Supplementary Information (SI) for Organic Chemistry Frontiers.

Supporting Information

Modular Assembly of Conformationally Dynamic Dinaphthocycloocta-1,5-dienes

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1 Experimental procedures and characterization data

1.1 General experimental

Chemicals were purchased from Sigma-Aldrich, Acros Organics, Alfa Aesar, chemPUR, abcr GmbH, TCI Europe or BLDpharm. Deuterated solvents were purchased from Deutero GmbH or Sigma-Aldrich. Technical grade solvents used during work-up and purification were distilled prior to use. The Bidentate Lewis acid **BDLA** was synthesized according to the literature,[1] stored and handled in a nitrogen-filled MBRAUN UNIlab glove box. Phthalazines **1b**-**1i** (Figure **S1**) were synthesized according to literature.[2–4]

Sensitive reactions were performed in dry glassware under nitrogen atmosphere using Schlenk techniques or in a nitrogen-filled MBRAUN UNIlab glove box. Oil baths or sand baths were used for all reactions requiring heating.

NMR spectra were measured on a Bruker Avance II 400 MHz, Avance III 400 MHz HD or Bruker Avance III HD 600 MHz spectrometer at 25 °C if not stated otherwise. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent signals. Coupling constants (*J*) are reported in Hertz (Hz). Multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet).

Flash chromatography was carried out with Silica 60 (0.04 – 0.063 mm) from Marcherey-Nagel GmbH & Co. KG. Automated flash chromatography was performed on an Advion Interchim puriFlash XS 520 Plus system using PF-30SIHP or PF-15SIHP columns. Thin layer chromatography was performed on Polygram®SIL G/UV254 from Macherey Nagel GmbH & Co. KG. Spots were visualized under UV-light and with basic $KMnO_4$ stain.

High-resolution mass spectra were recorded on a Bruker Impact II spectrometer featuring a quadrupole time-of-flight (Q-TOF) mass analyzer. Samples were dissolved in methanol.

Melting points were measured on a M5000 melting point meter from A. KRÜSS Optronic GmbH, Germany.

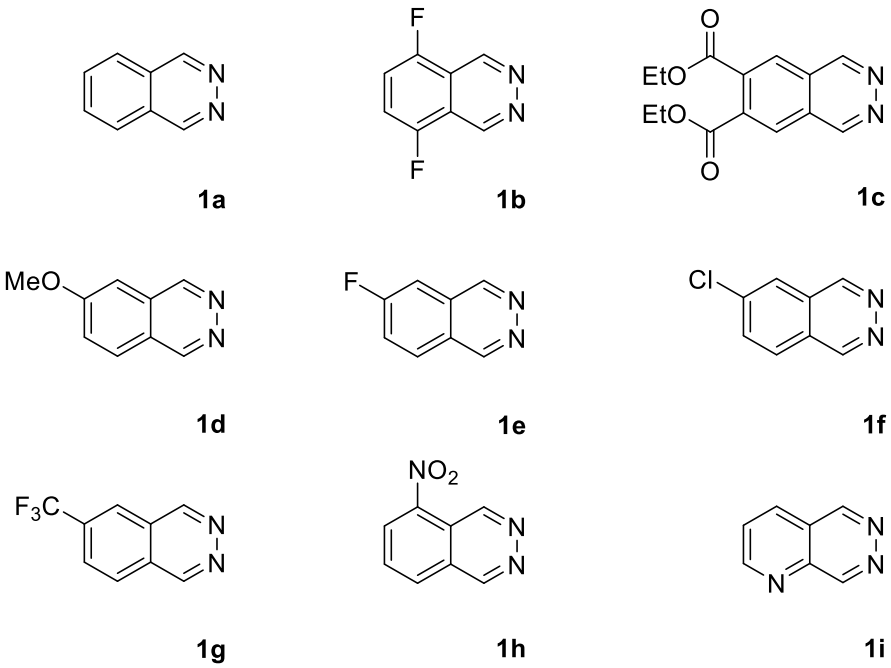
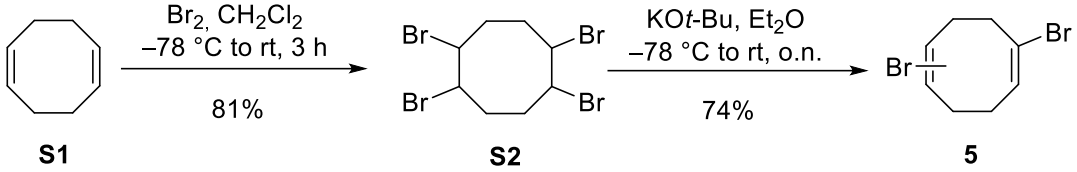


Figure S1. Overview of phthalazines and pyridazino-aromatics.

1.2 Synthesis of (1*E*,5*E*)-dibromocycloocta-1,5-diene (5)

The synthesis of (1*E*,5*E*)-dibromocycloocta-1,5-diene (**5**) was adapted from literature with slight modifications:[5]



Scheme S1. Synthesis scheme of (1*E*,5*E*)-dibromocycloocta-1,5-diene (**5**).

Synthesis of 1,2,5,6-tetrabromocyclooctane (S2**)**

A solution of bromine (6.45 mL, 125 mmol, 2.25 eq.) in anhydrous CH_2Cl_2 (100 mL) was slowly added to a solution of 1,5-cyclooctadiene (**S1**) (6.9 mL, 56 mmol, 1.0 eq.) in anhydrous CH_2Cl_2 (200 mL) at −78 °C under nitrogen atmosphere over 1.5 h. The resulting yellow suspension was allowed to warm to rt and stirred for another 3 h. Afterwards, a saturated aqueous solution of $Na_2S_2O_3$ (250 mL) was added. After stirring for 10 min, the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 200 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Cold hexane (50 mL) was added to the residual oil and the mixture was placed in the fridge overnight. Afterwards, the solvent was decanted and the remaining solid was washed with cold hexane (25 mL). The crude tetrabromide **S2** was obtained as a white solid (19.5 g, 45.6 mmol, 81%) which was used in the next step without further purification.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.12 – 4.17 (m, 4H), 3.02 – 1.90 (m, 8H) ppm.

Analytical data corresponds to literature.[5]

Synthesis of (1*E*,5*E*)-dibromocycloocta-1,5-diene (5)

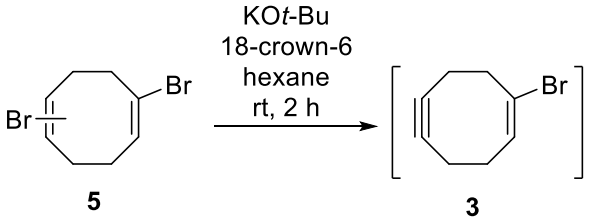
Diethyl ether (300 mL) was added to a stirred mixture of powdered tetrabromocyclooctane **S2** (10.0 g, 23.4 mmol, 1.00 eq.) and KO*t*-Bu (8.04 g, 70.2 mmol, 3.00 eq.) at −78 °C under nitrogen atmosphere over 30 min. The suspension was allowed to warm to rt and stirred overnight. Afterwards, a saturated aqueous NH_4Cl solution (120 mL) and water (100 mL) were added to the mixture and it was stirred for 10 min. The aqueous layer was separated and extracted with ethyl acetate (1 x 200 mL, 2 x 100 mL). The combined organic layers were washed with brine, dried ($MgSO_4$) and filtered. Silica gel (20 g) was added to the filtrate and it was concentrated *in vacuo*. Purification via column chromatography (180 g silica gel, cyclohexane) yielded the vinylbromide **5** as a pale yellow oil (mixture of isomers) (4.50 g, 16.9 mmol, 72%) which solidified upon storage at −20 °C.

Mixture of isomers:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.17 – 5.94 (m, 2H), 3.00 – 2.76 (m, 4H), 2.51 – 2.25 (m, 4H).

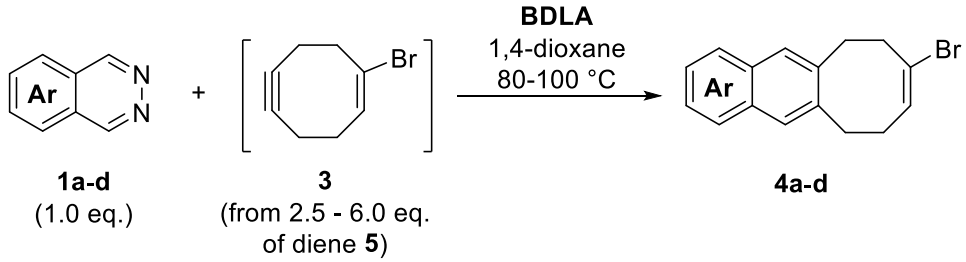
Analytical data corresponds to literature.[5]

1.3 **General procedure for the synthesis of cycloocta-naphthalenes** 4a-d **(GP1)**



Scheme S2. Synthesis of alkyne **3** from dibromocycloocta-1,5-diene **5**.

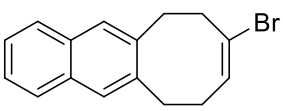
A solution of vinyl bromide **5** (665 mg, 2.50 mmol, 1.00 eq.) in anhydrous hexane (35 mL) was added dropwise to a suspension of KO*t*-Bu (1.13 g, 9.83 mmol, 3.93 eq.) and 18-crown-6 (0.16 mg, 0.62 mmol, 0.25 eq.) in anhydrous hexane (115 mL) at rt under nitrogen atmosphere. The resulting dark brown mixture was stirred for further 2 h at rt. Afterwards, a saturated aqueous solution of NH_4Cl (25 mL) and water (25 mL) was added. The aqueous phase was separated and extracted with pentane (3 x 25 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered and concentrated *in vacuo* (bath temp. < 40 °C) to obtain approx. 1 mL of a brown oil containing the crude alkyne **3**. The oil was transferred to a Schlenk tube, diluted with anhydrous 1,4-dioxane (15 mL) and degassed by three freeze-pump-thaw cycles. This solution was used in the following step without further purification.



Scheme S3. Synthesis cyclooctanaphthalenes **4a**-**d** via IEDDA reaction.

In a nitrogen filled glove box, phthalazine **1a**-**d** (1.00 mmol, 1.00 eq.) and **BDLA** catalyst (5.1 mg, 25 µmol, 2.5 mol%) were suspended in anhydrous 1,4-dioxane (15 mL). A stir bar was added, the flask was sealed and taken out of the glove box. A degassed solution of the crude alkyne **3** (obtained from 2.5 – 6.0 eq. of diene **5**) in anhydrous 1,4-dioxane (15 mL) was added to the phthalazine-**BDLA** suspension and stirred at the indicated temperature for the indicated time. Afterwards, the solvent was removed *in vacuo* and the residue was purified via column chromatography (conditions noted below). Additional purification steps are noted below.

Synthesis of (*E*)-8-bromo-6,7,10,11-tetrahydrocycloocta[*b*]-naphthalene (4a**)**



According to **GP1**, vinyl bromide **5** (1.06 g, 4.00 mmol, 4.00 eq.) in anhydrous hexane (50 mL) was treated with KO*t*-Bu (1.80 g, 15.7 mmol, 15.7 eq.) and 18-crown-6 (262 mg, 0.990 mmol, 0.990 eq.) in anhydrous hexane (120 mL). The crude alkyne **3** was dissolved in anhydrous 1,4-dioxane (15 mL), degassed and added to a suspension of phthalazine (**1a**) (131 mg, 1.00 mmol, 1.00 eq.) and **BDLA** catalyst (5.1 mg, 25 µmol, 2.5 mol%) in anhydrous 1,4-dioxane (10 mL). The mixture was stirred at 100 °C for 48 h. The crude product was purified via column chromatography [40 g silica gel, cyclohexane/toluene (95:5), dry loading (CH_2Cl_2)] to obtain a brown oil. Pentane (0.5 mL) was added and the mixture was placed in the fridge overnight. Afterwards, the solvent was removed with a cannula and the remaining solid was washed with cold pentane (0.5 mL) to obtain the substituted naphthalene **4a** as a pale yellow solid (206 mg, 717 µmol, 72%).

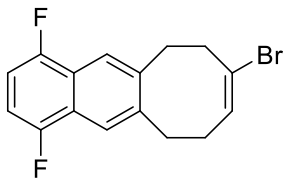
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.70 (m, 2H), 7.60 (s, 1H), 7.53 (s, 1H), 7.45 – 7.37 (m, 2H), 5.81 (t, *J* = 7.1 Hz, 1H), 3.24 (t, *J* = 7.1 Hz, 2H), 3.15 (t, *J* = 7.1 Hz, 2H), 3.09 (t, *J* = 7.1 Hz, 2H), 2.52 (q, *J* = 7.1 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 138.6, 137.6, 132.8, 132.6, 130.5, 128.7, 128.1, 127.3, 127.1, 125.5, 125.4, 124.2, 39.4, 33.6, 33.4, 30.3 ppm.

HRMS (ESI): *m/z* calculated for $C_{16}H_{15}Br+Na^+$: 309.0249 $[M+Na]^+$, found: 309.0250.

Melting point: 63 – 64 °C.

Synthesis of (*E*)-8-bromo-1,4-difluoro-6,7,10,11-tetrahydro-cycloocta[*b*]naphthalene (4b**)**



According to **GP1**, vinyl bromide **5** (665 mg, 2.50 mmol, 2.50 eq.) in anhydrous hexane (35 mL) was treated with KO*t*-Bu (1.13 g, 9.83 mmol, 9.83 eq.) and 18-crown-6 (164 mg, 0.620 mmol, 0.620 eq.) in anhydrous hexane (115 mL). The crude alkyne **3** was dissolved in anhydrous 1,4-dioxane (15 mL), degassed and added to a suspension of phthalazine **1b** (166 mg, 1.00 mmol, 1.00 eq.) and **BDLA** catalyst (5.1 mg, 25 µmol, 2.5 mol%) in anhydrous 1,4-dioxane (15 mL). The mixture was stirred at 80 °C for 24 h. The crude product was purified via column chromatography [30 g silica gel, cyclohexane/toluene (95:5), dry loading (CH_2Cl_2)] to obtain a yellow solid that was washed with a small amount of pentane (1 mL) to give the desired substituted naphthalene **4b** as a pale yellow solid (233 mg, 721 µmol, 72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 1H), 7.75 (s, 1H), 7.00 – 6.92 (m, 2H), 5.81 (t, *J* = 7.1 Hz, 1H), 3.27 (t, *J* = 7.1 Hz, 2H), 3.18 (t, *J* = 7.1 Hz, 2H), 3.11 (t, *J* = 7.1 Hz, 2H), 2.54 (q, *J* = 7.1 Hz, 2H) ppm.

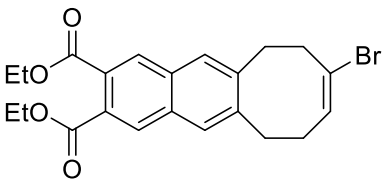
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 155.8 – 155.6 and 153.4 – 153.2 (m, 2C), 140.3, 139.3, 130.3, 124.0, 123.8 (dd, *J* = 15.2, 6.0 Hz), 123.6 (dd, *J* = 14.1, 6.0 Hz), 121.6 – 121.4 (m), 121.1 – 120.9 (m), 108.2 (dd, *J* = 22.2, 8.0 Hz), 108.1 (dd, *J* = 23.2, 9.0 Hz), 39.2, 33.7, 33.5, 30.0 ppm.

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ = -128.52 (dd, *J* = 148.5, 21.8 Hz) ppm.

HRMS (ESI): *m/z* calculated for $C_{16}H_{13}BrF_2$+Na^+: 345.0061 $[M+Na]^+$, found: 345.0057.

Melting point: 99 – 100 °C.

Synthesis of diethyl (*E*)-8-bromo-6,7,10,11-tetrahydrocyclo-octa[*b*]naphthalene-2,3-dicarboxylate (4c**)**



According to **GP1**, vinyl bromide **5** (1.02 g, 3.82 mmol, 2.55 eq.) in anhydrous hexane (40 mL) was treated with KO*t*-Bu (1.69 g, 14.7 mmol, 9.83 eq.) and 18-crown-6 (246 mg, 0.930 mmol, 0.620 eq.) in anhydrous hexane (90 mL). The crude alkyne **3** was dissolved in anhydrous 1,4-dioxane (6 mL), degassed and added to a suspension of phthalazine **1c** (411 mg, 1.50 mmol, 1.00 eq.) and **BDLA** catalyst (7.7 mg, 38 µmol, 2.5 mol%) in anhydrous 1,4-dioxane (9 mL). The mixture was stirred at 80 °C for 24 h. The crude product was purified via column chromatography [40 g silica gel, cyclohexane/EtOAc (98:2 to 62:38), dry loading (CH_2Cl_2)] to obtain a yellow solid. Pentane (0.5 mL) was added and the mixture was placed in the fridge overnight. Afterwards, the solvent was removed with a cannula and the remaining solid was washed with cold pentane (2 x 0.5 mL) to obtain the substituted naphthalene **4c** as a pale yellow solid (507 mg, 1.18 mmol, 78%).

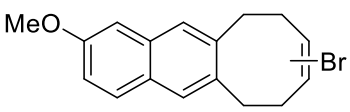
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (s, 1H), 8.13 (s, 1H), 7.67 (s, 1H), 7.59 (s, 1H), 5.78 (t, *J* = 7.0 Hz, 1H), 4.40 (two overlapping q, *J* = 7.1 Hz, 4H), 3.24 (t, *J* = 7.1 Hz, 2H), 3.16 (t, *J* = 7.2 Hz, 2H), 3.09 (t, *J* = 7.1 Hz, 2H), 2.52 (q, *J* = 7.0 Hz, 2H), 1.40 and 1.39 (two overlapping t, *J* = 7.1 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 168.1, 168.0, 141.7, 140.7, 132.7, 132.5, 130.3, 129.5, 129.4, 129.3, 128.9, 128.5, 128.4, 123.9, 61.7 (2C), 39.0, 33.6, 33.3, 29.9, 14.3 (2C) ppm.

HRMS (ESI): *m/z* calculated for $C_{22}H_{23}BrO_4$+Na^+: 453.0672 [M+Na]$^+$, found: 453.0672.

Melting point: 74 – 76 °C.

Synthesis of (*E*)-8-bromo-2-methoxy-6,7,10,11-tetrahydro-cycloocta[*b*]naphthalene and (*E*)-9-bromo-2-methoxy-6,7,10,11-tetrahydrocycloocta[*b*]naphthalene (4d**)**



According to **GP1**, vinyl bromide **5** (1.60 g, 6.00 mmol, 6.00 eq.) in anhydrous hexane (70 mL) was treated with KO*t*-Bu (2.70 g, 23.6 mmol, 23.6 eq.) and 18-crown-6 (393 mg, 1.49 mmol, 1.49 eq.) in anhydrous hexane (150 mL). The crude alkyne **3** was dissolved in anhydrous 1,4-dioxane (15 mL), degassed and added to a suspension of phthalazine **1d** (160 mg, 1.00 mmol, 1.00 eq.) and **BDLA** catalyst (5.1 mg, 25 µmol, 2.5 mol%) in anhydrous 1,4-dioxane (10 mL). The mixture was stirred at 100 °C for 72 h. The crude product was purified via column chromatography [35 g silica gel, cyclohexane/toluene (8:2), dry loading (CH_2Cl_2)] to obtain an orange oil. Pentane (0.5 mL) was added and the mixture was placed in the fridge overnight. Afterwards, the solvent was removed with a cannula and the remaining solid was washed with cold pentane (0.5 mL) to obtain the substituted naphthalene **4d** (mixture of 8-bromo and 9-bromo isomer) as a pale yellow solid (215 mg, 676 µmol, 68%).

Mixture of regioisomers:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 – 7.60 (m, 2H), 7.54 – 7.48 (m, 2H), 7.47 – 7.41 (m, 2H), 7.11 – 7.02 (m, 4H), 5.81 (t, *J* = 7.0 Hz, 2H), 3.93 – 3.87 (m, 6H), 3.25 – 3.15 (m, 4H), 3.16 – 3.03 (m, 8H), 2.56 – 2.45 (m, 4H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 157.5, 157.4, 139.1, 138.1, 136.1, 135.1, 133.8, 133.6, 130.6, 130.4, 128.8, 128.6, 128.5, 128.3, 128.1, 128.0, 127.7, 127.1, 124.3, 124.1, 118.3, 118.2, 105.3, 105.1, 55.4 (2C), 39.5, 39.4, 33.7, 33.4 (2C), 33.2, 30.3, 30.3 ppm.

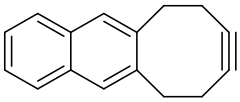
HRMS (ESI): *m/z* calculated for $C_{17}H_{17}BrO+Na^+$: 339.0355 $[M+Na]^+$, found: 339.0355.

Melting point: 80 – 81 °C.

1.4 General procedure for the synthesis of alkynes 6 (GP2)

A solution of vinyl bromide **4** (1.00 eq.) in a mixture of anhydrous hexane (10 mL) and anhydrous benzene (10 mL) was added dropwise to a suspension of KO*t*-Bu (2.5 eq.) and 18-crown-6 (0.25 eq.) in anhydrous hexane (45 mL) at 0 °C under nitrogen atmosphere. Afterwards, the mixture was stirred for 2 h at 0 °C and 1 h at rt. The resulting suspension was filtered and the filter cake was rinsed with EtOAc. The combined filtrates were washed with water and brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified via filtration over silica gel (3 – 4 g) with CH_2Cl_2 to afford the desired alkyne **6**. If additional purification was required, it is noted below.

Synthesis of 8,9-didehydro-6,7,10,11-tetrahydrocycloocta[*b*]-naphthalene (6a**)**



According to **GP2**, treatment of vinyl bromide **4a** (180 mg, 0.630 mmol, 1.00 eq.) with KO*t*-Bu (179 mg, 1.57 mmol, 2.50 eq.) and 18-crown-6 (41 mg, 0.16 mmol, 0.25 eq.) afforded the alkyne **6a** as a white solid (116 mg, 0.56 mmol, 89%).

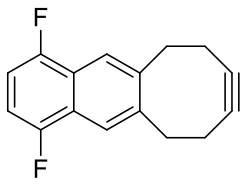
^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.82 – 7.73 (m, 2H), 7.66 (s, 2H), 7.49 – 7.37 (m, 2H), 3.45 (td, *J* = 12.3, 3.6 Hz, 2H), 3.07 (dt, *J* = 12.5, 2.9 Hz, 2H), 2.60 – 2.49 (m, 2H), 2.40 – 2.26 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 140.5 (2C), 132.8 (2C), 129.7 (2C), 127.3 (2C), 125.9 (2C), 99.2 (2C), 38.0 (2C), 24.1 (2C) ppm.

HRMS (APCI): *m/z* calculated for $C_{16}H_{14}+H^+$: 207.1168 $[M+H]^+$, found: 207.1175.

Melting point: slow degradation starting at 100 °C to give a yellow solid and finally a yellow oil above 110 °C.

Synthesis of 1,4-difluoro-8,9-didehydro-6,7,10,11-tetrahydro-cycloocta[*b*]naphthalene (6b**)**



According to **GP2**, treatment of vinyl bromide **4b** (220 mg, 0.680 mmol, 1.00 eq.) with KO*t*-Bu (195 mg, 1.70 mmol, 2.50 eq.) and 18-crown-6 (45 mg, 0.17 mmol, 0.25 eq.) afforded the crude alkyne **6b** as a pale yellow solid (145 mg) that was further purified via column chromatography [10 g silica gel, cyclohexane/toluene (9:1), crude dissolved in eluent with a few drops of CH_2Cl_2] to yield a white solid (103 mg, 0.42 mmol, 62%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.89 (s, 2H), 7.01 (dd, *J* = 7.5, 6.5 Hz, 2H), 3.50 (td, *J* = 12.3, 3.7 Hz, 2H), 3.11 (dt, *J* = 12.4, 2.9 Hz, 2H), 2.63 – 2.51 (m, 2H), 2.41 – 2.28 (m, 2H) ppm.

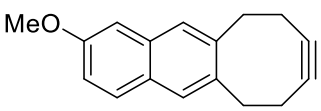
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 154.8 (dd, *J* = 248.9, 5.2 Hz, 2C), 142.5 (2C), 123.7 (dd, *J* = 13.2, 10.5 Hz, 2C), 122.4 (t, *J* = 3.0 Hz, 2C), 108.6 (dd, *J* = 18.2, 13.4 Hz, 2C), 99.1 (2C), 38.2 (2C), 24.0 (2C).

^{19}F{^{1}H} NMR (377 MHz, CD_2Cl_2): -129.26 ppm.

HRMS (APCI): *m/z* calculated for $C_{16}H_{12}F_2+H^+$: 243.0980 $[M+H]^+$, found: 243.0982.

Melting point: slow degradation starting at 100 °C to give a yellow solid and finally a yellow oil above 130 °C.

Synthesis of 2-methoxy-8,9-didehydro-6,7,10,11-tetrahydro-cycloocta[*b*]naphthalene (6d**)**



According to **GP2**, treatment of vinyl bromide **4d** (197 mg, 0.620 mmol, 1.00 eq.) with KO*t*-Bu (177 mg, 1.55 mmol, 2.50 eq.) and 18-crown-6 (41 mg, 0.16 mmol, 0.25 eq.) afforded the alkyne **6d** as a white solid (131 mg, 0.55 mmol, 89%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.70 – 7.63 (m, 1H), 7.57 (s, 1H), 7.56 (s, 1H), 7.12 – 7.03 (m, 2H), 3.90 (s, 3H), 3.49 – 3.36 (m, 2H), 3.08 – 2.98 (m, 2H), 2.59 – 2.46 (m, 2H), 2.39 – 2.23 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 158.0, 141.0, 138.0, 133.9, 129.5, 128.9, 128.7, 128.3, 118.7, 105.3, 99.4, 99.2, 55.6, 38.0, 37.8, 24.1, 24.1 ppm.

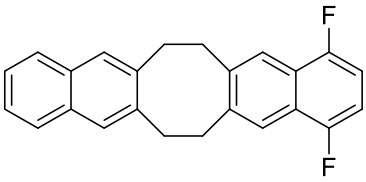
HRMS (ESI): *m/z* calculated for $C_{17}H_{16}O+Na^+$: 259.1093 $[M+Na]^+$, found: 259.1095.

Melting point: slow degradation starting at 140 °C to give a yellow solid and finally a yellow oil above 160 °C.

1.5 General procedure for the synthesis of arene-fused CODs (2) (GP3)

In a nitrogen filled glove box, (substituted) phthalazine **1** (1.0 eq.), alkyne **6** (1.0 eq.) and **BDLA** catalyst (5 mol%) were suspended in anhydrous 1,4-dioxane (2.0 mL) in a 4 mL-screw cap vial with a stir bar. The vial was sealed and taken out of the glove box. The mixture was stirred at the given temperature for the given time. Afterwards, the reaction mixture was concentrated *in vacuo*. Purification conditions are noted below.

Synthesis of 1,4-difluoro-6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b'*]dinaphthalene (2ab**)**



According to **GP3**, phthalazine **1b** (20 mg, 0.12 mmol, 1.0 eq.), alkyne **6a** (26.0 mg, 0.126 mmol, 1.05 eq.) and **BDLA** catalyst (1.2 mg, 6.0 µmol, 5.0 mol%) in 1,4-dioxane (2.0 mL) were stirred at 80 °C for 24 h. The mixture was concentrated *in vacuo* and the remaining solid was recrystallized from toluene. Dinaphthalene **2ab** was obtained as a white solid (26 mg, 76 µmol, 63%).

^{1}H NMR (400 MHz, CD_2Cl_2/CS_2): 7.67 (s, 2H), 7.65 – 7.58 (m, 2H), 7.45 (s, 2H), 7.33 – 7.26 (m, 2H), 6.86 (t, *J* = 6.9 Hz, 2H), 3.41 (s, 8H) ppm.

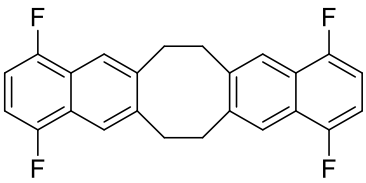
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2/CS_2): δ = 154.7 (dd, *J* = 249.1, 5.1 Hz, 2C), 141.3 (2C), 138.7 (2C), 132.9 (2C), 128.5 (2C), 127.4 (2C), 125.7 (2C), 123.7 (dd, *J* = 13.1, 10.4 Hz, 2C), 121.1 (t, *J* = 3.0 Hz, 2C), 108.3 (dd, *J* = 18.2, 13.2 Hz, 2C), 35.9 (2C), 35.5 (2C).

^{19}F{^{1}H} NMR (377 MHz, CD_2Cl_2/CS_2): δ = -127.61 ppm.

HRMS (ESI): *m/z* calculated for $C_{24}H_{18}F_2$+Na^+: 367.1269 [M+Na]$^+$, found: 367.1261.

Melting point: 233 – 234 °C.

Synthesis of 1,4,9,12-tetrafluoro-6,7,14,15-tetrahydrocyclo-octa[1,2-*b*:5,6-*b'*]dinaphthalene (2bb**)**



According to **GP3**, phthalazine **1b** (17 mg, 0.10 mmol, 1.1 eq.), alkyne **6b** (23 mg, 0.093 mmol, 1.0 eq.) and **BDLA** catalyst (1.0 mg, 4.7 µmol, 5.0 mol%) in 1,4-dioxane (2.0 mL) were stirred at 80 °C for 2 d. The mixture was concentrated *in vacuo* and filter over a silica plug with toluene. Dinaphthalene **2bb** was obtained as a white solid (26 mg, 0.068 mmol, 73%). Single crystals suitable for X-ray diffraction measurement (see 5.2) were obtained by recrystallization from toluene and slow cooling to rt over 24 h.

^{1}H NMR (200 MHz, $CDCl_3/CS_2$): δ = 7.66 (s, 4H), 6.84 (dd, *J* = 7.3, 6.4 Hz, 4H), 3.40 (s, 8H) ppm.

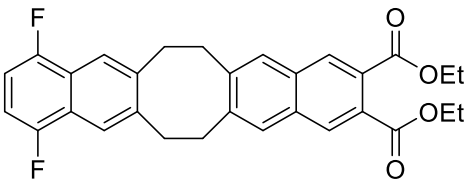
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3/CS_2$): δ = 154.2 (dd, *J* = 249.7, 5.2 Hz, 4C), 140.1 (br, 4C), 123.3 (dd, *J* = 13.2, 10.4 Hz, 4C), 120.9 (t, *J* = 2.9 Hz, 4C), 108.0 (dd, *J* = 18.1, 13.2 Hz, 4C), 35.2 (4C) ppm.

$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3/CS_2$): -127.2 ppm.

HRMS (APCI): *m/z* calculated for $C_{24}H_{16}F_4+H^+$: 381.1261 $[M+H]^+$, found: 381.1264.

Melting point: 273 – 275 °C (color change to dark brown).

Synthesis of diethyl 10-methoxy-6,7,14,15-tetrahydro-cycloocta[1,2-*b*:5,6-*b'*]dinaphthalene-2,3-dicarboxylate (2bc**)**



According to **GP3**, phthalazine **1c** (31.8 mg, 116 µmol, 1.00 eq.), alkyne **6b** (28.1 mg, 116 µmol, 1.00 eq.) and **BDLA** catalyst (1.2 mg, 5.8 µmol, 5.0 mol%) in 1,4-dioxane (2.0 mL) were stirred at 80 °C for 24 h. The mixture was concentrated *in vacuo* and purified via flash chromatography [12 g silica gel, cyclohexane/EtOAc (96:4 to 65:35, dry loading (CH_2Cl_2)]. Dinaphthalene **2bc** was obtained as a pale yellow solid (44 mg, 90 µmol, 78%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.00 (s, 2H), 7.65 (s, 2H), 7.54 (s, 2H), 6.86 (t, *J* = 7.0 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 4H), 3.40 (s, 8H), 1.33 (t, *J* = 7.1 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 168.0 (2C), 154.7 (dd, *J* = 248.2, 5.1 Hz, 2C), 132.6 (2C), 129.4 (2C), 129.0 (2C), 128.7 (2C), 123.6 (dd, *J* = 13.4, 10.5 Hz, 2C), 120.9 (t, *J* = 3.1 Hz, 2C), 108.3 (dd, *J* = 18.3, 13.3 Hz, 2C), 61.8 (2C), 35.1 (br, 4C), 14.3 (2C) ppm.

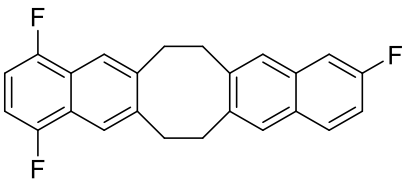
Due to peak broadening caused by conformational changes, four ^{13}C signals can't be detected (compare section 2.1).

^{19}F{^{1}H} NMR (377 MHz, CD_2Cl_2): δ = -129.16 ppm.

HRMS (ESI): *m/z* calculated for $C_{30}H_{26}F_2O_4$+Na^+: 511.1690 $[M+Na]^+$, found: 511.1690.

Melting point: 186 – 187 °C.

Synthesis of 1,4,10-trifluoro-6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b'*]dinaphthalene (2be**)**



According to **GP3**, phthalazine **1e** (16 mg, 0.11 mmol, 1.0 eq.), alkyne **6b** (27 mg, 0.11 mol, 1.0 eq.) and **BDLA** catalyst (1.1 mg, 5.5 µmol, 5.0 mol%) in 1,4-dioxane (2.0 mL) were stirred at 80 °C for 24 h. The mixture was concentrated *in vacuo*. The remaining yellow solid was dissolved in hot toluene, filtered over silica (4 g) and concentrated *in vacuo*. The remaining pale yellow solid was further purified via automated flash chromatography [12 g silica gel, cyclohexane/toluene (100:0 to 80:20, dry loading (toluene)]. Dinaphthalene **2be** was obtained as a white solid (25 mg, 69 µmol, 63%).

^{1}H NMR (400 MHz, $CDCl_3/CS_2$): δ = 7.64 (s, br, 2H), 7.58 (dd, *J* = 8.7, 5.8 Hz, 1H), 7.42 (s, 1H), 7.37 (s, 1H), 7.19 (d, *J* = 9.4 Hz, 1H), 7.05 (td, *J* = 8.7, 2.6 Hz, 1H), 6.83 (t, *J* = 6.9 Hz, 2H), 3.36 (s, 8H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3/CS_2$): δ = 160.2 (d, *J* = 245.6 Hz), 154.22 (d, *J* = 250.1 Hz), 154.16 (d, *J* = 250.1 Hz), 133.1 (d, *J* = 8.9 Hz), 129.3, 129.3 (d, *J* = 8.9 Hz), 128.0, 127.4 (d, *J* = 5.3 Hz), 123.6 – 123.1 (m, 2C), 120.9 – 120.7 (m, 2C), 115.5 (d, *J* = 25.3 Hz), 110.0 (d, *J* = 20.3 Hz), 108.3 – 107.6 (m, 2C), 36.3 – 34.3 (m, 4C) ppm.

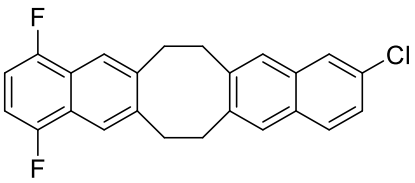
Due to peak broadening caused by conformational changes, four ^{13}C signals can't be detected (compare section 2.1).

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3/CS_2$): δ = -114.27, -127.20 (d, *J* = 21.6 Hz), -127.29 (d, *J* = 21.5 Hz) ppm.

HRMS (ESI): *m/z* calculated for $C_{24}H_{17}F_3$+Na^+: 385.1174 $[M+Na]^+$, found: 385.1175.

Melting point: 225 – 226 °C.

Synthesis of 10-chloro-1,4-difluoro-6,7,14,15-tetrahydrocyclo-octa[1,2-*b*:5,6-*b'*]dinaphthalene (2bf**)**



According to **GP3**, phthalazine **1f** (21 mg, 0.13 mmol, 1.1 eq.), alkyne **6b** (28 mg, 0.12 mmol, 1.0 eq.) and **BDLA** catalyst (1.2 mg, 5.8 µmol, 5.0 mol%) in 1,4-dioxane (2.0 mL) were stirred at 80 °C for 2 d. The mixture was concentrated *in vacuo* and remaining yellow solid was purified via flash chromatography [1 g silica gel, cyclohexane/toluene (9:1)]. Dinaphthalene **2bf** was obtained as a white, crystalline solid (33 mg, 0.086 mmol, 75%).

^{1}H NMR (400 MHz, $CDCl_3/CS_2$): 7.64 (s, 2H), 7.58 – 7.48 (m, 2H), 7.41 (s, 1H), 7.35 (s, 1H), 7.22 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.84 (t, *J* = 6.9 Hz, 2H), 3.36 (s, 8H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3/CS_2$): δ = 155.9 – 155.2 and 153.6 – 152.7 (m, 2C), 133.0, 131.1, 130.6, 128.5, 128.0, 127.2, 126.1, 125.7, 123.5 – 123.1 (m, 2C), 121.1 – 120.6 (m, 2C), 107.9 (dd, *J* = 21.2, 10.0 Hz, 2C), 35.4 and 35.1 (4C) ppm.

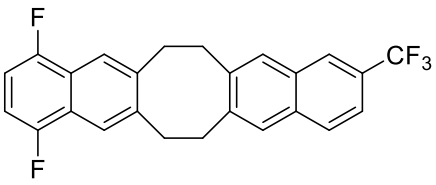
Due to peak broadening caused by conformational changes, four ^{13}C signals can't be detected (compare section 2.1).

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3/CS_2$): -127.18 (d, *J* = 21.7 Hz), -127.28 (d, *J* = 21.7 Hz) ppm.

HRMS (APCI): *m/z* calculated for $C_{24}H_{17}ClF_2+H^+$: 379.1060 $[M+H]^+$, found: 379.1062.

Melting point: 216 – 217 °C.

Synthesis of 1,4-difluoro-10-(trifluoromethyl)-6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b'*]dinaphthalene (2bg**)**



According to **GP3**, phthalazine **1g** (22 mg, 0.11 mmol, 1.0 eq.), alkyne **6b** (27 mg, 0.11 mol, 1.0 eq.) and **BDLA** catalyst (1.1 mg, 5.5 µmol, 5.0 mol%) in 1,4-dioxane (2.0 mL) were stirred at 80 °C for 24 h. The mixture was concentrated *in vacuo* and the remaining solid was recrystallized from toluene. Dinaphthalene **2bg** was obtained as a white solid (26 mg, 63 µmol, 57%).

^{1}H NMR (400 MHz, $CDCl_3/CS_2$): δ = 7.90 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.65 (s, 2H), 7.53 and 7.50 (two overlapping s, 2H), 7.45 (d, *J* = 8.5 Hz, 1H), 6.84 (t, *J* = 6.9 Hz, 2H), 3.40 (s, 8H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3/CS_2$): δ = 155.8 – 155.0 and 153.3 – 152.6 (m, 2C), 133.5, 131.1, 128.9, 128.03, 127.98, 127.1 (q, *J* = 32.1 Hz), 124.7 (q, *J* = 4.5 Hz), 124.3 (q, *J* = 272.4 Hz), 123.6 – 123.1 (m, 2C), 121.0 – 120.6 (m, 3C), 108.3 – 107.7 (m, 2C), 35.5 – 34.7 (m, 4C) ppm.

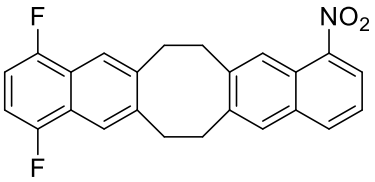
Due to peak broadening caused by conformational changes, four ^{13}C signals can't be detected (compare section 2.1).

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3/CS_2$): δ = -62.0, -127.2 (d, *J* = 21.6 Hz), -127.4c (d, *J* = 21.6 Hz) ppm.

HRMS (APCI): *m/z* calculated for $C_{25}H_{17}F_5$+Na^+: 435.1142 $[M+Na]^+$, found: 435.1134.

Melting point: 223 – 224 °C.

Synthesis of 1,4-difluoro-9-nitro-6,7,14,15-tetrahydrocyclo-octa[1,2-*b*:5,6-*b'*]dinaphthalene (2bh**)**



According to **GP3**, phthalazine **1h** (7.0 mg, 0.040 mmol, 1.0 eq.), alkyne **6b** (10 mg, 0.040 mmol, 1.0 eq.) and **BDLA** catalyst (0.5 mg, 2.5 µmol, 6.0 mol%) in 1,4-dioxane (2.0 mL) were stirred at 80 °C for 24 h. The mixture was concentrated *in vacuo* and the remaining solid was purified via automated flash chromatography [4 g silica gel, cyclohexane/toluene (100:0 to 50:50, dry loading (CH_2Cl_2)]. Dinaphthalene **2bh** was obtained as a pale yellow solid (12 mg, 31 µmol, 77%).

^{1}H NMR (200 MHz, $CDCl_3/CS_2$): δ = 8.26 (s, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.66 (s, 2H), 7.54 (s, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 6.88 – 6.80 (m, 3H), 3.57 – 3.31 (m, 8H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3/CS_2$): δ = 155.7 – 155.4 and 153.0 – 152.7 (m, 2C), 145.7, 133.7, 133.5, 128.8, 124.2, 123.6 – 123.2 (m, 5C), 121.2 – 121.0 (m), 120.8 – 120.6 (m), 108.3 – 107.8 (m, 2C), 35.7 – 34.7 (m, 4C) ppm.

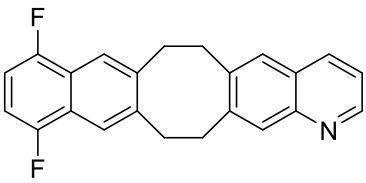
Due to peak broadening caused by conformational changes, four ^{13}C signals can't be detected (compare section 2.1).

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3/CS_2$): δ = -126.73 (d, *J* = 21.7 Hz), -127.38 (d, *J* = 21.7 Hz) ppm.

HRMS (APCI): *m/z* calculated for $C_{24}H_{17}F_2NO_2$+H^+: 390.1303 $[M+H]^+$, found: 390.1300.

Melting point: 254 – 256 °C (color change to dark brown).

Synthesis of 9,12-difluoro-6,7,14,15-tetrahydronaphtho-[2',3':5,6]cycloocta[1,2-*g*]quinoline (2bi**)**



According to **GP3**, phthalazine **1i** (16.7 mg, 128 µmol, 1.10 eq.), alkyne **6b** (28.0 mg, 116 µmol, 1.00 eq.) and **BDLA** catalyst (1.2 mg, 5.8 µmol, 6.0 mol%) in 1,4-dioxane (2.0 mL) were stirred at 80 °C for 24 h. The mixture was concentrated *in vacuo* and purified via column chromatography [5 g silica gel, toluene/EtOAc (9:1)]. Quinoline **2bi** was obtained as a white solid (33 mg, 96 µmol, 82%).

^{1}H NMR (200 MHz, CD_2Cl_2): δ = 8.68 (dd, *J* = 4.0, 2.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.63 (m, 3H), 7.43 (s, 1H), 7.21 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.86 (dd, *J* = 8.0, 6.0 Hz, 2H), 3.55 – 3.29 (m, 8H).

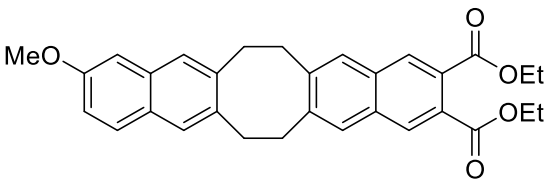
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 156.1 – 155.7 and 153.8 – 153.3 (m, 2C), 150.1, 147.9, 143.0, 141.2 (2C), 139.9, 135.2, 129.7, 128.0, 127.3, 123.9 – 123.3 (m, 2C), 121.3 – 120.6 (m, 3C), 108.2 (dd, *J* = 22.8, 8.8 Hz, 2C), 35.3 (2C), 35.1, 34.9 ppm.

^{19}F{^{1}H} NMR (377 MHz, CD_2Cl_2): δ = -128.97 (d, *J* = 22.6 Hz), -129.30 (d, *J* = 22.6 Hz) ppm.

HRMS (ESI): *m/z* calculated for $C_{23}H_{17}F_2N+Na^+$: 368.1221 $[M+Na]^+$, found: 368.1223.

Melting point: 216 – 217 °C (color change to dark brown).

Synthesis of diethyl 10-methoxy-6,7,14,15-tetrahydro-cycloocta[1,2-*b*:5,6-*b'*]dinaphthalene-2,3-dicarboxylate (2dc**)**



According to **GP3**, phthalazine **1c** (27.4 mg, 100 µmol, 1.00 eq.), alkyne **6d** (23.6 mg, 100 µmol, 1.00 eq.) and **BDLA** catalyst (1.0 mg, 5.0 µmol, 6.0 mol%) in 1,4-dioxane (2.0 mL) were stirred at 80 °C for 24 h. The mixture was concentrated *in vacuo* and purified via flash chromatography [12 g silica gel, cyclohexane/EtOAc (97:3 to 54:46, dry loading (CH_2Cl_2)]. Dinaphthalene **2dc** was obtained as a white solid (41 mg, 86 µmol, 86%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.01 (s, 2H), 7.79 – 7.45 (m, 3H), 7.35 (d, *J* = 4.6 Hz, 2H), 6.98 – 6.91 (m, 2H), 4.32 (q, *J* = 7.1 Hz, 4H), 3.81 (s, 3H), 3.34 (s, br, 8H), 1.34 (t, *J* = 7.1 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 167.8, 167.8, 157.4, 142.7 (br), 133.5, 132.3, 129.1, 129.1, 128.6, 128.5, 128.4, 128.3, 128.3, 127.9, 127.7, 126.9, 117.9, 105.1, 61.5 (2C), 55.3, 35.2 (br), 35.2 (br), 34.9 (br), 34.6 (br), 14.1(2C) ppm.

Due to peak broadening caused by conformational changes, four ^{13}C signals can't be detected (compare section 2.1).

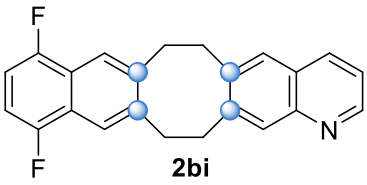
HRMS (ESI): *m/z* calculated for $C_{31}H_{30}O_5$+Na^+: 505.1985 $[M+Na]^+$, found: 505.1983.

Melting point: 143 – 146 °C.

2 Variable temperature (VT) NMR studies

2.1 VT ^{13}C NMR spectra of quinoline 2bi

For all synthesized dinaphthalenes **2**, several ^{13}C signals could not be observed or were detected as very broad peaks with low intensity. To show that this is due to conformational changes, ^{13}C NMR spectra of quinoline **2bi** were measured at different temperatures (Figure S2). With increasing the temperature up to 60 °C, three sharp signals emerged, which were assigned to the sp^2-hybridized carbon atoms of the cyclooctadiene core (Figure S3 and Figure S4).



2bi

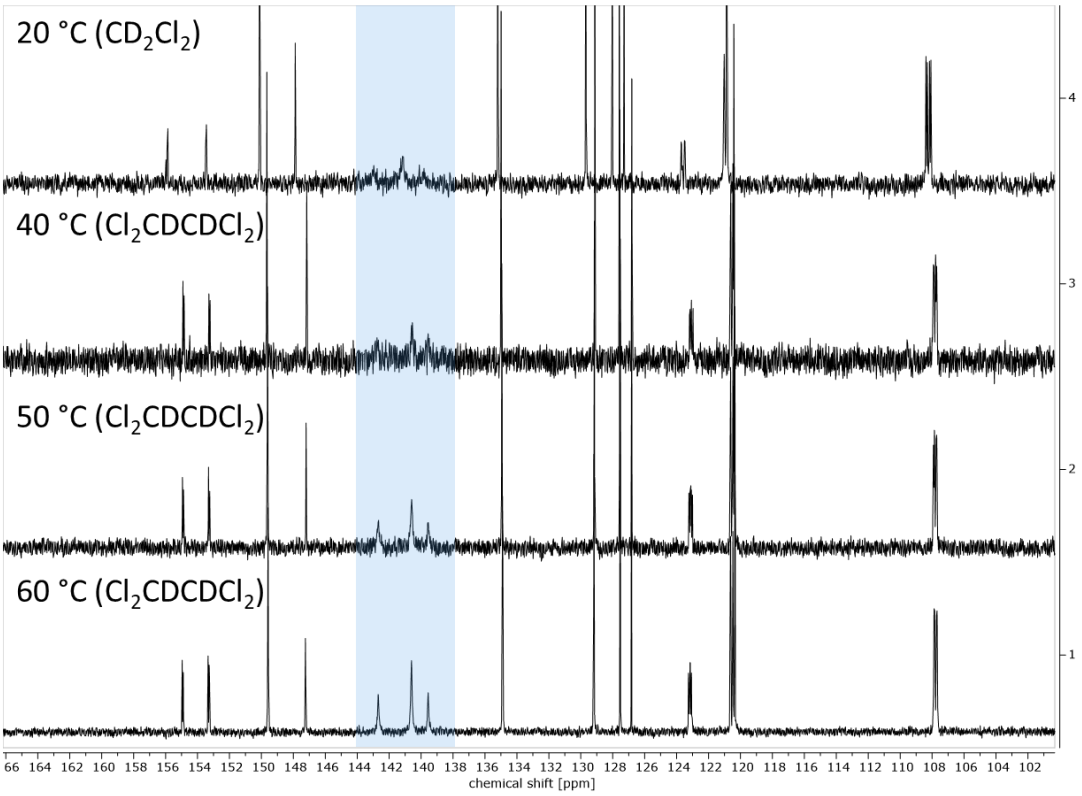


Figure S2. Excerpts of the ^{13}C{^{1}H} NMR spectra (151 MHz) of quinoline **2bi** at different temperatures.

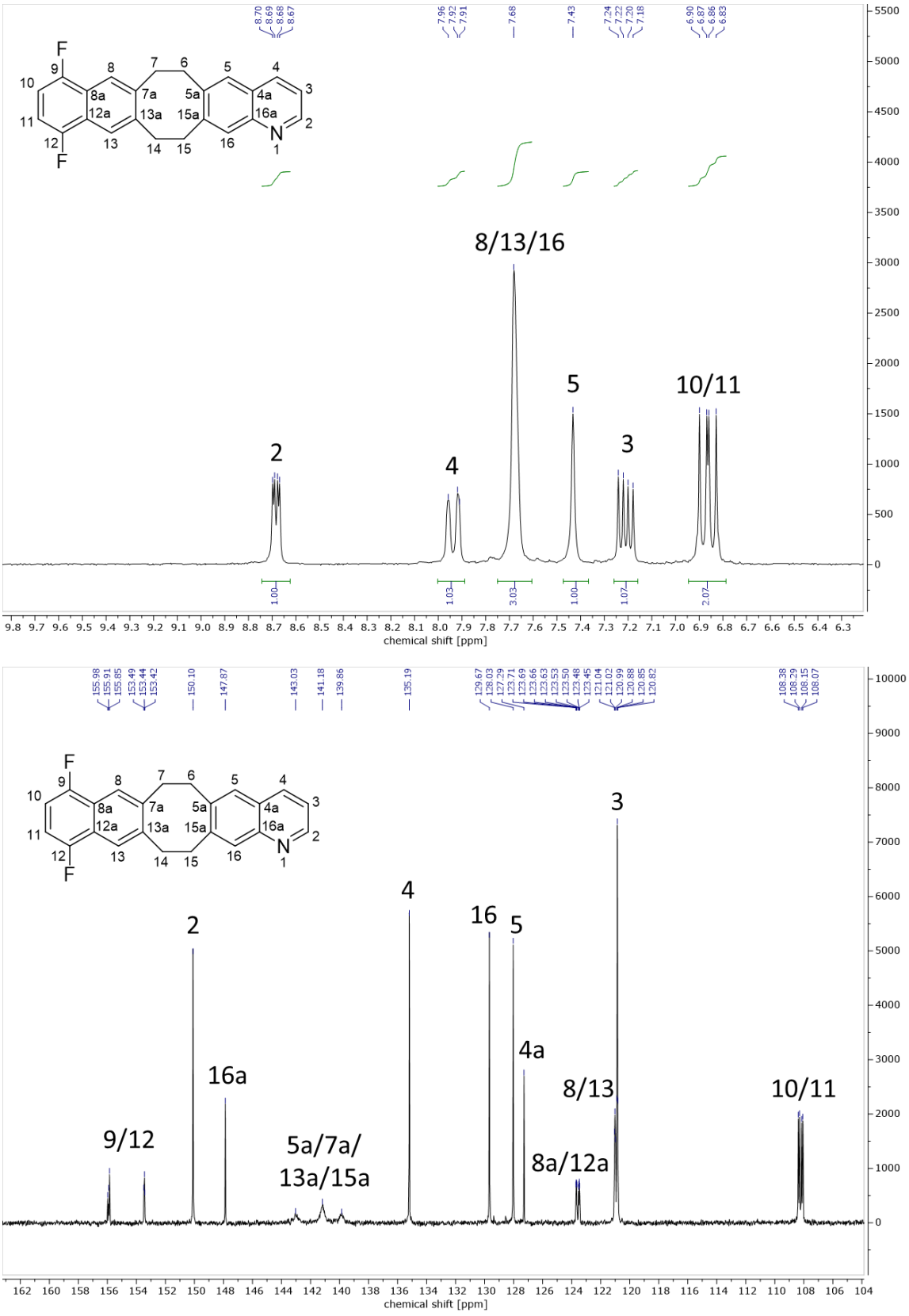


Figure S3. Assignment of the aromatic ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR signals (CD_2Cl_2) of quinoline **2bi**.

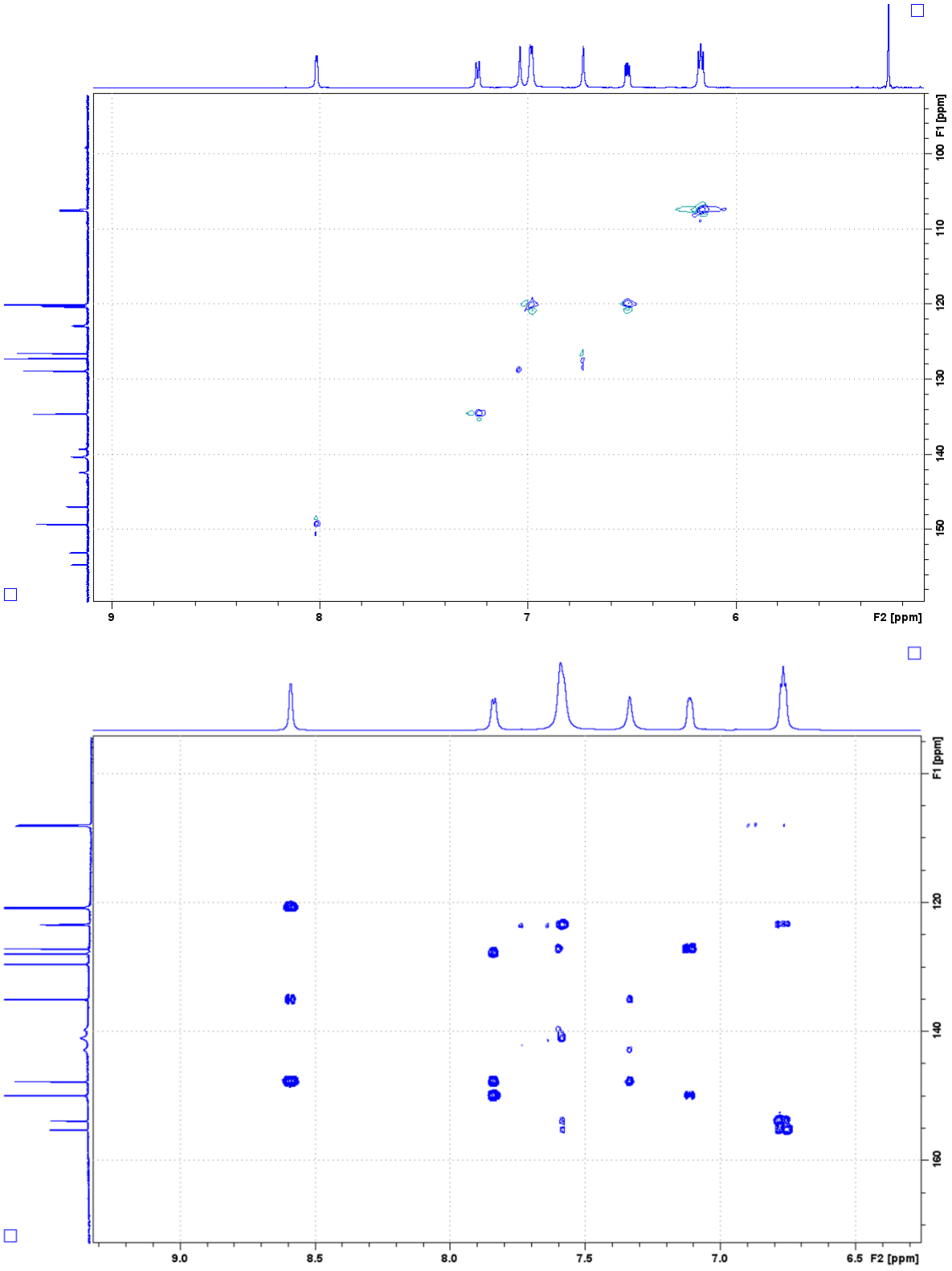


Figure S4. Excerpts of the ^{1}H-^{13}C HSQC (top) and ^{1}H-^{13}C HMBC (bottom) NMR spectra (CD_2Cl_2) of quinoline **2bi**.

2.2 VT ^{1}H NMR studies of the twist-boat/chair conversion

2.2.1 VT ^{1}H NMR spectra

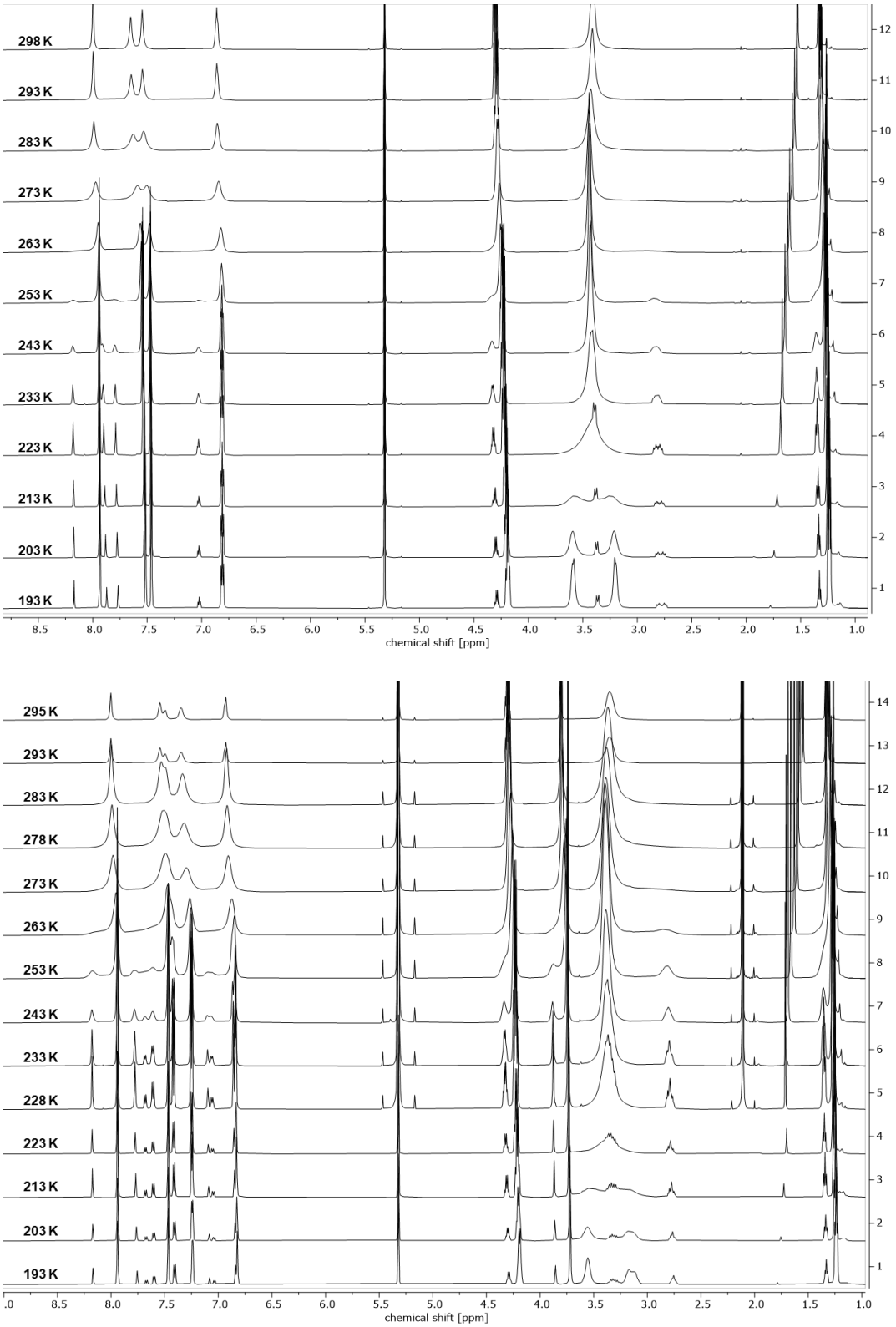


Figure S5. VT ^{1}H NMR spectra (600 MHz, CD_2Cl_2) of dinaphthalenes **2bc** (top) and **2dc** (bottom).

*Dinaphthalene **2bc***:

For the VT NMR analysis of dinaphthalene **2bc**, ^{1}H NMR signals at 223 K were assigned to the twist-boat (tb) and the chair (c) conformation by analyzing the 2D EXSY/NOESY spectrum (Figure S6).

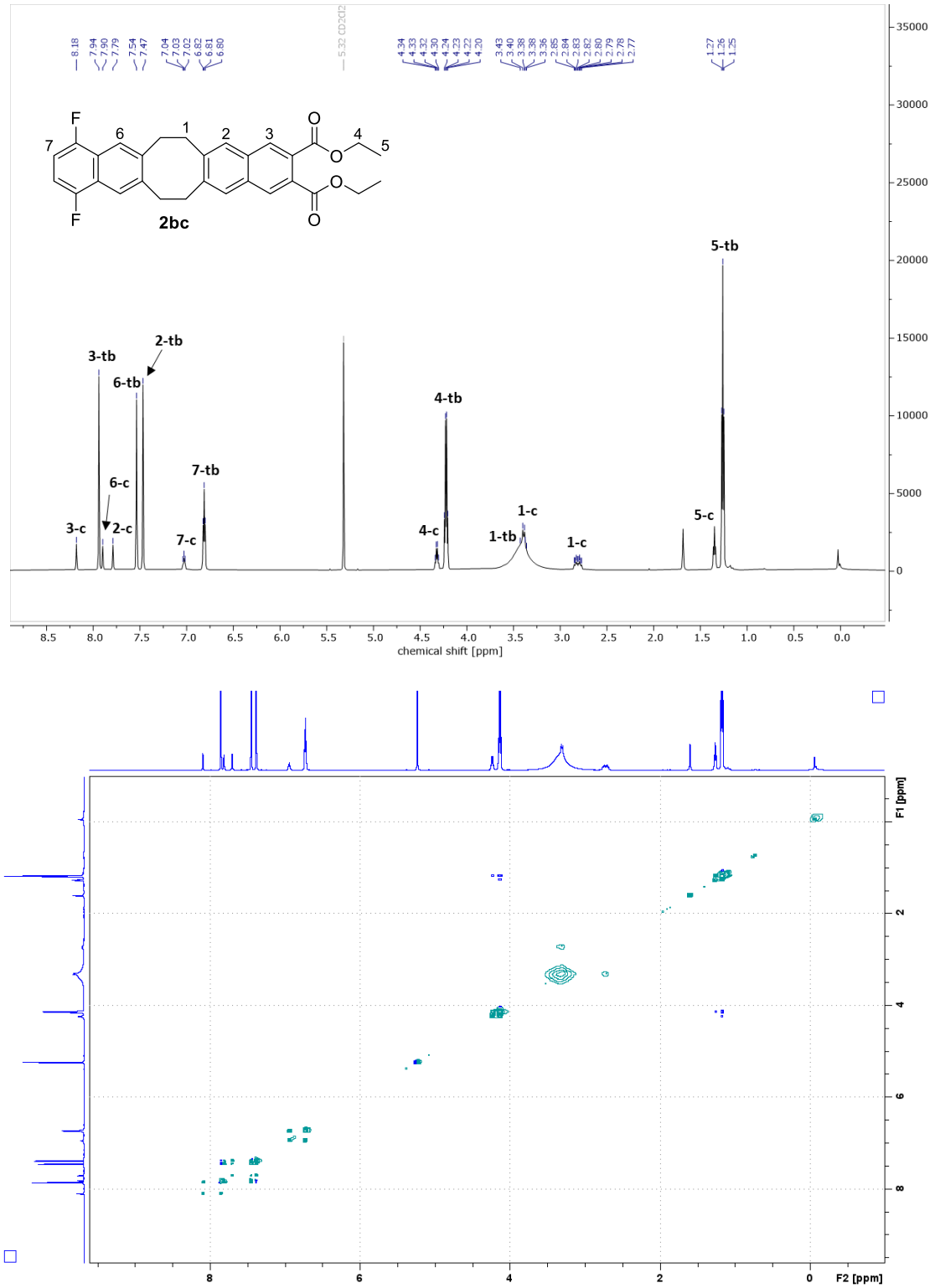


Figure S6. ^{1}H NMR spectrum with peak assignment (top) and ^{1}H-^{1}H EXSY/NOESY NMR spectrum (bottom) of dinaphthalene **2bc** at 223 K (600 MHz, CD_2Cl_2).

*Dinaphthalene **2dc***:

For the VT NMR analysis of dinaphthalene **2dc**, ^{1}H NMR signals at 228 K were assigned to the twist-boat (tb) and the chair (c) conformation by analyzing the 2D EXSY/NOESY spectrum (Figure S7).

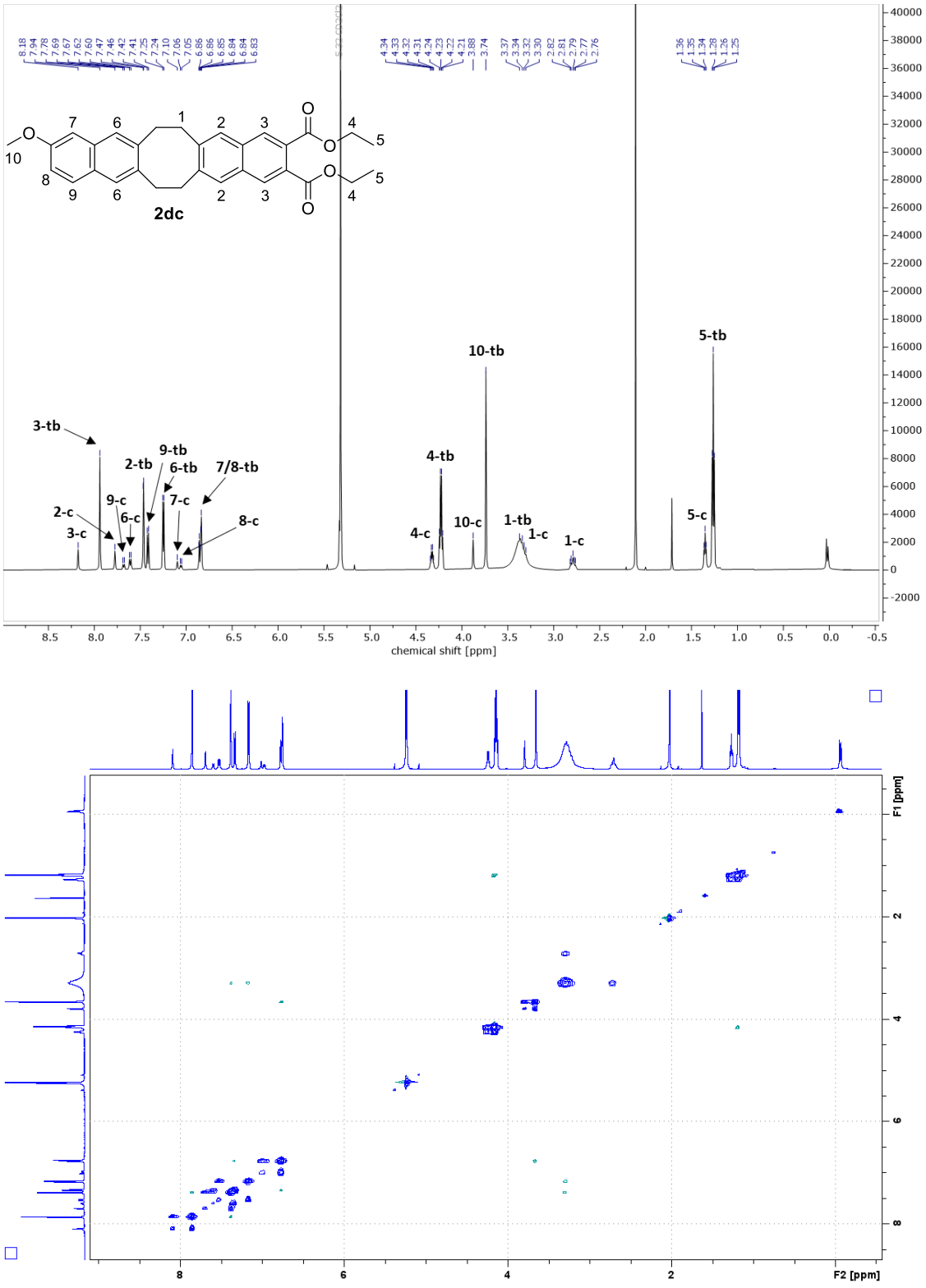


Figure S7. ^{1}H NMR spectrum with peak assignment (top) and ^{1}H-^{1}H EXSY/NOESY NMR spectrum (bottom) of dinaphthalene **2dc** at 228 K (600 MHz, CD_2Cl_2).

2.2.2 Thermodynamic study

The thermodynamic parameters of the twist-boat/chair equilibrium were studied by analyzing the ratio of twist-boat to chair conformation at different temperatures via integration of well separated signals in the ^{1}H NMR spectra. NMR spectra were measured on a Bruker Avance III HD 600 MHz spectrometer using CD_2Cl_2 as solvent and a sample concentration of 4 mg/mL. Changing the sample concentration to 8 mg/mL had virtually no effect on the equilibrium. Peak areas were obtained using the line fitting tool in MestReNova (version 14.2.1-27684). As significant peak broadening was observed around the coalescence temperature, the analysis was restricted to spectra acquired at and below 233 K. The ratios of twist-boat to chair conformer were used to calculate the equilibrium constants K_{eq} at different temperatures. A plot of $\ln K_{eq}$ vs. 1/T yielded a linear correlation that was fitted using OriginPro® 2020 (64-bit). ΔH^0 and ΔS^0 were determined from the slope and the y-intercept, respectively, of the linear fit using the following equation:

$$\ln K_{eq} = -\frac{\Delta H^0}{R} \cdot \frac{1}{T} + \frac{\Delta S^0}{R}$$

The Gibbs free energy difference ΔG^0 at 298 K of the two conformers was calculated from the following equation:

$$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0$$

*Dinaphthalene **2bc***:

The signals 2-c (δ_c = 7.79 ppm) and 2-tb (δ_{tb} = 7.47 ppm) were integrated at different temperatures to determine the populations of chair and twist-boat conformers, respectively, from which the equilibrium constants K_{eq} were calculated. The results are shown Table S1.

Table S1. Equilibrium constants K_{eq} of the tb/c equilibrium of dinaphthalene **2bc** at different temperatures determined from tb and c populations.

T [K]	Population of c	Population of tb	K_{eq}
193	0.1382	0.8618	0.160
203	0.1472	0.8528	0.173
213	0.1580	0.8420	0.188
223	0.1758	0.8242	0.213
228	0.1760	0.8240	0.214
233	0.1808	0.8192	0.221

The linear fit of $\ln K_{eq}$ vs. 1/T is shown in Figure S8 and was used to calculate the differences in enthalpy (ΔH^0) and entropy (ΔS^0) of tb and c conformer (Table S2).

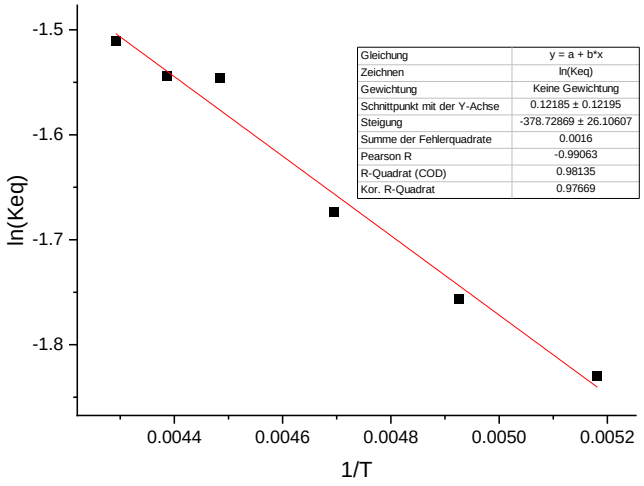


Figure S8. Linear fit of $\ln K_{eq}$ vs. 1/T of dinaphthalene **2dc**.

Table S2. Enthalpy (ΔH^0), entropy (ΔS^0) and Gibbs free energy (ΔG^0) difference of tb and c conformation of dinaphthalene **2bc** calculated from the linear fit of $\ln K_{eq}$ vs. 1/T.

y-intercept	slope [K]	ΔH^0 [kJ/mol]	ΔS^0 [J/K·mol]	ΔG^0 [kJ/mol] at 298 K
0.12±0.12	-378.7±26.1	3.1	1.0	2.8

*Dinaphthalene **2dc***:

The signals 10-c (δ_c = 3.88 ppm) and 10-tb (δ_{tb} = 3.74 ppm) were integrated at different temperatures to determine the populations of chair and twist-boat conformers, respectively, from which the equilibrium constants K_{eq} were calculated. The results are shown in Table S3.

Table S3. Equilibrium constants K_{eq} of the tb/c equilibrium of dinaphthalene **2dc** at different temperatures determined from tb and c populations.

T [K]	Population of c	Population of tb	K_{eq}
193	0.1738	0.8262	0.210
203	0.1846	0.8154	0.226
213	0.1904	0.8096	0.235
223	0.2003	0.7997	0.251
233	0.2068	0.7932	0.261

The linear fit of $\ln K_{eq}$ vs. 1/T is shown in Figure S9 and was used to calculate the differences in enthalpy (ΔH^0) and entropy (ΔS^0) of tb and c conformer (Table S4).

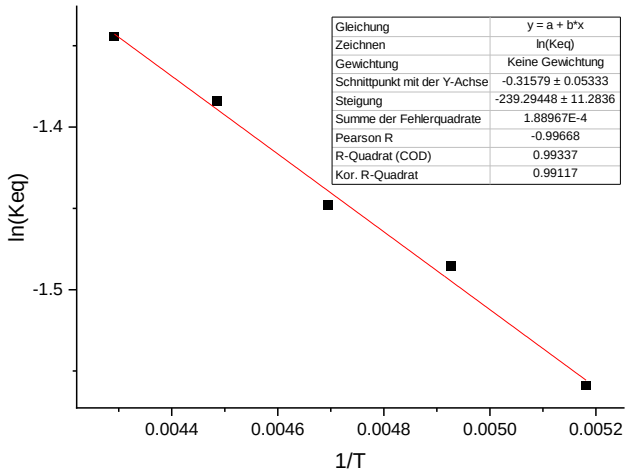


Figure S9. Linear fit of $\ln K_{eq}$ vs. 1/T of dinaphthalene **2dc**.

Table S4. Enthalpy (ΔH^0), entropy (ΔS^0) and Gibbs free energy (ΔG^0) difference of tb and c conformation of dinaphthalene **2dc** calculated from the linear fit of $\ln K_{eq}$ vs. 1/T.

y-intercept	slope [K]	ΔH^0 [kJ/mol]	ΔS^0 [J/K·mol]	ΔG^0 [kJ/mol] at 298 K
-0.32±0.07	-239.3±11.3	2.0	-2.6	2.8

2.2.3 Kinetic study

The kinetics of the twist-boat/chair conversion were studied below the coalescence temperature using the dynamic NMR (DNMR) lineshape analysis tool integrated in Brukers TopSpin (version 4.1.4). NMR spectra were measured on a Bruker Avance III HD 600 MHz spectrometer using CD_2Cl_2 as solvent and a sample concentration of 4 mg/mL. The temperatures of the measurements are given below in Table S5 and Table S7.

The chemical shifts of exchanging nuclei were identified and a region of the spectrum that showed well separated signals was used for the DNMR analysis. The selected region was simulated using an unequally populated two-site model. The rate constant k at each temperature was obtained by iterative refinement of the simulated spectrum until the best overlap (>90%) with the experimental data was obtained. A plot of ln(k/T) vs. 1/T yielded a linear correlation that was fitted using OriginPro® 2020 (64-bit). The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined from the slope and the y-intercept, respectively, of the linear fit using the Eyring–Polanyi equation:

$$\ln\frac{k}{T} = -\frac{\Delta H^{\ddagger}}{R}\cdot\frac{1}{T} + \ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}$$

The Gibbs free energy of activation $\Delta G^{\ddagger}$ at 298 K was calculated from the following equation:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\cdot\Delta S^{\ddagger}$$

*Dinaphthalene **2bc***:

The signals 2-c (δ_c = 7.79 ppm) and 2-tb (δ_{tb} = 7.47 ppm) were used for the determination of k via DNMR lineshape analysis. The results are shown in Table S5.

Table S5. Rate constants k for the twist-boat/chair conversion of dinaphthalene **2bc** determined via DNMR lineshape analysis at different temperatures.

T [K]	k [s^{-1}]
223	8.2
228	11.8
233	21.6
238	35.2
243	50.0
248	74.2

The linear fit of ln(k/T) vs. 1/T is shown in Figure S10 and was used to calculate the activation parameters (Table S6).

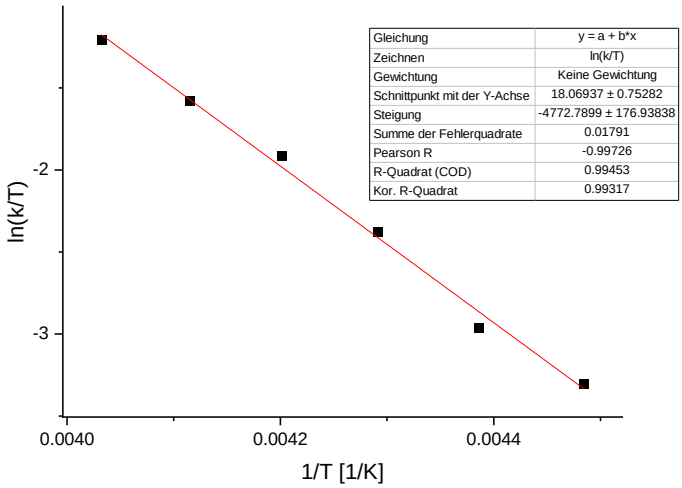


Figure S10. Linear fit of ln(k/T) vs. 1/T of dinaphthalene **2bc**.

Table S6. Activation parameters of the twist-boat/chair conversion of dinaphthalene **2bc** calculated from the linear fit of ln(k/T) vs. 1/T.

y-intercept	slope [K]	$\Delta H^{\ddagger}$ [kJ/mol]	$\Delta S^{\ddagger}$ [J/K·mol]	$\Delta G^{\ddagger}$ [kJ/mol] at 298 K
18.07±0.75	-4772±177	39.7	-47.3	53.8

*Dinaphthalene **2dc***:

The signals 10-c (δ_c = 3.88 ppm) and 10-tb (δ_{tb} = 3.74 ppm) belonging to the protons of the methoxy group were used for the determination of k via DNMR lineshape analysis. The results are shown in Table S7.

Table S7. Rate constants k for the twist-boat/chair conversion of dinaphthalene **2dc** determined via DNMR lineshape analysis at different temperatures.

T [K]	k [s^{-1}]
228	15.2
233	19.7
238	34.4
243	46.3
248	67.4
253	88.7
258	126.9

The linear fit of ln(k/T) vs. 1/T is shown in Figure S11 and was used to calculate the activation parameters (Table S8).

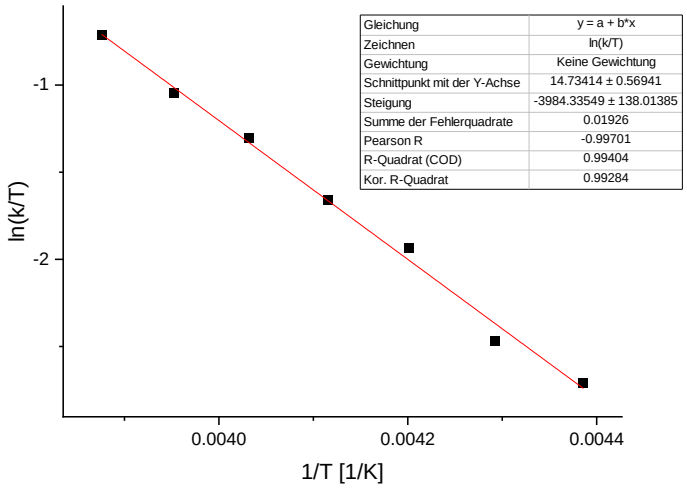


Figure S11. Linear fit of ln(k/T) vs. 1/T of dinaphthalene **2dc**.

Table S8. Activation parameters of the twist-boat/chair conversion of dinaphthalene **2dc** calculated from the linear fit of ln(k/T) vs. 1/T.

y-intercept	slope [K]	$\Delta H^{\ddagger}$ [kJ/mol]	$\Delta S^{\ddagger}$ [J/K·mol]	$\Delta G^{\ddagger}$ [kJ/mol] at 298 K
14.73±0.57	-3984±138	33.1	-75.0	55.5

2.2.4 Determination of the twist-boat to chair ratio above the coalescence temperature

At temperatures above the coalescence temperature T_c, the ratio of twist-boat to chair conformers was determined from the chemical shift of the coalesced signal of H-3 (δ_{obs}) relative to the chemical shifts of the corresponding signals assigned to the twist-boat (δ_{tb}) and chair (δ_c) conformation below T_c.[6] The following equations were used to calculate the population of twist-boat and chair, respectively:

$$Population\ of\ tb = \frac{\delta_c - \delta_{obs}}{\delta_c - \delta_{tb}}$$

$$Population\ of\ c = \frac{\delta_{obs} - \delta_{tb}}{\delta_c - \delta_{tb}}$$

The observed chemical shifts at 298 K and the corresponding chair and twist-boat populations of dinaphthalenes **2bc** and **2dc** are shown in Table S9.

Table S9. Populations of chair and twist-boat conformer at 298 K calculated from the observed chemical shifts of H-3.

Compound	δ_{obs} [ppm]	δ_c [ppm]	δ_{tb} [ppm]	Population of c	Population of tb
2bc	7.998	8.180	7.940	0.242	0.758
2dc	8.003	8.177	7.940	0.266	0.734

3 Theoretical calculations

3.1 Computational methods

Initial Geometry optimizations were carried out using extended tight binding (XTB),[7–11] followed by conformer screenings with the conformer rotamer ensemble sampling tool (CREST).[12–15] The resulting conformers of the twist-boat, chair and boat family were optimized by the means of Density Functional Theory (DFT) calculations. All calculations were carried out using the ORCA software package.[16] Geometry optimizations and frequency calculations were carried out on a PBE0/def2-TZVP/D4/CPCM(CH2Cl2) level of theory.[17–21] On all atoms, the def2/J auxiliary basis set was used for the RIJCOSX approximation.[22–32]

For a more accurate implicit solvation, single point energy calculations were carried out on a PBE0/def2-TZVPP/D4/SMD(CH2Cl2) level of theory to obtain both electrostatic and cavity-dispersion interactions.[33] Finally, single point energies were refined using the domain based local pair natural orbital (DLPNO)-CCSD(T) method.[34–38] Thermodynamic corrections as well as solvent interactions were taken from aforementioned DFT calculations.

Visualization of non-covalent interactions (NCIs) were carried out using the NCIPLOT software package and the visual molecular dynamics (VMD) program. Visualization was carried out using the VMD template supplied in the NCIPLOT software package.[39,40]

3.2 Calculated energies

Table S10. Calculated energies of dinaphthalene **2bc**.

	G_{abs}^{DFT}/Hartree	G_{rel}^{DFT}/kcal/mol	G_{abs}^{corr}/Hartree	G_{rel}^{corr}/kcal/mol
twist-boat	-1657.900	0.000	-1656.878	0.000
chair	-1657.899	1.100	-1656.874	2.554
twist	-1657.893	4.445	-1656.868	5.927

Table S11. Calculated energies of dinaphthalene **2dc**.

	G_{abs}^{DFT}/Hartree	G_{rel}^{DFT}/kcal/mol	G_{abs}^{corr}/Hartree	G_{rel}^{corr}/kcal/mol
twist-boat	-1573.920	0.000	-1572.970	0.000
chair	-1573.918	1.090	-1572.967	2.302
twist	-1573.912	4.769	-1572.961	5.998

3.3 Geometry data

*Dinaphthalene **2bc***:

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C30H26O4F2 – **2bc**_twistboat; G_rel = 0 kcal/mol

C	3.423182000	-4.158095000	-0.517876000
C	3.143357000	-3.796892000	-1.850109000
C	3.188284000	-2.483752000	-2.204944000
C	3.503836000	-1.454280000	-1.296441000
C	3.784605000	-1.818232000	0.045080000
C	3.731879000	-3.184989000	0.382047000
C	3.553561000	-0.094253000	-1.657411000
C	3.861891000	0.883785000	-0.745834000
C	4.127727000	0.516274000	0.603396000
C	4.093730000	-0.804146000	0.970768000
C	3.927337000	2.316061000	-1.203480000
C	3.042234000	3.324004000	-0.431559000
H	3.636200000	2.335455000	-2.255336000
H	4.965081000	2.665122000	-1.162297000
C	1.806961000	2.688640000	0.125567000
H	2.762760000	4.122466000	-1.121593000
H	3.612287000	3.791045000	0.372335000
C	1.842398000	2.061438000	1.403447000
C	3.071597000	2.103541000	2.270422000
C	4.378606000	1.572963000	1.633860000
H	2.858357000	1.515147000	3.164855000
H	3.243940000	3.131231000	2.609060000
H	4.998493000	1.162362000	2.433185000

H	4.945236000	2.393013000	1.190990000
F	4.000042000	-3.524443000	1.655112000
H	3.394766000	-5.195132000	-0.207856000
H	2.895219000	-4.550174000	-2.587234000
F	2.921892000	-2.135440000	-3.475854000
H	4.301615000	-1.078501000	1.998697000
H	3.342148000	0.179186000	-2.684536000
C	0.655101000	2.655082000	-0.618445000
C	-0.503752000	2.000784000	-0.159839000
C	-0.467705000	1.363370000	1.104994000
C	0.720129000	1.417704000	1.860472000
H	0.737417000	0.931772000	2.831104000
H	0.630991000	3.137817000	-1.590851000
C	-1.690083000	1.942122000	-0.920780000
C	-2.797213000	1.284828000	-0.457160000
C	-2.772259000	0.673116000	0.823477000
C	-1.625165000	0.709439000	1.573169000
C	-4.023561000	0.144516000	1.419100000
H	-1.612333000	0.258079000	2.558312000
C	-3.958357000	1.172151000	-1.382468000
H	-1.712204000	2.401847000	-1.902798000
O	-3.801754000	-0.886836000	2.227475000
C	-4.940325000	-1.441305000	2.911841000
H	-5.625499000	-0.632972000	3.168537000
H	-4.527335000	-1.865446000	3.826875000
C	-5.613884000	-2.496368000	2.071301000
H	-6.436356000	-2.939958000	2.636974000
H	-4.911068000	-3.289549000	1.808826000
H	-6.020570000	-2.067664000	1.154025000

O	-5.110954000	0.633482000	1.219405000
O	-4.408840000	2.099196000	-2.012000000
O	-4.369952000	-0.086320000	-1.496724000
C	-5.474724000	-0.340543000	-2.384614000
C	-6.801066000	-0.116467000	-1.703709000
H	-5.348922000	-1.383152000	-2.675522000
H	-5.365087000	0.291451000	-3.266607000
H	-6.897804000	-0.748392000	-0.819457000
H	-7.605419000	-0.370212000	-2.398220000
H	-6.921191000	0.925510000	-1.404705000

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C30H26O4F2 – **2bc**_chair, G_rel = 1.100 kcal/mol

C	8.493302000	-2.208015000	-0.047278000
C	8.541238000	-1.613188000	-1.322794000
C	7.388757000	-1.158959000	-1.886770000
C	6.135328000	-1.253334000	-1.250989000
C	6.087164000	-1.852039000	0.033136000
C	7.295522000	-2.314101000	0.590370000
C	4.937903000	-0.788403000	-1.827939000
C	3.734831000	-0.892647000	-1.176453000
C	3.686562000	-1.493338000	0.114255000
C	4.843788000	-1.959438000	0.685351000
C	2.495394000	-0.358985000	-1.829017000
C	1.989959000	0.980389000	-1.230057000
H	1.694257000	-1.101574000	-1.778158000
H	2.706799000	-0.206492000	-2.888433000
C	0.697294000	0.863112000	-0.481297000
H	1.848571000	1.692371000	-2.044604000

H	2.764686000	1.401782000	-0.583339000
C	0.645880000	0.258794000	0.808512000
C	1.884133000	-0.274221000	1.464105000
C	2.395226000	-1.611897000	0.866239000
H	1.668437000	-0.428579000	2.522452000
H	2.683968000	0.470062000	1.417533000
H	1.620906000	-2.038252000	0.222204000
H	2.540937000	-2.321331000	1.682257000
F	7.244512000	-2.881681000	1.808151000
H	9.394367000	-2.578456000	0.425216000
H	9.480213000	-1.516081000	-1.853114000
F	7.430475000	-0.591288000	-3.104820000
H	4.807022000	-2.425796000	1.663014000
H	4.974051000	-0.339474000	-2.813733000
C	-0.459956000	1.329918000	-1.052656000
C	-1.706293000	1.222073000	-0.405871000
C	-1.758827000	0.617156000	0.873860000
C	-0.561057000	0.153949000	1.453449000
H	-0.603342000	-0.296646000	2.440370000
H	-0.423103000	1.799406000	-2.030895000
C	-2.901777000	1.686636000	-0.991329000
C	-4.102234000	1.562808000	-0.345370000
C	-4.152033000	0.982892000	0.949162000
C	-3.002066000	0.515563000	1.530739000
C	-5.404518000	1.034190000	1.743865000
H	-3.036973000	0.090245000	2.527032000
C	-5.320345000	1.971755000	-1.096129000
H	-2.871817000	2.123789000	-1.983344000
O	-5.557093000	-0.038714000	2.512822000

C	-6.706308000	-0.065540000	3.379920000
H	-6.884464000	0.941135000	3.759217000
H	-6.407429000	-0.711133000	4.205393000
C	-7.914358000	-0.612449000	2.662737000
H	-8.749689000	-0.682950000	3.363127000
H	-7.712273000	-1.610384000	2.268641000
H	-8.211592000	0.038524000	1.839191000
O	-6.167136000	1.971545000	1.720129000
O	-5.399073000	2.986602000	-1.746544000
O	-6.268587000	1.042668000	-1.035093000
C	-7.496513000	1.309095000	-1.738602000
C	-8.435925000	2.158622000	-0.920617000
H	-7.915912000	0.321142000	-1.926583000
H	-7.255861000	1.781309000	-2.691777000
H	-8.010951000	3.144267000	-0.727295000
H	-8.663058000	1.681347000	0.033797000
H	-9.370010000	2.288903000	-1.472141000

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C30H26O4F2, **2bc**_twist, G_rel = 4.445 kcal/mol

C	8.654324000	-2.239348000	-0.148503000
C	8.807080000	-1.156092000	-1.035545000
C	7.712030000	-0.430382000	-1.391622000
C	6.418105000	-0.711885000	-0.911195000
C	6.264172000	-1.802855000	-0.020880000
C	7.415195000	-2.534905000	0.330629000
C	5.278492000	0.031578000	-1.270349000
C	4.028821000	-0.265502000	-0.785003000
C	3.872606000	-1.369554000	0.105048000

C	4.977935000	-2.099711000	0.466337000
C	2.876091000	0.599275000	-1.215387000
C	1.632256000	-0.149934000	-1.725394000
H	3.237430000	1.254119000	-2.009838000
H	2.590889000	1.269882000	-0.399327000
C	0.407099000	-0.049128000	-0.858986000
H	1.881393000	-1.202209000	-1.892373000
H	1.368773000	0.241459000	-2.709159000
C	0.434048000	-0.296795000	0.546653000
C	1.695655000	-0.650234000	1.284813000
C	2.538464000	-1.779397000	0.666381000
H	1.410727000	-0.942593000	2.296663000
H	2.314700000	0.243371000	1.407770000
H	1.955285000	-2.292536000	-0.104062000
H	2.725656000	-2.533451000	1.432508000
F	7.264660000	-3.567780000	1.177923000
H	9.508385000	-2.833304000	0.151737000
H	9.781166000	-0.899124000	-1.432422000
F	7.852960000	0.604258000	-2.238414000
H	4.862603000	-2.933127000	1.149598000
H	5.397555000	0.864310000	-1.953855000
C	-0.783236000	0.290954000	-1.454169000
C	-1.985720000	0.393347000	-0.730128000
C	-1.960685000	0.140586000	0.662224000
C	-0.734613000	-0.204742000	1.262087000
H	-0.721862000	-0.404102000	2.329326000
H	-0.805858000	0.491096000	-2.521010000
C	-3.207115000	0.749386000	-1.338391000
C	-4.359767000	0.847845000	-0.606828000

C	-4.341940000	0.562446000	0.783673000
C	-3.161573000	0.227708000	1.395077000
C	-5.614018000	0.459164000	1.540590000
H	-3.151287000	-0.008346000	2.452757000
C	-5.570933000	1.345422000	-1.314831000
H	-3.226074000	0.975083000	-2.398965000
O	-5.481954000	0.849255000	2.804157000
C	-6.639868000	0.731121000	3.651490000
H	-6.230807000	0.615246000	4.654893000
H	-7.184675000	-0.173577000	3.380106000
C	-7.511837000	1.956910000	3.550354000
H	-8.348590000	1.864050000	4.246405000
H	-7.914671000	2.069933000	2.542770000
H	-6.948796000	2.855864000	3.808824000
O	-6.636056000	0.024381000	1.063715000
O	-5.920790000	0.954493000	-2.402817000
O	-6.159451000	2.330798000	-0.644938000
C	-7.332083000	2.920323000	-1.237381000
C	-8.576407000	2.130078000	-0.920919000
H	-7.173507000	3.004283000	-2.313153000
H	-7.375374000	3.919585000	-0.804918000
H	-8.524803000	1.125574000	-1.342690000
H	-9.441091000	2.640428000	-1.351697000
H	-8.725671000	2.050553000	0.156942000

*Dinaphthalene **2dc***:

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C31H30O5, **2dc**_twistboat; G_rel = 0.00 kcal/mol

C	-2.17266	-5.18445	-0.74656
C	-1.61192	-4.76740	-1.97735
C	-1.84542	-3.50073	-2.45191
C	-2.64616	-2.60362	-1.70675
C	-3.20478	-3.01654	-0.47154
C	-2.94690	-4.33128	-0.01801
C	-2.91008	-1.29215	-2.15404
C	-3.67543	-0.40992	-1.43143
C	-4.21574	-0.82358	-0.18292
C	-3.98292	-2.10032	0.26123
C	-3.93144	0.96653	-1.98753
C	-3.53564	2.15957	-1.08316
H	-4.99158	1.06763	-2.24566
H	-3.37554	1.04662	-2.92382
C	-2.38533	1.82847	-0.18565
H	-4.38913	2.48663	-0.48794
H	-3.26594	2.99784	-1.72874
C	-2.61858	1.19678	1.06915
C	-4.01078	0.96624	1.59194
C	-4.95734	0.15193	0.67725
H	-4.48101	1.93101	1.81357
H	-3.91618	0.44281	2.54542
H	-5.55216	0.82231	0.05500
H	-5.66202	-0.38407	1.31654
H	-1.96861	-6.19248	-0.40393

O	-0.86022	-5.70058	-2.60288
H	-4.39889	-2.41836	1.21340
H	-2.48666	-0.97604	-3.10300
C	-1.09980	2.06453	-0.60066
C	0.01125	1.66781	0.16749
C	-0.21661	1.01454	1.40400
C	-1.54361	0.80165	1.82544
H	-1.71079	0.30636	2.77692
H	-0.92625	2.55515	-1.55386
C	1.33820	1.89342	-0.25354
C	2.40164	1.47836	0.50397
C	2.17285	0.79465	1.72657
C	0.89201	0.58670	2.16286
C	3.27438	0.19923	2.52679
H	0.72611	0.05496	3.09341
C	3.77498	1.88827	0.11436
H	1.51238	2.42843	-1.18013
O	4.16797	-0.40444	1.74981
C	5.30546	-1.00597	2.39255
H	5.58987	-0.39314	3.24838
H	6.09550	-0.96141	1.64291
C	5.01105	-2.42784	2.79901
H	4.71000	-3.02341	1.93485
H	4.21813	-2.46524	3.54756
H	5.91018	-2.87613	3.22776
O	3.31738	0.21421	3.73411
O	4.59453	2.31461	0.89407
O	3.97980	1.77569	-1.19214
C	5.25408	2.22782	-1.68326

C	5.26765	2.02013	-3.17244
H	6.03964	1.65600	-1.18464
H	5.37656	3.27948	-1.41506
H	5.13873	0.96512	-3.42207
H	6.22663	2.35264	-3.57478
H	4.47518	2.59461	-3.65606
H	-3.37321	-4.65456	0.92599
H	-1.42684	-3.16272	-3.39129
C	-0.27231	-5.34416	-3.83744
H	0.28049	-6.21849	-4.17537
H	0.41478	-4.50056	-3.71881
H	-1.03519	-5.08568	-4.57834

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C31H30O5, **2dc**_chair, G_rel = 1.090 kcal/mol

C	-7.286372000	-4.518402000	-1.705395000
C	-7.293051000	-3.819974000	-2.936225000
C	-6.237566000	-3.012698000	-3.280719000
C	-5.137518000	-2.875156000	-2.402328000
C	-5.127663000	-3.572083000	-1.169042000
C	-6.232044000	-4.395934000	-0.849602000
C	-4.029175000	-2.060622000	-2.715142000
C	-2.959271000	-1.919249000	-1.865910000
C	-2.952357000	-2.618615000	-0.626323000
C	-4.020060000	-3.422036000	-0.311345000
C	-1.823184000	-1.020134000	-2.252764000
C	-1.794957000	0.331684000	-1.490687000
H	-1.899146000	-0.813101000	-3.321525000
H	-0.868988000	-1.534343000	-2.105654000

C	-0.650804000	0.469588000	-0.532929000
H	-2.743792000	0.465231000	-0.963769000
H	-1.728665000	1.141822000	-2.218628000
C	-0.640955000	-0.233226000	0.707470000
C	-1.776105000	-1.129748000	1.100068000
C	-1.812554000	-2.481778000	0.338887000
H	-2.729096000	-0.612807000	0.956556000
H	-1.692936000	-1.333214000	2.168963000
H	-1.889665000	-3.287265000	1.071329000
H	-0.858940000	-2.627164000	-0.177112000
H	-8.136153000	-5.147575000	-1.466326000
O	-8.391258000	-4.021796000	-3.697661000
H	-4.017819000	-3.967363000	0.628404000
H	-4.027352000	-1.532011000	-3.664208000
C	0.411910000	1.275164000	-0.858526000
C	1.523194000	1.423843000	-0.006197000
C	1.532800000	0.726695000	1.226827000
C	0.432863000	-0.092053000	1.550378000
H	0.441173000	-0.618971000	2.499733000
H	0.402324000	1.820320000	-1.797434000
C	2.616169000	2.253895000	-0.329699000
C	3.678166000	2.391990000	0.522772000
C	3.701884000	1.671713000	1.745447000
C	2.643157000	0.869061000	2.083525000
C	4.931404000	1.653120000	2.575711000
H	2.669324000	0.305684000	3.009078000
C	4.723976000	3.381982000	0.147138000
H	2.599968000	2.814013000	-1.258267000
O	4.661207000	1.573584000	3.874610000

C	5.782241000	1.488957000	4.773602000
H	6.564891000	0.890580000	4.306306000
H	5.394550000	0.956515000	5.641830000
C	6.280043000	2.862542000	5.146669000
H	6.662672000	3.392162000	4.272808000
H	7.090277000	2.769604000	5.873367000
H	5.481383000	3.455366000	5.596810000
O	6.046702000	1.664499000	2.109954000
O	5.193207000	3.475425000	-0.961988000
O	5.006232000	4.202173000	1.154059000
C	5.995358000	5.220904000	0.915301000
C	7.396168000	4.693639000	1.097215000
H	5.763821000	5.994068000	1.647426000
H	5.845734000	5.623566000	-0.087200000
H	7.533073000	4.286100000	2.099984000
H	8.105420000	5.512928000	0.957844000
H	7.623172000	3.914486000	0.368630000
H	-6.231161000	-4.933998000	0.092742000
H	-6.222999000	-2.471248000	-4.218009000
C	-8.456189000	-3.351541000	-4.940138000
H	-9.402146000	-3.641277000	-5.393410000
H	-7.630947000	-3.650451000	-5.593812000
H	-8.433073000	-2.265780000	-4.804894000

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C31H30O5, **2dc**_twist, G_rel = 4.769 kcal/mol

C	8.60995	-2.16922	-0.05976
C	8.76936	-1.06146	-0.92645

C	7.68632	-0.33284	-1.32078
C	6.38642	-0.66321	-0.87187
C	6.23125	-1.77208	-0.00566
C	7.36272	-2.52221	0.39142
C	5.24298	0.06778	-1.24757
C	3.98236	-0.24307	-0.79828
C	3.82474	-1.35895	0.07431
C	4.93221	-2.08469	0.44230
C	2.83094	0.62132	-1.23887
C	1.58343	-0.12047	-1.75191
H	3.19874	1.26917	-2.03667
H	2.54169	1.30075	-0.43092
C	0.36041	-0.02744	-0.88043
H	1.83149	-1.17115	-1.93022
H	1.31491	0.28116	-2.73037
C	0.39349	-0.27888	0.52480
C	1.65566	-0.64496	1.25457
C	2.48654	-1.77516	0.62157
H	1.37397	-0.93933	2.26685
H	2.28256	0.24334	1.37595
H	1.89840	-2.26956	-0.15726
H	2.66496	-2.54255	1.37673
O	9.75594	-2.80977	0.26128
H	9.76930	-0.81338	-1.26356
H	4.80914	-2.93024	1.11314
H	5.37199	0.91263	-1.91860
C	-0.83444	0.31016	-1.46866
C	-2.03374	0.41028	-0.73826
C	-1.99899	0.16397	0.65508

C	-0.77020	-0.18257	1.24717
H	-0.75144	-0.38158	2.31443
H	-0.86342	0.51036	-2.53542
C	-3.26148	0.75569	-1.33960
C	-4.41025	0.85337	-0.60077
C	-4.37916	0.58345	0.79249
C	-3.19337	0.25697	1.39696
C	-5.64054	0.48701	1.56794
H	-3.17371	0.03153	2.45693
C	-5.63255	1.32736	-1.30540
H	-3.28982	0.97213	-2.40193
O	-5.50096	0.93811	2.81050
C	-6.64843	0.84693	3.67495
H	-6.22778	0.78834	4.67855
H	-7.18318	-0.07781	3.45594
C	-7.53779	2.05464	3.52002
H	-8.36488	1.98943	4.23056
H	-7.95431	2.10879	2.51320
H	-6.98290	2.97283	3.72230
O	-6.65773	0.00870	1.12444
O	-5.97297	0.93394	-2.39567
O	-6.24859	2.29199	-0.62973
C	-7.44107	2.84640	-1.21616
C	-8.65696	2.01278	-0.90031
H	-7.28822	2.94157	-2.29181
H	-7.51654	3.84123	-0.77797
H	-8.57209	1.01283	-1.32755
H	-9.54021	2.49510	-1.32561
H	-8.79903	1.92250	0.17757

H	7.21827	-3.36620	1.05379
H	7.81365	0.51525	-1.98566
C	9.65847	-3.93567	1.10972
H	9.03939	-4.71730	0.65829
H	9.24001	-3.66257	2.08335
H	10.67297	-4.30677	1.24140

3.4 Non-covalent interaction plots

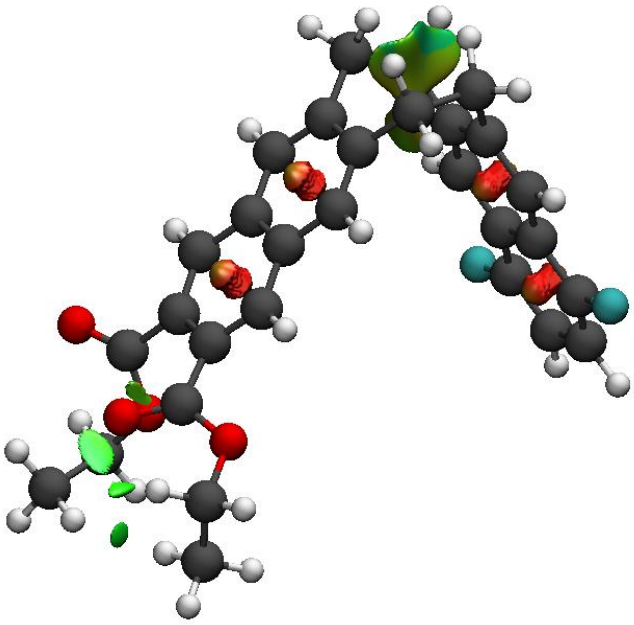

Figure S12. NCI plot of the twist-boat conformer of dinaphthalene **2bc**.

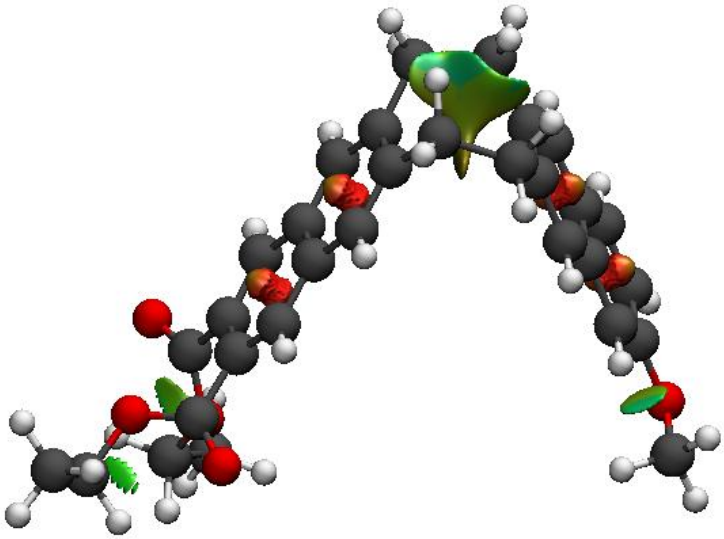

Figure S13. NCI plot of the twist-boat conformer of dinaphthalene **2dc**.

4 NMR spectra

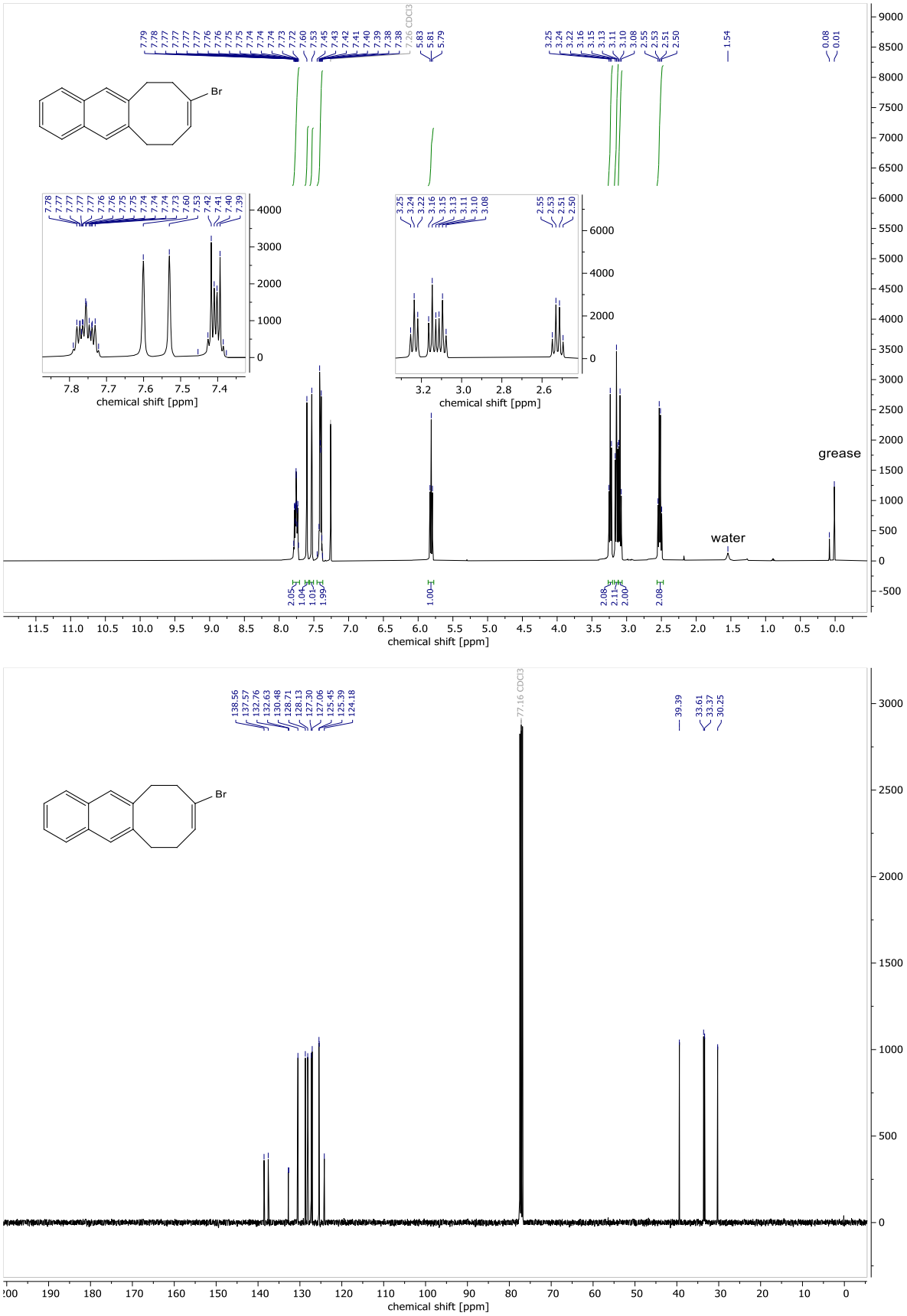

Figure S14. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra ($CDCl_3$) of (*E*)-8-bromo-6,7,10,11-tetrahydrocycloocta[*b*]naphthalene (**4a**).

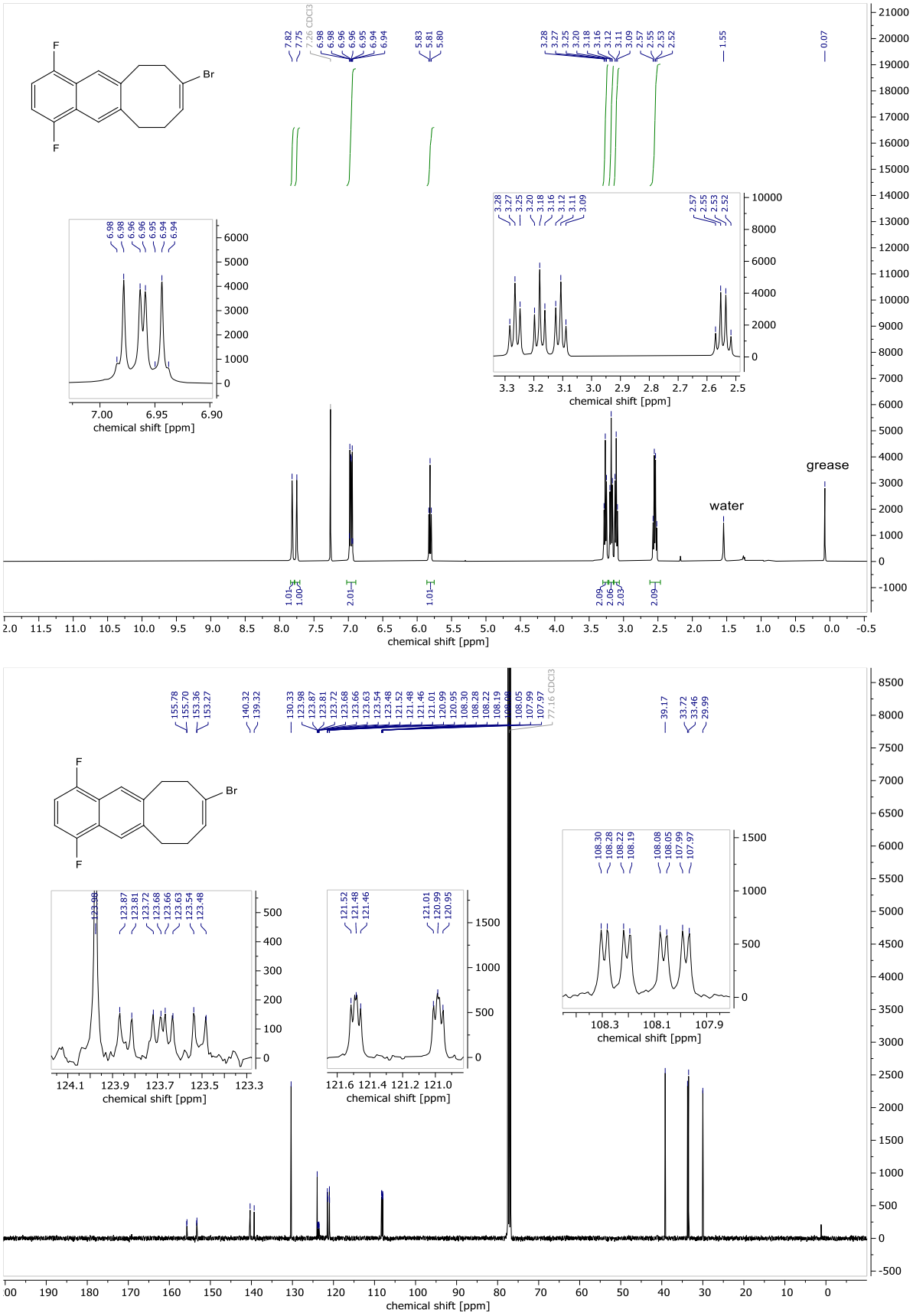

Figure S15. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra ($CDCl_3$) of (*E*)-8-bromo-1,4-difluoro-6,7,10,11-tetrahydrocycloocta[*b*]naphthalene (**4b**).

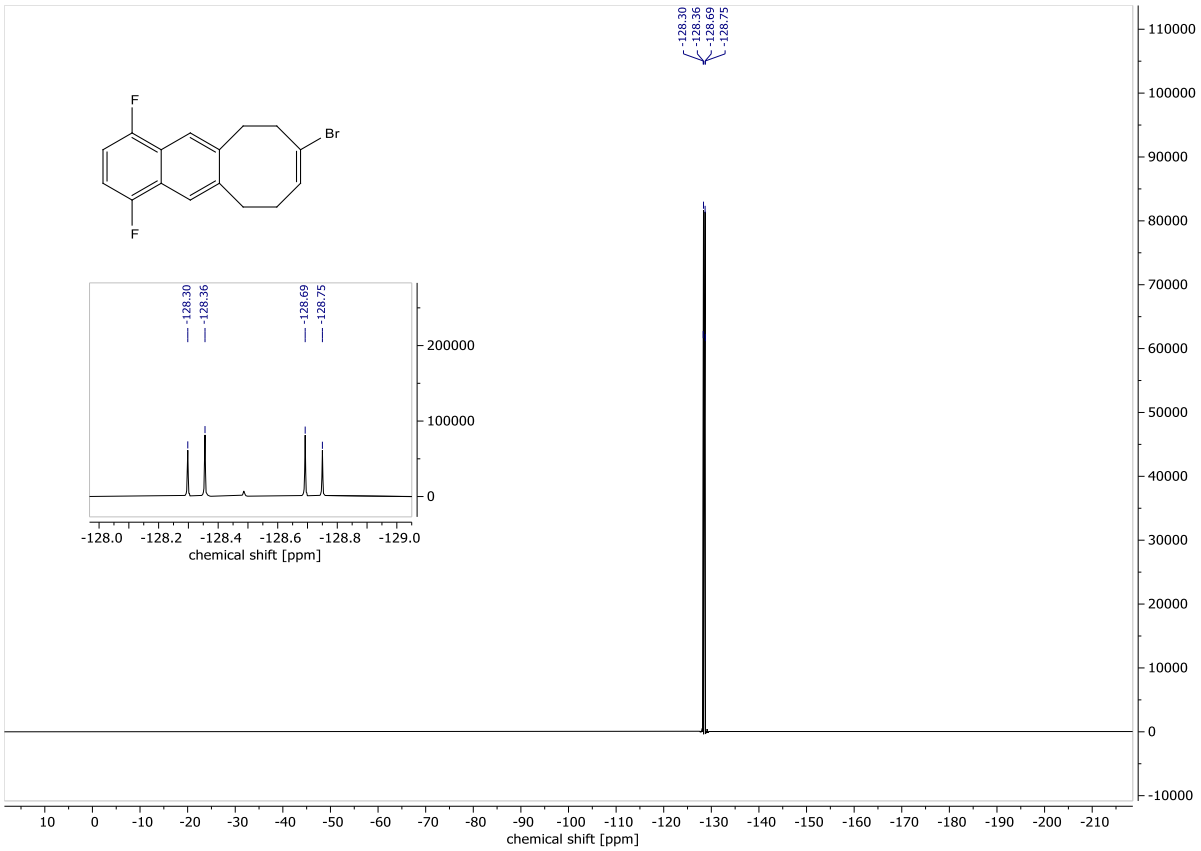

Figure S16. $^{19}F\{^{1}H\}$ (377 MHz) NMR spectrum ($CDCl_3$) of (*E*)-8-bromo-1,4-difluoro-6,7,10,11-tetrahydrocycloocta[*b*]naphthalene (**4b**).

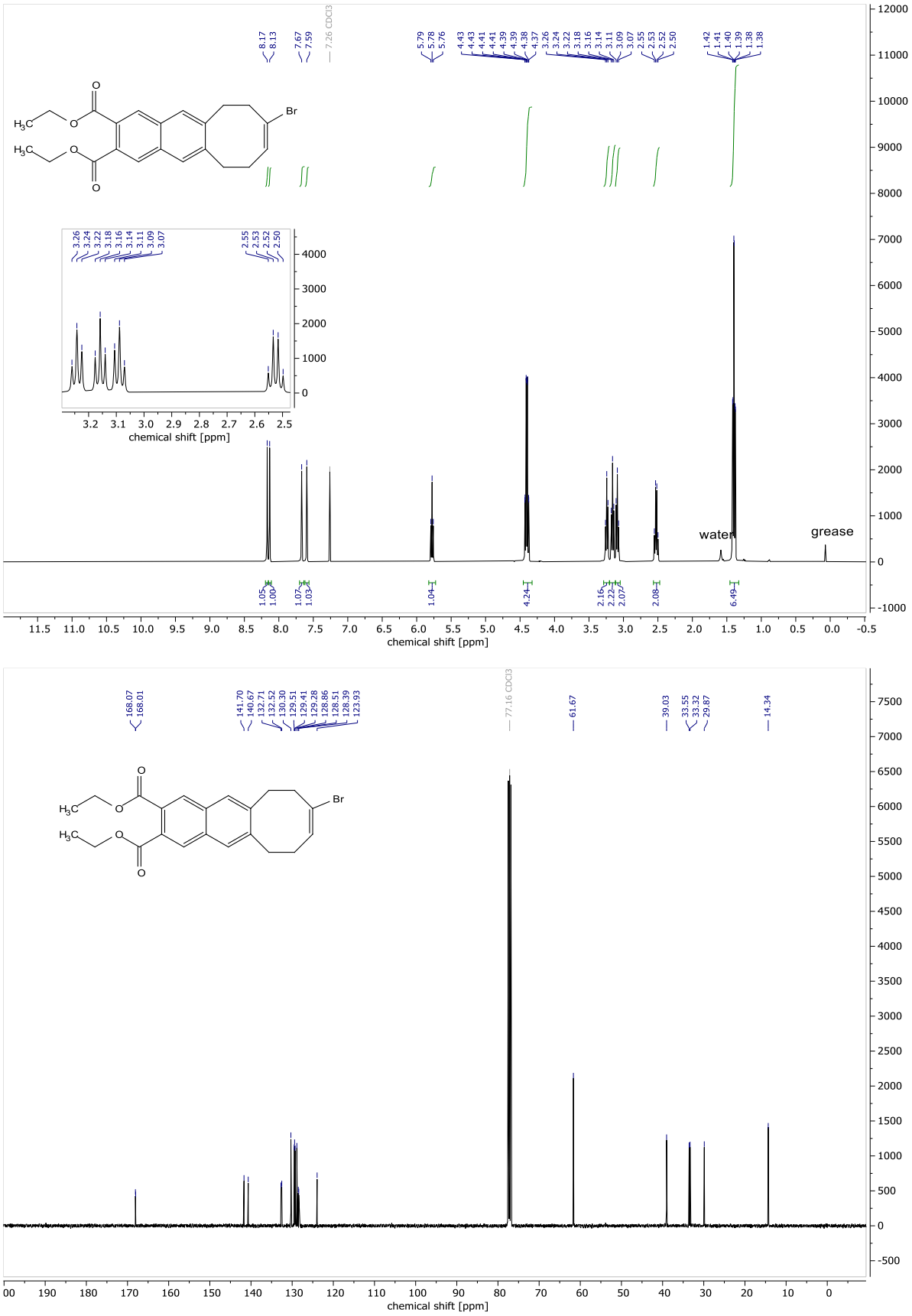

Figure S17. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra ($CDCl_3$) of diethyl (*E*)-8-bromo-6,7,10,11-tetrahydrocycloocta[*b*]naphthalene-2,3-dicarboxylate (**4c**).

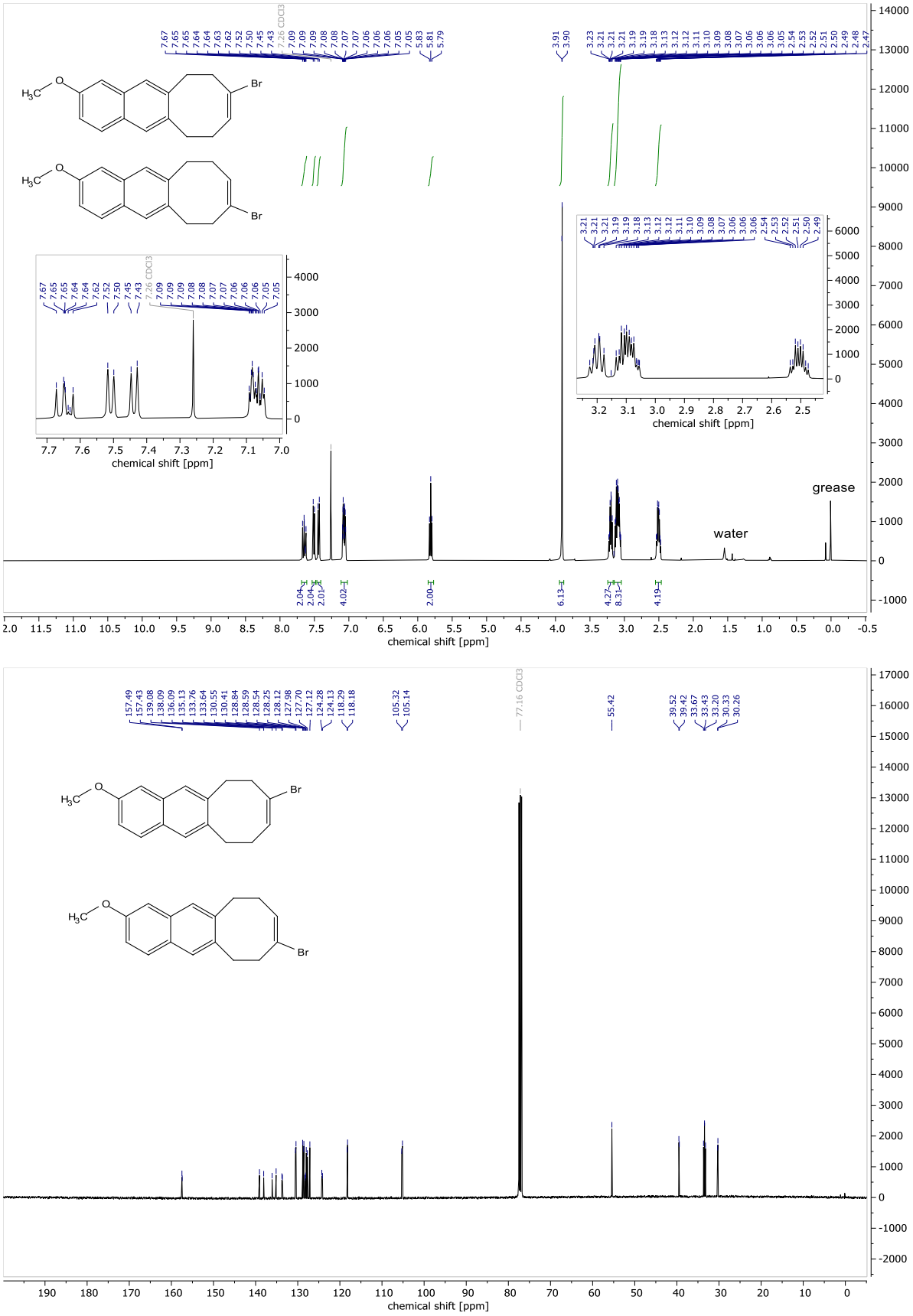

Figure S18. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra ($CDCl_3$) of (*E*)-8-bromo-2-methoxy-6,7,10,11-tetrahydrocycloocta[*b*]naphthalene and (*E*)-9-bromo-2-methoxy-6,7,10,11-tetrahydrocycloocta[*b*]naphthalene (**4d**).

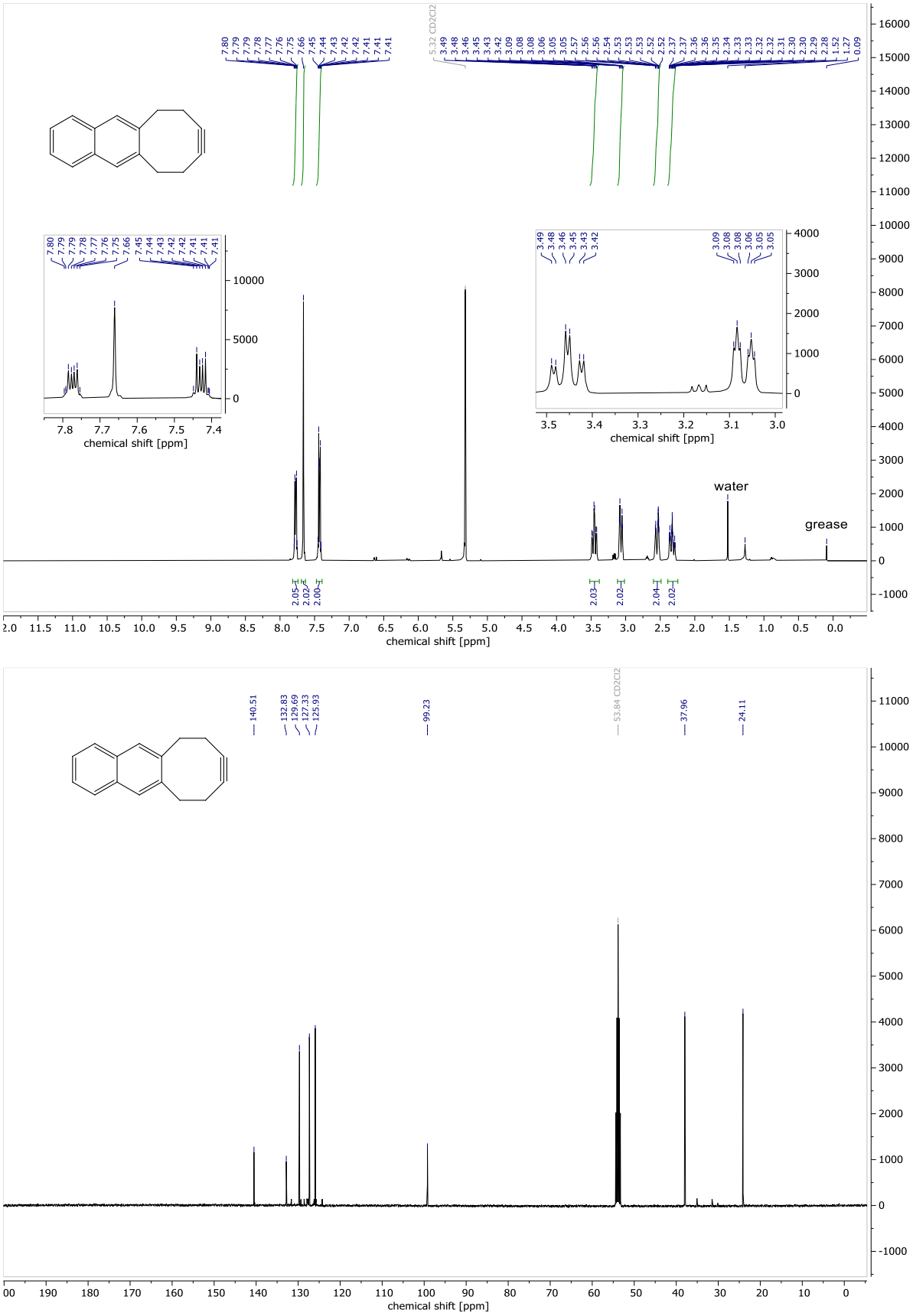

Figure S19. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra (CD_2Cl_2) of 8,9-didehydro-6,7,10,11-tetrahydrocycloocta[*b*]naphthalene (**6a**).

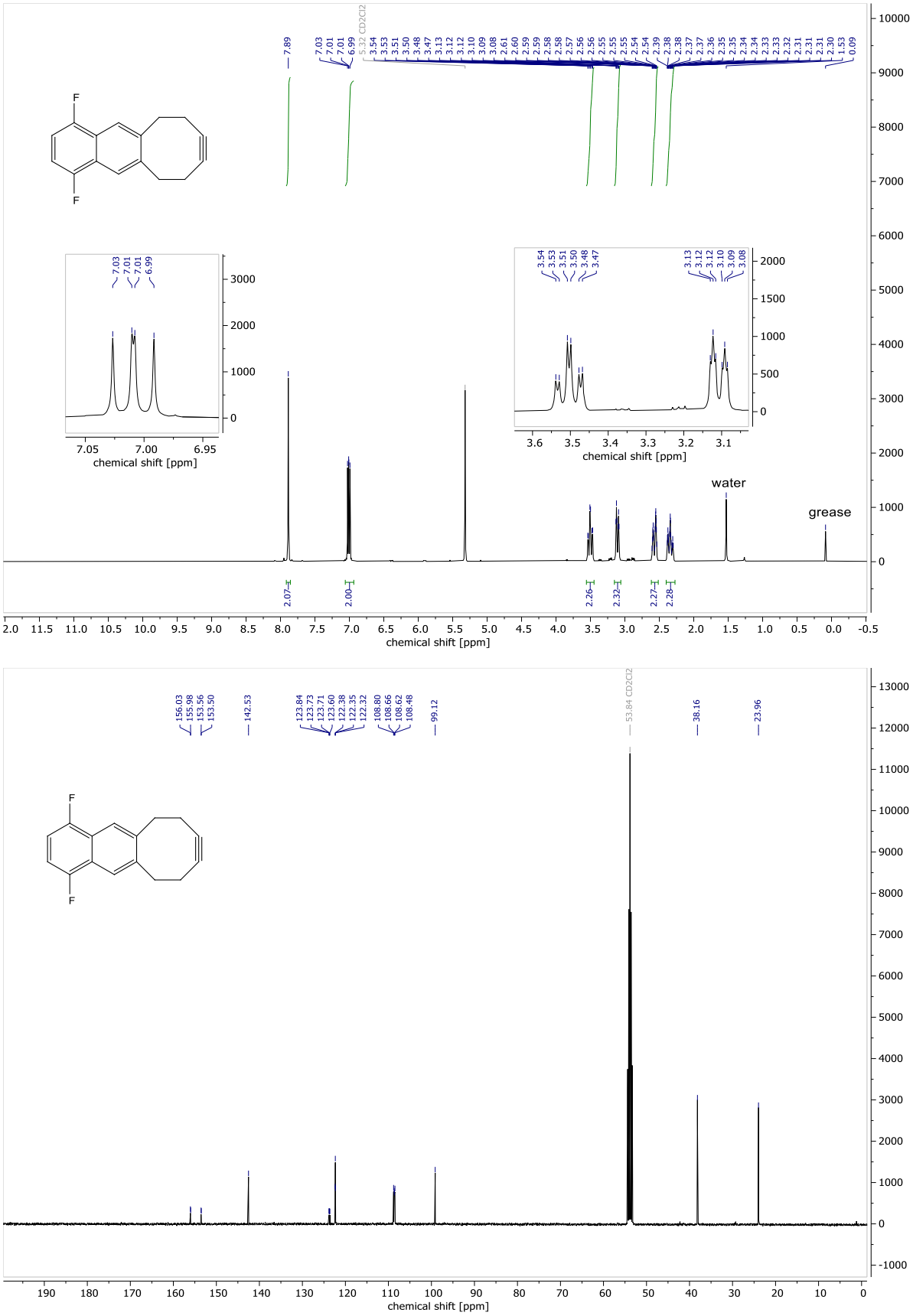

Figure S20. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra (CD_2Cl_2) of 1,4-difluoro-8,9-didehydro-6,7,10,11-tetrahydrocycloocta[*b*]naphthalene (**6b**).

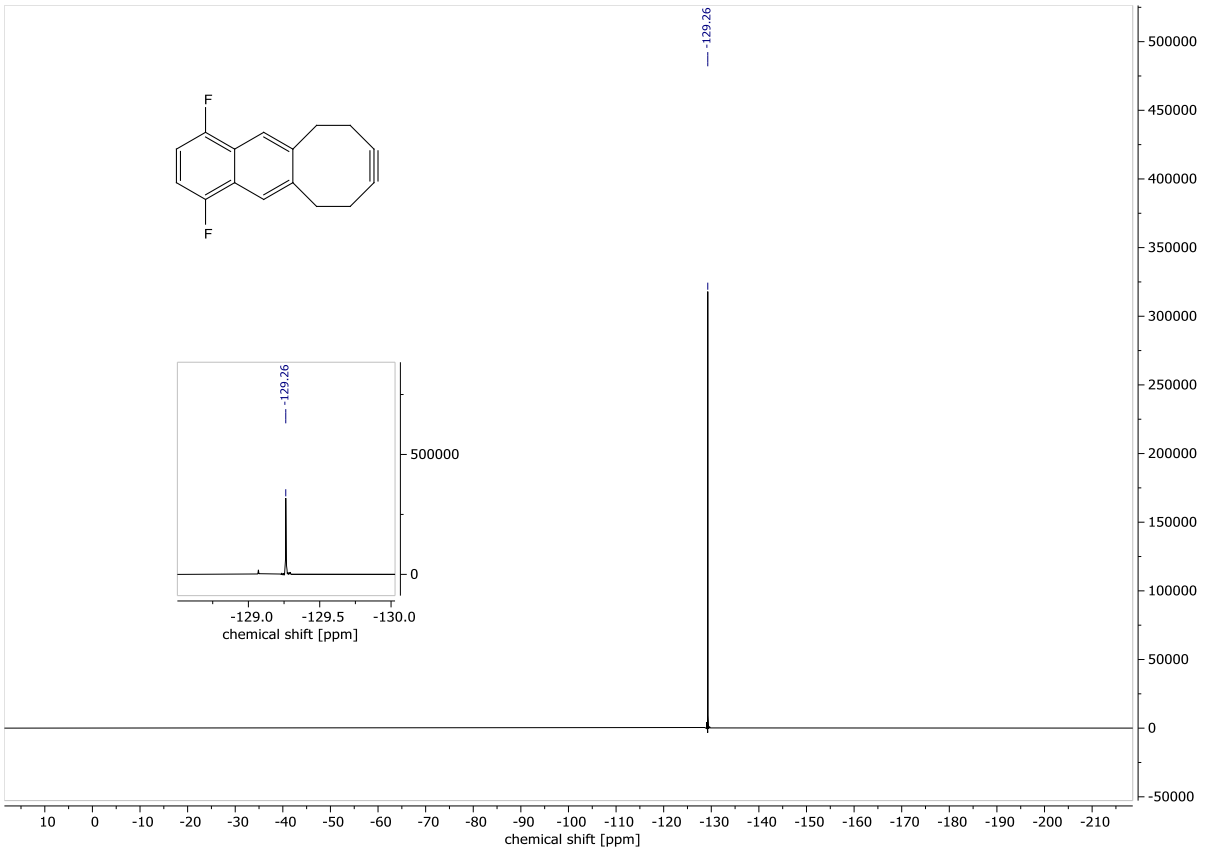

Figure S21. $^{19}F\{^{1}H\}$ (377 MHz) NMR spectrum (CD_2Cl_2) of 1,4-difluoro-8,9-didehydro-6,7,10,11-tetrahydrocycloocta[*b*]naphthalene (**6b**).

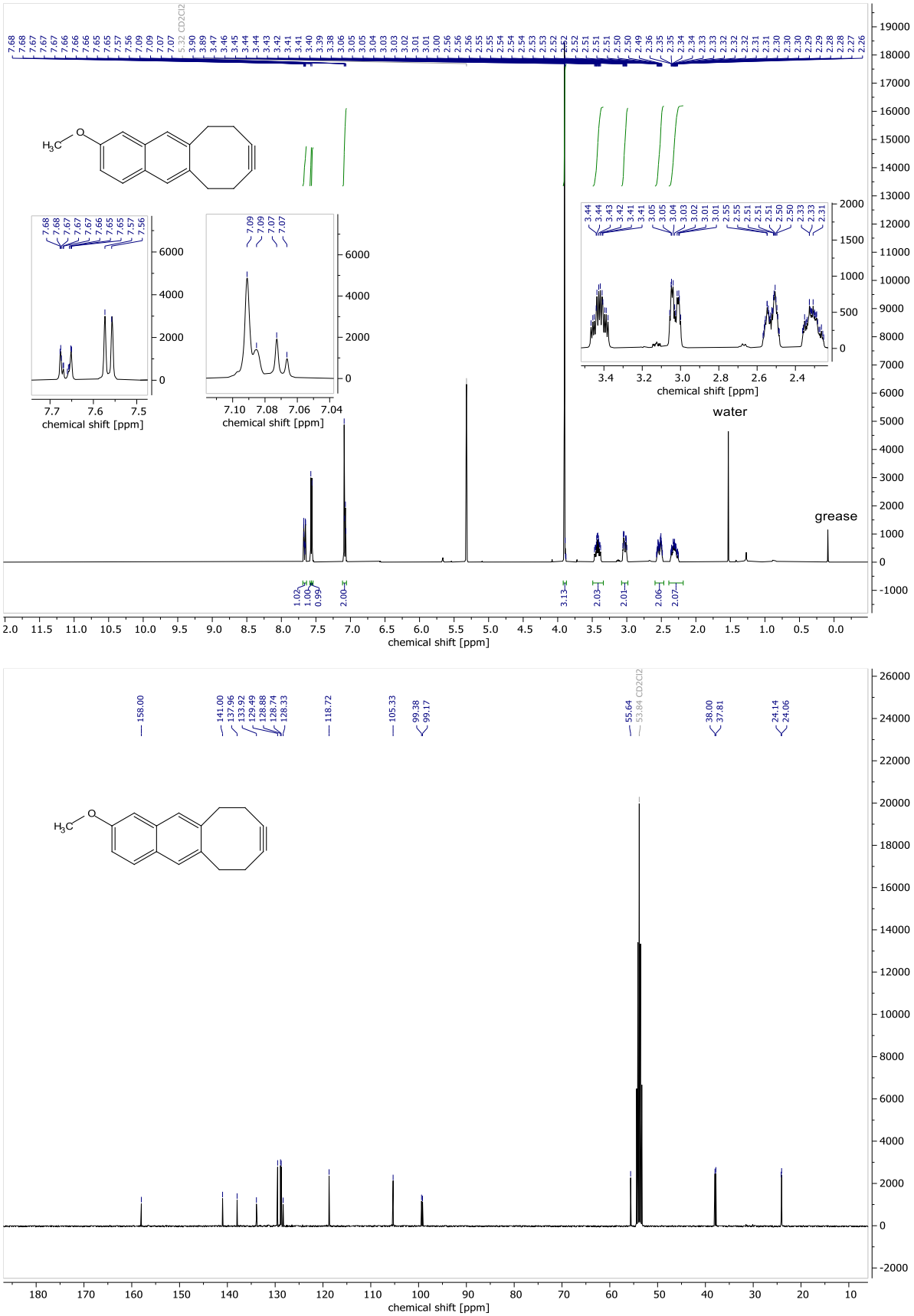

Figure S22. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra (CD_2Cl_2) of 2-methoxy-8,9-didehydro-6,7,10,11-tetrahydrocycloocta[*b*]naphthalene (**6d**).

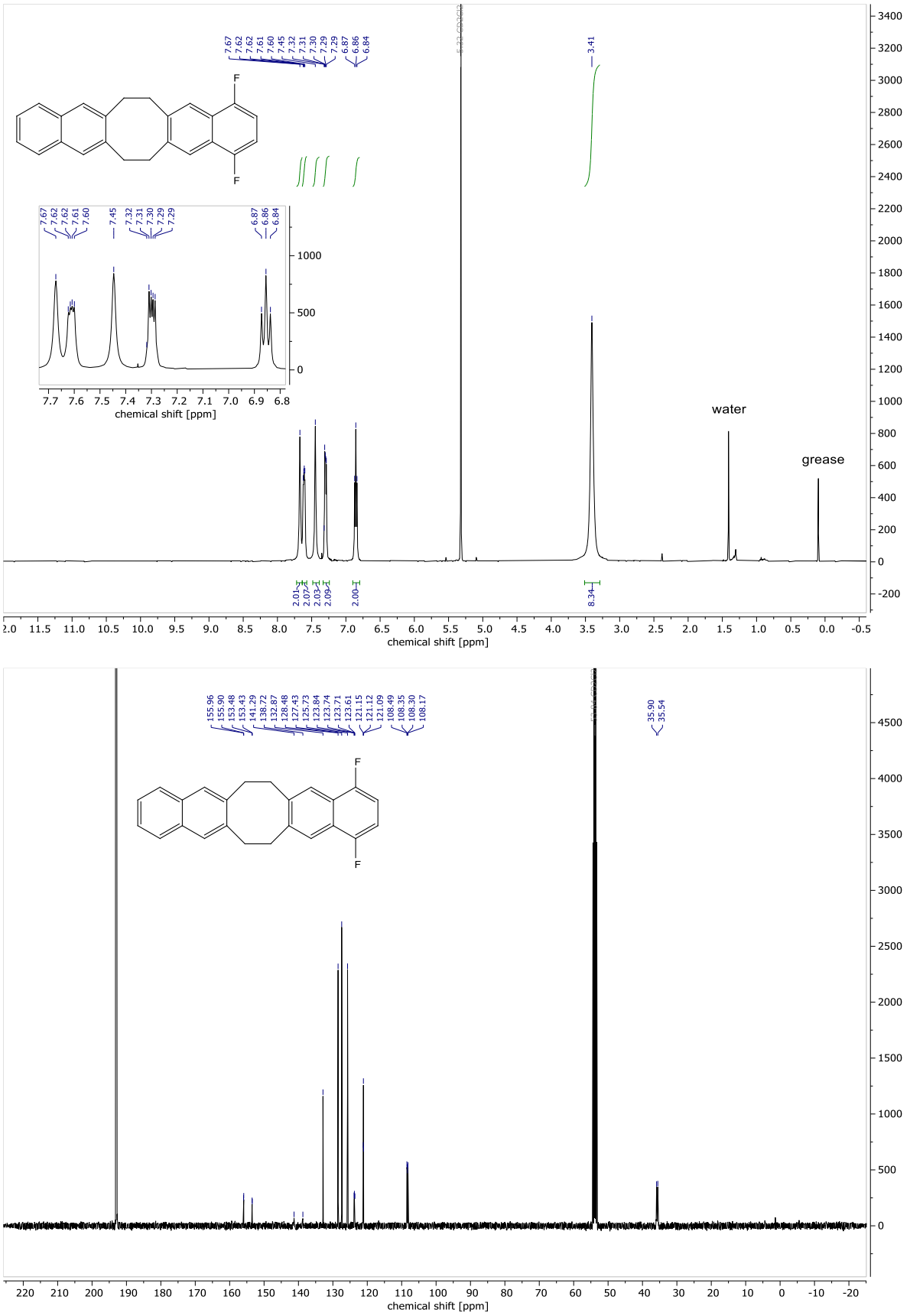

Figure S23. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra (CD_2Cl_2/CS_2) of 1,4-difluoro-6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b'*]dinaphthalene (**4ab**).

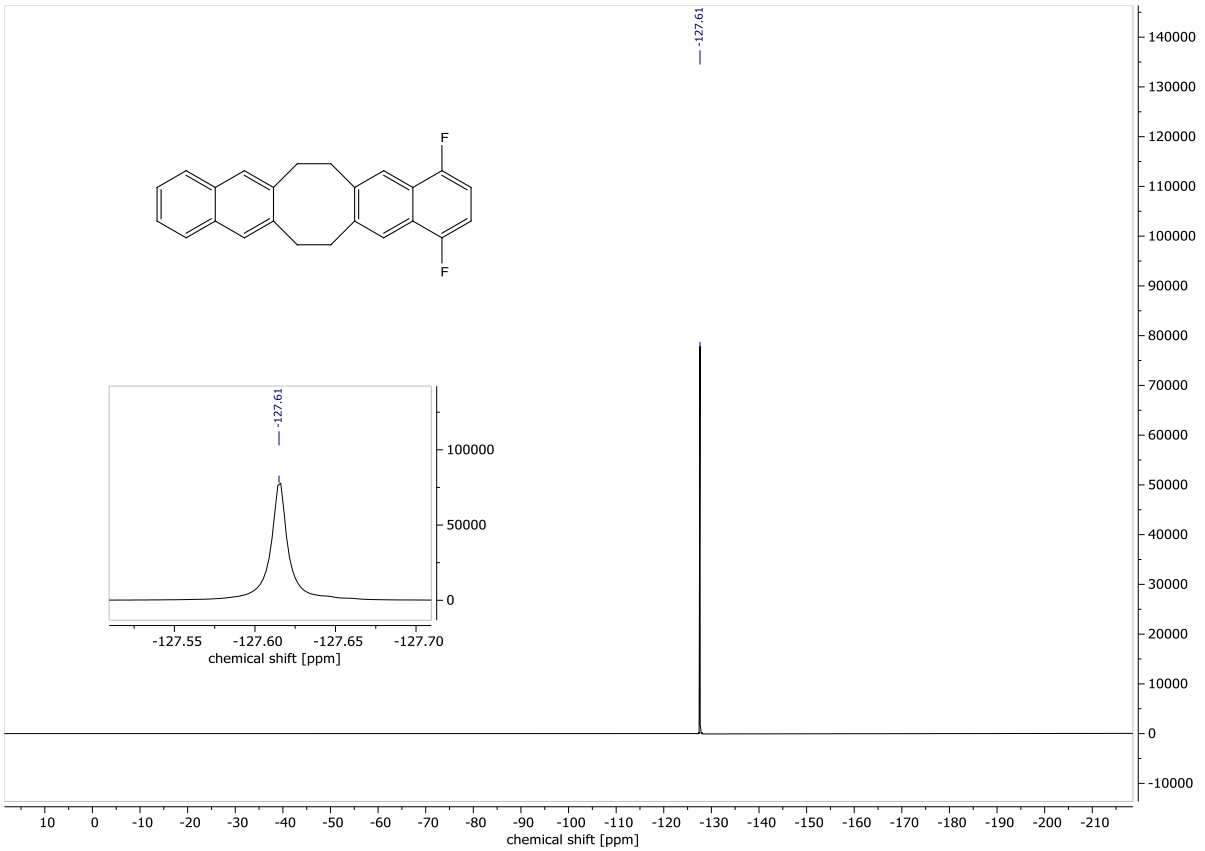

Figure S24. $^{19}F\{^{1}H\}$ (377 MHz) NMR spectrum (CD_2Cl_2/CS_2) of 1,4-difluoro-6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b'*]dinaphthalene (**4ab**).

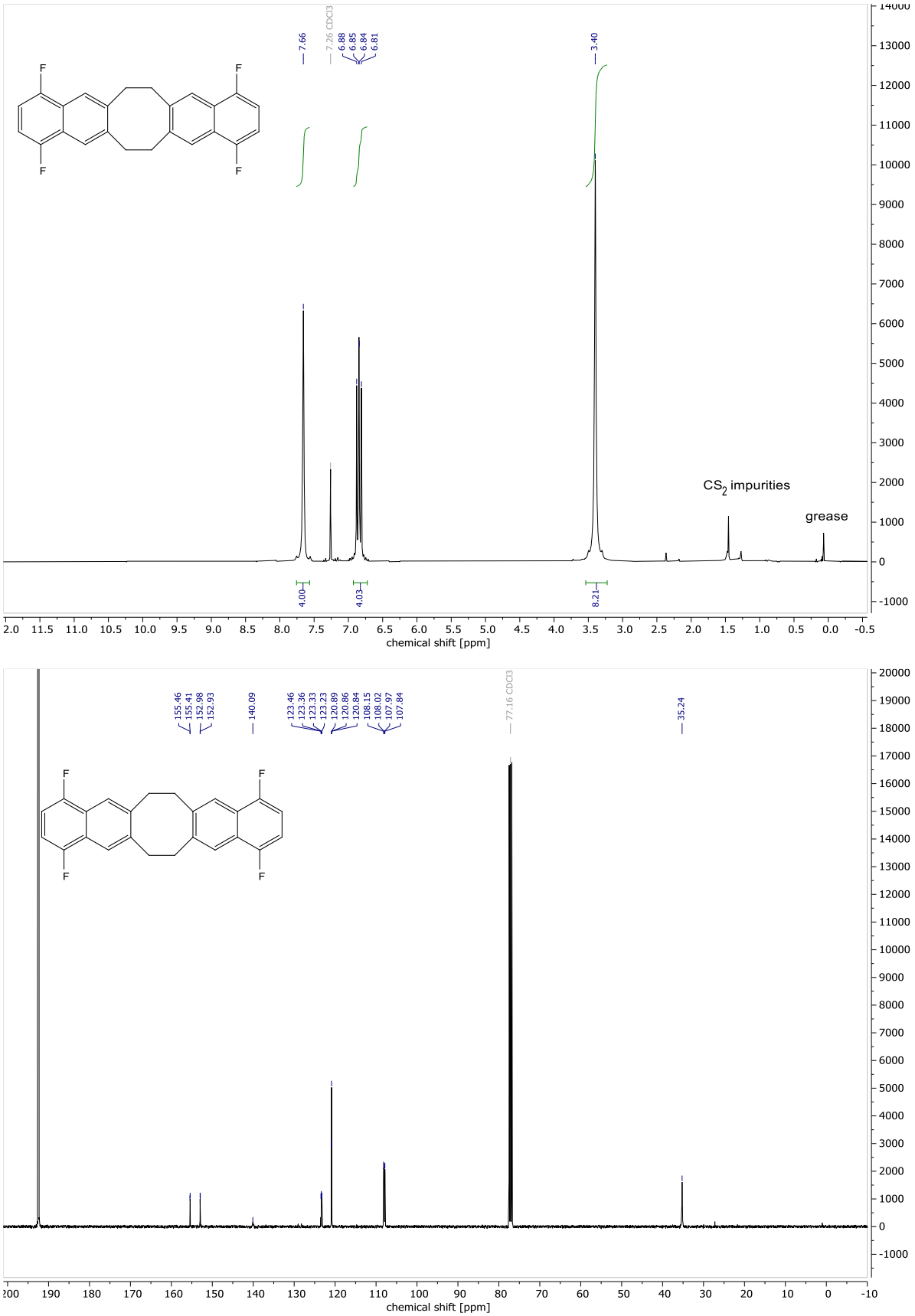

Figure S25. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra ($CDCl_3/CS_2$) of 1,4,9,12-tetrafluoro-6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b'*]dinaphthalene (**4bb**).

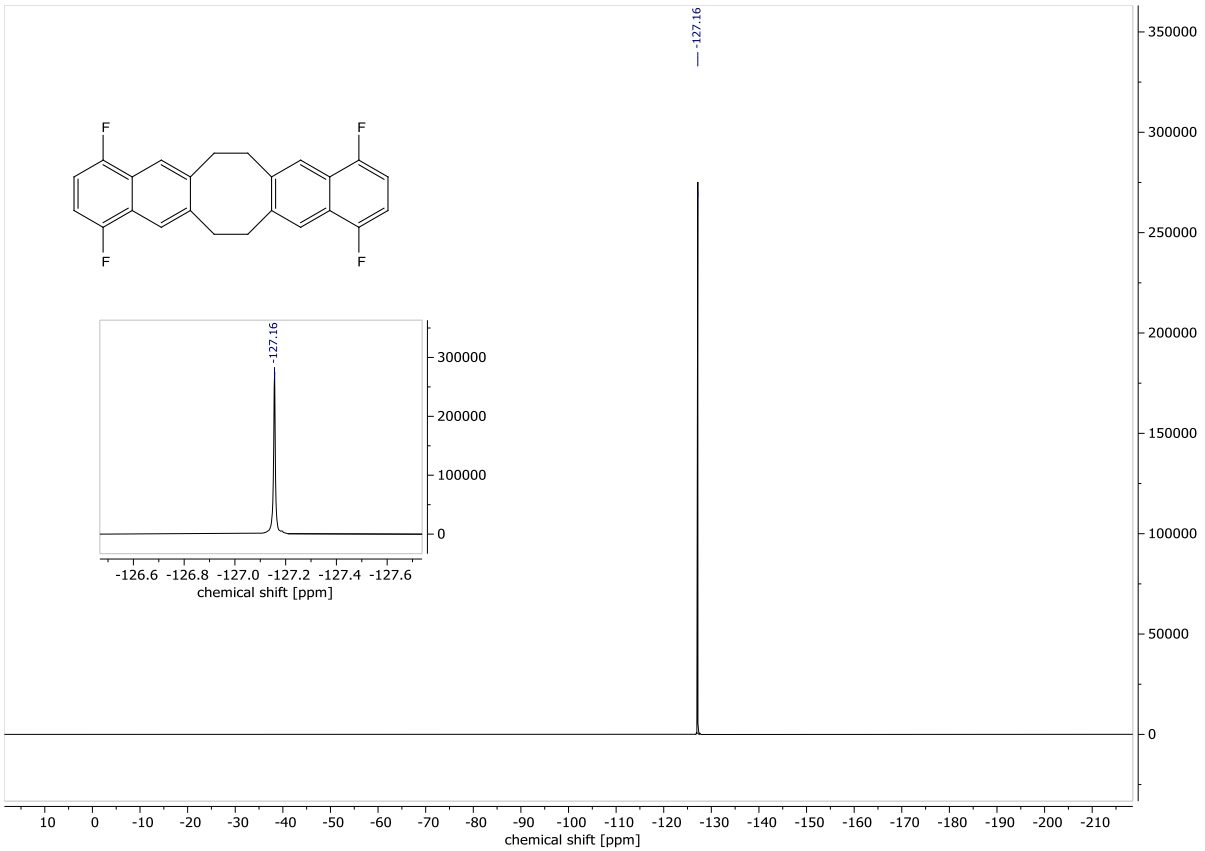

Figure S26. $^{19}F\{^{1}H\}$ (377 MHz) NMR spectrum ($CDCl_3/CS_2$) of 1,4,9,12-tetrafluoro-6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b'*]dinaphthalene (**4bb**).

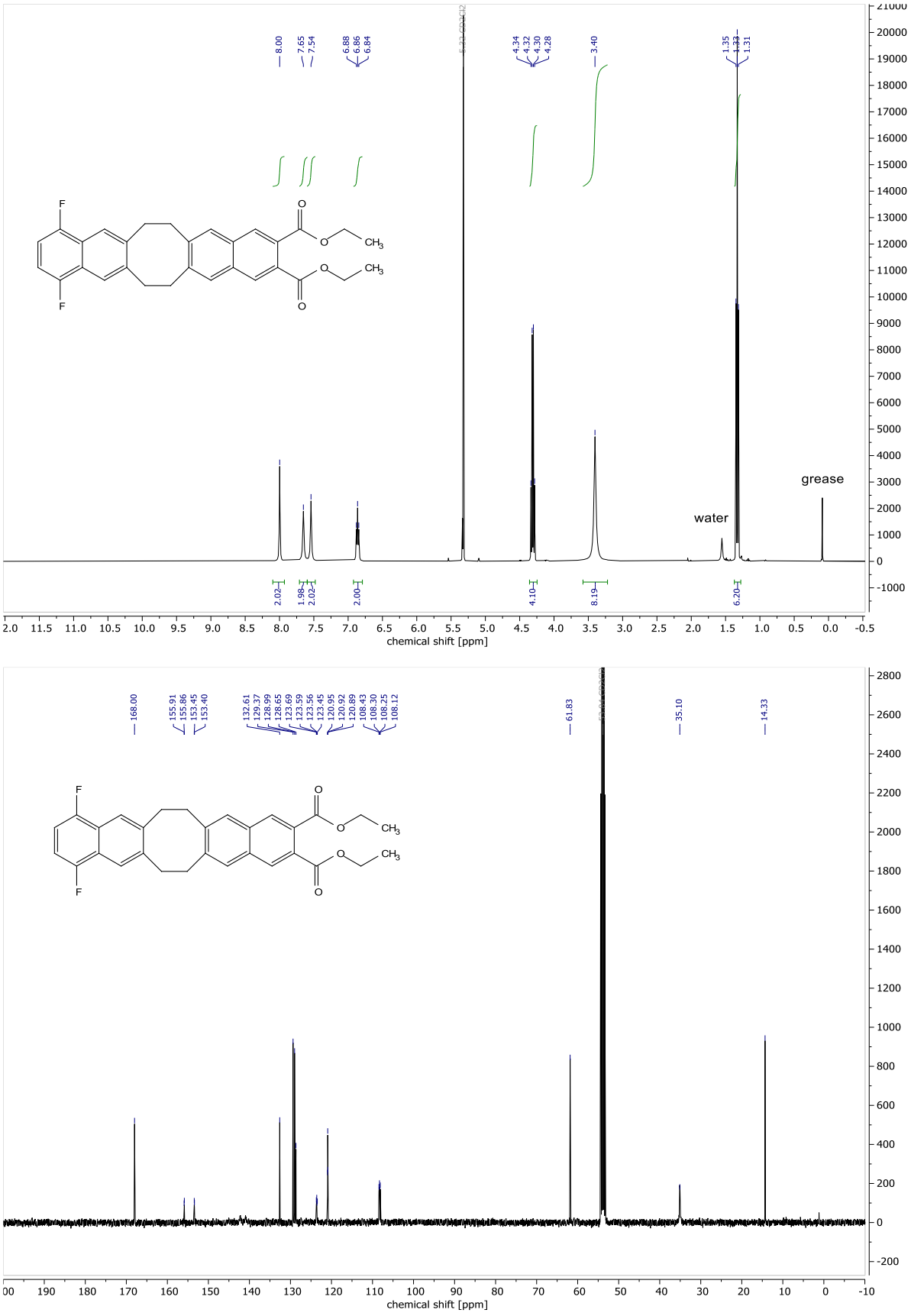

Figure S27. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra (CD_2Cl_2) of diethyl 10-methoxy-6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b'*]dinaphthalene-2,3-dicarboxylate (**4bc**).

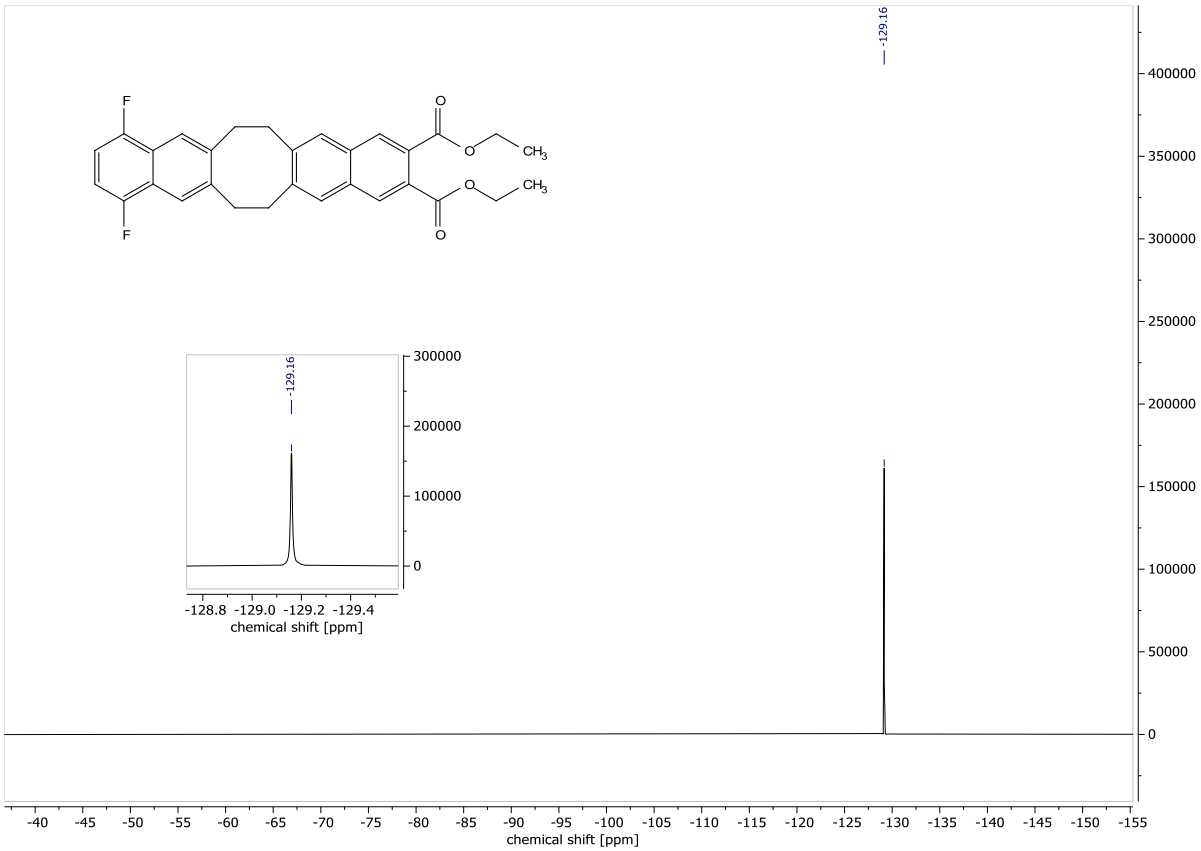

Figure S28. $^{19}F\{^{1}H\}$ (377 MHz) NMR spectrum (CD_2Cl_2) of diethyl 10-methoxy-6,7,14,15-tetrahydro-cycloocta[1,2-*b*:5,6-*b'*]dinaphthalene-2,3-dicarboxylate (**4bc**).

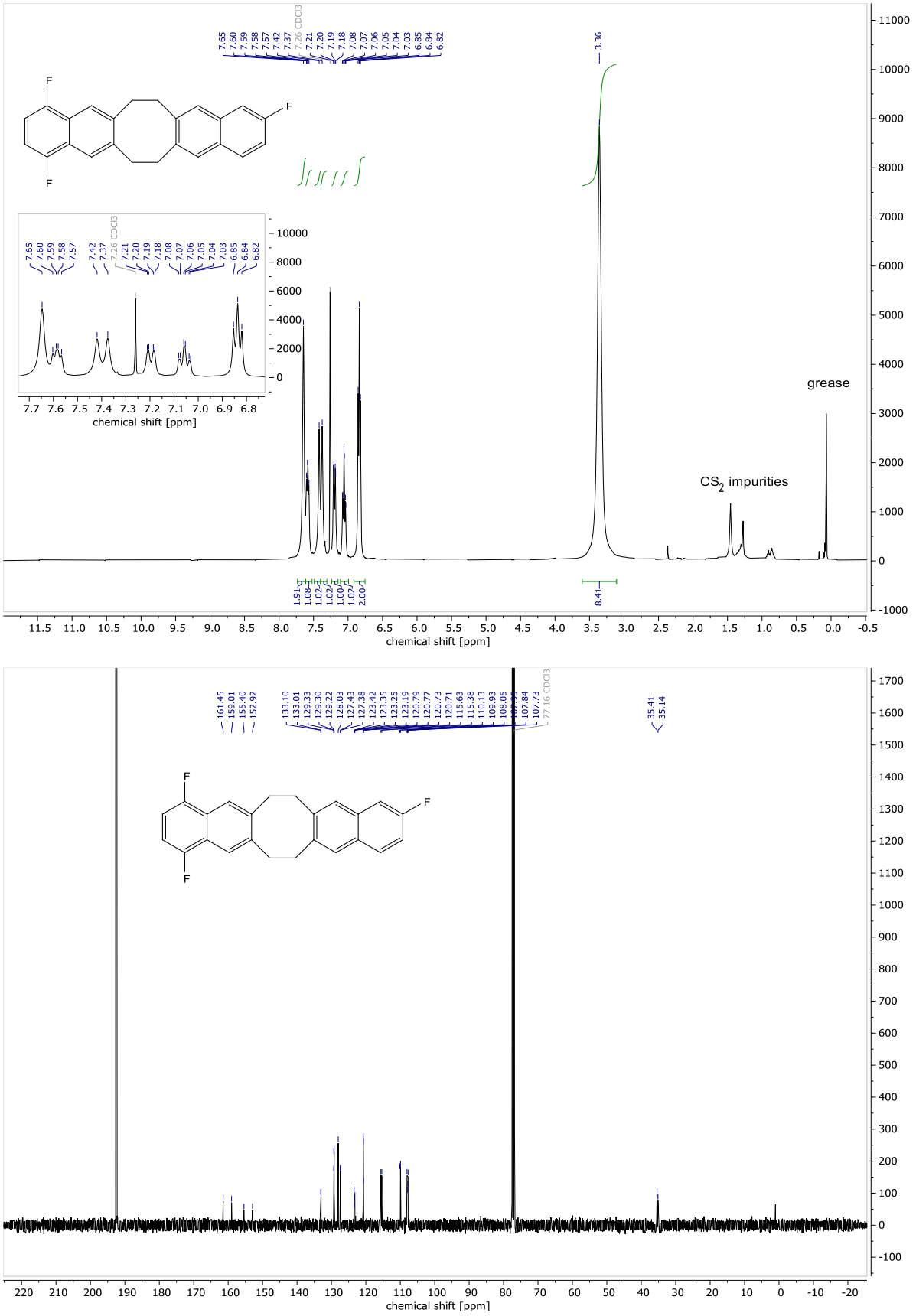

Figure S29. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra ($CDCl_3/CS_2$) of 1,4,10-trifluoro-6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b'*]dinaphthalene (**4be**).

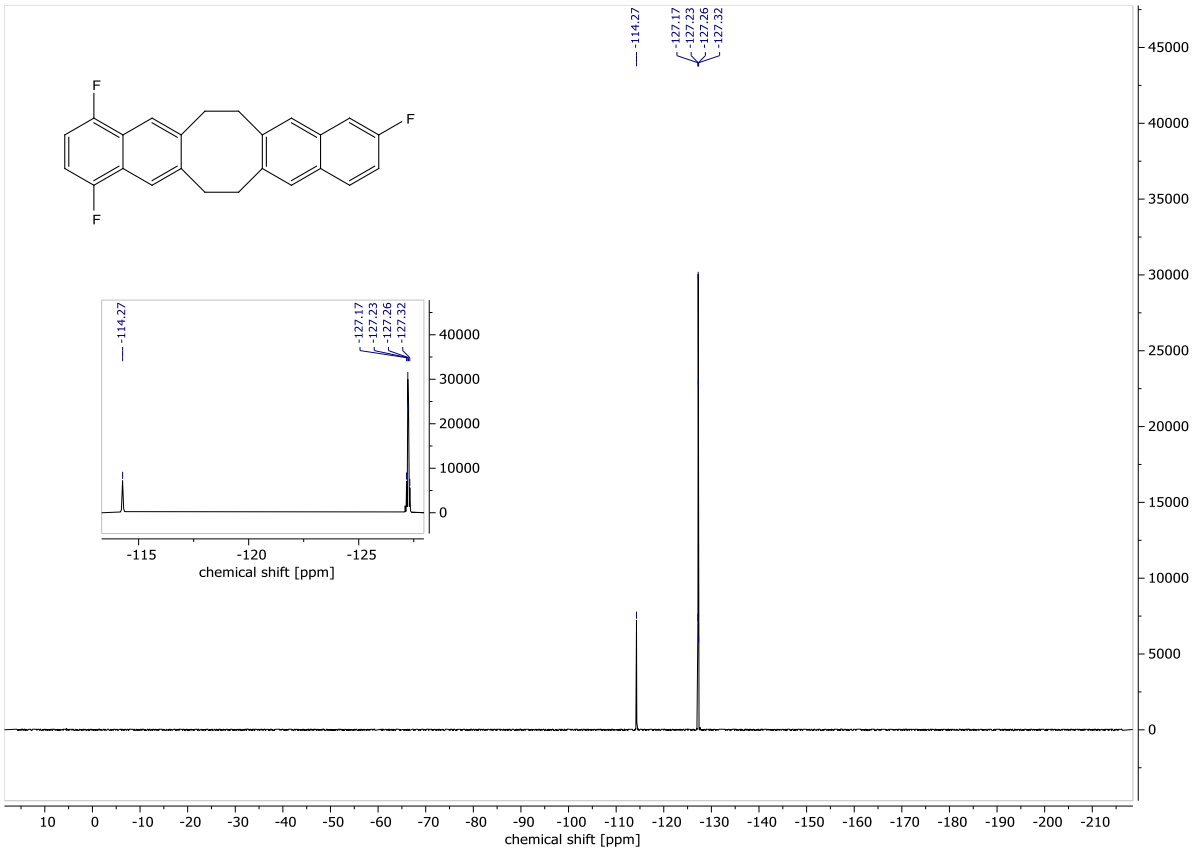

Figure S30. $^{19}F\{^{1}H\}$ (377 MHz) NMR spectrum ($CDCl_3/CS_2$) of 1,4,10-trifluoro-6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b'*]dinaphthalene (**4be**).

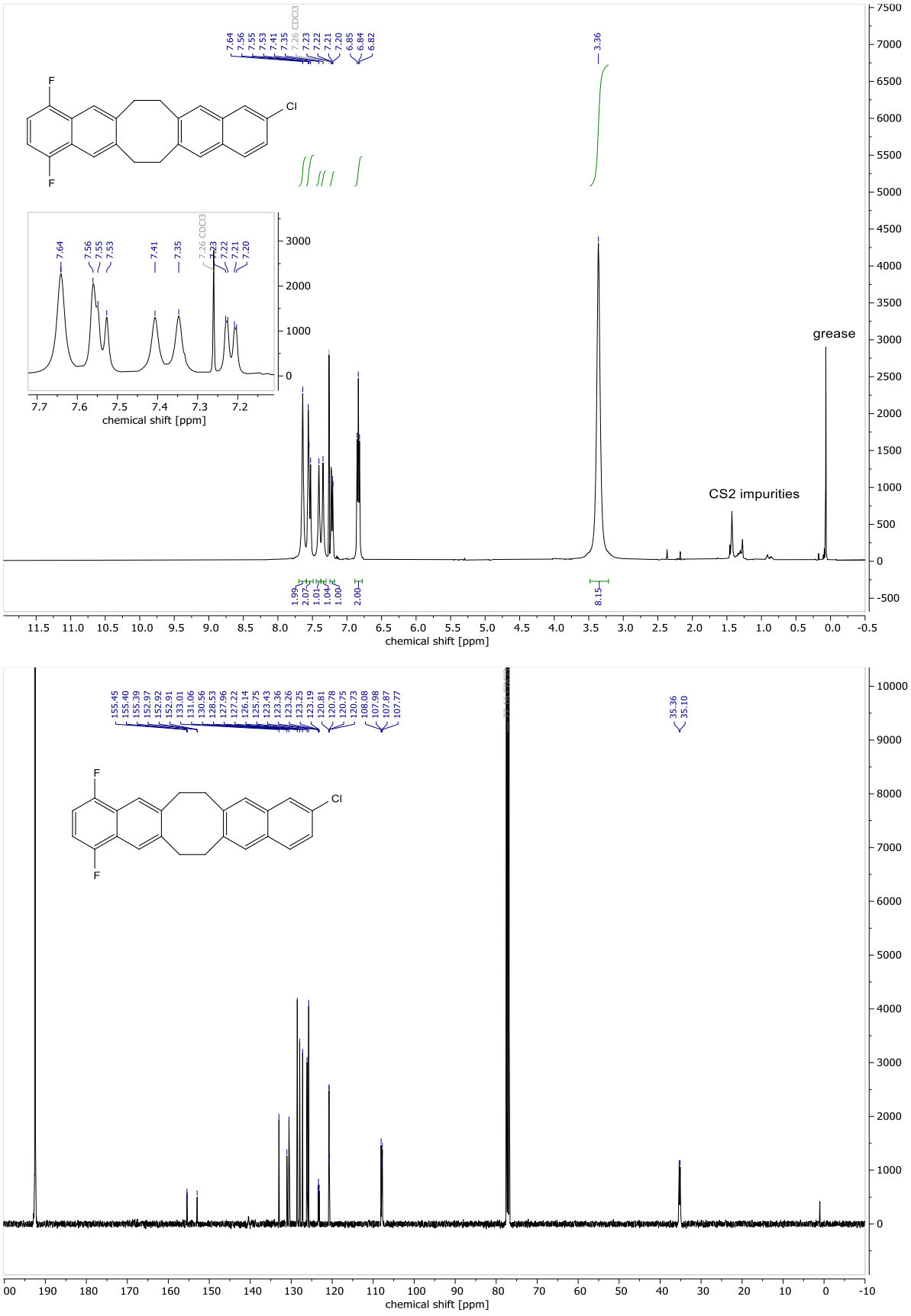

Figure S31. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra ($CDCl_3/CS_2$) of 10-chloro-1,4-difluoro-6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b'*]dinaphthalene (**4bf**).

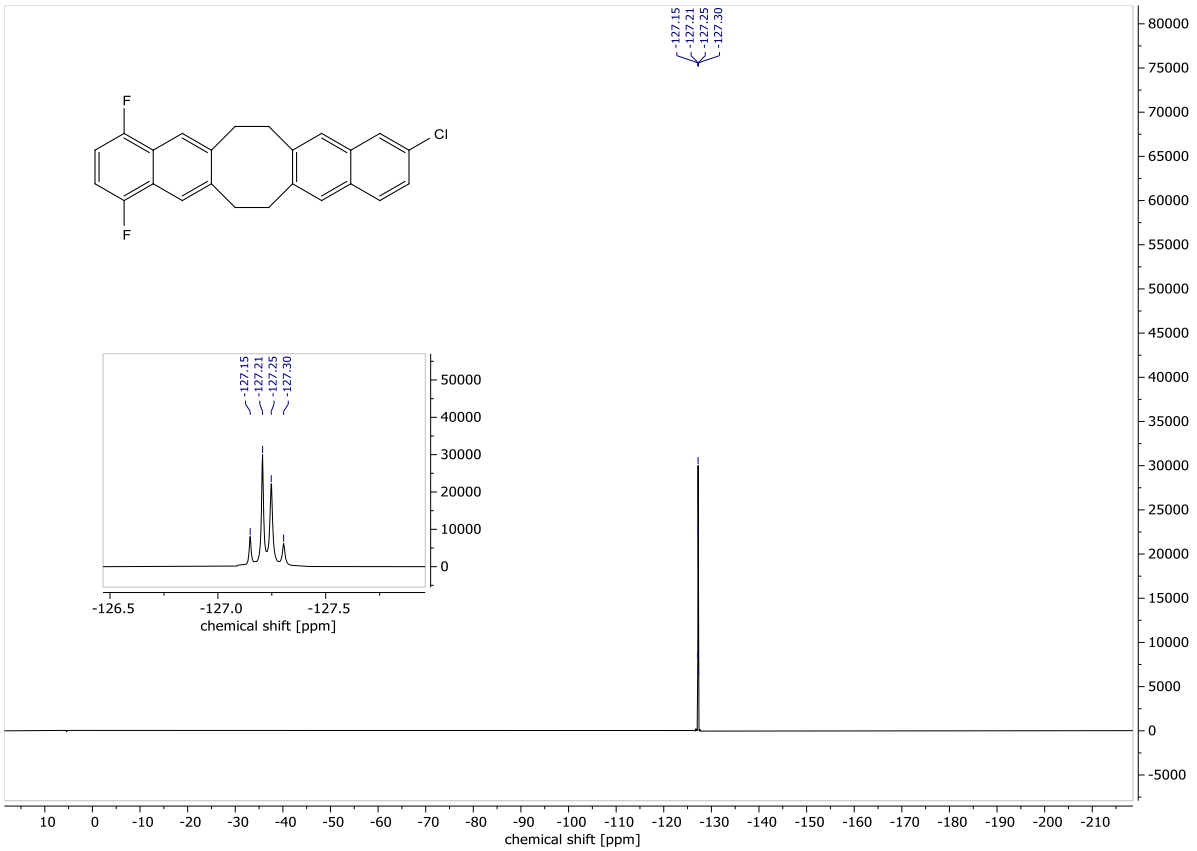

Figure S32. $^{19}F\{^{1}H\}$ (377 MHz) NMR spectrum ($CDCl_3/CS_2$) of 10-chloro-1,4-difluoro-6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b'*]dinaphthalene (4**bf**).

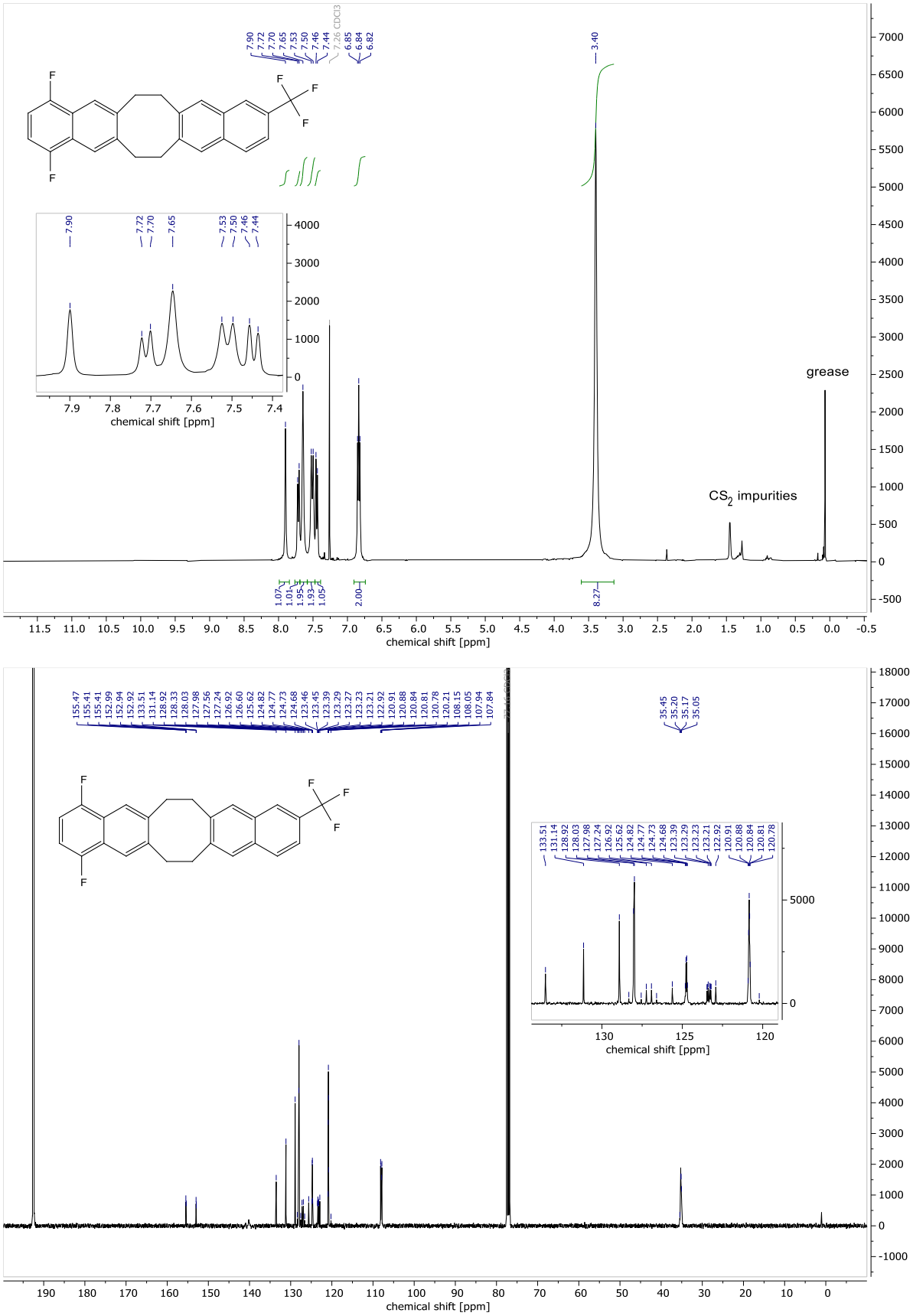

Figure S33. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra ($CDCl_3/CS_2$) of 1,4-difluoro-10-(trifluoromethyl)-6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b'*]dinaphthalene (**4bg**).

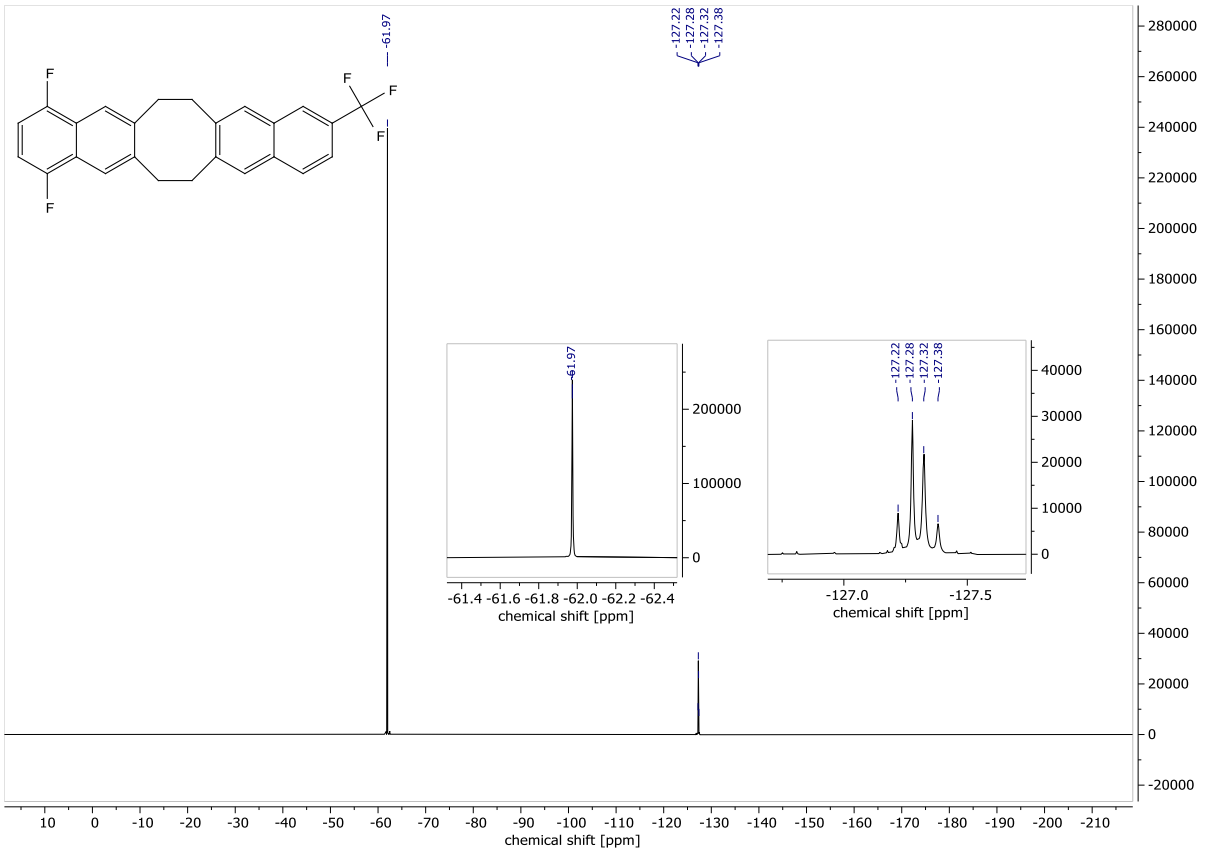

Figure S34. $^{19}F\{^{1}H\}$ (377 MHz) NMR spectrum ($CDCl_3/CS_2$) of 1,4-difluoro-10-(trifluoromethyl)-6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b'*]dinaphthalene (**4bg**).

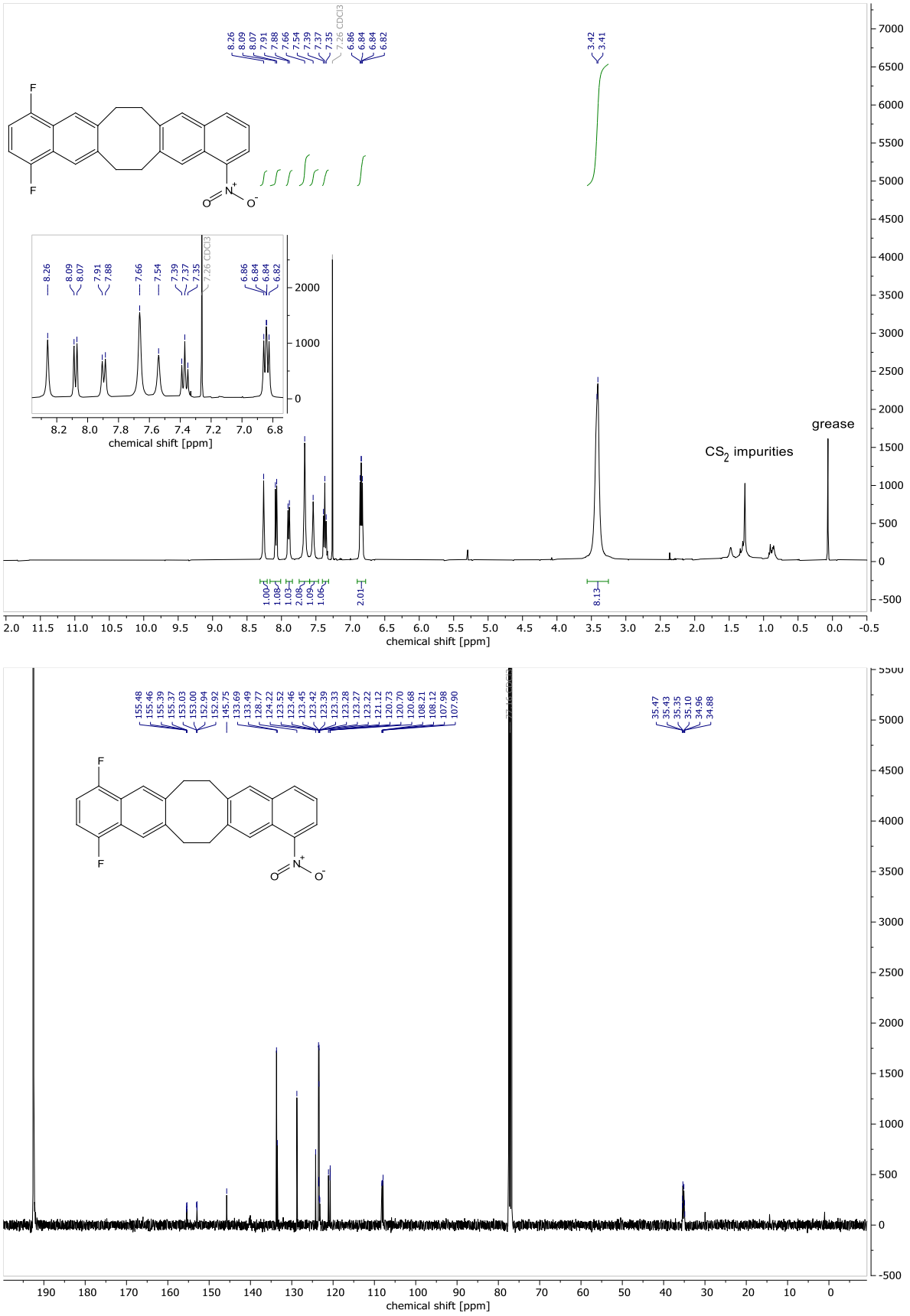

Figure S35. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra ($CDCl_3/CS_2$) of 1,4-difluoro-9-nitro-6,7,14,15-tetrahydrocycloocta[1,2-b:5,6-b']dinaphthalene (**4bh**).

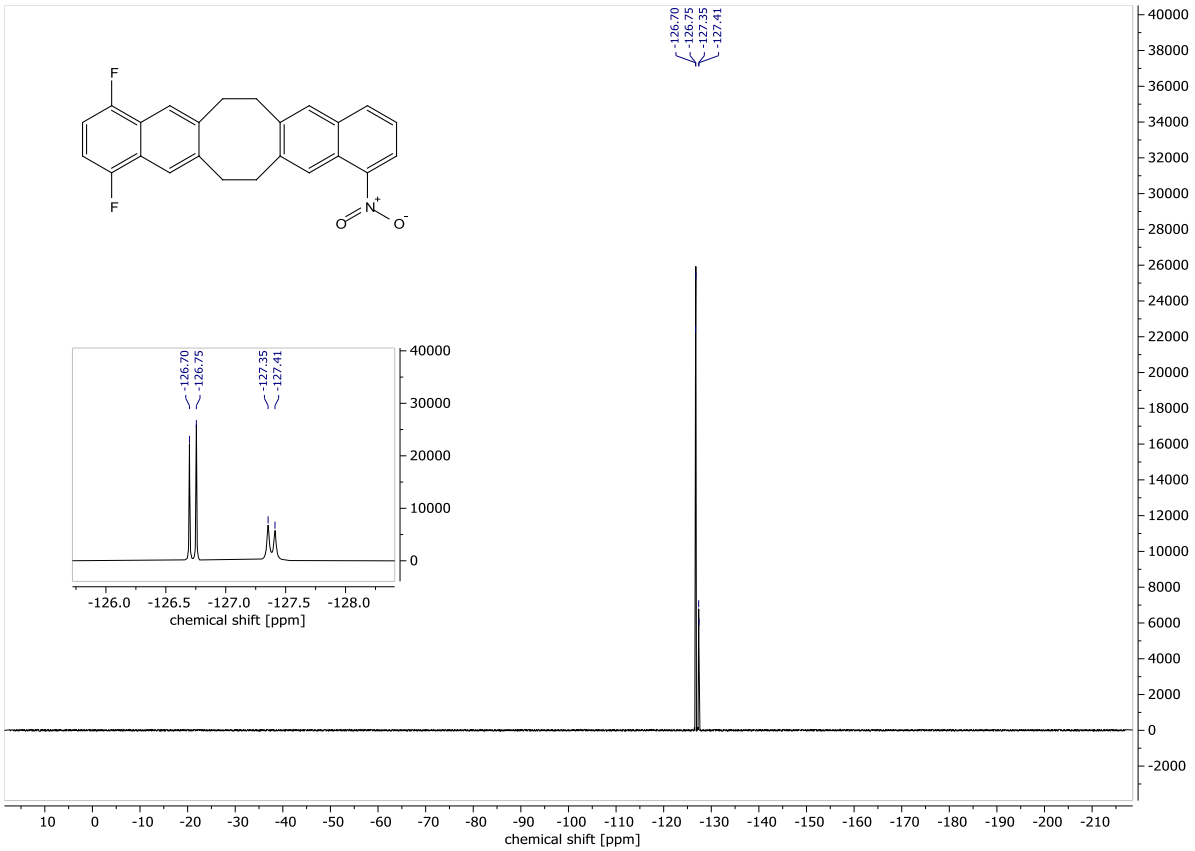

Figure S36. $^{19}F\{^{1}H\}$ (377 MHz) NMR spectrum ($CDCl_3/CS_2$) of 1,4-difluoro-9-nitro-6,7,14,15-tetrahydrocycloocta[1,2-b:5,6-b']dinaphthalene (**4bh**).

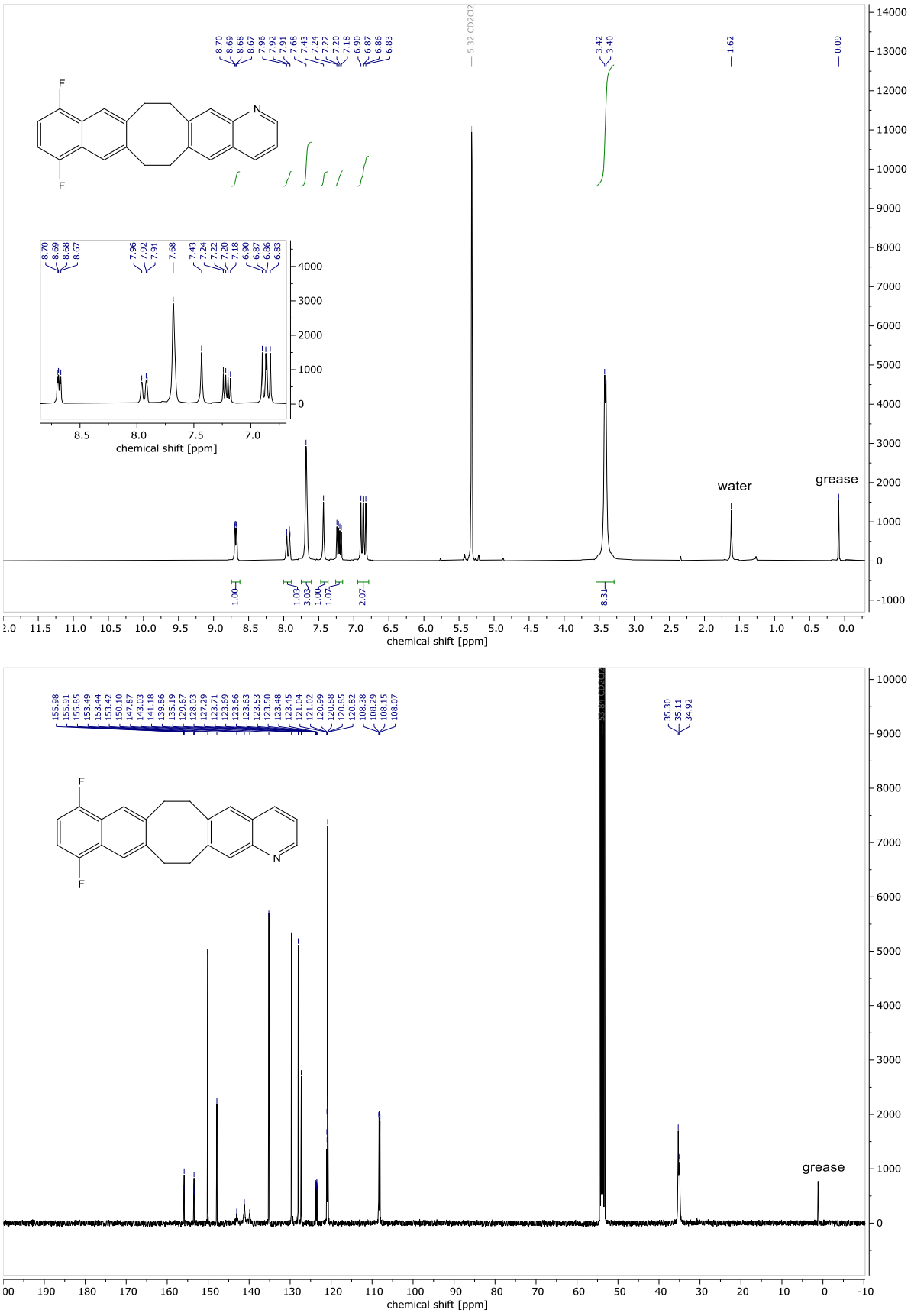

Figure S37. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra (CD_2Cl_2) of 9,12-difluoro-6,7,14,15-tetrahydronaphtho[2',3':5,6]cycloocta[1,2-*g*]quinoline (**4bi**).

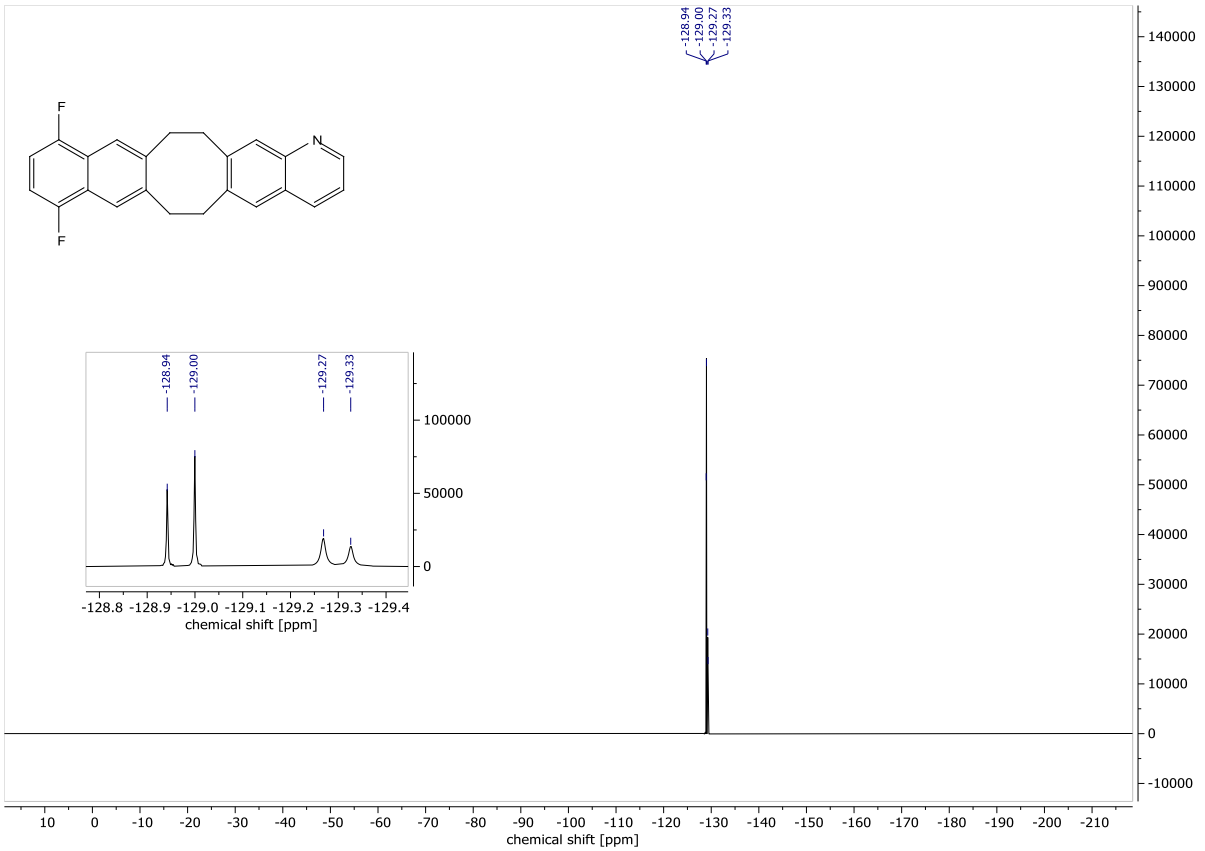

Figure S38. $^{19}F\{^{1}H\}$ (377 MHz) NMR spectrum (CD_2Cl_2) of 9,12-difluoro-6,7,14,15-tetrahydronaphtho[2',3':5,6]cycloocta[1,2-*g*]quinoline (**4bi**).

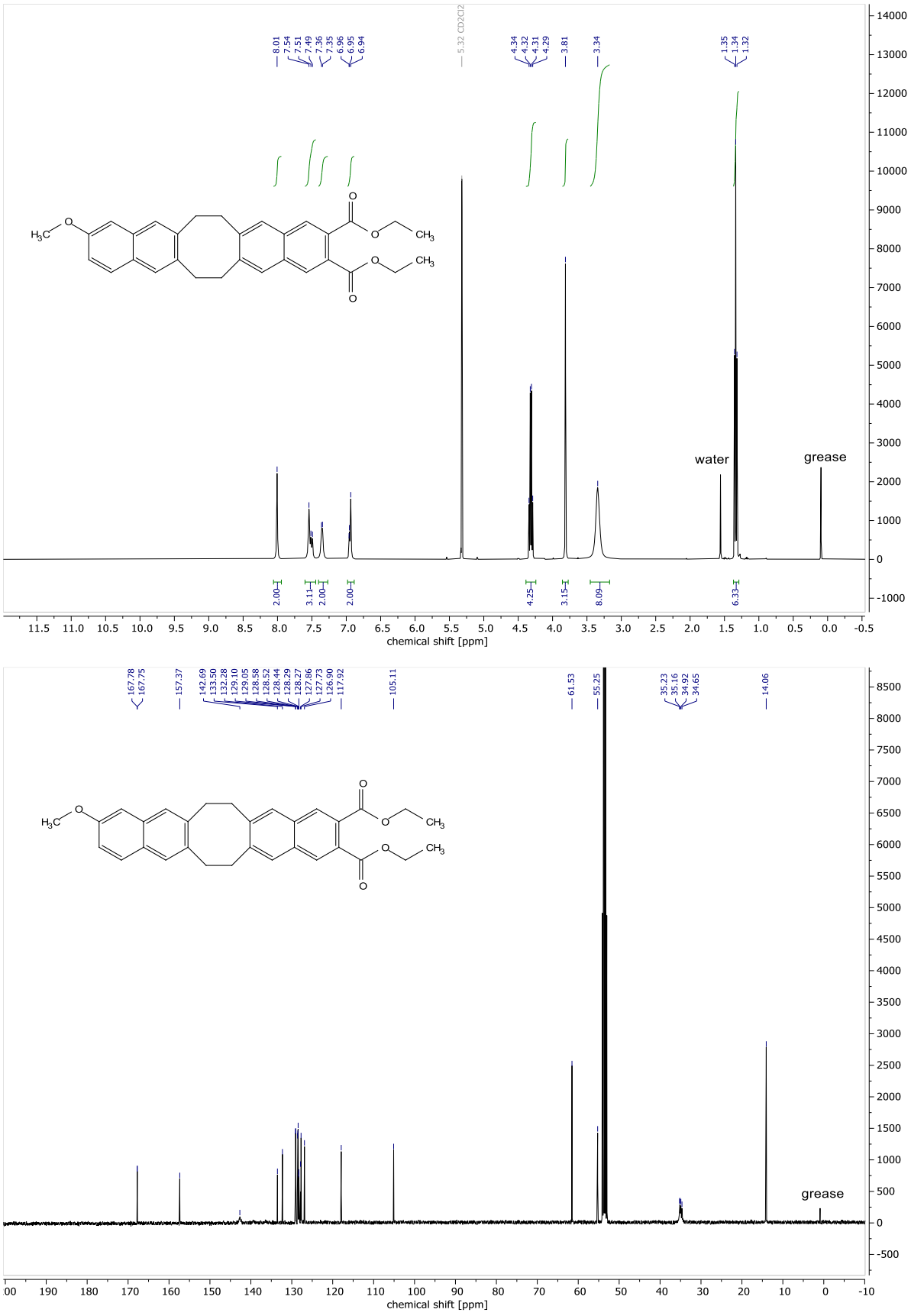

Figure S39. ^{1}H (400 MHz) (top) and $^{13}C\{^{1}H\}$ (101 MHz) (bottom) NMR spectra (CD_2Cl_2) of diethyl 10-methoxy-6,7,14,15-tetrahydro-cycloocta[1,2-*b*:5,6-*b'*]dinaphthalene-2,3-dicarboxylate (**4dc**).

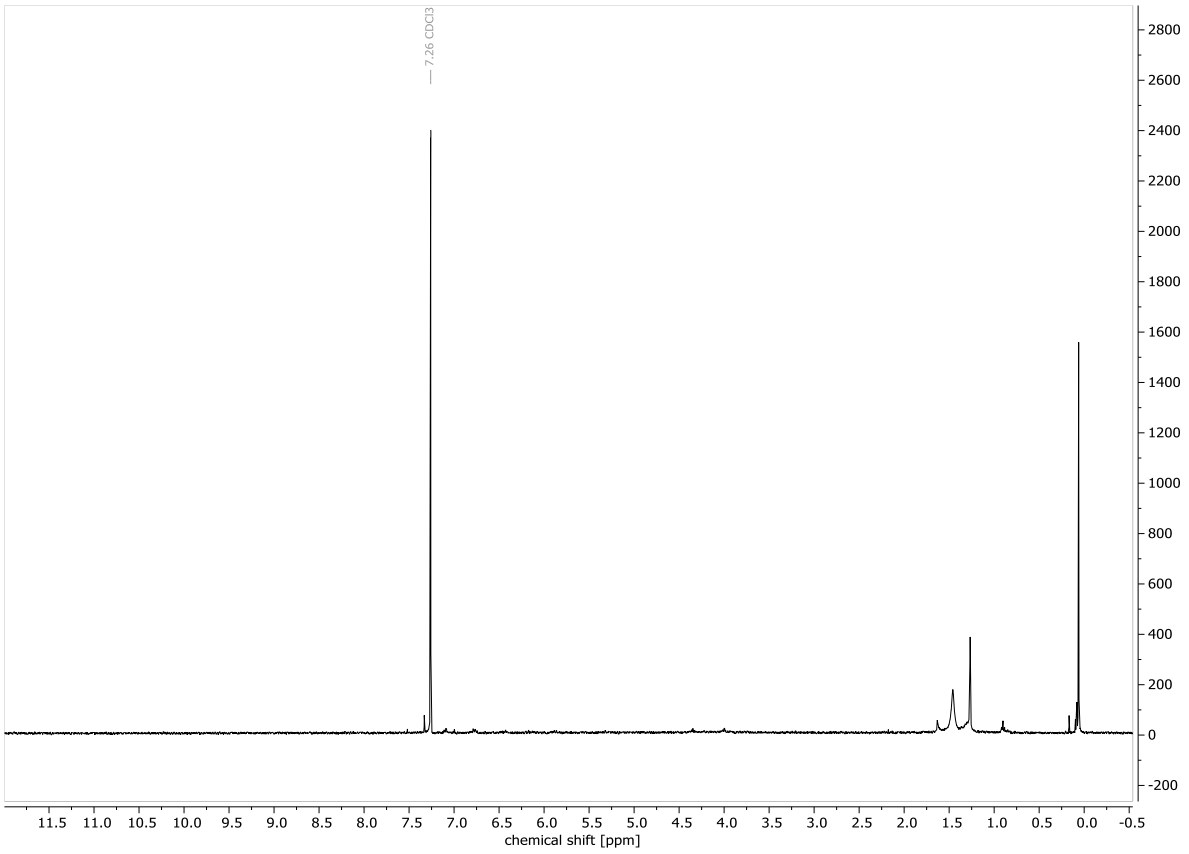

Figure S40. ^{1}H (400 MHz) NMR spectrum of a 1:1 mixture of $CDCl_3$ and CS_2 as a reference for the other NMR spectra using the same solvent system.

5 XRD analysis

5.1 General crystallographic experimental details

Suitable single crystals for X-ray structure determination were selected and transferred in protective perfluoropolyether oil on a microscope slide. The selected and mounted crystals were transferred to the cold gas steam on the diffractometer. The diffraction data were obtained at 100 K on a Bruker D8 three circle diffractometer, equipped with a PHOTON 100 CMOS detector and a IμS microfocus sources with Quazar mirror optics (Mo-Kα radiation, λ = 0.71073 Å).

The data obtained were integrated with SAINT and a semi-empirical absorption correction from equivalents with SADABS-2016/2 was applied.[41] The structures were solved by direct methods using SHELXT-2018/2.[42] Structure refinement was done using SHELXT-2018/3.[43] All non-hydrogen atoms were refined anisotropically and C-H hydrogen atoms were positioned at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2x or 1.5x (CH_3 hydrogens) the U_{eq} value of the atoms they are linked to.

5.2 Crystallographic details of 2bb

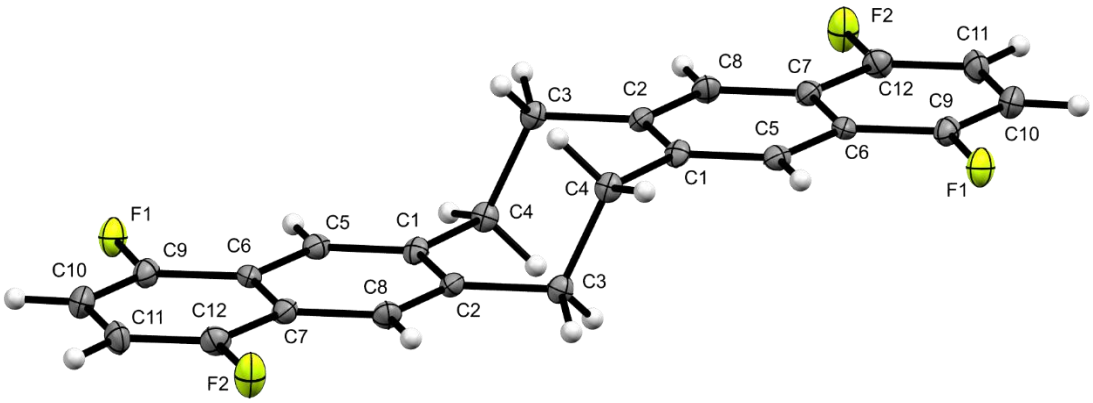

Figure S41. Thermal ellipsoid plot of **2bb** with the anisotropic displacement parameters drawn at the 50% probability level.

Crystal data and structure refinement for CCDC: 2433662.

Identification code	2433662	
Empirical formula	C24 H16 F4	
Formula weight	380.37	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 4.8992(13) Å	α= 90°.
	b = 8.306(2) Å	β= 91.874(13)°.
	c = 20.760(5) Å	γ = 90°.
Volume	844.3(4) $Å^3$	
Z	2	
Density (calculated)	1.496 Mg/m^3	
Absorption coefficient	0.117 mm^{-1}	
F(000)	392	
Crystal size	0.649 x 0.034 x 0.031 mm^3	
Theta range for data collection	2.641 to 29.571°.	
Index ranges	-6<=h<=6, 0<=k<=11, 0<=l<=28	
Reflections collected	2939	
Independent reflections	2939 [R(int) = ?]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745906 and 0.284011	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2939 / 0 / 128	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.1086, wR2 = 0.2769	
R indices (all data)	R1 = 0.1442, wR2 = 0.3015	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.459 and -0.367 $e.Å^{-3}$	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for CCDC: 2433662. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	2481(6)	5495(4)	7236(1)	22(1)
F(2)	5039(7)	11100(4)	6032(2)	26(1)
C(1)	8460(9)	5399(5)	5836(2)	13(1)
C(2)	9092(9)	6861(6)	5510(2)	15(1)
C(3)	11177(10)	6888(5)	4992(2)	14(1)
C(4)	9838(9)	3831(5)	5669(2)	14(1)
C(5)	6519(9)	5404(5)	6305(2)	14(1)
C(6)	5153(9)	6833(6)	6472(2)	14(1)
C(7)	5795(10)	8296(5)	6153(2)	14(1)
C(8)	7789(10)	8268(5)	5675(2)	16(1)
C(9)	3132(10)	6905(6)	6947(2)	16(1)
C(10)	1835(10)	8281(6)	7109(2)	20(1)
C(11)	2491(10)	9736(6)	6797(2)	19(1)
C(12)	4401(10)	9706(6)	6336(2)	18(1)

Bond lengths [Å] and angles [°] for CCDC: 2433662.

F(1)-C(9)	1.359(6)	H(3A)-C(3)-H(3B)	107.6
F(2)-C(12)	1.360(6)	C(1)-C(4)-C(3)#1	113.5(4)
C(1)-C(5)	1.383(6)	C(1)-C(4)-H(4A)	108.9
C(1)-C(2)	1.429(6)	C(3)#1-C(4)-H(4A)	108.9
C(1)-C(4)	1.512(6)	C(1)-C(4)-H(4B)	108.9
C(2)-C(8)	1.380(7)	C(3)#1-C(4)-H(4B)	108.9
C(2)-C(3)	1.507(6)	H(4A)-C(4)-H(4B)	107.7
C(3)-C(4)#1	1.563(6)	C(1)-C(5)-C(6)	121.1(4)
C(3)-H(3A)	0.9700	C(1)-C(5)-H(5)	119.4
C(3)-H(3B)	0.9700	C(6)-C(5)-H(5)	119.4
C(4)-H(4A)	0.9700	C(5)-C(6)-C(9)	123.5(4)
C(4)-H(4B)	0.9700	C(5)-C(6)-C(7)	119.4(4)
C(5)-C(6)	1.412(6)	C(9)-C(6)-C(7)	117.1(4)
C(5)-H(5)	0.9300	C(12)-C(7)-C(8)	123.6(4)
C(6)-C(9)	1.422(6)	C(12)-C(7)-C(6)	117.8(4)
C(6)-C(7)	1.423(6)	C(8)-C(7)-C(6)	118.6(4)
C(7)-C(12)	1.414(7)	C(2)-C(8)-C(7)	121.6(4)
C(7)-C(8)	1.415(7)	C(2)-C(8)-H(8)	119.2
C(8)-H(8)	0.9300	C(7)-C(8)-H(8)	119.2
C(9)-C(10)	1.356(7)	C(10)-C(9)-F(1)	119.9(4)
C(10)-C(11)	1.413(7)	C(10)-C(9)-C(6)	123.4(4)
C(10)-H(10)	0.9300	F(1)-C(9)-C(6)	116.7(4)
C(11)-C(12)	1.360(7)	C(9)-C(10)-C(11)	119.5(4)
C(11)-H(11)	0.9300	C(9)-C(10)-H(10)	120.3
C(5)-C(1)-C(2)	119.7(4)	C(11)-C(10)-H(10)	120.3
C(5)-C(1)-C(4)	119.1(4)	C(12)-C(11)-C(10)	118.6(5)
C(2)-C(1)-C(4)	121.2(4)	C(12)-C(11)-H(11)	120.7
C(8)-C(2)-C(1)	119.5(4)	C(10)-C(11)-H(11)	120.7
C(8)-C(2)-C(3)	119.6(4)	F(2)-C(12)-C(11)	119.0(4)
C(1)-C(2)-C(3)	120.9(4)	F(2)-C(12)-C(7)	117.4(4)
C(2)-C(3)-C(4)#1	114.6(4)	C(11)-C(12)-C(7)	123.6(4)
C(2)-C(3)-H(3A)	108.6		
C(4)#1-C(3)-H(3A)	108.6		
C(2)-C(3)-H(3B)	108.6		
C(4)#1-C(3)-H(3B)	108.6		

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+1

Anisotropic displacement parameters ($Å^2 x\ 10^3$) for CCDC: 2433662. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	23(2)	24(2)	19(1)	5(1)	8(1)	-1(1)
F(2)	31(2)	15(1)	34(2)	3(1)	15(1)	2(1)
C(1)	11(2)	15(2)	14(2)	2(2)	-1(2)	2(2)
C(2)	11(2)	18(2)	14(2)	-1(2)	1(2)	-4(2)
C(3)	14(2)	13(2)	15(2)	2(2)	1(2)	0(2)
C(4)	14(2)	13(2)	15(2)	3(2)	1(2)	2(2)
C(5)	14(2)	15(2)	13(2)	2(2)	-1(2)	-2(2)
C(6)	12(2)	18(2)	11(2)	-4(2)	0(2)	-2(2)
C(7)	12(2)	15(2)	16(2)	0(2)	0(2)	-1(2)
C(8)	17(2)	12(2)	19(2)	-1(2)	3(2)	-3(2)
C(9)	15(2)	20(2)	13(2)	2(2)	1(2)	-2(2)
C(10)	15(2)	25(2)	19(2)	-2(2)	5(2)	-2(2)
C(11)	18(2)	19(2)	20(2)	-4(2)	6(2)	2(2)
C(12)	20(2)	14(2)	18(2)	0(2)	2(2)	-2(2)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for CCDC: 2433662.

	x	y	z	U(eq)
H(3A)	12773	6290	5144	17
H(3B)	11740	7993	4925	17
H(4A)	9511	3052	6006	17
H(4B)	11793	4008	5658	17
H(5)	6107	4448	6515	17
H(8)	8232	9220	5468	19
H(10)	526	8268	7424	24
H(11)	1634	10694	6904	22

6 References

1 S. N. Kessler, M. Neuburger and H. A. Wegner, *Eur. J. Org. Chem.*, 2011, **2011**, 3238–3245.

2 S. N. Kessler and H. A. Wegner, *Org. Lett.*, 2012, **14**, 3268–3271.

3 J.-S. Kim, K.-J. Shin, D.-C. Kim, Y.-K. Kang, D.-J. Kim, K.-H. Yoo and S.-W. Park, *Bull. Korean Chem. Soc.*, 2002, **23**, 1425–1446.

4 M. Große, C. M. Leonhardt, P. A. R. Campbell and H. A. Wegner, *Org. Lett.*, 2025, **27**, 4893–4897.

5 B. R. Varga, M. Kállay, K. Hegyi, S. Béni and P. Kele, *Chem. Eur. J.*, 2012, **18**, 822–828.

6 W. Fu, T. M. Alam, J. Li, J. Bustamante, T. Lien, R. W. Adams, S. J. Teat, B. J. Stokes, W. Yang, Y. Liu and J. Q. Lu, *J. Am. Chem. Soc.*, 2020, **142**, 16651–16660.

7 C. Bannwarth, E. Caldeweyher, S. Ehlert, A. Hansen, P. Pracht, J. Seibert, S. Spicher and S. Grimme, *WIREs Comput. Mol. Sci.*, 2021, **11**, e1493.

8 S. Grimme, C. Bannwarth and P. Shushkov, *J. Chem. Theory Comput.*, 2017, **13**, 1989–2009.

9 C. Bannwarth, S. Ehlert and S. Grimme, *J. Chem. Theory Comput.*, 2019, **15**, 1652–1671.

10 P. Pracht, E. Caldeweyher, S. Ehlert and S. Grimme, *ChemRxiv*, 2019. DOI: 10.26434/chemrxiv.8326202.v1.

11 S. Ehlert, M. Stahn, S. Spicher and S. Grimme, *J. Chem. Theory Comput.*, 2021, **17**, 4250–4261.

12 P. Pracht, F. Bohle and S. Grimme, *Phys. Chem. Chem. Phys.*, 2020, **22**, 7169–7192.

13 P. Pracht, S. Grimme, C. Bannwarth, F. Bohle, S. Ehlert, G. Feldmann, J. Gorges, M. Müller, T. Neudecker, C. Plett, S. Spicher, P. Steinbach, P. A. Wesołowski and F. Zeller, *J. Chem. Phys.*, 2024, **160**, 114110.

14 P. Pracht and C. Bannwarth, *J. Chem. Theory Comput.*, 2022, **18**, 6370–6385.

15 S. Grimme, *J. Chem. Theory Comput.*, 2019, **15**, 2847–2862.

16 F. Neese, *WIREs Comput. Mol. Sci.*, 2022, **12**, e1606.

17 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.

18 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065.

19 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

20 V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995–2001.

21 C. Riplinger and F. Neese, *J. Chem. Phys.*, 2013, **138**, 34106.

22 L. Wittmann, I. Gordiy, M. Friede, B. Helmich-Paris, S. Grimme, A. Hansen and M. Bursch, *Phys. Chem. Chem. Phys.*, 2024, **26**, 21379–21394.

23 E. Caldeweyher, J.-M. Mewes, S. Ehlert and S. Grimme, *Phys. Chem. Chem. Phys.*, 2020, **22**, 8499–8512.

24 E. Caldeweyher, S. Ehlert, A. Hansen, H. Neugebauer, S. Spicher, C. Bannwarth and S. Grimme, *J. Chem. Phys.*, 2019, **150**, 154122.
25 E. Caldeweyher, C. Bannwarth and S. Grimme, *J. Chem. Phys.*, 2017, **147**, 34112.
26 F. Neese, *J. Comp. Chem.*, 2023, **44**, 381–396.
27 B. Helmich-Paris, B. de Souza, F. Neese and R. Izsák, *J. Chem. Phys.*, 2021, **155**, 104109.
28 M. Garcia-Ratés and F. Neese, *J. Comput. Chem.*, 2020, **41**, 922–939.
29 M. Garcia-Ratés and F. Neese, *J. Comput. Chem.*, 2019, **40**, 1816–1828.
30 D. Bykov, T. Petrenko, R. Izsák, S. Kossmann, U. Becker, E. Valeev and F. Neese, *Molec. Phys.*, 2015, **113**, 1961–1977.
31 F. Neese, F. Wennmohs, A. Hansen and U. Becker, *Chem. Phys.*, 2009, **356**, 98–109.
32 F. Neese, *J. Comp. Chem.*, 2003, **24**, 1740–1747.
33 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.
34 F. Neese, A. Hansen and D. G. Liakos, *J. Chem. Phys.*, 2009, **131**, 64103.
35 F. Neese, F. Wennmohs and A. Hansen, *J. Chem. Phys.*, 2009, **130**, 114108.
36 C. Riplinger, B. Sandhoefer, A. Hansen and F. Neese, *J. Chem. Phys.*, 2013, **139**, 134101.
37 C. Riplinger, P. Pinski, U. Becker, E. F. Valeev and F. Neese, *J. Chem. Phys.*, 2016, **144**, 24109.
38 G. Bistoni, C. Riplinger, Y. Minenkov, L. Cavallo, A. A. Auer and F. Neese, *J. Theo. Comp. Chem.*, 2017, **13**, 3220–3227.
39 W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graph.*, 1996, **14**, 33-8, 27-8.
40 J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J.-P. Piquemal, D. N. Beratan and W. Yang, *J. Chem. Theory Comput.*, 2011, **7**, 625–632.
41 L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3–10.
42 G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3–8.
43 G. M. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3–8.