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Supplementary Information

Effects of Counter Anions and *P*-Substituents on Optical and Photophysical Properties of 2-Phenylbenzo[*b*]phospholium Salts

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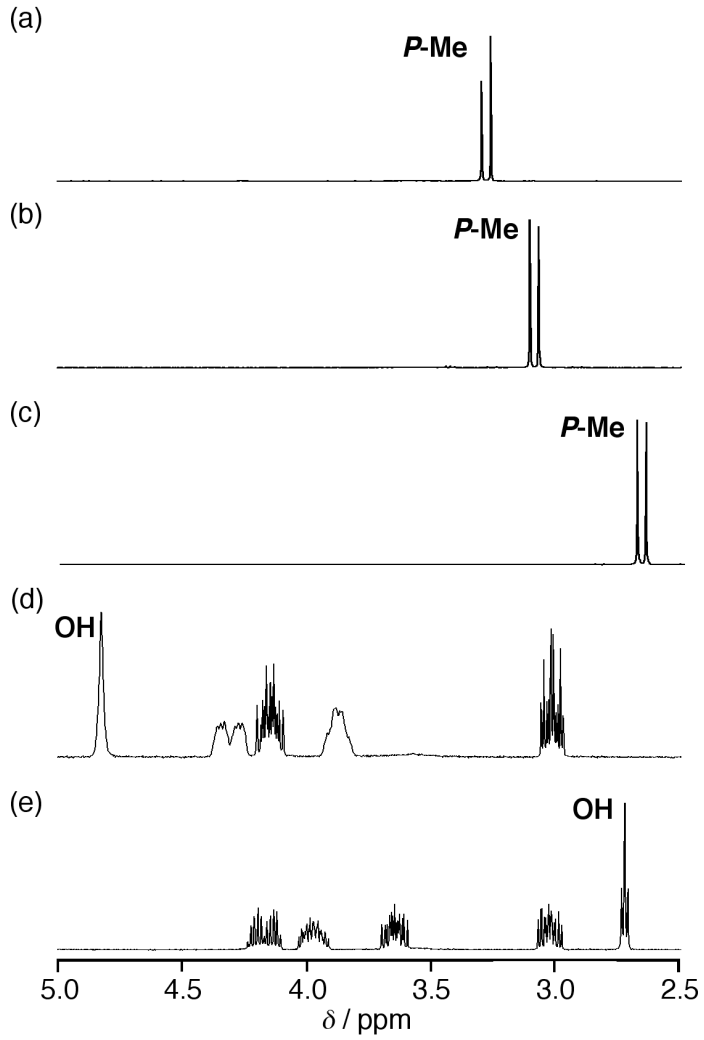

Fig. S1 ^{1}H NMR spectra (δ = 5.0–2.5 ppm) of (a) **9**, (b) **3**, (c) **4**, (d) **7**, and (e) **8** in CD_2Cl_2 (ca.10 mM).

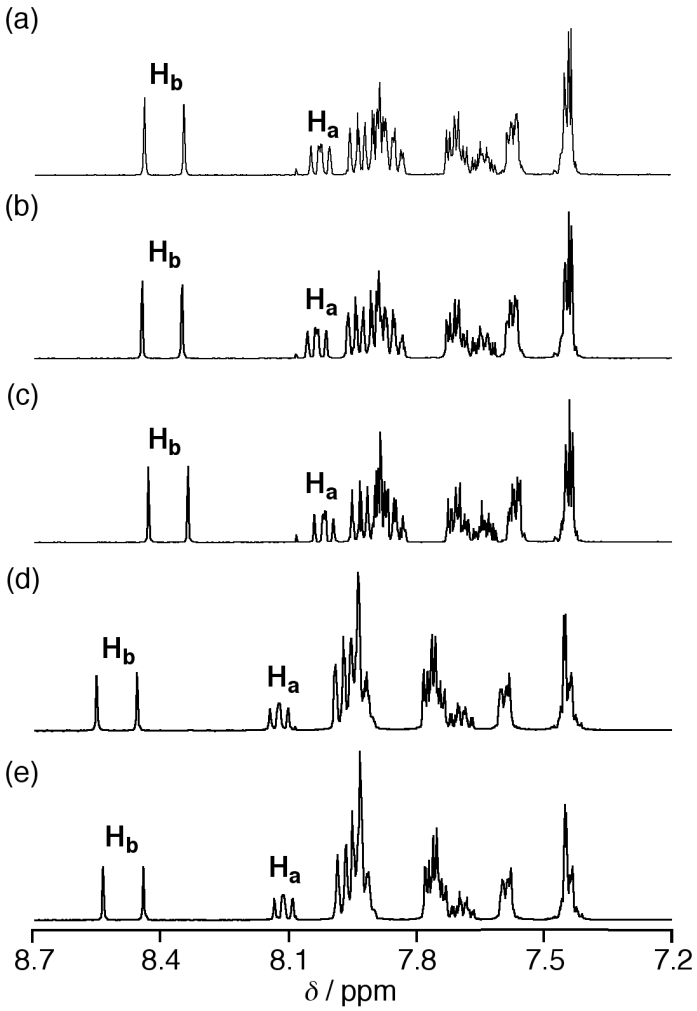

Fig. S2 ^{1}H NMR spectra (δ = 8.7–7.2 ppm) of (a) **9**, (b) **3**, (c) **4**, (d) **5**, and (e) **6** in CD_3OD (ca.10 mM).

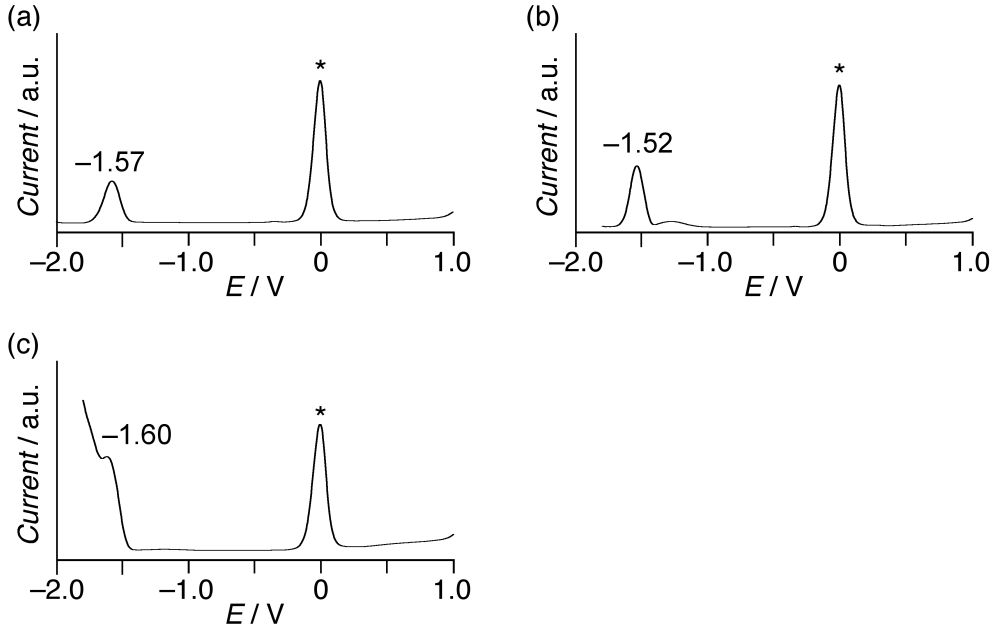

Fig. S3 Differential pulse voltammograms of (a) **4**, (b) **6**, and (c) **8**. Measured in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as a supporting electrolyte; Ag/Ag^+ [$AgNO_3$ (MeCN)] as a reference electrode; scan rate 60 mV s^{-1}. Asterisk (*) indicates Fc/Fc^+.

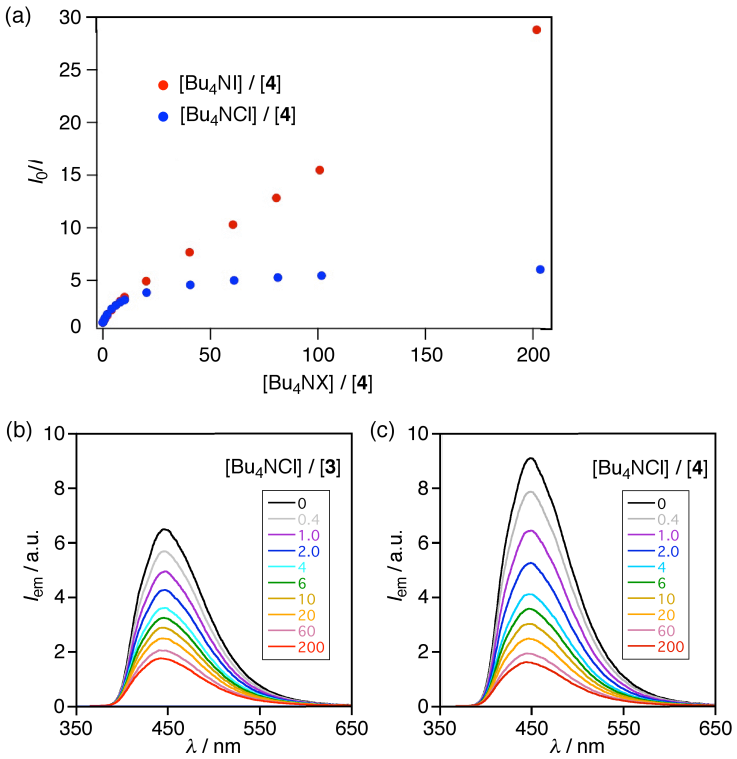

Fig. S4 Fluorescence titration measurements of **3** and **4** using Bu_4NX (X = I, Cl) in CH_2Cl_2 at 25 °C: λ_{ex} = 358 nm (λ_{abs}). (a) Stern–Volmer plots for **4**. I_0: Fluorescence intensity when [Bu_4NX] = 0. (b) Spectral changes for **3** (25 mM). (c) Spectral changes for **4** (25 mM).

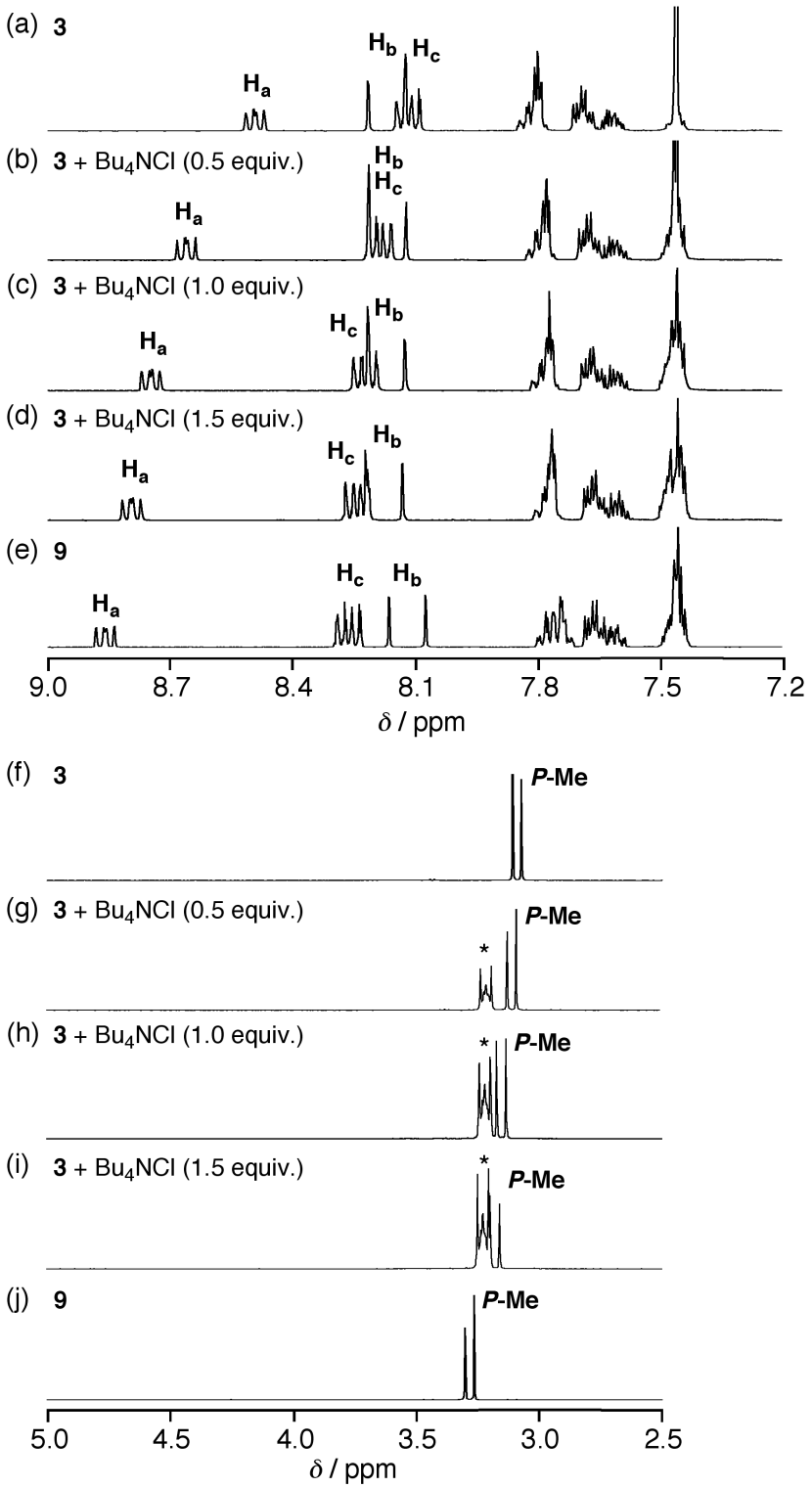

Fig. S5 ^{1}H NMR spectra of (a, f) **3**, (b–d, g–i) **3** + Bu_4NCl and (e, j) **9** in CD_2Cl_2 (**3**, **9**: ca. 10 mM). (a)–(e): δ 9.0–7.2 ppm; (f)–(j): δ 5.0–2.5 ppm. For the numbering of H_a, H_b and H_c, see: Scheme 1 in text. An asterisks in (g–i) indicate the N-methylene peak ($NCH_2CH_2CH_2CH_3$) of Bu_4N^+ ion.

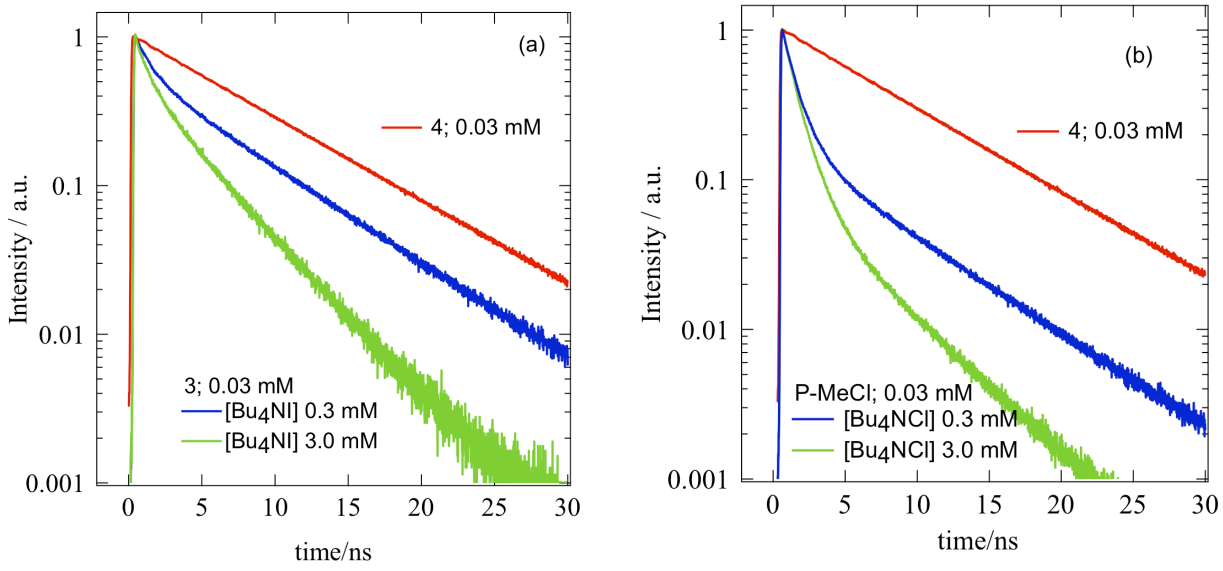

Fig. S6 Effect of salts (Bu_4NI and Bu_4NCl) on the decay curves of (a) **3** and (b) **9**. With increasing the concentration of halides, the intensity of the faster component increased, and the decay rate of the slower component increased. This fact indicates that there are at least two quenching mechanisms of the fluorescence; the CIP mechanism discussed in the text and the dynamic quenching effect due to the diffusional quenching from free halide ions.

^{1}H and ^{13}C{^{1}H} NMR Charts (**Figures S7–S21**) Asterisks (*) indicate the residual solvents.

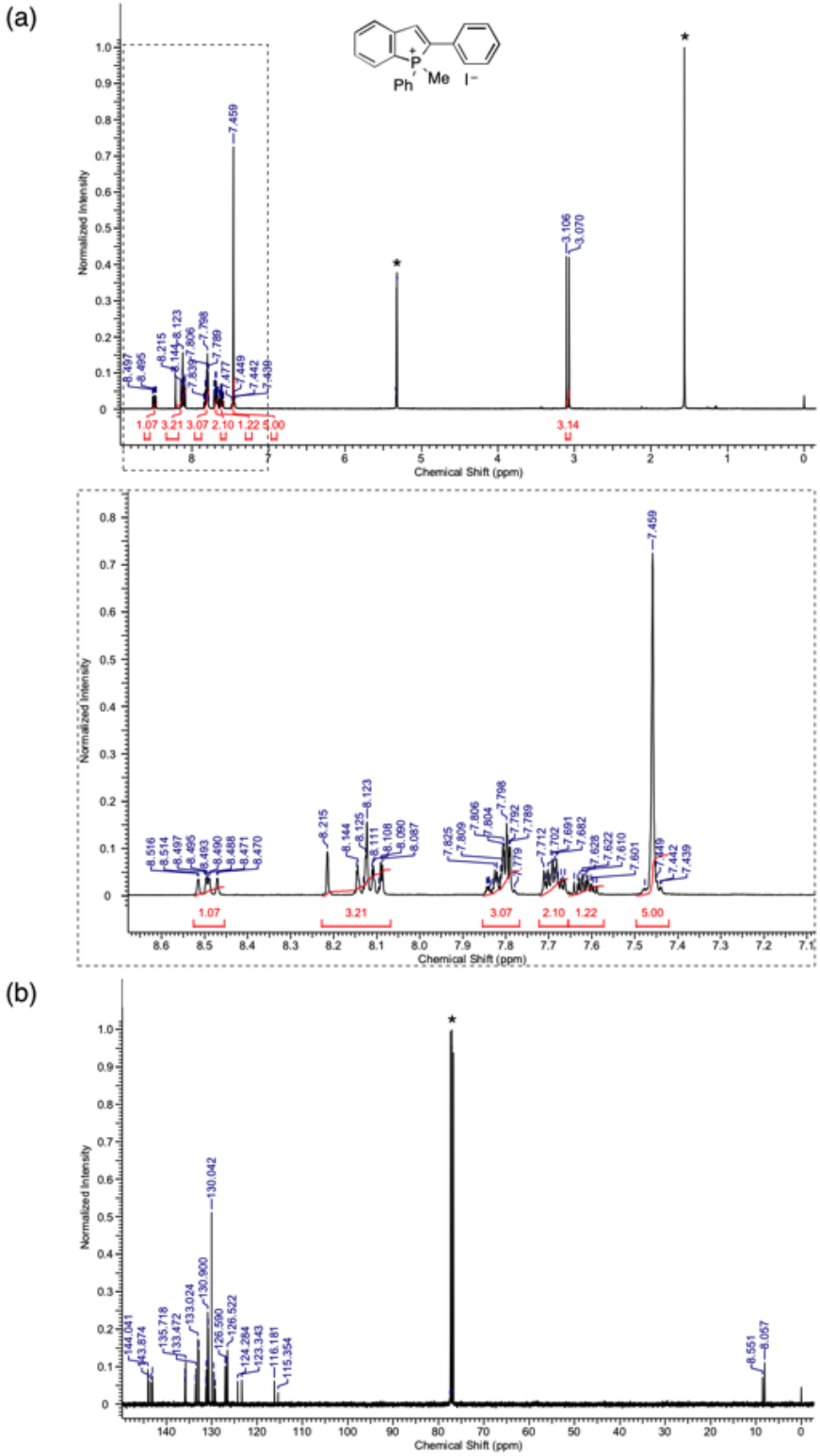

Figure S7. (a) ^{1}H NMR (in CD_2Cl_2) and (b) ^{13}C{^{1}H} NMR spectra (in $CDCl_3$) of **3**.

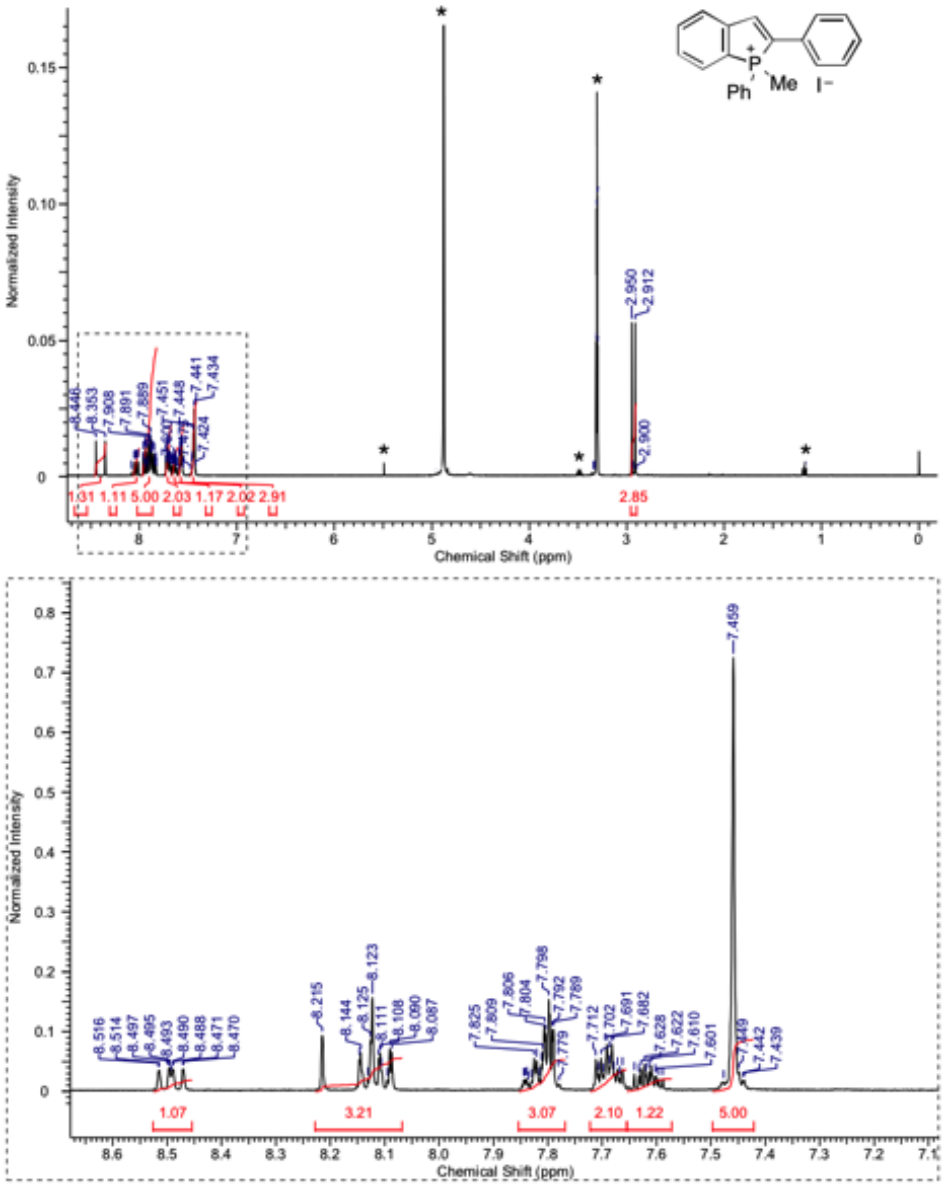

Figure S8. ^{1}H NMR spectra of **3** in CD_3OD.

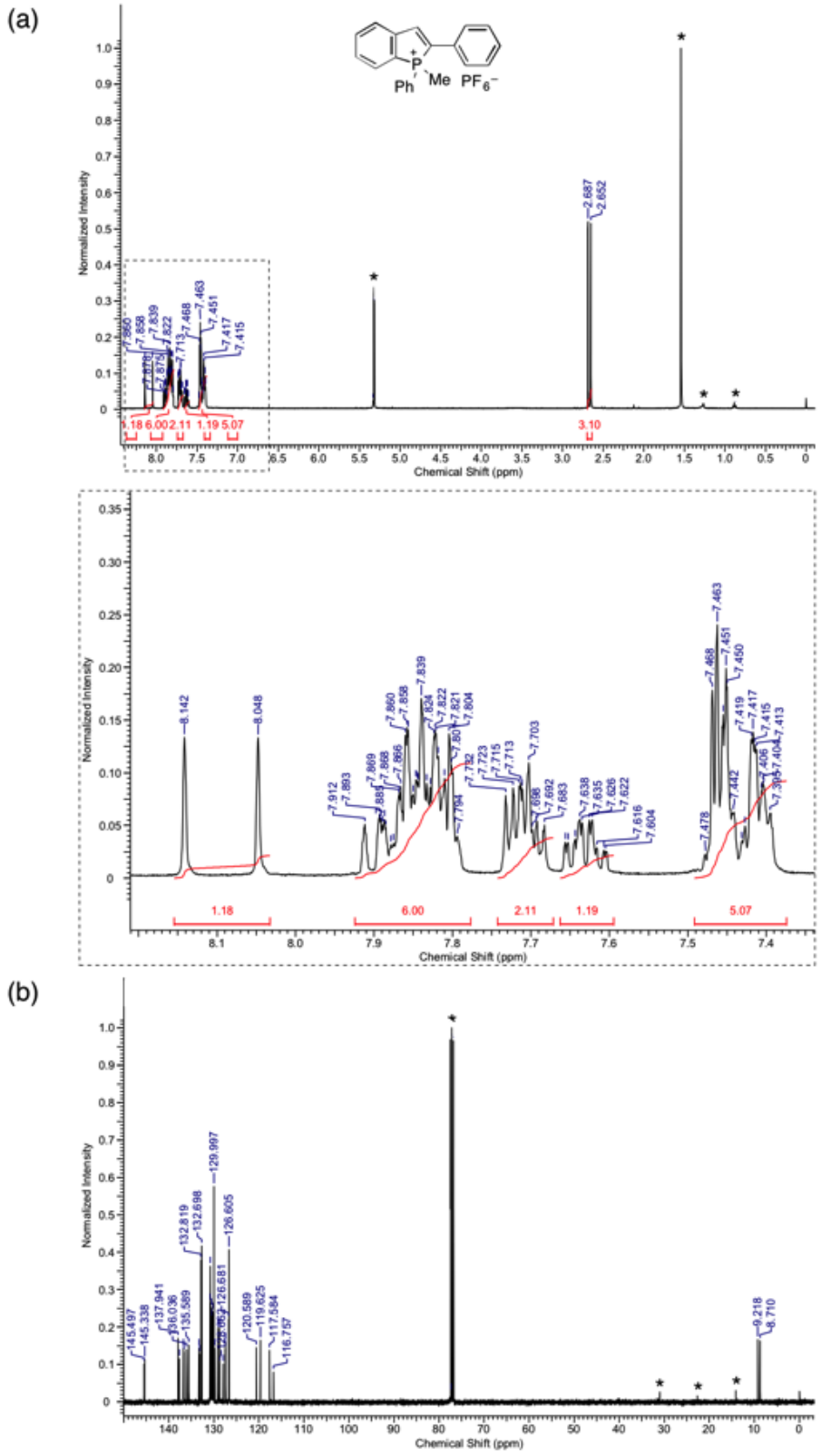

Figure S9. (a) ^{1}H NMR (in CD_2Cl_2) and (b) $^{13}C\{^{1}H\}$ NMR spectra (in $CDCl_3$) of **4**.

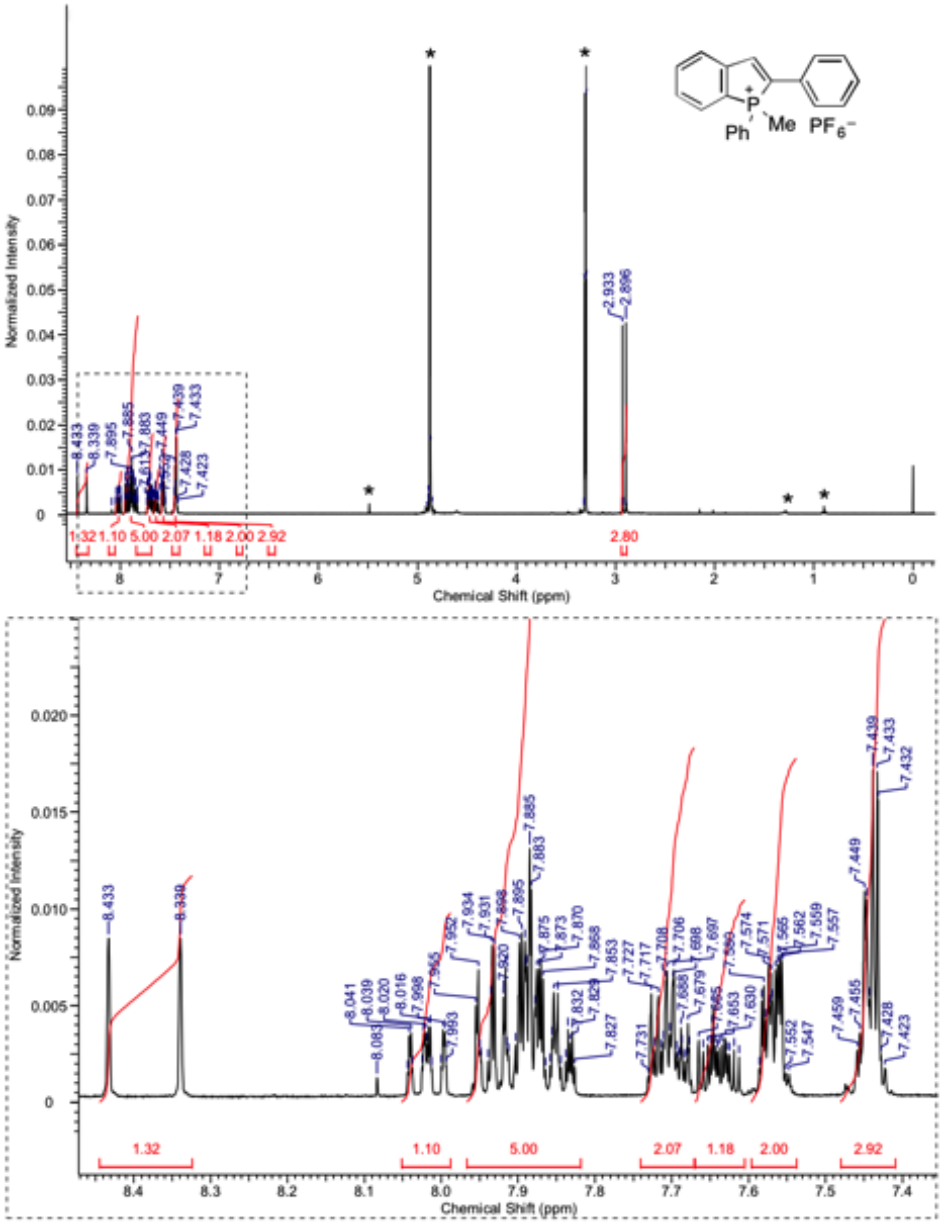

Figure S10. ^{1}H NMR spectra of **4** in CD_3OD.

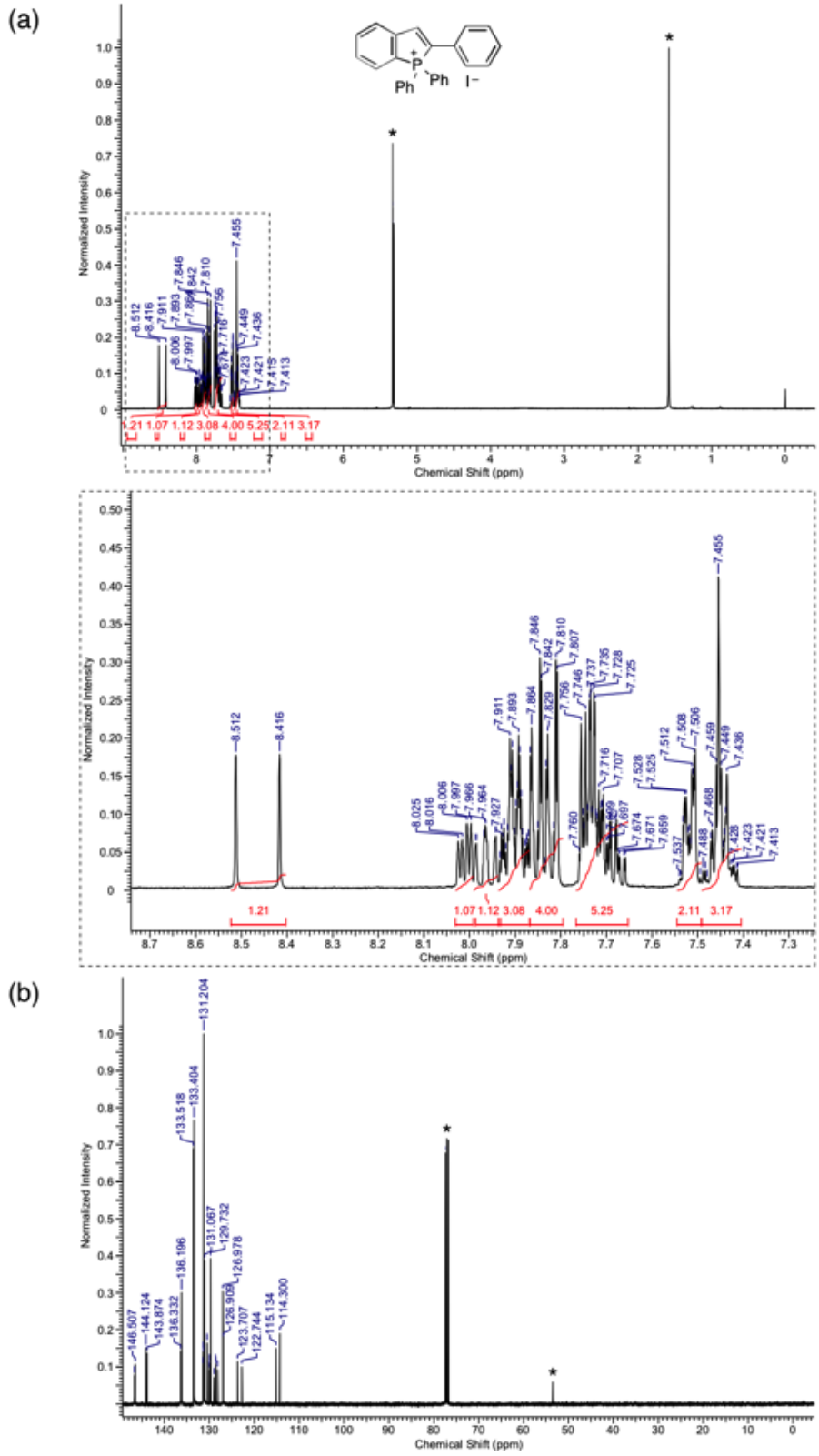

Figure S11. (a) ^{1}H NMR (in CD_2Cl_2) and (b) $^{13}C\{^{1}H\}$ NMR spectra (in $CDCl_3$) of **5**.

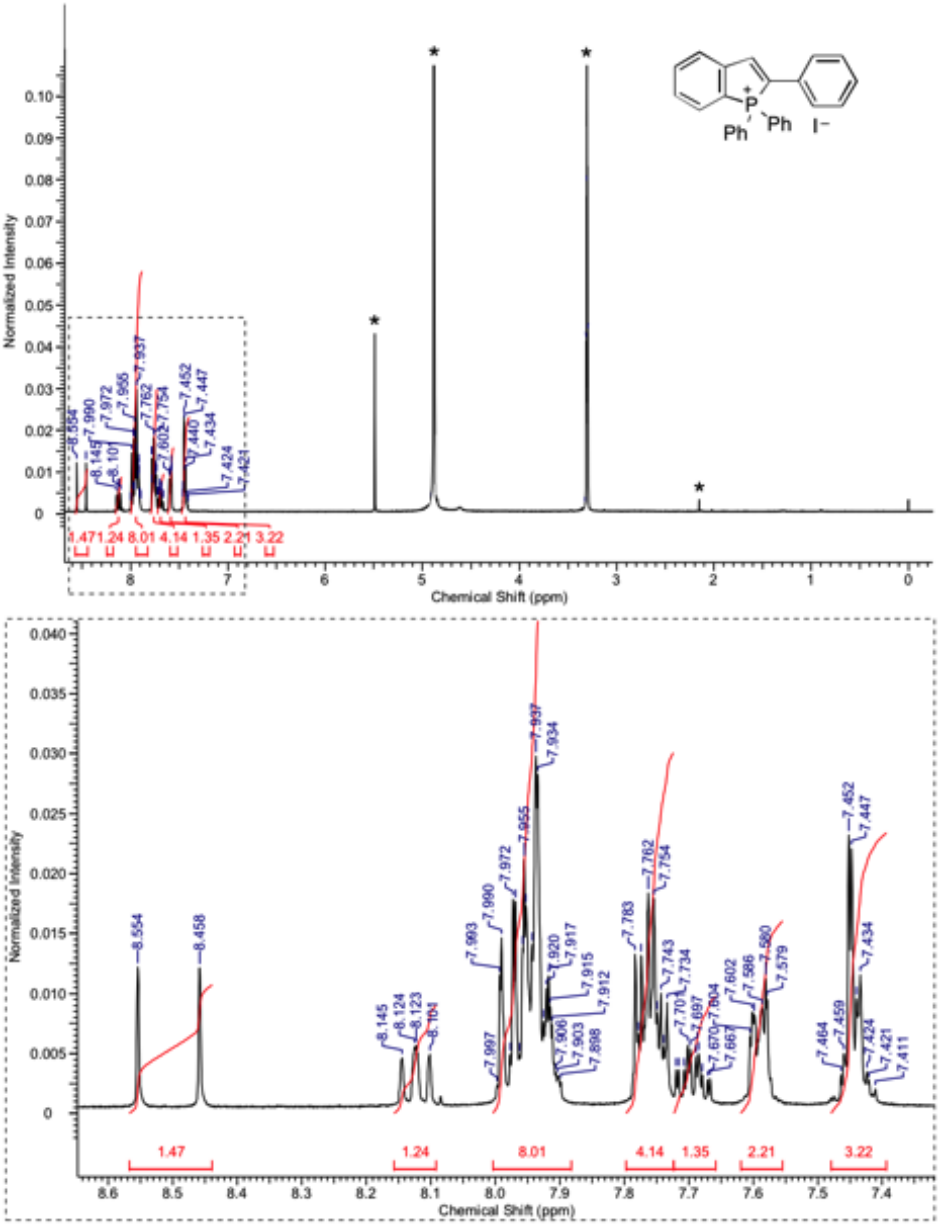

Figure S12. ^{1}H NMR spectra of **5** in CD_3OD.

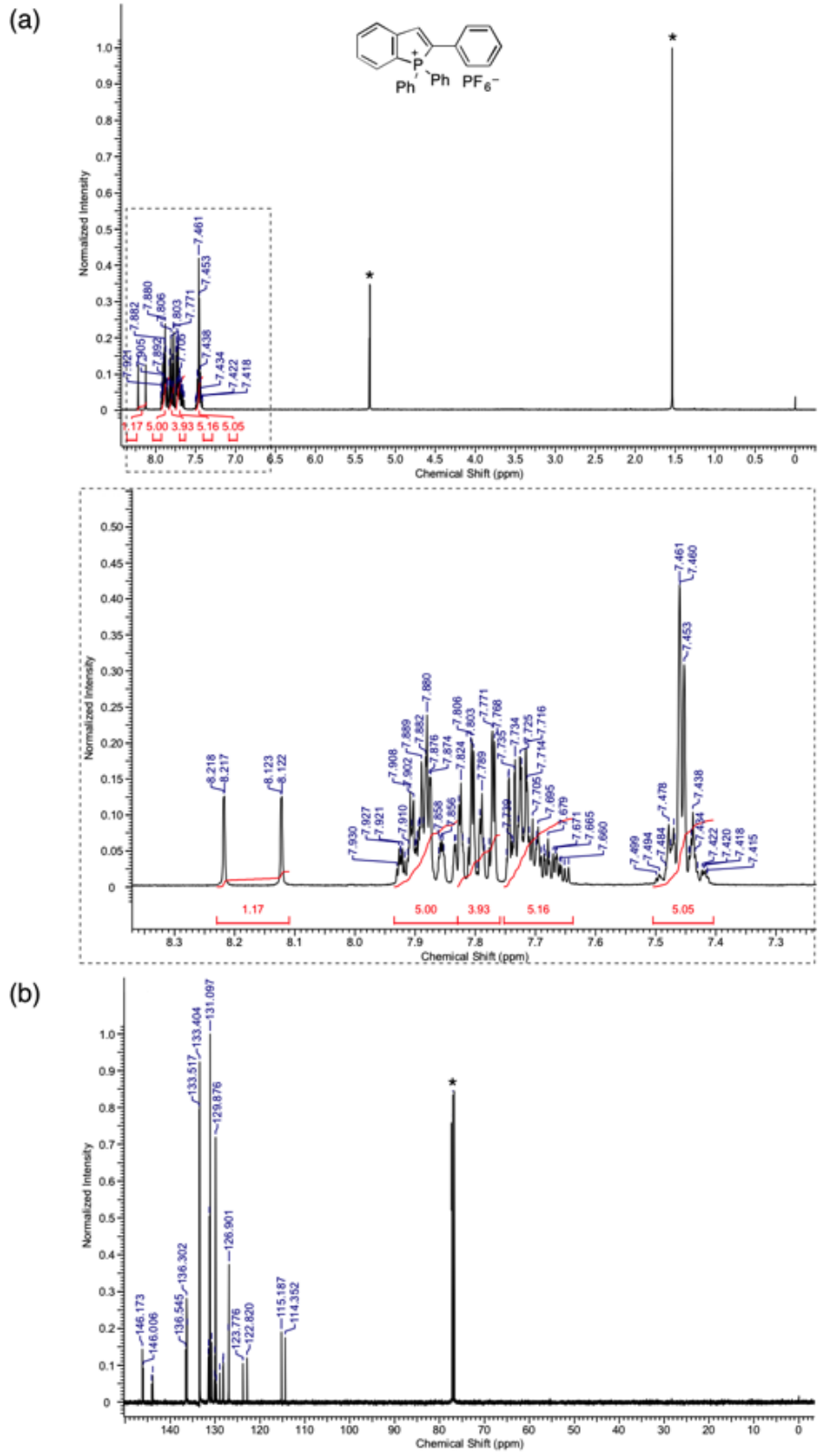

Figure S13. (a) ^{1}H NMR (in CD_2Cl_2) and (b) $^{13}C\{^{1}H\}$ NMR spectra (in $CDCl_3$) of **6**.

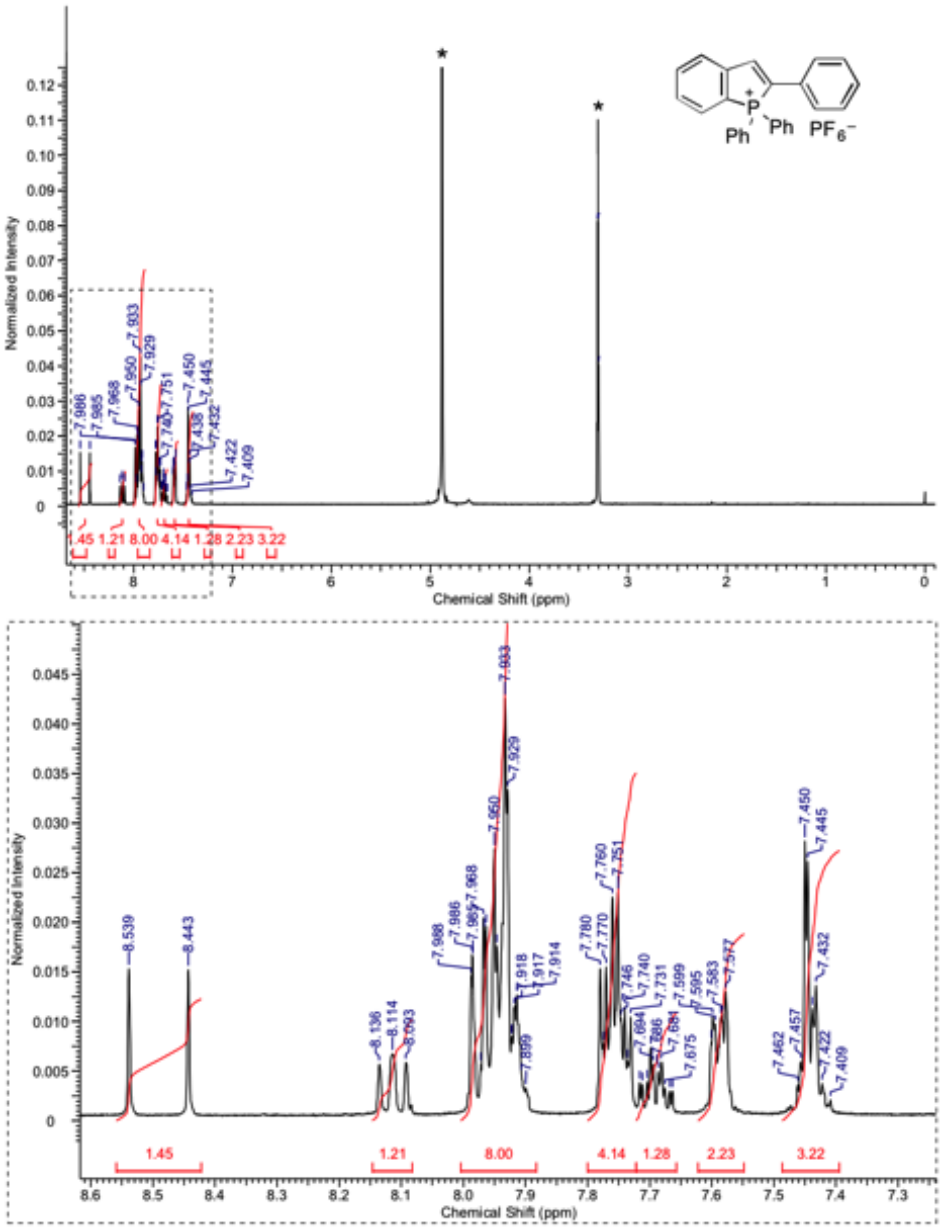

Figure S14. ^{1}H NMR spectra of **6** in CD_3OD.

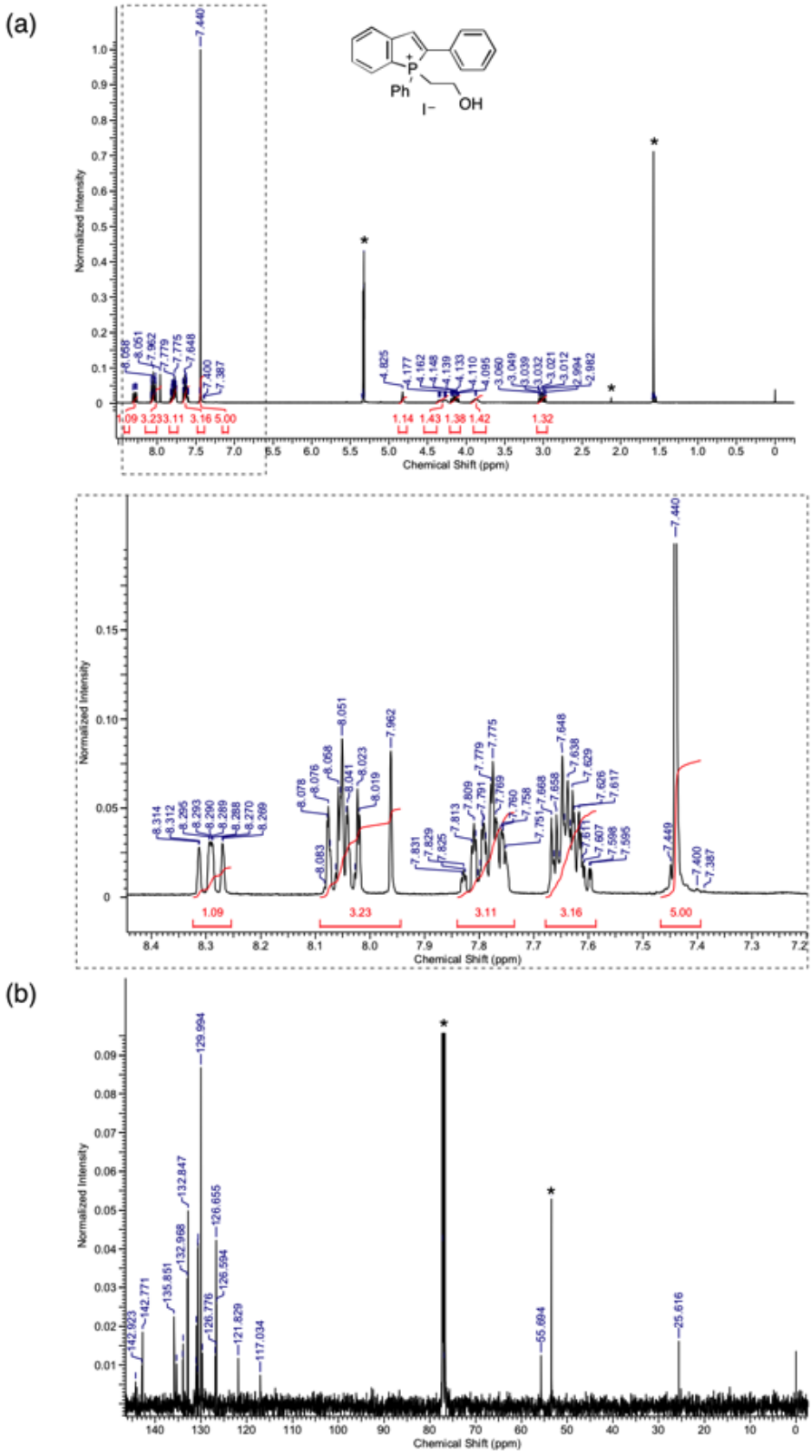

Figure S15. (a) ^{1}H NMR (in CD_2Cl_2) and (b) $^{13}C\{^{1}H\}$ NMR spectra (in $CDCl_3$) of **7**.

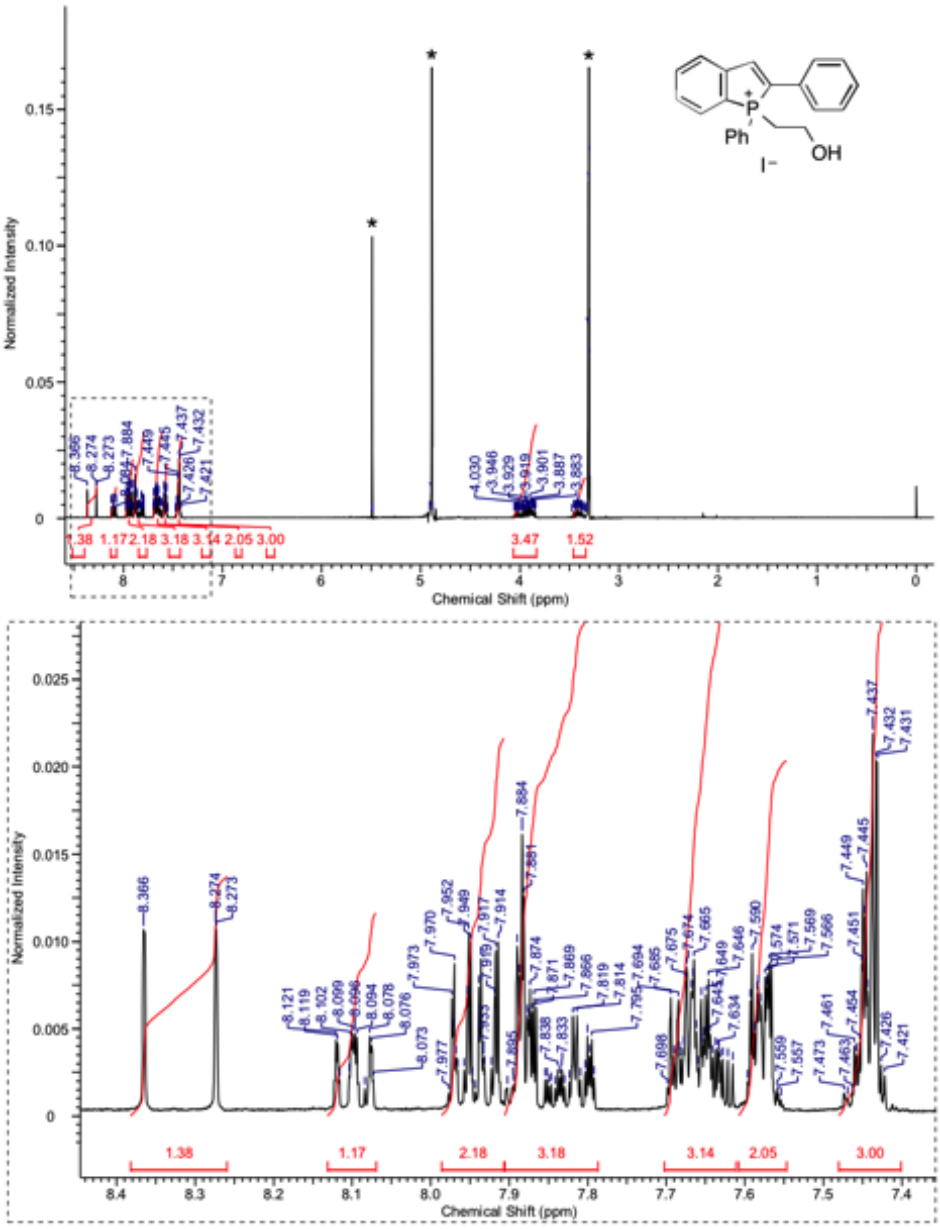

Figure S16. ^{1}H NMR spectra of **7** in CD_3OD.

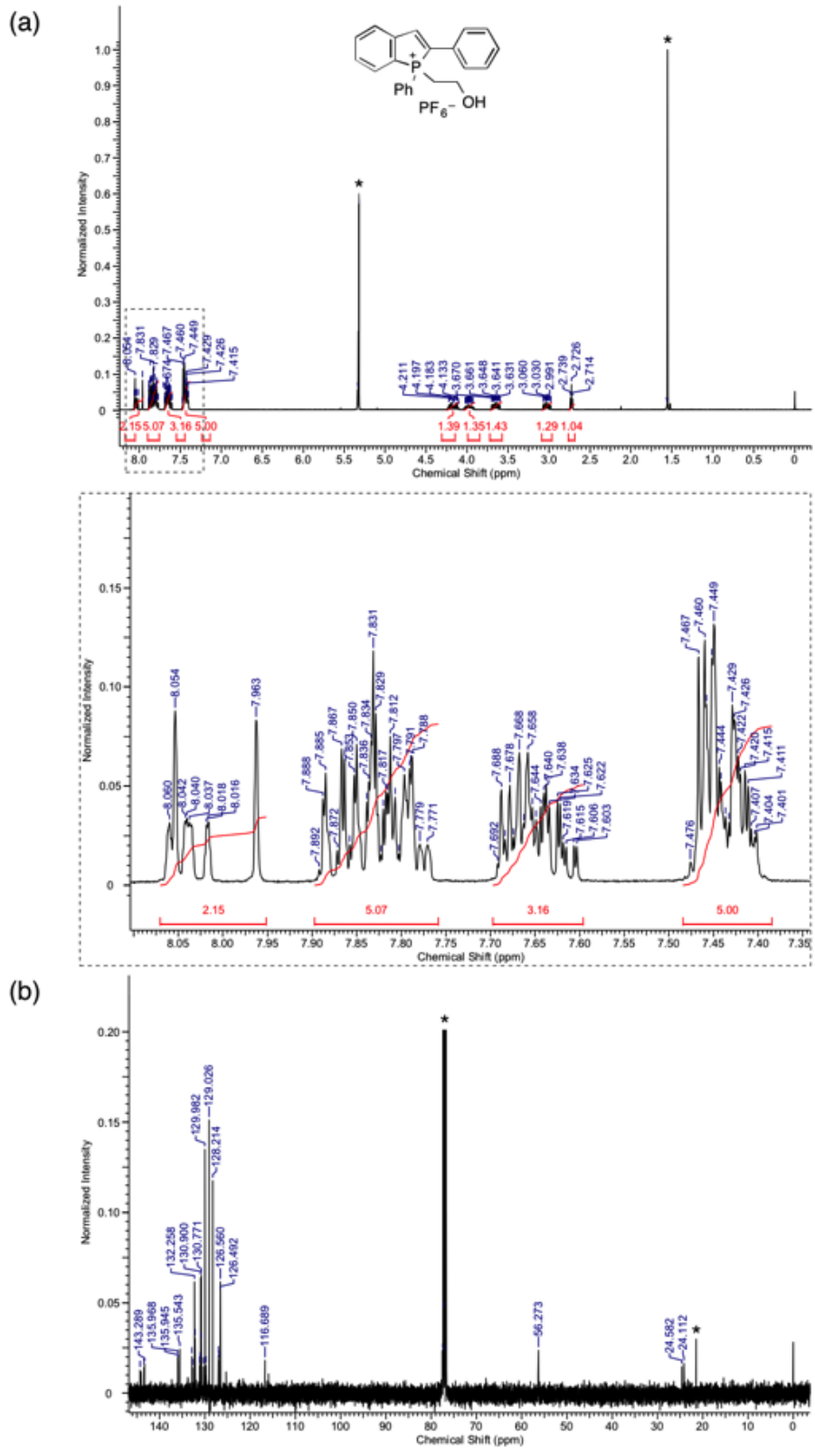

Figure S17. (a) ^{1}H NMR (in CD_2Cl_2) and (b) $^{13}C\{^{1}H\}$ NMR spectra (in $CDCl_3$) of **8**.

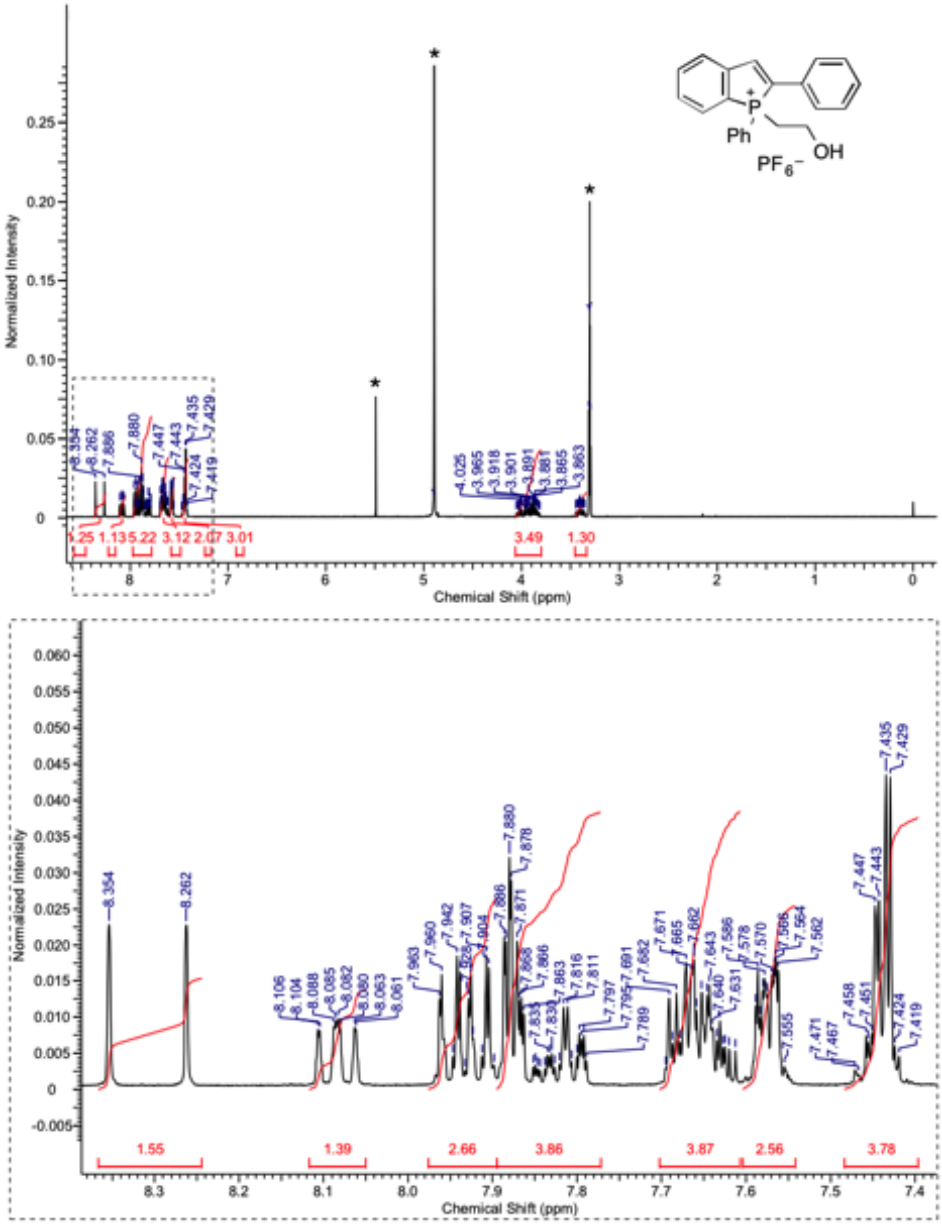

Figure S18. ^{1}H NMR spectra of **8** in CD_3OD.

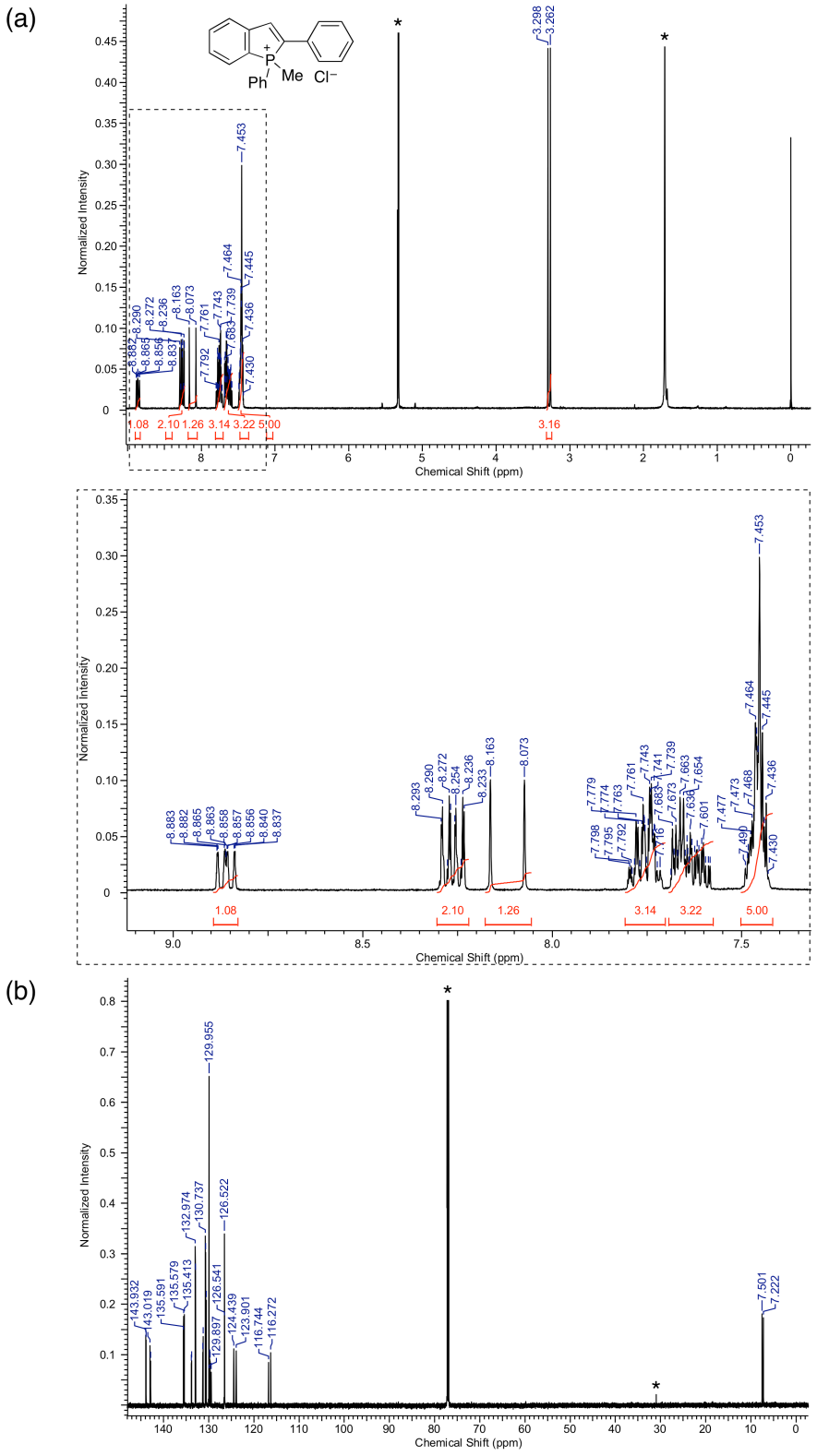

Figure S19. (a) ^{1}H NMR (in CD_2Cl_2) and (b) $^{13}C\{^{1}H\}$ NMR spectra (in $CDCl_3$) of **9**.

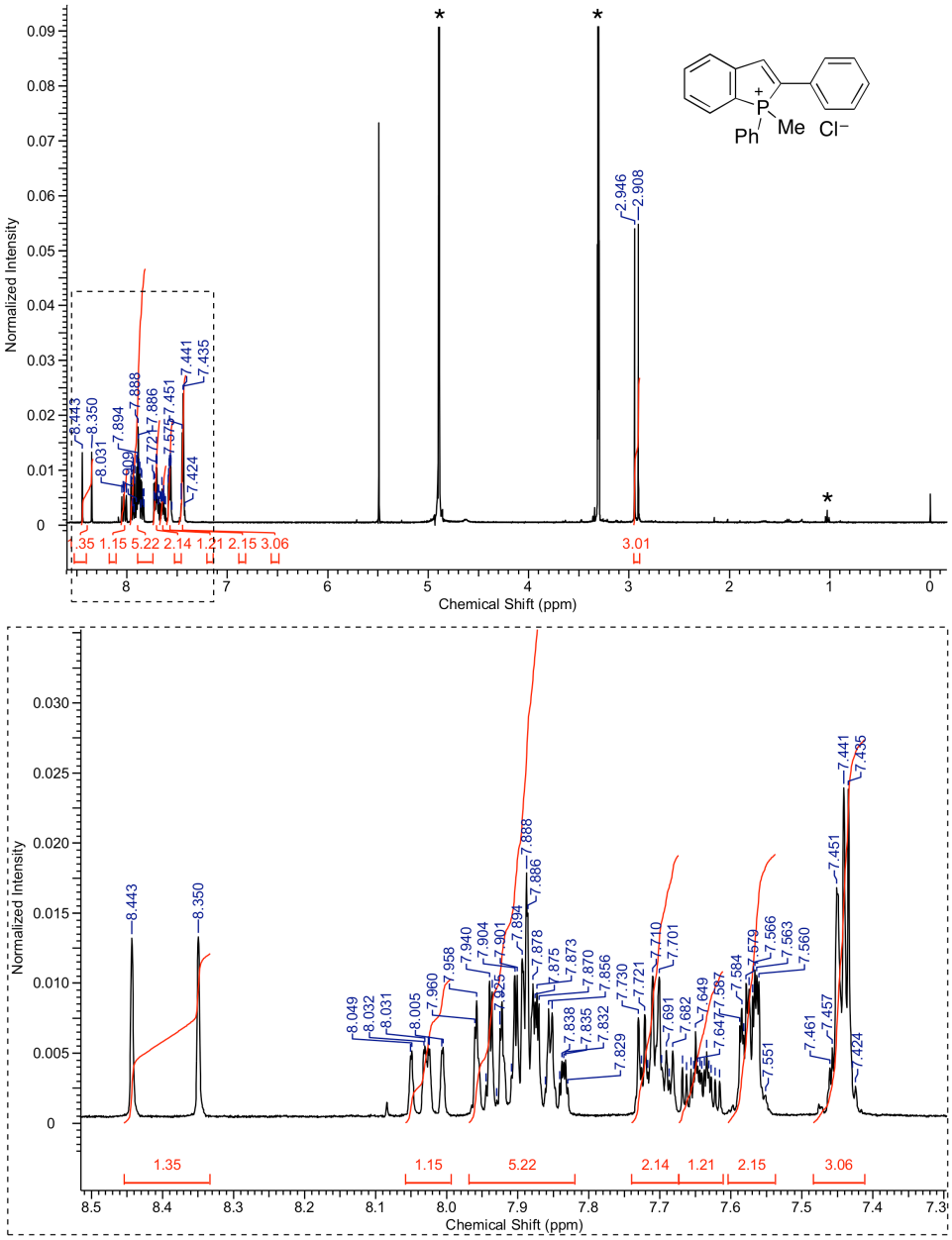

Figure S20. ^{1}H NMR spectra of **9** in CD_3OD.

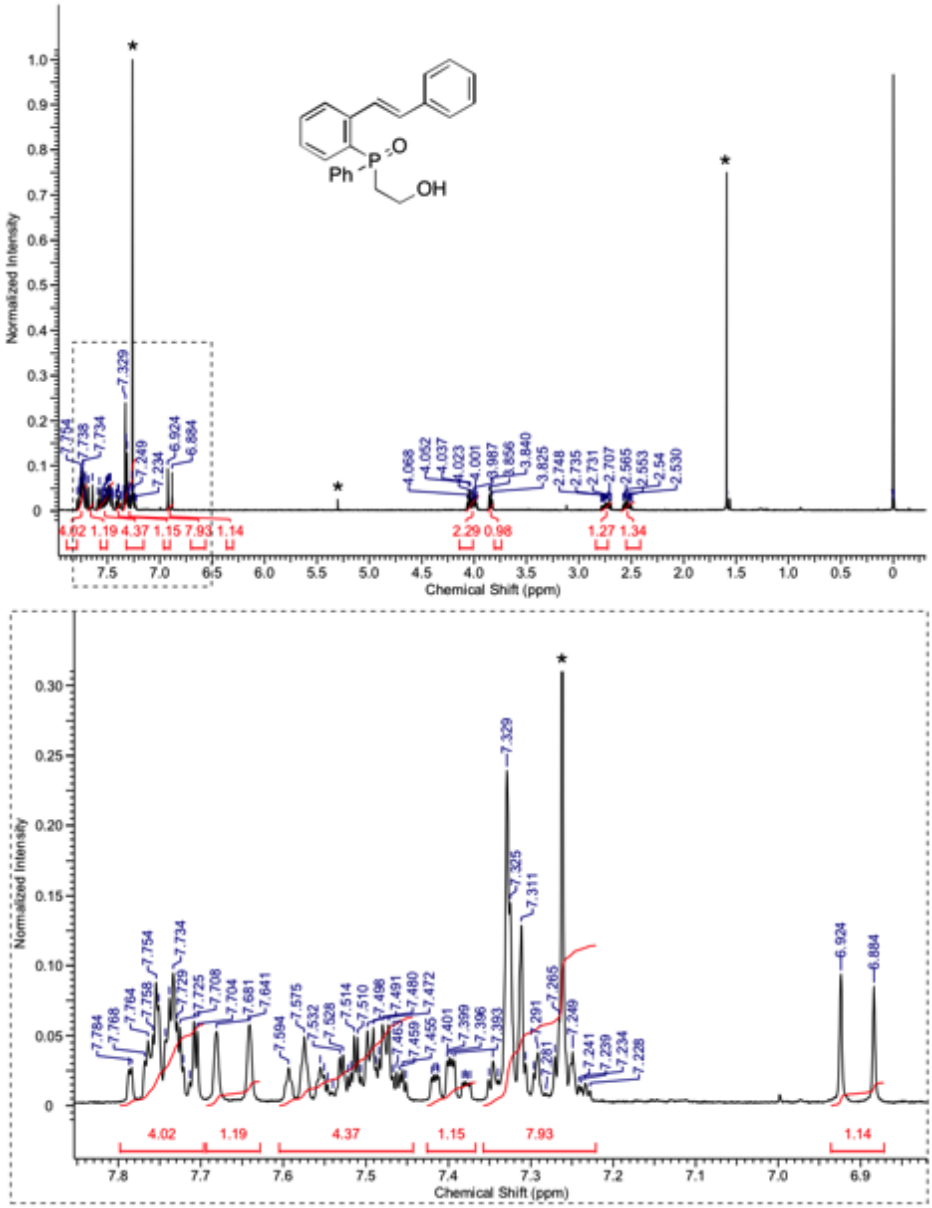

Figure S21. ^{1}H NMR spectra of **10** in $CDCl_3$.