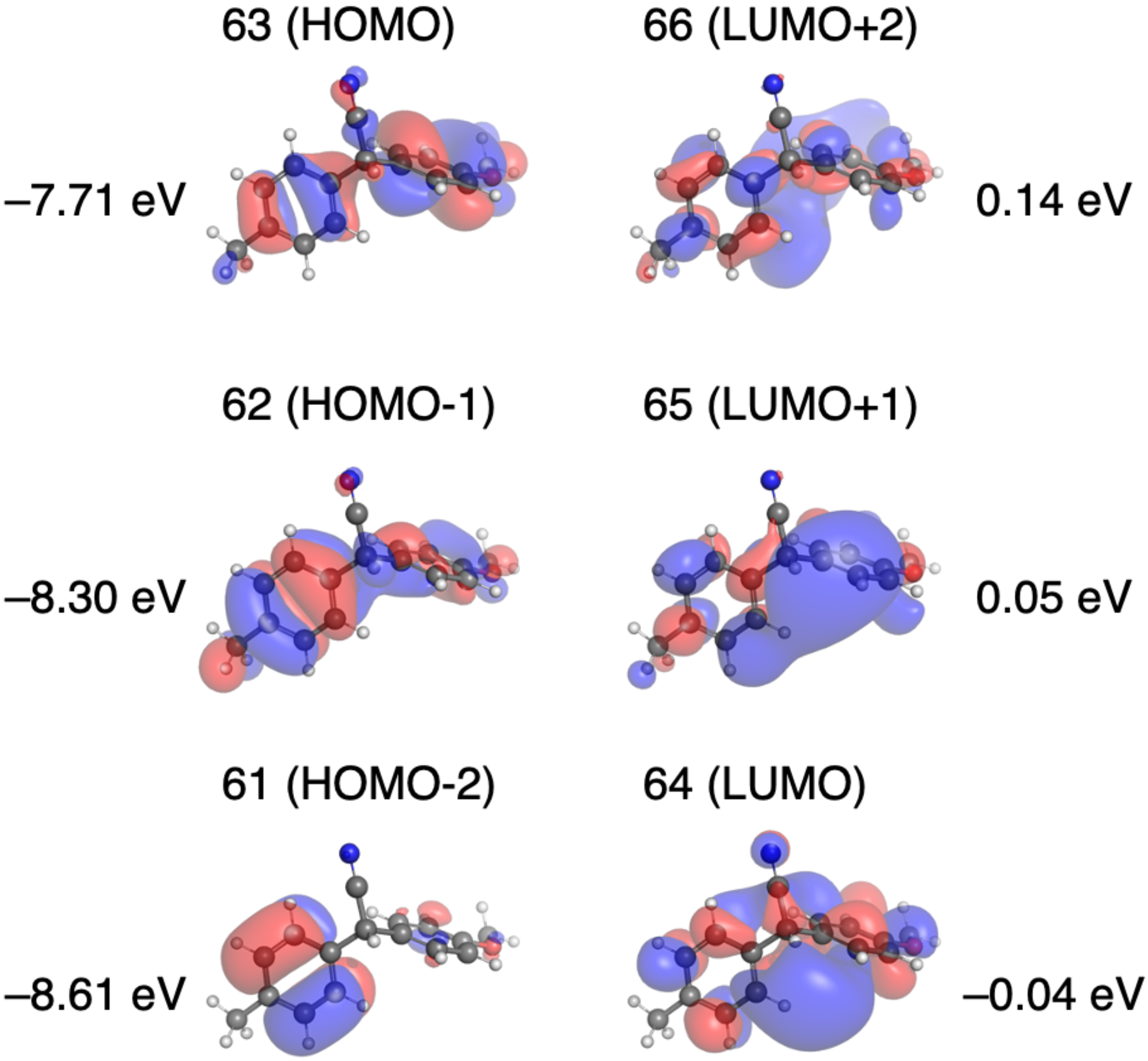


Figure S85. Molecular orbitals for **DAAN-Me/OMe**.

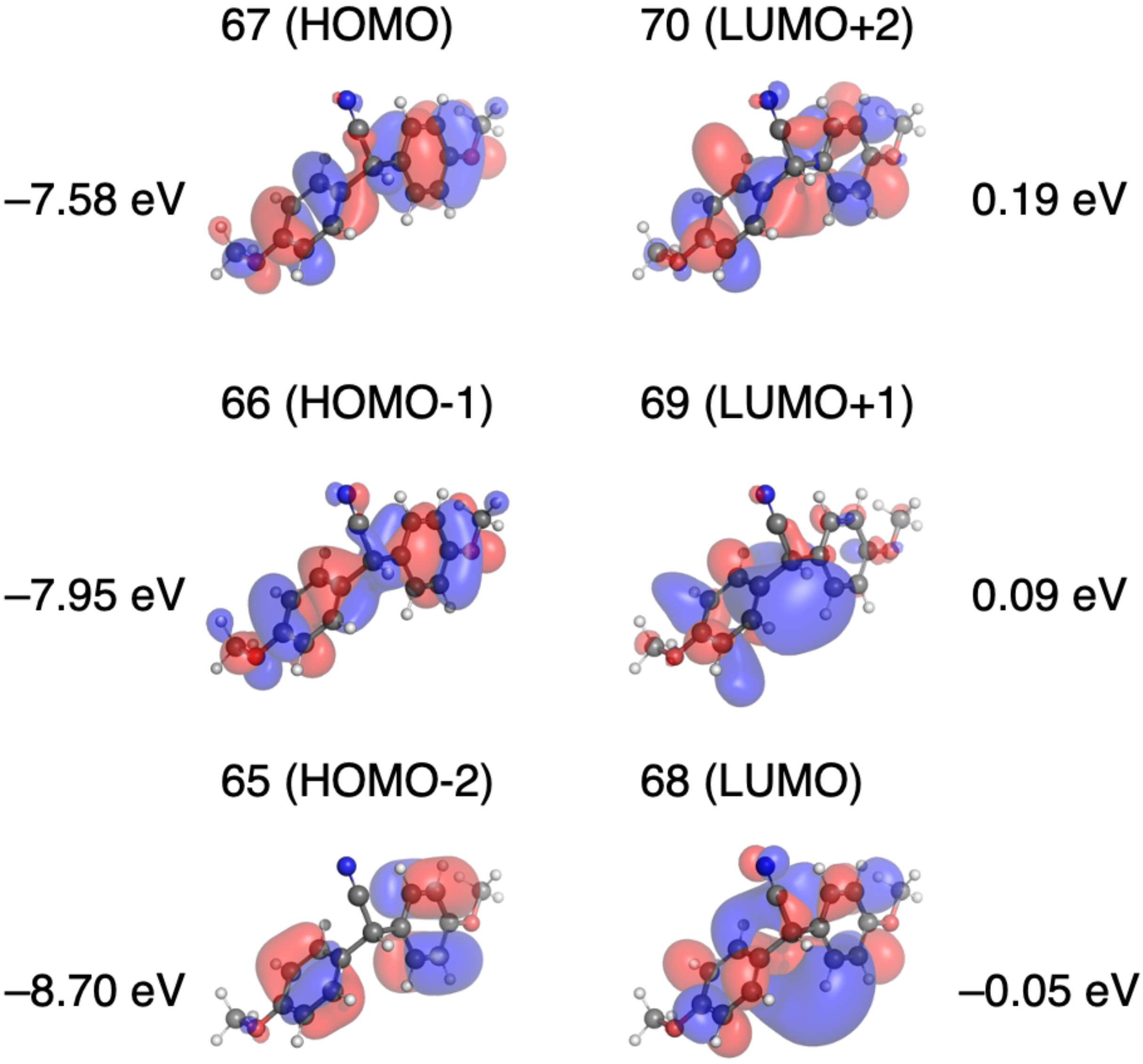


Figure S86. Molecular orbitals for **DAAN-OMe/OMe**.

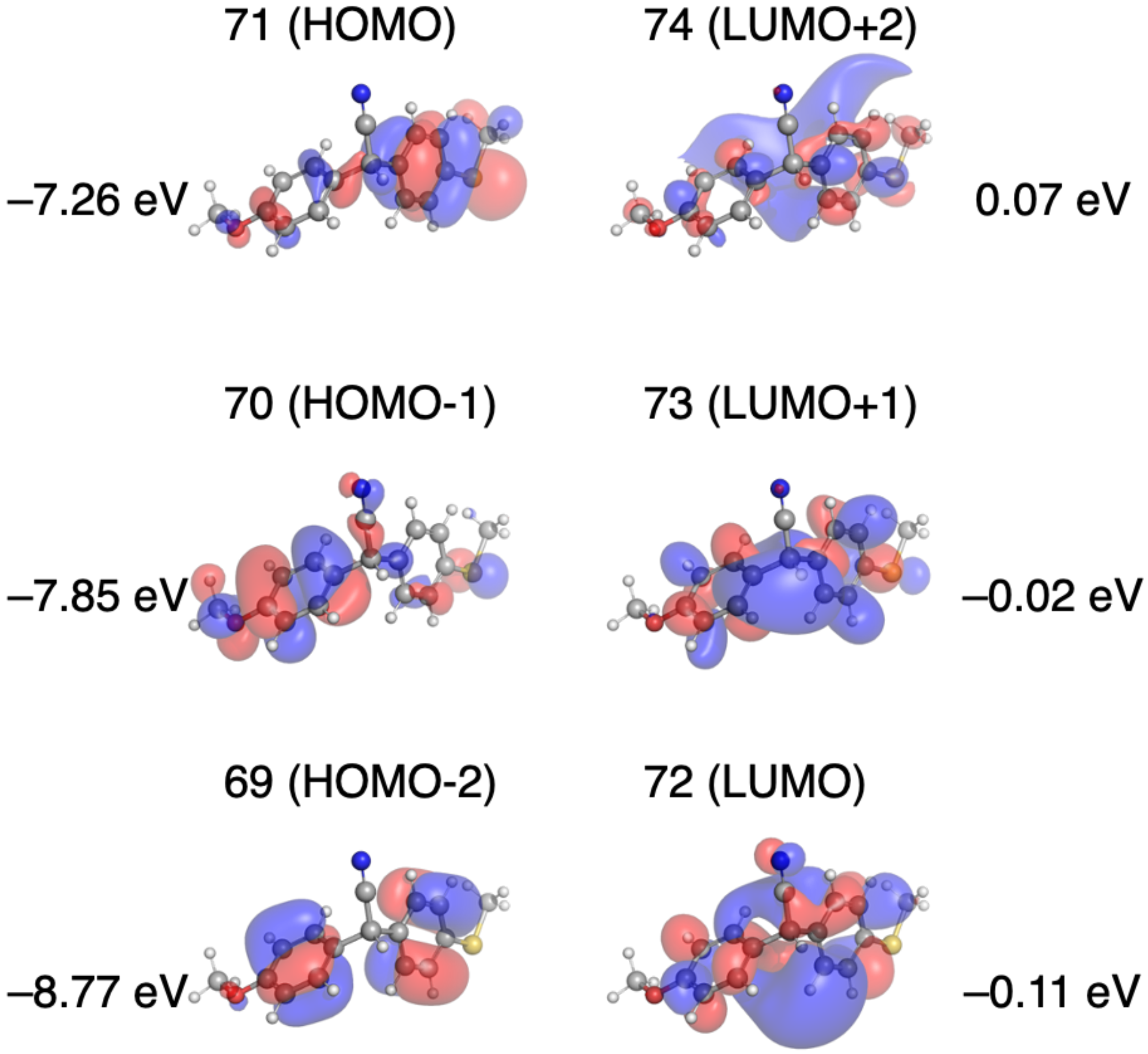


Figure S87. Molecular orbitals for **DAAN-SMe/OMe**.

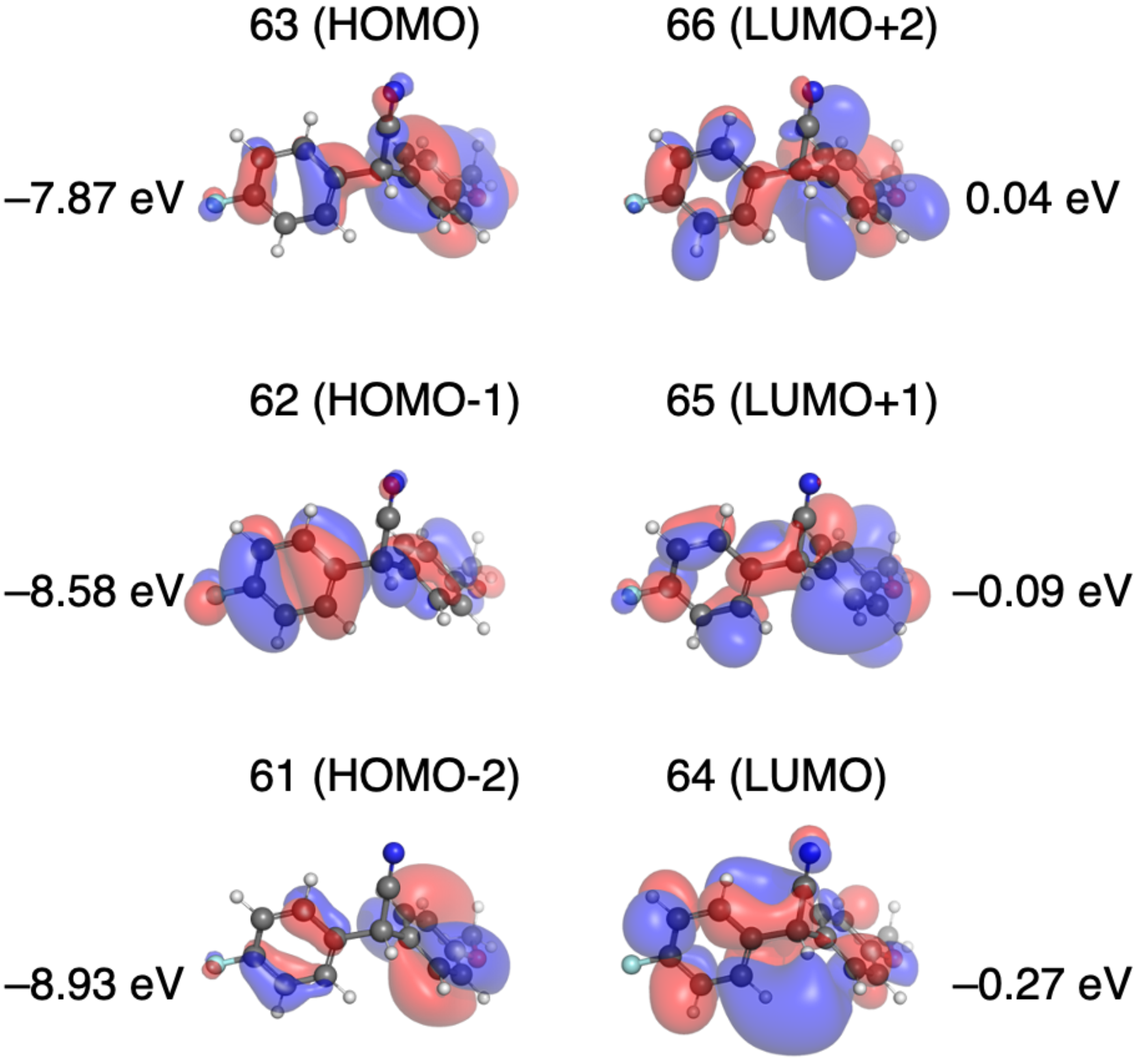


Figure S88. Molecular orbitals for **DAAN-F/OMe**.

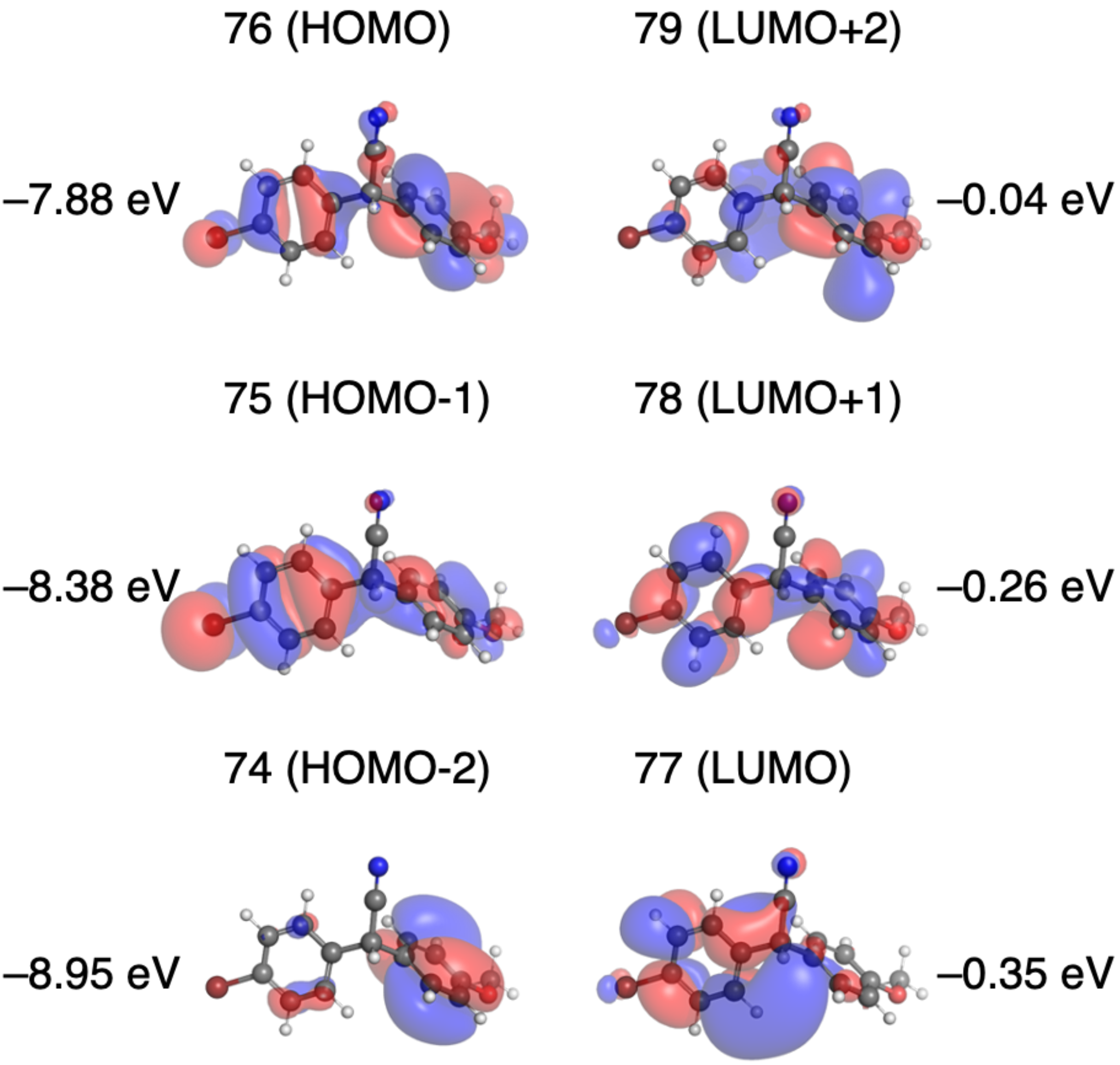


Figure S89. Molecular orbitals for **DAAN-Br/OMe**.

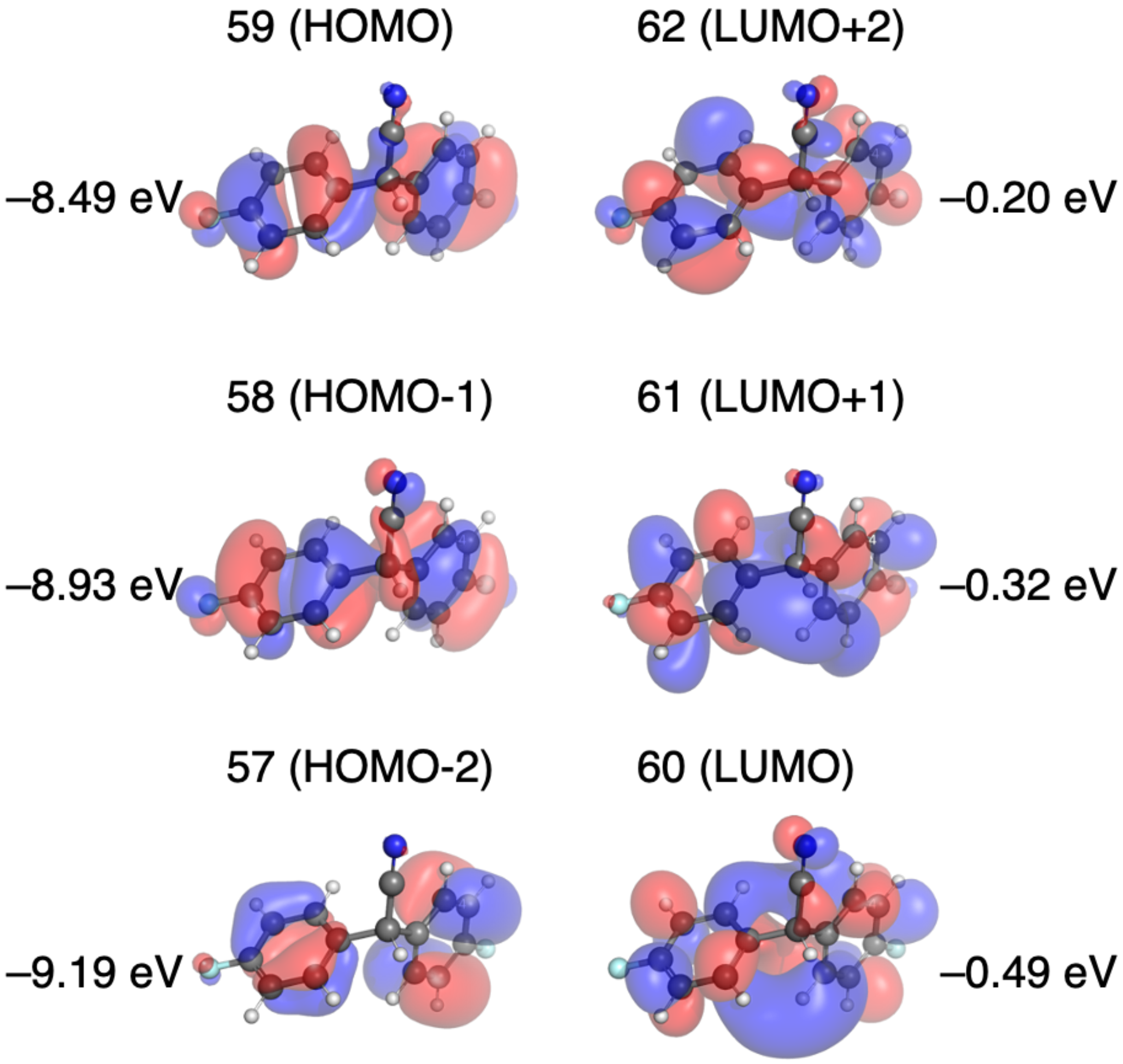


Figure S90. Molecular orbitals for **DAAN-F/F**.

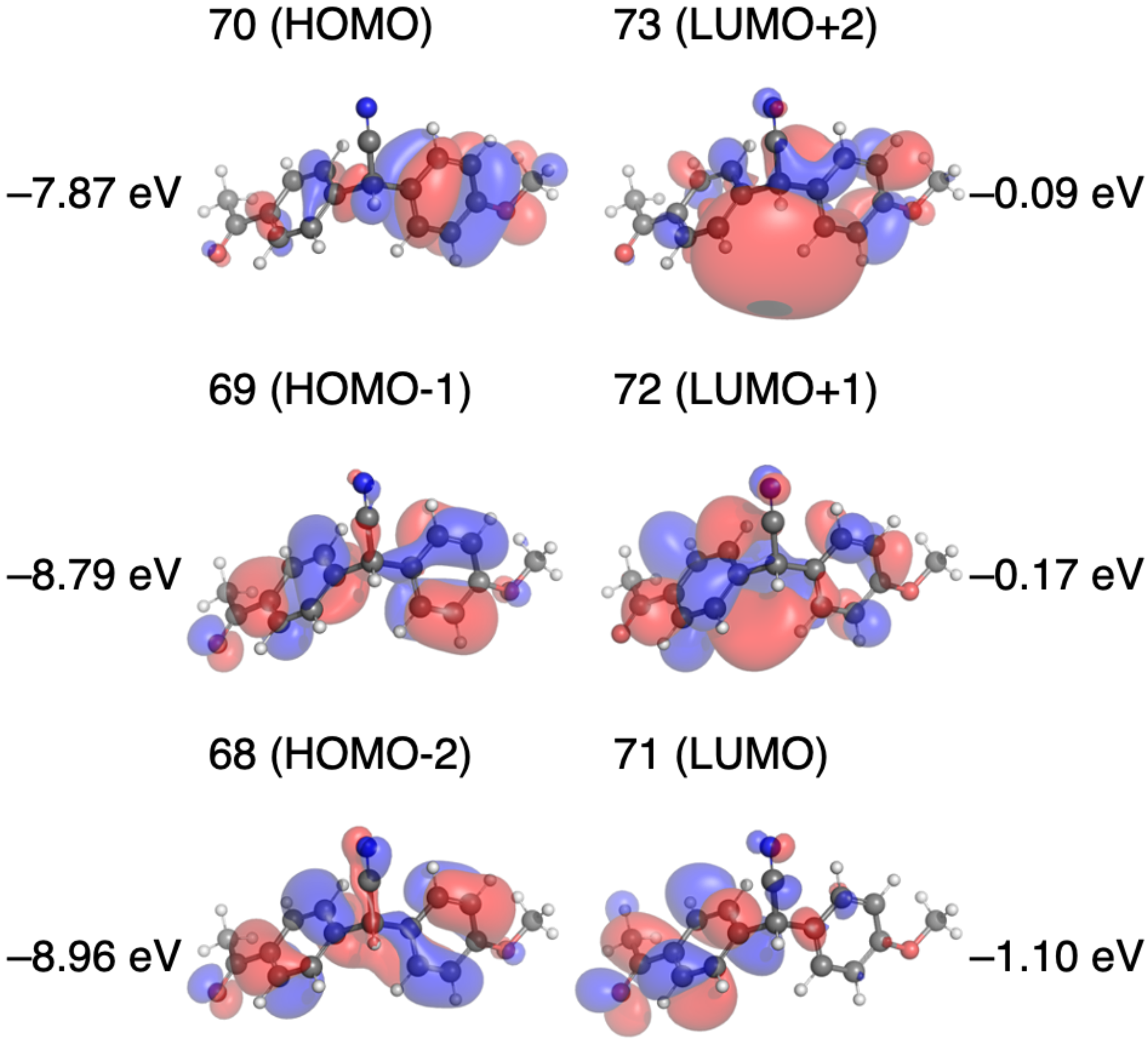


Figure S91. Molecular orbitals for **DAAN-Ac/OMe**.

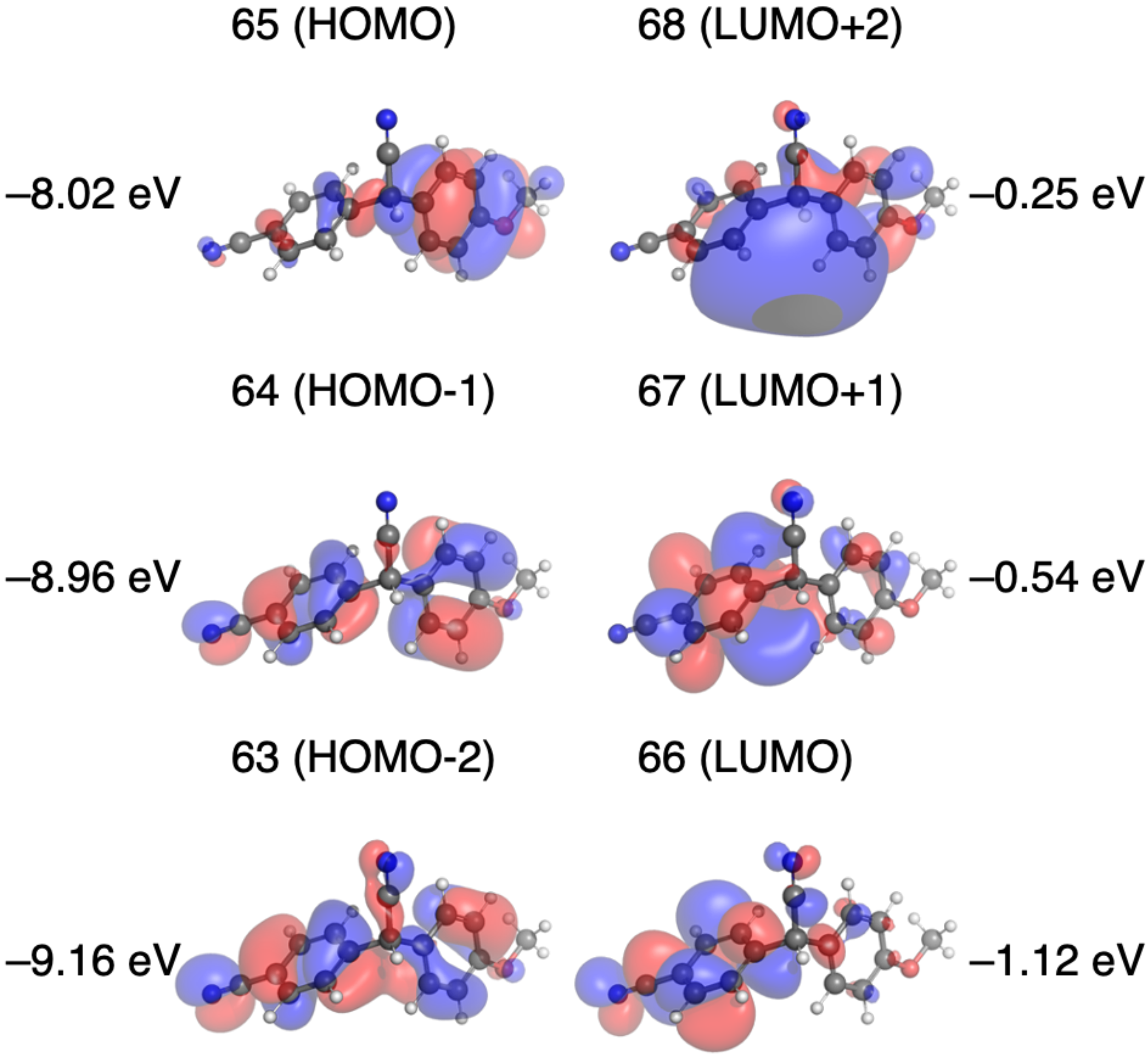


Figure S92. Molecular orbitals for **DAAN-CN/OMe**.

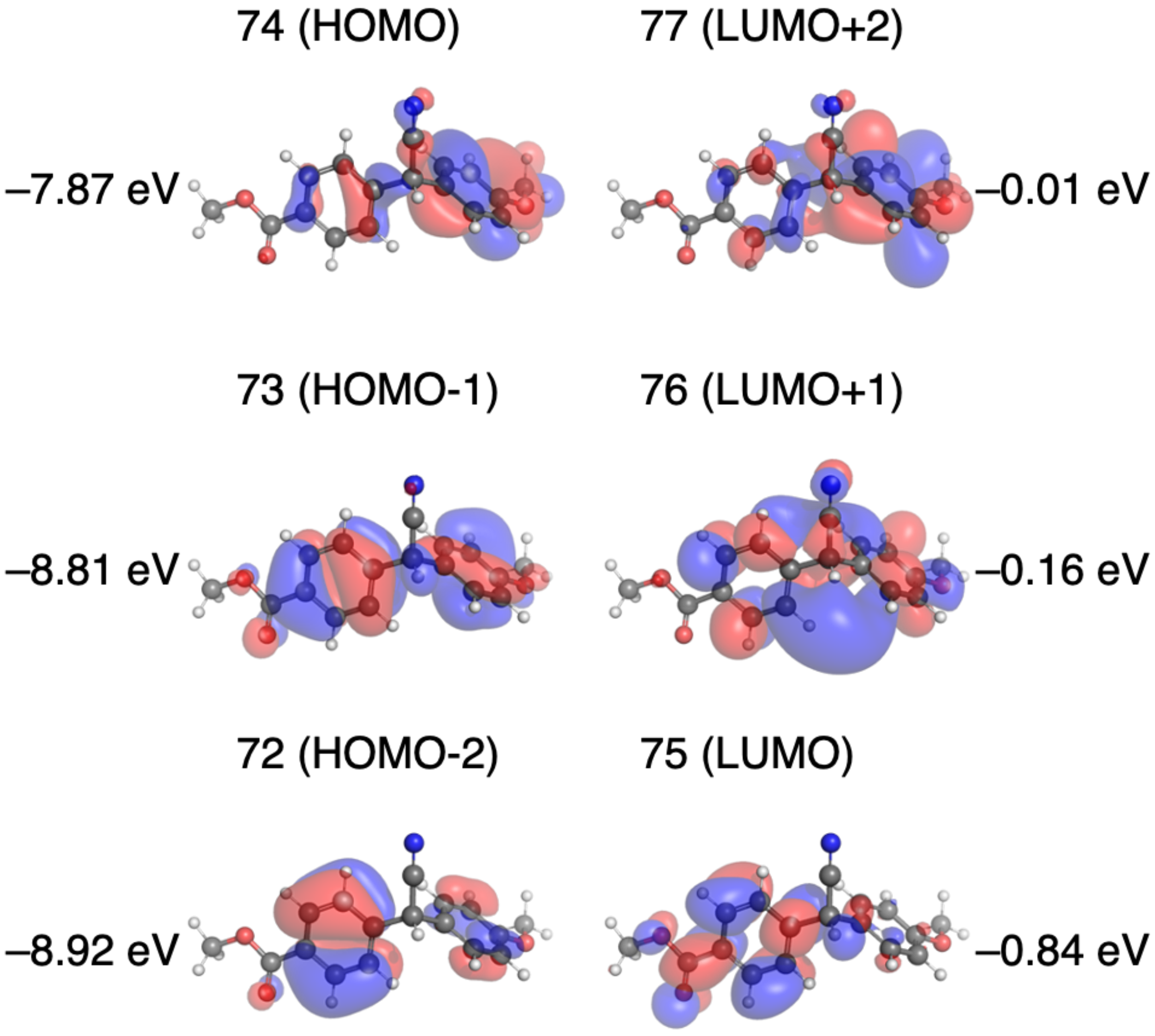


Figure S93. Molecular orbitals for **DAAN-COOMe/OMe**.

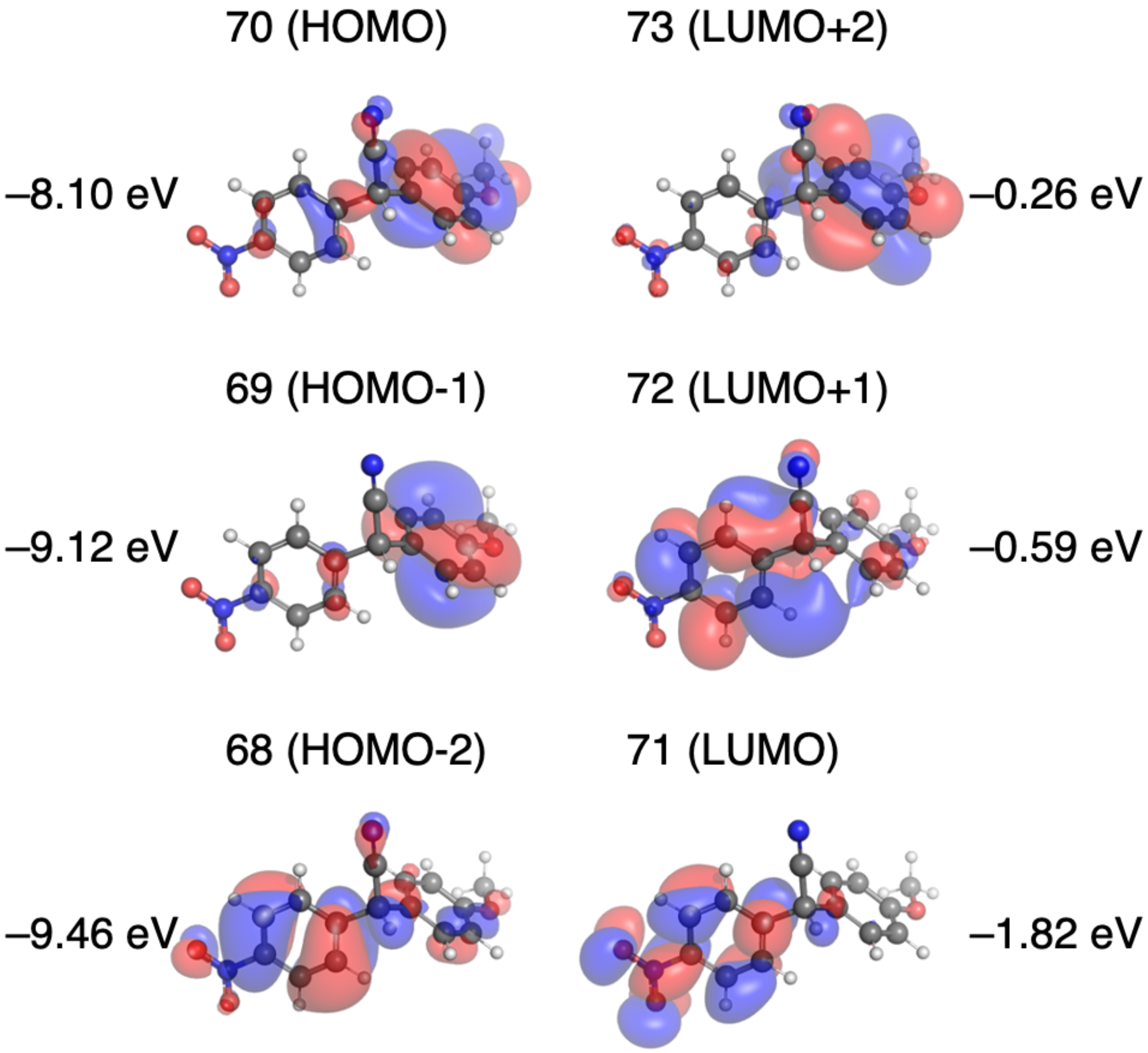


Figure S94. Molecular orbitals for **DAAN-NO$_2$/OMe**.

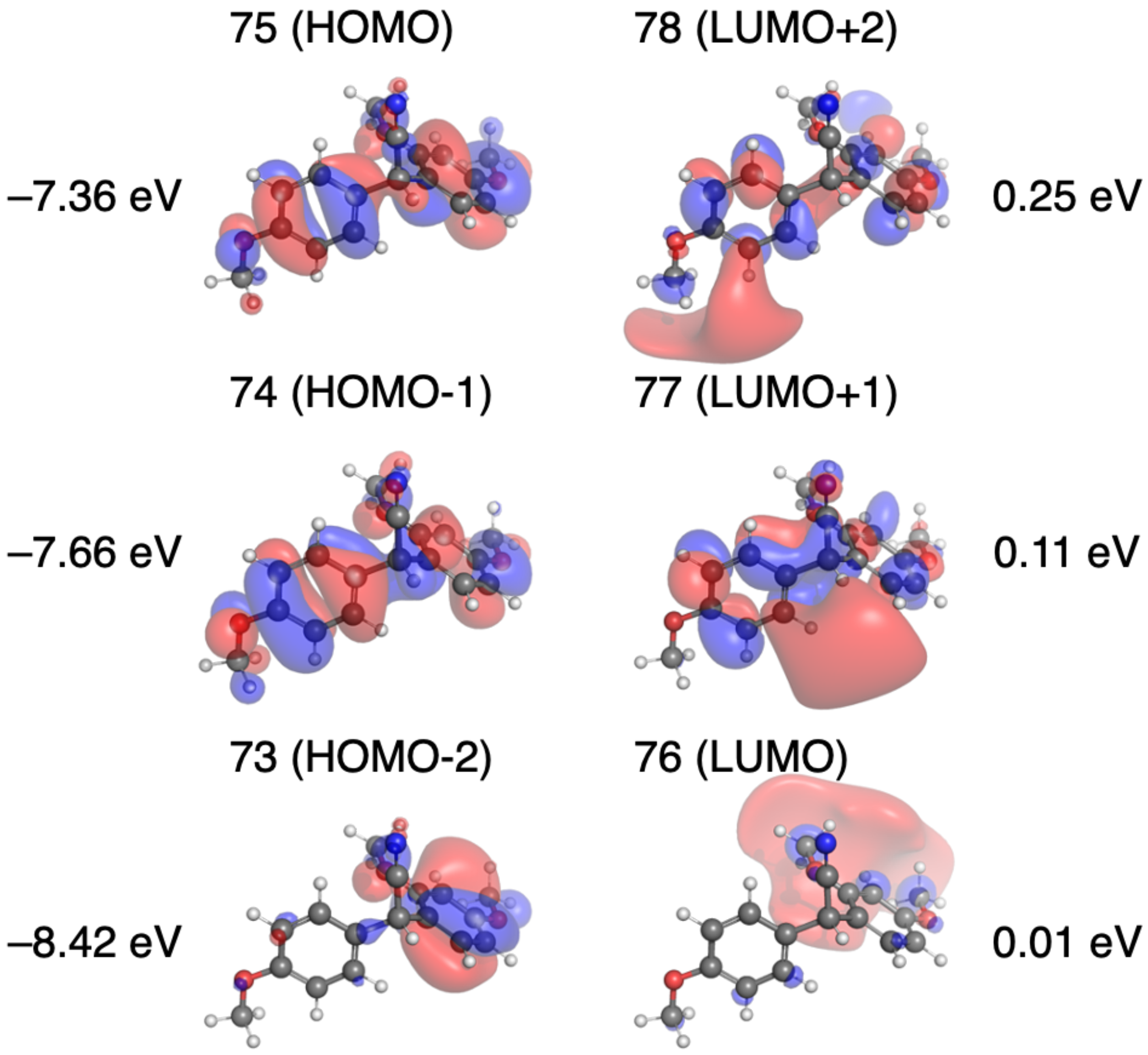


Figure S95. Molecular orbitals for **DAAN-OMe/diOMe**.

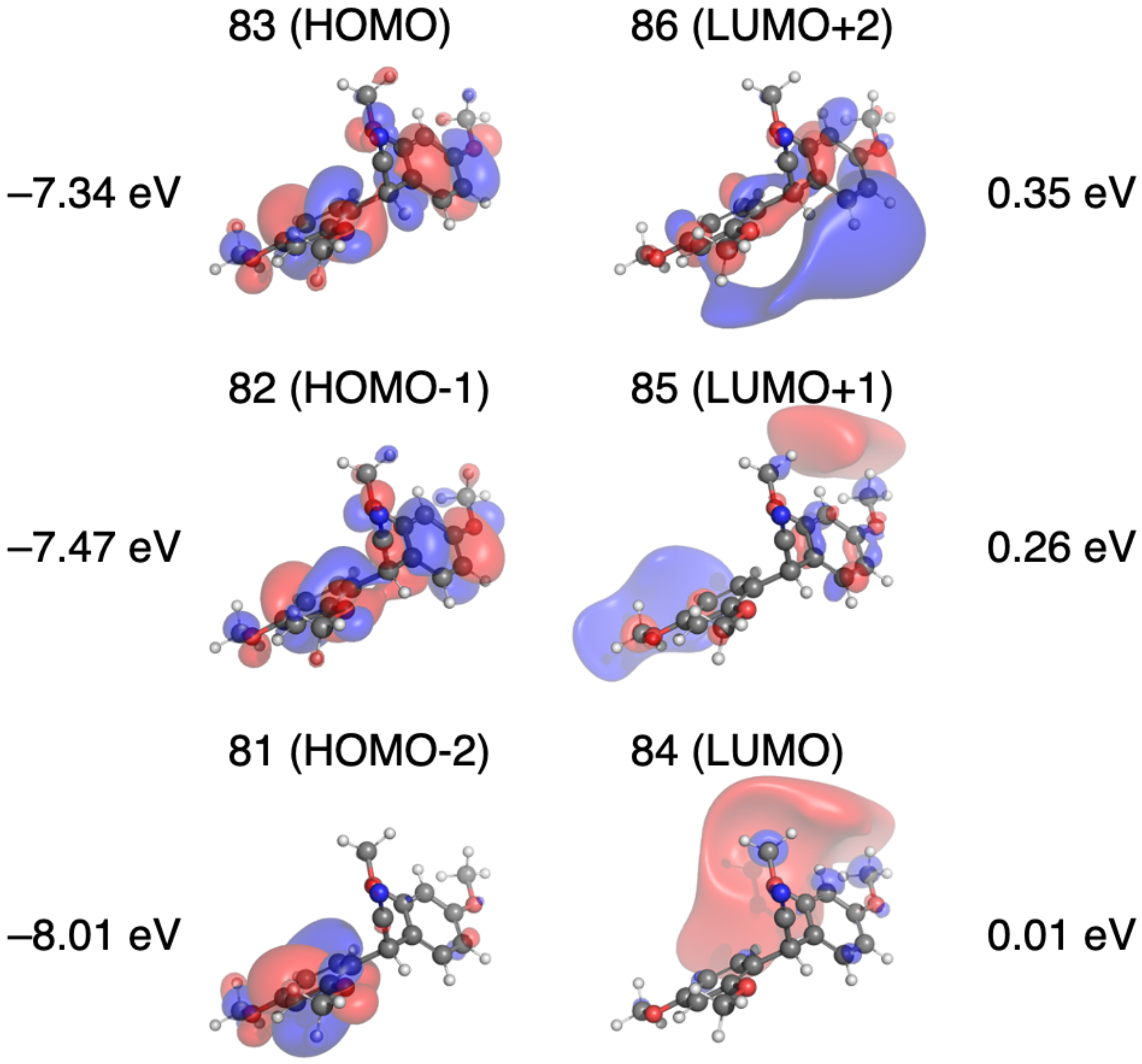


Figure S96. Molecular orbitals for **DAAN-diOMe/diOMe**.

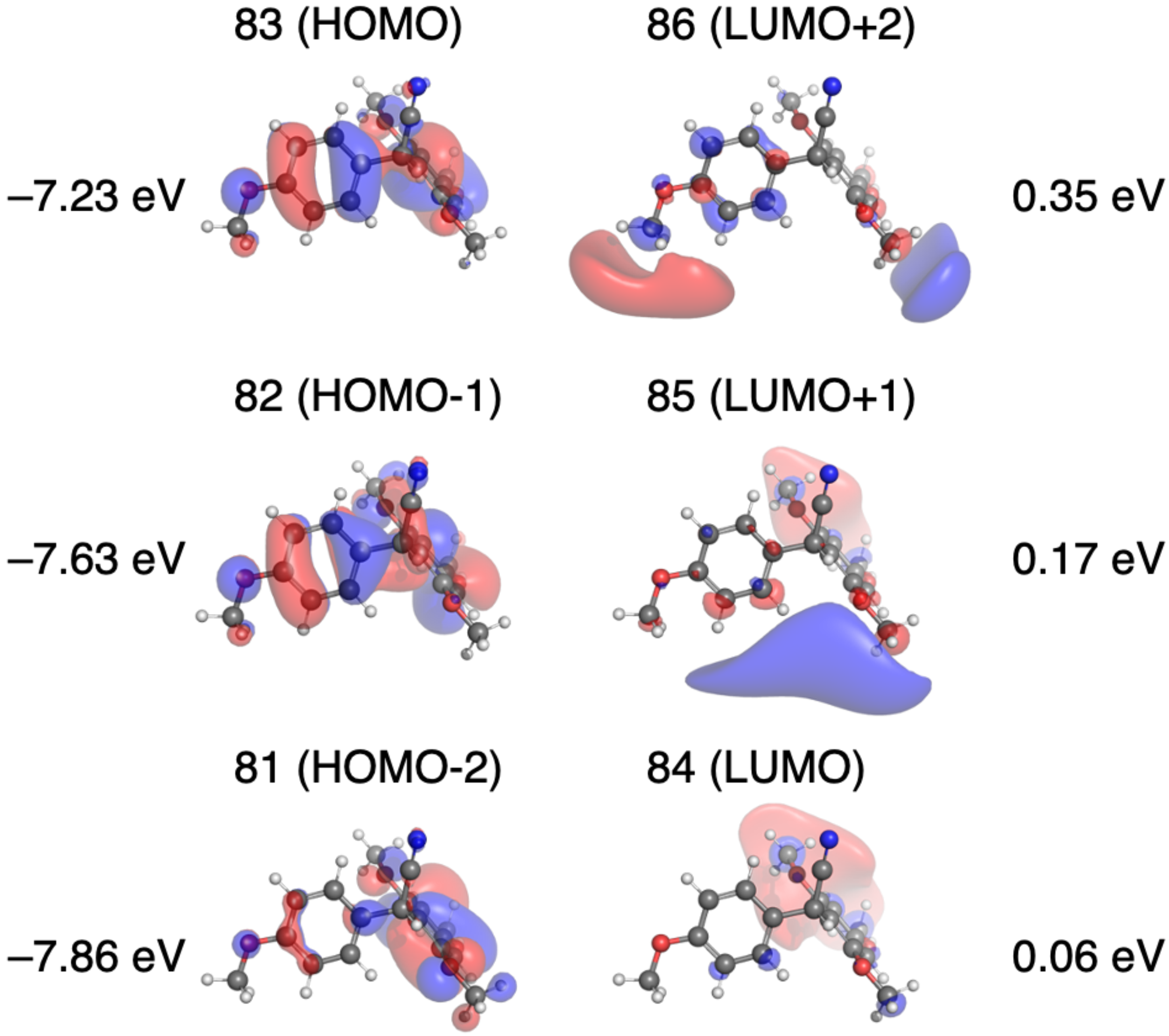


Figure S97. Molecular orbitals for **DAAN-OMe/triOMe**.

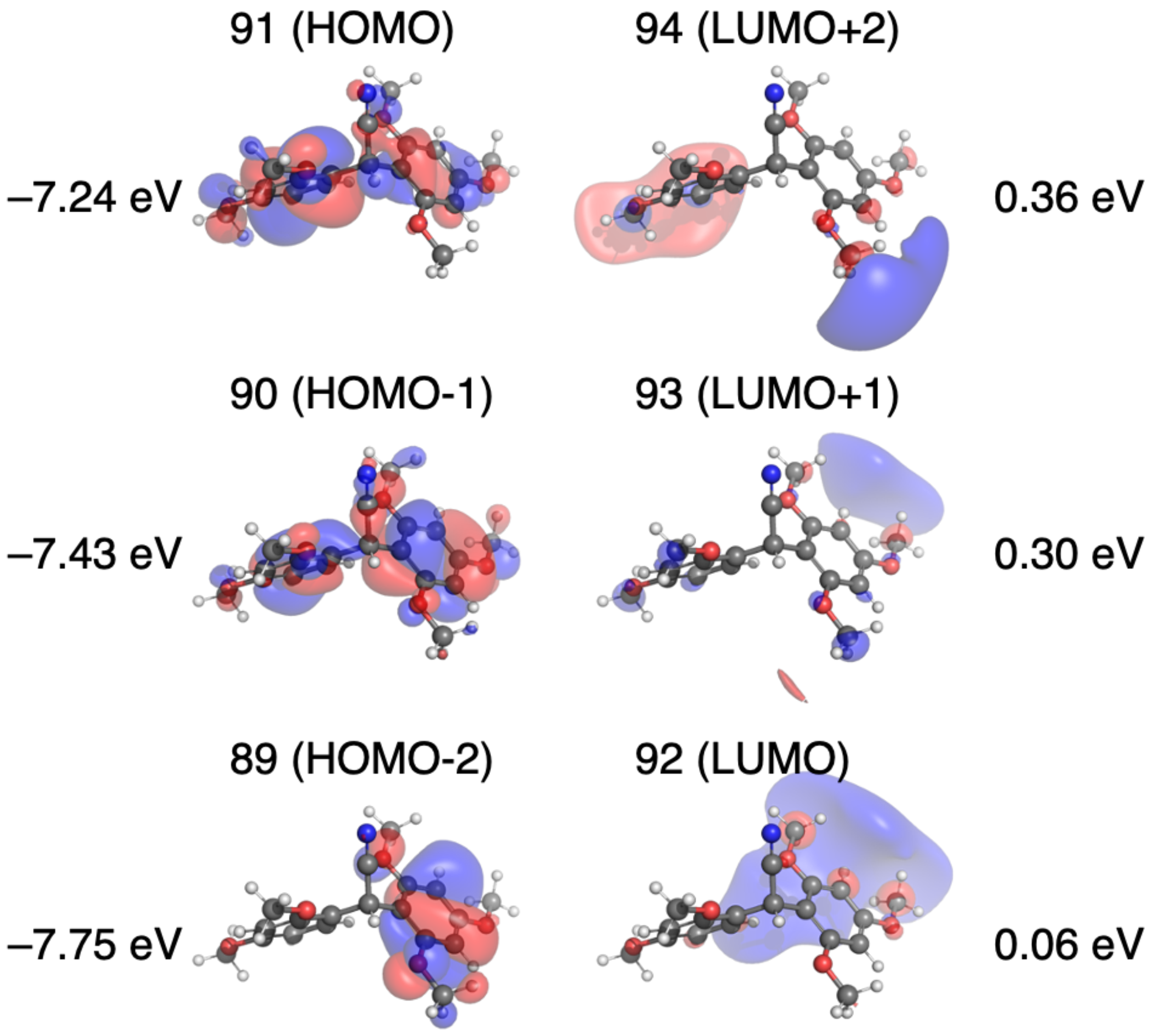


Figure S98. Molecular orbitals for **DAAN-diOMe/triOMe**.

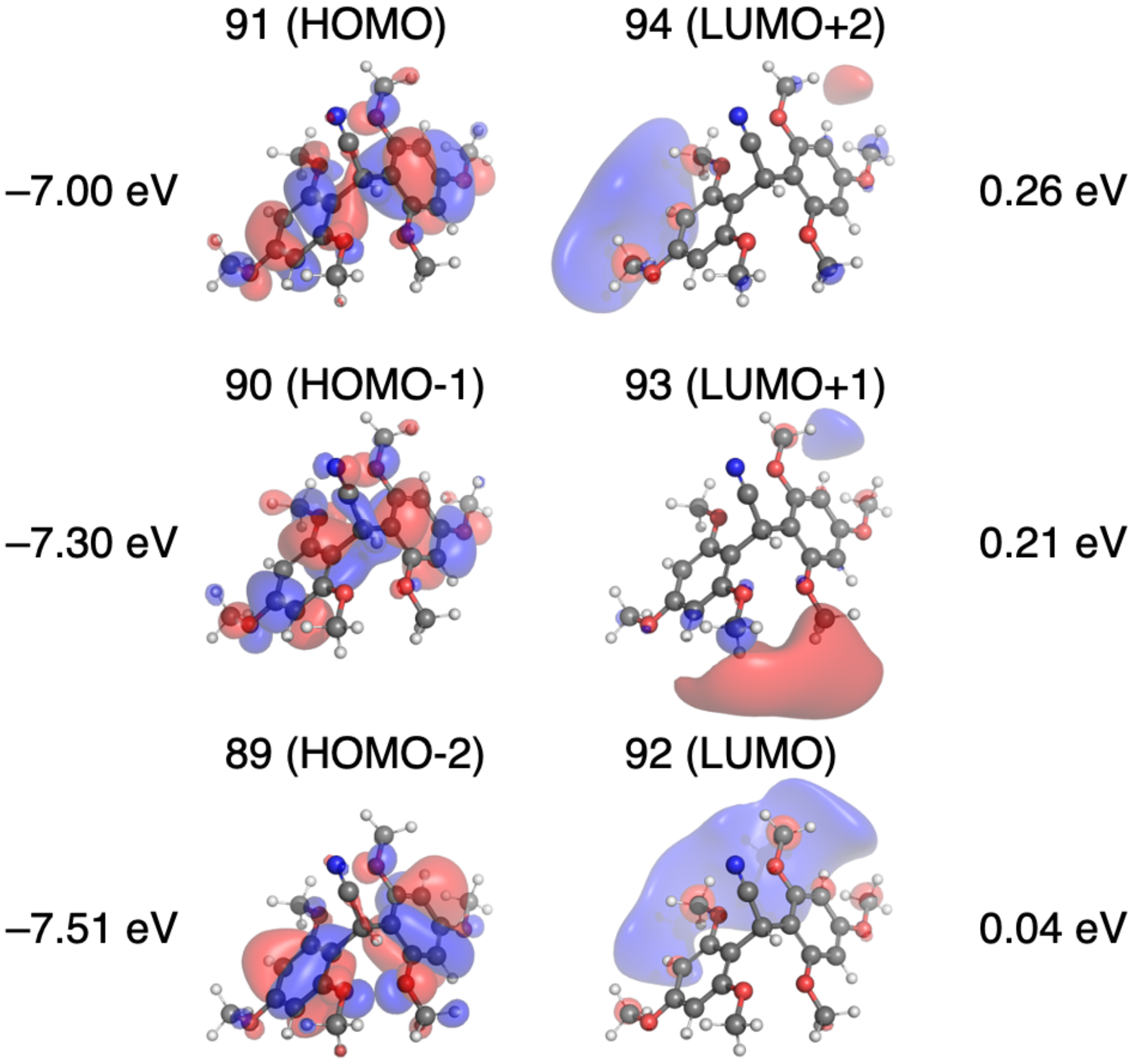


Figure S99. Molecular orbitals for **DAAN-triOMe/triOMe**.

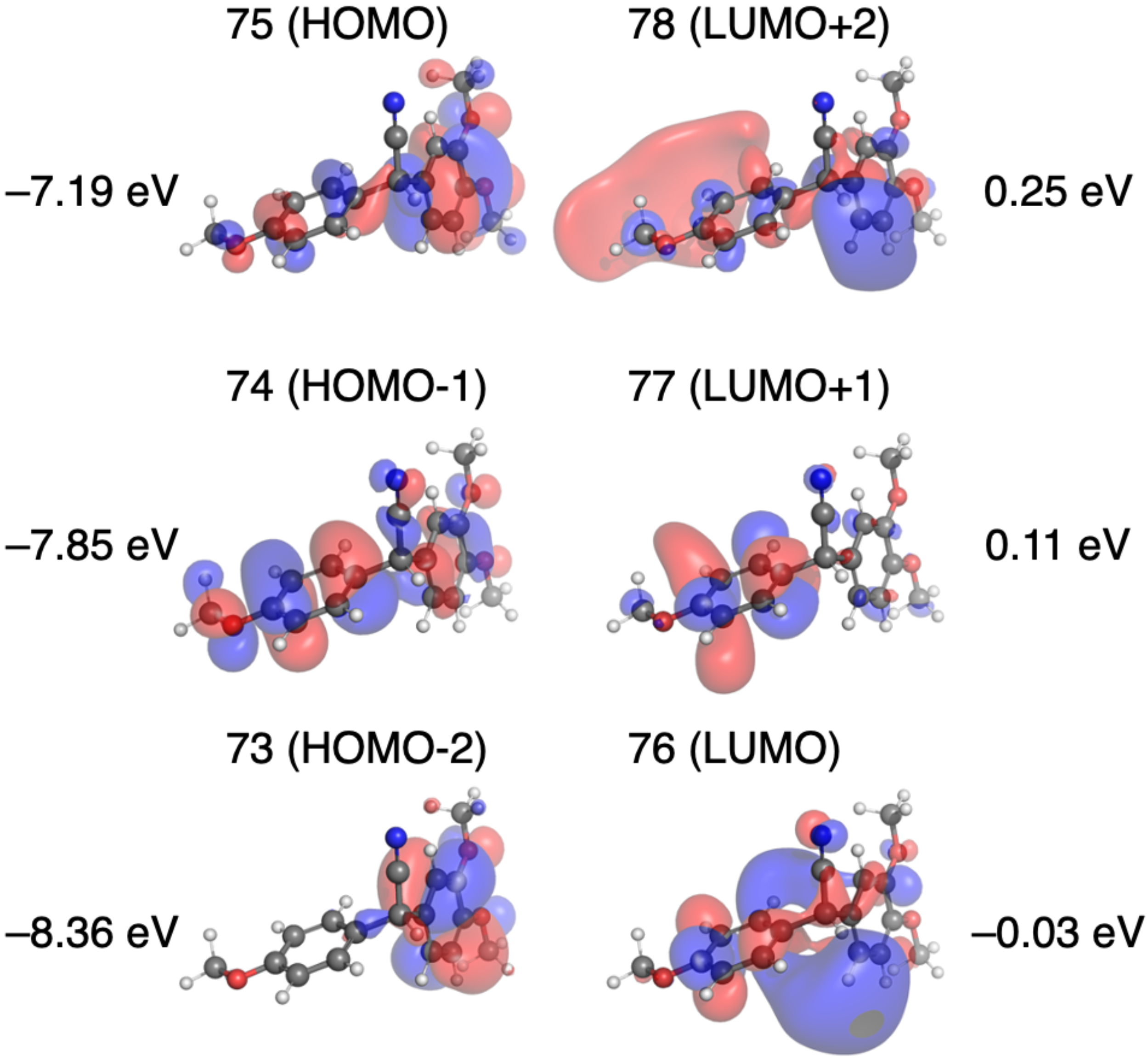


Figure S100. Molecular orbitals for **DAAN-OMe/diOMe-m**.

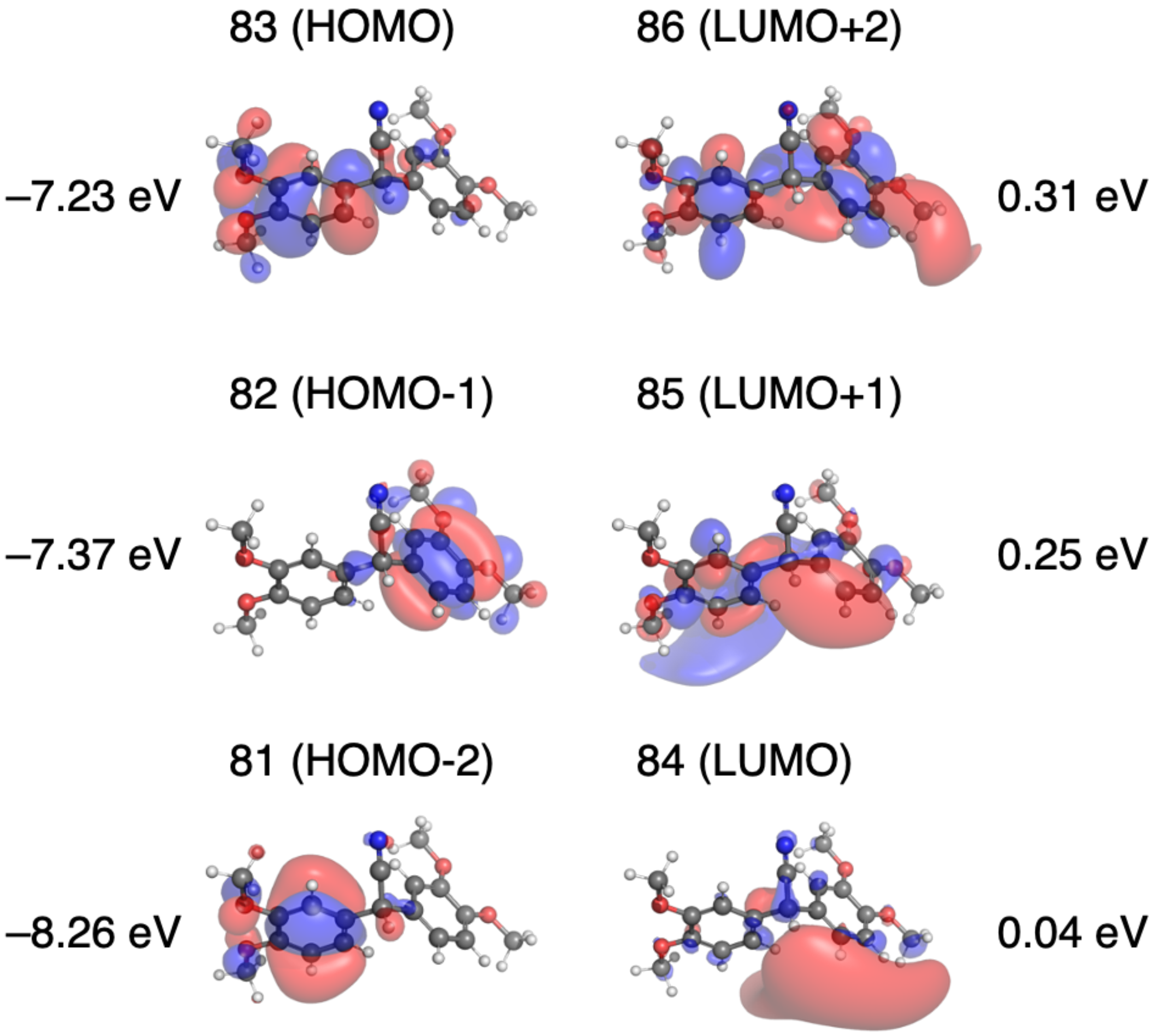
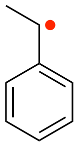


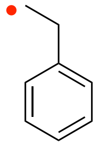
Figure S101. Molecular orbitals for **DAAN-diOMe-m/diOMe-m**.

Table S8. C-H bonding orbital ($\sigma_{C–H}$) energy level

	C–H bonding orbital ($\sigma_{C–H}$)	Orbital Number	$\sigma_{C–H}$ energy level / eV	ΔE |SOMO$_1$ – $\sigma_{C–H}$ | / eV	ΔE |SOMO$_2$ – $\sigma_{C–H}$ | / eV
triOMe/triOMe	HOMO	99	–7.00	0.96	0.13
OMe/diOMe-m	HOMO	75	–7.19	1.15	0.06
OMe/triOMe	HOMO	83	–7.23	1.20	0.10
diOMe-m/diOMe-m	HOMO	83	–7.23	1.20	0.10
diOMe/triOMe	HOMO	91	–7.24	1.20	0.11
SMe/OMe	HOMO	71	–7.26	1.22	0.13
diOMe/diOMe	HOMO	83	–7.34	1.31	0.21
OMe/diOMe	HOMO	75	–7.36	1.33	0.23
OMe/OMe	HOMO	67	–7.58	1.55	0.45
Ac/OMe	HOMO	70	–7.87	1.84	0.74
CN/OMe	HOMO	65	–8.02	1.98	0.89
H/Me	HOMO	55	–8.13	2.10	1.01
Me/OMe	HOMO–1	62	–8.30	2.26	1.17
H/H	HOMO	51	–8.37	2.33	1.24
Br/OMe	HOMO–1	75	–8.38	2.34	1.25
F/F	HOMO	59	–8.49	2.45	1.36
F/OMe	HOMO–1	62	–8.58	2.55	1.45
H/OMe	HOMO–1	58	–8.59	2.56	1.46
COOMe/OMe	HOMO–1	73	–8.81	2.78	1.68
NO_2/OMe	HOMO–2	68	–9.46	3.42	2.33



1-Phenylethyl radical
α–SOMO = –6.03 eV



2-Phenylethyl radical
α–SOMO = –7.13 eV

ΔE |SOMO$_1$ – $\sigma_{C–H}$| = | (α–SOMO level of 1-phenylethyl radical) – ($\sigma_{C–H}$ energy level) |

ΔE |SOMO$_2$ – $\sigma_{C–H}$| = | (α–SOMO level of 2-phenylethyl radical) – ($\sigma_{C–H}$ energy level) |

As shown in equation (S1), the BDE is the energy required for cleaving the hydrogen adduct (R–H) of the radical (R•) into R• and H•; the smaller this value, the more readily homolysis occurs and the greater the amount of thermodynamically stable radicals generated.

$$\mathrm{R-H} \longrightarrow \mathrm{R\cdot + H\cdot}$$

$$\mathrm{BDE\ (R\cdot)} = H_{298}(\mathrm{R\cdot}) + H_{298}(\mathrm{H\cdot}) - H_{298}(\mathrm{RH}) \tag{S1}$$

The RSE is a parameter that indicates the relative thermodynamic stability of the generated radicals by calculating how readily the hydrogen-abstraction reaction of a given radical occurs compared to that of the methyl radical, as shown in equation (S2).[6]

$$\mathrm{R-H} + \mathrm{CH_3\cdot} \longrightarrow \mathrm{R\cdot} + \mathrm{CH_4}$$

$$\mathrm{RSE\ (R\cdot)} = H_{298}(\mathrm{R\cdot}) + H_{298}(\mathrm{CH_4}) - H_{298}(\mathrm{RH}) - H_{298}(\mathrm{CH_3\cdot}) \tag{S2}$$

From the above definition, BDE and RSE can be related according to equation (S3).

$$\mathrm{RSE\ (R\cdot)} = \mathrm{BDE\ (R\cdot)} - \mathrm{BDE\ (CH_3\cdot)} \tag{S3}$$

Table S9. BDE and RSE of DAAN derivatives

	BDE / kJ mol^{-1}	RSE / kJ mol^{-1}
SMe/OMe	313	–120
OMe/OMe	313	–120
Me/OMe	315	–118
Ac/OMe	315	–118
CN/OMe	315	–118
COOMe/OMe	316	–118
F/OMe	316	–117
NO$_2$/OMe	316	–117
OMe/diOMe-m	316	–117
Br/OMe	316	–117
H/OMe	317	–117
H/Me	319	–114
F/F	319	–114
OMe/diOMe	320	–114
H/H	321	–113
diOMe-m/diOMe-m	323	–111
OMe/triOMe	327	–106
triOMe/triOMe	331	–103
diOMe/diOMe	333	–101
diOMe/triOMe	339	–95

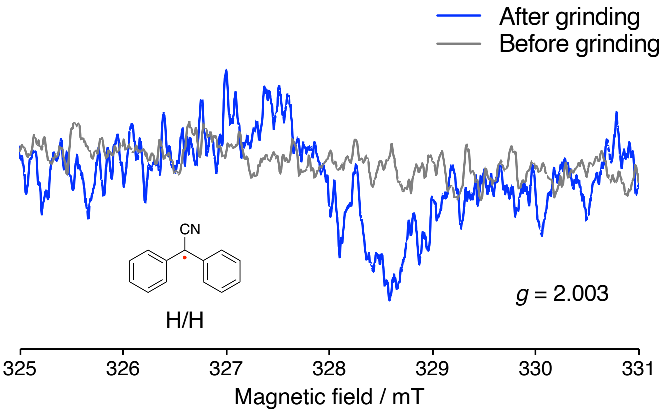


Figure S102. EPR spectra of a mixture of polystyrene and **DAAN-H/H** before and after ball milling.

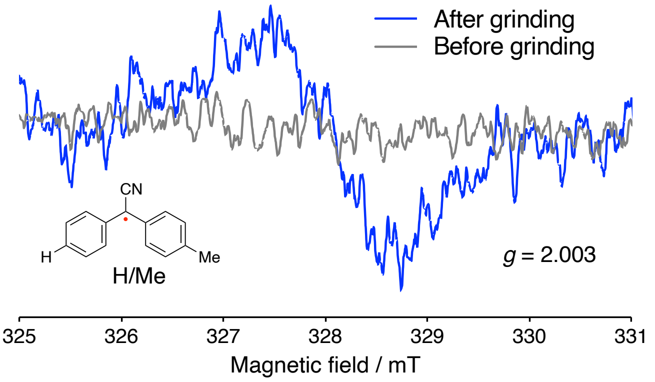


Figure S103. EPR spectra of a mixture of polystyrene and **DAAN-H/Me** before and after ball milling.

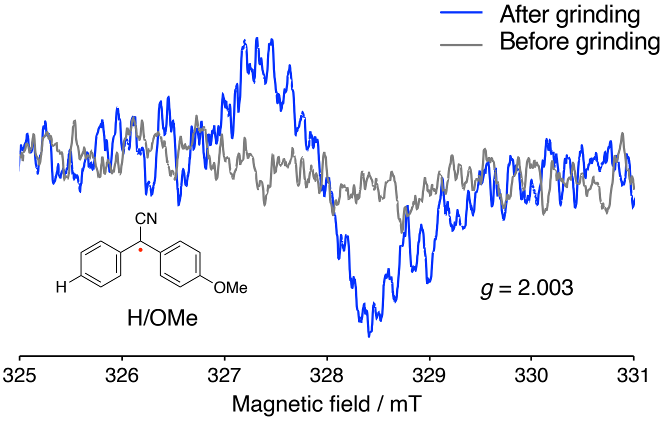


Figure S104. EPR spectra of a mixture of polystyrene and **DAAN-H/OMe** before and after ball milling.

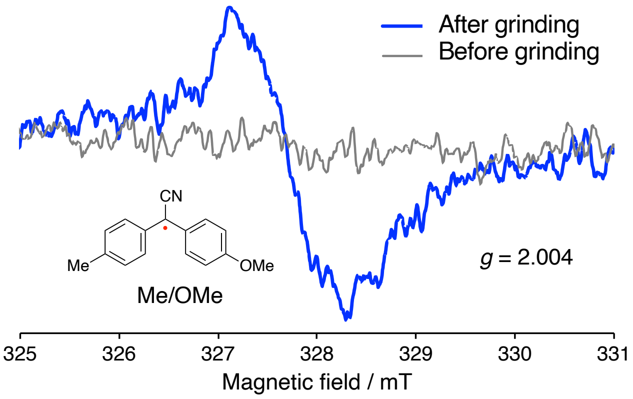


Figure S105. EPR spectra of a mixture of polystyrene and **DAAN-Me/OMe** before and after ball milling.

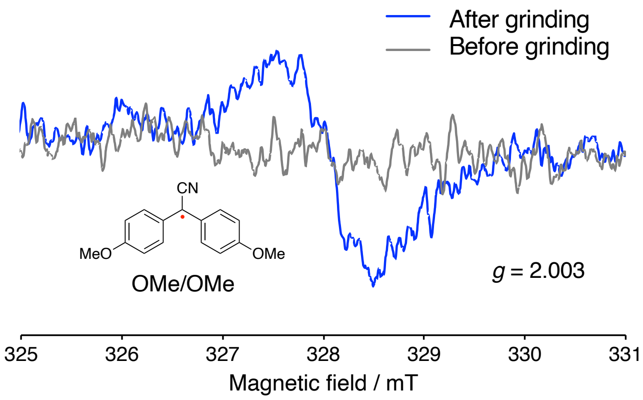


Figure S106. EPR spectra of a mixture of polystyrene and **DAAN-OMe/OMe** before and after ball milling.

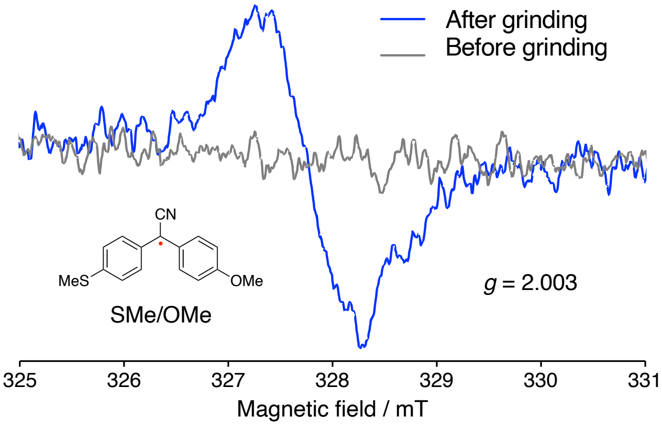


Figure S107. EPR spectra of a mixture of polystyrene and **DAAN-SMe/OMe** before and after ball milling.

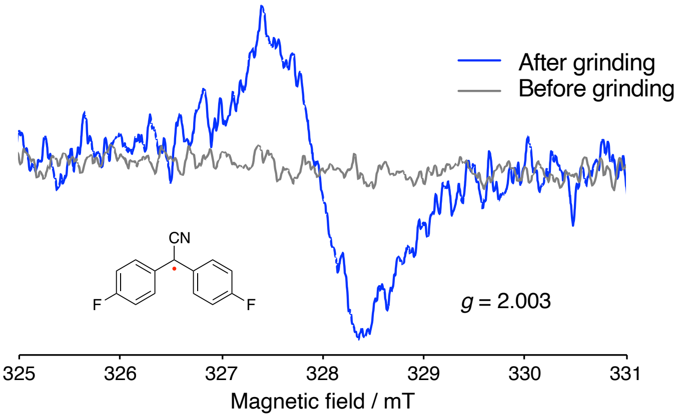


Figure S108. EPR spectra of a mixture of polystyrene and **DAAN-F/F** before and after ball milling.

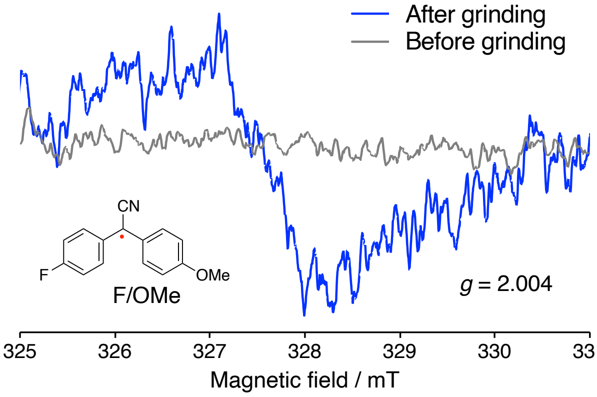


Figure S109. EPR spectra of a mixture of polystyrene and **DAAN-F/OMe** before and after ball milling.

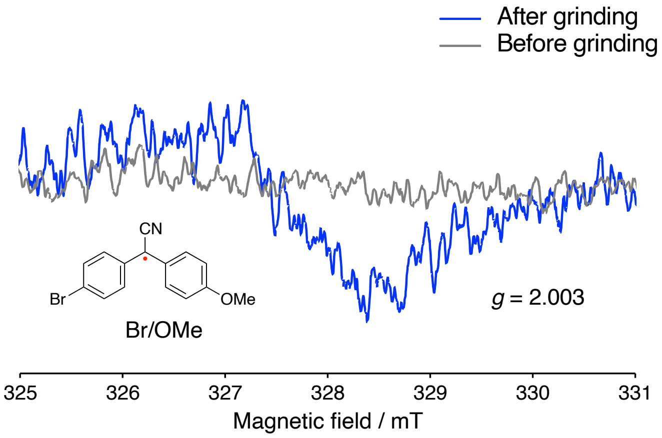


Figure S110. EPR spectra of a mixture of polystyrene and **DAAN-Br/OMe** before and after ball milling.

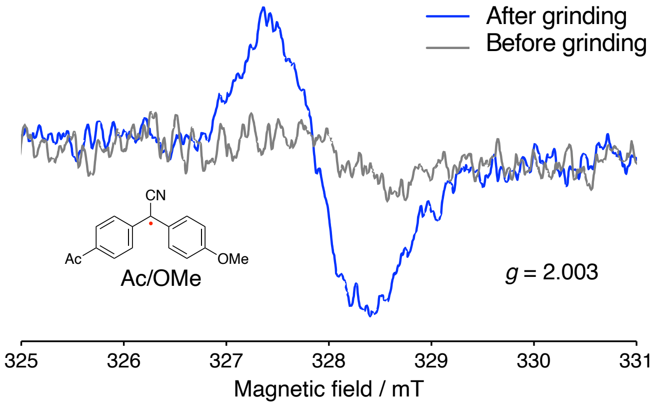


Figure S111. EPR spectra of a mixture of polystyrene and **DAAN-Ac/OMe** before and after ball milling.

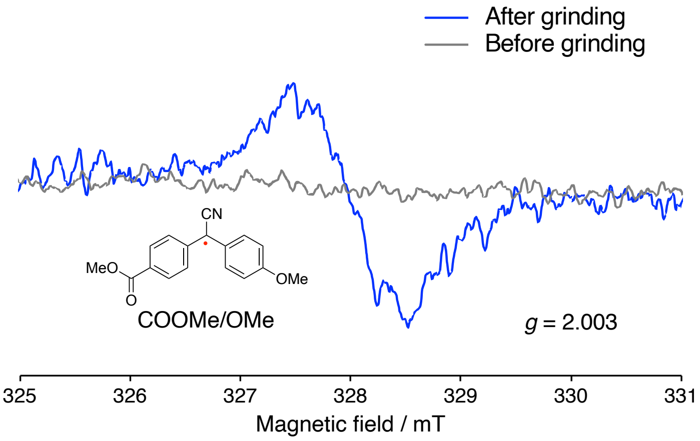


Figure S112. EPR spectra of a mixture of polystyrene and **DAAN-COOMe/OMe** before and after ball milling.

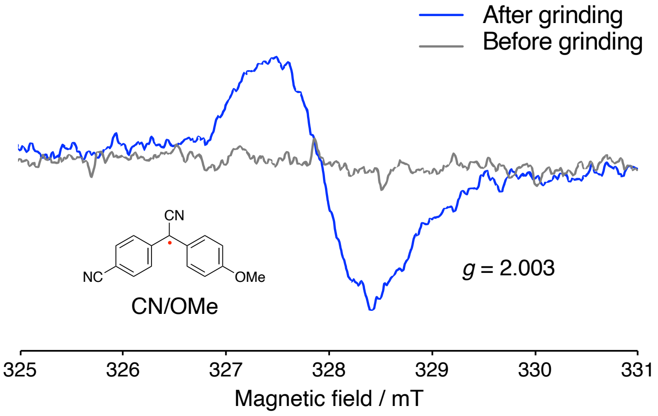


Figure S113. EPR spectra of a mixture of polystyrene and **DAAN-CN/OMe** before and after ball milling.

5.

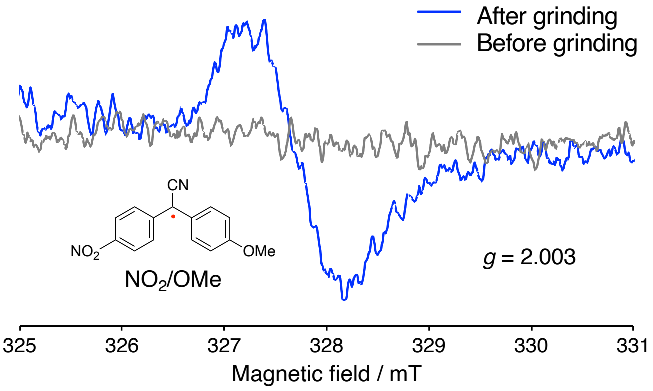


Figure S114. EPR spectra of a mixture of polystyrene and **DAAN-NO$_2$/OMe** before and after ball milling.

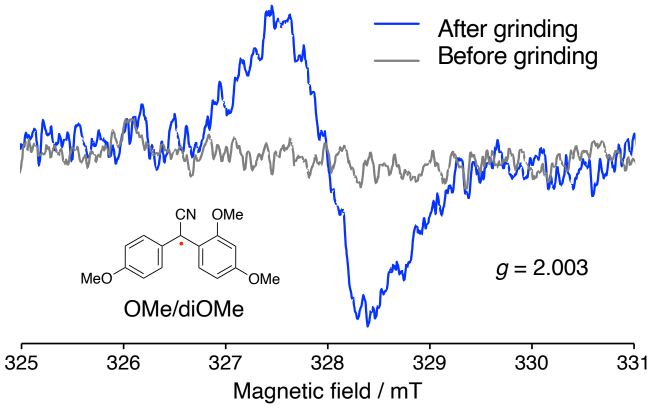


Figure S115. EPR spectra of a mixture of polystyrene and **DAAN-OMe/diOMe** before and after ball milling.

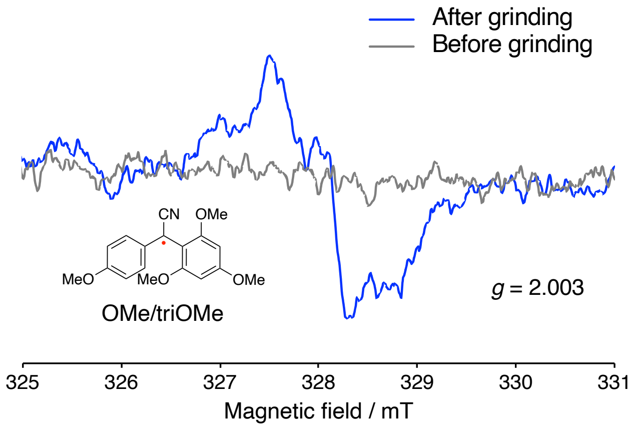


Figure S116. EPR spectra of a mixture of polystyrene and **DAAN-OMe/triOMe** before and after ball milling.

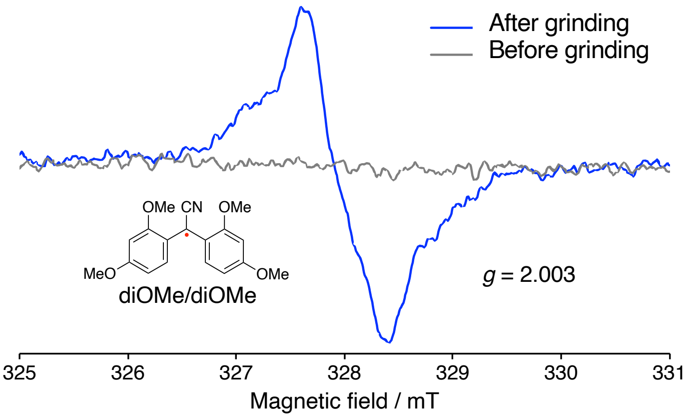


Figure S117. EPR spectra of a mixture of polystyrene and **DAAN-diOMe/diOMe** before and after ball milling.

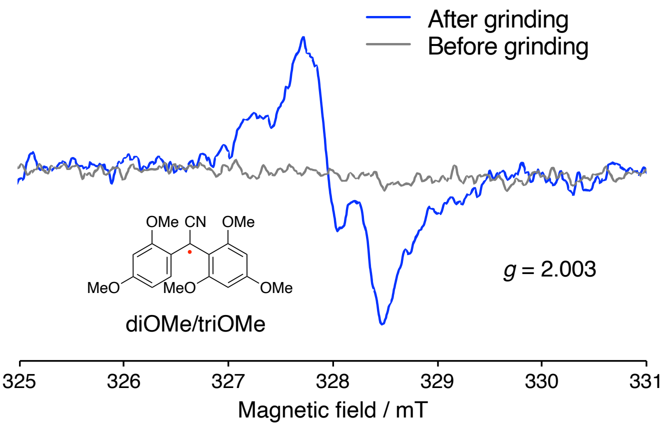


Figure S118. EPR spectra of a mixture of polystyrene and **DAAN-diOMe/triOMe** before and after ball milling.

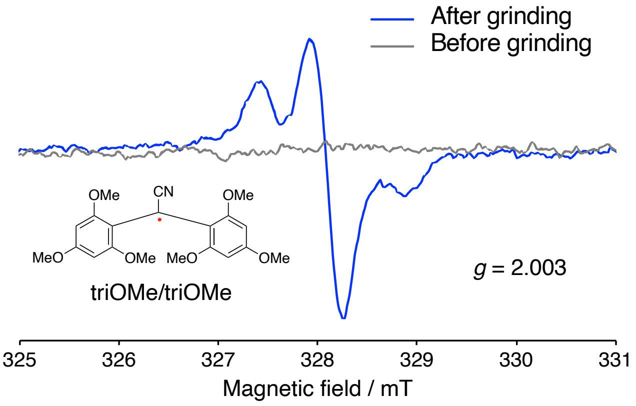


Figure S119. EPR spectra of a mixture of polystyrene and **DAAN-triOMe/triOMe** before and after ball milling.

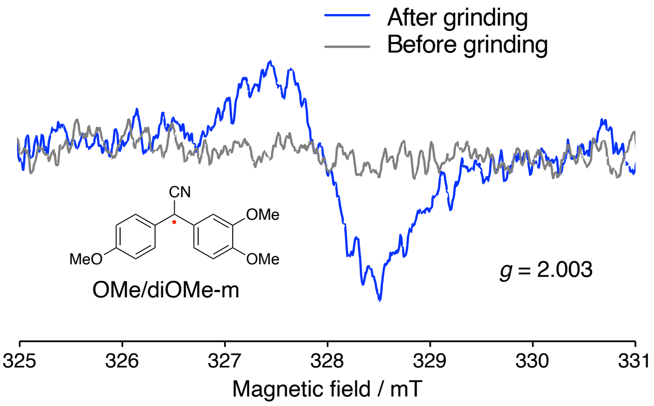


Figure S120. EPR spectra of a mixture of polystyrene and **DAAN-OMe/diOMe-m** before and after ball milling.

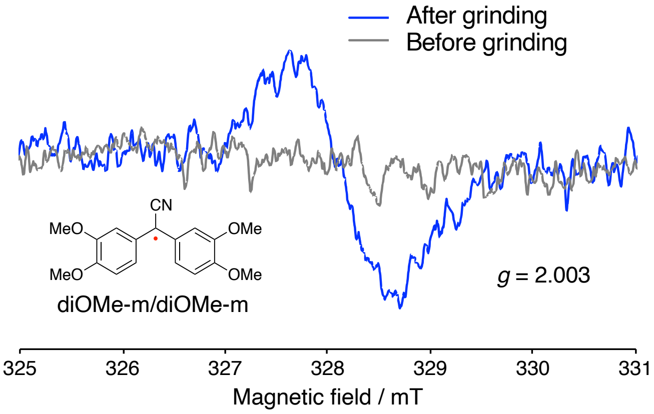


Figure S121. EPR spectra of a mixture of polystyrene and **DAAN-diOMe-m/diOMe-m** before and after ball milling.

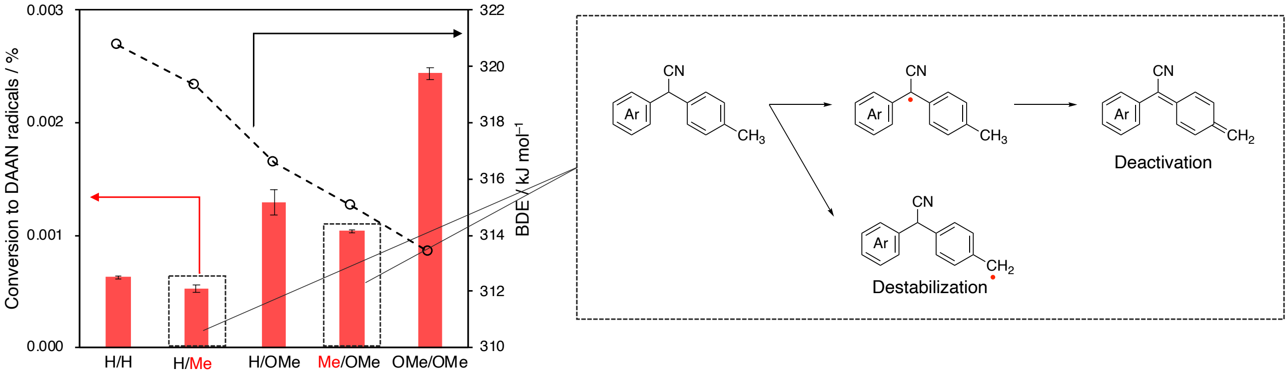


Figure S122. Plausible mechanism for the reduction of mechanoradical detection function of DAAN derivatives with methyl groups.

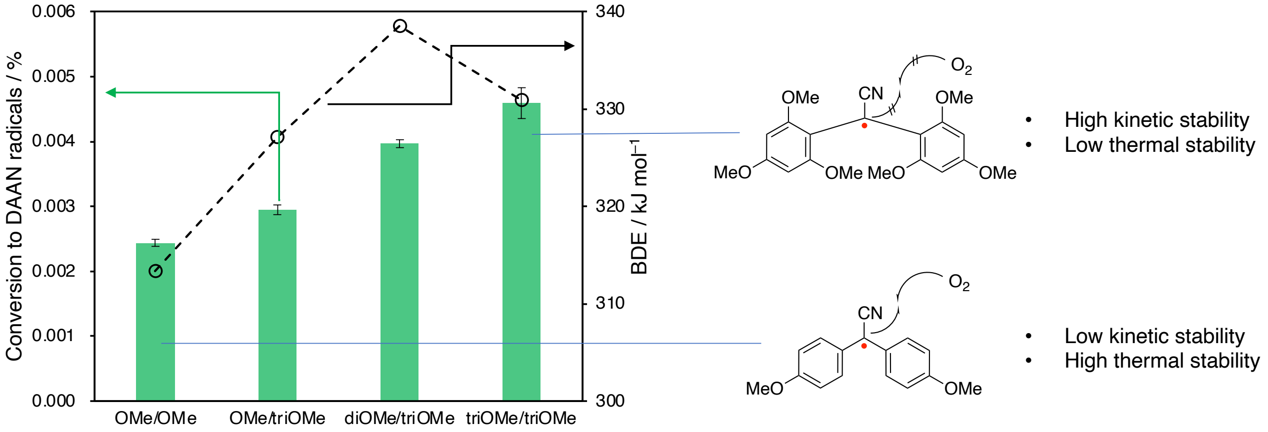


Figure S123. Plausible mechanism for the increase of mechanoradical detection function of DAAN derivatives with *ortho*-substituents.

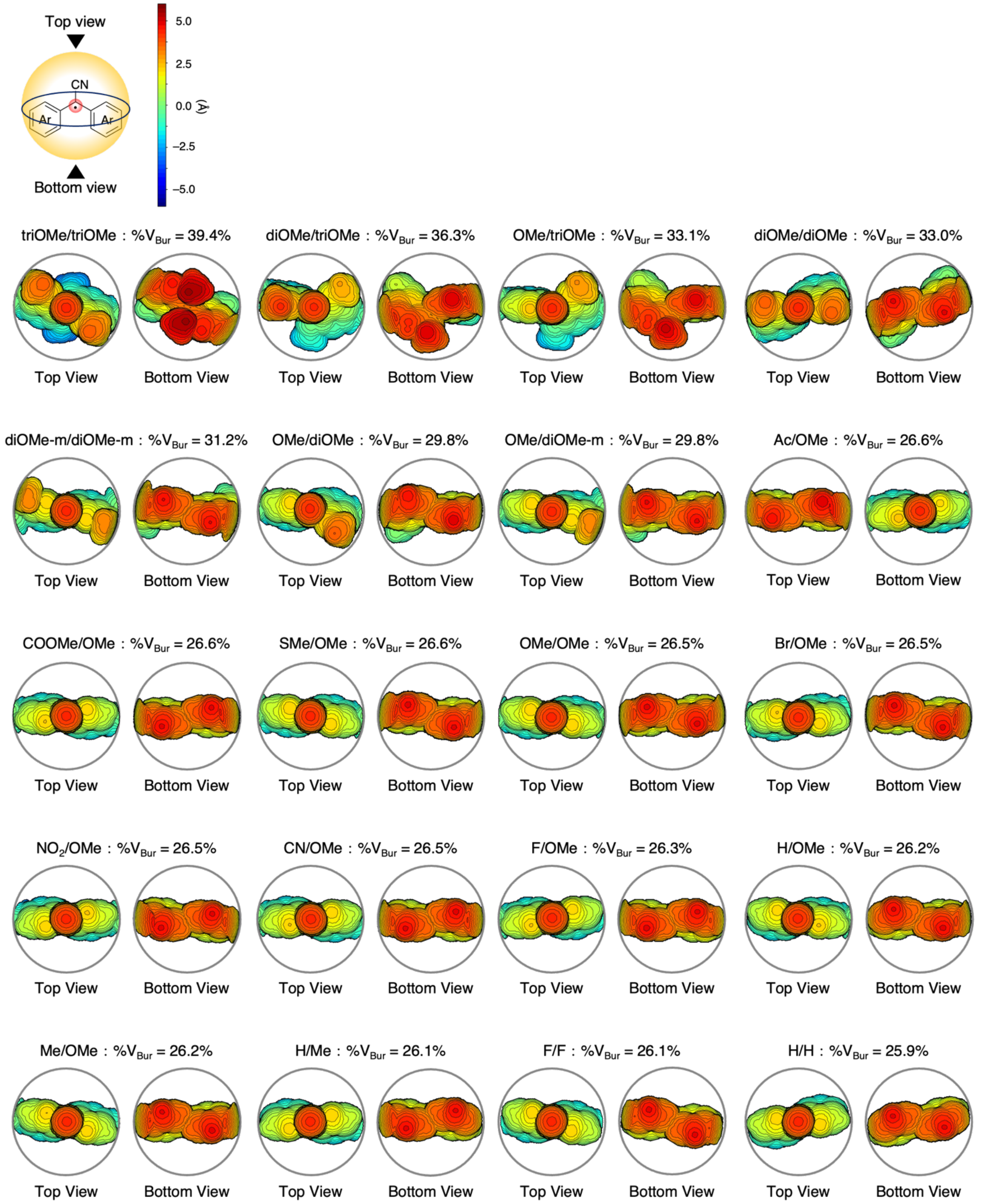


Figure S124. Steric maps of a series of DAAN radicals.

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