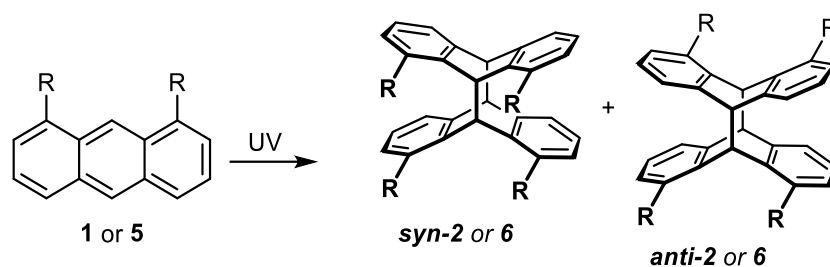


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Photo-dimerisation of alkynylantracenes **1** and **5**



Scheme S1

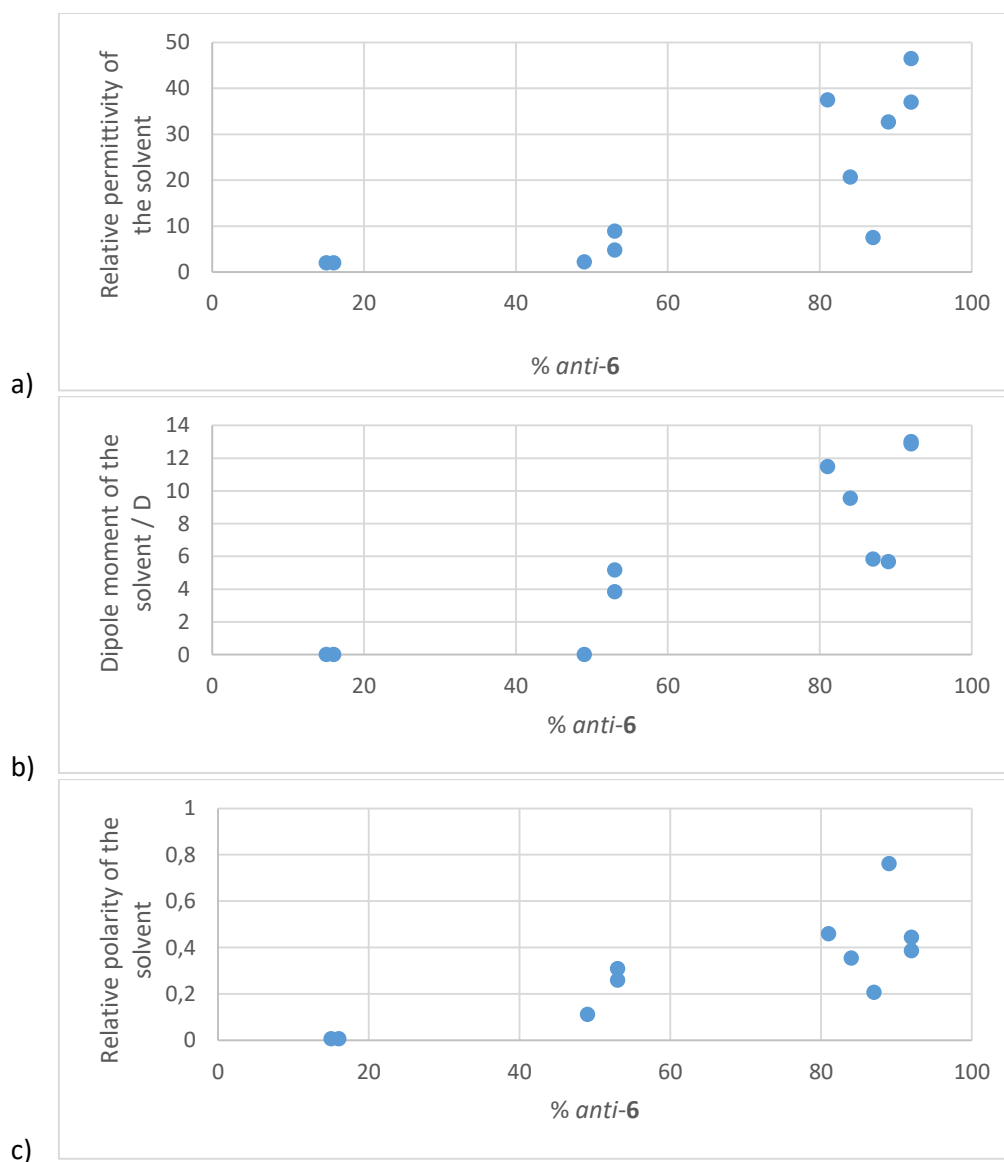
Table S1 NMR experiments for the photo-dimerisation of 1,8-diethynylantracene (**1**) in various deuterated solvents. The concentrations ($\pm 0.02 \text{ mg mL}^{-1}$) of reactant **1** as well as the irradiation times and the percentages ($\pm 1\%$) of isomers *syn*-**2** and *anti*-**2** are listed. Data for **5** \rightarrow *syn*-**6**/*anti*-**6** are listed in Table 1 (main text) and Table S2.

solvent	$c \text{ [mg mL}^{-1}\text{]}$	$t \text{ [h]}$	<i>syn</i> - 2 [%]	<i>anti</i> - 2 [%]
C_6D_6	3.33	3	21	79
toluene- d_8	3.33	3	21	79
CDCl_3	3.33	3	21	79
CD_2Cl_2	3.33	3	22	78
MeOD	3.33	3	22	78
THF- d_8	3.33	7	21	79
pyridine- d_5	3.33	7	25	75
acetone- d_6	3.33	3	26	74
CD_3CN	3.33	3	28	72
$\text{DMSO-}d_6$	3.33	15	33	67
methylcyclohexane- d_{14}	3.33	5	17	83
DMF- d_7	0.66	3	31	69
DMF- d_7	1.00	7	31	69
DMF- d_7	2.00	7	31	69
DMF- d_7	3.33	15	31	69
DMF- d_7	4.00	12	30	30
DMF- d_7	10.0	14	28	72
DMF- d_7	20.0	14	26	74
DMF- d_7	40.0	19	23	77

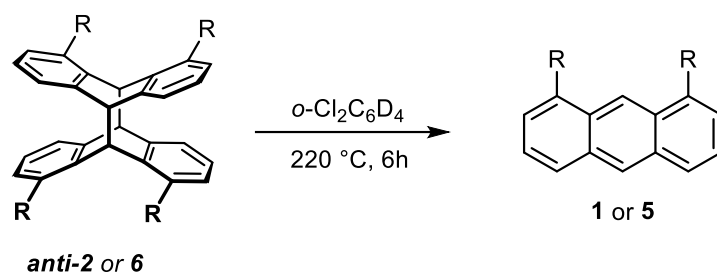
Photo-dimerisation of alkynylanthracenes **5** in different solvents

Table S2 NMR experiments for the photo-dimerization of dialkynylanthracene **5** in various deuterated solvents. Concentrations ($\pm 0.02 \text{ mg mL}^{-1}$) of reactant **5** as well as irradiation times and fractions ($\pm 1\%$) of isomers *syn-6* and *anti-6* are listed. In addition to Table 1 in the main text, solvent properties are listed here: dielectric constant ϵ , dipole moment μ and relative polarity *RP*. Plots of these parameters against the fraction of *anti-6* are provided below.

solvent	<i>c</i> [mg mL ⁻¹]	<i>t</i> [h]	<i>syn-6</i> [%]	<i>anti-6</i> [%]	ϵ	μ [D]	<i>RP</i> ^a
DMSO- <i>d</i> ₆	4.00	15	8	92	46.48	13	0.444
DMF- <i>d</i> ₇	4.00	9	8	92	37	12.88	0.386
CD ₃ CN	4.00	9	19	81	37.5	11.48	0.46
acetone- <i>d</i> ₆	4.00	3	16	84	20.7	9.54	0.355
THF- <i>d</i> ₈	4.00	9	13	87	7.58	5.84	0.207
MeOD	4.00	9	11	89	32.7	5.67	0.762
CD ₂ Cl ₂	4.00	9	47	53	8.93	5.17	0.309
CDCl ₃	4.00	9	47	53	4.81	3.84	0.259
C ₆ D ₆	4.00	3	51	49	2.28	0	0.111
cyclohexane- <i>d</i> ₁₂	4.00	9	85	15	2.02	0	0.006
cyclohexane- <i>d</i> ₁₂	20.0	25	85	15	2.02	0	0.006
methylcyclohexane- <i>d</i> ₁₄	4.00	9	84	16	2.02	0	
methylcyclohexane- <i>d</i> ₁₄	20.0	25	84	16	2.02	0	



Thermal cycloreversion reactions



Scheme S2

Table S3 ¹H NMR spectroscopic shifts of compounds **1**, *anti-2*, **5** and *anti-6* in *o*-C₆D₄Cl₂ at 298 K.^[a]

	1	<i>anti-2</i>	5	<i>anti-6</i> ^[b]
H9	9.47 (s)	5.88 (d)	9.46 (s)	n.a.
H10	8.21 (s)	4.71 (d)	8.20 (s)	n.a.
H4/H5	7.83 (d)	7.11 (d)	7.81 (d)	n.a.
H2/H7	7.68 (d)	6.96 (d)	7.58 (d)	n.a.
H3/H6	7.28 (t)	6.71 (t)	7.29 (dd)	n.a.
OH	–	–	3.85 (bs)	n.a.
CH ₃	–	–	1.76 (s)	n.a.
C≡CH	3.59 (s)	3.42 (s)	–	–

[a] For NMR assignments see Scheme 6 (main text). [b] n.a.: not assigned (due to poor solubility).

NMR Spectroscopic Data

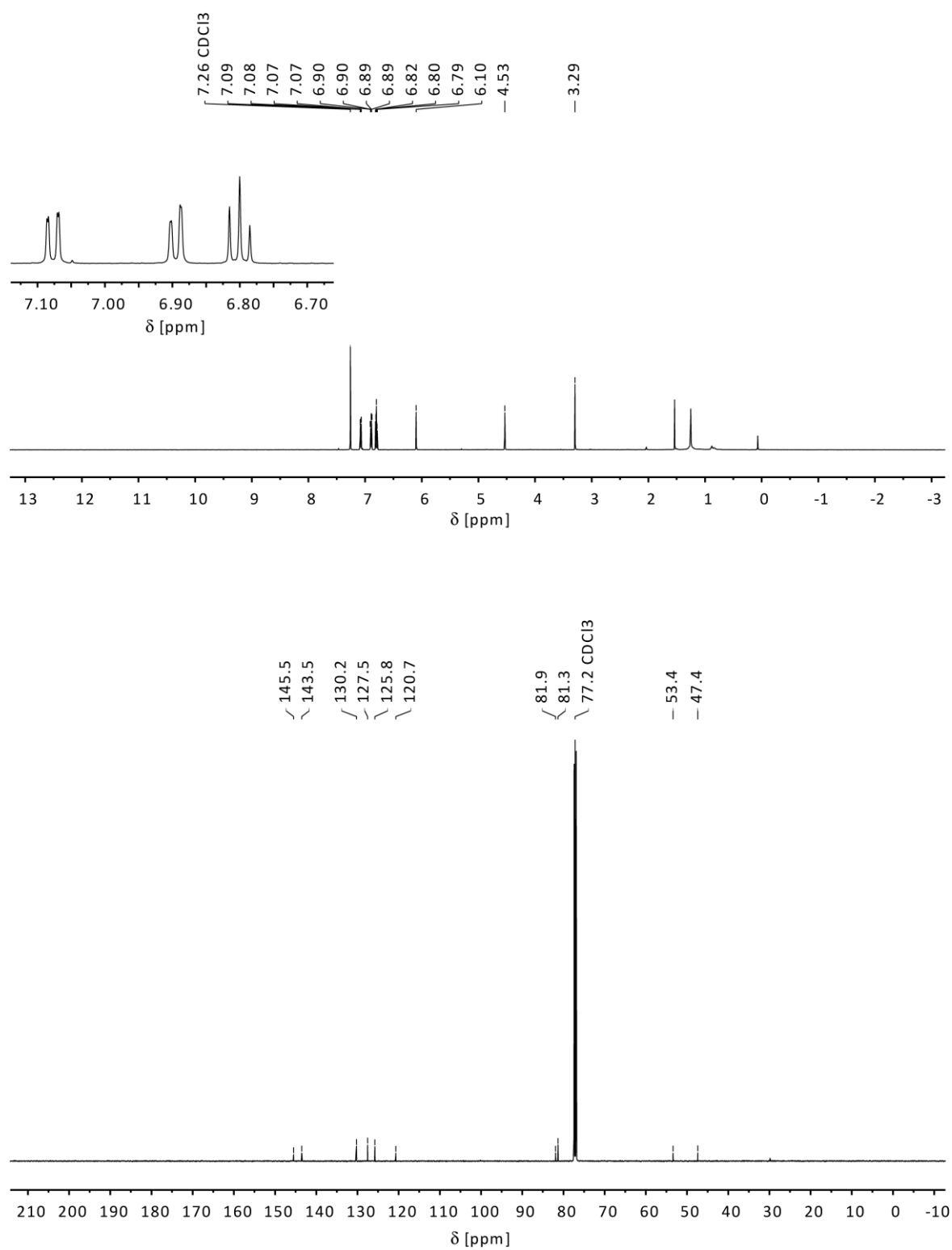


Fig. S1 NMR spectra, ^1H NMR (above), $^{13}\text{C}\{^1\text{H}\}$ NMR (below), of compound *syn-2*.

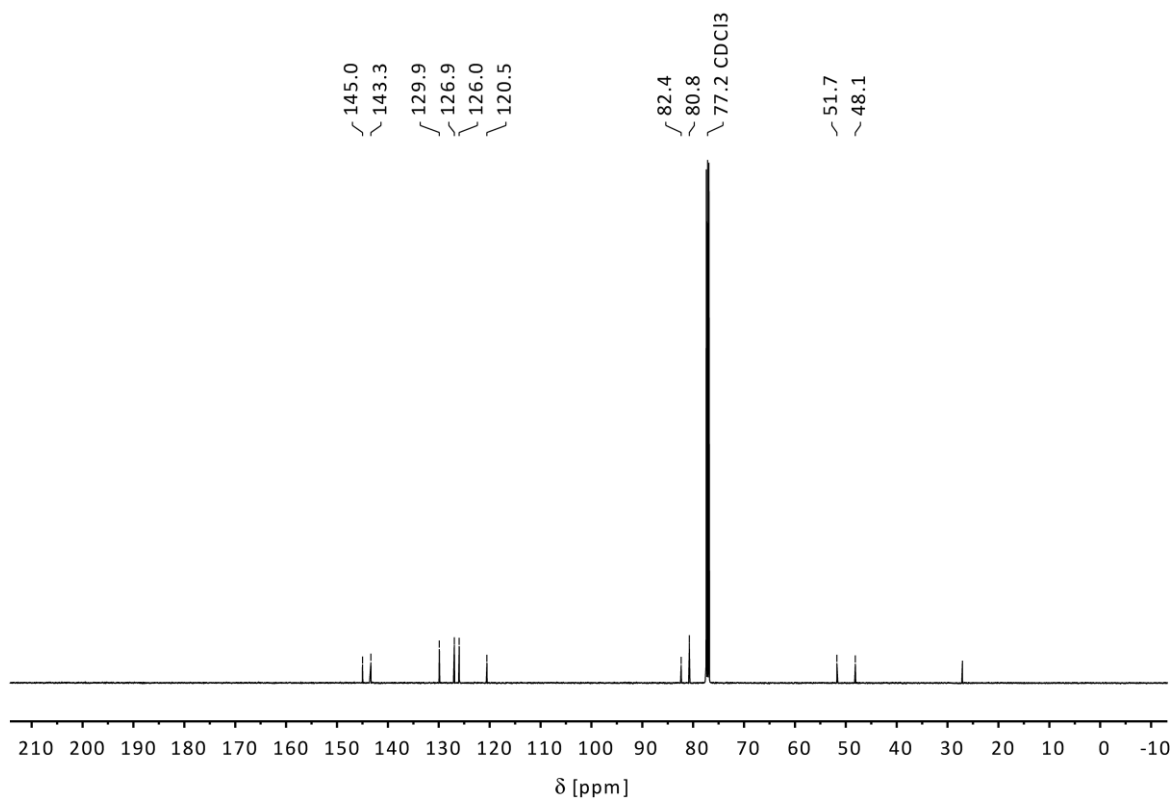
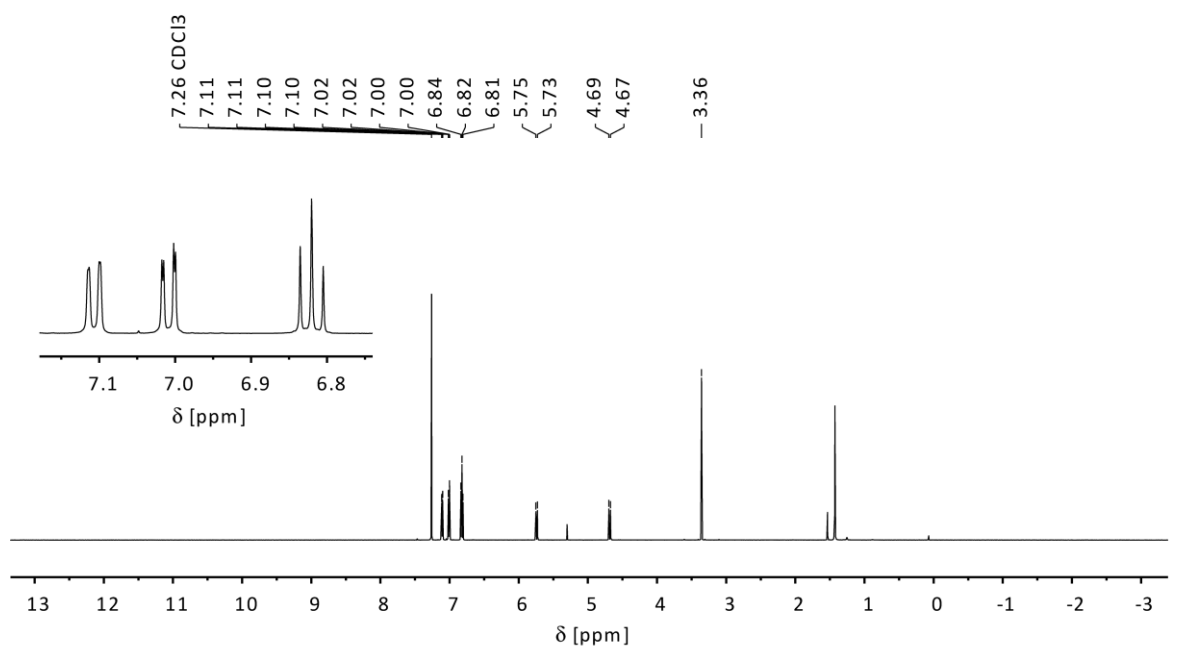


Fig. S2 NMR spectra, ^1H NMR (above), $^{13}\text{C}\{^1\text{H}\}$ NMR (below), of compound *anti-2*.

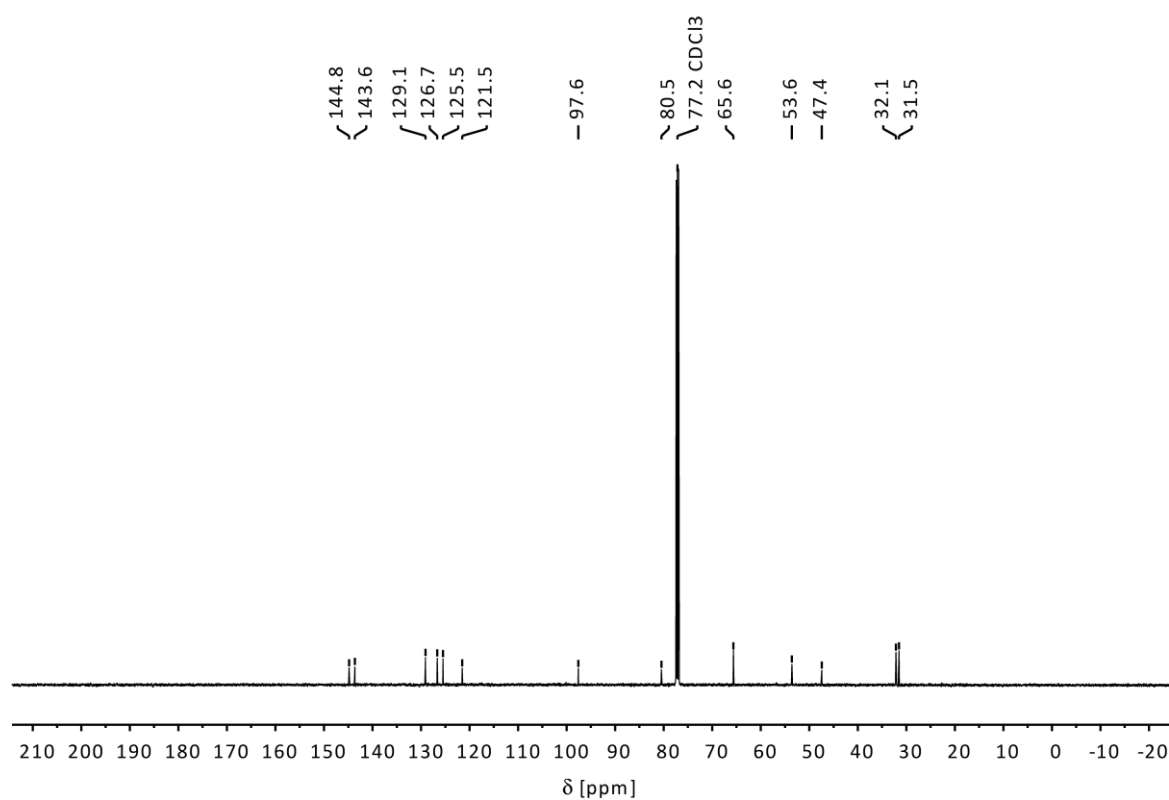
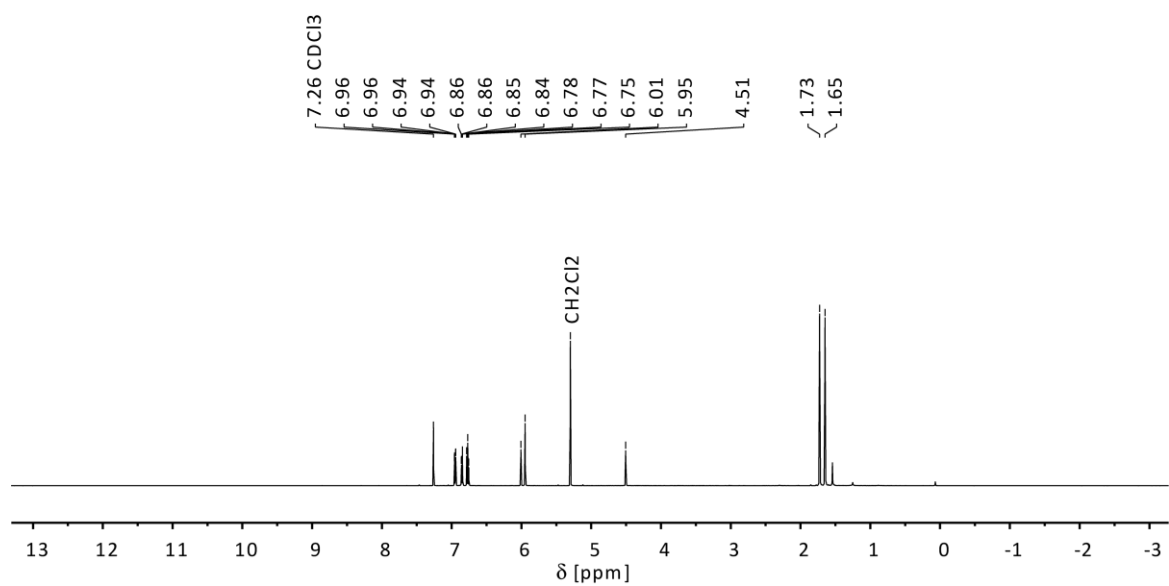


Fig. S3 NMR spectra, ^1H NMR (above), $^{13}\text{C}\{^1\text{H}\}$ NMR (below), of compound *syn-6*.

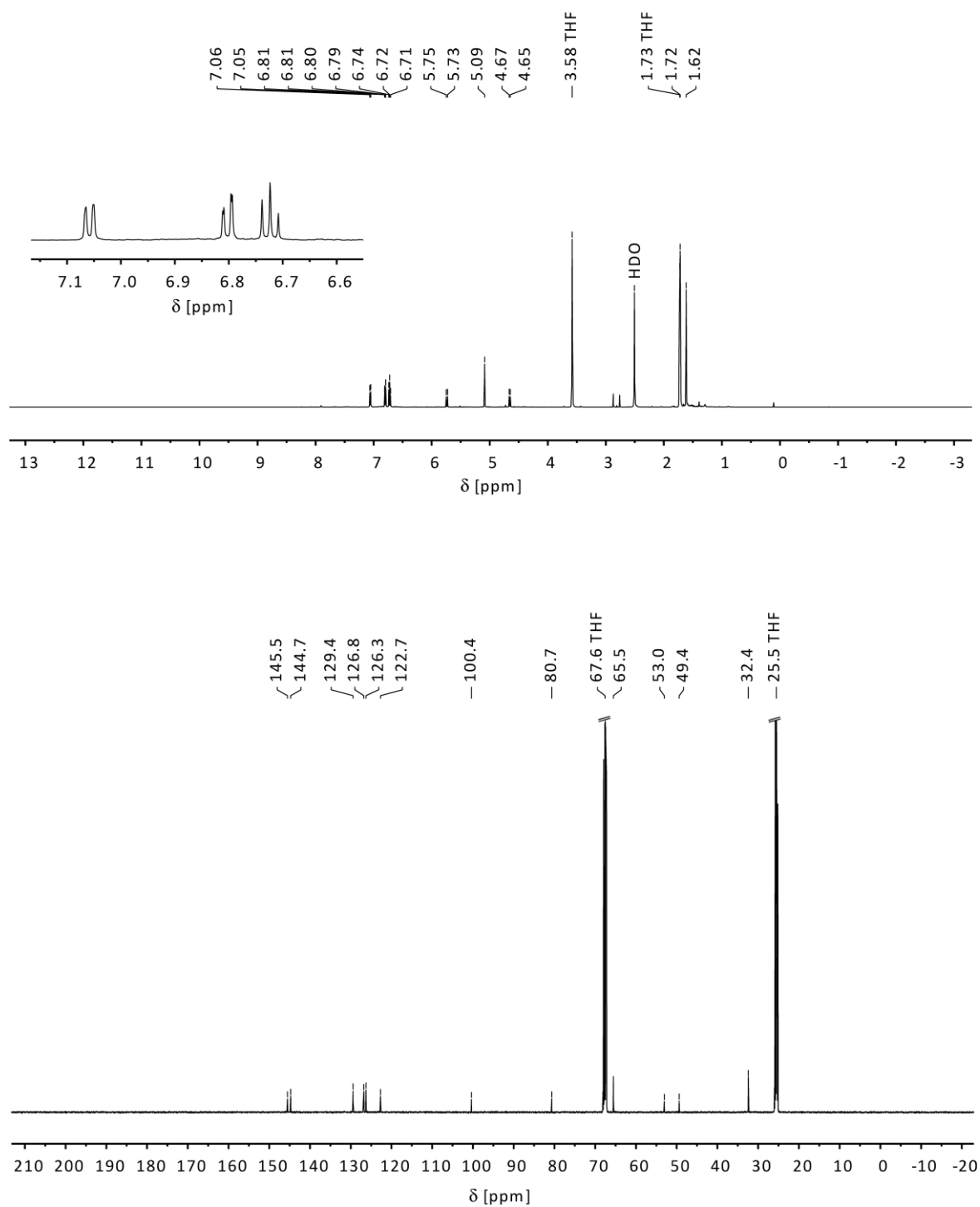


Fig. S4 NMR spectra, ^1H NMR (above), $^{13}\text{C}\{^1\text{H}\}$ NMR (below), of compound *anti-6*.

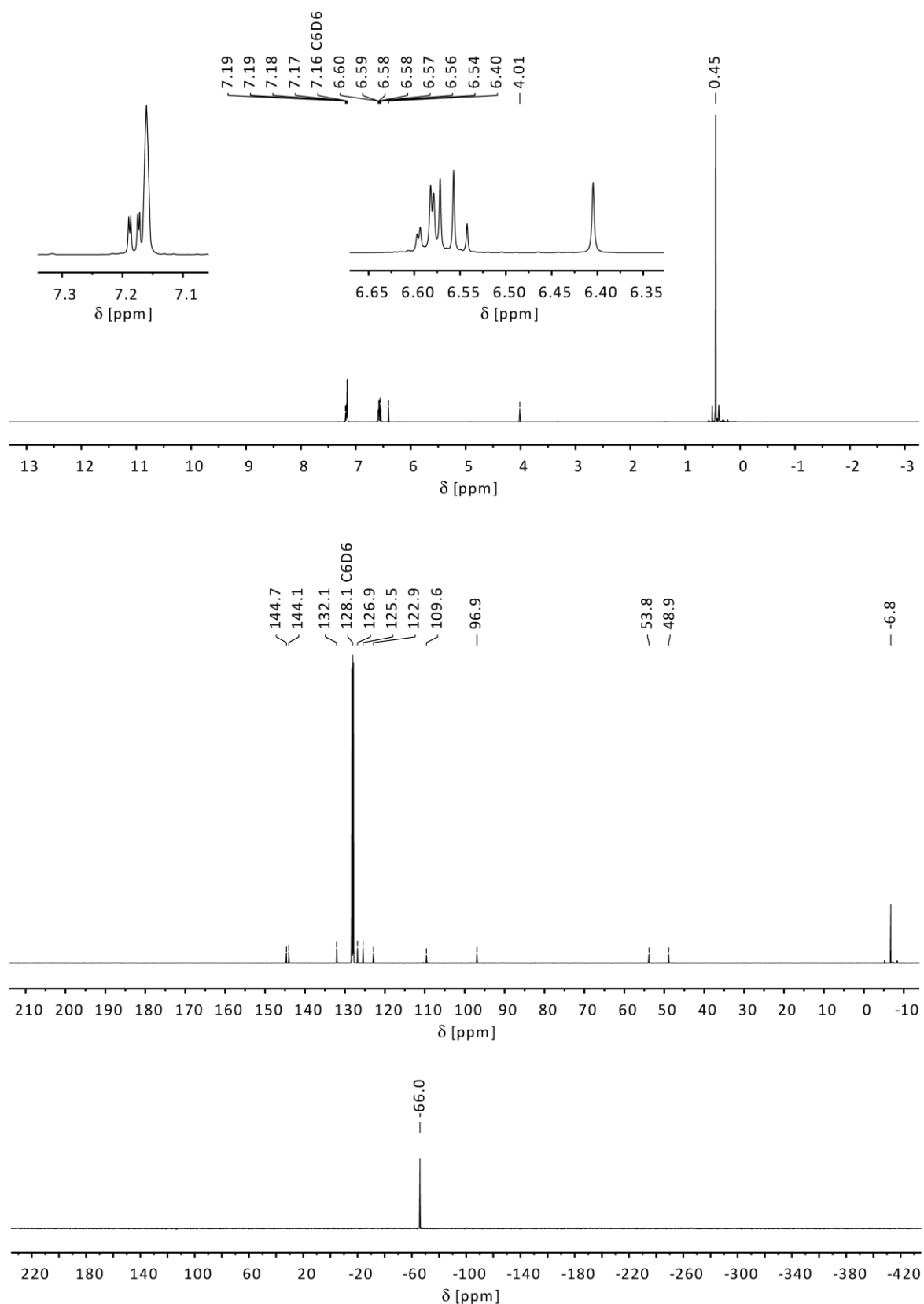


Fig. S5 NMR spectra, ^1H NMR (above), $^{13}\text{C}\{^1\text{H}\}$ NMR (centre), $^{119}\text{Sn}\{^1\text{H}\}$ NMR (below), of compound 7.

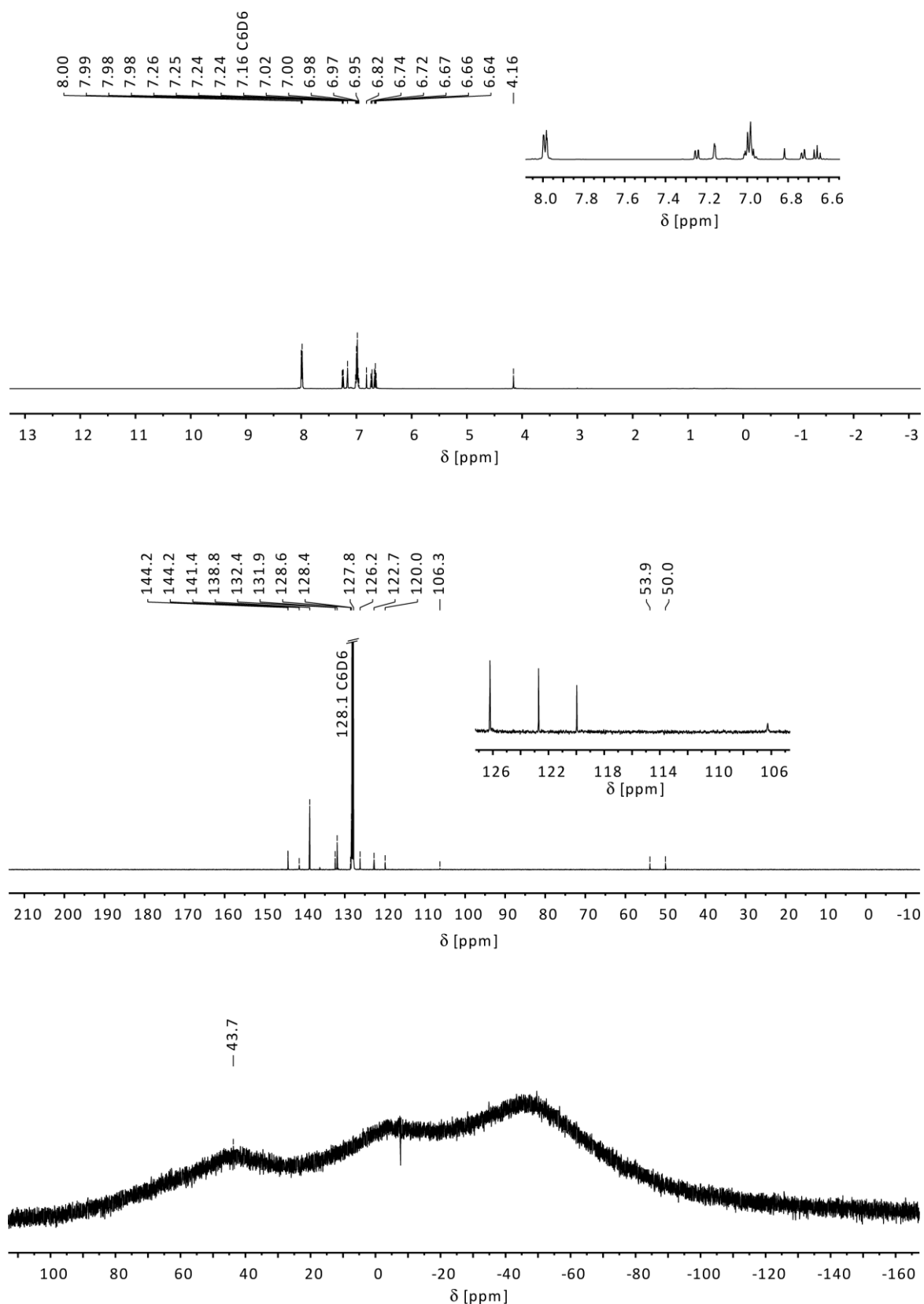


Fig. S6 NMR spectra, ^1H NMR (above), $^{13}\text{C}\{^1\text{H}\}$ NMR (centre), $^{11}\text{B}\{^1\text{H}\}$ NMR (below), of compound **8**.

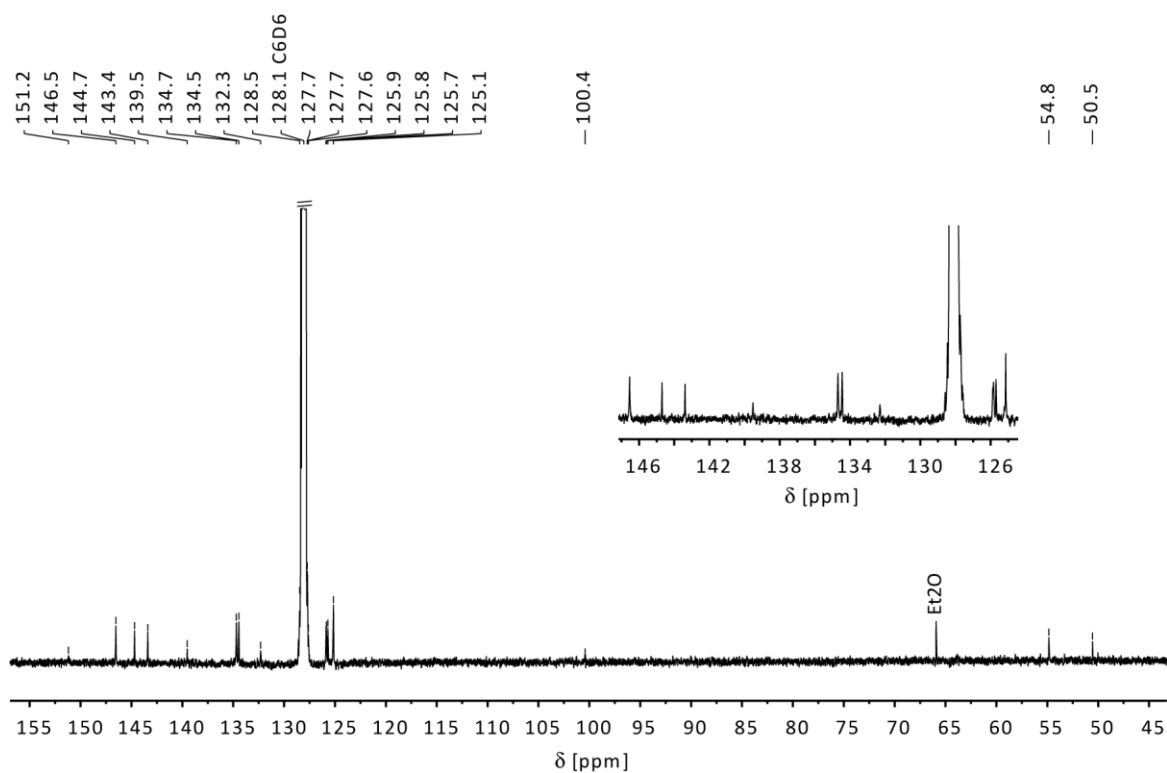
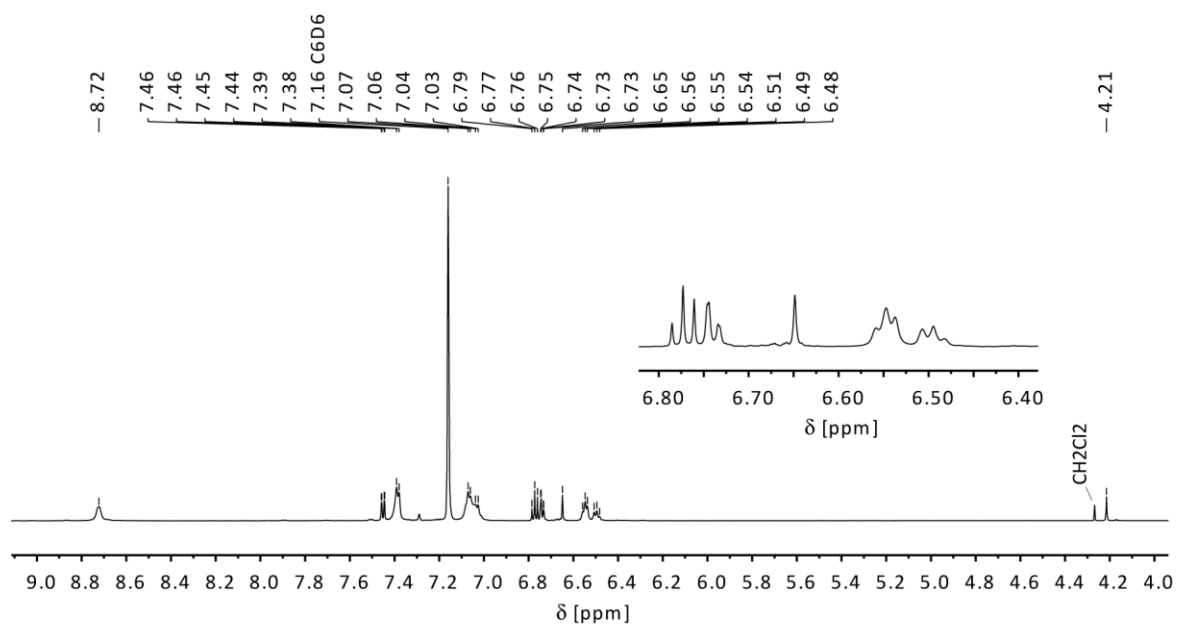


Fig. S7 NMR spectra, ^1H NMR (above), $^{13}\text{C}\{^1\text{H}\}$ NMR (below), of compound **9**.

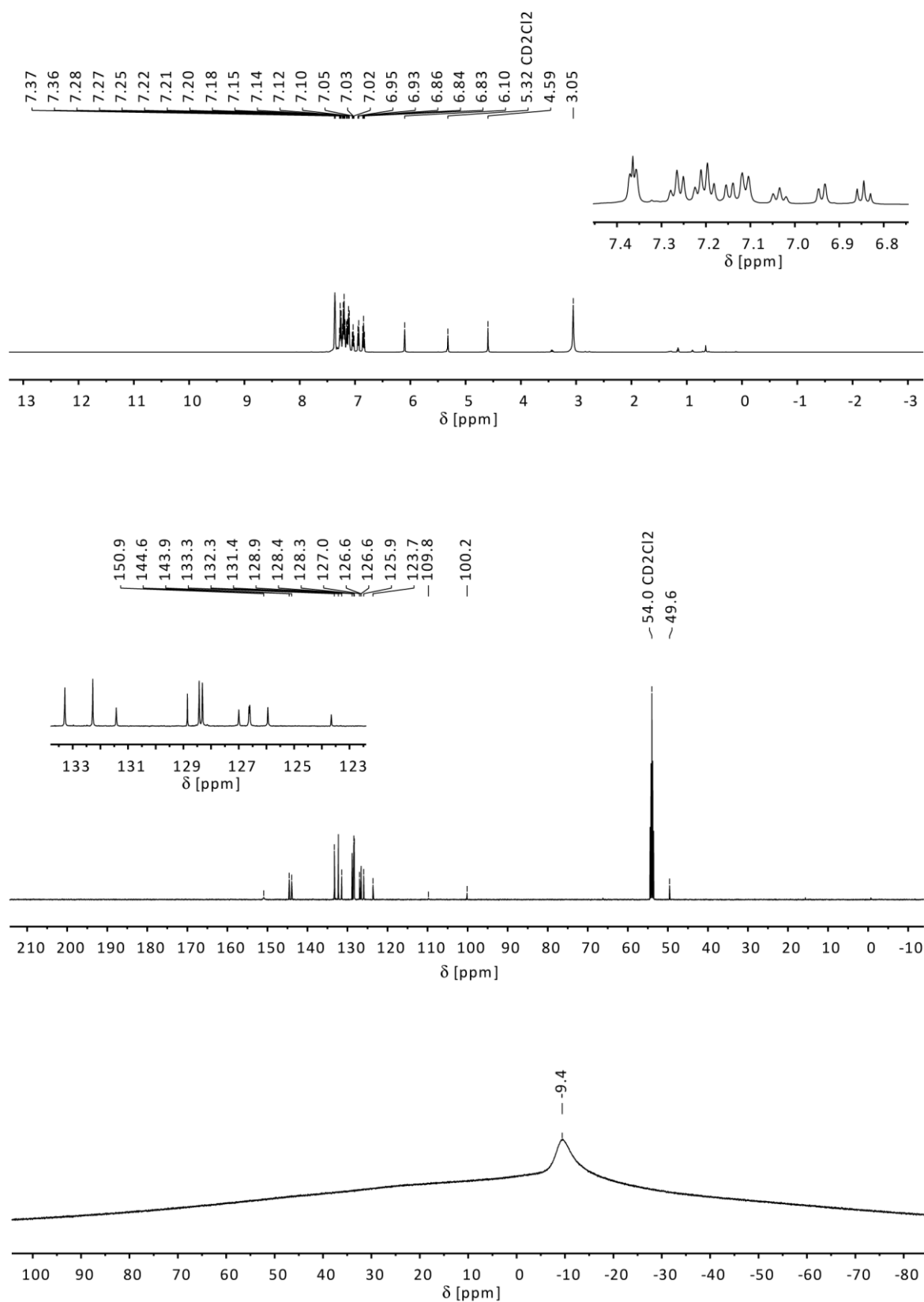


Fig. S8 NMR spectra, ¹H NMR (above), ¹³C{¹H} NMR (centre), ¹¹B{¹H} NMR (below), of compound **10**.

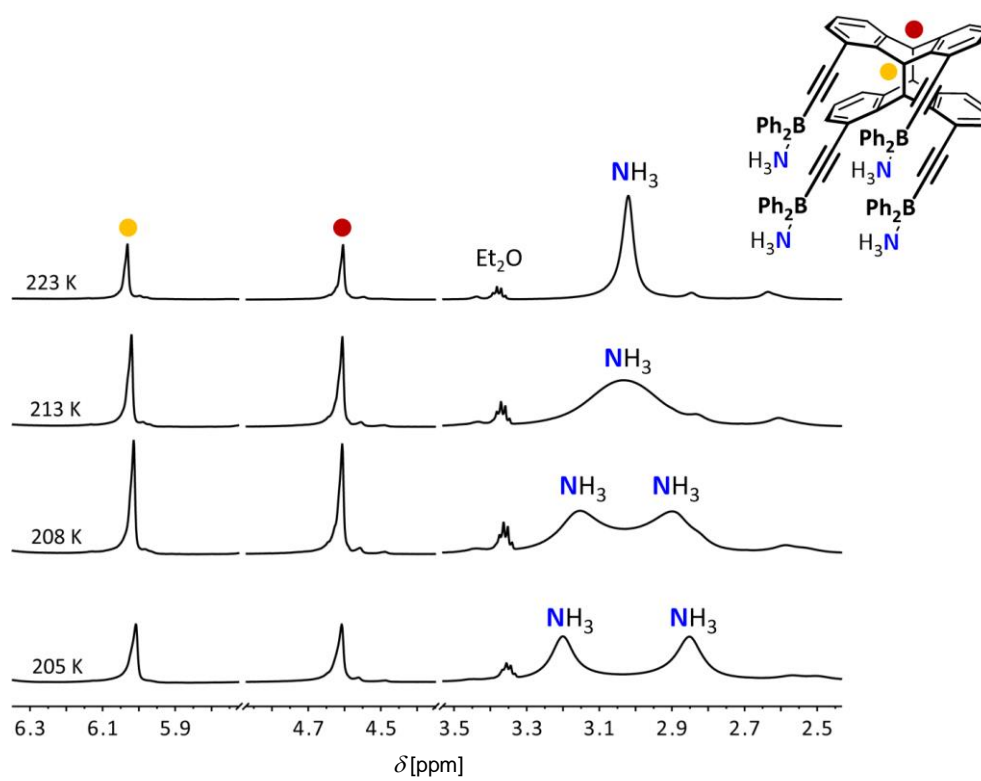


Fig. S9 Excerpts of the ^1H NMR spectra (600 MHz) of the ammonia adduct **10** at different temperatures in CD_2Cl_2 .

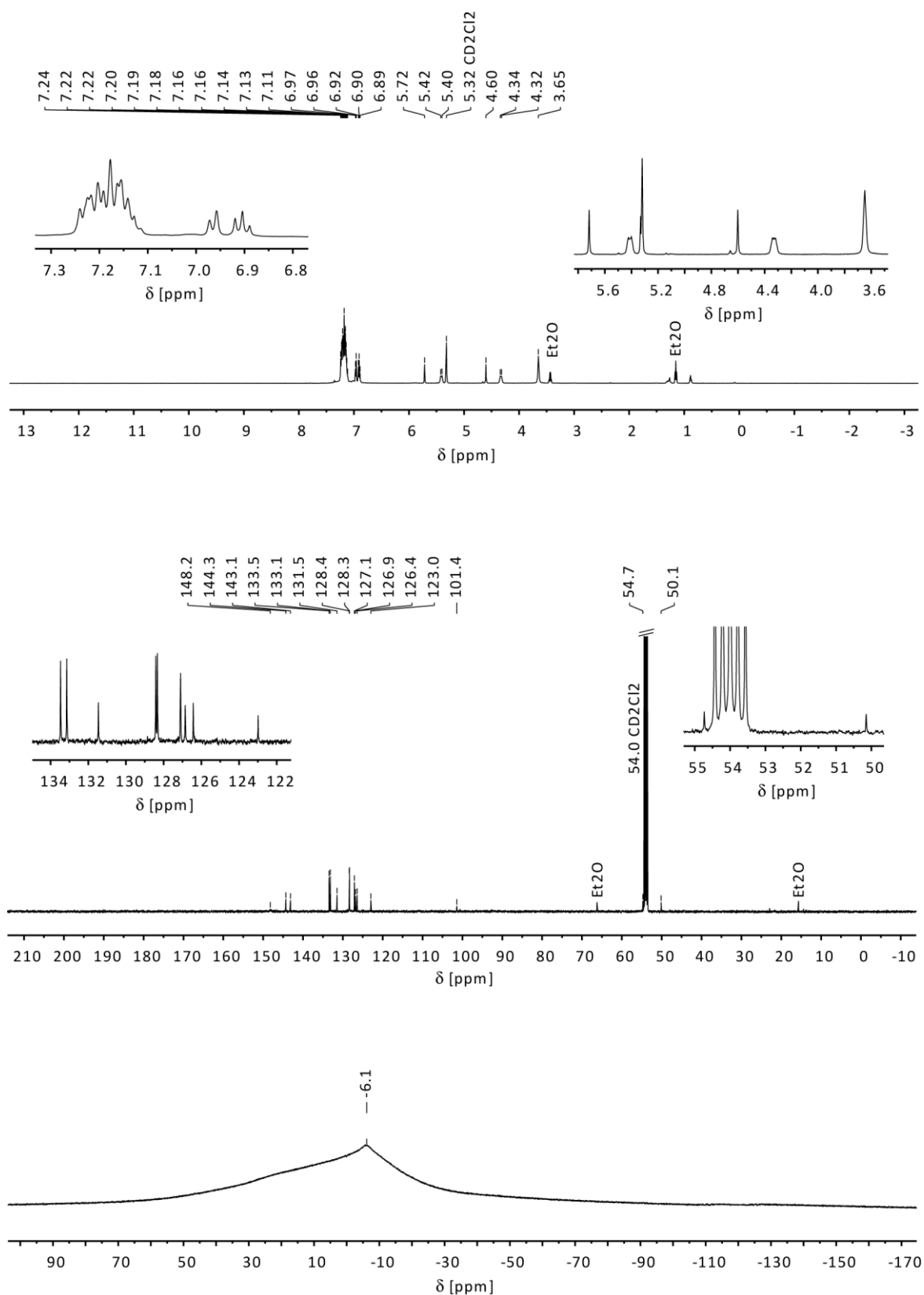


Fig. S10 NMR spectra, ¹H NMR (above), ¹³C{¹H} NMR (centre), ¹¹B{¹H} NMR (below), of compound **11**.

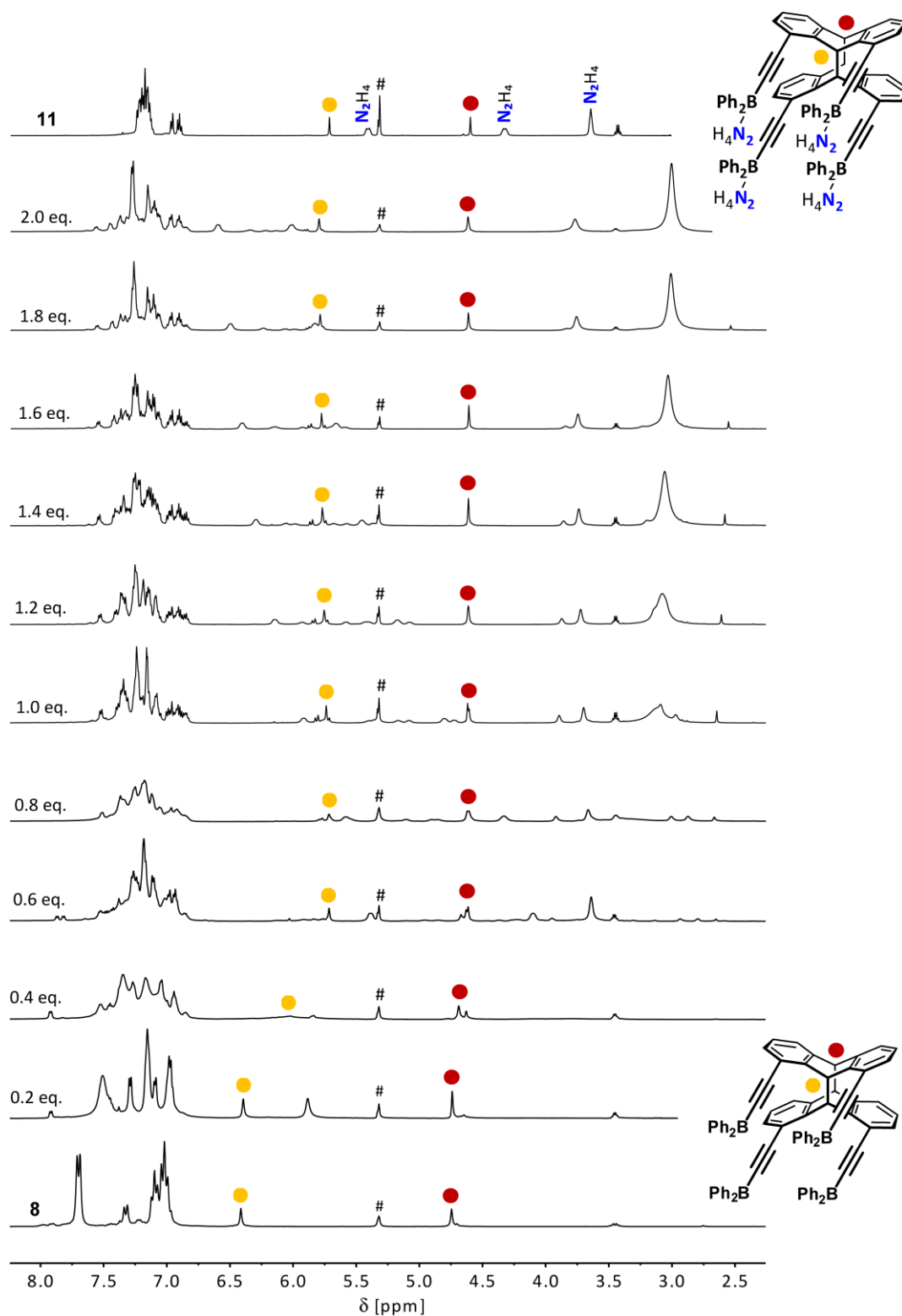


Fig. S11 ^1H NMR spectroscopy (500 MHz, 298 K) traces the adduct formation of tetraborane **8** by stepwise titration with hydrazine (0.2 eq. steps) in CD_2Cl_2 (#). After a total amount of two equivalents hydrazine, the oligomeric complex **12** ($[\mathbf{8}\cdot 5\text{N}_2\text{H}_4]_n$) was obtained as colourless crystals. ^1H NMR spectra of free tetraborane **8** (below) and its tetrahydrazine adduct **11** ($\mathbf{8}\cdot 4\text{N}_2\text{H}_4$, above) are shown, comparatively.

As shown in Fig. S11, strong dynamics are observed during the titration of **8** with hydrazine. Especially N_2H_4 -signals shift over a wide range of the NMR spectrum. The aromatic region indicates that a large number of different host/guest species are present at any time.

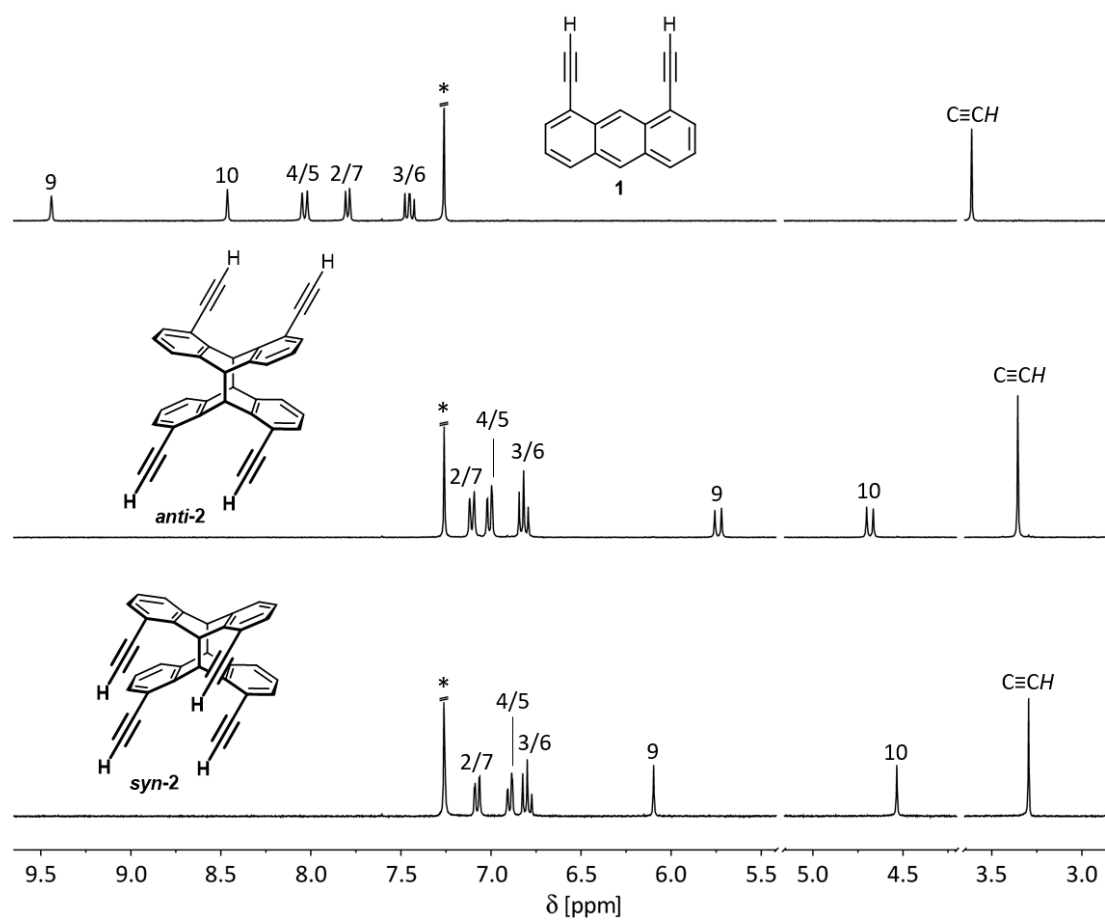


Fig. S12 Excerpts of the ^1H NMR spectra of anthracene monomer **1** (above) and its photo-isomers *anti*-**2** (centre) and *syn*-**2** (below).

UV-VIS Absorption Spectra

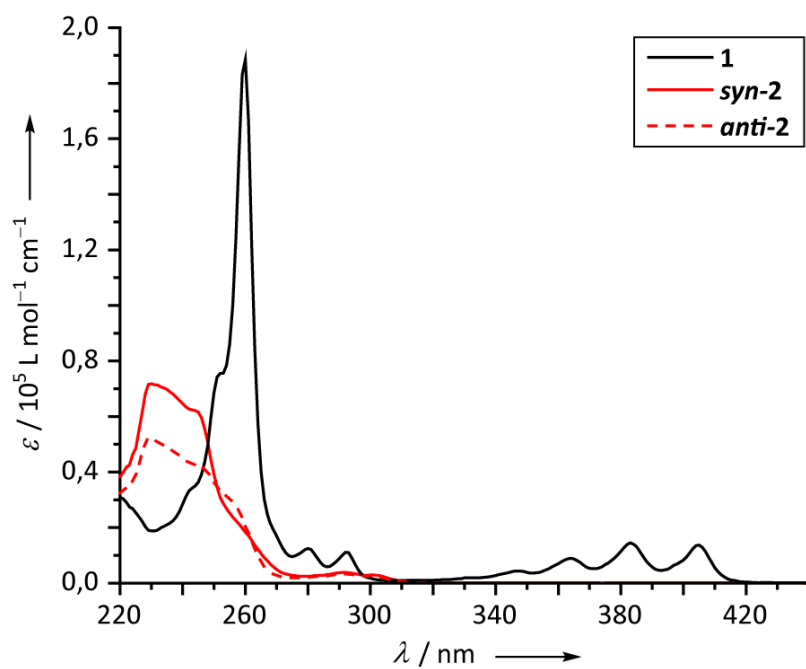


Fig. S13 Absorption spectra of 1,8-diethynylantracene **1** (black line, $8.0 \times 10^{-6} \text{ mol L}^{-1}$), as well as its photo-dimers **syn-2** (solid red line, $1.5 \times 10^{-5} \text{ mol L}^{-1}$) and **anti-2** (dotted red line, $1.4 \times 10^{-5} \text{ mol L}^{-1}$) in dichloromethane.

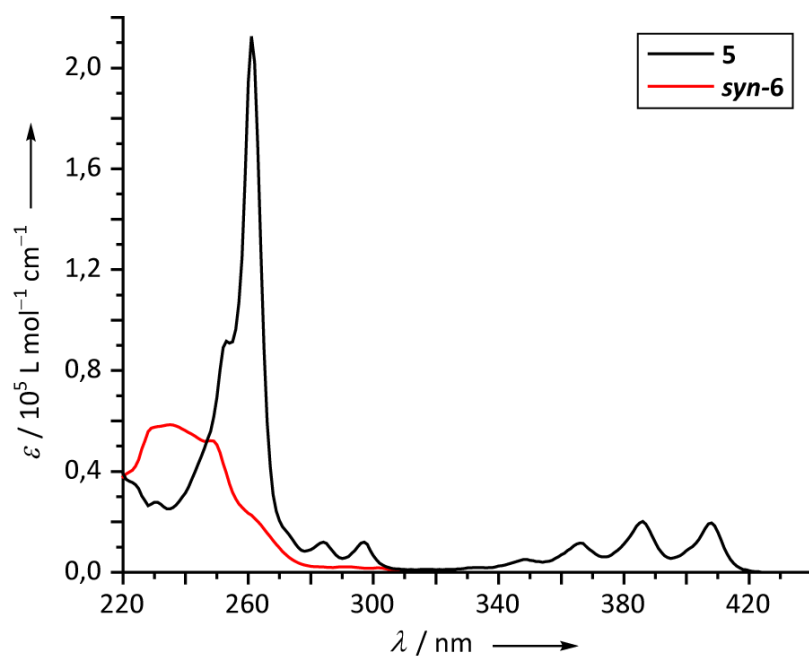


Fig. S14 Absorption spectra of dialkynylantracene **5** (black line, $5.3 \times 10^{-6} \text{ mol L}^{-1}$) and its photo-dimer **syn-6** (red line, $1.5 \times 10^{-5} \text{ mol L}^{-1}$) in dichloromethane.

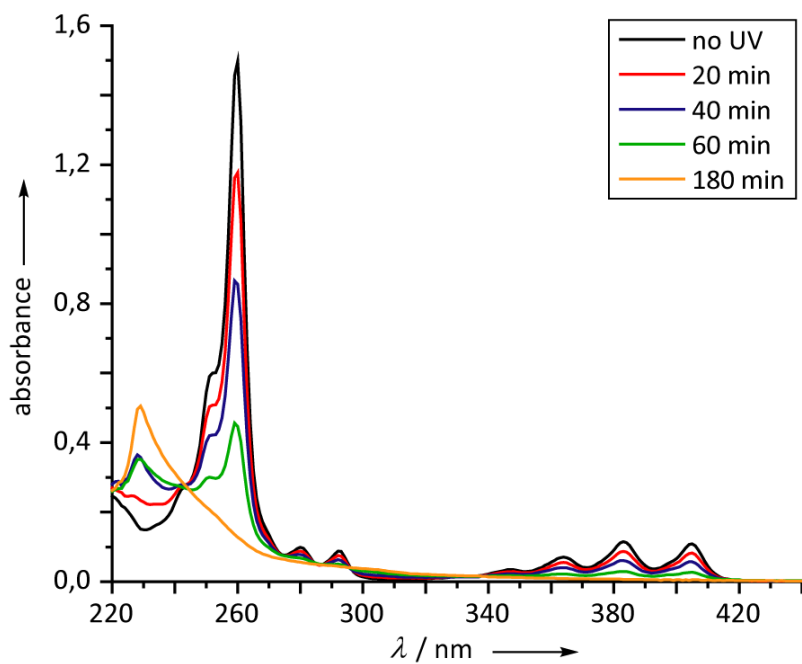


Fig. S15 Absorption spectra of 1,8-diethynylanthracene **1** (black line, $8.0 \times 10^{-6} \text{ mol L}^{-1}$) and the formed photo-isomers *syn-2* and *anti-2* in dichloromethane as a function of UV irradiation duration.

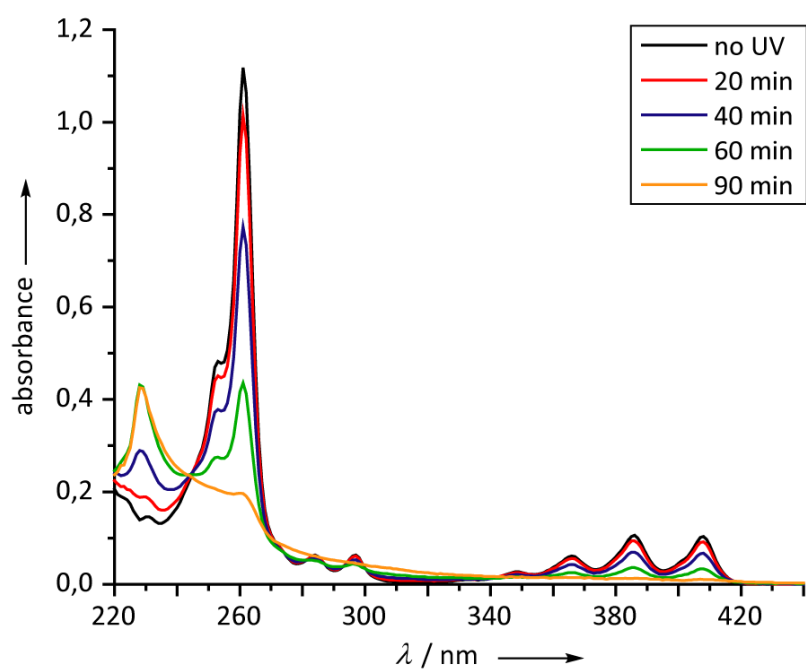


Fig. S16 Absorption spectra of dialkynylanthracene **5** (black line, $5.3 \times 10^{-6} \text{ mol L}^{-1}$) and the formed photo-isomers *syn-6* and *anti-6* in dichloromethane as a function of UV irradiation duration.

Crystallographic Data

General note: Solid state structures of compounds **4**, **4a**, **anti-2** and **10b** were determined, but are not mentioned or depicted in the main text.

Crystal structure determination: Suitable crystals were obtained by slow evaporation of saturated solutions from benzene (**syn-2**, **5**, **syn-6** and **10**), toluene (**anti-2**), *n*-hexane (**4a**), dichloromethane/*n*-pentane 1:4 (**4**), THF/*n*-hexane 1:1 (**anti-6**) or slowly grown from benzene (**9**), acetonitrile (**10b**) or dichloromethane (**11** and **12**) after adding the corresponding base to solutions of tetraborane **8**, respectively. They were selected, coated with PARATONE-N oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer into a nitrogen gas cold stream solidifying the oil. Data collection was performed on a *Rigaku SuperNova* diffractometer, a *SuperNova, Dual, Cu at zero*, diffractometer, a *SuperNova, Single source at offset, Eos*, diffractometer and a *Nonius KappaCCD* diffractometer. Using Olex2,² the structures were solved with the SHELXT³ structure solution program and refined with the SHELXL⁴ refinement package. Crystal and refinement details, as well as CCDC numbers are provided in Tables S4 and S5. CCDC 1952344-1952355 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

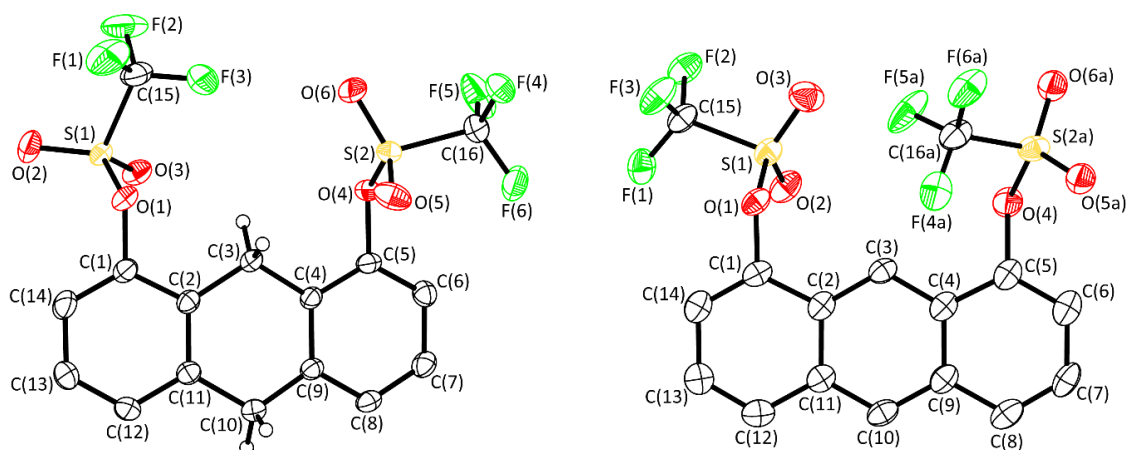


Fig. S17 Molecular structures of anthracene-1,8-diyl bis(trifluoromethanesulfonate) (**4**, right) and its precursor 9,10-dihydroanthracene-1,8-diyl bis(trifluoromethanesulfonate) (**4a**, left) in the crystalline state. Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms, except those of **4a** at C(3) and C(10), are omitted for clarity. Selected structural parameters are listed in Table S3.

Table S4 Selected structural parameters of 9,10-dihydroanthracene-1,8-diyl bis(trifluoromethanesulfonate) (**4a**) and anthracene-1,8-diyl bis(trifluoromethanesulfonate) (**4**).

Parameter	4a	4
$d[\text{C}(1)\text{--C}(2)]/\text{\AA}$	1.394(2)	1.423(4)
$d[\text{C}(2)\text{--C}(3)]/\text{\AA}$	1.484(2)	1.403(5)
$d[\text{C}(1)\cdots\text{C}(5)]/\text{\AA}$	4.958(2)	4.978(5)
$d[\text{C}(2)\text{--C}(11)]/\text{\AA}$	1.403(2)	1.435(4)
$d[\text{C}(1)\text{--O}(1)]/\text{\AA}$	1.436(2)	1.436(4)
$d[\text{S}(1)\text{--O}(1)]/\text{\AA}$	1.574(1)	1.565(2)

Parameter	4a	4
$d[\text{S}(1)\text{--O}(2)]/\text{\AA}$	1.415(1)	1.417(3)
$d[\text{S}(1)\text{--C}(15)]/\text{\AA}$	1.829(2)	1.839(3)
$\angle[\text{C}(14)\text{--C}(1)\text{--O}(1)]/^\circ$	118.5(1)	118.6(3)
$\angle[\text{C}(1)\text{--C}(2)\text{--C}(11)]/^\circ$	116.8(2)	116.0(3)
$\angle[\text{C}(2)\text{--C}(3)\text{--C}(4)]/^\circ$	114.7(1)	120.5(3)
$\tau[\text{Ar--Ar}]/^\circ$	19.4(1)	0.8(1)

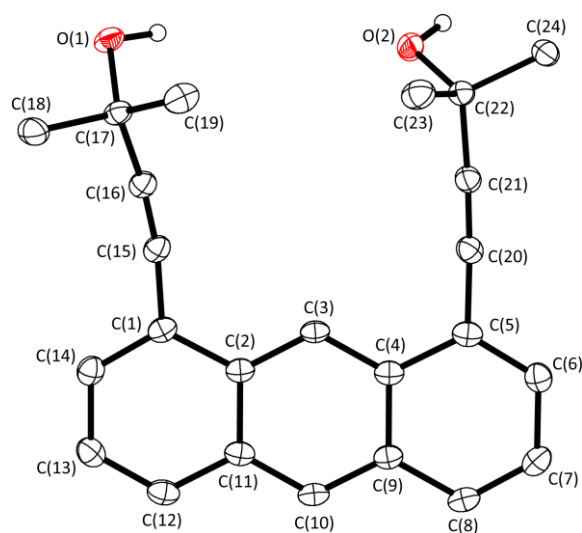


Fig. S18 Molecular structure of **5** in the crystalline state. Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms, except those of the hydroxyl-groups, are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.445(2), C(1)–C(15) 1.439(2), C(2)–C(3) 1.397(2), C(2)–C(11) 1.438(2), C(15)–C(16) 1.199(2), C(16)–C(17) 1.488(2), C(17)–C(18) 1.522(2), C(17)–O(1) 1.435(2); C(1)–C(2)–C(3) 122.6(1), C(1)–C(2)–C(11) 118.2(1), C(1)–C(15)–C(16) 171.5(2), C(15)–C(16)–C(17) 170.5(2), C(16)–C(17)–C(18) 107.7(1), C(16)–C(17)–O(1) 111.3(1), C(18)–C(17)–O(1) 106.3(1).

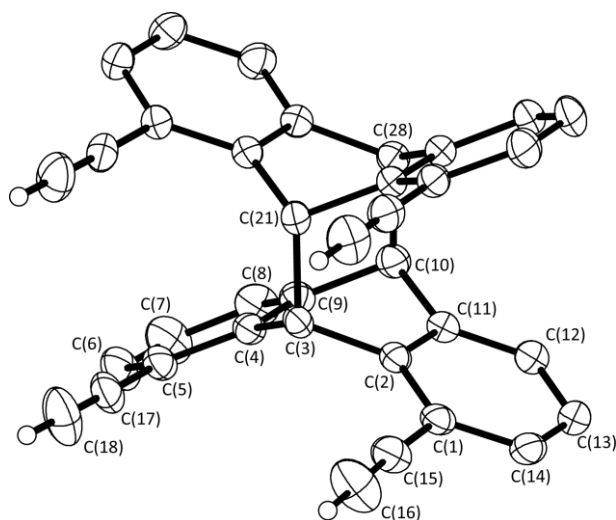


Fig. S19 Molecular structure of *syn-2* in the crystalline state. Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms, except those of the ethynyl groups, are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: C(1)–C(2) 1.403(1), C(1)–C(15) 1.438(1), C(2)–C(3) 1.520(1), C(2)–C(11) 1.397(1), C(3)–C(21) 1.615(1), C(10)–C(28) 1.616(1), C(15)–C(16) 1.189(2); C(1)–C(2)–C(3) 123.3(1), C(1)–C(2)–C(11) 119.3(1), C(1)–C(15)–C(16) 177.4(1), C(2)–C(3)–C(4) 107.9(1), C(2)–C(3)–C(21) 112.6(1), C(9)–C(10)–C(28) 112.9(1).

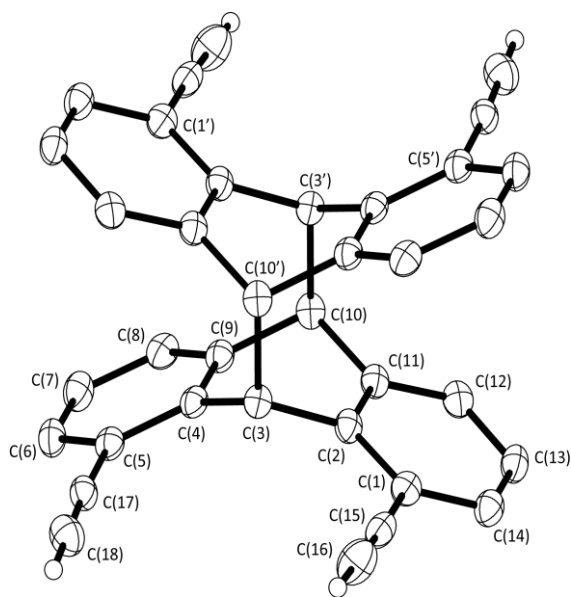


Fig. S20 Molecular structure of *anti-2* in the crystalline state. Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms, except those of the ethynyl groups, are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: C(1)–C(2) 1.401(3), C(1)–C(15) 1.446(3), C(2)–C(3) 1.516(2), C(2)–C(11) 1.395(3), C(3)–C(10') 1.613(2), C(10)–C(11) 1.515(3), C(15)–C(16) 1.182(3); C(1)–C(2)–C(3) 122.5(2), C(1)–C(2)–C(11) 120.1(2), C(1)–C(15)–C(16) 177.3(2), C(2)–C(3)–C(4) 108.3(1), C(2)–C(3)–C(10') 111.6(1), C(9)–C(10)–C(3') 110.8(1).

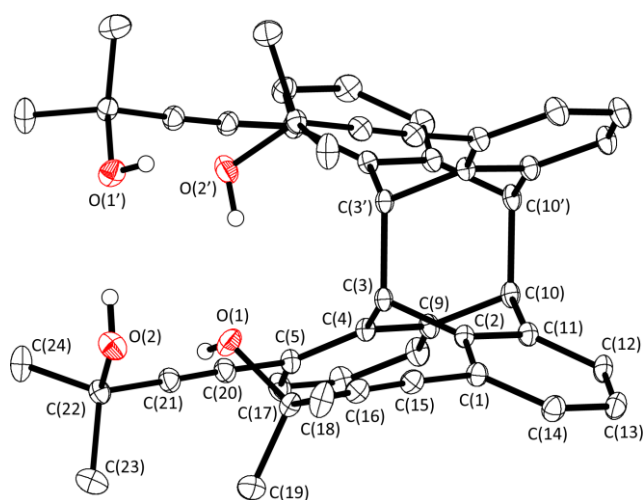


Fig. S21 Molecular structure of *syn-6* in the crystalline state. Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms, except those of the hydroxyl groups, are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.405(1), C(1)–C(15) 1.437(2), C(2)–C(3) 1.517(1), C(2)–C(11) 1.402(1), C(3)–C(3′) 1.614(2), C(10)–C(10′) 1.600(2), C(10)–C(11) 1.512(1), C(15)–C(16) 1.202(2), C(16)–C(17) 1.479(2), C(17)–C(18) 1.529(2), C(17)–O(1) 1.441(1); C(1)–C(2)–C(3) 123.5(1), C(1)–C(2)–C(11) 119.2(1), C(1)–C(15)–C(16) 177.6(1), C(2)–C(3)–C(4) 107.1(1), C(2)–C(3)–C(3′) 112.2(1), C(9)–C(10)–C(10′) 112.0(1), C(15)–C(16)–C(17) 178.3(1), C(16)–C(17)–C(18) 109.9(1), C(16)–C(17)–O(1) 110.0(1), C(18)–C(17)–O(1) 107.8(1).

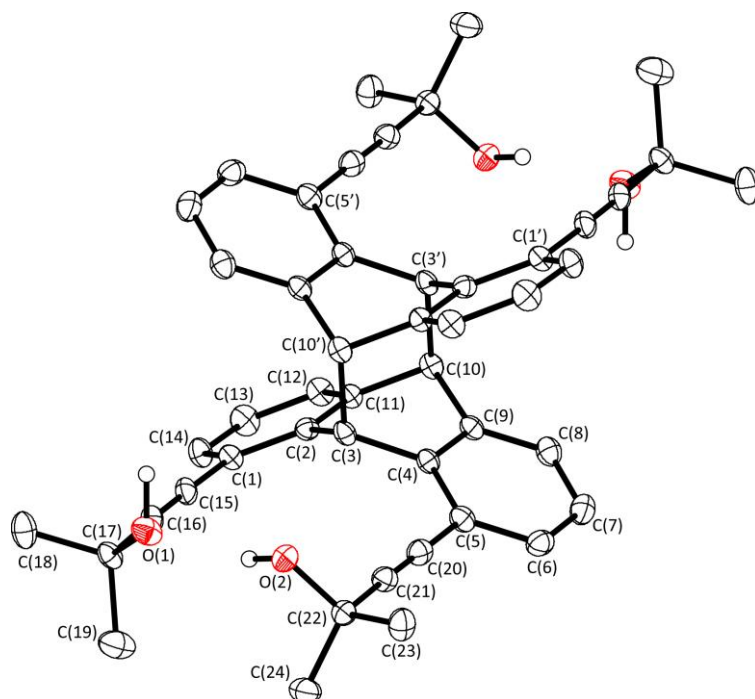


Fig. S22 Molecular structure of *anti-6* in the crystalline state. Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms, except those of the hydroxyl groups, are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.403(2), C(1)–C(15) 1.429(2), C(2)–C(3) 1.513(2), C(2)–C(11) 1.386(2), C(3)–C(10′) 1.609(2), C(10)–C(11) 1.513(2), C(15)–C(16) 1.198(2), C(16)–C(17) 1.477(2), C(17)–C(18) 1.521(2), C(17)–O(1) 1.439(2); C(1)–C(2)–C(3) 122.5(2), C(1)–C(2)–C(11) 119.8(2), C(1)–C(15)–C(16) 176.5(2), C(2)–C(3)–C(4) 107.7(1), C(2)–C(3)–C(10′) 111.6(1), C(3′)–C(10)–C(9) 111.8(1), C(15)–C(16)–C(17) 178.5(2), C(16)–C(17)–C(18) 110.2(1), C(16)–C(17)–O(1) 109.2(1), C(18)–C(17)–O(1) 109.7(1).

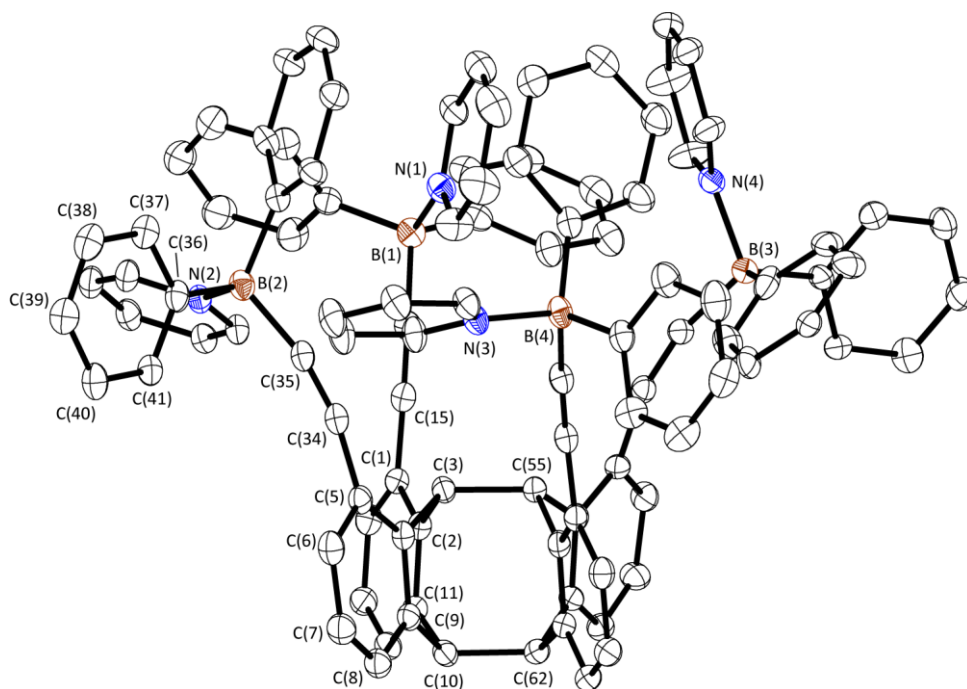


Fig. S23 Molecular structure of **9** in the crystalline state. Displacement ellipsoids are drawn at only 15% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.396(4), C(1)–C(15) 1.420(5), C(2)–C(3) 1.529(4), C(2)–C(11) 1.403(5), C(3)–C(55) 1.622(4), C(5)–C(34) 1.427(5), C(10)–C(62) 1.609(4), C(34)–C(35) 1.218(5), C(35)–B(2) 1.606(6), C(36)–B(2) 1.622(5), B(1)–N(1) 1.636(5), B(2)–N(2) 1.649(5), B(3)–N(3) 1.634(5), B(4)–N(4) 1.643(4); C(1)–C(2)–C(3) 123.6(3), C(1)–C(2)–C(11) 118.6(3), C(2)–C(3)–C(55) 114.7(3), C(5)–C(34)–C(35) 167.7(3), C(9)–C(10)–C(62) 114.1(3), C(34)–C(35)–B(2) 167.7(3), C(35)–B(2)–C(36) 109.4(3), C(35)–B(2)–N(2) 104.3(3), C(36)–C(37)–C(38) 121.8(4), C(36)–B(2)–N(2) 106.9(3), C(37)–C(36)–B(2) 122.4(4).

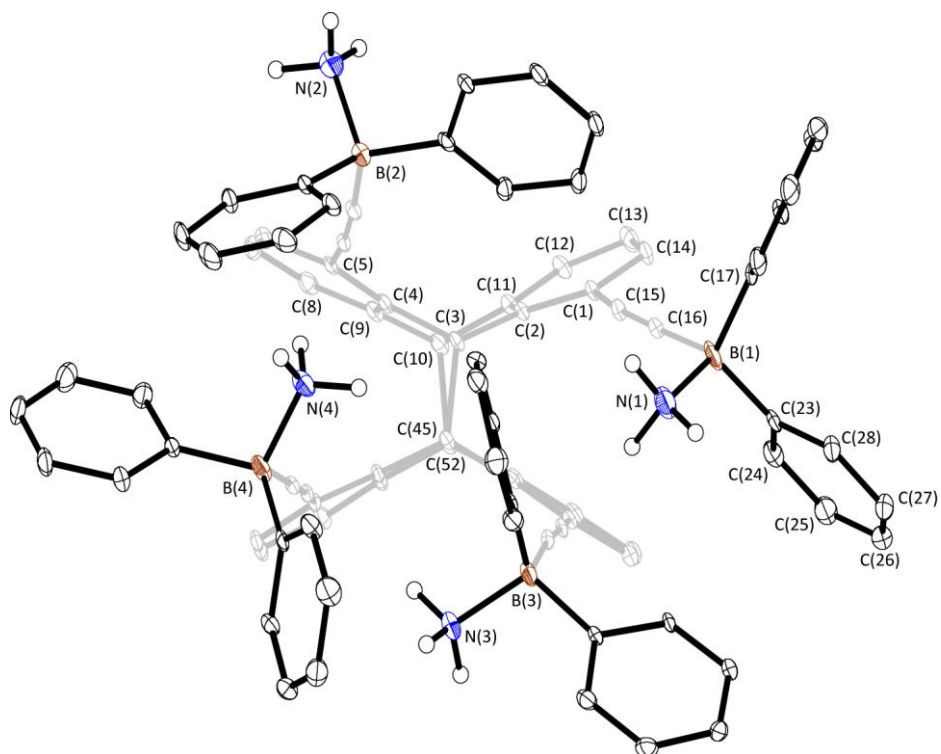


Fig. S24 Molecular structure of **10** in the crystalline state. Displacement ellipsoids are drawn at 30% (for C) and 50% (for B and N) probability levels. Carbon-bound hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.394(3), C(1)–C(15) 1.442(4), C(2)–C(3) 1.524(3), C(2)–C(11) 1.409(3), C(3)–C(45) 1.611(3), C(10)–C(52) 1.616(3), C(15)–C(16) 1.209(4), C(16)–B(1) 1.590(4), C(23)–B(1) 1.616(4), B(1)–N(1) 1.620(3), B(2)–N(2) 1.639(3), B(3)–N(3) 1.635(3), B(4)–N(4) 1.630(3); C(1)–C(2)–C(3) 124.8(2), C(1)–C(2)–C(11) 118.3(2), C(1)–C(15)–C(16) 165.1(3), C(2)–C(3)–C(45) 114.2(2), C(9)–C(10)–C(52) 114.5(2), C(15)–C(16)–B(1) 172.2(3), C(16)–B(1)–C(23) 111.5(2), C(16)–B(1)–N(1) 106.3(2), C(23)–C(24)–C(25) 122.7(3), C(23)–B(1)–N(1) 106.7(2), C(24)–C(23)–B(1) 124.2(2).

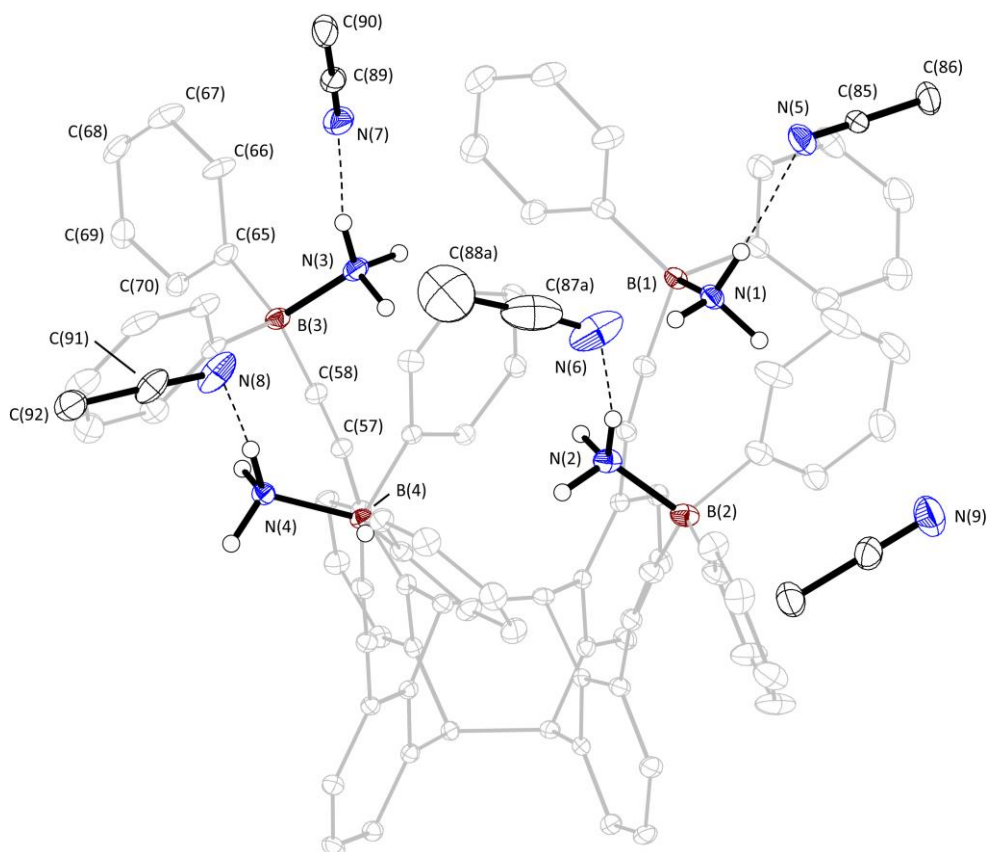


Fig S25 Molecular structure of **10b** (**8**·4NH₃·4MeCN) in the crystalline state. Single crystals were obtained, when a solution of **8** in acetonitrile was converted with an excess of gaseous ammonia. Displacement ellipsoids are drawn at 25% probability level. Carbon-bound hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(57)–C(58) 1.224(5), C(58)–B(3) 1.585(5), C(65)–C(66) 1.400(5), C(65)–B(3) 1.625(5), C(66)–C(67) 1.393(6), C(67)–C(68) 1.381(7), C(85)–C(86) 1.448(6), C(85)–N(5) 1.145(5), C(87a)–C(88a) 1.505(11), C(87a)–N(6) 1.177(10), C(89)–C(90) 1.466(8), C(89)–N(7) 1.159(7), C(91)–C(92) 1.455(7), C(91)–N(8) 1.158(6), B(1)–N(1) 1.635(5), B(2)–N(2) 1.600(6), B(3)–N(3) 1.608(6), B(4)–N(4) 1.625(5); C(57)–C(58)–B(3) 173.9(4), C(58)–B(3)–C(65) 110.8(3), C(58)–B(3)–N(3) 106.6(3), C(66)–C(65)–B(3) 122.3(3), C(66)–C(65)–C(70) 116.5(3), C(86)–C(85)–N(5) 178.7(5), C(88a)–C(87a)–N(6) 176.3(9), C(90)–C(89)–N(7) 177.7(8), C(92)–C(91)–N(8) 178.7(5).

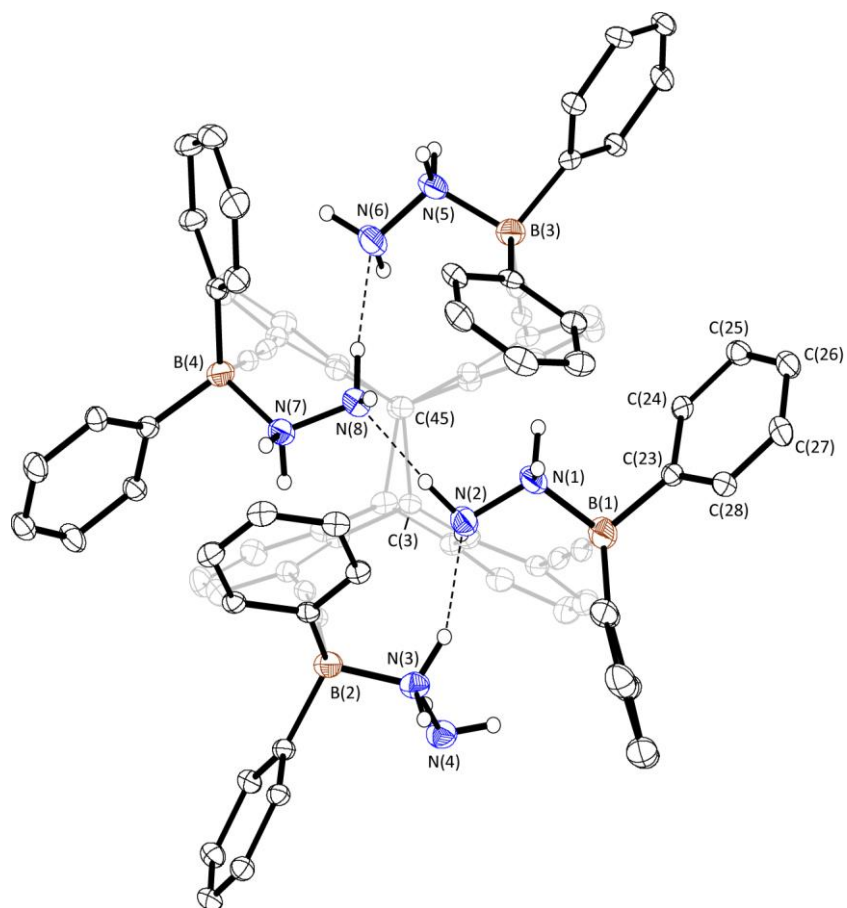


Fig. S26 Molecular structure of **11** in the crystalline state. Displacement ellipsoids are drawn at 30% (for C) and 50% (for B and N) probability levels. Carbon-bound hydrogen atoms are omitted for clarity. Dotted lines indicate hydrogen bonds. Selected bond lengths [\AA] and angles [$^\circ$]: C(23)–C(24) 1.405(6), C(23)–B(1) 1.612(7), C(24)–C(25) 1.391(7), C(25)–C(26) 1.382(8), B(1)–N(1) 1.631(6), B(2)–N(3) 1.626(6), B(3)–N(5) 1.625(7), B(4)–N(7) 1.618(6), N(1)–N(2) 1.456(5), N(3)–N(4) 1.459(5), N(5)–N(6) 1.456(5), N(7)–N(8) 1.459(5); C(23)–C(24)–C(25) 122.5(5), C(23)–B(1)–N(1) 105.0(4), C(24)–C(23)–C(28) 115.9(4), C(24)–C(23)–B(1) 120.8(5), B(1)–N(1)–N(2) 112.3(3), B(2)–N(3)–N(4) 114.2(3), B(3)–N(5)–N(6) 113.6(3), B(4)–N(7)–N(8) 118.0(3).

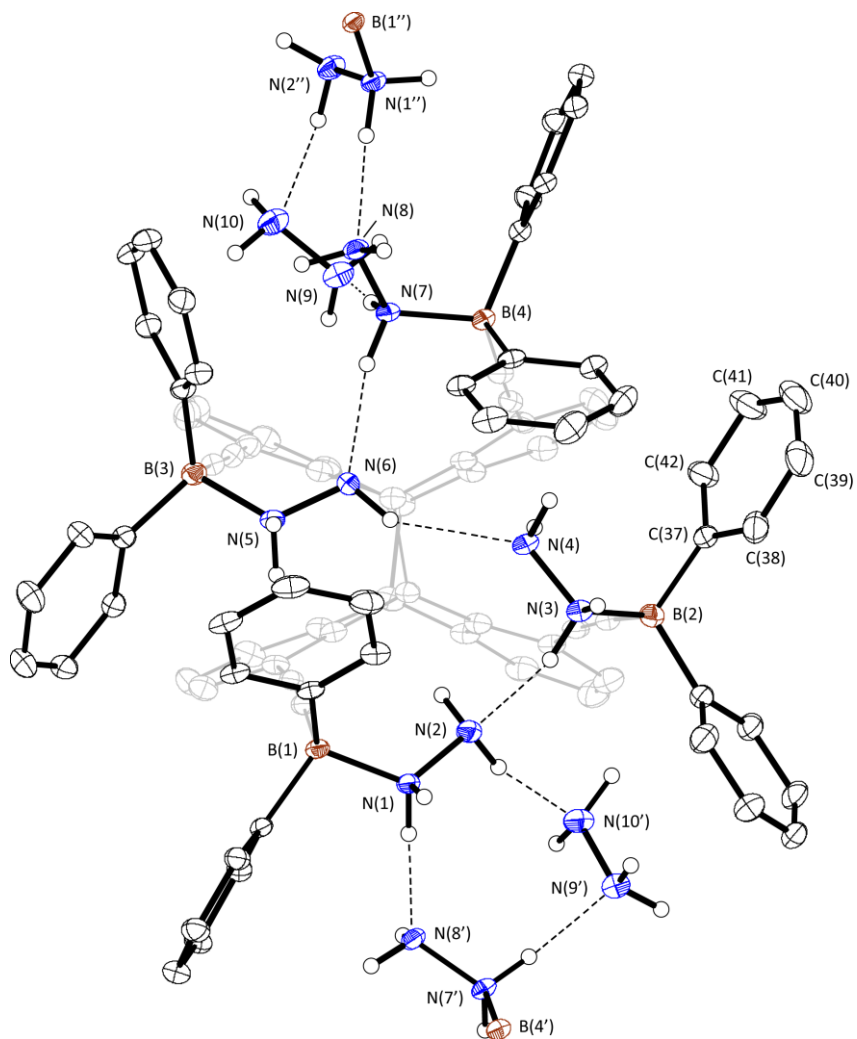


Fig. S27 Molecular structure of **12** in the crystalline state. Displacement ellipsoids are drawn at 30% probability level. Carbon-bound hydrogen atoms are omitted for clarity. Symmetry code: $-1/4 + y, 3/4 - x, -1/4 + z$ (for E') and $3/4 - y, 1/4 + x, 1/4 + z$ (for E''). Dotted lines indicate hydrogen bonds. Selected bond lengths [Å] and angles [°]: C(37)–C(38) 1.397(6), C(37)–B(2) 1.618(5), C(38)–C(39) 1.390(6), C(39)–C(40) 1.383(8), B(1)–N(1) 1.639(4), B(2)–N(3) 1.622(5), B(3)–N(5) 1.630(5), B(4)–N(7) 1.621(4), N(1)–N(2) 1.465(4), N(3)–N(4) 1.459(4), N(5)–N(6) 1.456(4), N(7)–N(8) 1.460(4), N(9)–N(10) 1.427(5); C(37)–C(38)–C(39) 122.1(5), C(37)–B(2)–N(3) 108.0(3), C(38)–C(37)–C(42) 116.5(4), C(38)–C(37)–B(2) 120.9(4), B(1)–N(1)–N(2) 117.4(2), B(2)–N(3)–N(4) 114.9(3), B(3)–N(5)–N(6) 115.0(2), B(4)–N(7)–N(8) 115.2(2).

Table S5 Crystallographic data for compounds **4a**, **4**, **5**, *syn-2*, *anti-2*, *syn-6* and *anti-6*.

	4a	4	5	<i>syn-2</i>	<i>anti-2</i>	<i>syn-6</i>	<i>anti-6</i> ^[a]
Empirical formula	C ₁₆ H ₁₀ F ₆ O ₂ S ₂	C ₁₆ H ₈ F ₆ O ₂ S ₂	C ₂₄ H ₂₂ O ₂	C ₃₆ H ₂₀	C ₃₆ H ₂₀ ·0.5 C ₇ H ₈	C ₅₄ H ₅₀ O ₄	C ₄₈ H ₄₄ O ₄ ·C ₄ H ₈ O
<i>M_r</i>	476.36	474.34	342.41	452.52	498.59	762.94	756.93
λ [Å]	1.54184	1.54184	1.54184	1.54184	0.71073	0.71073	0.71073
<i>T</i> [K]	100.0(1)	100.0(1)	100.0(1)	100.0(1)	100.0(1)	100.0(1)	100.0(1)
<i>F</i> (000)	480	476	1456	944	522	812	404
Crystal system	triclinic	triclinic	orthorhombic	monoclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2/ <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	9.5762(4)	5.4457(5)	11.74087(5)	10.03642(5)	10.1399(8)	11.1578(3)	9.8376(5)
<i>b</i> [Å]	10.0978(5)	9.7022(10)	32.16370(14)	20.42255(9)	11.8036(11)	11.0555(3)	11.0362(7)
<i>c</i> [Å]	10.1439(3)	17.3622(8)	9.77293(5)	12.53918(8)	12.2024(11)	17.2821	11.1225(6)
α [°]	87.983(3)	84.758(6)	90	90	104.246(4)	90	89.252(5)
β [°]	78.962(3)	87.356(7)	90	111.7520(4)	90.620(5)	98.594(2)	66.881(5)
γ [°]	69.485(4)	74.878(9)	90	90	111.016(5)	90	74.852(5)
<i>V</i> [Å ³]	901.16(7)	881.63(14)	3690.55(3)	2387.14(2)	1313.5(2)	2107.9(1)	1066.53(11)
<i>Z</i>	2	2	8	4	2	2	1
ρ _{calcd.} [g cm ⁻³]	1.756	1.787	1.233	1.259	1.261	1.202	1.179
μ [mm ⁻¹]	3.595	3.674	0.603	0.545	0.071	0.074	0.074
θ _{max} [°]	72.35	72.33	72.32	72.32	30.00	30.03	26.021
Index ranges <i>h</i>	-11 ≤ <i>h</i> ≤ 11	-6 ≤ <i>h</i> ≤ 6	-14 ≤ <i>h</i> ≤ 14	-12 ≤ <i>h</i> ≤ 12	-14 ≤ <i>h</i> ≤ 14	-15 ≤ <i>h</i> ≤ 15	-11 ≤ <i>h</i> ≤ 12
Index ranges <i>k</i>	-12 ≤ <i>k</i> ≤ 11	-11 ≤ <i>k</i> ≤ 11	-39 ≤ <i>k</i> ≤ 39	-25 ≤ <i>k</i> ≤ 25	-16 ≤ <i>k</i> ≤ 15	-15 ≤ <i>k</i> ≤ 15	-12 ≤ <i>k</i> ≤ 13
Index ranges <i>l</i>	-12 ≤ <i>l</i> ≤ 12	-21 ≤ <i>l</i> ≤ 19	-11 ≤ <i>l</i> ≤ 12	-15 ≤ <i>l</i> ≤ 15	-17 ≤ <i>l</i> ≤ 17	-24 ≤ <i>l</i> ≤ 24	-13 ≤ <i>l</i> ≤ 13
Reflexes collected	13616	11552	63776	81574	18989	47712	9733
Independent reflexes	3536	3434	6940	4718	7266	6166	4209
<i>R</i> _{int}	0.0191	0.0650	0.0249	0.0237	0.061	0.0338	0.0325
Observed reflexes, <i>I</i> > 2σ(<i>I</i>)	3333	2672	6850	4582	4680	5319	3268
Parameters	271	311	493	325	389	275	247
<i>R</i> ₁ , <i>I</i> > 2σ(<i>I</i>)	0.0312	0.0614	0.0256	0.0370	0.0624	0.0477	0.0509
<i>wR</i> ₂ , <i>I</i> > 2σ(<i>I</i>)	0.0842	0.1619	0.0675	0.0988	0.1315	0.1392	0.1234
<i>R</i> ₁ (all data)	0.0330	0.0769	0.0260	0.0377	0.1116	0.0548	0.0659
<i>wR</i> ₂ (all data)	0.0860	0.1782	0.0681	0.0994	0.1564	0.1452	0.1321
<i>GoF</i>	1.053	1.016	1.032	1.043	1.022	1.073	1.043
ρ _{max} /ρ _{min} [e Å ⁻³]	0.38/-0.37	0.48/-0.73	0.14/-0.17	0.25/-0.22	0.33/-0.25	0.47/-0.36	0.27/-0.21
Flack parameter	–	–	0.02(4)	–	–	–	–
CCDC number	1952344	1952345	1952346	1952347	1952348	1952349	1952350

[a] The unit cell contains one highly disordered thf solvent molecule, which was “squeezed” using the Olex2 routine, but included into the sum formula and dependent values.

Table S6 Crystallographic data for compounds **9**, **10**, **10b**, **11** and **12**.

	9 ^[a]	10 ^[b]	10b ^[c]	11 ^[d]	12 ^[e]
Empirical formula	C ₁₀₄ H ₇₆ B ₄ N ₄	C ₁₀₅ H ₈₉ B ₄ N ₄	C _{95.25} H _{84.87} B ₄ N _{9.62}	C _{87.33} H _{78.66} B ₄ Cl _{6.66} N ₈	C ₈₄ H ₇₆ B ₄ N ₁₀
<i>M_r</i>	1424.92	1450.04	1407.49	1519.63	1268.78
λ [Å]	1.54184	1.54184	1.54184	1.54184	1.54184
<i>T</i> [K]	100.0(1)	100.0(1)	100.0(1)	100.0(1)	100.0(1)
<i>F</i> (000)	2992	1534	5950	3168	10720
Crystal system	monoclinic	triclinic	orthorhombic	orthorhombic	tetragonal
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>Pbca</i>	<i>Pna</i> 2 ₁	<i>I</i> ₄ / <i>a</i>
<i>a</i> [Å]	14.0002(4)	14.4537(8)	19.2454(7)	23.0669(4)	26.4901(4)
<i>b</i> [Å]	40.8950(12)	14.7536(6)	28.1544(12)	22.8536(4)	26.4901(4)
<i>c</i> [Å]	17.3331(6)	20.5177(7)	29.7705(10)	15.3750(4)	44.9400(11)
α [°]	90	100.327(3)	90	90	90
β [°]	91.677(3)	98.165(4)	90	90	90
γ [°]	90	99.886(4)	90	90	90
<i>V</i> [Å ³]	9919.6(5)	4172.5(3)	16130.9(11)	8105.2(3)	31535.6(12)
<i>Z</i>	4	2	8	4	16
ρ _{calcd.} [g cm ⁻³]	0.954	1.154	1.159	1.245	1.069
μ [mm ⁻¹]	0.414	0.496	0.518	2.518	0.482
θ _{max} [°]	66.75	67.08	67.08	78.553	66.594
Index ranges <i>h</i>	-16 ≤ <i>h</i> ≤ 16	-15 ≤ <i>h</i> ≤ 17	-20 ≤ <i>h</i> ≤ 22	-29 ≤ <i>h</i> ≤ 29	-31 ≤ <i>h</i> ≤ 31
Index ranges <i>k</i>	-48 ≤ <i>k</i> ≤ 34	-17 ≤ <i>k</i> ≤ 17	-33 ≤ <i>k</i> ≤ 22	-28 ≤ <i>k</i> ≤ 29	-26 ≤ <i>k</i> ≤ 31
Index ranges <i>l</i>	-18 ≤ <i>l</i> ≤ 20	-21 ≤ <i>l</i> ≤ 24	-34 ≤ <i>l</i> ≤ 35	-19 ≤ <i>l</i> ≤ 19	-53 ≤ <i>l</i> ≤ 53
Reflexes collected	66655	28058	54697	91890	114503
Independent reflexes	17595	14901	14388	16668	13948
<i>R</i> _{int}	0.0692	0.0986	0.1485	0.0592	0.1541
Observed reflexes, <i>I</i> > 2σ(<i>I</i>)	10611	9295	8076	14362	9399
Parameters	1113	1097	1081	1126	963
<i>R</i> ₁ , <i>I</i> > 2σ(<i>I</i>)	0.0871	0.0598	0.0687	0.0605	0.0750
<i>wR</i> ₂ , <i>I</i> > 2σ(<i>I</i>)	0.2509	0.1279	0.1662	0.1554	0.1677
<i>R</i> ₁ (all data)	0.1196	0.1035	0.1349	0.0724	0.1095
<i>wR</i> ₂ (all data)	0.2793	0.1475	0.2177	0.1723	0.1949
<i>GoF</i>	1.051	0.931	1.011	1.063	1.023
ρ _{max} /ρ _{min} [e Å ⁻³]	0.50/-0.26	0.32/-0.27	0.28/-0.31	0.83/-0.44	0.28/-0.27
Flack parameter	–	–	–	0.006(7)	–
CCDC number	1952351	1952352	1952353	1952354	1952355

[a] As the crystal contains heavy disordered solvent molecules (chloroform and/or benzene), the squeeze algorithm of Olex2 was applied. Three phenyl groups were disordered in different ratios: (71:29), (59:41) and (59:41). All disordered phenyl groups were constrained to have idealised geometry (AFIX 66). Hydrogen atoms were taken into account using a riding model. [b] Hydrogen atoms bonded to nitrogen were refined isotropically, those ones bonded to carbon were taken into account using a riding model. On solvent benzene molecule was disordered in ration 53:47, both parts were constrained to an idealised hexagon. [c] Hydrogen atoms bonded to nitrogen were refined isotropically, those ones bonded to carbon were taken into account using a riding model. Approx. 5.6 molecules of acetonitrile were found per molecule. The occupation factors of these solvent molecules were refined, atoms of molecules with occupation below 25 % were refined isotropically, all others anisotropically. [d] Disordered CH₂Cl₂ with non-integer number. [e] Highly disordered CH₂Cl₂ was squeezed using the Olex2 routine. Bond lengths of hydrogens bonded to nitrogen were restrained with SADI to be equal. These hydrogens were refined isotropically.

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