Supporting Information for

Synthesis of a class of 5-((5-(pyrrol-2-yl-methylene)-pyrrol-2-yl)methylene)furan-2-ones and the formation of a furanone dipyrrin imino ether

Ji-Young Shin and David Dolphin*

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada, Tel: 1-604-822-3200, Fax: 1-604-822-9678

Content

<NMR Spectra>

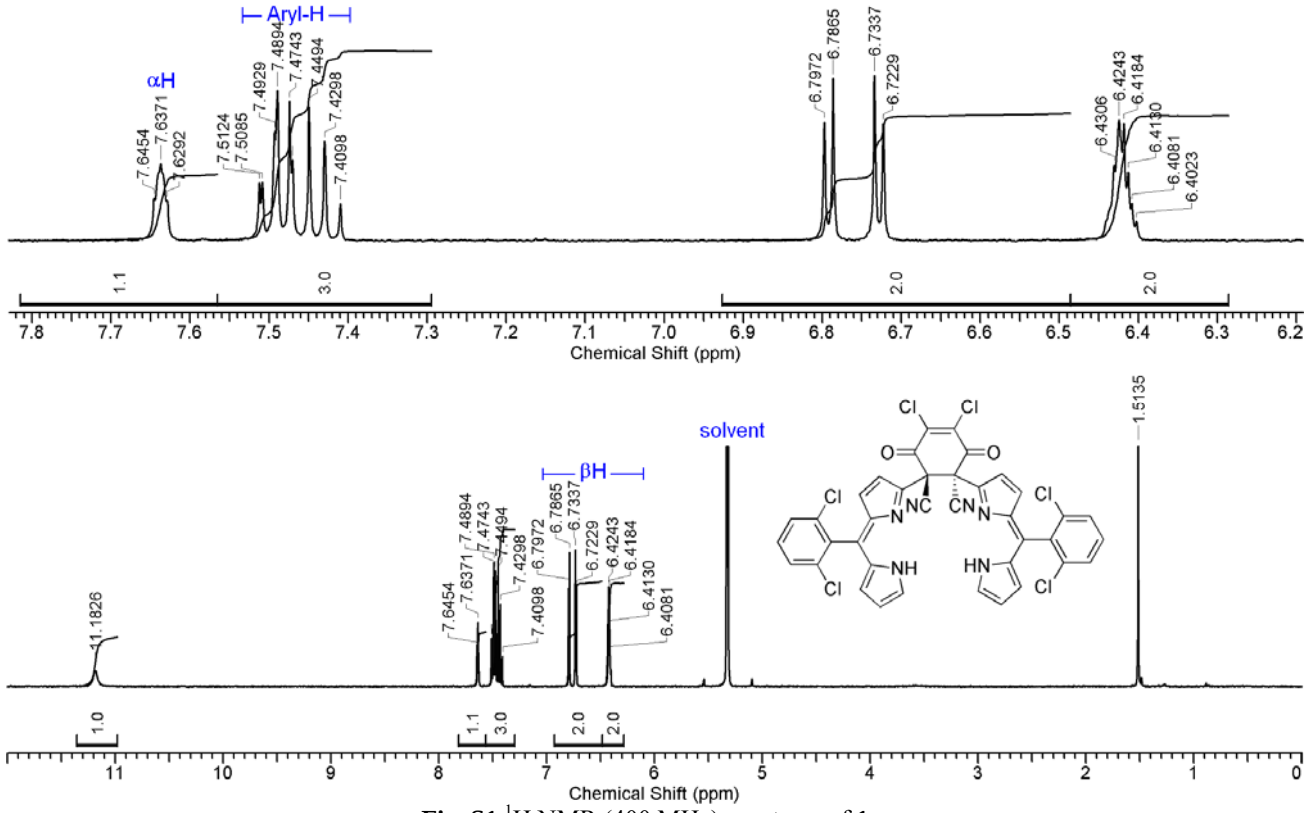

Fig. S1 ^{1}H NMR (400 MHz) spectrum of **1a**.

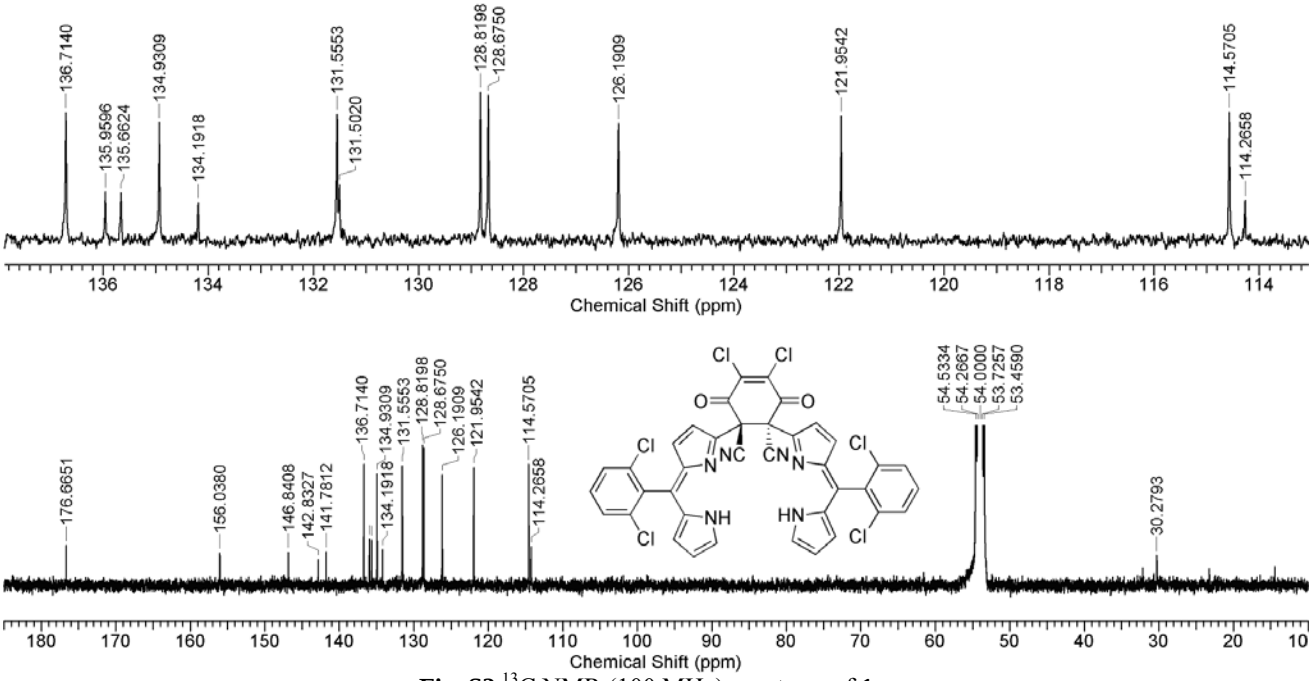

Fig. S2 ^{13}C NMR (100 MHz) spectrum of **1a**.

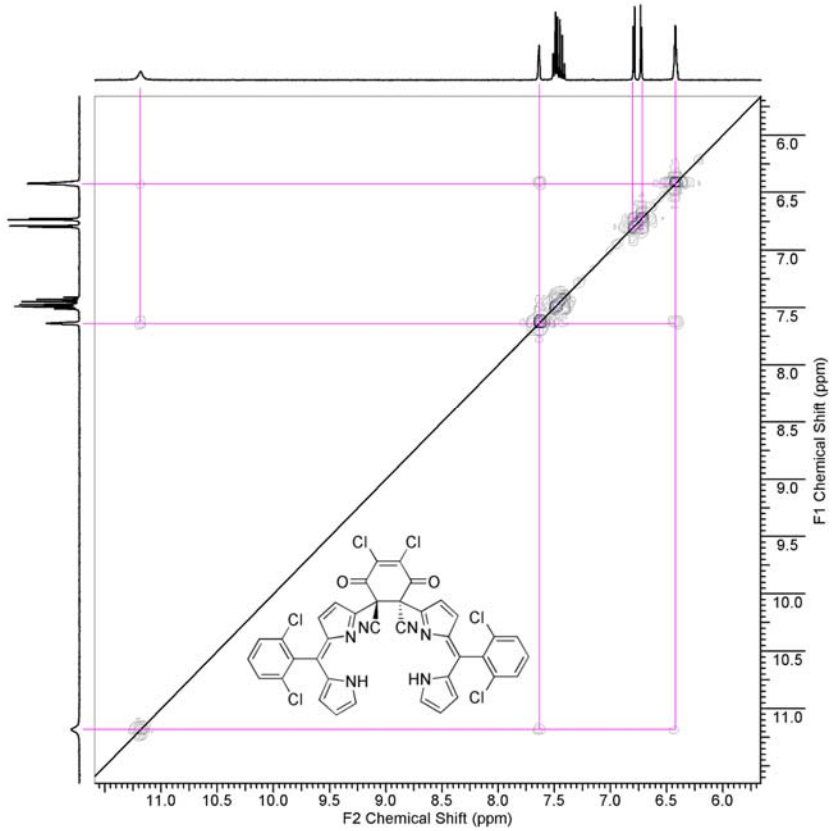

Fig. S3 HHCOSY NMR (F1 and F2: 400 MHz) spectrum of **1a**.

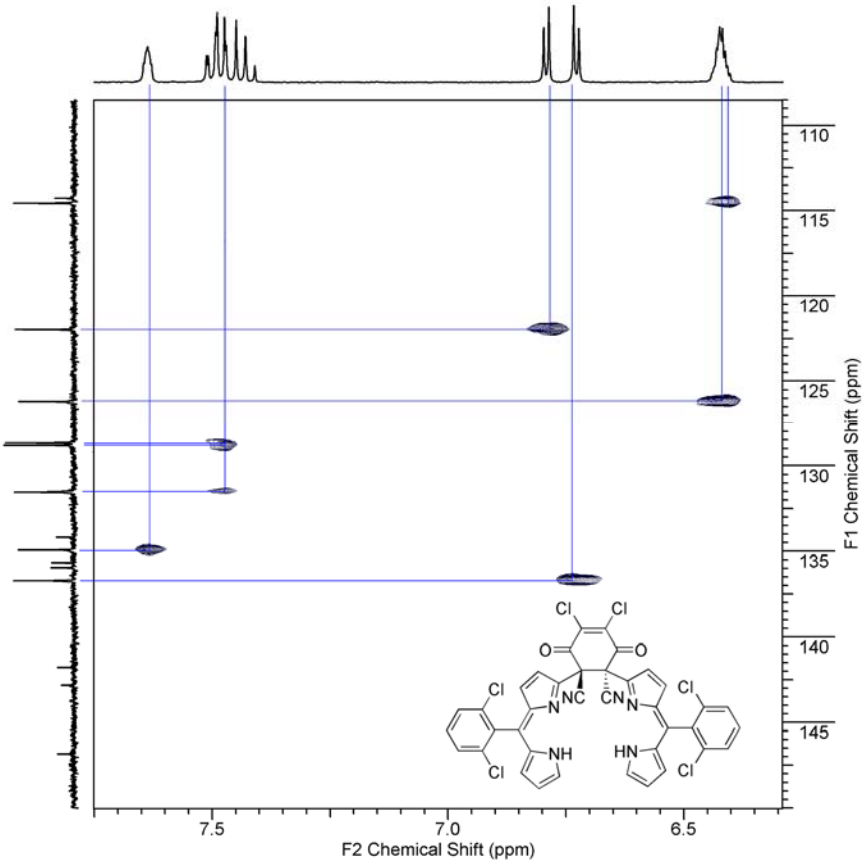

Fig. S4 HMQC NMR (F1: 100 MHz, F2: 400 MHz) spectra of **1a**.

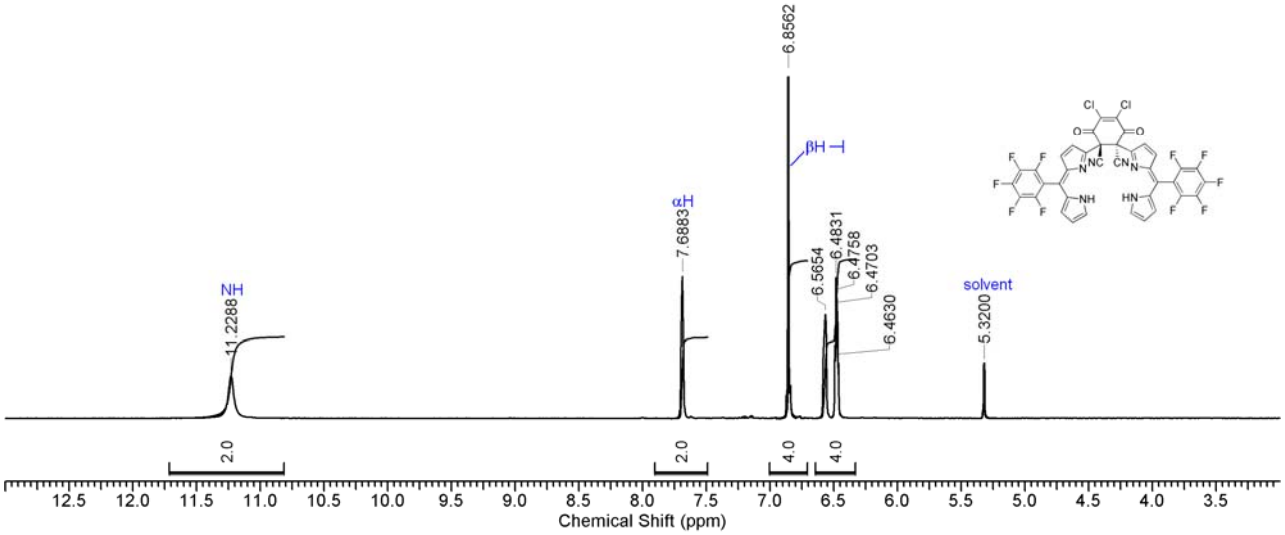

Fig. S5 ^{1}H NMR (300 MHz) spectrum of **1b**.

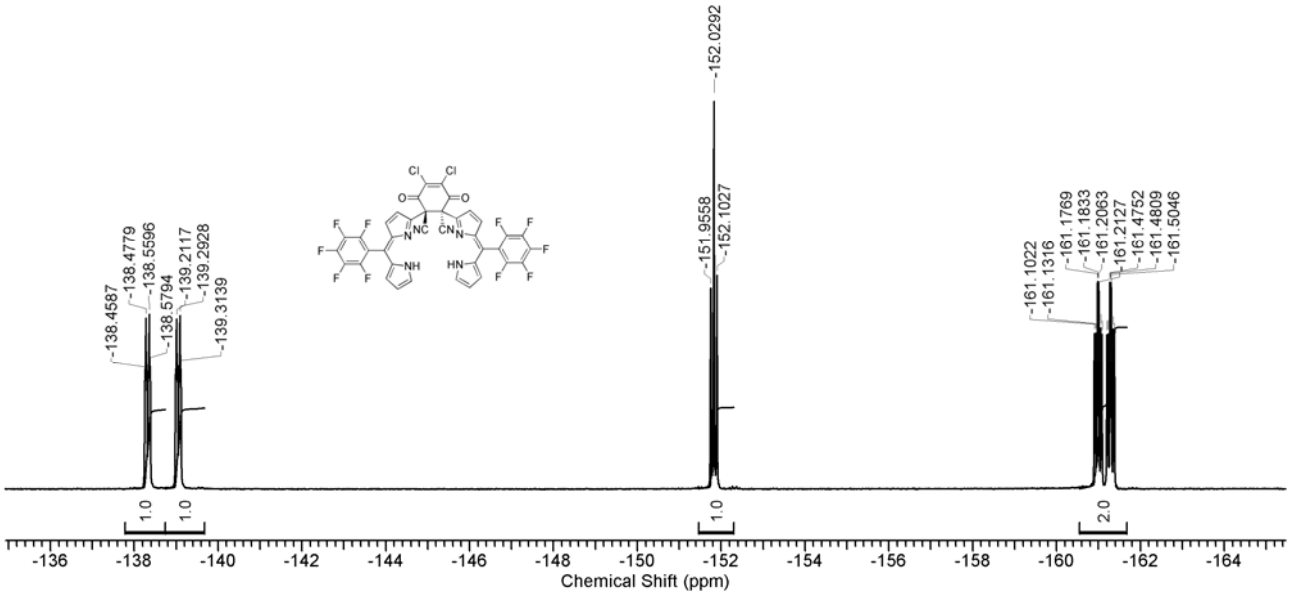

Fig. S6 ^{19}F NMR (282.4 MHz) spectrum of **1b**.

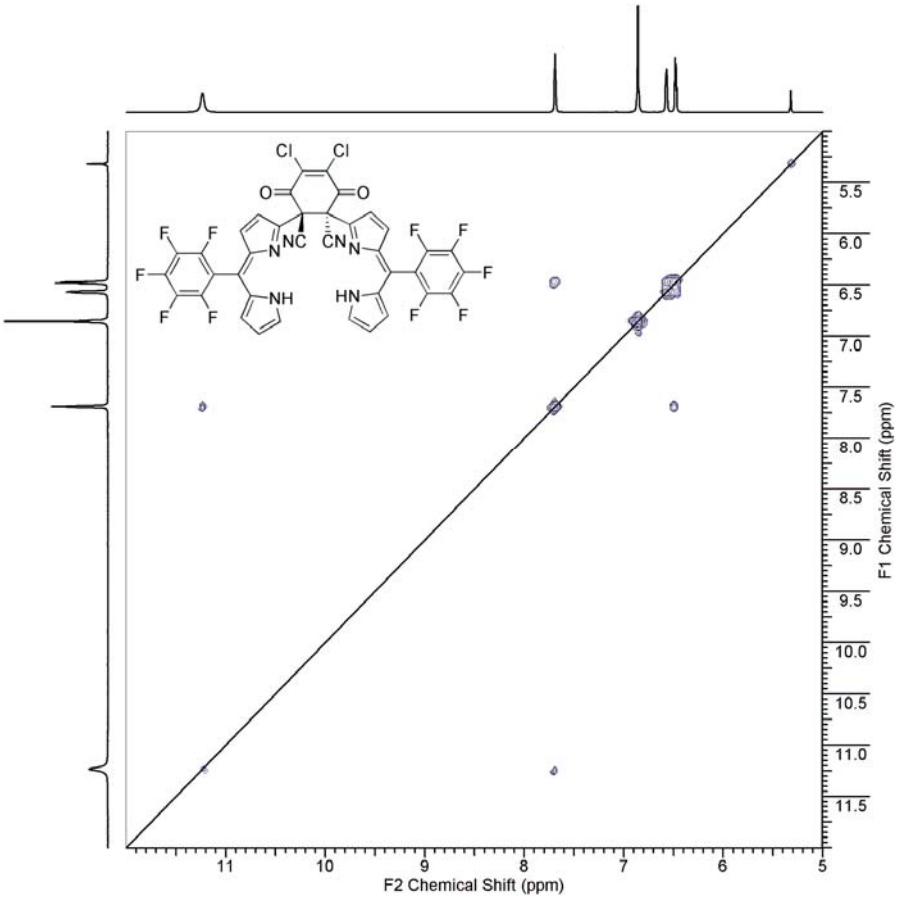

Fig. S7 HHCOSY NMR (F1 and F2: 400 MHz) spectrum of **1b**.

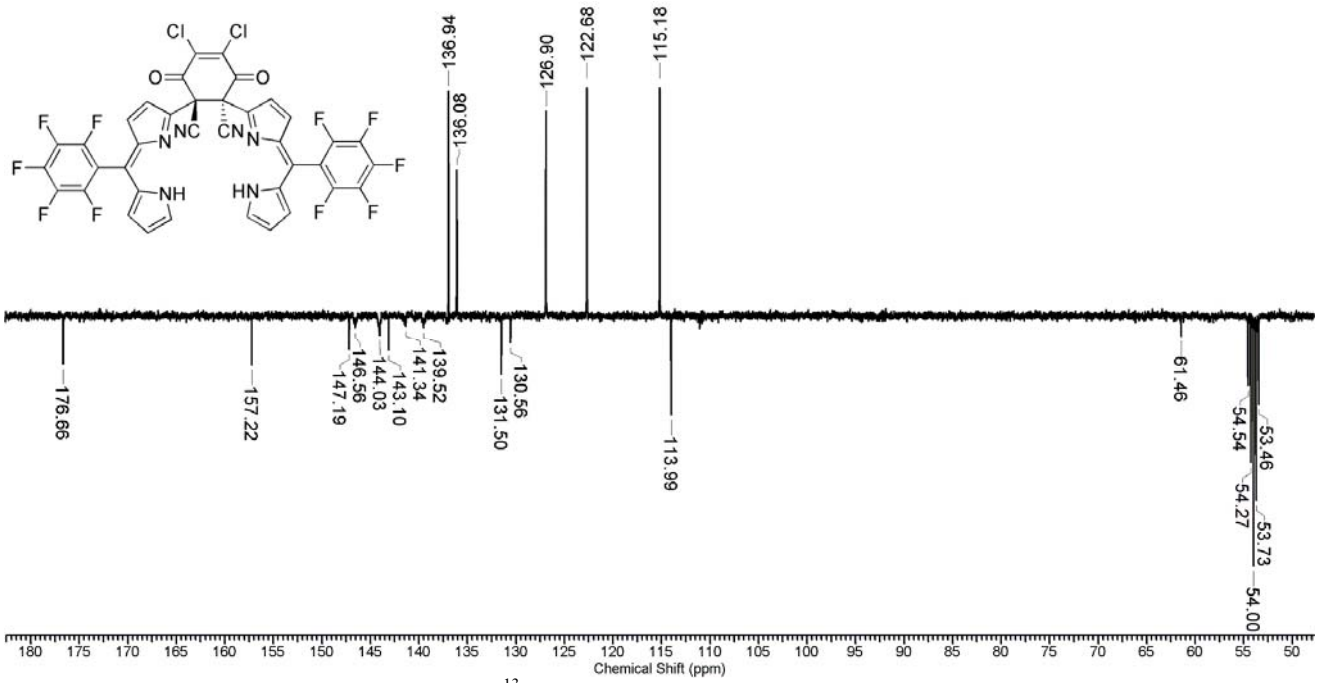

Fig. S8 ^{13}C NMR (100 MHz) spectrum of **1b**.

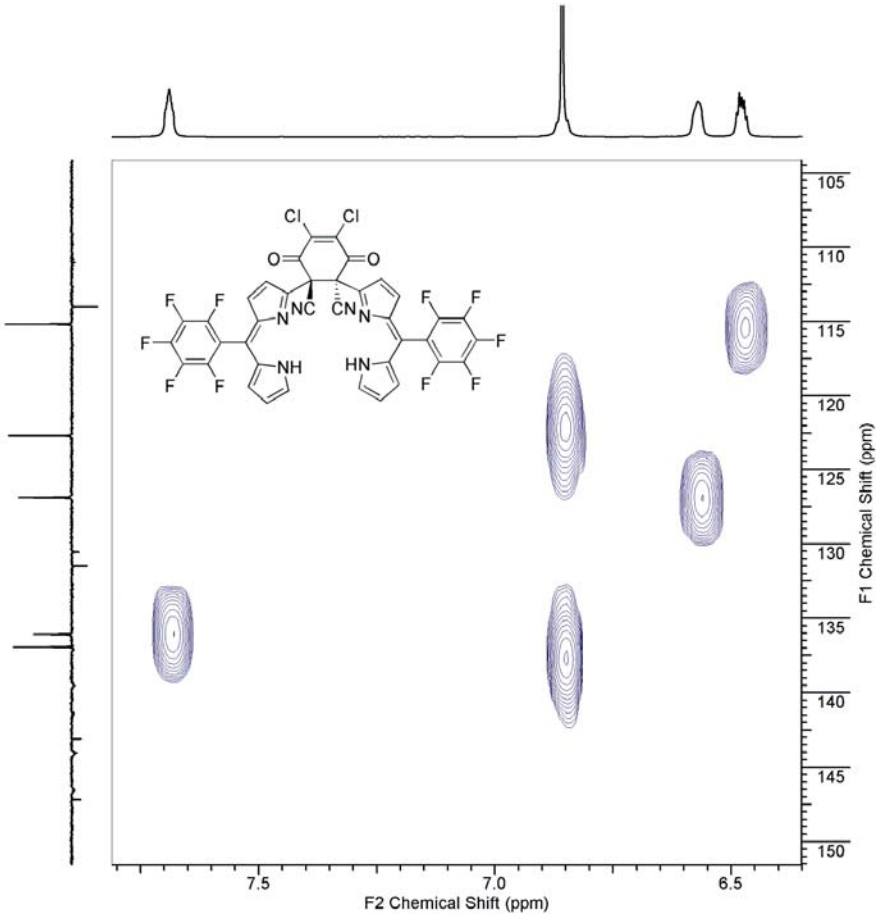

Fig. S9 HMQC NMR (F1: 100 MHz, F2: 400 MHz) spectra of **1b**.

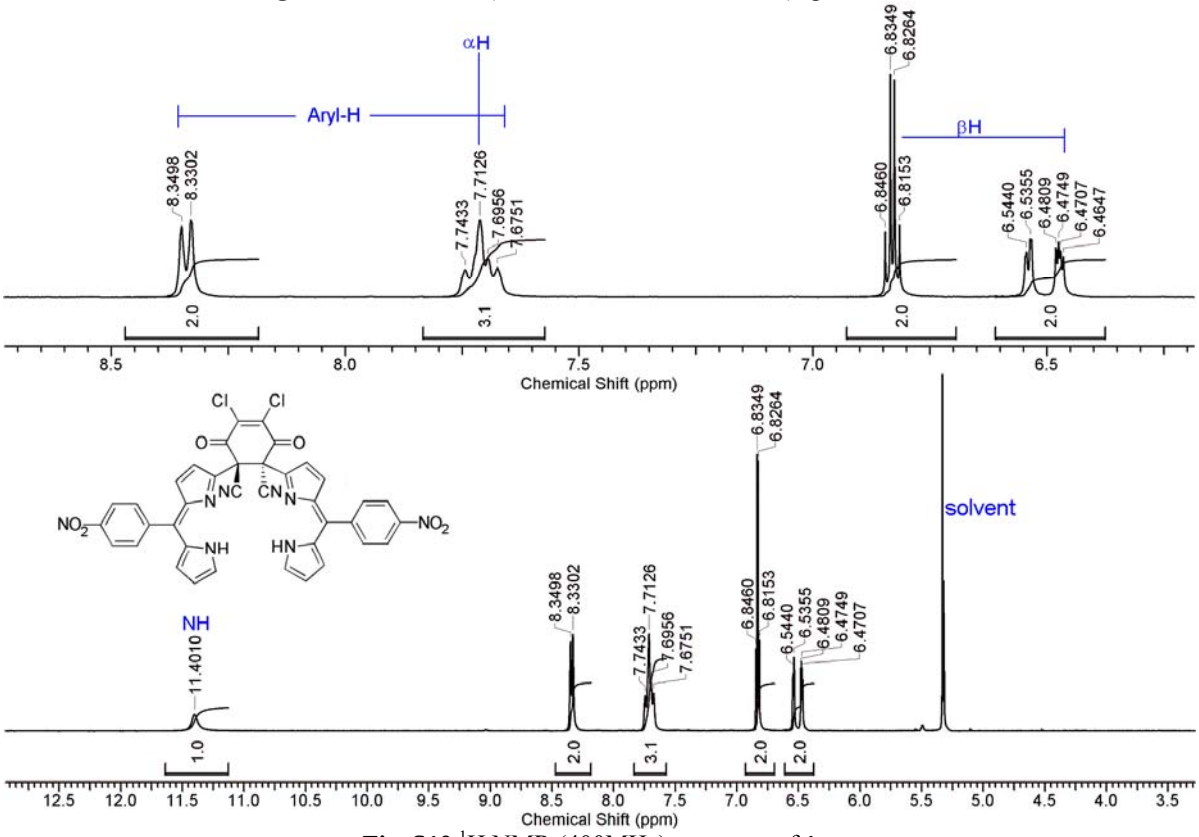

Fig. S10 ^{1}H NMR (400MHz) spectrum of **1c**.

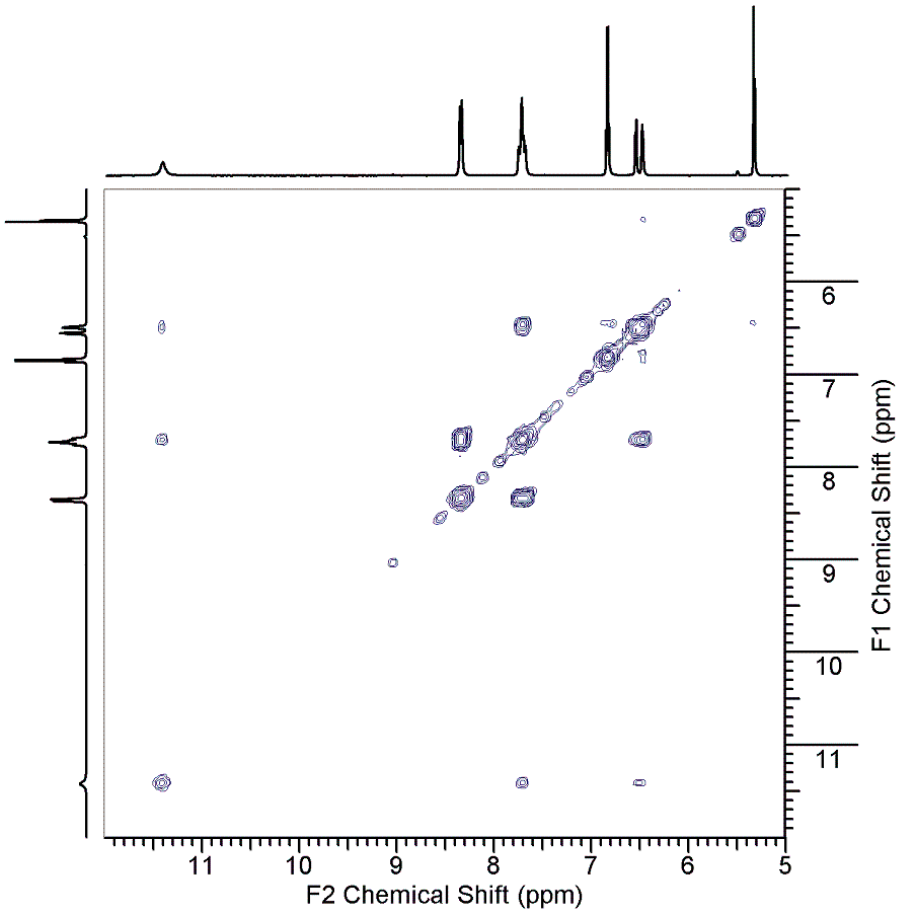

Fig. S11 HHCOSY NMR (F1 and F2: 400 MHz) spectrum of **1c**.

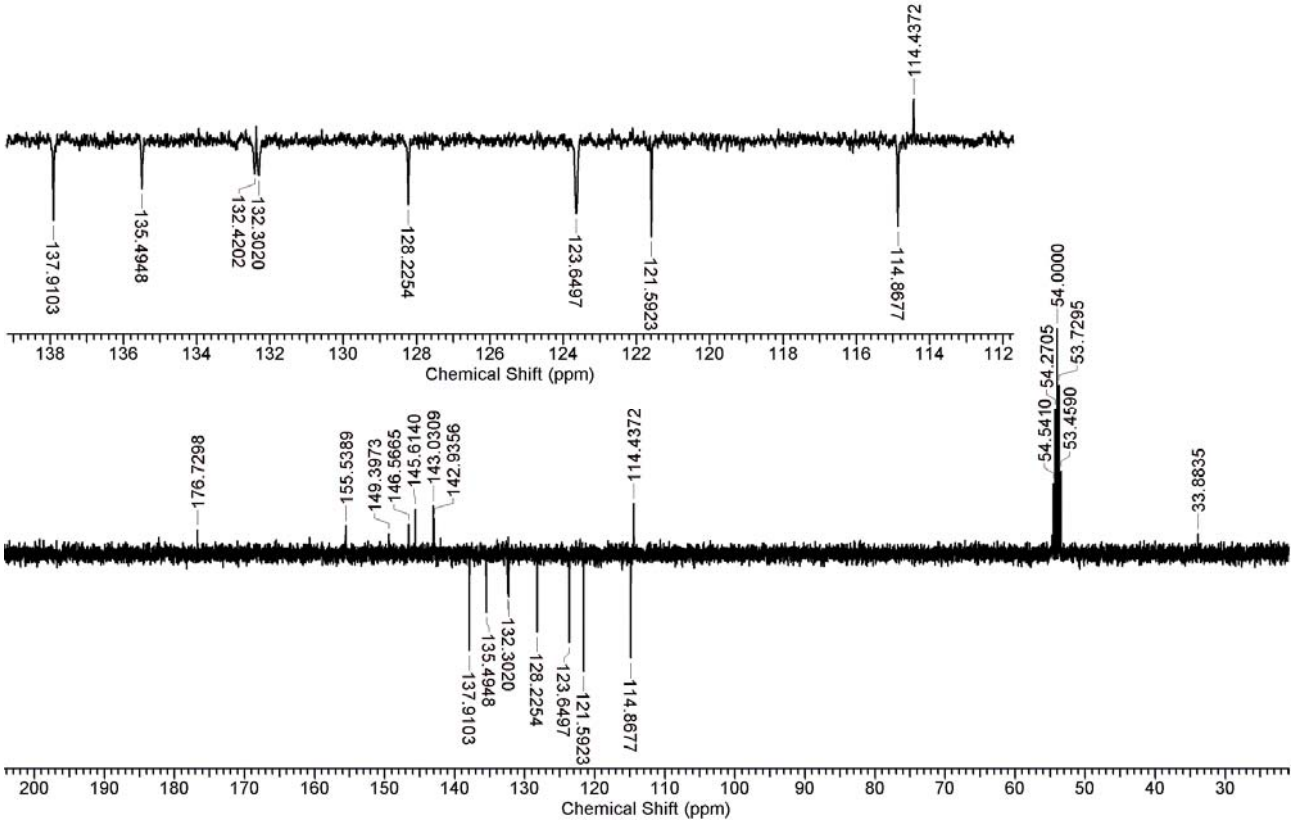

Fig. S12 APT NMR (100 MHz) spectrum of **1c**.

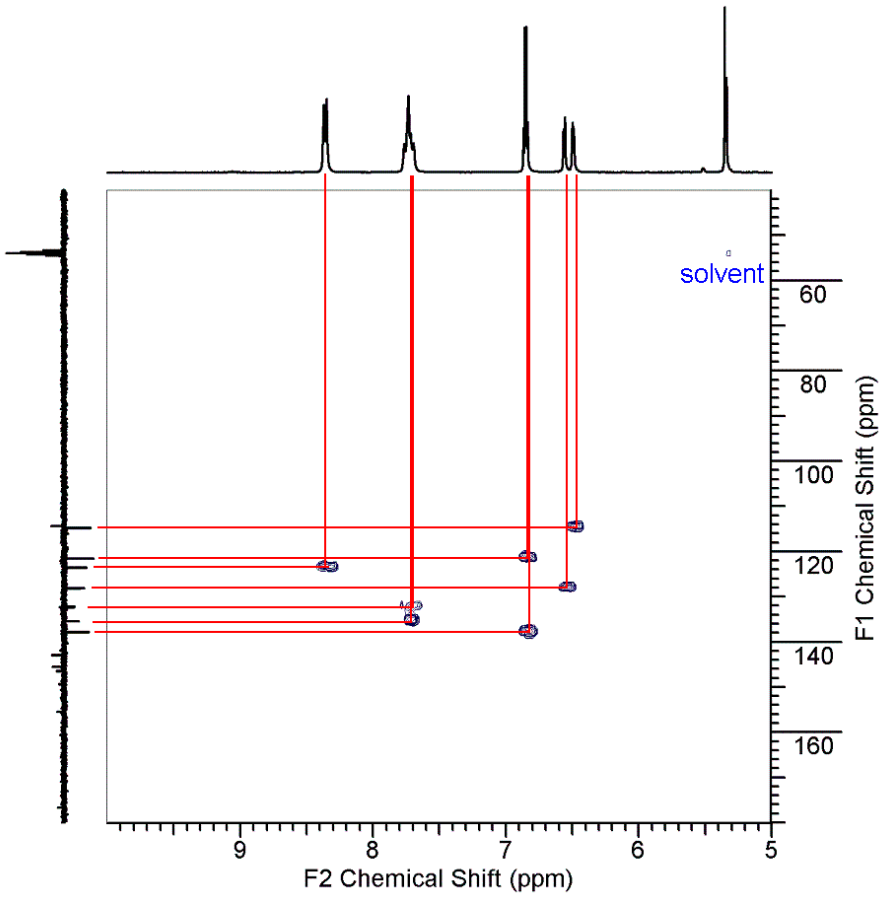

Fig. S13 HMQC NMR (F1: 100 MHz, F2: 400 MHz) spectrum of **1c**.

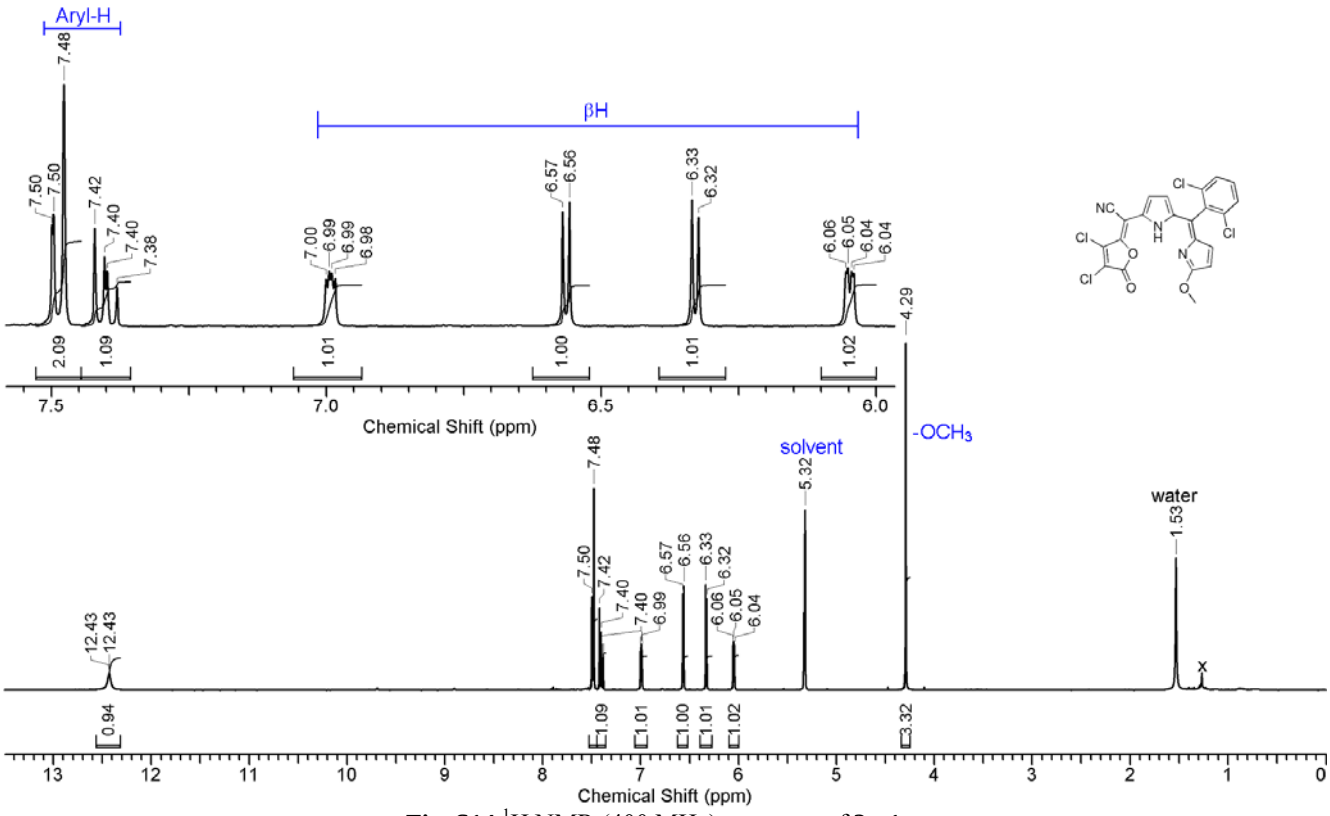

Fig. S14 ^{1}H NMR (400 MHz) spectrum of **2a-1**.

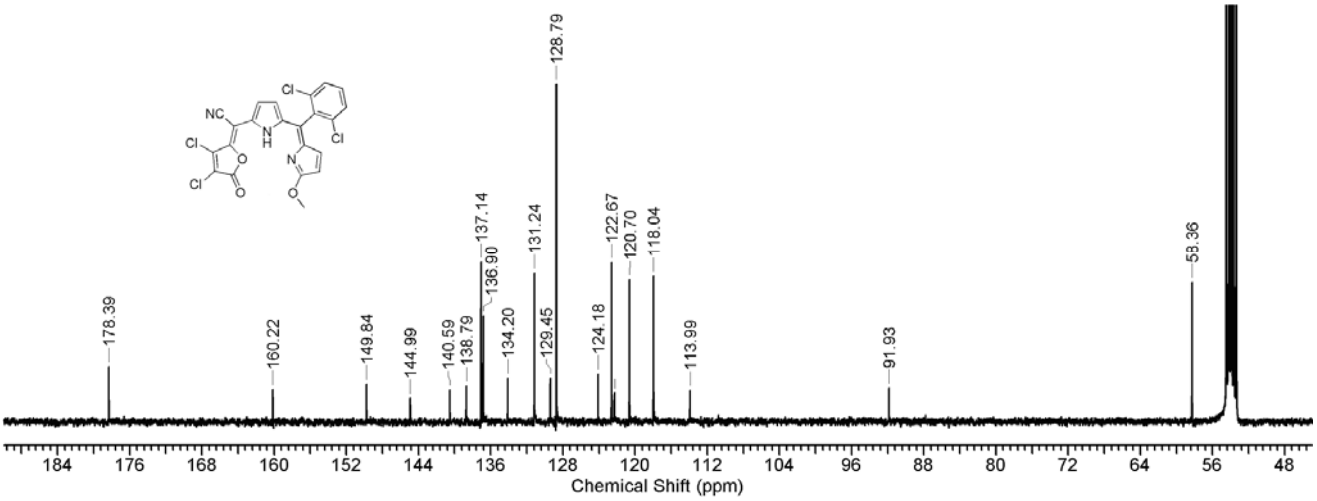

Fig. S15 ^{13}C NMR (100 MHz) spectrum of **2a-1**.

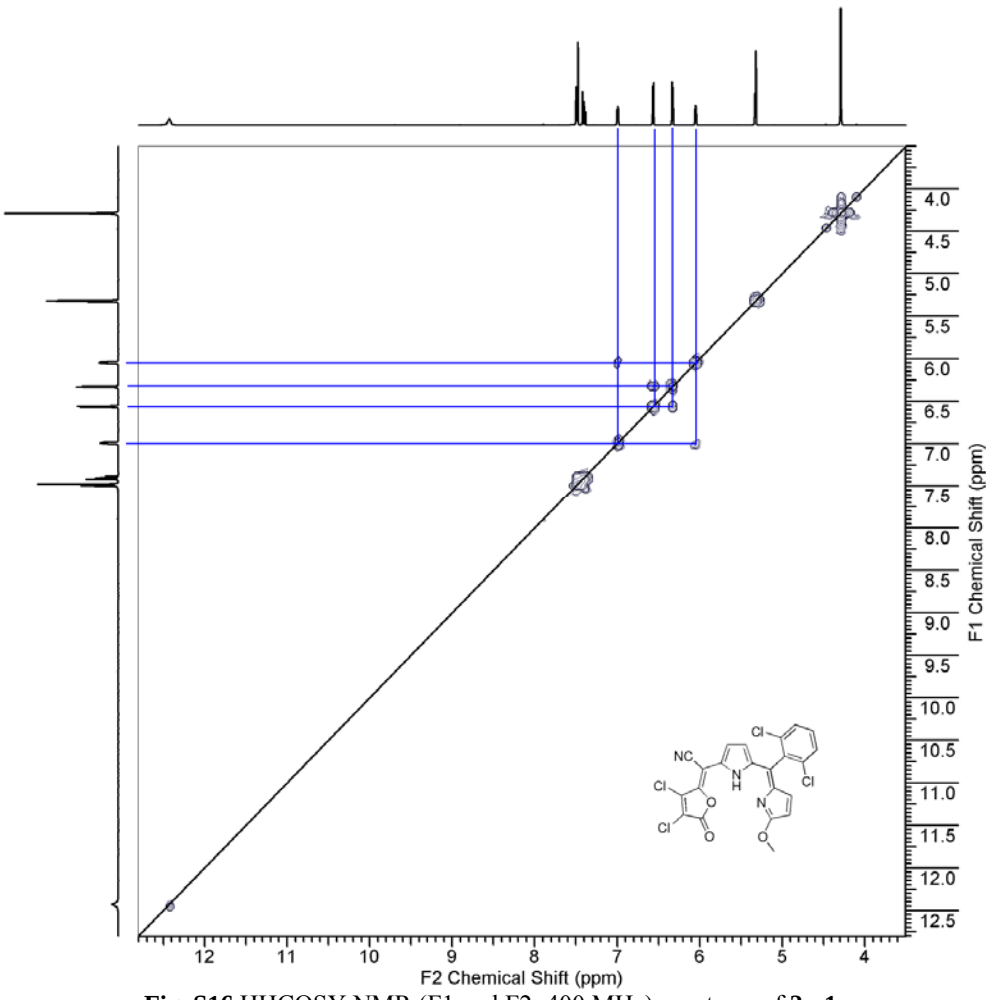

Fig. S16 HHCOSY NMR (F1 and F2: 400 MHz) spectrum of **2a-1**.

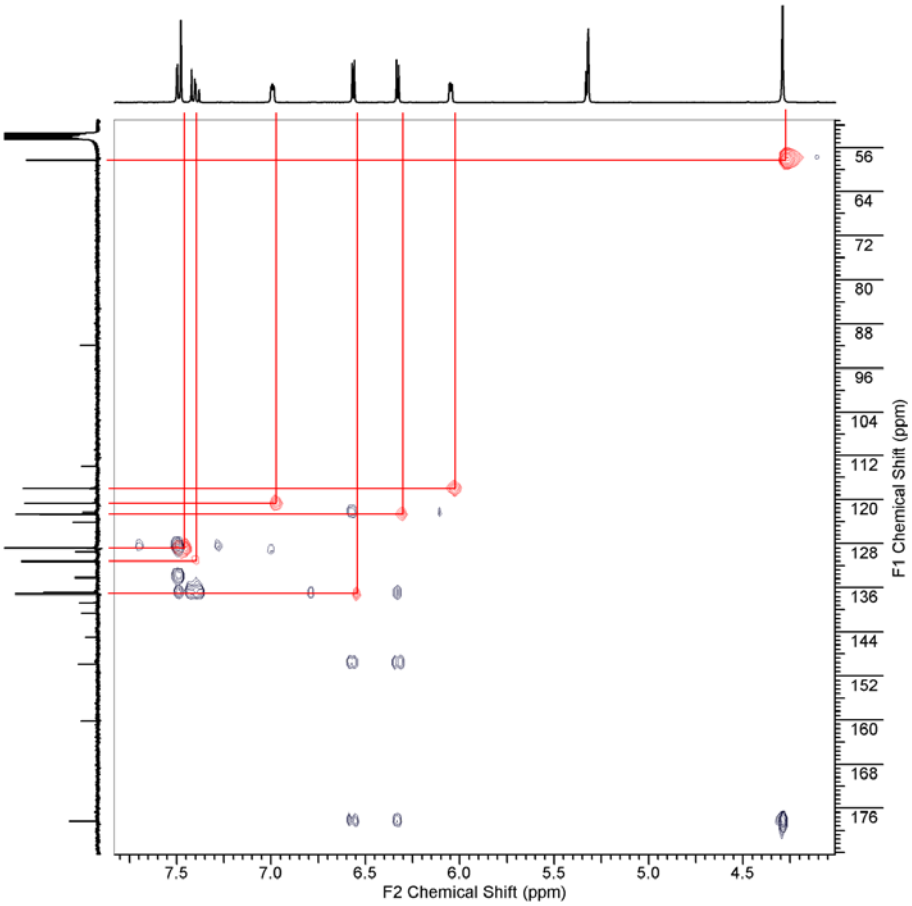

Fig. S17 HMQC(red) and HMBC(blue) NMR (F1: 100 MHz, F2: 400 MHz) spectra of **2a-1**.

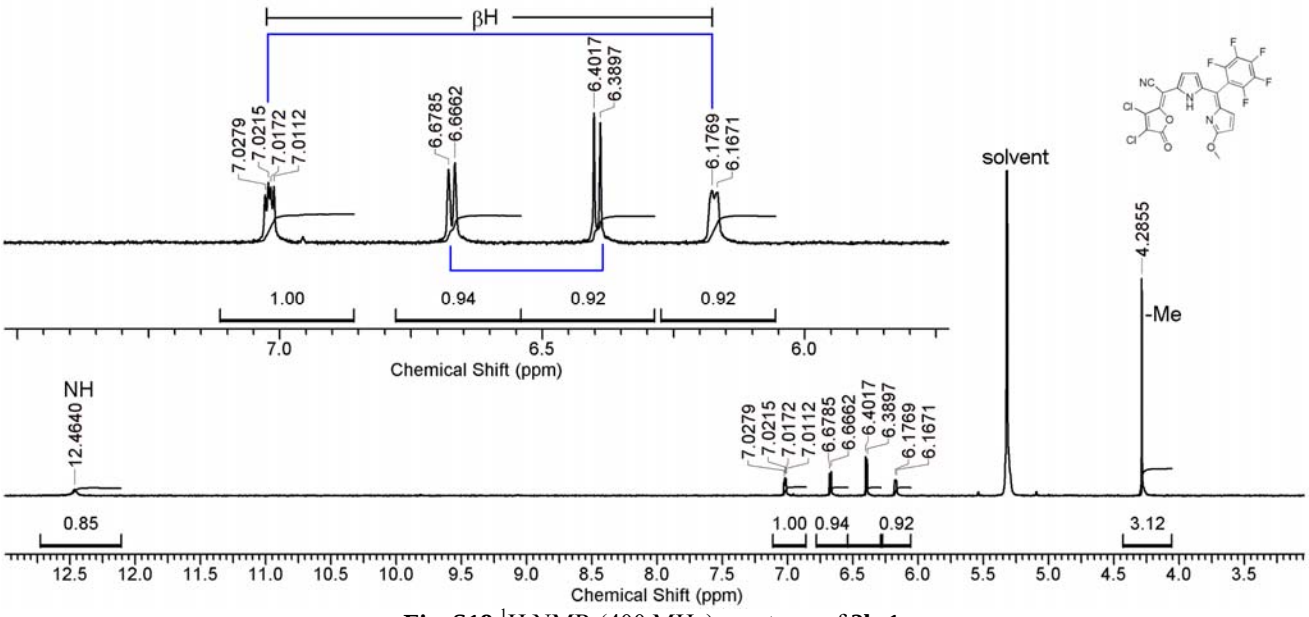

Fig. S18 ^{1}H NMR (400 MHz) spectrum of **2b-1**.

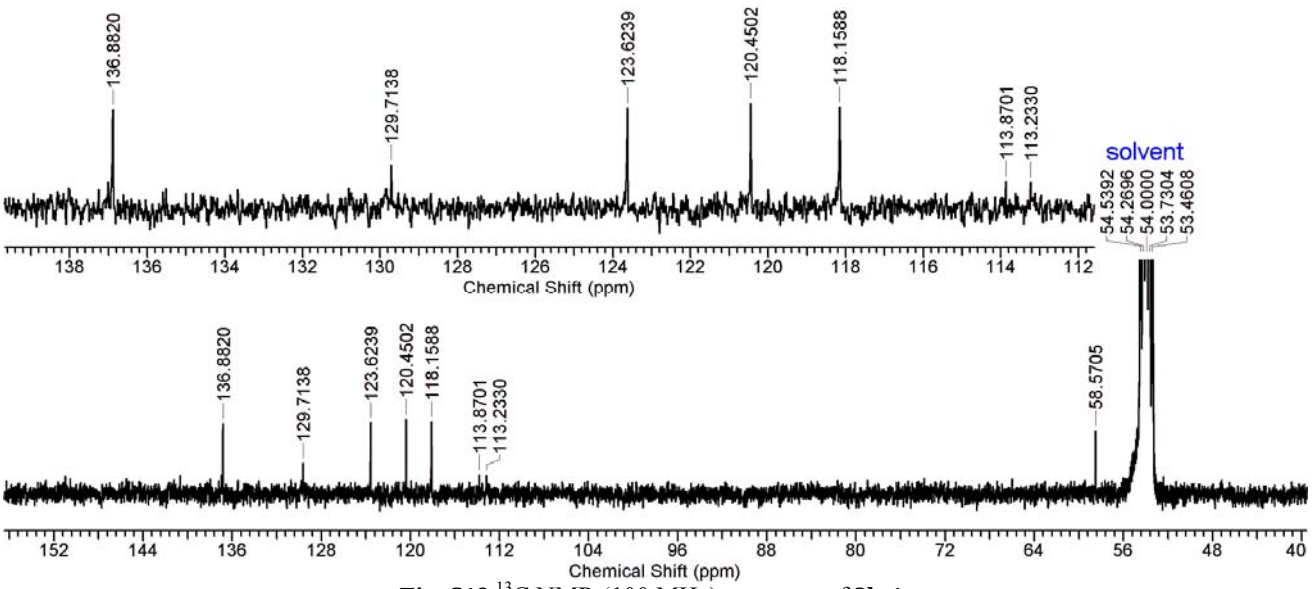

Fig. S19 ^{13}C NMR (100 MHz) spectrum of **2b-1**.

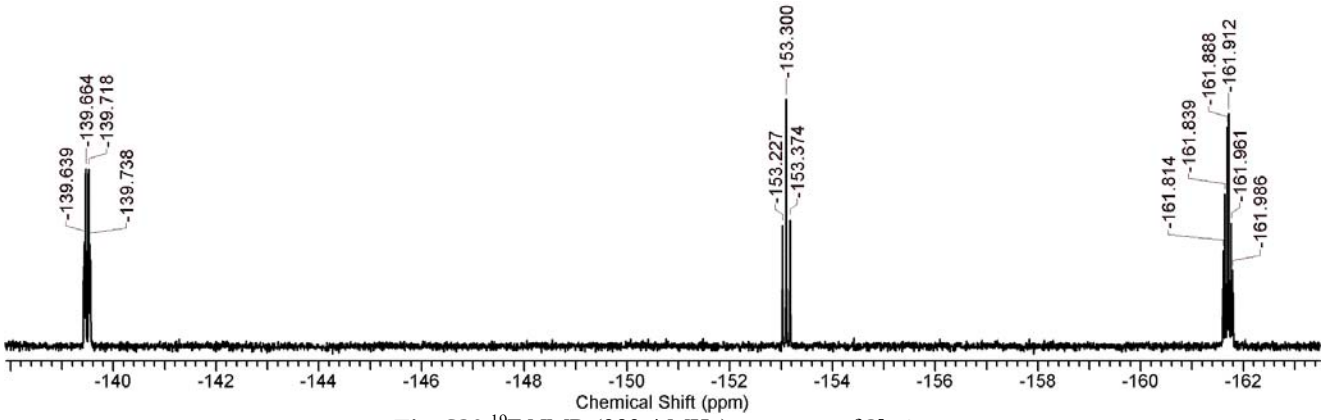

Fig. S20 ^{19}F NMR (282.4 MHz) spectrum of **2b-1**.

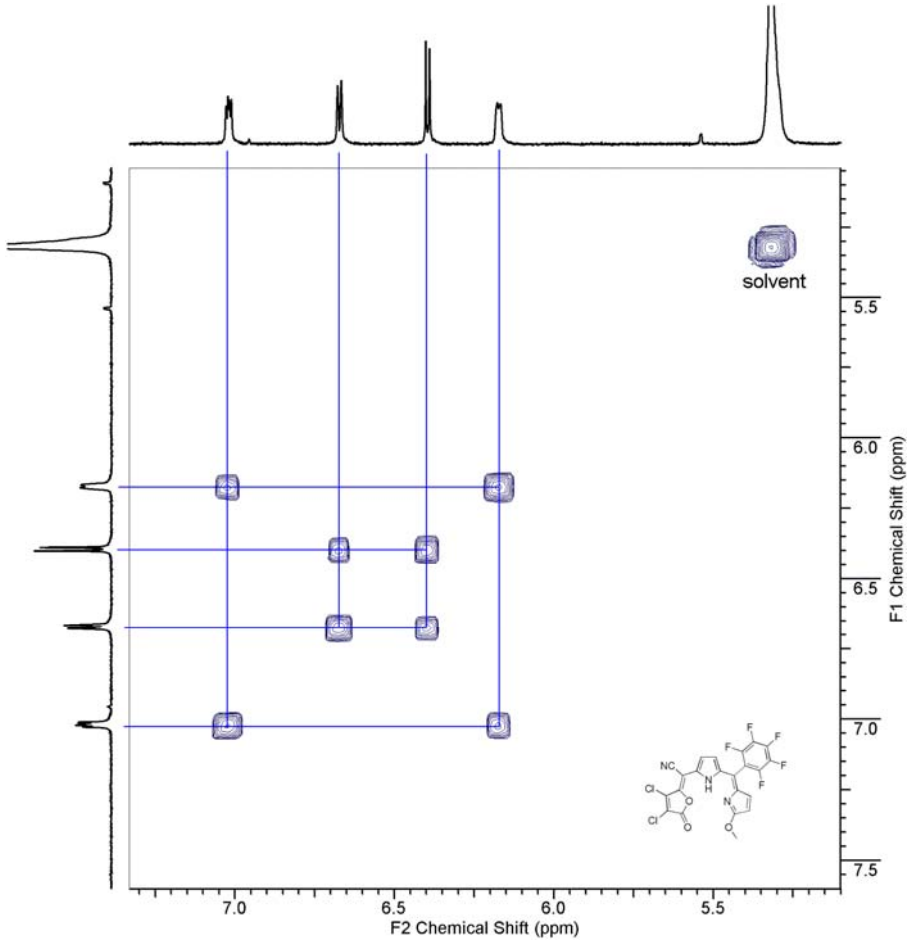

Fig. S21 HHCOSY NMR (F1 and F2: 400 MHz) spectrum of **2b-1**.

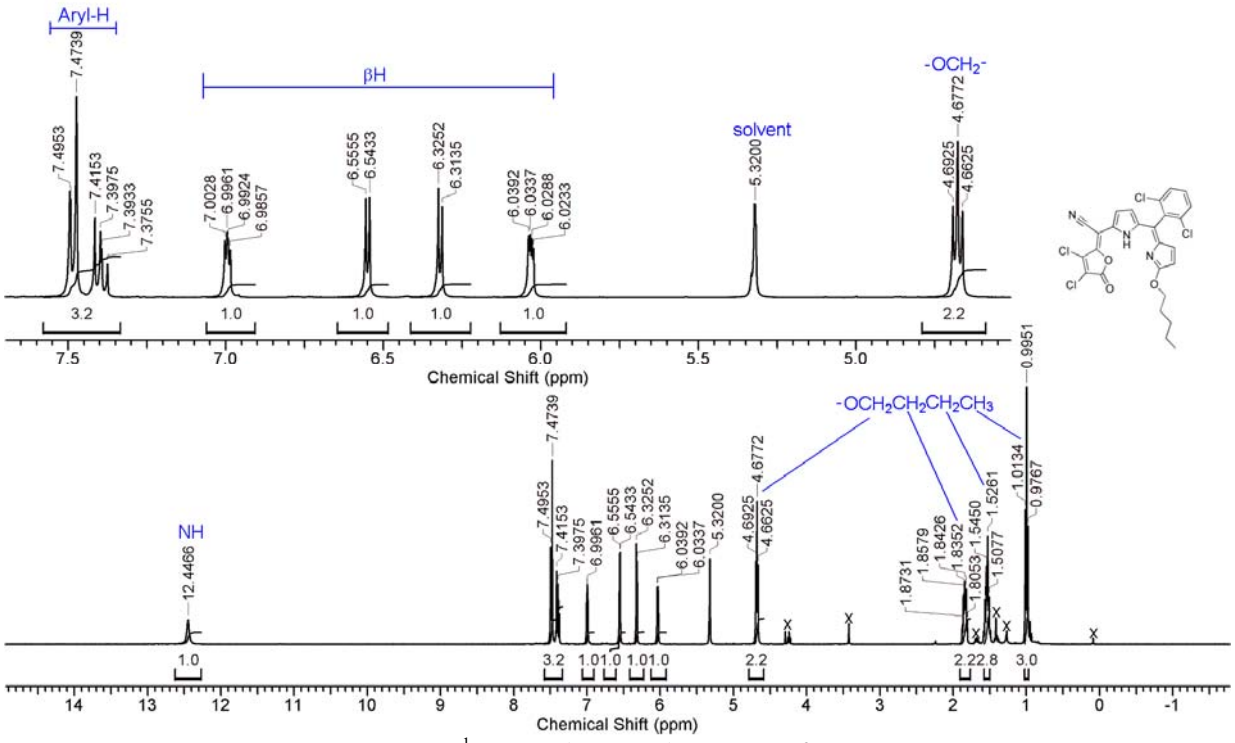

Fig. S22 ^{1}H NMR (400 MHz) spectrum of **2a-2**.

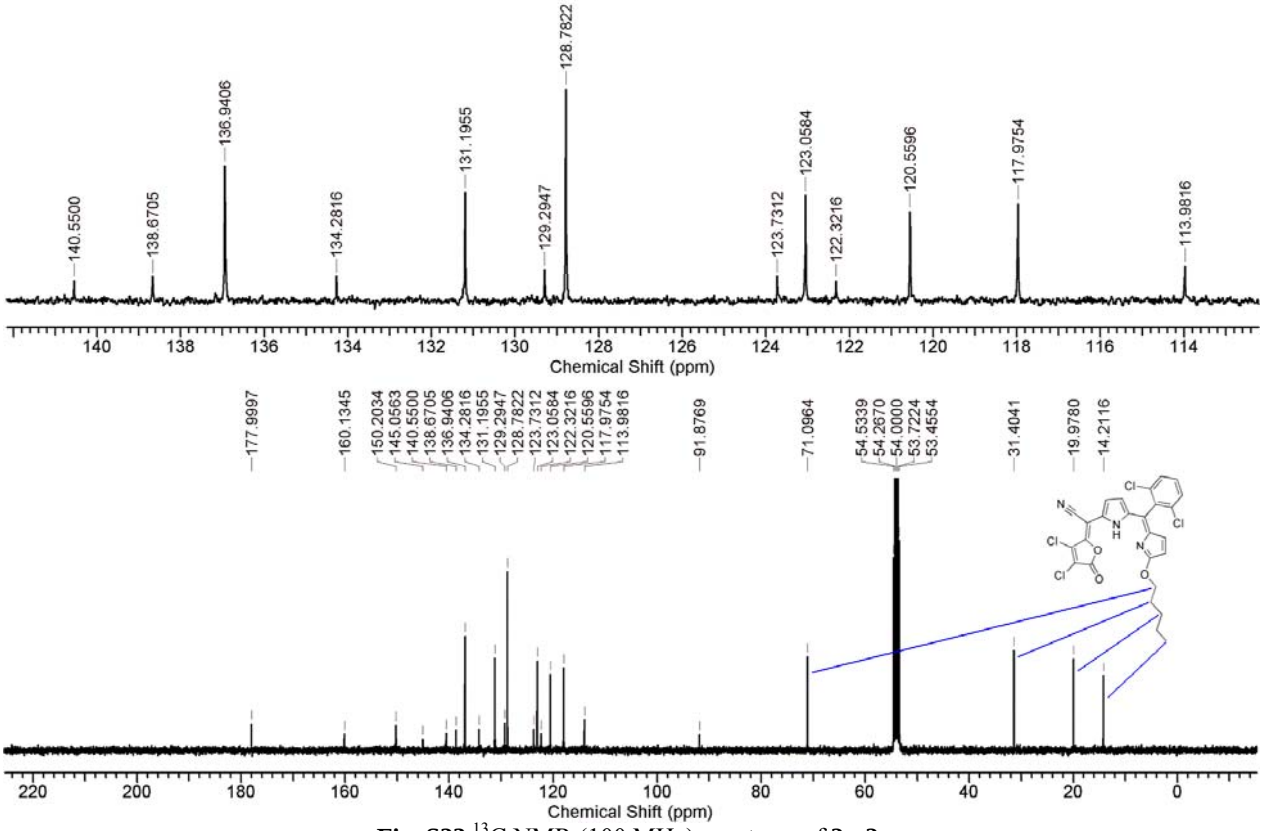

Fig. S23 ^{13}C NMR (100 MHz) spectrum of **2a-2**.

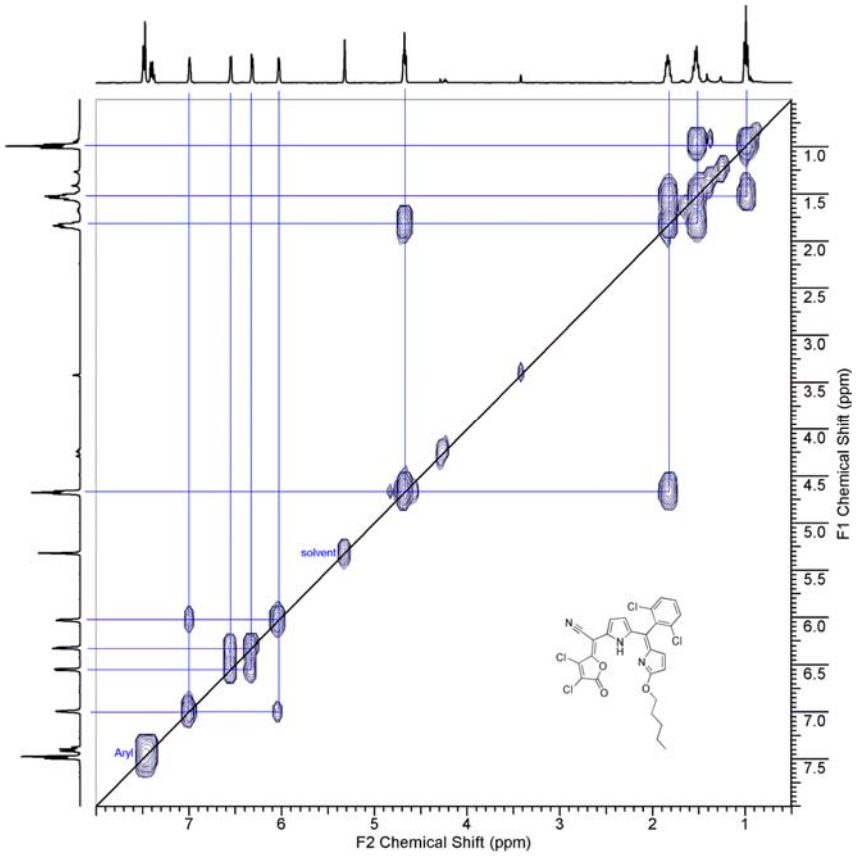

Fig. S24 HHCOSY NMR (F1 and F2: 400 MHz) spectrum of **2a-2**.

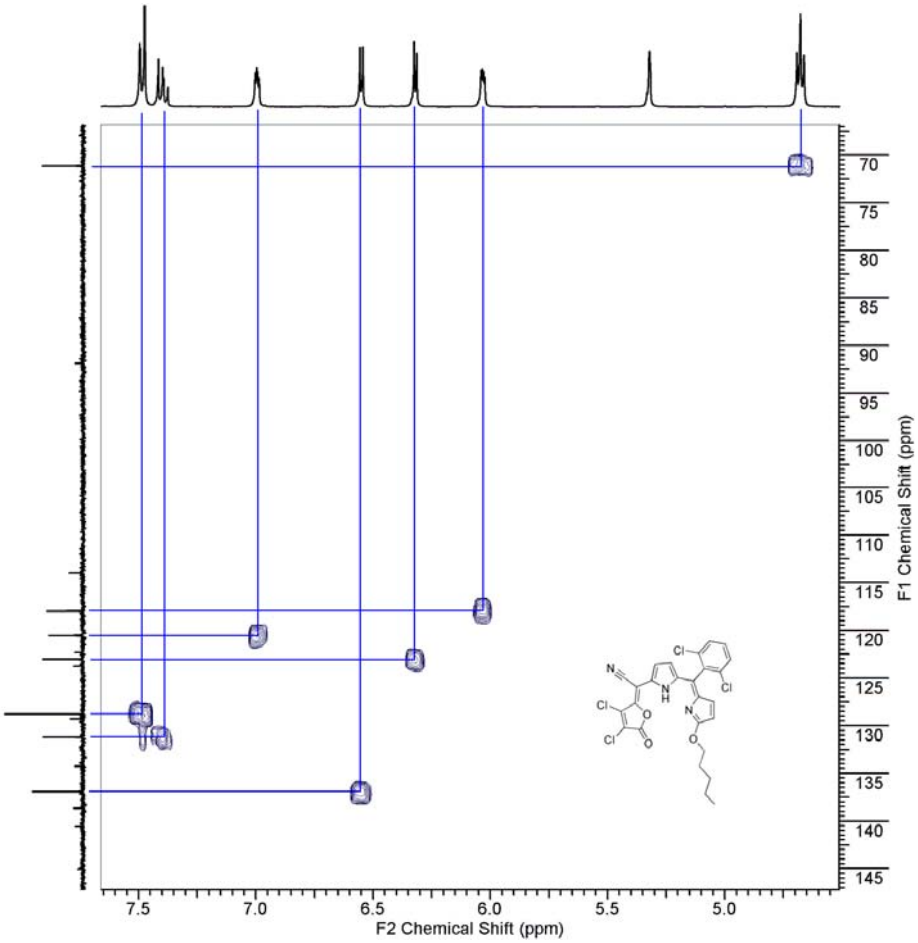

Fig. S25 HMQC NMR (F1: 100 MHz, F2: 400 MHz) spectrum of **2a-2**.

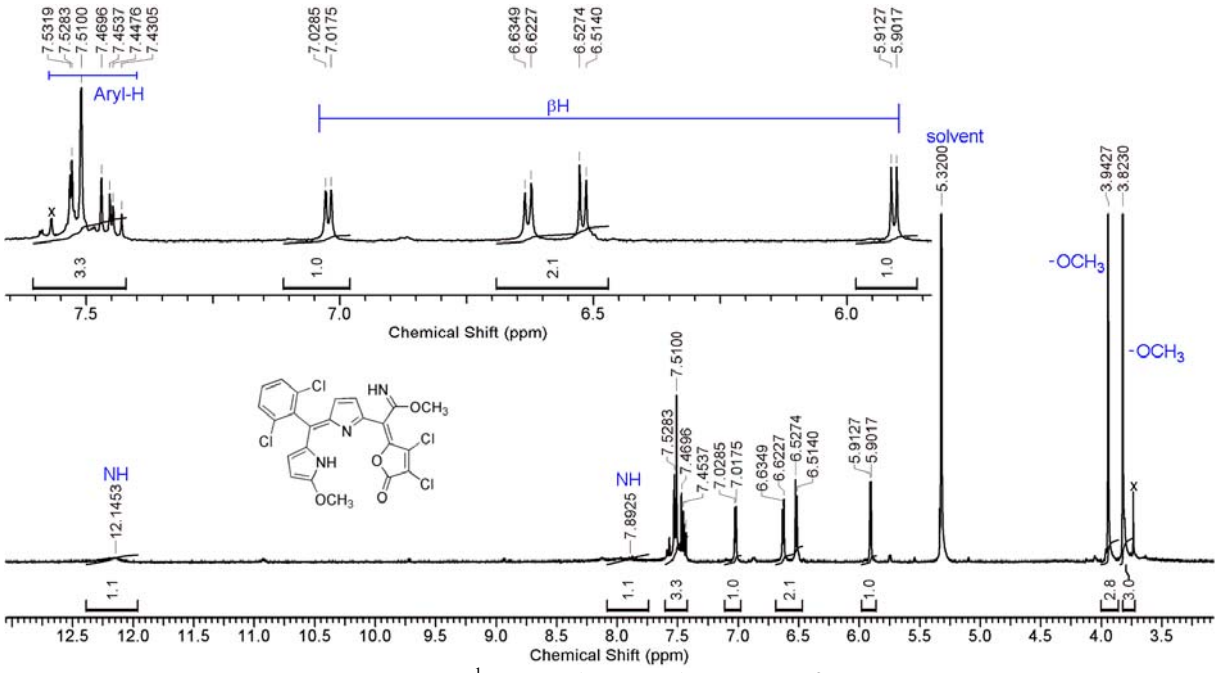

Fig. S26 ^{1}H NMR (400 MHz) spectrum of **3**.

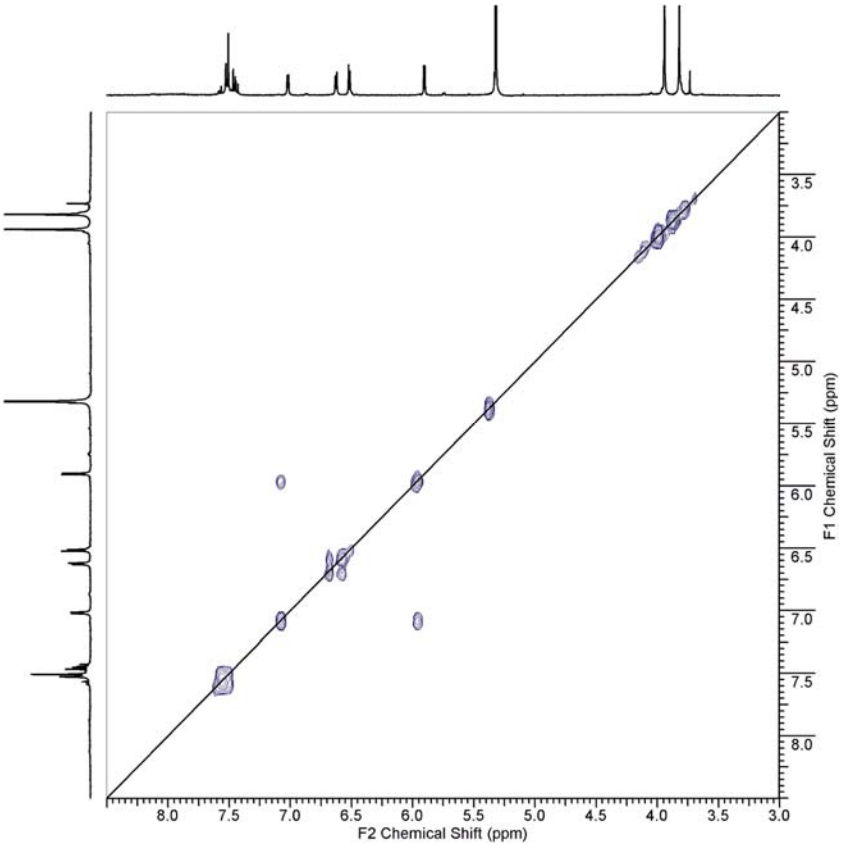

Fig. S27 HHCOSY NMR (F1 and F2: 400 MHz) spectrum of **3**.

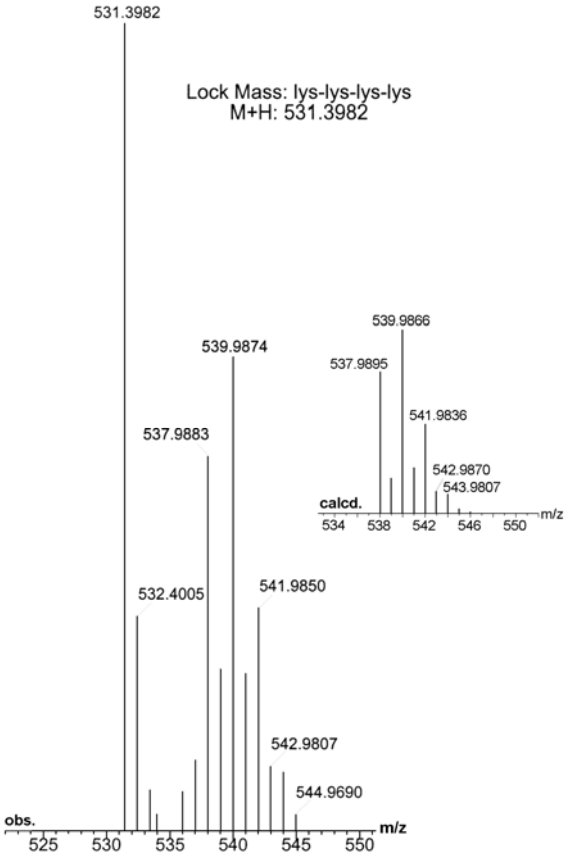

Fig. S28 HR ESI(+) TOF mass spectrum of **3**: calculated and observed spectra.

<Crystallographic data>

Crystallographic data of 2b-1

A crystalline red plate of $C_{22}H_8N_3O_3F_5Cl_2$ having approximate dimensions of 0.12 × 0.25 × 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 10.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Of the 20418 reflections that were collected, 4938 were unique (R_{int} = 0.024); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[S1] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 3.91 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[S2]), with minimum and maximum transmission coefficients of 0.890 and 0.954, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[S3]. 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[S4] on F^2 was based on 4938 reflections and 321 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors (R1 = 0.046 and wR2 = 0.102).

The standard deviation of an observation of unit weight[S5] was 0.99. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.41 and -0.32 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[S6]. Anomalous dispersion effects were included in Fcalc[S7]; the values for Δf' and Δf'' were those of Creagh and McAuley[S8]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[S9]. All refinements were performed using the SHELXTL[S10] crystallographic software package from Bruker-AXS.

Table S1. Parameters for the hydrogen-bonds of **2b-1**.

Donor --- H...Acceptor	D – H (Å)	H...A (Å)	D...A (Å)	D – H...A (°)
N(1) --H(1n) ..N(2)	0.84(3)	2.18(2)	2.7618(19)	127(2)
N(1) --H(1n) ..O(2)	0.84(3)	2.39(2)	2.8605(18)	116.3(18)

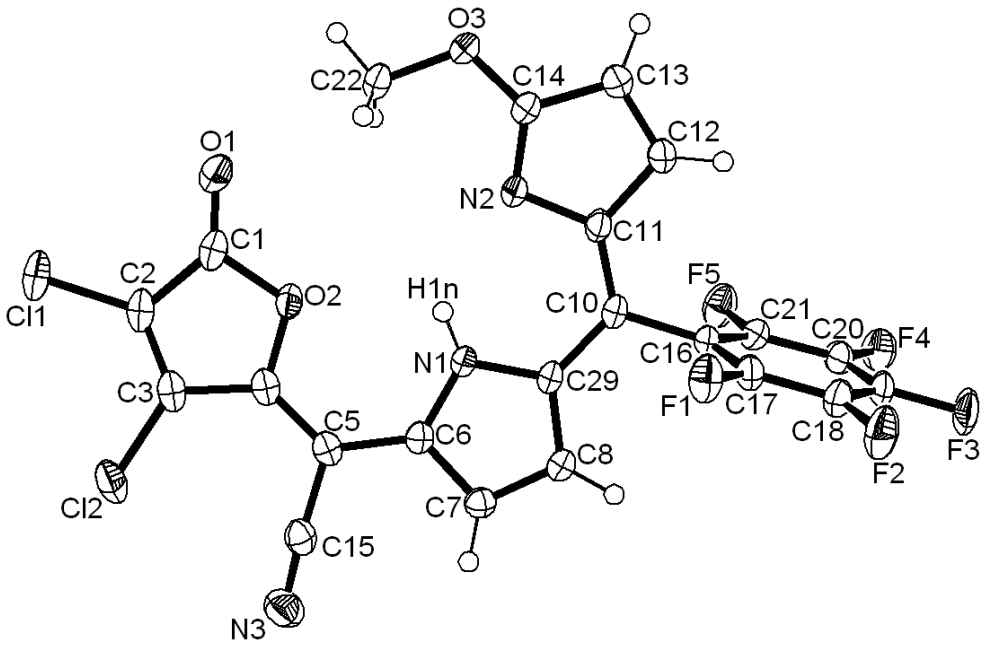

Fig. S29 ORTEP structure of **2b-1**. Thermal ellipsoids are scaled to the 50% probability level.

Crystallographic data of 2a-2

A crystalline black prism of $C_{25}H_{17}N_3O_3Cl_4$ having approximate dimensions of 0.40 × 0.45 × 0.55 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 56.2º. Data were collected in a series of ϕ and ω scans in 0.50º oscillations with 10.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Of the 38352 reflections that were collected, 5806 were unique (R_{int} = 0.028); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[S1] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 5.16 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[S2]), with minimum and maximum transmission coefficients of 0.674 and 0.814, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[S3]. 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[S4] on F^2 was based on 5806 reflections and 321 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors (R1 = 0.057 and wR2 = 0.118).

The standard deviation of an observation of unit weight[S5] was 1.08. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.51 and -0.38 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[S6]. Anomalous dispersion effects were included in Fcalc[S7]; the values for Δf' and Δf'' were those of Creagh and McAuley[S8]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[S9]. All refinements were performed using the SHELXTL[S10] crystallographic software package from Bruker-AXS.

Table S2. Parameters for the hydrogen-bonds of **2a-2**.

Donor --- H...Acceptor	D – H (Å)	H...A (Å)	D...A (Å)	D – H...A (°)
N(1) --H(1n) ..N(2)	0.88(2)	2.08(2)	2.730(2)	130(2)
C(7) --H(7c) ..O(2)	0.95	2.49	2.889(3)	111

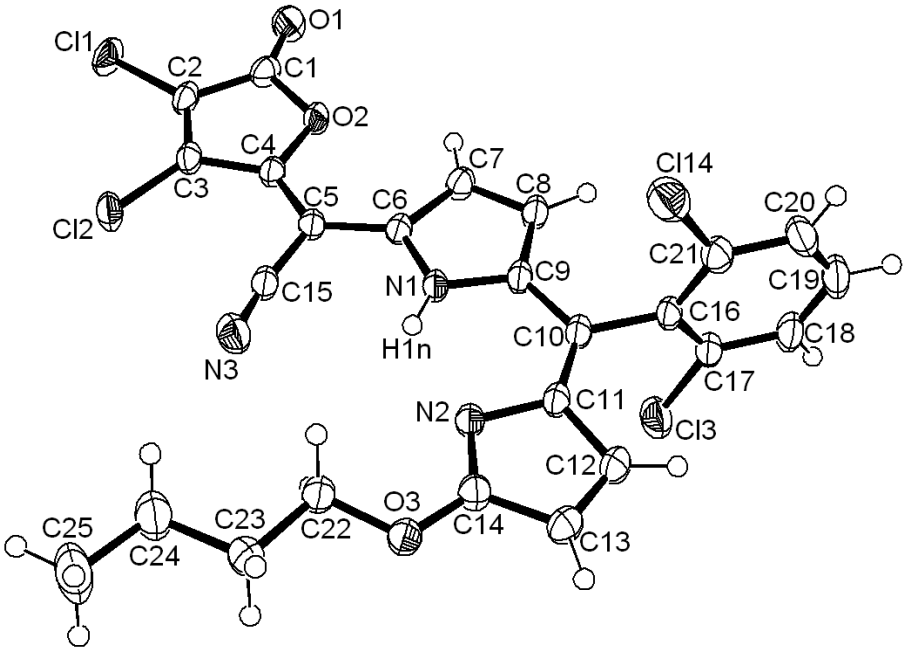

Fig. S30 ORTEP structure of **2a-2**. Thermal ellipsoids are scaled to the 50% probability level.

Table S3. Crystallographic data of 2a-2 and 2b-1.

	2a-2	**2b-1**
Formula	$C_{25}H_{17}Cl_4N_3O_3$	$C_{22}H_8Cl_2F_5N_3O_3$
*M*w	549.22	528.21
Crystal System	triclinic	triclinic
Space group	P-1	P-1
a / Å	7.5524(4)	7.0689(13)
b / Å	12.9084(7)	9.6348(19)
c / Å	13.1120(7)	16.074(3)
α / deg	102.326(2)	94.959(7)
β / deg	94.333(2)	95.467(7)
γ / deg	98.378(2)	106.429(7)
V / Å^3	1227.94(11)	1037.9(3)
Z	2	2
D_c / g cm^{-1}	1.485	1.690
μ(MoKα) cm^{-1}	0.71073	0.71073
Number of observed data ($I > 0.00\sigma(I)$)	5806	4938
Reflection / Parameter Ratio	18.09	15.38
R1[a]; *wR2*[b]	0.0574; 0.1179	0.0456; 0.1019
GOF	1.075	0.990
Numberof observed data ($I > 2\sigma(I)$)	4685	4046
(*R1*; *wR2*)[c]	0.0409; 0.1008	0.0347; 0.0926

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

Reference

S1. **SAINT.** Version 7.03A. Bruker AXS Inc., Madison, Wisconsin, USA. (1997-2003).

S2. **SADABS.** Bruker Nonius area detector scaling and absorption correction – V2.10, Bruker AXS Inc., Madison, Wisconsin, USA. (2003).

S3. **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.

S4. Least Squares function minimized: $\Sigma w(F_o^2 - F_c^2)^2$

S5. 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

S6. D. T. Cromer and J. T. Waber: *International Tables for X-ray Crystallography*, Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2A, (1974).

S7. J. A Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781.

S8. 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).

S9. 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).

S10. **SHELXTL.** Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA. (1997).