Electronic Supporting Information

Halochromic Generation of White Light Emission Using a Single Dithienophosphole Luminophore

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Experimental Section

Materials and Methods. All chemical reagents were purchased from commercial sources (Aldrich, Alfa Aesar, Strem) and were, unless otherwise noted, used without further purification Solvents were dried using an MBraun solvent purification system prior to use. 2,6-dibromodithieno[3,2-*b*:2',3'-*d*]phosphole (**2**),[1] 2-piperidinothiophene[2] and 2-piperidino-5-tribuylstannylthiophene (**3**)[3] were prepared according to reported procedures. All reactions and manipulations were carried out under a dry nitrogen atmosphere employing standard Schlenk techniques. ^{1}H, ^{13}C, and ^{31}P NMR were recorded on Bruker DRX400 and Avance (-II,-III) 400 MHz spectrometers. Chemical shifts were referenced to external 85% H_3PO_4 (^{31}P) or residual non-deuterated solvent peaks (^{1}H, ^{13}C). Elemental analyses were performed in the Department of Chemistry at the University of Calgary. Mass spectra were run on a Finnigan SSQ 7000 spectrometer or a Bruker Daltonics AutoFlex III system. All photophysical experiments were carried out on a Jasco FP-6600 spectrofluorometer and UV-vis-NIR Cary 5000 spectrophotometer. Fluorescence lifetime was measured by using Edinburgh Instruments Ltd FLS920P fluorescence spectrometer. Theoretical calculations have been carried out at the B3LYP/6-31G(d) level by using the GAUSSIAN 09 suite of programs using a PCM solvation model (solvent = CH_2Cl_2) for the protonated species.[4]

Synthesis of 1

To a solution of 2,6-dibromodithieno[3,2-*b*:2',3'-*d*]phosphole oxide **2** (1.4 g, 3.14 mmol) and 2-piperidino-5-tribuylstannylthiophene **3** (2.86 g, 6.28 mmol) in toluene (50 mL) was added $Pd(PPh_3)_4$ (0.22 g, 0.19 mmol). The mixture was refluxed at 120 ^{o}C for 24 h. After removing the solvent, the red residue was filtered through neutral alumina using $CHCl_3$. The filtrate was removed and the product was recrystallized using acetone to yield a red solid (0.76 g, 39% yield). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 20.3 ppm; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.84-7.78 (m, 2 H; Ph), 7.56 (qd, *J* = 8.0 and 1.6 Hz; 1H; Ph), 7.48-7.44 (m, 2 H; Ph), 6.95 (d, *J* = 2.4 Hz; 2 H; thiophene), 5.97 (d, 4 Hz; 2 H; thiophene), 3.17 (t, *J* = 5.2 Hz; 8 H; piperidine), 1.76 – 1.70 (m; 8 H; piperidine),

1.61 – 1.58 (m; 4 H; piperidine); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 160.0 (s), 142.2 (d, J(C,P) = 16 Hz), 141.7 (d, J(C,P) = 23.4 Hz), 138.8 (s), 137.7 (s), 132.4 (d, J(C,P) = 2.6 Hz), 131.0 (d, J(C,P) = 11.4 Hz), 128.9 (d, J(C,P) = 12.9 Hz), 124.2 (s), 121.2 (s), 119.0 (d, J(C,P) = 14.3 Hz), 104.5 (s), 52.1 (s), 25.2 (s), 23.7 (s); HRMS (MALDI-TOF): m/z = 618.1051 $[M + H]^+$ (calcd. 618.1051); elemental analysis calcd (%) for $C_{32}H_{31}OPS_4$: C 62.11, H 5.05, N 4.54; found: C 62.20, H 5.10, N 4.46.

Synthesis of 4

To a solution of **1** (100 mg, 0.16 mmol) in CH_2Cl_2 with stirring was added MeOTf (0.36 mmol) dropwise. The solution was left to stir overnight. The resulting mixture was filtered and washed with CH_2Cl_2 and recrystallized with acetone yielding brown crystals quantitatively. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 21.6 ppm,; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.85 – 7.93 (m; 2 H; Ph), 7.72 – 7.67 (m; 1 H; Ph), 7.60 – 7.57 (m; 6 H; thiophene), 7.39 (d; J = 4.4 Hz; 2 H; thiophene), 4.29 – 4.26 (m; 4 H; piperidine), 4.00 – 3.94 (m; 4 H; piperidine), 3.65 (s; 6 H; methyl), 2.10 – 1.95 (m; 8 H; piperidine), 1.84 – 1.71 (m; 4 H; piperidine); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 146.0 (s), 145.2 (s), 145.0 (s), 139.8 (s), 139.6 (d, J(C,P) = 2.4 Hz), 138.5 (s), 135.6 (s), 133.3 (d, J(C,P) = 3.0 Hz), 130.5 (d, J(C,P) =12.3 Hz), 129.2 (d, J(C,P) = 13.7), 128.2 (s), 127.1 (s), 123.9 (d, J(C,P) =50.3 Hz), 123.5 (d, J(C,P) = 14.6 Hz), 122.0 (s), 118.8 (s), 66.1 (s), 57.8 (s), 20.9 (s), 20.3 (s); HRMS (MALDI-TOF): m/z = 797.1070 $[M + H]^+$ (calcd. 797.1041).

Reference

1. Y. Dienes, S. Durben, T. Kárpáti, T. Neumann, U. Englert, L. Nyulászi and T. Baumgartner, *Chem. Eur. J.*, 2007, **13**, 7487-7500.
2. Z. Lu and R. J. Twieg, *Tetrahedron*, 2005, **61**, 903-918.
3. G. Sotgiu, M. Galeotti, C. Samorí, A. Bongini and A. Mazzanti, *Chem. Eur. J.*, 2011, **17**, 7947-7952.
4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Jr. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03*, revision E.01; Gaussian Inc.: Wallingford, CT, 2007.

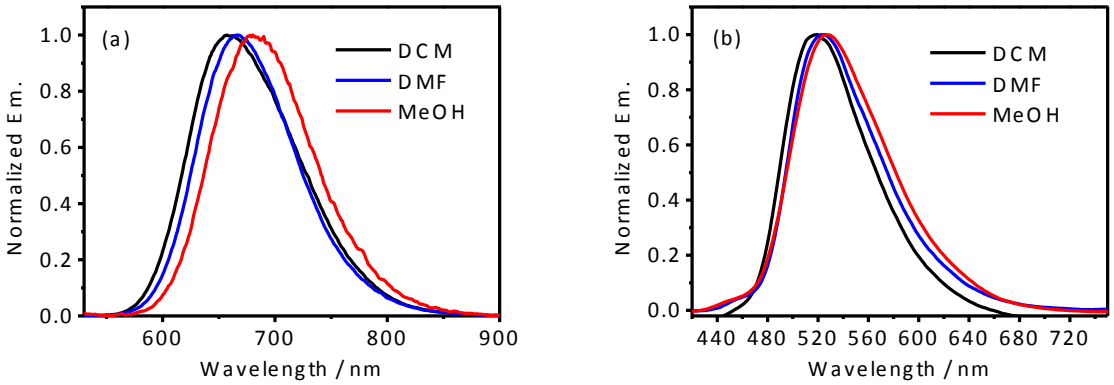

Fig. S1 Normalized emission spectra of (a) **1** and (b) **4** in different solvents

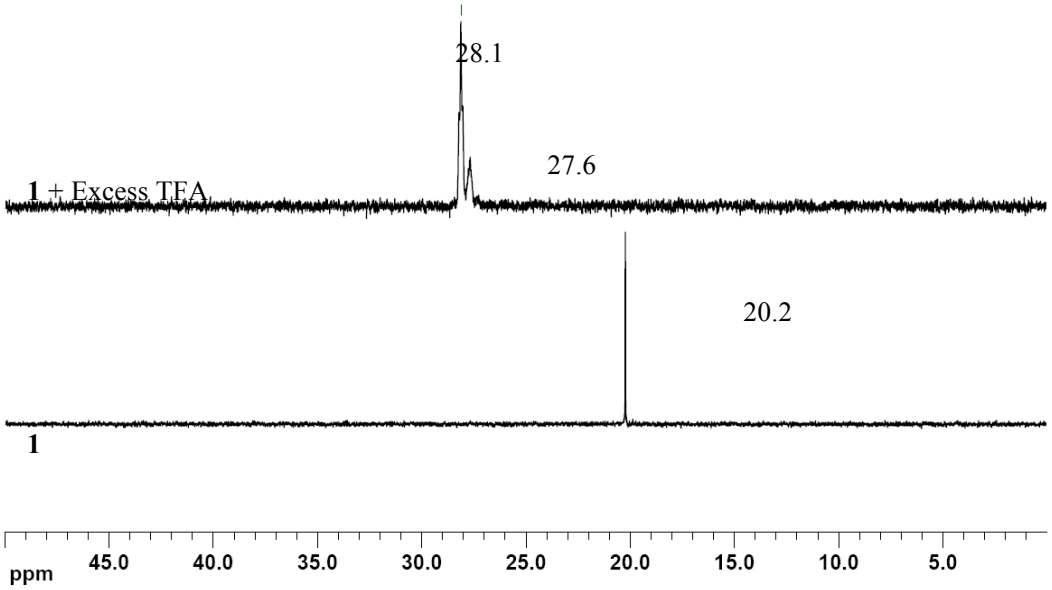

Fig. S2 ^{31}P NMR resonance signals before (bottom) and after (top) addition of excess of TFA in $CDCl_3$

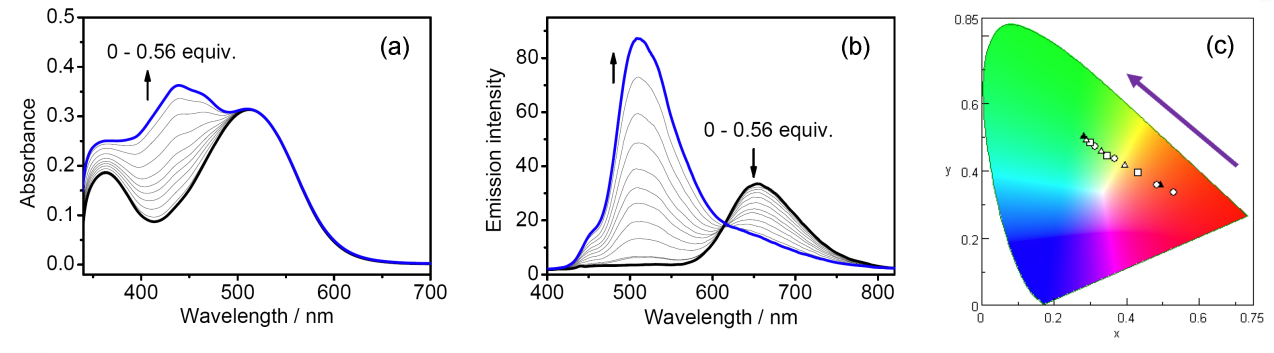

Fig. S3 (a) UV-vis absorption and (b) emission spectral changes as well as (c) CIE diagrams of **1** upon addition of **4** in dichloromethane solution.

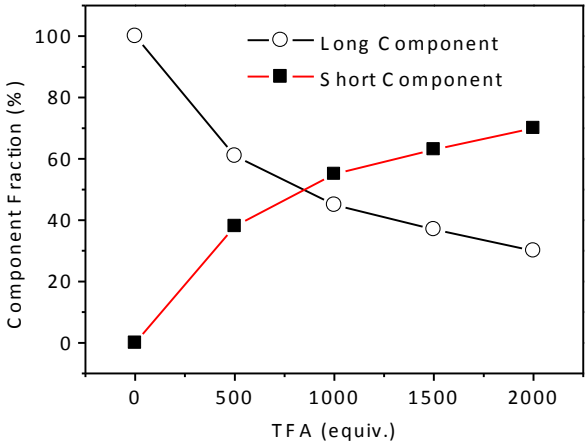

Fig. S4 Shifts in fractional intensity of the two lifetime components during the TFA titrating process of **1** in dichloromethane obtained from biexponential analysis.

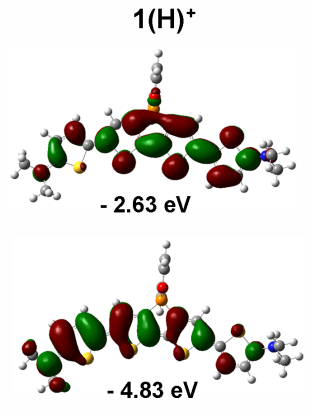

Fig. S5 HOMO (bottom) and LUMO (top) orbitals of monoprotonated species **1'(H)**$^+$ and it energies calculated at the B3LYP/6-31G(d) level.

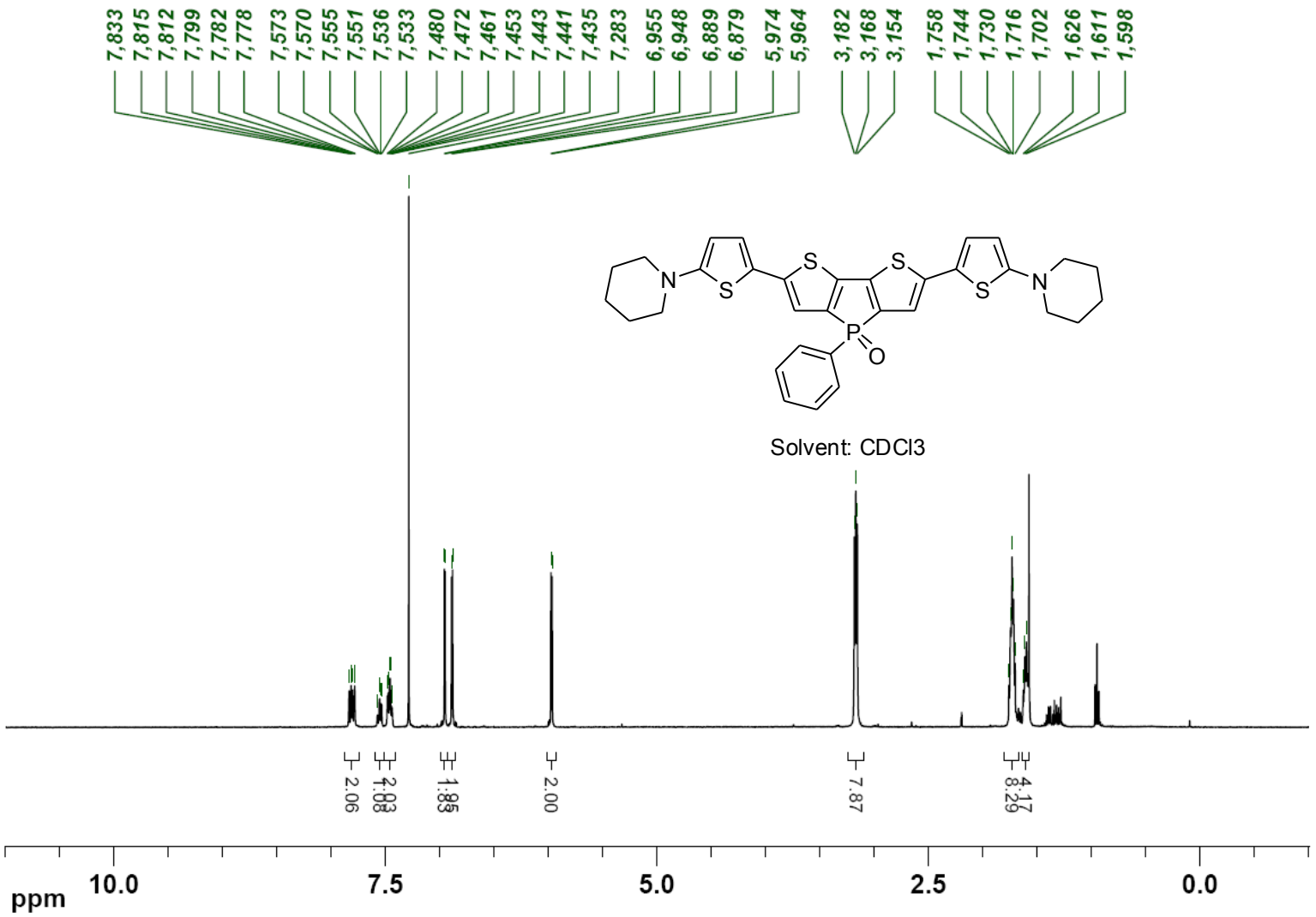

Fig. S6. ^{1}H NMR spectrum of **1** in $CDCl_3$

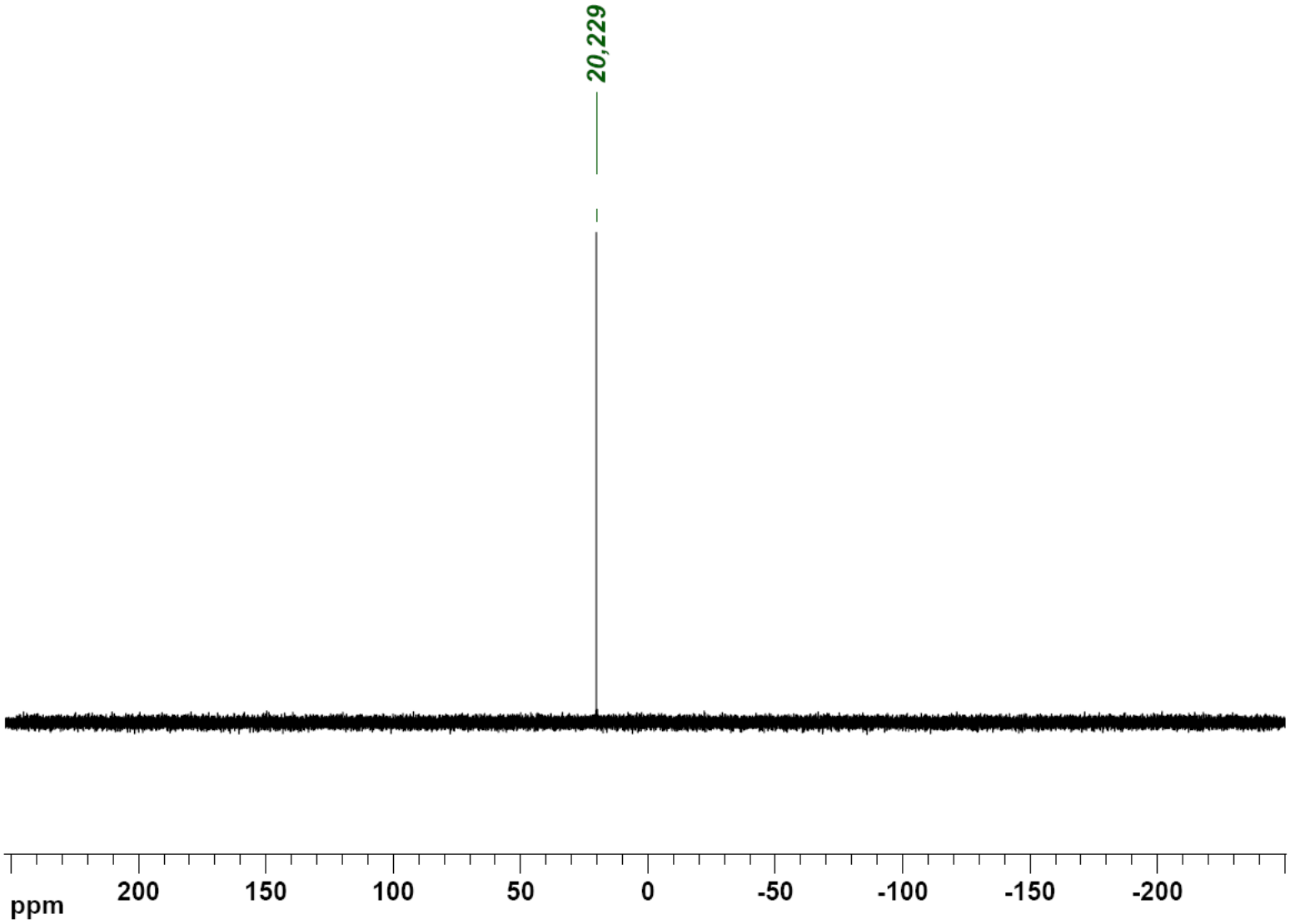

Fig. S7. ^{31}P NMR spectrum of **1** in $CDCl_3$

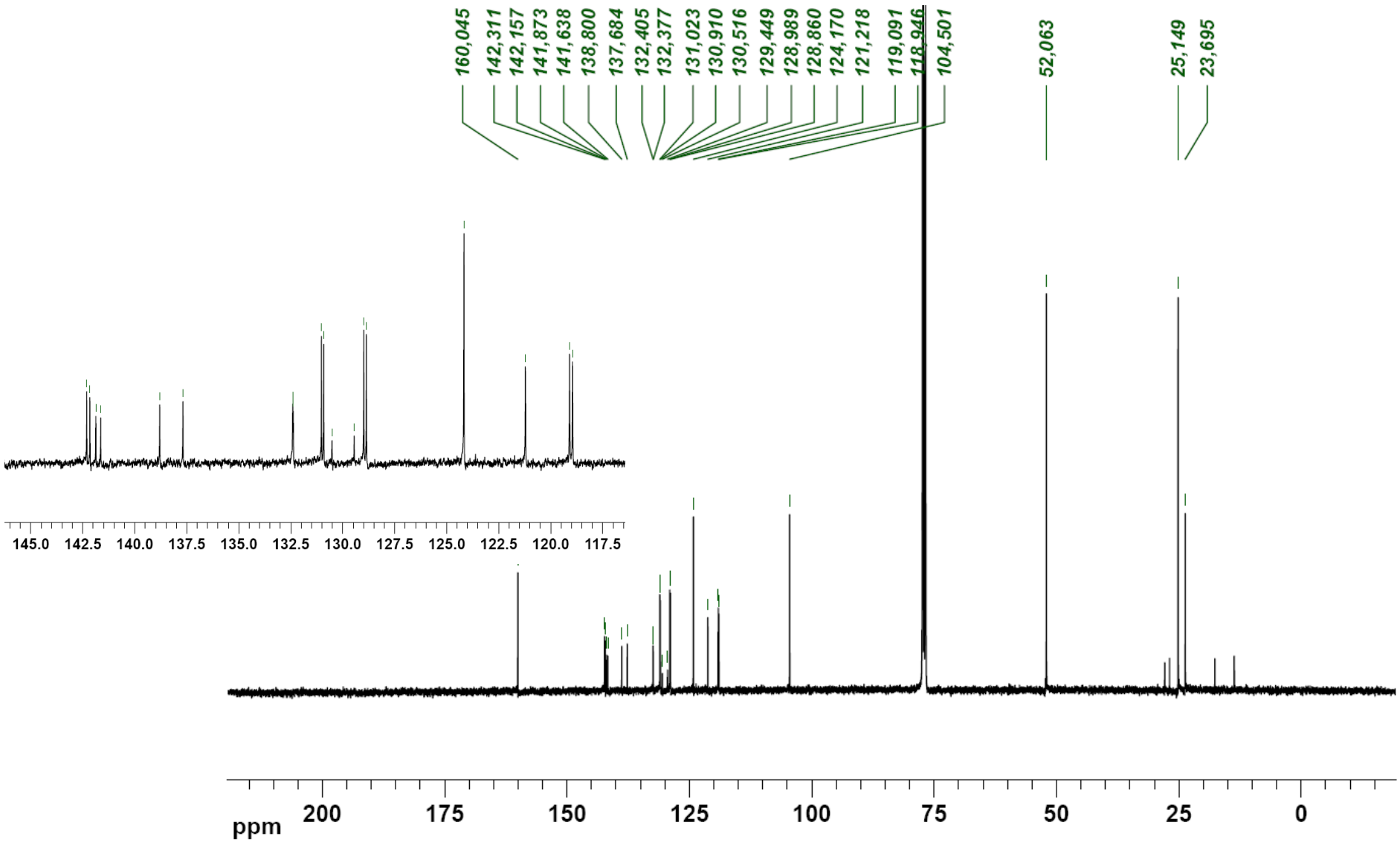

Fig. S8. ^{13}C NMR spectrum of **1** in $CDCl_3$

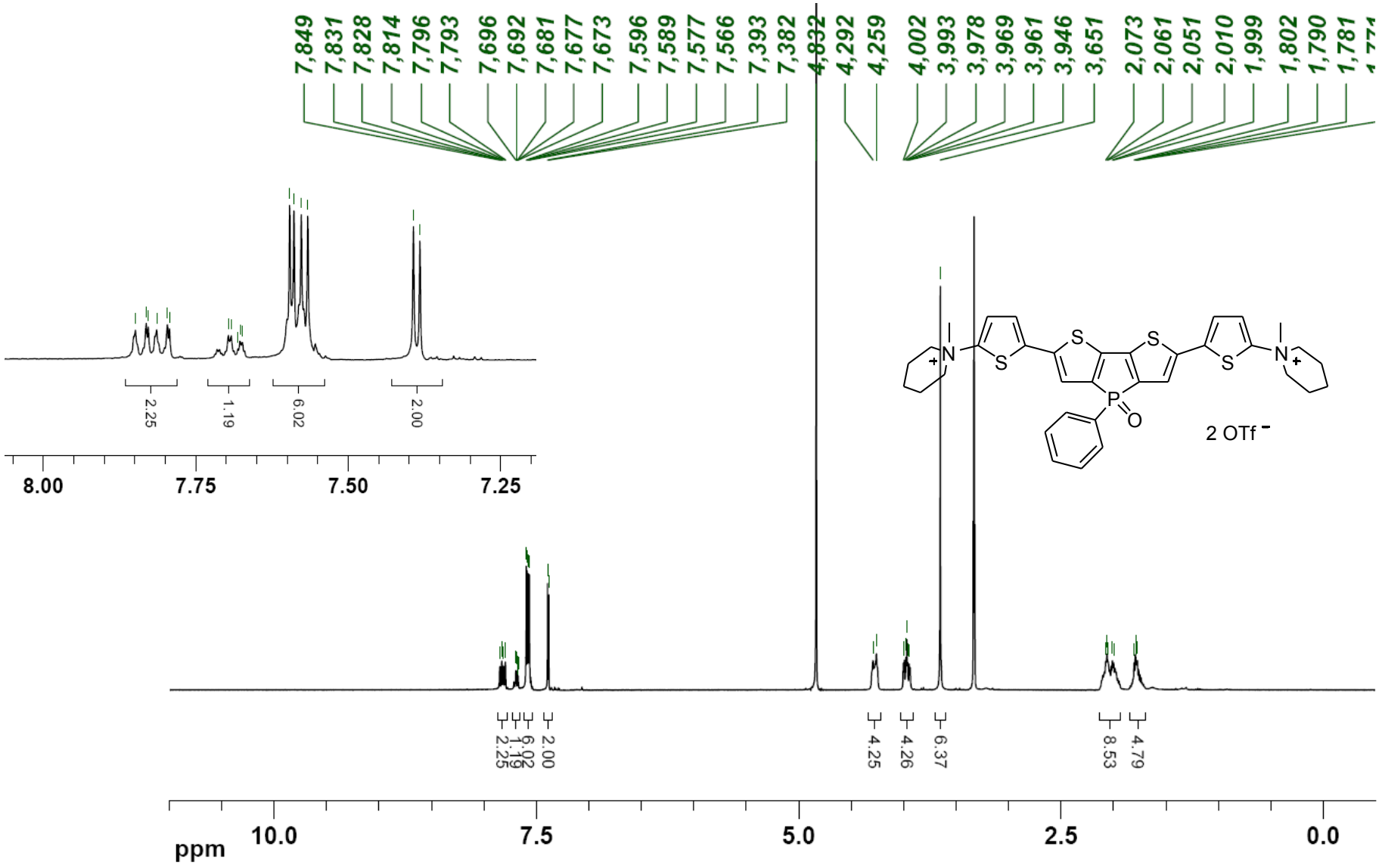

Fig. S9. ^{1}H NMR spectrum of **2** in CD_2Cl_2

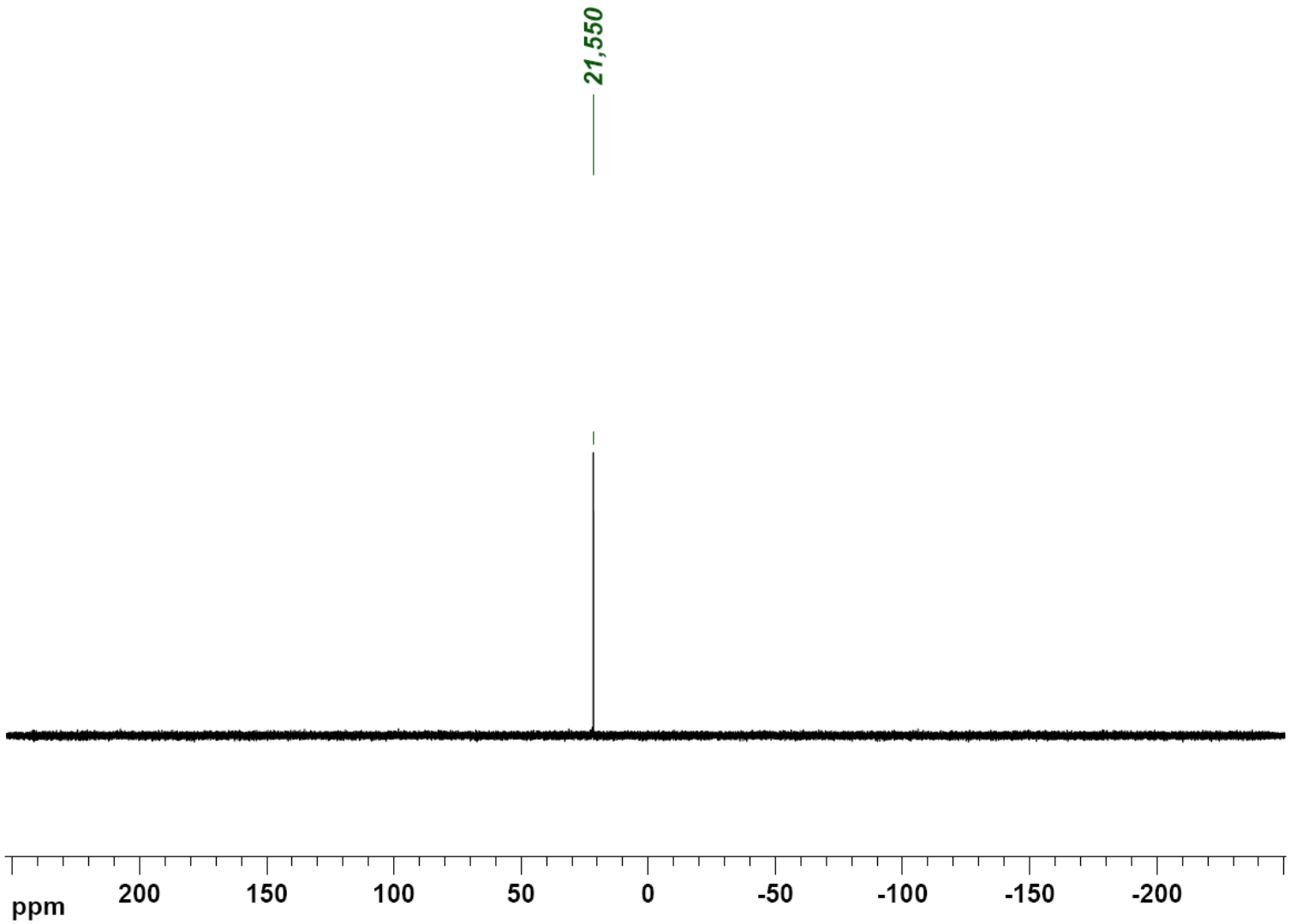

Fig. S10. ^{31}P NMR spectrum of **2** in CD_2Cl_2

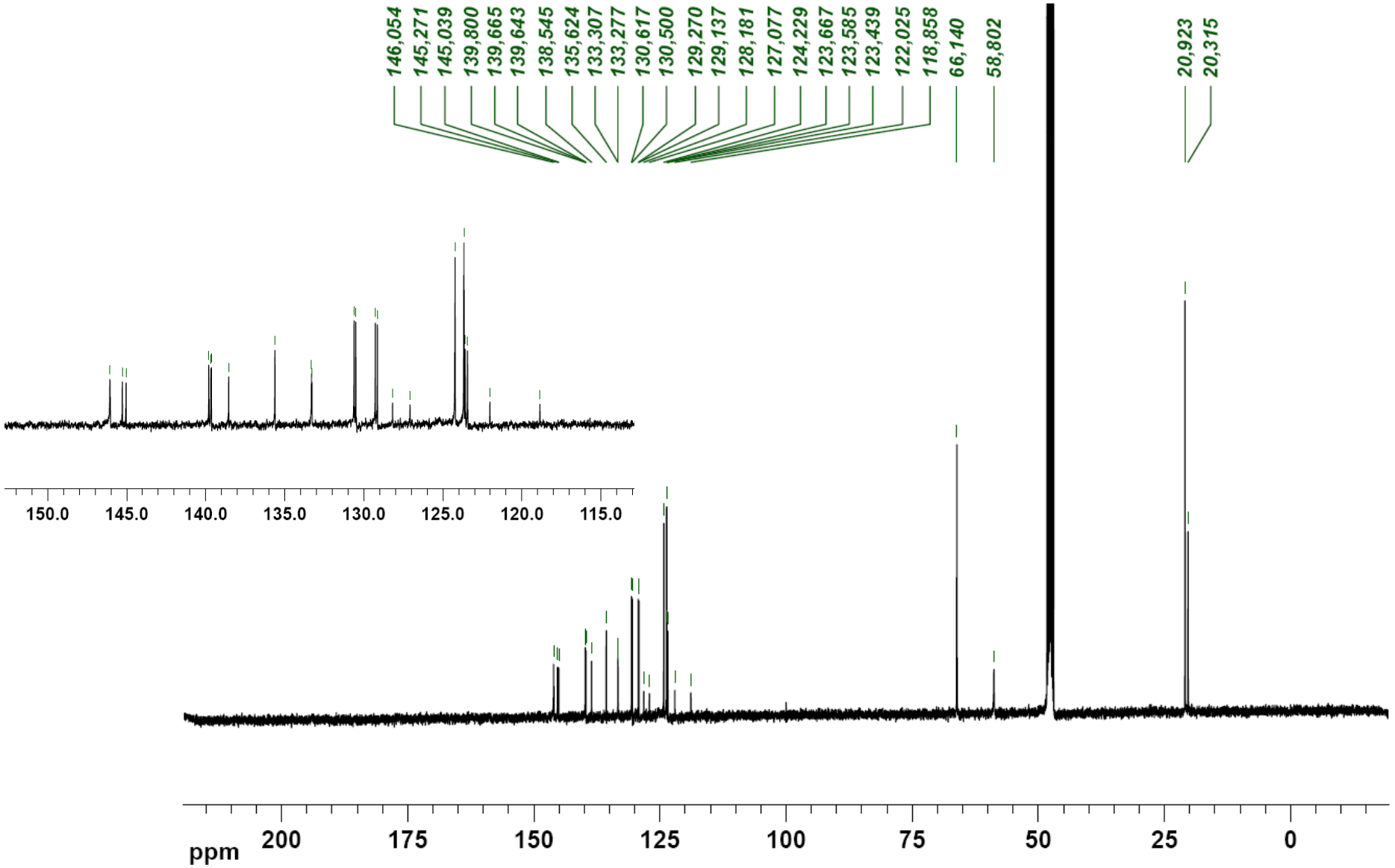

Fig. S11. ^{13}C NMR spectrum of **2** in CD_2Cl_2

Computational Data

1. Optimized structure coordinates of **1'**

C	-0.63678	-0.70872	-0.25229
C	-1.3161	0.41484	-0.6962
C	-2.72112	0.26816	-0.65403
C	-3.12429	-0.96663	-0.17562
S	-1.72311	-1.96345	0.24312
H	-3.42416	1.0255	-0.98333
C	0.80561	-0.60881	-0.30989
C	1.28529	0.59784	-0.7959
S	2.09134	-1.69151	0.1046
C	2.69642	0.66729	-0.81728
C	3.30319	-0.49019	-0.36122
H	3.26432	1.53485	-1.13343
P	-0.11767	1.69805	-1.22618
O	-0.2075	2.22678	-2.6265
C	-0.16135	3.02621	0.02665
C	-0.10051	2.77398	1.40499
C	-0.25989	4.34412	-0.43624
C	-0.13728	3.83319	2.30971
H	-0.02538	1.7535	1.77165
C	-0.2963	5.40249	0.47407
H	-0.30772	4.52451	-1.50603
C	-0.235	5.14809	1.84455
H	-0.0902	3.63467	3.37703
H	-0.3728	6.42403	0.11146
H	-0.26357	5.97231	2.55243
C	4.72121	-0.77217	-0.27829
C	5.73252	-0.23381	-1.043
S	5.39181	-1.87994	0.91167
C	7.02675	-0.70246	-0.68221
H	5.54585	0.45649	-1.85836
C	7.02499	-1.607	0.34762
H	7.93795	-0.38986	-1.18255
C	-4.46254	-1.48221	0.0068
C	-4.87841	-2.78432	0.17922
S	-5.84927	-0.40007	0.04044
C	-6.28716	-2.91617	0.32882
H	-4.1948	-3.6271	0.17804
C	-6.96605	-1.72722	0.27042
H	-6.78838	-3.86904	0.46657

N	-8.41366	-1.49299	0.37261
N	8.16711	-2.3022	0.95848
C	-8.90976	-2.03863	1.64425
H	-9.9355	-1.76333	1.77452
H	-8.82555	-3.10524	1.63174
H	-8.32932	-1.64448	2.45211
C	-9.09775	-2.15769	-0.74591
H	-8.94431	-3.2146	-0.68042
H	-10.14556	-1.94586	-0.6997
H	-8.70134	-1.79643	-1.67179
C	8.83215	-3.13521	-0.0538
H	9.25193	-2.50788	-0.81219
H	9.61061	-3.70525	0.40876
H	8.11801	-3.79884	-0.49482
C	9.12003	-1.31284	1.48193
H	9.9184	-1.81775	1.98449
H	9.51629	-0.73623	0.67236
H	8.61903	-0.66437	2.16996

2. Optimized structure coordinates of **5'**

C	0.61656	-0.41476	0.00808
C	1.30134	0.6634	0.55195
C	2.69608	0.46975	0.57632
C	3.08259	-0.75172	0.04592
S	1.68255	-1.6775	-0.50322
H	3.39762	1.18469	0.99418
C	-0.82452	-0.27574	0.01636
C	-1.28552	0.91379	0.56331
S	-2.11954	-1.31006	-0.48164
C	-2.69195	0.99206	0.60457
C	-3.30836	-0.13311	0.07974
H	-3.24604	1.81822	1.0359
P	0.12287	1.94522	1.15653
O	0.16097	2.26576	2.61656
C	0.25728	3.39266	0.07157
C	0.25547	3.29604	-1.32886
C	0.36166	4.64635	0.68991
C	0.35771	4.44951	-2.10313
H	0.17428	2.32685	-1.81538
C	0.46394	5.79791	-0.09298
H	0.36151	4.70863	1.77399
C	0.46181	5.69995	-1.48497
H	0.35613	4.37642	-3.18688

H	0.54456	6.76935	0.38575
H	0.54085	6.59749	-2.0917
C	-4.73372	-0.36279	-0.0257
C	-5.73693	0.57823	-0.15032
S	-5.41603	-1.98375	0.06687
C	-7.04575	0.02912	-0.18057
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C	-7.02425	-1.33504	-0.09058
H	-7.94031	0.63382	-0.28382
C	4.41328	-1.30057	-0.07448
C	4.8096	-2.60029	-0.32595
S	5.81756	-0.25035	0.09297
C	6.21692	-2.77928	-0.3736
H	4.10777	-3.41588	-0.45615
C	6.88415	-1.60407	-0.16751
H	6.68529	-3.74234	-0.54437
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N	-8.189	-2.23641	-0.09722
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H	8.96245	-3.16328	-1.11697
H	8.68927	-1.72161	-2.14271
C	8.89022	-1.83549	1.28922
H	8.73551	-2.90869	1.39819
H	9.95373	-1.59178	1.32593
H	8.34073	-1.29464	2.05963
C	-8.98455	-2.16594	1.19509
H	-9.4056	-1.16433	1.27814
H	-9.77768	-2.91498	1.15747
H	-8.30467	-2.35947	2.02468
C	-9.07709	-2.03909	-1.31142
H	-9.86624	-2.79244	-1.28785
H	-9.50817	-1.03982	-1.26235
H	-8.46257	-2.14436	-2.20522
H	8.52619	-0.41393	-0.15839
H	-7.82811	-3.19492	-0.16267

3. Optimized structure coordinates of **6'**

C	0.57611	-0.44381	0.15356
C	1.29379	0.71548	0.5036
C	2.69312	0.55269	0.46775
C	3.07196	-0.72497	0.09224

S	1.64755	-1.73916	-0.23626
H	3.4041	1.33003	0.72692
C	-0.84638	-0.32984	0.19698
C	-1.32049	0.93618	0.56975
S	-2.16985	-1.40407	-0.12363
C	-2.71247	1.0576	0.60007
C	-3.36138	-0.14381	0.25091
H	-3.25429	1.95662	0.86711
P	0.1041	1.98259	0.89559
O	0.35158	2.34619	2.45242
C	0.10086	3.50657	-0.04158
C	-0.72623	3.64257	-1.17149
C	0.9583	4.55585	0.34429
C	-0.6926	4.82594	-1.90641
H	-1.39146	2.838	-1.46871
C	0.97731	5.73348	-0.39765
H	1.59281	4.45927	1.22084
C	0.15486	5.86744	-1.52078
H	-1.33262	4.93707	-2.77601
H	1.62934	6.54818	-0.09855
H	0.17258	6.78915	-2.09452
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C	-5.79288	0.51256	0.45174
S	-5.42745	-1.96639	-0.24267
C	-7.0759	-0.01277	0.31576
H	-5.61348	1.54231	0.74178
C	-7.07487	-1.36401	-0.07219
H	-7.98034	0.5531	0.49371
C	4.39143	-1.28907	-0.04098
C	4.75914	-2.61273	-0.20241
S	5.81794	-0.25196	-0.04207
C	6.15827	-2.81832	-0.31612
H	4.04365	-3.4265	-0.2278
C	6.85307	-1.64331	-0.25165
H	6.60203	-3.80042	-0.43481
N	8.31557	-1.4741	-0.25232
N	-8.13279	-2.16078	-0.30659
C	9.00728	-2.35139	-1.27715
H	10.06609	-2.08898	-1.29064
H	8.88606	-3.3924	-0.98006
H	8.54744	-2.17364	-2.24885
C	8.92807	-1.64901	1.1285
H	8.75979	-2.67973	1.43978
H	9.99601	-1.43081	1.06781

H	8.42998	-0.96213	1.81261
C	-7.94564	-3.57973	-0.60458
H	-7.59393	-4.13271	0.2763
H	-8.89471	-4.00521	-0.93044
H	-7.22003	-3.70476	-1.41654
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H	-10.20937	-2.36157	-0.43122
H	-9.65908	-1.43966	0.98622
H	-9.6235	-0.70329	-0.63976
H	8.50849	-0.50708	-0.53801
H	-0.24253	3.0302	2.81409

4. Optimized structure coordinates of **1'(H^+)**

C	-0.56766	-0.38322	-0.09227
C	-1.28404	0.72641	-0.55644
C	-2.6694	0.53882	-0.51771
C	-3.04809	-0.70622	-0.01967
S	-1.61787	-1.6655	0.41229
H	-3.38651	1.28278	-0.85174
C	0.85469	-0.25329	-0.15014
C	1.30593	0.95722	-0.67747
S	2.17942	-1.29768	0.2651
C	2.70016	1.05017	-0.75698
C	3.3531	-0.09515	-0.28718
H	3.23399	1.90338	-1.15789
P	-0.12069	2.02302	-1.13675
O	-0.24683	2.47377	-2.5595
C	-0.17724	3.39601	0.0582
C	-0.05132	3.20507	1.44246
C	-0.34932	4.68755	-0.4564
C	-0.09954	4.30017	2.30261
H	0.08844	2.20649	1.84886
C	-0.39678	5.78123	0.41041
H	-0.43964	4.82222	-1.53015
C	-0.27236	5.58837	1.78674
H	0.00106	4.15138	3.37412
H	-0.52756	6.78227	0.00914
H	-0.30664	6.44062	2.45988
C	4.76138	-0.3336	-0.22697
C	5.78786	0.54855	-0.52696
S	5.43893	-1.89571	0.252
C	7.08305	0.01986	-0.38517
H	5.60408	1.56876	-0.84616

C	7.08589	-1.30295	0.05173
H	7.98319	0.5819	-0.59567
C	-4.35955	-1.24765	0.14495
C	-4.75619	-2.49209	0.62029
S	-5.77998	-0.27957	-0.27829
C	-6.15657	-2.68622	0.65011
H	-4.04958	-3.24605	0.94619
C	-6.83977	-1.58154	0.21555
H	-6.615	-3.60915	0.988
N	-8.28895	-1.44524	0.00974
N	8.15478	-2.09973	0.33227
C	-9.10002	-2.13735	1.08035
H	-10.15434	-1.91163	0.91403
H	-8.93259	-3.21073	1.00005
H	-8.7684	-1.77194	2.05176
C	-8.73203	-1.87192	-1.37926
H	-8.53299	-2.93904	-1.47629
H	-9.79745	-1.66032	-1.49361
H	-8.14441	-1.31404	-2.10805
C	7.96996	-3.53065	0.53406
H	7.71339	-4.05675	-0.3974
H	8.89218	-3.95545	0.93497
H	7.1742	-3.7083	1.26582
C	9.48465	-1.60682	-0.0081
H	10.23024	-2.28496	0.41066
H	9.63797	-1.53873	-1.09494
H	9.64121	-0.61656	0.43078
H	-8.50928	-0.44574	0.09276