Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

A Halogen Bonding Molecular Tweezer

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Electronic Supporting Information

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Synthesis and experimental

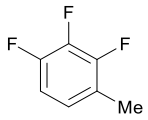
General Information

Commercially available chemicals were obtained from ABCR, Alfa Aesar, Carbolution, Fluorochem, Merck or VWR and used without further purification unless stated otherwise. Tetrahydrofuran, diethyl ether and pentane of technical grade were distilled before usage. Anhydrous tetrahydrofuran was stored over 3 Å molecular sieves and further dried on an aluminium oxide column using an MBraun MB SPS-800 solvent purification system. All other solvents and additives were dried according to literature procedures and stored over 3 Å molecular sieves. Degassing of solvents was performed using the freeze-pump-thaw method. Air and moisture sensitive reactions were performed using standard Schlenk-techniques. Column chromatography was performed using silica gel 60 M (0.04-0.063 mm, Machery-Nagel) and eluted products tracked by thin-layer chromatography on fluorescent coated TLC-plates (F254, Merck) using a UV-light at 254 nm and/or common TLC stains. Flash chromatography was performed with a Grace (Büchi) Reveleris® PREP Purification System with FlashPure silica cartridges. Nuclear magnetic resonance spectra were recorded on a Bruker DPX-250 (1H: 250 MHz, ^{19}F: 235 MHz, ^{13}C: 63 MHz), Avance III HD300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) or Avance Neo-400 (1H: 400 MHz, 19F: 376 MHz, 13C: 101 MHz) spectrometer at 25 °C/298.15 K. All shift values are given in ppm and all coupling constants (*J*) are printed in Hertz (Hz) and multiplicity is indicated with standard abbreviations: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), quin. (quintet), m (multiplet of higher or indeterminate order), dd (doublet of doublet) et cetera. GC/MS spectra were obtained with a Hewlett-Packard 5972 GC/MS System equipped with a Phenomenex Zebron ZB-5HT Inferno (25 m) column. Mass spectra of GC/MS unsuitable molecules were measured on a Jeol AccuTOF GCv with electron ionization (EI) as ionization technique or on a Bruker Esquire 6000 with electron spray ionization (ESI). Infrared spectra were obtained on a Shimadzu FTIR-8400s spectrometer equipped with a Specac Quest ATR through attenuated total reflection (ATR). Elemental analyses were performed on a vario MICRO cube from Elementar Analysensysteme GmbH. Crystal structures of single crystals were obtained with either a Rigaku SuperNova or a Stoe IPDS I.

Biphenyls **4** were prepared according to previously published methods.[1]

Synthesis

2,3,4-Trifluorotoluene (**1**)



1

Under argon atmosphere 1,2,3-trifluorobenzene (24.15 ml/30.91 g, 234 mmol,1.0 eq) is dissolved in anhydrous tetrahydrofuran (250 ml) and cooled to -78 °C. Afterwards sec-BuLi (1.3 M in cyclohexane, 180 ml, 234 mmol, 1.0 eq) is added dropwise over 1.5 hours. After complete addition, the reaction mixture is stirred for 2 hours. Methyl iodide (14.57 ml/33.22 g, 234 mmol, 1.0 eq) is added to the solution. The reaction mixture is stirred for 3 hours at -78 °C. The cooling is removed, and the mixture is continuously stirred while warming to room temperature overnight. Afterwards the reaction mixture is concentrated in vacuo to carefully remove most of the solvents as the product is volatile. The crude product is purified by fractional distillation with a Fischer Spaltrohr column® (head temperature 117 °C). The product is obtained as colorless liquid with a yield of 67% (22.8 g, 156 mmol).

^{1}H NMR: (250 MHz, Chloroform-*d*) δ = 6.95 – 6.73 (m, 2H), 2.41 – 2.27 (m, 3H) ppm.

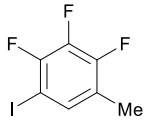
^{13}C{^{1}H}NMR: (63 MHz, Chloroform-*d*) δ = 150.06 (ddd, *J* = 246.8, 9.8, 2.6 Hz), 149.72 (ddd, *J* = 246.6, 10.1, 2.8 Hz), 140.15 (dt, *J* = 249.8, 15.5 Hz), 124.38 (dt, *J* = 7.8, 4.9 Hz), 123.11 – 121.85 (m), 111.46 (dd, *J* = 17.1, 4.0 Hz), 13.79 (t, *J* = 2.7 Hz) ppm.

^{19}F{^{1}H}NMR: (235 MHz, Chloroform-*d*) δ = -138.54 (dd, *J* = 19.7, 5.7 Hz), -139.20 (dd, *J* = 20.0, 5.8 Hz), -162.28 (td, *J* = 19.9, 1.4 Hz) ppm.

MS (EI_{pos}): calc´d for $C_7H_5F_3$ $[M]^+$: 147.0; found 147.0

2,3,4-Trifluoro-5-Iodotoluene (2)

Note: The Synthesis of **2** was most successful in a one-pot reaction.



2

Under argon atmosphere 1,2,3-trifluorobenzene (1.0 ml / 1.28 g, 9.7 mmol, 1.0 eq) is dissolved in anhydrous tetrahydrofuran (50 ml, 0.2 M) and cooled to -78°C. *n*-butyl lithium (2.5 M solution in hexanes, 4.1ml, 10.25 mmol, 1.05 eq) is added dropwise under rapid stirring. After complete addition, the mixture is stirred for 10 minutes at -78 °C. Methyl iodide (0.63 ml/1.44 g, 10.2 mmol, 1.05 eq) is added, and the solution stirred at -78 °C for 15 minutes. The cooling is removed, and the mixture is continuously stirred while warming to room temperature. The reaction mixture is cooled back down to -78 °C and *n*-butyl lithium (2.5 M solution in hexanes, 4.1ml, 10.25 mmol, 1.05 eq) is added dropwise under rapid stirring. After complete addition, the mixture is stirred for 10 minutes at -78 °C. Then iodine (2.59 g, 10.2 mmol, 1.05 eq) , dissolved in anhydrous tetrahydrofuran (ca. 10 ml) is added, and the solution stirred while warming to room temperature overnight.

The reaction is quenched by addition of sat. aqueous sodium sulfite solution (ca. 25 ml). The phases are separated, the aqueous phase is extracted with diethyl ether (3x20 ml). The combined organic phases are washed with sat. aqueous sodium thiosulfate solution, dried with magnesium sulfate, which is subsequently filtered off and most of the solvents carefully evaporated in vacuo, but no lower than 100 mbar, as the product is volatile. The crude containing residual solvent is purified by distillation under reduced pressure (50 mbar, 80 °C). The product is obtained as colorless liquid with a yield of 70% over two steps (1.9 g, 7.0 mmol).

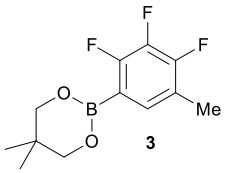
^{1}H NMR: (400 MHz, Chloroform-*d*) δ = 7.37 – 7.30 (m, 1H), 2.25 (s, 3H) ppm.

^{19}F{^{1}H} NMR: (376 MHz, Chloroform-*d*) δ = -116.31 (dd, *J* = 21.7, 7.1 Hz), -136.50 (dd, *J* = 19.6, 7.2 Hz), -156.91 (t, *J* = 20.6 Hz) ppm.

^{13}C{^{1}H} NMR (75 MHz, , Chloroform-*d*) δ = 150.09 (ddd, J = 249.3, 10.1, 2.6 Hz), 149.41 (ddd, J = 244.9, 11.2, 3.2 Hz), 141.87 – 137.15 (m), 133.08 (td, J = 4.1, 1.1 Hz), 124.19 (dd, J = 14.8, 3.9 Hz), 74.54 (ddd, J = 22.3, 4.6, 1.3 Hz), 13.88 (t, J = 2.5 Hz).

MS (EI_{pos}): calc´d for $C_7H_4F_3I$ $[M]^+$: 271.9, found 271.9.

5,5-Dimethyl-2-(2,3,4-trifluoro-5-methylphenyl)-1,3,2-dioxaborinane (**3**)



3

Under argon atmosphere 2,3,4-trifluorotoluene (1, 18.99 g, 130 mmol, 1.0 eq) is dissolved in anhydrous tetrahydrofuran (500 ml). The solution is cooled to -78 °C and sec-BuLi (1.3 M in cyclohexane, 110 ml, 143 mmol) is added dropwise to the solution over 1 hour. After complete addition the reaction mixture is stirred for 2 hours at -78 °C. Trimethyl borate (13.85 ml/14.86 g, 143 mmol, 1.1 eq) is added and the reaction mixture stirred for an hour while warming up to room temperature. The reaction is quenched with hydrochloric acid (2 M) and stirred vigorously for 2 hours. The mixture is diluted with diethyl ether (500 ml) for better phase separation and the phases are separated. The organic phase is extracted twice with brine and dried with magnesium sulfate, which is subsequently filtered of. The solvent is evaporated, and the residue dried in vacuo. The crude boronic acid was suspended in pentane to remove non-polar impurities and is precipitated by centrifugation. The liquid phase was discarded, and the precipitate was dried *in vacuo*.

The boronic acid is dissolved in tetrahydrofuran (100 ml) and 2,2-dimethyl-1,3-propanediol (14.89 g, 143 mmol, 1.1 eq) and magnesium sulfate (78.2 g, 650 mmol, 5 eq) are added. The suspension is stirred at room temperature overnight. The solid was filtered off and the solvent evaporated in vacuo. The crude was purified by flash column chromatography (silica, cyclohexane : diethyl ether 50%) to obtain the product in 62% yield (20.8 g, 80.6 mmol).

^{1}H NMR: (250 MHz, Chloroform-*d*) δ = 7.29 – 7.20 (m, 1H), 3.78 (s, 4H), 2.30 – 2.18 (m, 3H), 1.03 (s,6H) ppm.

^{19}F{^{1}H}NMR: (235 MHz, Chloroform-*d*) δ = -130.89 (dd, *J* = 20.9, 9.8 Hz), -134.65 (dd, *J* = 19.6, 9.8 Hz), -162.88 (t, *J* = 20.2 Hz) ppm.

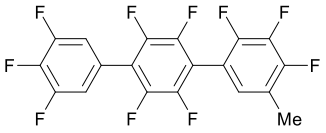
FTIR (ATR): 2960 (w), 2934 (w), 2911 (w), 1632 (w), 1483 (m), 1460 (m), 1339 (m), 1254 (s), 1229 (s),

1201 (s), 1188 (m), 957 (m), 687 (m), 675 (m).

MS (EI_{pos}): calc´d for $C_{12}H_{14}BF_3O_2$ $[M]^+$: 258.1; found 258.0

EA: calc´d for $C_{12}H_{14}BF_3O_2$: C, 55.85; H, 5.47; N, 0.00; found C, 56.03; H, 5.535; N, 0.00.

2,2',3,3',3'',4,4'',5',5'',6'-decafluoro-5-methyl-1,1':4',1''-terphenyl (5)



5

Via Negishi-Coupling:

Under argon atmosphere **4**-H (560 mg, 2 mmol, 1.0 eq) is dissolved in anhydrous Tetrahydrofuran (10 ml, 0.2 M) and cooled to -78°C. Then, n-butyl lithium (2.5 M solution in hexanes, 0.96 ml, 2.4 mmol, 1.2 eq) is added dropwise under rapid stirring. After complete addition, the mixture is stirred for 30 minutes at -78°C. Then a solution of $ZnCl_2$ (2M in 2-Methyl- Tetrahydrofuran, 1.25 ml, 2.5 mmol, 1.25 eq) is added, and the solution stirred at -78°C for 15 minutes, then continuously stirred while warming to room temperature. In the meantime, Tris(dibenzylidenaceton)dipalladium (55 mg, 6 µmol, 3 mol%) and XPhos (89 mg, 18 µmol, 9 mol%) is dissolved in anhydrous tetrahydrofuran (10 ml) and heated to 50°C for one hour. Formation of active catalyst can be observed by a color change. Then, room temperature aryl-zinc-chloride-solution is added via cannulation, followed by 2,3,4-trifluoro-5-iodotoluene (2, 2 mmol, 1.0 eq). The reaction mixture is heated to reflux for 72 hours. The reaction mixture is cooled to room temperature and quenched with sat. ammonium chloride solution. The phases are separated, and the aqueous phase is extracted with diethyl ether (3x20 ml). the combined organic phases are dried with magnesium sulfate, which is subsequently filtered off and the solvent evaporated *in vacuo*. The crude is purified by column chromatography (silica, pentane as eluent) and the product (Rf = 0.5) obtained as a white solid (629 mg, 74%).

Via Suzuki-Coupling:

Under Argon Atmosphere, Tris(dibenzylidenaceton)dipalladium (293 mg, 320 µmol, 10 mol%) and CyJohnPhos (337 mg, 960 µmol, 30 mol%) are dissolved in a degassed mixture of tetrahydrofuran (20 ml) and toluene (20 ml) and heated to 50°C for one hour. Formation of active catalyst can be observed by a color change. Then, degassed water (8 ml), potassium carbonate (1.77 g, 12.8 mmol, 4 eq), iodinated biphenyl **4**-I (1.3 g, 3.2 mmol, 1 eq) and boronic acid ester **3** (1.65 g, 6.4 mmol, 2 eq) are added. The reaction mixture is heated to reflux for 60 hours. After cooling to room temperature, the mixture is quenched with sat. ammonium chloride solution. The phases are separated, and the aqueous phase is extracted with diethyl ether (3x20 ml). the combined organic phases are dried with magnesium sulfate, which is subsequently filtered off and the solvent evaporated *in vacuo*. The crude is purified by column chromatography (silica, pentane as eluent) and the product (Rf = 0.5) obtained as a white solid (1.32 g, 97%).

^{1}H NMR: (250 MHz, Chloroform-*d*) δ 7.24 – 7.13 (m, 2H), 7.05 – 6.96 (m, 1H), 2.37 (t, *J* = 1.2 Hz, 2H).

^{13}C{^{1}H}NMR: (63 MHz, Chloroform-*d*) δ 151.27 (ddd, *J* = 251.3, 10.1, 4.2 Hz), 150.60 (ddd, *J* = 251.8, 9.9, 3.1 Hz), 145.26 (dd, *J* = 11.2, 3.3 Hz), 146.58 – 142.47 (m), 143.65 (dt, *J* = 249.6, 4.5 Hz), 146.11 – 141.80 (m), 146.27 – 142.05 (m), 142.57 – 137.92 (m), 126.31 (dd, *J* = 3.6, 1.8 Hz), 122.63 (dd, *J* = 14.7, 4.1 Hz), 118.11 (t, *J* = 16.1 Hz), 115.21 – 114.52 (m), 113.67 (t, *J* = 18.2 Hz), 111.09 (ddd, *J* = 13.0, 4.6, 2.3 Hz), 14.03 (t, *J* = 2.6 Hz).

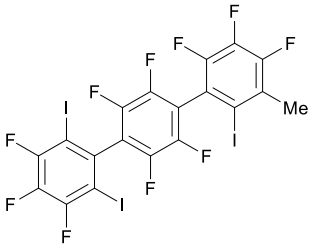
$^{19}F\{^{1}H\}$NMR: (235 MHz, Chloroform-*d*) δ -133.09 (d, *J* = 20.5 Hz), -133.83 (dd, *J* = 20.4, 8.7 Hz), -135.44 – -136.01 (m), -140.03 (ddd, *J* = 22.4, 12.3, 10.3 Hz), -142.75 – -143.44 (m), -157.85 (t, *J* = 20.6Hz), -159.05 (t, *J* = 20.4 Hz).

FTIR (ATR): 3103 (vw), 1618 (w), 1537 (m), 1481 (m), 1467 (s), 1284 (m), 1093 (m), 972 (m), 868 (m), 700 (m). 409 (m).

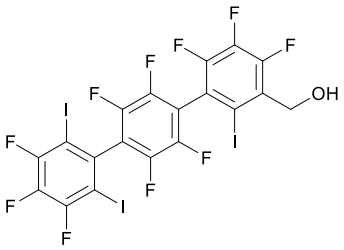
MS (EI+): calc´d for $C_{19}H_6F_{10}$ $[M]^+$: 424.0; found 424.0.

EA: Anal. calc´d for $C_{19}H_6F_{10}$: C, 53.79; H, 1.43; found C, 53.82; H, 1.268.

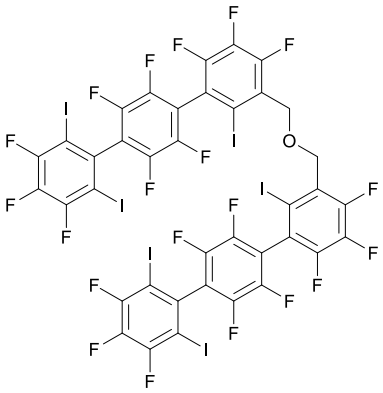
Synthesis of the iodinated terphenyls 6 & 7 and molecular Cleft 8



6



7



8

Terphenyl **5** (3 g, 7.07 mmol, 1.0 eq) is suspended in 125 ml triflic acid and cooled to 0 °C. Under vigorous stirring *N*-Iodosuccinimide (9.55 g, 42.43 mmol, 6.0 eq) is added within one hour in small portions. The reaction mixture is warmed up to room temperature and stirred for 3 h. The reaction mixture is poured onto ice and left to warm up to room temperature overnight. The resulting aqueous phase is extracted with diethyl ether (3x100 ml). The combined organic phases are extracted twice with saturated sodium bicarbonate solution and saturated sodium sulfite solution. Afterwards the organic phase is dried with magnesium sulfate, which is subsequently filtered off, and solvents evaporated *in vacuo*. The residue is purified by column chromatography (silica, pentane : diethyl ether gradient 0-25%). Methyl-terphenyl **6** elutes first (R_f=0.3, 100% pentane) yielding 2.25 g (39%) as a white solid, followed by **8** (R_f=0.2, pentane : diethyl ether 10%) yielding 780 mg (18%) as a yellow solid, and **7** (R_f=0.1, pentane : diethyl ether 25%) yielding up to 2.31 g (41%).

Methyl-Terphenyl **6**:

^{1}H NMR: (400 MHz, Chloroform-*d*) δ = 2.51 (dd, *J* = 3.1, 1.2 Hz, 3H) ppm.

^{13}C NMR: (101 MHz, Chloroform-*d*) δ = 151.77 (ddd, *J* = 249.6, 11.3, 4.2 Hz), 150.81 – 147.83 (m), 148.10 – 145.42 (m), 143.99 (dt, J = 250.5, 4.4 Hz), 145.43 – 142.81 (m), 143.43 (dt, *f* = 249.4, 4.6 Hz), 143.29 (dt, J = 250.1, 4.5 Hz), 141.67 – 138.36 (m), 138.61 (dt, J = 264.3, 18.3 Hz), 133.60 (d, J = 4.1 Hz), 127.97 (dd, J = 14.6, 4.1 Hz), 125.41 (t, J = 18.3 Hz), 118.71 – 118.33 (m), 118.38 – 118.15 (m), 99.18 (t, J = 4.0 Hz), 81.57 (td, J = 23.0, 5.5 Hz), 21.14 (t, J = 2.5 Hz) ppm.

$^{19}F\{^{1}H\}$NMR: (377 MHz, Chloroform-*d*) δ = -105.38 (td, J = 22.1, 9.8 Hz), -127.17 – -127.31 (m), -130.28 (dd, J = 21.1, 7.9 Hz), -137.62 (ddd, J = 23.6, 12.9, 2.7 Hz), -139.25 – -139.44 (m), -149.96 (t, J = 21.9 Hz), -157.47 (t, J = 20.8 Hz) ppm.

MS (EI_+): calc´d for $C_{19}H_3F_{10}I_3$ $[M]^+$: 801.7; found 801.7

FTIR (ATR): 1470 (m), 1456 (m), 1398 (m), 1107 (m), 1068 (m), 978 (m), 783 (m), 704 (m) 413 ()

EA: calc´d for C19H3F10I3: C, 28.46; H, 0.38; found C, 28.69; H, 0.404.

Hydroxymethyl-Terphenyl **7**:

^{1}H NMR: (400 MHz, Chloroform-*d*) δ = 4.95 (d, J = 4.5 Hz, 2H, CH_2), 2.1 (s, 1H, O*H*) ppm.

^{13}C{^{1}H}NMR: (101 MHz, Chloroform-*d*) δ = 151.92 (ddd, J = 249.6, 11.1, 4.2 Hz), 149.52 (ddd, J = 253.8, 10.3, 3.6 Hz), 148.25 – 145.54 (m), 144.27 (dt, J = 250.3, 4.2 Hz), 144.13 (dt, J = 250.7, 4.4 Hz), 143.57 (dt, J = 249.7, 4.6 Hz), 143.43 (dt, J = 250.2, 4.5 Hz), 141.94 – 138.67 (m), 138.76 (dt, J = 264.3, 18.3 Hz), 133.74 (d, J = 4.1 Hz), 128.11 (dd, J = 14.6, 4.1 Hz), 125.55 (t, J = 18.3 Hz), 118.66 (d, J = 18.7 Hz), 118.53 – 118.25 (m), 99.32 (t, J = 4.0 Hz), 81.71 (td, J = 23.0, 5.5 Hz), 21.28 (t, J = 2.5 Hz) ppm.

^{19}F{^{1}H}NMR: (377 MHz, Chloroform-*d*) δ = -105.19 – -105.46 (m), -125.94 – -126.07 (m), -129.71 (ddt, J = 21.0, 9.8, 3.1 Hz), -137.30 – -137.44 (m), -138.90 – -139.05 (m), -149.84 (t, J = 21.8 Hz), -155.93 (t, J = 20.8 Hz) ppm.

FTIR (ATR): 1618 (m), 1539 (m), 1450 (m), 1396 (m), 1068 (m), 977 (m), 706 (m)

MS (EI+): calc´d for C19H3F10I3O [M]+: 817.7; found 817.7

EA: calc´d for C19H3F10I3O: C, 27.90; H, 0.37; found: C, 28.32; H, 0.401.

Cleft **8**:

^{1}H NMR: (400 MHz, Chloroform-*d*) δ = 4.89 (d, J = 3.2 Hz, 4H) ppm.

^{13}C NMR: (101 MHz, Chloroform-*d*) δ 153.27 – 150.37 (m), 150.65 (ddd, J = 258.6, 10.3, 4.0 Hz), 148.67 (ddd, J = 256.8, 10.8, 4.1 Hz), 145.26 – 142.60 (m), 144.08 (dt, J = 250.6, 4.1 Hz), 143.46 (dt, J = 249.8, 4.3 Hz), 143.32 (dt, J = 250.0, 4.1 Hz), 140.02 (dt, J = 257.0, 16.0 Hz), 138.65 (dt, J = 264.5, 18.2 Hz), 133.47, 126.31 (dd, J = 13.1, 4.0 Hz), 125.71 (t, J = 18.4 Hz), 119.56 (d, J = 14.7 Hz), 117.90 (t, J = 18.4 Hz), 100.18 (d, J = 4.3 Hz), 81.52 (td, J = 23.3, 4.9 Hz), 69.80 (s) ppm.f

^{19}F{^{1}H}NMR: (377 MHz, Chloroform-*d*) δ -105.32 (ddd, J = 32.9, 21.9, 9.9 Hz), -125.15 (dd, J = 20.8, 10.1 Hz), -128.13 – -128.39 (m), -137.31 (ddd, J = 23.5, 13.0, 2.6 Hz), -138.86 – -139.07 (m), -149.81 (t, J = 22.0 Hz), -156.09 (t, J = 21.0 Hz) ppm.

FTIR (ATR): 2956 (vw), 2889 (vw), 1597 (w), 1496 (s), 1454 (s), 1396 (m), 1115 (m), 980 (m), 704 (m).

MS (EI_+): calc´d for C38H4F20I6O [M]+: 1618.4; found 801.7 (cleaved between the oxygen and the methylene group.)

EA: calc´d for $C_{38}H_4F_{20}I_6O$: C, 28.21; H, 0.25; found C, 29.39; H, 0.419.

Crystal Structure Data

Cleft **8** Single Crystal (CCDC No. 2296704)

***Table S1** Crystal structure data of tweezer-compound **8**.*

Identifier	DB-F41C2meas
Formula	$C_{38}H_4F_{20}I_6O$
Molecular Mass	1617.81 g/mol
Crystal System	Triclinic
Space Group	P -1 (2)
Lattice Parameters	
a	12.2390(7) Å
b	13.0222(7) Å
c	15.7212(8) Å
α	66.648(5)°
β	68.207(5)°
γ	73.564(5)°
Density [g/cm$_3$]	2,548
Crystal size [mm$_3$]	0.327 x 0.240 x 0.151
Volume [Å^3]	2108.7(2)
Z	2
Temperature [K]	170(2)
Diffraction Device	Xcalibur, Sapphire2
Radiation Type	0.71073 Å (Mo K)
F(000)	1476
Absorption coefficient [mm-1]	4,541
Absorption correction	Gaussian
Measurement range	2.7 - 26.0
Index range	-15 < h < 15 -16 < k < 16 -19 < l < 19
Measured reflexes	32425
Independent	8268
Observed	6315
R(int)	0,0361
Completeness (%) / theta (°)	99.8 / 25.242
Transmission (min / max)	0.397 / 0.630
R1 (observed/all)	0.0381 / 0.0567
wR2 (observed/all)	0.0854 / 0.0950
GooF = S	1,049
Rest electron density max./min. [e-/Å^3]	-1.034 / 1.331

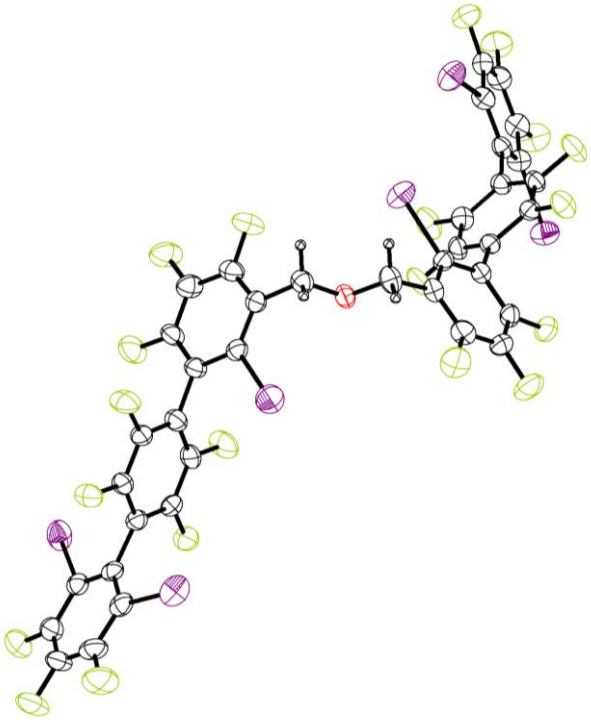


Table S2 *Fractional atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å²×10³) for DB-F41C2.*

Atom	*x*	*Y*	*z*	U(eq)
O(1)	0.0645(3)	0.3148(3)	0.3097(3)	0.0371(9)
C(1A)	0.4363(5)	-0.0923(5)	0.8862(4)	0.0372(13)
I(1A)	0.54392(4)	-0.17736(4)	0.78903(3)	0.05618(14)
F(1A)	0.5621(4)	-0.1905(3)	0.9873(3)	0.0650(11)
C(1B)	0.6421(5)	0.5144(5)	-0.3707(4)	0.0383(14)
I(1B)	0.72021(4)	0.60895(4)	-0.33551(3)	0.05078(13)
F(1B)	0.8157(3)	0.5067(4)	-0.5023(3)	0.0606(11)
C(2A)	0.4642(6)	-0.1185(5)	0.9704(5)	0.0454(15)
I(2A)	0.11125(4)	0.15538(4)	0.92498(4)	0.05781(14)
F(2A)	0.4163(5)	-0.1020(4)	1.1246(3)	0.0824(15)
C(3A)	0.3893(7)	-0.0732(6)	1.0417(5)	0.0545(19)
I(3A)	0.01801(5)	0.23355(4)	0.57440(4)	0.06117(15)
F(3A)	0.2219(5)	0.0489(4)	1.0958(3)	0.0794(14)
C(2B)	0.7077(5)	0.4787(5)	-0.4488(4)	0.0400(14)
I(2B)	0.32591(4)	0.35341(4)	-0.26119(4)	0.05423(13)
F(2B)	0.7302(3)	0.3762(3)	-0.5504(3)	0.0560(10)
C(4A)	0.2905(7)	0.0035(6)	1.0273(5)	0.0515(17)
F(4A)	0.4566(3)	0.1015(3)	0.6756(2)	0.0461(9)
C(3B)	0.6654(6)	0.4129(5)	-0.4752(4)	0.0414(14)
I(3B)	0.13476(4)	0.35315(4)	0.06136(4)	0.05398(13)
F(3B)	0.5140(3)	0.3205(3)	-0.4523(3)	0.0524(9)
C(5A)	0.2620(6)	0.0347(5)	0.9419(4)	0.0426(15)
F(5A)	0.3935(4)	0.1221(4)	0.5230(3)	0.0599(11)
C(4B)	0.5544(6)	0.3824(5)	-0.4236(4)	0.0388(14)
F(4B)	0.3297(3)	0.6593(3)	-0.3123(2)	0.0538(10)
C(6A)	0.3333(5)	-0.0155(5)	0.8716(4)	0.0348(13)
F(6A)	0.0739(3)	-0.0746(3)	0.7337(3)	0.0575(10)
C(5B)	0.4860(5)	0.4153(5)	-0.3430(4)	0.0378(13)
F(5B)	0.1809(3)	0.6942(3)	-0.1491(2)	0.0491(9)
C(7A)	0.2977(5)	0.0048(5)	0.7845(4)	0.0345(13)
F(7A)	0.1354(3)	-0.0934(3)	0.8849(2)	0.0497(9)
C(6B)	0.5295(5)	0.4835(4)	-0.3163(4)	0.0315(12)
F(6B)	0.4283(3)	0.4148(3)	0.0271(2)	0.0518(9)
C(8A)	0.3599(5)	0.0597(5)	0.6910(4)	0.0378(14)
F(8A)	0.3408(4)	-0.1285(3)	0.5259(3)	0.0620(11)
C(7B)	0.4556(5)	0.5160(5)	-0.2285(4)	0.0341(13)
F(7B)	0.5758(3)	0.3762(3)	-0.1366(3)	0.0547(10)
C(9A)	0.3283(6)	0.0694(5)	0.6120(4)	0.0400(14)
F(9A)	0.2972(4)	-0.1190(4)	0.3668(3)	0.0640(11)
C(8B)	0.3564(5)	0.5984(5)	-0.2290(4)	0.0346(13)

Atom	*x*	*Y*	*z*	U(eq)
F(8B)	0.2819(3)	0.7323(3)	0.0045(3)	0.0487(9)
C(10A)	0.2300(5)	0.0258(5)	0.6234(4)	0.0381(14)
F(10A)	0.1420(4)	0.0513(4)	0.2918(3)	0.0577(10)
C(9B)	0.2793(5)	0.6160(5)	-0.1449(4)	0.0325(12)
F(9B)	0.1393(4)	0.7538(3)	0.1757(3)	0.0637(11)
C(11A)	0.1690(5)	-0.0289(5)	0.7175(4)	0.0371(13)
C(10B)	0.2991(5)	0.5537(4)	-0.0558(4)	0.0311(12)
F(10B)	-0.0035(4)	0.6010(3)	0.2984(3)	0.0626(11)
C(12A)	0.1996(5)	-0.0385(5)	0.7959(4)	0.0373(13)
C(11B)	0.4032(5)	0.4761(5)	-0.0576(4)	0.0372(13)
C(13A)	0.1993(5)	0.0344(5)	0.5380(4)	0.0364(13)
C(12B)	0.4791(5)	0.4565(5)	-0.1407(4)	0.0375(13)
C(14A)	0.2603(5)	-0.0445(5)	0.4911(4)	0.0407(14)
C(13B)	0.2118(5)	0.5657(4)	0.0376(4)	0.0321(12)
C(15A)	0.2386(6)	-0.0404(5)	0.4102(5)	0.0442(15)
C(14B)	0.2101(5)	0.6552(5)	0.0639(4)	0.0364(13)
C(16A)	0.1567(5)	0.0474(5)	0.3731(4)	0.0406(14)
C(15B)	0.1369(6)	0.6675(5)	0.1506(4)	0.0402(14)
C(17A)	0.0919(5)	0.1275(5)	0.4163(4)	0.0346(13)
C(16B)	0.0646(6)	0.5879(5)	0.2134(4)	0.0441(15)
C(18A)	0.1144(5)	0.1190(5)	0.5003(4)	0.0373(13)
C(17B)	0.0626(5)	0.4963(5)	0.1912(4)	0.0370(13)
C(19A)	0.0046(5)	0.2213(5)	0.3707(4)	0.0412(14)
C(19B)	-0.0122(5)	0.4084(5)	0.2649(4)	0.0419(14)
C(18B)	0.1368(5)	0.4876(4)	0.1015(4)	0.0336(13)

Table S3 *Anisotropic displacement parameters ($Å^2×10^3$) for DB-F41C2.*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	0.038(2)	0.036(2)	0.036(2)	-0.0050(17)	-0.0153(19)	-0.0082(18)
C(1A)	0.041(3)	0.036(3)	0.035(3)	-0.011(3)	-0.008(3)	-0.012(3)
I(1A)	0.0607(3)	0.0484(3)	0.0474(3)	-0.0158(2)	-0.0117(2)	0.0036(2)
F(1A)	0.073(3)	0.059(2)	0.070(3)	-0.009(2)	-0.045(2)	-0.005(2)
C(1B)	0.037(3)	0.039(3)	0.040(3)	-0.016(3)	-0.010(3)	-0.005(3)
I(1B)	0.0485(3)	0.0594(3)	0.0513(3)	-0.0235(2)	-0.0108(2)	-0.0159(2)
F(1B)	0.040(2)	0.084(3)	0.055(2)	-0.034(2)	0.0109(18)	-0.022(2)
C(2A)	0.052(4)	0.045(4)	0.041(4)	-0.004(3)	-0.018(3)	-0.020(3)
I(2A)	0.0435(3)	0.0577(3)	0.0666(3)	-0.0294(2)	-0.0001(2)	-0.0082(2)
F(2A)	0.123(4)	0.099(3)	0.048(3)	-0.015(2)	-0.044(3)	-0.039(3)
C(3A)	0.080(5)	0.060(4)	0.039(4)	-0.008(3)	-0.030(4)	-0.028(4)
I(3A)	0.0685(3)	0.0561(3)	0.0584(3)	-0.0290(2)	-0.0165(3)	0.0029(2)
F(3A)	0.105(4)	0.097(3)	0.048(2)	-0.044(2)	-0.009(2)	-0.021(3)

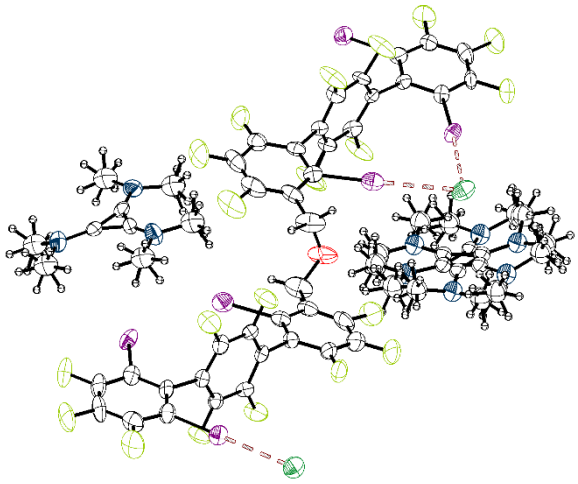
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(2B)	0.031(3)	0.048(3)	0.038(3)	-0.015(3)	-0.004(3)	-0.007(3)
I(2B)	0.0441(3)	0.0523(3)	0.0618(3)	-0.0224(2)	0.0013(2)	-0.0184(2)
F(2B)	0.054(2)	0.070(2)	0.045(2)	-0.0348(19)	0.0018(18)	-0.0092(19)
C(4A)	0.067(5)	0.061(4)	0.034(4)	-0.023(3)	-0.003(3)	-0.025(4)
F(4A)	0.048(2)	0.052(2)	0.041(2)	-0.0083(16)	-0.0100(17)	-0.0266(17)
C(3B)	0.044(4)	0.045(3)	0.032(3)	-0.019(3)	-0.004(3)	-0.001(3)
I(3B)	0.0566(3)	0.0492(3)	0.0600(3)	-0.0268(2)	-0.0055(2)	-0.0169(2)
F(3B)	0.061(2)	0.053(2)	0.053(2)	-0.0293(18)	-0.0093(19)	-0.0158(18)
C(5A)	0.045(4)	0.041(3)	0.042(4)	-0.013(3)	-0.005(3)	-0.018(3)
F(5A)	0.065(3)	0.078(3)	0.0311(19)	-0.0017(18)	-0.0076(18)	-0.036(2)
C(4B)	0.045(4)	0.035(3)	0.036(3)	-0.009(3)	-0.014(3)	-0.007(3)
F(4B)	0.064(2)	0.056(2)	0.0324(19)	-0.0126(17)	-0.0222(18)	0.0121(19)
C(6A)	0.040(3)	0.035(3)	0.034(3)	-0.013(2)	-0.009(3)	-0.014(3)
F(6A)	0.057(2)	0.079(3)	0.049(2)	-0.013(2)	-0.0199(19)	-0.035(2)
C(5B)	0.033(3)	0.046(3)	0.029(3)	-0.013(3)	-0.002(3)	-0.006(3)
F(5B)	0.045(2)	0.052(2)	0.041(2)	-0.0177(17)	-0.0155(17)	0.0128(17)
C(7A)	0.039(3)	0.034(3)	0.033(3)	-0.013(2)	-0.008(3)	-0.008(2)
F(7A)	0.054(2)	0.068(2)	0.0286(18)	-0.0069(17)	-0.0042(16)	-0.0359(19)
C(6B)	0.031(3)	0.035(3)	0.023(3)	-0.007(2)	-0.006(2)	-0.002(2)
F(6B)	0.060(2)	0.057(2)	0.0289(18)	-0.0052(16)	-0.0199(17)	0.0008(18)
C(8A)	0.040(3)	0.034(3)	0.042(3)	-0.010(3)	-0.013(3)	-0.012(3)
F(8A)	0.067(3)	0.059(2)	0.065(3)	-0.027(2)	-0.035(2)	0.016(2)
C(7B)	0.036(3)	0.036(3)	0.027(3)	-0.006(2)	-0.007(2)	-0.010(2)
F(7B)	0.042(2)	0.059(2)	0.044(2)	-0.0135(18)	-0.0132(17)	0.0151(18)
C(9A)	0.048(4)	0.040(3)	0.024(3)	-0.003(2)	-0.006(3)	-0.014(3)
F(9A)	0.065(3)	0.073(3)	0.069(3)	-0.049(2)	-0.024(2)	0.010(2)
C(8B)	0.042(3)	0.034(3)	0.026(3)	-0.007(2)	-0.011(3)	-0.004(2)
F(8B)	0.058(2)	0.0409(19)	0.047(2)	-0.0088(16)	-0.0109(18)	-0.0223(17)
C(10A)	0.045(4)	0.038(3)	0.032(3)	-0.011(3)	-0.014(3)	-0.004(3)
F(10A)	0.061(3)	0.081(3)	0.046(2)	-0.029(2)	-0.025(2)	-0.008(2)
C(9B)	0.031(3)	0.033(3)	0.035(3)	-0.012(2)	-0.013(3)	-0.003(2)
F(9B)	0.086(3)	0.051(2)	0.065(3)	-0.035(2)	-0.011(2)	-0.017(2)
C(11A)	0.036(3)	0.039(3)	0.039(3)	-0.007(3)	-0.013(3)	-0.017(3)
C(10B)	0.036(3)	0.033(3)	0.024(3)	-0.010(2)	-0.005(2)	-0.009(2)
F(10B)	0.067(3)	0.067(3)	0.043(2)	-0.032(2)	0.008(2)	-0.007(2)
C(12A)	0.044(4)	0.041(3)	0.027(3)	-0.010(3)	-0.007(3)	-0.014(3)
C(11B)	0.044(4)	0.032(3)	0.031(3)	-0.001(2)	-0.016(3)	-0.008(3)
C(13A)	0.038(3)	0.039(3)	0.033(3)	-0.010(3)	-0.012(3)	-0.009(3)
C(12B)	0.032(3)	0.039(3)	0.038(3)	-0.012(3)	-0.009(3)	-0.003(3)
C(14A)	0.042(4)	0.045(3)	0.035(3)	-0.014(3)	-0.015(3)	0.000(3)
C(13B)	0.035(3)	0.031(3)	0.027(3)	-0.008(2)	-0.011(2)	-0.003(2)
C(15A)	0.045(4)	0.048(4)	0.046(4)	-0.024(3)	-0.014(3)	-0.003(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(14B)	0.040(3)	0.032(3)	0.033(3)	-0.006(2)	-0.008(3)	-0.010(3)
C(16A)	0.040(3)	0.050(4)	0.037(3)	-0.010(3)	-0.015(3)	-0.016(3)
C(15B)	0.052(4)	0.035(3)	0.039(3)	-0.017(3)	-0.013(3)	-0.008(3)
C(17A)	0.038(3)	0.036(3)	0.029(3)	-0.004(2)	-0.009(3)	-0.015(3)
C(16B)	0.044(4)	0.049(4)	0.036(3)	-0.023(3)	-0.008(3)	0.005(3)
C(18A)	0.040(3)	0.035(3)	0.034(3)	-0.009(3)	-0.005(3)	-0.014(3)
C(17B)	0.035(3)	0.034(3)	0.034(3)	-0.005(3)	-0.010(3)	-0.004(2)
C(19A)	0.038(3)	0.044(3)	0.039(3)	-0.006(3)	-0.014(3)	-0.012(3)
C(19B)	0.032(3)	0.045(3)	0.037(3)	-0.008(3)	-0.008(3)	-0.001(3)
C(18B)	0.034(3)	0.030(3)	0.038(3)	-0.014(2)	-0.010(3)	-0.001(2)

Cleft **8** Co-Crystal with TDA-Cl (CCDC No. 2296703)

Table S4 *Co-Crystal structure data of tweezer-compound* ***8*** *and TDA-Cl.*

Identifier	DB-TDACl
Formula	$C_{56}H_{40}Cl_2F_{20}I_6N_6O$
Molecular Mass	2025.24
Crystal System	Monoclinic
Space Group	Pn (7)
Lattice Parameters	
a	13.4108(7)
b	19.3917(8)
c	13.6515(7)
α	90
β	112.993(7)
γ	90
Density [g/cm$_3$]	2.058
Crystal size [mm$_3$]	0.446 x 0.355 x 0.065
Volume [Å^3]	3268.1(3)
Z	2
Temperature [K]	170(2)
Diffraction Device	Xcalibur, Sapphire2
Radiation Type	0.71073 Å (Mo K)
F(000)	1916
Absorption coefficient [mm-1]	3,034
Absorption correction	Gaussian
Measurement range	2.9 - 26.5
Index range	-15 < h < 16
	-24 < k < 24
	-17 < l < 17
Measured reflexes	27643
Independent	9886
Observed	8679
R(int)	0.0405



Completeness (%) / theta (°)	99.8 / 25.242
Transmission (min / max)	0.439 / 0.843
R1 (observed/all)	0.0393 / 0.0493
wR2 (observed/all)	0.0795 / 0.0845
GooF = S	1.072
Rest electron density max./min. [e-/Å³]	-0.772 / 1.018
Flack*	0.57(3)

*The structure was refined as a two-component inversion twin.

Table S5 *Fractional atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å²×10³) for db-f41c2-tdacl.*

Atom	***x***	***Y***	***z***	**U(eq)**
I(1)	0.58621(6)	0.42854(4)	-0.12360(6)	0.04606(19)
C(1)	0.4754(9)	0.3800(5)	-0.0739(9)	0.041(2)
Cl(1)	0.7425(3)	0.50468(18)	-0.1966(3)	0.0607(8)
O(1)	0.4948(9)	0.8239(5)	0.4569(7)	0.074(3)
N(1)	0.5536(9)	0.3743(5)	0.4284(8)	0.056(3)
F(1)	0.4764(6)	1.1910(4)	1.1956(6)	0.064(2)
C(2)	0.4367(11)	0.3165(6)	-0.1108(10)	0.051(3)
Cl(2)	0.7342(3)	1.05301(16)	0.6872(2)	0.0554(8)
I(2)	0.30527(6)	0.42134(4)	0.13865(6)	0.04621(19)
N(2)	0.3933(9)	0.4425(5)	0.5680(8)	0.052(2)
F(2)	0.6101(7)	1.2730(3)	1.1470(6)	0.071(2)
C(3)	0.3651(10)	0.2815(5)	-0.0820(12)	0.055(3)
N(3)	0.2962(10)	0.2937(6)	0.3875(9)	0.067(3)
I(3)	0.38331(7)	0.62351(4)	0.28386(6)	0.0546(2)
F(3)	0.6849(6)	1.2354(3)	1.0008(6)	0.0560(17)
I(4)	0.59367(6)	0.91804(4)	0.68354(6)	0.0497(2)
C(4)	0.3279(10)	0.3128(5)	-0.0110(11)	0.052(3)
I(5)	0.65159(5)	1.10289(3)	0.85666(5)	0.03975(16)
C(5)	0.3646(8)	0.3768(5)	0.0306(9)	0.040(3)
C(6)	0.4747(8)	0.4818(5)	0.0431(8)	0.033(2)
I(6)	0.37471(6)	1.04543(4)	1.11321(6)	0.0495(2)
C(7)	0.4212(8)	0.5396(5)	-0.0092(8)	0.034(2)
F(8)	0.3388(6)	0.7745(3)	0.8289(6)	0.0637(19)
C(8)	0.4433(8)	0.6033(5)	0.0367(7)	0.033(2)
C(5T)	0.1855(13)	0.3063(8)	0.3795(11)	0.0772(17)
C(4T)	0.3077(13)	0.2469(8)	0.3120(11)	0.0772(17)
C(3T)	0.4666(9)	0.3734(5)	0.4487(8)	0.041(3)
C(38)	0.4800(9)	1.1076(5)	1.0712(8)	0.038(2)

Atom	*x*	*Y*	*z*	U(eq)
C(37)	0.5114(10)	1.1706(6)	1.1203(8)	0.043(3)
C(36)	0.5820(10)	1.2120(5)	1.0977(10)	0.050(3)
C(35)	0.6190(9)	1.1911(5)	1.0226(9)	0.040(2)
C(34)	0.5893(8)	1.1302(5)	0.9699(8)	0.032(2)
C(33)	0.5177(8)	1.0865(5)	0.9944(8)	0.031(2)
C(32)	0.5534(9)	0.9614(5)	0.9805(7)	0.039(3)
C(31)	0.4902(8)	1.0189(4)	0.9410(7)	0.026(2)
C(30)	0.4029(9)	1.0101(5)	0.8458(8)	0.037(2)
C(2T)	0.4050(9)	0.3985(6)	0.4989(9)	0.045(3)
F(9)	0.3282(7)	0.6630(3)	0.7066(7)	0.079(2)
C(9)	0.5216(8)	0.6125(4)	0.1386(8)	0.029(2)
C(10)	0.5809(8)	0.5563(5)	0.1902(8)	0.032(2)
F(10)	0.4213(8)	0.6649(4)	0.5668(7)	0.090(3)
F(11)	0.5591(8)	0.8793(4)	0.3045(6)	0.082(3)
C(11)	0.5572(8)	0.4918(5)	0.1417(8)	0.037(2)
F(12)	0.6721(7)	0.8430(4)	0.1920(6)	0.080(3)
F(13)	0.6562(6)	0.7142(3)	0.1136(6)	0.0627(19)
C(13)	0.5996(10)	0.7308(6)	0.1718(9)	0.046(3)
F(14)	0.6571(7)	0.5624(3)	0.2859(6)	0.067(2)
C(14)	0.6101(12)	0.7974(6)	0.2109(9)	0.056(3)
F(15)	0.6147(6)	0.4372(3)	0.1942(6)	0.066(2)
C(15)	0.5498(12)	0.8136(6)	0.2707(10)	0.058(3)
C(16)	0.4877(10)	0.7675(6)	0.2961(8)	0.049(3)
F(16)	0.3849(6)	0.6578(3)	-0.0154(5)	0.0597(19)
F(17)	0.3430(6)	0.5335(3)	-0.1057(5)	0.0532(18)
C(17)	0.4796(9)	0.7005(5)	0.2542(8)	0.041(2)
C(018)	0.4373(9)	0.4112(4)	-0.0013(9)	0.035(2)
F(18)	0.4711(7)	0.2836(4)	-0.1794(7)	0.076(2)
C(18)	0.5364(9)	0.6816(5)	0.1915(8)	0.035(2)
C(19)	0.4232(12)	0.7943(8)	0.3591(10)	0.068(4)
F(19)	0.3286(7)	0.2189(3)	-0.1189(7)	0.078(2)
C(29)	0.3873(10)	0.9491(5)	0.7903(8)	0.040(3)
C(28)	0.4543(8)	0.8948(5)	0.8255(8)	0.031(2)
C(27)	0.5365(10)	0.9016(5)	0.9240(9)	0.046(3)
C(26)	0.4976(8)	0.8323(5)	0.6858(8)	0.039(2)
C(25)	0.4469(8)	0.8325(5)	0.7559(8)	0.035(2)
C(24)	0.3884(10)	0.7749(6)	0.7624(9)	0.047(3)
C(23)	0.3821(10)	0.7182(6)	0.6981(11)	0.057(3)
C(22)	0.4314(12)	0.7210(7)	0.6275(11)	0.065(4)
C(21)	0.4913(9)	0.7761(6)	0.6179(8)	0.046(3)
C(20)	0.5429(12)	0.7760(7)	0.5395(10)	0.068(4)
F(20)	0.2574(6)	0.2778(3)	0.0178(7)	0.072(2)

Atom	*x*	*Y*	*z*	U(eq)
C(6T)	0.2975(14)	0.4385(8)	0.5935(12)	0.0772(17)
C(7T)	0.4528(13)	0.5075(8)	0.5882(11)	0.0772(17)
C(9T)	0.5674(14)	0.3302(8)	0.3517(11)	0.0772(17)
C(1T)	0.3712(10)	0.3428(5)	0.4339(8)	0.045(3)
C(8T)	0.6302(14)	0.4293(8)	0.4733(12)	0.0772(17)
C(3A)	0.5285(18)	1.1732(12)	0.5428(15)	0.035(2)
C(2A)	0.5041(18)	1.1134(10)	0.4873(15)	0.035(2)
N(1A)	0.6796(16)	1.1555(9)	0.4726(15)	0.057(2)
C(1A)	0.5938(17)	1.1481(11)	0.4954(15)	0.035(2)
N(2A)	0.4415(16)	1.0564(9)	0.4512(15)	0.057(2)
N(3A)	0.5014(16)	1.2216(9)	0.5952(14)	0.057(2)
C(4A)	0.766(2)	1.1983(12)	0.541(2)	0.060(2)
C(5A)	0.710(2)	1.1056(13)	0.414(2)	0.060(2)
C(6A)	0.476(2)	0.9993(11)	0.405(2)	0.060(2)
C(7A)	0.347(2)	1.0438(13)	0.473(2)	0.060(2)
C(8A)	0.406(2)	1.2094(12)	0.623(2)	0.060(2)
C(9A)	0.583(3)	1.269(2)	0.661(4)	0.060(2)
F(5A)	0.3067(18)	0.9402(9)	0.6933(17)	0.0679(18)
F(4A)	0.3342(19)	1.0625(10)	0.7958(16)	0.0679(18)
F(8A)	0.6487(18)	0.9657(8)	1.0694(14)	0.0679(18)
F(7A)	0.618(2)	0.8494(7)	0.9588(14)	0.0679(18)
C(1B)	0.554(2)	1.1156(14)	0.470(2)	0.035(2)
C(2B)	0.481(2)	1.1338(13)	0.5203(19)	0.035(2)
C(3B)	0.568(2)	1.1755(15)	0.529(2)	0.035(2)
N(1B)	0.581(2)	1.0778(11)	0.4075(19)	0.057(2)
N(2B)	0.398(2)	1.1158(12)	0.5430(19)	0.057(2)
N(3B)	0.624(2)	1.2325(12)	0.5742(19)	0.057(2)
C(4B)	0.670(3)	1.0862(17)	0.389(3)	0.060(2)
C(5B)	0.555(3)	1.0070(15)	0.400(3)	0.060(2)
C(6B)	0.338(3)	1.0617(17)	0.505(3)	0.060(2)
C(7B)	0.371(3)	1.1576(15)	0.612(3)	0.060(2)
C(8B)	0.607(4)	1.272(3)	0.659(5)	0.060(2)
C(9B)	0.730(2)	1.2387(16)	0.569(3)	0.060(2)
F(4B)	0.345(4)	1.0656(18)	0.818(3)	0.0679(18)
F(6B)	0.618(3)	0.9695(15)	1.080(3)	0.0679(18)
F(5B)	0.301(3)	0.9539(17)	0.695(3)	0.0679(18)
F(7B)	0.579(4)	0.8460(13)	0.972(2)	0.0679(18)

Table S6 *Anisotropic displacement parameters ($Å^2 \times 10^3$) for db-f41c2-tdacl.*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I(1)	0.0537(4)	0.0450(4)	0.0506(4)	-0.0085(3)	0.0324(4)	-0.0006(3)

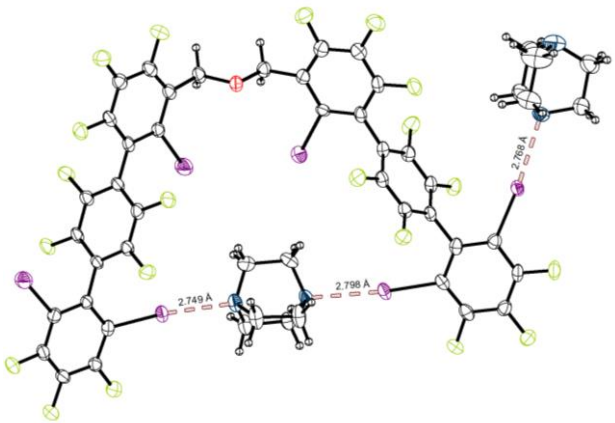
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.040(6)	0.025(5)	0.057(7)	-0.002(5)	0.019(6)	0.000(4)
Cl(1)	0.0594(19)	0.083(2)	0.0575(18)	-0.0101(16)	0.0425(17)	-0.0092(17)
O(1)	0.114(8)	0.061(6)	0.040(5)	-0.021(4)	0.022(5)	0.015(5)
N(1)	0.049(6)	0.057(6)	0.059(6)	-0.018(5)	0.019(5)	-0.018(5)
F(1)	0.083(5)	0.062(4)	0.066(4)	-0.029(4)	0.050(4)	-0.009(4)
C(2)	0.063(8)	0.034(6)	0.054(7)	-0.007(5)	0.019(7)	0.007(6)
Cl(2)	0.0621(19)	0.0641(19)	0.0558(17)	0.0062(14)	0.0403(16)	0.0132(15)
I(2)	0.0407(4)	0.0469(4)	0.0604(5)	0.0165(3)	0.0299(4)	0.0055(3)
N(2)	0.069(7)	0.044(5)	0.042(5)	-0.006(4)	0.023(5)	-0.006(5)
F(2)	0.094(6)	0.036(4)	0.081(5)	-0.029(3)	0.033(5)	-0.018(4)
C(3)	0.046(7)	0.017(5)	0.092(10)	-0.010(6)	0.016(7)	-0.009(5)
N(3)	0.087(9)	0.059(7)	0.054(6)	-0.010(5)	0.027(6)	-0.036(6)
I(3)	0.0580(5)	0.0682(5)	0.0472(4)	-0.0088(4)	0.0309(4)	-0.0020(4)
F(3)	0.058(4)	0.041(4)	0.072(5)	-0.005(3)	0.028(4)	-0.016(3)
I(4)	0.0519(5)	0.0595(5)	0.0413(4)	-0.0065(4)	0.0222(4)	0.0100(4)
C(4)	0.041(7)	0.021(5)	0.090(9)	0.004(5)	0.021(7)	-0.004(5)
I(5)	0.0433(4)	0.0356(3)	0.0496(4)	0.0052(3)	0.0282(3)	0.0039(3)
C(5)	0.029(5)	0.037(6)	0.054(7)	0.011(5)	0.016(5)	0.006(4)
C(6)	0.038(6)	0.024(5)	0.043(6)	-0.001(4)	0.022(5)	0.002(4)
I(6)	0.0576(5)	0.0575(5)	0.0452(4)	-0.0092(3)	0.0331(4)	-0.0117(4)
C(7)	0.039(6)	0.024(5)	0.039(6)	-0.004(4)	0.016(5)	0.000(4)
F(8)	0.079(5)	0.039(4)	0.078(5)	-0.006(3)	0.036(4)	-0.013(3)
C(8)	0.041(6)	0.029(5)	0.031(5)	0.002(4)	0.018(5)	0.012(4)
C(5T)	0.084(5)	0.089(4)	0.056(4)	-0.003(3)	0.025(3)	-0.010(4)
C(4T)	0.084(5)	0.089(4)	0.056(4)	-0.003(3)	0.025(3)	-0.010(4)
C(3T)	0.039(6)	0.040(6)	0.036(6)	0.003(5)	0.004(5)	-0.011(5)
C(38)	0.051(7)	0.033(5)	0.032(5)	-0.005(4)	0.018(5)	0.000(5)
C(37)	0.051(7)	0.045(6)	0.037(6)	-0.007(5)	0.021(5)	-0.008(5)
C(36)	0.051(7)	0.030(6)	0.063(8)	-0.021(5)	0.015(6)	-0.009(5)
C(35)	0.035(6)	0.033(6)	0.050(6)	-0.003(5)	0.015(5)	-0.009(5)
C(34)	0.034(6)	0.023(5)	0.043(6)	0.001(4)	0.020(5)	0.004(4)
C(33)	0.036(6)	0.025(5)	0.031(5)	0.002(4)	0.012(5)	0.006(4)
C(32)	0.048(7)	0.030(5)	0.020(5)	-0.005(4)	-0.006(5)	0.002(5)
C(31)	0.031(5)	0.022(5)	0.030(5)	0.000(4)	0.017(4)	-0.002(4)
C(30)	0.048(7)	0.025(5)	0.039(6)	0.004(4)	0.017(5)	0.014(5)
C(2T)	0.041(6)	0.046(6)	0.039(6)	0.014(5)	0.006(5)	-0.010(5)
F(9)	0.096(6)	0.031(4)	0.101(6)	-0.011(4)	0.030(5)	-0.012(4)
C(9)	0.033(5)	0.020(5)	0.037(5)	0.002(4)	0.018(5)	-0.001(4)
C(10)	0.030(5)	0.031(5)	0.035(5)	0.003(4)	0.013(5)	-0.002(4)
F(10)	0.112(7)	0.046(4)	0.091(6)	-0.045(4)	0.018(5)	0.011(4)
F(11)	0.133(8)	0.043(4)	0.065(5)	-0.018(3)	0.035(5)	-0.008(4)
C(11)	0.033(6)	0.029(5)	0.048(6)	0.009(4)	0.013(5)	0.005(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(12)	0.120(7)	0.045(4)	0.077(5)	-0.009(4)	0.041(5)	-0.036(4)
F(13)	0.083(5)	0.054(4)	0.067(5)	-0.015(3)	0.046(4)	-0.030(4)
C(13)	0.055(7)	0.041(6)	0.040(6)	-0.004(5)	0.019(6)	-0.014(5)
F(14)	0.067(5)	0.052(4)	0.049(4)	-0.004(3)	-0.011(4)	0.006(4)
C(14)	0.074(9)	0.048(7)	0.043(7)	0.001(5)	0.019(7)	-0.008(7)
F(15)	0.072(5)	0.032(3)	0.067(5)	0.010(3)	-0.004(4)	0.014(3)
C(15)	0.077(9)	0.037(7)	0.045(7)	-0.016(5)	0.009(7)	-0.003(6)
C(16)	0.058(8)	0.051(7)	0.032(6)	-0.008(5)	0.011(6)	0.003(6)
F(16)	0.082(5)	0.032(3)	0.046(4)	0.002(3)	0.003(4)	0.012(3)
F(17)	0.063(4)	0.032(3)	0.042(3)	-0.007(3)	-0.005(3)	0.010(3)
C(17)	0.046(6)	0.044(6)	0.031(5)	-0.008(5)	0.013(5)	-0.001(5)
C(018)	0.031(5)	0.021(5)	0.048(6)	0.008(4)	0.009(5)	0.005(4)
F(18)	0.096(6)	0.047(4)	0.095(6)	-0.033(4)	0.048(5)	-0.008(4)
C(18)	0.046(6)	0.024(5)	0.034(5)	-0.003(4)	0.016(5)	-0.002(4)
C(19)	0.081(10)	0.073(9)	0.047(7)	-0.021(6)	0.023(7)	0.022(8)
F(19)	0.075(5)	0.030(4)	0.114(7)	-0.018(4)	0.021(5)	-0.020(4)
C(29)	0.047(6)	0.038(6)	0.025(5)	-0.008(4)	0.002(5)	0.009(5)
C(28)	0.032(5)	0.030(5)	0.030(5)	0.000(4)	0.011(5)	0.005(4)
C(27)	0.056(7)	0.026(5)	0.043(6)	0.003(5)	0.006(6)	0.013(5)
C(26)	0.033(6)	0.038(6)	0.038(6)	0.000(4)	0.007(5)	0.007(5)
C(25)	0.032(5)	0.037(6)	0.029(5)	0.001(4)	0.004(4)	0.012(4)
C(24)	0.051(7)	0.042(6)	0.042(7)	-0.006(5)	0.014(6)	0.000(5)
C(23)	0.048(7)	0.028(6)	0.070(9)	-0.010(6)	-0.003(7)	0.001(5)
C(22)	0.081(10)	0.047(8)	0.055(8)	-0.022(6)	0.012(7)	0.016(7)
C(21)	0.048(7)	0.043(6)	0.035(6)	-0.011(5)	0.002(5)	0.012(5)
C(20)	0.076(9)	0.074(9)	0.049(7)	-0.019(7)	0.020(7)	0.041(8)
F(20)	0.062(5)	0.046(4)	0.118(7)	0.006(4)	0.046(5)	-0.017(3)
C(6T)	0.084(5)	0.089(4)	0.056(4)	-0.003(3)	0.025(3)	-0.010(4)
C(7T)	0.084(5)	0.089(4)	0.056(4)	-0.003(3)	0.025(3)	-0.010(4)
C(9T)	0.084(5)	0.089(4)	0.056(4)	-0.003(3)	0.025(3)	-0.010(4)
C(1T)	0.055(7)	0.034(6)	0.035(6)	0.008(5)	0.006(5)	-0.013(5)
C(8T)	0.084(5)	0.089(4)	0.056(4)	-0.003(3)	0.025(3)	-0.010(4)
C(3A)	0.045(8)	0.032(5)	0.028(5)	-0.004(4)	0.013(4)	-0.001(5)
C(2A)	0.045(8)	0.032(5)	0.028(5)	-0.004(4)	0.013(4)	-0.001(5)
N(1A)	0.063(6)	0.050(5)	0.054(5)	0.002(4)	0.019(5)	-0.007(4)
C(1A)	0.045(8)	0.032(5)	0.028(5)	-0.004(4)	0.013(4)	-0.001(5)
N(2A)	0.063(6)	0.050(5)	0.054(5)	0.002(4)	0.019(5)	-0.007(4)
N(3A)	0.063(6)	0.050(5)	0.054(5)	0.002(4)	0.019(5)	-0.007(4)
C(4A)	0.064(6)	0.052(4)	0.063(5)	-0.005(4)	0.025(5)	-0.002(4)
C(5A)	0.064(6)	0.052(4)	0.063(5)	-0.005(4)	0.025(5)	-0.002(4)
C(6A)	0.064(6)	0.052(4)	0.063(5)	-0.005(4)	0.025(5)	-0.002(4)
C(7A)	0.064(6)	0.052(4)	0.063(5)	-0.005(4)	0.025(5)	-0.002(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(8A)	0.064(6)	0.052(4)	0.063(5)	-0.005(4)	0.025(5)	-0.002(4)
C(9A)	0.064(6)	0.052(4)	0.063(5)	-0.005(4)	0.025(5)	-0.002(4)
F(5A)	0.064(4)	0.040(2)	0.056(3)	-0.018(2)	-0.024(3)	0.032(3)
F(4A)	0.064(4)	0.040(2)	0.056(3)	-0.018(2)	-0.024(3)	0.032(3)
F(8A)	0.064(4)	0.040(2)	0.056(3)	-0.018(2)	-0.024(3)	0.032(3)
F(7A)	0.064(4)	0.040(2)	0.056(3)	-0.018(2)	-0.024(3)	0.032(3)
C(1B)	0.045(8)	0.032(5)	0.028(5)	-0.004(4)	0.013(4)	-0.001(5)
C(2B)	0.045(8)	0.032(5)	0.028(5)	-0.004(4)	0.013(4)	-0.001(5)
C(3B)	0.045(8)	0.032(5)	0.028(5)	-0.004(4)	0.013(4)	-0.001(5)
N(1B)	0.063(6)	0.050(5)	0.054(5)	0.002(4)	0.019(5)	-0.007(4)
N(2B)	0.063(6)	0.050(5)	0.054(5)	0.002(4)	0.019(5)	-0.007(4)
N(3B)	0.063(6)	0.050(5)	0.054(5)	0.002(4)	0.019(5)	-0.007(4)
C(4B)	0.064(6)	0.052(4)	0.063(5)	-0.005(4)	0.025(5)	-0.002(4)
C(5B)	0.064(6)	0.052(4)	0.063(5)	-0.005(4)	0.025(5)	-0.002(4)
C(6B)	0.064(6)	0.052(4)	0.063(5)	-0.005(4)	0.025(5)	-0.002(4)
C(7B)	0.064(6)	0.052(4)	0.063(5)	-0.005(4)	0.025(5)	-0.002(4)
C(8B)	0.064(6)	0.052(4)	0.063(5)	-0.005(4)	0.025(5)	-0.002(4)
C(9B)	0.064(6)	0.052(4)	0.063(5)	-0.005(4)	0.025(5)	-0.002(4)
F(4B)	0.064(4)	0.040(2)	0.056(3)	-0.018(2)	-0.024(3)	0.032(3)
F(6B)	0.064(4)	0.040(2)	0.056(3)	-0.018(2)	-0.024(3)	0.032(3)
F(5B)	0.064(4)	0.040(2)	0.056(3)	-0.018(2)	-0.024(3)	0.032(3)
F(7B)	0.064(4)	0.040(2)	0.056(3)	-0.018(2)	-0.024(3)	0.032(3)

Cleft **8** Co-Crystal with DABCO (CCDC No. 2296705)

Table S7 *Co-crystal structure data of tweezer-compound* ***8*** *and DACBO.*



Identifier	db-helix-dabco
Formula	C50 H28 F20 I6 N4 O
Molecular Mass	1842,16
Crystal System	Triclinic
Space Group	P-1 (2)
Lattice Parameters	
a	8.4976(2)
b	15.4791(4)
c	21.9450(3)
α	87.441(2)
β	86.903(2)
γ	74.868(2)
Density [g/cm$_3$]	2,2
Crystal size [mm$_3$]	0.120 x 0.070 x 0.020
Volume [Å^3]	2780.99(11)
Z	2
Temperature [K]	110.0(6)
Diffraction Device	Xcalibur, Sapphire2
Radiation Type	1.54184 Å (Cu K)

F(000)	1724
Absorption coefficient [mm^{-1}]	27,305
Absorption correction	Semi-empirical from equivalents
Measurement range	3.5 - 74.7
Index range	-10 < h < 10 -19 < k < 19 -27 < l < 27
Measured reflexes	62949
Independent	11243
Observed	9821
R(int)	0,0832
Completeness (%) / theta (°)	100.0 / 67.684
Transmission (min / max)	0.11215 / 1.00000
R1 (observed/all)	0.0440 / 0.0507
wR2 (observed/all)	0.1175 / 0.1238
GooF = S	1,06
Rest electron density max./min. [e-/Å³]	-2.402 / 2.269

Table S8 *Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å²×10^3) for db-helix-dabco.*

Atom	***x***	***Y***	***z***	**U(eq)**
I(1)	1.18715(4)	0.67477(2)	0.08958(2)	0.01962(9)
I(2)	0.85692(5)	0.61881(3)	-0.14129(2)	0.03457(11)
I(3)	0.64152(5)	0.91138(3)	0.16116(2)	0.03553(11)
I(4)	0.64505(5)	0.90561(3)	0.35094(2)	0.03133(11)
I(5)	1.18694(4)	0.65147(2)	0.45551(2)	0.02168(9)
I(6)	0.72406(4)	0.66181(2)	0.68221(2)	0.02055(9)
F(1)	1.4815(4)	0.5940(2)	-0.00263(14)	0.0257(7)
F(2)	1.5003(4)	0.5281(2)	-0.11472(14)	0.0281(7)
F(3)	1.2297(5)	0.5362(3)	-0.17405(14)	0.0304(8)
F(4)	0.8640(4)	0.5875(2)	0.05922(15)	0.0277(7)
F(5)	0.9009(5)	0.8261(2)	-0.07773(15)	0.0298(8)
F(6)	0.5887(4)	0.6889(2)	0.10917(15)	0.0285(7)
F(7)	0.6162(5)	0.9244(2)	-0.03115(16)	0.0328(8)
F(8)	0.2997(4)	0.8305(2)	-0.01536(13)	0.0259(7)
F(9)	0.0071(4)	0.9179(2)	0.03424(16)	0.0305(7)
F(10)	-0.0113(4)	1.0003(2)	0.14013(16)	0.0297(7)
F(11)	-0.0127(4)	0.9961(3)	0.37838(17)	0.0327(8)
F(12)	-0.0130(5)	0.9101(3)	0.48656(17)	0.0336(8)
F(13)	0.2713(4)	0.8238(2)	0.53685(14)	0.0274(7)

Atom	*x*	*Y*	*z*	U(eq)
F(14)	0.5836(5)	0.9275(2)	0.53971(15)	0.0300(8)
F(15)	0.5814(4)	0.6808(2)	0.42185(14)	0.0269(7)
F(16)	0.8453(4)	0.8301(2)	0.59614(13)	0.0244(7)
F(17)	0.8331(4)	0.5804(2)	0.48233(15)	0.0258(7)
F(18)	1.0576(4)	0.5273(2)	0.72305(13)	0.0272(7)
F(19)	1.3559(5)	0.4782(2)	0.66991(15)	0.0315(8)
F(20)	1.4157(4)	0.5353(3)	0.55583(15)	0.0319(8)
O(1)	0.2717(5)	0.9566(2)	0.25774(15)	0.0205(8)
C(1)	1.1930(7)	0.6410(3)	-0.0030(2)	0.0168(10)
C(2)	1.3438(7)	0.6007(4)	-0.0310(2)	0.0193(10)
C(3)	1.3545(7)	0.5670(4)	-0.0886(2)	0.0208(10)
C(4)	1.2146(7)	0.5718(4)	-0.1188(2)	0.0208(11)
C(5)	1.0638(6)	0.6145(3)	-0.0937(2)	0.0178(10)
C(6)	1.0512(7)	0.6513(3)	-0.0356(2)	0.0161(9)
C(7)	0.8934(6)	0.7039(3)	-0.0103(2)	0.0155(9)
C(8)	0.8056(7)	0.6715(3)	0.0370(2)	0.0172(10)
C(9)	0.6630(7)	0.7229(4)	0.0619(2)	0.0204(11)
C(10)	0.5932(7)	0.8101(3)	0.0404(2)	0.0178(10)
C(11)	0.6767(7)	0.8419(3)	-0.0078(2)	0.0198(10)
C(12)	0.8250(7)	0.7908(4)	-0.0316(2)	0.0208(11)
C(13)	0.4365(7)	0.8654(3)	0.0671(2)	0.0169(10)
C(14)	0.2939(7)	0.8712(3)	0.0378(2)	0.0199(10)
C(15)	0.1441(7)	0.9168(4)	0.0619(2)	0.0221(11)
C(16)	0.1378(7)	0.9583(4)	0.1168(2)	0.0213(11)
C(17)	0.2742(7)	0.9591(3)	0.1476(2)	0.0194(10)
C(18)	0.4258(6)	0.9111(3)	0.1212(2)	0.0164(10)
C(19)	0.2592(7)	1.0129(4)	0.2035(2)	0.0211(11)
C(20)	0.2682(7)	1.0102(4)	0.3098(2)	0.0198(10)
C(21)	0.2745(7)	0.9538(3)	0.3678(2)	0.0190(10)
C(22)	0.1328(7)	0.9524(4)	0.4002(2)	0.0226(11)
C(23)	0.1286(7)	0.9086(4)	0.4565(2)	0.0221(11)
C(24)	0.2742(8)	0.8645(3)	0.4814(2)	0.0214(11)
C(25)	0.4235(7)	0.8602(3)	0.4503(2)	0.0168(10)
C(26)	0.4207(7)	0.9052(3)	0.3939(2)	0.0172(10)
C(27)	0.5730(7)	0.8073(3)	0.4795(2)	0.0181(10)
C(28)	0.6461(7)	0.8420(3)	0.5242(2)	0.0217(11)
C(29)	0.7798(7)	0.7915(3)	0.5537(2)	0.0182(10)
C(30)	0.8464(7)	0.7018(3)	0.5416(2)	0.0165(10)
C(31)	0.7741(7)	0.6666(3)	0.4965(2)	0.0201(11)
C(32)	0.6439(7)	0.7182(4)	0.4662(2)	0.0197(11)
C(33)	0.9838(7)	0.6442(3)	0.5753(2)	0.0156(10)
C(34)	0.9530(7)	0.6161(3)	0.6360(2)	0.0174(10)

Atom	*x*	*Y*	*z*	U(eq)
C(35)	1.0808(7)	0.5589(3)	0.6657(2)	0.0196(11)
C(36)	1.2338(7)	0.5323(4)	0.6391(2)	0.0206(11)
C(37)	1.2635(7)	0.5623(4)	0.5800(2)	0.0228(11)
C(38)	1.1396(7)	0.6169(3)	0.5477(2)	0.0199(11)
N(1)	0.1359(7)	0.8340(4)	0.7709(3)	0.0381(13)
N(5)	0.4217(6)	0.7458(3)	0.7347(2)	0.0254(10)
C(45)	0.3922(9)	0.8396(4)	0.7137(3)	0.0344(14)
C(46)	0.2188(9)	0.8924(5)	0.7361(3)	0.0402(16)
C(47)	0.4066(9)	0.7437(5)	0.8018(3)	0.0376(15)
C(48)	0.2349(10)	0.7971(5)	0.8234(4)	0.0453(18)
C(49)	0.2979(10)	0.7067(5)	0.7120(4)	0.0472(18)
C(50)	0.1290(11)	0.7597(7)	0.7337(6)	0.065(3)
N(3)	1.1953(6)	0.6943(3)	0.21313(19)	0.0243(10)
N(4)	1.2088(6)	0.6874(3)	0.3296(2)	0.0231(10)
C(39)	1.3436(8)	0.7163(5)	0.2305(2)	0.0314(14)
C(40)	1.3493(8)	0.7159(4)	0.3008(2)	0.0263(12)
C(41)	1.1944(10)	0.6049(4)	0.2371(3)	0.0372(16)
C(42)	1.2136(9)	0.5983(4)	0.3067(2)	0.0310(14)
C(43)	1.0551(9)	0.7596(5)	0.2408(3)	0.0405(16)
C(44)	1.0591(9)	0.7511(5)	0.3112(3)	0.0350(14)

Table S9 *Anisotropic displacement parameters ($Å^2×10^3$) for db-helix-dabco.*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I(1)	0.03079(19)	0.02011(16)	0.00846(14)	-0.00179(11)	0.00212(12)	-0.00786(14)
I(2)	0.0321(2)	0.0465(2)	0.02295(18)	-0.01638(16)	-0.00287(15)	-0.00352(18)
I(3)	0.0312(2)	0.0486(3)	0.02520(18)	-0.01498(17)	-0.00051(15)	-0.00541(19)
I(4)	0.0311(2)	0.0364(2)	0.02253(18)	0.00609(15)	0.00776(14)	-0.00460(17)
I(5)	0.0339(2)	0.02140(17)	0.00958(14)	-0.00314(12)	0.00858(12)	-0.00823(15)
I(6)	0.02824(19)	0.02226(17)	0.00975(14)	0.00057(11)	0.00506(12)	-0.00539(14)
F(1)	0.0257(17)	0.0289(17)	0.0209(15)	-0.0044(13)	-0.0012(13)	-0.0033(14)
F(2)	0.0262(18)	0.0322(18)	0.0199(15)	-0.0018(13)	0.0094(13)	0.0009(15)
F(3)	0.038(2)	0.0381(19)	0.0113(14)	-0.0127(13)	0.0058(13)	-0.0018(16)
F(4)	0.0319(18)	0.0175(15)	0.0296(17)	0.0107(13)	0.0046(14)	-0.0020(14)
F(5)	0.038(2)	0.0238(17)	0.0208(15)	0.0077(13)	0.0206(14)	-0.0014(15)
F(6)	0.0346(19)	0.0261(17)	0.0214(15)	0.0110(13)	0.0122(14)	-0.0061(15)
F(7)	0.043(2)	0.0174(16)	0.0265(17)	0.0098(13)	0.0212(15)	0.0056(15)
F(8)	0.0364(19)	0.0275(17)	0.0126(13)	-0.0086(12)	0.0022(13)	-0.0057(15)
F(9)	0.0271(18)	0.0341(19)	0.0304(17)	-0.0045(14)	-0.0035(14)	-0.0071(15)
F(10)	0.0251(18)	0.0306(18)	0.0304(17)	-0.0101(14)	0.0094(14)	-0.0026(15)
F(11)	0.0259(18)	0.038(2)	0.0323(18)	0.0047(15)	-0.0031(14)	-0.0052(16)
F(12)	0.0300(19)	0.0340(19)	0.0355(18)	0.0016(15)	0.0118(15)	-0.0091(16)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(13)	0.038(2)	0.0293(17)	0.0129(14)	0.0022(13)	0.0097(13)	-0.0080(15)
F(14)	0.048(2)	0.0130(14)	0.0260(16)	-0.0081(12)	-0.0122(15)	-0.0002(14)
F(15)	0.0368(19)	0.0238(16)	0.0206(15)	-0.0117(13)	-0.0071(14)	-0.0059(15)
F(16)	0.041(2)	0.0164(14)	0.0150(13)	-0.0062(11)	-0.0083(13)	-0.0040(14)
F(17)	0.0380(19)	0.0126(14)	0.0243(15)	-0.0082(12)	-0.0058(14)	0.0000(13)
F(18)	0.041(2)	0.0285(17)	0.0084(13)	0.0054(12)	0.0008(13)	-0.0042(15)
F(19)	0.035(2)	0.0334(19)	0.0193(15)	-0.0036(14)	-0.0054(14)	0.0053(16)
F(20)	0.0282(19)	0.042(2)	0.0199(15)	-0.0074(14)	0.0088(13)	0.0005(16)
O(1)	0.032(2)	0.0190(18)	0.0093(15)	-0.0004(14)	0.0015(14)	-0.0060(16)
C(1)	0.029(3)	0.014(2)	0.0067(19)	-0.0009(17)	0.0043(18)	-0.004(2)
C(2)	0.027(3)	0.019(2)	0.013(2)	0.0015(19)	0.002(2)	-0.008(2)
C(3)	0.024(3)	0.018(2)	0.015(2)	-0.0001(19)	0.010(2)	0.003(2)
C(4)	0.032(3)	0.021(2)	0.008(2)	-0.0038(18)	0.005(2)	-0.006(2)
C(5)	0.020(3)	0.021(2)	0.012(2)	-0.0013(19)	0.0016(19)	-0.005(2)
C(6)	0.025(3)	0.011(2)	0.009(2)	0.0015(17)	0.0049(18)	-0.001(2)
C(7)	0.022(3)	0.014(2)	0.010(2)	-0.0033(17)	0.0044(18)	-0.003(2)
C(8)	0.027(3)	0.013(2)	0.011(2)	0.0015(18)	0.0063(19)	-0.006(2)
C(9)	0.028(3)	0.023(3)	0.012(2)	0.0016(19)	0.007(2)	-0.011(2)
C(10)	0.023(3)	0.017(2)	0.013(2)	-0.0007(18)	0.0064(19)	-0.006(2)
C(11)	0.030(3)	0.014(2)	0.013(2)	-0.0016(18)	0.012(2)	-0.001(2)
C(12)	0.031(3)	0.022(3)	0.008(2)	0.0038(19)	0.007(2)	-0.007(2)
C(13)	0.024(3)	0.017(2)	0.009(2)	-0.0010(18)	0.0082(18)	-0.006(2)
C(14)	0.032(3)	0.017(2)	0.008(2)	-0.0019(18)	0.007(2)	-0.004(2)
C(15)	0.022(3)	0.023(3)	0.021(2)	0.000(2)	0.003(2)	-0.007(2)
C(16)	0.026(3)	0.020(2)	0.017(2)	0.000(2)	0.011(2)	-0.006(2)
C(17)	0.027(3)	0.014(2)	0.014(2)	0.0005(19)	0.009(2)	-0.002(2)
C(18)	0.022(3)	0.017(2)	0.010(2)	0.0000(18)	0.0025(18)	-0.004(2)
C(19)	0.036(3)	0.017(2)	0.008(2)	0.0004(19)	0.012(2)	-0.006(2)
C(20)	0.032(3)	0.017(2)	0.011(2)	-0.0002(19)	0.001(2)	-0.009(2)
C(21)	0.030(3)	0.015(2)	0.011(2)	-0.0039(18)	-0.001(2)	-0.003(2)
C(22)	0.027(3)	0.021(3)	0.020(2)	0.000(2)	-0.001(2)	-0.008(2)
C(23)	0.026(3)	0.020(2)	0.020(2)	-0.006(2)	0.007(2)	-0.005(2)
C(24)	0.040(3)	0.016(2)	0.008(2)	-0.0022(18)	0.003(2)	-0.007(2)
C(25)	0.028(3)	0.017(2)	0.0047(19)	-0.0049(17)	0.0042(18)	-0.004(2)
C(26)	0.024(3)	0.016(2)	0.012(2)	-0.0020(18)	0.0022(19)	-0.006(2)
C(27)	0.031(3)	0.017(2)	0.0066(19)	0.0017(18)	0.0006(19)	-0.008(2)
C(28)	0.037(3)	0.013(2)	0.015(2)	-0.0041(18)	-0.002(2)	-0.004(2)
C(29)	0.033(3)	0.016(2)	0.0081(19)	-0.0045(18)	-0.001(2)	-0.011(2)
C(30)	0.025(3)	0.016(2)	0.0080(19)	0.0010(17)	0.0042(18)	-0.004(2)
C(31)	0.034(3)	0.015(2)	0.011(2)	-0.0021(18)	0.004(2)	-0.005(2)
C(32)	0.033(3)	0.020(2)	0.008(2)	-0.0042(18)	0.001(2)	-0.010(2)
C(33)	0.027(3)	0.015(2)	0.0049(19)	-0.0027(17)	0.0033(18)	-0.006(2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(34)	0.024(3)	0.016(2)	0.009(2)	-0.0060(18)	0.0027(19)	-0.001(2)
C(35)	0.037(3)	0.018(2)	0.005(2)	0.0010(18)	0.000(2)	-0.010(2)
C(36)	0.027(3)	0.019(2)	0.014(2)	-0.0026(19)	-0.003(2)	-0.003(2)
C(37)	0.033(3)	0.024(3)	0.013(2)	-0.011(2)	0.009(2)	-0.009(2)
C(38)	0.039(3)	0.014(2)	0.0068(19)	-0.0050(17)	0.004(2)	-0.008(2)
N(1)	0.031(3)	0.030(3)	0.053(3)	-0.007(3)	0.009(3)	-0.007(2)
N(5)	0.029(3)	0.023(2)	0.023(2)	0.0007(19)	0.0057(19)	-0.007(2)
C(45)	0.041(4)	0.031(3)	0.030(3)	0.005(3)	0.012(3)	-0.010(3)
C(46)	0.041(4)	0.030(3)	0.041(4)	0.009(3)	0.007(3)	0.003(3)
C(47)	0.043(4)	0.034(3)	0.027(3)	0.008(3)	0.009(3)	0.002(3)
C(48)	0.050(5)	0.034(4)	0.043(4)	0.004(3)	0.017(3)	0.001(3)
C(49)	0.044(4)	0.039(4)	0.064(5)	-0.017(4)	0.000(4)	-0.018(3)
C(50)	0.041(5)	0.054(5)	0.103(8)	-0.040(5)	0.005(5)	-0.013(4)
N(3)	0.038(3)	0.025(2)	0.0116(19)	-0.0008(17)	0.0032(18)	-0.011(2)
N(4)	0.036(3)	0.019(2)	0.0137(19)	-0.0045(17)	0.0075(18)	-0.006(2)
C(39)	0.043(4)	0.044(4)	0.014(2)	0.003(2)	0.004(2)	-0.025(3)
C(40)	0.037(3)	0.026(3)	0.018(2)	-0.003(2)	-0.001(2)	-0.011(3)
C(41)	0.071(5)	0.030(3)	0.017(3)	-0.002(2)	0.007(3)	-0.025(3)
C(42)	0.056(4)	0.027(3)	0.016(2)	-0.002(2)	0.005(3)	-0.021(3)
C(43)	0.033(4)	0.048(4)	0.031(3)	-0.005(3)	-0.001(3)	0.006(3)
C(44)	0.036(4)	0.041(4)	0.022(3)	-0.010(3)	0.007(3)	0.002(3)

DFT Data

Method

Density Functional Theory (DFT) calculations were performed with the Gaussian16 suite of programs (Revision C.01).[2] The M06-2X functional[3] with a minimal augmented def2-TZVP(D) basis set including corresponding pseudopotentials[4], applying an additional diffuse function for chlorine and iodine nuclei, were used on an ultrafine grid. Geometries were optimized using symmetry restrictions were applicable to reduce computational costs. The nature of minima structures was confirmed by frequency calculations, with the absence of negative frequencies as indication of global minima (unless noted otherwise below). Optimizations were performed in gas phase and continued with the SMD18[5] intrinsic solvent model. Dispersion and Grimme entropy corrections[6] were applied to obtained energies using the *goodvibes* python script. [7] Obtained energies are given in Hartee.

Geometries

Open conformer of **8** in THF solution

E=-5308.389613 H=-5307.993974 G=-5308.169387

I	-5.05508600	-2.30701800	-2.56475000
I	-7.65127500	-1.41162700	2.90165400
I	-2.28401700	2.20987000	-2.01236900
I	1.86122000	1.84097700	-1.54562900
I	4.81739800	-2.91956900	-2.38732900
I	7.28744600	-1.66208300	3.05977900
F	-6.83624800	-4.83571700	-2.16920200
F	-8.48032400	-5.63213100	-0.22464200
F	-8.83192300	-4.14074800	1.96003600
F	-3.70562800	-1.89378300	0.69172500
F	-7.69203200	0.45935600	-0.10750800
F	-2.38647300	0.40957000	0.90890200
F	-6.37238300	2.76662600	0.10492400
F	-4.79786700	3.37803600	2.58533700
F	-3.52357900	5.71180700	2.94035900
F	-1.67846600	6.51391200	1.18088100
F	3.21359200	6.89964100	-0.29190400
F	5.53743500	6.21711700	0.81577100
F	6.27042500	3.63932200	0.95011700
F	6.51004100	1.92813900	-1.50839900
F	3.07946600	1.02020300	1.57269400
F	7.35912800	-0.59270500	-1.30366500
F	3.93297600	-1.49648300	1.77927200
F	7.94427100	-4.68491500	2.63390300
F	7.44385900	-6.40448300	0.65452100
F	6.10095700	-5.62954100	-1.51811900
O	0.33000900	4.70623100	-0.57102000
C	-6.29313900	-2.86282800	-0.98692300
C	-6.97545900	-4.06091900	-1.10175300
C	-7.83139900	-4.48412300	-0.10395500
C	-8.00556800	-3.70135800	1.02038700
C	-7.33296000	-2.49983400	1.15698000
C	-6.46584900	-2.06880900	0.14997100
C	-5.73612200	-0.78364100	0.28214400

C	-4.37525600	-0.75340600	0.54365300
C	-3.69086700	0.44097000	0.65206900
C	-4.33673800	1.65849200	0.49434800
C	-5.70070500	1.62739800	0.25058200
C	-6.38497000	0.43185900	0.14064700
C	-3.60757600	2.94391500	0.60193100
C	-3.89067800	3.75616600	1.69010600
C	-3.24489600	4.95897700	1.88484200
C	-2.29775500	5.35654400	0.96358200
C	-1.98686600	4.60226700	-0.15898400
C	-2.65574100	3.38864000	-0.32046200
C	-0.92203100	5.13093000	-1.07620200
C	1.39064000	5.09732400	-1.42008800
C	2.68449900	4.65480200	-0.79712600
C	3.53573700	5.60817700	-0.26012000
C	4.74439100	5.27585100	0.32099900
C	5.10729400	3.94819900	0.38431100
C	4.28885700	2.94476300	-0.11578800
C	3.08375200	3.31936000	-0.71283900
C	4.75783800	1.54481700	0.01028100
C	5.86200600	1.09586300	-0.69710100
C	6.30387700	-0.20879800	-0.58930000
C	5.66631300	-1.11686700	0.23954700
C	4.57214300	-0.66516300	0.95998800
C	4.12944800	0.63849200	0.85152500
C	6.13633000	-2.51991400	0.35148400
C	6.83765200	-2.94303400	1.48291100
C	7.27278100	-4.25316300	1.57481900
C	7.02250600	-5.15280400	0.55691100
C	6.32822300	-4.73801800	-0.56283000
C	5.88256400	-3.43300200	-0.67479200
H	-1.07045200	4.76168200	-2.09403800
H	-0.96381500	6.22400800	-1.10688000
H	1.38910600	6.18174000	-1.55440600
H	1.27497800	4.63577400	-2.40791400

closed conformer of **8** in THF solution

E=-5308. 388352 H=-5307.992599 G=-5308.167443

I	-5.05508600	-2.30701800	-2.56475000
I	-7.65127500	-1.41162700	2.90165400
I	-2.28401700	2.20987000	-2.01236900
I	1.86122000	1.84097700	-1.54562900
I	4.81739800	-2.91956900	-2.38732900
I	7.28744600	-1.66208300	3.05977900
F	-6.83624800	-4.83571700	-2.16920200
F	-8.48032400	-5.63213100	-0.22464200
F	-8.83192300	-4.14074800	1.96003600
F	-3.70562800	-1.89378300	0.69172500
F	-7.69203200	0.45935600	-0.10750800
F	-2.38647300	0.40957000	0.90890200
F	-6.37238300	2.76662600	0.10492400

F	-4.79786700	3.37803600	2.58533700
F	-3.52357900	5.71180700	2.94035900
F	-1.67846600	6.51391200	1.18088100
F	3.21359200	6.89964100	-0.29190400
F	5.53743500	6.21711700	0.81577100
F	6.27042500	3.63932200	0.95011700
F	6.51004100	1.92813900	-1.50839900
F	3.07946600	1.02020300	1.57269400
F	7.35912800	-0.59270500	-1.30366500
F	3.93297600	-1.49648300	1.77927200
F	7.94427100	-4.68491500	2.63390300
F	7.44385900	-6.40448300	0.65452100
F	6.10095700	-5.62954100	-1.51811900
O	0.33000900	4.70623100	-0.57102000
C	-6.29313900	-2.86282800	-0.98692300
C	-6.97545900	-4.06091900	-1.10175300
C	-7.83139900	-4.48412300	-0.10395500
C	-8.00556800	-3.70135800	1.02038700
C	-7.33296000	-2.49983400	1.15698000
C	-6.46584900	-2.06880900	0.14997100
C	-5.73612200	-0.78364100	0.28214400
C	-4.37525600	-0.75340600	0.54365300
C	-3.69086700	0.44097000	0.65206900
C	-4.33673800	1.65849200	0.49434800
C	-5.70070500	1.62739800	0.25058200
C	-6.38497000	0.43185900	0.14064700
C	-3.60757600	2.94391500	0.60193100
C	-3.89067800	3.75616600	1.69010600
C	-3.24489600	4.95897700	1.88484200
C	-2.29775500	5.35654400	0.96358200
C	-1.98686600	4.60226700	-0.15898400
C	-2.65574100	3.38864000	-0.32046200
C	-0.92203100	5.13093000	-1.07620200
C	1.39064000	5.09732400	-1.42008800
C	2.68449900	4.65480200	-0.79712600
C	3.53573700	5.60817700	-0.26012000
C	4.74439100	5.27585100	0.32099900
C	5.10729400	3.94819900	0.38431100
C	4.28885700	2.94476300	-0.11578800
C	3.08375200	3.31936000	-0.71283900
C	4.75783800	1.54481700	0.01028100
C	5.86200600	1.09586300	-0.69710100
C	6.30387700	-0.20879800	-0.58930000
C	5.66631300	-1.11686700	0.23954700
C	4.57214300	-0.66516300	0.95998800
C	4.12944800	0.63849200	0.85152500
C	6.13633000	-2.51991400	0.35148400
C	6.83765200	-2.94303400	1.48291100
C	7.27278100	-4.25316300	1.57481900
C	7.02250600	-5.15280400	0.55691100
C	6.32822300	-4.73801800	-0.56283000
C	5.88256400	-3.43300200	-0.67479200

H	-1.07045200	4.76168200	-2.09403800
H	-0.96381500	6.22400800	-1.10688000
H	1.38910600	6.18174000	-1.55440600
H	1.27497800	4.63577400	-2.40791400

Adduct of open conformer **8** and Chloride in THF

E=-5308.389613 H=-5307.993974 G=-5308.169387

C	10.80256400	-2.00412000	1.78672100
C	10.42845300	-0.86527100	2.47253500
C	9.28183100	-0.17386100	2.12361100
C	8.49201700	-0.62516000	1.06331800
C	8.87593700	-1.77569900	0.36909400
C	10.02423700	-2.45366900	0.73811500
C	7.25727000	0.10306100	0.67950000
C	6.00282500	-0.40821700	0.97270700
C	7.31129800	1.31387700	0.00909300
C	4.85045900	0.25771000	0.60385900
C	6.15859300	1.98090700	-0.35939800
C	4.90341500	1.46221400	-0.08217300
C	3.67359900	2.18164300	-0.48813600
C	3.39843800	3.39418000	0.12931500
C	2.78041200	1.72575000	-1.45881300
C	2.27262500	4.12531400	-0.18020700
C	1.62978200	2.43975700	-1.79800800
C	1.40037000	3.63401900	-1.13325500
C	0.64581500	1.96402600	-2.82850500
H	1.17844400	1.73296700	-3.75917900
H	-0.09209800	2.73990700	-3.04662500
F	0.31989100	4.36140800	-1.40015700
F	2.02811900	5.27719100	0.43038900
F	4.22882900	3.87548500	1.05099700
F	3.67484600	-0.27756700	0.91742000
F	5.89775400	-1.56585700	1.62113200
F	6.26714900	3.13967900	-1.00471700
F	8.49125800	1.85163100	-0.29175900
F	11.19884800	-0.46406400	3.47505200
F	11.90062300	-2.65984900	2.13127200
F	10.41735000	-3.54712100	0.09811000
I	3.21338400	-0.04903400	-2.48164400
I	8.79059000	1.50650100	3.24835200
I	7.79700500	-2.51792400	-1.24835400
O	0.00764800	0.80870200	-2.32777600
C	-0.69933500	0.12676900	-3.34484500
C	-1.48762200	-0.97959400	-2.70724400
H	0.00368900	-0.27534900	-4.08090000
H	-1.37735800	0.81271400	-3.86330700
C	-2.69186800	-0.76571300	-2.03218000
C	-0.99144700	-2.27318600	-2.75420200
C	-3.38715300	-1.83121500	-1.44977900
I	-3.46218800	1.18758000	-1.80727800
C	-1.65010500	-3.33840500	-2.17156800

F	0.16334600	-2.53547800	-3.36908200
C	-4.68049600	-1.63415300	-0.75284000
C	-2.84500900	-3.10337400	-1.52496700
F	-1.14406500	-4.56612000	-2.23599000
C	-4.76614900	-1.62600000	0.62884100
C	-5.82976400	-1.32833300	-1.46457500
F	-3.47757400	-4.13615800	-0.96988400
C	-5.93393800	-1.26049400	1.27264700
F	-3.69273900	-1.91869800	1.36052800
C	-6.99580200	-0.96759200	-0.82220600
F	-5.80206400	-1.32215400	-2.79565100
C	-7.06376700	-0.89772200	0.55977300
F	-5.94795100	-1.21317700	2.60388000
F	-8.05469700	-0.62613400	-1.55414400
C	-8.25315200	-0.31928700	1.23379400
C	-9.16424100	-1.12408200	1.91732400
C	-8.44287400	1.06787800	1.18207700
C	-10.25729200	-0.54845000	2.53956900
I	-8.95536200	-3.19169100	2.03236200
C	-9.54684600	1.61180600	1.81193700
I	-7.07869400	2.35453700	0.21891400
C	-10.45341000	0.81737500	2.48803000
F	-11.14805700	-1.28342300	3.19769900
F	-9.77381300	2.92233500	1.79675200
F	-11.50580600	1.36062500	3.08743900
Cl	-4.85847100	4.04016000	-1.25586700

Pincer-like complex of 8 and Chloride

E=-5768.778480 H=-5768.380320 G=-5768.557059

I	2.14879200	-1.28485400	2.47736900
I	2.14788300	1.78872900	7.77331100
I	-2.03442100	-1.45525400	1.90451300
I	-2.03442100	-1.45525400	-1.90451300
I	2.14879200	-1.28485400	-2.47736900
I	2.14788300	1.78872900	-7.77331100
F	5.19884700	-1.17643600	3.30180200
F	6.50243000	-0.11391400	5.36859300
F	5.18614400	1.17363600	7.30338300
F	1.10351100	2.52641500	4.18913000
F	0.63782800	-1.82489800	5.89552400
F	-1.51600700	2.60586700	3.67803500
F	-1.98049600	-1.74126800	5.39977100
F	-3.89960500	1.92955200	5.64616800
F	-6.41026900	1.94565200	4.68416900
F	-7.04456700	0.46807200	2.55674200
F	-7.04456700	0.46807200	-2.55674200
F	-6.41026900	1.94565200	-4.68416900
F	-3.89960500	1.92955200	-5.64616800
F	-1.98049600	-1.74126800	-5.39977100
F	-1.51600700	2.60586700	-3.67803500
F	0.63782800	-1.82489800	-5.89552400

F	1.10351100	2.52641500	-4.18913000
F	5.18614400	1.17363600	-7.30338300
F	6.50243000	-0.11391400	-5.36859300
F	5.19884700	-1.17643600	-3.30180200
O	-4.91501400	-0.46056600	0.00000000
C	3.11460100	-0.44386900	4.14341100
C	4.49065700	-0.54919400	4.23527000
C	5.18213000	-0.00272600	5.29974100
C	4.49090000	0.66112600	6.29385000
C	3.11440200	0.78112300	6.23053500
C	2.41898900	0.22812900	5.15590200
C	0.94277300	0.34705200	5.05156000
C	0.35106000	1.47637500	4.51293500
C	-1.00590600	1.51946400	4.25370100
C	-1.82291200	0.43260100	4.51814500
C	-1.24017300	-0.67029800	5.12235900
C	0.11525500	-0.71472900	5.37750500
C	-3.21286000	0.38583500	4.00528900
C	-4.19152400	1.16871300	4.59312000
C	-5.48248100	1.18839700	4.10782700
C	-5.79058200	0.41263300	3.00716000
C	-4.85229400	-0.39054000	2.37596200
C	-3.55303300	-0.38883000	2.89004000
C	-5.27184600	-1.18013100	1.16718900
C	-5.27184600	-1.18013100	-1.16718900
C	-4.85229400	-0.39054000	-2.37596200
C	-5.79058200	0.41263300	-3.00716000
C	-5.48248100	1.18839700	-4.10782700
C	-4.19152400	1.16871300	-4.59312000
C	-3.21286000	0.38583500	-4.00528900
C	-3.55303300	-0.38883000	-2.89004000
C	-1.82291200	0.43260100	-4.51814500
C	-1.24017300	-0.67029800	-5.12235900
C	0.11525500	-0.71472900	-5.37750500
C	0.94277300	0.34705200	-5.05156000
C	0.35106000	1.47637500	-4.51293500
C	-1.00590600	1.51946400	-4.25370100
C	2.41898900	0.22812900	-5.15590200
C	3.11440200	0.78112300	-6.23053500
C	4.49090000	0.66112600	-6.29385000
C	5.18213000	-0.00272600	-5.29974100
C	4.49065700	-0.54919400	-4.23527000
C	3.11460100	-0.44386900	-4.14341100
H	-4.77916300	-2.15777900	1.17287300
H	-6.35262200	-1.34831200	1.18614700
H	-6.35262200	-1.34831200	-1.18614700
H	-4.77916300	-2.15777900	-1.17287300
Cl	0.48342500	-2.57992800	0.00000000

8 in simulated cyclohexane solution

E=-5308.385751 H=-5307.988044 G=-5308.170218

C	-1.02290000	10.67534700	-2.48861700
C	-0.18543300	9.83857400	-3.20152700
C	0.31328000	8.68133400	-2.62874900
C	-0.03229600	8.34886700	-1.31632800
C	-0.87978900	9.19708600	-0.59840700
C	-1.36522400	10.35043700	-1.18974800
C	0.49144600	7.10992300	-0.68924500
C	0.00000000	5.86253300	-1.04122100
C	1.48290400	7.15786800	0.27740200
C	0.47441000	4.70985800	-0.44529900
C	1.95708200	6.00525100	0.87450400
C	1.45408500	4.75814200	0.53611800
C	1.96441900	3.53039100	1.19039000
C	3.28304200	3.16731400	0.94678700
C	1.21211500	2.72465800	2.04667400
C	3.84010000	2.03757900	1.50743000
C	1.74554000	1.57651000	2.63543300
C	3.06015700	1.25451000	2.33791100
C	0.95302500	0.67765900	3.53965100
H	0.45490300	1.27784500	4.31035400
H	1.60777700	-0.04123800	4.04021200
F	3.62278500	0.16494900	2.85431500
F	5.09622000	1.70479500	1.24927900
F	4.04020800	3.91078000	0.14774800
F	-0.02540900	3.53948400	-0.82673700
F	-0.94446800	5.76428400	-1.97172400
F	2.90470100	6.10518600	1.80171600
F	1.98606800	8.33081300	0.64986700
F	0.12526600	10.18322500	-4.44269200
F	-1.49334200	11.77987400	-3.04526800
F	-2.17347400	11.17336700	-0.53693800
I	-0.75333700	3.28046400	2.50296800
I	1.59344800	7.51274600	-3.77920900
I	-1.48214400	8.79051700	1.35119000
O	0.00000000	0.00000000	2.75052000
C	-0.95302500	-0.67765900	3.53965100
C	-1.74554000	-1.57651000	2.63543300
H	-1.60777700	0.04123800	4.04021200
H	-0.45490300	-1.27784500	4.31035400
C	-1.21211500	-2.72465800	2.04667400
C	-3.06015700	-1.25451000	2.33791100
C	-1.96441900	-3.53039100	1.19039000
I	0.75333700	-3.28046400	2.50296800
C	-3.84010000	-2.03757900	1.50743000
F	-3.62278500	-0.16494900	2.85431500
C	-1.45408500	-4.75814200	0.53611800
C	-3.28304200	-3.16731400	0.94678700
F	-5.09622000	-1.70479500	1.24927900
C	-0.47441000	-4.70985800	-0.44529900
C	-1.95708200	-6.00525100	0.87450400
F	-4.04020800	-3.91078000	0.14774800
C	0.00000000	-5.86253300	-1.04122100

F	0.02540900	-3.53948400	-0.82673700
C	-1.48290400	-7.15786800	0.27740200
F	-2.90470100	-6.10518600	1.80171600
C	-0.49144600	-7.10992300	-0.68924500
F	0.94446800	-5.76428400	-1.97172400
F	-1.98606800	-8.33081300	0.64986700
C	0.03229600	-8.34886700	-1.31632800
C	-0.31328000	-8.68133400	-2.62874900
C	0.87978900	-9.19708600	-0.59840700
C	0.18543300	-9.83857400	-3.20152700
I	-1.59344800	-7.51274600	-3.77920900
C	1.36522400	-10.35043700	-1.18974800
I	1.48214400	-8.79051700	1.35119000
C	1.02290000	-10.67534700	-2.48861700
F	-0.12526600	-10.18322500	-4.44269200
F	2.17347400	-11.17336700	-0.53693800
F	1.49334200	-11.77987400	-3.04526800

Complex of **8** and DABCO in simulated cyclohexane solution (tweezer like)

*We were not able to obtain a minimum-structure without negative frequencies. After several attempts, we chose a structure of lowest energy, where optimizations were fluctuating around differing by less than 0.05 kcal/mol. Negative Frequencies are associated with the distortion of the CH_2-O-CH_2-Linker. We attribute these fluctuations to the somewhat noisy nature of the chosen functional and basis sets.

E=-5653.722639 H=-5653.136871 G=-5653.324092

I	-4.04261200	-3.09111600	0.01269200
I	-9.50807600	-0.31854100	0.40800800
I	-2.16373300	1.92509700	-1.65678800
I	2.13473100	1.90308600	-1.64371600
I	4.07243100	-3.10506900	-0.00361900
I	9.50283100	-0.27055100	0.41537500
F	-6.12477700	-5.46244300	-0.03680900
F	-8.78844300	-5.57791000	0.05242400
F	-10.24706400	-3.34911900	0.23699400
F	-5.52186000	-0.95775300	2.45849700
F	-6.84420600	-0.13885100	-1.97334100
F	-4.22140400	1.36987700	2.50109400
F	-5.56153000	2.19606400	-1.92726200
F	-5.65779500	3.89035500	1.92424600
F	-4.47948500	6.29499600	2.05760700
F	-2.35469700	6.83592700	0.53202600
F	2.31776000	6.82483900	0.52287700
F	4.44304200	6.29324500	2.05130500
F	5.62845600	3.89174300	1.92356400
F	5.53313800	2.20194000	-1.92729200
F	4.20884200	1.35875700	2.50257400
F	6.83811900	-0.12069400	-1.97810600
F	5.52842700	-0.95848900	2.45381000
F	10.27885600	-3.29241500	0.24440600
F	8.84737600	-5.53790400	0.04887000

F	6.18286600	-5.45353900	-0.05317900
O	-0.01686700	4.65009500	-0.56101800
C	-6.14945700	-3.10411500	0.10563400
C	-6.80204900	-4.32243000	0.05701500
C	-8.18121700	-4.40068900	0.09979400
C	-8.92530300	-3.23985200	0.19344900
C	-8.30080700	-2.00612800	0.24381200
C	-6.90664800	-1.93249600	0.19998200
C	-6.21932700	-0.61665400	0.24092000
C	-5.54135700	-0.19190000	1.37180600
C	-4.86610900	1.01383900	1.39356400
C	-4.83737400	1.84418100	0.28342900
C	-5.53263000	1.42665000	-0.84240000
C	-6.20335000	0.21960000	-0.86425800
C	-4.11681600	3.13782800	0.31243800
C	-4.59485200	4.12519400	1.16366900
C	-4.00182200	5.36842700	1.24008300
C	-2.90616600	5.62921700	0.44097300
C	-2.38115400	4.68500300	-0.42969300
C	-2.99359700	3.43225400	-0.46438300
C	-1.18077400	5.06517400	-1.24652400
C	1.14966200	5.04844000	-1.25168800
C	2.34843000	4.67080500	-0.43119100
C	2.87154100	5.61887600	0.43646300
C	3.96749500	5.36301800	1.23669600
C	4.56402400	4.12124500	1.16349700
C	4.08824000	3.13024000	0.31527400
C	2.96313300	3.41897800	-0.46096600
C	4.81662300	1.84102900	0.28437200
C	5.51323600	1.43085600	-0.84338200
C	6.19486200	0.23007200	-0.86797400
C	6.21989600	-0.60736400	0.23602700
C	5.53961800	-0.19059300	1.36844800
C	4.85425900	1.00947700	1.39327900
C	6.92210700	-1.91532000	0.19374800
C	8.31679500	-1.97250400	0.24405000
C	8.95609700	-3.19864500	0.19460700
C	8.22614300	-4.36795300	0.09509800
C	6.84636500	-4.30584500	0.04553700
C	6.17922000	-3.09545900	0.09337700
H	-1.23087000	4.59525700	-2.23412200
H	-1.16237700	6.14952600	-1.39094900
H	1.13886700	6.13117700	-1.40911000
H	1.19608300	4.56641100	-2.23354300
C	-0.76323300	-2.77882000	-1.41177100
C	0.78875800	-2.71030900	-1.40009900
H	-1.12275500	-3.58155500	-2.05759000
H	-1.20387000	-1.84355800	-1.76252300
H	1.22590700	-3.40266800	-2.12118800
H	1.14724500	-1.70681700	-1.63828400
C	-0.76787400	-4.34607300	0.39759000
H	-1.11549500	-4.49690900	1.42082900

H	-1.22342200	-5.11552900	-0.22759700
C	0.78130200	-4.38405800	0.31118400
H	1.22876400	-4.66291200	1.26630400
H	1.12344900	-5.09788700	-0.43978800
C	0.80405100	-2.06407200	0.90333900
H	1.15547800	-2.36090000	1.89284800
H	1.25756700	-1.10079200	0.66164400
C	-0.74668900	-1.99438400	0.84802000
H	-1.18943700	-2.14712600	1.83342300
H	-1.09042100	-1.02864400	0.47264700
N	-1.25133500	-3.03632300	-0.05357600
N	1.28344400	-3.05766800	-0.06415900

Complex of 8 and DABCO in simulated cyclohexane solution (open form)

E=-5653,70951 H=-5653,123953 G=-5653,320779

I	-5.97849700	4.46757900	0.26776100
I	-9.70244900	-0.41161800	0.20112200
I	-1.96871400	0.42026300	1.40000600
I	4.09067200	-2.04885800	0.28507000
I	8.78093900	-0.64086000	3.14081800
I	10.85769400	1.12116300	-2.33275000
F	-8.82083300	5.73457500	0.56037200
F	-11.27793000	4.69787500	0.69000000
F	-11.65640700	2.06038500	0.54800900
F	-6.63716100	1.84291900	-2.14251200
F	-7.02283600	0.62498500	2.37692600
F	-4.59802400	0.14362300	-2.42543200
F	-4.99227800	-1.07657300	2.09517600
F	-4.97642300	-2.74472700	-1.73407700
F	-3.03370000	-4.55473100	-2.11919900
F	-0.65670400	-4.24600500	-0.94913100
F	0.80103200	0.68517700	-2.98154900
F	2.65869300	2.46417600	-3.69469800
F	5.15144200	2.27912000	-2.72195000
F	6.46917000	-1.65792500	-2.15709200
F	5.69489900	2.32456300	0.21328600
F	8.97171100	-1.71643800	-1.23795700
F	8.20183900	2.26503200	1.12830200
F	13.45192500	0.80680600	-0.62582000
F	13.89902700	0.12566200	1.91499900
F	11.87179600	-0.48619600	3.53986900
O	0.83257600	-1.10983900	0.11066600
C	-7.86156900	3.58346300	0.34653300
C	-8.95772600	4.41645700	0.48563300
C	-10.23432900	3.89165900	0.55529600
C	-10.41152600	2.52270100	0.48279100
C	-9.33658000	1.66474200	0.34287600
C	-8.04697200	2.20121300	0.27602800
C	-6.88222000	1.29103000	0.12745900
C	-6.23655900	1.13851100	-1.08837900
C	-5.18137600	0.25761200	-1.23545900

C	-4.72123000	-0.49968200	-0.16919700
C	-5.37420400	-0.35268900	1.04591100
C	-6.42761500	0.52839900	1.19184900
C	-3.59475600	-1.44779800	-0.33587600
C	-3.80106700	-2.55998800	-1.14170900
C	-2.81446800	-3.50146000	-1.34516900
C	-1.59281600	-3.32430600	-0.72376300
C	-1.32361300	-2.23664800	0.09314600
C	-2.34220000	-1.29591800	0.26302200
C	0.04636100	-2.10644300	0.72218800
C	1.22800000	-1.43702500	-1.20656200
C	2.31787900	-0.48410300	-1.60624000
C	2.02535600	0.55198800	-2.47933100
C	2.97171400	1.48569700	-2.85824100
C	4.24853300	1.37920800	-2.34849300
C	4.60371400	0.36053400	-1.47378300
C	3.61836800	-0.55688900	-1.10452700
C	6.00139000	0.32564700	-0.98268100
C	6.87604100	-0.68941900	-1.34262700
C	8.17354200	-0.71883200	-0.86920500
C	8.65459600	0.27077500	-0.02630400
C	7.78732100	1.29381000	0.32074100
C	6.48869400	1.32326100	-0.15173500
C	10.04638100	0.23361700	0.48758300
C	11.11926200	0.55030800	-0.34966100
C	12.41288400	0.50919600	0.14103200
C	12.65845300	0.16014100	1.45550900
C	11.59938200	-0.15225100	2.28661900
C	10.29825900	-0.12041300	1.81560500
H	-0.05745600	-1.81262400	1.76572700
H	0.56355100	-3.06920000	0.68631000
H	0.38411300	-1.35602200	-1.89632600
H	1.60306900	-2.46591500	-1.24699500
C	-10.61641900	-5.26415200	1.06887800
C	-10.48402100	-3.72462800	1.23358100
H	-11.66150900	-5.57531000	1.10783600
H	-10.08093600	-5.79220800	1.85914100
H	-11.44500800	-3.25758200	1.45628300
H	-9.79147400	-3.46294200	2.03588600
C	-10.84804600	-5.05880500	-1.29462300
H	-10.40277100	-5.34680000	-2.24819900
H	-11.86118500	-5.46210200	-1.26356000
C	-10.85413900	-3.51425800	-1.12274500
H	-10.50426100	-3.00588400	-2.02307600
H	-11.85267900	-3.13791000	-0.89310000
C	-8.62297900	-3.67365300	-0.27094100
H	-8.27352400	-3.25260400	-1.21574200
H	-7.95775800	-3.31719600	0.51871000
C	-8.67900100	-5.22526200	-0.31942000
H	-8.25304100	-5.60515400	-1.24905000
H	-8.12088000	-5.66548900	0.50840400
N	-10.06729300	-5.67883800	-0.22295800

N	-9.96804600	-3.14481900	-0.01223400

Complex of 6 and Quinuclidine in simulated cyclohexane solution

E=-2946,482252 H=-2946,077302 G= -2946,196074

C	4.52061100	1.36395300	0.54439000
C	5.52143600	0.52391100	0.09423000
C	5.19895900	-0.74826200	-0.33896400
C	3.88678300	-1.18882900	-0.32407400
C	2.87249300	-0.34271200	0.13010400
C	3.20236100	0.94300400	0.56440800
C	1.46175000	-0.80450200	0.14878700
C	0.86528500	-1.24809600	1.31707300
C	0.69411200	-0.81256000	-1.00497100
C	-0.44841200	-1.67948600	1.33122100
C	-0.61832700	-1.24317800	-0.99048900
C	-1.22355700	-1.67390400	0.18170600
C	-2.64206900	-2.10677600	0.21326400
C	-2.90620700	-3.44426800	0.46671500
C	-3.71899200	-1.23708000	0.01516500
C	-4.19842000	-3.92270000	0.50419700
C	-5.04131700	-1.69069400	0.04446800
C	-5.24146600	-3.04159500	0.28849300
C	-6.22545100	-0.79213200	-0.16222500
H	-6.26168400	-0.02422200	0.61210600
H	-6.15518000	-0.28339800	-1.12446700
H	-7.15422400	-1.35581300	-0.13411400
F	-6.47682600	-3.54531300	0.33109100
F	-4.43728600	-5.20752600	0.73992100
F	-1.90653100	-4.30086200	0.67176300
F	-0.97474500	-2.08876000	2.48145500
F	1.56110300	-1.25563900	2.45114700
F	4.86385500	2.57878600	0.94864800
F	6.77925100	0.93543400	0.07696100
F	6.18364300	-1.52712600	-0.76307100
F	1.22743800	-0.40246300	-2.15370000
F	-1.30432300	-1.23475900	-2.12886900
I	3.50784000	-3.12705900	-0.97654600
I	1.76626800	2.29386700	1.23077900
I	-3.32981800	0.81866800	-0.26483100
N	-2.39892600	3.50830100	-0.57113900
C	-1.24754300	3.33226900	-1.46336100
C	-1.93294000	3.90964000	0.75975400
C	-3.28381700	4.54342900	-1.11385600
C	-0.50359000	4.67208600	-1.68946700
H	-0.59082100	2.58710000	-1.00802700
H	-1.60942300	2.91245300	-2.40368300
H	-2.81571200	4.08593900	1.37729500
H	-1.39761200	3.06371200	1.19828000
C	-1.04143500	5.17479600	0.68431400
C	-2.58194100	5.92598300	-1.12162200
H	-4.19348900	4.56340900	-0.51157900

H	-3.56512300	4.23761900	-2.12308600
H	0.56358700	4.55696600	-1.48815500
H	-0.60616300	5.00267900	-2.72509900
H	-1.38161900	5.92909400	1.39571500
H	-0.00280100	4.94216100	0.93448500
H	-3.05162800	6.60250100	-0.40438000
H	-2.65897500	6.39228700	-2.10524300
C	-1.11008000	5.71704500	-0.74706000
H	-0.56359000	6.65719200	-0.82173500

6 in simulated cyclohexane solution

E= -2617,185873 H=-2616,981356 G=-2617,078709

C	-4.54093200	-1.43178700	0.09872600
C	-5.38636200	-0.34213300	0.01146400
C	-4.85178700	0.92889100	-0.08088200
C	-3.48097800	1.12051500	-0.08676500
C	-2.62343000	0.02104100	0.00362300
C	-3.16719200	-1.26265100	0.09626300
C	-1.15206800	0.21458200	0.00208000
C	-0.49165300	0.70954900	1.11472600
C	-0.38790000	-0.08897500	-1.11378000
C	0.87869800	0.89007400	1.11294500
C	0.98165400	0.09270300	-1.11642600
C	1.64641900	0.57525700	0.00180400
C	3.11467400	0.77444700	0.01077000
C	3.58931900	2.07589200	0.08476300
C	4.05041900	-0.26166200	-0.04034000
C	4.94088500	2.34849800	0.09047900
C	5.42781800	-0.02928900	-0.03790900
C	5.83431600	1.29626400	0.02589700
C	6.45827500	-1.11781700	-0.08950900
H	6.36690900	-1.77169200	0.77907200
H	6.32108100	-1.73188100	-0.98038200
H	7.46195700	-0.70209900	-0.10550800
F	7.13132700	1.60174300	0.03344600
F	5.37620800	3.59924300	0.15328400
F	2.73785300	3.09626300	0.14248600
F	1.46413400	1.36671900	2.20704300
F	-1.18152400	1.02136300	2.20780200
F	-5.08818000	-2.63546100	0.18917800
F	-6.69846200	-0.51499000	0.01546600
F	-5.69191100	1.95013900	-0.16753600
F	-0.97746600	-0.56205200	-2.20794100
F	1.66417100	-0.20224100	-2.21827500
I	3.37488600	-2.24214000	-0.06128400
I	-2.78046900	3.07165800	-0.26248600
I	-1.98717800	-2.96841000	0.25933100

Binding Constants

Experimental binding constants were determined by ^{19}F NMR-titration. To this end, a stock solution of the host in deuterated solvent was prepared at suitable concentration (1mM in cyclohexane-d12, 2mM in tetrahydrofuran-d8). All pipetting was performed with HAMMILTON® syringes. 500 µL stock solution were placed in a BOROECO-5-7® NMR tube. Guest-Solutions at suitable concentrations (5mM in cyclohexane, 25mM in tetrahydrofuran-d8) were added in volumes according to the given equivalents and measured straight away at 64 scans on a BRUKER AVANCE *neo-400*. ^{1}H NMR-spectra were recorded to confirm and correct relative equivalents through integration of characteristic signals if necessary. As an internal standard 1% 1,3,5-trifluorobenzene (-108 ppm) was added.

Calculation of the binding constants from collected shifts relative to the internal standard was performed via the website supramolecular.org[8], fitting the shifts of as many nuclei as possible. For the calculations, a 1:1 binding was assumed. 1:2 binding or 2:1 binding did not give reasonable results in all investigated cases.

Table S10 *Results of NMR-titrations.*

Host	**Guest**	**K [mol-1]**	**G [kcal mol^{-1}]**
8	TOA-Cl	1480±150	-4.32±0.44
8	DABCO	26.0±0.9	-1.93±0.07
6	TOA-Cl	4760±1280	-5.01±1.35
6	quinuclidine	3.6±0.3	-0.76±0.07

NMR of New Compounds

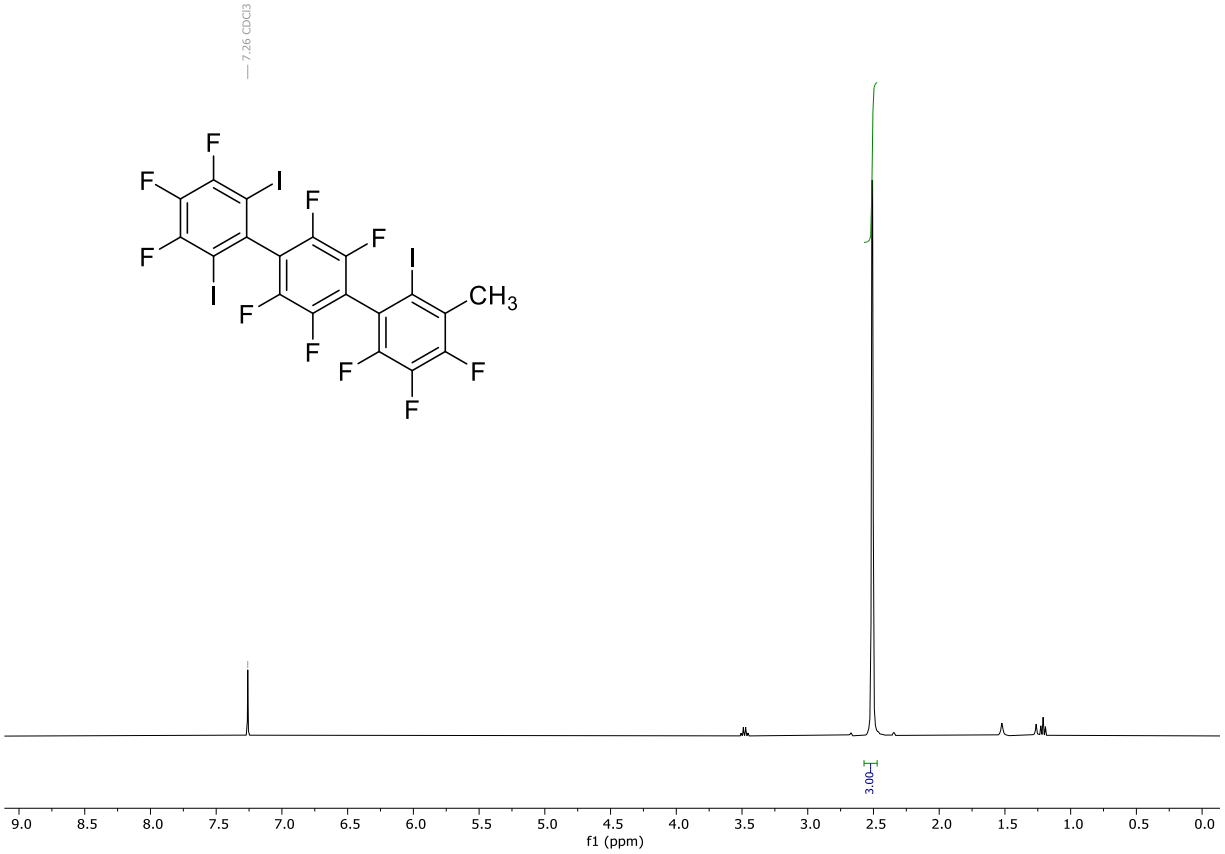


Figure S1 *^{1}H NMR spectrum of **6**.*

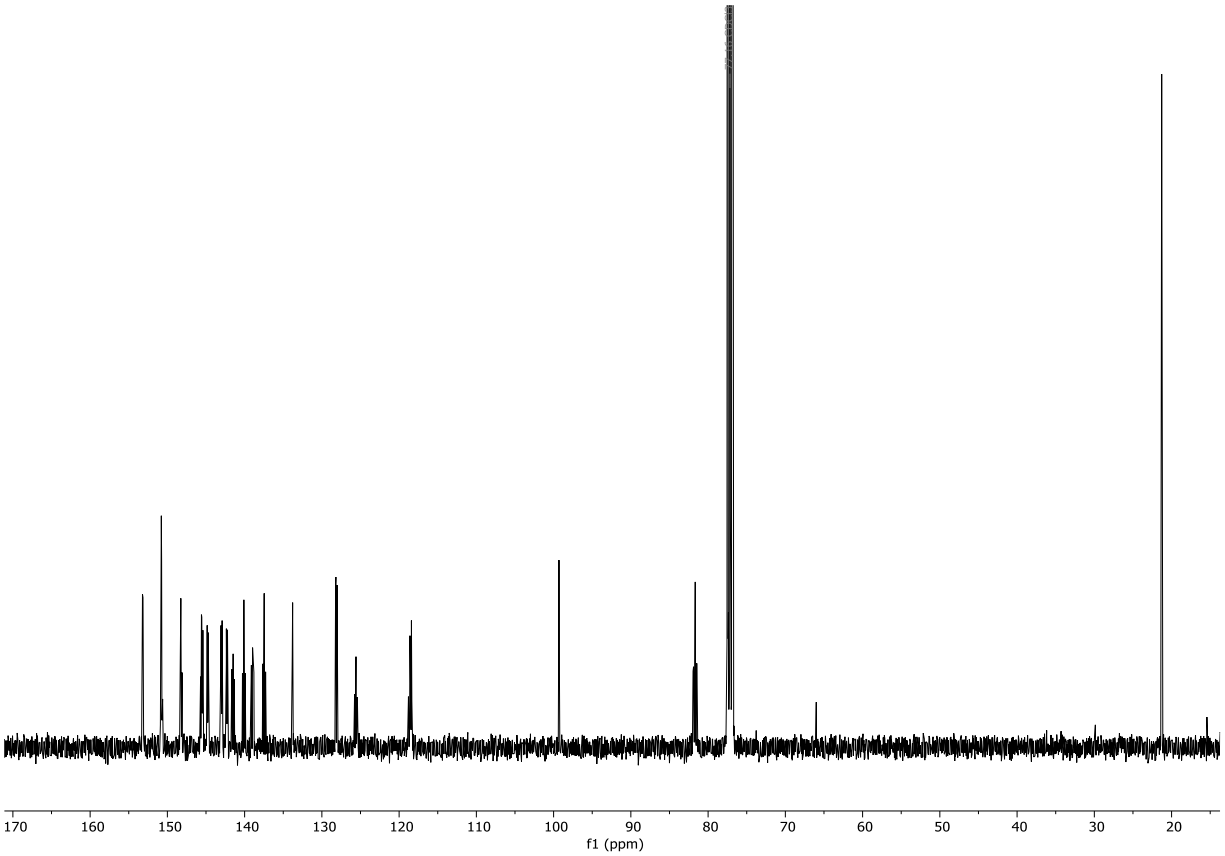


Figure S2 *^{13}C NMR spectrum of **6**.*

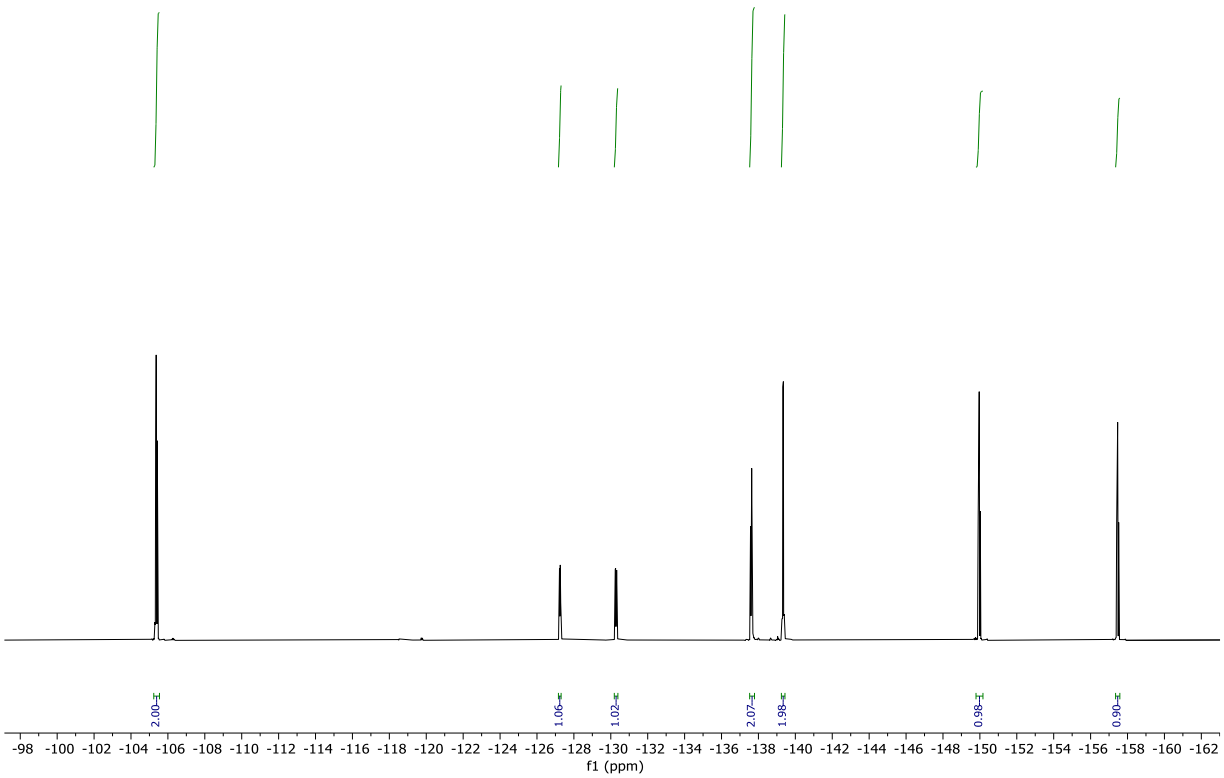


Figure S3 *^{19}F NMR spectrum of **6**.*

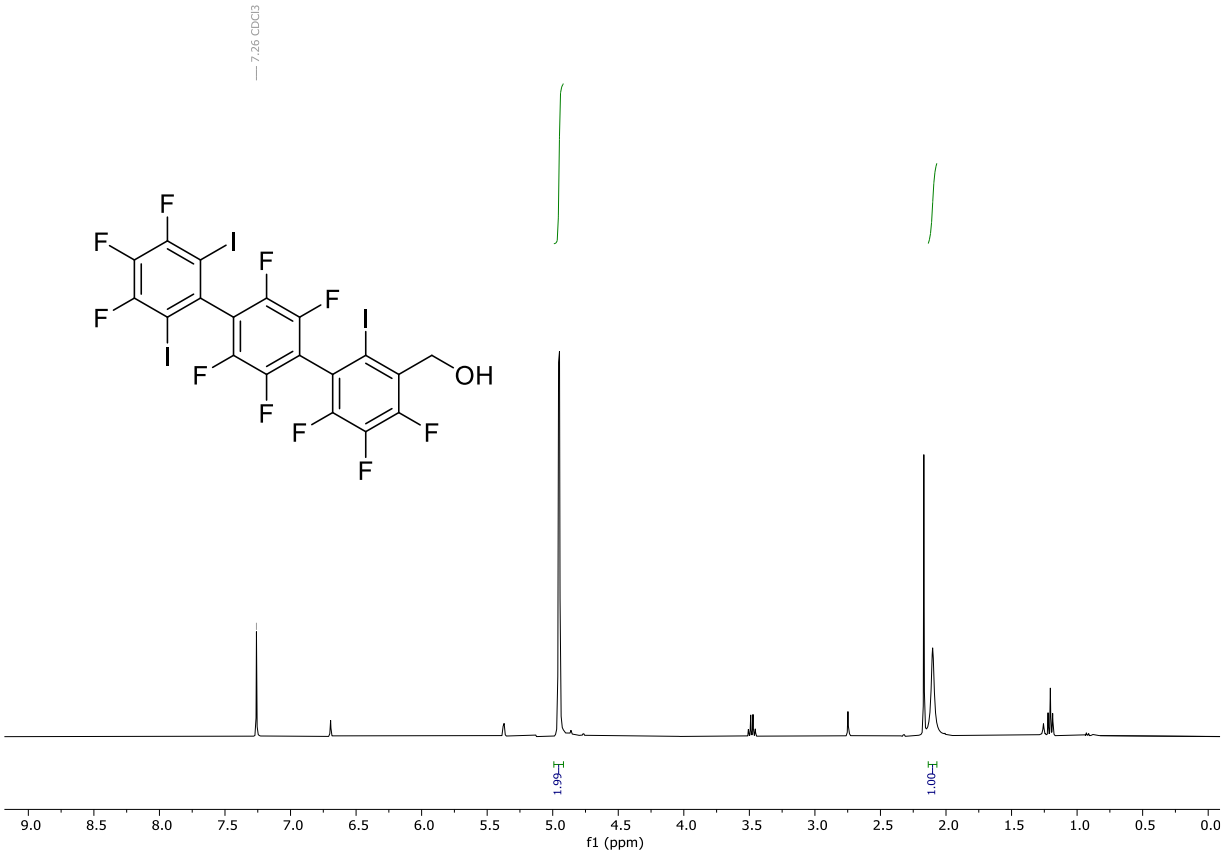


Figure S4 *^{1}H NMR spectrum of **7**.*

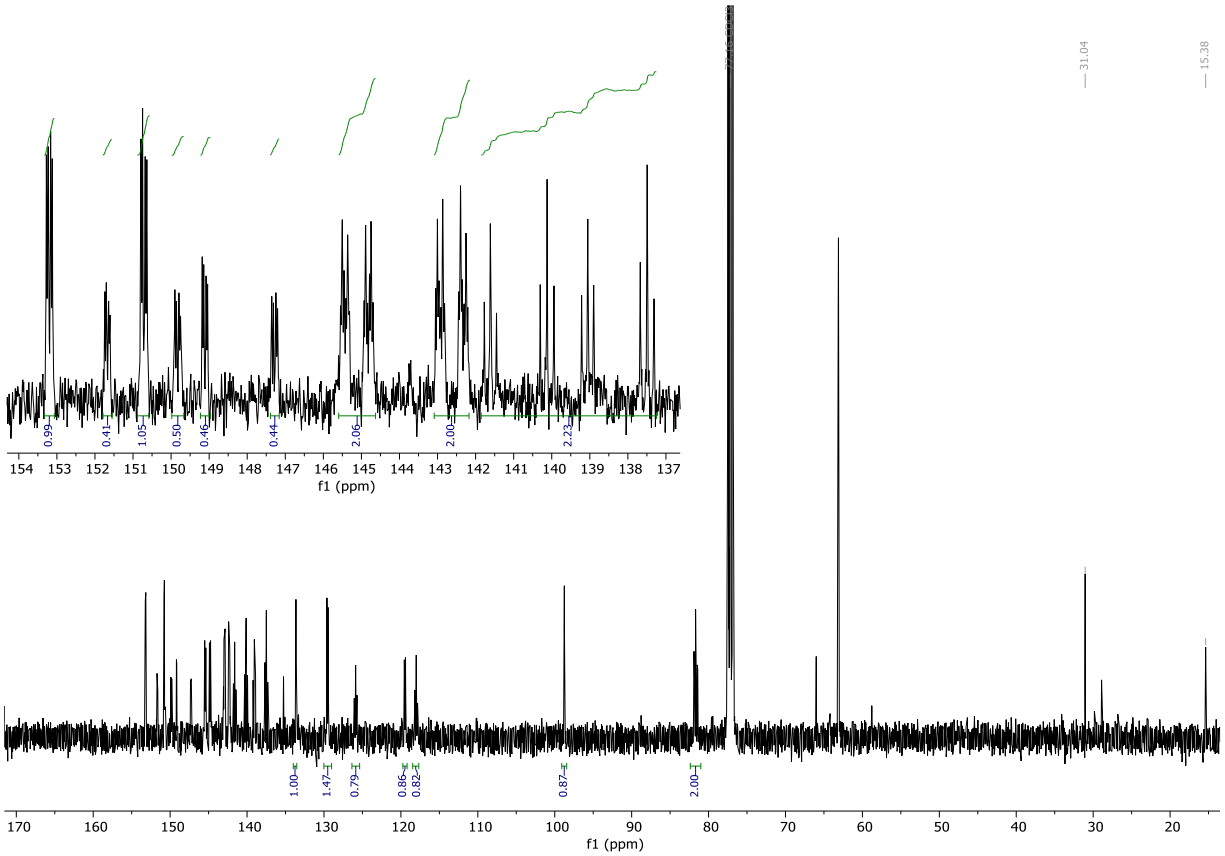


Figure S5 *^{13}C NMR spectrum of **7**.*

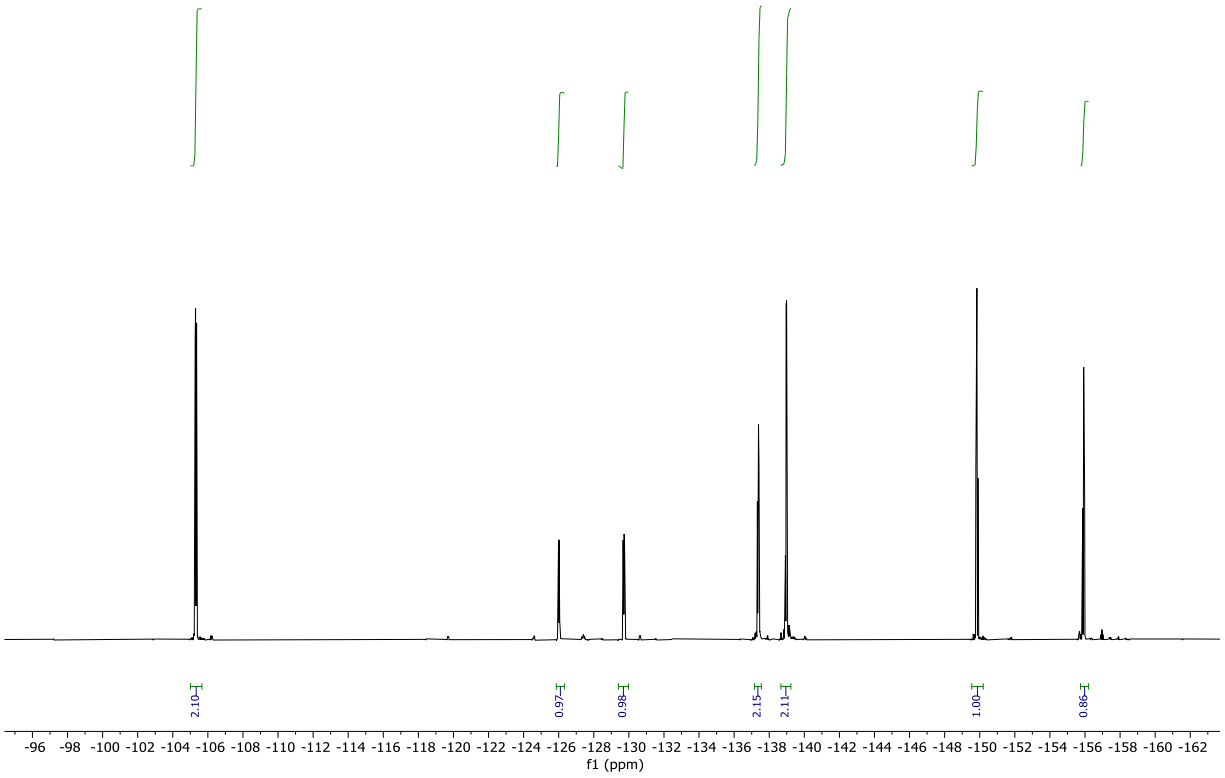


Figure 6 *^{19}F NMR spectrum of **7**.*

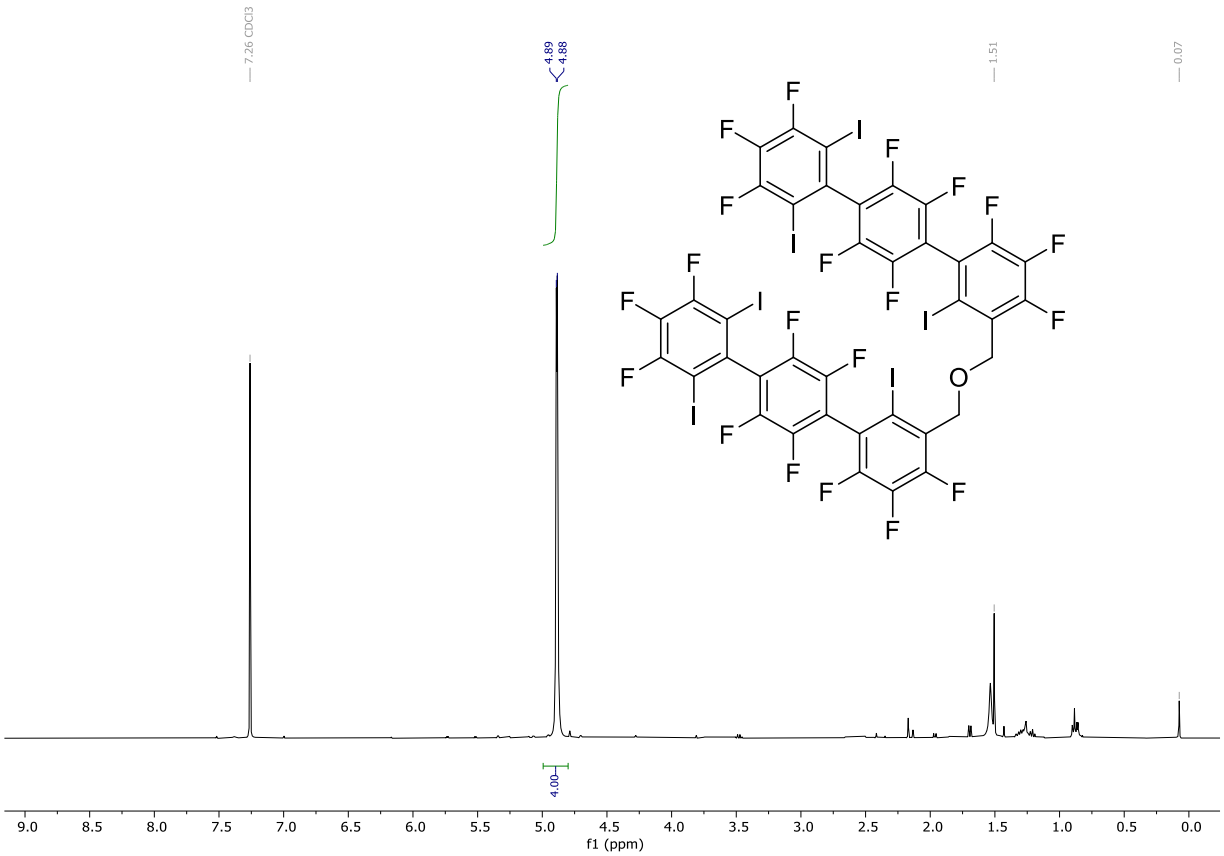


Figure 7 *^{1}H NMR spectrum of* ***8****.*

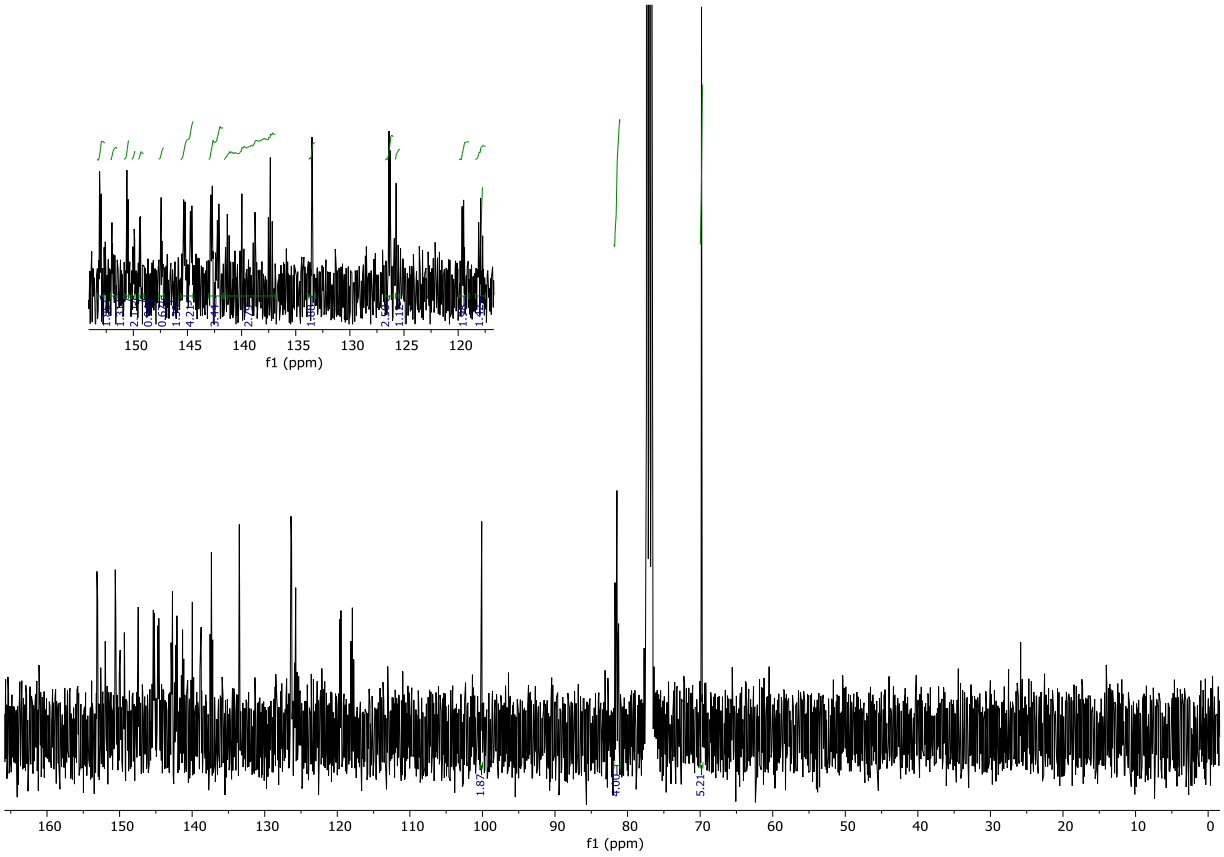


Figure 8 *^{13}C NMR of* ***8****.*

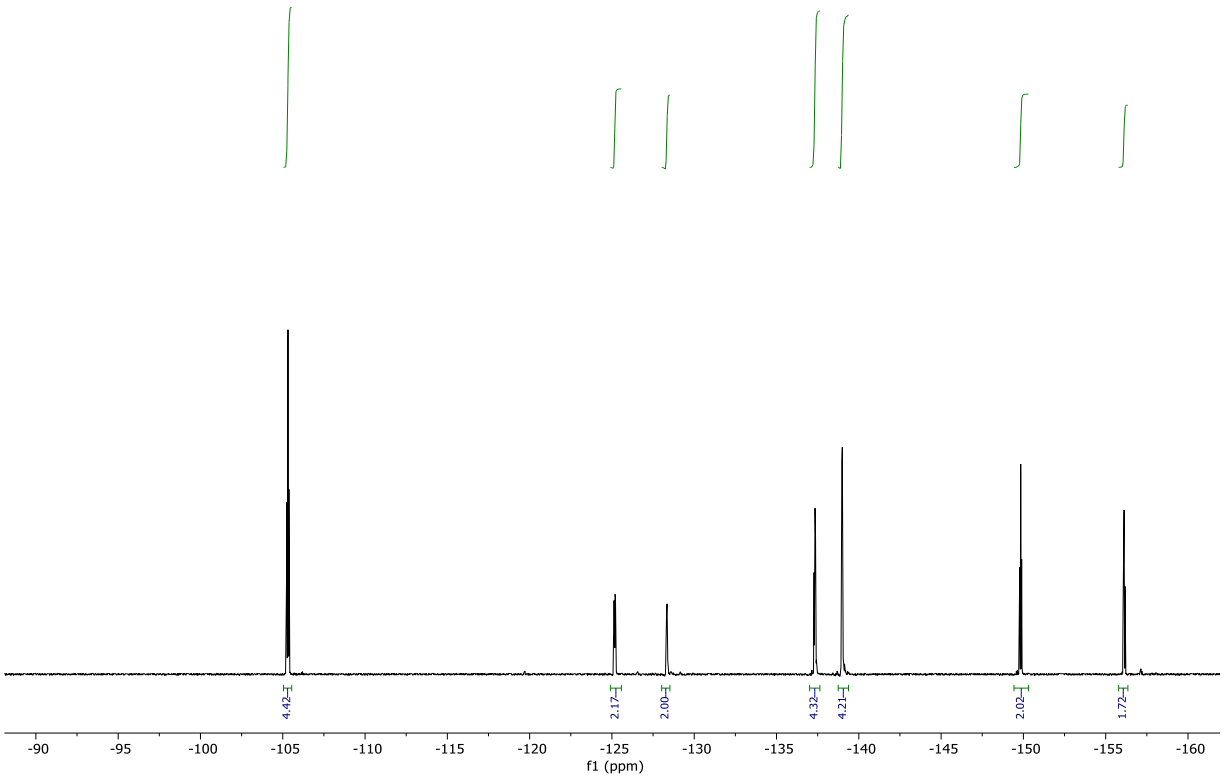


Figure 9 *^{19}F NMR spectrum of* ***8****.*

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