Supplementary Information

Efficient detection of polymeric mechanoradicals via fluorescent molecular probes stabilized by steric hindrance

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1. General Information

All commercially available polymers, 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. ^{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. Fluorescence Spectroscopy

Fluorescence measurements were carried out using a spectrofluorometer (JASCO FP-8550) between 350 and 750 nm.

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 0.25 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. Grinding 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 10–30 min at 30 Hz. All experiments were conducted at room temperature.

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 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

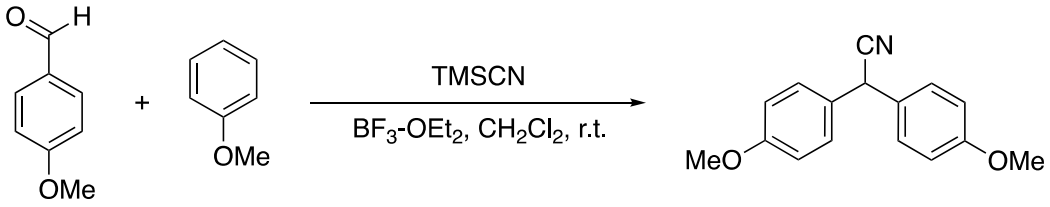
calculations were performed using the unrestricted M06-2X with the 6-311+G(d,p) to calculate the first doublet transitions.

4. Preparation of Polymer Samples

Polystyrene (61111) was purchased from ChemcoPlus and used without further purification. Polycarbonate (181676-1SET Lot#08) was purchased from Sigma-Aldrich, dissolved in chloroform and reprecipitated from methanol.

5. Synthesis Procedure

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



Scheme S1. Synthesis scheme of **DAAN-OMe/OMe**.

DAAN-OMe/OMe was synthesized according to the reported procedure.[1] 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 BF_3-OEt_2 (5.95 mL, 47.4 mmol, 1.2 equiv.) was added. 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, OCH_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.

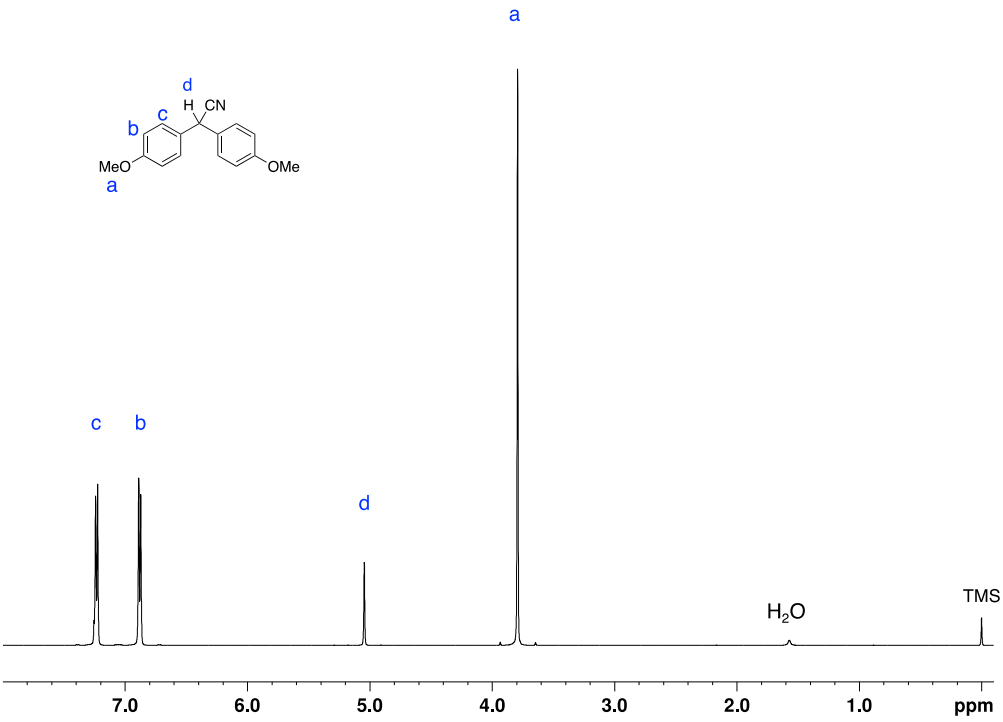


Figure S1. ^{1}H NMR spectrum of **DAAN-OMe/OMe** ($CDCl_3$, 500 MHz).

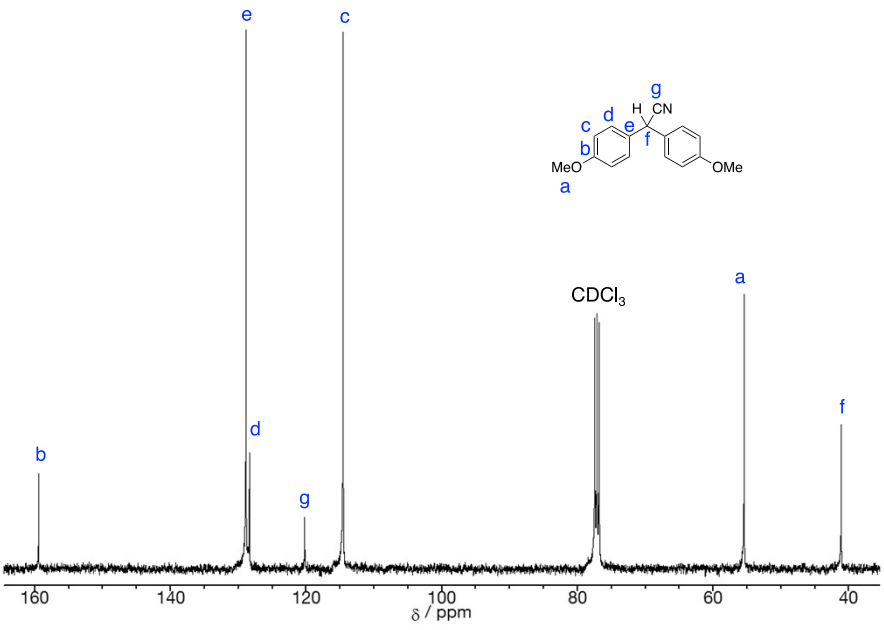
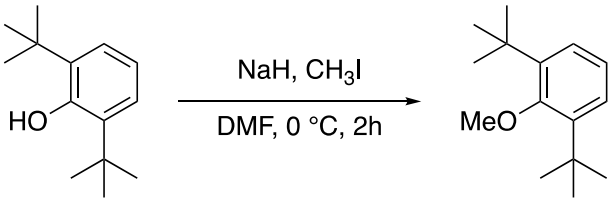


Figure S2. ^{13}C NMR spectrum of **DAAN-OMe/OMe** ($CDCl_3$, 100 MHz).

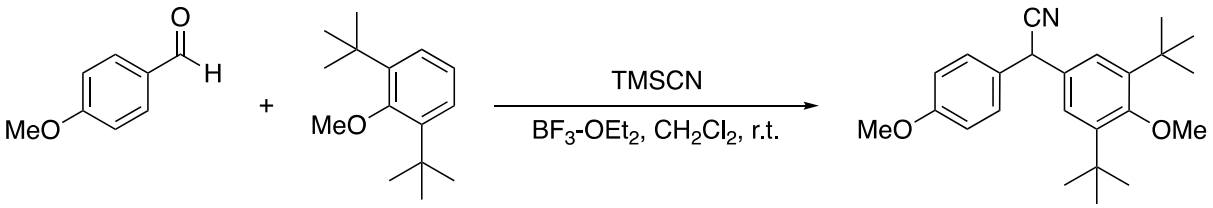
5.2. Synthesis of 1,3-di-*tert*-butyl-2-methoxybenzene



Scheme S2. Synthesis scheme of 1,3-di-*tert*-butyl-2-methoxybenzene.

2,6-Di-tert-butylphenol (9.36 g, 45 mmol), NaH (2.18 g, 54 mmol), and iodomethane (7.73 g, 54 mmol) were added to DMF (50 mL) at 0 °C for 3 h. The reaction mixture was poured into cold water, extracted with diethyl ether, and dried with Na_2SO_4. After filtration and evaporation, the crude product was purified by column chromatography on silica gel eluting with hexane and dried *in vacuo* to give 1,3-di-*tert*-butyl-2-methoxybenzene as colorless liquid (7.82 mg, 78% yield). The spectroscopic results were as reported.[2]

5.3. Synthesis of ***m*^{t}Bu$_2$-DAAN-OMe/OMe**



Scheme S3. Synthesis scheme of ***m*^{t}Bu$_2$-DAAN-OMe/OMe**.

To a stirred solution of 4-methoxybenzaldehyde (0.67 mL, 5.47 mmol), 1,3-di-*tert*-butyl-2-methoxybenzene (1.36 mL, 6.57 mmol, 1.2 equiv), and trimethylsilyl cyanide (1.02 mL, 8.21 mmol, 1.5 equiv) in CH_2Cl_2 (25 mL) at 0 °C BF_3-OEt_2 (0.82 mL, 6.57 mmol, 1.2 equiv) was added. After being stirred at room temperature for 7 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 and evaporation, the crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2/hexane (1/9, v/v) and dried *in vacuo* to give ***m*^{t}Bu$_2$-DAAN-OMe/OMe** as a white powder (1.68 g, 84% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.25 (d, J = 7.6 Hz, 2H, aromatic), 7.16 (s, 2H, aromatic), 6.90 (d, J = 6.9 Hz, 2H, aromatic), 5.02 (s, 1H, –C*H*(CN)–), 3.81 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 1.39 (s, 18H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 159.38, 144.56, 130.04, 128.93, 128.34, 126.01, 120.49, 114.48, 64.41, 55.44, 41.86, 36.00, 32.07.

^{13}C NMR (100 MHz, acetone-d_6): δ/ppm 159.52, 159.17, 144.23, 131.33, 129.21, 128.78, 125.98, 120.51, 114.48, 64.16, 54.85, 40.96, 35.74, 31.61.

FT-IR (NaBr, cm^{-1}): 2962, 2872, 2239, 1999, 1897, 1774, 1610, 1512, 1459, 1413, 1362, 1329, 1306, 1253, 1227, 1182, 1115, 1031, 1004, 929, 885, 837, 814, 772, 723, 658, 585, 550.

EI-MS (m/z): $[M]^+$ calcd for $C_{24}H_{31}NO_2$, 365.2355; found, 365.2361.

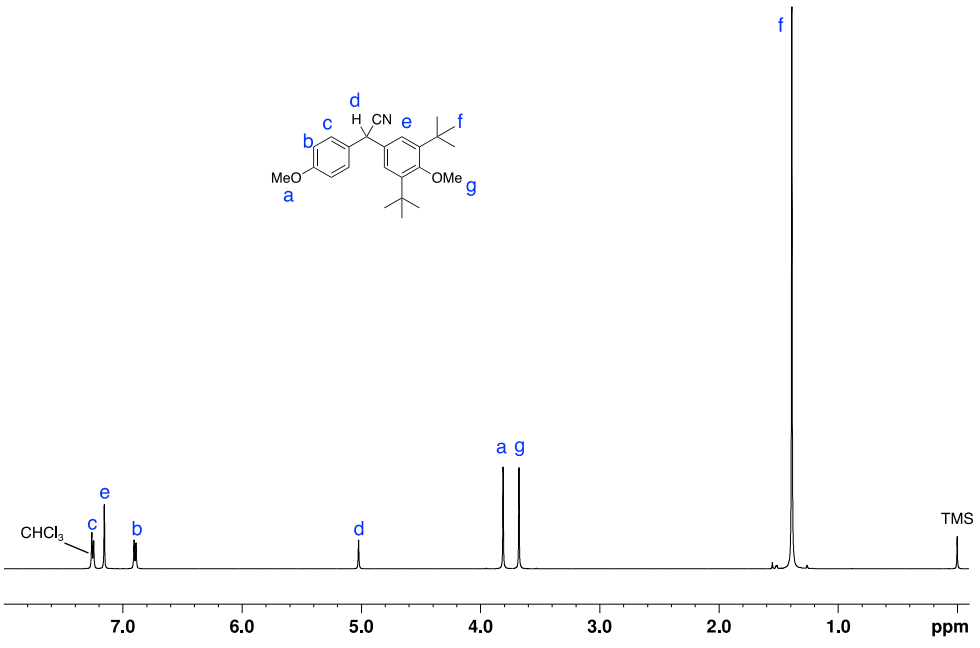


Figure S3. ^{1}H NMR spectrum of ***m*^{t}Bu$_2$-DAAN-OMe/OMe** ($CDCl_3$, 500 MHz).

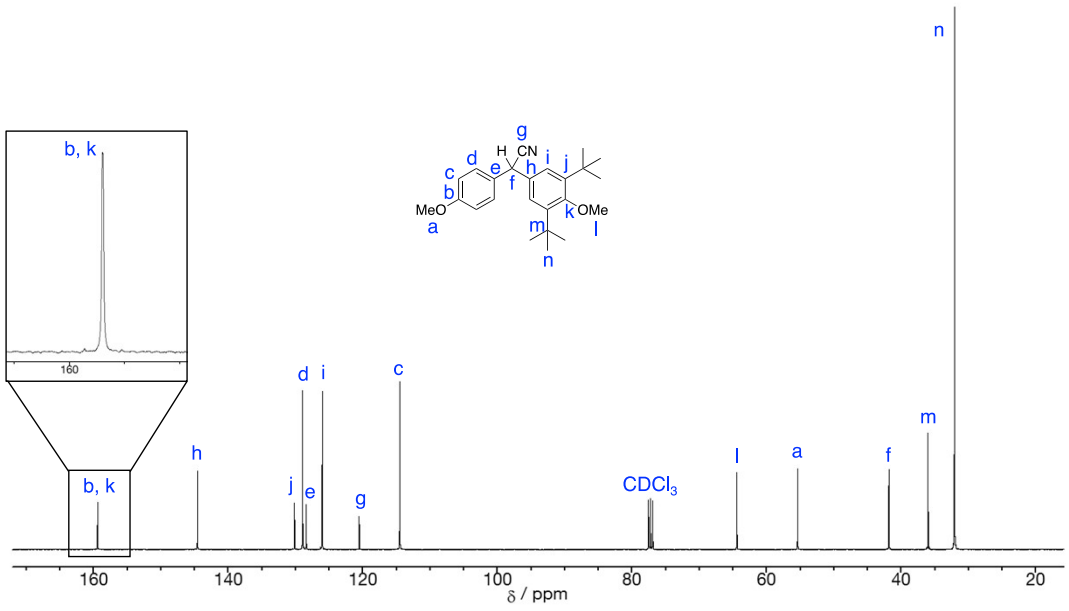


Figure S4. ^{13}C NMR spectrum of ***m*^{t}Bu$_2$-DAAN-OMe/OMe** ($CDCl_3$, 100 MHz).

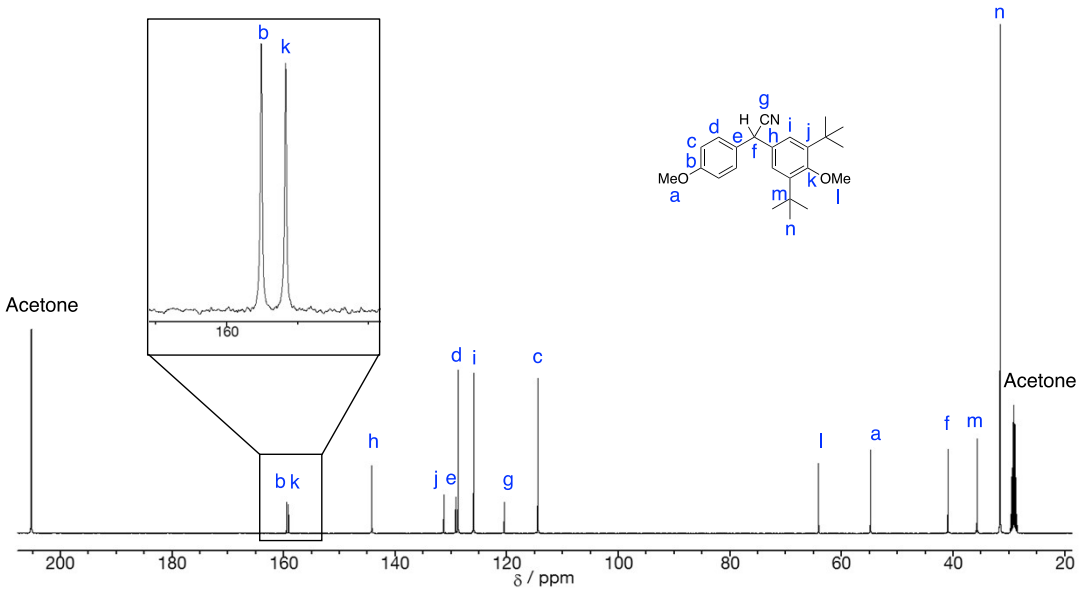
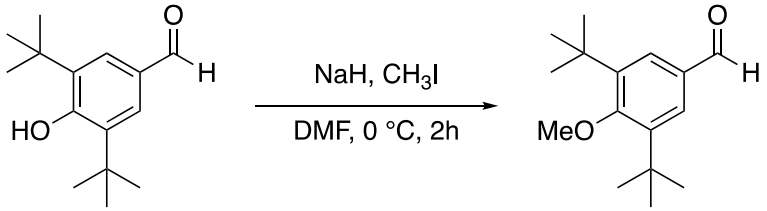


Figure S5. ^{13}C NMR spectrum of ***m*^{t}Bu$_2$-DAAN-OMe/OMe** (acetone-d_6, 100 MHz).

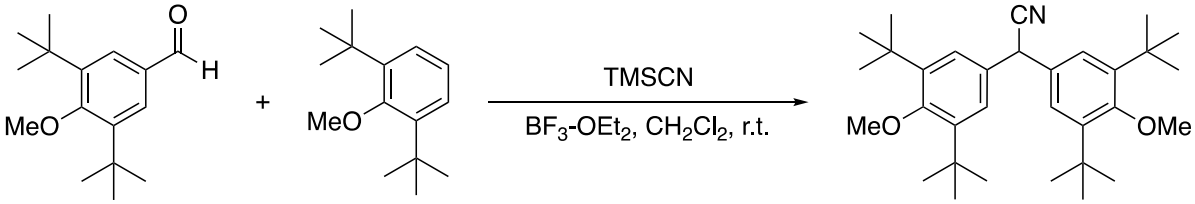
5.4. Synthesis of 3,5-di-*tert*-butyl-4-methoxybenzaldehyde



Scheme S4. Synthesis scheme of 3,5-di-*tert*-butyl-4-methoxybenzaldehyde.

3,5-Di-tert-butyl-4-hydroxybenzaldehyde (4.72 g, 20 mmol), NaH (0.81 g, 20 mmol), and iodomethane (4.29 g, 30 mmol) were added to DMF (50 mL) at 0 °C for 12 h. The reaction mixture was poured into cold water, extracted with diethyl ether, and dried with Na_2SO_4. After filtration and evaporation, the crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2/hexane (1/9, v/v) and dried *in vacuo* to give 1,3-di-*tert*-butyl-2-methoxybenzene as yellow liquid (4.01 mg, 80% yield). The spectroscopic results were as reported.[3]

5.5. Synthesis of ***m*^{t}Bu$_4$-DAAN-OMe/OMe**



Scheme S5. Synthesis of ***m*^{t}Bu$_4$-DAAN-OMe/OMe**.

To a stirred solution of 3,5-di-*tert*-butyl-4-methoxybenzaldehyde (0.99 mL, 4.47 mmol), 1,3-di-*tert*-butyl-2-methoxybenzene (1.11 mL, 5.36 mmol, 1.2 equiv), and trimethylsilyl cyanide (0.83 mL, 6.70 mmol, 1.5 equiv) in CH_2Cl_2 (25 mL) at 0 °C was added BF_3-OEt_2 (0.67 mL, 5.36 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 $MgSO_4$. After filtration and evaporation, the crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2/hexane (1/9, v/v) and dried *in vacuo* to give ***m*^{t}Bu$_4$-DAAN-OMe/OMe** as a white powder (1.17 g, 58% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.15 (s, 4H, aromatic), 5.01 (s, 1H, –C*H*(CN)–), 3.68 (s, 6H, OCH_3), 1.39 (s, 36H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 159.30, 144.43, 129.95, 126.16, 120.78, 64.43, 42.21, 36.01, 32.07.

FT-IR (NaBr, cm^{-1}): 2961, 2871, 2238, 1717, 1593, 1453, 1414, 1395, 1362, 1267, 1226, 1118, 1011, 928, 883, 795, 771, 680, 647.

EI-MS (m/z): $[M]^+$ calcd for $C_{32}H_{47}NO_2$, 477.3607; found, 477.3609.

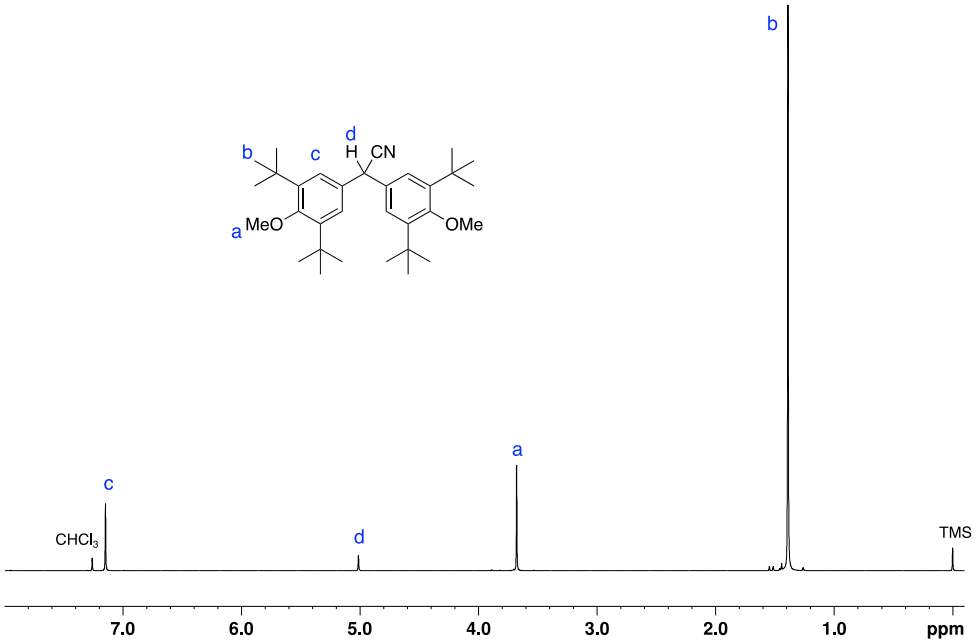


Figure S6. ^{1}H NMR spectrum of ***m*^{t}Bu$_4$-DAAN-OMe/OMe** ($CDCl_3$, 500 MHz).

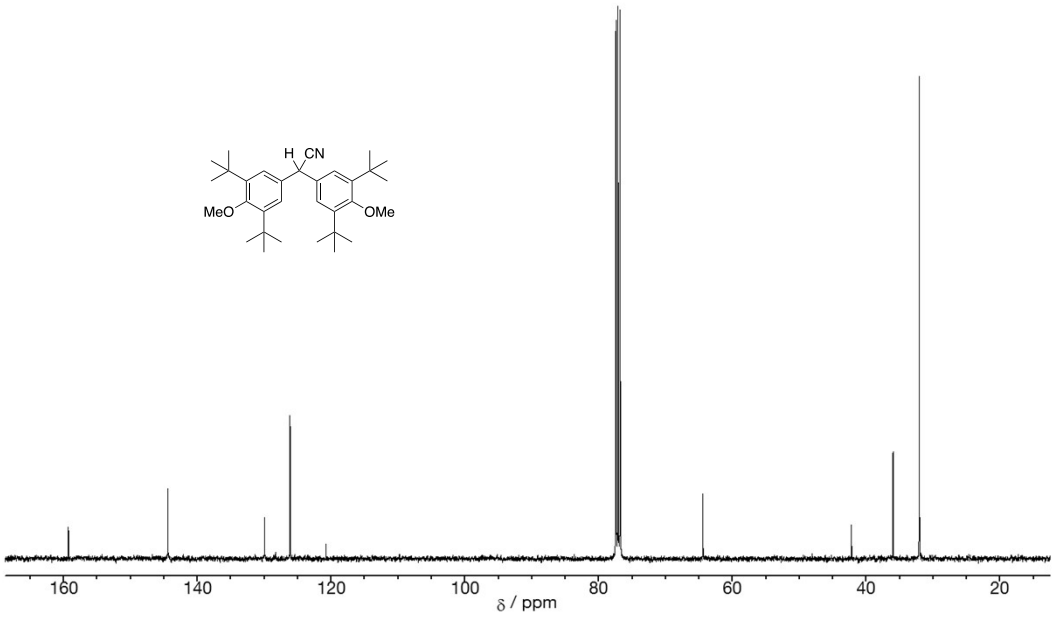


Figure S7. ^{13}C NMR spectrum of ***m*^{t}Bu$_4$-DAAN-OMe/OMe** ($CDCl_3$, 100 MHz).

6. Supplementary Figures

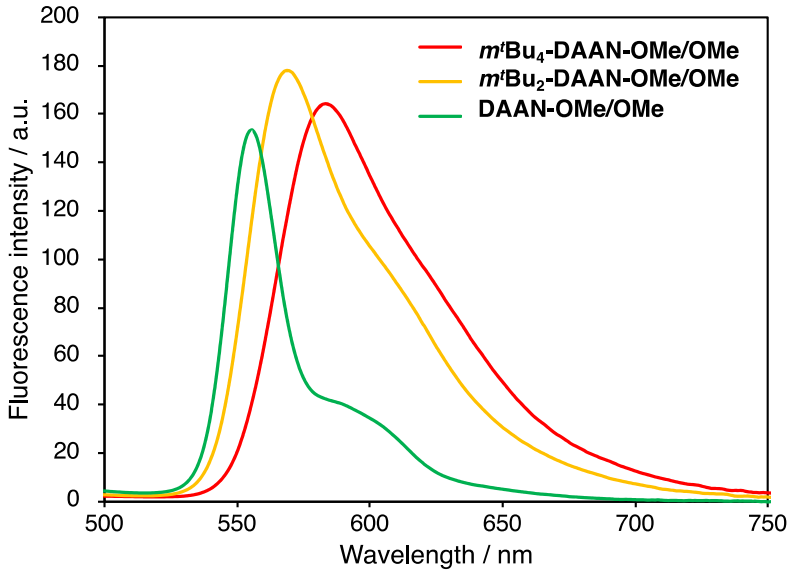


Figure S8. Fluorescence spectra (λ_{ex}=365 nm) of a mixture of polystyrene and DAAN derivatives after ball-milling for 30 min.

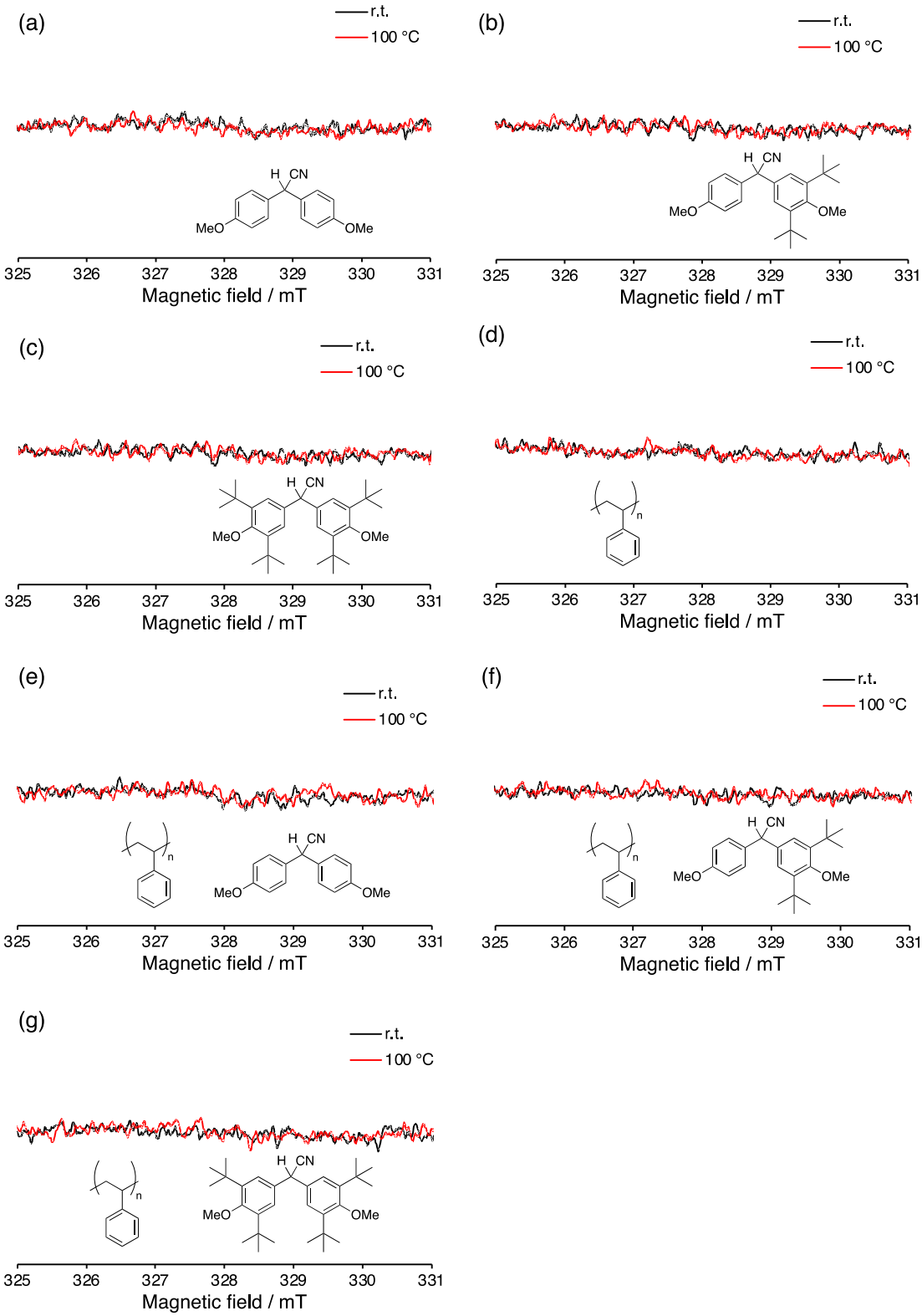


Figure S9. EPR spectra of (a) **DAAN-OMe/OMe**, (b) ***m*^{t}Bu$_2$-DAAN-OMe/OMe,** (c) ***m*^{t}Bu$_4$-DAAN-OMe/OMe,** (d) PS, (e) the mixture of **DAAN-OMe/OMe** and PS, (f) the mixture of ***m*^{t}Bu$_2$-DAAN-OMe/OMe** and PS, and (g) the mixture of ***m*^{t}Bu$_4$-DAAN-OMe/OMe** and PS at room temperature and 100 °C.

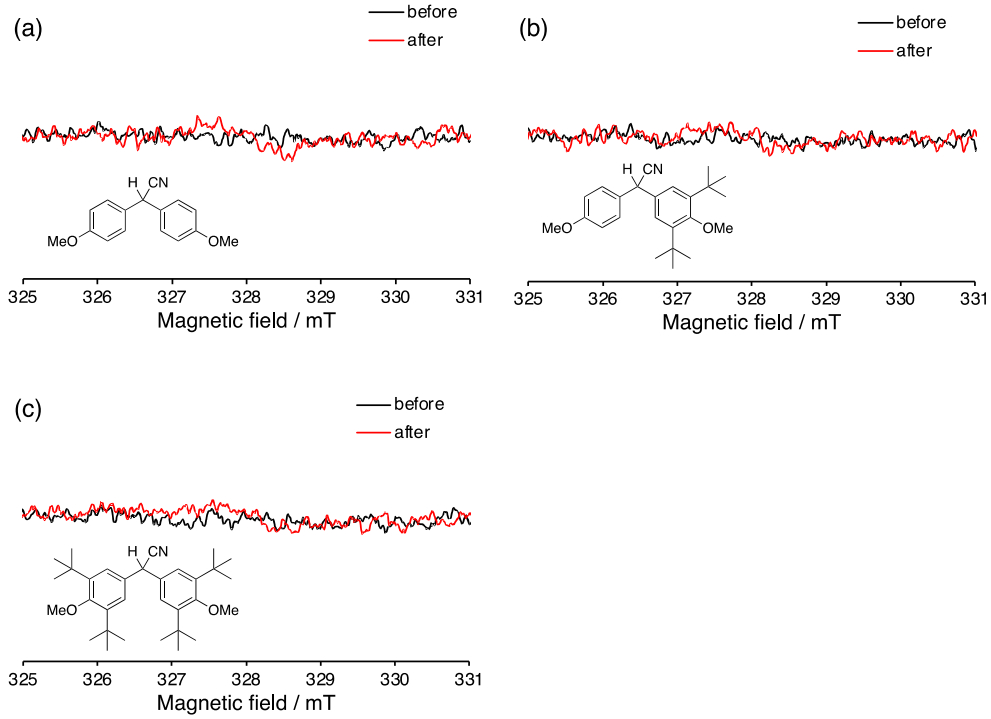


Figure S10. EPR spectra of (a) **DAAN-OMe/OMe**, (b) ***m*^{t}Bu$_2$-DAAN-OMe/OMe**, and (c) ***m*^{t}Bu$_4$-DAAN-OMe/OMe** before and after ball-milling for 30 min.

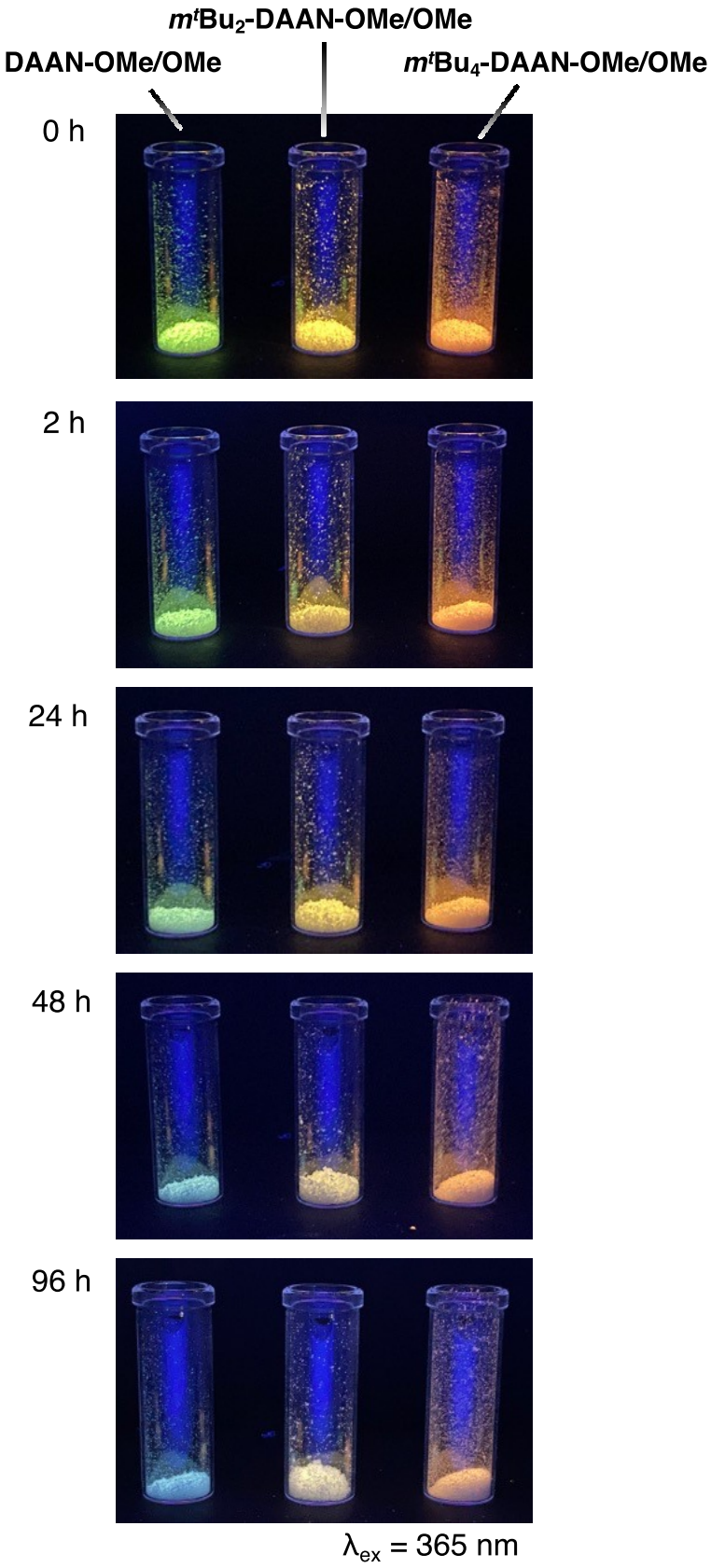


Figure S11. Photographs of the samples after ball-milling tests under UV irradiation (λ_{ex} = 365 nm).

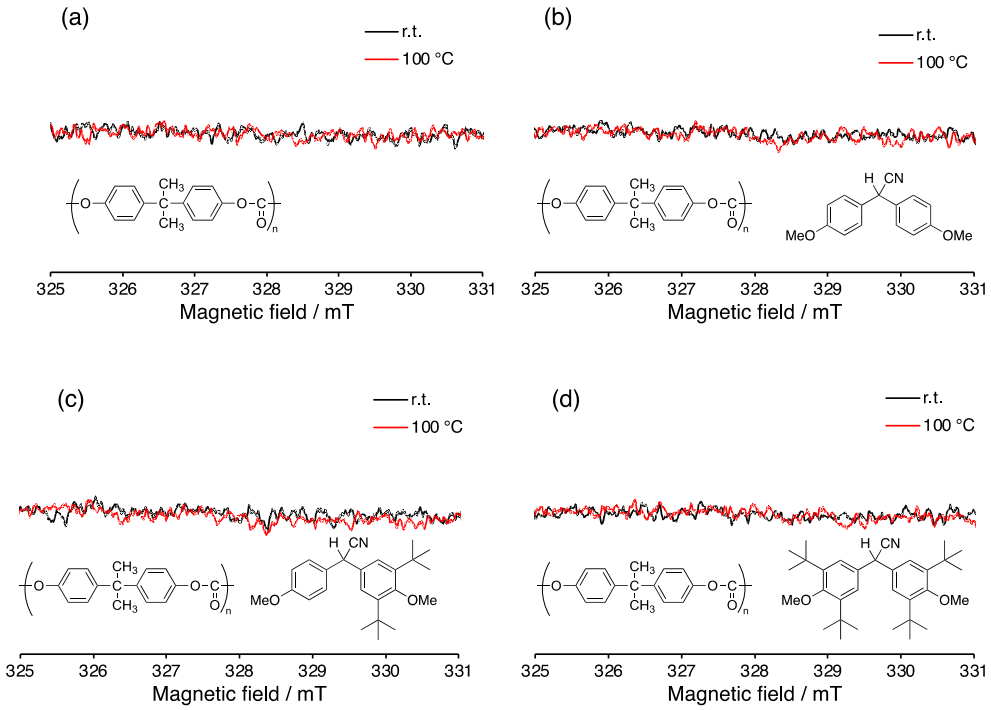


Figure S12. EPR spectra of (a) PC, (e) the mixture of **DAAN-OMe/OMe** and PC, (f) the mixture of ***m*^{t}Bu$_2$-DAAN-OMe/OMe** and PC, and (g) the mixture of ***m*^{t}Bu$_4$-DAAN-OMe/OMe** and PC at room temperature and 100 °C.

7. Calculated and Experimental Peak Wavelengths of DAAN Derivatives

Table S1. Calculated and Experimental peak wavelengths of DAAN derivatives

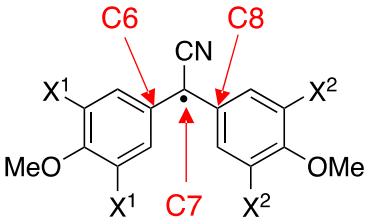
	$D_1 \rightarrow D_0$ / eV	Calculated fluorescence wavelength / nm	Experimental fluorescence wavelength / nm
DAAN-OMe/OMe	2.50	496	555
***m*^{t}Bu$_2$-DAAN-OMe/OMe**	2.41	515	568
***m*^{t}Bu$_4$-DAAN-OMe/OMe**	2.38	521	583

8. Calculated Fluorescence Properties of DAAN Derivatives Using UM06-2X/6-311+G(d,p)

Table S2. The relative orbital emission contributions are indicated ('up' = A, and 'down' =B)

	α-SOMO	Orbital emission contribution	Oscillator strength (*f*)
DAAN-OMe/OMe	67A	67A ← 68A (16%) 66B ← 67B (79%)	0.130
***m*^{t}Bu$_2$-DAAN-OMe/OMe**	99A	99A ← 100A (17%) 98B ← 99B (76%)	0.105
***m*^{t}Bu$_4$-DAAN-OMe/OMe**	131A	131A ← 32A (16%) 130B ← 131B (77%)	0.109

9. Calculated Angles of DAAN Derivatives Using UM06-2X/6-311+G(d,p)



DAAN-OMe/OMe : X^1, X^2 = H
***m*^{t}Bu$_2$-DAAN-OMe/OMe** : X^1 = H, X^2 = ^{t}Bu
***m*^{t}Bu$_4$-DAAN-OMe/OMe** : X^1, X^2 = ^{t}Bu

Table S3. Calculated angles of DAAN derivatives using UM06-2X/6-311+G(d,p)

	State	Dihedral angle / °	∠C6C7C8 / °
DAAN-OMe/OMe	D_0	44.3	125.4
	D_1	37.4	126.5
***m*^{t}Bu$_2$-DAAN-OMe/OMe**	D_0	44.8	125.4
	D_1	37.3	127.1
***m*^{t}Bu$_4$-DAAN-OMe/OMe**	D_0	49.2	124.9
	D_1	33.9	128.6

10. Cartesian Coordinates of All the Optimized Geometries by DFT Calculation

DAAN-OMe/OMe of D_0 state optimized with UM06-2X/6-311+G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.693211	0.529737	0.355087
2	6	0	2.447702	1.138675	0.400458
3	6	0	1.287665	0.482810	-0.042500
4	6	0	1.437852	-0.816211	-0.576856
5	6	0	2.671445	-1.426678	-0.630489
6	6	0	3.810903	-0.764754	-0.155317
7	1	0	4.557129	1.069738	0.717483
8	1	0	2.367547	2.144623	0.797123
9	1	0	0.577073	-1.327008	-0.989953
10	1	0	2.792085	-2.415878	-1.054417
11	6	0	-1.287679	0.482818	0.042532
12	6	0	-2.447703	1.138667	-0.400478
13	6	0	-1.437881	-0.816174	0.576952
14	6	0	-3.693216	0.529737	-0.355100
15	1	0	-2.367536	2.144596	-0.797190
16	6	0	-2.671478	-1.426632	0.630594
17	1	0	-0.577111	-1.326952	0.990091
18	6	0	-3.810923	-0.764727	0.155367
19	1	0	-4.557125	1.069724	-0.717540
20	1	0	-2.792131	-2.415809	1.054571
21	6	0	-0.000006	2.564734	-0.000001
22	7	0	0.000161	3.721664	-0.000376
23	8	0	4.972691	-1.450357	-0.244186
24	8	0	-4.972716	-1.450321	0.244246
25	6	0	6.153754	-0.815106	0.205107
26	1	0	6.088602	-0.571628	1.269665
27	1	0	6.957935	-1.528906	0.044663
28	1	0	6.353008	0.094892	-0.368392
29	6	0	-6.153774	-0.815071	-0.205062
30	1	0	-6.957964	-1.528851	-0.044578
31	1	0	-6.353007	0.094956	0.368399
32	1	0	-6.088631	-0.571641	-1.269631

33	6	0	-0.000004	1.148497	0.000013

***m*'Bu$_2$-DAAN-OMe/OMe** of D_0 state optimized with UM06-2X/6-311+G(d,p)

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000010654	-0.000005372	0.000002519
2	6	0.000003998	0.000003911	-0.000010208
3	6	0.000001257	-0.000000834	0.000003565
4	6	-0.000008544	-0.000003702	-0.000001137
5	6	0.000007507	0.000004171	-0.000008691
6	6	0.000002775	0.000001602	0.000013016
7	1	0.000001167	-0.000001902	0.000000730
8	1	0.000001298	-0.000000858	0.000000520
9	6	-0.000000125	-0.000003808	0.000000224
10	6	0.000005054	0.000001108	0.000001823
11	6	-0.000004186	0.000002417	-0.000001450
12	6	0.000000054	0.000003526	0.000000137
13	1	-0.000001222	0.000000052	-0.000000082
14	6	0.000005402	-0.000001148	0.000003943
15	1	-0.000000304	-0.000000637	-0.000000276
16	6	-0.000004741	-0.000002657	-0.000003773
17	6	-0.000001715	-0.000000701	0.000000239
18	7	-0.000000039	0.000000644	0.000000184
19	8	-0.000002134	0.000000624	-0.000001615
20	8	0.000000759	-0.000001269	0.000002699
21	6	-0.000002395	-0.000002682	-0.000001549
22	1	0.000003550	0.000000714	0.000000858
23	1	0.000000871	0.000000853	-0.000000126
24	1	0.000000751	0.000001904	0.000000734
25	6	0.000000477	0.000001330	-0.000002674
26	1	-0.000000139	-0.000000035	0.000000009
27	1	0.000000029	-0.000000458	0.000000842
28	1	0.000000134	0.000000107	0.000000934
29	6	-0.000000434	0.000000662	0.000004044
30	1	0.000001013	0.000000314	-0.000001318

31	6	-0.000001061	-0.000000517	0.000001311
32	6	-0.000000289	0.000000925	-0.000002813
33	1	0.000000180	-0.000000098	-0.000000243
34	1	-0.000000172	-0.000000574	0.000000326
35	1	-0.000000029	0.000000681	0.000000632
36	6	0.000000068	0.000001783	-0.000000137
37	1	0.000000446	-0.000000494	-0.000000498
38	1	-0.000000501	-0.000000339	-0.000000584
39	1	-0.000000043	-0.000001524	-0.000001880
40	6	0.000001742	-0.000002305	-0.000001956
41	1	-0.000000483	0.000000491	-0.000000182
42	1	0.000000301	0.000001461	-0.000000742
43	1	-0.000000668	0.000000068	0.000000325
44	6	-0.000000540	-0.000000162	-0.000004075
45	6	0.000000308	-0.000000166	0.000002190
46	1	-0.000000522	0.000000613	-0.000000301
47	1	0.000000294	0.000000422	0.000000293
48	1	0.000000271	-0.000000638	-0.000000408
49	6	-0.000000928	0.000000945	0.000002789
50	1	0.000001167	0.000000065	-0.000000549
51	1	0.000000136	-0.000000229	0.000000328
52	1	0.000001014	0.000000113	-0.000000409
53	6	0.000000416	0.000000893	-0.000000377
54	1	-0.000000366	0.000000794	0.000000327
55	1	-0.000000372	-0.000000265	0.000000414
56	1	-0.000000262	0.000000558	0.000000137
57	1	-0.000001090	-0.000001044	0.000002229
58	1	0.000001522	0.000000669	-0.000000267

***m*^{t}Bu$_4$-DAAN-OMe/OMe** of D_0 state optimized with UM06-2X/6-311+G(d,p)

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000001167	0.000002514	0.000000221
2	6	-0.000001647	-0.000000450	0.000003429
3	6	-0.000000853	-0.000001377	-0.000002338

4	6	0.000002055	0.000000605	0.000000874
5	6	0.000001461	-0.000003577	0.000000120
6	6	-0.000003792	-0.000000811	-0.000004150
7	1	-0.000000417	0.000000504	0.000000624
8	1	-0.000000856	-0.000000134	-0.000000764
9	6	-0.000001544	-0.000003458	-0.000000487
10	6	-0.000002006	-0.000002889	-0.000004257
11	6	0.000006787	-0.000005665	0.000000525
12	6	0.000000363	0.000000060	0.000001821
13	1	0.000000233	0.000000300	-0.000001402
14	6	-0.000003496	-0.000001867	-0.000006619
15	1	-0.000002471	-0.000005624	0.000001146
16	6	0.000001268	0.000001225	0.000001653
17	6	-0.000025581	-0.000000873	-0.000027662
18	7	0.000013241	-0.000001074	0.000010747
19	8	0.000003689	0.000002043	0.000005989
20	8	0.000002511	0.000001062	-0.000007430
21	6	-0.000001288	0.000002236	-0.000002865
22	1	0.000001630	0.000002601	0.000000745
23	1	-0.000000395	0.000001888	-0.000000659
24	1	0.000000228	0.000001238	-0.000002181
25	6	0.000000380	0.000003112	-0.000004569
26	1	0.000000588	-0.000000744	0.000000462
27	1	0.000000097	-0.000002236	-0.000001749
28	1	0.000002814	0.000004308	0.000001641
29	6	0.000014051	-0.000001664	0.000013540
30	1	0.000000562	0.000002937	-0.000001649
31	6	-0.000001041	-0.000001681	0.000002029
32	6	-0.000000029	-0.000000854	-0.000001552
33	1	0.000000262	0.000000147	-0.000002612
34	1	-0.000000070	-0.000000910	-0.000002300
35	1	0.000000095	0.000000127	-0.000001343
36	6	0.000005849	0.000006020	-0.000002731
37	1	-0.000000532	-0.000000072	-0.000001359
38	1	-0.000002079	0.000002639	0.000000831
39	1	-0.000002207	0.000006301	0.000007849
40	6	0.000003259	0.000000546	-0.000002178
41	1	0.000000332	0.000001371	-0.000001930

42	1	0.000001438	0.000000406	-0.000001145
43	1	0.000001479	0.000000237	-0.000000712
44	6	0.000000455	0.000000907	0.000005086
45	6	-0.000000687	-0.000003647	0.000001487
46	1	-0.000001031	-0.000001033	0.000001697
47	1	-0.000005995	-0.000009610	0.000000679
48	1	0.000000065	-0.000001415	0.000000597
49	6	0.000000015	-0.000002670	0.000004444
50	1	-0.000004735	-0.000004903	0.000001098
51	1	-0.000001052	-0.000000288	0.000001757
52	1	-0.000001179	-0.000000698	0.000001106
53	6	0.000001261	0.000003708	0.000000347
54	1	-0.000000656	-0.000000743	0.000001431
55	1	0.000000055	0.000002821	0.000001719
56	1	0.000000152	-0.000000483	0.000002345
57	6	-0.000000802	0.000000709	0.000001107
58	6	0.000000557	-0.000001012	0.000000169
59	1	-0.000000638	-0.000001593	0.000000477
60	1	0.000000644	-0.000001214	-0.000000581
61	1	-0.000000265	-0.000001314	0.000000518
62	6	0.000000038	-0.000000222	0.000001818
63	1	-0.000000257	-0.000000431	0.000000864
64	1	-0.000000698	-0.000001655	-0.000001316
65	1	0.000000083	-0.000000716	0.000001124
66	6	0.000001843	-0.000000097	-0.000000423
67	1	-0.000000321	0.000001045	-0.000000087
68	1	-0.000000113	-0.000000730	-0.000000071
69	1	0.000000303	-0.000000434	-0.000000130
70	6	-0.000002257	-0.000000502	0.000000563
71	6	0.000000508	0.000000276	-0.000000371
72	1	-0.000000701	0.000003116	-0.000000016
73	1	-0.000000563	0.000000847	0.000001631
74	1	0.000000012	0.000001273	0.000001304
75	6	-0.000000994	0.000000918	-0.000001538
76	1	-0.000000376	0.000001596	0.000000591
77	1	0.000000237	0.000002241	0.000000170
78	1	-0.000002051	0.000001790	-0.000001409
79	6	0.000001330	-0.000000028	0.000000029

80	1	0.000000397	0.000002773	0.000001177
81	1	0.000000722	0.000001571	0.000002238
82	1	0.000001156	0.000001379	0.000000763

DAAN-OMe/OMe of D_1 state optimized with UM06-2X/6-311+G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.711231	0.591201	0.283577
2	6	0	2.467640	1.166500	0.332591
3	6	0	1.273522	0.447799	-0.029414
4	6	0	1.463640	-0.901228	-0.490198
5	6	0	2.702495	-1.473174	-0.536788
6	6	0	3.853434	-0.748758	-0.136886
7	1	0	4.574284	1.174503	0.576546
8	1	0	2.370006	2.195403	0.656930
9	1	0	0.614028	-1.459414	-0.859282
10	1	0	2.841481	-2.485525	-0.897208
11	6	0	-1.273523	0.447799	0.029415
12	6	0	-2.467640	1.166499	-0.332596
13	6	0	-1.463642	-0.901228	0.490201
14	6	0	-3.711231	0.591201	-0.283582
15	1	0	-2.370004	2.195401	-0.656938
16	6	0	-2.702497	-1.473172	0.536791
17	1	0	-0.614031	-1.459413	0.859288
18	6	0	-3.853435	-0.748756	0.136885
19	1	0	-4.574282	1.174502	-0.576556
20	1	0	-2.841485	-2.485522	0.897214
21	6	0	-0.000003	2.510490	-0.000002
22	7	0	0.000013	3.667412	0.000006
23	8	0	5.019048	-1.416963	-0.199974
24	8	0	-5.019049	-1.416961	0.199974
25	6	0	6.203765	-0.742676	0.186600
26	1	0	6.147829	-0.427655	1.232072
27	1	0	7.010392	-1.460543	0.063052
28	1	0	6.382903	0.125852	-0.452854

29	6	0	-6.203766	-0.742673	-0.186601
30	1	0	-7.010394	-1.460538	-0.063049
31	1	0	-6.382901	0.125858	0.452851
32	1	0	-6.147832	-0.427656	-1.232073
33	6	0	-0.000001	1.089220	0.000002

***m*^{t}Bu$_2$-DAAN-OMe/OMe** of D_1 state optimized with UM06-2X/6-311+G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.450692	-0.903599	0.173841
2	6	0	-1.203310	-1.456085	0.106744
3	6	0	-0.001572	-0.684175	-0.086605
4	6	0	-0.149867	0.749891	-0.090531
5	6	0	-1.372709	1.358996	-0.063551
6	6	0	-2.549875	0.519453	-0.056297
7	1	0	-1.079438	-2.522202	0.250482
8	1	0	0.739076	1.351263	-0.184729
9	6	0	2.551812	-0.773915	-0.081892
10	6	0	3.695647	-1.371263	-0.695459
11	6	0	2.805736	0.346149	0.772050
12	6	0	4.967264	-0.876508	-0.517639
13	1	0	3.549570	-2.239961	-1.326473
14	6	0	4.070464	0.840374	0.950437
15	1	0	1.990780	0.780891	1.335486
16	6	0	5.173798	0.250312	0.298530
17	6	0	1.190989	-2.694712	-0.689114
18	7	0	1.136096	-3.798119	-1.032567
19	8	0	-3.742437	1.093940	-0.367631
20	8	0	6.370746	0.825850	0.526411
21	6	0	-4.224997	0.769409	-1.671988
22	1	0	-4.273374	-0.311575	-1.815573
23	1	0	-5.222319	1.199726	-1.751383
24	1	0	-3.568207	1.202817	-2.431193
25	6	0	7.512277	0.266733	-0.097364
26	1	0	8.354398	0.878837	0.215203

27	1	0	7.668173	-0.765677	0.227690
28	1	0	7.417732	0.300497	-1.186318
29	6	0	1.248086	-1.338049	-0.265757
30	6	0	-1.506750	2.885908	-0.032830
31	6	0	-0.136836	3.563066	0.109824
32	1	0	0.396674	3.214292	0.997714
33	1	0	0.495301	3.396830	-0.766117
34	1	0	-0.284871	4.640486	0.210316
35	6	0	-2.357347	3.285398	1.187659
36	1	0	-2.448955	4.374459	1.229228
37	1	0	-3.358489	2.858212	1.134310
38	1	0	-1.880145	2.948828	2.111823
39	6	0	-2.156447	3.430495	-1.319584
40	1	0	-1.645275	3.045996	-2.206511
41	1	0	-3.213478	3.178333	-1.377437
42	1	0	-2.072397	4.520739	-1.330050
43	6	0	-3.628623	-1.813734	0.582419
44	6	0	-4.949383	-1.081745	0.873090
45	1	0	-5.638890	-1.796565	1.329258
46	1	0	-4.805428	-0.255285	1.571247
47	1	0	-5.433797	-0.691957	-0.020706
48	6	0	-3.868300	-2.886449	-0.494344
49	1	0	-2.971077	-3.483988	-0.667354
50	1	0	-4.669054	-3.557503	-0.171223
51	1	0	-4.164953	-2.444261	-1.448212
52	6	0	-3.236774	-2.521761	1.898415
53	1	0	-2.353515	-3.150021	1.785023
54	1	0	-3.035837	-1.788361	2.683146
55	1	0	-4.061321	-3.159767	2.226612
56	1	0	5.796063	-1.361479	-1.016035
57	1	0	4.258355	1.679783	1.609167

***m*^{t}Bu$_4$-DAAN-OMe/OMe** of D_1 state optimized with UM06-2X/6-311+G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	3.711671	-1.019671	-0.414955
2	6	0	2.424488	-1.488190	-0.473151
3	6	0	1.284191	-0.737443	-0.032167
4	6	0	1.532524	0.617064	0.374779
5	6	0	2.801426	1.129065	0.486501
6	6	0	3.908325	0.259936	0.203917
7	1	0	2.232368	-2.464676	-0.899144
8	1	0	0.694130	1.223469	0.675115
9	6	0	-1.284187	-0.737514	0.031911
10	6	0	-2.424397	-1.488256	0.472992
11	6	0	-1.532585	0.616903	-0.375166
12	6	0	-3.711613	-1.019716	0.414987
13	1	0	-2.232243	-2.464772	0.898901
14	6	0	-2.801524	1.128918	-0.486717
15	1	0	-0.694243	1.223261	-0.675744
16	6	0	-3.908345	0.259856	-0.203835
17	6	0	0.000094	-2.781326	-0.000036
18	7	0	0.000176	-3.937953	0.000030
19	8	0	5.151433	0.662003	0.593670
20	8	0	-5.151573	0.662025	-0.593176
21	6	0	5.639432	-0.021253	1.747571
22	1	0	5.645488	-1.101704	1.592321
23	1	0	6.655464	0.334648	1.913586
24	1	0	5.015105	0.211099	2.614650
25	6	0	-5.639877	-0.021066	-1.747039
26	1	0	-6.655895	0.334983	-1.912834
27	1	0	-5.015694	0.211259	-2.614227
28	1	0	-5.646056	-1.101529	-1.591879
29	6	0	0.000029	-1.356382	-0.000115
30	6	0	-3.041514	2.592954	-0.882750
31	6	0	-1.720641	3.368441	-0.969244
32	1	0	-1.169281	3.321765	-0.027059
33	1	0	-1.077166	3.000016	-1.772868
34	1	0	-1.939419	4.418222	-1.176949
35	6	0	-3.901011	3.268716	0.202936
36	1	0	-4.061003	4.318695	-0.058439
37	1	0	-4.872970	2.786601	0.301929
38	1	0	-3.390579	3.233225	1.169041

39	6	0	-3.741032	2.714775	-2.249344
40	1	0	-4.780653	2.396544	-2.200994
41	1	0	-3.728287	3.760873	-2.567717
42	1	0	-3.219480	2.126203	-3.009195
43	6	0	-4.816838	-1.863595	1.086779
44	6	0	-4.357140	-2.174738	2.528652
45	1	0	-3.436931	-2.757859	2.556982
46	1	0	-4.192807	-1.249677	3.086619
47	1	0	-5.132406	-2.751439	3.039391
48	6	0	-4.996703	-3.194839	0.336712
49	1	0	-4.061614	-3.757257	0.295900
50	1	0	-5.742342	-3.808115	0.850455
51	1	0	-5.338412	-3.039449	-0.689125
52	6	0	-6.180988	-1.166496	1.222703
53	1	0	-6.809708	-1.778537	1.874395
54	1	0	-6.082841	-0.178057	1.674788
55	1	0	-6.708255	-1.056670	0.276720
56	6	0	3.041403	2.593100	0.882502
57	6	0	1.720575	3.368730	0.968365
58	1	0	1.169617	3.322035	0.025945
59	1	0	1.076716	3.000429	1.771739
60	1	0	1.939368	4.418503	1.176090
61	6	0	3.901455	3.268685	-0.202856
62	1	0	4.061452	4.318662	0.058519
63	1	0	4.873404	2.786455	-0.301393
64	1	0	3.391441	3.233190	-1.169181
65	6	0	3.740333	2.714917	2.249400
66	1	0	3.218343	2.126489	3.009061
67	1	0	4.779923	2.396508	2.201541
68	1	0	3.727615	3.761043	2.567682
69	6	0	4.817012	-1.863484	-1.086624
70	6	0	6.181189	-1.166373	-1.222194
71	1	0	6.810054	-1.778358	-1.873800
72	1	0	6.083144	-0.177895	-1.674218
73	1	0	6.708246	-1.056629	-0.276082
74	6	0	4.996731	-3.194808	-0.336664
75	1	0	4.061635	-3.757228	-0.296078
76	1	0	5.742463	-3.808031	-0.850336

77	1	0	5.338256	-3.039524	0.689252
78	6	0	4.357570	-2.174461	-2.528613
79	1	0	3.437335	-2.757532	-2.557158
80	1	0	4.193380	-1.249337	-3.086517
81	1	0	5.132902	-2.751148	-3.039268

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11. Extracted Results of TD-DFT Calculation

DAAN-OMe/OMe of D_1 state optimized with UM06-2X/6-311+G(d,p)

67A is SOMO.

Excited State 1: 2.116-A 2.4988 eV 496.18 nm f=0.1304 <S**2>=0.869

67A → 68A 0.39452

65B → 71B -0.10477

66B → 67B 0.89147

***m*^{t}Bu$_2$-DAAN-OMe/OMe** of D_1 state optimized with UM06-2X/6-311+G(d,p)

99A is SOMO.

Excited State 1: 2.128-A 2.4063 eV 515.25 nm f=0.1047 <S**2>=0.882

99A → 100A 0.41391

96B → 101B 0.10429

98B → 99B 0.86969

***m*^{t}Bu$_4$-DAAN-OMe/OMe** of D_1 state optimized with UM06-2X/6-311+G(d,p)

131A is SOMO.

Excited State 1: 2.134-A 2.3795 eV 521.04 nm f=0.1091 <S**2>=0.888

131A → 132A -0.39652

127B → 133B 0.10563

130B → 131B 0.88144

References

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