Supplementary Information

Effects of Boryl, Phosphino, and Phosphonio Substituents on Optical, Electrochemical, and Photophysical Properties of 2,5-Dithienylphospholes and 2-Phenyl-5-thienylphospholes

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Synthesis of 1b, 2b, 10, 11, and 12

Synthesis of 1b. A mixture of 1-phenyl-1,6-heptadiyne (0.900 g, 5.3 mmol), 2-bromothiophene (1.1 mL, 11 mmol), $PdCl_2(PPh_3)_2$ (0.151 g, 0.21 mmol), CuI (0.021 g, 0.11 mmol), NEt_3 (4 mL), and toluene (12 mL) was stirred for 14 h at room temperature. The resulting mixture was added to NH_4Cl aq (20 mL), and the aqueous layer was separated and extracted with AcOEt (3 × 20 mL). The combined organic extracts were washed with $NaHCO_3$ aq (20 mL), water (20 mL), and brine (20 mL) in this order, dried over Na_2SO_4, and evaporated to leave an oily residue, which was then chromatographed on silica gel using hexane as an eluent. Compound **1b** was isolated as a pale yellow oil (0.862 g, 64%): R_f = 0.6 (hexane/AcOEt = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.91 (tt, J = 7.0, 7.1 Hz, 2H), 2.58 (t, J = 7.0 Hz, 2H), 2.62 (t, J = 7.1 Hz, 2H), 6.94 (dd, J = 3.6, 5.1 Hz, 1H), 7.13 (dd, J = 1.1, 3.6 Hz, 1H), 7.18 (dd, J = 1.1, 5.1 Hz, 1H), 7.25–7.31 (m, 3H), 7.37–7.43 (m, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 18.7 (s), 18.9 (s), 27.7 (s), 74.3 (s), 81.3 (s), 89.0 (s), 93.3 (s), 123.7 (s), 123.9 (s), 126.0 (s), 126.8 (s), 127.6 (s), 128.2 (s), 131.1 (s), 131.5 (s) ppm; HRMS (ESI): m/z = 251.0888 ($[M + H]^+$, Calcd 251.0889).

Synthesis of 2b. According to a similar procedure described for the synthesis of **2a**, **2b** was prepared from **1b**. Compound **2b** was isolated as a yellow solid in 59% yield based on **1b**: R_f = 0.5 (hexane/AcOEt = 20/1); mp 134–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33–2.48 (m, 2H), 2.70–2.80 (m, 2H), 2.83–2.93 (m, 1H), 2.95–3.05 (m, 1H), 6.92 (ddd, J = 3.8, 5.1 Hz, J_{H-P} = 0.7 Hz, 1H), 6.98 (dd, J = 3.8 Hz, J_{H-P} = 0.6 Hz, 1H), 7.10–7.14 (m, 1H), 7.15 (ddd, J = 1.3, 5.1 Hz, J_{H-P} = 1.3 Hz, 1H), 7.19–7.28 (m, 5H), 7.43–7.50 (m, 4H) ppm; ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 29.3 (s), 29.7 (s), 30.1 (s), 124.5 (d, J_{C-P} = 8.3 Hz), 124.8 (d, J_{C-P} = 1.6 Hz), 126.6 (s), 127.7 (d, J_{C-P} = 10.6 Hz), 127.9 (s), 128.9 (s), 129.1 (d, J_{C-P} = 8.4 Hz), 130.1 (d, J_{C-P} = 1.5 Hz), 131.4 (s), 133.5 (d, J_{C-P} = 12.9 Hz), 134.0 (d, J_{C-P} = 19.7 Hz), 136.8 (s), 137.0 (d, J_{C-P} = 19.0 Hz), 140.6 (d, J_{C-P} = 23.6 Hz), 154.8 (d, J_{C-P} = 9.1 Hz), 155.5 (d, J_{C-P} = 9.1 Hz) ppm; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 37.4 ppm; HRMS (ESI): m/z = 359.1013 ($[M + H]^+$, Calcd 359.1018).

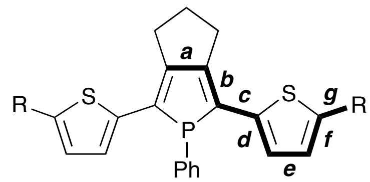
Synthesis of 10. To a solution of **2b** (0.362 g, 1.0 mmol) in THF (20 mL) was added a solution of LDA (in THF/PhEt/heptane, *ca.* 1.5 M × 1.0 mL, *ca.* 1.5 mmol) at −78 °C, and the reaction mixture was stirred for 1 h at same temperature. A solution of chlorodiphenylphosphine (0.30 mL, 1.6 mmol) was added to the reaction mixture, and the resulting solution was allowed to warm to room temperature and stirred for 29 h. After water (20 mL) was added to the mixture, the aqueous layer was separated and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, and evaporated to leave an oily residue, which was then chromatographed on silica gel using hexane/CH_2Cl_2 (10/1 to 5/1) as eluents. Compound **10** was isolated as a yellow solid (0.331 g, 60%) by recrystallization from CH_2Cl_2/MeOH: R_f = 0.5 (hexane/AcOEt = 20/1); mp 144–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31–2.42 (m, 2H), 2.63–2.83 (m, 3H), 2.93–3.03 (m, 1H), 6.95 (dd, J = 3.7 Hz, $J_{H–P}$ = 0.8 Hz, 1H), 7.07 (ddd, J = 3.7 Hz, $J_{H–P}$ = 0.6, 6.2 Hz, 1H), 7.10–7.14 (m, 1H) 7.18–7.27 (m, 5H), 7.29–7.46 (m, 14H) ppm; ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 29.5 (s), 29.7 (s), 30.1 (s), 125.3 (dd, $J_{C–P}$ = 8.0, 8.0 Hz) 126.8 (s), 127.8 (d, $J_{C–P}$ = 10.7 Hz), 128.8 (d, $J_{C–P}$ = 6.8 Hz), 128.9 (d, $J_{C–P}$ = 7.6 Hz), 128.9 (s), 129.1 (d, $J_{C–P}$ = 8.3 Hz), 129.2 (s), 129.3 (s), 130.2 (d, $J_{C–P}$ = 1.5 Hz), 131.1 (s), 133.3 (d, $J_{C–P}$ = 13.7 Hz), 133.3 (d, $J_{C–P}$ = 18.9 Hz), 133.5 (d, $J_{C–P}$ = 19.8 Hz), 134.1 (d, $J_{C–P}$ = 19.0 Hz), 136.9 (d, $J_{C–P}$ = 19.0 Hz), 137.0 (dd, $J_{C–P}$ = 1.5, 28.8 Hz), 137.5 (s), 137.5 (d, $J_{C–P}$ = 26.5 Hz), 138.3 (d, $J_{C–P}$ = 9.1 Hz), 138.4 (d, $J_{C–P}$ = 8.3 Hz), 147.4 (d, $J_{C–P}$ = 23.5 Hz), 155.6 (d, $J_{C–P}$ = 9.1 Hz), 155.9 (d, $J_{C–P}$ = 9.8 Hz) ppm; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = −18.9, 37.2 ppm; HRMS (ESI): m/z = 543.1447 ([M + H]$^+$, Calcd 543.1460).

Synthesis of 11. To a solution of **10** (0.240 g, 0.44 mmol) in $CHCl_3$ (8 mL) was added iodomethane (140 μL, 2.2 mmol), and the reaction mixture was stirred for 9 h at room temperature. The resulting mixture was evaporated under reduced pressure to leave a solid residue, which was then chromatographed on silica gel using CH_2Cl_2/MeOH (20/1) as eluents. Compound **11** was isolated as a yellow solid (0.137 g, 45%) by recrystallization from CH_2Cl_2/hexane: R_f = 0.4 (CH_2Cl_2/MeOH = 10/1); mp 122–125 °C; ^{1}H NMR (400 MHz, CD_2Cl_2, 20 mM): δ = 2.37–2.53 (m, 2H), 2.69–2.92 (m, 3H), 3.00 (d, $J_{H–P}$ = 13.6 Hz, 3H), 3.02–3.12 (m, 1H), 7.16–7.21 (m, 1H), 7.21 (dd, J = 4.1 Hz, $J_{H–P}$ = 2.0 Hz, 1H), 7.24–7.34 (m, 5H), 7.43–7.49 (m, 4H), 7.60 (ddd, J = 4.1 Hz, $J_{H–P}$ = 0.6, 8.4 Hz, 1H), 7.67–7.79 (m, 8H), 7.82–7.88 (m, 2H) ppm, ^{1}H NMR (400 MHz, CD_3OD): δ = 2.37–2.54 (m, 2H), 2.69–2.80 (m, 2H), 2.83–2.95 (m, 1H), 2.95 (d, $J_{H–P}$ = 14.4 Hz, 3H), 3.04–3.14 (m, 1H), 7.14–7.18 (m, 1H), 7.21–7.32 (m, 6H), 7.39–7.47 (m, 4H), 7.63 (ddd, J = 4.1 Hz, $J_{H–P}$ = 0.9, 8.5 Hz, 1H), 7.70–7.81 (m, 8H), 7.85–7.90 (m, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 13.1 (d, $J_{C–P}$ = 59.1 Hz), 29.7 (s), 30.0 (s), 30.1 (s), 112.9 (d, $J_{C–P}$ = 105.5 Hz), 112.9 (d, $J_{C–P}$ = 104.7 Hz), 120.2 (d, $J_{C–P}$ = 1.6, 91.8 Hz), 126.4 (d, $J_{C–P}$ = 8.0, 14.0 Hz), 127.7 (s), 128.0 (d, $J_{C–P}$ = 10.6 Hz), 129.0 (dd, $J_{C–P}$ = 1.9, 1.9 Hz), 129.1 (d, $J_{C–P}$ = 1.5 Hz), 129.4 (d, $J_{C–P}$ = 9.1 Hz), 130.7 (d, $J_{C–P}$ = 1.5 Hz), 130.8 (d, $J_{C–P}$ = 13.7 Hz), 130.8 (d,

$J_{C–P}$ = 12.9 Hz), 131.7 (d, $J_{C–P}$ = 12.2 Hz), 133.3 (d, $J_{C–P}$ = 11.3 Hz), 134.2 (d, $J_{C–P}$ = 20.5 Hz), 135.8 (d, $J_{C–P}$ = 3.1 Hz), 135.8 (d, $J_{C–P}$ = 3.0 Hz), 136.1 (d, $J_{C–P}$ = 19.0 Hz), 141.4 (s), 143.2 (d, $J_{C–P}$ = 9.1 Hz), 155.1 (dd, $J_{C–P}$ = 5.0, 23.2 Hz), 155.3 (d, $J_{C–P}$ = 8.3 Hz), 160.9 (d, $J_{C–P}$ = 10.6 Hz) ppm; ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 20 mM): δ = 14.6, 38.3 ppm; ^{31}P{^{1}H} NMR (162 MHz, CD_3OD): δ = 15.4, 38.7 ppm; HRMS (ESI): *m*/*z* = 557.1594 ([M – I]$^+$, Calcd 557.1616).

Synthesis of 12. A mixture of **11** (77 mg, 0.11 mmol), $NaPF_6$ (0.376 g, 2.2 mmol), CH_2Cl_2 (2 mL), and MeCN (2 mL) was stirred at room temperature. After 4 h, the mixture was washed with water (2 mL). $NaPF_6$ (0.381 g, 2.3 mmol) was then added, and the resulting mixture was stirred for 1 h. After addition of CH_2Cl_2 (10 mL), the mixture was washed with water (3 × 10 mL), dried over Na_2SO_4, and evaporated to leave a solid residue, which was then chromatographed on silica gel using CH_2Cl_2/MeOH (20/1) as eluents. Compound **12** was isolated as a yellow solid (65 mg, 82%) by recrystallization from CH_2Cl_2/hexane: R_f = 0.4 (CH_2Cl_2/MeOH = 10/1); mp 104–107 °C; IR (KBr): ν_{max} = 838 (P–F) cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.37–2.56 (m, 2H), 2.67–2.92 (m, 3H), 2.71 (d, $J_{H–P}$ = 13.2 Hz, 3H), 3.02–3.12 (m, 1H), 7.17–7.21 (m, 2H), 7.24–7.35 (m, 5H), 7.40 (ddd, J = 4.0 Hz, $J_{H–P}$ = 0.8, 8.4 Hz, 1H), 7.43–7.49 (m, 4H), 7.60–7.74 (m, 8H), 7.84–7.89 (m, 2H) ppm; ^{1}H NMR (400 MHz, CD_3OD): δ = 2.37–2.54 (m, 2H), 2.69–2.80 (m, 2H), 2.85–2.95 (m, 1H), 2.94 (d, $J_{H–P}$ = 14.0 Hz, 3H), 3.05–3.15 (m, 1H), 7.14–7.19 (m, 1H), 7.21–7.32 (m, 6H), 7.39–7.47 (m, 4H), 7.62 (ddd, J = 4.1 Hz, $J_{H–P}$ = 0.9, 8.5 Hz, 1H), 7.70–7.80 (m, 8H), 7.85–7.90 (m, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 11.7 (d, $J_{C–P}$ = 60.7 Hz), 29.7 (d, $J_{C–P}$ = 1.5 Hz), 30.0 (s), 30.1 (s), 112.4 (d, $J_{C–P}$ = 106.2 Hz), 112.4 (d, $J_{C–P}$ = 105.5 Hz), 119.9 (dd, $J_{C–P}$ = 1.6, 91.0 Hz), 126.3 (dd, $J_{C–P}$ = 8.0, 14.1 Hz), 127.7 (s), 128.0 (d, $J_{C–P}$ = 10.6 Hz), 128.9 (dd, $J_{C–P}$ = 1.9, 1.9 Hz), 129.1 (s), 129.4 (d, $J_{C–P}$ = 8.4 Hz), 130.7 (d, $J_{C–P}$ = 1.5 Hz), 130.9 (d, $J_{C–P}$ = 13.7 Hz), 130.9 (d, $J_{C–P}$ = 12.9 Hz), 131.7 (d, $J_{C–P}$ = 12.1 Hz), 133.0 (d, $J_{C–P}$ = 10.6 Hz), 134.2 (d, $J_{C–P}$ = 19.8 Hz), 136.0 (d, $J_{C–P}$ = 3.1 Hz), 136.0 (d, $J_{C–P}$ = 3.0 Hz), 136.1 (d, $J_{C–P}$ = 18.2 Hz), 141.6 (s), 142.8 (d, $J_{C–P}$ = 9.1 Hz), 155.3 (d, $J_{C–P}$ = 7.6 Hz), 155.5 (d, $J_{C–P}$ = 5.0, 23.9 Hz), 161.1 (d, $J_{C–P}$ = 10.6 Hz) ppm; ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = −144.5 (hept, $J_{P–F}$ = 711 Hz), 14.2, 38.2 ppm; ^{31}P{^{1}H} NMR (162 MHz, CD_3OD): δ = –144.6 (hept, $J_{P–F}$ = 708 Hz), 15.5, 38.6 ppm; HRMS (ESI): *m*/*z* = 557.1589 ([M – PF_6]$^+$, Calcd 557.1616).

Table S1 Bond lengths and torsion angles of **2a**, **3**, **7**, and $\mathbf{9}^{2+}$ obtained by the DFT method.[a]



	2a	**3**	**7**	$\mathbf{9}^{2+}$
bond lengths (Å)				
a	1.452	1.447	1.451	1.448
b	1.369	1.373	1.370	1.373
c	1.445	1.442	1.444	1.444
d	1.383	1.393	1.385	1.388
e	1.421	1.406	1.416	1.410
f	1.368	1.391	1.379	1.384
g	–	1.544	1.833	1.784
torsion angles (°)				
b-c-d	178.0	177.8	178.8	175.9

[a] Calculated by the B3LYP/6-31G(d) method.

Table S2 Optimized geometries of **2a**, **3**, **7**, and $\mathbf{9}^{2+}$ by the B3LYP/6-31G(d) method.

2a	*x*	*y*	*z*
C	-5.245480	-0.337629	-0.518740
C	-4.716382	0.832980	-0.990371
C	-3.295595	0.844230	-0.975841
C	-2.726413	-0.318083	-0.488250
S	-4.005713	-1.454484	-0.048818
H	-6.286818	-0.612790	-0.418215
H	-5.320569	1.664113	-1.338039
H	-2.702132	1.688304	-1.308707
C	-1.322229	-0.623839	-0.338473
C	-0.725755	-1.745101	0.172492
C	0.725754	-1.745101	0.172491
C	1.322228	-0.623840	-0.338474
P	0.000000	0.461219	-1.035936
C	0.000001	1.952706	0.064967
C	0.000002	3.219640	-0.535534
C	0.000001	1.864432	1.465946
C	0.000002	4.378070	0.246745
H	0.000001	3.299742	-1.620131
C	0.000001	3.018994	2.245732
H	0.000000	0.887230	1.940707
C	0.000002	4.278318	1.637249
H	0.000003	5.354006	-0.231602
H	0.000001	2.939141	3.329782
H	0.000003	5.177217	2.248167
C	2.726412	-0.318086	-0.488254
C	3.295595	0.844223	-0.975854
S	4.005712	-1.454491	-0.048833
C	4.716381	0.832980	-0.990366
H	2.702131	1.688294	-1.308727
C	5.245480	-0.337620	-0.518714
H	5.320569	1.664116	-1.338027
H	6.286817	-0.612772	-0.418165
C	-0.000001	-3.629121	1.475323
H	-0.000001	-4.722977	1.499569
H	-0.000001	-3.280219	2.514604

C	-1.238224	-3.047104	0.743382
H	-2.094693	-2.921253	1.414317
H	-1.569933	-3.714627	-0.065711
C	1.238223	-3.047104	0.743382
H	1.569931	-3.714627	-0.065712
H	2.094691	-2.921255	1.414316

3	*x*	*y*	*z*
C	5.274800	-0.398347	-0.183354
C	4.694260	-1.648523	0.006239
C	3.288625	-1.653986	0.026565
C	2.724255	-0.393689	-0.158928
S	3.996016	0.796806	-0.350204
H	5.298265	-2.539812	0.141827
H	2.691692	-2.546259	0.179602
C	1.320258	-0.067000	-0.196866
C	0.723587	1.161549	-0.335782
C	-0.723678	1.161550	-0.335720
C	-1.320343	-0.066994	-0.196723
P	-0.000051	-1.355511	-0.242866
C	0.000060	-2.095408	1.455199
C	0.000120	-3.493336	1.564887
C	0.000084	-1.320434	2.625720
C	0.000208	-4.107972	2.820165
H	0.000098	-4.102876	0.664339
C	0.000171	-1.933607	3.876849
H	0.000035	-0.236481	2.552638
C	0.000234	-3.328562	3.976119
H	0.000255	-5.192362	2.891509
H	0.000190	-1.324544	4.777071
H	0.000302	-3.803722	4.953487
C	-2.724345	-0.393653	-0.158623
C	-3.288727	-1.653875	0.027330
S	-3.996094	0.796798	-0.350272
C	-4.694363	-1.648396	0.007057
H	-2.691804	-2.546102	0.180676
C	-5.274893	-0.398282	-0.182969

H	-5.298374	-2.539630	0.142976
C	-0.000041	3.446792	-0.183941
H	-0.000061	4.395549	-0.728349
H	-0.000003	3.684978	0.886063
C	1.238093	2.570566	-0.510638
H	2.095038	2.801553	0.130576
H	1.573768	2.726614	-1.546363
C	-1.238196	2.570564	-0.510550
H	-1.573929	2.726604	-1.546257
H	-2.095107	2.801549	0.130711
B	6.771686	-0.022811	-0.233528
B	-6.771784	-0.022771	-0.233300
C	7.818269	-1.196679	-0.452372
C	7.753788	-2.04904	-1.584424
C	8.852066	-1.436052	0.496847
C	8.690010	-3.080265	-1.744925
C	9.749183	-2.489046	0.311587
C	9.691487	-3.325319	-0.808263
H	8.630975	-3.707654	-2.633160
H	10.520998	-2.659478	1.060627
C	7.191603	1.500527	-0.075782
C	6.881548	2.240966	1.092767
C	7.872904	2.180037	-1.126566
C	7.233345	3.595401	1.186174
C	8.194720	3.531284	-0.998054
C	7.883173	4.264267	0.153077
H	6.992893	4.136269	2.100611
H	8.704382	4.029898	-1.821142
C	-7.818334	-1.196751	-0.451714
C	-8.852114	-1.435842	0.497593
C	-7.753822	-2.049511	-1.583463
C	-9.749196	-2.488930	0.312708
C	-8.690003	-3.080831	-1.743594
C	-9.691473	-3.325593	-0.806849
H	-10.521000	-2.659124	1.061815
H	-8.630946	-3.708529	-2.631610
C	-7.191693	1.500653	-0.076322

C	-7.872739	2.179680	-1.127580
C	-6.881764	2.241685	1.091895
C	-8.194427	3.531035	-0.999844
C	-7.233396	3.596216	1.184501
C	-7.882980	4.264602	0.150937
H	-8.703882	4.029266	-1.823292
H	-6.993018	4.137555	2.098677
C	-8.231607	1.486075	-2.425744
H	-7.336849	1.214423	-3.000417
H	-8.796132	0.564433	-2.255535
H	-8.836240	2.141105	-3.061237
C	-6.242501	1.623715	2.321855
H	-5.410981	2.240162	2.683383
H	-6.971024	1.557772	3.140965
H	-5.856398	0.618844	2.143704
C	-8.998485	-0.593238	1.748262
H	-8.103507	-0.641670	2.379953
H	-9.165119	0.462141	1.509957
H	-9.842997	-0.939755	2.352638
C	-6.716963	-1.896566	-2.683363
H	-6.304510	-0.887854	-2.745938
H	-5.868201	-2.575242	-2.532651
H	-7.156120	-2.140908	-3.657326
C	8.231942	1.487064	-2.425019
H	8.796459	0.565347	-2.255181
H	7.337258	1.215673	-2.999932
H	8.836646	2.142407	-3.060122
C	6.241841	1.622482	2.322247
H	6.969687	1.557496	3.142029
H	5.409295	2.238059	2.682913
H	5.856979	0.617170	2.143909
C	6.716905	-1.895731	-2.684249
H	5.868006	-2.574248	-2.533601
H	6.304659	-0.886920	-2.746646
H	7.155965	-2.140008	-3.658270
C	8.998489	-0.593823	1.747768
H	9.165781	0.461524	1.509765

H	8.103301	-0.641894	2.379178
H	9.842632	-0.940943	2.352315
C	-10.694089	-4.439473	-0.995529
H	-10.755560	-5.078054	-0.105860
H	-11.702367	-4.043747	-1.174793
H	-10.43163	-5.074720	-1.847713
C	-8.234770	5.729904	0.255111
H	-7.614217	6.338213	-0.416159
H	-9.279646	5.912216	-0.023632
H	-8.086678	6.105821	1.272606
C	8.235113	5.729473	0.258091
H	9.279924	5.911876	-0.020825
H	7.614421	6.338260	-0.412617
H	8.087326	6.104759	1.275864
C	10.694123	-4.439119	-0.997307
H	11.702459	-4.043322	-1.176074
H	10.755336	-5.078206	-0.107981
H	10.431870	-5.073883	-1.849914

7	*x*	*y*	*z*
C	-5.267278	0.213741	-0.761168
C	-4.709603	1.215246	0.004900
C	-3.293161	1.216251	0.008163
C	-2.724787	0.210829	-0.756125
S	-4.003336	-0.733505	-1.516776
H	-5.310218	1.936471	0.548052
H	-2.700061	1.933753	0.564626
C	-1.321294	-0.069493	-0.945758
C	-0.725275	-1.064766	-1.674583
C	0.725253	-1.064787	-1.674567
C	1.321285	-0.069530	-0.945730
P	0.000004	1.068012	-0.335963
C	-0.000016	0.829958	1.502155
C	-0.000007	1.970866	2.317039
C	-0.000040	-0.437092	2.106468
C	-0.000021	1.850914	3.709621
H	0.000012	2.957544	1.859718

C	-0.000054	-0.556807	3.494581
H	-0.000048	-1.327295	1.483740
C	-0.000045	0.587408	4.298897
H	-0.000013	2.743617	4.329553
H	-0.000073	-1.542884	3.952030
H	-0.000056	0.491024	5.381471
C	2.724780	0.210754	-0.756066
C	3.293164	1.216175	0.008216
S	4.003322	-0.733664	-1.516626
C	4.709606	1.215157	0.004953
H	2.700071	1.933705	0.564648
C	5.267272	0.213647	-0.761114
H	5.310227	1.936398	0.548078
C	-0.000030	-3.121448	-2.682040
H	-0.000027	-3.677481	-3.624188
H	-0.000050	-3.856896	-1.869140
C	-1.238089	-2.198284	-2.532126
H	-2.095366	-2.721434	-2.095748
H	-1.568694	-1.816646	-3.509438
C	1.238053	-2.198321	-2.532098
H	1.568693	-1.816692	-3.509402
H	2.095305	-2.721496	-2.095699
C	-7.841383	1.380501	-0.557092
C	-8.025891	2.405085	-1.500091
C	-8.310187	1.576143	0.750425
C	-8.644609	3.602424	-1.141200
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C	-8.938548	2.771372	1.106859
H	-8.189147	0.791866	1.491593
C	-9.104376	3.787504	0.164390
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H	-9.298508	2.907533	2.123595
H	-9.595003	4.716238	0.443677
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C	-6.715473	-1.660071	1.306722
C	-8.640173	-2.155665	-0.065273
C	-7.124640	-2.630088	2.224201

H	-5.802385	-1.099150	1.484344
C	-9.055179	-3.116065	0.857075
H	-9.225358	-1.987477	-0.966695
C	-8.295988	-3.356970	2.004120
H	-6.526699	-2.816743	3.112764
H	-9.964088	-3.683672	0.674929
H	-8.612132	-4.112078	2.719086
C	7.841364	1.380467	-0.557222
C	8.310212	1.576230	0.750261
C	8.025820	2.404973	-1.500315
C	8.938566	2.771500	1.106570
H	8.189213	0.792014	1.491501
C	8.644529	3.602354	-1.141550
H	7.684333	2.260590	-2.522661
C	9.104340	3.787554	0.164008
H	9.298560	2.907755	2.123282
H	8.775930	4.386058	-1.883130
H	9.594962	4.716321	0.443198
C	7.471875	-1.406922	0.152903
C	8.640207	-2.155663	-0.065122
C	6.715567	-1.659933	1.306910
C	9.055251	-3.115974	0.857301
H	9.225353	-1.987562	-0.966585
C	7.124772	-2.629861	2.224464
H	5.802488	-1.098992	1.484517
C	8.296110	-3.356767	2.004403
H	9.964151	-3.683600	0.675172
H	6.526870	-2.816429	3.113072
H	8.612284	-4.111806	2.719429
P	-7.016074	-0.170570	-1.151521
P	7.016062	-0.170670	-1.151489

$\mathbf{9^{2+}}$	*x*	*y*	*z*
C	-5.241851	0.156826	-0.596044
C	-4.704304	1.285738	-0.003107
C	-3.296434	1.264067	0.066317
C	-2.719538	0.119406	-0.467393

S	-3.975849	-0.955769	-1.073632
H	-5.309221	2.106803	0.365048
H	-2.711923	2.065789	0.501565
C	-1.313747	-0.195659	-0.566256
C	-0.723886	-1.349952	-1.018903
C	0.723883	-1.349955	-1.018894
C	1.313745	-0.195666	-0.566240
P	0.000001	1.068330	-0.294149
C	-0.000010	1.432706	1.514775
C	0.000009	2.781301	1.905287
C	-0.000037	0.431608	2.500757
C	0.000001	3.124370	3.260211
H	0.000029	3.563568	1.149933
C	-0.000044	0.777342	3.850412
H	-0.000052	-0.61538	2.209896
C	-0.000025	2.123533	4.231375
H	0.000015	4.170323	3.553101
H	-0.000065	-0.001348	4.608100
H	-0.000031	2.388782	5.284711
C	2.719536	0.119391	-0.467358
C	3.296432	1.264047	0.066362
S	3.975849	-0.955795	-1.073571
C	4.704302	1.285719	-0.003061
H	2.711920	2.065771	0.501607
C	5.241849	0.156814	-0.596012
H	5.309218	2.106786	0.365090
C	-0.000004	-3.594436	-1.483757
H	-0.000001	-4.357280	-2.265971
H	-0.000011	-4.113678	-0.519453
C	-1.237515	-2.661097	-1.563509
H	-2.091761	-3.059778	-1.005473
H	-1.570238	-2.533788	-2.604165
C	1.237512	-2.661103	-1.563495
H	1.570248	-2.533795	-2.604146
H	2.091750	-3.059788	-1.005448
C	-7.908957	1.346456	-0.666047
C	-7.708703	2.389962	-1.589139

C	-8.839837	1.495440	0.374183
C	-8.439841	3.568556	-1.467773
H	-6.985679	2.291010	-2.394120
C	-9.565950	2.681641	0.485811
H	-9.001753	0.694676	1.088121
C	-9.368627	3.713717	-0.432427
H	-8.288217	4.371990	-2.181933
H	-10.287102	2.795364	1.289171
H	-9.939188	4.633339	-0.344059
C	-7.564617	-1.449183	0.310815
C	-6.861920	-1.691384	1.502163
C	-8.746201	-2.160404	0.033857
C	-7.338780	-2.640308	2.405893
H	-5.948780	-1.145967	1.719779
C	-9.213153	-3.106499	0.943649
H	-9.307398	-1.981194	-0.878501
C	-8.510126	-3.347146	2.127293
H	-6.793851	-2.828025	3.325874
H	-10.123861	-3.656344	0.727564
H	-8.877217	-4.086807	2.832415
C	7.908944	1.346466	-0.666056
C	8.839837	1.495460	0.374160
C	7.708670	2.389968	-1.589149
C	9.565943	2.681667	0.485776
H	9.001770	0.694699	1.088097
C	8.439801	3.568569	-1.467795
H	6.985635	2.291009	-2.394119
C	9.368599	3.713739	-0.432462
H	10.287105	2.795397	1.289126
H	8.288160	4.372000	-2.181955
H	9.939154	4.633365	-0.344104
C	7.564642	-1.449174	0.310814
C	8.746230	-2.160383	0.033841
C	6.861963	-1.691382	1.502171
C	9.213203	-3.106473	0.943627
H	9.307412	-1.981168	-0.878525
C	7.338845	-2.640301	2.405895

H	5.948821	-1.145973	1.719799
C	8.510194	-3.347127	2.127280
H	10.123914	-3.656309	0.727530
H	6.793930	-2.828023	3.325884
H	8.877302	-4.086784	2.832397
P	-6.973447	-0.190860	-0.847433
P	6.973444	-0.190858	-0.847427
C	-7.187970	-0.823748	-2.547799
H	-6.819598	-0.082874	-3.262090
H	-6.626323	-1.754085	-2.672485
H	-8.245632	-1.012912	-2.748413
C	7.187948	-0.823747	-2.547795
H	6.626305	-1.754089	-2.672471
H	6.819560	-0.082877	-3.262082
H	8.245608	-1.012904	-2.748424

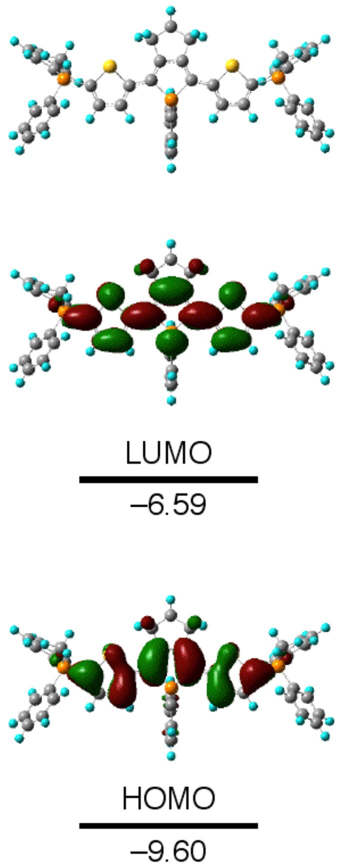


Fig. S1 Optimized structure and Kohn Sham diagrams of the HOMO and LUMO of $\mathbf{9}^{2+}$ calculated by the DFT method [B3LYP/6-31G(d)].

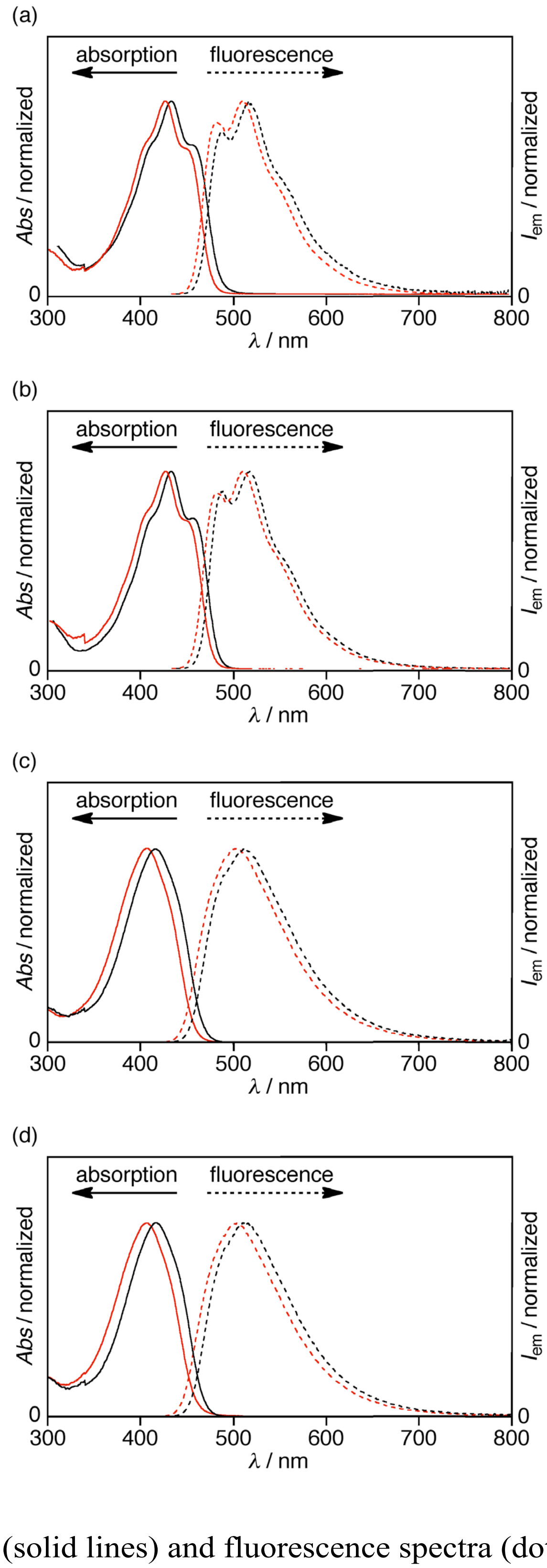


Fig. S2 UV-vis absorption (solid lines) and fluorescence spectra (dotted lines) of (a) **8**, (b) **9**, (c) **11**, and (d) **12** in CH_2Cl_2 (black) and in MeOH (red). λ_{ex} = absorption maxima.

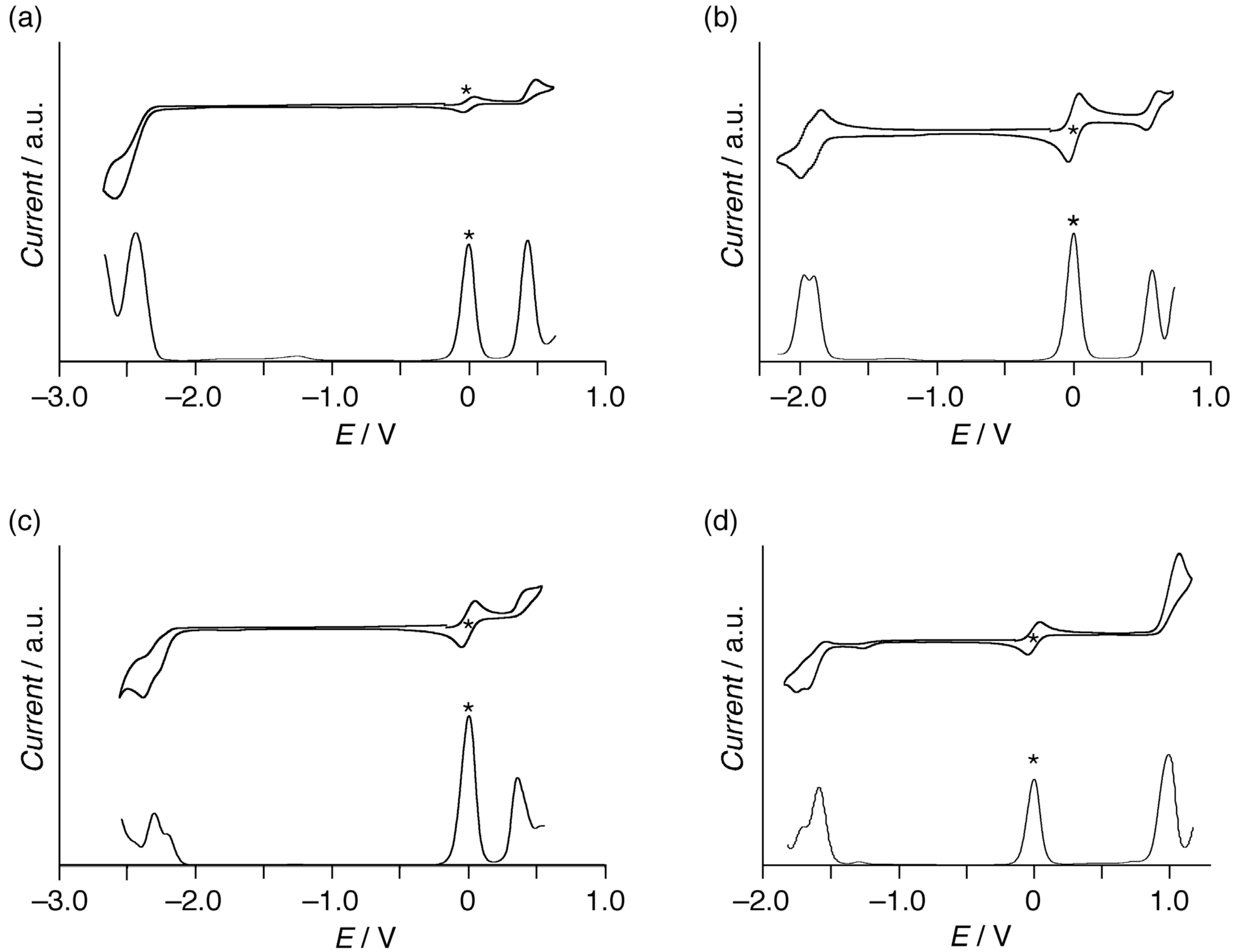
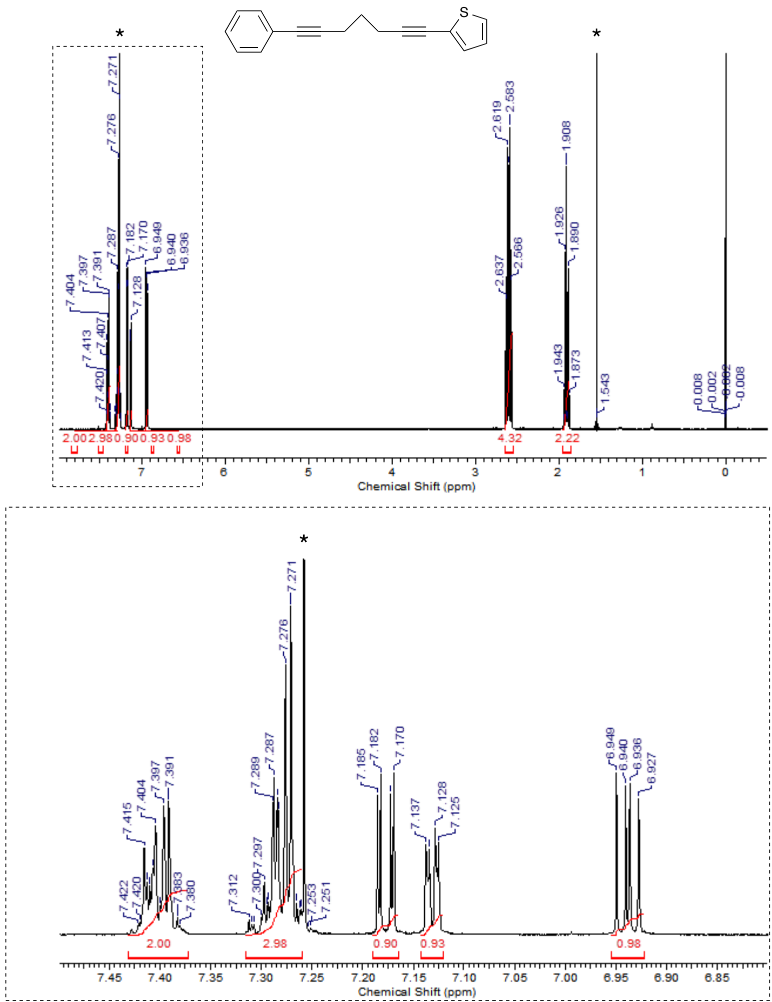


Fig. S3 Cyclic (upper) and differential pulse voltammograms (lower) of (a) **2a**, (b) **3**, (c) **7**, and (d) **9**. Measured in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as a supporting electrolyte; Ag/Ag^+ [$AgNO_3$ (MeCN)] as a reference electrode; scan rate 60 mV s^{-1}. Asterisk (*) indicates Fc/Fc^+.

^{1}H and ^{13}C{^{1}H} NMR Charts (**Figures S4–S20**) Asterisks (*) indicate the residual solvents.

(a)



(b)

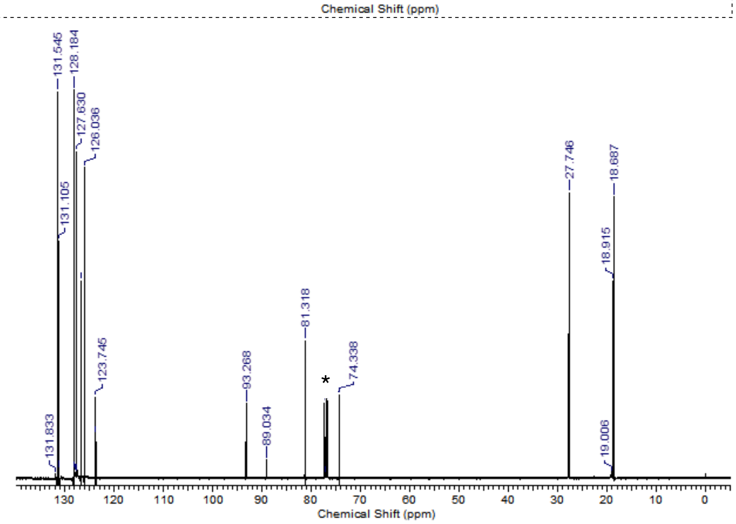
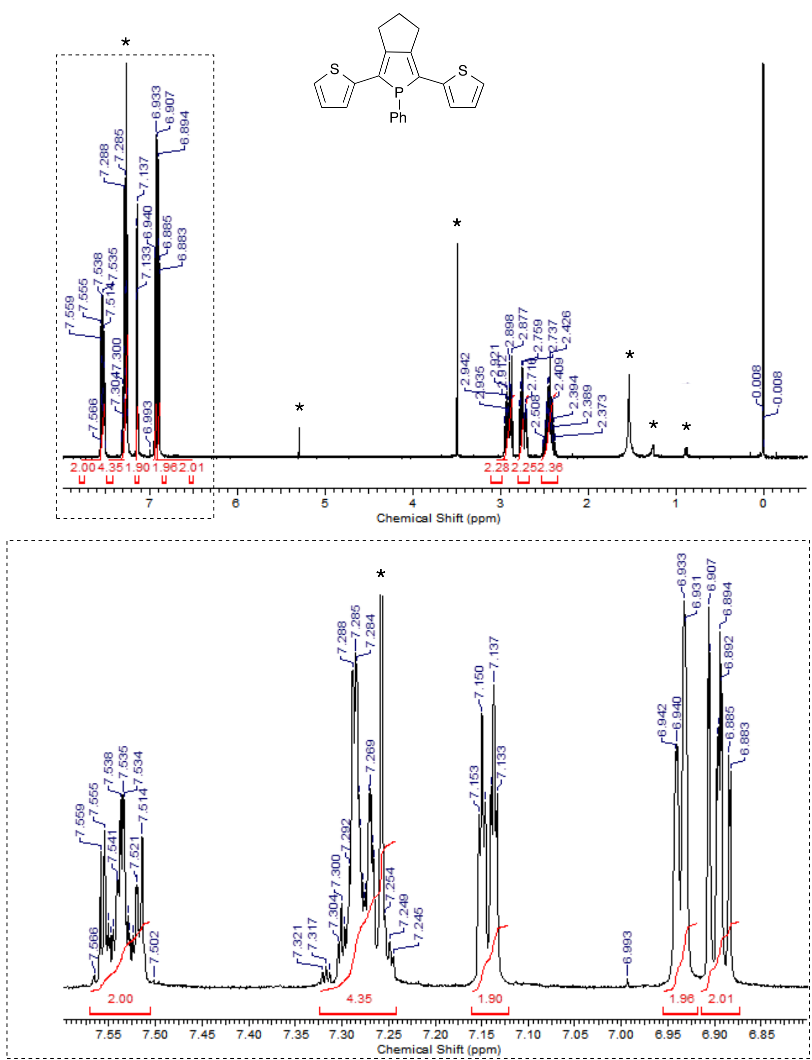


Fig. S4 (a) ^{1}H NMR and (b) ^{13}C{^{1}H} NMR spectra of **1b** in $CDCl_3$.

(a)



(b)

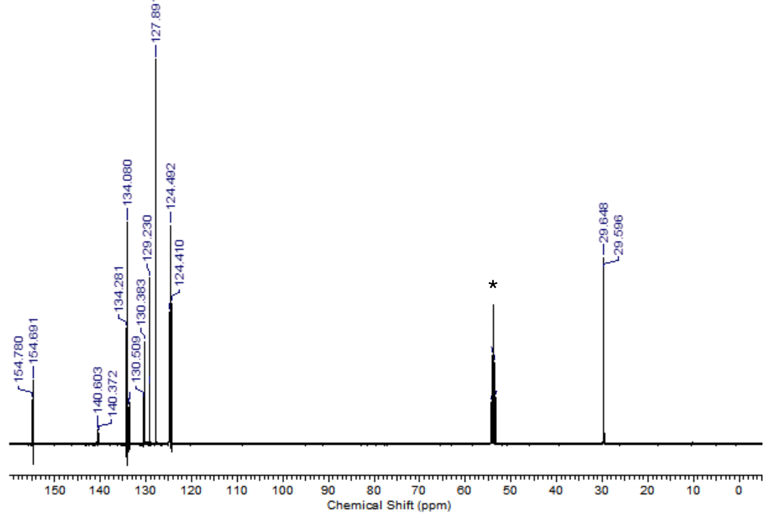


Fig. S5 (a) ^{1}H NMR (in $CDCl_3$) and (b) $^{13}C\{^1H\}$ NMR spectra (in CD_2Cl_2) of **2a**.

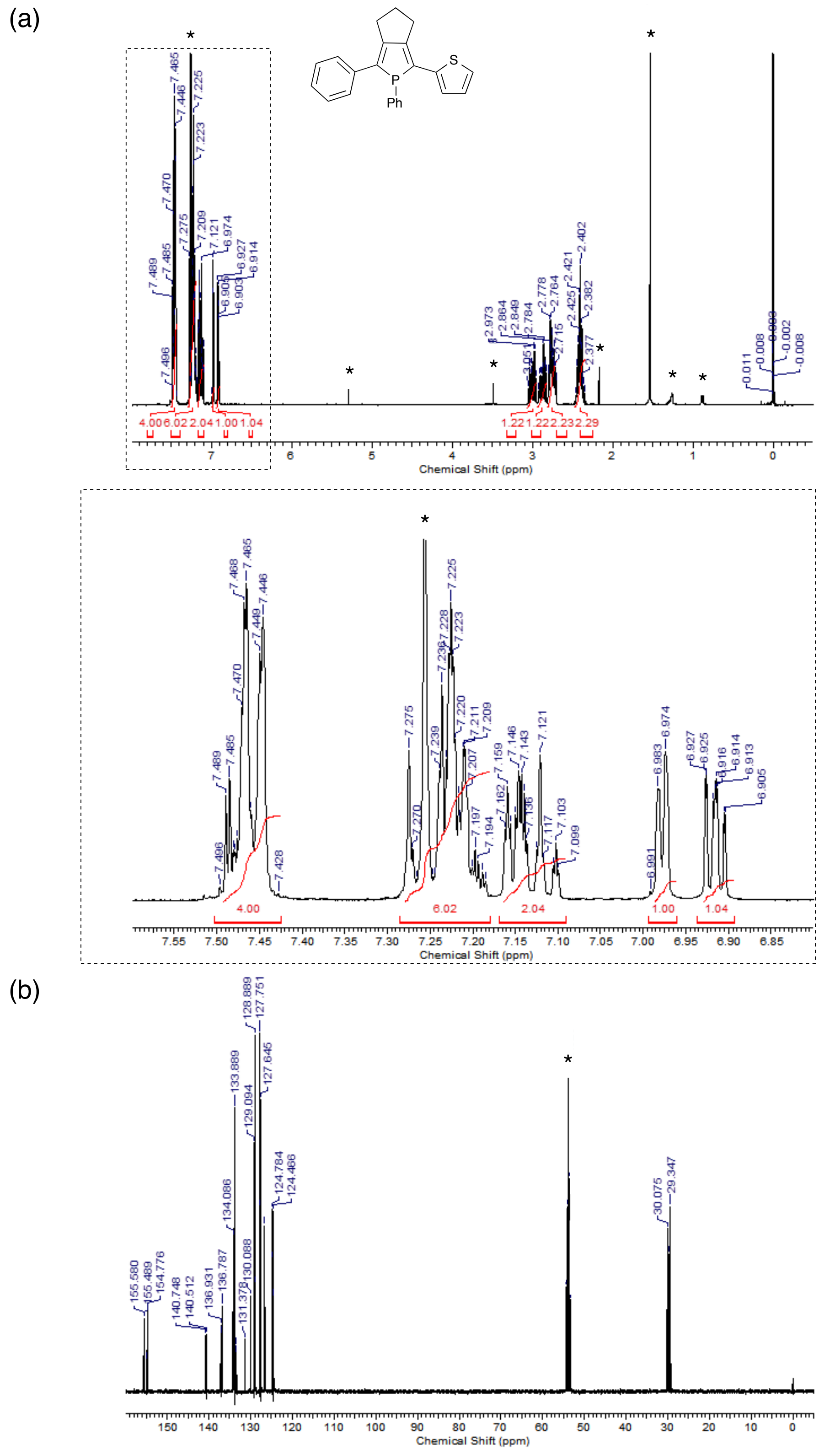


Fig. S6 (a) ^{1}H NMR (in $CDCl_3$) and (b) $^{13}C\{^{1}H\}$ NMR spectra (in CD_2Cl_2) of **2b**.

(a)

(b)

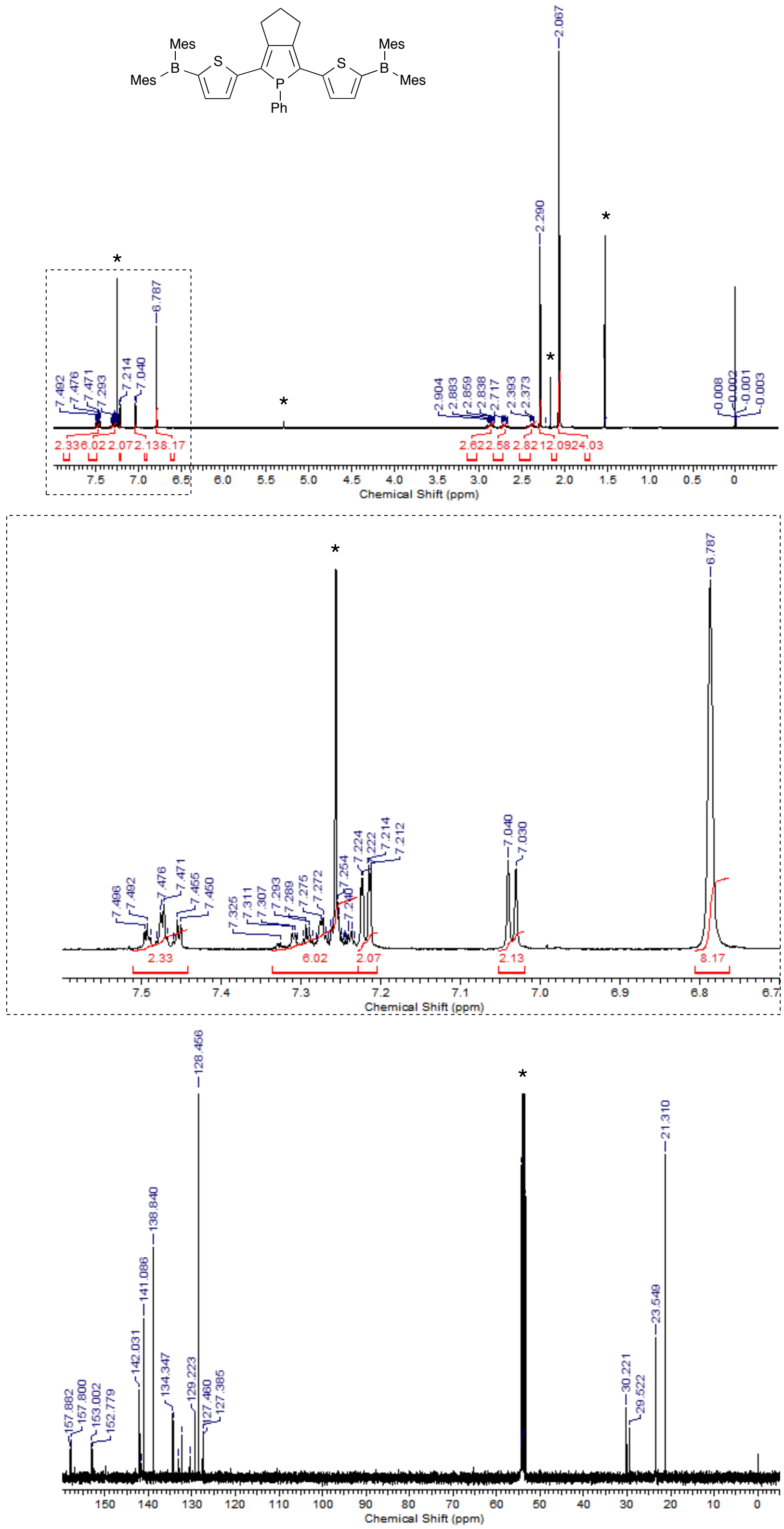
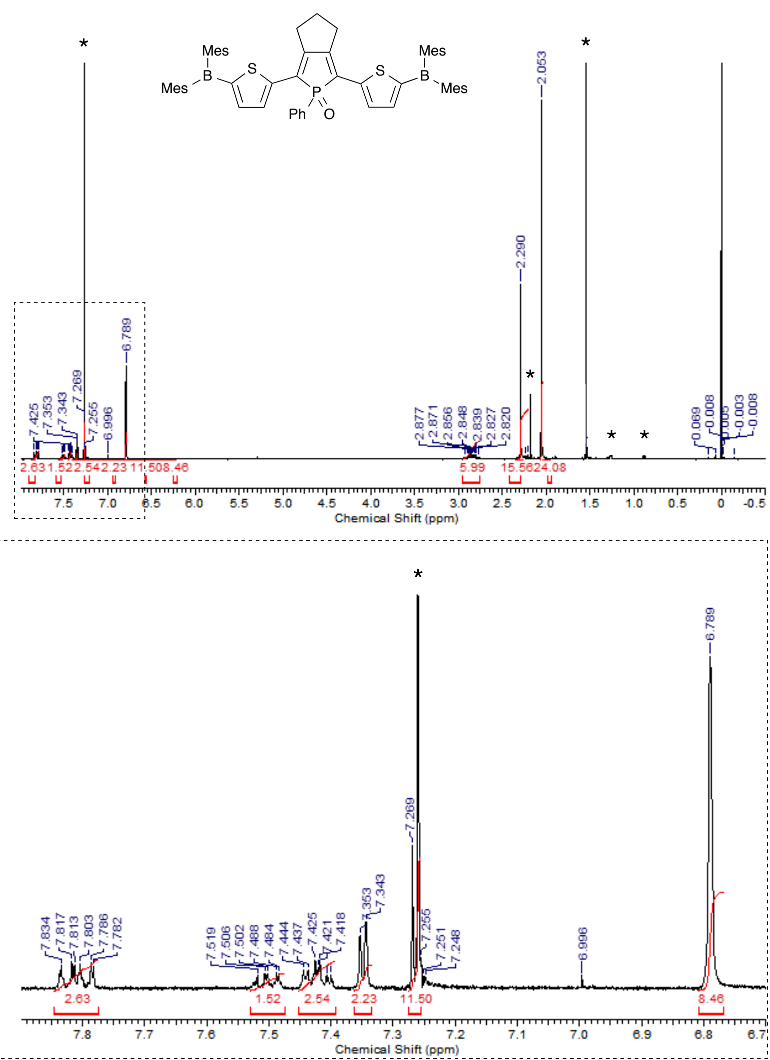


Fig. S7 (a) ^{1}H NMR (in $CDCl_3$) and (b) $^{13}C\{^{1}H\}$ NMR spectra (in CD_2Cl_2) of **3**.

(a)



(b)

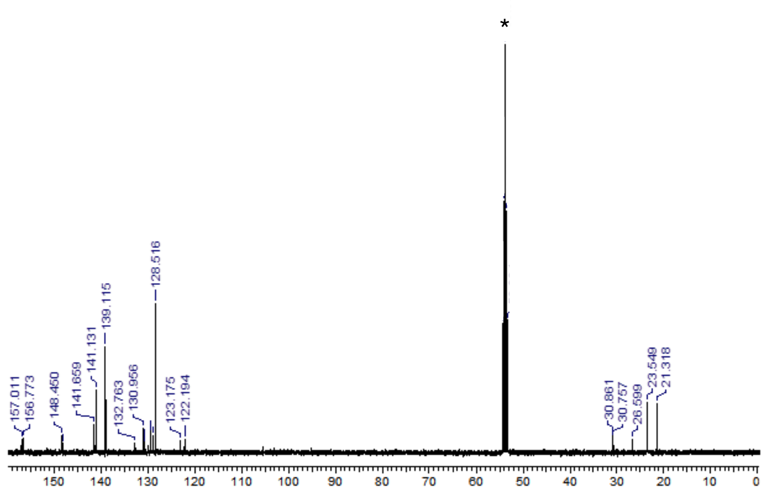
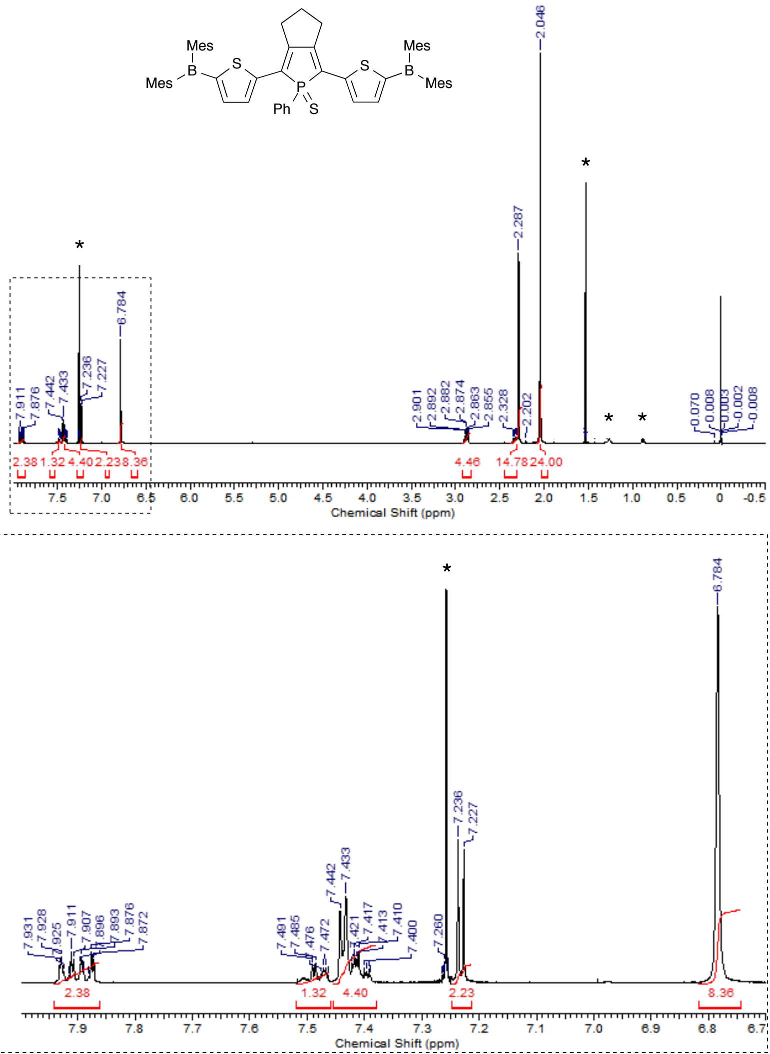


Fig. S8 (a) ^{1}H NMR (in $CDCl_3$) and (b) $^{13}C\{^{1}H\}$ NMR spectra (in CD_2Cl_2) of **4**.

(a)



(b)

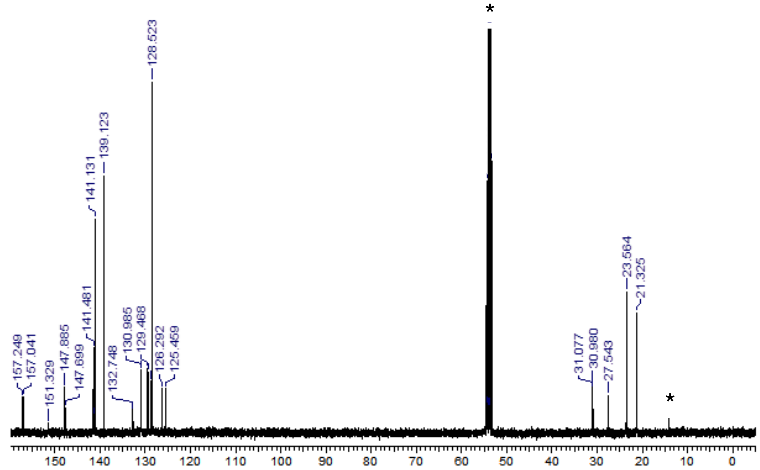


Fig. S9 (a) ^{1}H NMR (in $CDCl_3$) and (b) $^{13}C\{^{1}H\}$ NMR spectra (in CD_2Cl_2) of **5**.

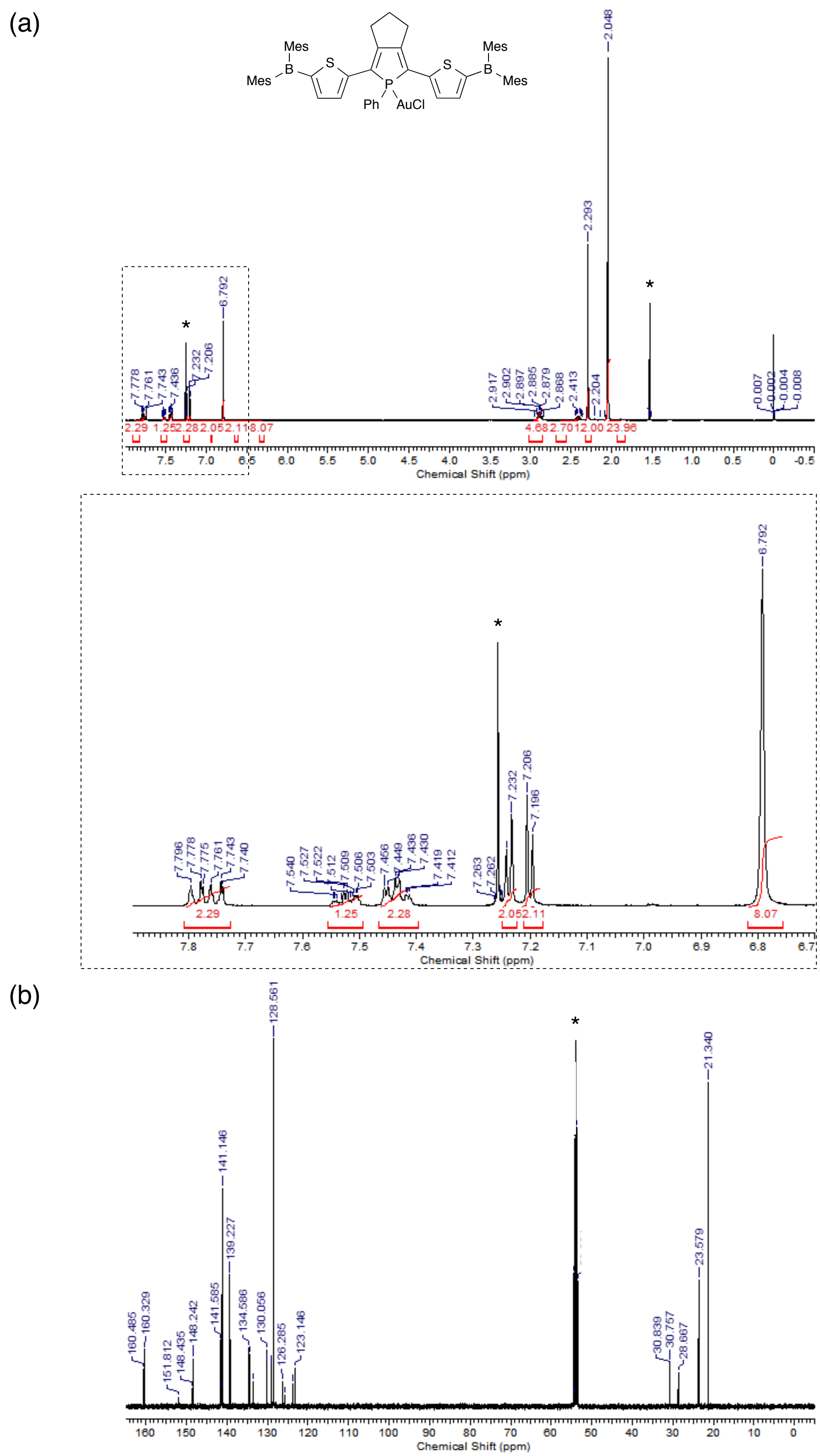


Fig. S10 (a) ^{1}H NMR (in $CDCl_3$) and (b) $^{13}C\{^{1}H\}$ NMR spectra (in CD_2Cl_2) of **6**.

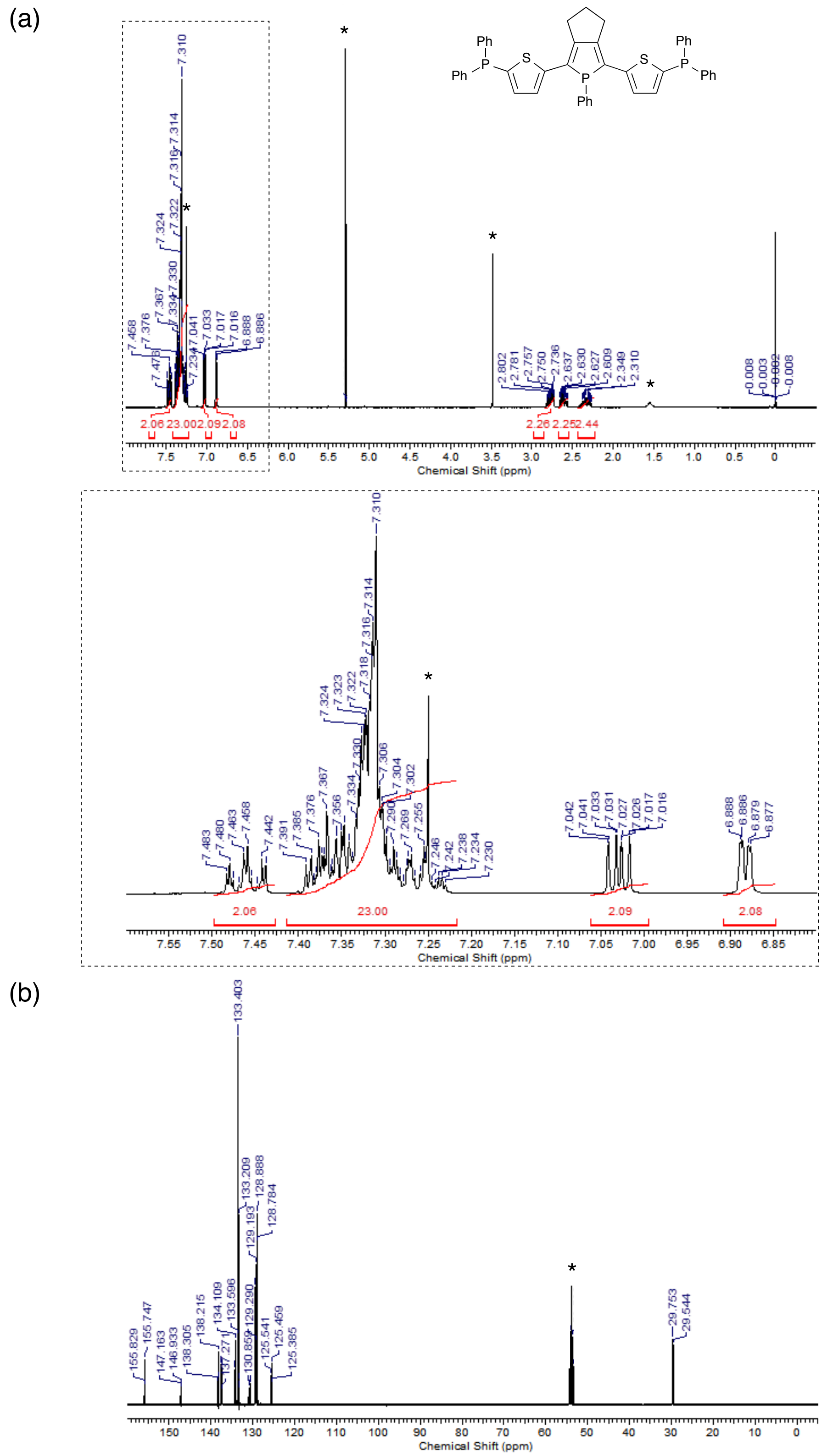
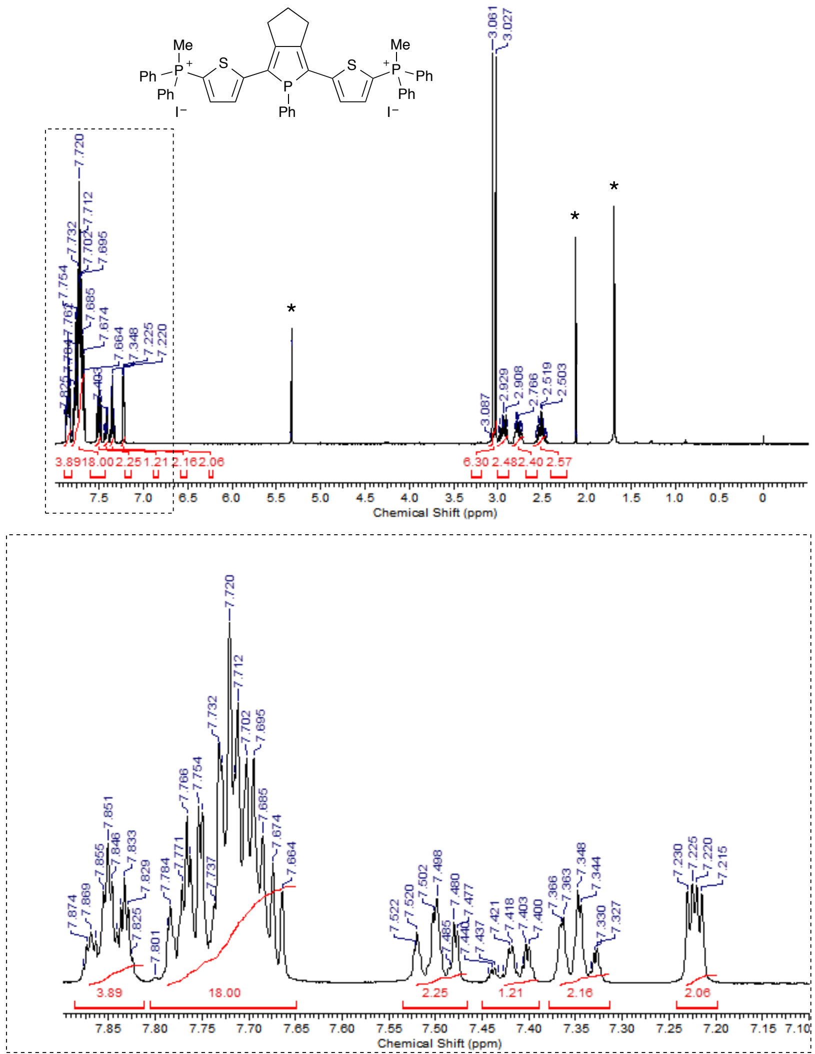


Fig. S11 (a) ^{1}H NMR (in $CDCl_3$) and (b) $^{13}C\{^{1}H\}$ NMR spectra (in CD_2Cl_2) of **7**.

(a)



(b)

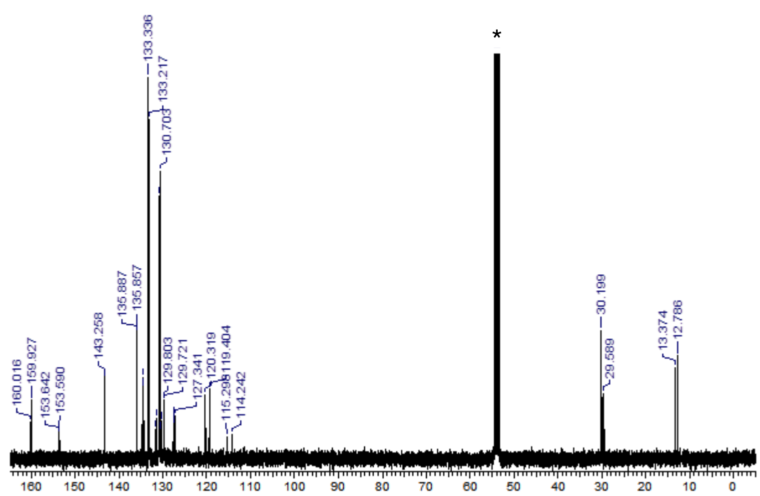


Fig. S12 (a) ^{1}H NMR and (b) $^{13}C\{^{1}H\}$ NMR spectra of **8** in CD_2Cl_2.

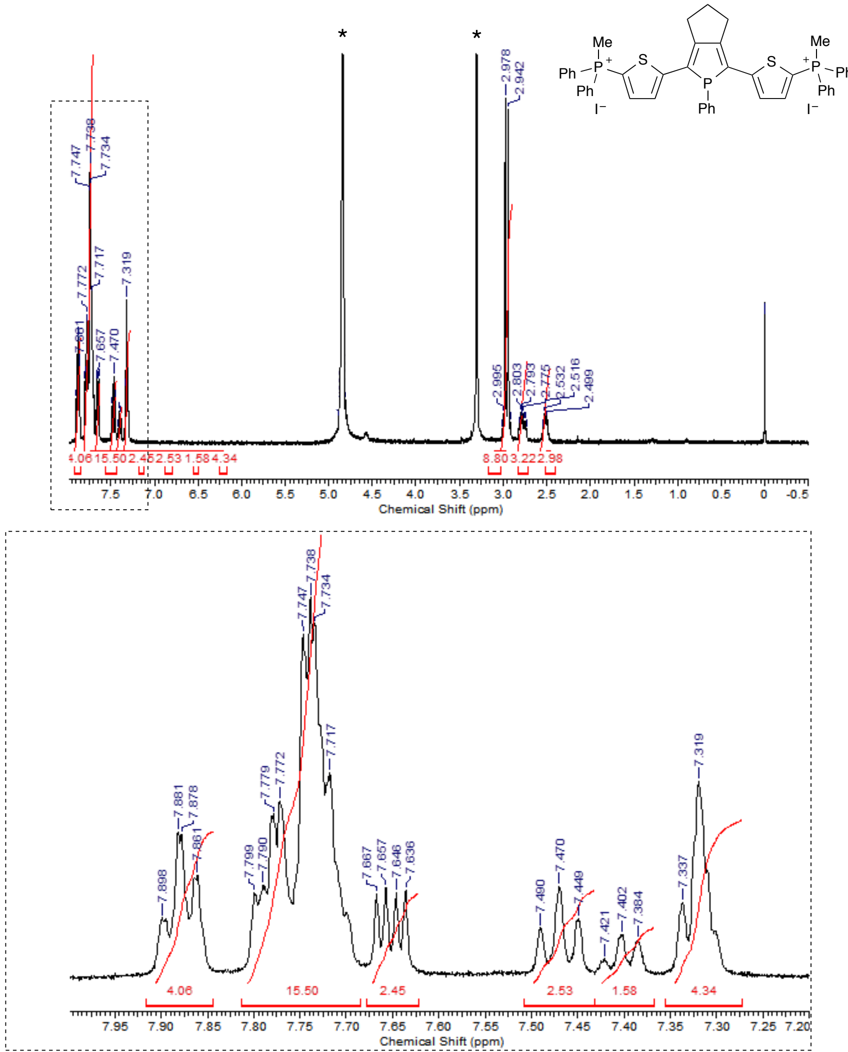


Fig. S13 ^{1}H NMR spectra of **8** in CD_3OD.

(a)

(b)

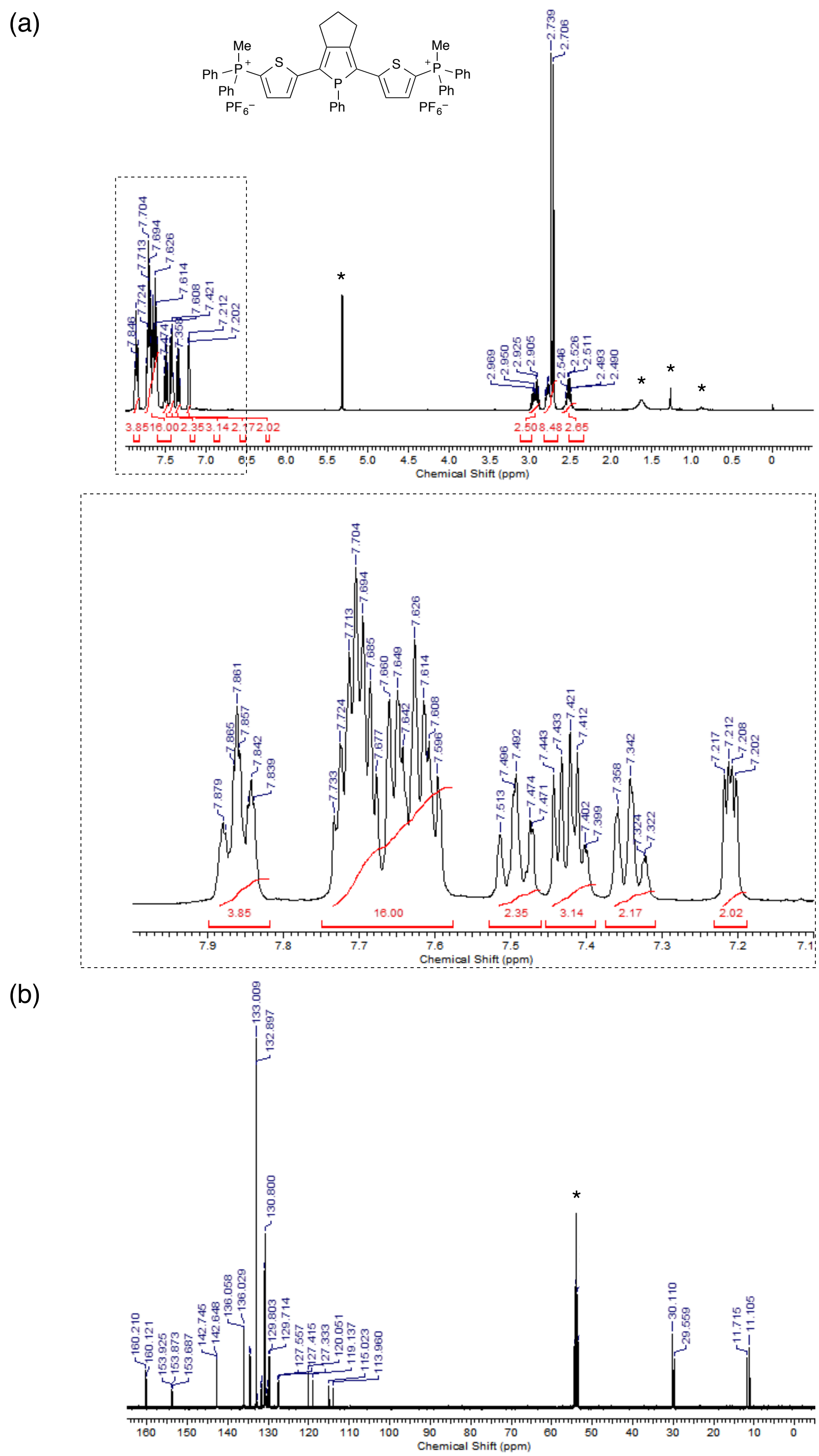


Fig. S14 (a) ^{1}H NMR and (b) ^{13}C{^{1}H} NMR spectra of **9** in CD_2Cl_2.

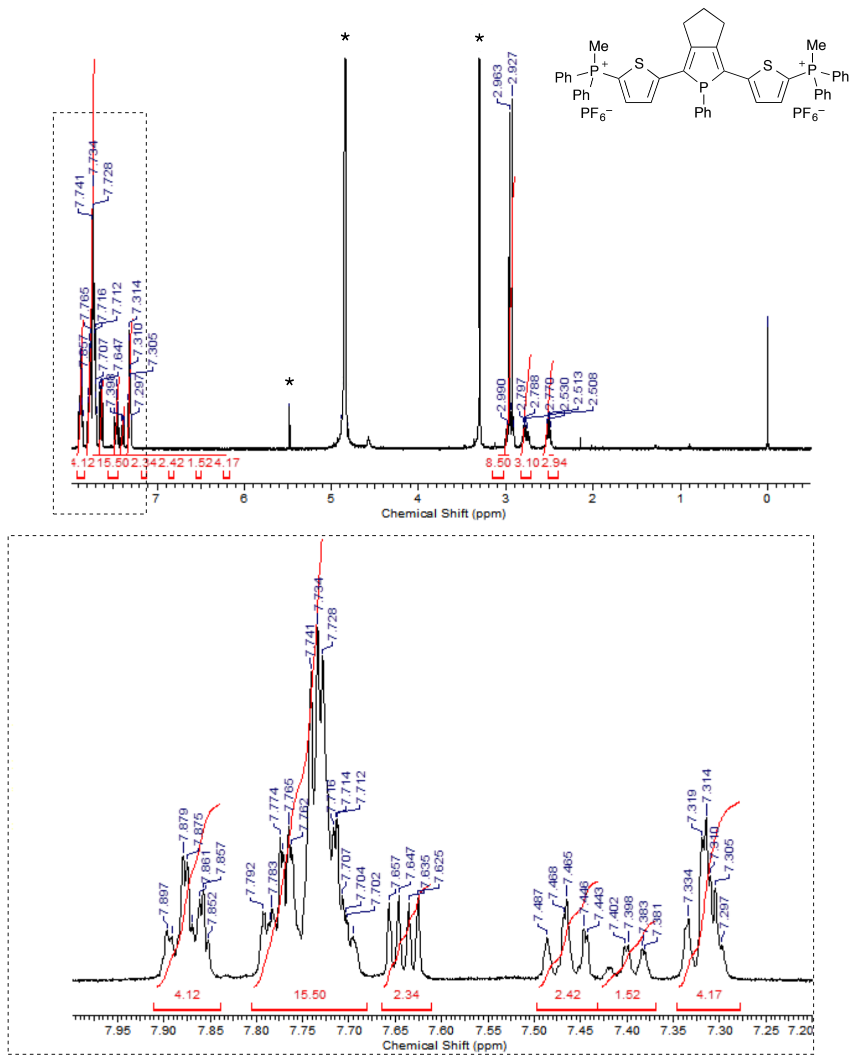


Fig. S15 ^{1}H NMR spectra of **9** in CD_3OD.

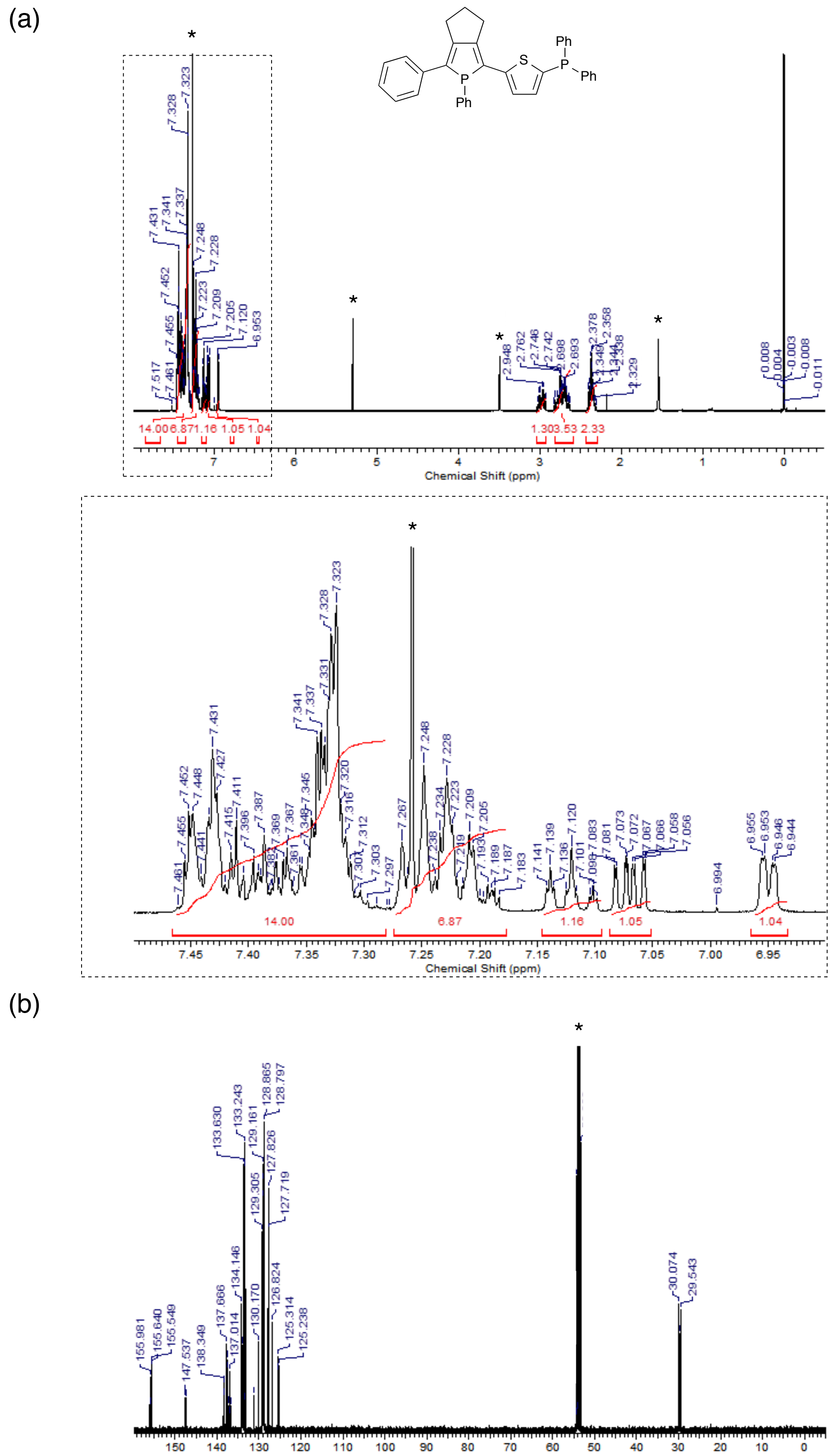


Fig. S16 (a) ^{1}H NMR (in $CDCl_3$) and (b) $^{13}C\{^{1}H\}$ NMR spectra (in CD_2Cl_2) of **10**.

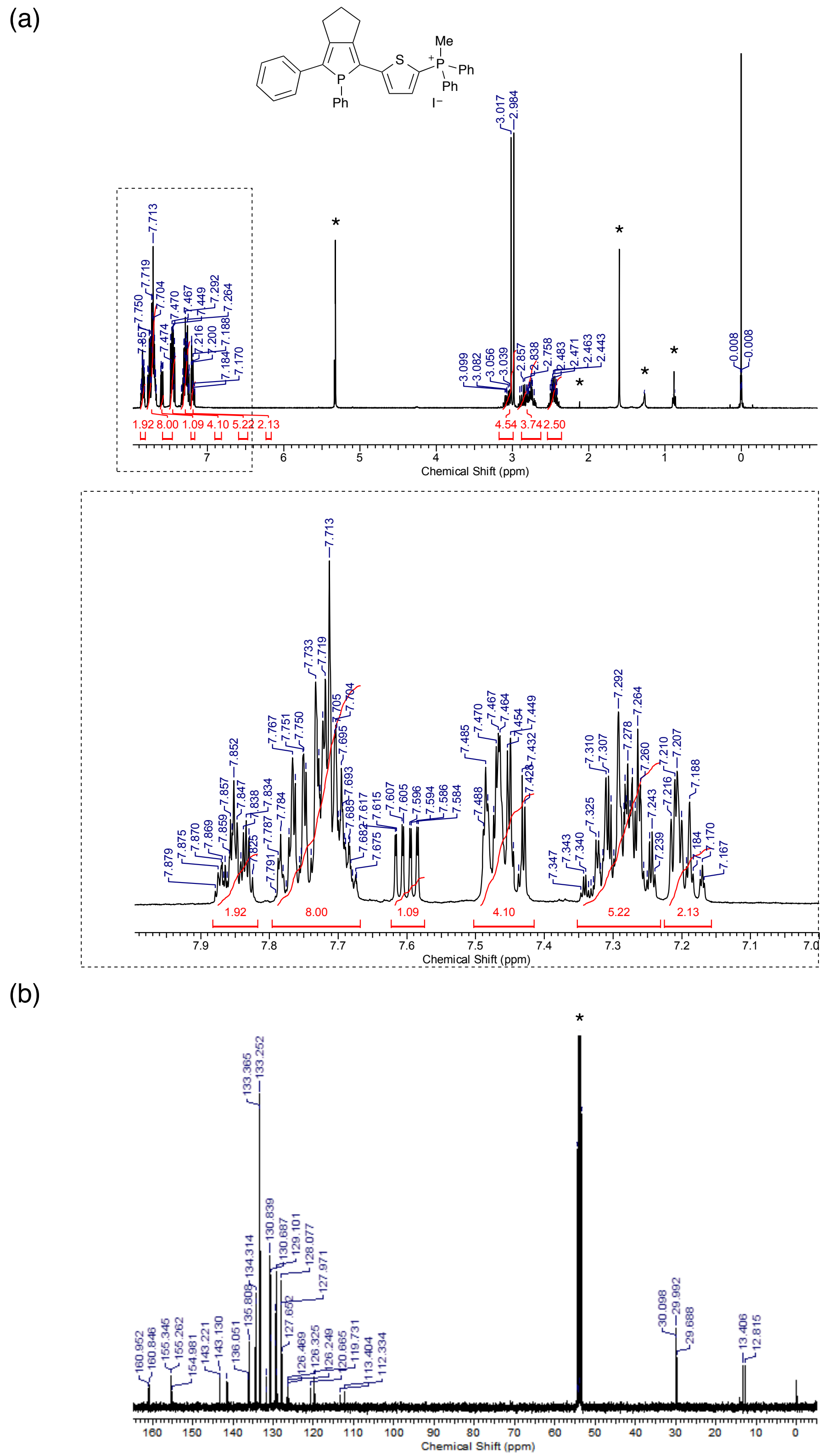


Fig. S17 (a) ^{1}H NMR and (b) $^{13}C\{^{1}H\}$ NMR spectra of **11** in CD_2Cl_2.

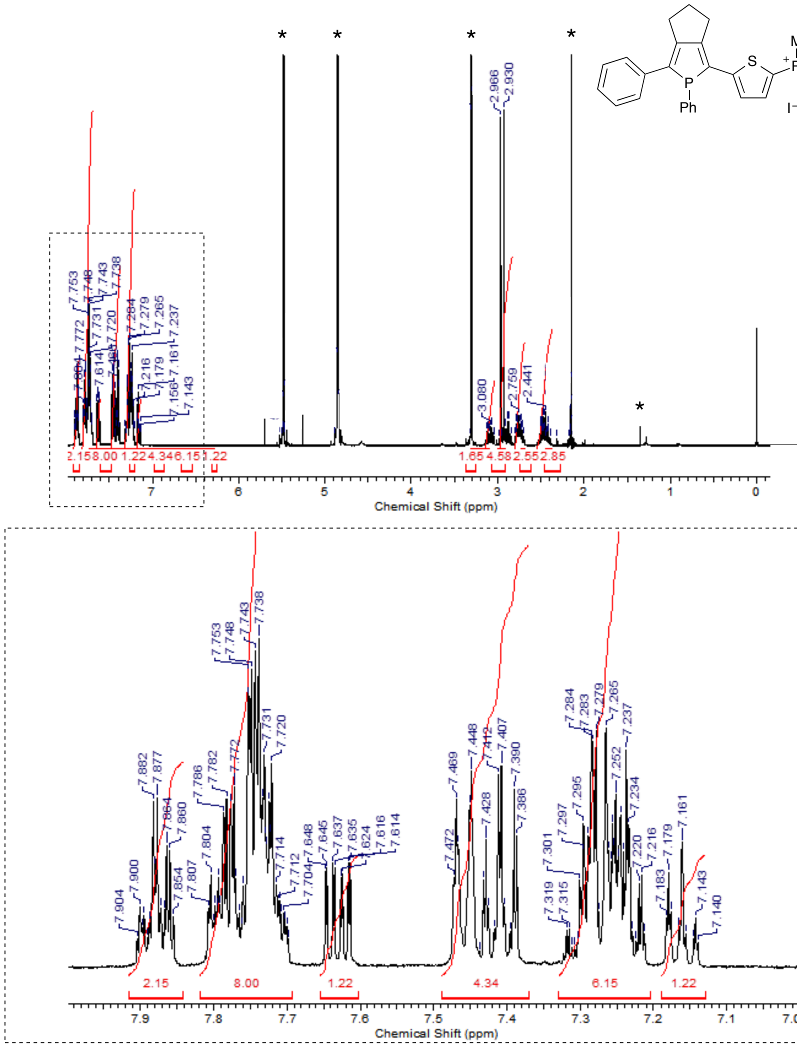
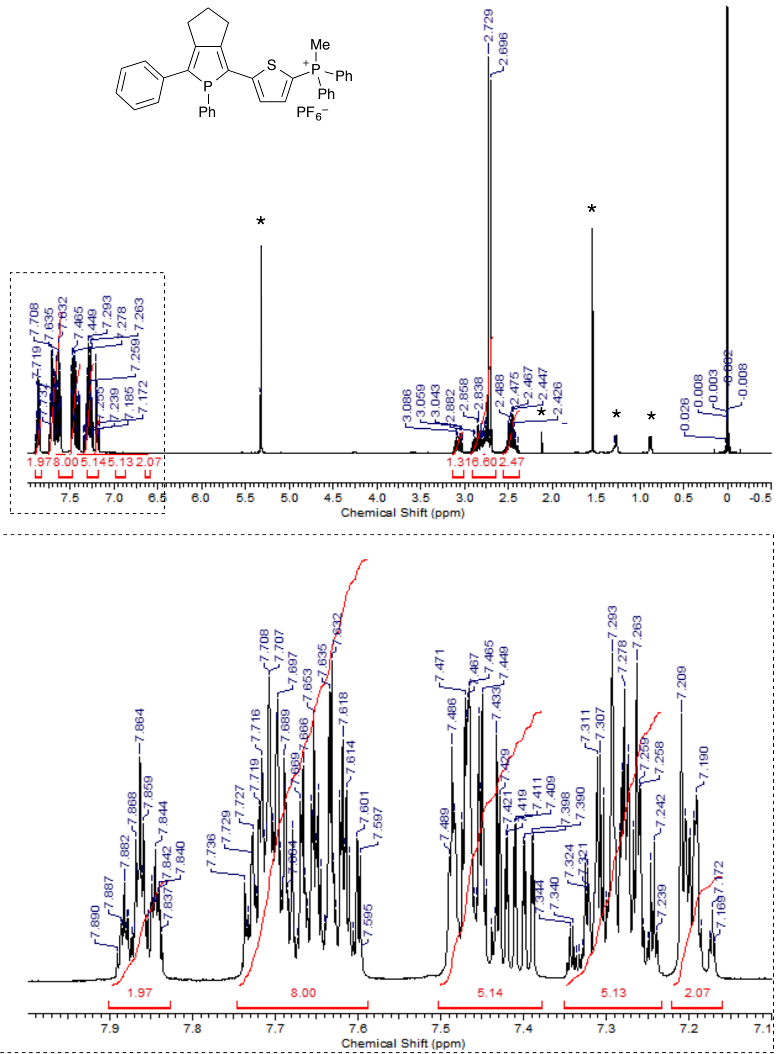


Fig. S18 ^{1}H NMR spectra of **11** in CD_3OD.

(a)



(b)

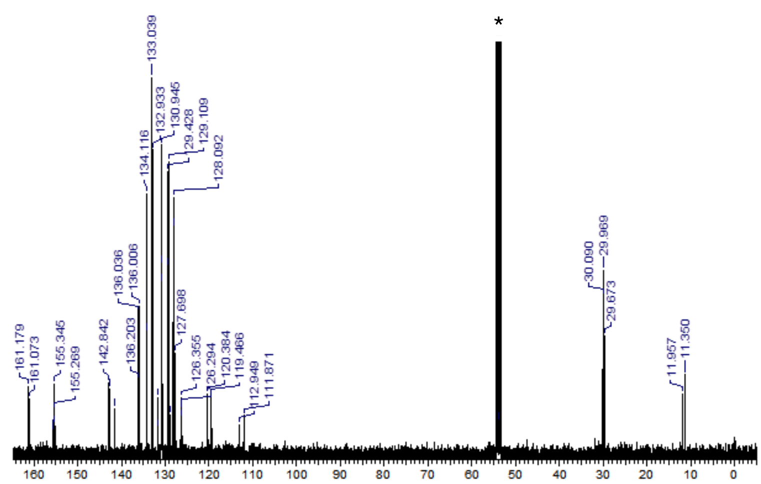


Fig. S19 (a) ^{1}H NMR and (b) $^{13}C\{^{1}H\}$ NMR spectra of **12** in CD_2Cl_2.

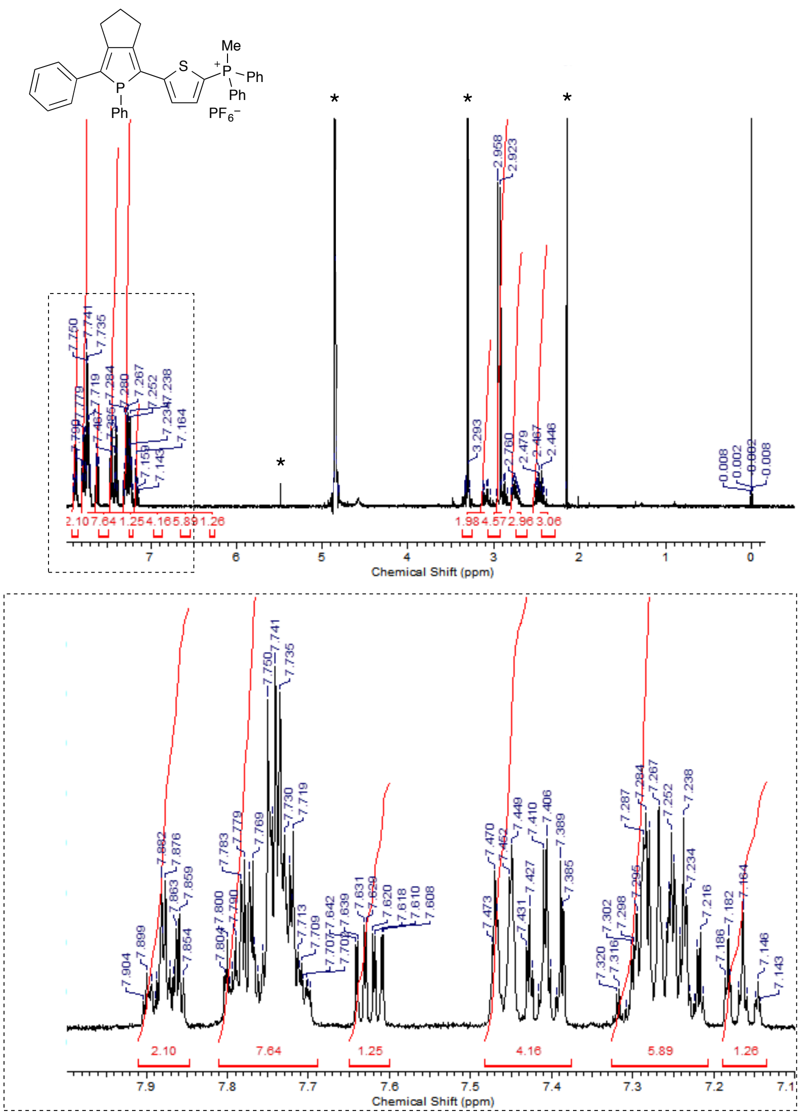


Fig. S20 ^{1}H NMR spectra of **12** in CD_3OD.