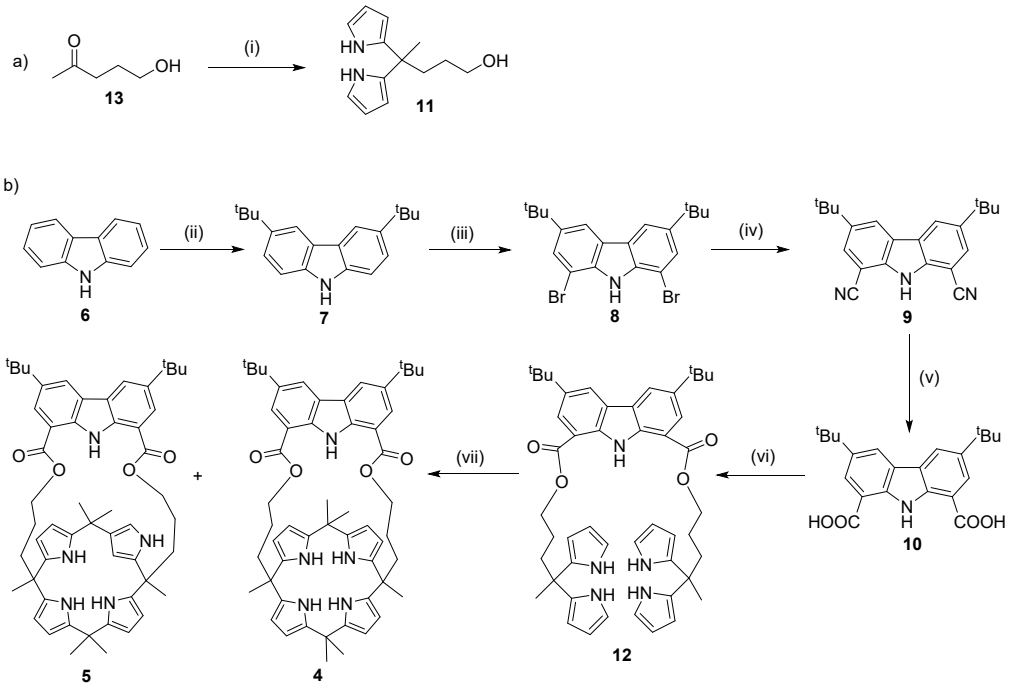
Supporting Information

Section S1. General information and instrumentation.

^{1}H NMR spectra were recorded on 400 and 600 MHz Bruker NMR spectrophotometers using TMS as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; br s, broad singlet; d, doublet; t, triplet; m, multiplet. ^{13}C NMR spectra were proton decoupled and recorded on a 100 MHz and 150 MHz Bruker spectrometer using TMS as the internal standard. Pyrrole was distilled at atmospheric pressure from CaH_2. Uv-vis and fluorescence titrations were performed using HPLC grade $CHCl_3$. All other chemicals and solvents were purchased from commercial sources and were used as such, unless otherwise mentioned. The compound **11** was prepared according to the reported literature procedure.[1] The dicarboxylic acid **10** was synthesized by slightly modifying the literature procedure.[2]

Section S2. Experimental section: synthetic scheme and synthetic procedures.

Synthetic Scheme



Scheme 1. Reagents and conditions: a) i) pyrrole, trifluoracetic acid, stirring, 0 °C to rt, 20 min. 35%; b) ii) ^{t}BuCl, anhydrous $ZnCl_2$, nitromethane, stirring, rt, 2.5 h, 75%; iii) Br_2, glacial AcOH, stirring, rt, 1h, 90%; iv) CuCN, N-Methyl-2-pyrrolidone **(**NMP), 180^{0}C, 12h, 65%; v) NaOH, EtOH/H_2O, reflux, 35h, 85%; vi) **11**, EDC.HCl, HOBt, DIPEA, DMF, stirring, rt, 10h, 27%; vii) Acetone, $BF_3(OEt)_2$, high dilution condition, stirring rt, 12% and 1% For **4** and **5**, respectively.

Synthetic procedures

4,4-di(1H-pyrrol-2-yl)pentan-1-ol (11)

To a mixture of pyrrole (25 mL, 0.36 mol) and 5-hydroxy- 2-pentanone (6.04 g, 59.15mmol), TFA (0.420 mL, 5.48 mmol) was added at 0˚C. After stirring at room temperature for 20 minutes, the reaction was quenched by adding 0.1(N) aqueous NaOH. Aqueous layer was extracted with dichloromethane (3 × 30 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated in vacuo. The residue was then purified by column chromatography over silica gel using 20% ethyl acetate in hexane (v/v) as eluent to give pure **11** (4.5 g, yield: 35%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ in ppm: 10.21(s, 2H), 6.55 (s, 2H), 5.84 (s, 2H), 5.70 (s, 2H), 4.31 (t, J = 5.12 Hz, 1H), 1.93-1.89 (m, 2H), 1.50 (s,

3H), 1.26-1.18 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ in ppm: 138.2, 116.7, 107.2, 104.2, 62.5, 38.7, 37.2, 27.8, 26.1. HRMS m/z for $C_{13}H_{19}N_2O$ $[M+H]^+$ calculated 219.1492, found 219.1487.

3, 6-di-tert-butyl-9H-carbazole (7)

Carbazole (3.34 g, 20 mmol) was suspended in nitromethane (100 mL) under argon atmosphere and anhydrous $ZnCl_2$ (18.1 g, 60 mmol) was added. To this suspension was added *tert*-butyl chloride (5.6 g, 4.55 mL, 60 mmol) dropwise via syringe while the solid slowly disappeared. The solution was stirred at room temperature for 2.5 h. After the completion of the reaction, the reaction mixture was poured in ice bath. Aqueous part was extracted by DCM (3 × 30 mL), dried over sodium sulfate and concentrated under reduced pressure to get the crude product. Crude product was then purified by silica gel column chromatography using 5% EtOAc in hexane (v/v) as eluent to afford the pure **7** (4.2 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ in ppm : 8.09 (s, 2H), 7.84 (s, 1H), 7.47 (d, J = 10.5 Hz, 2H), 7.33 (d, J = 9.2 Hz, 2H), 1.47 (s, 18H).^{13}C NMR (100 MHz, $CDCl_3$) δ in ppm : 144.92, 136.47, 126.78, 124.97, 116.10, 104.15, 35.07, 32.05.

1, 8-dibromo-3, 6-di-tert-butyl-9H-carbazole (8)

Compound **7** (3.1 g, 11.11 mmol) was dissolved in glacial acetic acid (100 mL). To this solution Br_2 (3.94 g, 1.27 mL, 24.66 mmol) was added drop wise via syringe at room temperature. After stirring the reaction mixture for 60 min, the volatile compounds were removed under reduced pressure. The residue was dissolved in excess hexane and washed with 1M aqueous NaOH solution. The aqueous solution was then extracted with hexane (2 × 30 mL). The combined hexane solution dried over sodium sulfate. Organic layer was then concentrated under reduced pressure and the product was washed with pentane to afford sufficiently pure **8** (4.5 g, 90%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ in ppm : 8.12 (s, 1H), 7.96 (s, 2H), 7.62 (d, 2H), 1.42 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ in ppm : 142.38, 138.18, 123.66, 123.47, 116.32, 110.14, 34.83, 32.18.

3, 6-di-tert-butyl-9H-carbazole-1, 8-dicarbonitrile (9)

In a 250 mL round bottomed flask compound **8** (6.33 g, 14.48 mmol) was dissolved in 100 mL N-Methyl-2-pyrrolidone (NMP). Then, CuCN (3.4 g, 37.88 mmol) was added to the solution and the resultant mixture was refluxed at 180°C for 12h. After cooling to room temperature the

solution was poured into a 500 mL beaker containing 200 mL ammonia and 100 mL ethyl acetate and the resultant mixture was stirred for 30 min. The precipitate was filtered through celite bed and then the filtrate was extracted with ethyl acetate (5 × 200 mL). The combined organic extracts were washed with brine (2 × 150 mL) and dried over anhydrous sodium sulfate. Organic layer was concentrated in vacuo and the crude product was purified by silica gel coloumn chromatography using 5% EtOAc in hexane (v/v) as eluent to get the pure product **9** (3.5g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ in ppm : 9.24 (s, 1H), 8.29 (s, 2H), 7.81 (d, J = 1.2 Hz, 2H), 1.45 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ in ppm : 144.15, 139.17, 128.53, 123.97, 122.31, 117.21, 94.41, 35.09, 31.85.

3,6-di-tert-butyl-9H-carbazole-1,8-dicarboxylic acid (10)

Compound **9** (1.8 g, 5.46 mmol) was dissolved in ethanol/water (1:2, v/v) followed by addition of NaOH (2.2 g, 54.63 mmol). The resultant mixture was refluxed for 35 h. After completion of the reaction, it was cooled to room temperature. EtOH was evaporated then diluted with H_2O and acidified with dilute HCl. Then, it was filtered through funnel. Residue was washed with cold water and dried to get the product **10** (2.1 g, 27%). The dicarboxylic acid **10** thus obtained was sufficiently pure and used directly in the next without further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ in ppm : 13.39 (s, 2H), 10.87 (s, 1H), 8.65 (s, 2H), 8.05 (s, 2H), 1.44 (s, 18H). ^{13}C NMR (100 MHz, DMSO-d_6) δ in ppm : 168.04, 141.90, 137.89, 125.03, 123.63, 123.00, 112.10, 34.55, 31.70.

bis(4,4-di(1H-pyrrol-2-yl)pentyl) 3,6-di-tert-butyl-9H-carbazole-1,8-dicarboxylate (12)

Compound **10** (900 mg, 2.456 mmol) and **11** (1.608 g, 7.37 mmol) were dissolved in dry DMF (15 mL) and cooled to 0 ˚C and then EDC.HCl (1.883 g, 9.823 mmol) was added under inert atmosphere followed by addition of DIPEA (1.587 g, 2.12 mL, 12.28 mmol) and HOBt (1.327 g, 9.823 mmol). The mixture was then stirred at room temperature for 10 h. After completion of the reaction DMF was evaporated under reduced pressure. Then water was added and extracted with ethyl acetate (2×300 mL). The combined organic layer was dried over anhydrous Na_2SO_4 to get the crude product. The crude product was purified by silica gel coloumn chromatography using 25% ethyl acetate in hexane (v/v) as eluent to afford the pure compound **12** (470 mg, 35%) as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ in ppm : 10.85 (s, 1H), 10.30 (s, 4H), 8.71 (s,

2H), 8.09 (s, 2H), 6.58 (s, 4H), 5.86 (s, 4H), 5.78 (s, 4H), 4.33 (t, J = 6.7 Hz, 4H), 2.17 – 2.12 (m, 4H), 1.69 – 1.63 (m, 4H), 1.59 (s, 6H), 1.44 (s, 18H). ^{13}C NMR (150 MHz, DMSO-d_6) δ in ppm : 166.36, 138.11, 137.80, 124.59, 123.75, 116.57, 111.23, 106.36, 103.82, 65.27, 38.33, 37.00, 34.62, 31.69, 25.17, 24.17. HRMS m/z for $C_{48}H_{57}N_5O_4$ $[M+H]^+$ calculated 768.4483, found 768.4484.

Synthesis of receptors 4 and 5

In a 500 mL round bottom flask, compound **12** (470 mg, 0.61 mmol) was dissolved in acetone (250 mL) and then $BF_3.OEt_2$ (130 mg, 0.115 mL, 0.92 mmol) was added. After stirring at room temperature for 4 h, the reaction mixture was quenched by adding triethyl amine (0.500 mL) Excess acetone was evaporated under reduced pressure and water was added and extracted with ethyl acetate (2×200 mL). Combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude mass was purified by silica gel coloumn chromatography using 5% and 8% ethyl acetate in hexane (v/v) as eluent to yield the pure product **4** (62 mg, 12%) and **5** (5.5 mg, 1%) as white solids, respectively.

Spectral data of **4**: ^{1}H NMR (600 MHz, $CDCl_3$) δ in ppm : 10.75 (s, 1H), 8.35 (d, J = 1.9 Hz, 2H), 8.20 (d, J = 1.9 Hz, 2H), 7.61 (d, J = 3.0 Hz, 4H), 5.91 (t, J = 3.1 Hz, 4H), 5.77 (t, J = 3.0 Hz, 4H), 4.38 (t, J = 6.4 Hz, 4H), 2.17 – 2.13 (m, 4H), 1.82 – 1.78 (m, 4H), 1.52 (s, 6H), 1.50 (s, 18H), 1.48 (s, 6H), 1.35 (s, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ in ppm : 167.65, 142.54, 138.68, 138.42, 136.22, 125.97, 124.19, 122.26, 112.21, 104.50, 103.25, 65.26, 39.21, 37.71, 35.58, 34.97, 32.08, 30.81, 29.65, 28.16, 25.70. HRMS m/z for $C_{54}H_{65}N_5O_4$ $[M+H]^+$ calculated 848.5109, found 848.5062.

Spectral data of **5**: ^{1}H NMR (600 MHz, $CDCl_3$) δ in ppm : 10.75 (s, 1H), 8.38 (s, 1H), 8.33 (s, 1H), 8.24 (s, 1H), 8.17 (s, 1H), 7.77 (brs, 1H), 7.65 (brs, 1H), 7.44 (brs, 1H), 7.14 (brs, 1H), 6.10-6.07 (m, 1H), 5.99-5.98 (m, 1H), 5.96-5.95 (m, 1H), 5.90-5.89 (m, 1H), 5.87-5.86 (m, 1H), 5.80-5.79 (s, 1H), 5.55 (brs, 1H), 5.14 (brs, 1H), 4.66-4.62 (m, 1H), 4.37-4.33 (m, 1H), 4.22-4.18 (m, 1H), 3.99-3.95 (m, 1H), 2..72-2.67 (m, 1H), 2.17-2.12 (m, 2H), 1.88-1.82 (m, 5H), 1.56 (s, 3H), 1.53 (s, 9H),1.52 (m, 6H), 1.47 (s, 12H), 1.30 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ in ppm : 167.38, 166.87, 142.61, 142.59, 142.33, 140.30, 138.66, 138.62, 137.61, 137.47, 136.33, 133.85, 132.63, 131.76, 126.89, 124.21, 124.18, 123.78, 122.14, 121.95, 112.59,

112.33, 111.77, 105.05, 104.93, 104.58, 103.46, 101.34, 100.39, 64.90, 64.22, 38.99, 38.95, 38.36, 36.36, 35.57, 34.79, 34.73, 34.43, 31.96, 31.80, 30.28, 29.84, 29.72, 29.64, 28.35, 27.70, 25.54, 25.19. HRMS m/z for $C_{54}H_{65}N_5O_4$ $[M+H]^+$ calculated 848.5109, found 848.5126.

Section S3. Theoretical methods.

The geometry optimization of the complex of fluoride with receptor **4** were performed at the PBE0-D4/def2-TZVP level of theory[4-7]without symmetry constrains by means of the Turbomole 7.7 software.[8] The optimization yielded to a C_2 symmetry complex. The minimum nature of the complex has been verified using frequency calculations.

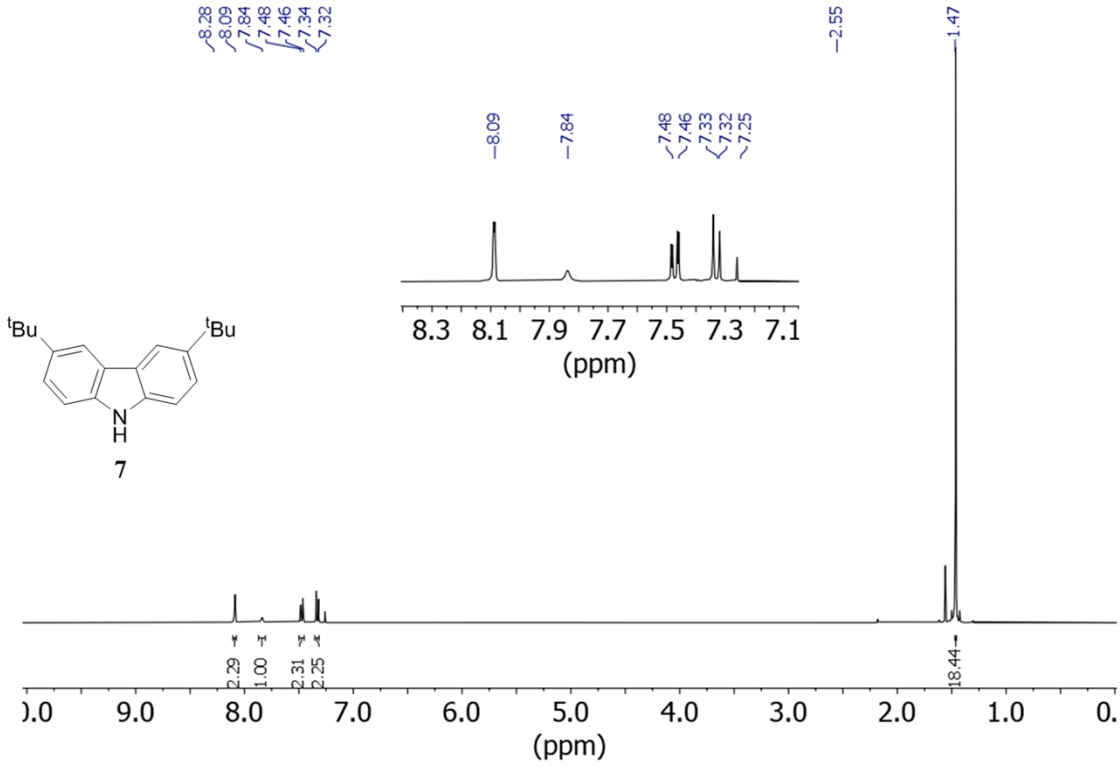


Figure S1. ^{1}H NMR spectrum of **7** recorded in $CDCl_3$.

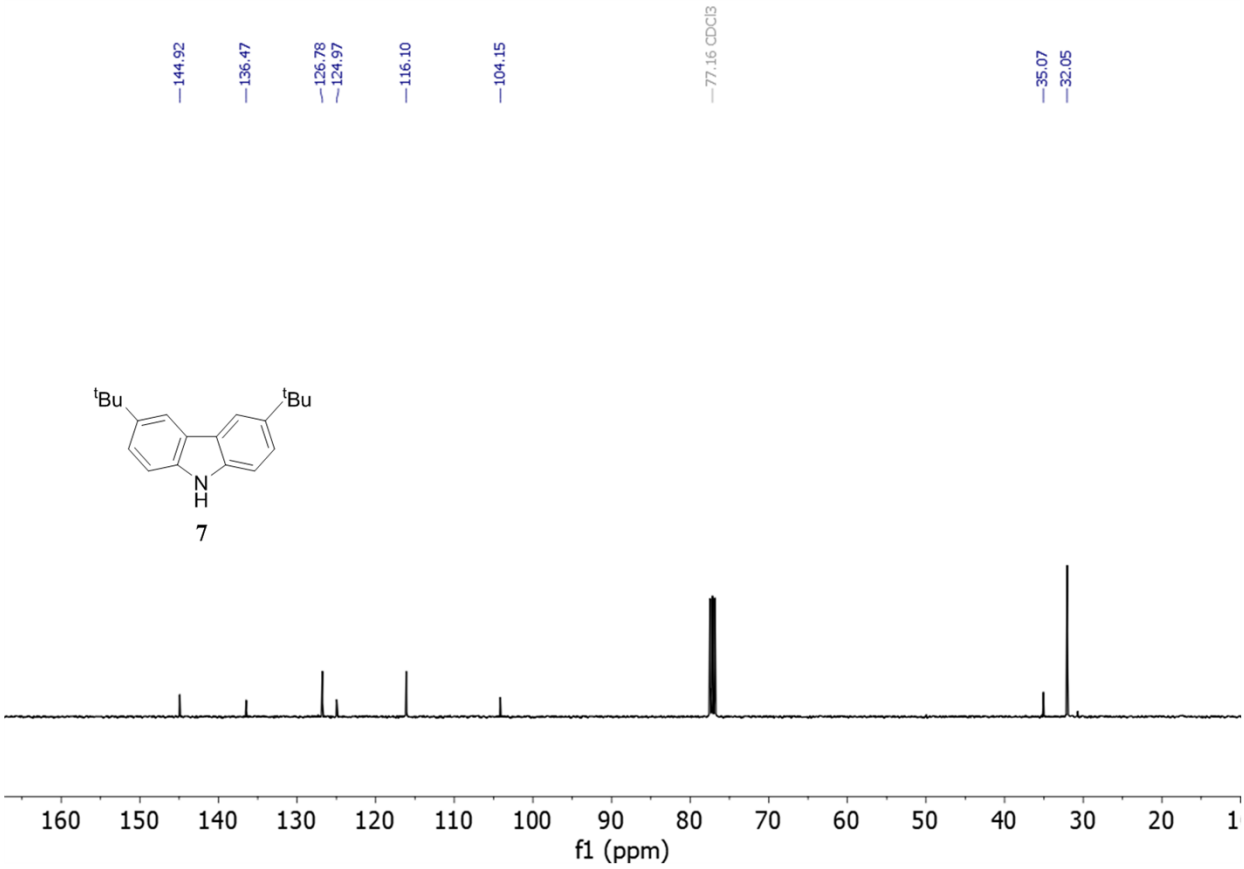


Figure S2. ^{13}C NMR spectrum of **7** recorded in $CDCl_3$.

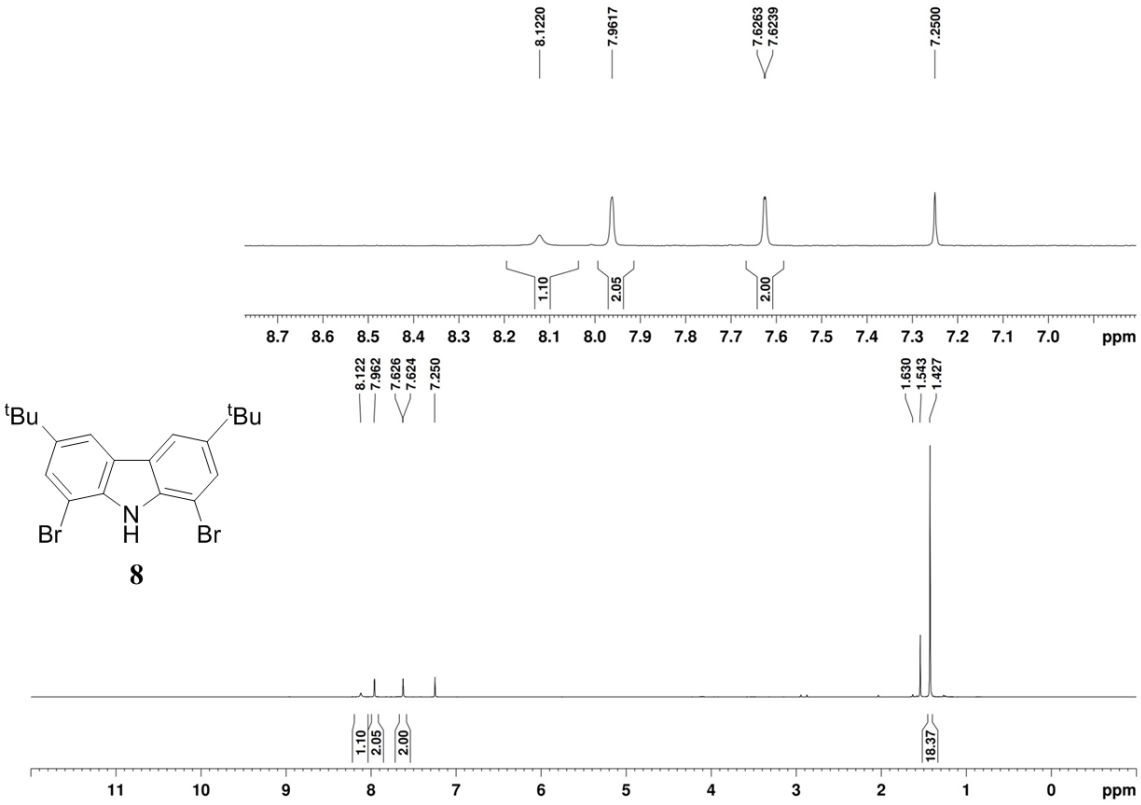


Figure S3. ^{1}H NMR spectrum of **8** recorded in $CDCl_3$.

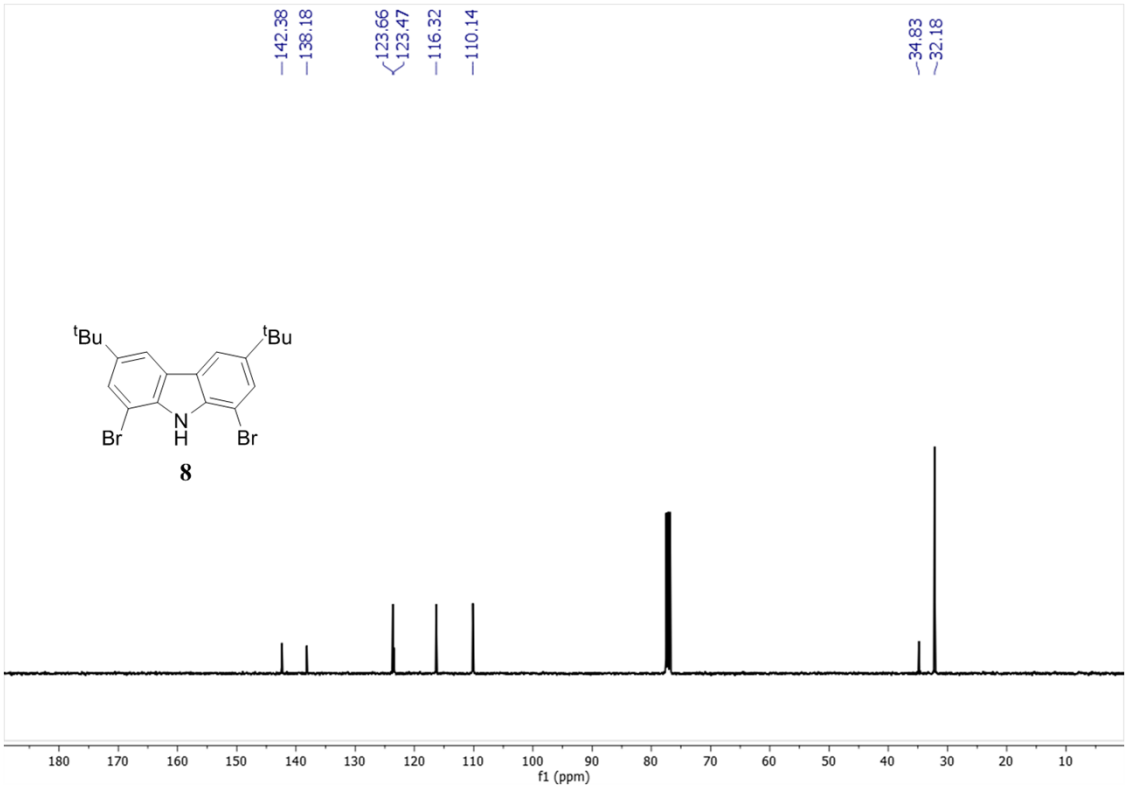


Figure S4. ^{13}C NMR spectrum of **8** recorded in $CDCl_3$.

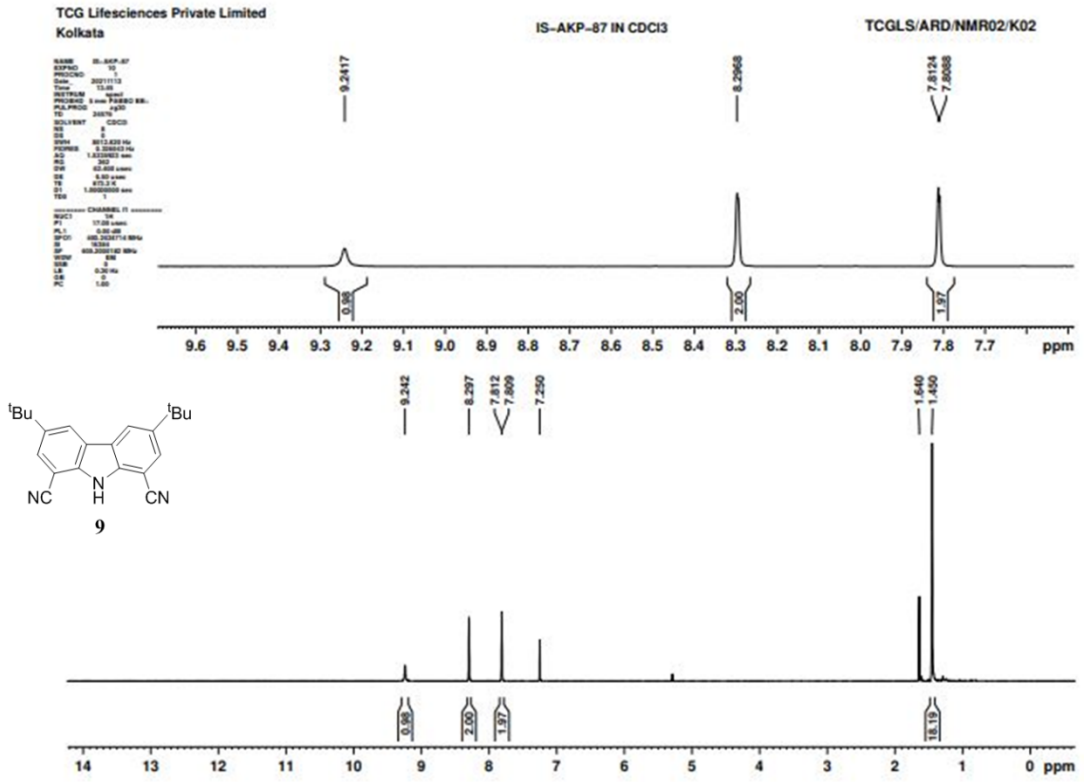


Figure S5. ^{1}H NMR spectrum of **9** recorded in $CDCl_3$.

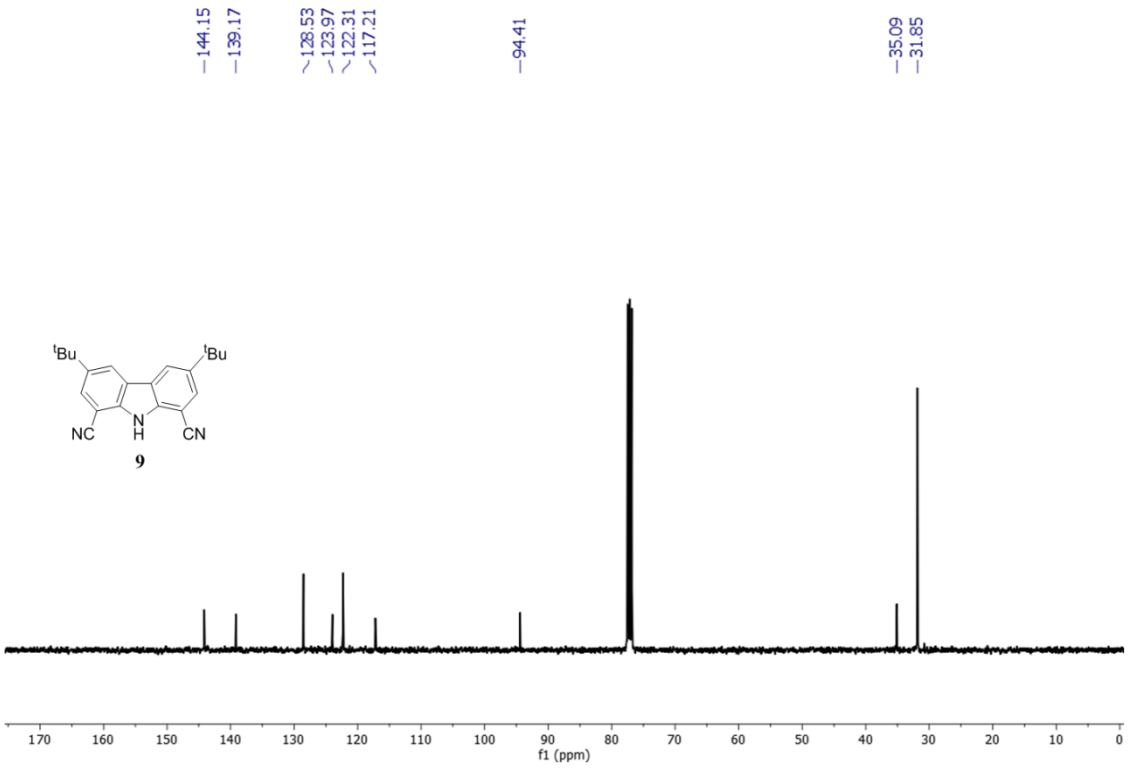


Figure S6. ^{13}C NMR spectrum of **9** recorded in $CDCl_3$.

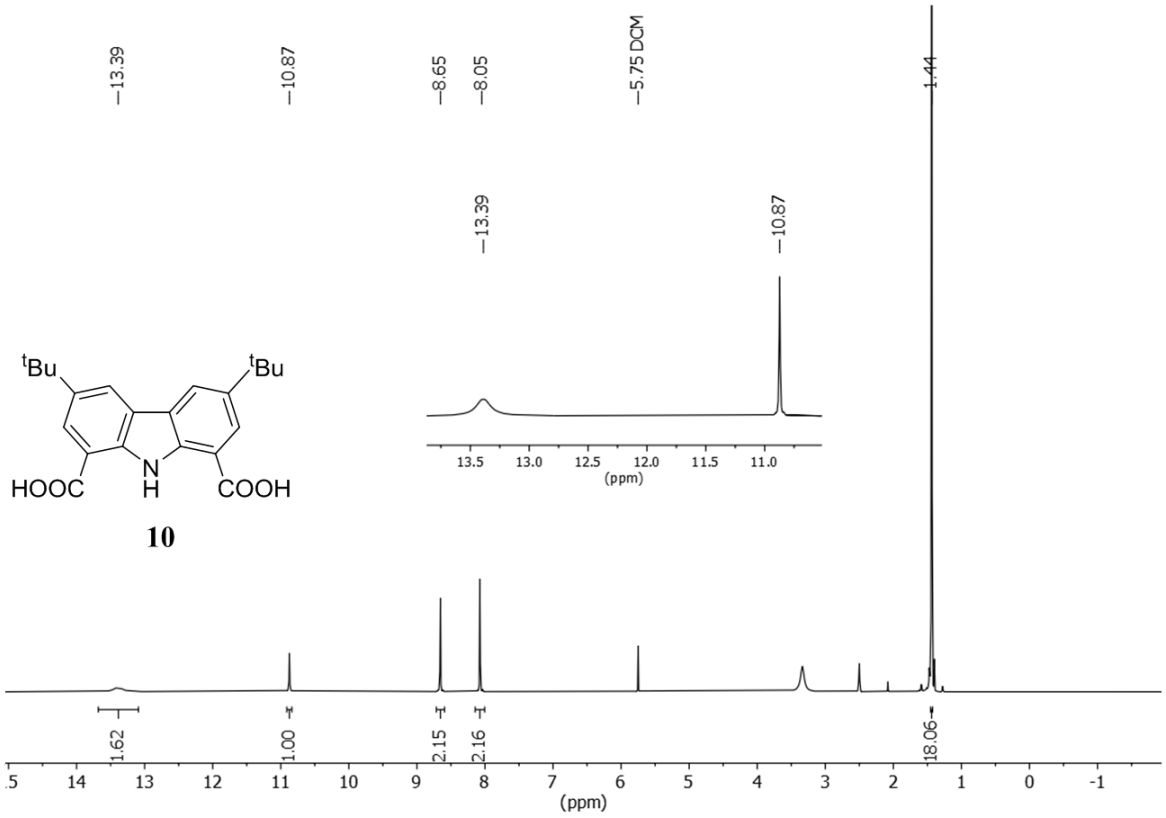


Figure S7. ^{1}H NMR spectrum of **10** recorded in DMSO-d_6.

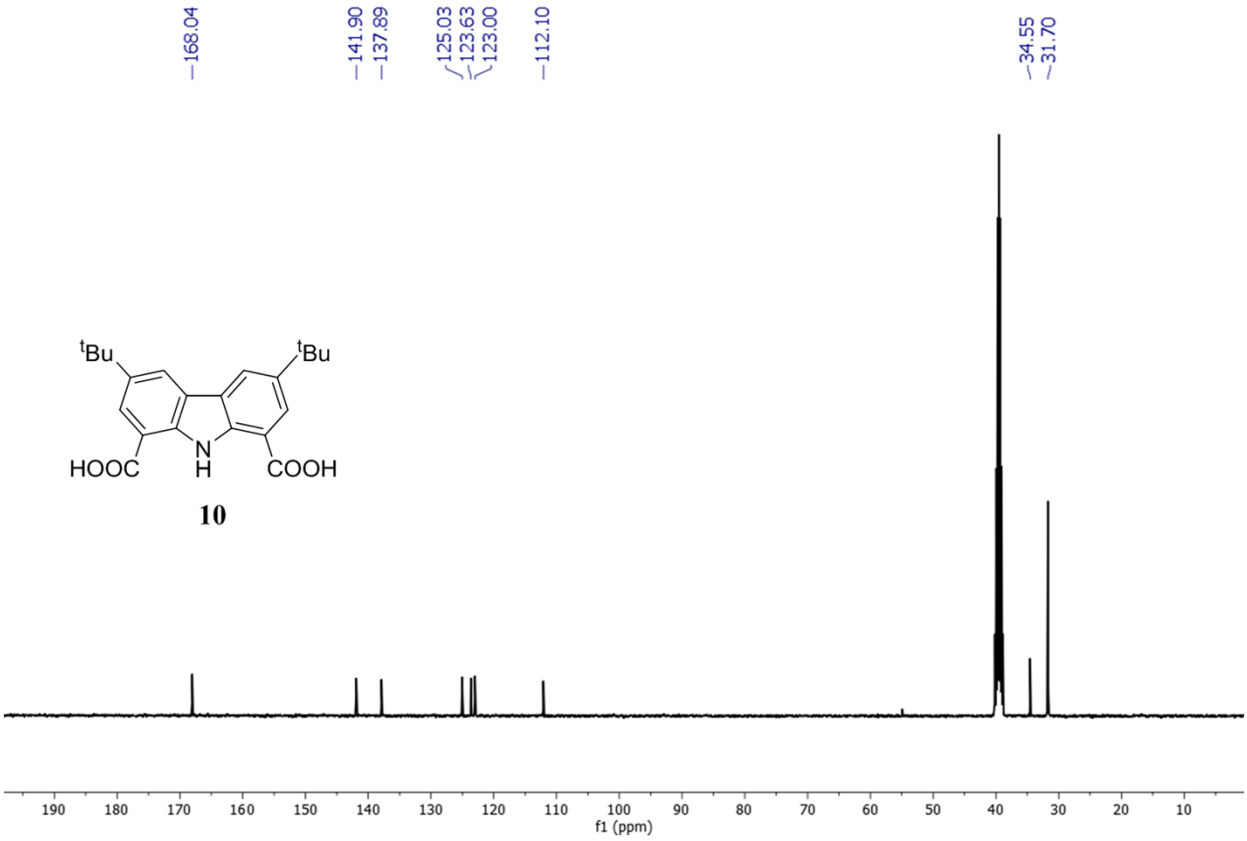


Figure S8. ^{13}C NMR spectrum of **10** recorded in DMSO-d_6 .

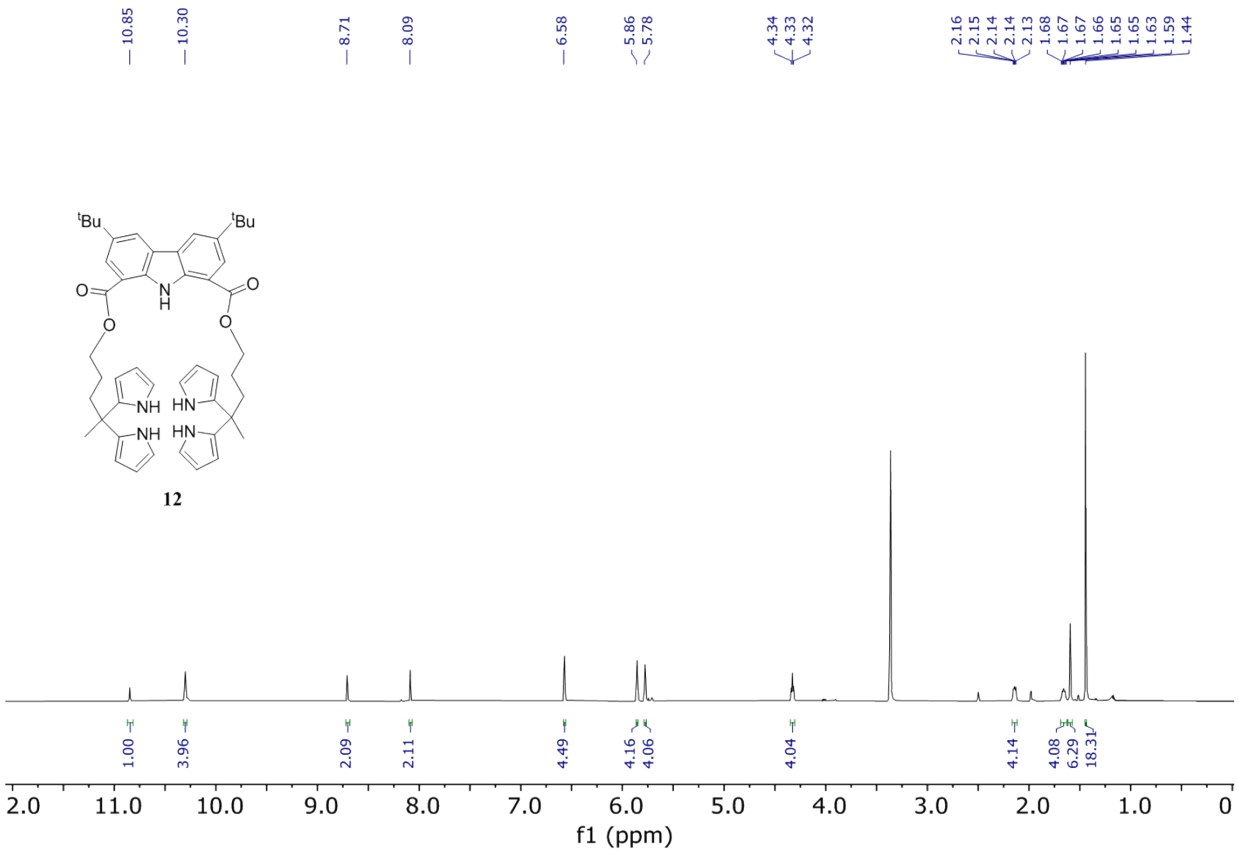


Figure S9. ^{1}H NMR spectrum of **12** recorded in DMSO-d_6 .

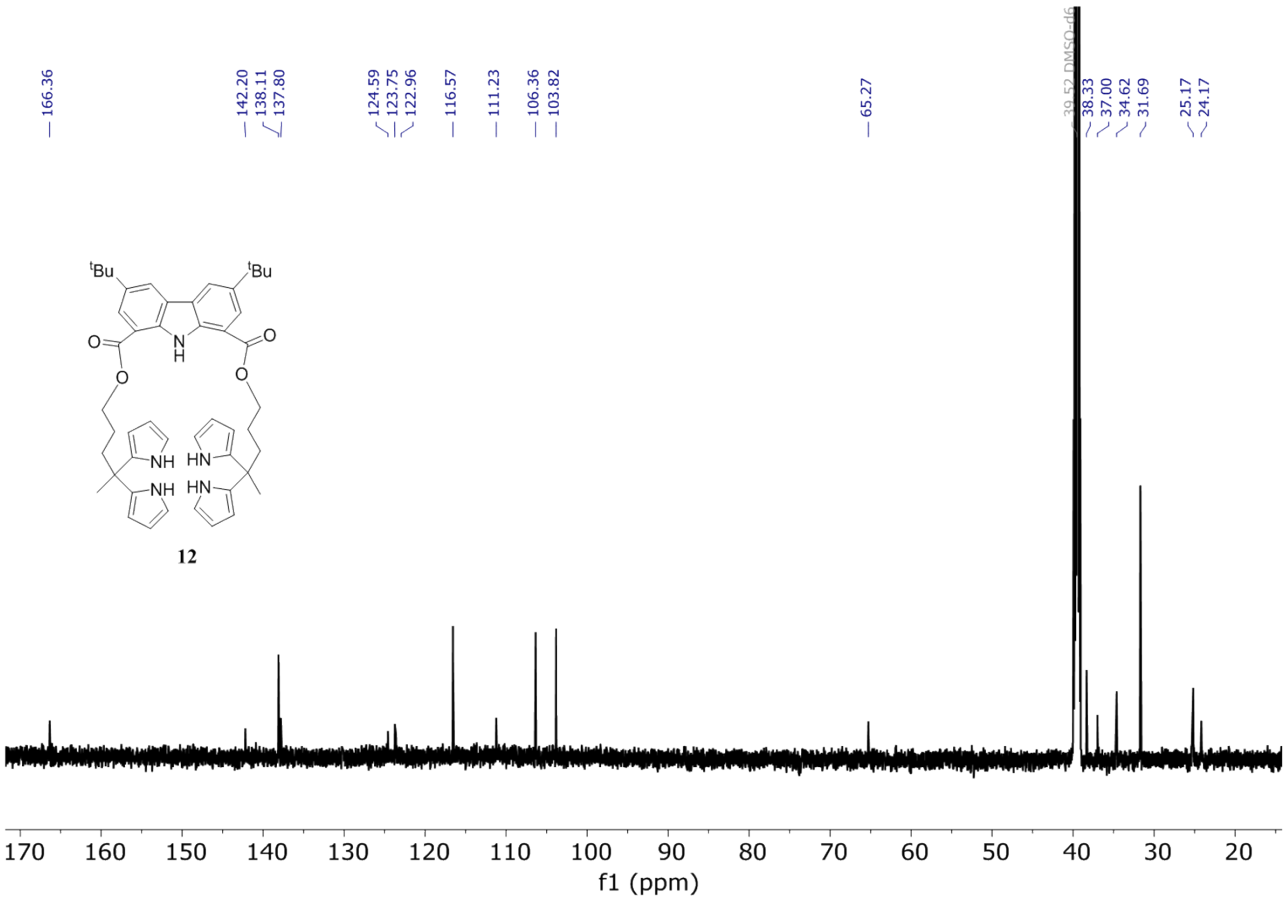


Figure S10. ^{13}C NMR spectrum of **12** recorded in DMSO-d_6.

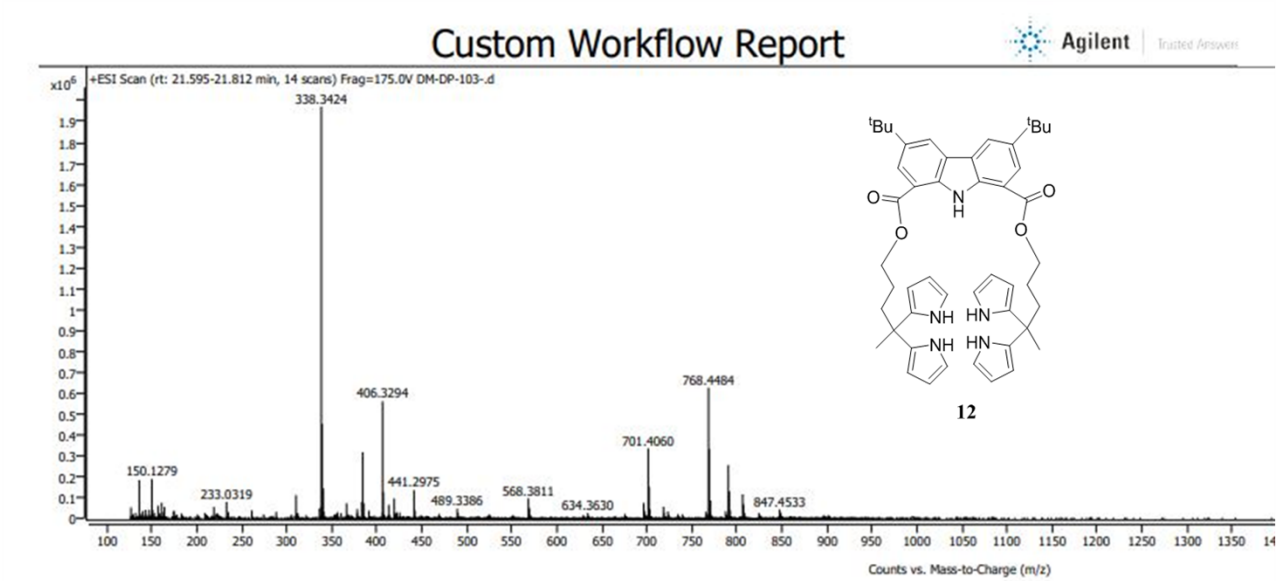


Figure S11. HRMS spectrum of **12.**

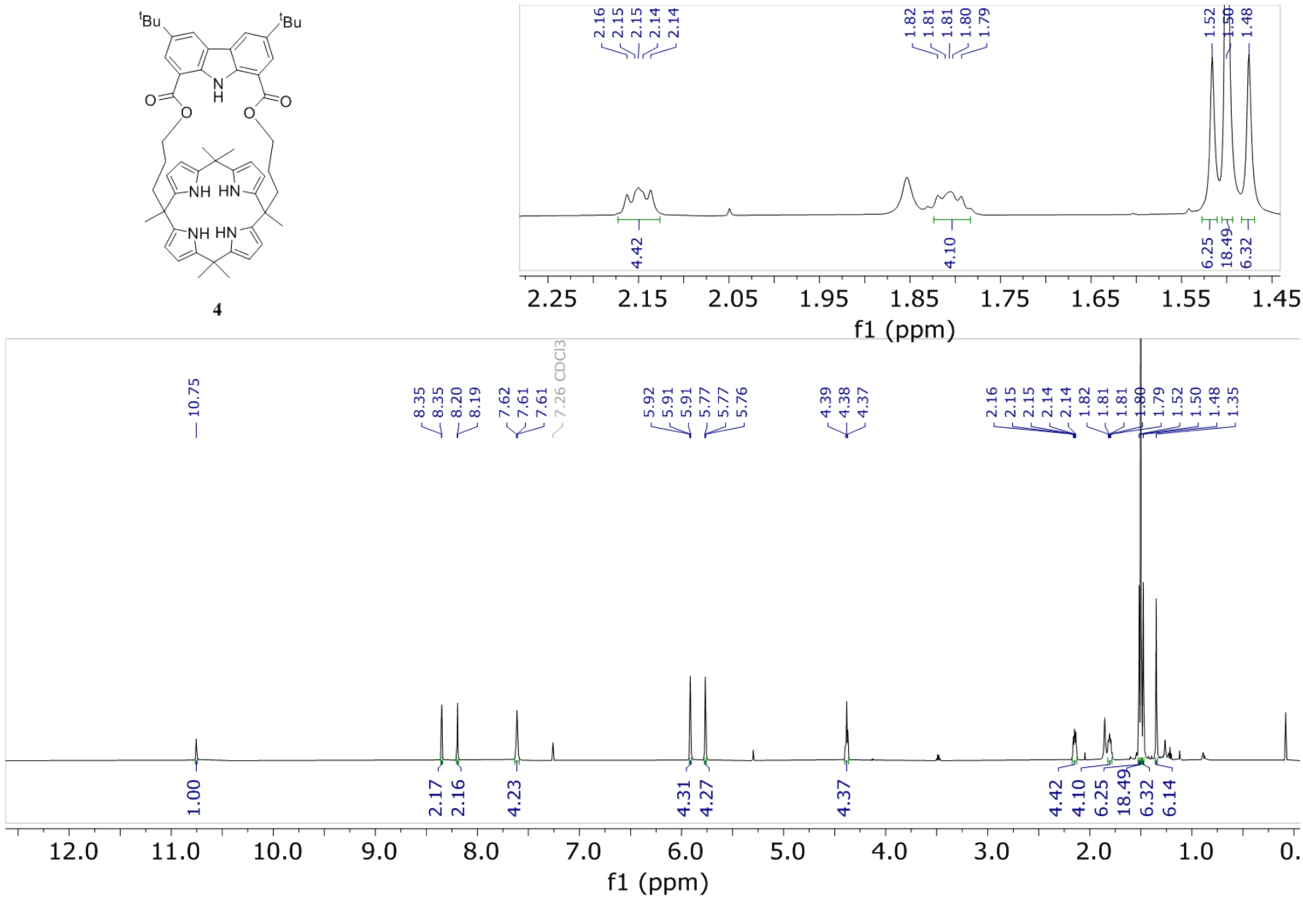


Figure S12. ^{1}H NMR spectrum of **4** recorded in $CDCl_3$.

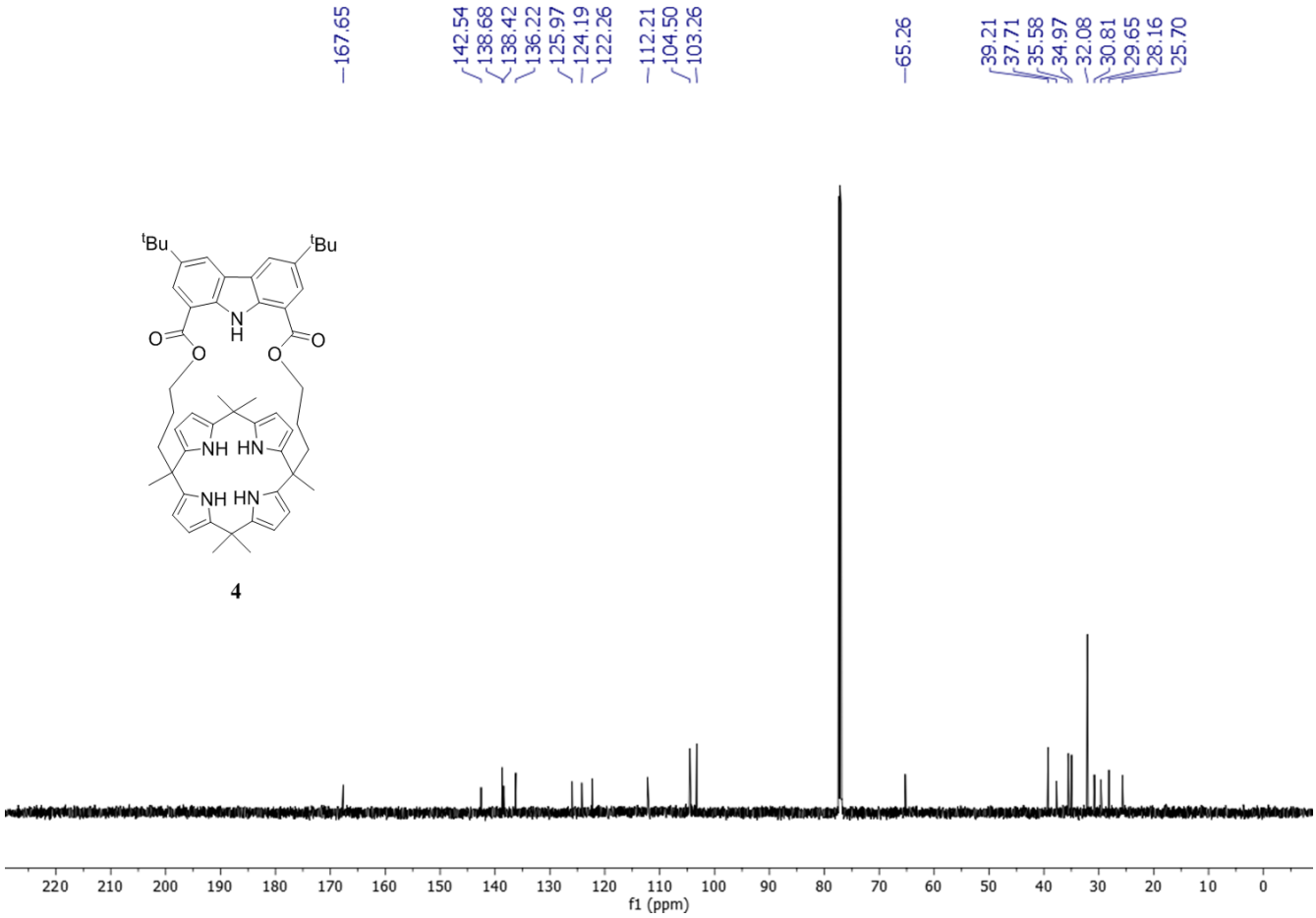


Figure S13. ^{13}C NMR spectrum of **4** recorded in $CDCl_3$.

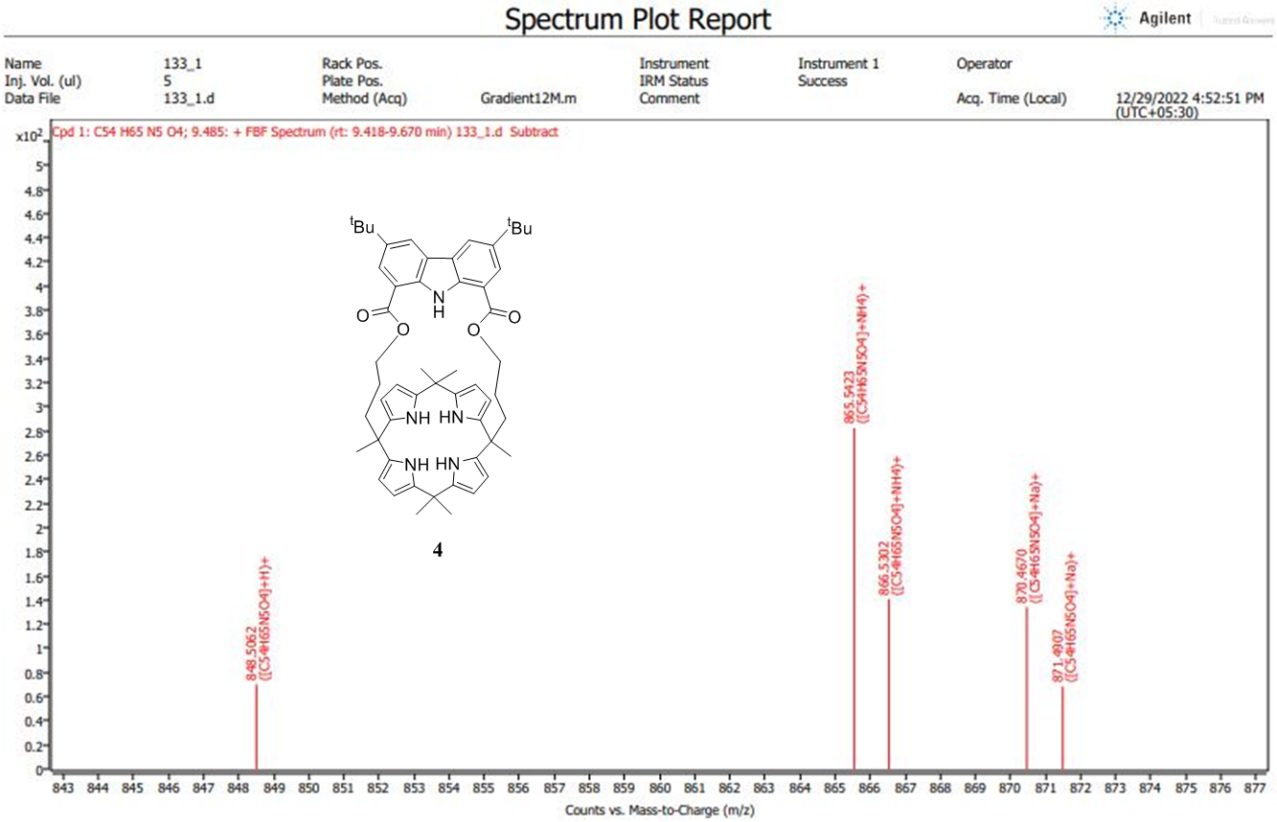


Figure S14. HRMS spectrum of **4.**

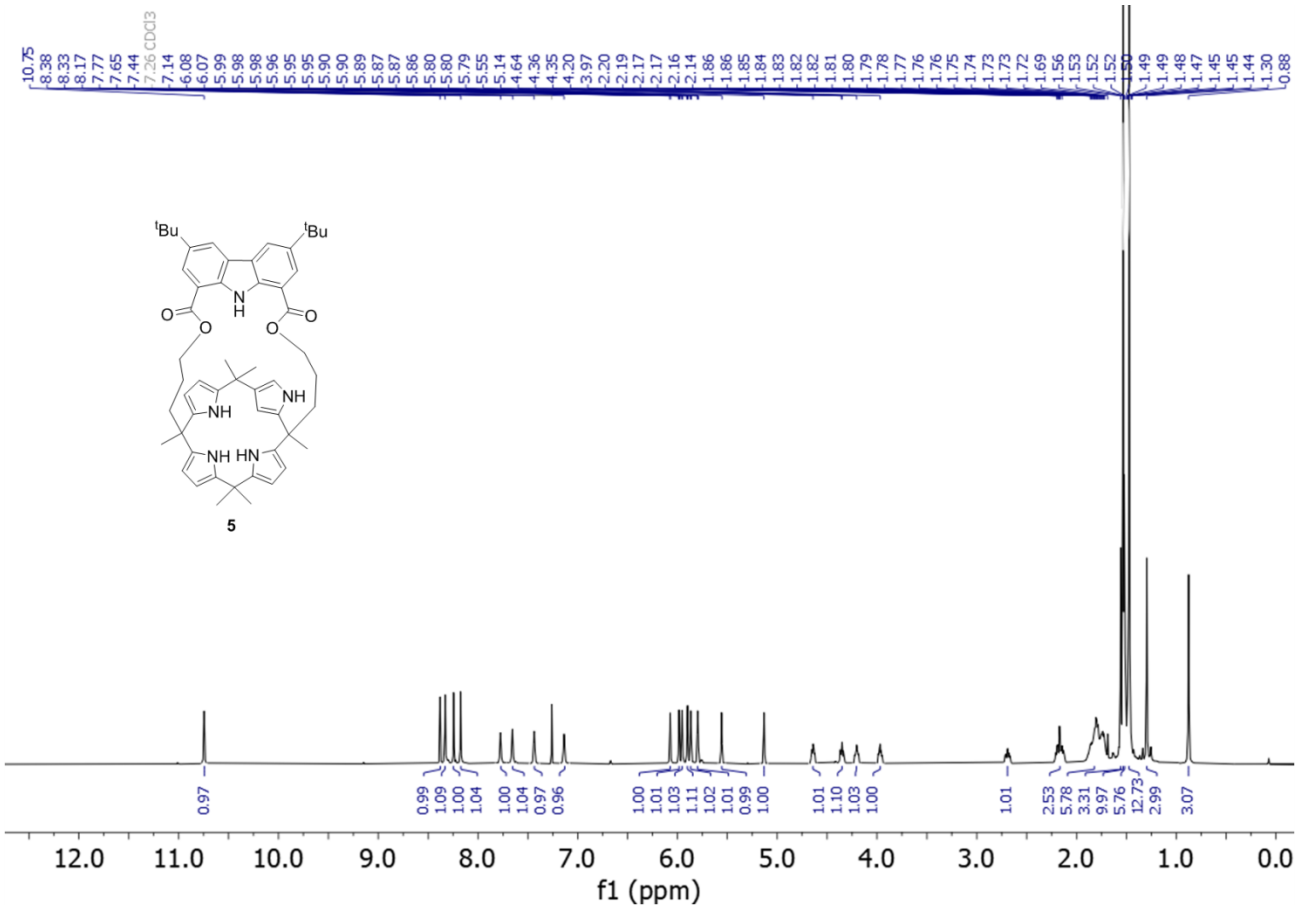


Figure S15. ^{1}H NMR spectrum of **5** recorded in $CDCl_3$.

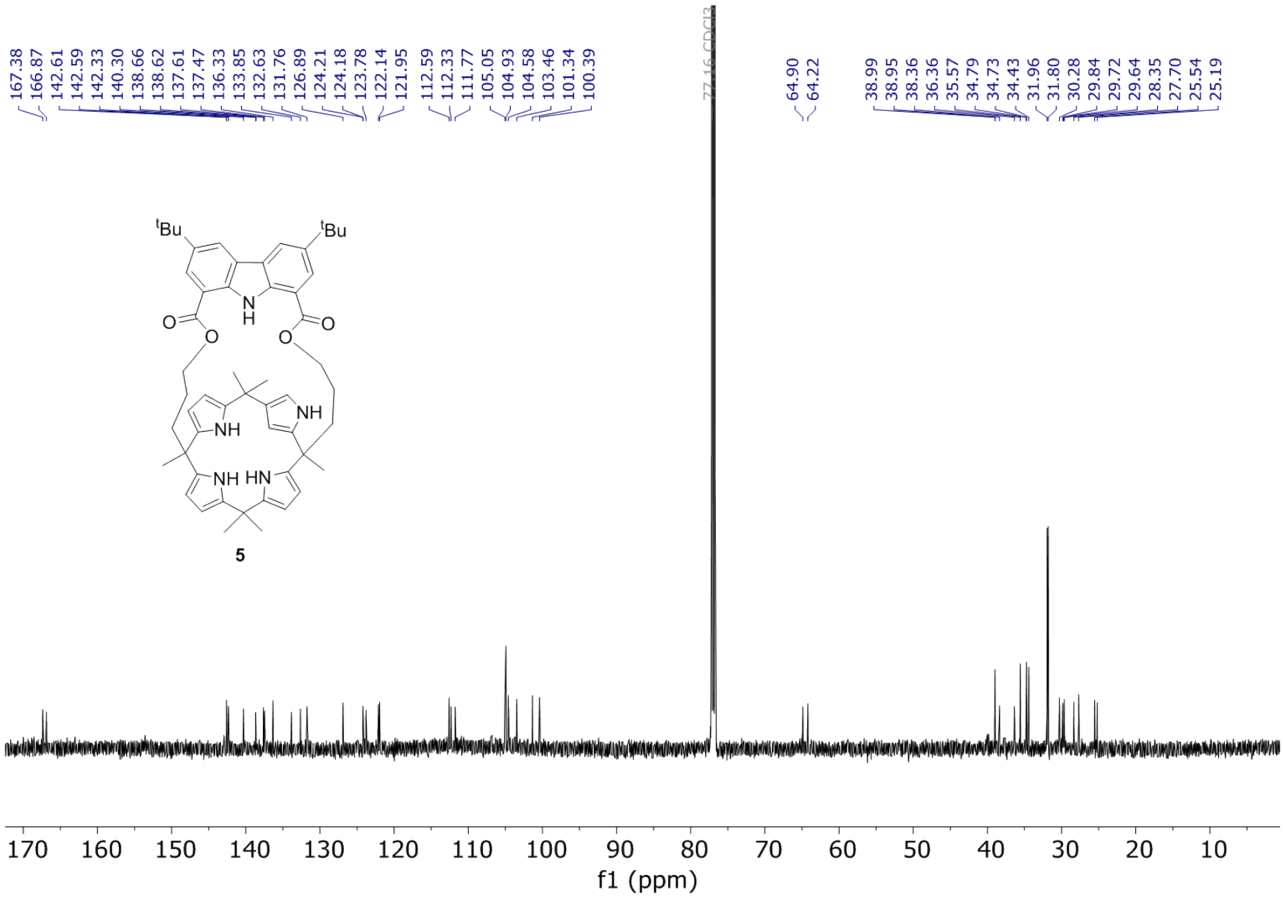


Figure S16. ^{13}C NMR spectrum of **5** recorded in $CDCl_3$.

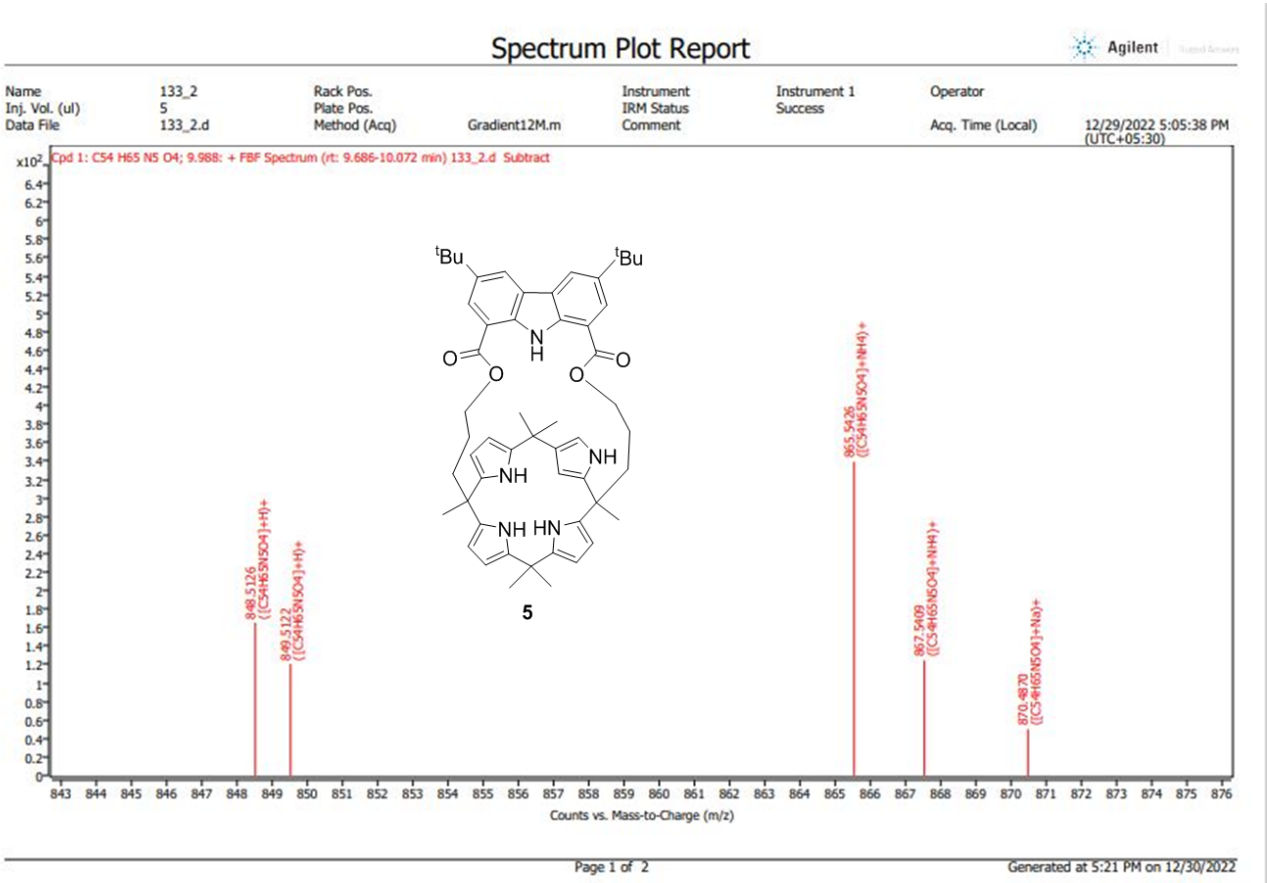


Figure S17. HRMS spectrum of **5.**

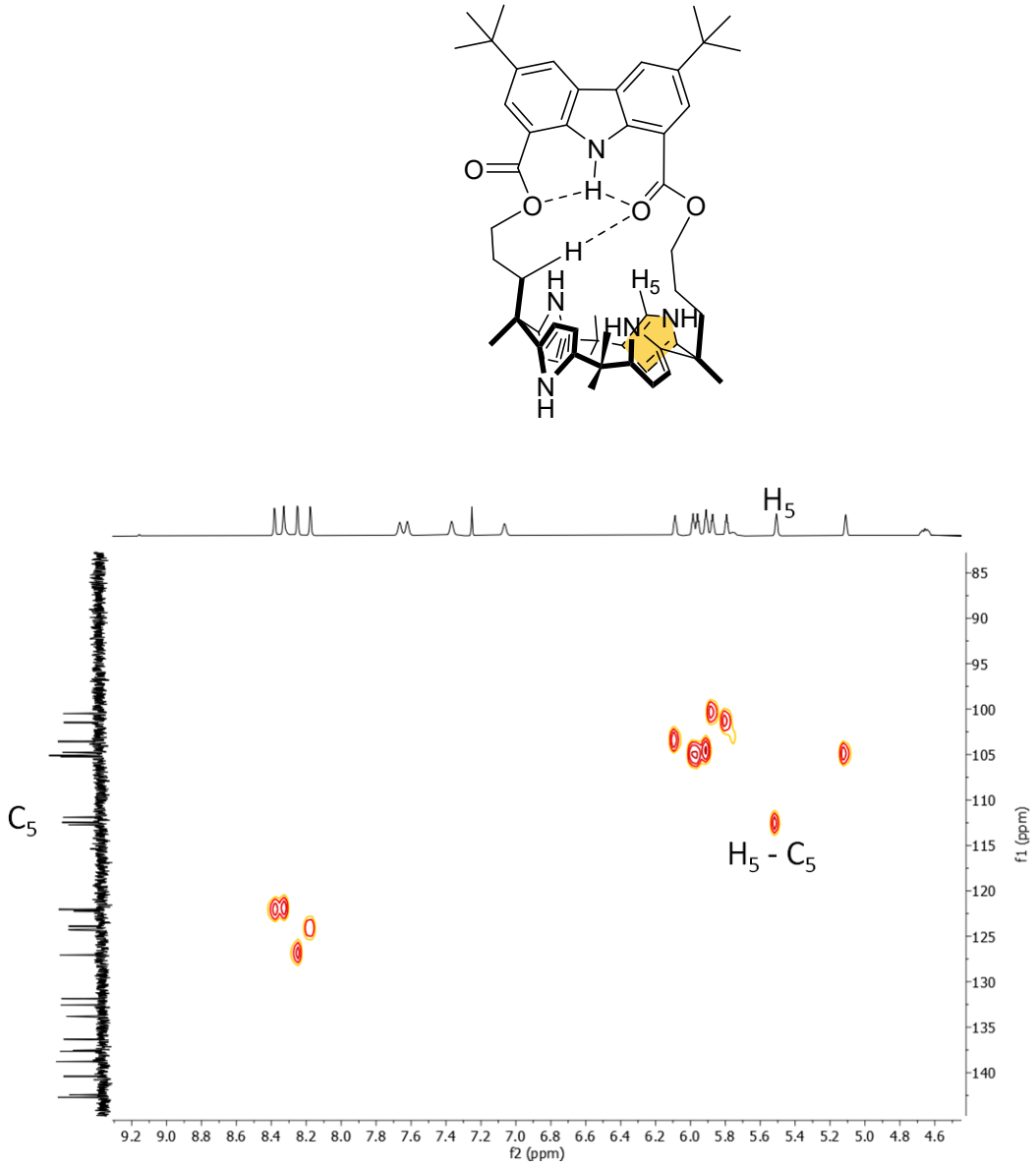


Figure S18. Partial view of the ^{1}H – ^{13}C HSQC NMR of receptor **5** recorded in $CDCl_3$. Figure S18 supports the contention that the proton signal corresponding to H_5 is α-CH of the of the inverted pyrrole ring of receptor **5** (H_5 - C_5 Correlation).

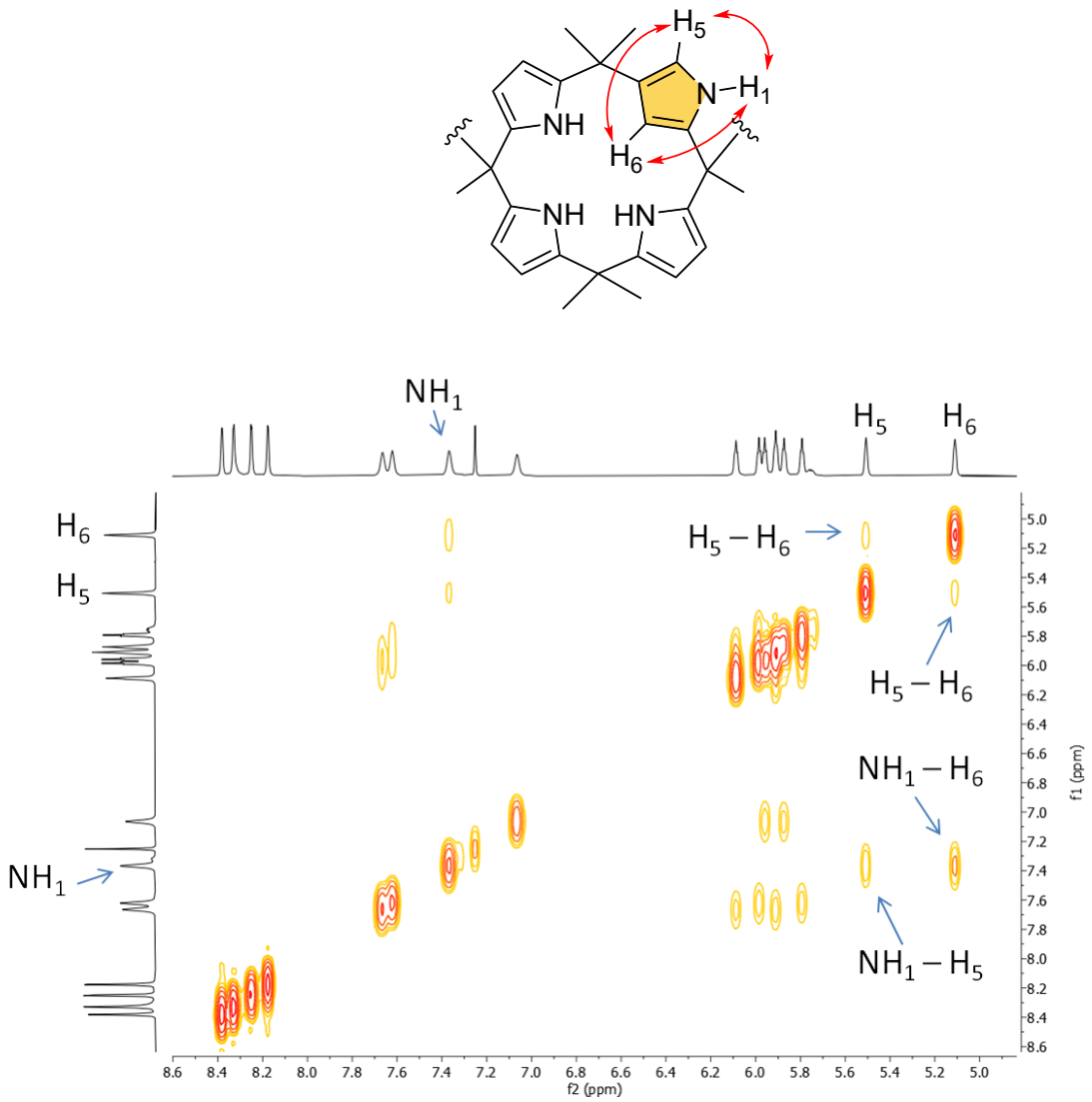


Figure S19. Partial view of $^{1}H - {}^{1}H$ COSY NMR of receptor **5** recorded in $CDCl_3$. The $^{1}H - {}^{1}H$ COSY spectrum of **5** supports the following contentions-

i) H_6 is the pyrrolic β-CH of the inverted pyrrole ring ($H_5 - H_6$ correlation)

ii) H_1 is the pyrrolic NH of the inverted pyrrole ring ($H_1 - H_5$ and $H_1 - H_6$ correlations)

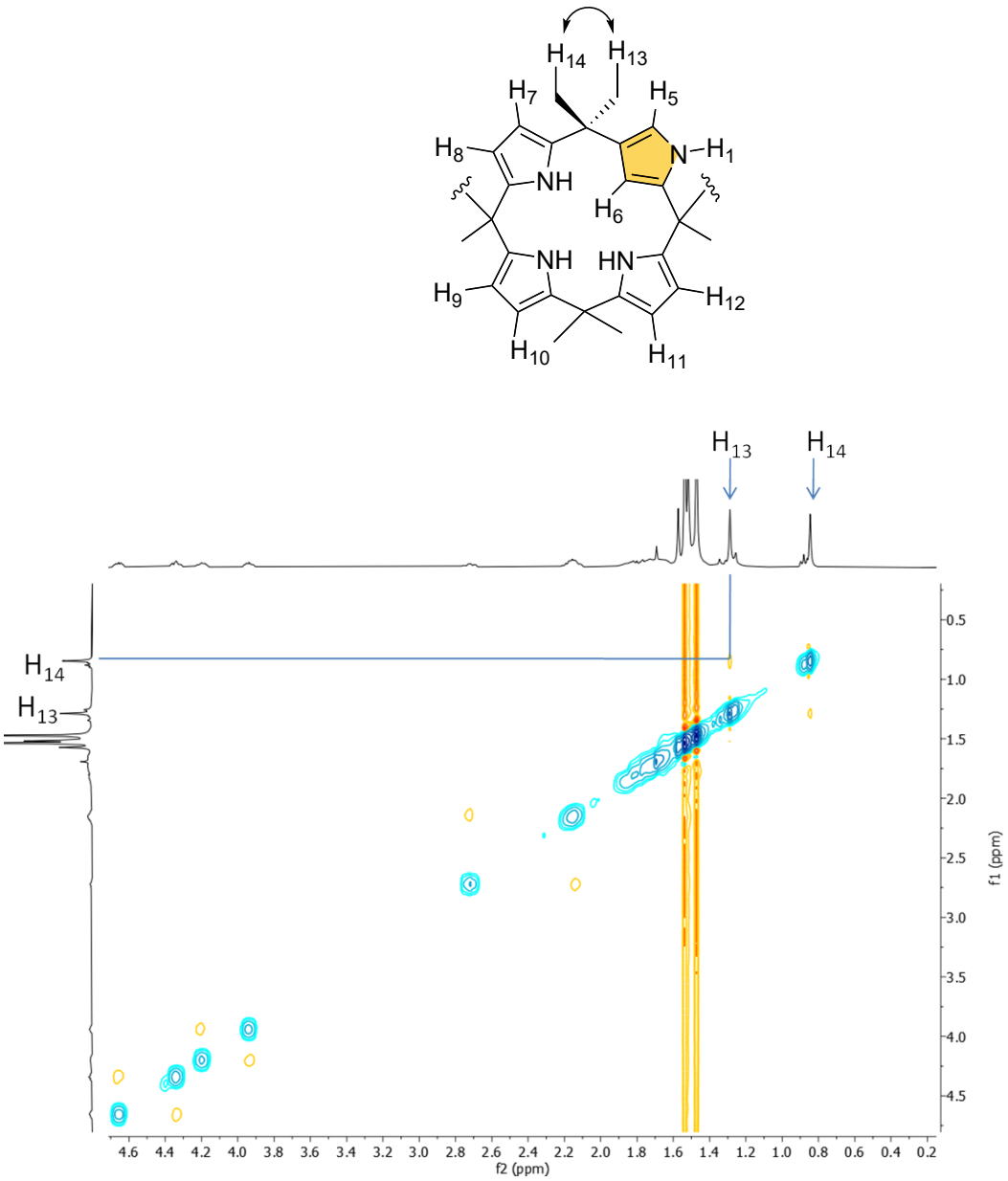


Figure S20. Partial view of $^{1}H - {}^{1}H$ NOESY NMR of receptor **5** recorded in $CDCl_3$. The $^{1}H - {}^{1}H$ NOESY spectrum supports the contention that H_{14} and H_{13} are the *meso*-methyl protons connected to the same *meso*-carbon.

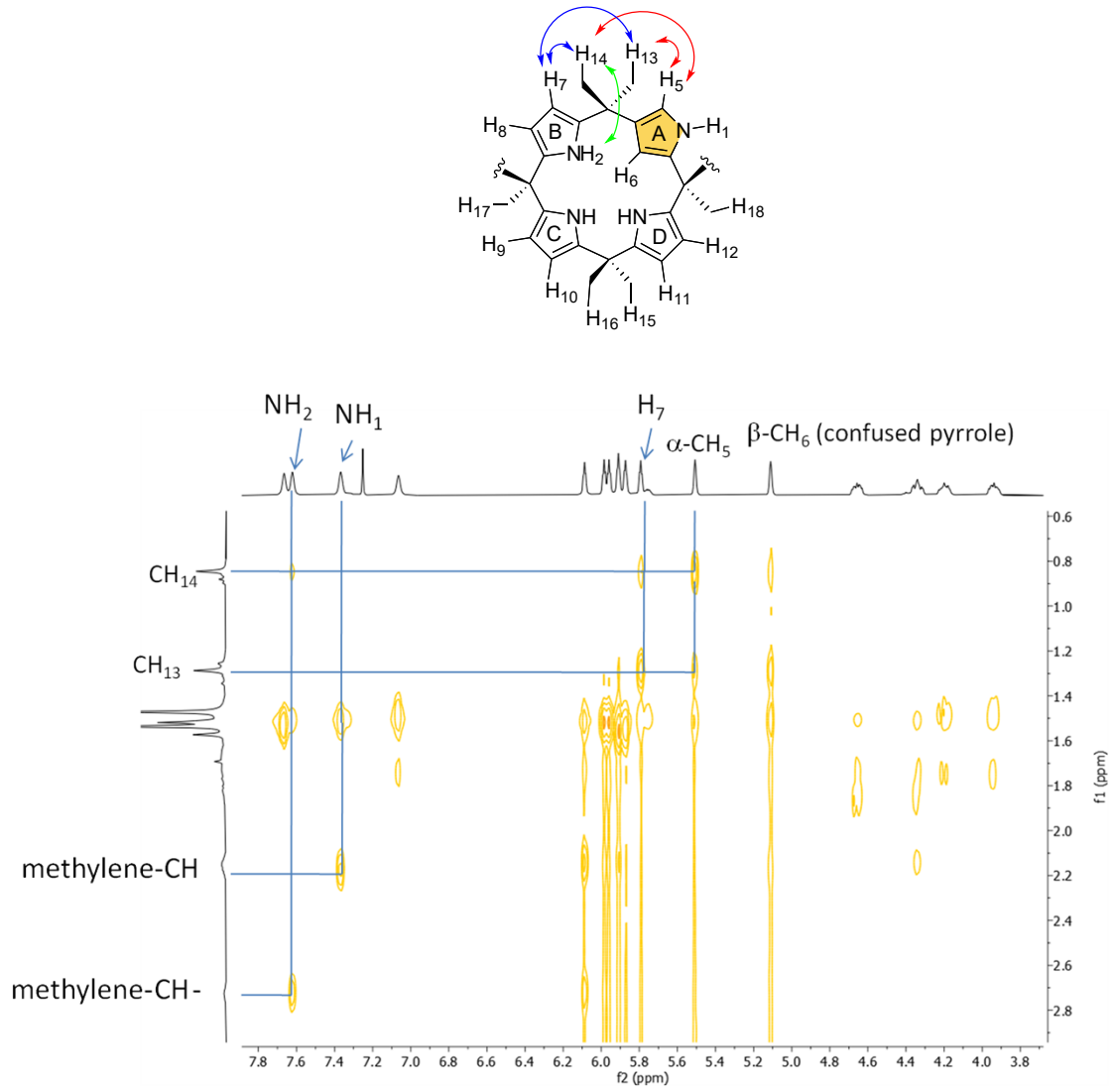


Figure S21. Partial view of $^1H - ^1H$ NOESY NMR of receptor **5** recorded in $CDCl_3$. The $^1H - ^1H$ NOESY spectrum supports the following contentions-

i) The H_{13} and H_{14} are protons corresponding to the *meso*- methyl groups attached to the *meso*-carbon to which one inverted pyrrole and one normal pyrrole rings are attached (H_{14} –H_5, H_{13} –H_5 and H_7 –H_{14}, H_7 –H_{13} correlation)

ii) H_2 is the pyrrolic NH of the normal pyrrole ring B and directed toward the cavity crafted by strap (H_{14} –H_2 correlation and methylene-CH-H_2 correlation).

iii) The *meso*-methyl group corresponding to the proton signal H_{14} resides on the side of the strap (H_{14} –H_2 correlation and no correlation between H_{13}-H_2).

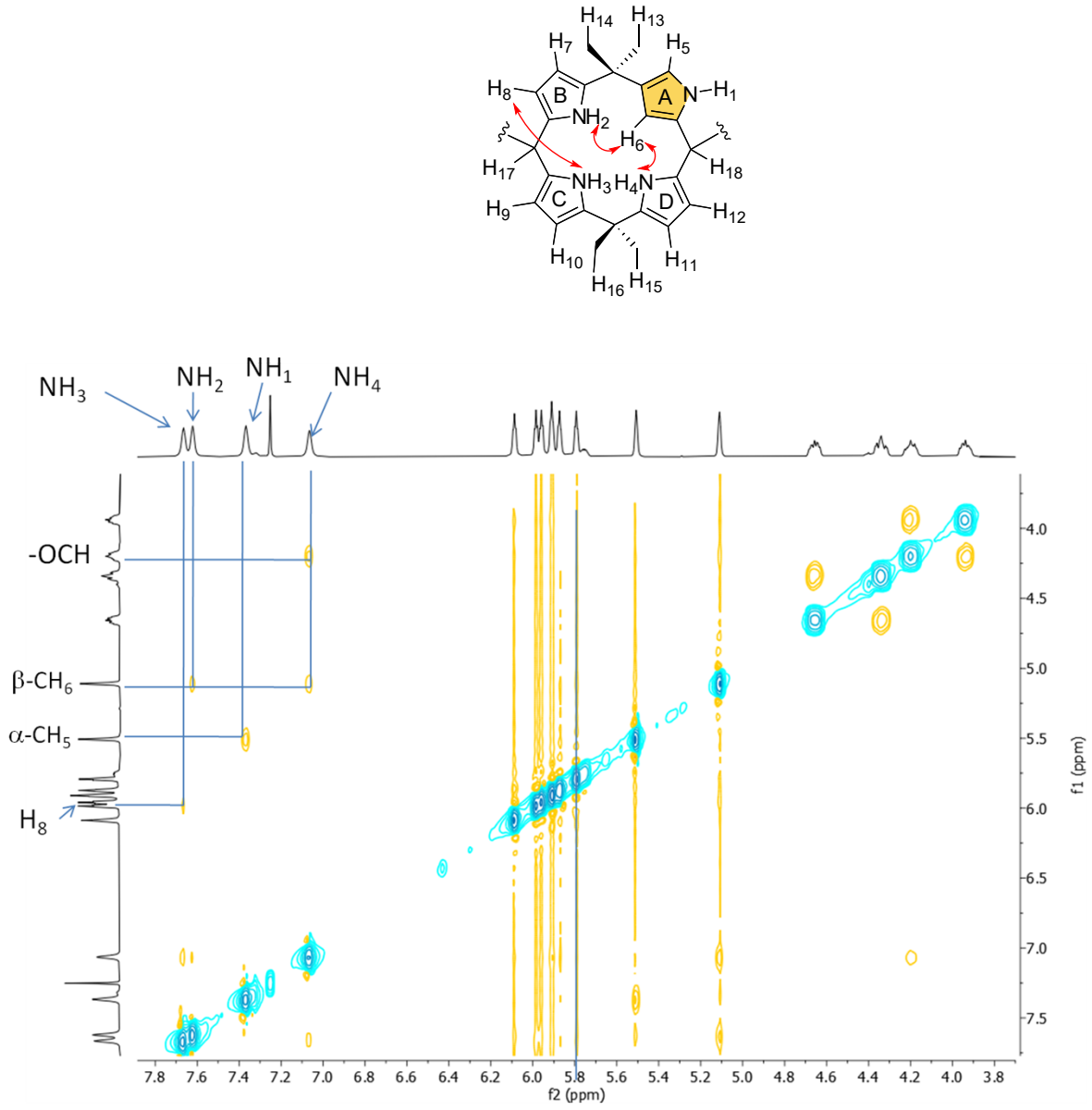


Figure S22. Partial view of the $^{1}H - {}^{1}H$ NOESY spectrum of receptor **5** recorded in $CDCl_3$. This figure supports the contention that H_4 is the pyrrolic NH of the pyrrole ring marked as D ($H_6 - H_4$, $H_6 - H_2$ correlation) and is pointed toward the cavity (-OCH-H_4 correlation). It also supports the notion that H_3 is the pyrrolic NH of the pyrrole ring marked as C (see also Figure S23) and pointing opposite to the strapped cavity (H_8-H_3 correlation).

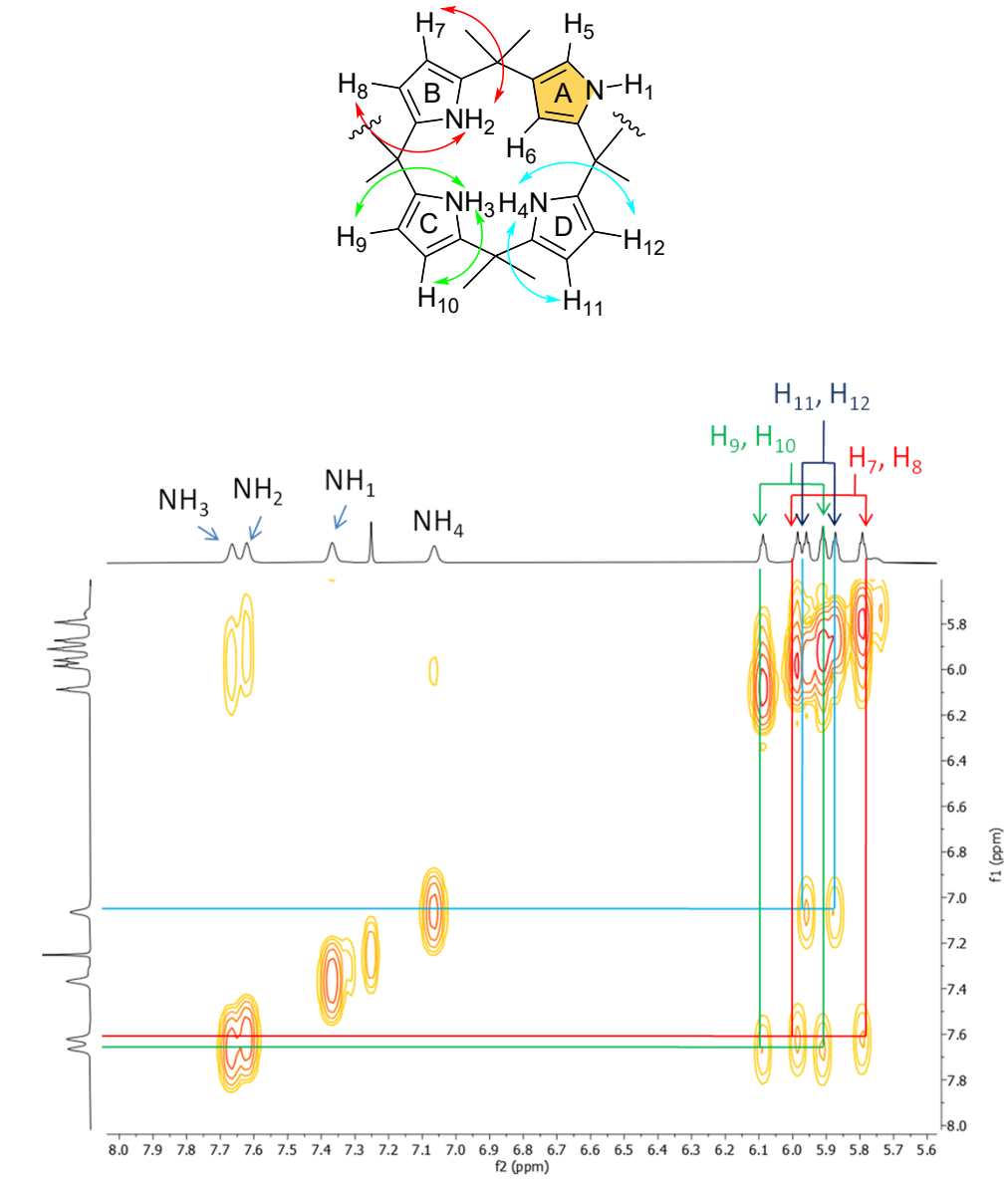


Figure S23. Partial view of $^{1}H - {}^{1}H$ COSY NMR of receptor **5** recorded in $CDCl_3$. The $^{1}H - {}^{1}H$ COSY spectrum of **5** supports the following contentions-

i) H_7 and H_8 are the β-pyrrolic CHs of pyrrole ring marked as B (H_2-H_7 and H_2-H_8 correlation).

ii) H_9 and H_{10} are the β-pyrrolic CHs of pyrrole ring marked as C (H_3-H_9 and H_3-H_{10} correlation).

iii) H_{11} and H_{12} are β-pyrrolic-CH of pyrrole ring marked as D (H_4-H_{11} and H_4-H_{12} correlation).

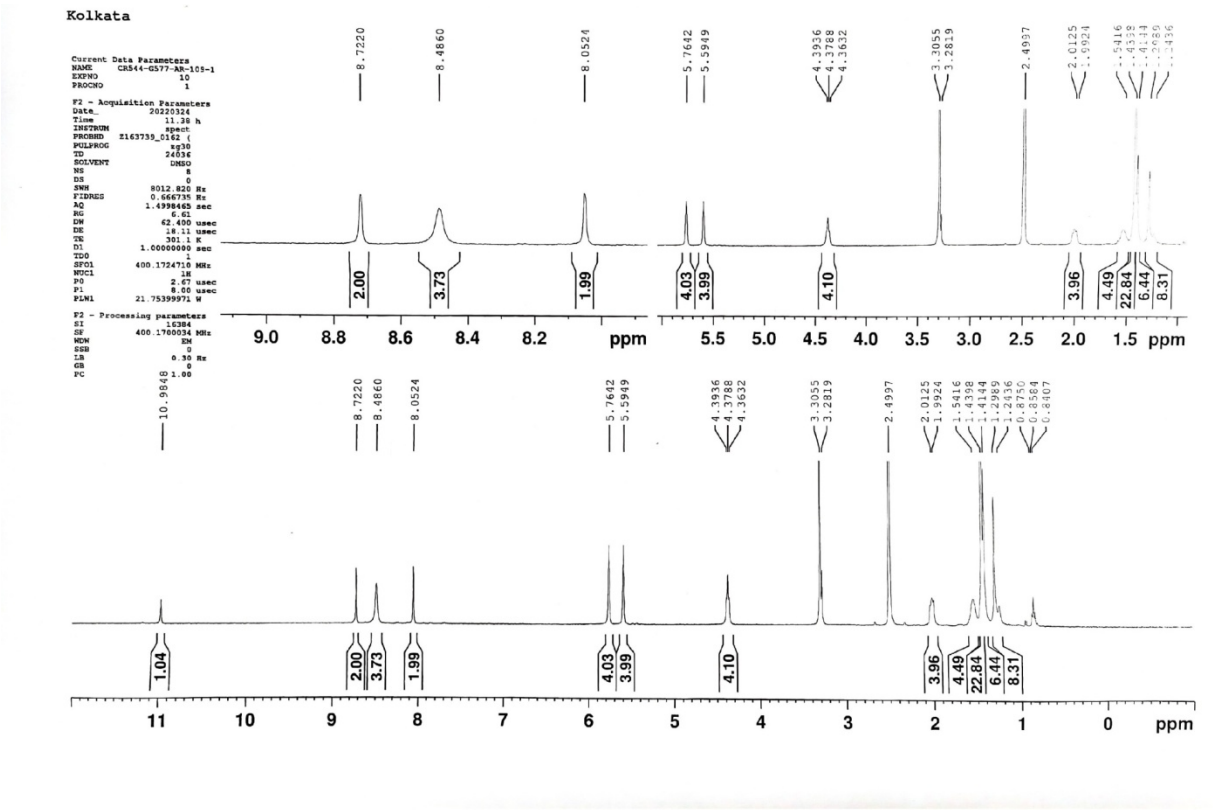


Figure S24. ^{1}H NMR spectrum of **4** recorded in DMSO-d_6.

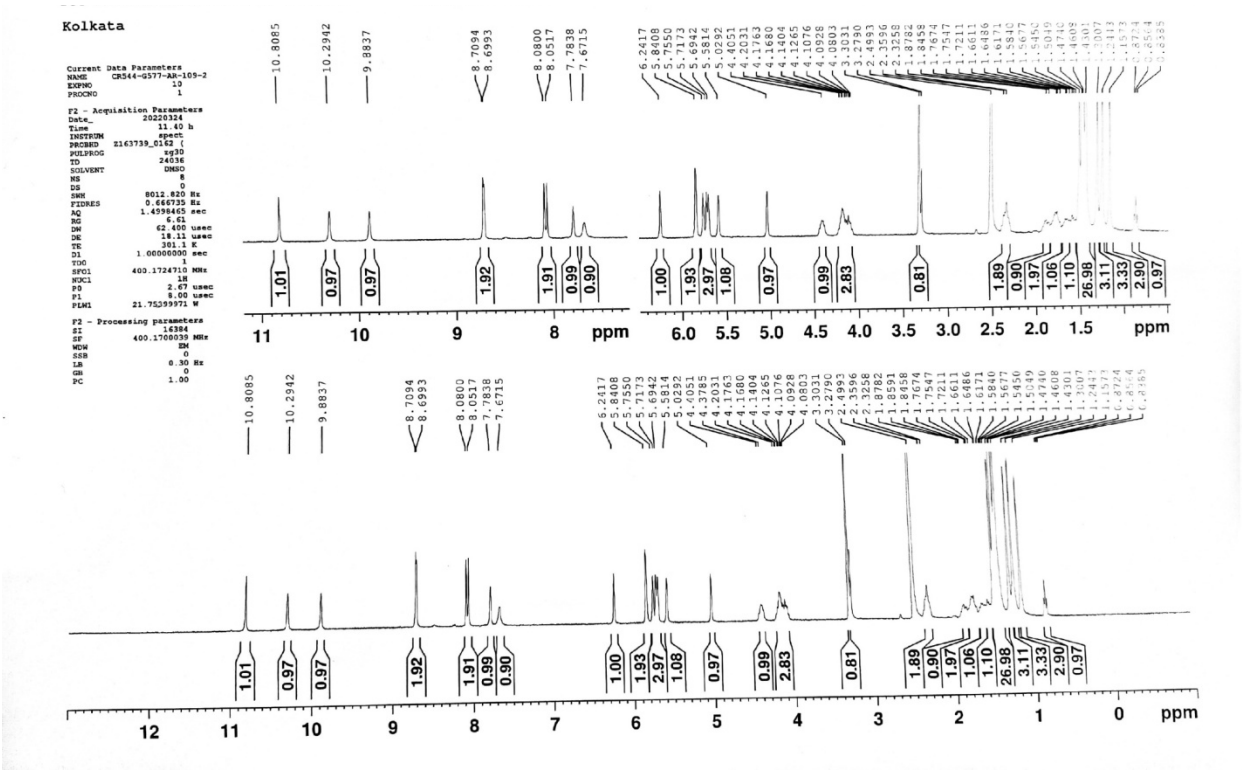


Figure S25. ^{1}H NMR spectrum of **5** recorded in DMSO-d_6.

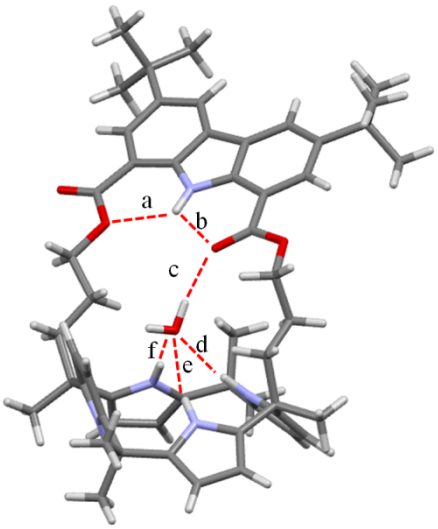


Figure S26. Single crystal X-ray structure of **4** showing various hydrogen bonding interactions. 'a' – 'f' indicates the corresponding distances as - a = 2.345 Å, b = 2.366 Å, c = 1.992 Å, d = 2.194 Å, e = 2.532 Å, f = 2.137 Å.

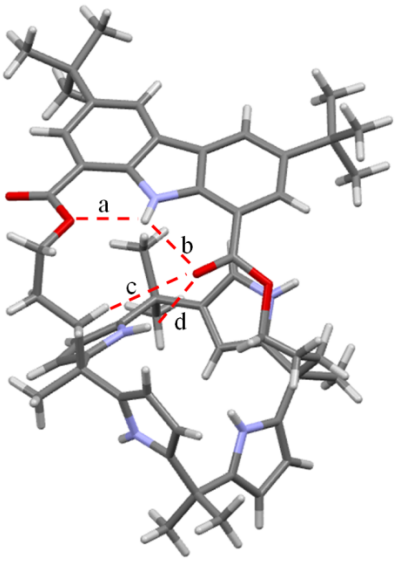


Figure S27. Single crystal X-ray structure of **4** showing various hydrogen bonding interactions. 'a' – 'd' indicates corresponding distances as - a = 2.250 Å, b = 2.300 Å, c = 2.914 Å, d = 3.009 Å.

Table S1. Selected crystal data and refinement parameters for receptor **4**•$CHCl_3$•H_2O.

Identification code	**4**•$CHCl_3$•H_2O
Empirical formula	$C_{55}H_{68}Cl_3N_5O_5$
Formula weight	985.49
Temperature/K	160.03
Crystal system	triclinic
Space group	P-1
a/Å	12.252(3)
b/Å	13.066(4)
c/Å	17.157(5)
α/°	103.800(9)
β/°	93.677(8)
γ/°	104.184(8)
Volume/Å^3	2564.0(12)
Z	2
ρ_{calc}g/cm^3	1.276
μ/mm^{-1}	0.232
F(000)	1048.0
Crystal size/mm^3	0.8 × 0.5 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.502 to 50.298
Index ranges	$-14 \leq h \leq 13$, $-15 \leq k \leq 15$, $-20 \leq l \leq 20$
Reflections collected	26193
Independent reflections	9165 [R_{int} = 0.0953, R_{sigma} = 0.1062]
Data/restraints/parameters	9165/0/628
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0736, wR_2 = 0.1861
Final R indexes [all data]	R_1 = 0.1041, wR_2 = 0.2195
Largest diff. peak/hole / e Å^{-3}	0.31/-0.49
CCDC	**2340636**

Table S2. Selected crystal data and refinement parameters for receptor **5**

Identification code	**5**
Empirical formula	$C_{54}H_{65}N_5O_4$
Formula weight	848.11
Temperature/K	273.15
Crystal system	monoclinic
Space group	C2/c
a/Å	38.9398(15)
b/Å	11.4985(4)
c/Å	25.6469(11)
α/°	90
β/°	124.788(3)
γ/°	90
Volume/Å^3	9430.9(7)
Z	8
ρ_{calc}g/cm^3	1.195
μ/mm^{-1}	0.075
F(000)	3648.0
Crystal size/mm^3	0.458 × 0.165 × 0.125
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.292 to 54.95
Index ranges	-50 ≤ h ≤ 50, -14 ≤ k ≤ 14, -33 ≤ l ≤ 33
Reflections collected	91860
Independent reflections	10777 [R_{int} = 0.2085, R_{sigma} = 0.1468]
Data/restraints/parameters	10777/492/645
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.1171, wR_2 = 0.2835
Final R indexes [all data]	R_1 = 0.2529, wR_2 = 0.3499
Largest diff. peak/hole / e Å^{-3}	0.88/-0.95
CCDC	**2340640**

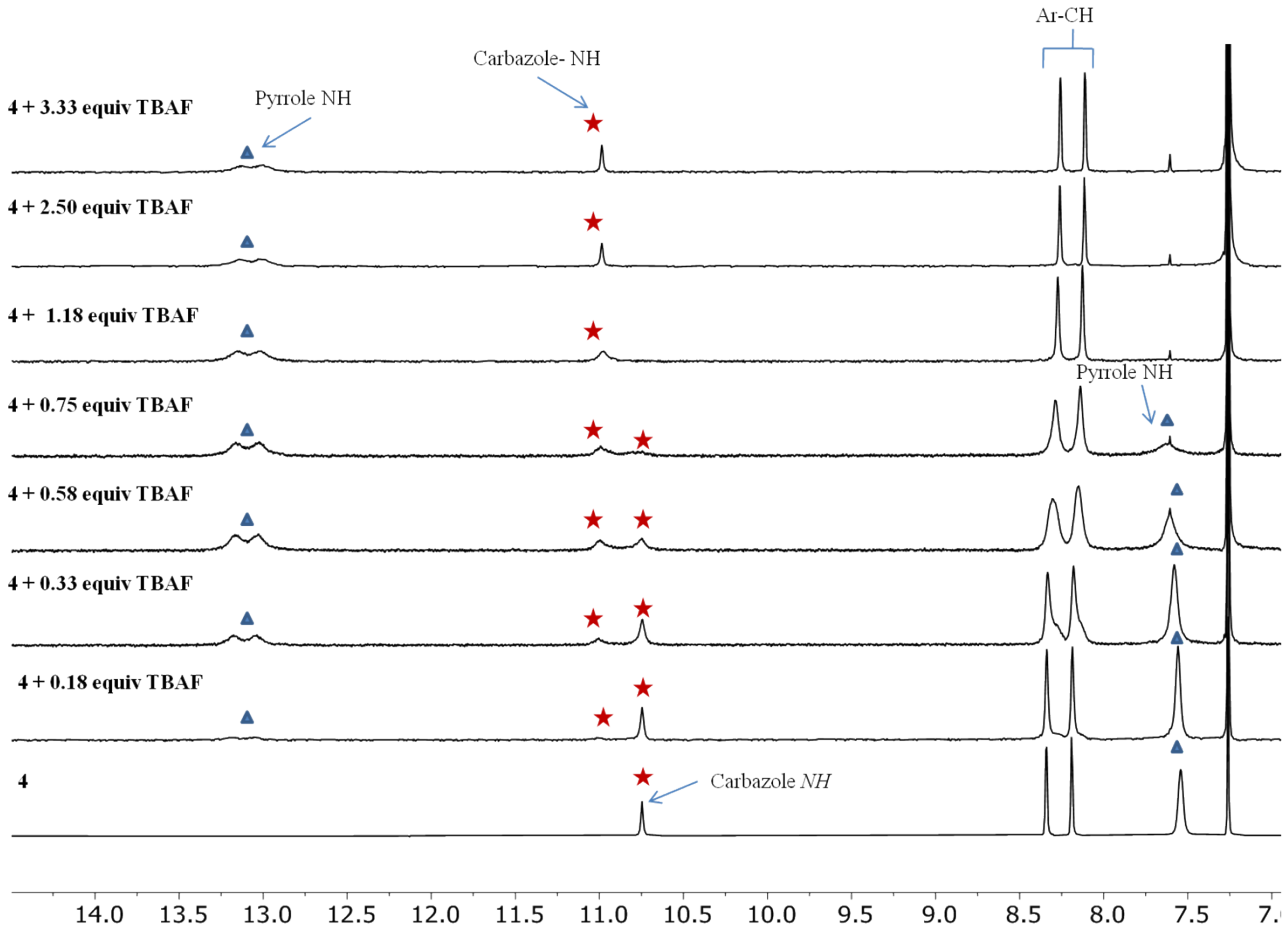


Figure S28. Partial ^{1}H NMR spectra recorded during the titration of receptor **4** (c = 8.25 mM) with TBAF in $CDCl_3$ (downfield region).

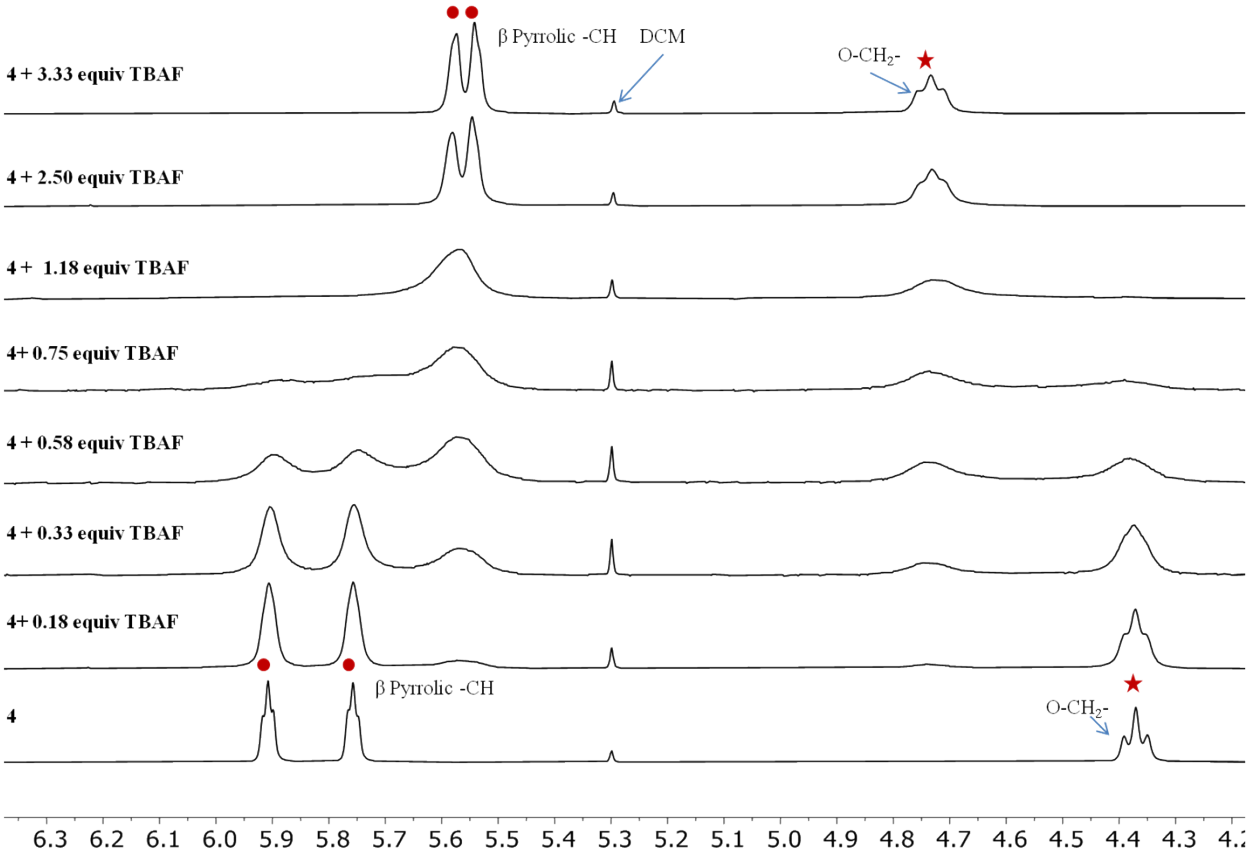


Figure S29. Partial ^{1}H NMR spectra recorded during the titration of receptor **4** (*c* = 8.25 mM) with TBAF in $CDCl_3$ (upfield region).

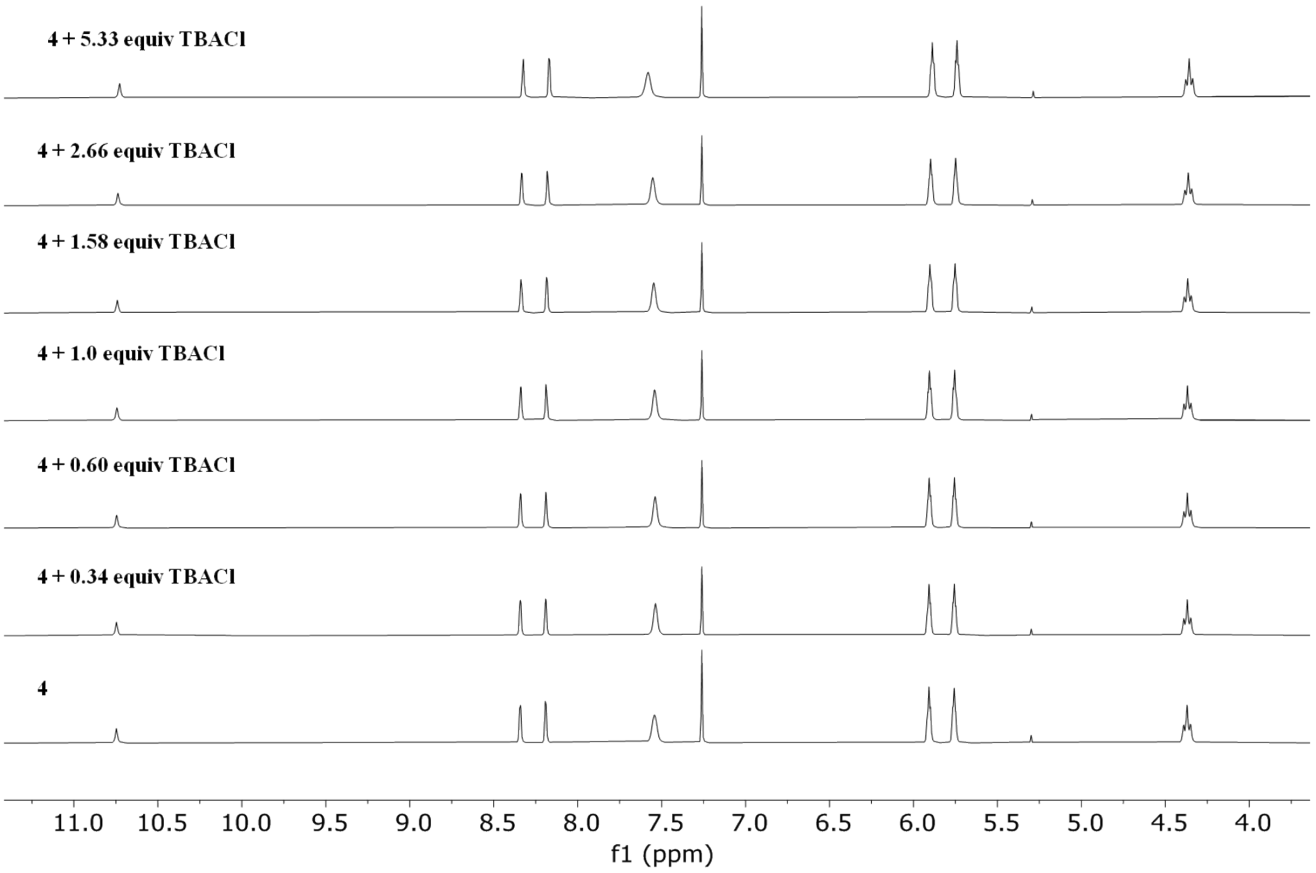


Figure S30. Partial ^{1}H NMR spectra recorded during the titration of receptor **4** (c = 5.66 mM) with TBACl in $CDCl_3$ (downfield region).

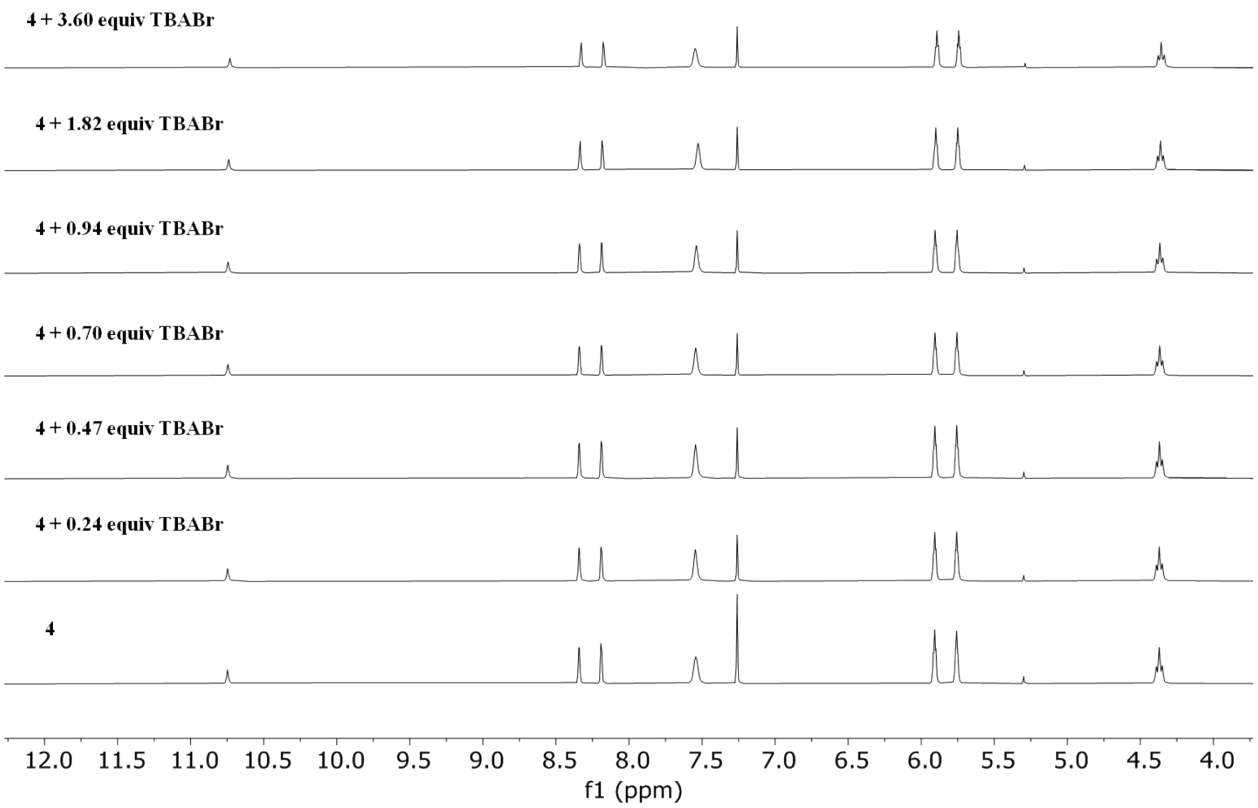


Figure S31. Partial ^{1}H NMR spectra recorded during the titration of receptor **4** (c = 8.25 mM) with TBABr in $CDCl_3$ (downfield region).

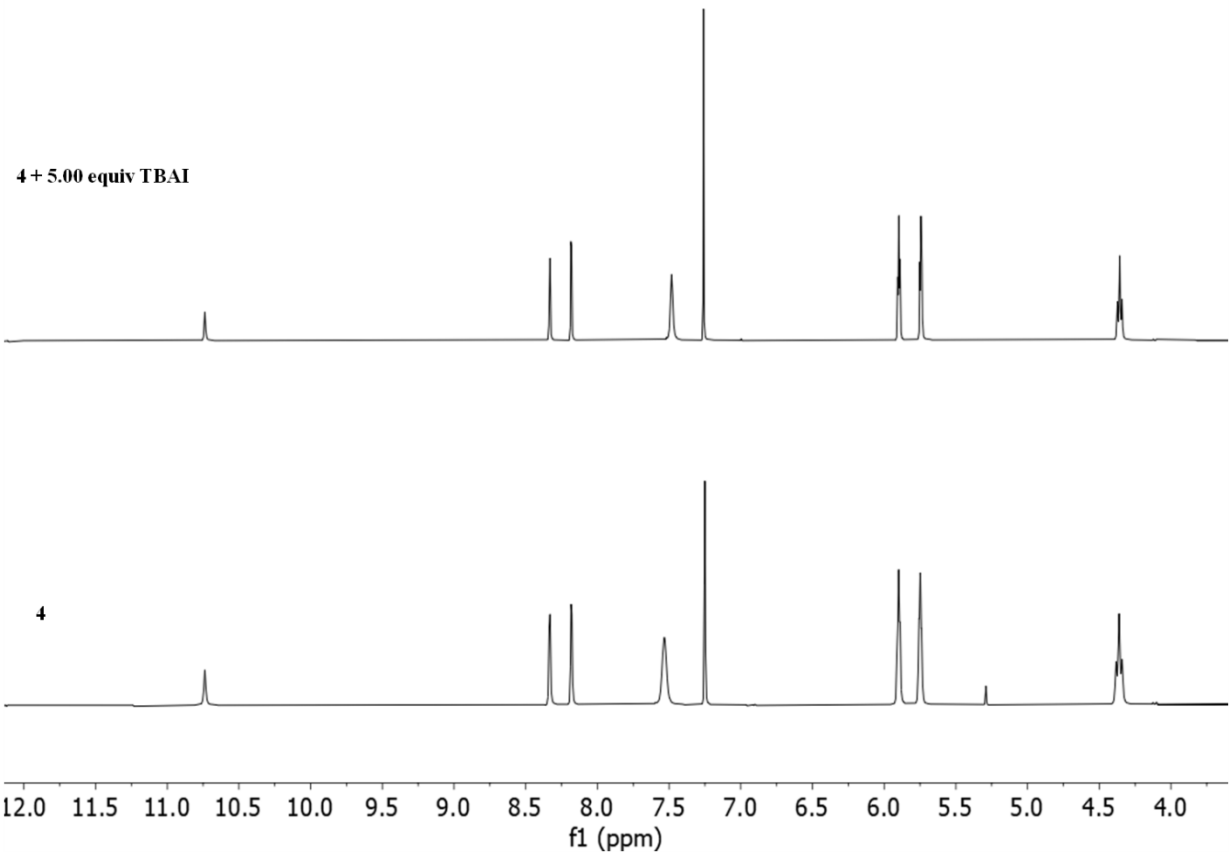


Figure S32. Partial ^{1}H NMR spectra recorded during the titration of receptor **4** (*c* = 4.72 mM) with TBAI in $CDCl_3$ (downfield region).

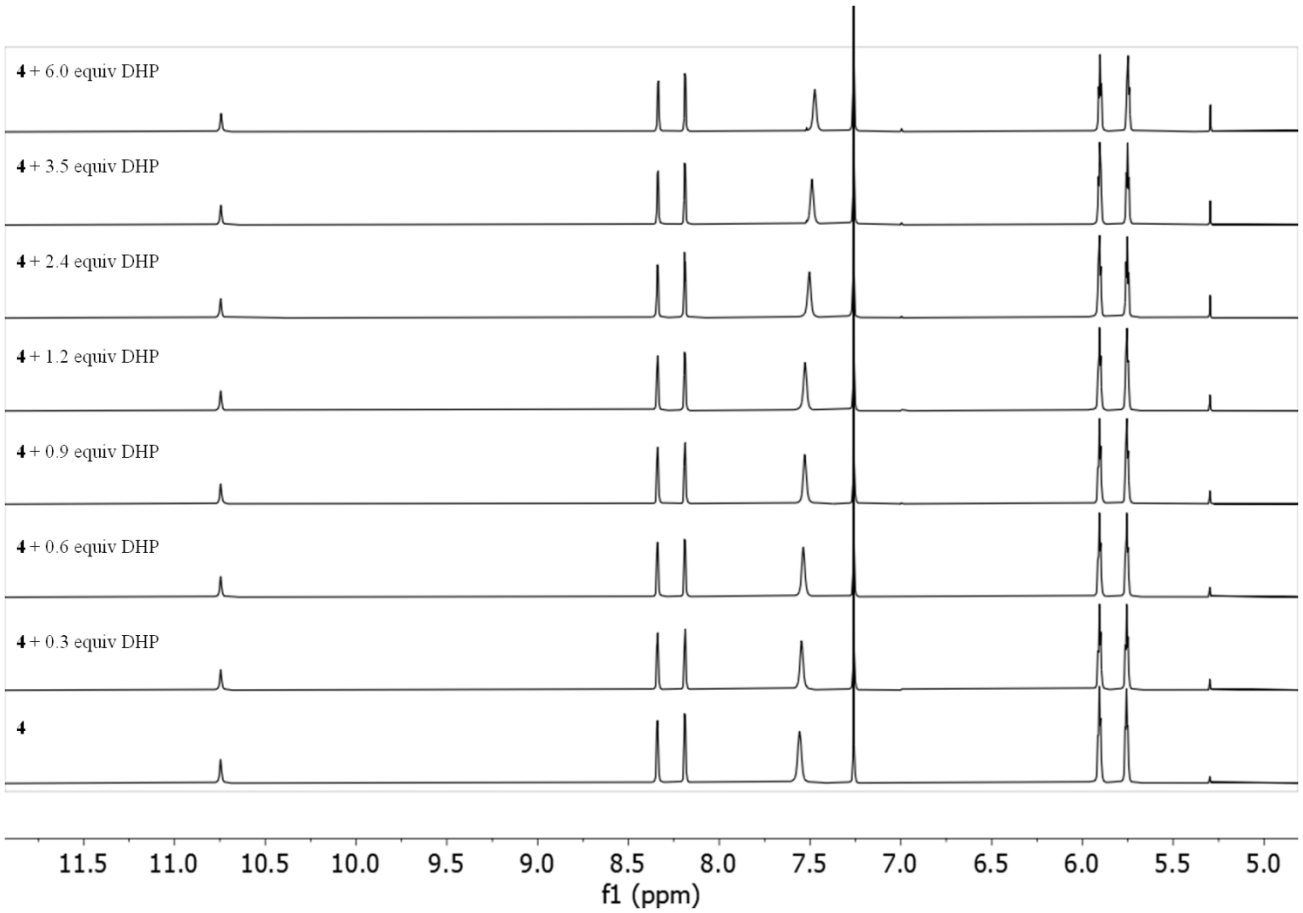


Figure S33. Partial ^{1}H NMR spectra recorded during the titration of receptor **4** (c = 4.24 mM) with $TBAH_2PO_4$ (DHP) in $CDCl_3$ (downfield region).

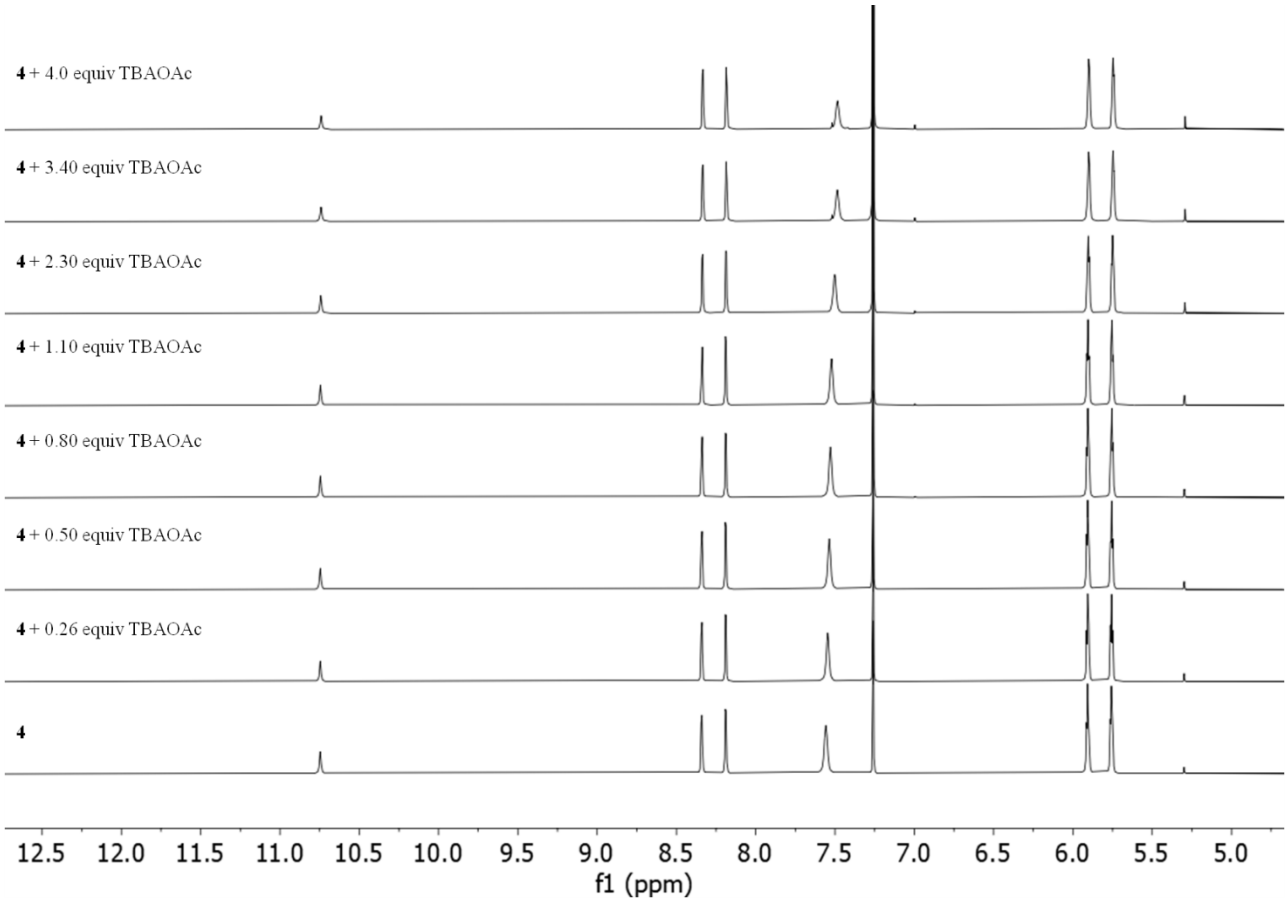


Figure S34. Partial ^{1}H NMR spectra recorded during the titration of receptor **4** (*c* = 5.19 mM) with TBAOAc in $CDCl_3$ (downfield region).

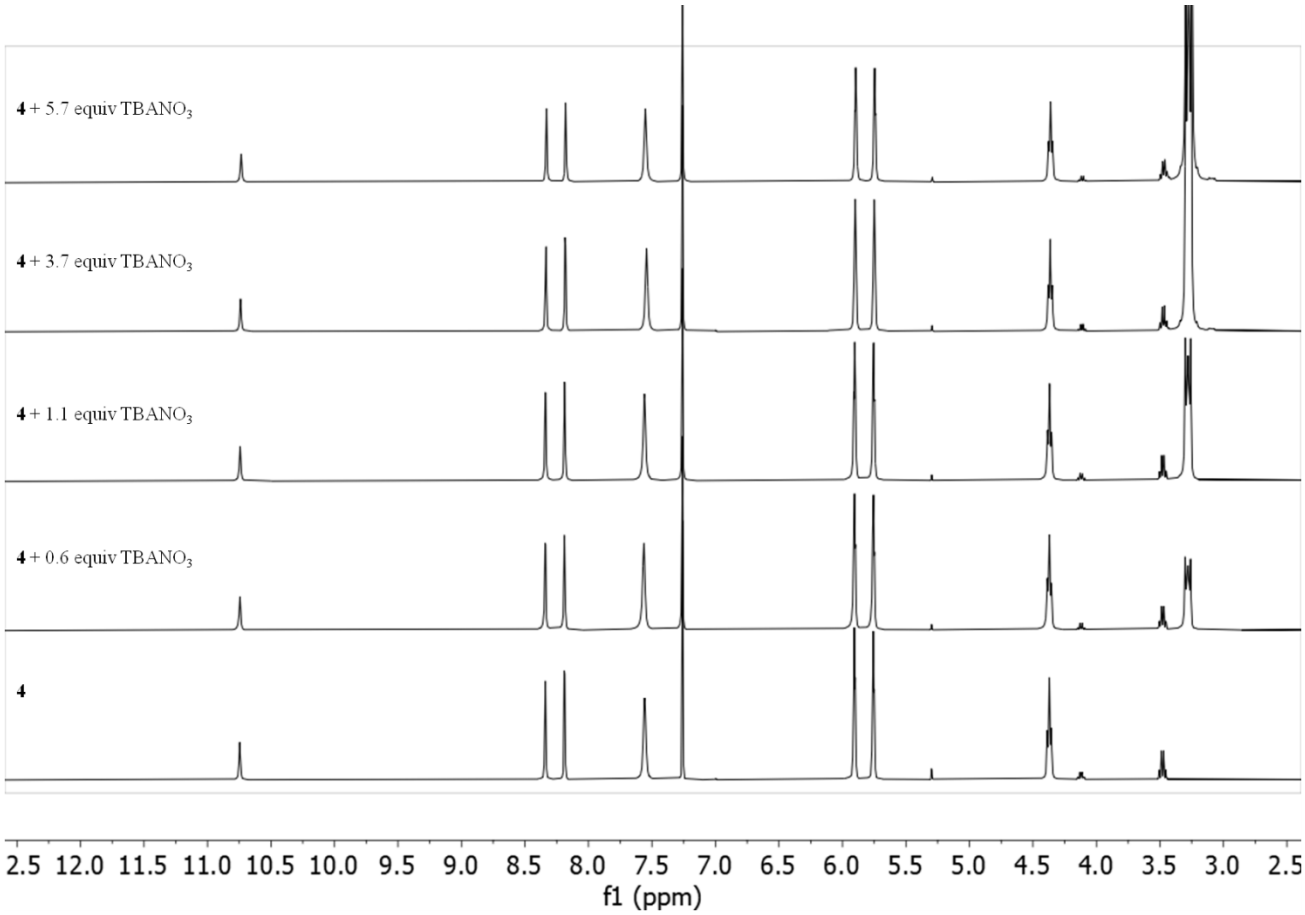


Figure S35. Partial ^{1}H NMR spectra recorded during the titration of receptor **5** (c = 6.13 mM) with $TBANO_3$ in $CDCl_3$ (downfield region).

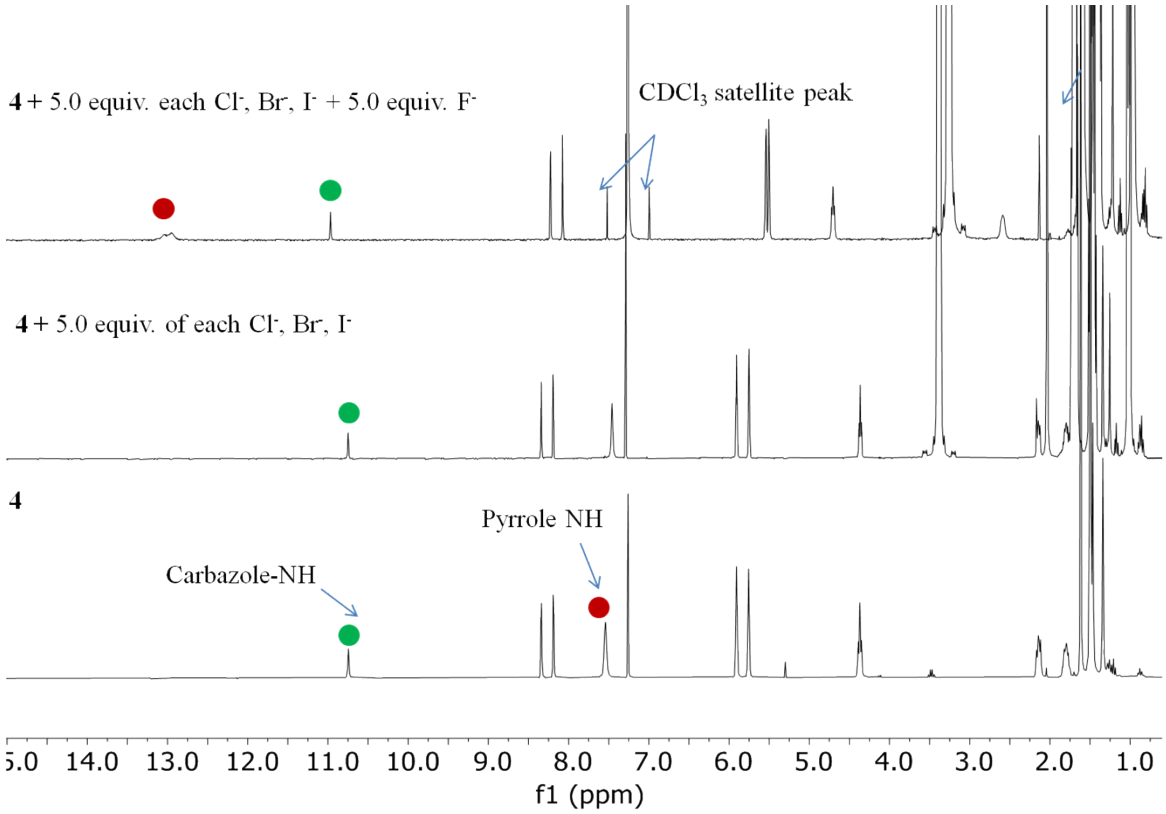


Figure S36. Partial ^{1}HNMR spectra before and after addition of TBAF (*ca*. 5.0 equivalent) to the $CDCl_3$ solution of **4** containing *ca.* 5.0 equiv**.** of TBACl, TBABr, and TBAI salts.

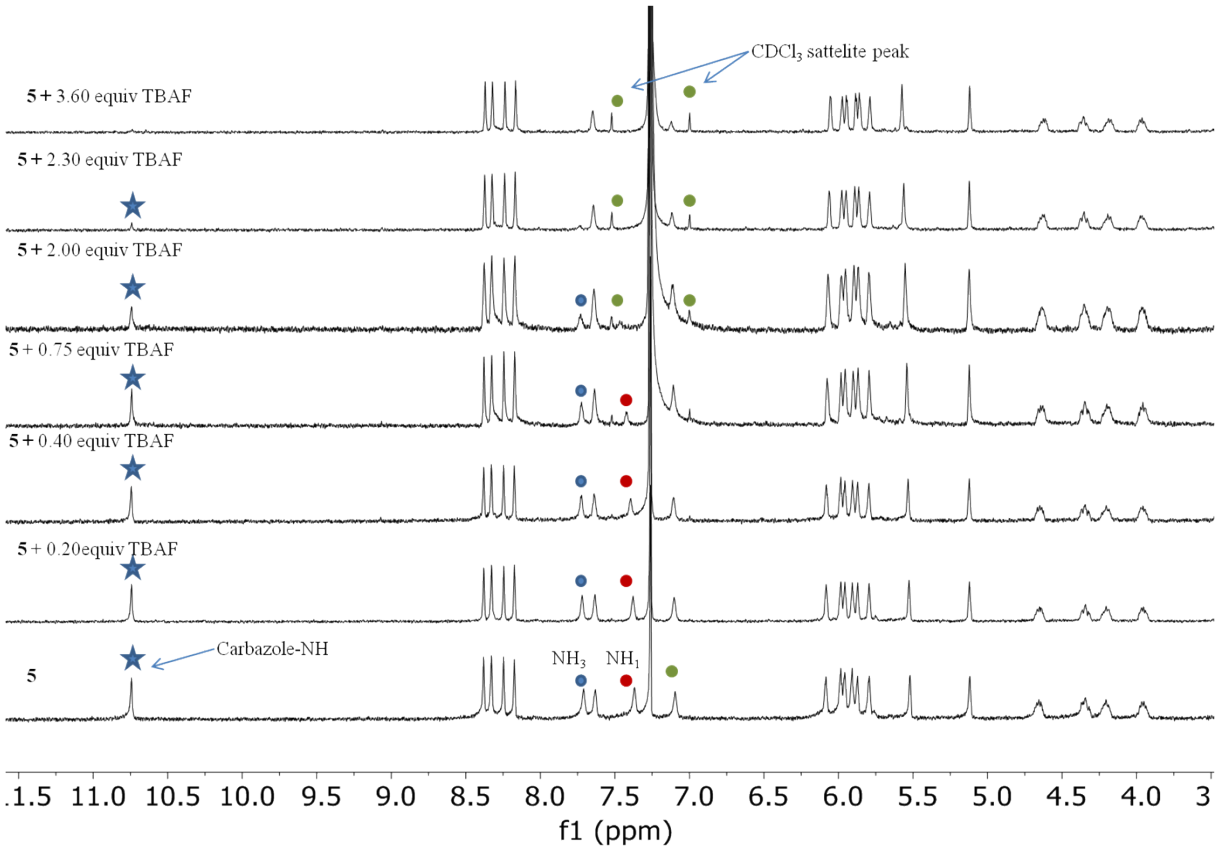


Figure S37. Partial ^{1}H NMR spectra recorded during the titration of receptor **5** (c = 5.20 mM) with TBAF in $CDCl_3$ (downfield region).

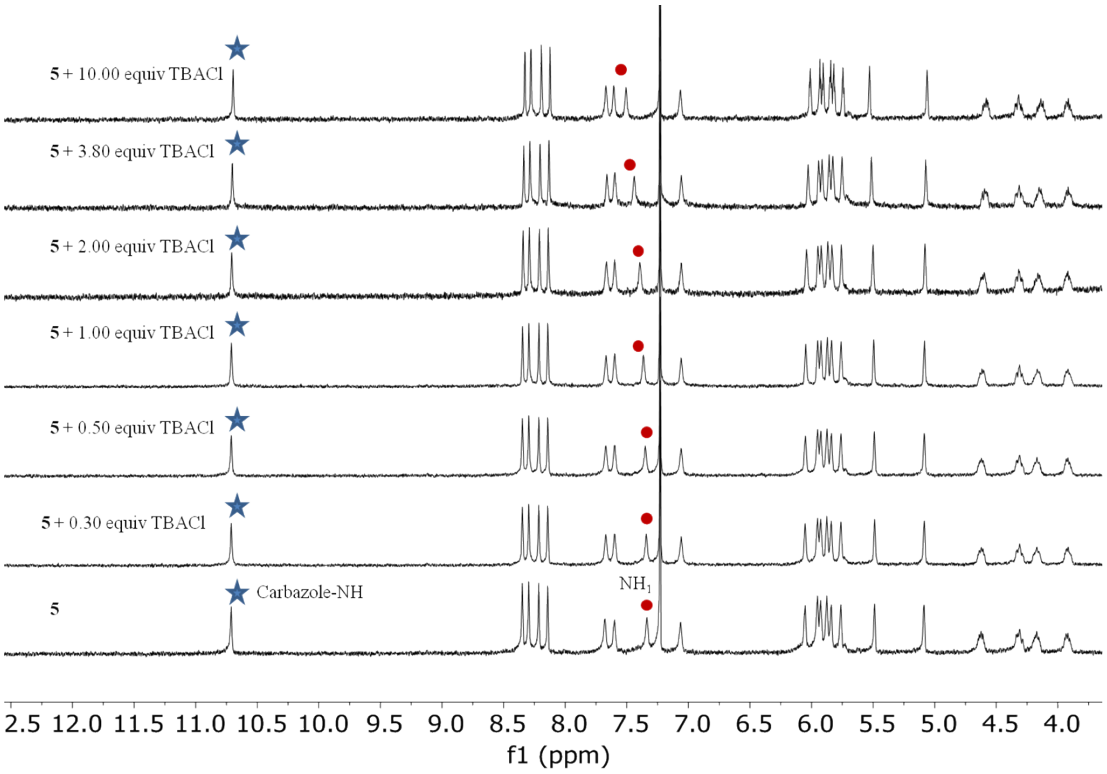


Figure S38. Partial ^{1}H NMR spectra recorded during the titration of receptor **5** (c = 5.42 mM) with TBACl in $CDCl_3$ (downfield region).

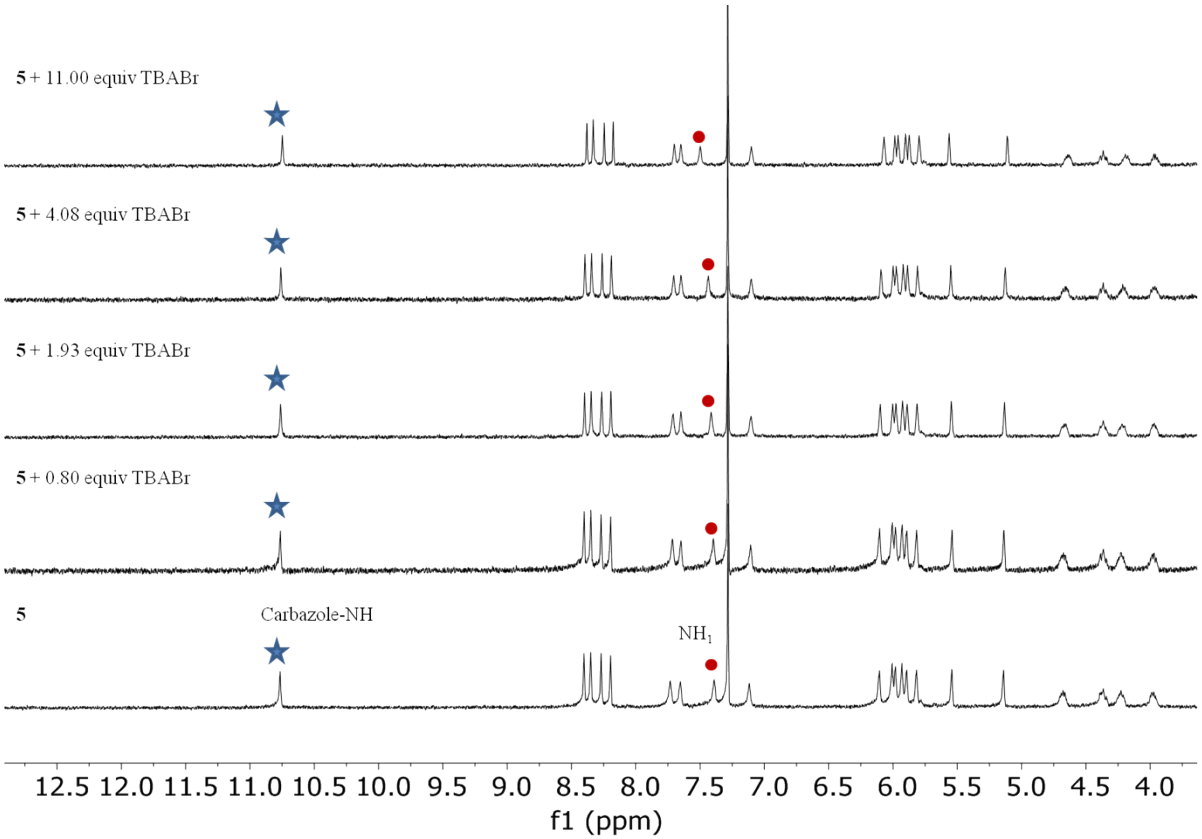


Figure S39. Partial ^{1}H NMR spectra recorded during the titration of receptor **5** (c = 4.95 mM) with TBABr in $CDCl_3$ (downfield region).

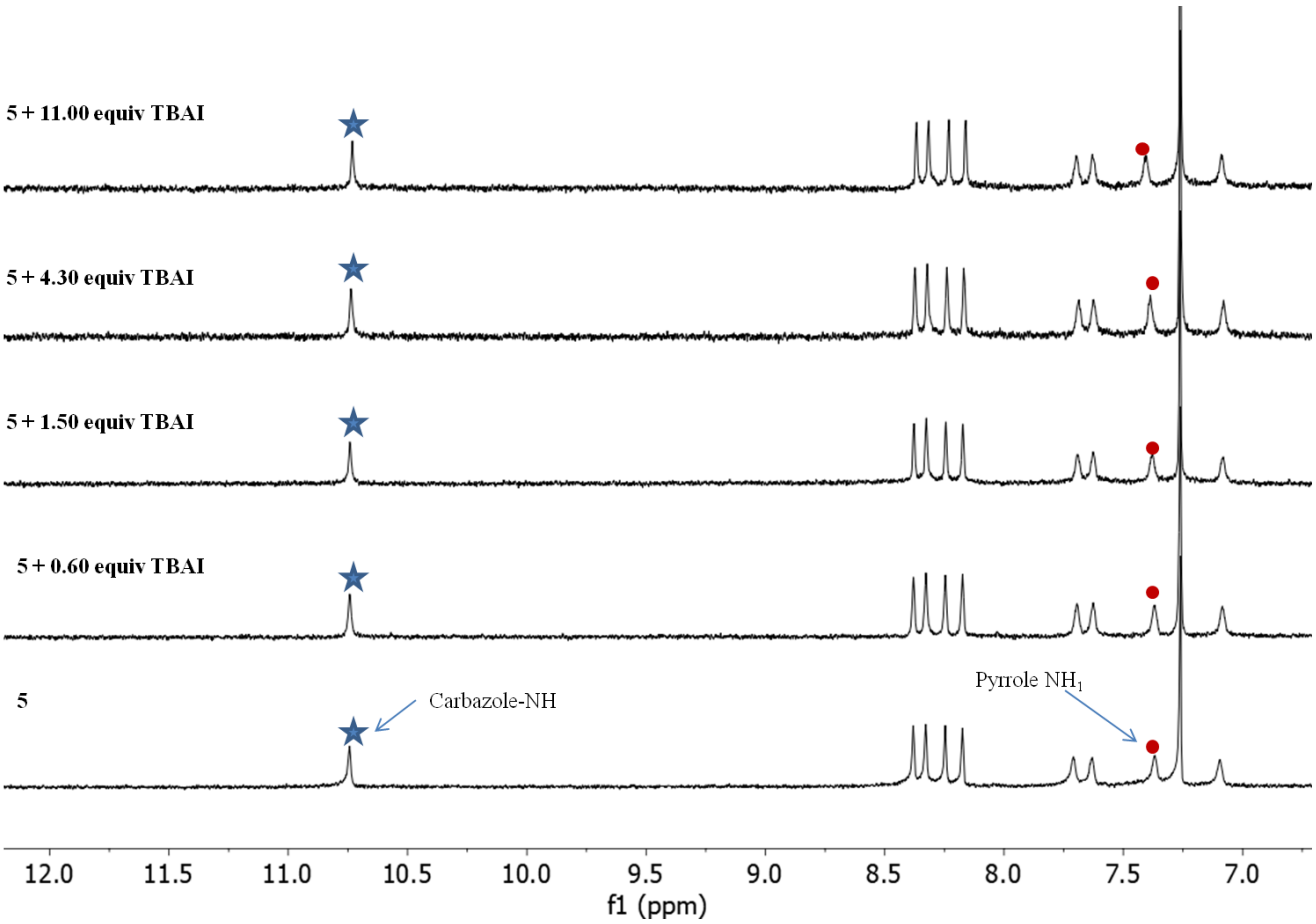


Figure S340. Partial ^{1}H NMR spectra recorded during the titration of receptor **5** (c = 4.95 mM) with TBAI in $CDCl_3$ (downfield region).

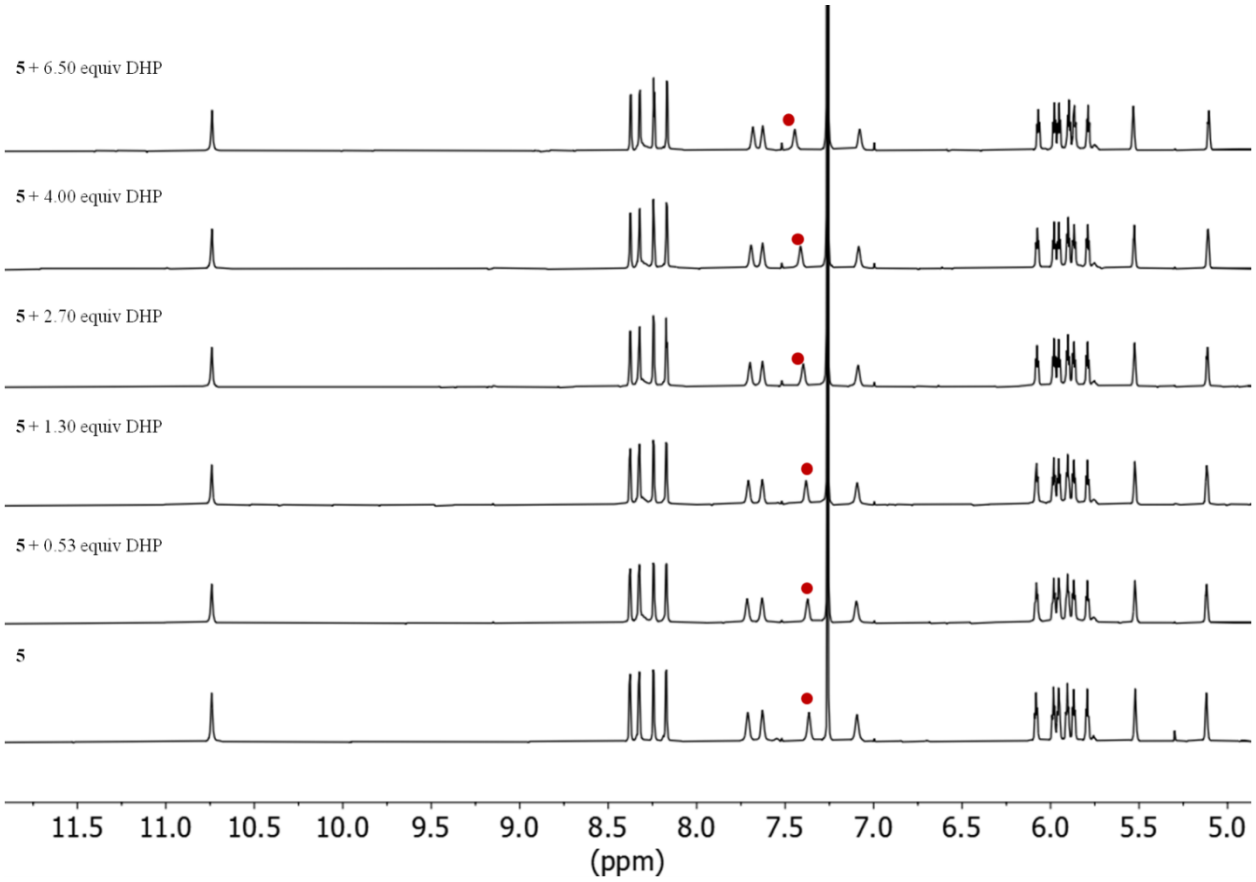


Figure S41. Partial ^{1}H NMR spectra recorded during the titration of receptor **5** (c = 3.77 mM) with $TBAH_2PO_4$ (DHP) in $CDCl_3$ (downfield region).

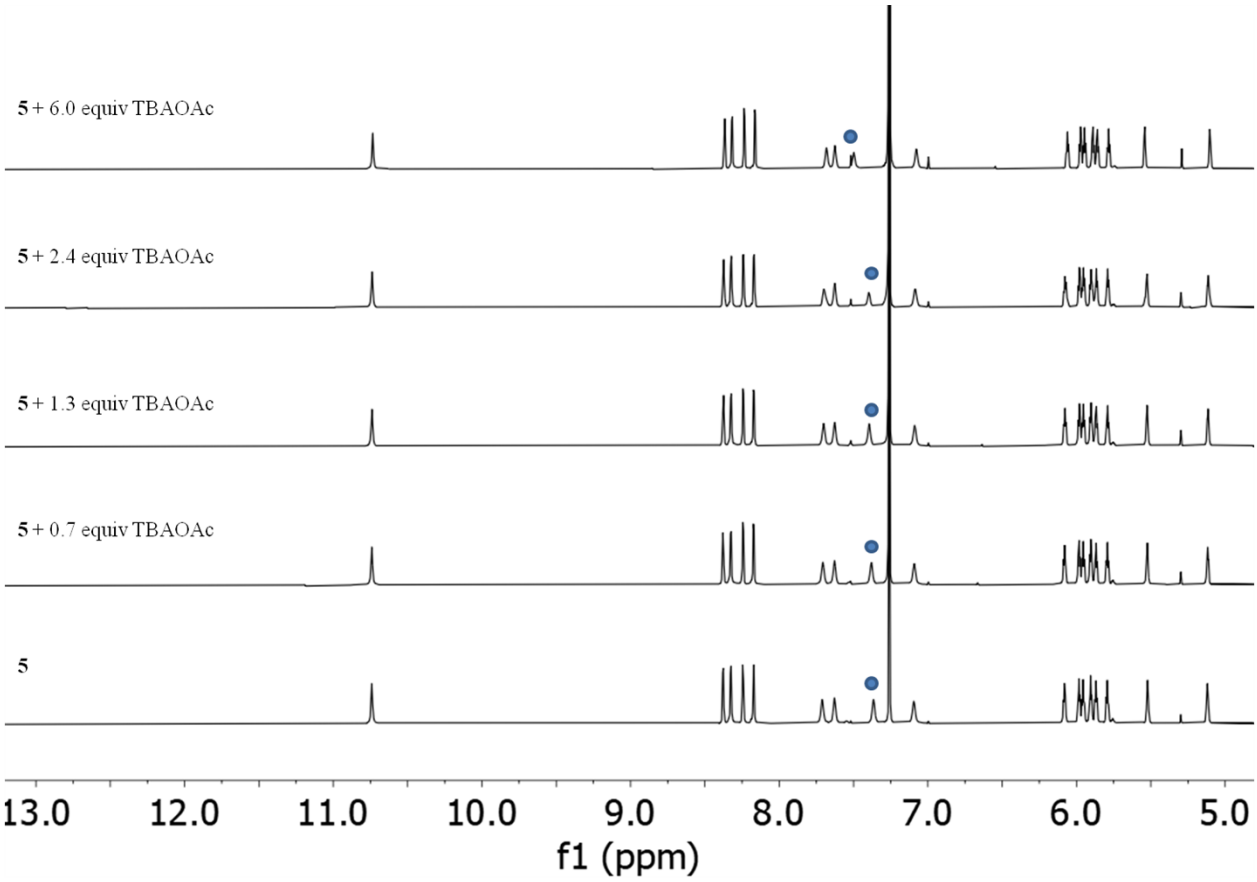


Figure S42. Partial ^{1}H NMR spectra recorded during the titration of receptor **5** (c = 3.77 mM) with TBAOAc in $CDCl_3$ (downfield region).

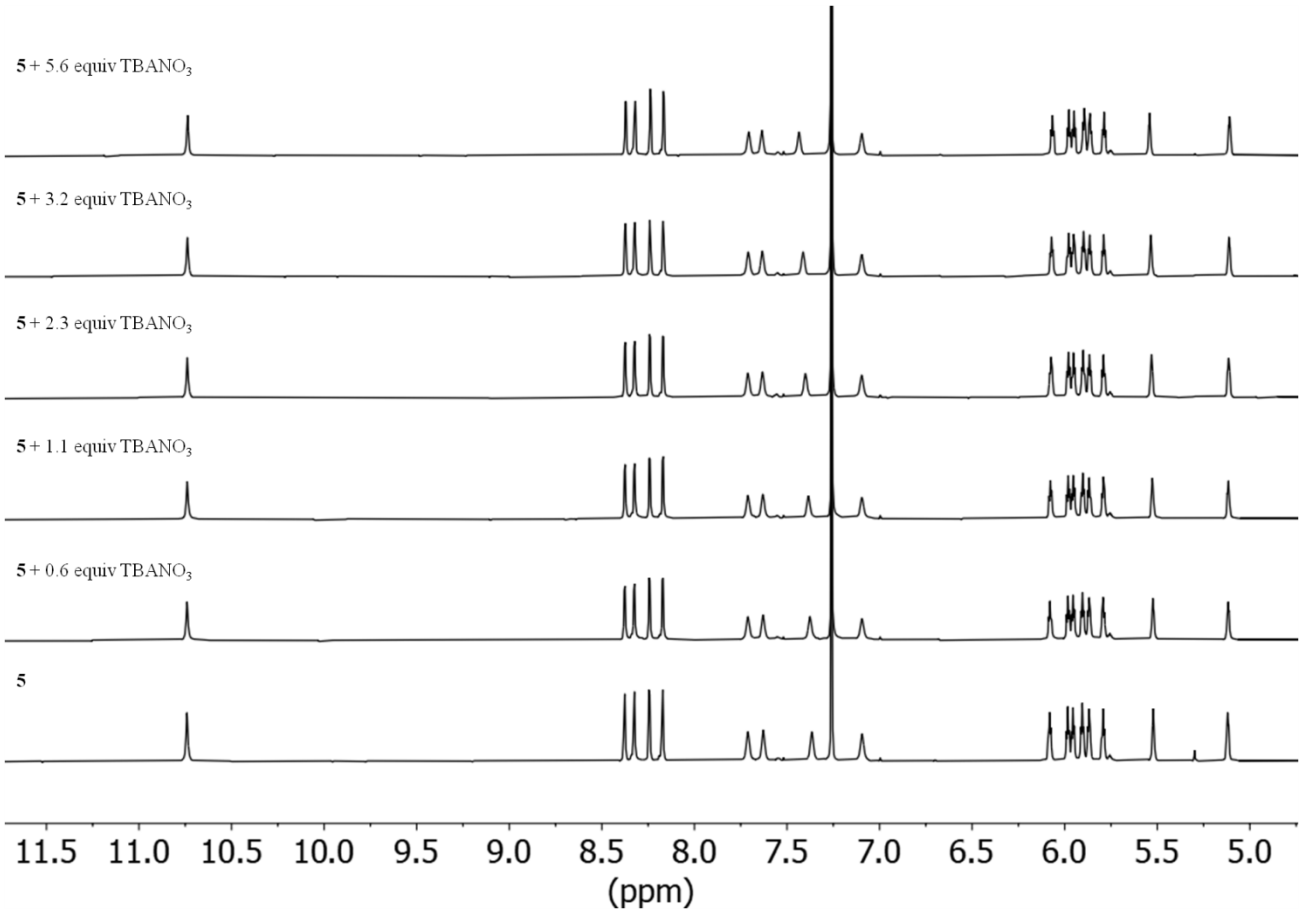


Figure S43. Partial ^{1}H NMR spectra recorded during the titration of receptor **5** (c = 2.83 mM) with $TBANO_3$ in $CDCl_3$ (downfield region).

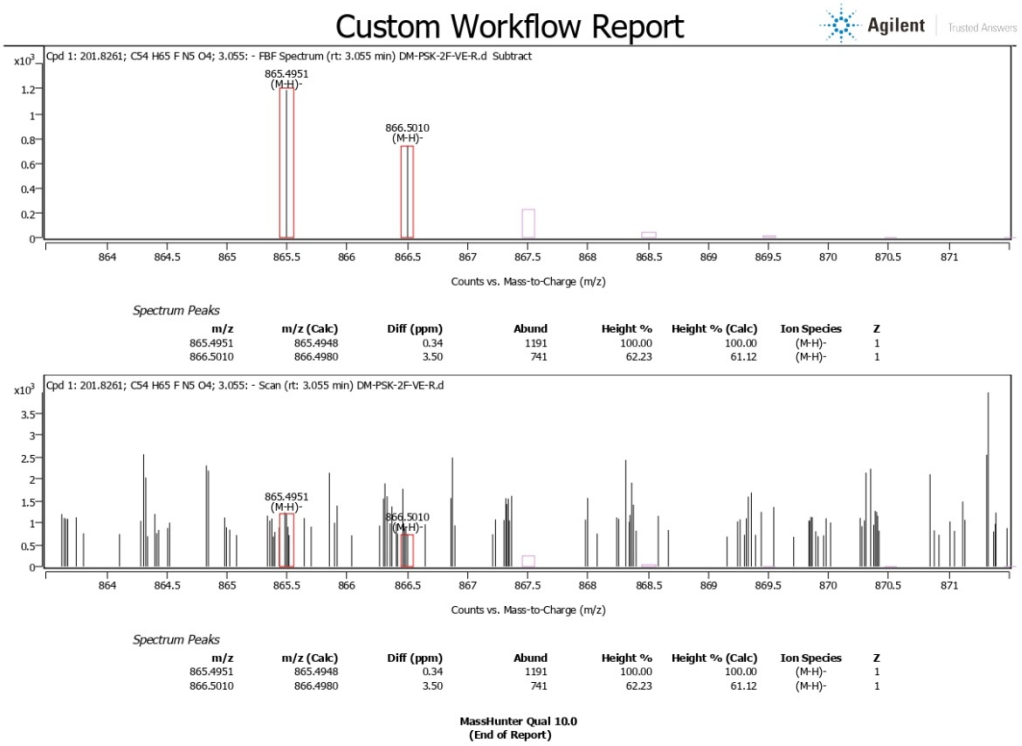


Figure S44. Mass spectra of receptor **4** recorded in the presence of TBAF. Note that the peak at m/z = 866.5010 corresponds to 1/1 **4**•F^- complex (calculated m/z value for **4**•F^- is 866.5026).

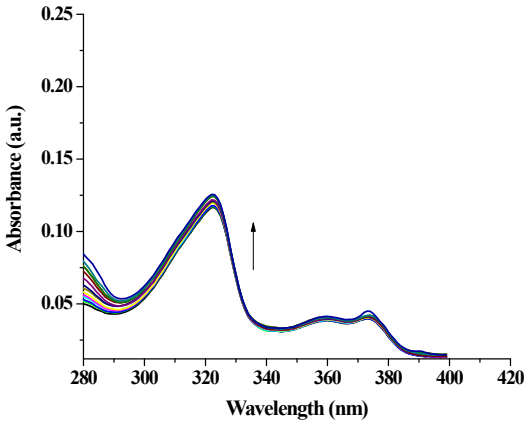


Figure S45. Change in absrobance of receptor **4** ($c = 4 \times 10^{-6}$ M) during incremental addition of fluoride anion (as tetrabutylammonium salt).

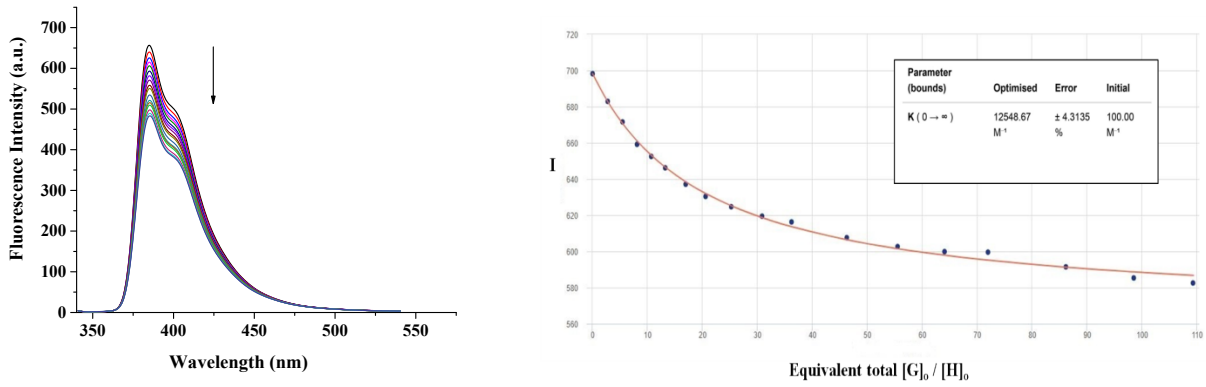


Figure S46. Change in emission of receptor **4** (c = 4.0 × 10^{-6} M) during incremental addition of tetrabutylammonium fluoride anion (0 to 4.37 × 10^{-4} M) (left panel) in $CHCl_3$ and corresponding binding isotherm analysis using BindFit v5.0.[3] The excitation wavelength was 330 nm.

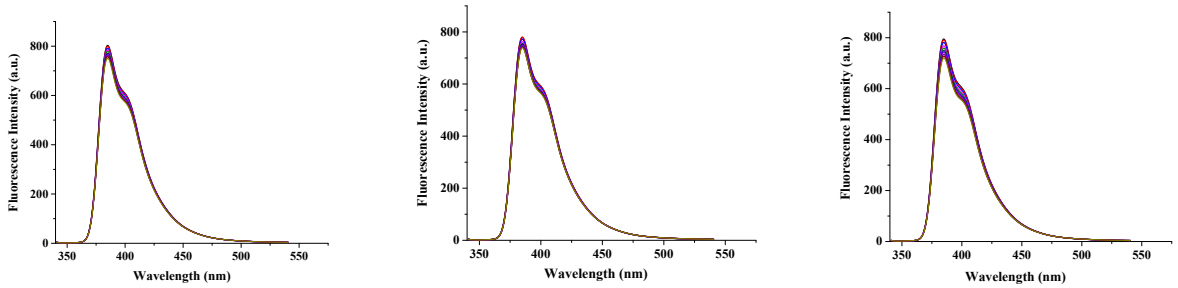


Figure S47. Change in emission of receptor **4** (c = 4.0 × 10^{-6} M) during incremental addition of chloride (0 to 4.31× 10^{-4} M) (left panel), bromide (0 to 4.31× 10^{-4} M) (centre panel) and iodide (0 to 4.31× 10^{-4} M) (right panel) anions (as their tetrabutylammonium salts) in $CHCl_3$. The excitation wavelength was 330 nm.

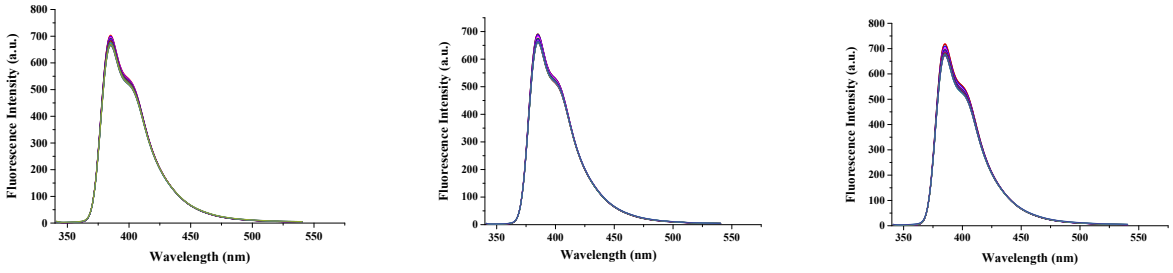


Figure S48. Change in emission of receptor **4** (c = 4.0 × 10^{-6} M) during incremental addition of dihydrogenphosphate (0 to 3.93 × 10^{-4} M) (left panel), nitrate (0 to 3.75 × 10^{-4} M) (centre panel) and acetate (0 to 3.85 × 10^{-4} M) (right panel) anions (as their tetrabutylammonium salts) in $CHCl_3$. The excitation wavelength was 330 nm.

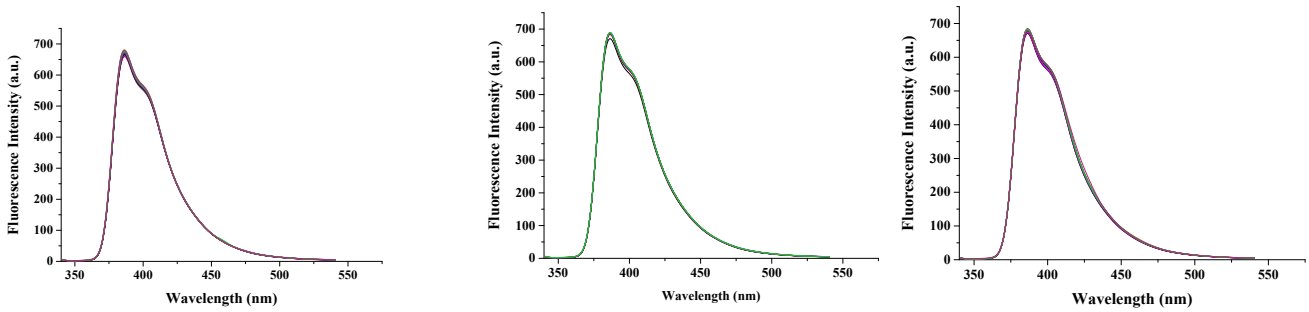


Figure S49. Change in emission of receptor **5** (c = 4.0 × 10^{-6} M) during incremental addition of fluoride (0 to 4.12× 10^{-4} M) (left panel), chloride (0 to 4.12× 10^{-4} M) (centre panel) and bromide (0 to 4.12× 10^{-4} M) (right panel) anions (as their tetrabutylammonium salts) in $CHCl_3$. The excitation wavelength was 330 nm.

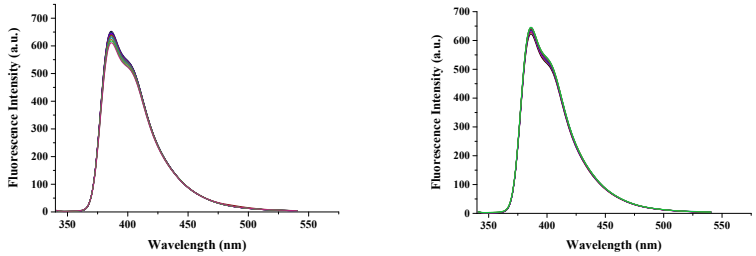


Figure S50. Change in emission of receptor **5** (c = 4.0 × 10^{-6} M) during incremental addition of iodide (0 to 4.15 × 10^{-4} M) (left panel) and dihydrogenphosphate (0 to 4.44 × 10^{-4} M) (right panel) anions (as their tetrabutylammonium salts) in $CHCl_3$. The excitation wavelength was 330 nm.

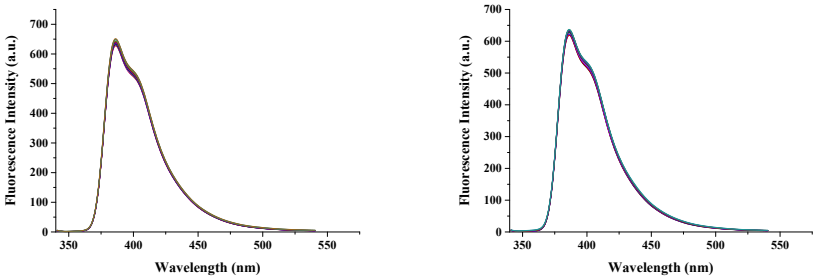


Figure S51. Change in emission of receptor **5** (c = 4.0 × 10^{-6} M) during incremental addition of acetate (0 to 4.12× 10^{-4} M) (left panel) and nitrate (0 to 4.12× 10^{-4} M) (right panel) anions (as their tetrabutylammonium salts) in $CHCl_3$. The excitation wavelength was 330 nm.

Cartesian coordinates of the fluoride complex with 4

C	1.7397997	-2.6066190	3.8062224
N	1.8949507	-1.3778037	3.2019389
H	1.2012662	-0.9137699	2.5845735
C	2.8533654	-2.8107137	4.6094817
H	3.0481844	-3.6877378	5.2178103
N	1.3351907	1.8622377	3.2436527
H	0.8486931	1.2480924	2.5616407
C	3.6924555	-1.6684860	4.4831408
H	4.6443843	-1.5083366	4.9786972
N	-1.8949507	1.3778037	3.2019389
H	-1.2012662	0.9137699	2.5845735
C	3.0742455	-0.7923656	3.6038861
N	-1.3351907	-1.8622377	3.2436527
H	-0.8486931	-1.2480924	2.5616407
C	3.5049044	0.5669829	3.0922763
C	4.9614284	0.8203796	3.5111275
H	5.2918747	1.8008313	3.1418645
H	5.6137932	0.0434284	3.0889657
H	5.0752441	0.8074119	4.6036388
C	2.6300954	1.6634192	3.6675640
C	2.8998390	2.6231368	4.6322203
H	3.8344738	2.7398076	5.1710476
C	1.7316051	3.4214716	4.7806294
H	1.6152457	4.2758086	5.4391796
C	0.7711273	2.9305819	3.9074328
C	-0.5682302	3.5176923	3.5063837
C	-0.7772120	4.8379896	4.2648215
H	-0.7942008	4.6691419	5.3497090
H	-1.7337194	5.2915500	3.9710597
H	0.0310934	5.5472220	4.0454296
C	-1.7397997	2.6066190	3.8062224
C	-2.8533654	2.8107137	4.6094817
H	-3.0481844	3.6877378	5.2178103
C	-3.6924555	1.6684860	4.4831408
H	-4.6443843	1.5083366	4.9786972
C	-3.0742455	0.7923656	3.6038861
C	-3.5049044	-0.5669829	3.0922763
C	-4.9614284	-0.8203796	3.5111275
H	-5.2918747	-1.8008313	3.1418645
H	-5.6137932	-0.0434284	3.0889657
H	-5.0752441	-0.8074119	4.6036388
C	-2.6300954	-1.6634192	3.6675640
C	-2.8998390	-2.6231368	4.6322203
H	-3.8344738	-2.7398076	5.1710476
C	-1.7316051	-3.4214716	4.7806294
H	-1.6152457	-4.2758086	5.4391796
C	-0.7711273	-2.9305819	3.9074328
C	0.5682302	-3.5176923	3.5063837
C	0.7772120	-4.8379896	4.2648215
H	0.7942008	-4.6691419	5.3497090
H	1.7337194	-5.2915500	3.9710597
H	-0.0310934	-5.5472220	4.0454296
C	-0.5486197	3.8133169	1.9703157
C	3.4300063	0.5917816	1.5457231
H	3.7655029	1.5675195	1.1660540
H	4.0752613	-0.1966272	1.1300422
H	2.4092837	0.4308346	1.1770295
C	-3.4300063	-0.5917816	1.5457231
H	-3.7655029	-1.5675195	1.1660540
H	-4.0752613	0.1966272	1.1300422
H	-2.4092837	-0.4308346	1.1770295
C	0.5486197	-3.8133169	1.9703157
C	-0.7404981	-4.4825299	1.4980768
C	-0.6868600	-5.0493548	0.0875947
C	0.7404981	4.4825299	1.4980768
C	0.6868600	5.0493548	0.0875947
C	0.0037255	-3.0253873	-4.9430074
C	-0.0741883	-3.4048359	-3.5892075

C	-0.1342917	-2.4934829	-2.5292439
C	-0.0545768	-1.1236304	-2.8451066
C	-0.0121265	-0.7192245	-4.2068874
C	0.0099988	-1.6616719	-5.2390280
H	-0.1284732	-4.4601303	-3.3267376
H	0.0401674	-1.3142382	-6.2712161
C	0.0545768	1.1236304	-2.8451066
C	0.1342917	2.4934829	-2.5292439
C	0.0741883	3.4048359	-3.5892075
C	-0.0037255	3.0253873	-4.9430074
C	-0.0099988	1.6616719	-5.2390280
C	0.0121265	0.7192245	-4.2068874
H	0.1284732	4.4601303	-3.3267376
H	-0.0401674	1.3142382	-6.2712161
N	0.0000000	-0.0000000	-2.0416343
C	-0.0558172	4.1126220	-6.0237721
C	-0.1400622	3.5184384	-7.4381130
H	-0.1870425	4.3308630	-8.1785400
H	0.7401334	2.9025225	-7.6741279
H	-1.0389586	2.8980217	-7.5652504
C	-1.3004555	4.9970760	-5.7946445
H	-1.2799979	5.4716143	-4.8044112
H	-1.3534781	5.7941165	-6.5530220
H	-2.2197128	4.3973510	-5.8588585
C	1.2151932	4.9849439	-5.9404969
H	1.1918002	5.7759650	-6.7067296
H	1.3083950	5.4690513	-4.9590962
H	2.1160318	4.3753499	-6.1009065
C	0.0558172	-4.1126220	-6.0237721
C	-1.2151932	-4.9849439	-5.9404969
H	-2.1160318	-4.3753499	-6.1009065
H	-1.1918002	-5.7759650	-6.7067296
H	-1.3083950	-5.4690513	-4.9590962
C	0.1400622	-3.5184384	-7.4381130
H	1.0389586	-2.8980217	-7.5652504
H	0.1870425	-4.3308630	-8.1785400
H	-0.7401334	-2.9025225	-7.6741279
C	1.3004555	-4.9970760	-5.7946445
H	2.2197128	-4.3973510	-5.8588585
H	1.2799979	-5.4716143	-4.8044112
H	1.3534781	-5.7941165	-6.5530220
C	-0.4923197	-2.9640482	-1.1675722
O	-1.1418417	-2.2964457	-0.3822949
O	-0.0681970	-4.2359204	-0.9572664
C	0.4923197	2.9640482	-1.1675722
O	1.1418417	2.2964457	-0.3822949
O	0.0681970	4.2359204	-0.9572664
H	0.0000000	-0.0000000	-1.0196758
F	-0.0000000	0.0000000	1.7216186
H	1.7019013	5.3006774	-0.2614836
H	0.0738695	5.9607445	0.0573179
H	0.9901096	5.3394512	2.1475327
H	1.5684225	3.7720770	1.5865753
H	-1.4328933	4.4283252	1.7313451
H	-0.6669271	2.8672053	1.4248650
H	-1.5684225	-3.7720770	1.5865753
H	-0.9901096	-5.3394512	2.1475327
H	1.4328933	-4.4283252	1.7313451
H	0.6669271	-2.8672053	1.4248650
H	-1.7019013	-5.3006774	-0.2614836
H	-0.0738695	-5.9607445	0.0573179

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