Supporting information

Double helicene possessing B-N dative bonds built on 1,4-dihydropyrrolo[3,2-*b*]pyrrole core

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1. Used reagents

All chemicals were commercially available and were used as received unless noted otherwise.

Sigma-Aldrich: iron(III) perchlorate hydrate, sodium borohydride >98%, benzaldehyde >99%, trifluoroacetic acid 99%, naphthalene-1-carbaldehyde 95%, trimethylaluminum solution 2 M in hexane

Chempur: toluene p. a., acetic acid p. a. >99,5%, magnesium sulfate anhydrous p., dimethylformamide HPLC grade, sulfuric acid 98% p. a., chromium(VI) oxide p. a., ammonia 25% p. a., potassium sodium tartrate tetrahydrate p. a.

Linegal chemicals: ethanol Line-Antybakteria, hexane fraction from kerosene p.

BLDpharm: 4-octylaniline 99,79%, 2,6-di-*tert*-butylpyridine 99,84%, 1-bromodibenzo[*b*,*d*]thiophene 99,91%, benzanthrone 98%

AmBeed: 2-nitrobenzaldehyde 98%

TCI: butanedione >98%

POCH: diethyl ether 99,5% (stab. BHT), nickel(II) acetate tetrahydrate, isopropanol HPLC grade, methanol HPLC grade, morpholine p. a.

ChemSolute: acetonitrile HPLC grade >99,9%

Stanlab: ethyl acetate p. a., dichloromethane p. a., sodium hydroxide p. a., hydrochloric acid 35-38% p. a.

Centro-Chem: methanol

Honeywell: tetrahydrofuran HPLC grade >99,9%, toluene HPLC grade >99,9%, dichloromethane HPLC grade >99,8%

Thermo Scientific: boron tribromide solution 1 M in dichloromethane, Red-Al solution 70% in toluene (around 3.5 M)

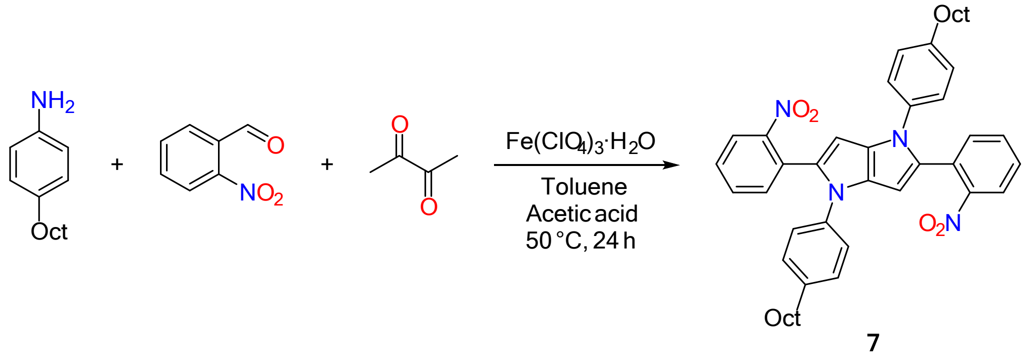
Roth: sodium sulfate anhydrous >99%

Fluka: thionyl chloride >99%

Dry and degassed solvents were obtained using MBRAUN Solvent Purification System.

2. Synthesis of organic compounds

Synthesis of TAPP 7



7
43%

This compound was synthesized based on the procedure published by Gryko's group.[1]

To a 250 mL round-bottom flask 4-octylaniline (5.00 g, 24.4 mmol, 2 equiv.) 2-nitrobenzaldehyde (3.68 g, 24.4 mmol, 2 equiv.), toluene (19 mL) and acetic acid (19 mL) were added. The resulting solution was stirred for one hour at 50 °C in open flask without a condenser. After one hour iron(III) perchlorate hydrate (272 mg, 0.731 mmol, 0.06 equiv.) and butanedione (1.1 g, 1.1 mL, 12 mmol, 1 equiv.) were added. The resulting dark solution was stirred for 23 hours at 50 °C in open flask without a condenser, while orange precipitate formed. When the reaction was finished, the solvents were evaporated and 20 mL of diethyl ether was added. The orange precipitate was filtered and subsequently washed with diethyl ether and acetonitrile. The crude product was recrystallized from 69 mL of ethyl acetate. Orange product was filtered and dried in vacuum at 80 °C for one hour. Yield: 3.79 g (12.2 mmol, 43%).

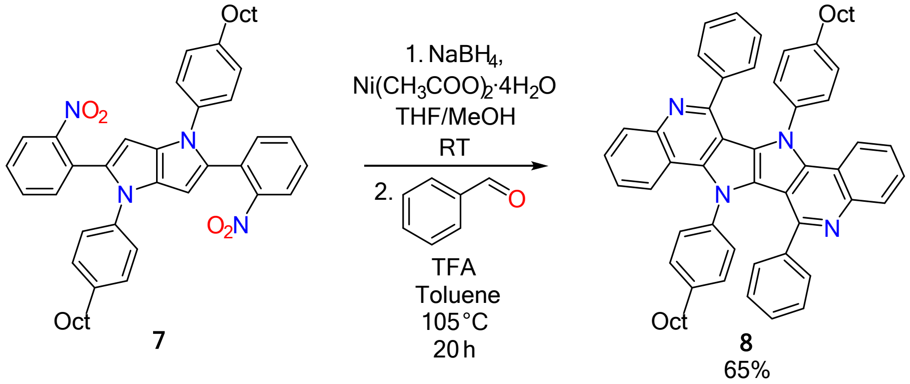
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.72 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 7.2 Hz, 2H), 7.42 (d, J = 6.7 Hz, 2H), 7.35 (t, J = 7.1 Hz, 2H), 7.09 (br. s, 8H), 6.35 (s, 2H), 2.57 (t, J = 7.8 Hz, 4H), 1.81 – 1.46 (m, 4H), 1.43 – 1.14 (m, 20H), 0.88 (t, J = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 149.0, 140.7, 136.3, 133.0, 132.1, 131.5, 130.4, 129.1, 128.3, 127.7, 124.5, 124.1, 95.3, 35.4, 31.9, 31.3, 29.4, 29.3, 29.2, 22.7, 14.1.

HR MS (APCI+): m/z calculated for $C_{46}H_{53}N_4O_4$ $[M+H]^+$: 725.4067; found 725.4069.

Melting point: 176.9-178.2 °C

Synthesis of DQPP 8



This compound was synthesized based on the procedure published by Gryko's group.[2]

Nickel(II) acetate tetrahydrate (343 mg, 1.38 mmol, 1 equiv.) and methanol (56 mL) were added to a 250 mL round-bottom flask. When the salt dissolved sodium borohydride (157 mg, 4.14 mmol, 3 equiv.) was added and black suspension formed. The flask was wrapped with aluminium foil and the mixture was stirred at room temperature for 15 minutes. In a separate 100 mL round-bottom flask **7** (1.00 g, 1.38 mmol, 1 equiv.) was dissolved in 56 mL of tetrahydrofuran. This solution was added into the reaction mixture and with limited light access more sodium borohydride (500-800 mg) was added, until TLC showed presence of only one, colorless product with strong blue fluorescence. The reaction mixture was filtered through celite, washed with tetrahydrofuran. The solvents were evaporated and 100 mL of water was added. The product was extracted three times with 100 mL of ethyl acetate. The combined organic phase was dried with magnesium sulfate. The solvent was evaporated in a 500 mL round-bottom flask and the residue was dissolved in 34 mL of toluene. Benzaldehyde (293 mg, 282 µL, 2.76 mmol, 2 equiv.) and trifluoroacetic acid (31.5 mg, 20.4 µL, 0.276 mmol, 0.2 equiv.) were added. The resulting dark brown solution was stirred at 105 °C, under an air condenser, for 20 hours. The solvent was evaporated and 20 mL of ethanol was added. After 30 minutes the brown precipitate was filtered and washed with ethanol. The crude product was recrystallized from 300 mL of ethyl acetate. Pale product was filtered and dried in vacuum at 100° C for one hour. Yield: 754 mg (0.901 mmol, 65%).

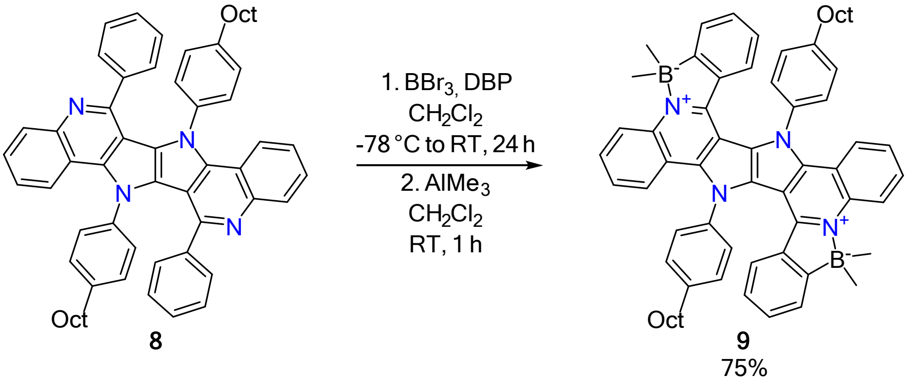
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.15 (br. s, 2H), 7.52 – 7.40 (m, 6H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 4H), 7.09 – 7.01 (m, 6H), 6.94 (d, *J* = 8.0 Hz, 4H), 6.89 (d, *J* = 8.5 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 4H), 1.79 – 1.68 (m, 4H), 1.49 – 1.31 (m, 20H), 0.93 (t, *J* = 6.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 153.5, 143.6, 141.7, 137.6, 129.7, 128.7, 128.6, 128.3, 128.0, 126.8, 124.9, 120.7, 117.6, 106.7, 35.7, 31.94, 30.9, 29.6, 29.5, 29.4, 22.7, 14.1.

HR MS (APCI+): m/z calculated for $C_{60}H_{61}N_4$ $[M+H]^+$: 837.4896; found 837.4880.

Melting point: 205.6-207.6 °C

Synthesis of N/C boron complex 9



A 50 mL Schlenk reaction vessel was evacuated and heated with a heat gun. After cooling down, the vessel was filled with argon and **8** (300 mg, 0.358 mmol, 1 equiv.) was added. The vessel was evacuated and filled with argon three times and dry and degassed dichloromethane (15 mL) and 2,6-di-*tert*-butylpyridine (274 mg, 322 µL, 1.43 mmol, 4 equiv.) were added. The resulting clear yellow solution was cooled down to -78 °C with a dry ice/isopropanol bath. Boron tribromide solution in dichloromethane (2.15 mL, 1 M, 2.15 mmol, 6 equiv.) was slowly added under stream of argon. The cooling bath was removed and the resulting yellow suspension with weak green fluorescence was stirred at room temperature for 24 hours. The solvent was evaporated. The reaction vessel was evacuated and filled with argon three times and 20 mL of dry and degassed dichloromethane was added. Slowly, under stream of argon, trimethylaluminum solution in hexane (1.08 mL, 2 M, 2.15 mmol, 6 equiv.) was added. The resulting suspension was stirred at room temperature for one hour, while strong blue fluorescence appeared. The reaction mixture was cooled down with a water/ice bath and 20 mL of water was carefully added. The resulting biphasic mixture was transferred into a separatory funnel and the phases were separated. The water phase was extracted four times with 10 mL of dichloromethane. The combined organic phase was dried with sodium sulfate. Approximately 10 g of silica gel was added, the solvent was evaporated and the product was filtered through a short pad of silica gel, washed with hexane/ethyl acetate 97:3 mixture. The solvents were evaporated and the crude product was recrystallized from 130 mL of ethyl acetate/acetonitrile 1:2 mixture. Yellow product was filtered and dried in vacuum at room temperature for one hour. Yield: 245 mg (0.267 mmol, 75%).

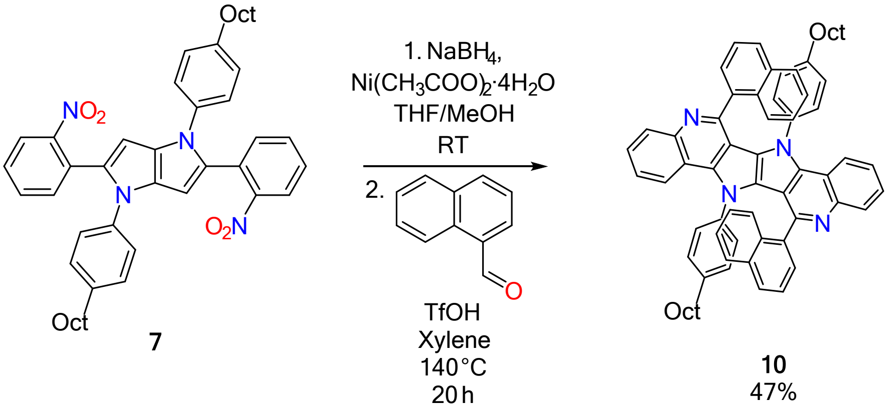
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.71 (d, J = 8.7 Hz, 2H), 7.63 (d, J = 7.2 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 7.2 Hz, 2H), 7.50 – 7.45 (m, 4H), 7.43 (d, J = 7.6 Hz, 2H), 7.24 – 7.10 (m, 8H), 6.61 (t, J = 7.2 Hz, 2H), 2.61 (t, J = 7.8 Hz, 4H), 1.62 – 1.55 (m, 4H), 1.41 – 1.30 (m, 20H), 0.94 (t, J = 6.8 Hz, 6H), 0.31 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 152.9, 145.5, 141.6, 138.4, 137.0, 136.1, 130.4, 130.2, 129.4, 128.2, 128.1, 127.2, 124.92, 124.87, 124.4, 123.5, 121.1, 118.0, 102.2, 35.7, 32.0, 31.5, 29.7, 29.5, 29.4, 29.3, 22.7, 14.2, 9.9.

HR MS (APCI+): m/z calculated for $C_{64}H_{71}B_2N_4$ $[M+H]^+$: 917.5856; found 917.5873.

Melting point: 242.0-242.8 °C

Synthesis of DQPP 10



This compound was synthesized based on the procedure published by Gryko's group.[2]

Nickel(II) acetate tetrahydrate (343 mg, 1.38 mmol, 1 equiv.) and methanol (56 mL) were added to a 250 mL round-bottom flask. When the salt dissolved sodium borohydride (157 mg, 4.14 mmol, 3 equiv.) was added and black suspension formed. The flask was wrapped with aluminium foil and the mixture was stirred at room temperature for 15 minutes. In a separate 100 mL round-bottom flask **7** (1.00 g, 1.38 mmol, 1 equiv.) was dissolved in 56 mL of tetrahydrofuran. This solution was added into the reaction mixture and with limited light access more sodium borohydride (500-800 mg) was added, until thin layer chromatography analysis showed presence of only one, colorless product with strong blue fluorescence. The reaction mixture was filtered through celite, washed with tetrahydrofuran. The solvents were evaporated and 100 mL of water was added. The product was extracted three times with 100 mL of ethyl acetate. The combined organic phase was dried with magnesium sulfate. The solvent was evaporated in a 500 mL round-bottom flask and the residue was dissolved in 34 mL of xylene. Naphthalene-1-carbaldehyde (431 mg, 375 µL, 2.76 mmol, 2 equiv.) and trifluoromethanesulfonic acid (41.4 mg, 24.4 µL, 0.276 mmol, 0.2 equiv.) were added. The resulting dark brown solution was stirred at 140 °C, under an air condenser, for 20 hours. The solvent was evaporated and 20 mL of ethanol was added. After 30 minutes brown precipitate was filtered and washed with ethanol. The crude product was recrystallized from 61 mL of ethyl acetate. Pale product was filtered and dried in vacuum at 100° C for one hour. Yield: 605 mg (0.646 mmol, 47%).

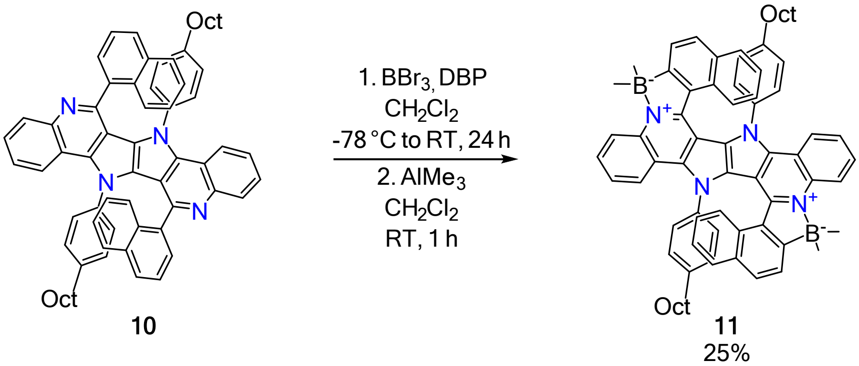
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.08 (d, J = 8.2 Hz, 2H), 7.75 (dd, J = 12.1, 8.2 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.5 Hz, 1H), 7.48 (d, J = 7.9 Hz, 2H), 7.45 – 7.34 (m, 6H), 7.33 – 7.26 (m, 2H), 7.23 (t, J = 7.6 Hz, 1H), 6.97 – 6.92 (m, 2H), 7.07 – 6.69 (m, 4H), 6.43 (dd, J = 8.4, 4.0 Hz, 2H), 6.51 – 6.19 (m, 4H), 2.63 – 2.42 (m, 4H), 1.72 – 1.59 (m, 4H), 1.47 – 1.29 (m, 20H), 0.93 (t, J = 6.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 152.7, 152.6, 144.6, 144.5, 142.9, 142.8, 140.8, 140.7, 140.7, 140.6, 136.5, 136.4, 133.9, 133.8, 131.9, 131.9, 130.2, 128.3, 128.3, 128.0, 127.5, 126.9, 126.8, 126.5, 126.3, 126.2, 125.8, 125.6, 124.9, 120.9, 120.9, 117.6, 108.4, 108.3, 35.5, 31.9, 30.5, 29.6, 29.4, 29.3, 22.7, 14.1. The excess number of signals is likely due to the presence of different atropisomers.

HR MS (APCI+): m/z calculated for $C_{68}H_{65}N_4$ $[M+H]^+$: 937.5209; found 937.5203.

Melting point: 251.9-252.7 °C

Synthesis of N/C boron complex 11



A 50 mL Schlenk reaction vessel was evacuated and heated with a heat gun. After cooling down, the vessel was filled with argon and **10** (336 mg, 0.358 mmol, 1 equiv.) was added. The vessel was evacuated and filled with argon three times and dry and degassed dichloromethane (15 mL) and 2,6-di-*tert*-butylpyridine (274 mg, 322 µL, 1.43 mmol, 4 equiv.) were added. The resulting clear yellow solution was cooled down to -78 °C with a dry ice/isopropanol bath. Boron tribromide solution in dichloromethane (2.15 mL, 1 M, 2.15 mmol, 6 equiv.) was slowly added under stream of argon. The cooling bath was removed and the resulting brown suspension with weak yellow fluorescence was stirred at room temperature for 24 hours. The solvent was evaporated. The reaction vessel was evacuated and filled with argon three times and 20 mL of dry and degassed dichloromethane was added. Slowly, under stream of argon, trimethylaluminum solution in hexane (1.08 mL, 2 M, 2.15 mmol, 6 equiv.) was added. The resulting suspension was stirred at room temperature for one hour, while strong green fluorescence appeared. The reaction mixture was cooled down with a water/ice bath and 20 mL of water was carefully added. The resulting biphasic mixture was transferred into a separatory funnel and the phases were separated. The water phase was extracted four times with 10 mL of dichloromethane. The combined organic phase was dried with sodium sulfate. Approximately 10 g of silica gel was added, the solvent was evaporated and the product was filtered through a short pad of silica gel, washed with hexane/ethyl acetate 19:1 mixture. The solvents were evaporated and the crude product was recrystallized from 160 mL of ethyl acetate/acetonitrile 1:2 mixture. Yellow product was filtered and dried in vacuum at room temperature for one hour. Yield: 90.0 mg (88.5 µmol, 25%).

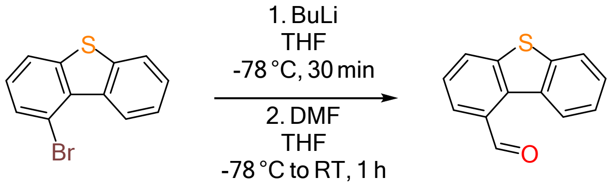
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.62 (d, J = 8.6 Hz, 2H), 8.57 – 8.49 (m, 2H), 7.85 – 7.77 (m, 2H), 7.71 (s, 4H), 7.64 (d, J = 8.7 Hz, 2H), 7.56 (t, J = 7.3 Hz, 2H), 7.46 – 7.32 (m, 4H), 7.06 (t, J = 7.5 Hz, 2H), 6.87 (dd, J = 8.0, 2.3 Hz, 2H), 6.53 (d, J = 8.1 Hz, 2H), 6.48 (dd, J = 7.9, 2.3 Hz, 2H), 6.40 (d, J = 8.0 Hz, 2H), 2.50 – 2.25 (m, 4H), 1.59 – 1.47 (m, 4H), 1.46 – 1.31 (m, 20H), 0.95 (t, J = 6.9 Hz, 6H), 0.31 (s, 6H), 0.25 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 174.8, 152.7, 143.04, 142.98, 138.5, 135.1, 132.9, 132.6, 131.6, 130.9, 130.0, 129.0, 128.20, 128.15, 126.6, 126.3, 125.9, 125.5, 124.6, 123.89, 123.85, 123.7, 121.0, 117.7, 105.3, 35.4, 32.0, 30.8, 29.6, 29.6, 29.4, 22.8, 14.2, 9.6, 9.1. The excess number of signals is likely due to the presence of two diastereoisomers.

HR MS (APCI+): m/z calculated for $C_{72}H_{75}B_2N_4$ $[M+H]^+$: 1017.6178; found 1017.6186.

Melting point: 255.6-256.8 °C (decomposition)

Synthesis of dibenzo[*b*,*d*]thiophene-1-carbaldehyde S1

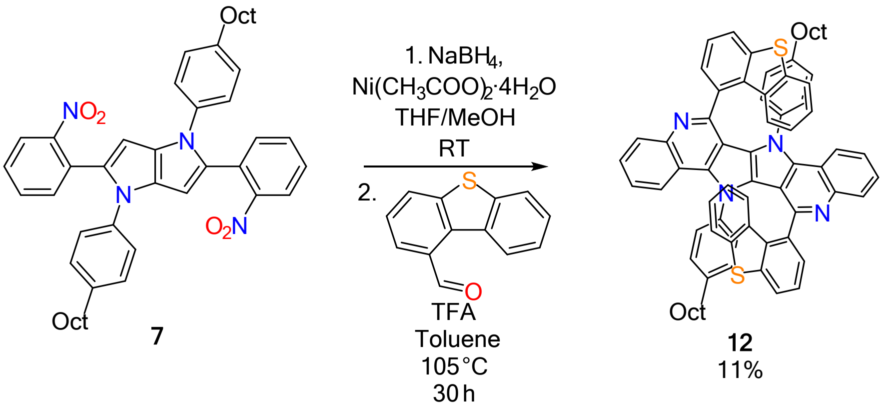


S1
87%

A 250 mL Schlenk reaction vessel was evacuated and heated with a heat gun. After cooling down, the vessel was filled with argon and 1-bromodibenzo[*b*,*d*]thiophene (3.54 g, 13.5 mmol, 1 equiv.) was added. The vessel was evacuated and filled with argon three times and dry and degassed tetrahydrofuran (71 mL) was added. The stopper was switched with a septum connected to a balloon with argon. The reaction mixture was cooled down to -78 °C with a dry ice/isopropanol bath. Butyllithium solution in hexane (8.1 mL, 2.5 M, 20 mmol, 1.5 equiv.) was slowly added and the resulting yellow solution was stirred for 30 minutes with cooling. Dry and degassed dimethylformamide (4.9 g, 5.2 mL, 67 mmol, 5 equiv.) was added. The mixture was stirred for 10 minutes with cooling, while white precipitate formed. The cooling bath was removed and the resulting suspension was stirred for one hour. Saturated water solution of sodium hydrogen carbonate (100 mL) was added. The biphasic mixture was transferred into a separatory funnel and the phases were separated. The water chase was extracted three times with 50 mL of ethyl acetate. Combined organic phase was dried with magnesium sulfate. The solvents were evaporated and the crude product was recrystallized from 320 mL of ethanol/water 7:9 mixture. Pale product was filtered and dried in vacuum at 80 °C for 5 hours. Yield: 2.48 g (11.7 mmol, 87%).

^{1}H NMR (600 MHz, $CDCl_3$) δ_H: 10.71 (s, 1H), 9.04 – 8.91 (m, 1H), 8.10 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.98 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.94 – 7.89 (m, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.57 – 7.49 (m, 2H).

Synthesis of DQPP 12



7

12
11%

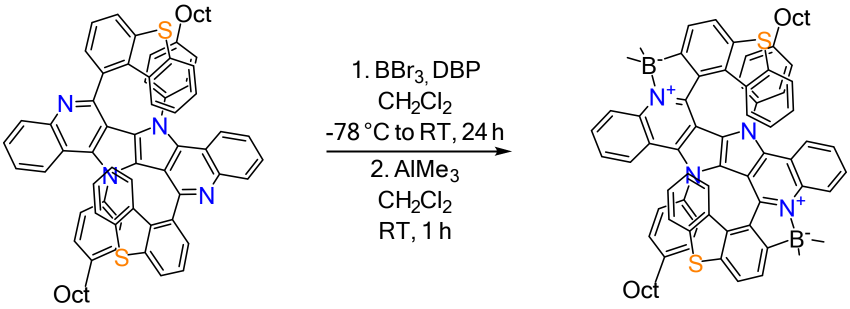
This compound was synthesized based on the procedure published by Gryko's group.[2]

Nickel(II) acetate tetrahydrate (1.03 g, 4.14 mmol, 1 equiv.) and methanol (170 mL) were added to a 250 mL round-bottom flask. When the salt dissolved sodium borohydride (497 mg, 12.4 mmol, 3 equiv.) was added and black suspension formed. The flask was wrapped with aluminium foil and the mixture was stirred at room temperature for 15 minutes. In a separate 250 mL beaker **7** (3.00 g, 4.14 mmol, 1 equiv.) was dissolved in 170 mL of tetrahydrofuran. This solution was transferred into the reaction mixture and a new portion of sodium borohydride (1.5-2.5 g) was added with limited light access, until TLC showed presence of the only colorless product with strong blue fluorescence. The reaction mixture was filtered through celite, washed with tetrahydrofuran. The solvents were evaporated and 150 mL of water was added. The product was extracted three times with 200 mL of ethyl acetate. The combined organic phase was dried with magnesium sulfate. The solvent was evaporated in a 1 L round-bottom flask and the residue was dissolved in 100 mL of toluene. **S1** (1.76 g, 8.28 mmol, 2 equiv.) and trifluoroacetic acid (94.4 mg, 61.3 µL, 0.828 mmol, 0.2 equiv.) were added. The resulting dark brown solution was stirred at 105 °C, under an air condenser, for 30 hours. The solvent was evaporated and 200 mL of ethanol was added. After 30 minutes of sonication brown precipitate was filtered and washed with ethanol. The crude product was suspended in 100 mL of ethanol, brought to boiling and refluxed for 30 minutes. It was quickly filtered before it cooled down and subsequently washed with ethanol. The pale product was dried in vacuum at 100° C for one hour. It was used in the next step without further purification. Yield: 459 mg (4.14 mmol, 11%).

HR MS (APCI+): m/z calculated for $C_{72}H_{65}N_4S_2$ $[M+H]^+$: 1049.4651; found 1049.4636.

Melting point: 261.2-270.0 °C

Synthesis of N/C boron complex 13



12 **13** 16%

A 50 mL Schlenk reaction vessel was evacuated and heated with a heat gun. After cooling down, the vessel was filled with argon and **12** (430 mg, 0.410 mmol, 1 equiv.) was added. The vessel was evacuated and filled with argon three times and dry and degassed dichloromethane (17 mL) and 2,6-di-*tert*-butylpyridine (314 mg, 368 µl, 1.64 mmol, 4 equiv.) were added. The resulting clear yellow solution was cooled down to -78 °C with a dry ice/isopropanol bath. Boron tribromide solution in dichloromethane (2.46 mL, 1 M, 2,46 mmol, 6 equiv.) was slowly added under stream of argon. The cooling bath was removed and the resulting brown suspension with weak orange fluorescence was stirred at room temperature for 24 hours. The solvent was evaporated. The reaction vessel was evacuated and filled with argon three times and 23 mL of dry and degassed dichloromethane was added. Slowly, under stream of argon, trimethylaluminum solution in hexane (3.69 mL, 2 M, 7.38 mmol, 18 equiv.) was added. The resulting suspension was stirred at room temperature for one hour, while strong green fluorescence appeared. The reaction mixture was cooled down with a water/ice bath and 20 mL of water was carefully added. The resulting biphasic mixture was transferred into a separatory funnel and the phases were separated. The water phase was extracted four times with 20 mL of dichloromethane. The combined organic phase was dried with sodium sulfate. Approximately 10 g of silica gel was added, the solvent was evaporated and the product was filtered through a short pad of silica gel, washed with hexane/ethyl acetate 19:1 mixture. The solvents were evaporated and the crude product was recrystallized as follows: the product was dissolved in 80 mL of boiling ethyl acetate and, with constant heating, 80 mL of acetonitrile were added. The resulting suspension was cooled down and placed in a freezer for three days. Yellow product was filtered and dried in vacuum at room temperature for one hour. Yield: 73.3 mg (0.410 mmol, 16%).

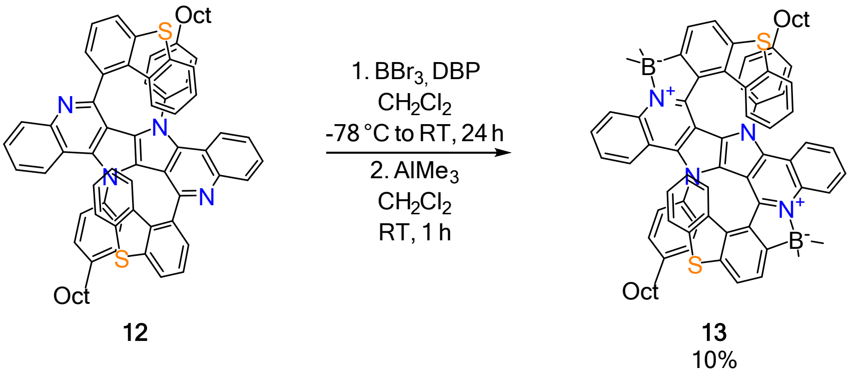
^{1}H NMR (500 MHz, CD_2Cl_2) δ_H: δ 8.67 (d, J = 8.5 Hz, 2H), 8.29 (d, J = 7.5 Hz, 2H), 7.92 (d, J = 7.0 Hz, 2H), 7.76 (d, J = 7.7 Hz, 2H), 7.65 (d, J = 7.7 Hz, 2H), 7.63 – 7.56 (m, 4H), 7.36 – 7.22 (m, 4H), 7.08 (t, J = 7.6 Hz, 2H), 6.88 (d, J = 7.9 Hz, 2H), 6.46 (d, J = 7.7 Hz, 2H), 6.40 (d, J = 7.7 Hz, 2H), 5.83 (d, J = 6.3 Hz, 2H), 2.53 – 2.36 (m, 4H), 1.69 – 1.48 (m, 4H), 1.41 – 1.26 (m, 20H), 0.90 (t, J = 6.0 Hz, 6H), 0.25 (s, 6H), 0.19 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ_C: 152.4, 143.5, 141.7, 139.5, 138.3, 137.3, 136.3, 134.0, 133.4, 130.7, 129.8, 128.2, 127.6, 127.5, 125.9, 125.8, 125.0, 124.87, 124.83, 124.20, 124.17, 122.9, 122.7, 120.7, 117.7, 105.2, 35.5, 32.2, 30.9, 29.9, 29.8, 29.7, 23.1, 14.4, 10.3, 10.0.

HR MS (APCI+): m/z calculated for $C_{76}H_{75}B_2N_4S_2$ $[M+H]^+$: 1129.5619; found 1129.5607.

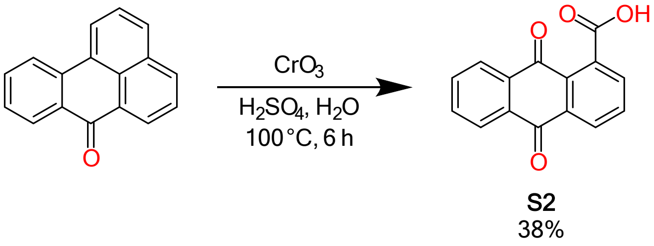
Melting point: 310.9-312.6 °C

Alternative synthesis of 13



A 50 mL Schlenk reaction vessel was evacuated and heated with a heat gun. After cooling down, the vessel was filled with argon and **12** (430 mg, 0.410 mmol, 1 equiv.) was added. The vessel was evacuated and filled with argon three times and dry and degassed dichloromethane (17 mL) and 2,6-di-*tert*-butylpyridine (314 mg, 368 µL, 1.64 mmol, 4 equiv.) were added. The resulting clear yellow solution was cooled down to -78 °C with a dry ice/isopropanol bath. Boron tribromide solution in dichloromethane (2.46 mL, 1 M, 2,46 mmol, 6 equiv.) was slowly added under stream of argon. The cooling bath was removed and the resulting brown suspension with weak orange fluorescence was stirred at room temperature for 24 hours. The solvent was evaporated. The reaction vessel was evacuated and filled with argon three times and 23 mL of dry and degassed dichloromethane was added. Slowly, under stream of argon, trimethylaluminum solution in hexane (3.69 mL, 2 M, 7.38 mmol, 18 equiv.) was added. The resulting suspension was stirred at room temperature for one hour, while strong green fluorescence appeared. The reaction mixture was cooled down with a water/ice bath and 20 mL of water were carefully added. The resulting biphasic mixture was transferred into a separatory funnel and the phases were separated. The water phase was extracted four times with 20 mL of dichloromethane. The combined organic phase was dried with sodium sulfate. Approximately 10 g of silica gel was added, the solvent was evaporated and the mixture was separated by flash chromatography on a RediSep Gold column. The eluent was hexane/dichloromethane gradient from pure hexane to pure dichloromethane. The solvents were evaporated from the fraction containing **13**. The remaining yellow solid was dried in vacuum at room temperature for one hour. Yield: 27.2 mg (0.240 mmol, 10%).

Synthesis of anthraquinone-1-carboxylic acid S2

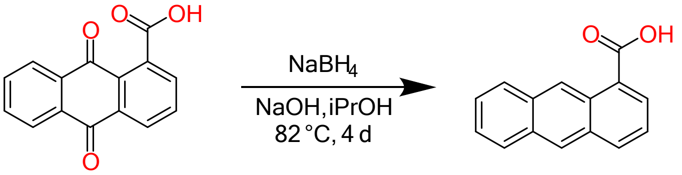


This compound was synthesized based on the procedure published by Tokumaru's group.[3]

Benzanthrone (10.0 g, 43.4 mmol, 1 equiv.) was dissolved in 120 mL of sulfuric acid in a 250 mL round-bottom flask. This red solution was added slowly with constant stirring into 600 mL of boiling water in a 1 L round-bottom flask. Chromium(VI) oxide (43.4 g, 434 mmol, 10 equiv.) was added and the resulting black suspension was refluxed for 6 hours. Next, the reaction mixture was allowed to cool down to room temperature and the brown precipitate was filtered. The product was dissolved in 10% ammonia solution and the insoluble impurities were filtered off. The filtrate was transferred into a 1 L round-bottom flask and brought to boiling. It was slowly acidified with concentrated hydrochloric acid until light brown precipitate formed. The mixture was cooled down to room temperature and the crude product was filtered and washed with water. It was recrystallized form 800 mL of ethanol. Yellow product was filtered and dried in vacuum at 100 °C for one hour. Yield: 4.21 g (16.7 mmol, 38%).

^{1}H NMR (500 MHz, DMSO) δ_H: 13.27 (br. s, 1H), 8.29 (dd, J = 7.7, 1.2 Hz, 1H), 8.25 – 8.20 (m, 1H), 8.20 – 8.15 (m, 1H), 7.99 – 7.93 (m, 3H), 7.85 (dd, J = 7.5, 1.2 Hz, 1H).

Synthesis of anthracene-1-carboxylic acid S3



S2

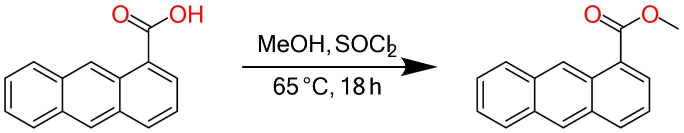
S3
61%

This compound was synthesized based on the procedure published by Plenio's group.[4]

S2 (4.21 g, 16.7 mmol, 1 equiv.), sodium hydroxide (200 mg, 5,00 mmol, 3 equiv.) and isopropanol (170 mL, HPLC grade) were added into a 500 mL three-necked flask. Argon was bubbled through the solvent for 15 minutes. The mixture was cooled down to 0 °C and sodium borohydride (6.31 g, 167 mmol, 10 equiv.) was added with constant stirring. The mixture changed color from yellow to grey and after an hour to purple. It was stirred at 0 °C for an hour and then the temperature was raised to 82 °C. The mixture was stirred at that temperature under an air condenser for 4 days. It was then cooled down and poured into a 1 L round-bottom flask with 400 mL of water. 40 mL of concentrated hydrochloric acid was added very slowly and carefully. The orange precipitate which formed was stirred for 30 minutes and then it was filtered and washed with water. The crude product was dried in vacuum at room temperature for 30 minutes and recrystallized from 280 mL of methanol. Yellow product was filtered and dried in vacuum at 100 °C for one hour. Yield: 2.25 g (10.1 mmol, 61%).

^{1}H NMR (500 MHz, DMSO) δ_H: 13.16 (br. s, 1H), 9.52 (s, 1H), 8.68 (s, 1H), 8.32 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 6.9 Hz, 1H), 8.16 – 8.06 (m, 2H), 7.61 – 7.52 (m, 3H).

Synthesis of methyl anthracene-1-carboxylate S4



S3

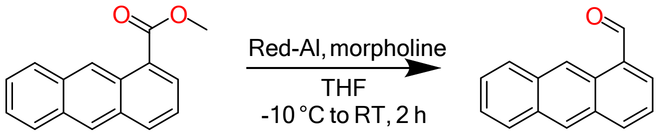
S4
88%

This compound was synthesized based on the procedure published by Plenio's group.[4]

S3 (2.25 g, 10.1 mmol, 1 equiv.) and methanol (45 mL, HPLC grade) were added into a 250 mL round-bottom flask. This suspension was cooled down to 0 °C and thionyl chloride (1.81 g, 1.10 mL, 15.2 mmol, 1.5 equiv.) was slowly added. The cooling bath was removed and the mixture was heated to 65 °C. The mixture was stirred at that temperature under an air condenser for 18 hours. It was then cooled down and poured into 200 mL of water. This emulsion was transferred into a separatory funnel and the product was extracted four times with 50 mL of ethyl acetate. The combined organic phases were washed with 50 mL of saturated sodium hydrogen carbonate solution and dried with magnesium sulfate. The solvent was evaporated and the crude product was recrystallized from 50 mL of methanol. Yellow product was filtered and dried in vacuum at room temperature for one hour. Yield: 2.10 g (8.88 mmol, 88%)

^{1}H NMR (600 MHz, $CDCl_3$) δ_H: 9.58 (s, 1H), 8.47 (s, 1H), 8.24 (d, J = 7.0 Hz, 1H), 8.19 (d, J = 8.5 Hz, 1H), 8.13 – 8.06 (m, 1H), 8.05 – 7.96 (m, 1H), 7.53 – 7.49 (m, 2H), 7.47 (dd, J = 8.4, 7.0 Hz, 1H), 4.06 (s, 3H).

Synthesis of anthracene-1-carbaldehyde S5



S4

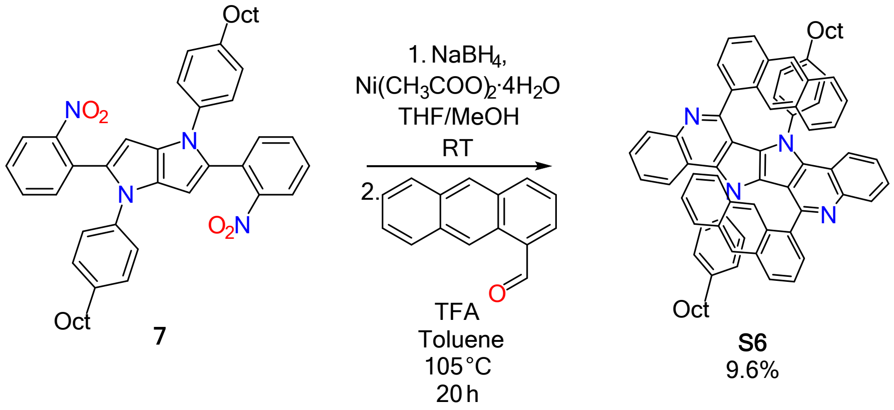
S5
60%

This compound was synthesized based on the procedure published by Zagotto's group.[5]

A 250 mL Schlenk flask was evacuated and heated with a heatgun. After cooling down it was filled with argon and it was then evacuated and filled with argon three more times. Red-Al solution in toluene (6.1 mL, 3.5 M, 22 mmol, 3 equiv.) and dry and degassed THF (6.8 mL) were added. In two separate Schlenk flasks morpholine (2.06 g, 2.07 mL, 23.6 mmol, 3.3 equiv.) and **S4** (1.69 g, 7.16 mmol, 1 equiv.) were dissolved in dry and degassed THF (1.7 mL and 6.8 mL, respectively). Red-Al solution was cooled down to -10 °C and connected to a bubbler through a septum. Morpholine solution was slowly added and the resulting mixture was stirred with constant cooling for one hour, during which colorless gas evolved. **S4** solution was slowly added and the cooling bath was removed. The resulting yellow solution was stirred at room temperature for one hour. 50 mL of concentrated potassium sodium tartrate solution was added and the product was extracted three times with 50 mL of dichloromethane. The combined organic phases were dried with magnesium sulfate. Approximately 10 g of silica gel was added, the solvent was evaporated and the product was filtered through a short pad of silica gel, washed with hexane/ethyl acetate 9:1 mixture. The solvents were evaporated and the crude product was recrystallized from 50 mL of methanol. Yellow product was filtered and dried in vacuum at 60 °C for one hour. Yield: 882 mg (4.28 mmol, 60%).

^{1}H NMR (600 MHz, $CDCl_3$) δ_H: 10.40 (s, 1H), 9.94 (s, 1H), 8.50 (s, 1H), 8.27 (d, J = 8.5 Hz, 1H), 8.15 (d, J = 7.1 Hz, 1H), 8.03 (d, J = 7.0 Hz, 1H), 8.00 (d, J = 6.7 Hz, 1H), 7.61 (dd, J = 8.4, 6.8 Hz, 1H), 7.58 – 7.53 (m, 2H).

Synthesis of DQPP S6



7

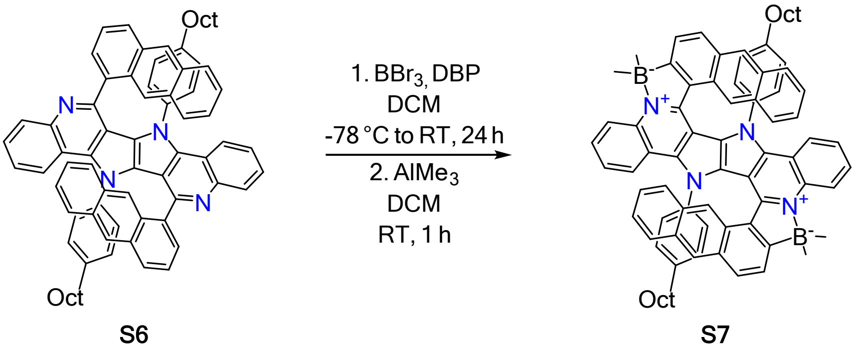
S6
9.6%

This compound was synthesized based on the procedure published by Gryko's group.[2]

Nickel(II) acetate tetrahydrate (172 g, 0.690 mmol, 1 equiv.) and methanol (28 mL) were added to a 250 mL round-bottom flask. When the salt dissolved sodium borohydride (78 mg, 2.07 mmol, 3 equiv.) was added and black suspension formed. The flask was wrapped with aluminium foil and the mixture was stirred at room temperature for 15 minutes. In a separate 100 mL beaker **7** (500 mg, 0.690 mmol, 1 equiv.) was dissolved in 28 mL of tetrahydrofuran. This solution was transferred into the reaction mixture and a new portion of sodium borohydride (300-400 mg) was added with limited light access, until TLC showed presence of the only colorless product with strong blue fluorescence. The reaction mixture was filtered through celite, washed with tetrahydrofuran. The solvents were evaporated and 50 mL of water was added. The product was extracted three times with 50 mL of ethyl acetate. The combined organic phase was dried with magnesium sulfate. The solvent was evaporated in a 250 mL round-bottom flask and the residue was dissolved in 17 mL of toluene. **S5** (285 mg, 1.38 mmol, 2 equiv.) and trifluoroacetic acid (15.7 mg, 10.2 µL, 0.138 mmol, 0.2 equiv.) were added. The resulting dark brown solution was stirred at 105 °C, under an air condenser, for 20 hours. The solvent was evaporated and 10 mL of ethanol was added. After 60 minutes of sonication brown precipitate was filtered and washed with ethanol. The pale product was dried in vacuum at 100° C for one hour. It was used in the next step without further purification. Yield: 68.6 mg (66.1 µmol, 9.6%).

HR MS (APCI+): m/z calculated for $C_{76}H_{69}N_4$ $[M+H]^+$: 1037.5522; found 1037.5533.

Synthesis of N/C boron complex S7



S6

S7
6.0%

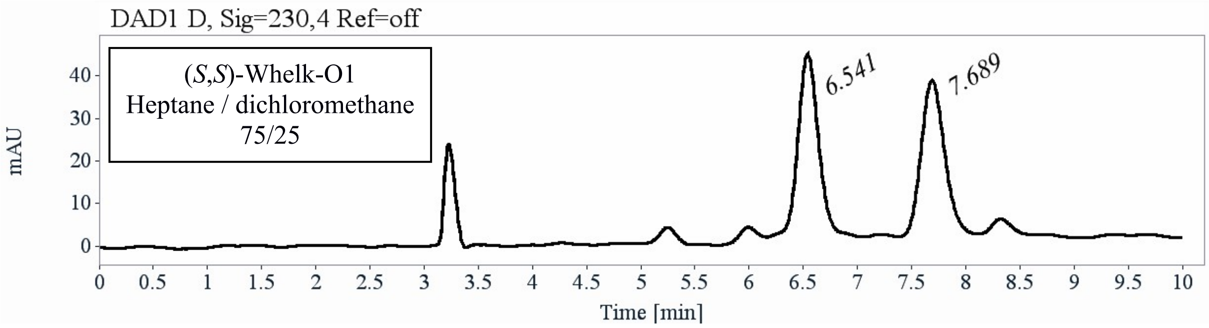
A 50 mL Schlenk reaction vessel was evacuated and heated with a heat gun. After cooling down, the vessel was filled with argon and **S6** (64.8 mg, 6.25 µmol, 1 equiv.) was added. The vessel was evacuated and filled with argon three times and dry and degassed dichloromethane (2.6 mL) and 2,6-di-*tert*-butylpyridine (47.8 mg, 56.1 µl, 0.25 mmol, 4 equiv.) were added. The resulting clear yellow solution was cooled down to -78 °C with a dry ice/isopropanol bath. Boron tribromide solution in dichloromethane (375 µL, 1 M, 0.375 mmol, 6 equiv.) was slowly added under stream of argon. The cooling bath was removed and the resulting brown suspension with weak orange fluorescence was stirred at room temperature for 24 hours. The solvent was evaporated. The reaction vessel was evacuated and filled with argon three times and 3.5 mL of dry and degassed dichloromethane was added. Slowly, under stream of argon, trimethylaluminum solution in hexane (187 µL, 2 M, 0.375 mmol, 18 equiv.) was added. The resulting suspension was stirred at room temperature for one hour, while strong green fluorescence appeared. The reaction mixture was cooled down with a water/ice bath and 4 mL of water was carefully added. The resulting biphasic mixture was transferred into a separatory funnel and the phases were separated. The water phase was extracted four times with 10 mL of dichloromethane. The combined organic phase was dried with sodium sulfate. Approximately 10 g of silica gel was added, the solvent was evaporated and the product was filtered through a short pad of silica gel, washed with hexane/ethyl acetate 19:1 mixture. The solvents were evaporated and the crude product was recrystallized from 16 mL of ethyl acetate/acetonitrile 1:1 mixture. Yellow product was filtered and dried in vacuum at room temperature for one hour. Yield: 4.2 mg ($3{,}8\cdot10^{-3}$ µmol, 6.0%). The amount of the product was too low to carry out analyses confirming its structure.

HR MS (APCI+): m/z calculated for $C_{80}H_{79}B_2N_4$ $[M+H]^+$: 1117.6491; found 1117.6494.

3. Separation of enantiomers

Analytical chiral HPLC separation for 13

The sample is dissolved in dichloromethane, injected on (*S*,*S*)-Whelk-O1 chiral column, with heptane / dichloromethane (75/25) as mobile phase, and detected with a UV detector at 230 nm. The flow-rate is 1 ml/min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.54	568	50.98	1.22		
7.69	546	49.02	1.61	1.32	3.12
Sum	1113	100.00			

Preparative separation for compound 13

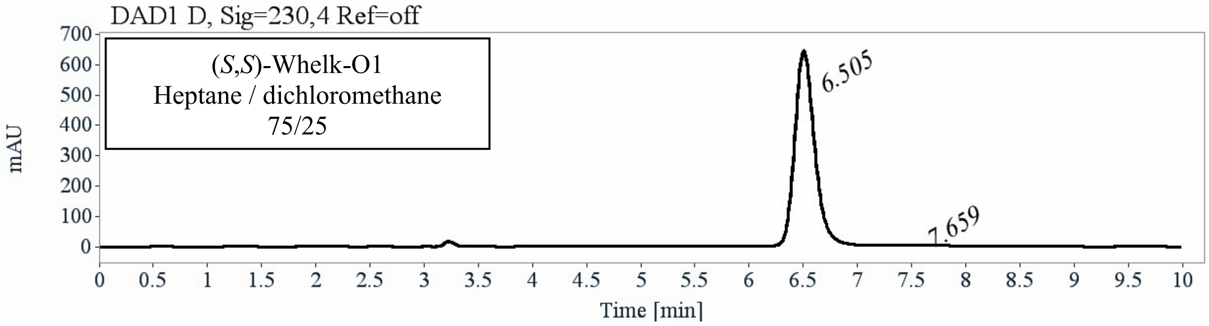
- Sample preparation: About 28 mg of compound **13** are dissolved in 5 mL of a mixture of dichloromethane and hexane (50/50).

- Chromatographic conditions: (*S*,*S*)-Whelk-O1 (250 x 10 mm), hexane / dichloromethane (75/25) as mobile phase, flow-rate = 5 mL/min, UV detection at 290 nm.

- Injections (stacked): 72 times 70 µL, every 4.3 minutes.

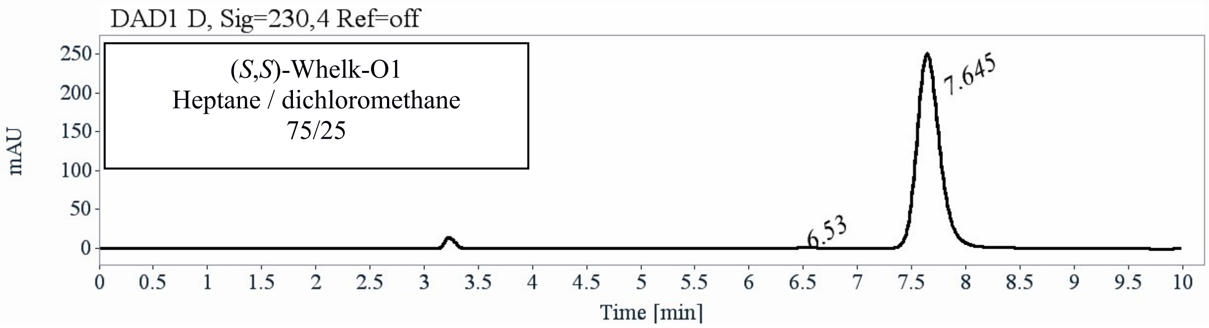
- Chromatograms of the collected fractions:

12 mg of the first eluted enantiomer with enantiomeric excess higher than 99%



RT [min]	Area	Area%
6.50	8110	99.58
7.66	34	0.42
Sum	8144	100.00

11 mg of the second eluted enantiomer with enantiomeric excess higher than 98.5 %



RT [min]	**Area**	**Area%**
6.53	21	0.57
7.64	3720	99.43
Sum	3741	100.00

Optical rotations

Optical rotations were measured on a Jasco P-2000 polarimeter with a halogen lamp (589, 578 and 546 nm), in a 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder.

λ (nm)	**13** first eluted on (*S*,*S*)-Whelk-O1 $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c = 0.17)	**13** second eluted on (*S*,*S*)-Whelk-O1 $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c = 0.16)
589	- 1200	+ 1200
578	- 1280	+ 1280
546	- 1530	+ 1530

Electronic Circular Dichroism

ECD and UV spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2°C. A CD quartz cell of 1 mm of optical pathlength was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted.

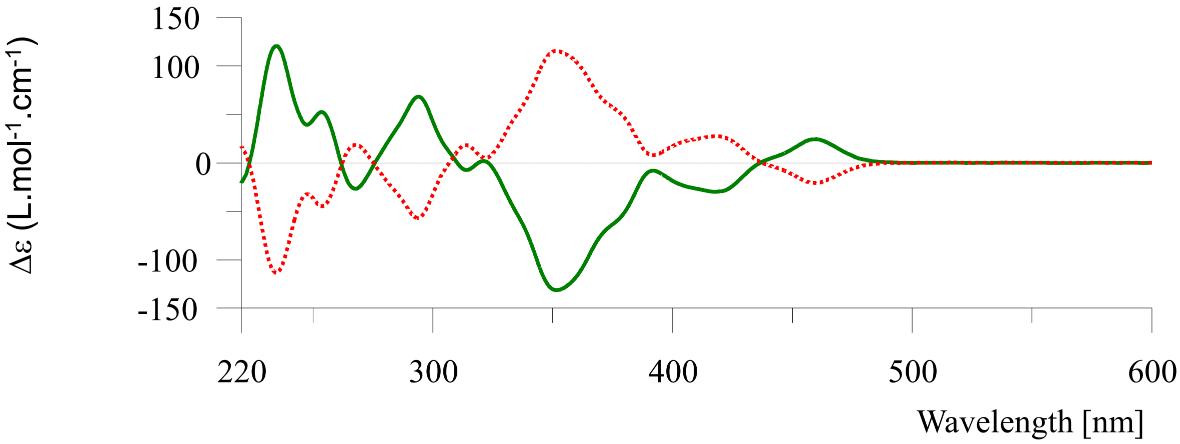
The baseline was always measured for the same solvent and in the same cell as the samples.

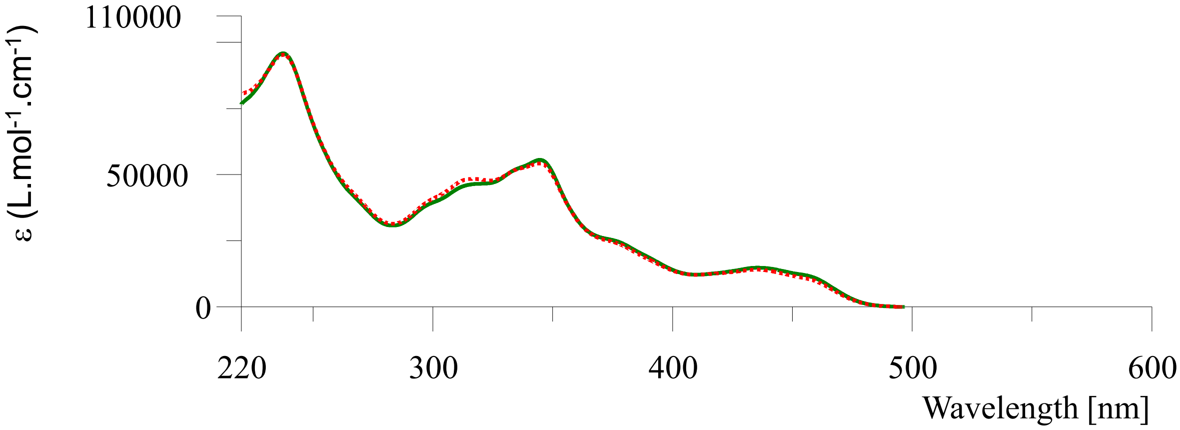
The spectra are presented without smoothing and further data processing.

13, first eluted on (*S*,*S*)-Whelk-O1: green solid line, concentration = 0.189 mmol.L^{-1} in dichloromethane.

13, second eluted on (*S*,*S*)-Whelk-O1: red dotted line, concentration = 0.179 mmol.L^{-1} in dichloromethane.

Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample.





4. UV/Vis spectra

All the absorption measurements were performed on a Shimadzu UV-3600i Plus UV-Vis-NIR Spectrophotometer. All the emission measurements were performed on an Edinburgh Instruments Spectrofluorometer FS5 equipped with a Hamamatsu R13456 PMT. HPLC grade solvents were used for all the measurements.

Fluorescence quantum yield was determined by comparison with a standard, according to formula 4.1, where *x* denotes values related to the studied compound, *st* denotes values related to the standard, *I* is the measured intensity of fluorescence at *λ* wavelength, *A* is the absorbance at the excitation wavelength and *n* is the refractive index of the solvent.[6] In all cases the standard was quinine sulfate dissolved in 0.1 M sulfuric acid and the excitation wavelength was 335 nm. Fluorescence quantum yield of the standard, equal to 0.51[7], and the refractive indices of the solvents, equal to: 1.49 for toluene,[8] 1.42 for dichloromethane,[9] 1.43 for dimethylformamide[10] and 1.33 for water,[10] were taken from literature.

$$\Phi_{f,x} = \Phi_{f,st}\frac{\int I_x d\lambda\left(1-10^{-A_{st}}\right)n_x^2}{\int I_{st} d\lambda\left(1-10^{-A_x}\right)n_{st}^2} \tag{4.1}$$

Figure S1 shows the absorption and emission spectra and Table S1 shows all the spectroscopic data of the studied compounds.

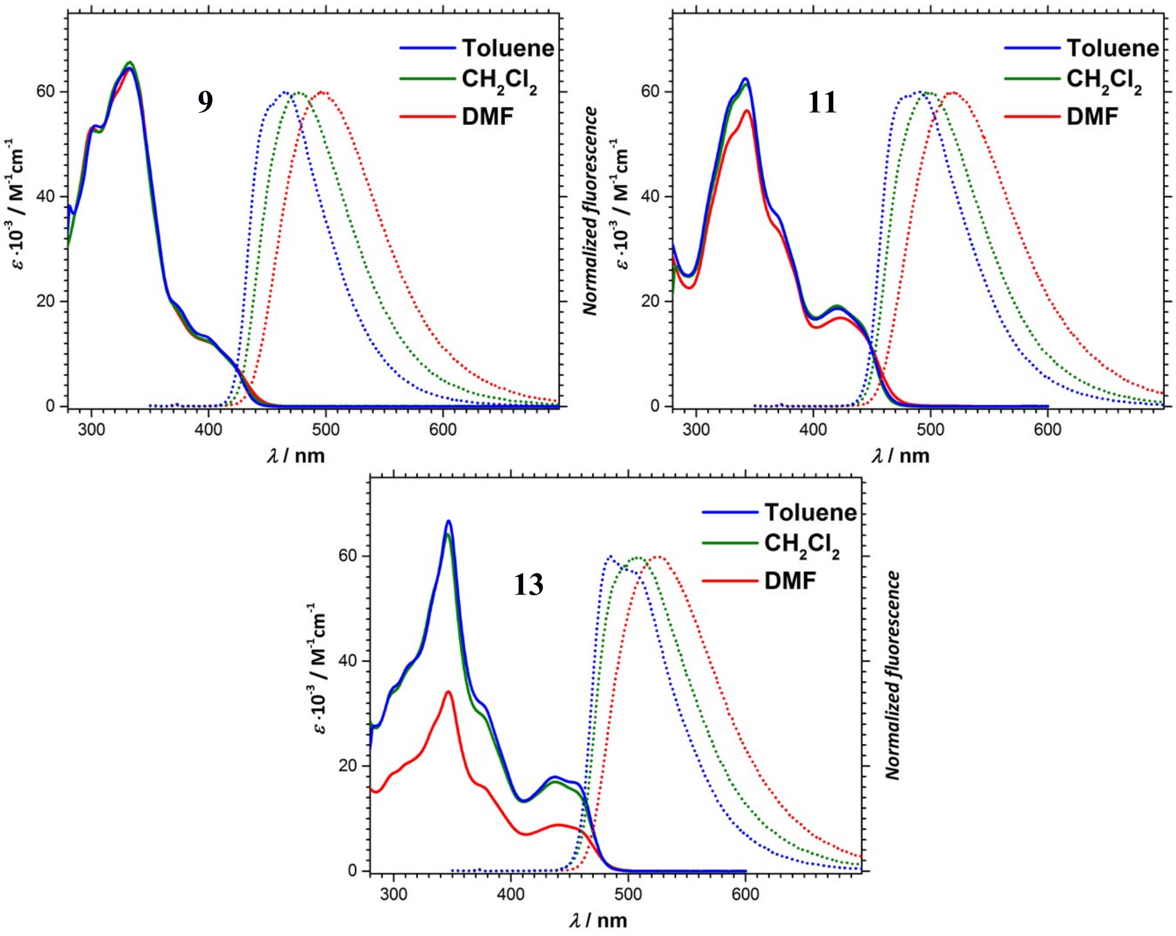


Figure S1: Absorption (solid line) and emission (dotted line) spectra of the new compounds: **9**, **11** and **13**.

Table S1: Spectroscopic data of the studied compounds. The values of λ_{abs} marked with an asterisk are estimated as due to band overlapping the maxima are not resolved.

Dye	Solvent	λ_{abs}/nm	$\varepsilon \cdot 10^{-3}$/M^{-1}cm^{-1}	λ_{em}/nm	Φ_{fl}	$\Delta\bar{\nu}$/cm^{-1}
9	Toluene	303 332 420*	54 65 8.5	465	0.27	2300
	CH_2Cl_2	301 333 420*	53 66 8.2	479	0.23	2900
	DMF	301 333 420*	53 64 8.5	495	0.29	3600
11	Toluene	343 420 440*	61 19 16	489	0.39	2300
	CH_2Cl_2	342 420 440*	63 19 15	499	0.32	2700
	DMF	343 423 440*	56 17 15	519	0.34	3500
13	Toluene	347 437 453*	67 18 17	485	0.34	1500
	CH_2Cl_2	346 438 453*	64 17 15	506	0.30	2300
	DMF	347 440 453*	34 8.8 8.3	525	0.38	3000

5. Crystal structures

Structural studies were performed using single crystal X-ray diffraction. Measurements were performed at 130 K on a Bruker APEX-II CCD diffractometer with a TRIUMPH monochromator using MoKα radiation. The Oxford Cryosystem Plus was used to maintain low temperature. Measurements were performed using APEX3 software.[11] The SAINT package[12] was applied to determine the unit cell parameters and integrate the collected reflections, and the SADABS software[13] was used to scale the data. Multi-scan absorption correction was applied during data scaling. The structures of **11** and **13** were solved with the SHELXT program using intrinsic phasing[14] and refined with the SHELXL refinement package[15] using Least Squares minimalisation. Non-hydrogen atoms were refined using an anisotropic thermal displacement model, whereas an isotropic model was applied for hydrogen atoms. The structures of the molecules were visualized in Olex2 program.[16] Crystallographic data and structure refinement parameters are presented in the table below.

Crystal data and structure refinement for compound 11 (CCDC 2415573)

Empirical formula	$C_{72}H_{74}B_2N_4$
Formula weight	1016.97
Temperature/K	130.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	20.2478(10)
b/Å	12.0654(6)
c/Å	24.4100(12)
α/°	90
β/°	106.520(2)
γ/°	90
Volume/Å^3	5717.1(5)
Z	4
ρ_{calc}g/cm^3	1.182
μ/mm^{-1}	0.068
F(000)	2176.0
Crystal size/mm^3	0.4 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.044 to 52.000
Index ranges	$-24 \leq h \leq 24$, $-14 \leq k \leq 14$, $-30 \leq l \leq 30$
Reflections collected	63992
Independent reflections	11218 [R_{int} = 0.0516, R_{sigma} = 0.0390]
Data/restraints/parameters	11218/1051/956
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0520, wR_2 = 0.1291
Final R indexes [all data]	R_1 = 0.0751, wR_2 = 0.1430
Largest diff. peak/hole / e Å^{-3}	0.43/-0.40

Crystal data and structure refinement for compound 13 (CCDC 2430266)

Empirical formula	$C_{76}H_{74}B_2N_4S_2$
Formula weight	1129.13
Temperature/K	130.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.8961(5)
b/Å	23.8496(8)
c/Å	17.9551(6)
α/°	90
β/°	105.520(2)
γ/°	90
Volume/Å^3	6146.3(4)
Z	4
ρ_{calc}g/cm^3	1.220
μ/mm^{-1}	0.135
F(000)	2400.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.01 to 50.998
Index ranges	$-17 \leq h \leq 18$, $-28 \leq k \leq 28$, $-21 \leq l \leq 21$
Reflections collected	96697
Independent reflections	11433 [R_{int} = 0.0401, R_{sigma} = 0.0231]
Data/restraints/parameters	11433/46/1047
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0420, wR_2 = 0.1026
Final R indexes [all data]	R_1 = 0.0546, wR_2 = 0.1122
Largest diff. peak/hole / e Å^{-3}	0.33/-0.54

There are B and C alerts in the checkcif – this is due to the disorder of the octyl groups. Alert B refers to a significant difference in the anisotropic displacement factors - and indeed these differences are significant - in the center of the molecule the factors are small, as can be seen from the ellipsoids, and in the periphery (including the disordered octyl chains) they are significant. This is due to the size of the molecule and the disorder of the octyl groups.

The minimum of the electron density map also occurs in an area of significant disorder near the end of one of the octyl groups.

The missing reflections were not measured because they were covered by the beamstop, which in no way affects the quality of the determined and refined structure.

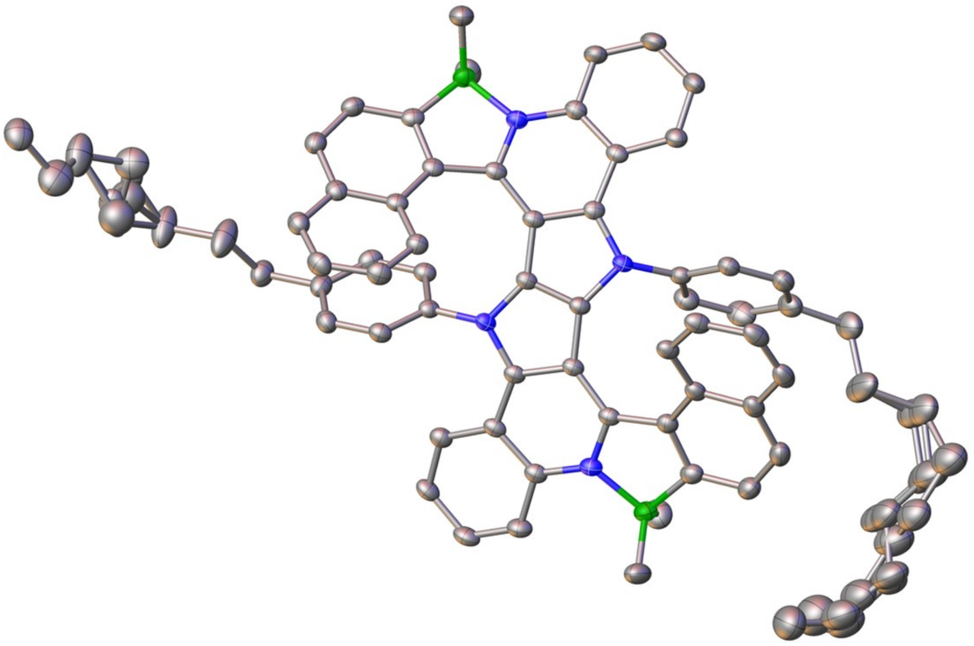


Figure S2: Structure **11** with anisotropic displacement model at 50% probability level. For clarity, all hydrogen atoms are omitted (CCDC 2415573).

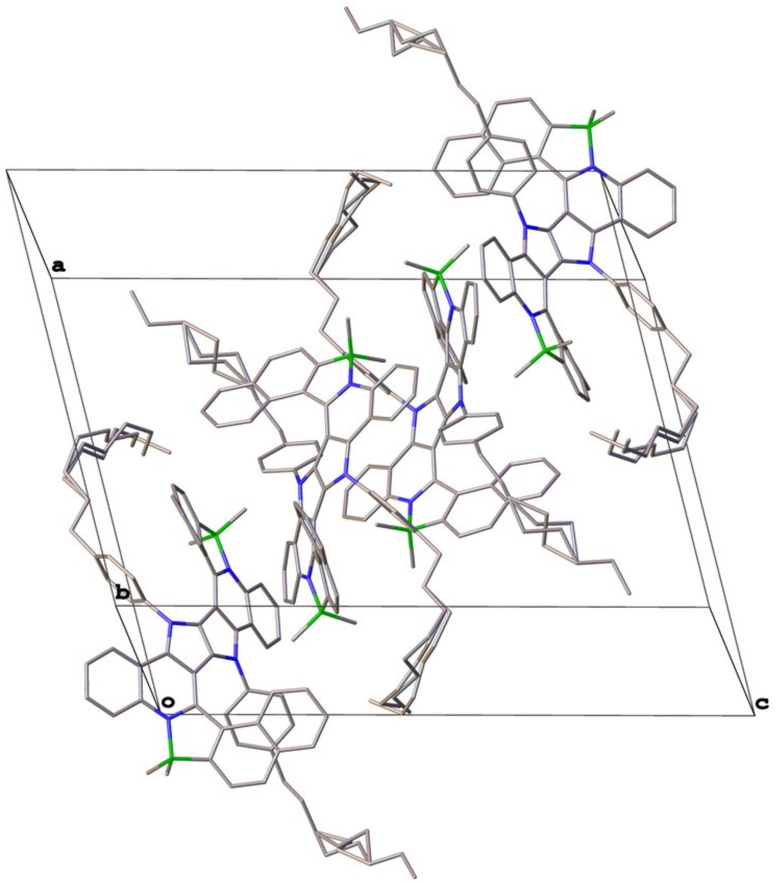


Figure S3: The unit cell of compound **11**. Hydrogen atoms are omitted.

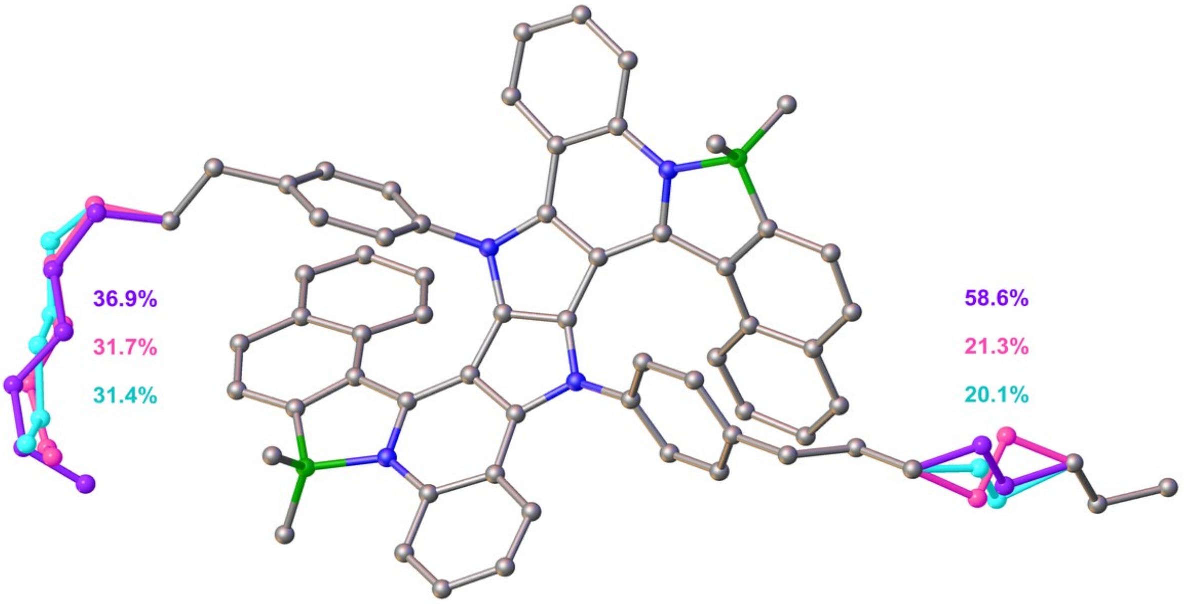


Figure S4: Disorder in octyl substituents of **11**. Occupancies of disordered fragments are indicated by appropriate colors.

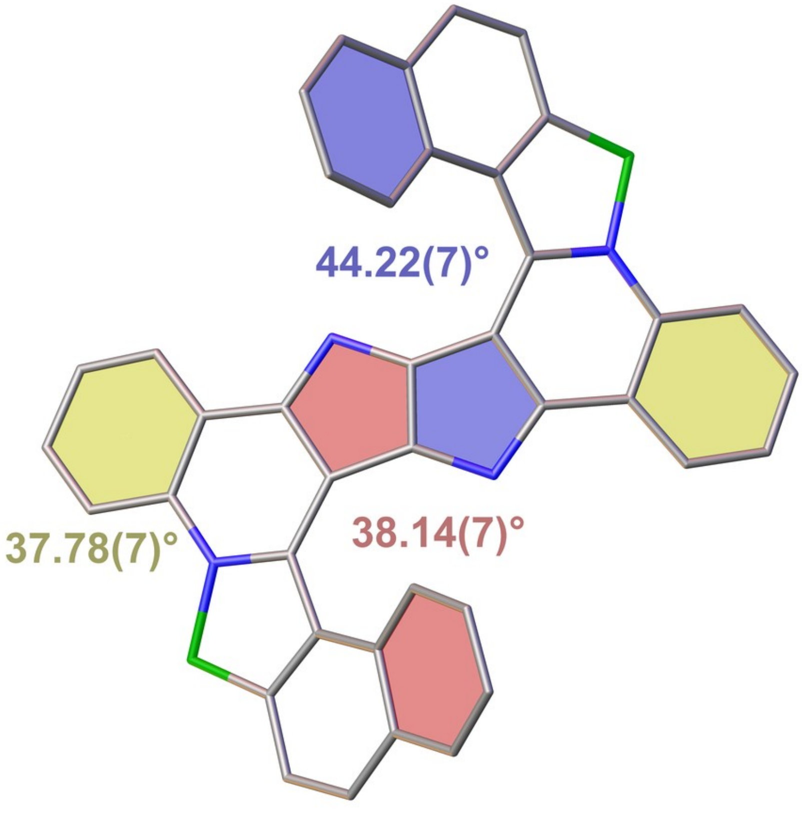
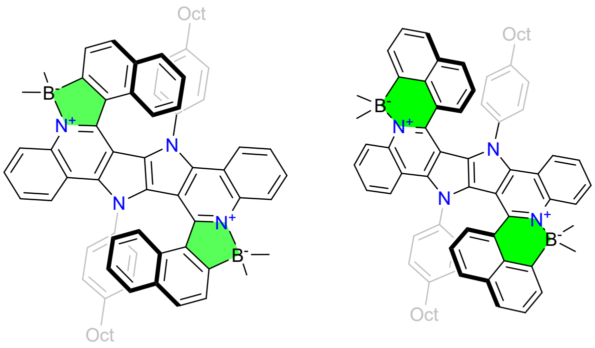


Figure S5: Angles between selected ring planes.



11 **11alt**

Figure S6: Two possible structures of boron complex formed from substrate **10**. The real structure of compound **11** is the one on the left.

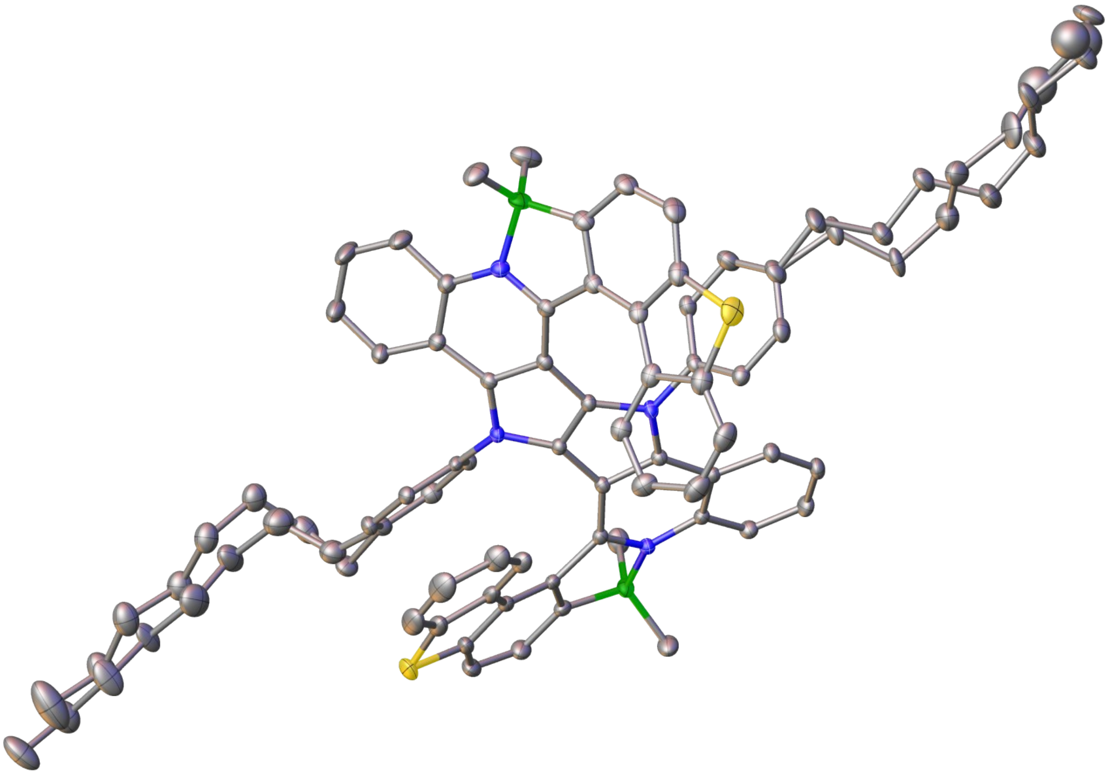


Figure S7: Structure **13** with anisotropic displacement model at 50% probability level. For clarity, all hydrogen atoms are omitted (CCDC 2430266).

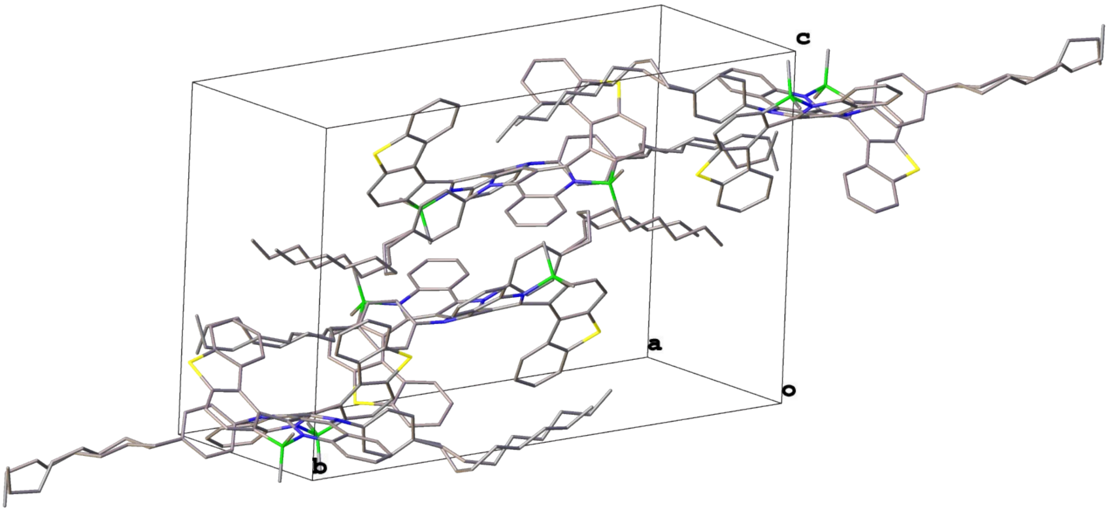


Figure S8: The unit cell of compound **13**. Hydrogen atoms are omitted.

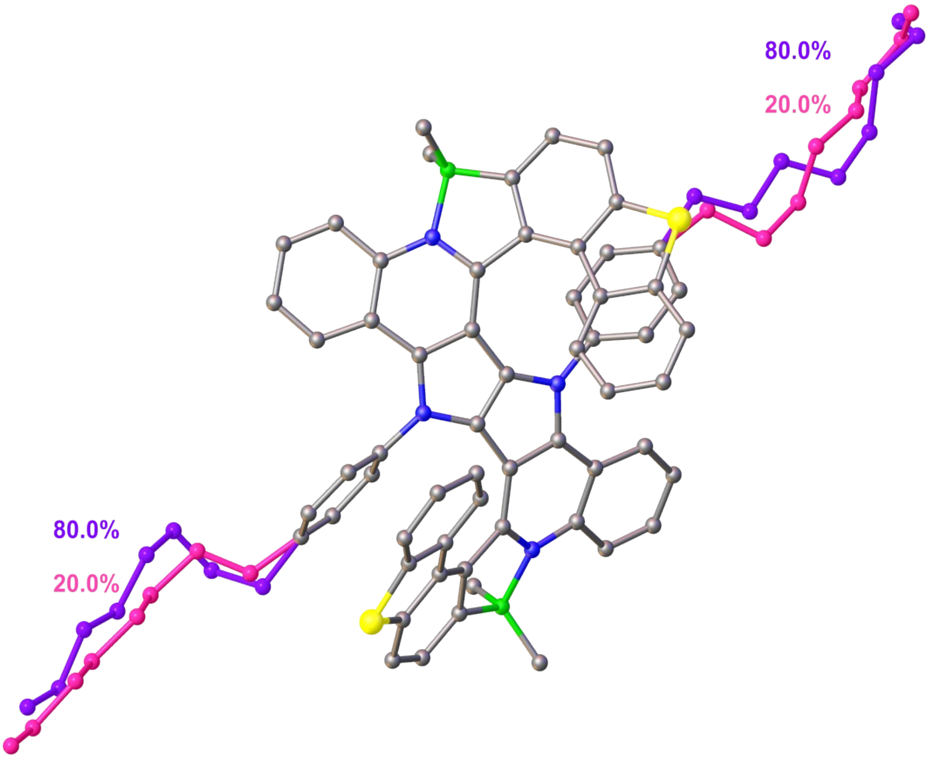


Figure S9: Disorder in octyl substituents of **13**. Occupancies of disordered fragments are indicated by appropriate colors.

6. Chiroptical properties

CD spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2 °C. A CD quartz cell of 1 mm optical pathlength was used. The CD spectrometer was purged with nitrogen before recording each spectrum. The baseline was acquired by measuring the pure solvent and the spectral range was cut at the cut-off wavelength of the relevant solvent (233 nm for dichloromethane, 284 nm for toluene).

A FLS1000 Edinburgh Instruments Fluorimeter, equipped with a PEM, a lock-in amplifier and an emission polarizer at 135°, was employed to acquire CPL spectra and obtain the corresponding dissymmetry factors (g_{lum}) in CH_2Cl_2 and in toluene (Fig. S10). The solutions were diluted as to have absorbance lower than 0.1, in order to minimize inner-filter effects. The absence of linearly polarized components in emission was confirmed by verifying that the CPL spectra did not change when excited through a horizontal polarizer.[17]

The g_{lum} values reported in Table 2 were obtained as the average of the values measured in the wavelength range falling inside the FWHM (full width at half maximum) of the corresponding emission band.

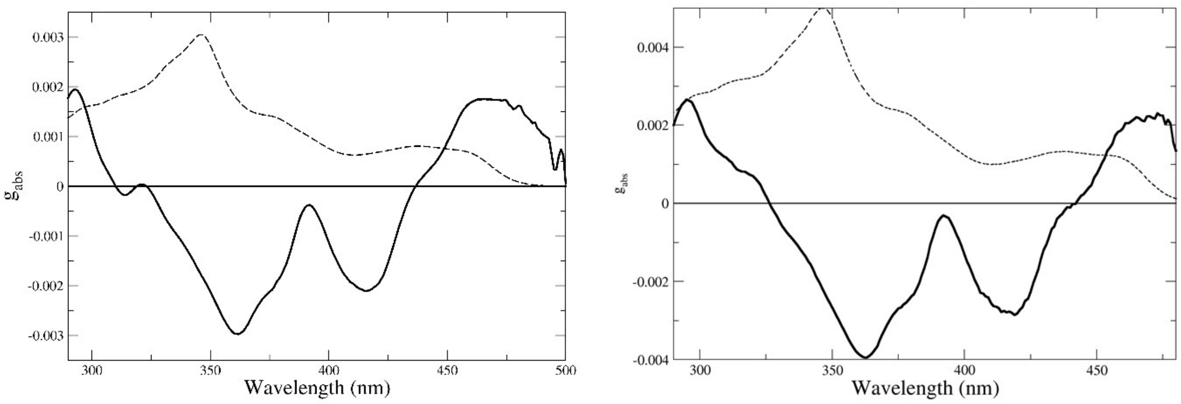


Figure S10: g_{abs} (full lines) of the first eluted fraction (E1) of **13**, as a function of absorption wavelength, in CH_2Cl_2 (left panel) and in toluene (right panel). The absorption spectra (dashed lines, arbitrary units) are reported as a reference for the position of the bands.

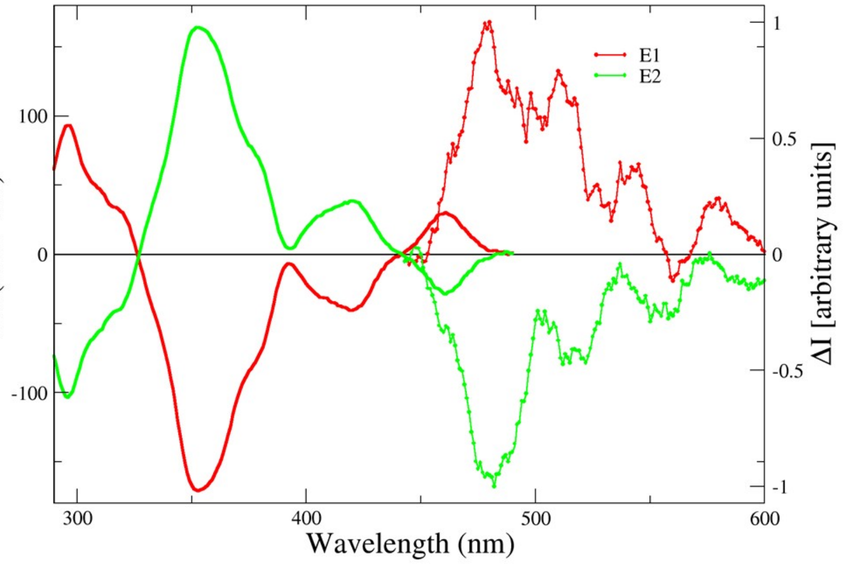


Figure S11: CD (full lines) and CPL (lines with dots) spectra of the enantiomers of **13** in toluene.

7. Theoretical calculations

Methods

Generalities

We have performed the DFT and TD-DFT calculations with Gaussian 16.[18] For all dyes the long octyl chains have been replaced by methyl groups during the calculations for obvious computational reasons. Default Gaussian16 thresholds and algorithms were used but for an improved optimization threshold (10^{-5} au on average residual forces), a stricter self-consistent field convergence criterion (10^{-10} a.u.) and the use of the *superfine* DFT integration grid, the largest pruned grid available in Gaussian.

Firstly, the S_0 geometries have been optimized with DFT and the vibrational frequencies have been analytically determined, using the M06-2X *meta*-GGA hybrid exchange-correlation functional.[19] These calculations were performed with the 6-311G(d,p) atomic basis set and account for solvent effects through the linear-response PCM approach considering toluene as solvent.[20] We selected toluene, since the least polar/protic medium is typically the one the best modeled by the PCM approach. Secondly, starting from the optimal ground-state geometries, we have used TD-DFT with the same functional and basis set to optimize the S_1 geometry and compute the vibrational frequencies. All optimized structures correspond to true minima of the potential energy surface. These very same geometries are used throughout.

0-0 energies

On the ground and excited-state geometries, the vertical transition energies were determined with TD-DFT and the same functional, but a larger basis set, namely 6-311+G(2d,p), in gas-phase as well as in solution using the cLR^2 variant of the PCM,[21] in its *non-equilibrium* limit.

As we are aware of the significant dependency of the TD-DFT results on the selected functional,[22] the obtained transition energies were also computed using CC2[23] with the Turbomole 7.3 code.[24] The CC2 energies were calculated in gas phase applying the resolution of identity scheme and the frozen-core approximations, and using the *aug*-cc-pVTZ atomic basis set. Combining the CC2 and TD-DFT data using a well-known protocol,[25] one can obtain accurate CC2-corrected estimates of the absorption, emission and 0-0 energies that can be straightforwardly compared to experimental values.

Absorption and ECD spectra

Using the optimal ground state geometries, absorption and ECD spectra were calculated in gas phase, at the TD-M06-2X/6-311+G(2d,p) level of theory, using 30 excited states (Figure S12). Each transition was assigned a Gaussian bandshape with a HWHM of 0.2 eV.

Vibronic calculations of absorption spectra

Vibronic calculations were carried out using the FCClasses 3 software,[26,27] employing the Vertical Gradient (VG), and Vertical Hessian (VH) PES models[28] within the time-dependent (TD) formalism.[29] While both approaches yield consistent results, the VH model was preferred for comparisons. Geometries, gradients, and Hessians were calculated following the methodology outlined above, with transition dipole moments determined using the LR-PCM protocol. All these calculations use TD-DFT without CC2 corrections. The Franck-Condon approximation was applied for the dipole expansion, and internal coordinates were employed. To align the simulated spectra with experimental observations, a Gaussian broadening of 0.050 eV was applied. For compound **9**, the first four excited states were included in the spectral representation, while the first six and seven states were considered for compounds **11** and **13**, respectively. The Internal Conversion (IC), have been evaluated in the VG, VH as well as in the adiabatic hessian (AH) models, using a 0.050 eV Lorentzian broadening and checking that the graph representing IC rates against adiabatic energies has the expected shape within the selected models (see below).[30]

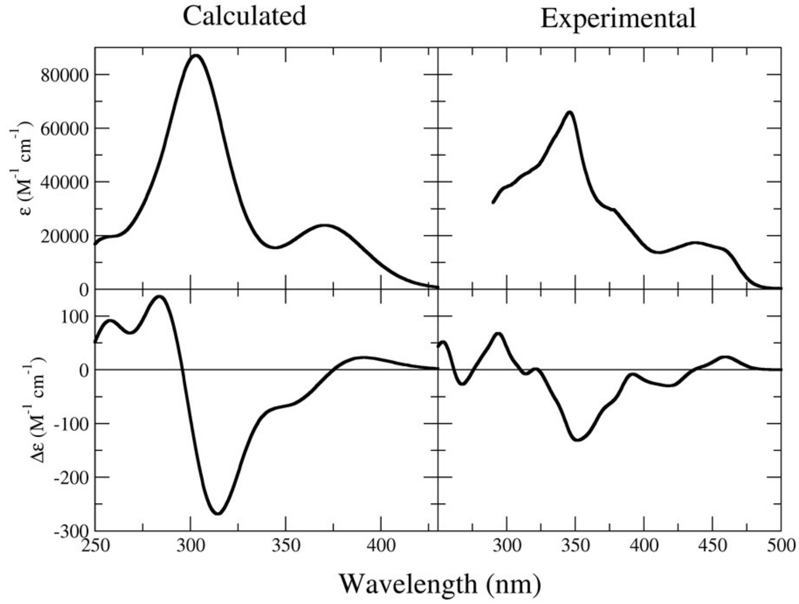
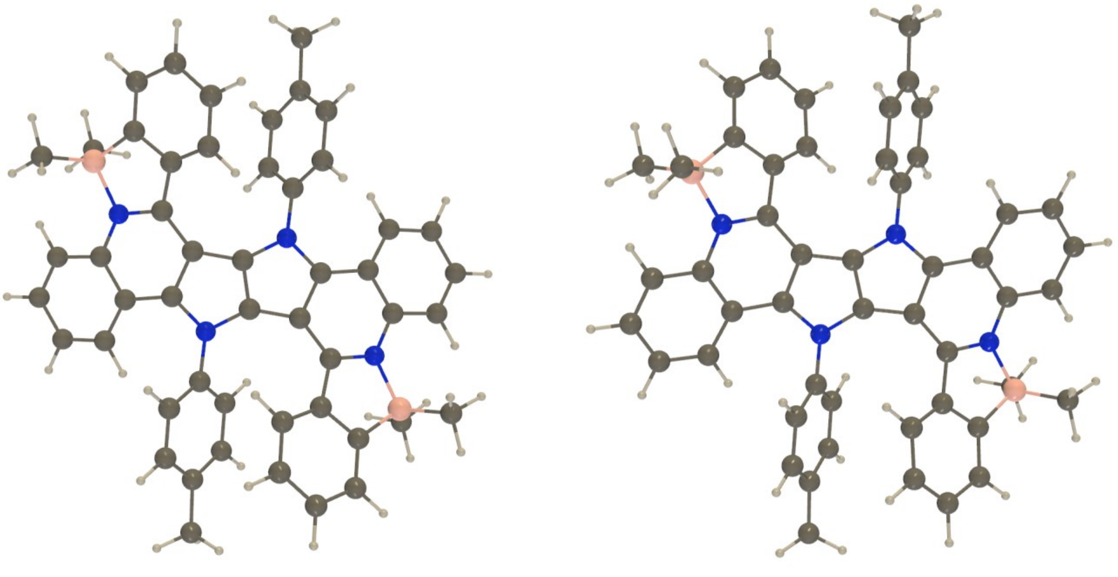


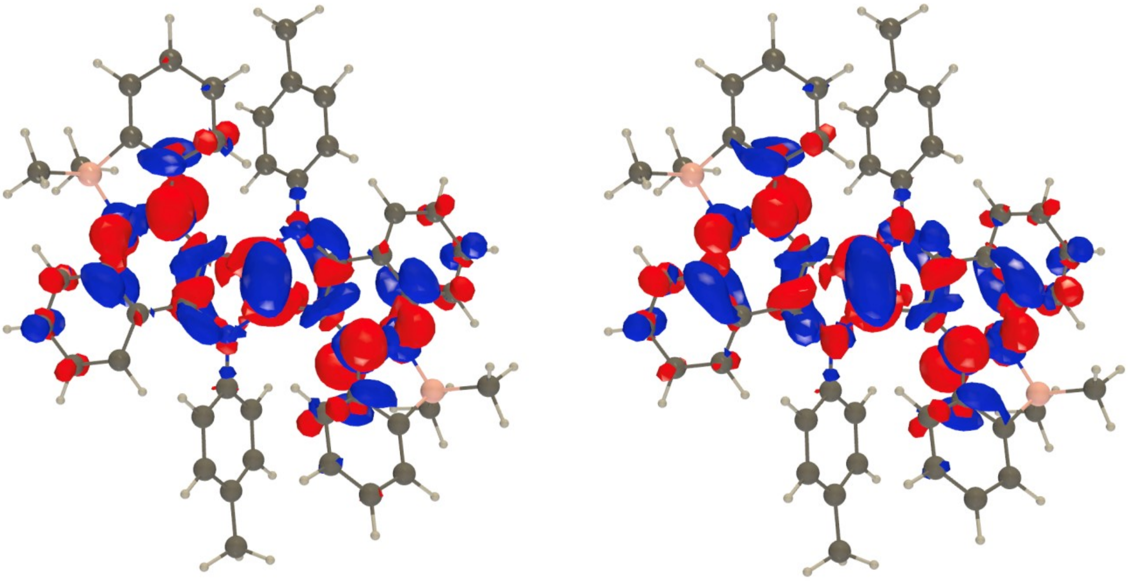
Figure S12: Calculated (left panel) and experimental (right panels) absorption (upper panels) and CD (lower panels) spectra for the E1 fraction of molecule **13**. The spectra correspond to a (M,M) configuration.

Additional theoretical results



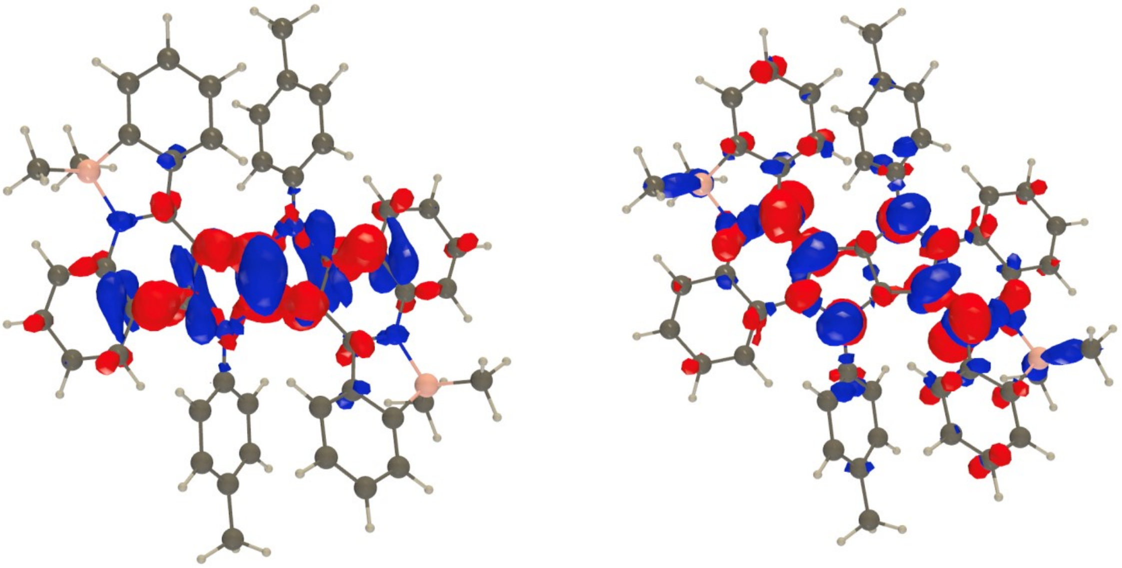
C_2 C_i

Figure S13: Two views of the C_2 (left) and C_i (right) ground-state minima found for **9**. Both structures are minimum of the potential energy surface.



345 nm (*f=0.372) B* sym

334 nm (*f=0.060) A* sym



322 nm (*f=0.300) B* sym

301 nm (*f=1.442) B* sym

Figure S14: Electron density difference (EDD) plots corresponding to the absorption to the lowest four states of **9**. The blue and red lobes represent regions of decrease and increase of density (threshold: 0.001 au). In all cases, we provide the TD-DFT transition wavelengths and oscillator strength (no CC2 correction).

Table S2: Theoretical best estimates for the vertical absorption and emission wavelengths (nm), as well as the adiabatic and 0-0 energies (eV).

Dye	$\lambda^{\text{vert-abs}}$ (nm)	$\lambda^{\text{vert-fl}}$ (nm)	ΔE^{adia} (eV)	$\Delta E^{0\text{–}0}$ (eV)
9	384	466	2.76	2.64
11	411	490	2.62	2.51
13	431	512	2.48	2.35

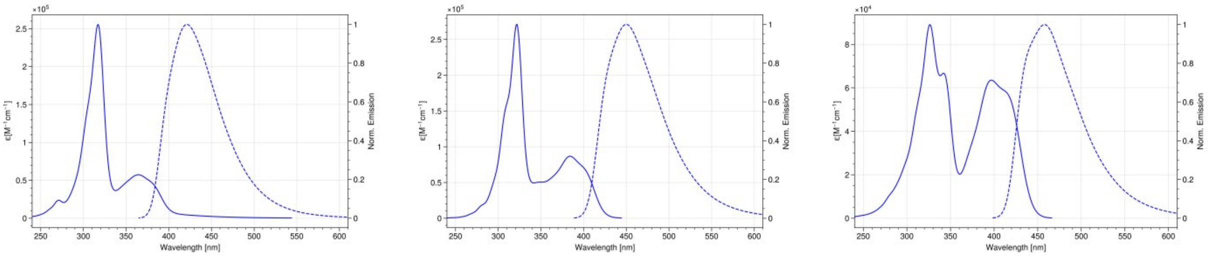


Figure S15: Computational absorption and emission spectra for molecules **9** (left), **11** (center), and **13** (right). Calculations (using TD-DFT with the LR-PCM model) were conducted in toluene solvent, using the VH model and the other parameters specified in the computational details.

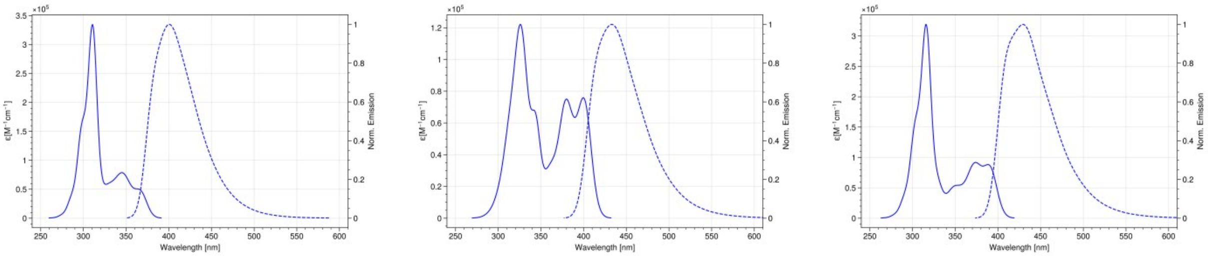


Figure S16: Computational absorption and emission spectra for molecules **9** (left), **11** (center), and **13** (right). Calculations (using TD-DFT with the LR-PCM model) were conducted in toluene solvent, using the VG model and the other parameters specified in the computational details.

The emission spectra shapes being reasonably reproduced for all three molecules we therefore tried to obtain the internal conversion rate (k_{IC}) is presented in Figure S17. The curve of k_{IC} as a function of adiabatic energy displays the expected behavior. However, since the adiabatic energy lies on the plateau of the kIC curve (after the inflexion point), reliable estimation of k_{IC} using the harmonic model is not feasible. This limitation arises from k_{IC} strong dependence of k_{IC} values on the arbitrary broadening parameter used in the model.

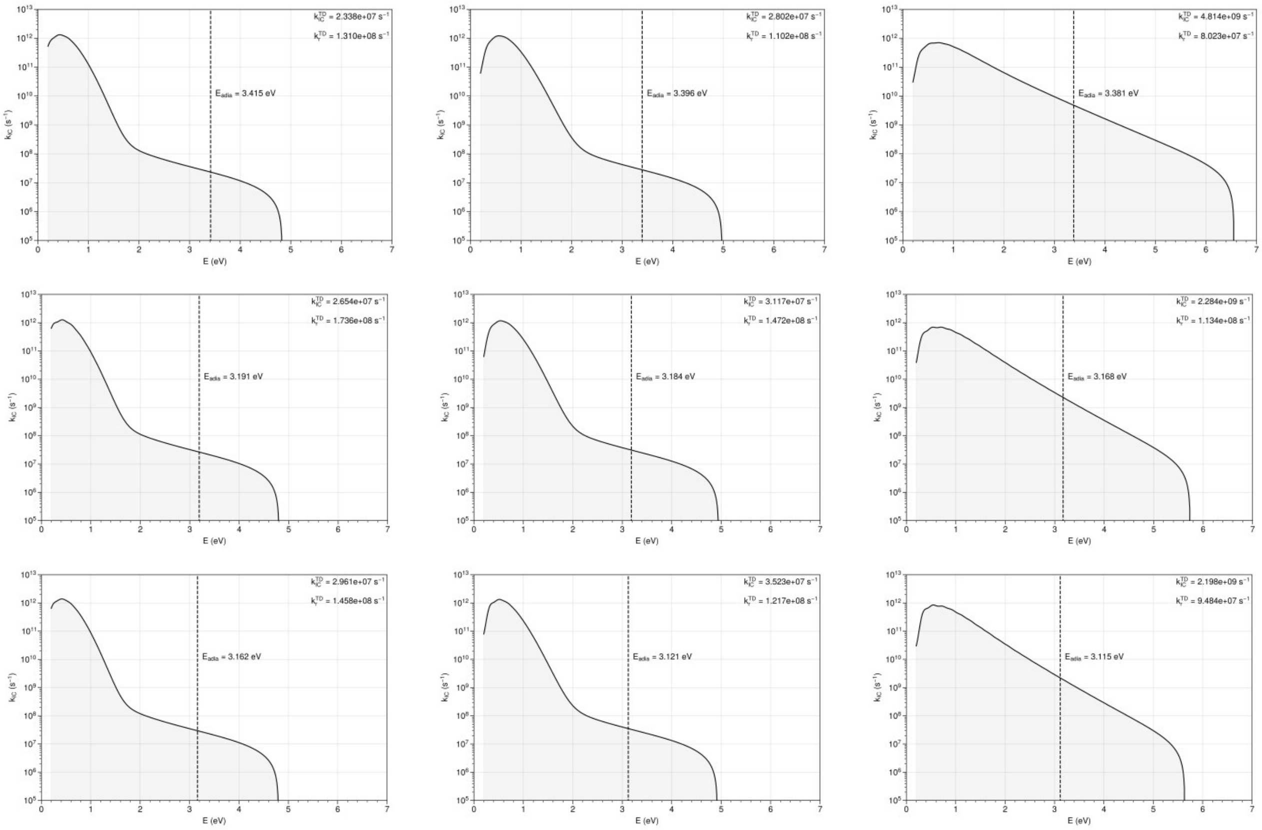


Figure S17: Internal conversion constant (k_{IC}) in function of the adiabatic energy for the three molecules (from top to bottom: **9**, **11**, and **13**) included in the study, using the VG (left), VH (central) and AH (right) models.

Cartesian coordinates

All structures are true minima of the PES.

9 (S_0), C_2 sym, G= -2198.387025 H

C	0.0025430	2.1204140	-0.0260320
C	1.1597450	1.3369640	0.1851320
C	2.4076080	2.0012610	0.2821670
C	1.4503680	3.9869290	-0.5743750
C	0.1243880	3.4795010	-0.4732000
C	0.6898690	-0.0137300	0.2671540
C	-0.6898690	0.0137300	0.2671540
C	-1.1597450	-1.3369640	0.1851320
C	-0.0025430	-2.1204140	-0.0260320
C	-2.4076080	-2.0012610	0.2821670
C	-0.1243880	-3.4795010	-0.4732000
C	-1.4503680	-3.9869290	-0.5743750
N	2.5383700	3.2535580	-0.1515940
N	-2.5383700	-3.2535580	-0.1515940
N	1.1161400	-1.3281110	0.0938240
N	-1.1161400	1.3281110	0.0938240
C	0.9397260	-4.2906380	-0.9345670
C	0.7059920	-5.5459560	-1.4418790
H	1.9514540	-3.9189060	-0.9165650
H	1.5379790	-6.1427110	-1.7942300
C	-0.9397260	4.2906380	-0.9345670
C	-0.7059920	5.5459560	-1.4418790
H	-1.9514540	3.9189060	-0.9165650
H	-1.5379790	6.1427110	-1.7942300
C	1.6601770	5.2805700	-1.0956940
C	0.6023300	6.0477330	-1.5165390
H	2.6694060	5.6535550	-1.1616840
H	0.7828980	7.0384500	-1.9149750
C	-1.6601770	-5.2805700	-1.0956940
C	-0.6023300	-6.0477330	-1.5165390
H	-2.6694060	-5.6535550	-1.1616840
H	-0.7828980	-7.0384500	-1.9149750
C	2.4831150	-1.7207230	-0.0493870
C	3.0417310	-2.6220920	0.8505730
C	3.2531630	-1.1535680	-1.0550380
C	4.3844730	-2.9491470	0.7384460
H	2.4228840	-3.0539790	1.6294080
C	4.6027690	-1.4730500	-1.1413370
H	2.8017410	-0.4525730	-1.7483730
C	5.1893850	-2.3646500	-0.2439740

H	4.8231020	-3.6496220	1.4407970
H	5.2106780	-1.0112360	-1.9113120
C	-2.4831150	1.7207230	-0.0493870
C	-3.2531630	1.1535680	-1.0550380
C	-3.0417310	2.6220920	0.8505730
C	-4.6027690	1.4730500	-1.1413370
H	-2.8017410	0.4525730	-1.7483730
C	-4.3844730	2.9491470	0.7384460
H	-2.4228840	3.0539790	1.6294080
C	-5.1893850	2.3646500	-0.2439740
H	-5.2106780	1.0112360	-1.9113120
H	-4.8231020	3.6496220	1.4407970
C	6.6667170	-2.6452960	-0.2944970
H	7.0478090	-2.5788740	-1.3141640
H	7.2027250	-1.9072910	0.3098870
H	6.8971770	-3.6353720	0.1005810
C	-6.6667170	2.6452960	-0.2944970
H	-7.0478090	2.5788740	-1.3141640
H	-7.2027250	1.9072910	0.3098870
H	-6.8971770	3.6353720	0.1005810
C	3.6565490	1.5103680	0.8594370
C	3.8243190	0.4053350	1.6937010
C	4.6940970	2.4073180	0.5739280
C	5.0990080	0.1196790	2.1576180
H	2.9803260	-0.2020630	1.9953930
C	5.9697280	2.0898530	1.0390220
C	6.1720550	0.9448790	1.8047730
H	5.2610440	-0.7373630	2.8007840
H	6.8062030	2.7499590	0.8292630
H	7.1659000	0.7074860	2.1692420
C	-3.6565490	-1.5103680	0.8594370
C	-3.8243190	-0.4053350	1.6937010
C	-4.6940970	-2.4073180	0.5739280
C	-5.0990080	-0.1196790	2.1576180
H	-2.9803260	0.2020630	1.9953930
C	-5.9697280	-2.0898530	1.0390220
C	-6.1720550	-0.9448790	1.8047730
H	-5.2610440	0.7373630	2.8007840
H	-6.8062030	-2.7499590	0.8292630
H	-7.1659000	-0.7074860	2.1692420
B	-4.1291740	-3.7195740	-0.1632520
B	4.1291740	3.7195740	-0.1632520
C	4.6362290	3.8293990	-1.7027050
H	4.2498950	4.6946430	-2.2506350
H	5.7285860	3.9176190	-1.7038440
H	4.3892090	2.9340070	-2.2843570

C	-4.6362290	-3.8293990	-1.7027050
H	-4.2498950	-4.6946430	-2.2506350
H	-5.7285860	-3.9176190	-1.7038440
H	-4.3892090	-2.9340070	-2.2843570
C	4.3844730	5.0330720	0.7563070
H	5.4569630	5.1017290	0.9714310
H	4.1010240	5.9847770	0.2965340
H	3.8738600	4.9682630	1.7232580
C	-4.3844730	-5.0330720	0.7563070
H	-5.4569630	-5.1017290	0.9714310
H	-4.1010240	-5.9847770	0.2965340
H	-3.8738600	-4.9682630	1.7232580

9 (S_1), C_1 sym, G= -2198.268143 H

C	-0.7594220	-1.9618230	-0.0408650
C	-1.5811240	-0.8266150	0.1917320
C	-2.9850400	-1.0152340	0.2793390
C	-2.7653220	-3.1884090	-0.6219310
C	-1.3376440	-3.1720540	-0.5159990
C	-0.6872880	0.2735660	0.2434790
C	0.6379170	-0.2452440	0.2602480
C	1.5477130	0.8245810	0.2624360
C	0.7487780	1.9724920	0.0254520
C	2.9616000	0.9532740	0.3333980
C	1.3389910	3.1661330	-0.4744020
C	2.7904200	3.1402190	-0.6028570
N	-3.5359140	-2.1404530	-0.1854020
N	3.5390220	2.0995380	-0.1955410
N	-0.6177380	1.6223940	0.0970150
N	0.5772490	-1.6096880	0.0930430
C	0.6316820	4.2883820	-0.9700170
C	1.2856790	5.3636840	-1.5246120
H	-0.4456860	4.3035530	-0.9304250
H	0.7207400	6.2101780	-1.8921480
C	-0.6103760	-4.2900080	-1.0031210
C	-1.2579070	-5.3750770	-1.5335790
H	0.4675260	-4.2824410	-0.9825890
H	-0.6831020	-6.2134000	-1.9056540
C	-3.3996800	-4.3234660	-1.1692690
C	-2.6629900	-5.3943030	-1.6088880
H	-4.4753410	-4.3301030	-1.2399010
H	-3.1697350	-6.2553600	-2.0269380
C	3.4215890	4.2698300	-1.1919490
C	2.6913800	5.3458970	-1.6274990
H	4.4946380	4.2553260	-1.2961700
H	3.2072030	6.1895090	-2.0713960

C	-1.7473940	2.4887780	-0.0153300
C	-1.9069310	3.5366590	0.8858310
C	-2.7016550	2.2378040	-0.9922130
C	-3.0416620	4.3293640	0.8057700
H	-1.1472030	3.7186300	1.6378300
C	-3.8406160	3.0306040	-1.0485360
H	-2.5574080	1.4211480	-1.6909260
C	-4.0329940	4.0779060	-0.1477060
H	-3.1707830	5.1456330	1.5079080
H	-4.5959950	2.8237860	-1.7983540
C	1.7323360	-2.4447460	-0.0351040
C	2.6873250	-2.1318470	-0.9933040
C	1.9161790	-3.5110200	0.8389620
C	3.8564450	-2.8800740	-1.0513220
H	2.5280710	-1.2953030	-1.6639760
C	3.0773150	-4.2626590	0.7512500
H	1.1586630	-3.7353100	1.5818900
C	4.0740510	-3.9437210	-0.1766970
H	4.6189620	-2.6183680	-1.7763680
H	3.2292480	-5.0903770	1.4350880
C	-5.3029200	4.8843270	-0.1690480
H	-5.6924300	4.9814180	-1.1830840
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H	-5.1471210	5.8821700	0.2421930
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H	6.1133510	-4.1477650	0.4164550
H	5.2722770	-5.6919920	0.2233130
C	-3.9807990	-0.1346550	0.8643240
C	-3.7581890	0.9551390	1.7103610
C	-5.2662650	-0.6107120	0.5619540
C	-4.8561520	1.6624850	2.1697900
H	-2.7579260	1.2288320	2.0224030
C	-6.3532430	0.1293580	1.0242460
C	-6.1476820	1.2663350	1.8012130
H	-4.7155150	2.5166070	2.8216410
H	-7.3660980	-0.1925870	0.8017660
H	-6.9986730	1.8336970	2.1625540
C	3.9327620	0.1138910	0.9439310
C	3.7278660	-0.9737710	1.8153610
C	5.2409280	0.5733150	0.6205300
C	4.8292940	-1.6804550	2.2622700
H	2.7309960	-1.2420830	2.1451250
C	6.3208360	-0.1641610	1.0862350
C	6.1239810	-1.2975870	1.8814750
H	4.6919440	-2.5289620	2.9238430

H	7.3331870	0.1495000	0.8459800
H	6.9756070	-1.8644580	2.2418560
B	5.1735330	1.9363090	-0.2391490
B	-5.1917210	-2.0230040	-0.2026170
C	-5.6928200	-1.9180640	-1.7437490
H	-5.6255540	-2.8528770	-2.3091630
H	-6.7481360	-1.6231500	-1.7470830
H	-5.1470670	-1.1521680	-2.3062680
C	5.6440620	1.7058150	-1.7818710
H	5.5358830	2.5950950	-2.4130470
H	6.7042400	1.4276990	-1.8006760
H	5.0890820	0.8913830	-2.2625590
C	-5.8903810	-3.1855460	0.6881650
H	-6.9220140	-2.8836500	0.9014010
H	-5.9504030	-4.1664490	0.2069320
H	-5.3966710	-3.3212320	1.6564260
C	5.9582670	3.1406370	0.5280470
H	6.9480510	2.7744960	0.8246900
H	6.1329290	4.0389680	-0.0731740
H	5.4499810	3.4505420	1.4479800

11 (S_0), C_2 sym, G= -2505.530907 H

C	-1.6417670	1.3364540	-0.2377860
C	-0.3033220	1.7383010	-0.0167180
C	0.0054280	3.1207600	-0.0046960
C	-2.1119520	3.6065320	-0.9452000
C	-2.6004560	2.2859110	-0.7272760
C	0.4457430	0.5240460	0.0710580
C	-0.4457430	-0.5240460	0.0710580
C	0.3033220	-1.7383010	-0.0167180
C	1.6417670	-1.3364540	-0.2377860
C	-0.0054280	-3.1207600	-0.0046960
C	2.6004560	-2.2859110	-0.7272760
C	2.1119520	-3.6065320	-0.9452000
N	-0.8442140	3.9853000	-0.5628760
N	0.8442140	-3.9853000	-0.5628760
N	1.7350070	0.0319810	-0.1038330
N	-1.7350070	-0.0319810	-0.1038330
C	3.9247220	-1.9882720	-1.1268740
C	4.7257310	-2.9461390	-1.7002390
H	4.3149030	-0.9912070	-1.0027110
H	5.7340480	-2.6895560	-2.0001180
C	-3.9247220	1.9882720	-1.1268740
C	-4.7257310	2.9461390	-1.7002390
H	-4.3149030	0.9912070	-1.0027110
H	-5.7340480	2.6895560	-2.0001180

C	-2.9560170	4.5683990	-1.5390220
C	-4.2390110	4.2463900	-1.9057320
H	-2.5738860	5.5649760	-1.6930060
H	-4.8734120	4.9997090	-2.3562770
C	2.9560170	-4.5683990	-1.5390220
C	4.2390110	-4.2463900	-1.9057320
H	2.5738860	-5.5649760	-1.6930060
H	4.8734120	-4.9997090	-2.3562770
C	2.8728510	0.8740800	-0.3181000
C	2.8421510	1.8050220	-1.3448240
C	3.9645810	0.8030970	0.5434010
C	3.9013410	2.6976600	-1.4903860
H	1.9844840	1.8502960	-2.0070460
C	5.0237150	1.6761200	0.3693390
H	3.9629710	0.0785710	1.3493180
C	4.9973540	2.6519500	-0.6346570
H	3.8594140	3.4493180	-2.2707030
H	5.8671470	1.6334740	1.0499310
C	-2.8728510	-0.8740800	-0.3181000
C	-3.9645810	-0.8030970	0.5434010
C	-2.8421510	-1.8050220	-1.3448240
C	-5.0237150	-1.6761200	0.3693390
H	-3.9629710	-0.0785710	1.3493180
C	-3.9013410	-2.6976600	-1.4903860
H	-1.9844840	-1.8502960	-2.0070460
C	-4.9973540	-2.6519500	-0.6346570
H	-5.8671470	-1.6334740	1.0499310
H	-3.8594140	-3.4493180	-2.2707030
C	6.1166150	3.6517330	-0.7377600
H	6.1651030	4.2519150	0.1757670
H	7.0812020	3.1529750	-0.8562150
H	5.9694440	4.3270770	-1.5806310
C	-6.1166150	-3.6517330	-0.7377600
H	-6.1651030	-4.2519150	0.1757670
H	-7.0812020	-3.1529750	-0.8562150
H	-5.9694440	-4.3270770	-1.5806310
C	1.2047080	3.7987400	0.4861530
C	1.2760390	5.0528810	-0.0952540
C	2.1119520	3.3752890	1.5076610
C	2.4225980	5.8473160	0.1423660
C	3.2481960	4.2017800	1.7343410
C	1.8927820	2.2799110	2.3805450
C	3.4024530	5.4079480	0.9919690
H	2.5175180	6.8135910	-0.3434980
C	4.1716890	3.8489510	2.7486340
C	2.7835390	1.9892560	3.3843690

H	0.9939080	1.6848310	2.2776760
H	4.2886990	6.0091480	1.1720180
C	3.9503810	2.7628340	3.5566000
H	5.0431260	4.4786510	2.8985880
C	-1.2047080	-3.7987400	0.4861530
C	-1.2760390	-5.0528810	-0.0952540
C	-2.1119520	-3.3752890	1.5076610
C	-2.4225980	-5.8473160	0.1423660
C	-3.2481960	-4.2017800	1.7343410
C	-1.8927820	-2.2799110	2.3805450
C	-3.4024530	-5.4079480	0.9919690
H	-2.5175180	-6.8135910	-0.3434980
C	-4.1716890	-3.8489510	2.7486340
C	-2.7835390	-1.9892560	3.3843690
H	-0.9939080	-1.6848310	2.2776760
H	-4.2886990	-6.0091480	1.1720180
C	-3.9503810	-2.7628340	3.5566000
H	-5.0431260	-4.4786510	2.8985880
H	2.5866160	1.1594100	4.0532660
H	4.6519030	2.5141710	4.3439640
H	-2.5866160	-1.1594100	4.0532660
H	-4.6519030	-2.5141710	4.3439640
B	0.0785670	-5.4124040	-0.8797380
B	-0.0785670	5.4124040	-0.8797380
C	0.1317380	5.5175420	-2.4871960
H	-0.7939290	5.6944000	-3.0443210
H	0.7987680	6.3597020	-2.7034750
H	0.6020090	4.6197670	-2.9045090
C	-0.1317380	-5.5175420	-2.4871960
H	0.7939290	-5.6944000	-3.0443210
H	-0.7987680	-6.3597020	-2.7034750
H	-0.6020090	-4.6197670	-2.9045090
C	-0.7879570	6.6978850	-0.1845660
H	-0.0546830	7.5092780	-0.1131740
H	-1.6401290	7.1064020	-0.7364450
H	-1.1235820	6.4870920	0.8363570
C	0.7879570	-6.6978850	-0.1845660
H	0.0546830	-7.5092780	-0.1131740
H	1.6401290	-7.1064020	-0.7364450
H	1.1235820	-6.4870920	0.8363570

11 (S_1), C_1 sym, G= -2505.419576 H

C	0.3667770	2.0813720	-0.2804270
C	1.3810110	1.1127210	-0.0468380
C	2.7376550	1.5302740	-0.0202940
C	2.1184710	3.5969930	-0.9905620

C	0.7223190	3.3692920	-0.7798520
C	0.7061910	-0.1328040	0.0020140
C	-0.6734410	0.1279200	-0.0001230
C	-1.3621540	-1.0932640	-0.0073140
C	-0.3607310	-2.0786800	-0.2176570
C	-2.7399230	-1.4755670	0.0074590
C	-0.7242040	-3.3582370	-0.7270140
C	-2.1412120	-3.5520160	-0.9949670
N	3.0715550	2.6923430	-0.5914610
N	-3.0785200	-2.6552670	-0.6476010
N	0.9038830	-1.4817480	-0.1249710
N	-0.8771260	1.4886170	-0.1487330
C	0.1818650	-4.3720230	-1.1237650
C	-0.2480880	-5.5213570	-1.7389710
H	1.2383360	-4.2396970	-0.9563890
H	0.4687490	-6.2791410	-2.0277160
C	-0.1936660	4.3660740	-1.2023190
C	0.2440330	5.5265910	-1.7879040
H	-1.2534350	4.2079570	-1.0835760
H	-0.4753420	6.2705510	-2.1057090
C	2.5352380	4.7996700	-1.5990150
C	1.6188910	5.7456840	-1.9848660
H	3.5906120	4.9628070	-1.7492920
H	1.9602420	6.6640760	-2.4464220
C	-2.5378020	-4.7494110	-1.6589690
C	-1.6218760	-5.7020720	-2.0099660
H	-3.5852210	-4.8854450	-1.8765900
H	-1.9571220	-6.6038920	-2.5086600
C	2.1936680	-2.0707730	-0.3183540
C	3.0109230	-1.5911160	-1.3303900
C	2.6477040	-3.0572530	0.5538460
C	4.3099350	-2.0791450	-1.4493370
H	2.6437830	-0.8246370	-2.0040990
C	3.9303090	-3.5536010	0.4062850
H	1.9989810	-3.4088290	1.3476430
C	4.7889810	-3.0553360	-0.5817050
H	4.9595340	-1.6776610	-2.2190260
H	4.2915000	-4.3092180	1.0954480
C	-2.1771870	2.0550580	-0.3473070
C	-2.6395090	3.0556230	0.5042590
C	-2.9959410	1.5297390	-1.3353660
C	-3.9337800	3.5216700	0.3588450
H	-1.9913020	3.4385630	1.2839810
C	-4.3060950	1.9880710	-1.4503930
H	-2.6238280	0.7472500	-1.9870610
C	-4.7939240	2.9788070	-0.6041200

H	-4.3034880	4.2862690	1.0335190
H	-4.9580630	1.5489010	-2.1971550
C	6.2096350	-3.5441880	-0.6564360
H	6.7363580	-3.3022720	0.2715260
H	6.2472170	-4.6284470	-0.7836170
H	6.7464550	-3.0794950	-1.4835000
C	-6.2268790	3.4306410	-0.6701150
H	-6.7507580	3.1339270	0.2436170
H	-6.2949940	4.5174730	-0.7537220
H	-6.7458110	2.9830470	-1.5177170
C	3.9065250	0.8316070	0.4938520
C	5.0429440	1.3882940	-0.0745390
C	3.9713940	-0.1645960	1.5200670
C	6.2945690	0.7828900	0.1821900
C	5.2474600	-0.7434750	1.7659100
C	2.8988480	-0.5110600	2.3784530
C	6.3826810	-0.2844590	1.0368550
H	7.1890330	1.1739670	-0.2926740
C	5.3831270	-1.7157530	2.7864020
C	3.0721240	-1.4239070	3.3900740
H	1.9385970	-0.0241910	2.2605680
H	7.3401210	-0.7585150	1.2315580
C	4.3183170	-2.0550830	3.5822720
H	6.3585870	-2.1623720	2.9511970
C	-3.8806850	-0.8426440	0.5488660
C	-5.0563020	-1.4263830	-0.0107250
C	-3.9700290	0.1706820	1.5739190
C	-6.2891120	-0.8351250	0.2585290
C	-5.2565540	0.7398360	1.8167340
C	-2.9008260	0.5425750	2.4067200
C	-6.3902790	0.2535540	1.1137980
H	-7.1868790	-1.2386690	-0.2010060
C	-5.3846170	1.7349000	2.8128320
C	-3.0622950	1.4909860	3.4022220
H	-1.9379130	0.0606820	2.2840280
H	-7.3551610	0.7083060	1.3158850
C	-4.3080980	2.1086850	3.5890460
H	-6.3602550	2.1808090	2.9794290
H	2.2440990	-1.6596010	4.0484770
H	4.4377530	-2.7841120	4.3747540
H	-2.2262890	1.7516730	4.0402920
H	-4.4297680	2.8603770	4.3601630
B	-4.6949340	-2.7129480	-0.9045540
B	4.6962140	2.7341800	-0.8792430
C	4.9216000	2.5844880	-2.4810230
H	4.6255020	3.4692300	-3.0537310

H	5.9877120	2.4222500	-2.6752920
H	4.3843090	1.7253630	-2.8985680
C	-4.9924530	-2.4584850	-2.4859900
H	-4.6738900	-3.2892390	-3.1255270
H	-6.0704360	-2.3317380	-2.6397600
H	-4.5034600	-1.5499810	-2.8567070
C	5.4426080	3.9984100	-0.1852080
H	6.5111610	3.7715740	-0.0979360
H	5.3754100	4.9349670	-0.7472270
H	5.0785770	4.1923300	0.8292120
C	-5.4123080	-4.0453690	-0.2972890
H	-6.4624640	-3.8129470	-0.0863360
H	-5.4214400	-4.9081100	-0.9714790
H	-4.9652330	-4.3674520	0.6495620

13 (S_0), C_2 sym, G= -3454.306491 H

C	-2.1172490	0.1630320	-0.6655160
C	-1.2388210	1.2592580	-0.4608810
C	-1.7814710	2.5665790	-0.3664420
C	-3.8408640	1.7595060	-1.2320590
C	-3.4641700	0.3948160	-1.0953310
C	0.0676200	0.6845430	-0.4478090
C	-0.0676200	-0.6845430	-0.4478090
C	1.2388210	-1.2592580	-0.4608810
C	2.1172490	-0.1630320	-0.6655160
C	1.7814710	-2.5665790	-0.3664420
C	3.4641700	-0.3948160	-1.0953310
C	3.8408640	-1.7595060	-1.2320590
N	-3.0061700	2.7871320	-0.8531170
N	3.0061700	-2.7871320	-0.8531170
N	1.4083340	1.0138350	-0.5794750
N	-1.4083340	-1.0138350	-0.5794750
C	4.3831020	0.5988370	-1.5109160
C	5.6165090	0.2598380	-2.0100980
H	4.1126910	1.6405100	-1.4619430
H	6.2977160	1.0402740	-2.3252590
C	-4.3831020	-0.5988370	-1.5109160
C	-5.6165090	-0.2598380	-2.0100980
H	-4.1126910	-1.6405100	-1.4619430
H	-6.2977160	-1.0402740	-2.3252590
C	-5.1169960	2.0782220	-1.7447780
C	-5.9900620	1.0889230	-2.1203750
H	-5.3952370	3.1158440	-1.8304920
H	-6.9663300	1.3533230	-2.5075030
C	5.1169960	-2.0782220	-1.7447780
C	5.9900620	-1.0889230	-2.1203750

H	5.3952370	-3.1158440	-1.8304920
H	6.9663300	-1.3533230	-2.5075030
C	1.8634220	2.3517410	-0.7953880
C	1.3023000	3.0998180	-1.8203680
C	2.8145940	2.9082110	0.0543120
C	1.6755720	4.4311980	-1.9767560
H	0.5616150	2.6510650	-2.4731260
C	3.2074220	4.2216020	-0.1394770
H	3.2226930	2.3120640	0.8644940
C	2.6253850	5.0099490	-1.1392540
H	1.2097260	5.0266740	-2.7538530
H	3.9452240	4.6604590	0.5230990
C	-1.8634220	-2.3517410	-0.7953880
C	-2.8145940	-2.9082110	0.0543120
C	-1.3023000	-3.0998180	-1.8203680
C	-3.2074220	-4.2216020	-0.1394770
H	-3.2226930	-2.3120640	0.8644940
C	-1.6755720	-4.4311980	-1.9767560
H	-0.5616150	-2.6510650	-2.4731260
C	-2.6253850	-5.0099490	-1.1392540
H	-3.9452240	-4.6604590	0.5230990
H	-1.2097260	-5.0266740	-2.7538530
C	2.9910500	6.4641800	-1.2536490
H	2.6755410	6.9971130	-0.3511680
H	4.0712280	6.5935720	-1.3497390
H	2.5072640	6.9299310	-2.1121990
C	-2.9910500	-6.4641800	-1.2536490
H	-2.6755410	-6.9971130	-0.3511680
H	-4.0712280	-6.5935720	-1.3497390
H	-2.5072640	-6.9299310	-2.1121990
C	-1.1738020	3.8216060	0.1179090
C	-1.8800480	4.8813650	-0.4633530
C	-0.1424860	4.0704620	1.0641350
C	-1.4304350	6.1961010	-0.3012570
C	0.2649370	5.4123600	1.1861750
C	-0.3282060	6.4656150	0.4854680
H	-1.9615980	7.0111750	-0.7826340
C	0.5578950	3.2305020	2.0377110
H	0.0365190	7.4784390	0.6163430
C	1.5207410	3.9606910	2.7653630
C	1.1738020	-3.8216060	0.1179090
C	1.8800480	-4.8813650	-0.4633530
C	0.1424860	-4.0704620	1.0641350
C	1.4304350	-6.1961010	-0.3012570
C	-0.2649370	-5.4123600	1.1861750
C	0.3282060	-6.4656150	0.4854680

H	1.9615980	-7.0111750	-0.7826340
C	-0.5578950	-3.2305020	2.0377110
H	-0.0365190	-7.4784390	0.6163430
C	-1.5207410	-3.9606910	2.7653630
B	3.2305910	-4.3848930	-1.1669130
B	-3.2305910	4.3848930	-1.1669130
C	-3.2074220	4.5817650	-2.7797660
H	-4.0965700	4.1983710	-3.2901950
H	-3.1505270	5.6533490	-3.0023630
H	-2.3319490	4.1115990	-3.2424180
C	3.2074220	-4.5817650	-2.7797660
H	4.0965700	-4.1983710	-3.2901950
H	3.1505270	-5.6533490	-3.0023630
H	2.3319490	-4.1115990	-3.2424180
C	-4.5099030	5.0350460	-0.4031740
H	-4.3591880	6.1176500	-0.3252180
H	-5.4702940	4.8997720	-0.9100890
H	-4.6183600	4.6599680	0.6201460
C	4.5099030	-5.0350460	-0.4031740
H	4.3591880	-6.1176500	-0.3252180
H	5.4702940	-4.8997720	-0.9100890
H	4.6183600	-4.6599680	0.6201460
C	2.3634190	3.3647500	3.7012260
C	2.2282720	2.0092940	3.9445420
H	3.1020800	3.9554470	4.2296650
H	2.8768240	1.5217440	4.6619080
C	-2.3634190	-3.3647500	3.7012260
C	-2.2282720	-2.0092940	3.9445420
H	-3.1020800	-3.9554470	4.2296650
H	-2.8768240	-1.5217440	4.6619080
C	0.3929130	1.8760720	2.3660970
C	1.2309950	1.2754970	3.2932640
H	-0.3952690	1.2959630	1.9059430
H	1.1081030	0.2262150	3.5324320
C	-0.3929130	-1.8760720	2.3660970
C	-1.2309950	-1.2754970	3.2932640
H	0.3952690	-1.2959630	1.9059430
H	-1.1081030	-0.2262150	3.5324320
S	1.5327340	5.6582330	2.3680960
S	-1.5327340	-5.6582330	2.3680960

13 (S_1), C_1 sym, G= -3454.198385 H

C	0.1648700	2.1124700	-0.6268980
C	1.2604670	1.2273100	-0.4086180
C	2.5930780	1.7465280	-0.3330590
C	1.7909060	3.7801970	-1.3019740

C	0.3975710	3.4311170	-1.0987400
C	0.6921020	-0.0513260	-0.4465670
C	-0.7161190	0.0745280	-0.4503640
C	-1.2721970	-1.2236910	-0.4599650
C	-0.1651250	-2.0926890	-0.6978480
C	-2.5809480	-1.7752590	-0.3752490
C	-0.3896910	-3.4164700	-1.1628030
C	-1.7605660	-3.7974140	-1.3126640
N	2.8074980	2.9742940	-0.9423930
N	-2.7908440	-2.9890390	-0.9116590
N	1.0186100	-1.3802600	-0.5938560
N	-1.0373810	1.3930560	-0.5655040
C	0.6153850	-4.3145890	-1.6106730
C	0.2866460	-5.5297460	-2.1506320
H	1.6541990	-4.0351050	-1.5495380
H	1.0698490	-6.1957500	-2.4893410
C	-0.6006630	4.3465340	-1.5211050
C	-0.2751170	5.5505830	-2.0898950
H	-1.6418260	4.0919870	-1.4127940
H	-1.0574400	6.2306290	-2.4007200
C	2.0812800	5.0325700	-1.9125970
C	1.0816710	5.8896490	-2.2834890
H	3.1142910	5.2937360	-2.0738760
H	1.3386480	6.8383350	-2.7398940
C	-2.0633270	-5.0587610	-1.8722410
C	-1.0640130	-5.9068410	-2.2745480
H	-3.0975990	-5.3445760	-1.9720560
H	-1.3197210	-6.8709980	-2.6965480
C	2.3628360	-1.8293480	-0.7894500
C	3.1305050	-1.2366910	-1.7816390
C	2.9021190	-2.7970270	0.0531200
C	4.4671550	-1.5997880	-1.9145710
H	2.6942810	-0.4804090	-2.4245510
C	4.2223620	-3.1753280	-0.1177160
H	2.2919460	-3.2241550	0.8427740
C	5.0304490	-2.5662190	-1.0859880
H	5.0792160	-1.1097110	-2.6632480
H	4.6516050	-3.9221680	0.5411280
C	-2.3751500	1.8565900	-0.7633980
C	-2.9179210	2.8058800	0.0976090
C	-3.1358310	1.3005250	-1.7820010
C	-4.2335640	3.1986840	-0.0774590
H	-2.3112230	3.2102510	0.9018090
C	-4.4678660	1.6772790	-1.9211930
H	-2.6953370	0.5649980	-2.4461240
C	-5.0348470	2.6230130	-1.0711850

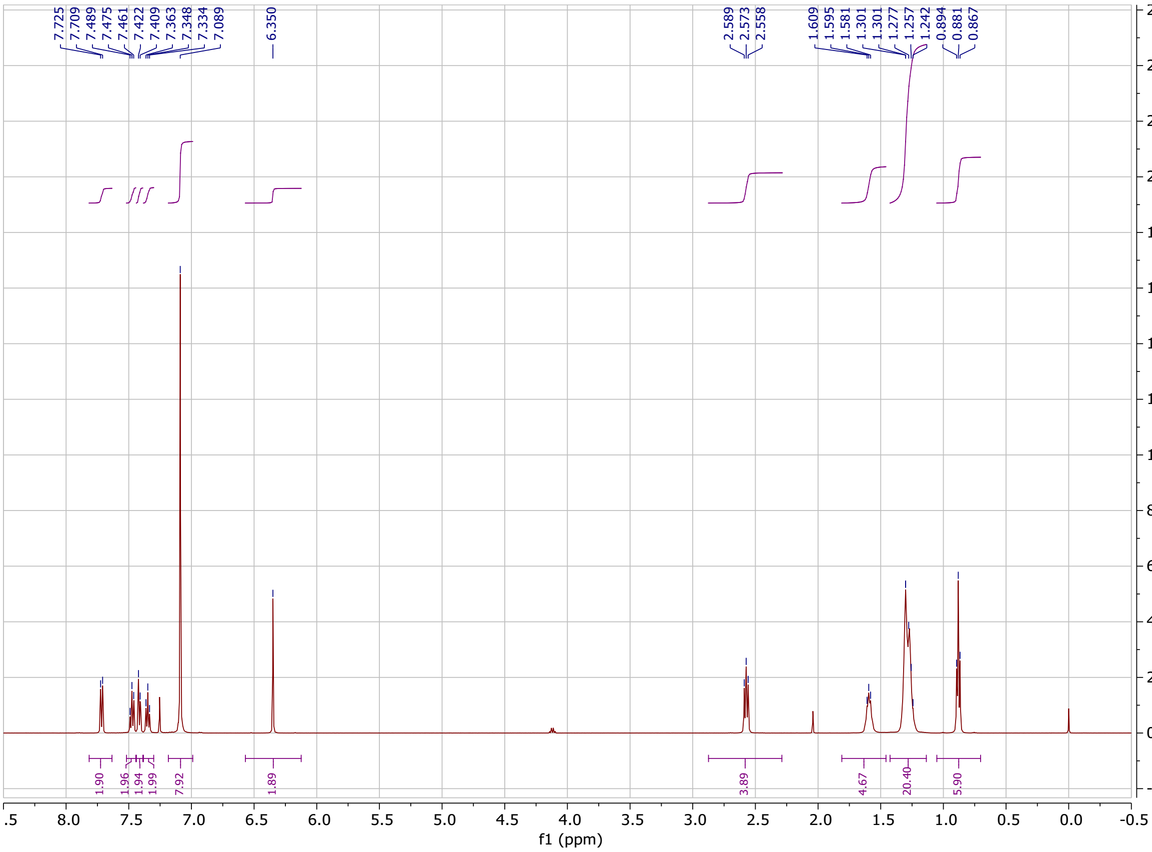
H	-4.6636370	3.9332090	0.5944510
H	-5.0725020	1.2181890	-2.6951430
C	6.4887920	-2.9213510	-1.1748450
H	6.9995080	-2.6147790	-0.2567180
H	6.6270170	-3.9991890	-1.2840550
H	6.9693340	-2.4211510	-2.0155460
C	-6.4888330	2.9938790	-1.1682050
H	-7.0119360	2.6808390	-0.2592020
H	-6.6147910	4.0745430	-1.2629230
H	-6.9664760	2.5119260	-2.0211630
C	3.8068240	1.2006020	0.1830900
C	4.9008430	1.9217960	-0.3993570
C	4.0759850	0.1657270	1.1356510
C	6.2014900	1.4760230	-0.2259920
C	5.4231100	-0.2354710	1.2551550
C	6.4790140	0.3659560	0.5717380
H	7.0182800	2.0063150	-0.7061950
C	3.2362120	-0.5442540	2.0836940
H	7.4937030	0.0104990	0.7107380
C	3.9580040	-1.5259630	2.8032430
C	-3.8269790	-1.1942680	0.1302560
C	-4.8898660	-1.8992990	-0.4595530
C	-4.0797070	-0.1727950	1.0893200
C	-6.2042300	-1.4571920	-0.2877100
C	-5.4230220	0.2264050	1.2183670
C	-6.4758710	-0.3650860	0.5146640
H	-7.0184710	-1.9838320	-0.7752080
C	-3.2394980	0.5243970	2.0616850
H	-7.4898110	-0.0062550	0.6526490
C	-3.9711160	1.4797550	2.7985420
B	-4.3883420	-3.2215920	-1.2100520
B	4.3961260	3.2081470	-1.2112050
C	4.6934060	3.0702130	-2.8076780
H	4.3018670	3.9032120	-3.4016640
H	5.7767030	3.0419030	-2.9727760
H	4.2795210	2.1442740	-3.2239860
C	-4.6120110	-3.1460360	-2.8183570
H	-4.2259890	-4.0129990	-3.3638780
H	-5.6875070	-3.0955280	-3.0221330
H	-4.1599470	-2.2497460	-3.2584670
C	4.9913190	4.5664530	-0.5315560
H	6.0632600	4.4278140	-0.3509100
H	4.9012060	5.4676470	-1.1467660
H	4.5342800	4.7805670	0.4408400
C	-5.0097670	-4.5350500	-0.4813370
H	-6.0927240	-4.4013570	-0.3819230

H	-4.8700370	-5.4748490	-1.0243690
H	-4.6173680	-4.6743870	0.5316040
C	3.3532990	-2.3885900	3.7124880
C	1.9931240	-2.2584520	3.9457110
H	3.9388210	-3.1377740	4.2320850
H	1.4978120	-2.9206880	4.6447800
C	-3.3746480	2.3227640	3.7334590
C	-2.0162600	2.1962880	3.9661270
H	-3.9664690	3.0554500	4.2688530
H	-1.5276950	2.8456320	4.6819650
C	1.8765030	-0.3874850	2.4021000
C	1.2686410	-1.2460720	3.3075370
H	1.3054140	0.4143450	1.9541560
H	0.2172420	-1.1273480	3.5410130
C	-1.8813940	0.3673410	2.3802390
C	-1.2801640	1.2065690	3.3061250
H	-1.2998150	-0.4186930	1.9180790
H	-0.2285960	1.0903050	3.5379820
S	5.6579460	-1.5183300	2.4202550
S	-5.6706420	1.4827850	2.4105060

8. NMR spectra

All NMR spectra were collected with 500 MHz and 600 MHz Varian spectrometers at room temperature, except for **13** ^{1}H NMR, which was collected at -40°C – this was based on our previous experience with double helicenes.[31] Chemical shifts (δ, ppm) were determined with tetramethylsilane as the internal reference. *J* values are given in Hz. Data is presented as following: chemical shift, multiplicity (s – singlet, br. s – broad singlet, d – doublet, dd – doublet of doublets, t – triplet, m – multiplet), *J*-coupling, number of protons.

TAPP 7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7.461
7.422
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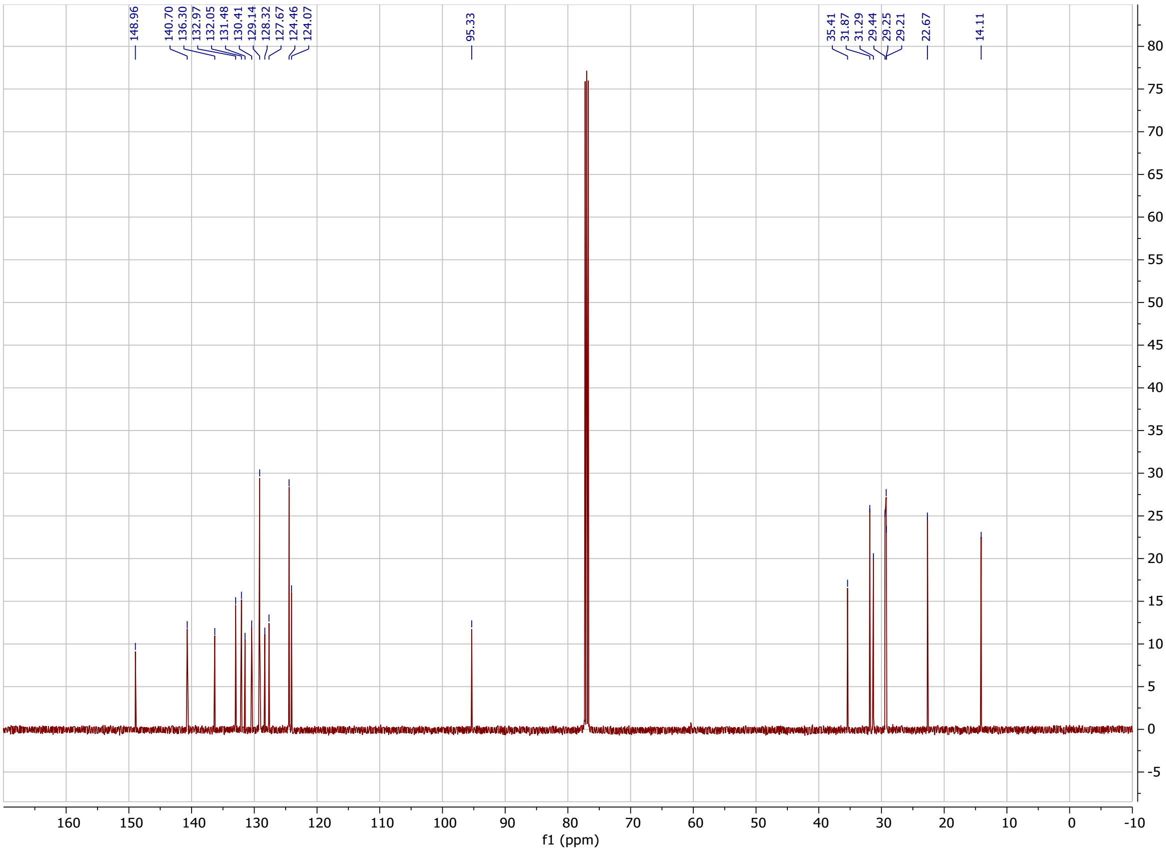
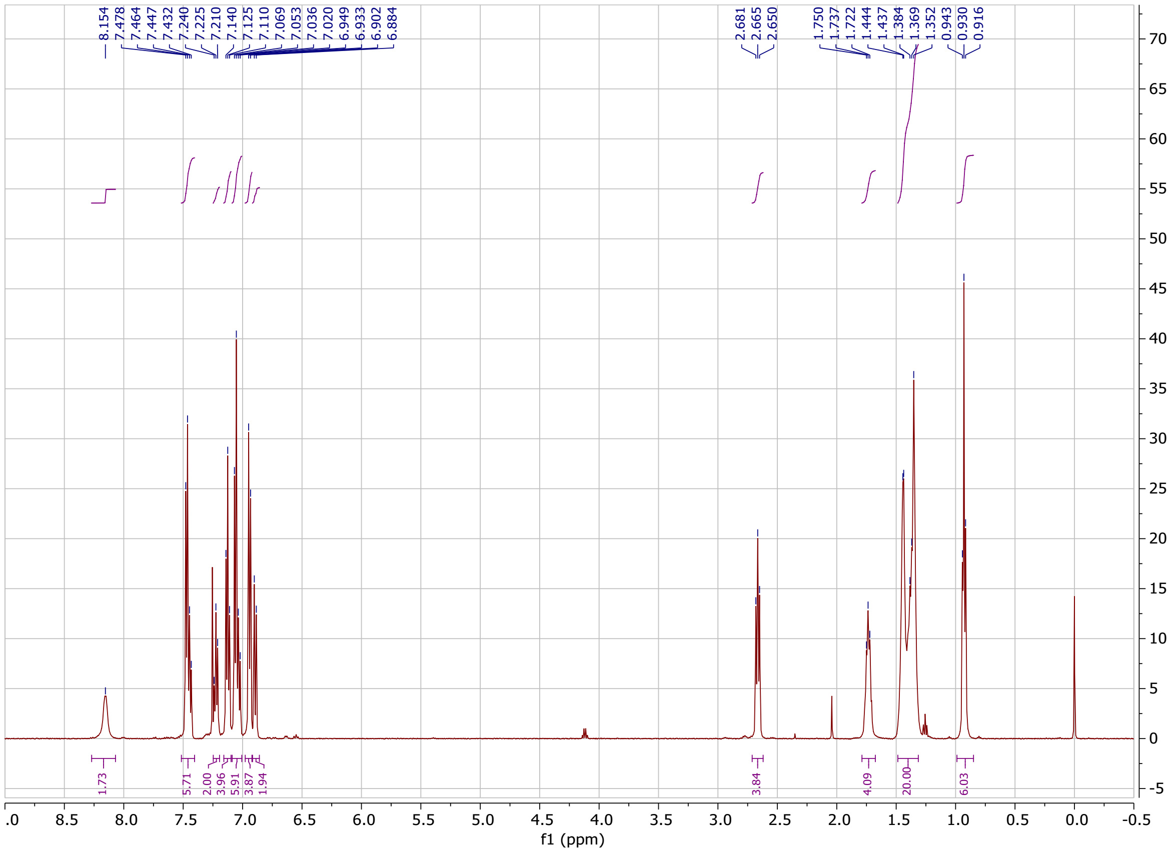
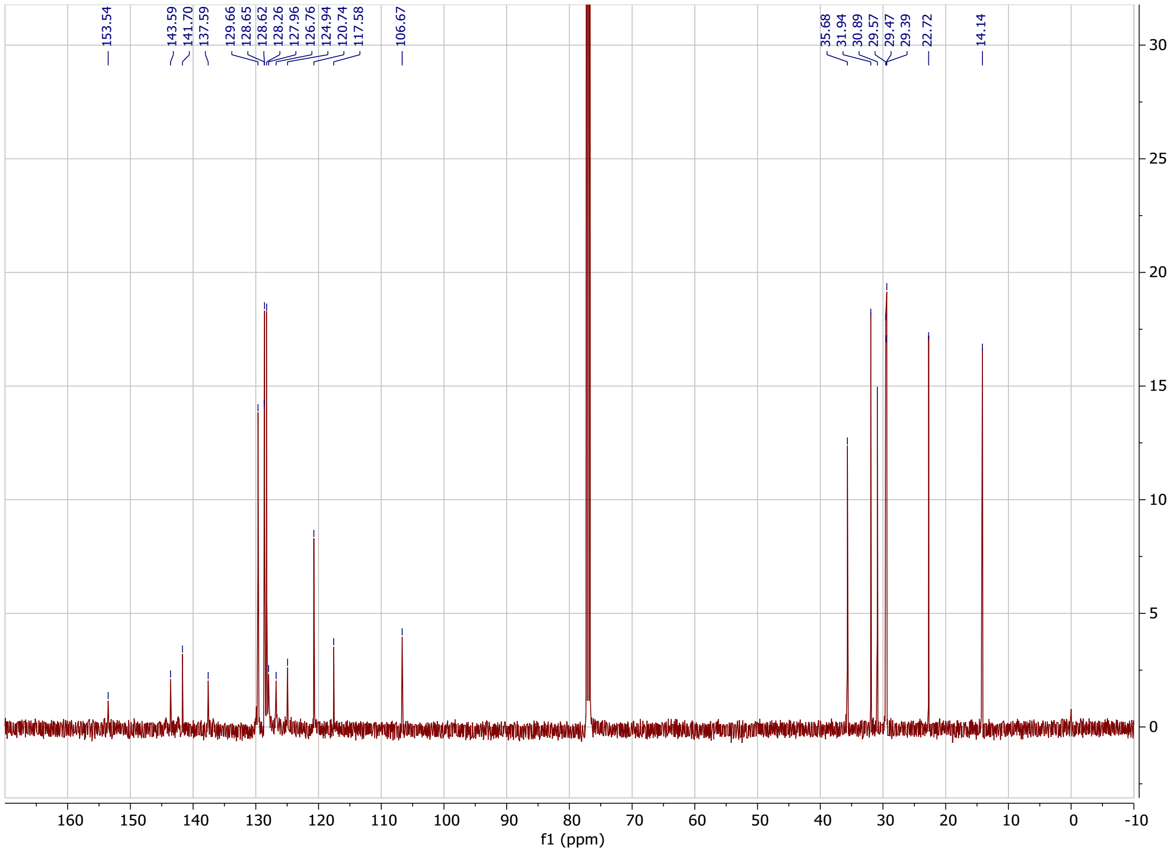
7.348
7.334
7.089
6.350
2.589
2.573
2.558
1.609
1.595
1.581
1.301
1.301
1.277
1.257
1.242
0.894
0.881
0.867
1.90
1.96
1.94
1.99
7.92
1.89
3.89
4.67
20.40
5.90
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


148.96
140.70
136.30
132.97
132.05
131.48
130.41
129.14
128.32
127.67
124.46
124.07
95.33
35.41
31.87
31.29
29.44
29.25
29.21
22.67
14.11
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

DQPP 8

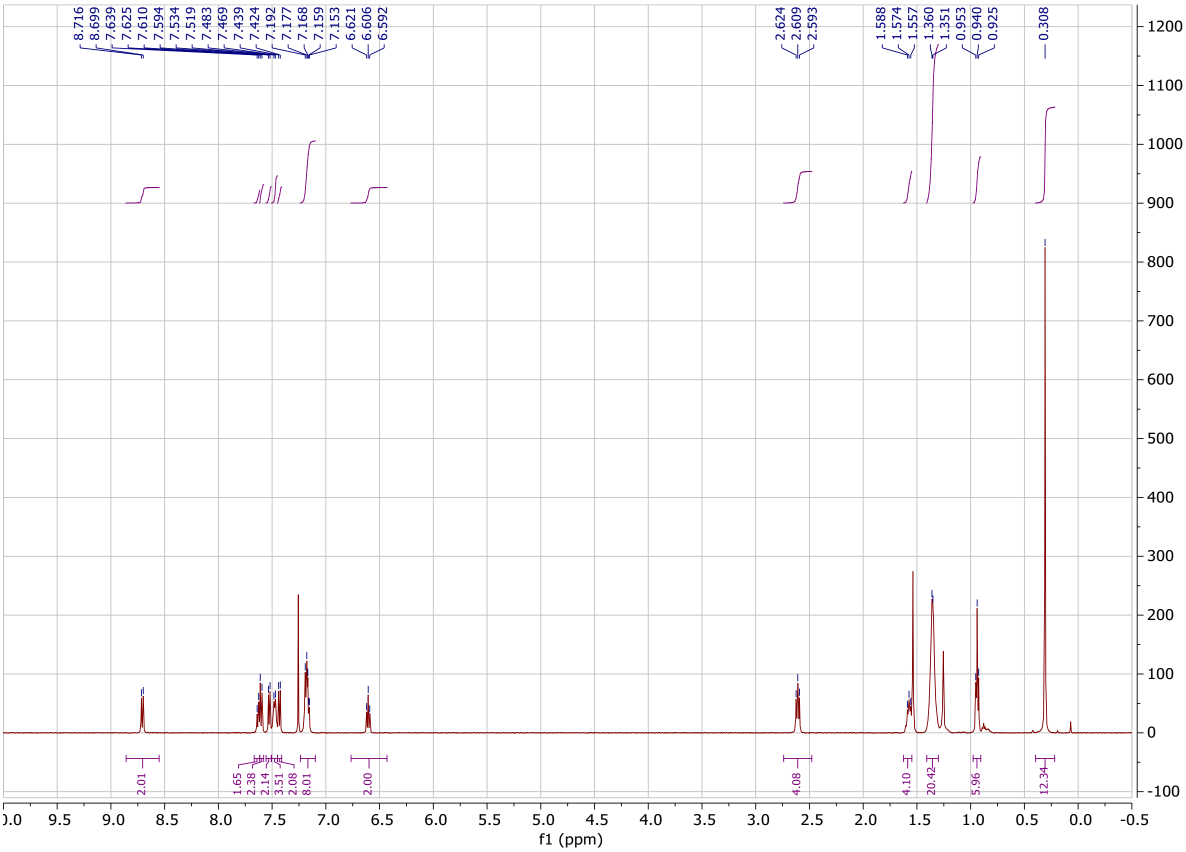


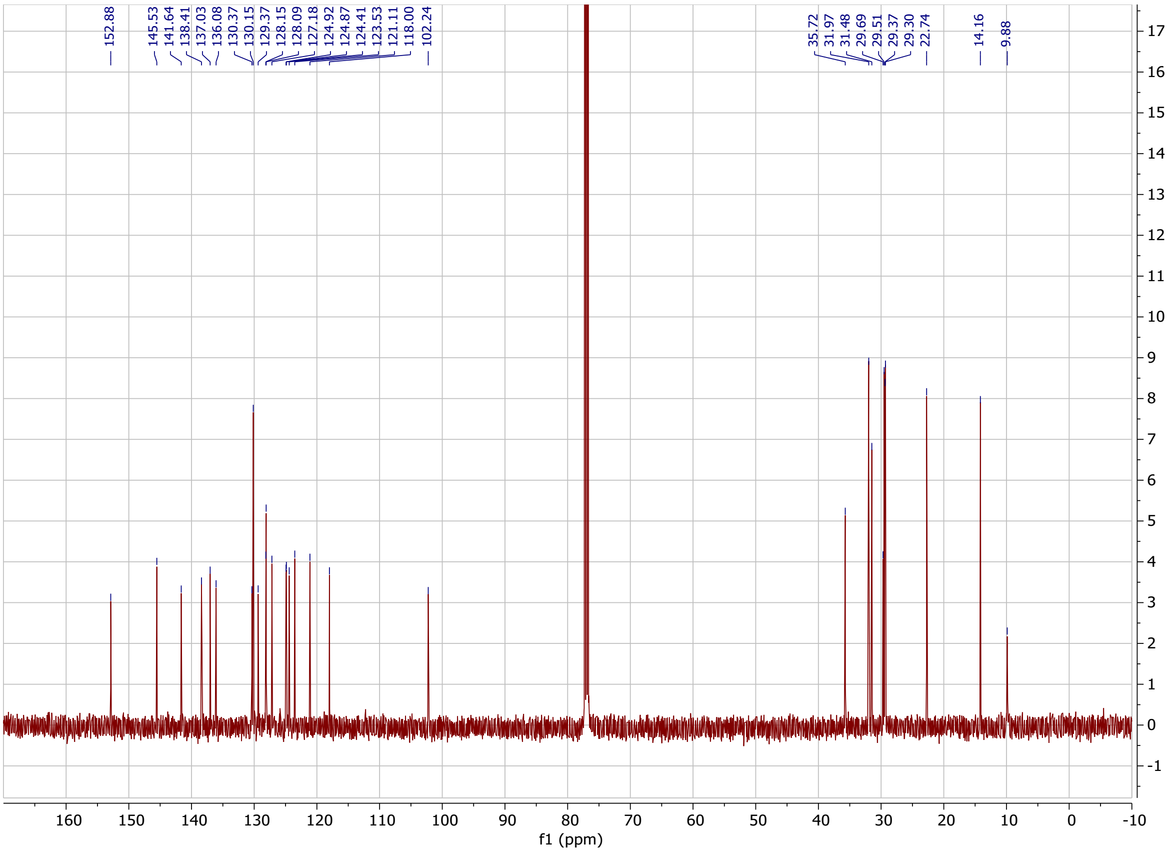
8.154
7.478
7.464
7.447
7.432
7.240
7.225
7.210
7.140
7.125
7.110
7.069
7.053
7.036
7.020
6.949
6.933
6.902
6.884
2.681
2.665
2.650
1.750
1.737
1.722
1.444
1.437
1.384
1.369
1.352
0.943
0.930
0.916
1.73
5.71
2.00
3.96
5.91
3.87
1.94
3.84
4.09
20.00
6.03
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5



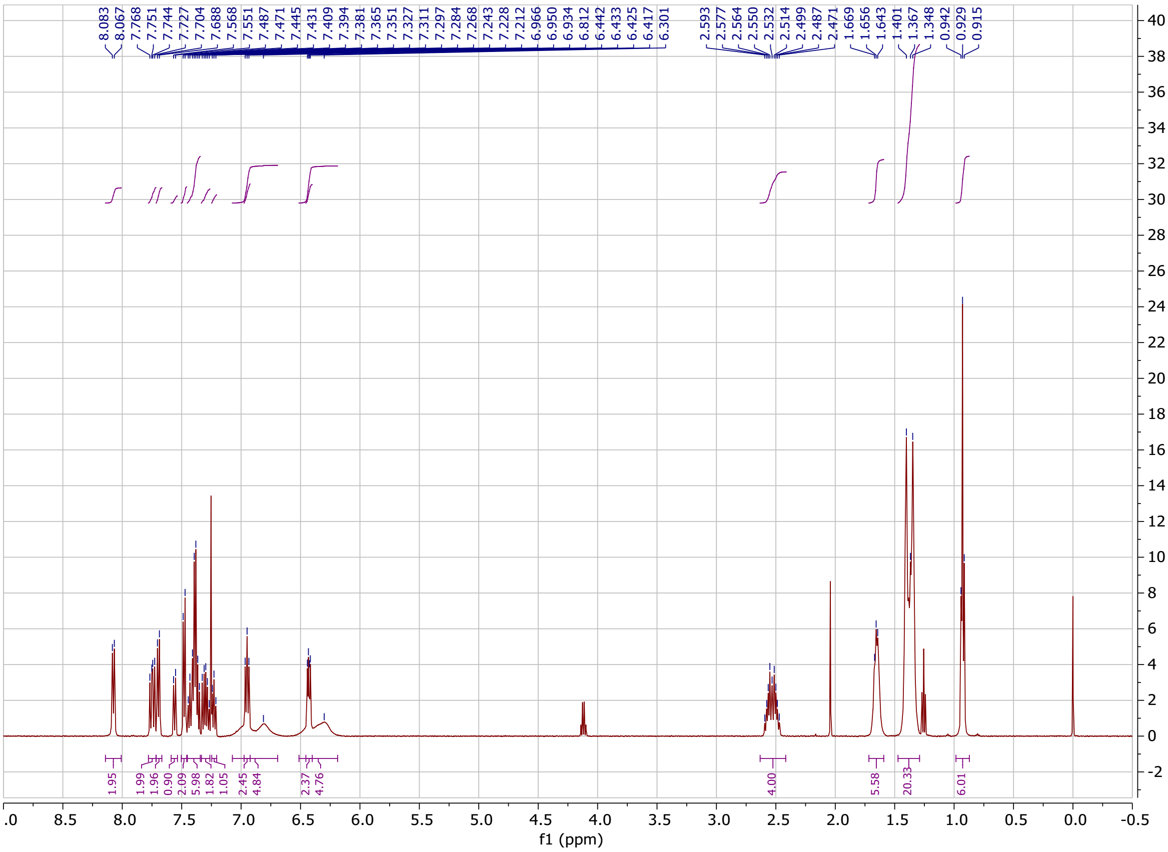
153.54
143.59
141.70
137.59
129.66
128.65
128.62
128.26
127.96
126.76
124.94
120.74
117.58
106.67
35.68
31.94
30.89
29.57
29.47
29.39
22.72
14.14
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
30
25
20
15
10
5
0

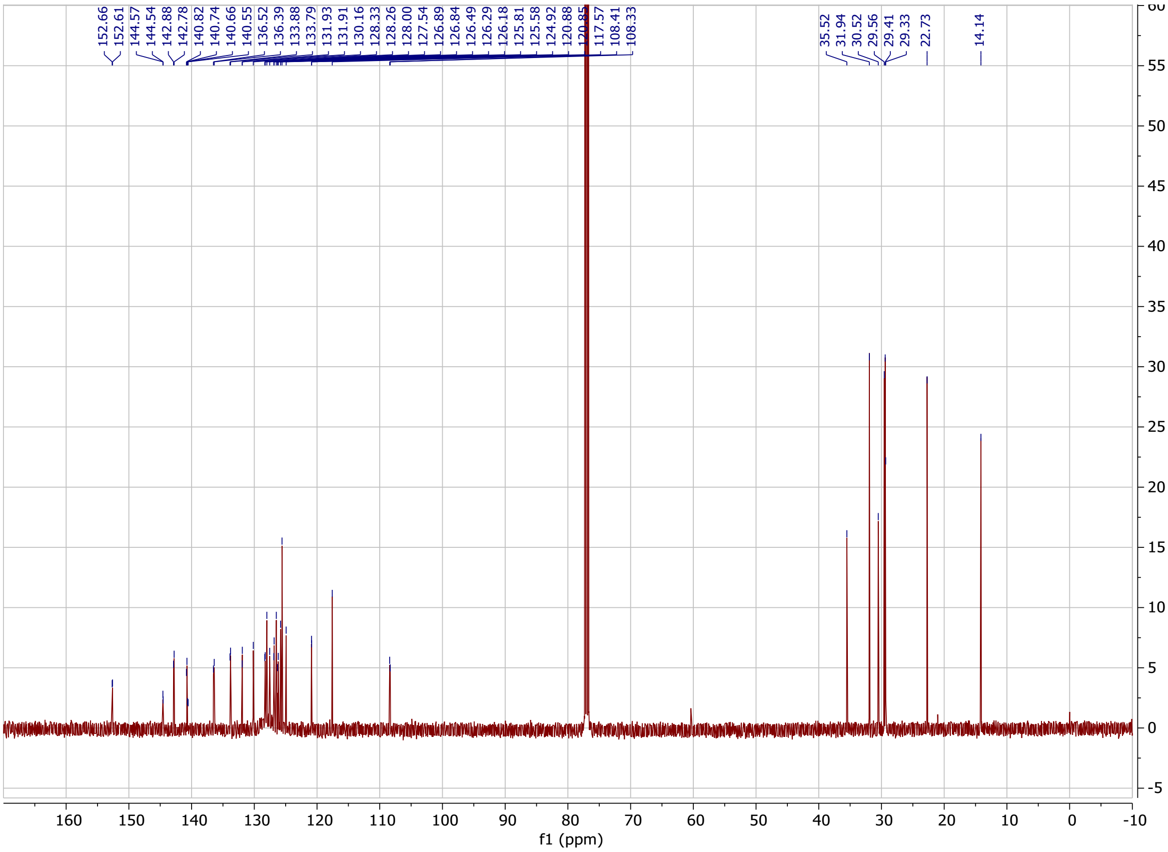
N/C boron complex 9



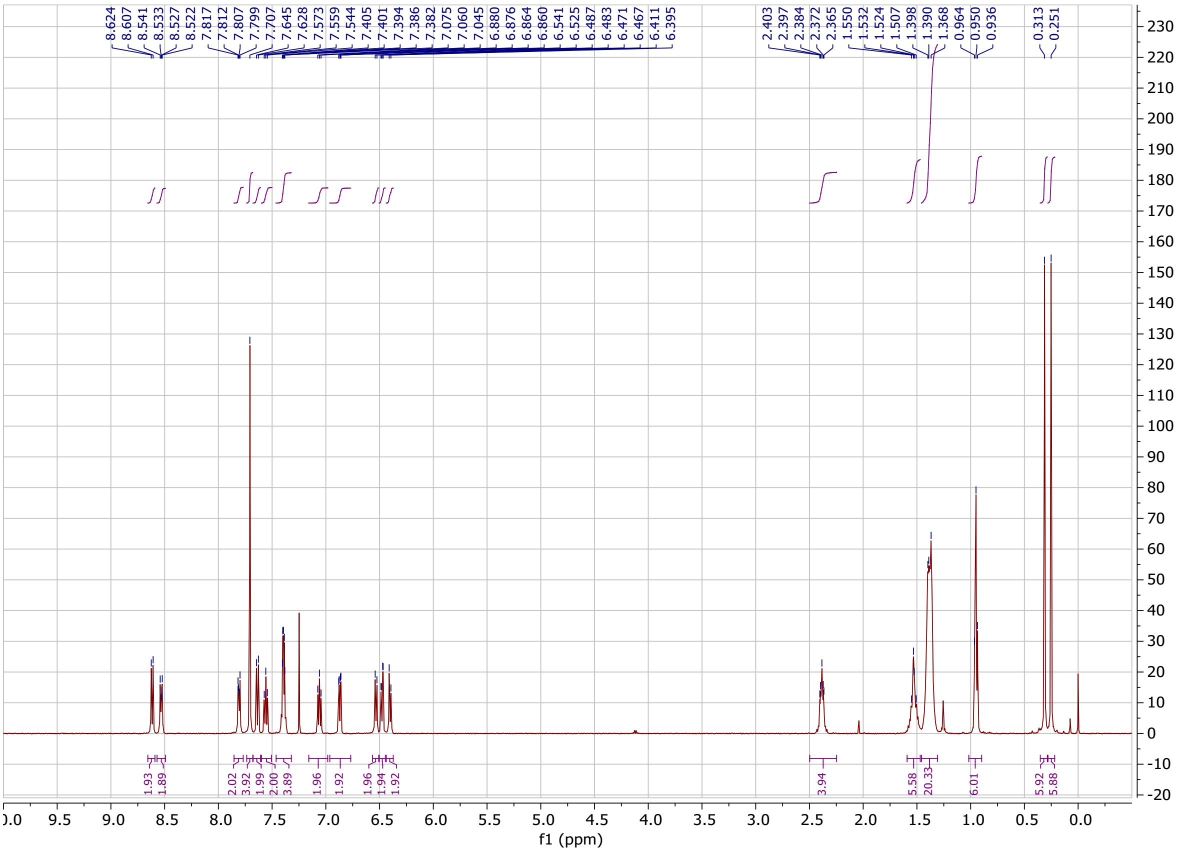


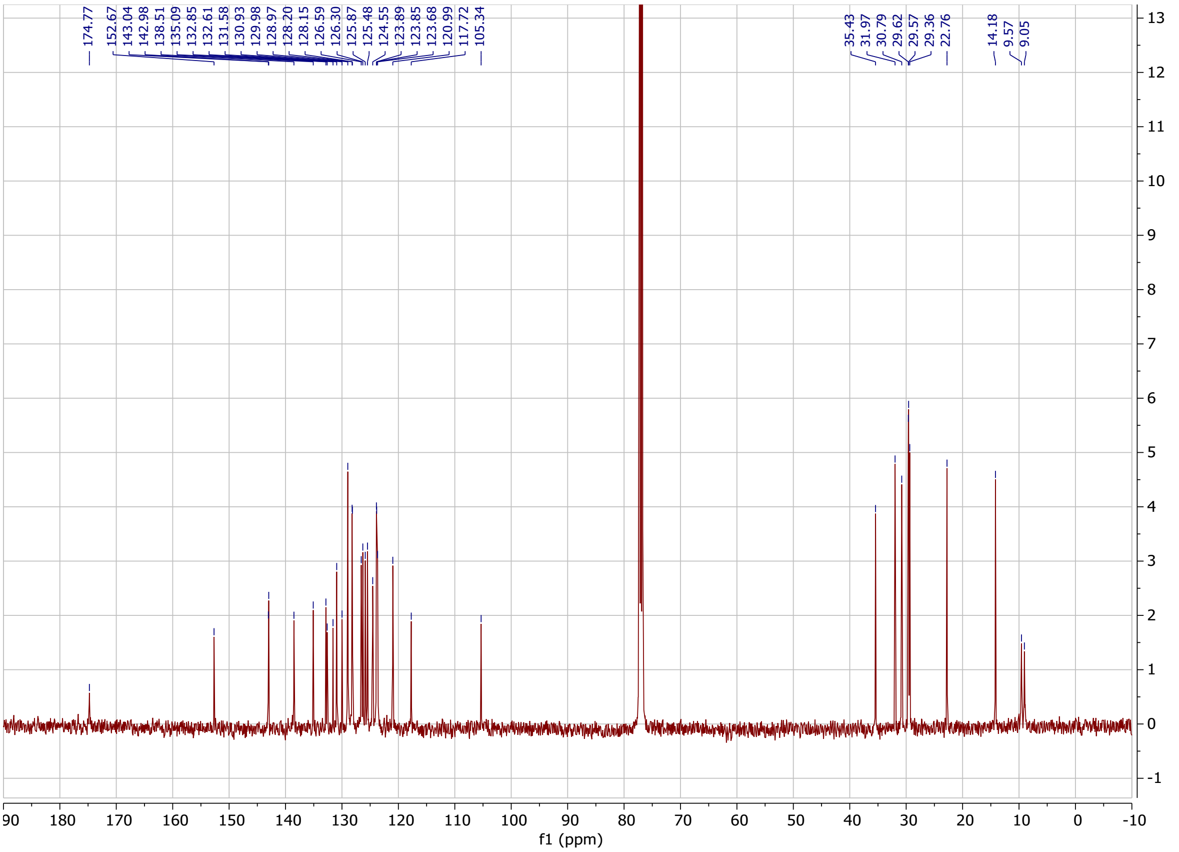
DQPP 10


8.083
8.067
7.768
7.751
7.744
7.727
7.704
7.688
7.568
7.551
7.487
7.471
7.445
7.431
7.409
7.394
7.381
7.365
7.351
7.327
7.311
7.297
7.284
7.268
7.243
7.228
7.212
6.966
6.950
6.934
6.812
6.442
6.433
6.425
6.417
6.301
2.593
2.577
2.564
2.550
2.532
2.514
2.499
2.487
2.471
1.669
1.656
1.643
1.401
1.367
1.348
0.942
0.929
0.915
1.95
1.99
1.96
0.90
2.09
5.98
1.82
1.05
2.45
4.84
2.37
4.76
4.00
5.58
20.33
6.01
f1 (ppm)

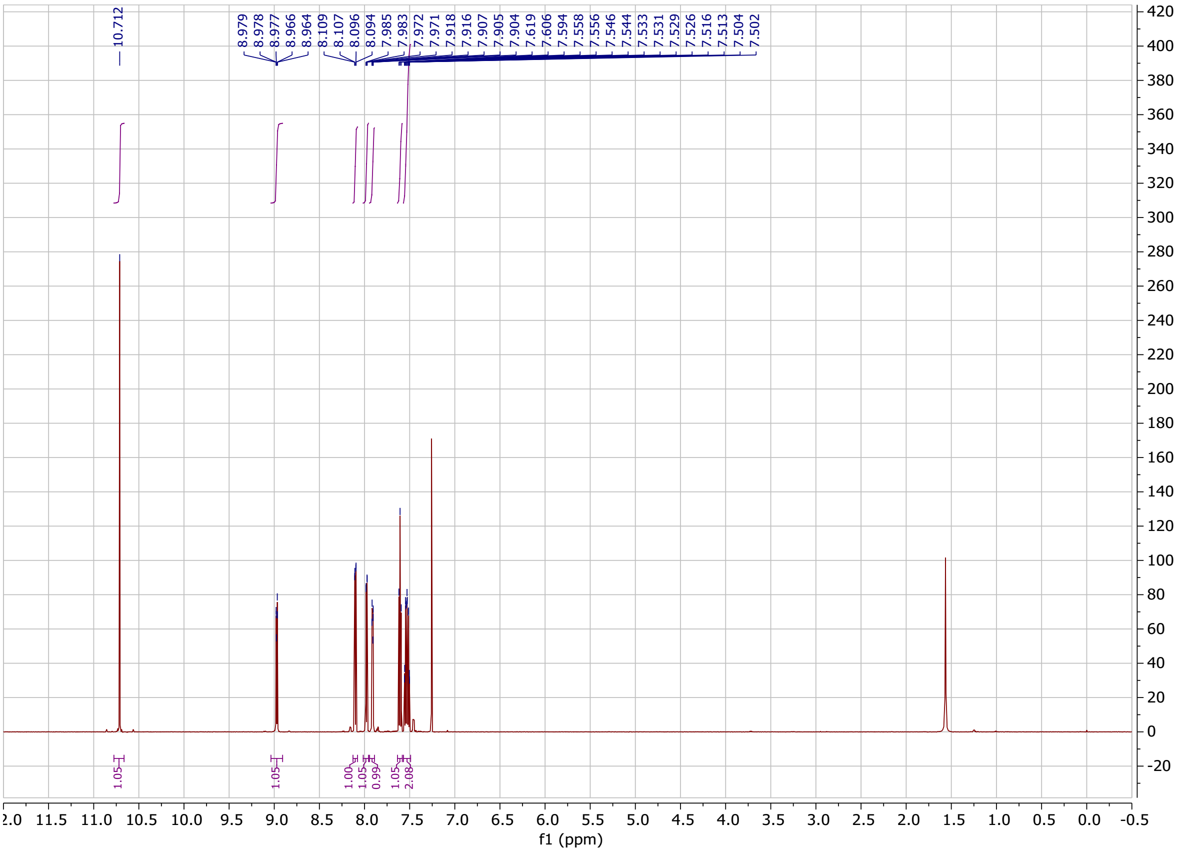

152.66
152.61
144.57
144.54
142.88
142.78
140.82
140.74
140.66
140.55
136.52
136.39
133.88
133.79
131.93
131.91
130.16
128.33
128.26
128.00
127.54
126.89
126.84
126.49
126.29
126.18
125.81
125.58
124.92
120.88
120.85
117.57
108.41
108.33
35.52
31.94
30.52
29.56
29.41
29.33
22.73
14.14
f1 (ppm)

N/C boron complex 11

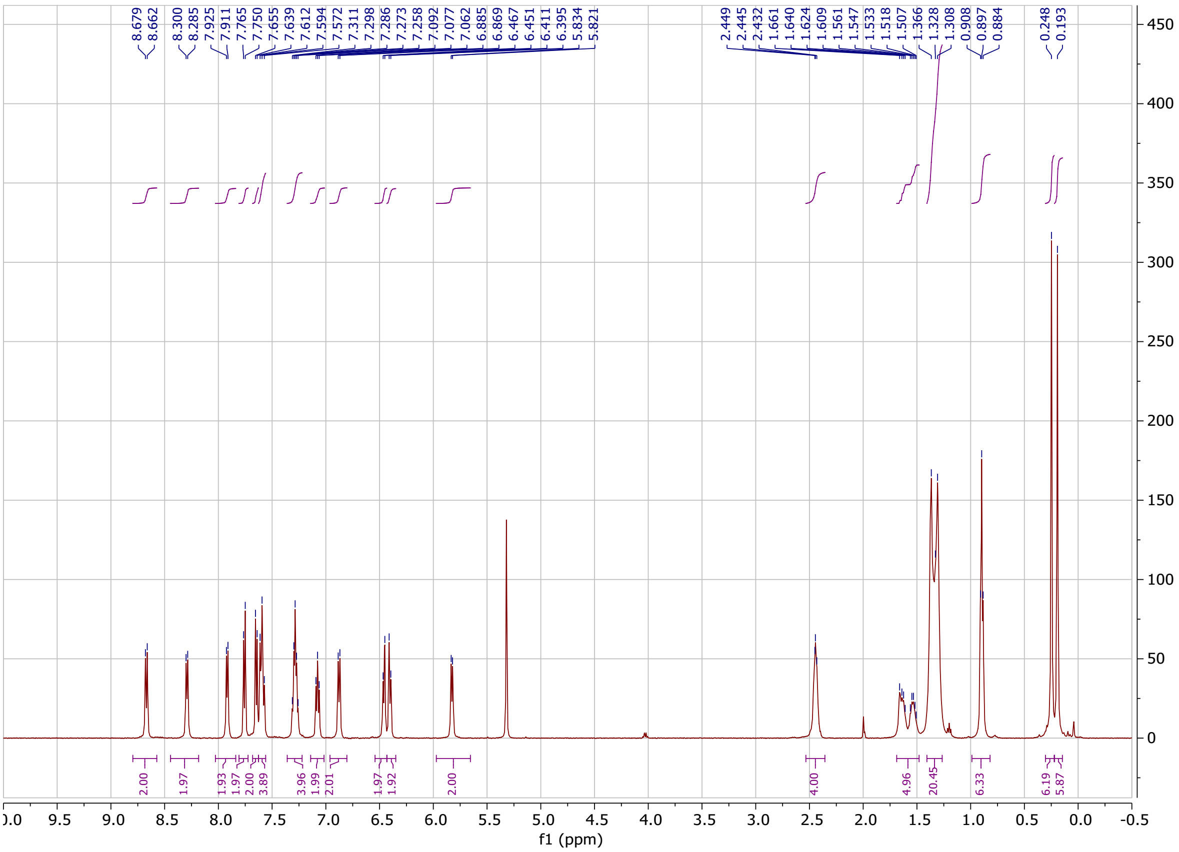


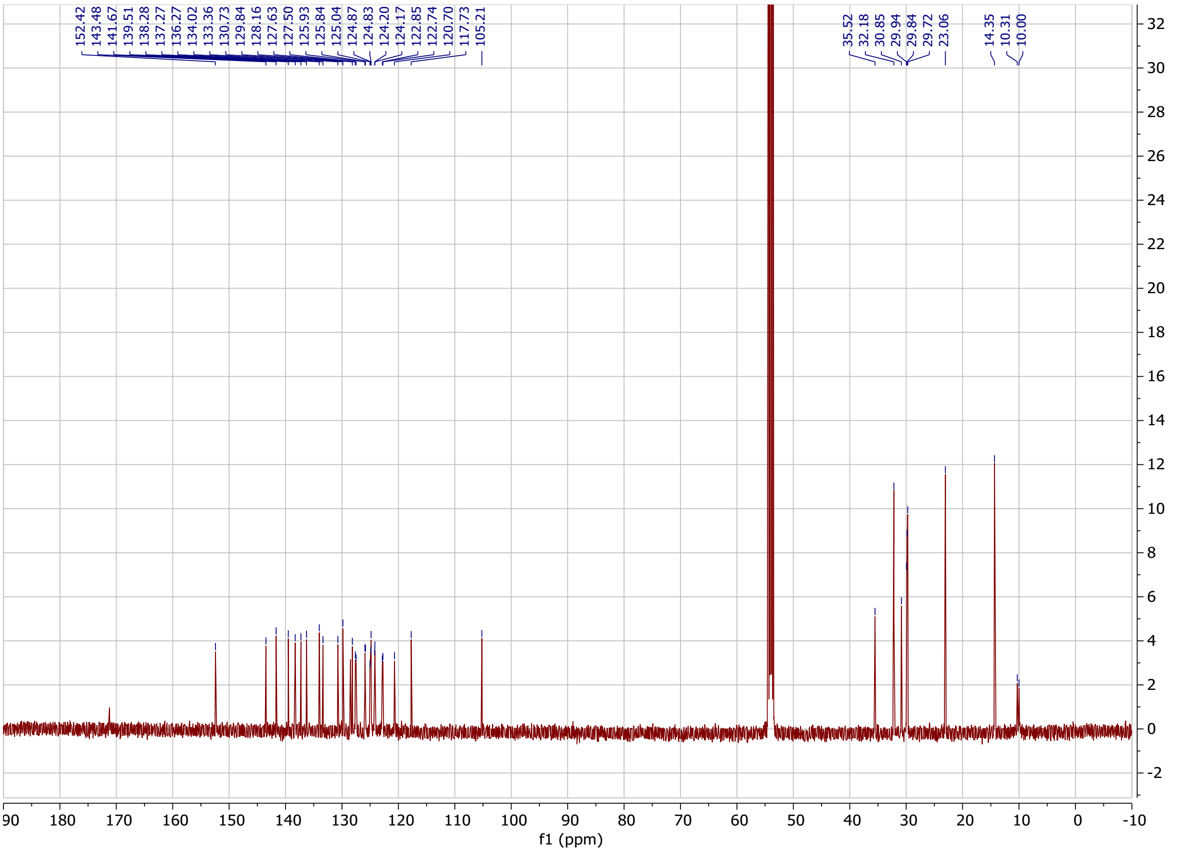


Dibenzo[*b*,*d*]thiophene-1-carbaldehyde S1

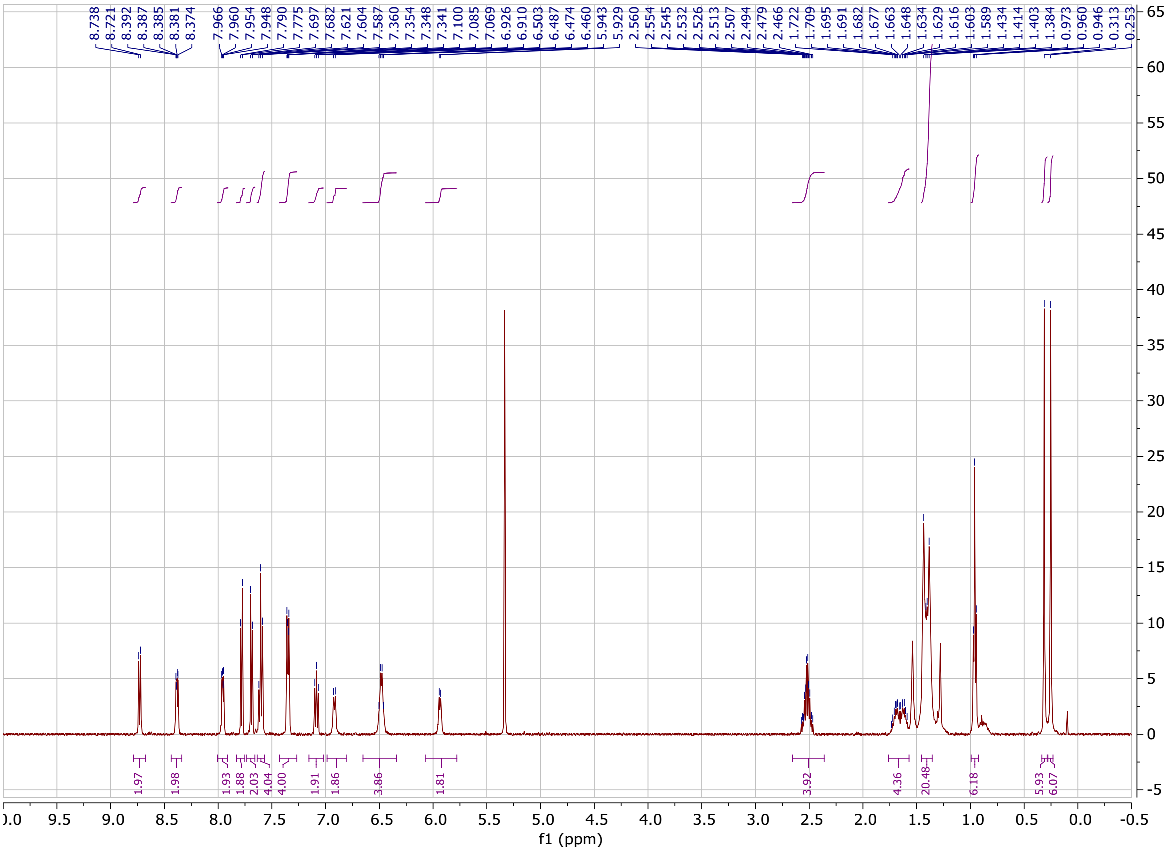


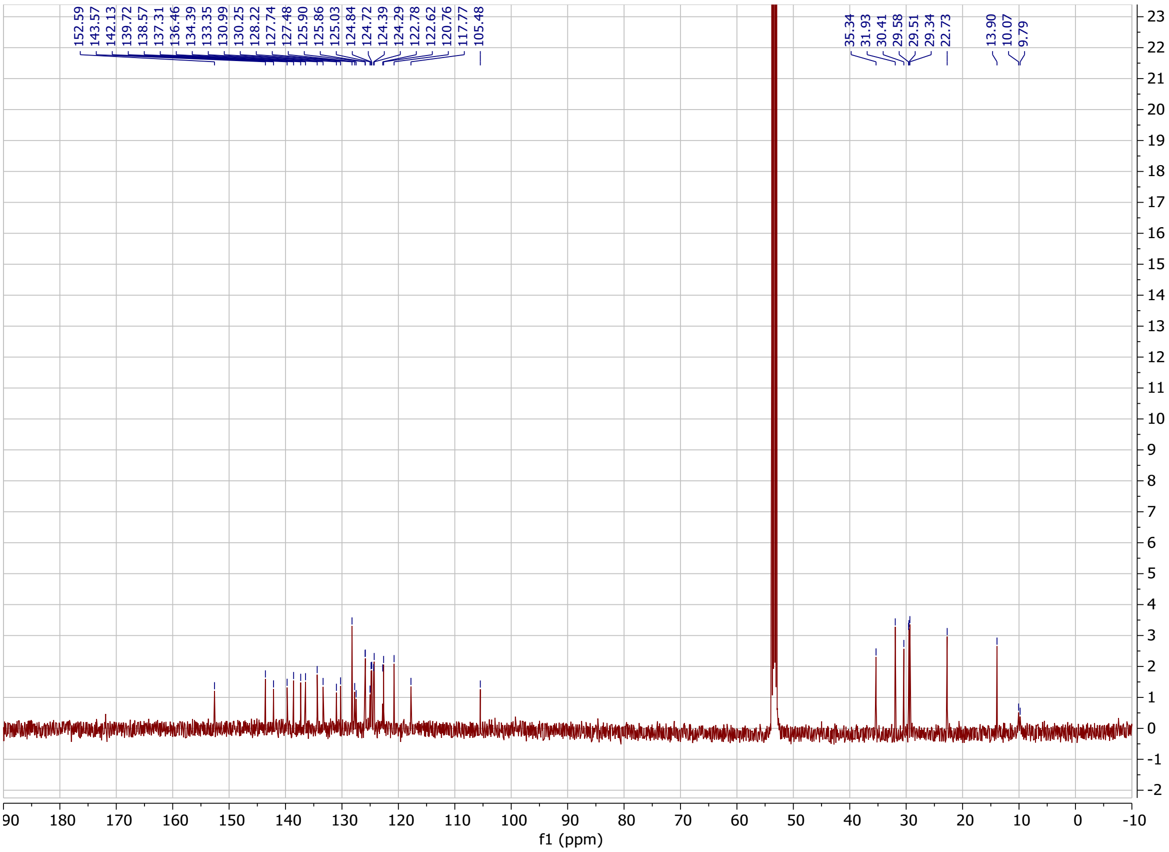
N/C boron complex 13



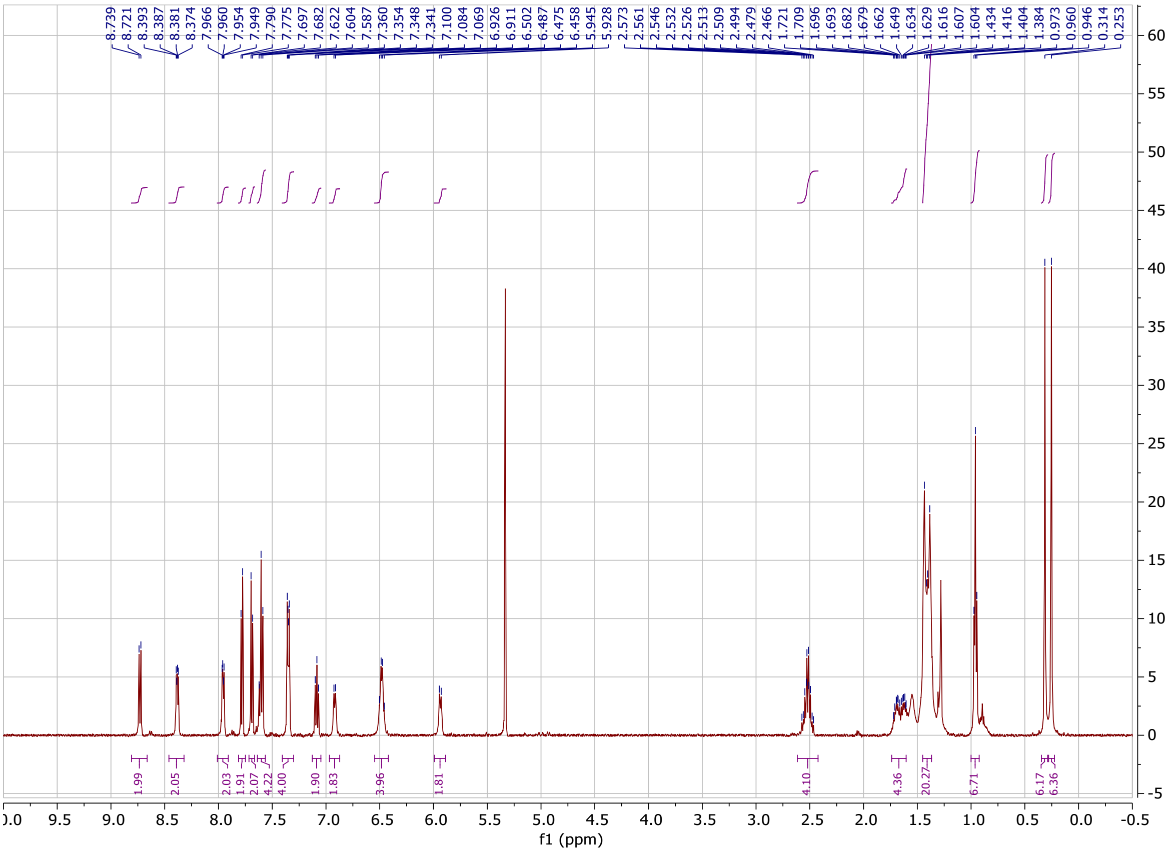


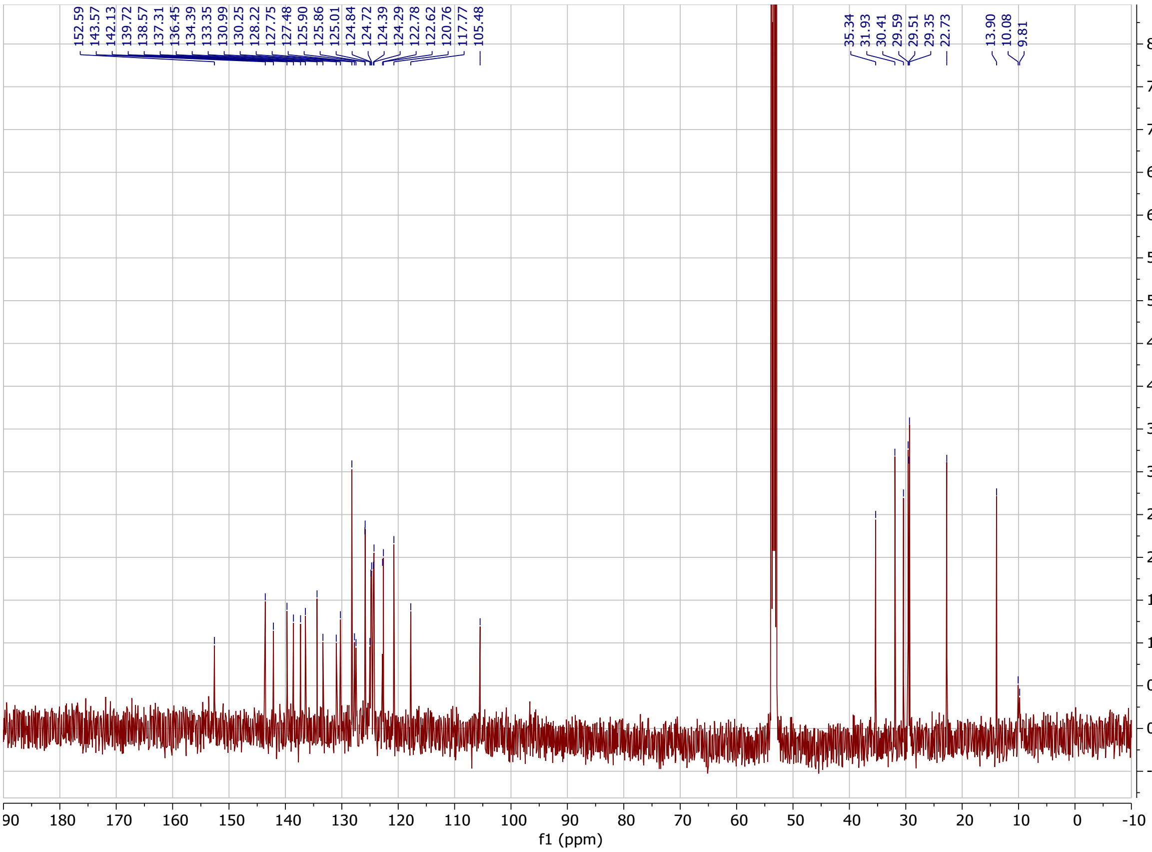
First enantiomer of 13



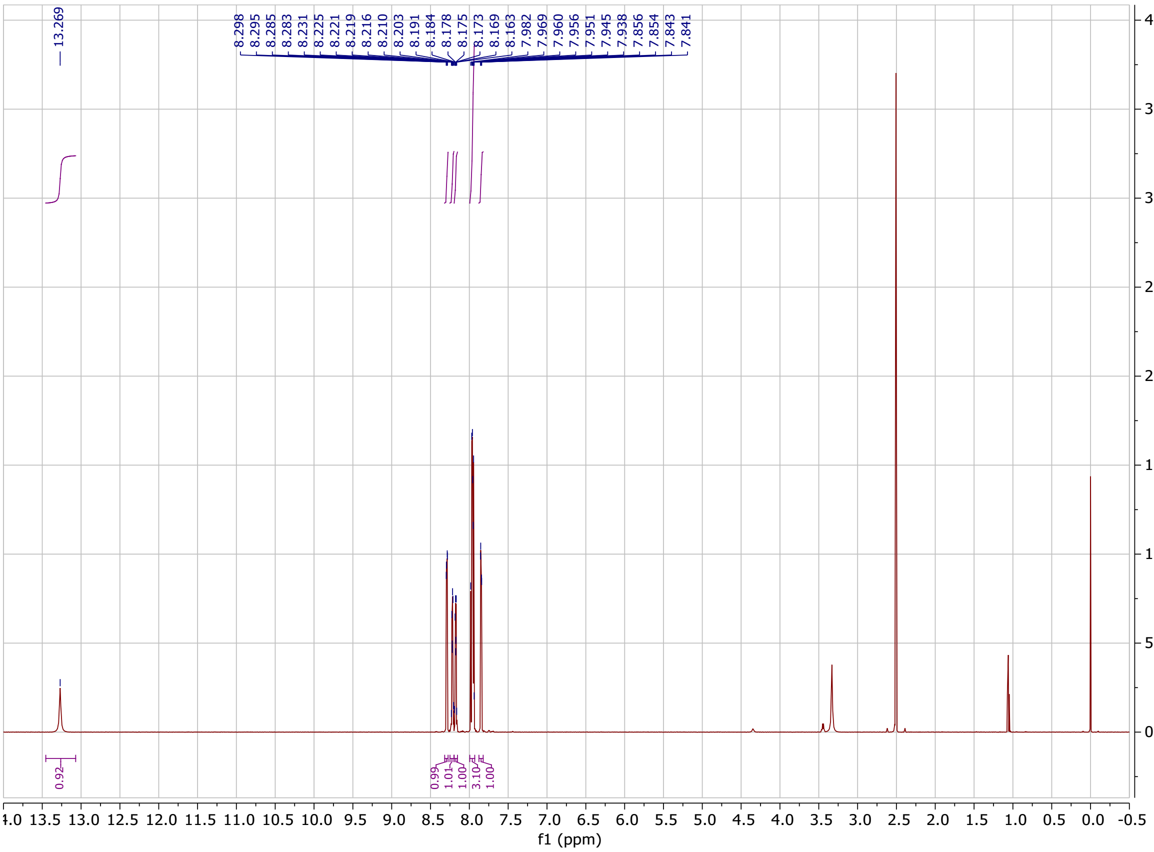


Second enantiomer of 13

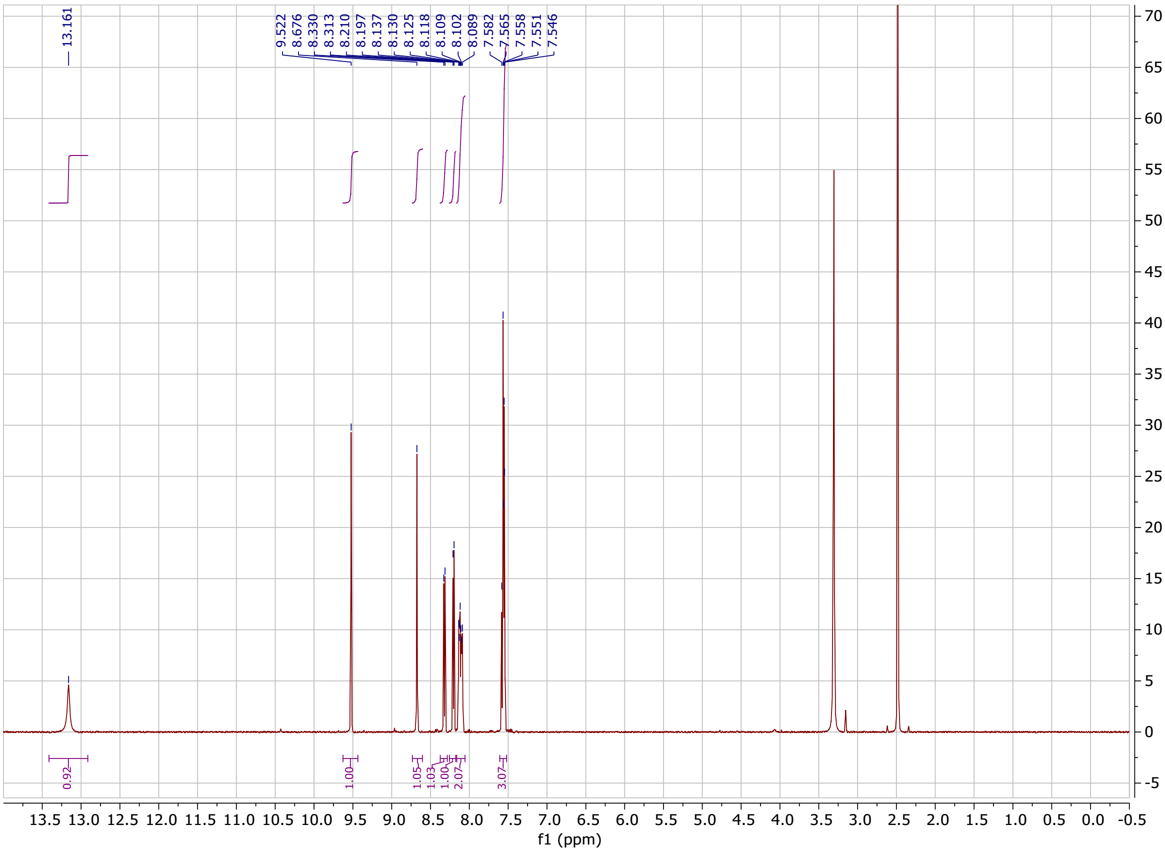




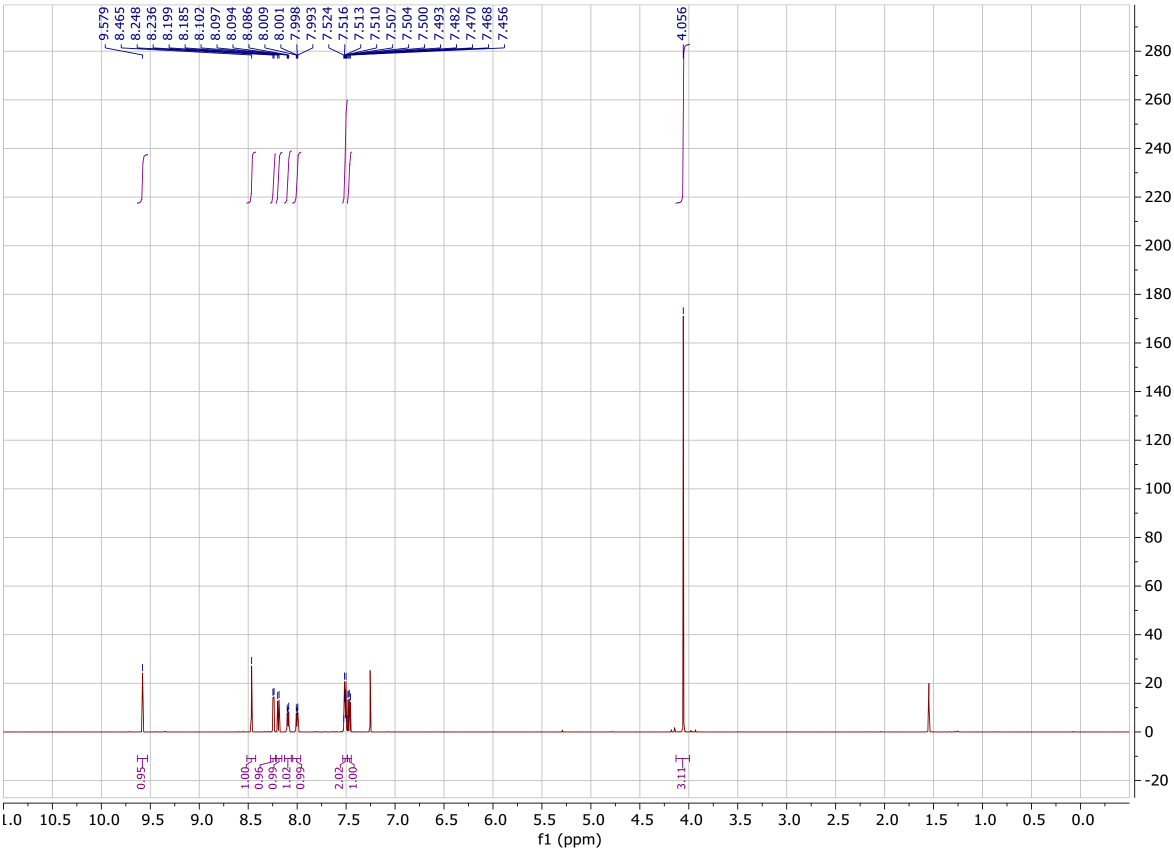
Anthraquinone-1-carboxylic acid S2



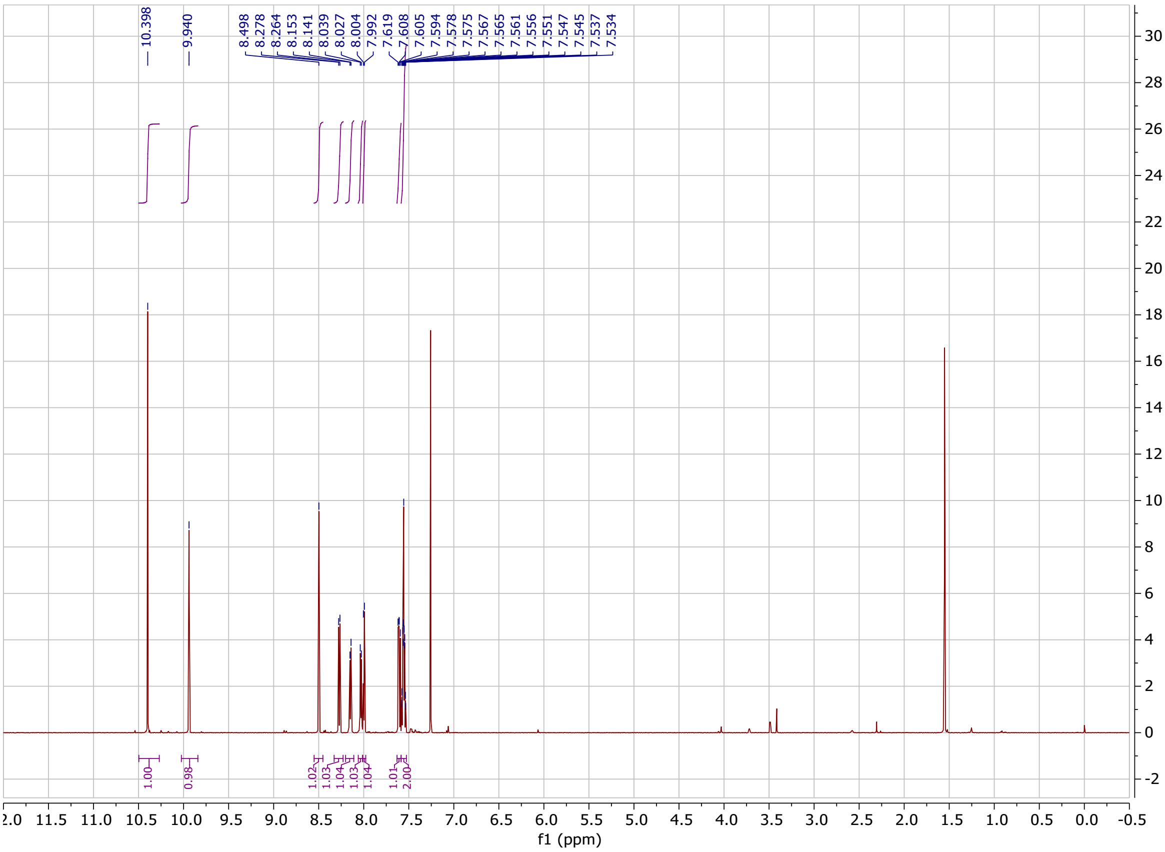
Anthracene-1-carboxylic acid S3



Methyl anthracene-1-carboxylate S4



Anthracene-1-carbaldehyde S5



9. References

1. Tasior, M., Vakuliuk, O., Koga, D., Koszarna, B., Górski, K., Grzybowski, M., Kielesiński, Ł., Krzeszewski, M., Gryko, D. T. Method for the Large-Scale Synthesis of Multifunctional 1,4-Dihydro-pyrrolo[3,2-*b*]pyrroles. *J. Org. Chem.* **85**, *21*, 13529–13543 (2020).
2. Tasior, M., Chotkowski, M., Gryko, D. T. Extension of Pyrrolopyrrole π-System: Approach to Constructing Hexacyclic Nitrogen-Containing Aromatic Systems. *Org. Lett.* **17**, *24*, 6106–6109 (2015).
3. Karatsu, T., Kitamura, A., Zeng, H., Arai, T., Sakuragi, H., Tokumaru, K. Photoisomerization and Photocyclization Reactions of 1-Styrylanthracene. *Bull. Chem. Soc. Jpn.* **68**, *3*, 920–928 (1995).
4. Kaps, A., Plenio, H. Facile Synthesis of Triptycene-Azolium Salts and NHC-Metal Complexes. *Eur. J. Inorg. Chem.* **26**, *18*, e202300178 (2023).
5. Zagotto, G., Palumbo, M., Uriarte, E., Bonsignore, L., Delogu, G., Podda, G. Synthesis of 2H,9H-naphtho[2,3-b:7,6-b′]dipyran-2,9-diones as potential DNA-reactive agents. *Il Farm.* **53**, *10–11*, 675–679 (1998).
6. Würth, C., Grabolle, M., Pauli, J., Spieles, M., Resch-Genger, U. Relative and absolute determination of fluorescence quantum yields of transparent samples. *Nat. Protoc.* **8**, *8*, 1535–1550 (2013).
7. *Standardization and Quality Assurance in Fluorescence Measurements I: Techniques*. vol. 5 (Springer Berlin Heidelberg, 2008).
8. Nain, A. K., Chandra, P., Pandey, J. D., Gopal, S. Densities, Refractive Indices, and Excess Properties of Binary Mixtures of 1,4-Dioxane with Benzene, Toluene, *o*-Xylene, *m*-Xylene, *p*-Xylene, and Mesitylene at Temperatures from (288.15 to 318.15) K. *J. Chem. Eng. Data* **53**, *11*, 2654–2665 (2008).
9. Nath, J., Mishra, S. K. Relative permittivities and refractive indices of binary mixtures of cyclohexanone with dichloromethane, trichloromethane, 1,2-dichloroethane, trichloroethene and cyclohexane at T = 303.15 K. *Fluid Phase Equilibria* **145**, *1*, 89–97 (1998).
10. Krivacic, J. R., Urry, D. W. Ultraviolet and visible refractive indices of spectro-quality solvents. *Anal. Chem.* **42**, *6*, 596–599 (1970).
11. Bruker AXS Inc., Madison, Wisconsin, USA. APEX3. (2017).
12. Bruker AXS Inc., Madison, Wisconsin, USA. SAINT. (2019).
13. Bruker AXS Inc., Madison, Wisconsin, USA. SADABS. (2016).
14. Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. Found. Adv.* **71**, *1*, 3–8 (2015).
15. Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Crystallogr. Sect. C Struct. Chem.* **71**, *1*, 3–8 (2015).
16. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschmann, H. *OLEX2*: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42**, *2*, 339–341 (2009).
17. Longhi, G., Castiglioni, E., Koshoubu, J., Mazzeo, G., Abbate, S. Circularly Polarized Luminescence: A Review of Experimental and Theoretical Aspects. *Chirality* **28**, *10*, 696–707 (2016).
18. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Petersson, G. A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A. V., Bloino, J., Janesko, B. G., Gomperts, R., Mennucci, B., Hratchian, H. P., Ortiz, J. V., Izmaylov, A. F., Sonnenberg, J. L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V. G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Montgomery, J. A., Jr., Peralta, J. E., Ogliaro, F., Bearpark, M. J., Heyd, J. J., Brothers, E. N., Kudin, K. N., Staroverov, V. N., Keith, T. A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A. P., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Millam, J. M., Klene, M., Adamo, C., Cammi, R., Ochterski, J. W., Martin, R. L., Morokuma, K., Farkas, O., Foresman, J. B., Fox, D. J. Gaussian 16, Revision A.03; Gaussian Inc.: Wallingford, CT. (2016).

19. Zhao, Y., Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **120**, *1–3*, 215–241 (2008).
20. Tomasi, J., Mennucci, B., Cammi, R. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* **105**, *8*, 2999–3094 (2005).
21. Guido, C. A., Chrayteh, A., Scalmani, G., Mennucci, B., Jacquemin, D. Simple Protocol for Capturing Both Linear-Response and State-Specific Effects in Excited-State Calculations with Continuum Solvation Models. *J. Chem. Theory Comput.* **17**, *8*, 5155–5164 (2021).
22. Laurent, A. D., Jacquemin, D. TD-DFT benchmarks: A review. *Int. J. Quantum Chem.* **113**, *17*, 2019–2039 (2013).
23. Christiansen, O., Koch, H., Jørgensen, P. The second-order approximate coupled cluster singles and doubles model CC2. *Chem. Phys. Lett.* **243**, *5–6*, 409–418 (1995).
24. TURBOMOLE V7.3/V7.5/V7.8, *a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH*, 1989−2007; TURBOMOLE GmbH. http://www.turbomole.com.
25. Jacquemin, D., Duchemin, I., Blase, X. 0–0 Energies Using Hybrid Schemes: Benchmarks of TD-DFT, CIS(D), ADC(2), CC2, and BSE/ *GW* formalisms for 80 Real-Life Compounds. *J. Chem. Theory Comput.* **11**, *11*, 5340–5359 (2015).
26. Santoro, F., Cerezo, J. (v3-0.1-177-g4b1514a) http://www.pi.iccom.cnr.it/fcclasse. (2021).
27. Cerezo, J., Santoro, F. *FCclasses3*: Vibrationally-resolved spectra simulated at the edge of the harmonic approximation. *J. Comput. Chem.* **44**, *4*, 626–643 (2023).
28. Santoro, F., Jacquemin, D. Going beyond the vertical approximation with time-dependent density functional theory. *WIREs Comput. Mol. Sci.* **6**, *5*, 460–486 (2016).
29. Avila Ferrer, F. J., Cerezo, J., Soto, J., Improta, R., Santoro, F. First-principle computation of absorption and fluorescence spectra in solution accounting for vibronic structure, temperature effects and solvent inhomogenous broadening. *Comput. Theor. Chem.* **1040–1041**, 328–337 (2014).
30. Humeniuk, A., Bužančić, M., Hoche, J., Cerezo, J., Mitrić, R., Santoro, F., Bonačić-Koutecký, V. Predicting fluorescence quantum yields for molecules in solution: A critical assessment of the harmonic approximation and the choice of the lineshape function. *J. Chem. Phys.* **152**, *5*, 054107 (2020).
31. Kusy, D., Górski, K., Bertocchi, F., Galli, M., Vanthuyne, N., Terenziani, F., Gryko, D. T. Synthesis and Chiroptical Activity of π-Expanded Electron-Rich Heterohelicenes Based on the 1,4-Dihydropyrrolo[3,2-*b*]pyrrole Core. *Chem. – Eur. J.* e202404632 (2025) doi:10.1002/chem.202404632.