Supporting Information

Duplex *vs* folding: tuning the self-assembly of synthetic recognition-encoded aniline oligomers

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1. Experimental Procedures

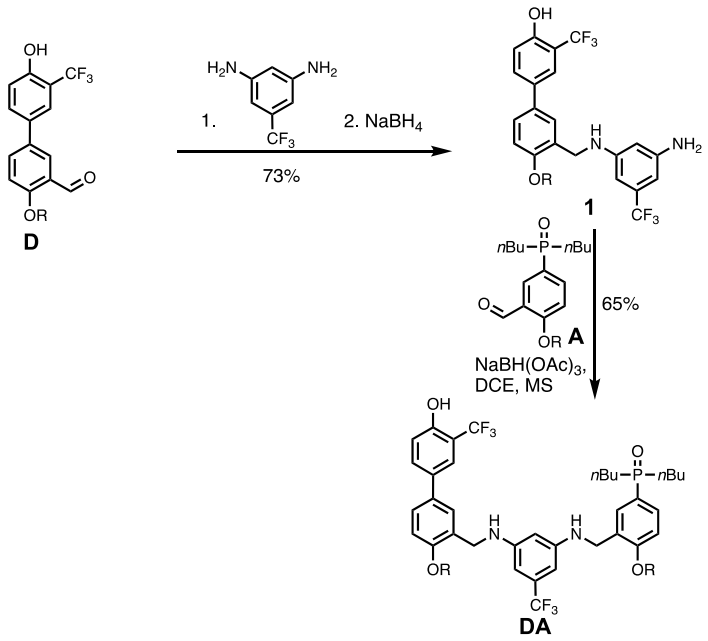
The reagents and materials used in the synthesis were bought from commercial sources, without prior purification. Thin layer chromatography was carried out using Merck 60 F254 silica gel precoated aluminium plates. Column chromatography was carried out either manually on Macherey-Nagel silica gel 60 (70-230 mesh) or on an automated system (Combiflash Companion, Combiflash Rf+ or Combiflash Rf Lumen) using prepacked cartridges of silica (25µ or 50µ PuriFlash® Columns). All NMR spectroscopy was carried out on a Bruker AVI250, AVI400, DPX400, AVIII400, 500 MHz AVIII HD Smart Probe, AV600 MHz Cryo spectrometers using the residual solvent as the internal standard. All chemical shifts (δ) are quoted in ppm and coupling constants given in Hz. ES+ was carried out on a Waters LCT-TOF spectrometer or a Waters Xevo G2-S bench top QTOF machine.

2. Synthesis and characterisation of homo- and hetero-dimers

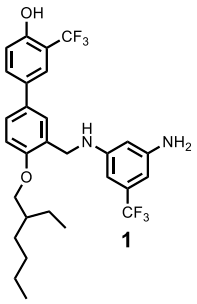
The monomers **A** and **D** and the dimers **AA**, **DD** used in this work were synthesised following the synthetic procedure that we recently reported.[1] Using similar procedures we synthesised mixed dimers and analogue homodimers, as reported here. In all the following schemes, the generic symbol R represents an ethylhexyl alkyl chain.

2.1 Synthesis of dimer DA

The dimer **DA** was prepared as reported in the following scheme:



2.1.1 Synthesis of 1



Monomer **D** (100 mg, 0.237 mmol, 1 equiv) and 5-(trifluoromethyl)-1,3-phenylenediamine (208 mg, 1.184 mmol, 5 equiv) were dissolved in dry DCE (2 mL). Molecular sieves (3 Å) were added, and the mixture was mixed overnight on an orbital shaker, under N_2 atmosphere. Then, $NaBH_4$ (90 mg, 2.37

mmol, 10 equiv) and MeOH (0.5 mL) were added, and the mixture was shaken for 2 hours. The solution was filtered, MS were washed with DCM and a saturated solution of $NaHCO_3$ was added. The mixture was stirred until complete solubilisation. The organic phase was extracted, and the aqueous phase washed (3x) with EtOAc. The organic layers were collected and dried over $MgSO_4$, the solvent was evaporated and the residue purified *via* combiflash chromatography (PE:EtOAc), giving the desired compound **1** (96 mg, 73% yield).

^{1}H-NMR (500 MHz, Methanol-d_4) δ 7.58 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.46 (s, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.29 (s, 1H), 6.27 (s, 1H), 6.18 (d, *J* = 2.2 Hz, 1H), 4.32 (s, 2H), 3.94 (d, *J* = 5.4 Hz, 2H), 1.80 – 1.68 (m, 1H), 1.58 – 1.20 (m, 8H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H).

^{13}C-NMR (126 MHz, Methanol-d_4) δ 156.2, 154.4, 150.0, 148.6, 131.9, 131.7, 131.5 (d, *J* = 30.8 Hz), 130.7, 127.5, 126.1, 125.6, 124.5 (q, *J* = 271.5 Hz), 124.0 (q, *J* = 271.3 Hz), 116.6, 116.6 (q, *J* = 30.4 Hz), 111.1, 101.7, 100.5 (q, *J* = 3.9 Hz), 99.7 (q, *J* = 4.1 Hz), 70.0, 42.2, 39.4, 30.4, 28.8, 23.7, 22.6, 12.9, 10.11.

^{19}F-NMR (471 MHz, Methanol-d_4) δ -63.91, -64.72.

HRMS (ES+): Calculated for $C_{29}H_{33}F_6N_2O_2$ 555.5446 a.m.u., found 555.5472 a.m.u.

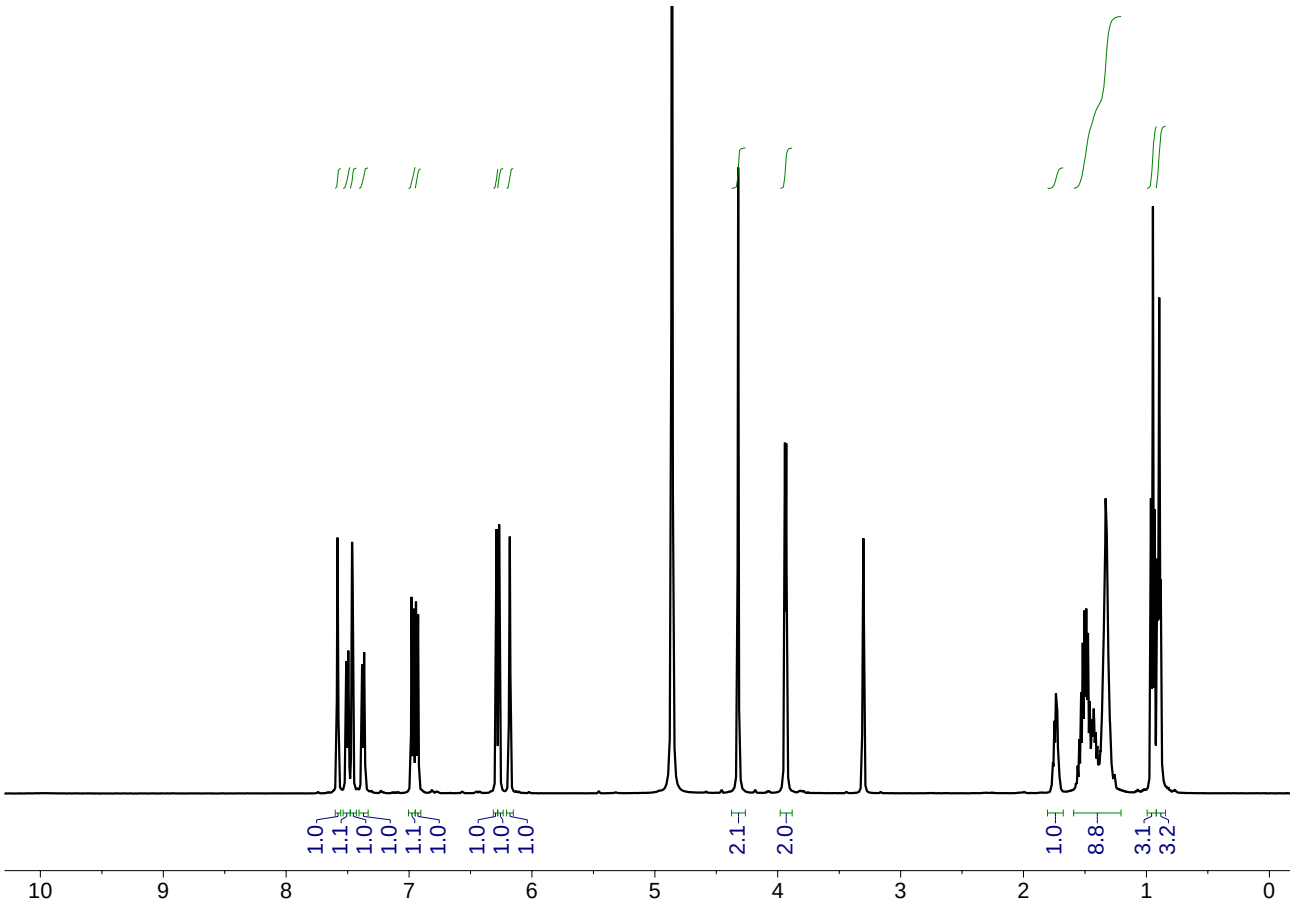


Figure S1.1. ^{1}H-NMR spectrum (500 MHz, Methanol-d_4) of **1**.

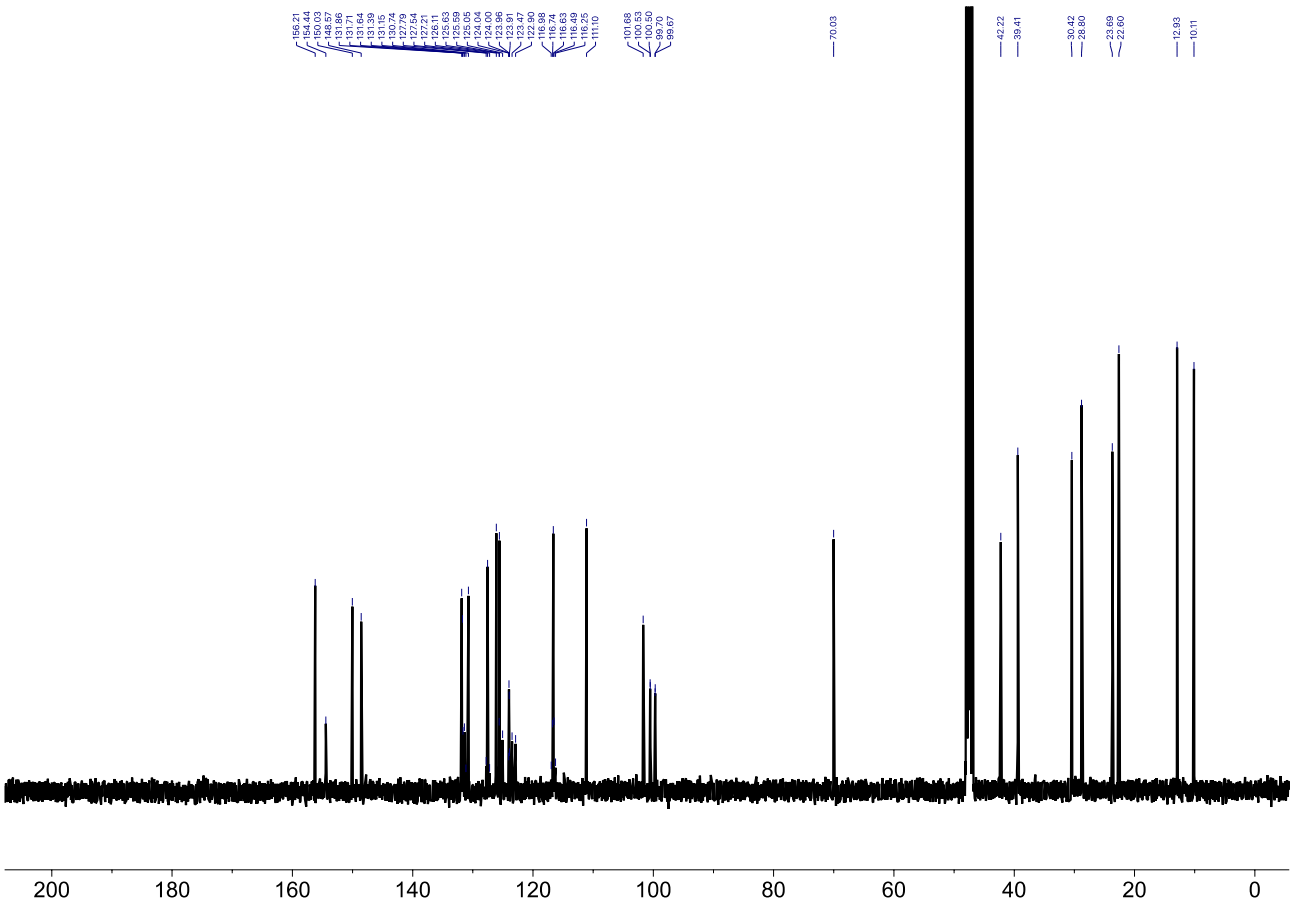


Figure S1.2. ^{13}C-NMR spectrum (126 MHz, Methanol-d_4) of **1**.

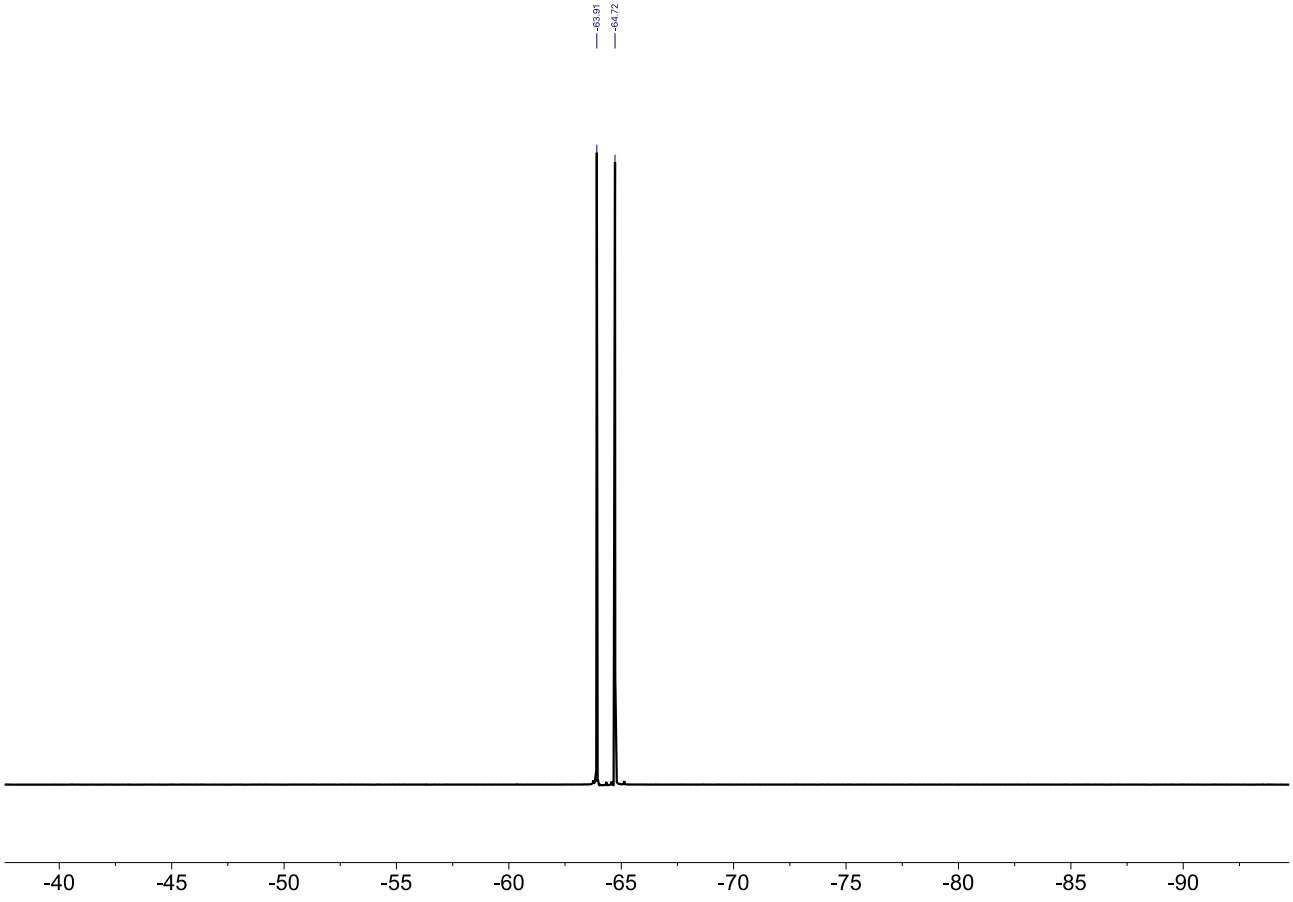
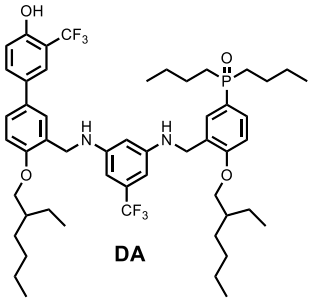


Figure S1.3. ^{19}F-NMR spectrum (471 MHz, Methanol-d_4) of **1**.

2.1.2 Synthesis of DA



DA

Compound **1** (38 mg, 0.0685 mmol, 1 equiv) and the acceptor monomer **A** (54 mg, 0.137 mmol, 2 equiv) were dissolved in dry DCE (1 mL). Molecular sieves (3 Å) were added, and the mixture was mixed overnight on an orbital shaker, under N_2 atmosphere. After imine formation $NaBH(OAc)_3$ (14 mg, 0.0685 mmol, 1 equiv) was added and the mixture was shaken for 12 hours. Then, in order to fully complete the reduction $NaBH(OAc)_3$ (30 mg, 0.137 mmol, 2 equiv) was added and the mixture was shaken for further 6 hours. Then the solution was filtered, MS washed with DCM and a saturated solution of $NaHCO_3$ was added. The mixture was stirred until complete solubilisation. The organic phase was extracted, and the aqueous phase was washed (3x) with EtOAc. The organic layers were collected and dried over $MgSO_4$, the solvent was evaporated and the residue was purified via combiflash chromatography (PE:EtOAc), giving the desired dimer **DA** (42 mg, 65% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.60 (s, 1H), 7.58 – 7.49 (m, 2H), 7.41 – 7.29 (m, 3H), 7.15 (d, *J* = 8.5 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.23 (s, 1H), 6.19 (s, 1H), 6.05 (s, 1H), 4.32 (s, 4H), 4.20 (bs, 2H), 3.91 (s, 4H), 2.06 – 1.96 (m, 2H), 1.97 – 1.84 (m, 2H), 1.83 – 1.69 (m, 4H), 1.57 – 1.36 (m, 10H), 1.39 – 1.23 (m, 15H), 0.98 – 0.84 (m, 12H), 0.80 (t, *J* = 7.1 Hz, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 159.74 (d, *J* = 2.8 Hz), 156.1, 154.9, 149.32 (d, *J* = 40.6 Hz), 149.25 (d, *J* = 40.7 Hz), 132.09 (q, *J* = 31.3 Hz), 132.0, 131.4, 131.4, 131.3, 130.9, 130.81 (d, *J* = 10.6 Hz), 127.66 (d, *J* = 191.7 Hz), 127.59 (d, *J* = 11.4 Hz), 127.31 (d, *J* = 22.2 Hz), 126.0, 124.43 (q, *J* = 4.9 Hz), 124.32 (d, *J* = 272.5 Hz), 124.11 (d, *J* = 272.4 Hz), 122.3, 121.5, 118.0, 116.88 (q, *J* = 30.2 Hz), 111.2, 111.08 (d, *J* = 12.5 Hz), 100.1, 99.1, 70.35 (d, *J* = 27.8 Hz), 43.4, 39.28 (d, *J* = 16.4 Hz), 30.61 (d, *J* = 12.1 Hz), 29.21 (d, *J* = 68.8 Hz), 28.99 (d, *J* = 6.1 Hz), 23.95 (d, *J* = 13.9 Hz), 23.84 (d, *J* = 16.9 Hz), 23.27 (d, *J* = 4.1 Hz), 22.91 (d, *J* = 8.6 Hz), 13.93 (d, *J* = 5.0 Hz), 13.3, 11.05 (d, *J* = 6.5 Hz).

^{19}F-NMR (471 MHz, $CDCl_3$) δ -62.25, -63.38.

^{31}P-NMR (202 MHz, $CDCl_3$) δ 44.23.

HRMS (ES+): Calculated for $C_{52}H_{72}F_6N_2O_4P$ 933.5134 a.m.u., found 933.5153 a.m.u.

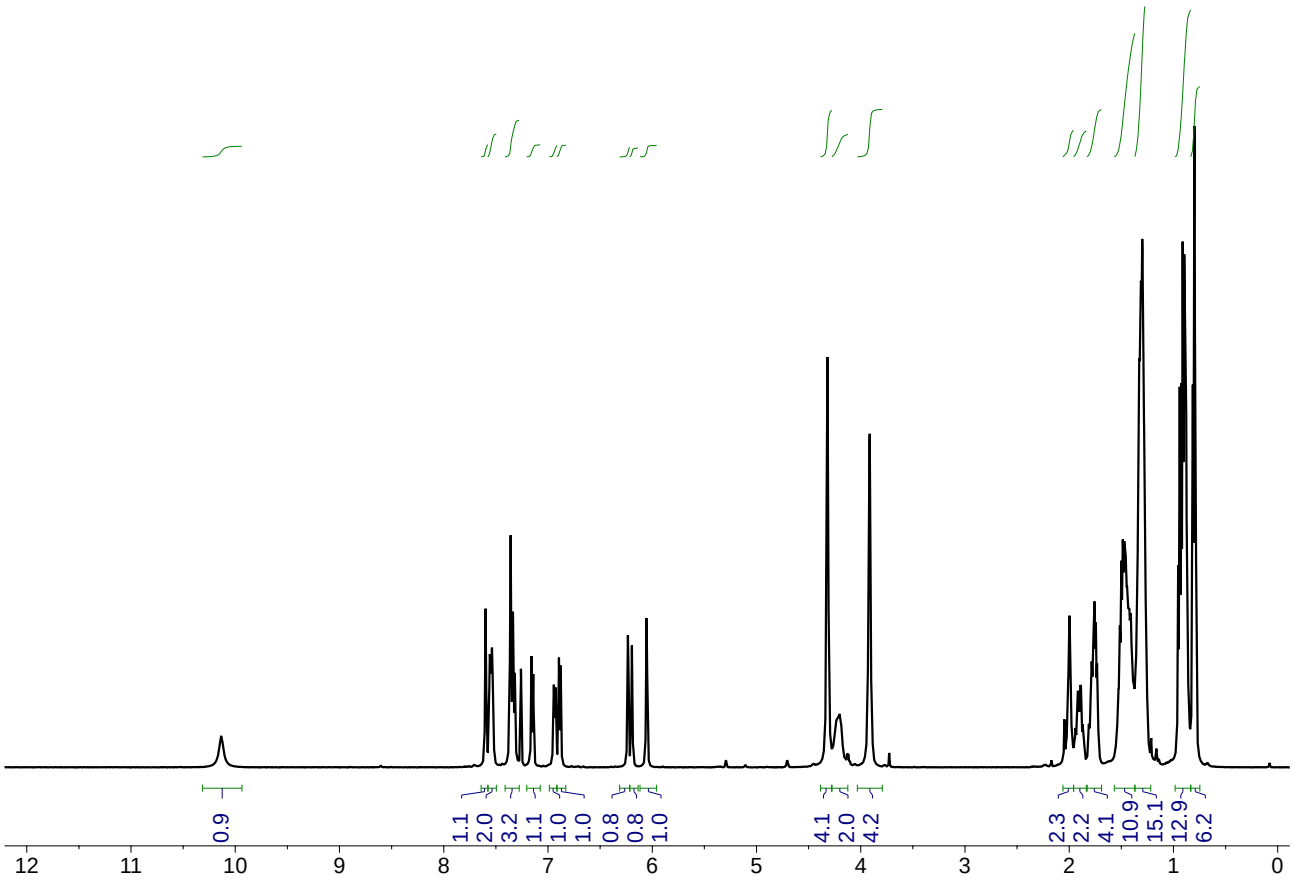


Figure S1.4. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **DA**.

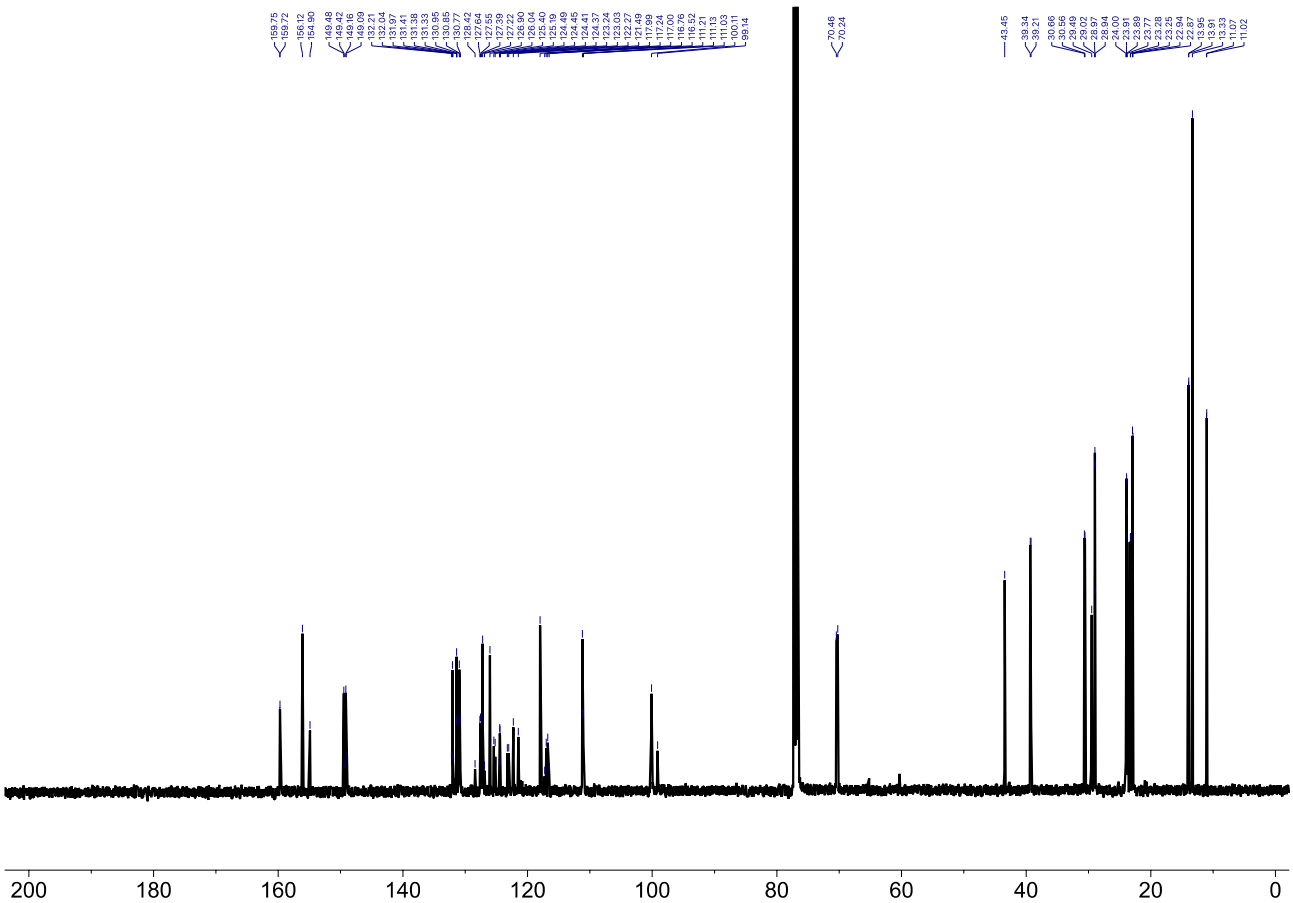


Figure S1.5. ^{13}C-NMR spectrum (126 MHz, $CDCl_3$) of **DA**.

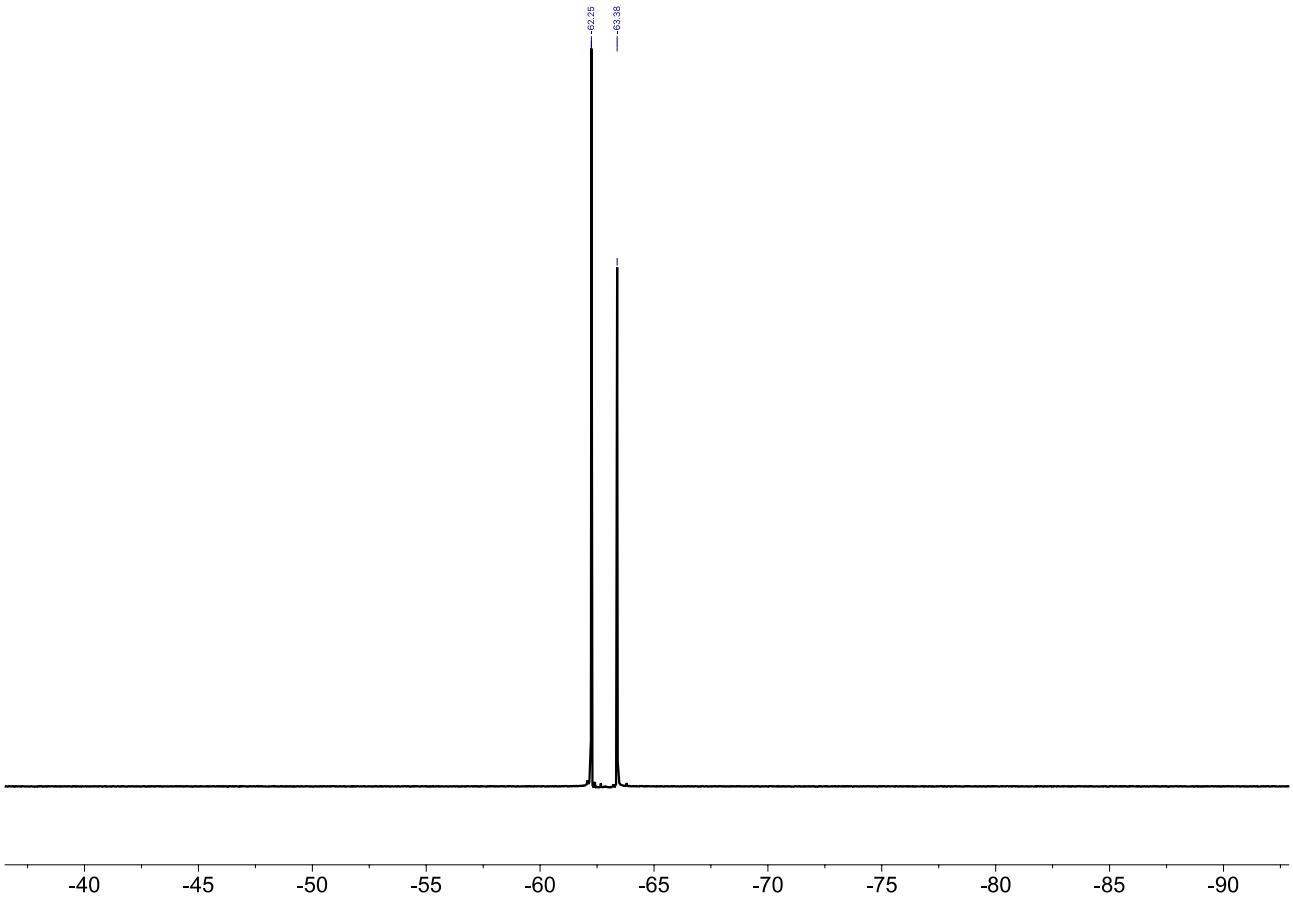


Figure S1.6. ^{19}F-NMR spectrum (471 MHz, $CDCl_3$) of **DA**.

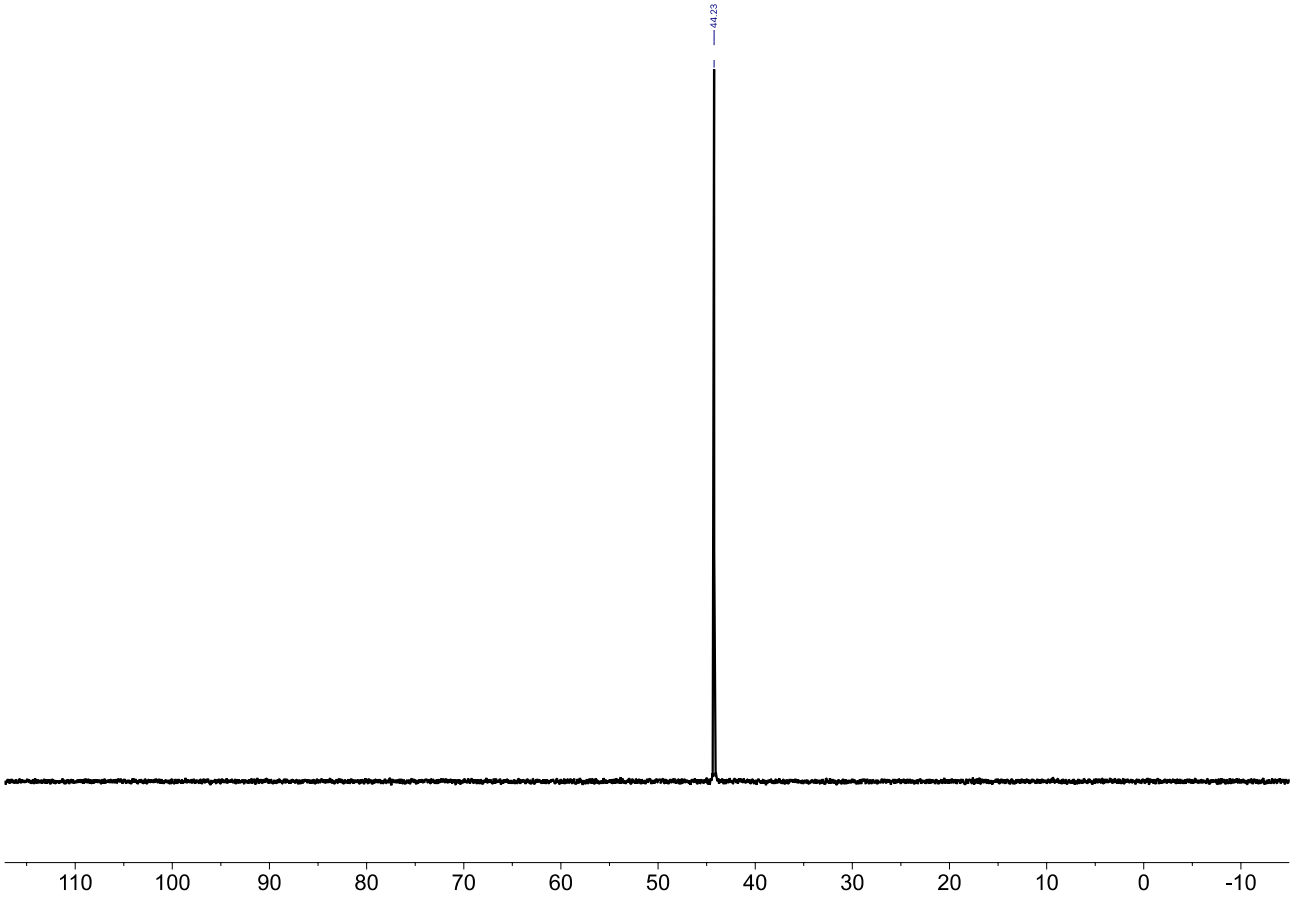


Figure S1.7. ^{31}P-NMR spectrum (202 MHz, $CDCl_3$) of **DA**.

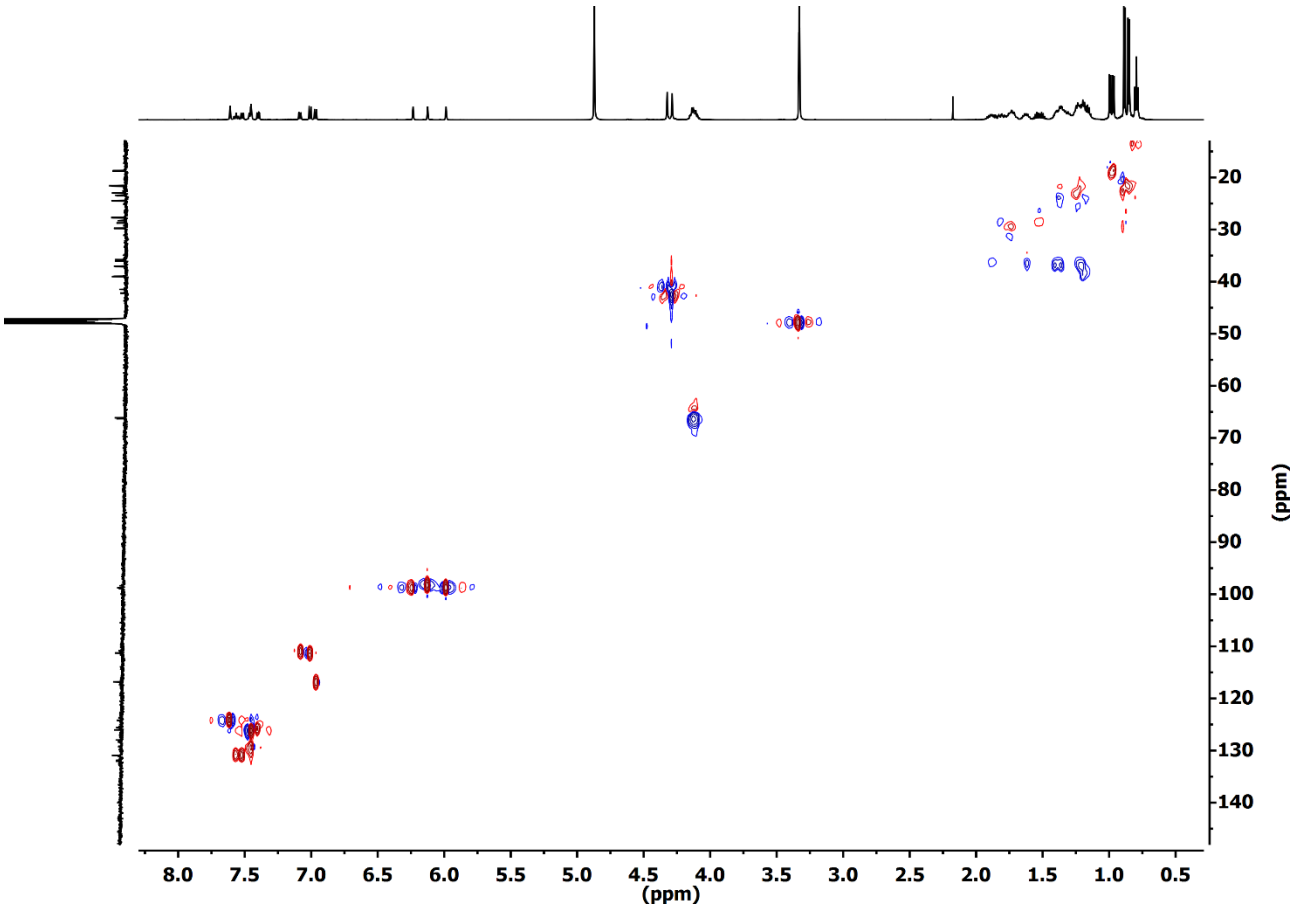


Figure S1.8. ^{1}H-^{13}C HSQC spectrum of **DA**.

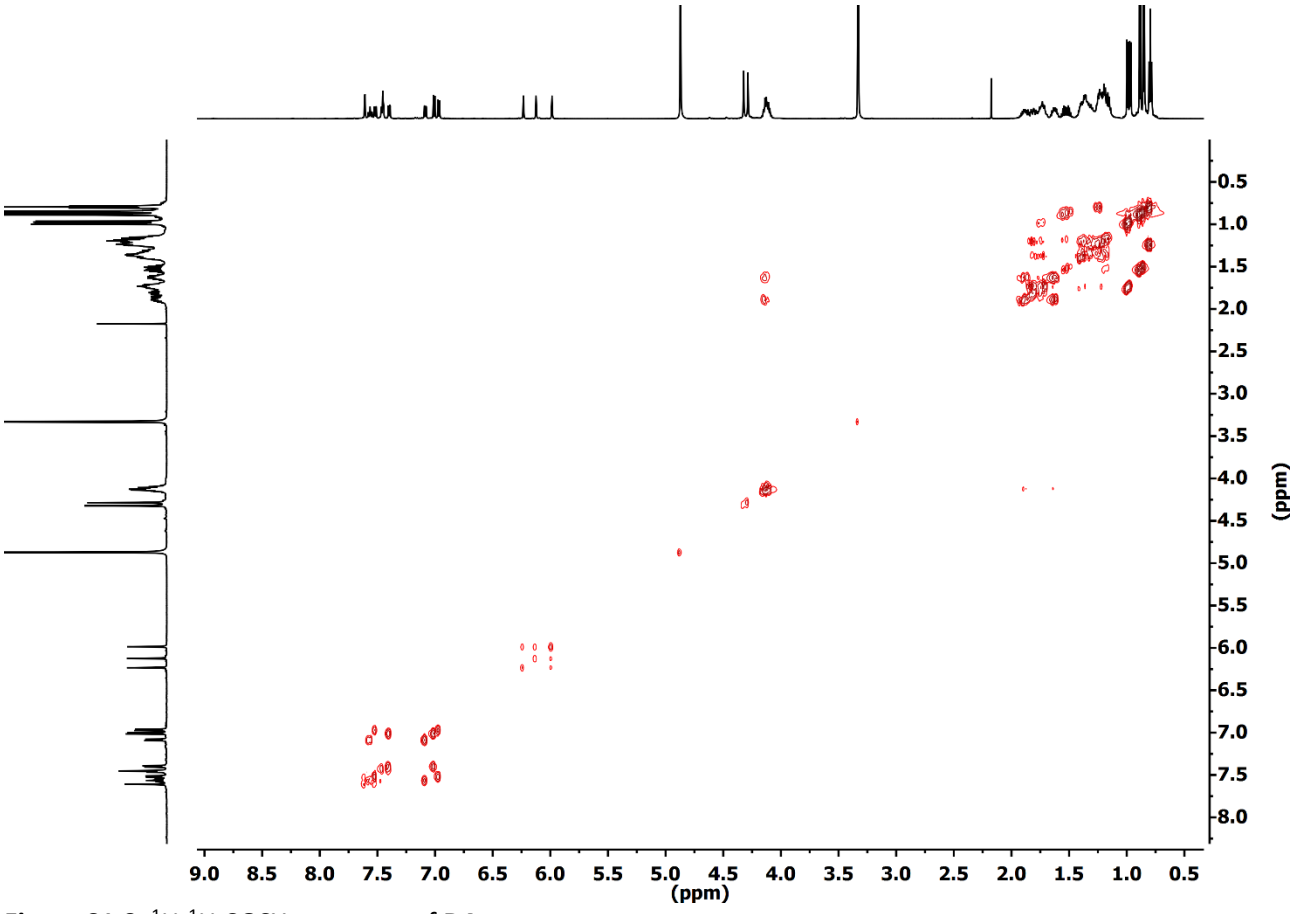
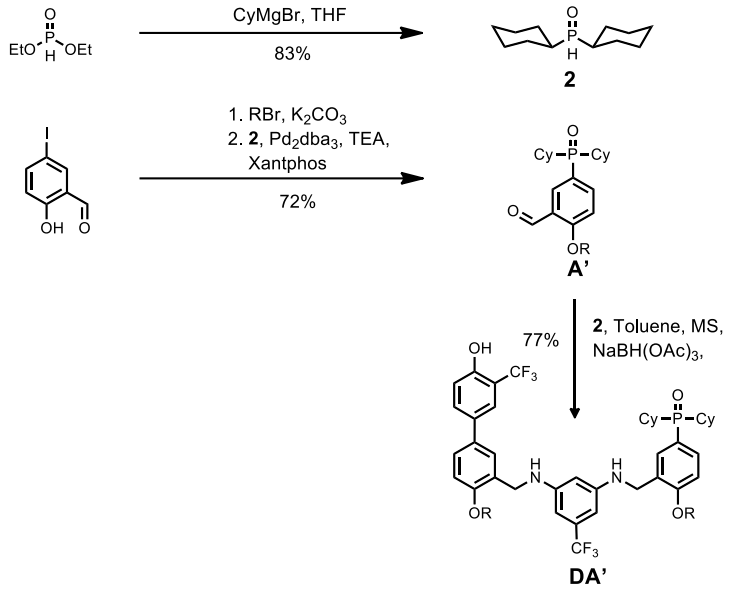


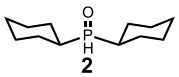
Figure S1.9. ^{1}H-^{1}H COSY spectrum of **DA**.

2.2 Synthesis of dimer DA'

The dimer **DA'** was prepared as reported in the following scheme:



2.2.1 Synthesis of 2



To a commercial solution of cyclohexylmagnesim bromide (11 ml, 11.0 mmol, 3 equiv) cooled at 0 °C was added dropwise over 15 min a solution of diethylphosphite in 15 ml of THF (500 mg, 3.62 mmol, 1 equiv) under N_2 atmosphere. When the addition was complete, the reaction was stirred overnight at room temperature. The residual Grignard reagent was quenched at 0 °C with diluted HCl (0.1 M, 20 ml) and the reaction mixture extracted (3x) with ethyl acetate. The organic layers were collected, dried over Na_2SO_4. The solvent was removed and the crude absorbed on silica and purified through flash column chromatography (EtOAc:MeOH) giving the desired compound as white solid (638 mg, 83%).

^{1}H-NMR: (500 MHz, $CDCl_3$) δ 6.31 (dt, *J* = 433.8, 3.0 Hz, 1H), 2.00 (d, *J* = 12.9 Hz, 2H), 1.86 (m, 4H), 1.75 (m, 6H), 1.47 (m, 4H), 1.28 (m, 6H).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 34.80 (d, *J* = 64.6 Hz), 26.20, 26.09, 25.97, 25.76, 24.95 (d, *J* = 3.6 Hz).

^{31}P NMR: (202 MHz, $CDCl_3$) δ 49.48 (d, J = 433.8 Hz).

HRMS (ES+): Calculated for $C_{12}H_{24}OP$ 215.1564 a.m.u., found 215.1558 a.m.u.

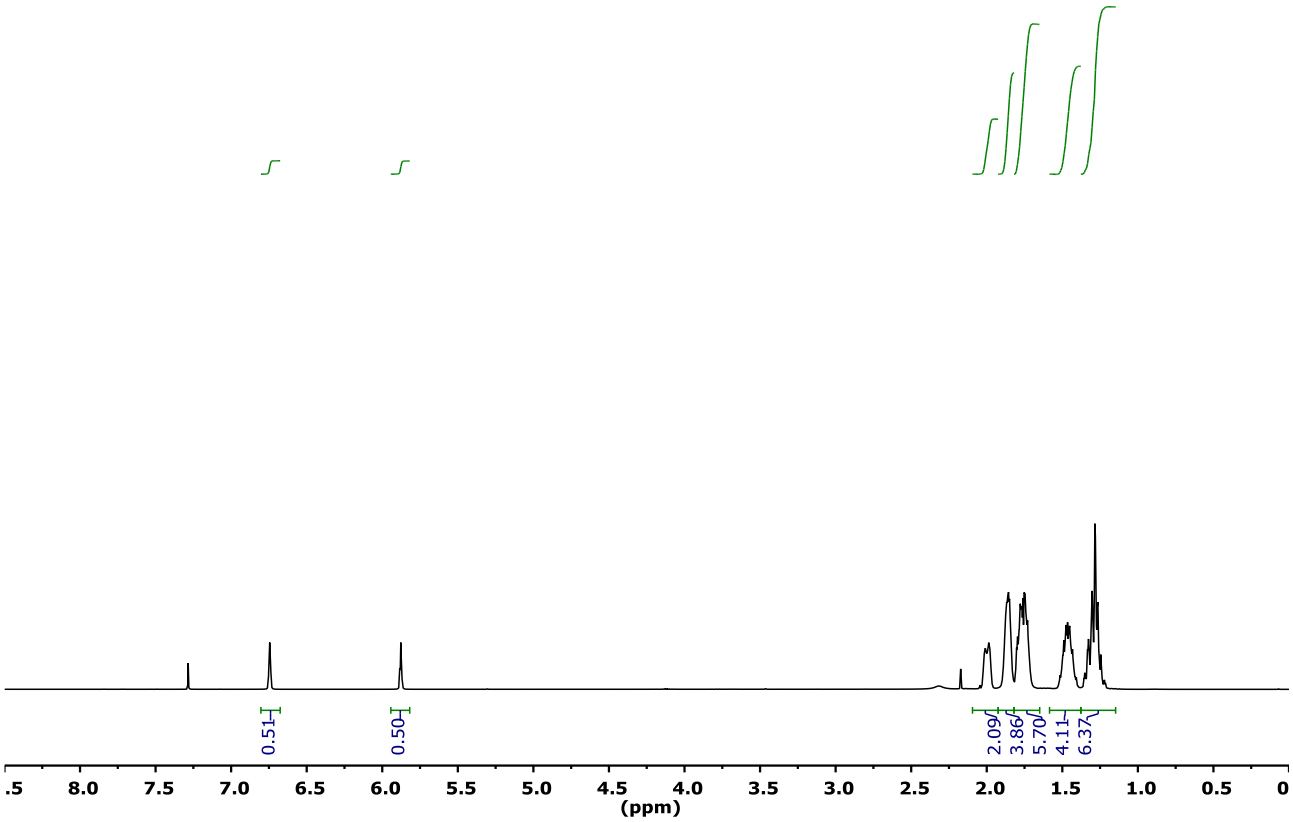


Figure S1.10. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **2**.

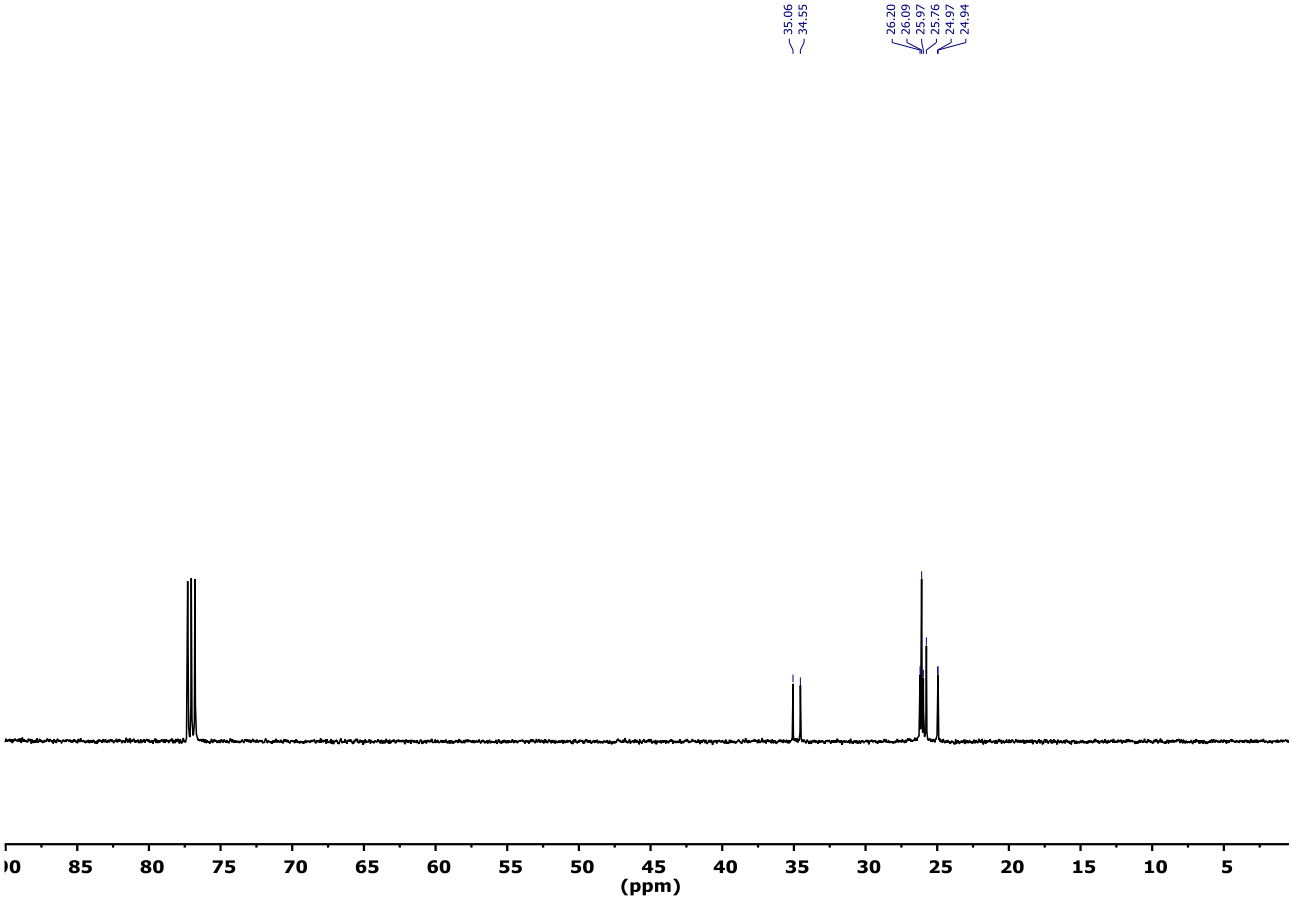


Figure S1.11. ^{13}C-NMR spectrum (126 MHz, $CDCl_3$) of **2**.

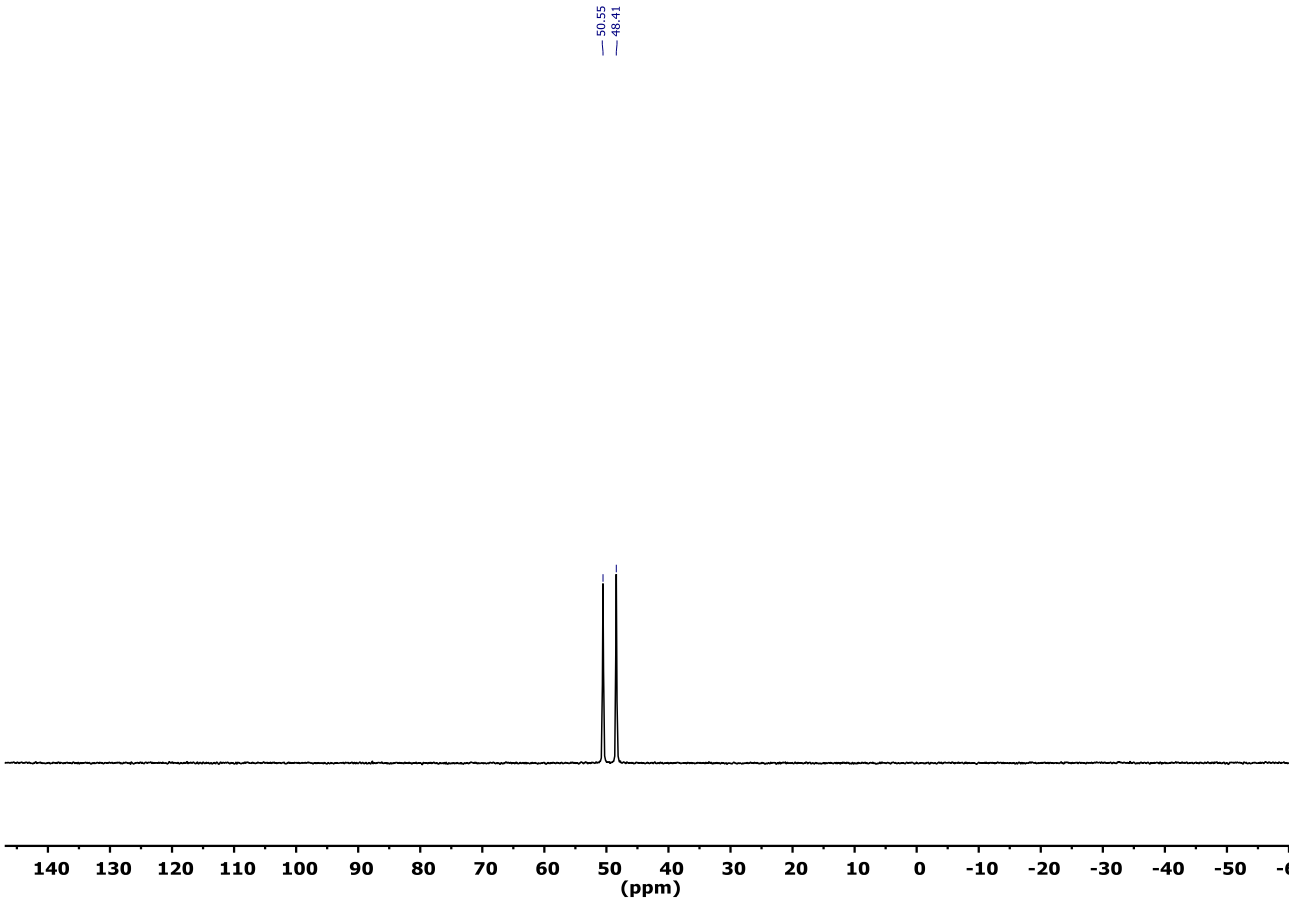
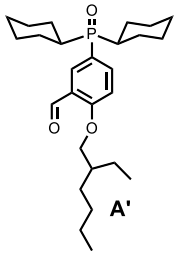


Figure S1.12. ^{31}P-NMR spectrum (202 MHz, $CDCl_3$) of **2**.

2.2.2 Synthesis of A'.



2-hydroxy-5-iodobenzaldehyde (0.5 g, 2.016 mmol, 1 equiv) and 3-(bromomethyl) heptane (1.43 mL, 8.064 mmol, 4 equiv) were dissolved in dry DMF (8 mL); anhydrous K_2CO_3 (1.1 g, 8.064 mmol, 4 equiv) was added and the mixture was stirred at 120°C for 3.5 hours. Then, the reaction mixture was extracted 3 times with EtOAc and LiCl 5% solution. The organic layers were collected, dried over Na_2SO4, concentrated under vacuum and purified by flash column chromatography (PE:EtOAc), giving 0.5 g of a colourless oil, which is freshly used for the next synthetic step.

The obtained alkylated iodobenzaldehyde (0.5 g, 1.389 mmol, 1 equiv) was mixed with the phosphine oxide **2** (357 mg, 1.666 mmol, 1.2 equiv), Xantphos (80 mg, 0.139 mmol, 0.1 equiv) and Pd_2dba_3 (127 mg, 0.139 mmol, 0.1 equiv); finally, previously degassed dioxane (8 mL, N_2 bubbling) and triethylamine (570 µl, 4.164 mmol, 3 equiv) were added, and the solution was stirred under nitrogen atmosphere, in dark conditions, for 90 minutes. The rection mixture was extracted with brine/EtOAc (4x) dried over Na_2SO_4 and the solvent evaporated. The crude was purified through column chromatography EtOAc: MeOH (from 0% to 3%) to obtain the pure **A'** (645 mg, 72% yield over 2 steps).

^{1}H-NMR: (500 MHz, $CDCl_3$) δ 10.56 (d, *J* = 1.8 Hz, 1H), 8.07 (td, *J* = 8.9, 2.1 Hz, 1H), 7.90 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.15 (dd, *J* = 8.7, 1.3 Hz, 1H), 4.06 (dd, *J* = 5.5, 1.6 Hz, 2H), 2.06 (d, *J* = 10.4 Hz, 4H), 1.91 – 1.69 (m, 6H), 1.61 – 1.45 (m, 3H), 1.40 – 0.86 (m, 24H).

^{13}C-NMR: (126 MHz, $CDCl_3$) δ 189.27, 163.68, 140.58 (d, *J* = 7.3 Hz), 130.11 (d, *J* = 10.9 Hz), 124.31 (d, *J* = 10.3 Hz), 121.48 (d, *J* = 88.5 Hz), 112.71 (d, *J* = 10.0 Hz), 71.13, 39.38, 35.15 (d, *J* = 67.6 Hz), 30.60, 29.08, 26.31 (dd, *J* = 12.9, 7.4 Hz), 25.65 (d, *J* = 41.7 Hz), 24.61, 23.97, 22.98, 14.05, 11.19.

^{31}P-NMR: (202 MHz, $CDCl_3$) δ 45.19.

HRMS (ES+): Calculated for $C_{27}H_{44}O_3P$ 447.3029 a.m.u., found 447.3082 a.m.u.

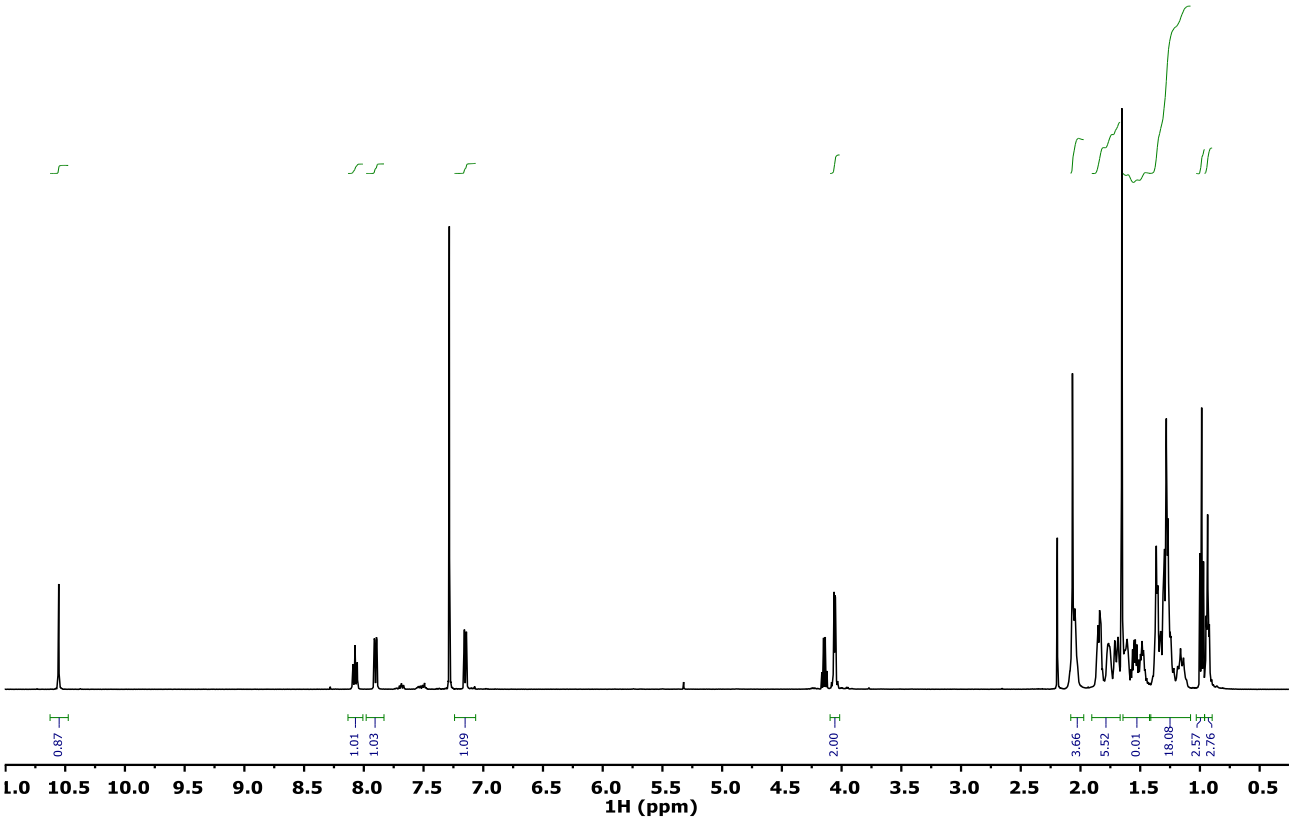


Figure S1.13. ^{1}H-NMR spectrum (500 MHz, Chloroform-*d*) of **A'**.

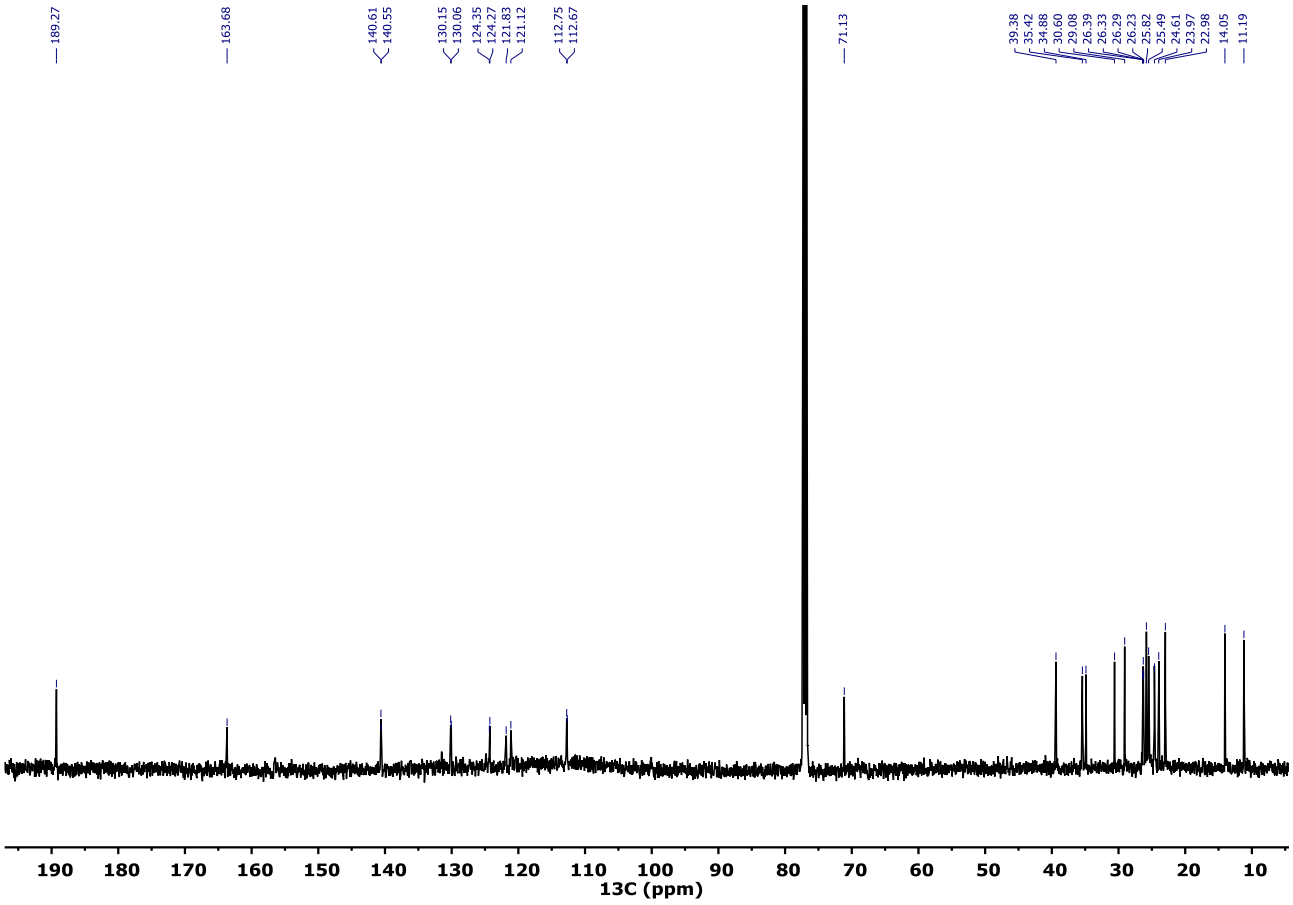


Figure S1.14. ^{13}C-NMR spectrum (126 MHz, Chloroform-*d*) of **A'**.

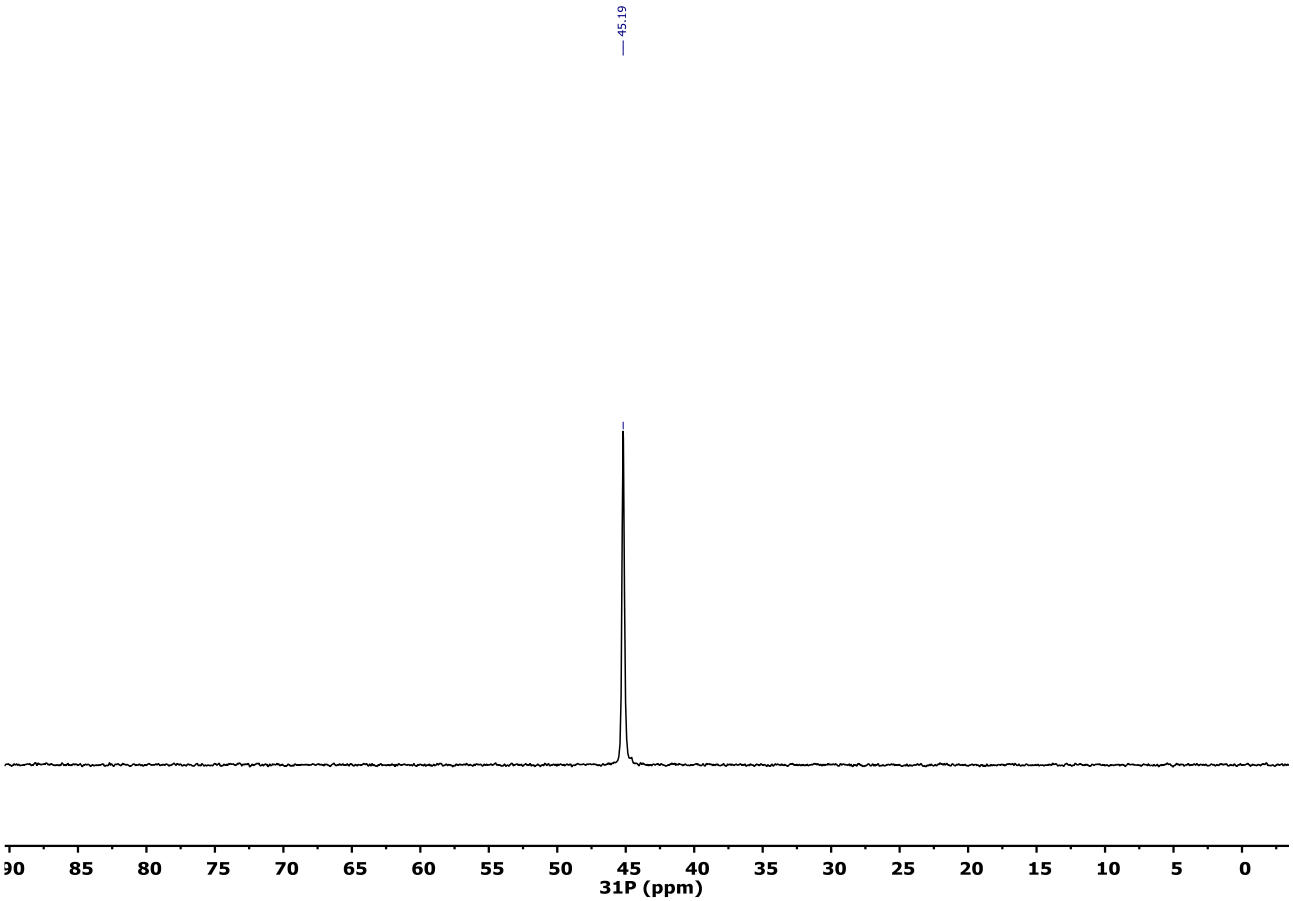
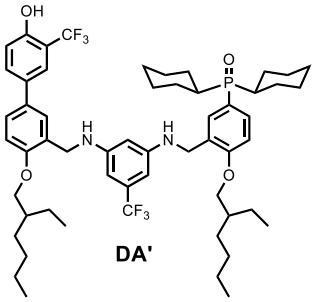


Figure S1.15. ^{31}P-NMR spectrum (202 MHz, Chloroform-*d*) of **A'**.

2.2.3 Synthesis of DA'



DA'

Compound **1** (25 mg, 0.045 mmol, 1 equiv) and the acceptor monomer **A'** (24 mg, 0.054 mmol, 1.2 equiv) were dissolved in dry toluene (0.5 mL). Molecular sieves (3 Å) were added, and the mixture was refluxed 4h using a Dean-Stark apparatus under N_2 atmosphere. After complete imine formation $NaBH(OAc)_3$ (38 mg, 0.180 mmol, 4 equiv) was added and the mixture was stirred for 2 hours. Upon complete reduction the reaction mixture was partitioned between brine and EtOAc and extracted (4x) with ethyl acetate. The organic layers were collected, dried over Na_2SO_4, the solvent evaporated and the crude purified through flash chromatography (PE:EtOAc), giving the desired dimer **DA'** (34 mg, 77% yield).

^{1}H NMR: (600 MHz, $CDCl_3$) δ 10.17 (s, 1H) 7.68 – 7.59 (m, 2H), 7.45 (td, J = 9.4, 8.9, 2.0 Hz, 1H), 7.36 (m, 3H), 7.30 (d, J = 8.6 Hz, 1H), 6.96 (dd, J = 8.4, 2.2 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.26 – 6.19 (m, 2H), 6.13 (t, J = 2.2 Hz, 1H), 4.35 (d, J = 4.1 Hz, 4H), 3.96 (m, 2H), 3.95 – 3.91 (m, 2H), 2.04 – 1.92 (m, 4H), 1.78 (m, 11H), 1.75 – 1.61 (m, 9H), 1.41 – 1.13 (m, 20H), 1.01 – 0.96 (m, 14H)

^{13}C NMR: (151 MHz, $CDCl_3$) δ 159.85 (d, J = 2.9 Hz), 156.18, 155.26, 149,64, 149.21, 132.72 (q, J = 32 Hz), 132.34, 132.14, 131.98 (d, *J* = 9.6 Hz), 131.43, 131.17, 127.77, 127.47, 127.34 (d, *J* = 10.6 Hz), 125.95, 125.26 (d, *J* = 20.9 Hz), 124.42 (q, J= 5 H, 123.45 (d, *J* = 21.3 Hz), 119.19 (d, *J* = 92.4 Hz), 118.44, 116.96 (d, *J* = 30.1 Hz), 111.26, 110.91 (d, *J* = 12.3 Hz), 100.28, 99.65, 70.54, 70.32, 60.43, 43.60, 43.45, 39.42 (d, *J* = 14.8 Hz), 34.85 (d, *J* = 67.7 Hz), 30.75 (d, *J* = 13.1 Hz), 29.13 (d, *J* = 4.2 Hz), 26.36, 26.26 (d, *J* = 3.6 Hz), 26.17, 25.70, 25.32, 24.41 (d, *J* = 3.2 Hz), 24.09 (d, *J* = 14.9 Hz), 23.84, 23.07, 14.05 (d, *J* = 6.2 Hz), 11.19 (d, *J* = 5.0 Hz).

^{19}F NMR: (565 MHz, $CDCl_3$) δ -61.99, -63.16.

^{31}P NMR: (202 MHz, $CDCl_3$) δ 44.04

HRMS (ES+): Calculated for $C_{56}H_{76}F_6N_2O_4P$ 985.5447 a.m.u., found 985.5396 a.m.u.

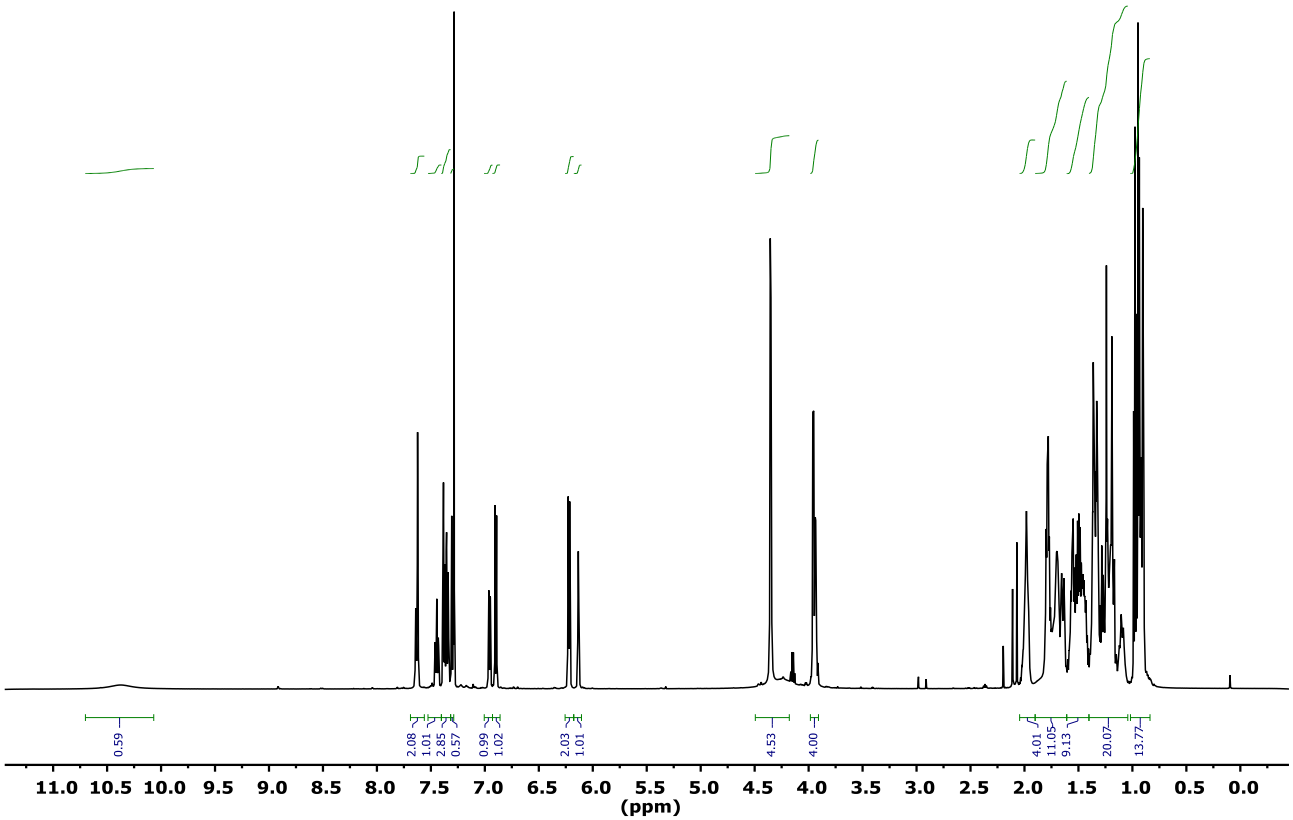


Figure S1.16. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **DA'**.

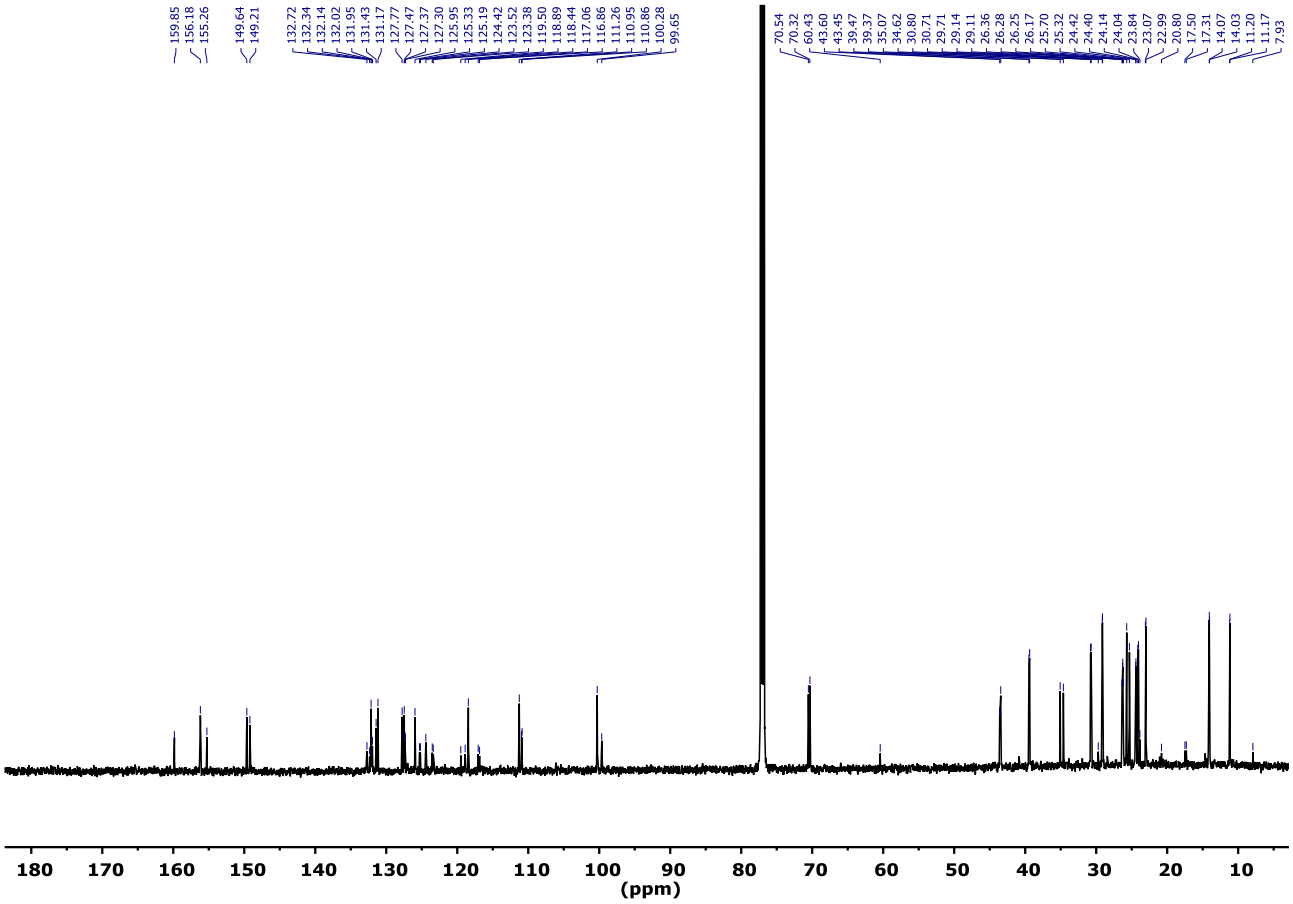


Figure S1.17. ^{13}C-NMR spectrum (126 MHz, $CDCl_3$) of **DA'**.

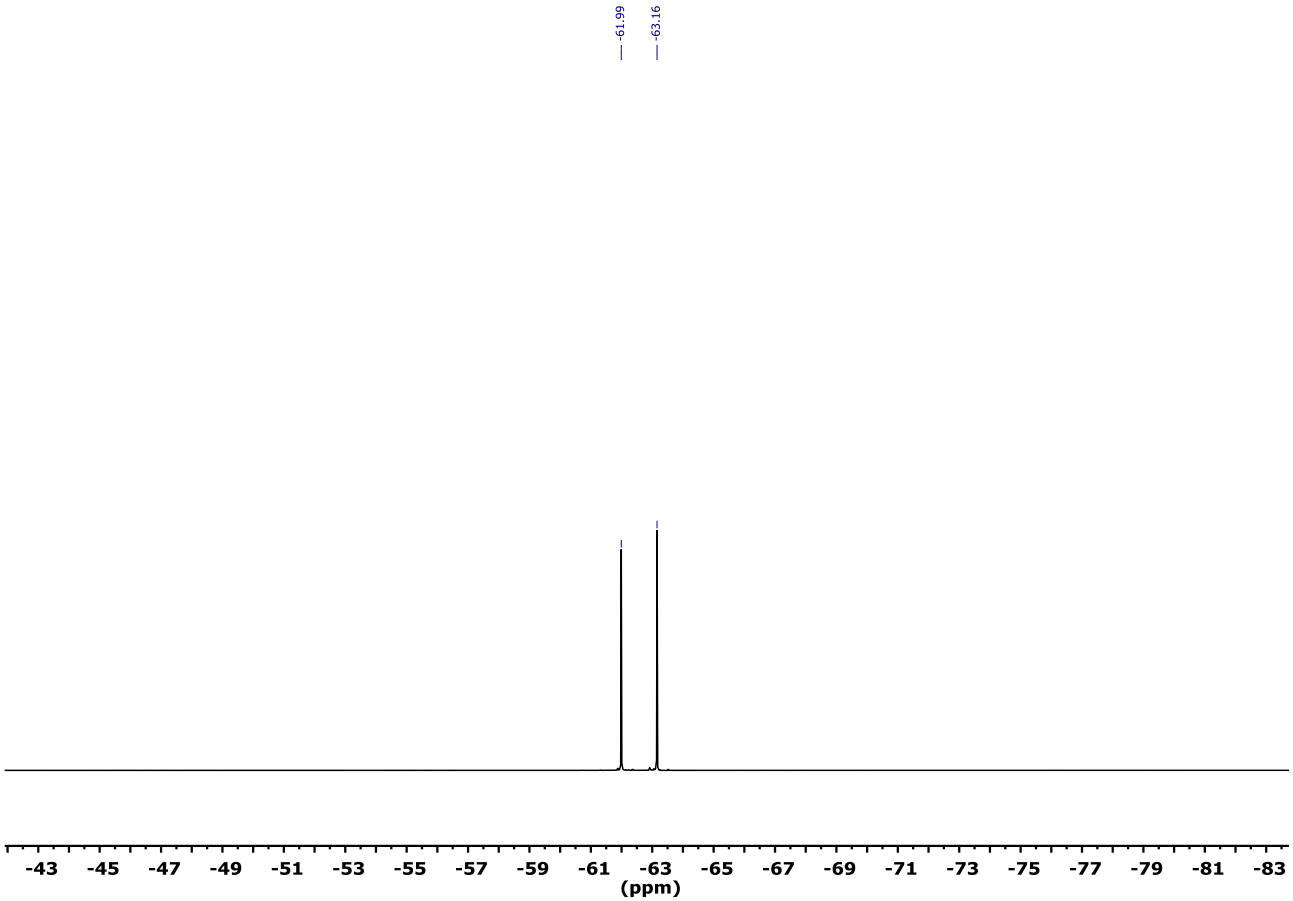


Figure S1.18. ^{19}F-NMR spectrum (475 MHz, $CDCl_3$) of **DA'**.

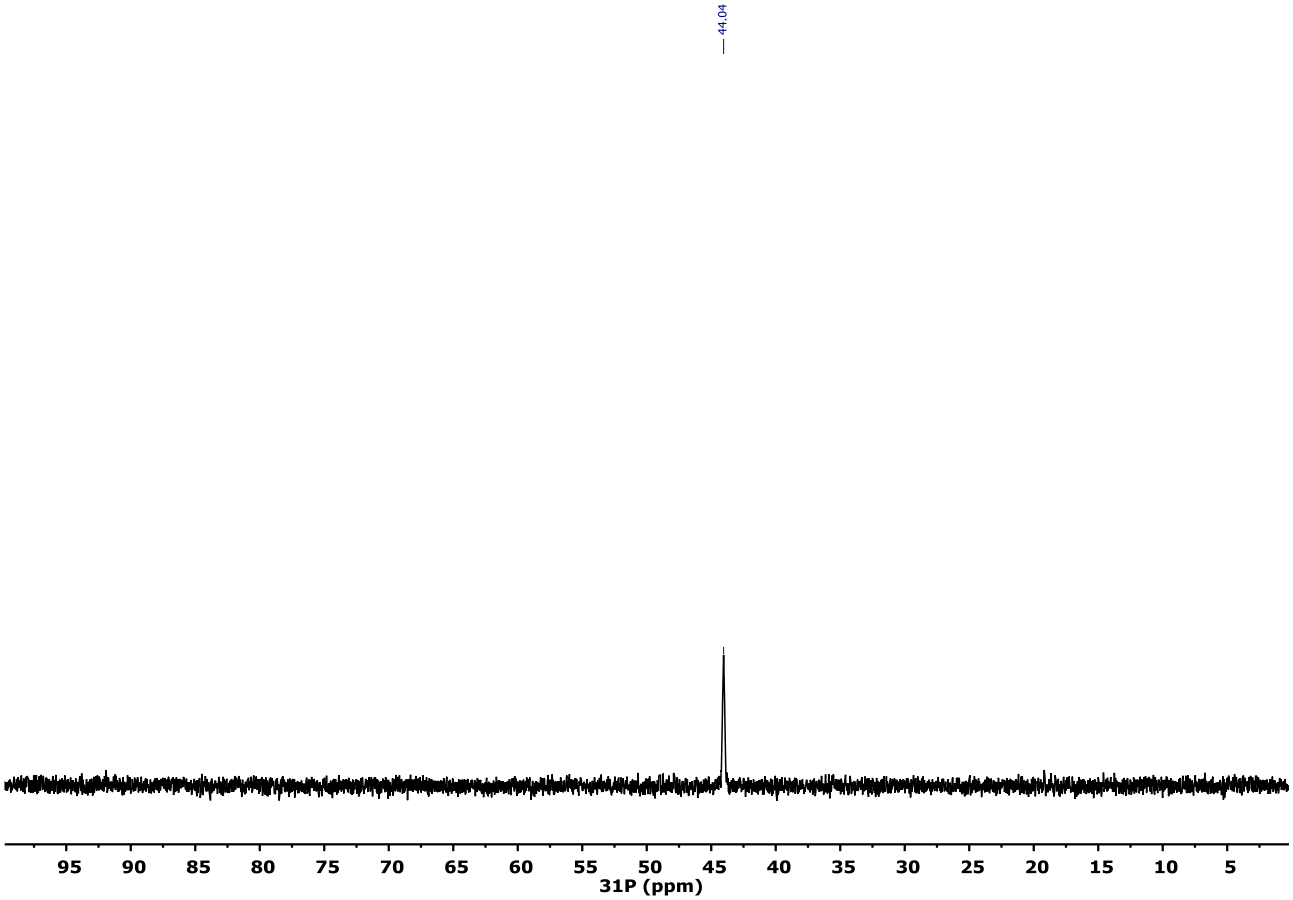


Figure S1.19. ^{31}P-NMR spectrum (202 MHz, $CDCl_3$) of **DA'**.

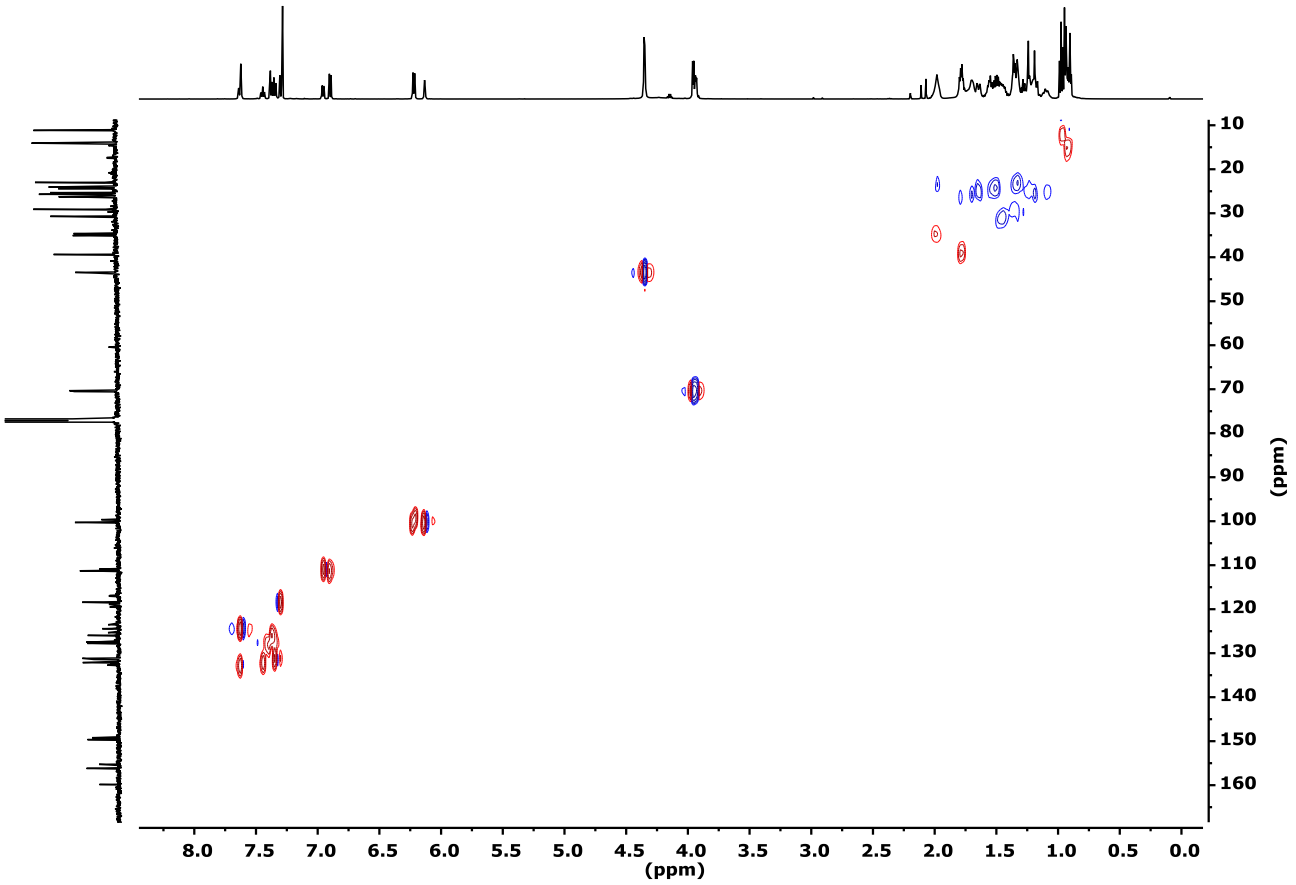


Figure S1.20. ^{1}H-^{13}C HSQC spectrum of **DA'**.

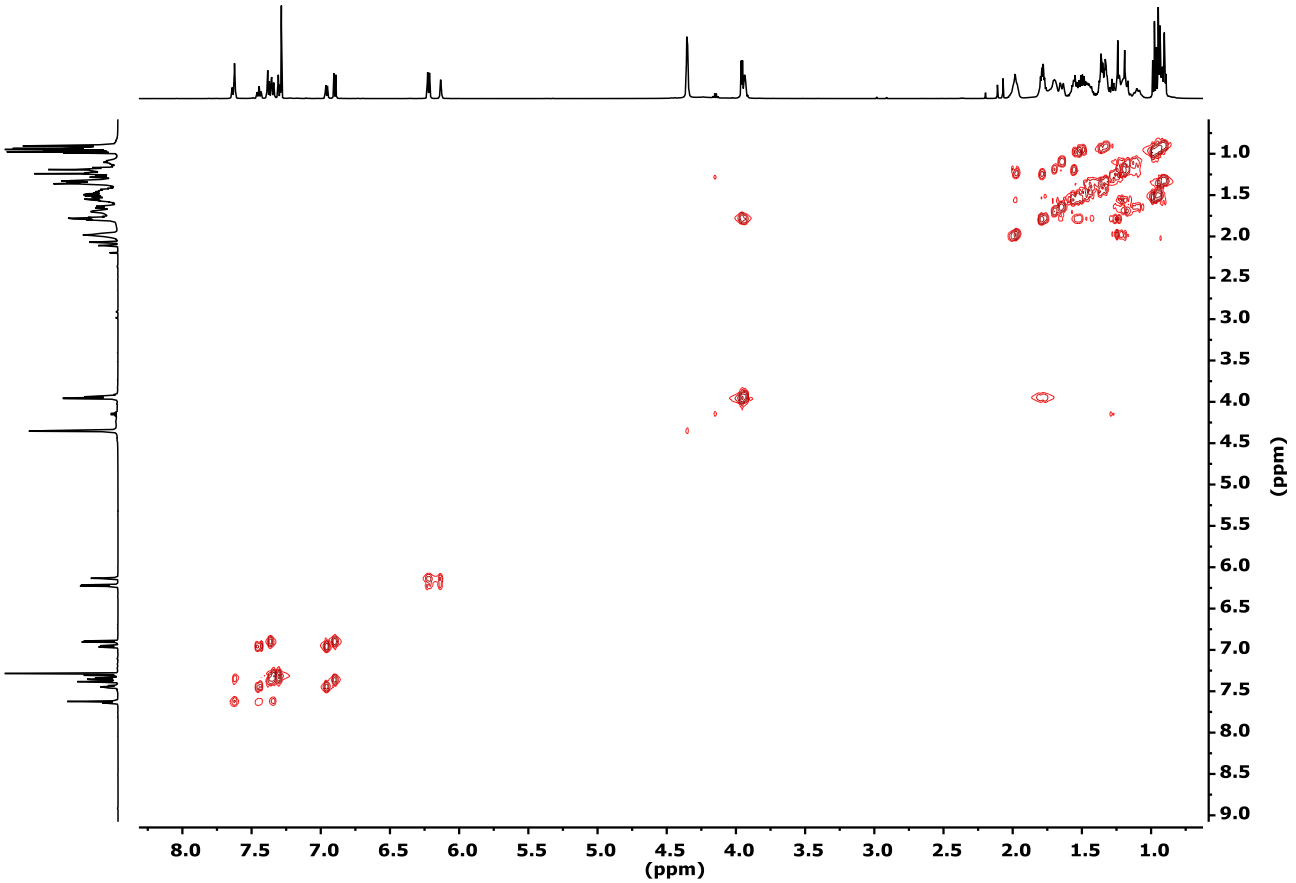
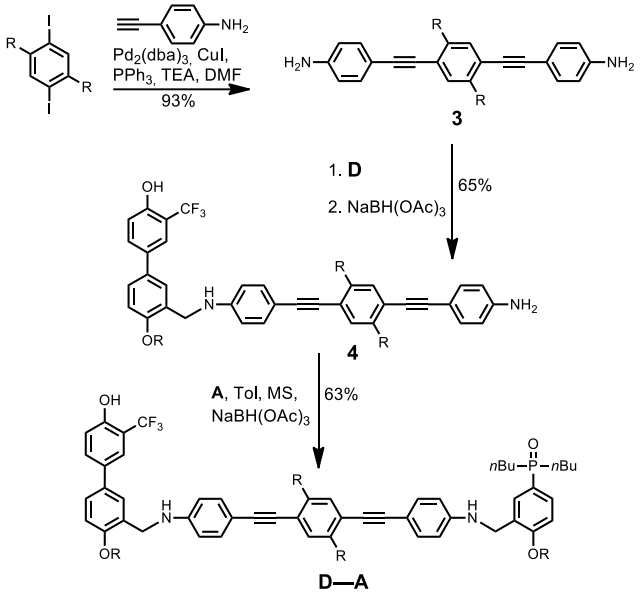


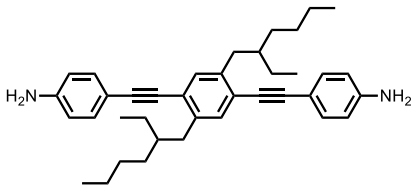
Figure S1.21. ^{1}H-^{1}H COSY spectrum of **DA'**.

2.3 Synthesis of dimer D—A

Dimer **D—A** was prepared as reported in the following scheme:



2.3.1 Synthesis of 3.



3

1,4-bis(2-ethylhexyl)-2,5-diiodobenzene (326.0 mg, 0.59 mmol, 1 equiv), $Pd_2(dba)_3$ (53.9 mg, 0.059 mmol, 0.1 equiv), CuI (22.4 mg, 0.12 mmol, 0.2 equiv) and PPh_3 (30.85 mg, 0.12 mmol, 0.2 equiv) were mixed in degassed Et_3N (1 ml) under nitrogen. A solution of 4-ethynylaniline (172.23 mg, 1.47 mmol, 2.5 equiv) in degassed dry DMF (1 ml) was added to the reaction mixture. The mixture was covered with aluminium foil to prevent light and stirred at 50 °C for 2 hours. After that, the reaction was cooled down to room temperature, diluted with EtOAc (30 ml) and washed with 5% aqueous LiCl solution (3x25 ml). The and organic phase was dried with anhydrous $MgSO_4$ and the solvent removed in vacuum the crude product was purified via flash chromatography (eluent PE:EtOAc 7:3) to yield the pure product as orange solid (292 mg, 93% yield).

^{1}H NMR (400.0 MHz, $CDCl_3$):7.36 (d, *J* = 8.5 Hz, 4H), 7.29 (s, 2H), 6.67 (d, *J* = 8.2 Hz, 4H), 3.84 (s, 4H), 2.83 – 2.65 (m, 4H), 1.46 – 1.19 (m, 16H), 1.01 – 0.72 (m, 12H).

^{13}C NMR (100.6 MHz, $CDCl_3$): 146.52, 140.75, 133.16, 132.79, 122.77, 114.77, 94.32, 86.98, 40.22, 38.55, 32.57, 28.94, 25.56, 23.15, 14.15, 10.80.

HRMS (**ASAP+**)**:** Calculated for $C_{38}H_{48}N_2$ 532.3817 a.m.u., found 532.3810 a.m.u.

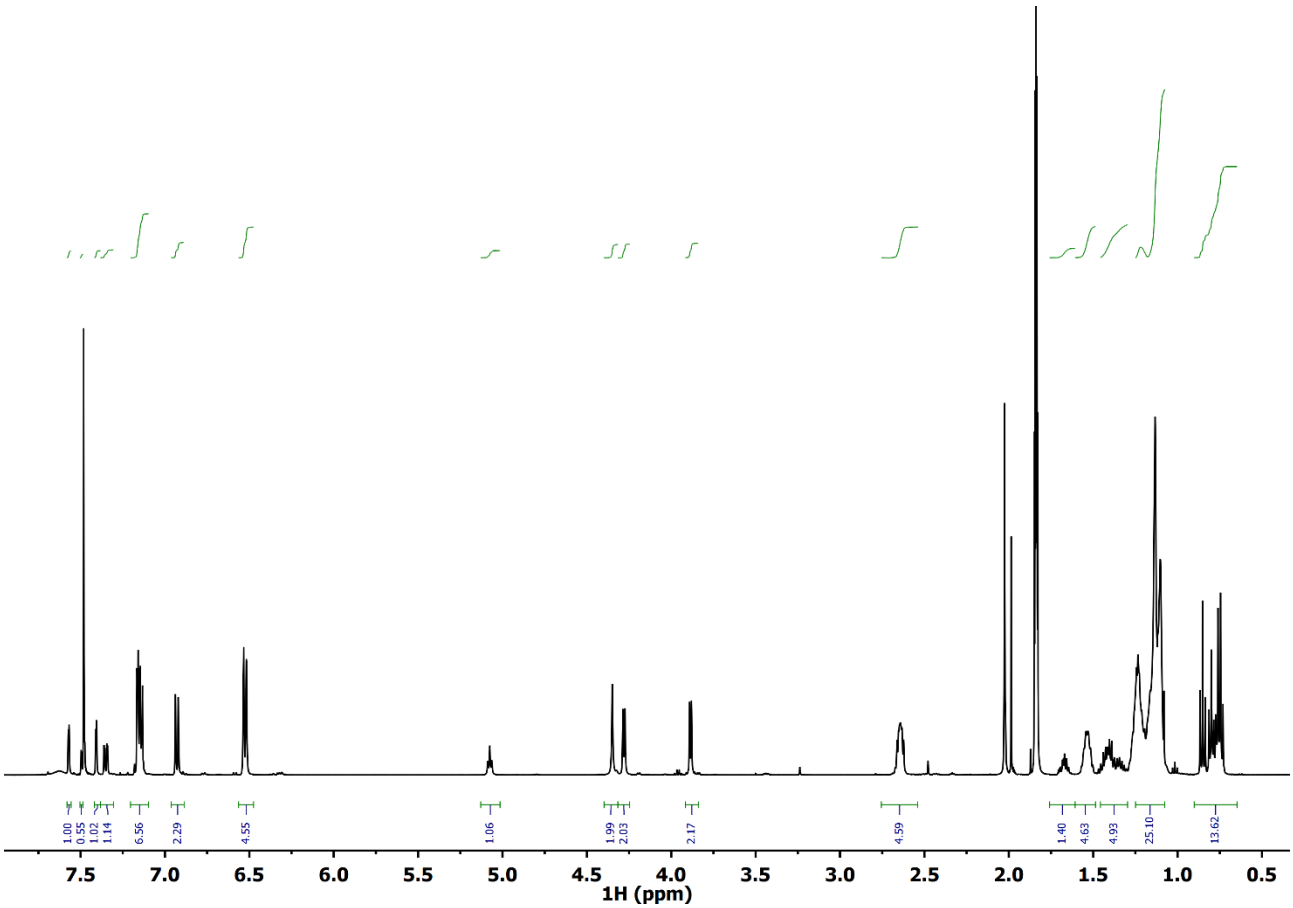


Figure S1.22. ^{1}H-NMR spectrum (400 MHz, Chloroform-*d*) of **3**.

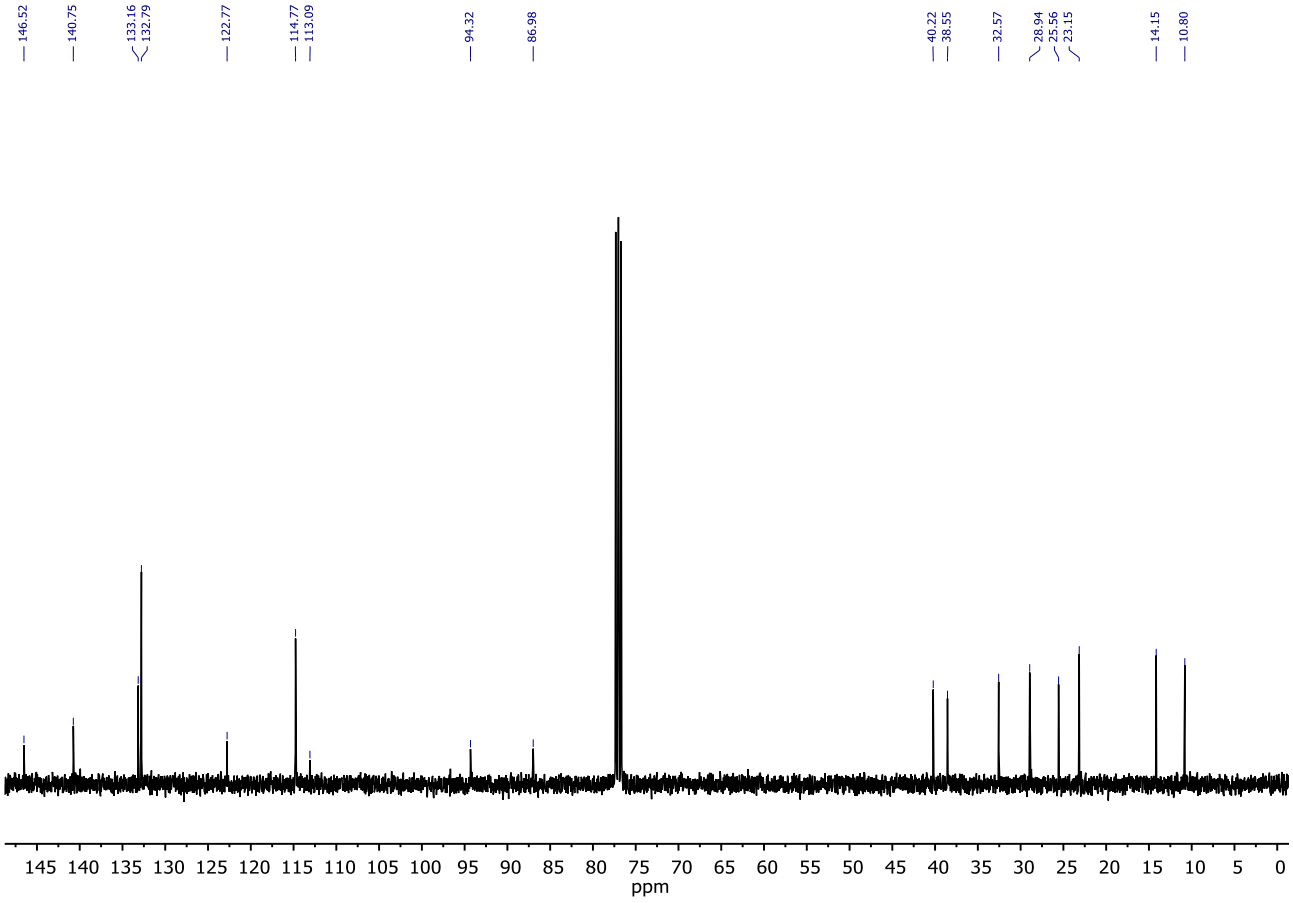
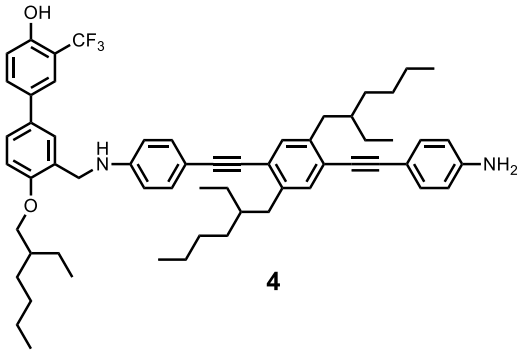


Figure S1.23. ^{13}C-NMR spectrum (100.6 MHz, Chloroform-*d*) of **3**.

2.3.2 Synthesis of 4



4

Compound **3** (250 mg, 0.47 mmol, 2 equiv) and the donor monomer **D** (89 mg, 0.235 mmol, 1 equiv) were dissolved in dry toluene (2 mL). Molecular sieves (3 Å) were added, and the mixture was refluxed 2h using a Dean-Stark apparatus under N_2 atmosphere. After complete imine formation $NaBH(OAc)_3$ (200 mg, 0.94 mmol, 4 equiv) was added and the mixture was stirred for 2 hours. Upon complete reduction, the reaction mixture was partitioned between brine and EtOAc and extracted (4x) with ethyl acetate. The organic layers were collected, dried over Na_2SO_4, the solvent evaporated and the crude purified through quick flash chromatography (PE:EtOAc), giving the desired compound **4** (139 mg, 65% yield) that was immediately used for the synthesis of **D—A**.

^{1}H NMR: (500 MHz, Methanol-d_4) δ 7.57 (d, *J* = 2.3 Hz, 1H), 7.49 (m, 1H), 7.41 (d, *J* = 2.5 Hz, 1H), 7.35 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.20 – 7.09 (m, 6H), 6.93 (dd, *J* = 8.5, 1.3 Hz, 2H), 6.58 – 6.49 (m, 4H), 5.08 (t, *J* = 6.1 Hz, 1H), 4.35 (s, 2H), 4.28 (d, *J* = 6.1 Hz, 2H), 3.89 (d, *J* = 5.4 Hz, 2H), 2.73 – 2.54 (m, 4H) 1.63-1.02 (series of m, 31H), 0.95-0.70 (m, 18H)

^{19}F NMR: (565 MHz, Toluene-d_8) δ -61.27

HRMS (ES+): Calculated for $C_{60}H_{74}F_3N_2O_2$ 911.5702 a.m.u., found 911.5647 a.m.u.

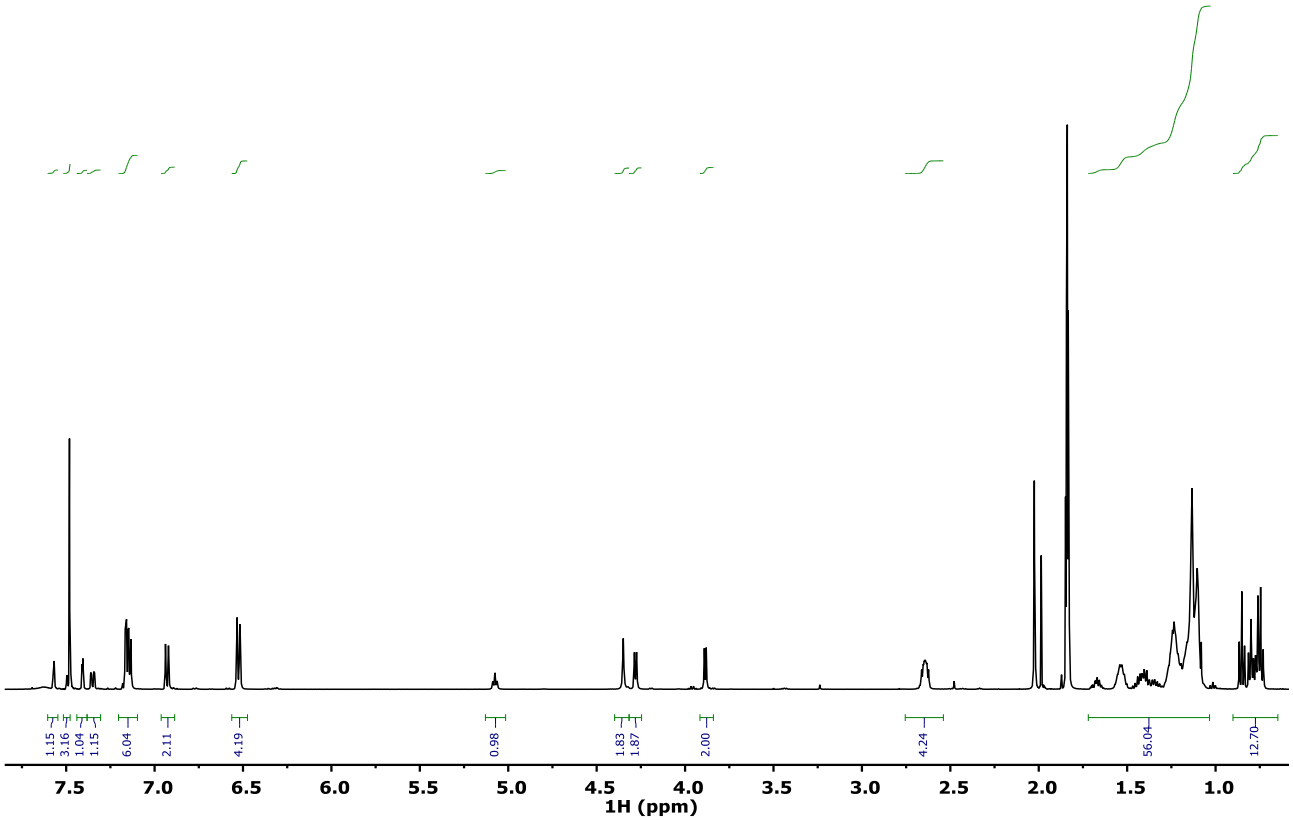


Figure S1.24 ^{1}H-NMR spectrum (500 MHz, Methanol-d_4) of **4**.

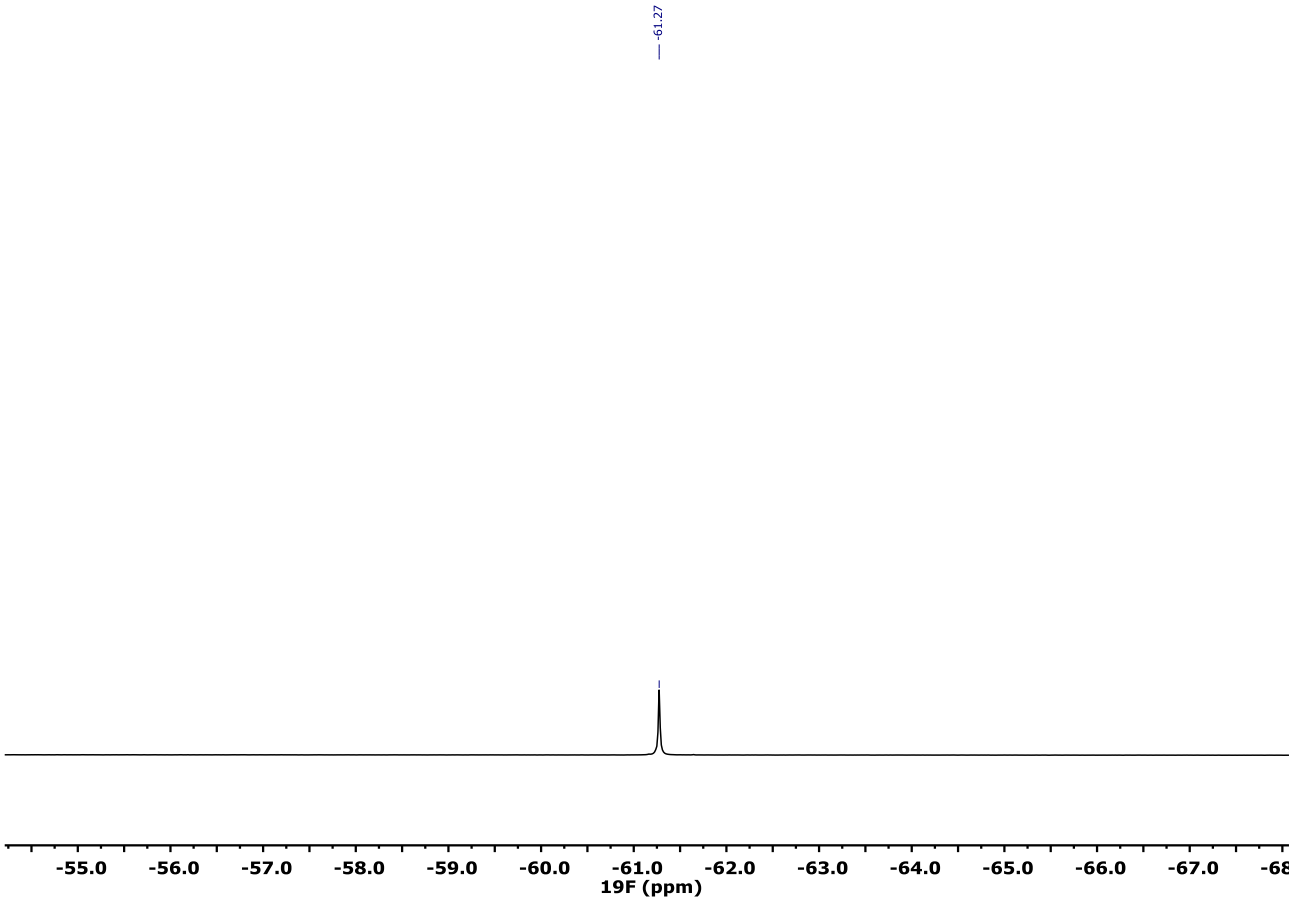
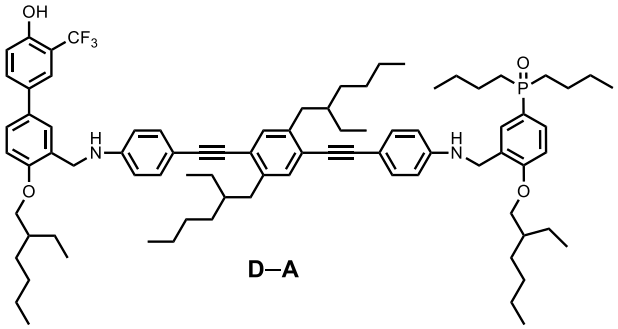


Figure S1.25. ^{19}F-NMR spectrum (565 MHz, Toluene-d_8) of **4**.

2.3.3 Synthesis of D—A.



D—A

Compound **1** (50 mg, 0.055 mmol, 1 equiv) and acceptor monomer **A** (43 mg, 0.11, 2 equiv) were dissolved in dry toluene (0.7 mL). Molecular sieves (3 Å) were added and the mixture was mixed overnight under N_2 atmosphere. After complete imine formation $NaBH(OAc)_3$ (42 mg, 1.1 mmol, 20 equiv) was added and the mixture was shaken for 2 hours. The mixture was partitioned between brine and Ethyl acetate, then the organic phase extracted and the aqueous phase washed (3x) with EtOAc. The organic layers were collected and dried over $MgSO_4$, the solvent evaporated and the residue purified via flash chromatography (PE:EtOAc), giving the desired heterodimer **D—A** (44.7 mg, 63% yield).

^{1}H NMR: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.37 (s, 1H), 7.69 (d, *J* = 2.3 Hz, 1H), 7.64 (ddd, *J* = 10.5, 8.2, 2.0 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.45 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.37 – 7.27 (m, 5H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.01 (dd, *J* = 8.6, 3.0 Hz, 1H), 6.66 (dd, *J* = 8.5, 6.4 Hz, 2H), 6.63 – 6.56 (m, 2H), 4.45 (d, *J* = 5.4 Hz, 4H), 4.03 (d, *J* = 5.5 Hz, 2H), 4.00 (d, *J* = 5.4 Hz, 2H), 2.78 (m, 4H), 2.02 – 1.86 (m, 2H), 1.82 (m, 4H), 1.75 – 1.45 (m, 12H), 1.44 – 1.22 (m, 44H), 1.05 – 0.82 (m, 30H).

^{13}C NMR: (126 MHz, CD_2Cl_2) δ 159.87, 156.59, 154.65, 148.45, 148.02, 141.68, 132.63, 132.59, 131.96, 131.86, 131.70, 131.17, 127.43, 127.07, 126.46, 122.59, 122.44, 117.78, 116.59, 112.64 (d, J = 9 Hz), 111.58 (d, J = 15.2 Hz), 111.32, 94.82 (d, J = 27.2 Hz), 86.29, 86.19, 70.54, 70.42, 43.37, 42.91, 39.54, 39.44, 34.09, 31.91, 30.73 (d, J = 6.7 Hz), 30.61, 29.67, 29.63, 29.57, 29.55, 29.35, 29.12 (d, J = 4.9 Hz), 24.09 (d, J = 3.7 Hz), 24.03, 23.92, 23.43 (d, J = 4.1 Hz), 23.04 (d, J = 3.7 Hz), 22.68, 13.86, 13.83, 13.31, 10.99, 10.97.

^{19}F NMR: (565 MHz, Toluene-d_8) δ -61.28.

^{31}P NMR: (202 MHz, Toluene-d_8) δ 42.96.

HRMS (ES+): Calculated for $C_{83}H_{113}F_3N_2O_4P$ 1289.8390 a.m.u., found 1289.8342 a.m.u.

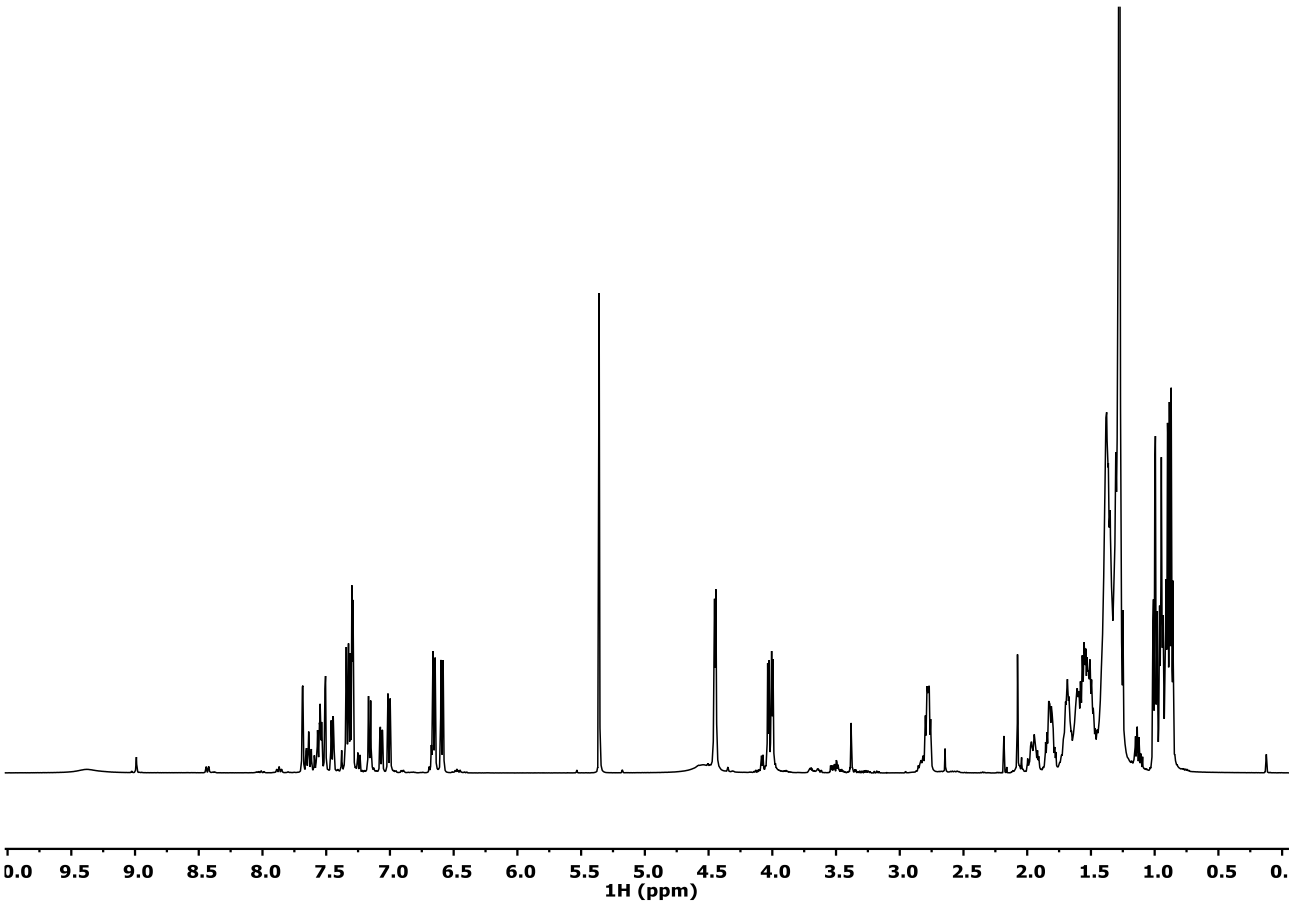


Figure S1.26. 500 MHz ^{1}H-NMR spectrum of **D—A** in CD_2Cl_2.

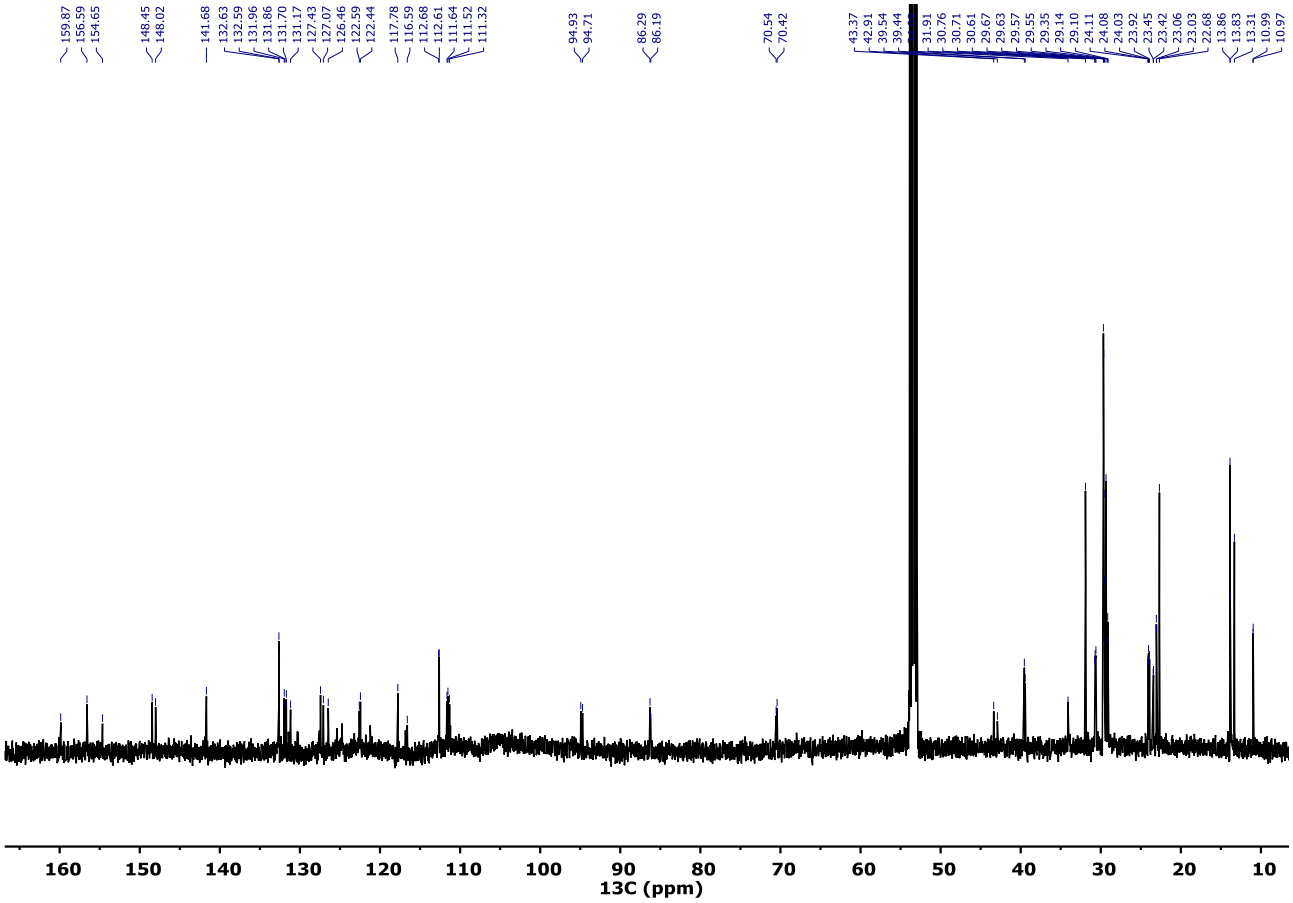


Figure S1.27. ^{13}C-NMR spectrum of **D—A** in CD_2Cl_2.

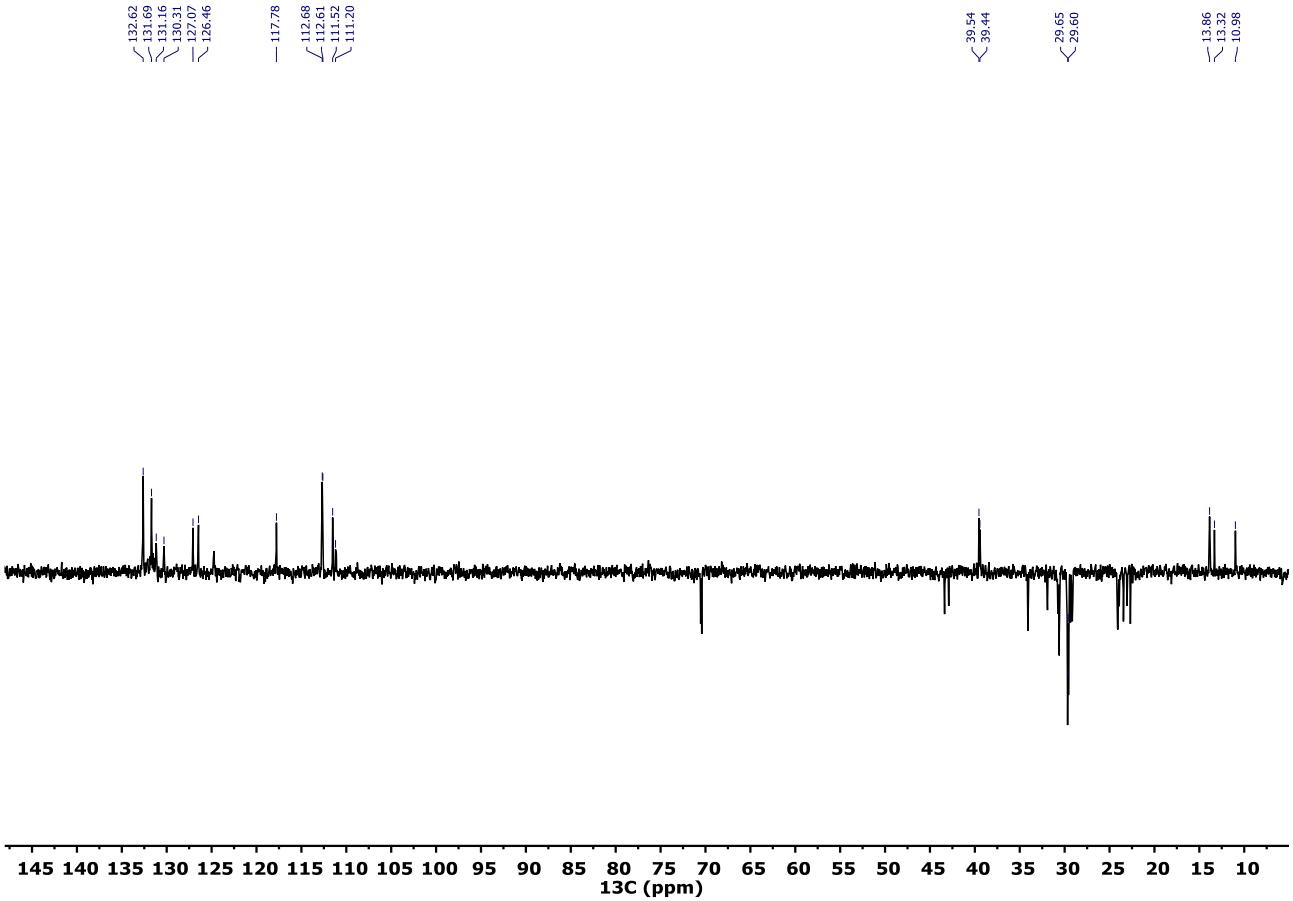


Figure S1.28. DEPT ^{13}C-NMR spectrum of **D—A** in CD_2Cl_2.

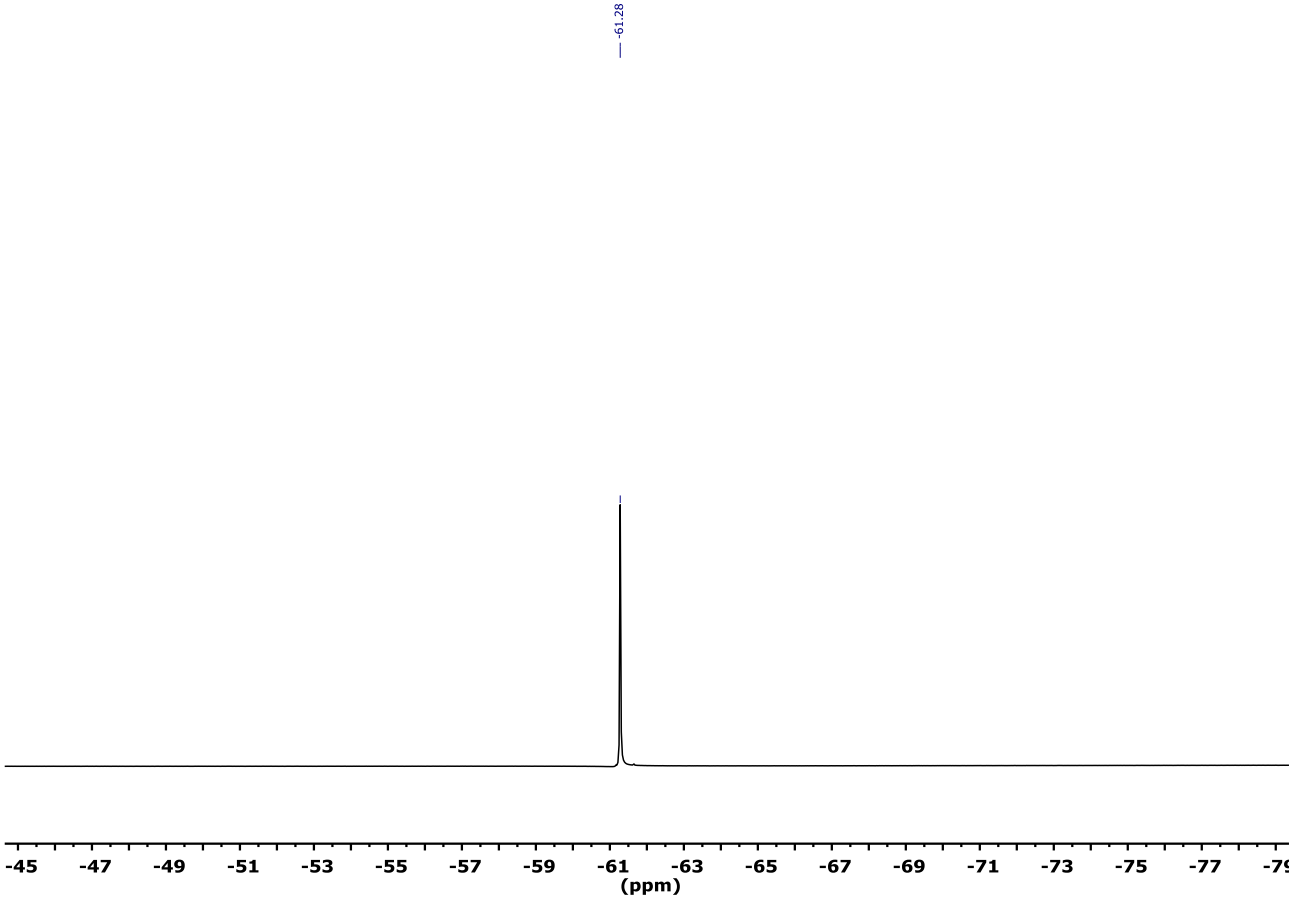


Figure S1.29. 565 MHz ^{19}F-NMR spectrum of **D—A** in Toluene-d_8.

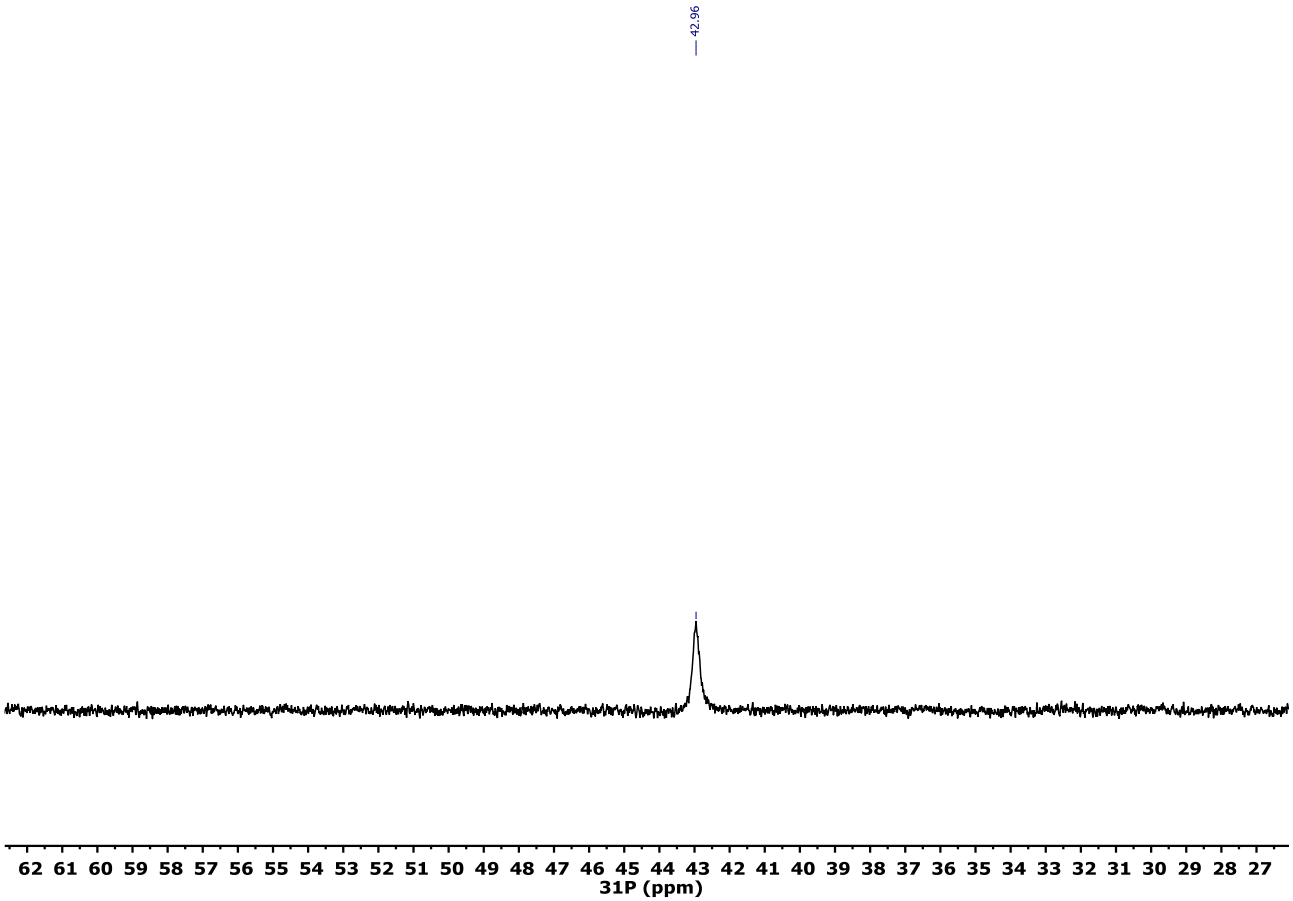


Figure S1.30. 202 MHz ^{1}H-NMR spectrum of **D—A** in Toluene-d_8.

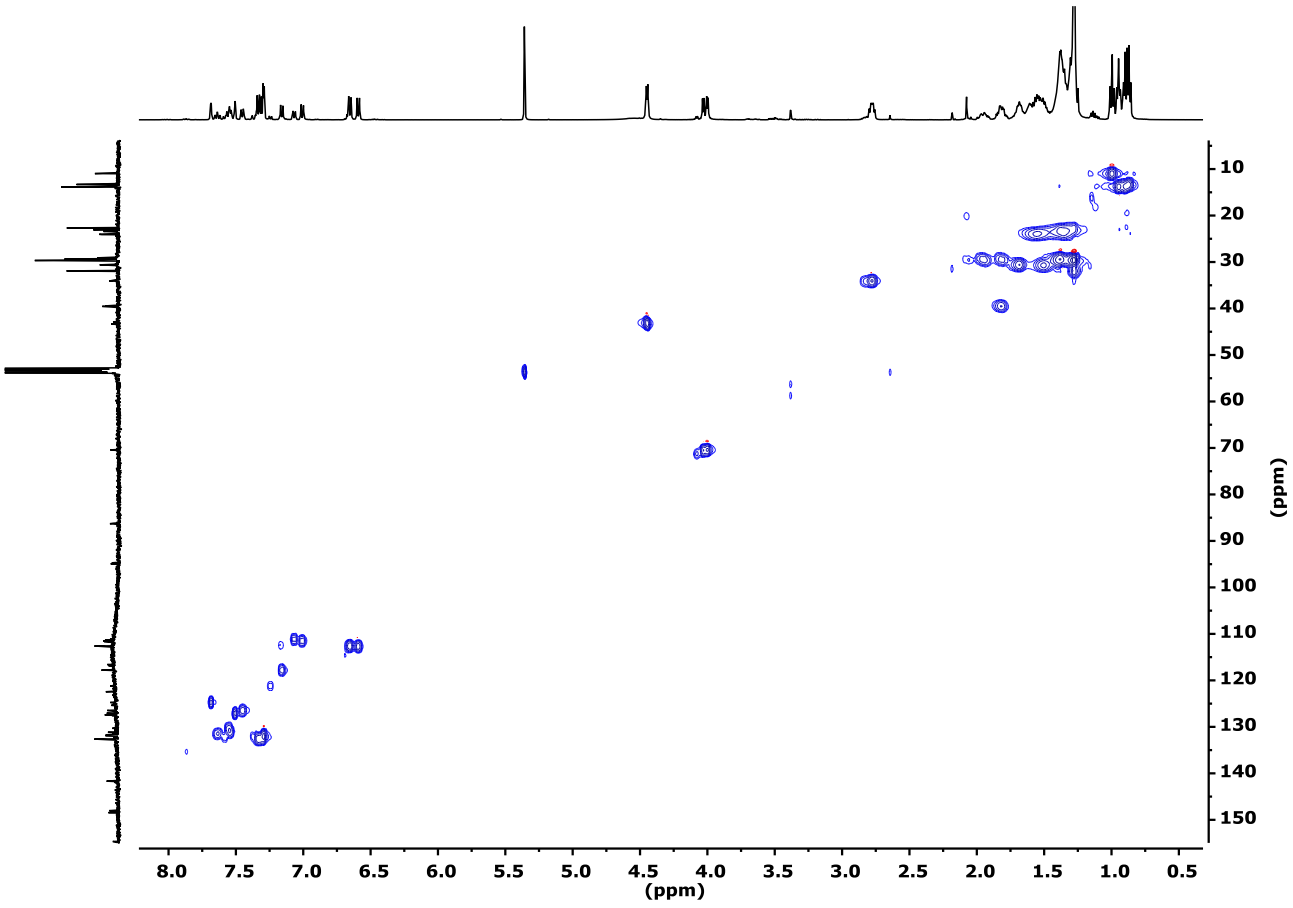


Figure S1.31. ^{1}H-^{13}C HSQC spectrum of **D—A** in $CDCl_3$.

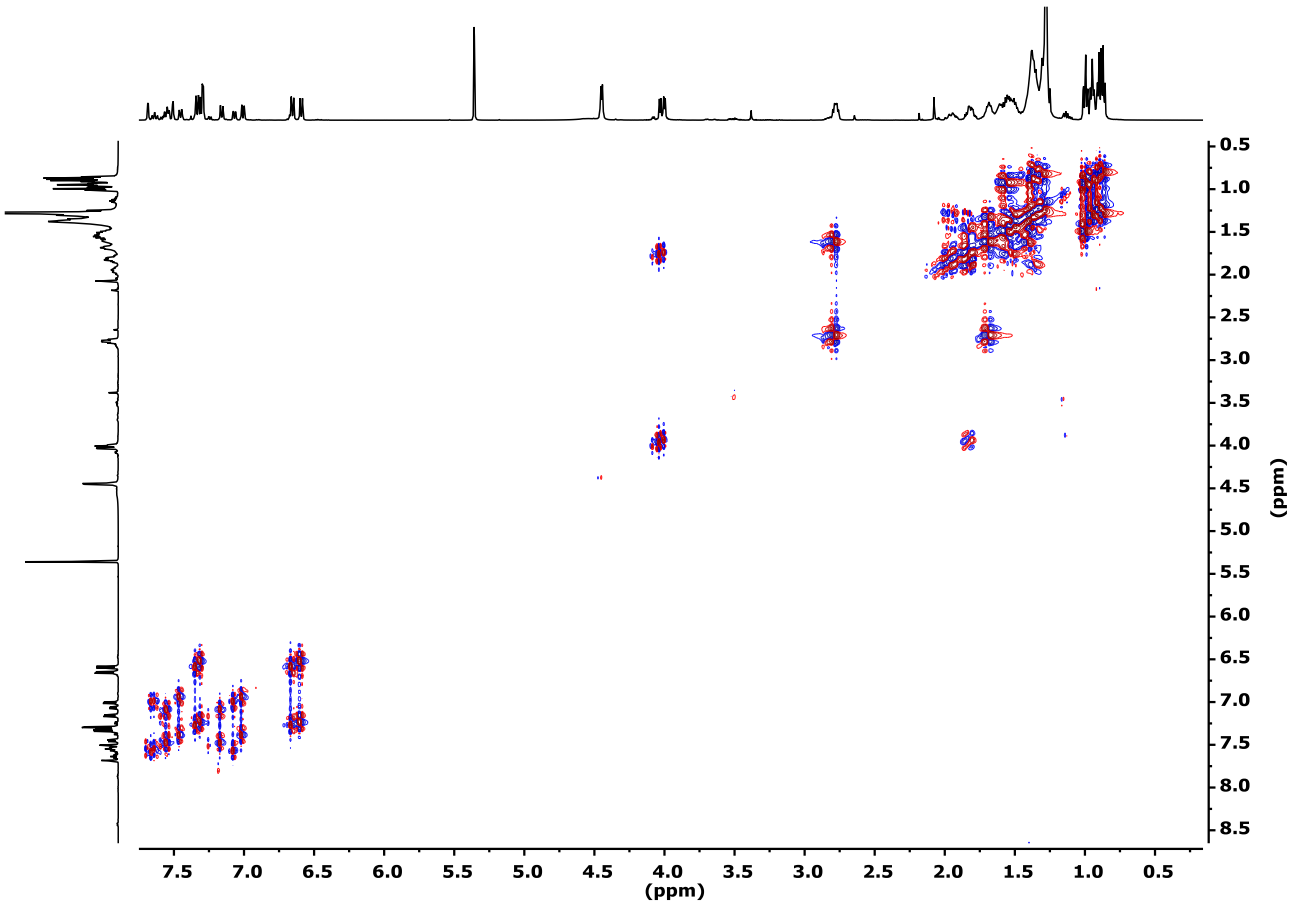
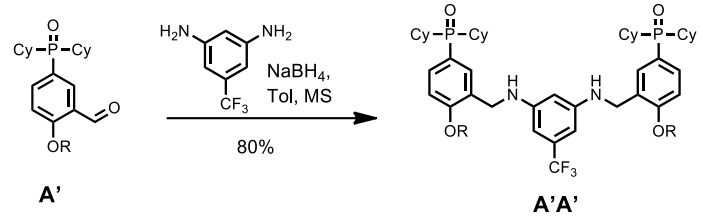
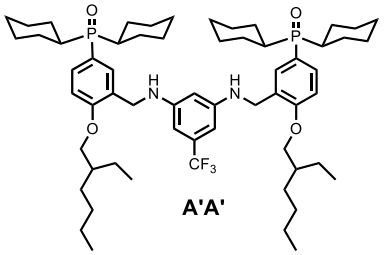


Figure S1.32. ^{1}H-^{1}H COSY spectrum of **D—A** in $CDCl_3$.

2.4 Synthesis of dimer A'A'

Dimer **A'A'** was prepared as reported in the following scheme:





Monomer **A'** (100 mg, 0.22. mmol, 3 equiv) and 5-(trifluoromethyl)-1,3-phenylenediamine (13 mg, 0.07 mmol, 1 equiv) were dissolved in dry toluene (2 mL). Molecular sieves (3 Å) were added and the mixture was stirred at 110 °C for 6 hours overnight on an orbital shaker, under N_2 atmosphere. Then, $NaBH_4$ (53 mg, 1.4 mmol, 20 equiv) and MeOH (2.5 mL) were added and the mixture was shaken for 2 hours (^{1}H-NMR was used to confirm fully imine reduction). Then the solution was partitioned between brine and ethyl acetate and the aqueous phase was washed (3x) with EtOAc. The organic layers were collected and dried over $MgSO_4$, the solvent was evaporated and the residue was purified *via* flash column chromatography (gradient EtOAc 100% to EtOAc:MeOH 9:1), giving the desired compound **1** (58.2 mg, 80% yield).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.59 (ddd, *J* = 9.9, 8.3, 1.9 Hz, 1H), 7.46 (dd, *J* = 9.3, 1.9 Hz, 1H), 6.98 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.19 (d, *J* = 1.9 Hz, 1H), 6.01 (s, 1H), 4.34 (d, *J* = 3.9 Hz, 4H), 4.33 (br s, 2H) 3.96 (dd, *J* = 5.5, 2.3 Hz, 2H), 2.10 – 2.02 (m, 3H), 2.02 – 1.83 (m, 8H), 1.84 – 1.74 (m, 6H), 1.72 – 1.60 (m, 8H), 1.58 – 1.40 (m, 12H), 1.39 – 1.29 (m, 8H), 1.29 – 1.05 (m, 20H), 0.99 – 0.87 (m, 12H).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 159.42 (d, J = 2.7 Hz), 149.23, 132.75 (d, J = 8 Hz), 132.22 (q, J = 31.5 Hz), 131.05 (d, J = 9.6 Hz), 125.90 (d, J= 10.3 Hz), 125.50, 123.33, 120.67, 119.95, 110.71 (d, J = 11.6 Hz), 100.10, 99.33, 70.39, 43.25, 39.39, 35.42, 34.88, 30.71, 29.11, 29.09, 26.49, 26.38, 26.28, 25.82, 25.46, 24.55 (d, J = 3.4 Hz), 24.07, 23.00, 14.05, 11.19, 11.16.

^{31}P NMR: (202 MHz, $CDCl_3$) δ 45.19.

HRMS (ES+): Calculated for $C_{61}H_{94}F_3N_2O_4P_2$ 1037.6641 a.m.u., found 1037.6620 a.m.u.

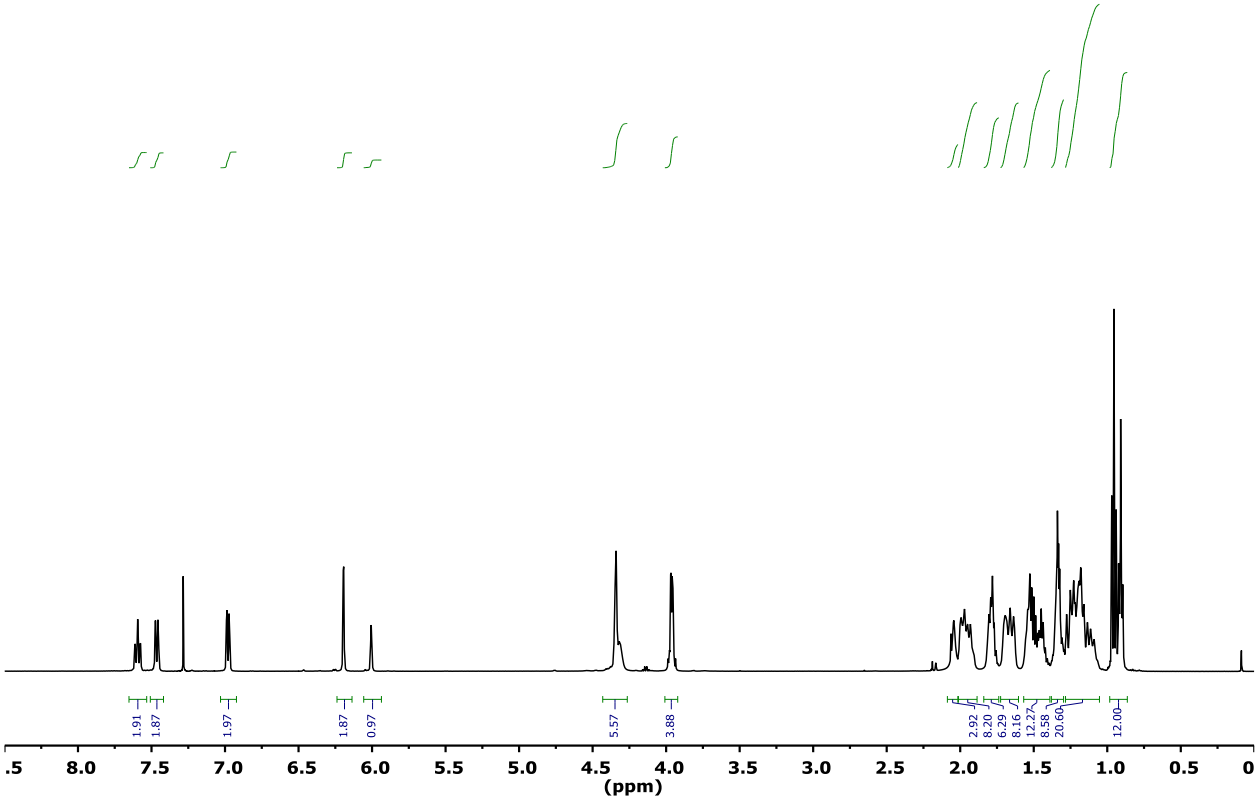


Figure S1.33. 600 MHz ^{1}H NMR spectrum of **A'A'** in $CDCl_3$.

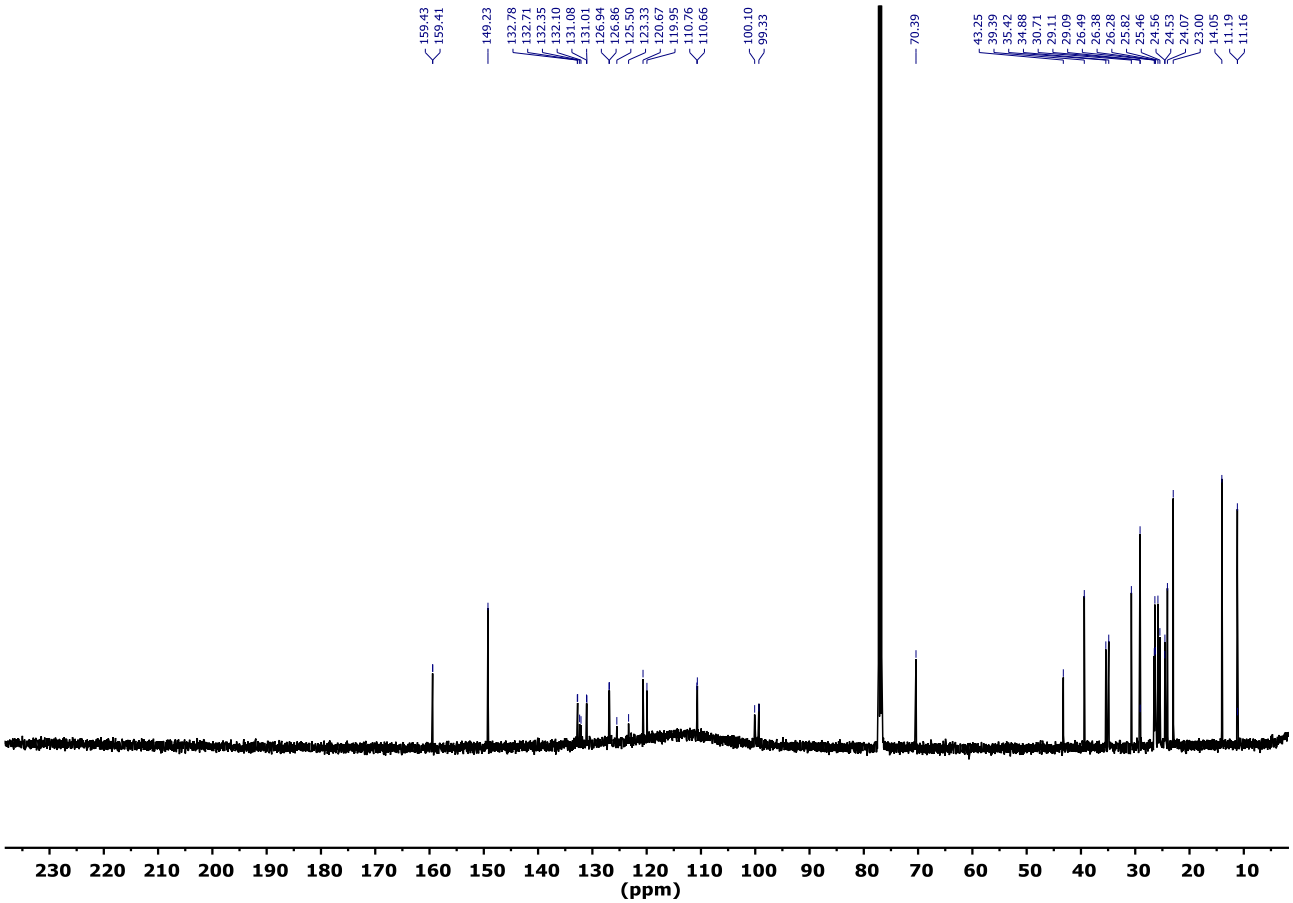


Figure S1.34.126 MHz ^{13}C NMR spectrum of **A'A'** in $CDCl_3$.

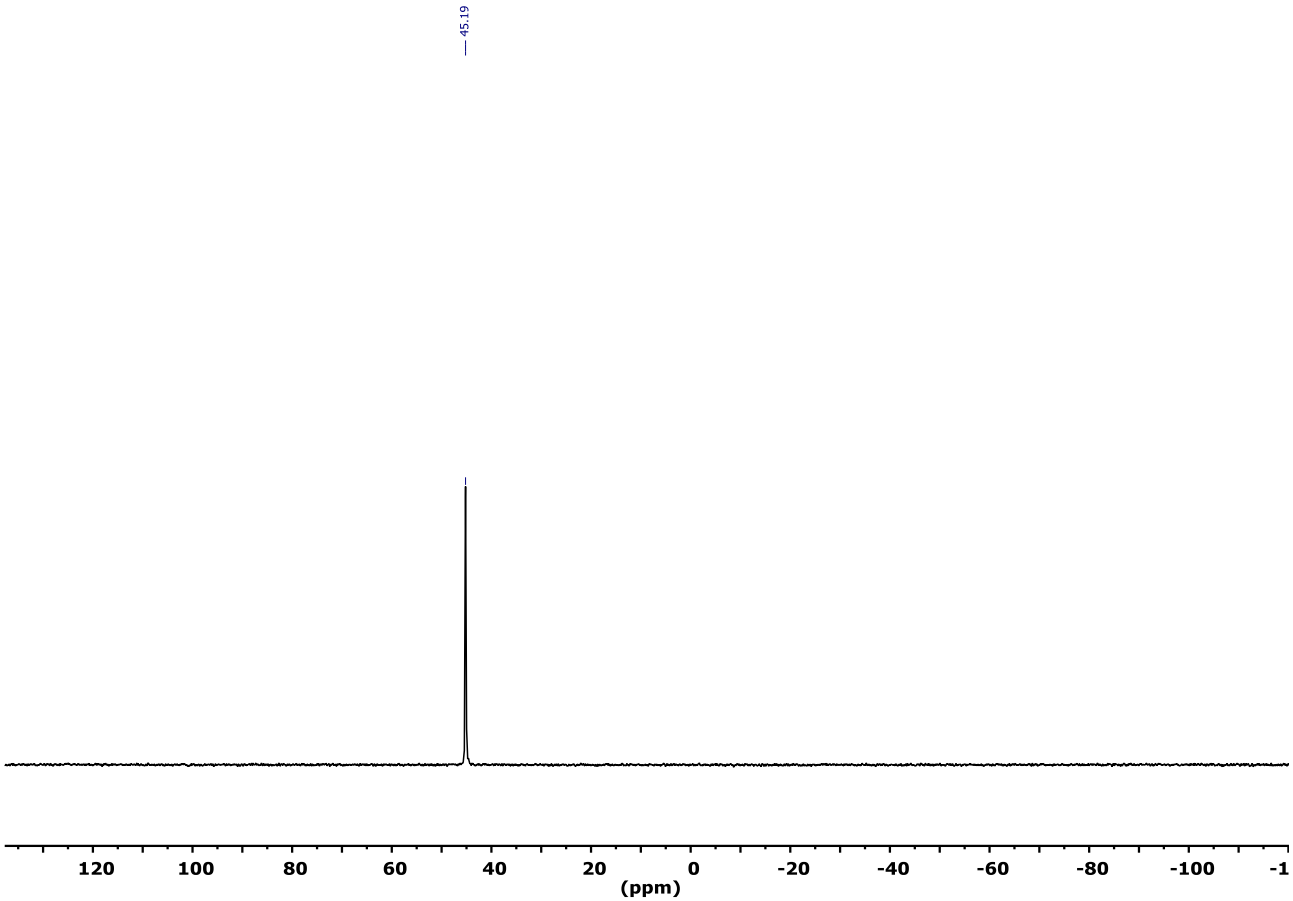


Figure S1.35. 202 MHz ^{31}P NMR spectrum of **A'A'** in Toluene-d_8.

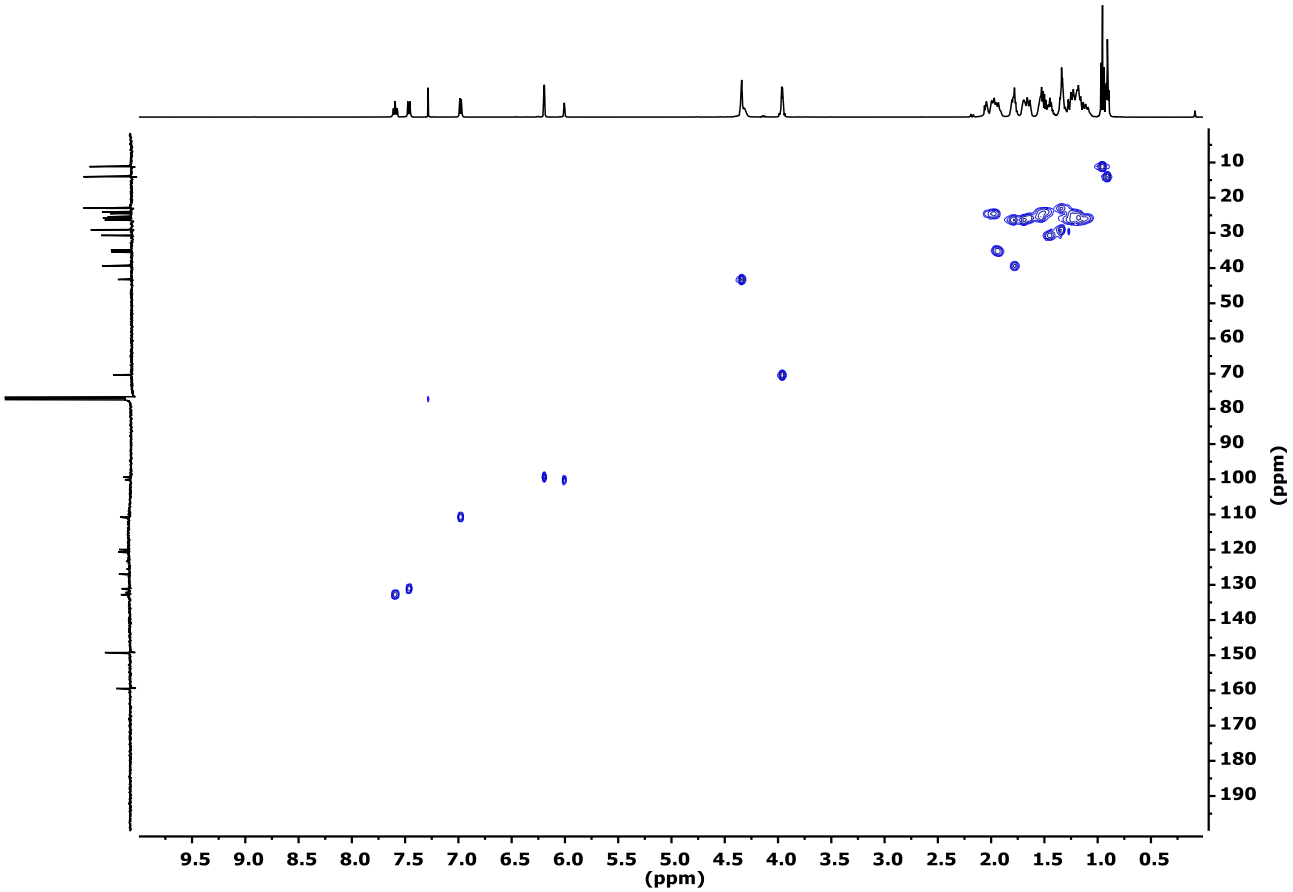


Figure S1.36. 500 MHz HSQC spectrum of **A'A'** in $CDCl_3$.

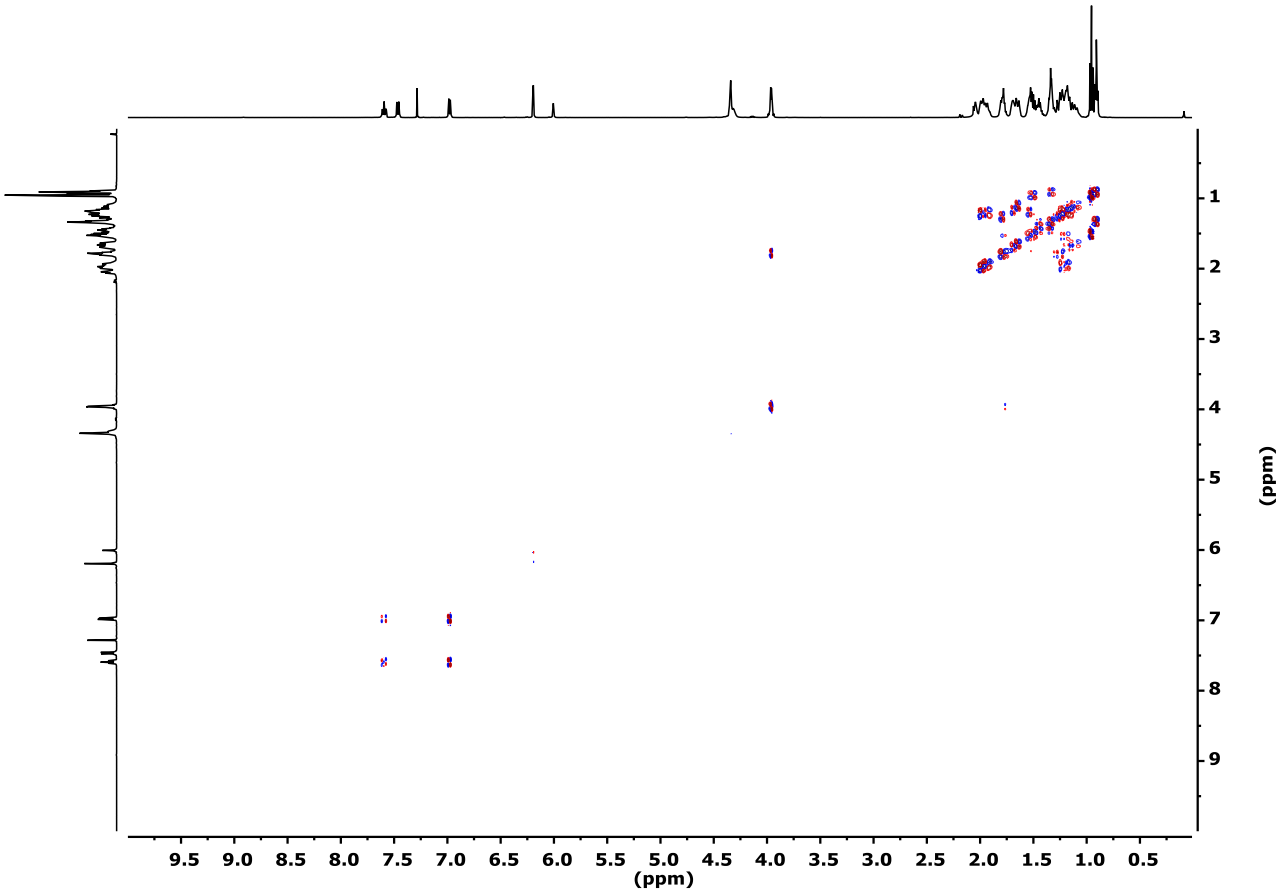
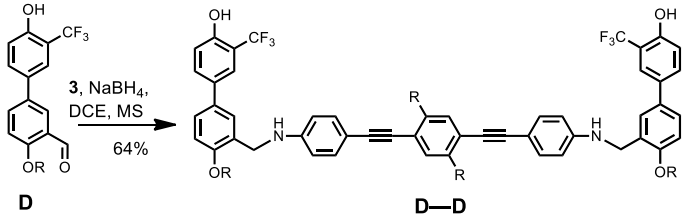
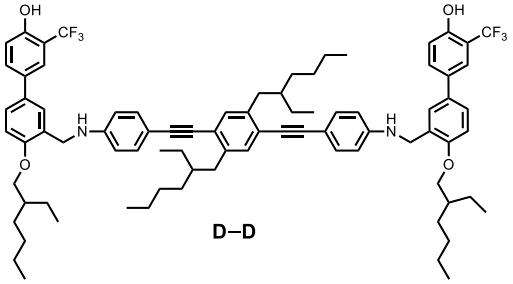


Figure S1.37. 500 MHz COSY spectrum of **A'A'** in $CDCl_3$.

2.5 Synthesis of dimer D—D

Dimer **D—D** was prepared as reported in the following scheme:





Monomer **D** (68.1 mg, 0.172 mmol, 2 equiv) and **4** (46.0 mg, 0.086 mmol, 1 equiv) were mixed in degassed dry DCE (1 ml) with molecular sieves (3Å) under nitrogen. The reaction mixture was stirred over weekend at room temperature. The end of the reaction was checked with ^{1}H-NMR. $NaBH_4$ (65.1 mg, 1.72 mmol, 20 equiv) and MeOH (0.2 ml) were added, and the reaction mixture was stirred for 2 hours. The reaction mixture was quenched with saturated aqueous Na_2CO_3 solution and extracted with EtOAc (3x). The organic phase was dried with anhydrous $MgSO_4$. The solvent was removed and the crude product was purified with flash chromatography (PE:EtOAc 7:3) to yield the product as white solid (71.3 mg, 0.055 mmol, 64% yield).

^{1}H NMR: (400.0 MHz, $CDCl_3$) δ 7.65 (d, J = 2.3 Hz, 2H), 7.54 (dd, J = 8.5, 2.3 Hz, 2H), 7.47 (d, J = 2.4 Hz, 2H), 7.42 (dd, J = 8.4, 2.4 Hz, 2H), 7.36 (d, J = 8.7 Hz, 4H), 7.27 (s, 2H), 7.06 – 6.93 (m, 4H), 6.64 (d, J = 8.7 Hz, 4H), 4.44 (s, 4H), 3.98 (d, J = 5.4 Hz, 4H), 2.83 – 2.63 (m, 4H), 1.85 – 1.74 (m, 4H), 1.63 – 1.41 (m, 5H), 1.41 – 1.23 (m, 23H), 1.03 – 0.80 (m, 20H).

^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 171.41, 156.65, 152.75, 148.18, 140.62, 133.46, 133.06, 132.73, 131.81, 131.55, 127.46, 127.32, 126.68, 124.93 (d, J = 4.9 Hz), 122.76, 118.01, 112.75, 111.84, 111.46, 94.63, 86.92, 70.39, 60.51, 43.61, 40.16, 39.50, 38.55, 32.53, 30.79, 29.15, 28.90, 25.56, 24.13, 23.09, 21.06, 14.13, 11.22, 10.78.

^{19}F NMR: (376.5 MHz, $CDCl_3$): δ -61.13

HRMS (ASAP+): Calculated for $C_{82}H_{99}F_6N_2O_4$ 1289.7504 a.m.u., found 1289.7468 a.m.u.

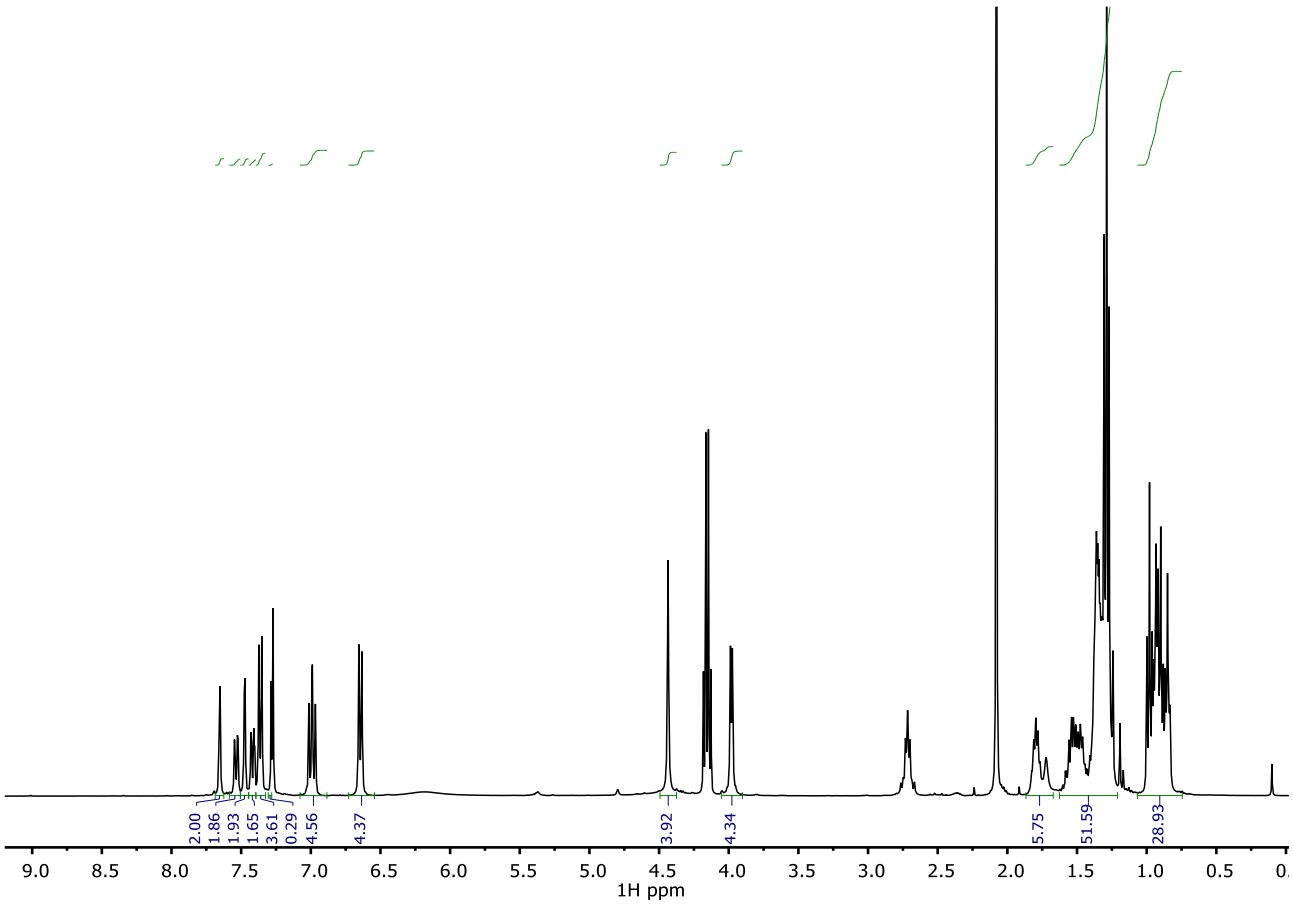


Figure S1.38. 400 MHz ^{1}H NMR spectrum of **D—D** in $CDCl_3$.

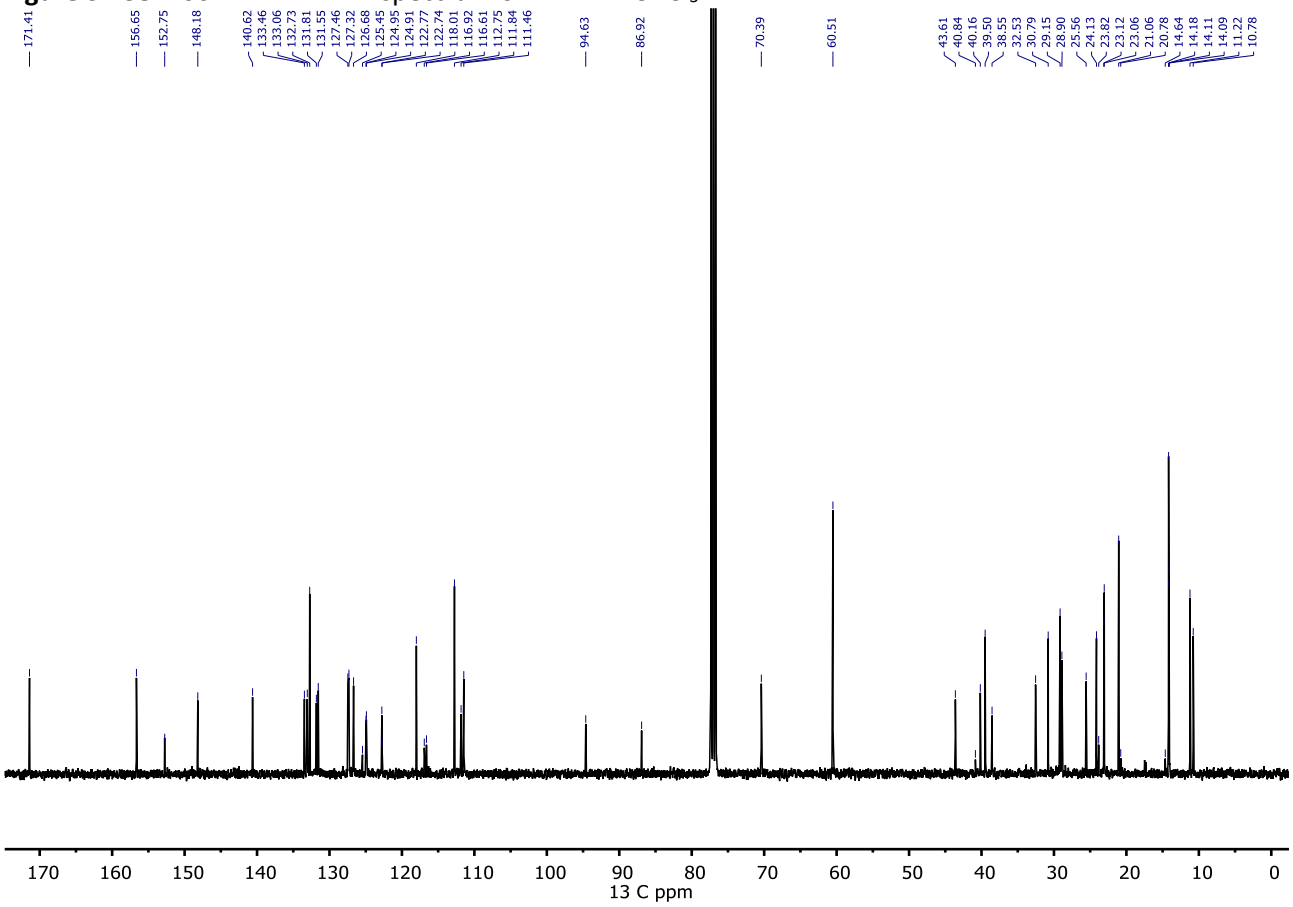


Figure S1.39.100.6 MHz ^{13}C NMR spectrum of **D—D** in $CDCl_3$.

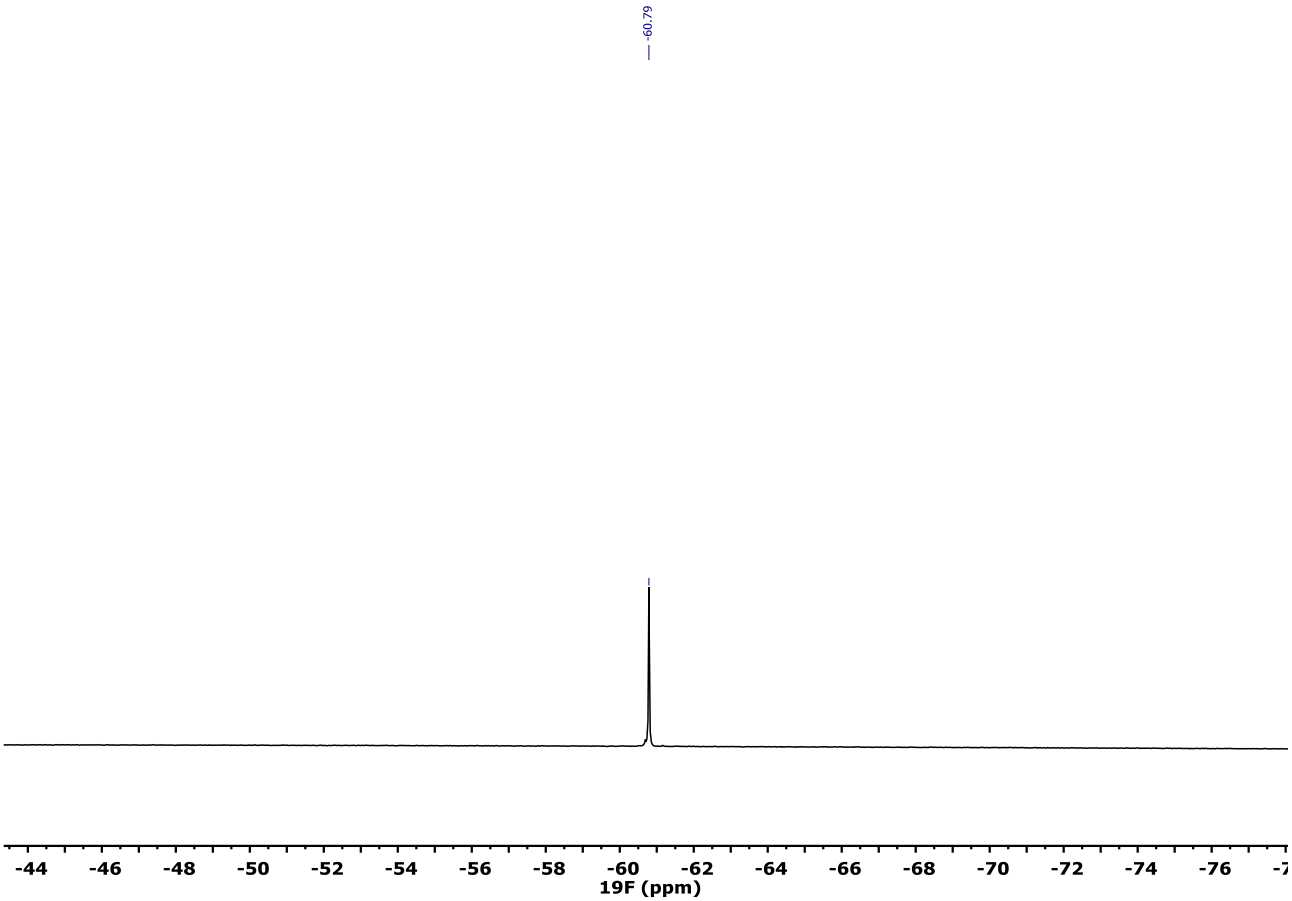


Figure S1.40. 376.5 MHz ^{19}F NMR spectrum of **D—D** in $CDCl_3$.

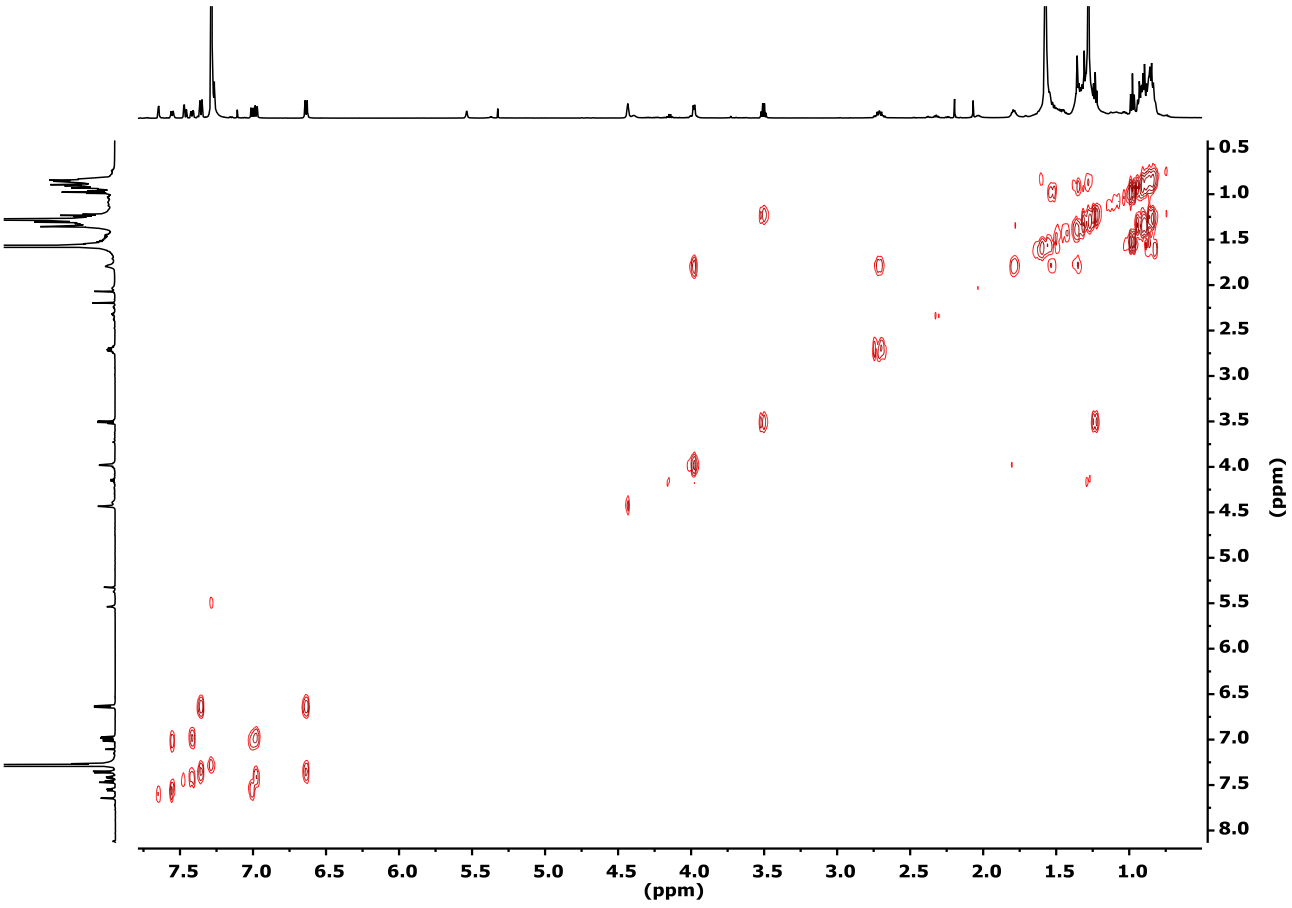
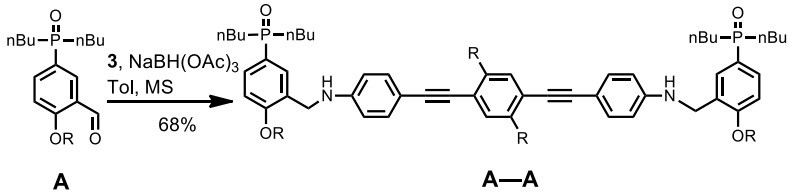
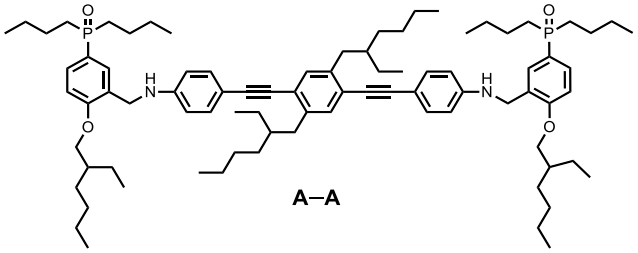


Figure S1.41. 600 MHz COSY spectrum of **D—D** in $CDCl_3$.

2.6. Synthesis of dimer A—A

Dimer **A—A** was prepared as reported in the following scheme:





Monomer **A** (68 mg, 0.173 mmol, 1 equiv) and **3** (46 mg, 0.086 mmol, 0.5 equiv) were dissolved in degassed dry toluene (1 ml). The flask was equipped with a dean-stark apparatus, containing molecular sieves and dry toluene. The reaction mixture was refluxed for 3 hours, then the heating was turned off, $NaBH(OAc)_3$ (4 eq) was added and the mixture was stirred for 2 hours. Then the reaction was quenched with saturated aqueous Na_2CO_3 solution and stirred until complete solubilization. The mixture was extracted with EtOAc (3x), the organic fractions were collected and dried with anhydrous $MgSO_4$ and the solvent evaporated in vacuum. The crude product was purified with flash chromatography (EtOAc:MeOH 95:0.5) to yield the product as pale yellow oil (75.2 mg, 68% yield).

^{1}H NMR (400.0 MHz, $CDCl_3$)**:** δ_H = 7.66 (ddd, *J* = 10.5, 8.2, 2.0 Hz, 2H), 7.51 (dd, *J* = 10.4, 2.1 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 4H), 7.26 (s, 2H), 7.01 (dd, *J* = 8.3, 2.0 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 4H), 4.42 (s, 4H), 3.99 (d, *J* = 5.4 Hz, 4H), 2.71 (d, *J* = 7.3 Hz, 4H), 2.00 – 1.84 (m, 4H), 1.84 – 1.70 (m, 7H), 1.66 (t, *J* = 5.1 Hz, 4H), 1.61 – 1.43 (m, 5H), 1.43 – 1.18 (m, 43H), 1.07 – 0.66 (m, 38H).

^{13}C NMR (100.6 MHz, $CDCl_3$)**:** δ_C = 189.11, 159.53 (d, *J* = 2.9 Hz), 147.74, 140.59, 133.06, 132.68, 131.75 (d, *J* = 9.1 Hz), 130.27 (d, *J* = 10.8 Hz), 127.27 (d, *J* = 11.3 Hz), 123.61, 122.71 (d, *J* = 12.3 Hz), 112.81, 110.99 (d, *J* = 12.1 Hz), 94.49, 86.94, 70.43, 43.25, 40.16, 39.43, 38.51, 32.49, 30.75, 30.17, 29.49, 29.13, 28.89, 25.55, 24.30 – 23.98 (m), 23.52 (d, *J* = 4.1 Hz), 23.12, 23.04, 14.11 (d, *J* = 4.9 Hz), 13.61, 11.24, 10.79, 1.03.

^{31}P NMR (162.0 MHz, $CDCl_3$)**:** δ_P = 40.66

HRMS (ASAP+): Calculated for $C_{84}H_{127}N_2O_4P_2$ 1289.9266 a.m.u., found 1289.9234 a.m.u.

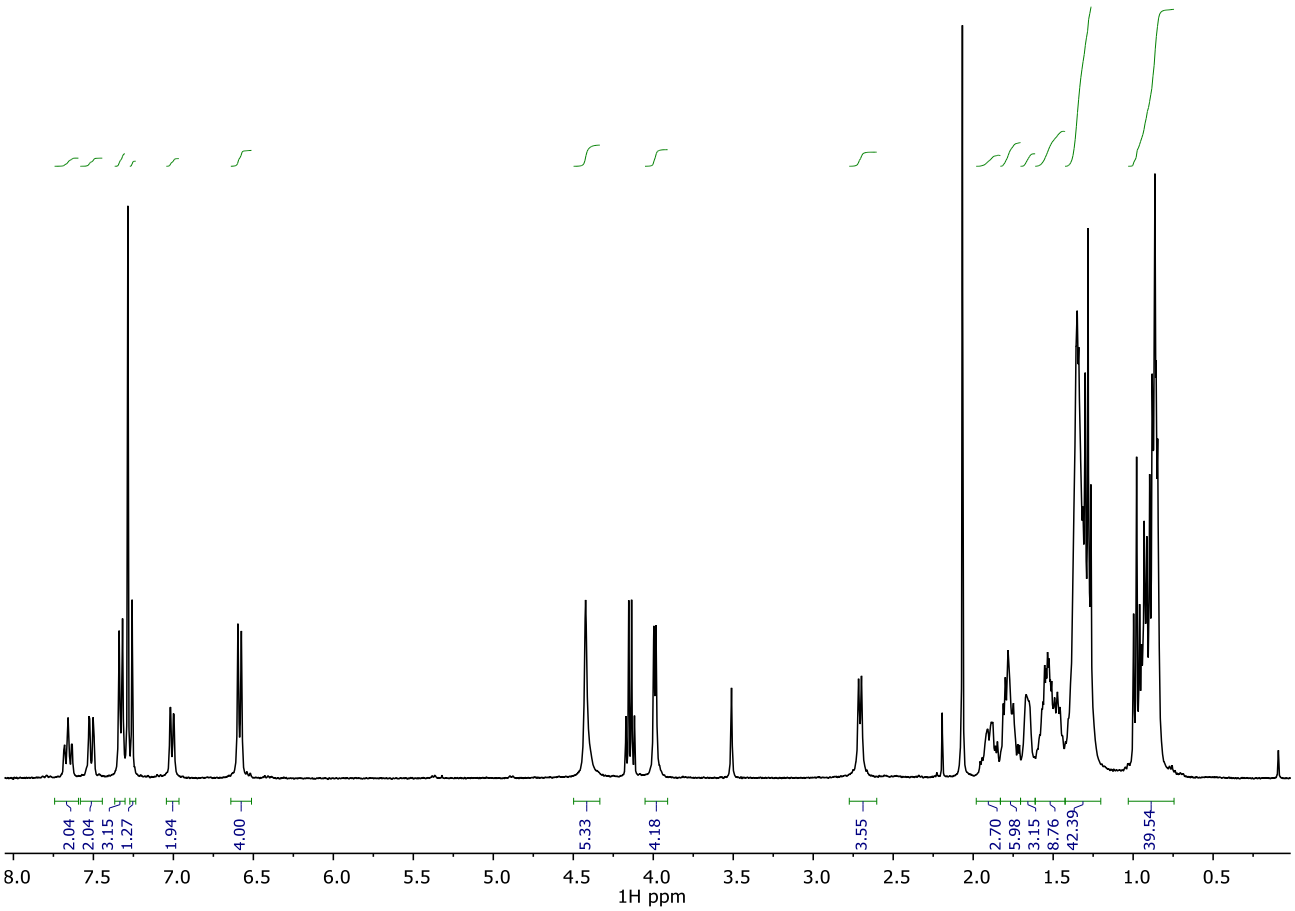


Figure S1.42. 400 MHz ^{1}H NMR spectrum of **A—A** in $CDCl_3$.

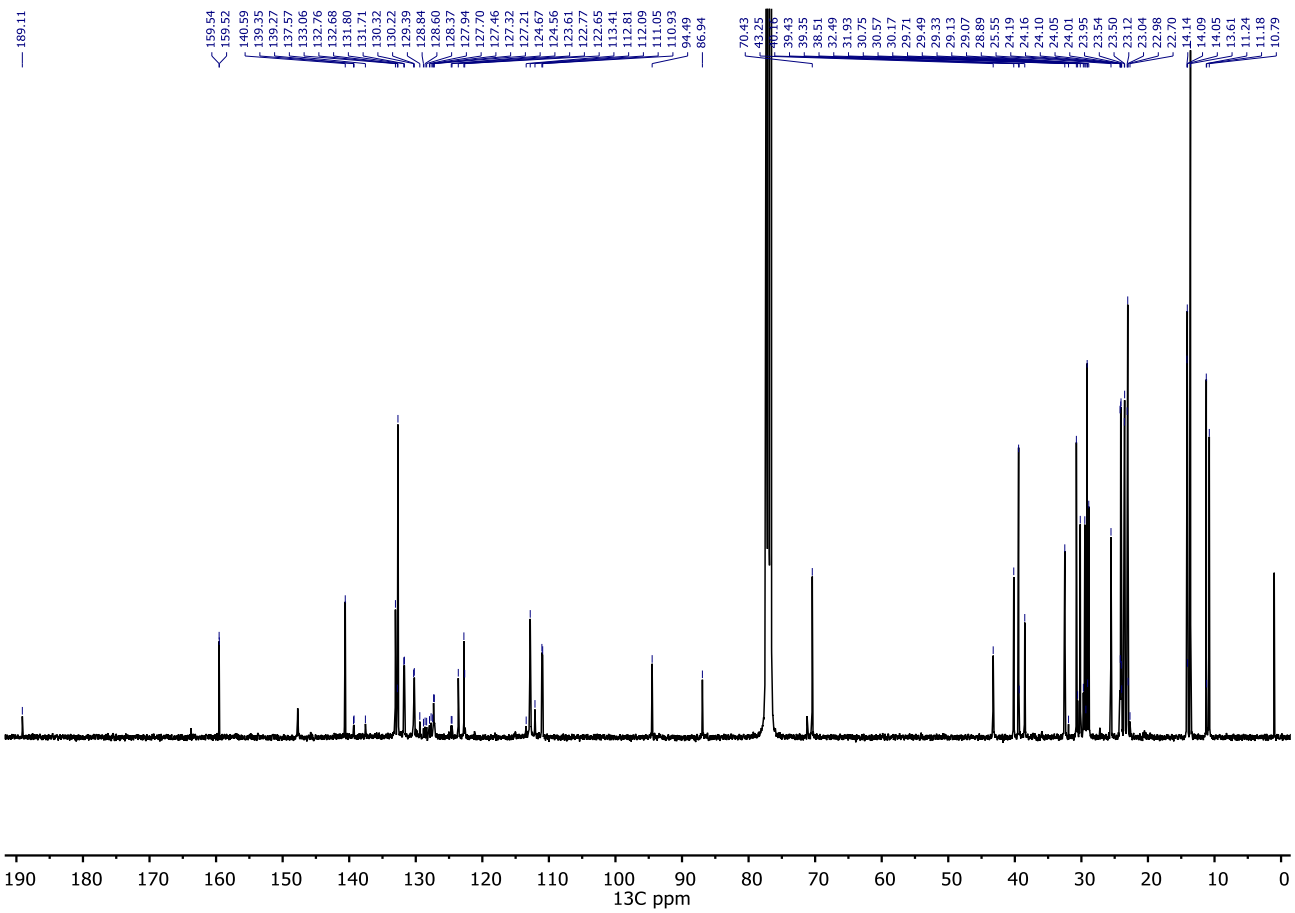


Figure S1.43.100.6 MHz ^{13}C NMR spectrum of **A—A** in $CDCl_3$.

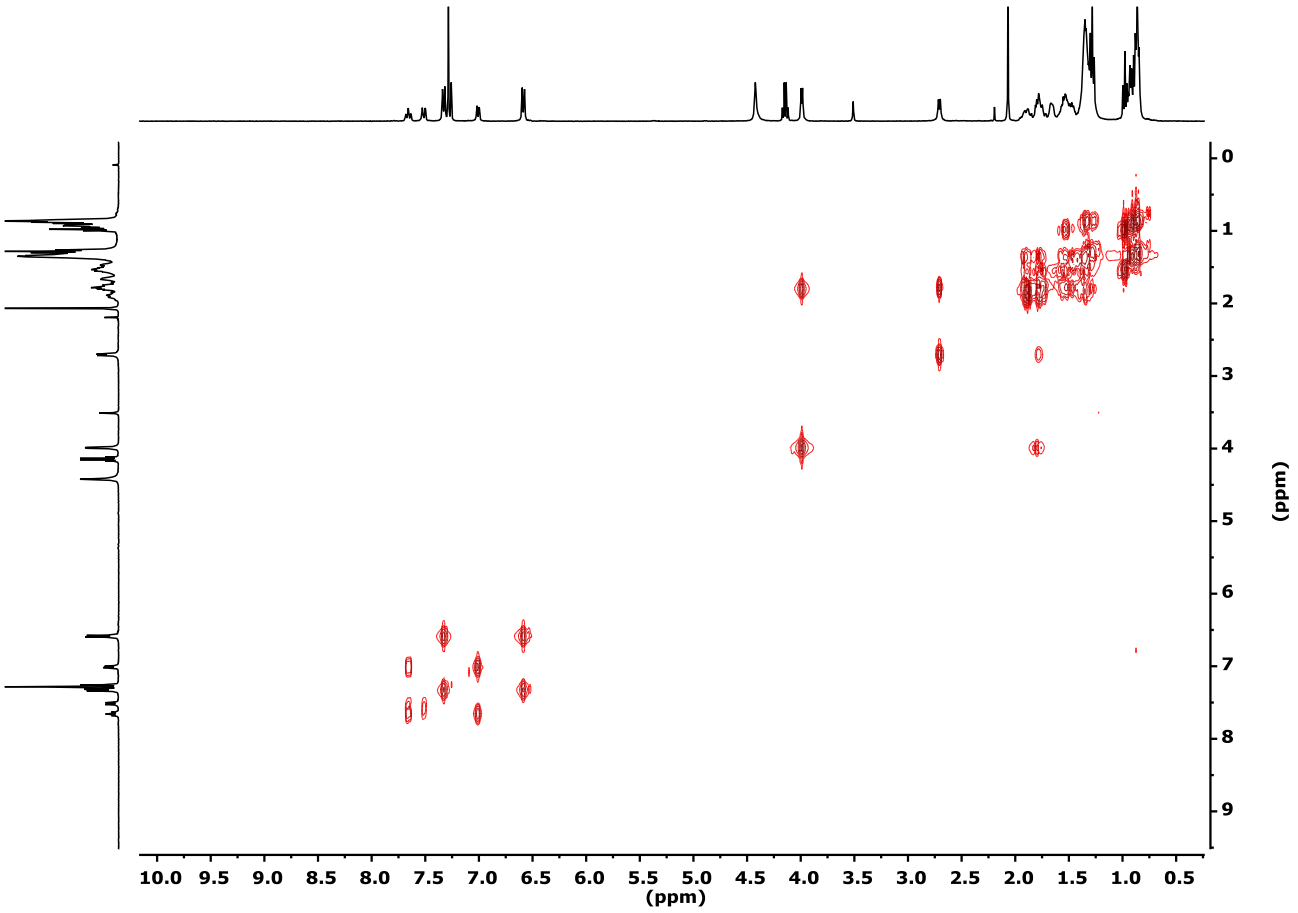


Figure S1.44. 600 MHz COSY spectrum of **A—A** in $CDCl_3$.

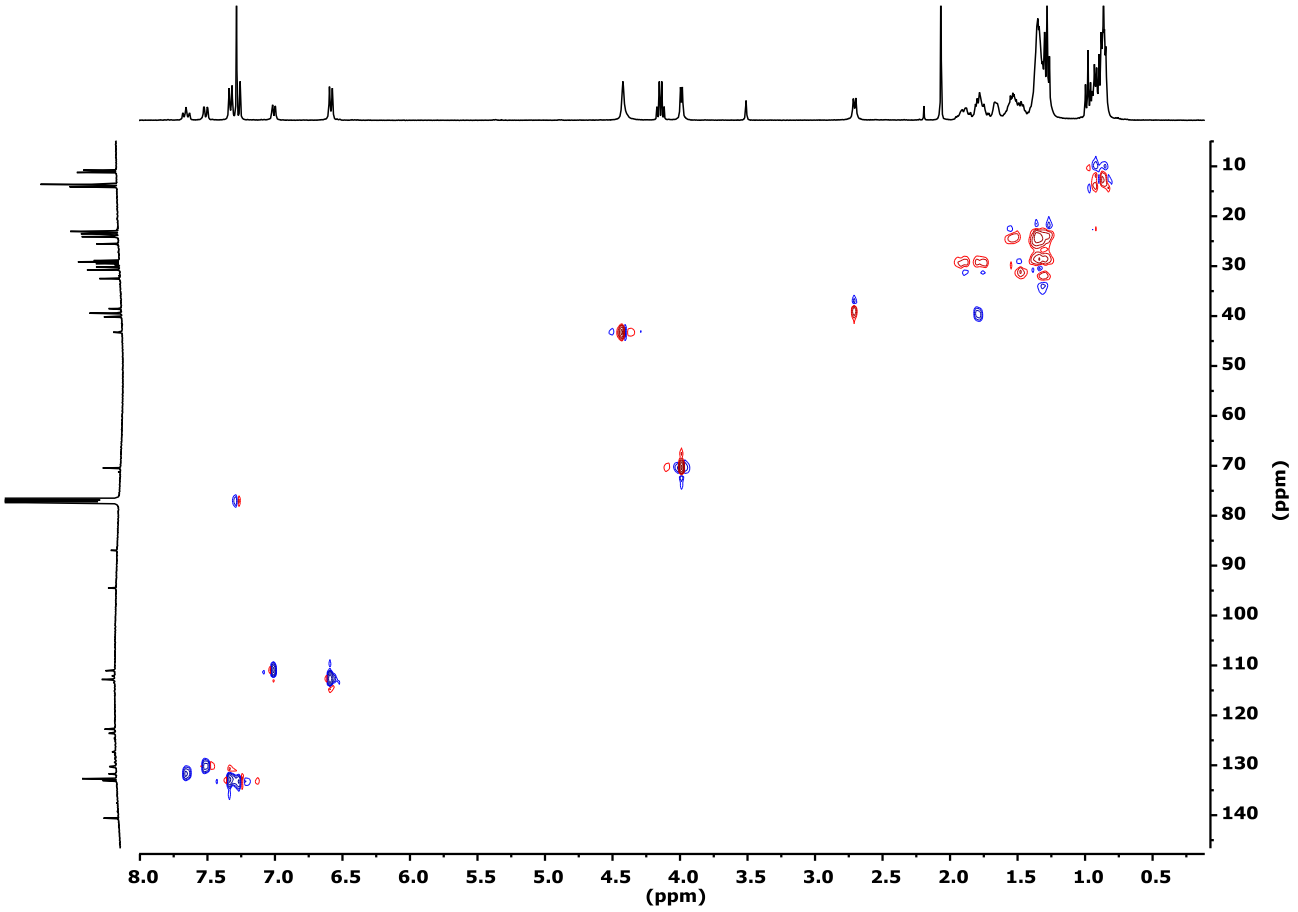


Figure S1.45. 600 MHz HSQC spectrum of **A—A** in $CDCl_3$.

3. NMR spectroscopy studies

All binding constants were measured by ^{19}F and ^{1}H-NMR titrations in a Bruker 500 MHz AVIII HD Smart Probe and Bruker Avance III 600MHz spectrometers. The host (H, phenol derivatives **D**, **DD**, **D—D**) was dissolved in toluene-*d8* or chloroform-*d3* at a known concentration. The guest (G, phosphine oxide derivatives **A**, **AA**, **A'**, **A'A'**, **A—A**) was dissolved in the host solution and made to a known concentration. 500 µl of H were added to an NMR tube and the spectrum was recorded. Known volumes of G in H solution were added to the NMR tube, and the spectra were recorded after each addition. The chemical shifts of the host spectra were monitored as a function of guest concentration and analysed using a purpose written software in Microsoft Excel. Errors were calculated as two times the standard deviation from the average value (95% confidence limit).

Self-association constants of mixed dimers were measured by ^{19}F and ^{1}H NMR titrations in a Bruker 500 MHz AVIII HD Smart Probe and Bruker Avance III 600MHz spectrometers. The dimer (**DA**, **DA'**, **D—A**) was dissolved in toluene-*d8* or chloroform-*d3* at a known concentration and then subsequently diluted. ^{19}F and ^{1}H-NMR spectra were recorded for each concentration.

^{19}F and ^{1}H (donor -CF_3 and -*OH*) NMR chemical shifts and limiting complexation-induced changes in chemical shifts of the free host (ppm) were obtained by fitting the titration data measured in toluene-*d8* and chloroform-*d3* at 298 K to a 1:1 binding isotherm.

3.1 Titration of D vs A'

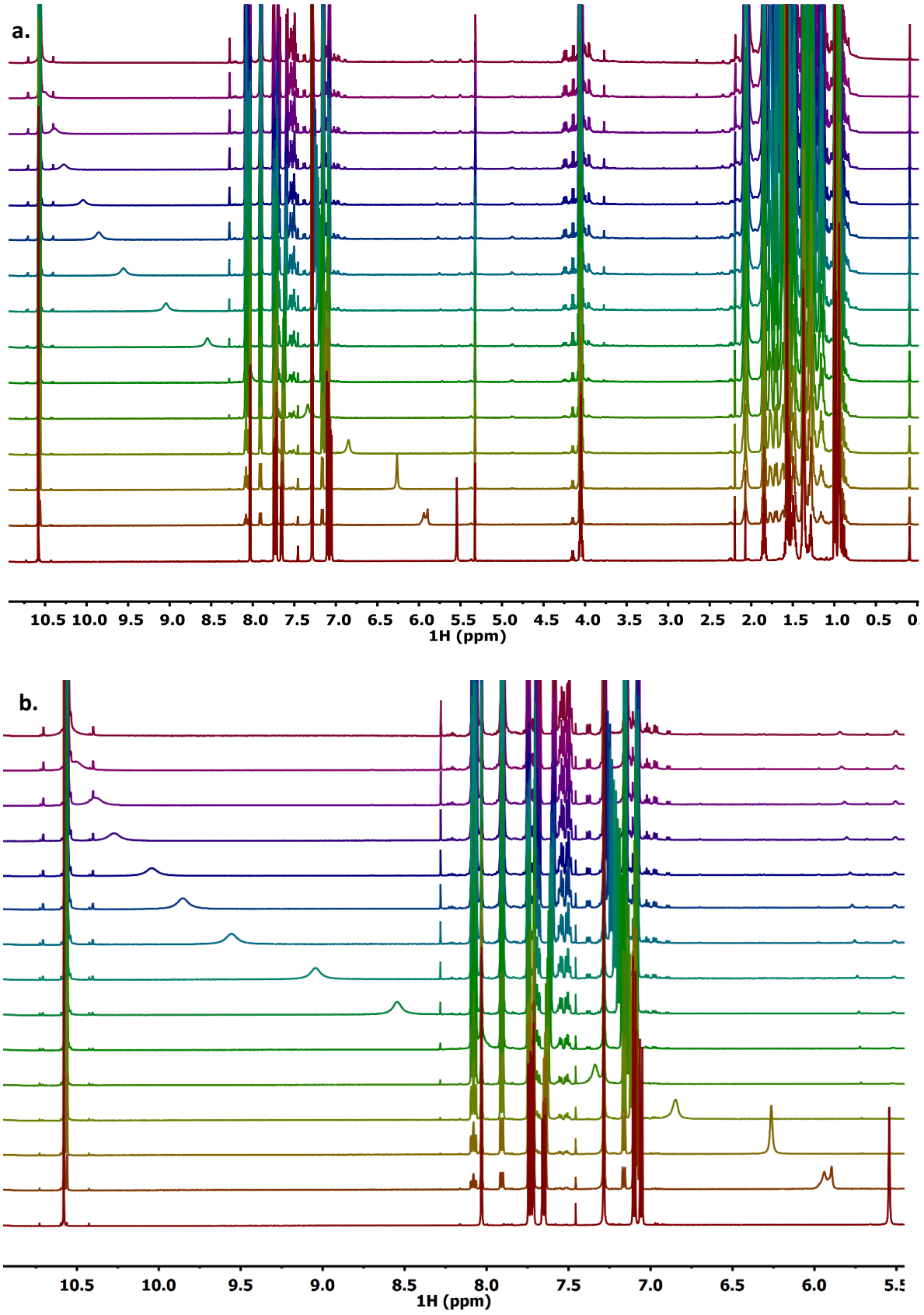


Fig. S3.1 Titration of **A'** (40.6 mM) into **D** (2.3 mM) in $CDCl_3$ (^{1}H-NMR 600 MHz): **a.** complete ^{1}H stacked spectra; **b.** detail of the -OH shift.

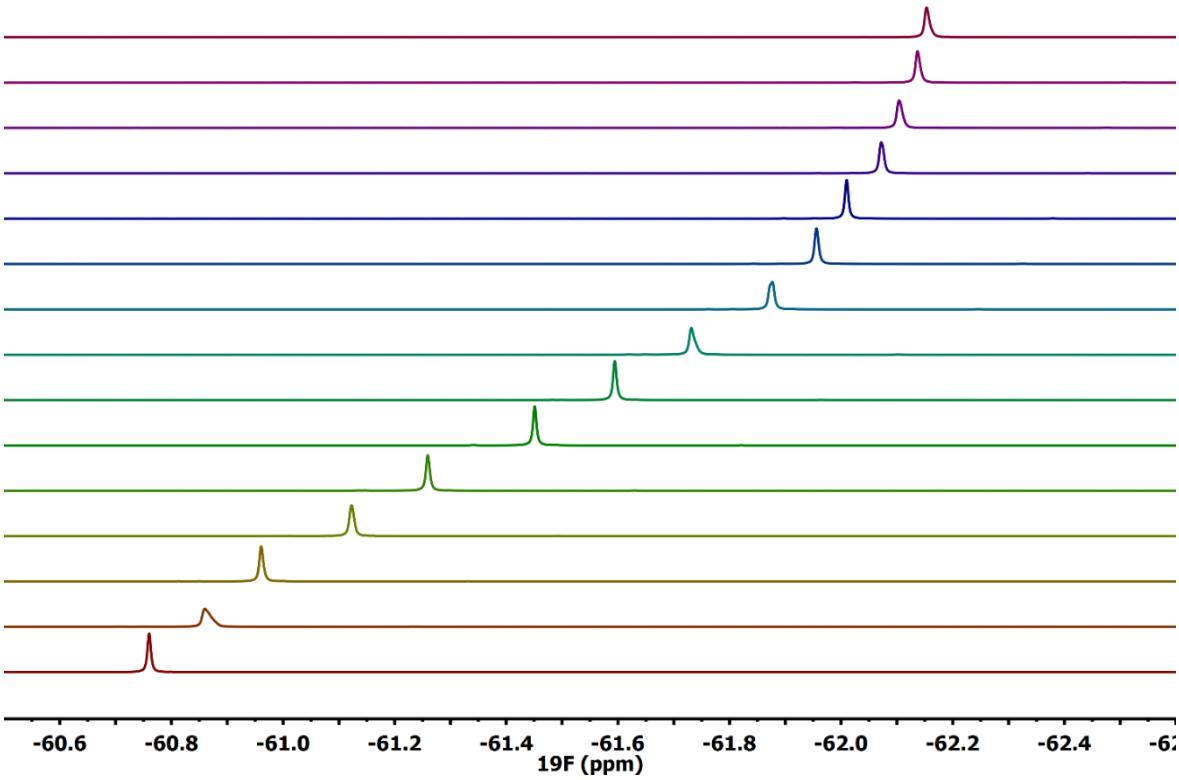


Fig. S3.2 Titration of **A'** (40.6 mM) into **D** (2.3 mM) in $CDCl_3$ (^{19}F-NMR 600 MHz).

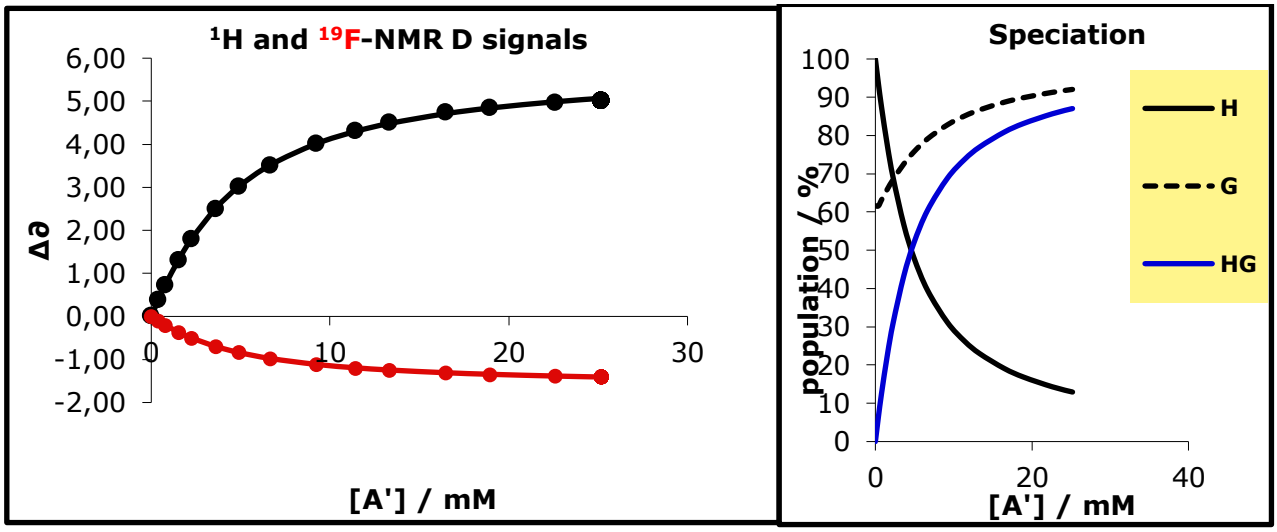


Fig. S3.3 Plot of the change in chemical shift of the **D** ^{19}F (**red**) and ^{1}H (**black**) signal in $CDCl_3$ as a function of **[A']** (the line represents the best fit to a 1:1 binding isotherm) and speciation as a function of **[A']** obtained from the average of the two constants obtained from the ^{19}F and ^{1}H fitting.

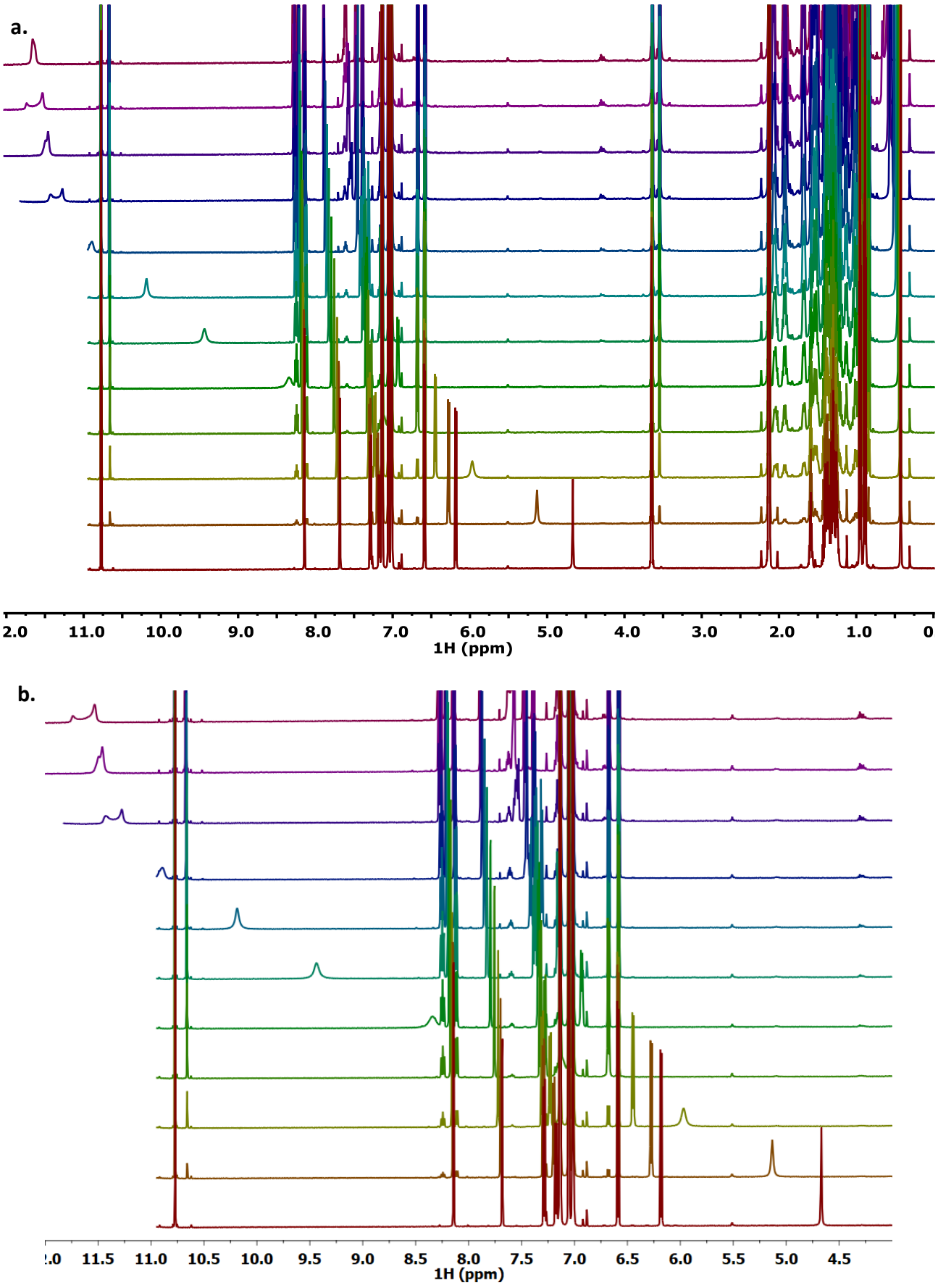


Fig. S3.4 Titration of **A'** (7.00 mM) into **D** (2.00 mM) in Toluene-d_8 (^{1}H-NMR 600 MHz): **a.** complete ^{1}H stacked spectra; **b.** detail of the -OH shift.

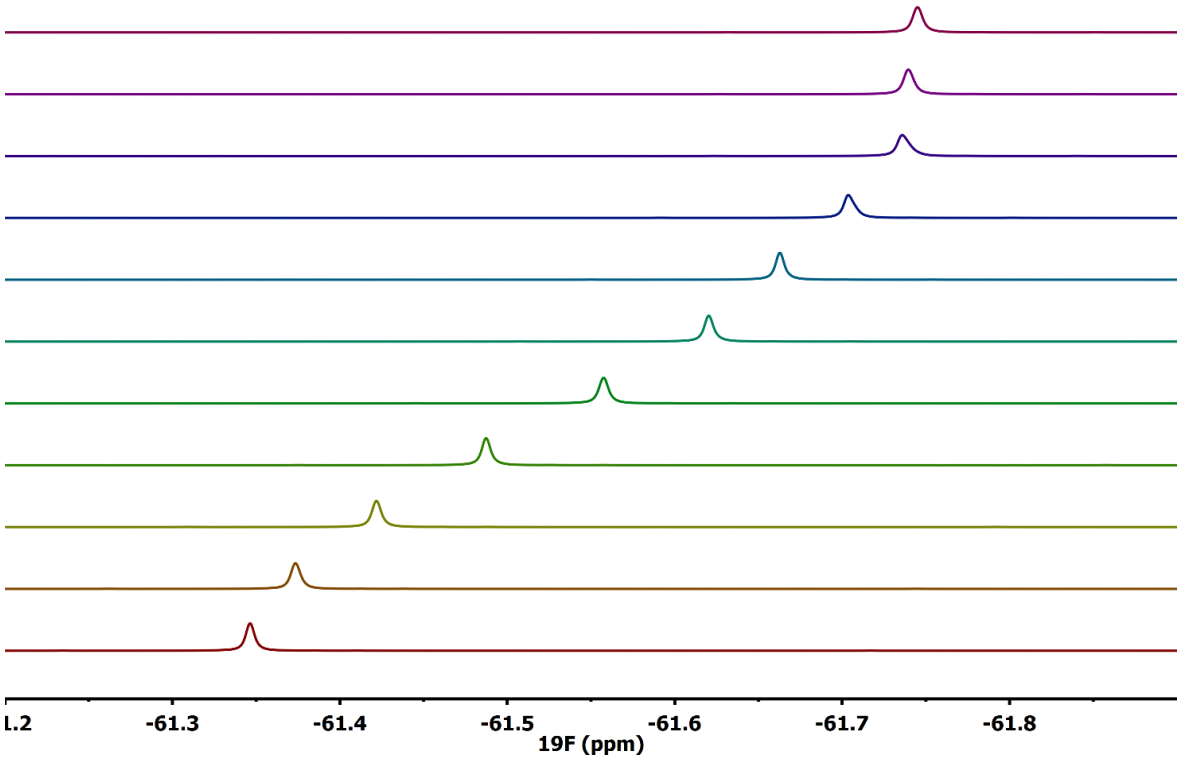


Fig. S3.5 Titration of **A'** (7.00 mM) into **D** (2.00 mM) in Toluene-d_8 (^{19}F-NMR 565 MHz).

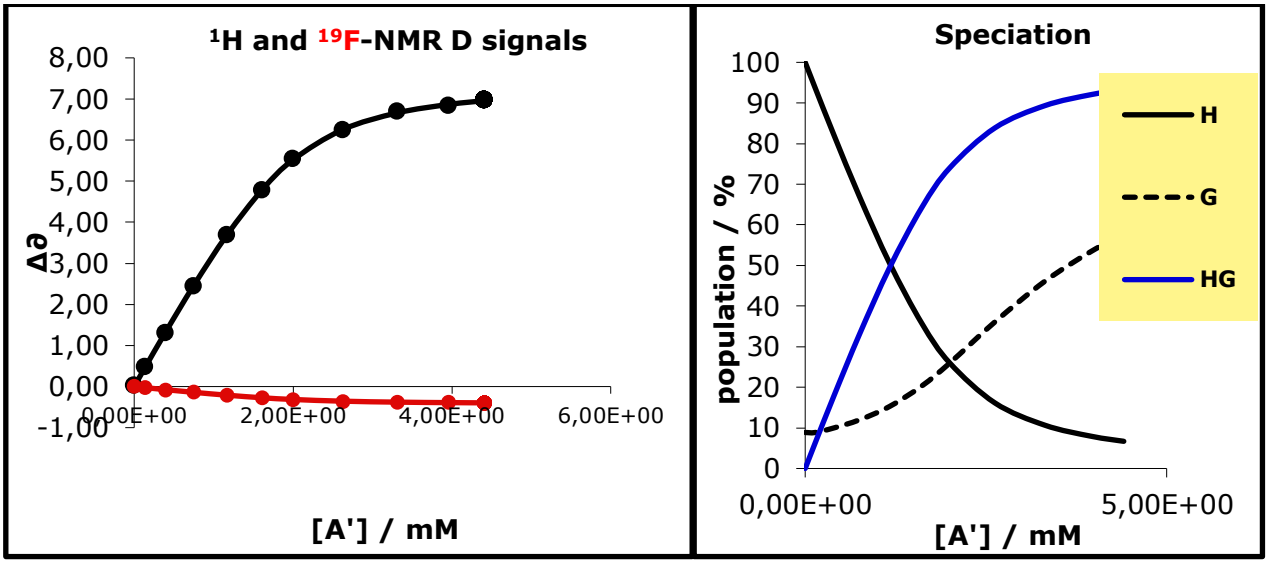


Fig. S3.6 Plot of the change in chemical shift of the **D** ^{19}F (**red**) and ^{1}H (**black**) signal in Toluene-d_8 as a function of **[A']** (the line represents the best fit to a 1:1 binding isotherm) and speciation as a function of **[A']** obtained from the average of the two constants obtained from ^{19}F and ^{1}H fitting.

3.2 Titration of DD vs A'A'

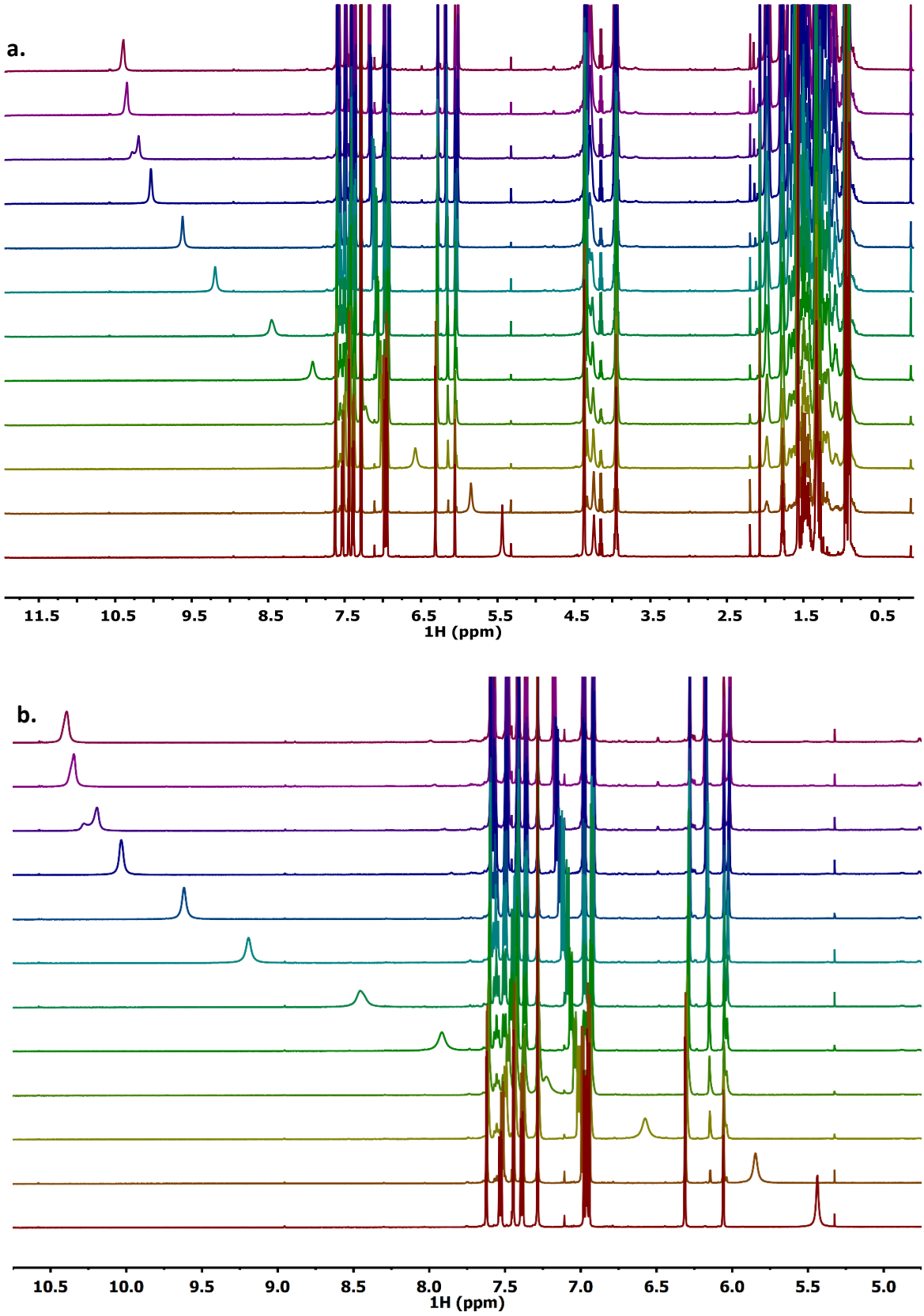


Fig. S3.7 Titration of **A'A'** (10.0 mM) into **DD** (2.0 mM) in $CDCl_3$ (^{1}H-NMR 600 MHz): **a.** complete ^{1}H stacked spectra; **b.** detail of the -OH shift.

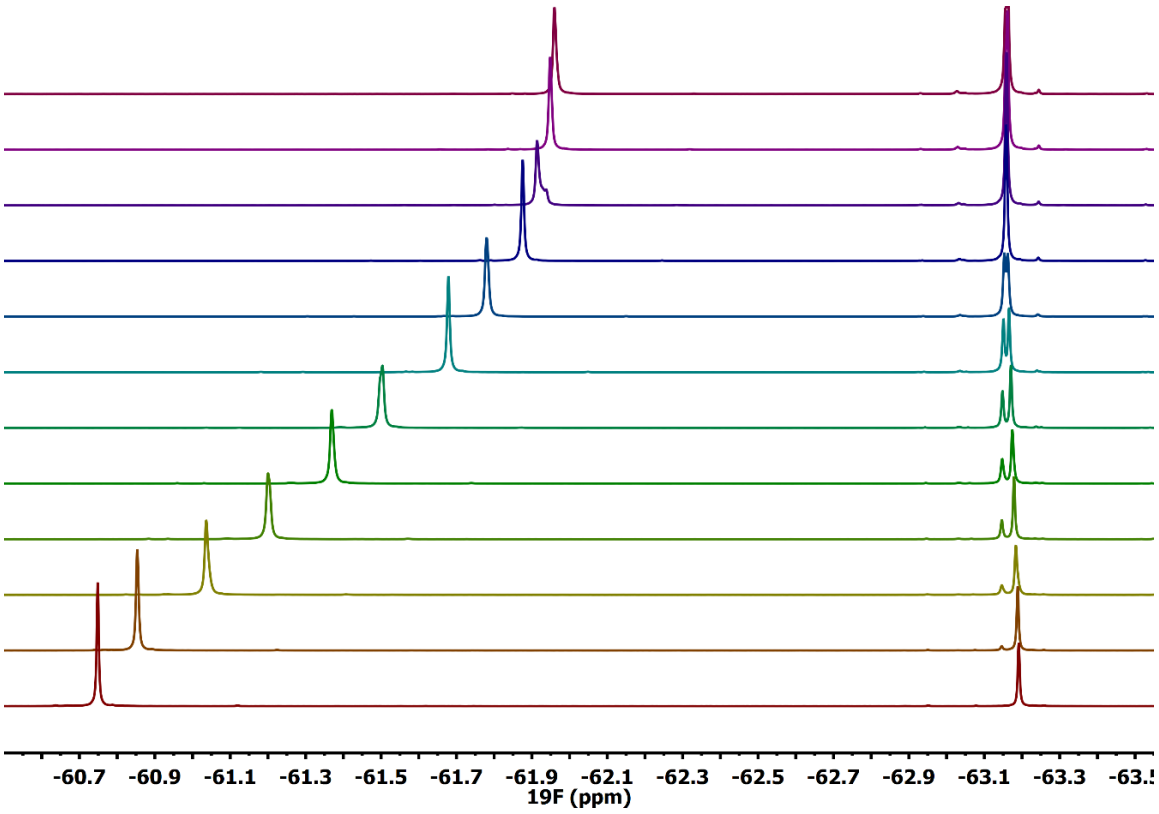


Fig. S3.8 Titration of **A'A'** (10.0 mM) into **DD** (2.0 mM) in $CDCl_3$ (^{19}F-NMR 565 MHz)

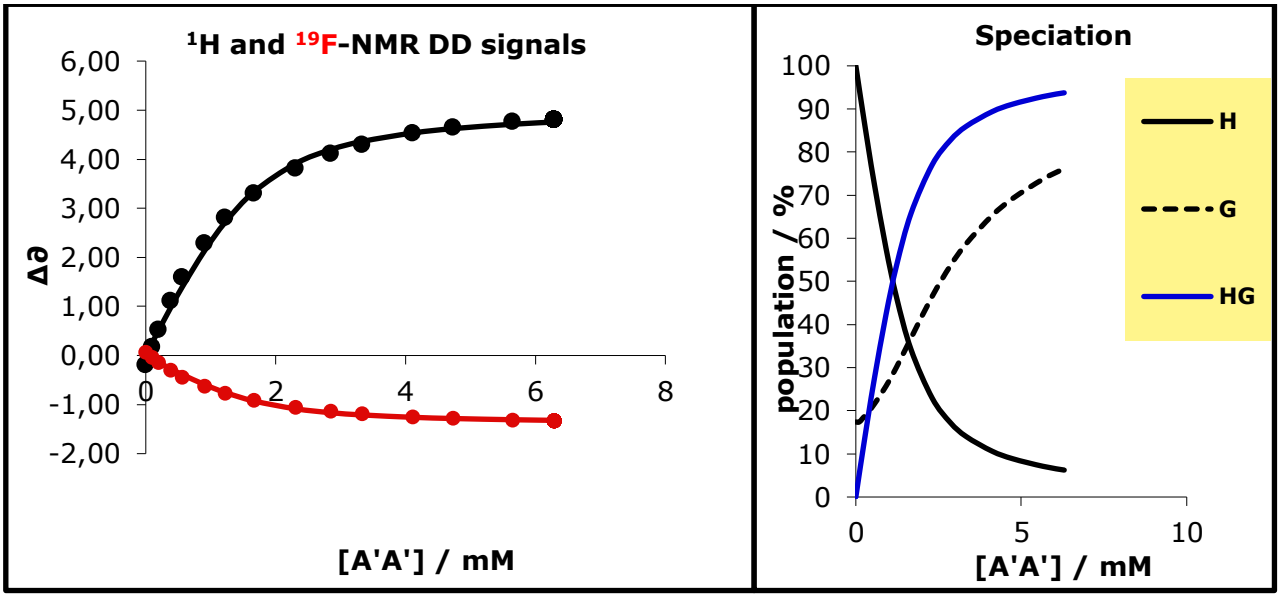


Fig. S3.9 Plot of the change in chemical shift of the **DD** ^{19}F (**red**) and ^{1}H (**black**) signal in CDCl3 as a function of **[A'A']** (the line represents the best fit to a 1:1 binding isotherm) and speciation as a function of **[A'A']** obtained from the average of the two constants obtained from ^{19}F and ^{1}H fitting.

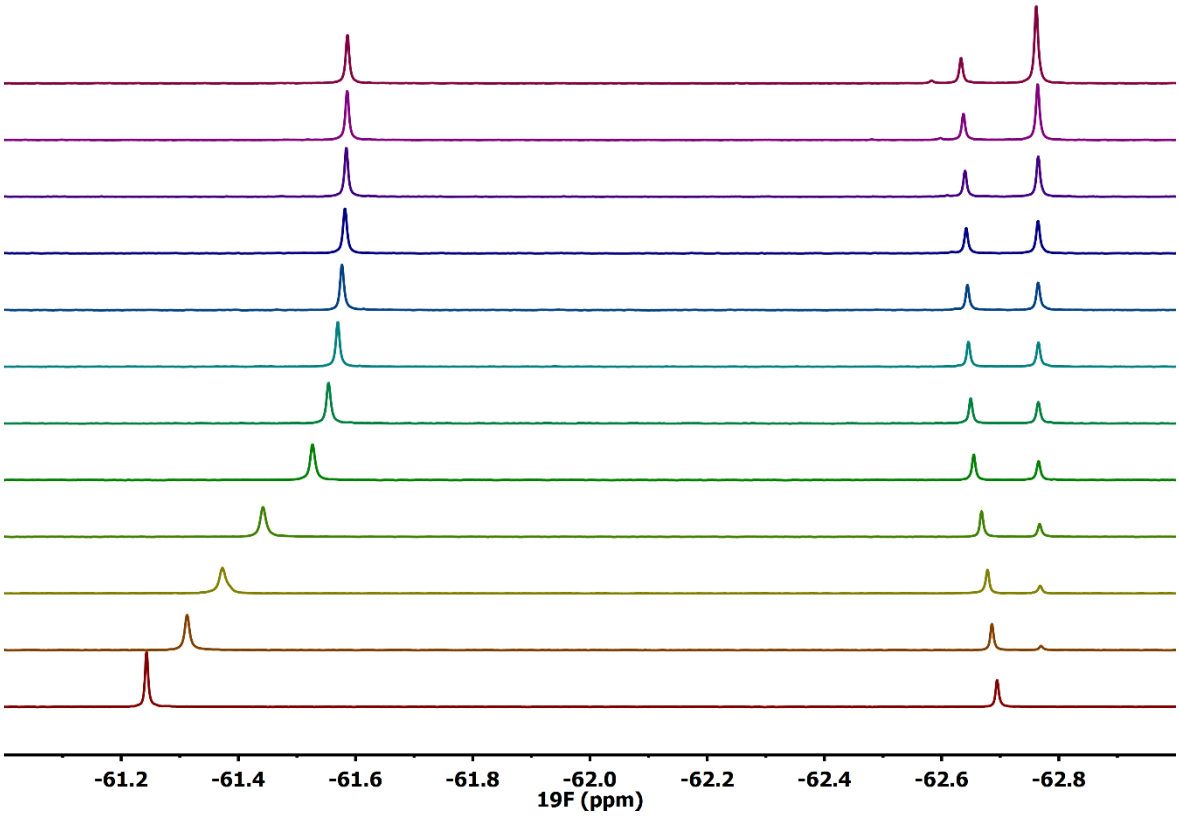


Fig. S3.10 Titration of **A'A'** (1 mM) into **DD** (0.1 mM) in Toluene-d_8 (^{19}F-NMR 600 MHz)

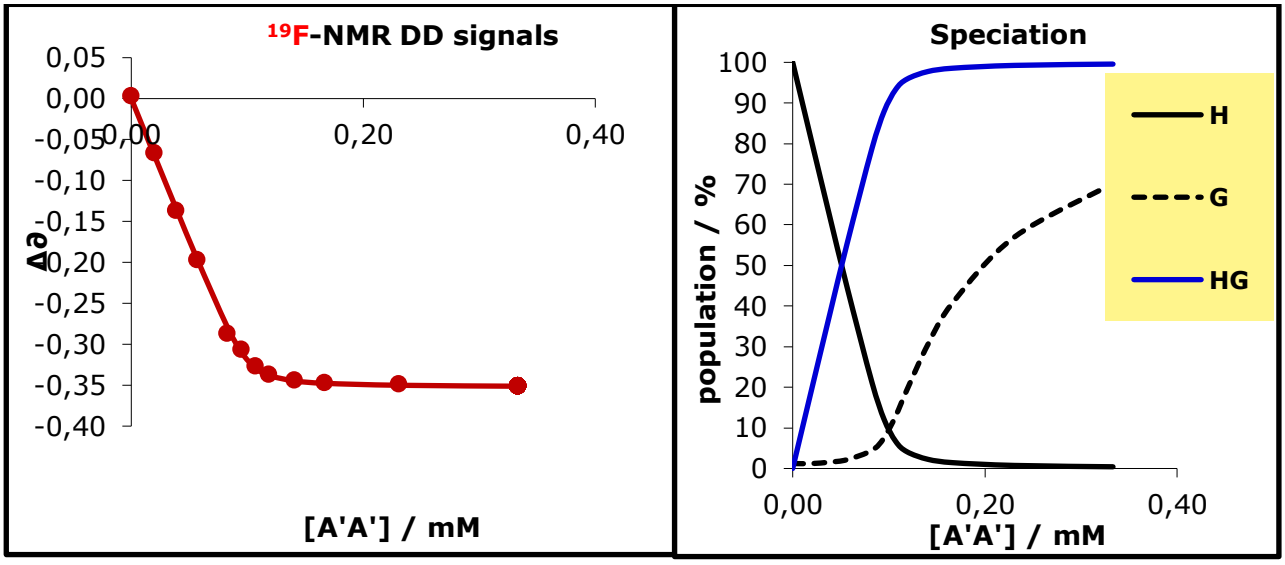


Fig. S3.11 Plot of the change in chemical shift of the **DD** ^{19}F (**red**) signal in Toluene-d_8 as a function of **[A'A']** (the line represents the best fit to a 1:1 binding isotherm) and speciation as a function of **[A'A']** obtained from the average of the two constants obtained from ^{19}F and ^{1}H fitting.

3.3 Titration of D—D vs A—A

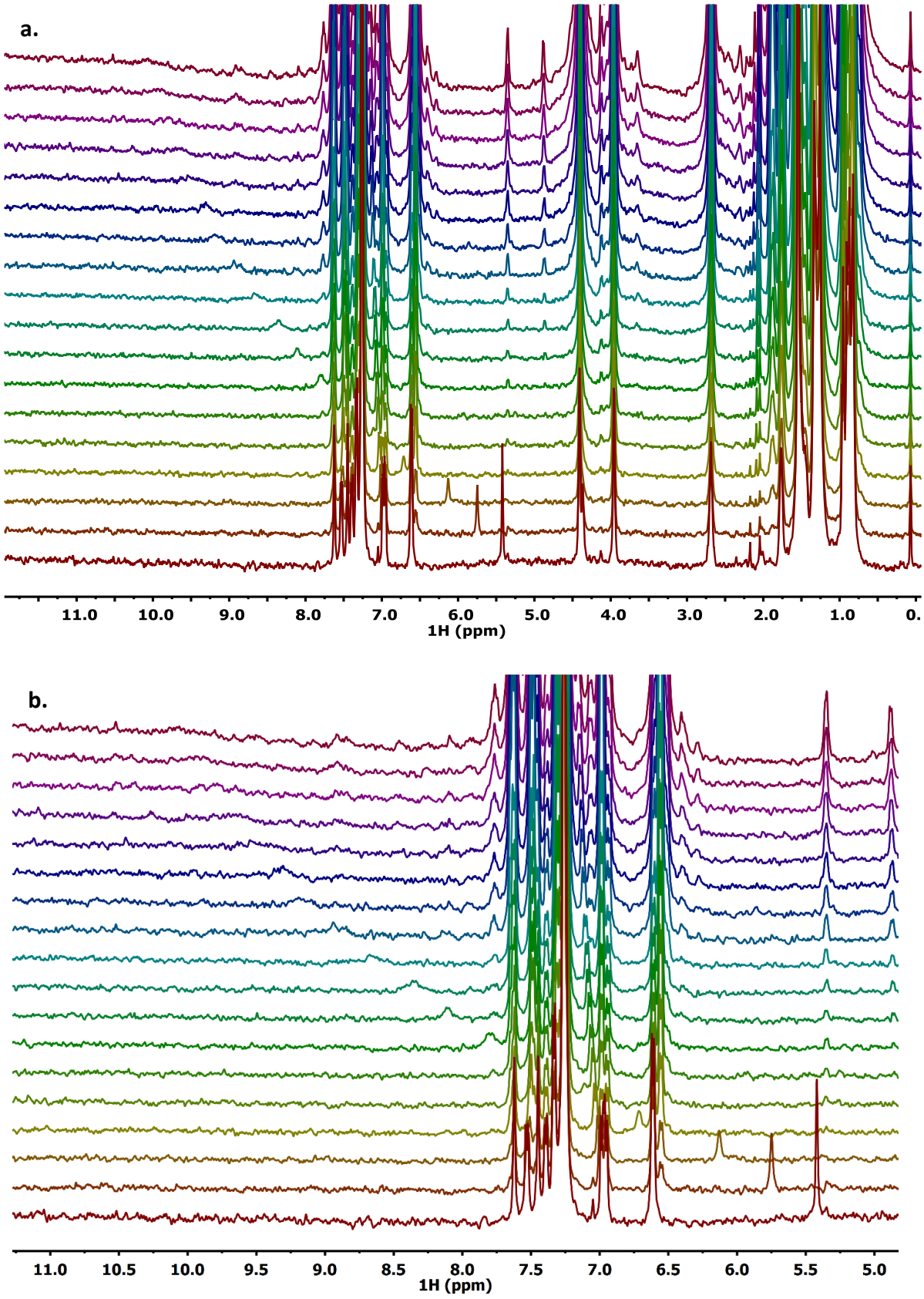


Fig. S3.12 Titration of **A—A** (20.54 mM) into **D—D** (0.5 mM) in $CDCl_3$ (^{1}H-NMR 400 MHz): **a.** complete ^{1}H stacked spectra; **b.** detail of the -OH shift.

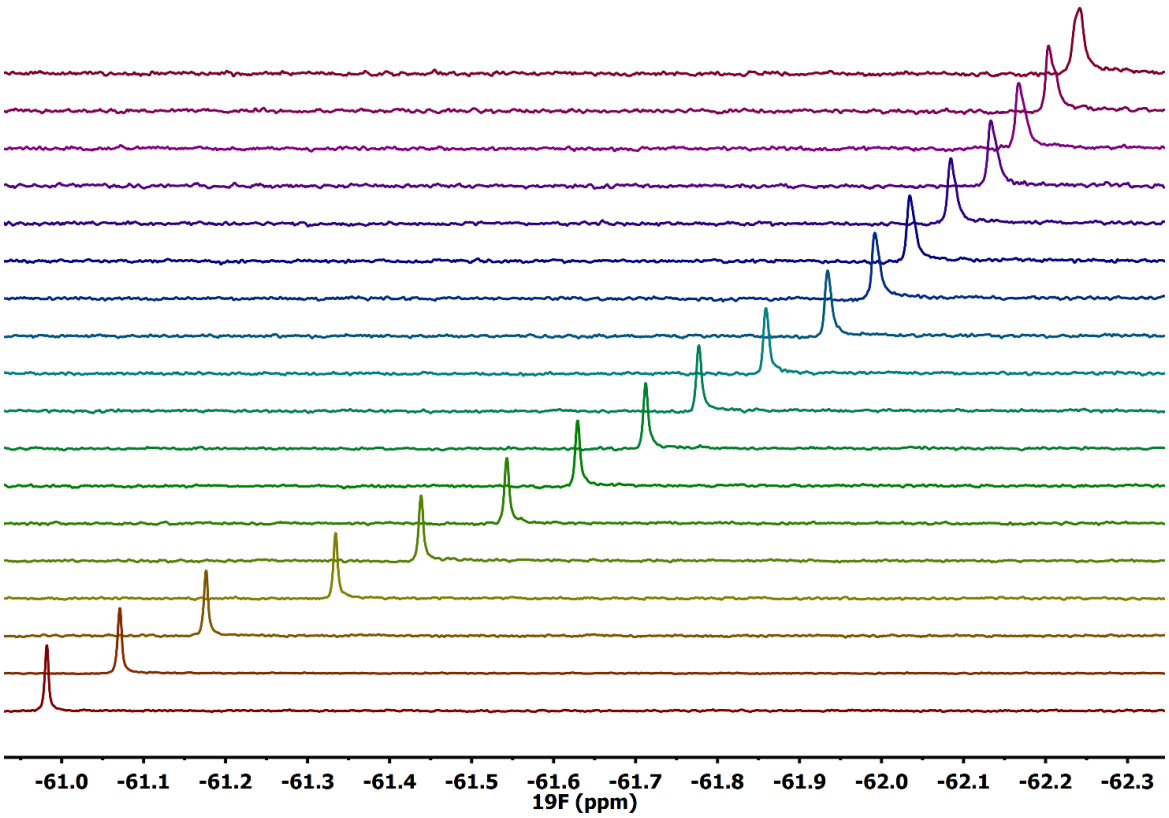


Fig. S3.13 Titration of **A—A** (20.54 mM) into **D—D** (0.5 mM) in $CDCl_3$ (^{19}F-NMR 376 MHz)

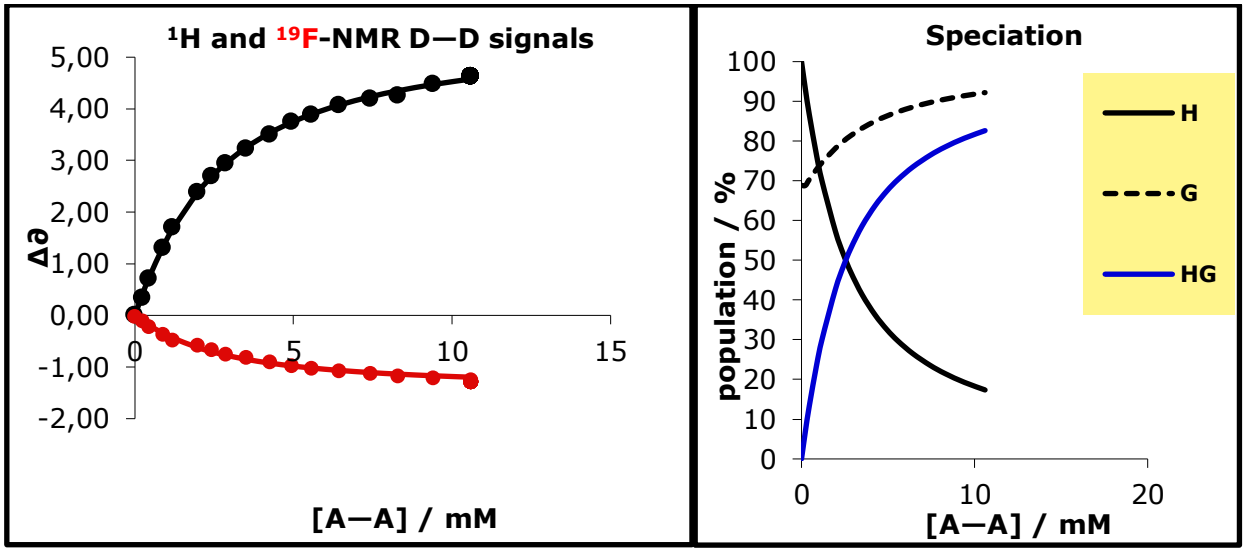


Fig. S3.14 Plot of the change in chemical shift of the **D—D** ^{19}F (**red**) signal in $CDCl_3$ as a function of **[A—A]** (the line represents the best fit to a 1:1 binding isotherm) and speciation as a function of **[A—A]** obtained from the average of the two constants obtained from ^{19}F and ^{1}H fitting.

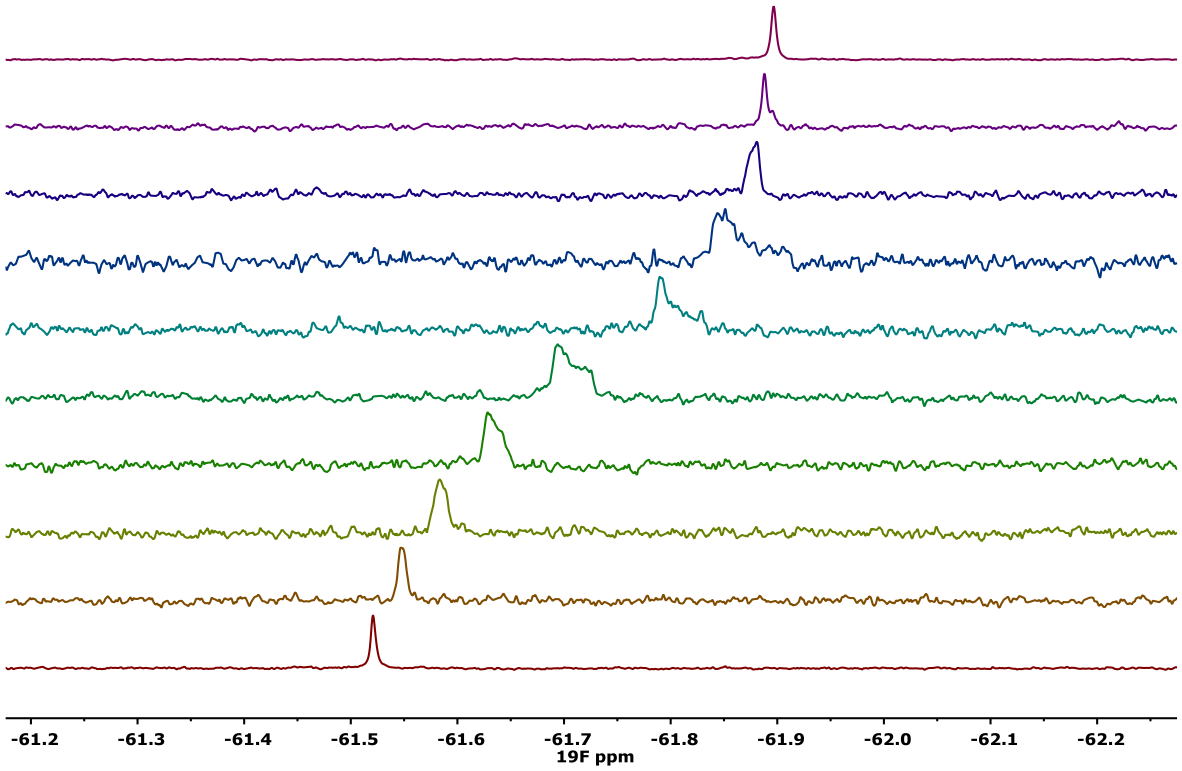


Fig. S3.15 Titration of **A—A** (1.0 mM) into **D—D** (0.1 mM) in toluene-d_8 (^{19}F-NMR 376 MHz)

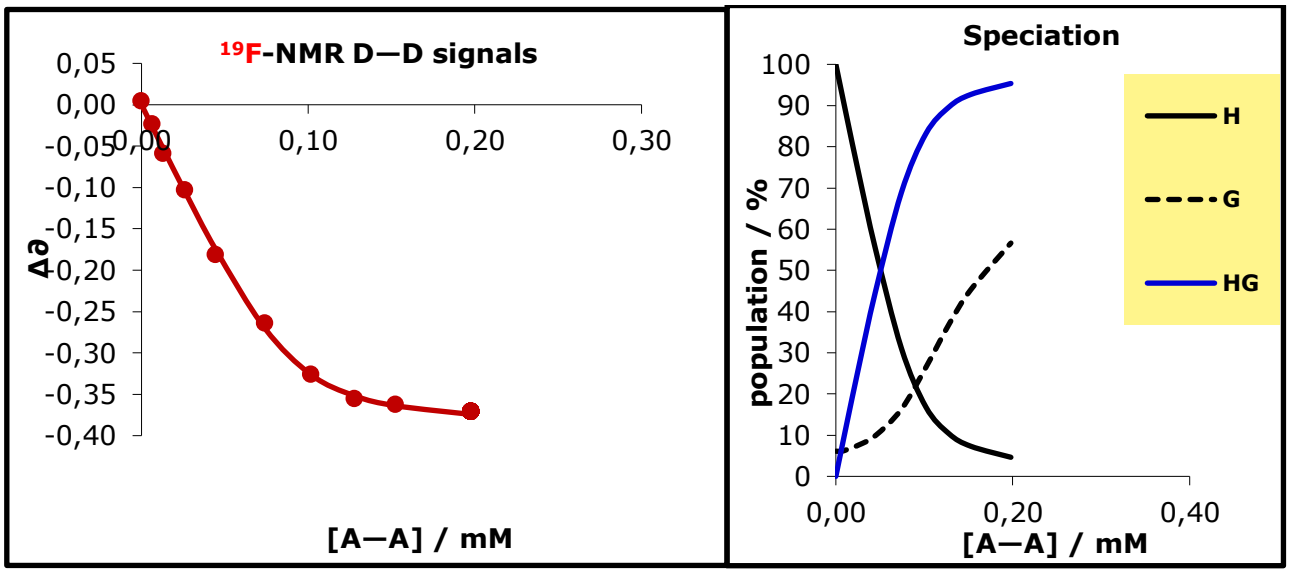


Fig. S3.16 Plot of the change in chemical shift of the **D—D** ^{19}F (**red**) signal in toluene-d_8 as a function of **[A—A]** (the line represents the best fit to a 1:1 binding isotherm) and speciation as a function of **[A—A]**.

3.4 Dilution of DA

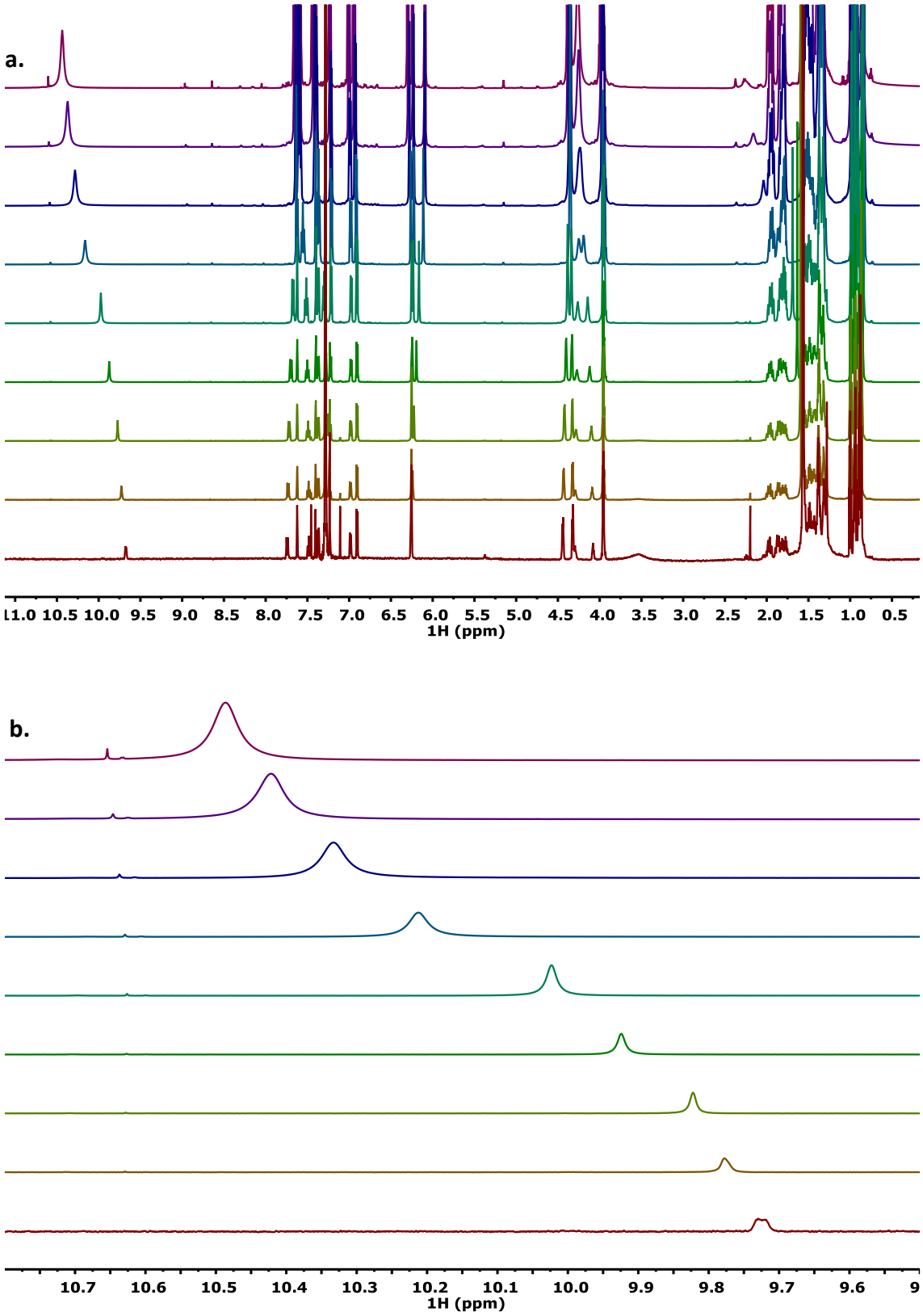


Fig. S3.17 Dilution of **DA** (top to bottom 130 – 95.3 – 60.4 – 30.8 – 10 – 5 – 2 – 1 – 0.2 mM) in $CDCl_3$ (^{1}H-NMR 600 MHz): **a.** complete ^{1}H stacked spectra; **b.** detail of the -OH shift.

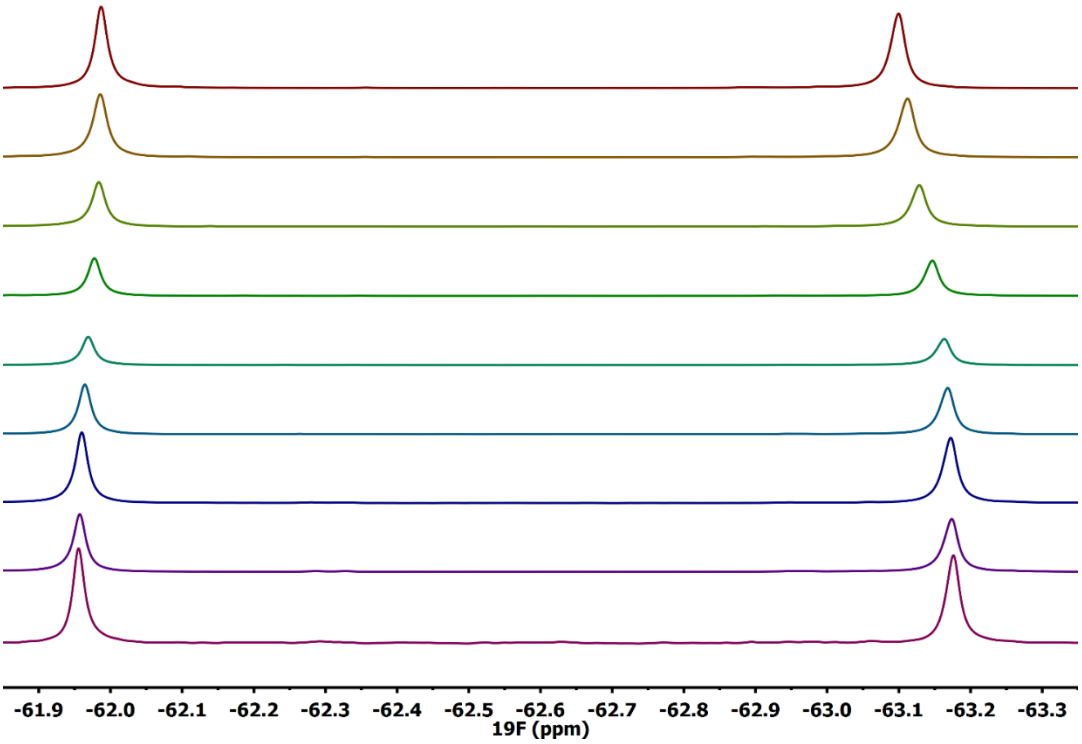


Fig. S3.18 Dilution of **DA** (top to bottom 130 – 95.3 – 60.4 – 30.8 – 10 – 5 – 2 – 1 – 0.2 mM) in $CDCl_3$ (^{19}F-NMR 600 MHz)

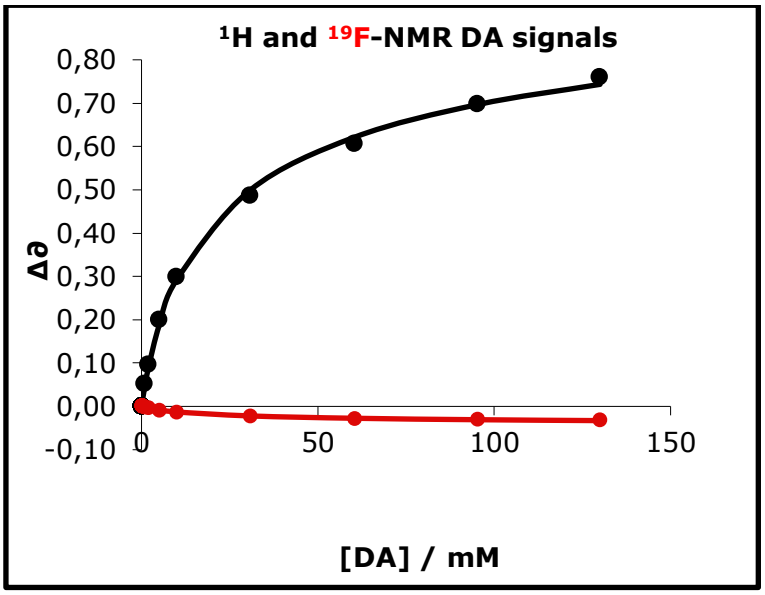


Fig. S3.19 Plot of the change in chemical shift upon dilution of a solution of the **DA** ^{19}F (**red**) and ^{1}H (**black**) signal in $CDCl_3$ as a function of **[DA]** (the line represents the best fit to a 1:1 binding isotherm).

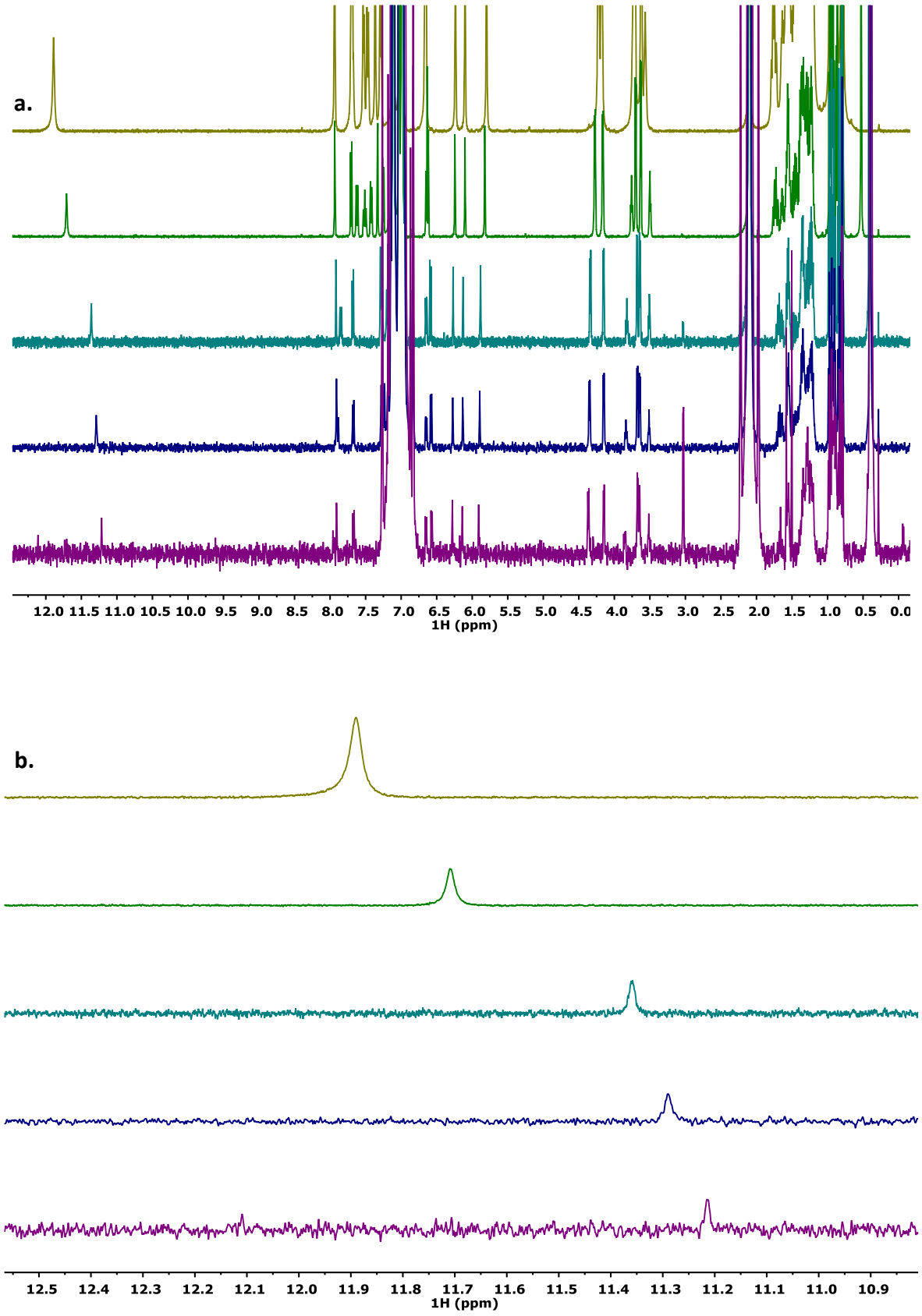


Fig. S3.20 Dilution of **DA** (top to bottom 44 – 4.4 – 0.44 – 0.22 – 0.044 mM) in Toluene-d8 (^{1}H-NMR 400 MHz): **a.** complete ^{1}H stacked spectra; **b.** detail of the -OH shift.

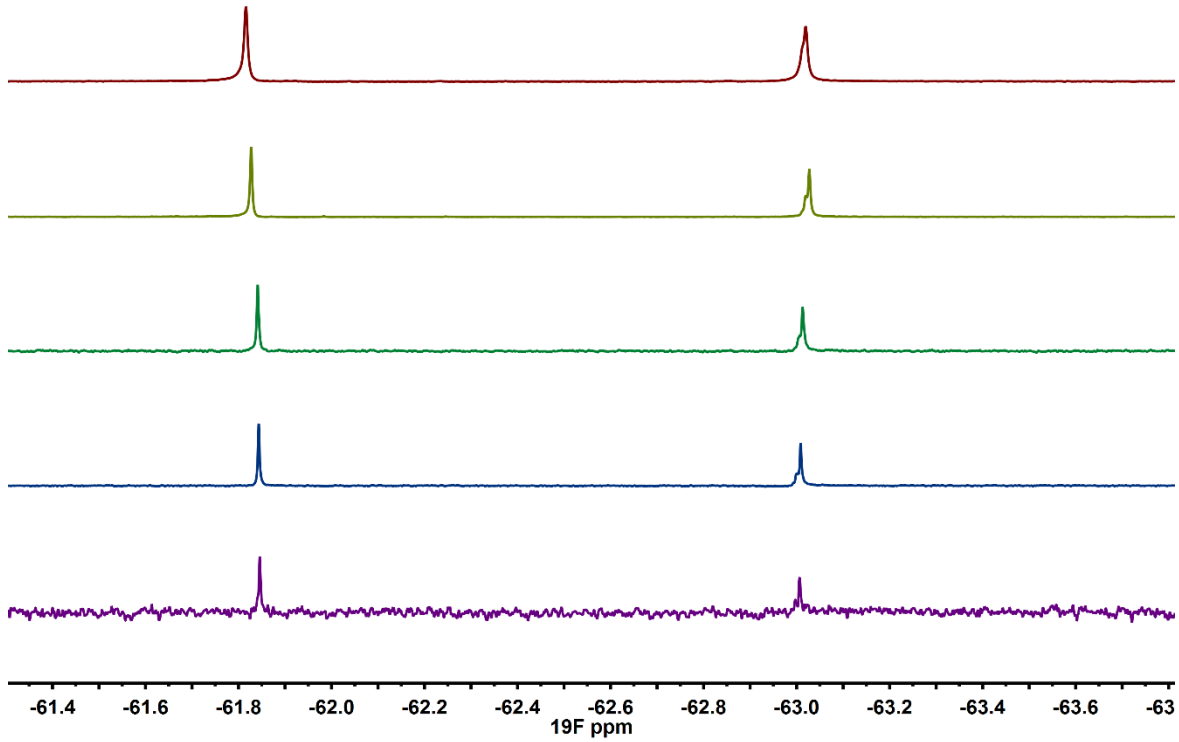


Fig. S3.21 Dilution of **DA** (top to bottom 44 – 4.4 – 0.44 – 0.22 – 0.044 mM) Toluene-d8 (^{19}F-NMR 376 MHz)

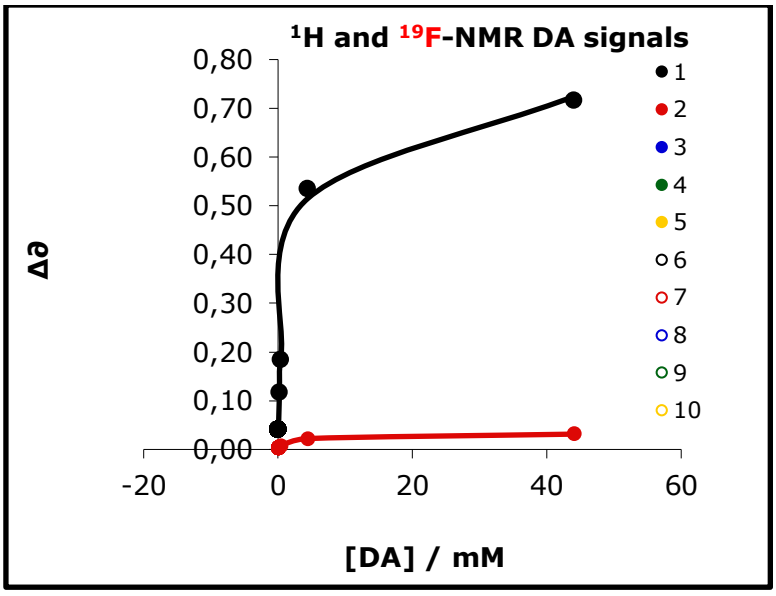


Fig. S3.22 Plot of the change in chemical shift upon dilution of a solution of the **DA** ^{19}F (**red**) and ^{1}H (**black**) signal in Toluene-d_8 as a function of **[DA]** (the line represents the best fit to a 1:1 binding isotherm).

3.5 Dilution of DA'

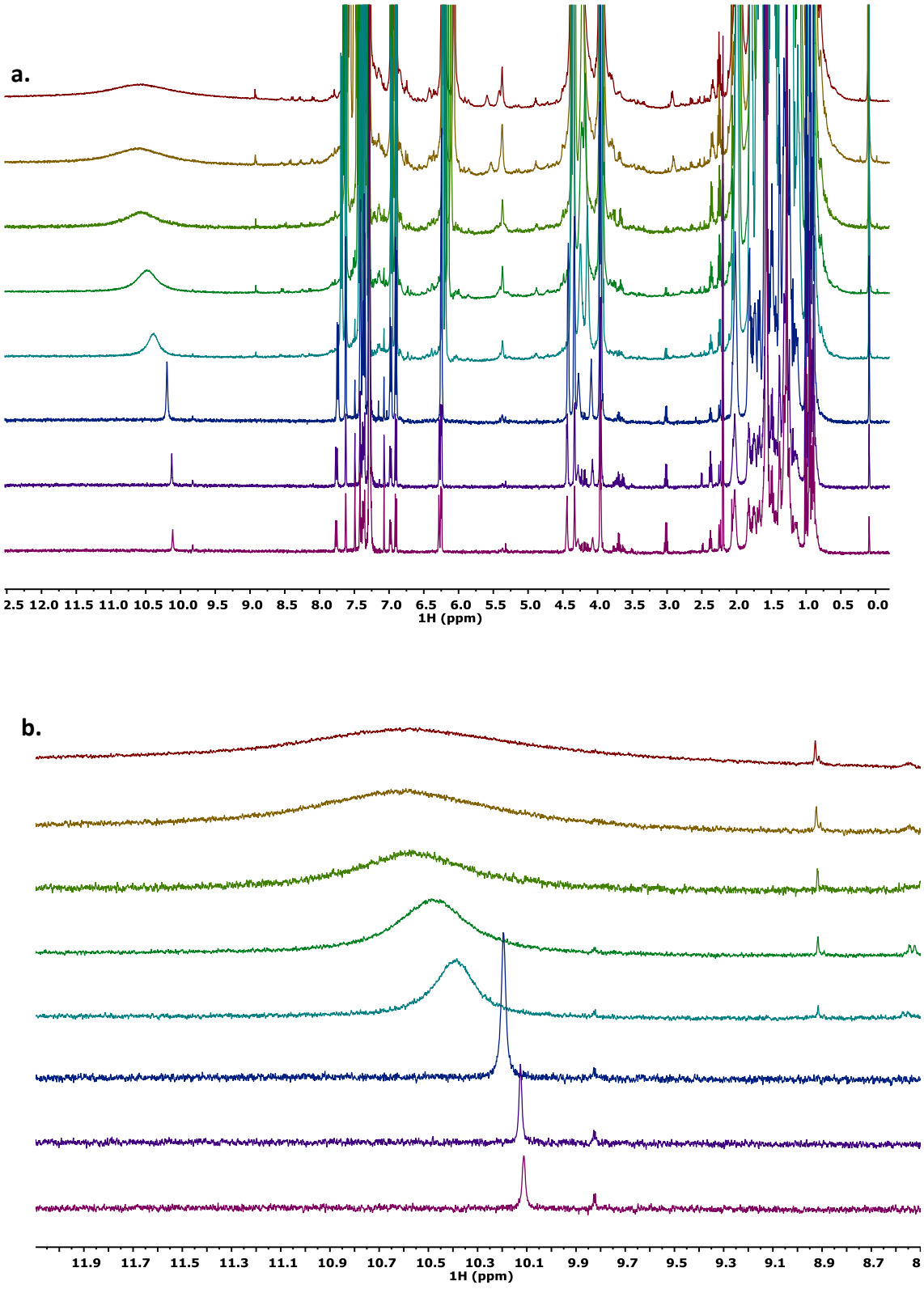


Fig. S3.23 Dilution of **DA'** (top to bottom 76 – 50 – 30 – 15 – 5 – 1 – 0.25 – 0.1 mM) in $CDCl_3$ (^{1}H-NMR 600 MHz): **a.** complete ^{1}H stacked spectra; **b.** detail of the -OH shift.

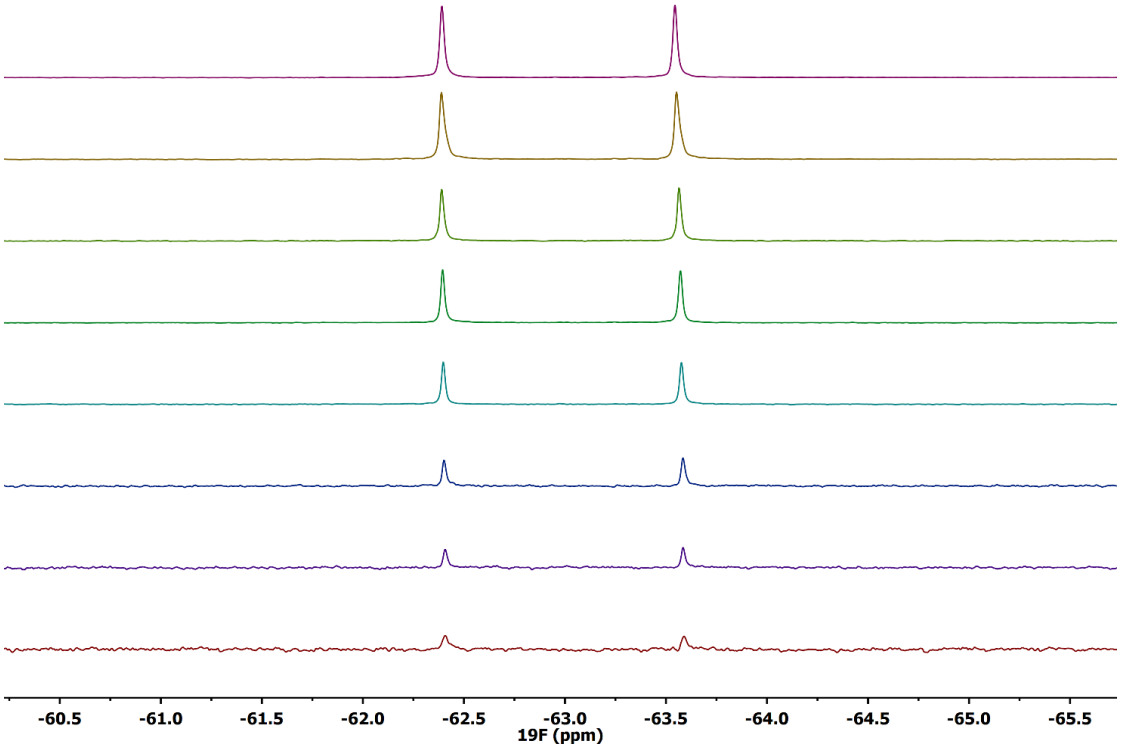


Fig. S3.24 Dilution of **DA'** (top to bottom 76 – 50 – 30 – 15 – 5 – 1 – 0.25 – 0.1 mM) in $CDCl_3$ (^{19}F-NMR 565 Hz)

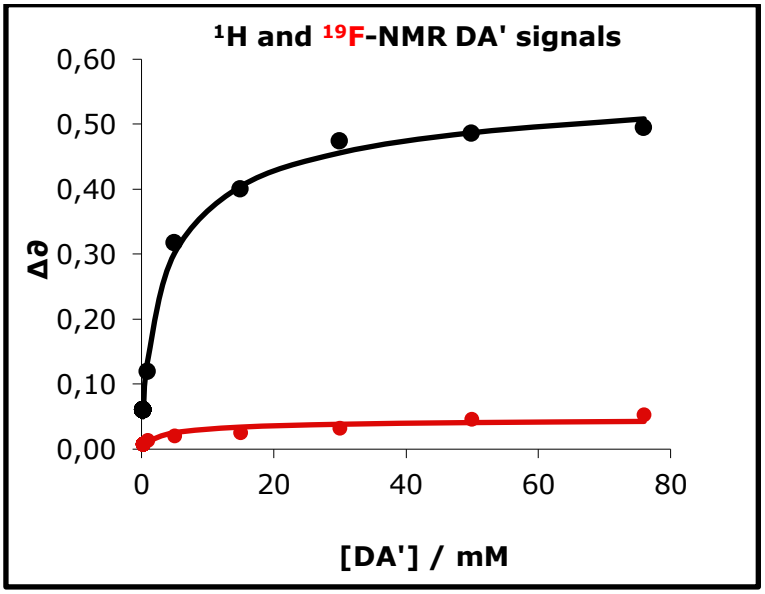


Fig. S3.25 Plot of the change in chemical shift upon dilution of a solution of the **DA'** ^{19}F (**red**) and ^{1}H (**black**) signal in $CDCl_3$ as a function of **[DA']** (the line represents the best fit to a 1:1 binding isotherm).

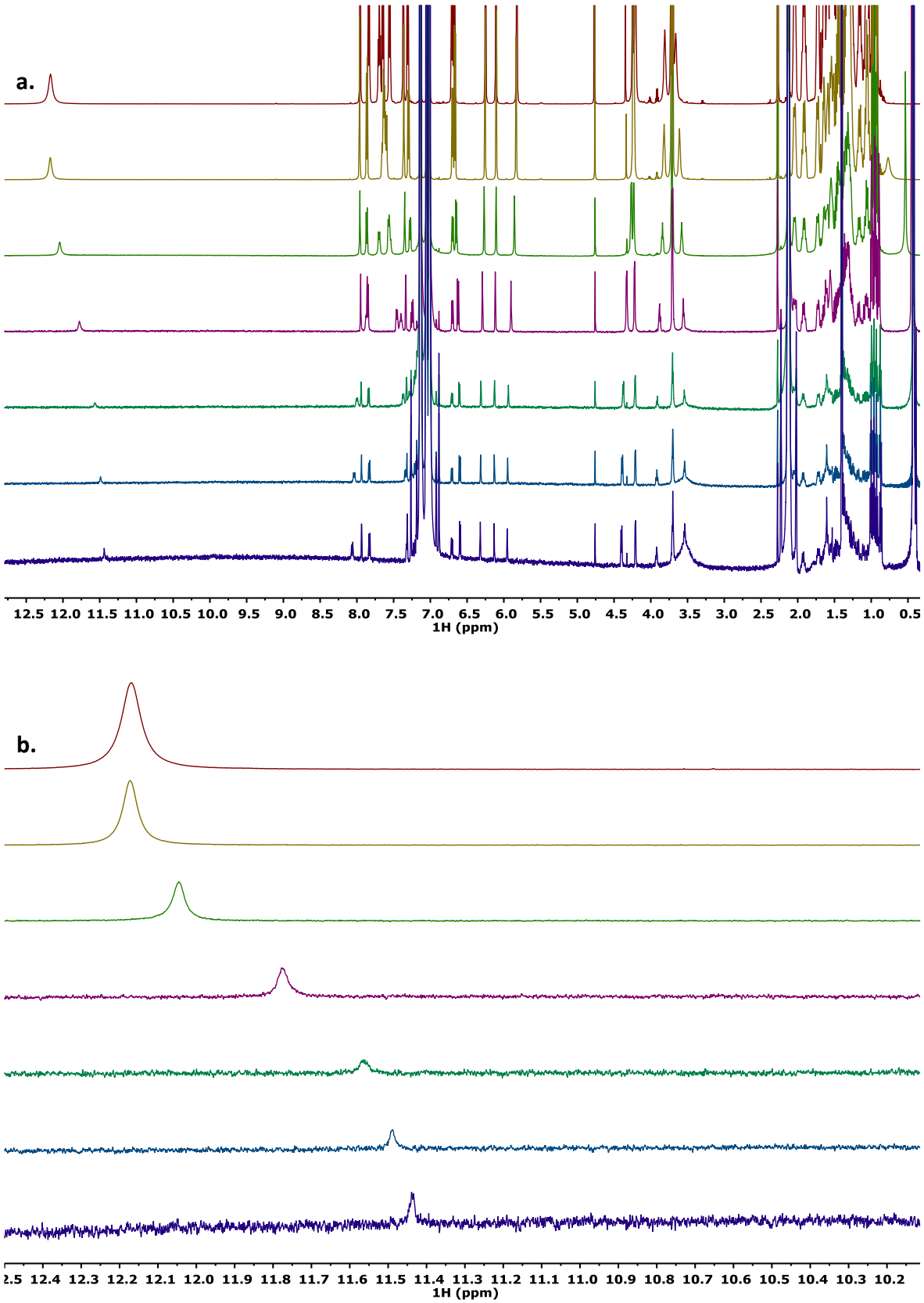


Fig. S3.26 Dilution of **DA'** (top to bottom 60 – 20 – 5 – 1 – 0.25 – 0.125 – 0.040 mM) in Toluene-d_8 (^{1}H-NMR 600 MHz): **a.** complete ^{1}H stacked spectra; **b.** detail of the -OH shift.

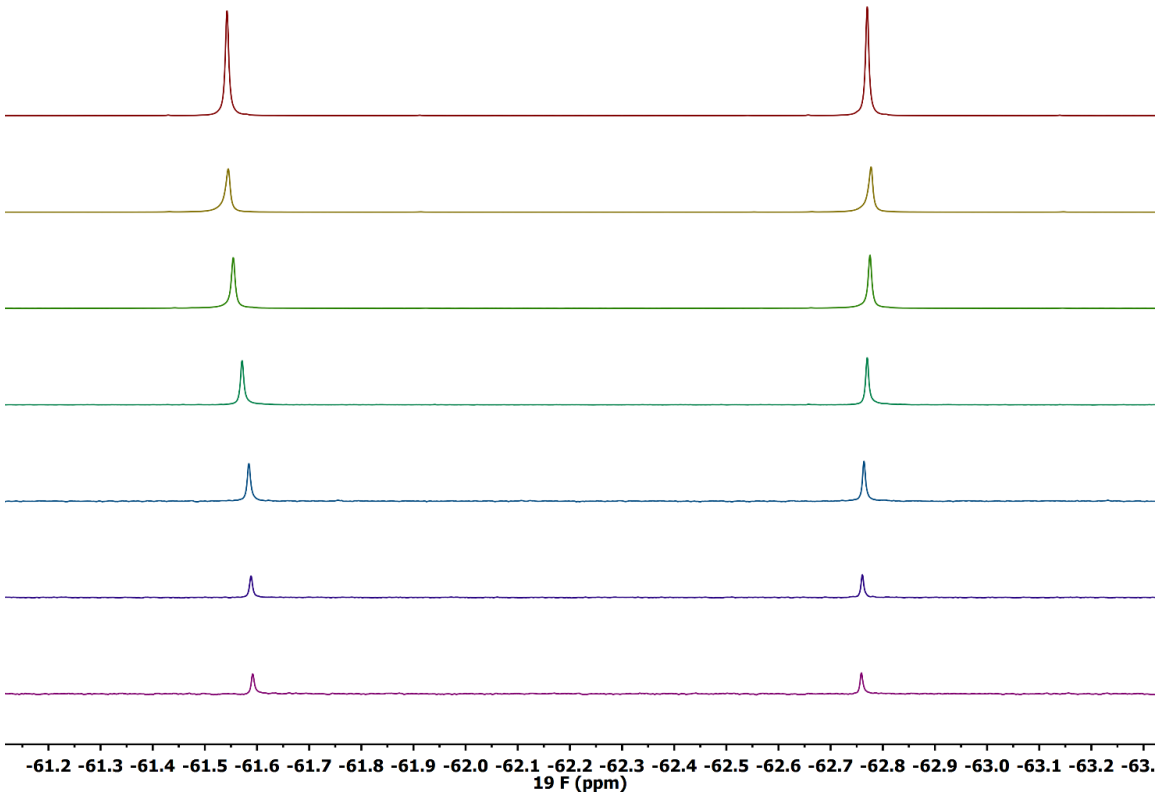


Fig. S3.27 Dilution of **DA'** (top to bottom 60 – 20 – 5 – 1 – 0.25 – 0.125 – 0.040 mM) in Toluene-d_8 (^{19}F-NMR 565 MHz)

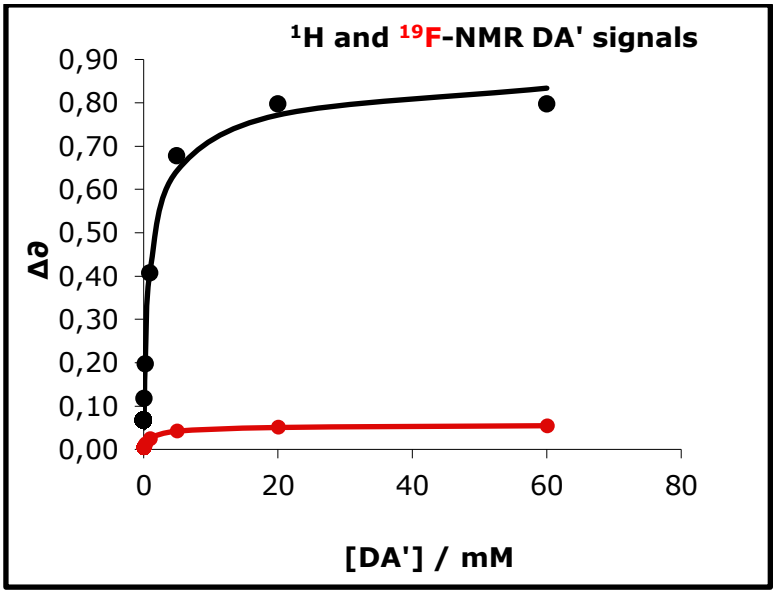


Fig. S3.28 Plot of the change in chemical shift upon dilution of a solution of the **DA'** ^{19}F (**red**) and ^{1}H (**black**) signal in toluene-d_8 as a function of **[DA']** (the line represents the best fit to a 1:1 binding isotherm).

3.6 Dilution of D—A

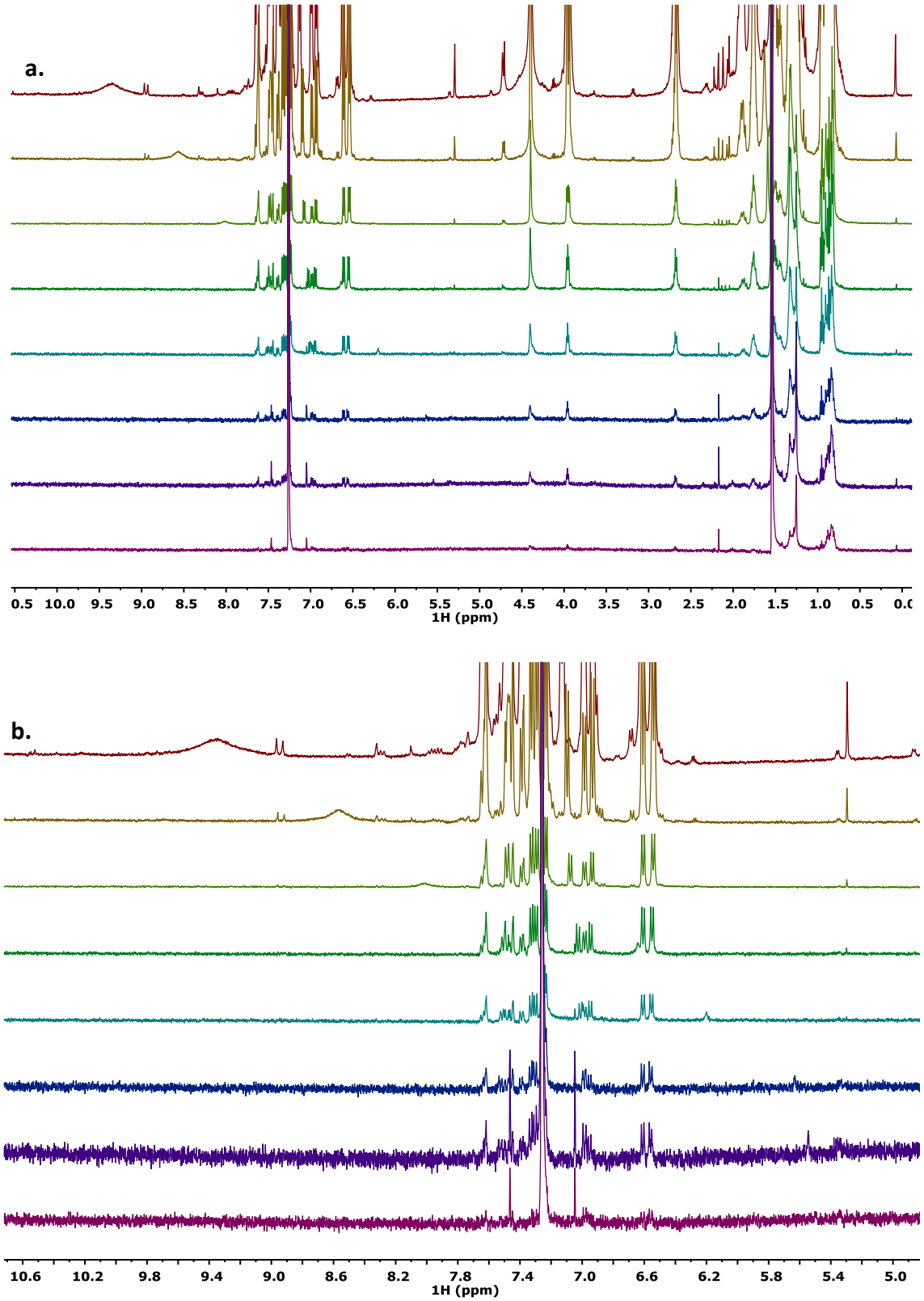


Fig. S3.29 Dilution of **D—A** (top to bottom 60.6 – 30.2 – 10 – 5 – 1 – 0.5 – 0.1 – 0.050) in $CDCl_3$ (^{1}H-NMR 400 MHz): **a.** complete ^{1}H stacked spectra; **b.** detail of the -OH shift.

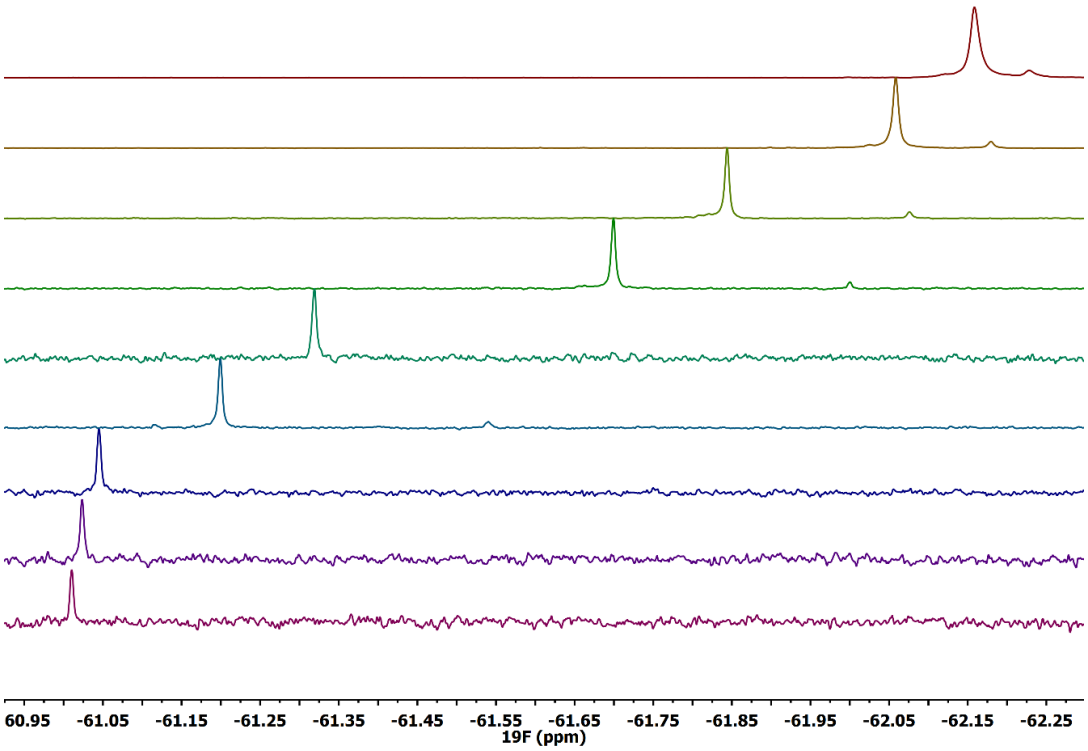


Fig. S3.30 Dilution of **D—A** (top to bottom 60.6 – 30.2 – 10 – 5 – 1 – 0.5 – 0.1 – 0.050 – 0.025 mM) in $CDCl_3$ (^{19}F-NMR 376 MHz)

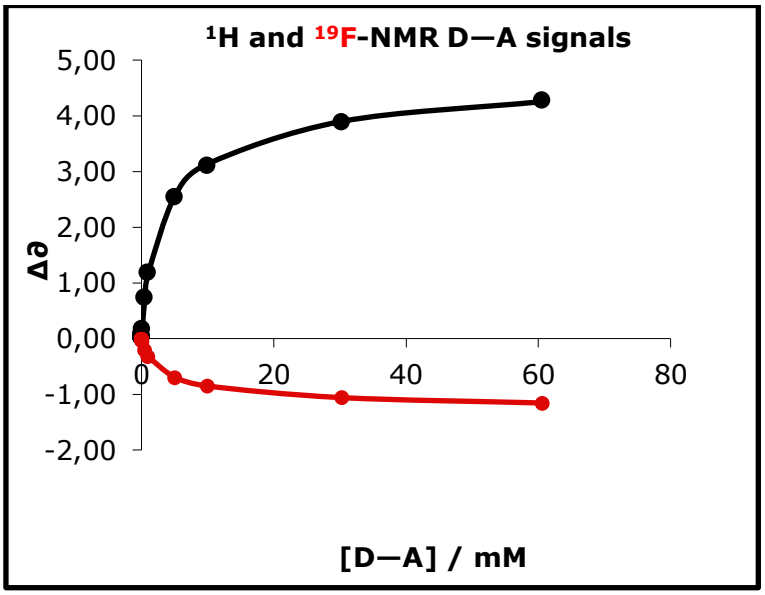


Fig. S3.31 Plot of the change in chemical shift upon dilution of a solution of the **D—A** ^{19}F (**red**) and ^{1}H (**black**) signal in $CDCl_3$ as a function of **[D—A]** (the line represents the best fit to a 1:1 binding isotherm).

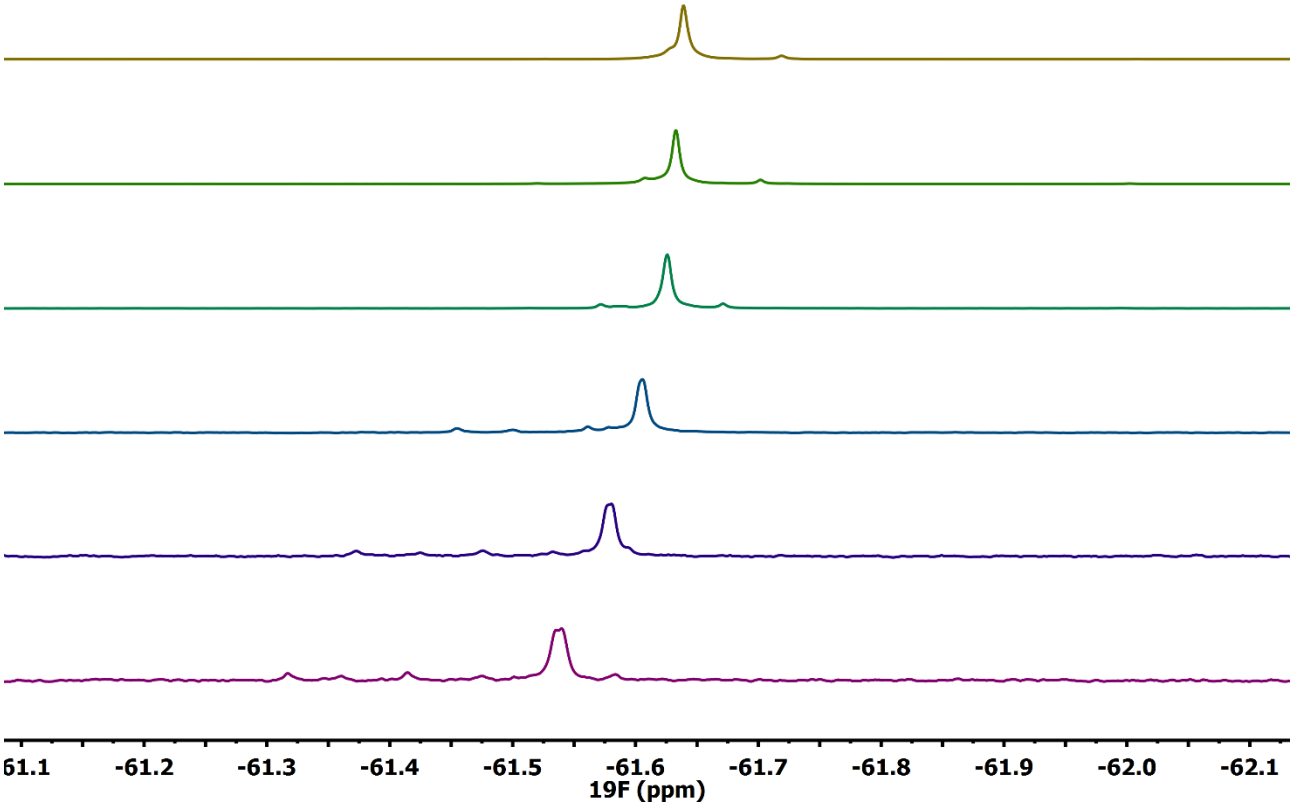


Fig. S3.32 Dilution of **D—A** (top to bottom 18 – 10 – 5 – 1 – 0.25 – 0.1 mM) in Toluene-d_8 (^{19}F-NMR 565 MHz)

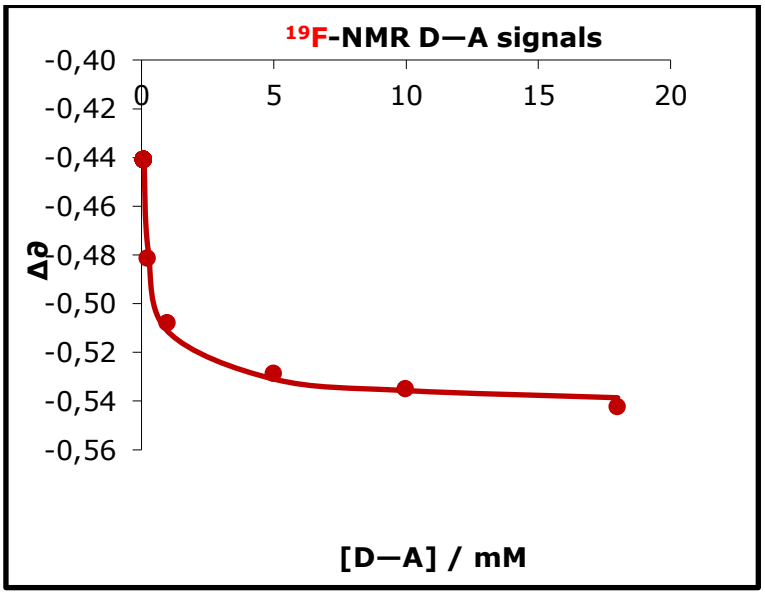


Fig. S3.33 Plot of the change in chemical shift upon dilution of a solution of the **D—A** ^{19}F (**red**) signal in toluene-d_8 as a function of **[D—A]** (the line represents the best fit to a 1:1 binding isotherm).

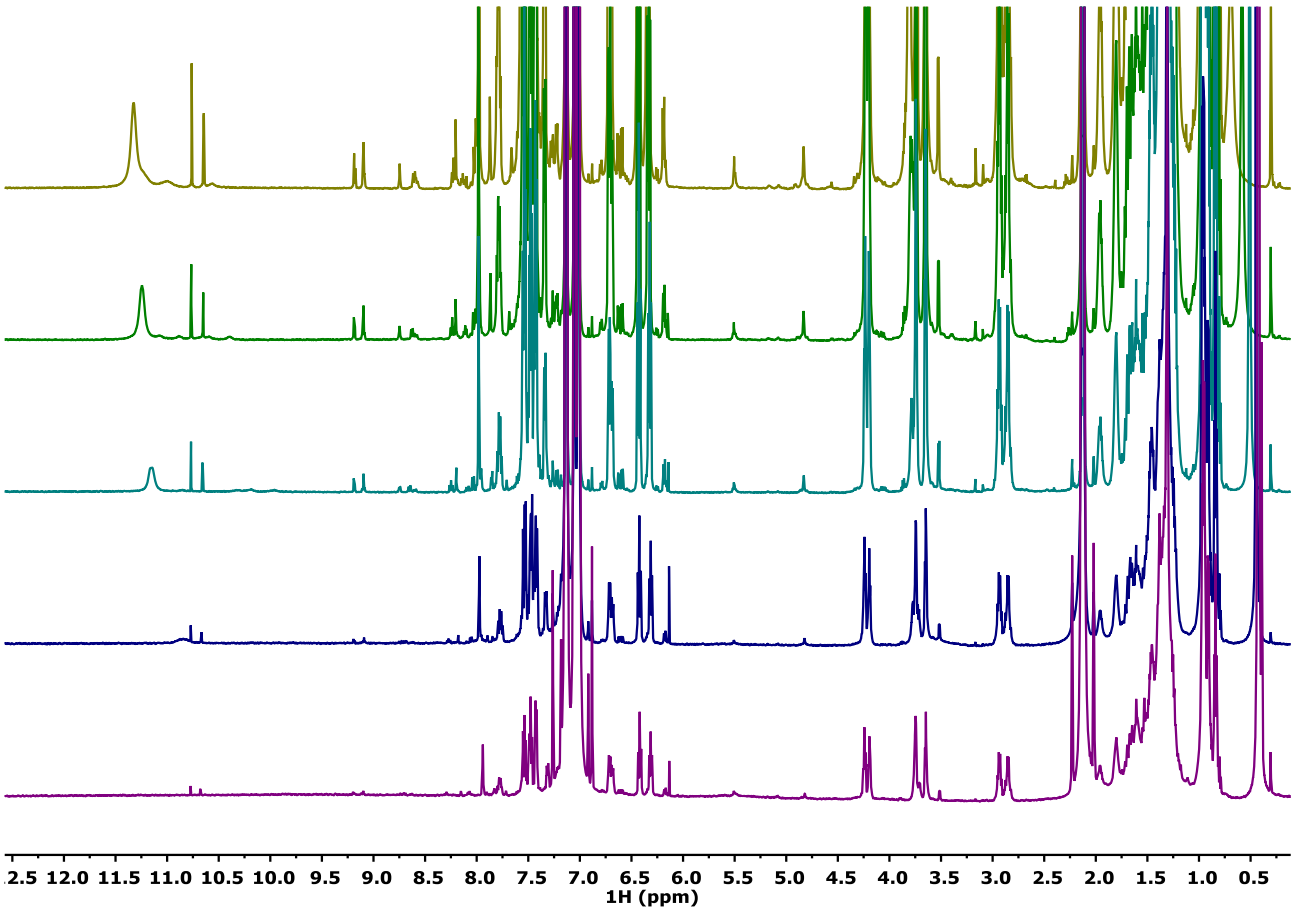


Fig. S3.34 Dilution of **D—A** (top to bottom 18 – 10 – 5 – 1 – 0.25) in $CDCl_3$ (^{1}H-NMR 600 MHz). In this case the fitting is not possible: the -OH proton signal is too broad to be detected already at 0.25 mM concentration.

3.7 Log K values from fitting

Solvent	Complex	log K_{obs} (M^{-1})
	D●A	2.30
	DD●AA	3.45
	DA●DA	1.48
	D●A'	2.46
$CDCl_3$	**DD●A'A'**	3.50
	DA'●DA'	1.47
	D●A	2.30
	D-D● A-A	2.69
	D-A● D-A	2.26
	D●A	3.46
	DD●AA	5.70
	DA●DA	2.47
	D●A'	3.74
Toluene	**DD●A'A'**	6.00
	DA'●DA'	2.80
	D●A	3.46
	D-D● A-A	5.53
	D-A● D-A	5.03

Table S3.1 Summary of the average log*K* used to calculate the effective molarities (EM_d and EM_f) and the K_{fold} reported in Table 1 (main text).

4. Bibliography

1 L. Gabrielli, D Núñez-Villanueva, C. A. Hunter, *Chem. Sci*., **2020**, *11*, 561.