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Electronic Supporting Information for:

Regioselective addition of DDQ on a quinoid ring: an entry into chiral zwitterionic bridging ligands

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Table S1: Structural analysis and refinement of **11a**

Compound	**11a**
CCDC	1572929
Formula	$C_{22}H_{22}N_4O_4$
M_w	473.33
Crystal system	monoclinic
Measurement temperature (K)	293
Space group	P $2_1/c$
a (Å)	13.4139(16)
b (Å)	19.1246(19)
c (Å)	9.4516(9)
β/ °	103.255(10)
V (Å^3)	2360.1(4)
Z	4
Dc (g.cm^{-3})	1.343
Crystal colour	red
Crystal size (mm^3)	0.01×0.05×0.05
μ(Mo-Kα) (cm^{-1})	2.776
N° of unique refl.	6451
N° of observed refl.[$F^2 > 4\sigma F^2$]	3612
N° parameters refined/restraints	321/27
R_1 [$F^2>4\sigma F^2$]	0.0820
wR_1 [$F^2>4\sigma F^2$]	0.2048
R_2 [all refl.]	0.1383
wR_2 [all refl.]	0.2342
Goodness of fit [all refl.]	1.032
Largest diff. peak/hole /e. Å^{-3}	+0.445; -0.417

Determination of the enantiomerization barrier of 11a

A solution of about 0.5 mg of the second eluted enantiomer in 1 mL of the mixture hexane / ethanol + trifluoroacetic acid (0,1% v/v) / dichloromethane (10/80/10 v/v/v) was thermostated at 25 °C and 10 µL of this solution were injected on (*S*,*S*)-Whelk-O1 every 12 minutes. The decreasing percentage of the second eluted enantiomer was monitored and transferred to a kinetic analysis giving the following values, $k_{enantiomerization}$= 8.88 10^{-5} s^{-1}, $t_{1/2}$= 65 minutes and $\Delta G^{\neq}$ = 96.2 kJ.mol^{-1}.

Table S2: time decreasing percentage of the second enantiomer of **11a** in the acidic mobile phase

Time (min)	% enantiomer	ln ((%t-50%)/(%(t=0)-50%))
0	87.59	0.0000
12	83.35	-0.1197
24	79.42	-0.2451
36	75.62	-0.3834
48	72.69	-0.5048

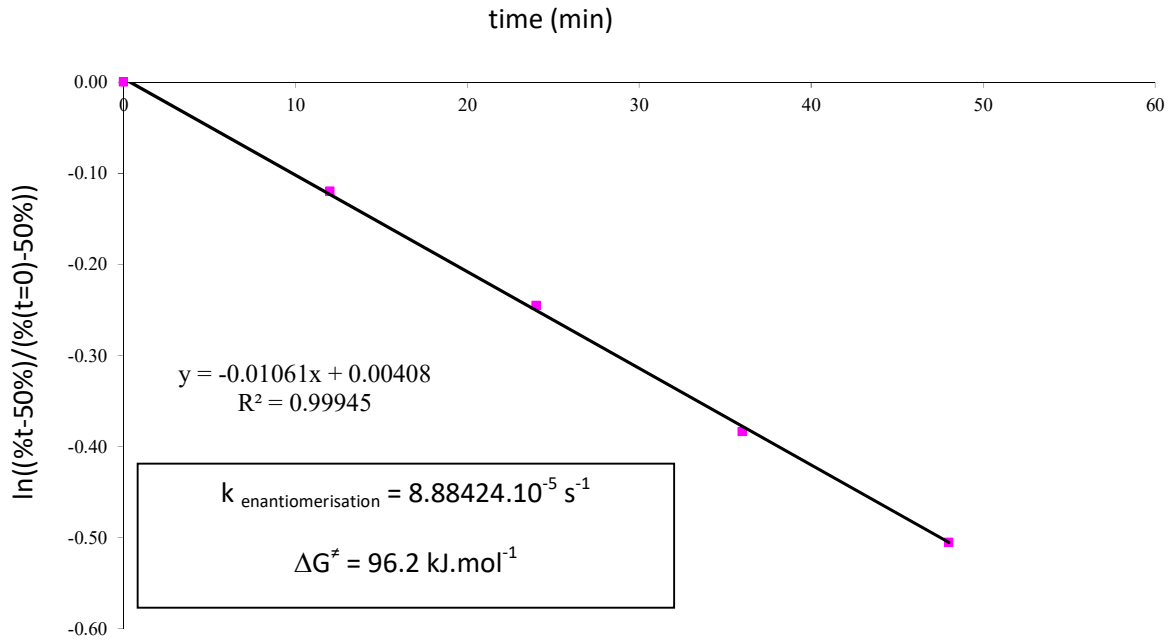


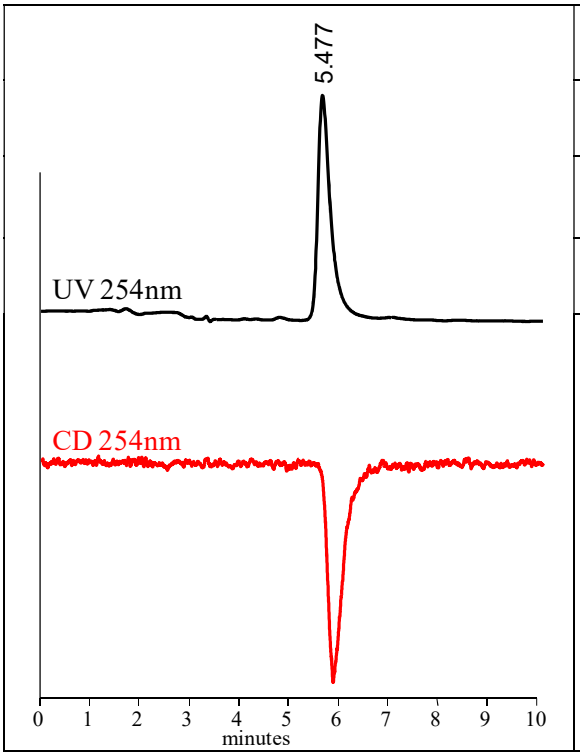
Fig S1: Determination of the enantiomerization barrier of **11a**

Preparative chiral HPLC separation and optical purity analysis of 11a enantiomers

• Sample preparation: About 70 mg of the racemic **11a** are dissolved in 15 mL of a mixture ethanol / dichloromethane (2/1).
• Chromatographic conditions: stationary phase: (*S*,*S*)-Whelk-O1; mobile phase: hexane / ethanol + trifluoroacetic acid (0,1%) / dichloromethane (10/80/10); flow-rate = 5 mL/min; UV detection at 254 nm.
• Injections (stacked): 60 times 250 µL, every 8 minutes.
• Collection: each enantiomer was collected in a flask containing sodium carbonate in ethanol, because racemization occurs in acidic media.
• First fraction: 25 mg of the first eluted with ee > 99%; • Second fraction: 25 mg of the second eluted with ee > 96

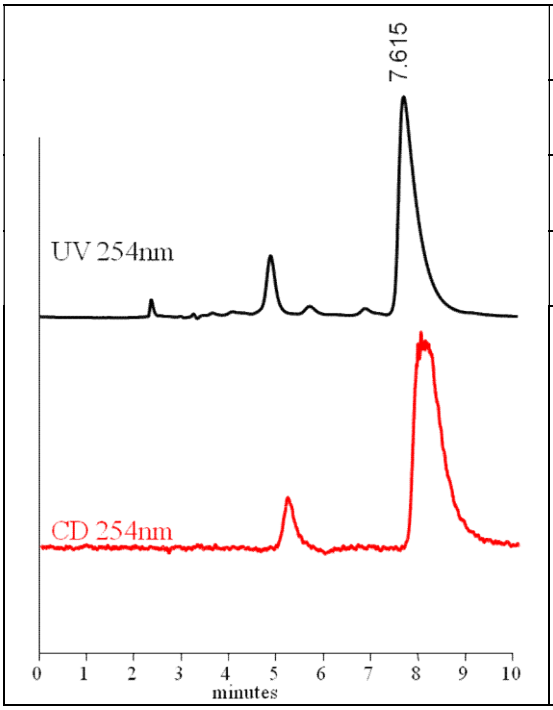
• Chromatograms and HPLC data of the collected fractions:

- first eluted enantiomer :



RT [min]	Area	Area%
5.48	2782	99.62
8.10	11	0.38
Sum	2793	100.00

- second eluted enantiomer :



RT [min]	Area	Area%
5.65	226	1.69
7.61	13134	98.31
Sum	13361	100.00

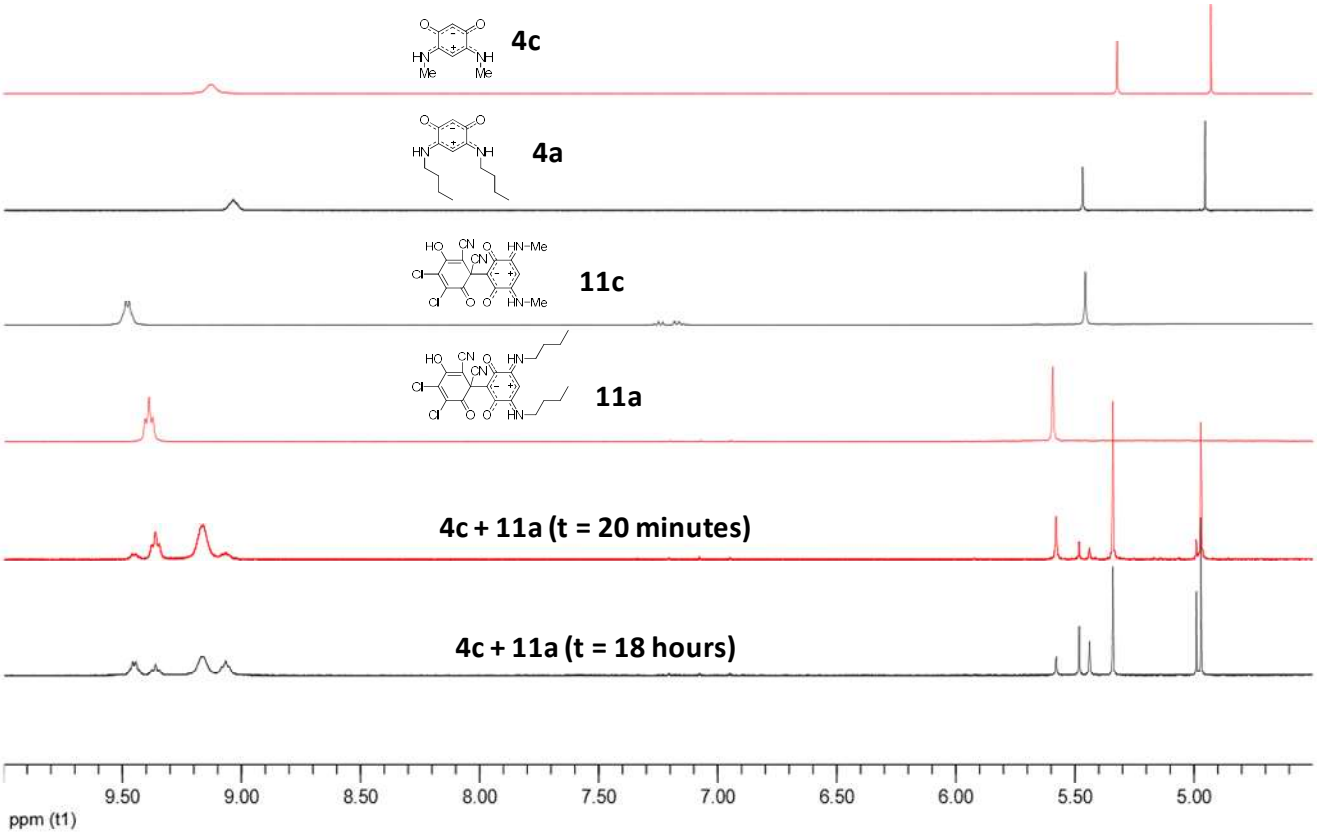


Fig S2: Partial views of the ^{1}H NMR spectra (in DMSO-d_6) of **4a**, **4c**, **11a**, **11c** and of an equimolar mixture of **4c** and **11a** after 20 minutes and 18 hours.

^{1}H and ^{13}C NMR spectra of 11a-c

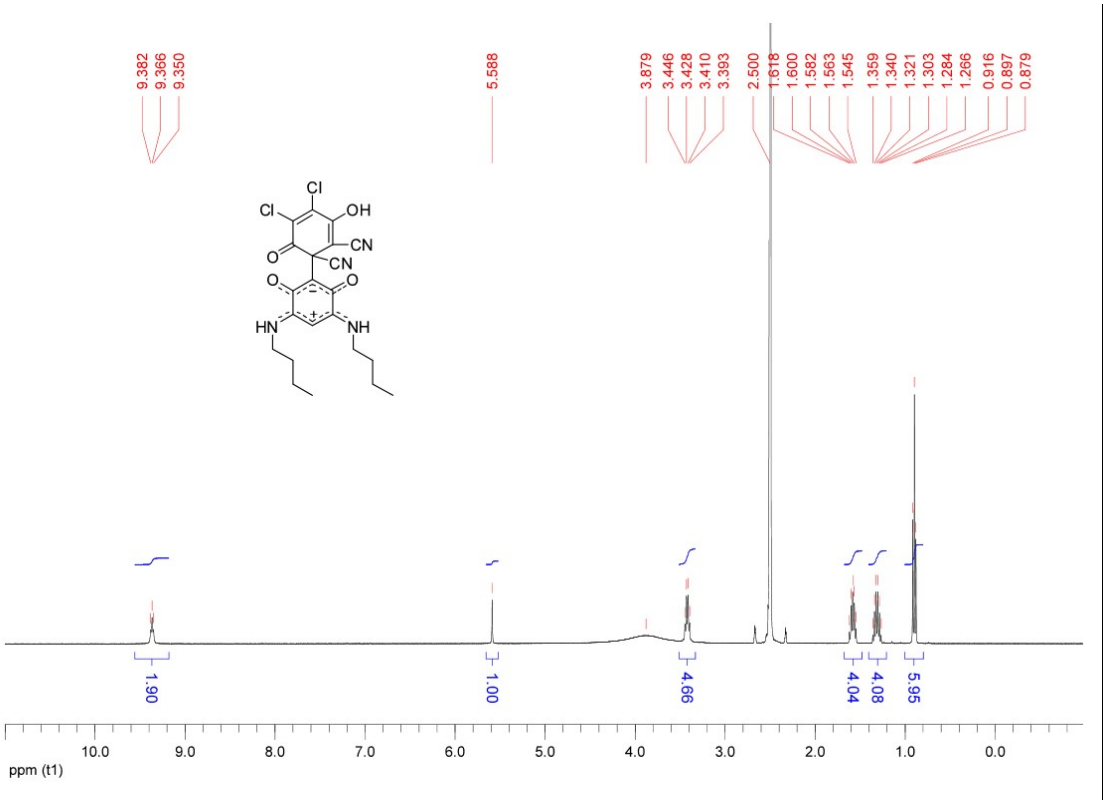


Fig. S3: ^{1}H NMR spectrum of **11a** in DMSO-d_6 (400 MHz, 294 K).

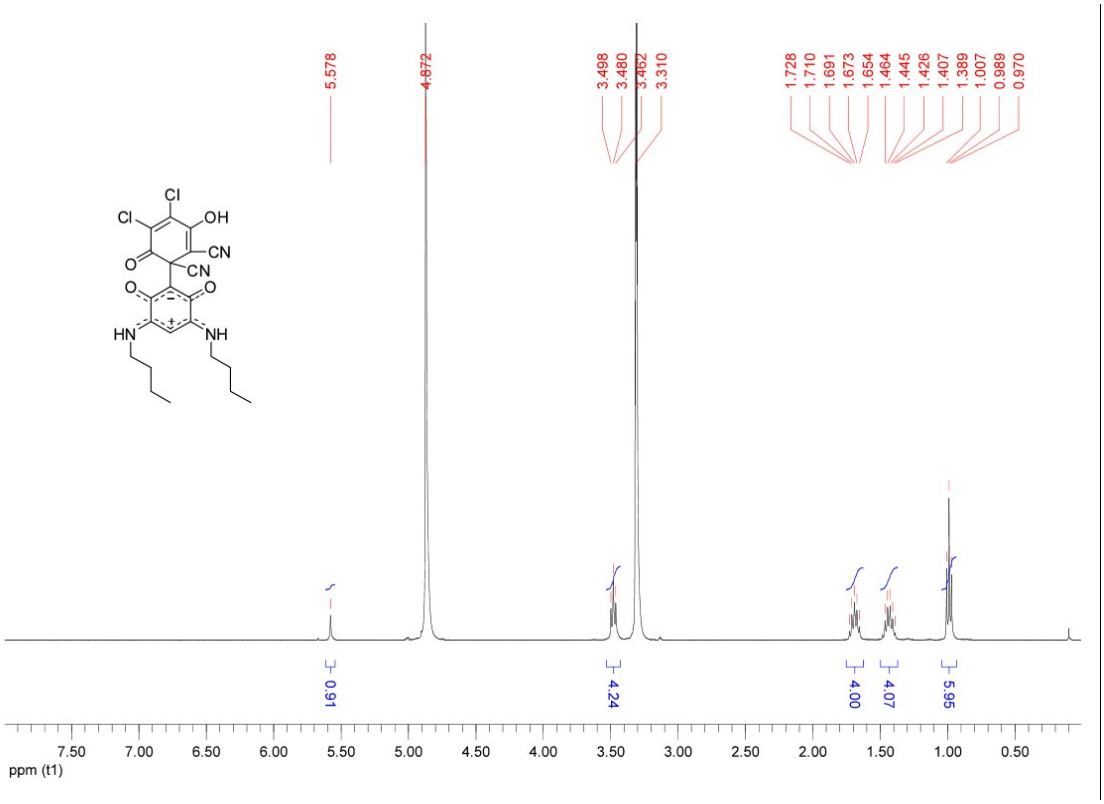


Fig. S4: ^{1}H NMR spectrum of **11a** in MeOD-d_4 (400 MHz, 294 K).

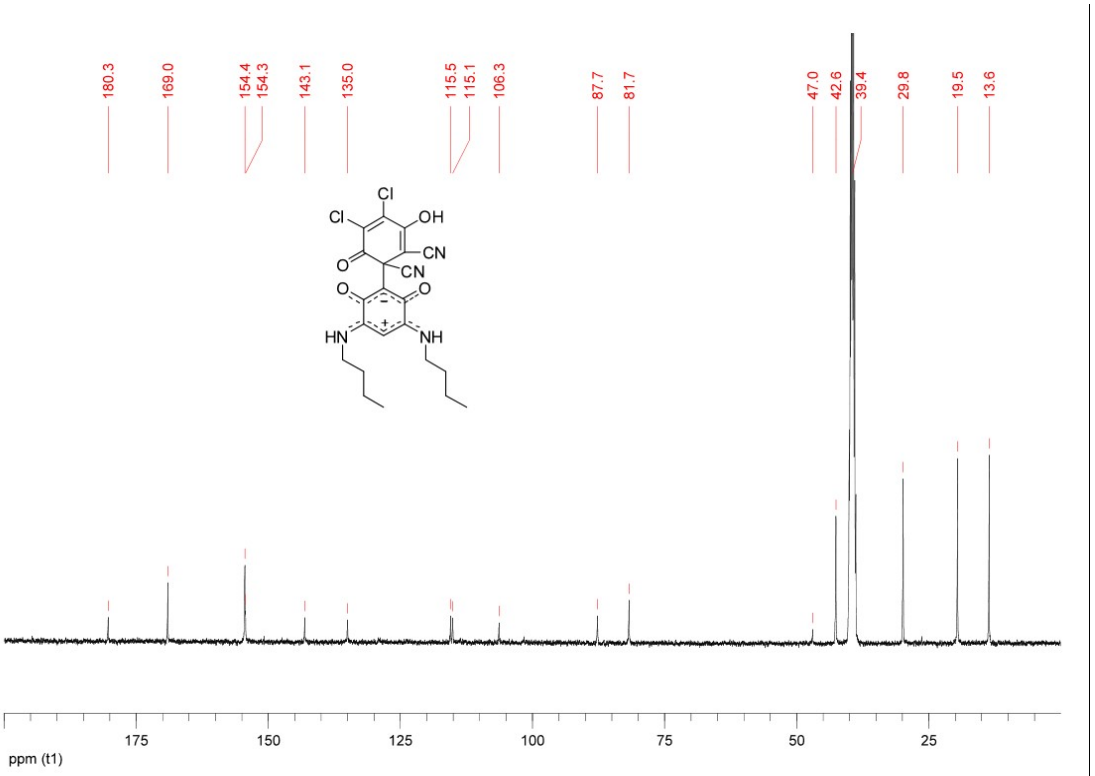


Fig. S5: ^{13}C NMR spectrum of **11a** in DMSO-d_6 (100 MHz, 294 K).

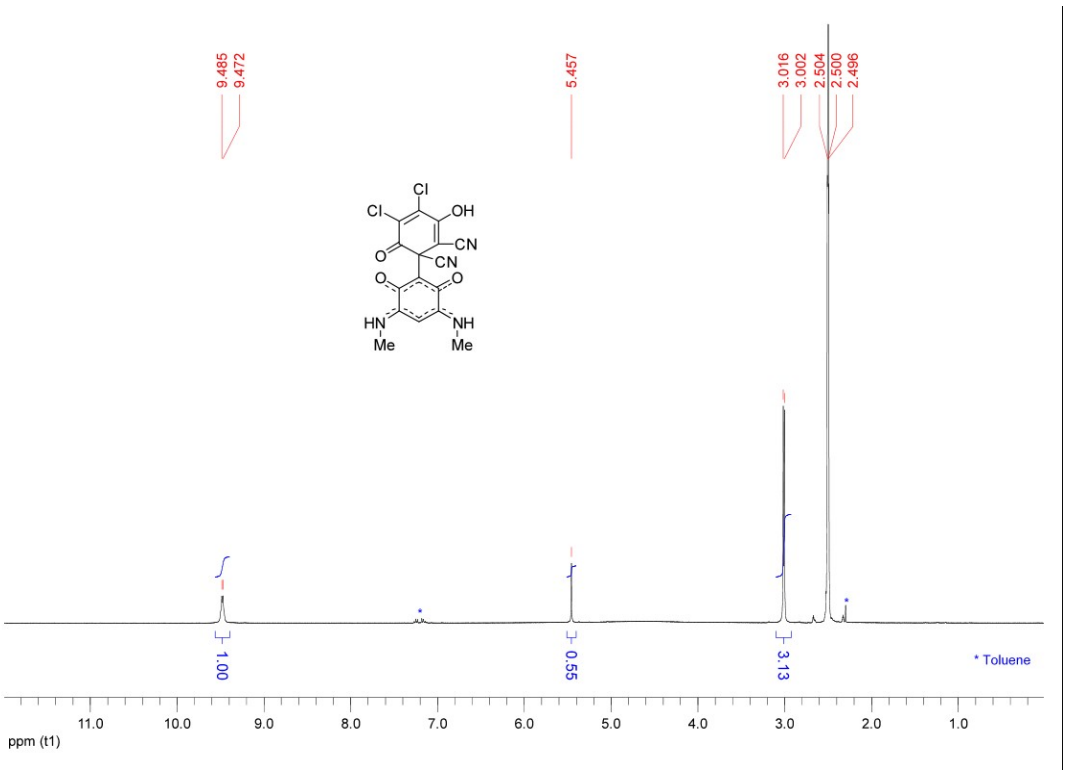


Fig. S6: ^{1}H NMR spectrum of **11b** in DMSO-d_6 (400 MHz, 294 K)

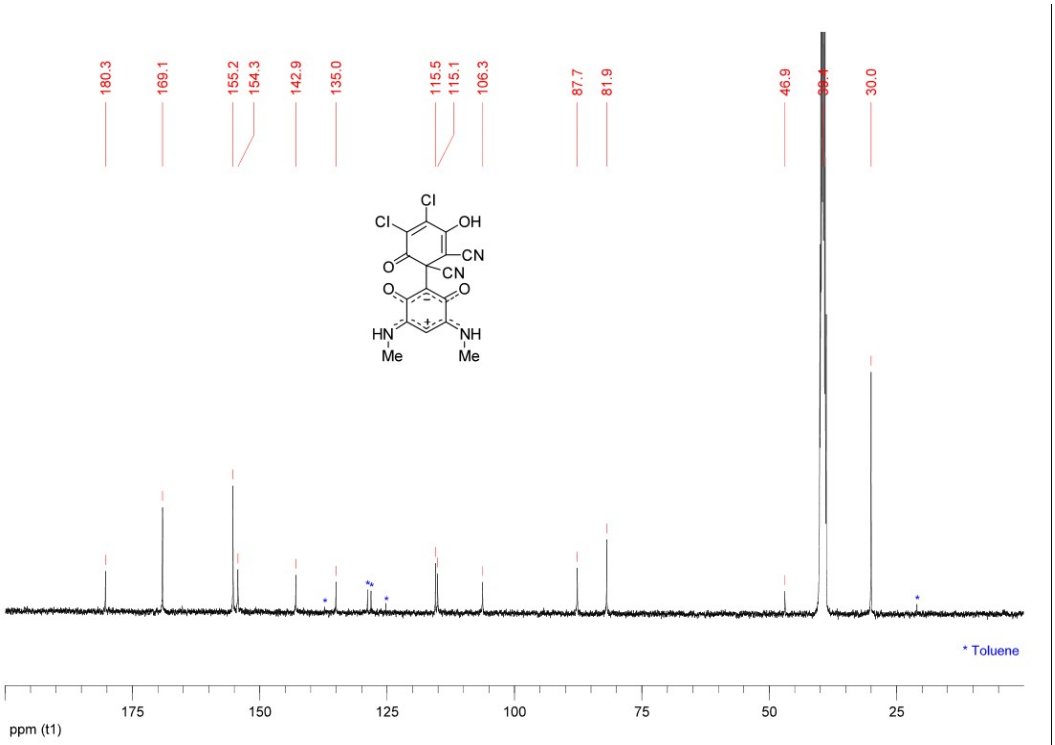


Fig. S7: ^{13}C NMR spectrum of **11b** in DMSO-d_6 (100 MHz, 294 K).

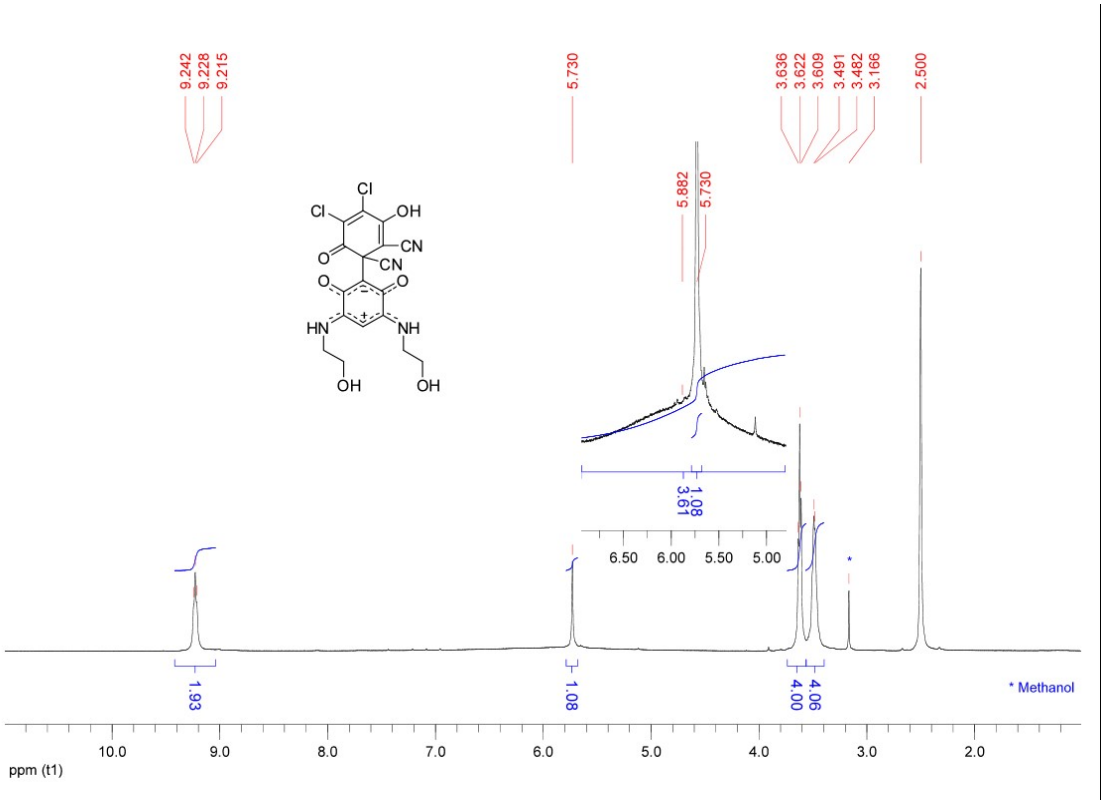


Fig. S8: ^{1}H NMR spectrum of **11c** in DMSO-d_6 (400 MHz, 294 K).

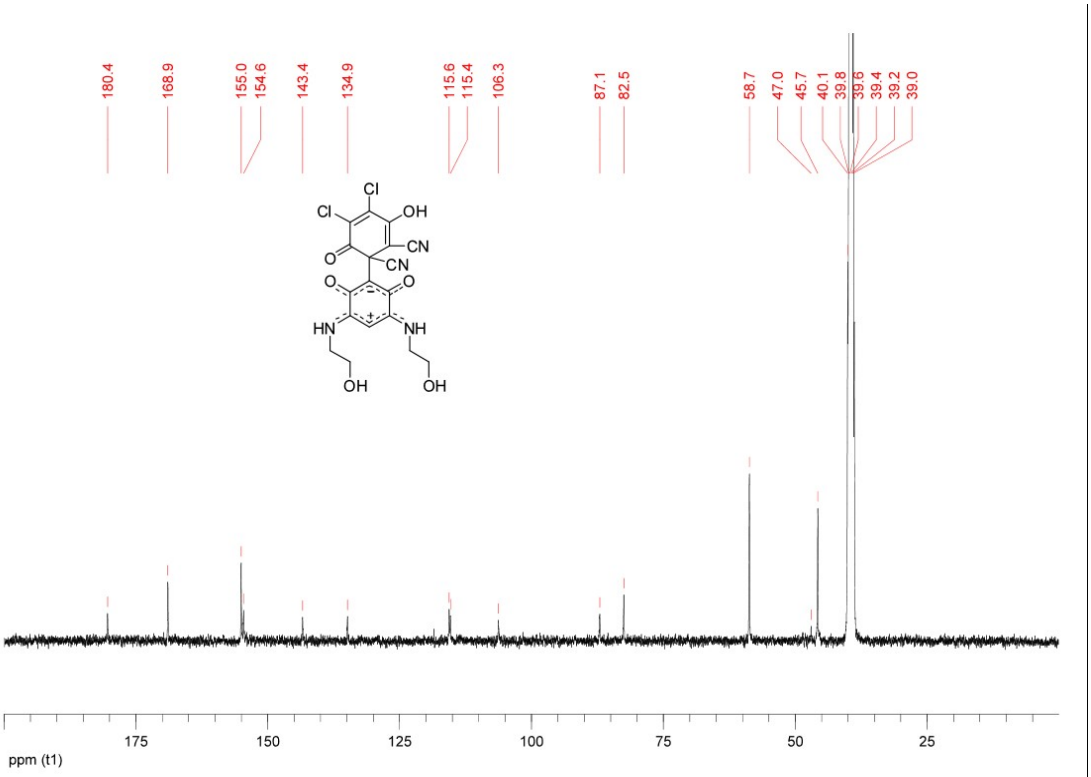


Fig. S9: ^{13}C NMR spectrum of **7c** in DMSO-d_6 (100 MHz, 294 K).