Supporting Information

Facile synthesis of dicyanovinyl-di(*meso*-aryl)dipyrromethenes via a dipyrromethene-DDQ adduct

Ji-Young Shin*, Brian O. Patrick and David Dolphin*

Experimental and NMR data

Experimental and NMR data

General

All chemicals were purchased from commercial suppliers and used without further purification. Column chromatography of all products was carried out using silica gel (particle size: 0.040-0.063 mm, 230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance 300 and 400 NMR spectrometers in CD_2Cl_2. Mass spectra were determined on EI or ESI mass spectrometers. Optical spectra were recorded with a Cary 5000 UV-vis spectrophotometer using a 1 cm cell. The crystals were grown by diffusion of hexane into CH_2Cl_2 solutions. Data were collected and integrated using the Bruker SAINT software package and corrected for absorption effects using the multi-scan technique (SADABS). The structures were solved by direct methods and all refinements were performed using the SHELXTL crystallographic software package from Bruker-AXS.

Procedure

Dipyrromethane 1:

Meso-2,6-dichlorophenyldipyrromethane was prepared following the reference method.[S1]
Column chromatography on silica gel using a mixed eluent of CH_2Cl_2 and hexane (3:1), followed by recrystallization from CH_2Cl_2 and hexane yielded an off-white solid in 60% yield.

Compounds 2-4:

DDQ (2.29 g, 10.09 mmol) was added into a CH_2Cl_2 (150 mL) solution of *meso*-2,6-dichlorophenyldipyrromethane (1.11g, 3.85 mmol). After stirring for 2 days, the reaction mixture was concentrated and column chromatographed on silica gel using CH_2Cl_2. Three fractions were collected (first red (**3**), second yellow (**2**), and third blue) and each was recrystallized from CH_2Cl_2 and hexane (yields: 30% (330 mg) and 8% (124 mg) for **2**, and **3**, respectively). A small amount of compound **3** was lost during the isolation due to its poor solubility. Compound **4** was prepared by the addition of Et_3N (0.5 mL) into a CH_2Cl_2 (75 mL) solution of **3** (30 mg, 37.4 μmol) and purified by column chromatography on silica gel using CH_2Cl_2 as eluent (80% yield).

Spectral data of ***2*** : ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 12.36 (bs, 1H, NH), 7.66 (s, 2H, αH), 7.47 (dd, J = 8.6, ^{dd}J = 1.2, 2H, *meta*-H), 7.39 (t, J = 7.2, 1H, *para*-H), 6.39 (m, 4H, βH); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 145.11 (αC), 140.45, 136.02, 135.49, 135.25, 130.93 (*para*-C), 128.60 (*meta*-C), 127.29 (βC), 118.96 (βC); *m/z* HREIMS found 288.02273 (100%), calcd. 288.02210 for $C_{15}H_{10}N_2{}^{35}Cl_2$ (M^+); λ_{max} (nm, CH_2Cl_2, log ε) 431 (4.49).

Spectral data of ***3*** : ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 11.18 (bs, 2H, NH), 7.64 (m, 2H, αH), 7.52-7.40 (m, 6H, Aryl-H), 6.79 (d, J = 4.3, 2H, βH of inner pyrrole), 6.73 (d, J = 4.3, 2H, βH of inner pyrrole), 6.42 (m, 4H, βH of terminal pyrrole);^{13}C NMR (100 MHz, CD_2Cl_2) δ = 176.67, 156.04, 146.84, 142.83, 141.78, 136.71 (βC), 135.96, 135.66, 134.93 (αC), 134.19, 131.56 (*para*-C), 131.50, 128.82 (*meta*-C), 128.68 (*meta*-C), 126.19 (βC), 121.95 (βC), 114.57 (βC), 114.27, 30.28 (sp^{3}C); *m/z* HRESIMS found 802.9671, calcd. 802.9691 for $C_{38}H_{19}N_6O_2{}^{35}Cl_5{}^{37}Cl$ ($[M+H]^+$); λ_{max} (nm, CH_2Cl_2, log ε) 500 (4.64).

Spectral data of ***4*** : ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 12.94 (bs, 2H, NH), 7.59 (m, 2H, αH), 7.54-7.42 (m, 6H, Aryl-H), 7.16 (d, J = 4.5, 2H, βH of inner pyrrole), 6.72 (d, J = 4.3, 2H, βH of inner pyrrole), 6.47 (dd, 2H, J =

4.1, ^{dd}J = 1.2, βH of terminal pyrrole), 6.42 (dd, 2H, J = 4.3, ^{dd}J = 2.2, βH of terminal pyrrole); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 140.04, 136.82 (αC), 135.95, 134.58, 133.75, 133.57 (βC), 131.47, 128.77 (Aryl-C), 126.19 (βC), 125.77 (βC), 119.57, 115.38 (βC), 114.09; *m/z* HREIMS found 650.03271 (100%), calcd. 650.03471 for $C_{34}H_{18}N_6{}^{35}Cl_4$ (M^+); λ_{max} (nm, CH_2Cl_2, log ε) 335 (4.18), 492 (3.59), 680 (4.31), 735 (4.50).

Compound 5:

$AlCl_3$ (300 mg) in MeOH (15 mL) was added into a THF (35 mL) solution of **3** (54 mg, 67.3 μmol). After refluxing for 2 days, the reaction mixture was poured into water and extracted with CH_2Cl_2. The result solution was evaporated and the residue was column chromatographed on silica gel using CH_2Cl_2. The fastest pink fraction was collected and recrystallized from CH_2Cl_2 and hexane (10 mg, 30%)

Spectral data of **5** : ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 12.43 (bs, 2H, NH), 7.54-7.35 (m, 6H, Aryl-H), 6.99 (dd, J = 4.0, ^{dd}J = 2.4, 2H, βH), 6.56 (d, J = 4.8, 2H, βH), 6.33 (d, 2H, J = 4.8, βH), 6.05 (dd, 2H, J = 4.4, ^{dd}J = 1.6, βH), 4.29 (s, 6H, OMe); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 178.39, 160.22, 149.84, 144.99, 140.59, 138.79, 137.14 (βC), 136.90, 134.20, 131.24 (Aryl-C), 129.45, 128.79 (Aryl-C), 124.18, 122.67 (βC), 122.00, 120.70 (βC), 118.04 (βC), 113.99, 91.93, 58.36; *m/z* HRESIMS found 505.9636 (100%), calcd. 505.9633 for $C_{22}H_{12}N_3{}^{35}Cl_4O_3$ [$(M+H)^+$]; λ_{max} (nm, CH_2Cl_2, log ε) 332 (4.51), 420 (3.94), 542 (4.48), 735 (4.50).

NMR spectra of **2**, **3** and **4**.

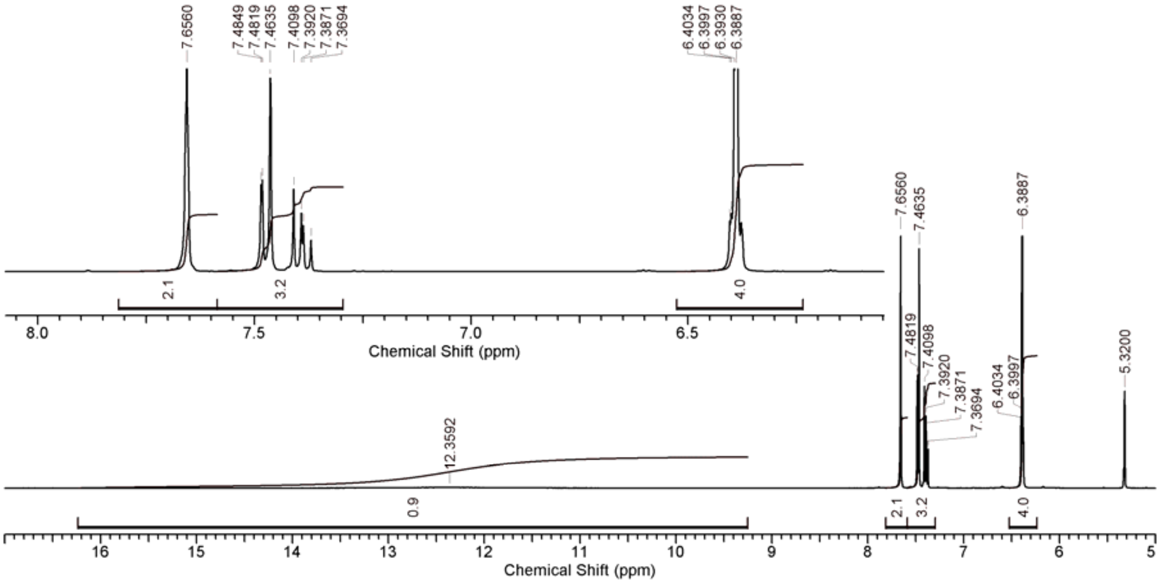

Figure S1. ^{1}H NMR (400 MHz) spectrum of **2** in CD_2Cl_2.

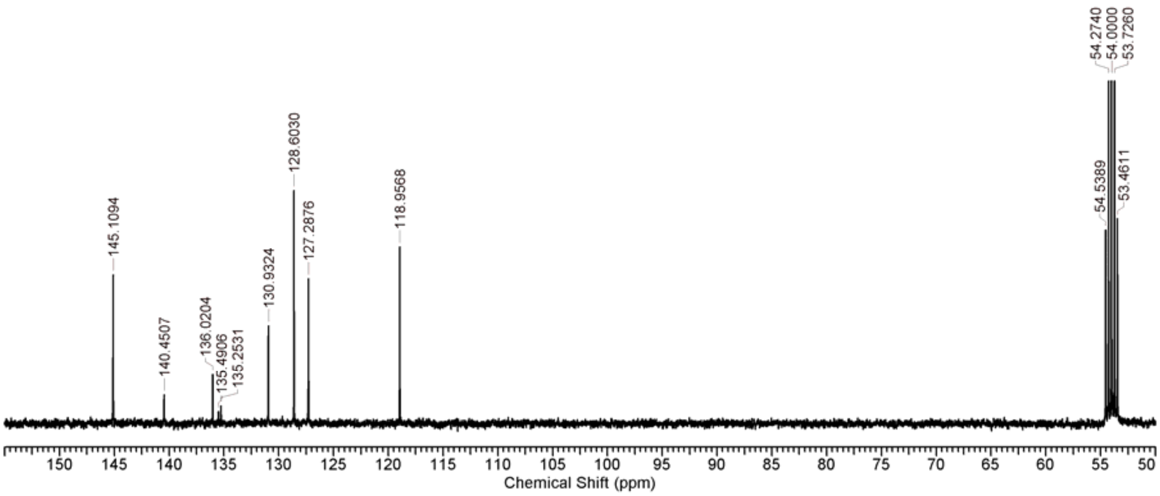

Figure S2. ^{13}C NMR (100 MHz) spectrum of **2** in CD_2Cl_2.

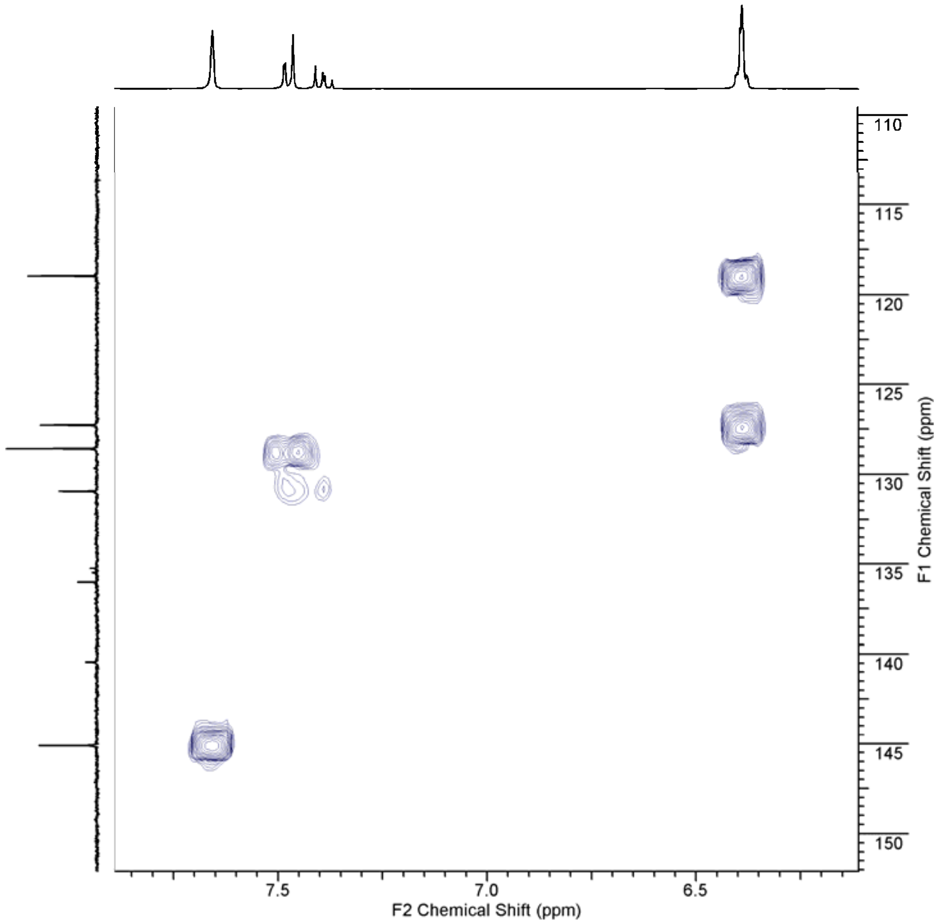

Figure S3. HMQC NMR (F1 = 100 MHz and F2 = 400 MHz) spectrum of **2** in CD_2Cl_2.

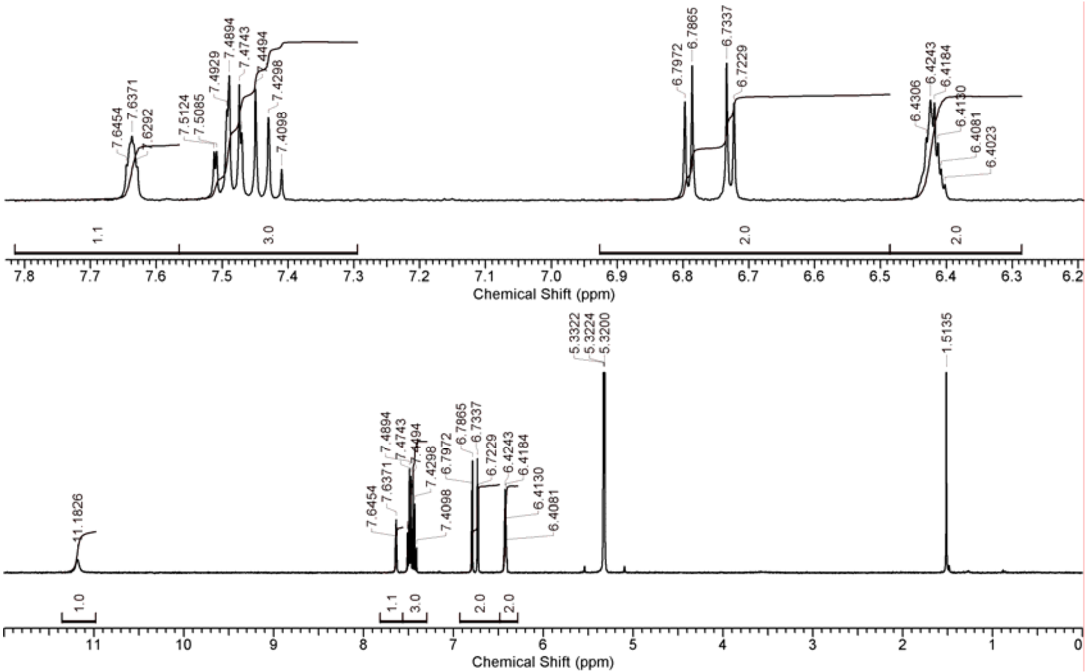

Figure S4. ^1H NMR (400 MHz) spectrum of **3** in CD_2Cl_2.

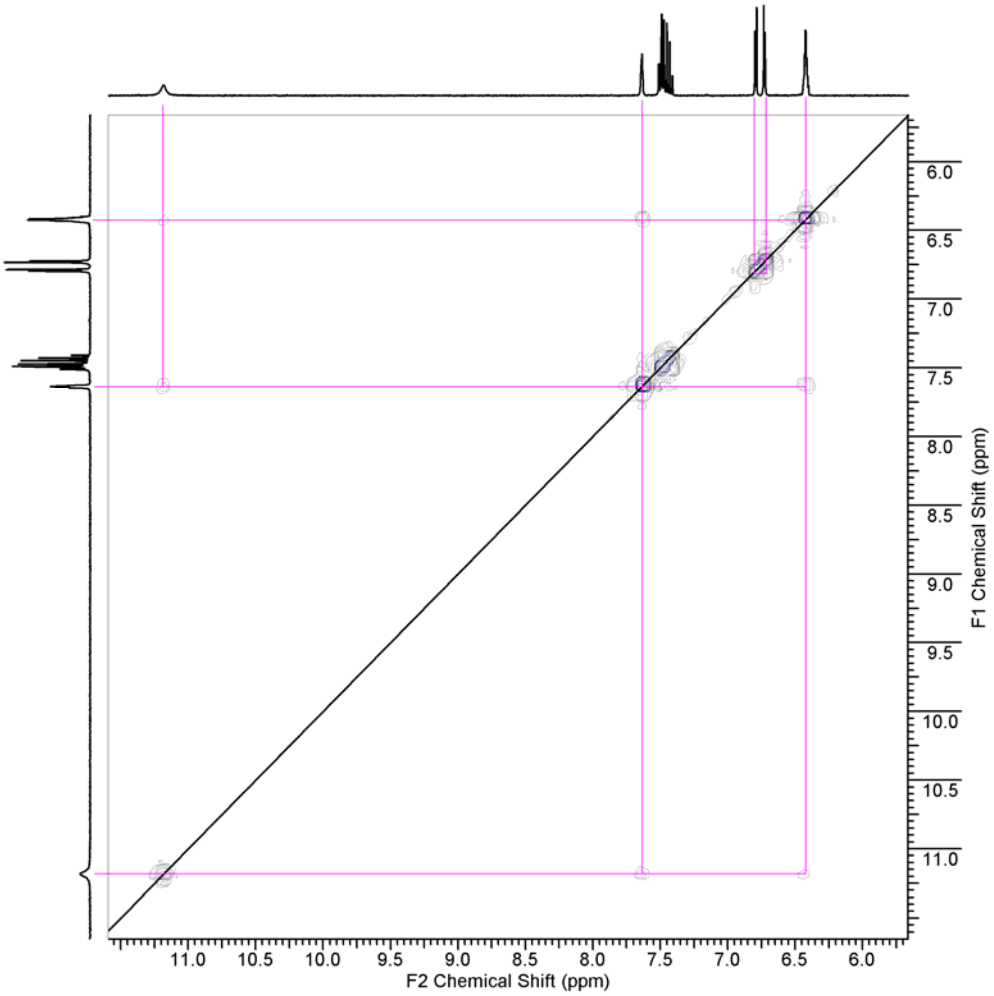

Figure S5. HH COSY NMR (F1 = F2 = 400 MHz) spectrum of **3** in CD_2Cl_2.

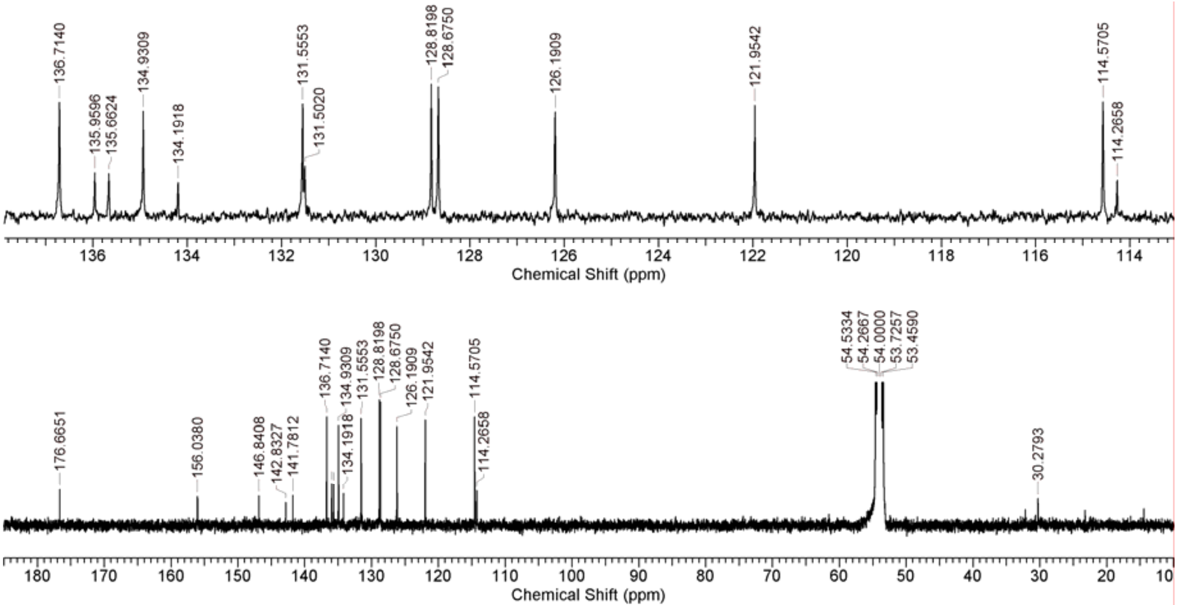

Figure S6. ^{13}C NMR (100 MHz) spectrum of **3** in CD_2Cl_2.

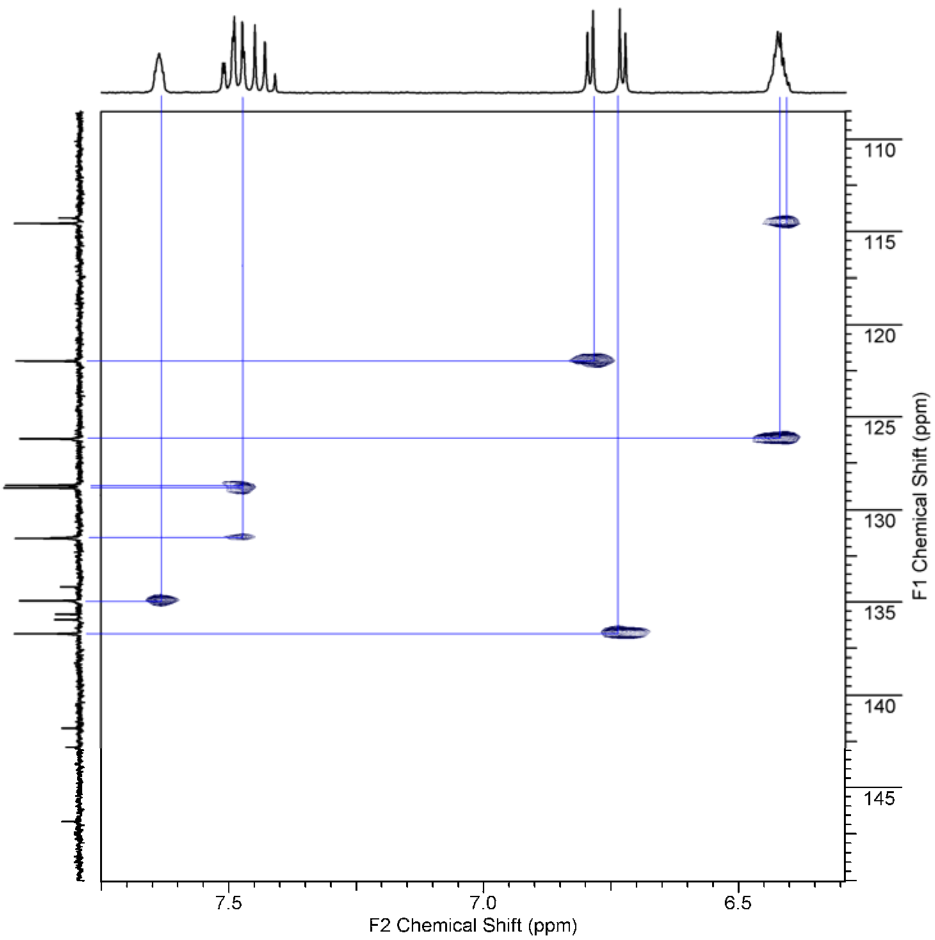

Figure S7. HMQC NMR (F1 = 100 MHz and F2 = 400 MHz) spectrum of **3** in CD_2Cl_2.

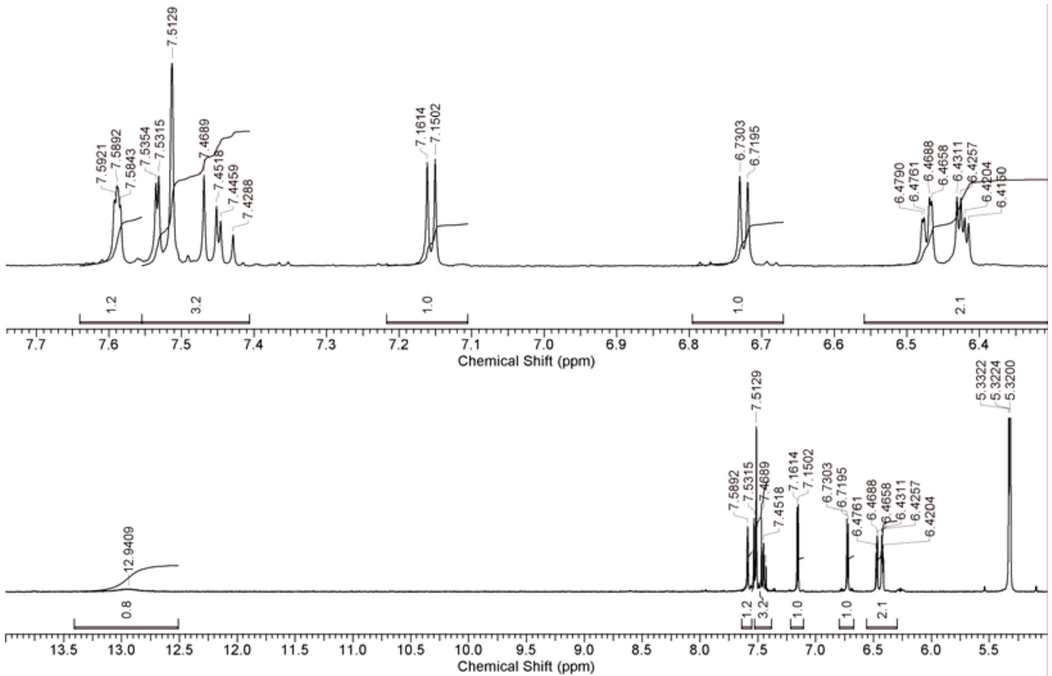

Figure S8. ^{1}H NMR (400 MHz) spectrum of **4** in CD_2Cl_2.

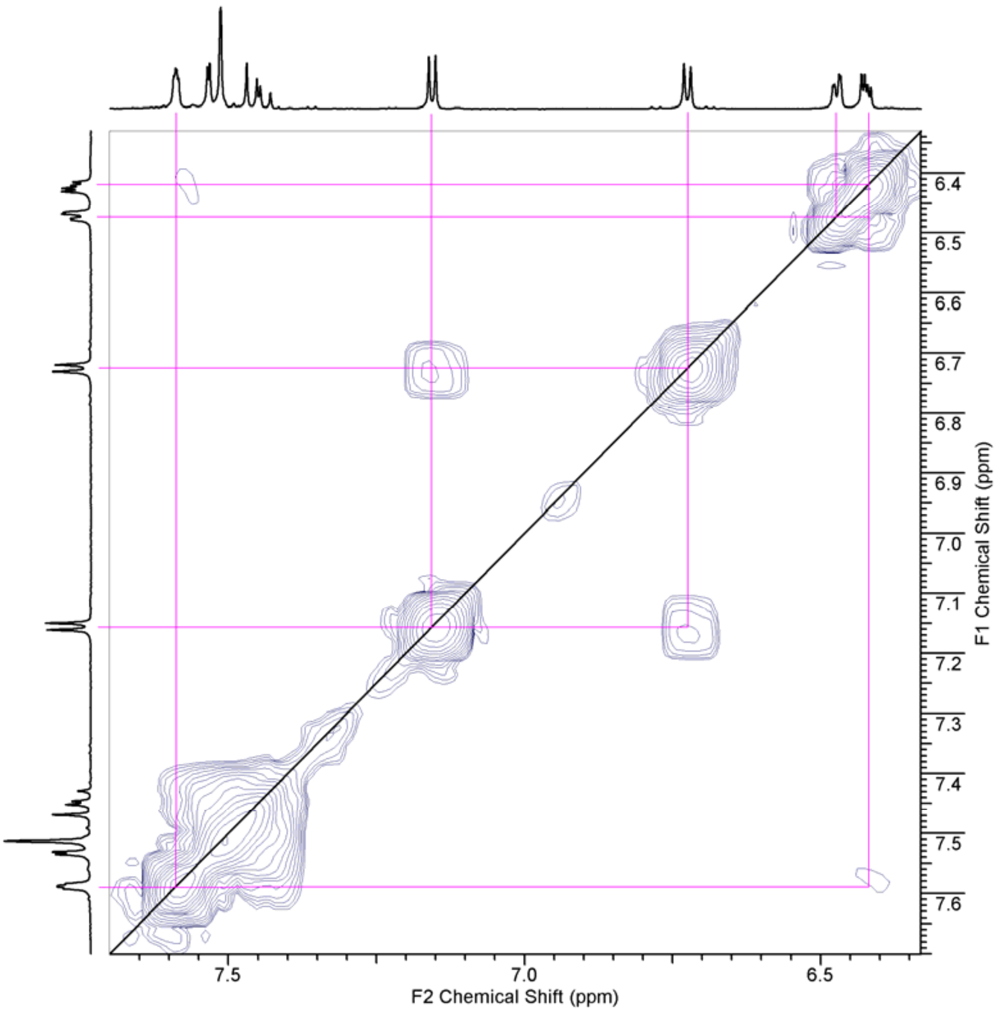

Figure S9. HH COSY NMR (F1 = F2 = 400 MHz) spectrum of **4** in CD_2Cl_2.

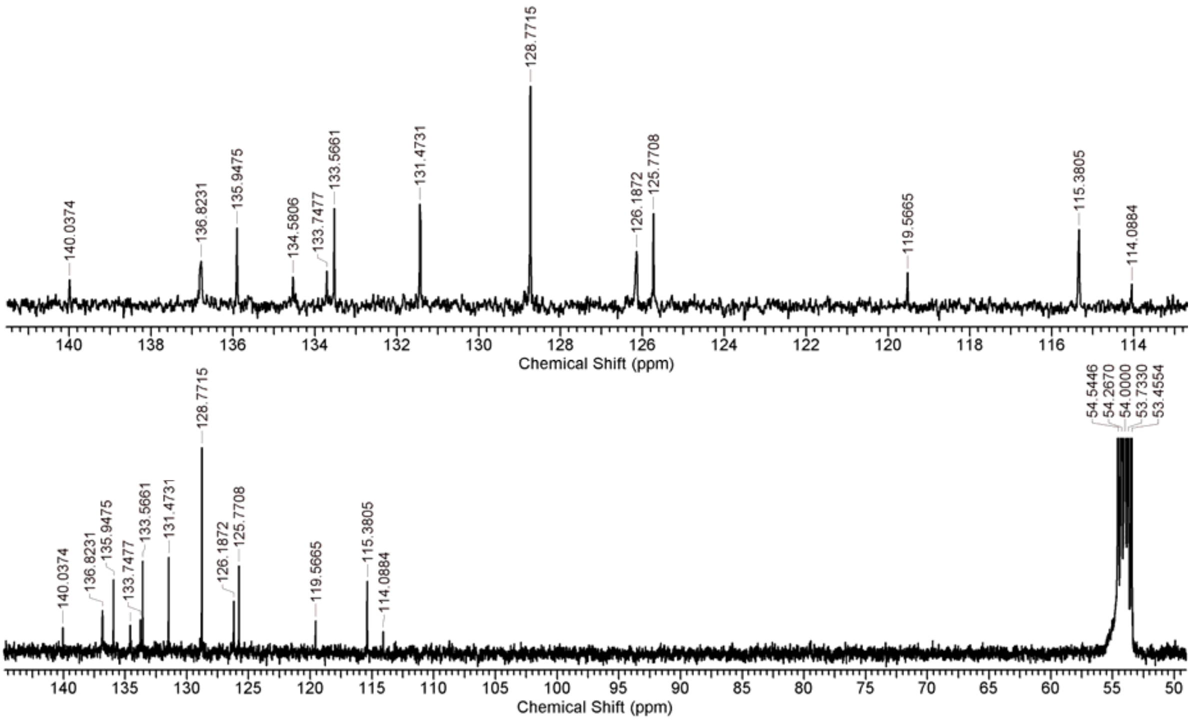

Figure S10. ^{13}C NMR (100 MHz) spectrum of **4** in CD_2Cl_2.

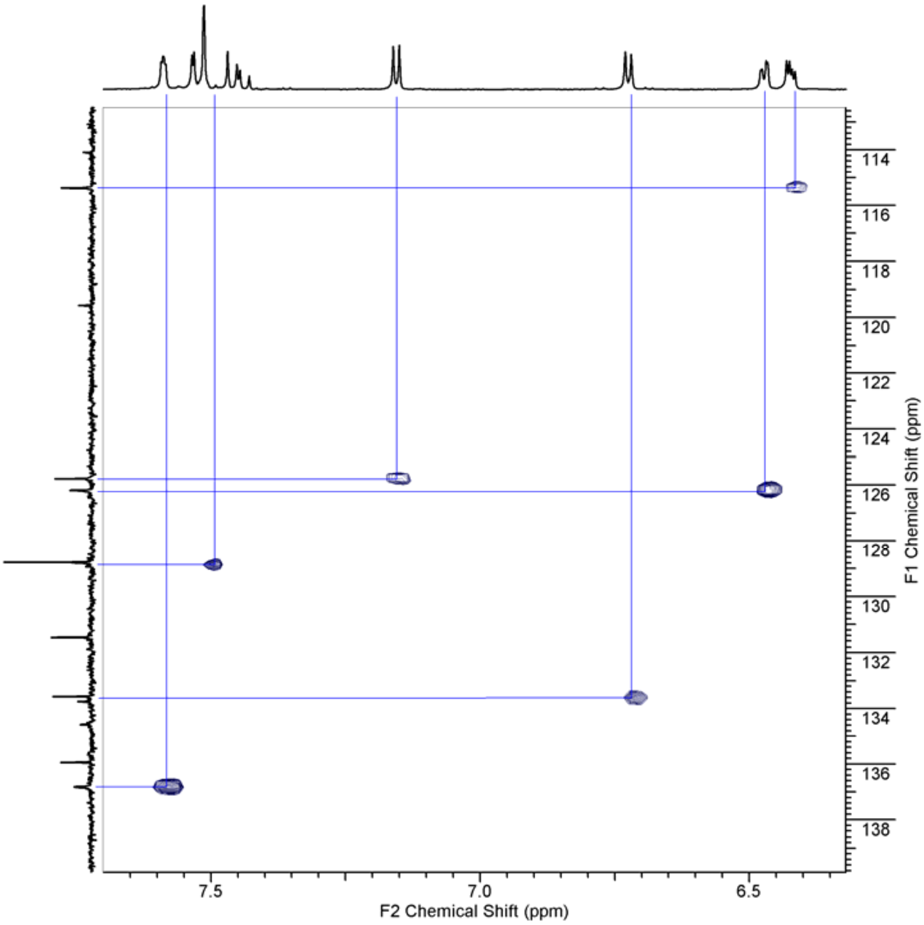

Figure S11. HMQC NMR (F1 = 100 MHz and F2 = 400 MHz) spectrum of **4** in CD_2Cl_2.

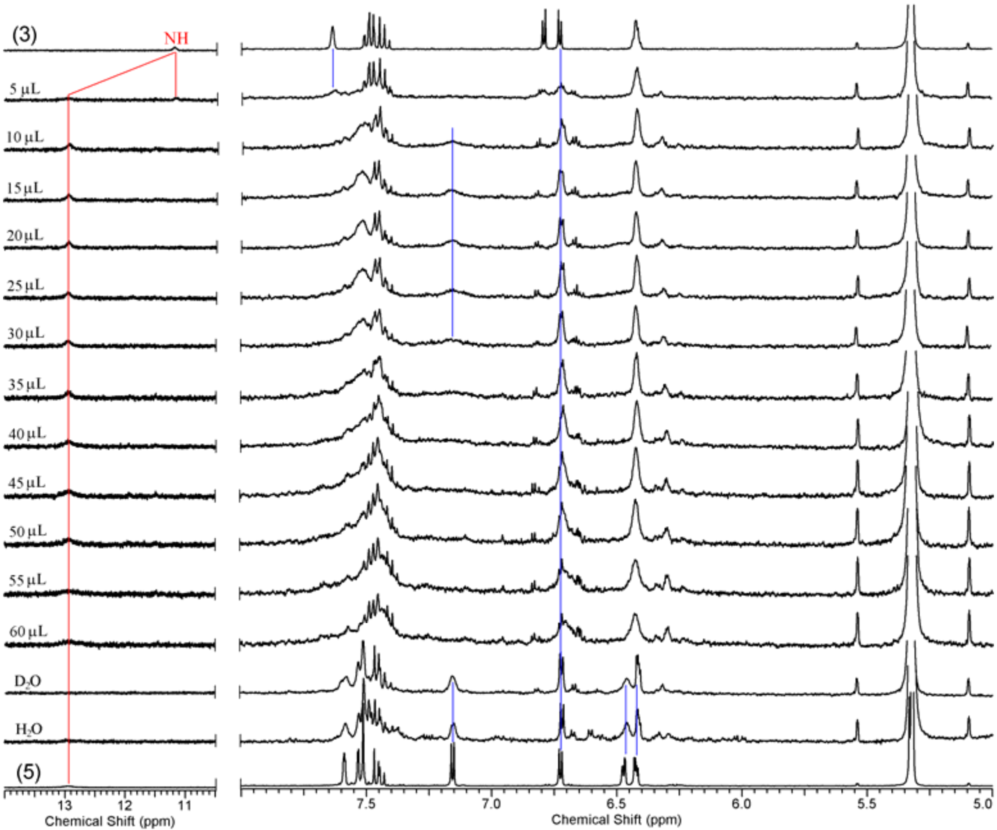

Figure S12. ^{1}H NMR spectral changes of CD_2Cl_2 (1 mL) solution of **3** (1 μmole) by adding Et_3N (5 ~ 60 μL) followed by D_2O and H_2O; for the comparison, the ^{1}H NMR spectrum of **4** in CD_2Cl_2 has been added as the last spectrum.

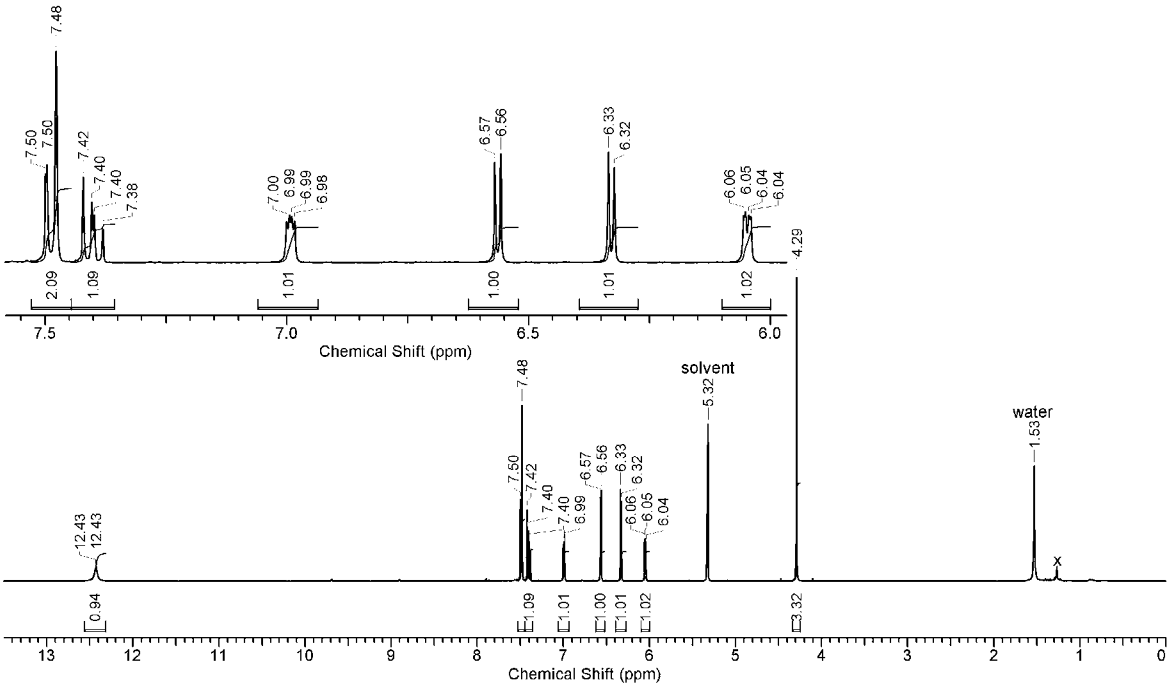

Figure S13. ^{1}H NMR (400 MHz) spectra of **5** in CD_2Cl_2.

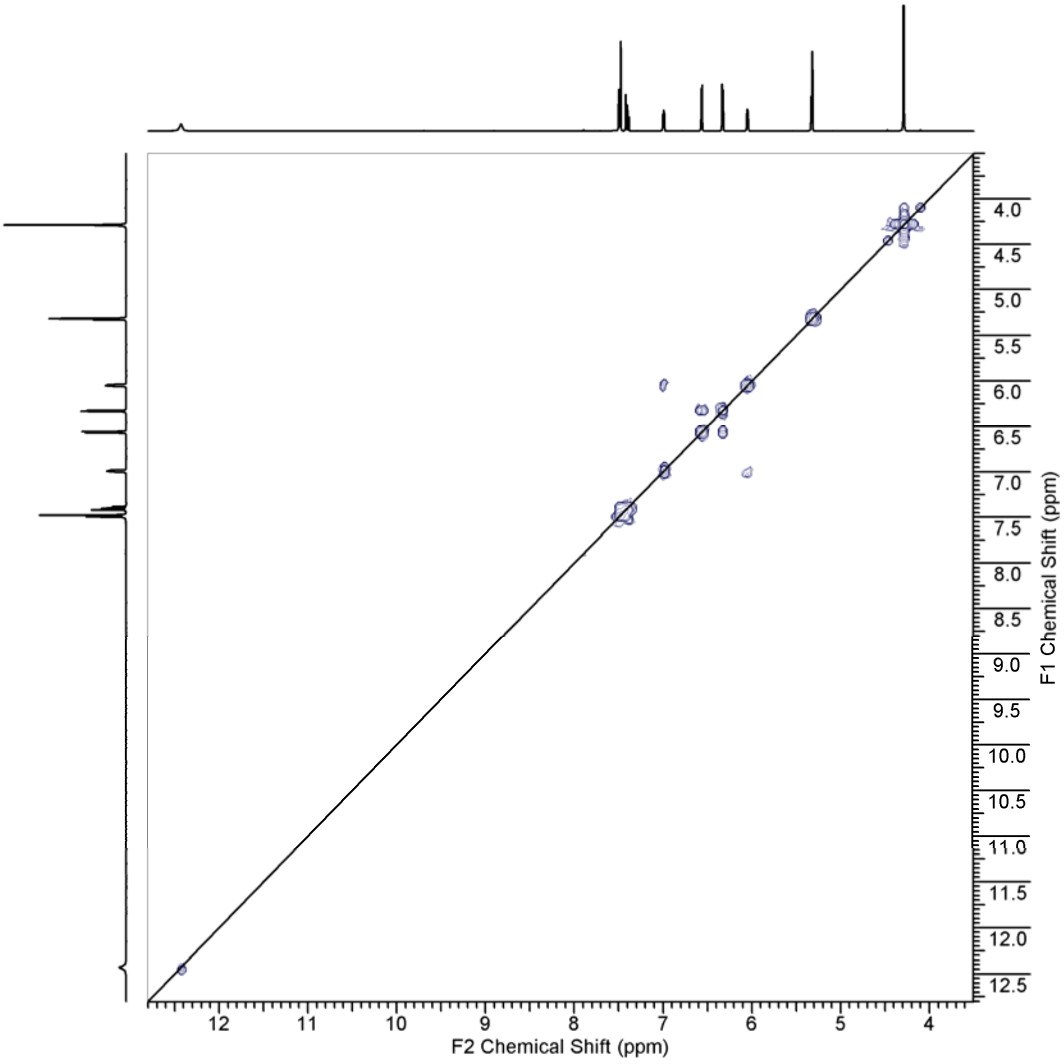

Figure S14. HH COSY NMR (F1 = F2 = 400 MHz) spectrum of **5** in CD_2Cl_2.

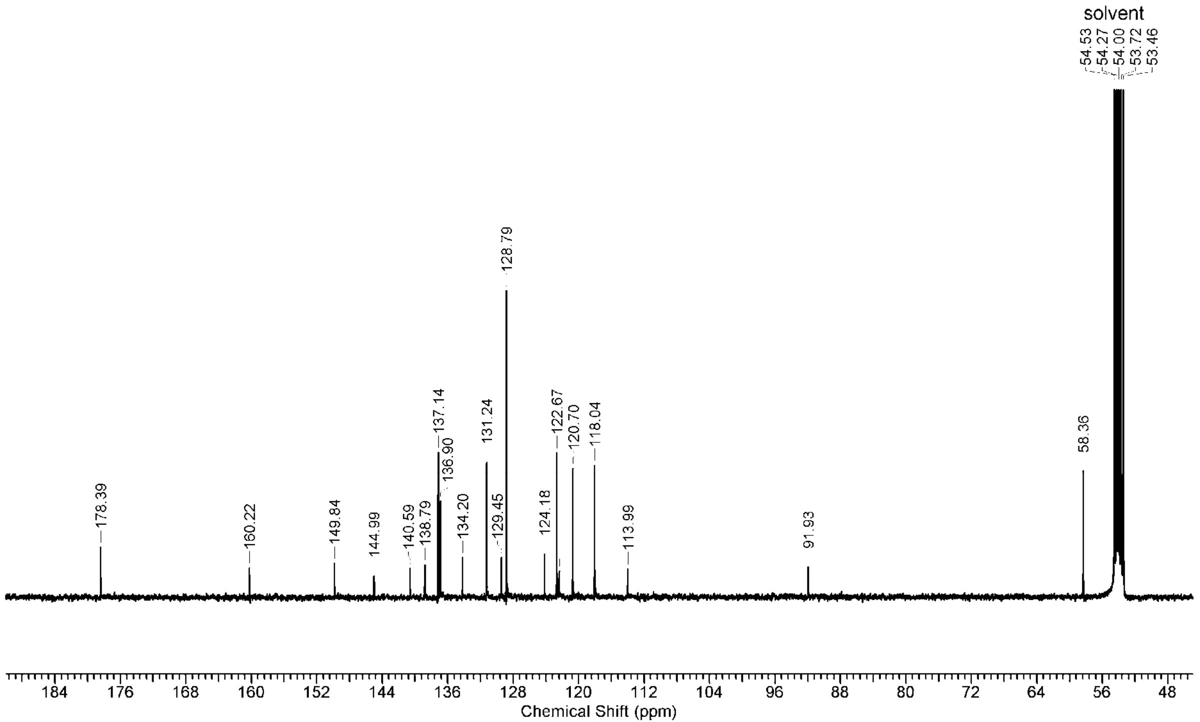

Figure S15. ^{13}C NMR (100 MHz) spectrum of **5** in CD_2Cl_2.

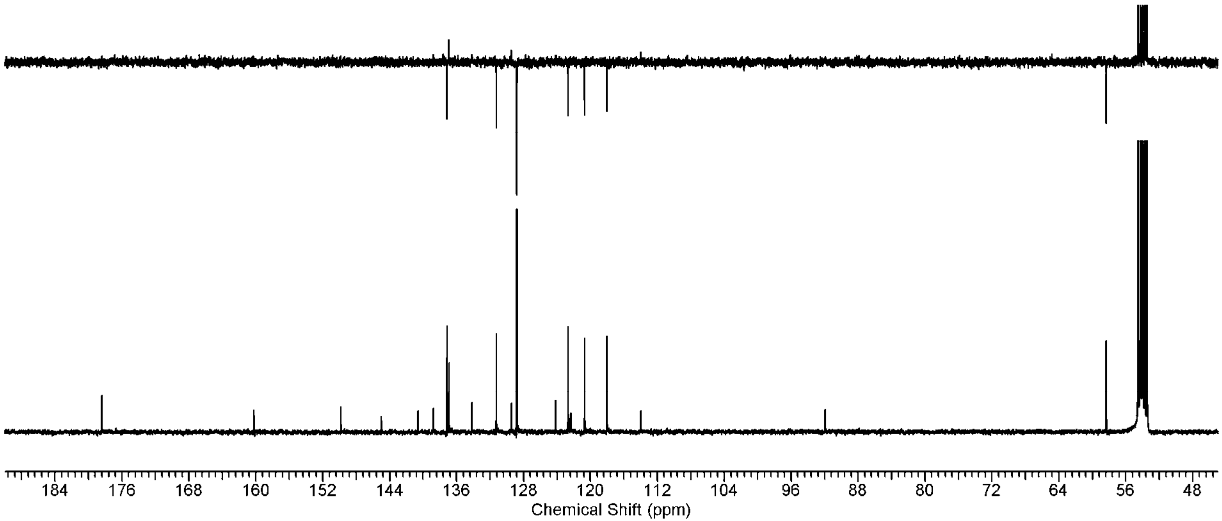

Figure S16. 45 deg APT (up) and ^{13}C NMR (down) spectra (100 MHz) of **5** in CD_2Cl_2.

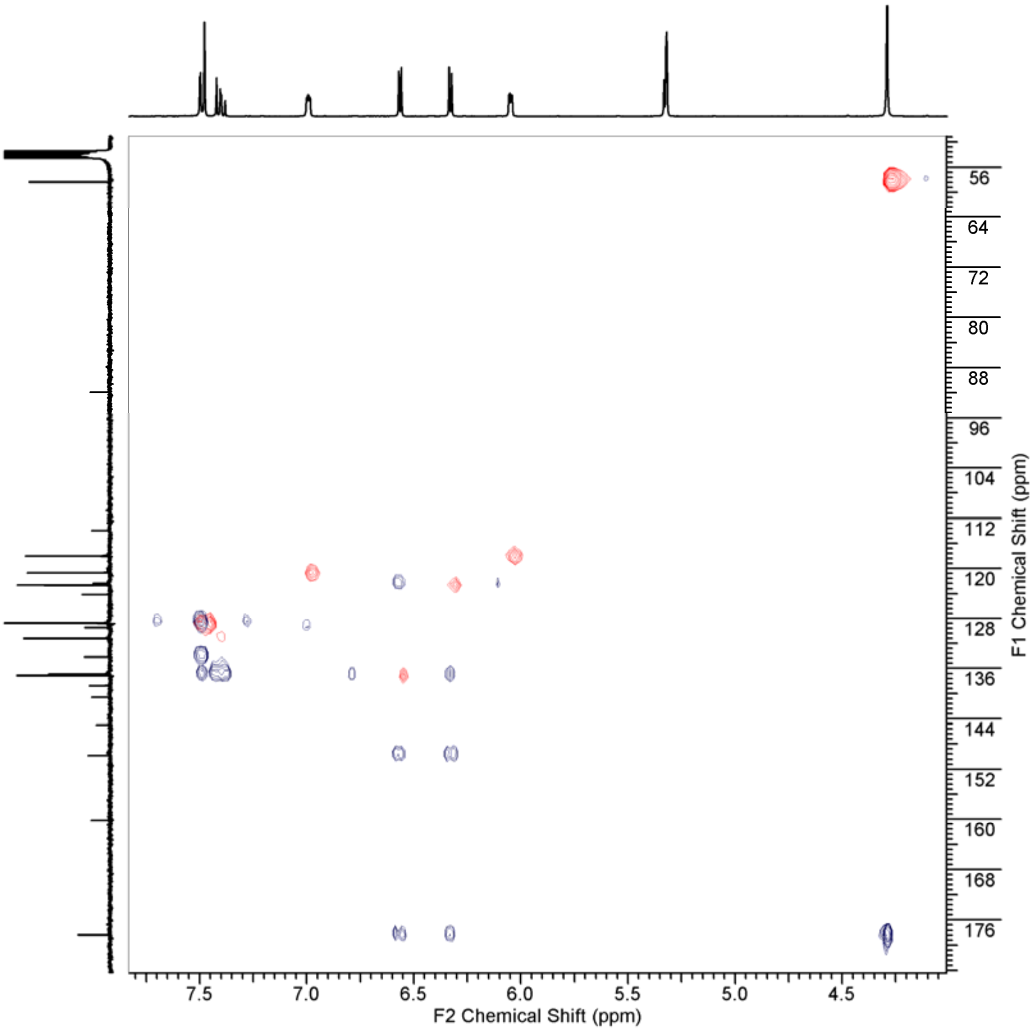

Figure S17. HMQC (red) and HMBC (blue) NMR (F1 = 400 MHz, F2 = 100 MHz) spectra of **5** in CD_2Cl_2.

Crystallographic data

Crystallographic data of 3

A red crystal of $C_{38}H_{18}N_6O_2Cl_6{\cdot}CH_2Cl_2$ having approximate dimensions of 0.04 × 0.22 × 0.50 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -100.0 ± 0.1ºC to a maximum 2θ value of 56.0º. Data were collected in a series of ϕ and ω scans in 0.50º oscillations with 20.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Of the 33043 reflections that were collected, 9356 were unique (R_{int} = 0.032); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[S2] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 6.19 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[S3]), with minimum and maximum transmission coefficients of 0.892 and 0.976, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[S4]. The molecule crystallizes with CH_2Cl_2 in the lattice. One solvent molecule was modelled, however a second was disordered in such a way that it was not possible to achieve a reasonable model. As a result the PLATON/SQUEEZE[S5] program was used to generate a data set free of any electron density in the region of the disordered solvent. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement[S6] on F^2 was based on 9356 reflections and 504 variable parameters and converged (largest parameter shift was 0.00 times its esd with unweighted and weighted agreement factors (R1 = 0.077 and wR2 = 0.174).

The standard deviation of an observation of unit weight[S7] was 1.17. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.95 and -1.38 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[S8]. Anomalous dispersion effects were included in Fcalc[S9]; the values for Δf' and Δf" were those of Creagh and McAuley[S10]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[S11]. All refinements were performed using the SHELXTL[S12] crystallographic software package from Bruker-AXS.

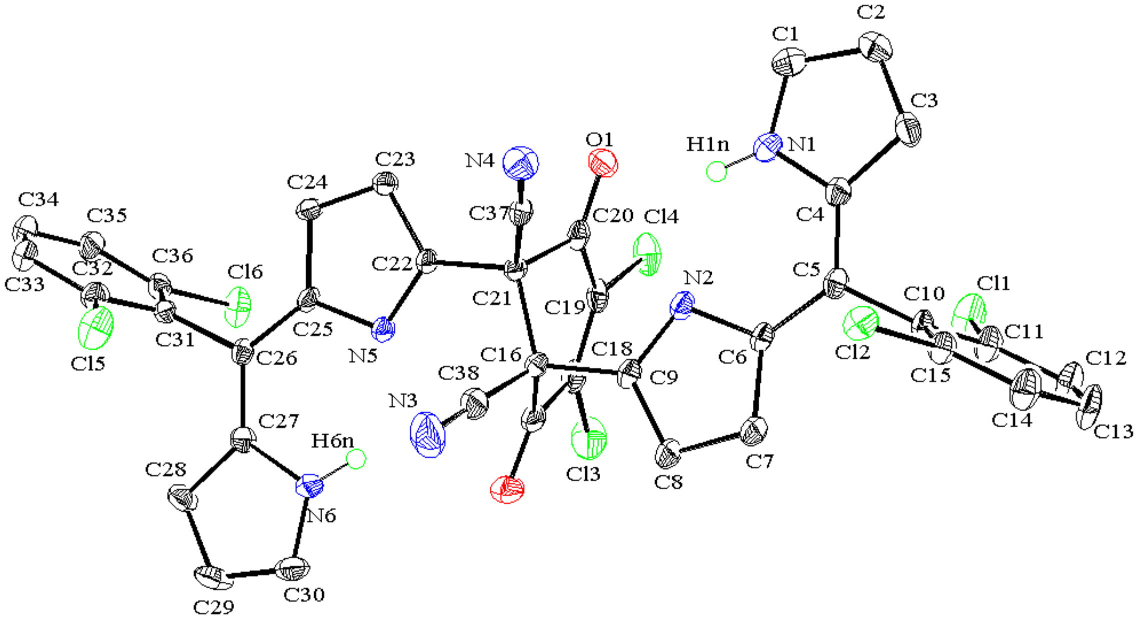

Figure S18. ORTEP structure of **3**. Thermal ellipsoids are scaled to the 50% probability level.

Table S1. Parameters of the hydrogen-bonds for **3**.

Donor --- H...Acceptor	D - H	H...A	D...A	D - H...A
N(1) --H(1n) ...O(1)	0.77(4)	2.55(3)	3.155(3)	137(3)
N(1) --H(1n) ..N(2)	0.77(4)	2.25(3)	2.765(3)	125(3)
N(6) --H(6n) ..O(2)	0.80(4)	2.50(3)	3.158(3)	140(3)
N(6) --H(6n) ..N(5)	0.80(4)	2.19(3)	2.758(3)	128(3)

Crystallographic data of 4

An irregular green crystal of $C_{34}H_{18}N_6Cl_4$ having approximate dimensions of 0.17 × 0.20 × 0.30 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -100.0 ± 0.1°C to a maximum 2θ value of 56.0°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 20.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Of the 63004 reflections that were collected, 7054 were unique (R_{int} = 0.038); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[S2] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 4.39 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[S3]), with minimum and maximum transmission coefficients of 0.868 and 0.928, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[S4]. All non-hydrogen atoms were refined anisotropically. All N-H hydrogen atoms were located in difference maps and refined isotropically. All other hydrogen atoms were placed in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement[S6] on F^2 was based on 7054 reflections and 405 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors (R1 = 0.053 and wR2 = 0.082).

The standard deviation of an observation of unit weight[S7] was 1.02. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.32 and -0.33 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[S8]. Anomalous dispersion effects were included in Fcalc[S9]; the values for Δf' and Δf'' were those of Creagh and McAuley[S10]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[S11]. All refinements were performed using the SHELXTL[S12] crystallographic software package from Bruker-AXS.

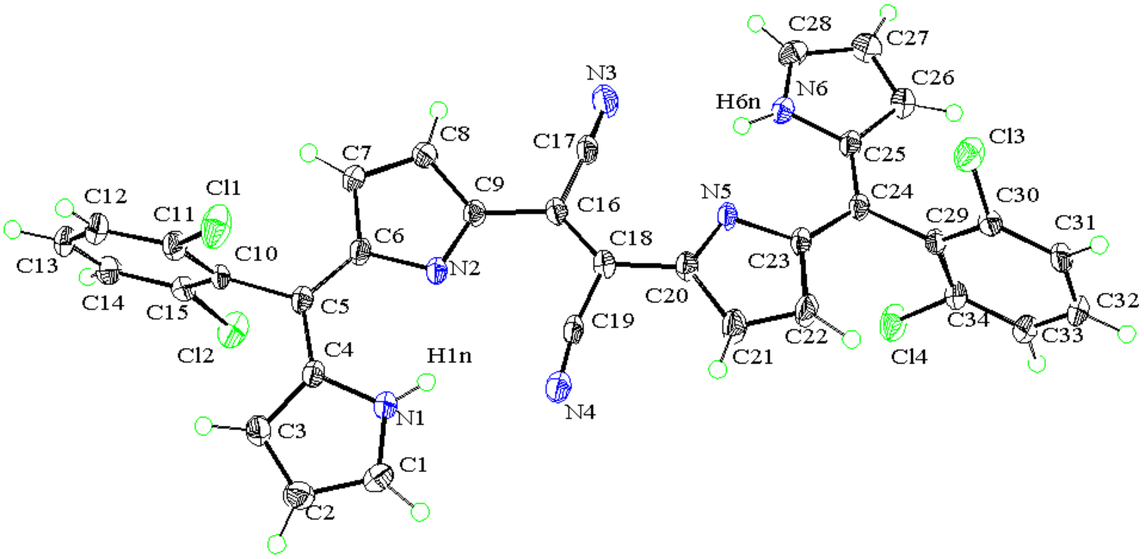

Figure S19. ORTEP structure of **4**. Thermal ellipsoids are scaled to the 50% probability level.

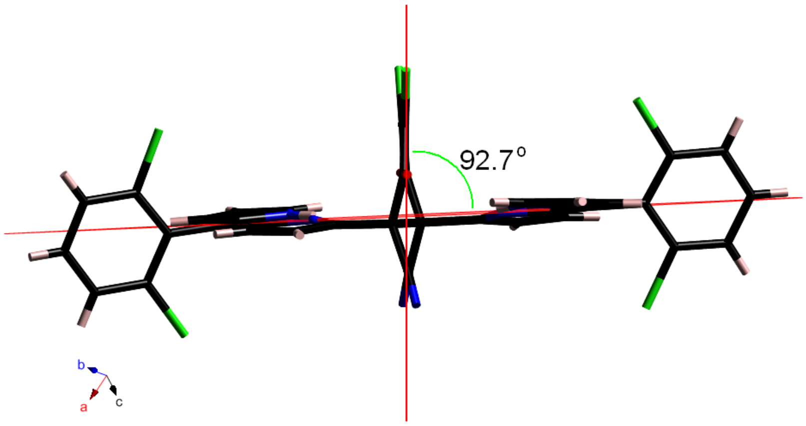

Figure S20. Perpendicular planes for crystal structure of **4**.

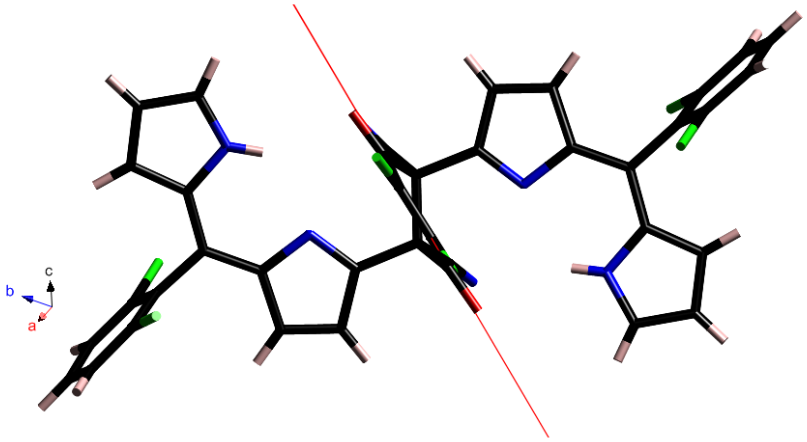

Figure S21. C2 symmetric axis for crystal structure of **4**.

Table S2. Parameters of the hydrogen-bonds for **4**.

Donor --- H...Acceptor	D - H	H...A	D...A	D - H...A
N(1) --H(1n) ..N(2)	0.83(2)	2.16(2)	2.7338(19)	126.3(17)
N(1) --H(1n) ..N(4)	0.83(2)	2.31(2)	3.008(2)	142.9(18)
N(6) --H(6n) ..N(3)	0.87(2)	2.52(2)	3.264(2)	144.0(17)
N(6) --H(6n) ..N(5)	0.87(2)	2.13(2)	2.7542(19)	127.7(17)

Crystallographic data of 5

An irregular violet crystal of $C_{22}H_{11}N_3O_3Cl_4$ having approximate dimensions of 0.12 × 0.18 × 0.40 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -100.0 ± 0.1ºC to a maximum 2θ value of 56.0º. Data were collected in a series of ϕ and ω scans in 0.50º oscillations with 20.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Of the 36940 reflections that were collected, 5085 were unique (R_{int} = 0.029); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[S2] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 5.95 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[S3]), with minimum and maximum transmission coefficients of 0.864 and 0.931, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[S4]. All non-hydrogen atoms were refined anisotropically. All C-H hydrogen atoms were placed in calculated positions but were not refined. The N-H hydrogen atom was located in a difference map and refined isotropically. The final cycle of full-matrix least-squares refinement[S6] on F^2 was based on 5085 reflections and 294 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors (R1 = 0.053 and wR2 = 0.082).

The standard deviation of an observation of unit weight[S7] was 1.03. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.37 and -0.35 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[S8]. Anomalous dispersion effects were included in Fcalc[S9]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[S10]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[S11]. All refinements were performed using the SHELXTL[S12] crystallographic software package from Bruker-AXS.

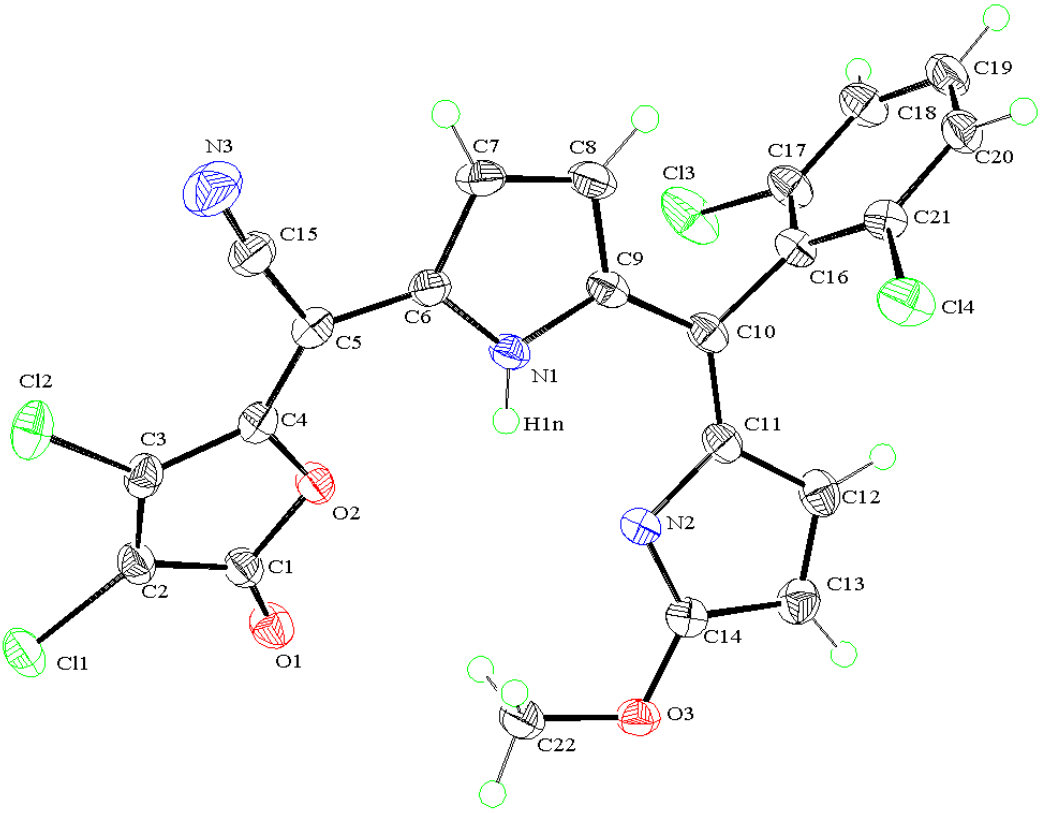

Figure S22. ORTEP structure of **6**. Thermal ellipsoids are scaled to the 50% probability level.

Table S3. Parameters of the hydrogen-bonds for **5**.

Donor --- H...Acceptor	D - H	H...A	D...A	D - H...A
N(1) --H(1n) ..O(2)	0.839(19)	2.360(19)	2.7781(16)	111.4(14)
N(1) --H(1n) ..N(2)	0.839(19)	2.140(17)	2.7383(18)	128.1(16)

Table S4. Crystallographic Data of **3, 4** and **5**.

	3	**4**	**5**
Formula	$C_{39}H_{20}N_6O_2Cl_8$	$C_{34}H_{18}N_6Cl_4$	$C_{22}H_{11}N_3Cl_4O_3$
Mw	888.21	652.34	507.14
cryst syst	triclinic	monoclinic	triclinic
Space group	*P*-1 (# 2)	$P\ 2_1/c$ (#14)	*P*-1 (# 2)
a/Å	11.2796(18)	14.1530(16)	7.8137(8)
b/Å	12.066(2)	10.3574(11)	9.9057(11)
c/Å	14.734(2)	20.116(2)	14.0847(16)
α/deg	83.100(8)	90.0	84.895(5)
β/deg	79.807(8)	92.535(5)	77.368(5)
γ/deg	89.782(8)	90.0	81.828(2)
V/Å^3	1959.0(6)	2945.8(6)	1051.0(2)
Z	2	4	2
D_c/g cm^{-3}	1.506	1.471	1.603
μ(MoKα)cm^{-1}	6.19	4.39	5.95
No. of obsd data (I>0.00σ(I))	9356	7054	5085
Reflection / Parameter Ratio	18.56	17.42	17.30
$R1^a$; $wR2^b$	0.077; 0.174	0.053; 0.082	0.038; 0.079
GOF	1.17	1.02	1.03
No. of obsd data (I>2σ(I))	6694	5367	4365
($R1$; $wR2$) ^{c}	(0.053; 0.163)	(0.033; 0.073)	(0.030; 0.074)

[a] R1 = Σω||Fo|-|Fc|| / Σω|Fo|, [b] $wR2 = \sqrt{\Sigma\{\omega(Fo^2-Fc^2)^2\}} / \Sigma\omega(Fo^2)^2$ [c] refined on F, I>2σ(I)

Reference

S1. C. H. Lee, J. S. Lindsey, *Tetrahedron*, **1994**, *50*, 11427-11440.

S2. **SAINT.** Version 7.03A. Bruker AXS Inc., Madison, Wisconsin, USA. (1997-2003).

S3. **SADABS.** Bruker Nonius area detector scaling and absorption correction – V2.10, Bruker AXS Inc., Madison, Wisconsin, USA. (2003).

S4. **SIR97.** A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115-119.

S5. **SQUEEZE.** P. v.d. Sluis and A. L. Spek, *Acta Crystallogr., Sect A*, 1990, **46**, 194-201.

S6. Least Squares function minimized: $\Sigma w(F_o^2 - F_c^2)^2$

S7. Standard deviation of an observation of unit weight: $[\Sigma w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$
Where: N_o = number of observations
N_v = number of variables

S8. D. T. Cromer and J. T. Waber: *International Tables for X-ray Crystallography*, Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2A, (1974).

S9. J. A Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781.

S10. D. C. Creagh and W. J. McAuley: *International Tables for Crystallography*, Vol. C, (A. J. C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

S11. D. C. Creagh and J. H. Hubbell: *International Tables for Crystallography*, Vol. C, (A. J. C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

S12. **SHELXTL.** Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA. (1997).

- Perfluorophenyl substituted dipyrromethane formed a DDQ adduct in higher yield (~ 20%). The (a) ^{1}H and (b) ^{19}F NMR spectra (in CD_2Cl_2) are included below.