Direct triple annulations: a way to design large triazastarphenes with intertwined hexagonal packing

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Contents

A. Materials, Methods and synthesis

All the chemical reagents were purchased and used as received (3-amino-2-naphthoic acid provided by fluorochem; BrettPhos, 5-bromo-1,2,3-trimethoxybenzene and 1-bromo-3,5-di-tert-butylbenzene by Sigma-aldrich; diphenyl chlorophosphate and triisopropylsilylacetylene by TCI; 1-bromo-3,5-bis(trifluoromethyl)benzene and 2-aminobenzophenone by Alfa Aesar. Solvents used below were dried and freshly distilled before use. For TAN derivatives, 2-amino-4'-methylbenzophenone was obtained by the reported method[1].

Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments.

Mass spectra were performed by the CESAMO (Bordeaux, France) on a Qexactive mass spectrometer (ion trap, Thermo) or on a QStar Elite mass spectrometer (TOF, Applied Biosystems). The instruments are equipped with an ESI source and spectra were recorded in the positive mode. The spray voltage was maintained at a value between 3200 V and 4500V. The capillary temperature was set between room temperature and 320°C. Samples were introduced by injection through a 20 µL sample loop into a flow (from 300 to 400 µL/min) of methanol from the LC pump.Melting points were recorded by differential scanning calorimetry and confirmed by a melting point apparatus (MP90 Mettler Toledo).

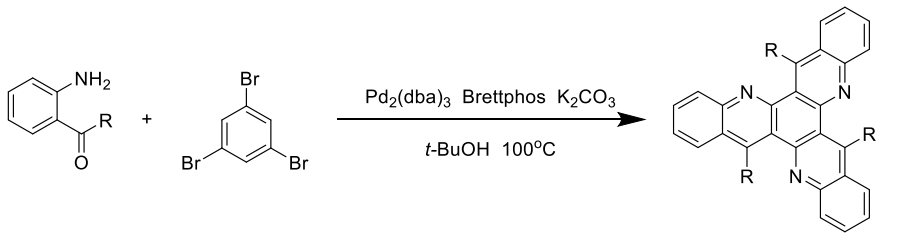
Triazatrinaphthylene (TAN) derivatives **TAN-Ph** and **TAN-MePh** were synthesized following the route shown in **Scheme S-A.1**. Triazatrianthrylene (TAA) derivatives **TAA-Ph**, **TAA-Tips**, **TAA-OMePh**, **TAA-tBuPh** and **TAA-CF3Ph** were synthesized following the route shown in **Scheme S-A.2**.

For TAA derivatives, 3-amino-2-naphthoic acid was modified into its Weinreb amide counterpart before reacting with Grignard reagent and organolithium compounds to get ketone derivatives. The final products were synthesized by one-pot reactions between amino-ketones and 1,3,5-tribromobenzene with quite high yield (about 75%).

Scheme S-A.3 describes reaction carried out with mono and dibromobenzene which stopped after the coupling reaction.

Reactions with sterically hindered reactants described in **Scheme S-A.4** failed to led to triazatrinaphthylene (TAN) or triazatrianthrylene (TAA) derivatives.

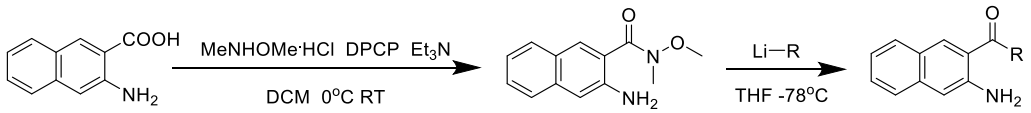
Scheme S-A.5 describes the steps and intermediates in the last reaction. The first intermediate is likely obtained in the reaction mixture. Then, the order in which the other steps are performed are speculative.



R = Ph [1]

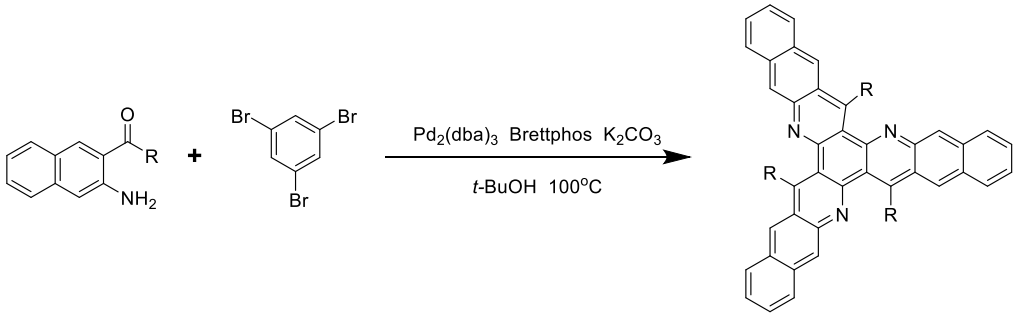
R = p-Tol [2]

Scheme S-A.1. Synthetic route of TAN derivatives.



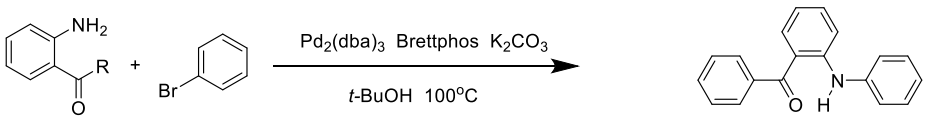
[8]

R = ~Ph [9]
R = ~≡—Si(*i*Pr)$_3$ [10]
R = ~Ph(OMe)$_3$ [11]
R = ~Ph(tBu)$_2$ [12]
R = ~Ph(CF$_3$)$_2$ [13]

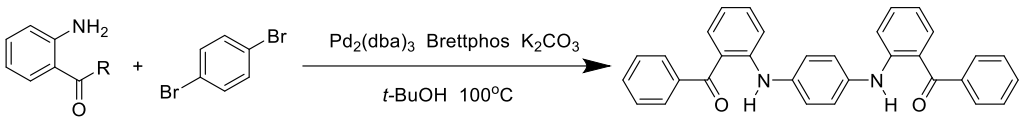


R = ~Ph [3]
R = ~≡−Si(*i*Pr)$_3$ [4]
R = ~Ph(OMe)$_3$ [5]
R = ~Ph(tBu)$_2$ [6]
R = ~Ph(CF$_3$)$_2$ [7]

Scheme S-A.2. Synthetic route of TAA derivatives.

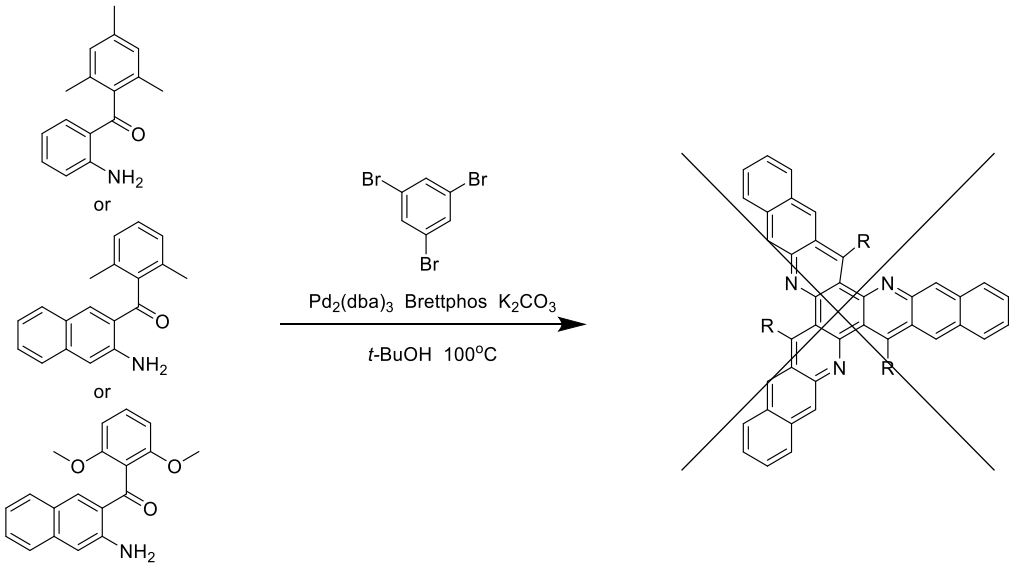


[14]

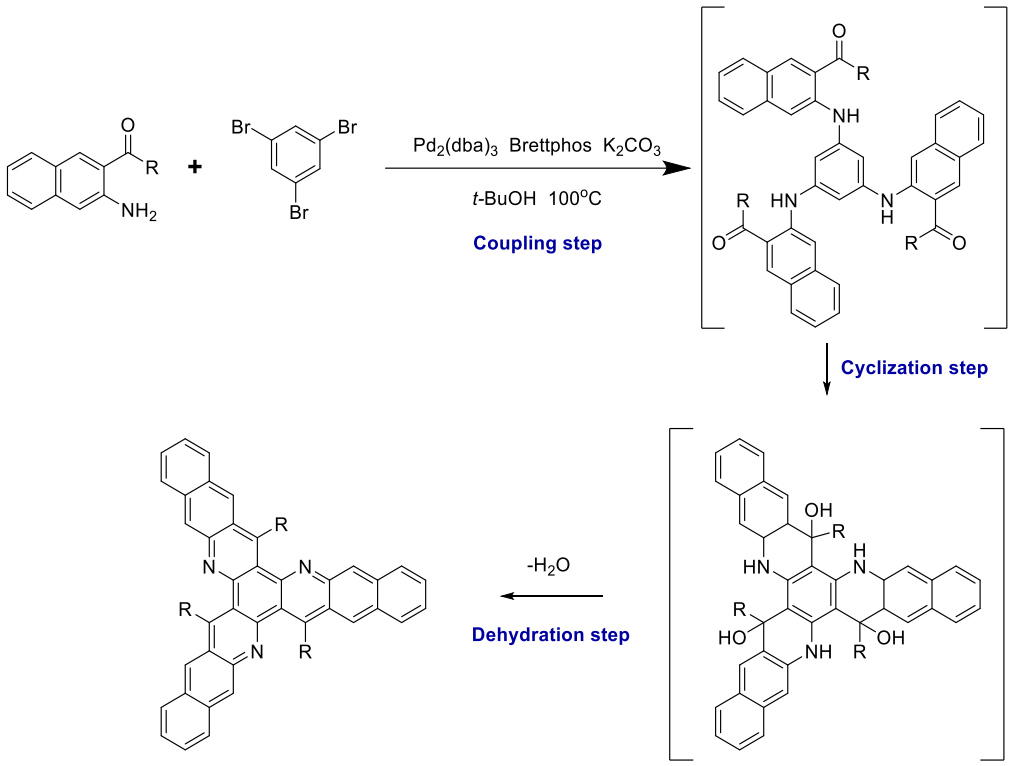


[15]

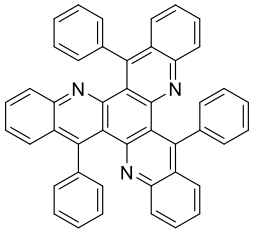
Scheme S-A.3. Synthetic route of TAA derivatives.



Scheme S-A.4. Unsuccessful synthetic route of TAA derivatives.



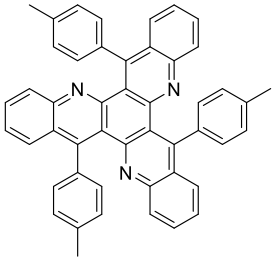
Scheme S-A.5. Plausible steps and intermediates.



1. 6,12,18-triphenyl-5,11,17-triazatrinaphthylene (TAN-Ph)

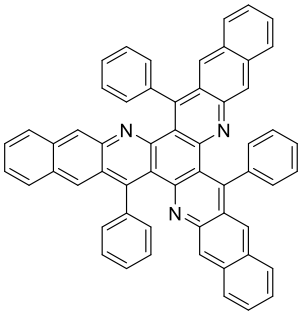
0.94 g (3.00 mmol, 1.0 eq.) of 1,3,5-tribromobenzene, 1.95 g (9.85 mmol, 3.3 eq.) of 2-aminobenzophenone , 2.48 g (17.92 mmol, 6.0 eq.) of potassium carbonate, 0.027 g (0.03 mmol, 0.01 eq.) of $Pd_2(dba)_3$ and 0.048 g (0.09 mmol, 0.03 eq.) of BrettPhos were added into a dry round-bottom flask. Then, 30 mL *t*-butanol were added into the flask. The mixture was stirred at reflux for 72 hours under nitrogen by an aluminium heating block. After cooling to room temperature, the reaction mixture was filtered and the filtrate was dried under reduced pressure. The residue was purified by column chromatography over silica gel using pentane:dichloromethane (4:1) as eluent to yield 1.20 g of light yellow solid (66%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (m, 15H; Ar-H), 7.36 (m, 9H; Ar-H), 7.16 (d, 3H, *J* = 7.9 Hz; Ar-H).
^{13}C NMR (151 MHz, CD_2Cl_2) δ = 150.1, 148.8, 146.7, 142.6, 130.3, 129.9, 129.6, 128.5, 128.2, 127.7, 127.0, 126.8, 123.5
HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{45}H_{28}N_3$ 610.2277; found 610.2272.
Mp: >400°C.
NMR Spectra [1]



2. 6,12,18-tri-p-tolyl-5,11,17-triazatrinaphthylene (TAN-MePh)

0.13 g (0.41 mmol, 1.0 eq.) of 1,3,5-tribromobenzene, 0.31 g (1.47 mmol, 3.3 eq.) of 2-amino-4'-methylbenzophenone , 0.36 g (2.61 mmol, 6.0 eq.) of potassium carbonate, 0.004 g (0.004 mmol, 0.01 eq.) of $Pd_2(dba)_3$ and 0.007 g (0.013 mmol, 0.03 eq.) of BrettPhos were added into a dry round-bottom flask. 20 mL *t*-butanol were added into the flask. The mixture was stirred at reflux for 72 hours under nitrogen by an aluminium heating block. After cooling to room temperature, the reaction mixture was filtered and the filtrate was dried under reduced pressure. The residue was then purified by column chromatography over silica gel with pentane:dichloromethane (7:3) as eluent to give 0.21 g of light yellow solid (74%).
^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.61 (ddd, 3H, *J* = 8.5, 1.4, 0.6 Hz; Ar-H), 7.56 (ddd, 3H, *J* = 8.3, 5.7, 1.4 Hz; Ar-H), 7.37 (m, 9H; Ar-H), 7.22 (d, 6H, *J* = 8.0 Hz; Ar-H), 7.17 (ddd, 3H, *J* = 8.4, 1.3, 0.6 Hz; Ar-H), 2.56 (s, 9H; CH_3).
^{13}C NMR (75 MHz, CD_2Cl_2): *δ* = 150.1, 148.8, 146.6, 139.2, 136.3, 130.0, 129.6, 129.4, 128.9, 128.1, 127.6, 126.7, 123.5, 21.6.
HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{48}H_{34}N_3$ 652.2747; found 652.2737.
Mp: 268-270°C
NMR Spectra [2]



3. *7,15,23-triphenyl-6,14,22-triazatriantrylene (TAA-Ph)*

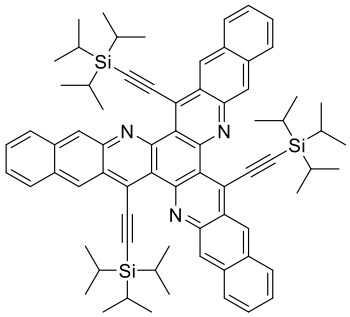
0.096 g (0.30 mmol, 1.0 eq.) of 1,3,5-tribromobenzene, 0.25 g (1.01 mmol, 3.3 eq.) of 2-amino-3-benzoylnaphthalene, 0.25 g (1.83 mmol, 6.0 eq.) of potassium carbonate, 0.003 g (0.0031 mmol, 0.01 eq.) of $Pd_2(dba)_3$ and 0.005 g (0.0092 mmol, 0.03 eq.) of BrettPhos were added into a dry round-bottom flask. Then, 20 mL of *t*-butanol were added into the flask. The mixture was stirred at reflux for 72 hours under nitrogen by an aluminium heating block. After cooling to room temperature, the reaction mixture was filtered and the filtrate was dried under reduced pressure. The residue was purified by column chromatography over silica gel using pentane:dichloromethane (7:3) as eluent to yield 0.20 g of light yellow solid (87%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (s, 3H; Ar-H), 7.94 (d, 3H, *J* = 8.1 Hz; Ar-H), 7.84 (d, 3H, *J* = 8.1 Hz; Ar-H), 7.75 (s, 3H; Ar-H), 7.68 (m, 9H; Ar-H), 7.45 (m, 12H; Ar-H).

^{13}C NMR (150.9 MHz, $C_2D_2Cl_4$): *δ* =150.6, 148.5, 142.6, 141.5, 133.8, 131.7, 129.2, 128.8, 128.2, 128.1, 127.2, 127.1, 126.6, 126.5, 126.4, 125.8, 122.6.

HRMS (FD-TOF) m/z: [M + H]+ Calcd for $C_{57}H_{33}N_3$ 759.2674; found 759.2696.

Mp: >400°C.NMR Spectra [3]



4. *7,15,23-tri(triisopropylsilylethynyl)-6,14,22-triazatriantrylene (TAA-Tips)*

0.081 g (0.26 mmol, 1.0 eq.) of 1,3,5-tribromobenzene, 0.30 g (0.85 mmol, 3.3 eq.) of 1-(3-(2-aminonaphthalenyl)-3-(triisopropylsilyl)-2-propyn-1-one, 0.21 g (1.50 mmol, 6.0 eq.) of potassium carbonate, 0.002 g (0.0026 mmol, 0.01 eq.) of $Pd_2(dba)_3$ and 0.004 g (0.0078 mmol, 0.03 eq.) of BrettPhos were added into a dry round-bottom flask. Then, 20 mL of *t*-butanol were added into the flask. The mixture was stirred at reflux for 72 hours under nitrogen by an aluminium heating block. After cooling to room temperature, the reaction mixture was filtered and the filtrate was dried under reduced pressure. The residue was purified by column chromatography over silica gel with pentane:dichloromethane (4:1) as eluent to give 0.20 g of light yellow solid (74%).

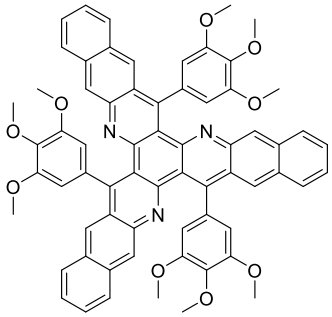
^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.49 (s, 3H; Ar-H), 9.01 (s, 3H; Ar-H), 8.11 (m, 6H; Ar-H), 7.60 (m, 6H; Ar-H), 1.50 (m, 9H; CH), 1.36 (d, 54H, *J* = 6.8 Hz; CH_3).

^{13}C NMR (150.9 MHz, $C_2D_2Cl_4$): *δ* = 149.7, 143.2, 134.2, 132.5, 128.8, 128.0, 127.7, 127.6, 127.3, 127.0, 127.0, 126.6, 125.2, 111.28, 104.6, 19.0, 11.7.

HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{72}H_{82}N_3Si_3$ 1072.5811; found 1072.5802.

Mp: >400°C.

NMR Spectra [4]



5. 7,15,23-tri(3,4,5-trimethoxyphenyl)-6,14,22-triazatriantrylene (TAA-OMePh)

0.34 g (1.08 mmol, 1.0 eq.) of 1,3,5-tribromobenzene, 1.20 g (3.56 mmol, 3.3 eq.) of 2-amino-3-(3,4,5-trimethoxy)benzoylnaphthalene, 0.90 g (6.50 mmol, 6.0 eq.) of potassium carbonate, 0.010 g (0.011 mmol, 0.01 eq.) of $Pd_2(dba)_3$ and 0.018 g (0.032 mmol, 0.03 eq.) of BrettPhos were added into a dry round-bottom flask. Then, 20 mL of *t*-butanol were added into the flask. The mixture was stirred at reflux for 72 hours under nitrogen by an aluminium heating block. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was dried under reduced pressure. The residue was purified by column chromatography over silica gel with dichloromethane:ethyl acetate (19:1) as eluent to give 0.40 g of yellow solid (36%).

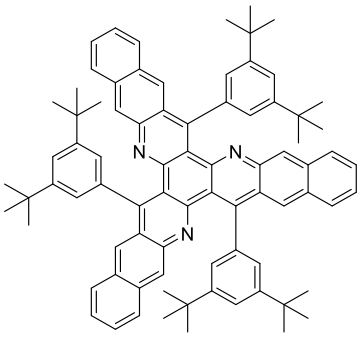
^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.39 (s, 3H; Ar-H), 7.98 (s, 3H; Ar-H), 7.96 (d, 6H, *J* = 7.8 Hz; Ar-H), 7.49 (m, 6H; Ar-H), 6.73 (s, 6H; Ar-H), 4.17 (s, 9H; CH_3), 3.78 (s, 18H; CH_3).

^{13}C NMR (150.9 MHz, $C_2D_2Cl_4$): *δ* =153.4, 150.4, 148.01, 142.8, 137.17, 137.0, 133.9, 131.8, 129.0, 127.8, 127.4, 127.0 (x2 CH, see HSQC), 126.4, 126.0, 122.5, 106.9, 61.4, 56.4.

HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{66}H_{52}O_9N_3$ 1030.3698; found 1030.3664.

Mp: 331-334°C

NMR Spectra [5]



6. 7,15,23-tri(3,5-di-tert-butylphenyl)-6,14,22-triazatriantrylene (TAA-tBuPh)

0.11 g (0.35 mmol, 1.0 eq.) of 1,3,5-tribromobenzene, 0.41 g (1.15 mmol, 3.3 eq.) of (2-amino-3-(3,5-di-tert-butyl)benzoylnaphthalene, 0.29 g (2.10 mmol, 6.0 eq.) of potassium carbonate, 0.0032 g (0.0035 mmol, 0.01 eq.) of $Pd_2(dba)_3$ and 0.0056 g (0.011 mmol, 0.03 eq.) of BrettPhos were added into a dry round-bottom flask. Then, 20 mL of *t*-butanol were added into the flask. The mixture was stirred at reflux for 72 hours under nitrogen by an aluminium heating block. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was dried under reduced pressure. The residue was purified by column chromatography over silica gel with dichloromethane:ethyl acetate (19:1) as eluent to give 0.20 g of yellow solid (53%).

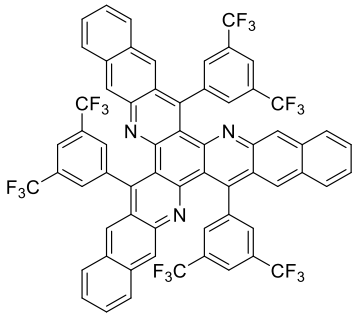
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (s, 3H; Ar-H), 7.88 (t, 6H, *J* = 8.0 Hz; Ar-H), 7.74 (dd, 6H, *J* = 4.7, 3.0 Hz; Ar-H), 7.45 (ddd, 6H, *J* =19.0, 10.8, 6.2 Hz; Ar-H), 7.32 (d, 6H, *J* = 1.7 Hz; Ar-H), 1.38 (s, 54H; CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 151.2, 150.9, 149.9, 143.1, 140.9, 134.1, 132.1, 129.3, 128.1, 127.8, 127.5, 126.8, 126.6, 125.6, 124.1, 123.3, 120.4, 35.2, 31.9

HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{81}H_{82}N_3$ 1096.6503; found 1096.6470.

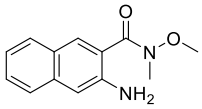
Mp: >400°C.

NMR Spectra [6]



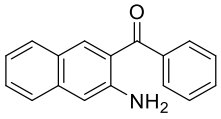
7. 7,15,23-tri(3,5-di-trifluoromethylphenyl)-6,14,22-triazatriantrylene (TAA-CF_3Ph)

0.20 g (0.63 mmol, 1.0 eq.) of 1,3,5-tribromobenzene, 0.80 g (2.09 mmol, 3.3 eq.) of 2-amino-3-(3,5-bis(trifluoromethyl))benzoylnaphthalene, 0.53 g (3.81 mmol, 6.0 eq.) of potassium carbonate, 0.0058 g (0.0063 mmol, 0.01 eq.) of $Pd_2(dba)_3$ and 0.010 g (0.019 mmol, 0.03 eq.) of BrettPhos were added into a dry round-bottom flask. Then, 20 mL of *t*-butanol were added into the flask. The mixture was stirred at reflux for 72 hours under nitrogen by an aluminium heating block. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was dried under reduced pressure. The residue was finally purified by column chromatography over silica gel using dichloromethane:ethyl acetate (19:1) as eluent to give 0.32 g of yellow solid (42%).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (s, 3H; Ar-H), 8.01 (s, 6H; Ar-H), 7.92 (m, 9H; Ar-H), 7.68 (s, 3H; Ar-H), 7.53 (dddd, 6H, *J* = 9.5, 7.9, 6.6, 1.1 Hz; Ar-H).
^{13}C NMR (75 MHz, CD_2Cl_2): δ = 149.6, 145.2, 144.0, 142.4, 134.5, 132.4, 131.9, 131.4, 129.9, 128.7, 127.4, 127.1, 126.8, 126.5, 125.8, 122.7, 120.7.
HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{63}H_{28}N_3F_{18}$ 1168.1990, found 1168.1960.
NMR Spectra [7]



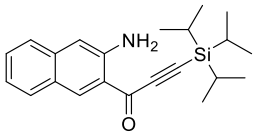
8. 2-amino-N-methoxy-N-methyl-3-naphthamide

1.00 g (5.34 mmol, 1.0 eq.) of 3-amino-2-naphthoic acid was dissolved in 50 mL dichloromethane and cooled down to 0 °C. 1.72 g (6.41 mmol, 1.2 eq.) of diphenyl chlorophosphate were added dropwise and stirred for 10 min. Then, 1.30 g (12.82 mmol, 2.4 eq.) of triethylamine were added and the mixture was stirred for 10 min following by addition of 0.62 g (6.41 mmol, 1.2 eq.) of *N,O*-dimethylhydroxylamine hydrochloride. After overnight stirring and return to room temperature, the reaction mixture was poured into water and extracted with dichloromethane, then the organic phase was collected and the organic solvent was removed under reduced pressure. The residue was finally purified by column chromatography over silica gel with dichloromethane:ethyl acetate (1:1) as eluent to give 0.98 g of brown oil (80%).
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (s, 1H; Ar-H), 7.69 (dd, 1H, *J* = 8.2, 0.6 Hz; Ar-H), 7.57 (d, 1H, *J* = 8.3 Hz; Ar-H), 7.40 (ddd, 1H, *J* = 8.2, 6.8, 1.3 Hz; Ar-H), 7.23 (m, 1H; Ar-H), 7.03 (s, 1H; Ar-H), 4.63 (s, 2H; NH), 3.58 (s, 3H; CH_3), 3.39 (s, 3H; CH_3).
^{13}C NMR (150 MHz, CD_2Cl_2): δ = 169.4, 143.2, 135.58, 129.3, 128.5, 127.7, 126.7, 125.6, 123.0, 110.4, 61.4, 34.2.
HRMS (ESI-Ion trap) m/z: [M + H]+ Calcd for $C_{13}H_{15}N_2O_2$231.1128, found 231.1125.
NMR Spectra [8]



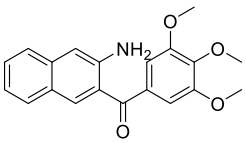
9. 2-amino-3-benzoylnaphthalene

1.30 g (5.91 mmol, 1.0 eq.) of 2-amino-N-methoxy-N-methyl-3-naphthamide were dissolved in 30 mL of freshly distilled THF and cooled to 0 °C. Then, 8.8 mL (17.7 mmol, 3 eq.) of 2 mol/L phenylmagnesium chloride solution were added dropwise to the solution. The mixture was stirred at 0° C for 5 hours, then carefully quenched with 5 mL of water. After THF evaporation under reduced pressure, the residue was dissolved in dichloromethane and washed with water. Then the organic phase was collected and the organic solvent was removed under reduced pressure. The residue was then purified by column chromatography over silica gel using dichloromethane as eluent to give 1.00 g of orange powder (68%).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (s, 1H; Ar-H), 7.80 (m, 2H; Ar-H), 7.53 (m, 6H; Ar-H), 7.19 (ddd, 1H, *J* = 8.1, 6.7, 1.2 Hz; Ar-H), 7.03 (s, 1H; Ar-H), 5.42 (s, 2H; NH).
^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 199.1, 146.1, 139.5, 137.1, 136.1, 132.1, 130.0, 129.3, 129.1, 128.3, 125.8, 125.3, 122.8, 122.7, 110.5.
HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{17}H_{13}NONa$ 270.0889; found 270.0899.
NMR Spectra [9]



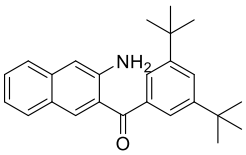
10. 1-(3-(2-aminonaphthalenyl)-3-(triisopropylsilyl)-2-propyn-1-one

0.66 g (3.60 mmol, 3.0 eq.) of tri*iso*propylsilylacetylene were dissolved in 20 mL of freshly distilled THF and cooled down to -78 °C. Then, 2.25 mL (3.60 mmol, 3.0 eq.) of 1.6M n-BuLi solution were added drop by drop. After stirring -78 °C for 2 hours, 0.28 g (1.20 mmol, 1.0 eq.) of 2-amino-N-methoxy-N-methyl-3-naphthamide, dissolved in 20 mL of THF, were added to the mixture drop by drop. Then, the mixture was stirred and was kept at room temperature overnight. After the reaction, 10 mL of water were slowly added to quench the excess of organolithium compounds, and then THF was removed under reduced pressure. 150 mL of water and 150 mL of dichloromethane were added to the residue. The aqueous phase was extracted three times with dichloromethane. The combined solution was concentrated under reduced pressure. The residue was purified by column chromatography over silica gel with dichloromethane as eluent to give 0.31 g of orange solid (65%).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.87 (s, 1H; Ar-H), 7.69 (d, 1H, *J* = 8.3 Hz; Ar-H), 7.52 (d, 1H, *J* = 8.3 Hz; Ar-H), 7.42 (m, 1H; Ar-H), 7.20 (ddd, 1H, *J* = 8.1, 6.7, 1.2 Hz; Ar-H), 6.92 (s, 1H; Ar-H), 5.82 (s, 2H; NH), 1.22 (m, 21H; CH_3CHCH_3).
^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 179.7, 146.3, 138.2, 138.0, 129.9, 129.7, 126.0, 125.3, 122.8, 122.3, 110.1, 103.5, 97.4, 18.8, 11.3.
HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{22}H_{30}NOSi$ 352.2091; found 352.2097.
NMR Spectra [10]



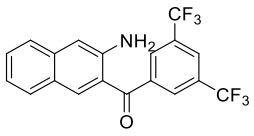
11. 2-amino-3-(3,4,5-trimethoxy)benzoylnaphthalene

3.86 g (15.63 mmol, 3.0 eq.) of 5-bromo-1,2,3-trimethoxybenzene were dissolved in 25 mL of freshly distilled THF and cooled down to -78 °C. Then, 6.25 mL (15.63 mmol, 3.0 eq.) of 2.5 M n-BuLi solution were added drop by drop and the mixture was stirred at -78 °C for 2 hours. After addition of 1.20 g (5.21 mmol, 1.0 eq.) of 2-amino-N-methoxy-N-methyl-3-naphthamide, again dissolved in 20 mL of THF drop by drop, the mixture was stirred and was allowed to rise its temperature to -10 °C in 3 hours. After the reaction, 10 mL of water were carefully added to quench the excess lithium compound and the resulting mixture was concentrated under reduced pressure. Then, 200 mL of water and 200 mL of dichloromethane were added, and the aqueous phase was extracted three times with dichloromethane. The combined solution was concentrated under reduced pressure. The residue was purified by column chromatography over silica gel with dichloromethane:ethyl acetate (9:1) as eluent to give 1.60 g of yellow solid (90%).
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.00 (s, 1H; Ar-H), 7.65 (d, 1H, *J* = 8.2 Hz; Ar-H), 7.58 (d, 1H, *J* = 7.9 Hz; Ar-H), 7.44 (ddd, 1H, *J* = 9.7, 5.5, 2.1 Hz; Ar-H), 7.20 (ddd, 1H, *J* = 8.1, 6.8, 1.2 Hz; Ar-H), 7.05 (s, 3H; Ar-H), 5.42 (s, 2H; NH), 3.96 (s, 3H; CH_3), 3.86 (s, 6H; CH_3).
^{13}C NMR (150.9 MHz, $CDCl_3$): *δ* = 197.9, 153.0, 145.9, 141.9, 137.0, 135.5, 134.4, 129.2, 125.9, 125.4, 123.2, 123.0, 110.5, 107.7, 61.1, 56.5.
HRMS (ESI-Ion trap) m/z: [M + H]+ Calcd for $C_{20}H_{20}NO_4$ 338.1387; found 338.1378.
NMR Spectra [11]



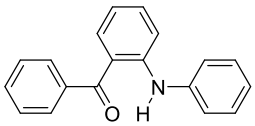
12. 2-amino-3-(3,5-di-tert-butyl)benzoylnaphthalene

3.51 g (13.03 mmol, 3.0 eq.) of 1-bromo-3,5-di-*tert*-butylbenzene were dissolved in 25 mL of freshly distilled THF and cooled down to -78 °C. Then, 5.21 mL (13.03 mmol, 3.0 eq.) of 2.5 M n-BuLi solution were added drop by drop, and the mixture was stirred at -78 °C for 2 hours. 1.00 g (4.34 mmol, 1.0 eq.) of 2-amino-N-methoxy-N-methyl-3-naphthamide dissolved in 20 mL of THF were then added to the mixture drop by drop. The mixture was stirred and allowed to heat to -10 °C in 3 hours. After the reaction, 10 mL of water was slowly added to quench the excess of lithium reagent, and then THF was removed under reduced pressure. 200 mL of water and 200 mL of dichloromethane were added, and the aqueous phase was extracted three times with dichloromethane. The combined solution was concentrated under reduced pressure. The residue was purified by column chromatography over silica gel with cyclohexane:ethyl acetate (7:3) as eluent to give 0.4 g of yellow solid (26%).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (s, 1H; Ar-H), 7.70 (m, 1H; Ar-H), 7.67 (d, 2H, *J* = 1.8 Hz; Ar-H), 7.60 (dd, 2H, *J* =11.1, 8.3 Hz; Ar-H), 7.44 (ddd, 1H, *J* = 8.3, 6.8, 1.2 Hz; Ar-H), 7.19 (ddd, 1H, *J* = 8.1, 6.8, 1.2 Hz; Ar-H), 7.05 (s, 1H; Ar-H), 5.56 (s, 2H; NH), 1.39 (s, 18H; CH_3).
^{13}C NMR (75 MHz, $CDCl_3$): *δ* =199.9, 150.9, 146.3, 138.8, 137.0, 136.4, 129.2, 129.1, 126.2, 125.9, 125.3, 124.6, 123.1, 122.8, 110.4, 35.1, 31.5.
HRMS (ESI-Ion trap) m/z: [M + H]+ Calcd for $C_{25}H_{30}NO$ 360.2322; found 360.2314.
NMR Spectra [12]



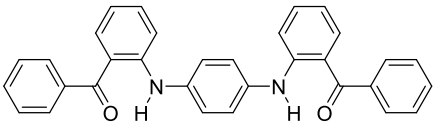
13. 2-amino-3-(3,5-bis(trifluoromethyl))benzoylnaphthalene

3.82 g (13.03 mmol, 3.0 eq.) of 1-bromo-3,5-bis(trifluoromethyl)benzene were dissolved in 25 mL of freshly distilled THF and cooled down to -78 °C. Then, 5.21 mL (13.03 mmol, 3.0 eq.) of 2.5 M n-BuLi solution were added drop by drop and the mixture was stirred at -78 °C for 2 hours. After addition drop by drop of 1.00 g (4.34 mmol, 1.0 eq.) of 2-amino-N-methoxy-N-methyl-3-naphthamide dissolved in 20 mL of THF, the mixture was stirred and was allowed to heat to -10 °C in 3 hours. After the reaction, 10 mL of water were carefully added to quench the excess lithium compound, and then THF was removed under reduced pressure. 200 mL of water and 200 mL of dichloromethane were added, and the aqueous phase was extracted three times with dichloromethane. The combined solution was concentrated under reduced pressure and the residue was purified by column chromatography over silica gel with dichloromethane:cycohexane (6:4) as eluent to give 0.6 g of yellow solid (36%).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20 (s, 2H; Ar-H), 8.10 (s, 1H; Ar-H), 7.85 (s, 1H; Ar-H), 7.60 (m, 2H; Ar-H), 7.47 (t, 1H, *J* = 7.6 Hz; Ar-H), 7.22 (t, 1H, *J* = 7.5 Hz; Ar-H), 7.14 (s, 1H; Ar-H), 5.68 (s, 2H; NH).
^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 195.89, 146.27,141.56, 137.76, 136.27, 132.14 (q, $^{2}J_{(C-H)}$ = 32 Hz), 130.02, 129.73 (q, $^{3}J_{(C-H)}$ = 4 Hz), 129.5, 125.8, 125.5, 125.3 (sextuplet, $^{3}J_{(C-H)}$ = 4 Hz), 123.3, 123.1 (q, $^{1}J_{(C-H)}$ = 273 Hz), 121.2, 111.1.
HRMS (ESI-Ion trap) m/z: [M + H]+ Calcd for $C_{19}H_{12}F_6NO$ 384.0818; found 384.0810.
NMR Spectra [13]



14. 2-Phenylaminobenzophenone

1.00 g (6.37 mmol, 1 eq.) of bromobenzene, 1.49 g (7.54 mmol, 1.2 eq.) of 2-Aminobenzophenone, 1.76 g (12.7 mmol, 2.0 eq.) of potassium carbonate, 0.020 g (0.022 mmol, 0.0035 eq.) of $Pd_2(dba)_3$ and 0.030 g (0.056 mmol, 0.0088 eq.) of BrettPhos were added into a dry round-bottom flask. Then, 20 mL of *t*-butanol were added into the flask. The mixture was stirred at reflux for 72 hours under nitrogen by an aluminium heating block. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was dried under reduced pressure. The residue was finally purified by column chromatography over silica gel using dichloromethane:pentane (1:3) as eluent to give 1.29 g of yellow solid (74%).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.18 (s, 1H; N-H), 7.74 (m, 2H), 7.54 (m, 4H), 7.36 (m, 6H), 7.12 (m, 1H), 6.73 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$): *δ* =199.2, 148.1, 140.6, 139.9, 135.1, 134.3, 131.5, 129.5, 129.5, 128.2, 123.6, 122.3, 119.8, 116.7, 114.7.
HRMS (ESI-Ion trap) m/z: [M + Na]+ Calcd for $C_{19}H_{15}NONa$ 296.1046, found 296.1034.
NMR Spectra [14]



15. *[1,4-Phenylenebis(imino-2,1-phenylene)]bis(phenylmethanone)*

0.76 g (3.2 mmol, 1 eq.) of 1,4-dibromobenzene, 1.49 g (7.54 mmol, 2.4 eq.) of 2-Aminobenzophenone, 1.76 g (12.7 mmol, 4.0 eq.) of potassium carbonate, 0.020 g (0.022 mmol, 0.007 eq.) of $Pd_2(dba)_3$ and 0.030 g (0.056 mmol, 0.017 eq.) of BrettPhos were added into a dry round-bottom flask. Then, 20 mL of *t*-butanol were added into the flask. The mixture was stirred at reflux for 72 hours under nitrogen by an aluminium heating block. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was dried under reduced pressure. The residue was finally purified by column chromatography over silica gel using dichloromethane:pentane (1:1) as eluent to give 1.49 g of yellow solid (99%).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.11 (s, 2H; N-H), 7.72 (m, 4H), 7.52 (m, 8H), 7.32 (m, 8H), 6.70 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.3, 148.7, 140.0, 136.5, 135.2, 134.5, 131.4, 129.5, 128.3, 124.0, 119.5, 116.4, 114.6.
HRMS (ESI-Ion trap) m/z: [M + Na]+ Calcd for $C_{32}H_{24}N_2O_2Na$ 491.1730, found 491.1718.
NMR Spectra [15]

B. Electronic properties

UV-visible absorption spectra in solution were recorded with a UV-1650PC Shimadzu spectrophotometer. Cyclic voltammetry analyses were performed using a potentiostat/galvanostat Autolab PGSTAT100 and a three-electrode device. In the CV medium, the ferrocene/ferrocenium (Fc/Fc^+) couple has always been measured at 0,6 V vs $Ag/AgCl_{sat}$ [2]. Taking into account the NHE formal potential on the fermi level (-4.75 eV) and our reference electrode potential against NHE potential (0.2 V), LUMO has been estimated following the equation 1 and the half-wave reduction potential $E_{½}^{red}$ vs Ag/AgCl:[3].

$$LUMO = -4.95 - E_{½}^{red}\ [eV] \qquad (1)$$

where $E_{½}^{red}$ is the half-wave reduction potential.

To compare, C_{60}/C_{60}^- potential in THF is -0.23V vs. Ag/AgCl[4].

Table S-B.1. Optical, electrochemical and electronic properties of TAN and TAA derivatives

Compounds	λ_{abs} (nm)[a]	E_g^{opt} (eV)[b]	$E_{½}^{red}$ (V)[c]	LUMO (eV)[d]	HOMO (eV)[e]	$LUMO_{calc}$ (eV)[f]	$HOMO_{calc}$ (eV)[f]	λ_{calc} (nm)[g]
TAN-Ph	232, 298	3.10	-1.47	-3.48	-6.58	-2.12	-5.99	284
TAN-MePh	233, 297	3.05	-1.49	-3.46	-6.51	-2.10	-5.88	284
TAA-Ph	278, 351	2.56	-1.11	-3.83	-6.39	-2.56	-5.39	330
TAA-Tips	286, 371	2.38	-0.80	-4.15	-6.53	-2.86	-5.44	357
TAA-OMePh	278, 354	2.53	-1.15	-3.80	-6.33	-2.56	-5.39	330
TAA-tBuPh	279, 352	2.55	-1.21	-3.74	-6.29	-2.50	-5.36	331
TAA-CF_3Ph	280, 353	2.56	-0.88	-4.07	-6.63	-2.76	-5.55	334

a: Two main absorption features for each compound. b: Optical bandgap calculated from the threshold of UV-vis absorption spectrum. c: Half-wave reduction potential vs Ag/AgCl. d: LUMO energy level calculated from $E_{½}^{red}$ using equation 1. e: HOMO energy level estimated from LUMO energy and optical bandgap values. f: HOMO and LUMO energy level calculated at the B3LYP/6-31G(d) level in THF. g: Maximum absorption wavelength calculated at the CAM-B3LYP/6-311G(d) level in DCM.

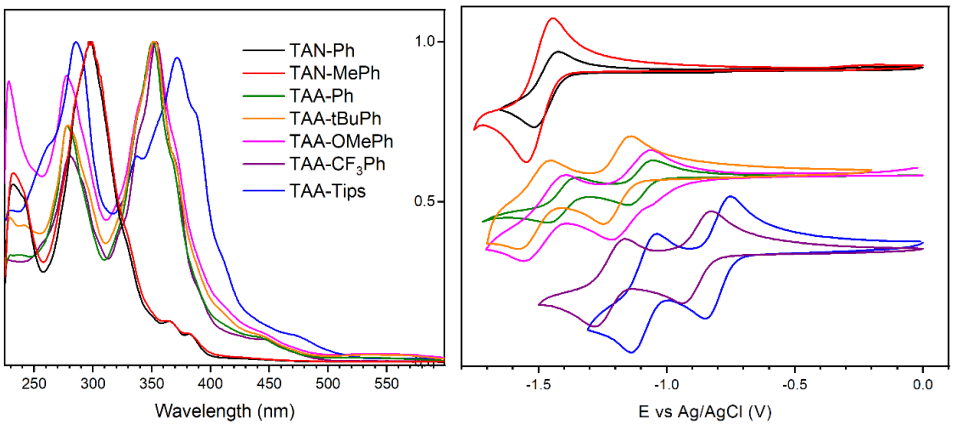


Figure S-B.1. Normalized UV-vis spectra in DCM (top) and cyclic voltam-mograms in THF (bottom) of TANs and TAAs. Cyclic volt-ammograms were recorded at 0.1 V/s in 1 mM THF solution (0.25 M Bu4NPF6, glassy carbon as working electrode, Ag/AgCl as reference electrode).

C. Thermal properties

Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were performed by using a STA 449 F5 Jupiter Simultaneous Thermal Analyzer (TG-DTG, DTA, DSC) from NETZSCH under an argon flow at a heating rate of 20 $K.min^{-1}$. The point of 5% weight loss was used to determine the temperature of thermal decomposition (Td). The different thermograms are depicted in **Figure S-C.1**.

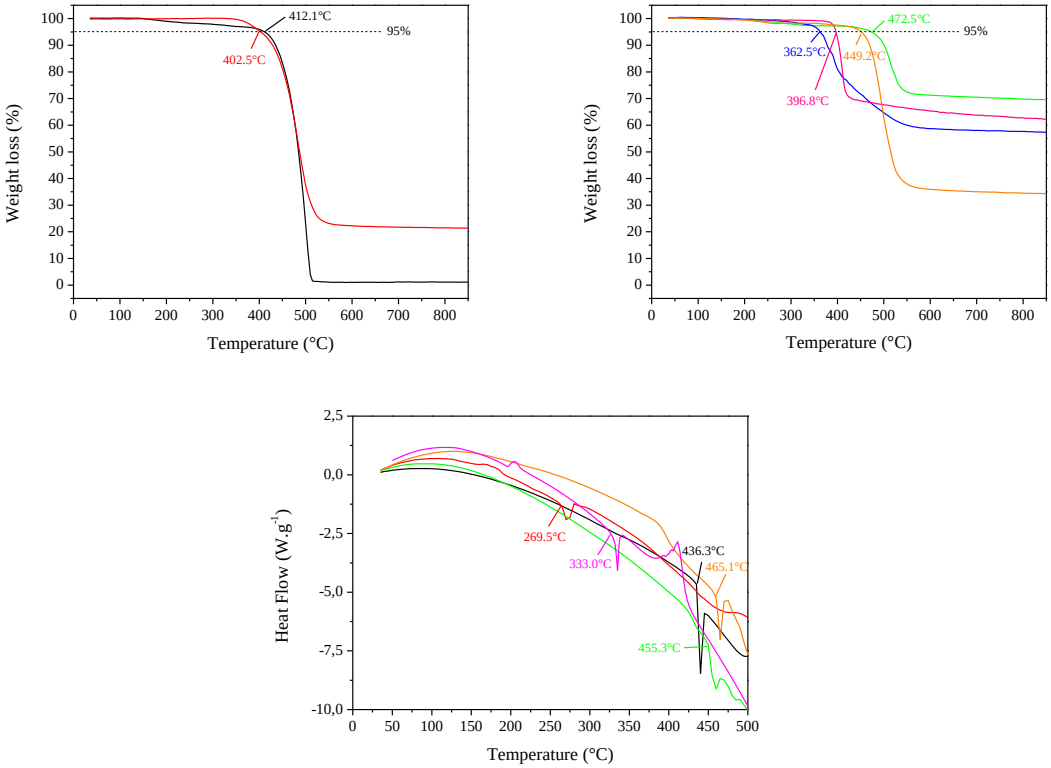


Figure S-C.1. TGA (A,B) and DSC (C) curves for TAN-Ph (black), TAN-MePh (red), TAA-Ph (green), TAA-Tips (blue), TAA-OMePh (pink) and TAA-tBuPh (Orange).

TAN-Ph and TAN-MePh showed high thermal stability with decomposition temperature (Td) of 412°C and 402°C, respectively, the decomposition process occurring in a steep single stage. Moreover, TAA-Ph and TAA-tBuPh appeared to be even more thermally stable with decomposition temperature of 449°C and 472°C, respectively, and, once again, through a steep single decomposition stage. This suggests that the introduction of azaanthrylene arms has a beneficial effect on the thermal stability. Nonetheless, the nature of the branches also strongly affects the thermal stability. Thus TAA-OMePh and TAA-Tips are much less stable, with decomposition temperature of 397°C and 362°C, respectively, and a decomposition pathway involving at least two different steps in the last case.

On the other hand, DSC curves of TAA-OMePh and TAA-Tips exhibited no feature of any phase transition before the decomposition stage. By contrast, the DSC traces of TAN-MePh and TAA-OMePh showed an endothermic feature at 269°C (H = - 54 $J.g^{-1}$) and 333°C (H = -34 $J.g^{-1}$), respectively, that can be unambiguously assigned to melting since this temperature is far below the decomposition temperature. Similar features were also found for TAN-Ph, TAA-Ph and TAA-tBuPh at 436°C (H = - 92 $J.g^{-1}$), 455°C (H = - 44 $J.g^{-1}$) and 465°C (H = - 86 $J.g^{-1}$) indicating that melting took place just before the decomposition process.

D. Crystallographic data

Single crystals of all the compounds were obtained by solution diffusion method using dichloromethane and methanol as solvents. Crystallographic data were acquired at CESAMO (ISM, UMR 5255 CNRS) on a Bruker APEX 2 DUO. A single crystal was mounted and immersed in a stream of nitrogen gas [T = 150(2) K]. Data were collected, using a microfocus sealed tube of Mo Kα radiation (k = 0.71073 Å) on a KappaCCD diffractometer. Data collection and cell refinement were performed using APEX2 2013.10-0 (Bruker AXS Inc.), and SAINT v8.34A (Bruker AXS Inc.). Data reduction was performed using SAINT v8.34A (Bruker AXS Inc.). Correction for absorption was performed using multi-scan integration as included in SADABS V2012/1 (Bruker AXS). Structure solutions were found by charge flipping methods (SUPERFLIP (Palatinus & Chapuis, 2007) EDMA (Palatinus et al., 2012)) and refined with (SHELXL) (G.M. Sheldrick , A short history of SHELX, Acta Crystallographica Section A, 64 (2008), pp. 112–122). Crystallographic data of all the compounds are presented in **table S-D.1**. and **table S-D.2**.

Table S-D.1. Crystallographic parameters for **TAN-Ph**, **TAN-MePh** and **TAA-Ph**.

	TAN-Ph	TAN-MePh	TAA-Ph
Chemical formula	C_{45} H_{27} N_3	$C_{48}H_{33}N_3$	C_{38} H_{22} N_2
Formula weight	609.69	651.77	506.57
Crystal system	Triclinic	Triclinic	Trigonal
Space group	P -1	P -1	R 3 :H
a / Å	11.4220(5)	11.2751(10)	26.890(2)
b / Å	11.8638(6)	12.3505(11)	26.890(2)
c / Å	13.6400(7)	13.4070(12)	9.3703(8)
α/ º	115.445(2)	99.461(3)	90
β/ º	98.835(2)	92.650(3)	90
γ/ º	107.484(2)	108.041(3)	120
V / Å^3	1503.75(13)	1741.6(3)	5867.6(10)
Z	2	2	9
Dcalc /mg·m^{-3}	1.347	1.243	1.290
Temperature / K	120	120	120
No. of reflections measured	46762	44512	11458
No. of independent reflections	5703	8436	5457
Residuals: R	0.0406	0.0486	0.0559
Residuals: wR^2	0.1065	0.1159	0.0995
Goodness of fit indicator	1.009	1.026	1.006

Table S-D.2. Crystallographic parameters for **TAA-Tips**, **TAA-OMe-Ph** and **TAA-tBuPh**.

	TAA-Tips	TAA-OMePh	TAA-tBuPh
Chemical formula	C_{73} H_{83} Cl_2 N_3 Si_3	C_{66} H_{51} N_3 O_9	C_{81} H_{81} N_3
Formula weight	1157.59	1030.09	1096.48
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P 21/n	P -1	P -1
a / Å	18.2212(10)	11.2358(6)	14.2405(16)
b / Å	10.4445(5)	15.7124(9)	17.0268(18)
c / Å	33.2572(19)	16.9610(10)	17.130(2)
α/ º	90	68.562(2)	118.098(3)
β/ º	91.409(2)	84.545(2)	99.825(4)
γ/ º	90	75.900(2)	99.093(3)
V / Å^3	6327.3(6)	2703.1(3)	3471.8(7)
Z	4	2	2
*D*calc /mg·m^{-3}	1.215	1.266	1.049
Temperature / K	120	120	120
No. of reflections measured	98701	89514	101981
No. of independent reflections	13996	12760	13903
Residuals: R	0.0649	0.0496	0.0942
Residuals: wR^2	0.1747	0.1164	0.2703
Goodness of fit indicator	1.055	1.009	1.022

1. *Geometrical parameters for each individual molecules*

All molecular structures exhibit twists and bendings in single crystals. Bending and twisting angles are summarized in **table S-D.3**.

Table S-D.3. Molecular structural parameters deduced from XRD.

	Twist angle (°)[a]	Distance (Å)[b]	Bending angle (°)[c]	Bending radius (Å)[d]
TAN-Ph	19, 11, 4	0.73, 0.3, 0.28	-8.7, 3.5, 3.3	16, 40, 42
TAN-MePh	24, 8, 8	0.73, 0.65, 0.02	-8.7, 7.7, 0.2	16, 18, 821
TAA-Ph	13, 13, 13 11, 11, 11	0.12, 0.12, 0.12 0.27, 0.27, 0.27	1.4, 1.4, 1.4 3.2, 3.2, 3.2	101, 101, 101 43, 43, 43
TAA-Tips	13, 13, 10	0.48, 0.39, 0.17	-5.7, 4.6, 2.0	24, 30, 70
TAA-OMePh	27, 25, 3	0.87, 0.32, 0.32	-10.3, 3.8, 3.8	14, 36, 36
TAA-tBuPh	5, 3, 3	0.2, 0.17, 0.07	2.4, 2.0, 0.8	57, 70, 180
TAA-CF_3Ph	/	/	/	/

a: Twist angles between the mean plane of the central ring and the mean plane of each branch; b: distances from the centroid of the third phenyl ring and the mean plane of central ring; c: Bending angles between the mean plane of the central ring and the line connecting the centroids of third and central phenyl rings. d: Bending radius (Å) calculated as the radius of circle connecting the centroid of the first and third ring and tangent to the mean plane of the first ring.

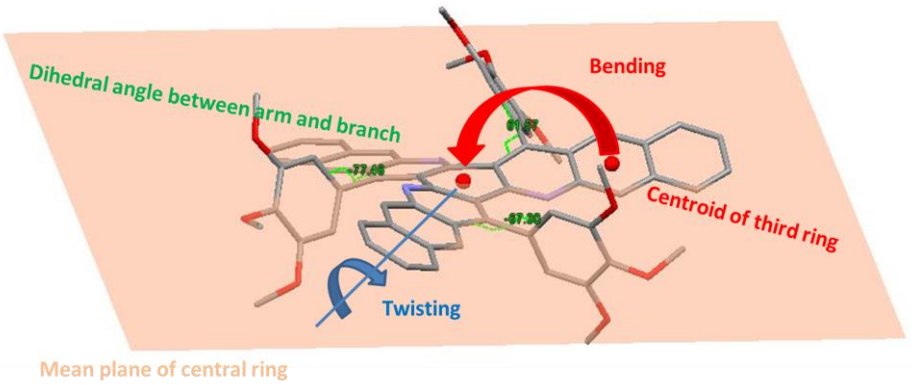


Figure S-D.1. Graphical representation of geometrical parameters for a single molecule listed in **Table S-D.3.**

2. *Molecules and their closer neighbors in packing*

Figures showing the molecular packing in single crystals are reported below. Only one geometrical conformation exists for **TAN-Ph**, **TAN-MePh**, **TAA-Tips**, **TAA-OMePh** and **TAA-tBuPh**. The reference molecule is dark red colored. Intermolecular contacts between this molecule and its first neighbors are shown in light blue. Molecule **TAA-Ph** exhibits two different conformations in the single crystal, colored in red and blue in the Figures below.
Close contacts between carbon atoms belonging to neighboring molecules were determined using the following criteria: a distance threshold of 2*VdW radius + 0.2 Å was applied for **TAN-Ph**, **TAN-MePh**, **TAA-Tips** and **TAA-tBuPh**, and of 2*VdW radius + 0.3 Å for **TAA-Ph** and **TAA-OMePh**. The color code is defined as follows: pink molecules can be deduced from the reference molecule (in red) by a translation operation. Molecules in light green are deduced from the reference one by an inversion operation. In **TAA-Ph**, two non-equivalent geometries are shown in red and blue for reference molecules. Then, light blue molecules correspond to the blue one after a translation operation. In all Figures, lateral substituents (branches) and hydrogen atoms have been hidden for clarity, as well as contacts from these atoms. For each compound, crystalline packing is shown normal to the three lattice planes *ab*, *bc* and *ac*.

TAN-Ph

Description: two arms of the reference molecule are connected via extended □π-stacking with two arms of two inversed molecules, suggesting one efficient charge transport pathway in the □π-stacking direction.

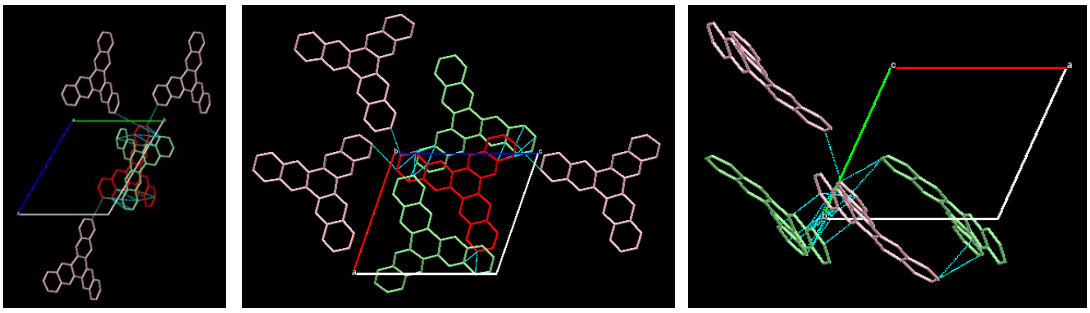


Figure S-D.2. Following three planes (100), (010) and (001), a molecule in red is represented with their closer neighbors (Symmetry operation are an inversion with the light green neighbors and identity with the light red neighbors). Blue lines correspond to C-C contacts with a distance smaller than 3.6 Å.

TAN-MePh

Description: two arms of the reference are connected via extended □π-stacking with two arms of two inversed molecules, suggesting one efficient charge transport pathway in the □π-stacking direction.

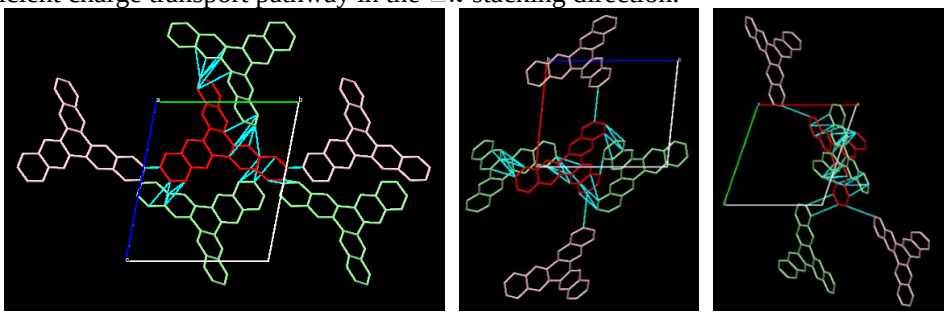


Figure S-D.3. Following three planes (100), (010) and (001), a molecule in red is represented with their closer neighbors (Symmetry operation are an inversion with the light green neighbors and identity with the light red neighbors). Blue lines correspond to C-C contacts with a distance smaller than 3.6 Å.

TAA-Ph

Arms of the two reference non-equivalent molecules (red and blue) are connected via small π-π stacking with neighbouring molecules in all directions, suggesting several but not particularly efficient charge transport pathway.

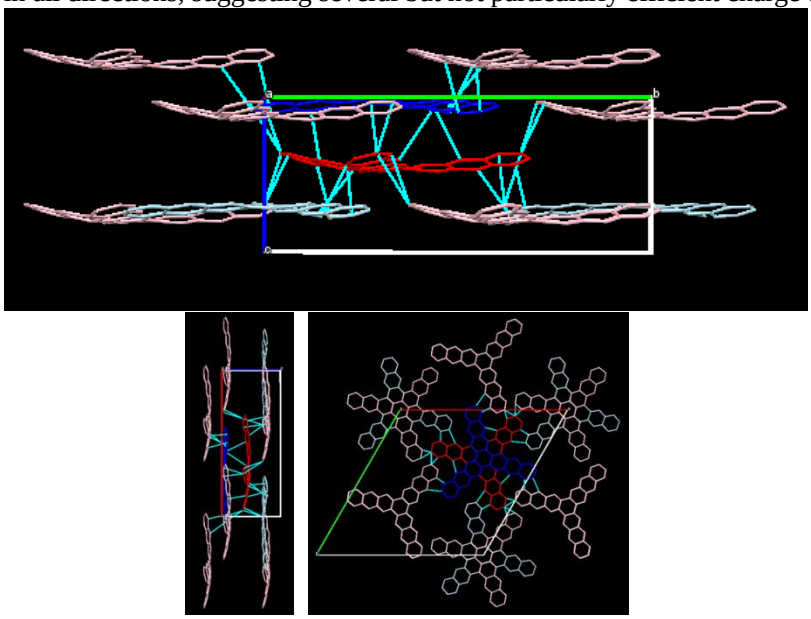


Figure S-D.4. Following three planes (100), (010) and (001), two molecules with geometry called A and B are collored in red and blue respectivly. Their closer neighbors are represented (neighbors in light red and in light blue follow the A and B geometry,respectivly). Blue lines correspond to C-C contacts with a distance smaller than 3.7 Å.

TAA-Tips

One arm of one molecule is connected via extended π-π stacking with one arm of two inversed molecules, suggesting one efficient charge transport pathway in the π-stacking direction.

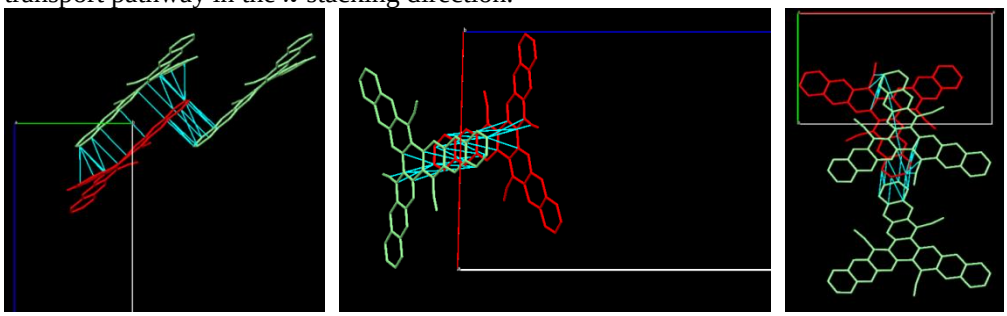


Figure S-D.5. Following three planes (100), (010) and (001), a molecule in red is represented with their closer neighbors (Symmetry operation are an inversion with the light green neighbors). Blue lines correspond to C-C contacts with a distance smaller than 3.6 Å.

TAA-OMePh

One arm of one molecule is connected via extended π-π stacking with one arm of three inversed molecules; suggesting 2D charge transport pathway within molecular layers.

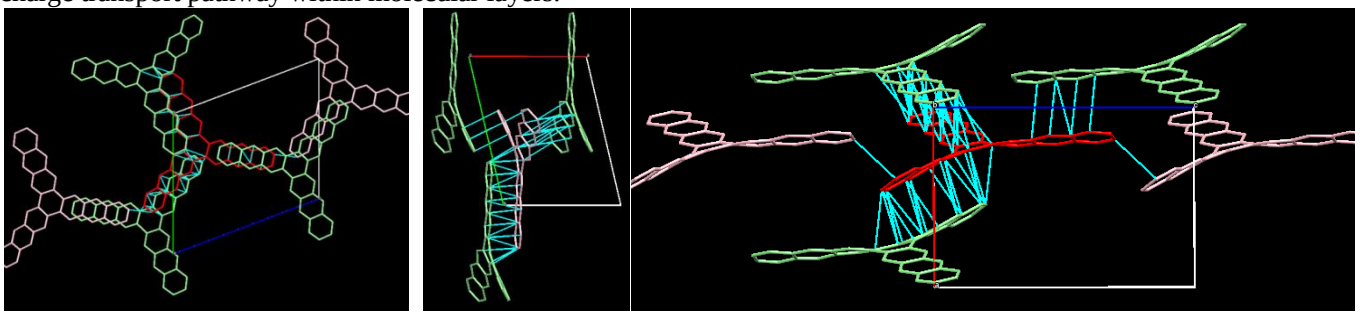


Figure S-D.6.: Following three planes (100), (010) and (001), a molecule in red is represented with their closer neighbors (Symmetry operation are an inversion with the light green neighbors and identity with the light red neighbors). Blue lines correspond to C-C contacts with a distance smaller than 3.7 Å.

TAA-tBuPh

No π-π interactions between molecules, suggesting no charge transport.

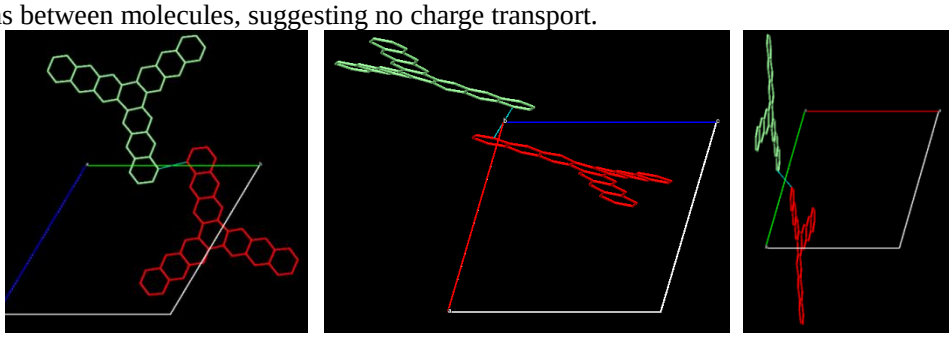
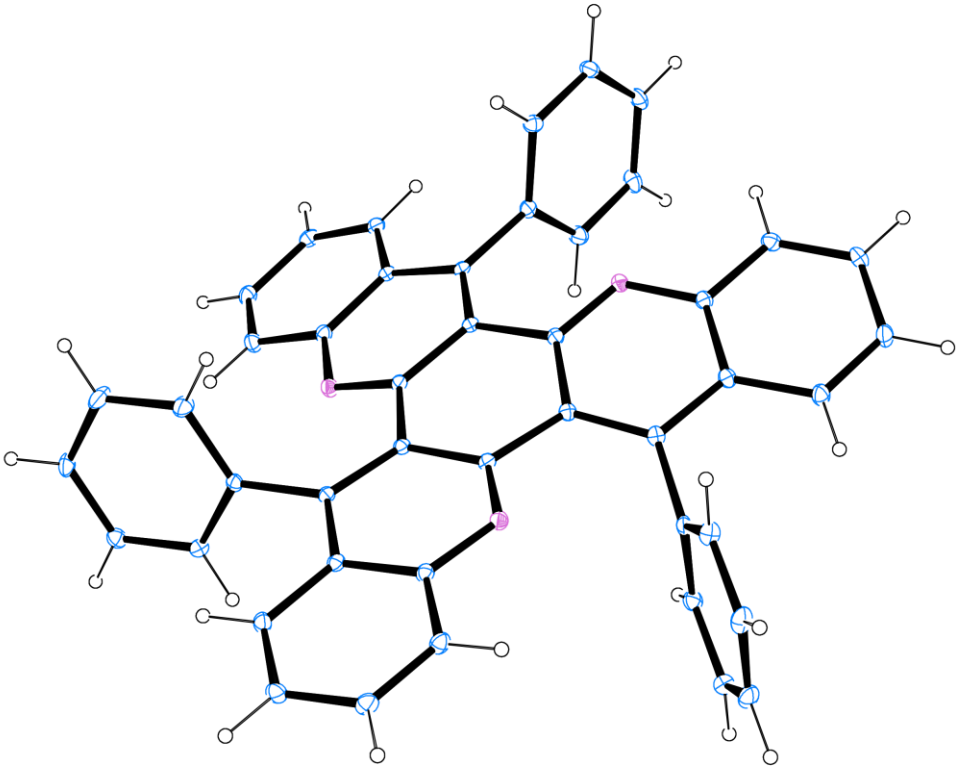


Figure S-D.7. Following three planes (100), (010) and (001), a molecule in red is represented with their closer neighbors (Symmetry operation are an inversion with the light green neighbors). Blue lines correspond to C-C contacts with a distance smaller than 3.6 Å.

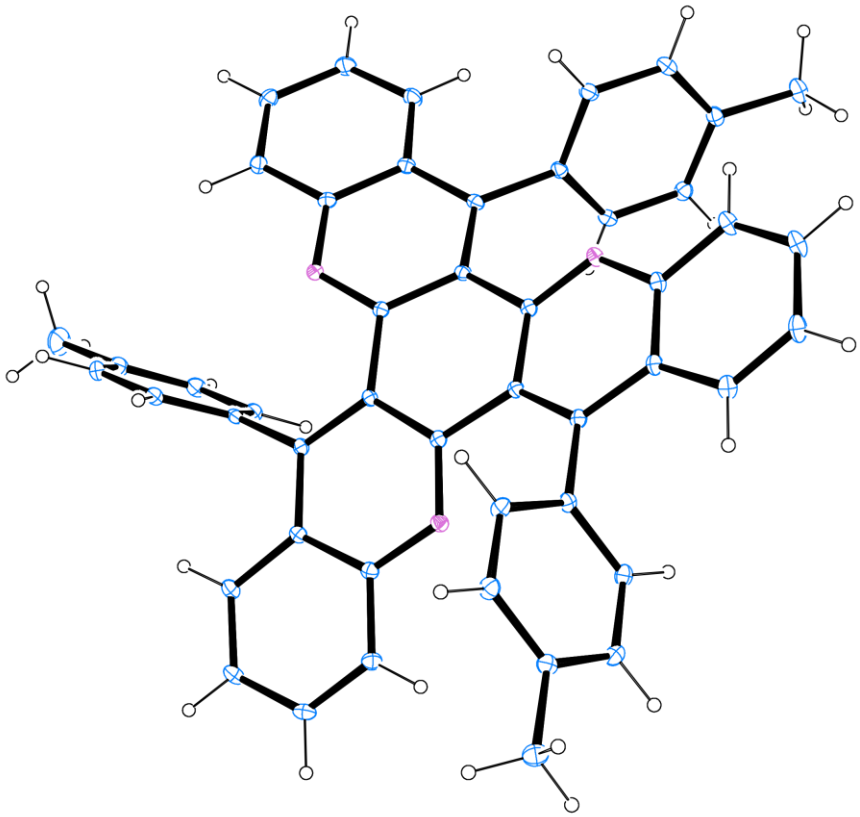
3. *Thermal ellipsoid plot*

Figures showing the atomic displacements in each chemical structures are reported below. The ellipsoid contour probability has been set at 20 %.

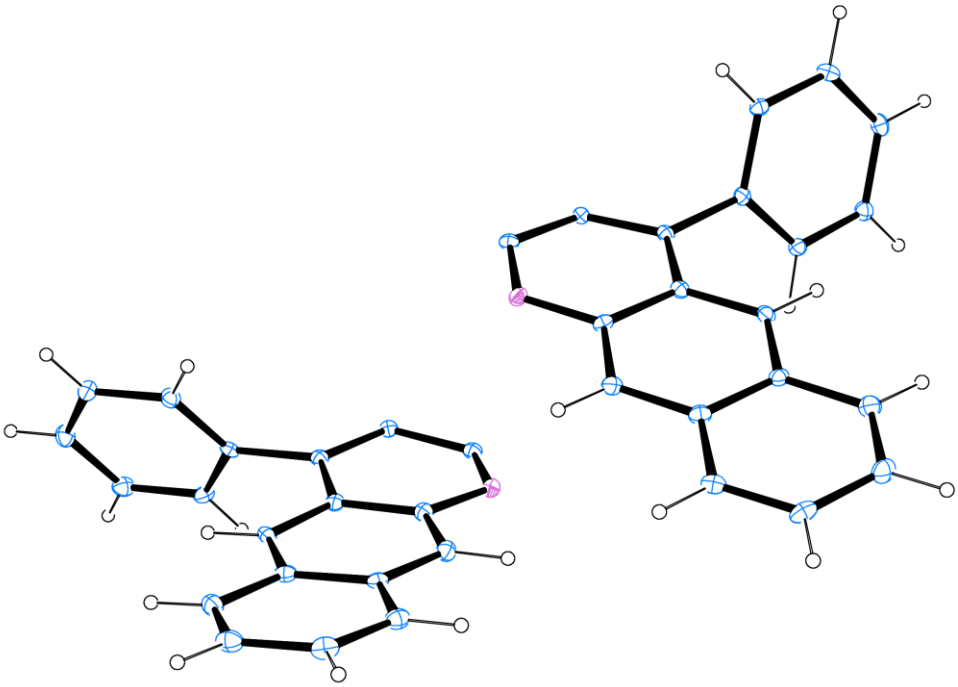
TAN-Ph



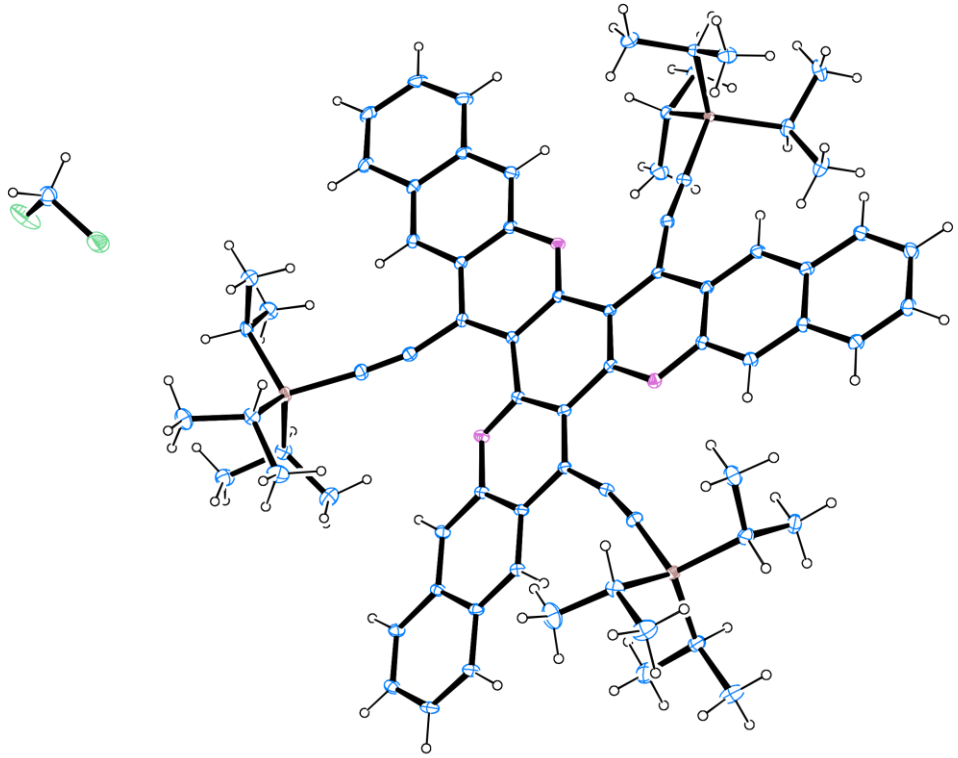
TAN-MePh



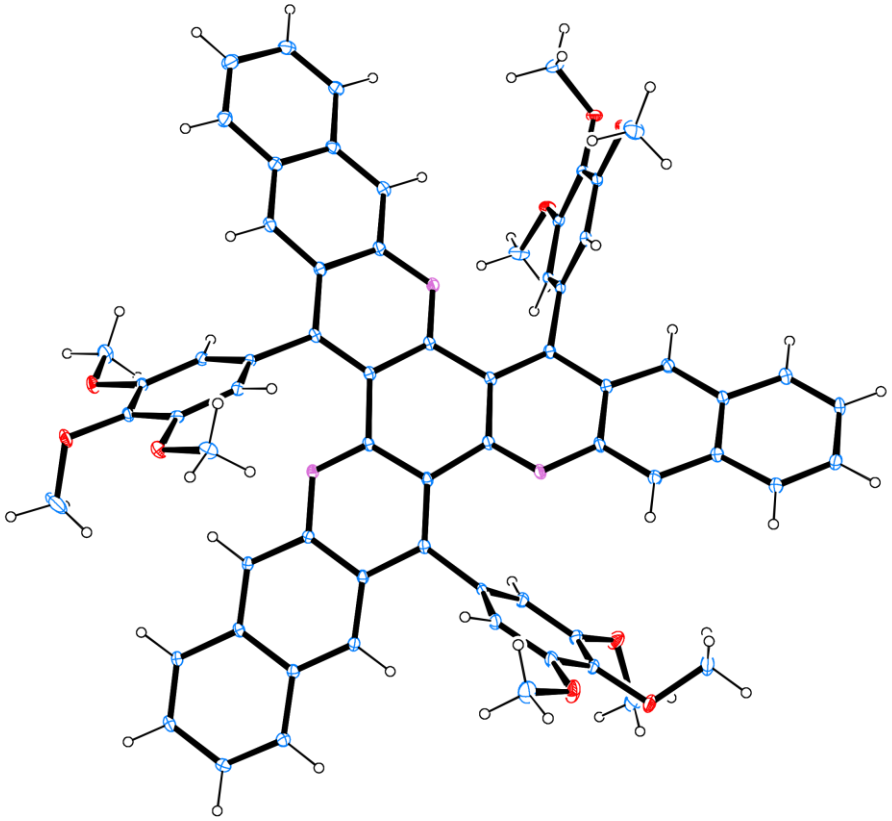
TAA-Ph



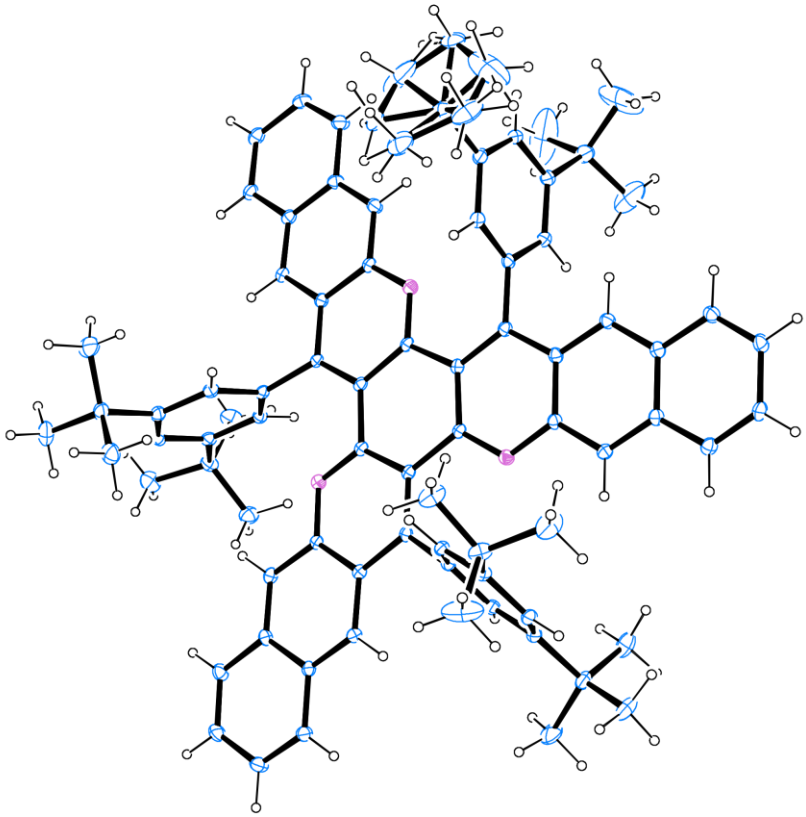
TAA-Tips



TAA-OMePh



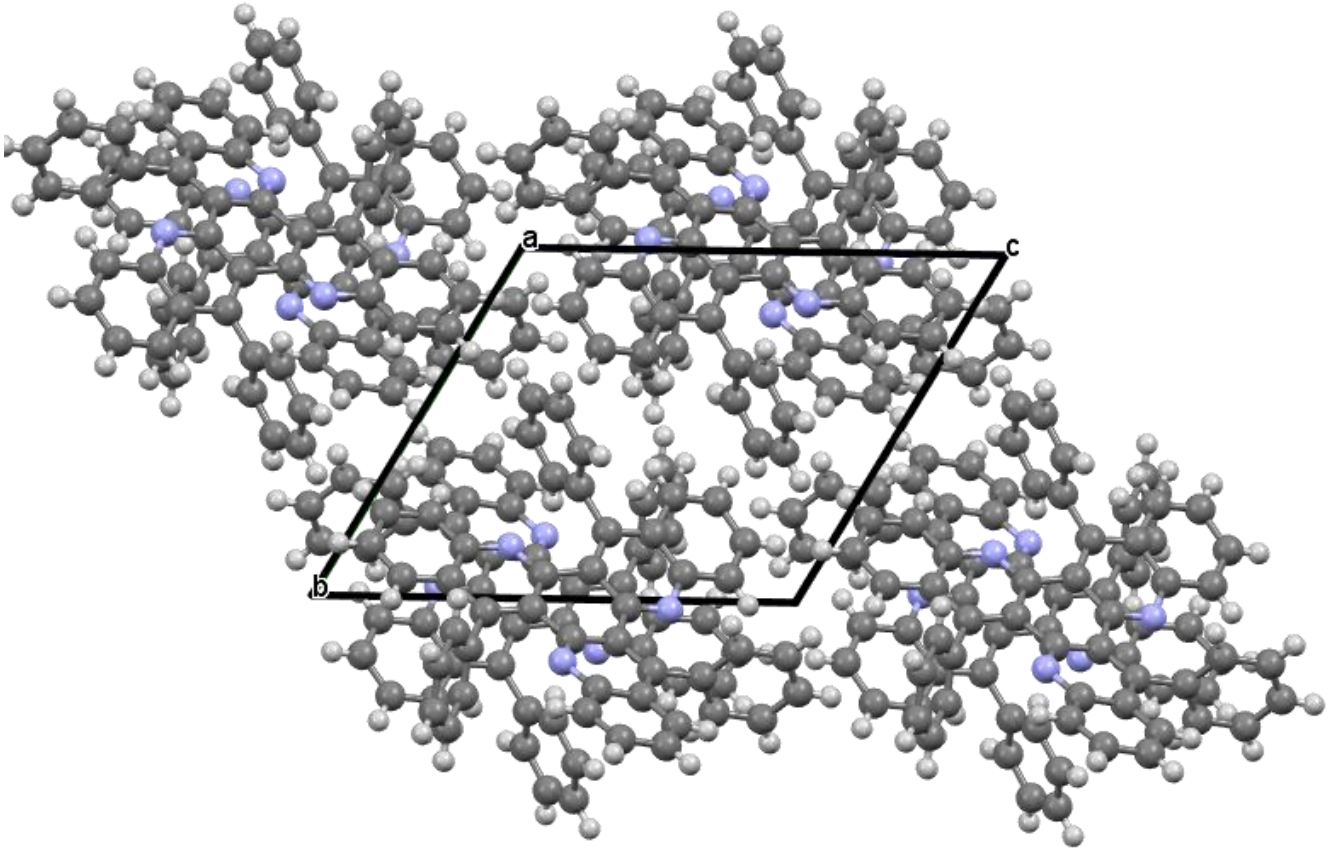
TAA-tBuPh

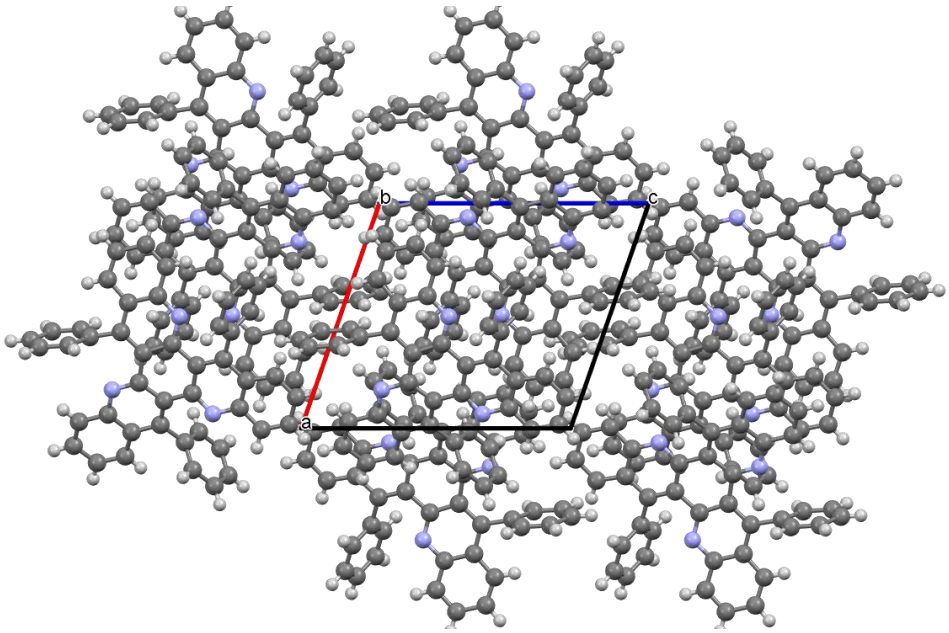


4. *Representation of packing with whole molecular structure*

Figures below show the complete molecular structures of all molecules whom any atom is included in a unit cell.

TAN-Ph





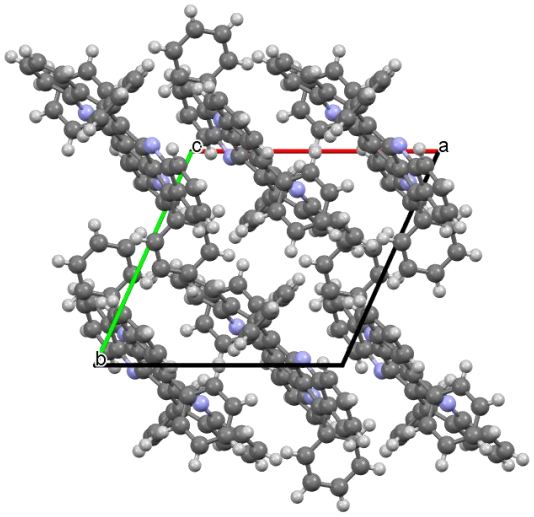
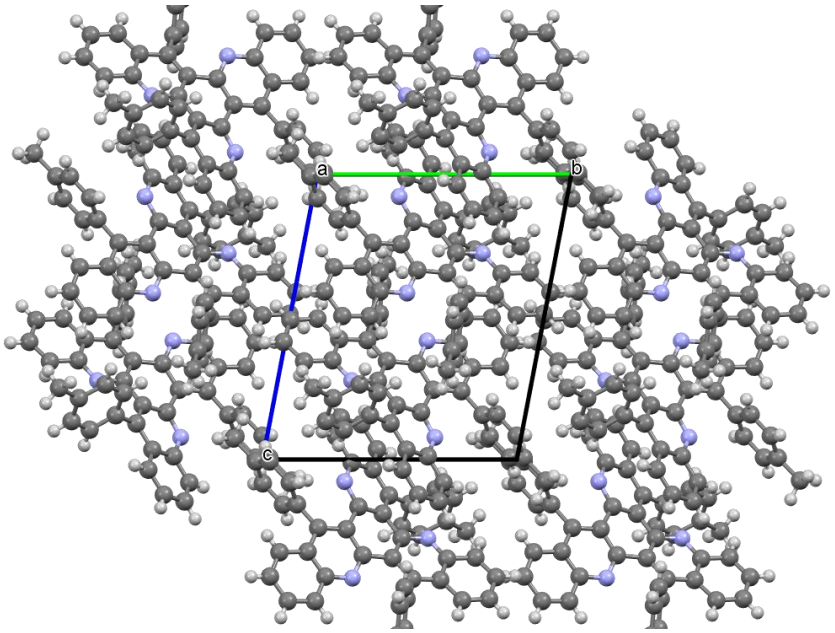


Figure S-D.2. Following three planes (100), (010) and (001).

TAN-MePh



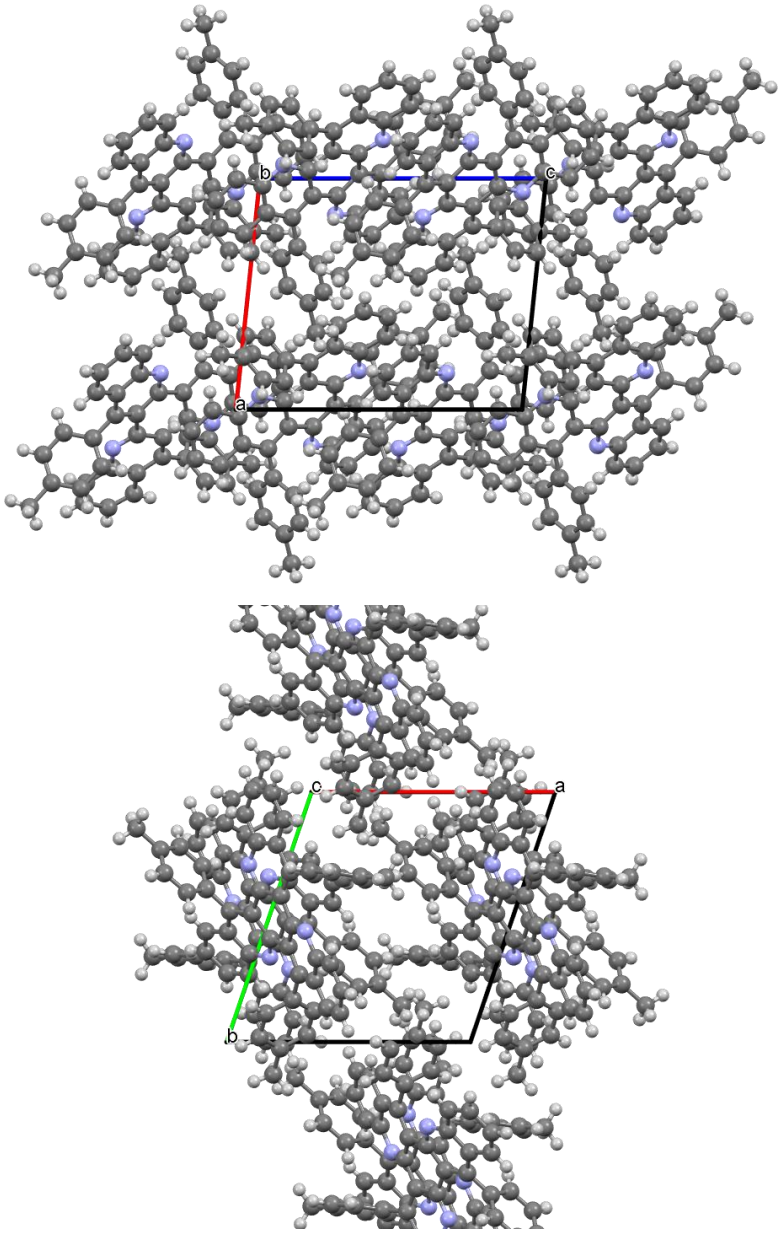
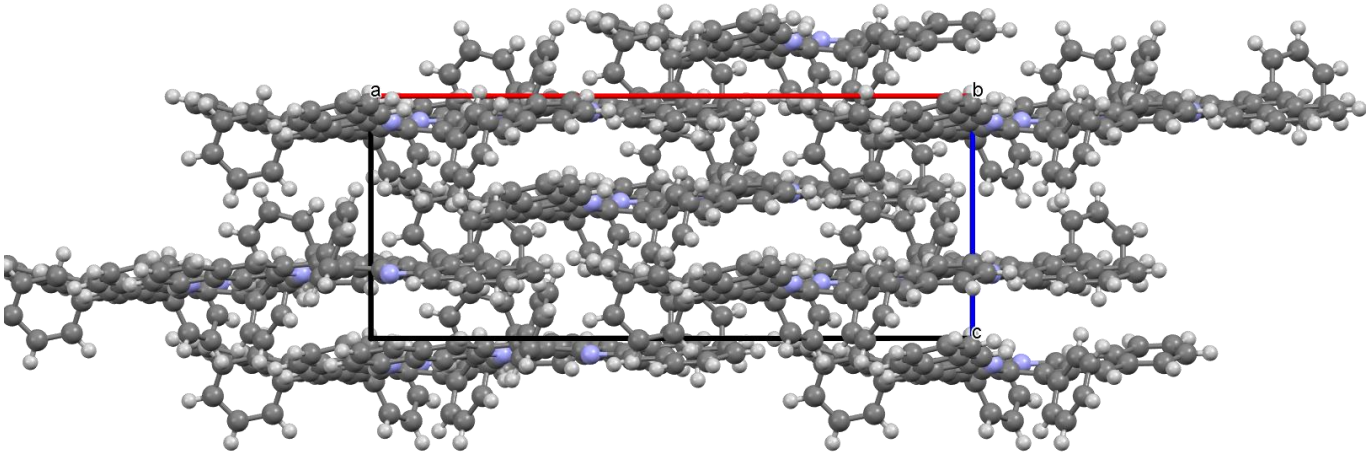
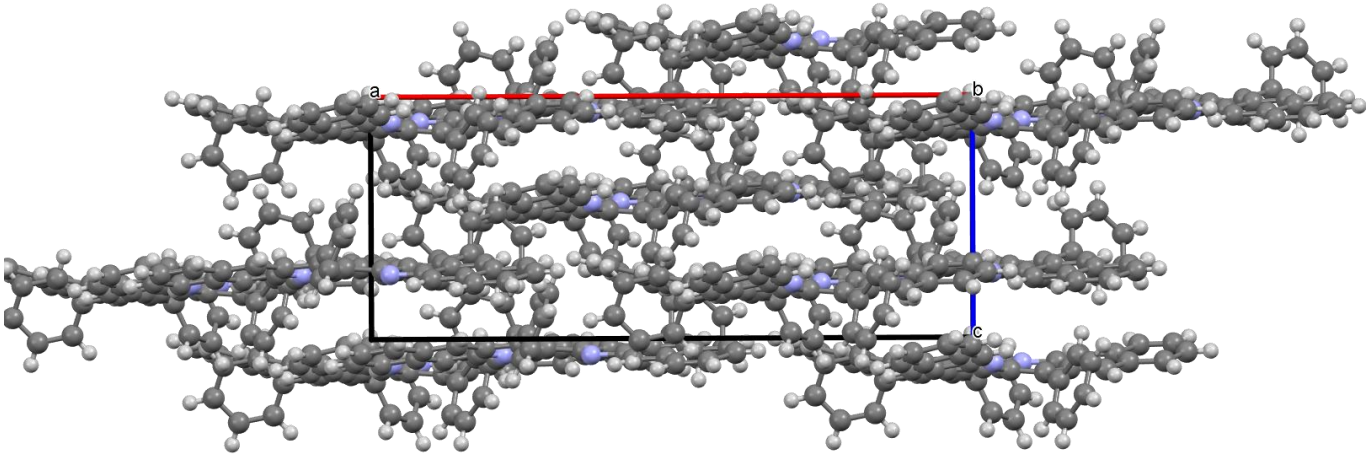


Figure S-D.3. Following three planes (100), (010) and (001).

TAA-Ph





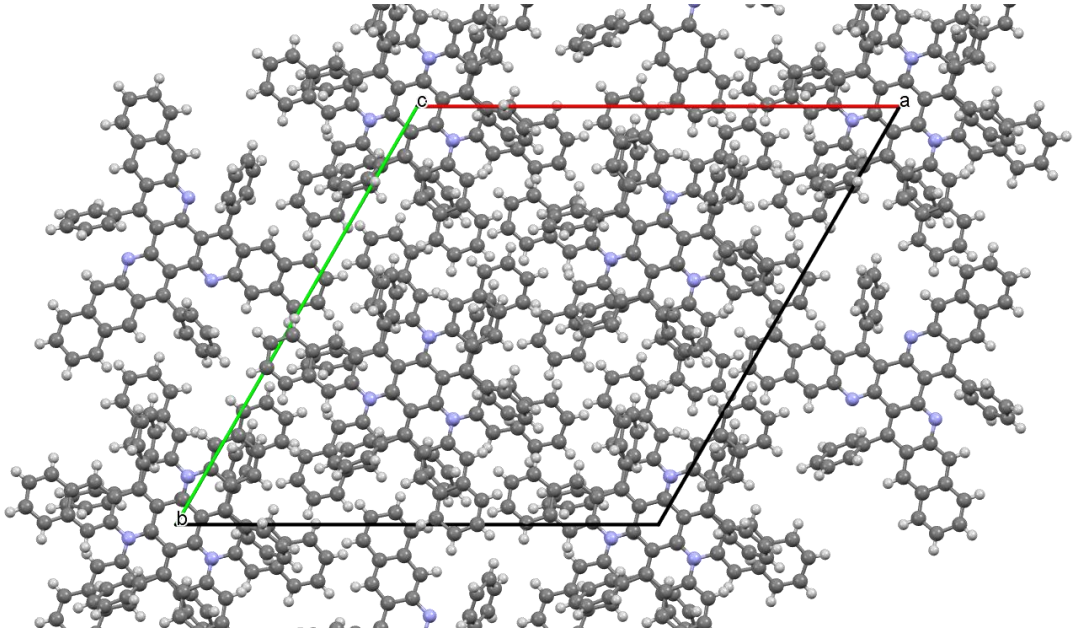
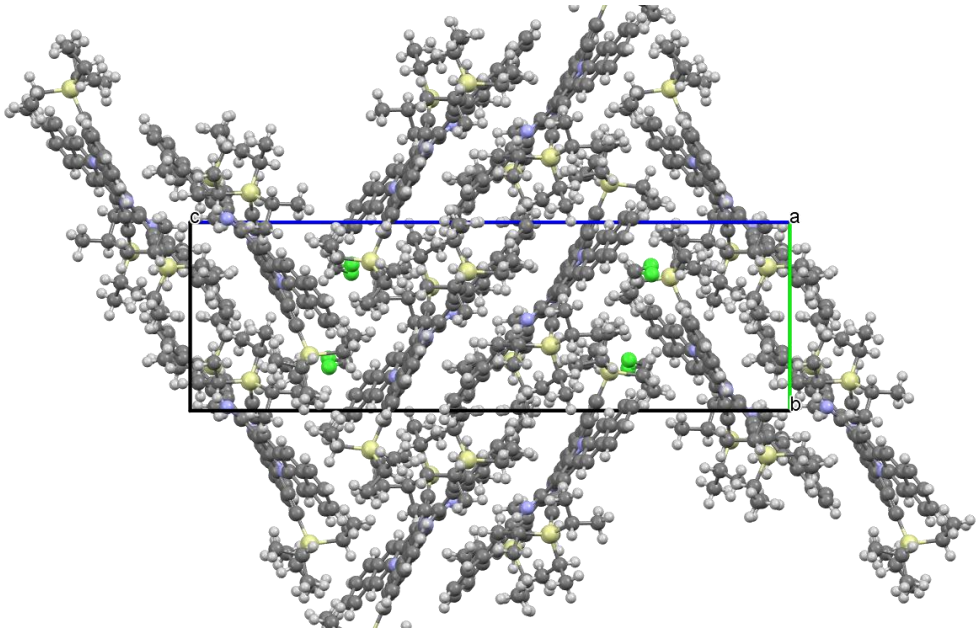


Figure S-D.4. Following three planes (100), (010) and (001).

TAA-Tips



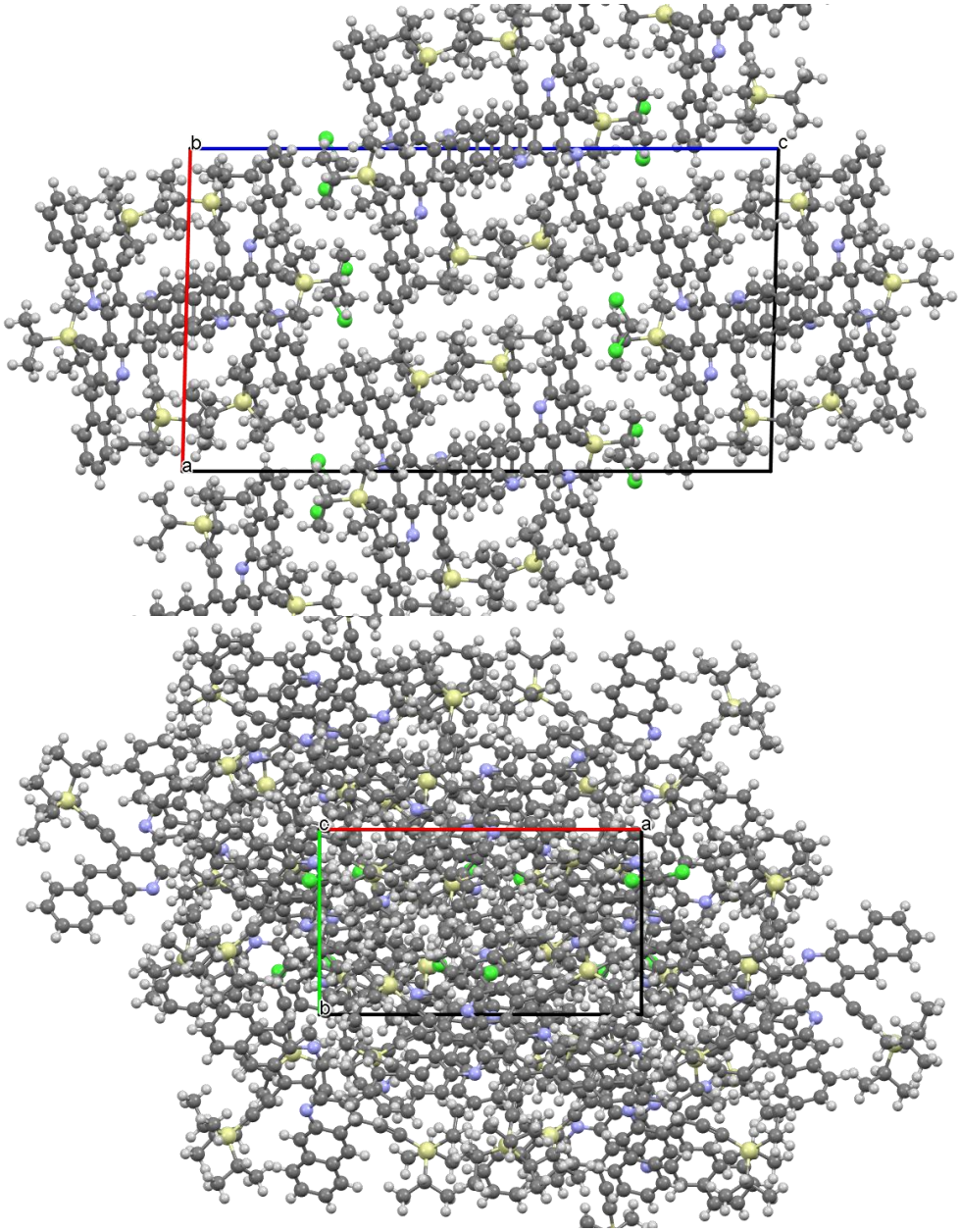
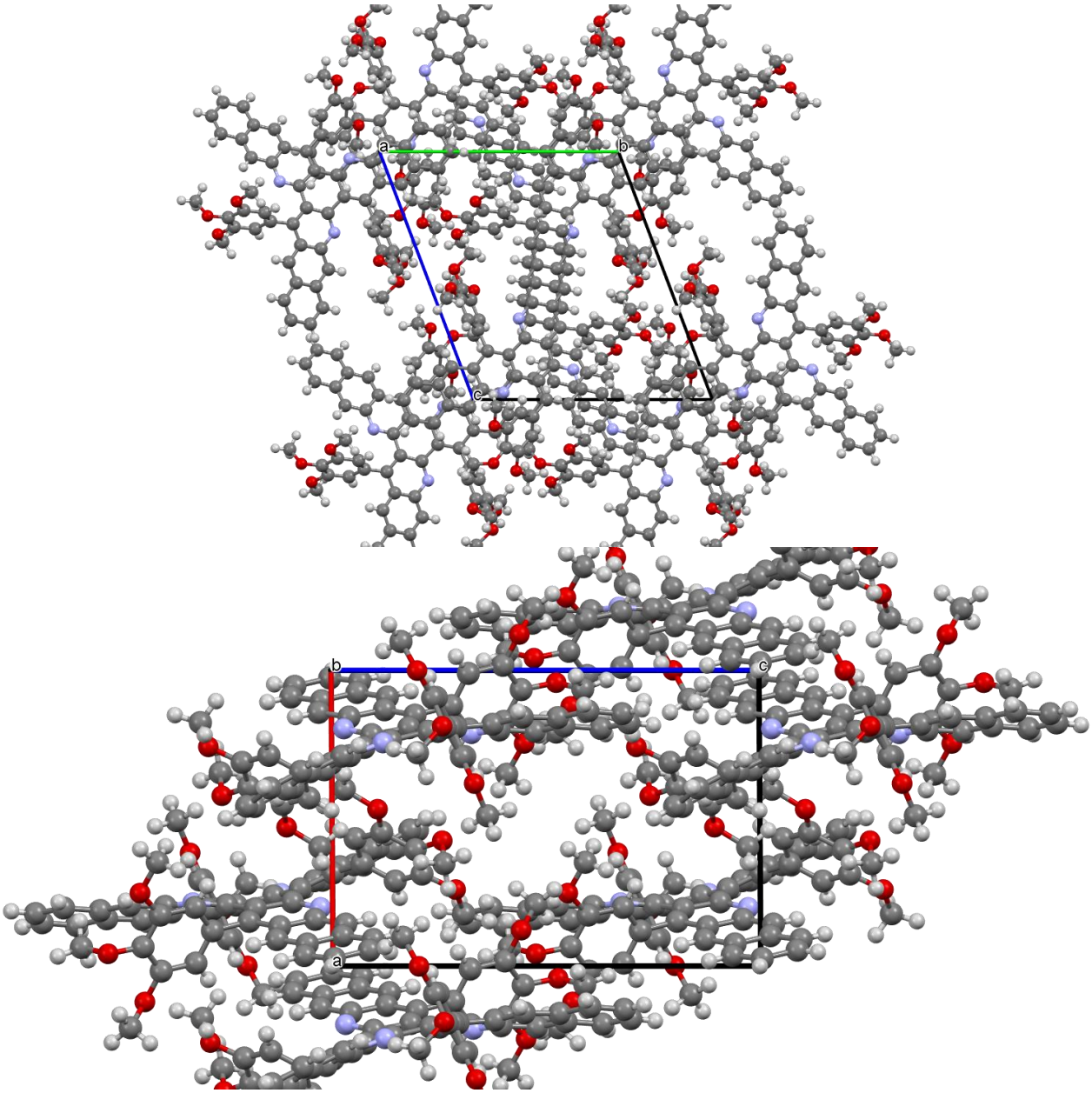


Figure S-D.5. Following three planes (100), (010) and (001).

TAA-OMePh



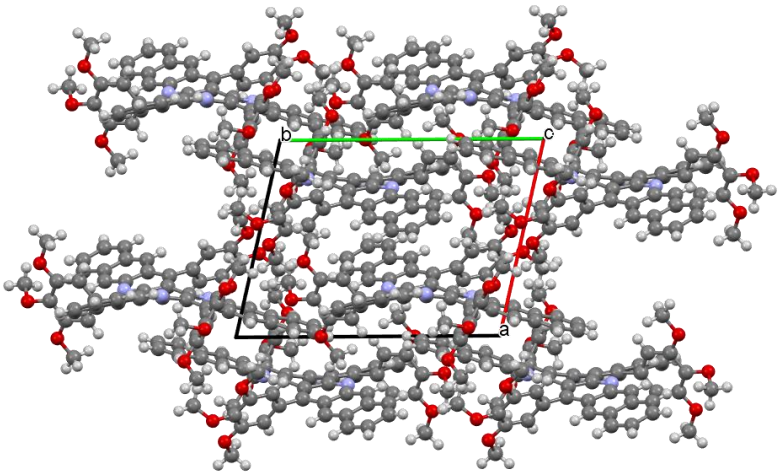
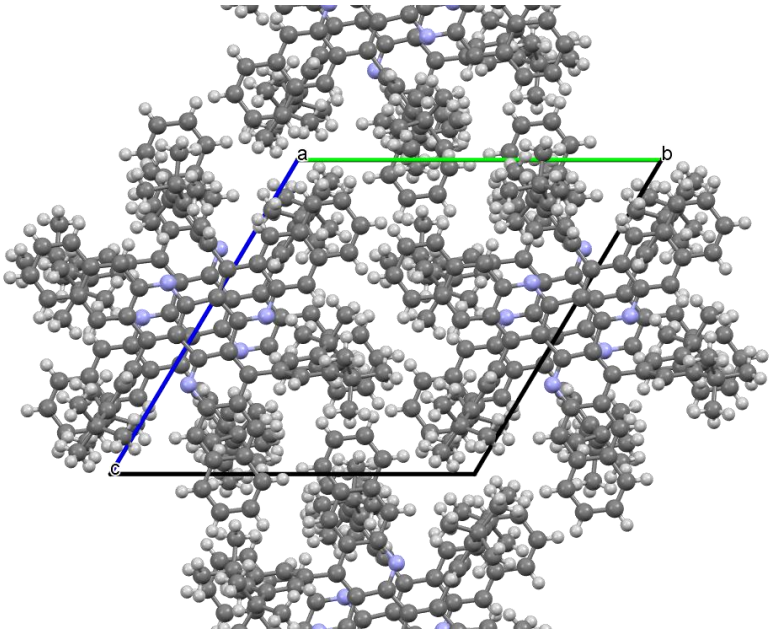


Figure S-D.6.: Following three planes (100), (010) and (001).

TAA-tBuPh



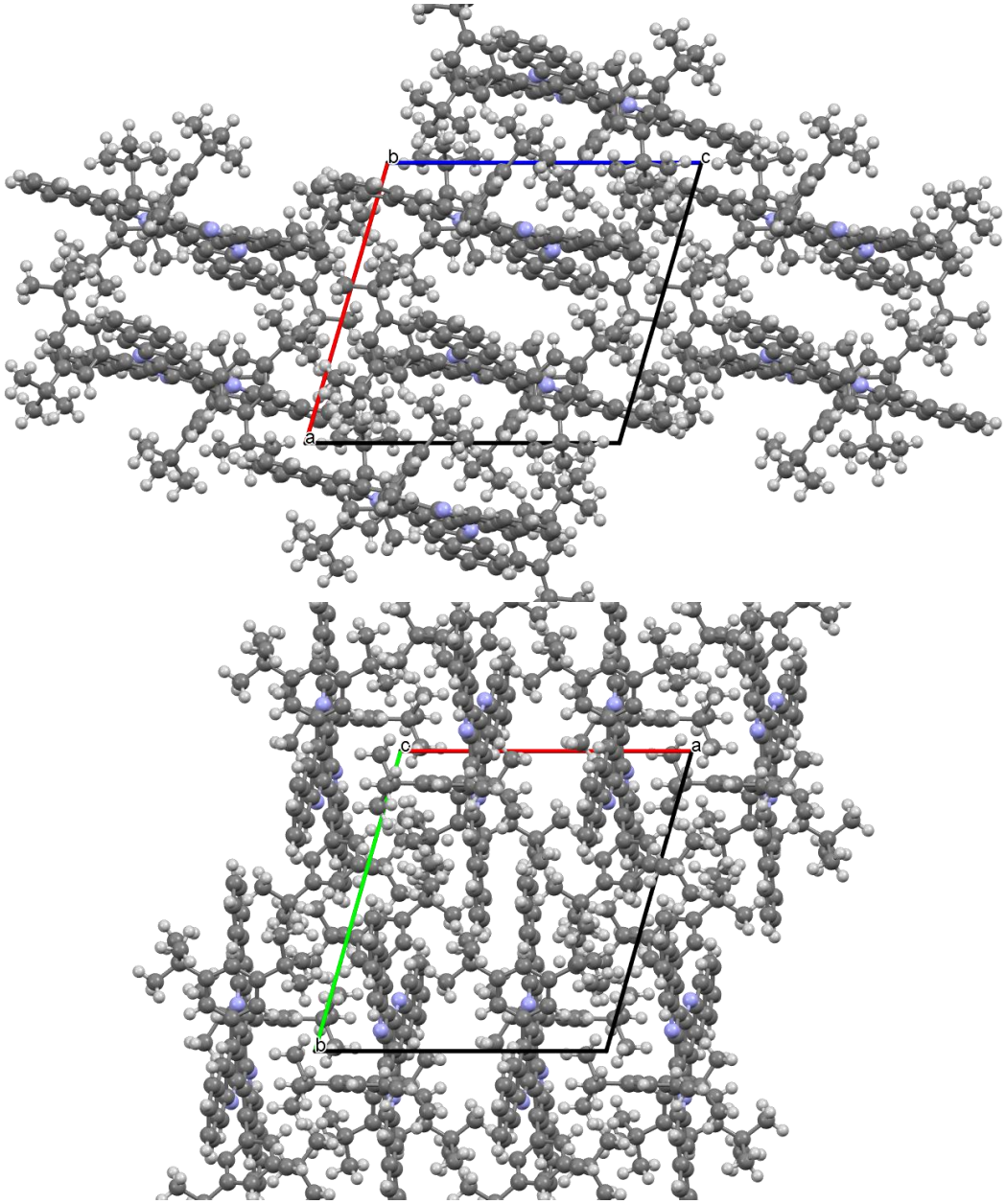


Figure S-D.7. Following three planes (100), (010) and (001).

E. DFT calculations

Molecular geometries were optimized using the density functional theory (DFT) at the B3LYP/6-31G(d) level. Each structure was characterized as a minimum of the potential energy surface on the basis of its positive force constants issued by normal mode calculations. Internal reorganization energies for holes (λ_h) and electrons (λ_e) were calculated at the same level of theory, using the expression derived from the four point adiabatic potential approach:[5–8]

$$\lambda_h = E^{(+)}(M) - E^{(0)}(M) + E^{(+)}(M^+) - E^{(0)}(M^+) \quad \text{SI1}$$

$$\lambda_e = E^{(-)}(M) - E^{(0)}(M) + E^{(-)}(M^-) - E^{(0)}(M^-) \quad \text{SI2}$$

where $E^{(0)}(M)$, $E^{(+)}(M^+)$ and $E^{(-)}(M^-)$ denote the ground-state energy of the neutral, positively and negatively charged states, respectively; $E^{(+)}(M)$ $[E^{(-)}(M)]$ is the energy of the neutral molecule in the optimized geometry of the cation [anion], and $E^{(0)}(M^+)$ $[E^{(0)}(M^-)]$ is the energy of the cation [anion] in the optimized geometry of the neutral molecule. Ionization energies (IE) and electron affinities (EA) are defined as:

$$IE = E^{(+)}(M^+) - E^{(0)}(M) \quad \text{SI3}$$

$$EA = E^{(0)}(M) - E^{(-)}(M^-) \quad \text{SI4}$$

Transfer integrals J_{ij} characterizing hole (electron) coupling between molecular pairs *ij* within the crystals were obtained by employing the projection method involving the HOMOs (LUMOs) of monomers *i* and *j*.[9] Since the TAN-Ph compound possesses nearly degenerate HOMO (H) and HOMO-1 (H–1) levels (E_{H-1} = -5.657 eV and E_H = -5.637 eV, as calculated at the B3LYP/6-31G(d) level using the crystal geometry), effective transfer integrals for hole transport in this compound were also computed as:

$$J_h = \frac{1}{\sqrt{2}}\left\{J_{H-1,H-1}^2 + J_{H-1,H}^2 + J_{H,H-1}^2 + J_{H,H}^2\right\}^{1/2} \quad \text{SI5}$$

in line with previous works.[10–12]

Transition energies towards the first optically allowed excited states were computed by means of time-dependent DFT at the CAM-B3LYP/6-311G(d) level. Solvent effects were taken into account in these calculations by using the Integral Equation Formalism of the Polarizable Continuum Model (IEF-PCM)[13]. All calculations were performed with the ORCA[14] and Gaussian[15] programs.

1. *Molecular orbitals*

A graphical representation of molecular orbitals (MOs) of the various compounds, calculated at the B3LYP/6-31G(d) level in gas phase, is given in the figures below.

TAN-Ph

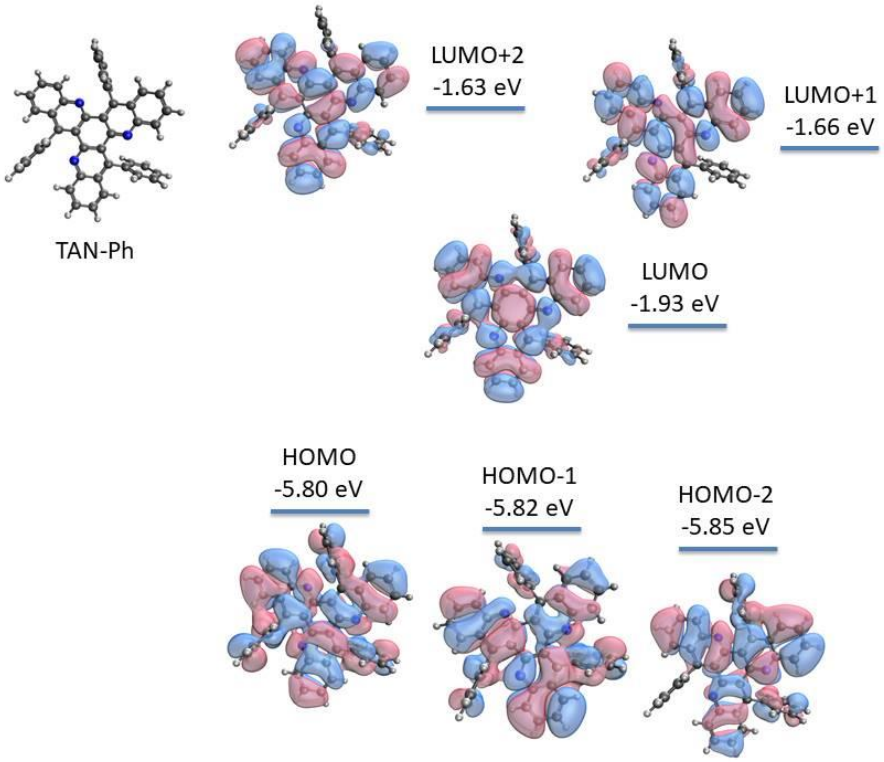


Figure S-E.1. Representation of molecular orbital of TAN-Ph.

TAN-MePh

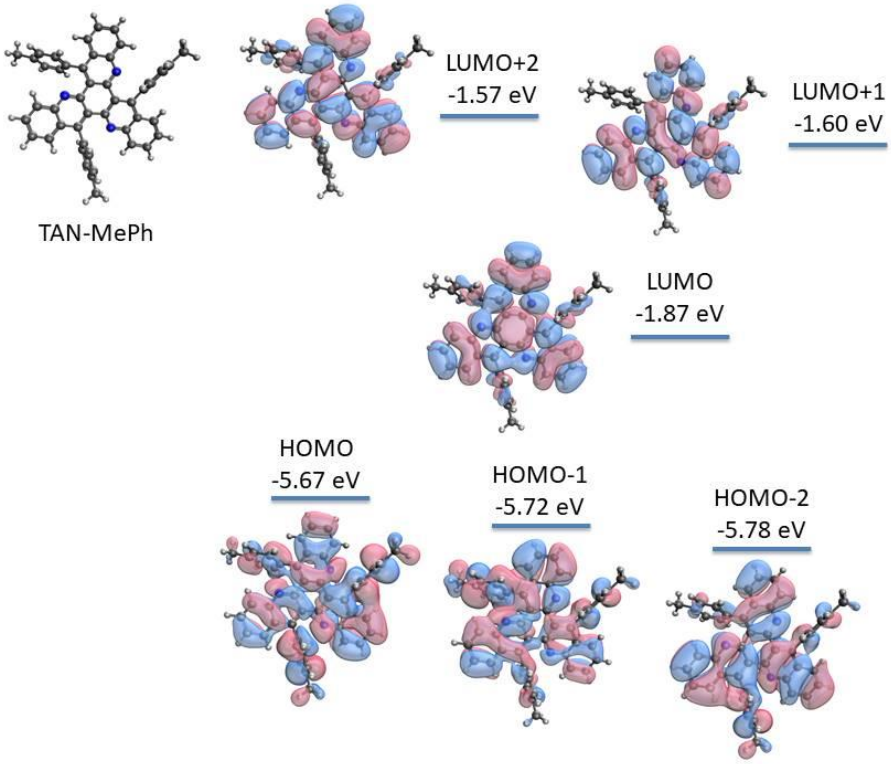


Figure S-E.2. Representation of molecular orbital of TAN-MePh.

TAA-Ph

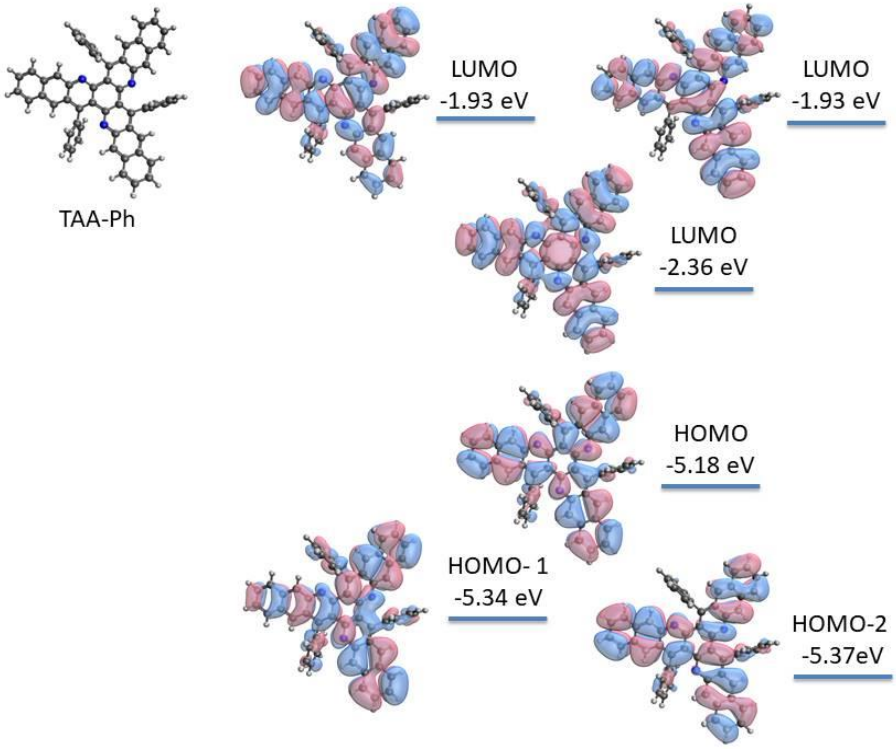


Figure S-E.3. Representation of molecular orbital of TAA-Ph.

TAA-OMePh

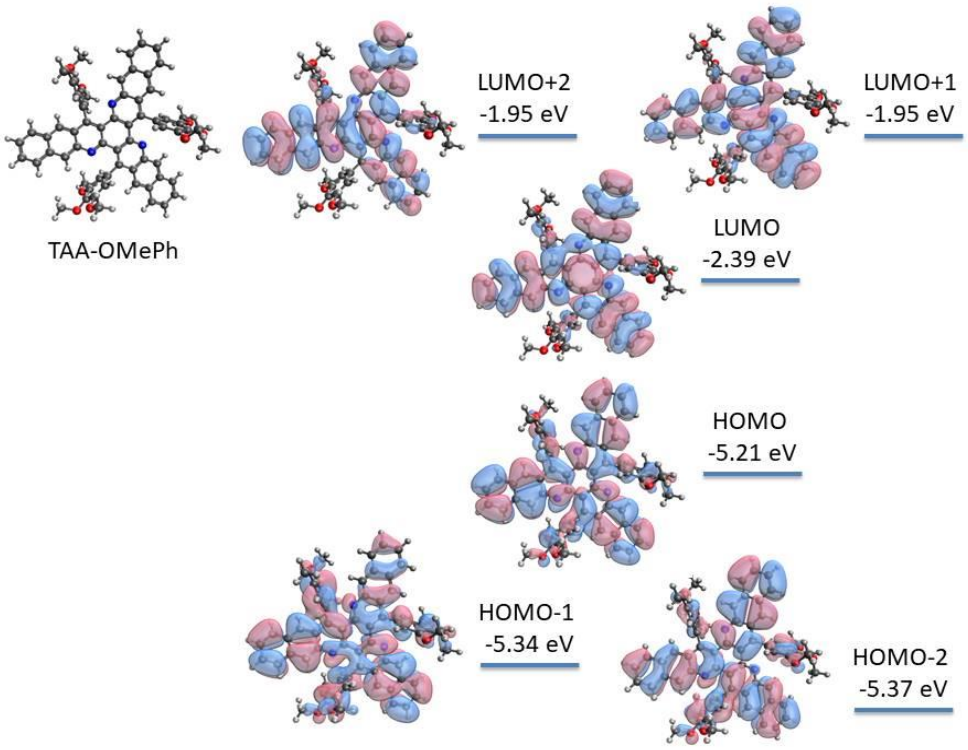


Figure S-E.4. Representation of molecular orbital of TAA-OMePh.

TAA-Tips

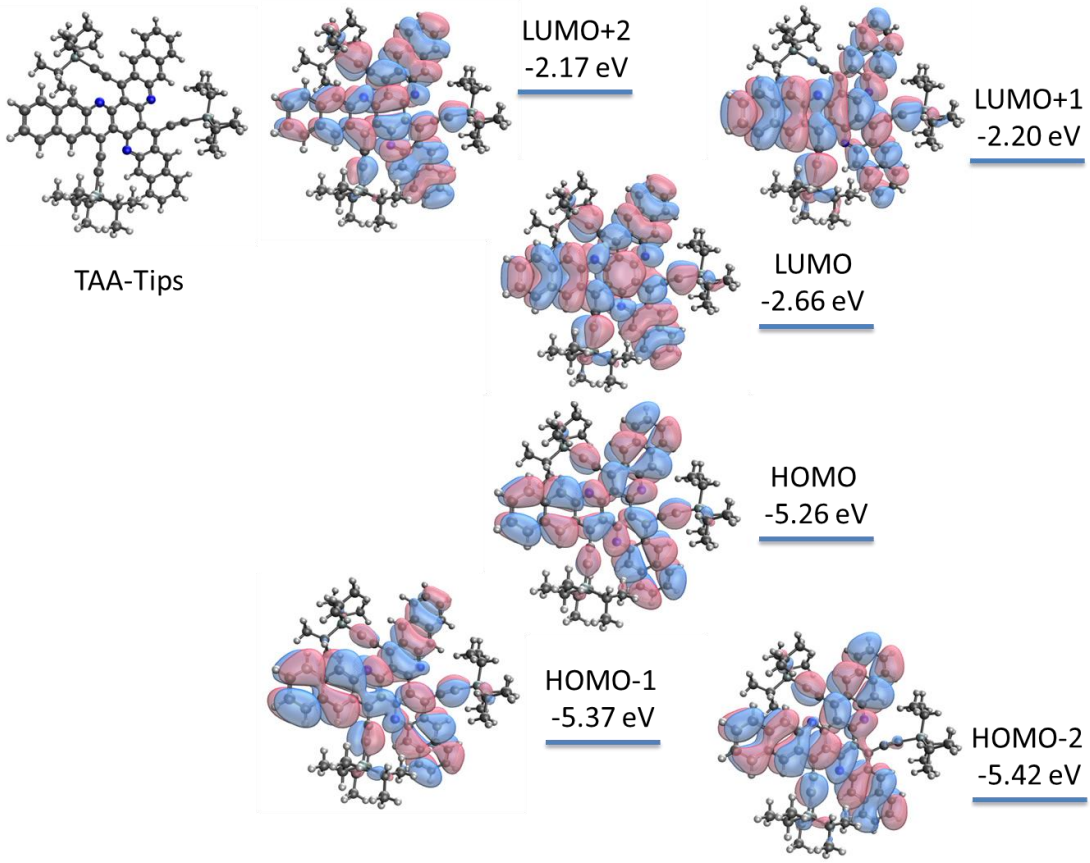


Figure S-E.5. Representation of molecular orbital of TAA-Tips.

TAA-tBuPh

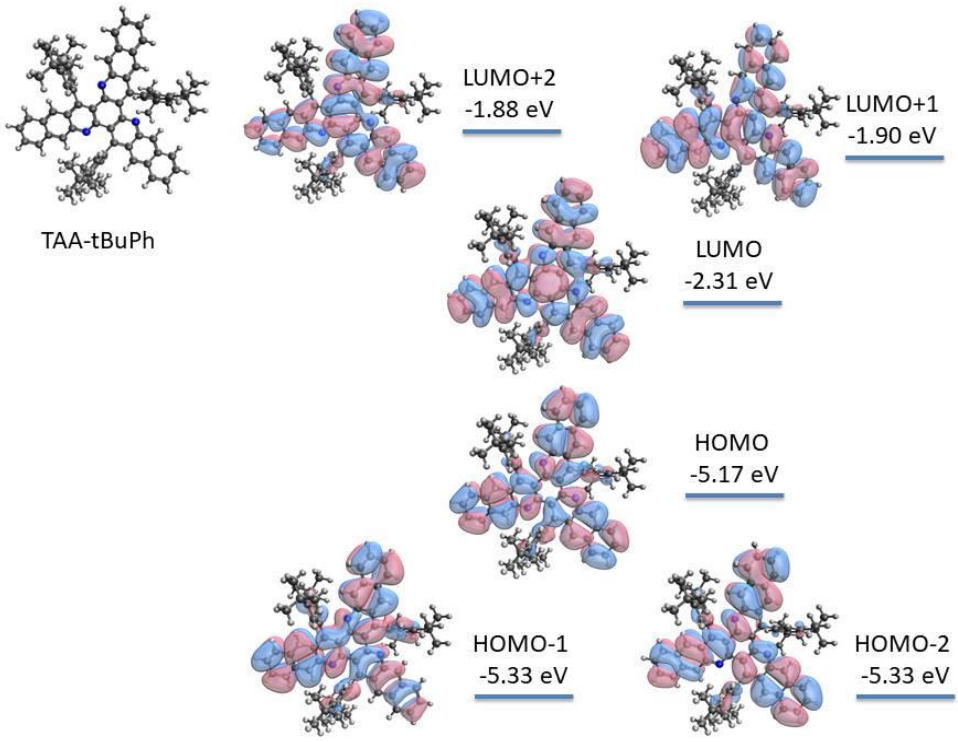


Figure S-E.6. Representation of molecular orbital of TAA-tBuPh.

TAA-CF$_3$Ph

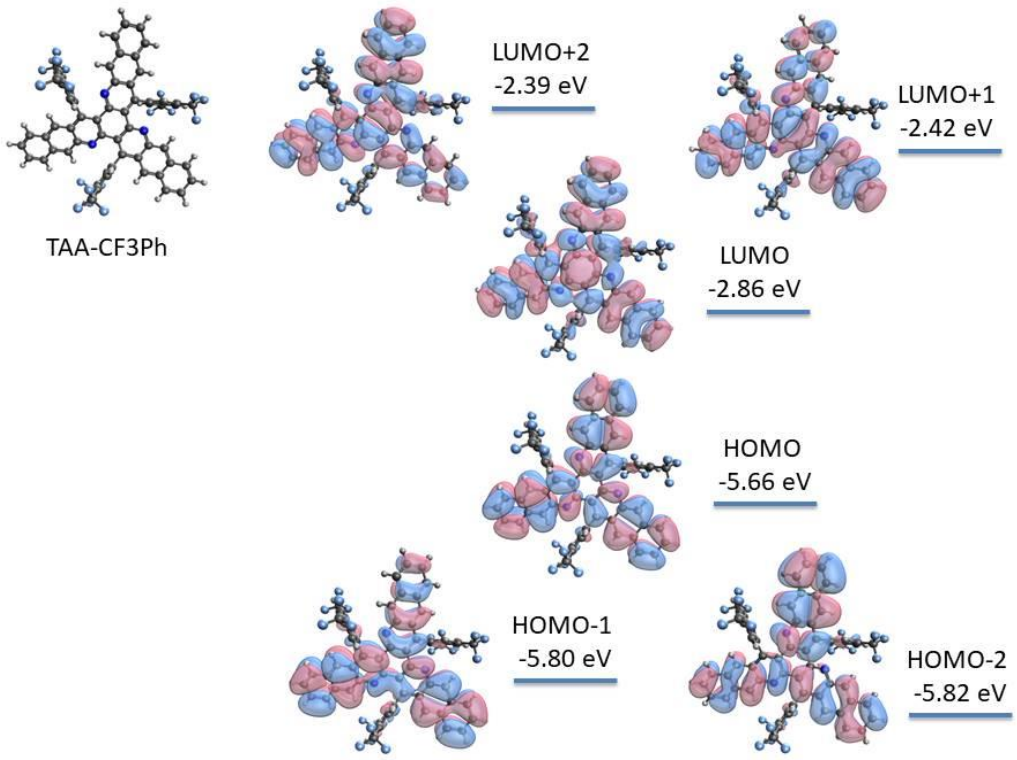


Figure S-E.7. Representation of molecular orbital of TAA-CF3Ph.

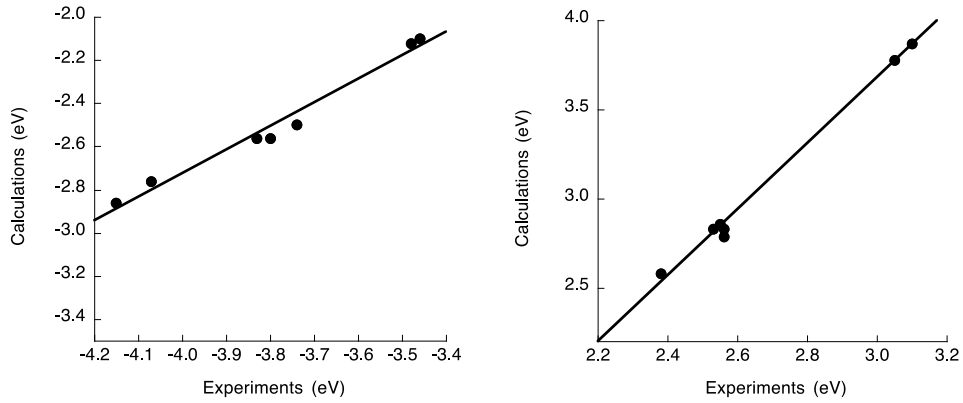


Figure S-E.8. Correlation between experimental and IEFPCM:B3LYP/6-31G(d) calculations in THF for (left) LUMO energies and (right) HOMO-LUMO gaps.

2. *Absorption spectra*

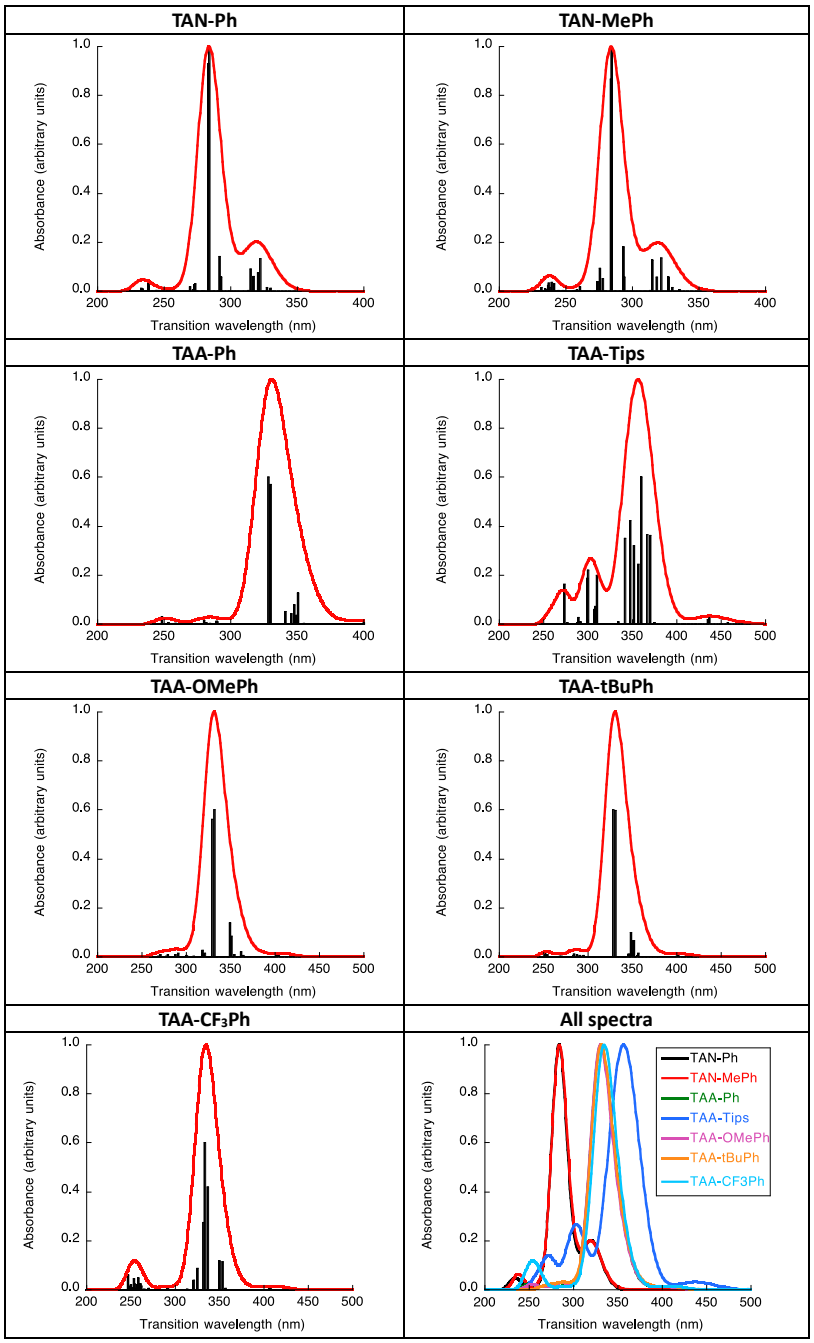


Figure S-E.9. Oscillator strengths (black bars) associated to electron excitations calculated at the IEFPCM/CAM-B3LYP/6-311G(d) level, and normalized spectra (lines), in which each transition has been enlarged by using a Gaussian function with a full width at half maximum (FWHM) equal to 0.3 eV.

3. *Calculated absorption properties*

TAN-Ph

(HOMO = MO 159; LUMO = MO 160)

```
Excited State   1:      Singlet-A      3.7646 eV  329.35 nm  f=0.0280
     147 ->160        -0.12649
     155 ->161         0.15423
     155 ->162        -0.14473
     156 ->160         0.28720
     157 ->160         0.23417
     157 ->162        -0.12274
     158 ->160        -0.12393
     158 ->162         0.14420
     159 ->160         0.38013
     159 ->161        -0.13791

 Excited State   2:      Singlet-A      3.7970 eV  326.54 nm  f=0.0342
     154 ->160         0.12710
     154 ->161         0.11615
     156 ->160        -0.13493
     157 ->160         0.36749
     158 ->160         0.17947
     158 ->162         0.25513
     159 ->160        -0.19218
     159 ->161        -0.27894
     159 ->162        -0.15156

 Excited State   3:      Singlet-A      3.8507 eV  321.98 nm  f=0.2804
     155 ->160        -0.30425
     155 ->161         0.10121
     156 ->161        -0.10199
     156 ->162         0.12589
     158 ->160         0.42418
     159 ->160         0.19251
     159 ->161        -0.17100
     159 ->162         0.13357

 Excited State   4:      Singlet-A      3.8713 eV  320.27 nm  f=0.1604
     145 ->160         0.12264
     155 ->160         0.31366
     155 ->161        -0.12961
     156 ->160        -0.10523
     156 ->161         0.17472
     158 ->160         0.31522
     158 ->161        -0.17930
     159 ->160         0.27464
     159 ->161         0.11035
     159 ->162        -0.11132

 Excited State   5:      Singlet-A      3.9111 eV  317.01 nm  f=0.1270
     148 ->160        -0.13679
     154 ->160        -0.14331
     155 ->161        -0.12928
     155 ->162         0.10828
     156 ->160        -0.22746
     156 ->161         0.12854
     158 ->160        -0.15513
     158 ->161         0.19597
```

```
    158 ->162         0.25718
    159 ->160         0.19206
    159 ->161        -0.17767
    159 ->162         0.30530

Excited State   6:      Singlet-A      3.9440 eV  314.36 nm  f=0.1944
    154 ->160        -0.17700
    154 ->161        -0.12373
    154 ->162        -0.15913
    155 ->160         0.13938
    156 ->160         0.30997
    156 ->161         0.16270
    158 ->160         0.21988
    158 ->161         0.17676
    159 ->160        -0.26210
    159 ->161        -0.10215
    159 ->162         0.10922

Excited State   7:      Singlet-A      3.9687 eV  312.40 nm  f=0.0069
    146 ->160         0.13663
    154 ->160         0.36980
    154 ->161         0.14360
    155 ->160         0.12647
    155 ->162        -0.11048
    156 ->162        -0.24931
    157 ->160        -0.13046
    158 ->161         0.30816
    159 ->162         0.18573

Excited State   8:      Singlet-A      4.2409 eV  292.35 nm  f=0.1219
    149 ->160        -0.12412
    150 ->160        -0.16837
    153 ->160        -0.14617
    157 ->161         0.51764
    157 ->162        -0.24057
    158 ->164        -0.12327
    159 ->162         0.10257
    159 ->163        -0.13479

Excited State   9:      Singlet-A      4.2548 eV  291.40 nm  f=0.3018
    149 ->160        -0.16611
    150 ->160         0.13359
    152 ->160         0.13702
    157 ->161         0.20412
    157 ->162         0.44742
    158 ->162         0.22286
    158 ->163        -0.13040
    159 ->161         0.18763
    159 ->164         0.12041

Excited State  10:      Singlet-A      4.3758 eV  283.34 nm  f=2.1090
    157 ->161        -0.12313
    157 ->164         0.10719
    158 ->161        -0.41910
    158 ->162         0.10116
    159 ->160        -0.10743
    159 ->161         0.11305
    159 ->162         0.43041
```

```
 Excited State  11:      Singlet-A      4.3840 eV  282.81 nm  f=1.9613
     157 ->162        -0.24488
     157 ->163        -0.11737
     158 ->160         0.10487
     158 ->161         0.12680
     158 ->162         0.36789
     159 ->161         0.40219
     159 ->162        -0.11663
```

TAN-MePh

(HOMO = MO 171; LUMO = MO 172)

```
Excited State   1:      Singlet-A      3.7093 eV  334.25 nm  f=0.0152
     160 -> 172       -0.14537
     167 -> 172       -0.21200
     168 -> 173        0.15688
     168 -> 174       -0.14716
     169 -> 172        0.21732
     169 -> 174       -0.15061
     170 -> 173       -0.10774
     171 -> 172        0.44551
     171 -> 173       -0.15262

 Excited State   2:      Singlet-A      3.7620 eV  329.57 nm  f=0.0341
     167 -> 172        0.13423
     169 -> 172        0.32183
     169 -> 173        0.14495
     170 -> 172        0.30444
     170 -> 174        0.25383
     171 -> 172       -0.15808
     171 -> 173       -0.23627
     171 -> 174       -0.15589

 Excited State   3:      Singlet-A      3.7985 eV  326.40 nm  f=0.1199
     157 -> 172        0.12658
     160 -> 174        0.11348
     167 -> 172        0.12260
     167 -> 173       -0.15723
     168 -> 172        0.39252
     168 -> 174       -0.16560
     169 -> 172        0.13757
     169 -> 173        0.11080
     170 -> 172       -0.22470
     171 -> 173        0.21256
     171 -> 174       -0.16669

 Excited State   4:      Singlet-A      3.8660 eV  320.71 nm  f=0.2781
     167 -> 172        0.16614
     167 -> 173       -0.11706
     168 -> 172        0.15669
     169 -> 172       -0.25236
     170 -> 172        0.41980
     170 -> 173       -0.13460
     171 -> 172        0.24169

 Excited State   5:      Singlet-A      3.9042 eV  317.57 nm  f=0.1165
     159 -> 172        0.13420
     166 -> 172       -0.20543
     167 -> 172        0.23631
```

```
    167 -> 173       -0.22690
    168 -> 174        0.10586
    169 -> 174       -0.17962
    170 -> 173        0.13641
    170 -> 174        0.24306
    171 -> 172        0.16584
    171 -> 173       -0.20446
    171 -> 174        0.24979

Excited State   6:      Singlet-A      3.9416 eV  314.56 nm  f=0.2567
    166 -> 174        0.10627
    167 -> 172        0.30770
    167 -> 173        0.10876
    168 -> 172       -0.21680
    168 -> 173       -0.11433
    169 -> 174        0.12875
    170 -> 172       -0.22493
    170 -> 173       -0.19938
    171 -> 172        0.24760
    171 -> 173        0.10487
    171 -> 174       -0.11795

Excited State   7:      Singlet-A      3.9608 eV  313.03 nm  f=0.0056
    158 -> 172        0.12080
    166 -> 172        0.36131
    167 -> 174        0.21088
    168 -> 174       -0.15022
    169 -> 172       -0.11634
    170 -> 173        0.32180
    171 -> 172        0.10161
    171 -> 174        0.21319

Excited State   8:      Singlet-A      4.2287 eV  293.20 nm  f=0.1159
    162 -> 172       -0.19331
    165 -> 172       -0.13126
    166 -> 173       -0.14516
    169 -> 173        0.49989
    169 -> 174       -0.21730
    171 -> 175       -0.13116

Excited State   9:      Singlet-A      4.2397 eV  292.43 nm  f=0.3677
    161 -> 172       -0.18679
    164 -> 172       -0.13147
    166 -> 173       -0.12637
    166 -> 174       -0.12433
    169 -> 173        0.13226
    169 -> 174        0.32059
    170 -> 174        0.35575
    170 -> 175       -0.12208
    171 -> 173        0.22462
    171 -> 174        0.11386
    171 -> 176        0.10379

Excited State  10:      Singlet-A      4.3654 eV  284.01 nm  f=2.0390
    166 -> 173        0.13692
    170 -> 173       -0.43074
    171 -> 174        0.43263

Excited State  11:      Singlet-A      4.3781 eV  283.19 nm  f=1.7665
```

```
     166 -> 174        0.14387
     169 -> 173       -0.13410
     169 -> 174       -0.33589
     169 -> 175       -0.11937
     170 -> 172        0.12174
     170 -> 174        0.25902
     171 -> 173        0.39310
```

TAA-Ph

(HOMO = MO 198; LUMO = MO 199)

```
Excited State   1:      Singlet-A      2.9668 eV  417.90 nm  f=0.0022
     196 -> 201       -0.26901
     197 -> 200        0.25232
     198 -> 199        0.58087

 Excited State   2:      Singlet-A      3.0863 eV  401.72 nm  f=0.0438
     196 -> 199       -0.33130
     196 -> 200        0.10992
     197 -> 199        0.47921
     198 -> 200        0.19187
     198 -> 201        0.23923

 Excited State   3:      Singlet-A      3.1024 eV  399.64 nm  f=0.0231
     196 -> 199        0.47952
     197 -> 199        0.33206
     197 -> 200        0.14726
     198 -> 200        0.22447
     198 -> 201       -0.20707

 Excited State   4:      Singlet-A      3.4967 eV  354.58 nm  f=0.0099
     187 -> 199        0.14779
     191 -> 200       -0.10289
     192 -> 201       -0.14797
     194 -> 199       -0.11506
     196 -> 200        0.37741
     196 -> 202        0.10652
     197 -> 200       -0.12544
     197 -> 201        0.39761
     198 -> 205        0.12180

 Excited State   5:      Singlet-A      3.5424 eV  350.00 nm  f=0.5487
     187 -> 201       -0.11482
     191 -> 199        0.13044
     191 -> 201       -0.11019
     192 -> 199        0.20129
     192 -> 200       -0.11714
     193 -> 199        0.10254
     194 -> 199        0.14177
     195 -> 199       -0.27875
     196 -> 201        0.14166
     197 -> 199       -0.18226
     197 -> 200        0.17911
     198 -> 200        0.34177
     198 -> 201       -0.10827

 Excited State   6:      Singlet-A      3.5496 eV  349.29 nm  f=0.1609
     185 -> 199       -0.12424
     192 -> 199        0.15731
     193 -> 200       -0.10960
```

```
    194 -> 199        0.20452
    194 -> 200       -0.17095
    194 -> 201        0.10131
    195 -> 199        0.38513
    196 -> 200        0.16567
    198 -> 200        0.18685
    198 -> 201        0.21634

Excited State   7:      Singlet-A      3.5674 eV  347.55 nm  f=0.3331
    187 -> 200        0.11833
    191 -> 199       -0.28068
    192 -> 199        0.15926
    192 -> 201        0.11423
    193 -> 199       -0.17232
    194 -> 200        0.15376
    195 -> 199       -0.20304
    196 -> 199        0.19660
    196 -> 200        0.12939
    198 -> 201        0.32831

Excited State   8:      Singlet-A      3.5923 eV  345.14 nm  f=0.1852
    181 -> 199        0.10932
    192 -> 199       -0.18601
    193 -> 201        0.11920
    194 -> 199        0.39957
    194 -> 201       -0.10506
    195 -> 200       -0.17048
    195 -> 201        0.17541
    196 -> 201        0.12872
    197 -> 200        0.11553
    197 -> 201        0.11591
    198 -> 200       -0.19772

Excited State   9:      Singlet-A      3.6380 eV  340.80 nm  f=0.2251
    182 -> 199        0.11692
    185 -> 200        0.10658
    191 -> 199       -0.18271
    191 -> 200       -0.10898
    193 -> 199        0.41848
    193 -> 200        0.13336
    193 -> 201        0.12982
    195 -> 200       -0.12671
    195 -> 201       -0.18081
    196 -> 200       -0.13816
    197 -> 201        0.15364
    198 -> 201        0.13830

Excited State  10:      Singlet-A      3.7588 eV  329.85 nm  f=2.4562
    192 -> 199        0.18127
    193 -> 199        0.13841
    195 -> 201       -0.10306
    196 -> 200        0.13521
    196 -> 201        0.33507
    197 -> 200        0.31472
    197 -> 201       -0.13922
    198 -> 200       -0.27344
    198 -> 202       -0.16342

Excited State  11:      Singlet-A      3.7800 eV  328.00 nm  f=2.5836
```

```
     191 -> 199        0.19858
     196 -> 200       -0.32799
     196 -> 201        0.13607
     197 -> 200        0.14629
     197 -> 201        0.35290
     198 -> 201        0.23615
     198 -> 203       -0.14136
```

TAA-tBuPh

(HOMO = MO 294; LUMO = MO 295)

```
Excited State   1:      Singlet-A      2.9726 eV  417.08 nm  f=0.0010
     292 -> 297       -0.26503
     293 -> 296        0.24686
     294 -> 295        0.57941

 Excited State   2:      Singlet-A      3.0916 eV  401.04 nm  f=0.0398
     292 -> 295       -0.36831
     293 -> 295        0.44919
     293 -> 296        0.12036
     294 -> 296        0.14904
     294 -> 297        0.26887

 Excited State   3:      Singlet-A      3.1078 eV  398.95 nm  f=0.0168
     292 -> 295        0.44891
     293 -> 295        0.37137
     293 -> 296        0.10295
     294 -> 296        0.26244
     294 -> 297       -0.16525

 Excited State   4:      Singlet-A      3.4867 eV  355.59 nm  f=0.0672
     290 -> 295        0.12634
     291 -> 295        0.35235
     291 -> 296        0.14324
     291 -> 297       -0.16194
     292 -> 296        0.31216
     293 -> 296       -0.15631
     293 -> 297        0.22306

 Excited State   5:      Singlet-A      3.4994 eV  354.30 nm  f=0.0285
     282 -> 295        0.15300
     290 -> 295       -0.25626
     290 -> 296        0.23504
     291 -> 295        0.36428
     291 -> 297       -0.11403
     292 -> 296       -0.13678
     293 -> 296        0.10733
     293 -> 297       -0.25880

 Excited State   6:      Singlet-A      3.5315 eV  351.08 nm  f=0.2874
     283 -> 295       -0.10778
     290 -> 295        0.38537
     290 -> 296       -0.14663
     291 -> 296        0.15989
     291 -> 297       -0.11781
     292 -> 296       -0.13725
     292 -> 297       -0.19674
     293 -> 297       -0.22653
     294 -> 296       -0.12089
```

```
 Excited State   7:      Singlet-A      3.5514 eV  349.11 nm  f=0.2900
     284 -> 296        0.10117
     285 -> 295        0.20665
     286 -> 295        0.10638
     288 -> 295       -0.12068
     289 -> 295        0.20133
     290 -> 295        0.12107
     292 -> 295       -0.13701
     292 -> 296       -0.19640
     293 -> 295       -0.14915
     293 -> 299        0.11039
     294 -> 296        0.36267
     294 -> 297       -0.12394

 Excited State   8:      Singlet-A      3.5635 eV  347.92 nm  f=0.4331
     283 -> 296        0.11389
     284 -> 295       -0.22361
     285 -> 295        0.10593
     286 -> 295       -0.11503
     287 -> 295       -0.20362
     289 -> 295       -0.10984
     292 -> 295        0.16219
     292 -> 296        0.11866
     293 -> 295       -0.13834
     293 -> 297       -0.10625
     294 -> 296        0.16485
     294 -> 297        0.35988

 Excited State   9:      Singlet-A      3.5929 eV  345.08 nm  f=0.0497
     279 -> 295        0.10034
     284 -> 295       -0.10103
     289 -> 295        0.41839
     289 -> 297        0.25877
     291 -> 297       -0.11651
     294 -> 297        0.19669

 Excited State  10:      Singlet-A      3.7571 eV  330.00 nm  f=2.6292
     285 -> 295        0.10957
     290 -> 295        0.11274
     292 -> 297        0.37040
     293 -> 296        0.35538
     294 -> 296       -0.28068
     294 -> 298       -0.15643
     294 -> 299        0.11442

 Excited State  11:      Singlet-A      3.7811 eV  327.90 nm  f=2.6360
     284 -> 295        0.11543
     289 -> 295       -0.13527
     292 -> 296       -0.35989
     293 -> 297        0.37682
     294 -> 297        0.23967
     294 -> 298       -0.10815
     294 -> 299       -0.13490
```

TAA-OMePh

(HOMO = MO 270; LUMO = MO 271)

```
Excited State   1:      Singlet-A      2.9642 eV  418.28 nm  f=0.0015
     268 -> 272       -0.12192
     268 -> 273        0.24124
```

```
    269 -> 272        0.22701
    269 -> 273        0.13916
    270 -> 271        0.58015

Excited State   2:      Singlet-A      3.0745 eV  403.26 nm  f=0.0445
    268 -> 271        0.27162
    268 -> 272       -0.10353
    269 -> 271        0.51748
    270 -> 272        0.15778
    270 -> 273        0.25869

Excited State   3:      Singlet-A      3.0959 eV  400.48 nm  f=0.0206
    268 -> 271        0.51674
    269 -> 271       -0.26924
    269 -> 272       -0.13009
    270 -> 272       -0.25394
    270 -> 273        0.16466

Excited State   4:      Singlet-A      3.4193 eV  362.60 nm  f=0.0238
    257 -> 271       -0.15319
    258 -> 271       -0.14268
    258 -> 272        0.11871
    266 -> 271        0.44223
    266 -> 272       -0.27347
    267 -> 271        0.24171
    269 -> 272        0.14794

Excited State   5:      Singlet-A      3.4364 eV  360.80 nm  f=0.0874
    257 -> 271       -0.12704
    257 -> 273        0.11985
    258 -> 271        0.17483
    266 -> 271       -0.26604
    266 -> 273        0.10130
    267 -> 271        0.41738
    267 -> 272        0.19888
    267 -> 273       -0.19840
    268 -> 272        0.13310
    269 -> 272        0.13924

Excited State   6:      Singlet-A      3.5078 eV  353.45 nm  f=0.0421
    259 -> 271        0.16953
    260 -> 272       -0.12911
    261 -> 273       -0.15833
    267 -> 271        0.16128
    268 -> 272       -0.29652
    268 -> 273       -0.23065
    269 -> 272       -0.13131
    269 -> 273        0.36500
    270 -> 277       -0.11695

Excited State   7:      Singlet-A      3.5412 eV  350.12 nm  f=0.3662
    259 -> 273       -0.11221
    260 -> 272        0.10061
    261 -> 271        0.30988
    265 -> 271       -0.20075
    268 -> 271        0.12293
    268 -> 272        0.13221
    268 -> 275       -0.10630
    269 -> 271       -0.15112
```

```
     269 -> 272        0.13114
     270 -> 272        0.37637

 Excited State   8:      Singlet-A      3.5535 eV  348.91 nm  f=0.6149
     260 -> 271       -0.26476
     261 -> 271        0.15018
     262 -> 271       -0.12773
     265 -> 271        0.21578
     265 -> 273        0.10637
     268 -> 271       -0.10979
     268 -> 272       -0.20545
     269 -> 271       -0.14752
     269 -> 273       -0.13461
     270 -> 272        0.15112
     270 -> 273        0.30000

 Excited State   9:      Singlet-A      3.5796 eV  346.36 nm  f=0.0039
     256 -> 271        0.12765
     260 -> 271        0.18893
     262 -> 271       -0.15285
     265 -> 271        0.31898
     265 -> 273        0.20993
     268 -> 271        0.14087
     269 -> 275        0.10138
     270 -> 273       -0.30407

 Excited State  10:      Singlet-A      3.7428 eV  331.26 nm  f=2.6282
     261 -> 271       -0.14008
     267 -> 271        0.10741
     268 -> 273        0.36648
     269 -> 272       -0.34958
     270 -> 272        0.28388
     270 -> 274        0.16581

 Excited State  11:      Singlet-A      3.7711 eV  328.77 nm  f=2.4596
     260 -> 271        0.13617
     263 -> 271       -0.18000
     265 -> 271        0.11280
     268 -> 272        0.33021
     269 -> 273        0.34884
     270 -> 273        0.24432
     270 -> 275       -0.12926
```

TAA-Tips

(HOMO = MO 288; LUMO = MO 289)

```
Excited State   1:      Singlet-A      2.7164 eV  456.43 nm  f=0.0131
     286 -> 291        0.24514
     287 -> 290       -0.21951
     288 -> 289        0.59973

 Excited State   2:      Singlet-A      2.8424 eV  436.19 nm  f=0.0597
     286 -> 289       -0.22690
     287 -> 289        0.56174
     287 -> 290       -0.13683
     288 -> 290       -0.19717
     288 -> 291       -0.17762

 Excited State   3:      Singlet-A      2.8592 eV  433.64 nm  f=0.0360
     286 -> 289        0.56112
```

```
    287 -> 289        0.22586
    287 -> 290       -0.13532
    288 -> 290       -0.15585
    288 -> 291        0.23801

Excited State   4:      Singlet-A      3.3169 eV  373.79 nm  f=0.0113
    284 -> 290       -0.13074
    285 -> 291       -0.15180
    286 -> 290        0.38351
    286 -> 291        0.11144
    287 -> 290       -0.10912
    287 -> 291        0.40591
    288 -> 291       -0.18075
    288 -> 297       -0.10904

Excited State   5:      Singlet-A      3.3506 eV  370.04 nm  f=0.6795
    285 -> 289       -0.36979
    286 -> 291        0.17960
    287 -> 289        0.18569
    287 -> 290        0.26953
    288 -> 290        0.37314

Excited State   6:      Singlet-A      3.3865 eV  366.11 nm  f=0.6891
    284 -> 289        0.32907
    284 -> 290       -0.11704
    286 -> 289       -0.18188
    286 -> 290        0.29193
    288 -> 291        0.39709

Excited State   7:      Singlet-A      3.4570 eV  358.65 nm  f=1.1279
    281 -> 289        0.15302
    283 -> 290        0.10266
    285 -> 289        0.13002
    286 -> 291       -0.26353
    287 -> 290       -0.28916
    288 -> 290        0.38332
    288 -> 292        0.12996

Excited State   8:      Singlet-A      3.4854 eV  355.72 nm  f=0.4620
    276 -> 289       -0.15091
    281 -> 290       -0.10992
    282 -> 289        0.32885
    282 -> 291       -0.14095
    283 -> 291       -0.15419
    284 -> 289        0.13723
    285 -> 289        0.11928
    286 -> 290        0.18874
    287 -> 291       -0.25667
    288 -> 291       -0.20116

Excited State   9:      Singlet-A      3.5352 eV  350.71 nm  f=0.6046
    273 -> 289       -0.15355
    273 -> 290       -0.10309
    278 -> 289       -0.10283
    280 -> 289        0.16427
    281 -> 289       -0.21636
    281 -> 290       -0.18117
    282 -> 289        0.24399
    282 -> 290        0.14423
```

```
     283 -> 289       -0.20024
     286 -> 290       -0.16584
     287 -> 291        0.24547
     288 -> 291        0.14542

 Excited State  10:      Singlet-A      3.5772 eV  346.60 nm  f=0.7937
     273 -> 289        0.12780
     280 -> 289       -0.20327
     282 -> 289        0.16758
     282 -> 290       -0.12923
     282 -> 291       -0.17486
     283 -> 289        0.29091
     286 -> 290       -0.22754
     287 -> 291        0.25403
     288 -> 291        0.14370

 Excited State  11:      Singlet-A      3.6360 eV  340.99 nm  f=0.6576
     271 -> 289        0.10661
     274 -> 289        0.12195
     280 -> 291        0.10484
     281 -> 289        0.38598
     281 -> 291        0.13756
     282 -> 290       -0.11417
     283 -> 289       -0.13410
     286 -> 291        0.22305
     287 -> 290        0.16256
```

TAA-CF_3Ph

(HOMO = MO 294; LUMO = MO 295)

```
Excited State   1:      Singlet-A      2.9269 eV  423.61 nm  f=0.0032
     292 -> 297       -0.26963
     293 -> 296       -0.25810
     294 -> 295        0.58414

 Excited State   2:      Singlet-A      3.0439 eV  407.32 nm  f=0.0315
     292 -> 295       -0.16707
     292 -> 296       -0.12865
     293 -> 295        0.56460
     293 -> 297       -0.11885
     294 -> 296       -0.26940
     294 -> 297        0.12134

 Excited State   3:      Singlet-A      3.0565 eV  405.65 nm  f=0.0363
     292 -> 295        0.56099
     293 -> 295        0.16197
     293 -> 296       -0.16561
     294 -> 296       -0.12086
     294 -> 297       -0.27663

 Excited State   4:      Singlet-A      3.4812 eV  356.16 nm  f=0.0242
     286 -> 295        0.16465
     290 -> 296        0.13769
     291 -> 297       -0.16927
     292 -> 296       -0.36822
     293 -> 297        0.42621
     294 -> 296        0.11535
     294 -> 307        0.13166
```

```
Excited State   5:      Singlet-A      3.5151 eV  352.72 nm  f=0.4461
    286 -> 297        0.12860
    290 -> 296       -0.10245
    291 -> 295       -0.37550
    291 -> 296       -0.10014
    292 -> 296        0.21658
    293 -> 295        0.19837
    294 -> 296        0.38871

Excited State   6:      Singlet-A      3.5417 eV  350.07 nm  f=0.4491
    286 -> 296       -0.13331
    290 -> 295       -0.36730
    290 -> 296        0.11950
    292 -> 295        0.21005
    292 -> 296       -0.10446
    293 -> 296        0.11469
    294 -> 297        0.41521

Excited State   7:      Singlet-A      3.6847 eV  336.49 nm  f=1.6076
    288 -> 296        0.10402
    288 -> 297        0.10847
    289 -> 295        0.31925
    289 -> 296        0.10880
    291 -> 295        0.17915
    292 -> 296       -0.23123
    292 -> 297        0.12158
    293 -> 296       -0.12108
    293 -> 297       -0.25715

    294 -> 296        0.27839

Excited State   8:      Singlet-A      3.7237 eV  332.96 nm  f=2.3040
    288 -> 295        0.15324
    289 -> 295        0.14230
    289 -> 296        0.11694
    290 -> 295       -0.10921
    292 -> 297       -0.32625
    293 -> 296        0.36740
    293 -> 297       -0.11448
    294 -> 297       -0.25620

Excited State   9:      Singlet-A      3.7414 eV  331.38 nm  f=1.0557
    287 -> 295        0.10386
    287 -> 296       -0.10647
    288 -> 296        0.15522
    289 -> 295        0.38836
    289 -> 297        0.11806
    290 -> 295        0.10120
    292 -> 296        0.27106
    293 -> 297        0.27302
    294 -> 296       -0.13546
```

4. *Ionization energies (IE), Electron affinities (AE)*

Table S-E.1a: Total electronic energies of the neutral and charged systems used to calculate the IP, EA and internal reorganization energies for holes and electrons. All values are given in atomic units and are issued from B3LYP/6-31G(d) calculations in the gas phase.

compound	neutral (optimized)	anion (optimized)	cation (optimized)
TAN-Ph	-1895.362357	-1895.396003	-1895.114186
TAN-MePh	-2013.315957	-2013.348170	-2013.072927
TAA-Ph	-2356.275805	-2356.329814	-2356.050654
TAA-Tips	-3825.225748	-3825.294413	-3825.000768
TAA-OMePh	-3386.940213	-3386.996633	-3386.717890
TAA-tBuPh	-3299.804369	-3299.858166	-3299.582773

compound	anion (in the geometry of the neutral compound)	cation (in the geometry of the neutral compound)	neutral (in the geometry of the anion)	neutral (in the geometry of the cation)
TAN-Ph	-1895.394242	-1895.110397	-1895.360615	-1895.35765
TAN-MePh	-2013.346423	-2013.069302	-2013.314078	-2013.311643
TAA-Ph	-2356.328504	-2356.049940	-2356.274506	-2356.273467
TAA-Tips	-3825.291814	-3824.999355	-3825.224374	-3825.224270
TAA-OMePh	-3386.994908	-3386.715321	-3386.938495	-3386.936612
TAA-tBuPh	-3299.857166	-3299.581356	-3299.802454	-3299.803037

Table S-E.1b: Ionization energies (IE), Electron affinities (AE) and Internal Reorganization Energies (λi), for Hole (h) and Electron (e) Transport

Compounds	IE (eV)[a]	EA (eV)[a]	λ_h (eV)[b]	λ_e (eV)[b]
TAN-Ph	6.753	0.916	0.231	0.095
TAN-MePh	6.613	0.877	0.216	0.099
TAA-Ph	6.126	1.470	0.083	0.071
TAA-Tips	6.122	1.868	0.079	0.108
TAA-OMePh	6.049	1.535	0.168	0.094
TAA-tBuPh	6.030	1.464	0.075	0.079

a: calculated from differences in the total energies of the charged and neutral molecules in their optimized geometries. b: calculated using the four point adiabatic potential approach (see ESI section 5 for details).

5. *Transfer integrals*

Table S-E.2. Transfer integrals (with absolute values larger than 2 meV) between a reference molecule (i) and its first neighbors (j), calculated for holes (h) and electrons (e) at the B3LYP/6-31G(d) level.

Compound	Direction[a]	d_{i-j} (Å)[b]	J_h (meV)[c]	J_e (meV)[c]	Dimer relation[d]
TAN-Ph	(0.52, 0.02, 0.13)	5.853	12 (68)	67	$\bar{1}$
P$\bar{1}$	(-0.48, 0.02, 0.13)	6.075	15 (24)	5	$\bar{1}$
	(-0.52, -1.02; -0.12)	10.888	0	2	$\bar{1}$
	±(0, 0, 1)	13.640	7 (10)	5	1
	(-0.52, -1.02, -1.13)	13.721	1 (4)	2	$\bar{1}$
	±(1, 1, 0)	13.777	1 (9)	2	1
	±(1, 1, 1)	13.748	7 (6)	2	1
TAN-MePh	(0.02, 0.03, 0.46)	6.162	15	3	$\bar{1}$
P$\bar{1}$	(0.02, 0.03,-0.53)	7.272	15	47	$\bar{1}$
	(0.02, -0.96, -0,53)	12.952	8	3	$\bar{1}$
	(0.02, 1.03, 0.46)	13.181	7	14	$\bar{1}$
	(1.02, 0.03, -0.53)	13.812	13	1	$\bar{1}$
	±(1, 1, 0)	13.907	0	6	1
	(1.02, 1.03, 0.46)	14.540	6	1	$\bar{1}$
TAA-Ph	(0, 0, -0.45)	4.194	39	72	A→B
R3	(0, 0, 0.55)	5.177	8	8	A→B
	(-2/3, -1/3, 0.22)	15.660	0	12	A→B
	(1/3, 2/3, 0.22)	15.660	0	12	A→B
	(1/3, -1/3, 0.22)	15.660	0	12	A→B
	±(-1/3, 1/3, 1/3)	15.836	10	6	1
	±(-1/3, -2/3, 1/3)	15.836	10	6	1
	±(2/3, 1/3, 1/3)	15.836	10	6	1
TAA-Tips	(0.09, 0.22, -0.22)	7.881	7	90	$\bar{1}$
P2_1/n	(-0.41, ±1/2, 0.28)	13.131	0	2	2_1
	(0.09, 1.22, -0.22)	14.792	2	9	$\bar{1}$
	(0.59, ± 1/2, 0.28)	15.036	3	2	$2_{/1}$
TAA-OMePh	(-0.43, 0.61, -1/3)	9.522	23	85	$\bar{1}$
P$\bar{1}$	(0.57, -0.39, -1/3)	10.464	39	85	$\bar{1}$
	-(0.43, -0.39, -1/3)	11.771	2	1	$\bar{1}$
	(-0.43, -0.39, 2/3)	11.933	7	41	$\bar{1}$
	(0.57, 0.61, -1/3)	12.150	1	1	1
	±(0, 1, 0)	15.712	5	3	1
	±(0, 0,1)	16.961	4	7	1
	±(0, -1, 1)	18.432	3	0	
TAA-tBuPh					
P$\bar{1}$	(-0.46, -0.96, -0.94)	15.902	3	3	$\bar{1}$

[a] Crystallographic directions corresponding to intermolecular vectors joining one central molecule with its neighbours are given in the basis of direct lattice vectors. [b] d_{i-j} is the distance (in Å) between the centers of mass of molecules i and j. [c] values in parentheses are calculated using equation SI5 accounting for the close degeneracy of the two highest occupied MOs. [d] Symmetry relationship linking molecules i and j. When i and j possess identical geometry, symmetry operations are given, otherwise dimers are described as A→B. B→B dimers do not have close contacts, so that all integral transfers for those dimers are negligible.

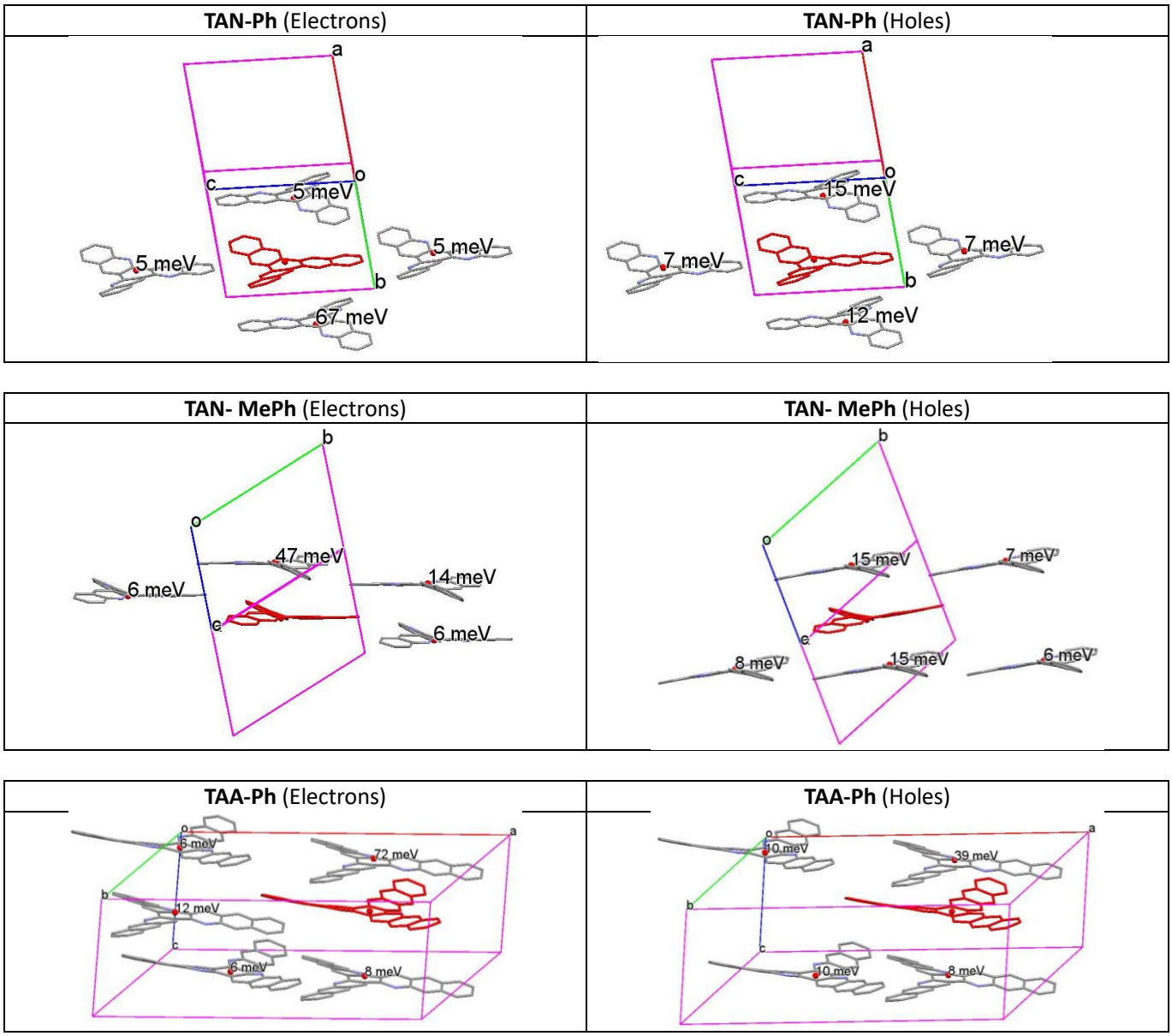


Figure S-E.10. Molecular packing within the investigated crystals, with values of the main electron and hole transfer integrals between the reference molecule (in red) and its first neighbors for TAN-Ph, TAN-PhMe an TAA-Ph. Lattice vectors a, b and c are represented in red, green and blue, respectively. In all structures, lateral substituents and hydrogen atoms have been omitted for clarity.

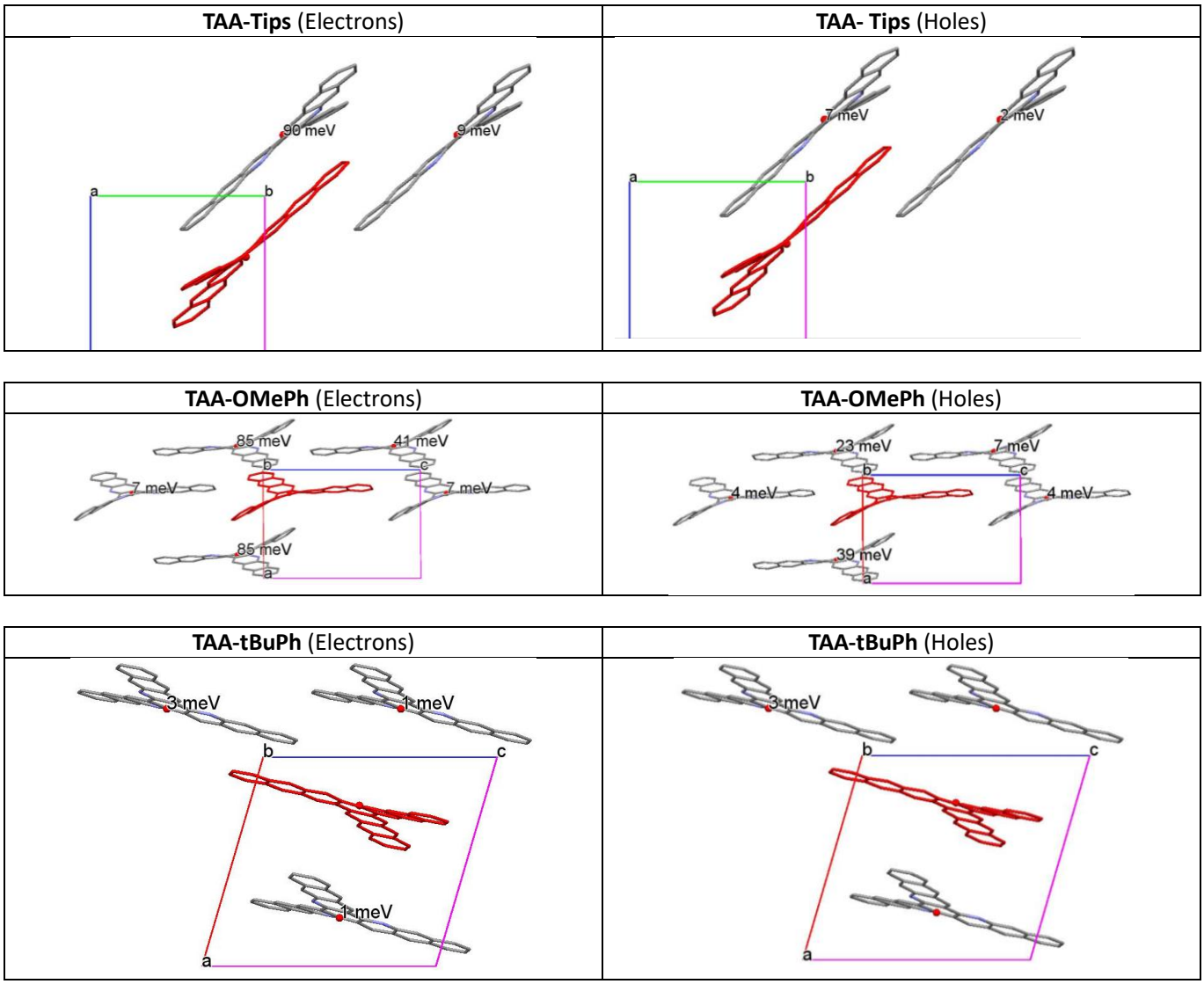


Figure S-E.11. Molecular packing within the investigated crystals, with values of the main electron and hole transfer integrals between the reference molecule (in red) and its first neighbors for TAA-Tips, TAA-OMePh and TAAtBuPh. Lattice vectors a, b and c are represented in red, green and blue, respectively. In all structures, lateral substituents and hydrogen atoms have been omitted for clarity.

6. *Molecular structures*

TAN-Ph

No imaginary frequency
Energies (in atomic units):
Electronic energy = -1895.36235747
Zero-point correction= 0.587338
Thermal correction to Energy= 0.621996
Thermal correction to Enthalpy= 0.622940
Thermal correction to Gibbs Free Energy= 0.515976
Sum of electronic and zero-point Energies= -1894.775019
Sum of electronic and thermal Energies= -1894.740361
Sum of electronic and thermal Enthalpies= -1894.739417
Sum of electronic and thermal Free Energies= -1894.846381
Cartesian coordinates (in Angströms):

N	-0.71886500	-2.69736500	0.00232200
N	2.65463600	0.67357900	0.40521500
N	-1.90953500	1.91998900	-0.46378500
C	0.37545300	1.39881700	-0.00541100
C	0.19875800	-3.68495300	-0.06168400
C	2.13458300	3.04861000	0.36423700
C	0.76180600	2.74378300	0.10903700
C	-3.72293200	0.31813000	-0.22675400
C	-1.40287800	-0.40915700	-0.01833000
C	1.39368000	0.38949500	0.13360600
C	2.02138300	-2.05115700	-0.13436200
C	1.05249600	-1.04407200	-0.00196400
C	1.59851100	-3.41589100	-0.16437000
C	-3.22684300	1.62775300	-0.51050900
C	-2.77166500	-0.72184800	0.01186100
C	3.04727700	1.96023500	0.51754200
C	-1.03108500	0.97349700	-0.18899700
C	3.48921100	-1.80111800	-0.30692000
C	-0.33385100	-1.43411800	0.02054800
C	-0.16637900	3.91846400	0.01752500
C	2.63943200	4.37490700	0.49775100
H	1.96234700	5.21340500	0.38554400
C	4.38833600	-2.03575000	0.74236600
H	4.00643500	-2.32707300	1.71692500
C	-3.33032400	-2.07980000	0.31199600
C	-4.13363900	2.68066100	-0.81482700
H	-3.71292700	3.65885000	-1.02500900
C	2.01016800	-5.81169200	-0.29661100
H	2.70378300	-6.64224900	-0.39624900
C	2.48817900	-4.52132800	-0.29893000
H	3.55125800	-4.33721400	-0.39903000
C	-0.26755300	-5.02933300	-0.05801400
H	-1.33779400	-5.18756200	0.02968100
C	5.76010200	-1.87585500	0.54956200
H	6.44362200	-2.05384900	1.37600000
C	-5.48829900	2.44900400	-0.81430600
H	-6.18089100	3.25523300	-1.04102500
C	-3.43621400	-2.51631400	1.63903200
H	-3.04328000	-1.89416900	2.43859600
C	3.97104100	4.59547500	0.76548400
H	4.33870700	5.61346200	0.86227900

C	-0.32373400	4.60848000	-1.19173700
H	0.16677000	4.23573200	-2.08673900
C	-1.58358900	5.56321100	1.10398400
H	-2.06568500	5.93432400	2.00478500
C	0.62191800	-6.07089700	-0.16847300
H	0.26492400	-7.09737600	-0.16599500
C	4.41829200	2.21726600	0.79738000
H	5.07705500	1.36082000	0.89967400
C	4.87024100	3.50946200	0.91677100
H	5.91859100	3.70495300	1.12611900
C	-5.99041200	1.15986600	-0.50371400
H	-7.06382000	0.99102500	-0.49188300
C	-4.44805600	-4.11025900	-0.41123500
H	-4.84666300	-4.72399000	-1.21512900
C	-5.13461500	0.12182000	-0.21391400
H	-5.53163400	-0.85831800	0.02211100
C	-3.86272700	-2.87971100	-0.70806300
H	-3.79955200	-2.54233000	-1.73895300
C	-1.11858600	5.75240200	-1.25628300
H	-1.23635700	6.27260900	-2.20356200
C	3.99502000	-1.44149800	-1.56284100
H	3.30758300	-1.27670600	-2.38819600
C	-0.78562800	4.42074400	1.16927700
H	-0.65144300	3.90520400	2.11643500
C	-4.02532700	-3.74489800	1.93635500
H	-4.09414500	-4.07187300	2.97073500
C	-1.75711900	6.23152800	-0.10951900
H	-2.37461400	7.12449200	-0.15939700
C	6.25544800	-1.49404100	-0.69995200
H	7.32480300	-1.37255600	-0.85103800
C	-4.52810900	-4.55031800	0.91229300
H	-4.98883600	-5.50692700	1.14426300
C	5.36744500	-1.28212900	-1.75590000
H	5.74281900	-0.99617200	-2.73510800

TAN-MePh

No imaginary frequency
Energies (in atomic units):
Electronic energy = -2013.31595666
Zero-point correction= 0.669843 (Hartree/Particle)
Thermal correction to Energy= 0.710247
Thermal correction to Enthalpy= 0.711191
Thermal correction to Gibbs Free Energy= 0.590075
Sum of electronic and zero-point Energies= -2012.646114
Sum of electronic and thermal Energies= -2012.605710
Sum of electronic and thermal Enthalpies= -2012.604765
Sum of electronic and thermal Free Energies= -2012.725881
Cartesian coordinates (in Angströms):

N	-1.13398800	2.43813200	-0.52801900
N	2.68358100	-0.28489000	0.55992100
N	-1.59556900	-2.30602400	-0.14376900
C	-0.80807200	-1.24980300	-0.04824600
C	3.00760100	2.12543600	0.52978100
C	-0.63858200	1.25192100	-0.22741700
C	1.20748800	-2.62170100	-0.15024400
C	0.62768700	-1.35177300	-0.00546500

C	0.81909500	1.17473400	0.02399900
C	1.63239900	2.30778200	0.18458000
C	1.42364700	-0.12120900	0.19904200
C	3.48117000	0.79190600	0.72551900
C	-1.46357700	0.07844200	-0.08006700
C	1.16910700	3.72793100	0.05555800
C	-3.39064800	1.55154300	-0.33653000
C	-3.84400500	-0.83272100	0.23177000
C	-1.06086500	-3.54307300	-0.21963200
C	2.67969600	-2.87323200	-0.26745100
C	-2.47079100	2.60910000	-0.61536400
C	0.70609300	4.42996200	1.17481100
H	0.60722100	3.91553800	2.12702500
C	-2.85720400	0.25100400	-0.07472000
C	0.35108200	-3.76110900	-0.25616900
C	1.30614000	4.41938800	-1.15417800
H	1.67338900	3.89470000	-2.03200800
C	4.83401700	0.56740400	1.10382400
H	5.15114600	-0.46201200	1.23687000
C	3.40680000	-3.43925400	0.78725200
H	2.91298600	-3.62803200	1.73656800
C	-2.95675400	3.90302800	-0.95102300
H	-2.22211800	4.67476400	-1.15788400
C	5.43037700	-3.49378300	-0.56776000
C	-5.81483800	-2.77173500	0.86157400
C	3.33867800	-2.64570500	-1.48185900
H	2.78955500	-2.21936500	-2.31724500
C	-4.64944100	-1.38844100	-0.76990500
H	-4.50612800	-1.08306300	-1.80281900
C	-4.05511400	-1.23824600	1.55565800
H	-3.44829200	-0.81049400	2.34924600
C	3.92524900	3.19999900	0.71596200
H	3.58442700	4.21813100	0.56969000
C	5.23015800	2.95455000	1.07748400
H	5.91619000	3.78625000	1.21369800
C	0.82176500	-5.09766600	-0.40892100
H	1.88855000	-5.28075000	-0.45965300
C	5.69090300	1.62806700	1.27465000
H	6.72552100	1.45515000	1.55896000
C	-0.06223300	-6.14948000	-0.48587100
H	0.31528500	-7.16232000	-0.59793300
C	4.76074500	-3.73524800	0.63961200
H	5.30684400	-4.16397700	1.47753500
C	-4.30870000	4.14857400	-0.98172500
H	-4.67906700	5.13916500	-1.23220100
C	-4.78386300	1.85128400	-0.35130700
H	-5.49634900	1.07007800	-0.11441700
C	0.46618200	6.46754300	-0.13749900
C	-1.46131500	-5.92699500	-0.42402600
H	-2.14295600	-6.77135200	-0.48419100
C	-5.02032400	-2.19522300	1.86149700
H	-5.15975200	-2.49914200	2.89694600
C	0.35036800	5.77416000	1.07401600
H	-0.02007900	6.29442000	1.95493500
C	4.69266300	-2.94462400	-1.62405500
H	5.18391100	-2.74964000	-2.57513700
C	-5.60999800	-2.34964200	-0.45882400
H	-6.21390900	-2.77705200	-1.25673700
C	-5.22734900	3.11460700	-0.67000000

H	-6.29370700	3.32367700	-0.67988600
C	0.95298000	5.76423600	-1.24800500
H	1.05939200	6.27773100	-2.20148500
C	-1.95199500	-4.64960200	-0.29871900
H	-3.01583900	-4.43776000	-0.25980300
C	0.11609100	7.93475400	-0.23413900
H	0.97990700	8.56977200	0.00561600
H	-0.68489100	8.20296700	0.46336200
H	-0.21158100	8.20359700	-1.24423800
C	6.88995200	-3.84765900	-0.73650800
H	7.42246800	-3.82120300	0.22029800
H	7.39341900	-3.15757700	-1.42241600
H	7.01227400	-4.85894400	-1.14785700
C	-6.88237300	-3.78599600	1.20194700
H	-6.58369200	-4.41466500	2.04804900
H	-7.09710300	-4.44297000	0.35228300
H	-7.82573300	-3.29677300	1.48046600

TAA-Ph

No imaginary frequency
Energies (in atomic units):
Electronic energy = -2356.27580455
Zero-point correction= 0.727021 (Hartree/Particle)
Thermal correction to Energy= 0.769949
Thermal correction to Enthalpy= 0.770894
Thermal correction to Gibbs Free Energy= 0.646359
Sum of electronic and zero-point Energies= -2355.548783
Sum of electronic and thermal Energies= -2355.505855
Sum of electronic and thermal Enthalpies= -2355.504911
Sum of electronic and thermal Free Energies= -2355.629446
Cartesian coordinates (in Angströms):

N	2.30247100	-1.57376500	0.11718500
C	3.54902000	-1.04378100	0.00475600
C	3.75778500	0.36407400	-0.21046000
C	2.59876900	1.21711700	-0.23096500
C	2.83934400	2.66654300	-0.52249900
C	2.61369800	3.16694200	-1.81139400
H	2.20070100	2.51184900	-2.57374500
C	2.90382900	4.49695500	-2.11719200
H	2.71665900	4.87079800	-3.12051200
C	3.43666200	5.34226600	-1.14281800
H	3.66491200	6.37760400	-1.38175800
C	3.68477600	4.84463400	0.13912300
H	4.10831500	5.49198000	0.90299600
C	3.39537500	3.51531900	0.44481700
H	3.58332900	3.13370200	1.44450800
C	1.33918400	0.64919400	-0.03773800
C	1.24672400	-0.79285400	0.08958000
C	5.07075400	0.82542600	-0.39297800
H	5.24877400	1.87921400	-0.57664700
C	6.16929000	-0.04200000	-0.33514400
C	5.95313500	-1.44997300	-0.09106700
C	4.64425900	-1.91603700	0.06647300
H	4.44351300	-2.96999400	0.23551700
C	7.08835400	-2.31777200	-0.03097900
H	6.92188300	-3.37615700	0.15355600
C	8.35636900	-1.82857800	-0.20254100

H	9.21056200	-2.49862800	-0.15450900
C	8.57028600	-0.43927600	-0.44604400
H	9.58375400	-0.07109700	-0.58022500
C	7.50945600	0.42517500	-0.51035500
H	7.66863500	1.48479900	-0.69529900
N	-2.42056800	-1.18580000	-0.49604300
C	-2.59206600	-2.53395200	-0.44062400
C	-1.54029300	-3.41149400	0.00182600
C	-0.24646900	-2.83279900	0.25496100
C	0.82815400	-3.77003300	0.71136800
C	1.41723000	-4.68080400	-0.17649600
H	1.14091300	-4.65696300	-1.22693500
C	2.36962600	-5.59447000	0.27398900
H	2.82560700	-6.28657500	-0.42951600
C	2.73222600	-5.62535600	1.62290400
H	3.47045100	-6.34105600	1.97506100
C	2.12900400	-4.73938500	2.51784500
H	2.39506300	-4.76318800	3.57148400
C	1.18063900	-3.82197700	2.06645200
H	0.71611300	-3.13169400	2.76530900
C	-0.07944800	-1.45614500	0.09466000
C	-1.25759600	-0.65660600	-0.19491300
C	-1.82442800	-4.77909800	0.13878400
H	-1.05461100	-5.45440600	0.49536800
C	-3.08211700	-5.30451100	-0.18587700
C	-4.12064100	-4.42173400	-0.66589800
C	-3.84879400	-3.05408000	-0.77558100
H	-4.61573200	-2.35723800	-1.10080400
C	-5.39585800	-4.97853600	-0.99532300
H	-6.17484000	-4.31123500	-1.35564300
C	-5.63241100	-6.32120000	-0.85985100
H	-6.60583100	-6.73183700	-1.11432300
C	-4.60835000	-7.19292700	-0.38433500
H	-4.81599100	-8.25468700	-0.28319200
C	-3.37310300	-6.69860100	-0.05741400
H	-2.58985500	-7.36004600	0.30503700
N	0.25063100	2.73774700	0.30068400
C	-0.83811200	3.54988500	0.36299300
C	-2.17251800	3.04249400	0.18358400
C	-2.33220600	1.62784200	-0.02922600
C	-3.74511200	1.13853000	-0.13644500
C	-4.41704600	1.16793800	-1.36569800
H	-3.87958200	1.46900200	-2.26065900
C	-5.75825500	0.79550600	-1.44852600
H	-6.26394500	0.81767400	-2.41062700
C	-6.45103100	0.39966700	-0.30140200
H	-7.49692500	0.11123800	-0.36572500
C	-5.79387900	0.39132900	0.93031400
H	-6.32641400	0.09601400	1.83070700
C	-4.45335800	0.76873700	1.01421400
H	-3.94670100	0.76412700	1.97552600
C	-1.19545600	0.82019600	-0.08564500
C	0.10094900	1.45515900	0.06085500
C	-3.24635800	3.94386500	0.25209300
H	-4.25985000	3.58179600	0.11918500
C	-3.04502800	5.30981500	0.48901000
C	-1.70169400	5.81091800	0.67081300
C	-0.63062800	4.91430400	0.60462800
H	0.39254500	5.25713100	0.72710600

C	-1.51766300	7.20878000	0.91018700
H	-0.50565200	7.58225000	1.04546800
C	-2.59046500	8.05872700	0.96820600
H	-2.43706400	9.11885900	1.15123700
C	-3.91681600	7.56464900	0.78988600
H	-4.75440000	8.25504400	0.83975000
C	-4.13553800	6.23237900	0.55753100
H	-5.14502700	5.85212500	0.42096200

TAA-tBuPh

No imaginary frequency
Energies (in atomic units):
Electronic energy = -3299.80437280
Zero-point correction= 1.404666
Thermal correction to Energy= 1.481420
Thermal correction to Enthalpy= 1.482364
Thermal correction to Gibbs Free Energy= 1.284034
Sum of electronic and zero-point Energies= -3298.399707
Sum of electronic and thermal Energies= -3298.322953
Sum of electronic and thermal Enthalpies= -3298.322009
Sum of electronic and thermal Free Energies= -3298.520339
Cartesian coordinates (in Angströms):

N	-1.72456500	2.04623700	0.59100500
N	2.75247900	0.58377400	-0.25699900
N	-0.82759200	-2.56993500	-0.43894800
C	-3.05266100	1.81641600	0.76914000
C	-3.86289100	2.89224500	1.15596700
H	-3.38705100	3.85814000	1.29813400
C	-5.24103000	2.73577300	1.33576200
C	-6.09169000	3.81726100	1.72567700
H	-5.64475200	4.79481200	1.88941200
C	-7.43844600	3.62798400	1.89059400
H	-8.07345800	4.45819600	2.18802000
C	-8.02134500	2.34391900	1.67501800
H	-9.09157200	2.21424500	1.81098800
C	-7.24101300	1.28225400	1.29978100
H	-7.68161300	0.30200000	1.13440900
C	-5.83093900	1.43466100	1.11661000
C	-5.01497600	0.36239600	0.73323600
H	-5.46971100	-0.60896700	0.57305600
C	-3.63131700	0.51718300	0.55436000
C	-2.74988200	-0.56281600	0.19534200
C	-1.38737400	-0.29947600	0.03943100
C	-0.93331700	1.06901000	0.21169400
C	1.46790300	0.35815600	-0.10011600
C	0.48291300	1.42142600	-0.04267100
C	0.91489900	2.73543300	-0.23108400
C	2.32167800	2.98632300	-0.40576800
C	2.86772300	4.26355700	-0.60810700
H	2.21154800	5.12571800	-0.65100300
C	4.24768500	4.45977200	-0.74911800
C	4.80886600	5.76035700	-0.94576300
H	4.13617300	6.61362400	-0.98802300
C	6.16183700	5.93114600	-1.07645600
H	6.57522100	6.92506200	-1.22458800
C	7.04039000	4.80857000	-1.01939300

H	8.11075000	4.96394200	-1.12500500
C	6.54408800	3.54523800	-0.83434900
H	7.21101000	2.68757300	-0.79211100
C	5.13822400	3.32280600	-0.69416100
C	4.59457700	2.04680100	-0.51710900
H	5.23166500	1.16775300	-0.48265400
C	3.21254100	1.85644700	-0.38116700
C	-0.37823600	-1.36136400	-0.19195900
C	1.03773100	-1.06022200	-0.06539700
C	1.93422400	-2.12943400	-0.01332100
C	1.43415800	-3.46602000	-0.20559500
C	2.23897200	-4.61494200	-0.15767500
H	3.29405800	-4.52038400	0.07384900
C	1.71658700	-5.88989200	-0.41230700
C	2.53420300	-7.06234100	-0.37209200
H	3.58925800	-6.95002300	-0.13397500
C	2.00452800	-8.29964600	-0.62824200
H	2.63733600	-9.18234600	-0.59527400
C	0.61988200	-8.44170500	-0.94013400
H	0.21768400	-9.43115200	-1.14056100
C	-0.19902600	-7.34433900	-0.98691000
H	-1.25521600	-7.44972700	-1.22215400
C	0.31341700	-6.03485400	-0.72622400
C	-0.49623800	-4.89426600	-0.74779300
H	-1.56093600	-4.96930300	-0.94938000
C	0.03067700	-3.62347500	-0.48125200
C	-3.39418600	-1.90799500	0.04225400
C	-3.95207100	-2.28096400	-1.17883000
H	-3.84000200	-1.61238100	-2.02736300
C	-4.62576100	-3.50398900	-1.32767900
C	-4.73140700	-4.32870400	-0.20290600
H	-5.24757400	-5.27733700	-0.29253000
C	-4.20410500	-3.97024000	1.05238700
C	-3.54684100	-2.74347700	1.15791900
H	-3.12287000	-2.42257300	2.10229600
C	-5.21919600	-3.88227700	-2.69889700
C	-5.91080100	-5.25871600	-2.68444400
H	-6.74819400	-5.28872700	-1.97798800
H	-5.21370200	-6.06316200	-2.42312200
H	-6.31146400	-5.48014200	-3.68017600
C	-6.26832800	-2.82305800	-3.11347500
H	-7.08933600	-2.78044900	-2.38834300
H	-6.69395100	-3.06945000	-4.09415100
H	-5.83109100	-1.82164400	-3.18184700
C	-4.09085500	-3.92415300	-3.75679200
H	-4.49976100	-4.18460600	-4.74097800
H	-3.33438400	-4.67250400	-3.49403000
H	-3.58290000	-2.95910900	-3.85094700
C	-4.37095300	-4.92775700	2.24843500
C	-5.87651800	-5.15202900	2.52666000
H	-6.37351400	-4.20694500	2.77444800
H	-6.01093600	-5.83801900	3.37217200
H	-6.39203700	-5.58394400	1.66240800
C	-3.70353400	-6.28450300	1.91886800
H	-3.81038300	-6.97749200	2.76264400
H	-2.63412200	-6.15575100	1.71714500
H	-4.15552100	-6.75857200	1.04107400
C	-3.72416600	-4.37913200	3.53452100
H	-4.17392400	-3.42911100	3.84481300

H	-2.64613600	-4.22449800	3.41391400
H	-3.86636700	-5.09428200	4.35275200
C	3.40013300	-1.99665400	0.26335600
C	4.33754500	-2.20815000	-0.75903600
H	3.97026700	-2.40096600	-1.76017200
C	5.70805900	-2.14646100	-0.50290000
C	6.11933900	-1.88046500	0.81736100
H	7.18160500	-1.83196100	1.02631200
C	5.21271000	-1.69026000	1.86456600
C	3.84334900	-1.76283800	1.56365700
H	3.10427900	-1.61805500	2.34624300
C	6.76810500	-2.36594600	-1.60039900
C	6.13796900	-2.64386400	-2.97850400
H	5.51546800	-1.80853800	-3.31812100
H	5.52005500	-3.54885400	-2.96972500
H	6.92870900	-2.79135600	-3.72293600
C	7.65547300	-3.57709700	-1.22590100
H	7.05463000	-4.48984600	-1.13949700
H	8.17194700	-3.42623200	-0.27221400
H	8.41853800	-3.74492000	-1.99602200
C	7.65426800	-1.10375300	-1.72617400
H	8.42139700	-1.25031800	-2.49662700
H	8.16653900	-0.86872400	-0.78720500
H	7.05282300	-0.23196900	-2.00942900
C	5.65789200	-1.40807600	3.31257800
C	7.19041600	-1.35346700	3.45956100
H	7.66233400	-2.30271000	3.18101100
H	7.45313200	-1.14875600	4.50362600
H	7.63135100	-0.55869600	2.84707300
C	5.12677300	-2.52536500	4.24200300
H	4.03417700	-2.59205700	4.21660700
H	5.42528900	-2.33300900	5.28001500
H	5.52781300	-3.50258100	3.94897300
C	5.08365300	-0.04578600	3.76952400
H	5.44062100	0.76570500	3.12534600
H	5.39343800	0.17312600	4.79895800
H	3.98935400	-0.03451000	3.74106500
C	0.00863800	3.92550700	-0.31877400
C	-0.05367500	4.85014400	0.72804400
H	0.51330900	4.64779200	1.63186900
C	-0.84306600	6.00275900	0.63401000
C	-1.56449300	6.20846300	-0.55226200
H	-2.18012300	7.09282900	-0.64130700
C	-1.50782400	5.31291100	-1.63038800
C	-0.70073200	4.17634600	-1.49599500
H	-0.62824500	3.45845300	-2.30783500
C	-2.29498100	5.53561100	-2.93688900
C	-3.25900700	4.34619300	-3.16239500
H	-2.72042700	3.39704500	-3.25004600
H	-3.83442500	4.49034600	-4.08534200
H	-3.96536800	4.25090900	-2.33008300
C	-1.30843400	5.62786300	-4.12519700
H	-0.62009300	6.47156600	-3.99868800
H	-1.85503600	5.77336200	-5.06522300
H	-0.70653600	4.71901800	-4.22735200
C	-3.13150200	6.82909300	-2.91052600
H	-3.87817500	6.81654000	-2.10839100
H	-3.66923700	6.93867700	-3.85917300
H	-2.50528700	7.71941600	-2.78203600

C	-0.88211800	6.99670200	1.81243400
C	-1.81060700	8.19660600	1.54443000
H	-1.48611200	8.77990200	0.67521900
H	-1.80557800	8.86693300	2.41149100
H	-2.84694800	7.88153900	1.37689900
C	0.54336100	7.54219100	2.06856200
H	1.24900200	6.74041100	2.30951200
H	0.53873700	8.24712400	2.90918700
H	0.92445600	8.06950900	1.18619100
C	-1.38728400	6.27650200	3.08503500
H	-2.40356200	5.89154900	2.94072300
H	-1.40564800	6.97015100	3.93484100
H	-0.74827800	5.43081600	3.35803600

TAA-OMePh

No imaginary frequency
Energies (in atomic units):
Electronic energy = -3386.94021309
Zero-point correction= 1.019443
Thermal correction to Energy= 1.087450
Thermal correction to Enthalpy= 1.088394
Thermal correction to Gibbs Free Energy= 0.905323
Sum of electronic and zero-point Energies= -3385.920770
Sum of electronic and thermal Energies= -3385.852763
Sum of electronic and thermal Enthalpies= -3385.851819
Sum of electronic and thermal Free Energies= -3386.034890
Cartesian coordinates (in Angströms):

O	3.50851700	-6.95201100	-0.28555800
O	3.40706800	4.79943600	3.25969700
O	2.10897900	-6.20448000	-2.44716200
O	4.24773700	5.66269000	-1.26009900
O	3.26833200	-5.66365200	2.05194000
O	-7.63307300	0.03682000	-1.14011800
O	4.28505900	6.41824300	1.31002700
O	-6.98945100	1.09139500	1.25132400
O	-5.64966900	-0.33695000	-3.08846300
N	0.32233000	2.80044000	-0.03540700
N	-2.47541000	-1.00537300	0.60003700
N	2.16702600	-1.58702500	-0.53443900
C	2.64677800	1.14782300	0.01217900
C	0.13674400	1.50084400	0.01137000
C	-1.53151100	5.94026200	-0.34170700
C	-0.74198000	3.63906200	-0.14597900
C	1.86445400	-5.50954300	-1.29859700
C	3.81760500	5.16836600	0.98656900
C	3.39054700	4.28684400	1.99509100
C	2.63950100	-5.89289700	-0.18940900
C	-1.18180300	0.89659500	-0.00667800
C	1.34580700	0.64207400	-0.01800600
C	-2.28719900	1.72214300	-0.21023800
C	-0.31650300	-2.79468000	0.19677200
C	-3.68314700	1.22257300	-0.42215100
C	3.00228500	2.56594100	0.33812200
C	-1.61521600	-3.29432200	0.56476400
C	-2.87926900	5.45021200	-0.52138200
C	-0.49494200	5.01843300	-0.16548000

H	0.53280000	5.34974200	-0.04789600
C	-0.14363800	-1.41905100	0.03675600
C	0.76129100	-3.82639300	0.04572900
C	0.91676400	-4.48662500	-1.17671400
H	0.31892100	-4.17842000	-2.02545800
C	3.83014400	4.73459600	-0.35110900
C	-1.29957500	-0.56172700	0.21740800
C	1.17593100	-0.78966400	-0.21035400
C	2.46588600	-5.22951300	1.03758700
C	-2.08667100	3.14513800	-0.28762100
C	-3.12132700	4.07052700	-0.49441900
H	-4.13744100	3.71646100	-0.62897500
C	3.44192400	3.42854000	-0.67153500
H	3.44516900	3.08441000	-1.69829400
C	-5.97498100	0.98868100	0.34211600
C	1.51310600	-4.21052500	1.15990400
H	1.36645700	-3.69770300	2.10256400
C	-4.21698200	-4.13149300	1.37184100
C	-1.89560300	-4.65666100	0.75379200
H	-1.11422000	-5.39094800	0.59228500
C	3.74601900	0.25931000	-0.26224400
C	2.99511600	2.98366400	1.67222400
H	2.66055200	2.29794300	2.44085500
C	6.12388400	-0.23009100	-0.58098900
C	-4.66059300	1.40201100	0.56880100
H	-4.37316200	1.83296700	1.52006200
C	-2.66932200	-2.33932900	0.78106600
C	-1.30637400	7.35238100	-0.36573500
H	-0.29119800	7.71736600	-0.22998300
C	-4.03940700	0.67620700	-1.65481000
H	-3.30711000	0.54150000	-2.44385000
C	-3.93172100	6.39762900	-0.72083600
H	-4.94430700	6.02589300	-0.85843000
C	-3.67403100	7.74308200	-0.73790200
H	-4.48309900	8.45229000	-0.88983400
C	5.80239100	-1.58842100	-0.95530700
C	1.35324900	-5.87269100	-3.60093900
H	0.27919000	-6.03406000	-3.44040900
H	1.70411700	-6.54230600	-4.38852900
H	1.51803900	-4.83152000	-3.90845500
C	-2.34395600	8.22617400	-0.55706600
H	-2.15927800	9.29692600	-0.57347700
C	-3.16502500	-5.09733100	1.14940100
C	5.09232800	0.65545900	-0.24178000
H	5.34712300	1.67281000	0.03347500
C	-6.33167800	0.41106000	-0.89535200
C	-6.69649900	1.66646800	2.51494700
H	-5.94249400	1.08382300	3.06062500
H	-7.63539200	1.65565800	3.07173900
H	-6.34634600	2.70219500	2.41492000
C	-3.93930600	-2.77423400	1.18205100
H	-4.70877700	-2.02212500	1.32911000
C	3.43768000	-1.10574800	-0.59734300
C	3.14390900	-5.03493700	3.31702100
H	3.37261100	-3.96241100	3.26101700
H	3.87159400	-5.52622400	3.96579800
H	2.13791100	-5.16701500	3.73685000
C	4.46335400	-1.99278100	-0.94832700
H	4.18800100	-3.01492000	-1.19129500

C	-5.35515200	0.26274900	-1.88735700
C	6.86937700	-2.47484700	-1.30242000
H	6.62372200	-3.49603500	-1.58346000
C	-3.45567900	-6.48416900	1.34291300
H	-2.66188500	-7.20799500	1.17500800
C	8.17150200	-2.04918400	-1.28095700
H	8.97310500	-2.73283600	-1.54736300
C	-5.74192000	-5.94041200	1.94978700
H	-6.72568400	-6.28497100	2.25712400
C	4.83445200	-6.59627000	-0.67078700
H	4.84657500	-6.14061500	-1.66971600
H	5.40812200	-7.52643300	-0.69351500
H	5.28736300	-5.90935200	0.05547600
C	7.49643200	0.17100300	-0.56959000
H	7.73515700	1.19315100	-0.28576300
C	-5.50559700	-4.60230000	1.77555600
H	-6.29502300	-3.87327400	1.94187700
C	-7.97878700	-1.25315300	-0.62940500
H	-7.33601900	-2.03021600	-1.06092000
H	-9.01573400	-1.43127100	-0.92480000
H	-7.90454000	-1.27412100	0.46429000
C	-4.70389800	-6.89423800	1.73091800
H	-4.91155100	-7.95105000	1.87445200
C	4.28934300	5.28548600	-2.62687400
H	4.98318800	4.45130800	-2.79514200
H	4.64613800	6.16461900	-3.16688700
H	3.29538500	5.00712000	-3.00150400
C	2.99145700	3.96078700	4.32511900
H	1.94800300	3.64013300	4.20588800
H	3.08319500	4.56334900	5.23083400
H	3.63231800	3.07368700	4.41433500
C	8.48983000	-0.70930000	-0.90932000
H	9.52878200	-0.39140700	-0.89754800
C	3.28148100	7.42965600	1.36567000
H	2.79770700	7.55955700	0.38834500
H	3.79342100	8.35603700	1.63855600
H	2.52481700	7.19637600	2.12511500
C	-6.53300400	0.39339300	-3.94485700
H	-7.51068500	0.54030300	-3.47711400
H	-6.64135700	-0.20966300	-4.84958800
H	-6.09944800	1.36719600	-4.20978900

TAA-Tips

No imaginary frequency
Energies (in atomic units):
Electronic energy = -3825.22574738
Zero-point correction= 1.339983
Thermal correction to Energy= 1.422327
Thermal correction to Enthalpy= 1.423271
Thermal correction to Gibbs Free Energy= 1.213229
Sum of electronic and zero-point Energies= -3823.885765
Sum of electronic and thermal Energies= -3823.803421
Sum of electronic and thermal Enthalpies= -3823.802477
Sum of electronic and thermal Free Energies= -3824.012519
Cartesian coordinates (in Angströms):

Si	6.71250400	-0.70728800	-0.79375100

Si	-4.43240700	-4.80950300	1.36505400
Si	-2.50037300	6.06956200	0.18773200
N	-0.21120000	-2.90736700	-0.32360000
N	2.53941700	0.86380300	0.64865500
N	-1.89757200	1.47117100	-1.11586900
C	0.27531300	1.29593300	-0.14034800
C	-5.36331700	1.36748600	-2.31478000
C	-2.50114900	-1.22487400	-0.45497800
C	0.85773000	-3.75152600	-0.33279300
C	-3.13357500	0.96712200	-1.40086400
C	2.47941700	-8.34333000	-0.62036800
H	2.29267300	-9.41124800	-0.69445400
C	2.41617600	-1.84465300	-0.19358400
C	1.29626600	-1.01359800	-0.09004300
C	6.74239900	-3.15261600	-2.39213800
H	7.11410800	-3.66595900	-3.28961000
H	5.65188400	-3.09568500	-2.46523300
H	6.98342600	-3.79164700	-1.53311000
C	1.40377700	0.43619100	0.14357100
C	-0.01438700	-1.61074000	-0.21353000
C	1.68364700	3.15926600	0.60566300
C	0.41109800	2.66615600	0.11350600
C	-3.20911500	-6.15202900	1.97578600
H	-3.77686200	-6.77127100	2.68767500
C	-5.20925900	-3.93279800	2.89107700
H	-4.35445300	-3.39761000	3.33301300
C	-7.59608600	1.75076700	-3.20661200
H	-8.31130400	2.38588200	-3.72227200
C	-1.19146000	-0.73894000	-0.37802900
C	0.61357700	-5.12700000	-0.43760400
H	-0.41946300	-5.45236000	-0.49166900
C	6.73874500	1.15876100	-1.23186300
H	6.29891500	1.65879800	-0.35661300
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C	1.65904000	-6.05526800	-0.48087200
C	7.67644400	-1.03406300	0.83169800
H	8.73270100	-0.82511000	0.60082000
C	4.20022300	3.96021800	1.67594300
C	3.45484900	6.31570400	1.62878700
H	2.68519300	7.04919600	1.40239000
C	-0.98763200	0.68156300	-0.59104500
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C	1.43006300	-7.46329100	-0.57983800
H	0.40424500	-7.82060000	-0.62002500
C	3.82389200	-7.87087100	-0.56570900
H	4.64200100	-8.58513600	-0.59935400
C	-5.75027400	-4.89337000	3.96884300
H	-6.09562400	-4.32931900	4.84603600
H	-4.98969500	-5.60130900	4.31650900
H	-6.60448700	-5.47687800	3.60554500
C	3.02074800	-5.57626200	-0.42819200
C	-8.00264700	0.45943900	-2.75965500
H	-9.02180900	0.12880400	-2.94022400
C	3.17900000	4.93627900	1.37602000
C	2.21469800	-3.27322500	-0.28868100
C	3.76009100	-1.37778300	-0.29233900
C	-6.31612500	2.19073000	-2.99118800
H	-6.00290700	3.17428800	-3.33232500
C	3.26186100	-4.19809300	-0.34071000

H	4.28546400	-3.84080300	-0.30490800
C	-2.92461300	-2.50509500	0.01107700
C	2.71347000	2.19308700	0.88066400
C	-4.05225800	1.78936500	-2.06332500
H	-3.72135600	2.77513600	-2.37106900
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C	-4.84438000	-0.76809900	-1.21737900
H	-5.14839100	-1.76071700	-0.90483100
C	4.94724500	-1.15531200	-0.49040100
C	1.94844800	4.50894700	0.85638300
H	1.18234000	5.24519400	0.64282100
C	4.66075200	6.70779000	2.14861800
H	4.85751900	7.75964600	2.33698600
C	5.66684000	5.74289500	2.44917300
H	6.61569400	6.07343600	2.86293200
C	3.93690900	2.61037500	1.42149500
H	4.67878000	1.84845800	1.63938700
C	5.44321800	4.41071900	2.22035900
H	6.20764100	3.67226500	2.44929200
C	-3.50225900	-3.47819800	0.48000700
C	-7.11767300	-0.36086900	-2.10956500
H	-7.42309600	-1.34767800	-1.77055700
C	4.08502900	-6.52883100	-0.47240500
H	5.10870100	-6.16477500	-0.43245400
C	8.15679500	1.72839400	-1.43130500
H	8.64005000	1.30296100	-2.31960500
H	8.81235800	1.53593600	-0.57320900
H	8.12023300	2.81637700	-1.57787100
C	7.38374500	-1.75830100	-2.26001300
H	7.10014200	-1.18875600	-3.15858700
C	5.84049500	1.49319200	-2.43778400
H	5.80949100	2.57756000	-2.60960500
H	4.81184100	1.15070600	-2.28394900
H	6.21354900	1.03160000	-3.36120200
C	7.24635700	-0.08277900	1.96498300
H	6.18612700	-0.21676700	2.21343800
H	7.39902900	0.97039700	1.70147100
H	7.82367200	-0.27913500	2.87883000
C	7.58024600	-2.49884100	1.30054800
H	8.15966000	-2.65193400	2.22134000
H	7.96382400	-3.20154500	0.55230900
H	6.54184700	-2.77735000	1.51763200
C	8.92255800	-1.87156000	-2.25613200
H	9.28065900	-2.45196500	-1.39704000
H	9.41801500	-0.89487700	-2.22182200
H	9.27426300	-2.38519100	-3.16118200
C	-5.66760400	-5.60187700	0.12591500
H	-5.01629900	-6.15593800	-0.56714600
C	-2.02100500	-5.53518400	2.74007000
H	-1.35765000	-6.31974400	3.12867000
H	-2.35003100	-4.93202800	3.59467800
H	-1.42286100	-4.88643900	2.09039200
C	-2.72033400	-7.08490500	0.85190400
H	-2.25372700	-6.52313700	0.03382200
H	-3.53691300	-7.67430000	0.42014300
H	-1.97094000	-7.79249500	1.23265600
C	-6.47255000	-4.60551400	-0.72818100
H	-7.09618700	-5.13931700	-1.45863100
H	-5.81478100	-3.93157600	-1.28699000

H	-7.14415200	-3.99154600	-0.11665100
C	-6.60400900	-6.62955600	0.79328200
H	-7.32342900	-6.14144900	1.46173200
H	-6.05788600	-7.37475900	1.38412800
H	-7.18553500	-7.17370700	0.03676800
C	-6.26513500	-2.87135200	2.52890800
H	-7.17650600	-3.33098000	2.12699800
H	-5.89294800	-2.15736800	1.78597700
H	-6.56019400	-2.29891800	3.41886900
C	-1.59974900	7.44776100	1.17640900
H	-2.35377900	8.23666500	1.32588500
C	-4.02310200	5.49448900	1.20537400
H	-3.56746000	5.03880400	2.09846300
C	-2.82995600	6.71025500	-1.59150200
H	-1.84158400	7.07246400	-1.91424200
C	-4.85987600	4.39871100	0.52110700
H	-5.62366000	4.00961300	1.20820100
H	-4.24488400	3.55391500	0.19631500
H	-5.38917000	4.78573700	-0.35827600
C	-3.79515400	7.91147000	-1.63778500
H	-3.83855400	8.33562500	-2.65015600
H	-3.49561600	8.71818100	-0.95813300
H	-4.81642500	7.61562500	-1.36928000
C	-3.25286900	5.62740100	-2.59991200
H	-4.24903900	5.23096700	-2.36977000
H	-2.54952400	4.78796500	-2.60819100
H	-3.29544100	6.04075100	-3.61710600
C	-4.92555800	6.64613900	1.69209100
H	-5.42204500	7.15514600	0.85739300
H	-4.37201800	7.40316400	2.25900100
H	-5.71674200	6.26012700	2.34910800
C	-0.42314800	8.08521500	0.41379200
H	0.06620000	8.85479300	1.02686100
H	-0.74336400	8.56607900	-0.51709900
H	0.34130500	7.34335900	0.15086200
C	-1.15229600	6.96762500	2.57084000
H	-0.41971200	6.15498400	2.49866500
H	-1.99208300	6.59830500	3.17051500
H	-0.68256100	7.78570500	3.13390000
C	-1.36969200	4.61167300	0.05094800

TAA-CF_3Ph

No imaginary frequency
Energies (in atomic units):
Electronic energy = -4378.50118483
Zero-point correction= 0.755392
Thermal correction to Energy= 0.820681
Thermal correction to Enthalpy= 0.821625
Thermal correction to Gibbs Free Energy= 0.639278
Sum of electronic and zero-point Energies= -4377.745793
Sum of electronic and thermal Energies= -4377.680504
Sum of electronic and thermal Enthalpies= -4377.679560
Sum of electronic and thermal Free Energies= -4377.861907
Cartesian coordinates (in Angströms):

C	-0.18416500	-3.68977600	-0.33558400
C	-0.44525800	-1.39199600	-0.15210900

C	0.98716600	-1.18324500	-0.04314600
C	1.80515800	-2.30440800	0.07316300
C	1.23062700	-3.61206000	-0.07505400
C	-1.36881600	-0.24912500	0.05025100
C	1.51763800	0.19453400	-0.13916500
C	0.62289100	1.32327200	0.00146000
C	-0.80363000	1.06570700	0.29750100
C	1.14121200	2.60048100	-0.20308400
C	2.54175000	2.75378000	-0.48696100
C	3.33568000	1.55677600	-0.59608100
C	-2.75371800	-0.38476900	0.14402400
C	-3.54465300	0.73515000	0.57985900
C	-2.84936000	1.94368500	0.94013900
C	-4.94164900	0.70270000	0.71210800
C	-5.65718500	1.79648200	1.21755500
C	-4.94582700	2.99015000	1.61371800
C	-3.55630500	3.03391800	1.46100300
H	-5.49129500	-0.18784300	0.42752600
H	-3.00051600	3.92392700	1.73820300
C	1.96821500	-4.80318000	-0.00285200
C	1.36925400	-6.05125900	-0.21766800
C	-0.78646000	-4.93486300	-0.55452700
C	-0.04460900	-6.12009500	-0.50991700
H	-1.85473400	-4.95772300	-0.74813600
H	3.03104600	-4.76761000	0.21166300
C	3.16746700	3.99444800	-0.68375400
C	4.53393400	4.08914200	-0.97837400
C	4.69908600	1.64501200	-0.90499200
C	5.32068500	2.88263300	-1.09666200
H	2.58924100	4.90889600	-0.60481600
H	5.26658500	0.72493400	-1.00130700
N	-0.97512000	-2.58177400	-0.32217200
N	2.79169100	0.32012400	-0.43514200
N	-1.50637300	2.07369300	0.75948500
C	-5.68836500	4.09370600	2.13735300
C	-7.05095500	4.02364300	2.26053400
H	-7.60638400	4.86775900	2.65971200
C	-7.75496400	2.84687300	1.86739100
H	-8.83568400	2.81249800	1.97290600
C	-7.07925700	1.76766200	1.36161900
H	-7.61405500	0.86955600	1.06275800
H	-5.14576800	4.98785500	2.43356400
C	-0.63850100	-7.40182400	-0.72958300
H	-1.70209100	-7.45043700	-0.94823400
C	0.11530500	-8.54385900	-0.66491800
H	-0.34733200	-9.51223600	-0.83386300
C	1.51039000	-8.47662300	-0.37562000
H	2.08980300	-9.39437500	-0.32850400
C	2.11755100	-7.26795500	-0.15861300
H	3.18076600	-7.21369200	0.06178700
C	6.71150000	2.99404100	-1.40902000
C	7.29098100	4.22195100	-1.58966500
H	8.34868300	4.29620600	-1.82654400
C	6.51628200	5.41401900	-1.46983600
H	6.99583100	6.37774900	-1.61667100
C	5.18021800	5.34937600	-1.17393600
H	4.58815900	6.25676800	-1.08414000
H	7.29528300	2.08159800	-1.50011600
C	0.31209700	3.84899500	-0.23752200

C	-0.22496300	4.27788200	-1.45378700
C	0.13387400	4.64500800	0.90016000
C	-0.95808000	5.46646600	-1.52652800
H	-0.08456800	3.67803100	-2.34711500
C	-0.60538400	5.82322000	0.82406500
H	0.54627400	4.32515600	1.85056600
C	-1.15739400	6.24318300	-0.38922600
H	-1.73186800	7.16028500	-0.44341400
C	3.26054900	-2.23098800	0.42001400
C	4.25973300	-2.40263500	-0.54554000
C	3.63310700	-2.06028300	1.75577000
C	5.60359700	-2.35455600	-0.18133000
H	3.98552300	-2.53687700	-1.58604000
C	4.98297900	-2.03065500	2.11802000
H	2.86969300	-1.93597200	2.51674200
C	5.97603100	-2.16945800	1.15271600
H	7.02258300	-2.13459600	1.43123600
C	-3.50416900	-1.64059600	-0.17652300
C	-3.84989500	-1.93275400	-1.49988200
C	-3.96232600	-2.47876800	0.84563700
C	-4.60081000	-3.06999000	-1.79808100
H	-3.51045200	-1.28538800	-2.30128600
C	-4.70754000	-3.61838100	0.54178100
H	-3.71252000	-2.25762400	1.87770700
C	-5.02779400	-3.92477300	-0.78135200
H	-5.59879700	-4.81543000	-1.01630700
C	-1.47866100	5.93343600	-2.86074100
C	-0.90476900	6.59783400	2.07828400
C	6.66619800	-2.39465900	-1.24533000
C	5.35714300	-1.90678700	3.57204000
C	-5.00337200	-3.34856800	-3.22301200
C	-5.22465700	-4.49475600	1.65271600
F	-4.09325800	-2.88098300	-4.10368800
F	-5.15085900	-4.67225200	-3.45106000
F	-6.18433900	-2.76214500	-3.52708100
F	7.81982600	-2.92766200	-0.79126000
F	6.28062900	-3.10656600	-2.32386600
F	6.96325400	-1.14237000	-1.68711100
F	5.34826800	-3.11117700	4.18897800
F	6.59402800	-1.38961900	3.73131000
F	4.49260300	-1.11579200	4.24392500
F	-5.32997700	-5.78457300	1.26340800
F	-4.42254600	-4.45945900	2.73779800
F	-6.45551600	-4.10450300	2.05846100
F	-2.53113800	6.76824100	-2.72719300
F	-0.52834500	6.60077600	-3.55588400
F	-1.87282200	4.89702600	-3.63226700
F	-2.06037100	6.16869500	2.65460100
F	-1.06111500	7.91617500	1.83557000
F	0.06572200	6.46231600	3.00463600

F. NMR spectra of final compounds

1. *TAN-Ph*

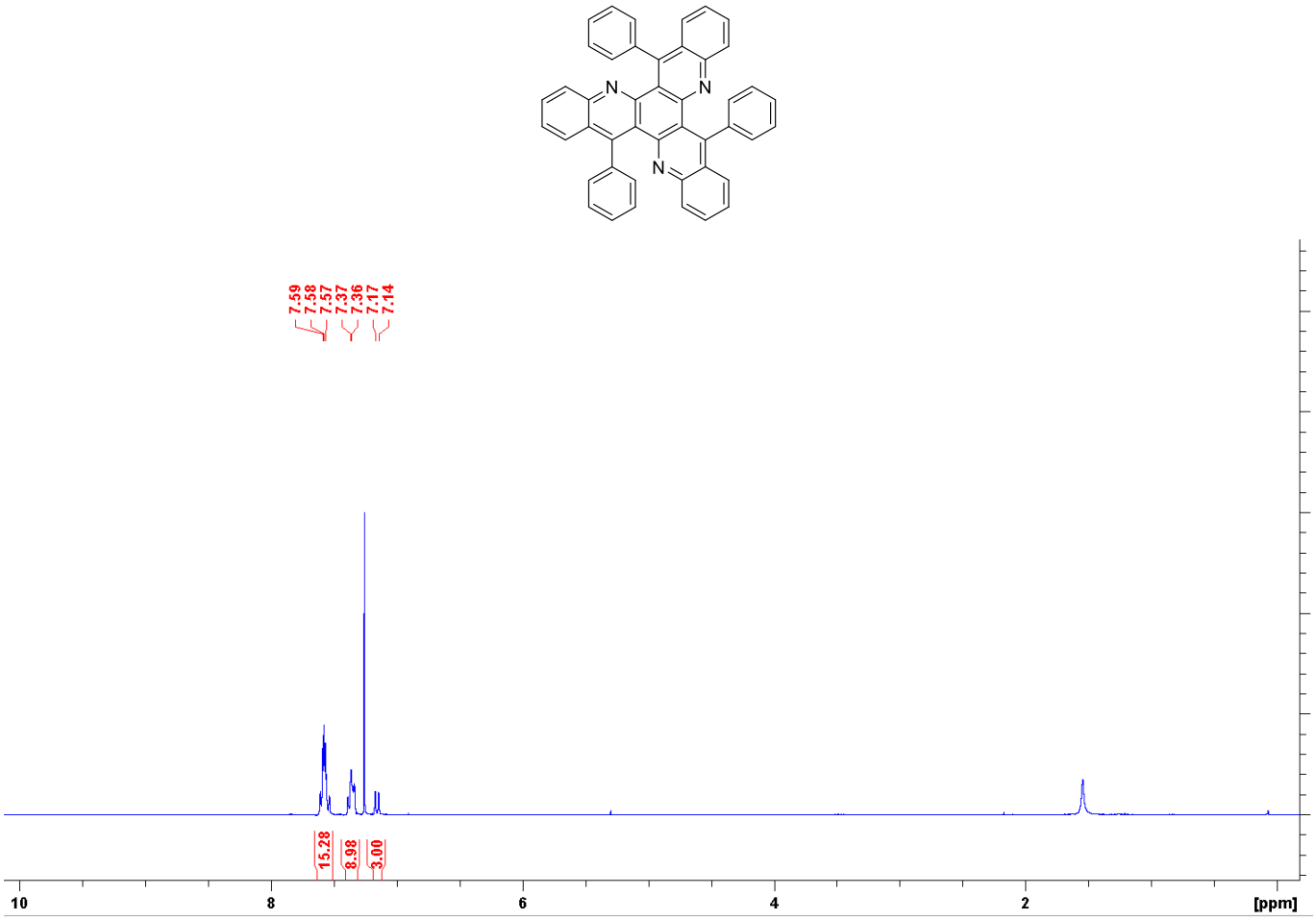


Figure S-F.1: ^{1}H NMR Spectrum (300 MHz, $CDCl_3$).

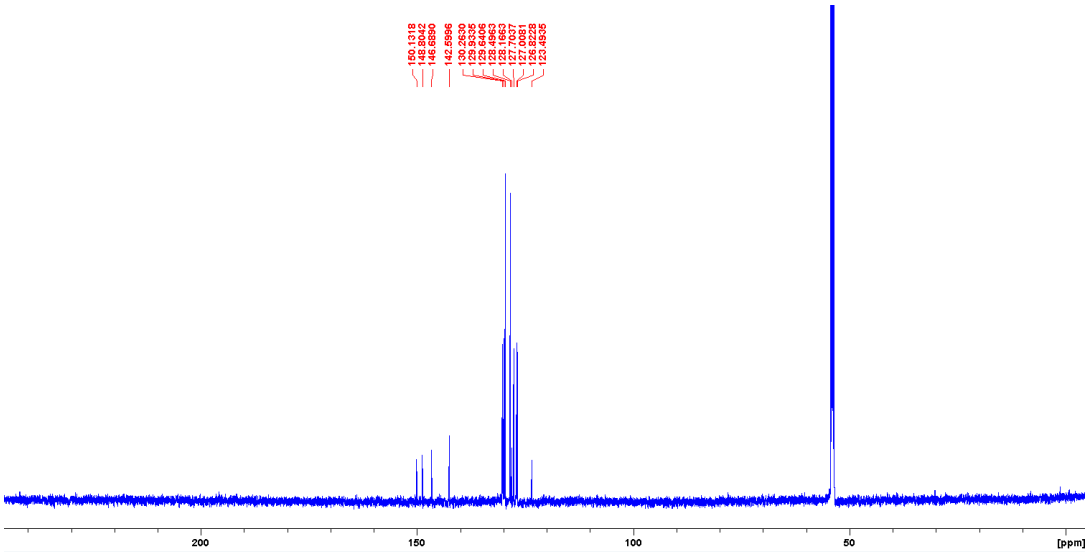


Figure S-F.2: ^{13}C NMR Spectrum (151 MHz, CD_2Cl_2).

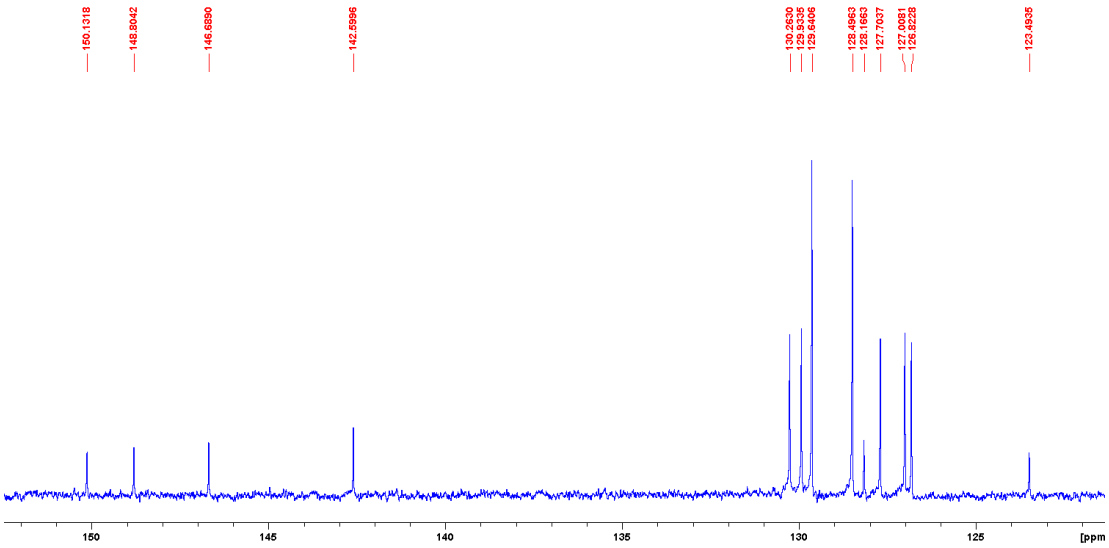


Figure S-F.3: ^{13}C NMR Spectrum, extension, (151 MHz, CD_2Cl_2).

2. *TAN-MePh*

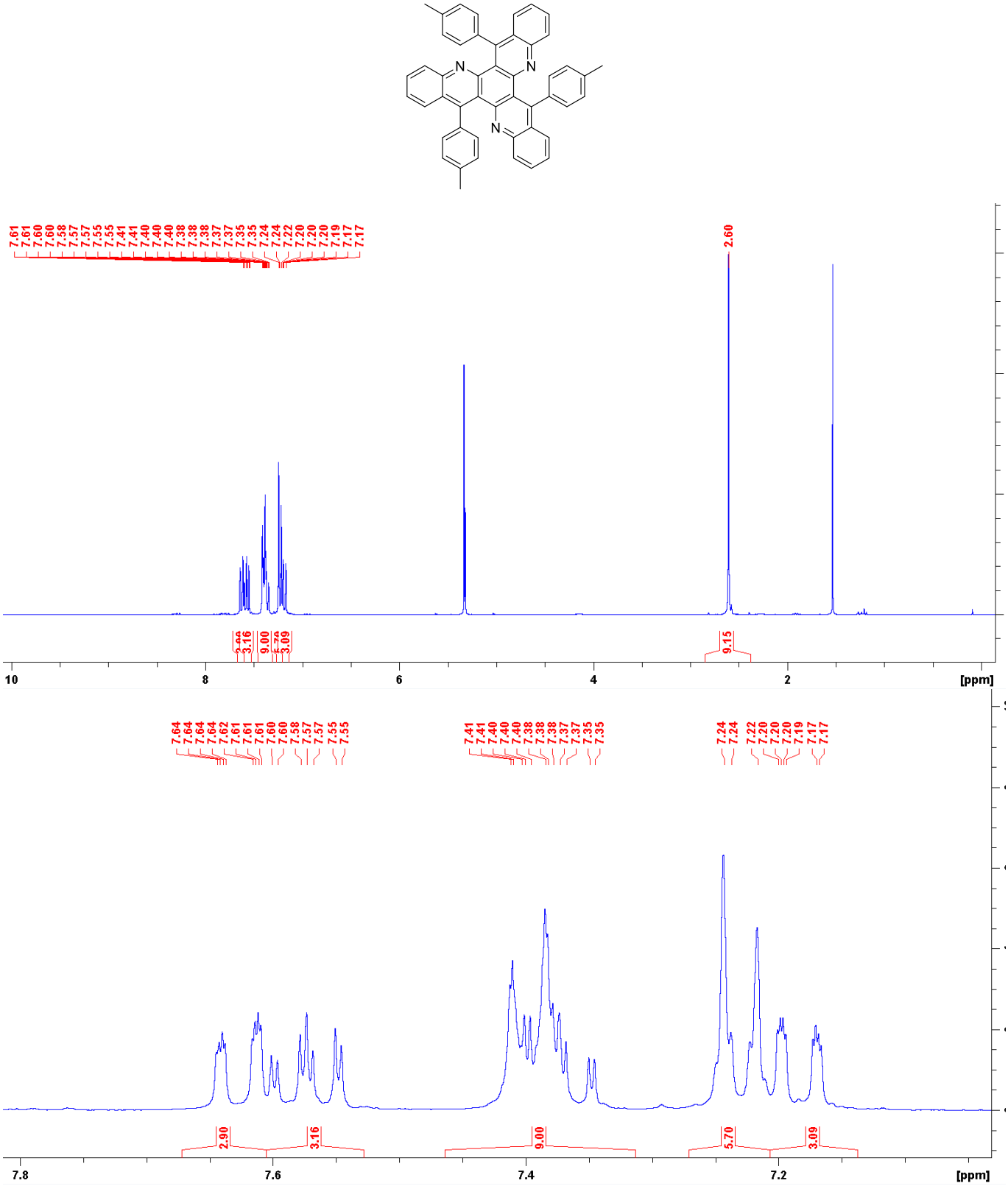


Figure S-F.4: ^{1}H NMR Spectrum (300 MHz, CD_2Cl_2).

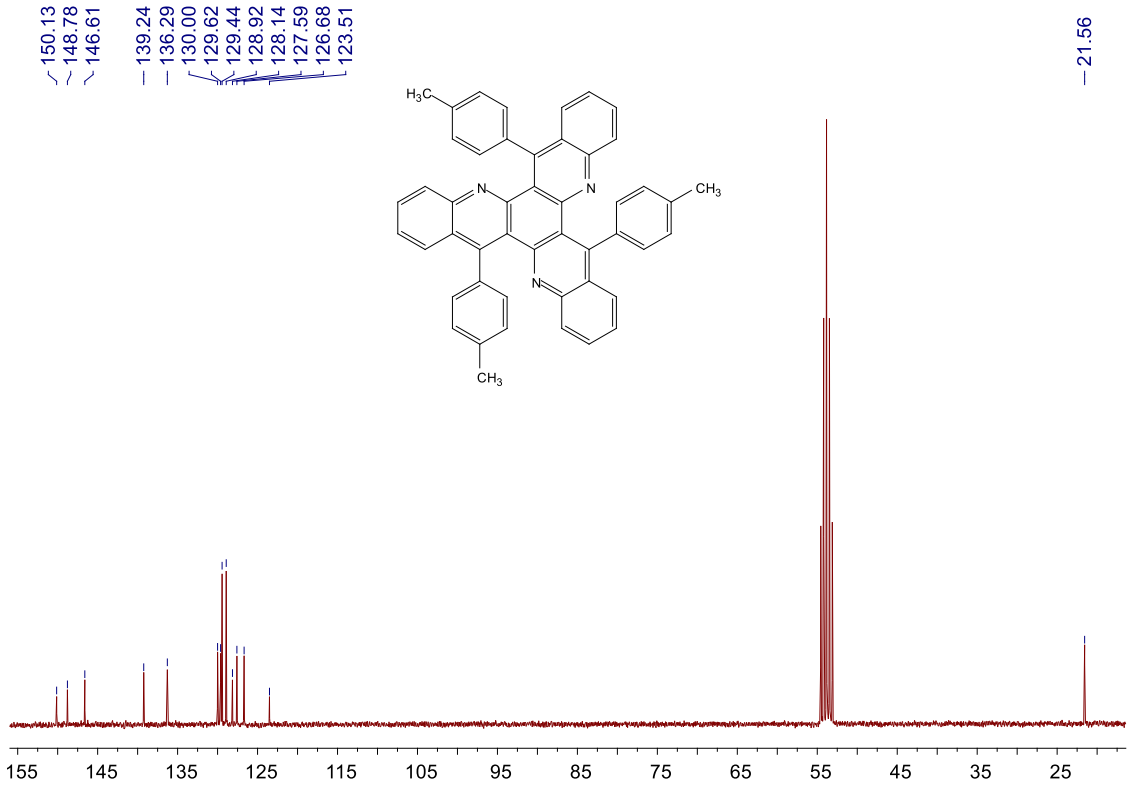


Figure S-F.5: ^{13}C NMR Spectrum (75 MHz, CD_2Cl_2).

3. *TAA-Ph*

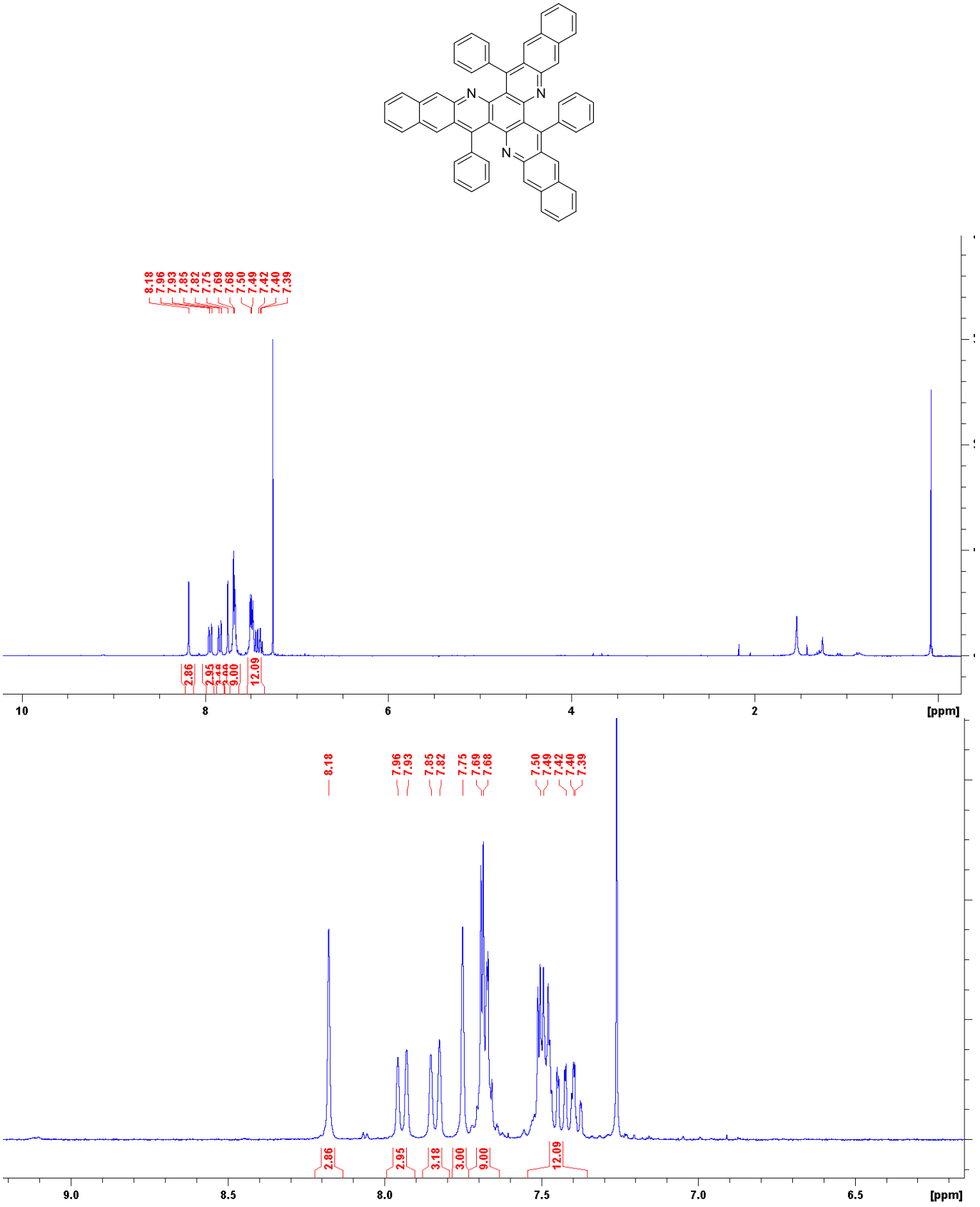


Figure S-F.6: ^{1}H NMR Spectrum (300 MHz, $CDCl_3$).

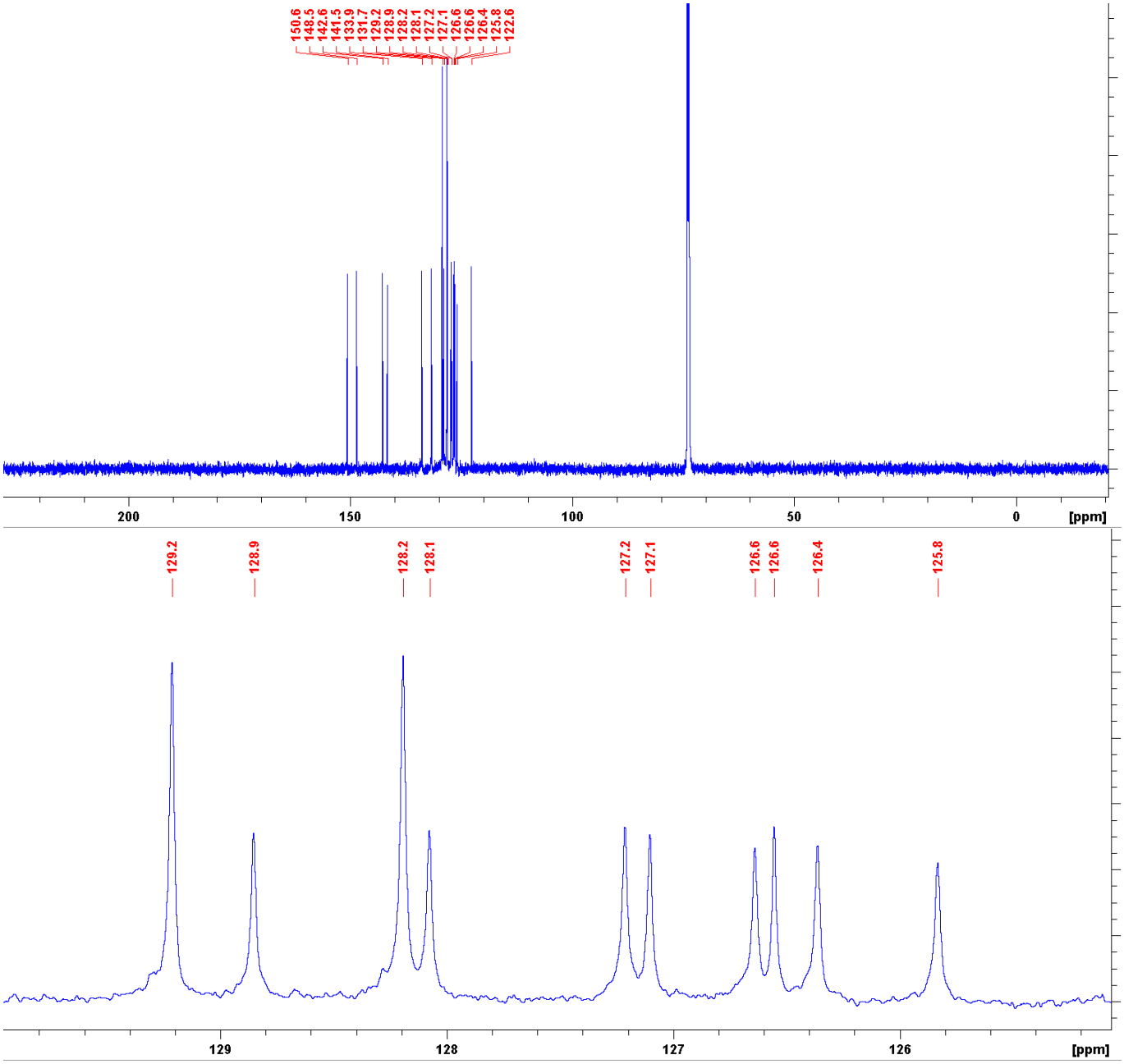


Figure S-F.7: ^{13}C NMR full Spectrum and expanded (150.9 MHz, $C_2D_2Cl_4$).

4. *TAA-Tips*

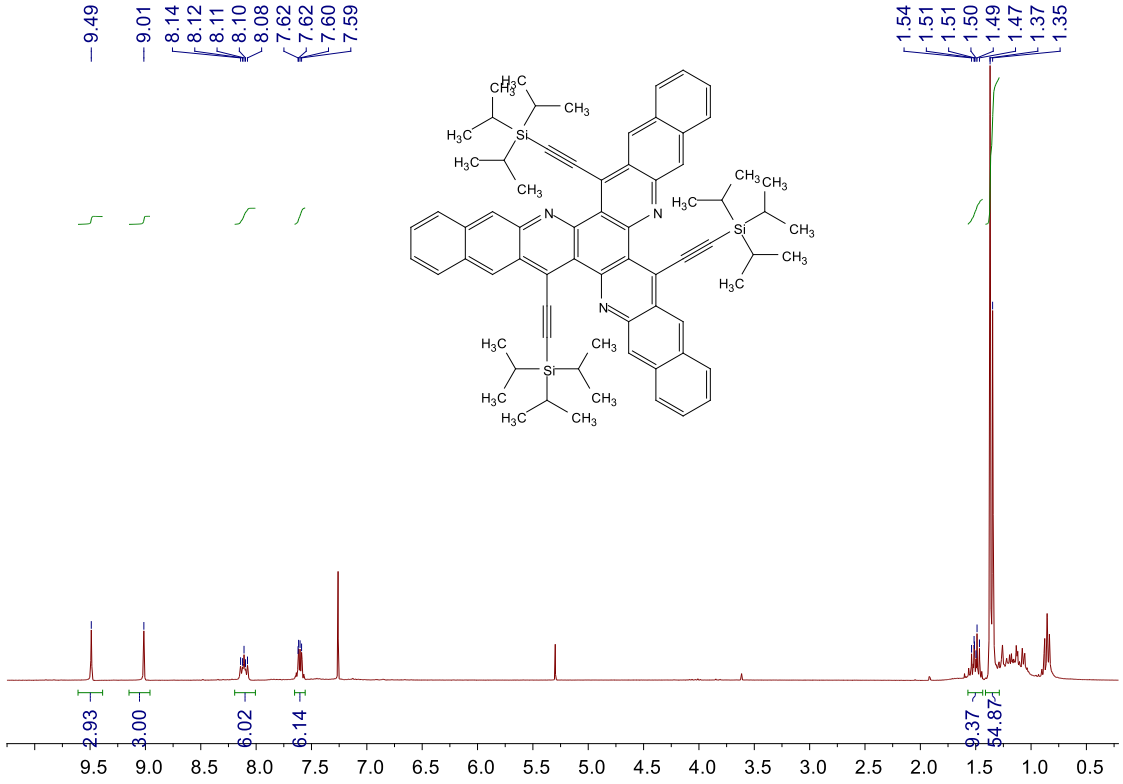
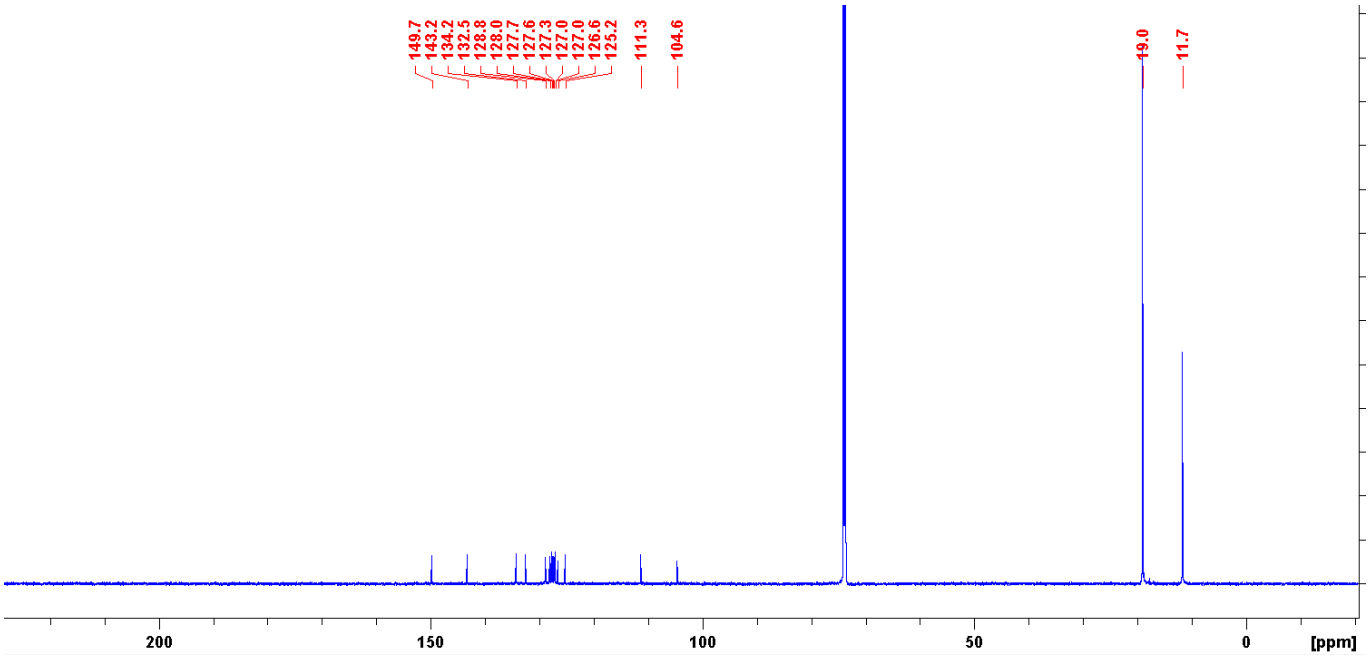


Figure S-F.8: ^{1}H NMR Spectrum (300 MHz, $CDCl_3$).



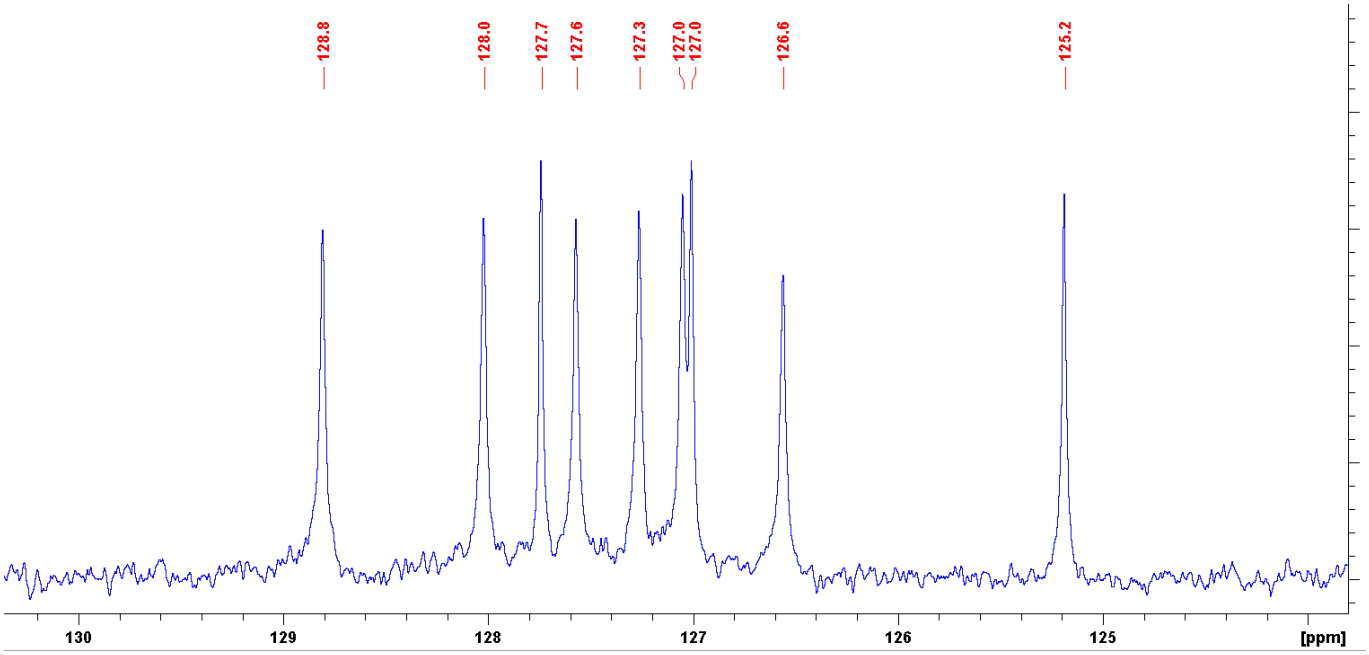


Figure S-F.9: ^{13}C NMR full Spectrum and expanded (150.9 MHz, $C_2D_2Cl_4$).

5. *TAA-OMePh*

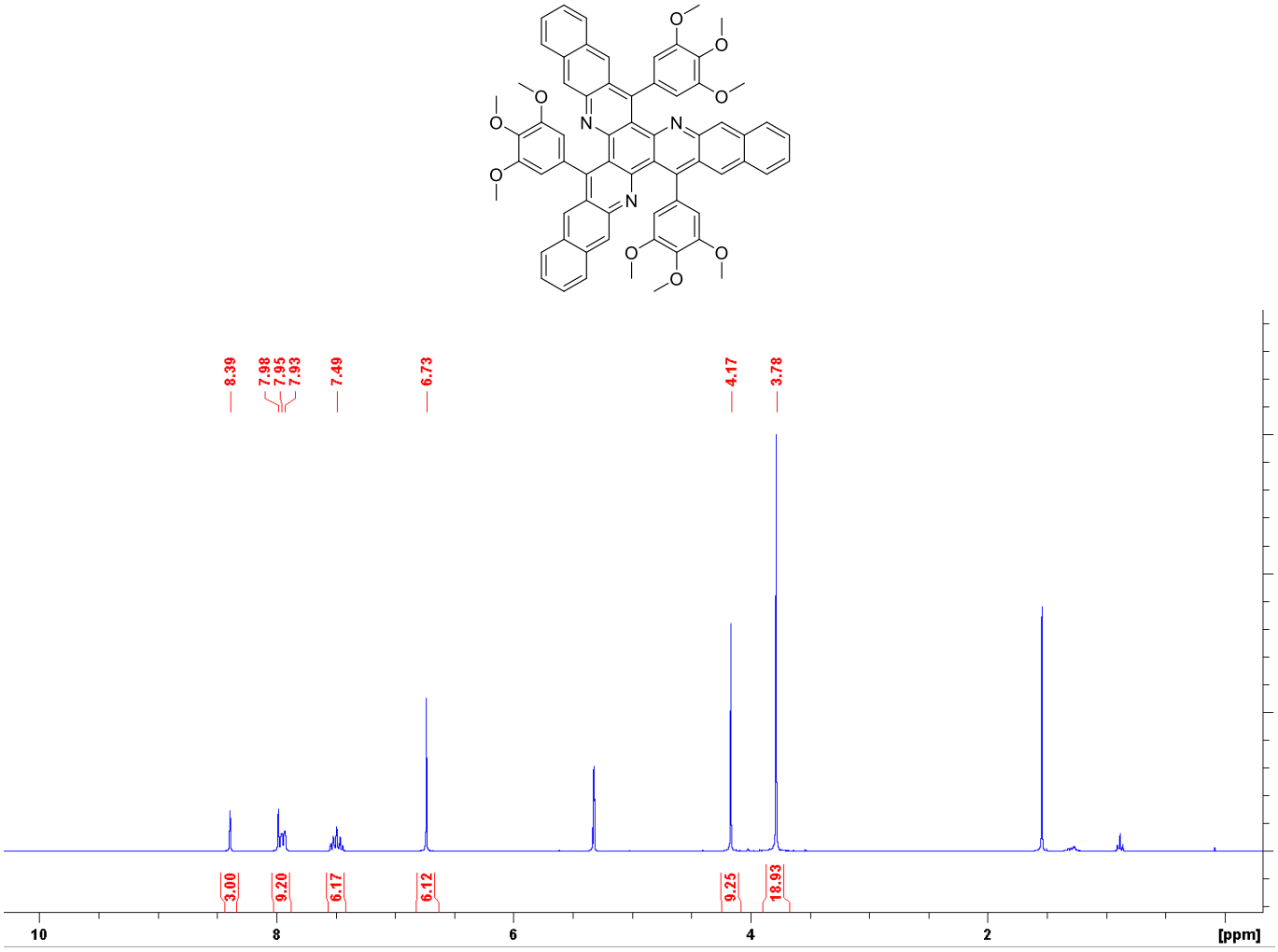


Figure S-F.10: ^{1}H NMR Spectrum (300 MHz, CD_2Cl_2).

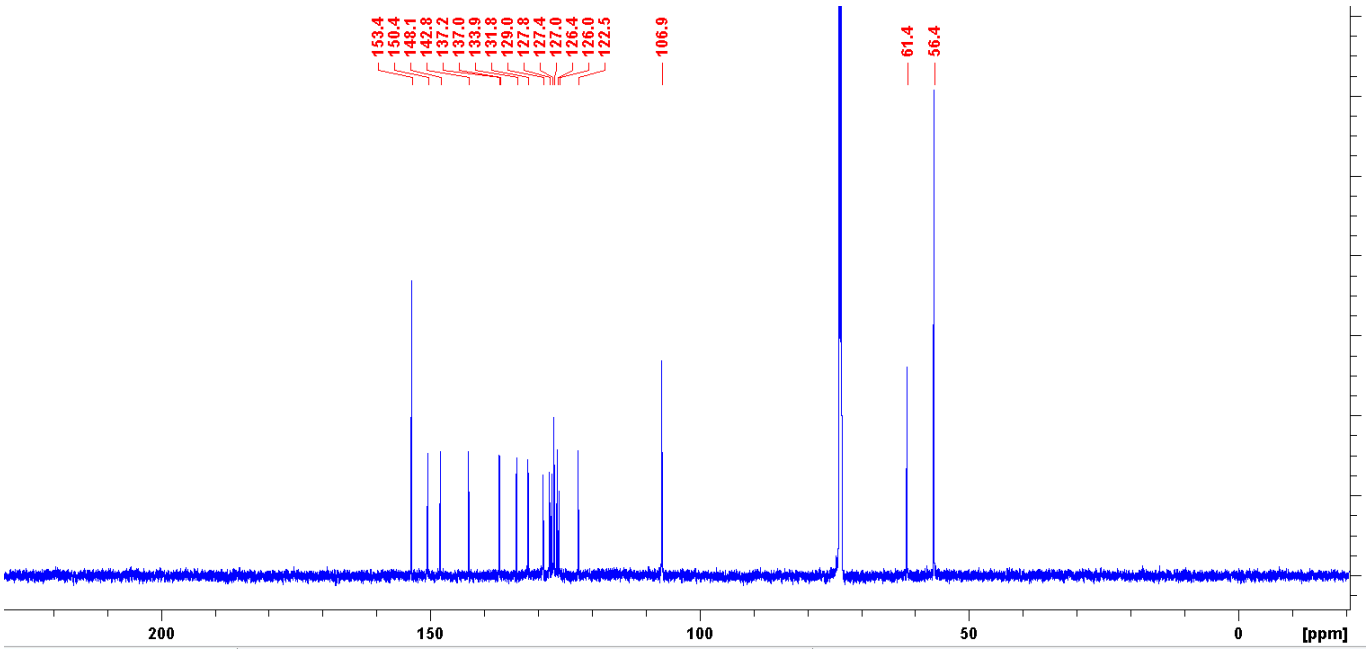


Figure S-F.11: ^{13}C NMR Spectrum, (150.9 MHz, $C_2D_2Cl_4$).

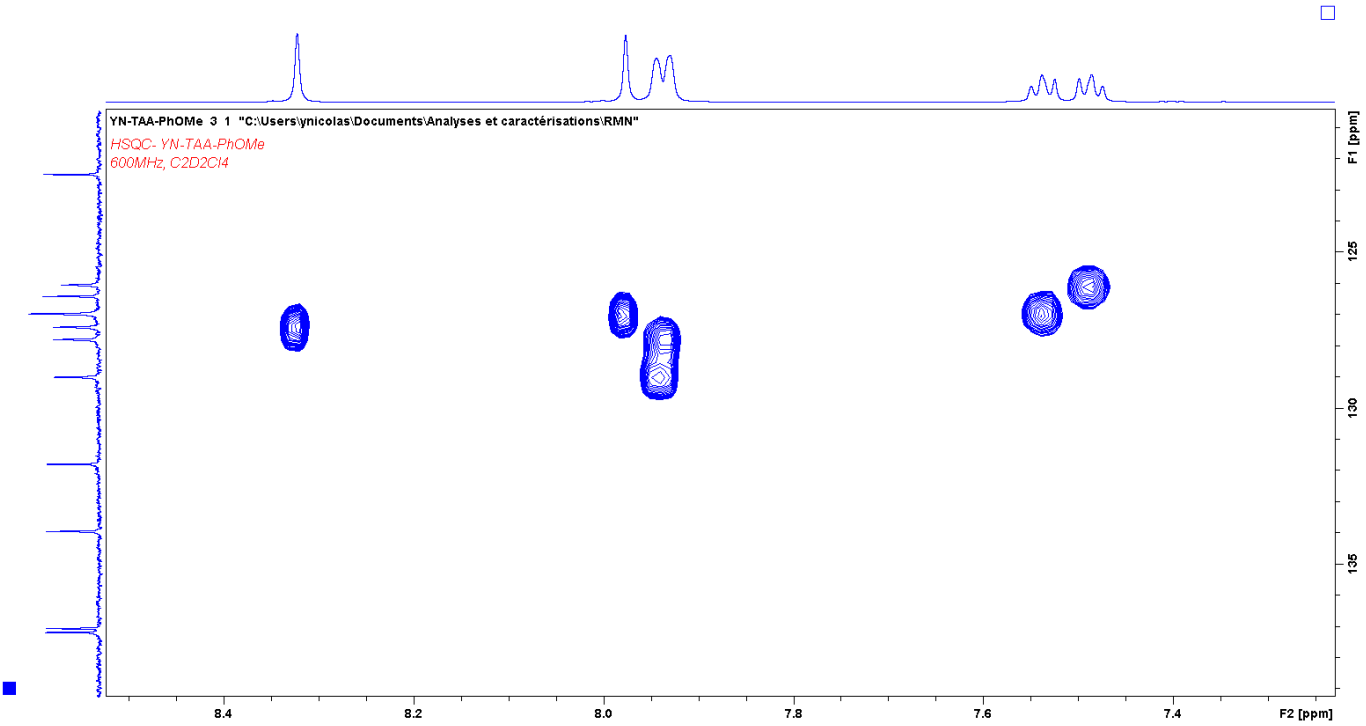


Figure S-F.12: HSQC NMR Spectrum, (^{1}H 600MHz, $C_2D_2Cl_4$).

6. *TAA-tBuPh*

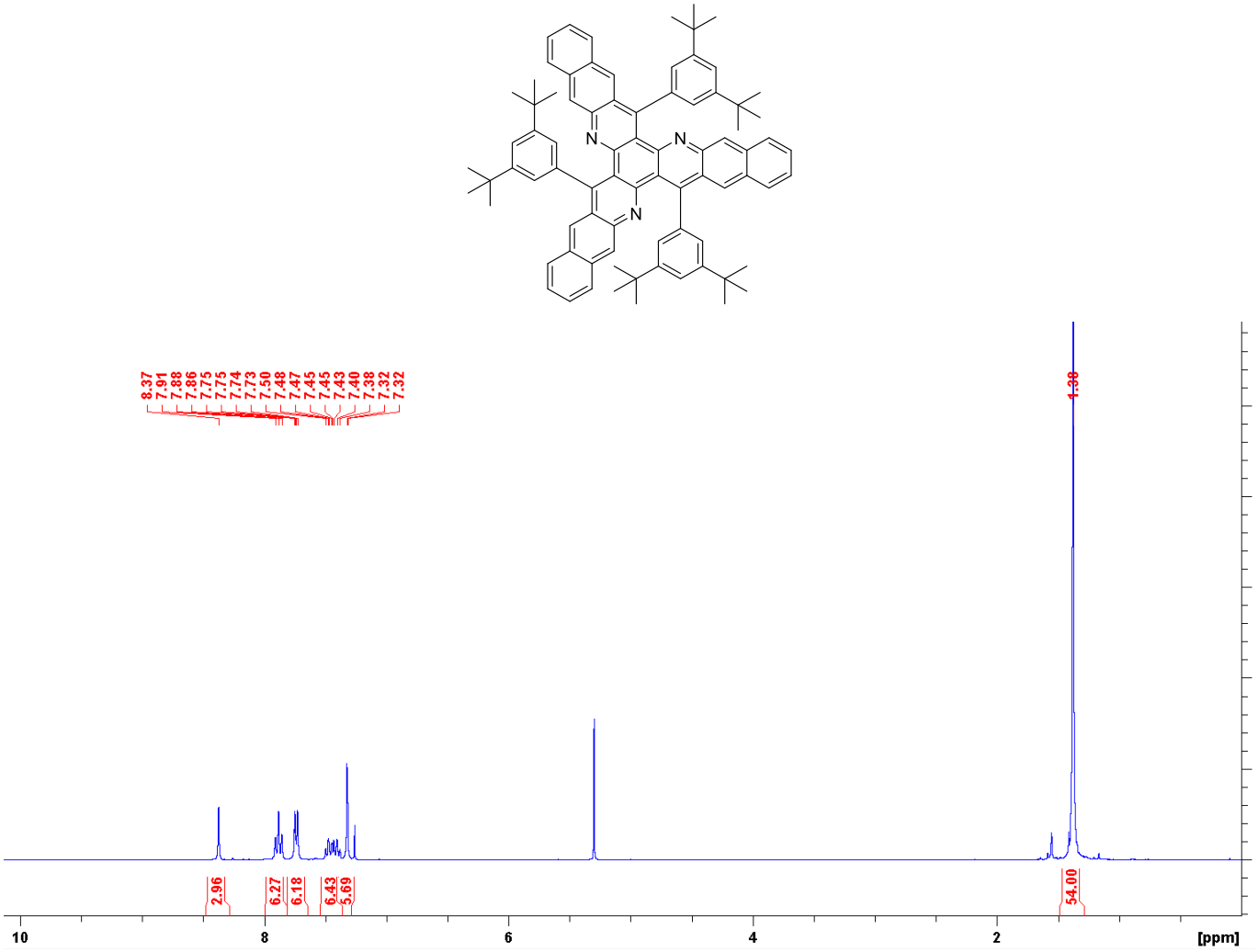


Figure S-F.13: ^{1}H NMR Spectrum (300 MHz, $CDCl_3$).

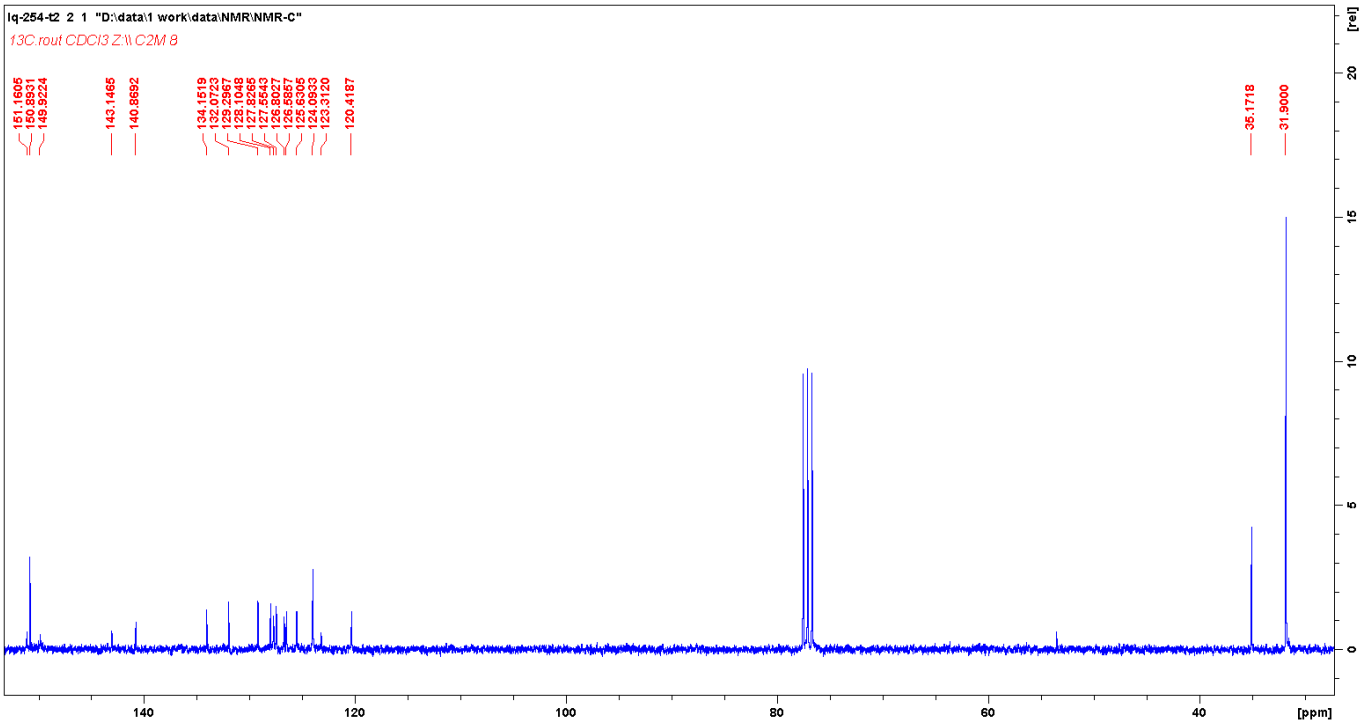


Figure S-F.14: ^{13}C NMR Spectrum (75 MHz, $CDCl_3$).

7. *TAA-CF3Ph*

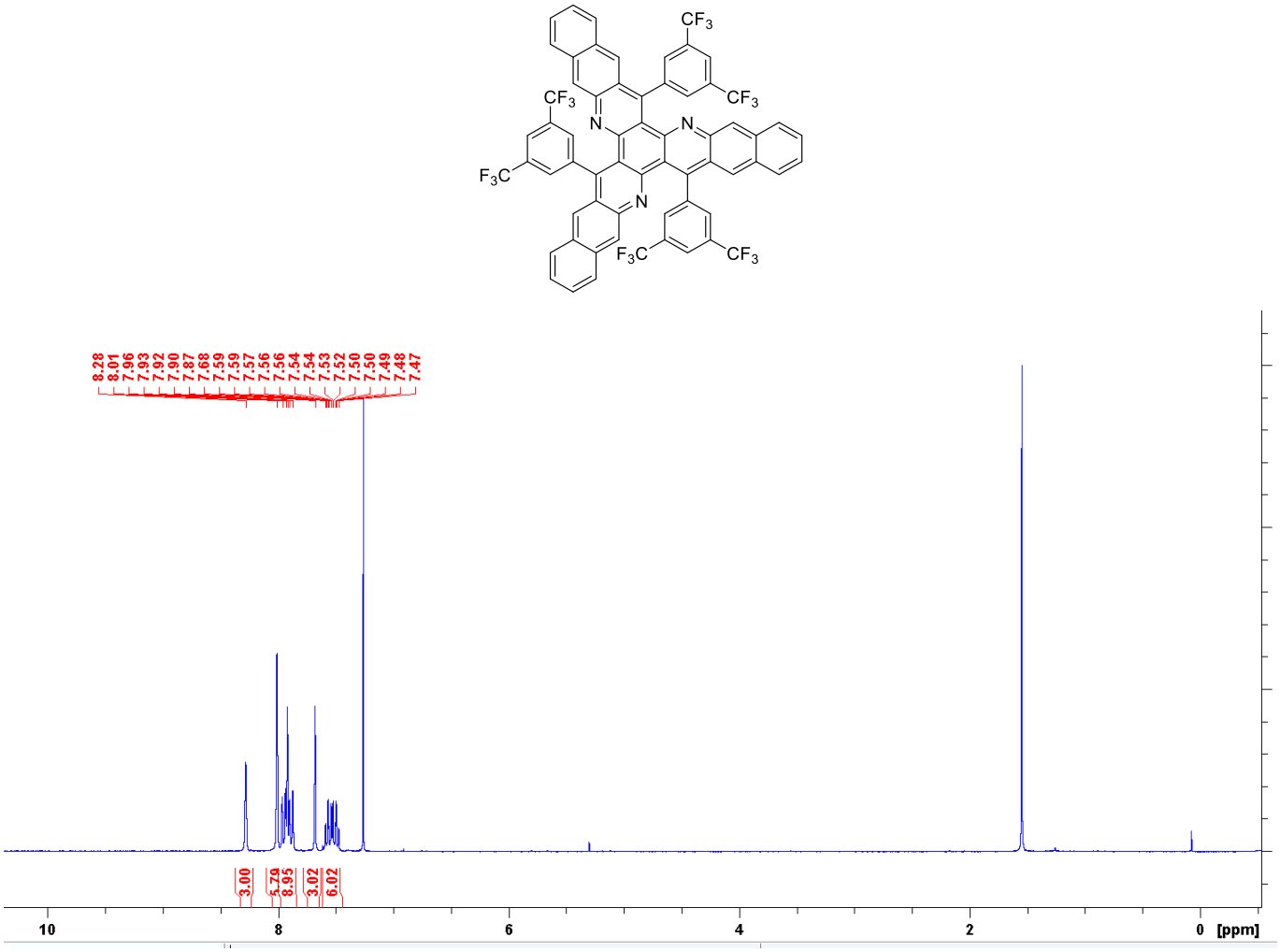


Figure S-F.15: ^{1}H NMR Spectrum (300 MHz, $CDCl_3$).

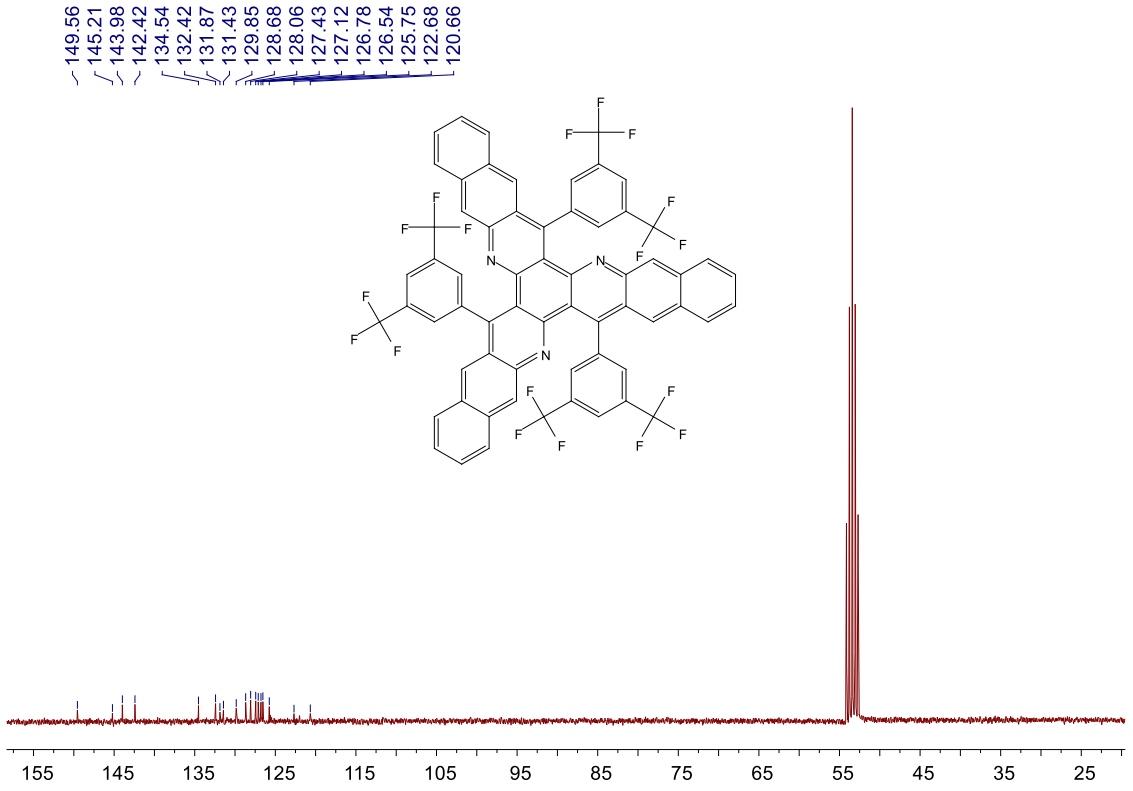


Figure S-F.16: ^{13}C NMR Spectrum (75 MHz, CD_2Cl_2).

8. *2-amino-N-methoxy-N-methyl-3-naphthamide*

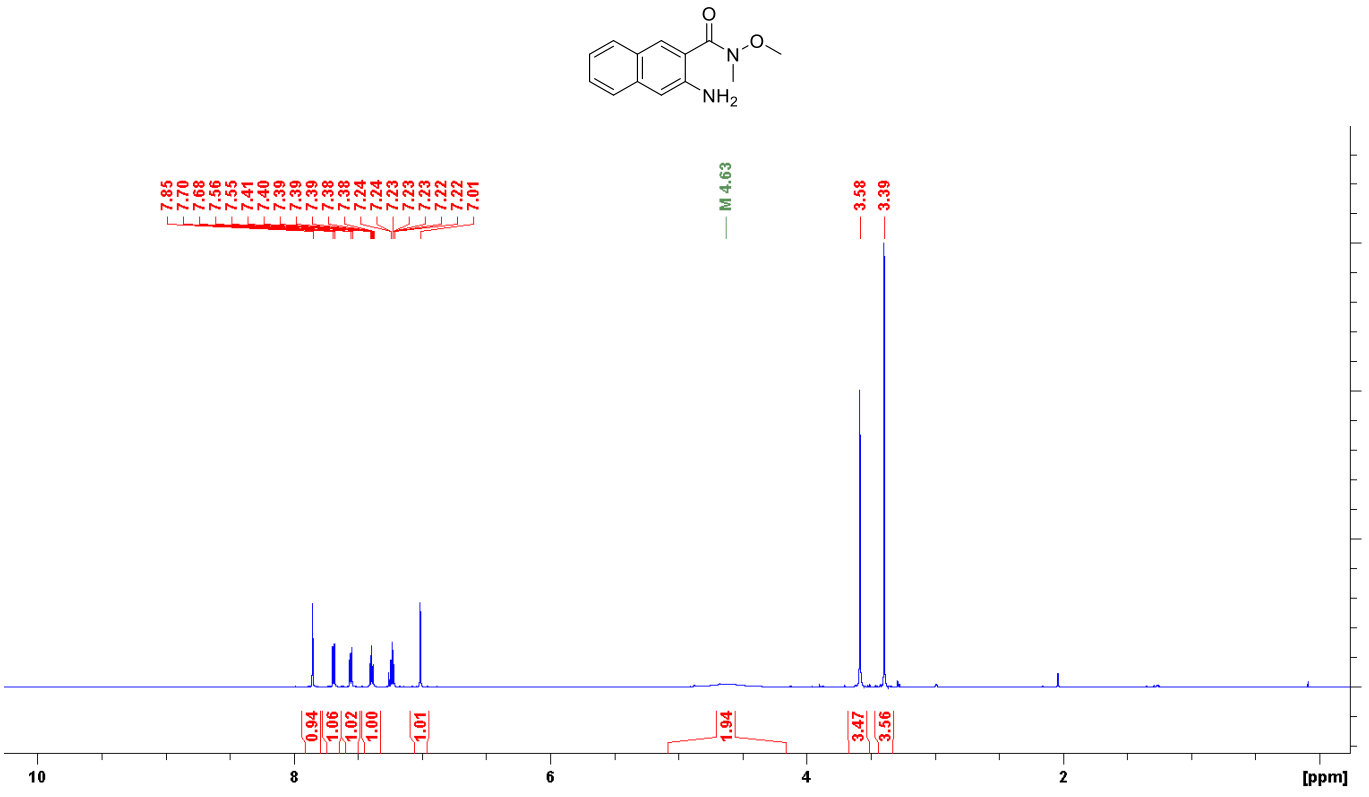


Figure S-F.17: ^{1}H NMR Spectrum (600 MHz, $CDCl_3$).

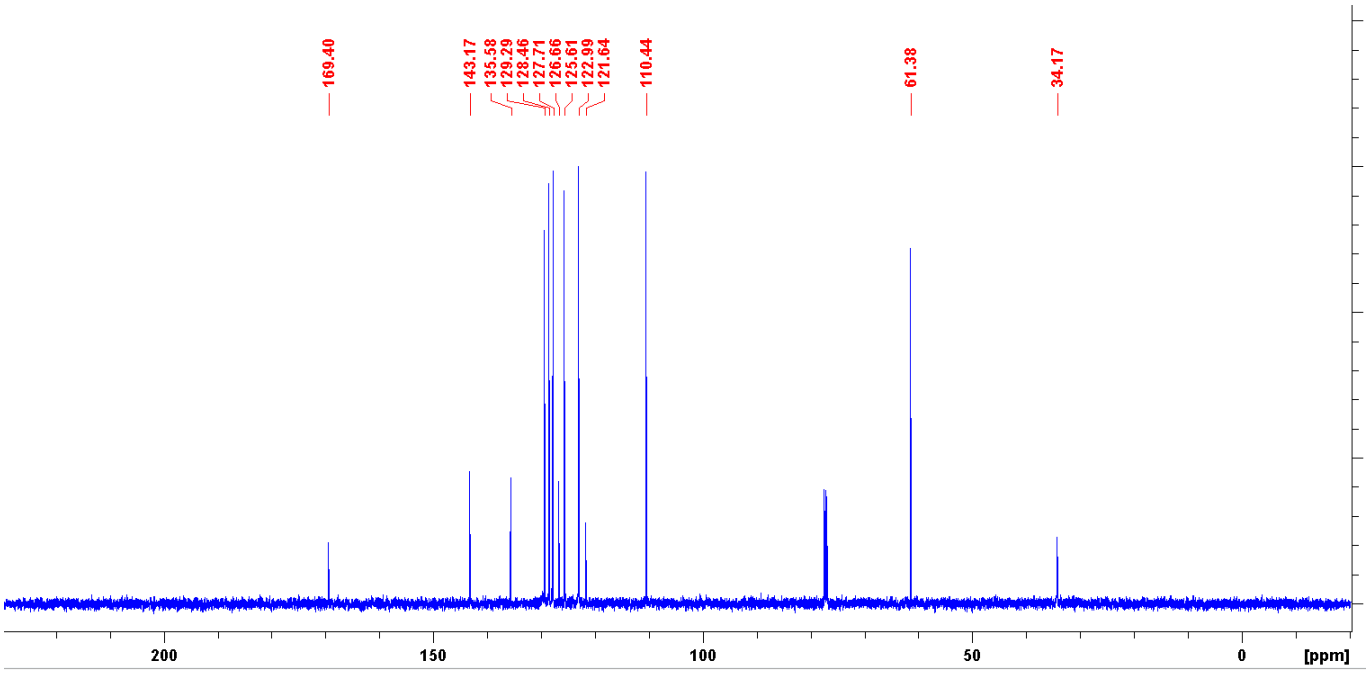


Figure S-F.18: ^{13}C NMR Spectrum (150 MHz, $CDCl_3$).

9. *2-amino-3-benzoylnaphthalene*

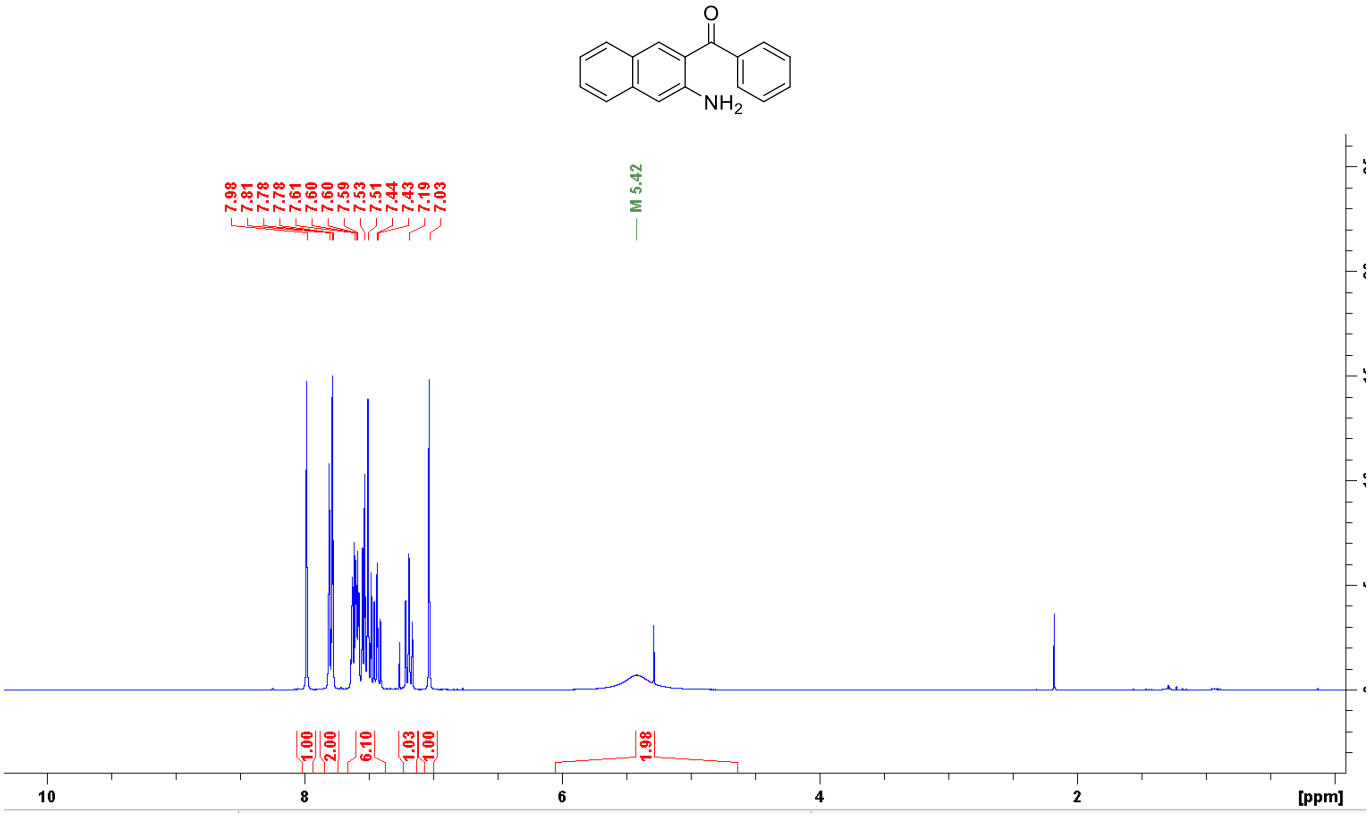


Figure S-F.19: ^{1}H NMR Spectrum (300 MHz, $CDCl_3$).

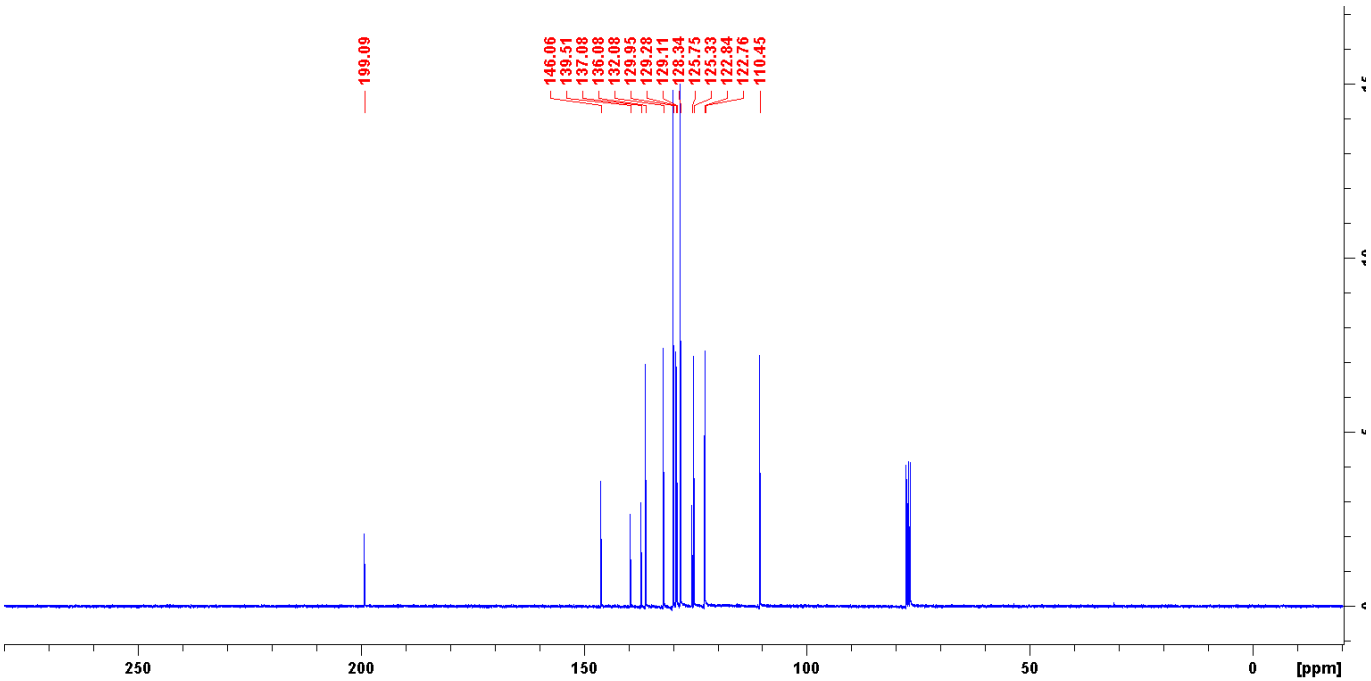


Figure S-F.20: ^{13}C NMR Spectrum (75 MHz, $CDCl_3$).

10. 1-(3-(2-aminonaphthalenyl)-3-(triisopropylsilyl)-2-propyn-1-one

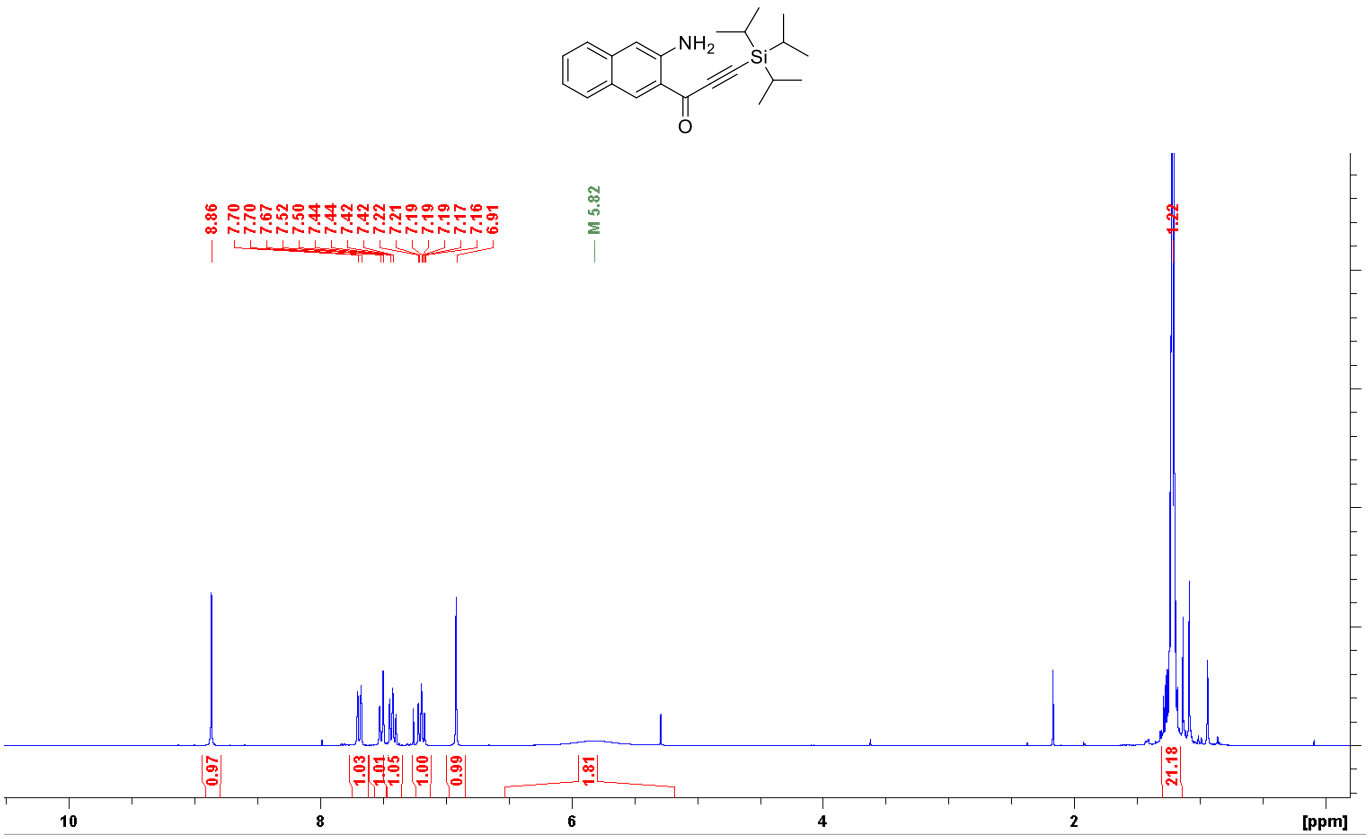


Figure S-F.21: ^{1}H NMR Spectrum (300 MHz, $CDCl_3$).

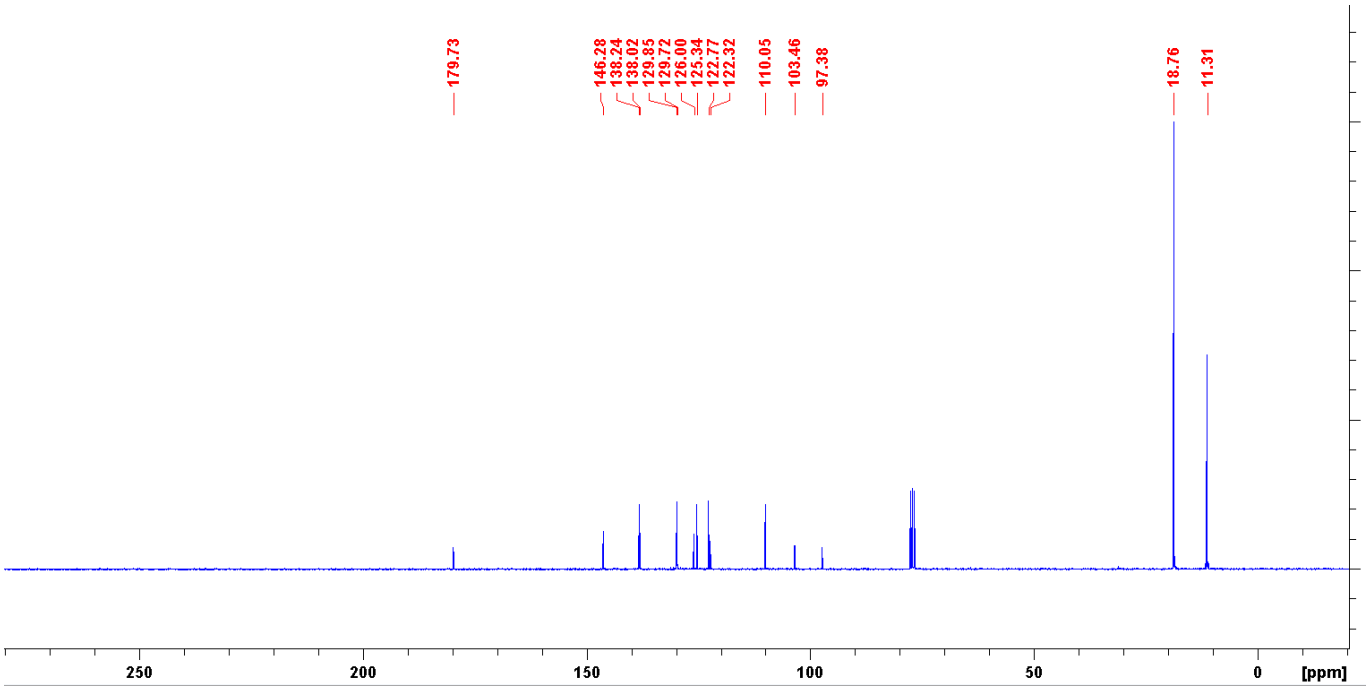


Figure S-F.22: ^{13}C NMR Spectrum (75 MHz, $CDCl_3$).

11. *2-amino-3-(3,4,5-trimethoxy)benzoylnaphthalene*

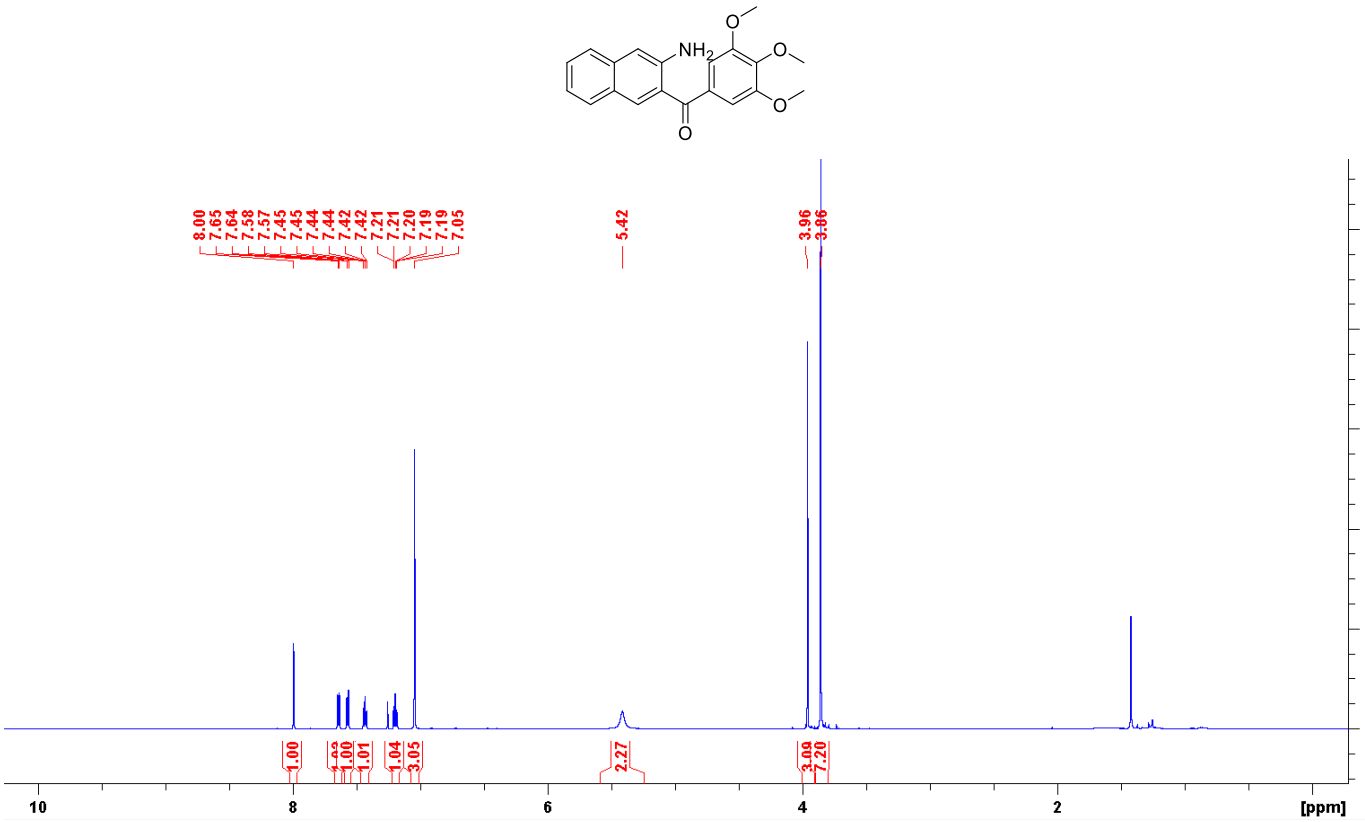


Figure S-F.23: ^{1}H NMR Spectrum (600 MHz, $CDCl_3$).

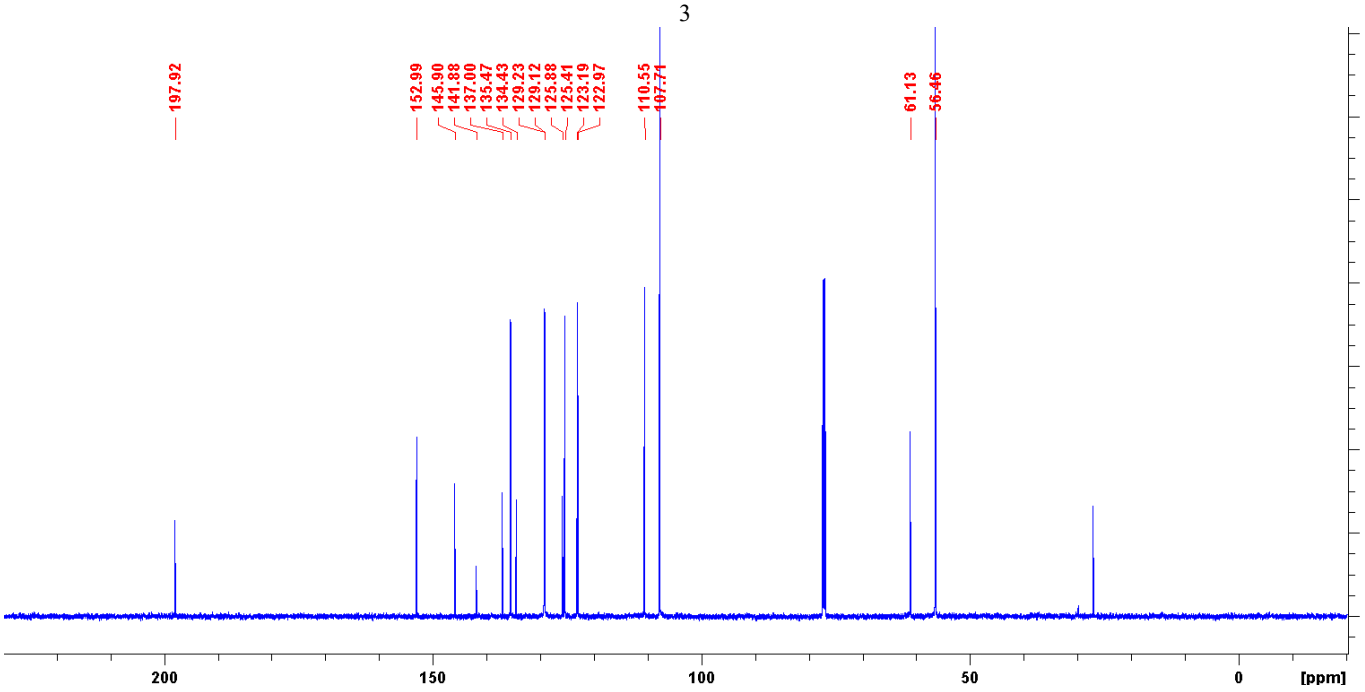


Figure S-F.24: ^{13}C NMR Spectrum (150 MHz, $CDCl_3$).

12. *2-amino-3-(3,5-di-tert-butyl)benzoylnaphthalene*

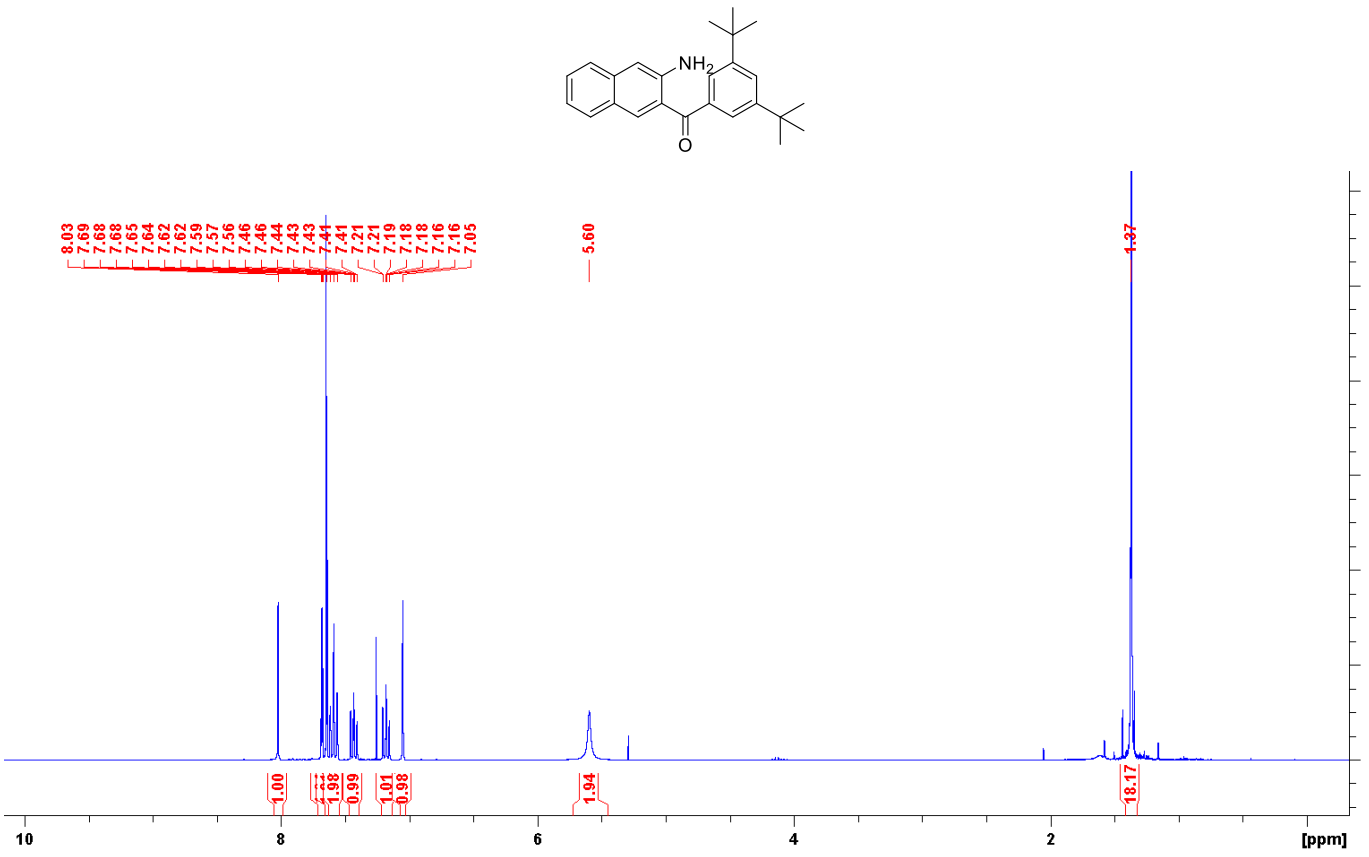


Figure S-F.25: ^{1}H NMR Spectrum (300 MHz, $CDCl_3$).

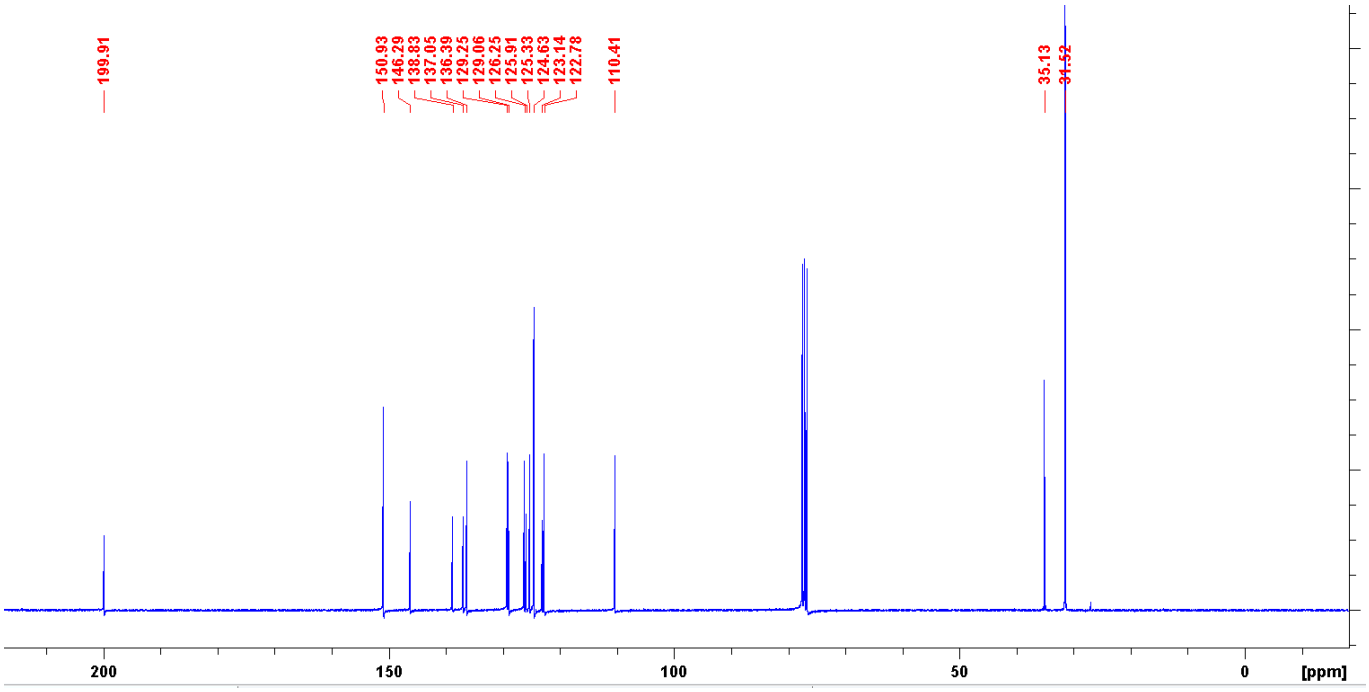


Figure S-F.26: ^{13}C NMR Spectrum (75 MHz, $CDCl_3$).

13. *2-amino-3-(3,5-bis(trifluoromethyl))benzoylnaphthalene*

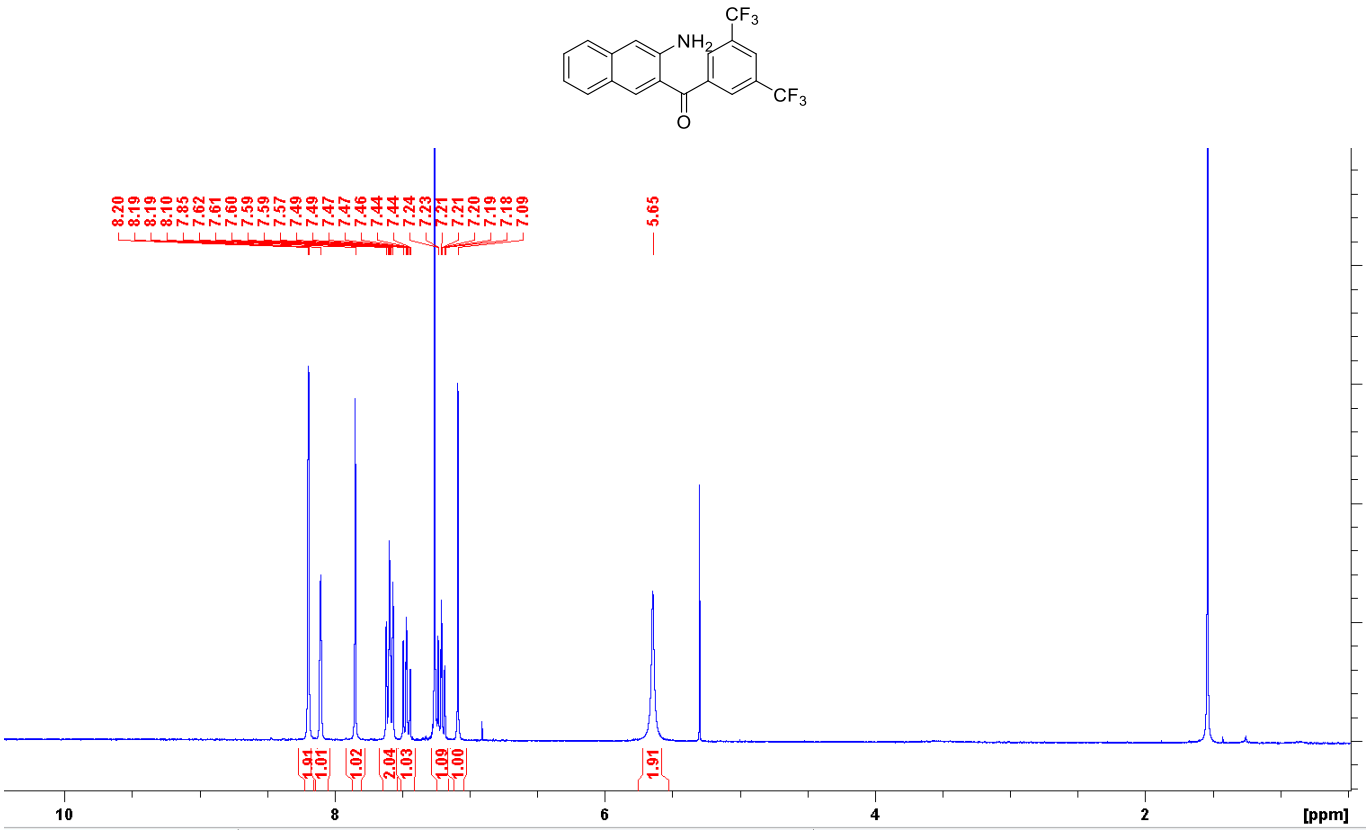
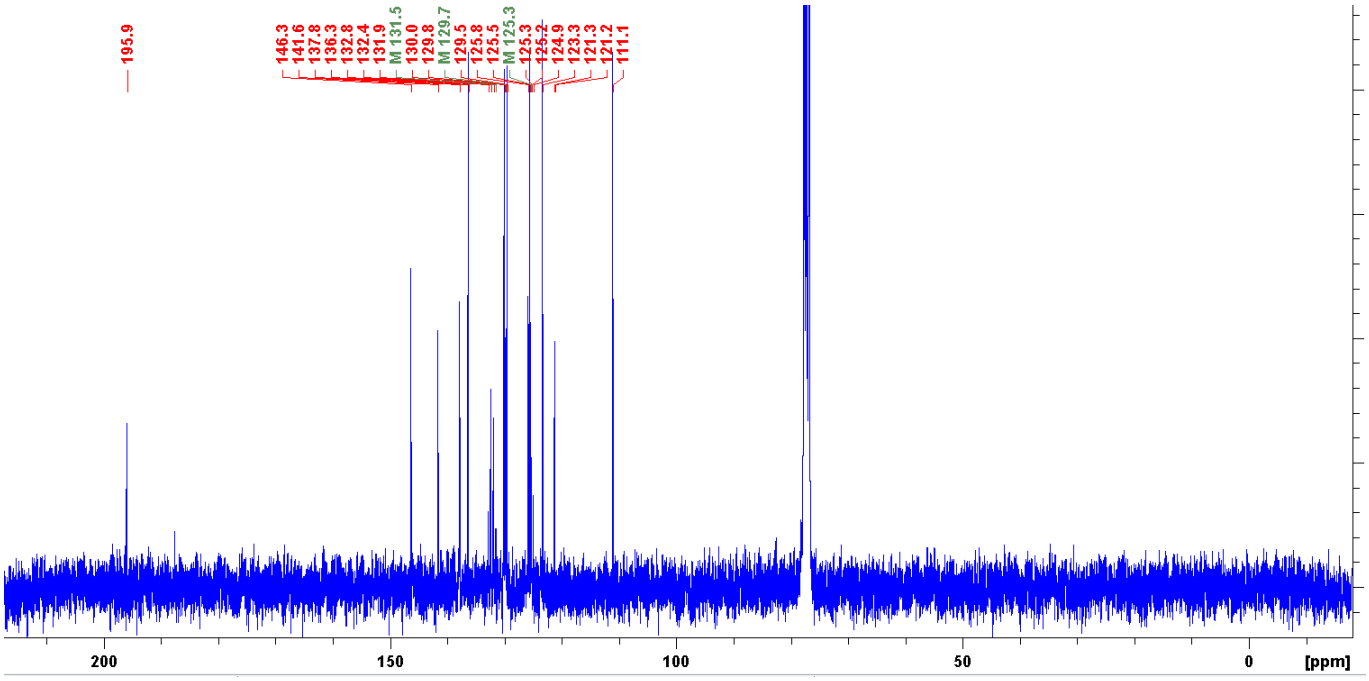


Figure S-F.27: ^{1}H NMR Spectrum (300 MHz, $CDCl_3$).



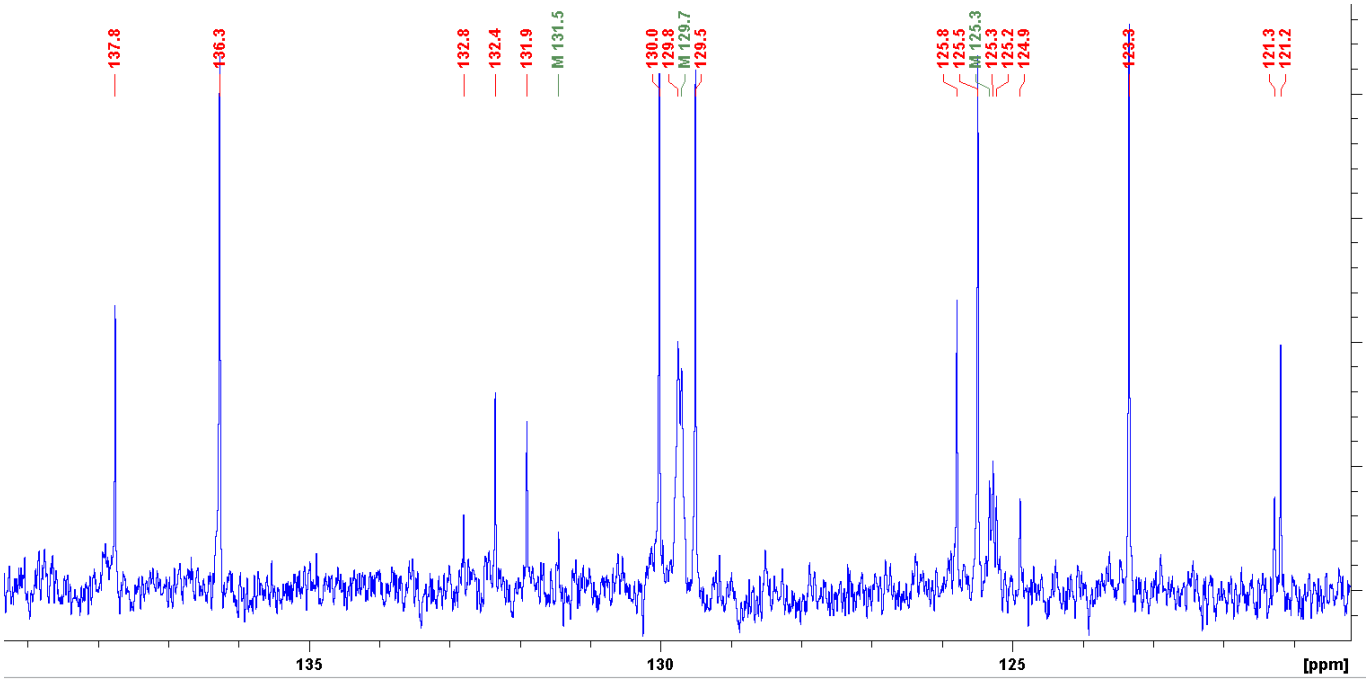
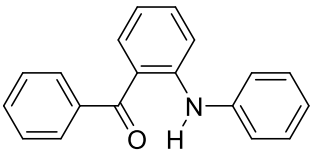


Figure S-F.28: ^{13}C NMR full Spectrum and expanded (75 MHz, $CDCl_3$).

14. 2-Phenylaminobenzophenone



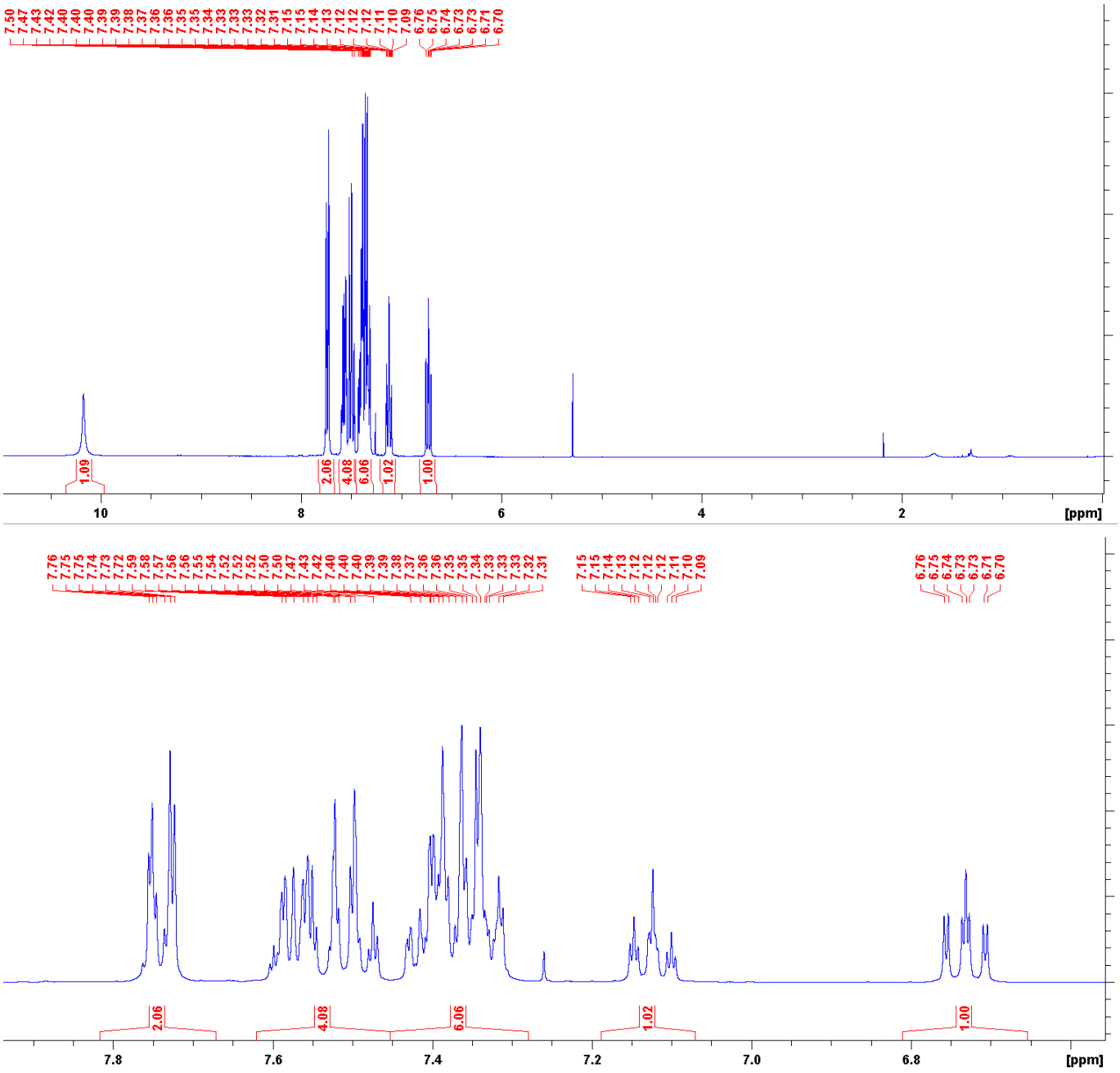


Figure S-F.29: ^{1}H NMR Spectrum (300 MHz, $CDCl_3$).

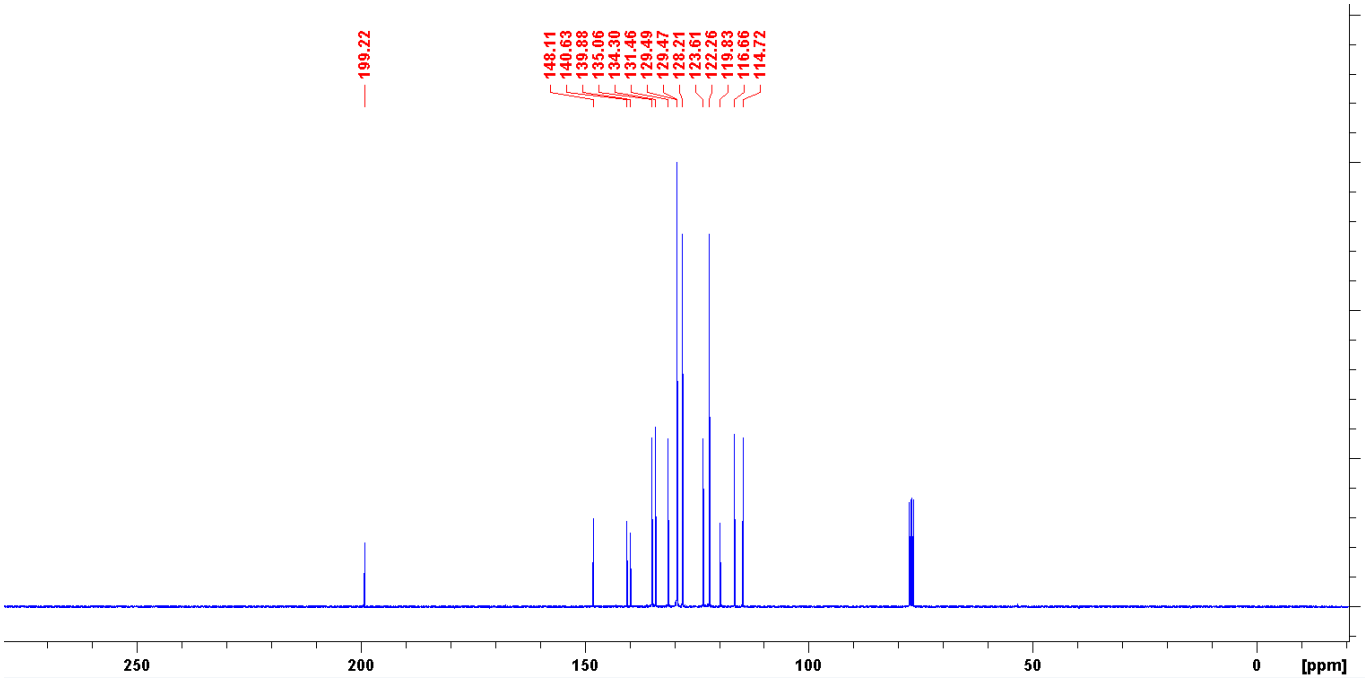
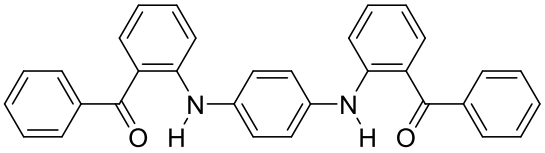


Figure S-F.30: ^{13}C NMR Spectrum (75 MHz, $CDCl_3$).

15. *[1,4-Phenylenebis(imino-2,1-phenylene)]bis(phenylmethanone)*



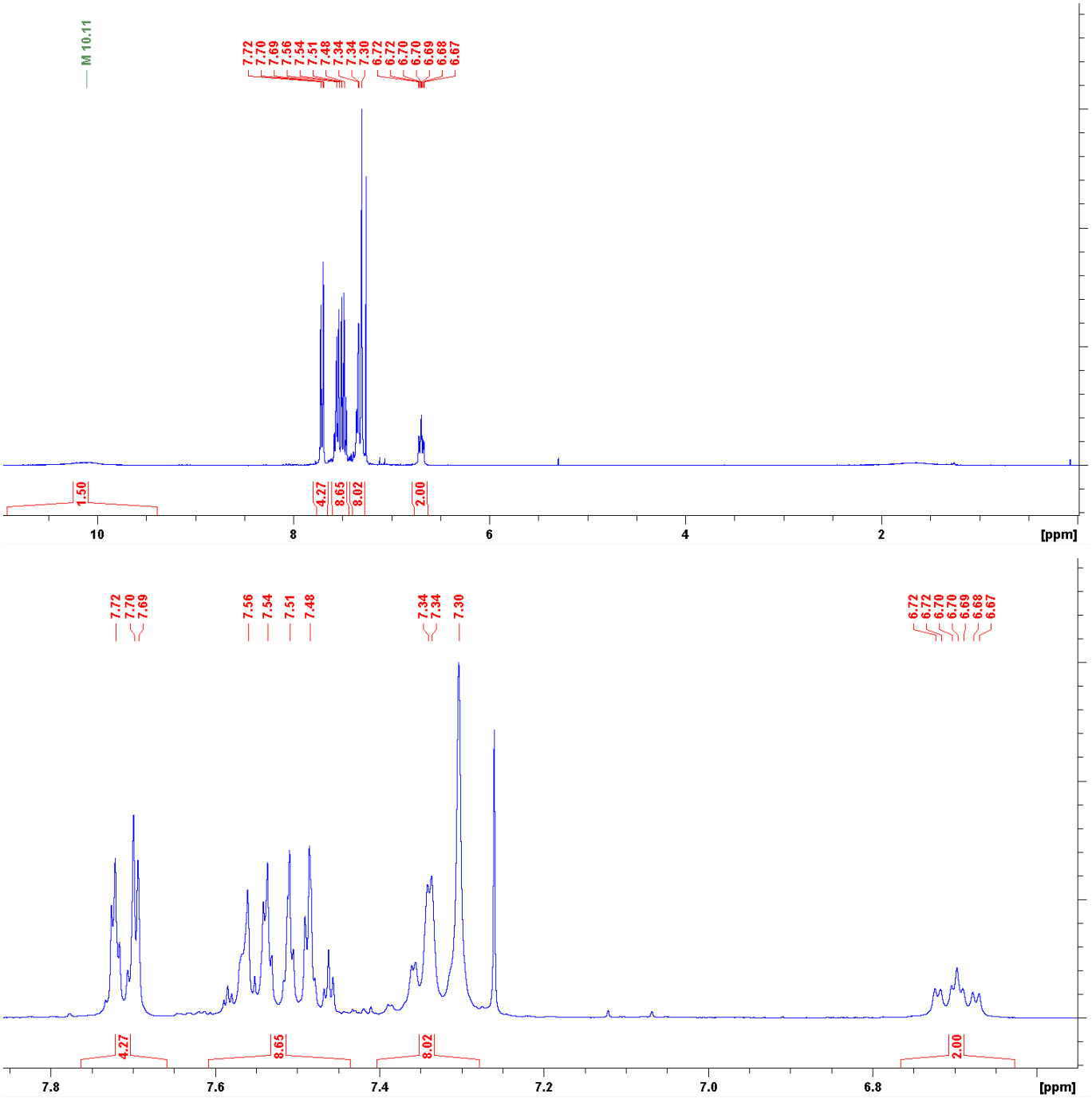


Figure S-F.31: ^{1}H NMR Spectrum (300 MHz, $CDCl_3$).

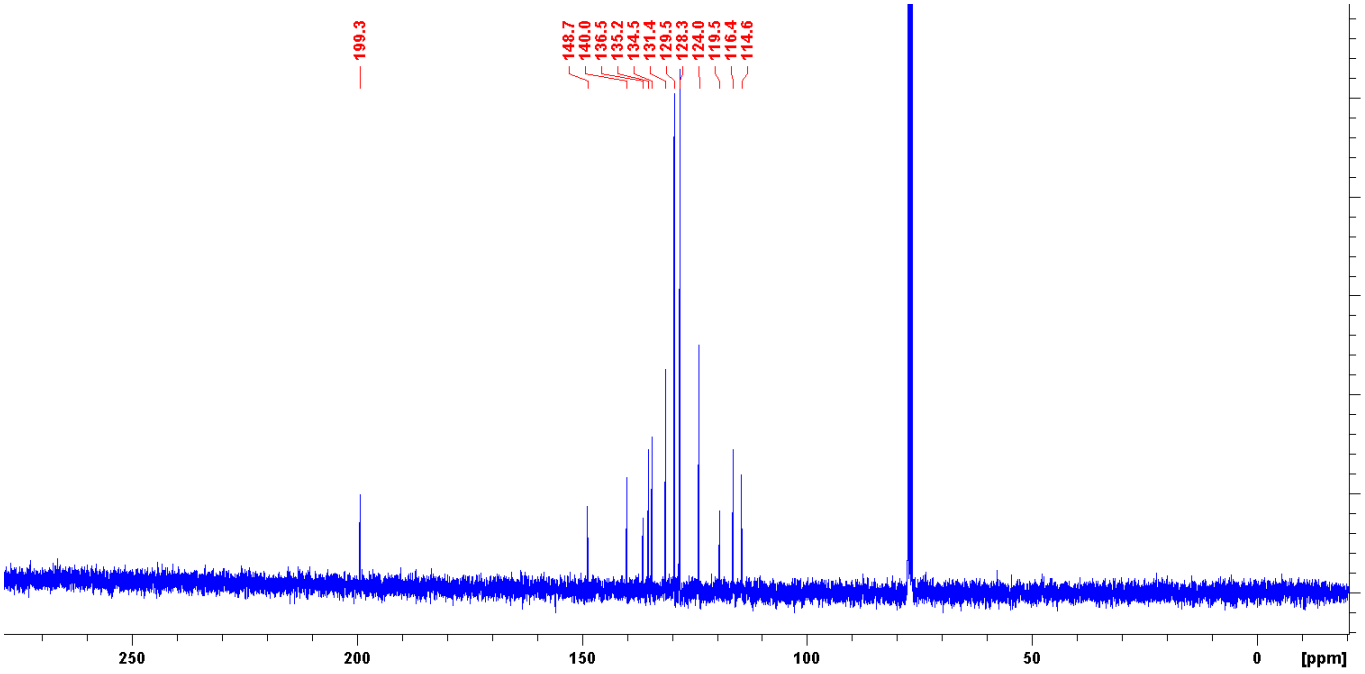


Figure S-F.32: ^{13}C NMR Spectrum (75 MHz, $CDCl_3$).

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