Supporting Information

Color-tunable emissive heptagon-embedded polycyclic aromatic dicarboximides

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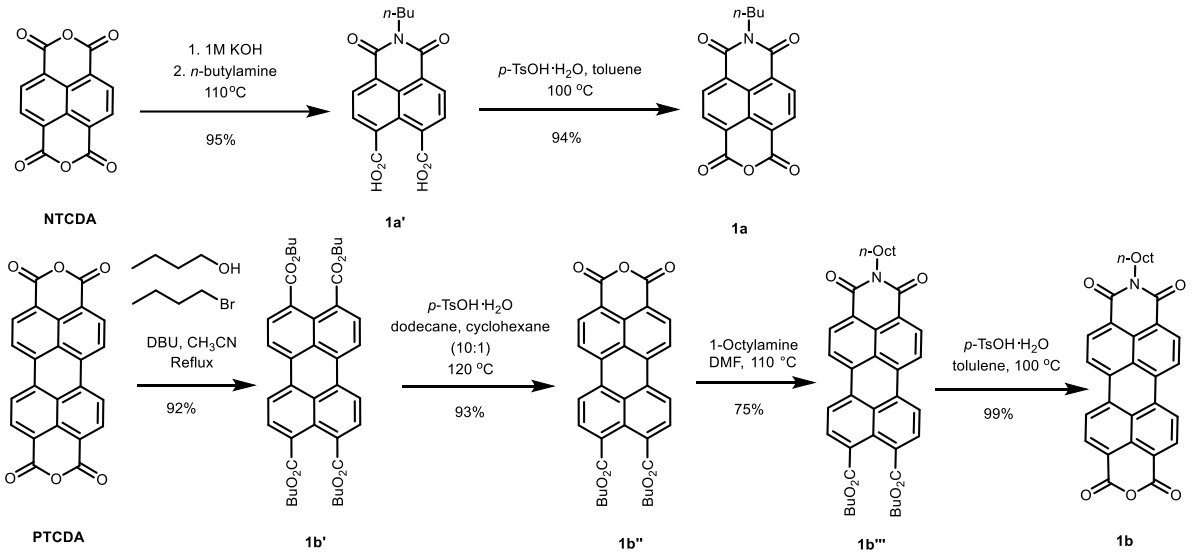
I. General Information

All another starting materials, reagents, and solvents were obtained from commercial sources and were used without further purification. Reactions were monitored by Thin-Layer Chromatography and visualized by UV. Purification of the reaction products was carried out by column chromatography on Merck silica gel 60. ^{1}H NMR,^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker Avance-600, Bruker Avance-500, Bruker Avance-400, or JEOL-400 spectrometer in $CDCl_3$ by using tetramethylsilane (δ = 0 ppm) or residual non-deuterated solvent peak as an internal standard. ^{1}H NMR data are assumed to be first order with apparent singlet, doublets, triplets and multiplets reported as s, d, t and m. The structures of known compounds were confirmed by comparing their ^{1}H NMR and ^{13}C NMR data with those in the literature. Melting points were recorded with Buchi Melting Point M-565 apparatus. Infrared spectra were recorded with a Bruker ALPHA FT-IR spectrometer. High resolution mass spectra (HRMS) were obtained on a Bruker micro TOF spectrometer in the APCI mode and JEOL *AccuTOF™-DART® 4G*. UV-Vis spectroscopy was performed on a UV-Vis spectrophotometer (Shimadzu UV2600) and all fluorescence spectra were recorded using a spectrofluorometer (Horiba FluoroMax4+, integration time 0.1 s, slit width 3 nm). The fluorescence quantum yields in solution were determined by using the dilution method (A < 0.05). The quantum efficiencies were measured by comparing between solvents as a blank and sample according to this equation (original from Horiba with sphere cuvette correction): Φ_F = Δ Area under emission curve /Δ Area under absorption curve the default mode for quantum yield measurement was set at slit width 3–2.8 nm, integration time 1 sec.

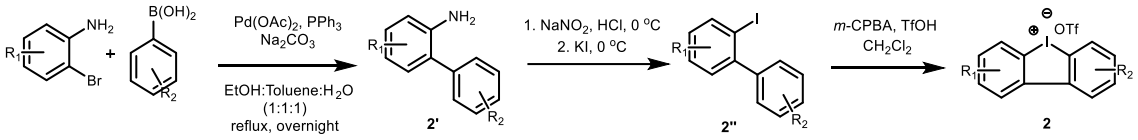
II. General Procedure for Preparation of the Starting Materials



A. Preparation of Naphthalene Carboximide and Perylene Carboximide Derivatives (1)

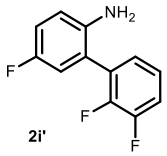
Naphthalene Carboximide and Perylene Carboximide Derivatives (1a and 1b) were prepared according to the reported procedures.[1] The structures of known compounds were confirmed by comparing their ^{1}H NMR and ^{13}C NMR data with those in the literature.

B. General Procedure for Preparation of the Cyclic Diaryliodonium Salts (2)



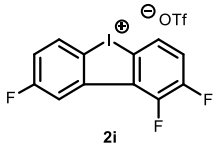
2-(Trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2a**), 2-fluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2b**), diphenyleniodonium trifluoromethanesulfonate (**2c**), 2-methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2d**), 2-methoxydibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2e**), 2,8-bis(trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2f**), 2,8-difluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2g**), 3,7-difluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2h**), were prepared according to the reported procedures.[1] The structures of known compounds were confirmed by comparing their ^{1}H NMR and ^{13}C NMR data with those in the literature. Below are summarized characterization data for newly synthesized substrates.

2',3',5-Trifluoro-[1,1'-biphenyl]-2-amine (2i'):



Prepared following the general procedure using 2-bromo-4-fluoroaniline (2.0 g, 10.58 mmol) and purified by column chromatography on silica gel using 10% EtOAc/Hexanes as eluent to obtain a light-brown oil (2.36 g, 99% yield); IR (neat): 3467, 3377, 2917, 1585, 1470, 1263 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.25–7.08 (m, 3H), 6.94 (td, *J* = 8.5, 3.0 Hz, 1H), 6.86 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.74 (dd, *J* = 8.8, 4.8 Hz, 1H), 3.55 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.1 (d, $J_{C,F}$ = 235.0 Hz), 151.2 (d, $J_{C,F}$ = 248.0 Hz), 148.0 (d, $J_{C,F}$ = 247.5 Hz), 140.4, 128.1 (d, $J_{C,F}$ = 12.5 Hz), 126.4, 124.7 (dd, $J_{C,F}$ = 7.5, 5.0 Hz), 121.2 (dd, $J_{C,F}$ = 7.5, 1.25 Hz), 117.3 (d, $J_{C,F}$ = 23.8 Hz), 117.1 (d, $J_{C,F}$ = 6.3 Hz), 117.0 (d, $J_{C,F}$ = 2.5 Hz), 116.4 (d, $J_{C,F}$ = 22.5 Hz) ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ = -126.78 (s), -136.89 (d, *J* = 22.3 Hz), -139.37 (d, *J* = 21.1 Hz) ppm; HRMS (APCI) *m/z* calcd for $C_{12}H_8F_3N+H^+$: 224.0682 [*M*+H]$^+$; found: 224.0686

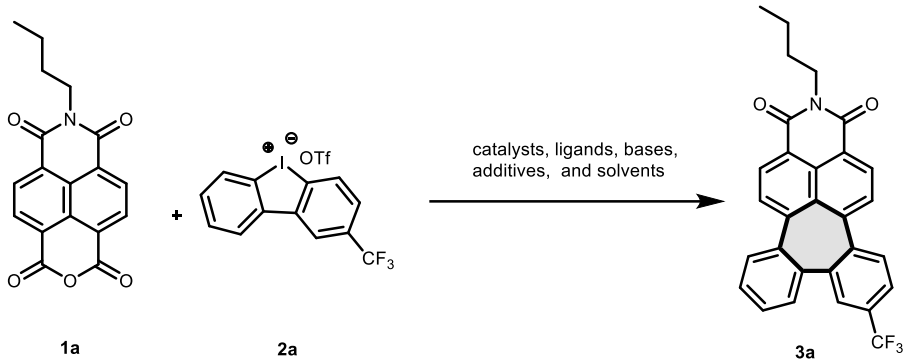
1,2,8-Trifluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2i):



Prepared following the general procedure using 2',3',5-trifluoro-[1,1'-biphenyl]-2-amine (**2i'**) (2.36 g, 10.58 mmol) and dried under vacuum to afford a white solid (3.91 g, 77% yield, 2 steps); Mp: 274.5–275.2 °C; IR (neat): 3086, 1572, 1221, 1020 cm^{-1}; ^{1}H NMR (400 MHz, DMSO) δ = 8.27–8.13 (m, 1H), 8.10–7.93 (m, 2H), 7.88–7.70 (m, 1H), 7.69–7.57 (m, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ = 162.46 (d, $J_{C,F}$ = 247.0 Hz), 151.2 (d, $J_{C,F}$ = 220.0 Hz), 149.1 (d, $J_{C,F}$ = 246.0 Hz), 140.4, 132.8 (d, $J_{C,F}$ = 9.0 Hz), 131.0 (d, $J_{C,F}$ = 9.0 Hz), 127.5 (dd, $J_{C,F}$ = 7.5, 4.8 Hz), 120.0 (d, $J_{C,F}$ = 19.0 Hz), 119.3 (d, $J_{C,F}$ = 23.0 Hz), 116.6 (dd, $J_{C,F}$ = 25.9, 16.0 Hz), 115.9, 115.7 (d, $J_{C,F}$ = 3.0 Hz) ppm; ^{19}F NMR (376 MHz, DMSO) δ = -109.23, -135.04 (d, *J* = 20.3 Hz), -136.60 (d, *J* = 20.1 Hz) ppm; HRMS (APCI) *m/z* calcd for $C_{12}H_5F_3I^+$: 332.9383 [*M*-OTf]$^+$; found: 332.9384.

III. Optimization of Reaction Conditions

Table S1 Screening for optimal reaction conditions.[a]



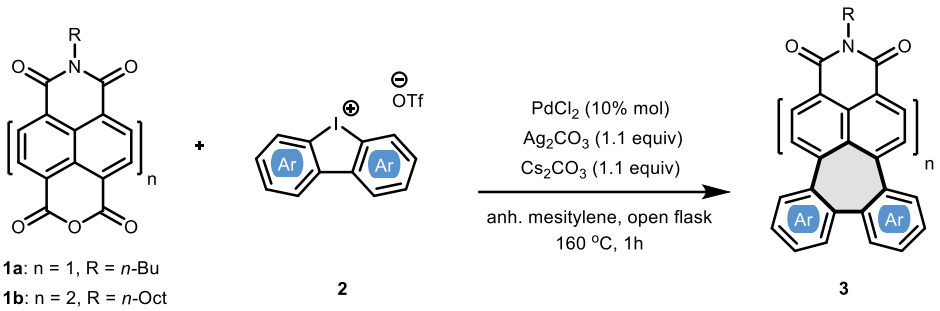
1a 2a 3a

Entry	Catalyst	Ligand	Base	Additive	Solvent	% Yield[b]
1[c]	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	-	DMSO	44%
2[c]	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	-	sulfolane	19%
3[c]	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	-	mesitylene	43%
4[c]	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	-	NMP	4%
5[c]	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	-	1,2-DCB	21%
6[c]	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	-	1-chloronaphthalene	41%
7[d]	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	-	mesitylene	27%
8	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	-	mesitylene	50%
9	$PdCl_2$	PPh_3	Cs_2CO_3	-	mesitylene	60%
10	$Pd(TFA)_2$	PPh_3	Cs_2CO_3	-	mesitylene	45%
11	$Pd(PPh_3)_4$	PPh_3	Cs_2CO_3	-	mesitylene	32%
12	$PdCl_2(PhCN)_2$	PPh_3	Cs_2CO_3	-	mesitylene	34%
13	$PdCl_2(PPh_3)_2$	PPh_3	Cs_2CO_3	-	mesitylene	44%
14	$PdCl_2$	$P(4\text{-}CF_3Ph)_3$	Cs_2CO_3	-	mesitylene	17%
15	$PdCl_2$	$P(4\text{-}OMePh)_3$	Cs_2CO_3	-	mesitylene	33%
16	$PdCl_2$	$P(4\text{-}FPh)_3$	Cs_2CO_3	-	mesitylene	45%
17	$PdCl_2$	P(*o*-furly)$_3$	Cs_2CO_3	-	mesitylene	28%
18	$PdCl_2$	-	Cs_2CO_3	-	mesitylene	61%
19	$PdCl_2$	-	K_2CO_3	-	mesitylene	23%
20	$PdCl_2$	-	K_3PO_4	-	mesitylene	23%
21	$PdCl_2$	-	CsF	-	mesitylene	20%
22	$PdCl_2$	-	KOAc	-	mesitylene	12%

23	$PdCl_2$		Cs_2CO_3	CuI (0.1 equiv)	mesitylene	52%
24	$PdCl_2$	-	Cs_2CO_3	CuBr (0.1 equiv)	mesitylene	51%
25	$PdCl_2$	-	Cs_2CO_3	$CuSO_4.H_2O$ (0.1 equiv)	mesitylene	28%
26	$PdCl_2$	-	Cs_2CO_3	$CuCl_2$ (0.1 equiv)	mesitylene	24%
27	**$PdCl_2$**	**-**	**Cs_2CO_3**	**Ag_2CO_3**	**mesitylene**	**84%**
28	$PdCl_2$	-	Cs_2CO_3	AgOAc	mesitylene	trace
29	$PdCl_2$	-	Cs_2CO_3	$AgClO_4$	mesitylene	25%
30	$PdCl_2$	-	Cs_2CO_3	AgTFA	mesitylene	38%
31	$PdCl_2$	-	Cs_2CO_3	Ag_2O	mesitylene	55%
32	$PdCl_2$	-	Cs_2CO_3	Ag_2CO_3 (2.2 equiv)	mesitylene	73%
33	$PdCl_2$	-	Cs_2CO_3	Ag_2CO_3	mesitylene[e]	52%

Conditions: (a) naphthalene monoanhydride (**1a**, 0.25 mmol, 1 equiv), cyclic diphenyliodonium salt (**2a**, 0.50 mmol, 2 equiv), catalyst (0.025 mmol, 0.1 equiv), ligand (0.050 mmol, 0.2 equiv), base (0.275 mmol, 1.1 equiv), additive (0.275 mmol, 1.1 equiv), solvent (3.2 ml), 160 ^oC, 1h., (b) Isoated yields, (c) solvent (1.6 ml), (d) solvent (0.8 ml), DMSO = dimethyl sulfoxide, NMP = *N*-methyl-2-pyrrolidone, 1,2 DCB = 1,2-dichlorobenzene, $P(4\text{-}CF_3Ph)_3$ = tris(4-trifluoromethylphenyl)phosphine, $P(4\text{-}OMePh)_3$ = tris(4-methoxyphenyl)phosphine, $P(4\text{-}FPh)_3$ = tris(4-fluorophenyl)phosphine, P(*o*-furly)$_3$ = tri(2-furyl)phosphine, (e) reagent grade without prior purification.

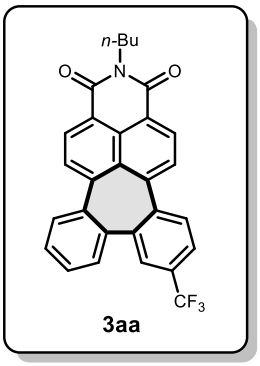
IV. Synthesis of Dibenzopleiadiene Polycyclic Aromatic Dicarboximides Derivatives



A 10 mL oven-dried Schlenk tube was charged with palladium (II) chloride (4.4 mg, 2.5 µmol, 0.1 equiv), silver carbonate (75 mg, 0.275 mmol, 1.1 equiv), cesium carbonate (89 mg, 0.275 mmol, 1.1 equiv), **1** (0.25 mmol, 1.0 equiv) and cyclic diaryliodonium triflate **2** (0.50 mmol, 2.0 equiv) in anhydrous mesitylene (3.20 mL). The reaction mixture was stirred at 160 °C for 1 h under ambient atmosphere. The reaction mixture was allowed to cool to rt, filtered, and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography to give the corresponding product **3**.

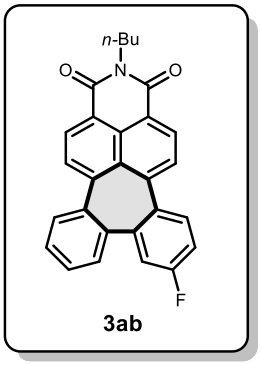
V. Characterization of the Products

2-Butyl-11-(trifluoromethyl)-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-cd]pyridine-1,3(2H)-dione (3aa):



Prepared following the general procedure using 7-butyl-1H-isochromeno[6,5,4-def]isoquinoline-1,3,6,8(7H)-tetraone (**1a**) (81 mg, 0.25 mmol), 2-(trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2a**) (248 mg, 0.50 mmol) and purified by column chromatography silica gel using 50% CH_2Cl_2/Hexanes as eluent to obtain the product as a yellow solid (98.7 mg, 84% yield); Mp: 278.5–281.4 °C (from CH_2Cl_2/Hexanes); IR (neat): 3065, 2962, 2856, 1582, 1444, 1096 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ =) 8.62 (d, *J* = 7.6 Hz, 2H), 8.00 (dd, *J* = 7.7, 2.6 Hz, 2H), 7.97 (s, 1H), 7.73 (d, *J* = 7.4 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.52 (dt, *J* = 22.9, 7.2 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 4.19 (t, *J* = 7.4 Hz, 2H), 1.76–1.69 (m, 2H), 1.51–1.41 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.07, 164.05, 143.2, 142.7, 142.0, 139.6, 139.0, 137.0, 136.3, 134.5, 134.1, 131.3, 130.95, 130.9, 129.7, 129.5, 127.8, 127.7, 127.5, 125.19, 125.16, 124.0 (q, $J_{C,F}$ = 271.0 Hz), 122.1, 121.5, 40.5, 30.3, 20.5, 14.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.65 (s) ppm; HRMS (DART) *m/z* calcd for $C_{29}H_{20}F_3NO_2$+H^+: 472.1519 [*M*+H]$^+$; found: 472.1525; UV/Vis ($CHCl_3$): λ_{max} (ε) = 404 nm (11900 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 404 nm): λ_{em} = 470 nm; Quantum yield ($CHCl_3$): 0.42.

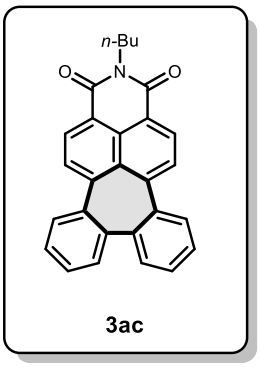
2-Butyl-11-fluoro-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-cd]pyridine-1,3(2H)-dione (3ab):



3ab

Prepared following the general procedure using 7-butyl-1H-isochromeno[6,5,4-def]isoquinoline-1,3,6,8(7H)-tetraone (**1a**) (81 mg, 0.25 mmol), 2-fluorodibenzo[b,d]iodol-5- ium trifluoromethanesulfonate (**2b**) (223 mg, 0.50 mmol) and purified by column chromatography silica gel using 50% CH_2Cl_2/Hexanes as eluent to obtain the product as a yellow solid (60.4 mg, 57% yield); Mp: 257.7–259.2 °C (from CH_2Cl_2/Hexanes); IR (neat): 3055, 2959, 2854, 1641, 1175 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.62 (dd, *J* = 8.9, 7.8 Hz,2H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.72 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.58–7.39 (m, 3H), 7.20 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.16 (dd, *J* = 6.6, 1.4 Hz, 2H), 4.20 (t, *J* = 7.6 Hz, 2H), 1.77–1.71 (m, 2H), 1.49–1.41 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 164.2 (x2), 163.2 (d, $J_{C,F}$ = 248.0 Hz), 143.4, 142.8, 140.4 (d, $J_{C,F}$ = 8.3 Hz), 139.5, 137.2, 136.22, 136.2, 135.8 (d, $J_{C,F}$ = 3.3 Hz), 134.1, 131.2, 131.1, 130.8, 129.5, 129.4, 127.7, 127.3, 127.1, 121.5, 121.3, 117.19 (d, $J_{C,F}$ = 22.3 Hz), 116.11 (d, $J_{C,F}$ = 21.3 Hz), 40.4, 30.4, 20.6, 14.0 ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ = -112.88 (s) ppm; HRMS (APCI) *m/z* calcd for $C_{28}H_{20}FNO_2$+H^+: 422.1551 [*M*+H]$^+$; found: 422.1553; UV/Vis ($CHCl_3$): λ_{max} (ε) = 409 nm (20400 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 409 nm): λ_{em} = 467 nm; Quantum yield ($CHCl_3$): 0.70.

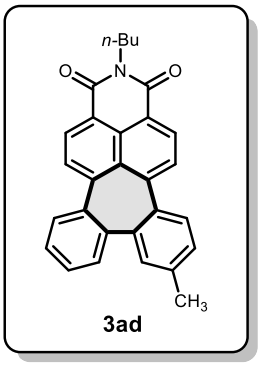
2-Butyl-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-cd]pyridine-1,3(2H)-dione (3ac) [1]:



3ac

Prepared following the general procedure using 7-butyl-1H-isochromeno[6,5,4-def]isoquinoline-1,3,6,8(7H)-tetraone (**1a**) (81 mg, 0.25 mmol), diphenyleniodonium trifluoromethanesulfonate (**2a**) (214 mg, 0.50 mmol) and purified by column chromatography silica gel using 50% CH_2Cl_2/Hexanes as eluent to obtain the product as a yellow solid (33.2 mg, 33% yield); Mp: 220.2–222.1 °C (from CH_2Cl_2/Hexanes); IR (neat): 3064, 2958, 1643, 1568, 1387, 1086 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.62 (d, *J* = 7.7 Hz, 2H), 8.01 (d, *J* = 7.7 Hz, 2H), 7.74 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.63–7.32 (m, 4H), 7.19 (dd, *J* = 7.8, 1.2 Hz, 2H), 4.20 (t, *J* = 7.5 Hz, 2H), 1.80–1.65 (m, 2H), 1.54–1.38 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H) ppm; UV/Vis ($CHCl_3$): λ_{max} (ε) = 412 nm (22700 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 412 nm): λ_{em} = 470 nm; Quantum yield ($CHCl_3$): 0.79.

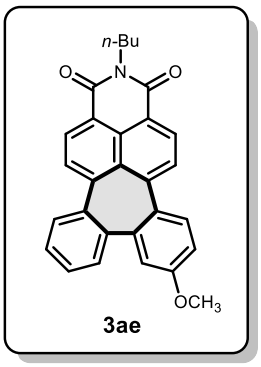
2-Butyl-11-methyl-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-cd]pyridine-1,3(2H)-dione (3ad):



3ad

Prepared following the general procedure using 7-butyl-1H-isochromeno[6,5,4-def]isoquinoline-1,3,6,8(7H)-tetraone (**1a**) (81 mg, 0.25 mmol), 2-methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2d**) (221 mg, 0.50 mmol) and purified by column chromatography silica gel using 50% CH_2Cl_2/Hexanes as eluent to obtain the product as a yellow solid (41.4 mg, 39% yield); Mp: 217.1–218.1 °C (from CH_2Cl_2/Hexanes); IR (neat): 3025, 2917, 2853, 1640, 1084 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.60 (dd, *J* = 7.7, 2.9 Hz, 2H), 7.97 (dd, *J* = 7.7, 4.2 Hz, 2H), 7.74 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.54 (s, 1H), 7.52–7.42 (m, 2H), 7.29–7.24 (m, 1H), 7.17 (d, *J* = 8.6 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 4.20 (t, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.78–1.70 (m, 2H), 1.56–1.38 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.4 (x2), 143.9, 143.8, 139.5, 139.3, 138.4, 138.0, 136.9, 136.2, 134.0, 133.9, 131.5, 131.12, 131.0, 130.8, 129.9, 129.2, 128.9, 127.7, 127.1, 126.8, 121.3, 121.0, 40.9, 30.4, 21.3, 20.6, 14.0 ppm; HRMS (APCI) *m/z* calcd for $C_{29}H_{23}NO_2$+H^+: 418.1802 [*M*+H]$^+$; found: 418.1800; UV/Vis ($CHCl_3$): λ_{max} (ε) = 416 nm (23200 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 416 nm): λ_{em} = 475 nm; Quantum yield ($CHCl_3$): 0.81.

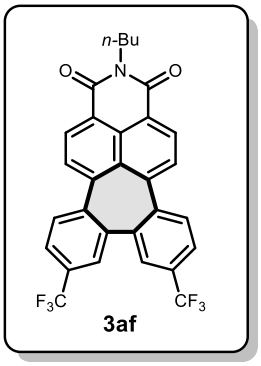
2-Butyl-11-methoxy-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-cd]pyridine-1,3(2H)-dione (3ae):



3ae

Prepared following the general procedure using 7-butyl-1H-isochromeno[6,5,4-def]isoquinoline-1,3,6,8(7H)-tetraone (**1a**) (81 mg, 0.25 mmol), 2-methoxydibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2e**) (229 mg, 0.50 mmol) and purified by column chromatography silica gel using 50% CH_2Cl_2/Hexanes as eluent to obtain the product as a yellow solid (24.7 mg, 23% yield); Mp: 174.2–176.1 °C (from CH_2Cl_2/Hexanes); IR (neat): 2956, 2830, 1642, 1087 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.61 (dd, *J* = 9.7, 7.8 Hz, 2H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.57–7.39 (m, 1H), 7.24 (d, *J* = 2.7 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.01 (dd, *J* = 8.8, 2.7 Hz, 1H), 4.20 (t, *J* = 7.3 Hz, 2H), 3.92 (s, 3H), 1.77–1.72 (m, 2H), 1.53–1.39 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 164.4, 164.4, 160.2, 143.8, 143.7, 139.6, 139.5, 138.2, 136.0, 135.7, 134.0, 132.5, 131.2, 131.0, 130.8, 129.3, 129.1, 127.8, 127.1, 126.4, 121.4, 120.6, 115.7, 114.9, 55.7, 40.4, 30.4, 20.6, 14.0 ppm ; HRMS (APCI) *m/z* calcd for $C_{29}H_{23}NO_3$+H^+: 434.1751 [*M*+H]$^+$; found: 434.1752; UV/Vis ($CHCl_3$): λ_{max} (ε) = 426 nm (15000 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 426 nm): λ_{em} = 494 nm; Quantum yield ($CHCl_3$): 0.93.

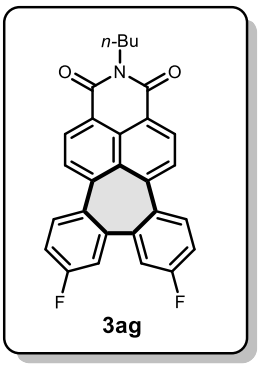
2-Butyl-8,11-bis(trifluoromethyl)-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-cd]pyridine-1,3(2H)-dione (3af) [1]:



3af

Prepared following the general procedure using 7-butyl-1H-isochromeno[6,5,4-def]isoquinoline-1,3,6,8(7H)-tetraone (**1a**) (81 mg, 0.25 mmol), 2,8-bis(trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2f**) (282 mg, 0.50 mmol) and purified by column chromatography silica gel using 10% EtOAc/Hexanes as eluent to obtain the product as a light-yellow solid (118.6 mg, 88% yield); Mp: >300 °C (from CH_2Cl_2/Hexanes); IR (neat): 3067, 2970, 2880, 1646, 1121 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.68 (d, *J* = 7.7 Hz, 2H), 8.07 (d, *J* = 7.7 Hz, 2H), 7.96 (s, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 4.20 (td, *J* = 7.1, 2.5 Hz, 2H), 1.87–1.64 (m, 2H), 1.52–1.39 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ = -62.67 (s) ppm; UV/Vis ($CHCl_3$): λ_{max} (ε) = 396 nm (21800 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 396 nm): λ_{em} = 462 nm; Quantum yield ($CHCl_3$): 0.24.

2-Butyl-8,11-difluoro-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-cd]pyridine-1,3(2H)-dione (3ag):

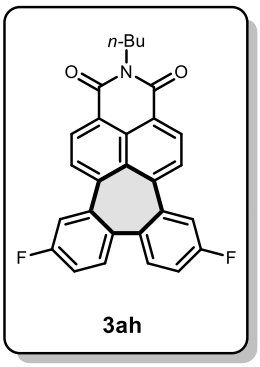


3ag

Prepared following the general procedure using 7-butyl-1H-isochromeno[6,5,4-def]isoquinoline-1,3,6,8(7H)-tetraone (**1a**) (81 mg, 0.25 mmol), 2,8-difluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2g**) (232 mg, 0.50 mmol) and purified by column chromatography silica gel using 50% CH_2Cl_2/Hexanes as eluent to obtain the product as a yellow solid (79.3 mg, 72% yield); Mp: >280°C (decomposition) (from CH_2Cl_2/Hexanes); IR (neat): 3077, 2963, 2857, 1643, 1085 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.62 (d, *J* = 7.7 Hz, 2H), 7.96 (d, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 11.4 Hz, 2H), 7.18 (dd, *J* = 6.4, 3.5 Hz, 4H), 4.19 (t, *J* = 7.2 Hz, 2H), 1.76–1.71 (m, 2H), 1.50–1.42 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 164.0, 163.0 (d, J_{CF} = 249.0 Hz), 142.3, 139.0 (d, J_{CF} = 7.5 Hz), 136.2 (d, J_{CF} = 8.8 Hz), 135.9, 135.6 (d, J_{CF} = 2.5 Hz), 131.0, 127.6, 127.1, 121.3, 117.1 (d, J_{CF} = 22.5 Hz), 116.5 (d, J_{CF} = 20.0Hz), 40.3, 30.2, 20.4, 13.9 ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ = -112.43 (s) ppm; HRMS (APCI) *m/z* calcd for $C_{28}H_{19}F_2NO_2$+H^+: 440.1457 [*M*+H]$^+$; found: 440.1458; UV/Vis ($CHCl_3$): λ_{max} (ε) = 407 nm (11900 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 407 nm): λ_{em} = 466 nm; Quantum yield ($CHCl_3$): 0.70.

.

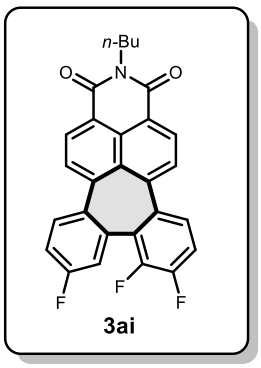
2-Butyl-7,12-difluoro-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-cd]pyridine-1,3(2H)-dione (3ah):



3ah

Prepared following the general procedure using 7-butyl-1H-isochromeno[6,5,4-def]isoquinoline-1,3,6,8(7H)-tetraone (**1a**) (81 mg, 0.25 mmol), 3,7-difluorodibenzo[b,d]iodol-5-iumtrifluoromethanesulfonate (**2h**) (232 mg, 0.50 mmol) and purified by column chromatography silica gel using 50% CH_2Cl_2/Hexanes as eluent to obtain the product as a yellow solid (79.4 mg, 72% yield); Mp: 250.7–252.3 °C (from CH_2Cl_2/Hexanes); IR (neat): 3064, 2962, 2874, 1644, 1118 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.64 (d, *J* = 7.7 Hz, 2H), 8.00 (d, *J* = 7.7 Hz, 2H), 7.65 (dd, *J* = 8.7, 5.8 Hz, 2H), 7.25–7.16 (m, 2H), 6.91 (dd, *J* = 10.2, 2.7 Hz, 2H), 4.20 (t, *J* = 7.2 Hz, 2H), 1.77–1.72 (m, 2H), 1.49–1.42 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.1, 162.6 (d, J_{CF} = 247.0 Hz), 142.2, 141.2 (d, J_{CF} = 8.0 Hz), 135.8, 133.6 (d, J_{CF} = 3.0 Hz), 132.8 (d, J_{CF} = 8.0 Hz), 131.2, 127.8, 127.5, 122.0, 120.0 (d, J_{CF} = 22.0 Hz), 116.4 (d, J_{CF1} = 21.0 Hz), 40.5, 30.4, 20.6, 14.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -113.48 (s) ppm; HRMS (APCI) *m/z* calcd for $C_{28}H_{19}F_2NO_2$+H^+: 440.1457 [*M*+H]$^+$; found: 440.1450; UV/Vis ($CHCl_3$): λ_{max} (ε) = 408 nm (14200 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 408 nm): λ_{em} = 468 nm; Quantum yield ($CHCl_3$): 0.63.

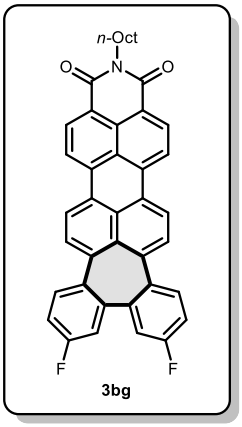
2-Butyl-8,10,11-trifluoro-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-cd]pyridine-1,3(2H)-dione (3ai):



3ai

Prepared following the general procedure using 7-butyl-1H-isochromeno[6,5,4-def]isoquinoline-1,3,6,8(7H)-tetraone (**1a**) (81 mg, 0.25 mmol), 1,2,8-trifluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2g**) (241 mg, 0.50 mmol) and purified by column chromatography silica gel using 50% CH_2Cl_2/Hexanes as eluent to obtain the product as a yellow solid (84.3 mg, 74% yield); Mp: 279.2–280.3 °C (from CH_2Cl_2/Hexanes); IR (neat): 2964, 2856, 1642, 1153 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.62 (t, *J* = 8.0 Hz, 2H), 7.98 (dd, *J* = 7.7, 4.6 Hz, 2H), 7.51 (ddd, *J* = 9.6, 5.7, 2.6 Hz, 1H), 7.30–7.24 (m, 2H), 7.22–7.10 (m, 2H), 6.91 (ddd, *J* = 8.9, 5.0, 1.7 Hz, 1H), 4.19 (t, *J* = 7.6 Hz, 2H), 1.76–1.72 (m, 2H), 1.50–1.43 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ =164.03, 164.0, 162.0 (d, J_{CF} = 236.3 Hz), 151.2 (d, J_{CF} = 251.5 Hz), 147.7 (d, J_{CF} = 249.2 Hz), 142.2, 141.6, 137.1 (d, J_{CF} = 2.5 Hz), 136.5 (d, J_{CF} = 3.0 Hz), 136.4 (d, J_{CF} = 8.4 Hz), 136.0, 131.7 (d, J_{CF} = 10.0 Hz), 131.3, 131.1, 129.9 (dd, J_{CF} = 6.5, 4.1 Hz), 127.7, 127.24, 127.22, 127.0 (d, J_{CF} = 9.0 Hz), 121.9, 121.5, 118.9 (dd, J_{CF} = 23.2, 8.9 Hz), 117.7 (d, J_{CF} = 16.1 Hz), 117.2 (d, J_{CF} = 21.3 Hz), 40.5, 30.3, 20.5, 14.0 ppm; ^{19}F NMR (417 MHz, $CDCl_3$) δ = -113.26 (s), -135.12 (d, *J* = 20.8 Hz), -138.41 (d, *J* = 20.8 Hz) ppm; HRMS (APCI) *m/z* calcd for $C_{28}H_{18}F_3NO_2$+H^+: 458.1362 [*M*+H]$^+$; found: 458.1361; UV/Vis ($CHCl_3$): λ_{max} (ε) = 401 nm (24800 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 401 nm): λ_{em} = 472 nm; Quantum yield ($CHCl_3$): 0.50.

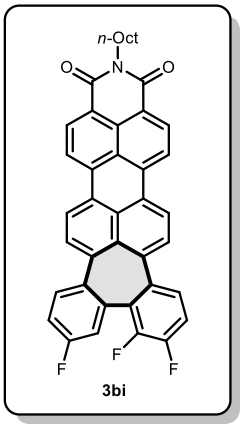
10,13-Difluoro-2-octanoyl-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':9,10]peryleno[3,4-cd]pyridine-1,3(2H)-dione (3bg):



3bg

Prepared following the general procedure using 9-octyl-1H-isochromeno[6',5',4':10,5,6]anthra[2,1,9-def]isoquinoline-1,3,8,10(9H)-tetraone (**1b**) (125.9 mg, 0.25 mmol), 2,8-difluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2g**) (232 mg, 0.50 mmol) and purified by column chromatography silica gel using 50% CH_2Cl_2/Hexanes as eluent to obtain the product as a purple solid (91.2 mg, 59% yield); Mp: >300 °C (from $CHCl_3$/Acetone); IR (neat): 3080, 2921, 2852, 1649, 1133 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.60 (d, *J* = 8.1 Hz, 2H), 8.48 (d, *J* = 8.1 Hz, 2H), 8.43 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 9.7 Hz, 2H), 7.16 (d, *J* = 6.6 Hz, 4H), 4.18 (t, *J* = 7.6 Hz, 2H), 1.85–1.67 (m, 2H), 1.48–1.21 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ = 163.7, 162.5 (d, J_{CF} = 246.0 Hz), 139.1, 139.05 (d, J_{CF} = 8.8 Hz), 138.6, 136.6, 136.5, 135.6 (d, J_{CF} = 7.5 Hz), 131.4, 129.4, 128.1, 127.9, 127.2, 125.8, 123.9, 120.6, 120.3, 116.3 (d, J_{CF} = 22.5 Hz), 116.1 (d, J_{CF} = 21.3 Hz), 40.4, 31.7, 29.3, 29.2, 28.0, 27.2, 22.6, 14.1 ppm ; ^{19}F NMR (471 MHz, $CDCl_3$) δ = -111.71 (s) ppm; HRMS (APCI) *m/z* calcd for $C_{42}H_{31}F_2NO_2+H^+$: 620.2396 $[M+H]^+$; found: 620.2394; UV/Vis ($CHCl_3$): λ_{max} (ε) = 540 nm (35500 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 532 nm): λ_{em} = 611 nm; Quantum yield ($CHCl_3$): 0.59.

10,12,13-Trifluoro-2-octanoyl-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':9,10]peryleno[3,4-cd]pyridine-1,3(2H)-dione (3bi):



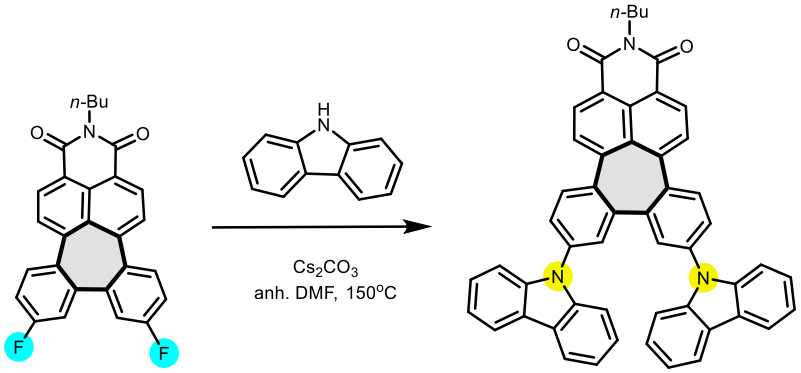
3bi

Prepared following the general procedure 9-octyl-1H-isochromeno[6',5',4':10,5,6]anthra[2,1,9-def]isoquinoline-1,3,8,10(9H)-tetraone (**1b**) (125.9 mg, 0.25 mmol), 1,2,8-trifluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (241mg, 0.50 mmol) and purified by column chromatography silica gel using 50% CH_2Cl_2/Hexanes as eluent to obtain the product as a purple solid (98.4 mg, 62% yield); Mp: >300 °C (from $CHCl_3$/Acetone); IR (neat): 2924, 2852, 1650, 1130 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.54 (dd, *J* = 8.0, 1.0 Hz, 2H), 8.41 (dd, *J* = 11.3, 8.1 Hz, 2H), 8.36 (dd, *J* = 8.1, 3.1 Hz, 2H), 7.91–7.76 (m, 2H), 7.50 (ddd, *J* = 8.2, 5.6, 2.5 Hz, 1H), 7.25–7.07 (m, 3H), 6.90 (dd, *J* = 9.2, 4.3 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 2H), 1.76–1.72 (m, 2H), 1.45–1.25 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (151 MHz, CD_2Cl_2) δ = 163.6 (x2), 161.8 (d, J_{CF} = 248.2 Hz), 150.7 (d, J_{CF} = 250.5 Hz), 147.4 (d, J_{CF} = 249.3 Hz), 139.5, 138.6 (d, J_{CF} = 3.0 Hz), 138.5, 138.3, 137.9 (d, J_{CF} = 3.0 Hz), 136.4, 136.3, 135.8 (d, J_{CF} = 7.6 Hz), 132.1 (d, J_{CF} = 6.0 Hz), 131.2, 131.17, 129.6, 129.3 (dd, J_{CF} = 6.0, 4.5 Hz), 128.7, 128.3, 128.2, 128.1, 127.4, 127.1 (d, J_{CF} = 9.0 Hz), 126.1, 124.0, 123.8, 121.4, 121.3, 120.6, 120.58, 118.0 (dd, J_{CF} = 22.7, 9.0 Hz), 117.2 (d, J_{CF} = 16.6 Hz),116.6 (d, J_{CF} = 21.1 Hz), 40.3, 31.9, 29.4, 29.3, 28.1, 27.2, 22.7, 13.9 ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ = -114.36 (s), -136.42 (d, *J* = 20.8 Hz), -139.45 (d, *J* = 20.7 Hz) ppm; HRMS (APCI) *m/z* calcd for $C_{42}H_{30}F_3NO_2+H^+$: 638.2301 $[M+H]^+$; found: 638.2305; UV/Vis ($CHCl_3$): λ_{max} (ε) = 550 nm (41800 $mol^{-1}dm^3cm^{-1}$; Fluorescence ($CHCl_3$, λ_{ex} = 550 nm): λ_{em} = 599 nm; Quantum yield ($CHCl_3$): 0.60.

VI. Synthesis of push-pull heptagon-embedded PADIs

The nucleophilic substitution to synthesize push-pull heptagon-embedded PADIs was adapted from the previous literature. [2]

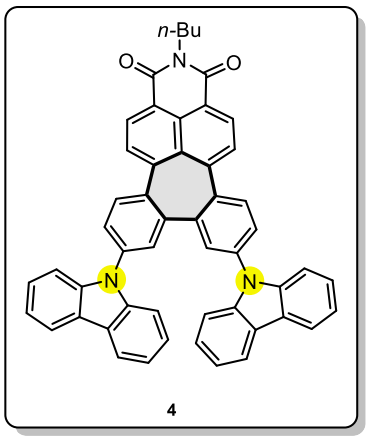
Synthesis of Compound 4



3ag **4**

To a Schlenk flask under argon was added **3ag** (43.9 mg, 0.1 mmol), carbazole (50.1 mg, 0.3 mmol), cesium carbonate (162.5 mg, 0.5 mmol), and anhydrous DMF (1.0 mL). The reaction mixture was then heated to 150 °C and stirred for overnight. The residue was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O and brine, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The crude product was purified by column chromatography on a silica gel with 50% CH_2Cl_2/Hexanes as eluent to give compound **4.**

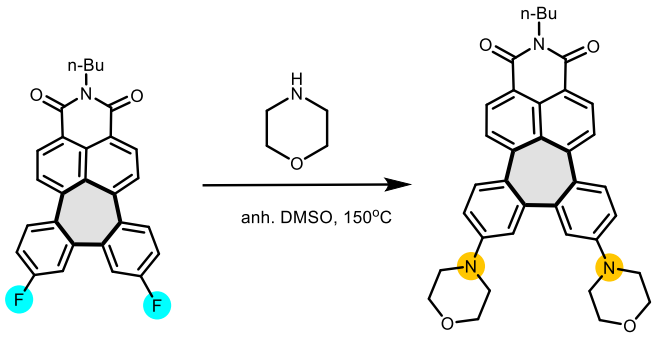
2-Butyl-8,11-di(9H-carbazol-9-yl)-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-cd]pyridine-1,3(2H)-dione (4):



4

Light-yellow solid (32.4 mg, 44% yield); Mp: >300 °C (from CH_2Cl_2/MeOH); IR (neat): 3048, 2958, 2856, 1652, 1476, 1220 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.73 (d, *J* = 7.7 Hz, 2H), 8.18 (d, *J* = 7.7 Hz, 2H), 8.12 (d, *J* = 7.6 Hz, 4H), 8.00 (d, *J* = 1.9 Hz, 2H), 7.74 (dd, *J* = 8.4, 1.9 Hz, 2H), 7.49 (dd, *J* = 10.9, 8.5 Hz, 6H), 7.34 (t, *J* = 7.6 Hz, 4H), 7.31–7.16 (m, 4H), 4.25 (t, *J* = 7.8 Hz, 2H), 1.82–1.77 (m, 2H), 1.53–1.47 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 164.2, 142.7, 140.4 (x2), 139.1, 139.05, 138.3, 136.2, 136.0, 131.3, 128.3, 128.0, 127.6, 127.4, 126.4 (x2), 123.9 (x2), 121.8, 120.7 (x2). 120.6 (x2), 109.8 (x2), 40.5, 30.4, 20.6, 14.0 ppm; HRMS (APCI) *m/z* calcd for $C_{52}H_{35}N_3O_2+H^+$: 734.2804 $[M+H]^+$; found: 734.2802; UV/Vis ($CHCl_3$): λ_{max} (ε) = 434 nm (25600 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 434 nm): λ_{em} = 536 nm; Quantum yield ($CHCl_3$): 0.77.

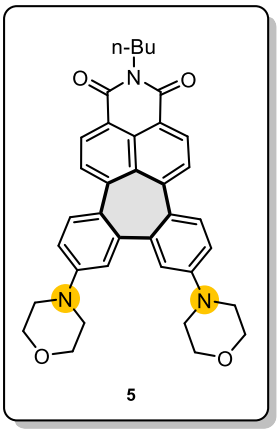
Synthesis of Compound 5



3ag **5**

To a Schlenk flask under argon was added **3ag** (43.9 mg, 0.1 mmol), morpholine (0.1 ml, 1.2 mmol) and anhydrous DMSO (0.5 mL). The reaction mixture was then heated to 150 °C and stirred for overnight. The residue was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O and brine, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The crude product was purified by column chromatography on a silica gel with CH_2Cl_2 as eluent to give compound **5.**

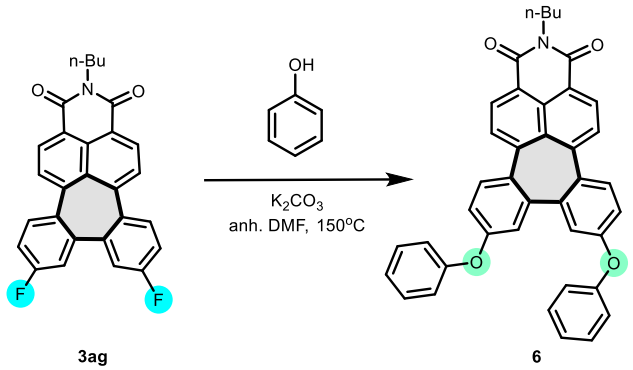
2-Butyl-8,11-dimorpholino-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-cd]pyridine-1,3(2H)-dione (5):



5

Orange solid (25.3 mg, 44% yield); Mp: > 250°C (decomposition) (from CH_2Cl_2/MeOH); IR (neat): 3036, 2923, 2852, 1648, 1546, 1448, 1230 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.56 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 2.6 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.99 (dd, *J* = 8.8, 2.6, 2H), 4.19 (t, *J* = 7.2 Hz, 2H), 3.94–3.86 (m, 8H), 3.34–3.25 (m, 8H), 1.75–1.71 (m, 2H), 1.49–1.45 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.5, 151.9, 144.0, 139.6, 135.4, 135.3, 131.2, 131.1, 128.0, 125.9, 120.4, 116.2, 115.9, 66.9, 48.6, 40.3, 30.4, 20.6, 14.0 ppm; HRMS (APCI) *m/z* calcd for $C_{36}H_{35}N_3O_4+H^+$: 574.2700 $[M+H]^+$; found: 574.2704; UV/Vis ($CHCl_3$): λ_{max} (ε) = 459 nm (27000 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 459 nm): λ_{em} = 578 nm; Quantum yield ($CHCl_3$): 0.75.

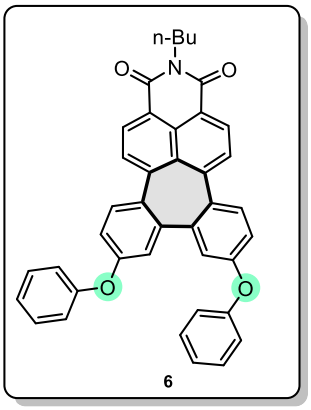
Synthesis of Compound 6



3ag **6**

To a Schlenk flask under argon was added **3ag** (43.9 mg, 0.1 mmol), phenol (39.5 mg, 0.4 mmol), potassium carbonate (55.3 mg, 0.4 mmol), and anhydrous DMF (1.5 mL). The reaction mixture was then heated to 150 °C and stirred for overnight. The residue was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O and brine, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The crude product was purified by column chromatography on a silica gel with 50% CH_2Cl_2/Hexanes as eluent to give compound **6.**

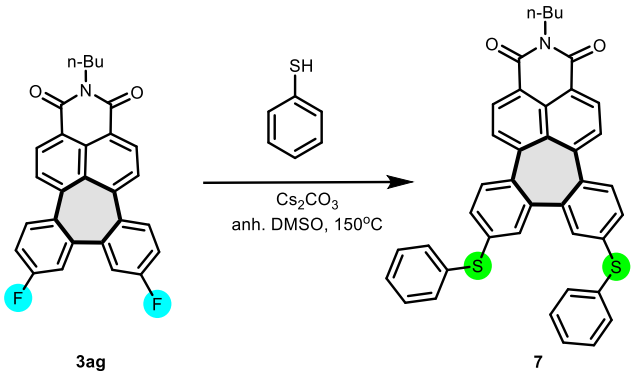
2-Butyl-8,11-diphenoxy-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-cd]pyridine-1,3(2H)-dione (6):



6

Light-yellow solid (34.9 mg, 59% yield); Mp: 224.8–225.9 °C (from CH_2Cl_2/MeOH); IR (neat): 3041, 2929, 2872, 1646, 1487, 1221 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.61 (d, *J* = 7.7 Hz, 2H), 7.95 (d, *J* = 7.7 Hz, 2H), 7.43–7.31 (m, 4H), 7.25 (s, 2H), 7.16 (dd, *J* = 17.5, 8.1 Hz, 4H), 7.10–7.02 (m, 6H), 4.20 (t, *J* = 7.5 Hz, 2H), 1.78–1.72 (m, 2H), 1.51–1.42 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 164.3, 158.4, 156.2, 143.2, 139.3, 135.9, 135.8, 134.3, 131.1, 130.2 (x2), 127.8, 126.8, 124.3, 121.0, 119.7 (x2), 119.6, 119.0, 40.4, 30.8, 20.6, 14.0 ppm; HRMS (APCI) *m/z* calcd for $C_{40}H_{29}NO_4$+H^+: 588.2169 $[M+H]^+$; found: 588.2170; UV/Vis ($CHCl_3$): λ_{max} (ε) = 426 nm (24400 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 426 nm): λ_{em} = 490 nm; Quantum yield ($CHCl_3$): 0.93.

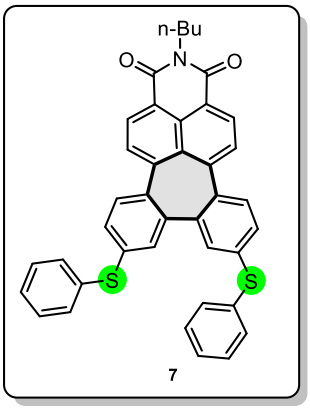
Synthesis of Compound 7



3ag **7**

To a Schlenk flask under argon was added **3ag** (43.9 mg, 0.1 mmol), thiophenol (0.1 ml, 1.05 mmol), cesium carbonate (130.0 mg, 0.4 mmol), and anhydrous DMSO (1.5 mL). The reaction mixture was then heated to 150 °C and stirred for overnight. The residue was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O and brine, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The crude product was purified by column chromatography on a silica gel with 50% CH_2Cl_2/Hexanes as eluent to give compound **7**.

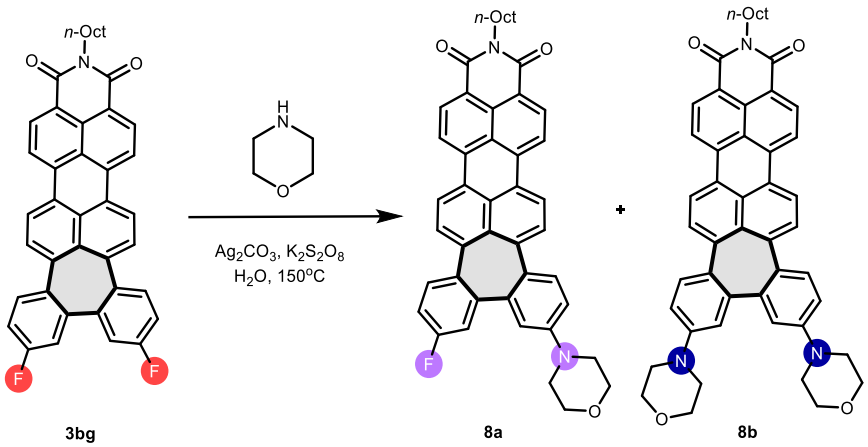
2-Butyl-8,11-bis(phenylthio)-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-cd]pyridine-1,3(2H)-dione (7):



7

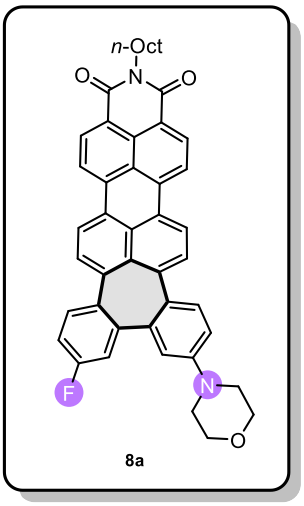
Yellow solid (33.0 mg, 53% yield); Mp: > 146 °C (decomposition) °C (from CH_2Cl_2/MeOH); IR (neat): 2959, 2854, 1650, 1566, 1345, 1068 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.59 (d, *J* = 7.8 Hz, 2H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 1.9 Hz, 2H), 7.45 (dd, *J* = 8.0, 1.5 Hz, 4H), 7.41–7.29 (m, 6H), 7.27–7.22 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.18 (t, *J* = 7.2 Hz, 2H), 1.75–1.71 (m, 2H), 1.49–1.42 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 164.2, 143.0, 139.1, 138.2, 137.7, 135.9, 134.7, 133.7, 132.8 (x2), 131.1, 129.8, 129.7 (x2), 128.3 (x2), 127.8, 127.0, 121.4, 40.4, 30.5, 20.5, 14.0 ppm; HRMS (APCI) *m/z* calcd for $C_{40}H_{29}NO_2S_2+H^+$: 620.1712 $[M+H]^+$; found: 620.1715; UV/Vis ($CHCl_3$): λ_{max} (ε) = 433 nm (18500 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 432 nm): λ_{em} = 505 nm; Quantum yield ($CHCl_3$): 0.73.

Synthesis of Compound 8a and 8b



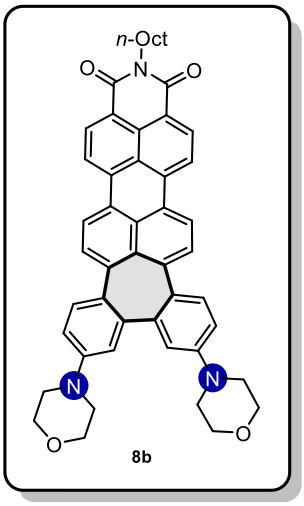
To a Schlenk flask under argon was added **3bg** (67.3 mg, 0.1 mmol), morpholine (2.0 mL, 23 mmol), silver carbonate (44 mg, 0.16 mmol), potassium persulfate (518 mg, 1.9 mmol), and water (28.8 µL, 0.16 mmol). The reaction mixture was then heated to 150 °C and stirred for 60 h. The residue was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O and brine, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The crude product was purified by column chromatography on a silica gel with CH_2Cl_2 to 1% CH_2Cl_2/MeOH as eluent to give compound **8a** and **8b.**

13-Fluoro-10-morpholino-2-octyl-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':9,10]peryleno[3,4-cd]pyridine-1,3(2H)-dione (8a):



Dark purple solid (28.5 mg, 42% yield); Mp: : > 300 °C (from CH_2Cl_2/MeOH); IR (neat): 3077, 2923, 2850, 1650, 1561, 1162 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.53 (dd, *J* = 8.1, 1.9 Hz, 2H), 8.39 (dd, *J* = 8.1, 3.0 Hz, 2H), 8.33 (dd, *J* = 8.2, 2.3 Hz, 2H), 7.79 (dd, *J* = 11.4, 8.0 Hz, 2H), 7.42 (dd, *J* = 9.9, 2.3 Hz, 1H), 7.18–7.07 (m, 4H), 7.00 (dd, *J* = 8.8, 2.7 Hz, 1H), 4.16 (t, *J* = 7.6 Hz, 2H), 3.93–3.90 (m, 4H), 3.35–3.26 (m, 4H), 1.78–1.72 (m, 2H), 1.43–1.25 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H) ppm;^{13}C NMR (125 MHz, $CDCl_3$) δ = 164.1 (x2), 162.8 (d, J_{CF} = 247.5 Hz), 151.3, 141.1 (d, J_{CF} = 7.5 Hz), 140.1, 139.3 , 139.28, 138.3, 137.2, 137.6, 137.0 (d, J_{CF} = 2.5 Hz), 135.7 (d, J_{CF} = 7.5 Hz), 134.8, 132.3, 131.6 , 131.57, 129.9, 128.1, 128.07, 127.5, 127.4, 127.3, 126.2, 124.3, 123.9, 120.9, 120.6, 120.2, 120.1, 116.4 (d, J_{CF} = 22.5 Hz), 116.2, 116.0, 115.7 (d, J_{CF} = 21.3 Hz), 66.9, 48.7, 40.6, 32.0, 29.5, 29.4, 28.3, 27.4, 22.8, 14.3 ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ = -114.09 (s) ppm; HRMS (DART) *m/z* calcd for $C_{46}H_{39}FN_2O_3+H^+$: 687.3017 $[M+H]^+$; found: 687.3013; UV/Vis ($CHCl_3$): λ_{max} (ε) = 564 nm (30600 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 570 nm): λ_{em} = 678 nm; Quantum yield ($CHCl_3$): 0.19.

10,13-Dimorpholino-2-octyl-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':9,10]peryleno[3,4-cd]pyridine-1,3(2H)-dione (8b):



8b

Dark purple solid (28.4 mg, 38% yield); Mp: > 300 °C (from CH_2Cl_2/MeOH); IR (neat): 2920, 2848, 1648, 1557, 1349, 1120 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.48 (d, *J* = 8.1 Hz, 2H), 8.33 (d, *J* = 8.1 Hz, 2H), 8.26 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 2.7 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.98 (dd, *J* = 8.8, 2.6 Hz, 2H), 4.16 (t, *J* = 7.5 Hz, 2H), 3.93–3.90 (m, 8H), 3.34–3.25 (m, 8H), 1.76–1.72 (m, 2H), 1.43–1.25 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 164.1, 151.2, 140.4, 139.8, 139.0, 137.3, 134.8, 132.3, 131.5, 129.8, 127.4, 127.2, 127.1, 126.0, 124.1, 120.3, 119.7, 116.0, 115.8, 66.9, 48.9, 40.6, 32.0, 29.5, 29.4, 28.3, 27.4, 22.8, 14.3 ppm; HRMS (DART) *m/z* calcd for $C_{50}H_{47}N_3O_4+H^+$: 734.3639 $[M+H]^+$; found: 734.3645; UV/Vis ($CHCl_3$): λ_{max} (ε) = 581 nm (32400 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 586 nm): λ_{em} = 695 nm; Quantum yield ($CHCl_3$): 0.17.

VII. X-ray Single Crystal Analysis

Experimental details

The X-ray crystallographic data of **4** was collected on a Bruker CCD diffractometer controlled by *APEX3* software, and the cell refinement and data reduction were carried out by *SAINT*.[3] Absorption correction was done by a multi-scan method using *SADABS*.[4] The structure solution was done by an intrinsic phasing method in *SHELXT* software.[5] The structure was then refined on F^2 by a full-matrix least-squares method using *the SHELXL* program package.[6] All non-hydrogen atoms were treated anisotropically, while the H atoms were refined by a riding model. Olex2[7] and Mercury[8] software packages were used to prepare molecular graphics and materials for publication.

CCDC 2178872 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table S2 Crystal data, data collection, and refinement details for **4**.

Compound	**4**
Empirical formula	$C_{52}H_{35}N_3O_2$
Formula weight	733.83
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a/Å	9.0827(12)
b/Å	14.2076(18)
c/Å	15.2875(19)
α/°	101.390(4)
β/°	104.212(4)
γ/°	96.122(5)
Volume/Å^3	1849.6(4)
Z	2
ρ_{calc}g/cm^3	1.318
μ/mm^{-1}	0.630
F(000)	768.0
Crystal size/mm^3	0.05 × 0.05 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.432 to 144.544
Index ranges	-11 ≤ h ≤ 11, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18
Reflections collected	63100
Independent reflections	7167 [R_{int} = 0.0227, R_{sigma} = 0.0125]
Data/restraints/parameters	7167/0/515
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0426, wR_2 = 0.1234
Final R indexes [all data]	R_1 = 0.0467, wR_2 = 0.1274
Largest diff. peak/hole / e Å^{-3}	0.36/-0.22

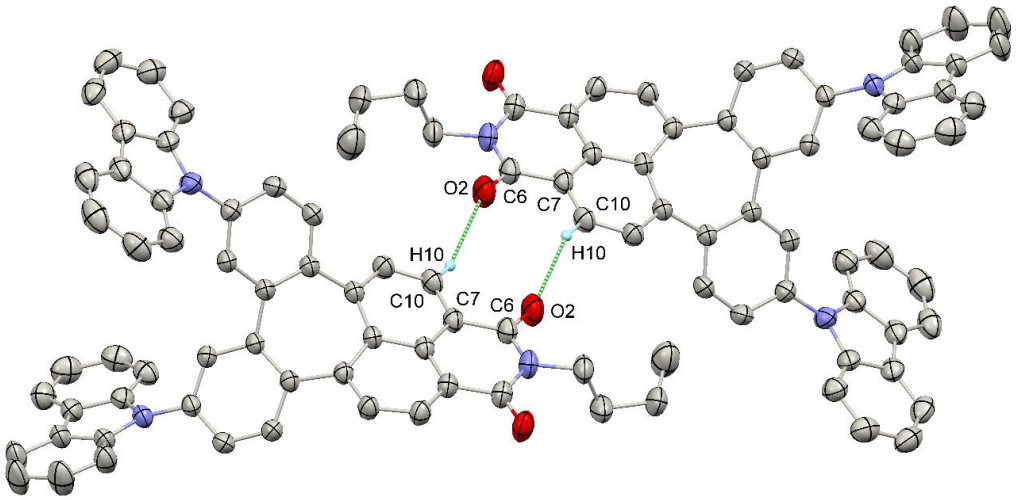


Figure S1 A view of molecular packing of **4** showing an $R_2^2(10)$ motif constructed from two C10—H10···O2 interactions (light green dash lines) in the extended structure.

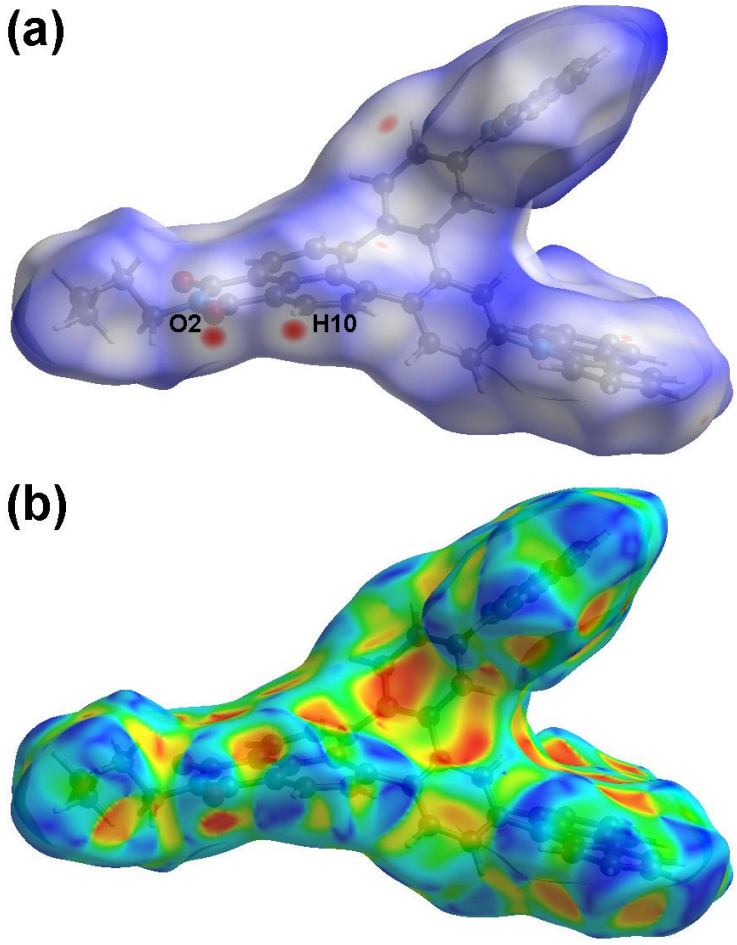


Figure S2 (a) A view of the three-dimensional Hirshfeld surface of **4** plotted over d_{norm} in the range −0.13 to 1.78 a.u. (b) A view of the shape-index Hirshfeld surface plotted over d_{norm} in the range -1.00 to 1.00 a.u.). The presence of red spots near the oxygen (O2) and hydrogen (H1) supports the occurrence of the $R_2^2(10)$ C–H···O interactions and the shape index property of the Hirshfeld surface suggests the absence of the π-π interactions. Both the surfaces are computed by *Crystal Explorer 17.5* software (Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *Crystal Explorer 17.5*. The University of Western Australia.).

VIII. Photophysical Properties

Table S3 The photophysical properties of all compounds in $CHCl_3$.

Compound	λ_{ab}[a] [nm]	λ_{em}[b] [nm]	Stokes shifts [cm^{-1}]	ε [M^{-1} cm^{-1}]	Fluorescent quantum yield[c] [Φ_F]
3aa	404	470	3480	11900	0.42
3ab	409	467	3040	20400	0.70
3ac	412	470	3000	22700	0.79
3ad	416	475	2990	23200	0.81
3ae	426	494	3230	15000	0.93
3af	396	462	3610	21800	0.24
3ag	407	466	3100	11900	0.70
3ah	408	468	3100	14200	0.63
3ai	401	472	3750	24800	0.50
3bg	540	611	2150	35500	0.59
3bi	550	599	1490	41800	0.60[d]
4	434	536	4390	25600	0.77
5	459	578	4490	27000	0.75
6	426	490	3070	24400	0.93
7	433	505	3290	18500	0.73
8a	564	678	2981	30600	0.19
8b	581	695	2820	32400	0.17

[a] Absorption maxima in $CHCl_3$ (10^{-5} mol/L). [b] Emission maxima in $CHCl_3$ (10^{-6} mol/L). [c] Absolute quantum yield in $CHCl_3$ (10^{-6} mol/L) was determined by an integrating sphere system. [d] λ_{ex} = 500 nm.

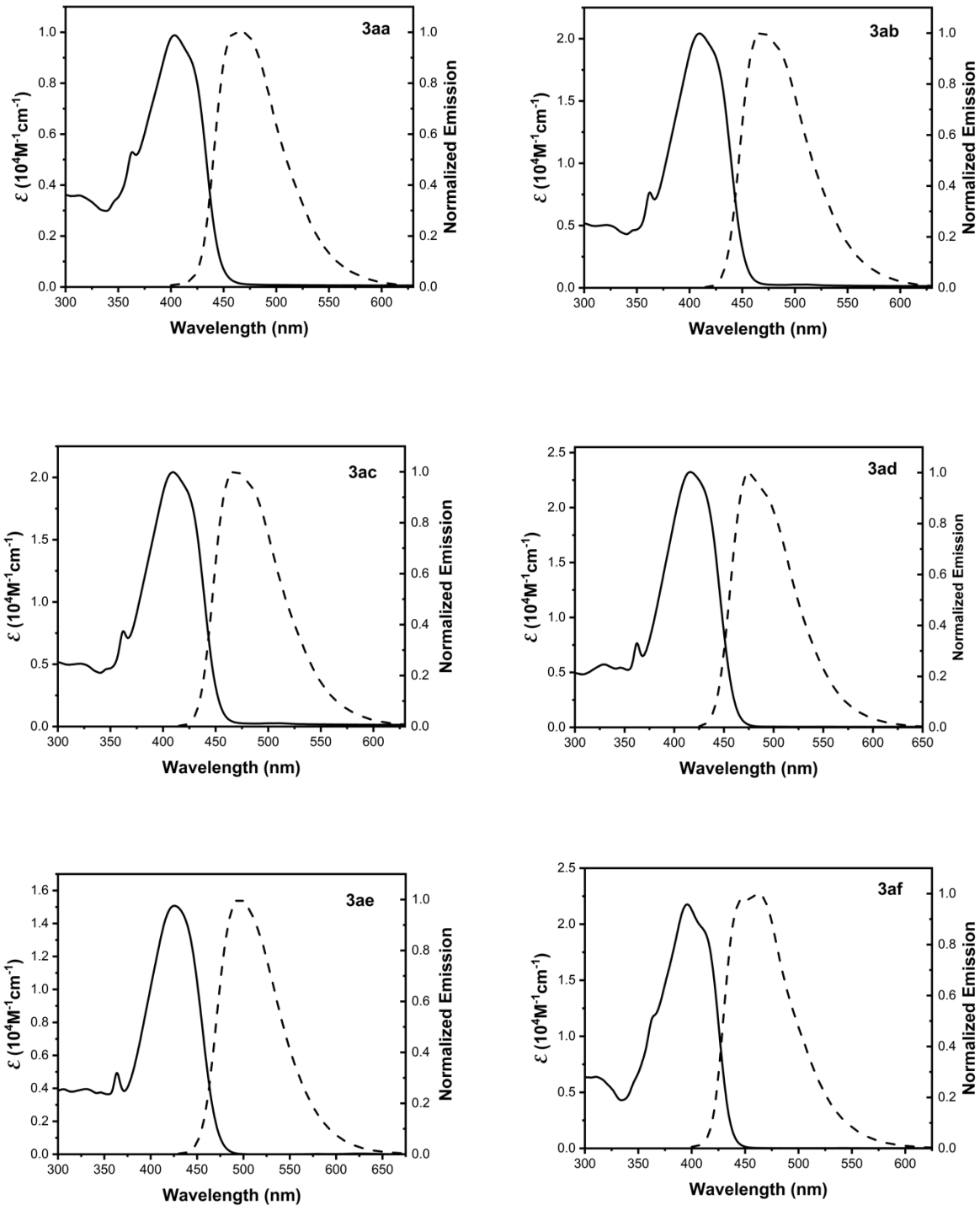


Figure S3.1 UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) of all compounds in $CHCl_3$.

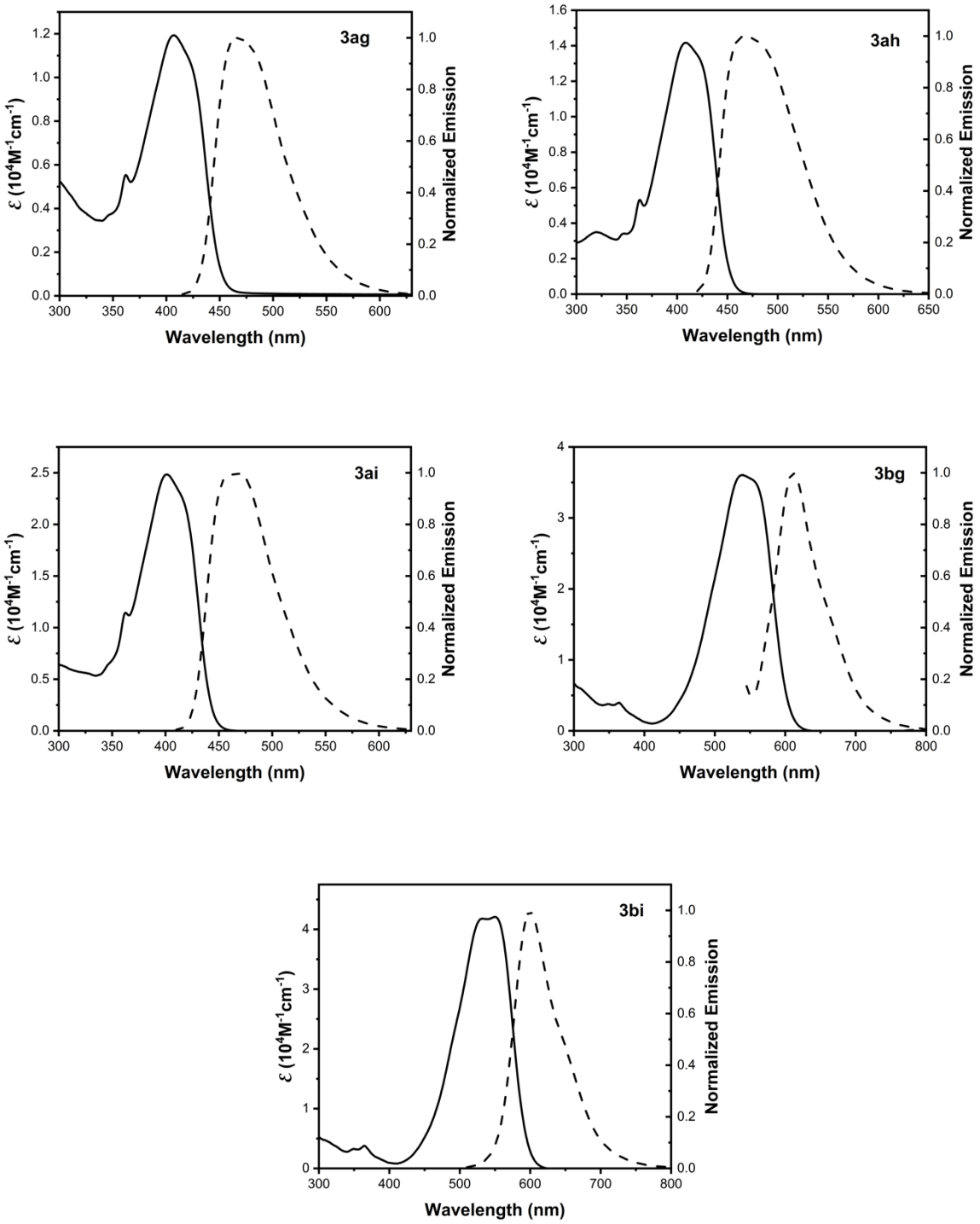


Figure S3.2 UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) of all compounds in $CHCl_3$. (con.)

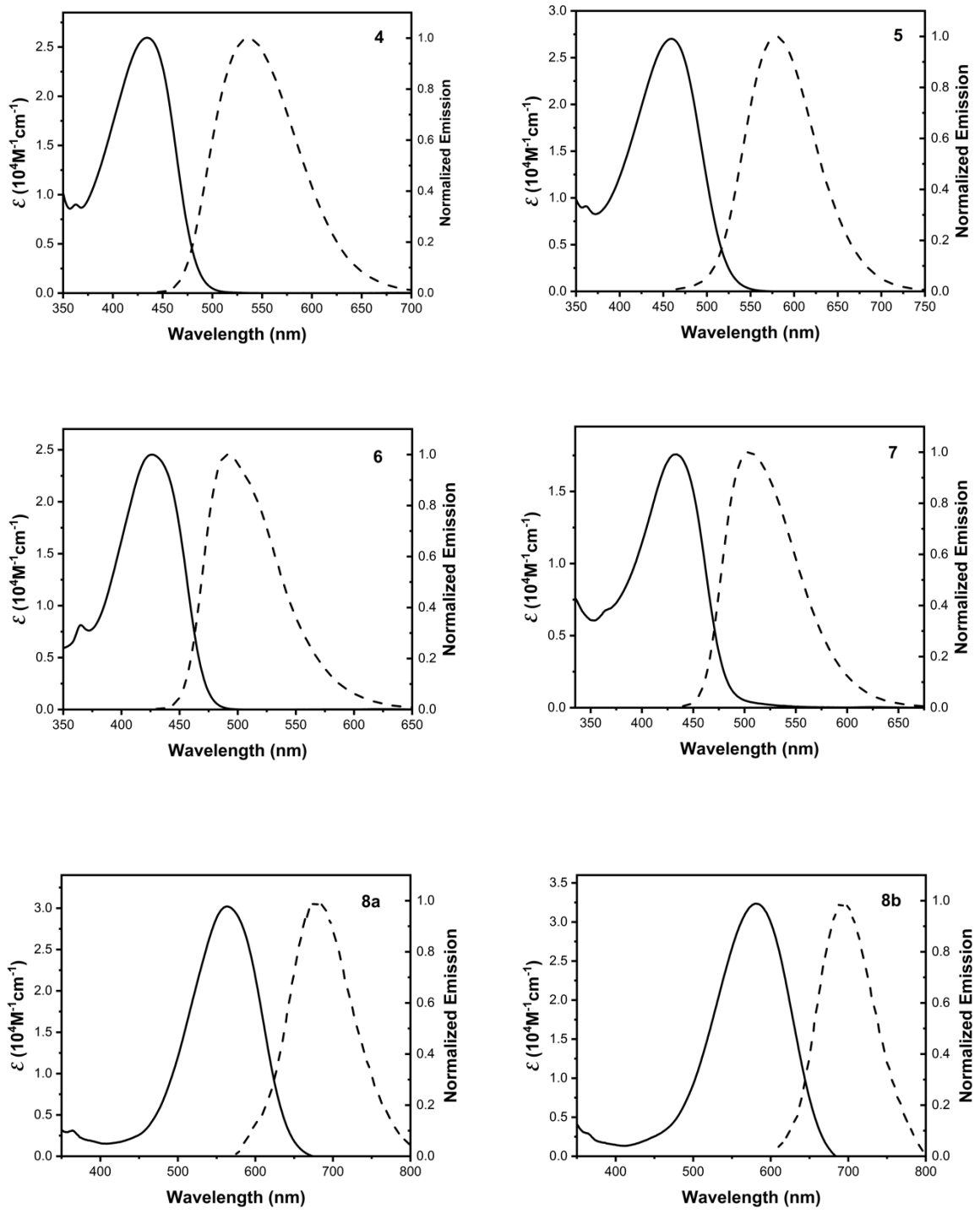


Figure S3.3 UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) of all compounds in $CHCl_3$. (con.)

IX. DFT Calculations

Computation details

Density functional theory and time-dependent density functional theory (TD-DFT) calculations were performed to determine electronic structures and electronic transition energies of **3ag, 3bg, 4, 5, 6, 7, 8a**, and **8b** model compounds, in which the butyl- and octyl-group were truncated to methyl-group. All calculations were performed with Gaussian 09 package.[9] Ground-state geometry optimizations were calculated in gas phase with B3LYP functional [10-12] and 6-31G(d) [13,14,15] basis set. The frequency calculation for each optimized geometry was carried out to ensure that each stationary point corresponds to the true minimum. The TD-DFT was performed in chloroform solvent for five singlet excited states using CAM-B3LYP functional[16] and 6-31++G(d,p) basis set.[13,14,15] Conductor like polarizable continuum model (CPCM)[17,18] was used with chloroform parameters. Molecular orbitals were plotted using GaussView 5.0. [19]

We performed time-dependent density functional theory (TD-DFT) to calculate the electronic structures and electronic transition energies of compounds **3ag, 3bg, 4, 5, 6, 7, 8a**, and **8b** (Table S4). While the calculated absorption energies are shifted from the experimental absorption energies by 30 – 50 nm as also found in other works,[20,21,22,1] the overall trend of the calculated absorption wavelengths is in the order of **3ag** < **6** < **7** ~ **4** < **5** < **3bg** < **8a** < **8b** (Table S3), in good agreement with the experiment.

Table S4 Calculated electronic transition energies (in eV and nm) and oscillator strength (f) of **3ag, 3bg, 4, 5, 6, 7, 8a and 8b** using CAM-B3LYP/6-31++G(d,p).

	Calculation				Experiment	
	Band assignment	**Energy (eV)**	λ_{ab} **(nm)**	f	λ_{ab} **(nm)**	ε
3ag	H-0 → L+0 (96.9%)	3.27	378.8	0.614	407	11900
6	H-0 → L+0 (94.3%)	3.16	391.8	0.774	426	24400
7	H-0 → L+0 (90.2%)	3.14	394.6	0.808	433	18500
4	H-4→ L+0 (37.3%) H-0 → L+0 (59.0%)	3.16	392.1	0.848	434	25600
5	H-0 → L+0 (90.8%)	3.03	409.1	0.791	459	27000
3bg	H-0 → L+0 (96.9%)	2.42	512.3	1.111	540	35500
8a	H-0 → L+0 (94.8%)	2.35	526.6	1.204	564	30600
8b	H-0 → L+0 (94.8%)	2.31	536.2	1.283	581	32400

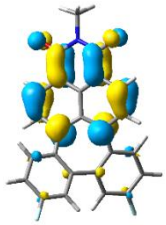
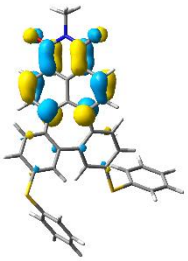
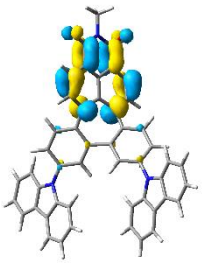
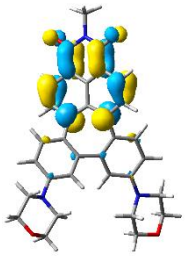
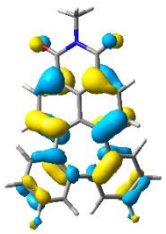
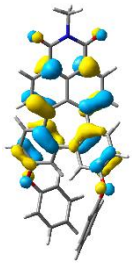
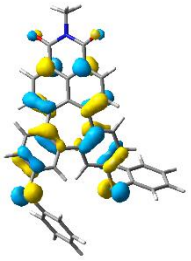
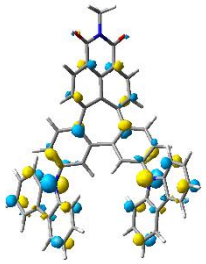
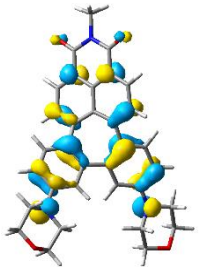
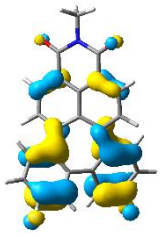
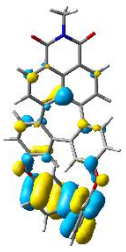
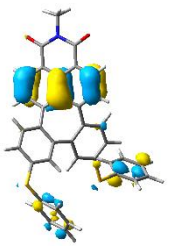
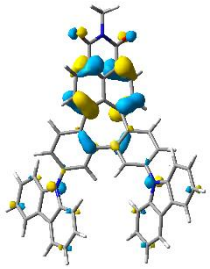
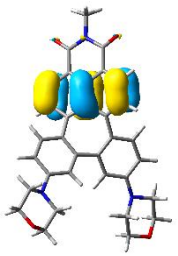
					
LUMO	-1.91	-1.82	-1.86	-1.93	-1.75
					
HOMO	-7.47	-7.21	-7.15	-7.03	-6.87
					
HOMO-4	-9.19	-8.59	-8.71	-7.69	-8.64
LUMO-HOMO	5.56	5.39	5.29	5.10	5.12
	3ag	**6**	**7**	**4**	**5**

Figure S4 Frontier molecular orbitals (MOs), MO energies, and HOMO-LUMO energy gaps (in eV) of **3ag, 6, 7, 4**, and **5**.

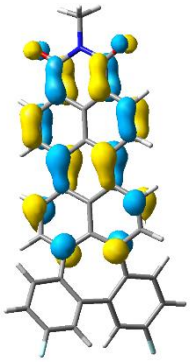
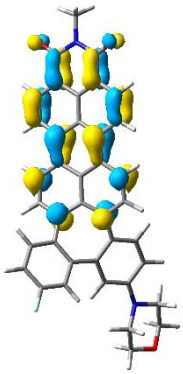
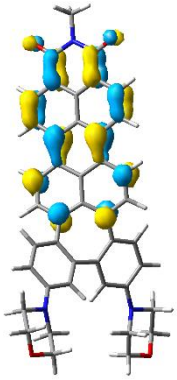
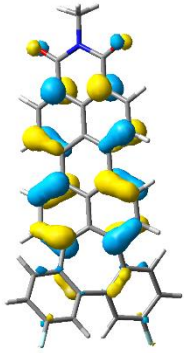
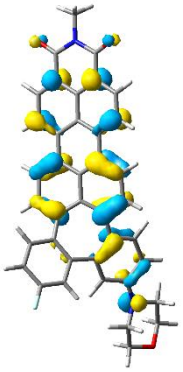
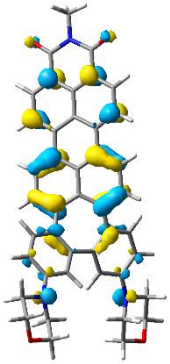
			
LUMO	-2.30	-2.25	-2.20
			
HOMO	-6.69	-6.53	-6.42
LUMO-HOMO	4.39	4.28	4.22
	3bg	**8a**	**8b**

Figure S5 Frontier molecular orbitals (MOs), MO energies, and HOMO-LUMO energy gaps (in eV) of **3bg, 8a**, and **8b**.

Cartesian coordinates of optimized structures

3ag

C	1.99204300	-1.87783300	1.53261100
C	0.60189400	-1.99143300	1.39535300
C	-0.13734800	-1.13205500	0.58309200
C	0.53108600	-0.00052900	0.00098000
C	1.96543800	-0.00137000	0.00176500
C	2.68238200	-0.94175700	0.78569600
C	-0.13544200	1.13174800	-0.58236400
C	0.60523100	1.99051900	-1.39399000
C	1.99552100	1.87538100	-1.52997000
C	2.68276300	0.93827800	-0.78210300
C	-1.48249500	-1.57304200	0.12557600
C	-1.48061700	1.57409300	-0.12603400
C	-2.58267100	-0.72522100	-0.14566600
C	-3.76455400	-1.28166900	-0.66553500
C	-3.86347000	-2.64269400	-0.89650200
C	-2.80599000	-3.50212500	-0.63229300
C	-1.63122900	-2.95241100	-0.13545400
C	-2.58201300	0.72745800	0.14399700
C	-3.76381500	1.28508600	0.66280600
C	-3.86151200	2.64617200	0.89387900
C	-2.80284300	3.50448200	0.63082400
C	-1.62816400	2.95356900	0.13509700
C	4.16484800	-0.93648800	0.82884000
N	4.81295800	-0.00471400	0.00289600
C	4.16365800	0.92500700	-0.81905500
O	4.79980700	-1.70531300	1.53921700
O	4.81672700	1.68641100	-1.52130800
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H	-2.89223700	4.56501100	0.84008900
H	-0.77784200	3.60788100	-0.02064600
H	6.63175500	-0.74883300	0.66665200
H	6.63607700	-0.17841300	-1.03378000
H	6.63905400	1.00290200	0.28568800
F	-5.00504800	3.14172000	1.40426200
F	-5.00703100	-3.13708900	-1.40791000

4

C	4.90394800	0.83329600	2.27529300
C	3.51406500	1.00059300	2.21705800
C	2.77242600	0.67445800	1.08176300
C	3.43885100	-0.00261600	0.00203200
C	4.87374500	-0.00282200	0.00217300
C	5.59238600	0.40808200	1.15450300
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C	4.90368800	-0.83915200	-2.27178000

C	5.59083600	-0.41361500	-1.15073200
C	1.42712800	1.28579600	0.91634200
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C	-0.98140800	2.74766600	0.55500600
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C	1.26886500	2.60219200	1.39825800
C	0.32825800	-0.69943400	-0.24555100
C	-0.84588400	-1.44866500	-0.06333400
C	-0.98459600	-2.74770200	-0.55381700
C	0.08834400	-3.32260300	-1.24424000
C	1.26678000	-2.60547300	-1.39473900
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C	7.07177800	-0.38497100	-1.17661500
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O	7.72382600	-0.68589300	-2.16841300
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H	5.46437200	-1.10499800	-3.16165800
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H	9.54195500	0.29631300	0.95275600

H	9.54458200	0.68275100	-0.79833000
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H	-0.83950100	-7.52723400	1.53207800
H	-0.20309100	-5.31850700	0.61327100
H	-0.19496100	5.31740500	-0.61104200
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H	-3.20172600	8.21867300	-1.67099000
H	-5.00431500	6.68821600	-0.90876700
H	-6.48702700	4.57102200	0.06853400
H	-3.20378800	1.05133100	1.45463600
H	-5.63663700	0.67664600	1.69936800
H	-7.26946300	2.41189500	1.01622500

5

C	-3.83535000	1.18519100	2.10596100
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C	-1.68809200	0.83467400	0.98186000
C	-2.34281200	-0.01284100	0.02177200
C	-3.77779000	-0.01992600	0.00565700
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C	-0.18515600	2.78832700	1.00155600
C	0.78257200	-0.72395300	-0.07632400
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O	-6.64341100	1.01304000	2.01342900
O	-6.60081700	-1.06988200	-2.05211900
C	-8.08861200	-0.05368600	-0.07213800
C	3.18122600	4.82933400	-0.75399800
C	4.44756300	2.77219200	-0.55134800
C	5.70752000	3.62738000	-0.40883800
C	4.48736200	5.60325400	-0.59843900
C	4.59342300	-2.81364800	0.02836100
C	3.37653000	-4.90658400	0.19032700
C	4.55288600	-5.46330700	0.99281300
C	5.71661000	-3.45194100	0.84166200
N	3.28286200	3.52267600	-0.08746800
N	3.30999800	-3.45423600	0.34449200

O	5.77951700	-4.85283500	0.62300500
O	5.58892200	4.86063900	-1.09982400
H	2.36590200	5.40977400	-0.31838300
H	2.96374500	4.69736500	-1.82832400
H	4.56307100	1.87427100	0.06384400
H	4.33801900	2.45462700	-1.60397600
H	6.56717900	3.10750400	-0.84217300
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H	4.64781700	5.84993100	0.46417800
H	4.54661900	-1.74780000	0.25976600
H	4.82181600	-2.91522600	-1.04732600
H	2.45299700	-5.35048000	0.57427400
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H	4.66613400	-6.53443100	0.80141600
H	4.36497300	-5.31376800	2.06878000
H	6.68494500	-3.04371800	0.53692300
H	5.56293000	-3.24110900	1.91295700
H	-4.40655000	1.59400400	2.93272900
H	-1.94742500	1.92032100	2.81057500
H	-1.86460300	-1.94111200	-2.75795300
H	-4.32549800	-1.63871500	-2.93578500
H	2.74934400	0.91657600	-0.58278200
H	1.03658400	4.53424700	0.99254800
H	-1.02991800	3.34263500	1.39599900
H	2.74716300	-0.88575700	0.73421400
H	1.09942800	-4.52371800	-0.86231700
H	-0.96664300	-3.35460600	-1.30973700
H	-8.44163500	-1.08462400	-0.15369400
H	-8.44007900	0.49778400	-0.94785400
H	-8.45431000	0.40600800	0.84318700

6

C	3.97470100	1.15452300	2.14921200
C	2.59269700	1.32077900	1.99336000
C	1.90872800	0.85611600	0.86900200
C	2.62445800	0.04129800	-0.07570600
C	4.05722300	0.03031500	0.00451500
C	4.71651800	0.58130600	1.13331900
C	2.00614800	-0.76356700	-1.09439600
C	2.80430000	-1.23815600	-2.13633500
C	4.19737000	-1.09361700	-2.13620800
C	4.83136400	-0.53234100	-1.04310500
C	0.57997900	1.44481300	0.55899000
C	0.64444700	-1.33487500	-0.93258300
C	-0.49106800	0.78506900	-0.08663600
C	-1.65896100	1.50394200	-0.39792400
C	-1.80288500	2.84442300	-0.05249900
C	-0.75560200	3.50778700	0.58980300
C	0.40988600	2.81222400	0.86980800
C	-0.48165600	-0.66253900	-0.40503500
C	-1.68409100	-1.36845800	-0.21819800
C	-1.79665800	-2.71478300	-0.55092300
C	-0.69732700	-3.38822900	-1.08751300
C	0.49294300	-2.70059000	-1.26071300
C	6.19195700	0.54275600	1.24664200
N	6.89989800	0.00492500	0.16429000

C	6.31246400	-0.52392500	-0.99613800
O	6.79499800	0.96139200	2.22743400
O	6.99895800	-0.95916100	-1.91245300
C	8.36148300	0.00333900	0.27780200
O	-2.90394000	3.60187800	-0.37330300
O	-2.95569000	-3.44223400	-0.41956100
C	-3.72356100	-2.85808400	1.80857400
C	-3.96111500	-3.02896100	0.44208800
C	-5.24247600	-2.88051700	-0.08695400
C	-4.78697600	-2.52328400	2.64681100
C	-6.07656500	-2.37168500	2.12989100
C	-6.30049500	-2.55550200	0.76377800
C	-4.13779500	3.00780100	-0.59301300
C	-4.84319700	3.40783200	-1.72746300
C	-6.12405300	2.90083000	-1.95095300
C	-4.69916900	2.11264100	0.32168800
C	-5.97445100	1.60173800	0.07942300
C	-6.69093800	1.99335400	-1.05413700
H	-2.72101000	-2.99180400	2.20255000
H	-5.39422100	-3.02861200	-1.15133800
H	-4.60721800	-2.39201400	3.71034900
H	-6.90207700	-2.12085800	2.78991900
H	-7.30137500	-2.44698400	0.35496600
H	-4.38216300	4.11072300	-2.41402900
H	-6.67561900	3.21338400	-2.83338800
H	-4.14394800	1.82440600	1.20858800
H	-6.40582100	0.89503800	0.78284500
H	-7.68524500	1.59556000	-1.23563300
H	4.48986800	1.52891200	3.02757000
H	2.04412300	1.87367400	2.74895700
H	2.33580600	-1.78214900	-2.95009400
H	4.80063800	-1.47704900	-2.95220900
H	-2.45768500	1.00718100	-0.93443800
H	-0.85721200	4.56088900	0.83073400
H	1.23618800	3.35225700	1.31859200
H	-2.53723200	-0.85623600	0.20871400
H	-0.78208200	-4.44227400	-1.33062000
H	1.35535300	-3.24900600	-1.62316100
H	8.66517500	-0.58653600	1.14626200
H	8.72297400	1.02529200	0.41546100
H	8.76311300	-0.42589900	-0.63721100

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C	-3.80739300	1.23527000	2.17185500
C	-2.41479300	1.12936800	2.06629000
C	-1.79605300	0.48784800	0.99234100
C	-2.62234900	-0.22385100	0.05499400
C	-4.03300000	0.04002000	0.07643100
C	-4.61121000	0.76286600	1.15129000
C	-2.13643500	-1.18170600	-0.90143100
C	-2.97754100	-1.55047300	-1.95248800
C	-4.31677600	-1.14596400	-2.01604900
C	-4.86641900	-0.41925900	-0.97604900
C	-0.37048000	0.80016700	0.71244000
C	-0.91272700	-1.98935000	-0.66154600
C	0.57679300	-0.08203000	0.14277700
C	1.86348000	0.39842600	-0.15735300

C	2.25474300	1.70884700	0.11988500
C	1.32750200	2.57921900	0.70118200
C	0.04364600	2.12480200	0.96738300
C	0.30437200	-1.51452300	-0.12060000
C	1.34327200	-2.42569200	0.14070100
C	1.23221100	-3.78298800	-0.15383600
C	0.03388000	-4.25582500	-0.70268400
C	-1.01035900	-3.37209300	-0.92837700
C	-6.06959500	1.01195200	1.20408400
N	-6.83190100	0.56357900	0.11797000
C	-6.31952200	-0.12816400	-0.99105800
O	-6.61247500	1.58857500	2.13868400
O	-7.04641400	-0.47297500	-1.91461400
C	-8.26931600	0.84714700	0.16942800
C	4.62151400	-3.83053000	1.56471300
C	3.99928200	-3.98628300	0.32057800
C	4.57333300	-3.41413500	-0.82391800
C	5.80974900	-3.10260100	1.66340700
C	6.37157700	-2.52023900	0.52706300
C	5.75055000	-2.67488400	-0.71562900
C	3.88207000	3.93758600	-0.45874500
C	3.20500200	4.51185300	-1.54415200
C	3.21728300	5.89492000	-1.71786800
C	4.58216200	4.75495000	0.43651600
C	4.60583100	6.13860500	0.24575300
C	3.92065000	6.71018300	-0.82660700
S	3.94859000	2.15542000	-0.25094900
S	2.51205000	-4.98464300	0.19657300
H	4.17331300	-4.27553500	2.44776600
H	4.09625600	-3.55030400	-1.78976100
H	6.28941300	-2.98516700	2.63123600
H	7.29188500	-1.94840900	0.60679600
H	6.18929900	-2.22814400	-1.60363700
H	2.67307400	3.87511000	-2.24447300
H	2.68686300	6.33583800	-2.55755000
H	5.10313200	4.30641900	1.27693900
H	5.15338300	6.76789400	0.94210700
H	3.93515000	7.78703300	-0.97041000
H	-4.26985000	1.74388800	3.01117600
H	-1.79580500	1.60576800	2.81959000
H	-2.59586100	-2.21435600	-2.72130200
H	-4.95587500	-1.45036100	-2.83804900
H	2.56846900	-0.26905400	-0.64218600
H	1.59277100	3.60870800	0.91642200
H	-0.67897800	2.83081900	1.36226700
H	2.25248100	-2.05726500	0.60015400
H	-0.08916500	-5.31047200	-0.93264600
H	-1.94881000	-3.76787700	-1.30117600
H	-8.71407900	0.46655900	-0.74719200
H	-8.43009500	1.92418100	0.25851500
H	-8.71240300	0.36181500	1.04276400

3bg

C	-0.08116700	-2.08045700	1.24196900
C	-1.46220200	-2.17841700	1.05702800
C	-2.18786300	-1.20159200	0.38425800
C	-1.50140600	-0.00021200	-0.00005800

C	-0.06115000	0.00005200	-0.00035700
C	0.65307000	-1.04955500	0.66514200
C	-2.18842300	1.20096600	-0.38406300
C	-1.46350500	2.17804200	-1.05728200
C	-0.08253200	2.08058500	-1.24282500
C	0.65224900	1.04996600	-0.66621000
C	-3.52674700	-1.56125500	-0.15520400
C	-3.52715900	1.56022300	0.15601500
C	-4.63466800	-0.68927800	-0.27032300
C	-5.81464500	-1.15386600	-0.87713900
C	-5.90379000	-2.45374400	-1.34380500
C	-4.83859300	-3.33733600	-1.23744900
C	-3.66567500	-2.87420900	-0.65448900
C	-4.63476600	0.68792300	0.27160500
C	-5.81463500	1.15220700	0.87886500
C	-5.90395700	2.45207900	1.34552100
C	-4.83904700	3.33596800	1.23874200
C	-3.66623800	2.87315300	0.65532400
C	2.12074400	-1.01449600	0.72270000
C	2.82113700	0.00084700	-0.00096700
C	2.11981300	1.01554000	-0.72428500
C	2.86598500	-1.94813400	1.44909800
C	4.26352000	-1.92737500	1.46234900
C	4.96131000	-0.97336400	0.73982500
C	4.25079100	0.00137400	-0.00117400
C	2.86457900	1.94926400	-1.45096700
C	4.26199500	1.92929500	-1.46452600
C	4.96188400	0.97625200	-0.74211000
C	6.44008100	-0.98277300	0.75411600
C	6.44215000	0.99329400	-0.76135000
N	7.08842300	0.00364000	-0.00184400
C	8.55422900	-0.02149500	0.01827600
O	7.08031400	1.82097200	-1.40066300
O	7.09574400	-1.80263300	1.38608200
H	0.41677200	-2.87653900	1.78289900
H	-1.97477200	-3.06552600	1.41580000
H	-1.97660200	3.06492100	-1.41585900
H	0.41493900	2.87679900	-1.78399200
H	-6.66515400	-0.49479000	-1.00811700
H	-4.92228100	-4.34551300	-1.62885400
H	-2.81076000	-3.54007700	-0.61508500
H	-6.66491800	0.49290800	1.01017900
H	-4.92286600	4.34413300	1.63014800
H	-2.81152400	3.53925800	0.61554700
H	2.36528100	-2.71675900	2.02592400
H	4.82521200	-2.66104900	2.03119800
H	4.82233500	2.66344000	-2.03387600
H	2.36354300	2.71758000	-2.02791600
H	8.91212700	0.09372000	1.04431900
H	8.90717900	0.79636500	-0.60569800
H	8.91352500	-0.98030000	-0.36363100
F	-7.04623300	2.85888100	1.93317400
F	-7.04617400	-2.86083700	-1.93105400

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C	-0.53040000	-2.23780000	0.92880000
C	-1.91130000	-2.30790000	0.73260000

C	-2.63710000	-1.24510000	0.20610000
C	-1.95090000	-0.00030000	-0.00010000
C	-0.51010000	0.00000000	-0.00040000
C	0.20440000	-1.13590000	0.50330000
C	-2.63770000	1.24410000	-0.20600000
C	-1.91270000	2.30730000	-0.73300000
C	-0.53190000	2.23790000	-0.92990000
C	0.20350000	1.13630000	-0.50450000
C	-3.97610000	-1.52430000	-0.37960000
C	-3.97650000	1.52280000	0.38050000
C	-5.08090000	-0.64220000	-0.36820000
C	-6.25660000	-1.01800000	-1.04490000
C	-6.37320000	-2.23620000	-1.70350000
C	-5.29160000	-3.11610000	-1.70430000
C	-4.11480000	-2.75260000	-1.06040000
C	-5.08100000	0.64020000	0.36970000
C	-6.25640000	1.01570000	1.04710000
C	-6.37310000	2.23380000	1.70580000
C	-5.29180000	3.11410000	1.70590000
C	-4.11520000	2.75110000	1.06130000
C	1.67220000	-1.11360000	0.55790000
C	2.37300000	0.00090000	-0.00100000
C	1.67130000	1.11480000	-0.55960000
C	2.41810000	-2.15150000	1.12520000
C	3.81540000	-2.13490000	1.13810000
C	4.51340000	-1.07870000	0.57540000
C	3.80280000	0.00150000	-0.00120000
C	2.41670000	2.15310000	-1.12680000
C	3.81380000	2.13730000	-1.13980000
C	4.51400000	1.08180000	-0.57750000
C	5.99170000	-1.09100000	0.58680000
C	5.99380000	1.10260000	-0.59250000
N	6.64010000	0.00350000	-0.00210000
C	8.10580000	-0.02440000	0.01400000
O	6.63260000	2.02290000	-1.08900000
O	6.64800000	-2.00130000	1.07940000
H	-0.03300000	-3.10300000	1.35130000
H	-2.42440000	-3.23690000	0.96010000
H	-2.42640000	3.23610000	-0.96030000
H	-0.03500000	3.10320000	-1.35270000
H	-7.08850000	-0.32120000	-1.06590000
H	-5.35100000	-4.06760000	-2.22540000
H	-3.25940000	-3.41770000	-1.11460000
H	-7.08800000	0.31850000	1.06860000
H	-5.35130000	4.06560000	2.22700000
H	-3.26010000	3.41650000	1.11500000
H	1.91790000	-3.00190000	1.57310000
H	4.37710000	-2.95020000	1.58200000
H	4.37410000	2.95350000	-1.58370000
H	1.91610000	3.00330000	-1.57450000
H	8.46420000	-0.06720000	1.04550000
H	8.45860000	0.87930000	-0.47760000
H	8.46480000	-0.91390000	-0.50950000
C	-7.37754636	-2.85913562	-3.90243421
C	-8.32074300	-3.79614437	-1.78383004
C	-8.62121318	-3.29451092	-4.65028939
H	-6.59566851	-3.65958019	-3.98192890

H	-6.96022199	-1.93251576	-4.37556014
C	-9.56487782	-4.23100742	-2.53124366
H	-7.58613071	-4.64349058	-1.75744700
H	-8.58706653	-3.54780432	-0.72371661
H	-8.35418816	-3.54417372	-5.70993628
H	-9.35514027	-2.44660943	-4.67844513
H	-9.98195198	-5.15786268	-2.05844944
H	-10.34665307	-3.43051720	-2.45054015
N	-7.67723510	-2.59197479	-2.44141378
O	-9.26641066	-4.49714547	-3.99258859
F	-7.51602226	2.54518978	2.35330684

8b

C	1.85222200	1.27746800	-2.05842100
C	0.47156700	1.44490900	-1.94325400
C	-0.25673800	0.88751200	-0.89616000
C	0.43087000	-0.00064300	-0.00010400
C	1.87174000	-0.00087500	0.00013300
C	2.58695300	0.62684200	-1.07175500
C	-0.25728000	-0.88864800	0.89569700
C	0.47044600	-1.44644700	1.94299500
C	1.85110000	-1.27942700	2.05867300
C	2.58627700	-0.62884800	1.07232100
C	-1.59704200	1.44854000	-0.59217300
C	-1.59777400	-1.44906700	0.59139400
C	-2.70859700	0.73660500	-0.08165600
C	-3.87821300	1.43086400	0.25366300
C	-4.02724900	2.81734200	0.08189600
C	-2.92720700	3.51293600	-0.44929000
C	-1.75309700	2.83779900	-0.75577000
C	-2.70896700	-0.73652400	0.08091800
C	-3.87890800	-1.43019600	-0.25444400
C	-4.02859600	-2.81662700	-0.08280600
C	-2.92887800	-3.51282800	0.44822400
C	-1.75445300	-2.83826900	0.75480200
C	4.05350100	0.57114900	-1.10648700
C	4.75499000	-0.00112100	0.00095500
C	4.05272400	-0.57330400	1.10771200
C	4.79952900	1.07127800	-2.17930400
C	6.19614200	1.04778700	-2.18097100
C	6.89529100	0.52876400	-1.10261400
C	6.18500500	-0.00110900	0.00146300
C	4.79847300	-1.07336900	2.18070800
C	6.19496800	-1.04978200	2.18313500
C	6.89610300	-0.53078500	1.10559900
C	8.37255500	0.53189800	-1.11957100
C	8.37485300	-0.53710400	1.13085300
N	9.02098000	-0.00110100	0.00364700
C	10.48627500	0.01342300	-0.02534600
O	9.01506000	-0.98325600	2.07629000
O	9.03006900	0.97351700	-2.05541300
H	2.35093400	1.73576700	-2.90453100
H	-0.04247900	2.06309700	-2.67250500
H	-0.04408700	-2.06454500	2.67197200
H	2.34944600	-1.73791600	2.90489800
H	-4.68190500	0.86849400	0.71415700
H	-2.96891900	4.58297900	-0.61469800

H	-0.90939200	3.41871200	-1.11355600
H	-4.68237000	-0.86744200	-0.71486400
H	-2.97109600	-4.58287900	0.61344400
H	-0.91102700	-3.41961100	1.11255000
H	4.29859300	1.49180700	-3.04324600
H	6.75788000	1.44153500	-3.02175800
H	6.75544200	-1.44363000	3.02456700
H	4.29734400	-1.49397900	3.04450100
H	10.84607400	-0.56377000	-0.88085000
H	10.83917500	-0.42176900	0.90683500
H	10.84437700	1.04039500	-0.13192200
C	-5.25822600	-4.92190800	-0.43896300
C	-6.49525100	-2.86448300	-0.10087600
C	-6.44134700	-5.43376500	-1.26122300
H	-5.34615700	-5.29285900	0.59824900
H	-4.33575900	-5.32570900	-0.86722900
C	-7.62623700	-3.45326200	-0.94024900
H	-6.70147400	-3.05215600	0.96786800
H	-6.46504500	-1.78335000	-0.24942000
H	-6.53945100	-6.51733100	-1.14677100
H	-6.27295400	-5.20426900	-2.32627800
H	-8.59350400	-3.08263100	-0.58772700
H	-7.49544700	-3.15867800	-1.99470500
C	-5.25574100	4.92330900	0.43791600
C	-6.49388400	2.86644600	0.10041300
C	-6.43845400	5.43590900	1.26029700
H	-5.34366500	5.29415300	-0.59933400
H	-4.33300600	5.32671100	0.86597300
C	-7.62440300	3.45600200	0.93987100
H	-6.70020300	3.05395100	-0.96833800
H	-6.46422500	1.78534000	0.24925000
H	-6.53598900	6.51951000	1.14570100
H	-6.27002100	5.20647500	2.32536000
H	-8.59192100	3.08578400	0.58760500
H	-7.49356700	3.16158200	1.99436800
N	-5.21112400	-3.46175500	-0.49007600
N	-5.20936800	3.46313800	0.48921800
O	-7.66878500	-4.86757000	-0.82850000
O	-7.66625600	4.87029900	0.82783700

X. References

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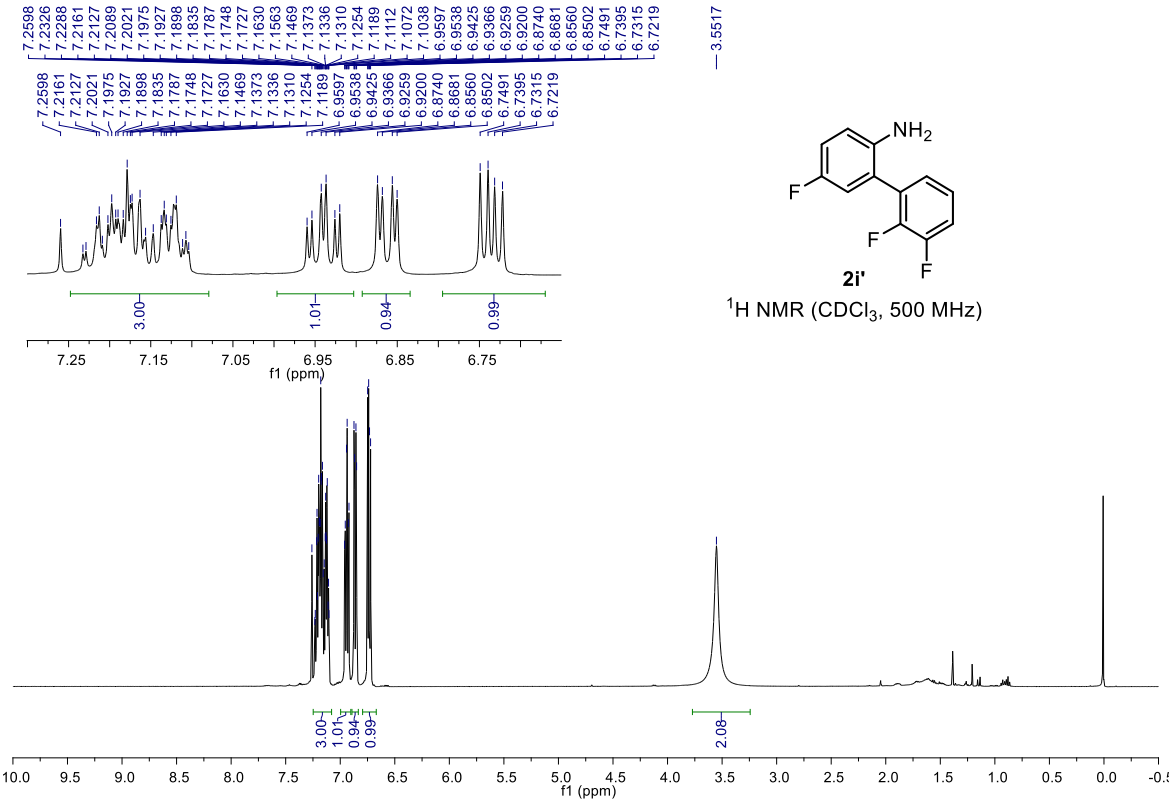
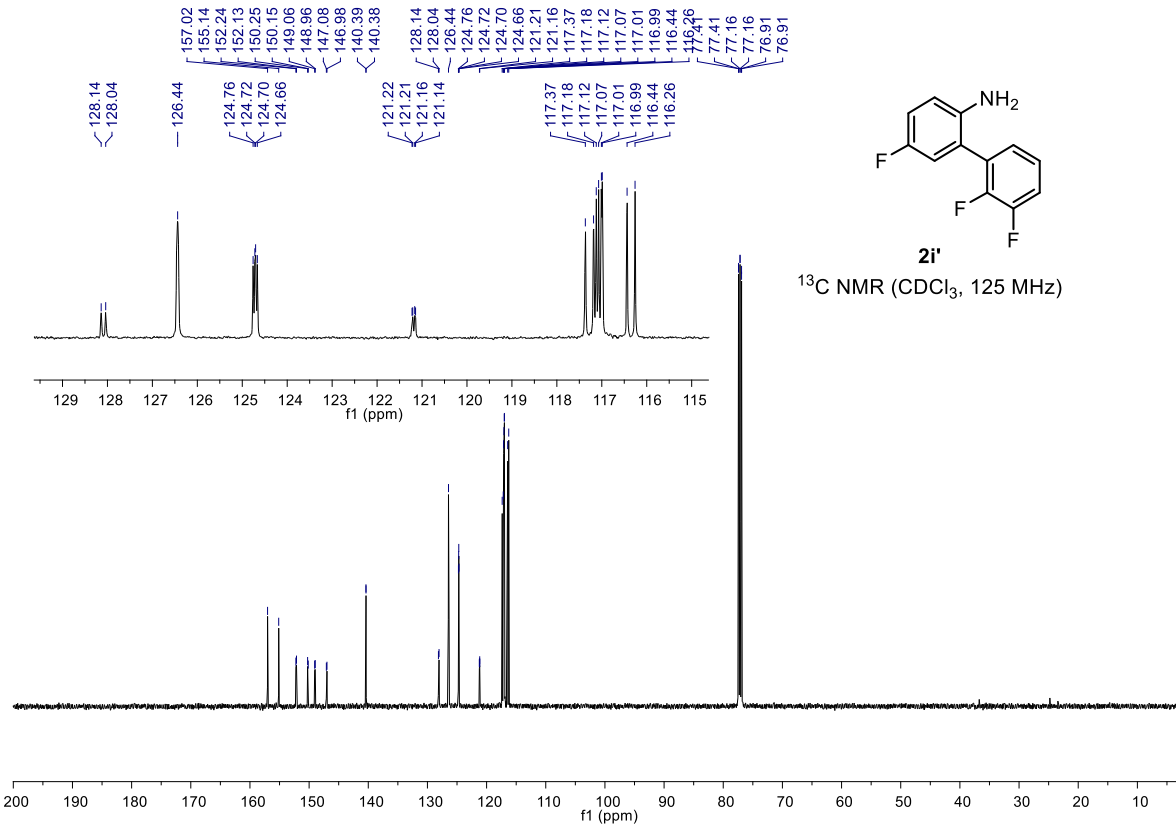
XI. NMR Spectra



2i'

^{1}H NMR ($CDCl_3$, 500 MHz)



2i'

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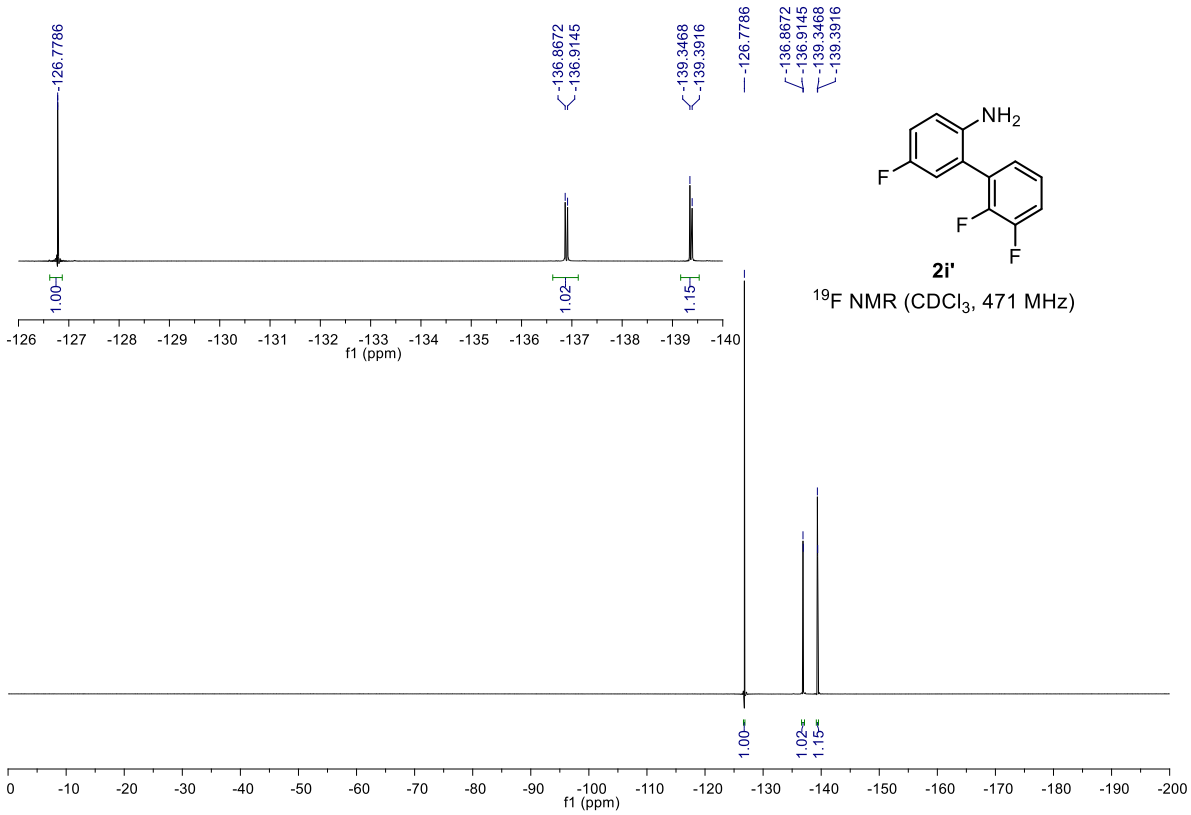

2i'

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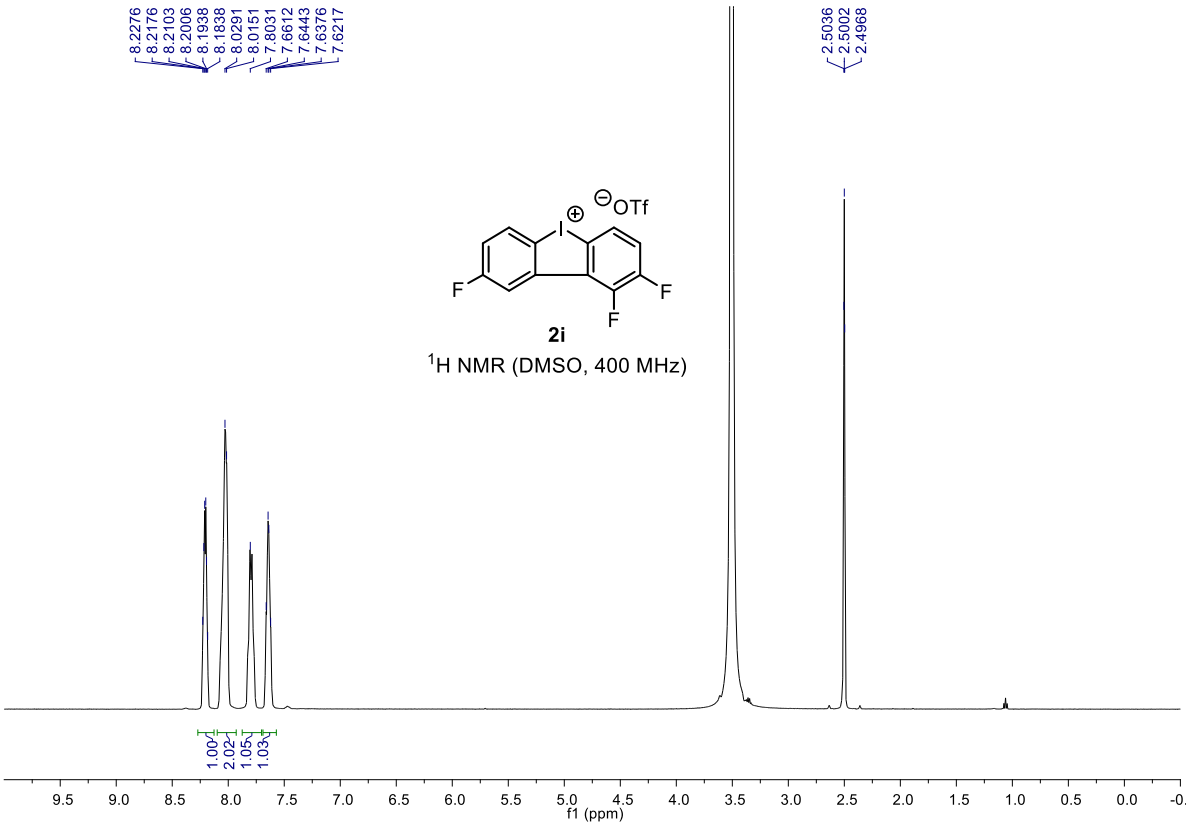
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8.2006
8.1938
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8.0291
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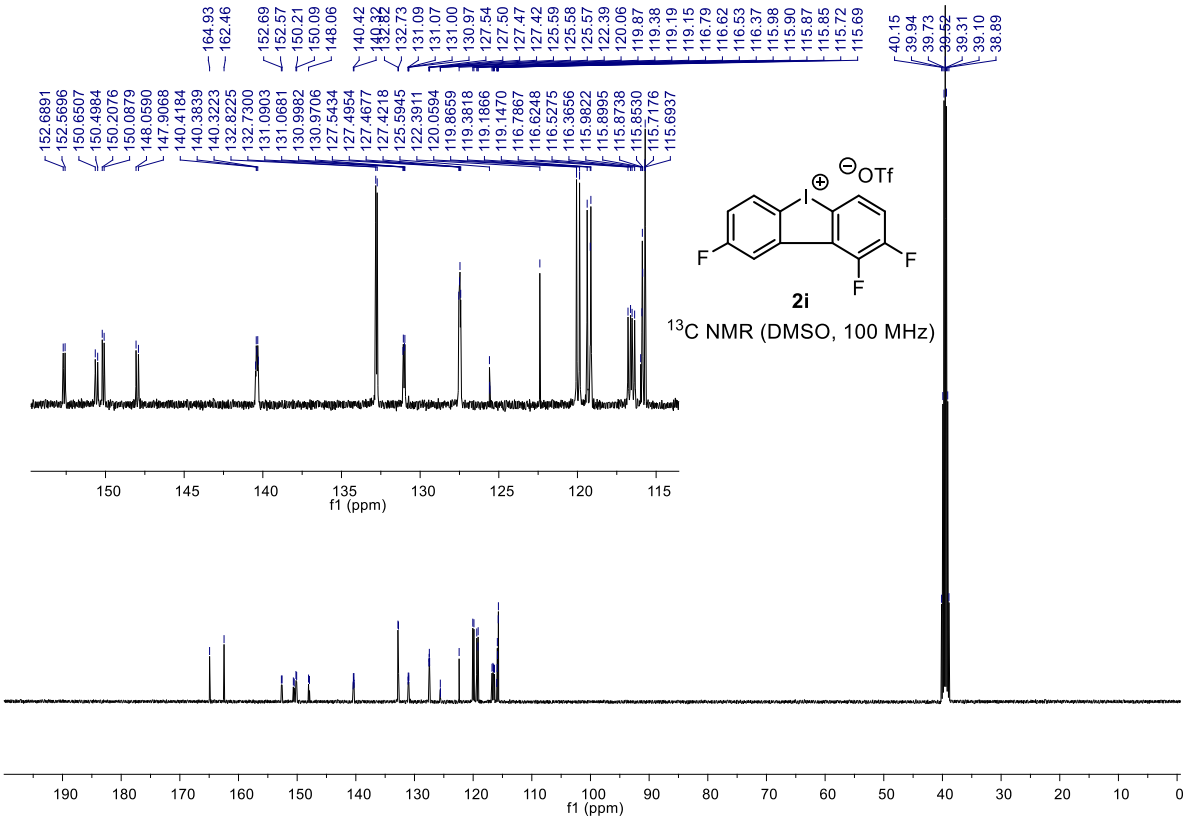
7.8031
7.6612
7.6443
7.6376
7.6217
2.5036
2.5002
2.4968
OTf
F
F
F
2i
1H NMR (DMSO, 400 MHz)
1.00
2.02
1.05
1.03
f1 (ppm)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162.46
152.69
152.57
150.21
150.09
148.06
140.42
132.73
131.09
131.07
131.00
130.97
127.54
127.50
127.47
127.42
125.59
125.58
125.57
122.39
120.06
119.87
119.38
119.19
119.15
116.79
116.62
116.53
116.37
115.98
115.90
115.87
115.85
115.72
115.69
40.15
39.94
39.73
39.52
39.31
39.10
38.89
152.6891
152.5696
150.6507
150.4984
150.2076
150.0879
148.0590
147.9068
140.4184
140.3839
140.3223
132.8225
132.7300
131.0903
131.0681
130.9982
130.9706
127.5434
127.4954
127.4677
127.4218
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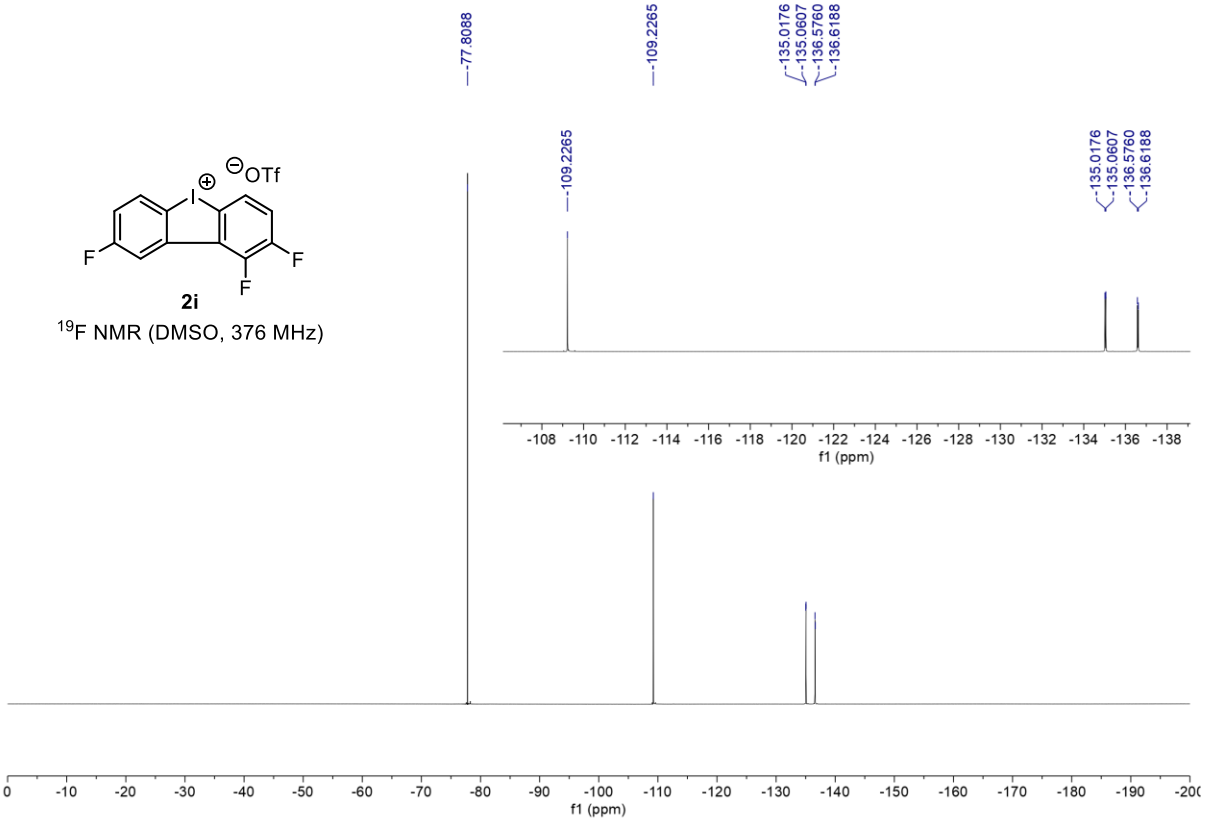
122.3911
120.0594
119.8659
119.3818
119.1866
119.1470
116.7867
116.6248
116.5275
116.3656
115.9822
115.8995
115.8738
115.8530
115.7176
115.6937
OTf
F
F
F
2i
13C NMR (DMSO, 100 MHz)
f1 (ppm)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-135.0607
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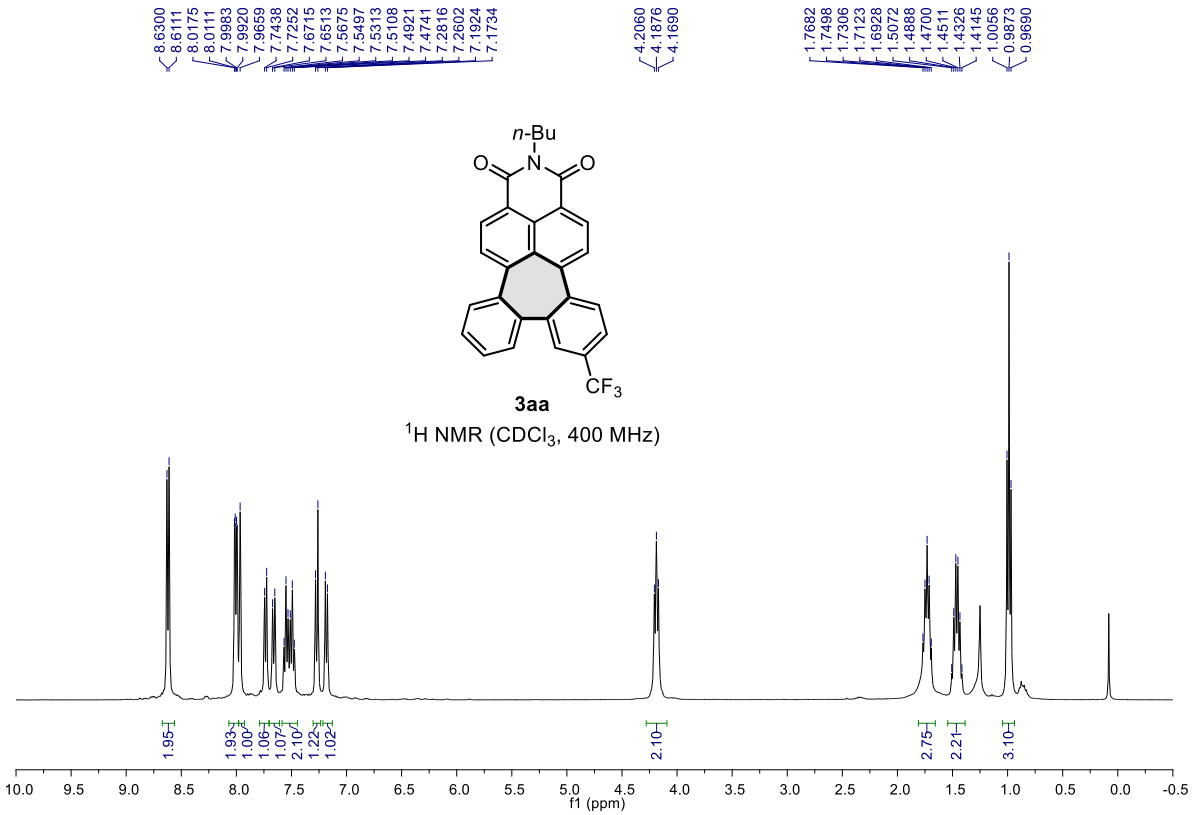
-136.6188
OTf
I
F
F
F
2i
19F NMR (DMSO, 376 MHz)
f1 (ppm)



3aa

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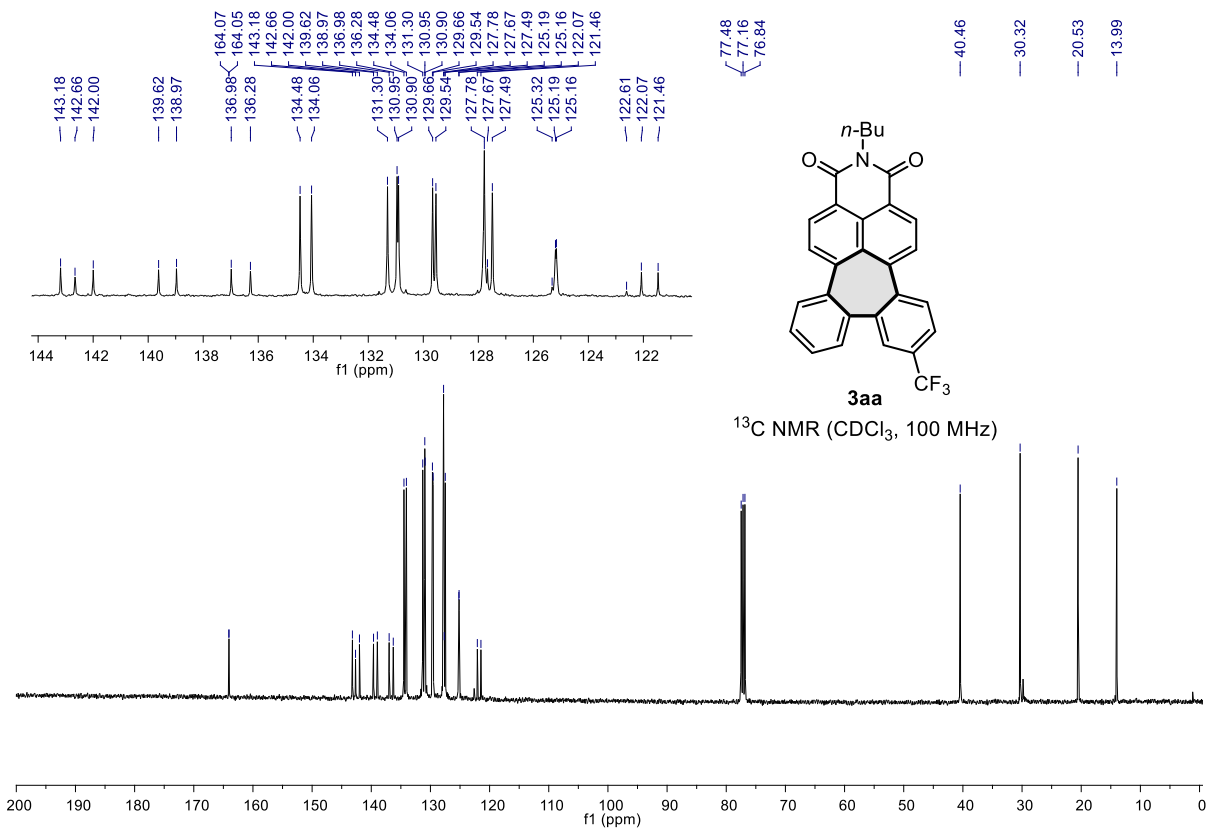

3aa

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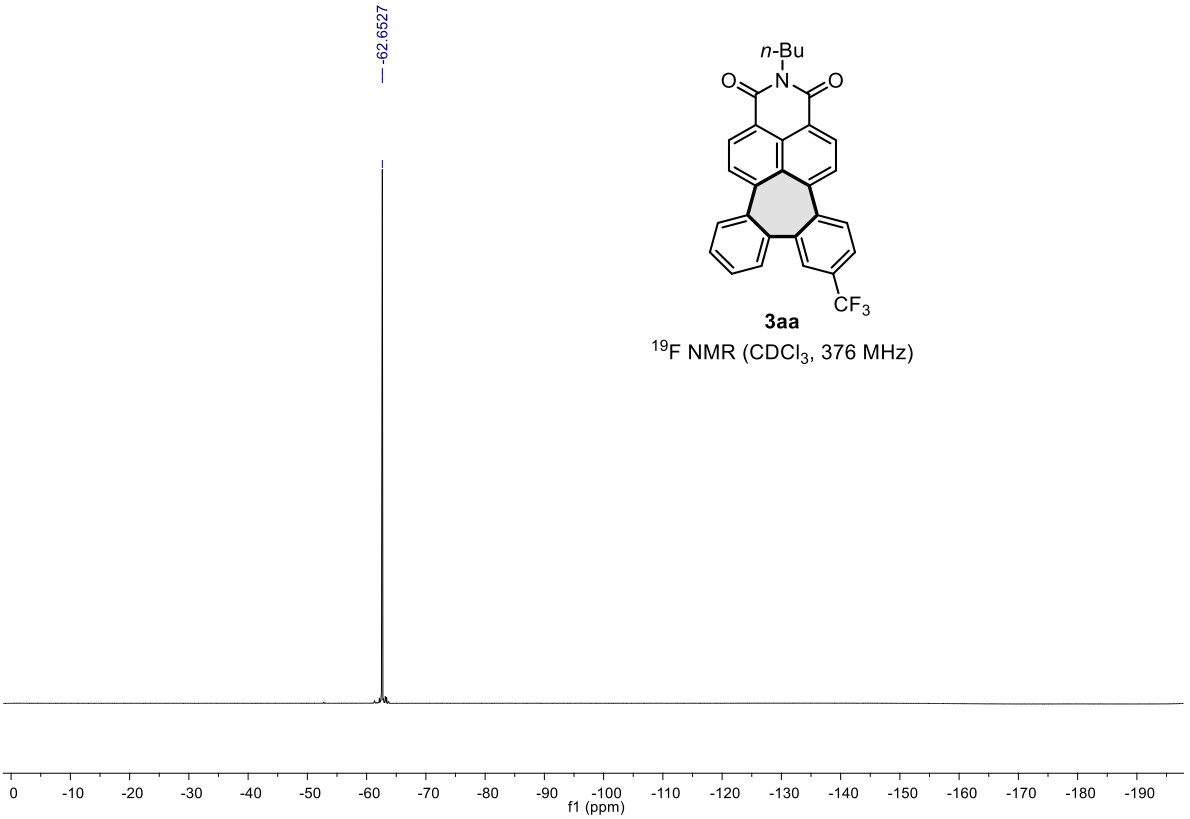

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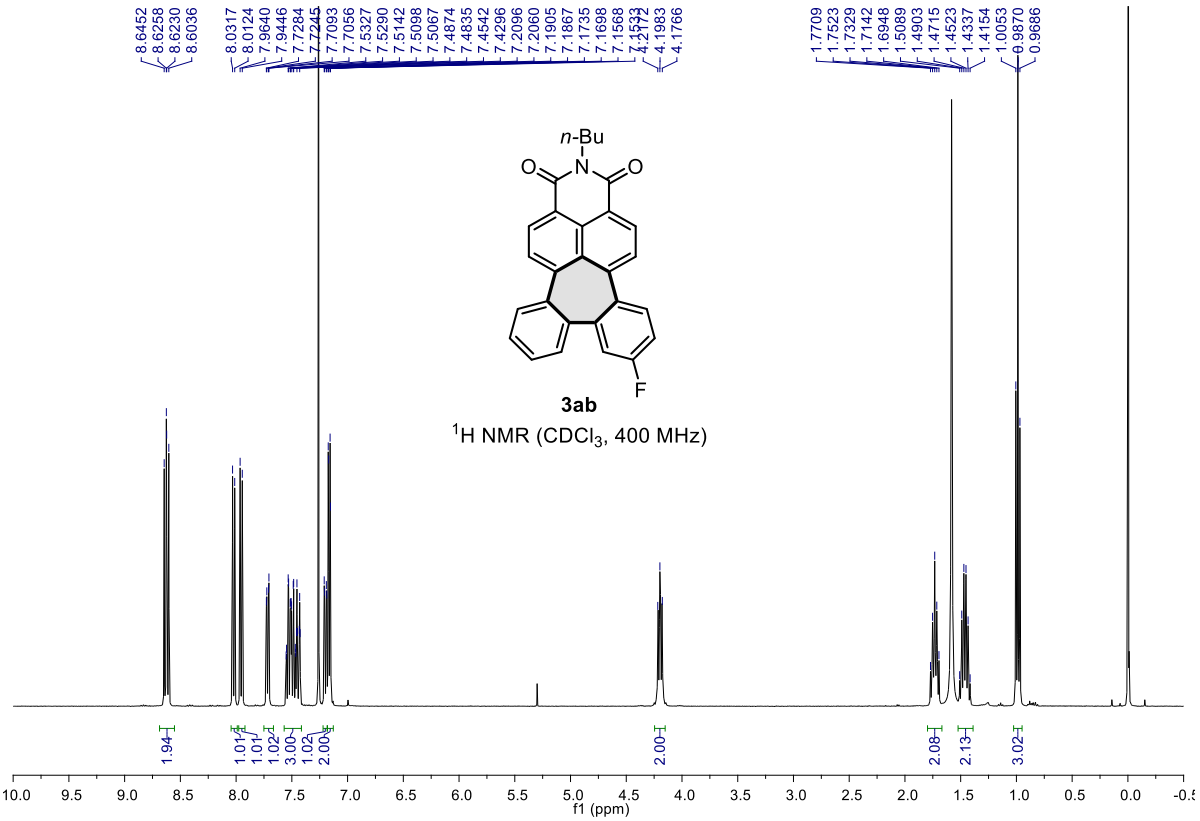
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7.9640
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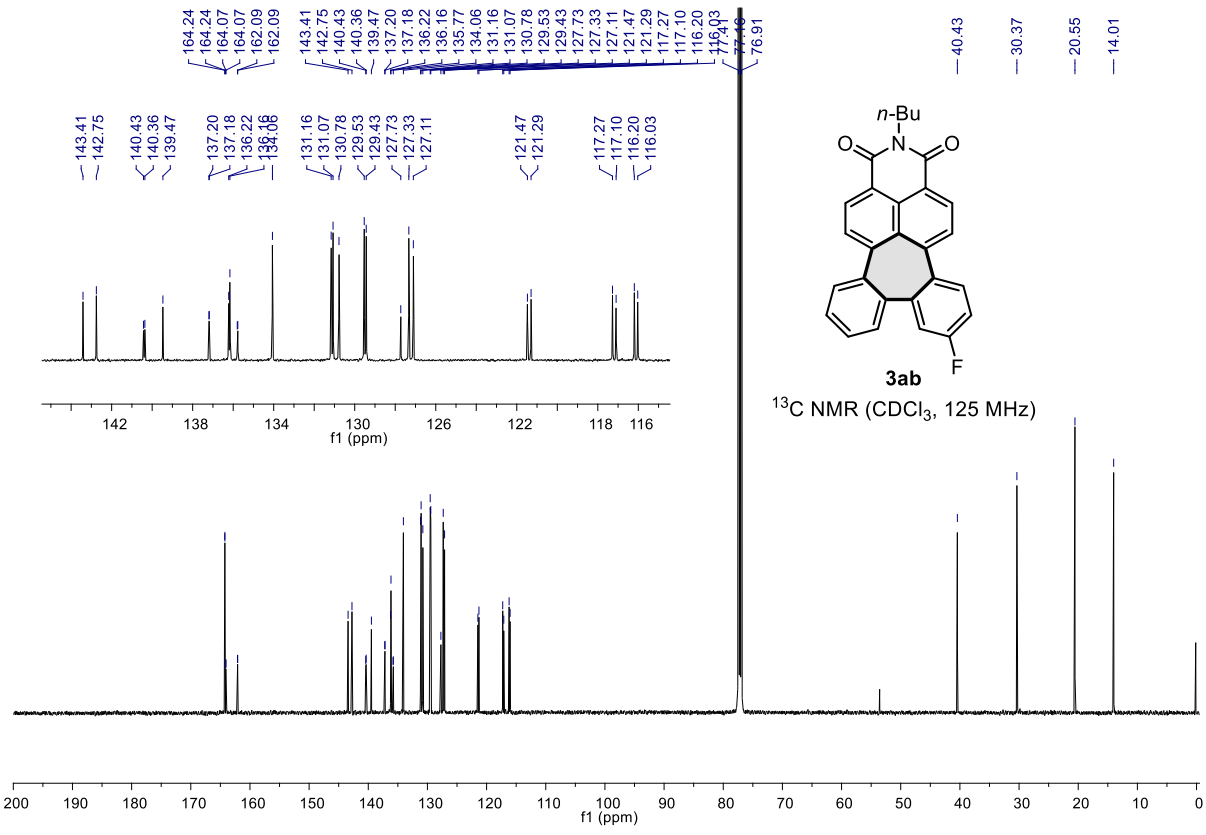
7.7093
7.7056
7.5327
7.5290
7.5142
7.5098
7.5067
7.4874
7.4835
7.4542
7.4296
7.2096
7.2060
7.1905
7.1867
7.1735
7.1698
7.1568
7.1533
4.2172
4.1983
4.1766
1.7709
1.7523
1.7329
1.7142
1.6948
1.5089
1.4903
1.4715
1.4523
1.4337
1.4154
1.0053
0.9870
0.9686
n-Bu
O
N
O
F
3ab
1H NMR (CDCl3, 400 MHz)
1.94
1.01
1.01
1.02
3.00
1.02
2.00
2.00
2.08
2.13
3.02
f1 (ppm)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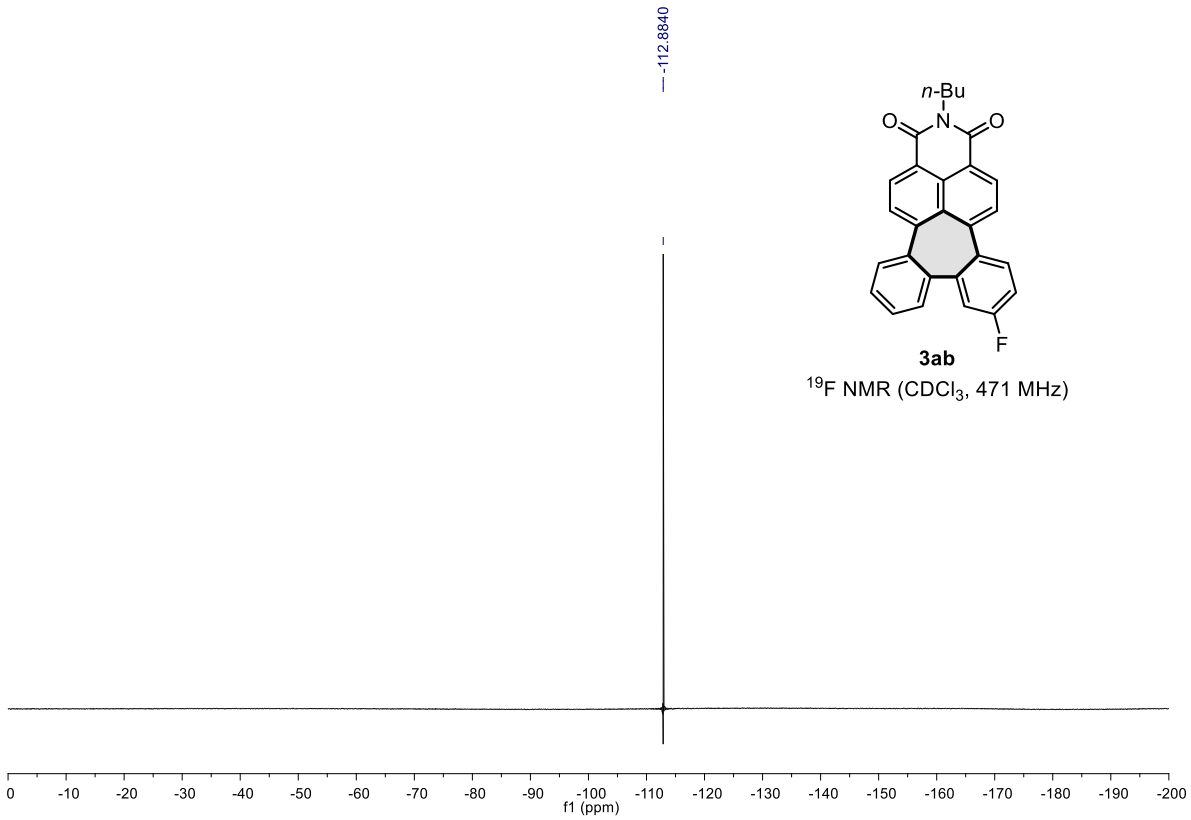
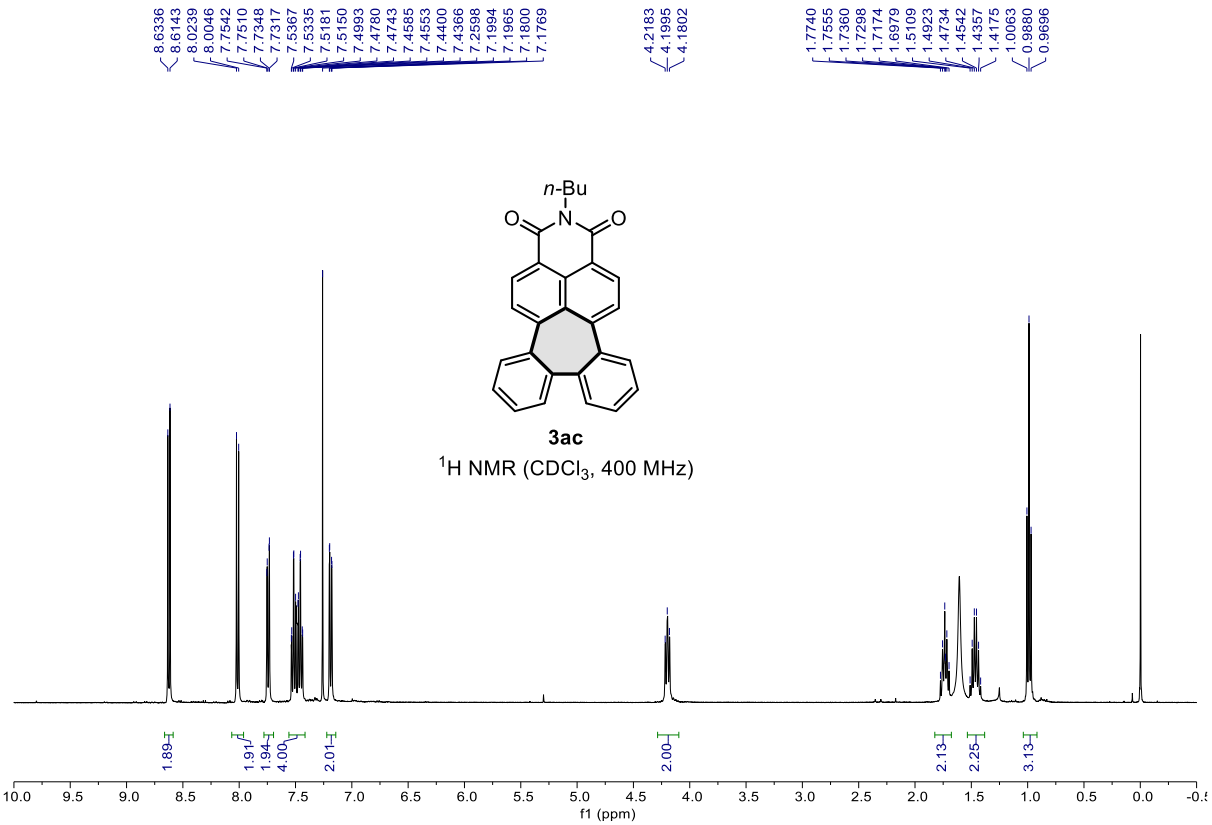
164.24
164.07
164.07
162.09
162.09
143.41
142.75
140.43
140.36
139.47
137.20
137.18
136.22
131.16
131.07
130.78
129.53
129.43
127.73
127.33
127.11
121.47
121.29
117.27
117.10
116.20
116.03
77.48
77.16
76.91
40.43
30.37
20.55
14.01
n-Bu
O
N
O
F
3ab
13C NMR (CDCl3, 125 MHz)
f1 (ppm)



3ab

^{19}F NMR ($CDCl_3$, 471 MHz)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7.7542
7.7510
7.7348
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7.5367
7.5335
7.5181
7.5150
7.4993
7.4780
7.4743
7.4585
7.4553
7.4400
7.4366
7.2598
7.1994
7.1965
7.1800
7.1769
4.2183
4.1995
4.1802
1.7740
1.7555
1.7360
1.7298
1.7174
1.6979
1.5109
1.4923
1.4734
1.4542
1.4357
1.4175
1.0063
0.9880
0.9696
n-Bu
N
O
O
3ac
1H NMR (CDCl3, 400 MHz)
1.89
1.91
1.94
4.00
2.01
2.00
2.13
2.25
3.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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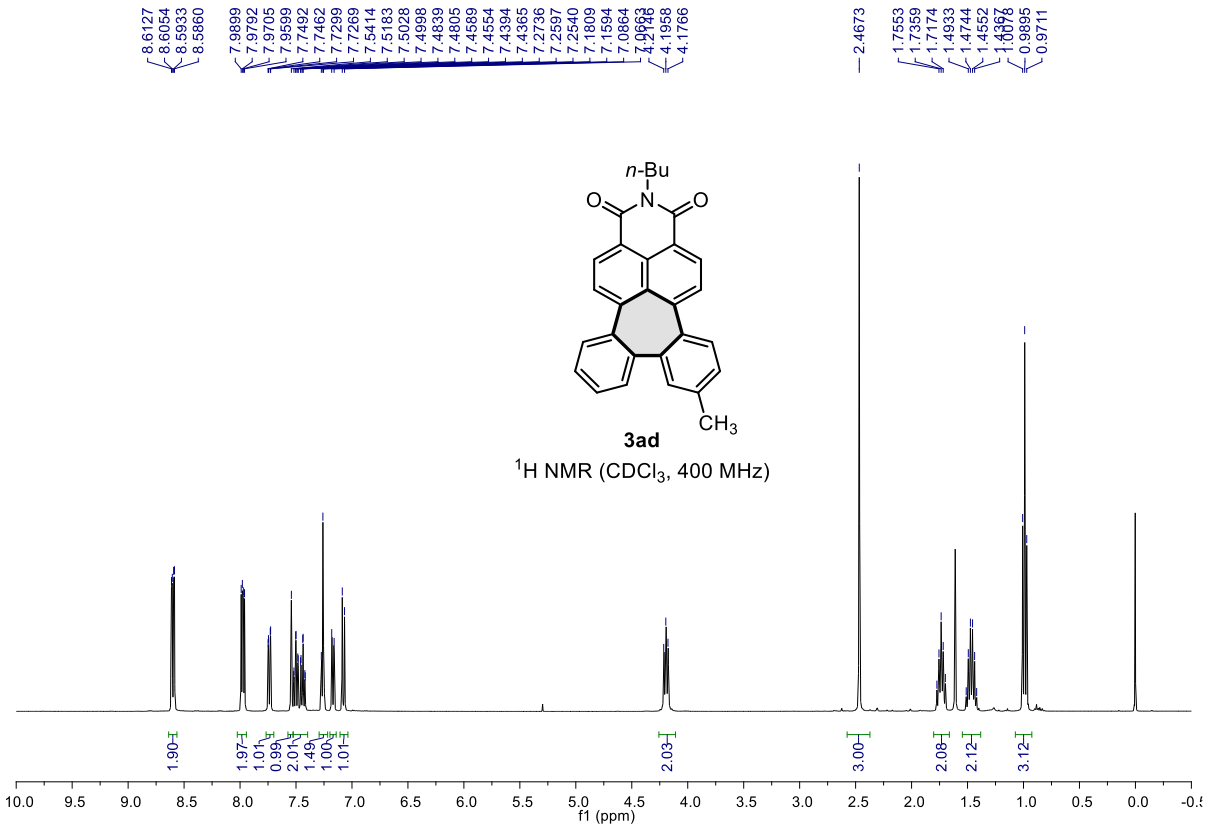
f1 (ppm)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7.7269
7.5414
7.5183
7.5028
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7.4554
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7.1594
7.0864
4.2043
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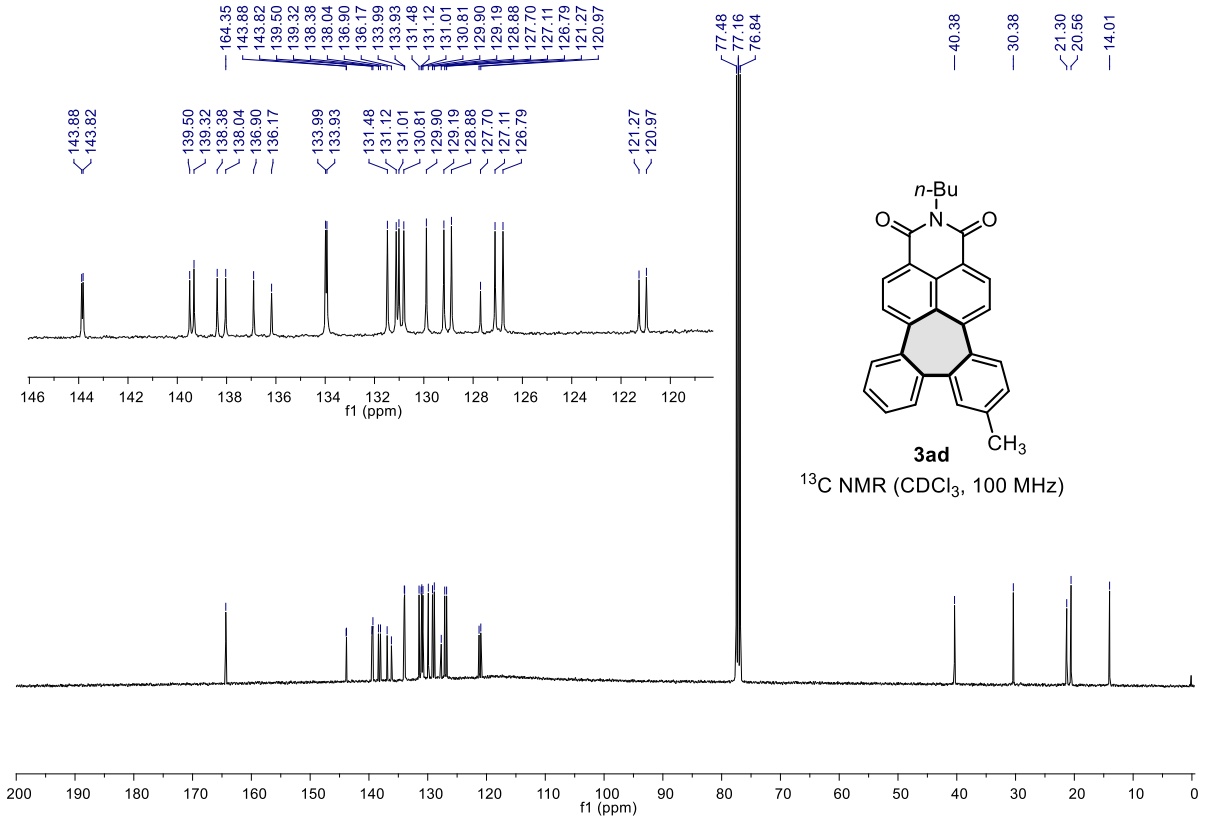
2.4673
1.7553
1.7359
1.7174
1.4933
1.4744
1.4552
1.0078
0.9895
0.9711
n-Bu
N
O
O
CH3
3ad
1H NMR (CDCl3, 400 MHz)
1.90
1.97
1.01
0.99
2.01
1.49
1.00
1.01
2.03
3.00
2.08
2.12
3.12
f1 (ppm)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131.12
131.01
130.81
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129.19
128.88
127.70
127.11
126.79
121.27
120.97
77.48
77.16
76.84
40.38
30.38
21.30
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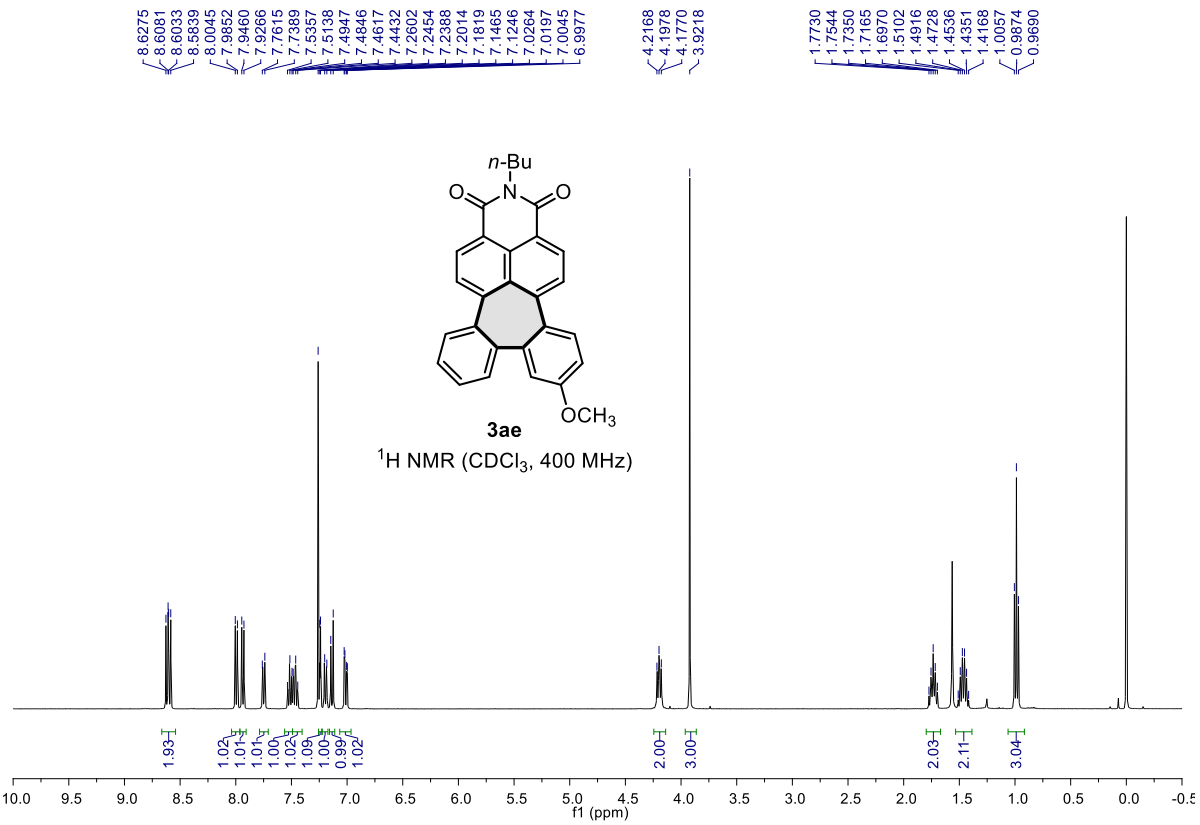
n-Bu
N
O
O
CH3
3ad
13C NMR (CDCl3, 100 MHz)
f1 (ppm)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7.7615
7.7389
7.5357
7.5138
7.4947
7.4846
7.4617
7.4432
7.2602
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7.2388
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6.9977
4.2168
4.1978
4.1770
3.9218
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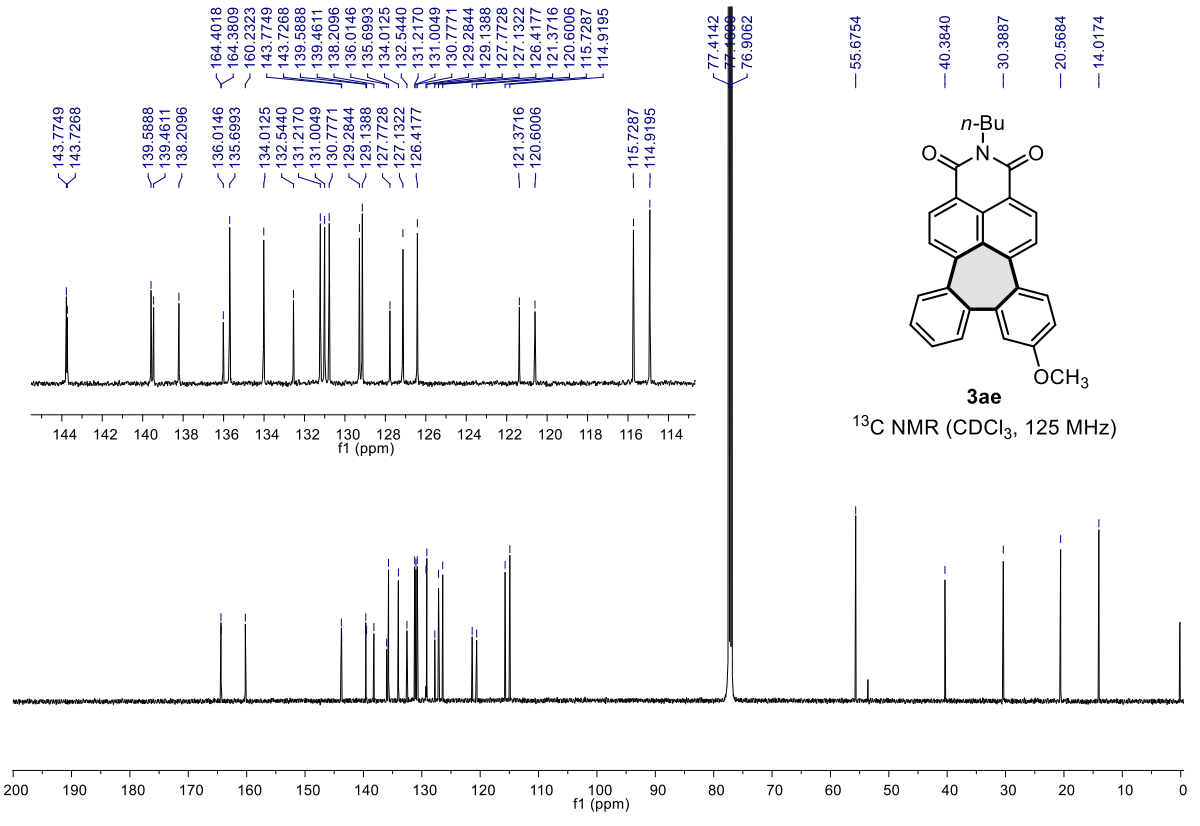
1.7350
1.7165
1.6970
1.5102
1.4916
1.4728
1.4536
1.4351
1.4168
1.0057
0.9874
0.9690
n-Bu
N
O
O
OCH3
3ae
1H NMR (CDCl3, 400 MHz)
1.93
1.02
1.01
1.01
1.00
1.02
1.09
1.00
0.99
1.02
2.00
3.00
2.03
2.11
3.04
f1 (ppm)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132.5440
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131.0049
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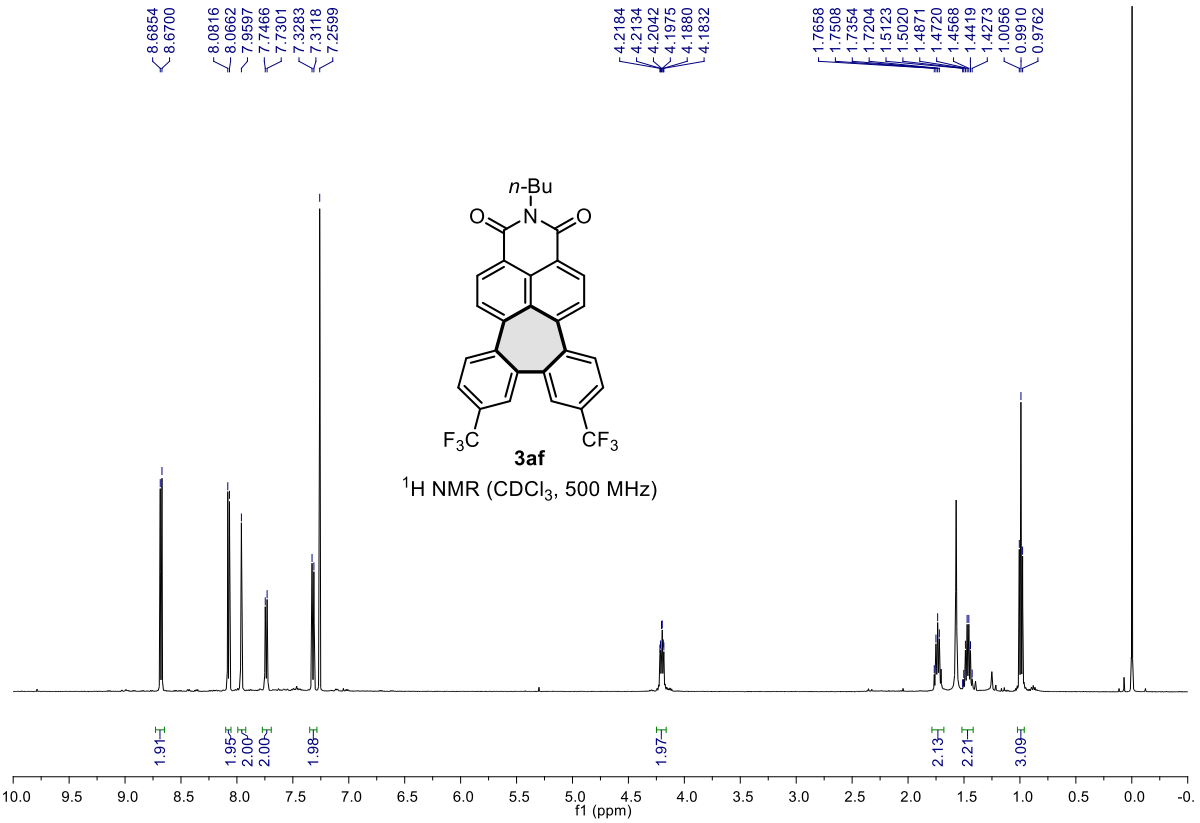
N
O
O
OCH3
3ae
13C NMR (CDCl3, 125 MHz)
f1 (ppm)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7.3118
7.2599
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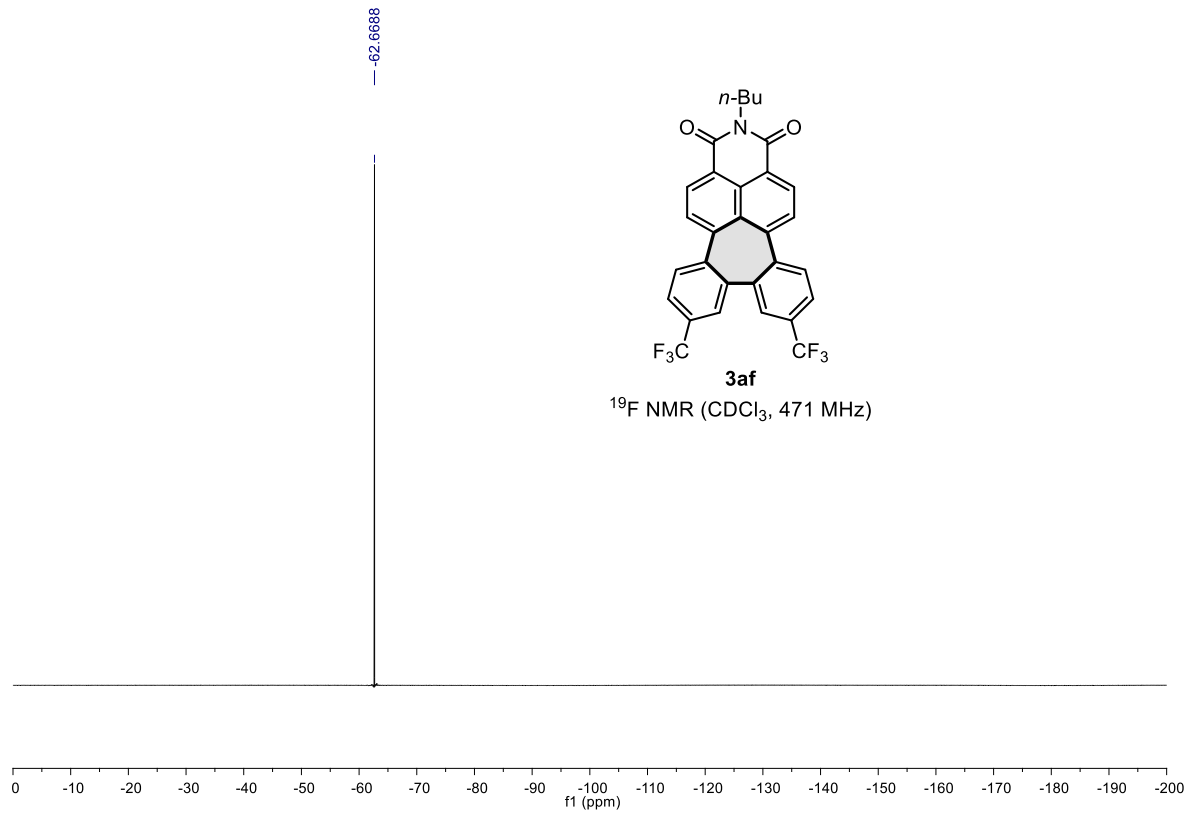
4.2134
4.2042
4.1975
4.1880
4.1832
1.7658
1.7508
1.7354
1.7204
1.5123
1.5020
1.4871
1.4720
1.4568
1.4419
1.4273
1.0056
0.9910
0.9762
n-Bu
O
N
O
F3C
CF3
3af
1H NMR (CDCl3, 500 MHz)
1.91
1.95
2.00
2.00
1.98
1.97
2.13
2.21
3.09
f1 (ppm)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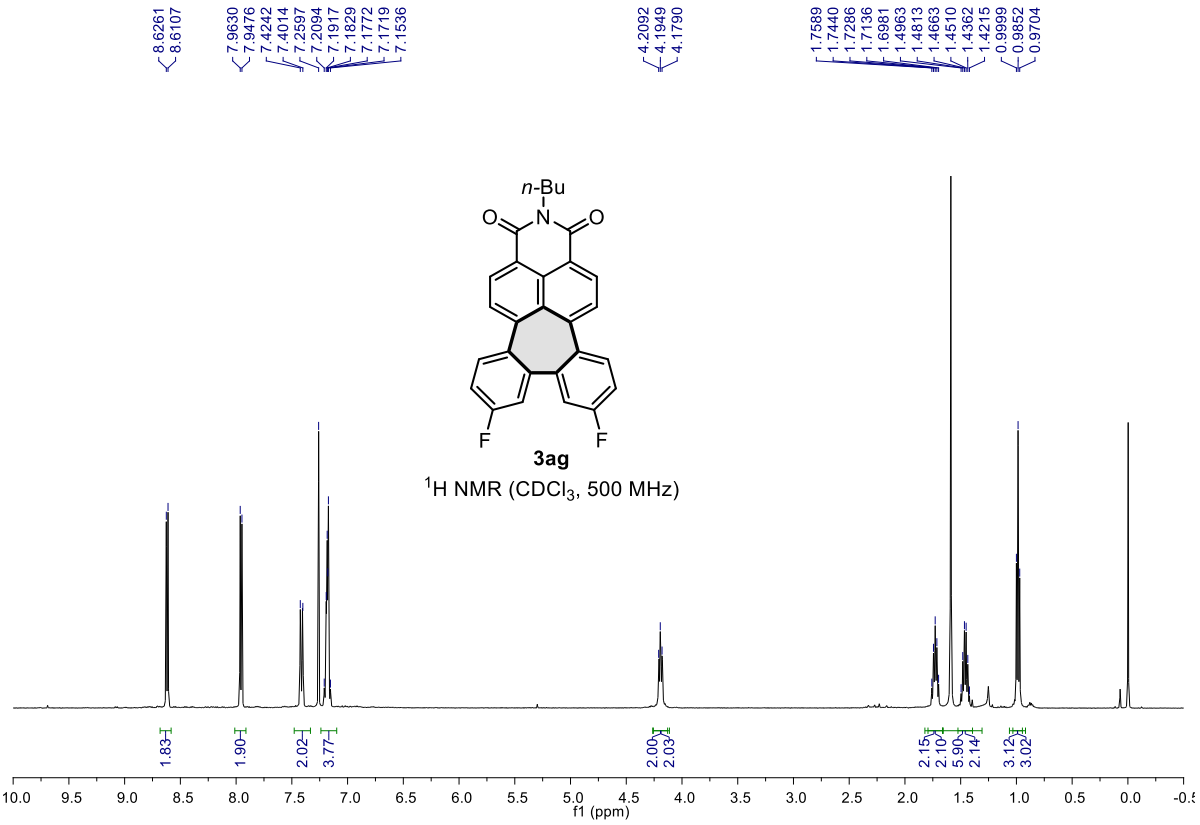
n-Bu
O
N
O
F3C
CF3
3af
19F NMR (CDCl3, 471 MHz)
f1 (ppm)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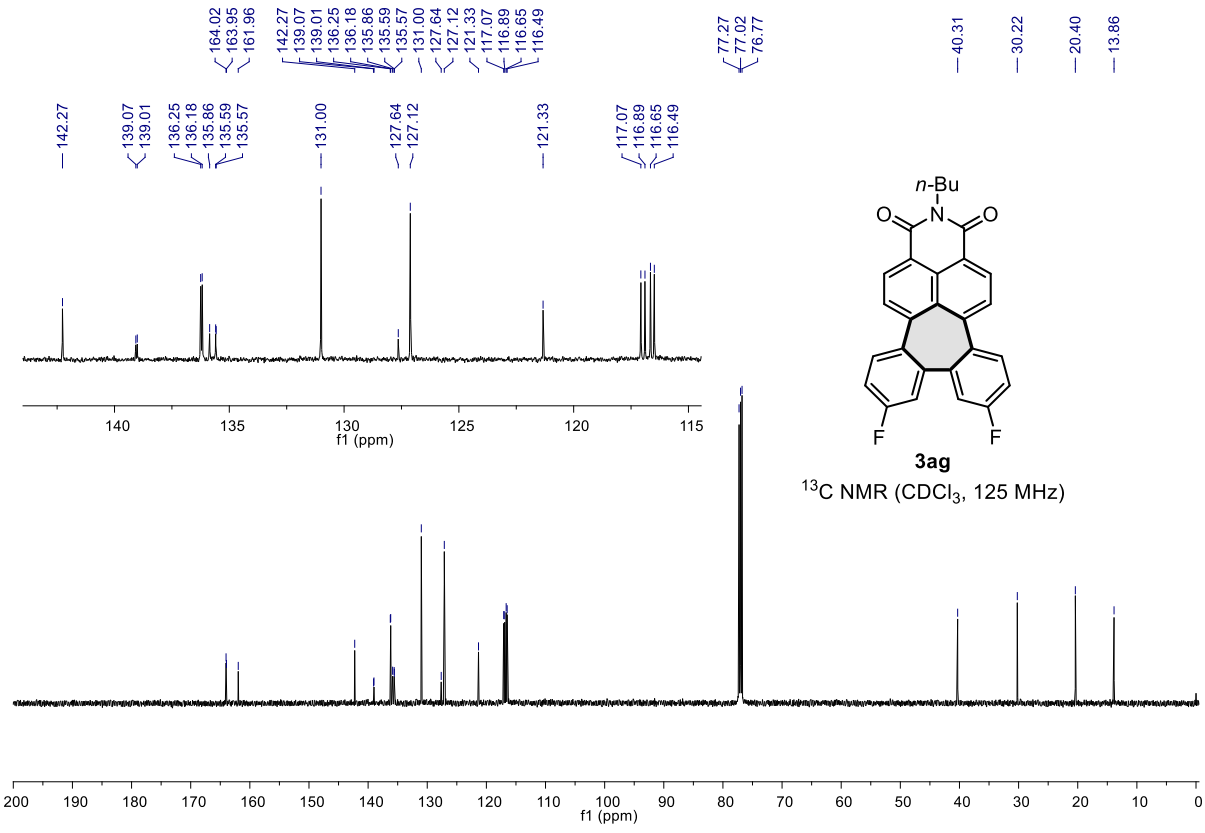
7.1917
7.1829
7.1772
7.1719
7.1536
4.2092
4.1949
4.1790
1.7589
1.7440
1.7286
1.7136
1.6981
1.4963
1.4813
1.4663
1.4510
1.4362
1.4215
0.9999
0.9852
0.9704
n-Bu
O
N
O
F
F
3ag
1H NMR (CDCl3, 500 MHz)
1.83
1.90
2.02
3.77
2.00
2.03
2.15
2.10
5.90
2.14
3.12
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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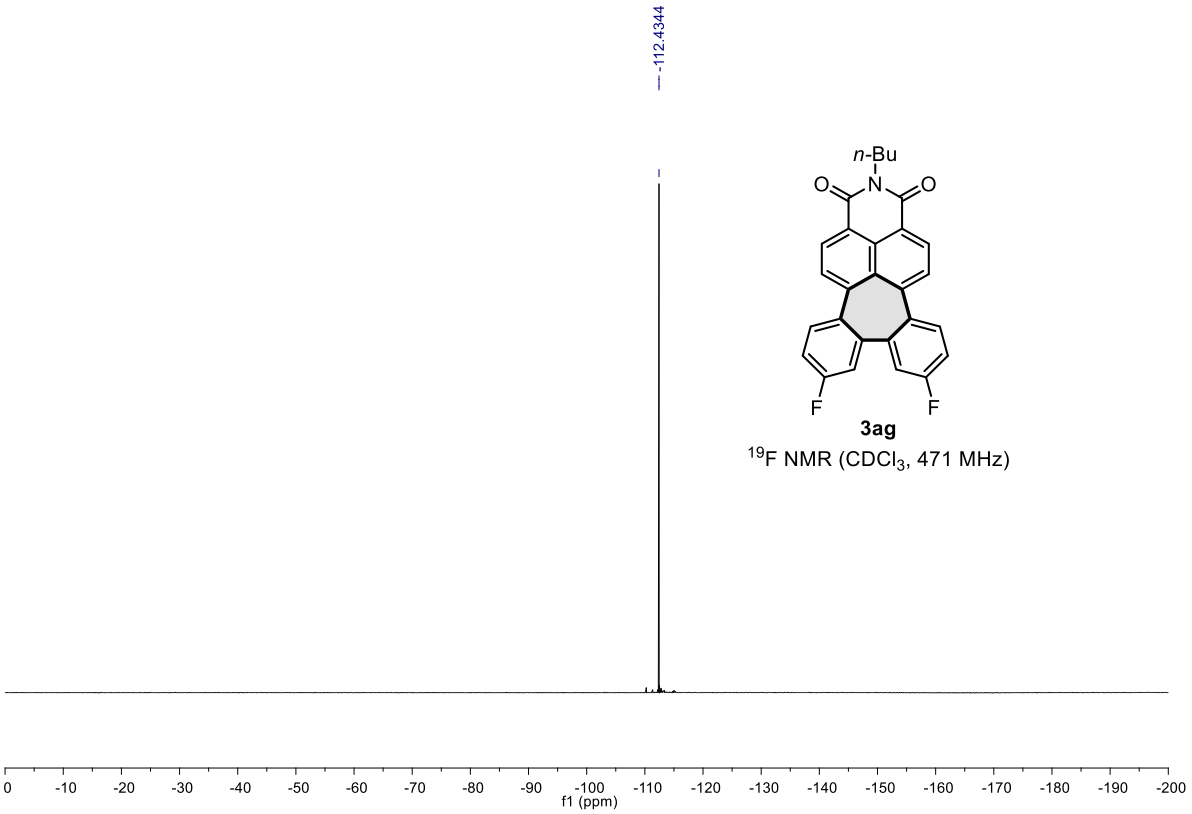
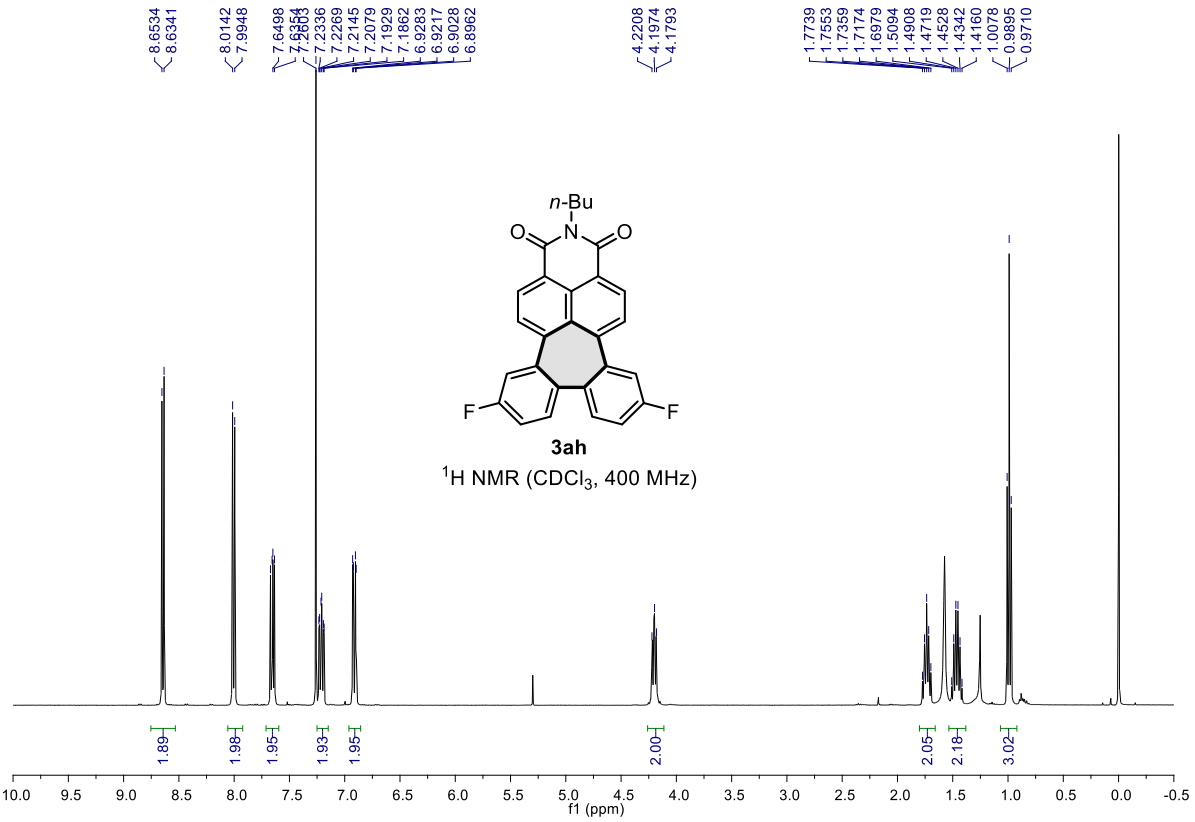
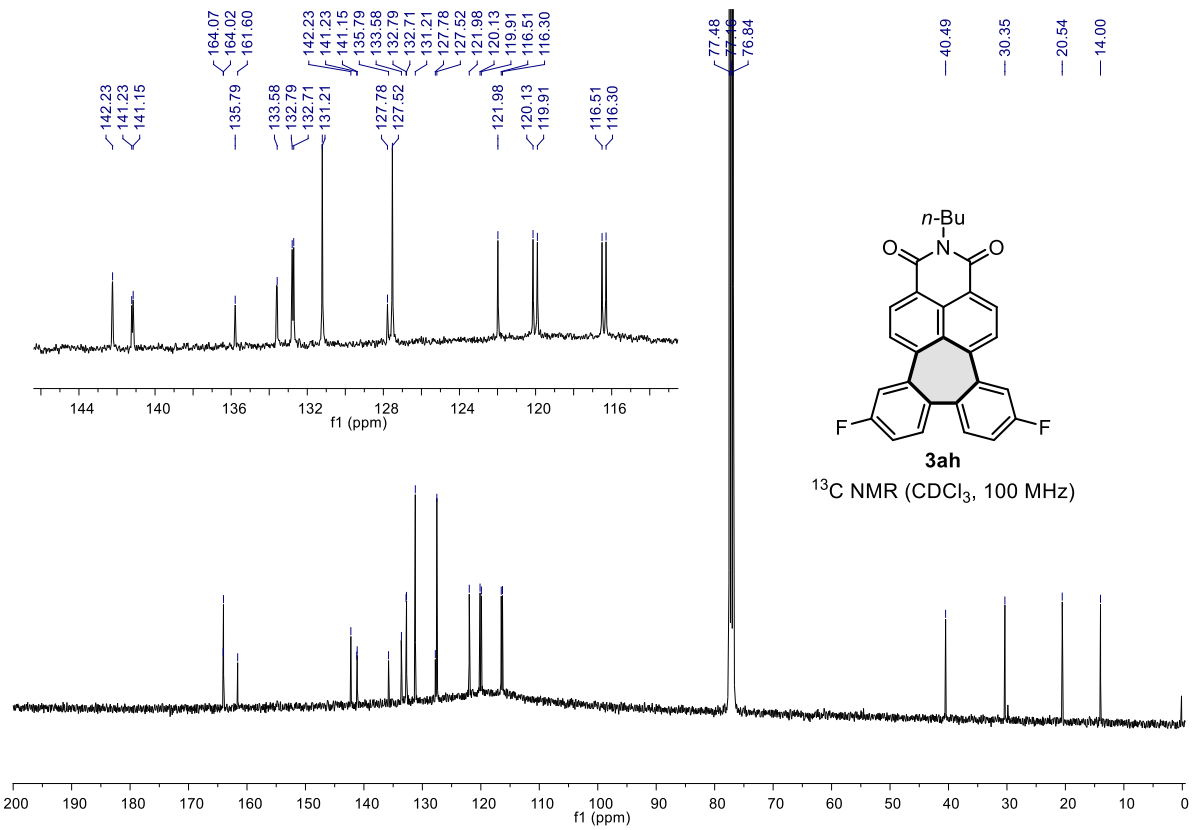
161.96
142.27
139.07
139.01
136.25
136.18
135.86
135.59
135.57
131.00
127.64
127.12
121.33
117.07
116.89
116.65
116.49
77.27
77.02
76.77
40.31
30.22
20.40
13.86
n-Bu
O
N
O
F
F
3ag
13C NMR (CDCl3, 125 MHz)
140 135 130 125 120 115
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

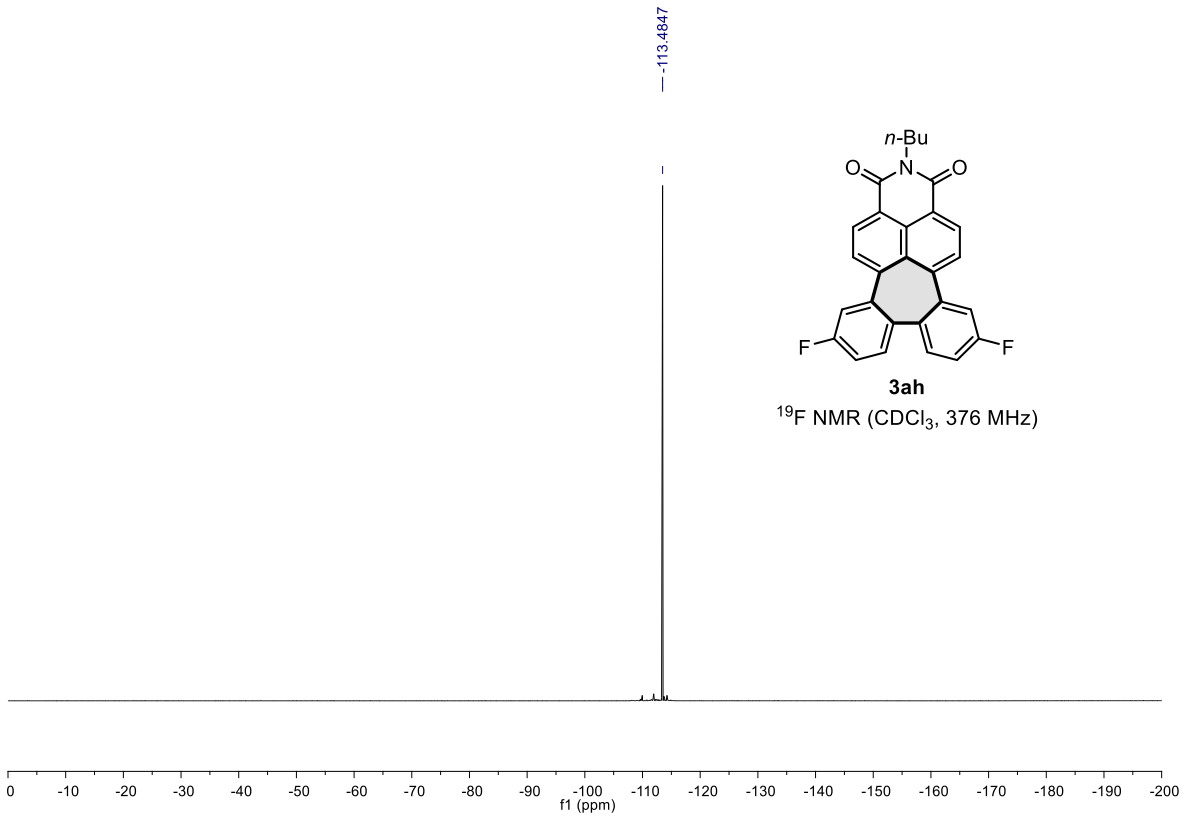


3ag

^{19}F NMR ($CDCl_3$, 471 MHz)

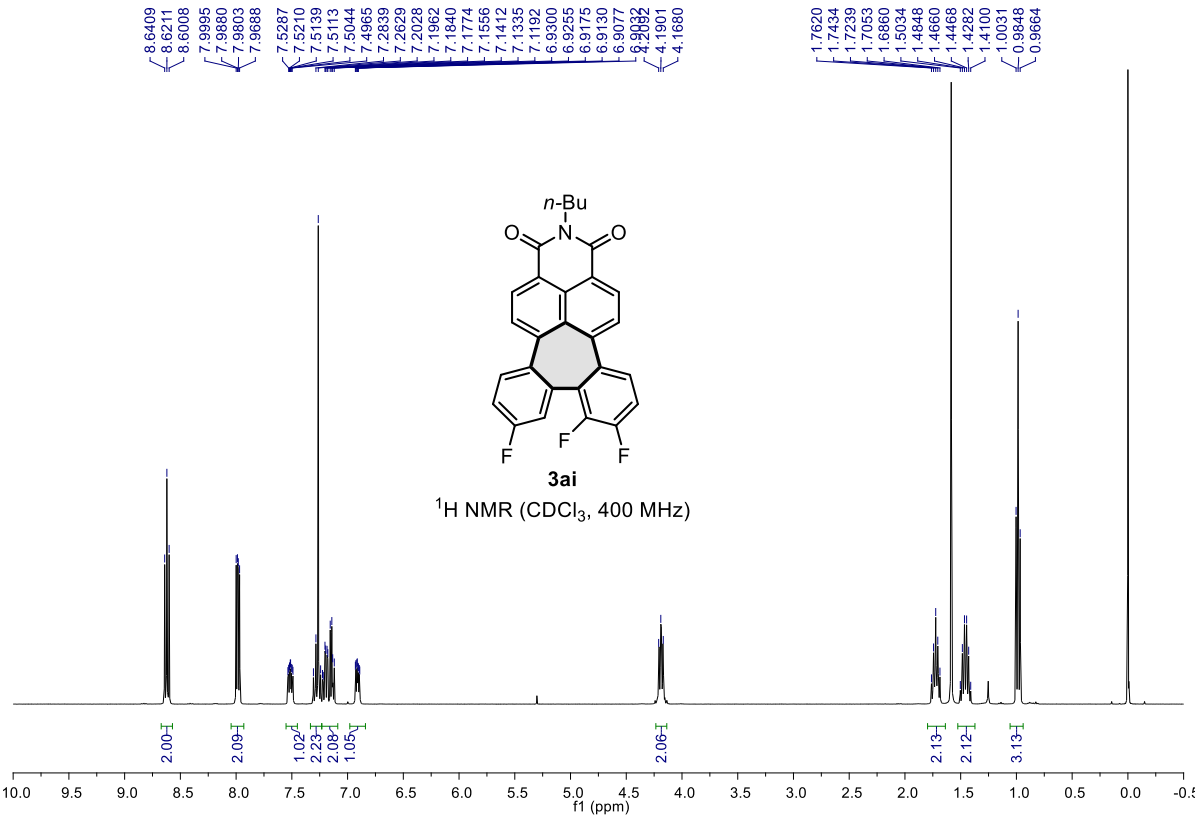

8.6534
8.6341
8.0142
7.9948
7.6498
7.6354
7.2603
7.2336
7.2269
7.2145
7.2079
7.1929
7.1862
6.9283
6.9217
6.9028
6.8962
4.2208
4.1974
4.1793
1.7739
1.7553
1.7359
1.7174
1.6979
1.5094
1.4908
1.4719
1.4528
1.4342
1.4160
1.0078
0.9895
0.9710
n-Bu
O
N
O
F
F
3ah
1H NMR (CDCl3, 400 MHz)
1.89
1.98
1.95
1.93
1.95
2.00
2.05
2.18
3.02
f1 (ppm)

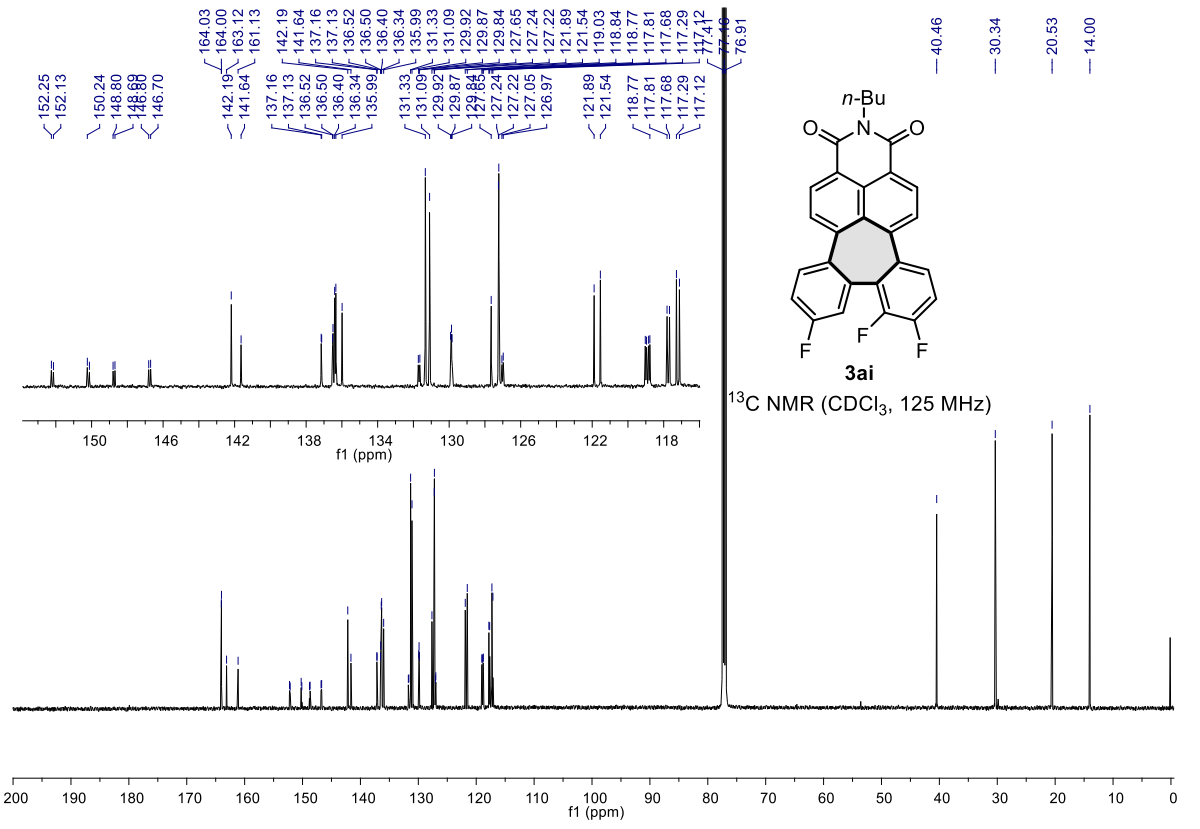

164.07
164.02
161.60
142.23
141.23
141.15
135.79
133.58
132.79
132.71
131.21
127.78
127.52
121.98
120.13
119.91
116.51
116.30
77.48
77.16
76.84
40.49
30.35
20.54
14.00
n-Bu
O
N
O
F
F
3ah
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

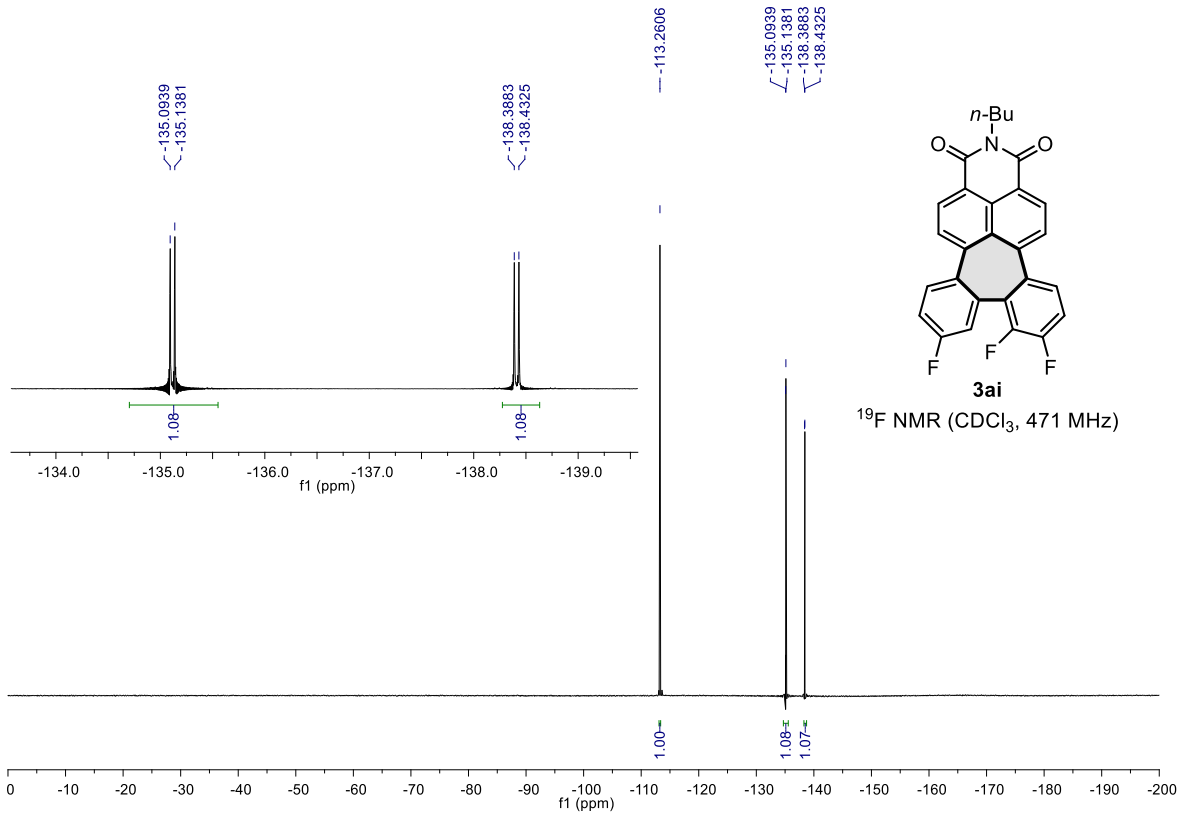


3ah

^{19}F NMR ($CDCl_3$, 376 MHz)

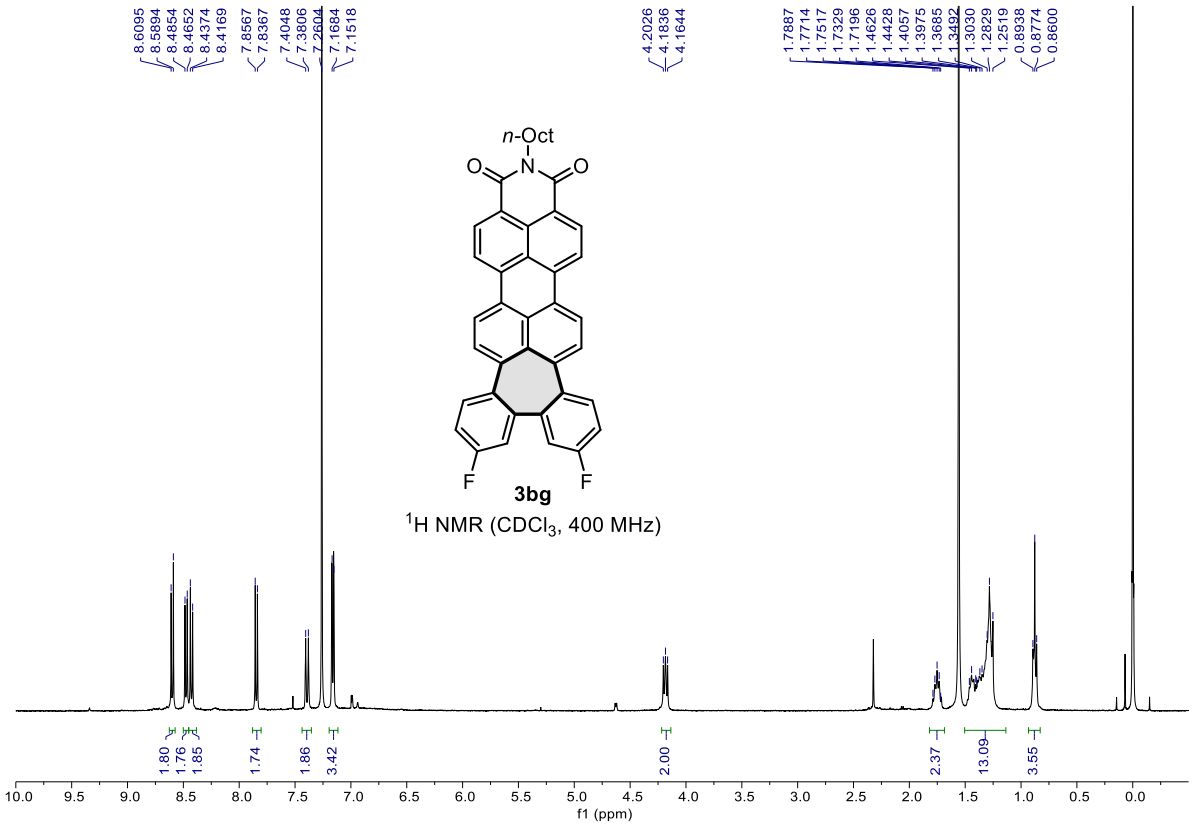

8.6409
8.6211
8.6008
7.9995
7.9880
7.9803
7.9688
7.5287
7.5210
7.5139
7.5113
7.5044
7.4965
7.2839
7.2629
7.2028
7.1962
7.1840
7.1774
7.1556
7.1412
7.1335
7.1192
6.9300
6.9255
6.9175
6.9130
6.9077
4.1901
4.1680
1.7620
1.7434
1.7239
1.7053
1.6860
1.5034
1.4848
1.4660
1.4468
1.4282
1.4100
1.0031
0.9848
0.9664
n-Bu
O
N
O
F
F
F
3ai
1H NMR (CDCl3, 400 MHz)
2.00
2.09
1.02
2.23
2.08
1.05
2.06
2.13
2.12
3.13
f1 (ppm)

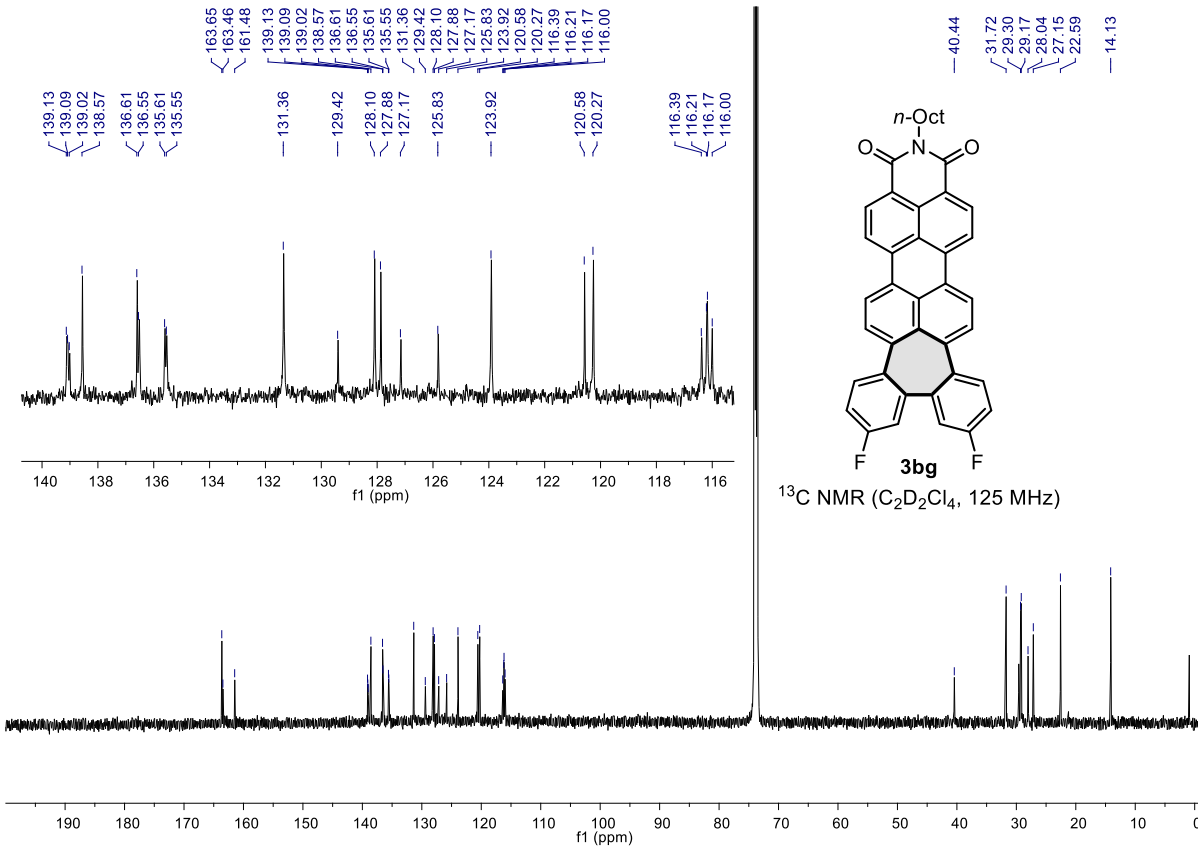

164.03
164.00
163.12
161.13
152.25
152.13
150.24
148.80
146.70
142.19
141.64
137.16
137.13
136.52
136.50
136.40
136.34
136.52
136.50
136.40
136.34
135.99
131.33
131.09
131.33
129.92
129.87
129.84
127.24
127.22
127.65
127.24
127.05
126.97
121.89
121.54
119.03
118.84
118.77
117.81
117.68
117.29
117.12
77.41
76.91
40.46
30.34
20.53
14.00
n-Bu
O
N
O
F
F
F
3ai
13C NMR (CDCl3, 125 MHz)
f1 (ppm)

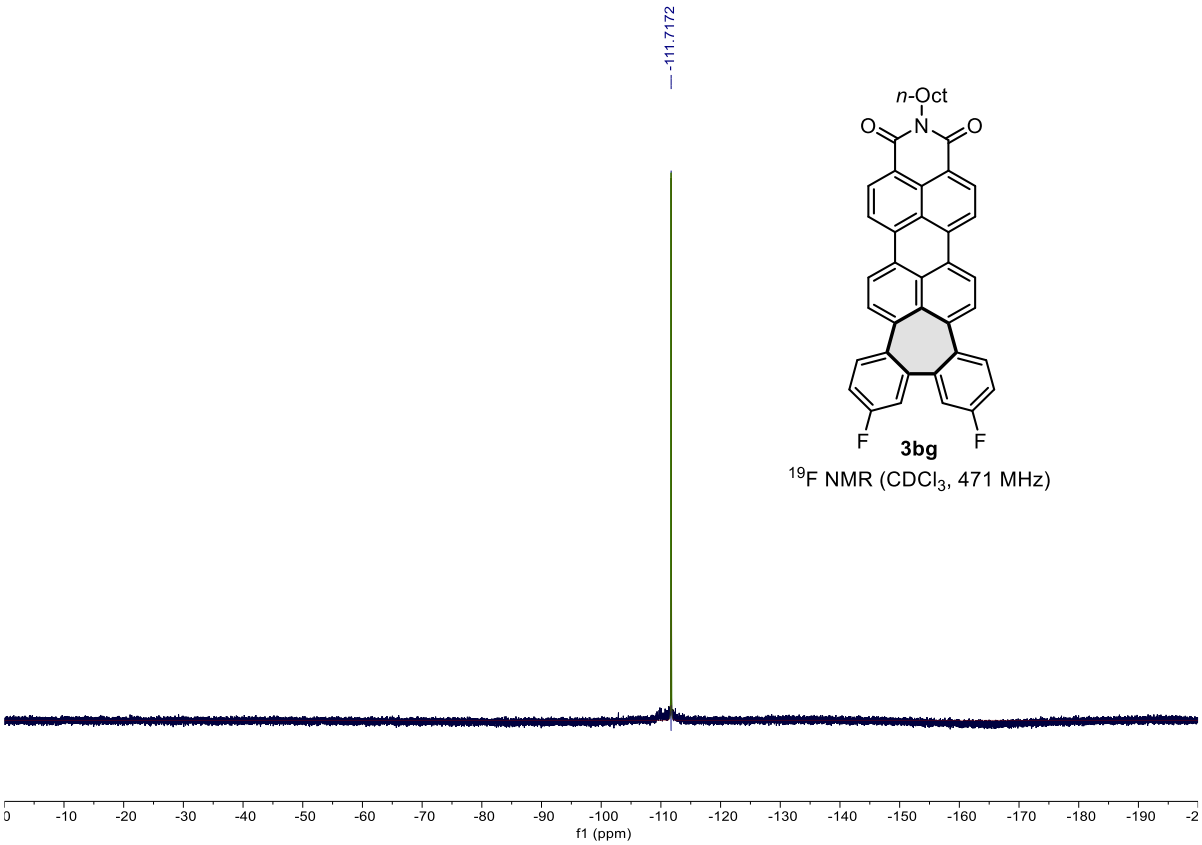


3ai

^{19}F NMR ($CDCl_3$, 471 MHz)

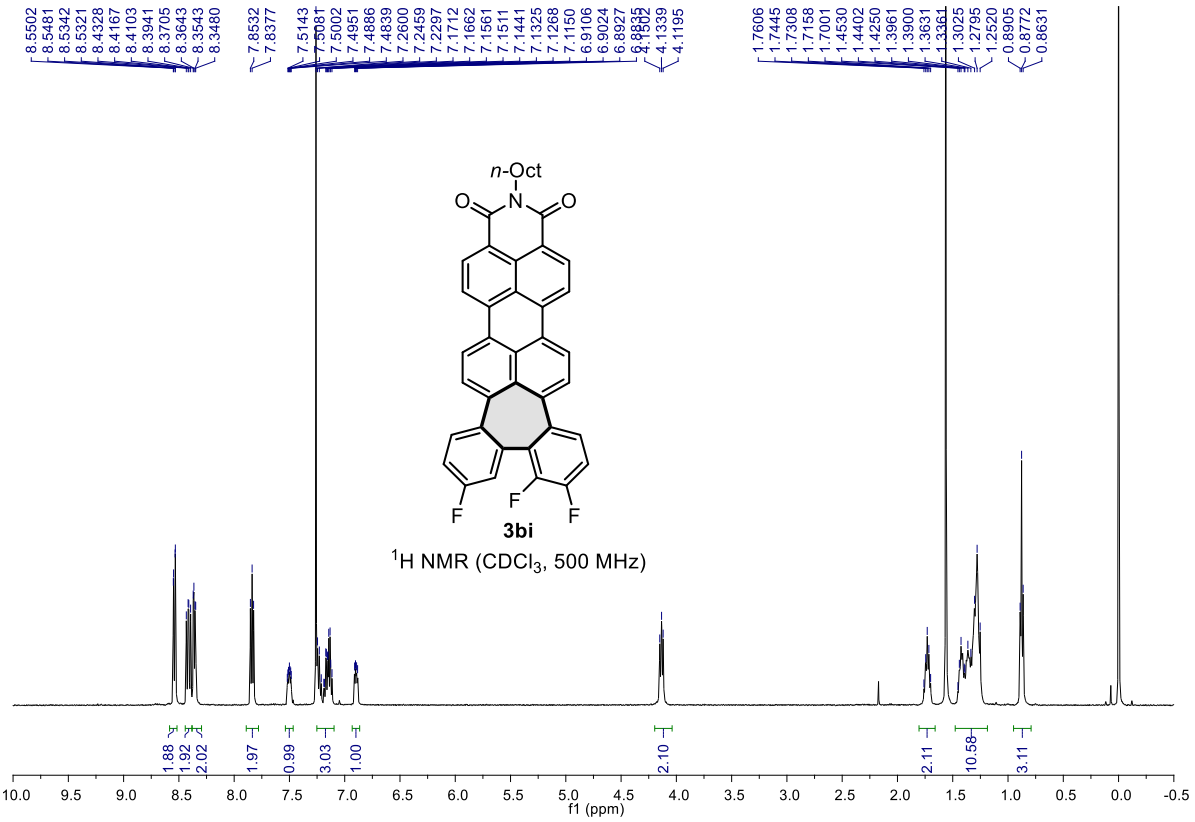

8.6095
8.5894
8.4854
8.4652
8.4374
8.4169
7.8567
7.8367
7.4048
7.3806
7.2604
7.1684
7.1518
4.2026
4.1836
4.1644
1.7887
1.7714
1.7517
1.7329
1.7196
1.4626
1.4428
1.4057
1.3975
1.3685
1.3492
1.3030
1.2829
1.2519
0.8938
0.8774
0.8600
n-Oct
O
N
O
F
F
3bg
1H NMR (CDCl3, 400 MHz)
1.80
1.76
1.85
1.74
1.86
3.42
2.00
2.37
13.09
3.55
f1 (ppm)

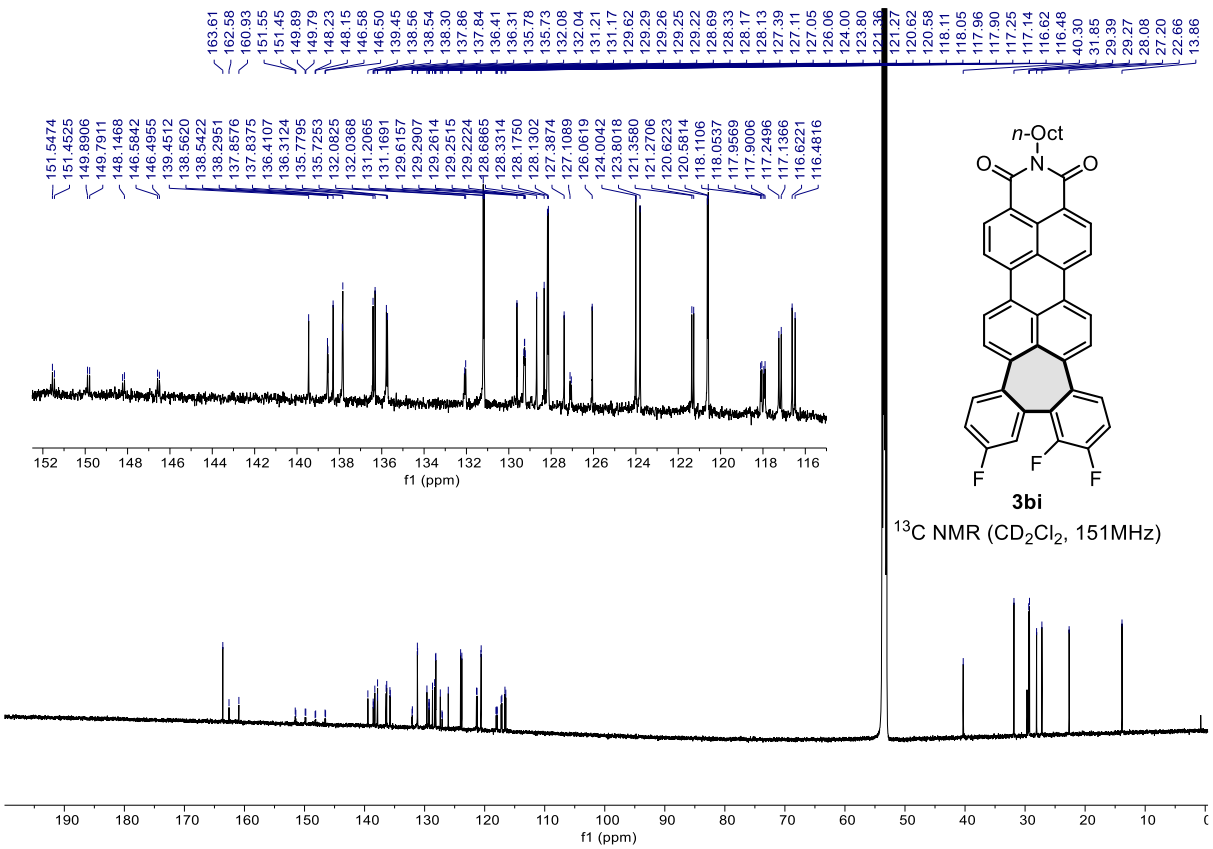

163.65
163.46
161.48
139.13
139.09
139.02
138.57
136.61
136.55
135.61
135.55
131.36
129.42
128.10
127.88
127.17
125.83
123.92
120.58
120.27
116.39
116.21
116.17
116.00
40.44
31.72
29.30
29.17
28.04
27.15
22.59
14.13
n-Oct
O
N
O
F
F
3bg
13C NMR (C2D2Cl4, 125 MHz)
f1 (ppm)

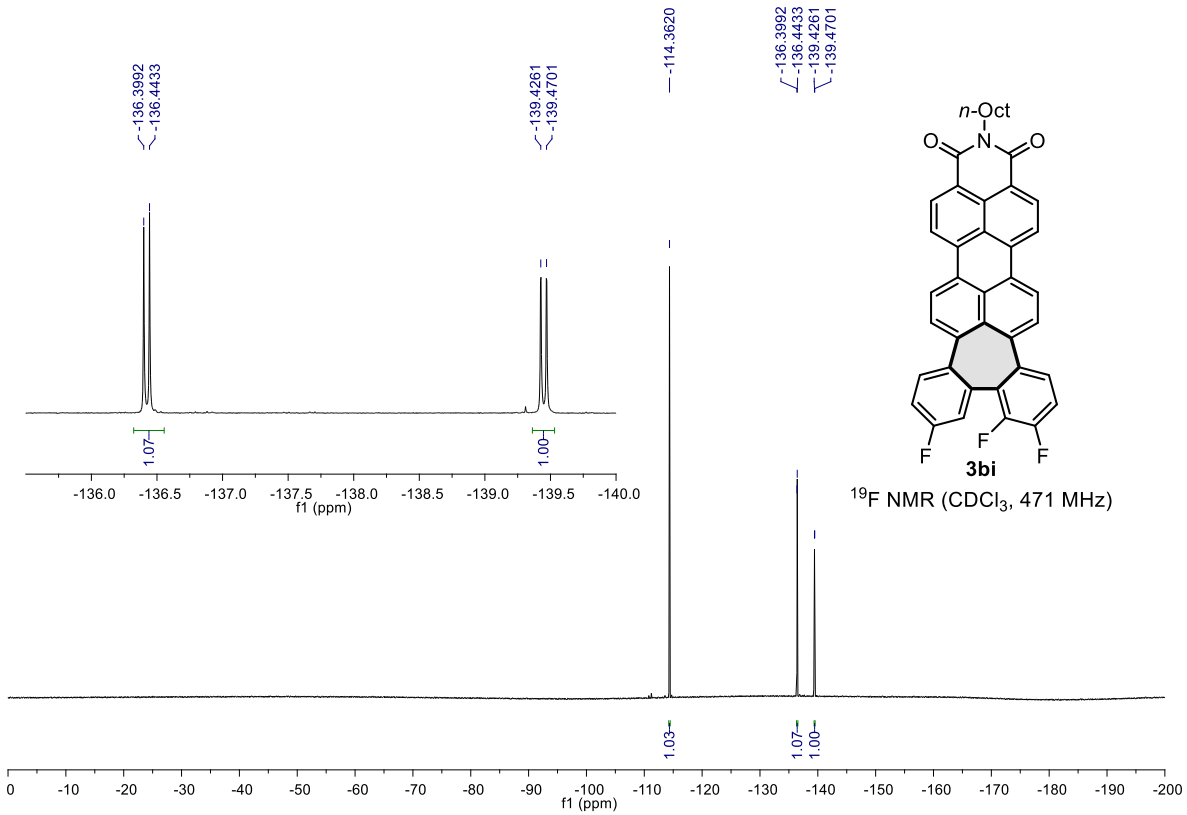


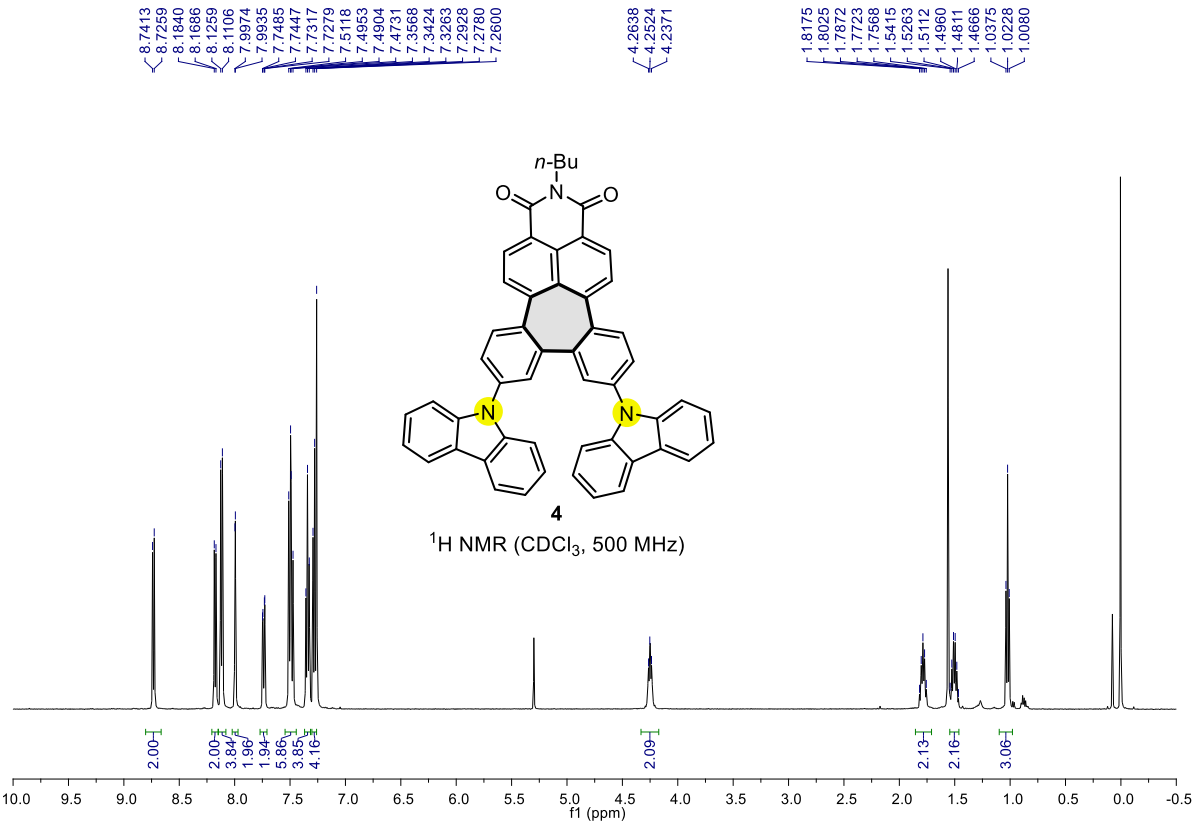
3bg

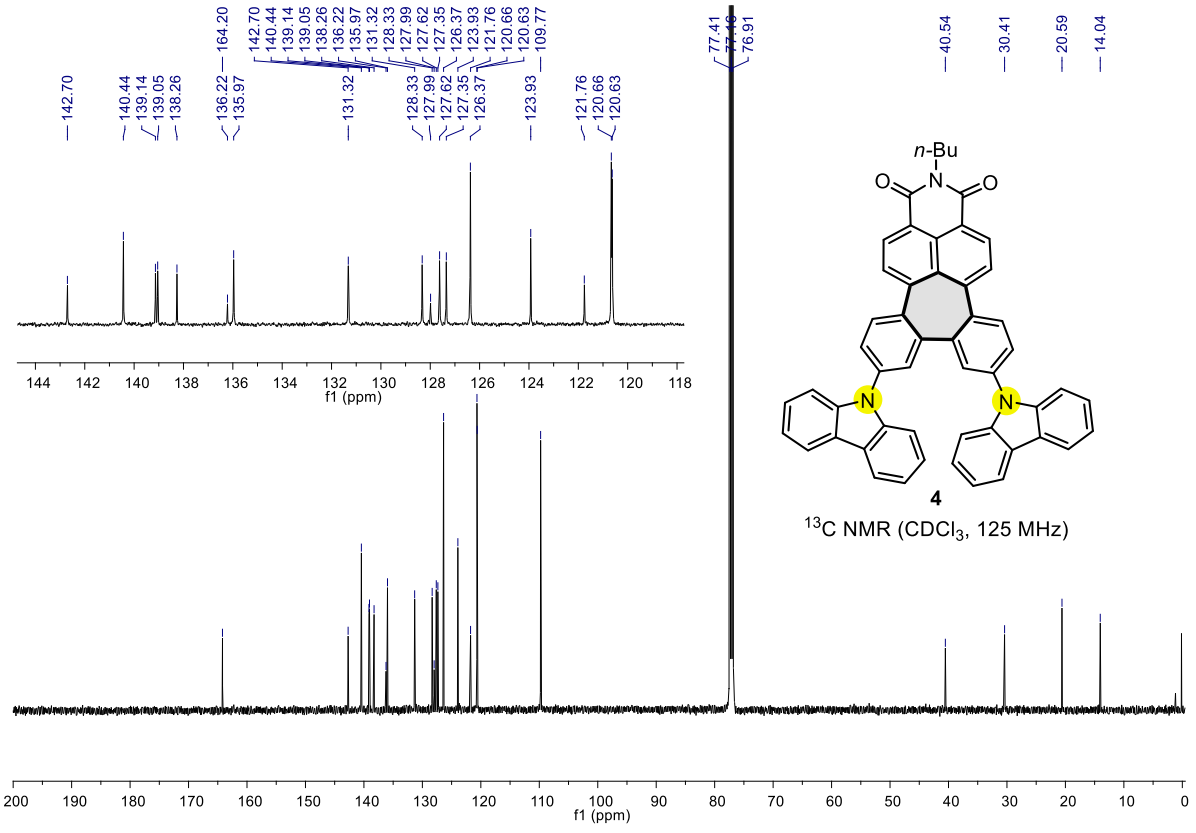
^{19}F NMR ($CDCl_3$, 471 MHz)

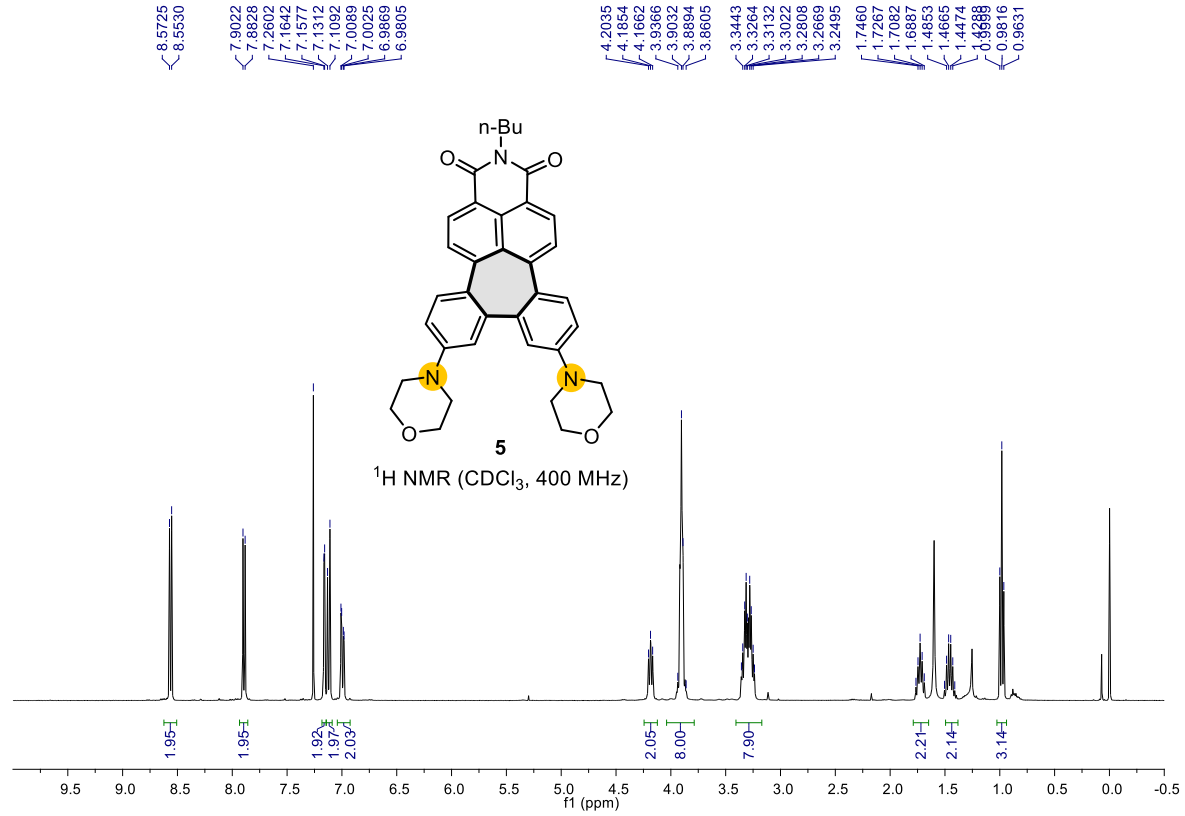

n-Oct
N
O
O
F
F
F
3bi
1H NMR (CDCl3, 500 MHz)
f1 (ppm)

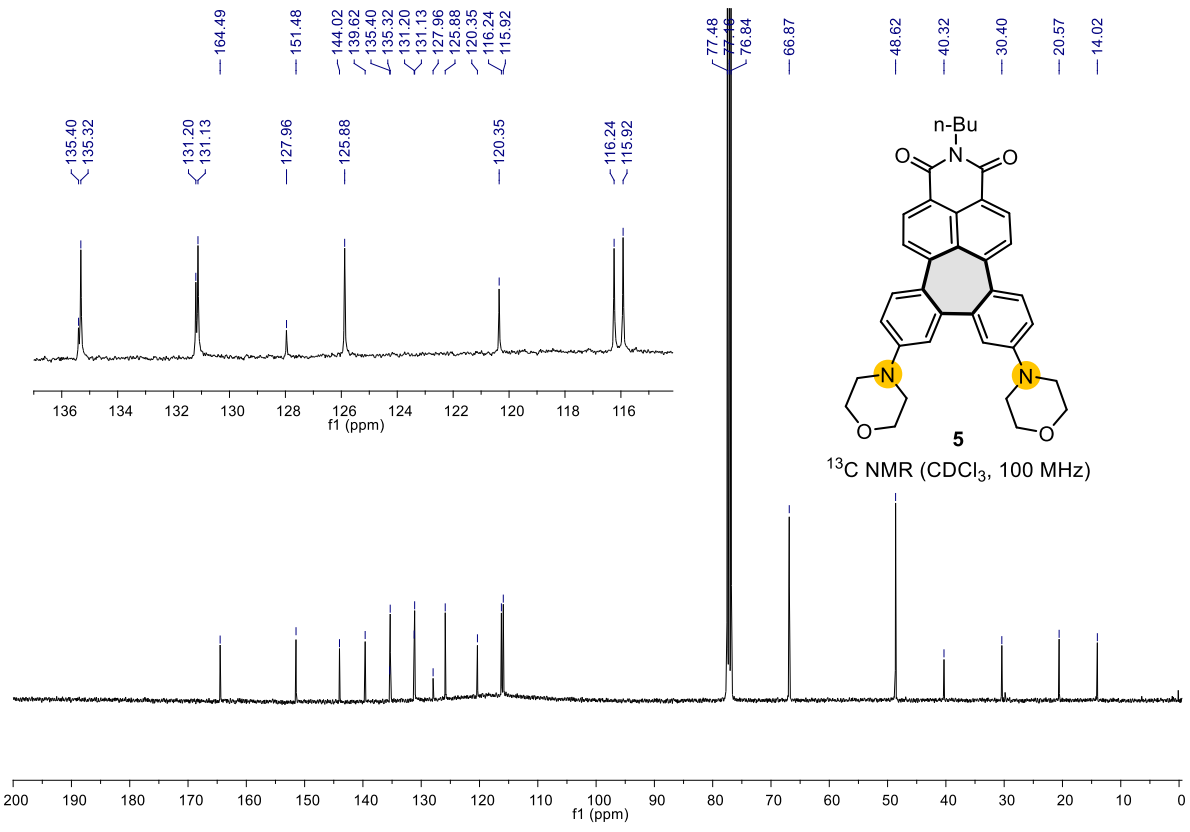

n-Oct
N
O
O
F
F
F
3bi
13C NMR (CD2Cl2, 151MHz)
f1 (ppm)

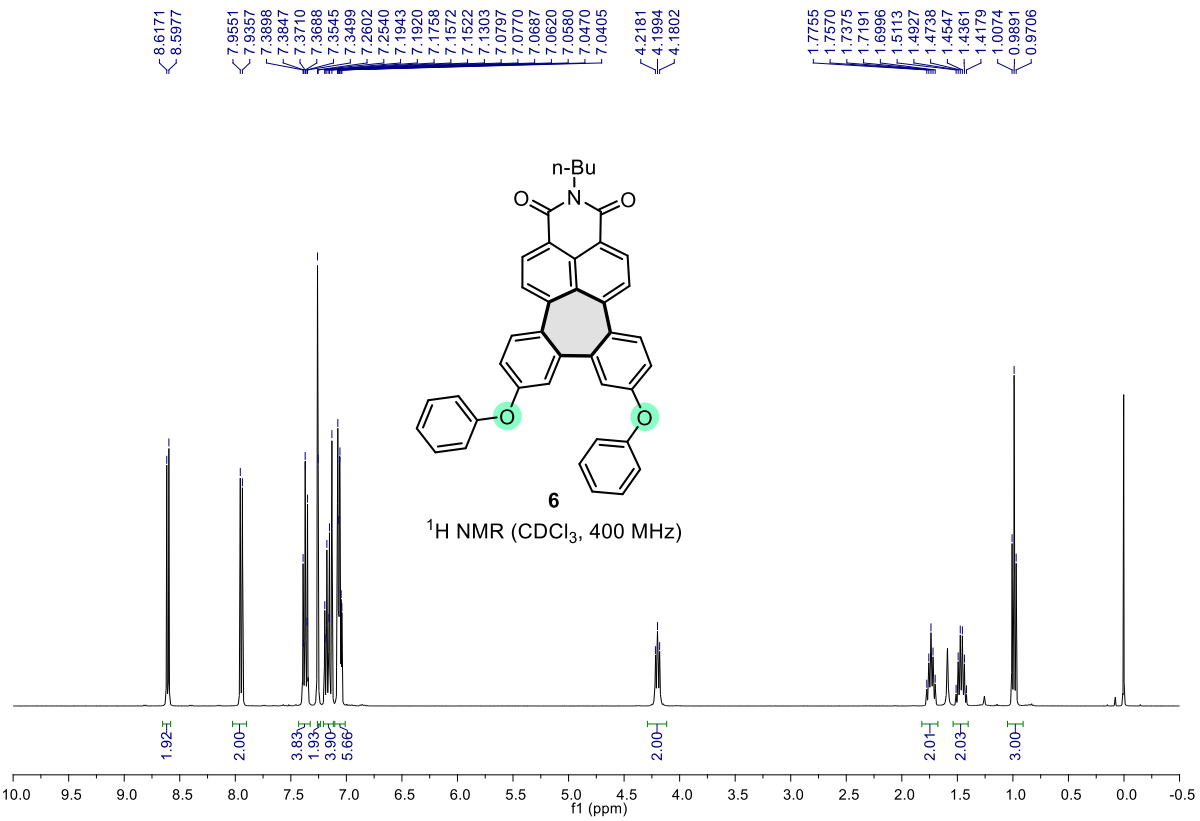

-136.3992
-136.4433
-139.4261
-139.4701
-114.3620
1.07
1.00
1.03
f1 (ppm)
n-Oct
O
N
O
F
F
F
3bi
19F NMR (CDCl3, 471 MHz)

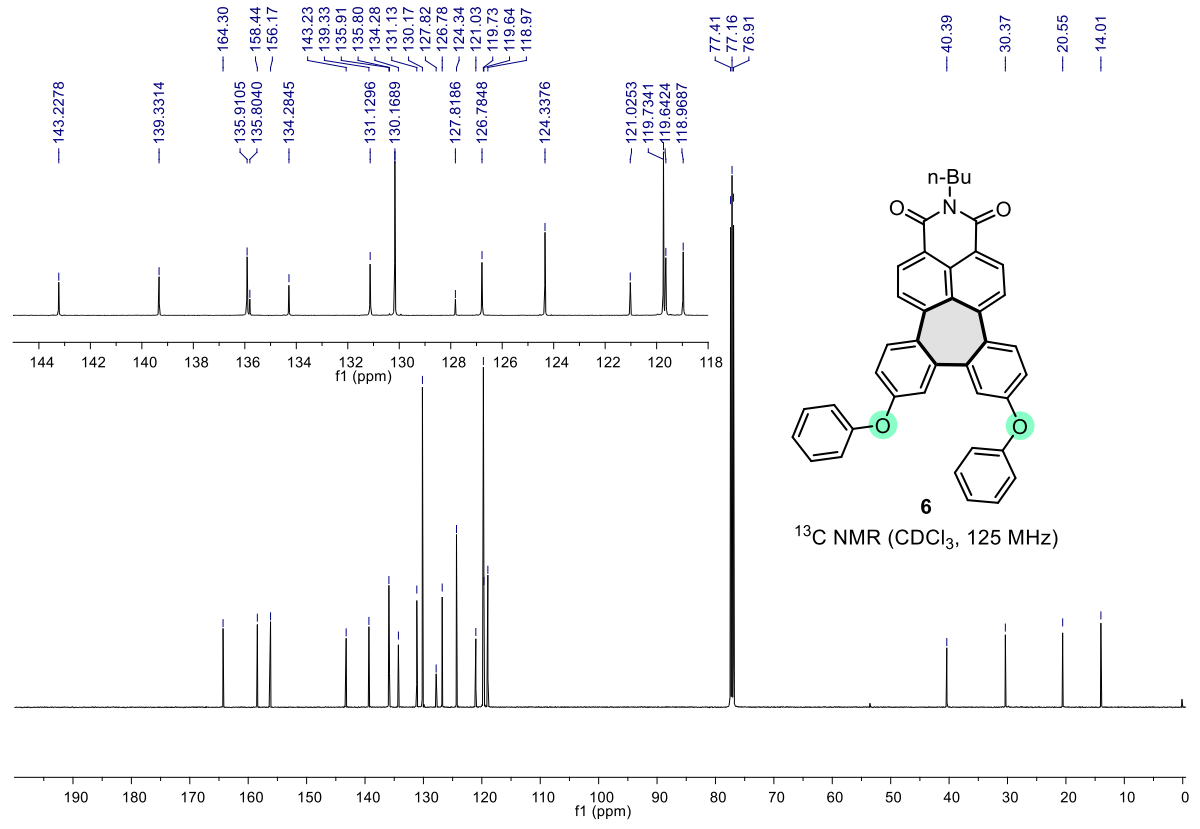

8.7413
8.7259
8.1840
8.1686
8.1259
8.1106
7.9974
7.9935
7.7485
7.7447
7.7317
7.7279
7.5118
7.4953
7.4904
7.4731
7.3568
7.3424
7.3263
7.2928
7.2780
7.2600
4.2638
4.2524
4.2371
1.8175
1.8025
1.7872
1.7723
1.7568
1.5415
1.5263
1.5112
1.4960
1.4811
1.4666
1.0375
1.0228
1.0080
n-Bu
O
N
O
N
N
4
1H NMR (CDCl3, 500 MHz)
2.00
2.00
3.84
1.96
1.94
5.86
3.85
4.16
2.09
2.13
2.16
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

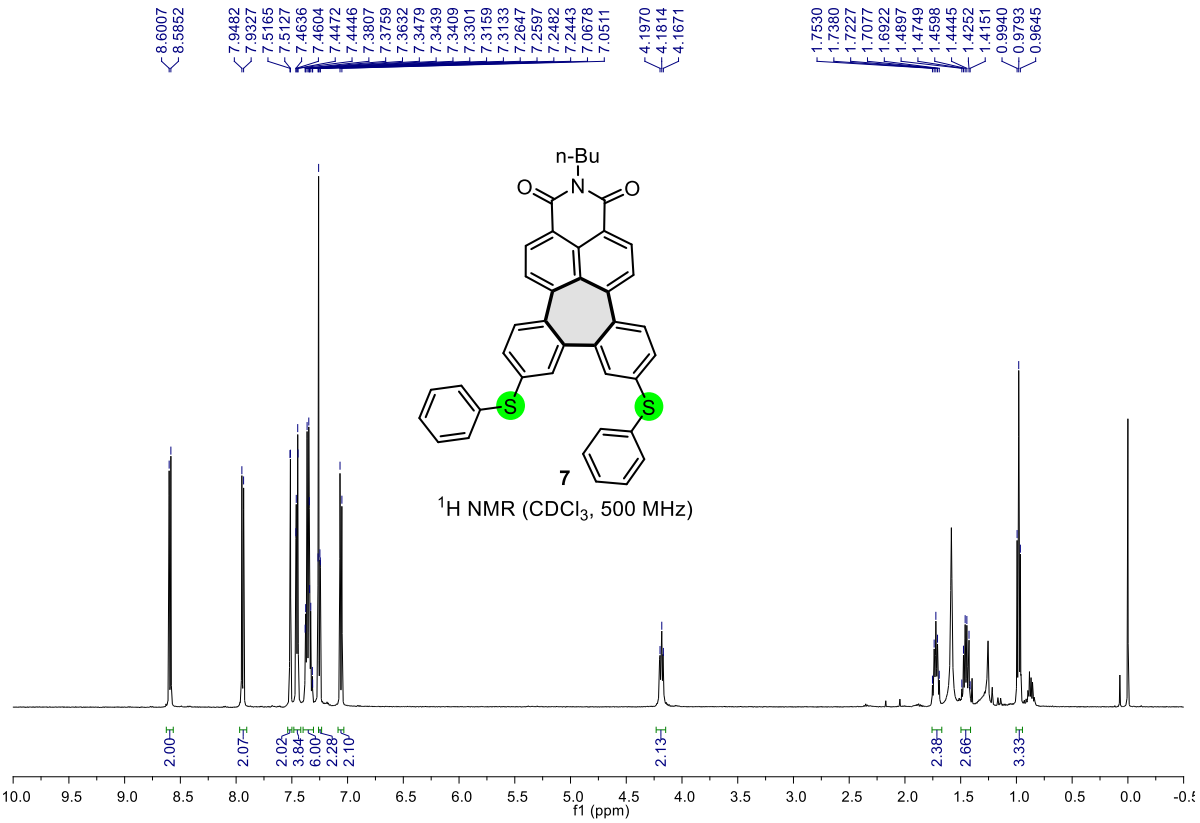

142.70
140.44
139.14
139.05
138.26
136.22
135.97
164.20
131.32
128.33
127.99
127.62
127.35
126.37
123.93
121.76
120.66
120.63
109.77
77.41
77.16
76.91
40.54
30.41
20.59
14.04
n-Bu
O
N
O
N
N
4
13C NMR (CDCl3, 125 MHz)
144 142 140 138 136 134 132 130 128 126 124 122 120 118
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

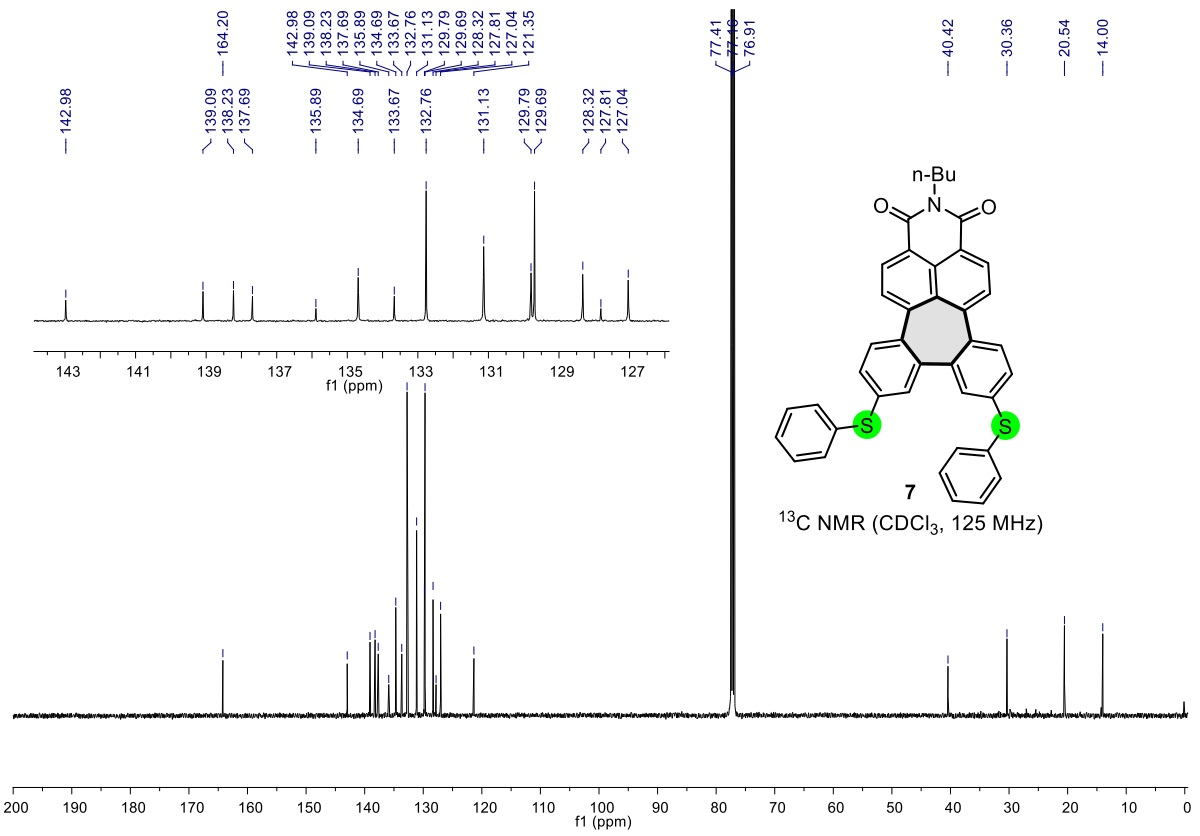

8.5725
8.5530
7.9022
7.8828
7.2602
7.1642
7.1577
7.1312
7.1092
7.0089
7.0025
6.9869
6.9805
4.2035
4.1854
4.1662
3.9366
3.9032
3.8894
3.8605
3.3443
3.3264
3.3132
3.3022
3.2808
3.2669
3.2495
1.7460
1.7267
1.7082
1.6887
1.4853
1.4665
1.4474
0.9816
0.9631
n-Bu
5
1H NMR (CDCl3, 400 MHz)
1.95
1.95
1.92
1.97
2.03
2.05
8.00
7.90
2.21
2.14
3.14
f1 (ppm)

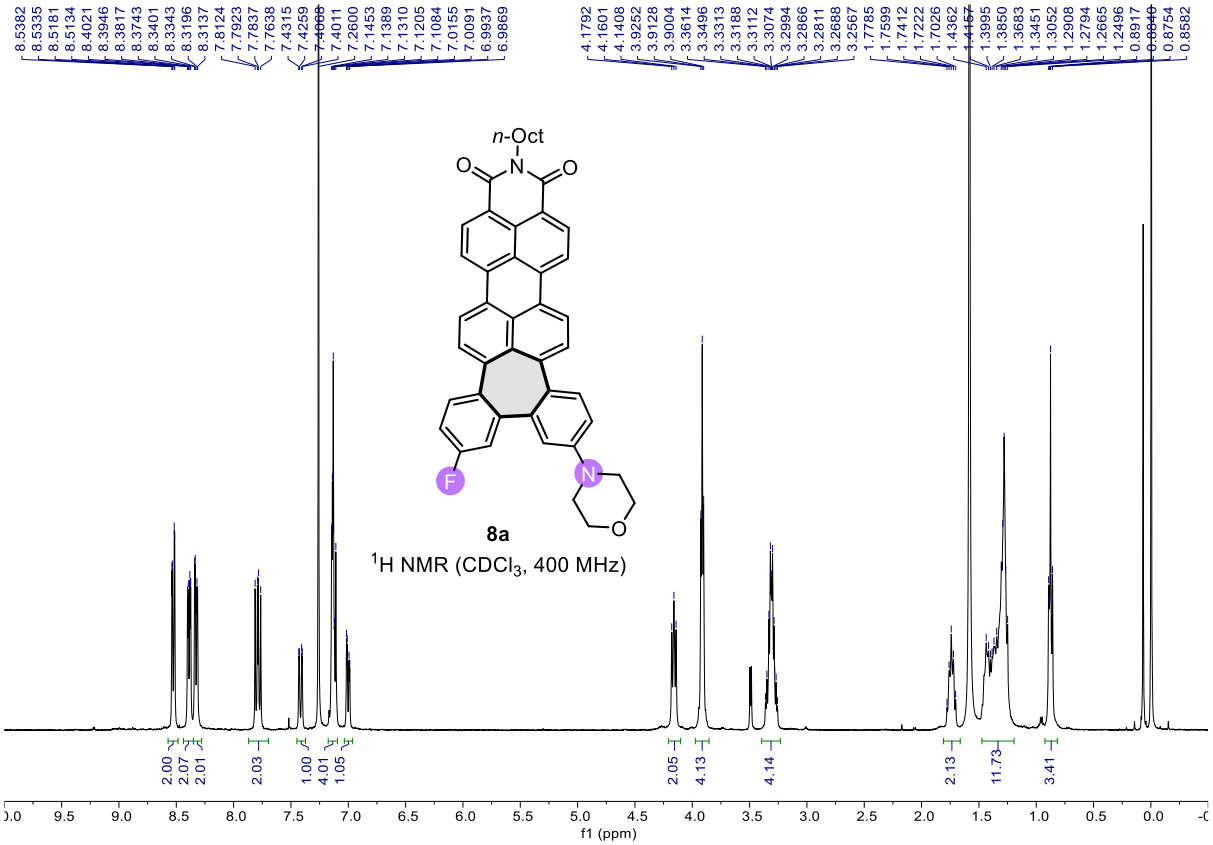

164.49
151.48
144.02
139.62
135.40
135.32
131.20
131.13
127.96
125.88
120.35
116.24
115.92
77.48
77.16
76.84
66.87
48.62
40.32
30.40
20.57
14.02
n-Bu
5
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

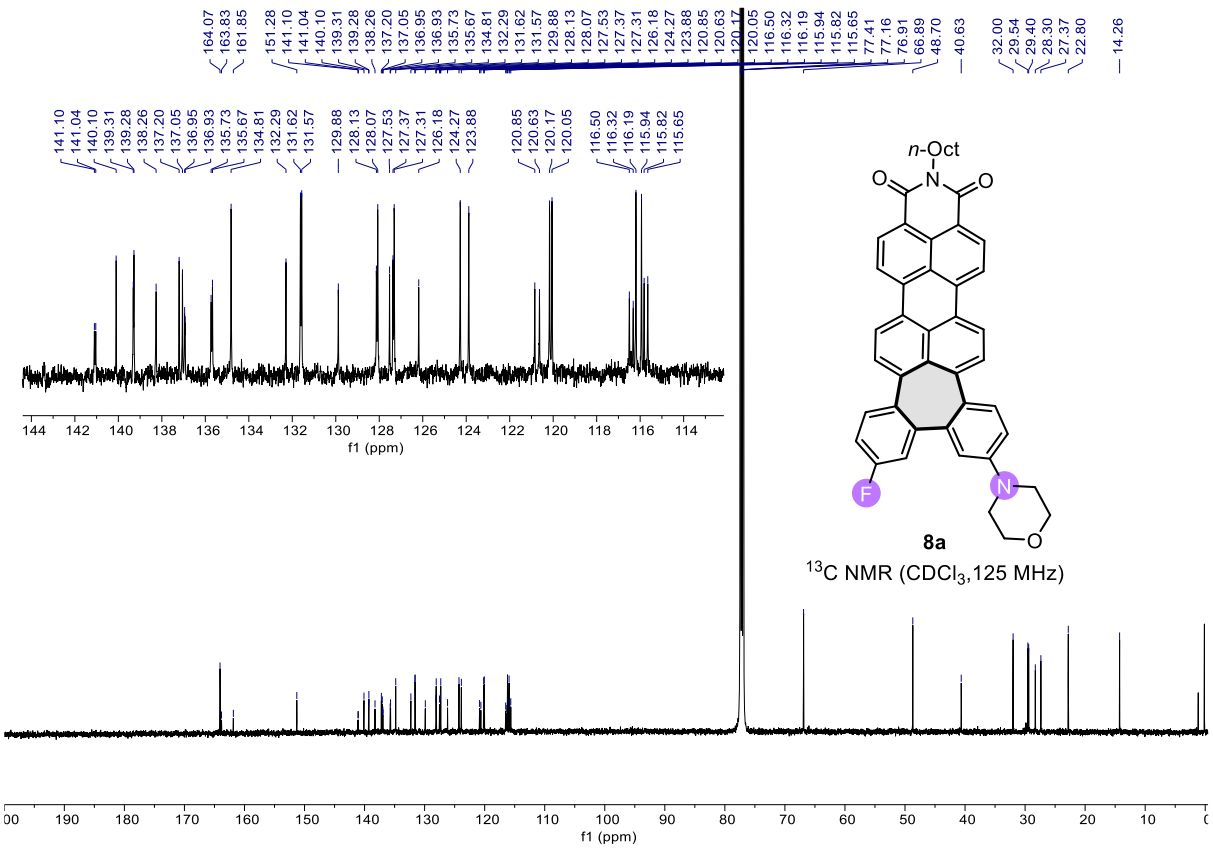

8.6171
8.5977
7.9551
7.9357
7.3898
7.3847
7.3710
7.3688
7.3545
7.3499
7.2602
7.2540
7.1943
7.1920
7.1758
7.1572
7.1522
7.1303
7.0797
7.0770
7.0687
7.0620
7.0580
7.0470
7.0405
4.2181
4.1994
4.1802
1.7755
1.7570
1.7375
1.7191
1.6996
1.5113
1.4927
1.4738
1.4547
1.4361
1.4179
1.0074
0.9891
0.9706
n-Bu
N
O
O
O
O
6
1H NMR (CDCl3, 400 MHz)
1.92
2.00
3.83
1.93
3.90
5.66
2.00
2.01
2.03
3.00
f1 (ppm)

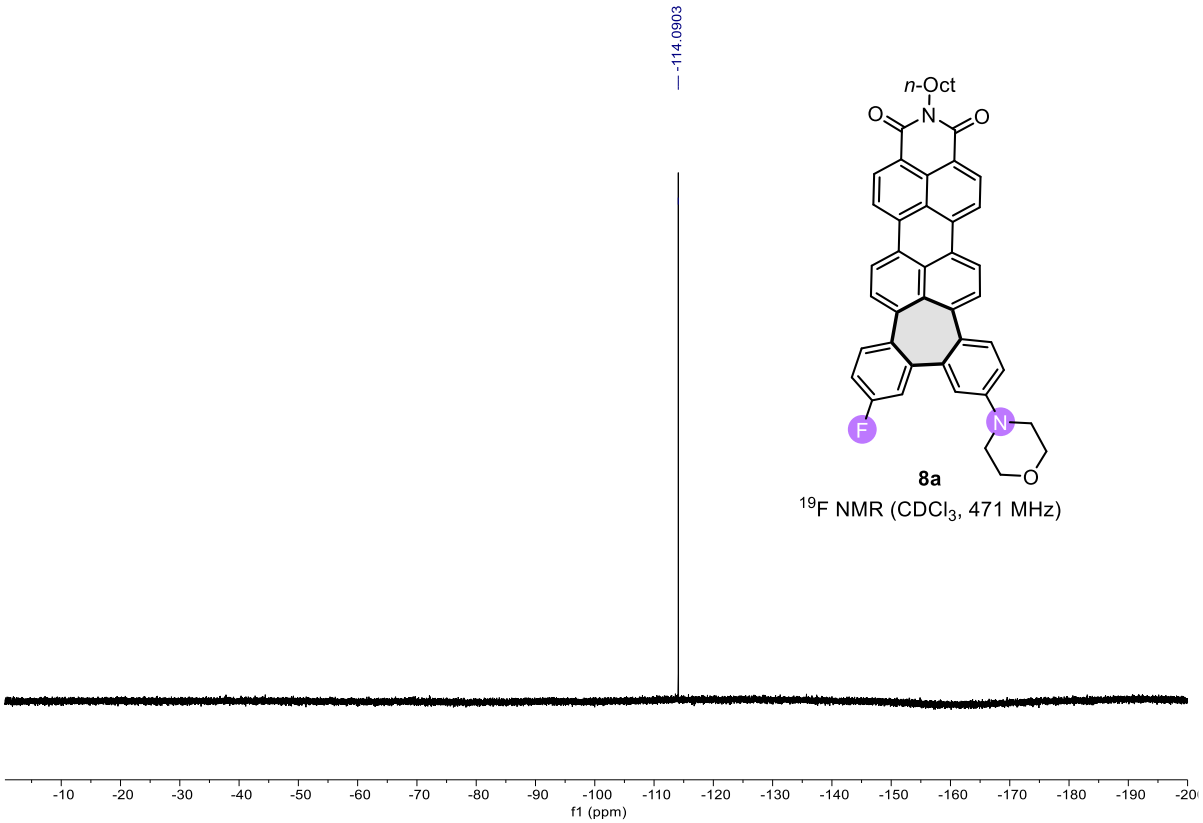

164.30
158.44
156.17
143.23
139.33
135.91
135.80
134.28
131.13
130.17
127.82
126.78
124.34
121.03
119.73
119.64
118.97
77.41
77.16
76.91
40.39
30.37
20.55
14.01
143.2278
139.3314
135.9105
135.8040
134.2845
131.1296
130.1689
127.8186
126.7848
124.3376
121.0253
119.7341
119.6424
118.9687
n-Bu
N
O
O
O
O
6
13C NMR (CDCl3, 125 MHz)
f1 (ppm)


8.6007
8.5852
7.9482
7.9327
7.5165
7.5127
7.4636
7.4604
7.4472
7.4446
7.3807
7.3759
7.3632
7.3479
7.3439
7.3409
7.3301
7.3159
7.3133
7.2647
7.2597
7.2482
7.2443
7.0678
7.0511
4.1970
4.1814
4.1671
1.7530
1.7380
1.7227
1.7077
1.6922
1.4897
1.4749
1.4598
1.4445
1.4252
1.4151
0.9940
0.9793
0.9645
n-Bu
O
N
O
S
S
7
1H NMR (CDCl3, 500 MHz)
2.00
2.07
2.02
3.84
6.00
2.28
2.10
2.13
2.38
2.66
3.33
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.98
139.09
138.23
137.69
135.89
134.69
133.67
132.76
131.13
129.79
129.69
128.32
127.81
127.04
121.35
164.20
77.41
77.16
76.91
40.42
30.36
20.54
14.00
143 141 139 137 135 133 131 129 127
f1 (ppm)
n-Bu
O
N
O
S
S
7
13C NMR (CDCl3, 125 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

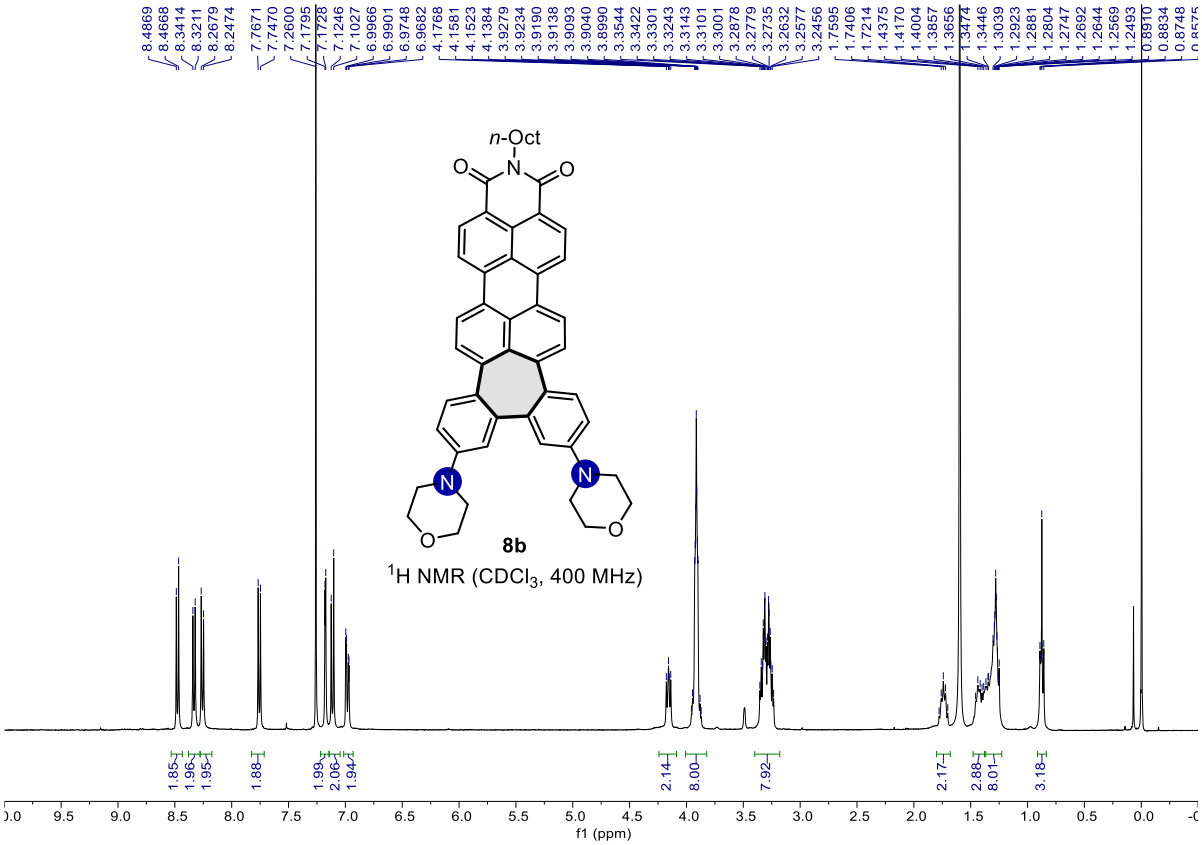

n-Oct
8a
1H NMR (CDCl3, 400 MHz)
f1 (ppm)

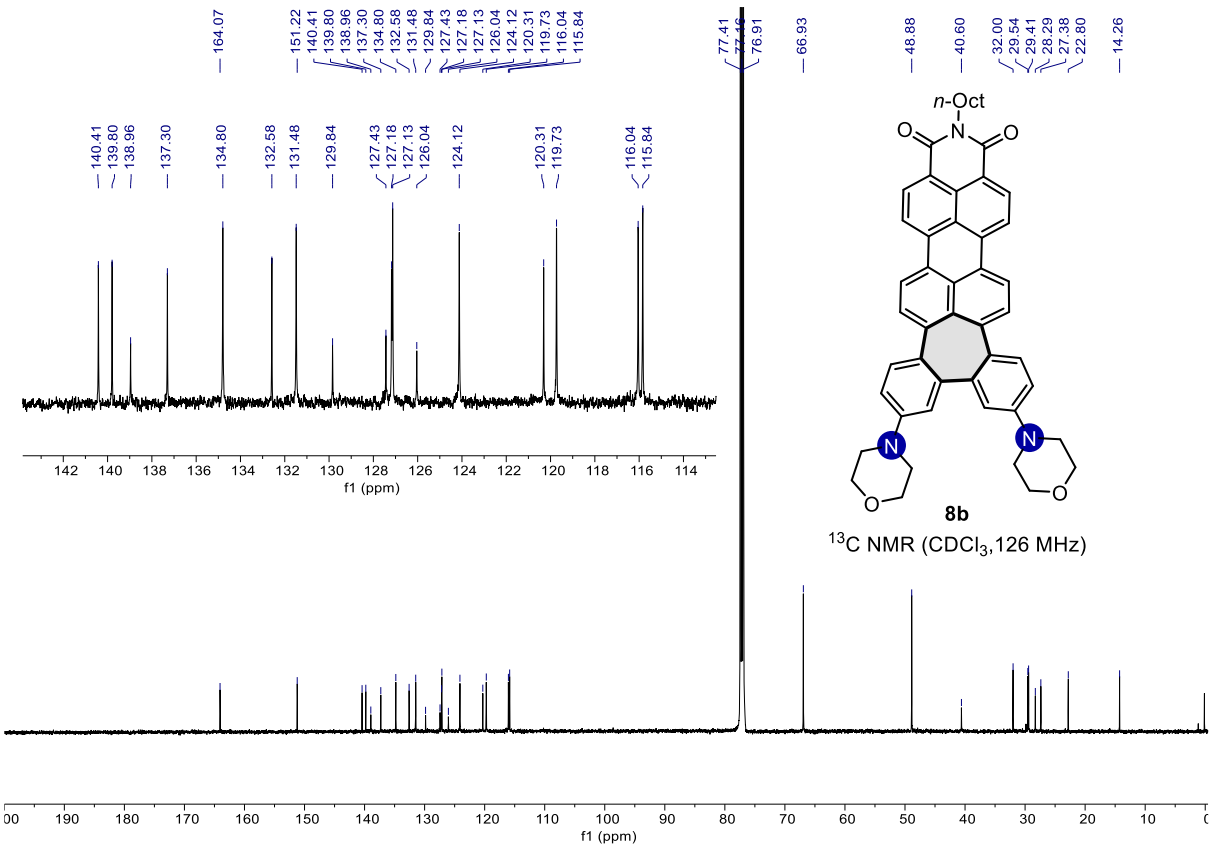

n-Oct
8a
13C NMR (CDCl3,125 MHz)
f1 (ppm)



8a

^{19}F NMR ($CDCl_3$, 471 MHz)


n-Oct
8b
1H NMR (CDCl3, 400 MHz)
f1 (ppm)


n-Oct
8b
13C NMR (CDCl3,126 MHz)
f1 (ppm)