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Conjugated Donor-Acceptor Molecular Systems Involving the 1,3-Indandione-Derived Electron Accepting Moieties.

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Synthesis of 2-(4-(diisopropylamino)benzylidene)-1H-indene-1,3(2H)-dione (1c).

To the mixture of 0.146 g (1 mmol) of 1,3-indandione and 0.205 g (1 mmol) of 4-N-diisopropylaminobenzaldehyde in 20 ml of acetic acid were added three drops of concentrated HCl, the solution was refluxed for 30 min, cooled to room temperature and poured into ice water. The precipitate formed was filtered off and washed with cold ethanol. Red solid, yield 0.23 g (66%), m.p. 177-178°C, from ethanol. ^{1}H NMR, $CDCl_3$, δ, ppm: 8.46 d (2H, H-2'6'); 7.86 m (2H, 5,6-H); 7.72 m (2H, H-4,7); 7.69 s (1H, =CH); 6.91 d (2H, *J* = (9.3 Hz, H-3',5'); 4.08 m (2H, CH-*i*-Pr); 1.36 d (12H, *J* = 6.8 Hz, CH_3). ^{13}C NMR, $CDCl_3$, δ, ppm: 191.3; 189.8; 152.9; 146.7; 142.2; 137.4; 134.2; 134.0; 122.5; 122.2; 122.1; 121.5; 114.2; 48.1; 20.5.
Calculated: C 79.25%, H 6.95%, N 4.20%. Found: C 79.14%, H 7.02%, N 4.17%.

Synthesis of 1,3-bis-dicyanovinyl-2-(4-diisopropylaminobenzylidene)-indane (3c).

The mixture of 0.24 g (1 mmol) of 1,3-bisdicyanovinylindane and 0.25 g (1.2 mmol) of 4-N-diisopropylaminobenzaldehyde in 10 ml of acetic anhydride was heated at 70°C for 2h and cooled. The precipitated solid was filtered off, washed with diethyl ether and dried. Dark-green solid, yield 0.35 g, (74%), m.p. 240-242°C, from acetonitrile. ^{1}H NMR, $CDCl_3$, δ, ppm: 8.63 s (1H, =CH); 8.54 m (2H, 4,7-H); 7.72 m (2H, 5,6-H); 7.55 d (2H, *J* = 9.3 Hz, H-2',6'); 6.92 d (2H, *J* = (9.3 Hz, H-3',5'); 4.14 m (2H, CH-*i*-Pr); 1.40 d (12H, *J* = 6.8 Hz, CH_3). ^{13}C NMR, $CDCl_3$, δ, ppm: 161.4; 153,6; 146.5; 137.7; 146.5; 137.7; 133.7; 125.1; 122.8; 122.3; 115.2; 114.6; 114.2; 69.6; 48.8; 20.9.
Calculated: C 78.30%, H 5.40%, N 16.31%. Found: 78.21%, H 5.42%, N 16.35%.

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NMR spectra

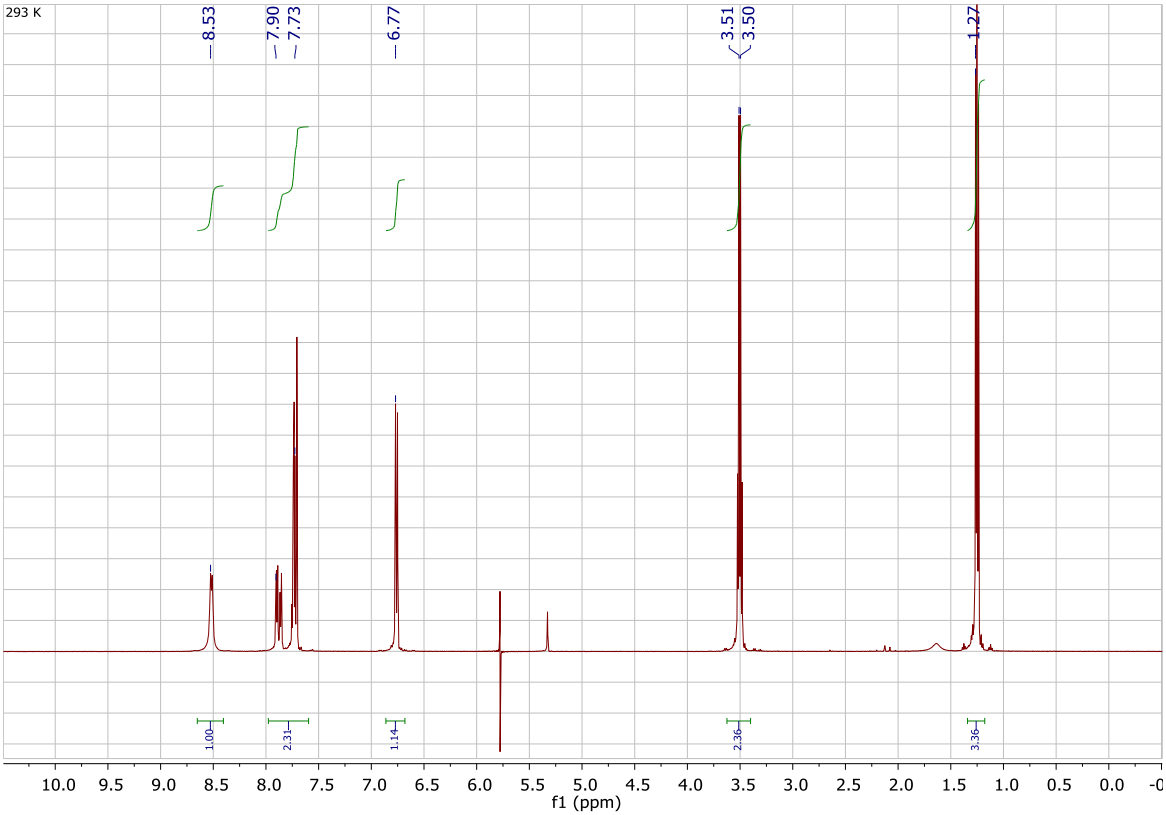

Fig. S1. ^{1}H NMR spectrum of **1b** in CD_2Cl_2.

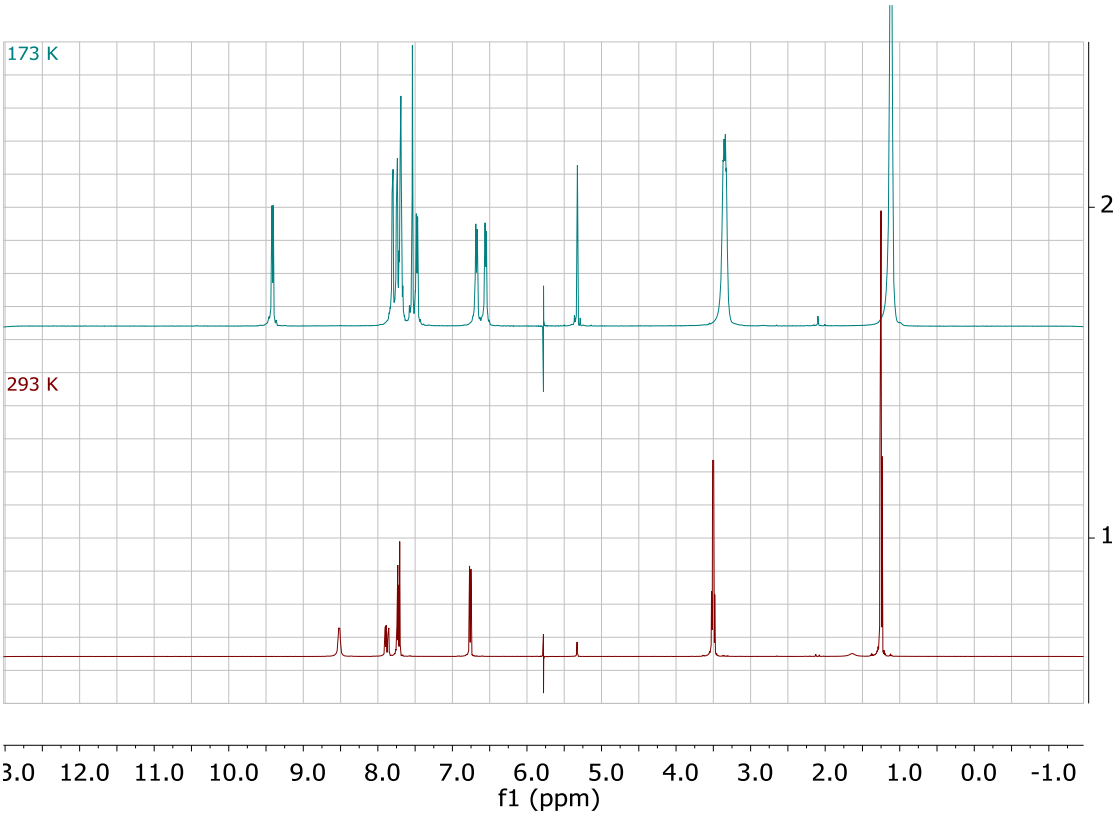

Fig. S2. Variable temperature ^{1}H NMR spectra of **1b** in CD_2Cl_2 at RT (brown) and 173 K (green).

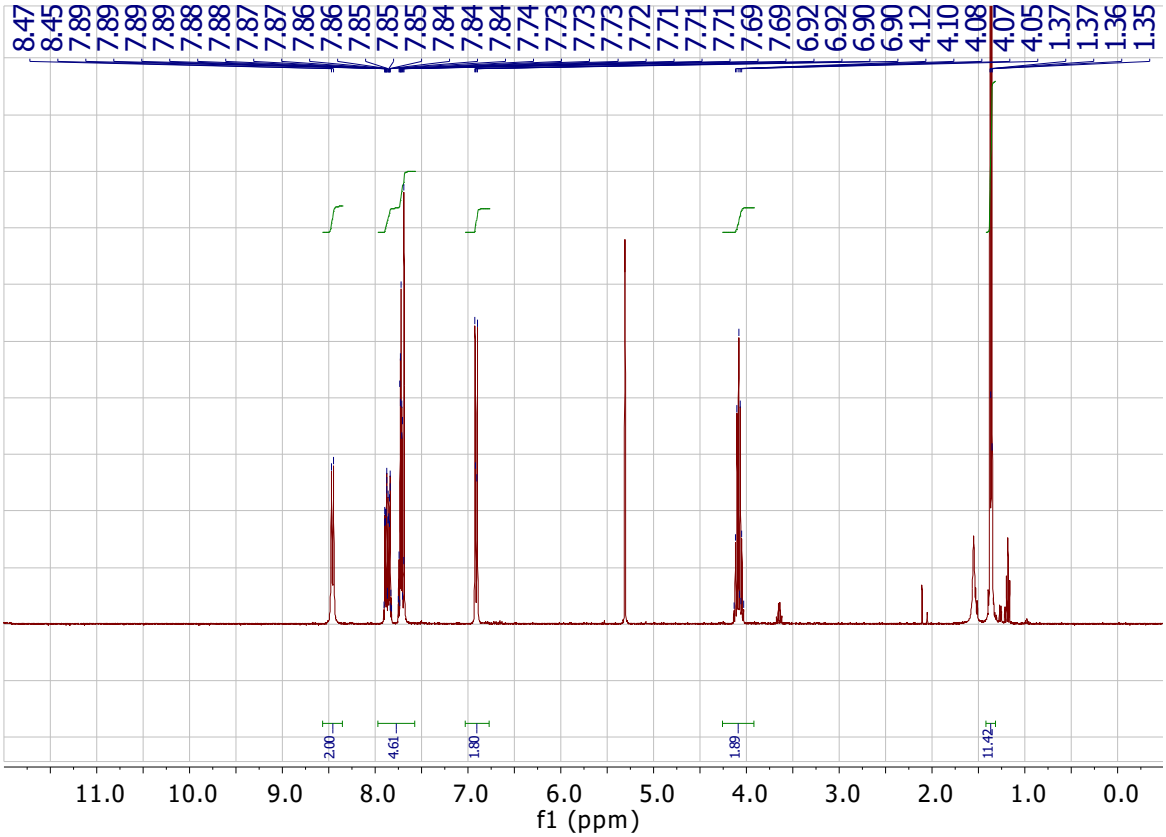

Fig. S3. ^{1}H NMR spectrum of **1c** in CD_2Cl_2.

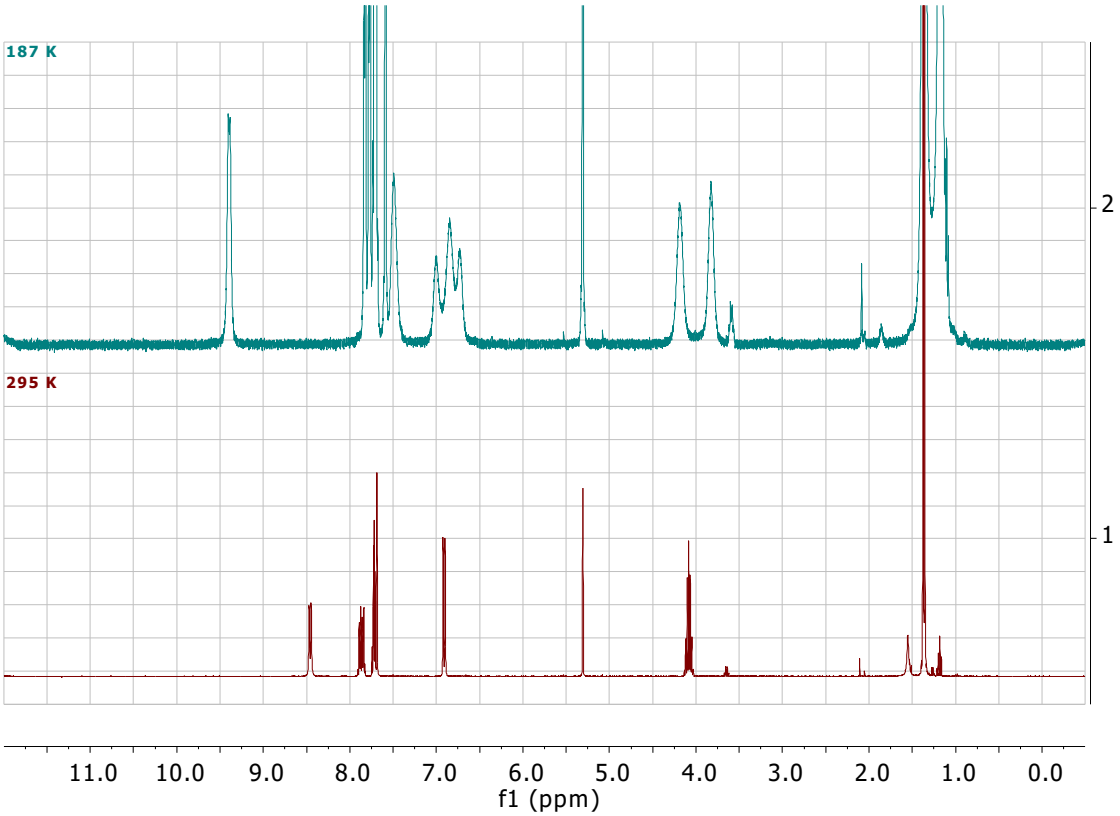

Fig. S4. Variable temperature ^{1}H-NMR spectra of **1c** in CD_2Cl_2 at RT (brown) 233 K (green) and 187 K (blue).

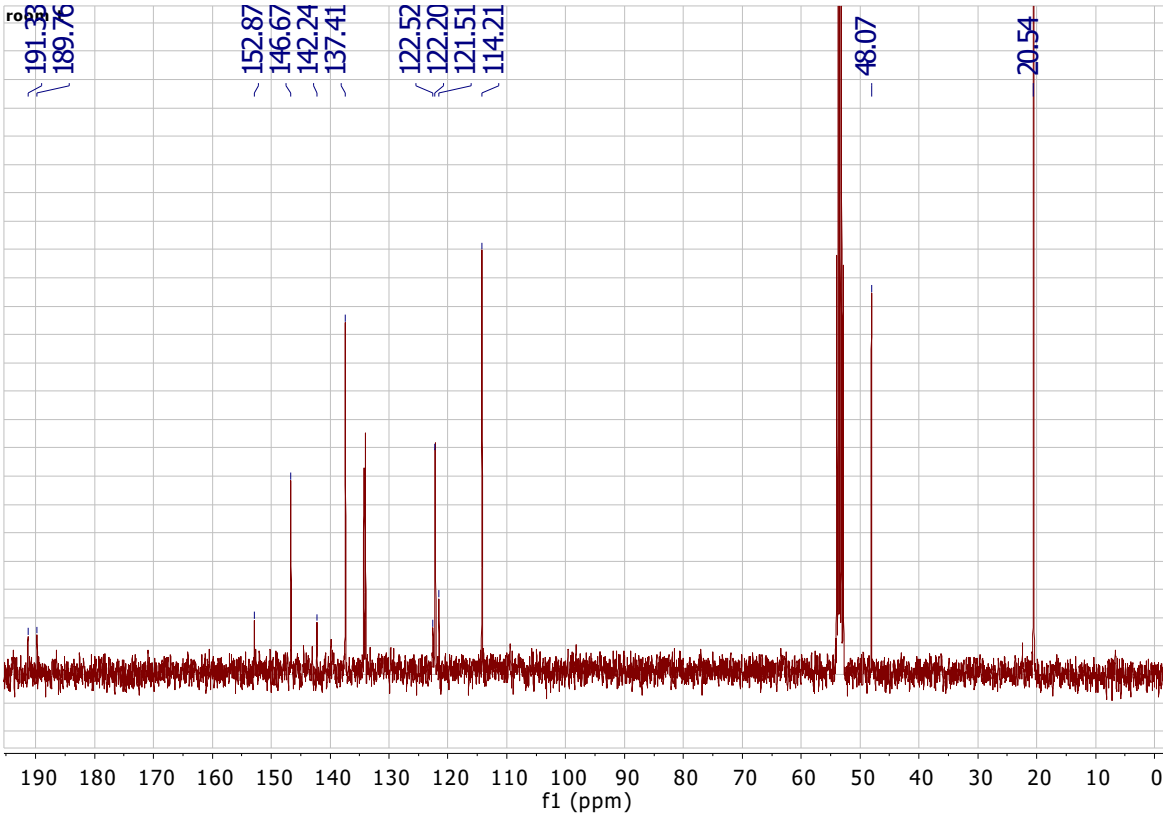

Fig. S5. ^{13}C NMR spectrum of **1c** in CD_2Cl_2.

Fig. S6. ^{1}H NMR spectrum of **2b** in CD_2Cl_2.

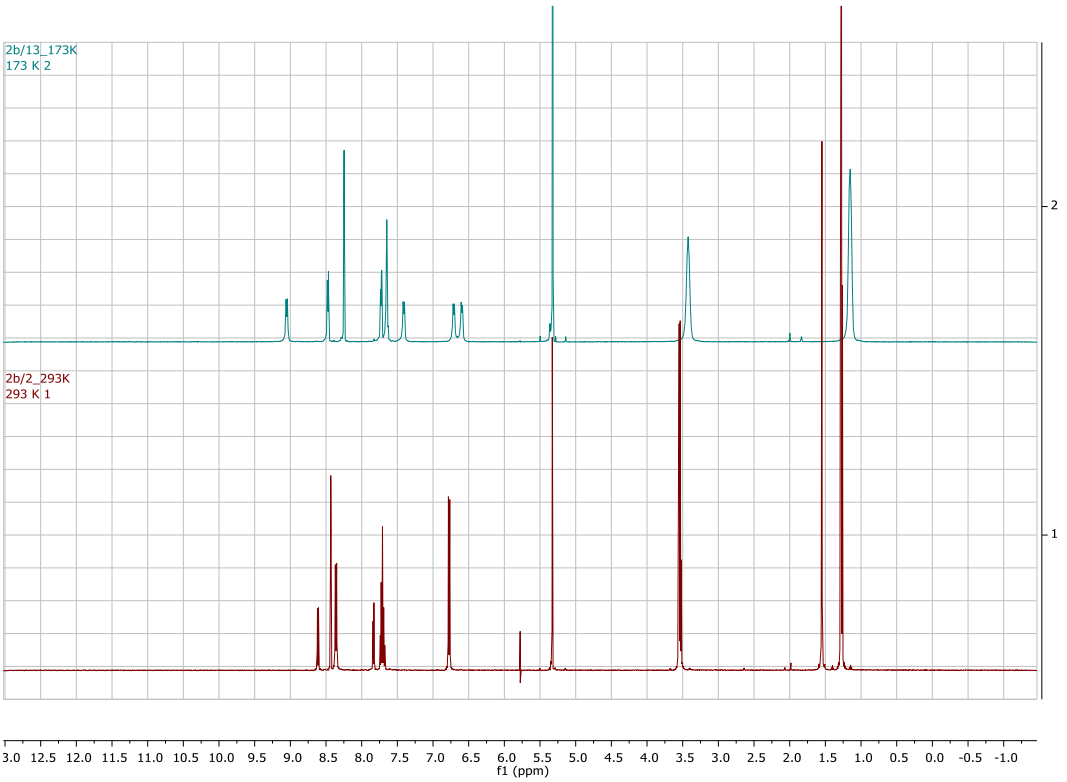

Fig. S7. Variable temperature ^{1}H NMR spectra of **2b** in CD_2Cl_2 at RT (brown) and 173 K (green).

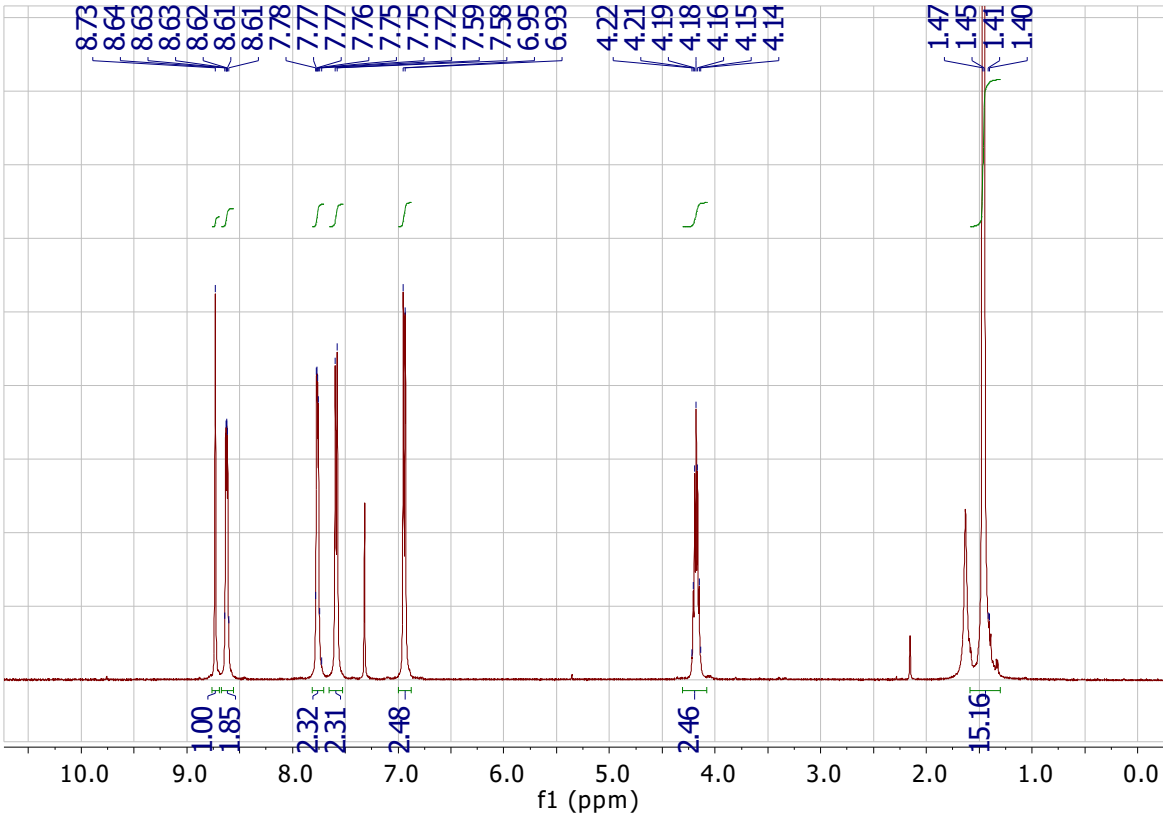

Fig. S8. ^{1}H NMR spectrum of **3c** in CD_2Cl_2.

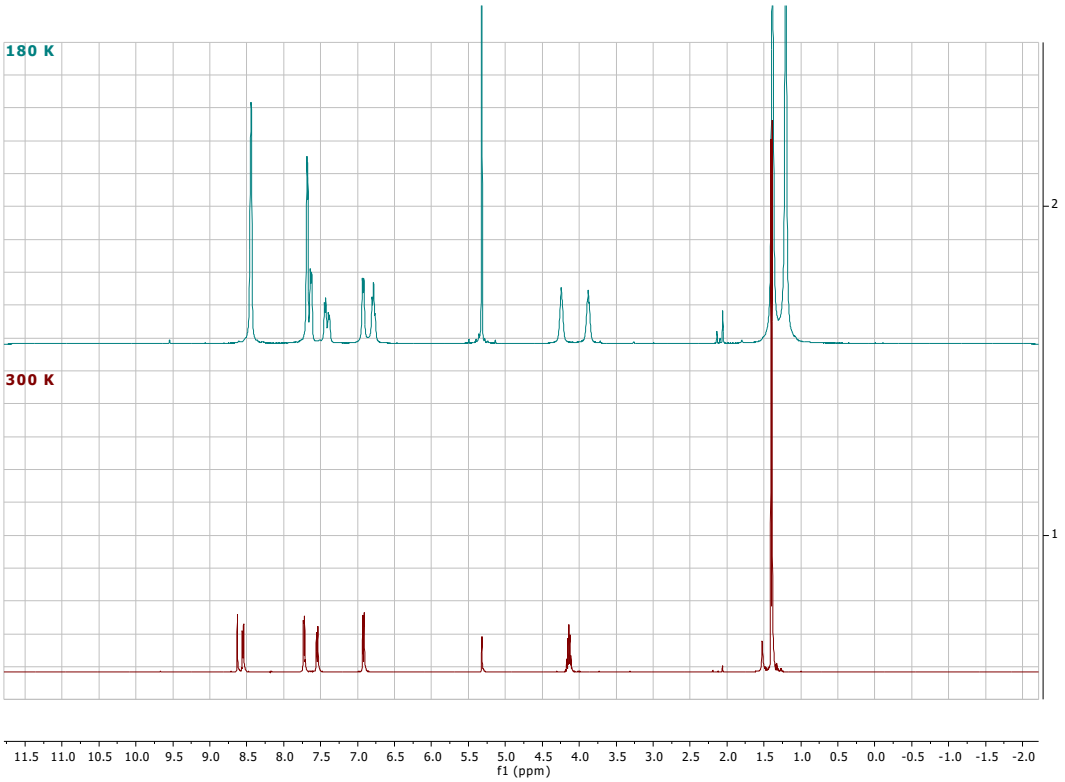

Fig. S9. ^{1}H NMR spectrum of **3c** in CD_2Cl_2 at 300 (brown) and 180 K (green).

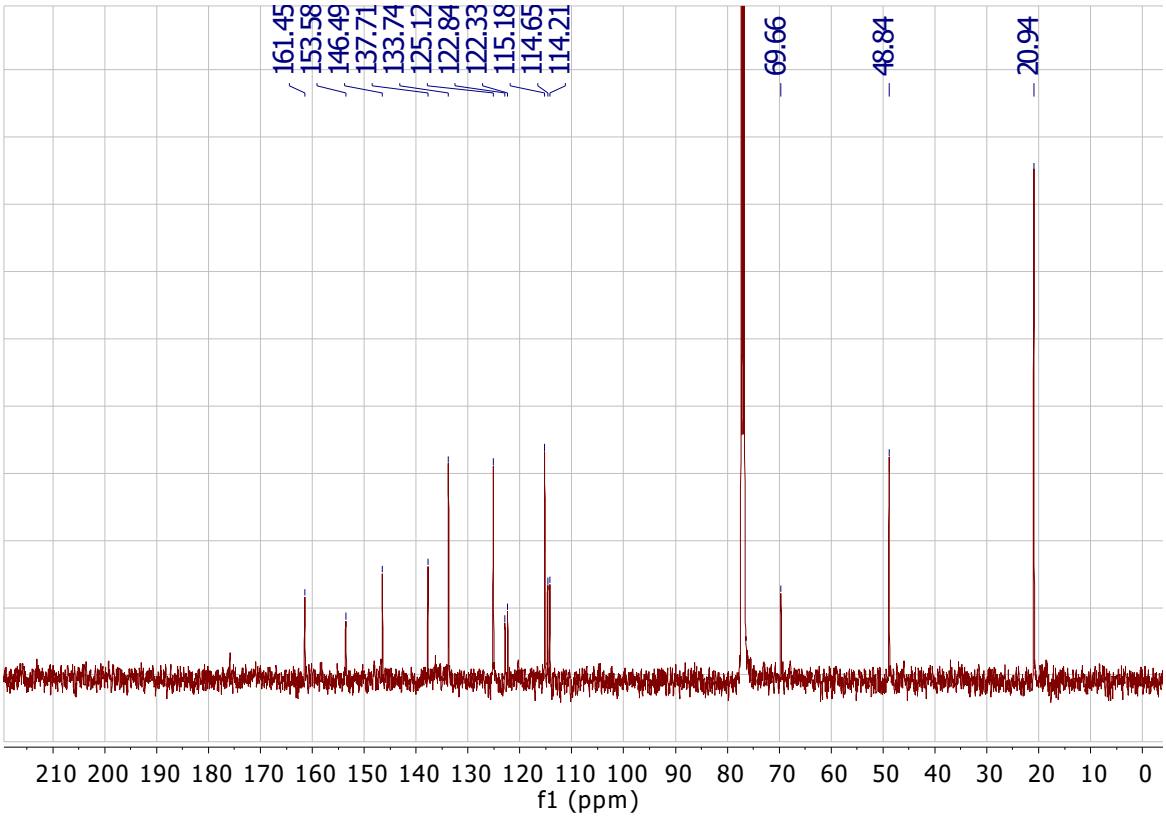

Fig. S10. ^{13}C NMR spectrum of **3c** in $CDCl_3$ at RT.

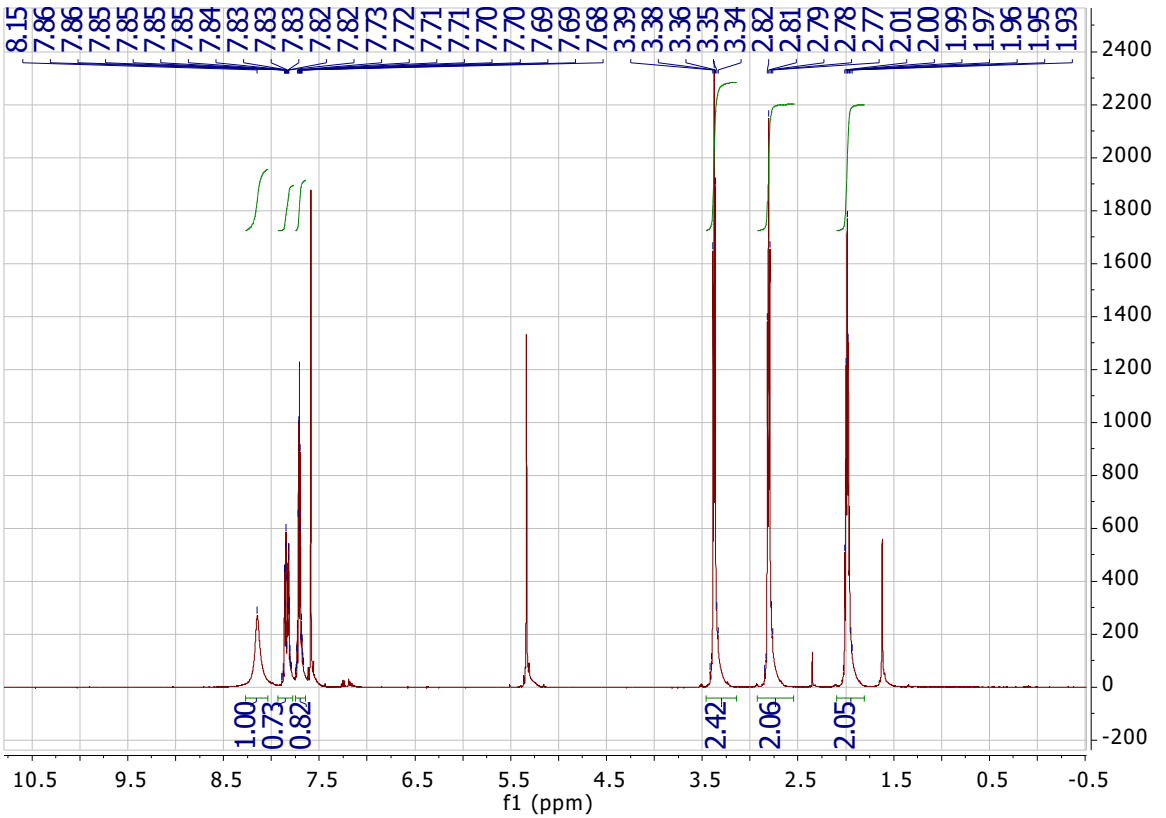

Fig. S11. ^{1}H NMR spectrum of **4** in CD_2Cl_2 at RT.

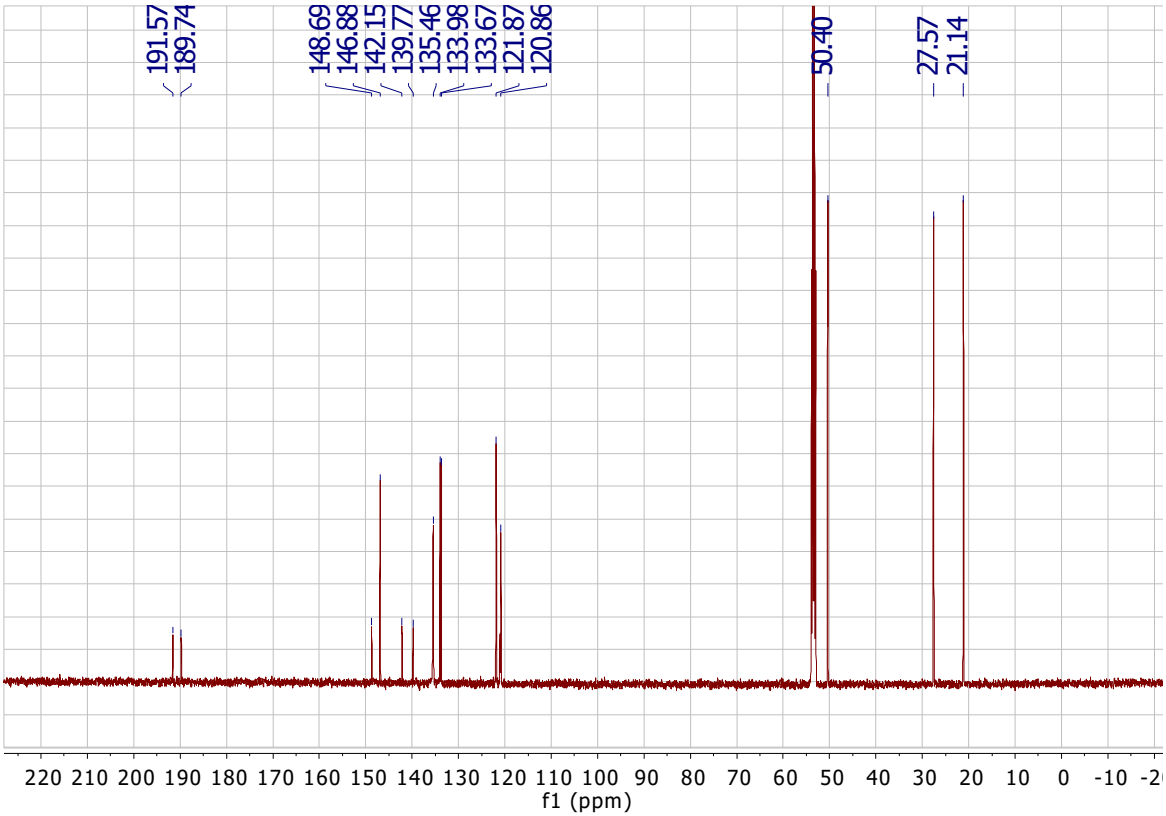

Fig. S12. ^{13}C NMR spectrum of **4** in CD_2Cl_2 at RT.

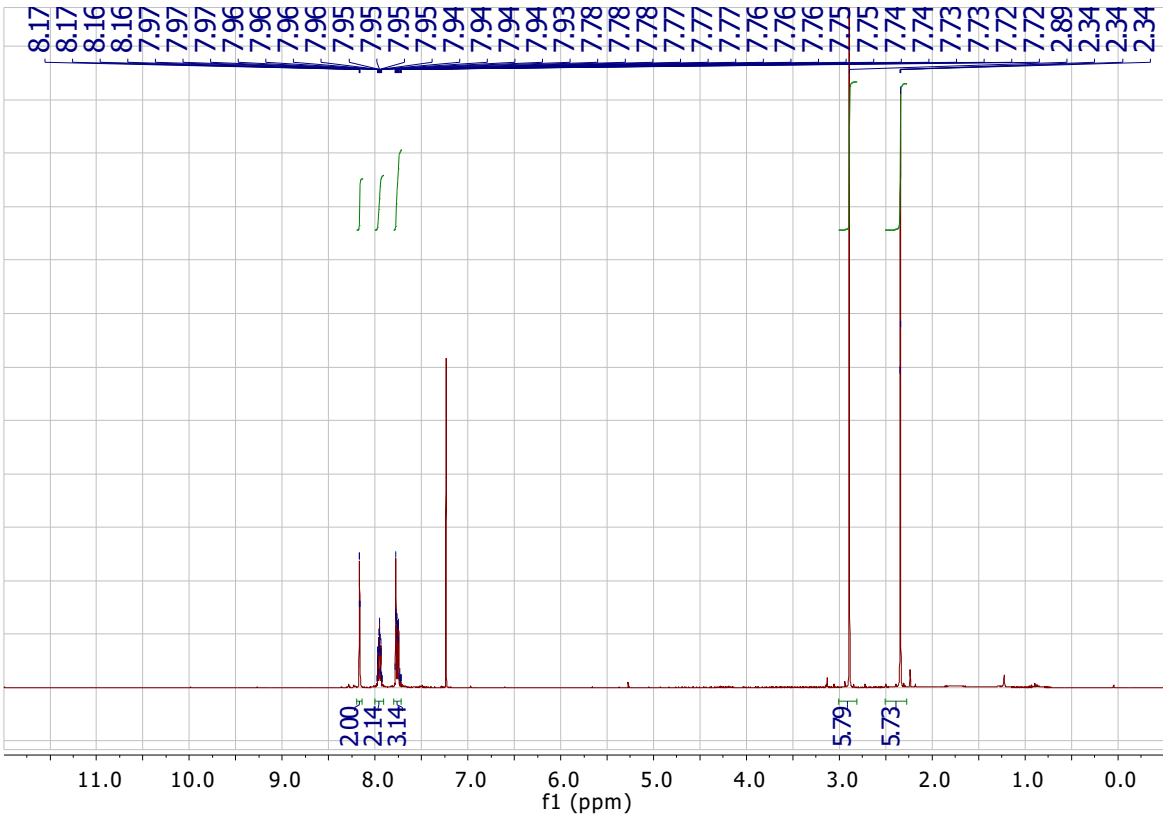

Fig. S13. ^{1}H NMR spectrum of **5** in $CDCl_3$.

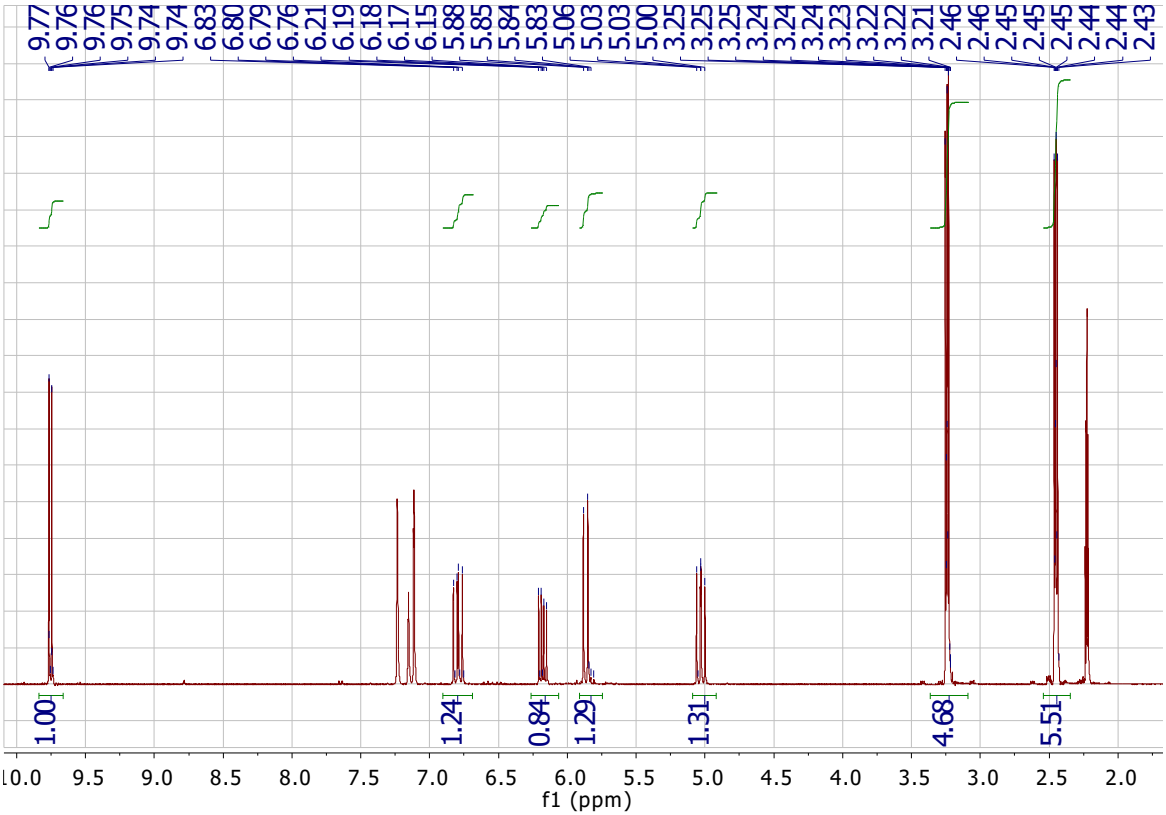

Fig. S14. ^{1}H NMR spectrum of **6b** in toluene$_{d8}$ at RT.

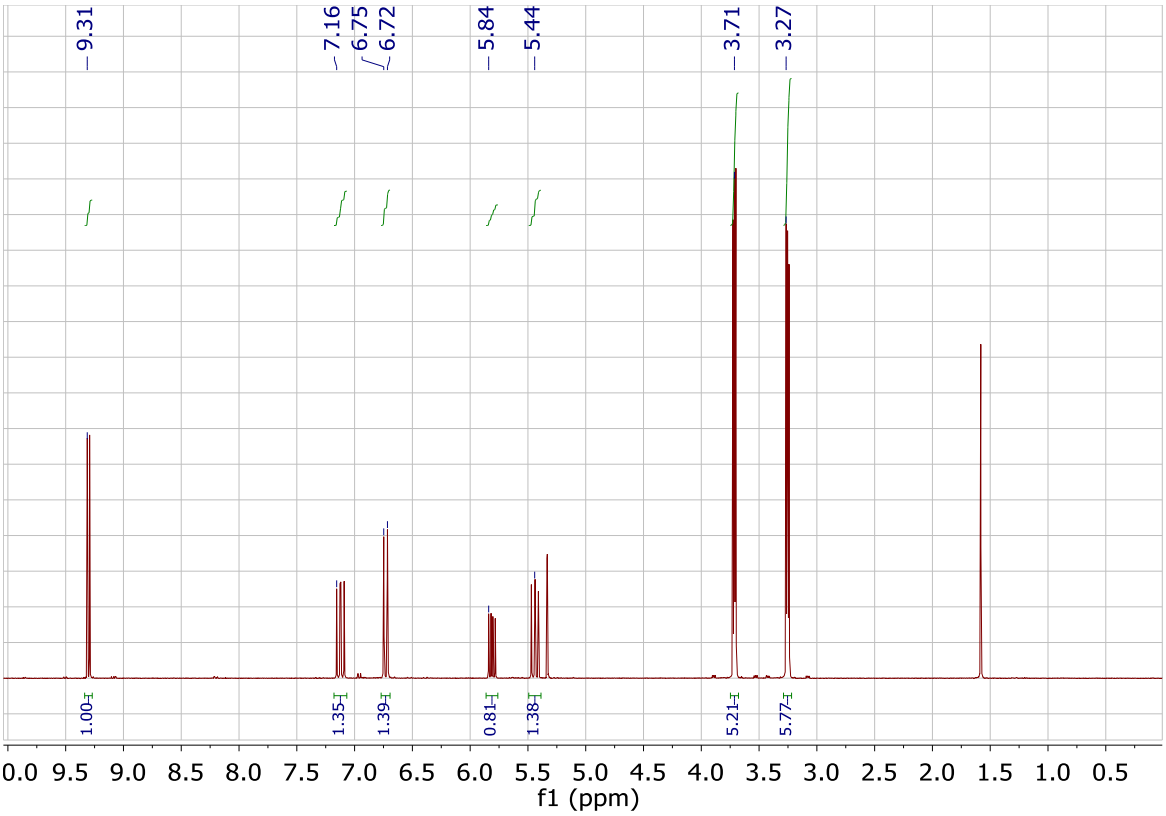

Fig. S15. ^{1}H NMR spectrum of **6b** in CD_2Cl_2 at RT.

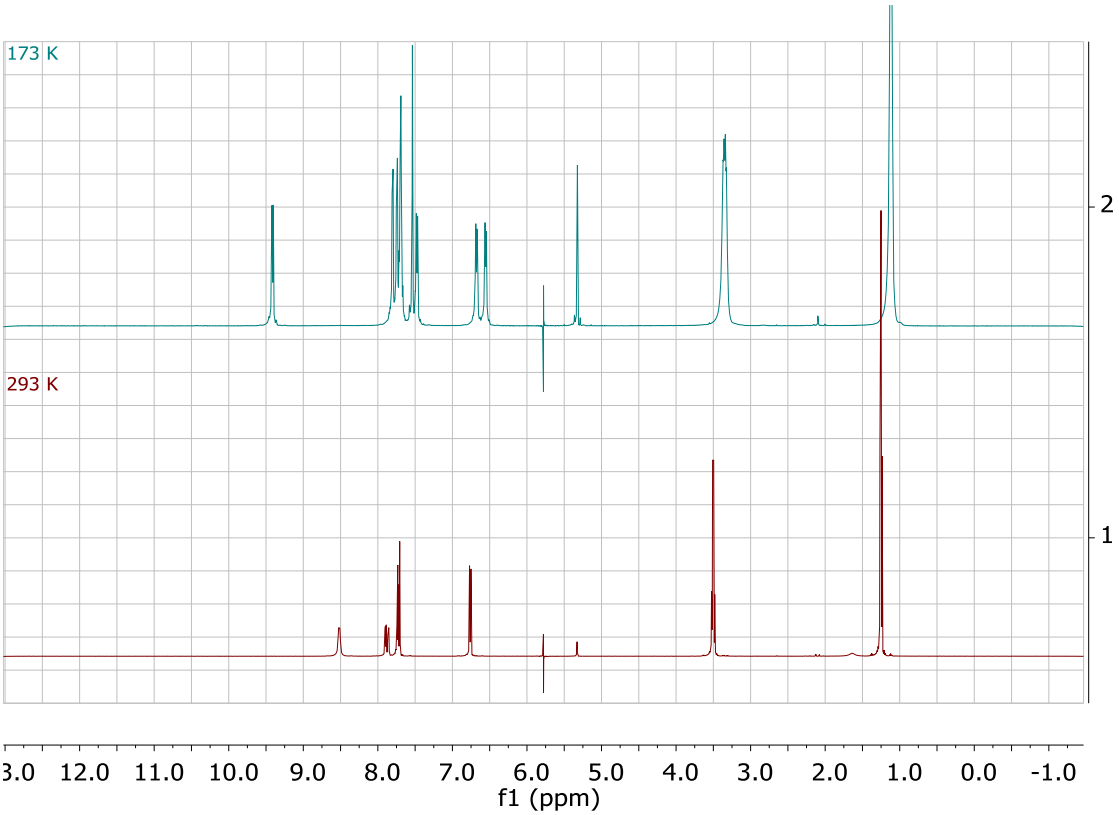

Fig. S16. ^{1}H NMR spectrum of **6b** in CD_2Cl_2 at 295 (brown) and 195 K (green).

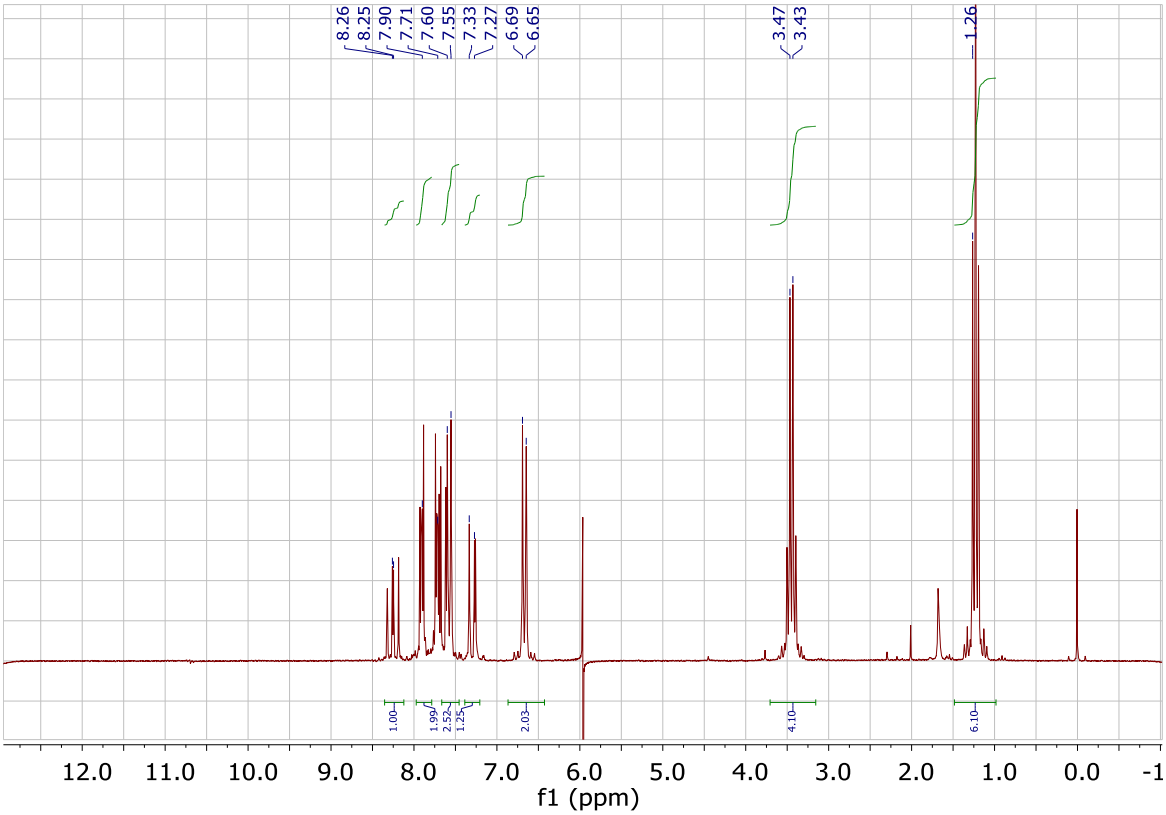

Fig. S17. ^{1}H NMR spectrum of **7b** in $CDCl_3$.

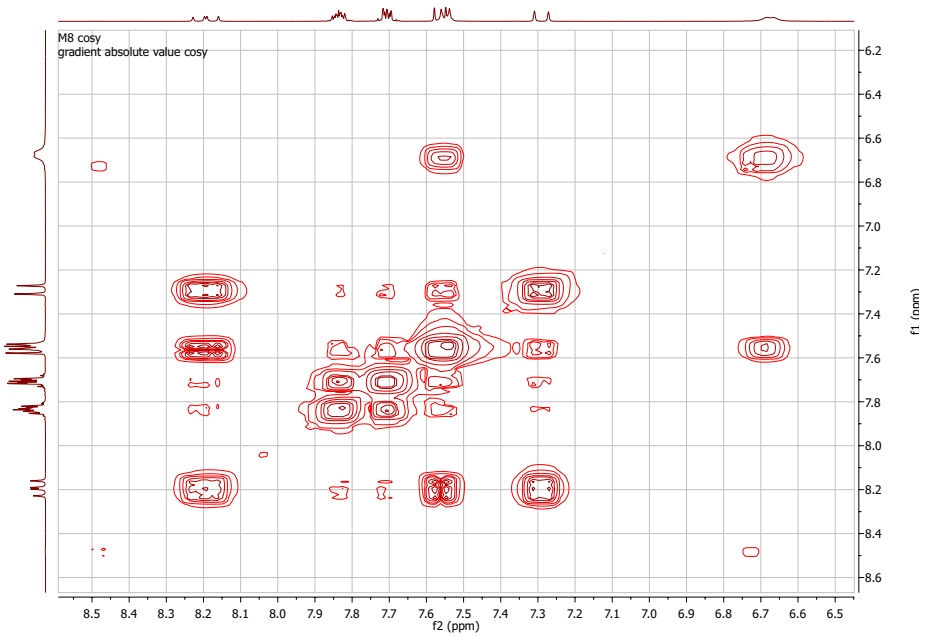

Fig. S18. COSY spectrum of **7b** in CD_2Cl_2 at RT.

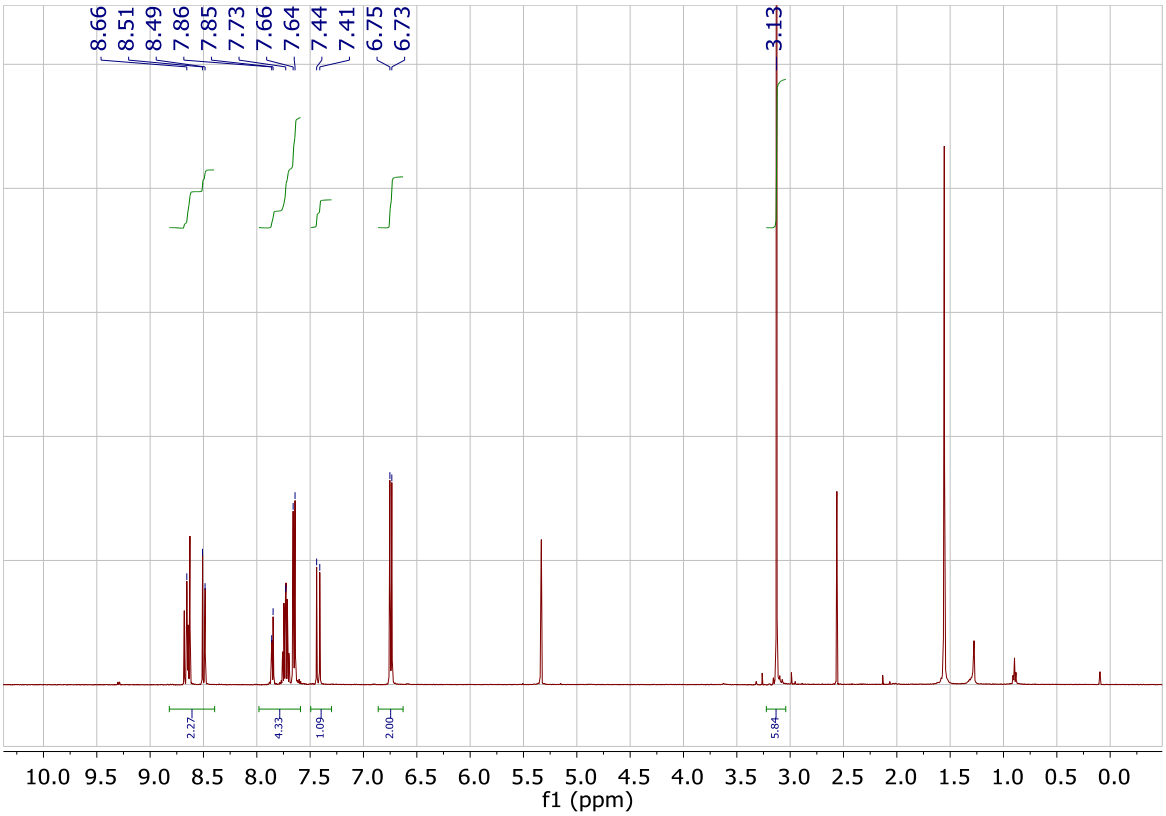

Fig. S19. ^1H NMR spectrum of **8b** in CD_2Cl_2.

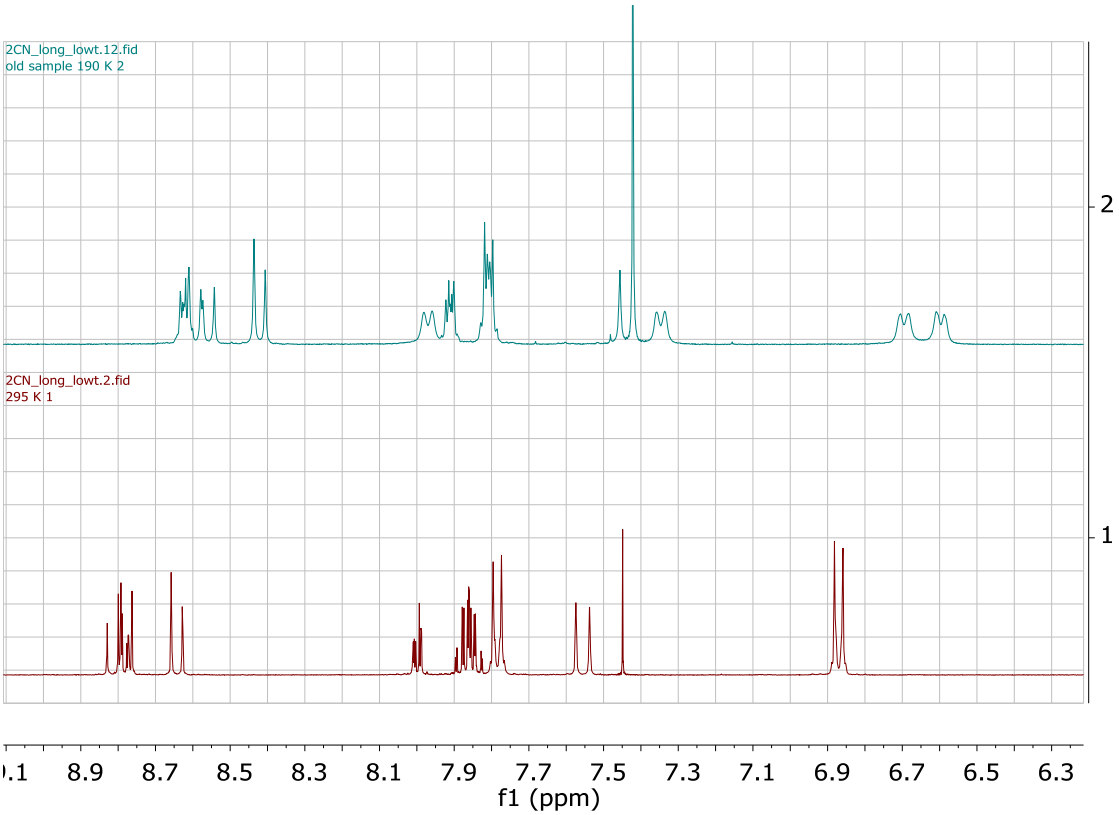

Fig. S20. ^{1}H NMR spectrum of **8b** in CD_2Cl_2 at 295 (brown) and 190 K (green).

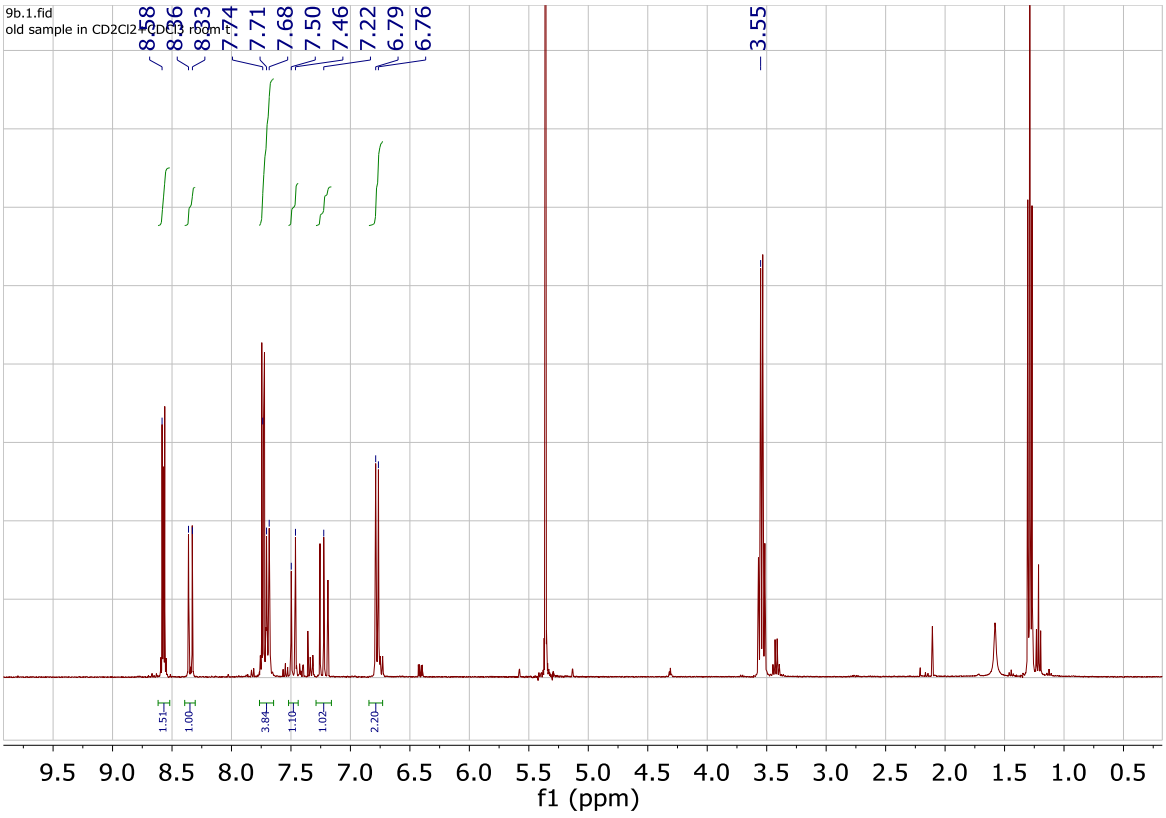

Fig. S21. ^{1}H NMR spectrum of **9b** in CD_2Cl_2.

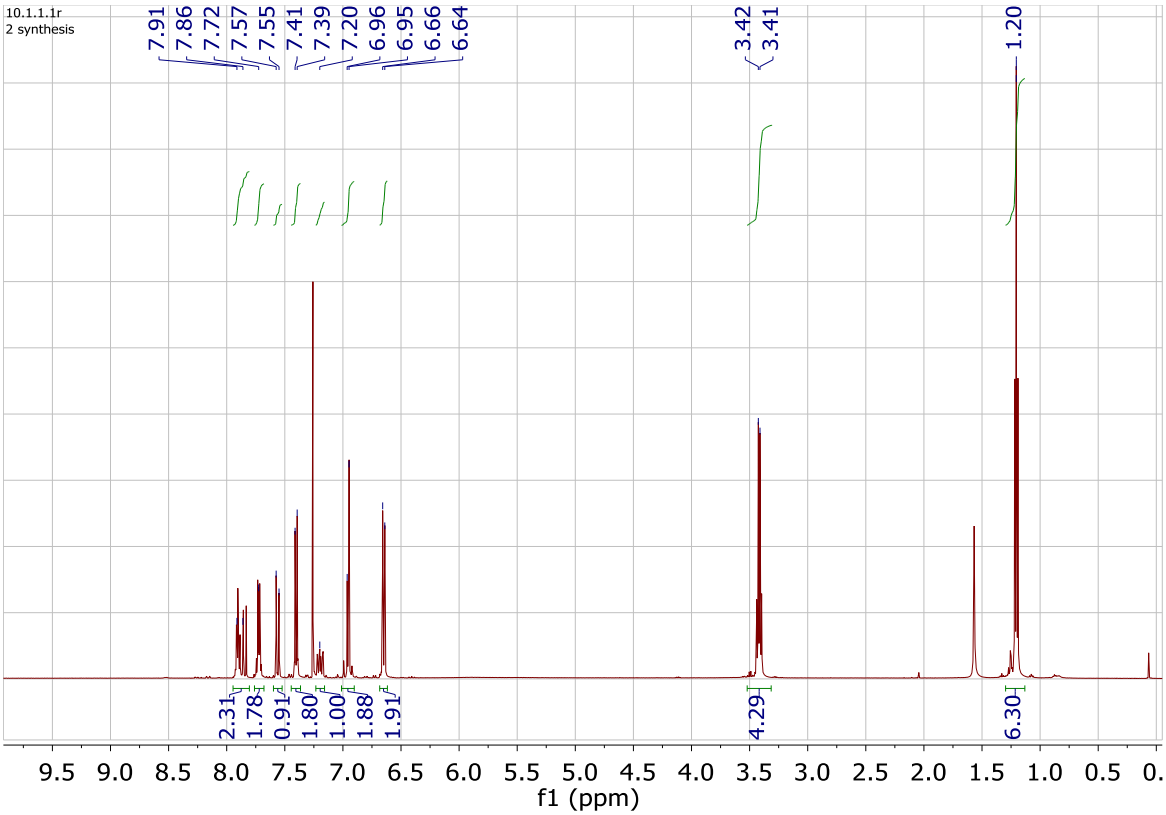

Fig. S22. ^{1}H-NMR spectrum of **10b** in in $CDCl_3$.

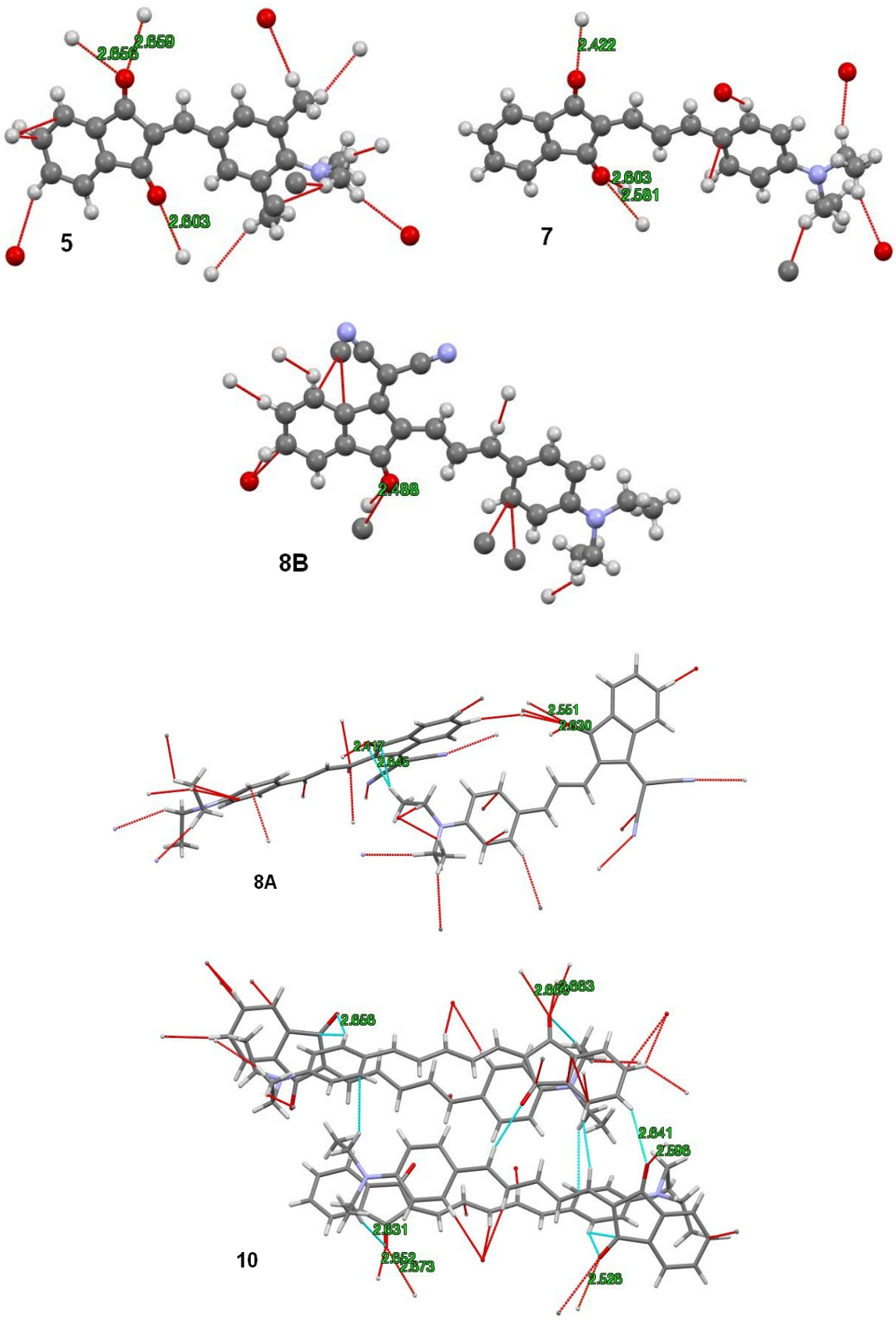

Fig. S23. Short contacts within the X-Ray structures of **5**, **7**, **8** and **10**. Only selected O···HC bond lengths are shown.

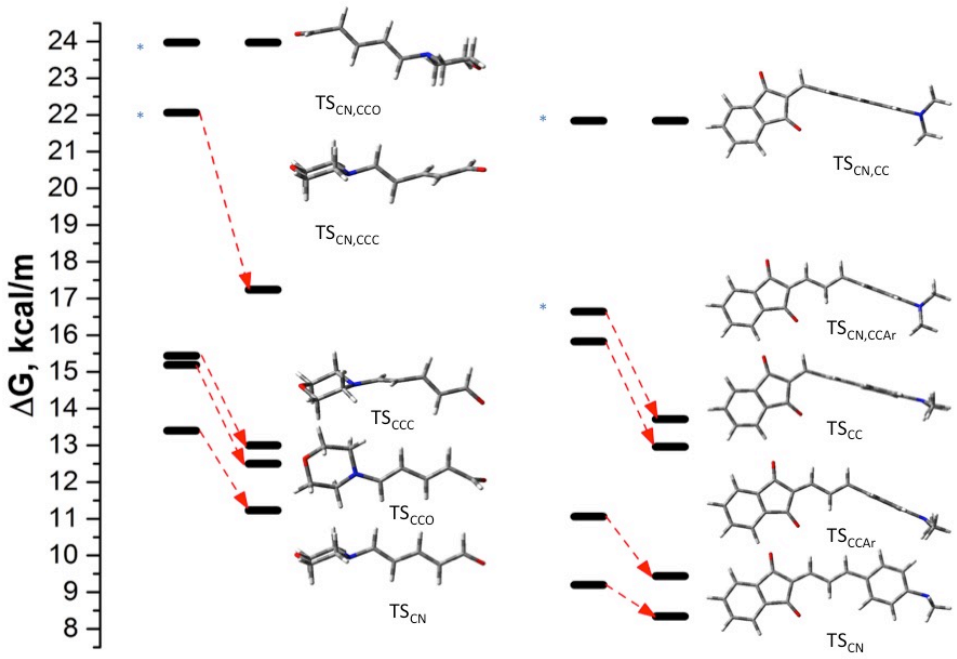

Fig. S24. Corrections of the calculated barriers to rotation for derivatives **6b** and **7a**. Two higher barriers (blue asterisks) are used to correct the lower barriers: $TS_{CN,CCO}$ for $TS_{CN,C-CC}$ and TS_{C-CC}; $TS_{CN,C-CC}$ for TS_{C-CO} and TS_{CN} (**6d**); $TS_{CN,CC}$ for $TS_{CN,CCAr}$ and TS_{CC}; $TS_{CN,CCAr}$ for TS_{CCAr} and TS_{CN} (**7a**).

Table S1. Calculated for derivative **1a** energies (a.u.) in dichloromethane: EE - electronic energies, ZPE - ZPE corrected energies, FE_{RT} - free energies at 298 K, FE_{204} - free energies at 204 K. B_{X-Y} – rotation barrier about X-Y bond (kcal/mol, corrected). Bonds (a), (b) and (c) are also shown in Chart 3.

	GS	TS_{C-C}	TS_{C-N}	$TS_{C-C,C-N}$
	DZ			
EE	-900.26287	-900.24331	-900.24553	-900.23498
ZPE	-899.97729	-899.9597	-899.96112	-899.9521
FE_{RT}	-900.02498	-900.00644	-900.00659	-899.99679
FE_{204K}	-900.00567	-899.98753	-899.98835	-899.97881

B_{C-C}(b): 10.00; B_{C-N}(c): 9.66 (kcal/mol, corrected).

	TZ			
EE	-900.48034	-900.46125	-900.46307	-900.4529
ZPE	-900.19459	-900.17696	-900.17815	-900.16917
FE_{RT}	-900.24266	-900.22369	-900.22384	-900.21381

B_{C-C}(b): 10.23; B_{C-N}(c): 9.89 (kcal/mol, corrected).

Table S2. Calculated (DZ) for derivative **2a** energies (a.u.) in dichloromethane.

	GS	TS_{C-C}	TS_{C-N}	$TS_{C-C,C-N}$
EE	-1,048.8271	-1,048.8082	-1,048.8078	-1,048.7998
ZPE	-1,048.521	-1,048.504	-1,048.5033	-1,048.4961
FE_{RT}	-1,048.5741	-1,048.5574	-1,048.5551	-1,048.5467

B_{C-C}(b): 9.13; B_{C-N}(c): 9.89 (kcal/mol, corrected).

Table S3. Calculated (DZ) for derivative **3a** energies (a.u.) in dichloromethane.

	GS	TS_{C-C}	TS_{C-N}	$TS_{C-C,C-N}$
EE	-1,197.387	-1,197.3659	-1,197.3681	-1,197.3548
ZPE	-1,197.0609	-1,197.0409	-1,197.0433	-1,197.0303
FE_{RT}	-1,197.1185	-1,197.0977	-1,197.0992	-1,197.0852

B_{C-C}(b): 11.74; B_{C-N}(c): 10.51 (kcal/mol, corrected).

Table S4. Calculated (DZ) for derivative **4** energies (a.u.) in dichloromethane.

	GS	TS_{C-C}	GS_{anh}	$TS_{C-C,\ anh}$
EE	-1055.138	-1055.1176	-1055.136	-1055.1165
ZPE	-1054.78	-1054.7616	-1054.7766	-1054.7596
FE_{248}	-1054.8177	-1054.7987	-1054.8116	-1054.7957

B_{C-C}: 11.92; B_{C-CAnh}: 9.98 kcal/mol

Table S5. Calculated (DZ) for derivative **5** energies (a.u.) in dichloromethane.

	GS	TS_{C-C}	TS_{C-N}	$TS_{C-C,C-N}$
EE	-978.8849	-978.8708	-978.8804	-978.8697
ZPE	-978.5450	-978.5330	-978.5417	-978.5325
FE_{RT}	-978.5949	-978.5826	-978.5915	-978.5813

B_{C-C}(b): 6.77; B_{C-N}(c): 2.08 (kcal/mol, corrected).

Table S6. Calculated (TZ) for derivative **6d** energies (a.u.) in dichloromethane.

	GS	TS_{C-CO}	TS_{C-N}	TS_{C-C}	$TS_{C-C,C-N}$	$TS_{C-CO,C-N}$
EE	-556.1613	-556.1358	-556.1393	-556.1356	-556.1249	-556.1215
ZPE	-555.9506	-555.9266	-555.9299	-555.9263	-555.9164	-555.9133
FE_{225K}	-555.9773	-555.9531	-555.956	-555.9527	-555.9422	-555.9391

B_{C-C}: 13.00; B_{C-CO}: 13.01; B_{C-N}: 11.37(kcal/mol, corrected).

Table S7. Calculated (DZ) for derivative **7a** energies (a.u.) in dichloromethane.

	GS	TS_{C-C}	TS_{C-N}	TS_{C-CAr}	$TS_{C-CAr,C-N}$	$TS_{C-C,C-N}$
EE	-977.6829	-977.6551	-977.6674	-977.6637	-977.6552	-977.6456
ZPE	-977.3639	-977.3383	-977.3498	-977.3462	-977.3386	-977.3297
FE_{215K}	-977.3958	-977.3706	-977.3811	-977.3782	-977.3693	-977.3610

B_{C-C}(b): 12.96; B_{C-CAr}: 9.44; B_{C-N}(c): 8.34 (kcal/mol, corrected).

Table S8. Calculated (DZ) for derivative **8a** energies (a.u.) in dichloromethane.

	GS	TS_{C-C}	TS_{C-N}	TS_{C-CAr}	$TS_{C-CAr,C-N}$
EE	-1,126.2514	-1,126.2202	-1,126.2341	-1,126.2294	-1,126.2208
ZPE	-1,125.9114	-1,125.8827	-1,125.8954	-1,125.8911	-1,125.8833
FE_{225K}	-1,125.9489	-1,125.9207	-1,125.9323	-1,125.929	-1,125.9194

B_{C-C}(b): 10.57; B_{C-CAr}: 9.44 10.35; B_{C-N}(c): 8.34 9.14 (kcal/mol, corrected).

Table S9. Calculated (DZ) for derivative **9a** energies (a.u.) in dichloromethane.

	GS	$TS_{C-C(a)}$	$TS_{C-C(b)}$	TS_{C-CAr}	$TS_{C-N(c)}$	$TS_{C-C,C-N}$
EE	-1,274.8114	-1,274.7926	-1,274.7788	-1,274.7888	-1,274.793	-1,274.78
ZPE	-1,274.4512	-1,274.4328	-1,274.4207	-1,274.4303	-1,274.4342	-1,274.4222
FE_{242K}	-1,274.4962	-1,274.4777	-1,274.4665	-1,274.4748	-1,274.4782	-1,274.4654

B_{C-C}(a): 9.93; B_{C-C}(b): 14.75; B_{C-CAr}: 9.44 11.33; B_{C-N}(c): 8.34 10.09 (kcal/mol, corrected).

Table S10. Calculated dipole moments μ (D) and zero-frequency hyperpolarizabilities $\beta_{0*}10^{30}$ (esu) for six unique rotamers of eight of derivative **1a** in dichloromethane.

	GS	TSA1	TSA2	TSD1	TSD2	TSDA
	DZ (CH_2Cl_2)					
μ (D)	8.0514	2.9789	2.4390	0.6585	2.170	2.9864
$\beta_{0*}10^{30}$ (esu)	135.99	5.53	8.87	32.26	32.64	8.79
	TZ (CH_2Cl_2)					
	7.9862	2.9367	2.4144	0.6668	2.1416	2.9378
	131.69	5.236	8.874	31.51	31.169	8.52
	DZ (CH_2Cl_2)					
	7.5878	2.9221	2.4299	0.6940	2.0778	2.8464
	116.34	4.664	7.991	29.28	28.98	7.442

Averaging:
(2*TSA1+TSA2+TSD1+TSD2+2*TSDA)/8

Table S11. Calculated (TZ) dipole moments μ (D) for ten unique rotamers of ten of derivative **6a** in benzene and chloroform.

	GS	TS1a	TS1b	TS1c	TS2a	TS2b	TS2c	TS3a	TS3b	TS3c
	Benzene									
μ (D)	11.371	6.588	9.654	6.80	6.558	10.457	5.335	6.31	11.371	5.281
	Chloroform									
μ (D)	12.828	7.130	10.908	7.348	6.975	11.748	5.659	6.84	12.82	4.721

Averaging:
(TS1a+TS1b+TS1c+TS2a+TS2b+TS2c+TS3a+TS3b+TS3c)/10

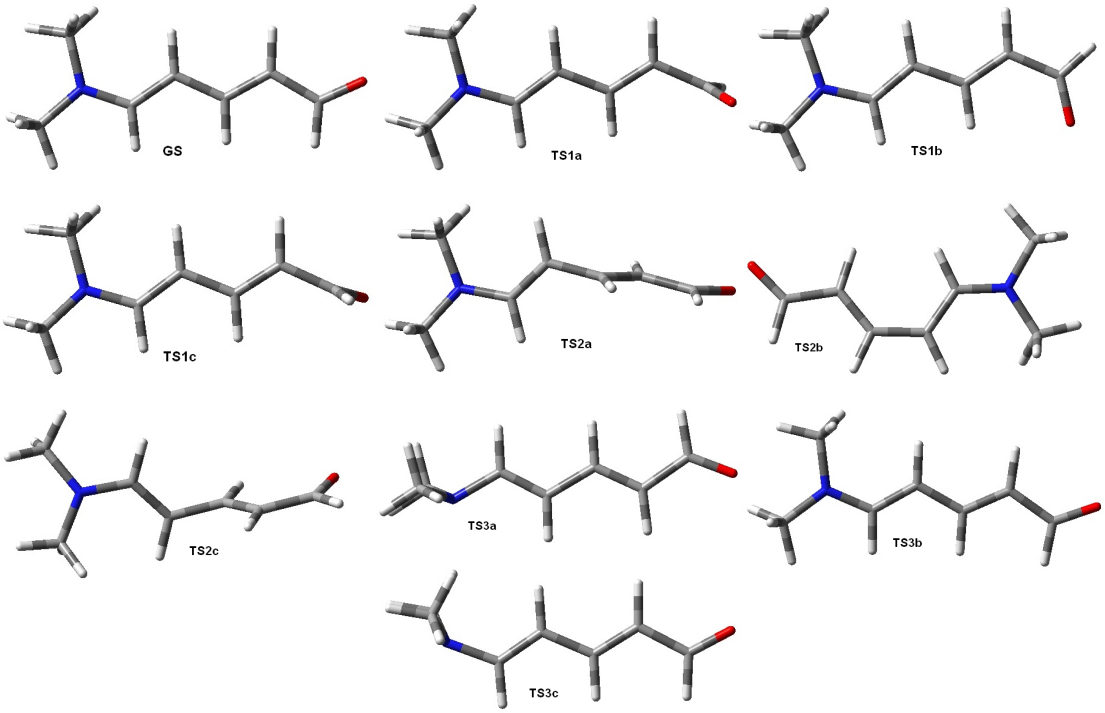

Fig. S25. Ten unique rotamers of ten of **6a** present in benzene solution at RT.

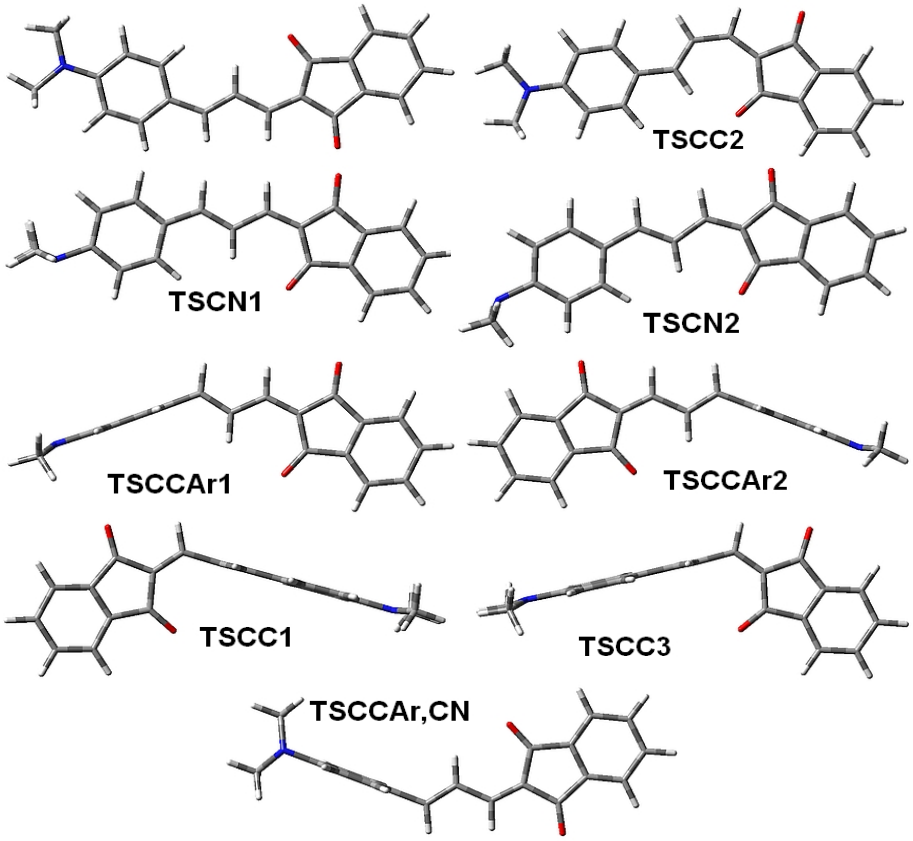

Fig. S26. Nine unique rotamers of 18 of **6a** present in dichloromethane and chloroform solutions at RT.

Table S12. Calculated (DZ) dipole moments μ (D) and zero-frequency hyperpolarizabilities $\beta_{0*}10^{30}$ (esu) for nine unique rotamers of 18 of derivative **7a** in dichloromethane and chloroform.

Dichloromethane:

	GS	TS_{CC2}	TS_{CN1}	TS_{CN2}	TS_{CCAr1}	TS_{CCAr2}	TS_{CC1}	TS_{CC2}	$TS_{CCAr,CN}$
μ (D)	11.258	11.471	2.947	3.136	3.631	3.329	3.329	3.631	1.482
$\beta_{0*}10^{30}$	345.9	316.62	105.06	104.5	24.67	25.43	25.43	24.67	11.47

Chloroform:

	GS	TS_{CC2}	TS_{CN1}	TS_{CN2}	TS_{CCAr1}	TS_{CCAr2}	TS_{CC1}	TS_{CC2}	$TS_{CCAr,CN}$
μ (D)	10.509	10.733	2.836	3.031	3.521	3.380	3.556	3.268	1.432
$\beta_{0*}10^{30}$	292.09	266.57	92.01	91.60	19.14	19.08	22.18	22.86	11.01

Averaging:

$(3*GS+TS_{CC2}+2*TS_{CN1}+2*TS_{CN2}+4*TS_{CCAr,CN}+2*TS_{CCAr1}+2*TS_{CCAr2}+TS_{CC1}+TS_{CC2})/18$