Supporting Information

Zwitterionic Ladder Stilbenes with Phosphonium and Borate-Bridges: Intramolecular Cascade Cyclization and Structure-Photophysical Properties Relationship

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1. NMR Spectra

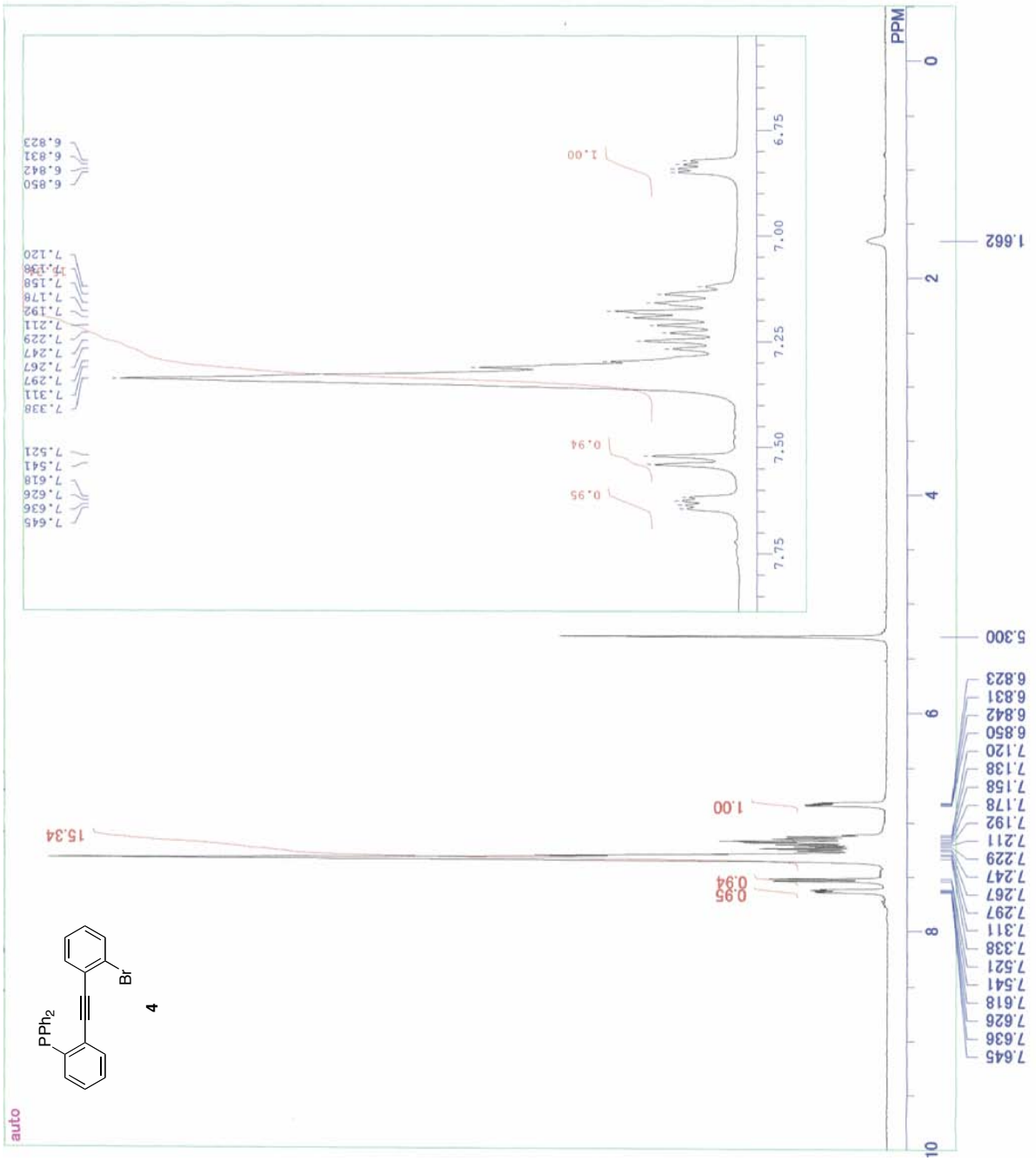

Figure S1. ^{1}H NMR spectrum of **4** (400 MHz, CD_2Cl_2).

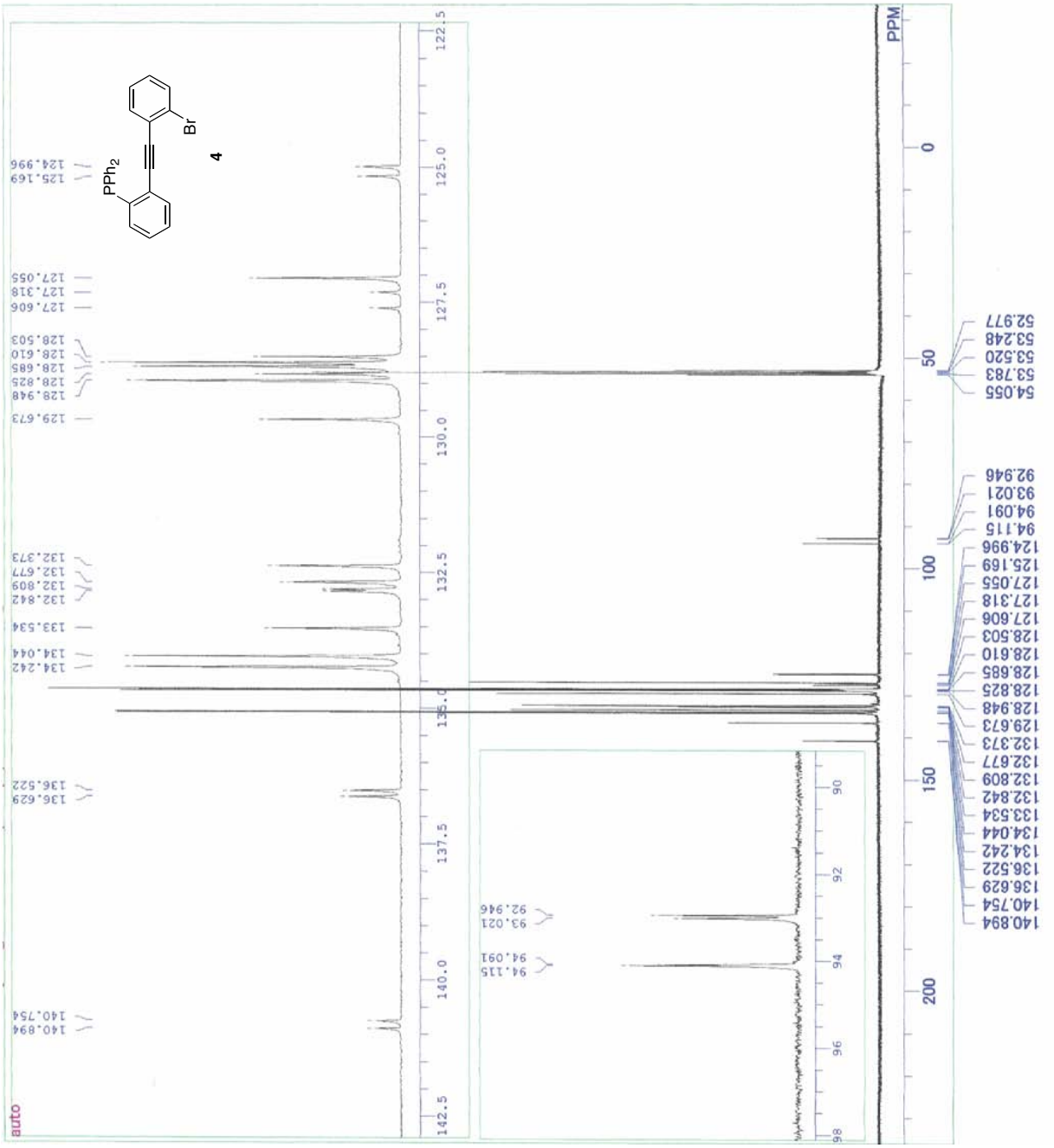

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **4** (100 MHz, CD_2Cl_2).

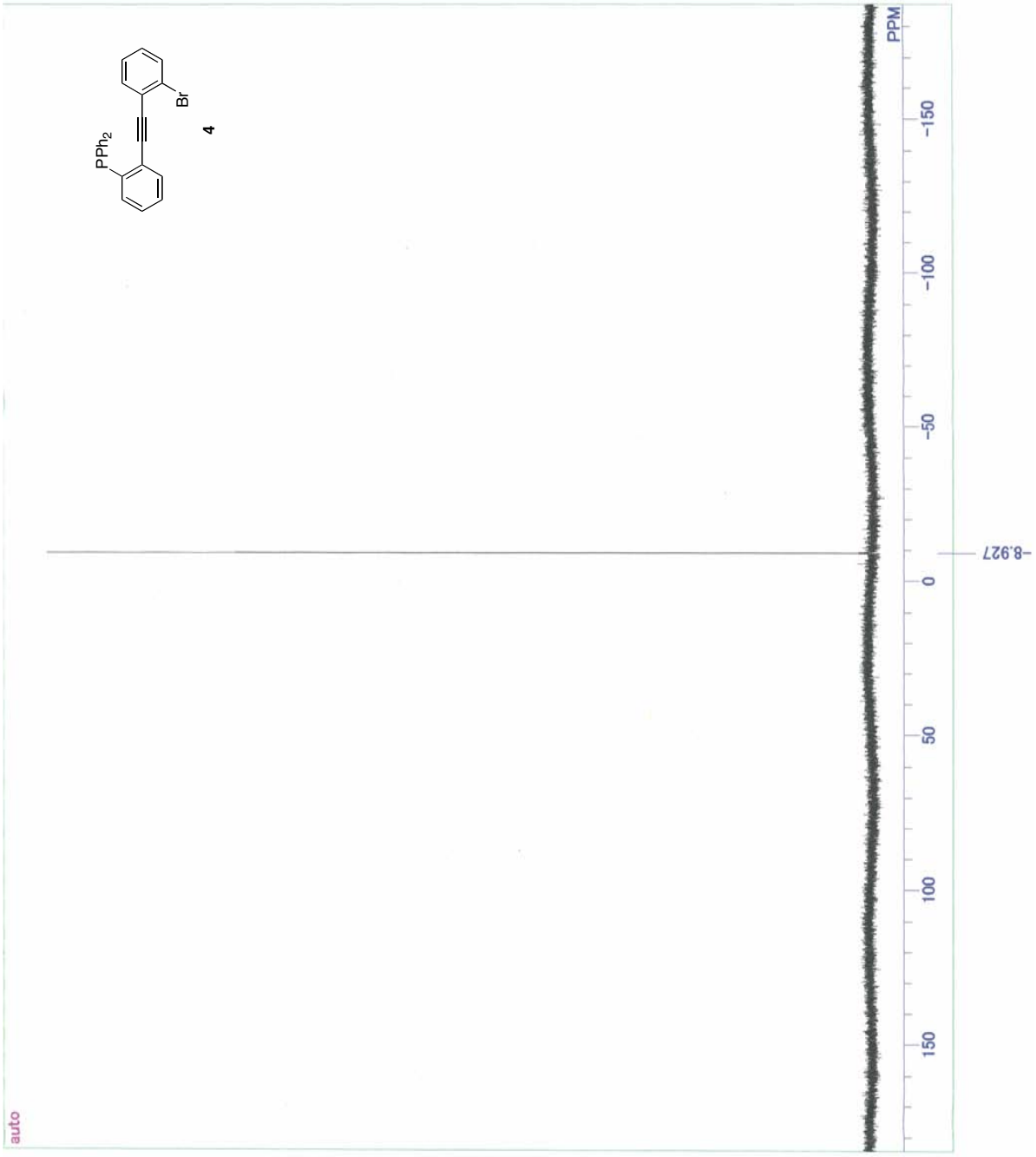

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **4** (162 MHz, CD_2Cl_2).

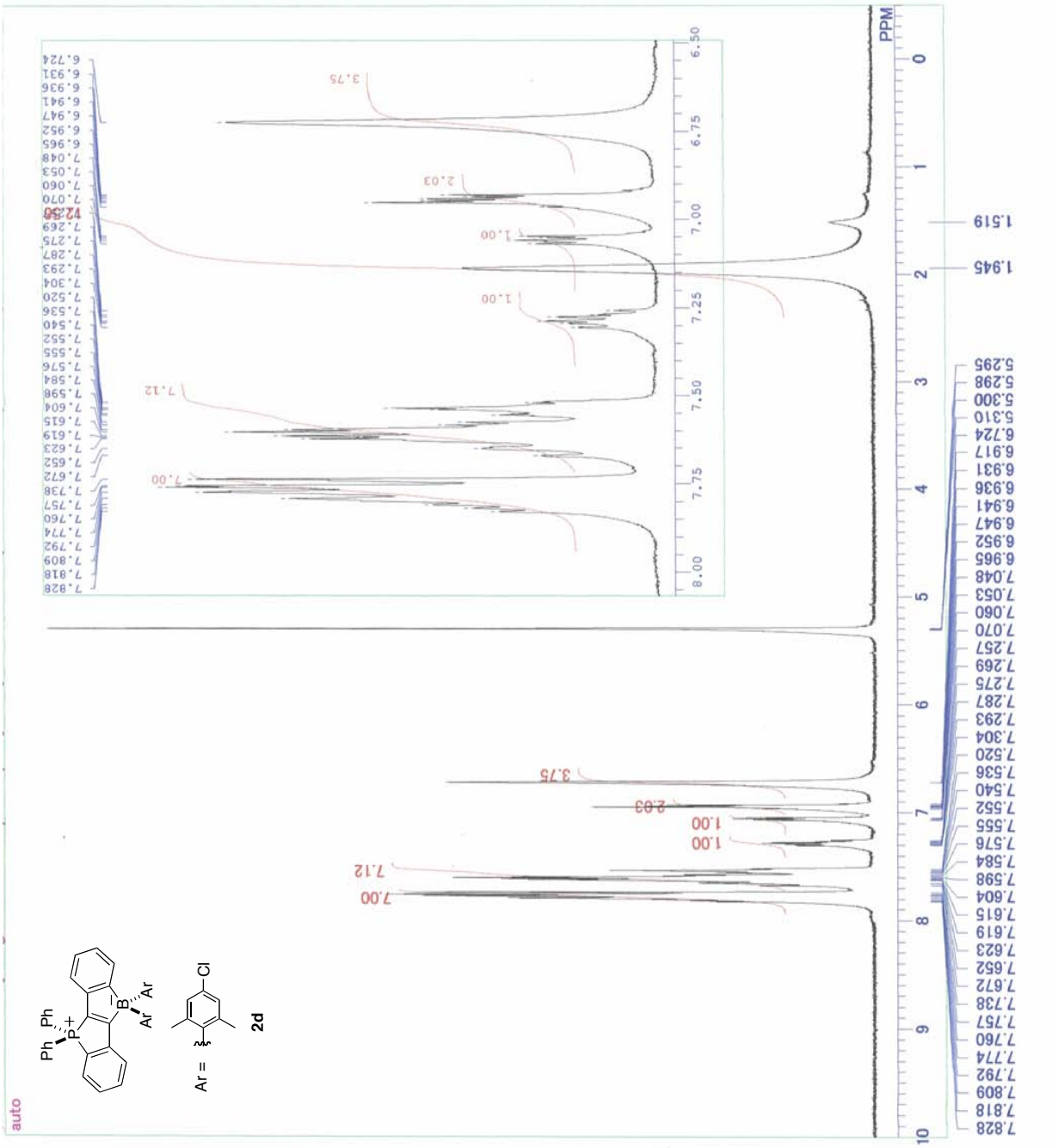

Figure S4. ^{1}H NMR spectrum of **2d** (400 MHz, CD_2Cl_2).

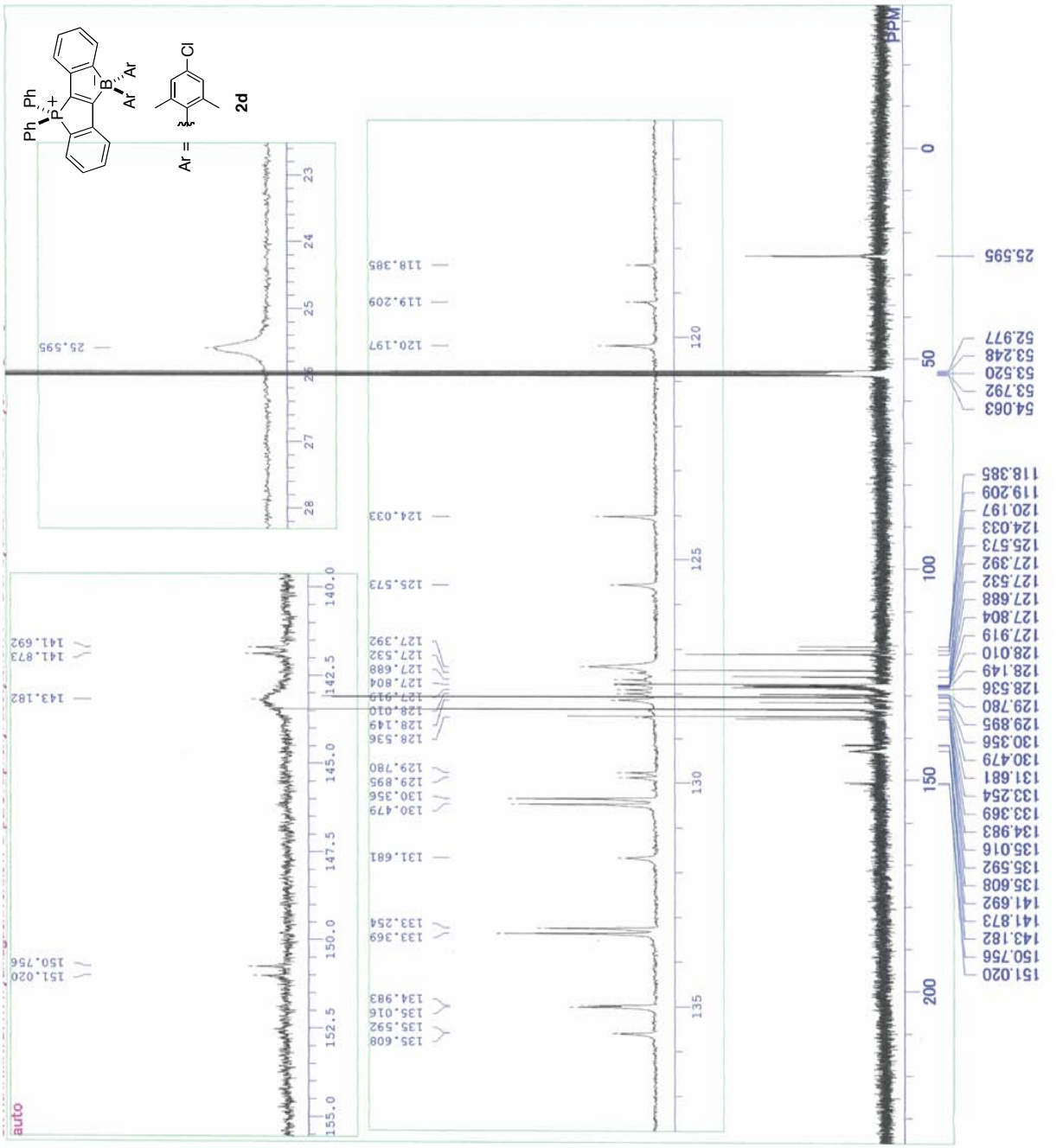

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **2d** (100 MHz, CD_2Cl_2).

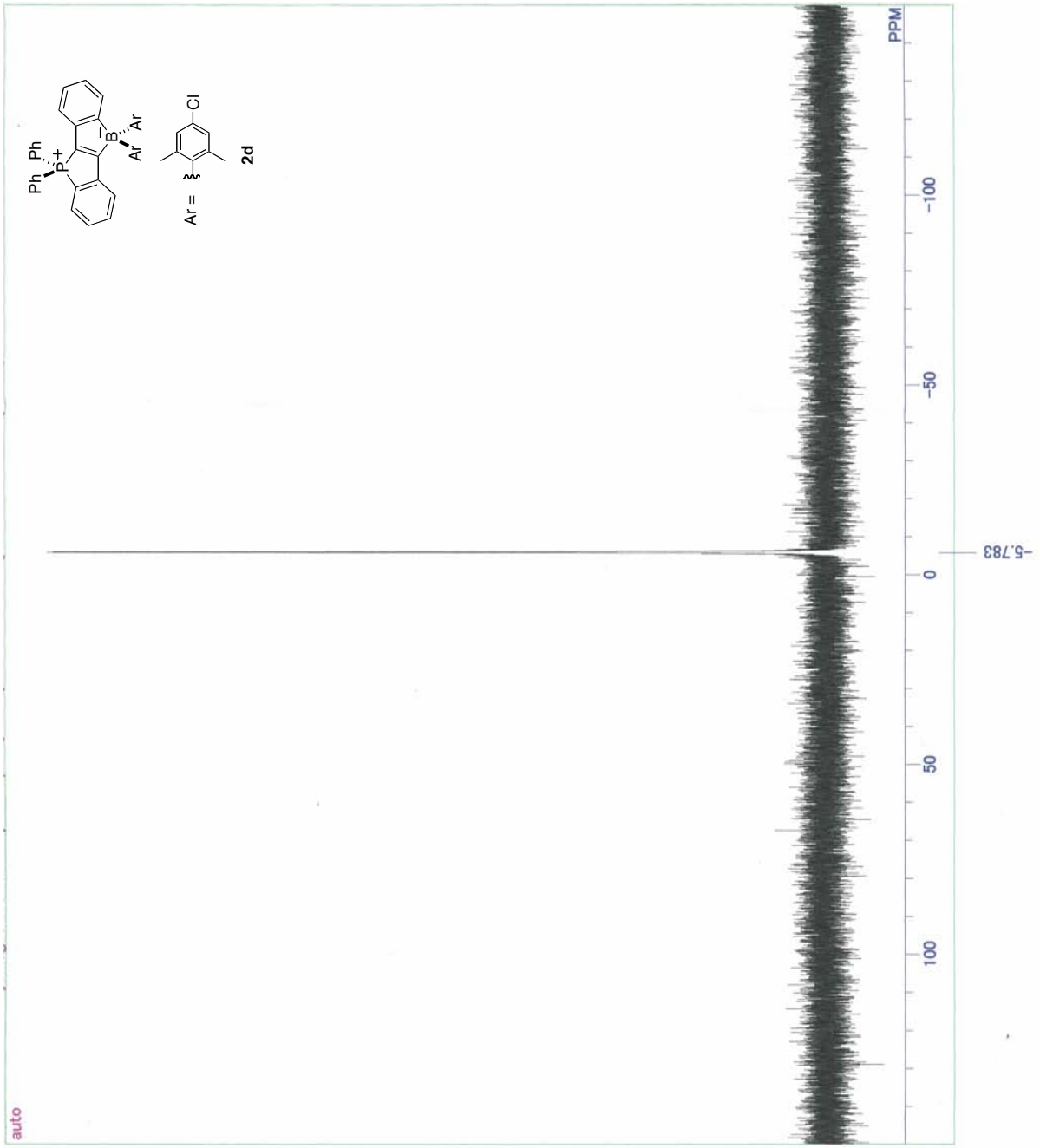

Figure S6. $^{11}B\{^{1}H\}$ NMR spectrum of **2d** (128 MHz, CD_2Cl_2).

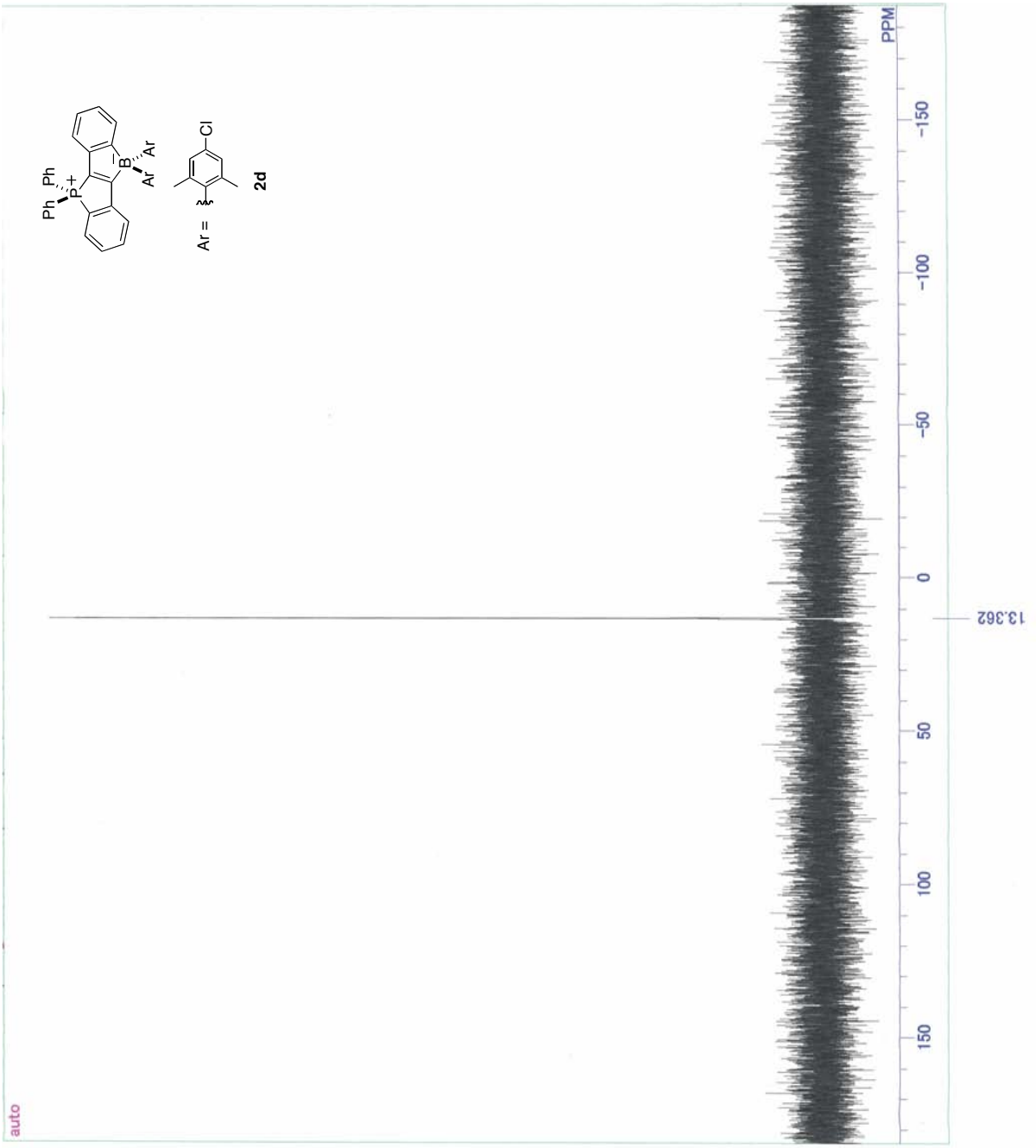

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of **2d** (162 MHz, CD_2Cl_2).

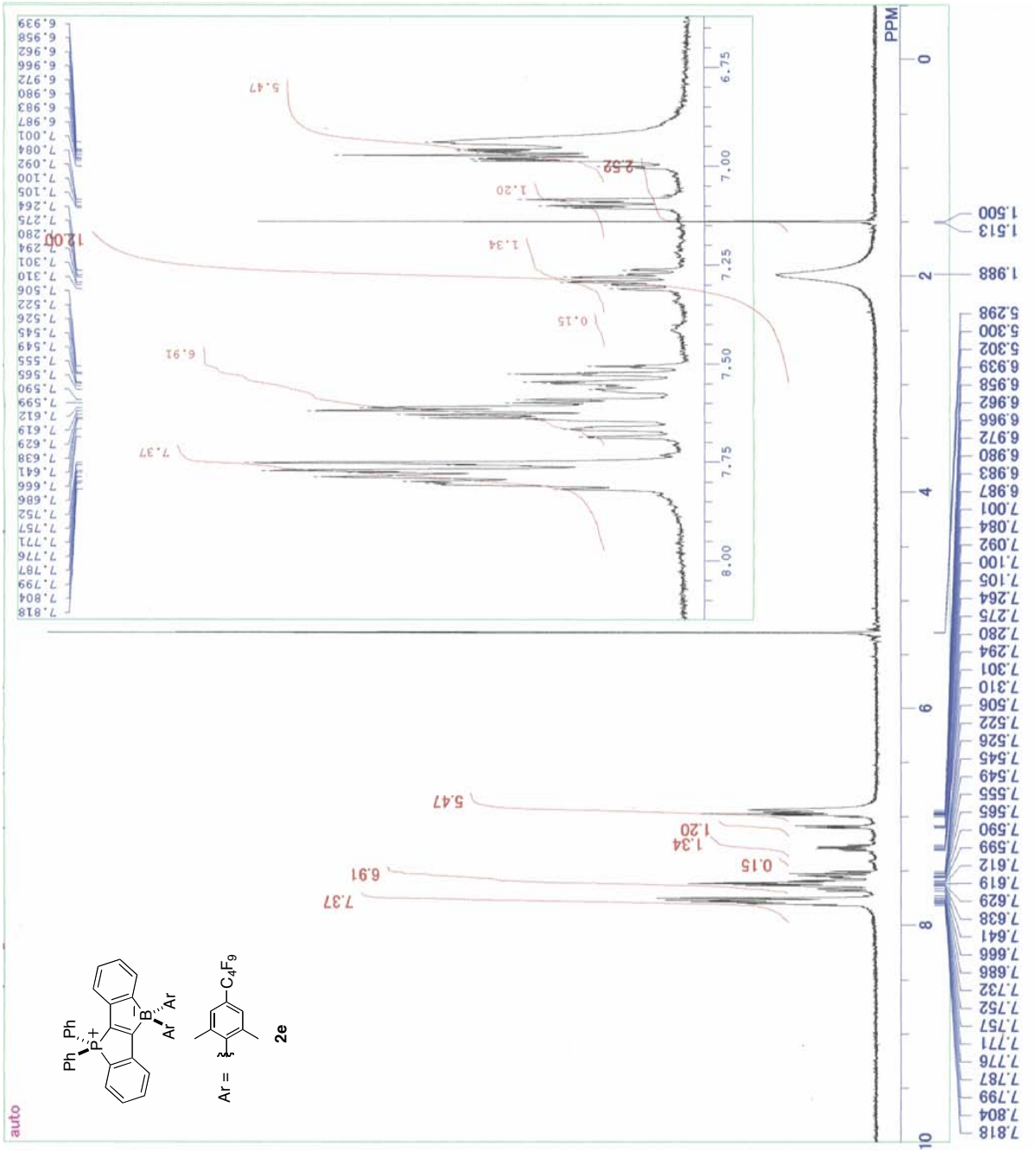

Figure S8. ^{1}H NMR spectrum of **2e** (400 MHz, CD_2Cl_2).

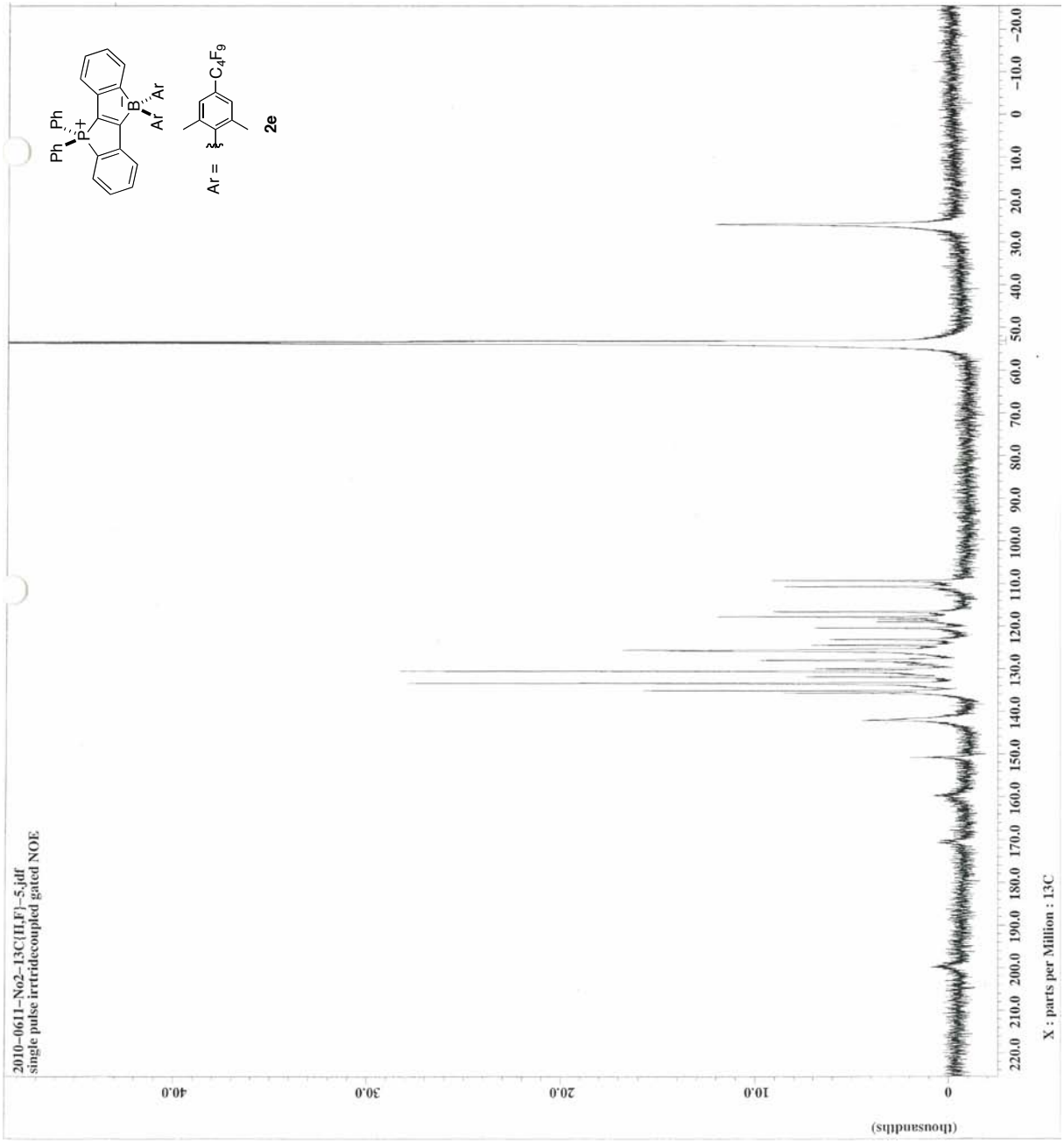

Figure S9. $^{13}C\{^{1}H,^{19}F\}$ NMR spectrum of **2e** (150 MHz, CD_2Cl_2).

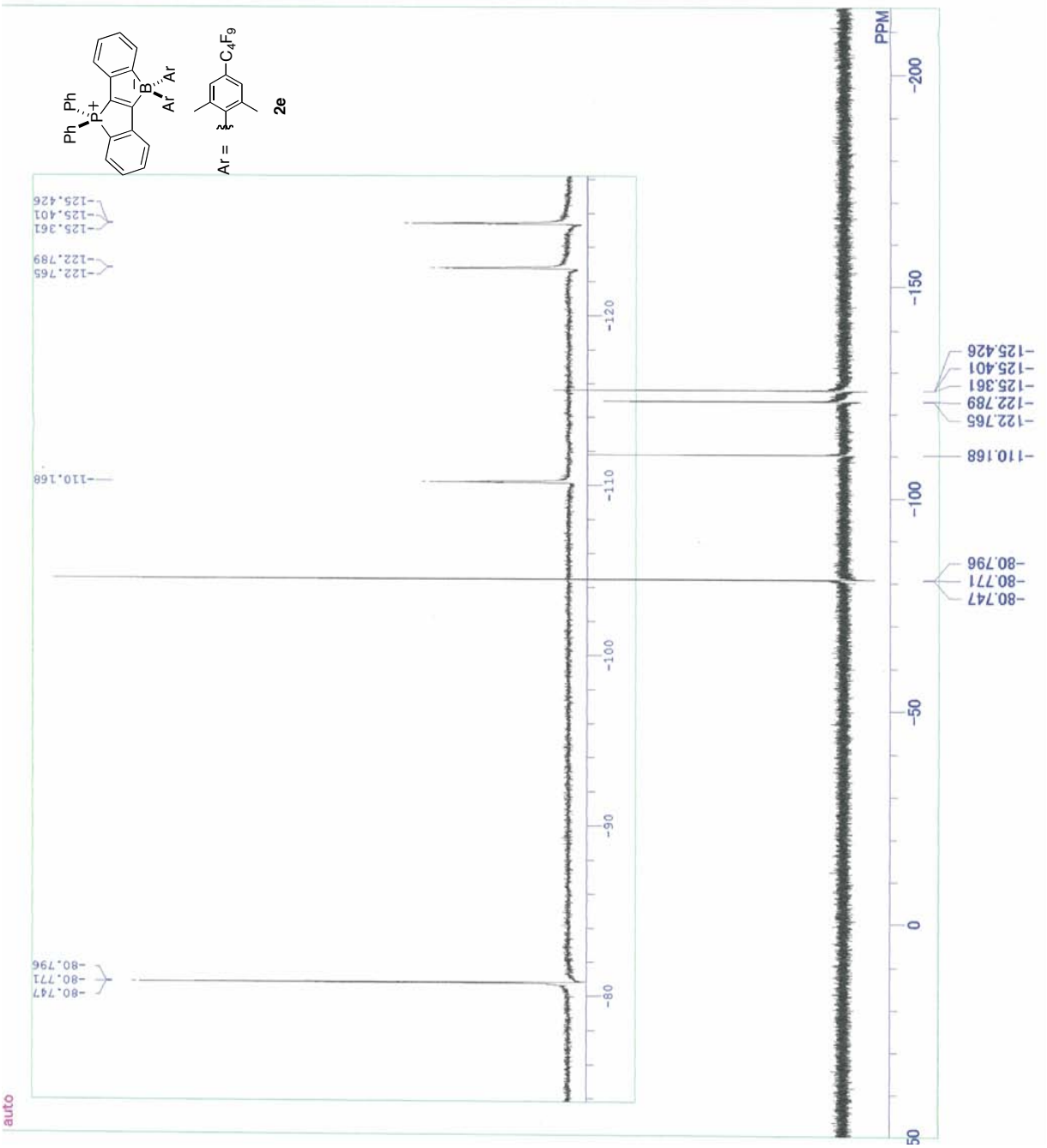

Figure S10. $^{19}F\{^{1}H\}$ NMR spectrum of **2e** (376 MHz, $CDCl_3$).

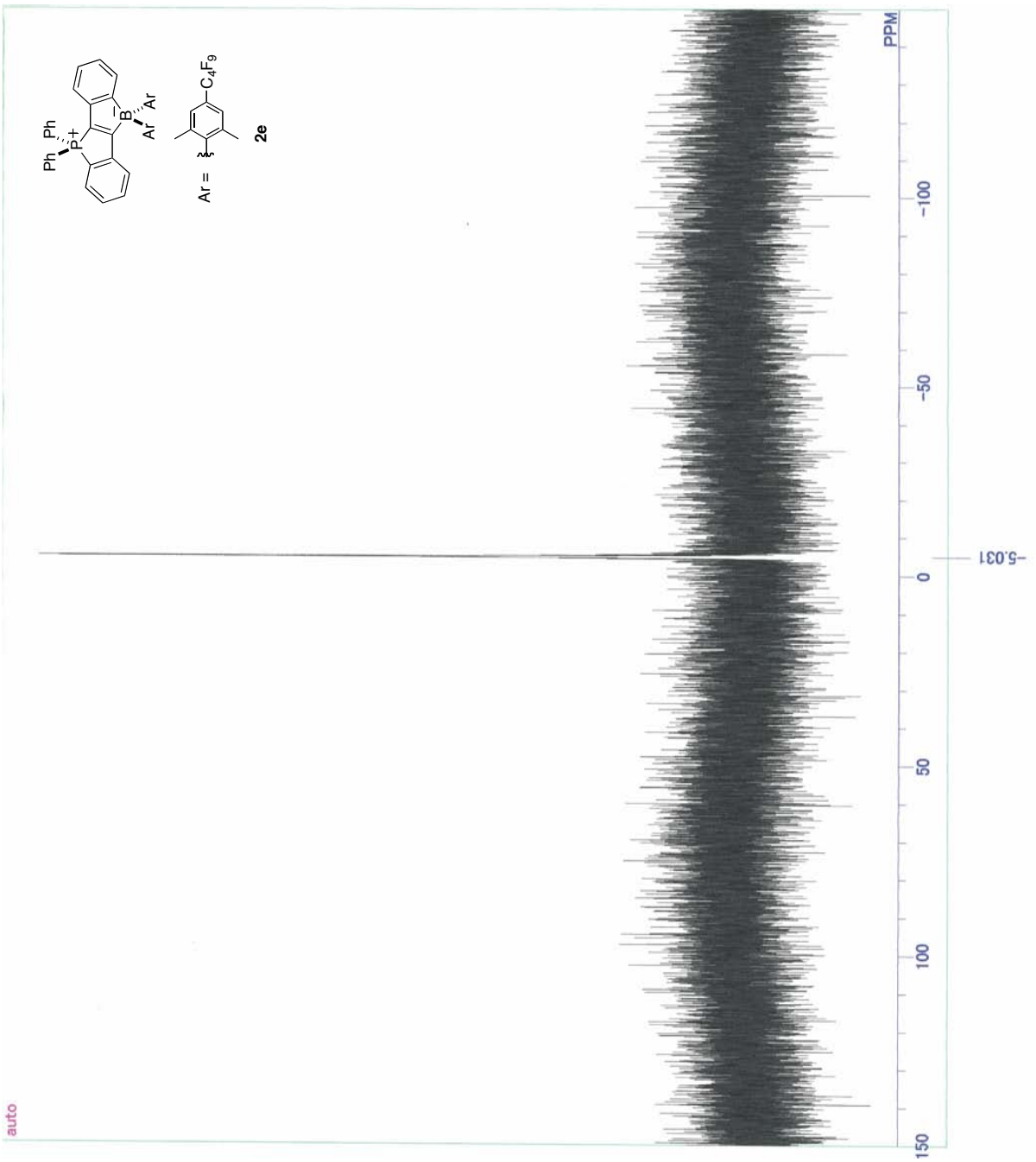

Figure S11. $^{11}B\{^{1}H\}$ NMR spectrum of **2e** (128 MHz, CD_2Cl_2).

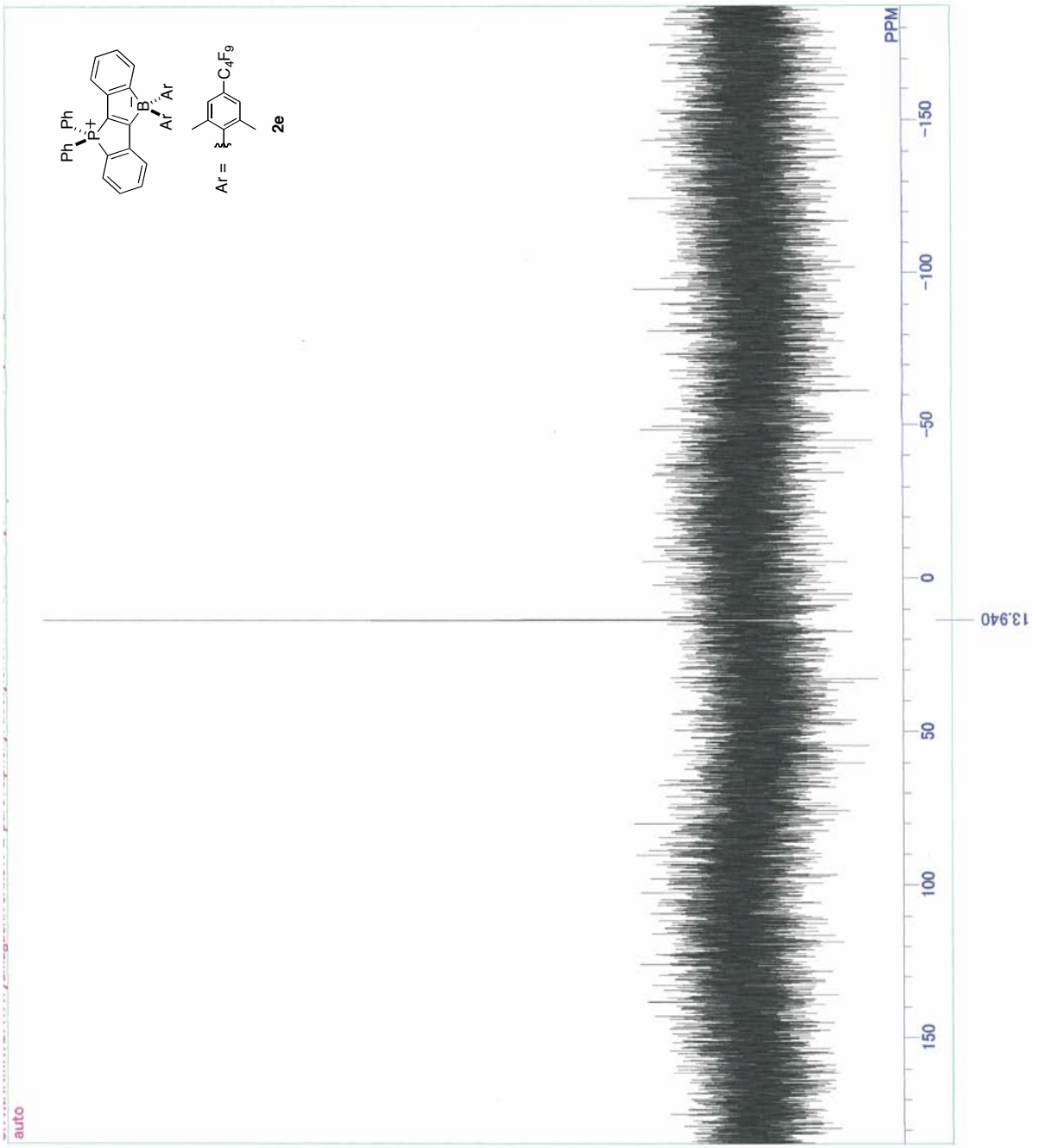

Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of **2e** (162 MHz, CD_2Cl_2).

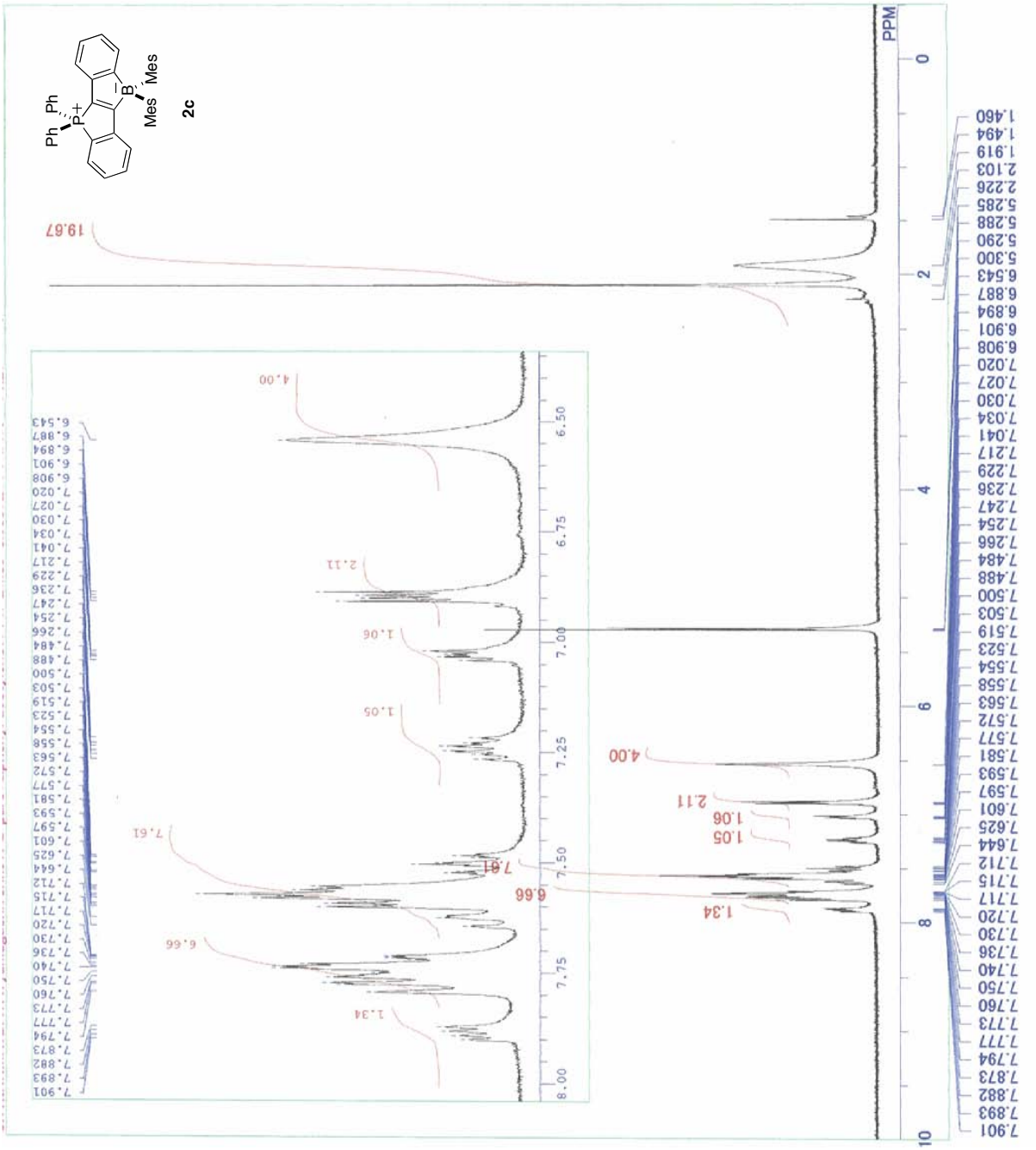

Figure S13. ^{1}H NMR spectrum of **2c** (400 MHz, CD_2Cl_2).

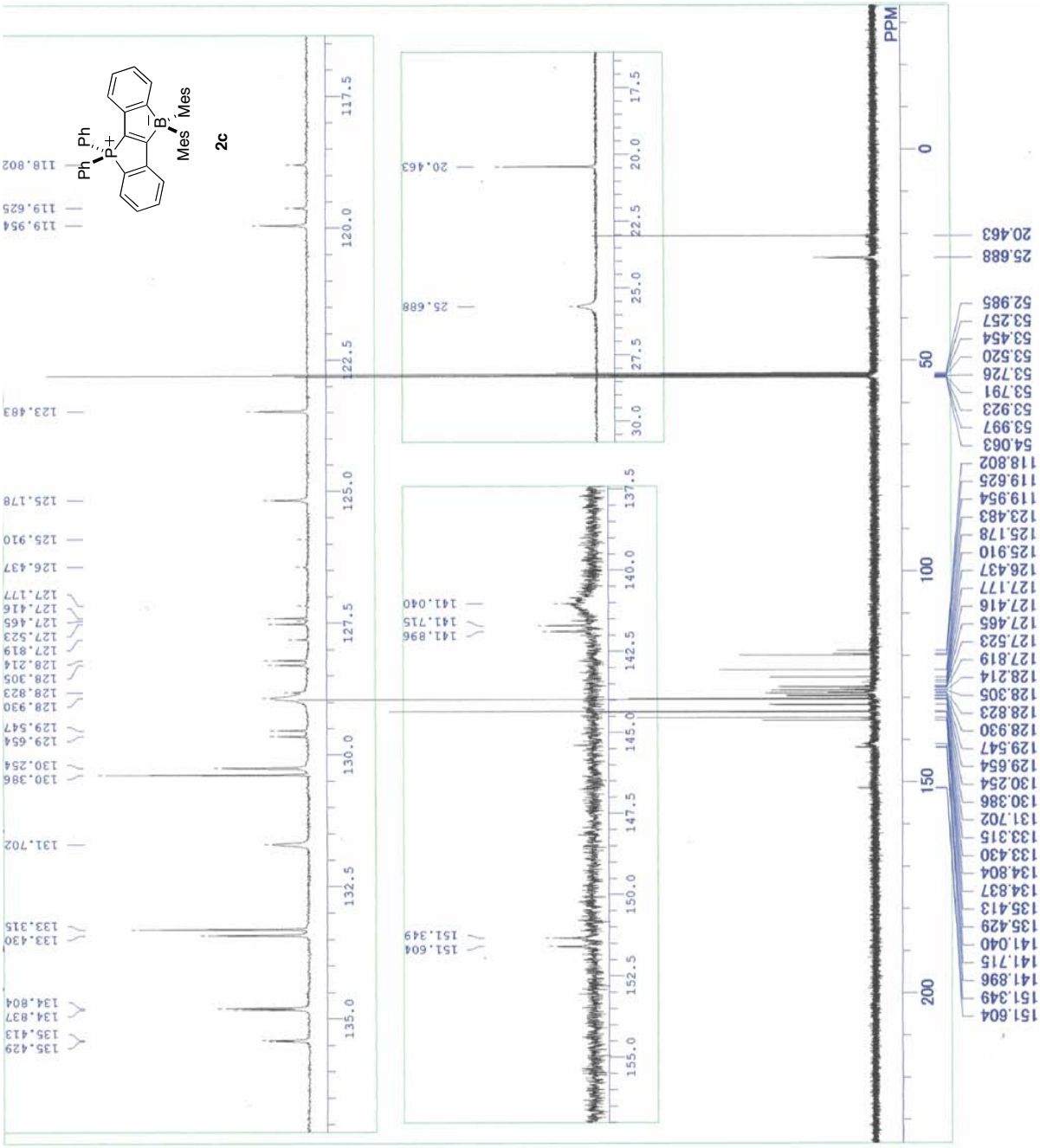

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **2c** (100 MHz, CD_2Cl_2).

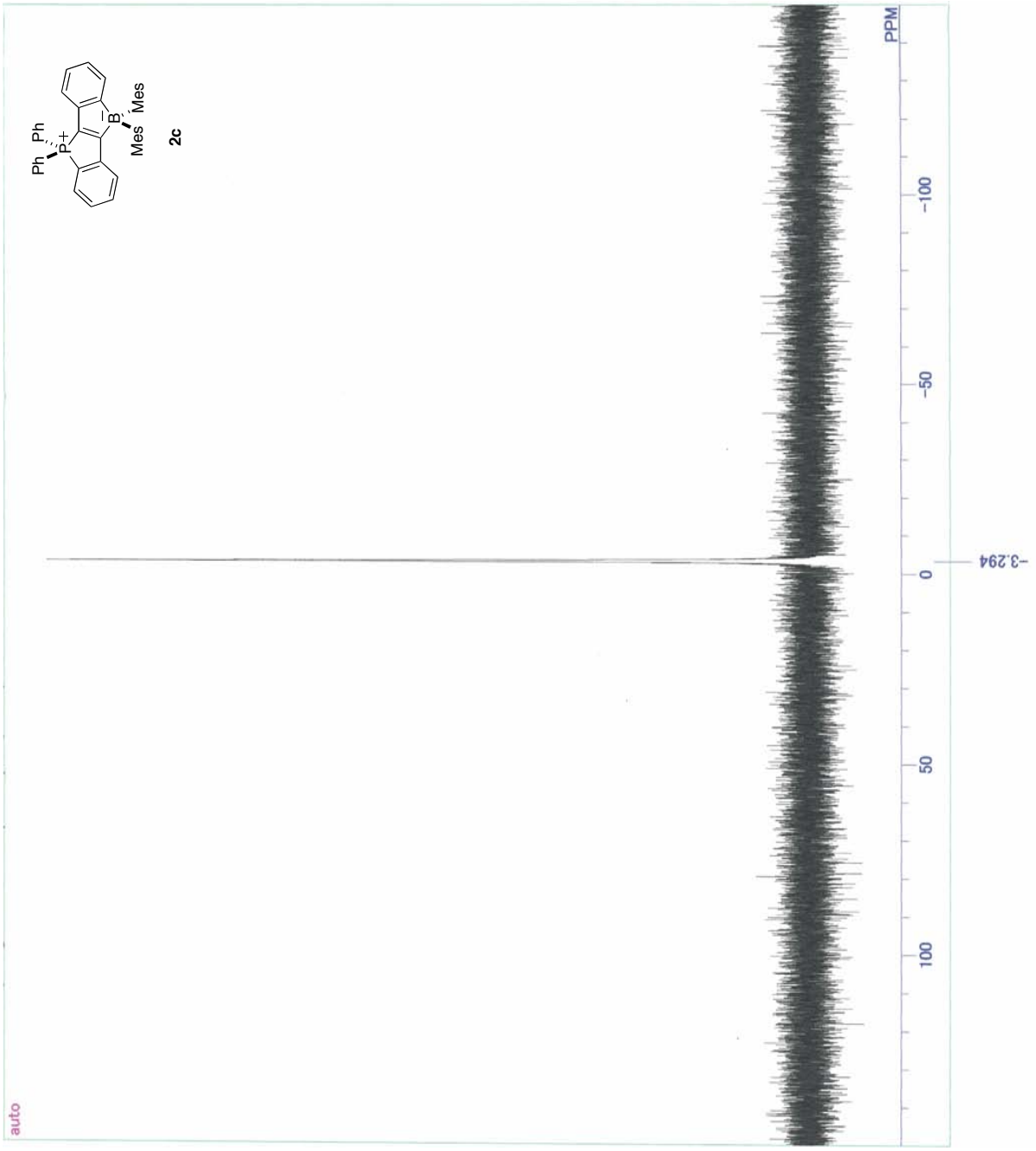

Figure S15. $^{11}B\{^{1}H\}$ NMR spectrum of **2c** (128 MHz, THF-d_8).

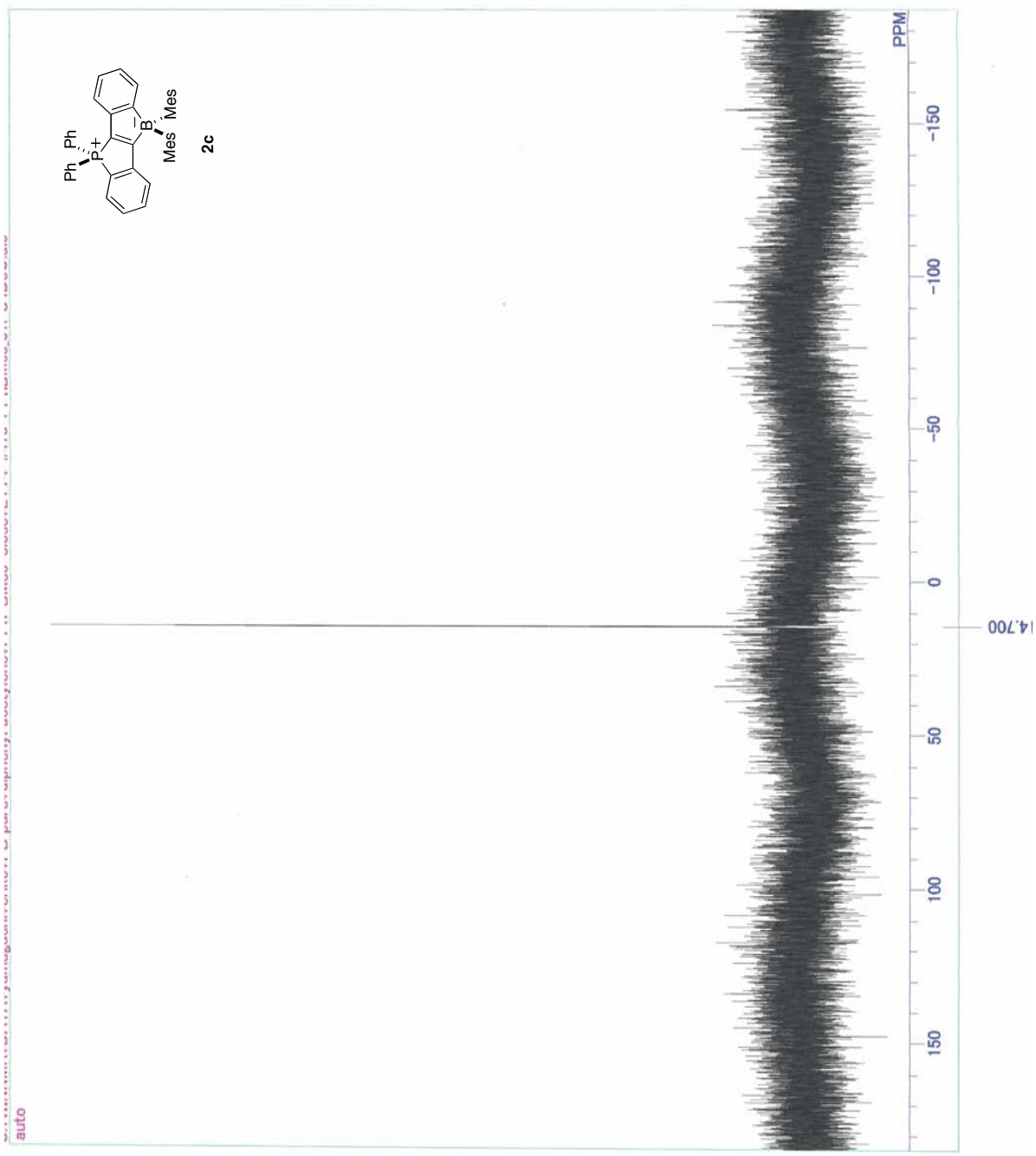

Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of **2c** (162 MHz, THF-d_8).

2. Photophysical Properties

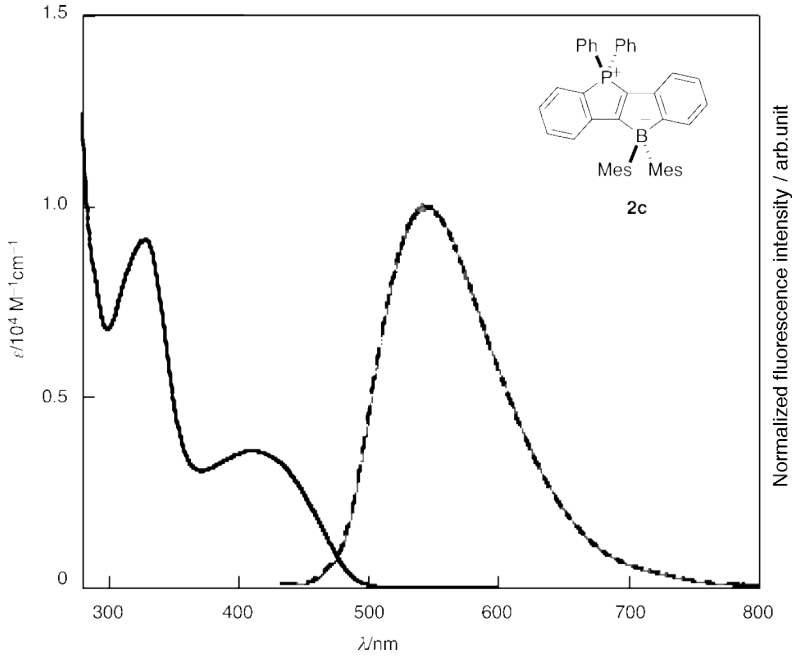

Figure S17. UV-visible absorption (solid line) and fluorescence spectra (broken line) of **2c** in THF. The fluorescence spectrum was obtained upon excitation at the longest absorption maximum wavelength.

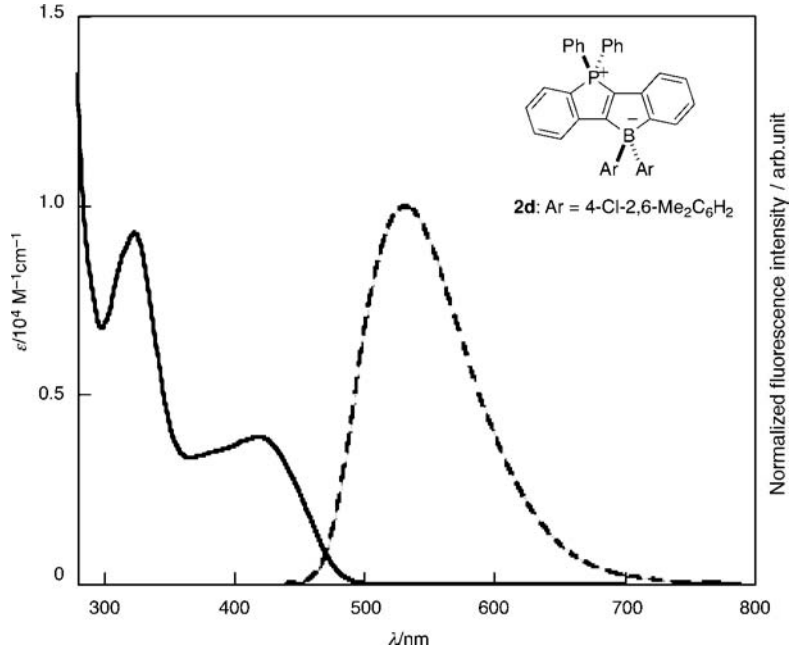

Figure S18. UV-visible absorption (solid line) and fluorescence spectra (broken line) of **2d** in THF. The fluorescence spectrum was obtained upon excitation at the longest absorption maximum wavelength.

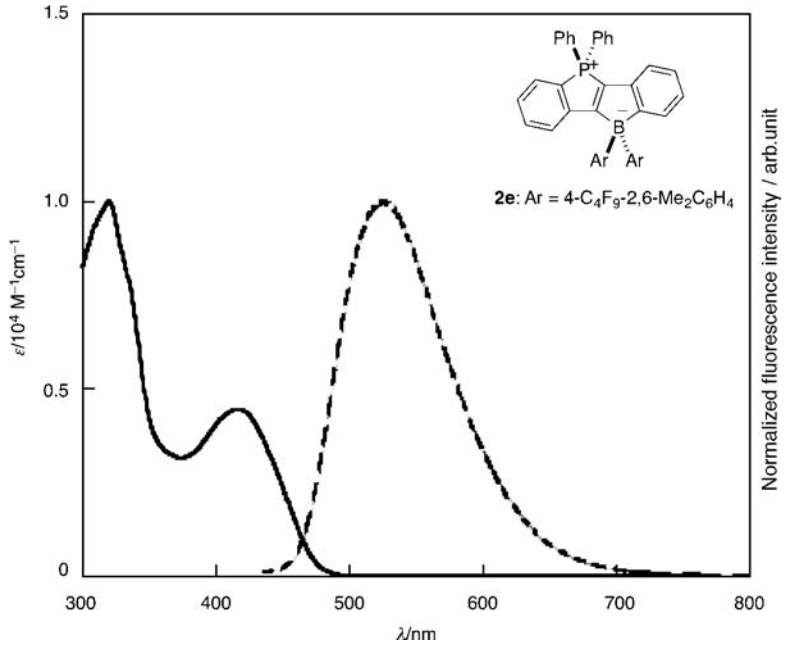

Figure S19. UV-visible absorption (solid line) and fluorescence spectra (broken line) of **2e** in THF. The fluorescence spectrum was obtained upon excitation at the longest absorption maximum wavelength.

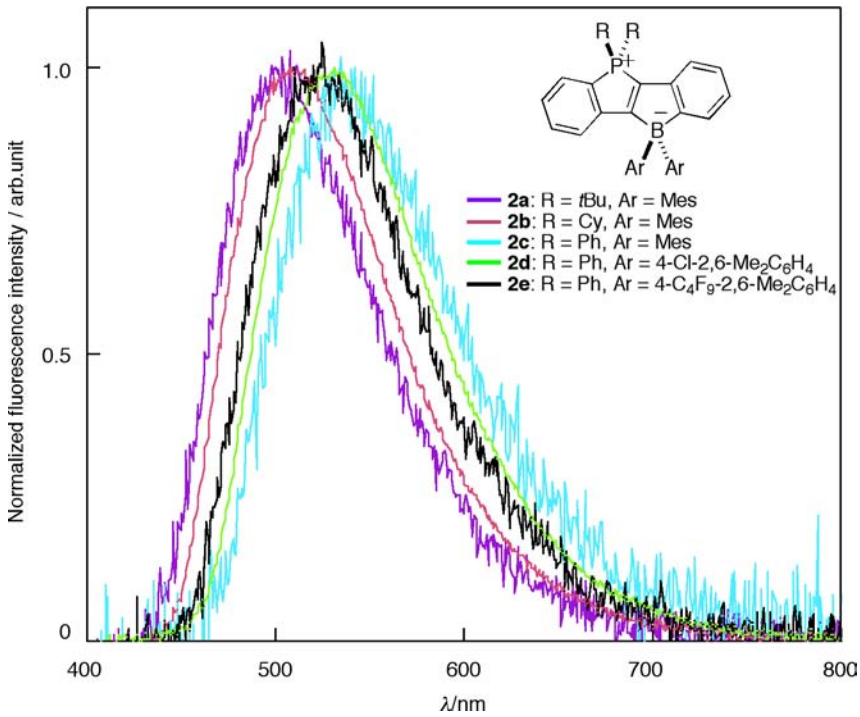

Figure S20. Fluorescence spectra of **2a–e** in a PMMA matrix.

3. Theoretical Calculations

Table S1. Energy Changes for Intramolecular Double Cyclization of **1** to **2**.

reactant	TS^{P}		TS^{PB}		**2**
	ΔE / kcal mol^{-1} [b]	ν_i / cm^{-1} [c]	ΔE / kcal mol^{-1} [b]	ν_i / cm^{-1} [c]	ΔE / kcal mol^{-1} [b]
1a	+27.2	174.02*i*	+35.3	172.73*i*	–3.9
1c	+30.4	170.52*i*	+39.0	178.71*i*	+3.0
1e	+29.1	179.14*i*	+36.9	170.55*i*	–2.5

[a]Calculated at the B3LYP/def2-SV(P) level of theory. [b]Energies relative to **1**. [c]Imaginary frequencies identified with frequency analyses.

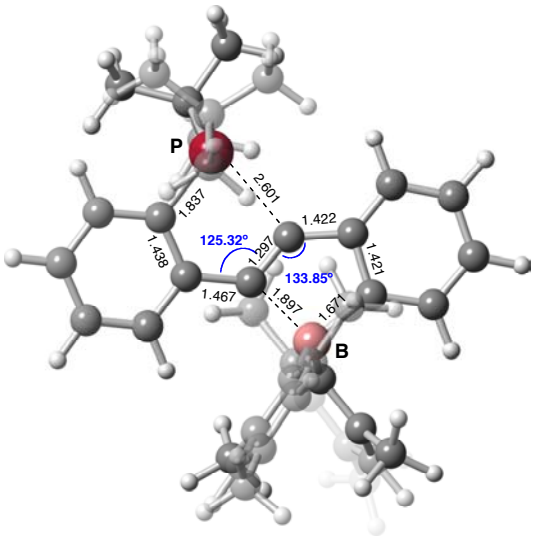

Figure S21. Optimized geometries of TS^{PB} for the reactions of **1a**, calculated at the B3LYP/def2-SV(P) level. Selected bond lengths (Å), interatomic distances (Å), and bond angles (deg) are given.

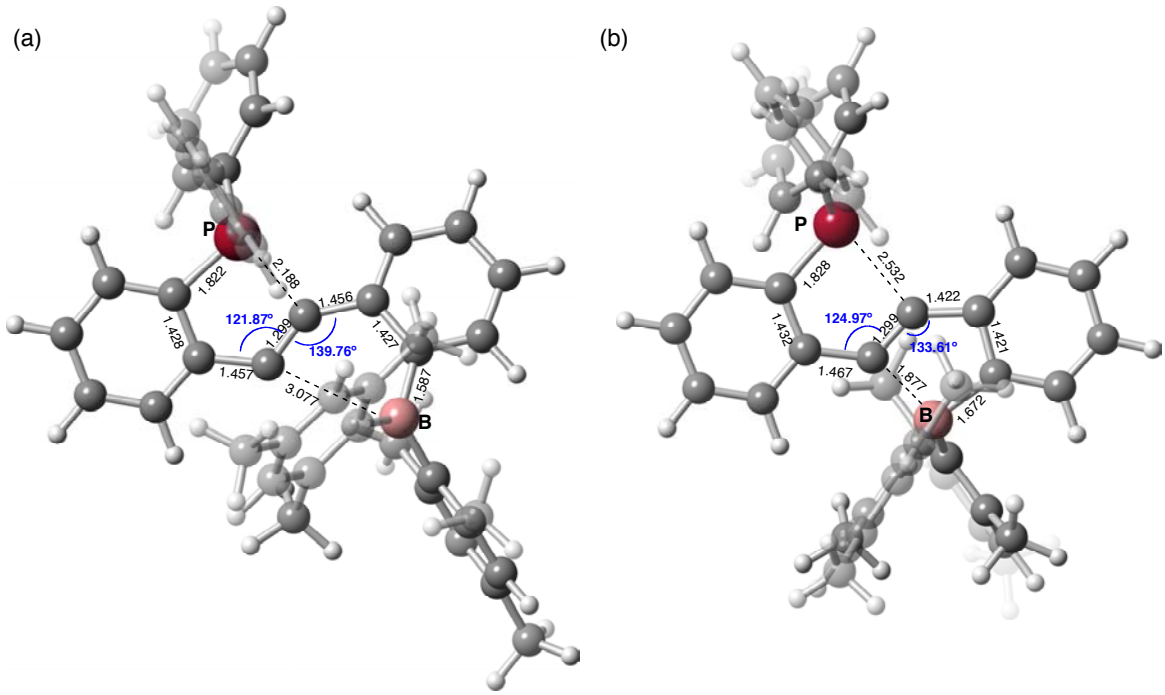

Figure S22. Optimized geometries of (a) $\mathbf{TS^{P}}$ and (b) $\mathbf{TS^{PB}}$ for the reactions of **1c**, calculated at the B3LYP/def2-SV(P) level. Selected bond lengths (Å), interatomic distances (Å), and bond angles (deg) are given.

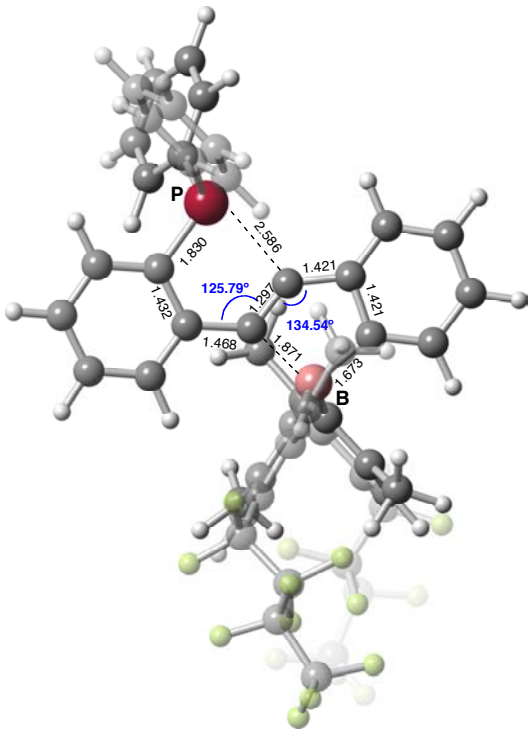

Figure S23. Optimized geometries of $\mathbf{TS^{PB}}$ for the reactions of **1e**, calculated at the B3LYP/def2-SV(P) level. Selected bond lengths (Å), interatomic distances (Å), and bond angles (deg) are given.

Table S2. Cartesian Coordinates of $\mathbf{TS^P}$ for the Reaction of **1a**[a]

atom	*x*	*y*	*z*
C	-2.8981313	0.4899878	1.5090015
C	-1.5484639	0.5578818	1.9812183
C	-1.2695635	1.3326260	3.1205778
H	-0.2395135	1.3780897	3.4830258
C	-2.2828215	2.0429317	3.7705988
H	-2.0454996	2.6449721	4.6538830
C	-3.5949597	1.9938354	3.2912512
H	-4.3886527	2.5577887	3.7914692
C	-3.8991093	1.2176132	2.1633832
H	-4.9319702	1.1976934	1.8077346
C	-0.5412325	-0.1674195	1.2237863
C	-0.8309134	-0.8394875	0.1547109
C	-0.1468837	-1.6202173	-0.8644863
C	1.2538610	-1.4112790	-1.0491674
C	1.9359422	-2.2903994	-1.9131602
H	3.0188010	-2.1752636	-2.0319756
C	1.2797168	-3.2848266	-2.6456972
H	1.8438435	-3.9341593	-3.3230551
C	-0.1010783	-3.4411607	-2.4989276
H	-0.6358858	-4.2148282	-3.0597150
C	-0.7978660	-2.6224623	-1.6083392
H	-1.8707179	-2.7696705	-1.4708505
P	-3.0658782	-0.5745326	0.0241720
C	1.6901684	1.3061765	-0.6703296
C	1.8314668	2.2604292	0.3815488
C	1.4793563	3.5997424	0.1732490
H	1.5783701	4.3059848	1.0060670
C	1.0146861	4.0671622	-1.0620994
C	0.9087923	3.1384906	-2.1008280
H	0.5707279	3.4814048	-3.0857682
C	1.2220685	1.7799427	-1.9288045
B	2.0992971	-0.2139327	-0.4378735
C	3.5065567	-0.6011761	0.1978472
C	4.7168661	-0.0124319	-0.2717785
C	5.9467930	-0.3958590	0.2817238
H	6.8652801	0.0616796	-0.1046771
C	6.0388957	-1.3335789	1.3170273
C	4.8488086	-1.9043557	1.7790620

(Table S2 continued)

atom	*x*	*y*	*z*
H	4.8910516	-2.6375735	2.5932272
C	3.6002081	-1.5780310	1.2293194
C	2.3445108	1.8800602	1.7553733
H	2.1977538	2.7100534	2.4686291
H	3.4216021	1.6386576	1.7382056
H	1.8198024	0.9923397	2.1476950
C	0.6307853	5.5158996	-1.2527862
H	-0.3529129	5.7348010	-0.7924614
H	0.5599243	5.7804394	-2.3223473
H	1.3635328	6.1956937	-0.7806562
C	1.0708959	0.8863995	-3.1470501
H	0.8578624	1.4919431	-4.0451276
H	0.2485156	0.1590083	-3.0305902
H	1.9799810	0.2953763	-3.3545103
C	4.7476415	1.0275520	-1.3769457
H	5.7827494	1.1957824	-1.7216771
H	4.3441646	1.9982192	-1.0396036
H	4.1509972	0.7280544	-2.2562010
C	7.3783112	-1.7365205	1.8886160
H	7.2819710	-2.1127156	2.9223241
H	8.0882745	-0.8899279	1.8967733
H	7.8436916	-2.5437668	1.2890133
C	2.3825530	-2.2915823	1.7818654
H	2.0726299	-3.1171300	1.1142760
H	1.5089815	-1.6248949	1.8882441
H	2.6032971	-2.7326691	2.7700792
C	-3.7547635	0.5415319	-1.3814239
C	-4.2585315	-2.0038183	0.5458603
C	-3.4994470	-0.1792979	-2.7224879
H	-4.0797551	-1.1116974	-2.8199733
H	-3.8003119	0.4856084	-3.5547010
H	-2.4314487	-0.4233353	-2.8575282
C	-5.2467796	0.8958124	-1.2567461
H	-5.5284823	1.5694539	-2.0897515
H	-5.8990101	0.0087704	-1.3210945
H	-5.4727283	1.4290998	-0.3181449
C	-2.9134746	1.8358611	-1.3509401
H	-3.1744159	2.4526523	-2.2319998

(Table S2 continued)

atom	*x*	*y*	*z*
H	-3.1097954	2.4361339	-0.4474171
H	-1.8291637	1.6327151	-1.3941440
C	-5.4905706	-1.5499737	1.3509913
H	-5.2070586	-1.0773539	2.3044876
H	-6.1347438	-0.8525267	0.7902511
H	-6.1042796	-2.4393854	1.5954915
C	-4.7309312	-2.7940053	-0.6894323
H	-3.8944931	-3.1349982	-1.3231512
H	-5.2728985	-3.6974061	-0.3504406
H	-5.4258884	-2.2132629	-1.3189306
C	-3.3955806	-2.9225364	1.4396388
H	-4.0168265	-3.7618988	1.8072172
H	-2.5371176	-3.3472615	0.8923548
H	-3.0020137	-2.3854675	2.3206535

[a] Calculated at the B3LYP/def2-SV(P) level.

Table S3. Cartesian Coordinates of **TS^{PB}** for the Reaction of **1a**[a]

atom	*x*	*y*	*z*
C	-2.4682909	-0.5869085	-1.3381818
C	-1.0341224	-0.6907110	-1.3464027
C	-0.4375164	-1.4788807	-2.3464886
H	0.6452208	-1.5695596	-2.3641434
C	-1.1988926	-2.1504656	-3.3050034
H	-0.6944255	-2.7557996	-4.0646601
C	-2.5912612	-2.0557412	-3.2903932
H	-3.1960689	-2.5838517	-4.0339648
C	-3.2125057	-1.2754345	-2.3088827
H	-4.3032669	-1.2144405	-2.3058122
C	-0.2497548	0.0128018	-0.3255822
C	-0.7421177	0.7348573	0.6327824
C	-0.1836362	1.3615082	1.7811149
C	1.1845197	0.9791517	1.7383649
C	1.9995528	1.5333922	2.7375640
H	3.0728228	1.3284417	2.7540714
C	1.4629607	2.3569387	3.7379340
H	2.1235119	2.7562262	4.5151556

(Table S3 continued)

atom	*x*	*y*	*z*
C	0.0988001	2.6847535	3.7573753
H	-0.2999407	3.3335945	4.5437194
C	-0.7426100	2.1931443	2.7581378
H	-1.8065547	2.4488539	2.7315359
P	-3.2427486	0.4151119	-0.0073786
C	1.8224316	-1.5288507	0.4415219
C	2.5075439	-2.2073865	-0.6146960
C	2.7672456	-3.5873623	-0.5359786
H	3.2970650	-4.0680755	-1.3676228
C	2.3807109	-4.3674291	0.5535678
C	1.6829837	-3.7170454	1.5747464
H	1.3403926	-4.3017488	2.4369519
C	1.3950259	-2.3445556	1.5370535
B	1.5158532	0.0878618	0.3645140
C	2.6155635	1.0355512	-0.4254080
C	3.9759698	0.9366461	-0.0017239
C	4.9621920	1.7752637	-0.5466875
H	5.9957423	1.6637176	-0.1960525
C	4.6790891	2.7377523	-1.5173464
C	3.3480768	2.8422148	-1.9272454
H	3.0855942	3.5902373	-2.6849477
C	2.3277539	2.0328057	-1.4002074
C	3.0375690	-1.5428016	-1.8776146
H	3.0676608	-2.2751071	-2.7047419
H	4.0686875	-1.1698991	-1.7397276
H	2.4528951	-0.6746665	-2.2076734
C	2.7101569	-5.8395281	0.6357264
H	1.8976540	-6.4122214	1.1187782
H	3.6269821	-6.0144845	1.2329703
H	2.8855755	-6.2730579	-0.3649187
C	0.6058257	-1.8088110	2.7153176
H	0.3168596	-2.6324434	3.3910686
H	-0.3182347	-1.2980460	2.3966939
H	1.1793193	-1.0769997	3.3082227
C	4.4864548	-0.0849531	1.0049885
H	5.3651425	0.3143606	1.5431236
H	4.8114359	-1.0168545	0.5043280
H	3.7413549	-0.3904277	1.7506447

(Table S3 continued)

atom	*x*	*y*	*z*
C	5.7515758	3.6494988	-2.0673176
H	5.5349953	3.9498418	-3.1083502
H	6.7440581	3.1642921	-2.0526625
H	5.8362069	4.5806264	-1.4722984
C	0.9332155	2.2967744	-1.9328534
H	0.2459282	2.6381828	-1.1404389
H	0.4768863	1.3975726	-2.3814893
H	0.9592155	3.0790197	-2.7119151
C	-4.3458115	-0.7408963	1.0491842
C	-4.1451481	1.8868690	-0.8306263
C	-4.5229323	-0.0717181	2.4299600
H	-5.0895040	0.8723401	2.3747554
H	-5.0835259	-0.7554986	3.0954992
H	-3.5490691	0.1390369	2.9050722
C	-5.7247504	-1.0562848	0.4423753
H	-6.2556015	-1.7663331	1.1058567
H	-6.3597258	-0.1587857	0.3518477
H	-5.6490001	-1.5333284	-0.5494220
C	-3.5479636	-2.0482011	1.2361615
H	-4.0762036	-2.6882264	1.9680757
H	-3.4504503	-2.6148950	0.2958523
H	-2.5323476	-1.8597245	1.6277047
C	-5.1185834	1.5034794	-1.9613363
H	-4.5989994	1.0162309	-2.8022826
H	-5.9320112	0.8420518	-1.6206534
H	-5.5855710	2.4263559	-2.3563489
C	-4.8918130	2.6881023	0.2543434
H	-4.2310518	2.9548233	1.0984612
H	-5.2652230	3.6314906	-0.1869110
H	-5.7663325	2.1457087	0.6527169
C	-3.0180109	2.7651594	-1.4165238
H	-3.4668245	3.6439426	-1.9177758
H	-2.3332378	3.1309276	-0.6329470
H	-2.4181387	2.2204133	-2.1659279

[a] Calculated at the B3LYP/def2-SV(P) level.

Table S4. Cartesian Coordinates of $\mathbf{TS^P}$ for the Reaction of **1c**[a]

atom	*x*	*y*	*z*
C	-2.5233080	-0.0191910	1.9094413
C	-1.1649175	-0.1342831	2.3337884
C	-0.8642139	0.1447770	3.6768616
H	0.1716764	0.0579386	4.0151578
C	-1.8729232	0.5349540	4.5652628
H	-1.6207948	0.7506643	5.6088183
C	-3.1975609	0.6589075	4.1314962
H	-3.9795585	0.9732620	4.8299330
C	-3.5232397	0.3842419	2.7950432
H	-4.5595824	0.4885688	2.4571771
C	-0.1982713	-0.5349934	1.3202531
C	-0.5536566	-0.7948153	0.0985206
C	0.0266347	-1.2640588	-1.1520424
C	1.4284463	-1.1041444	-1.3672141
C	1.9888147	-1.7313386	-2.4973625
H	3.0705381	-1.6612943	-2.6557377
C	1.2124179	-2.4135771	-3.4391813
H	1.6837185	-2.8690719	-4.3162934
C	-0.1677558	-2.5145829	-3.2437956
H	-0.7931476	-3.0514017	-3.9647986
C	-0.7472458	-1.9568967	-2.1029993
H	-1.8185865	-2.0870165	-1.9285315
P	-2.7069321	-0.4075048	0.1390958
C	-3.2309122	1.1609422	-0.6631615
C	-2.2236295	2.0825183	-1.0042907
H	-1.1711838	1.8456976	-0.8184986
C	-2.5595762	3.3143953	-1.5725363
H	-1.7633446	4.0209146	-1.8264064
C	-3.8986799	3.6365653	-1.8171655
H	-4.1595123	4.5994212	-2.2682012
C	-4.9048559	2.7235655	-1.4827473
H	-5.9555053	2.9713468	-1.6664069
C	-4.5764338	1.4932143	-0.9051415
H	-5.3744692	0.7938790	-0.6410106
C	-4.0935773	-1.5935853	-0.0368759
C	-4.4869979	-2.4204617	1.0331137
H	-4.0435530	-2.2832018	2.0229112

(Table S4 continued)

atom	*x*	*y*	*z*
C	-5.4459585	-3.4202616	0.8418443
H	-5.7431545	-4.0499987	1.6866782
C	-6.0235222	-3.6158223	-0.4165380
H	-6.7746111	-4.3983242	-0.5631125
C	-5.6302433	-2.8077043	-1.4902059
H	-6.0722363	-2.9560824	-2.4807862
C	-4.6689097	-1.8116027	-1.3066595
H	-4.3674062	-1.1952287	-2.1593923
C	2.0987393	1.3482795	-0.2767167
C	2.3049006	1.9488415	1.0007925
C	2.0465999	3.3124826	1.1902844
H	2.1946504	3.7434964	2.1874426
C	1.6197986	4.1443492	0.1482591
C	1.4497545	3.5608955	-1.1105113
H	1.1460369	4.1949468	-1.9522665
C	1.6645941	2.1913645	-1.3391008
B	2.4034640	-0.1968653	-0.5042241
C	3.7970832	-0.8381654	-0.0846851
C	5.0327009	-0.2095997	-0.4156019
C	6.2473173	-0.8172746	-0.0655290
H	7.1847790	-0.3250806	-0.3495734
C	6.3016934	-2.0250598	0.6388552
C	5.0870858	-2.6391062	0.9627498
H	5.0999117	-3.5896542	1.5089271
C	3.8502357	-2.0862703	0.6012740
C	2.7890123	1.1541717	2.1953100
H	2.7516060	1.7667277	3.1130588
H	3.8289796	0.8083285	2.0635152
H	2.1644772	0.2573638	2.3525745
C	1.3405695	5.6101410	0.3854085
H	1.3265631	6.1799084	-0.5602067
H	2.0997487	6.0656224	1.0468982
H	0.3578425	5.7575106	0.8753011
C	1.4555618	1.6948023	-2.7588718
H	1.2952838	2.5448049	-3.4445397
H	0.5800215	1.0282414	-2.8440629
H	2.3201979	1.1232103	-3.1386556

(Table S4 continued)

atom	*x*	*y*	*z*
C	5.1097187	1.1082905	-1.1650783
H	6.1484366	1.3165952	-1.4751588
H	4.7692555	1.9549779	-0.5438832
H	4.4854637	1.1143654	-2.0752268
C	7.6213921	-2.6315116	1.0551867
H	7.9042058	-2.3111387	2.0773739
H	8.4399369	-2.3256742	0.3799782
H	7.5766522	-3.7352205	1.0629928
C	2.6019636	-2.8599869	0.9763181
H	2.2088563	-3.4230208	0.1094054
H	1.7850099	-2.2063026	1.3282495
H	2.8229183	-3.5929610	1.7719288

[a] Calculated at the B3LYP/def2-SV(P) level.

Table S5. Cartesian Coordinates of **TS^{PB}** for the Reaction of **1c**[a]

atom	*x*	*y*	*z*
C	-1.9441077	-0.4489784	-1.4990700
C	-0.5132642	-0.5095107	-1.4965736
C	0.1171937	-1.0402451	-2.6354563
H	1.2018347	-1.1132545	-2.6528372
C	-0.6226840	-1.4884398	-3.7327877
H	-0.0969369	-1.8991015	-4.6006814
C	-2.0186612	-1.4233504	-3.7266320
H	-2.5974920	-1.7787562	-4.5846070
C	-2.6729617	-0.9063112	-2.6036736
H	-3.7671100	-0.8654124	-2.5899999
C	0.2073192	-0.0324559	-0.3113179
C	-0.3536731	0.3814544	0.7842203
C	0.1439126	0.7293944	2.0705174
C	1.5384976	0.4774049	1.9645679
C	2.2986671	0.7961589	3.1006650
H	3.3842582	0.6712163	3.0952284
C	1.6892430	1.2755005	4.2691444

(Table S5 continued)

atom	*x*	*y*	*z*
H	2.3090337	1.4943924	5.1453469
C	0.3031266	1.4858768	4.3354947
H	-0.1520262	1.8661081	5.2555586
C	-0.4887322	1.2216075	3.2173112
H	-1.5694135	1.3927567	3.2295653
P	-2.7569032	0.1803895	0.0128042
C	-3.9411507	-1.1094612	0.5584537
C	-3.4406450	-2.1501969	1.3625105
H	-2.3874883	-2.1501137	1.6626476
C	-4.2812771	-3.1856765	1.7794682
H	-3.8807424	-3.9914673	2.4024188
C	-5.6309294	-3.1860516	1.4097486
H	-6.2905027	-3.9939511	1.7421478
C	-6.1373729	-2.1492932	0.6183489
H	-7.1926174	-2.1456088	0.3269219
C	-5.2991783	-1.1140822	0.1922297
H	-5.7064705	-0.3092431	-0.4264107
C	-3.7226878	1.6677619	-0.4288570
C	-3.4981019	2.3639532	-1.6299084
H	-2.7918474	1.9729162	-2.3672022
C	-4.1770367	3.5592974	-1.8891651
H	-3.9938398	4.0904610	-2.8286012
C	-5.0835274	4.0734030	-0.9573589
H	-5.6138554	5.0083842	-1.1639036
C	-5.3061836	3.3905408	0.2446630
H	-6.0095666	3.7898223	0.9822813
C	-4.6253483	2.2014855	0.5127908
H	-4.8001623	1.6841311	1.4618782
C	2.4160639	-1.5116233	0.0533415
C	3.1736602	-1.8055511	-1.1239942
C	3.5903334	-3.1193134	-1.4018071
H	4.1735122	-3.3014239	-2.3127525
C	3.2920815	-4.1981215	-0.5689734
C	2.5134034	-3.9248346	0.5587003
H	2.2298229	-4.7526286	1.2194074
C	2.0693996	-2.6316982	0.8733312
B	1.9413501	0.0254570	0.4060804
C	2.9207806	1.2658362	-0.0838909

(Table S5 continued)

atom	*x*	*y*	*z*
C	4.2877577	1.2090727	0.3272533
C	5.1709236	2.2629039	0.0420964
H	6.2132915	2.1755302	0.3731089
C	4.7744667	3.4101185	-0.6478285
C	3.4373772	3.4714601	-1.0449429
H	3.0874335	4.3585581	-1.5859673
C	2.5164302	2.4455328	-0.7716564
C	3.6090335	-0.7741583	-2.1551082
H	3.7517440	-1.2609377	-3.1368442
H	4.5704538	-0.3024679	-1.8842130
H	2.8987719	0.0534895	-2.2831247
C	3.7921359	-5.5926629	-0.8647962
H	4.0025003	-5.7293201	-1.9405664
H	3.0596047	-6.3615470	-0.5592307
H	4.7325683	-5.8074896	-0.3191975
C	1.2011260	-2.5177892	2.1105839
H	0.9833777	-3.5191307	2.5211494
H	0.2358704	-2.0280693	1.8945372
H	1.6793397	-1.9262170	2.9088293
C	4.9181738	0.0216328	1.0421174
H	5.7121705	0.3654818	1.7293915
H	5.3928728	-0.6725268	0.3224430
H	4.2080148	-0.5840887	1.6188610
C	5.7359179	4.5451634	-0.9155387
H	5.4156711	5.1530194	-1.7805425
H	6.7567616	4.1743320	-1.1195368
H	5.8085170	5.2284987	-0.0459963
C	1.0999537	2.6885522	-1.2564548
H	0.3786197	2.7492472	-0.4232873
H	0.7442958	1.8895199	-1.9295672
H	1.0425021	3.6398937	-1.8137383

[a] Calculated at the B3LYP/def2-SV(P) level.

Table S6. Cartesian Coordinates of $\mathbf{TS^P}$ for the Reaction of **1e**[a]

atom	*x*	*y*	*z*
C	-3.5780798	-2.5171291	2.1186075
C	-2.1899623	-2.1979346	2.2137623
C	-1.6750601	-1.8357240	3.4691080
H	-0.6130424	-1.5916435	3.5558045
C	-2.5092586	-1.7822551	4.5914667
H	-2.0923894	-1.4953190	5.5622662
C	-3.8709002	-2.0844366	4.4820342
H	-4.5196836	-2.0321616	5.3617737
C	-4.4080684	-2.4490517	3.2388844
H	-5.4761115	-2.6746988	3.1549508
C	-1.4195064	-2.2728073	0.9804561
C	-1.9460531	-2.6051435	-0.1551424
C	-1.5593200	-2.8452394	-1.5359698
C	-0.3629534	-2.2379911	-2.0245446
C	0.1069259	-2.6411960	-3.2898575
H	1.0473788	-2.2220684	-3.6639338
C	-0.6050279	-3.5303702	-4.1009681
H	-0.2212923	-3.8032866	-5.0891342
C	-1.8068868	-4.0708308	-3.6341576
H	-2.3745468	-4.7743133	-4.2518604
C	-2.2681570	-3.7410182	-2.3582641
H	-3.1787987	-4.2103147	-1.9773845
P	-4.0815760	-2.9195004	0.4128035
C	-5.3072339	-1.6189586	-0.0225278
C	-4.7977605	-0.3353139	-0.2961600
H	-3.7175769	-0.1573995	-0.2869857
C	-5.6643330	0.7276346	-0.5620581
H	-5.2516438	1.7247266	-0.7421720
C	-7.0479757	0.5174834	-0.5814520
H	-7.7263999	1.3497036	-0.7941655
C	-7.5607305	-0.7579122	-0.3229003
H	-8.6423871	-0.9276372	-0.3311159
C	-6.6983197	-1.8220375	-0.0371777
H	-7.1171532	-2.8073130	0.1838699
C	-4.9655598	-4.5243478	0.4461157
C	-4.8163731	-5.4251845	1.5173796
H	-4.2461409	-5.1333447	2.4029374
C	-5.3994939	-6.6954239	1.4618625

(Table S6 continued)

atom	*x*	*y*	*z*
H	-5.2786467	-7.3804240	2.3070739
C	-6.1350300	-7.0881448	0.3394931
H	-6.5922498	-8.0817316	0.3002381
C	-6.2753640	-6.2056921	-0.7386238
H	-6.8432052	-6.5064258	-1.6248553
C	-5.6893091	-4.9388985	-0.6916701
H	-5.8027147	-4.2653117	-1.5469519
C	-0.3517459	0.2670999	-0.8698218
C	-0.0914664	0.8712174	0.3947493
C	-0.8101575	2.0050255	0.7942049
H	-0.6283489	2.4355710	1.7818478
C	-1.7540608	2.5924152	-0.0510676
C	-1.9695225	2.0508363	-1.3183442
H	-2.6820317	2.5293652	-1.9951236
C	-1.2981551	0.8919435	-1.7334488
B	0.4128865	-1.0630204	-1.3076846
C	2.0025120	-1.1656659	-1.2431556
C	2.8311822	-0.1501001	-1.8000710
C	4.2266465	-0.2685003	-1.7363058
H	4.8543755	0.5093573	-2.1779244
C	4.8244434	-1.3656167	-1.1125435
C	4.0226255	-2.3700193	-0.5692745
H	4.4902562	-3.2315972	-0.0866004
C	2.6251290	-2.2985253	-0.6453888
C	0.9300157	0.3148564	1.3629723
H	0.8754628	0.8396597	2.3318889
H	1.9588129	0.4273452	0.9790193
H	0.7609953	-0.7605204	1.5441752
C	-2.4990586	3.8259420	0.3915437
C	-1.6235135	0.3817752	-3.1253396
H	-2.1884846	1.1426467	-3.6903168
H	-2.2361838	-0.5356396	-3.0957974
H	-0.7206175	0.1377679	-3.7099345
C	2.2675884	1.0802412	-2.4858948
H	3.0649971	1.6302720	-3.0136267
H	1.8043684	1.7751539	-1.7634773
H	1.4917837	0.8295444	-3.2294322
C	6.3271514	-1.4510030	-1.0018806

(Table S6 continued)

atom	*x*	*y*	*z*
C	1.8327320	-3.4547895	-0.0722676
H	1.4877143	-4.1304398	-0.8766644
H	0.9328019	-3.1250715	0.4758472
H	2.4565630	-4.0519049	0.6149159
F	-3.7196919	3.9087854	-0.2151463
F	-2.7047188	3.8109847	1.7318127
C	-1.7365343	5.1448183	0.0525337
C	-2.5304325	6.4645512	0.3002831
C	-1.6423658	7.7453535	0.3014569
F	-1.3909406	5.1196449	-1.2511366
F	-0.6087243	5.1739506	0.7966547
F	-3.1593667	6.4141947	1.4890795
F	-3.4471101	6.6088480	-0.6735934
F	-0.8635095	7.7794505	-0.7803770
F	-0.8783768	7.7891271	1.3900291
F	-2.4323452	8.8191431	0.2928641
C	6.8779095	-0.7585032	0.2859208
C	8.3805159	-1.0392914	0.5991606
C	9.0048530	-0.0694518	1.6476855
F	6.7422607	-2.7464065	-0.9657404
F	6.9264296	-0.8527355	-2.0625931
F	6.1587695	-1.1760751	1.3479911
F	6.7043057	0.5755130	0.1497030
F	8.4937680	-2.2866737	1.0900189
F	9.1161485	-0.9412319	-0.5234888
F	8.2370558	0.0039355	2.7358034
F	9.1542779	1.1498668	1.1359716
F	10.2044610	-0.5305640	2.0032947

[a] Calculated at the B3LYP/def2-SV(P) level.

Table S7. Cartesian Coordinates of $\mathbf{TS}^{\mathbf{PB}}$ for the Reaction of **1e**[a]

atom	*x*	*y*	*z*
C	-3.3076573	2.7888153	-1.6483066
C	-2.2466165	1.8589822	-1.4017400
C	-1.8120274	1.0667993	-2.4786338

(Table S7 continued)

atom	*x*	*y*	*z*
H	-1.0160198	0.3447461	-2.3169120
C	-2.3901654	1.1784940	-3.7457495
H	-2.0270337	0.5414681	-4.5581971
C	-3.4259115	2.0870042	-3.9767018
H	-3.8828905	2.1719687	-4.9672092
C	-3.8806596	2.8858584	-2.9225110
H	-4.6986257	3.5917952	-3.0986331
C	-1.6799876	1.7709045	-0.0499624
C	-2.0917834	2.4284138	0.9893082
C	-1.7944885	2.3852554	2.3782823
C	-0.8640247	1.3160369	2.4745620
C	-0.3413400	1.0821416	3.7556584
H	0.4098436	0.3055497	3.9193520
C	-0.7709086	1.8329047	4.8598540
H	-0.3584681	1.6119999	5.8499444
C	-1.7114623	2.8646874	4.7196808
H	-2.0275220	3.4425440	5.5937438
C	-2.2293756	3.1606096	3.4581363
H	-2.9487373	3.9713778	3.3103622
P	-3.9156981	3.7880417	-0.2403847
C	-5.7156842	3.4704661	-0.0953050
C	-6.1230991	2.3861053	0.7027331
H	-5.3761017	1.7919373	1.2393212
C	-7.4780635	2.0614275	0.8129670
H	-7.7838451	1.2137396	1.4339838
C	-8.4386143	2.8229700	0.1385693
H	-9.5000650	2.5716528	0.2294429
C	-8.0411397	3.9098991	-0.6481368
H	-8.7899686	4.5089670	-1.1759435
C	-6.6865833	4.2350031	-0.7676103
H	-6.3881736	5.0876567	-1.3845126
C	-3.6950480	5.5533378	-0.6576222
C	-2.8059236	5.9663439	-1.6661114
H	-2.2919755	5.2242324	-2.2828290
C	-2.5753863	7.3280522	-1.8882210
H	-1.8829945	7.6354412	-2.6782504
C	-3.2245427	8.2904235	-1.1090604
H	-3.0428744	9.3550617	-1.2861864

(Table S7 continued)

atom	*x*	*y*	*z*
C	-4.1042625	7.8868966	-0.0972770
H	-4.6121569	8.6343006	0.5203744
C	-4.3335993	6.5290566	0.1338922
H	-5.0171455	6.2282118	0.9343845
C	-0.9872069	-0.7663019	0.4607106
C	-0.3193174	-1.4546338	-0.6020423
C	-0.7502133	-2.7251210	-1.0159580
H	-0.2219829	-3.2277925	-1.8298871
C	-1.8429412	-3.3528554	-0.4223803
C	-2.5245367	-2.6894821	0.5967766
H	-3.3958613	-3.1627872	1.0553814
C	-2.1258490	-1.4180033	1.0325049
B	-0.4920463	0.7288960	0.9525478
C	1.1204289	1.0794006	0.8351765
C	2.0196968	0.1717629	1.4761001
C	3.3934090	0.4450007	1.5376354
H	4.0563273	-0.2641140	2.0407740
C	3.9275584	1.6043133	0.9784307
C	3.0670839	2.5007999	0.3470052
H	3.4744400	3.4160425	-0.0892584
C	1.6862008	2.2637191	0.2782433
C	0.8846457	-0.9202699	-1.3634238
H	0.9262521	-1.3747746	-2.3691059
H	1.8340475	-1.1706846	-0.8576339
H	0.8864899	0.1713271	-1.4821528
C	-2.2696743	-4.7264512	-0.8713757
C	-2.9825316	-0.8004790	2.1186376
H	-3.8529363	-1.4437980	2.3337660
H	-3.3631011	0.1928585	1.8282305
H	-2.4280364	-0.6620701	3.0612960
C	1.6061232	-1.1557842	2.0948975
H	2.2508429	-1.3914783	2.9601808
H	1.7233515	-1.9851842	1.3721651
H	0.5623458	-1.1895922	2.4299152
C	5.4088353	1.8657367	1.0414566
C	0.8706769	3.3394577	-0.4116296
H	0.1643813	3.8319530	0.2778605
H	0.2756004	2.9386496	-1.2496937

(Table S7 continued)

atom	*x*	*y*	*z*
H	1.5343991	4.1204334	-0.8207819
F	-3.6047643	-4.9158961	-0.6825782
F	-2.0094579	-4.9058387	-2.1931276
C	-1.5365502	-5.8685495	-0.0995135
C	-2.0659003	-7.3101350	-0.3708848
C	-1.1195626	-8.4418300	0.1328479
F	-1.6532525	-5.6387766	1.2248019
F	-0.2260447	-5.8239583	-0.4298180
F	-2.2417737	-7.5012351	-1.6918006
F	-3.2471982	-7.4649556	0.2544600
F	-0.7778338	-8.2418739	1.4064238
F	-0.0165970	-8.5019208	-0.6093095
F	-1.7574975	-9.6096584	0.0406591
C	6.1902914	1.2240586	-0.1486719
C	7.6934517	1.6270313	-0.2575691
C	8.5342992	0.7117050	-1.1981981
F	5.6792255	3.2003829	1.0128321
F	5.9397463	1.3600392	2.1853355
F	5.5922886	1.5824111	-1.3041619
F	6.1143091	-0.1210121	-0.0262478
F	7.7730291	2.8805660	-0.7402845
F	8.2776125	1.5865297	0.9545482
F	7.9360945	0.5681442	-2.3817164
F	8.7148737	-0.4893960	-0.6542351
F	9.7287654	1.2737452	-1.3903453

[a] Calculated at the B3LYP/def2-SV(P) level.

Table S8. Cartesian Coordinates of **1e** in S_1[a]

atom	*x*	*y*	*z*
C	-2.9323478	4.5171321	8.6835697
C	-1.7397845	3.7282291	8.4857324
C	-1.5705967	3.1645711	7.1817433
H	-0.6898229	2.5430177	7.0018378
C	-2.4972513	3.3777005	6.1767448
H	-2.3279743	2.9249787	5.1938266
C	-3.6611599	4.1563628	6.3928787
H	-4.3915182	4.3064113	5.5932412
C	-3.8702125	4.7132525	7.6492060
H	-4.7745900	5.3031829	7.8358306
C	-0.8071013	3.5164563	9.5066160
C	0.0256937	3.3256226	10.4031901
C	0.9438305	3.1681299	11.4526413
C	2.1847553	2.4121442	11.3384615
C	3.0349345	2.4511876	12.4808914
H	3.9840171	1.9087799	12.4244314
C	2.7177450	3.1030964	13.6634937
H	3.4065236	3.0714664	14.5140154
C	1.4908080	3.8030702	13.7638850
H	1.2224565	4.3214554	14.6907541
C	0.6361221	3.8366510	12.6798932
H	-0.3049279	4.3907925	12.7466261
P	-3.1961621	5.2296336	10.2955749
C	-4.6584338	4.5994034	11.1375928
C	-4.7717665	3.1942808	11.2414216
H	-3.9989627	2.5496335	10.8123100
C	-5.8688745	2.6293523	11.8883157
H	-5.9498813	1.5413518	11.9655943
C	-6.8623701	3.4512724	12.4374775
H	-7.7236559	3.0042332	12.9430776
C	-6.7570371	4.8433778	12.3361441
H	-7.5395856	5.4853488	12.7517423
C	-5.6592449	5.4217180	11.6961931
H	-5.5974448	6.5087899	11.6072876
C	-3.0488944	7.0173952	10.3885000
C	-2.6799869	7.7524723	9.2417343
H	-2.5521506	7.2393876	8.2853804
C	-2.4864285	9.1312758	9.3315833

(Table S8 continued)

atom	*x*	*y*	*z*
H	-2.2118693	9.6975830	8.4369443
C	-2.6351033	9.7860228	10.5601903
H	-2.4740860	10.8662472	10.6267007
C	-2.9710366	9.0581303	11.7095421
H	-3.0654649	9.5661929	12.6738716
C	-3.1682943	7.6805380	11.6315525
H	-3.3973044	7.1161600	12.5401017
C	1.6363556	0.8968647	9.0775222
C	1.8160309	1.0425549	7.6714564
C	0.9855812	0.3599596	6.7693266
H	1.1523032	0.4924743	5.6931494
C	-0.0392904	-0.4914176	7.1979751
C	-0.2184843	-0.6333089	8.5779849
H	-1.0073244	-1.3019659	8.9441229
C	0.5810744	0.0428177	9.5121205
B	2.6435019	1.5609836	10.1263983
C	4.2152277	1.2865032	9.9482947
C	4.7468181	-0.0338604	9.9046466
C	6.1212679	-0.2437788	9.7240867
H	6.5009492	-1.2726205	9.7036211
C	7.0219879	0.8159178	9.5638635
C	6.5005630	2.1124300	9.6006459
H	7.1807579	2.9626847	9.4676320
C	5.1334859	2.3639169	9.8008251
C	2.8877645	1.9424398	7.0894810
H	2.7692322	2.0398252	5.9959000
H	3.9024585	1.5551536	7.2864210
H	2.8474215	2.9582979	7.5210563
C	-0.9345589	-1.2055166	6.2112175
H	-1.8466550	-0.6153120	5.9912625
H	-1.2695370	-2.1836005	6.6007593
H	-0.4207483	-1.3804350	5.2488754
C	0.2792302	-0.1898580	10.9791708
H	-0.3978945	-1.0528408	11.1081803
H	-0.2069354	0.6924498	11.4325361
H	1.1886136	-0.3790300	11.5738514
C	3.8638570	-1.2552799	10.0676433
H	4.4716701	-2.1737872	10.1448927

(Table S8 continued)

atom	*x*	*y*	*z*
H	3.1705529	-1.3787039	9.2171925
H	3.2404958	-1.1914120	10.9776780
C	8.5020796	0.5643968	9.3862401
H	9.0055735	1.4243018	8.9097346
H	8.6910021	-0.3289192	8.7634337
H	9.0026733	0.3910402	10.3596620
C	4.6959486	3.8165401	9.8454949
H	4.5782739	4.1701290	10.8864042
H	3.7231666	3.9826175	9.3540113
H	5.4429493	4.4658564	9.3548862

[a] Calculated at the B3LYP/def2-SV(P) level.

4. Complete Reference for Ref. 24

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