

## A new P-heterocyclic type of phosphonium–iodonium ylides based on dibenzophosphole

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#### 1. Experimental

$^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra were recorded on Bruker Avance 400 and Agilent 400-MR spectrometers, both operating at 400, 100, 376 and 162 MHz, respectively; Bruker Avance 500, operating at 500, 125, 470 and 202 MHz. The solvent signals were used as internal references, *viz.*,  $\delta$  7.26 ( $\text{CDCl}_3$ ) and  $\delta$  2.49 ( $\text{DMSO-d}_6$ ) for  $^1\text{H}$  and  $\delta$  77.1 ( $\text{CDCl}_3$ ) and  $\delta$  39.5 ( $\text{DMSO-d}_6$ ) for  $^{13}\text{C}$ . The  $^{19}\text{F}$  chemical shifts were referenced to  $\text{C}_6\text{F}_6$ ; 85%  $\text{H}_3\text{PO}_4$  was used as external reference for  $^{31}\text{P}$ .

Infrared spectra were recorded on a Thermo Scientific Nicolet IR200 FT IR spectrometer equipped with an attenuated total reflection (ATR) accessory with a ZnSe crystal. The angle of incidence was  $45^\circ$  and the spectral resolution was  $4\text{ cm}^{-1}$ . A total of 20 scans were collected.

High-resolution electrospray ionization (ESI) mass spectra were recorded on an Agilent LC/MSD 1100 SL instrument with atmospheric pressure ESI (AP-ESI) in the positive ion mode (ion trap mass analyzer). Conditions: drying gas (nitrogen) temperature  $300^\circ\text{C}$ ; drying gas feed rate  $12\text{ dm}^3\text{ min}^{-1}$ , ion source voltage 5000 V, capillary voltage 150 V, acetonitrile as solvent.

*5-Phenyl-5H-benzo[b]phosphindole 1* was prepared as reported [S1].

*5-(2-Oxo-2-phenylethyl)-5-phenyl-5H-benzo[b]phosphindol-5-ium bromide 2* [S2]. A mixture of *5-phenyl-5H-benzo[b]phosphindole 1* (2.00 g, 7.7 mmol) and 2-bromo-1-phenylethane-2-one (1.58 g, 8.0 mmol) in MeCN (10 ml) was stirred at  $80^\circ\text{C}$  for 2 h. The resulting precipitate was filtered off, washed with acetonitrile ( $3\times 6\text{ ml}$ ), then with diethyl ether (10 ml), and dried on a glass filter at room temperature.

The yield was 3.17 g (90%), white powder, mp  $245\text{--}247^\circ\text{C}$ .

$^1\text{H}$  NMR ( $\text{DMSO-d}_6$ , 400 MHz)  $\delta$ : 6.36 (d, 2 H,  $\text{CH}_2\text{COPh}$ ,  $^2J_{\text{P,H}} = 12.2\text{ Hz}$ ); 7.50 (t, 2 H,  $\text{H}_{\text{arom}}$ ,  $J = 7.6\text{ Hz}$ ); 7.55–7.65 (m, 4 H,  $\text{H}_{\text{arom}}$ ); 7.68 (tdd, 2 H,  $\text{H}_{\text{arom}}$ ,  $J = 7.5\text{ Hz}$ ,  $J = 4.3\text{ Hz}$ ,  $J = 0.9\text{ Hz}$ ); 7.82 (tt, 2 H,  $\text{H}_{\text{arom}}$ ,  $J = 7.7\text{ Hz}$ ,  $J = 1.4\text{ Hz}$ ); 7.97–8.02 (m, 2 H,  $\text{H}_{\text{arom}}$ ); 8.29–8.37 (m, 4 H,  $\text{H}_{\text{arom}}$ ); 8.95–9.02 (m, 2 H,  $\text{H}_{\text{arom}}$ ).

$^{13}\text{C}$  NMR ( $\text{DMSO-d}_6$ , 100 MHz),  $\delta$ : 36.98 (d,  $^1J_{\text{C,P}} = 58.0\text{ Hz}$ ,  $\text{CH}_2\text{COPh}$ ); 118.22 (d,  $\text{C}_{\text{ipso}}$ ,  $^1J_{\text{C,P}} = 87.7\text{ Hz}$ ); 120.82 (d,  $\text{C}_{\text{ipso}}$ ,  $^1J_{\text{C,P}} = 93.9\text{ Hz}$ ); 123.68 (d,  $\text{C}_{\text{arom}}$ ,  $J_{\text{C,P}} = 9.9\text{ Hz}$ ); 129.00 (s,  $\text{C}_{\text{arom}}$ ); 129.24 (s,  $\text{C}_{\text{arom}}$ ); 130.22 (d,  $\text{C}_{\text{arom}}$ ,  $J_{\text{C,P}} = 13.7\text{ Hz}$ ); 130.75 (d,  $\text{C}_{\text{arom}}$ ,  $J_{\text{C,P}} = 12.2\text{ Hz}$ ); 132.03 (d,  $\text{C}_{\text{arom}}$ ,  $J_{\text{C,P}} = 12.2\text{ Hz}$ ); 133.25 (d,  $\text{C}_{\text{arom}}$ ,  $J_{\text{C,P}} = 9.9\text{ Hz}$ ); 134.45 (d,  $\text{C}_{\text{arom}}$ ,  $J_{\text{C,P}} = 6.1\text{ Hz}$ ); 134.75 (d,  $\text{C}_{\text{arom}}$ ,

$J_{C,P} = 3.1$  Hz); 135.11 (s,  $C_{arom}$ ); 136.06 (d,  $C_{arom}$ ,  $J_{C,P} = 2.3$  Hz); 144.03 (d,  $C_{arom}$ ,  $J_{C,P} = 19.1$  Hz); 193.42 (d,  ${}^2J_{C,P} = 6.9$ , COPh).

${}^{31}P$  NMR (DMSO- $d_6$ , 162 MHz),  $\delta$ : 24.05.

IR,  $\nu/cm^{-1}$ : 1657 (COPh).

*1-Phenyl-2-(5-phenyl-5H-5 $\lambda^5$ -benzo[b]phosphindol-5-ylidene)ethan-1-one* **3** [S2]. To a suspension of phosphonium salt **2** (3.00 g, 6.5 mmol) in anhydrous methanol (30 ml) in a dry argon atmosphere, a solution sodium methoxide (6.7 mmol) in anhydrous methanol (5 ml) was gradually added, the temperature being maintained at 0 °C. The mixture was stirred for 2 h, and the formation of a yellowish-green ylide precipitate was observed. The precipitate was separated by filtration, washed with cold methanol (2 $\times$ 3 ml), and dried in air.

Yield 2.20 g (89%), yellow-green powder, mp 203–205 °C.

${}^1H$  NMR (chloroform- $d$ , 400 MHz),  $\delta$ : 4.43 (d, 1 H, PCH,  ${}^2J_{P,H} = 29.0$  Hz); 7.33–7.42 (m, 5 H,  $H_{arom}$ ); 7.43–7.53 (m, 3 H,  $H_{arom}$ ); 7.58–7.73 (m, 4 H,  $H_{arom}$ ); 7.92 (dd, 2 H,  $H_{arom}$ ,  $J = 7.7$  Hz,  $J = 2.5$  Hz); 7.97–8.03 (m, 2 H,  $H_{arom}$ ); 8.16 (t, 2 H,  $H_{arom}$ ,  $J = 8.5$  Hz).

${}^{13}C$  NMR (chloroform- $d$ , 100 MHz),  $\delta$ : 46.46 (d,  ${}^1J_{C,P} = 110.6$  Hz, PCH); 121.56 (d,  $C_{arom}$ ,  $J_{C,P} = 9.2$  Hz); 126.12 (d,  $C_{ipso}$ ,  ${}^1J_{C,P} = 90.9$  Hz); 126.81 (d,  $C_{arom}$ ,  $J_{C,P} = 0.92$  Hz); 127.72 (s,  $C_{arom}$ ); 128.95 (d,  $C_{arom}$ ,  $J_{C,P} = 13.1$  Hz); 129.48 (d,  $C_{arom}$ ,  $J_{C,P} = 11.2$  Hz); 129.64 (s,  $C_{arom}$ ); 129.65 (d,  $C_{ipso}$ ,  ${}^1J_{C,P} = 95.3$  Hz); 130.98 (d,  $C_{arom}$ ,  $J_{C,P} = 11.8$  Hz); 131.26 (d,  $C_{arom}$ ,  $J_{C,P} = 9.8$  Hz); 132.01 (d,  $C_{arom}$ ,  $J_{C,P} = 3.0$  Hz); 132.97 (d,  $C_{arom}$ ,  $J_{C,P} = 2.2$  Hz); 139.66 (d,  $C_{arom}$ ,  $J_{C,P} = 13.8$  Hz); 186.98 (d,  ${}^2J_{C,P} = 1.8$  Hz, COPh).

${}^{31}P$  NMR (chloroform- $d$ , 162 MHz),  $\delta$ : 16.79.

IR,  $\nu/cm^{-1}$ : 1499 (COPh).

*[2-Oxo-2-phenyl-1-(5-phenyl-5H-5 $\lambda^5$ -benzo[b]phosphindol-5-ylidene)ethyl](phenyl)iodonium tetrafluoroborate* **4**. To a suspension of ylide **3** (2.00 g, 5.3 mmol) in anhydrous methanol (10 ml) in a dry argon atmosphere, a solution of (diacetoxyiodo)benzene (1.70 g, 5.3 mmol) in anhydrous methanol (5 ml) was added, the temperature being maintained at 0 °C. The disappearance of the ylide precipitate was observed. The mixture was stirred for 1 h. Then, a 50% aqueous  $HBF_4$  solution (0.7 ml, 5.6 mmol) was added, the temperature being maintained at 0 °C. The solution was stirred for 1 h, diethyl ether (10 ml) was added and stirred for an additional 1 h. The precipitate was filtered off, washed with diethyl ether (3 $\times$ 20 ml), and dried in air.

Yield 2.20 g (89%), white powder, mp 165–167 °C (decomp.).

${}^1H$  NMR (DMSO- $d_6$ , 400 MHz),  $\delta$ : 6.70–8.40 (m, 23 H,  $H_{arom}$ ).

${}^{13}C$  NMR (DMSO- $d_6$ , 125 MHz),  $\delta$ : 21.53 (d, PCI,  ${}^1J_{C,P} = 101.7$  Hz); 119.02 (s,  $C_{ipso}$ ); 122.94 (d,  $C_{arom}$ ,  $J_{C,P} = 9.1$  Hz); 123.64 (d,  $C_{ipso}$ ,  ${}^1J_{C,P} = 91.3$  Hz); 126.14 (d,  $C_{ipso}$ ,  ${}^1J_{C,P} = 93.0$  Hz); 127.93 (s,  $C_{arom}$ ); 128.19 (s,  $C_{arom}$ ); 129.64 (d,  $C_{arom}$ ,  $J_{C,P} = 14.5$  Hz); 130.26 (s,  $C_{arom}$ ); 130.73 (s,  $C_{arom}$ ); 131.06 (s,  $C_{arom}$ ); 132.68 (s,  $C_{arom}$ ); 133.28 (s,  $C_{arom}$ ); 133.61 (d,  $C_{arom}$ ,  $J_{C,P} = 10.9$  Hz); 134.98 (s,  $C_{arom}$ ); 137.07 (s,  $C_{arom}$ ); 137.92 (d,  $C_{arom}$ ,  $J_{C,P} = 7.3$  Hz); 142.88 (d,  $C_{arom}$ ,  $J_{C,P} = 19.5$  Hz); 192.44 (s, COPh).

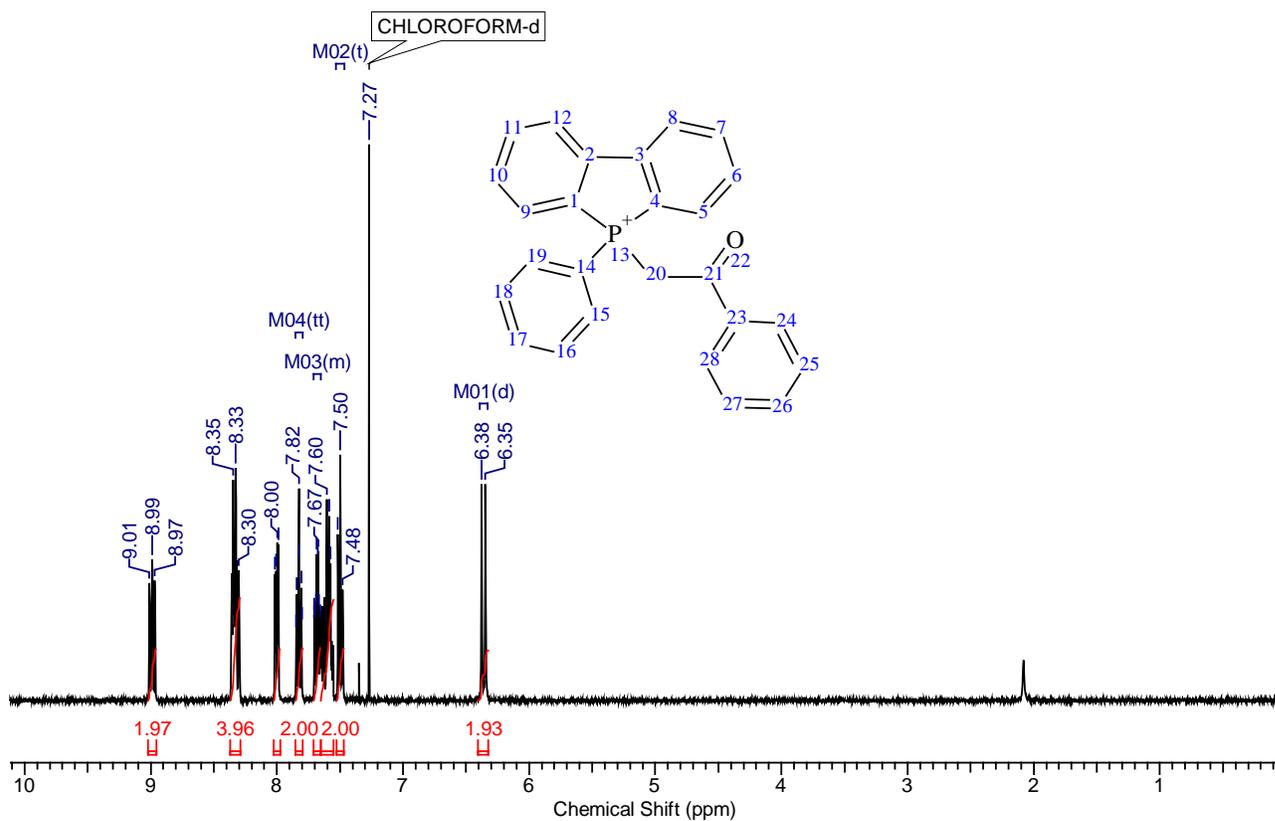
${}^{19}F$  NMR (DMSO- $d_6$ , 376 MHz),  $\delta$ : -148.18 [ ${}^{11}BF_4$ ] $^-$ , -148.12 [ ${}^{10}BF_4$ ] $^-$ .

${}^{31}P$  NMR (DMSO- $d_6$ , 162 MHz),  $\delta$ : 25.79.

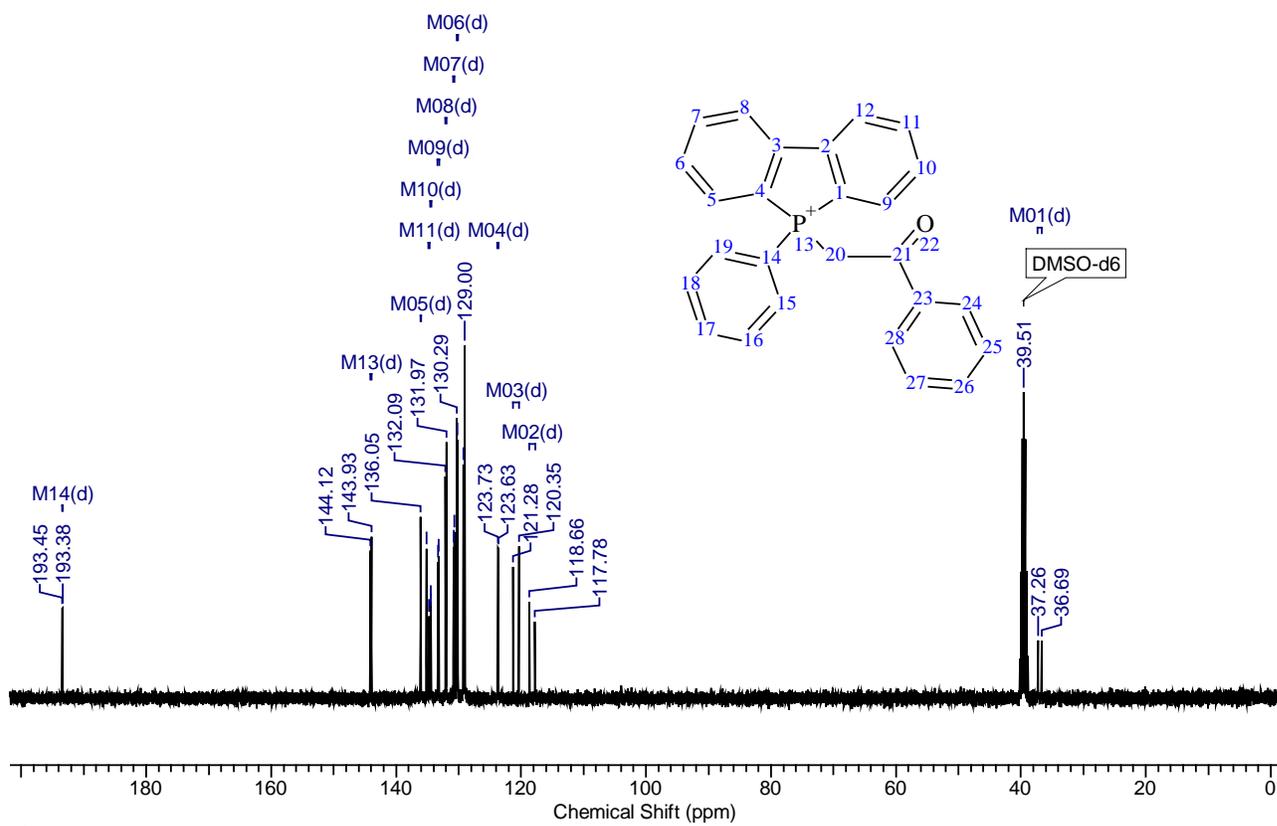
IR,  $\nu/cm^{-1}$ : 1349 (COPh); 1075, 1029 ( $BF_4^-$ ).

High-resolution ESI mass spectrum: found  $m/z$  581.0526 [ $M$ ] $^+$ ; calculated for  $C_{32}H_{23}IOP$  581.0526.

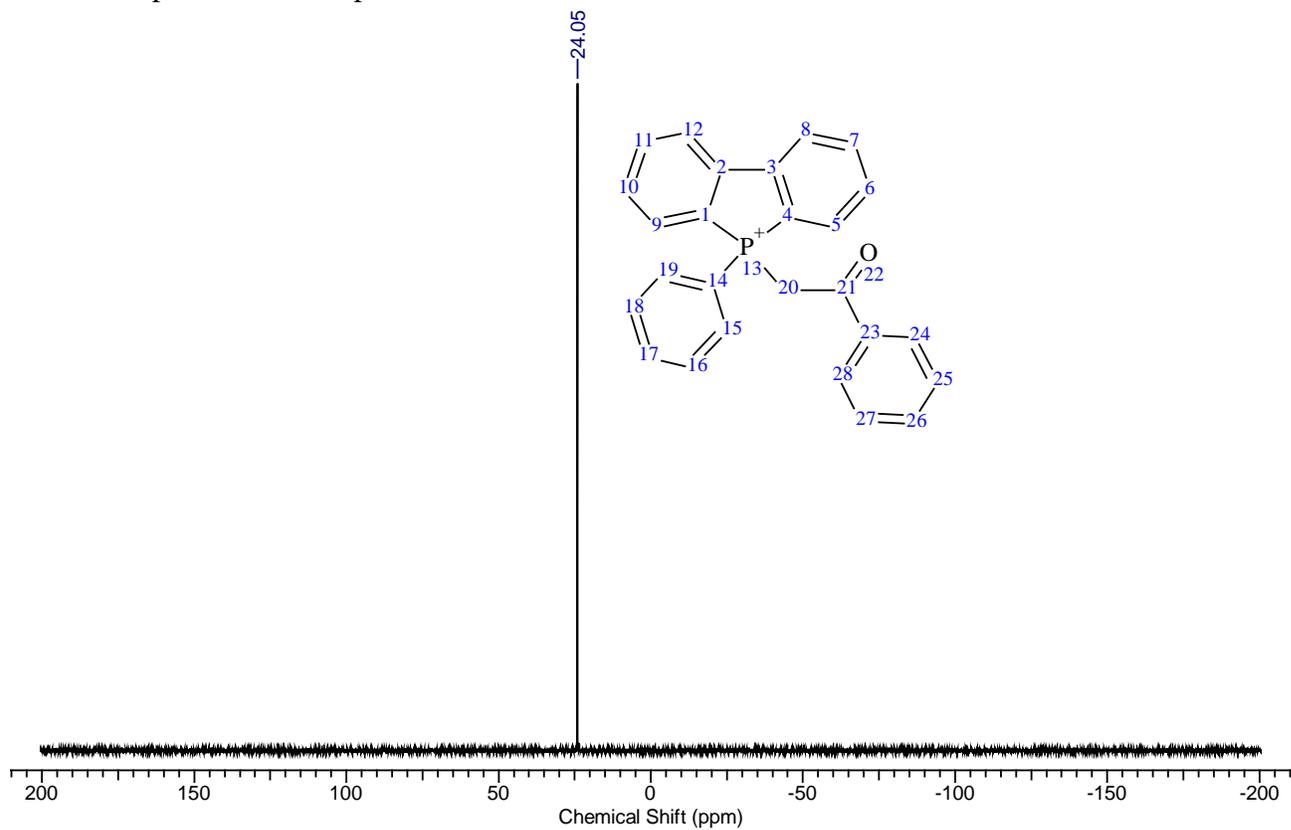
## 2. NMR spectra of compounds 2-4



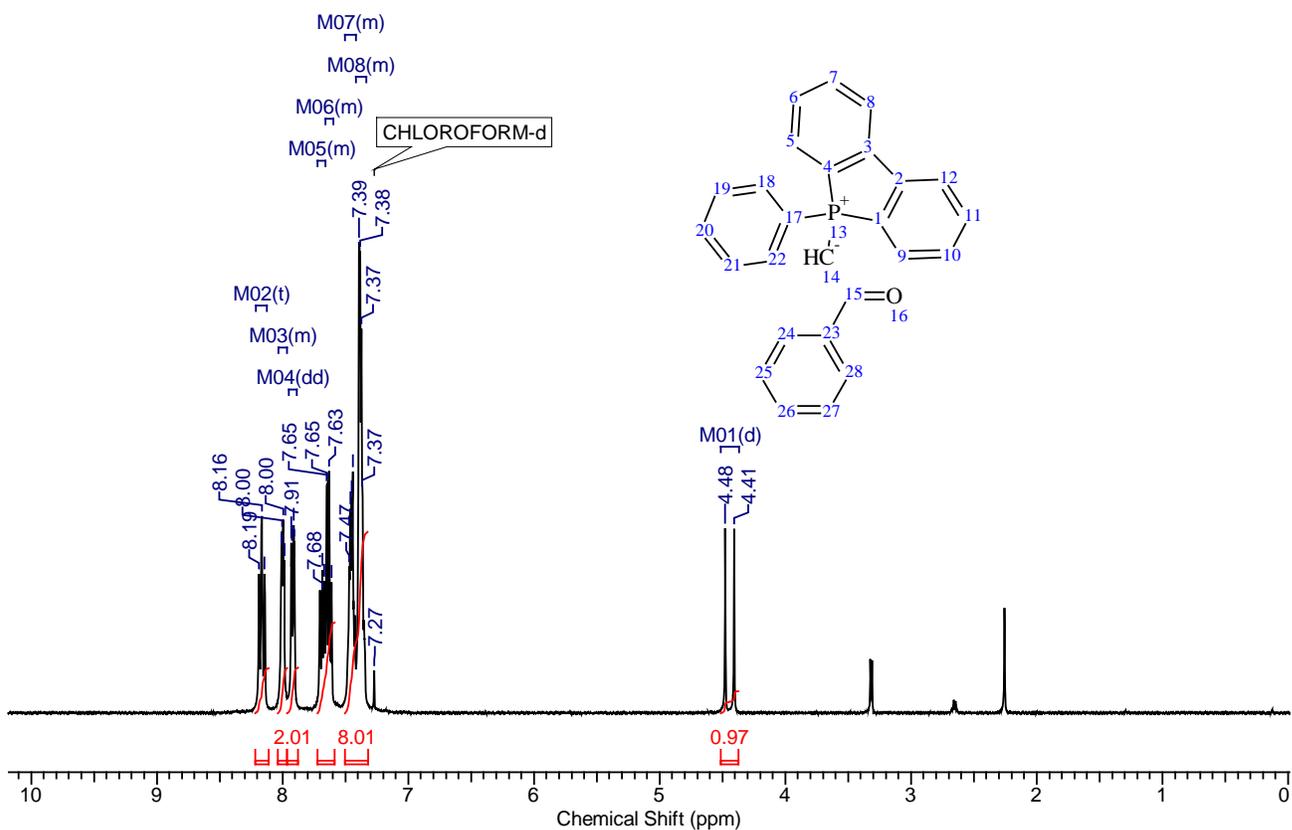
<sup>1</sup>H NMR spectrum of compound 2



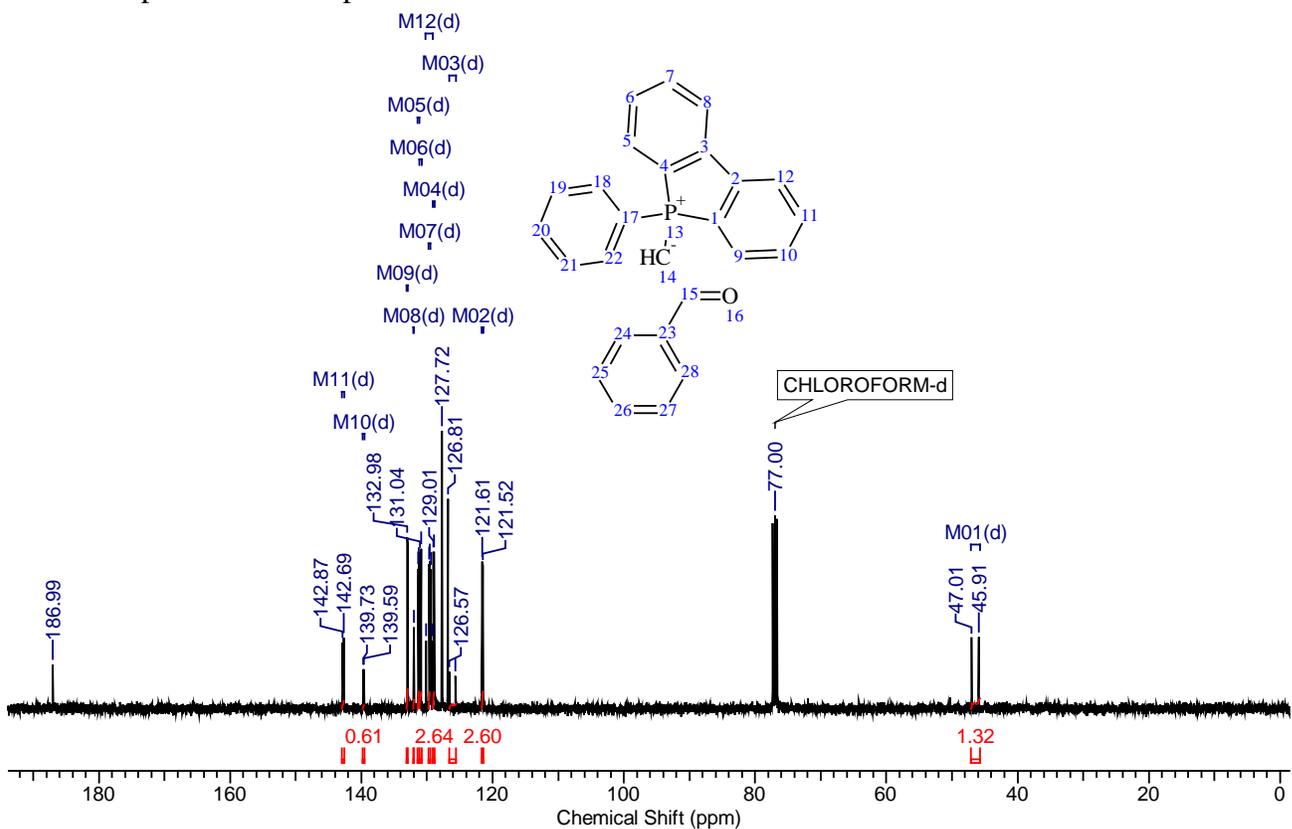
<sup>13</sup>C NMR spectrum of compound **2**



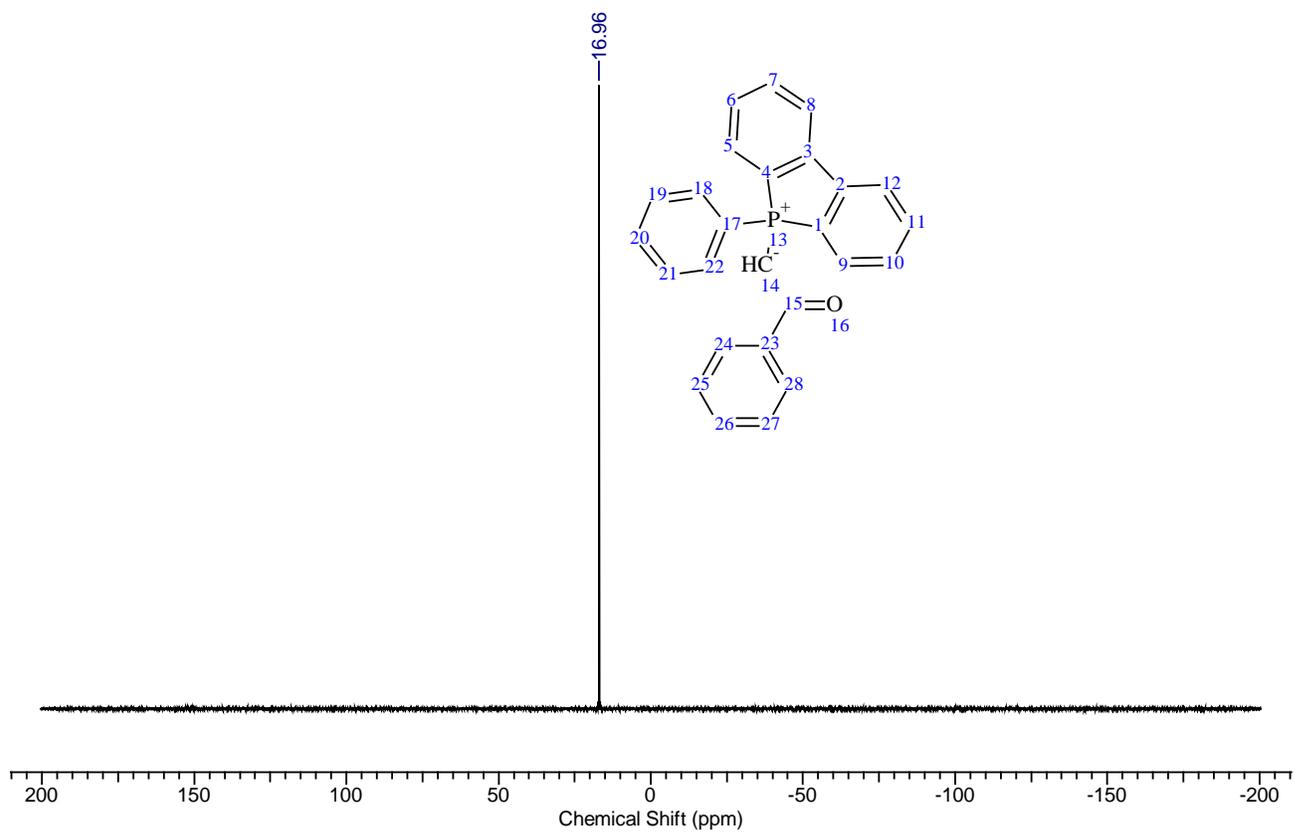
<sup>31</sup>P NMR spectrum of compound **2**



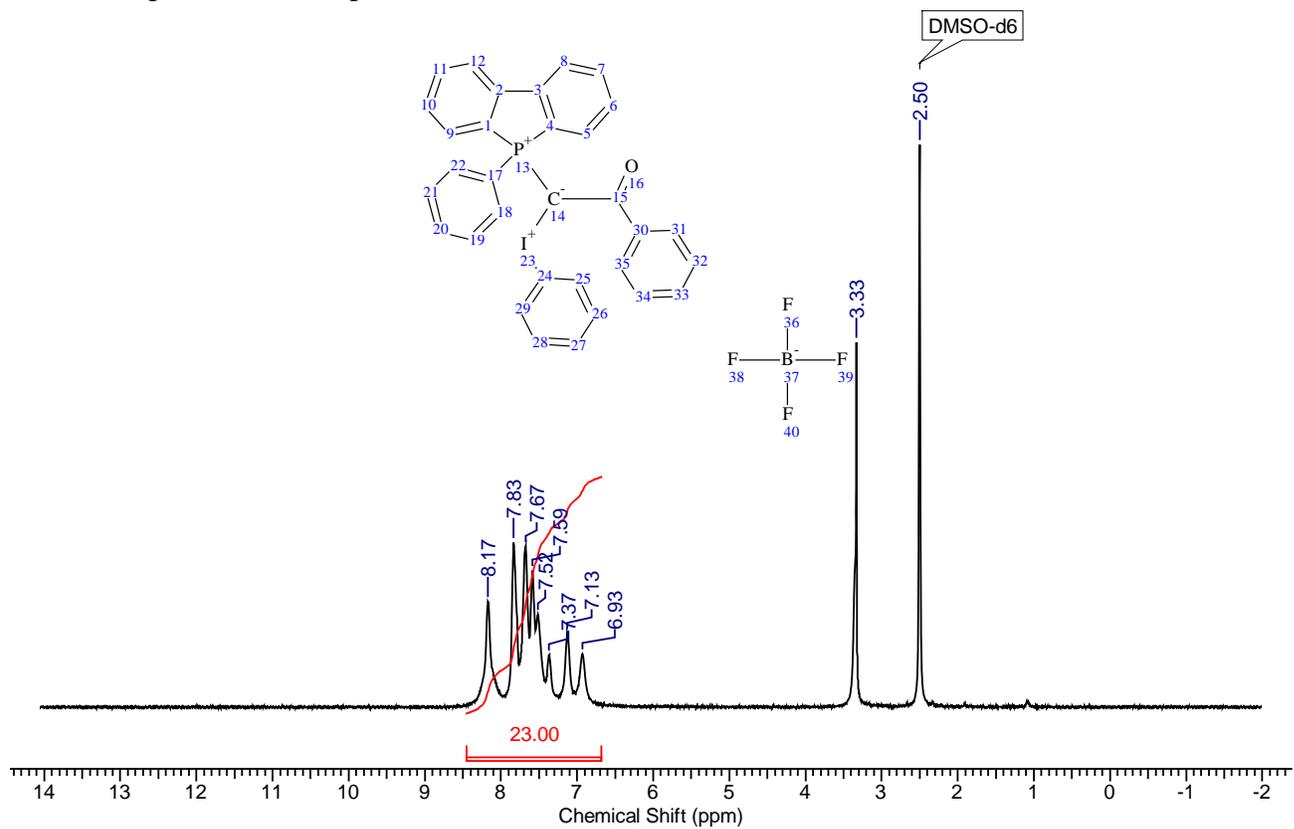
<sup>1</sup>H NMR spectrum of compound **3**



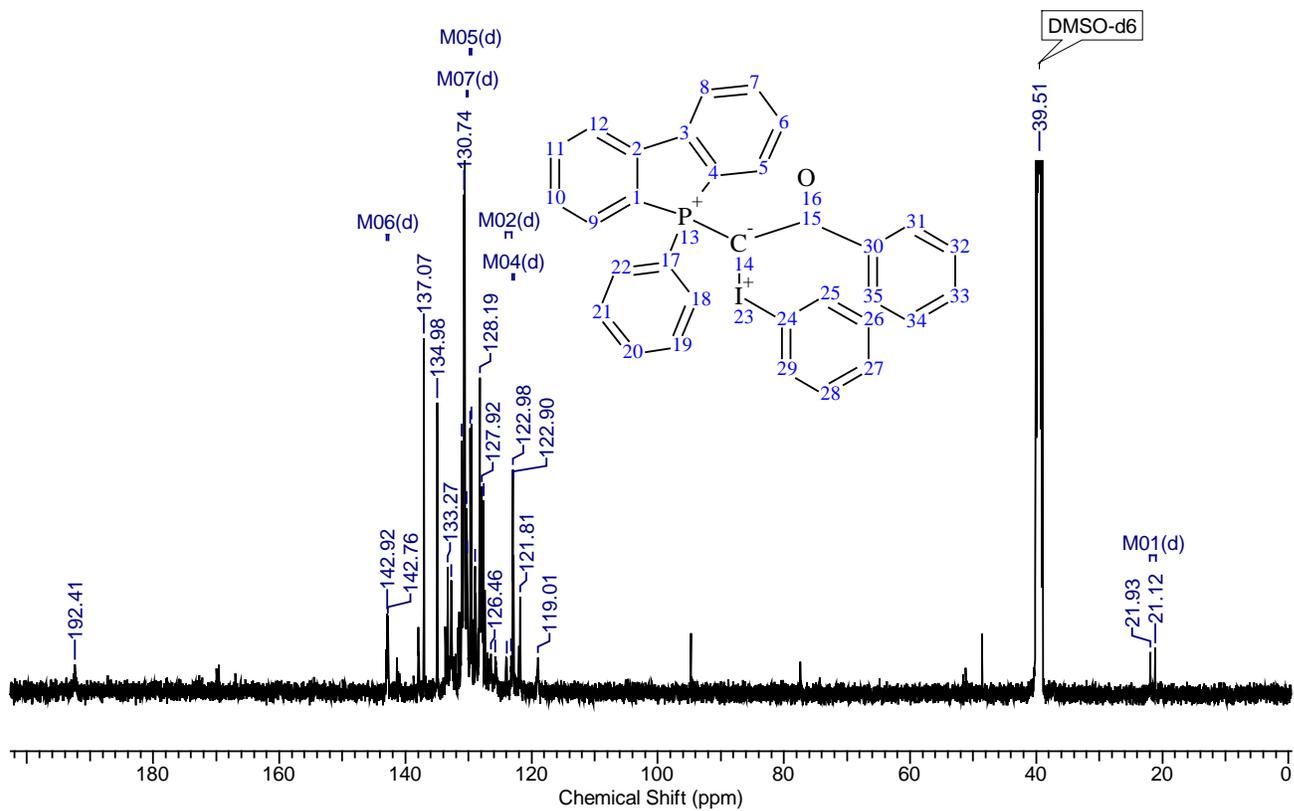
<sup>13</sup>C NMR spectrum of compound **3**



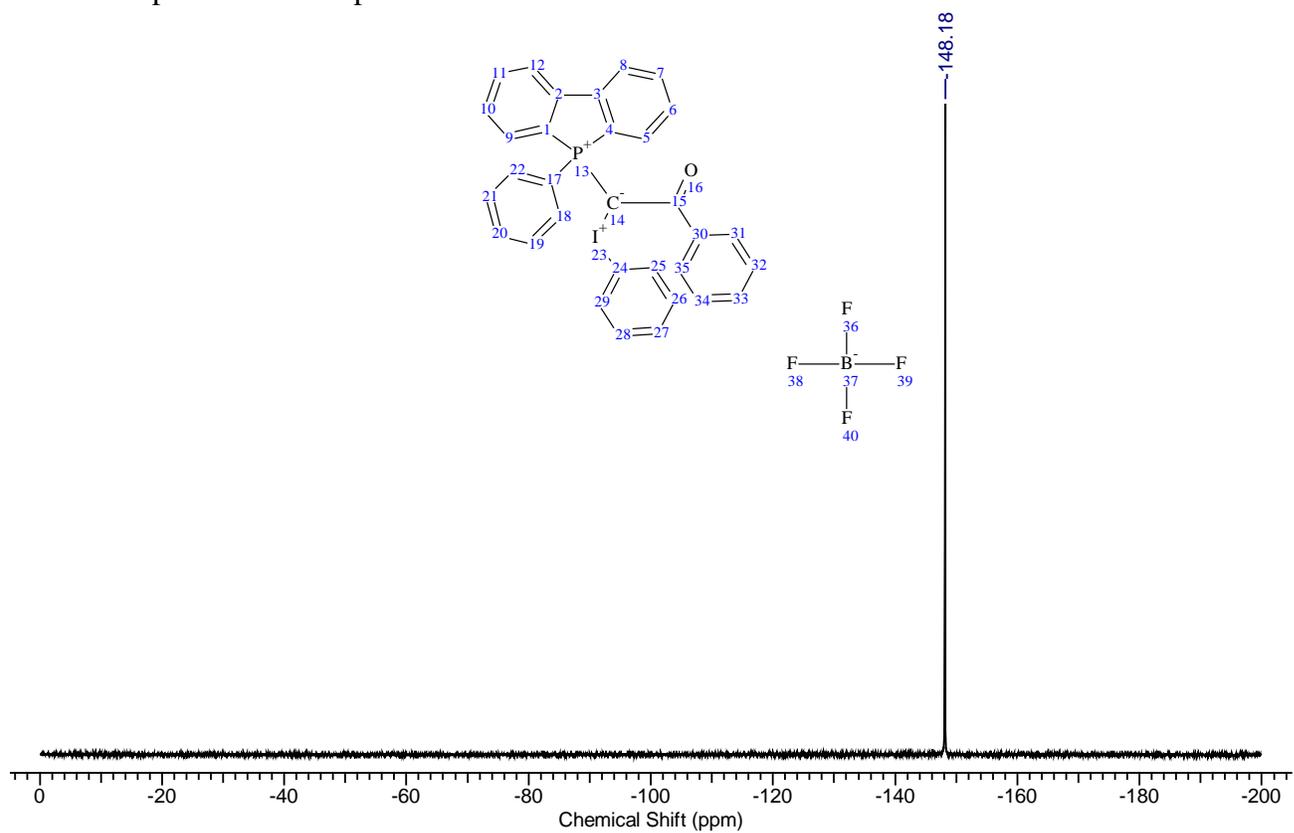
<sup>31</sup>P NMR spectrum of compound **3**



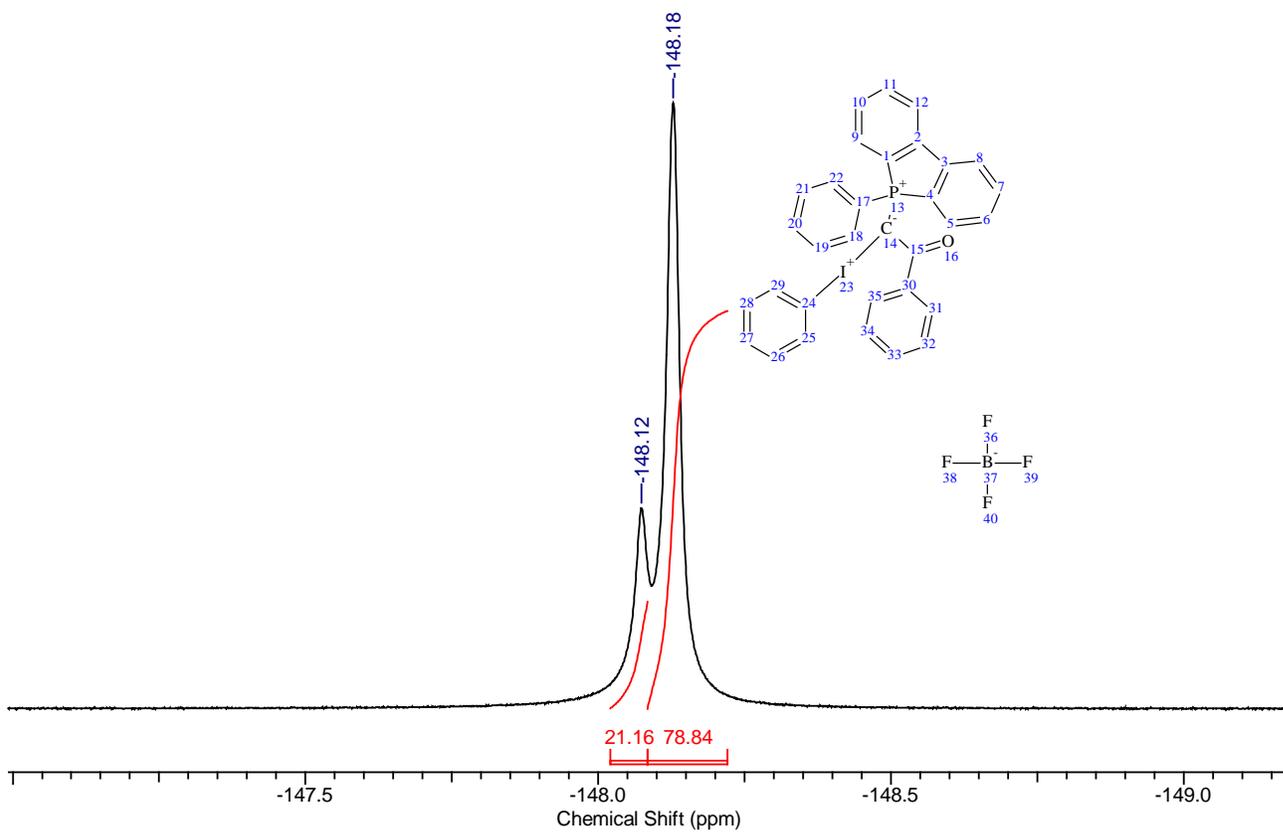
<sup>1</sup>H NMR spectrum of compound **4**



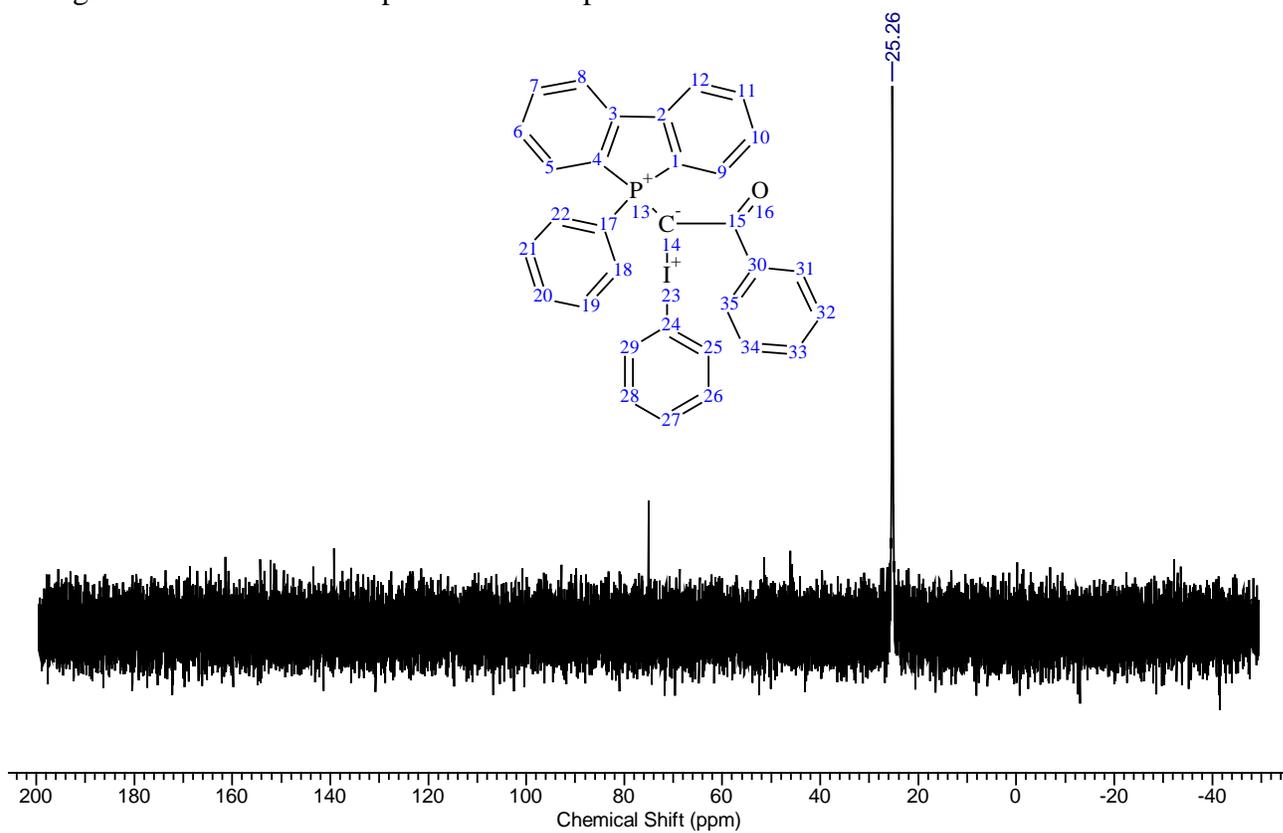
<sup>13</sup>C NMR spectrum of compound **4**



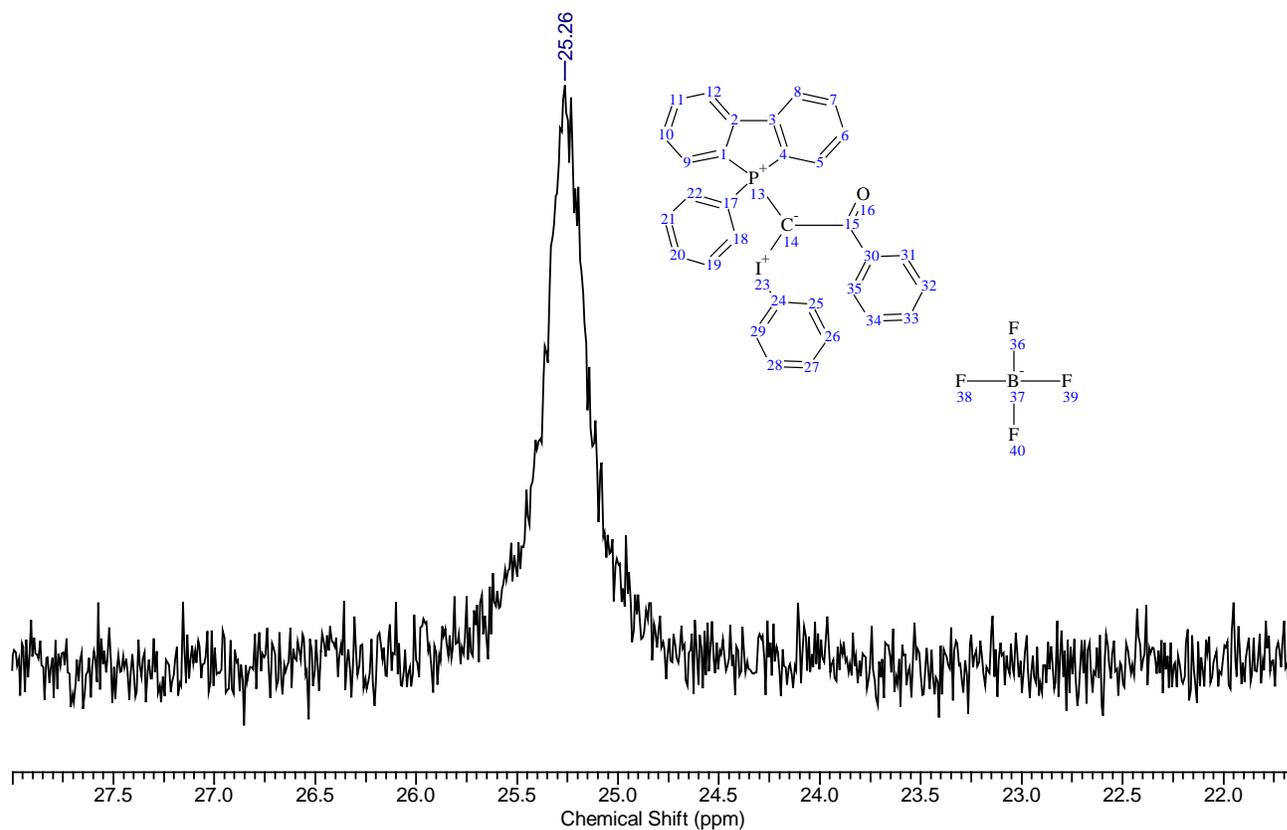
<sup>19</sup>F NMR spectrum of compound **4**



A fragment of the <sup>19</sup>F NMR spectrum of compound **4**



<sup>31</sup>P NMR spectrum of compound **4**



A fragment of the  $^{31}\text{P}$  NMR spectrum of compound 4

### 3. References

- [S1] J. Cornforth, R. H. Cornforth and R. T. Gray, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2289; (b) S. Affandi, R. L. Green, B. T. Hsieh, M. S. Holt, J. H. Nelson and E. C. Alyea, *Synth. React. Inorg. Met.-Org. Chem.*, 1987, **17**, 307.
- [S2] I. F. Wilson and J. C. Tebby, *J. Chem. Soc., Perkin Trans. 1*, 1972, 2713.