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Supporting Information

Dibenzopleiadiene-Embeded Polyaromatics via [4+3] Annulative Decarbonylation/Decarboxylation

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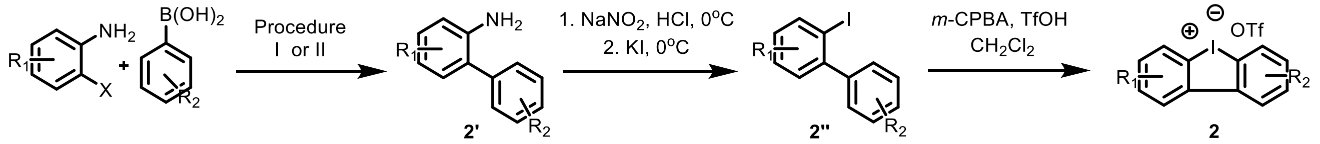
I. General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on 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. 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 or aluminium oxide 60 PF_{254} (Type E). 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 and ESI mode. Melting points were recorded with Buchi Melting Point M-565 apparatus. 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): $\Phi = \Delta$ Area under emission curve /Δ Area under absorption curve the default mode for quantum yield measurement was set at slit width 3 nm, integration time 1 sec.

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

Diphenyleniodonium trifluoromethanesulfonate (**2a**), 2-fluorodibenzo[*b,d*]iodol-5-iumtrifluoromethane sulfonate (**2b**), 2-cyanodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2c**), 2-(trifluoromethyl)dibenzo[*b,d*] iodol-5-ium trifluoromethanesulfonate (**2e**), 2-methyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2g**), 2,8-dimethyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2h**), 2-methoxydibenzo[*b,d*]iodol-5-iumtrifluoro methanesulfonate (**2i**), 3-methyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2j**), 3-cyanodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2k**), 3-methoxydibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2l**), 2,4-dimethyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2n**), benzo[b]naphtho[2,1-*d*]iodol-11-iumtrifluoro methanesulfonate (**2o**) and benzo[b]thieno[2,3-*d*]iodol-4-ium trifluoromethanesulfonate (**2p**) 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.



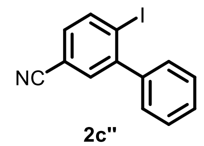
A. General Procedure for the Preparation of 2-Aminobiaryl Derivatives (2'):

Procedure I (when X = I): 2-Iodoaniline derivative (1.0 equiv), arylboronic acid (1.2 equiv), K_3PO_4 (2.5 equiv), $Pd(PPh_3)_4$ (0.01 equiv) and EtOH (0.5 M) were added to a round-bottom flask. The reaction was stirred at a reflux for 12 h under argon atmosphere, followed by removal of EtOH by rotary evaporation. The residue was extracted with EtOAc, and the combined organic layers were washed with H_2O and brine, dried over anhydrous $MgSO_4$, concentrated by rotary evaporation. The crude product was purified by column chromatography on a silica gel to afford the desired 2-aminobiaryl derivatives **(2')**.

Procedure II (when X = Br): 2-Bromoaniline derivative (1.0 equiv), arylboronic acid (1.2 equiv), Na_2CO_3 (2.5 equiv), $Pd(OAc)_2$ (0.01 equiv), PPh_3 (0.04 equiv) and EtOH:toluene:H_2O (1:1:1, 0.2 M) were added to a round-bottom flask. The reaction was stirred at a reflux for 12 h under argon atmosphere. The residue was extracted with EtOAc, and the combined organic layers were washed with H_2O and brine, dried over anhydrous $MgSO_4$, concentrated by rotary evaporation. The crude product was purified by column chromatography on a silica gel to afford the desired 2-aminobiaryl derivatives **(2')**.

B. General Procedure for the Preparation of 2-Iodobiaryl from 2-Aminobiaryl (2''): To a solution of **2'** (1.0 equiv) in THF (0.5 M) was added 4 M aqueous HCl (0.5 M), and the solution was cooled to 0 °C. An aqueous solution of $NaNO_2$ (1.5 equiv) was added slowly to the reaction below 5 °C and stirred for 1 hour at the same temperature. A solution of KI (3.0 equiv) in H_2O (0.5 M) was added at same temperature and then slowly warmed up to rt and stirred for 1 h. The phases were separated, and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation.The crude product was purified by a column chromatography on a silica gel to afford the desired 2-iodobiaryl derivatives. Below are summarized characterization data for newly synthesized substrates.

6-Iodo-[1,1'-biphenyl]-3-carbonitrile (2c''):

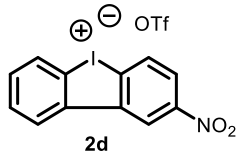


2c''

Prepared following the general procedure using 6-amino-[1,1'-biphenyl]-3-carbonitrile (**2c''**) (0.48 g, 2.5 mmol) and purified by column chromatography on silica gel using hexane and was isolated as a white solid (0.69 g, 90% yield); Mp: 84.0–86.0 °C; IR (neat): 3052, 2225, 1578, 1456, 969, 819, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 1.9 Hz, 1H), 7.46 (dd, *J* = 5.1, 1.8 Hz, 3H), 7.34–7.26 (m, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.2, 142.3, 140.7, 132.8, 131.5, 129.1, 128.7, 128.5, 118.2, 112.5, 105.1; HRMS (APCI) *m/z* calcd for $C_{13}H_8NI+Na^+$: 327.9594 $[M+Na]^+$; found: 327.9593.

C. General Procedure for the Preparation of Cyclic Diaryliodonium Salts (2): To a stirred solution of **2''** (1.0 equiv) in CH_2Cl_2 (0.5 M) was added *m*-CPBA (1.5 equiv) and TfOH (3.0 equiv). The solution was stirred for 1 h at room temperature, followed by removal of CH_2Cl_2 by rotary evaporation. To the solid residue was added Et_2O (20 mL), and the resulting mixture was stirred for 20 min. The solid precipitate was collected by vacuum filtration, washed with Et_2O for three times, and dried under vacuum to afford cyclic diaryliodonium salt derivatives. Below are summarized characterization data for newly synthesized substrates.

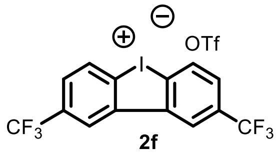
2-Nitrodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2d):



2d

Prepared following the general procedure using 2-iodo-5-nitro-1,1'-biphenyl (**2d''**) (0.90 g, 2.80 mmol) and dried under vacuum to afford a white solid (1.10 g, 83% yield); Mp: 281.9–283.9 °C; IR (neat): 3097, 1531, 1220, 1021 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 9.23 (s, 1H), 8.76 (d, *J* = 7.9 Hz, 1H), 8.47 (s, 2H), 8.25 (d, *J* = 8.2 Hz, 1H), 7.90 (t, *J* = 7.6 Hz, 1H), 7.79 (t, *J* = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ = 149.9, 143.6, 140.1, 132.2, 132.1, 130.9, 130.5 (x2), 128.0, 124.6, 122.8, 121.1; ^{19}F NMR (376 MHz, DMSO) δ = -77.8; HRMS (APCI) *m/z* calcd for $C_{12}H_7INO_2^+$: 323.9516 $[M\text{-OTf}]^+$; found: 323.9520.

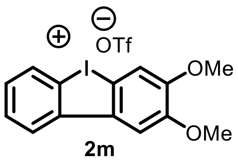
2,8-Bis(trifluoromethyl)dibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2f):



2f

Prepared following the general procedure using 2-iodo-3',5-bis(trifluoromethyl)-1,1'-biphenyl (**2f''**) (1.0 g, 2.40 mmol) and dried under vacuum to afford a white solid (0.91 g, 67% yield); Mp: >280 °C; IR (neat): 3106, 1599, 1256, 1026 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ = 9.24 (s, 2H), 8.47 (d, *J* = 8.6 Hz, 2H), 8.11 (d, *J* = 9.9 Hz, 2H); ^{13}C NMR (100 MHz, DMSO) δ = 142.0, 131.8, 131.7 (q, $J_{C,F}$ = 33 Hz) , 127.7, 126.8, 124.8, 123.7 (q, $J_{C,F}$= 273 Hz); ^{19}F NMR (376 MHz, DMSO) δ = -60.8, -77.8; HRMS (APCI) *m/z* calcd for $C_{14}H_6F_6I^+$: 414.9413 $[M\text{-OTf}]^+$; found: 414.9416.

2,3-Dimethoxydibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2m):

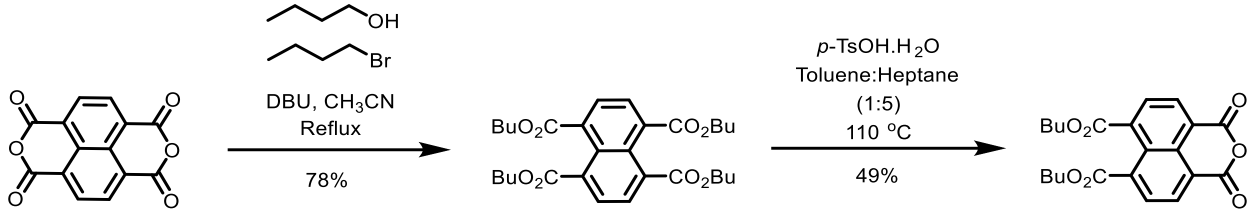


2m

Prepared following the general procedure using 2-iodo-3',4'-dimethoxy-1,1'-biphenyl (**2m''**) (0.70 g, 2.00 mmol) and dried under vacuum to afford a cream solid (0.63 g, 65% yield); Mp: 250 °C (decomposition); IR (neat): 3021, 2850, 1503, 1238, 1023 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ = 8.40 (d, *J* = 7.9 Hz, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.87 (s, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.66–7.49 (m, 2H), 3.95 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ = 151.5, 150.9, 142.0, 134.6, 130.5, 130.5, 129.7, 126.7, 121.2, 111.7, 111.8, 108.9, 56.4, 56.1; ^{19}F NMR (376 MHz, DMSO) δ = -77.7; HRMS (APCI) *m/z* calcd for $C_{14}H_{12}IO_2^+$: 338.9876 $[M\text{-OTf}]^+$; found: 338.9877.

III. Synthesis of Naphthalene and Perylene Monoanhydride Derivatives (1b–1e)

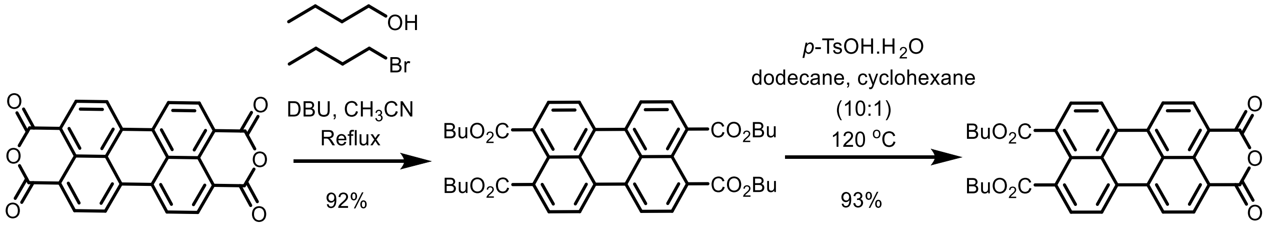
A. Preparation of Naphthalene and Perylene Dicarboxylic Acid Anhydride Containing Ester Groups (1b and 1c)



NTCDA **1b'** **1b**

Tetrabutyl naphthalene-1,4,5,8-tetracarboxylate (1b'): To a suspension of 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTCDA) (**1f**, 1.00 g, 3.70 mmol) in 60 mL of acetonitrile was added *n*-butanol (2.10 mL, 22.4 mmol), 1-bromobutane (2.50 mL, 22.4 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (4.50 mL, 29.8 mmol). The mixture was heated at reflux overnight and then cooled to room temperature. After solvent removal under reduced pressure, the residue was extracted with EtOAc, and the combined organic layers were washed with H_2O and brine, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The resulting crude product was purified by column chromatography on silica gel using CH_2Cl_2 as the eluent to afford **4** as a colorless solid (1.55 g, 78%). NMR spectra matched those previously reported.[2]

Dibutyl 1,3-dioxo-1H,3H-benzo[*de*]isochromene-6,7-dicarboxylate (1b): Compound **1b**' (1.55 g, 2.90 mmol), *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O, 0.56 g, 2.90 mmol), 0.2 mL toluene and 1.0 mL heptane were added to a round-bottom flask. The reaction mixture was stirred at 110 °C for overnight (16 h). After solvent removal under reduced pressure, the residue was extracted with EtOAc, and the combined organic layers were washed with H_2O and brine, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The resulting crude product was purified by column chromatography on silica gel using 20% EtOAc/hexane to afford **1b** as an off–white solid (0.57 g, 49%). Mp: 100.1–102.4 °C (from CH_2Cl_2); IR (neat): 2957, 1779, 1713, 1277, 1029 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.61 (d, *J* = 7.5 Hz, 2H), 8.14 (d, *J* = 7.5 Hz, 2H), 4.33 (t, *J* = 6.8 Hz, 4H), 1.80–1.72 (m, 4H), 1.50–1.41 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.1, 159.5, 137.0, 132.8, 131.0, 130.0, 126.4, 121.3, 66.9, 30.6, 19.3, 13.8; HRMS (APCI) *m/z* calcd for $C_{22}H_{22}O_7+H^+$: 399.1438 $[M+H]^+$; found: 399.1437.

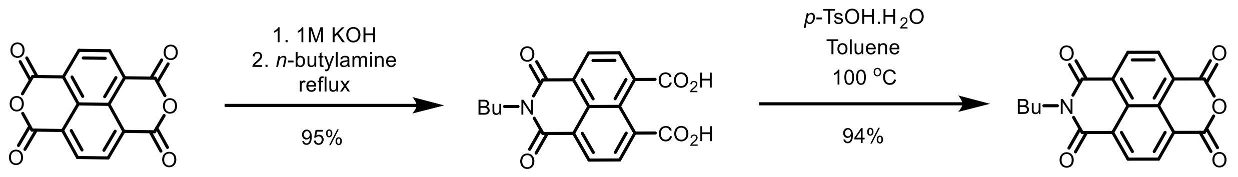


PTCDA **1c'** **1c**

Tetrabutyl perylene-3,4,9,10-tetracarboxylate (1c'): To a suspension of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) (**1g**, 2.00 g, 5.10 mmol) in 80 mL of acetonitrile was added *n*-butanol (3.30 mL, 30.6 mmol), 1-bromobutane (3.30 mL, 30.6 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (6.10 mL, 40.8 mmol). The mixture was heated at reflux overnight and then cooled to room temperature. After solvent removal under reduced pressure, the residue was extracted with EtOAc, and the combined organic layers were washed with H_2O and brine, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The resulting crude product was purified by column chromatography on silica gel using CH_2Cl_2 as an eluent to afford **1c**' as an orange solid (3.06 g, 92%). NMR spectra matched those previously reported.[3]

Dibutyl 1,3-dioxo-1H,3H-benzo[10,5]anthra[2,1,9-*def*]isochromene-8,9-dicarboxylate (1c): Compound **1c**' (1.00 g, 1.90 mmol), *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O, 0.30 g, 1.90 mmol), 0.30 mL cyclohexane and 3.00 mL dodecane were added to a round-bottom flask. The reaction mixture was stirred at 120 °C until color change from orange to red. The solid was then isolated by filtration followed by washing with boiling hexane then with acetonitrile to yield the dibutyl-3,4-dicarboxylate-9,10-carboxylic monoanhydride **1c** as a bright red powdery solid (0.75 g, 93%). NMR spectra matched those previously reported.[3]

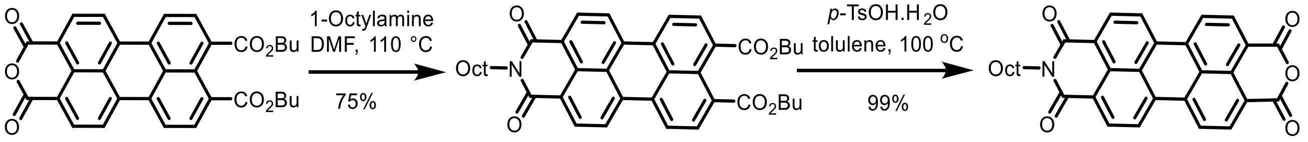
B. Preparation of Naphthalene Carboximide and Perylene Carboximide Derivatives (1d and 1e)



NTCDA **1d'** **1d**

Tetrabutyl perylene-3,4,9,10-tetracarboxylate (1d'): 1,4,5,8-Naphthalenetetracarbxylic dianhydride (NTCDA) (**1f**, 1.00 g, 3.70 mmol) was suspended in H_2O (160 mL). 1.0 M KOH solution (18 mL, 18 mmol) was added and the reaction mixture was stirred at room temperature until complete dissolution of the starting material. The pH was set to 6.3 with a 1.0 M phosphoric acid solution. *n*-Butylamine (0.37 mL, 3.70 mmol) was added and the pH was set at 6.3 using the 1.0 M phosphoric acid solution. The reaction mixture was set to reflux overnight. The homogeneous solution was then allowed to cool back to room temperature and was acidified to pH 1–2 with 2.0 M HCl. Filtration gave 1.20 g (95%) of an off-white solid which was directly used in the next step without further purifications. NMR spectra matched those previously reported.[4]

7-Butyl-1H-isochromeno[6,5,4-*def*]isoquinoline-1,3,6,8(7H)-tetraone (1d): A mixture of **1d**' (0.91 g, 2.67 mmol) and *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O, 3.05 g, 16.0 mmol) in toluene (80 mL) was stirred at 100 °C for 12 h. Then, the mixture was cooled to room temperature and the solvent was evaporated to dryness. To the resulting solid, water was added and the suspension was sonicated for 10 min. The precipitate was filtered, washed several times with water and dried under vacuum to give an off-white solid (0.81 g, 94%). NMR spectra matched those previously reported.[4]

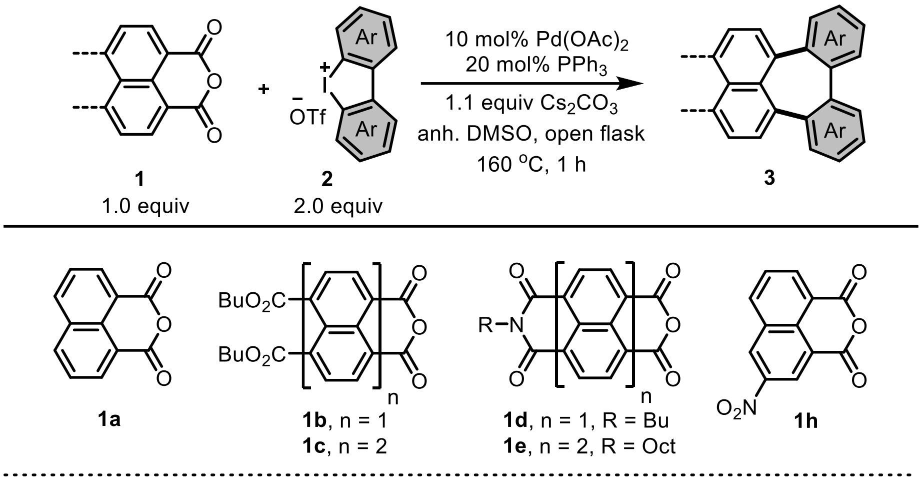


1c **1e'** **1e**

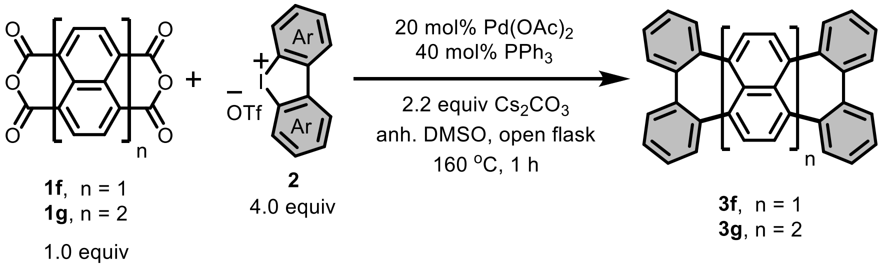
Dibutyl 2-octanoyl-1,3-dioxo-2,3-dihydro-1H-benzo[10,5]anthra[2,1,9-def]isoquinoline-8,9-dicarboxylate (1e'): Compound **1c** (1.29 g, 2.47 mmol), octylamine (4.10 mL, 24.7 mmol) and dimethylformamide (13 mL) were added to a round-bottom flask, which was stirred at 120 °C for 45 minutes. The reaction was then precipitated by addition to a 20% solution of hydrochloric acid (2.0 M, aqueous) in methanol (50 mL). The precipitate was isolated by fitration, washed with 20% water in methanol (100 mL), air dried and purified by column chromatography on silica gel using CH_2Cl_2 as the eluent to afford **1e'** as a red solid (1.17 g, 75%). NMR spectra matched those previously reported.[5]

9-Octanoyl-1H-isochromeno[6',5',4':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10(9H)-tetraone (1e): A mixture of **1e**' (1.75 g, 2.75 mmol) and *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O, 3.14 g, 16.52 mmol) in toluene (60 mL) was stirred at 100 °C for 3 h. Then the mixture was cooled to room temperature and the solvent was evaporated to dryness. To the resulting solid, water was added and the precipitate was filtered, washed several times with MeOH and dried in the oven to give **1e** as a dark red solid (1.37 g, 99%).^{1}H NMR and ^{13}C NMR were not recorded due to low solubility of **1e**. However, IR spectra and MS(EI) matched those previously reported.[6]

IV. Synthesis of Dibenzopleiadiene Derivatives

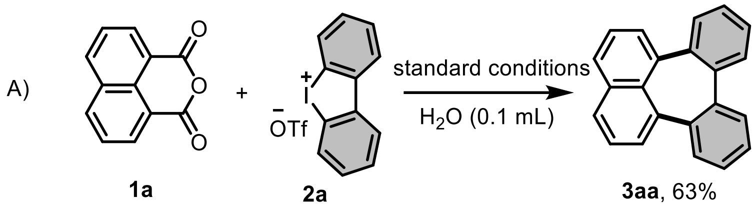


General procedure A: A 10 mL oven-dried Schlenk tube was charged with Palladium (II) acetate (5.1 mg, 22.5 μmol, 0.1 equiv), triphenylphosphine (11.8 mg, 45.0 μmol, 0.2 equiv), cesium carbonate (80.6 mg, 0.245 mmol, 1.1 equiv), **1** (0.225 mmol, 1.0 equiv) and cyclic diaryliodonium triflate **2** (0.45 mmol, 2.0 equiv) in dry DMSO (1.40 mL). The reaction mixture was stirred at 160 °C for 1 h under ambient atmosphere. The reaction mixture was allowed to cool to rt and extracted with ethyl acetate (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**.

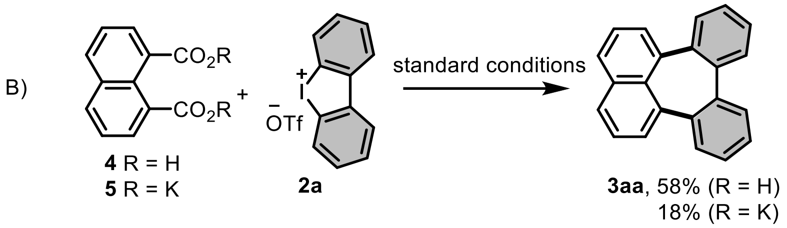


General procedure B: A 10 mL oven-dried Schlenk tube was charged with Palladium (II) acetate (10.2 mg, 45 μmol, 0.2 equiv), triphenylphosphine (23.6 mg, 90.0 μmol, 0.4 equiv), cesium carbonate (161.3 mg, 0.495 mmol, 2.2 equiv), **1** (0.225 mmol, 1.0 equiv) and cyclic diaryliodonium triflate **2** (0.90 mmol, 4.0 equiv) in dry DMSO (3.00 mL). The reaction mixture was stirred at 160 °C for 1 h under ambient atmosphere. The reaction mixture was allowed to cool to rt and extracted with ethyl acetate (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. Control Experiments



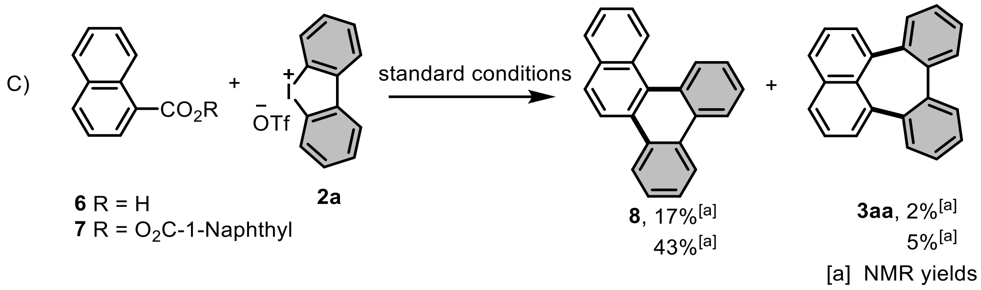
A) A 10 mL oven-dried Schlenk tube was charged with Palladium (II) acetate (5.1 mg, 22.5 μmol, 0.1 equiv), triphenylphosphine (11.8 mg, 45.0 μmol, 0.2 equiv), cesium carbonate (80.6 mg, 0.245 mmol, 1.1 equiv), **1a** (44.6 mg, 0.225 mmol, 1.0 equiv), cyclic diaryliodonium triflate **2a** (192.7 mg, 0.45 mmol, 2.0 equiv) and H_2O (0.1 mL) in dry DMSO (1.40 mL). The reaction mixture was stirred at 160 °C for 1 h under ambient atmosphere. The reaction mixture was allowed to cool to rt and extracted with ethyl acetate (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 on aluminium oxide 60 PF_{254} (Type E) followed by silica gel using hexane as eluent to give the product **3aa** (39.6 mg, 63% yield).



Preparation of compound 5: A 250 mL round-bottomed flask was charged with naphthalene-1,8- dicarboxylic acid (0.75 g, 3.48 mmol, 1.0 equiv), dry ethanol (15 mL) and dry THF (60 mL). To this mixtrue, a solution of potassium *tert*-butoxide (0.78 g, 6.96 mmol, 2.0 equiv) in dry ethanol (10 mL) was added dropwise over 30 min. After the addition was complete, the reaction mixture was stirred for another 1 h at room temperature. After removing the ethanol by slow evaporation on rotary evaporator, diethyl ether (20 mL) was added. The resulting solid was triturated sequentially with ethanol (2 x 5 mL) and diethyl ether (2 x 10 mL) and dried under vacuum for 1 h to provide **5** as a white solid (0.96 g, 94% yield). IR (neat): 3211, 3039, 1696, 1564, 1400 cm^{-1}; ^1H NMR (400 MHz, D_2O) δ = 7.96 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 6.9 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, D_2O) δ = 177.5, 137.7, 134.2, 129.8, 126.9, 126.5, 125.2.

B) A 10 mL oven-dried Schlenk tube was charged with Palladium (II) acetate (5.1 mg, 22.5 μmol, 0.1 equiv), triphenylphosphine (11.8 mg, 45.0 μmol, 0.2 equiv), cesium carbonate (80.6 mg, 0.245 mmol, 1.1 equiv), **4**[7a] or **5** (0.225 mmol, 1.0 equiv) and cyclic diaryliodonium triflate **2a** (192.7 mg, 0.45 mmol, 2.0 equiv) in dry DMSO (1.40 mL). The reaction mixture was stirred at 160 °C for 1 h under ambient atmosphere. The reaction mixture was allowed to cool to rt and extracted with ethyl acetate (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 on aluminium oxide 60 PF_{254} (Type E) followed by silica gel using hexane as eluent to give the product **3aa** (36.4 mg, 58% yield (from **4**) and 11.2 mg, 18% yield (from **5**), respectively).

C)



6 R = H
7 R = O$_2$C-1-Naphthyl

2a

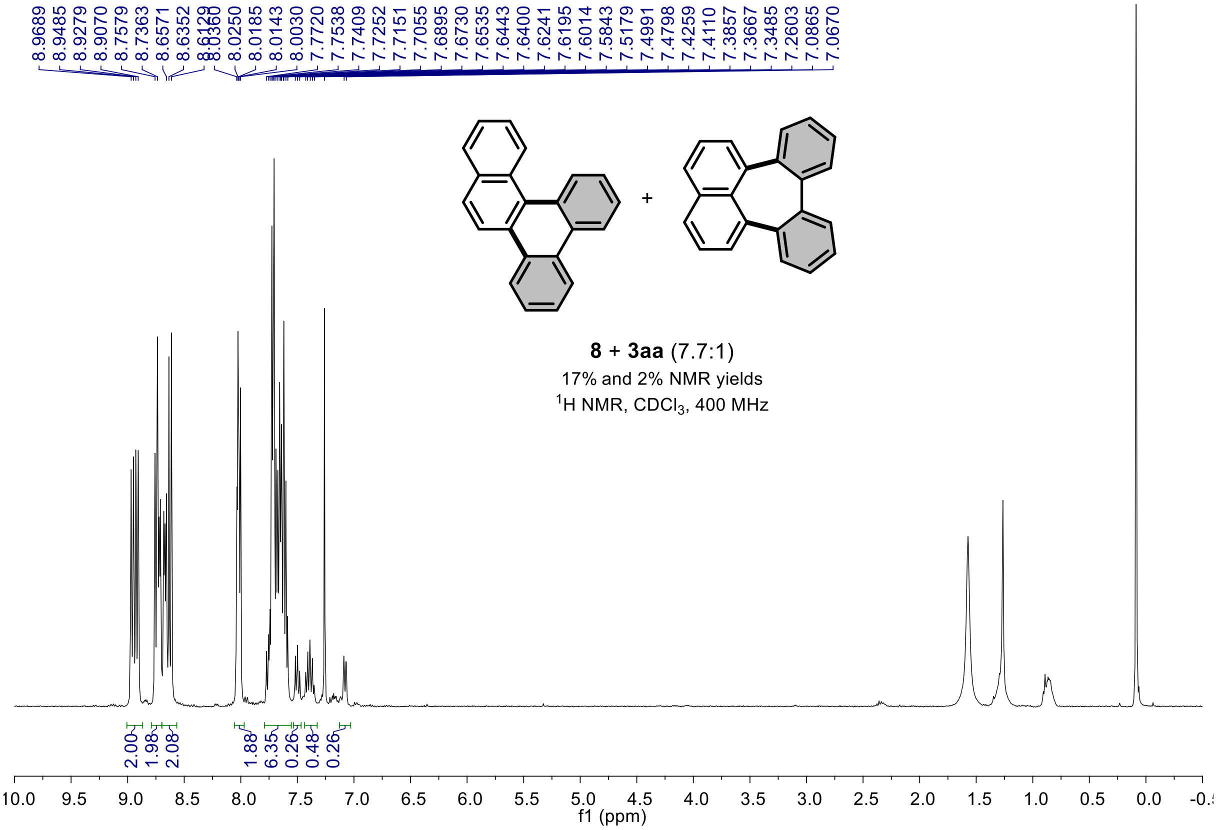
8, 17%[a]
43%[a]

3aa, 2%[a]
5%[a]

[a] NMR yields

Preparation of compound 7: 1-Naphthoic acid (**6**) (1.00 g, 5.81 mmol, 2.0 equiv) was dissolved in dichloromethane (7 mL), and *N,N'*-dicyclohexylcarbodiimide (DCC) (0.60 g, 2.90 mmol, 1.0 equiv) was added in one portion, which resulted in immediate formation of white precipitate. The reaction was stirred for 1 h at room temperature and then filtered to remove dicyclohexylurea (DCU) and washed with cold Et$_2$O. The filtrate was concentrated to afford **7** as an off–white solid (0.85 g, 45% yield). NMR spectra matched those previously reported.[7b]

C) A 10 mL oven-dried Schlenk tube was charged with Palladium (II) acetate (5.1 mg, 22.5 μmol, 0.1 equiv), triphenylphosphine (11.8 mg, 45.0 μmol, 0.2 equiv), cesium carbonate (80.6 mg, 0.245 mmol, 1.1 equiv), **6** or **7** (0.225 mmol, 1.0 equiv) and cyclic diaryliodonium triflate **2a** (192.7 mg, 0.45 mmol, 2.0 equiv) in dry DMSO (1.40 mL). The reaction mixture was stirred at 160 °C for 1 h under ambient atmosphere. The reaction mixture was allowed to cool to rt and extracted with ethyl acetate (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 on aluminium oxide 60 PF$_{254}$ (Type E) followed by silica gel using hexane as eluent to give the isomer products **8** and **3aa** (12.0 mg (from **6**), and 30.2 mg (from **7**), respectively).



8 + **3aa** (7.7:1)
17% and 2% NMR yields
^{1}H NMR, CDCl$_3$, 400 MHz

Figure S1. NMR of regioisomeric products isolated from the reaction between **6** and **2a**.

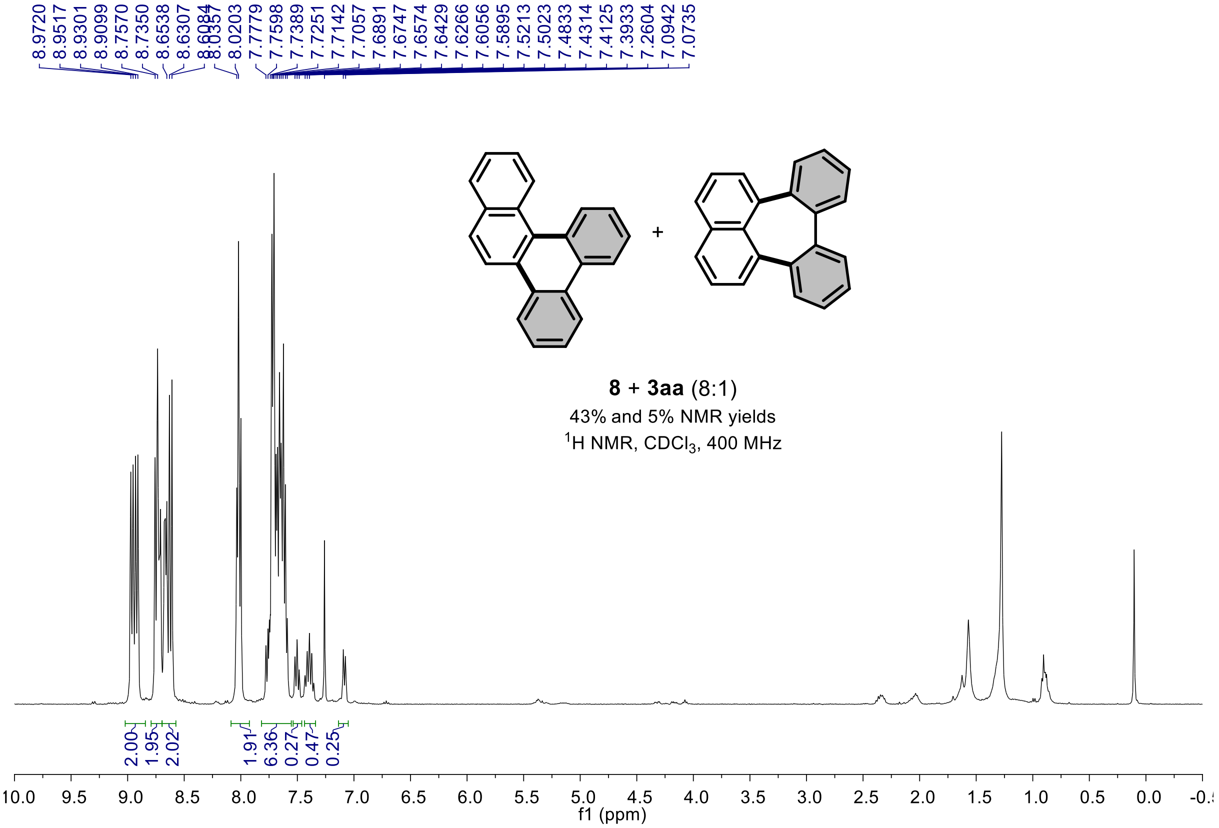
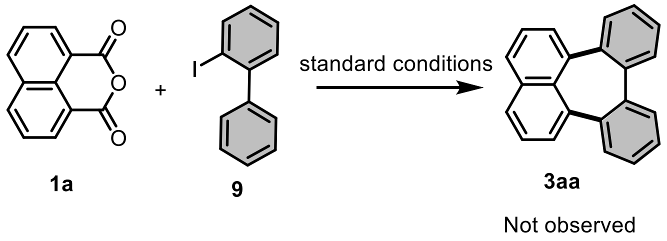


Figure S2. NMR of regioisomeric products isolated from the reaction between **7** and **2a**.

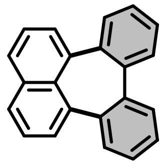
D)



D) A 10 mL oven-dried Schlenk tube was charged with Palladium (II) acetate (5.1 mg, 22.5 μmol, 0.1 equiv), triphenylphosphine (11.8 mg, 45.0 μmol, 0.2 equiv), cesium carbonate (80.6 mg, 0.245 mmol, 1.1 equiv), **1a** (44.6 mg, 0.225 mmol, 1.0 equiv) and 2-iodo-1,1'-biphenyl **9** (126.1 mg, 0.45 mmol, 2.0 equiv) in dry DMSO (1.40 mL). The reaction mixture was stirred at 160 °C for 1 h under ambient atmosphere. The reaction mixture was allowed to cool to rt and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and the volatiles were removed under reduced pressure. No product **3aa** was observed by TLC.

VI. Characterization of the Products

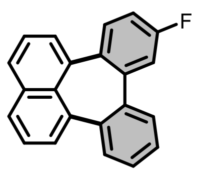
Dibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene (3aa)[8]:



3aa

Prepared following the general procedure A using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), diphenyleniodonium trifluoromethanesulfonate (**2a**) (192.7 mg, 0.45 mmol) and purified by column chromatography on aluminium oxide 60 PF$_{254}$ (Type E) followed by silica gel using hexane as eluent to obtain the product as an off–white solid (53.0 mg, 85% yield); Mp: 158.0–159.3 °C (from Hexane); IR (neat): 3045, 2919, 2850, 1484, 1261 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.77–7.72 (m, 4H), 7.66 (d, J = 7.4 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.43–7.35 (m, 4H), 7.08 (d, J = 7.5 Hz, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 141.8, 139.1, 138.9, 137.5, 134.1, 133.0, 130.7, 128.4, 127.9, 127.5, 127.0, 126.0; HRMS (APCI) *m/z* calcd for $C_{22}H_{14}$+H$^+$: 279.1168 [M+H]$^+$; found: 279.1167; UV/Vis (CHCl$_3$): λ_{max} (ε) = 339 nm (11600 mol^{-1}dm^{3}cm^{-1}). Fluorescence (CHCl$_3$, λ_{ex} = 339 nm): λ_{em} = 398 nm. Quantum yield (CHCl$_3$): 0.29.

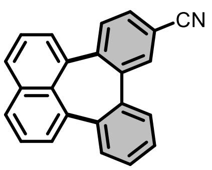
12-Fluorodibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene (3ab):



3ab

Prepared following the general procedure A using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), 2-fluorodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2b**) (200.8 mg, 0.45 mmol) and purified by column chromatography on aluminium oxide 60 PF$_{254}$ (Type E) followed by silica gel using hexane as eluent to obtain the product as an off-white solid (47.9 mg, 72% yield); Mp: 133.0–135.5 °C (from CH$_2$Cl$_2$/Hexane); IR (neat): 3044, 2960, 2849, 1725, 1489, 1262 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.78–7.73 (m, 4H), 7.70–7.69 (m, 1H), 7.52–7.49 (m, 2H), 7.42–7.38 (m, 3H), 7.10–7.03 (m, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 163.7, 161.2, 141.7, 140.9 (d, $J_{C,F}$ = 7.8 Hz), 138.6, 137.9, 137.2, 136.5, 136.0 (d, $J_{C,F}$ = 8.1 Hz), 134.2, 133.0, 130.6, 128.9, 128.0, 127.7, 127.4, 127.1, 126.9, 126.1, 126.0, 116.8 (d, $J_{C,F}$ = 22.3 Hz), 115.3 (d, $J_{C,F}$ = 21.1 Hz); ^{19}F NMR (376 MHz, CDCl$_3$) δ = -116.0 ; HRMS (APCI) *m/z* calcd for $C_{22}H_{13}F$+H$^+$: 297.1074 [M+H]$^+$; found: 297.1072.

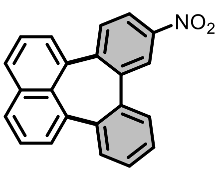
Dibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene-12-carbonitrile (3ac):



3ac

Prepared following the general procedure A using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), 2-cyanodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2c**) (203.9 mg, 0.45 mmol) and purified by column chromatography on silica gel using 5% EtOAc/hexane to obtain the product as an off–white solid (41.4 mg, 61% yield); Mp: 180.8–182.4 °C (from CH$_2$Cl$_2$/Hexane); IR (neat): 3048, 2919, 2223, 1489, 1262 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.92 (s, 1H), 7.82–7.75 (m, 4H), 7.61–7.59 (m, 2H), 7.55–7.53 (m, 2H), 7.45–7.42 (m, 2H), 7.14 (d, J = 8.2 Hz, 1H), 7.09–7.07 (m, 1H); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 146.4, 141.9, 140.3, 138.7, 136.9, 136.7, 135.9, 134.7, 134.4, 134.2, 133.1, 131.0, 130.6, 129.4, 128.9, 128.3, 127.9, 127.8, 127.6, 126.5, 126.1, 119.0, 111.5; HRMS (APCI) *m/z* calcd for $C_{23}H_{13}N$+H$^+$: 304.1121 [M+H]$^+$; found: 304.1122.

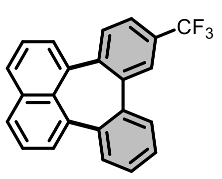
12-Nitrodibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene (3ad):



3ad

Prepared following the general procedure A using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), 2-nitrodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2d**) (212.9 mg, 0.45 mmol) and purified by column chromatography on silica gel using 5% EtOAc/hexane to obtain the product as a yellow solid (40.3 mg, 55% yield); Mp: 175.3–176.3 °C (from CH$_2$Cl$_2$/Hexane); IR (neat): 3044, 2919, 2850, 1726, 1581, 1340 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.51 (s, 1H), 8.16 (dd, J = 8.7, 2.4 Hz, 1H), 7.84–7.76 (m, 4H), 7.68 (d, J = 7.1 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 7.48–7.44 (m, 2H), 7.20 (d, J = 8.7 Hz, 1H), 7.10 (dd, J = 7.5, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 148.2, 147.3, 141.8, 140.4, 138.7, 136.9, 136.8, 135.3, 135.1, 134.2, 133.2, 130.8, 129.5, 129.1, 128.4, 128.3, 127.9, 127.7, 126.5, 126.1, 125.7, 122.5; HRMS (APCI) *m/z* calcd for $C_{22}H_{13}NO_2$+H$^+$: 324.1027 [M+H]$^+$; found: 324.1028.

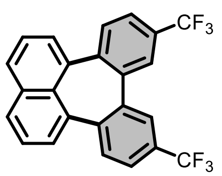
12-(Trifluoromethyl)dibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene (3ae):



3ae

Prepared following the general procedure A using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), 2-(trifluoromethyl)dibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2e**) (223.3 mg, 0.45 mmol) and purified by column chromatography on aluminium oxide 60 PF_{254} (Type E) followed by silica gel using hexane as eluent to obtain the product as a white solid (56.5 mg, 73% yield); Mp: 144.5–146.7 °C (from CH_2Cl_2/Hexane); IR (neat): 3059, 1614, 1562, 1278, 1135 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.90 (s, 1H), 7.77 (dd, *J* = 11.3, 7.2 Hz, 4H), 7.63 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.46–7.40 (m, 2H), 7.17 (d, *J* = 8.2 Hz, 1H), 7.09 (dd, *J* = 7.5, 1.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.2, 141.8, 139.6, 138.8, 137.7, 137.0, 136.1, 134.5, 134.1, 133.1, 130.7, 129.8 (q, $J_{C,F}$ = 32.5 Hz), 129.1, 128.5, 128.4, 127.7, 127.7, 127.6 (d, $J_{C,F}$ = 3.7 Hz), 127.4, 126.3, 126.1, 124.7 (d, $J_{C,F}$ = 3.7 Hz),124.3 (q, $J_{C,F}$ = 272.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.5; HRMS (APCI) *m/z* calcd for $C_{23}H_{13}F_3$+H^+: 347.1042 [*M*+H]$^+$; found: 347.1045.

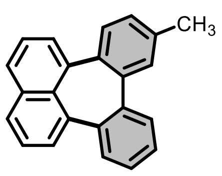
9,12-Bis(trifluoromethyl)dibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene (3af):



3af

Prepared following the general procedure using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), 2,8-bis(trifluoromethyl)dibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2f**) (253.9 mg, 0.45 mmol) and purified by column chromatography on aluminium oxide 60 PF_{254} (Type E) followed by silica gel using hexane as eluent to obtain the product as a white solid (75.2 mg, 81% yield); Mp: 251.5–254.4 °C (from CH_2Cl_2/Hexane); IR (neat): 3057, 2925, 1735, 1397, 1172 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.86 (s, 2H), 7.80 (t, *J* = 7.3 Hz, 4H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.3, 138.7, 138.3, 135.6, 134.7, 133.1, 130.2 (q, $J_{C,F}$ = 32.9 Hz), 128.6, 128.1, 127.5 (d, $J_{C,F}$ = 3.7 Hz), 126.4,125.4 (d, $J_{C,F}$ = 3.5 Hz), 124.2 (q, $J_{C,F}$ = 273.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.5; Elemental analysis calcd for $C_{24}H_{12}F_6$: C 69.57, H 2.92, found: C 69.74, H 3.12; UV/Vis ($CHCl_3$): λ_{max} (ε) = 339 nm (17900 $mol^{-1}dm^3cm^{-1}$). Fluorescence ($CHCl_3$, λ_{ex} = 339 nm): λ_{em} = 423 nm. Quantum yield ($CHCl_3$): 0.26.

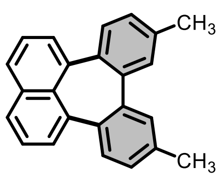
12-Methyldibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene (3ag):



3ag

Prepared following the general procedure using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), 2-methyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2g**) (198.9 mg, 0.45 mmol) and purified by column chromatography on aluminium oxide 60 PF_{254} (Type E) followed by silica gel using hexane as eluent to obtain the product as an off–white solid (38.5 mg, 59% yield); Mp: 144.7–146.9 °C (from CH_2Cl_2/Hexane); IR (neat): 3048, 2922, 2853, 1492, 1263 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.75–7.70 (m, 4H), 7.67–7.65 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.50–7.46 (m, 3H), 7.41–7.34 (m, 2H), 7.20–7.17 (m, 1H), 7.08–7.05 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.7, 139.1, 139.0, 138.8, 138.7, 137.6, 137.5, 137.4, 134.06, 134.05, 133.0, 131.3, 130.6, 129.3, 128.3, 127.8, 127.5, 127.2, 127.0, 126.6, 126.01, 126.0, 21.2; HRMS (APCI) *m/z* calcd for $C_{23}H_{16}$+H^+: 293.1325 [*M*+H]$^+$; found: 293.1328.

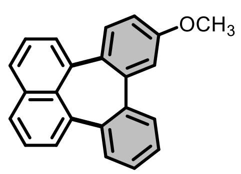
9,12-Dimethyldibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene (3ah):



3ah

Prepared following the general procedure using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), 2,8-dimethyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2h**) (205.3 mg, 0.45 mmol) and purified by column chromatography on aluminium oxide 60 PF_{254} (Type E) followed by silica gel using hexane as eluent to obtain the product as an off-white solid (38.5 mg, 63% yield); Mp: 156.8–158.2 °C (from Hexane); IR (neat): 3037, 2913, 1606, 1493, 1260, 1073 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.71 (t, *J* = 7.8 Hz, 4H), 7.47 (t, *J* = 7.6 Hz, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.0, 138.8, 138.6, 137.5 (x2), 134.1, 133.0, 131.2, 129.2, 127.1, 126.6, 125.9, 21.2; HRMS (APCI) *m/z* calcd for $C_{24}H_{18}$+H^+: 307.1481 [*M*+H]$^+$; found: 307.1480.

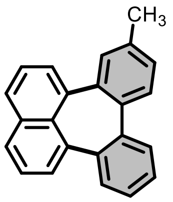
12-Methoxydibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene (3ai):



3ai

Prepared following the general procedure A using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), 2-methoxydibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2i**) (206.2 mg, 0.45 mmol) and purified by column chromatography on silica gel using 1% EtOAc/hexane to obtain the product as a pale yellow solid (50.3 mg, 72% yield); Mp: 80.0–81.7 °C (from Hexane); IR (neat): 3043, 2921, 1585, 1491, 1262, 1018 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.76–7.66 (m, 5H), 7.48 (dd, *J* = 15.4, 7.8 Hz, 2H), 7.41–7.37 (m, 2H), 7.19 (d, *J* = 2.6 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 6.94 (dd, *J* = 8.7, 2.7 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 159.2, 141.7, 140.0, 138.9, 138.6, 137.4, 137.2, 135.5, 134.6, 134.1, 133.0, 130.5, 128.6, 127.9, 127.5, 127.0, 126.8, 126.3, 126.0, 126.0, 115.4, 114.4, 55.6; HRMS (APCI) *m/z* calcd for $C_{23}H_{16}O+H^+$: 309.1274 [*M*+H]$^+$; found: 309.1272.

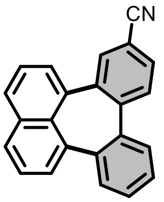
13-Methyldibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene (3aj)[8]**:**



3aj

Prepared following the general procedure A using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), 3-methyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2j**) (198.9 mg, 0.45 mmol) and purified by column chromatography on aluminium oxide 60 PF$_{254}$ (Type E) followed by silica gel using hexane as eluent to obtain the product as an off–white solid (48.4 mg, 74% yield); Mp: 80.1–82.1 °C (from CH$_2$Cl$_2$/Hexane); IR (neat): 3043, 2916, 1604, 1484, 1261 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.78–7.72 (m, 4H), 7.65 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.52–7.48 (m, 2H), 7.42–7.34 (m, 2H), 7.23 (d, *J* = 7.1 Hz, 1H), 7.08 (d, *J* = 1.2 Hz, 1H), 6.91 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 141.6, 141.5, 139.0, 138.8, 138.1, 137.5, 137.5, 136.2, 134.6, 134.0, 132.9, 130.7, 130.4, 128.7, 128.1, 127.8, 127.4 (x2), 127.0, 126.9, 126.0, 126.0, 21.3; HRMS (APCI) *m/z* calcd for $C_{23}H_{16}+H^+$: 293.1325 [*M*+H]$^+$; found: 293.1329.

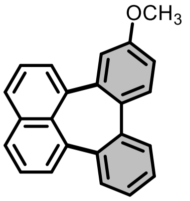
Dibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene-13-carbonitrile (3ak):



3ak

Prepared following the general procedure A using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), 3-cyanodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2k**) (203.9 mg, 0.45 mmol) and purified by column chromatography on silica gel using 5% EtOAc/hexane to obtain the product as an off–white solid (41.4 mg, 61% yield); Mp: 117.9–118.9 °C (from CH$_2$Cl$_2$/Hexane); IR (neat): 3050, 2921, 2262, 1456, 1264 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.80–7.76 (m, 3H), 7.73–7.71 (m, 2H), 7.65–7.60 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.43–7.41 (m, 2H), 7.34 (s, 1H), 7.10–7.09 (m, 1H); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 143.7, 142.9, 142.0, 138.6, 137.6, 137.3, 136.7, 135.3, 134.9, 133.9, 131.5, 130.8, 130.7, 129.6, 128.6, 128.1, 127.9, 127.5, 127.5, 126.4, 126.2, 118.9, 112.1; HRMS (APCI) *m/z* calcd for $C_{23}H_{13}N+H^+$: 304.1121 [*M*+H]$^+$; found: 304.1120.

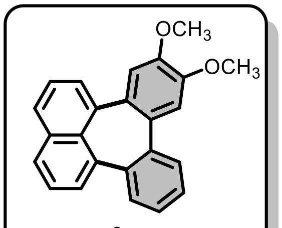
13-Methoxydibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene (3al)[8]**:**



3al

Prepared following the general procedure A using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), 3-methoxydibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2l**) (206.2 mg, 0.45 mmol) and purified by column chromatography on silica gel using 1% EtOAc/hexane to obtain the product as an off–white solid (48.4 mg, 54% yield); Mp: 89.0–91.0 °C (from CH$_2$Cl$_2$/Hexane); IR (neat): 3046, 2924, 1601, 1484, 1263, 1041 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.78–7.72 (m, 4H), 7.62–7.58 (m, 2H), 7.52–7.50 (m, 2H), 7.38– 7.33 (m, 2H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.97 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.62 (d, *J* = 2.6 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 159.7, 142.9, 141.3, 138.7, 138.6, 137.5, 137.4, 134.0, 133.0, 132.0, 131.8, 130.3, 127.9, 127.8, 127.7, 127.4, 127.0, 126.9, 126.1, 126.0, 118.7, 113.8, 55.6; HRMS (APCI) *m/z* calcd for $C_{23}H_{16}O+H^+$: 309.1274 [*M*+H]$^+$; found: 309.1278.

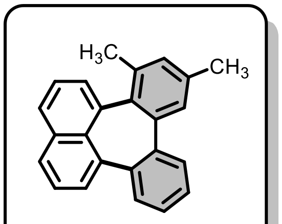
13-Methoxydibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene (3am):



3am

Prepared following the general procedure A using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), 2,3-dimethoxydibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2m**) (219.7 mg, 0.45 mmol) and purified by column chromatography on silica gel using 5% EtOAc/hexane to obtain the product as a pale yellow solid (45.7 mg, 60% yield); Mp: 161.1–163.9 °C (from CH_2Cl_2/Hexane); IR (neat): 3043, 2927, 1601, 1490, 1233, 1089 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.77–7.70 (m, 4H), 7.65 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.52–7.47 (m, 2H), 7.42–7.33 (m, 2H), 7.16 (s, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.60 (s, 1H), 4.00 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.1, 148.7, 141.5, 138.9, 138.8, 137.4 (x2), 134.4, 134.1, 133.0, 131.5, 130.1, 128.1, 127.8, 127.5, 126.9 (x2), 126.2, 126.0, 126.0, 116.6, 113.3, 56.2, 56.2; HRMS (APCI) *m/z* calcd for $C_{24}H_{18}O_2+H^+$: 339.1380 $[M+H]^+$; found: 339.1378.

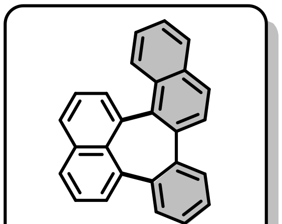
12,14-Dimethyldibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene (3an):



3an

Prepared following the general procedure A using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), 4-metheyliumyl-2-methyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2n**) (205.3 mg, 0.45 mmol) and purified by column chromatography on aluminium oxide 60 PF_{254} (Type E) followed by silica gel using hexane as eluent to obtain the product as an off-white solid (42.6 mg, 60% yield); Mp: 161.1–163.9 °C (from CH_2Cl_2/Hexane); IR (neat): 3032, 2919, 1604, 1453, 1256, 1036 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.77 (t, *J* = 8.0 Hz, 2H), 7.70 (dd, *J* = 15.3, 7.9 Hz, 2H), 7.50–7.41 (m, 3H), 7.38–7.28 (m, 3H), 7.09 (s, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 2.39 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.9, 139.9, 139.8, 139.2, 137.8, 137.4, 137.4, 137.2, 133.6, 133.5, 132.6, 132.3, 130.8, 130.4, 129.8, 127.8, 127.42, 126.8, 126.7, 125.9, 125.7, 124.1, 22.9, 21.1; HRMS (APCI) *m/z* calcd for $C_{24}H_{18}+H^+$: 307.1481 $[M+H]^+$; found: 307.1485.

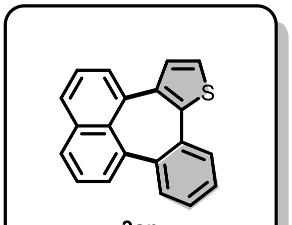
Benzo[6,7]cyclohepta[2,1-*a*:3,4,5-*d'e'*]dinaphthalene (3ao):



3ao

Prepared following the general procedure A using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), benzo[*b*]naphtho[2,1-*d*]iodol-11-ium trifluoromethanesulfonate (**2o**) (215.2 mg, 0.45 mmol) and purified by column chromatography on aluminium oxide 60 PF_{254} (Type E) followed by silica gel using hexane as eluent to obtain the product as a brown solid (47.4 mg, 60% yield); Mp: 100.2–101.8 °C (from CH_2Cl_2/Hexane); IR (neat): 3049, 2920, 2849, 1493, 1234, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.90 (t, *J* = 7.4 Hz, 2H), 7.82–7.80 (m, 3H), 7.73–7.71 (m, 3H), 7.56–7.48 (m, 2H), 7.45–7.31 (m, 4H), 7.25–7.21 (m, 1H), 7.03 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 142.8, 141.9, 139.0, 137.7, 137.3, 136.5, 134.1, 134.0, 133.7, 133.0, 132.2, 131.9, 130.8, 128.8, 128.5, 128.2, 128.1, 127.7, 127.4, 126.7, 126.3, 126.2, 126.0, 125.9, 125.8, 124.1; HRMS (APCI) *m/z* calcd for $C_{26}H_{16}+H^+$: 329.1325 $[M+H]^+$; found: 329.1324.

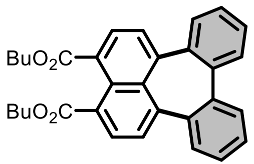
Benzo[6,7]naphtho[1',8':3,4,5]cyclohepta[1,2-*b*]thiophene (3ap):



3ap

Prepared following the general procedure A using 1,8-naphthalic anhydride (**1a**) (44.6 mg, 0.225 mmol), benzo[*b*]thieno[2,3-*d*]iodol-4-ium trifluoromethanesulfonate (**2p**) (195.4 mg, 0.45 mmol) and purified by column chromatography on aluminium oxide 60 PF_{254} (Type E) followed by silica gel using hexane as eluent to obtain the product as a brown solid (32.5 mg, 51% yield); Mp: 114.4–116.2 °C (decomposition) (from CH_2Cl_2/Hexane); IR (neat): 3042, 2917, 1489, 1461, 1045 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.74–7.64 (m, 5H), 7.51–7.44 (m, 2H), 7.36–30 (m, 3H), 7.18–7.16 (m, 1H), 7.02 (d, *J* = 5.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 140.7, 139.6, 138.7, 138.0, 137.7, 134.8, 134.3, 133.5, 132.7, 132.3, 129.2, 129.2, 128.9, 128.3, 128.2, 127.2, 126.1, 125.9, 125.8, 125.1; HRMS (APCI) *m/z* calcd for $C_{20}H_{12}S+H^+$: 285.0732 $[M+H]^+$; found: 285.0734.

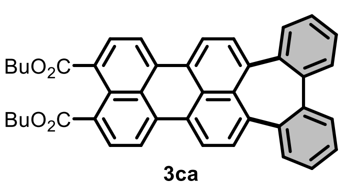
Dibutyl dibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]naphthalene-3,4-dicarboxylate (3ba):



3ba

Prepared following the general procedure A using dibutyl 1,3-dioxo-1H,3H-benzo[*de*]isochromene-6,7-dicarboxylate (**1b**) (89.6 mg, 0.225 mmol), diphenyleniodonium trifluoromethanesulfonate (**2a**) (192.7 mg, 0.45 mmol) and purified by column chromatography on silica gel using 10% EtOAc/hexane to obtain the product as a pale yellow solid (49.7 mg, 46% yield); Mp: 73.8–75.1 °C (from CH_2Cl_2/Hexane); IR (neat): 2957, 2929, 1708, 1574, 1454, 1260 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 7.4 Hz, 2H), 7.73 (d, *J* = 7.4 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 4.40–4.23 (m, 4H), 1.80–1.75 (m, 4H), 1.53–1.43 (m, 4H), 0.99 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.7, 141.2, 140.2, 140.0, 138.1, 133.9, 130.1, 129.6, 128.7, 128.7, 128.6, 126.6, 126.0, 65.4, 30.8, 19.4, 14.0; HRMS (APCI) *m/z* calcd for $C_{32}H_{30}O_4^+$: 478.2144 $[M]^+$; found: 478.2145; UV/Vis ($CHCl_3$): λ_{max} (ε) = 368 nm (15200 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 368 nm): λ_{em} = 449 nm. Quantum yield ($CHCl_3$): 0.03.

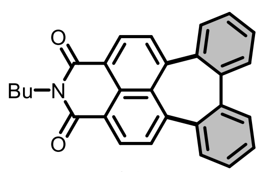
Dibutyl dibenzo[4,5:6,7]cyclohepta[1,2,3-*cd*]perylene-1,18-dicarboxylate (3ca):



3ca

Prepared following the general procedure A using dibutyl 1,3-dioxo-1H,3H-benzo[10,5]anthra[2,1,9-*def*]isochromene-8,9-dicarboxylate (**1c**) (117.6 mg, 0.225 mmol), diphenyleniodonium trifluoromethanesulfonate (**2a**) (192.7 mg, 0.45 mmol) and purified by column chromatography on silica gel using 20% EtOAc/hexane to obtain the product as a red solid (53.7 mg, 40% yield); Mp: 119.0–120.6 °C (from CH_2Cl_2/Hexane); IR (neat): 3049, 2955, 1705, 1562, 1254, 1158 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.30 (d, *J* = 8.0 Hz, 2H), 8.23 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 7.9 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.47–7.40 (m, 4H), 7.15 (d, *J* = 7.6 Hz, 2H), 4.34–4.31 (m, 4H), 1.81–1.74 (m, 4H), 1.53–1.43 (m, 4H), 0.99 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.1, 141.2, 140.0, 139.0, 138.8, 134.6, 133.5, 130.8, 130.4, 129.7, 129.3, 129.1, 128.96, 128.6, 128.4, 128.1, 127.4, 122.8, 119.8, 65.3, 30.9, 19.5, 14.0; HRMS (APCI) *m/z* calcd for $C_{42}H_{34}O_4^-$: 602.2457 $[M]^-$; found: 602.2448; UV/Vis ($CHCl_3$): λ_{ex} (ε) = 514 nm (42200 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 485 nm): λ_{em} = 555 nm. Quantum yield ($CHCl_3$): 0.79.

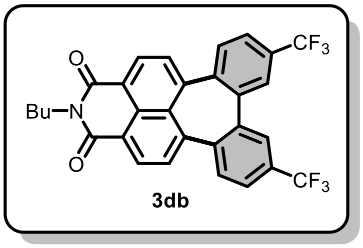
2-Butyl-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-*cd*]pyridine-1,3(2H)-dione (3da):



3da

Prepared following the general procedure A using 7-butyl-1H-isochromeno[6,5,4-*def*]isoquinoline-1,3,6,8(7H)-tetraone (**1d**) (72.7 mg, 0.225 mmol), diphenyleniodonium trifluoromethanesulfonate (**2a**) (192.7 mg, 0.45 mmol) and purified by column chromatography on silica gel using 10% EtOAc/hexane to obtain the product as a yellow solid (24.5 mg, 27% yield); Mp: 210.6–212.7 °C (from CH_2Cl_2/Hexane); IR (neat): 3056, 2957, 1644, 1567, 1234, 1154 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.61 (d, *J* = 7.7 Hz, 2H), 8.00 (d, *J* = 7.7 Hz, 2H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.53–7.47 (m, 4H), 7.18 (d, *J* = 7.6 Hz, 2H), 4.20 (t, *J* = 7.4 Hz, 2H), 1.78–1.70 (m, 2H), 1.51–1.40 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.3, 143.8, 139.6, 138.4, 136.4, 134.0, 131.1, 130.9, 129.3, 129.0, 127.7, 127.20, 121.3, 40.4, 30.4, 20.6, 14.0; HRMS (APCI) *m/z* calcd for $C_{28}H_{21}NO_2+H^+$: 404.1645 $[M+H]^+$; found: 404.1644; UV/Vis ($CHCl_3$): λ_{max} (ε) = 412 nm (18800 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 412 nm): λ_{em} = 471 nm. Quantum yield ($CHCl_3$): 0.76.

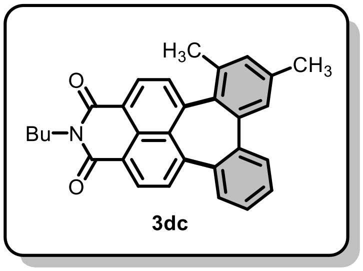
2-Butyl-8,11-bis(trifluoromethyl)-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-*cd*]pyridine-1,3(2H)-dione (3db):



3db

Prepared following the general procedure A using 7-butyl-1H-isochromeno[6,5,4-*def*]isoquinoline-1,3,6,8(7H)-tetraone (**1d**) (72.7 mg, 0.225 mmol), 2,8-bis(trifluoromethyl)dibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2f**) (253.9 mg, 0.45 mmol) and purified by column chromatography on silica gel using 10% EtOAc/hexane to obtain the product as a light-yellow solid (45.9 mg, 38% yield); Mp: > 300 °C (from CH_2Cl_2/Hexane); IR (neat): 3067, 2969, 1646, 1580, 1232, 1124 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66 (d, *J* = 7.7 Hz, 2H), 8.06 (d, *J* = 7.7 Hz, 2H), 7.96 (s, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.19 (t, *J* = 7.3 Hz, 2H), 1.84–1.63 (m, 2H), 1.50–1.41 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.9, 142.9, 141.6, 137.8, 136.4, 134.8, 131.6 (q, $J_{C,F}$ = 33.3), 131.3, 128.2, 128.3, 127.8 (q, $J_{C,F}$ = 3.3 Hz), 126.0 (q, $J_{C,F}$ = 3.4 Hz), 122.5 (q, $J_{C,F}$ = 273.7 Hz), 122.4, 40.6, 30.4, 20.6, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.7; HRMS (APCI) *m/z* calcd for $C_{30}H_{19}F_6NO_2$+H$^+$: 540.1393 [*M*+H]$^+$; found: 540.1395; UV/Vis ($CHCl_3$): λ_{max} (ε) = 396 nm (29400 mol^{-1}dm^{3}cm^{-1}); Fluorescence ($CHCl_3$, λ_{ex} = 396 nm): λ_{em} = 462 nm. Quantum yield ($CHCl_3$): 0.25.

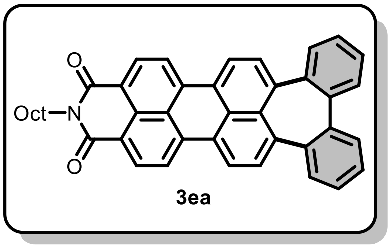
2-Butyl-11,13-dimethyl-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':4,5]naphtho[1,8-cd]pyridine-1,3(2H)-dione (3dc):



3dc

Prepared following the general procedure A using 7-butyl-1H-isochromeno[6,5,4-*def*]isoquinoline-1,3,6,8(7H)-tetraone (**1d**) (72.7 mg, 0.225 mmol), 4-metheyliumyl-2-methyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2n**) (205.3 mg, 0.45 mmol) and purified by column chromatography on silica gel using 5% EtOAc/hexane to obtain the product as a yellow solid (12.7 mg, 13% yield); Mp: 246.4–248.1 °C (from CH_2Cl_2/Hexane); IR (neat): 3056, 2957, 1690, 1640, 1324, 1035 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.59 (d, *J* = 7.7 Hz, 1H), 8.54 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 6.9 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 8.1 Hz, 1H), 7.34 (s, 1H), 7.16 (s, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 4.20 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.99 (s, 3H), 1.79–1.71 (m, 2H), 1.52–1.43 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.5, 164.3, 143.5, 140.2, 139.8, 139.0, 138.6, 137.7, 137.4, 135.4, 133.5, 133.0, 131.2, 131.0 (x2), 130.8, 130.01, 129.1, 129.0, 128.5, 127.3, 126.0, 120.8 (x2), 40.4, 30.5, 23.1, 21.3, 20.6, 14.1; HRMS (APCI) *m/z* calcd for $C_{30}H_{25}NO_2$+H$^+$: 432.1958 [*M*+H]$^+$; found: 432.1957; UV/Vis ($CHCl_3$): λ_{max} (ε) = 416 nm (23800 mol^{-1}dm^{3}cm^{-1}); Fluorescence ($CHCl_3$, λ_{ex} = 416 nm): λ_{em} = 479 nm. Quantum yield ($CHCl_3$): 0.90.

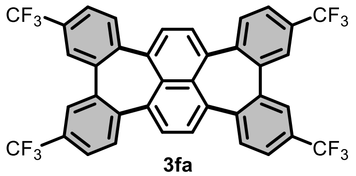
2-Octanoyl-1H-dibenzo[4',5':6',7']cyclohepta[1',2',3':9,10]peryleno[3,4-*cd*]pyridine-1,3(2H)-dione (3ea):



3ea

Prepared following the general procedure A using 9-octyl-1H-isochromeno[6',5',4':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10(9H)-tetraone (**1e**) (113.3 mg, 0.225 mmol), diphenyleniodonium trifluoromethanesulfonate (**2a**) (192.7 mg, 0.45 mmol) and purified by column chromatography on silica gel using 75% CH_2Cl_2/hexane to obtain the product as a purple solid (17.0 mg, 13% yield); Mp: > 300 °C (from CH_2Cl_2/Hexane); IR (neat): 2954, 1650, 1561, 1297, 1135 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.50 (d, *J* = 8.0 Hz, 2H), 8.34 (d, *J* = 8.0 Hz, 2H), 8.29 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.73 (d, *J* = 7.1 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.1 Hz, 2H), 7.16 (d, *J* = 7.5 Hz, 2H), 4.15 (t, *J* = 7.5 Hz, 2H), 1.79–1.71 (m, 2H), 1.39–1.28 (m, 10H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.0, 140.9, 140.2, 139.9, 138.7, 137.0, 133.5, 131.6, 130.5, 129.8, 128.8, 128.7, 128.2, 128.1, 127.4, 126.2, 124.0, 120.9, 120.3, 40.7, 32.0, 29.6, 29.5, 28.3, 27.4, 22.9, 14.3; HRMS (APCI) *m/z* calcd for $C_{42}H_{33}NO_2$+H$^+$: 584.2584 [*M*+H]$^+$; found: 584.2571; UV/Vis ($CHCl_3$): λ_{max} (ε) = 546 nm (31000 mol^{-1}dm^{3}cm^{-1}); Fluorescence ($CHCl_3$, λ_{ex} = 500 nm): λ_{em} = 619 nm. Quantum yield ($CHCl_3$): 0.51.

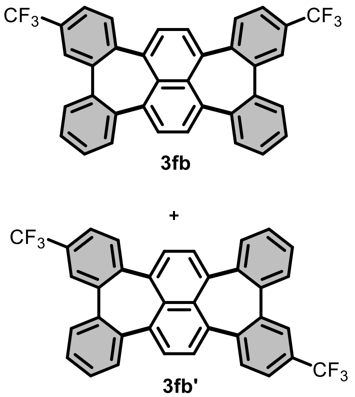
3,6,13,16-Tetrakis(trifluoromethyl)dibenzo[4,5:6,7]cyclohepta[1,2,3-*de*]dibenzo[4,5:6,7]cyclohepta[1,2,3-*ij*]naphthalene (3fa):



3fa

Prepared following the general procedure B using using 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) (**1f**) (60.3 mg, 0.225 mmol), bis(trifluoromethyl)dibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2f**) (507.7 mg, 0.90 mmol) and purified by column chromatography on silica gel using hexane as eluent to obtain the product as a yellow solid (60.3 mg, 38% yield); Mp: 301.8–302.3 °C (from CH_2Cl_2/Hexane); IR (neat): 2926, 1614, 1340, 1120 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.86 (s, 4H), 7.73 (s, 4H), 7.66 (d, *J* = 7.6 Hz, 4H), 7.21 (d, *J* = 8.2 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.9, 139.0, 138.0, 135.8, 133.7, 130.7 (q, $J_{C,F}$ = 33.0 Hz), 127.4 (d, $J_{C,F}$ = 3.6 Hz), 127.1, 125.7 (d, $J_{C,F}$ = 3.5 Hz), 124.1 (q, $J_{C,F}$ = 273.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.5; HRMS (APCI) *m/z* calcd for $C_{38}H_{16}F_{12}+H^+$: 701.1133 [*M*+H]$^+$; found: 701.1135; UV/Vis ($CHCl_3$): λ_{max} (ε) = 393 nm (24000 $mol^{-1}dm^3cm^{-1}$); Fluorescence ($CHCl_3$, λ_{ex} = 393 nm): λ_{em} = 457 nm. Quantum yield ($CHCl_3$): 0.17.

3,13-bis(trifluoromethyl)dibenzo[4,5:6,7]cyclohepta[1,2,3-de]dibenzo[4,5:6,7]cyclohepta[1,2,3-ij] naphthalene (3fb) /3,16-Bis(trifluoromethyl)dibenzo[4,5:6,7]cyclohepta[1,2,3-de]dibenzo[4,5:6,7] cyclohepta[1,2,3ij] naphthalene (3fb'):



3fb

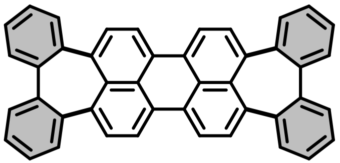
+

3fb'

(1:1)

Prepared following the general procedure B using using 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) (**1f**) (60.3 mg, 0.225 mmol), 2-(trifluoromethyl)dibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2e**) (507.7 mg, 0.90 mmol) and purified by column chromatography on silica gel using hexane as eluent to obtain the product as a yellow solid (33.0 mg, 26% yield); ^1H NMR (400 MHz, $CDCl_3$, * marked as another regioisomer) δ = 7.88 (s, 4H, both isomers), 7.67–7.64 (m, 12H, both isomers), 7.59 (d, *J* = 8.2 Hz, 4H, both isomers), 7.49–7.40 (m, 8H, both isomers), 7.19 (d, *J* = 3.8 Hz, 2H), 7.17* (d, *J* = 3.8 Hz, 2H), 7.11 (d, *J* = 2.4 Hz, 2H), 7.09* (d, *J* = 3.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.1, 140.6, 139.4, 139.1, 137.5, 137.0, 136.2, 133.5, 133.1, 130.5, 129.4, 128.5, 128.4, 127.4, 126.7, 126.5, 124.9, 124.4 (q, $J_{C,F}$ = 273.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.51, -62.52*; HRMS (APCI) *m/z* calcd for $C_{36}H_{18}F_6+H^+$: 565.1385 [*M*+H]$^+$; found: 565.1384.

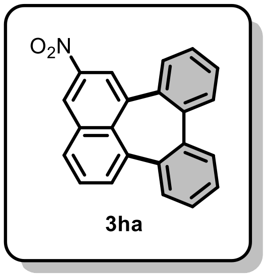
Dibenzo[4,5:6,7]cyclohepta[1,2,3-*cd*]dibenzo[4,5:6,7]cyclohepta[1,2,3-*lm*]perylene (3ga):



3ga

Prepared following the general procedure B using 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) (**1g**) (88.3 mg, 0.225 mmol), diphenyleniodonium trifluoromethanesulfonate (**2a**) (385.4 mg, 0.90 mmol) and purified by preparative thin-layer chromatography on silica gel using 20% CH_2Cl_2/hexane to obtain the product as a red solid (2.4 mg, 2% yield); IR (neat): 3050, 2919, 2850, 1684 cm^{-1}; ^1H NMR (400 MHz, $C_2D_2Cl_4$, 120 °C) δ = 8.32 (d, *J* = 8.0 Hz, 4H), 7.84 (d, *J* = 7.9 Hz, 4H), 7.71 (d, *J* = 7.6 Hz, 4H), 7.50–7.44 (m, 8H), 7.20 (d, *J* = 7.4 Hz, 4H); ^{13}C NMR (101 MHz, $C_2D_2Cl_4$, 120 °C) δ = 141.5, 140.3, 139.1, 138.6, 137.3, 132.9, 130.0 (x2), 128.0, 127.7, 127.6, 120.8 ; HRMS (APCI) *m/z* calcd for $C_{44}H_{24}+H^+$: 553.1951 [*M*+H]$^+$; found: 553.1953.

2-Nitrodibenzo[4,5:6,7]cyclohepta[1,2,3-de]naphthalene (3ha):



3ha

Prepared following the general procedure A using 3-nitro-1,8-naphthalic anhydride (**1h**)[9] (54.7 mg, 0.225 mmol), diphenyleniodonium trifluoromethanesulfonate (**2a**) (192.7 mg, 0.45 mmol) and purified by column chromatography on silica gel using 5% EtOAc/hexane to obtain the product as a yellow solid (39.3 mg, 54% yield); Mp: 189.1–190.2 °C (from CH_2Cl_2/Hexane); IR (neat): 3066, 1756, 1526, 1327 cm^{-1}; ^1H NMR (400 MHz,) δ = 8.66 (d, *J* = 2.2 Hz, 1H), 8.48 (d, *J* = 2.2 Hz, 1H), 7.97–7.85 (m, 2H), 7.73–7.61 (m, 3H), 7.55–7.37 (m, 4H), 7.14 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.07 (dd, *J* = 7.7, 1.5 Hz, 1H); ^{13}C NMR (101 MHz,) δ = 145.8, 141.1, 140.2, 140.0, 139.7, 138.8, 138.4, 138.1, 134.1, 134.0, 131.7, 130.8 (x2), 130.2, 129.3, 129.0, 128.9, 128.8, 128.5, 128.0, 123.3, 119.3; HRMS (ESI) *m/z* calcd for $C_{22}H_{13}NO_2^+$: 323.0946 $[M]^+$; found: 323.0937.

VII. X-ray Single Crystal Analysis

The diffraction data were collected on a Bruker CCD diffractometer controlled by *APEX3* software and the cell refinement and data reduction were carried out by *SAINT*.[10] Absorption correction was done by multi-scan method using *SADABS*.[11] The structure solution was done by intrinsic phasing method in *SHELXT* software.[12] The structure was then refined on F^2 by full-matrix least-squares method using *SHELXL* program package.[13] All non-hydrogen atoms were treated anisotropically while the H atoms were refined by a riding model with d(C—H) = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic hydrogen atoms, with d(C—H) = 0.99 Å and U_{iso}(H) = 1.2U_{eq}(C) for $–CH_2–$ hydrogen atoms and d(C–H) = 0.98 Å, U_{iso}(H) = 1.5U_{eq}(C) for the terminal methyl hydrogen atoms. Software packages used to prepare molecular graphics and materials for publication were Olex^2.[14] and Mercury.[15]

Table S1. Crystal data and structure refinement for **3dc**.

Identification code	**3dc**
CCDC number	2014875
Empirical formula	$C_{30}H_{25}NO_2$
Formula weight	431.51
Temperature/K	273.15
Crystal system	monoclinic
Space group	C2/c
a/Å	29.740(4)
b/Å	4.6409(6)
c/Å	34.041(5)
α/°	90
β/°	108.029(7)
γ/°	90
Volume/Å^3	4467.7(11)
Z	8
ρ_{calc}g/cm^3	1.283
μ/mm^{-1}	0.626
F(000)	1824.0
Crystal size/mm^3	0.05 × 0.05 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.912 to 136.482
Index ranges	$-33 \leq h \leq 35$, $-5 \leq k \leq 5$, $-39 \leq l \leq 40$
Reflections collected	16010
Independent reflections	4084 [R_{int} = 0.0334, R_{sigma} = 0.0308]
Data/restraints/parameters	4084/0/301
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0521, wR_2 = 0.1416
Final R indexes [all data]	R_1 = 0.0599, wR_2 = 0.1466
Largest diff. peak/hole / e Å^{-3}	0.17/-0.16

Table S2. Bond Lengths for **3dc.**

Bond	Length/Å	Bond	Length/Å
O1–C5	1.222(2)	C21–C25	1.513(3)
O2–C9	1.223(2)	C8–C16	1.374(3)
N1–C5	1.393(3)	C18–C19	1.487(3)
N1–C9	1.394(3)	C18–C24	1.392(3)
N1–C4	1.465(3)	C14–C20	1.479(3)
C13–C7	1.418(3)	C14–C15	1.385(3)
C13–C12	1.445(3)	C16–C15	1.392(3)
C13–C14	1.433(3)	C19–C20	1.399(3)
C7–C6	1.414(3)	C19–C27	1.393(3)
C7–C8	1.417(3)	C22–C23	1.379(3)
C12–C17	1.488(3)	C20–C30	1.407(3)
C12–C11	1.380(3)	C23–C24	1.378(3)
C17–C21	1.420(3)	C23–C26	1.511(3)
C17–C18	1.407(3)	C4–C3	1.512(3)
C11–C10	1.391(3)	C3–C2	1.502(3)
C6–C5	1.472(3)	C30–C29	1.375(4)
C6–C10	1.375(3)	C27–C28	1.384(4)
C9–C8	1.469(3)	C28–C29	1.371(5)
C21–C22	1.390(3)	C2–C1	1.498(4)

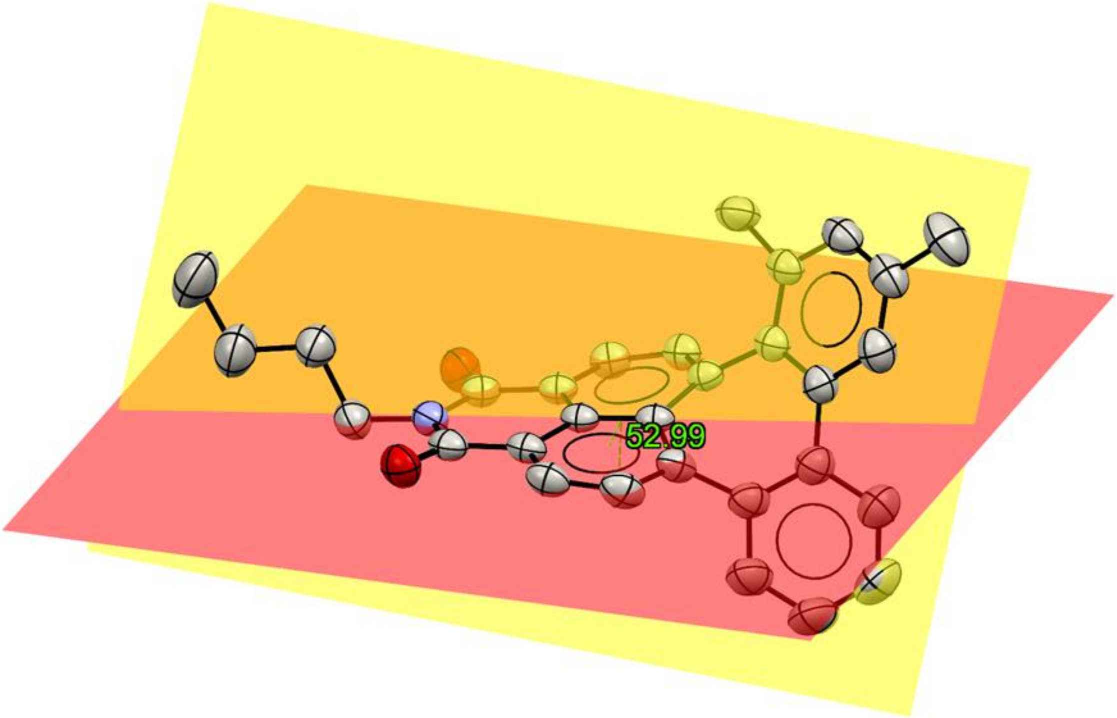


Figure S3. The mean plane (red plane) is constructed from 10 atoms in the naphthyl group (C6 to C8 and C10 to C16). The mean plane (yellow plane) is constructed from 12 atoms in biphenyl group (C17 to C24 and C27 to C30). The intersecting angle between two planes is about 53.0 Å.

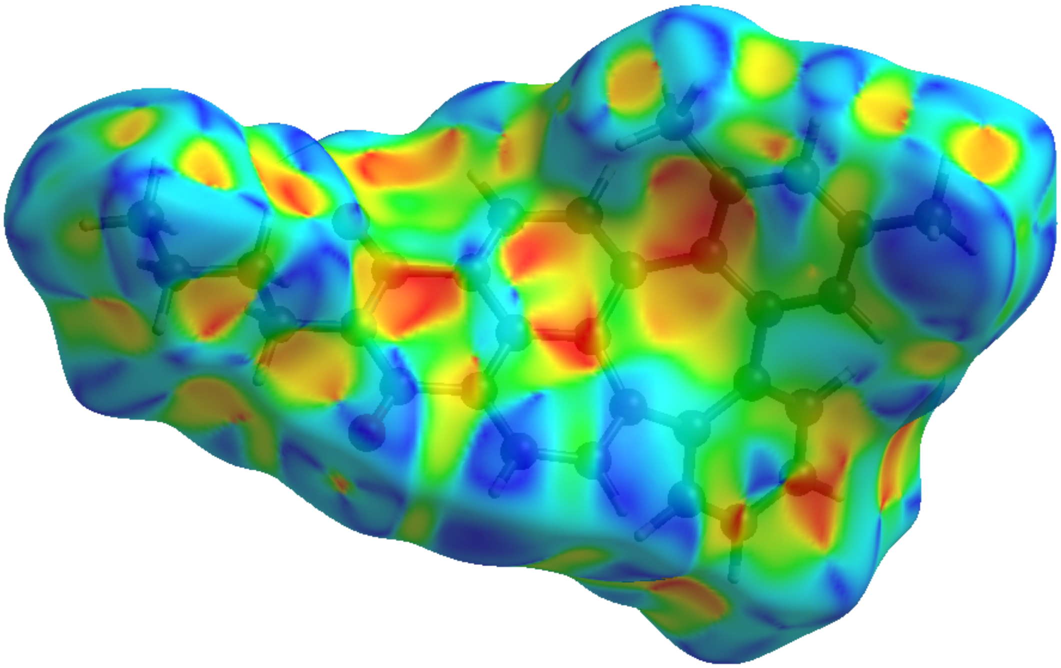


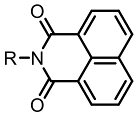
Figure S4. Shape index Hirshfeld surface plotted over d_{norm} in the range -1.0000 to 1.0000 a.u. The surface is computed by *Crystal Explorer 17.5* software.[16] The presence of adjacent orange and blue triangular regions in the shape index Hirshfeld surface confirms that π–π interactions occur in the crystal structure of **3dc**.

VIII. Photophysical Properties

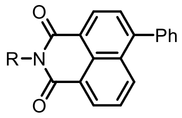
Table S3. The photophysical properties of compounds **3aa**, **3af**, **3ba**, **3ca**, **3da**, **3db**, **3dc**, **3ea** and **3fa** in $CHCl_3$ and reference compounds.

Compounds	λ_{ab}[a] [nm]	λ_{em}[b] [nm]	Stokes shifts [nm]	ε [M^{-1} cm^{-1}]	Fluorescent quantum yield[c] [Φ]
3aa	339	398	59	11600	0.29
3af	339	423	84	17900	0.26
3ba	368	449	81	15200	0.03
3ca	514	555	41	47400	0.79[d]
3da	412	471	59	18800	0.76
3db	396	462	66	29400	0.25
3dc	416	479	63	23800	0.90
3ea	546	619	73	31000	0.51[e]
3fa	393	454	61	24000	0.17
10[f]	334	380	66	NA	0.007
11[f]	355	420	46	17100	0.78
12[f]	370	447	77	27400	0.18
13[f]	525	580	55	NA	0.57

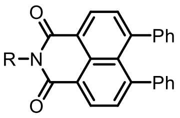
[a] Absorption maxima in $CHCl_3$ (10^{-5} mol/L). [b] Emission maxima in $CHCl_3$ (10^{-6} mol/L). [c] Absolute quantum yield in $CHCl_3$ (10^{-6} mol/L) determined with an integrating sphere system. [d] λ_{ex} = 485 nm. [e] λ_{ex} = 500 nm. [f] data taken from references.[17]



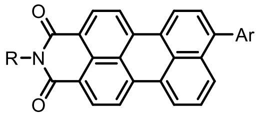
10
R = 2,6-di-*tert* butyl phenyl



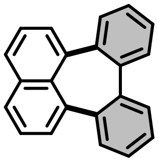
11
R = $CH(C_6H_{13})_2$



12
R = Bu



13
R = $CH(C_6H_{13})_2$
Ar = 4-methoxynaphth-1-yl



3aa

ε = 11600 M^{-1}cm-1
λ_{abs} = 339 nm
λ_{ex} = 398 nm
[Φ] = 0.29

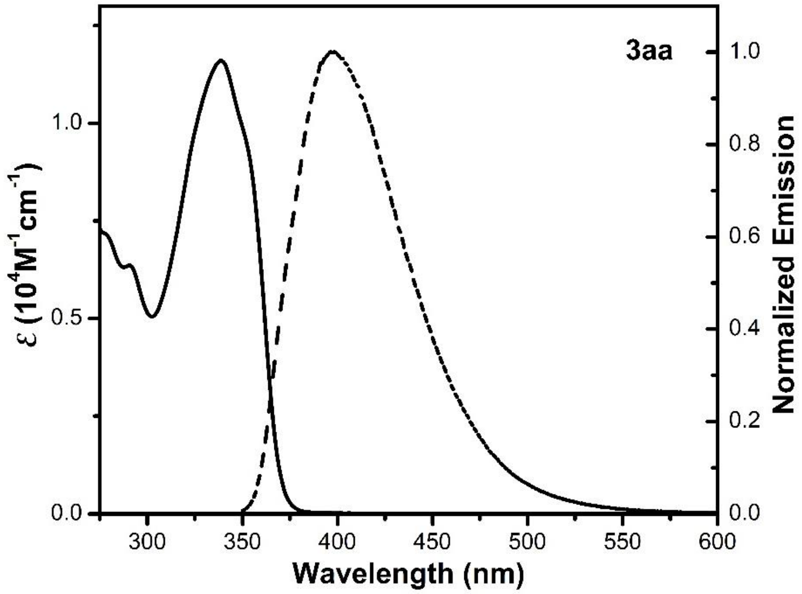
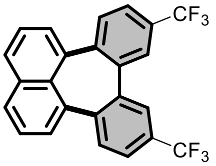


Figure S5. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3aa** in CHCl$_3$.



3af

ε = 17900 M^{-1}cm-1
λ_{abs} = 339 nm
λ_{ex} = 423 nm
[Φ] = 0.26

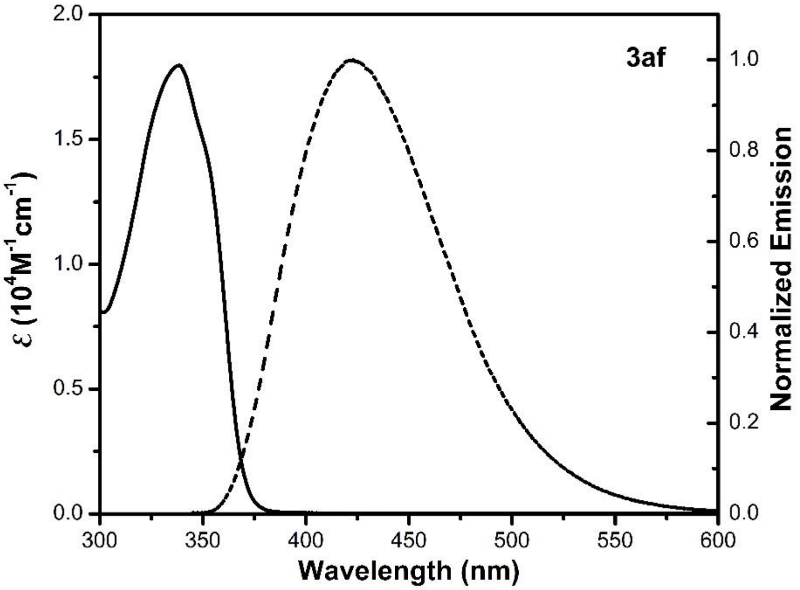
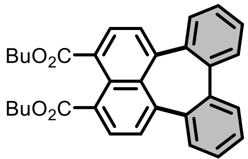


Figure S6. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3af** in CHCl$_3$.



3ba

ε = 15200 M^{-1}cm^{-1}
λ_{abs} = 368 nm
λ_{ex} = 449 nm
[Φ] = 0.03

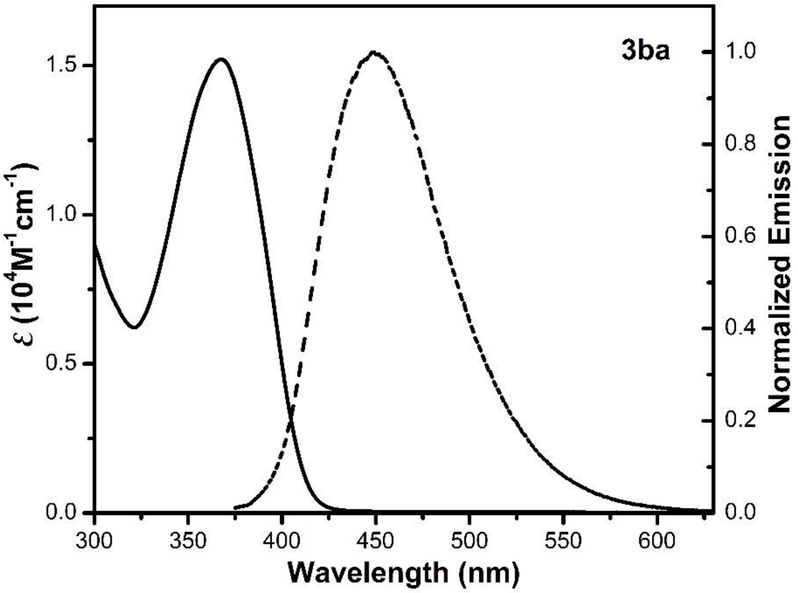
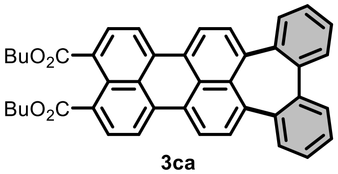


Figure S7. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3ba** in $CHCl_3$.



3ca

ε = 42200 M^{-1}cm^{-1}
λ_{abs} = 514 nm
λ_{ex} = 555 nm
[Φ] = 0.79

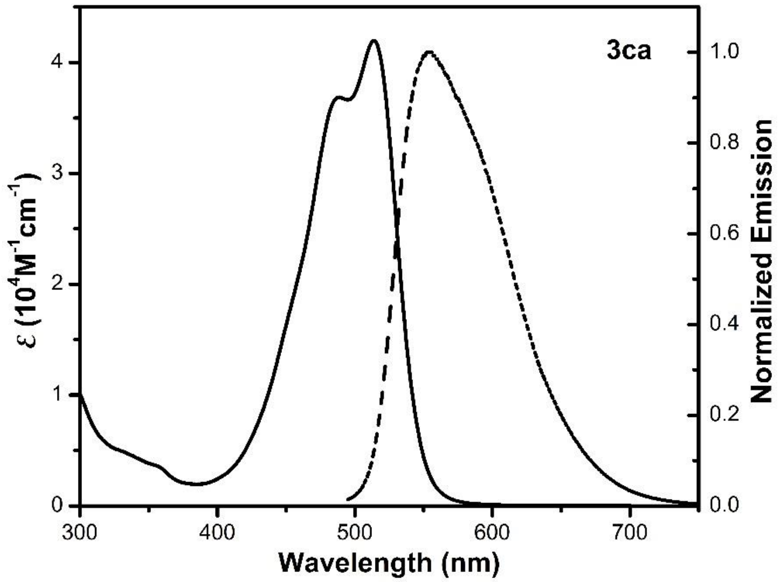
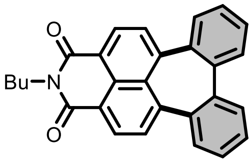


Figure S8. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3ca** in $CHCl_3$.



3da

ε = 18800 M^{-1}cm-1
λ_{abs} = 442 nm
λ_{ex} = 471 nm
[Φ] = 0.76

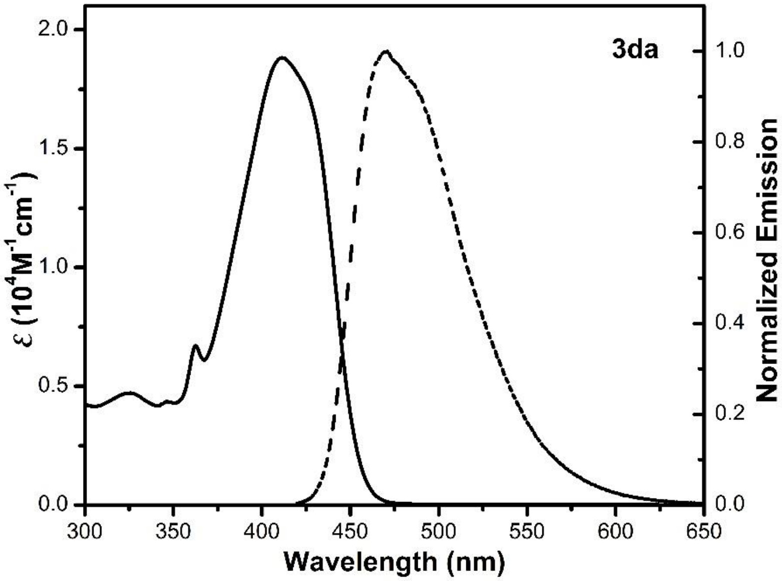
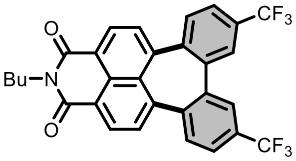


Figure S9. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3da** in $CHCl_3$.



3db

ε = 26400 M^{-1}cm^{-1}
λ_{abs} = 396 nm
λ_{ex} = 462 nm
[Φ] = 0.25

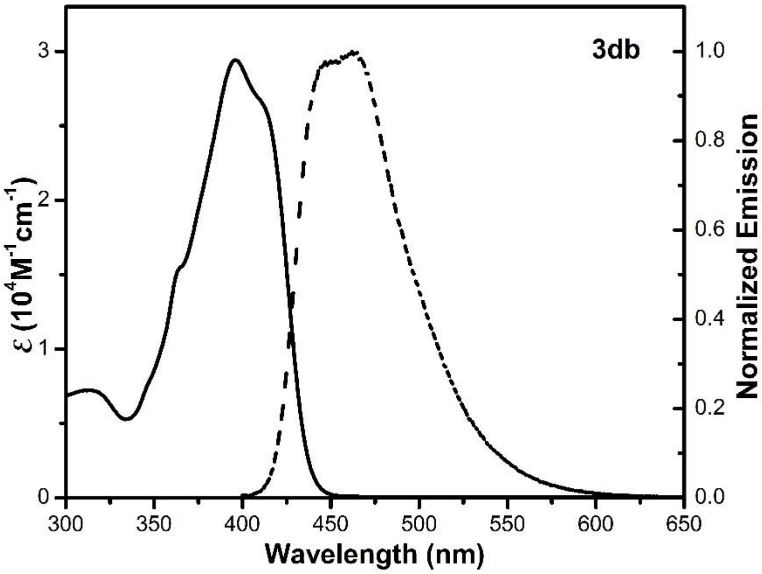
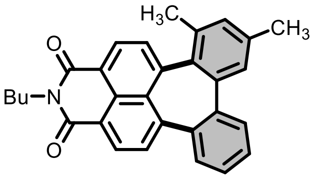


Figure S10. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3db** in $CHCl_3$.



3dc

ε = 23800 M^{-1}cm-1
λ_{abs} = 416 nm
λ_{ex} = 479 nm
[Φ] = 0.90

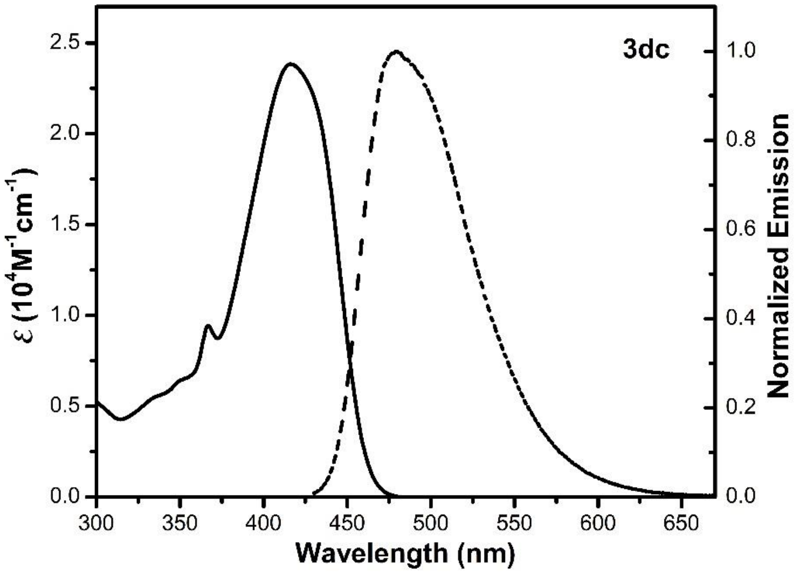
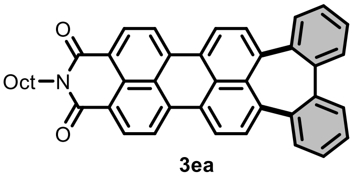


Figure S11. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3dc** in $CHCl_3$.



3ea

ε = 31000 $M^{-1}cm^{-1}$
λ_{abs} = 546 nm
λ_{ex} = 619 nm
[Φ] = 0.51

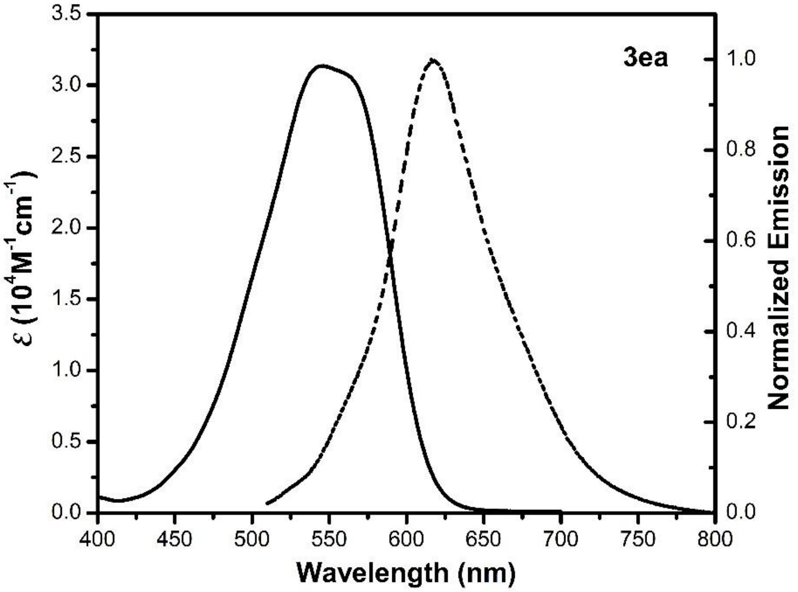
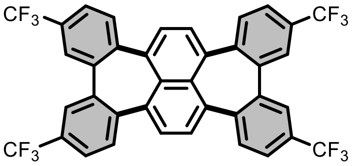


Figure S12. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3ea** in $CHCl_3$.



3fa

ε = 24000 M^{-1}cm^{-1}
λ_{abs} = 393 nm
λ_{ex} = 454 nm
[Φ] = 0.17

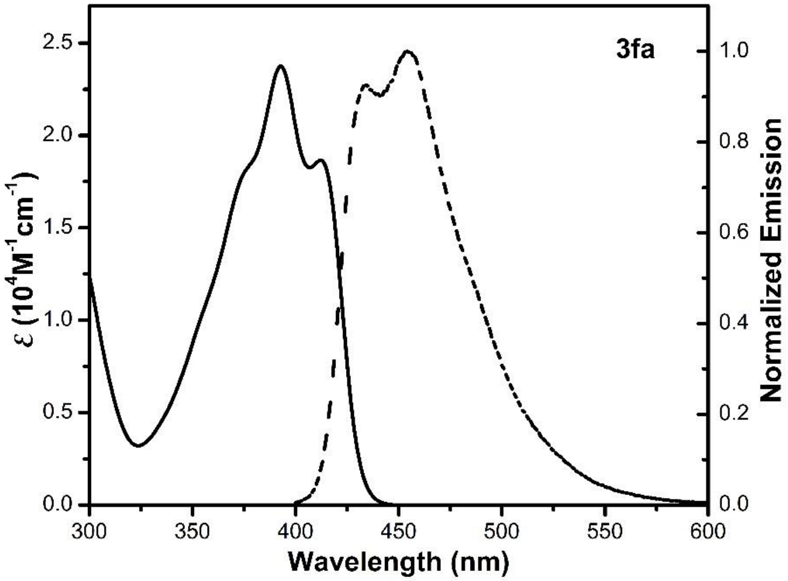


Figure S13. UV/Vis absorption spectra (solid lines) and fluorescence emission spectra (dashed line) obtained for compounds **3fa** in CHCl$_3$.

IX. DFT Calculations

Computation details

Density functional theory and time-dependent density functional theory (TD-DFT) calculation were performed to determine electronic structures and electronic transition energies of **3aa**, **3da, 3db**, **3fa,** and **3ea** model compounds, in which the Bu group was truncated to Me group. All calculations were performed with Gaussian 09 package.[18] Ground-state geometry optimizations were calculated in gas phase with B3LYP functional [19-21] and 6-31G(d) [22-24] basis set. The frequency calculations for each optimized geometry was carried out to ensure that each stationary point corresponds to the true minima. The TD-DFT was performed in chloroform solvent for ten singlet excited states using CAM-B3LYP functional[25] and 6-31++G(d,p) basis set.[22-24] Conductor like polarizable continuum model (CPCM)[26-27] was used with chloroform parameters. Molecular orbitals were plotted using Jimp2 visualizing program.[28-29]

We performed time-dependent density functional theory (TD-DFT) to calculate the electronic structures and electronic transition energies of compounds **3aa**, **3da, 3db**, **3fa,** and **3ea** (Table S4 and Figure S14). The calculated absorption energies are slightly shifted from the experimental absorption energies as also found in other works. [30-32] In general, the calculated absorption energies are in good agreement with the experiment.

Table S4. Calculated electronic transition energies (in eV and nm) and oscillator strength (*f*) of **3aa**, **3da**, **3db**, **3fa**, and **3ea** using CAM-B3LYP/6-31++G(d,p).

	Calculation				**Experiment**	
	Band assignment	**Energy (eV)**	**λ_{ab} (nm)**	***f***	**λ_{ab} (nm)**	***f***
3aa	H-0 → L+0(96.54%)	3.86	321.5	0.398	339	11600
	H-1 → L+1(68.78%)	5.21	238.1	0.508		
3da	H-0 → L+0(96.44%)	3.25	381.3	0.619	412	18800
3db	H-0 → L+0(97.08%)	3.32	373.4	0.648	396	29400
D_2-3fa	H-0 → L+0(96.48%)	3.32	373.3	0.732	393	24000
C_{2h}-3fa	H-0 → L+0(96.69%)	3.38	367.1	0.832		
3ea	H-0 → L+0(97.55%)	2.40	515.9	1.120	546	31000

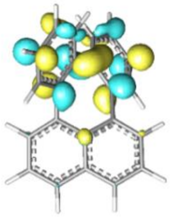
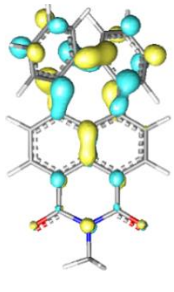
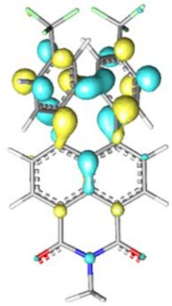
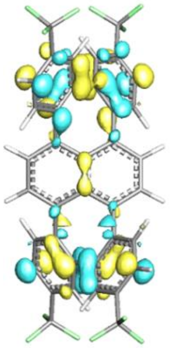
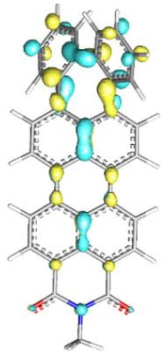
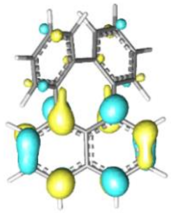
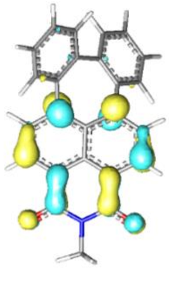
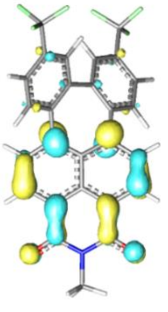
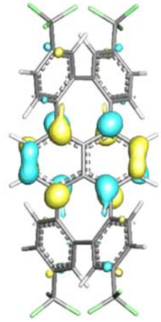
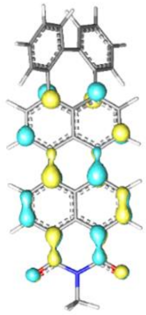
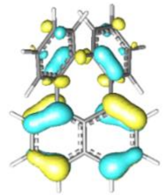
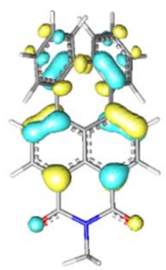
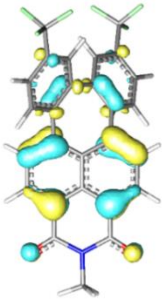
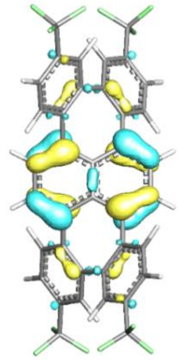
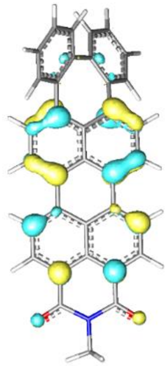
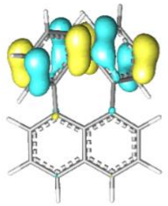
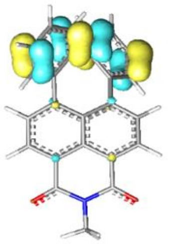
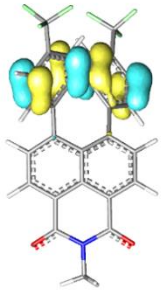
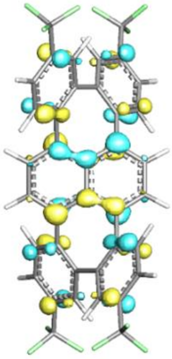
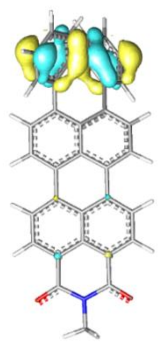
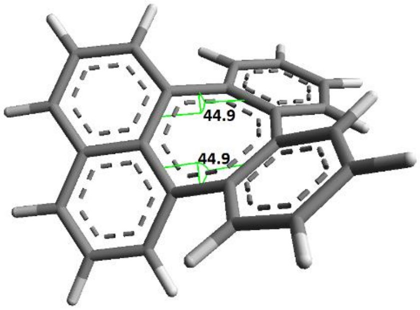
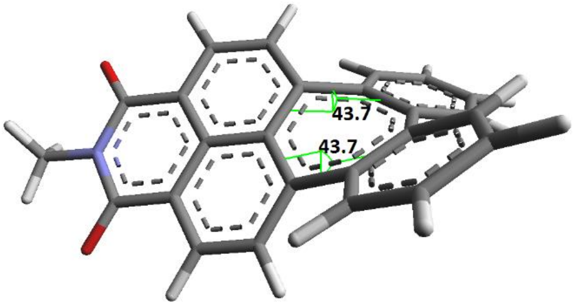
					
LUMO+1	-0.86	-1.43	-2.00	-1.95	-1.42
					
LUMO	-1.34	-2.48	-2.87	-2.38	**-**2.81
					
HOMO	-5.34	-5.88	-6.31	-5.83	**-**5.28
					
HOMO-1	-6.24	-6.64	-7.18	-6.91	-6.44
LUMO-HOMO	4.00	3.40	3.44	3.45	2.47
	3aa	**3da**	**3db**	***D*$_2$-3fa**	**3ea**

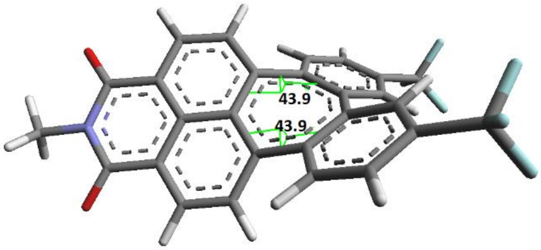
Figure S14. Frontier molecular orbitals (MOs), MO energies, and HOMO-LUMO energy gaps (in eV) of **3aa**, **3da**, **3db**, **3fa,** and **3ea**.



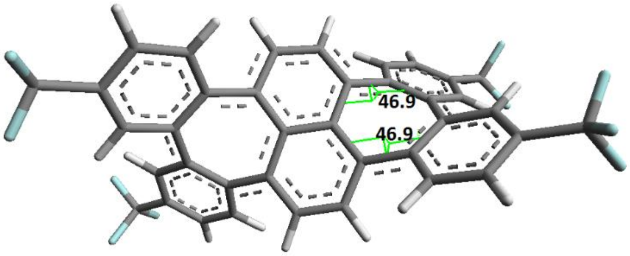
3aa



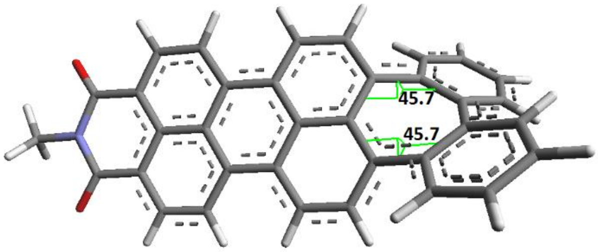
3da



3db



D_2-**3fa**



3ea

Figure S15. Optimized geometries of **3aa**, **3da**, **3db**, **3fa**, and **3ea.** The dihedral angle between naphthalene and dibenzo-moiety are shown in degree (°).

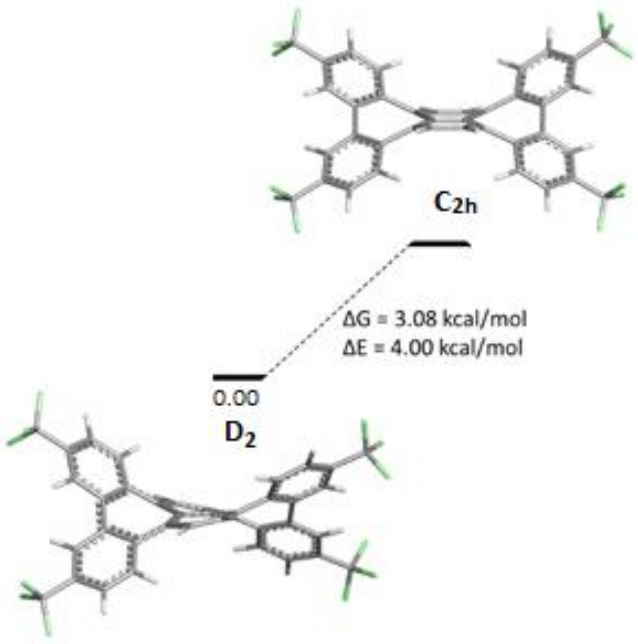


Figure S16. Relative energies of **3fa** in the twisted conformation of D_2 symmetry and the twisted-saddle conformation with C_{2h} symmetry.

Cartesian coordinates of optimized structures

3aa

C	-2.884964	1.920153	1.481595
C	-1.488198	2.035068	1.326829
C	-0.755218	1.149227	0.546149
C	-1.426972	0.000000	0.000000
C	-2.864799	0.000000	0.000000
C	-3.568539	0.965081	0.768573
C	-0.755218	-1.149227	-0.546149
C	-1.488198	-2.035069	-1.326828
C	-2.884963	-1.920153	-1.481595
C	-3.568539	-0.965082	-0.768573
C	0.588991	1.576032	0.060178
C	0.588991	-1.576032	-0.060178
C	1.688431	0.719475	-0.176641
C	2.864377	1.260753	-0.730257
C	2.988248	2.612170	-1.029962
C	1.911484	3.463172	-0.785847
C	0.733584	2.941499	-0.263205
C	1.688431	-0.719474	0.176641
C	2.864377	-1.260753	0.730257
C	2.988248	-2.612169	1.029962
C	1.911485	-3.463172	0.785847
C	0.733584	-2.941499	0.263205
H	-3.417188	2.632384	2.106060
H	-0.976751	2.874521	1.788071
H	-0.976751	-2.874521	-1.788071
H	-3.417188	-2.632384	-2.106060
H	3.691300	0.591426	-0.946170
H	1.974351	4.520801	-1.027187
H	-0.119381	3.598951	-0.132350
H	3.691300	-0.591425	0.946170
H	1.974351	-4.520800	1.027187
H	-0.119381	-3.598951	0.132351
H	3.908645	2.990994	-1.465880
H	3.908645	-2.990994	1.465879
H	-4.654843	0.924530	0.787491
H	-4.654843	-0.924531	-0.787491

3da

C	-1.564122	-2.062883	-1.273004
C	-0.174263	-2.157111	-1.121991
C	0.565462	-1.198762	-0.429506
C	-0.103000	-0.000419	-0.000805
C	-1.537937	-0.001545	-0.001603
C	-2.254746	-1.036943	-0.655150
C	0.563148	1.199015	0.429115
C	-0.178386	2.156474	1.120930
C	-1.568375	2.060101	1.270767
C	-2.255512	1.032894	0.651895
C	1.911028	-1.577006	0.081833
C	1.908749	1.579105	-0.080966
C	3.008390	-0.698755	0.240424
C	4.186319	-1.188923	0.836034
C	4.312079	-2.508763	1.251830
C	3.237713	-3.381341	1.083715
C	2.058904	-2.910890	0.518232

C	3.007596	0.702462	-0.238300
C	4.185440	1.194221	-0.832772
C	4.309754	2.514167	-1.248642
C	3.233943	3.385192	-1.081756
C	2.055206	2.913115	-0.517462
C	-3.736752	-1.038457	-0.697761
N	-4.384987	-0.004988	-0.003134
C	-3.735964	1.025057	0.689364
O	-4.372659	-1.895109	-1.298855
O	-4.390356	1.872166	1.284502
C	-5.850891	0.019847	0.016143
H	-2.122590	-2.822722	-1.809201
H	0.335760	-3.032049	-1.511729
H	0.330215	3.032123	1.510940
H	-2.129311	2.818686	1.806404
H	5.012653	-0.503021	0.992716
H	3.303812	-4.413556	1.415782
H	1.208417	-3.580127	0.446142
H	5.012898	0.509460	-0.988522
H	3.298880	4.417451	-1.413920
H	1.203676	3.581136	-0.446403
H	-6.203257	-0.827689	-0.567231
H	-6.208652	-0.045455	1.046631
H	-6.210742	0.958464	-0.412309
H	5.233453	-2.846222	1.718145
H	5.231117	2.852875	-1.714072

3db

C	3.081917	-1.489722	1.912593
C	1.691702	-1.633719	1.802204
C	0.952392	-0.974252	0.821773
C	1.619044	-0.001171	0.000767
C	3.053472	-0.001665	0.001667
C	3.770516	-0.742980	0.975635
C	0.954078	0.972294	-0.821547
C	1.694579	1.631013	-1.801624
C	3.084925	1.485885	-1.910656
C	3.770695	0.738987	-0.972220
C	-0.393093	-1.507028	0.473043
C	-0.391182	1.506398	-0.473730
C	-1.491262	-0.739960	0.021144
C	-2.669303	-1.402326	-0.366393
C	-2.791905	-2.785061	-0.298164
C	-1.716550	-3.547964	0.158380
C	-0.540360	-2.909618	0.523438
C	-1.490374	0.740605	-0.022061
C	-2.667773	1.404260	0.365230
C	-2.788938	2.787098	0.296823
C	-1.712719	3.548763	-0.159763
C	-0.537099	2.909141	-0.524411
C	5.254476	-0.728117	1.015988
N	5.902371	-0.002845	0.004555
C	5.253033	0.718305	-1.004591
O	5.887521	-1.320538	1.879467
O	5.904009	1.303804	-1.859698
C	7.369049	0.014922	-0.021849
C	-4.081725	3.457883	0.678020
F	-3.867303	4.669408	1.236407

F	-4.872032	3.657440	-0.402081
F	-4.793306	2.721766	1.558322
C	-4.085462	-3.454343	-0.679438
F	-4.795670	-2.717808	-1.560500
F	-4.876468	-3.652073	0.400485
F	-3.872486	-4.666521	-1.236938
H	3.640754	-2.014269	2.680103
H	1.183192	-2.320936	2.470701
H	1.187005	2.318434	-2.470625
H	3.645723	2.009416	-2.677593
H	-3.497913	-0.821380	-0.754176
H	-1.785838	-4.630028	0.193857
H	0.309413	-3.514515	0.818912
H	-3.497037	0.824216	0.752966
H	-1.780854	4.630896	-0.195462
H	0.313364	3.513157	-0.819695
H	7.722065	-0.568386	0.825382
H	7.727243	-0.413683	-0.961015
H	7.726636	1.045195	0.043796

D_2-3fa

C	-0.675516	0.190715	-2.417373
C	0.675526	-0.190665	-2.417379
C	1.397282	-0.280728	-1.237603
C	0.716953	-0.000020	-0.000002
C	-0.716969	-0.000023	-0.000001
C	-1.397284	0.280733	-1.237599
C	1.397282	0.280687	1.237597
C	0.675526	0.190626	2.417374
C	-0.675514	-0.190756	2.417369
C	-1.397283	-0.280781	1.237594
C	2.730003	-0.943959	-1.257104
C	2.729994	0.943932	1.257097
C	3.832319	-0.590974	-0.446697
C	5.004336	-1.362553	-0.516499
C	5.116574	-2.450846	-1.374910
C	4.036593	-2.797906	-2.187460
C	2.865493	-2.056850	-2.112477
C	3.832311	0.590972	0.446682
C	5.004317	1.362567	0.516487
C	5.116544	2.450849	1.374913
C	4.036563	2.797880	2.187477
C	2.865474	2.056809	2.112490
C	6.403819	3.225654	1.454720
F	6.183640	4.533515	1.715514
F	7.204299	2.759447	2.441994
F	7.111080	3.151907	0.306266
C	6.403864	-3.225627	-1.454704
F	6.183721	-4.533473	-1.715603
F	7.111059	-3.151950	-0.306205
F	7.204394	-2.759335	-2.441898
C	-2.730013	-0.943994	1.257093
C	-3.832319	-0.590989	0.446683
C	-5.004349	-1.362554	0.516457
C	-5.116603	-2.450869	1.374835
C	-4.036630	-2.797957	2.187385
C	-2.865526	-2.056907	2.112438
C	-6.403863	-3.225697	1.454643

F	-7.203926	-2.760137	2.442560
F	-6.183586	-4.533735	1.714502
F	-7.111589	-3.151198	0.306529
C	-2.730003	0.943964	-1.257092
C	-3.832309	0.590985	-0.446673
C	-5.004326	1.362570	-0.516449
C	-5.116568	2.450875	-1.374840
C	-4.036595	2.797931	-2.187406
C	-2.865504	2.056862	-2.112457
C	-6.403813	3.225729	-1.454653
F	-7.203864	2.760212	-2.442598
F	-7.111563	3.151212	-0.306555
F	-6.183505	4.533769	-1.714473
H	-1.168997	0.390506	-3.363317
H	1.169011	-0.390423	-3.363329
H	1.169010	0.390396	3.363322
H	-1.168997	-0.390532	3.363315
H	5.836499	-1.117598	0.133492
H	4.098556	-3.658483	-2.845262
H	2.011781	-2.367542	-2.704790
H	5.836481	1.117630	-0.133508
H	4.098519	3.658445	2.845296
H	2.011762	2.367474	2.704819
H	-5.836506	-1.117573	-0.133527
H	-4.098595	-3.658554	2.845164
H	-2.011827	-2.367636	2.704750
H	-5.836484	1.117608	0.133541
H	-4.098553	3.658515	-2.845203
H	-2.011806	2.367560	-2.704788

C_{2h}-**3fa**

C	0.698360000	1.448187000	-1.952924000
C	-0.701506000	1.448054000	-1.947941000
C	-1.419730000	0.878100000	-0.904699000
C	-0.721820000	-0.003611000	-0.010993000
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C	1.424126000	0.878749000	-0.914535000
C	-1.413360000	-0.885686000	0.887268000
C	-0.687678000	-1.456847000	1.924706000
C	0.712174000	-1.456973000	1.919604000
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C	-3.867761000	0.731605000	-0.082072000
C	-5.041779002	1.430569000	0.247183000
C	-5.154603002	2.803784000	0.063088000
C	-4.072450000	3.517006000	-0.453552000
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C	-3.867475000	-0.737834000	0.082938000
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C	2.767519000	1.447374000	-0.610959000
C	5.053337002	-1.434248000	-0.273325000

C	5.166616002	-2.807826000	-0.091952000
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F	6.668052002	4.587809002	-0.354533000
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H	5.892469002	0.887774000	0.633341000
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3ea

C	-0.530384	-2.237828	0.928849
C	-1.911252	-2.307890	0.732609
C	-2.637126	-1.245066	0.206084
C	-1.950936	-0.000328	-0.000133
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C	5.993794	1.102606	-0.592507
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H	8.458631	0.879272	-0.477573
H	8.464823	-0.913852	-0.509529

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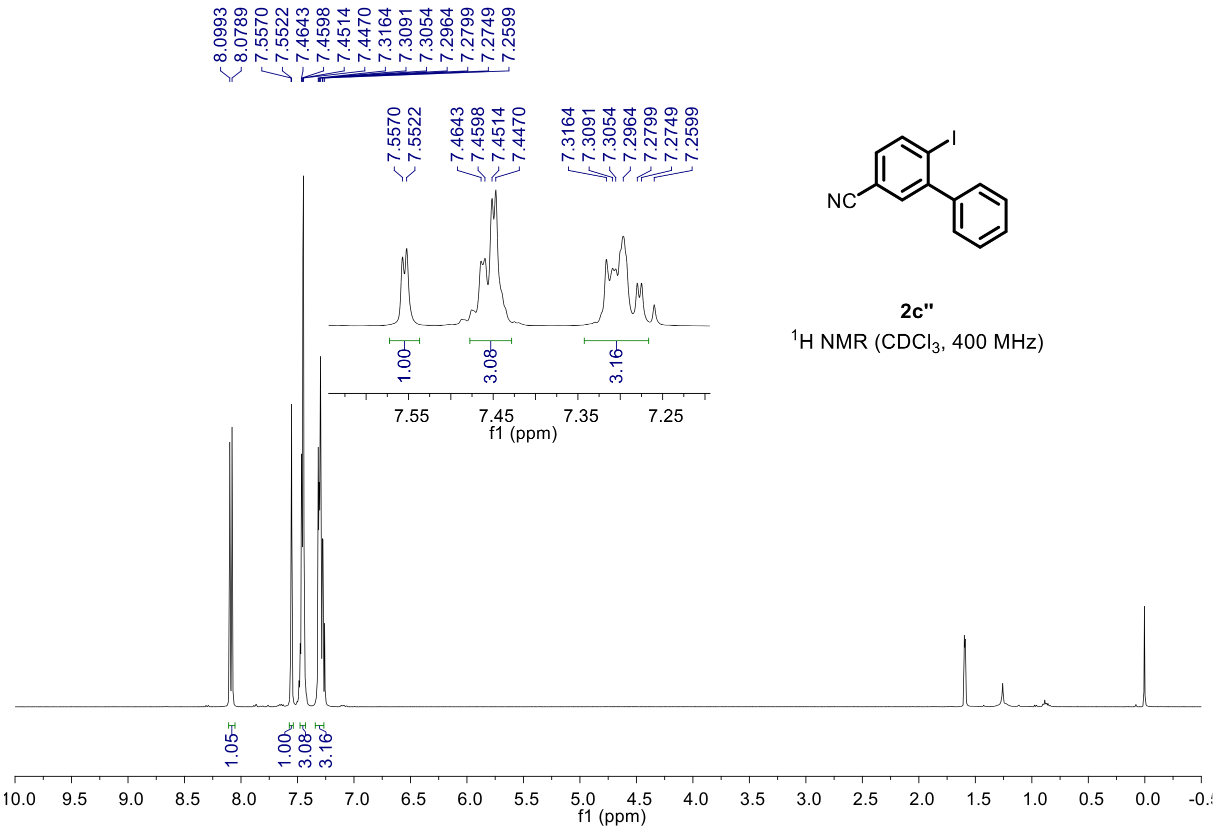
XI. NMR Spectra



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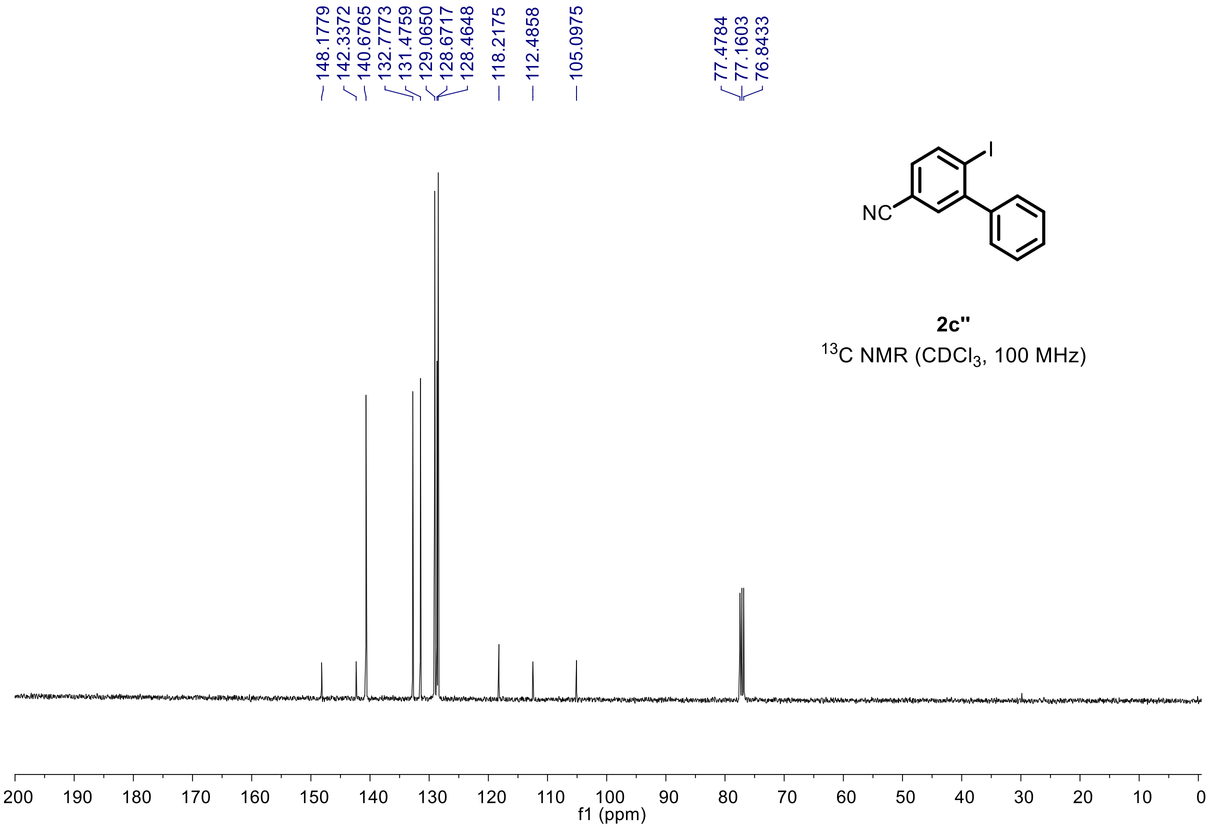

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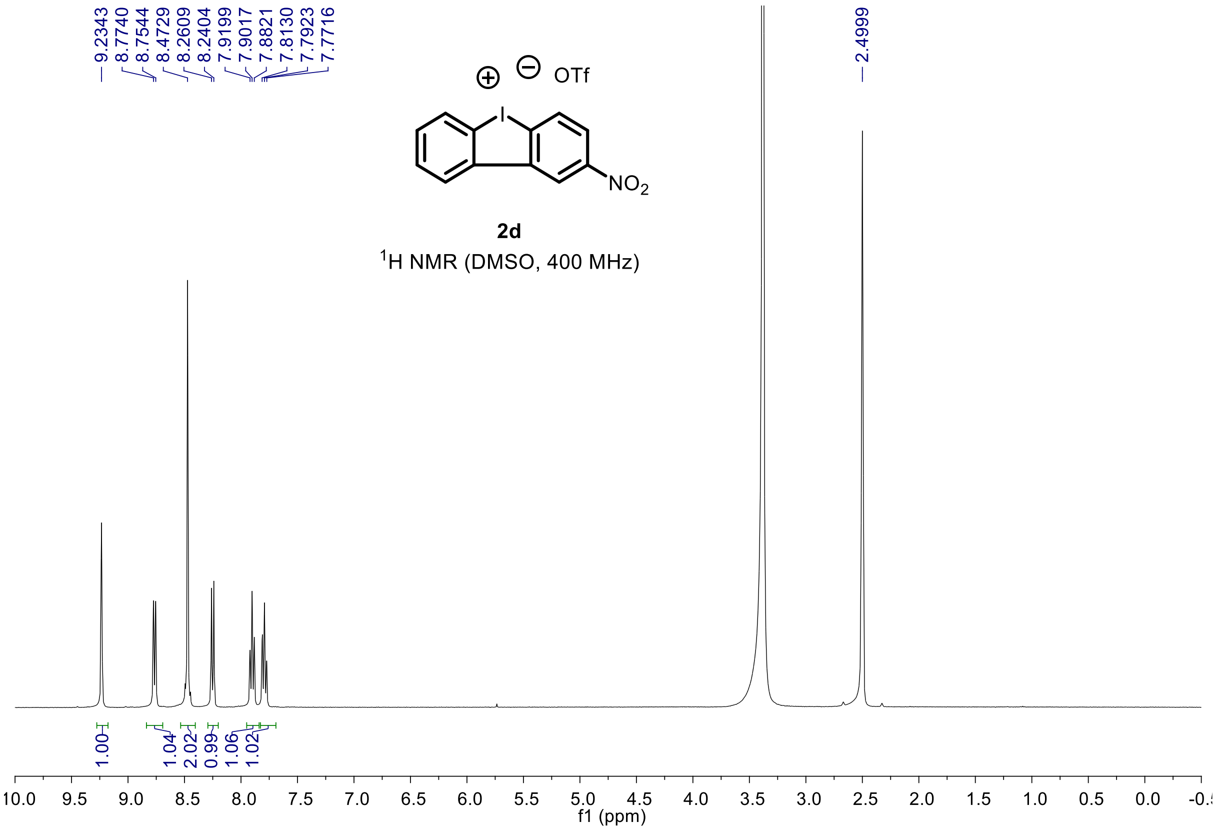
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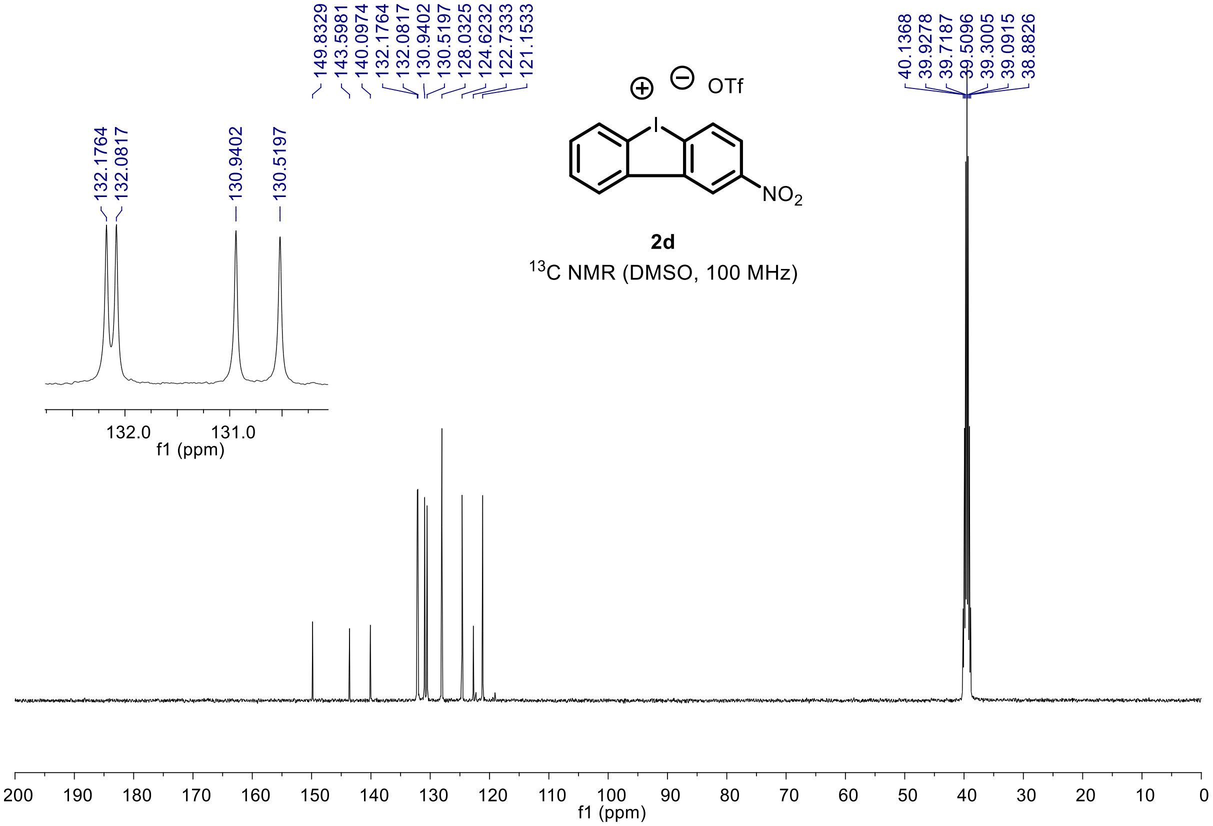
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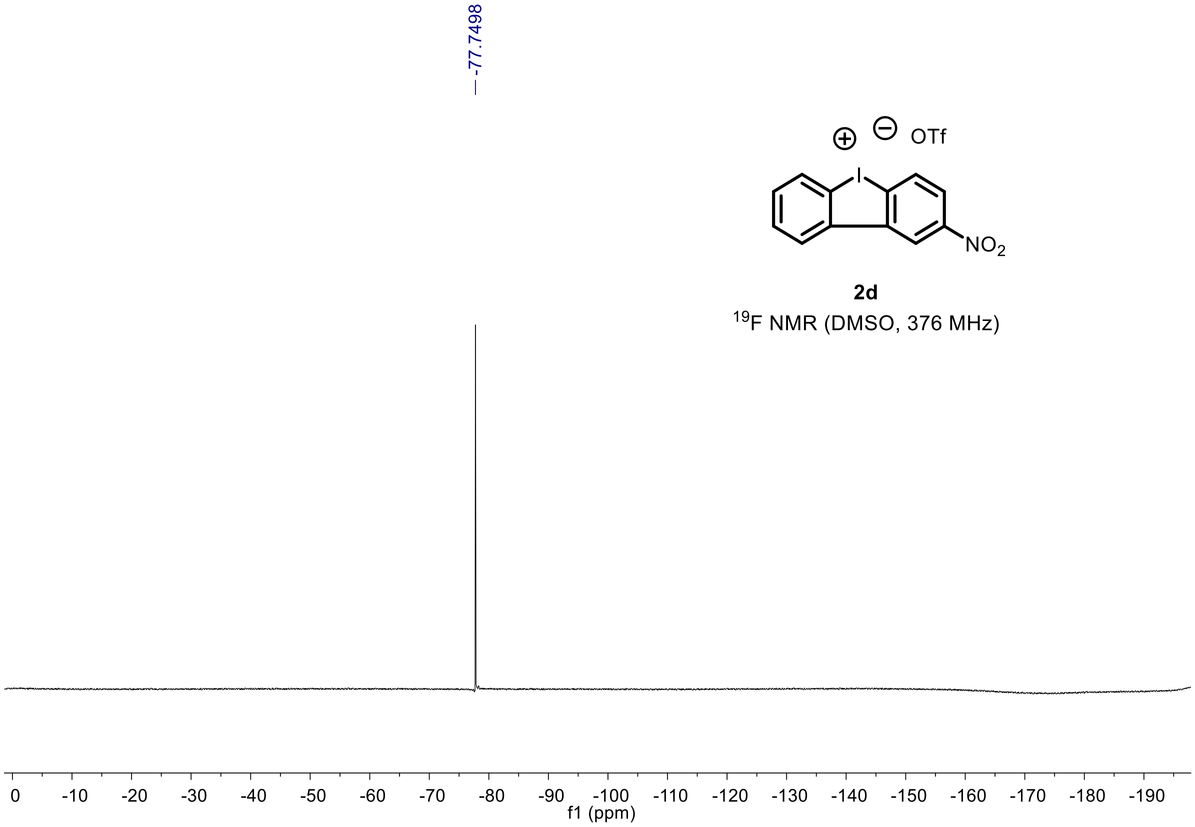

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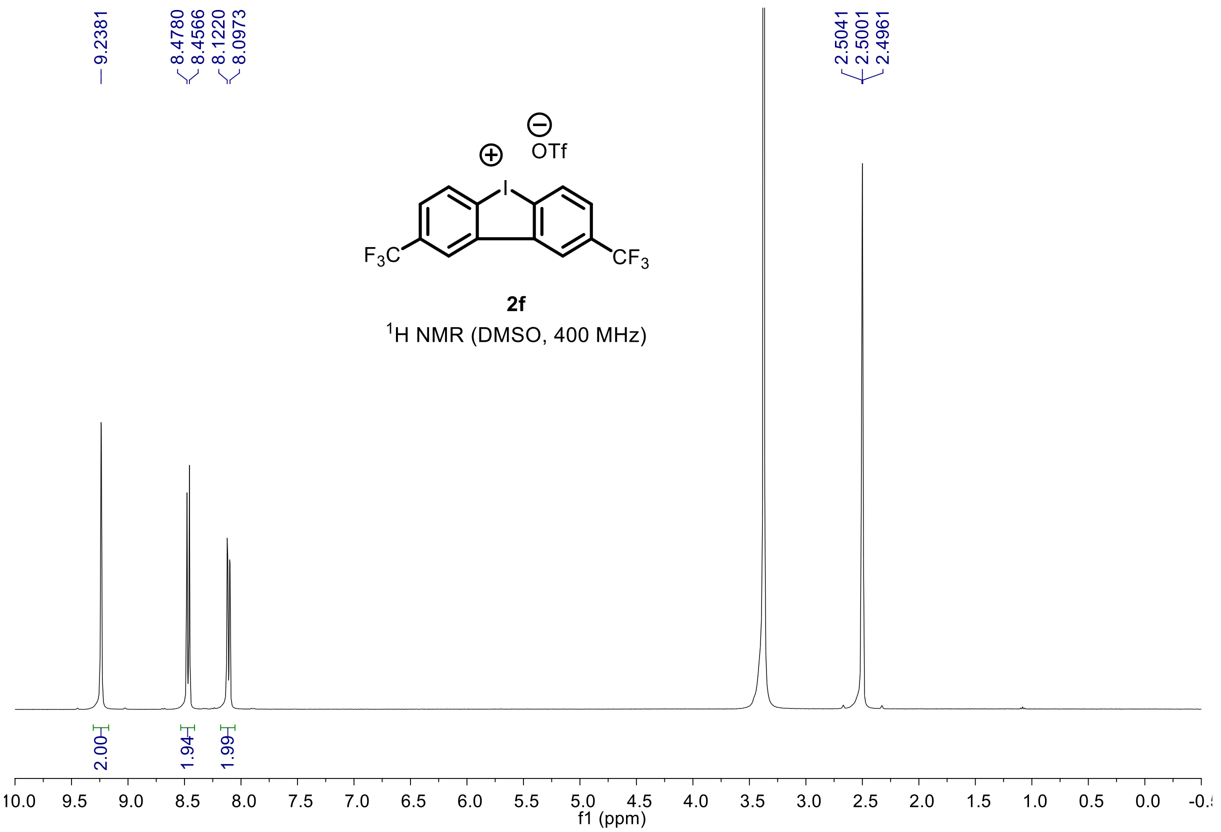

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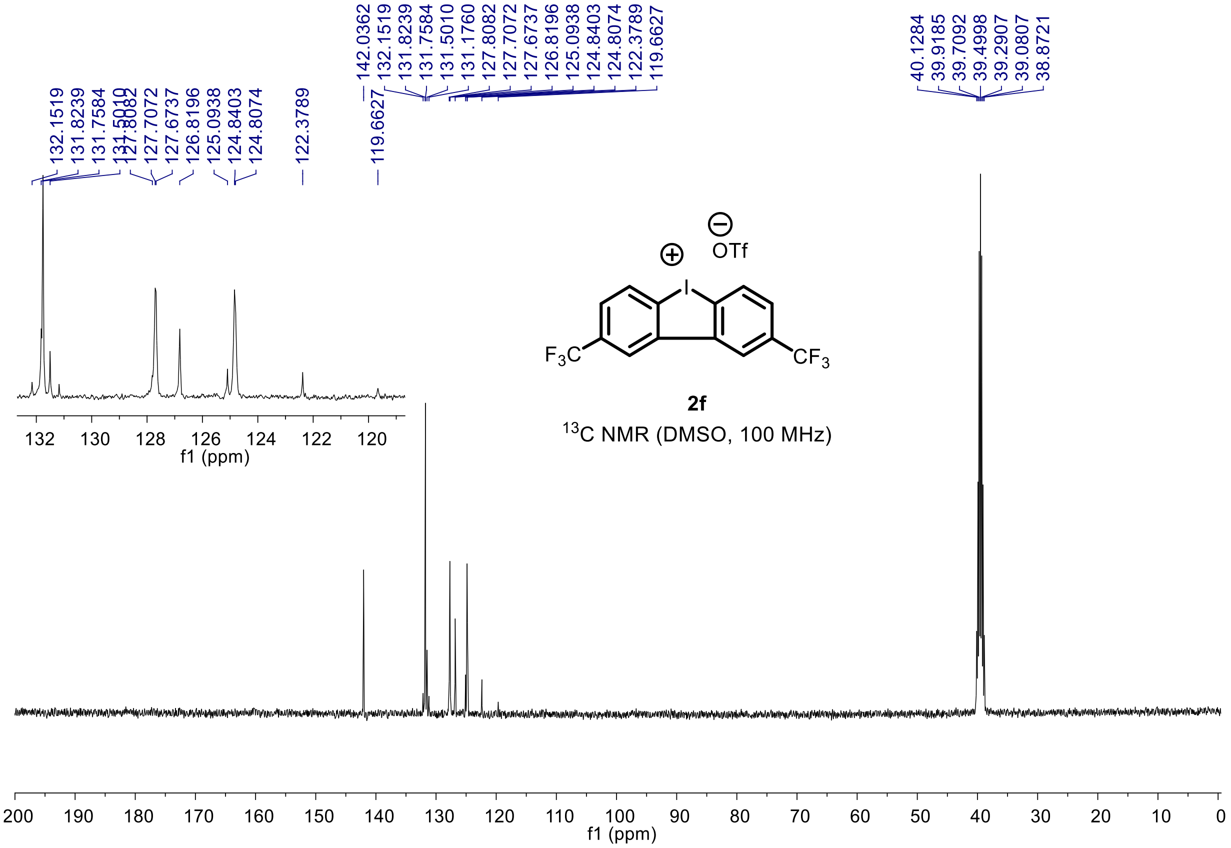

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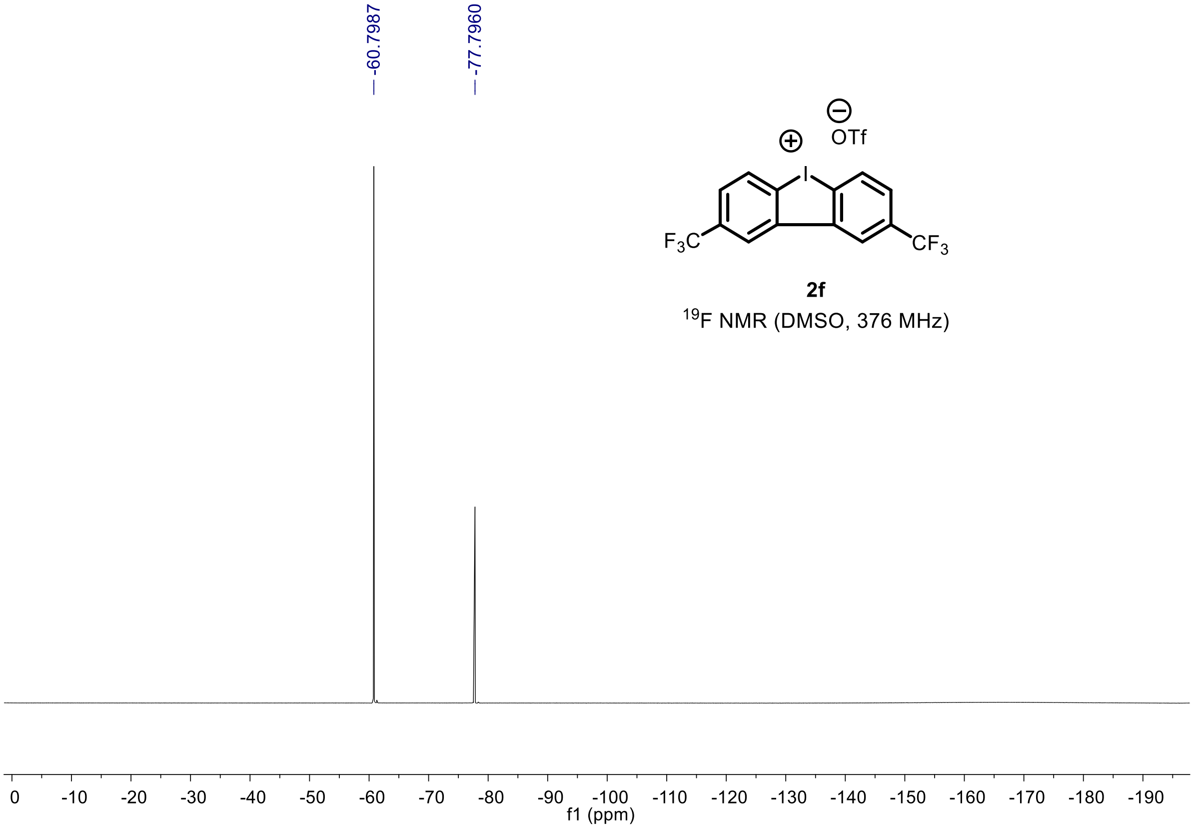

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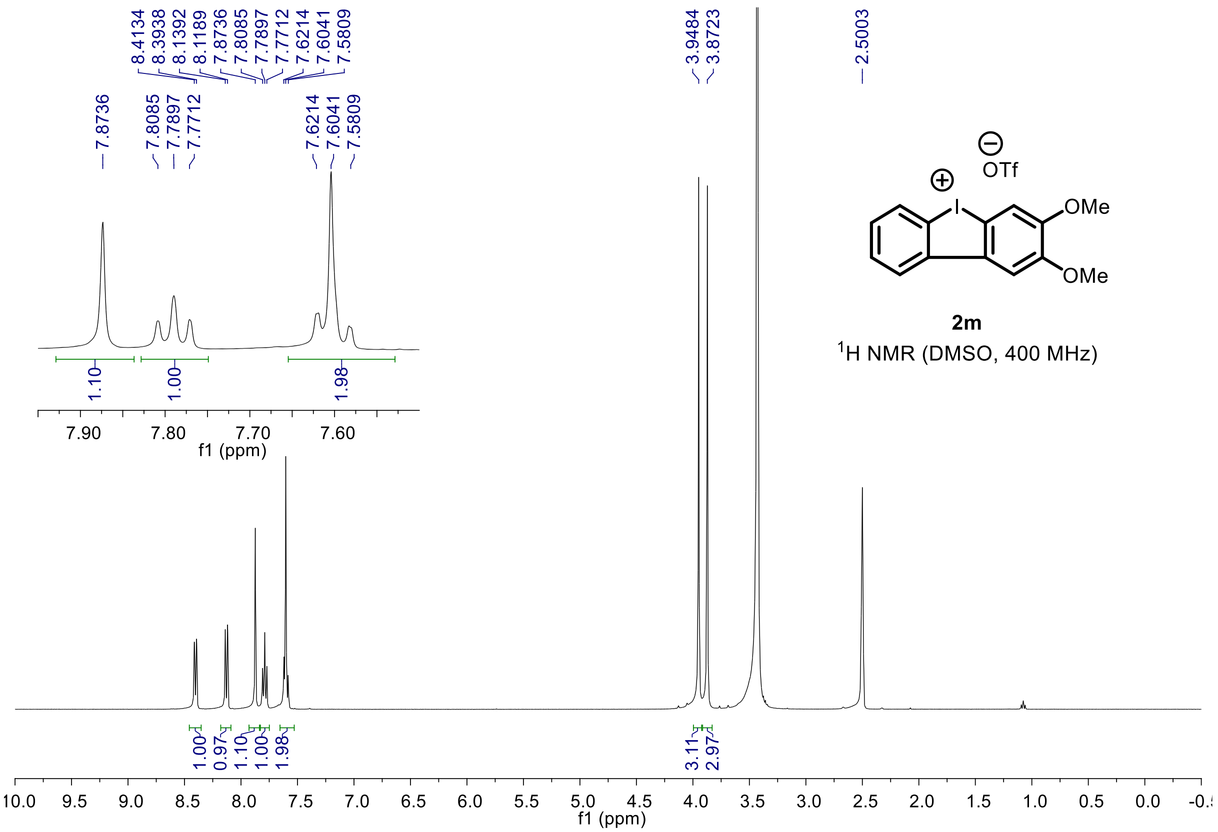

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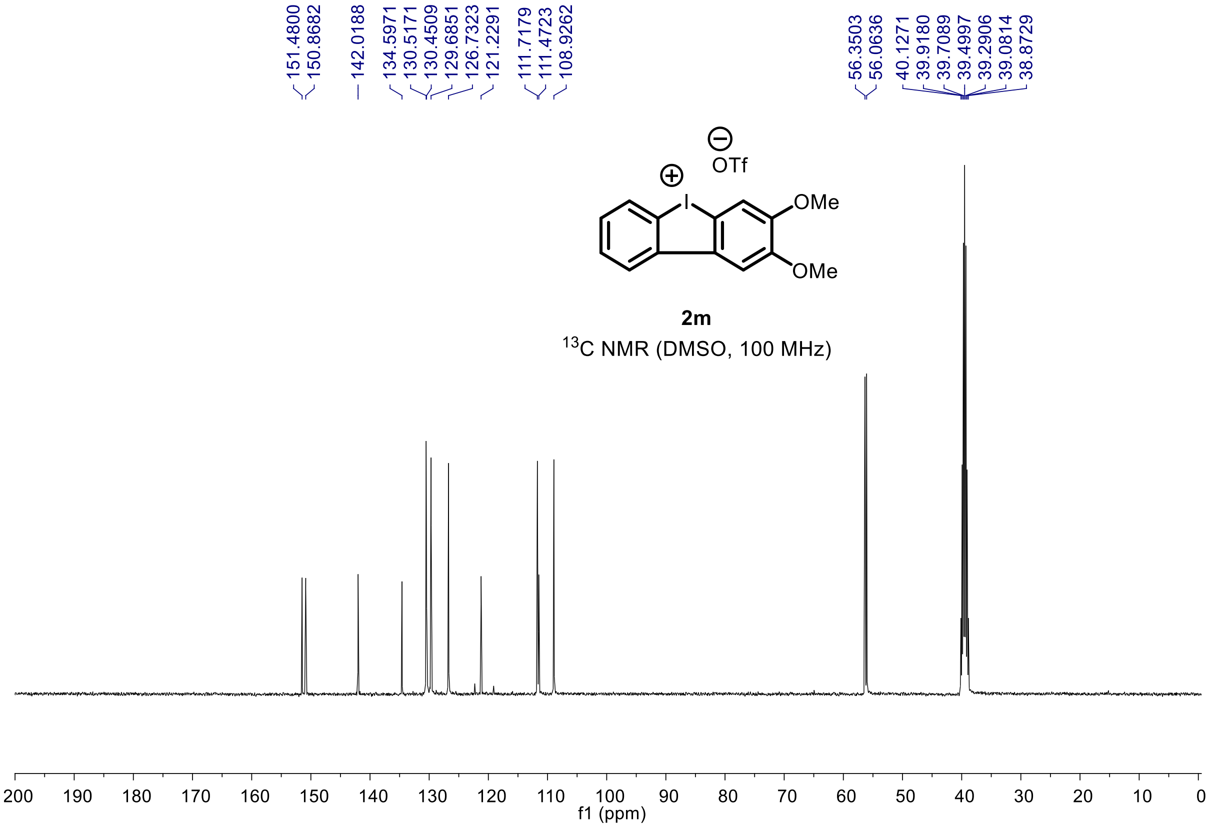

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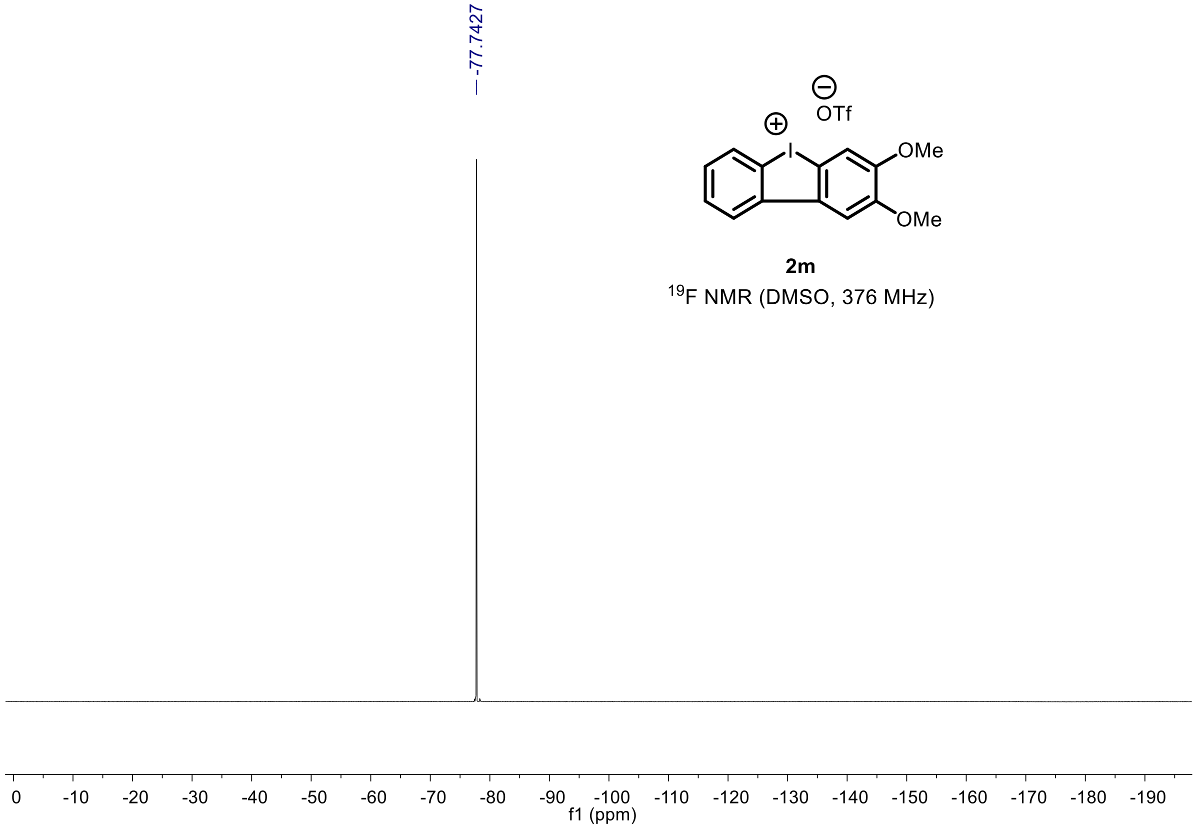

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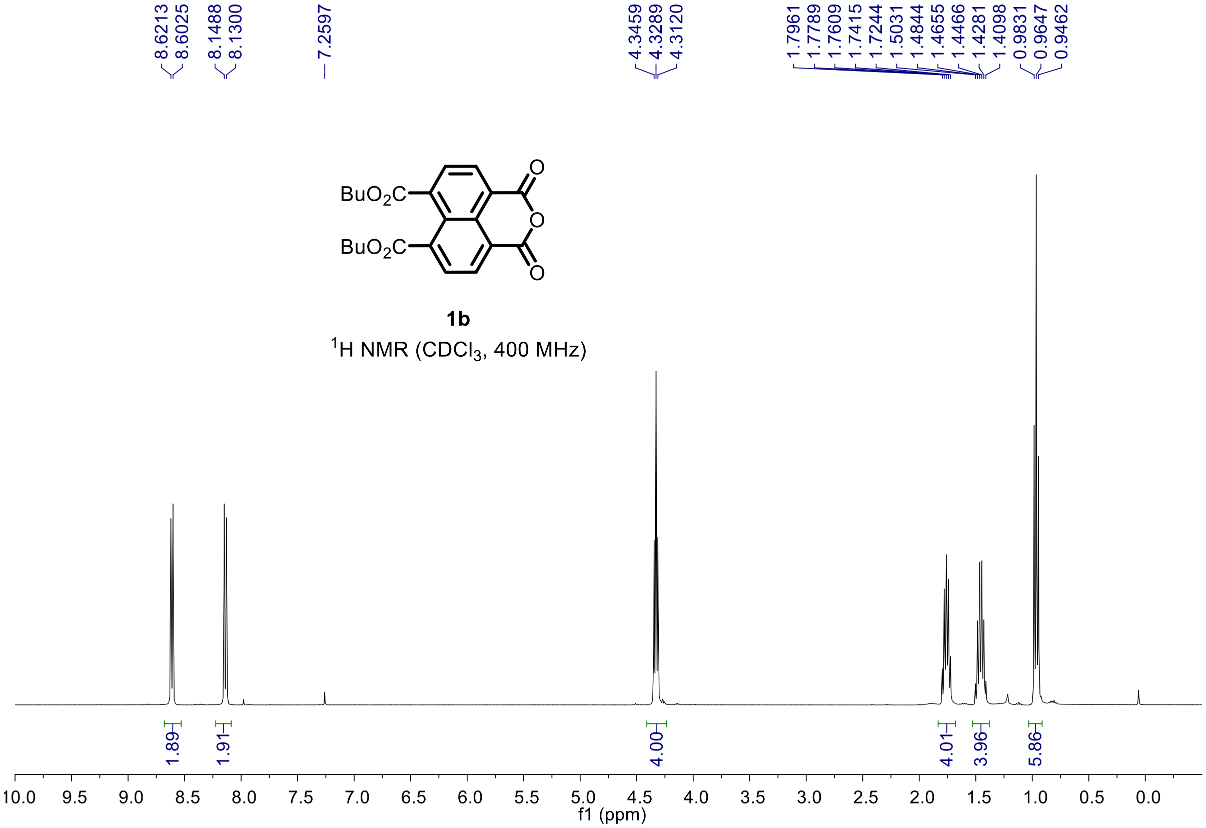

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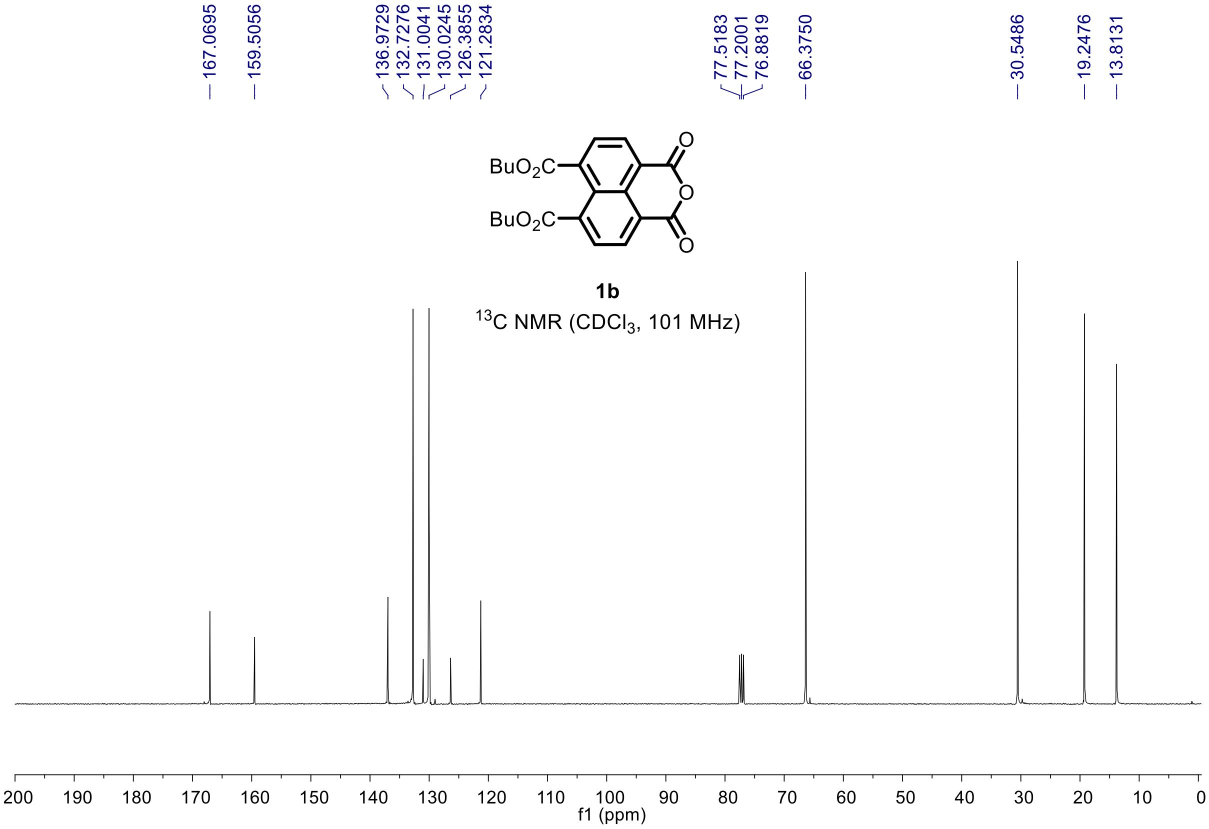

1b

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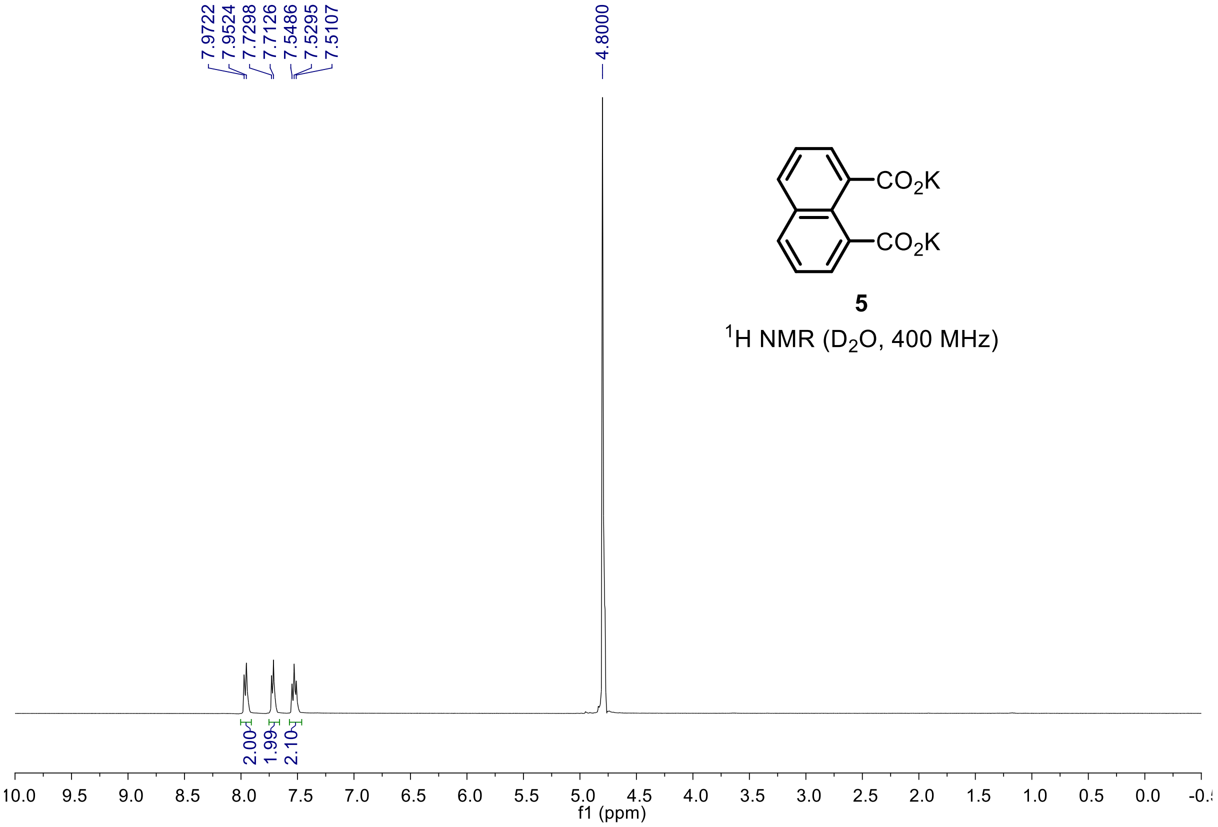

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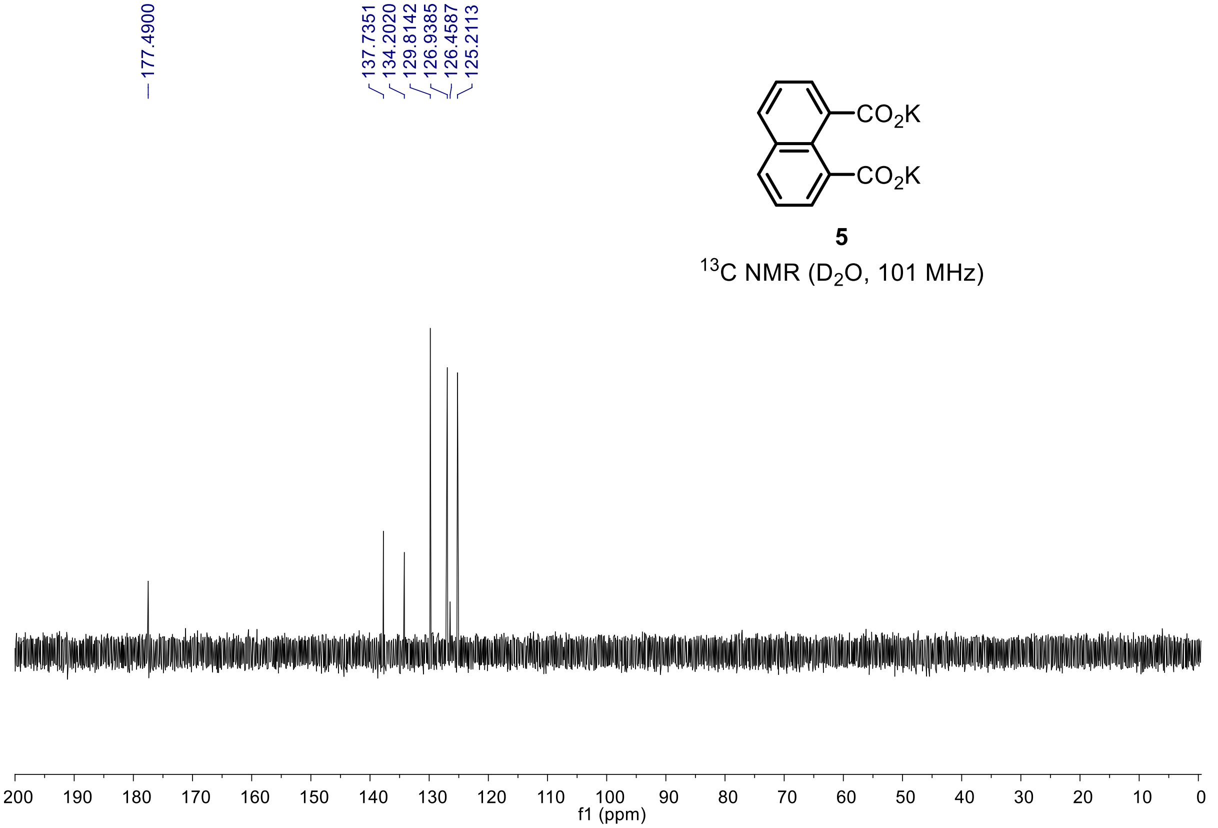

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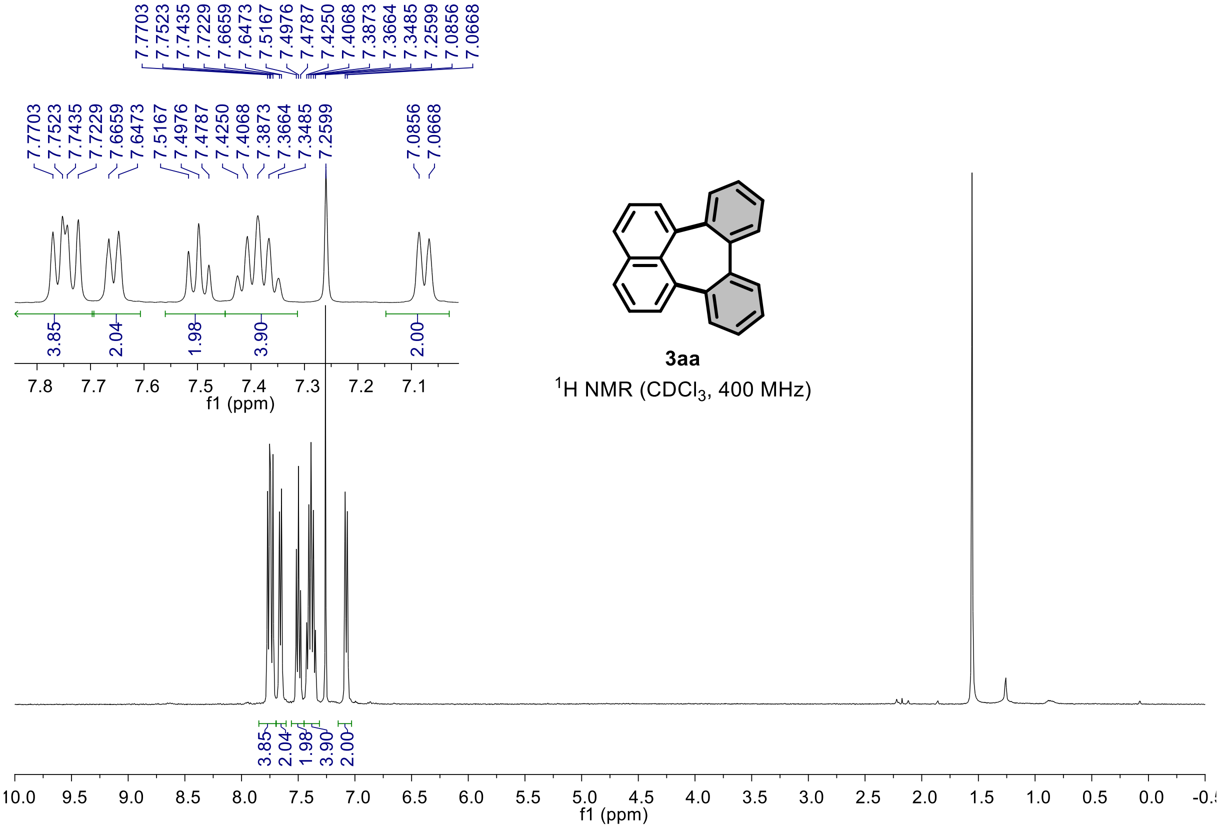

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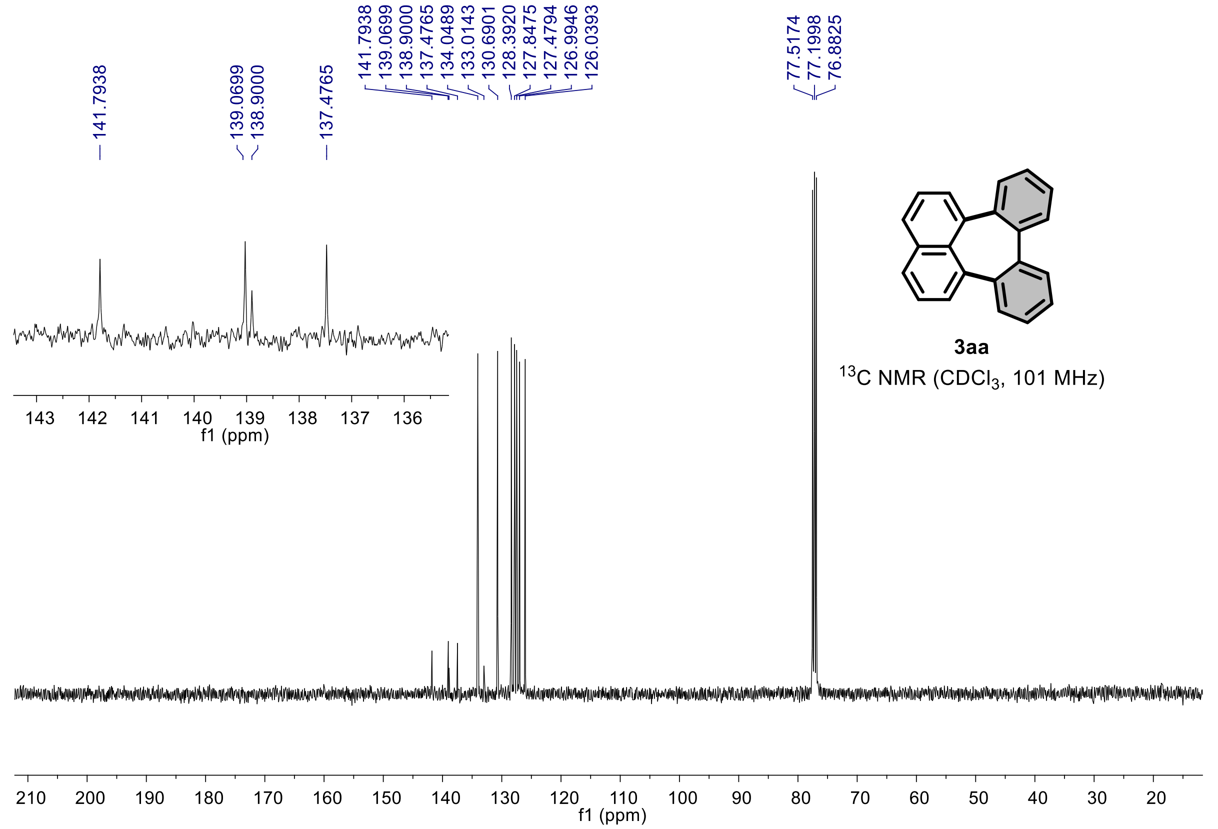

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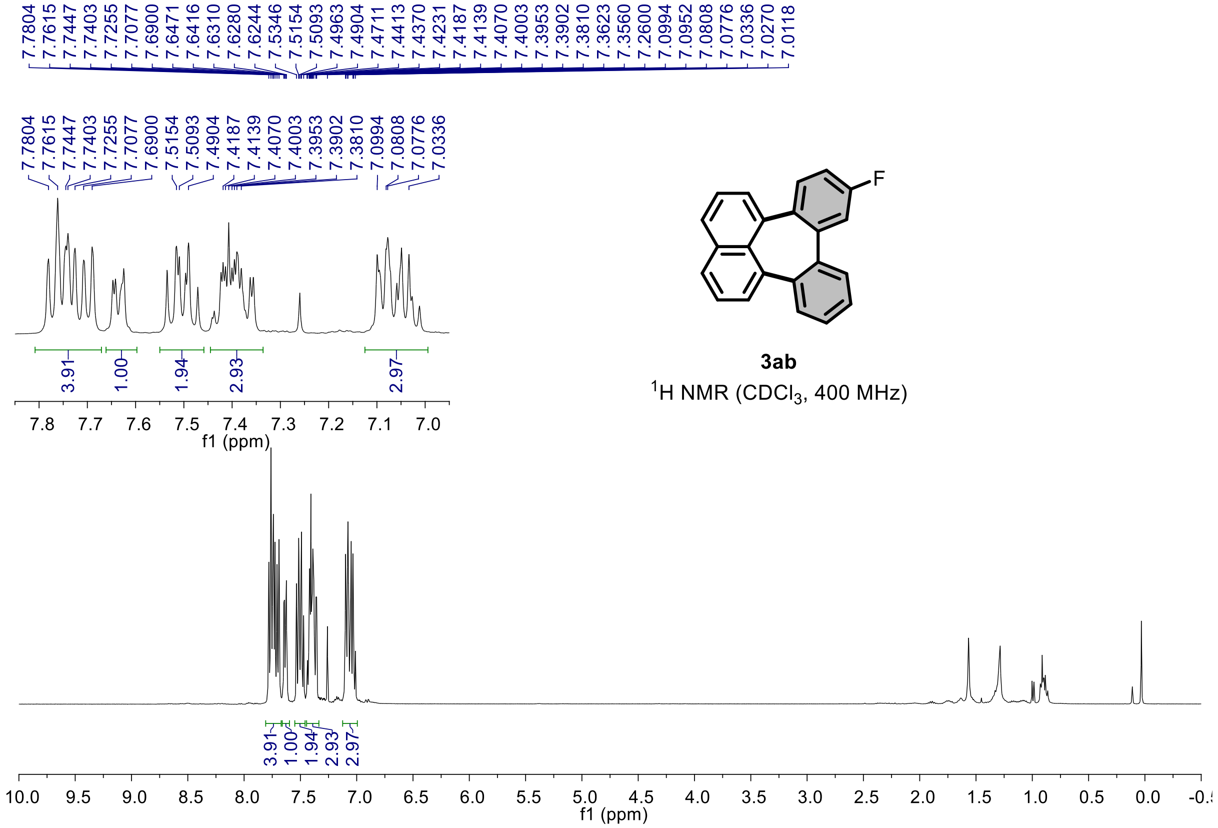

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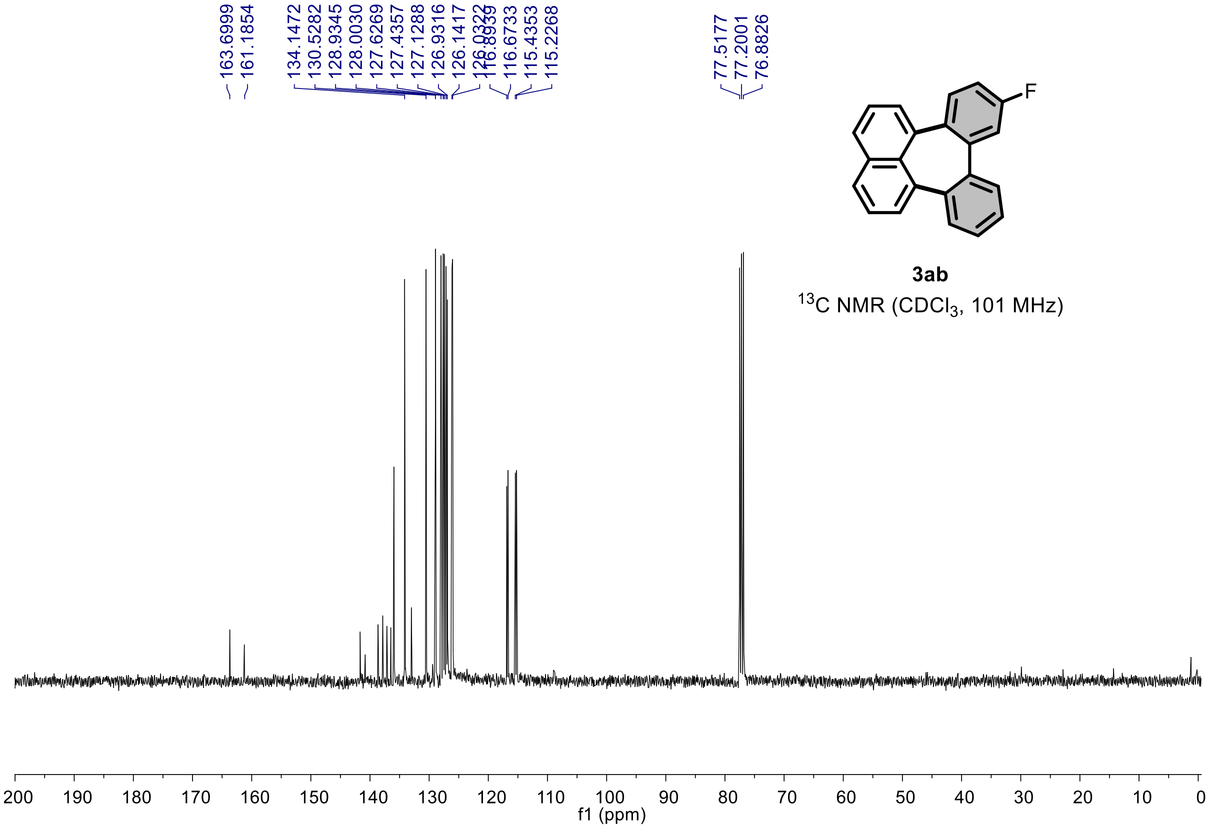

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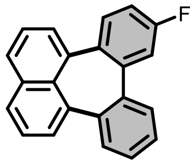

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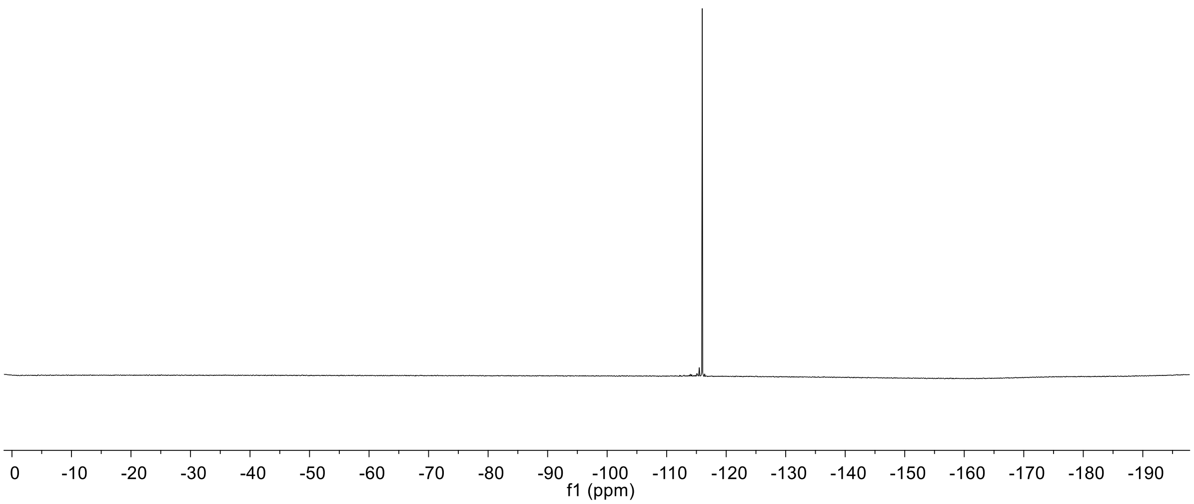
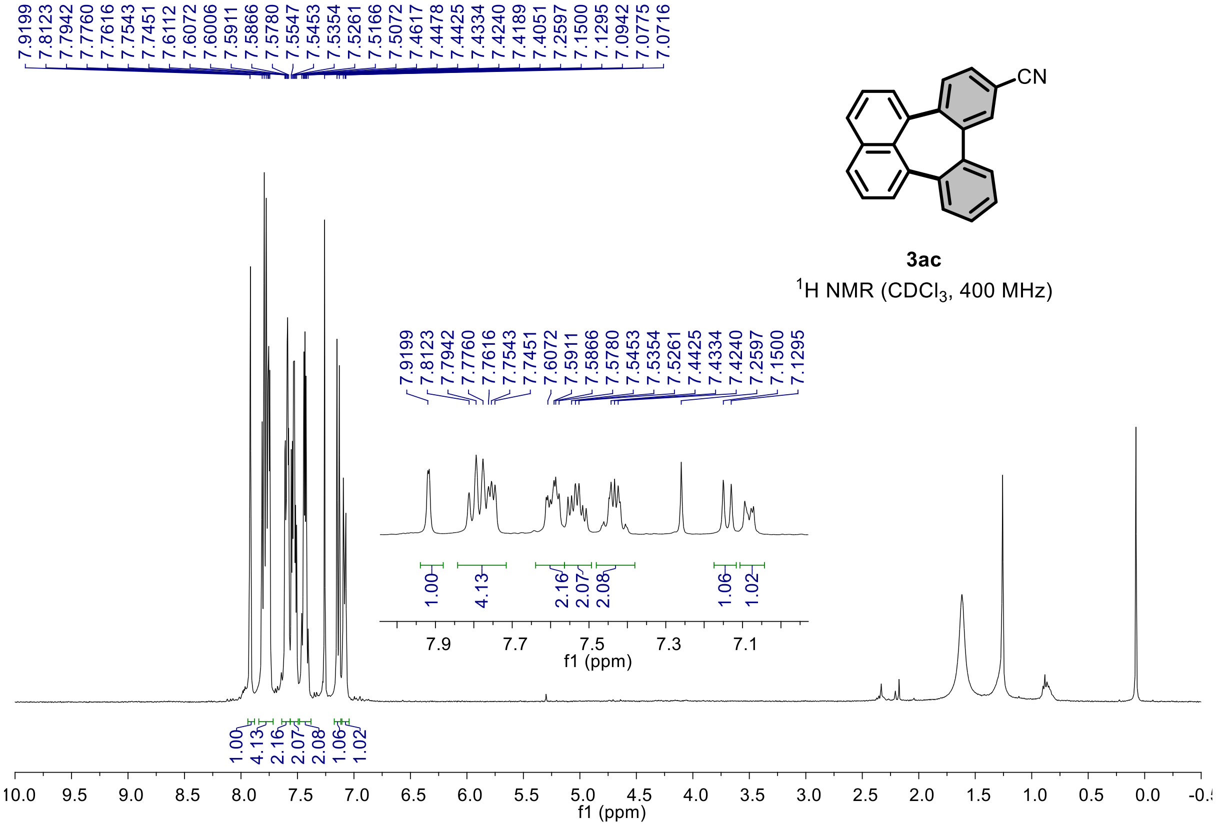
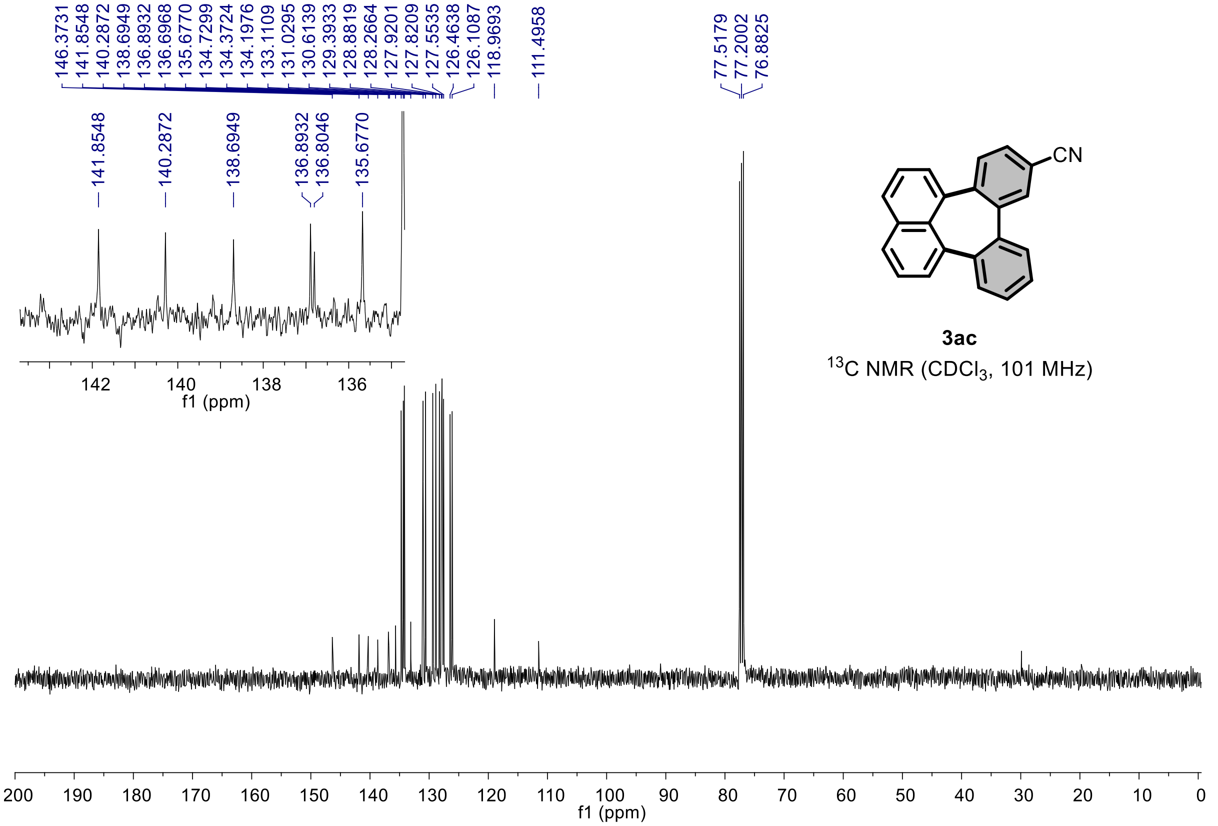




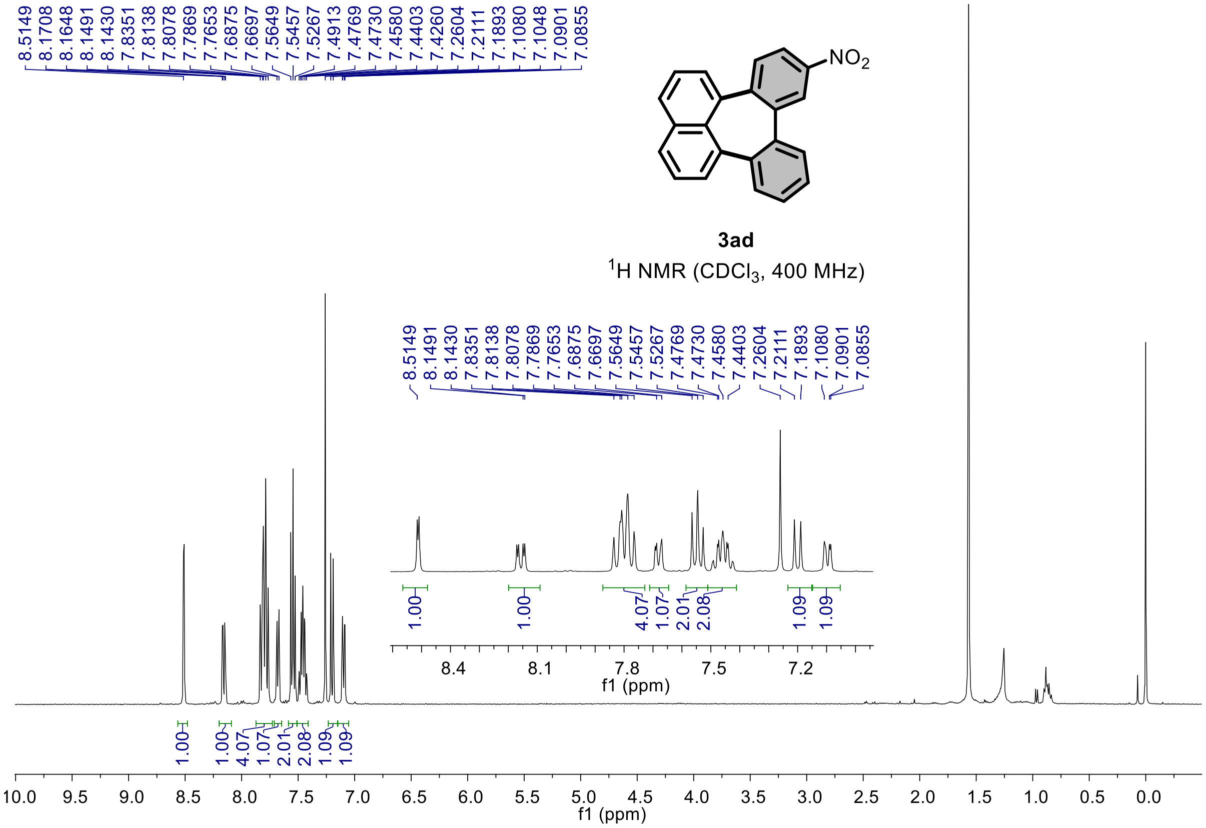
3ac

^{1}H NMR ($CDCl_3$, 400 MHz)



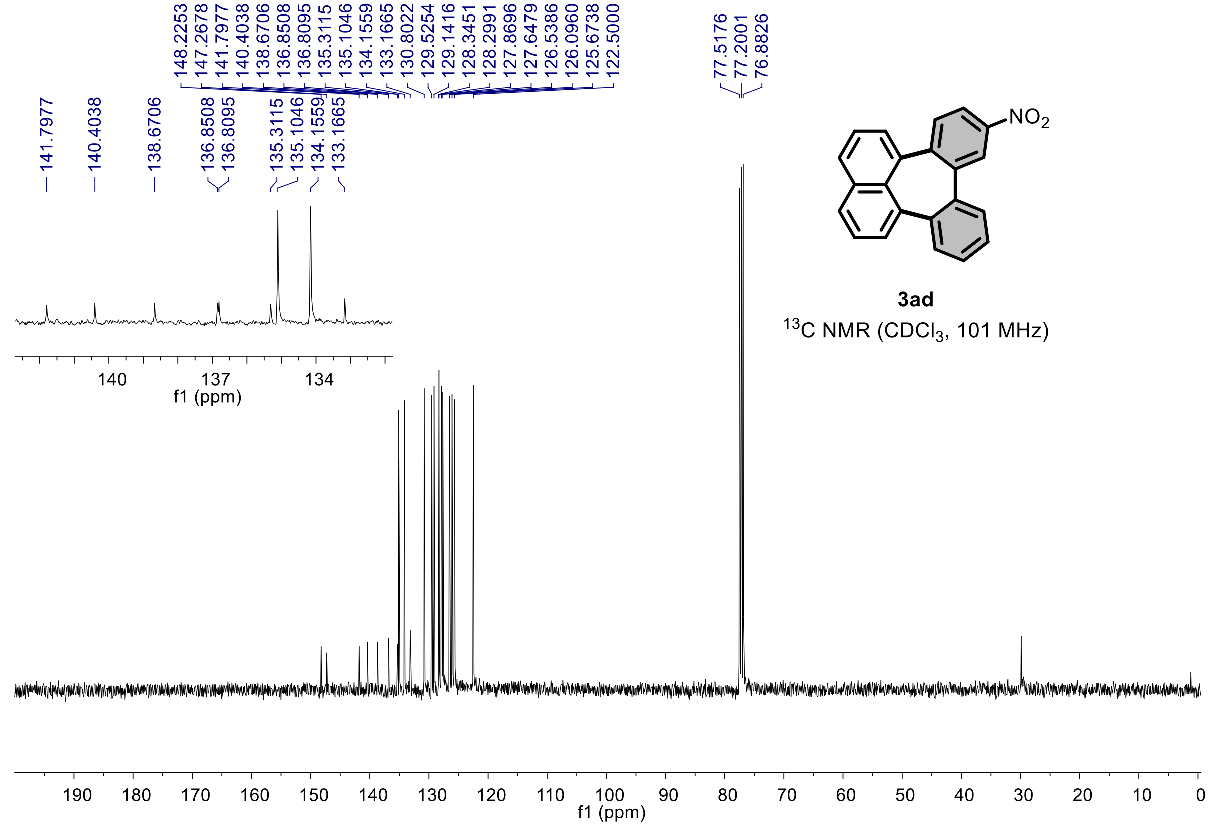
3ac

^{13}C NMR ($CDCl_3$, 101 MHz)



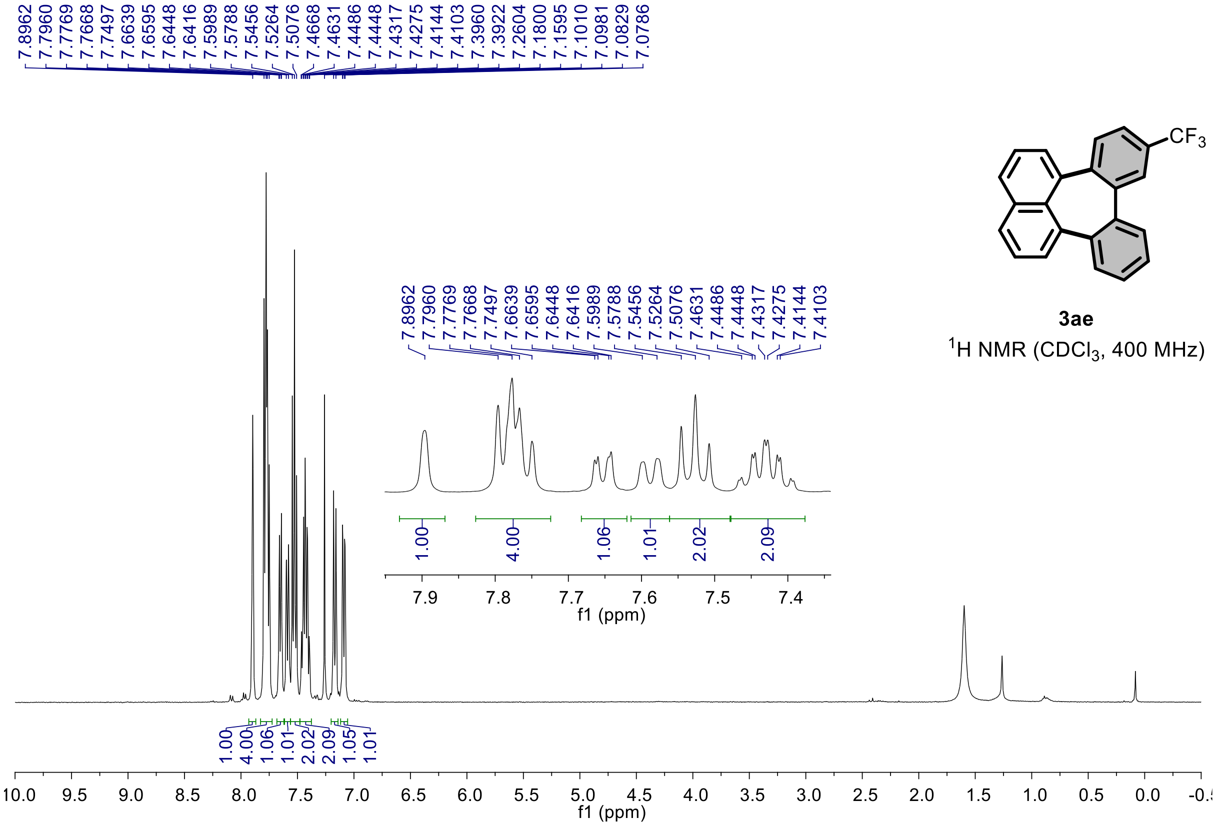
3ad

^{1}H NMR (CDCl$_3$, 400 MHz)



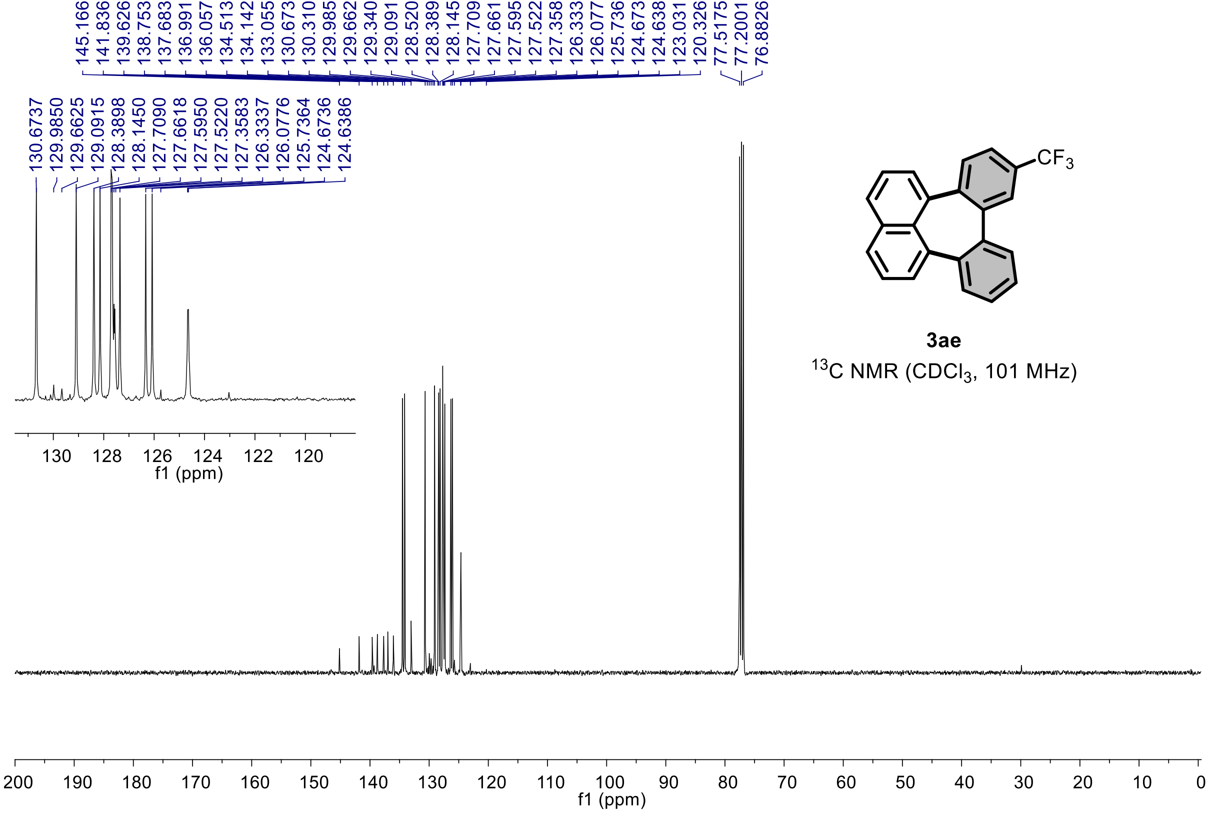
3ad

^{13}C NMR (CDCl$_3$, 101 MHz)



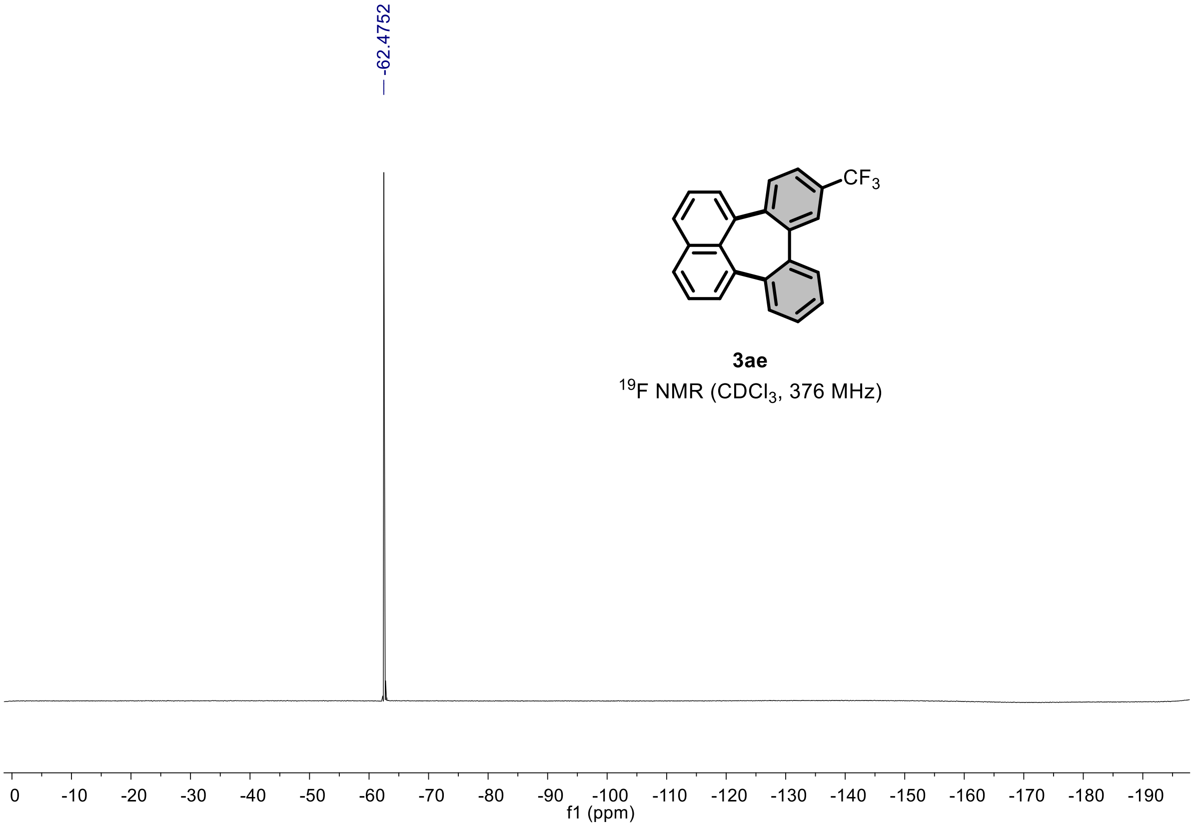
3ae

^{1}H NMR (CDCl$_3$, 400 MHz)



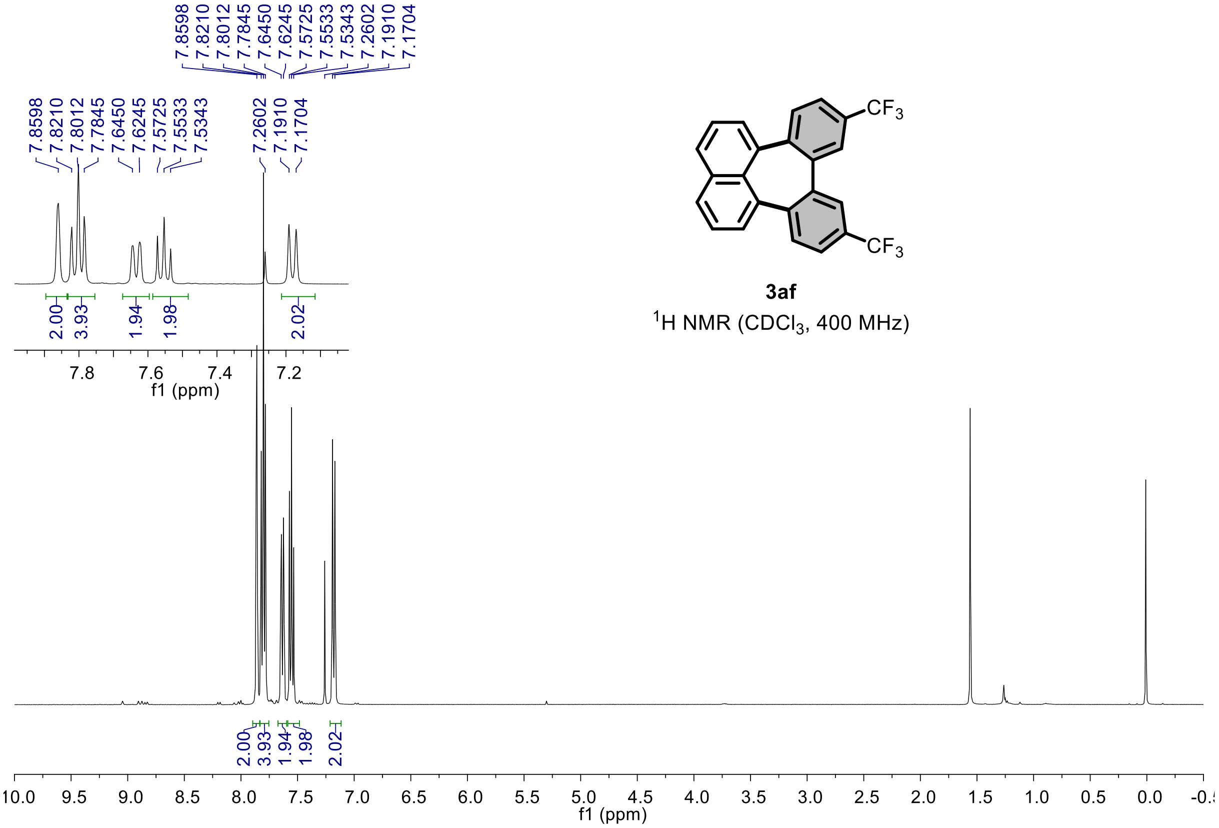
3ae

^{13}C NMR (CDCl$_3$, 101 MHz)



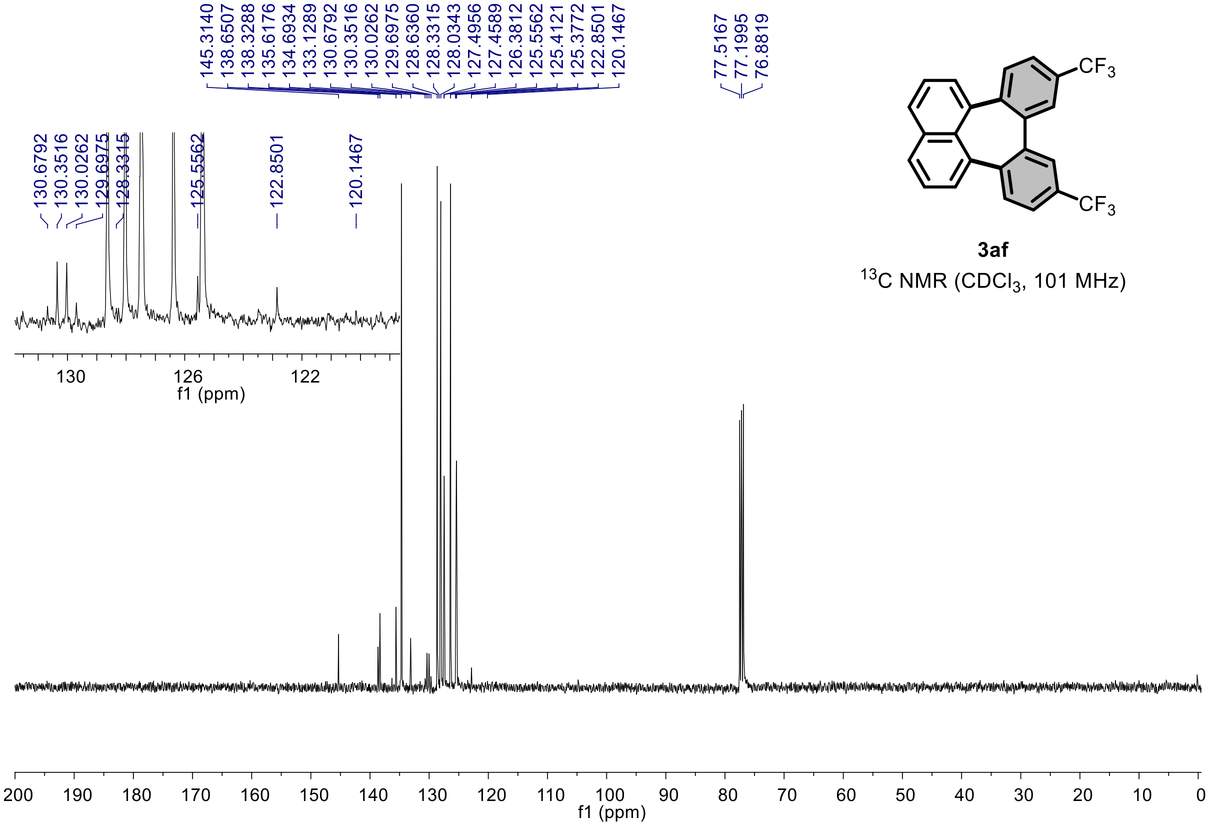
3ae

^{19}F NMR (CDCl$_3$, 376 MHz)



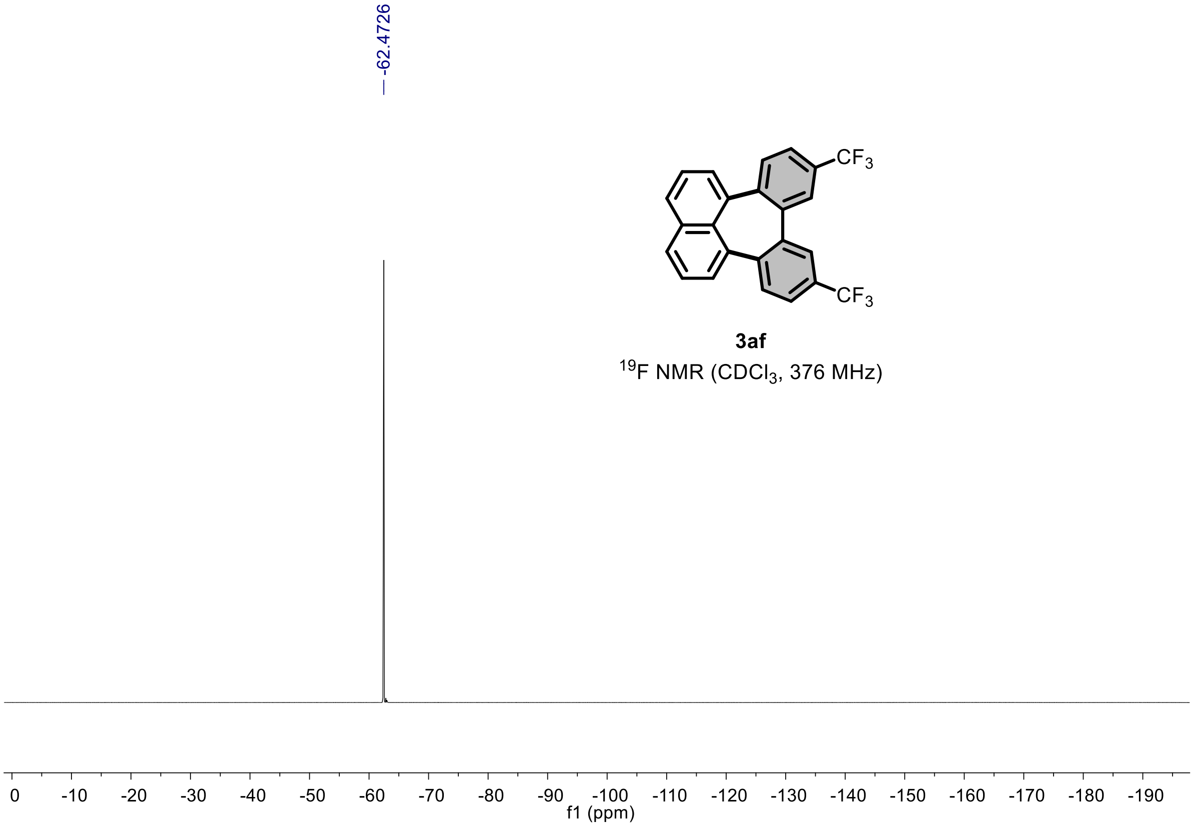
3af

^{1}H NMR (CDCl$_3$, 400 MHz)



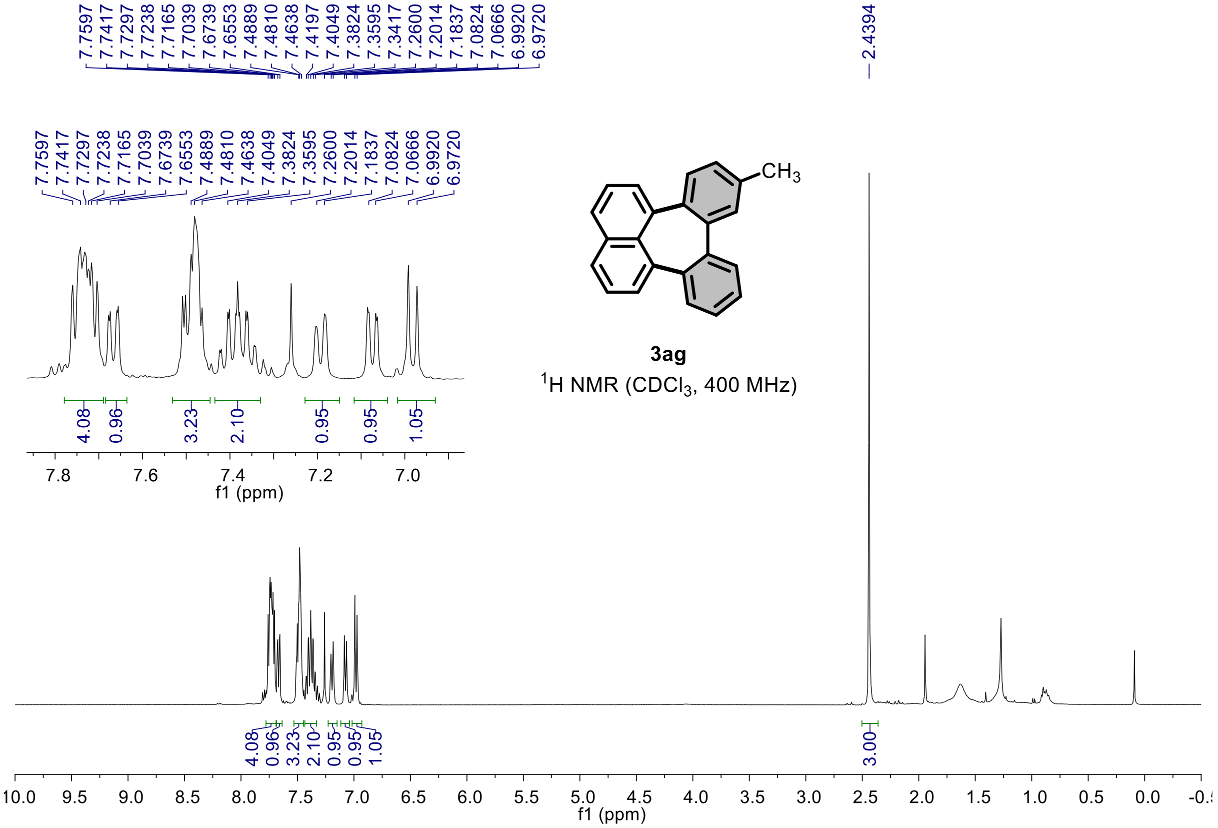
3af

^{13}C NMR (CDCl$_3$, 101 MHz)



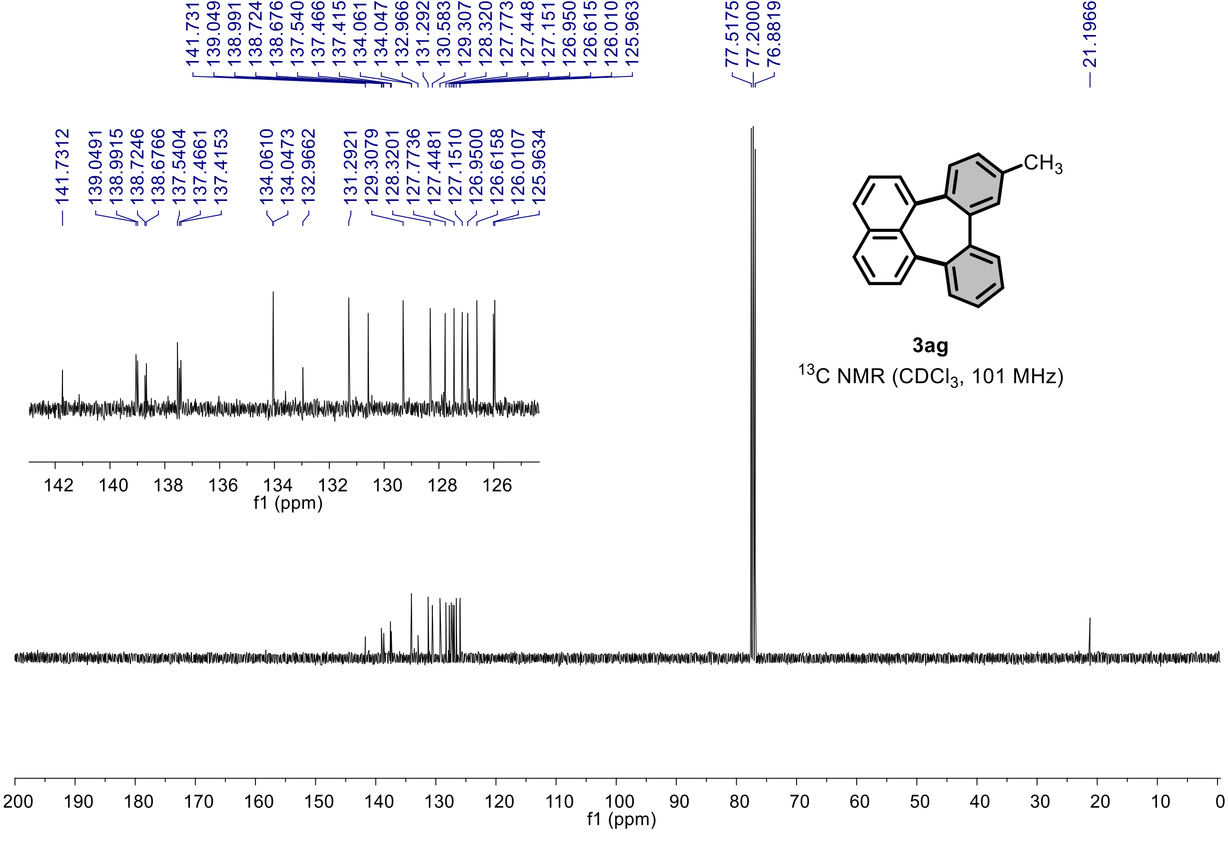
3af

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



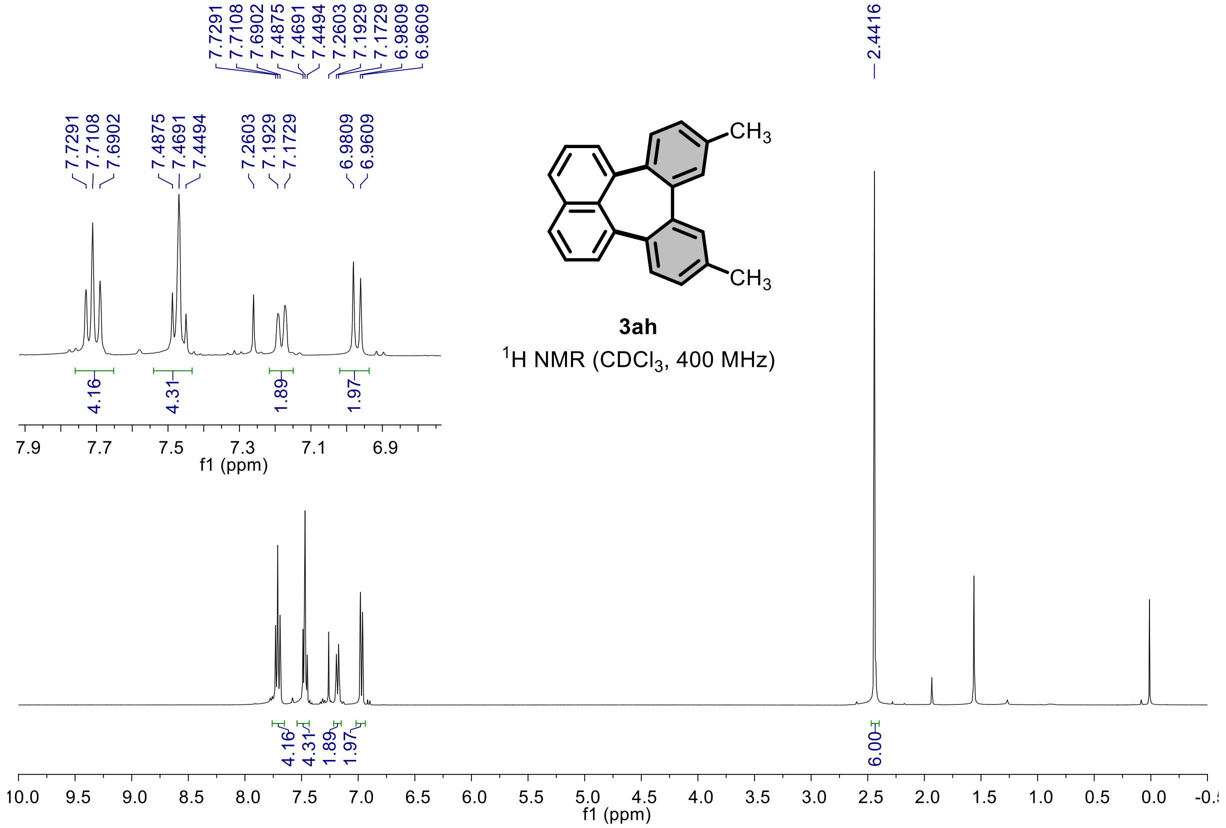
3ag

^{1}H NMR ($CDCl_3$, 400 MHz)



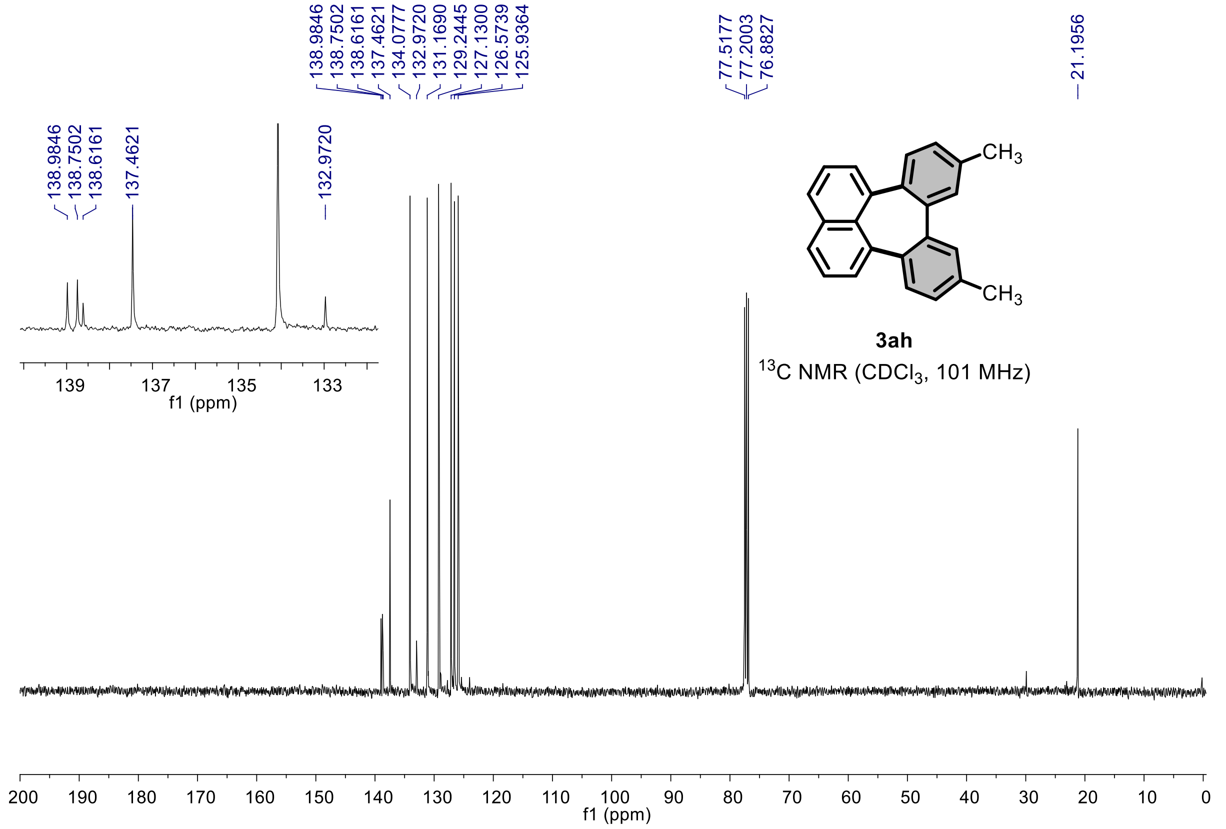
3ag

^{13}C NMR ($CDCl_3$, 101 MHz)



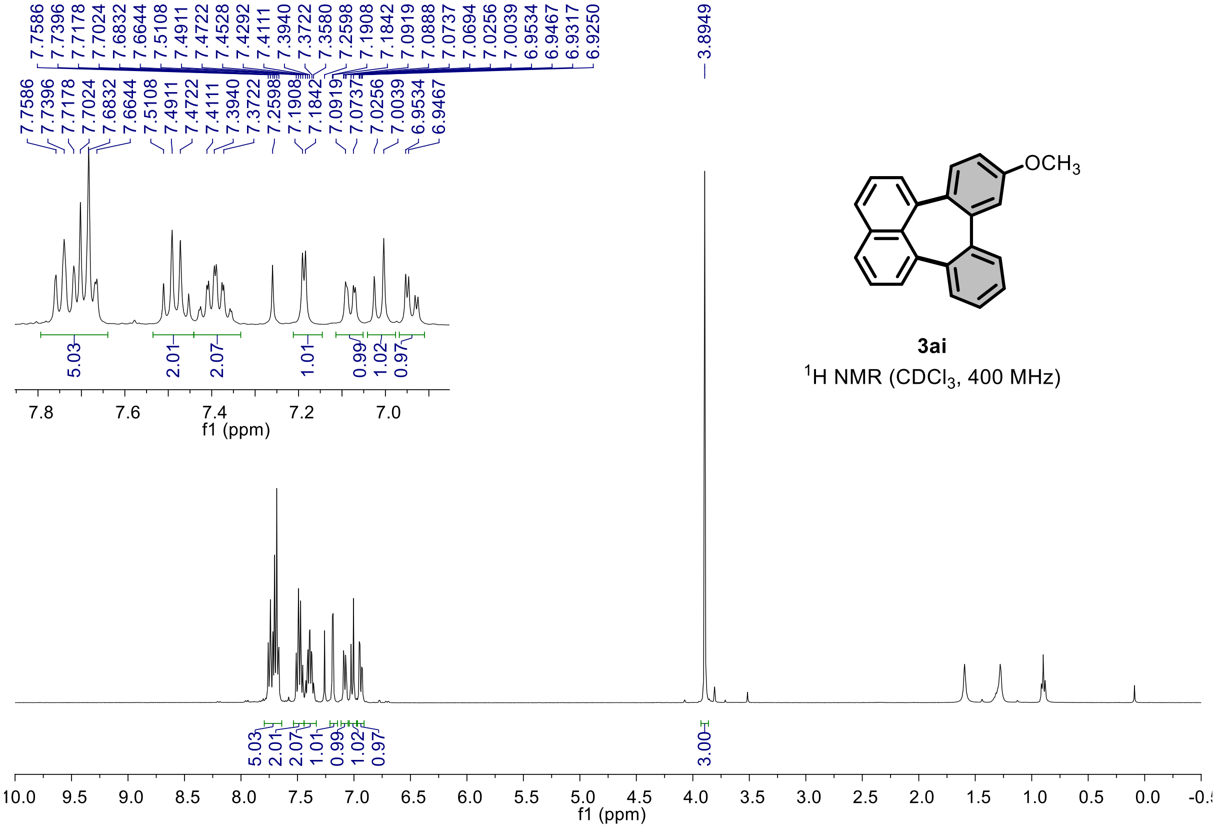
3ah

^{1}H NMR (CDCl$_3$, 400 MHz)



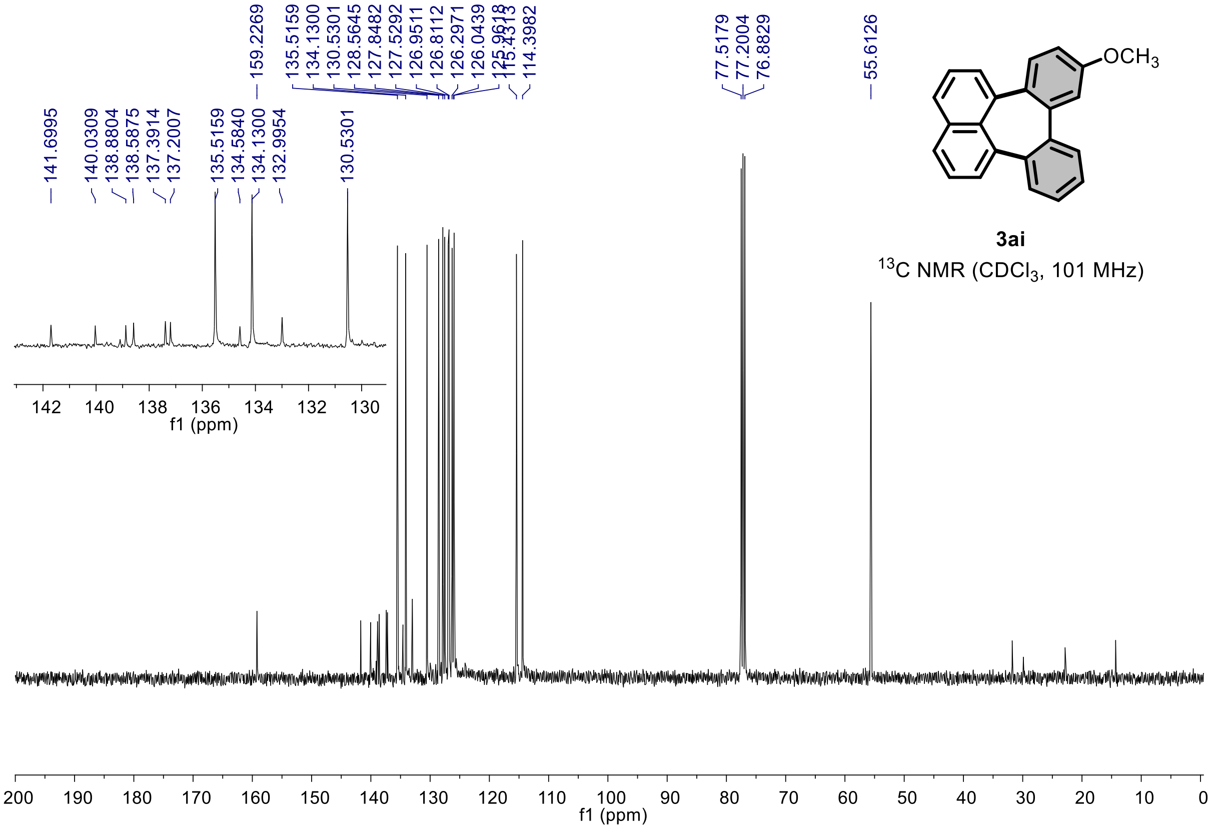
3ah

^{13}C NMR (CDCl$_3$, 101 MHz)



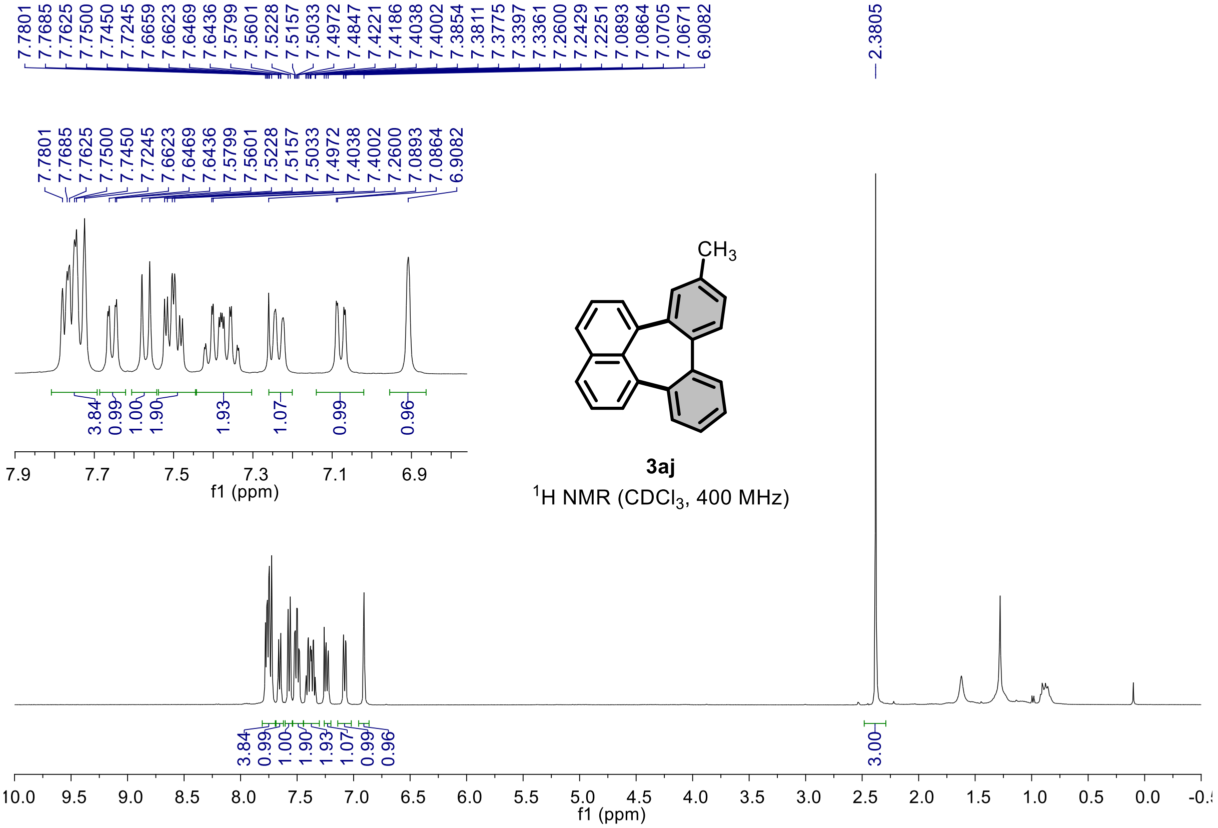
3ai

^{1}H NMR (CDCl$_3$, 400 MHz)



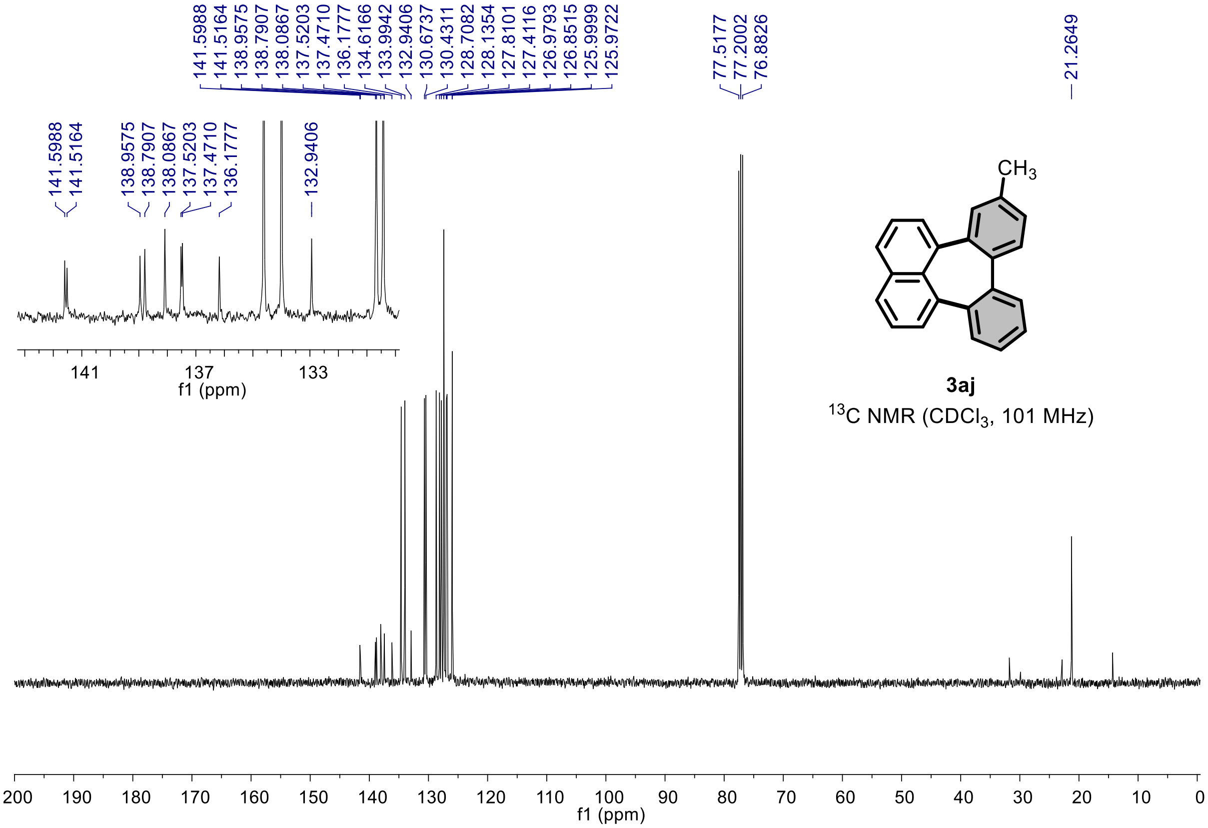
3ai

^{13}C NMR (CDCl$_3$, 101 MHz)



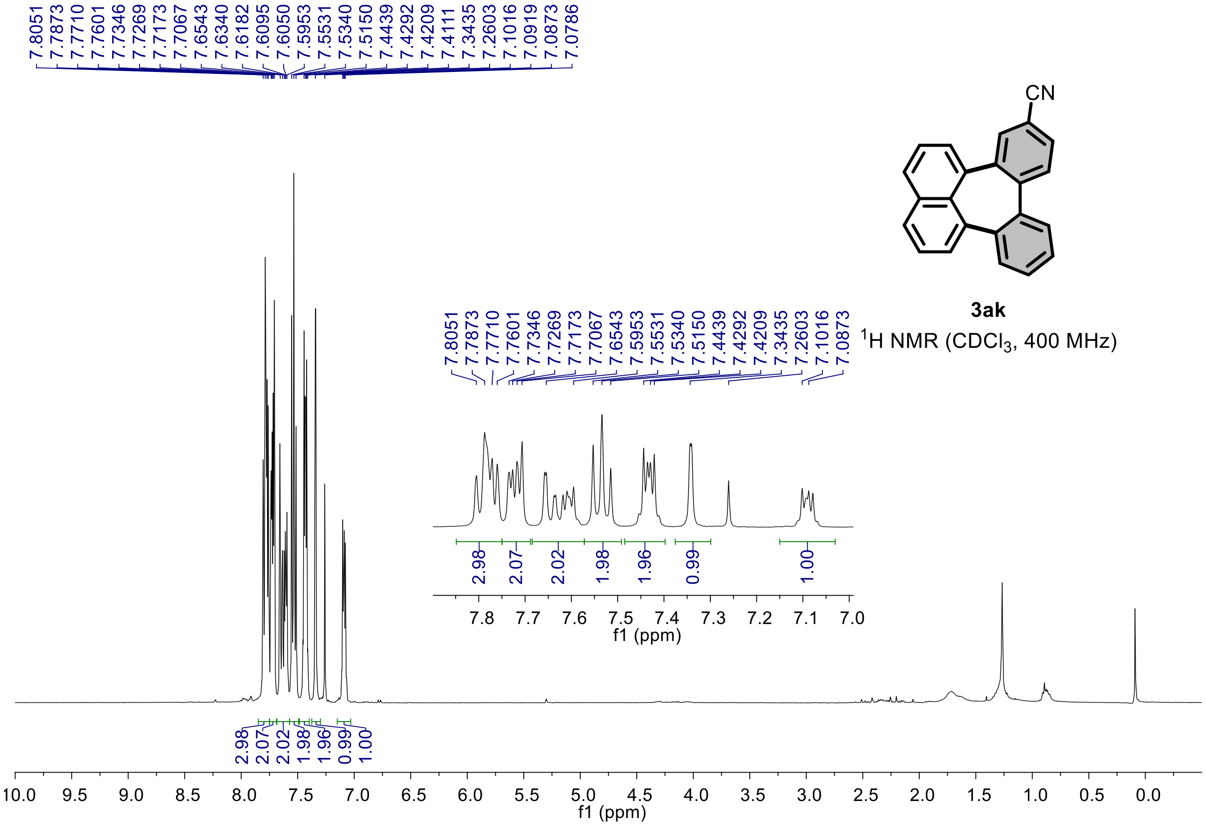
3aj

^{1}H NMR (CDCl$_3$, 400 MHz)



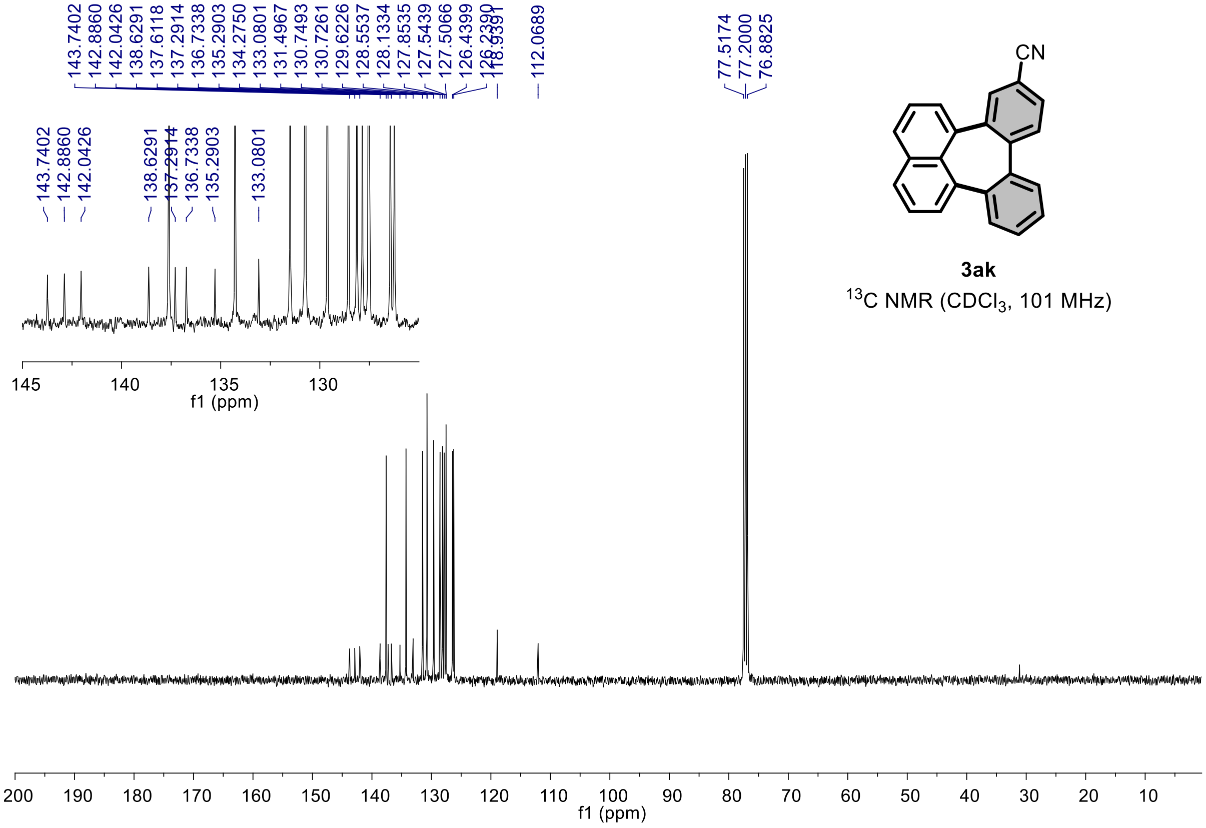
3aj

^{13}C NMR (CDCl$_3$, 101 MHz)



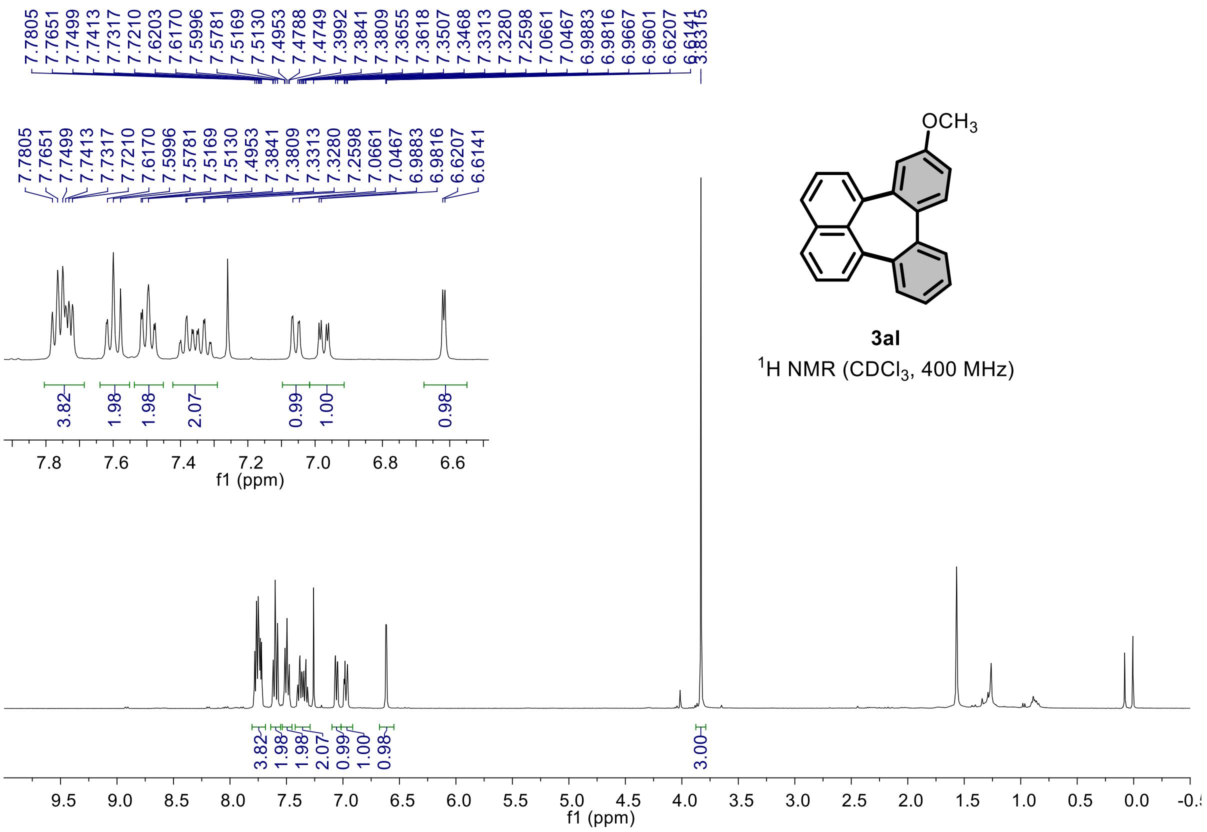
3ak

^{1}H NMR (CDCl$_3$, 400 MHz)



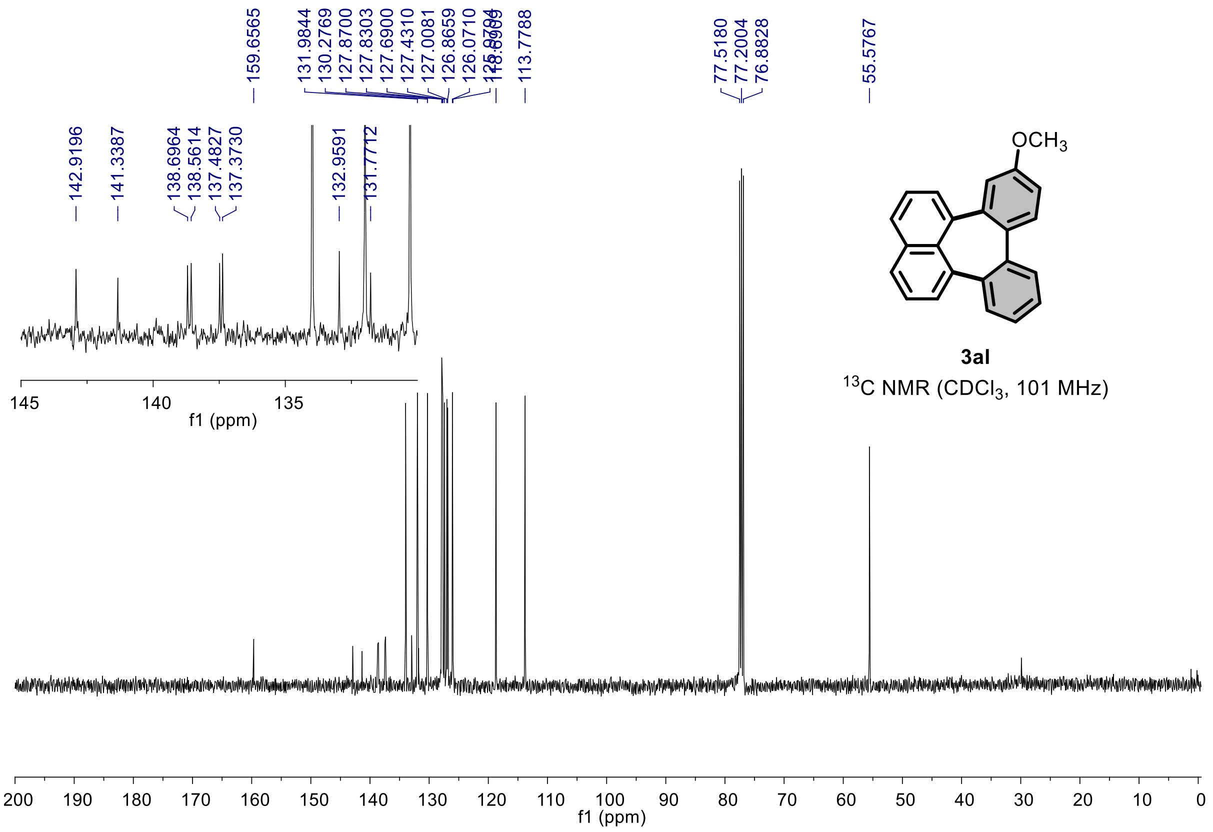
3ak

^{13}C NMR (CDCl$_3$, 101 MHz)



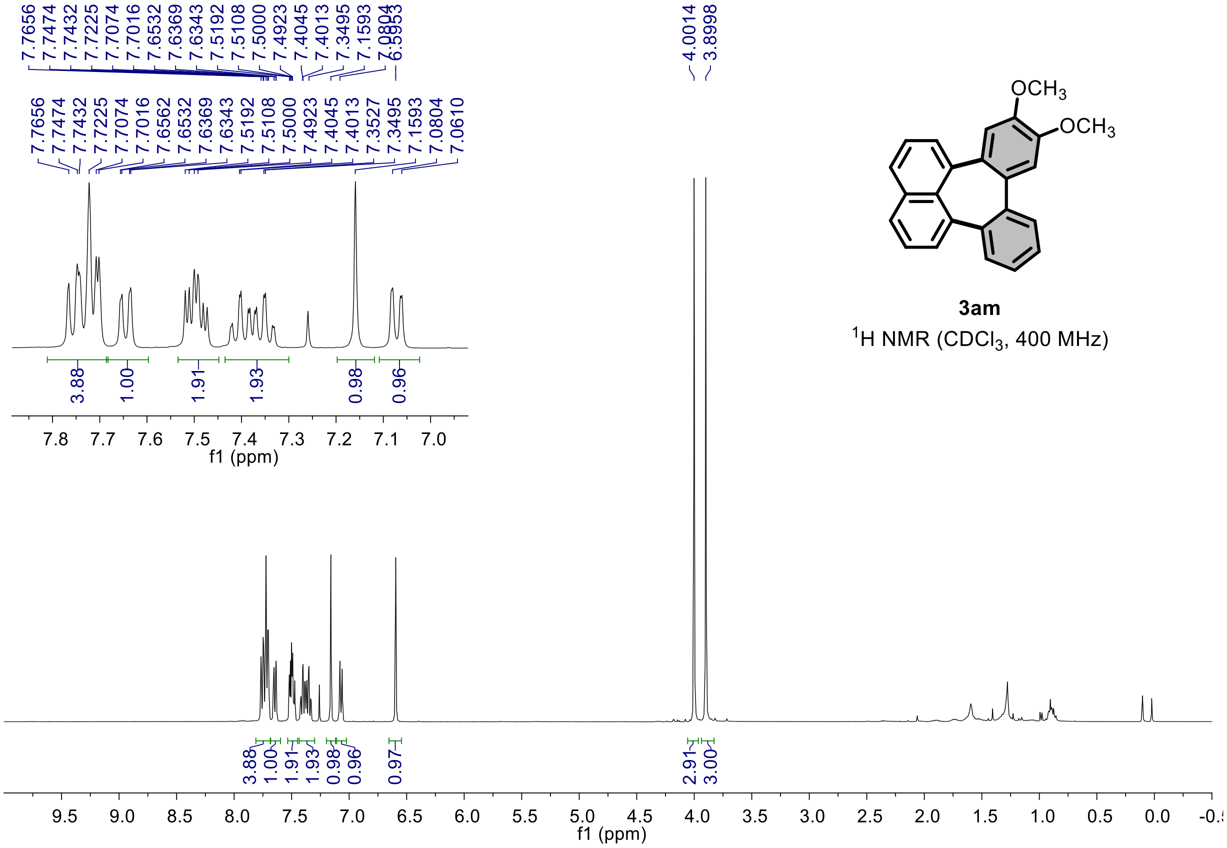
3al

^{1}H NMR (CDCl$_3$, 400 MHz)



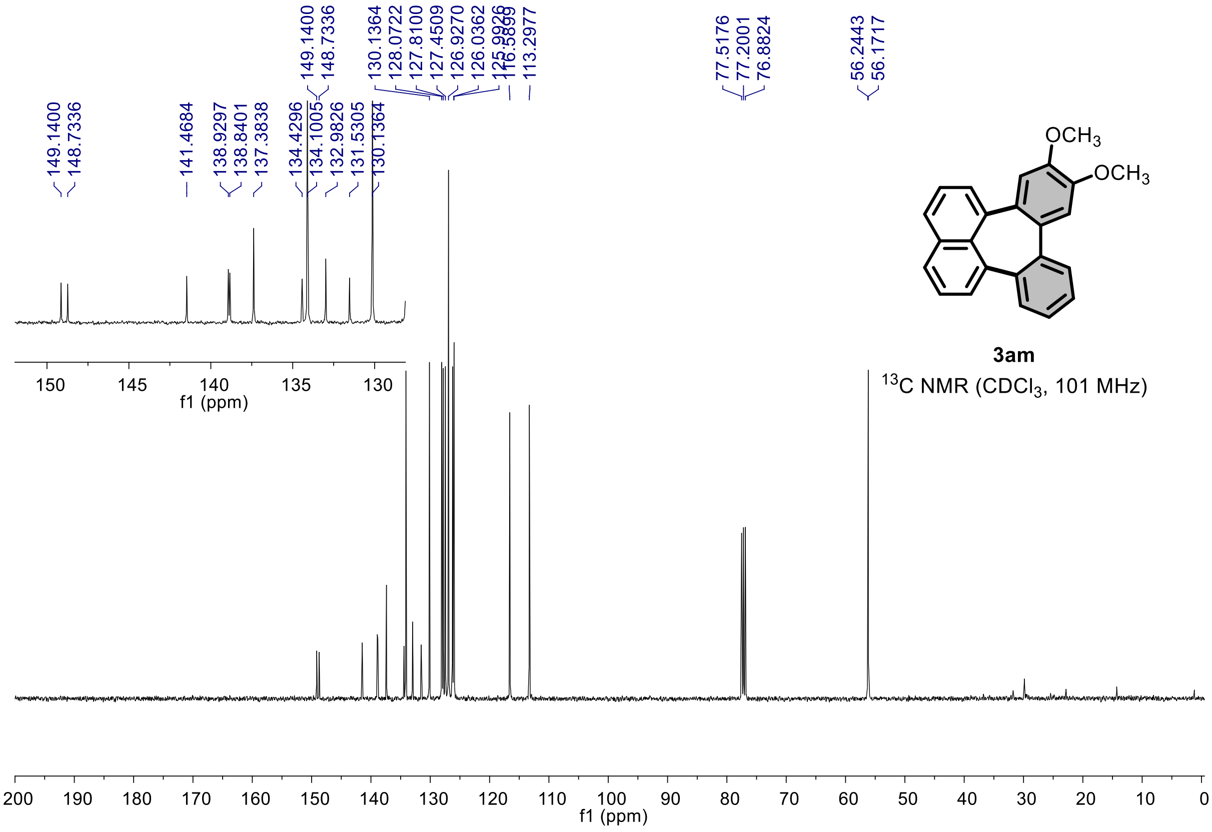
3al

^{13}C NMR (CDCl$_3$, 101 MHz)



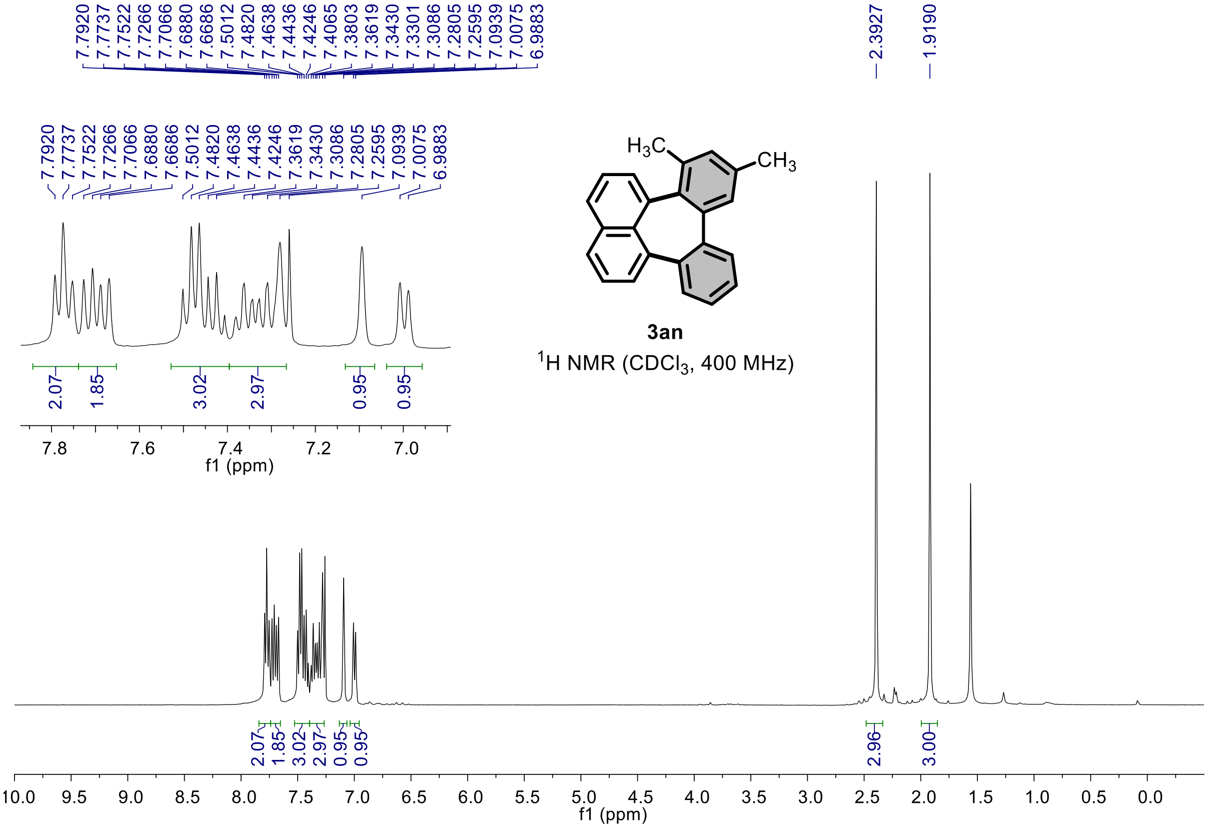
3am

^{1}H NMR (CDCl$_3$, 400 MHz)



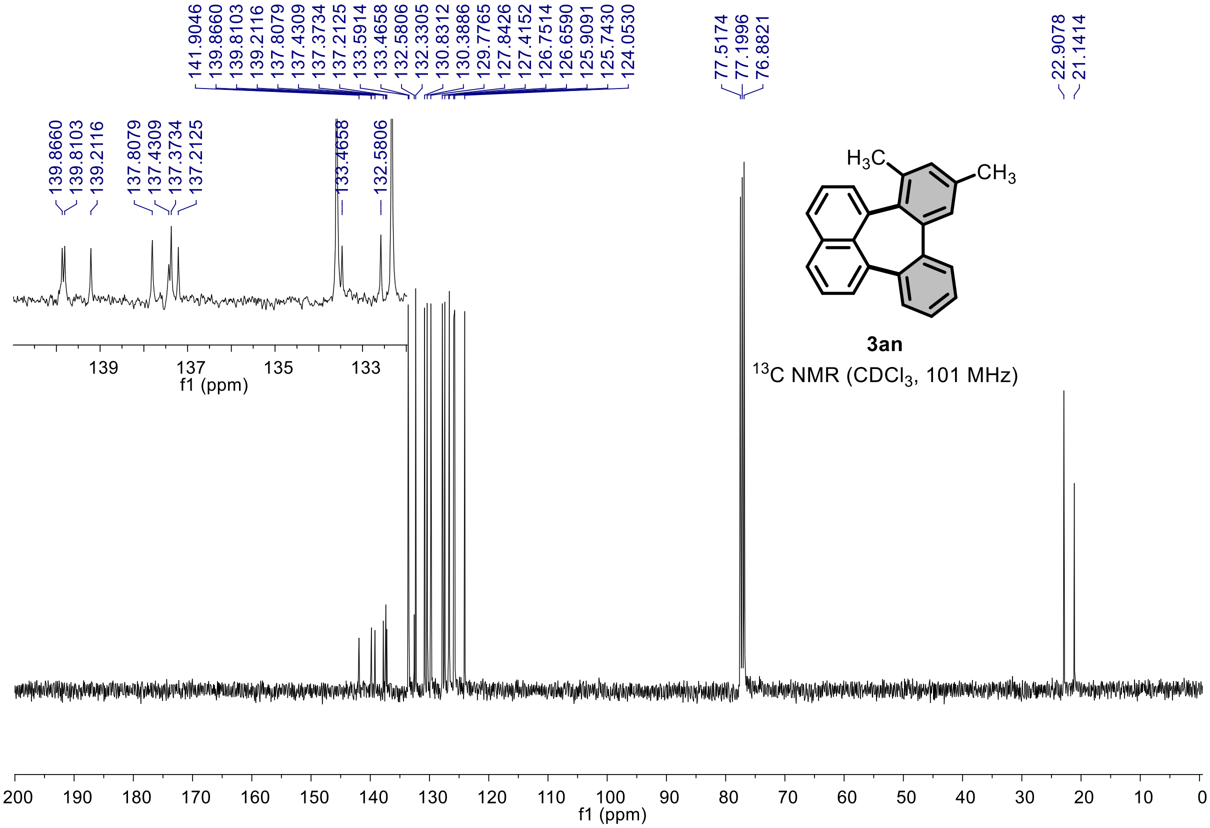
3am

^{13}C NMR (CDCl$_3$, 101 MHz)



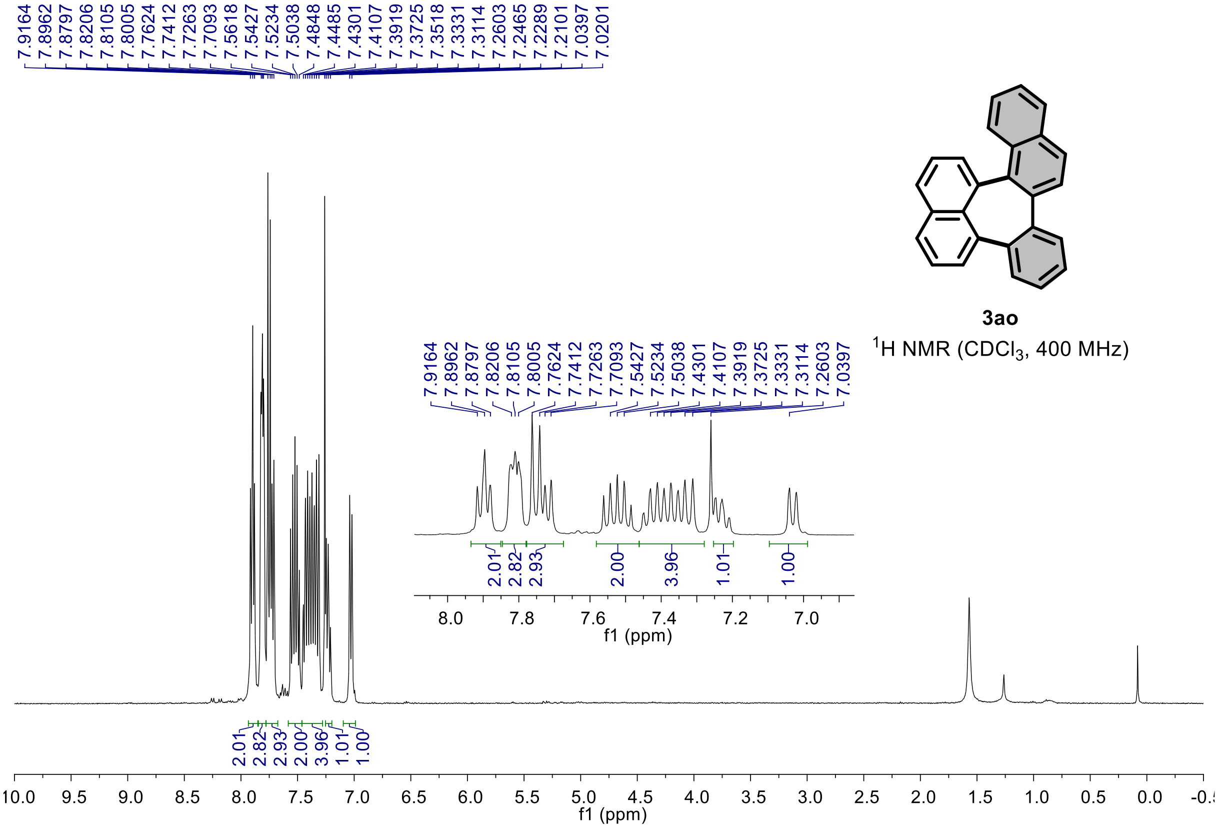
3an

^{1}H NMR (CDCl$_3$, 400 MHz)



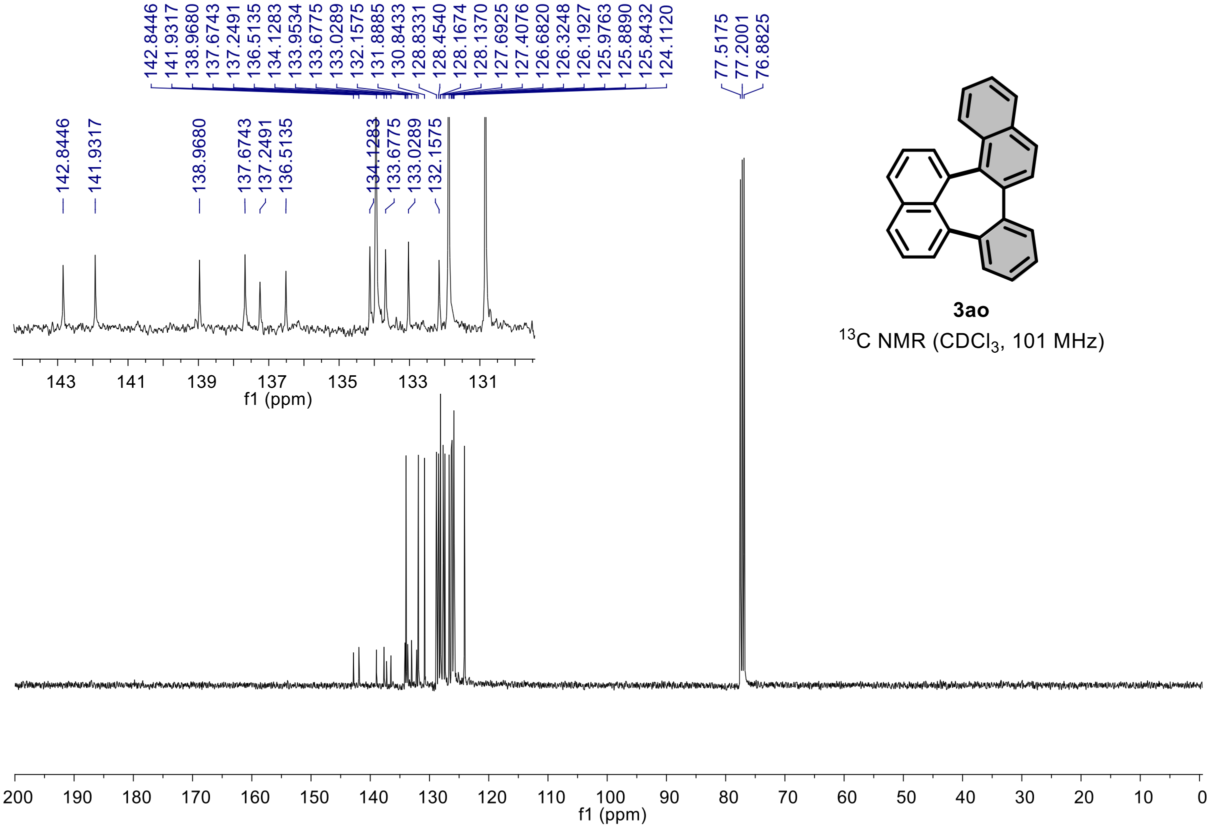
3an

^{13}C NMR (CDCl$_3$, 101 MHz)



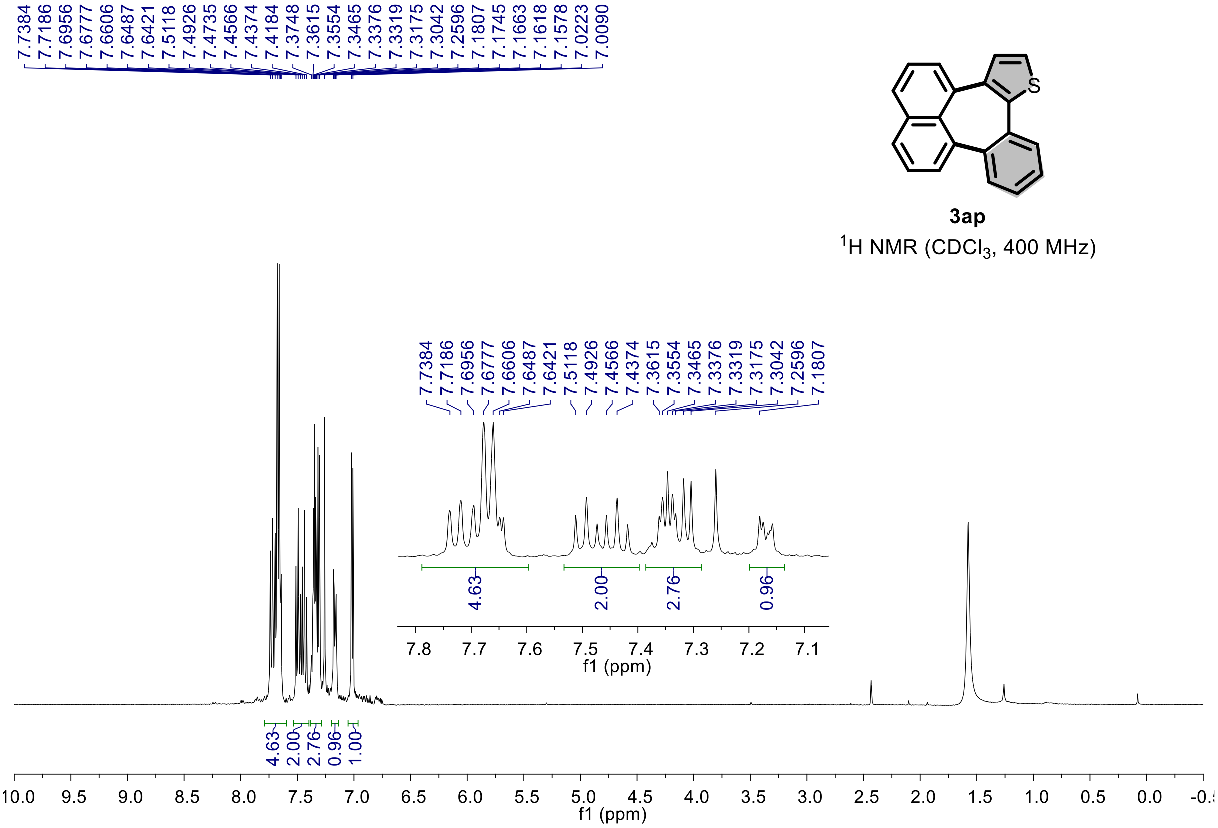
3ao

^{1}H NMR (CDCl$_3$, 400 MHz)



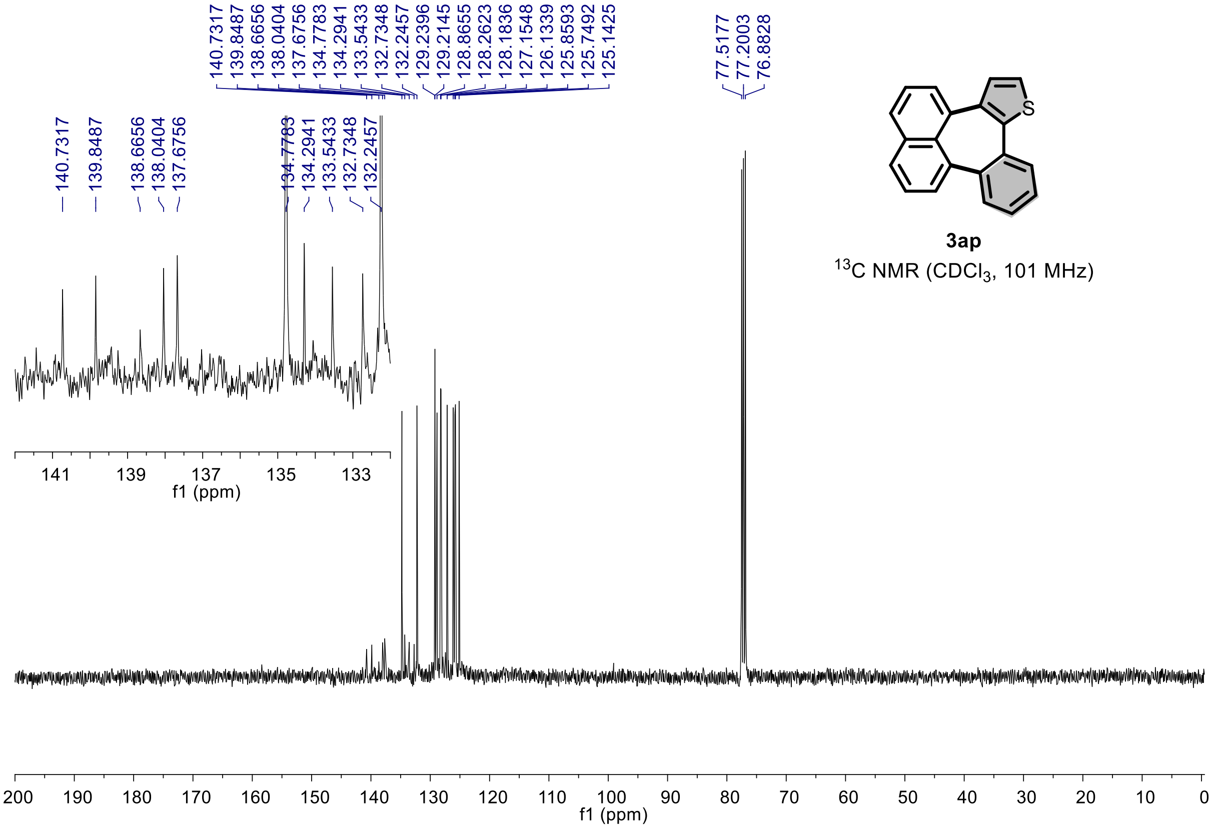
3ao

^{13}C NMR (CDCl$_3$, 101 MHz)



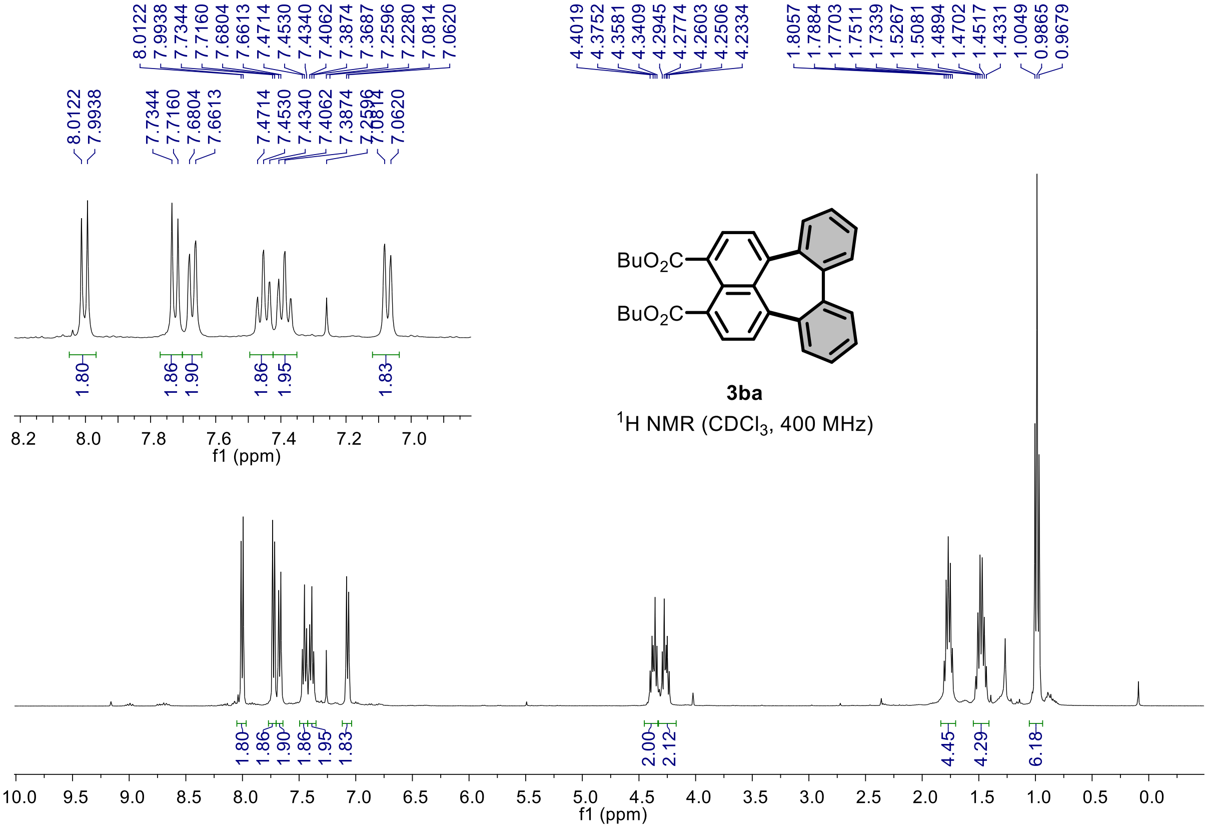
3ap

^{1}H NMR (CDCl$_3$, 400 MHz)



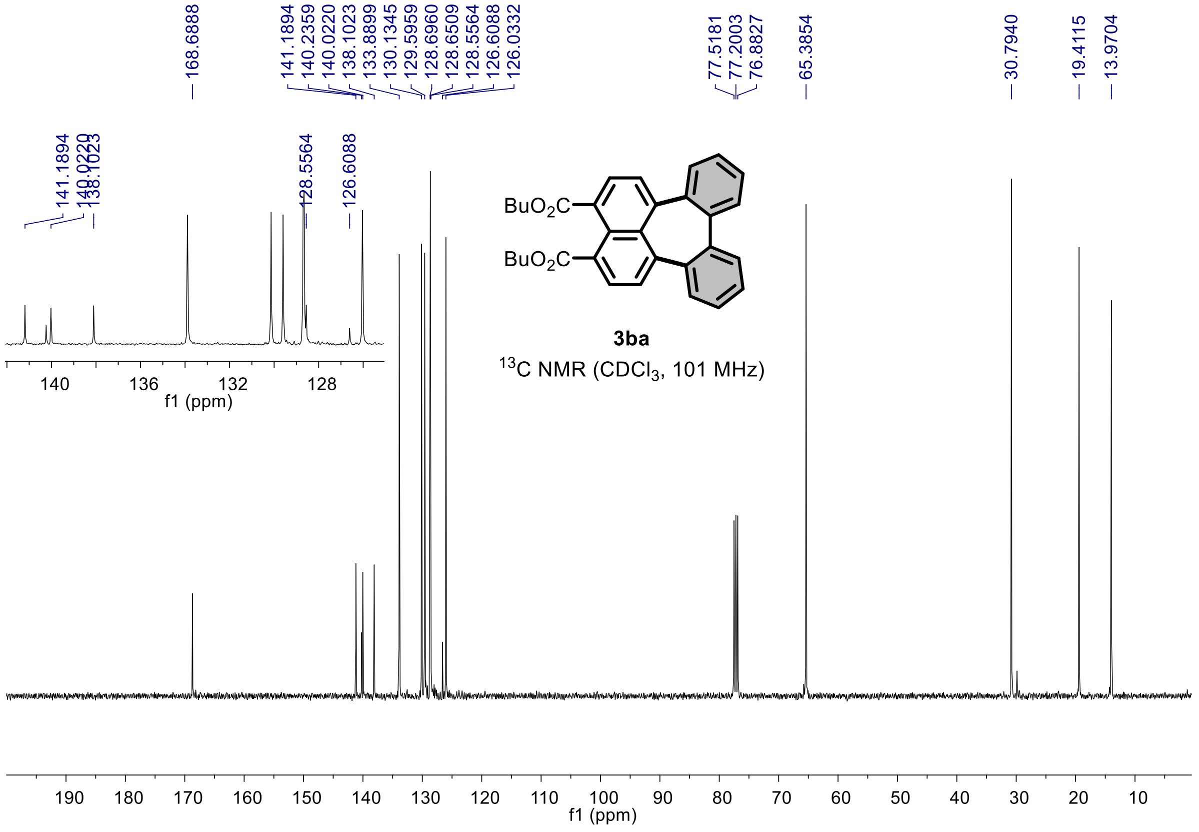
3ap

^{13}C NMR (CDCl$_3$, 101 MHz)



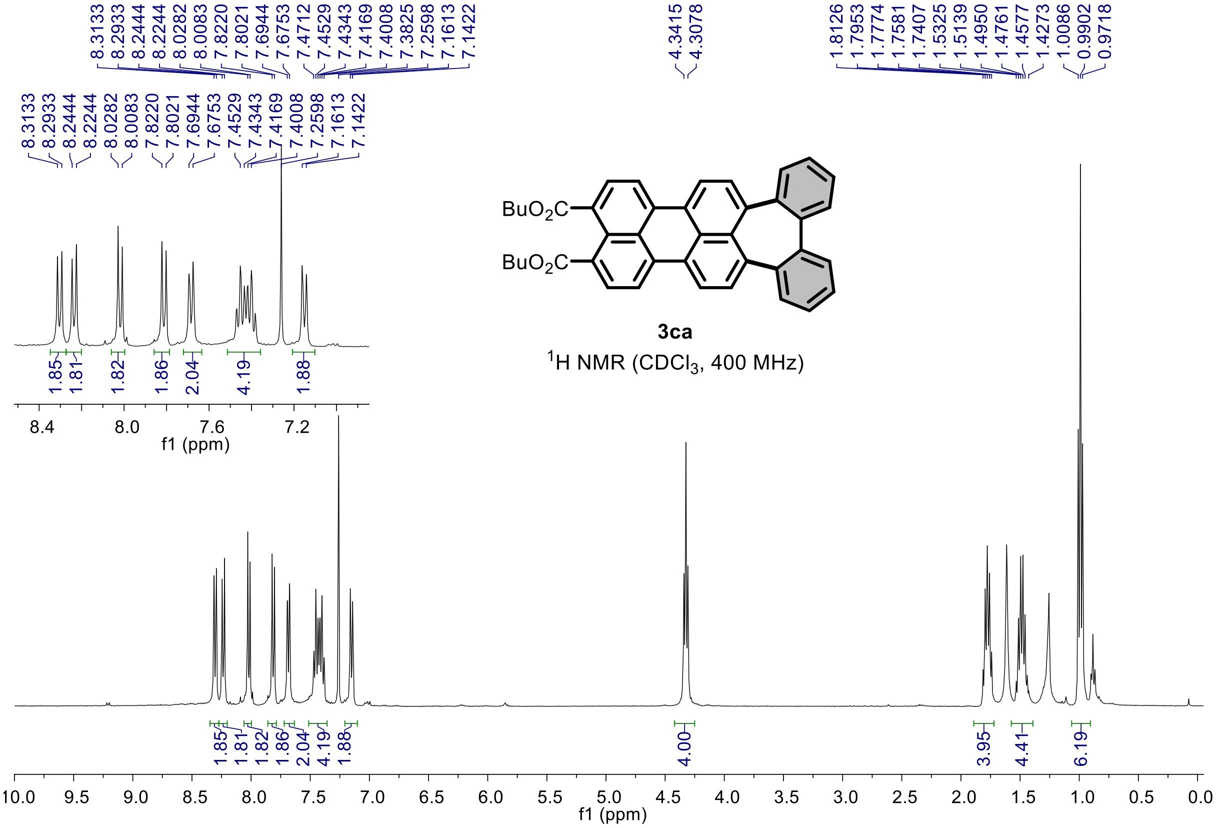
3ba

^1H NMR ($CDCl_3$, 400 MHz)



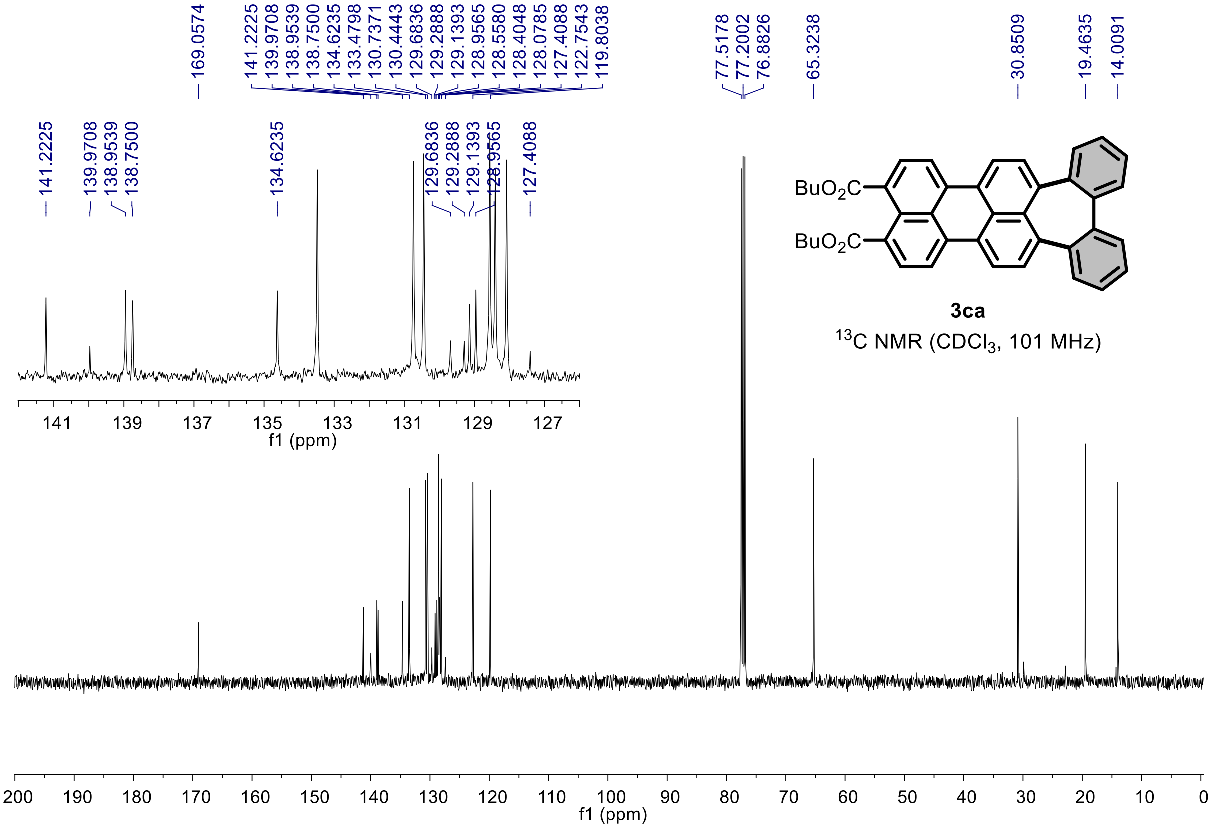
3ba

^{13}C NMR ($CDCl_3$, 101 MHz)



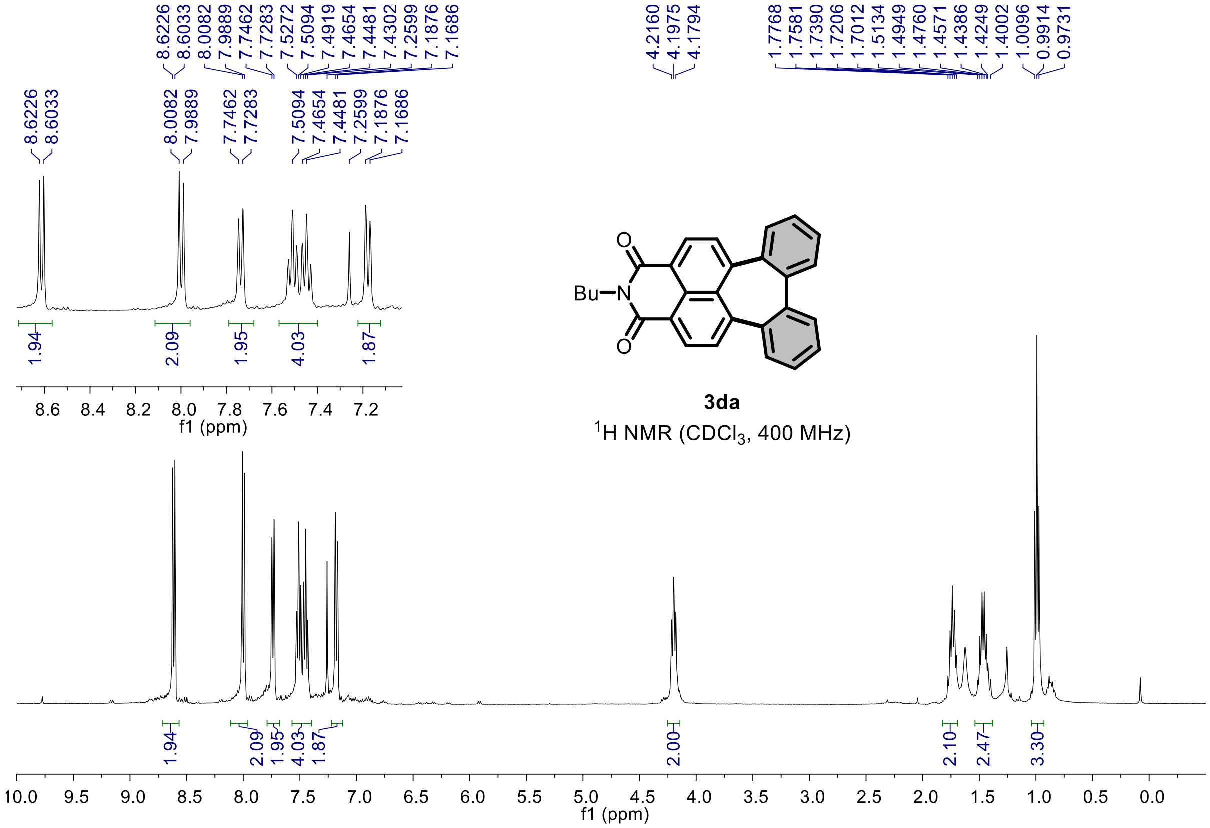
3ca

^{1}H NMR (CDCl$_3$, 400 MHz)



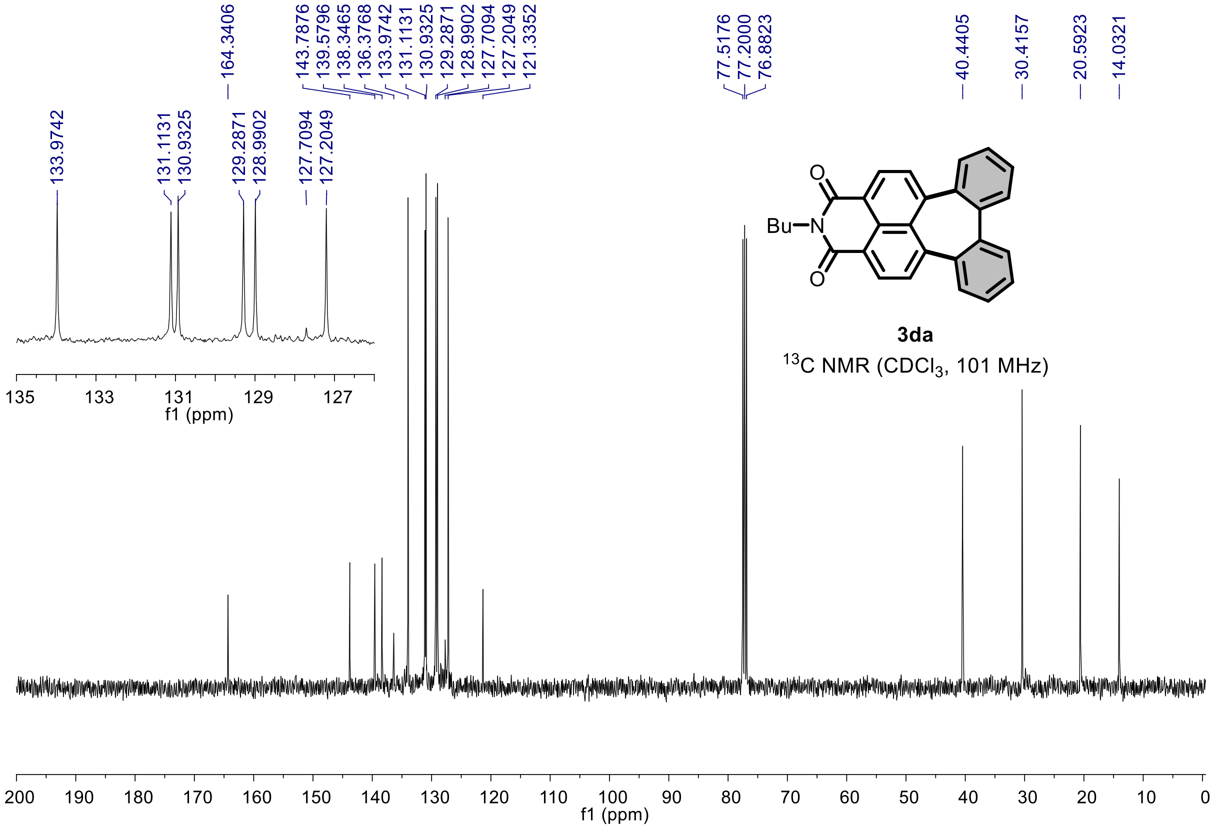
3ca

^{13}C NMR (CDCl$_3$, 101 MHz)



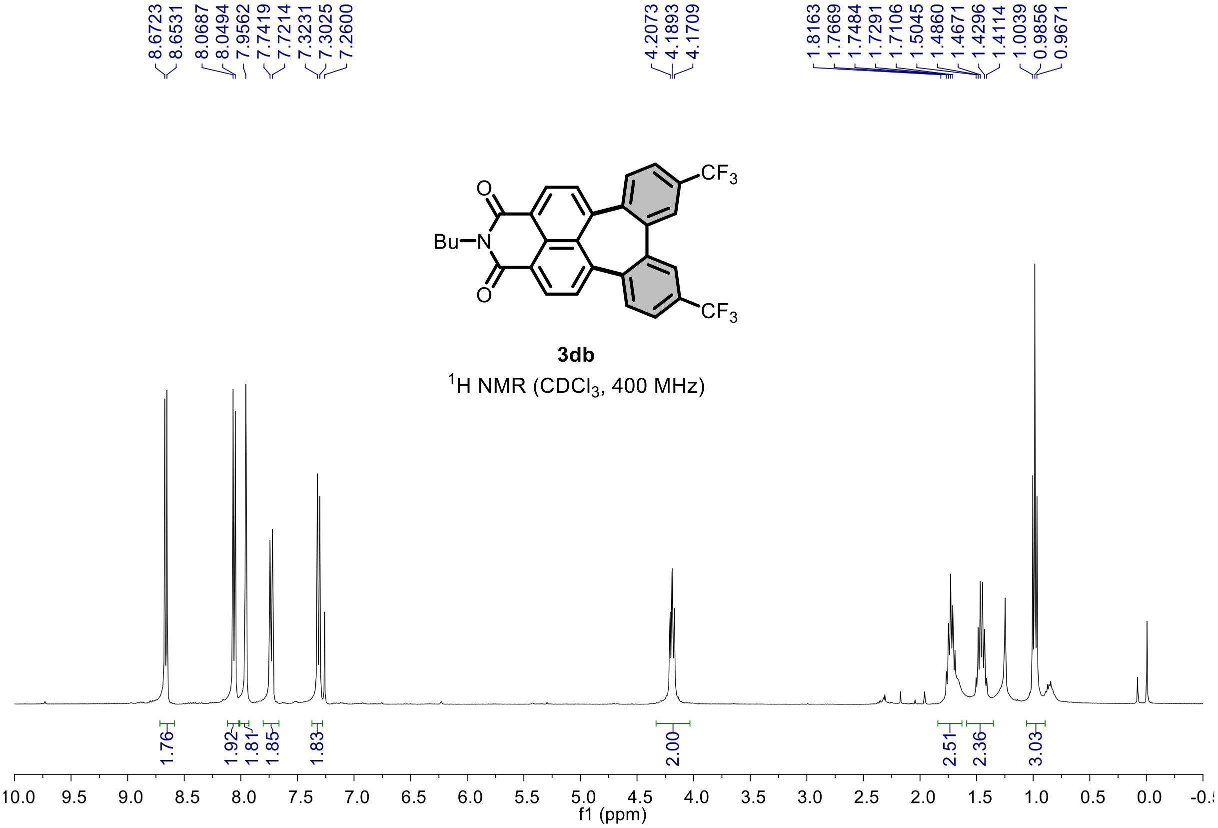
3da

^{1}H NMR (CDCl$_3$, 400 MHz)



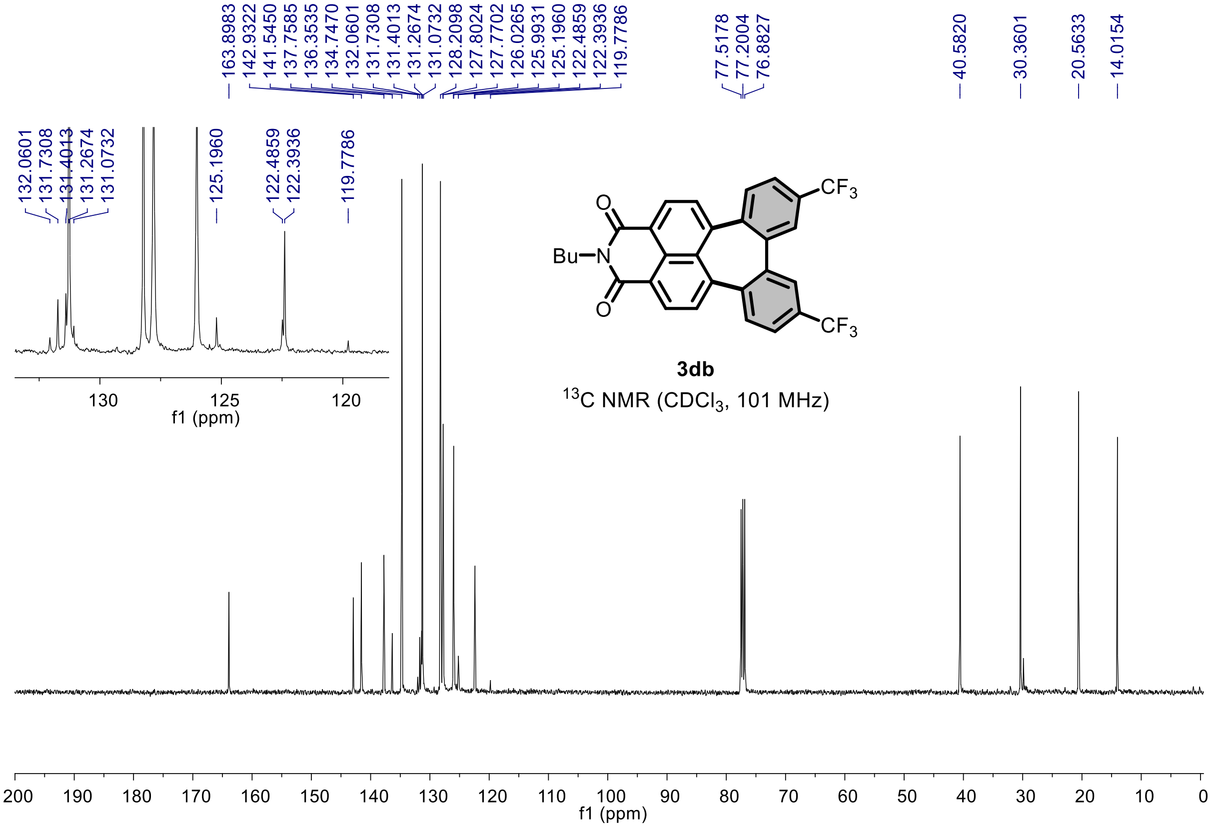
3da

^{13}C NMR (CDCl$_3$, 101 MHz)



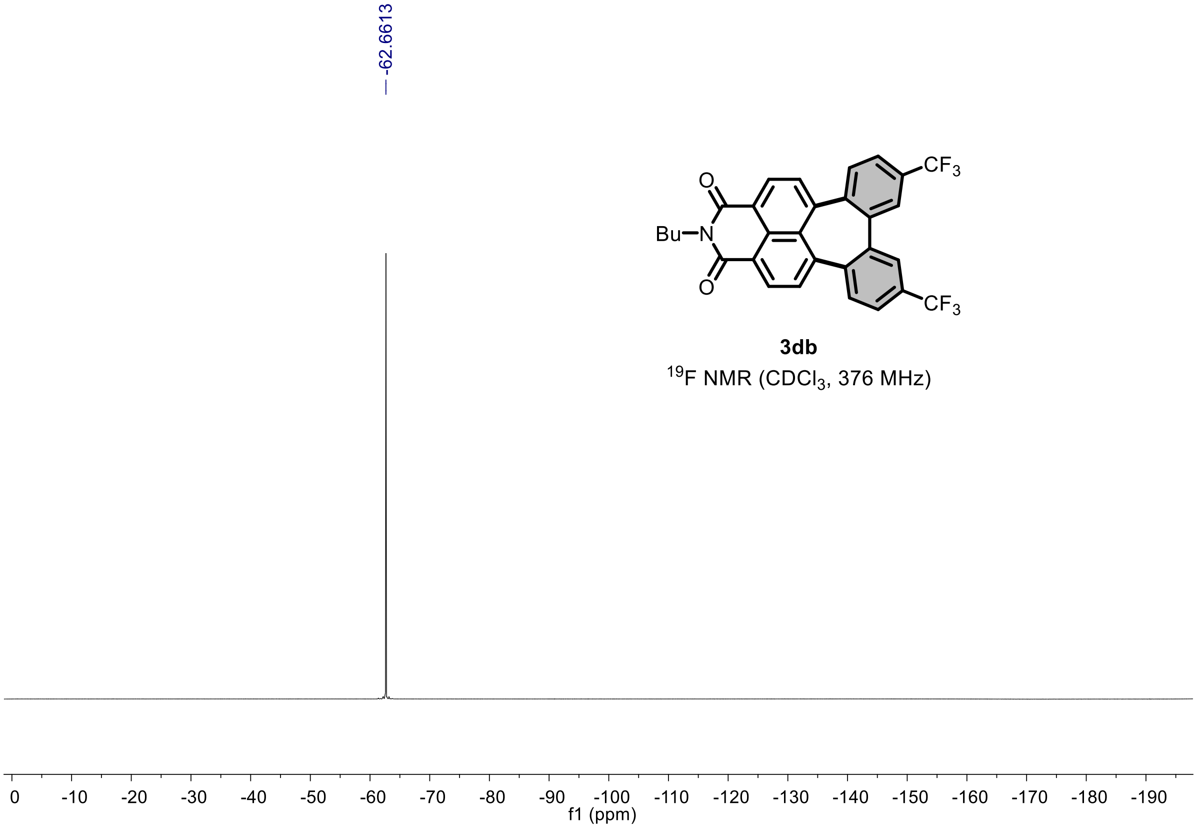
3db

^{1}H NMR ($CDCl_3$, 400 MHz)



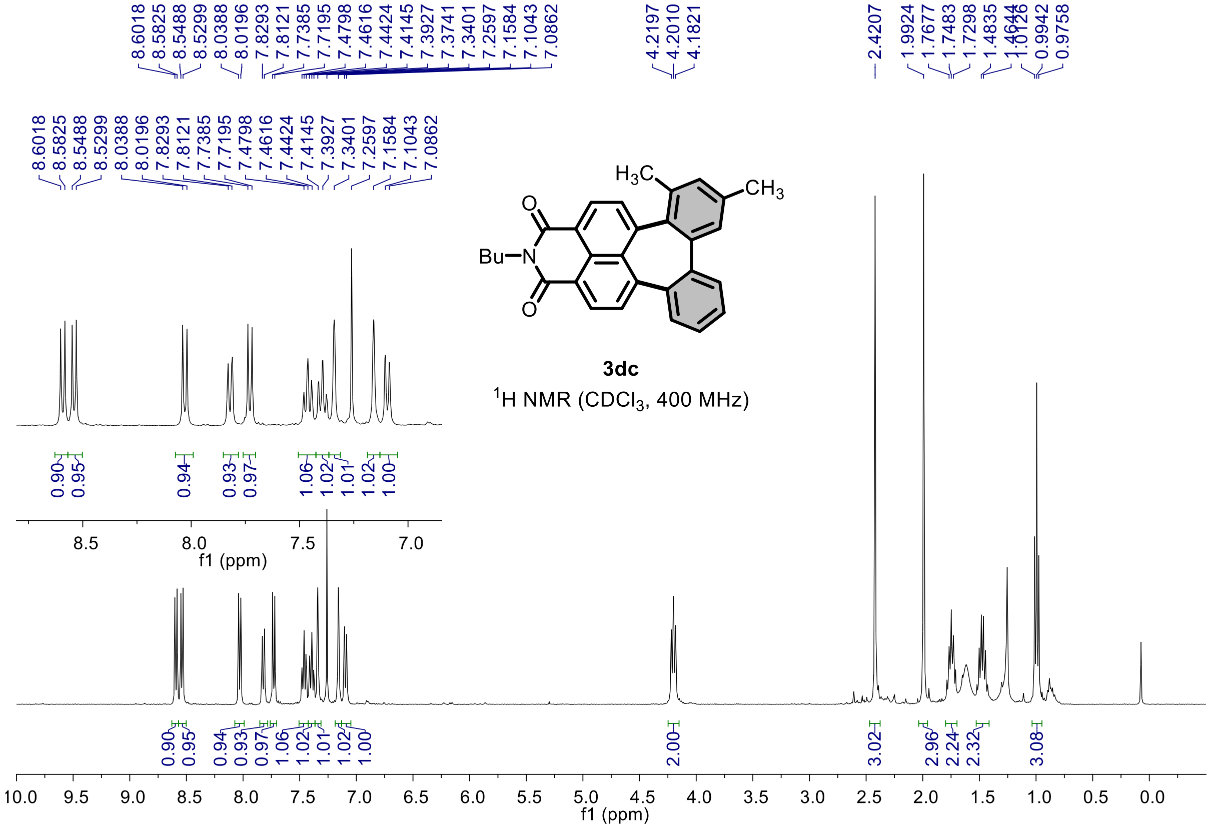
3db

^{13}C NMR ($CDCl_3$, 101 MHz)



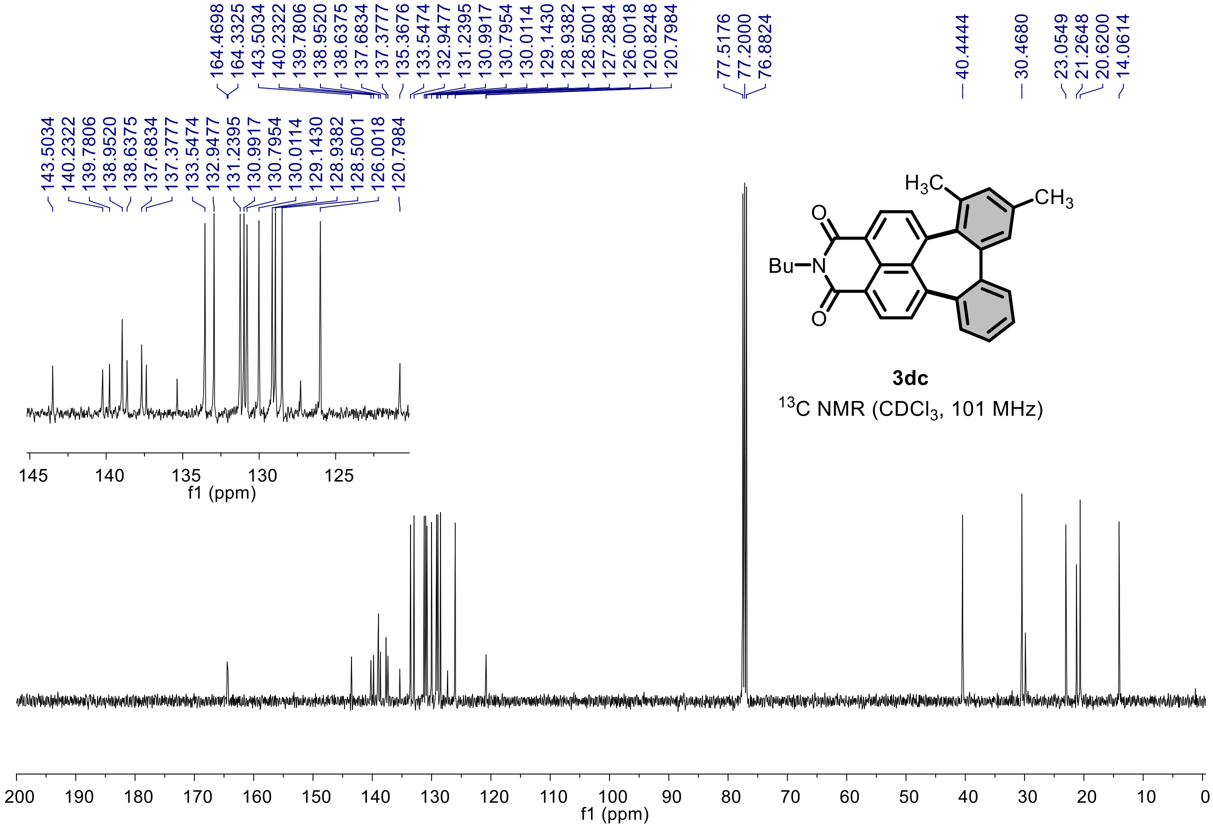
3db

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



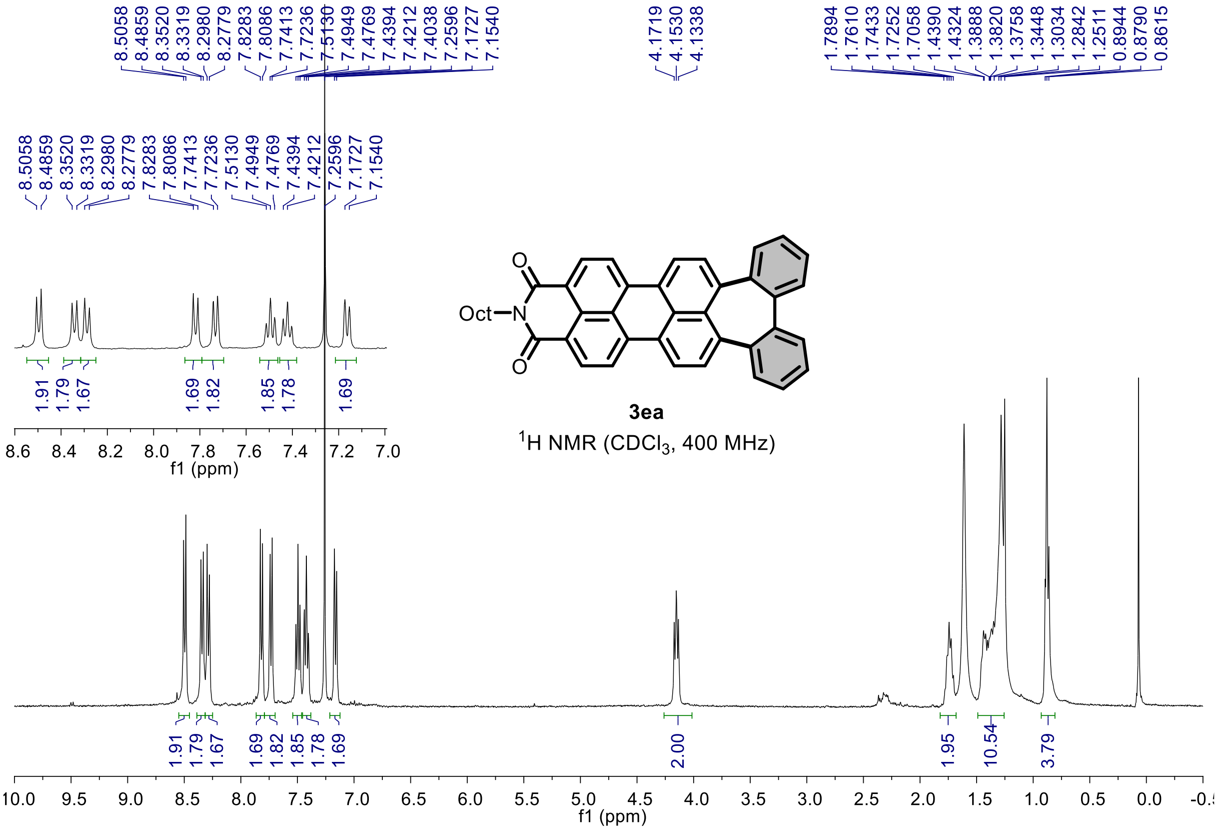
3dc

^1H NMR ($CDCl_3$, 400 MHz)



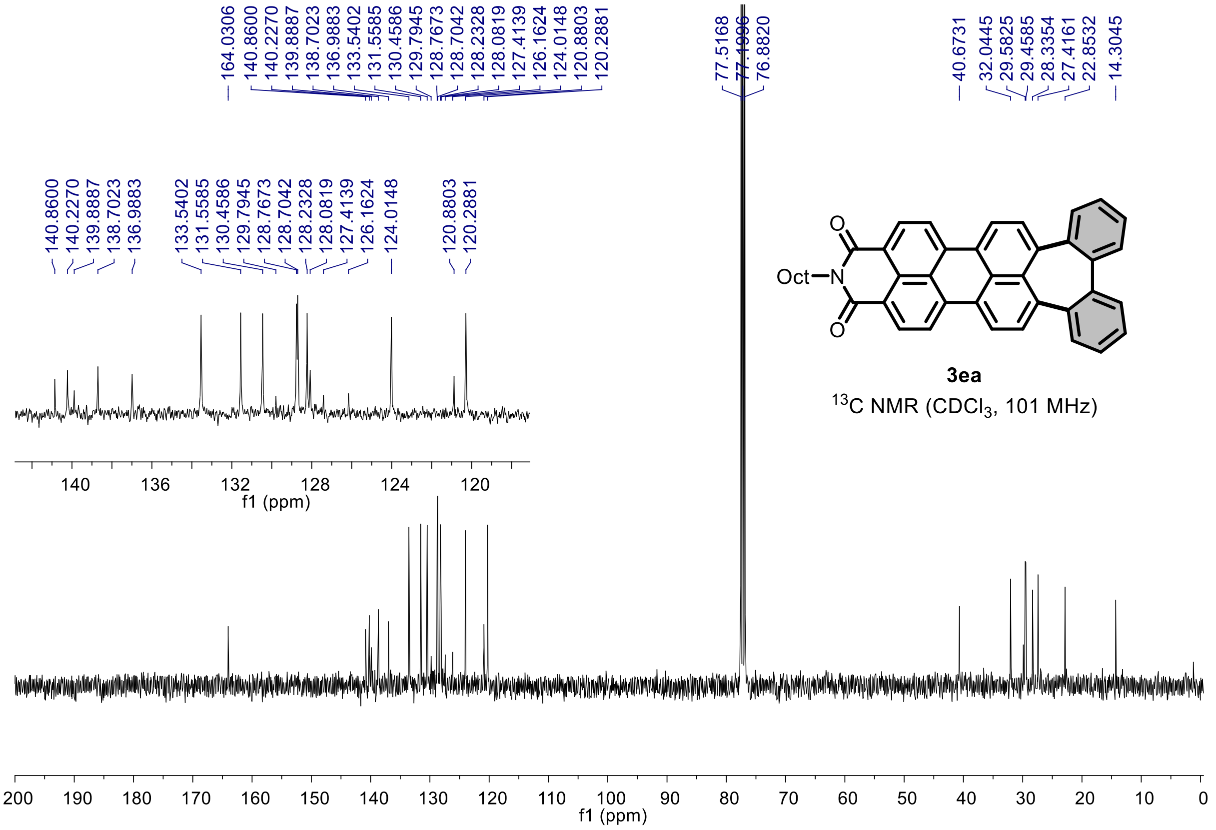
3dc

^{13}C NMR ($CDCl_3$, 101 MHz)



3ea

^{1}H NMR (CDCl$_3$, 400 MHz)



3ea

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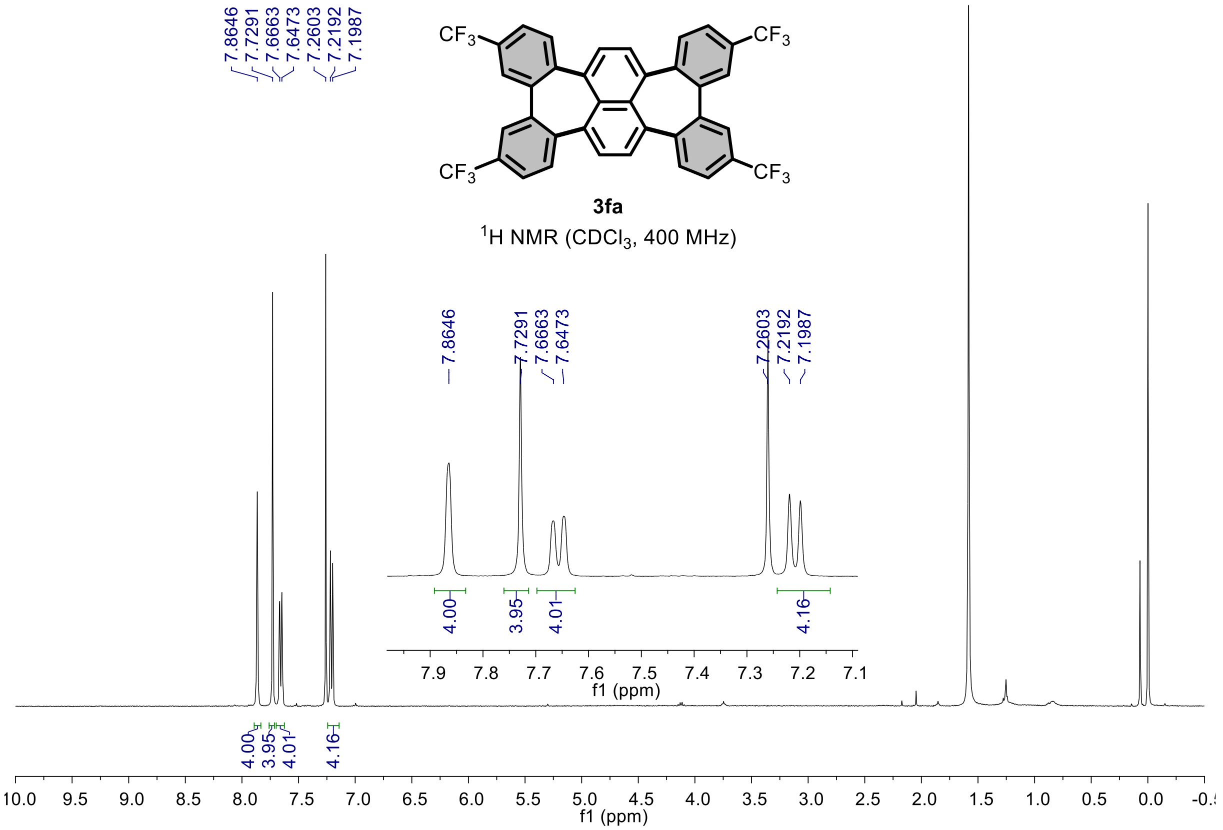

3fa

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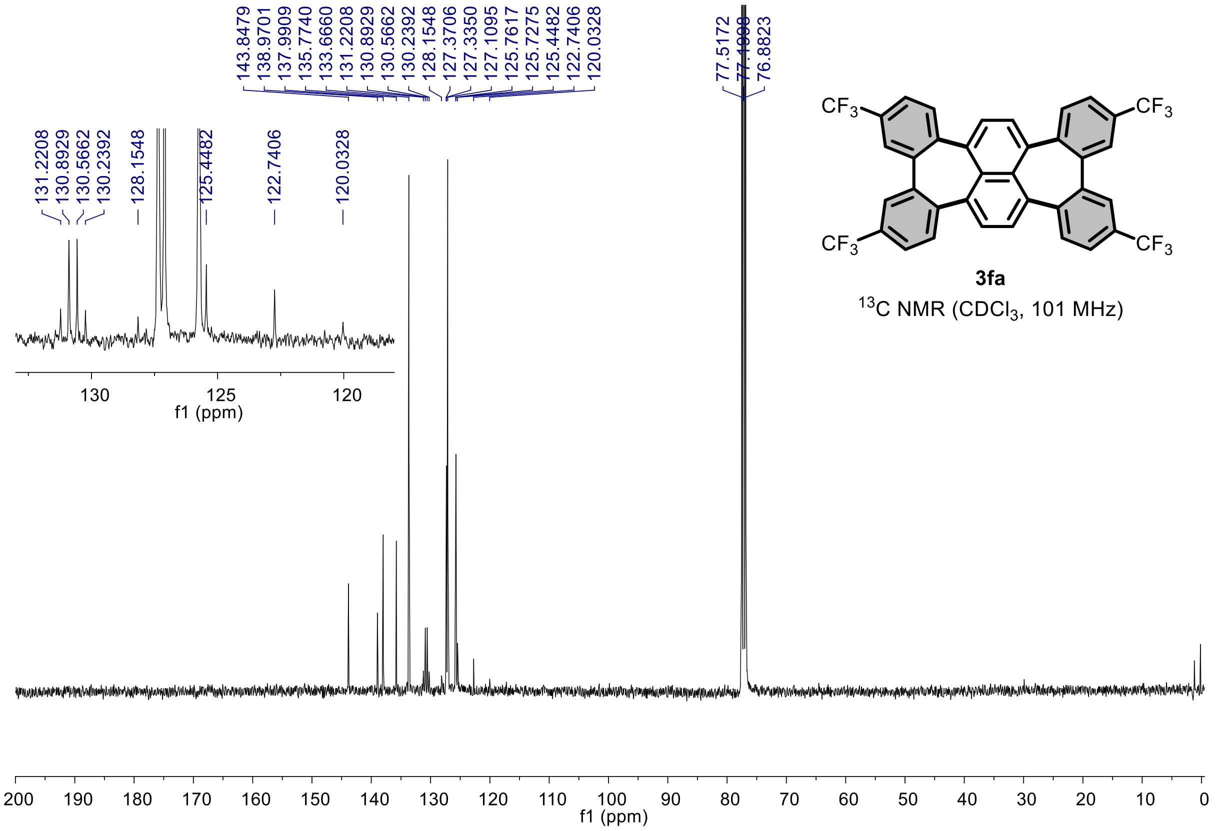

3fa

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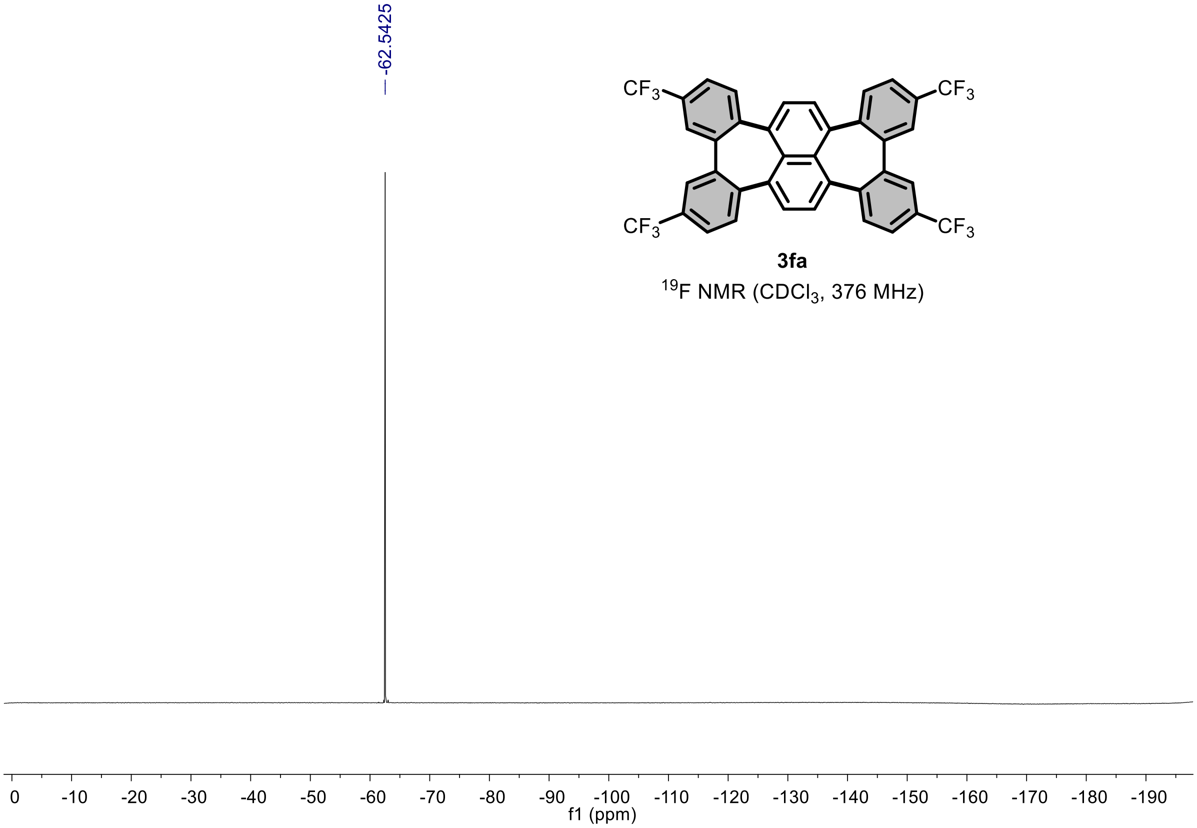
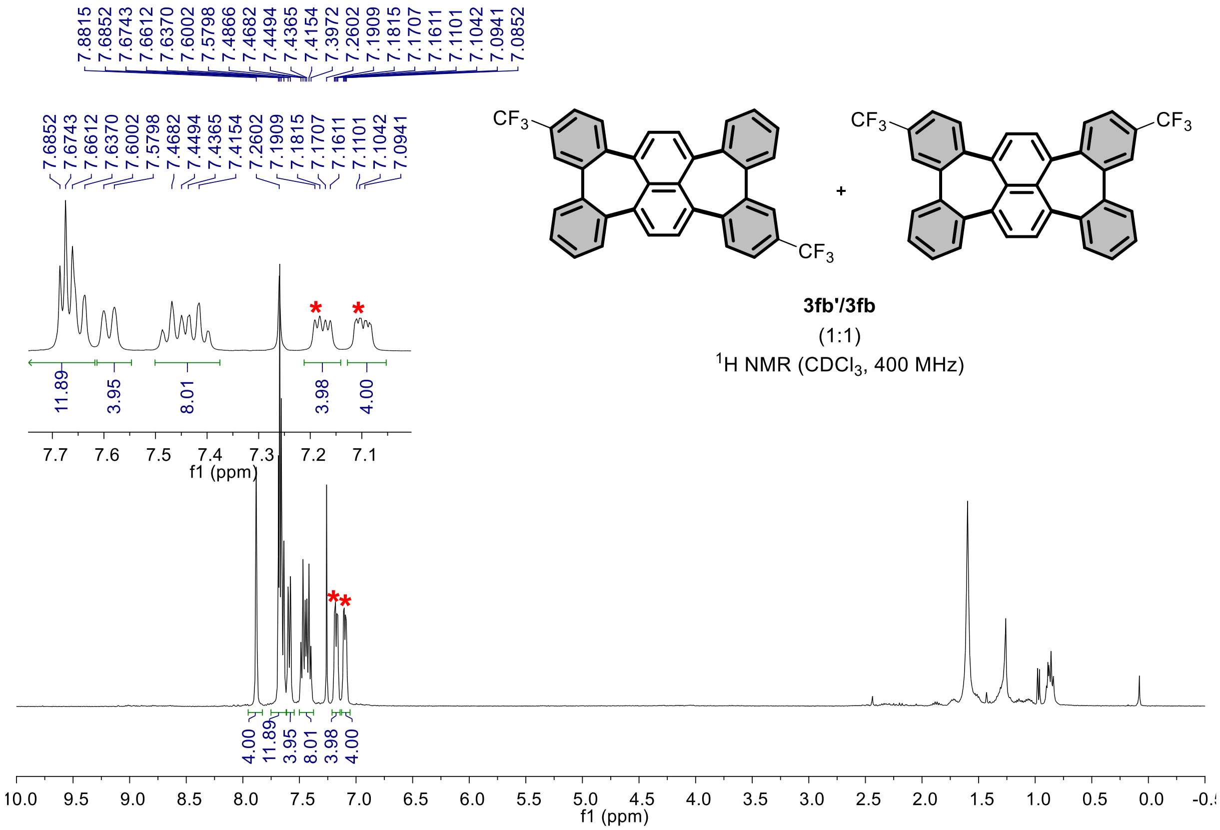


3fa

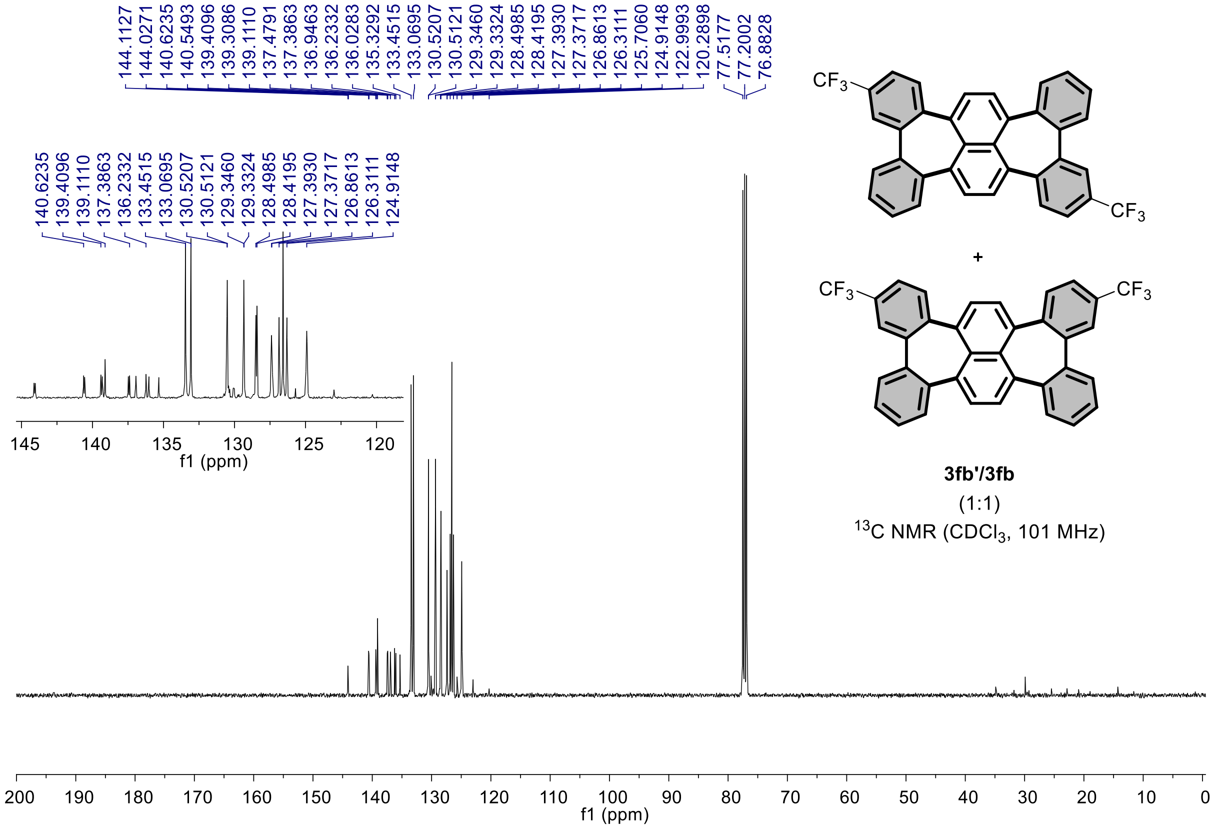
^{19}F NMR (CDCl$_3$, 376 MHz)



3fb'/3fb

(1:1)

^{1}H NMR ($CDCl_3$, 400 MHz)



3fb'/3fb

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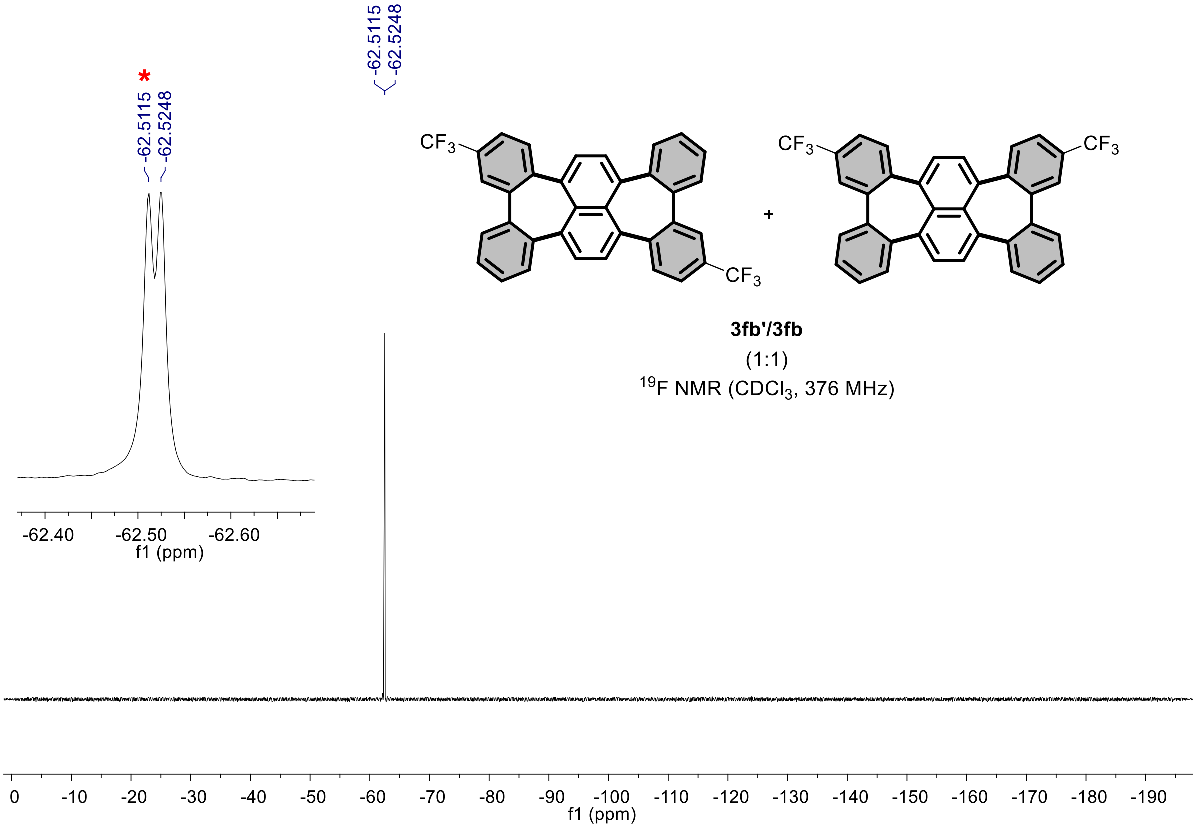

3fb'/3fb

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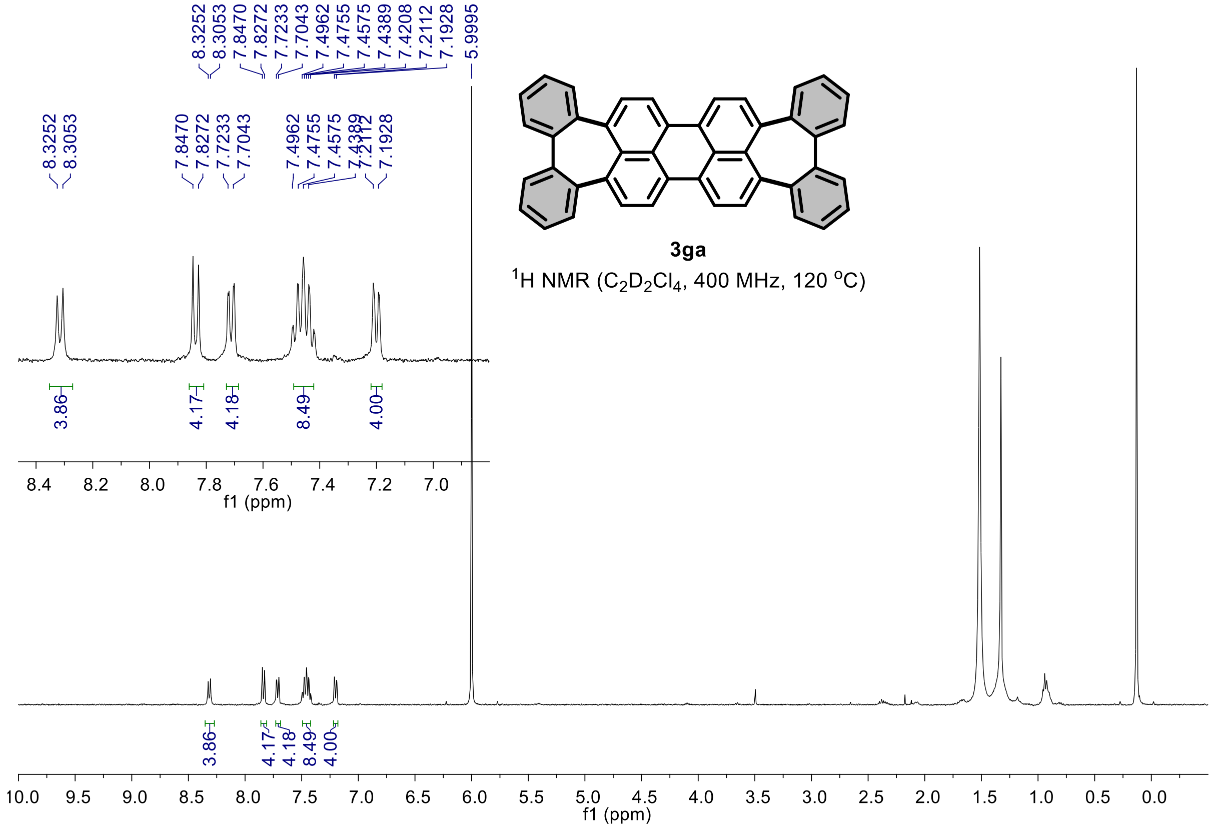
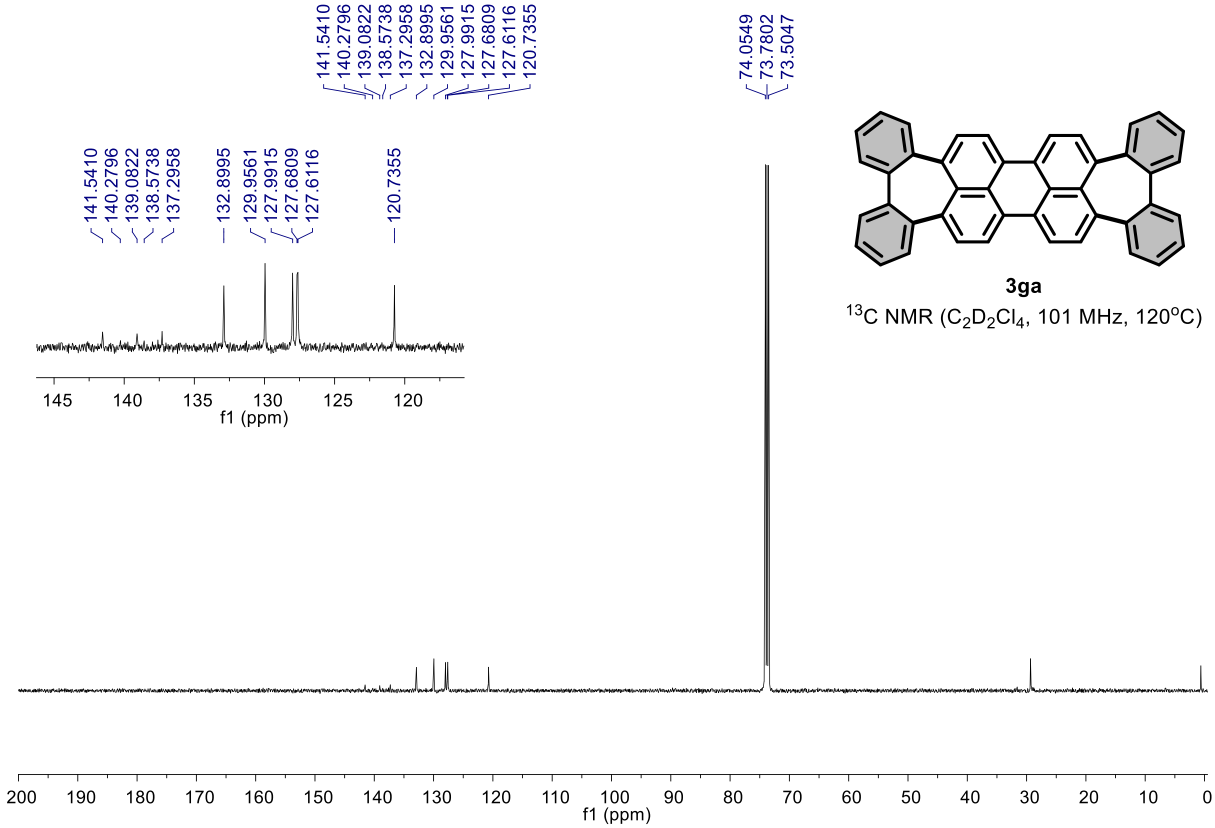
^{19}F NMR (CDCl$_3$, 376 MHz)



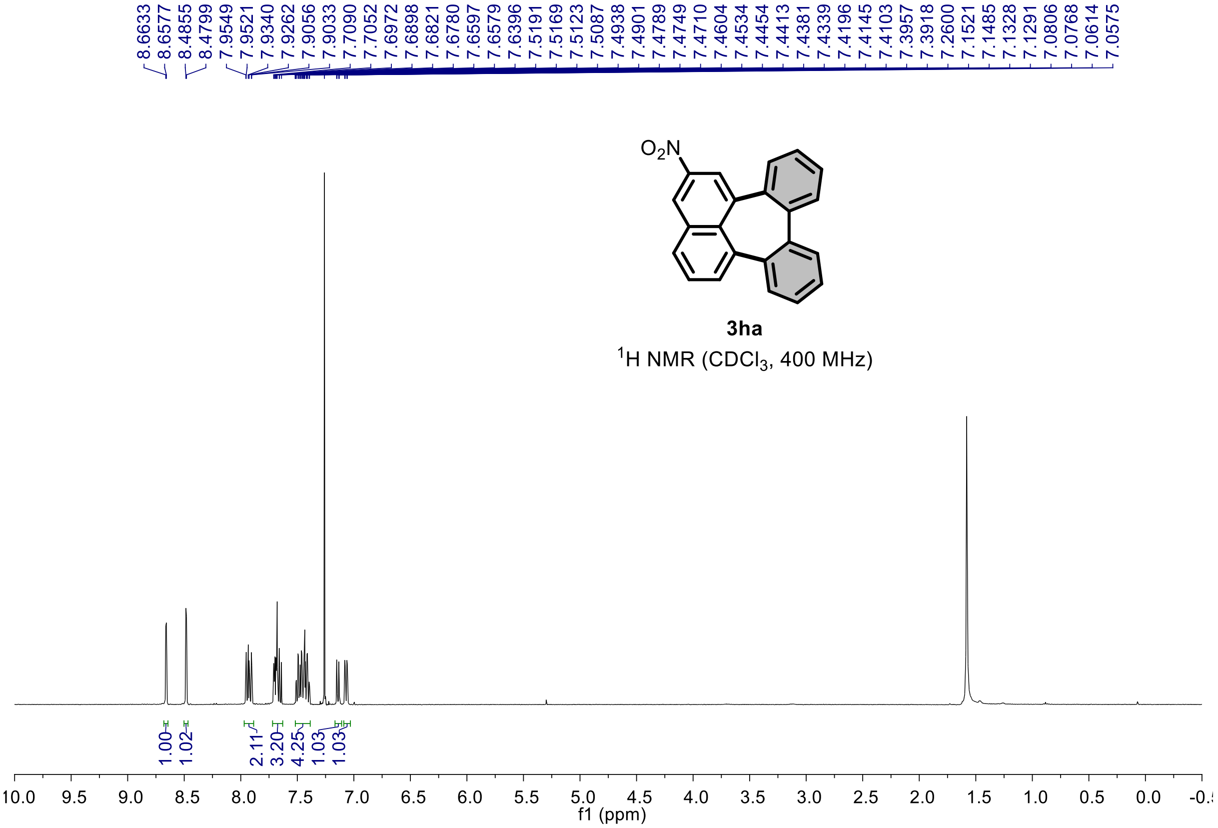
3ga

^{1}H NMR ($C_2D_2Cl_4$, 400 MHz, 120 ^{o}C)



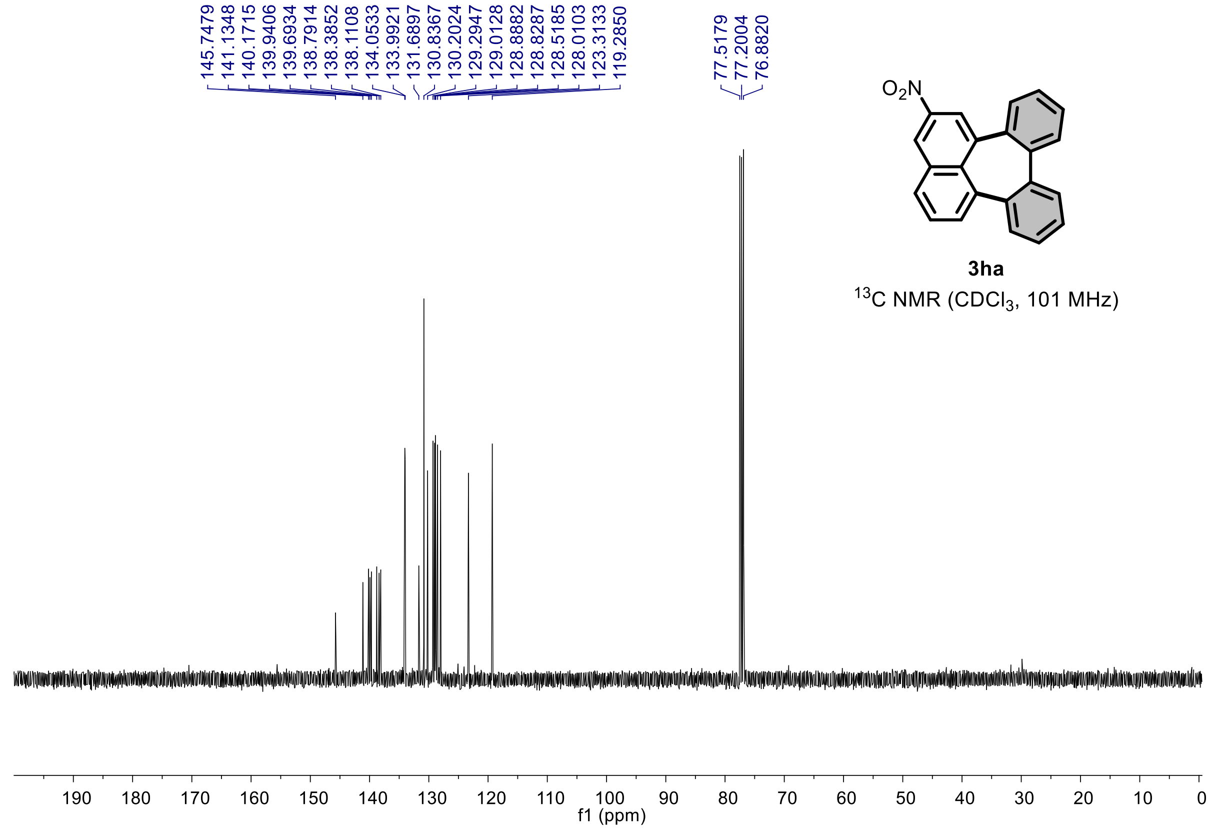
3ga

^{13}C NMR ($C_2D_2Cl_4$, 101 MHz, 120^{o}C)



3ha

^{1}H NMR (CDCl$_3$, 400 MHz)



3ha

^{13}C NMR (CDCl$_3$, 101 MHz)