Electronic Supplementary Information for

Facile synthesis of luminescent benzo-1,2-dihydrophosphinines from a phosphaalkene

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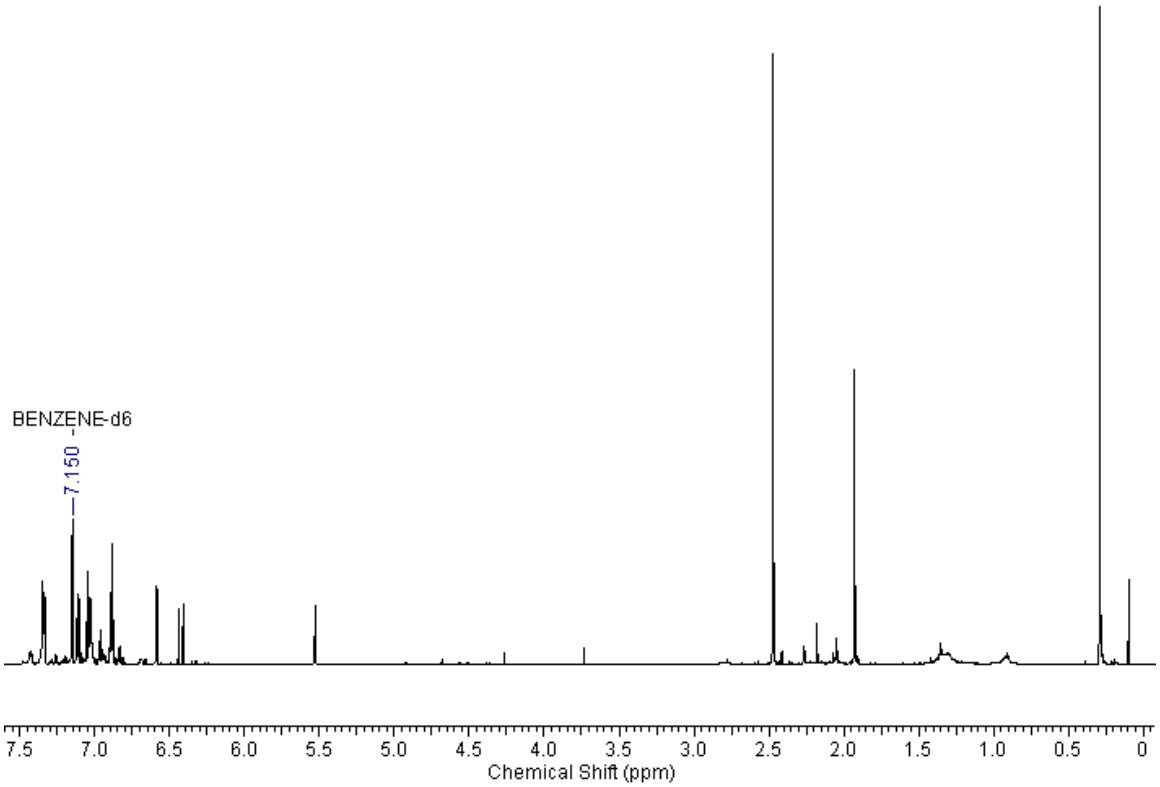
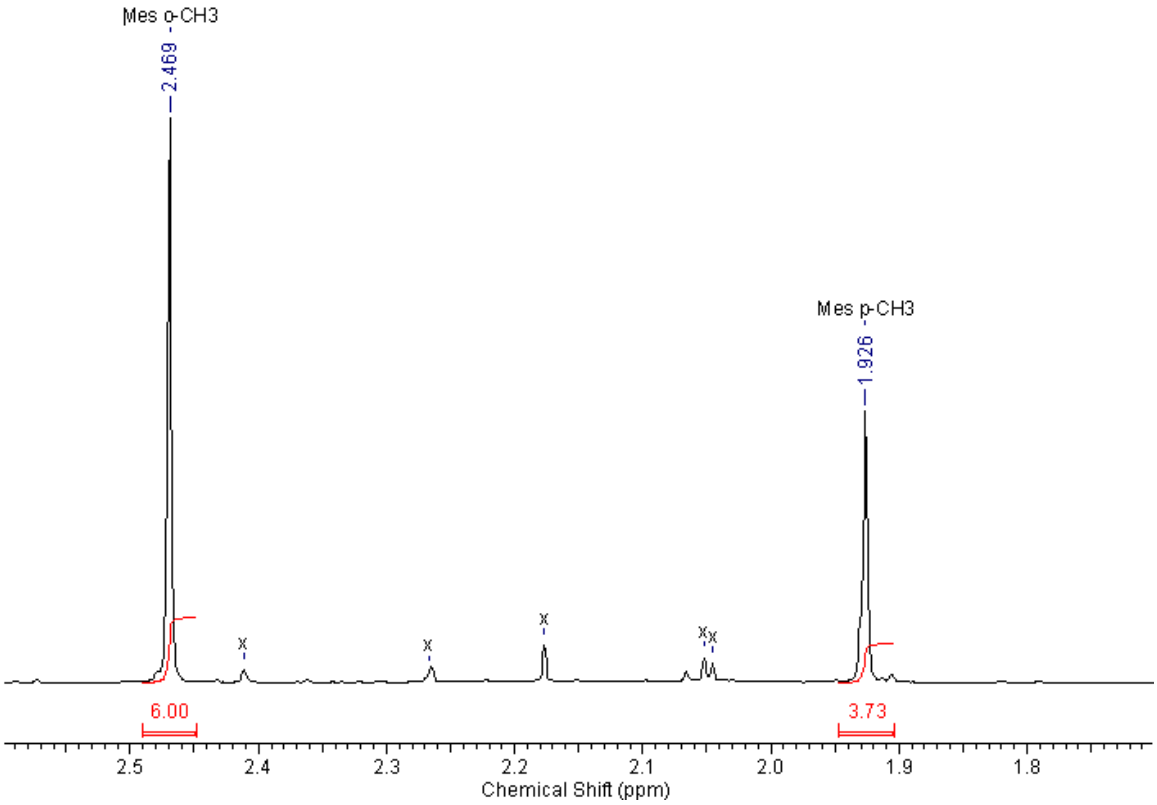
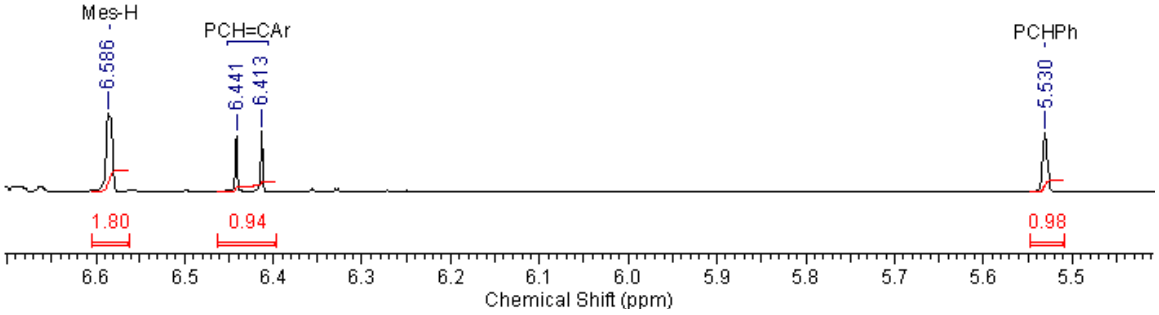
Fig. S1 ^{1}H NMR Spectrum of **4a** in C_6D_6 at 25 °C.







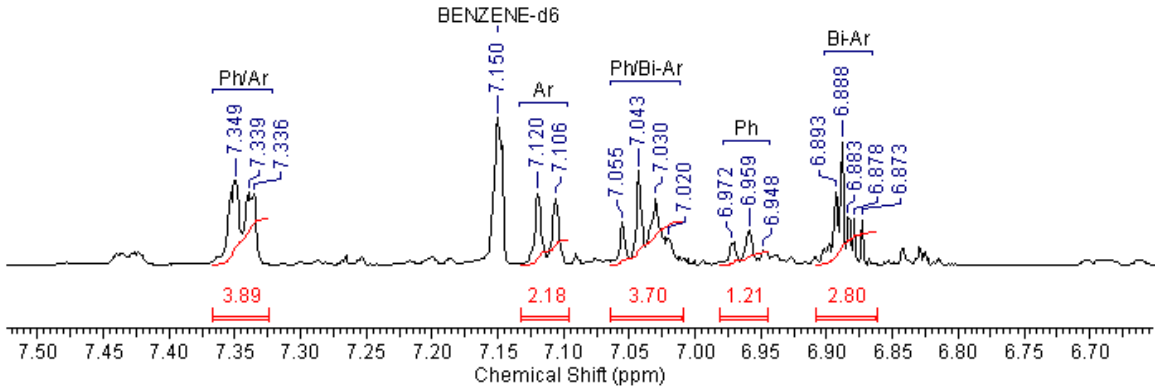
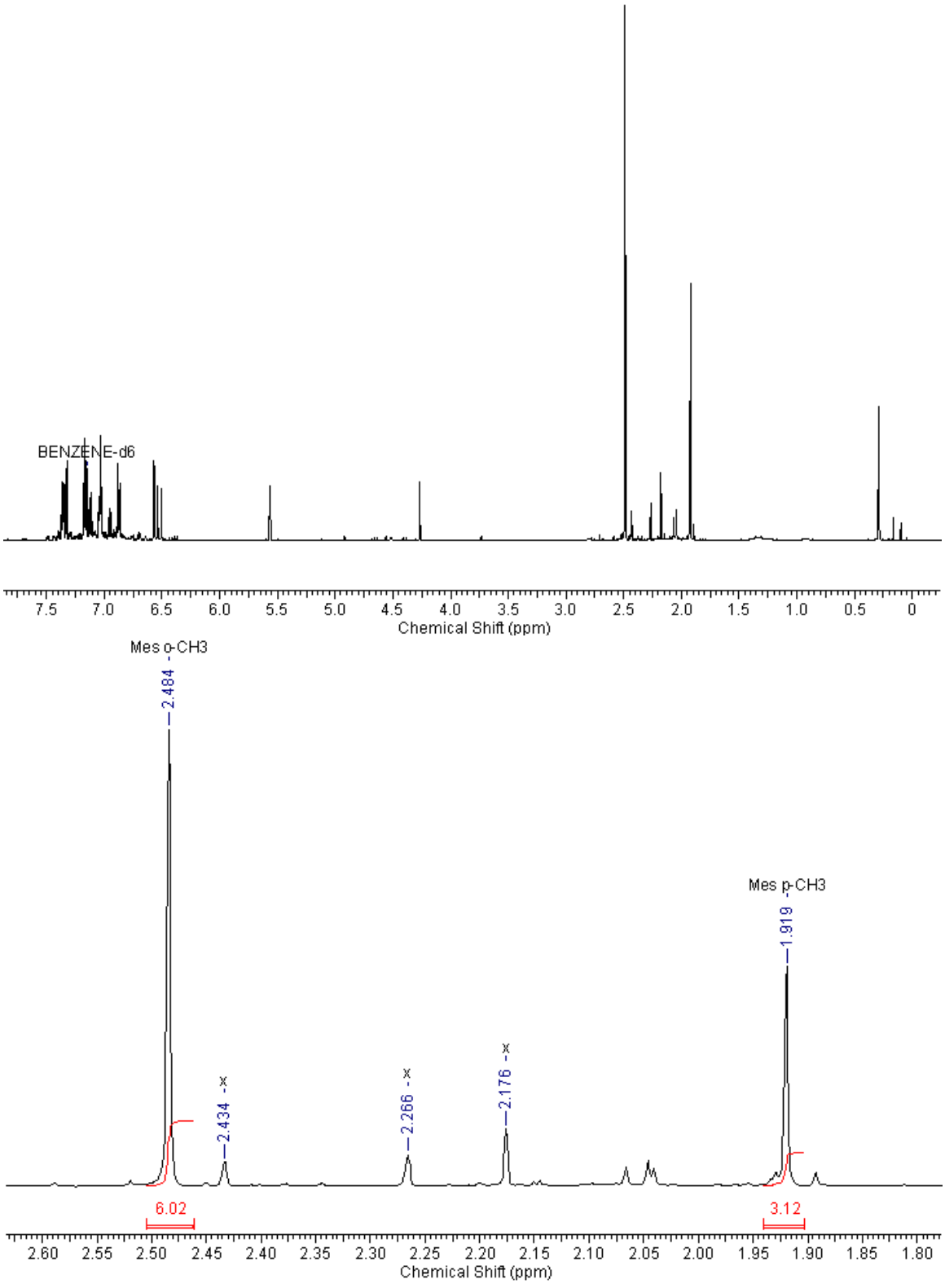
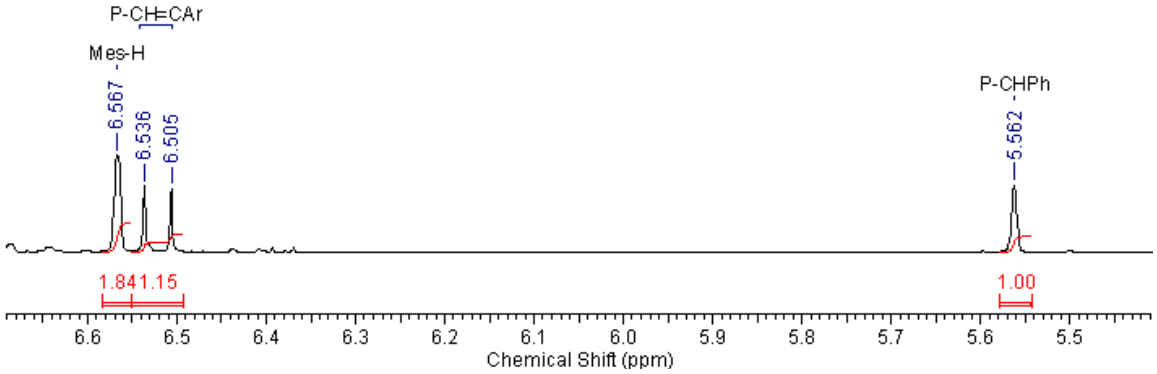


Fig. S2 ^{1}H NMR Spectrum of **4b** in C_6D_6 at 25 °C.





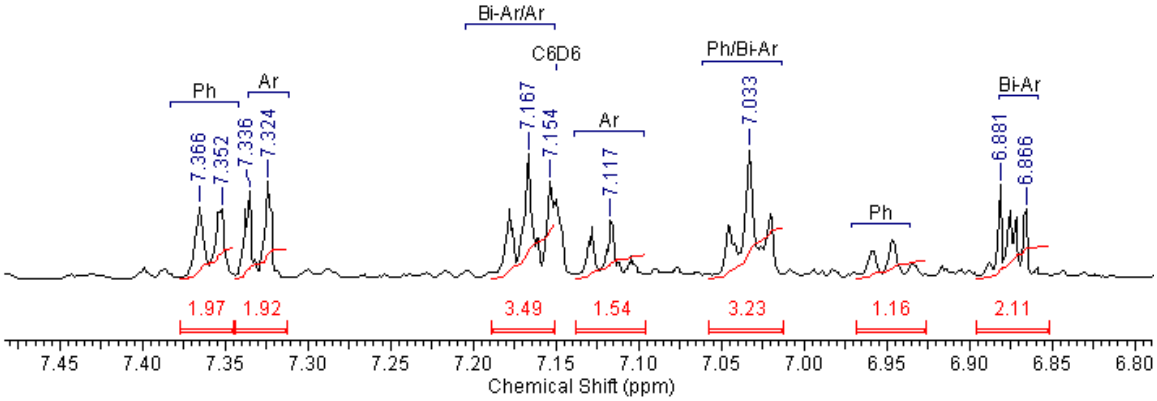
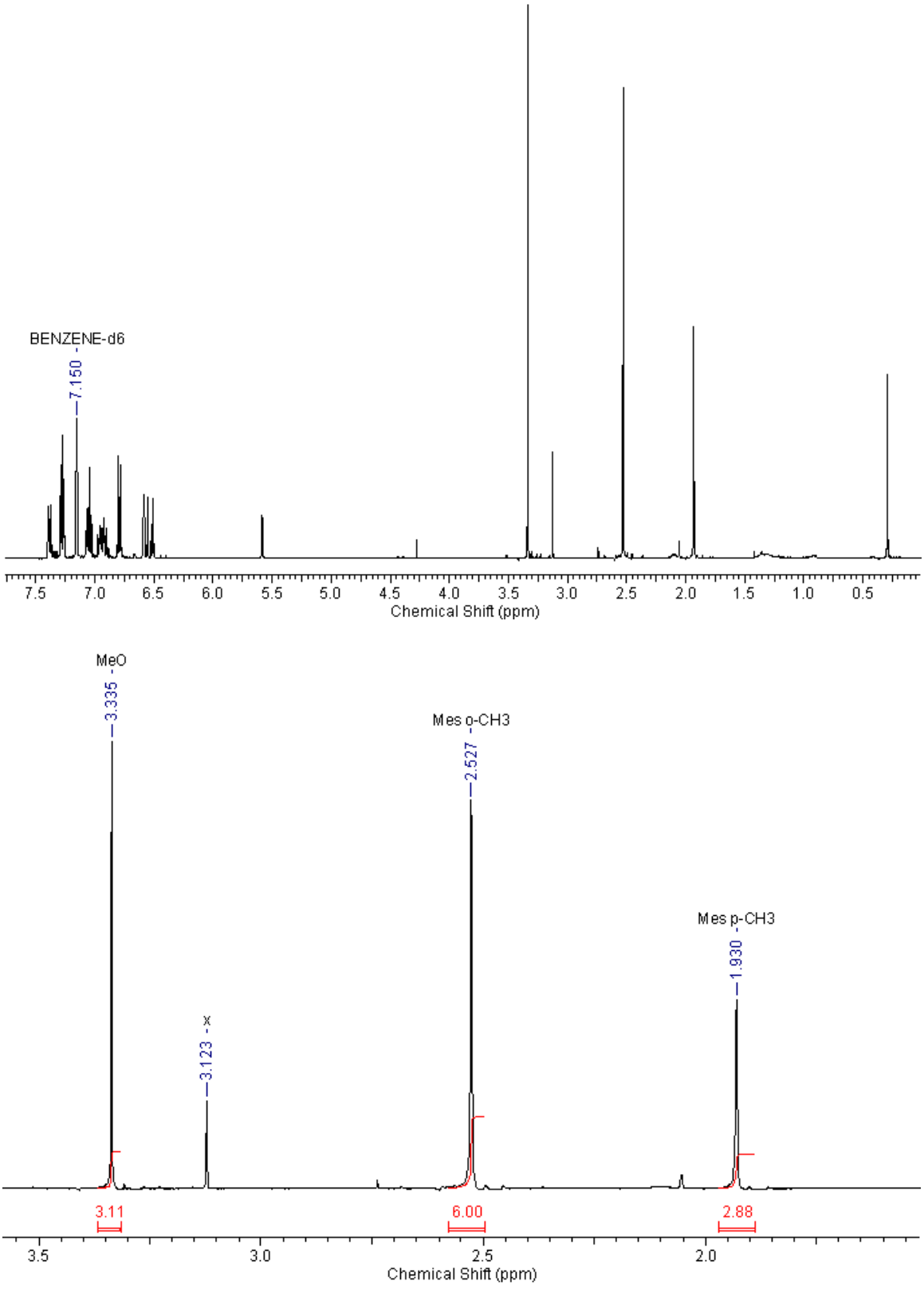
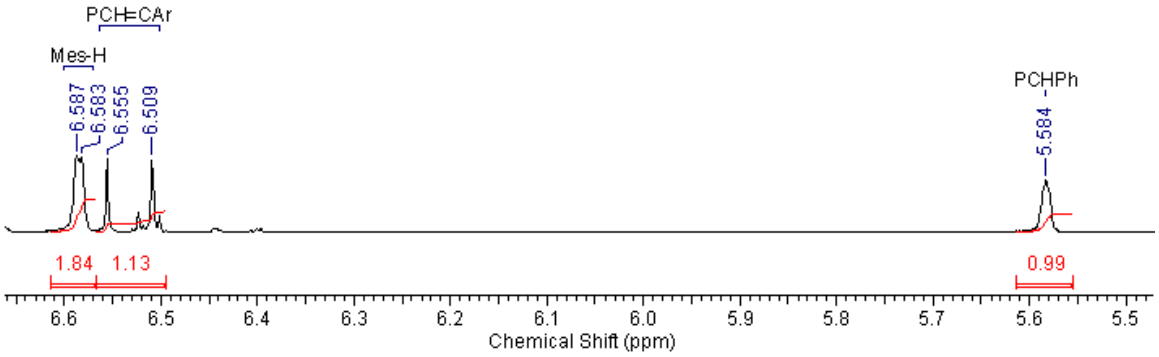
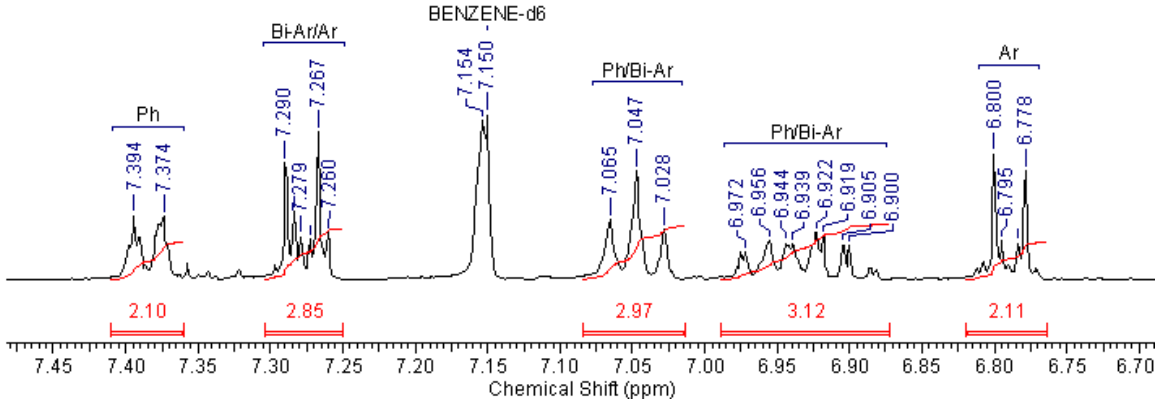


Fig. S3 ^{1}H NMR Spectrum of **4c** in C_6D_6 at 25 °C.







X-ray Structure of 6a:

Crystals of **6a** were grown by slow diffusion of hexanes into a concentrated Et_2O/C_6D_6 solution containing **6a**. A colourless crystal was mounted on a glass fibre. Data were collected at low temperature (150(2) K) on a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997-2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN.[1] The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The crystal data and refinement parameters are listed in Table S1. The reflection data and systematic absences were consistent with a triclinic space group: P $\bar{1}$.

The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G. M., 2001) suite of programs was used to solve the structure by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. Full-matrix least squares refinement of F^2 gave $R_1 = 6.19$ for 2σ data and $wR_2 = 20.05$ for all data (GOOF = 1.070).

The crystallographic information file (CIF) can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Tel: +44 1223 336408, Fax: +44 1223 336033, email: data_request@ccdc.cam.ac.uk). The Cambridge Crystallographic Data Centre (CCDC) retrieval number for **6a** is included in Table S1.

Table S1. X-Ray Crystallographic Data for **6a**

CCDC#	842631
Formula	$C_{31}H_{26}F_3PS$
Fw	518.61
Wavelength	0.71073
T(K)	150(2)
Crystal system	triclinic
Space group	$P\ \bar{1}$
a (Å)	10.6836(5)
b (Å)	10.8849(5)
c (Å)	13.1140(5)
α (deg)	69.316(3)
β (deg)	74.491(2)
γ (deg)	74.934(2)
V(Å^3)	1351.41(11)
Z	2
D_{calc} (g cm^{-1})	1.274
Absorption coefficient (mm^{-1})	0.217
F(000)	540
Crystal size (mm^3)	0.125 x 0.3 x 0.35
θ range for data collection (deg)	2.04 to 27.48
Reflections collected	10114
Independent reflections	6195; R(int) = 0.037
Completeness (%)	98.1
Absorption correction	Semi-empirical from equivalents
Data/restraints/parameters	6195/0/328
Goodness-of-fit F^2	1.070
Final R indices [I>2σ(I)]	R_1 = 0.0619; wR_2 = 0.1745
R indices (all data)	R_1 = 0.1064; wR_2 = 0.2005
Largest diff. peak and hole (e Å^{-3})	0.517; -0.422

X-ray Structure of 6b:

Crystals of **6b** were grown by slow diffusion of hexanes into a concentrated Et_2O/C_6D_6 solution containing **6b**. A colourless crystal was mounted on a glass fibre. Data were collected at low temperature (150(2) K) on a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997-2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN.[1] The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The crystal data and refinement parameters are listed in Table S2. The reflection data and systematic absences were consistent with a triclinic space group: P $\bar{1}$.

The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G. M., 2001) suite of programs was used to solve the structure by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. The P=S group was disordered between P51 and S51 and was modeled using 2 sulfur sites with 1/2 occupancy. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. Full-matrix least squares refinement of F^2 gave $R_1 = 5.25$ for 2σ data and $wR_2 = 14.04$ for all data (GOOF = 1.049).

The crystallographic information file (CIF) can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Tel: +44 1223 336408, Fax: +44 1223 336033, email: data_request@ccdc.cam.ac.uk). The Cambridge Crystallographic Data Centre (CCDC) retrieval number for **6b** is included in Table S2.

Table S2. X-Ray Crystallographic Data for **6b**

CCDC#	842629
Formula	$C_{30}H_{27}PS$
Fw	450.61
Wavelength	0.71073
T(K)	150(2)
Crystal system	triclinic
Space group	$P\ \bar{1}$
a (Å)	11.3067(3)
b (Å)	11.8222(3)
c (Å)	20.3297(6)
α (deg)	87.8245(14)
β (deg)	76.1635(12)
γ (deg)	62.4285(13)
V(Å^3)	2330.59(11)
Z	4
D_{calc} (g cm^{-1})	1.284
Absorption coefficient (mm^{-1})	0.224
F(000)	952
Crystal size (mm^3)	0.3 x 0.35 x 0.375
θ range for data collection (deg)	2.04 to 30.03
Reflections collected	16932
Independent reflections	13308; R(int) = 0.031
Completeness (%)	97.1
Absorption correction	Semi-empirical from equivalents
Data/restraints/parameters	13308/0/593
Goodness-of-fit F^2	1.049
Final R indices [I>2σ(I)]	R_1 = 0.0525; wR_2 = 0.1286
R indices (all data)	R_1 = 0.0756; wR_2 = 0.1404
Largest diff. peak and hole (e Å^{-3})	0.964; -0.719

X-Ray Structure of 6c

Crystals of **6c** were grown by slow diffusion of hexanes into a concentrated Et_2O/C_6D_6 solution containing **6c**. A colourless crystal was mounted on a glass fibre. Data were collected at low temperature (150(2) K) on a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997-2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN.[1] The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The crystal data and refinement parameters are listed in Table S3. The reflection data and systematic absences were consistent with a monoclinic space group: P2(1)/c.

The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G. M., 2001) suite of programs was used to solve the structure by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. Full-matrix least squares refinement of F^2 gave $R_1 = 4.63$ for 2σ data and $wR_2 = 12.46$ for all data (GOOF = 1.045).

The crystallographic information file (CIF) can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Tel: +44 1223 336408, Fax: +44 1223 336033, email: data_request@ccdc.cam.ac.uk). The Cambridge Crystallographic Data Centre (CCDC) retrieval number for **6c** is included in Table S3.

Table S3. X-Ray Crystallographic Data for **6c**

CCDC#	842630
Formula	$C_{31}H_{29}OPS$
Fw	480.64
Wavelength	0.71073
T(K)	150(2)
Crystal system	monoclinic
Space group	$P2(1)/c$
a (Å)	10.1635(3)
b (Å)	14.1370(4)
c (Å)	17.8587(4)
α (deg)	90.000
β (deg)	102.1929(14)
γ (deg)	90.000
V(Å^3)	2508.08(12)
Z	2
D_{calc} (g cm^{-1})	1.273
Absorption coefficient (mm^{-1})	0.215
F(000)	1016
Crystal size (mm^3)	0.3 x 0.325 x 0.45
θ range for data collection (deg)	2.04 to 27.48
Reflections collected	19121
Independent reflections	6004; R(int) = 0.047
Completeness (%)	99.9
Absorption correction	Semi-empirical from equivalents
Data/restraints/parameters	6004/0/311
Goodness-of-fit F^2	1.046
Final R indices [I>2σ(I)]	R_1 = 0.0463; wR_2 = 0.1122
R indices (all data)	R_1 = 0.0720; wR_2 = 0.1246
Largest diff. peak and hole (e Å^{-3})	0.206; -0.376

Fig S4. UV-vis spectra of **4a-c** in THF. The spectra were recorded at 6.0 x 10^{-5} M (**4a**), 7.5 x 10^{-5} M (**4b**), and 5.3 x 10^{-5} M (**4c**).

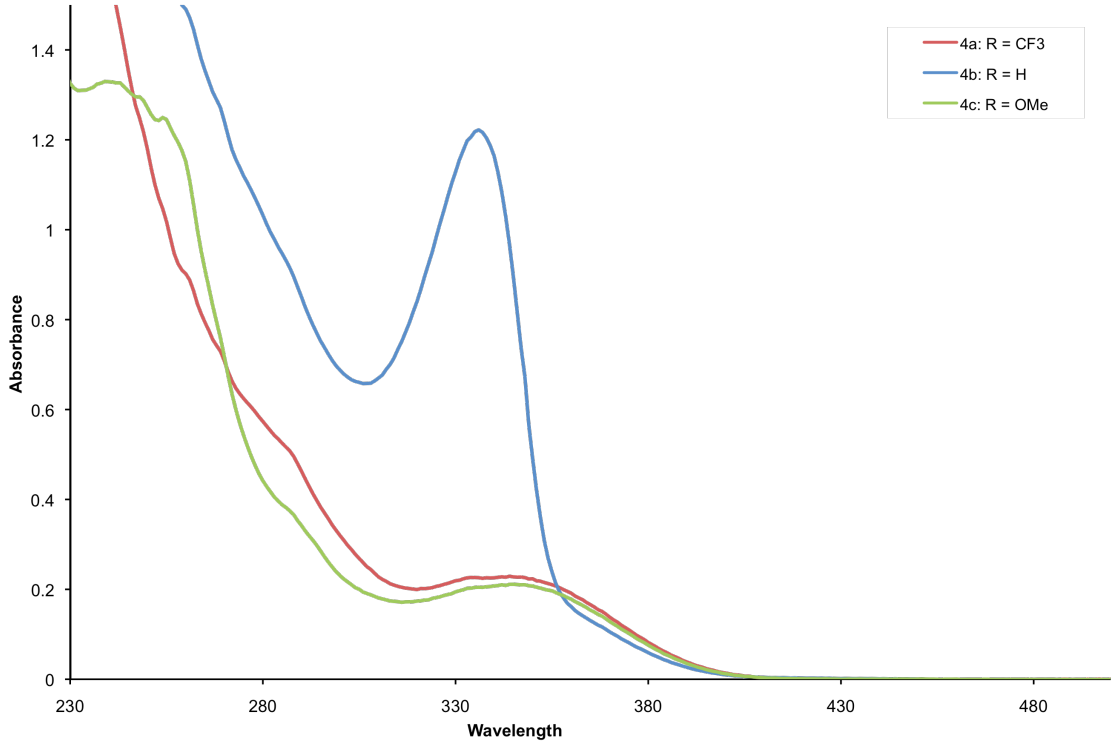
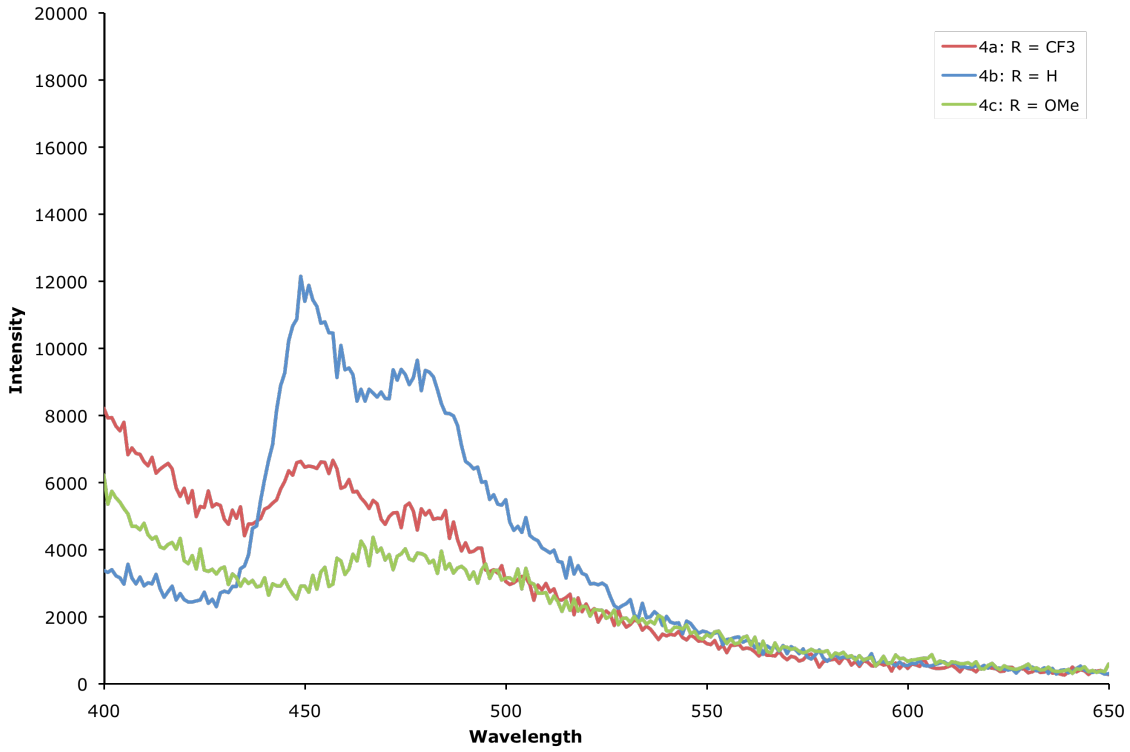


Fig S5. Emission spectra of **4a-c** in THF.



References

1. Z. Otwinowski and W. Minor in *Methods in Enzymology, Vol. 276: Macromolecular Crystallography, Part A*. Edited by C. W. Carter Jr. and R. M. Sweet; Academic Press: New York, 1997; p. 307.