Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for

Push-pull flexibly-bridged bis(haloBODIPYs): Solvent and spacer switchable red emission

César Ray,[a] Jorge Bañuelos,[b]* Teresa Arbeloa,[b] Beatriz L. Maroto,[a] Florencio Moreno,[a] Antonia R. Agarrabeitia,[a] María J. Ortiz,[a] Iñigo López-Arbeloa[b] and Santiago de la Moya[a]*

a. Departamento de Química Orgánica I, Facultad de CC. Químicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040, Madrid, Spain. E-mail: santmoya@ucm.es.

b. Departamento de Química Física, Universidad del País Vasco-EHU, Apartado 644, 48080, Bilbao, Spain. E-mail: Jorge.banuelos@ehu.es.

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1. Tables

Table S1. Photophysical properties of flexible bis(BODIPYs) **1-3** in different solvents (2 μM). See Experimental Section in article for details.

Bis(BODIPY)	Solvent	λ_{ab}[a] (nm)	ε[b] (10^4 $M^{-1}cm^{-1}$)	λ_{fl}[c] (nm)	$\Delta\nu_{St}$[d] (cm^{-1})	ϕ_{fl}[e]	τ[f] (ns)
1	Cyclohexane	529.0	12.4	544.0	520	0.170	1.15 (97%) - 4.70 (3%)
	$CHCl_3$	525.5	8.3	544.5	665	0.140	0.23 (32%) -1,15 (86%)
	Acetone	508.5 469.5	5.5 5.8	537.5	1060	0.005	-
	Methanol	511.0 469.5	5.4 5.5	535.5	895	<0.001	-
2	Ciclohexane	516.0	12.2	523.5	280	0.300	0.75 (63%) - 1.75 (37%)
	$CHCl_3$	515.5	9.5	524.5	330	0.160	0.15 (56%) - 1.14 (44%)
	Acetone	508.0	7.1	520.0	455	0.005	-
	Methanol	508.5	7.1	519.0	400	0.005	-
3	Cyclohexane	518.0	11.0	550.0	1125	0.030	0.06 (96%) - 0.35 (4%)
	$CHCl_3$	516.0	9.9	535.0	690	0.003	-
	Acetone	508.0	7.6	528.5	765	0.001	-
	Methanol	509.0	7.3	526.5	655	0.002	-

[a]Maximum absorption wavelength. [b]Molar absorption. [c]Maximun fluorescence wavelength. [d]Stokes shift. [e]Fluorescence quantum yield. [f] Lifetime (probability into parenthesis).

Table S2. Photophysical properties of flexible bis(BODIPYs) **4-7** in different solvents (2 μM). See Experimental Section in article for details.

Bis(BODIPY)	Solvent	λ_{ab}[a] (nm)	ε[b] (10^4 $M^{-1}cm^{-1}$)	λ_{fl}[c] (nm)	$\Delta\nu_{St}$[d] (cm^{-1})	ϕ_{fl}[e]	τ[f] (ns)
4	Cyclohexane	521.5	10.4	570.0	1650	0.370[g]	0.09 (32%) - 1.82 (68%)
	$CHCl_3$	521.0	9.6	573.5	1760	0.200[g]	0.08 (51%)-0.64 (7%)-4.19 (42%)
	Acetone	515.0	9.5	527.0	445	0.003	-
	Methanol	517.0	8.4	526.0	330	0.005	-
5	Cyclohexane	521.5	12.0	527.5	220	0.530	0.36 (19%) - 4.48 (81%)
	$CHCl_3$	521.5	10.1	562.5	1400	0.210[g]	0.26 (54%) - 3.62 (46%)
	Acetone	516.0	9.1	526.0	370	0.010	0.07 (78%) - 0.20 (22%)
	Methanol	516.0	8.9	524.5	315	0.010	0.09 (94%) - 0.27 (6%)
6	Cyclohexane	550.0	9.1	600.0	1515	0.540[g]	1.16 (12%) - 4.01 (88%)
	$CHCl_3$	549.5	9.2	609.0	1780	0.060[g]	0.05 (48%) - 0.87 (52%)
	Acetone	543.0	7.1	554.0	365	0.020	0.35 (82%) - 0.55 (18%)
	Methanol	538.0	7.9	550	405	0.130	0.39 (85%) - 0.59 (15%)
7	Cyclohexane	546.5	4.0	595.5	1505	0.380	0.92 (9%) - 3.12 (91%)
	$CHCl_3$	543.0	3.6	596.0	1640	0.150	0.05 (40%)-0.81 (59%)-2.81 (1%)
	Acetone	~520	3.2	-	-	<0.001	-
	Methanol	~520	3.2	-	-	<0.001	-

[a]Maximum absorption wavelength. [b]Molar absorption. [c]Maximun fluorescence wavelength. [d]Stokes shift. [e]Fluorescence quantum yield. [f] Lifetime (probability into parenthesis). [g]This data should be taken into account with care, since dual emission is recorded; the ICT emission as the main band, but with a shoulder from the LE emission.

2. Figures

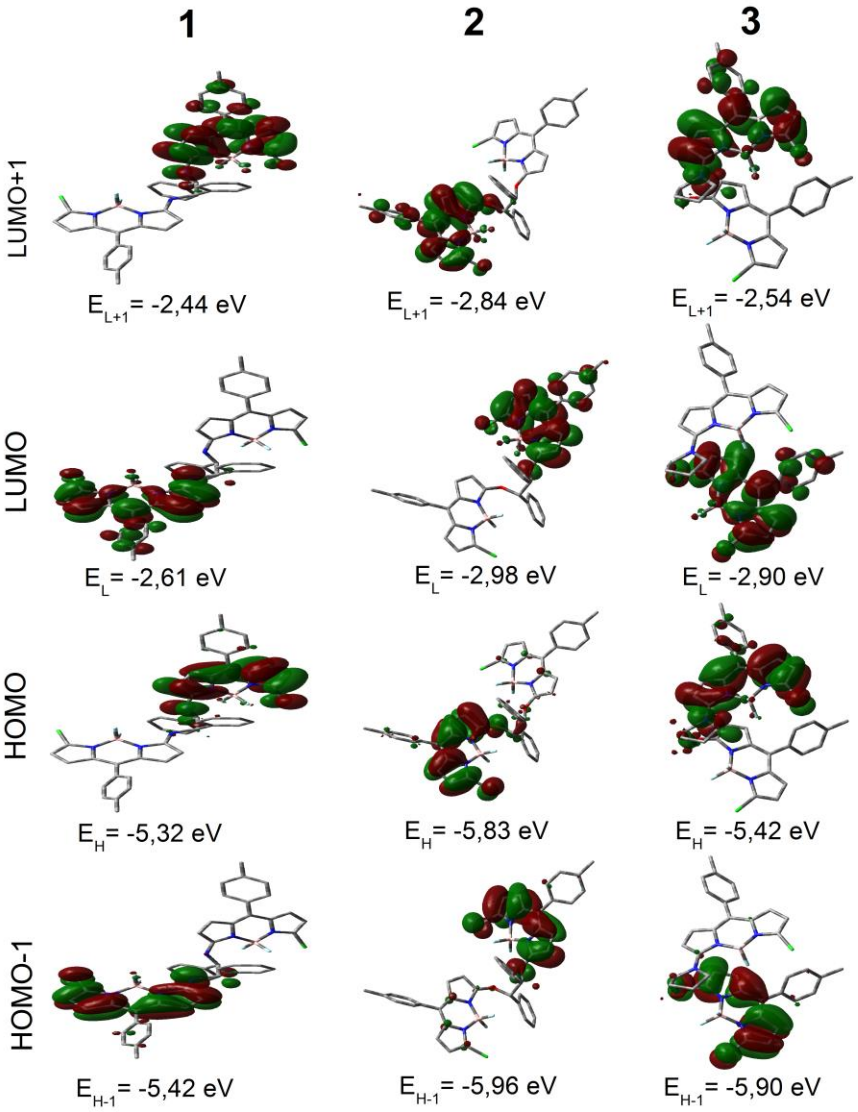


Fig. S1. Key molecular orbitals and energies computed for bis(BODIPYs) **1**-**3** (see Experimental Section in the article).

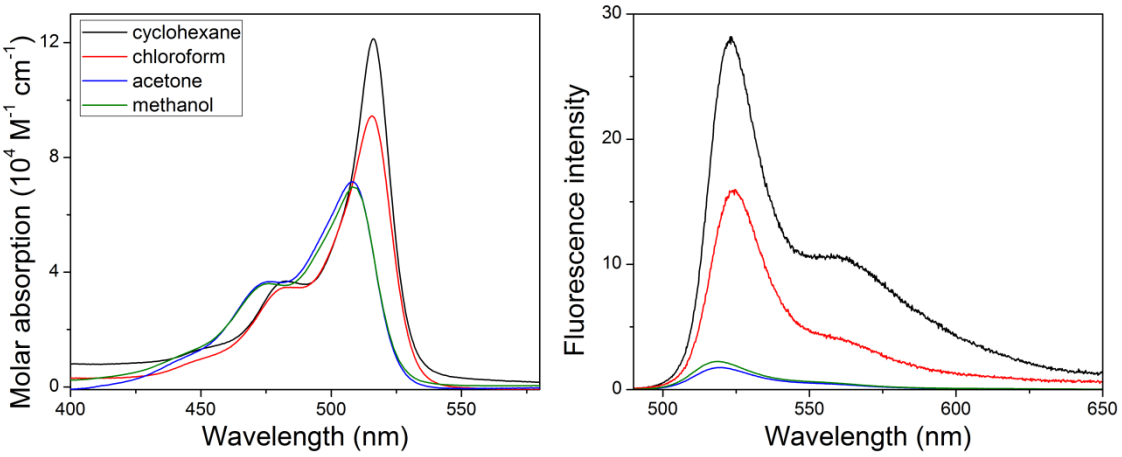


Fig. S2. Absorption (left) and fluorescence (right) spectra of **2** in solvents of different polarity (diluted solutions; see Experimental Section in the article).

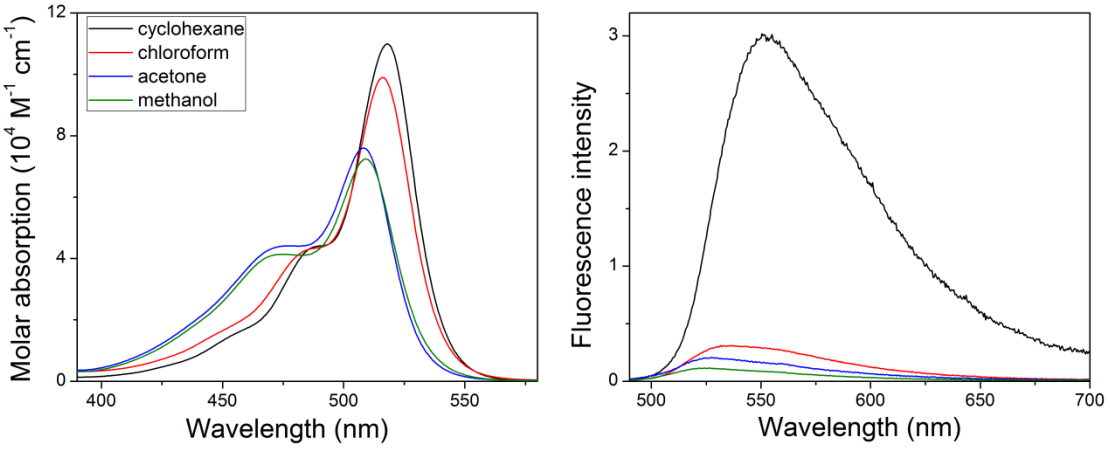


Fig. S3. Absorption (left) and fluorescence (right) spectra of **3** in solvents of different polarity (diluted solutions; see Experimental Section in the article).

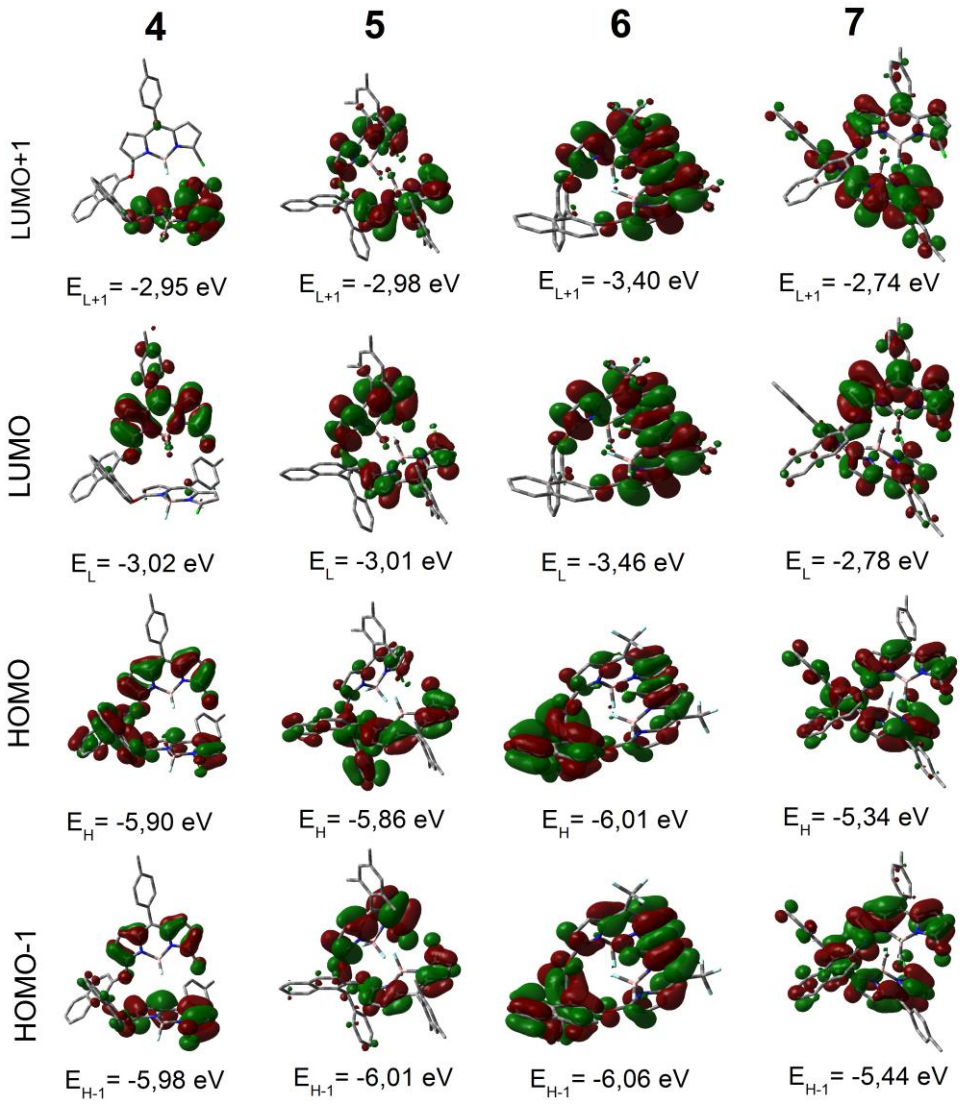


Fig. S4. Key molecular orbitals and energies computed for bis(BODIPYs) **4**-**7** (see Experimental Section in the article).

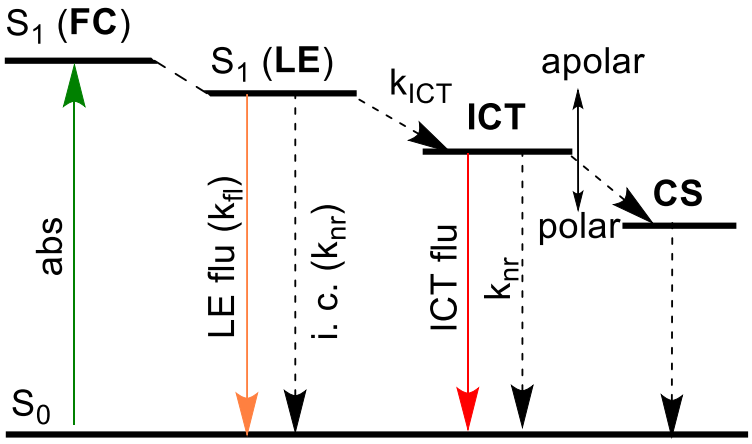


Fig. S5. Energetic diagram of the photoinduced charge transfer (FC: Frank-Condon excited state; LE: locally excited state; ICT: intramolecular charge transfer state; CS: charge separation state).

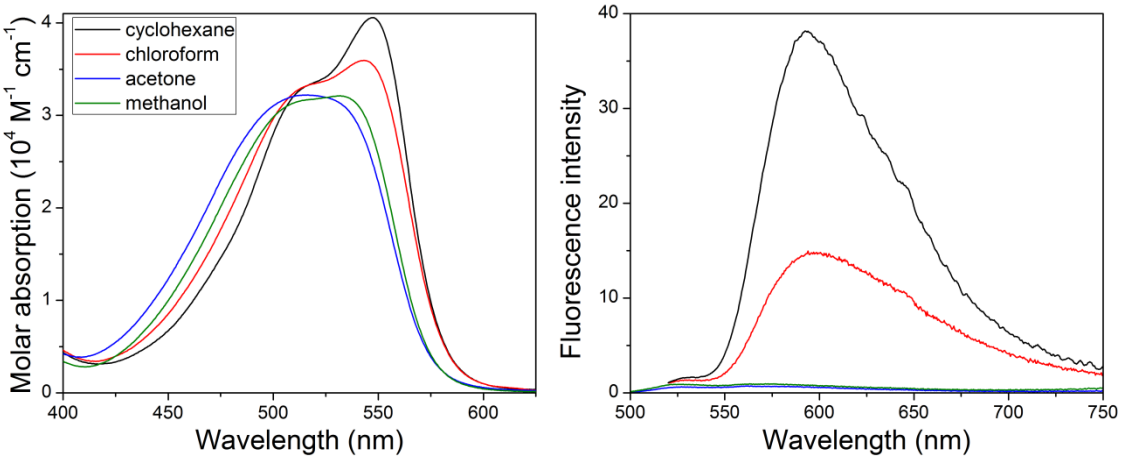
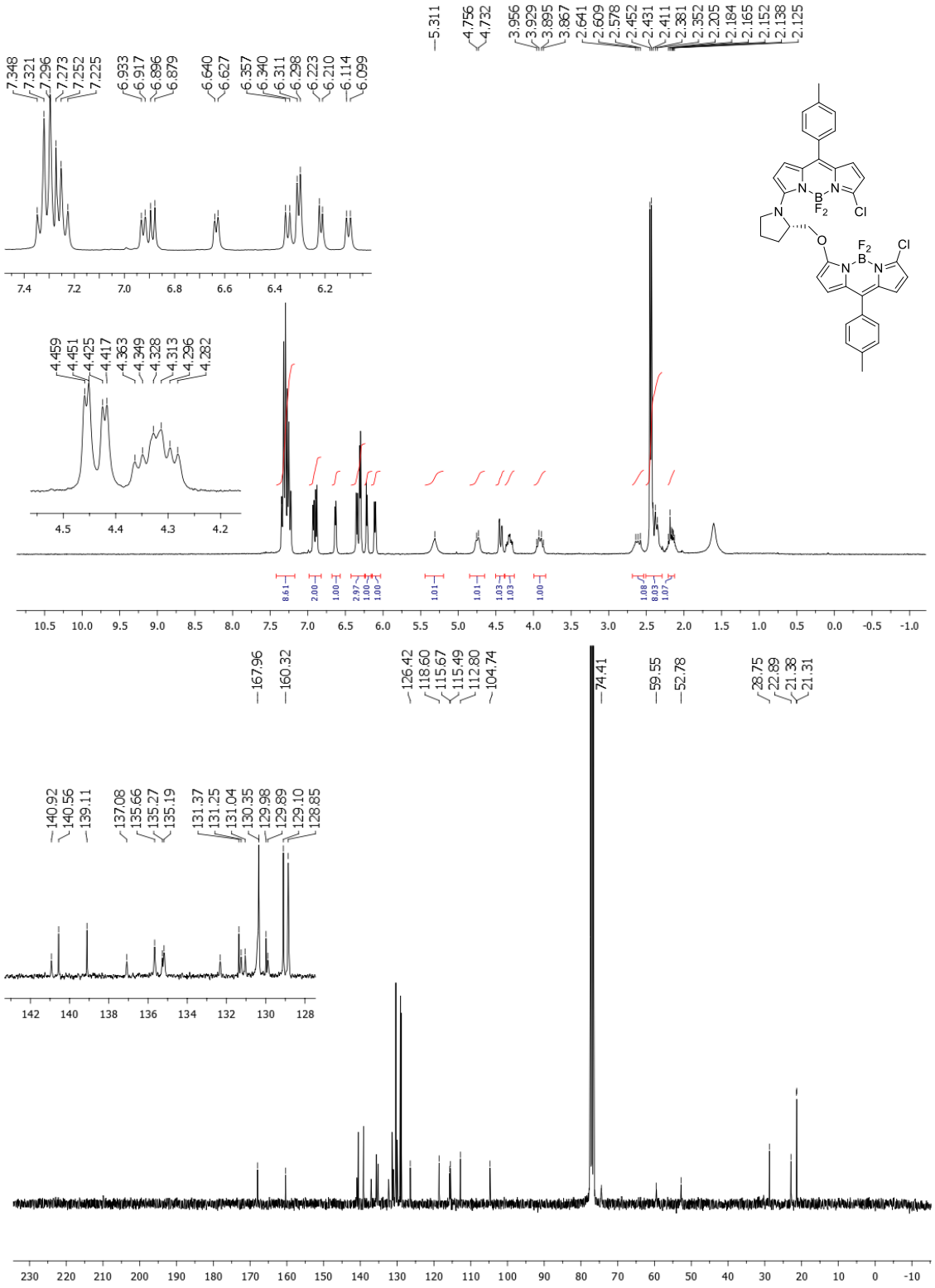


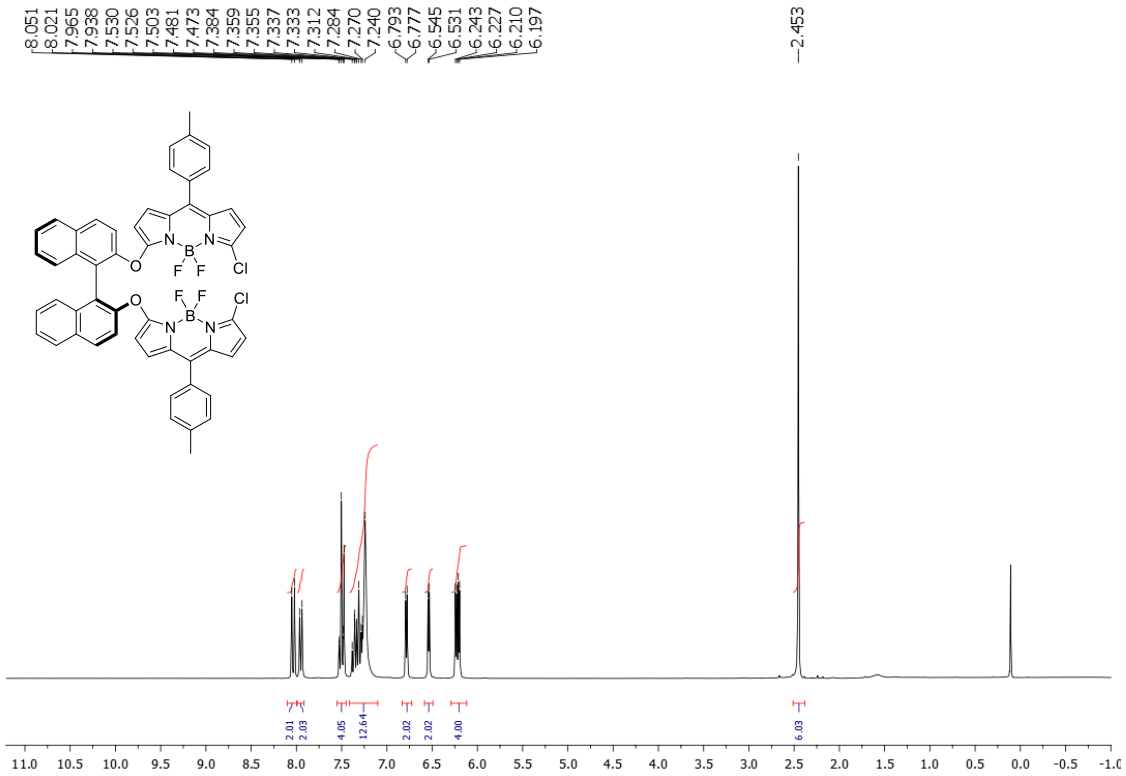
Fig. S6. Absorption (left) and fluorescence (right) spectra of **7** in solvents of different polarity (diluted solutions; see Experimental Section in the article).

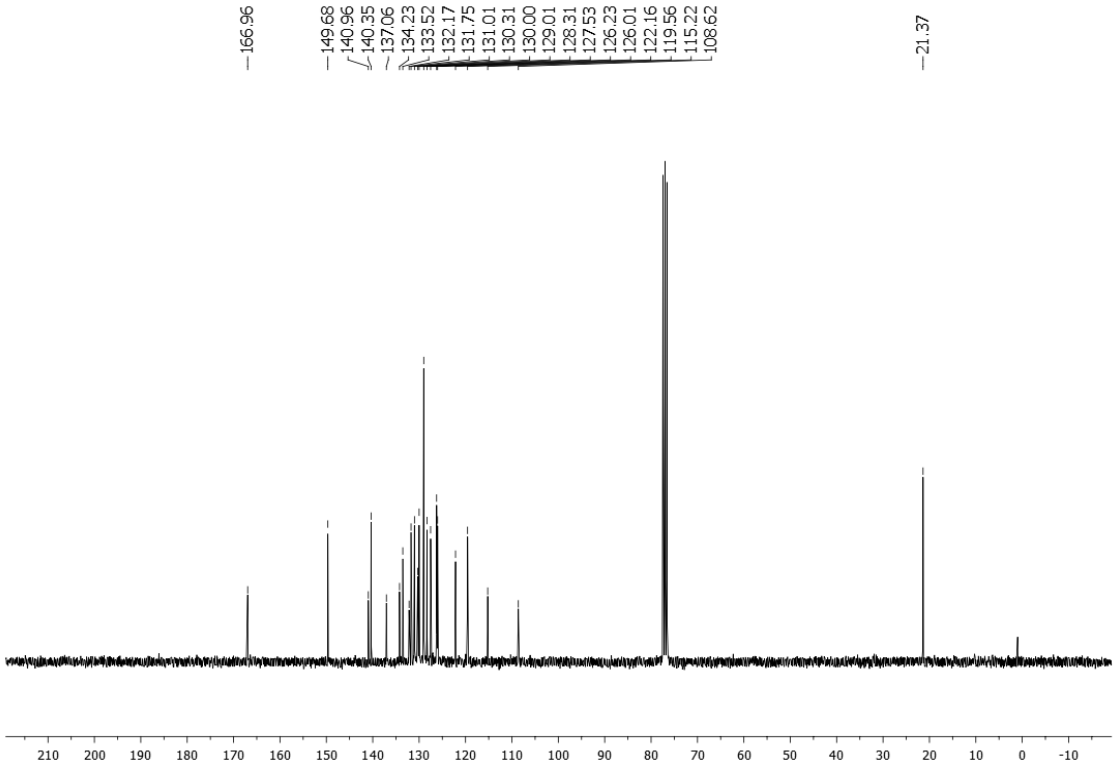
3. ^{1}H NMR and ^{13}C NMR spectra

^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectra of **3**

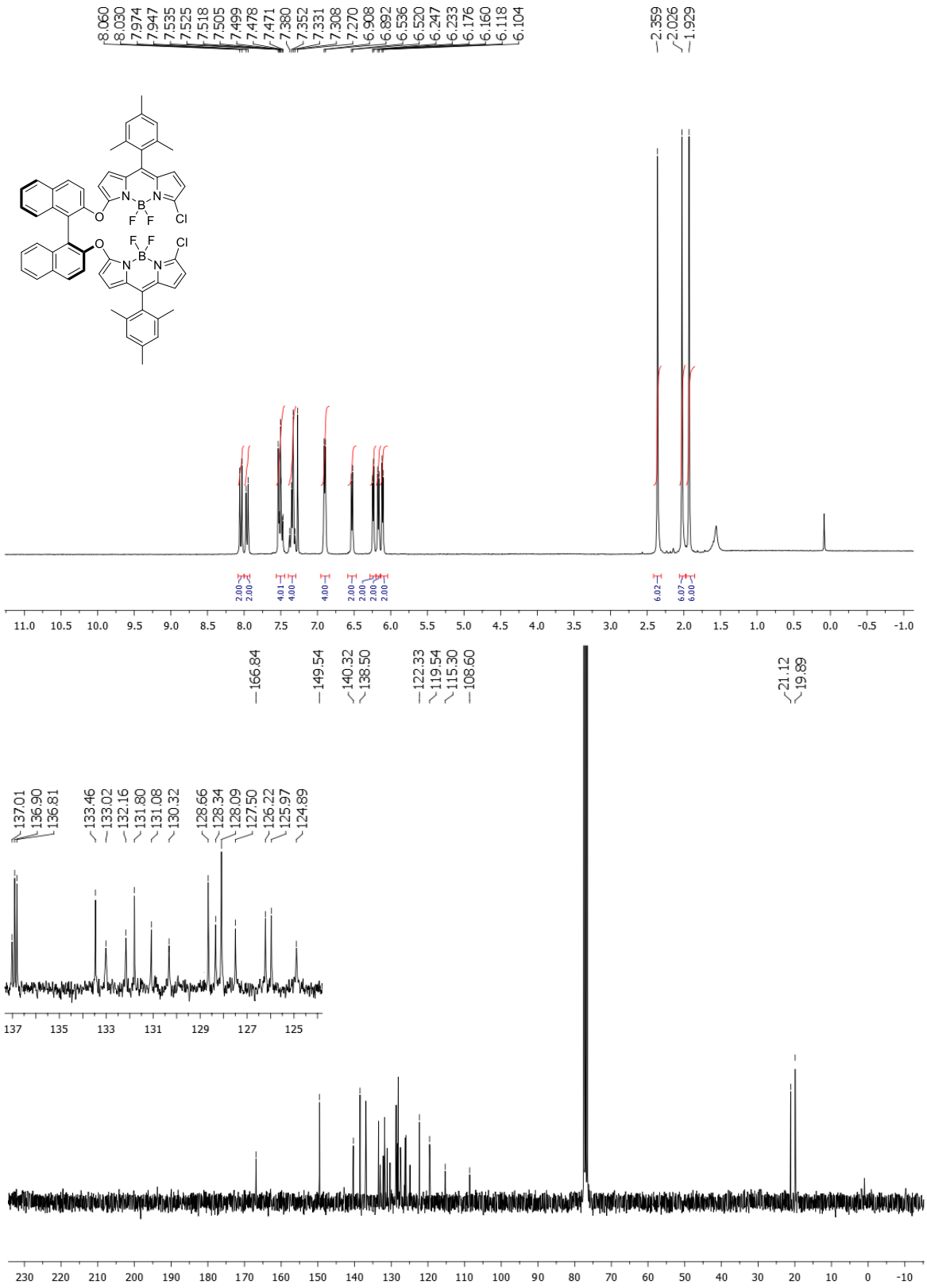


^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectra of **4**

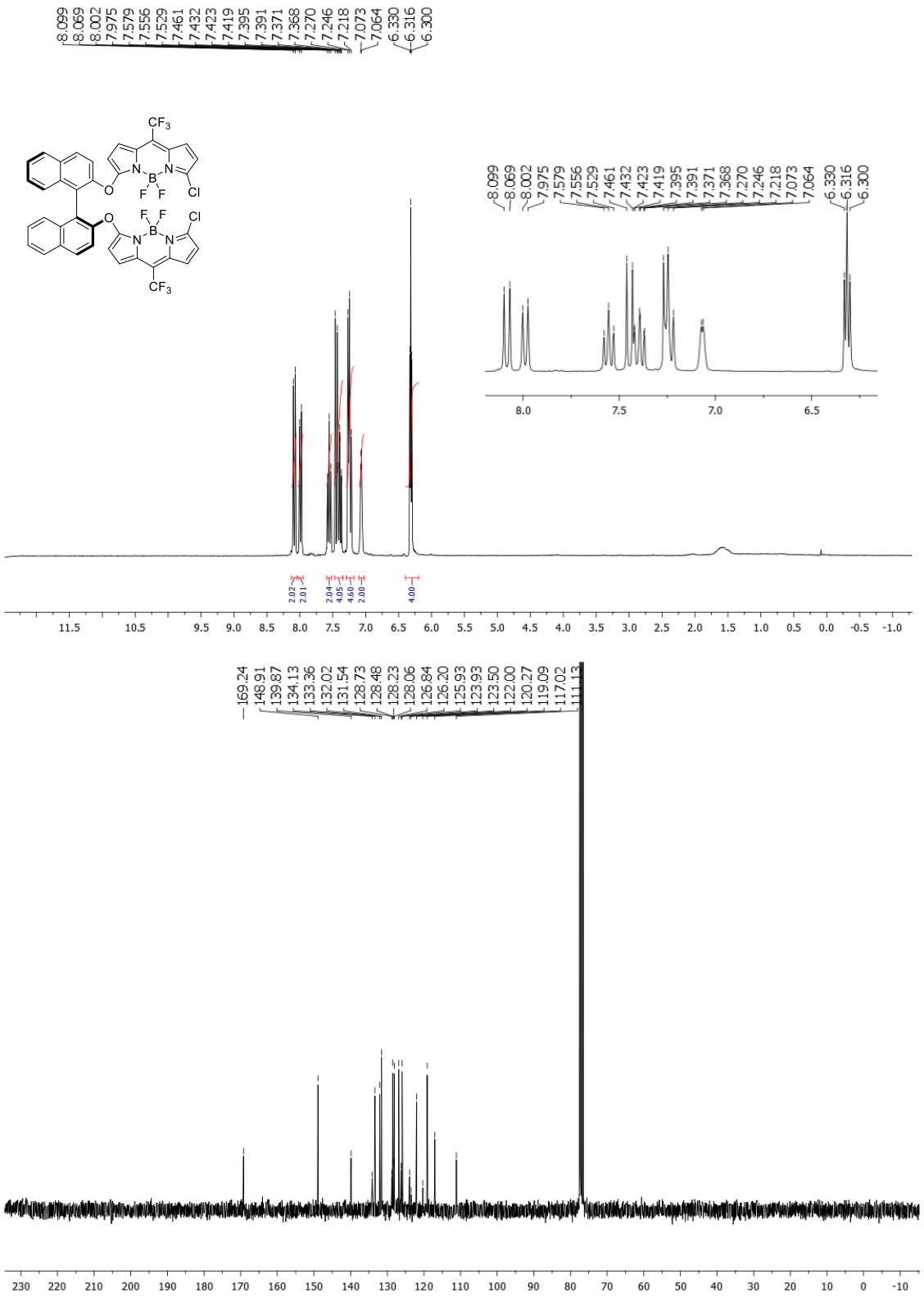




^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectra of **5**



^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectra of **6**



^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectra of **7**