Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Hetero-Diels-Alder Reactions of 2*H*-Phospholes with Allenes: Synthesis and Functionalization of 6-Methylene-1-phosphanorbornenes

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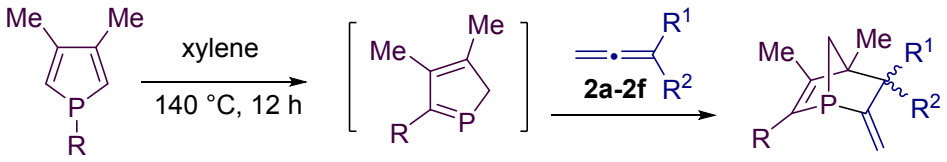
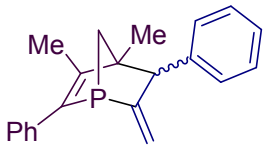
General information

All reactions were performed under nitrogen using solvents dried by standard methods. NMR spectra were obtained using Bruker AV300 spectrometer. All spectra were recorded in $CDCl_3$ and $(CD_3)_2SO$. All coupling constants (*J* values) were reported in hertz (Hz). Chemical shifts were expressed in parts per million (ppm) downfield from internal TMS (^1H). HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-Tof HRMS spectrometer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Melting Point: heating rate: 4°C/min, the thermometer was not corrected. Silica gel (200-300 mesh) was used for the chromatographic separations. All commercially available reagents were used without further purification. All new compounds were synthetic in small scale, and were purified by column chromatography. Compounds **1a-1d**[1] and **2a-2f**[2] were prepared according to literature method. The purity of the new compounds are acceptable according to NMR spectra analysis.

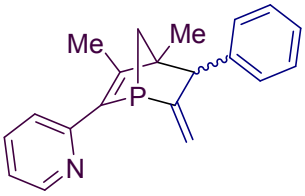
Experimental Procedures and Characterization Data



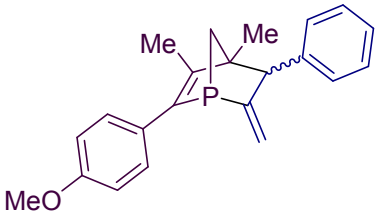
1a-1e 2H-phospholes **3** (*endo* + *exo*)



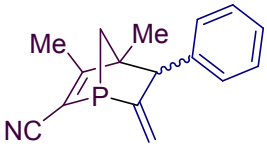
3aa (*endo* + *exo*) 98%
exo : *endo* = 0.85 : 1



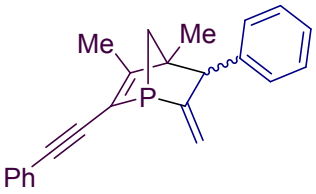
exo-**3ba** 41%
endo-**3ba** 49%



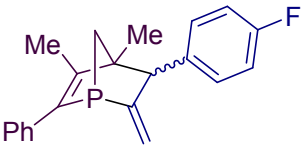
3ca (*endo* + *exo*) 89%
exo : *endo* = 0.86 : 1



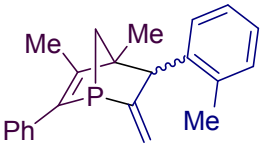
exo **- 3da** 21%
endo - **3da** 53%



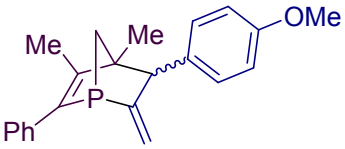
3ea (*endo* + *exo*) 98%
exo : *endo* = 0.60 : 1



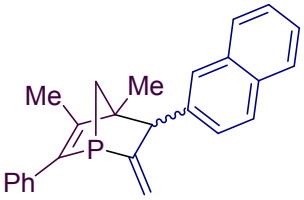
3ab (*endo* + *exo*) 81%
exo : *endo* = 0.81 : 1



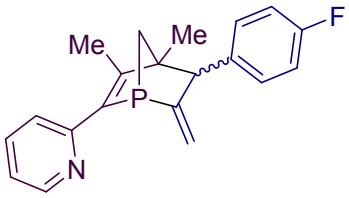
3ac (*endo* + *exo*) 83%
exo : *endo* = 1 : 0.60



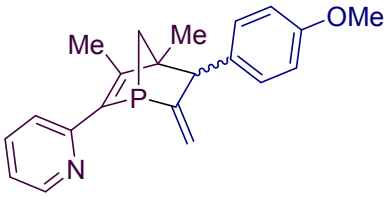
3ad (*endo* + *exo*) 83%
exo : *endo* = 1 : 0.83



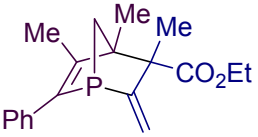
3ae (*endo* + *exo*) 89%
exo : *endo* = 1 : 0.60



exo **- 3bb** 33%
endo - **3bb** 37%



exo **- 3bd** 33%
endo - **3bd** 43%



3af (*endo* + *exo*) 35%
exo : *endo* = 1 : 0.38

General procedure for the reaction of phosphole 1 with allenes 2

A solution of phosphole **1** (0.5 mmol) and allenes **2** (1 mmol) in xylenes (5 mL) was stirred at 140 °C in oil bath for 12 h under nitrogen. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography providing **3**.

3aa (*endo* + *exo*) colorless liquid, dichloromethane/petroleum ether = 1:10, R_f = 0.40, 149 mg, 98%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -15.7 (exo), -15.2 (endo), exo:endo = 0.85:1. **^1H NMR** ($CDCl_3$; 300 MHz): δ 0.97 (s, 2.57H, CH_3, exo), 1.28 (s, 3H, CH_3, endo), 1.31 (s, 3H, CH_3, endo), 1.52-1.60 (m, 1.84H, CH_2, exo + endo), 1.76-1.86 (m, 1.87H, CH_2, exo + endo), 1.89 (s, 2.52H, CH_3, exo), 3.14 (s, 0.85H, CH, exo), 3.46 (s, 1H, CH, endo), 5.29 (d, J = 24.3 Hz, 0.85H, CH_2, exo), 5.40 (d, J = 24.3 Hz, 1H, CH_2, endo), 5.94 (*pseudo*-t, J = 12.5 Hz, 1.82H, CH_2 exo + endo), 6.96-7.42 (m, 18.7H, CH, exo + endo). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 12.9 (s, CH_3, exo), 16.1 (s, CH_3, endo), 20.4 (s, CH_3, endo), 21.0 (s, CH_3, exo), 44.4 (d, J_{CP} = 2.4 Hz, CH_2, exo), 50.8 (d, J_{CP} = 0.7 Hz, CH_2, endo), 53.6 (d, J_{CP} = 2.4 Hz, CH, exo), 57.1 (d, J_{CP} = 1.8 Hz, CH, endo), 64.0 (d, J_{CP} = 5.9 Hz, C, exo), 64.6 (d, J_{CP} = 5.5 Hz, C, endo), 121.3 (d, J_{CP} = 29.1 Hz, CH_2, endo), 122.7 (d, J_{CP} = 29.8 Hz, CH_2, exo), 126.4 (s, CH, endo), 126.5 (s, CH, exo), 126.6 (s, CH, exo), 127.8 (s, CH, endo), 128.0 (s, CH, endo), 128.1 (s, CH, exo), 128.2 (s, CH, endo), 128.3 (s, CH, endo), 128.5 (s, CH, exo), 128.6 (s, CH, exo), 129.7 (s, CH, exo), 130.1 (s, CH, endo), 138.9 (d, J_{CP} = 8.0 Hz, C, endo), 139.1 (d, J_{CP} = 7.4 Hz, C, exo), 140.0 (d, J_{CP} = 16.7 Hz, C, endo), 141.4 (s, C, endo), 141.7 (d, J_{CP} = 15.8 Hz, C, exo), 142.8 (s, C, exo), 151.7 (d, J_{CP} = 1.3 Hz, C, exo), 154.6 (d, J_{CP} = 1.3 Hz, C, endo), 156.7 (d, J_{CP} = 19.6 Hz, C, endo), 159.1 (d, J_{CP} = 20.1 Hz, C, exo). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}P$ 305.1454; Found 305.1454.

exo-**3ba:** colorless liquid, ethyl acetate/petroleum ether = 1:15, R_f = 0.20, 50 mg, 41%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -18.41. **^1H NMR** ($CDCl_3$; 300 MHz): δ 0.99 (s, 3H, CH_3), 1.55-1.63 (m, 1H, CH_2), 1.80-1.88 (m, 1H, CH_2), 2.12 (s, 3H, CH_3), 3.19 (s, H, CH), 5.41 (d, J = 32.0 Hz, 1H, CH_2), 6.03 (d, J = 13.4 Hz, 1H, CH_2), 7.06-7.10 (m, 1H, CH), 7.15-7.20 (m, 2H, CH), 7.23-7.37 (m, 4H, CH), 7.60-7.65 (m, 1H, CH), 8.61-8.62 (s, 1H, CH). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 13.1 (s, CH_3), 20.2 (s, CH_3), 44.0 (d, J_{CP} = 2.2 Hz, CH_2), 53.5 (d, J_{CP} = 2.4 Hz, CH), 64.5 (d, J_{CP} = 6.1 Hz, C), 120.9 (s, CH), 122.9(d, J_{CP} = 1.7 Hz, CH), 123.1(d, J_{CP} = 29.9 Hz, CH_2), 126.4 (s, CH), 128.0 (s, CH), 130.0 (s, CH), 135.9 (s, CH), 141.4 (d, J_{CP} = 15.2 Hz, C), 142.6 (s, C), 149.3 (s, CH), 157.6 (d, J_{CP} = 20.9 Hz, C), 158.5 (d, J_{CP} = 19.8 Hz, C), 159.1 (d,

J_{CP} = 1.9 Hz, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}NP$ 306.1406; Found 306.1407.

endo-**3ba:** colorless liquid, ethyl acetate/petroleum ether = 1:15, R_f = 0.25, 75 mg, 49%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -17.7. **^1H NMR** ($CDCl_3$; 300 MHz): δ 1.35 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.56-1.64 (m, 1H, CH_2), 1.83-1.90 (m, 1H, CH_2), 3.52 (d, H, *J* = 2.3 Hz, CH), 5.33 (d, *J* = 31.7 Hz, 1H, CH_2), 5.98 (dd, *J* = 13.1 Hz, *J* = 1.3 Hz, 1H, CH_2), 6.95-6.97 (m, 2H, CH), 7.09-7.14 (m, 1H, CH), 7.17-7.22 (m, 3H, CH), 7.35-7.38 (m, 1H, CH), 7.63-7.69 (m, 1H, CH), 8.64-8.66 (s, 1H, CH). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 16.4 (s, CH_3), 20.7 (s, CH_3), 50.4 (d, J_{CP} = 0.9 Hz, CH_2), 57.2 (d, J_{CP} = 2.0 Hz, CH), 65.0 (d, J_{CP} = 5.6 Hz, C), 120.9 (s, Ph, CH), 121.4(d, J_{CP} = 29.4 Hz, CH_2), 123.1(d, J_{CP} = 7.9 Hz, CH), 126.5 (s, CH), 127.8 (s, CH), 129.7 (s, CH), 136.9 (s, CH), 140.1 (d, J_{CP} = 16.1 Hz, C), 141.1 (s, C), 149.5 (s, CH), 156.1 (d, J_{CP} = 1.9 Hz, C), 156.4 (d, J_{CP} = 19.4 Hz, C), 157.6 (d, J_{CP} = 21.2 Hz, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}NP$ 306.1406; Found 306.1405.

3ca: colorless liquid, ethyl acetate/petroleum ether = 1:10, R_f = 0.35, 148 mg, 89%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -16.9 (exo), -16.3 (endo), exo:endo = 0.86:1. **^1H NMR** ($CDCl_3$; 300 MHz): δ 0.96 (s, 2.57H, CH_3, exo), 1.27 (s, 3H, CH_3, endo), 1.30 (s, 3H, CH_3, endo), 1.51-1.58 (m, 1.87H, CH_2, exo + endo), 1.74-1.84 (m, 1.86H, CH_2), 1.88 (s, 2.59H, CH_3, exo), 3.14 (s, 0.68H, CH, exo), 3.45 (s, 1H, CH, endo), 3.77 (s, 2.60H, OCH_3, exo), 3.79 (s, 3H, OCH_3, endo), 5.29 (d, *J* = 31.5 Hz, 1H, CH_2, endo), 5.37 (d, *J* = 31.6 Hz, 0.85H, CH_2, exo), 5.91 (*pseudo*-t, *J* = 12.9 Hz, 1.85H, CH_2 exo + endo), 7.09-7.49 (m, 16.81H, CH, exo + endo). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 12.9 (s, CH_3, exo), 16.0 (s, CH_3, endo), 20.5 (s, CH_3, exo), 21.0 (s, CH_3, endo), 44.2 (s, CH_2, exo), 50.5 (s, CH_2, endo), 53.6 (d, J_{CP} = 2.4 Hz, CH, exo), 55.3 (s, OCH_3, exo + endo), 57.1 (d, J_{CP} = 1.5 Hz, CH, endo), 63.9 (d, J_{CP} = 5.9 Hz, C, exo), 64.5 (d, J_{CP} = 5.4 Hz, C, endo), 113.7 (s, CH, exo), 113.8 (s, CH, endo), 121.1 (d, J_{CP} = 29.0 Hz, CH_2, endo), 122.5 (d, J_{CP} = 29.6 Hz, CH_2, exo), 126.4 (s, CH, exo), 126.6 (s, CH, endo), 127.8 (s, CH, exo), 128.0 (s, CH, endo), 129.3 (d, J_{CP} = 7.4 Hz, CH, exo), 129.7 (s, CH, exo), 129.8 (d, J_{CP} = 7.7 Hz, CH, endo), 130.1 (s, CH, endo), 131.2 (d, J_{CP} = 20.9 Hz, C, exo), 131.4 (d, J_{CP} = 20.6 Hz, C, endo), 139.3 (d,

J_{CP} = 16.2 Hz, C, endo), 141.1 (d, J_{CP} = 15.2 Hz, C, exo), 141.5 (s, C, endo), 142.9 (s, C, exo), 150.3 (s, C, exo), 153.2 (s, C, endo), 156.7 (d, J_{CP} = 20.1 Hz, C, endo), 158.2 (s, C, exo + endo), 159.2 (d, C, J_{CP} = 20.0 Hz, exo). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{24}OP$ 355.1559; Found 355.1557.

exo-**3da:** light yellow liquid, ethyl acetate/petroleum ether = 1:10, R_f = 0.24, 27 mg, 21%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -18.2. **^1H NMR** ($CDCl_3$; 300 MHz): δ 0.94 (s, 3H, CH_3), 1.56-1.63 (m, 1H, CH_2), 1.81-1.96 (m, 1H, CH_2), 2.15 (s, 3H, CH_3), 3.05 (s, 1H, CH), 5.46 (d, *J* = 33.3 Hz, 1H, CH_2), 6.01 (dd, *J* = 13.8 Hz, *J* = 1.7 Hz, 1H, CH_2), 6.84-6.87 (m, 2H, CH), 7.09-7.12 (m, 2H, CH), 7.23-7.34 (m, 3H, CH). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 16.0 (s, CH_3), 19.1 (s, CH_3), 45.1 (d, J_{CP} = 4.4 Hz, CH_2), 52.5 (d, J_{CP} = 2.3 Hz, CH), 63.1 (d, J_{CP} = 6.7 Hz, C), 113.4 (d, J_{CP} = 21.2 Hz, C), 117.2 (d, J_{CP} = 25.6 Hz, C), 126.0 (d, J_{CP} = 31.3 Hz, CH_2), 127.1 (s, CH), 128.3 (s, CH), 129.9 (s, CH), 140.7 (s, C), 154.9 (d, J_{CP} = 20.0 Hz, C), 180.2 (s, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}NP$ 254.1093; Found 254.1092.

endo-**3da:** light yellow liquid, ethyl acetate/petroleum ether = 1:10, R_f = 0.28, 66 mg, 53%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -18.0. **^1H NMR** ($CDCl_3$; 300 MHz): δ 1.32 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.59-1.67 (m, 1H, CH_2), 1.79-1.85 (m, 1H, CH_2), 3.55 (t, 1H, *J* = 2.4 Hz, CH), 5.40 (dd, *J* = 24.1 Hz, *J* = 2.0 Hz, 1H, CH_2), 6.00 (dd, *J* = 13.7 Hz, *J* = 2.1 Hz, 1H, CH_2), 6.91-6.93 (m, 2H, CH), 7.21-7.30 (m, 3H, CH). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 19.3 (s, CH_3), 19.6 (s, CH_3), 50.8 (d, J_{CP} = 3.5 Hz, CH_2), 56.2 (d, J_{CP} = 2.0 Hz, CH), 64.5 (d, J_{CP} = 6.9 Hz, C), 111.8 (d, J_{CP} = 22.2 Hz, C), 117.1 (d, J_{CP} = 26.0 Hz, C), 124.4 (d, J_{CP} = 30.5 Hz, CH_2), 127.3 (s, CH), 128.2 (s, CH), 129.2 (s, CH), 139.2 (s, C), 152.8 (d, J_{CP} = 20.0 Hz, C), 178.2 (s, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}NP$ 254.1093; Found 254.1090.

3ea: light yellow liquid, ethyl acetate/petroleum ether = 1:20, R_f = 0.35, 161 mg, 98%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -16.1 (exo), -15.4 (endo), exo:endo = 0.60:1. **^1H NMR** ($CDCl_3$; 300 MHz): δ 0.91 (s, 1.79H, CH_3, exo), 1.25 (s, 3H, CH_3, endo), 1.44 (s, 3H, CH_3, endo), 1.49-1.59 (m, 1.59H, CH_2, exo + endo), 1.72-1.84 (m, 1.62H, CH_2), 2.04 (s, 1.80H, CH_3, exo), 3.09 (s, 0.68H, CH, exo), 3.44 (s, 1H, CH, endo), 5.31 (d, *J* = 30.7 Hz, 1H, CH_2, endo), 5.41 (d, *J* = 30.5 Hz, 0.68H, CH_2, exo),

5.96 (d, J = 15.2 Hz, 1H, CH_2, endo), 6.00 (d, J = 14.9 Hz, 0.68H, CH_2, exo), 7.09-7.49 (m, 16.34H, CH, exo + endo). **^{13}C{^{1}H} NMR** ($CDCl_3$; 75 MHz): δ 14.8 (s, CH_3, exo), 18.0 (s, CH_3, endo), 19.8 (s, CH_3, exo), 20.3 (s, CH_3, endo), 44.8 (d, J_{CP} = 3.6 Hz, CH_2, exo), 50.8 (d, J_{CP} = 2.4 Hz, CH_2, endo), 53.5 (s, CH, exo), 57.2 (s, CH, endo), 62.8 (d, J_{CP} = 6.8 Hz, C, exo), 63.6 (d, J_{CP} = 6.3 Hz, C, endo), 86.7 (d, J_{CP} = 26.1 Hz, C, exo), 86.8 (d, J_{CP} = 26.5 Hz, C, endo), 96.2 (d, J_{CP} = 5.2 Hz, C, endo), 96.4 (d, J_{CP} = 5.0 Hz, C, exo), 121.9 (d, J_{CP} = 14.2 Hz, C, endo), 122.4 (d, J_{CP} = 29.6 Hz, CH_2, endo), 123.2 (d, J_{CP} = 13.1 Hz, C, exo), 124.0 (d, J_{CP} = 1.5 Hz, C, exo), 124.0 (d, J_{CP} = 1.4 Hz, C, endo), 124.1 (d, J_{CP} = 30.3 Hz, CH_2, exo), 126.7 (s, CH), 126.8 (s, CH), 128.0 (s, CH), 128.2 (s, CH), 128.4 (s, CH), 129.7 (s, CH), 130.0 (s, CH), 131.5 (s, CH), 131.5 (s, CH), 131.6 (s, CH), 131.6 (s, CH), 140.8 (s, C, endo), 142.2 (s, C, exo), 155.4 (d, J_{CP} = 20.3 Hz, C, endo), 157.4 (d, C, J_{CP} = 20.5 Hz, exo), 164.5 (s, C, endo), 167.2 (s, C, exo). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{22}P$ 329.1454; Found 329.1456.

3ab: colorless liquid, dichloromethane /petroleum ether = 1:20, R_f = 0.36, 131 mg, 81%. **^{31}P{^{1}H} NMR** ($CDCl_3$; 121 MHz): δ -15.9 (exo), -15.4 (endo), exo:endo = 0.81:1. **^{1}H NMR** ($CDCl_3$; 300 MHz): δ 0.97 (s, 2.42H, CH_3, exo), 1.30 (s, 6H, $2CH_3$, endo), 1.52-1.59 (m, 1.86H, CH_2, exo + endo), 1.71-1.84 (m, 1.83H, CH_2, exo + endo), 1.89 (s, 2.40H, CH_3, exo), 3.14 (s, 0.80H, CH, exo), 3.45 (d, 1H, CH, endo), 5.33 (dd, J = 31.2 Hz, J = 26.6 Hz, 1.81H, CH_2, exo + endo), 5.94 (*pseudo*-t, J = 12.0 Hz, 1.81H, CH_2, exo + endo), 6.89-7.36 (m, 16.31H, CH, exo + endo). **^{13}C{^{1}H} NMR** ($CDCl_3$; 75 MHz): δ 12.8 (s, CH_3, exo), 16.0 (s, CH_3, endo), 20.4 (s, CH_3, exo), 20.9 (s, CH_3, endo), 44.2 (d, J_{CP} = 2.6 Hz, CH_2 exo), 50.6 (d, J_{CP} = 0.8 Hz, CH_2 endo), 52.8 (d, J_{CP} = 2.3 Hz, CH, exo), 56.4 (d, J_{CP} = 1.7 Hz, CH, endo), 63.8 (d, J_{CP} = 5.5 Hz, C, exo), 64.4 (d, J_{CP} = 4.7 Hz, C, endo), 114.7 (d, J_{CP} = 21.0 Hz, CH, exo), 114.8 (s, J_{CP} = 20.9 Hz, CH, endo), 121.3 (d, J_{CP} = 29.2 Hz, CH_2, endo), 122.8 (d, J_{CP} = 29.8 Hz, CH_2, exo), 126.4 (s, CH, exo), 126.5 (s, CH, endo), 128.0 (d, J_{CP} = 7.5 Hz, CH, exo), 128.2 (s, CH, exo), 128.3 (s, CH, endo), 128.5 (d, J_{CP} = 7.7 Hz, CH, endo), 131.0 (d, J_{CP} = 6.5 Hz, exo), 131.3 (d, J_{CP} = 7.8 Hz, CH, endo), 137.0 (d, J_{CP} = 3.0 Hz, C, endo), 138.5 (d, J_{CP} = 3.2 Hz, C, exo), 138.8 (d, J_{CP} = 20.4 Hz, C, endo), 138.9 (d,

J_{CP} = 19.9 Hz, C, exo), 140.2 (d, J_{CP} = 17.0 Hz, C, endo), 141.7 (d, J_{CP} = 15.9 Hz, C, exo), 151.4 (d, J_{CP} = 1.4 Hz, C, endo), 154.4 (d, J_{CP} = 1.2 Hz, C, exo), 156.8 (d, J_{CP} = 19.9 Hz, C, endo), 159.1 (d, J_{CP} = 20.3 Hz, C, exo), 161.7 (s, C, J_{CF} =243.3 Hz, exo), 161.8 (d, J_{CP} = 243.4 Hz, C, endo). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{21}FP$ 323.1359; Found 323.1357.

3ac: colorless liquid, dichloromethane /petroleum ether = 1:20, R_f = 0.33, 132 mg, 83%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -16.8 (exo), -14.5 (endo), exo:endo = 1:0.60. **^1H NMR** ($CDCl_3$; 300 MHz): δ 0.99 (s, 3H, CH_3, exo), 1.30 (s, 1.82H, CH_3, endo), 1.44 (s, 1.80H, CH_3, endo), 1.44-1.57 (m, 1H, CH_2, exo), 1.60-1.67 (m, 0.62H, CH_2, endo), 1.77-1.81 (m, 0.62H, CH_2, endo), 1.94 (s, 3H, CH_3, exo), 1.96-2.02 (m, 1H, CH_2, exo), 2.39 (s, 3H, CH_3, exo), 2.44 (s, 1.64H, CH_3, endo), 3.52 (s, 1H, CH, exo), 3.85 (d, 0.60H, J = 2.3 Hz, CH, endo), 5.16 (d, J = 31.6 Hz, 0.62H, CH_2, endo), 5.32 (d, J = 32.0 Hz, 1H, CH_2, exo), 5.84 (dd, J = 13.1 Hz, J = 1.4 Hz, 0.62H, CH_2, endo), 5.93 (d, J = 13.5 Hz, 1H, CH_2, exo), 6.81-7.35 (m, 14.7H, CH, exo + endo). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 13.0 (s, CH_3, exo), 16.4 (s, CH_3, endo), 18.9 (s, CH_3, exo), 20.7 (s, CH_3, endo), 20.8 (s, CH_3, exo), 21.2 (s, CH_3, endo), 44.8 (d, J_{CP} = 2.3 Hz, CH_2, exo), 47.9 (d, J_{CP} = 2.6 Hz, CH, exo), 51.2 (s, CH_2, endo), 51.7 (d, J_{CP} = 1.7 Hz, CH, endo), 65.0 (d, J_{CP} = 5.9 Hz, C, exo), 65.6 (d, J_{CP} = 5.4 Hz, C, endo), 120.8 (d, J_{CP} = 29.0 Hz, CH_2, endo), 122.6 (d, J_{CP} = 29.9 Hz, CH_2, exo), 125.8 (s, CH, endo), 126.0 (s, CH, exo), 126.1 (s, CH, exo), 126.2 (s, CH, endo), 126.3 (s, CH, exo), 126.4 (s, CH, endo), 128.0 (d, J_{CP} = 7.5 Hz, CH, exo), 128.2 (s, CH, exo), 128.3 (s, CH, endo), 128.5 (d, J_{CP} = 7.6 Hz, CH, endo), 128.9 (s, CH, endo), 129.0 (s, CH, exo), 129.8 (s, CH, endo), 130.1 (s, CH, exo), 137.5 (s, C, exo), 137.9 (s, C, endo), 139.0 (d, J_{CP} = 20.4 Hz, C, endo), 139.1 (d, J_{CP} = 20.0 Hz, C, exo), 139.9 (s, C, endo), 140.1 (d, J_{CP} = 18.4 Hz, C, endo), 141.3 (s, C, exo), 141.5 (d, J_{CP} = 15.9 Hz, C, exo), 151.8 (d, J_{CP} = 1.2 Hz, C, endo), 154.9 (d, J_{CP} = 1.5 Hz, C,exo), 158.1 (d, J_{CP} = 19.7 Hz, C, endo), 160.1 (d, J_{CP} = 20.0 Hz, C, exo). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{24}P$ 319.1610; Found 319.1608.

3ad: colorless liquid, dichloromethane /petroleum ether = 1:20, R_f = 0.35, 139 mg, 83%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -16.0 (exo), -15.5 (endo), exo:endo =

1:0.83. **^{1}H NMR** ($CDCl_3$; 300 MHz): δ 0.98 (s, 3H, CH_3, exo), 1.30 (s, 2.50H, CH_3, endo), 1.31 (s, 2.51H, CH_3, endo), 1.50-1.58 (m, 1.87H, CH_2, exo + endo), 1.74-1.83 (m, 1.82H, CH_2, exo + endo), 1.88 (s, 3H, CH_3, exo), 3.11 (s, 1H, CH, exo), 3.42 (d, 0.84H, J = 2.3 Hz, CH, endo), 3.73 (s, 2.49H, OCH_3, endo), 3.77 (s, 3H, OCH_3, exo), 5.35 (dd, J = 31.7 Hz, J = 25.9 Hz, 1.84H, CH_2, exo + endo), 5.89-5.98 (m, 1.84H, CH_2, exo + endo), 6.73-7.35 (m, 16.36H, CH, exo + endo). **^{13}C{^{1}H} NMR** ($CDCl_3$; 75 MHz): δ 12.9 (s, CH_3, exo), 16.1 (s, CH_3, endo), 20.4 (s, CH_3, exo), 30.1 (s, CH_3, endo), 44.4 (d, J_{CP} = 2.3 Hz, CH_2, exo), 50.6 (d, J_{CP} = 0.7 Hz, CH_2 endo), 52.7 (d, J_{CP} = 2.4 Hz, CH, exo), 55.2 (s, OCH_3, exo), 55.3 (s, OCH_3, endo), 56.3 (d, J_{CP} = 1.7 Hz, CH, endo), 63.9 (d, J_{CP} = 5.9 Hz, C, exo), 64.3 (d, J_{CP} = 5.4 Hz, C, endo), 113.2 (s, CH, endo), 113.4 (s, CH, exo), 121.0 (d, J_{CP} = 29.0 Hz, CH_2, endo), 122.5 (d, J_{CP} = 29.7 Hz, CH_2, exo), 126.3 (s, CH, endo), 128.0 (s, CH, exo), 128.1 (s, CH, exo), 128.2 (s, CH, exo), 128.3 (s, CH, endo), 128.5 (s, CH, endo), 128.6 (s, CH, endo), 130.9 (s, CH, exo), 133.3 (s, C, endo), 134.8 (s, C, exo), 138.9 (d, J_{CP} = 6.4 Hz, C, endo), 139.2 (d, J_{CP} = 5.8 Hz, C, exo), 139.9 (d, J_{CP} = 16.8 Hz, C, endo), 141.5 (d, J_{CP} = 15.5 Hz, C, exo), 151.8 (s, C, exo), 154.6 (s, C, endo), 157.0 (d, J_{CP} = 19.4 Hz, C, endo), 158.2 (s, C, exo), 158.4 (s, C, endo), 159.3 (d, J_{CP} = 19.8 Hz, C, exo) . **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{24}OP$ 305.1559; Found 305.1558.

3ae: light yellow liquid, petroleum ether, R_f = 0.30, 158 mg, 89%. **^{31}P{^{1}H} NMR** ($CDCl_3$; 121 MHz): δ -16.0 (exo), -15.5 (endo), exo:endo = 1:0.60.. **^{1}H NMR** ($CDCl_3$; 300 MHz): δ 0.98 (s, 1.96H, CH_3, exo), 1.26 (s, 3H, CH_3, endo), 1.33 (s, 3H, CH_3, endo), 1.56-1.63 (m, 1.70H, CH_2, exo + endo), 1.79-1.97 (m, 1.72H, CH_2), 1.92 (s, 2.04H, CH_3, exo), 3.31 (s, 0.68H, CH, exo), 3.60 (s, 1H, CH, endo), 5.31 (d, J = 30.7 Hz, 1H, CH_2, endo), 5.41 (d, J = 30.5 Hz, 0.68H, CH_2, exo), 5.96 (d, J = 15.2 Hz, 1H, CH_2, endo), 6.00 (d, J = 14.9 Hz, 0.68H, CH_2, exo), 7.00-7.79 (m, 20.55H, CH, exo + endo). **^{13}C{^{1}H} NMR** ($CDCl_3$; 75 MHz): δ 13.0 (s, CH_3, exo), 16.2 (s, CH_3, endo), 20.6 (s, CH_3, exo), 21.1 (s, CH_3, endo), 44.6 (d, J_{CP} = 2.4 Hz, CH_2, exo), 50.8 (s, CH_2, endo), 53.8 (d, J_{CP} = 2.3 Hz, CH, exo), 57.3 (s, CH, endo), 64.3 (d, J_{CP} = 5.9 Hz, C, exo), 64.8 (d, J_{CP} = 5.4 Hz, C, endo), 121.6 (d, J_{CP} = 29.0 Hz, CH_2, endo), 123.0 (d, J_{CP} = 29.8 Hz, CH_2, exo), 125.6 (s, CH), 125.7 (s, CH), 126.1 (s, CH), 126.1 (s, CH),

126.5 (s, CH), 126.6 (s, CH), 127.4 (s, CH), 127.6 (s, CH), 127.7 (s, CH), 127.7 (s, CH), 127.8 (s, CH), 128.1 (s, CH), 128.2 (s, CH), 128.3 (s, CH), 128.4 (s, CH), 128.7 (s, CH), 128.8 (s, CH), 128.9 (s, CH), 132.4 (s, C, exo), 132.5 (s, C, endo), 133.2 (s, C, endo), 133.4 (s, C, exo), 138.9 (d, J_{CP} = 19.9 Hz, C, endo), 139.0 (s, C, endo), 139.1 (d, C, J_{CP} = 19.9 Hz, exo), 140.2 (d, J_{CP} = 17.0 Hz, C, endo), 140.4 (s, C, exo), 141.9 (d, J_{CP} = 15.8 Hz, C, exo), 151.8 (d, J_{CP} = 1.2 Hz, C, endo), 154.7 (d, J_{CP} = 1.1 Hz, C, exo), 156.8 (d, J_{CP} = 19.7 Hz, C, endo), 159.1 (d, J_{CP} = 20.1 Hz, C, exo). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{24}P$ 355.1608; Found 355.1608.

exo-**3bb** **:** light yellow liquid, ethyl acetate/petroleum ether = 1:15, R_f = 0.25, 33 mg, 33%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -19.4. **^1H NMR** ($CDCl_3$; 300 MHz): δ 0.99 (s, 3H, CH_3), 1.58-1.64 (m, 1H, CH_2), 1.74-1.81 (m, 1H, CH_2), 2.10 (s, 3H, CH_3), 3.18 (s, H, CH), 5.40 (d, *J* = 31.9 Hz, 1H, CH_2), 6.03 (d, *J* = 13.3 Hz, 1H, CH_2), 6.96-7.02 (m, 2H, CH), 7.08-7.15 (m, 3H, CH), 7.34-7.37 (m, 1H, CH), 7.61-7.66 (m, 1H, CH), 8.61-8.62 (s, 1H, CH). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 13.1 (s, CH_3), 20.1 (s, CH_3), 43.9 (d, J_{CP} = 2.4 Hz, CH_2), 52.8 (d, J_{CP} = 2.6 Hz, CH), 64.4 (d, J_{CP} = 5.2 Hz, C), 114.8 (d, J_{CF} = 21.0 Hz, CH), 121.0 (s, CH), 122.9(d, J_{CP} = 8.6 Hz, CH), 123.2(d, J_{CP} = 29.9 Hz, CH_2), 131.3(d, J_{CP} = 7.4 Hz, CH), 135.9 (s, CH), 138.2 (d, J_{CP} = 3.3 Hz, C), 141.4 (d, J_{CP} = 15.2 Hz, C), 149.3 (s, CH), 157.5 (d, J_{CP} = 20.9 Hz, C), 158.4 (d, J_{CP} = 20.1 Hz, C), 159.0 (d, J_{CP} = 1.7 Hz, C), 161.6 (d, J_{CF} = 241.1 Hz, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}FNP$ 324.1312; Found 324.1310

endo-**3bb** **:** light yellow liquid, ethyl acetate/petroleum ether = 1:15, R_f = 0.30, 60 mg, 37%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -18.5. **^1H NMR** ($CDCl_3$; 300 MHz): δ 1.34 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.55-1.63 (m, 1H, CH_2), 1.83-1.89 (m, 1H, CH_2), 3.50 (d, H, *J* = 2.3 Hz, CH), 5.31 (d, *J* = 31.5 Hz, 1H, CH_2), 5.99 (dd, *J* = 13.0 Hz, *J* = 1.4 Hz, 1H, CH_2), 6.86-6.91 (m, 4H, CH), 7.11-7.14 (m, 1H, CH), 7.34-7.37 (m, 1H, CH), 7.64-7.69 (m, 1H, CH), 8.64-8.66 (s, 1H, CH). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 16.4 (s, CH_3), 20.6 (s, CH_3), 50.2 (d, J_{CP} = 1.0 Hz, CH_2), 56.5 (d, J_{CP} = 2.0 Hz, CH), 64.9 (d, J_{CP} = 6.0 Hz, C), 114.6 (d, J_{CF} = 21.1 Hz, CH), 121.0 (s, CH), 121.5(d, J_{CP} = 29.2 Hz, CH_2), 123.1(d, J_{CP} = 8.1 Hz, CH), 131.0 (s, CH), 136.0 (s, CH), 136.8 (s, C), 140.4 (d, J_{CP} = 12.6 Hz, C), 149.5 (s, CH), 155.8 (d, J_{CP} = 1.7 Hz,

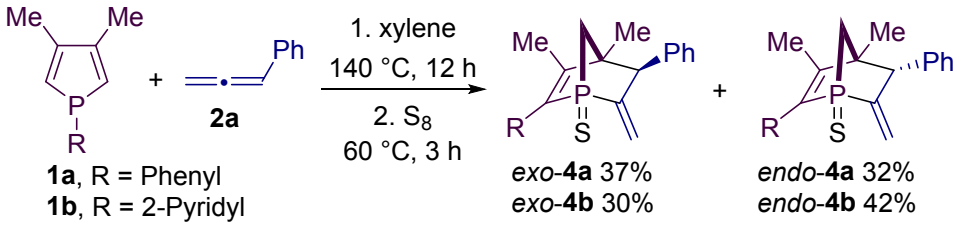
C), 156.4 (d, J_{CP} = 19.5 Hz, C), 157.4 (d, J_{CP} = 21.0 Hz, C), 161.7 (d, J_{CF} = 243.3 Hz, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}FNP$ 324.1312; Found 324.1314.

exo-**3bd** **:** light yellow liquid, ethyl acetate/petroleum ether = 1:20, R_f = 0.20, 56 mg, 33%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -18.5. **^1H NMR** ($CDCl_3$; 300 MHz): δ 1.00 (s, 3H, CH_3), 1.56-1.64 (m, 1H, CH_2), 1.77-1.85 (m, 1H, CH_2), 2.11 (s, 3H, CH_3), 3.17 (s, H, CH), 3.81 (s, 3H, OCH_3), 5.42 (d, *J* = 32.0 Hz, 1H, CH_2), 6.03 (d, *J* = 13.4 Hz, 1H, CH_2), 6.84-6.87 (m, 2H, CH), 7.08-7.11 (m, 3H, CH), 7.35-7.38 (m, 1H, CH), 7.61-7.67 (m, 1H, CH), 8.61-8.63 (s, 1H, CH). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 13.1 (s, CH_3), 20.2 (s, CH_3), 44.0 (d, J_{CP} = 2.2 Hz, CH_2), 52.7 (d, J_{CP} = 2.6 Hz, CH), 55.2 (s, OCH_3), 64.5 (d, J_{CP} = 6.0 Hz, C), 113.4 (s, CH), 120.9 (s, CH), 122.8 (s, J_{CP} = 8.7 Hz, CH), 122.9 (d, J_{CP} = 30.0 Hz, CH_2), 130.8 (s, CH), 134.6 (s, C), 135.9 (s, CH), 141.2 (d, J_{CP} = 15.0 Hz, C), 149.3 (s, CH), 157.7 (d, J_{CP} = 21.2 Hz, C), 158.2 (s, C), 158.7 (d, J_{CP} = 19.7 Hz, C), 159.2 (d, J_{CP} = 1.8 Hz, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}NOP$ 336.1512; Found 336.1513.

endo-**3bd** **:** light yellow liquid, ethyl acetate/petroleum ether = 1:20, R_f = 0.25, 72 mg, 43%. **^{31}P NMR** ($CDCl_3$; 121 MHz): δ -18.0. **^1H NMR** ($CDCl_3$; 300 MHz): δ 1.33 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.54-1.61 (m, 1H, CH_2), 1.82-1.88 (m, 1H, CH_2), 3.46 (t, 1H, *J* = 2.3 Hz, CH), 3.75 (s, 3H, OCH_3), 5.32 (d, *J* = 31.7 Hz, 1H, CH_2), 5.97 (dd, *J* = 13.0 Hz, *J* = 1.1 Hz, 1H, CH_2), 6.73-6.75 (m, 2H, CH), 6.86-6.89 (m, 2H, CH), 7.08-7.12 (m, 1H, CH), 7.35-7.37 (m, 1H, CH), 7.62-7.66 (m, 1H, CH), 8.64-8.65 (s, 1H, CH). **^{13}C NMR**$\{^1H\}$ ($CDCl_3$; 75 MHz): δ 16.5 (s, CH_3), 20.7 (s, CH_3), 50.2 (d, J_{CP} = 0.8 Hz, CH_2), 55.1 (s, OCH_3), 56.5 (d, J_{CP} = 2.0 Hz, CH), 64.8 (d, J_{CP} = 5.5 Hz, C), 113.1 (s, CH), 120.9 (s, CH), 121.2(d, J_{CP} = 29.4 Hz, CH_2), 123.0(d, J_{CP} = 7.9 Hz, CH), 130.5 (s, CH), 133.0 (s, C), 135.9 (s, CH), 140.0 (d, J_{CP} = 16.1 Hz, C), 149.4 (s, CH), 156.2 (d, J_{CP} = 1.7 Hz, C), 156.7 (d, J_{CP} = 19.2 Hz, C), 157.6 (d, J_{CP} = 21.1 Hz, C), 158.3 (s, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}NOP$ 336.1512; Found 336.1511.

3af colorless liquid, dichloromethane/petroleum ether = 1:20, R_f = 0.45, 55 mg, 35%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -19.6 (exo), -15.2 (endo), exo:endo = 1:0.38. **^1H NMR** ($CDCl_3$; 300 MHz): δ 1.11 (t, *J* = 7.1 Hz, 1.13 H, CH_3, endo), 1.21 (s,

3H, CH_3, exo), 1.27 (t, J = 7.1 Hz, 3H, CH_3, exo), 1.35 (s, 3H, CH_3, exo), 1.46 (s, 1.13H, CH_3, endo), 1.47 (s, 1.14H, CH_3, endo), 1.58-1.64 (m, 1.77H, CH_2, exo + endo), 1.69 (s, 1.16H, CH_3, endo), 1.90 (s, 3H, CH_3, exo), 2.36-2.43 (m, 1H, CH_2, exo + endo), 3.94-4.23 (m, 2.78H, CH_2, exo + endo), 5.51 (d, J = 30.9 Hz, 1H, CH_2, exo), 5.55 (d, J = 32.5 Hz, 0.38H, CH_2, endo), 5.86 (d, J = 12.9 Hz, 1H, CH_2, exo), 5.91 (d, J = 14.0 Hz, 0.38H, CH_2, endo), 7.21-7.35 (m, 6.92H, CH, exo + endo). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 13.9 (s, CH_3, endo), 14.2 (s, CH_3, exo), 14.6 (s, CH_3, endo), 16.5 (s, CH_3, exo), 17.8 (s, CH_3, exo), 17.9 (s, CH_3, endo), 22.3 (s, CH_3, exo), 23.5 (s, CH_3, endo), 47.1 (s, CH_2, endo), 47.4 (s, CH_2, exo), 54.5 (d, J_{CP} = 2.0 Hz, C, endo), 55.4 (d, J_{CP} = 2.2 Hz, C, exo), 60.7 (s, CH_2, endo), 60.9 (s, CH_2, exo), 65.9 (d, J_{CP} = 5.7 Hz, C, endo), 66.2(d, J_{CP} = 6.3 Hz, C, exo), 120.7 (d, J_{CP} = 29.3 Hz, CH_2, exo), 122.7 (d, J_{CP} = 30.6 Hz, CH_2, endo), 126.3 (s, CH), 126.5 (s, CH), 128.0 (s, CH), 128.1 (s, CH), 128.3 (s, CH), 128.4 (s, CH), 138.6 (d, J_{CP} = 20.1 Hz, C, exo), 138.8 (d, J_{CP} = 20.0 Hz, C, endo), 141.7 (d, J_{CP} = 16.4 Hz, C, exo), 141.8 (d, J_{CP} = 16.0 Hz, C, endo), 152.5 (s, C, endo), 153.3 (s, C, exo), 156.6 (d, J_{CP} = 20.3 Hz, C, endo), 157.9 (d, J_{CP} = 22.7 Hz, C, endo), 174.7 (s, CO, endo), 175.1 (s, CO, exo). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{23}O_2P$ 315.1508; Found 315.1509.



A solution of phosphole **1** (10 mmol) and allenes **2** (20 mmol) in xylenes (20 mL) was stirred at 140 °C in oil bath for 12 h under nitrogen. When the reaction liquid return to room temperature, add S_8 (11 mmol) powder to the solution, and place it in a 60 °C oil bath for 3 hours. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography providing **4.**

exo-**4a** **:** white solid, m.p. 188.5-189.2 ℃. ethyl acetate/petroleum ether = 1:10, R_f = 0.35, 1.25 g, 37%. **^{31}P NMR** ($CDCl_3$; 121 MHz): δ 47.2 . **^1H NMR** ($CDCl_3$; 300

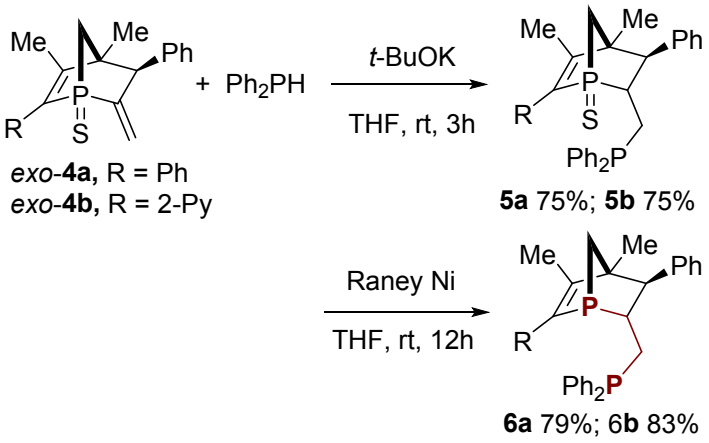
MHz): δ 1.00 (s, 3H, CH_3), 1.97 (d, J = 2.5 Hz, 3H, CH_3), 2.04-2.12 (m, 1H, CH_2), 2.24-2.30 (m, 1H, CH_2), 3.47 (dd, J = 9.2 Hz, J = 1.5 Hz, 1H, CH), 5.71 (dd, J = 41.8 Hz, J = 1.9 Hz, 1H, CH_2), 6.27 (dd, J = 21.6 Hz, J = 2.5 Hz, H, CH_2), 7.18-7.21 (m, 2H, CH), 7.24-7.28 (m, 3H, CH), 7.29-7.31 (m, 2H, CH), 7.33-7.40 (m, 3H, CH). **^{13}C NMR**{^{1}H} ($CDCl_3$; 75 MHz): δ 14.0 (d, J_{CP} = 11.6 Hz, CH_3), 19.6 (d, J_{CP} = 13.9 Hz, CH_3), 47.1 (d, J_{CP} = 57.6 Hz, CH_2), 49.4 (d, J_{CP} = 16.5 Hz, C), 52.7 (d, J_{CP} = 13.7 Hz, CH), 125.2 (d, J_{CP} = 8.8 Hz, CH_2), 127.3 (s, CH), 127.6 (s, CH), 128.2 (s, CH), 128.4 (s, CH), 129.0 (d, J_{CP} = 5.5 Hz, CH), 129.7 (s, CH), 132.5 (d, J_{CP} = 10.1 Hz, C), 134.6 (d, J_{CP} = 69.0 Hz, C), 140.0 (d, J_{CP} = 2.9 Hz, C), 149.0 (d, J_{CP} = 64.6 Hz, C), 156.7 (d, J_{CP} = 15.9 Hz, C) **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}PS$ 337.1174; Found 337.1172.

endo-**4a:** white solid, m.p. 155.4-156.3 ℃. ethyl acetate/petroleum ether = 1:10, R_f = 0.33, 1.07 g, 32%. **^{31}P NMR** ($CDCl_3$; 121 MHz): δ 49.1. **^{1}H NMR** ($CDCl_3$; 300 MHz): δ 1.29 (d, J = 2.1 Hz, 3H, CH_3), 1.41 (s, 3H, CH_3), 2.05-2.11 (m, 1H, CH_2), 2.32-2.39 (m, 1H, CH_2), 3.72 (d, J = 2.0 Hz, 1H, CH), 5.69 (dd, J = 41.7 Hz, J = 1.1 Hz, 1H, CH_2), 6.24 (dd, J = 21.6 Hz, J = 2.3 Hz,1 H, CH_2), 7.02-7.05 (m, 2H, CH), 7.25-7.26 (m, 3H, CH), 7.32-7.35 (m, 3H, CH), 7.39-7.44 (m, 2H, CH). **^{13}C NMR**{^{1}H} ($CDCl_3$; 75 MHz): δ 16.0 (d, J_{CP} = 12.0 Hz, CH_3), 20.1 (d, J_{CP} = 13.7 Hz, CH_3), 50.2 (d, J_{CP} = 16.4 Hz, C), 54.0 (d, J_{CP} = 57.5 Hz, CH_2), 56.5 (d, J_{CP} = 14.2 Hz, CH), 124.1 (d, J_{CP} = 8.3 Hz, CH_2), 127.5 (s, CH), 127.6 (s, CH), 128.2 (s, CH), 128.3 (s, CH), 129.1 (s, CH), 129.3 (d, J_{CP} = 5.6 Hz, CH), 132.5 (d, J_{CP} = 9.9 Hz, C), 133.3 (d, J_{CP} = 68.3 Hz, C), 138.7 (d, J_{CP} = 5.6 Hz, C), 147.5 (d, J_{CP} = 64.4 Hz, C), 154.3 (d, J_{CP} = 14.2 Hz, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}PS$ 337.1174; Found 337.1172

exo-**4b** : white solid, m.p. 159.3-159.9 ℃. ethyl acetate/petroleum ether = 1:3, R_f = 0.25, 1.01 g, 30%. **^{31}P{^{1}H} NMR** ($CDCl_3$; 121 MHz): δ 45.9. **^{1}H NMR** ($CDCl_3$; 300 MHz): δ 1.01 (s, 3H, CH_3), 2.05-2.11 (m, 1H, CH_2), 2.17 (s, 3H, CH_3), 2.25-2.31 (m, 1H, CH_2), 3.51 (d, J = 8.5 Hz, 1H, CH), 5.73 (d, J = 42.2 Hz, 1H, CH_2), 6.32 (d, J = 21.6 Hz, 1H, CH_2), 7.18-7.20 (m, 3H, CH), 7.29-7.34 (m, 3H, CH), 7.54-7.57 (m, 1H, CH), 7.69-7.74 (m, 1H, CH), 8.64-8.66 (s, 1H, CH). **^{13}C{^{1}H} NMR** ($CDCl_3$; 75

MHz): δ 14.2 (d, J_{CP} = 11.3 Hz, CH_3), 19.4 (d, J_{CP} = 14.1 Hz, CH_3), 47.0 (d, J_{CP} = 58.4 Hz, CH_2), 49.8 (d, J_{CP} = 16.3 Hz, C), 52.6 (d, J_{CP} = 13.7 Hz, CH), 122.2 (s, CH), 124.4 (d, J_{CP} = 2.9 Hz, CH), 125.6 (d, J_{CP} = 8.9 Hz, CH_2), 127.4 (s, Ph, CH), 128.5 (s, CH), 129.7 (s, CH), 133.3 (d, J_{CP} = 69.3 Hz, C), 136.0 (s, Ph, CH), 139.8 (d, J_{CP} = 2.9 Hz, C), 148.6 (d, J_{CP} = 65.5 Hz, C), 149.6 (s, Ph, CH), 152.1 (d, J_{CP} = 13.8 Hz, C), 161.3 (d, J_{CP} = 14.3 Hz, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}NPS$ 338.1127; Found 338.1125.

endo-**4b** : white solid, m.p. 174.7-175.4 ℃. ethyl acetate/petroleum ether = 1:3, R_f = 0.28, 1.42 g, 42% **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ 48.0. **^1H NMR** ($CDCl_3$; 300 MHz): δ 1.42 (s, 3H, CH_3), 1.47 (d, J = 1.3 Hz, 3H, CH_3), 2.05-2.11 (m, 1H, CH_2), 2.40-2.47 (m, 1H, CH_2), 3.73 (s, H, CH), 5.71 (d, J = 42.1 Hz, H, CH_2), 6.29 (dd, J = 21.8 Hz, J = 1.7 Hz, H, CH_2), 7.03 (s, 2H, CH), 7.18-7.22 (m, 3H, CH), 7.53-7.56 (m, 1H, CH), 7.72-7.77 (m, 1H, CH), 8.65-8.67 (s, 1H, CH). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 16.4 (d, J_{CP} = 11.3 Hz, CH_3), 19.8 (d, J_{CP} = 13.7 Hz, CH_3), 50.6 (d, J_{CP} = 16.1 Hz, C), 53.5 (d, J_{CP} = 57.9 Hz, CH_2), 56.6 (d, J_{CP} = 14.3 Hz, CH), 122.1 (s, CH), 124.2 (d, J_{CP} = 7.4 Hz, CH_2), 124.3 (d, J_{CP} = 3.1 Hz, CH), 127.5 (s, CH), 128.2 (s, CH), 129.2 (s, CH), 132.6 (d, J_{CP} = 68.9 Hz, C), 136.0 (s, CH), 138.5 (d, J_{CP} = 5.9 Hz, C), 147.4 (d, J_{CP} = 65.1 Hz, C), 149.7 (s, CH), 152.3 (d, J_{CP} = 17.9 Hz, C), 158.8 (d, J_{CP} = 12.5 Hz, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}NPS$ 338.1127; Found 338.1125.



A solution of *exo*-**4** (1 mmol), diphenylphosphine (1.2 mmol) and *t*-BuOK (1.2 mmol) in THF (5 mL) was stirred at room temperature for 3 h under nitrogen. The

resulting solution was evaporated to dryness and the crude product was purified by column chromatography providing **5.**

5a: white solid, m.p. 192.9-193.3 ℃. ethyl acetate/petroleum ether = 1:10, R_f = 0.35, 392 mg, 75%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -21.0 (d, J_{PP} = 30.1 Hz), 58.7 (d, J_{PP} = 31.1 Hz). **^1H NMR** ($CDCl_3$; 300 MHz): δ 0.88 (s, 3H, CH_3), 1.83-1.98 (m, 2H, CH_2), 2.05 (d, J = 1.7 Hz, 3H, CH_3), 2.26-2.32 (m, 1H, CH_2), 2.43 (s, 1H, CH), 2.76 (s, 1H, CH), 2.95-3.01 (m, 1H, CH_2), 6.85-6.90 (m, 2H, CH), 7.09-7.13 (m, 4H, CH), 7.21-7.24 (m, 6H, CH), 7.28-7.35 (m, 4H, CH), 7.42-7.44 (s, 4H, CH). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 13.7 (d, J_{CP} = 11.5 Hz, CH_3), 19.6 (d, J_{CP} = 16.8 Hz, CH_3), 30.4 (d, J_{CP} = 16.9 Hz, CH_2), 45.0 (dd, J_{CP} = 44.8 Hz, J_{CP} = 8.9 Hz, CH), 47.4 (dd, J_{CP} = 54.1 Hz, J_{CP} = 2.2 Hz, CH_2), 49.8 (d, J_{CP} = 21.3 Hz, C), 56.3 (d, J_{CP} = 7.4 Hz, CH), 127.2 (s, CH), 127.6 (s, CH), 128.1 (s, CH), 128.3 (s, CH), 128.4 (s, CH), 128.5 (s, CH), 129.2 (s, CH), 129.5 (d, J_{CP} = 5.3 Hz, CH), 131.5 (s, CH), 131.7 (s, CH), 132.7 (d, J_{CP} = 34.3 Hz, C), 133.2 (d, J_{CP} = 21.4 Hz, C), 133.9 (s, CH), 134.2 (s, CH), 135.6 (d, J_{CP} = 13.8 Hz, C), 139.2 (d, J_{CP} = 12.5 Hz, C), 140.2 (d, J_{CP} = 5.5 Hz, C), 157.4 (d, J_{CP} = 15.3 Hz, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{33}P_2S$ 523.1173; Found 523.1174.

5b: white solid, m.p. 155.3-156.1 ℃. ethyl acetate/petroleum ether = 1:5, R_f = 0.20, 390 mg, 75%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -21.14 (d, J_{PP} = 30.0 Hz), 58.30 (d, J_{PP} = 30.0 Hz). **^1H NMR** ($CDCl_3$; 300 MHz): δ 0.89 (s, 3H, CH_3), 1.97-2.12 (m, 2H, CH_2), 2.20 (d, J = 2.3 Hz, 3H, CH_3), 2.67-2.33 (m, 1H, CH_2), 2.41-2.47 (m, 1H, CH), 2.79-2.82 (m, 1H, CH), 2.90-2.99 (m, 1H, CH_2), 6.85-6.90 (m, 2H, CH), 7.06-7.13 (m, 4H, CH), 7.20-7.22 (m, 7H, CH), 7.25-7.29 (m, 3H, CH), 7.69-7.78 (m, 2H, CH), 8.69-8.70 (m, 1H, CH). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 13.9 (d, J_{CP} = 11.1 Hz, CH_3), 19.2 (d, J_{CP} = 16.7 Hz, CH_3), 30.2 (d, J_{CP} = 16.7 Hz, CH_2), 45.0 (dd, J_{CP} = 45.2 Hz, J_{CP} = 9.2 Hz, CH), 47.1 (dd, J_{CP} = 54.8 Hz, J_{CP} = 2.1 Hz, CH_2), 50.2 (d, J_{CP} = 21.0 Hz, C), 56.1 (d, J_{CP} = 7.4 Hz, CH), 122.2 (s, CH), 125.0 (d, J_{CP} = 2.6 Hz, CH), 127.2 (s, CH), 128.0 (s, CH), 128.2 (s, J_{CP} = 13.6 Hz, CH), 128.3 (s, CH), 128.5 (s, CH), 129.1 (s, CH), 131.5 (s, CH), 131.8 (s, CH), 132.4 (s, C), 133.9 (s, CH), 134.2 (s, CH), 135.9 (d, J_{CP} = 13.9 Hz, C), 136.1 (s, CH), 139.2 (d, J_{CP} = 12.9 Hz, C),

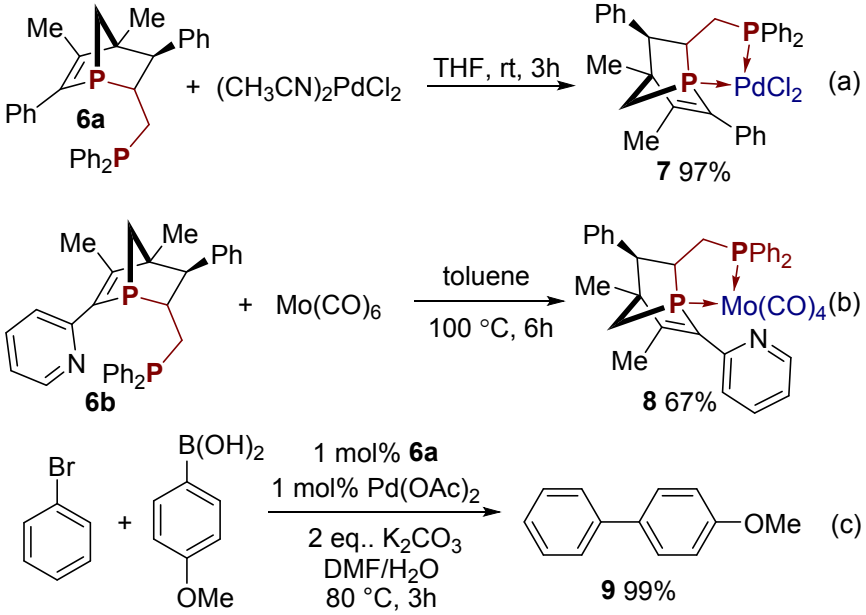
140.1 (d, J_{CP} = 5.6 Hz, C), 149.5 (s, CH), 152.6 (d, J_{CP} = 12.4 Hz, C), 162.0 (d, J_{CP} = 13.7 Hz, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{32}NP_2S$ 524.1725; Found 524.1727.

Raney nickel(~25 equiv) in a Schlenk tube was washed 3 times with EtOH, 3 times with THF[3]. A suspension of freshly prepared Raney nickel and **5** (0.2 mmol) in THF (5 mL) was stirred at room temperature until complete conversion observed by TLC analysis. The solution was filtered and the black solid was washed three times with THF and the crude product was quickly purified by column chromatography providing **6.** After desulfurisation was completed, the nickel waste was destroyed by addition of diluted HCl and subsequently concentrated HCl.

6a: white solid, m.p. 113.5-114.1 ℃. ethyl acetate/petroleum ether = 1:20, R_f = 0.38, 78 mg, 79%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -9.9 (d, J_{PP} = 30.1 Hz), -19.4 (d, J_{PP} = 31.2 Hz). **^1H NMR** ($CDCl_3$; 300 MHz): δ 0.88 (s, 3H, CH_3), 1.44-1.50 (m, H, CH_2), 1.76-1.83 (m, H, CH_2), 2.00 (s, 3H, CH_3), 2.13-2.20 (m, 1H, CH), 2.25-2.35 (m, 2H, CH_2), 2.38-2.43 (m, 1H, CH), 6.89-6.93 (m, 2H, CH), 7.08-7.13 (m, 4H, CH), 7.16-7.26 (m, 10H, CH), 7.35-7.46 (m, 4H, CH). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 12.5 (s, CH_3), 20.3 (s, CH_3), 34.7 (dd, J_{CP} = 14.6 Hz, J_{CP} = 6.3 Hz, CH_2), 44.8 (dd, J_{CP} = 4.5 Hz, J_{CP} = 2.4 Hz, CH_2), 45.5 (dd, J_{CP} = 16.0 Hz, J_{CP} = 9.7 Hz, CH), 56.5 (dd, J_{CP} = 7.4 Hz, J_{CP} = 3.6 Hz, CH), 64.7 (d, J_{CP} = 5.3 Hz, C), 126.2 (s, CH), 126.3 (s, CH), 128.1 (s, CH), 128.2 (d, J_{CP} = 19.7Hz, CH), 128.3 (s, CH), 128.5 (s, Ph, CH), 128.7 (dd, J_{CP} = 7.2 Hz, J_{CP} = 1.3 Hz, CH), 129.2 (s, CH), 132.0 (s, CH), 132.3 (s, CH), 133.2 (s, CH), 133.5 (s, CH), 138.3 (d, J_{CP} = 12.3 Hz, C), 138.5 (d, J_{CP} = 12.3 Hz, C), 139.5 (d, J_{CP} = 18.8 Hz, C), 139.6 (d, J_{CP} = 19.7 Hz, C), 140.0 (s, C), 155.5 (s, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{33}P_2$ 491.2052; Found 491.2051.

6b: white solid, m.p. 113.9-114.5 ℃. ethyl acetate/petroleum ether = 1:10, R_f = 0.35, 82 mg, 83%. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$; 121 MHz): δ -20.98 (d, J_{PP} = 32.1 Hz), -13.41 (d, J_{PP} = 31.7 Hz). **^1H NMR** ($CDCl_3$; 300 MHz): δ 0.90 (s, 3H, CH_3), 1.46-1.52 (m, 1H, CH_2), 1.76-1.84 (m, 1H, CH_2), 2.10-2.23 (m, 1H, CH_2), 2.17 (s, 3H, CH_3), 2.27-2.29 (m, 1H, CH_2), 2.33-2.42 (m, 2H, CH), 6.91-6.96 (m, 2H, CH), 7.08-7.13 (m, 5H, CH), 7.16-7.27 (m, 9H,CH), 7.52-7.54 (m, 1H, CH), 7.64-7.70 (m, 1H, CH),

8.64-8.65 (m, 1H, CH). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$; 75 MHz): δ 12.8 (s, CH_3), 20.1 (s, CH_3), 34.5 (dd, J_{CP} = 14.0 Hz, J_{CP} = 6.0 Hz, CH_2), 44.2 (dd, J_{CP} = 4.6 Hz, J_{CP} = 2.3 Hz, CH_2), 45.3 (dd, J_{CP} = 16.1 Hz, J_{CP} = 10.2 Hz, CH), 56.5 (dd, J_{CP} = 7.5 Hz, J_{CP} = 4.0 Hz, CH), 65.1 (d, J_{CP} = 5.5 Hz, C), 120.8 (s, CH), 123.6 (dd, J_{CP} = 7.7 Hz, J_{CP} = 2.0 Hz, CH), 126.4 (s, CH), 128.0 (s, CH), 128.1 (d, J_{CP} = 0.8 Hz, CH), 128.2 (s, CH), 128.3 (d, J_{CP} = 6.1 Hz, CH), 128.4 (s, CH), 129.3 (s, CH), 132.3 (d, J_{CP} = 17.5 Hz, CH), 133.3 (d, J_{CP} = 19.1 Hz, CH), 136.0 (s, CH), 138.6 (d, J_{CP} = 13.4 Hz, C), 138.7 (d, J_{CP} = 13.4 Hz, C), 139.5 (d, J_{CP} = 18.2 Hz, C), 142.9 (s, C), 149.2 (s, CH), 158.4 (d, J_{CP} = 20.6 Hz, C), 160.0 (d, J_{CP} = 1.8 Hz, C). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{32}NP_2$ 492.2004; Found 492.2001.



A 10 mL Schlenk tube containing a stirring bar was charged with **6a** (56 mg, 0.11 mmol), $Pd(CH_3CN)_2Cl_2$ (29 mg, 0.11 mmol), THF (3 mL) under nitrogen, sequentially. The resulting mixture was stirred at room temperature. After 3 h, ^{31}P NMR spectroscopy showed the total conversion of **6a** into complex **7**. After evaporation of the solvent, complex **7** was washed with hexanes (3×5 mL), and then dried under vacuum and recovered as a yellow solid. Yield: 70 mg (97%).

7: yellow solid, m.p. > 250 °C. **$^{31}P\{^1H\}$ NMR** ($(CD_3)_2SO$; 121 MHz): δ -58.3 (d, J_{PP} = 11.7 Hz), 85.7 (d, J_{PP} = 13.2 Hz). **^1H NMR** ($(CD_3)_2SO$; 300 MHz): δ 0.87 (s, 3H, CH_3), 1.38-1.52 (m, 1H, CH_2), 2.03 (s, 3H, CH_3), 2.33-2.39 (m, 1H, CH_2), 2.73-3.03 (m, 4H, CH, CH_2), 6.79-6.86 (m, 2H, Ph), 7.02-7.16 (m, 2H, CH), 7.24-7.33 (m, 7H,

CH), 7.46-7.58 (m, 5H, CH) , 7.71-7.73 (m, 2H, CH) , 7.86-7.93 (m, 2H, CH). **$^{13}C\{^{1}H\}$ NMR** ($(CD_3)_2SO$; 75 MHz): δ 13.5 (d, J_{CP} = 8.1 Hz, CH_3), 20.0 (d, J_{CP} = 13.2 Hz, CH_3), 30.2 (dd, J_{CP} = 34.1 Hz, J_{CP} = 10.4 Hz, CH_2), 44.6 (d, J_{CP} = 37.4 Hz, CH_2), 48.3 (dd, J_{CP} = 27.5 Hz, J_{CP} = 17.7 Hz, CH), 51.5 (d, J_{CP} = 20.3 Hz, CH), 64.5 (d, J_{CP} = 7.4 Hz, C), 127.4 (s, C), 127.6 (s, CH), 128.1 (s, C), 128.3 (s, CH), 128.7 (d, J_{CP} = 11.2 Hz, CH), 129.0 (s, CH), 129.2 (s, CH), 130.1 (s, C), 130.7 (d, J_{CP} = 4.6 Hz, CH), 131.6 (s, CH), 132.3 (s, CH), 132.8 (s, CH), 133.0 (s, CH), 134.0 (s, CH), 134.2 (s, CH), 135.5 (d, J_{CP} = 13.1 Hz, C), 140.6 (d, J_{CP} = 5.0 Hz, C), 162.1 (d, J_{CP} = 8.5 Hz, C). **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{32}Cl_2P_2PdNa$ 689.0283; Found 689.0282.

A 10 mL Schlenk tube containing a stirring bar was charged with **6b** (60 mg, 0.12 mmol), $Mo(CO)_6$ (31 mg, 0.12 mmol), toluene (2 mL) under nitrogen, sequentially. The resulting mixture was stirred at 100 ℃. After 3 h, ^{31}P NMR spectroscopy showed the total conversion of **6b** into complex **8**. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography providing **8.** Yield: 56 mg (67%).

8: yellow solid, m.p. 139.4-140.2 °C, ethyl acetate/petroleum ether = 1:5, R_f = 0.25. **$^{31}P\{^{1}H\}$ NMR** ($CDCl_3$; 121 MHz): δ 53.67 (d, J_{PP} = 14.5 Hz), 61.64 (d, J_{PP} = 14.5 Hz). **^{1}H NMR** ($CDCl_3$; 300 MHz): δ 0.98 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 1.96-2.00 (m, 1H, CH_2), 2.11-2.17 (m, 1H, CH_2), 2.31-2.43 (m, 1H, CH_2), 2.49-2.55 (m, 2H, CH), 2.84-2.89 (m, 1H, CH_2), 6.93-6.97 (m, 1H, CH), 7.12-7.15 (m, 1H, CH), 7.21-7.23 (m, 6H,CH), 7.30-7.39 (m, 8H, CH), 7.52-7.64 (m, 4H, CH). **$^{13}C\{^{1}H\}$ NMR** ($CDCl_3$; 75 MHz): δ 12.6 (d, J_{CP} = 5.0 Hz, CH_3), 19.9 (d, J_{CP} = 7.5 Hz, CH_3), 28.5 (dd, J_{CP} = 21.8 Hz, J_{CP} = 10.7 Hz, CH_2), 46.4 (d, J_{CP} = 24.0 Hz, CH_2), 54.1 (d, J_{CP} = 17.7 Hz, CH), 56.0 (dd, J_{CP} = 23.9 Hz, J_{CP} = 20.5 Hz, CH), 63.0 (s, C), 124.6 (s, CH), 127.2 (s, CH), 128.3 (s, CH), 128.4 (s, CH), 128.5 (s, CH), 128.9 (s, CH), 129.0 (s, CH), 130.4 (s, CH), 130.6 (s, CH), 132.5 (s, CH), 132.6 (s, CH), 136.1 (s, CH), 136.7 (d, J_{CP} = 19.1 Hz, C), 137.3 (d, J_{CP} = 32.8 Hz, C), 138.8 (d, J_{CP} = 29.7 Hz, C), 141.1 (d, J_{CP} = 3.8 Hz, C), 148.9 (s, CH), 155.6 (d, J_{CP} = 14.0 Hz, C), 160.2 (s, C), 208.5 (t, J_{CP} = 8.2 Hz, CO); 209.4 (t, J_{CP} = 8.7 Hz, CO) 217.1 (dd, J_{CP} = 28.0 Hz, J_{CP} = 8.6 Hz,

CO), 217.8 (dd, J_{CP} = 25.8 Hz, J_{CP} = 8.8 Hz, CO). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{32}MoNO_4P_2$ 702.0855; Found 702.0852.

A mixture of bromobenzene (1 mmol, 105 μL), 4-Methoxyphenylboronic acid (1 mmol, 182 mg), $Pd(OAC)_2$ (0.01 mmol, 2.24 mg), 6a (0.01 mmol, 4.9 mg), K_2CO_3 (2 mmol, 276 mg), distilled water (2.5 mL) and DMF (2.5 mL) was stirred at 80 °C in oil bath for 3 h under nitrogen. Ethyl acetate (10 mL) was then added to the reaction solution. The solution were washed 3 times with water. The organic phase was dried with $MgSO_4$. After filtration, the solution was evaporated to dryness. The crude product was purified by column chromatography providing **9**.

9[4]: white solid. dichloromethane/petroleum ether = 1:8, R_f = 0.35. 183 mg, 99%. **^{1}H NMR** ($CDCl_3$; 300 MHz): δ 3.82 (s, 3H, OCH_3), 6.96 (d, J_{CP} = 8.7 Hz, 2H), 7.28 (t, J_{CP} = 7.3 Hz, 1H), 7.40 (t, J_{CP} = 7.3 Hz, 2H), 7.50-7.55 (m, 4H). **^{13}C{^{1}H} NMR** ($CDCl_3$; 75 MHz): δ 55.4 (s, OCH_3), 114.2 (s, CH), 126.7 (s, CH), 126.8 (s, CH), 128.2 (s, CH), 128.8 (s, CH), 133.8 (s, C), 140.9 (s, C), 159.2 (s, C).

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X-ray crystallographic studies of compound 4a

Crystal Structure of Compound *exo*-4a

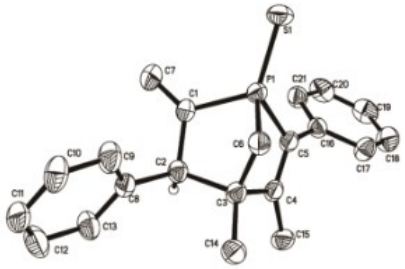


Table 1 Crystal data and structure refinement for *exo*-4a.

Identification code	***exo*-4a**
Empirical formula	$C_{21}H_{21}PS$
Formula weight	336.41
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.5968(3)
b/Å	10.8680(5)
c/Å	19.5365(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1825.30(13)
Z	4
ρ_{calc}g/cm^3	1.224
μ/mm^{-1}	2.356
F(000)	712.0
Crystal size/mm^3	0.15 × 0.12 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.054 to 141.77
Index ranges	$-10 \le h \le 10$, $-13 \le k \le 13$, $-13 \le l \le 23$
Reflections collected	7505
Independent reflections	3456 [R_{int} = 0.0323, R_{sigma} = 0.0405]
Data/restraints/parameters	3456/0/210
Goodness-of-fit on F^2	1.024

Final R indexes [I>=2σ (I)]	R_1 = 0.0434, wR_2 = 0.1104
Final R indexes [all data]	R_1 = 0.0500, wR_2 = 0.1165
Largest diff. peak/hole / e Å^{-3}	0.29/-0.25
Flack parameter	-0.018(15)

Table 2 Bond Lengths for *exo*-4a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	P1	1.9378(14)	C5	C16	1.469(5)
P1	C1	1.827(3)	C8	C9	1.386(6)
P1	C5	1.823(4)	C8	C13	1.369(6)
P1	C6	1.816(4)	C9	C10	1.382(6)
C1	C2	1.527(5)	C10	C11	1.351(8)
C1	C7	1.295(6)	C11	C12	1.365(8)
C2	C3	1.593(5)	C12	C13	1.390(6)
C2	C8	1.520(5)	C16	C17	1.389(6)
C3	C4	1.541(5)	C16	C21	1.379(6)
C3	C6	1.545(5)	C17	C18	1.387(6)
C3	C14	1.514(5)	C18	C19	1.361(7)
C4	C5	1.336(5)	C19	C20	1.376(8)
C4	C15	1.497(6)	C20	C21	1.395(6)

Table 3 Bond Angles for *exo*-4a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	P1	S1	120.14(14)	C4	C5	P1	105.8(3)
C5	P1	S1	121.54(13)	C4	C5	C16	128.1(3)
C5	P1	C1	98.89(17)	C16	C5	P1	125.8(3)
C6	P1	S1	125.99(14)	C3	C6	P1	94.9(2)
C6	P1	C1	91.25(17)	C9	C8	C2	122.8(4)
C6	P1	C5	91.29(18)	C13	C8	C2	119.8(4)
C2	C1	P1	106.4(2)	C13	C8	C9	117.4(4)
C7	C1	P1	125.0(4)	C10	C9	C8	120.9(5)
C7	C1	C2	128.6(4)	C11	C10	C9	121.2(5)
C1	C2	C3	105.6(3)	C10	C11	C12	118.7(4)
C8	C2	C1	113.8(3)	C11	C12	C13	120.8(5)
C8	C2	C3	115.1(3)	C8	C13	C12	120.9(5)
C4	C3	C2	104.9(3)	C17	C16	C5	119.5(3)
C4	C3	C6	103.9(3)	C21	C16	C5	122.4(3)
C6	C3	C2	105.4(3)	C21	C16	C17	118.1(4)
C14	C3	C2	113.7(3)	C18	C17	C16	120.9(4)
C14	C3	C4	114.4(3)	C19	C18	C17	120.5(5)

C14	C3	C6	113.4(3)	C18	C19	C20	119.6(4)
C5	C4	C3	114.0(3)	C19	C20	C21	120.1(5)
C5	C4	C15	125.5(3)	C16	C21	C20	120.7(4)
C15	C4	C3	120.1(3)				

Table 4 Torsion Angles for *exo*-4a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	P1	C1	C2	-166.18(19)	C5	P1	C6	C3	-47.1(2)
S1	P1	C1	C7	13.5(5)	C5	C16	C17	C18	176.3(4)
S1	P1	C5	C4	165.7(2)	C5	C16	C21	C20	-174.9(4)
S1	P1	C5	C16	-20.6(4)	C6	P1	C1	C2	-32.4(3)
S1	P1	C6	C3	-178.66(15)	C6	P1	C1	C7	147.3(4)
P1	C1	C2	C3	1.2(3)	C6	P1	C5	C4	31.0(3)
P1	C1	C2	C8	128.4(3)	C6	P1	C5	C16	-155.3(3)
P1	C5	C16	C17	130.4(4)	C6	C3	C4	C5	-34.9(4)
P1	C5	C16	C21	-52.1(5)	C6	C3	C4	C15	152.2(4)
C1	P1	C5	C4	-60.5(3)	C7	C1	C2	C3	-178.4(5)
C1	P1	C5	C16	113.2(3)	C7	C1	C2	C8	-51.2(6)
C1	P1	C6	C3	51.8(2)	C8	C2	C3	C4	162.6(3)
C1	C2	C3	C4	-71.0(3)	C8	C2	C3	C6	-88.0(4)
C1	C2	C3	C6	38.4(4)	C8	C2	C3	C14	36.8(5)
C1	C2	C3	C14	163.3(3)	C8	C9	C10	C11	-3.3(9)
C1	C2	C8	C9	-50.9(5)	C9	C8	C13	C12	-0.9(8)
C1	C2	C8	C13	129.3(4)	C9	C10	C11	C12	1.4(9)
C2	C3	C4	C5	75.5(4)	C10	C11	C12	C13	0.7(10)
C2	C3	C4	C15	-97.4(4)	C11	C12	C13	C8	-0.9(10)
C2	C3	C6	P1	-58.6(3)	C13	C8	C9	C10	2.9(7)
C2	C8	C9	C10	-176.9(5)	C14	C3	C4	C5	-159.2(4)
C2	C8	C13	C12	178.9(5)	C14	C3	C4	C15	27.9(5)
C3	C2	C8	C9	71.2(5)	C14	C3	C6	P1	176.3(3)
C3	C2	C8	C13	-108.6(4)	C15	C4	C5	P1	170.5(3)
C3	C4	C5	P1	-1.9(4)	C15	C4	C5	C16	-3.0(6)
C3	C4	C5	C16	-175.4(3)	C16	C17	C18	C19	-1.3(8)
C4	C3	C6	P1	51.5(3)	C17	C16	C21	C20	2.7(7)
C4	C5	C16	C17	-57.4(6)	C17	C18	C19	C20	2.5(8)
C4	C5	C16	C21	120.1(5)	C18	C19	C20	C21	-1.1(8)
C5	P1	C1	C2	59.1(3)	C19	C20	C21	C16	-1.5(8)
C5	P1	C1	C7	-121.2(4)	C21	C16	C17	C18	-1.3(7)

X-ray crystallographic studies of compound 6b

Crystal Structure of Compound 6b

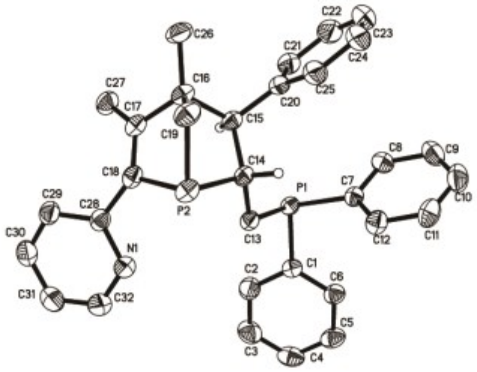


Table 5 Crystal data and structure refinement for 6b

Identification code	202008152
Empirical formula	$C_{32}H_{31}NP_2$
Formula weight	491.52
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.9742(2)
b/Å	10.3221(2)
c/Å	21.5772(4)
α/°	90
β/°	97.4710(19)
γ/°	90
Volume/Å^3	2644.31(9)
Z	4
ρ_{calc}g/cm^3	1.235
μ/mm^{-1}	1.638
F(000)	1040.0
Crystal size/mm^3	0.16 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.034 to 134.136
Index ranges	$-14 \le h \le 12$, $-7 \le k \le 12$, $-23 \le l \le 25$
Reflections collected	9907
Independent reflections	4727 [R_{int} = 0.0319, R_{sigma} = 0.0441]
Data/restraints/parameters	4727/0/318
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0447, wR_2 = 0.1095
Final R indexes [all data]	R_1 = 0.0620, wR_2 = 0.1238

Largest diff. peak/hole / e Å^{-3} 0.32/-0.18

Table 6 Bond Lengths for 6a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.386(4)	C16	C17	1.527(3)
C1	C6	1.382(3)	C16	C19	1.537(3)
C1	P1	1.843(2)	C16	C26	1.528(3)
C2	C3	1.384(4)	C17	C18	1.358(3)
C3	C4	1.368(4)	C17	C27	1.497(3)
C4	C5	1.369(4)	C18	C28	1.464(3)
C5	C6	1.385(4)	C18	P2	1.848(2)
C7	C8	1.391(3)	C19	P2	1.848(3)
C7	C12	1.388(3)	C20	C21	1.378(4)
C7	P1	1.835(2)	C20	C25	1.388(4)
C8	C9	1.392(4)	C21	C22	1.387(4)
C9	C10	1.374(5)	C22	C23	1.371(5)
C10	C11	1.368(4)	C23	C24	1.363(5)
C11	C12	1.378(4)	C24	C25	1.381(4)
C13	C14	1.527(3)	C28	C29	1.396(3)
C13	P1	1.861(2)	C28	N1	1.345(3)
C14	C15	1.559(3)	C29	C30	1.374(4)
C14	P2	1.890(2)	C30	C31	1.370(4)
C15	C16	1.594(3)	C31	C32	1.367(4)
C15	C20	1.511(3)	C32	N1	1.334(4)

Table 7 Bond Angles for 6a

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	P1	118.36(19)	C18	C17	C16	111.9(2)
C6	C1	C2	117.7(2)	C18	C17	C27	127.8(2)
C6	C1	P1	123.88(19)	C27	C17	C16	119.6(2)
C3	C2	C1	121.1(3)	C17	C18	C28	128.2(2)
C4	C3	C2	120.5(3)	C17	C18	P2	110.18(19)
C3	C4	C5	119.2(3)	C28	C18	P2	120.90(17)
C4	C5	C6	120.7(3)	C16	C19	P2	99.13(15)
C1	C6	C5	120.9(3)	C21	C20	C15	120.0(2)
C8	C7	P1	116.68(18)	C21	C20	C25	117.5(3)
C12	C7	C8	118.9(2)	C25	C20	C15	122.5(2)
C12	C7	P1	124.44(19)	C20	C21	C22	121.1(3)
C7	C8	C9	119.7(3)	C23	C22	C21	120.2(3)

C10	C9	C8	120.5(3)	C24	C23	C22	119.8(3)
C11	C10	C9	119.8(3)	C23	C24	C25	120.0(3)
C10	C11	C12	120.5(3)	C24	C25	C20	121.5(3)
C11	C12	C7	120.6(3)	C29	C28	C18	123.9(2)
C14	C13	P1	115.90(16)	N1	C28	C18	114.6(2)
C13	C14	C15	116.25(18)	N1	C28	C29	121.4(2)
C13	C14	P2	111.74(15)	C30	C29	C28	119.0(3)
C15	C14	P2	106.91(14)	C31	C30	C29	119.7(3)
C14	C15	C16	106.50(18)	C32	C31	C30	117.6(3)
C20	C15	C14	114.03(18)	N1	C32	C31	124.8(3)
C20	C15	C16	114.17(19)	C32	N1	C28	117.3(2)
C17	C16	C15	103.06(18)	C1	P1	C13	97.19(10)
C17	C16	C19	104.1(2)	C7	P1	C1	103.02(10)
C17	C16	C26	115.2(2)	C7	P1	C13	104.36(10)
C19	C16	C15	105.47(19)	C18	P2	C14	95.76(10)
C26	C16	C15	113.9(2)	C18	P2	C19	87.72(12)
C26	C16	C19	113.9(2)	C19	P2	C14	87.28(11)

Table 8 Torsion Angles for 6a.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
C1	C2	C3	C4	-1.2(5)	C16	C19	P2	C18	-43.49(17)
C2	C1	C6	C5	-1.3(4)	C17	C16	C19	P2	51.20(19)
C2	C1	P1	C7	171.3(2)	C17	C18	C28	C29	-39.0(4)
C2	C1	P1	C13	64.7(2)	C17	C18	C28	N1	139.7(3)
C2	C3	C4	C5	-0.1(5)	C17	C18	P2	C14	-60.89(18)
C3	C4	C5	C6	0.7(5)	C17	C18	P2	C19	26.14(19)
C4	C5	C6	C1	0.0(4)	C18	C28	C29	C30	173.8(2)
C6	C1	C2	C3	1.9(4)	C18	C28	N1	C32	-174.7(2)
C6	C1	P1	C7	-12.3(2)	C19	C16	C17	C18	-35.7(3)
C6	C1	P1	C13	-118.9(2)	C19	C16	C17	C27	153.7(2)
C7	C8	C9	C10	-0.2(4)	C20	C15	C16	C17	156.4(2)
C8	C7	C12	C11	-0.8(4)	C20	C15	C16	C19	-94.7(2)
C8	C7	P1	C1	111.59(19)	C20	C15	C16	C26	30.9(3)
C8	C7	P1	C13	-147.35(18)	C20	C21	C22	C23	-1.2(5)
C8	C9	C10	C11	-0.8(5)	C21	C20	C25	C24	1.5(4)
C9	C10	C11	C12	0.9(5)	C21	C22	C23	C24	2.5(6)
C10	C11	C12	C7	-0.1(4)	C22	C23	C24	C25	-1.8(6)
C12	C7	C8	C9	1.0(4)	C23	C24	C25	C20	-0.3(5)
C12	C7	P1	C1	-68.8(2)	C25	C20	C21	C22	-0.8(4)

C12	C7	P1	C13	32.3(2)	C26	C16	C17	C18	-161.2(2)
C13	C14	C15	C16	132.6(2)	C26	C16	C17	C27	28.3(3)
C13	C14	C15	C20	-100.6(2)	C26	C16	C19	P2	177.47(19)
C13	C14	P2	C18	-75.74(17)	C27	C17	C18	C28	1.1(4)
C13	C14	P2	C19	-163.17(17)	C27	C17	C18	P2	171.1(2)
C14	C13	P1	C1	169.46(17)	C28	C18	P2	C14	109.93(19)
C14	C13	P1	C7	63.99(18)	C28	C18	P2	C19	-163.0(2)
C14	C15	C16	C17	-76.9(2)	C28	C29	C30	C31	2.3(4)
C14	C15	C16	C19	32.0(2)	C29	C28	N1	C32	4.0(4)
C14	C15	C16	C26	157.6(2)	C29	C30	C31	C32	0.9(4)
C14	C15	C20	C21	130.6(2)	C30	C31	C32	N1	-1.8(5)
C14	C15	C20	C25	-50.2(3)	C31	C32	N1	C28	-0.6(5)
C15	C14	P2	C18	52.50(16)	N1	C28	C29	C30	-4.9(4)
C15	C14	P2	C19	-34.93(16)	P1	C1	C2	C3	178.5(2)
C15	C16	C17	C18	74.2(2)	P1	C1	C6	C5	-177.7(2)
C15	C16	C17	C27	-96.4(2)	P1	C7	C8	C9	-179.4(2)
C15	C16	C19	P2	-56.9(2)	P1	C7	C12	C11	179.5(2)
C15	C20	C21	C22	178.5(2)	P1	C13	C14	C15	47.0(2)
C15	C20	C25	C24	-177.7(3)	P1	C13	C14	P2	170.07(11)
C16	C15	C20	C21	-106.7(3)	P2	C14	C15	C16	7.0(2)
C16	C15	C20	C25	72.5(3)	P2	C14	C15	C20	133.84(17)
C16	C17	C18	C28	-168.5(2)	P2	C18	C28	C29	152.0(2)
C16	C17	C18	P2	1.4(2)	P2	C18	C28	N1	-29.3(3)
C16	C19	P2	C14	52.39(17)					

X-ray crystallographic studies of compound 7

Crystal Structure of Compound 7

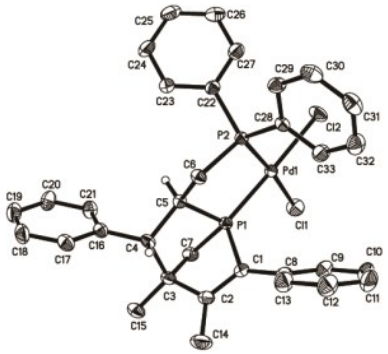


Table 9 Crystal data and structure refinement for 7.

Identification code	202008137
Empirical formula	$C_{33}H_{32}Cl_2P_2Pd$
Formula weight	667.82
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.55252(15)
b/Å	13.96012(19)
c/Å	18.4085(2)
α/°	90
β/°	94.0277(11)
γ/°	90
Volume/Å^3	2961.49(6)
Z	4
ρ_{calc}g/cm^3	1.498
μ/mm^{-1}	7.892
F(000)	1360.0
Crystal size/mm^3	0.11 × 0.1 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.956 to 134.14
Index ranges	$-13 \le h \le 13$, $-16 \le k \le 16$, $-21 \le l \le 14$
Reflections collected	11646
Independent reflections	5279 [R_{int} = 0.0495, R_{sigma} = 0.0555]
Data/restraints/parameters	5279/0/345
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0502, wR_2 = 0.1284
Final R indexes [all data]	R_1 = 0.0564, wR_2 = 0.1359
Largest diff. peak/hole / e Å^{-3}	1.28/-1.17

Table 10 Bond Lengths for 7.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.353(6)	C17	C18	1.378(7)
C1	C8	1.483(6)	C18	C19	1.373(8)
C1	P1	1.813(4)	C19	C20	1.394(8)
C2	C3	1.530(6)	C20	C21	1.388(7)
C2	C14	1.499(7)	C22	C23	1.392(6)
C3	C4	1.608(6)	C22	C27	1.382(7)
C3	C7	1.554(6)	C22	P2	1.819(4)
C3	C15	1.523(6)	C23	C24	1.372(8)
C4	C5	1.549(5)	C24	C25	1.376(9)
C4	C16	1.517(6)	C25	C26	1.378(9)
C5	C6	1.523(5)	C26	C27	1.383(7)
C5	P1	1.836(4)	C28	C29	1.381(6)
C6	P2	1.854(4)	C28	C33	1.383(6)
C7	P1	1.814(5)	C28	P2	1.811(4)
C8	C9	1.380(7)	C29	C30	1.404(7)
C8	C13	1.393(7)	C30	C31	1.371(8)
C9	C10	1.386(8)	C31	C32	1.377(8)
C10	C11	1.371(9)	C32	C33	1.384(7)
C11	C12	1.357(9)	Cl1	Pd1	2.3534(11)
C12	C13	1.399(8)	Cl2	Pd1	2.3477(11)
C16	C17	1.390(6)	P1	Pd1	2.1996(10)
C16	C21	1.381(6)	P2	Pd1	2.2622(10)

Table 11 Bond Angles for 7

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C8	128.9(4)	C16	C21	C20	122.0(5)
C2	C1	P1	106.1(3)	C23	C22	P2	121.6(4)
C8	C1	P1	124.3(3)	C27	C22	C23	118.4(4)
C1	C2	C3	113.0(4)	C27	C22	P2	120.0(3)
C1	C2	C14	125.8(4)	C24	C23	C22	120.5(5)
C14	C2	C3	120.8(4)	C23	C24	C25	120.7(5)
C2	C3	C4	103.2(3)	C24	C25	C26	119.5(5)
C2	C3	C7	104.2(4)	C25	C26	C27	119.9(5)

C7	C3	C4	107.1(3)	C22	C27	C26	121.0(5)
C15	C3	C2	115.0(4)	C29	C28	C33	119.8(4)
C15	C3	C4	114.2(4)	C29	C28	P2	121.8(3)
C15	C3	C7	112.2(4)	C33	C28	P2	118.4(3)
C5	C4	C3	105.4(3)	C28	C29	C30	120.2(4)
C16	C4	C3	114.3(3)	C31	C30	C29	119.4(5)
C16	C4	C5	114.0(3)	C30	C31	C32	120.3(5)
C4	C5	P1	105.0(3)	C31	C32	C33	120.6(5)
C6	C5	C4	120.6(3)	C28	C33	C32	119.7(5)
C6	C5	P1	106.9(3)	C1	P1	C5	100.41(19)
C5	C6	P2	106.8(3)	C1	P1	C7	92.1(2)
C3	C7	P1	94.3(3)	C1	P1	Pd1	119.54(15)
C9	C8	C1	121.0(5)	C5	P1	Pd1	107.70(13)
C9	C8	C13	118.7(5)	C7	P1	C5	91.2(2)
C13	C8	C1	120.2(4)	C7	P1	Pd1	138.01(15)
C8	C9	C10	120.4(5)	C6	P2	Pd1	108.91(14)
C11	C10	C9	120.5(5)	C22	P2	C6	106.16(19)
C12	C11	C10	120.2(5)	C22	P2	Pd1	113.75(14)
C11	C12	C13	120.3(6)	C28	P2	C6	106.16(19)
C8	C13	C12	120.0(5)	C28	P2	C22	107.15(19)
C17	C16	C4	119.0(4)	C28	P2	Pd1	114.16(13)
C21	C16	C4	123.0(4)	Cl2	Pd1	Cl1	95.89(4)
C21	C16	C17	118.0(4)	P1	Pd1	Cl1	89.53(4)
C18	C17	C16	120.6(5)	P1	Pd1	Cl2	174.23(4)
C19	C18	C17	121.2(5)	P1	Pd1	P2	84.88(4)
C18	C19	C20	119.3(4)	P2	Pd1	Cl1	174.37(4)
C21	C20	C19	119.0(5)	P2	Pd1	Cl2	89.67(4)

Table 12 Torsion Angles for 7

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
C1	C2	C3	C4	-73.8(5)	C14	C2	C3	C4	98.9(5)
C1	C2	C3	C7	38.0(5)	C14	C2	C3	C7	-149.3(5)
C1	C2	C3	C15	161.2(4)	C14	C2	C3	C15	-26.1(7)
C1	C8	C9	C10	179.9(5)	C15	C3	C4	C5	-156.4(4)
C1	C8	C13	C12	-179.2(5)	C15	C3	C4	C16	-30.3(5)
C2	C1	C8	C9	131.7(6)	C15	C3	C7	P1	-177.5(3)
C2	C1	C8	C13	-50.3(7)	C16	C4	C5	C6	104.0(4)
C2	C1	P1	C5	62.8(4)	C16	C4	C5	P1	-135.5(3)
C2	C1	P1	C7	-28.8(4)	C16	C17	C18	C19	-1.2(8)

C2	C1	P1	Pd1	-179.9(3)	C17	C16	C21	C20	-0.2(7)
C2	C3	C4	C5	78.1(4)	C17	C18	C19	C20	0.7(9)
C2	C3	C4	C16	-155.8(3)	C18	C19	C20	C21	0.1(8)
C2	C3	C7	P1	-52.6(3)	C19	C20	C21	C16	-0.4(8)
C3	C4	C5	C6	-129.7(4)	C21	C16	C17	C18	1.0(7)
C3	C4	C5	P1	-9.3(3)	C22	C23	C24	C25	-1.7(10)
C3	C4	C16	C17	109.7(4)	C23	C22	C27	C26	-0.3(8)
C3	C4	C16	C21	-70.2(5)	C23	C22	P2	C6	-13.1(5)
C3	C7	P1	C1	46.3(3)	C23	C22	P2	C28	-126.2(4)
C3	C7	P1	C5	-54.1(3)	C23	C22	P2	Pd1	106.7(4)
C3	C7	P1	Pd1	-172.64(17)	C23	C24	C25	C26	2.4(10)
C4	C3	C7	P1	56.4(3)	C24	C25	C26	C27	-2.0(9)
C4	C5	C6	P2	170.9(3)	C25	C26	C27	C22	1.0(8)
C4	C5	P1	C1	-53.3(3)	C27	C22	C23	C24	0.6(9)
C4	C5	P1	C7	39.0(3)	C27	C22	P2	C6	168.8(4)
C4	C5	P1	Pd1	-179.1(2)	C27	C22	P2	C28	55.6(4)
C4	C16	C17	C18	-178.9(4)	C27	C22	P2	Pd1	-71.5(4)
C4	C16	C21	C20	179.7(5)	C28	C29	C30	C31	1.2(8)
C5	C4	C16	C17	-128.9(4)	C29	C28	C33	C32	1.1(7)
C5	C4	C16	C21	51.3(6)	C29	C28	P2	C6	-89.8(4)
C5	C6	P2	C22	89.5(3)	C29	C28	P2	C22	23.3(4)
C5	C6	P2	C28	-156.7(3)	C29	C28	P2	Pd1	150.2(3)
C5	C6	P2	Pd1	-33.4(3)	C29	C30	C31	C32	-1.7(8)
C6	C5	P1	C1	75.8(3)	C30	C31	C32	C33	1.8(8)
C6	C5	P1	C7	168.1(3)	C31	C32	C33	C28	-1.5(8)
C6	C5	P1	Pd1	-50.0(3)	C33	C28	C29	C30	-0.9(7)
C7	C3	C4	C5	-31.5(4)	C33	C28	P2	C6	89.3(4)
C7	C3	C4	C16	94.6(4)	C33	C28	P2	C22	-157.6(3)
C8	C1	C2	C3	169.5(4)	C33	C28	P2	Pd1	-30.7(4)
C8	C1	C2	C14	-2.8(9)	P1	C1	C2	C3	-1.4(5)
C8	C1	P1	C5	-108.6(4)	P1	C1	C2	C14	-173.7(5)
C8	C1	P1	C7	159.8(4)	P1	C1	C8	C9	-59.0(6)
C8	C1	P1	Pd1	8.7(4)	P1	C1	C8	C13	119.1(5)
C8	C9	C10	C11	-1.2(9)	P1	C5	C6	P2	51.4(3)
C9	C8	C13	C12	-1.2(8)	P2	C22	C23	C24	-177.6(5)
C9	C10	C11	C12	-0.2(10)	P2	C22	C27	C26	178.0(4)
C10	C11	C12	C13	0.9(10)	P2	C28	C29	C30	178.1(4)
C11	C12	C13	C8	-0.2(10)	P2	C28	C33	C32	-178.0(4)
C13	C8	C9	C10	1.8(8)					

X-ray crystallographic studies of compound 8

Crystal Structure of Compound 8

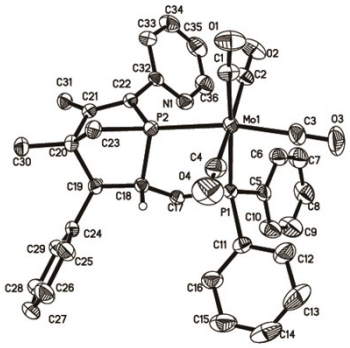


Table 13Crystal data and structure refinement for 8

Identification code	202009166
Empirical formula	$C_{36}H_{31}MoNO_4P_2$
Formula weight	699.50
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	13.3804(4)
b/Å	15.4864(5)
c/Å	16.7675(6)
α/°	105.320(3)
β/°	91.827(3)
γ/°	92.381(3)
Volume/Å^3	3344.8(2)
Z	4
ρ_{calc}g/cm^3	1.389
μ/mm^{-1}	4.425
F(000)	1432.0
Crystal size/mm^3	0.15 × 0.12 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.618 to 134.16
Index ranges	-11 ≤ h ≤ 15, -18 ≤ k ≤ 18, -20 ≤ l ≤ 19
Reflections collected	25314
Independent reflections	11932 [R_{int} = 0.0357, R_{sigma} = 0.0481]
Data/restraints/parameters	11932/0/797
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0371, wR_2 = 0.0894
Final R indexes [all data]	R_1 = 0.0483, wR_2 = 0.0977

Largest diff. peak/hole / e Å^{-3}	0.42/-0.51

Table 14 Bond Lengths for 8

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	Mo1	1.993(3)	C1'	Mo1'	1.986(3)
C1	O1	1.144(4)	C1'	O1'	1.142(4)
C2	Mo1	2.057(4)	C2'	Mo1'	2.051(4)
C2	O2	1.128(5)	C2'	O2'	1.131(4)
C3	Mo1	1.975(4)	C3'	Mo1'	1.995(4)
C3	O3	1.148(5)	C3'	O3'	1.141(5)
C4	Mo1	2.022(4)	C4'	Mo1'	2.029(3)
C4	O4	1.136(5)	C4'	O4'	1.127(4)
C5	C6	1.377(5)	C5'	C6'	1.373(5)
C5	C10	1.392(5)	C5'	C10'	1.382(5)
C5	P1	1.825(3)	C5'	P1'	1.833(3)
C6	C7	1.377(6)	C6'	C7'	1.380(6)
C7	C8	1.368(7)	C7'	C8'	1.363(7)
C8	C9	1.351(7)	C8'	C9'	1.363(6)
C9	C10	1.381(6)	C9'	C10'	1.382(5)
C11	C12	1.382(6)	C11'	C12'	1.391(5)
C11	C16	1.388(5)	C11'	C16'	1.378(4)
C11	P1	1.823(3)	C11'	P1'	1.838(3)
C12	C13	1.401(7)	C12'	C13'	1.373(6)
C13	C14	1.362(8)	C13'	C14'	1.359(7)
C14	C15	1.370(8)	C14'	C15'	1.370(6)
C15	C16	1.380(6)	C15'	C16'	1.388(5)
C17	C18	1.517(4)	C17'	C18'	1.518(4)
C17	P1	1.846(3)	C17'	P1'	1.853(3)
C18	C19	1.542(4)	C18'	C19'	1.546(4)
C18	P2	1.863(3)	C18'	P2'	1.862(3)
C19	C20	1.609(4)	C19'	C20'	1.610(4)
C19	C24	1.509(4)	C19'	C24'	1.518(4)
C20	C21	1.535(4)	C20'	C21'	1.528(4)
C20	C23	1.544(4)	C20'	C23'	1.547(4)
C20	C30	1.517(4)	C20'	C30'	1.524(4)
C21	C22	1.345(4)	C21'	C22'	1.342(5)
C21	C31	1.498(4)	C21'	C31'	1.503(4)
C22	C32	1.476(4)	C22'	C32'	1.473(4)
C22	P2	1.832(3)	C22'	P2'	1.831(3)

C23	P2	1.834(3)	C23'	P2'	1.840(3)
C24	C25	1.389(5)	C24'	C25'	1.387(5)
C24	C29	1.386(5)	C24'	C29'	1.389(5)
C25	C26	1.395(5)	C25'	C26'	1.384(5)
C26	C27	1.368(7)	C26'	C27'	1.381(6)
C27	C28	1.365(7)	C27'	C28'	1.363(6)
C28	C29	1.396(5)	C28'	C29'	1.386(5)
C32	C33	1.391(5)	C32'	C33'	1.385(5)
C32	N1	1.333(4)	C32'	N1'	1.339(5)
C33	C34	1.391(6)	C33'	C34'	1.389(6)
C34	C35	1.347(7)	C34'	C35'	1.368(7)
C35	C36	1.372(6)	C35'	C36'	1.379(6)
C36	N1	1.340(5)	C36'	N1'	1.332(5)
Mo1	P1	2.5448(8)	Mo1'	P1'	2.5387(8)
Mo1	P2	2.4923(8)	Mo1'	P2'	2.4877(8)

Table 15 Bond Angles for 8

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O1	C1	Mo1	175.7(4)	O1'	C1'	Mo1'	175.9(3)
O2	C2	Mo1	173.2(3)	O2'	C2'	Mo1'	172.4(3)
O3	C3	Mo1	177.2(5)	O3'	C3'	Mo1'	174.9(4)
O4	C4	Mo1	175.0(4)	O4'	C4'	Mo1'	174.6(3)
C6	C5	C10	117.7(4)	C6'	C5'	C10'	118.5(3)
C6	C5	P1	119.9(3)	C6'	C5'	P1'	119.9(3)
C10	C5	P1	122.2(3)	C10'	C5'	P1'	121.6(3)
C5	C6	C7	120.8(4)	C5'	C6'	C7'	120.1(4)
C8	C7	C6	121.0(4)	C8'	C7'	C6'	121.2(4)
C9	C8	C7	118.8(4)	C9'	C8'	C7'	119.1(4)
C8	C9	C10	121.4(4)	C8'	C9'	C10'	120.4(4)
C9	C10	C5	120.3(4)	C9'	C10'	C5'	120.6(4)
C12	C11	C16	117.4(4)	C12'	C11'	P1'	121.5(3)
C12	C11	P1	118.9(3)	C16'	C11'	C12'	117.9(3)
C16	C11	P1	123.7(3)	C16'	C11'	P1'	120.6(3)
C11	C12	C13	120.7(5)	C13'	C12'	C11'	120.3(4)
C14	C13	C12	120.5(5)	C14'	C13'	C12'	121.3(4)
C13	C14	C15	119.4(5)	C13'	C14'	C15'	119.5(4)
C14	C15	C16	120.4(5)	C14'	C15'	C16'	119.8(4)
C15	C16	C11	121.5(5)	C11'	C16'	C15'	121.2(3)
C18	C17	P1	108.9(2)	C18'	C17'	P1'	109.9(2)
C17	C18	C19	117.1(2)	C17'	C18'	C19'	117.4(2)
C17	C18	P2	110.0(2)	C17'	C18'	P2'	111.3(2)

C19	C18	P2	106.6(2)	C19'	C18'	P2'	106.41(19)
C18	C19	C20	105.4(2)	C18'	C19'	C20'	105.5(2)
C24	C19	C18	113.6(2)	C24'	C19'	C18'	113.4(2)
C24	C19	C20	117.2(3)	C24'	C19'	C20'	116.9(2)
C21	C20	C19	100.7(2)	C21'	C20'	C19'	101.2(2)
C21	C20	C23	103.5(3)	C21'	C20'	C23'	103.8(2)
C23	C20	C19	107.0(2)	C23'	C20'	C19'	106.8(2)
C30	C20	C19	114.3(3)	C30'	C20'	C19'	113.7(3)
C30	C20	C21	115.4(3)	C30'	C20'	C21'	116.5(3)
C30	C20	C23	114.5(3)	C30'	C20'	C23'	113.6(3)
C22	C21	C20	112.8(3)	C22'	C21'	C20'	112.7(3)
C22	C21	C31	126.2(3)	C22'	C21'	C31'	126.8(3)
C31	C21	C20	120.0(3)	C31'	C21'	C20'	119.7(3)
C21	C22	C32	124.3(3)	C21'	C22'	C32'	126.8(3)
C21	C22	P2	108.7(2)	C21'	C22'	P2'	108.9(2)
C32	C22	P2	125.9(2)	C32'	C22'	P2'	123.1(2)
C20	C23	P2	97.5(2)	C20'	C23'	P2'	97.1(2)
C25	C24	C19	123.3(3)	C25'	C24'	C19'	123.2(3)
C29	C24	C19	118.5(3)	C25'	C24'	C29'	118.3(3)
C29	C24	C25	118.2(3)	C29'	C24'	C19'	118.4(3)
C24	C25	C26	120.1(4)	C26'	C25'	C24'	120.5(3)
C27	C26	C25	120.8(4)	C27'	C26'	C25'	120.6(4)
C28	C27	C26	120.0(4)	C28'	C27'	C26'	119.3(3)
C27	C28	C29	119.8(4)	C27'	C28'	C29'	120.7(4)
C24	C29	C28	121.1(4)	C28'	C29'	C24'	120.6(4)
C33	C32	C22	121.5(3)	C33'	C32'	C22'	122.0(3)
N1	C32	C22	116.1(3)	N1'	C32'	C22'	115.3(3)
N1	C32	C33	122.3(3)	N1'	C32'	C33'	122.7(3)
C34	C33	C32	118.6(4)	C32'	C33'	C34'	118.5(4)
C35	C34	C33	119.0(4)	C35'	C34'	C33'	119.2(4)
C34	C35	C36	119.2(4)	C34'	C35'	C36'	118.3(4)
N1	C36	C35	123.7(4)	N1'	C36'	C35'	123.9(4)
C1	Mo1	C2	85.28(14)	C1'	Mo1'	C2'	84.31(14)
C1	Mo1	C4	85.44(15)	C1'	Mo1'	C3'	93.07(14)
C1	Mo1	P1	174.22(11)	C1'	Mo1'	C4'	86.98(14)
C1	Mo1	P2	100.65(11)	C1'	Mo1'	P1'	179.23(10)
C2	Mo1	P1	100.47(10)	C1'	Mo1'	P2'	100.86(10)
C2	Mo1	P2	92.40(11)	C2'	Mo1'	P1'	95.73(10)
C3	Mo1	C1	93.63(16)	C2'	Mo1'	P2'	95.11(12)
C3	Mo1	C2	88.49(19)	C3'	Mo1'	C2'	94.19(16)

C3	Mo1	C4	91.9(2)	C3'	Mo1'	C4'	85.30(15)
C3	Mo1	P1	87.10(12)	C3'	Mo1'	P1'	87.70(11)
C3	Mo1	P2	165.71(12)	C3'	Mo1'	P2'	163.94(11)
C4	Mo1	C2	170.72(15)	C4'	Mo1'	C2'	171.24(14)
C4	Mo1	P1	88.80(12)	C4'	Mo1'	P1'	92.99(10)
C4	Mo1	P2	89.51(11)	C4'	Mo1'	P2'	87.46(9)
P2	Mo1	P1	78.71(2)	P2'	Mo1'	P1'	78.37(2)
C32	N1	C36	117.2(3)	C36'	N1'	C32'	117.3(3)
C5	P1	C17	101.41(15)	C5'	P1'	C11'	101.52(14)
C5	P1	Mo1	122.64(11)	C5'	P1'	C17'	103.64(15)
C11	P1	C5	101.99(16)	C5'	P1'	Mo1'	120.63(11)
C11	P1	C17	104.73(16)	C11'	P1'	C17'	103.73(14)
C11	P1	Mo1	114.28(12)	C11'	P1'	Mo1'	114.56(10)
C17	P1	Mo1	109.76(10)	C17'	P1'	Mo1'	110.89(9)
C18	P2	Mo1	106.71(9)	C18'	P2'	Mo1'	105.64(9)
C22	P2	C18	98.46(13)	C22'	P2'	C18'	98.36(13)
C22	P2	C23	89.39(14)	C22'	P2'	C23'	89.36(14)
C22	P2	Mo1	125.73(10)	C22'	P2'	Mo1'	129.12(11)
C23	P2	C18	87.53(14)	C23'	P2'	C18'	87.75(14)
C23	P2	Mo1	137.84(11)	C23'	P2'	Mo1'	134.90(11)

Table 16 Torsion Angles for 8

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
C5	C6	C7	C8	-0.7(8)	C5'	C6'	C7'	C8'	-0.1(8)
C6	C5	C10	C9	0.0(7)	C6'	C5'	C10'	C9'	-0.2(6)
C6	C5	P1	C11	-150.9(3)	C6'	C5'	P1'	C11'	-107.5(3)
C6	C5	P1	C17	101.1(3)	C6'	C5'	P1'	C17'	145.1(3)
C6	C5	P1	Mo1	-21.5(4)	C6'	C5'	P1'	Mo1'	20.4(4)
C6	C7	C8	C9	0.8(9)	C6'	C7'	C8'	C9'	0.6(9)
C7	C8	C9	C10	-0.5(10)	C7'	C8'	C9'	C10'	-0.8(8)
C8	C9	C10	C5	0.1(9)	C8'	C9'	C10'	C5'	0.7(7)
C10	C5	C6	C7	0.3(7)	C10'	C5'	C6'	C7'	-0.1(7)
C10	C5	P1	C11	34.7(4)	C10'	C5'	P1'	C11'	72.2(3)
C10	C5	P1	C17	-73.3(4)	C10'	C5'	P1'	C17'	-35.2(3)
C10	C5	P1	Mo1	164.1(3)	C10'	C5'	P1'	Mo1'	-159.9(3)
C11	C12	C13	C14	-0.2(9)	C11'	C12'	C13'	C14'	0.2(9)
C12	C11	C16	C15	-1.8(7)	C12'	C11'	C16'	C15'	-1.4(6)
C12	C11	P1	C5	70.4(4)	C12'	C11'	P1'	C5'	30.1(4)
C12	C11	P1	C17	175.8(4)	C12'	C11'	P1'	C17'	137.4(3)

C12	C11	P1	Mo1	-64.1(4)	C12'	C11'	P1'	Mo1'	-101.5(3)
C12	C13	C14	C15	-1.6(9)	C12'	C13'	C14'	C15'	-1.5(9)
C13	C14	C15	C16	1.7(9)	C13'	C14'	C15'	C16'	1.3(7)
C14	C15	C16	C11	0.1(8)	C14'	C15'	C16'	C11'	0.1(6)
C16	C11	C12	C13	1.9(7)	C16'	C11'	C12'	C13'	1.2(7)
C16	C11	P1	C5	-108.3(3)	C16'	C11'	P1'	C5'	-152.0(3)
C16	C11	P1	C17	-3.0(4)	C16'	C11'	P1'	C17'	-44.7(3)
C16	C11	P1	Mo1	117.2(3)	C16'	C11'	P1'	Mo1'	76.3(3)
C17	C18	C19	C20	-138.1(3)	C17'	C18'	C19'	C20'	-139.2(3)
C17	C18	C19	C24	92.3(3)	C17'	C18'	C19'	C24'	91.6(3)
C17	C18	P2	C22	80.2(2)	C17'	C18'	P2'	C22'	81.1(2)
C17	C18	P2	C23	169.2(2)	C17'	C18'	P2'	C23'	170.1(2)
C17	C18	P2	Mo1	-51.1(2)	C17'	C18'	P2'	Mo1'	-53.7(2)
C18	C17	P1	C5	-165.5(2)	C18'	C17'	P1'	C5'	-153.8(2)
C18	C17	P1	C11	88.7(2)	C18'	C17'	P1'	C11'	100.5(2)
C18	C17	P1	Mo1	-34.4(2)	C18'	C17'	P1'	Mo1'	-23.0(2)
C18	C19	C20	C21	81.9(3)	C18'	C19'	C20'	C21'	81.5(3)
C18	C19	C20	C23	-25.9(3)	C18'	C19'	C20'	C23'	-26.8(3)
C18	C19	C20	C30	-153.8(3)	C18'	C19'	C20'	C30'	-152.9(3)
C18	C19	C24	C25	53.3(4)	C18'	C19'	C24'	C25'	49.4(4)
C18	C19	C24	C29	-124.9(3)	C18'	C19'	C24'	C29'	-127.9(3)
C19	C18	P2	C22	-47.7(2)	C19'	C18'	P2'	C22'	-47.9(2)
C19	C18	P2	C23	41.3(2)	C19'	C18'	P2'	C23'	41.1(2)
C19	C18	P2	Mo1	-179.07(17)	C19'	C18'	P2'	Mo1'	177.36(16)
C19	C20	C21	C22	-73.8(3)	C19'	C20'	C21'	C22'	-73.3(3)
C19	C20	C21	C31	95.4(3)	C19'	C20'	C21'	C31'	96.9(3)
C19	C20	C23	P2	54.3(3)	C19'	C20'	C23'	P2'	54.8(2)
C19	C24	C25	C26	-177.5(4)	C19'	C24'	C25'	C26'	-177.4(3)
C19	C24	C29	C28	178.0(4)	C19'	C24'	C29'	C28'	178.6(3)
C20	C19	C24	C25	-70.1(4)	C20'	C19'	C24'	C25'	-73.8(4)
C20	C19	C24	C29	111.7(3)	C20'	C19'	C24'	C29'	109.0(3)
C20	C21	C22	C32	166.7(3)	C20'	C21'	C22'	C32'	165.5(3)
C20	C21	C22	P2	-1.9(3)	C20'	C21'	C22'	P2'	-2.3(3)
C20	C23	P2	C18	-54.0(2)	C20'	C23'	P2'	C18'	-54.24(19)
C20	C23	P2	C22	44.5(2)	C20'	C23'	P2'	C22'	44.1(2)
C20	C23	P2	Mo1	-166.41(14)	C20'	C23'	P2'	Mo1'	-164.24(13)
C21	C20	C23	P2	-51.5(2)	C21'	C20'	C23'	P2'	-51.6(2)
C21	C22	C32	C33	67.0(4)	C21'	C22'	C32'	C33'	59.5(5)
C21	C22	C32	N1	-110.1(4)	C21'	C22'	C32'	N1'	-119.3(4)
C21	C22	P2	C18	60.7(2)	C21'	C22'	P2'	C18'	61.2(2)

C21	C22	P2	C23	-26.7(2)	C21'	C22'	P2'	C23'	-26.5(2)
C21	C22	P2	Mo1	178.38(17)	C21'	C22'	P2'	Mo1'	179.27(17)
C22	C32	C33	C34	-174.1(3)	C22'	C32'	C33'	C34'	-177.6(4)
C22	C32	N1	C36	175.0(3)	C22'	C32'	N1'	C36'	178.5(3)
C23	C20	C21	C22	36.8(3)	C23'	C20'	C21'	C22'	37.3(3)
C23	C20	C21	C31	-154.1(3)	C23'	C20'	C21'	C31'	-152.5(3)
C24	C19	C20	C21	-150.6(3)	C24'	C19'	C20'	C21'	-151.4(3)
C24	C19	C20	C23	101.6(3)	C24'	C19'	C20'	C23'	100.3(3)
C24	C19	C20	C30	-26.3(4)	C24'	C19'	C20'	C30'	-25.8(4)
C24	C25	C26	C27	-0.2(7)	C24'	C25'	C26'	C27'	-0.1(6)
C25	C24	C29	C28	-0.3(6)	C25'	C24'	C29'	C28'	1.2(5)
C25	C26	C27	C28	-0.8(7)	C25'	C26'	C27'	C28'	-0.8(6)
C26	C27	C28	C29	1.2(7)	C26'	C27'	C28'	C29'	1.9(6)
C27	C28	C29	C24	-0.6(7)	C27'	C28'	C29'	C24'	-2.1(6)
C29	C24	C25	C26	0.7(6)	C29'	C24'	C25'	C26'	-0.1(5)
C30	C20	C21	C22	162.7(3)	C30'	C20'	C21'	C22'	163.0(3)
C30	C20	C21	C31	-28.2(4)	C30'	C20'	C21'	C31'	-26.8(4)
C30	C20	C23	P2	-178.0(2)	C30'	C20'	C23'	P2'	-179.1(2)
C31	C21	C22	C32	-1.7(5)	C31'	C21'	C22'	C32'	-3.9(6)
C31	C21	C22	P2	-170.2(3)	C31'	C21'	C22'	P2'	-171.7(3)
C32	C22	P2	C18	-107.7(3)	C32'	C22'	P2'	C18'	-107.2(3)
C32	C22	P2	C23	164.9(3)	C32'	C22'	P2'	C23'	165.2(3)
C32	C22	P2	Mo1	10.1(3)	C32'	C22'	P2'	Mo1'	10.9(3)
C32	C33	C34	C35	-1.3(7)	C32'	C33'	C34'	C35'	-0.9(7)
C33	C32	N1	C36	-2.1(5)	C33'	C32'	N1'	C36'	-0.3(6)
C33	C34	C35	C36	-0.8(8)	C33'	C34'	C35'	C36'	-0.1(8)
C34	C35	C36	N1	1.6(8)	C34'	C35'	C36'	N1'	1.0(8)
C35	C36	N1	C32	-0.2(6)	C35'	C36'	N1'	C32'	-0.8(7)
N1	C32	C33	C34	2.9(6)	N1'	C32'	C33'	C34'	1.1(6)
P1	C5	C6	C7	-174.3(4)	P1'	C5'	C6'	C7'	179.6(4)
P1	C5	C10	C9	174.5(4)	P1'	C5'	C10'	C9'	-179.9(3)
P1	C11	C12	C13	-177.0(4)	P1'	C11'	C12'	C13'	179.2(4)
P1	C11	C16	C15	176.9(4)	P1'	C11'	C16'	C15'	-179.3(3)
P1	C17	C18	C19	177.1(2)	P1'	C17'	C18'	C19'	172.3(2)
P1	C17	C18	P2	55.3(2)	P1'	C17'	C18'	P2'	49.4(2)
P2	C18	C19	C20	-14.5(3)	P2'	C18'	C19'	C20'	-13.9(3)
P2	C18	C19	C24	-144.1(2)	P2'	C18'	C19'	C24'	-143.1(2)
P2	C22	C32	C33	-126.4(3)	P2'	C22'	C32'	C33'	-134.3(3)
P2	C22	C32	N1	56.5(4)	P2'	C22'	C32'	N1'	46.9(4)

Computational Methods and Results

Computational Methods

Gaussian 09 program was employed to perform the theoretical study. The geometry optimization was carried out by using the B3LYP functional with 6-31G(d, p) basis set and accounting for the xylene solvent (ε=2.3879) effect by employing the SMD solvation model (B3LYP-D3/6-31G(d, p)/SMD_{xylene}). Then, frequency calculations at the same level of theory were carried out to identify all of the stationary points as minima (zero imaginary frequency) and to provide corrections for free energies.

Energies, Cartesian coordinates, and representative vibrational frequencies of the listed compounds

R1

Zero-point correction= 0.213783
Thermal correction to Energy= 0.226226
Thermal correction to Enthalpy= 0.227170
Thermal correction to Gibbs Free Energy= 0.174596
Sum of electronic and zero-point Energies= -806.271103
Sum of electronic and thermal Energies= -806.258660
Sum of electronic and thermal Enthalpies= -806.257716
Sum of electronic and thermal Free Energies= -806.310290

Cartesian coordinates

C	3.351257	-0.747288	0.779495
C	1.969463	-0.935095	0.765004
C	1.137078	-0.115325	-0.018538
C	1.737714	0.899455	-0.787152
C	3.118752	1.083672	-0.774913
C	3.931850	0.262823	0.010648
H	3.973655	-1.388566	1.396820
H	1.519529	-1.711058	1.376453
H	1.117726	1.527904	-1.417950
H	3.561425	1.866831	-1.383615
H	5.007637	0.410476	0.023377
C	-0.325197	-0.343909	-0.060006

C	-1.309265	0.728740	0.149623
C	-2.597707	0.292786	0.063468
P	-1.001138	-1.893782	-0.368197
C	-0.894602	2.142811	0.475285
H	-1.673423	2.671490	1.029398
H	0.016383	2.154604	1.079373
H	-0.684414	2.725800	-0.429069
C	-3.845012	1.109382	0.230234
H	-3.640453	2.150169	0.489480
H	-4.434153	1.108287	-0.696069
H	-4.490033	0.684683	1.009653
C	-2.722266	-1.170667	-0.226410
H	-3.278916	-1.352502	-1.157065
H	-3.290279	-1.685703	0.561732

Vibrational frequencies

50.7291	72.7691	87.1760
96.4660	149.9935	163.6256
202.4181	262.8709	283.4856
301.7068	338.7600	401.0441
421.7467	474.0633	508.1287
528.6414	585.7738	626.2751
647.6596	674.3658	713.7829
721.8047	727.1593	775.2756
826.2394	862.6786	934.0646
966.1837	978.8417	998.2775

R2

Zero-point correction= 0.137716

Thermal correction to Energy= 0.145415

Thermal correction to Enthalpy= 0.146359

Thermal correction to Gibbs Free Energy= 0.105104

Sum of electronic and zero-point Energies= -347.603685

Sum of electronic and thermal Energies= -347.595986

Sum of electronic and thermal Enthalpies= -347.595042

Sum of electronic and thermal Free Energies= -347.636297

Cartesian coordinates

C	2.523653	-0.209570	0.000019
C	3.613462	0.509000	-0.000095
H	4.090719	0.821549	0.927177
H	4.090573	0.821269	-0.927551
C	1.421080	-0.926197	0.000109
H	1.518605	-2.012292	0.000088
C	0.044730	-0.395177	0.000039

C	-1.037904	-1.289448	0.000003
C	-0.224845	0.985283	0.000083
C	-2.351857	-0.820872	-0.000055
H	-0.845281	-2.359249	-0.000038
C	-1.536023	1.451266	0.000016
H	0.604544	1.686719	0.000107
C	-2.607064	0.551097	-0.000067
H	-3.175613	-1.528871	-0.000116
H	-1.725747	2.520874	0.000074
H	-3.629193	0.917705	-0.000057

Vibrational frequencies

60.8055	119.4915	210.8901
335.7596	335.8245	415.1324
441.6804	452.6845	616.4282
632.2691	650.2847	711.5306
783.3399	832.2605	859.0010
876.8012	908.0697	933.2579
976.0430	1000.1293	1013.2624
1016.0304	1053.8970	1099.2421
1127.5271	1193.8356	1214.3275
1230.6682	1323.9540	1366.7080

TS1

Zero-point correction= 0.353249
Thermal correction to Energy= 0.373752
Thermal correction to Enthalpy= 0.374697
Thermal correction to Gibbs Free Energy= 0.303498
Sum of electronic and zero-point Energies= -1153.870903
Sum of electronic and thermal Energies= -1153.850400
Sum of electronic and thermal Enthalpies= -1153.849455
Sum of electronic and thermal Free Energies= -1153.920654

Cartesian coordinates

C	-4.475664	-1.561666	-0.810706
C	-3.194030	-1.244968	-0.364984
C	-2.882807	0.054569	0.082700
C	-3.906924	1.021584	0.065219
C	-5.188424	0.702406	-0.380081
C	-5.479835	-0.590532	-0.821037
H	-4.688886	-2.568622	-1.158197
H	-2.412162	-1.998078	-0.385480
H	-3.698717	2.022769	0.428578
H	-5.963070	1.464034	-0.376189

H	-6.478246	-0.838185	-1.169095
C	-1.532970	0.373154	0.582036
C	-0.767706	1.524991	0.188071
C	0.483761	1.587020	0.774599
P	-0.632400	-0.724995	1.605232
C	-1.254337	2.524702	-0.835077
H	-0.423478	2.925099	-1.421359
H	-1.965970	2.068752	-1.526755
H	-1.759013	3.376140	-0.363326
C	1.517820	2.647596	0.574801
H	2.461598	2.201754	0.231678
H	1.217822	3.409641	-0.147266
H	1.739146	3.152620	1.523987
C	0.699670	0.550890	1.829779
H	0.537308	0.998537	2.824351
H	1.708815	0.129473	1.833582
C	0.580224	-1.726946	-0.165323
C	0.330370	-3.027566	-0.100260
H	0.723034	-3.693669	-0.867709
H	-0.264176	-3.477592	0.688097
C	1.292899	-0.774063	-0.842010
H	0.765373	-0.132893	-1.543261
C	2.712347	-0.526055	-0.668310
C	3.351595	0.473098	-1.435589
C	3.498862	-1.257617	0.250807
C	4.716256	0.718194	-1.301925
H	2.763839	1.049457	-2.145249
C	4.858595	-1.000597	0.387741
H	3.026347	-2.032386	0.846559
C	5.478250	-0.014104	-0.387821
H	5.185429	1.486959	-1.909338
H	5.442580	-1.574607	1.101691
H	6.540712	0.181165	-0.279571

Vibrational frequencies

-253.4298	25.9154	43.2580
55.1793	65.0797	72.3178
82.1286	98.3819	103.8396
132.6384	143.3172	150.1277
190.5526	207.8878	239.4710
266.3472	278.6450	287.6638
335.8349	344.1220	367.0836
385.1487	412.6510	420.4906
424.0796	463.0980	474.7580

495.3465 518.7197 529.6511

TS2

Zero-point correction= 0.353699
Thermal correction to Energy= 0.373990
Thermal correction to Enthalpy= 0.374934
Thermal correction to Gibbs Free Energy= 0.303624
Sum of electronic and zero-point Energies= -1153.862159
Sum of electronic and thermal Energies= -1153.841868
Sum of electronic and thermal Enthalpies= -1153.840924
Sum of electronic and thermal Free Energies= -1153.912234

Cartesian coordinates

C	3.203817	-2.834211	0.759146
C	2.409805	-1.693658	0.649174
C	2.917204	-0.511463	0.077167
C	4.243449	-0.516583	-0.389882
C	5.037665	-1.657450	-0.279039
C	4.522406	-2.820098	0.298102
H	2.789869	-3.737286	1.198697
H	1.378024	-1.718129	0.986391
H	4.649229	0.388810	-0.831268
H	6.061618	-1.636991	-0.641040
H	5.141593	-3.707978	0.385893
C	2.057898	0.681435	-0.082801
C	1.212472	1.209908	0.925472
C	0.353137	2.216942	0.461780
P	1.778007	1.397504	-1.657036
C	1.188602	0.734432	2.357444
H	0.287805	0.142622	2.560041
H	2.052668	0.109027	2.586453
H	1.185613	1.579140	3.053761
C	-0.495553	3.071286	1.359950
H	0.093234	3.910815	1.754105
H	-1.346238	3.490000	0.815609
H	-0.878312	2.517725	2.221355
C	0.775420	2.750733	-0.872725
H	1.462343	3.596837	-0.707613
H	-0.044521	3.107534	-1.499415
C	-1.130985	0.644463	-0.589807
C	-0.527110	0.301708	-1.755320
H	-0.769591	0.826125	-2.676894
H	-0.089052	-0.685496	-1.876504
C	-2.119201	0.526646	0.285152

H	-2.075938	1.042934	1.240454
C	-3.351065	-0.265051	0.078428
C	-4.309790	-0.302572	1.106017
C	-3.610948	-0.988486	-1.099188
C	-5.485776	-1.038865	0.966854
H	-4.126462	0.252506	2.022934
C	-4.784817	-1.724214	-1.237869
H	-2.884588	-0.966451	-1.905512
C	-5.729182	-1.754294	-0.206765
H	-6.211570	-1.053096	1.775053
H	-4.966321	-2.276585	-2.155664
H	-6.644192	-2.328281	-0.319040

Vibrational frequencies

-328.9142	18.4335	33.2257
46.8515	64.6275	74.7999
84.4644	105.5848	127.9529
147.9386	156.1790	170.2741
196.6467	221.7679	252.8587
270.7634	280.1574	299.9415
330.9949	336.0258	349.4406
402.2522	418.6746	421.0502
433.9341	458.0364	504.5806
507.6305	518.9666	540.8392

TS3

Zero-point correction= 0.352861

Thermal correction to Energy= 0.373584

Thermal correction to Enthalpy= 0.374528

Thermal correction to Gibbs Free Energy= 0.301198

Sum of electronic and zero-point Energies= -1153.863206

Sum of electronic and thermal Energies= -1153.842483

Sum of electronic and thermal Enthalpies= -1153.841539

Sum of electronic and thermal Free Energies= -1153.914868

Cartesian coordinates

C	1.892541	3.447638	-0.157312
C	1.478717	2.144445	0.114977
C	2.396430	1.077792	0.095253
C	3.740149	1.361709	-0.209028
C	4.152275	2.665437	-0.482138
C	3.230393	3.714439	-0.456965
H	1.166243	4.255302	-0.143062
H	0.432769	1.936836	0.320419

H	4.464813	0.552939	-0.211358
H	5.196122	2.862855	-0.709118
H	3.551492	4.729673	-0.670415
C	1.957822	-0.298079	0.410355
C	2.162548	-1.421125	-0.438333
C	1.555438	-2.587186	0.031318
P	0.941195	-0.658792	1.790353
C	2.843108	-1.354066	-1.782534
H	2.261127	-1.893139	-2.537888
H	2.967552	-0.325475	-2.123877
H	3.835349	-1.820456	-1.753505
C	1.662471	-3.929888	-0.632291
H	2.632264	-4.399002	-0.415289
H	0.883568	-4.609056	-0.274251
H	1.577792	-3.856585	-1.720492
C	1.140296	-2.476942	1.464235
H	1.974052	-2.809671	2.105243
H	0.262928	-3.068773	1.732639
C	-1.046347	-0.870984	0.321020
C	-0.776835	-1.846819	-0.580849
H	-0.409977	-1.612586	-1.575562
H	-1.070996	-2.878259	-0.405887
C	-1.903366	0.041878	0.776093
H	-1.625965	0.674413	1.615773
C	-3.256128	0.289195	0.235469
C	-4.033191	1.310024	0.811585
C	-3.807619	-0.441663	-0.831957
C	-5.313326	1.594897	0.338076
H	-3.623923	1.884993	1.638626
C	-5.085674	-0.156972	-1.305301
H	-3.223411	-1.235776	-1.286357
C	-5.846335	0.862424	-0.723915
H	-5.894033	2.388873	0.799047
H	-5.492649	-0.733377	-2.131507
H	-6.843243	1.081229	-1.095019

Vibrational frequencies

-290.8163	14.2095	25.7475
41.9642	54.2181	75.7250
78.2759	90.8665	101.1702
111.3034	133.2383	143.1609
187.0879	219.9891	247.8966
251.8203	274.9917	286.2032
330.2195	332.3013	360.4885

390.5810	414.3868	418.2680
424.8265	470.3177	493.5696
500.3699	520.1001	532.3293

TS4

Zero-point correction= 0.353543
Thermal correction to Energy= 0.373828
Thermal correction to Enthalpy= 0.374772
Thermal correction to Gibbs Free Energy= 0.304014
Sum of electronic and zero-point Energies= -1153.860833
Sum of electronic and thermal Energies= -1153.840548
Sum of electronic and thermal Enthalpies= -1153.839604
Sum of electronic and thermal Free Energies= -1153.910362

Cartesian coordinates

P	0.077887	-0.508883	-1.317674
C	-1.078178	1.109682	1.265946
C	-1.327247	-0.205155	0.973379
H	-0.646403	-0.956466	1.362399
C	-0.038155	2.064706	-0.555684
C	1.241574	1.597024	-0.195170
C	1.464779	0.243709	-0.554025
C	-0.707501	1.156074	-1.543257
H	-0.443258	1.490403	-2.559440
H	-1.797113	1.134416	-1.479309
C	-1.205986	2.077812	2.151945
H	-1.693702	1.876383	3.106125
H	-0.864337	3.095256	1.997300
C	-2.637430	-0.687346	0.501877
C	-3.697884	0.192785	0.216132
H	-3.549705	1.260206	0.350253
C	-4.931996	-0.291778	-0.214051
H	-5.736273	0.406526	-0.428467
C	-5.139752	-1.664808	-0.364057
H	-6.101669	-2.041063	-0.698956
C	-4.096116	-2.550344	-0.078369
H	-4.244687	-3.620575	-0.191115
C	-2.860407	-2.068059	0.343824
H	-2.048707	-2.761438	0.548057
C	-0.428237	3.517848	-0.532013
H	0.021508	4.062938	0.301393
H	-1.513566	3.635140	-0.475872
H	-0.086813	4.008172	-1.453203
C	2.193409	2.434260	0.620143

H	2.667902	3.212284	0.009747
H	2.984250	1.830599	1.067018
H	1.657704	2.938904	1.430224
C	2.681960	-0.523547	-0.207503
C	3.962600	-0.034764	-0.524307
H	4.054076	0.921187	-1.031018
C	5.107139	-0.769782	-0.218408
H	6.085023	-0.373614	-0.476914
C	4.998465	-2.012828	0.409006
H	5.889867	-2.585387	0.647369
C	3.734172	-2.514501	0.725216
H	3.637849	-3.479340	1.214852
C	2.589578	-1.779010	0.420259
H	1.611025	-2.173146	0.679365

Vibrational frequencies

-381.0863	26.3838	40.8727
47.1448	58.1582	64.9208
95.6622	104.7744	130.1700
140.6481	150.2811	178.5320
196.5700	209.4728	260.2450
276.0288	279.0411	285.2150
335.2232	340.0552	381.8108
410.8629	417.1986	421.9307
434.0126	463.1285	494.1762
511.9481	517.6131	539.3049

Int1

Zero-point correction= 0.359220
Thermal correction to Energy= 0.378139
Thermal correction to Enthalpy= 0.379083
Thermal correction to Gibbs Free Energy= 0.312592
Sum of electronic and zero-point Energies= -1153.928989
Sum of electronic and thermal Energies= -1153.910070
Sum of electronic and thermal Enthalpies= -1153.909126
Sum of electronic and thermal Free Energies= -1153.975617

Cartesian coordinates

C	3.360373	2.384988	-0.134003
C	2.240688	1.563558	-0.263629
C	2.361978	0.161516	-0.222559
C	3.642945	-0.384630	-0.020238
C	4.761969	0.436012	0.106828
C	4.626438	1.825426	0.047775

H	3.241190	3.464317	-0.166183
H	1.257847	2.007392	-0.380364
H	3.756901	-1.463567	0.030187
H	5.741665	-0.009451	0.254197
H	5.498042	2.465028	0.150797
C	1.183914	-0.717634	-0.347940
C	0.129088	-0.588708	-1.188599
C	-0.996538	-1.579939	-0.868143
P	0.888475	-2.143962	0.834444
C	-0.032201	0.418933	-2.289147
H	-0.807949	1.150755	-2.033136
H	0.896533	0.957992	-2.482938
H	-0.348926	-0.067356	-3.218108
C	-2.021404	-1.798656	-1.977595
H	-2.761940	-2.542250	-1.664702
H	-2.555913	-0.877237	-2.226058
H	-1.537602	-2.168686	-2.887042
C	-0.253208	-2.870258	-0.457635
H	0.308299	-3.299950	-1.292394
H	-0.923058	-3.630548	-0.041235
C	-0.611980	-1.321634	1.579557
C	-0.728702	-0.977244	2.863184
H	-1.610699	-0.459658	3.235093
H	0.055484	-1.188712	3.584546
C	-1.670728	-1.106402	0.496923
H	-2.487789	-1.816583	0.684939
C	-2.269557	0.285240	0.431937
C	-3.598748	0.455414	0.020500
C	-1.512761	1.430706	0.722474
C	-4.152150	1.729475	-0.121250
H	-4.205746	-0.420818	-0.192261
C	-2.060777	2.705199	0.578091
H	-0.492807	1.317266	1.071646
C	-3.382026	2.860916	0.151299
H	-5.184849	1.836074	-0.440916
H	-1.456017	3.578315	0.806894
H	-3.809474	3.853442	0.043386

Vibrational frequencies

29.7284	44.5763	60.8139
82.0120	89.8330	108.9236
139.8977	176.8846	194.2802
213.9814	248.3966	255.9304
274.8422	288.4170	298.2034

315.7837	333.1281	343.3403
376.2498	420.0165	424.4112
427.1538	448.4441	482.6653
498.3559	515.0167	518.9103
563.0629	585.2611	616.8169

Int2

Zero-point correction= 0.359131
Thermal correction to Energy= 0.378202
Thermal correction to Enthalpy= 0.379146
Thermal correction to Gibbs Free Energy= 0.310677
Sum of electronic and zero-point Energies= -1153.931496
Sum of electronic and thermal Energies= -1153.912425
Sum of electronic and thermal Enthalpies= -1153.911481
Sum of electronic and thermal Free Energies= -1153.979949

Cartesian coordinates

C	3.555765	-2.646727	0.955809
C	2.597399	-1.640317	0.834510
C	2.840967	-0.501414	0.045452
C	4.066729	-0.418684	-0.639407
C	5.025398	-1.422849	-0.516563
C	4.775320	-2.540121	0.284503
H	3.345131	-3.519039	1.568048
H	1.639953	-1.741119	1.336082
H	4.265860	0.445937	-1.266143
H	5.968662	-1.334521	-1.048000
H	5.521067	-3.324162	0.377198
C	1.826767	0.561890	-0.098699
C	1.099779	1.153824	0.877567
C	-0.010385	2.067001	0.318261
P	1.223968	1.127039	-1.773354
C	1.203279	0.920712	2.355723
H	0.294024	0.435111	2.732893
H	2.056258	0.288688	2.607013
H	1.303321	1.868445	2.896321
C	-0.552767	3.110768	1.290325
H	0.239366	3.809954	1.575316
H	-1.360731	3.678703	0.820151
H	-0.944967	2.665902	2.209354
C	0.614421	2.692062	-0.950003
H	1.440881	3.364984	-0.704571
H	-0.121259	3.224899	-1.561996
C	-1.045122	1.052118	-0.225383

C	-0.526610	0.425730	-1.508814
H	-1.139127	0.713164	-2.371488
H	-0.502350	-0.667406	-1.471645
C	-2.184285	0.756081	0.428388
H	-2.371504	1.302065	1.351055
C	-3.235794	-0.226837	0.127372
C	-4.167692	-0.513466	1.147030
C	-3.393421	-0.900261	-1.101018
C	-5.191069	-1.439063	0.962809
H	-4.076826	-0.000768	2.101451
C	-4.420560	-1.824628	-1.286689
H	-2.725963	-0.693505	-1.926016
C	-5.322254	-2.104432	-0.258238
H	-5.888043	-1.639693	1.771557
H	-4.518522	-2.325706	-2.245662
H	-6.119939	-2.825829	-0.408223

Vibrational frequencies

13.0224	32.3521	45.0621
73.1578	90.5185	102.6030
131.3707	151.6615	207.6245
216.6048	225.3503	253.9338
271.7632	287.8532	297.7161
302.7338	333.5400	351.5625
368.7987	417.4756	420.4597
427.5793	462.4312	498.9278
509.9339	532.3174	535.6321
565.8908	578.0459	616.8298

Int3

Zero-point correction= 0.359265
Thermal correction to Energy= 0.378415
Thermal correction to Enthalpy= 0.379359
Thermal correction to Gibbs Free Energy= 0.310411
Sum of electronic and zero-point Energies= -1153.932004
Sum of electronic and thermal Energies= -1153.912854
Sum of electronic and thermal Enthalpies= -1153.911909
Sum of electronic and thermal Free Energies= -1153.980858

Cartesian coordinates

C	2.877443	-3.172206	-0.044436
C	2.099747	-2.040141	-0.279626
C	2.597451	-0.752273	-0.008371
C	3.909069	-0.638270	0.486112

C	4.686917	-1.772111	0.721849
C	4.174374	-3.043999	0.459726
H	2.469925	-4.157164	-0.253848
H	1.088767	-2.150177	-0.661748
H	4.321770	0.349699	0.665835
H	5.698548	-1.660153	1.101732
H	4.781120	-3.926473	0.639862
C	1.768502	0.439954	-0.261180
C	1.524491	1.472492	0.579388
C	0.502649	2.465379	0.012835
P	0.722196	0.627995	-1.808755
C	1.987886	1.608706	1.999919
H	1.123677	1.737752	2.664649
H	2.548171	0.734115	2.333607
H	2.617802	2.496173	2.135302
C	0.511368	3.852266	0.652595
H	1.498172	4.318336	0.565275
H	-0.215340	4.502374	0.154375
H	0.249189	3.812659	1.714803
C	0.783542	2.473661	-1.506067
H	1.768679	2.885413	-1.743336
H	0.016306	3.012210	-2.073110
C	-0.880505	0.590760	-0.841193
C	-0.896061	1.763947	0.120920
H	-1.101175	1.454041	1.152488
H	-1.675928	2.483797	-0.163082
C	-1.784615	-0.392281	-1.013774
H	-1.544112	-1.141143	-1.768979
C	-3.053436	-0.654297	-0.318884
C	-3.667368	-1.906597	-0.526167
C	-3.704662	0.257377	0.536430
C	-4.862104	-2.244704	0.103634
H	-3.189333	-2.623470	-1.188936
C	-4.902839	-0.079922	1.163676
H	-3.288465	1.241676	0.702931
C	-5.486546	-1.331538	0.956279
H	-5.307316	-3.219713	-0.072466
H	-5.385653	0.642568	1.815658
H	-6.419549	-1.589656	1.448303

Vibrational frequencies

12.8510	27.5397	40.8458
69.8652	91.6148	101.4145
112.3161	165.0614	205.2123

224.9537	230.9343	256.7641
266.8804	269.2383	286.5398
295.7734	313.9034	335.0139
374.3563	416.6140	419.2820
453.9184	467.3445	479.8445
508.0135	527.0735	537.7466
553.0309	573.6860	587.4285

Int4

Zero-point correction= 0.358555
Thermal correction to Energy= 0.377749
Thermal correction to Enthalpy= 0.378693
Thermal correction to Gibbs Free Energy= 0.310575
Sum of electronic and zero-point Energies= -1153.926638
Sum of electronic and thermal Energies= -1153.907444
Sum of electronic and thermal Enthalpies= -1153.906500
Sum of electronic and thermal Free Energies= -1153.974618

Cartesian coordinates

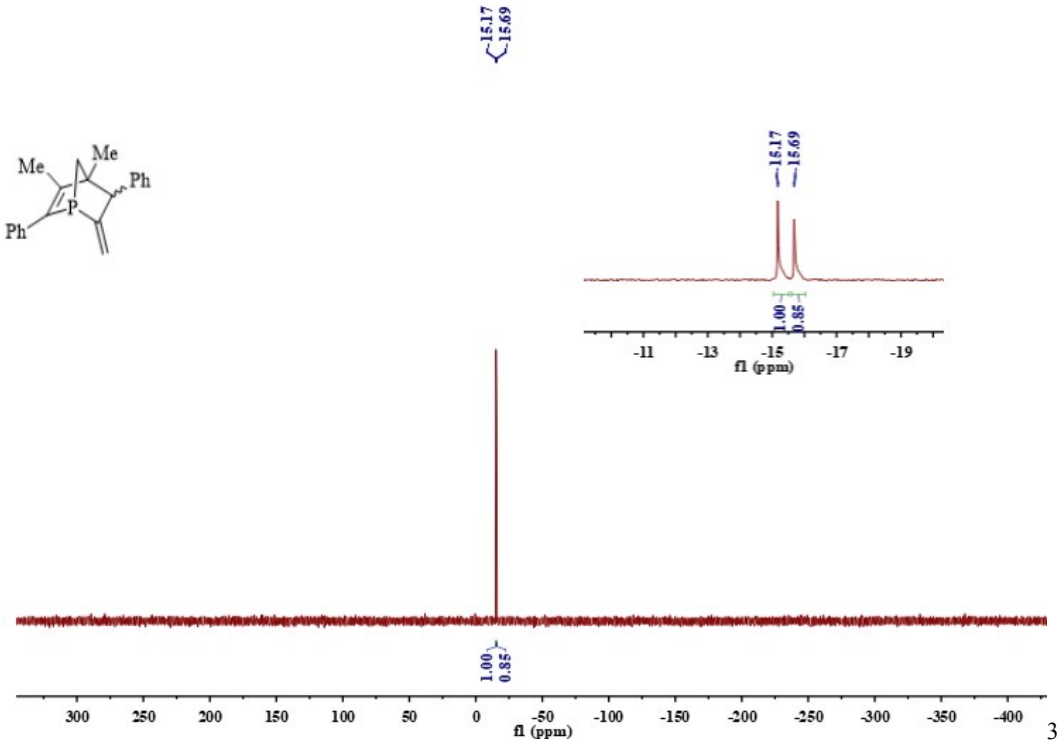
P	-0.084144	-0.368805	-1.142348
C	-1.042141	1.365332	0.771882
C	-1.143040	-0.129232	0.464708
H	-0.636197	-0.706844	1.244657
C	-0.149862	2.080958	-0.258170
C	1.267911	1.570626	0.064281
C	1.478202	0.301906	-0.362152
C	-0.508689	1.393068	-1.595562
H	0.113879	1.751920	-2.419854
H	-1.564365	1.508402	-1.860572
C	-1.642534	1.952530	1.808417
H	-2.256417	1.379968	2.497582
H	-1.563185	3.018607	1.995497
C	-2.540000	-0.682888	0.281224
C	-3.602996	0.096011	-0.198973
H	-3.449928	1.154985	-0.378199
C	-4.861681	-0.466716	-0.417112
H	-5.670726	0.157064	-0.786829
C	-5.084797	-1.819600	-0.157050
H	-6.065442	-2.255667	-0.323004
C	-4.035897	-2.605933	0.325600
H	-4.196735	-3.659075	0.538108
C	-2.779157	-2.041825	0.539130
H	-1.966683	-2.662032	0.910147
C	-0.298281	3.599524	-0.299792

H	-0.037618	4.069335	0.652976
H	-1.332155	3.869830	-0.534147
H	0.352147	4.024536	-1.070279
C	2.156495	2.396571	0.946202
H	2.512802	3.297465	0.432454
H	3.022966	1.834507	1.297477
H	1.586795	2.735297	1.820549
C	2.680066	-0.526027	-0.157861
C	3.971123	-0.005987	-0.365739
H	4.079895	1.018052	-0.708604
C	5.103578	-0.795142	-0.166569
H	6.089524	-0.371719	-0.336122
C	4.972735	-2.126004	0.234899
H	5.854370	-2.741516	0.386823
C	3.697446	-2.663172	0.426768
H	3.583473	-3.699542	0.731507
C	2.565818	-1.874961	0.226842
H	1.579975	-2.305740	0.379219

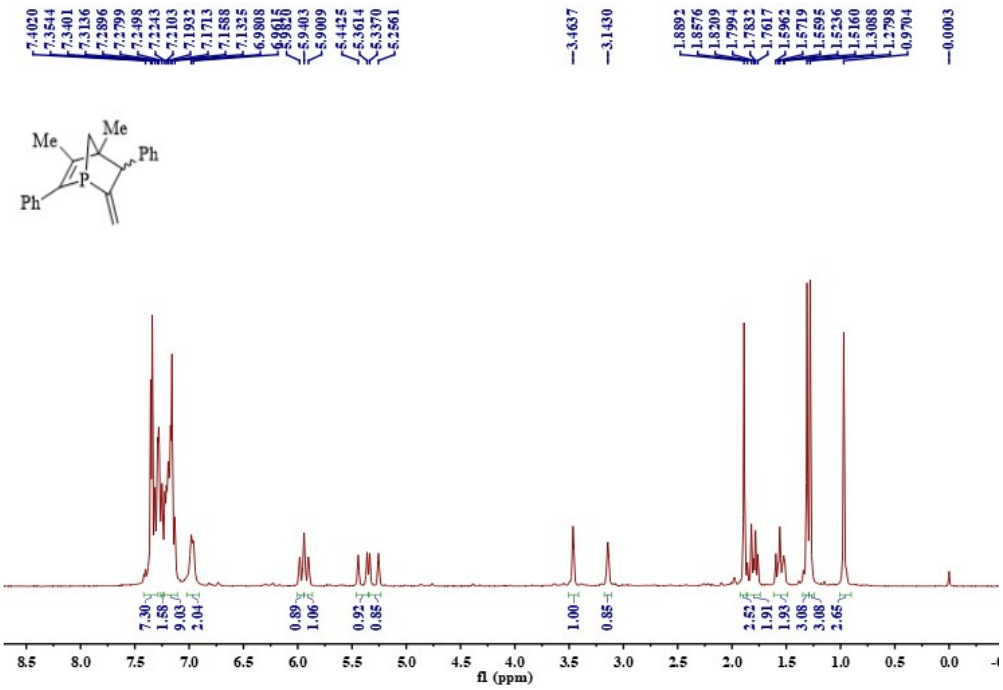
Vibrational frequencies

23.8329	39.3535	48.3536
59.2607	70.1064	102.3191
125.3865	154.7946	199.0914
230.7223	238.7384	247.4182
263.5747	270.9244	290.0218
317.5016	327.5022	349.0841
382.1026	398.3211	416.9156
420.7122	451.1714	491.6484
510.3031	524.1126	541.4747
543.7639	579.7945	620.4590

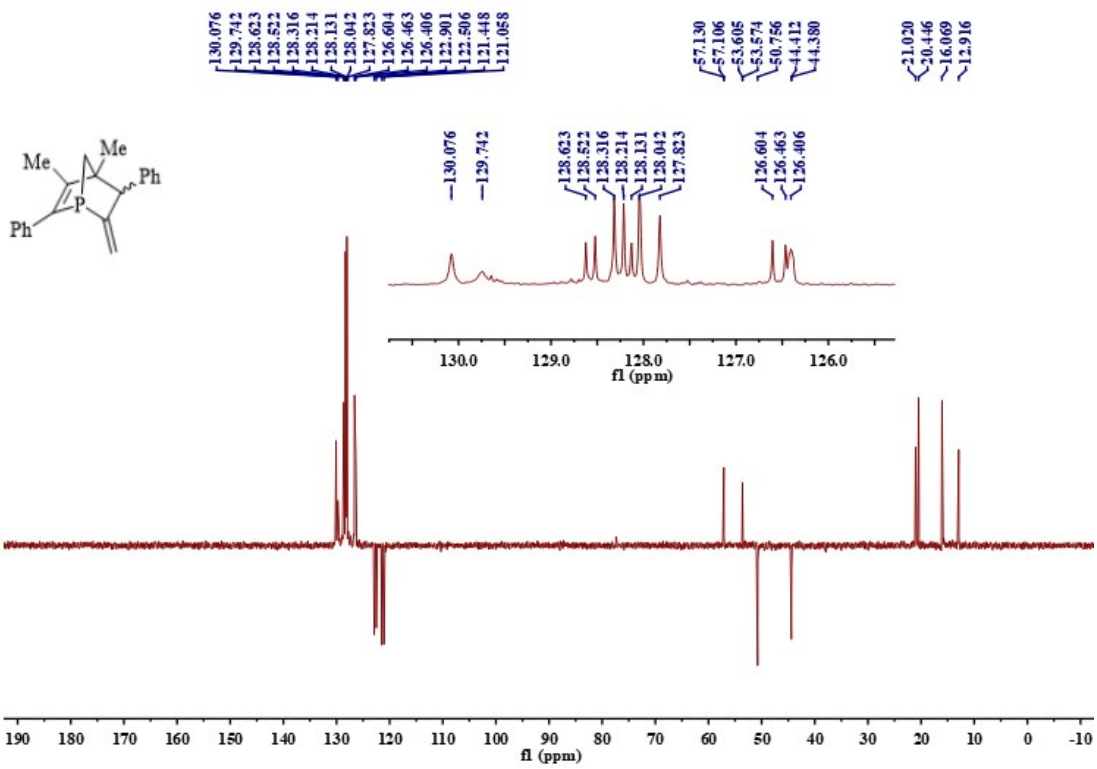
NMR spectrums



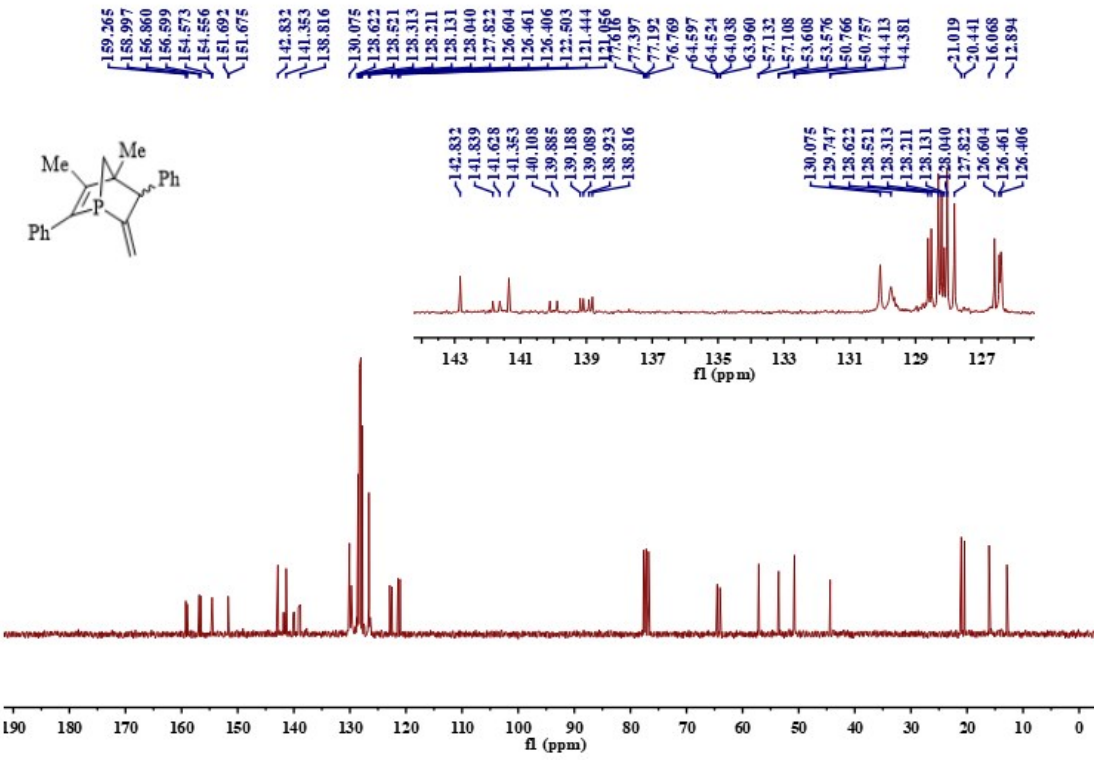
^{31}P (CDCl$_3$, 121 MHz) NMR of **3aa**



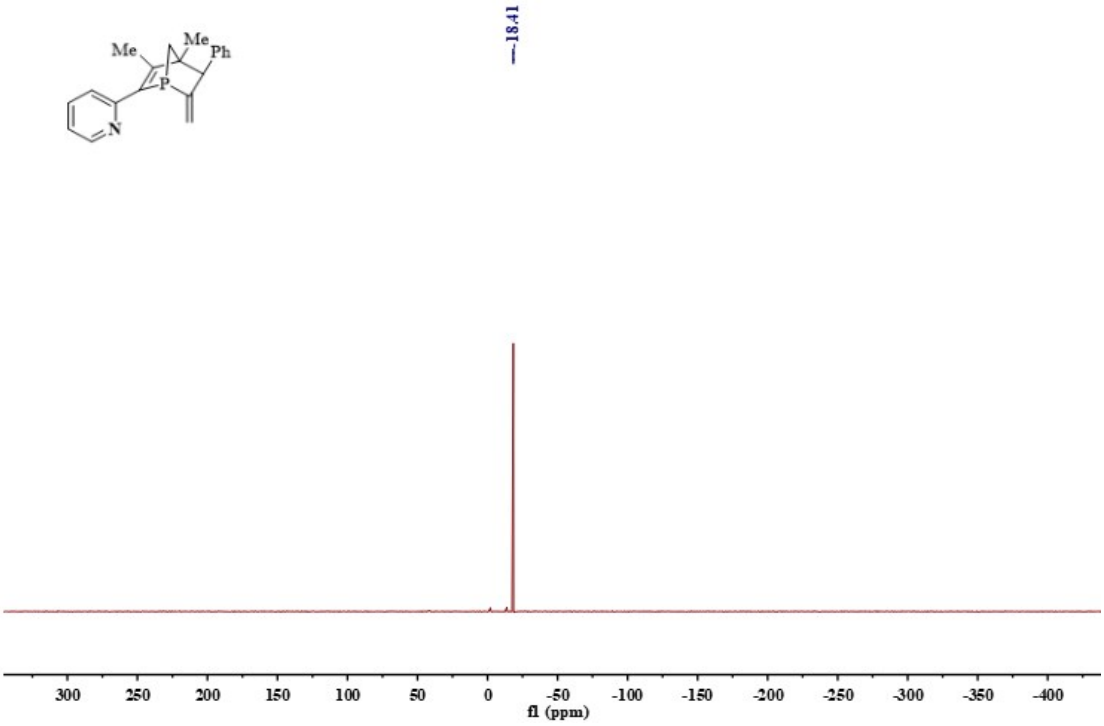
^{1}H (CDCl$_3$, 300 MHz) NMR of **3aa**



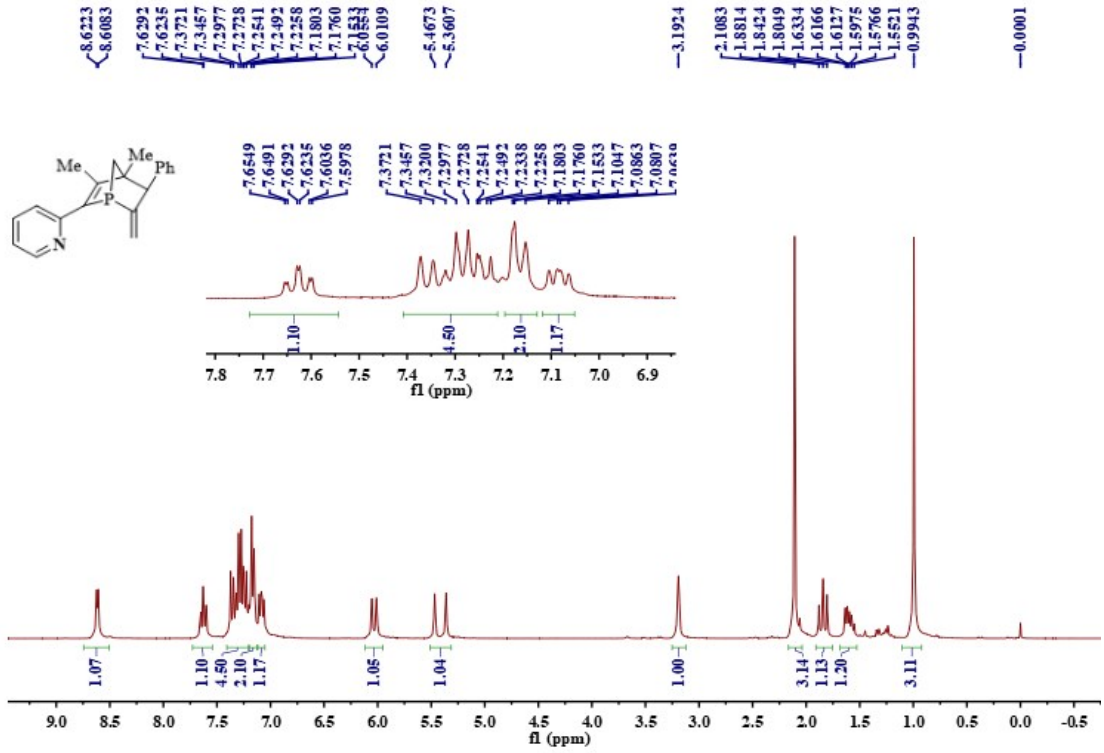
Dept135 ($CDCl_3$, 75 MHz) NMR of **3aa**



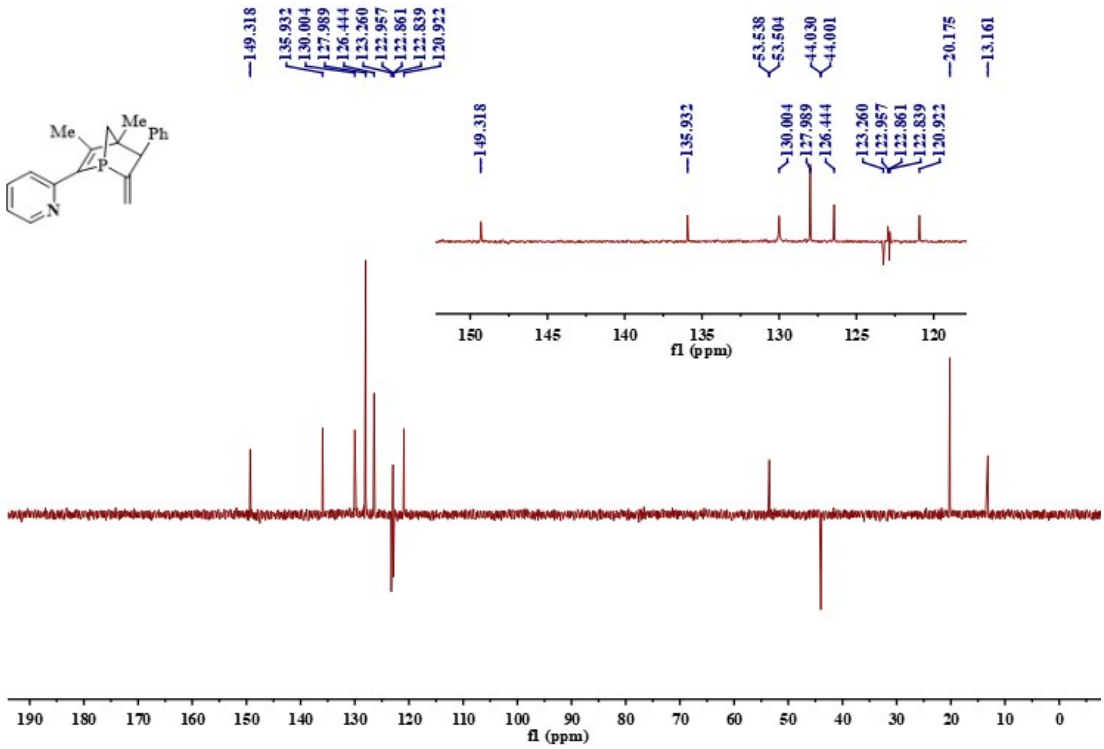
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of **3aa**



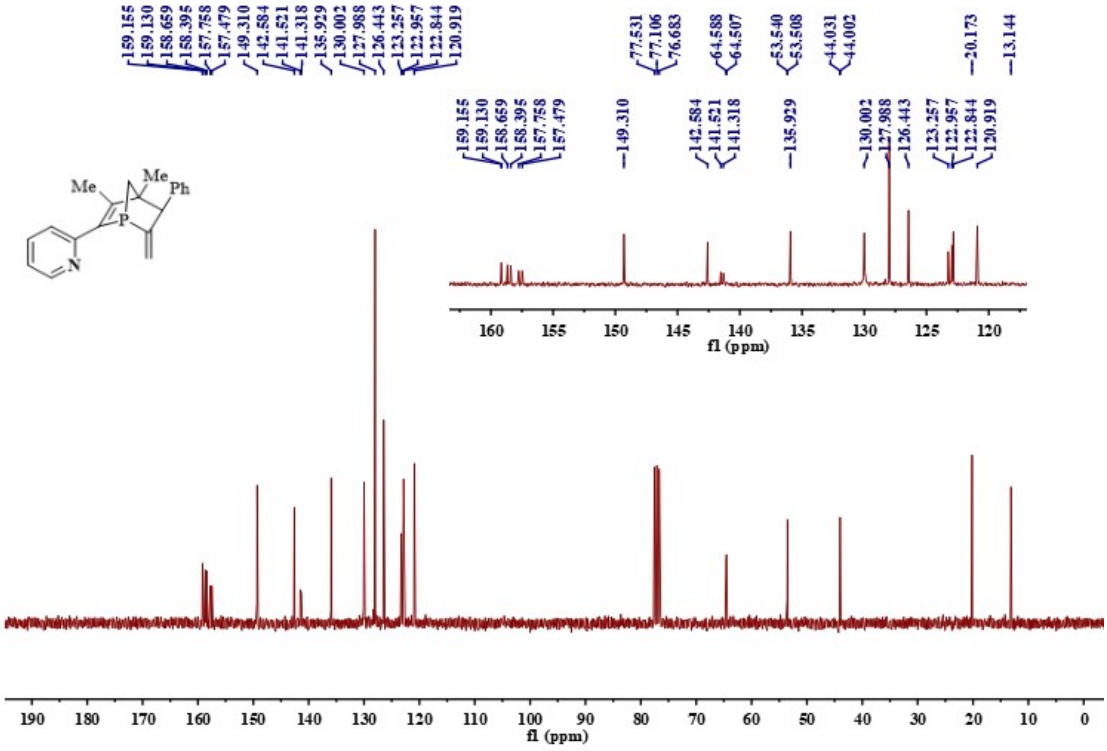
^{31}P ($CDCl_3$, 121 MHz) NMR of *exo*-**3ba**



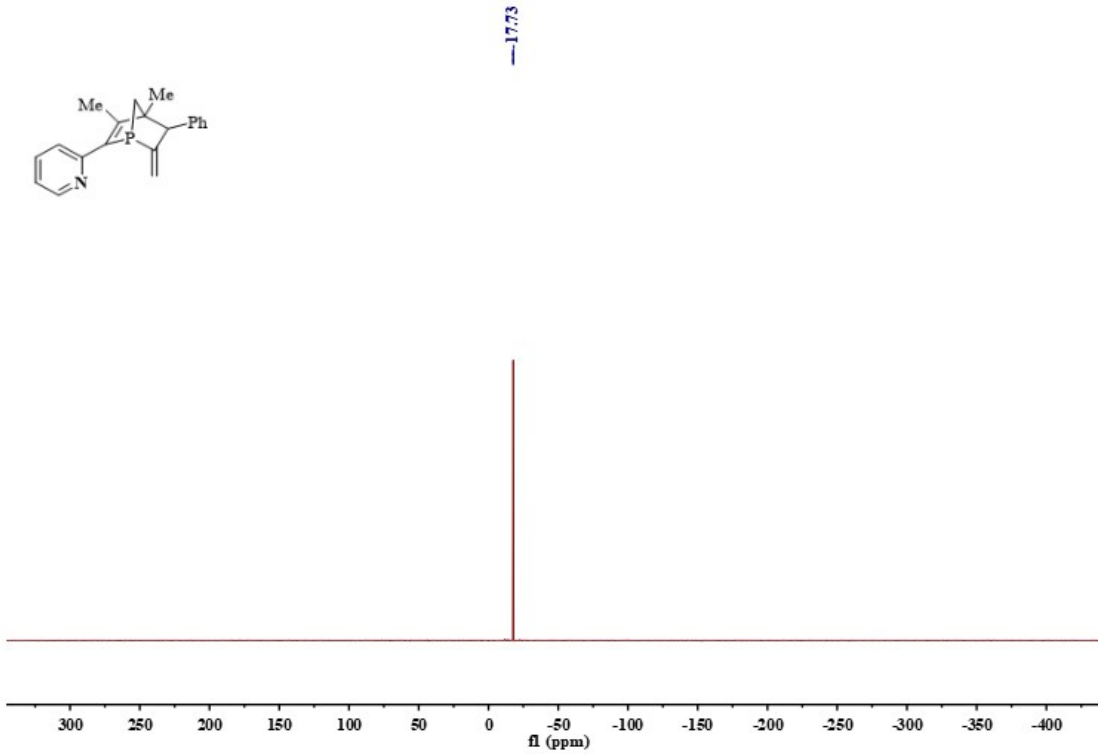
^{1}H ($CDCl_3$, 300 MHz) NMR of *exo*-**3ba**



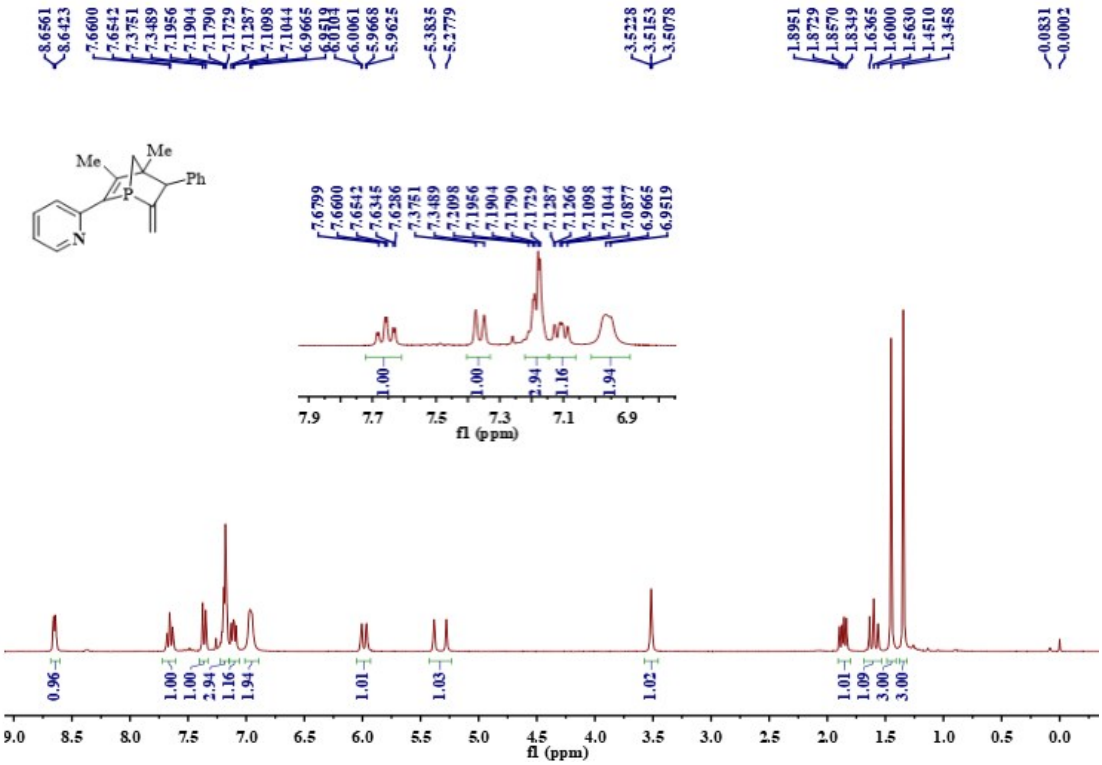
Dept135 ($CDCl_3$, 75 MHz) NMR of *exo*-**3ba**



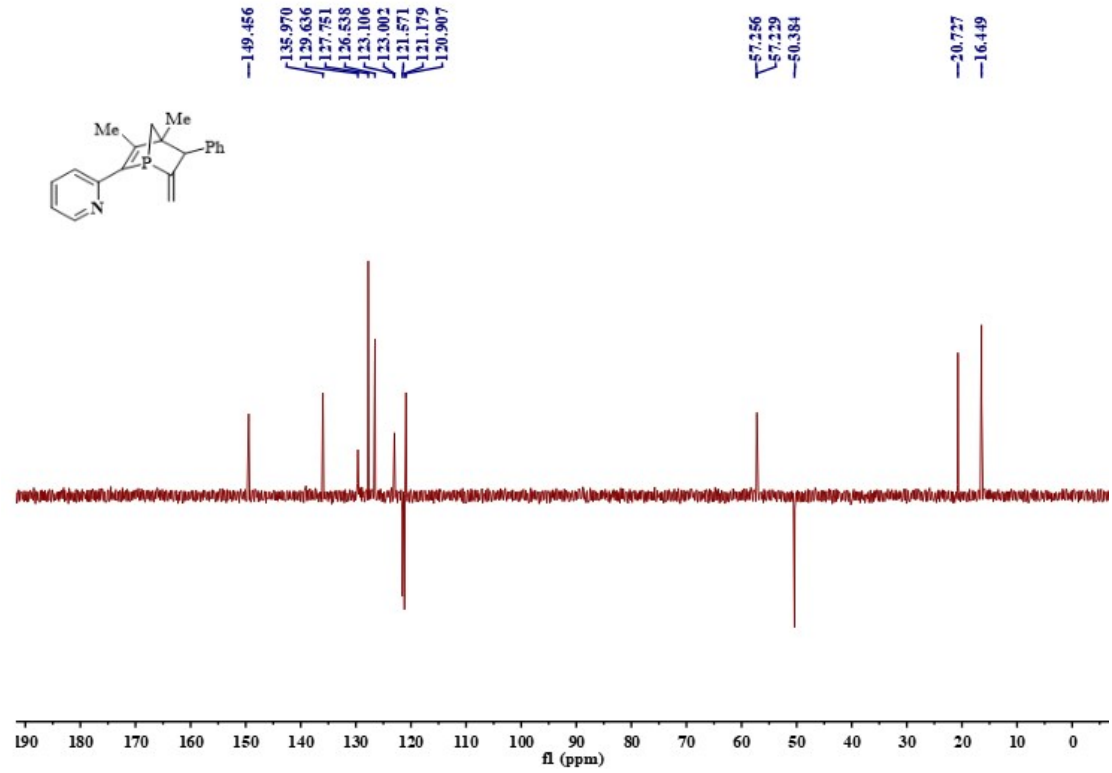
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of *exo*-**3ba**



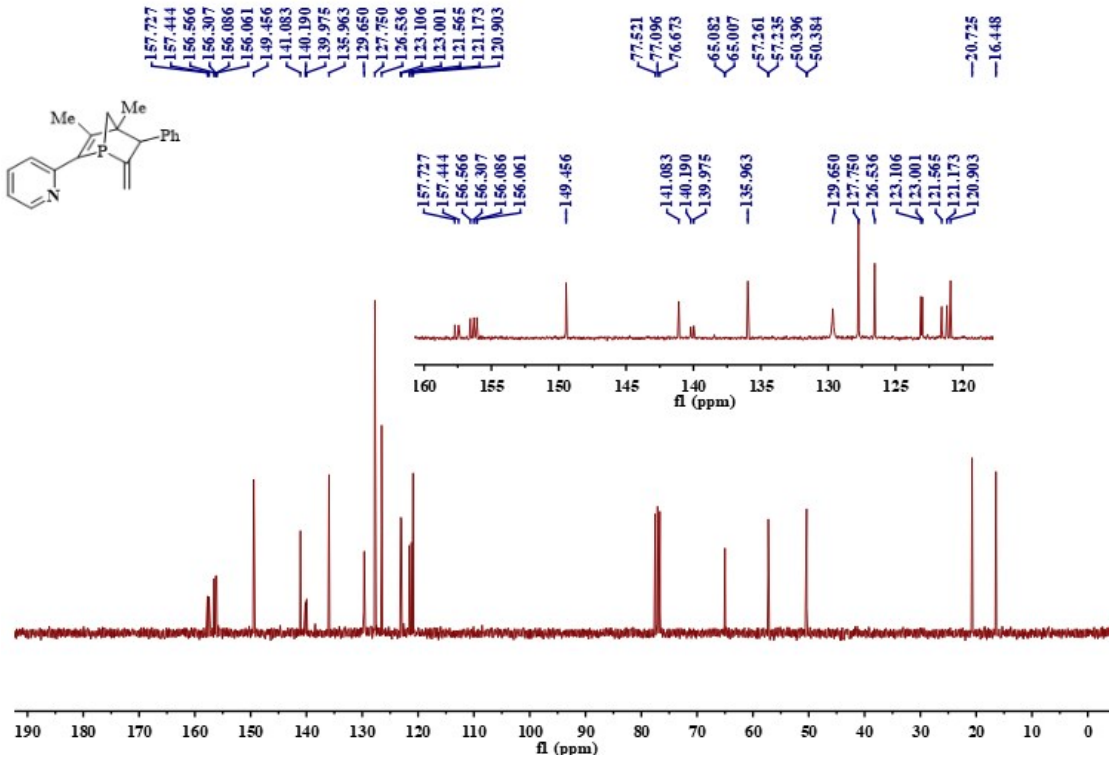
^{31}P ($CDCl_3$, 121 MHz) NMR of *endo*-**3ba**



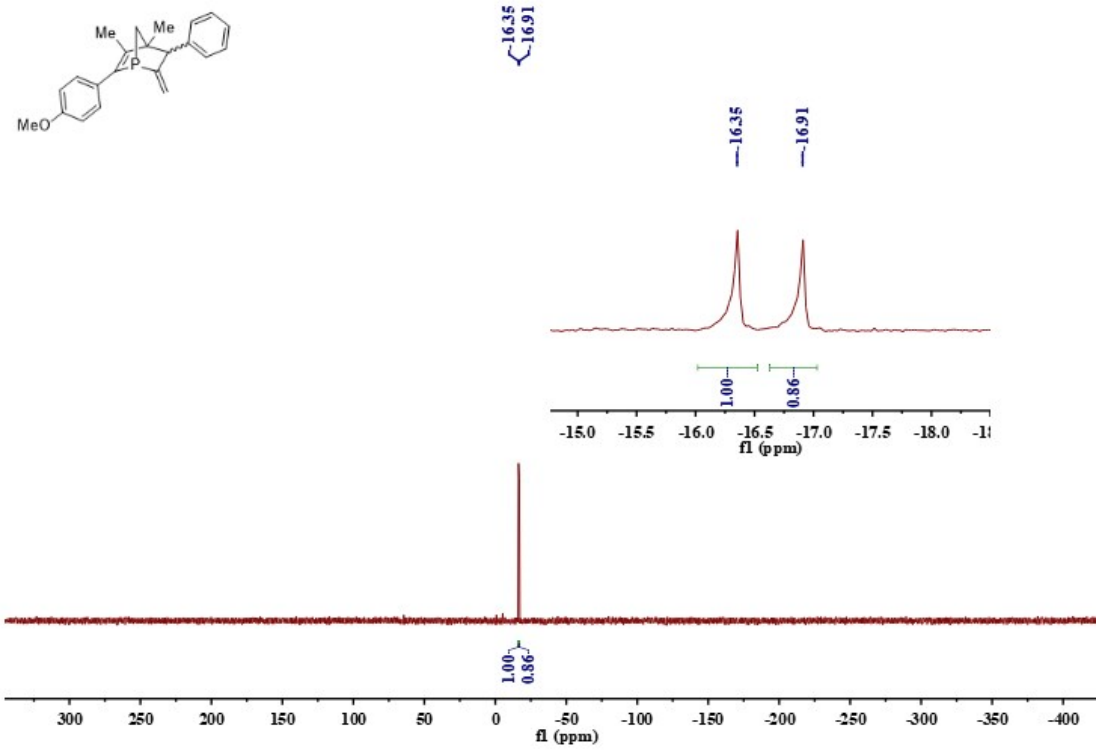
^{1}H ($CDCl_3$, 300 MHz) NMR of *endo*-**3ba**



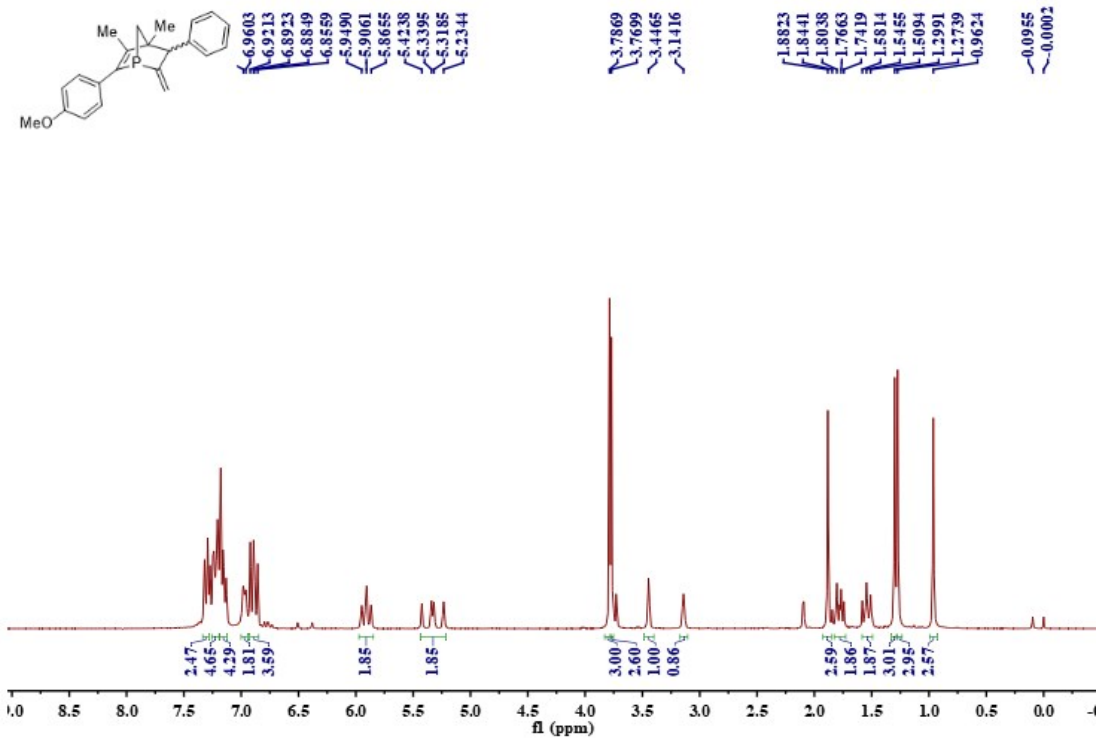
Dept135 ($CDCl_3$, 75 MHz) NMR of *endo*-**3ba**



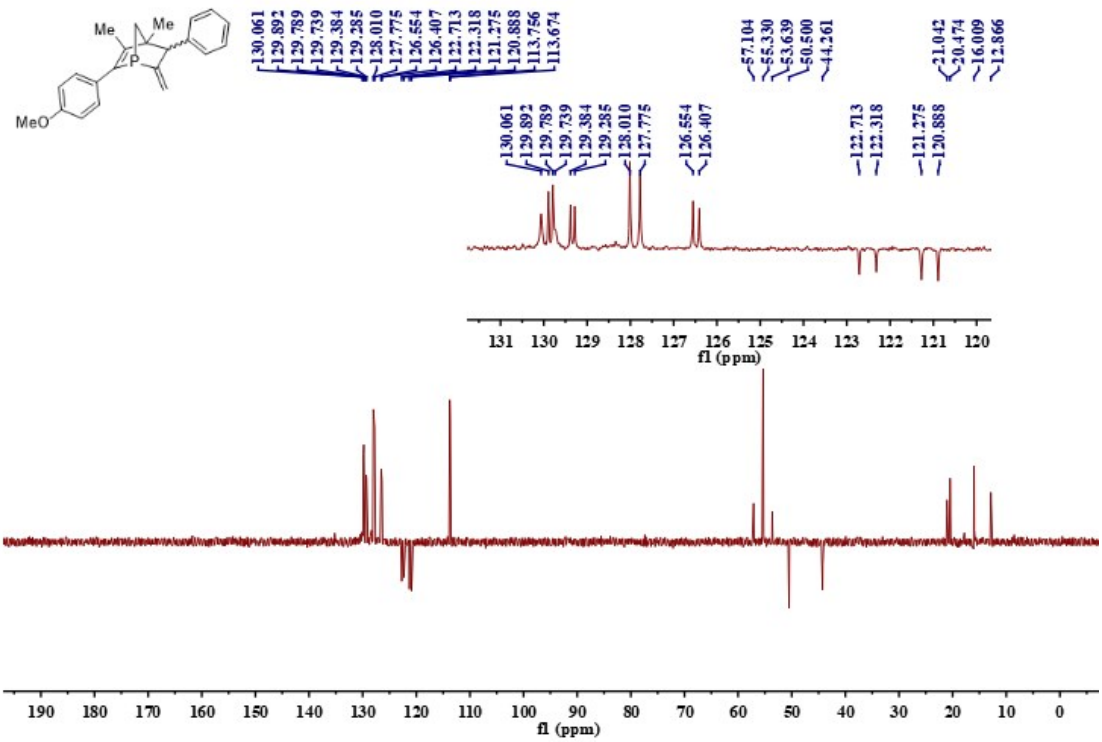
$^{13}C\{^1H\}$ ($CDCl_3$, 75 MHz) NMR of *endo*-**3ba**



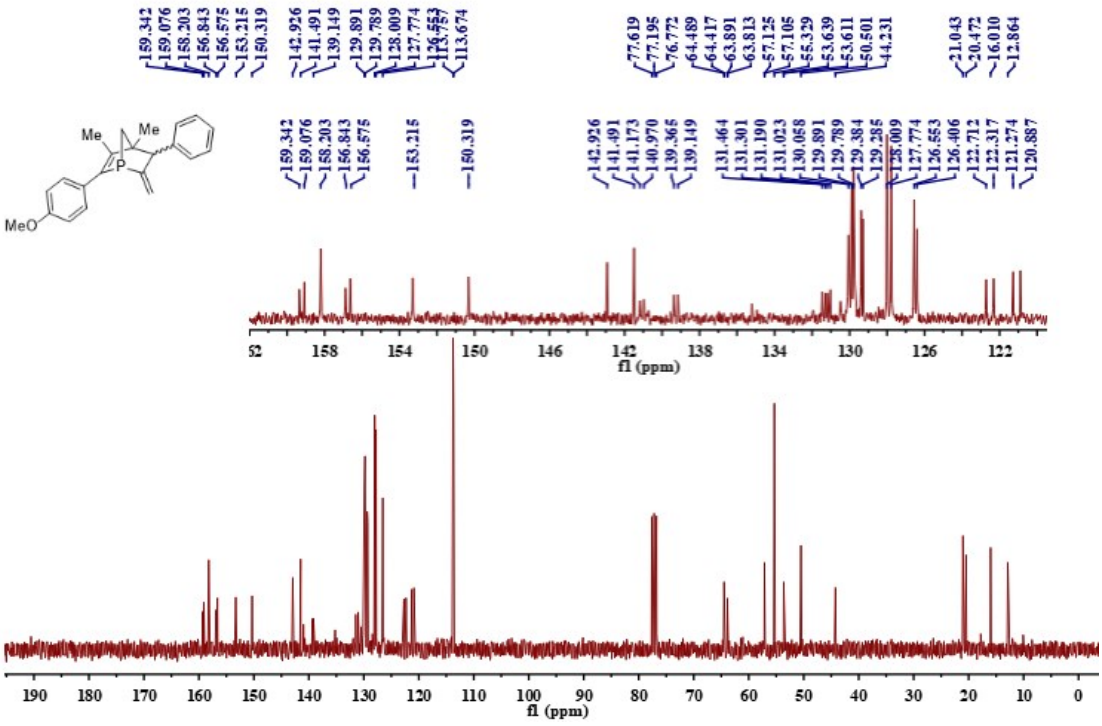
^{31}P ($CDCl_3$, 121 MHz) NMR of **3ca**



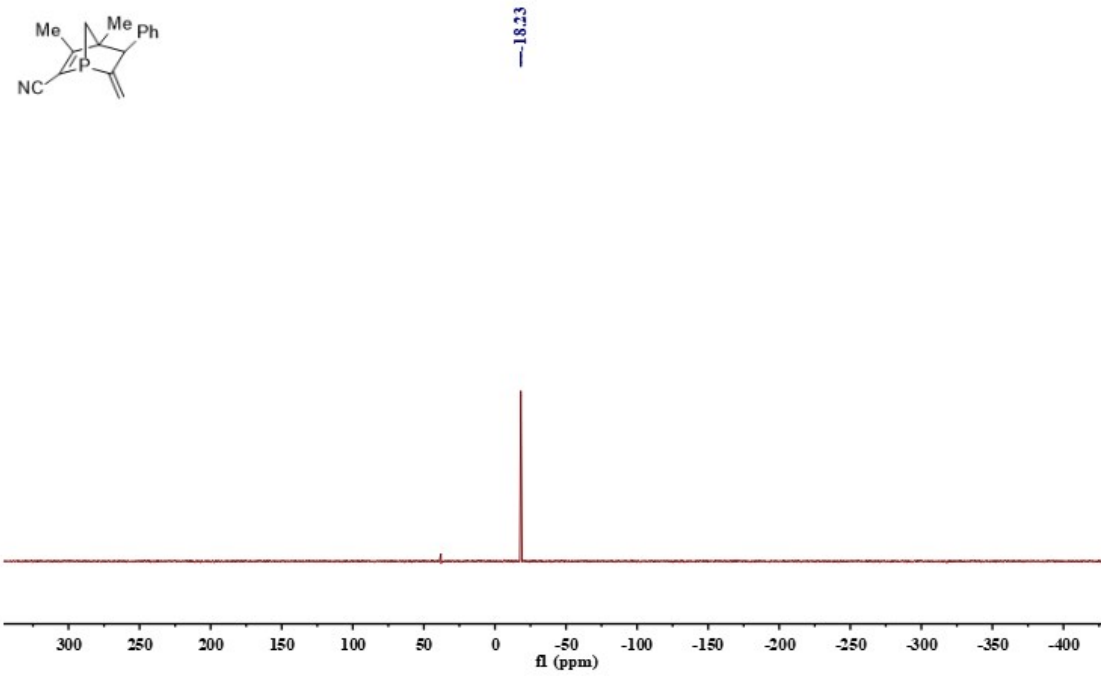
^{1}H ($CDCl_3$, 300 MHz) NMR of **3ca**



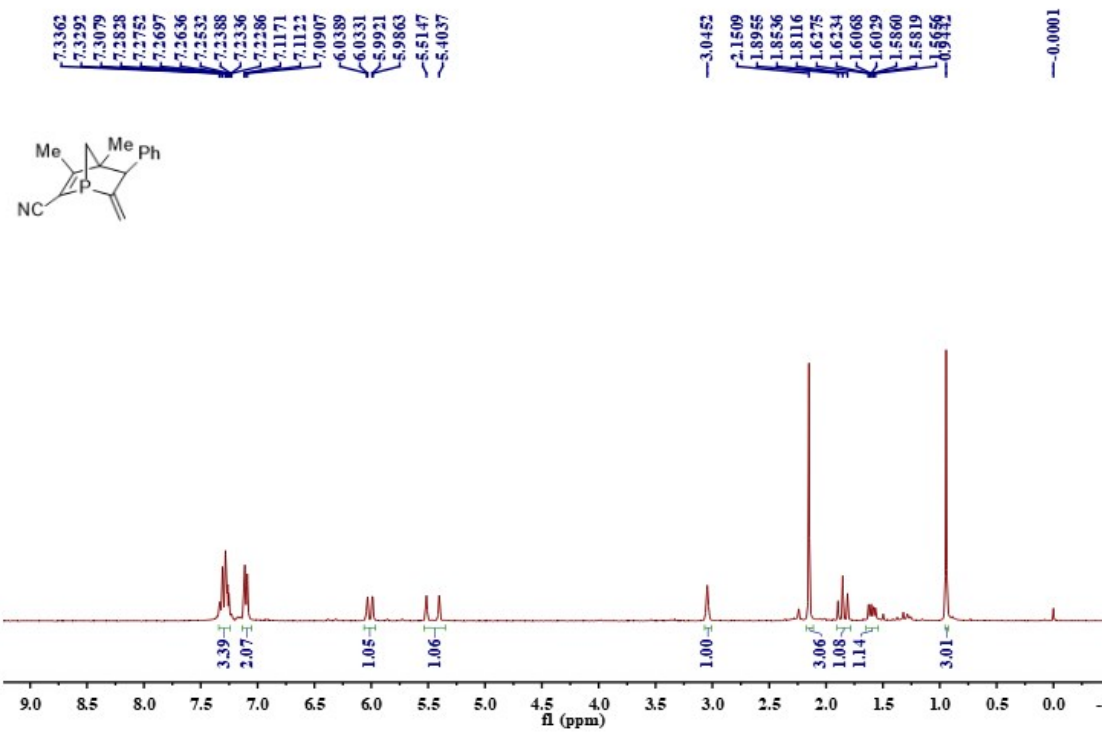
Dept135 ($CDCl_3$, 75 MHz) NMR of **3ca**



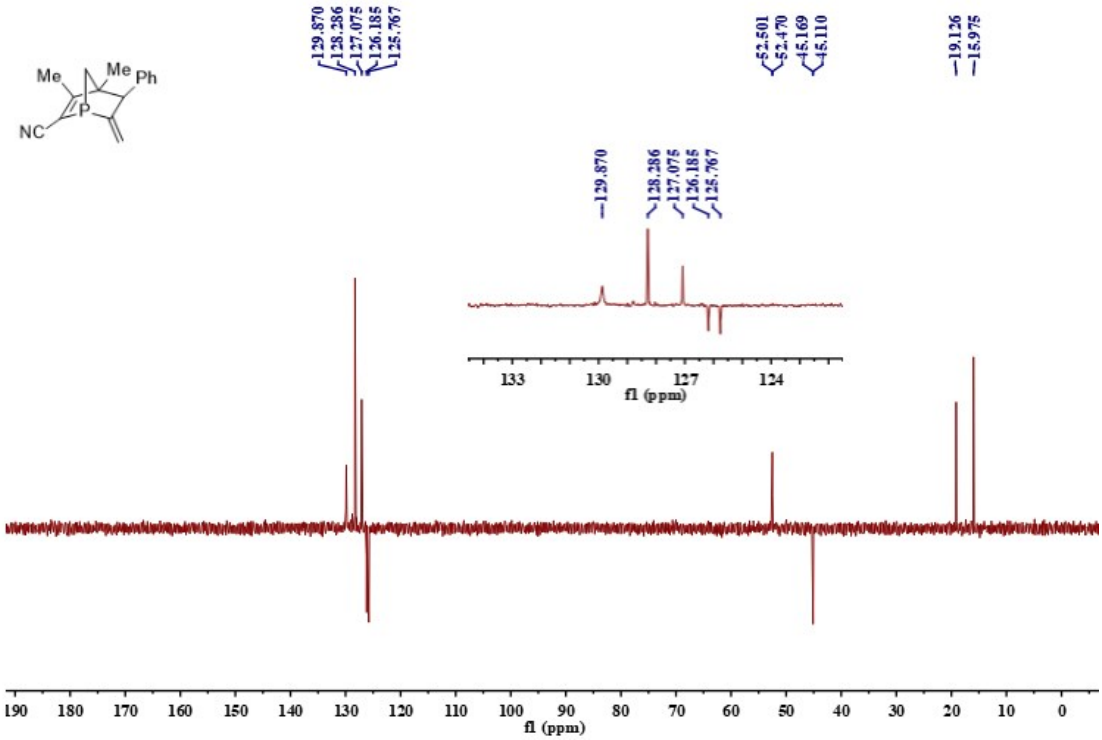
^{13}C $\{^1H\}$ ($CDCl_3$, 75 MHz) NMR of **3ca**



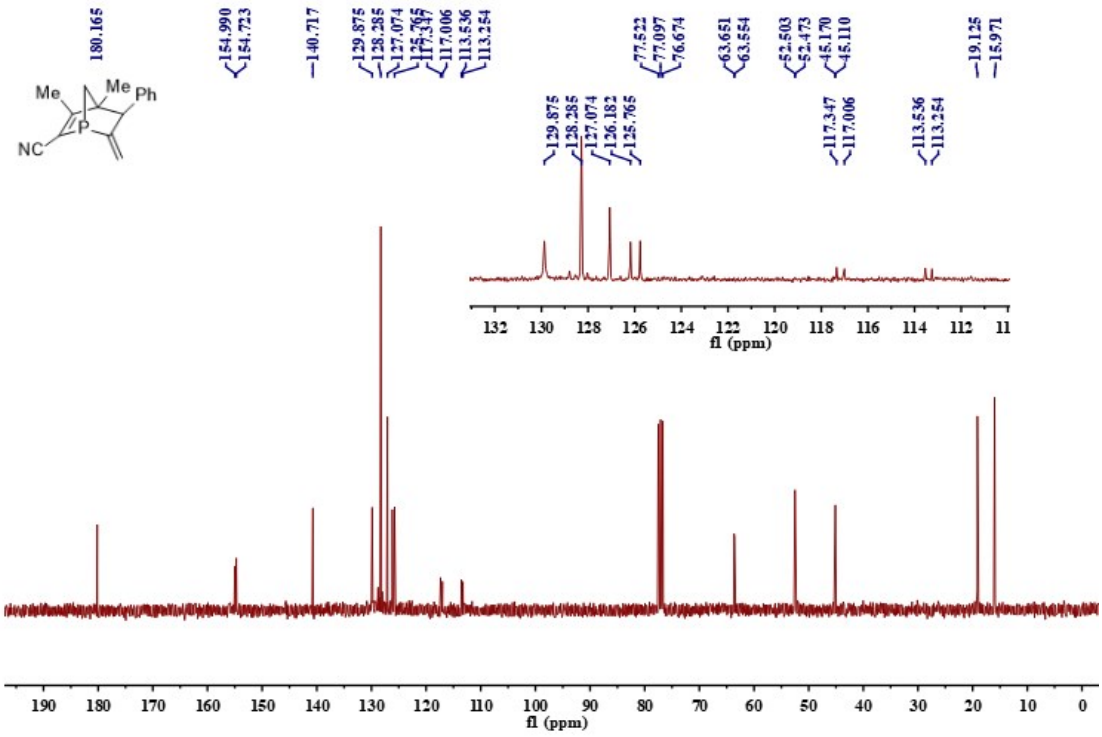
^{31}P ($CDCl_3$, 121 MHz) NMR of *exo*-**3da**



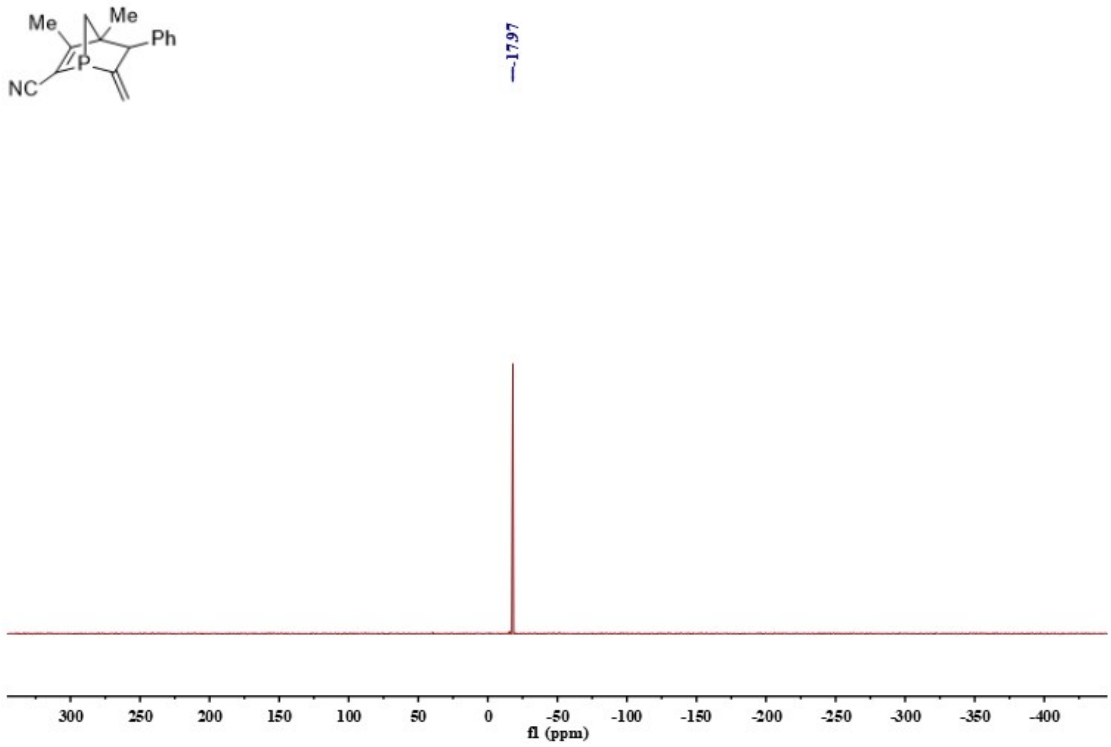
^{1}H ($CDCl_3$, 300 MHz) NMR of *exo*-**3da**



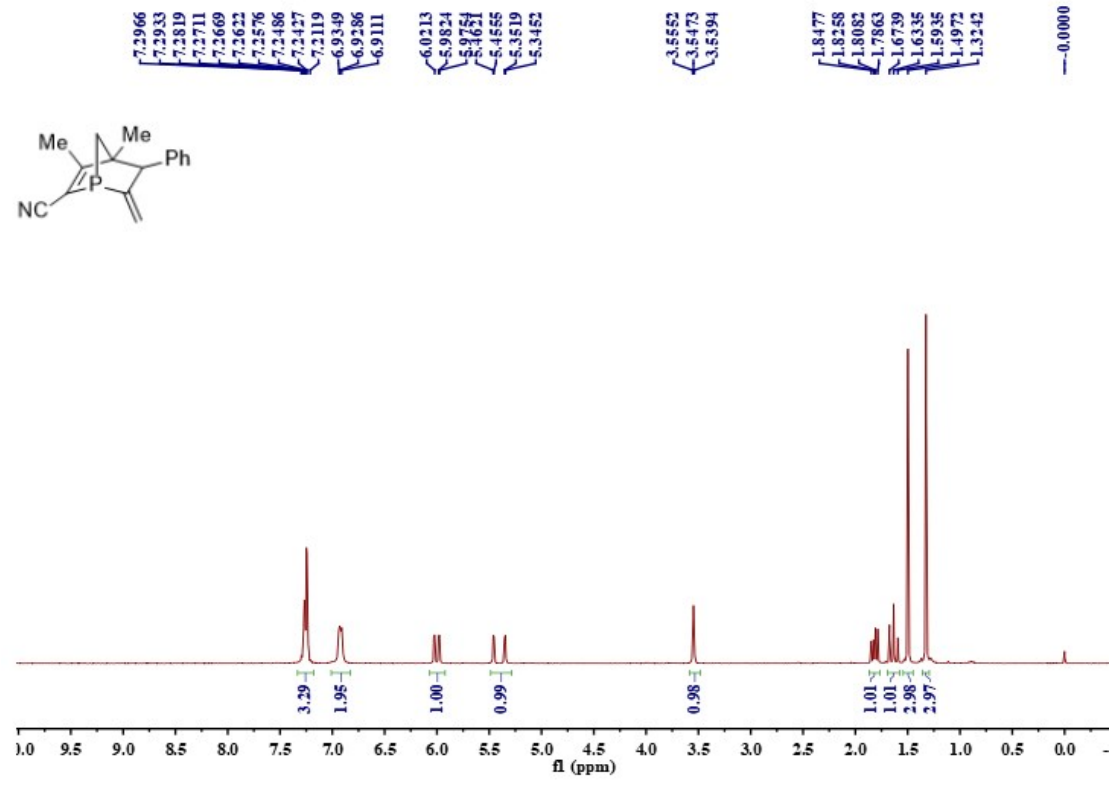
Dept135 ($CDCl_3$, 75 MHz) NMR of *exo*-**3da**



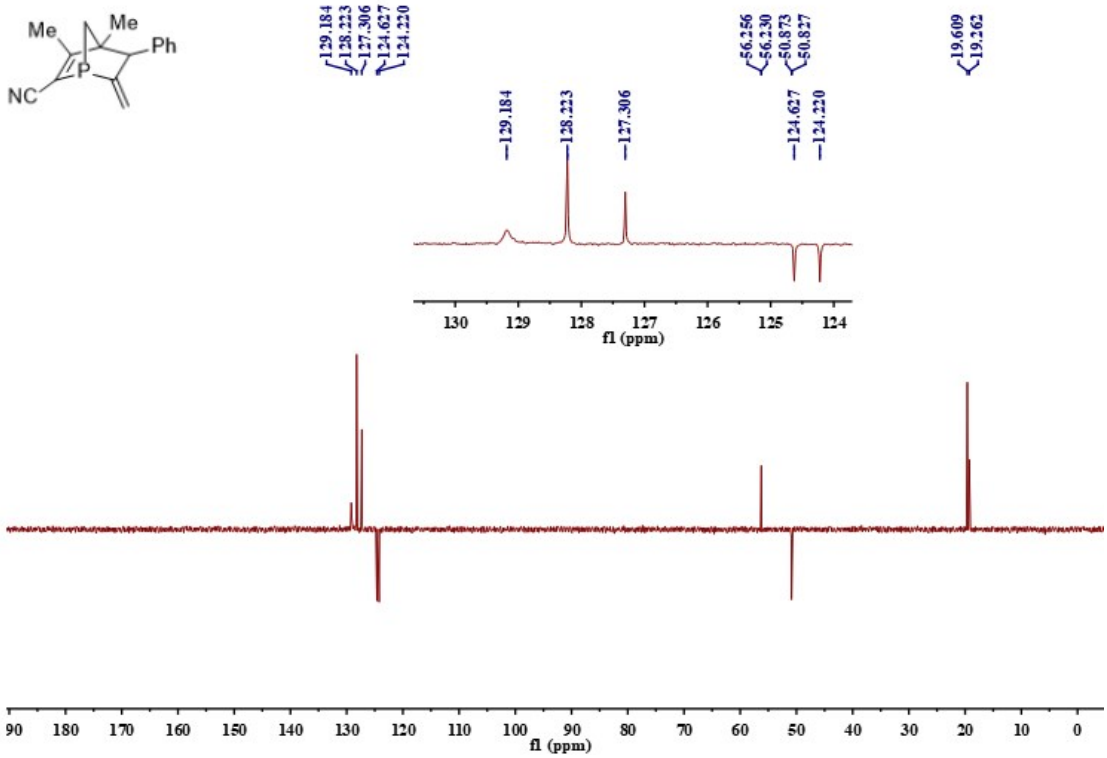
^{13}C $\{^1H\}$ ($CDCl_3$, 75 MHz) NMR of *exo*-**3da**



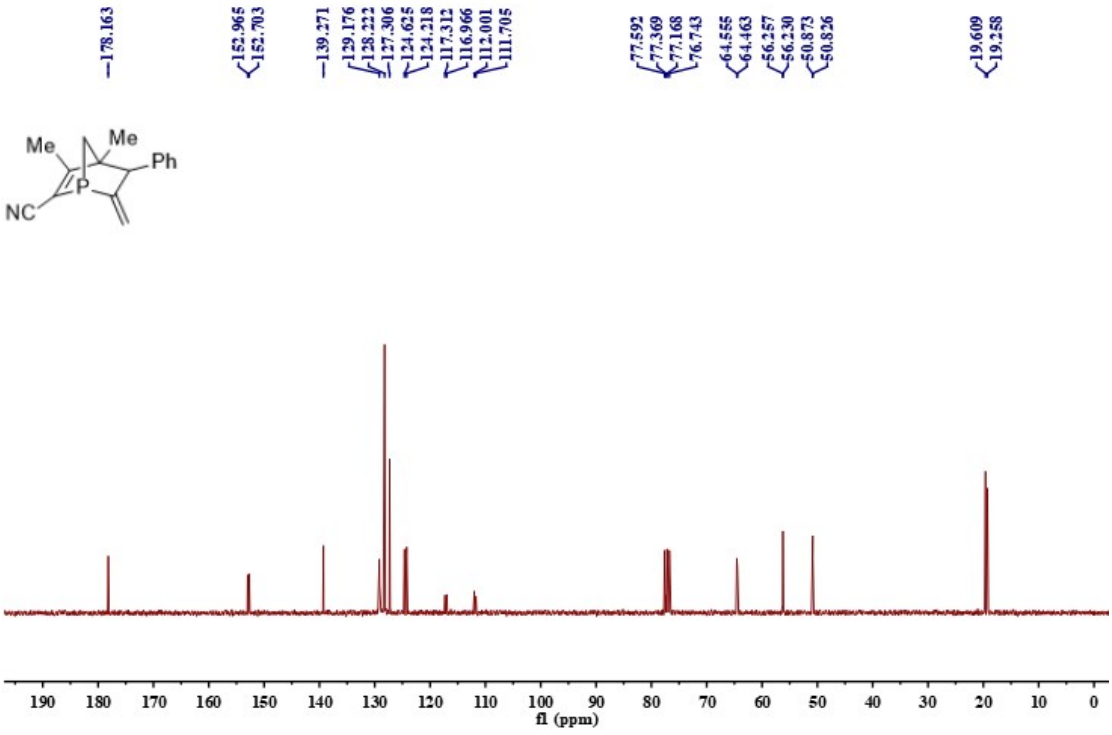
^{31}P ($CDCl_3$, 121 MHz) NMR of *endo*-**3da**



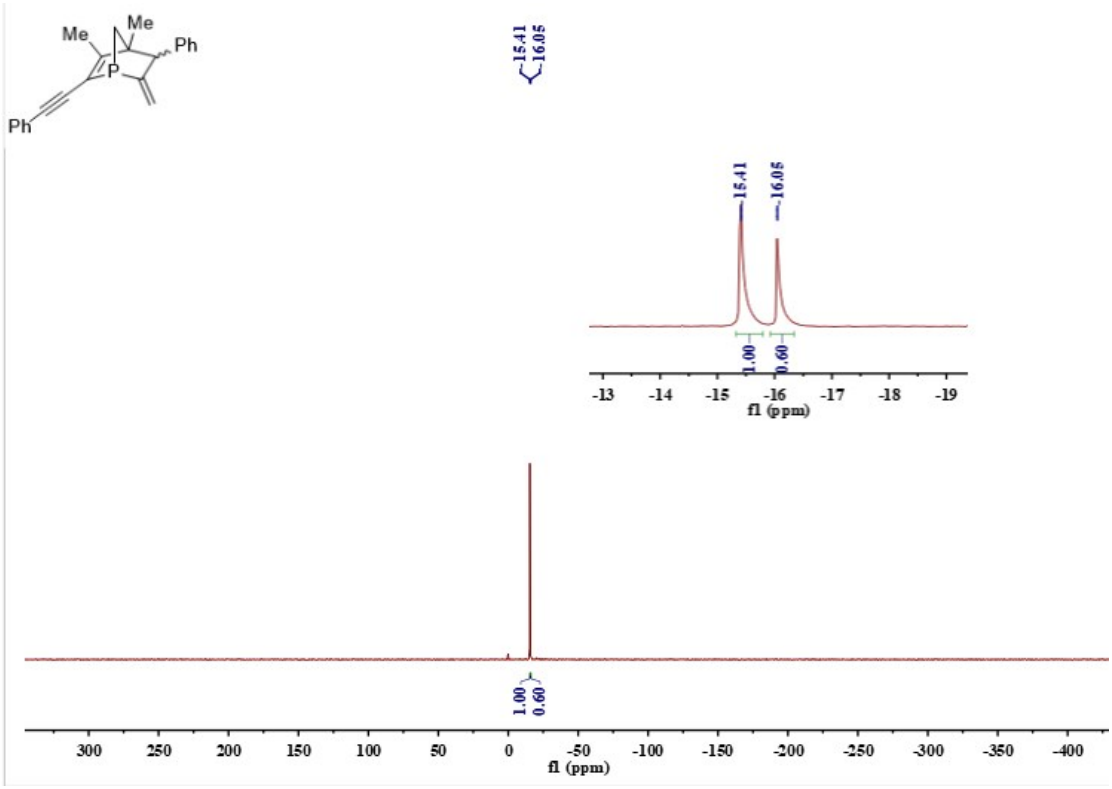
^{1}H ($CDCl_3$, 300 MHz) NMR of *endo*-**3da**



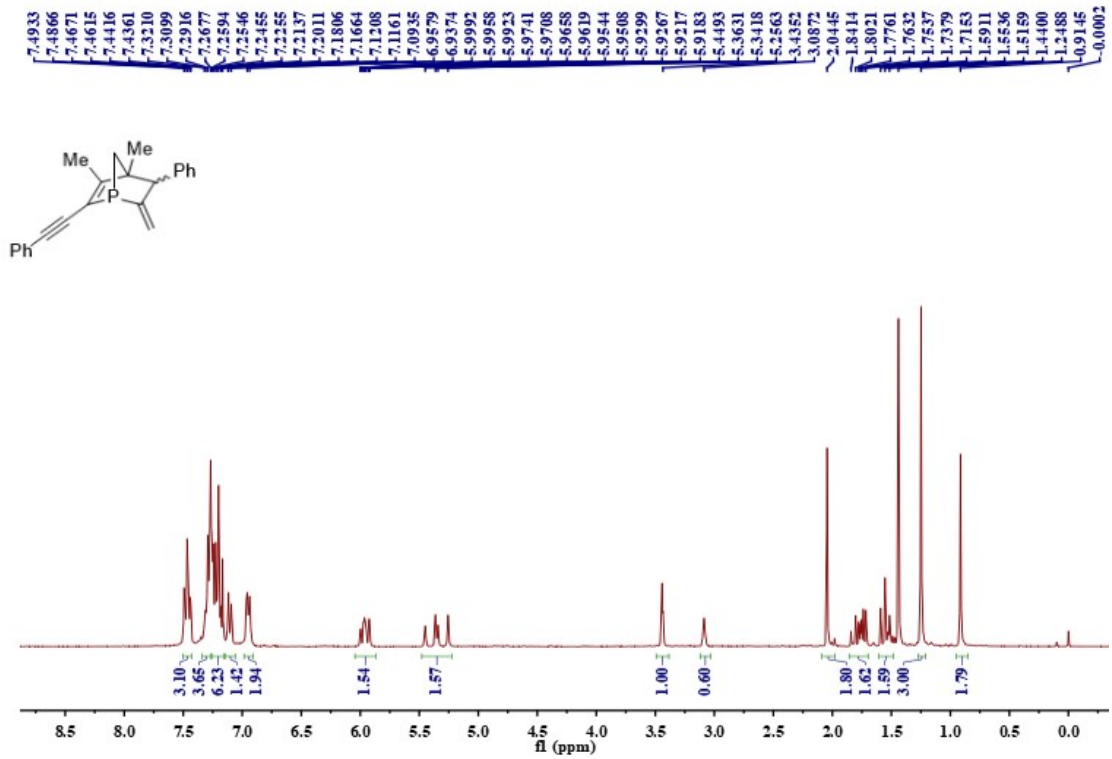
Dept135 ($CDCl_3$, 75 MHz) NMR of *endo*-**3da**



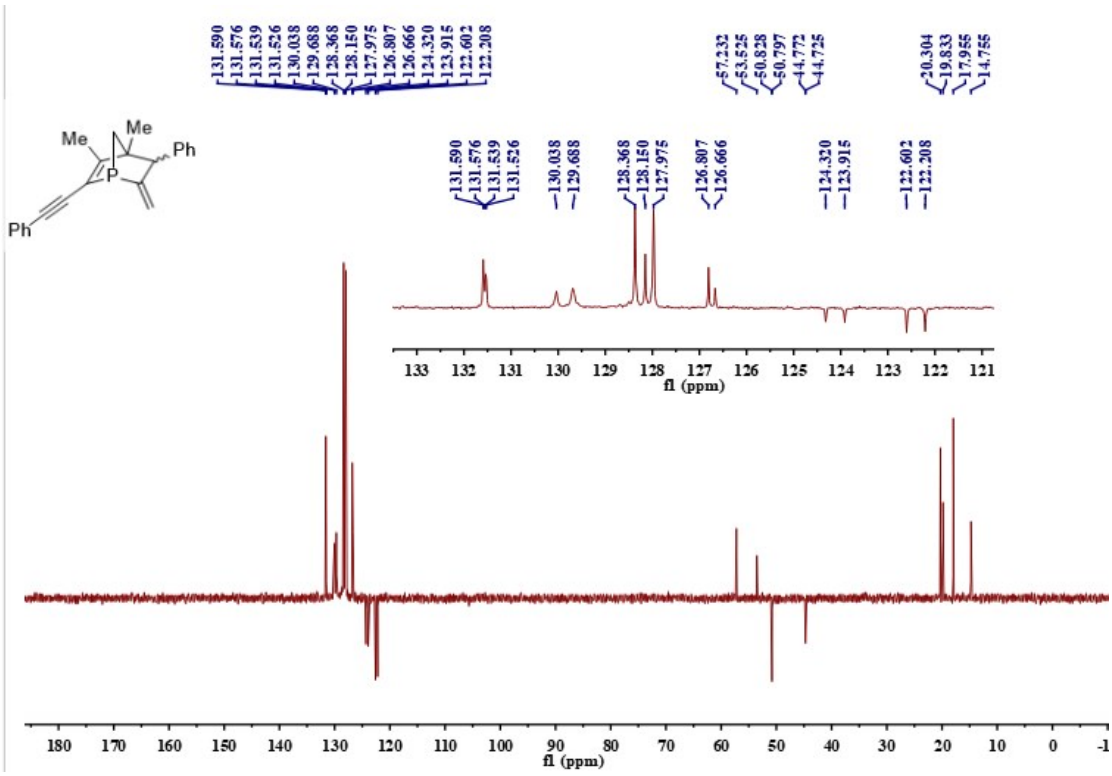
^{13}C $\{^1H\}$ ($CDCl_3$, 75 MHz) NMR of *endo*-**3da**



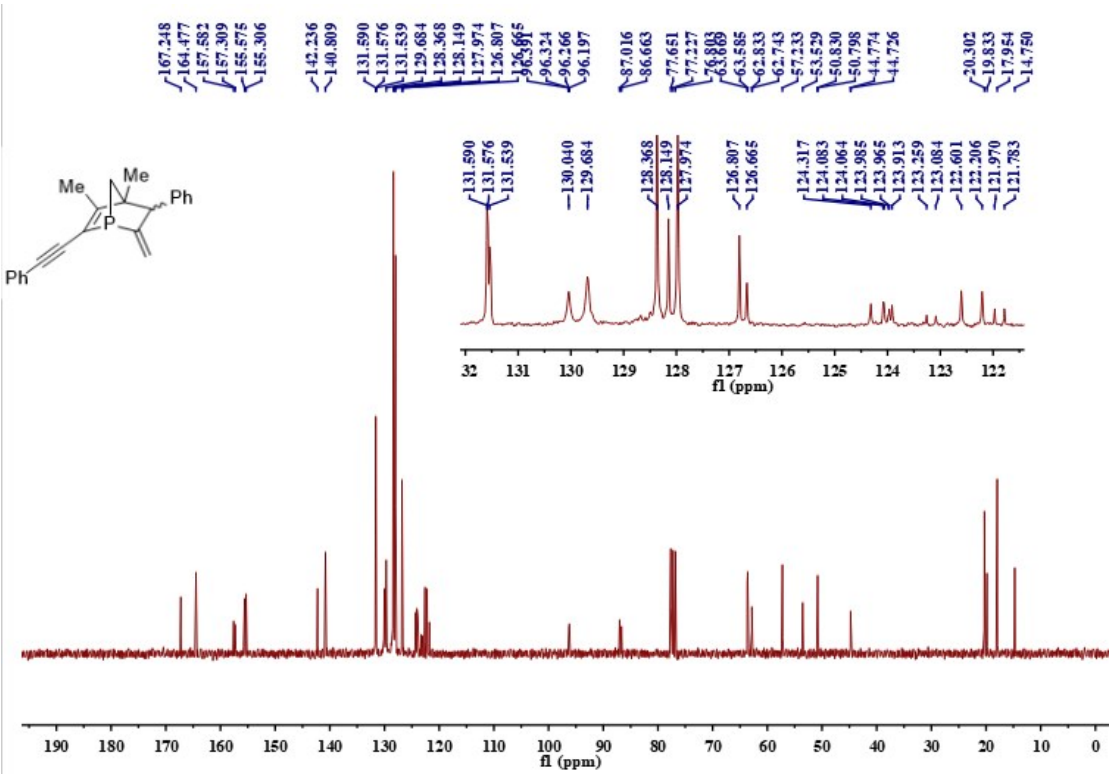
^{31}P ($CDCl_3$, 121 MHz) NMR of **3ea**



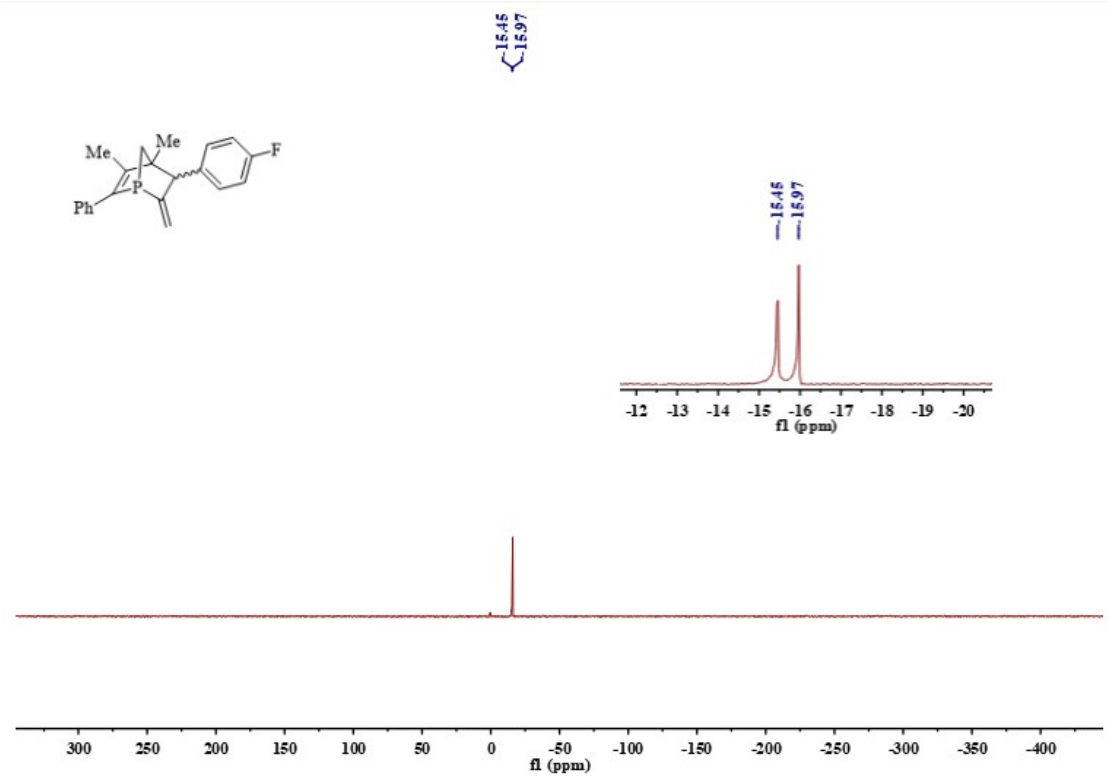
^{1}H ($CDCl_3$, 300 MHz) NMR of **3ea**



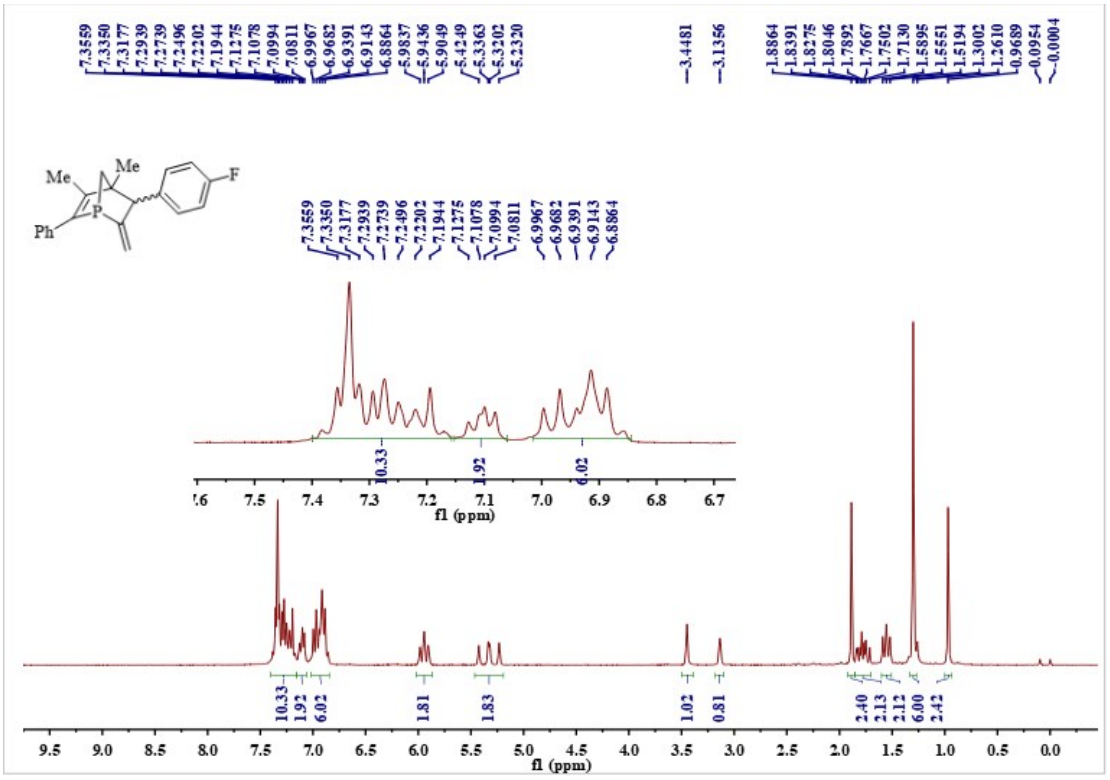
Dept135 ($CDCl_3$, 75 MHz) NMR of **3ea**



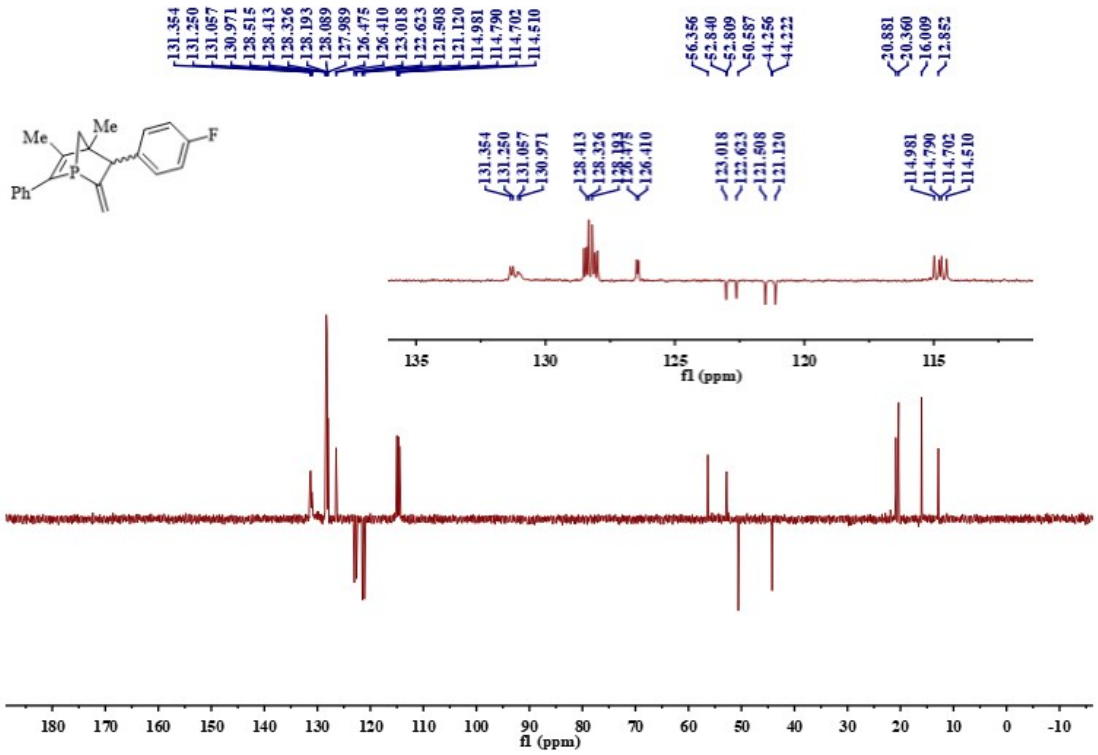
^{13}C $\{^1H\}$ ($CDCl_3$, 75 MHz) NMR of **3ea**



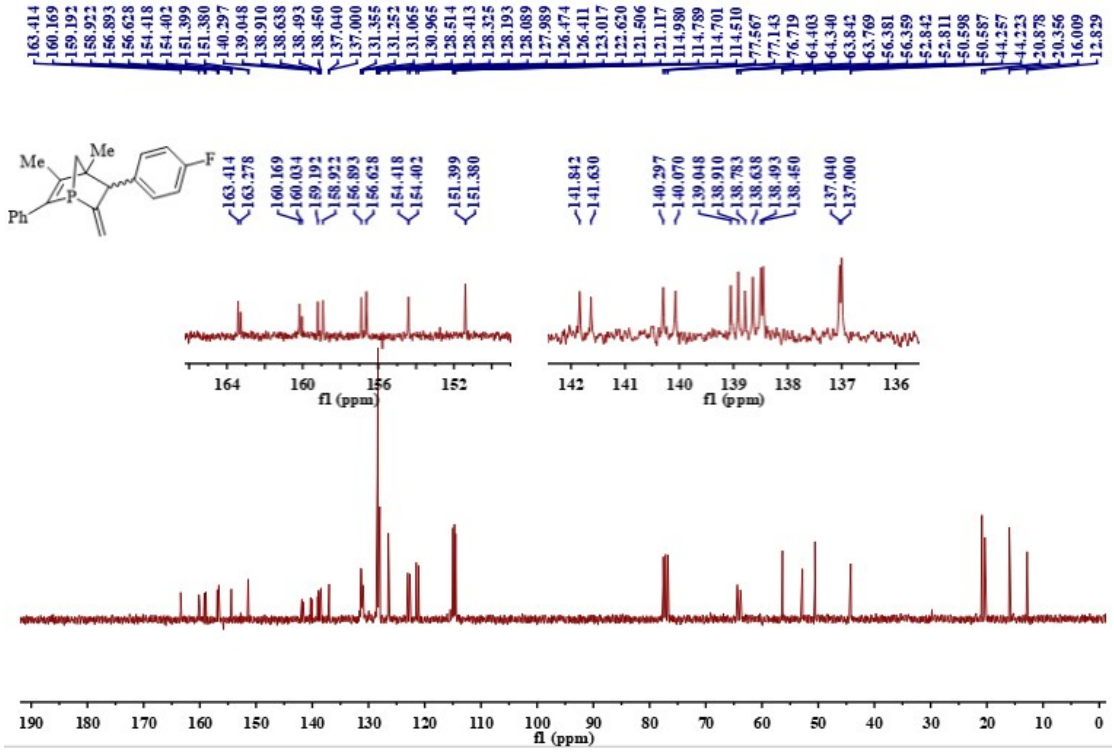
^{31}P ($CDCl_3$, 121 MHz) NMR of **3ab**



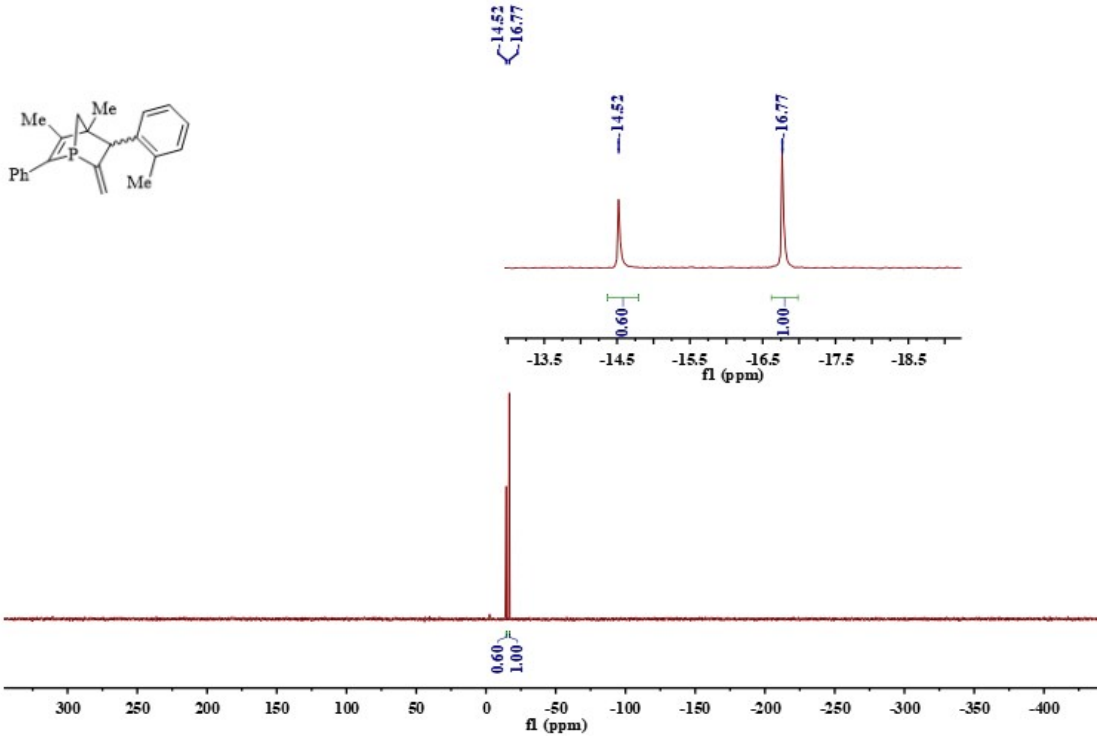
^{1}H ($CDCl_3$, 300 MHz) NMR of **3ab**



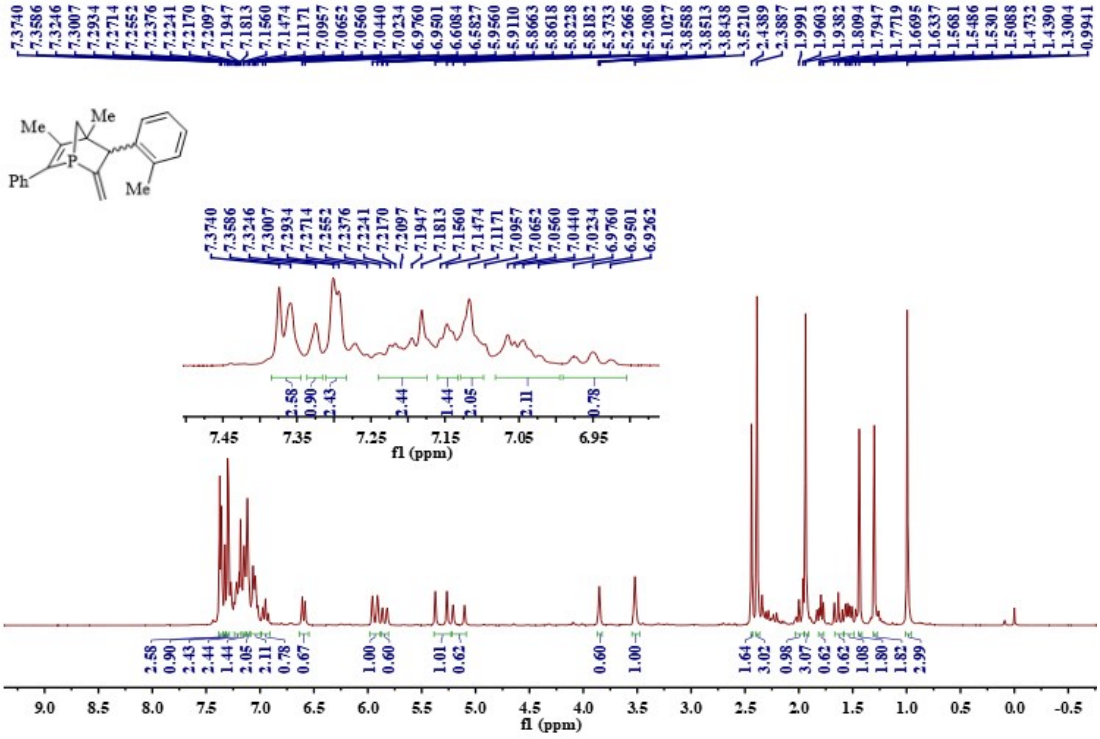
Dept135 ($CDCl_3$, 75 MHz) NMR of **3ab**



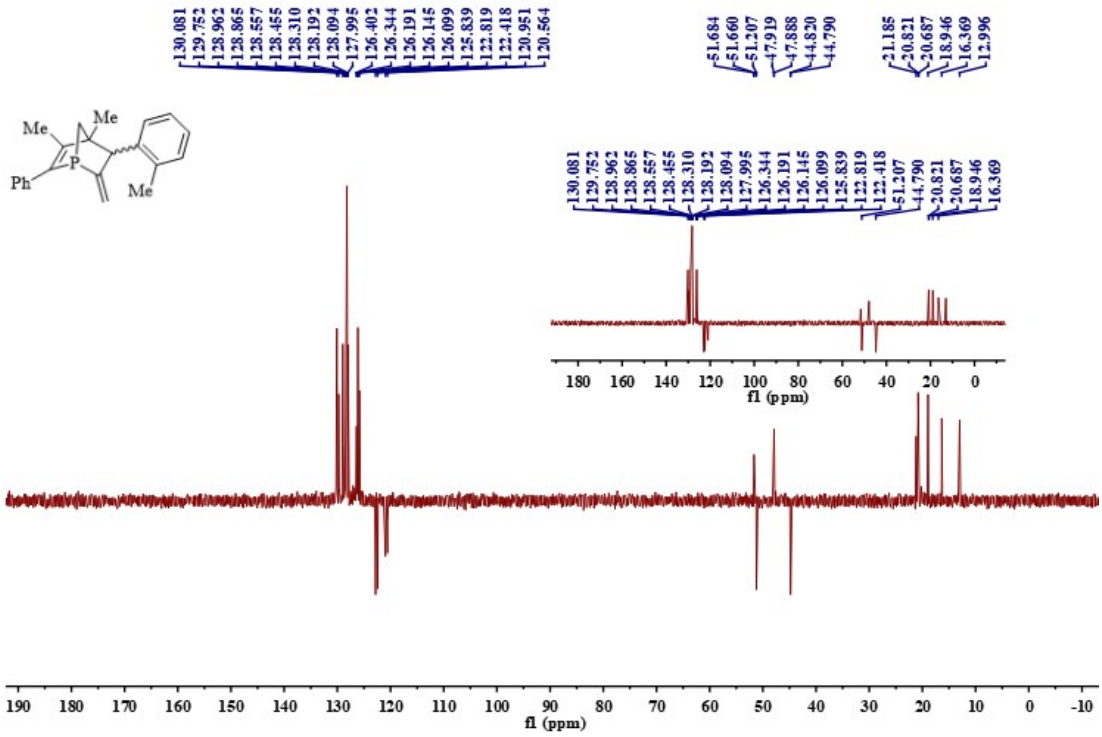
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of **3ab**



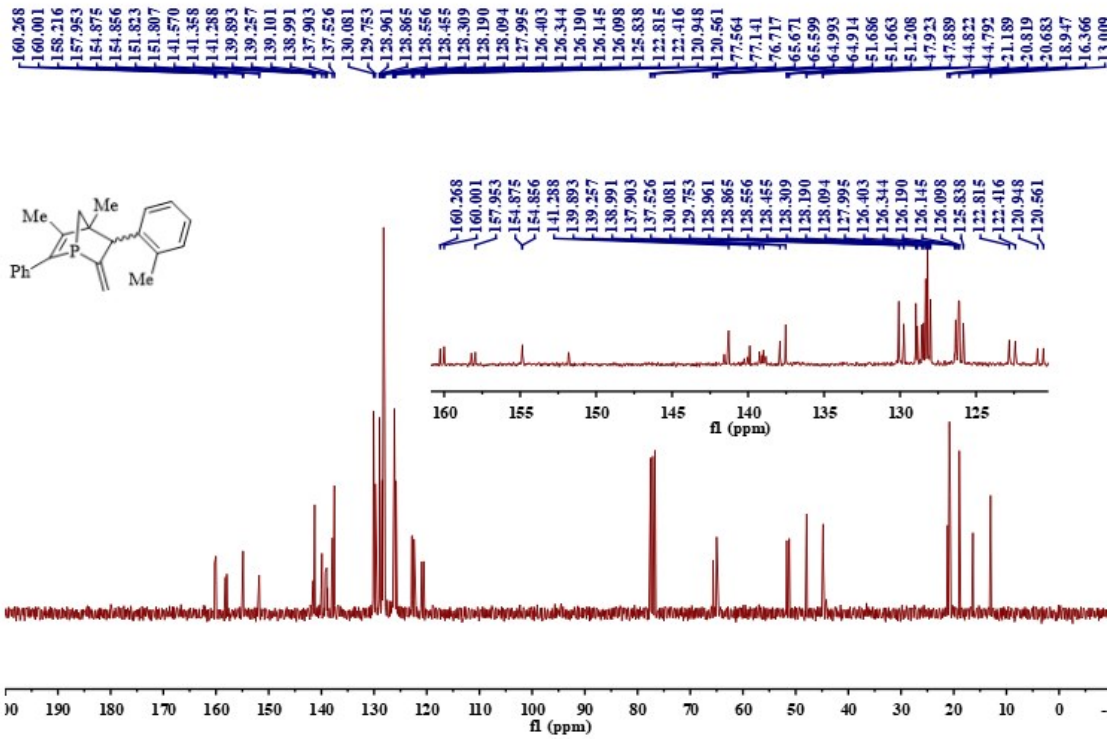
^{31}P ($CDCl_3$, 121 MHz) NMR of **3ac**



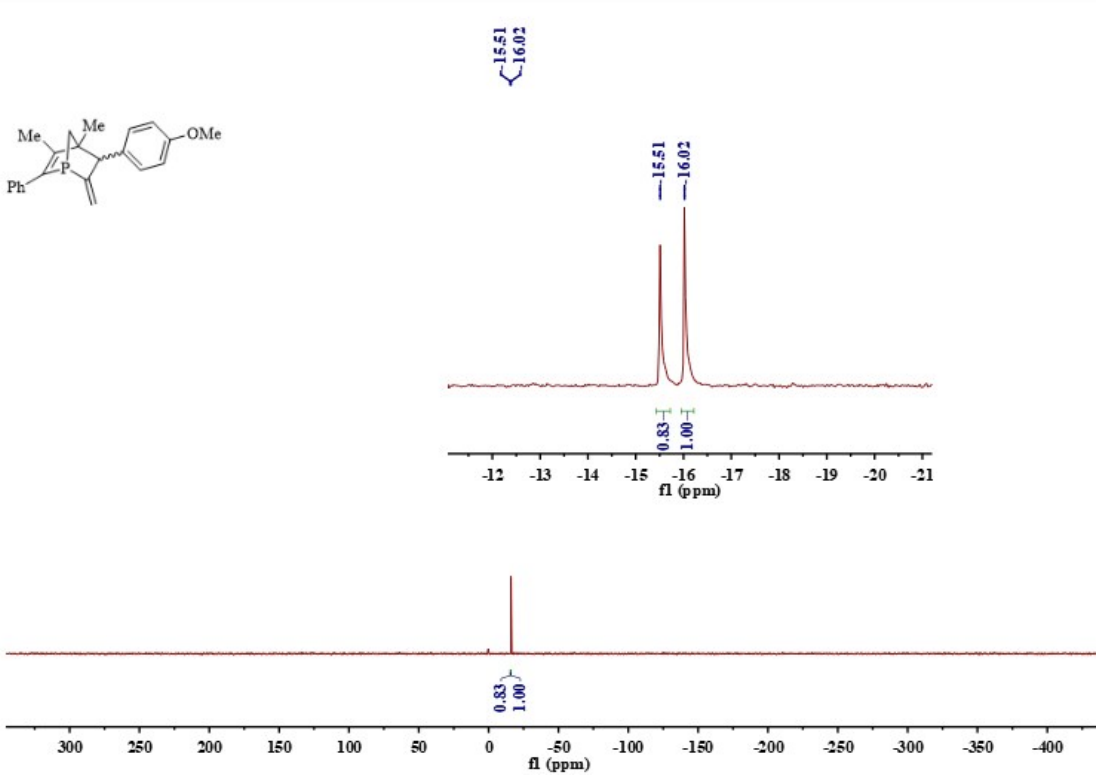
^{1}H ($CDCl_3$, 300 MHz) NMR of **3ac**



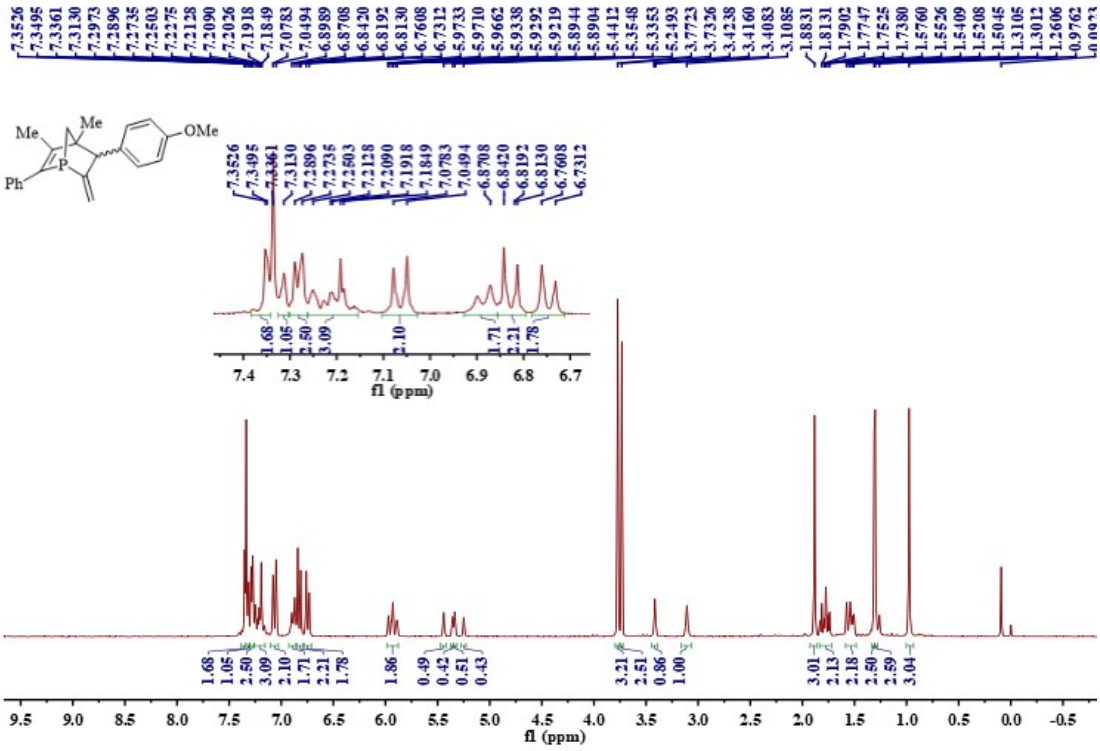
Dept135 ($CDCl_3$, 75 MHz) NMR of **3ac**



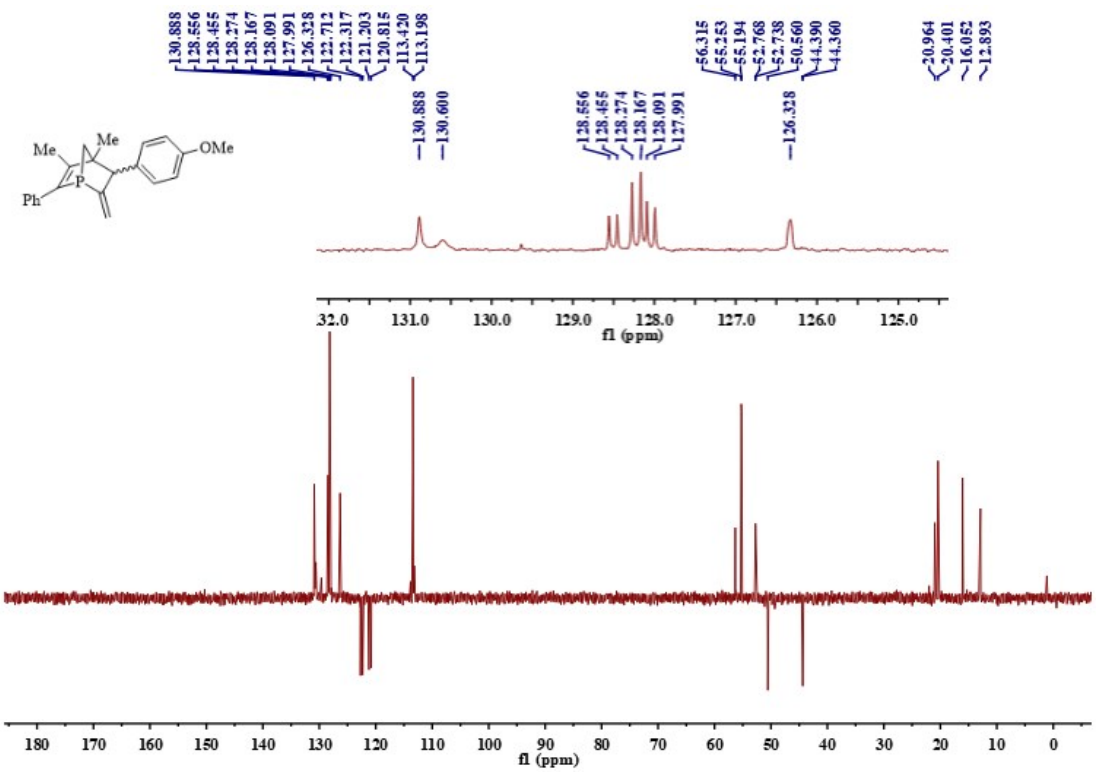
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of **3ac**



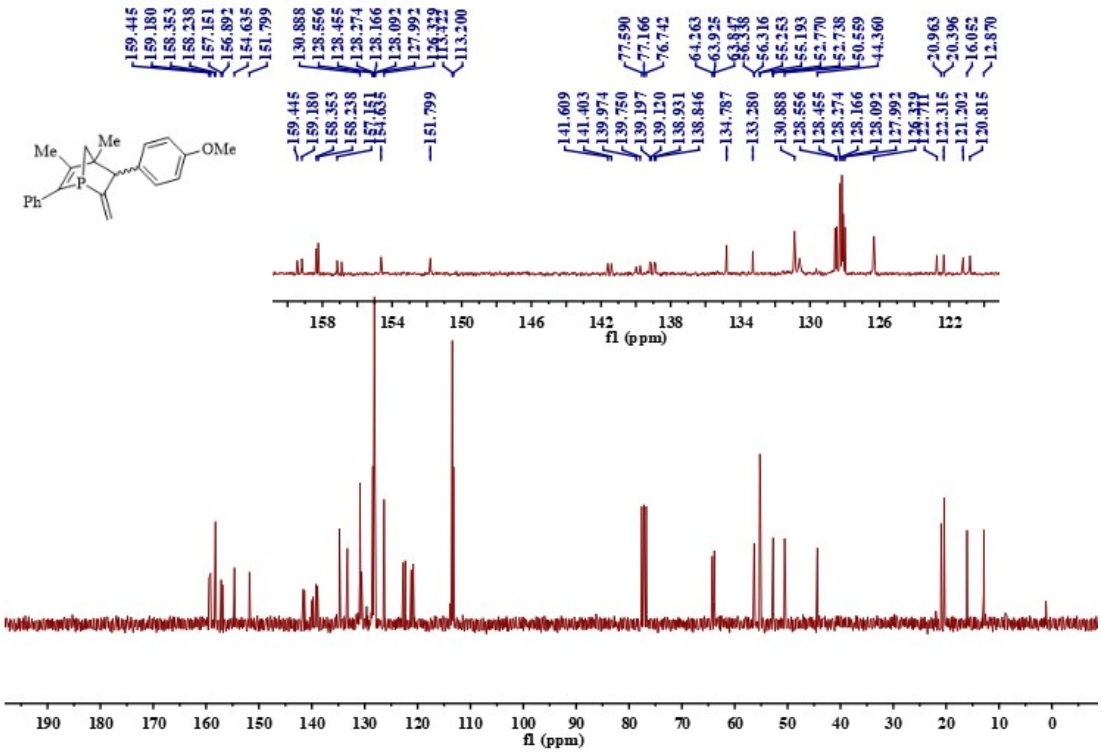
^{31}P ($CDCl_3$, 121 MHz) NMR of **3ad**



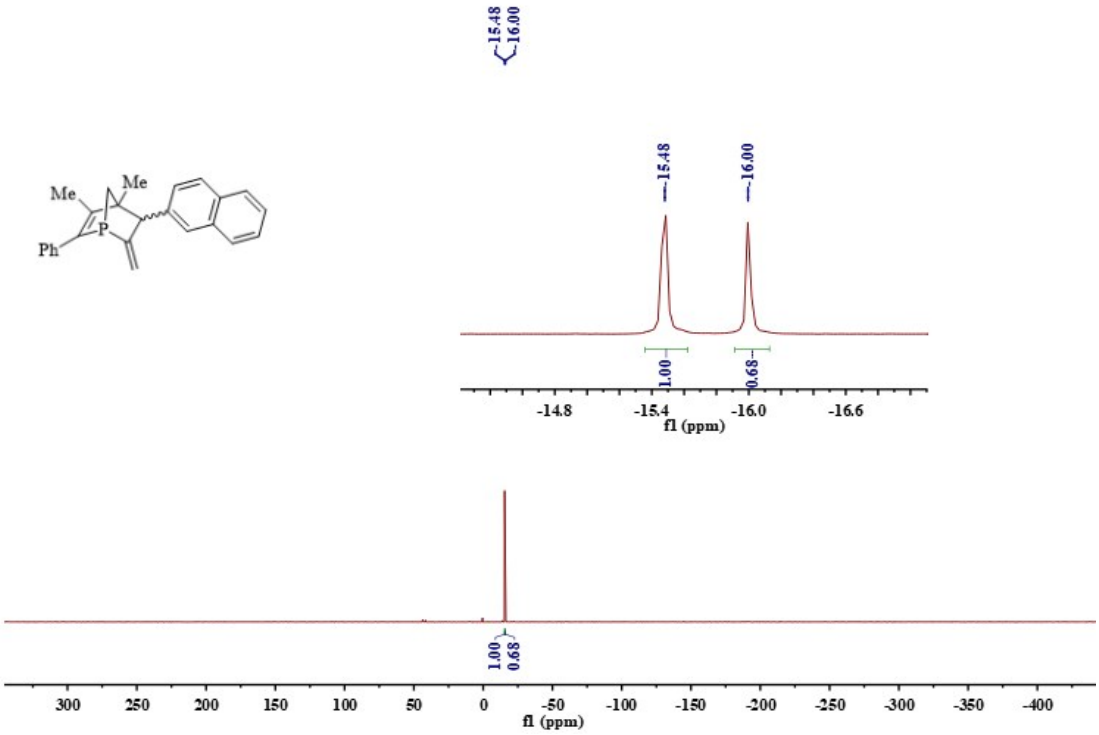
^{1}H ($CDCl_3$, 300 MHz) NMR of **3ad**



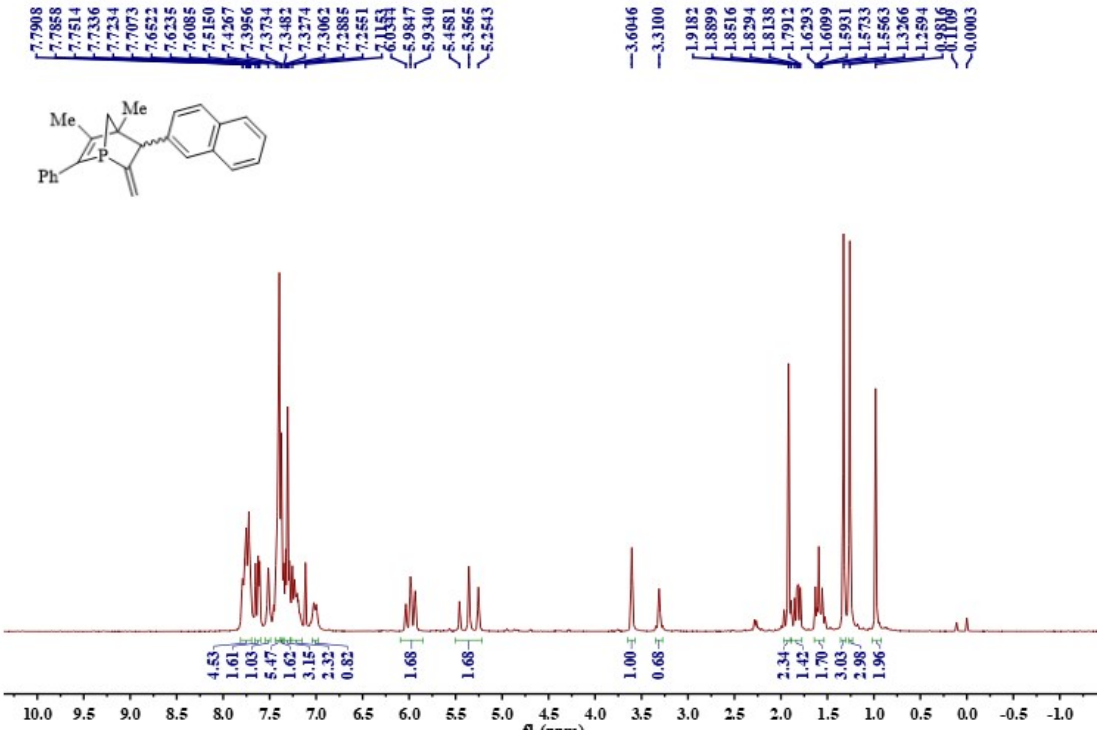
Dept135 ($CDCl_3$, 75 MHz) NMR of **3ad**



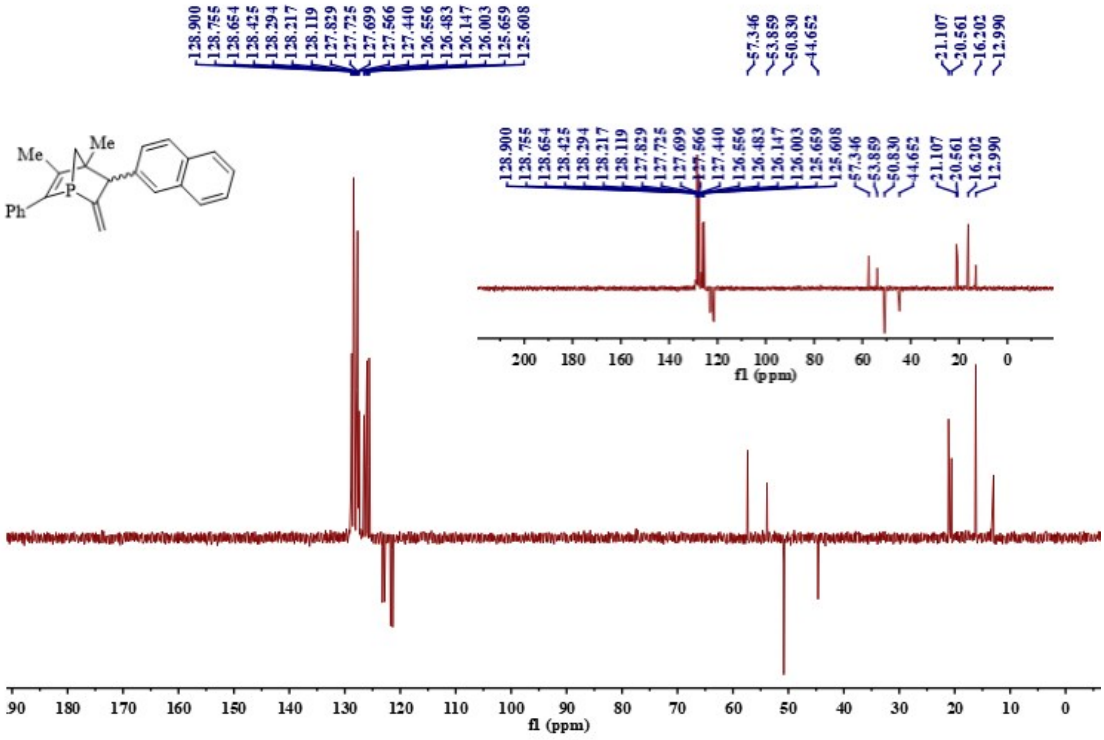
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of **3ad**



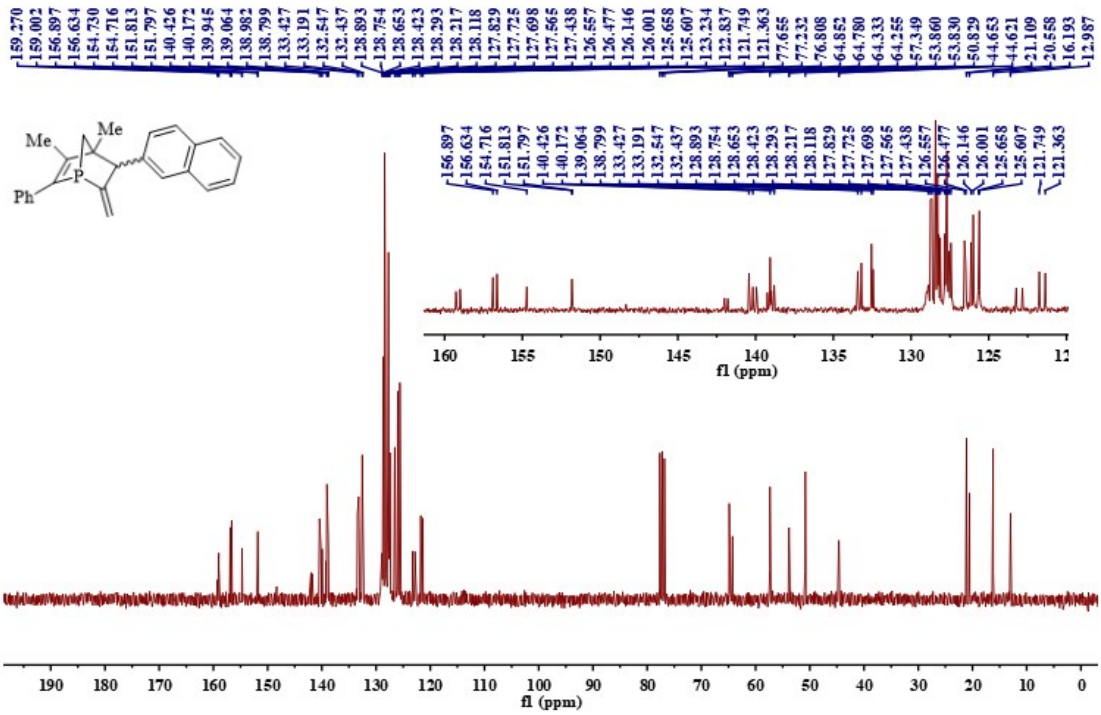
^{31}P ($CDCl_3$, 121 MHz) NMR of **3ae**



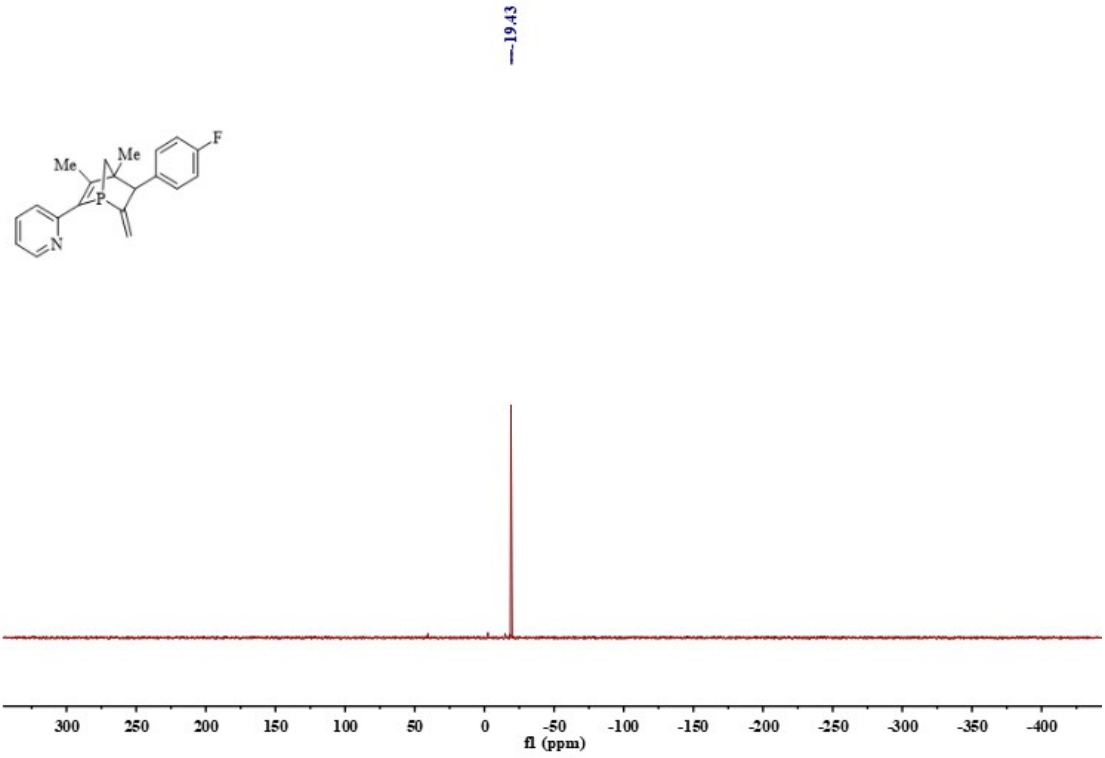
^{1}H ($CDCl_3$, 300 MHz) NMR of **3ae**



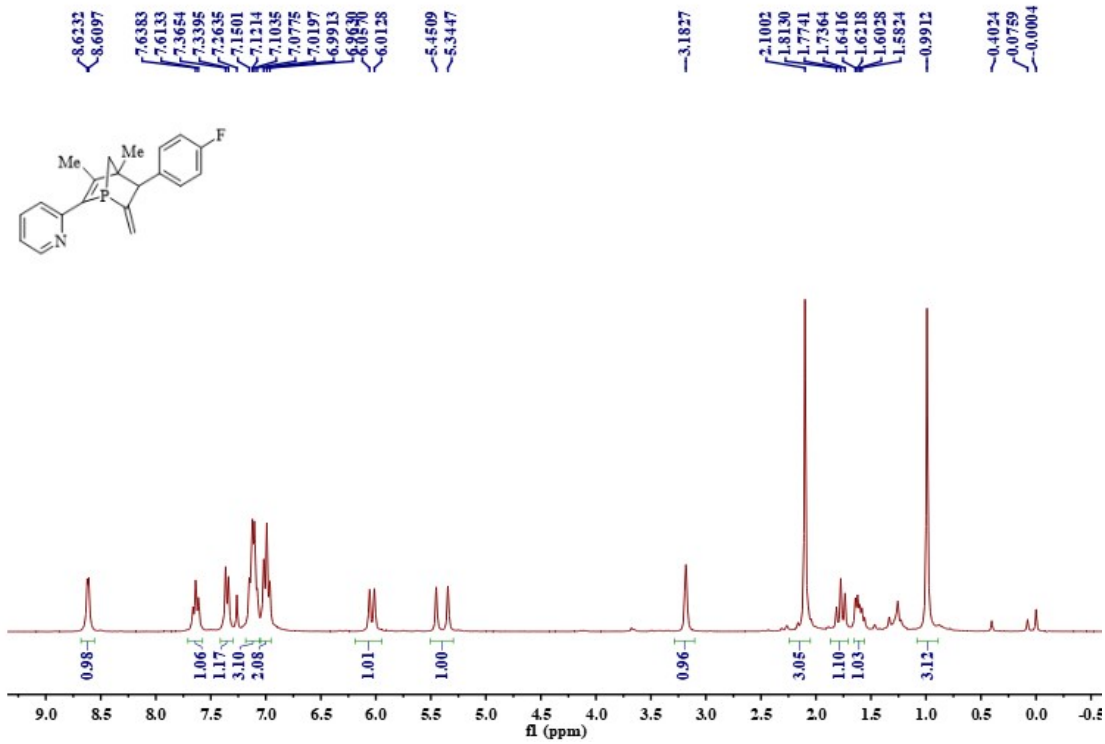
Dept135 ($CDCl_3$, 75 MHz) NMR of **3ae**



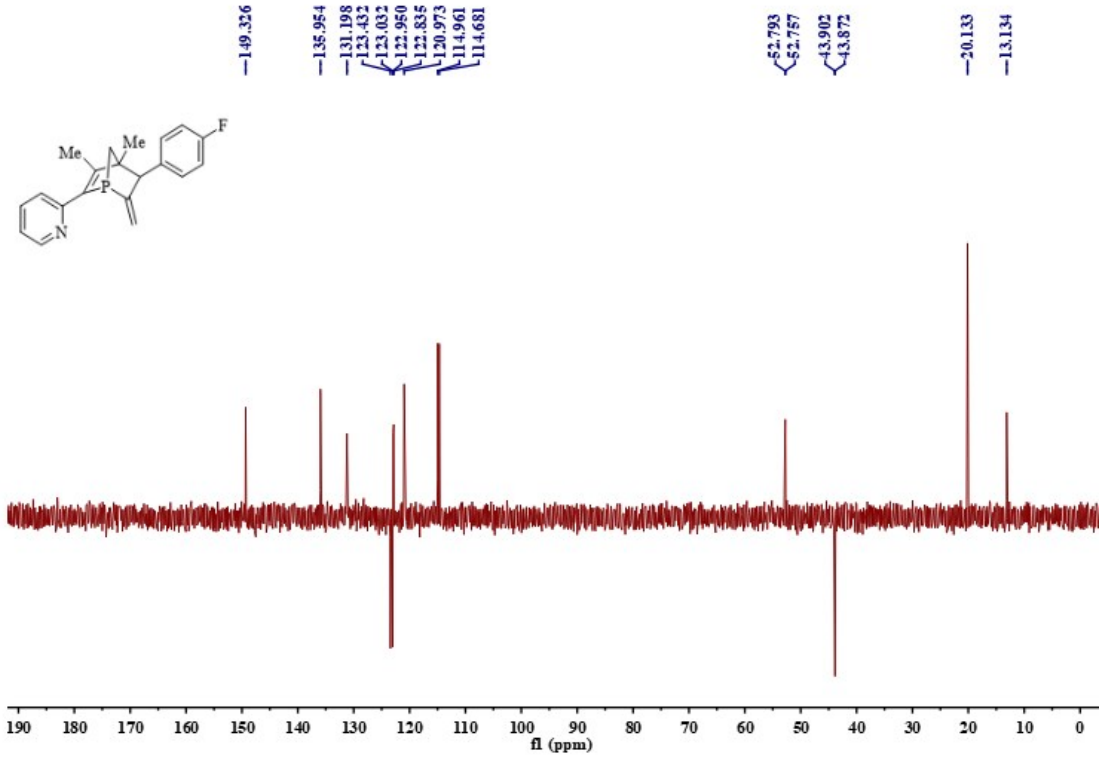
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of **3ae**



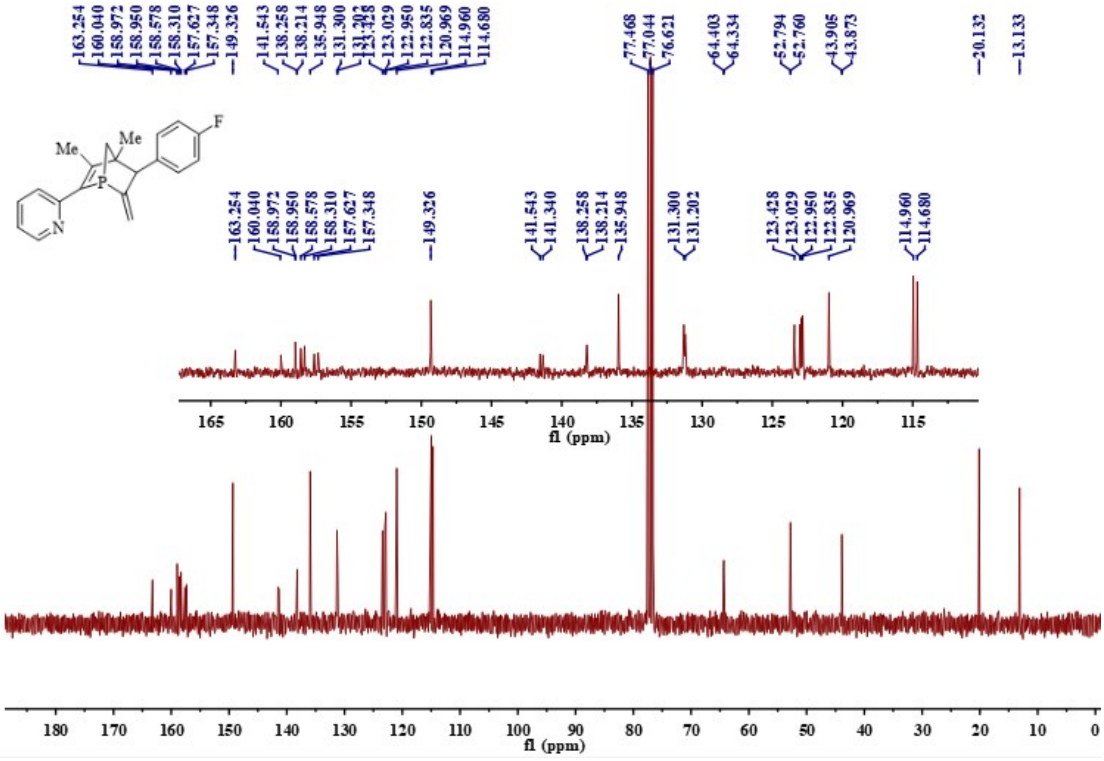
^{31}P ($CDCl_3$, 121 MHz) NMR of *exo*-**3bb**



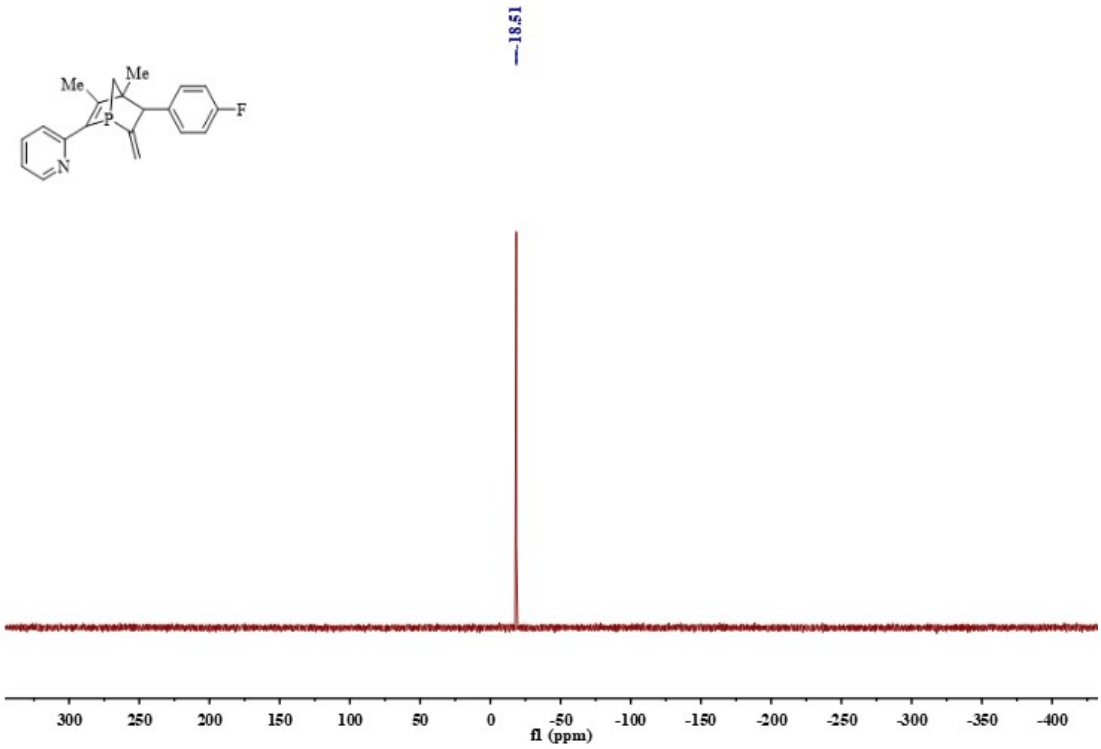
^{1}H ($CDCl_3$, 300 MHz) NMR of *exo*-**3bb**



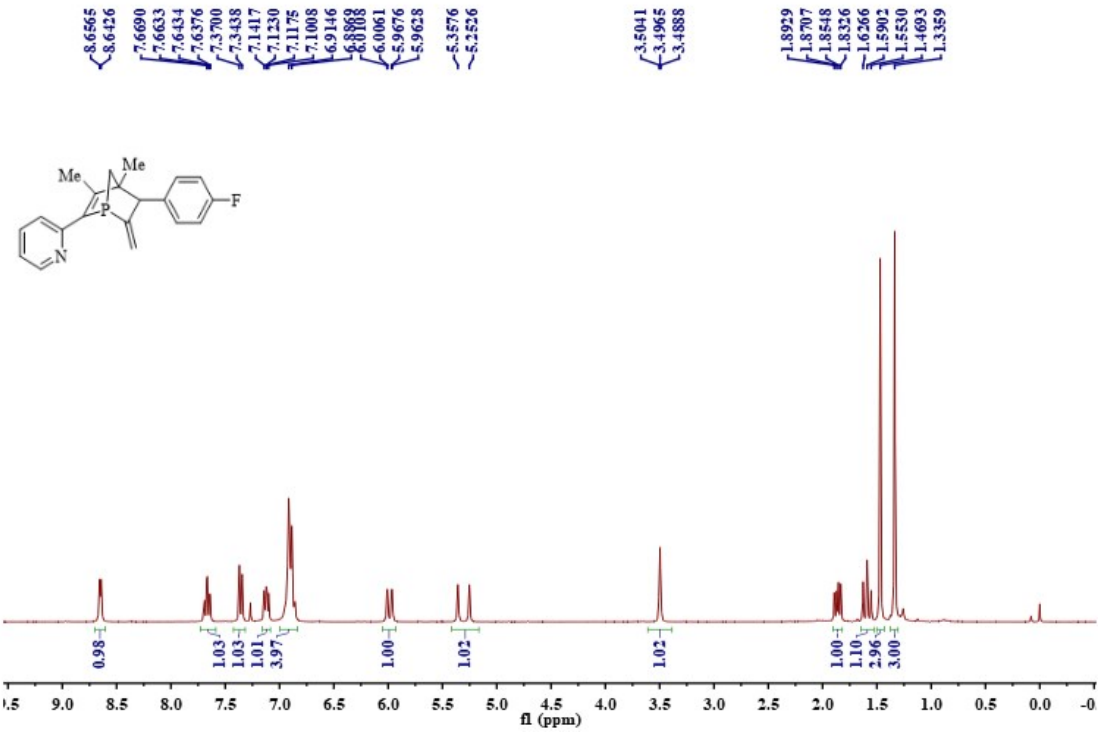
Dept135 ($CDCl_3$, 75 MHz) NMR of *exo*-**3bb**



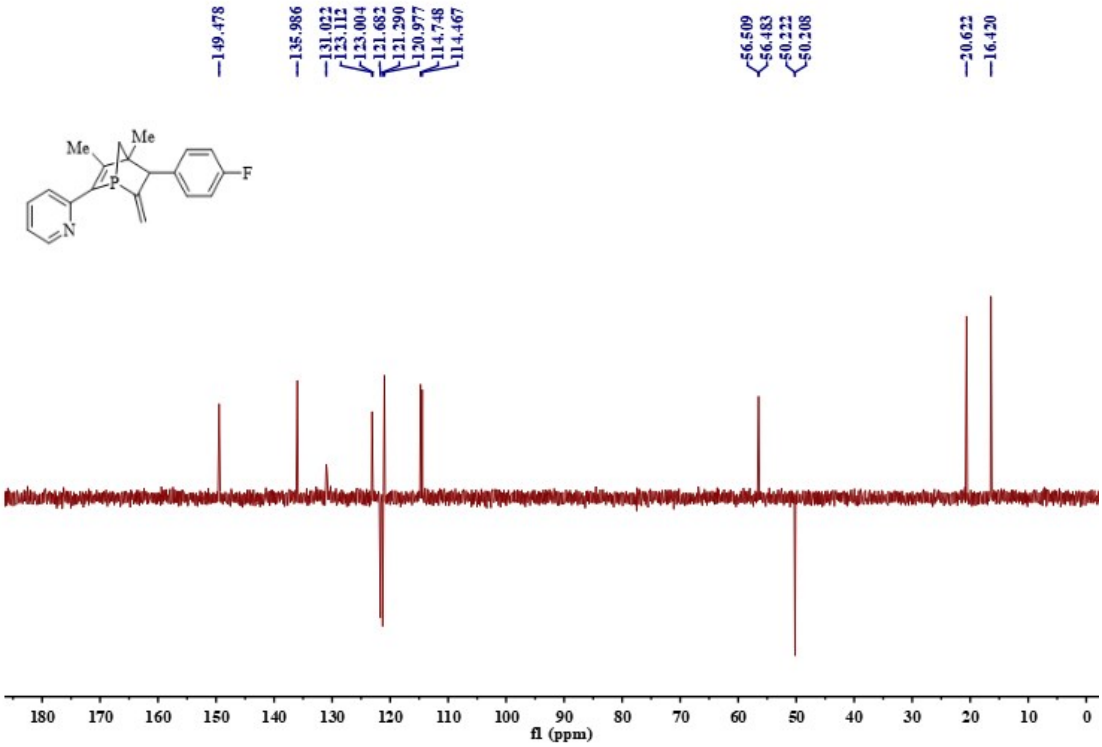
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of *exo*-**3bb**



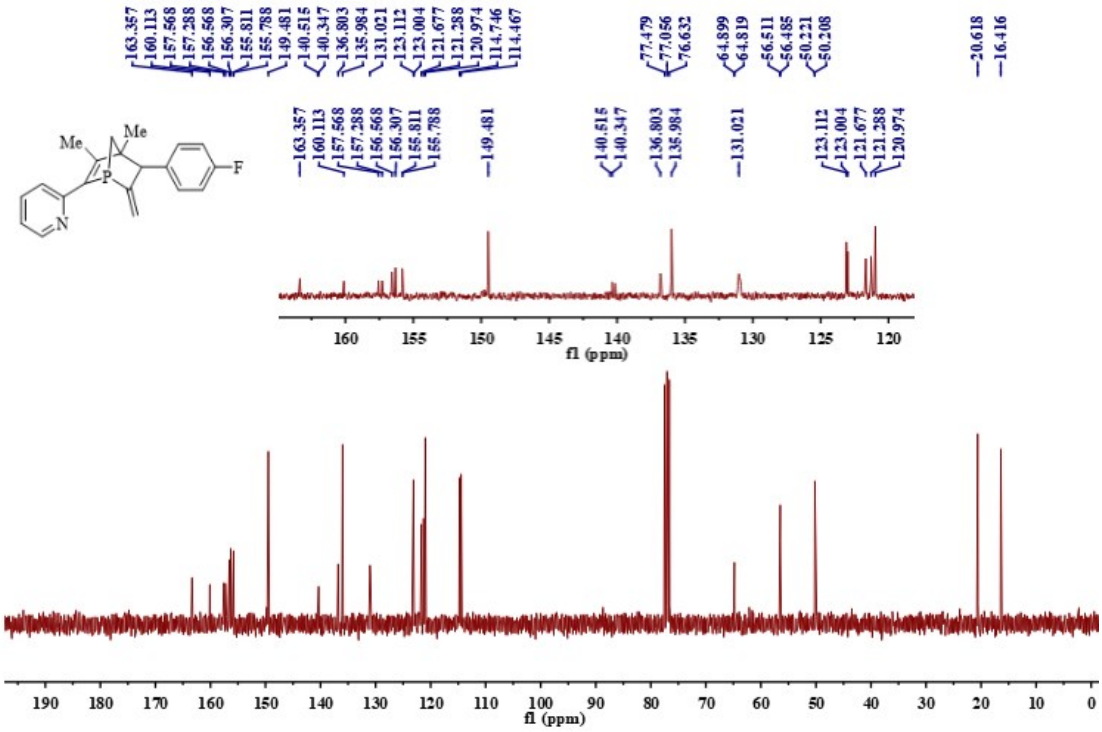
^{31}P ($CDCl_3$, 121 MHz) NMR of *endo*-**3bb**



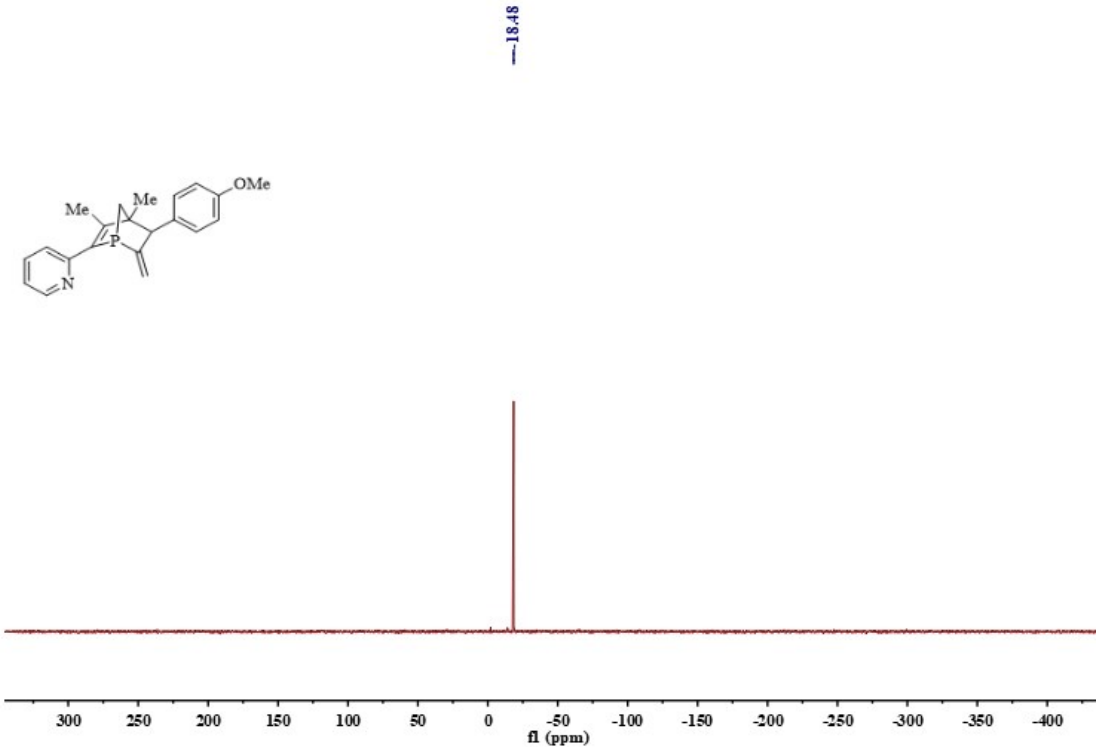
^{1}H ($CDCl_3$, 300 MHz) NMR of *endo*-**3bb**



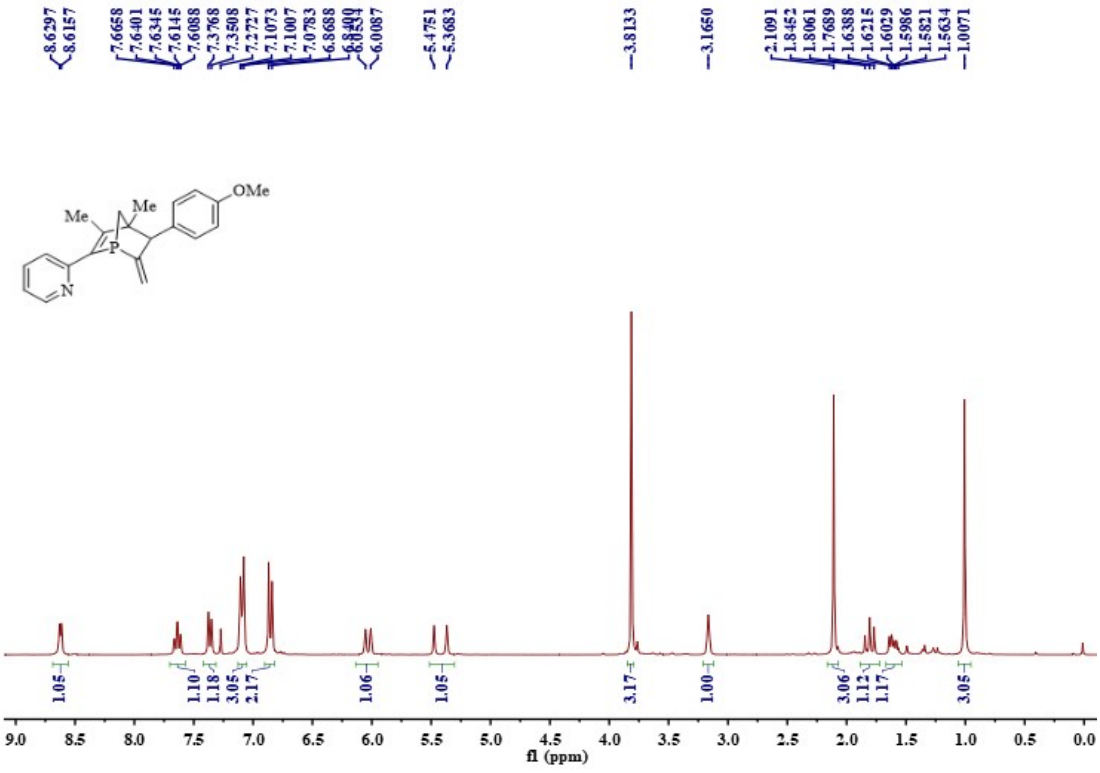
Dept135 ($CDCl_3$, 75 MHz) NMR of *endo*-**3bb**



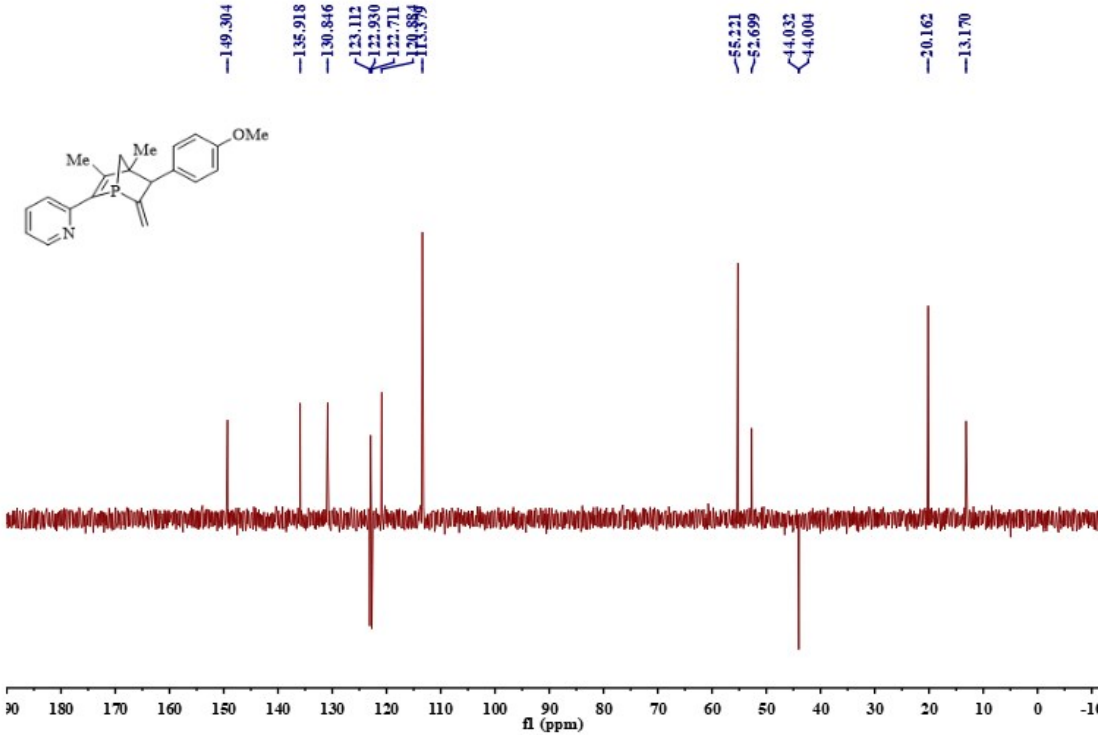
^{13}C $\{^1H\}$ ($CDCl_3$, 75 MHz) NMR of *endo*-**3bb**



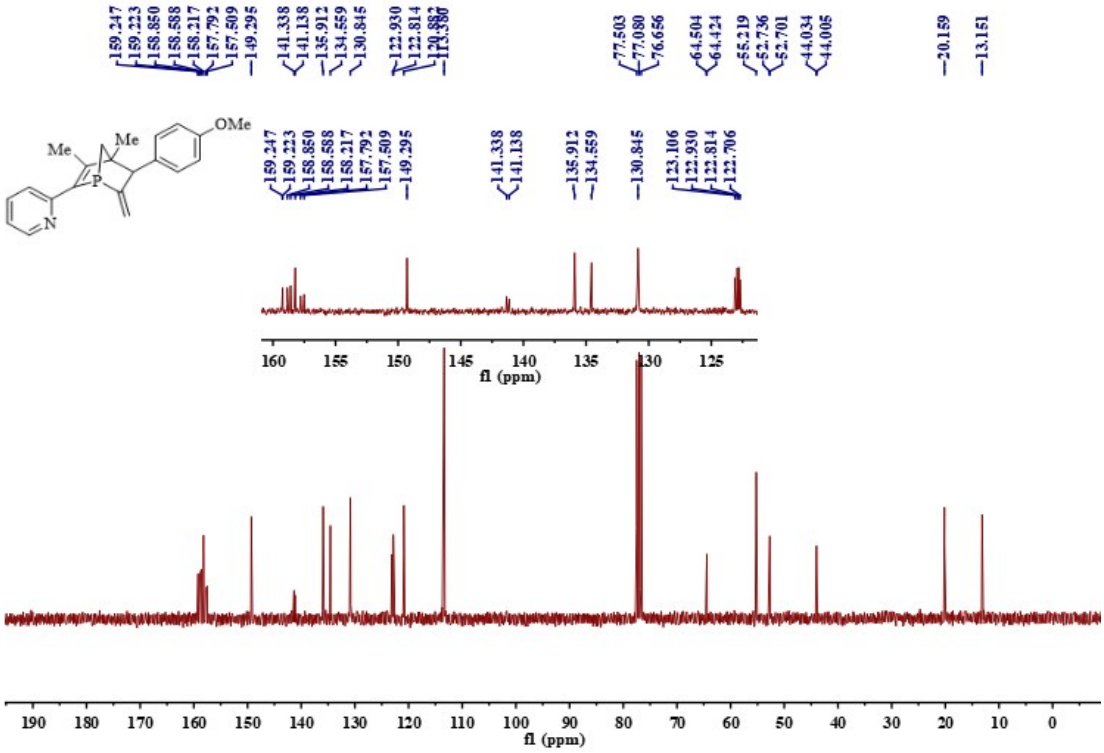
^{31}P ($CDCl_3$, 121 MHz) NMR of *exo*-**3bd**



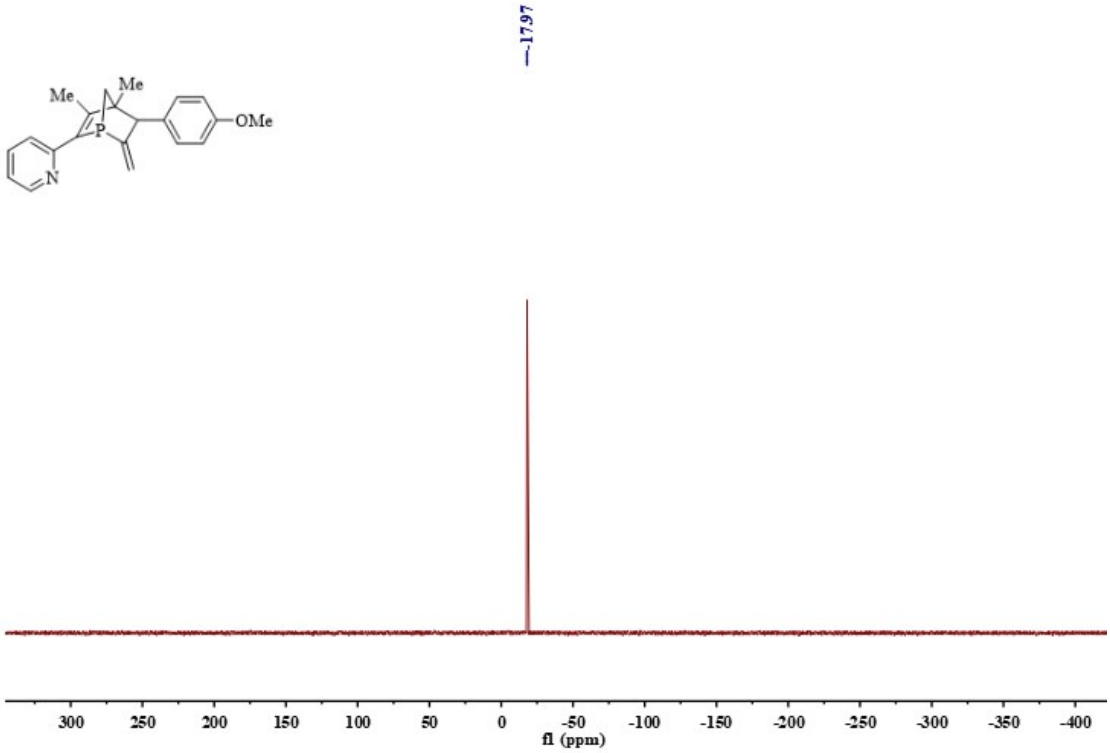
^{1}H ($CDCl_3$, 300 MHz) NMR of *exo*-**3bd**



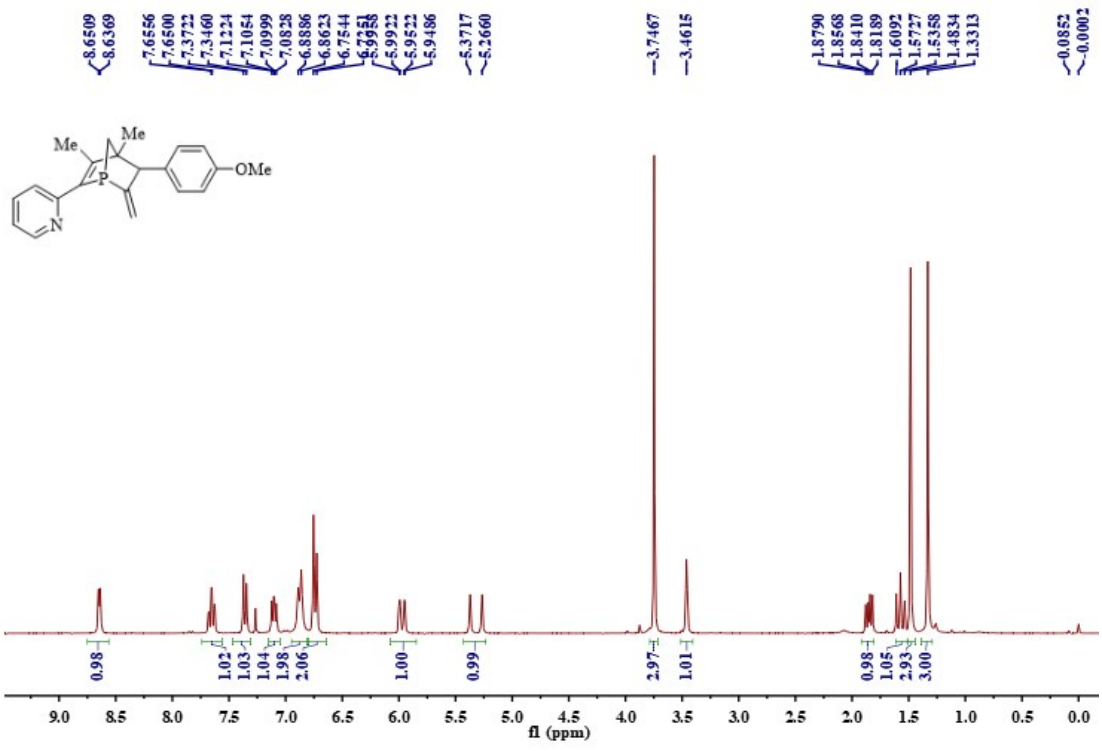
Dept135 ($CDCl_3$, 75 MHz) NMR of *exo*-**3bd**



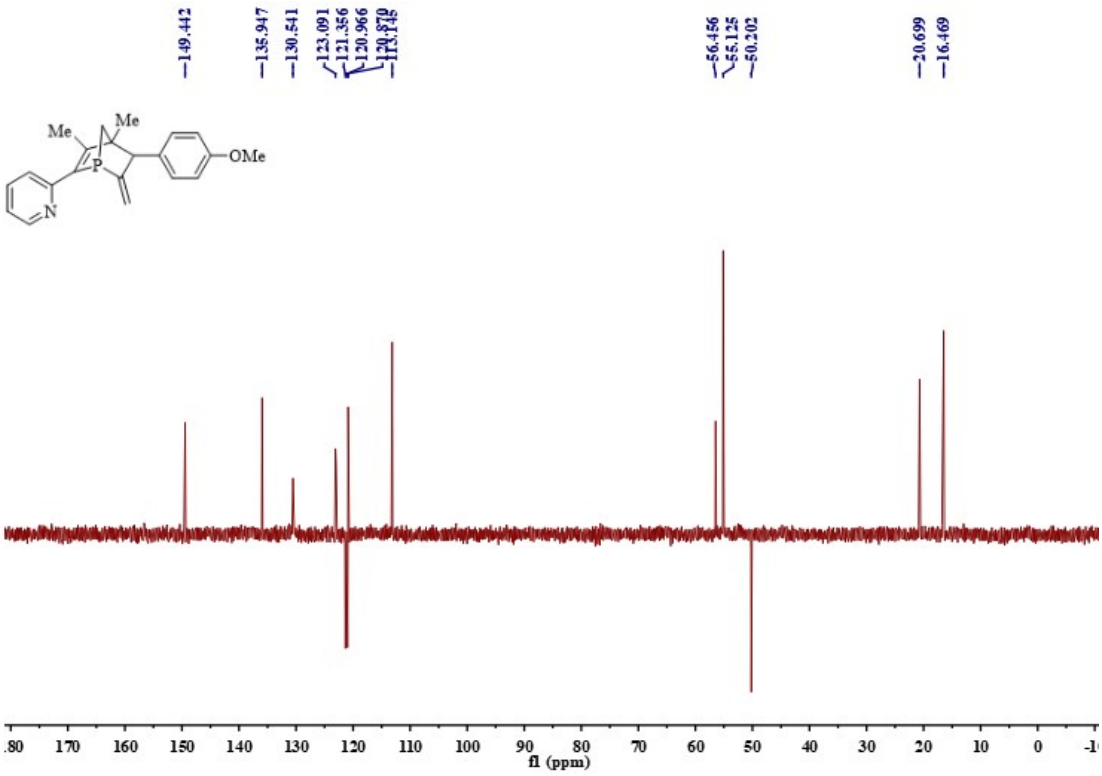
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of *exo*-**3bd**



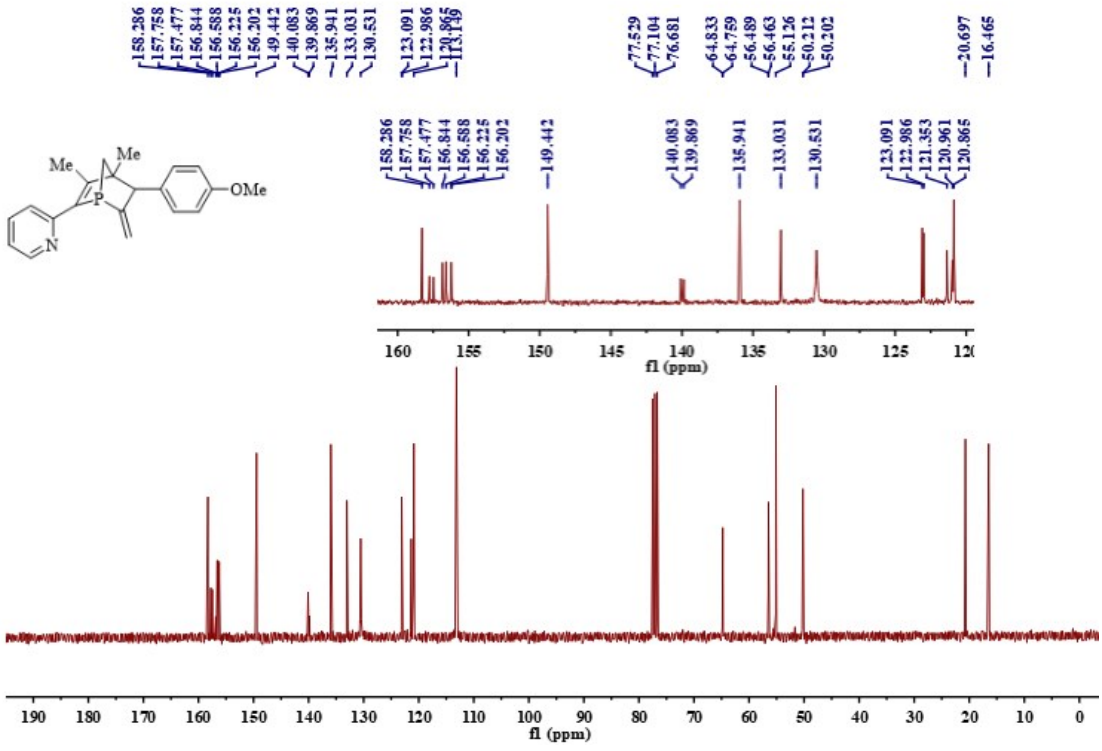
^{31}P ($CDCl_3$, 121 MHz) NMR of *endo*-**3bd**



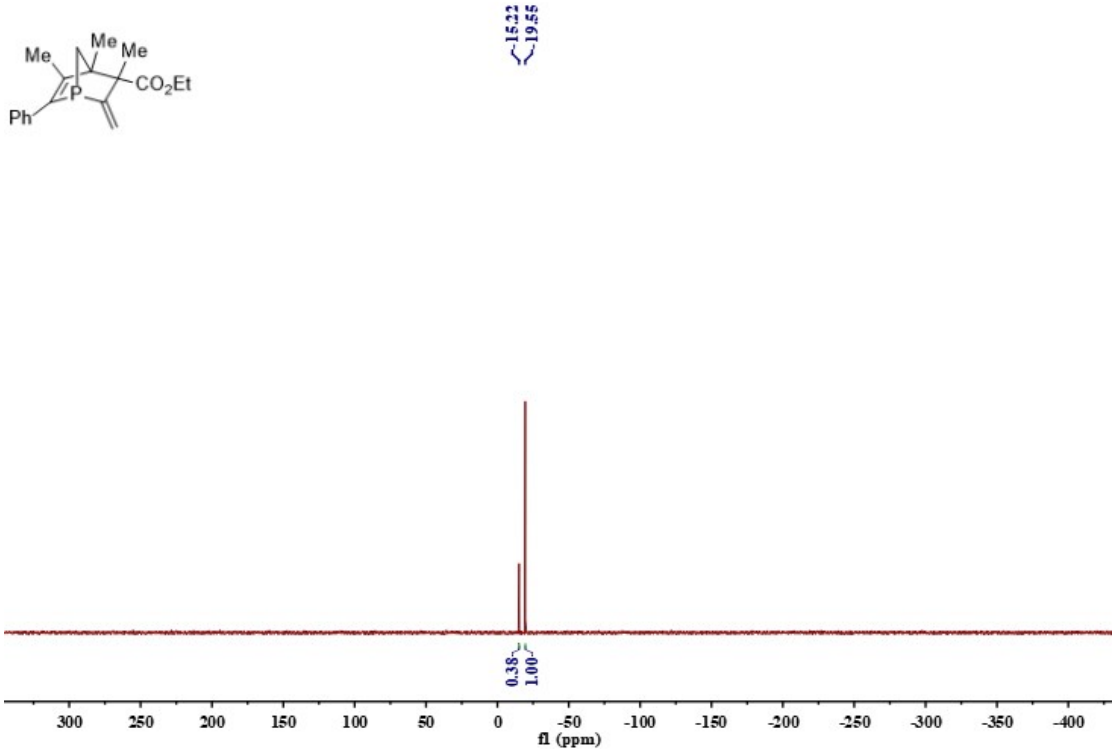
^{1}H ($CDCl_3$, 300 MHz) NMR of *endo*-**3bd**



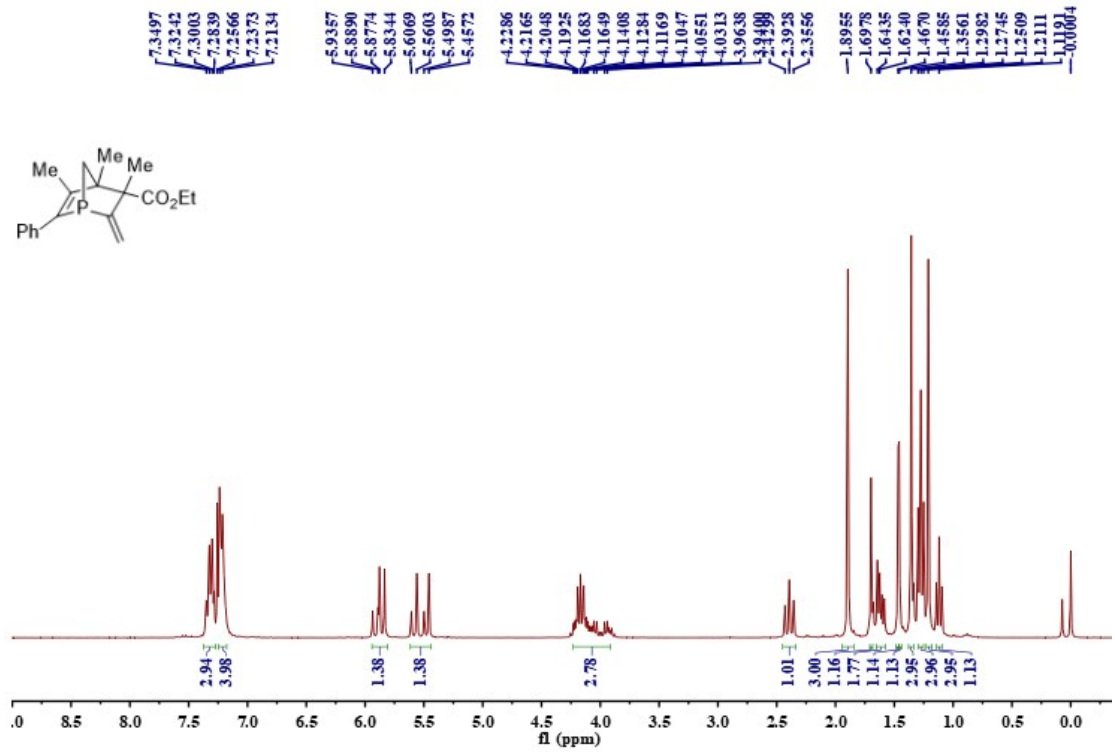
Dept135 ($CDCl_3$, 75 MHz) NMR of *endo*-**3bd**



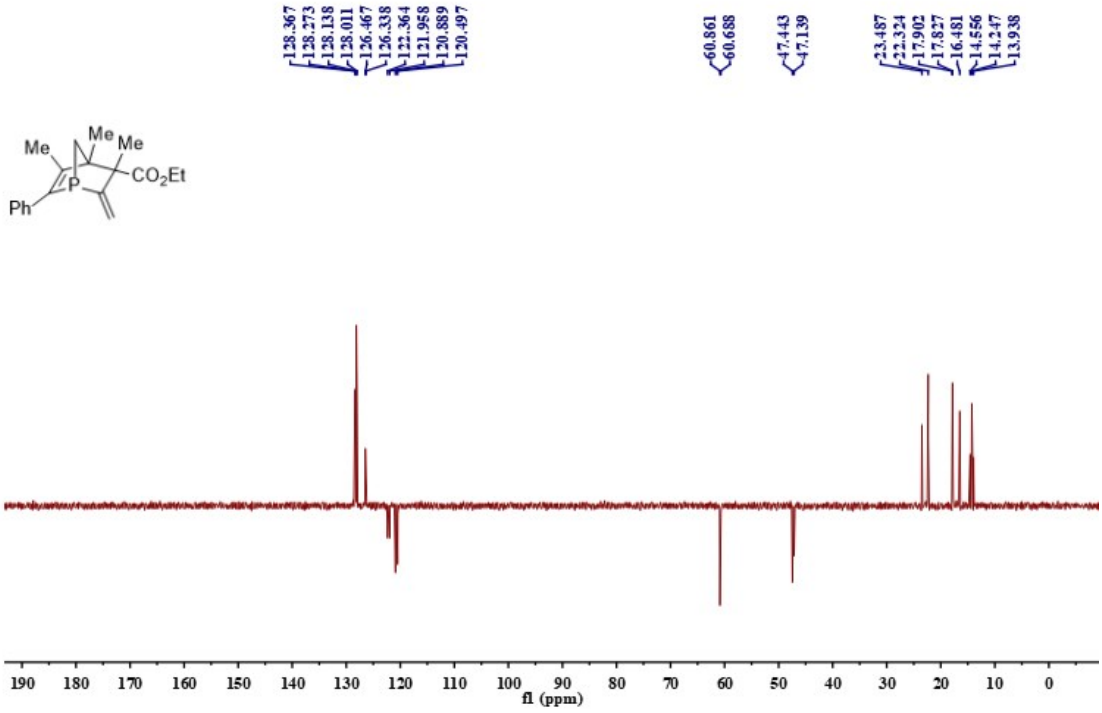
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of *endo*-**3bd**



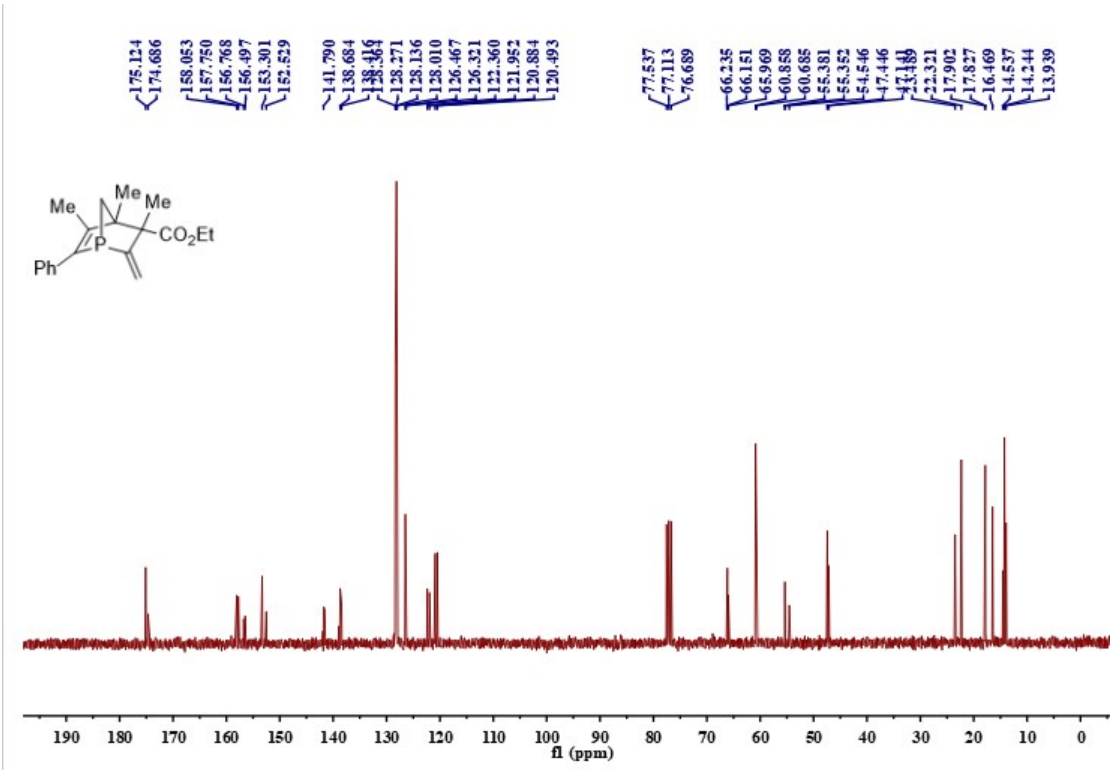
^{31}P ($CDCl_3$, 121 MHz) NMR of **3af**



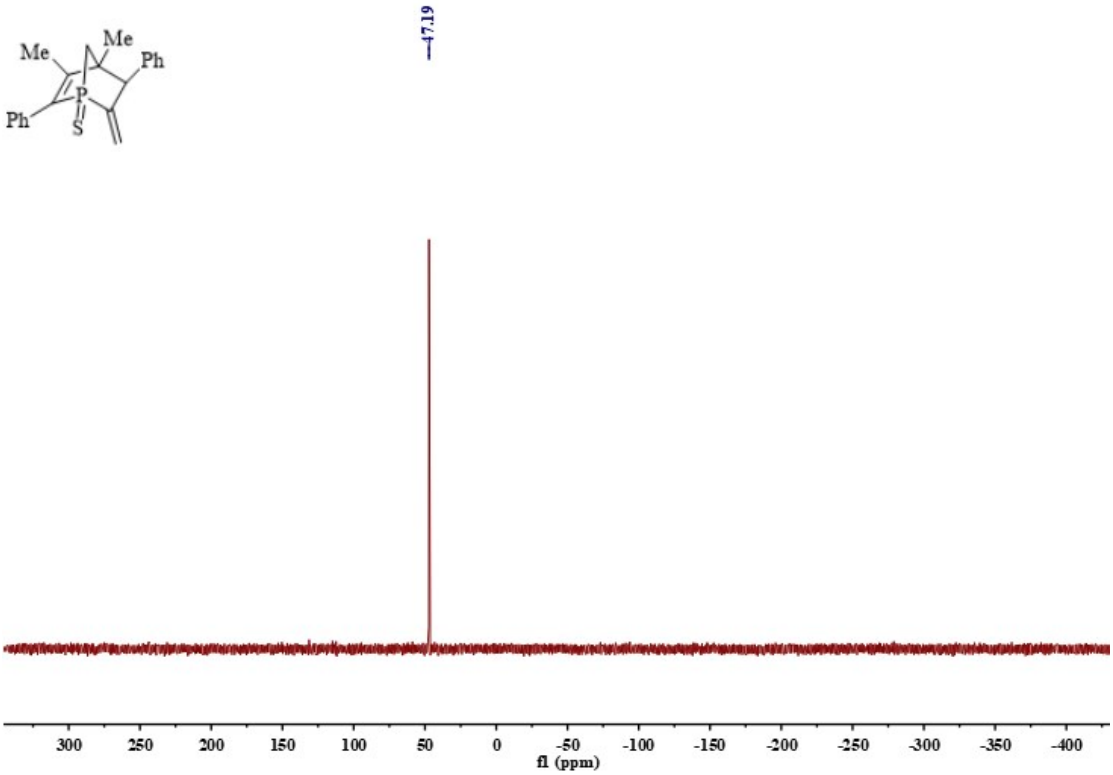
^{1}H ($CDCl_3$, 300 MHz) NMR of **3af**



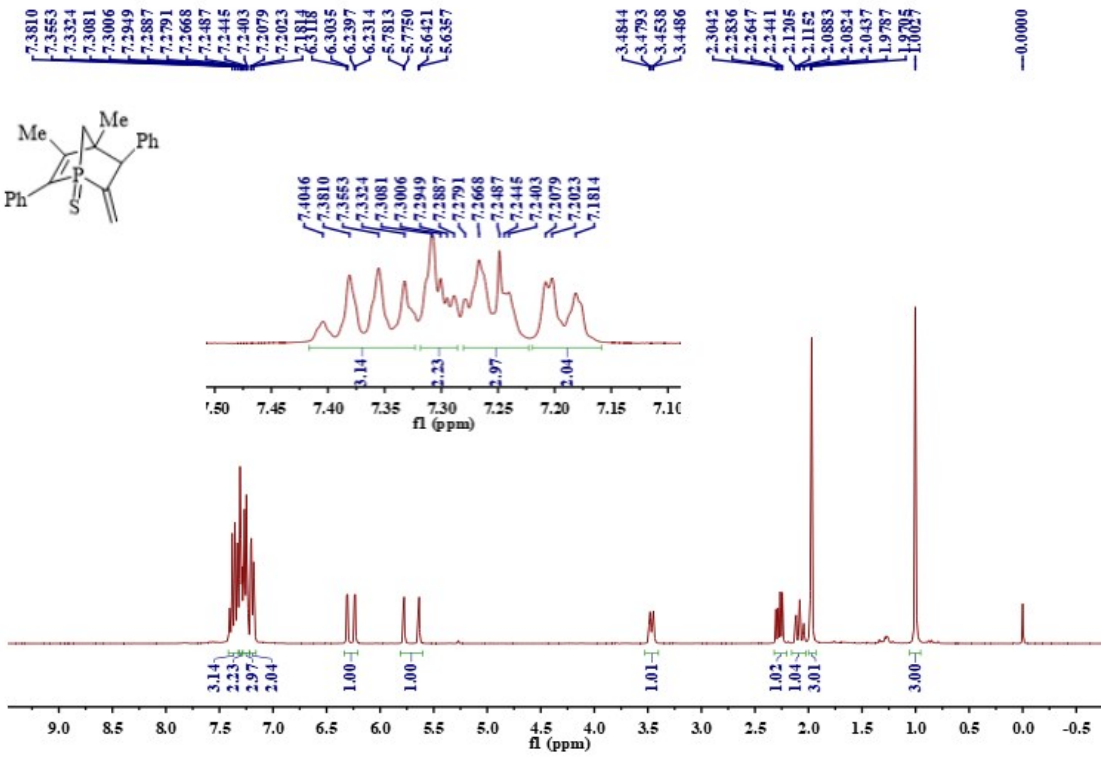
Dept135 ($CDCl_3$, 75 MHz) NMR of **3af**



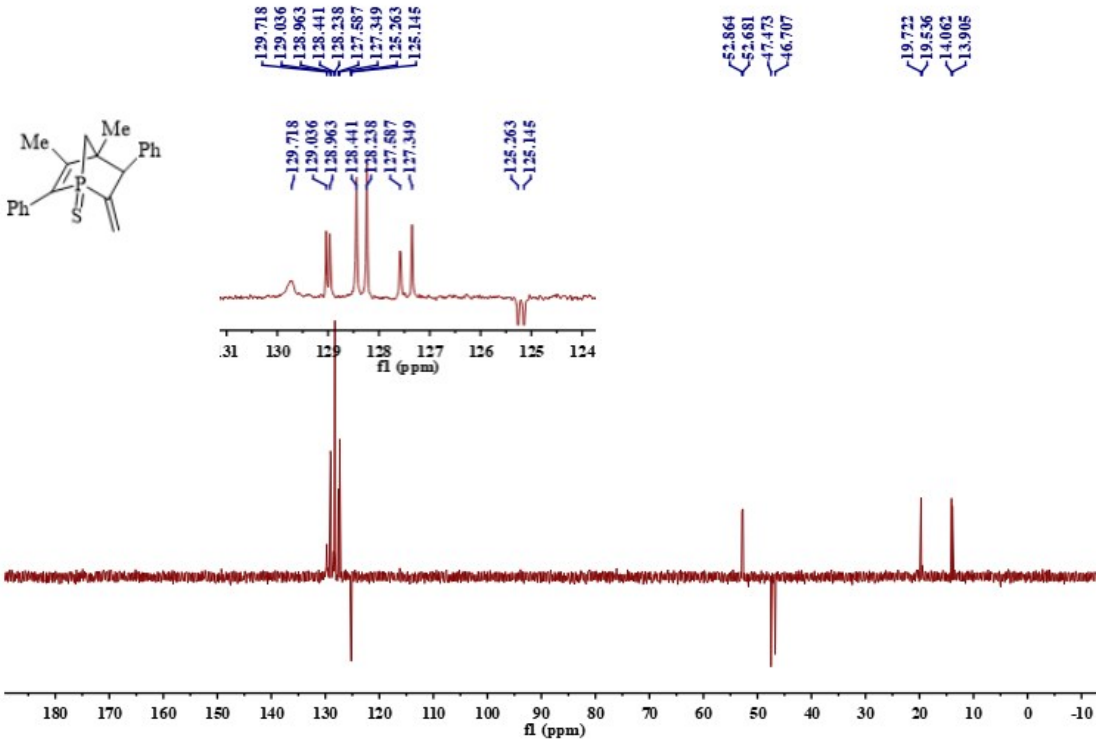
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of **3af**



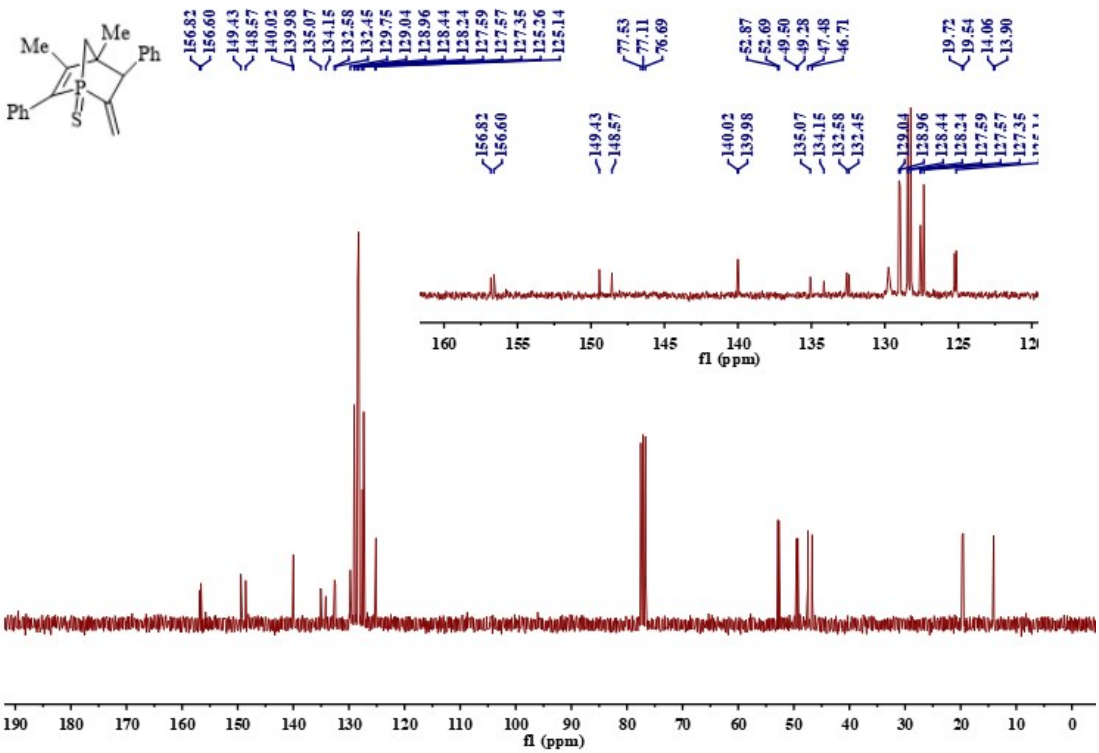
^{31}P ($CDCl_3$, 121 MHz) NMR of *exo*-**4a**



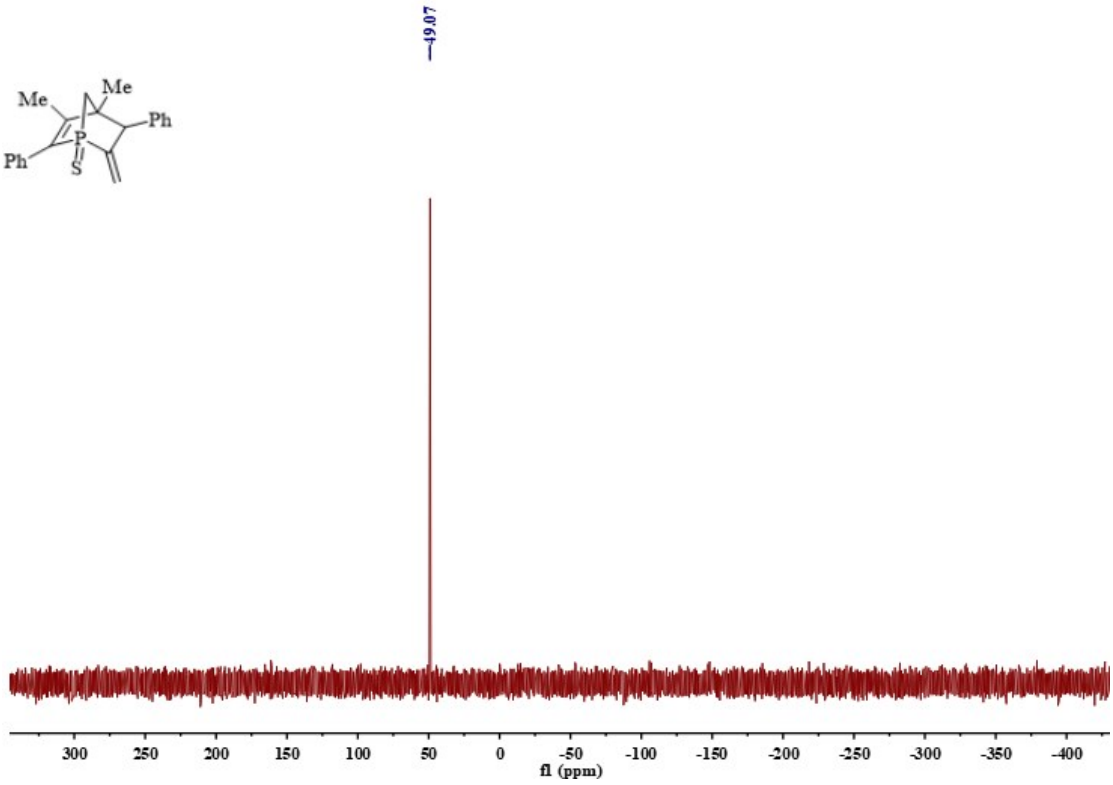
^{1}H ($CDCl_3$, 300 MHz) NMR of *exo*-**4a**



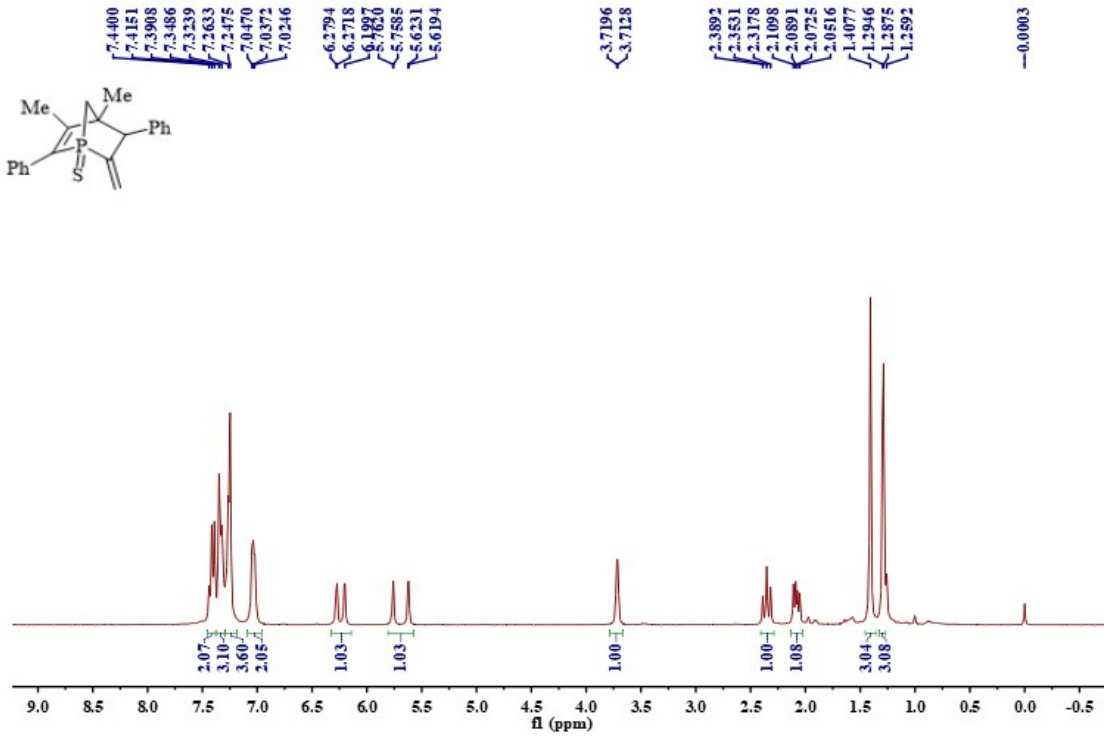
Dept135 ($CDCl_3$, 75 MHz) NMR of *exo*-**4a**



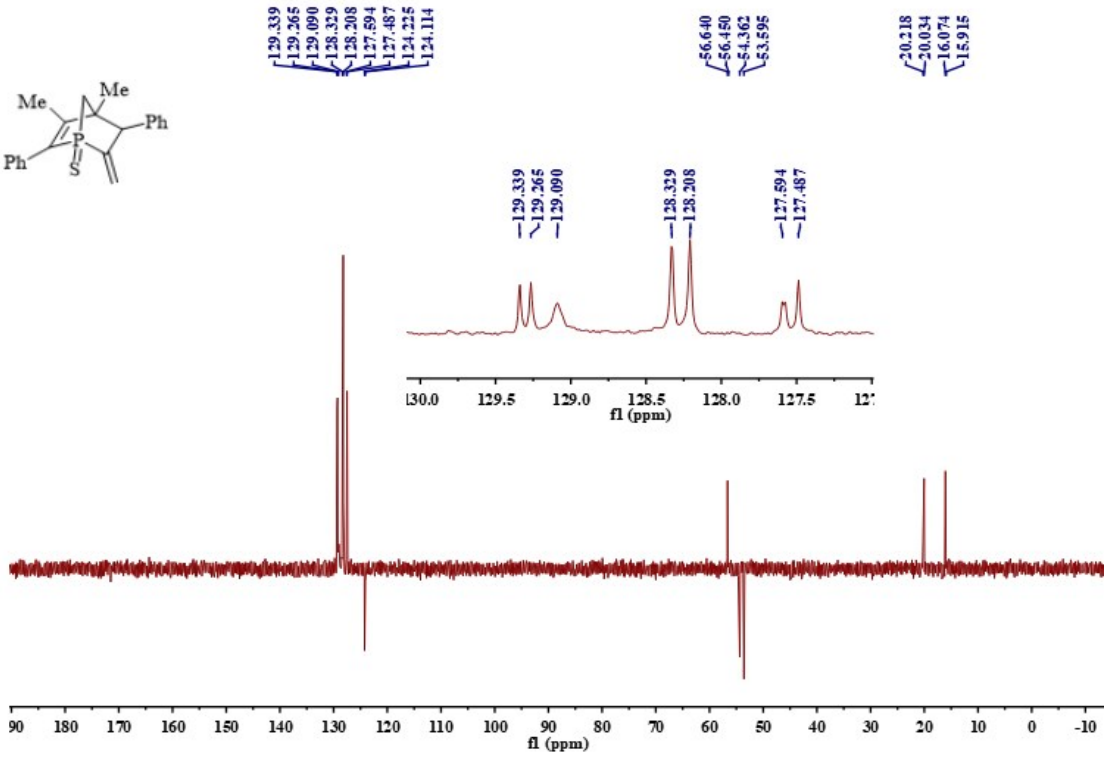
^{13}C $\{^1H\}$ ($CDCl_3$, 75 MHz) NMR of *exo*-**4a**



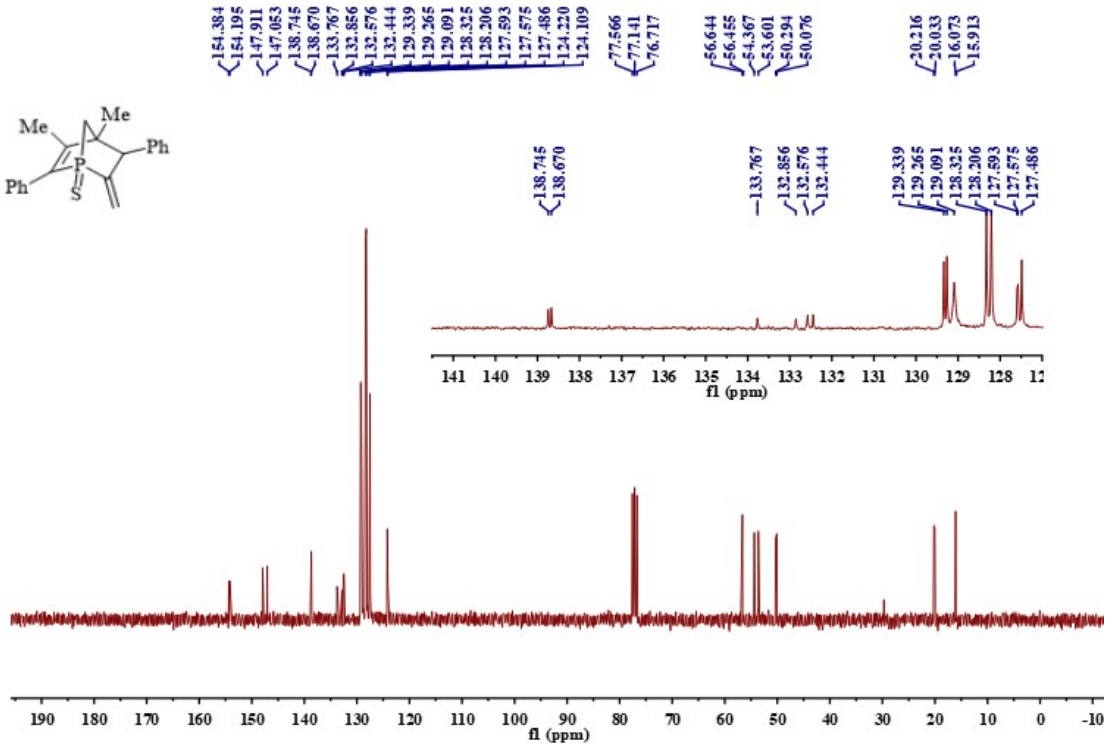
^{31}P ($CDCl_3$, 121 MHz) NMR of *endo*-**4a**



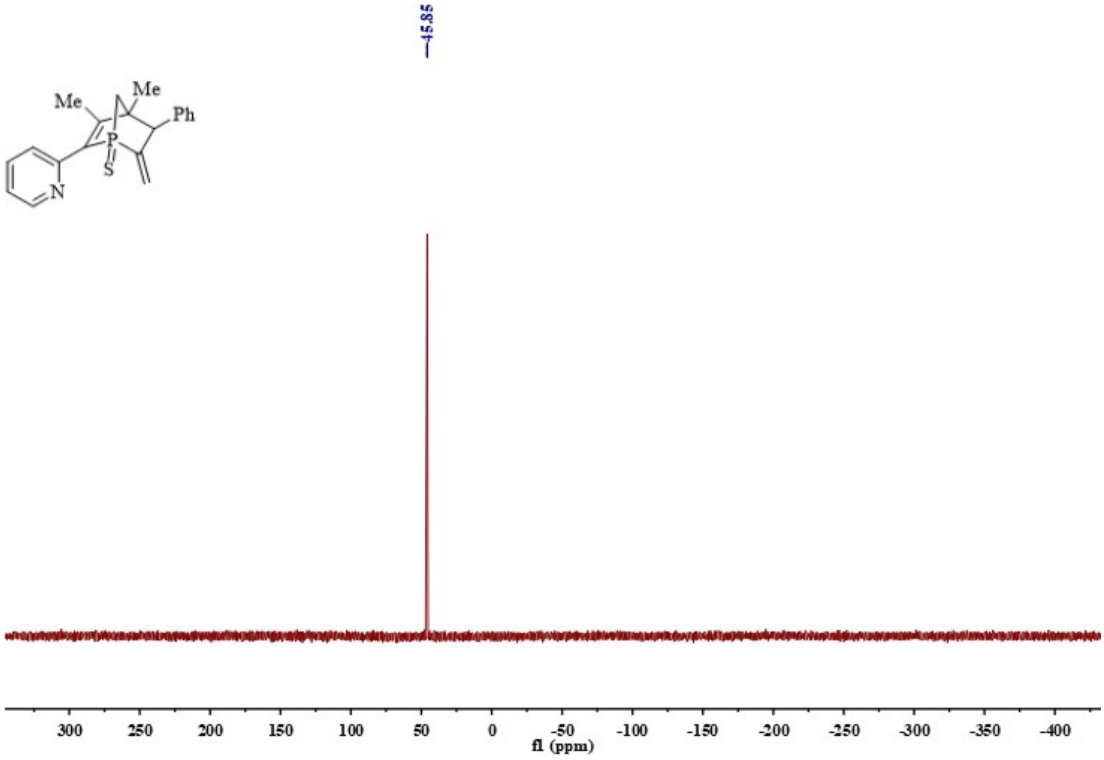
^{1}H ($CDCl_3$, 300 MHz) NMR of *endo*-**4a**



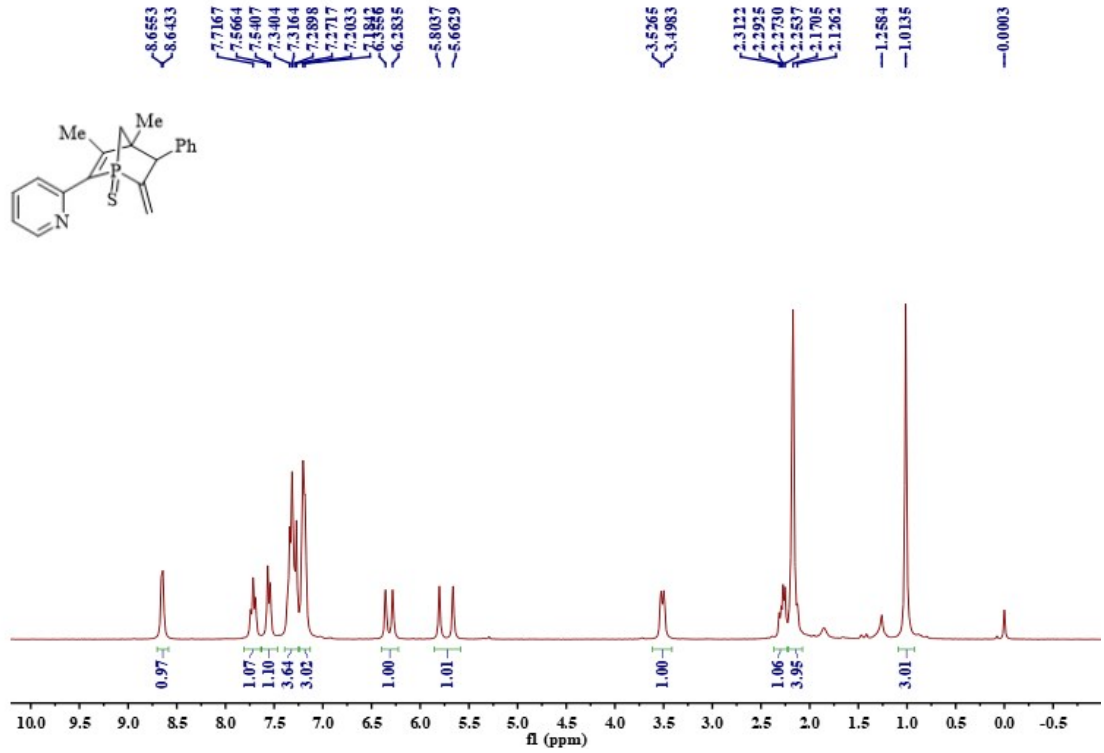
Dept135 ($CDCl_3$, 75 MHz) NMR of *endo*-**4a**



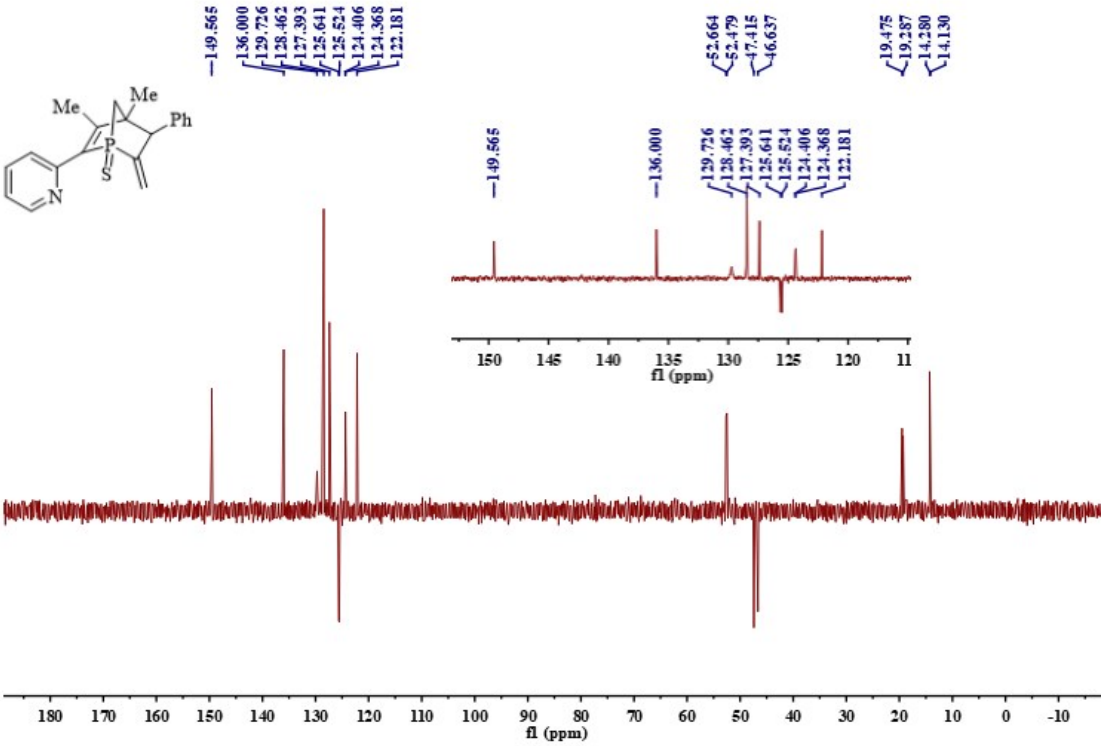
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of *endo*-**4a**



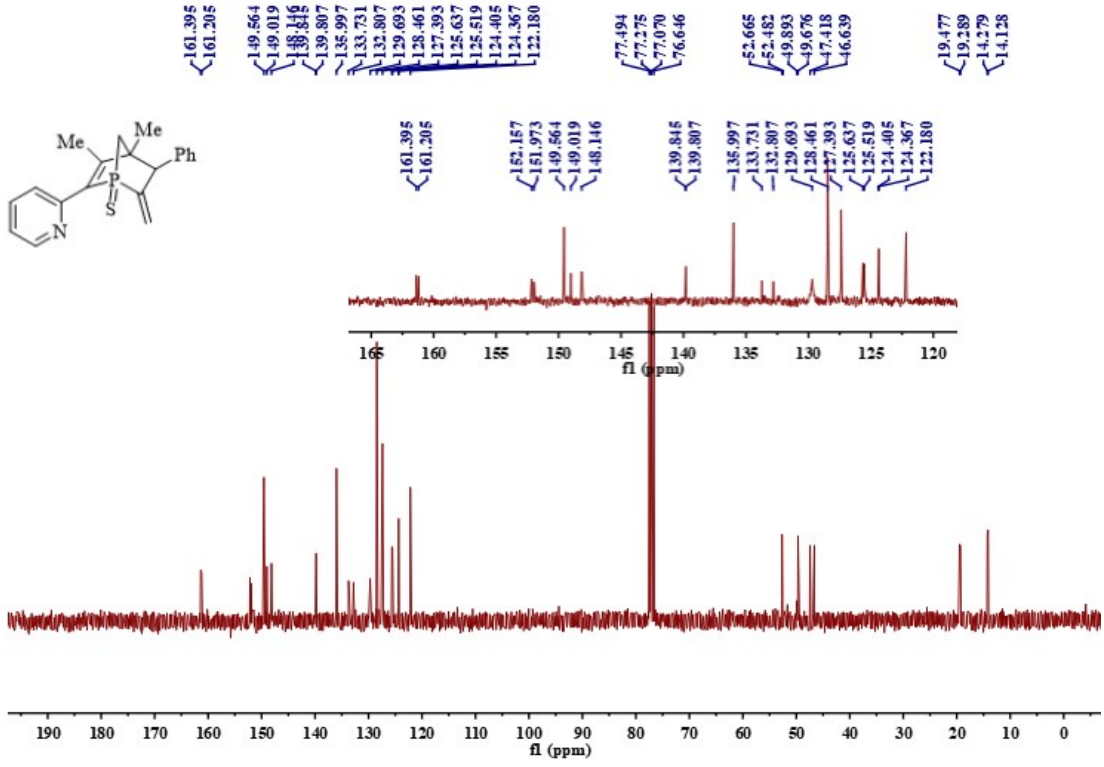
^{31}P ($CDCl_3$, 121 MHz) NMR of *exo*-**4b**



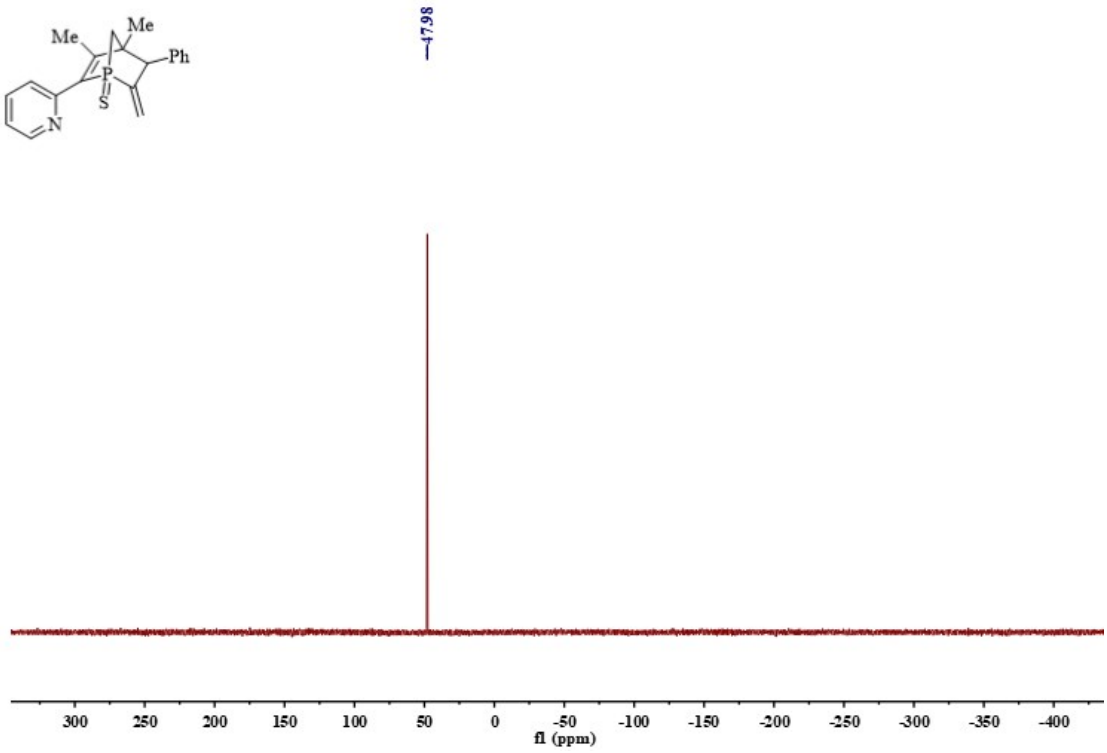
^{1}H ($CDCl_3$, 300 MHz) NMR of *exo*-**4b**



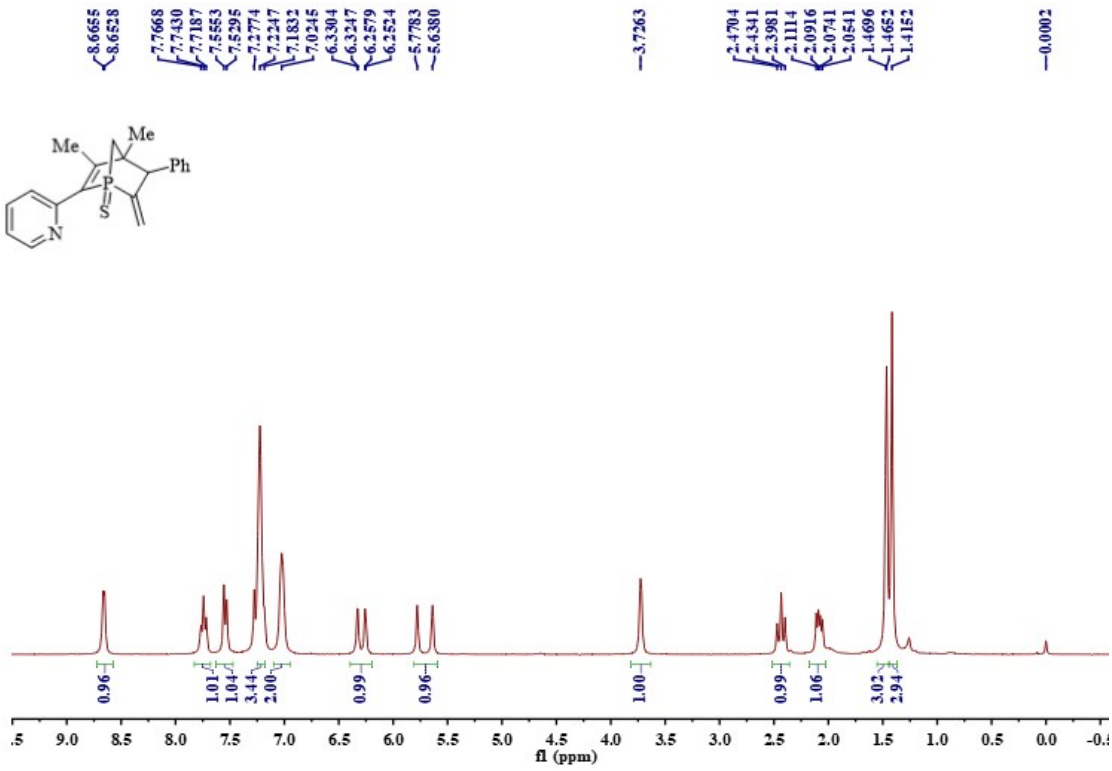
Dept135 ($CDCl_3$, 75 MHz) NMR of *exo*-**4b**



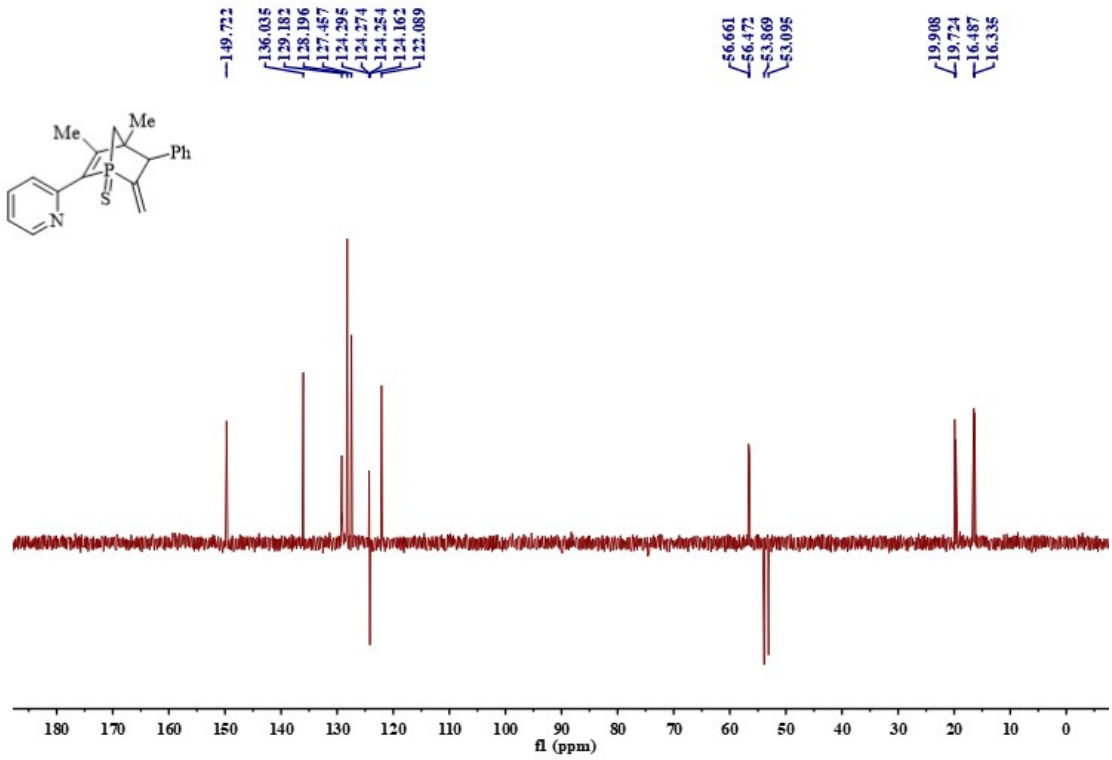
^{13}C $\{^1H\}$ ($CDCl_3$, 75 MHz) NMR of *exo*-**4b**



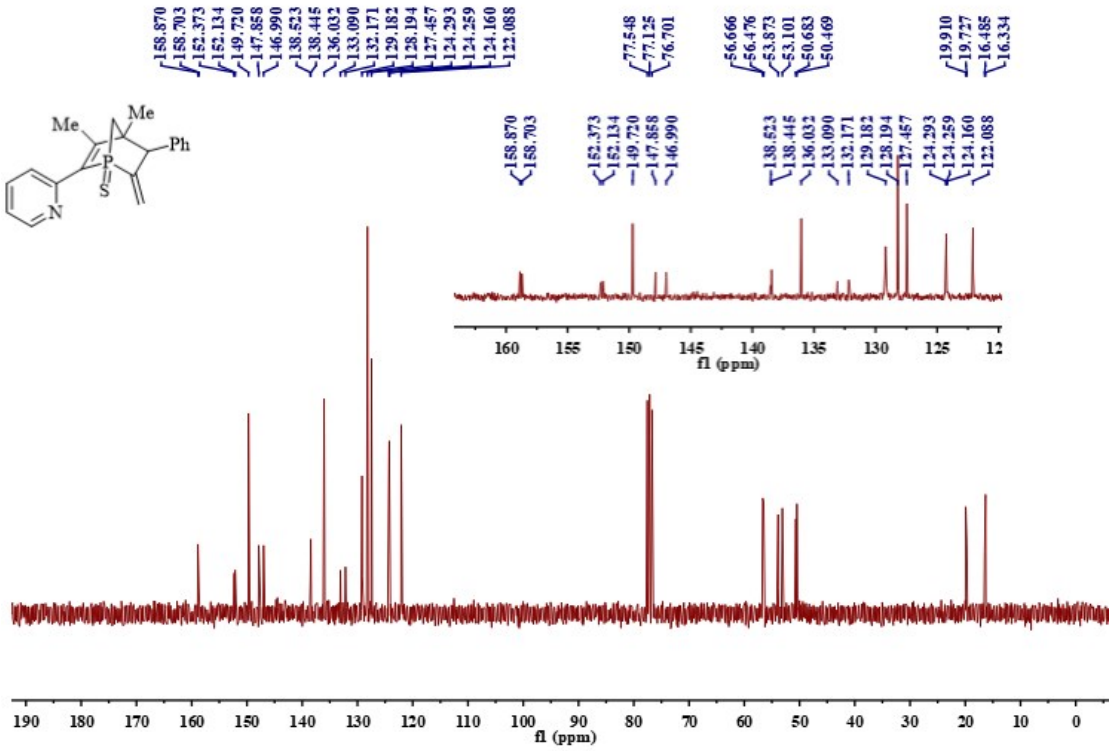
^{31}P ($CDCl_3$, 121 MHz) NMR of *endo*-**4b**



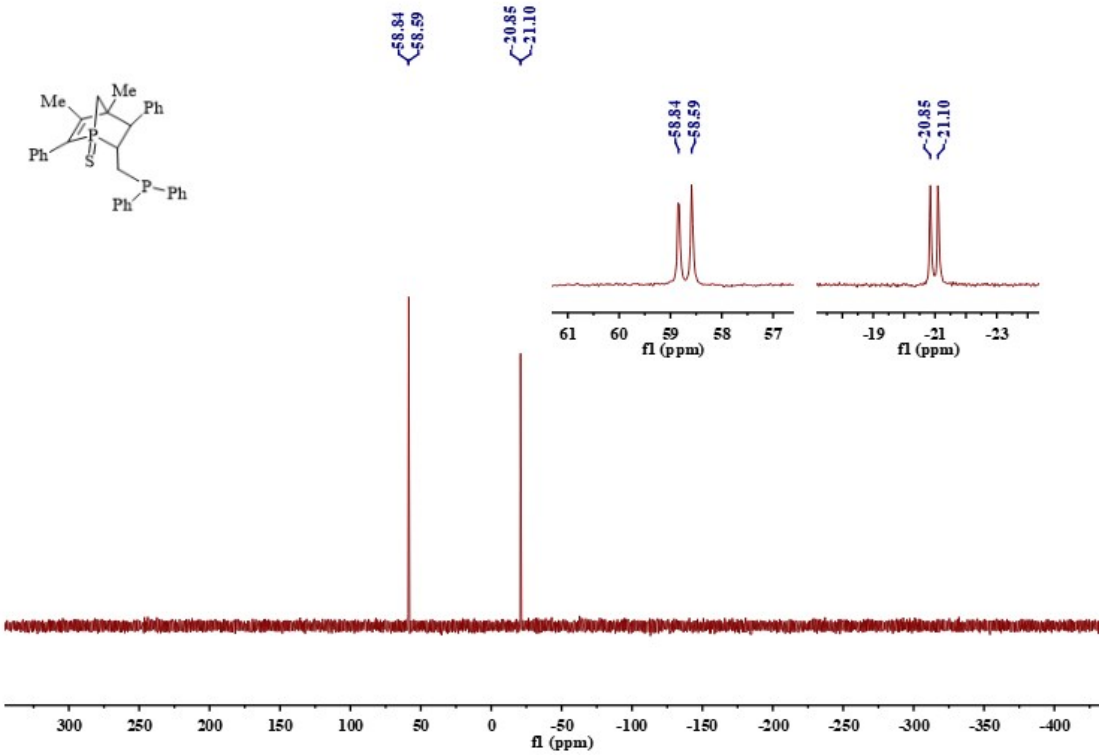
^{1}H ($CDCl_3$, 300 MHz) NMR of *endo*-**4b**



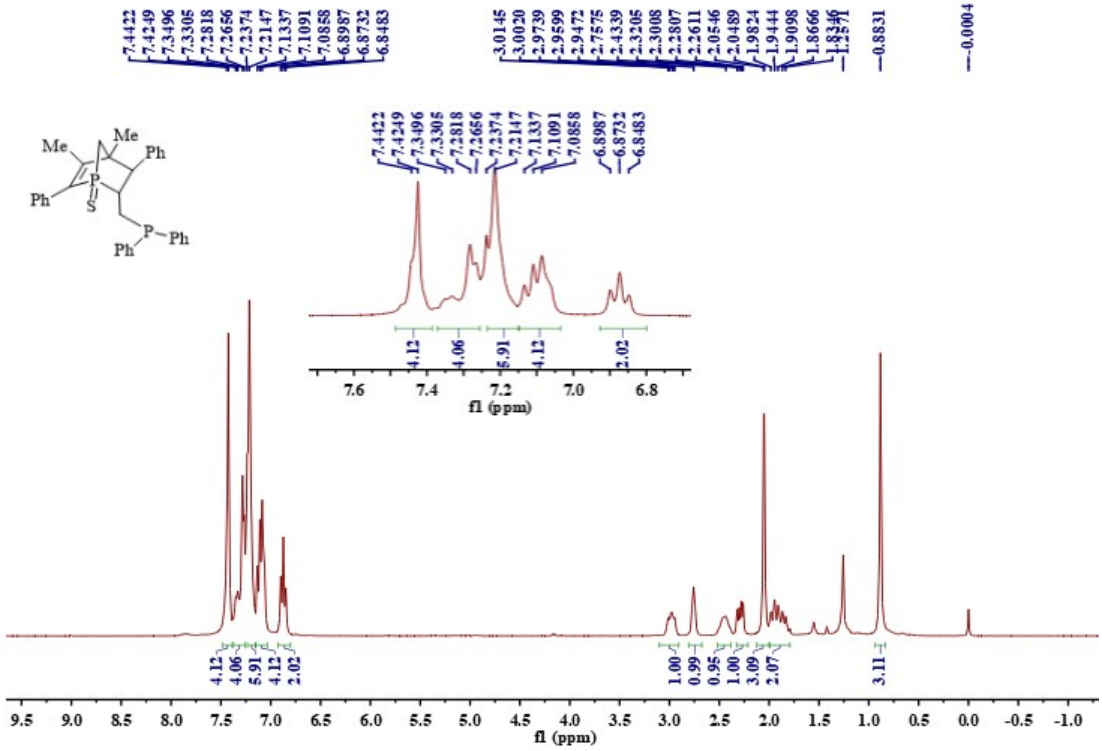
Dept135 ($CDCl_3$, 75 MHz) NMR of *endo*-**4b**



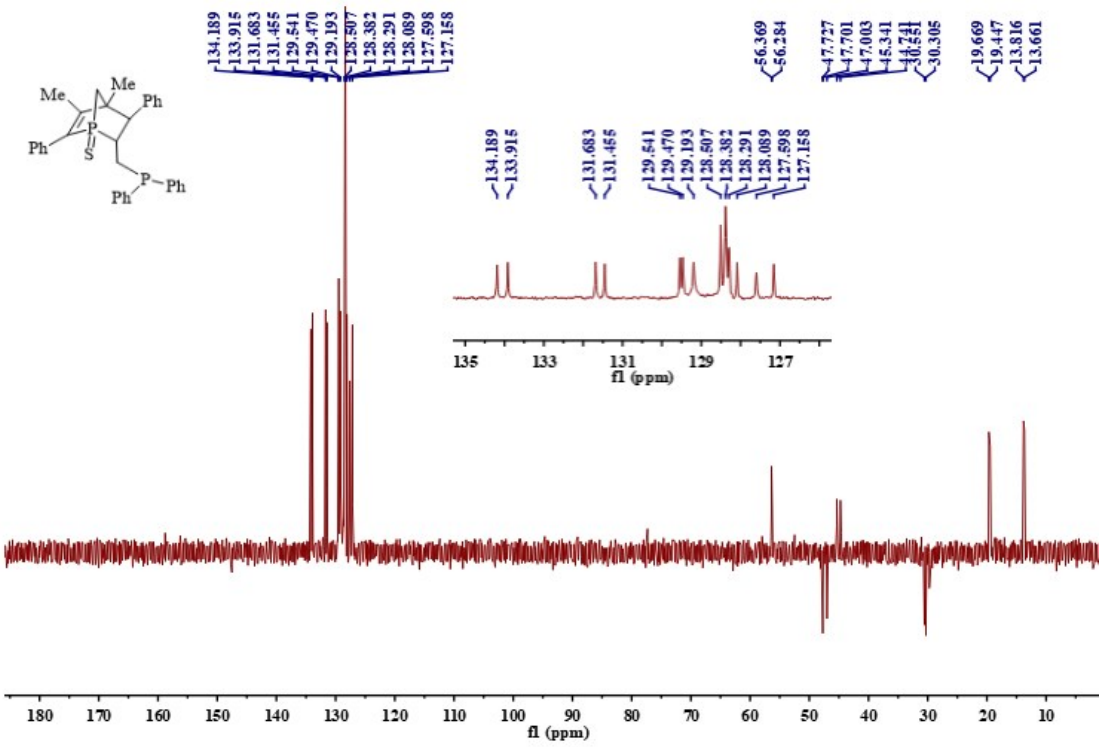
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of *endo*-**4b**



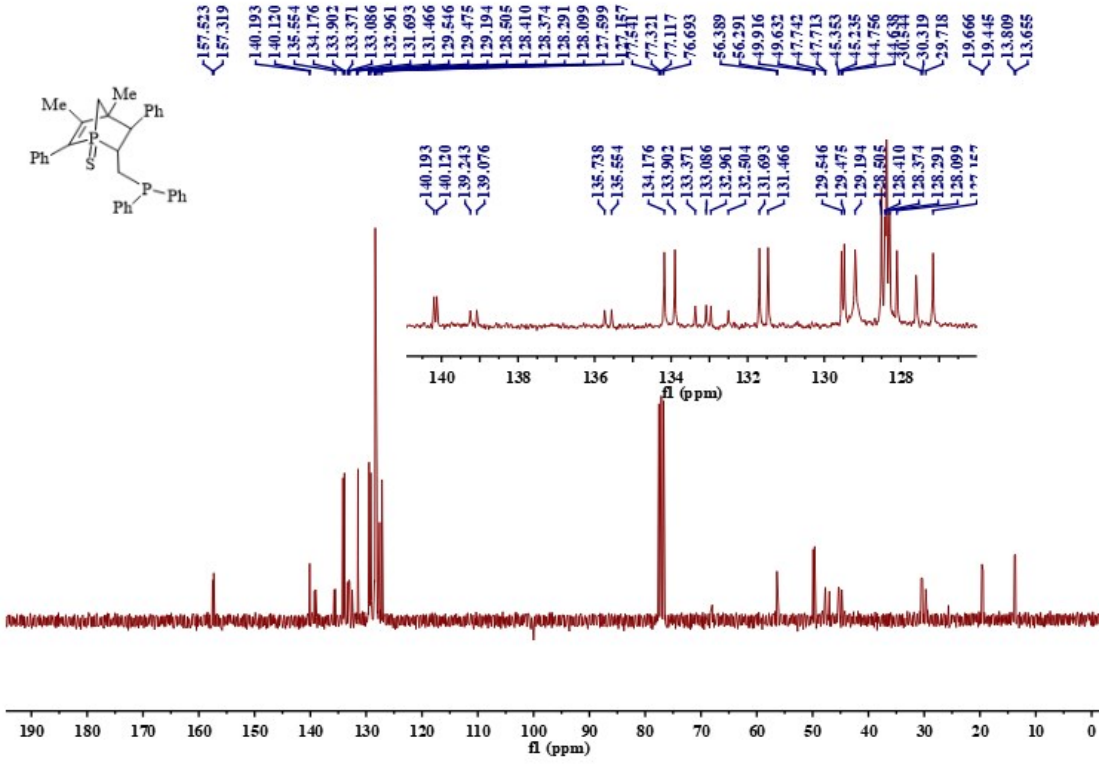
^{31}P ($CDCl_3$, 121 MHz) NMR of **5a**



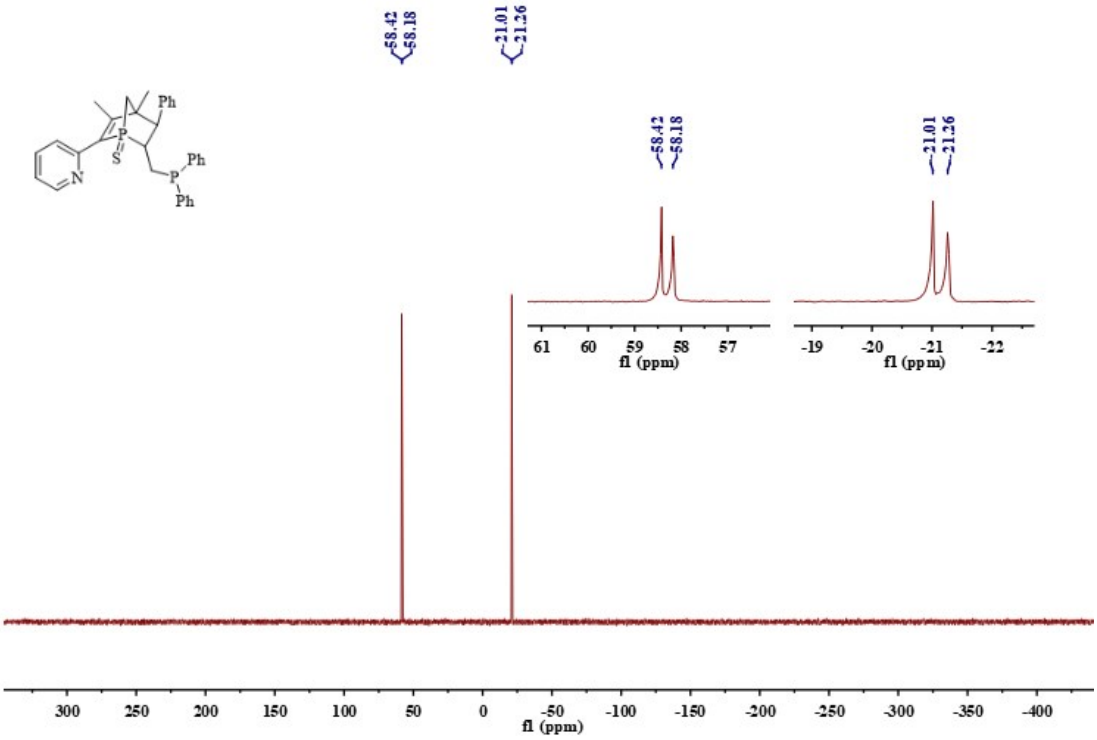
^{1}H ($CDCl_3$, 300 MHz) NMR of **5a**



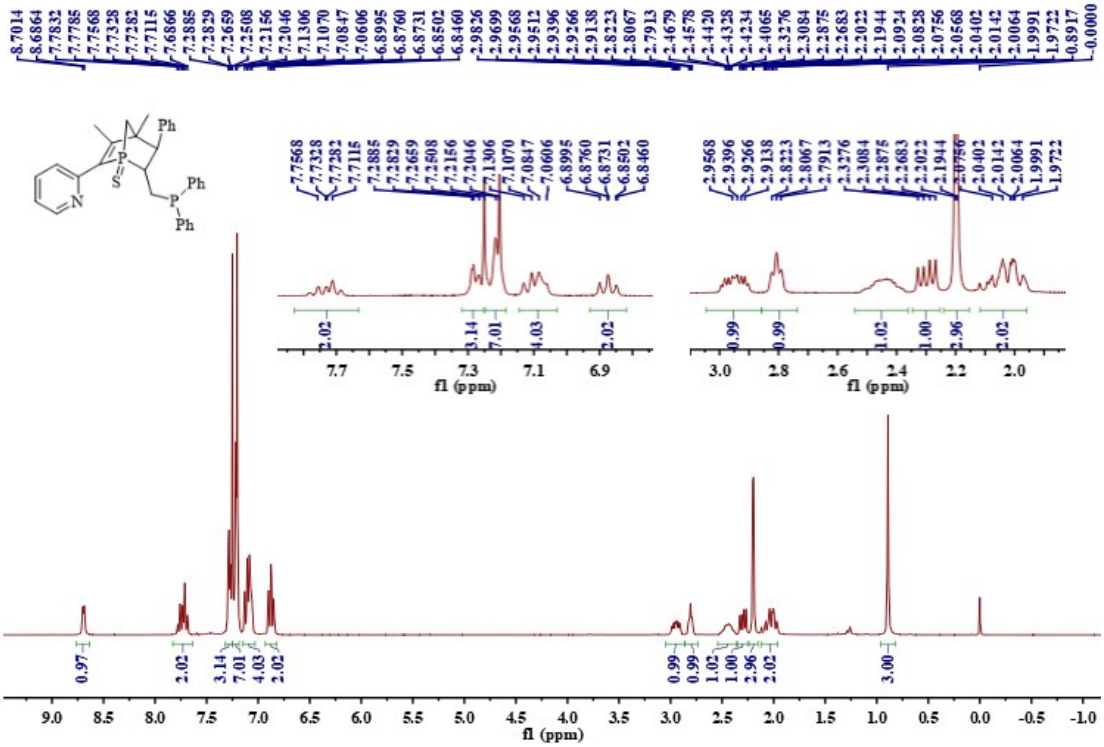
Dept135 ($CDCl_3$, 75 MHz) NMR of **5a**



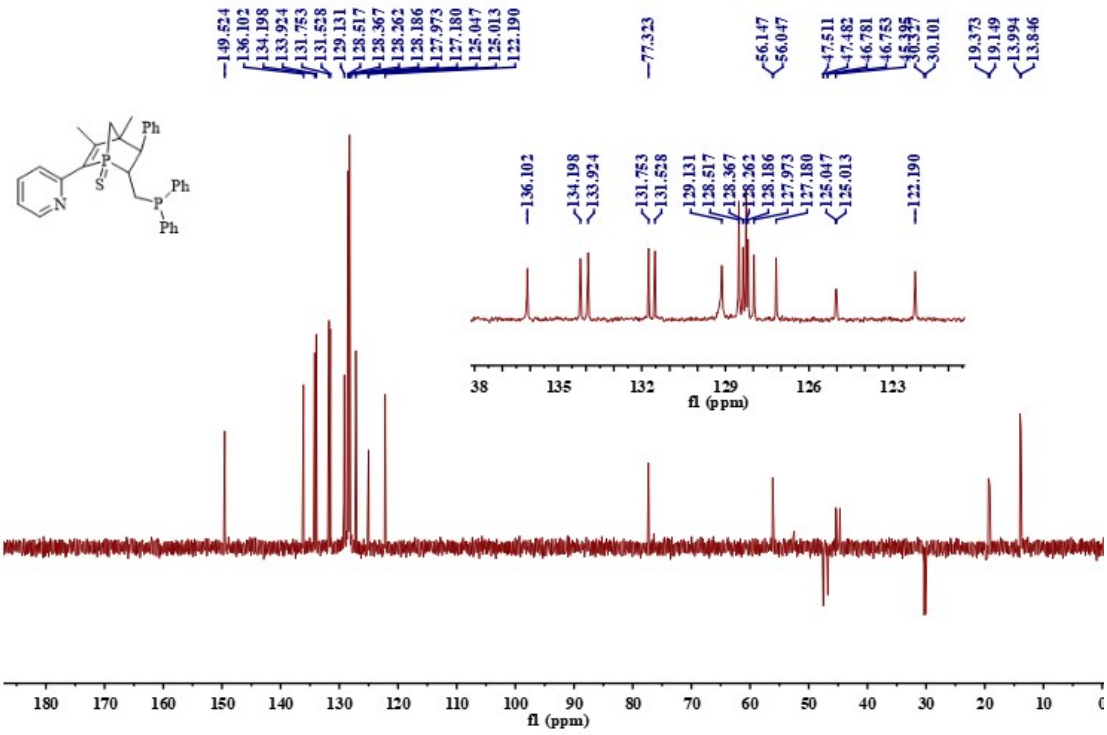
^{13}C $\{^1H\}$ ($CDCl_3$, 75 MHz) NMR of **5a**



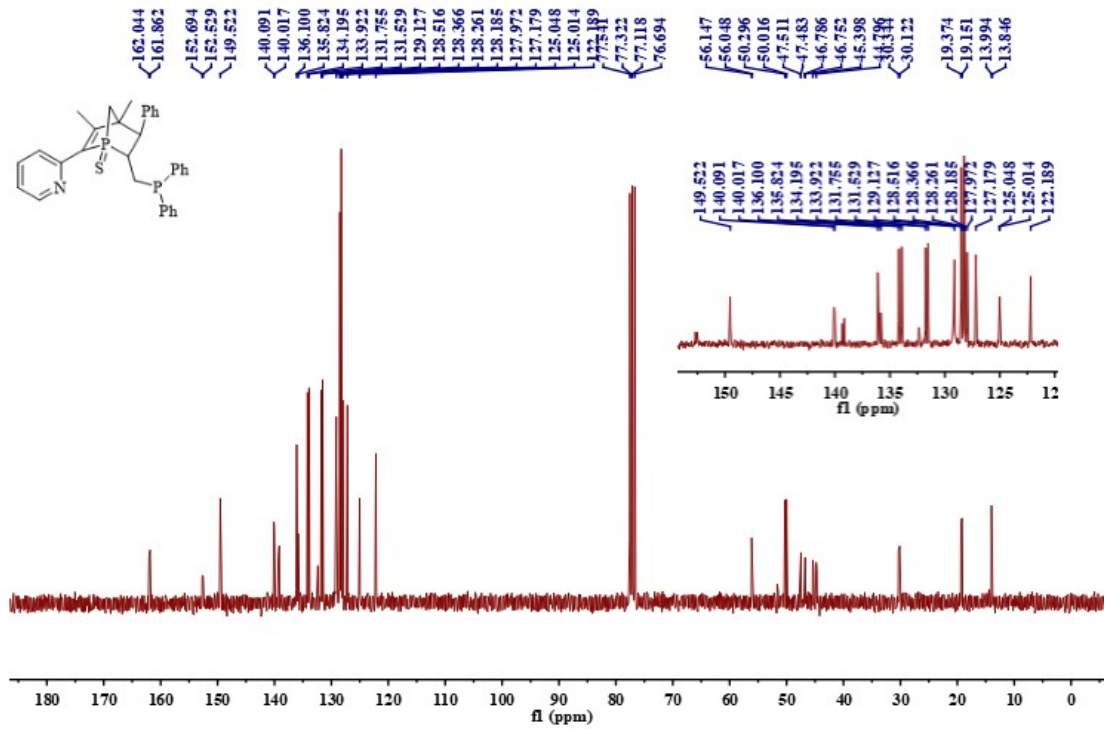
^{31}P ($CDCl_3$, 121 MHz) NMR of **5b**



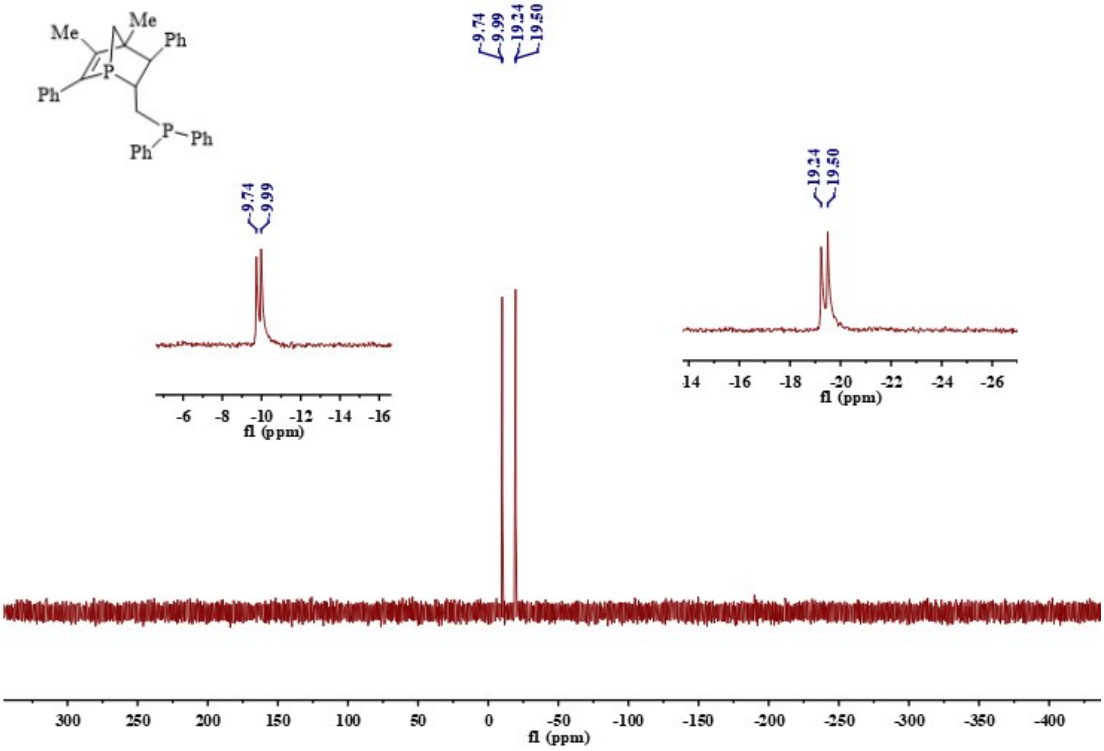
^{1}H ($CDCl_3$, 300 MHz) NMR of **5b**



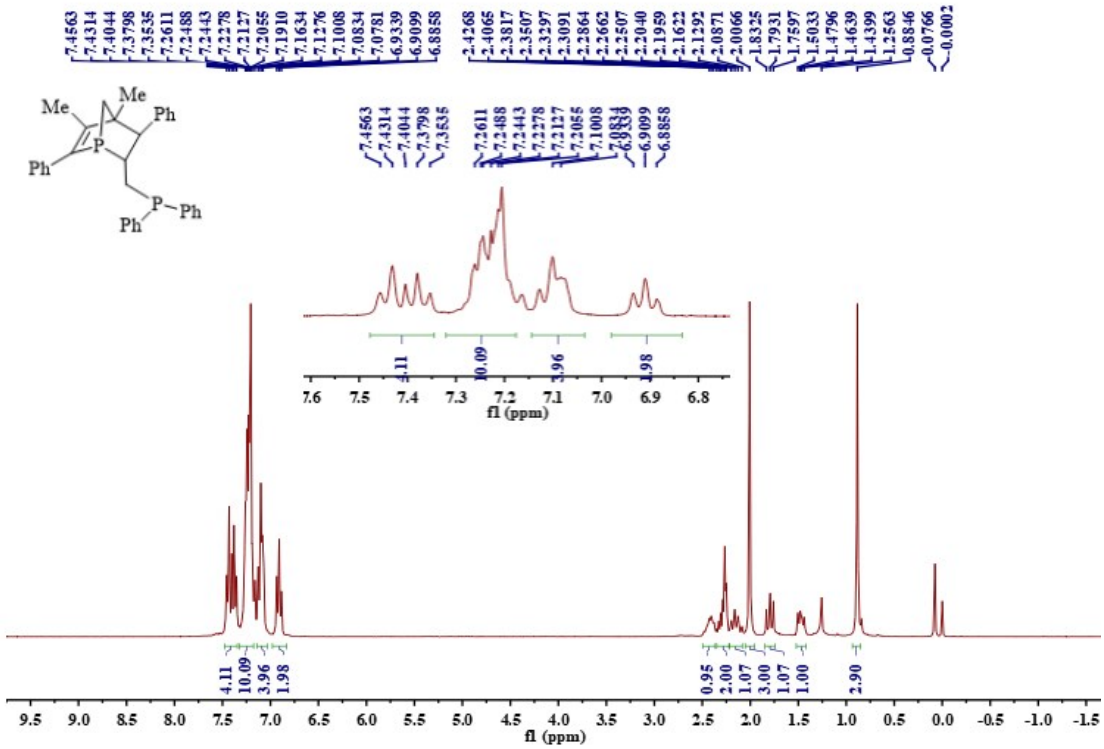
Dept135 ($CDCl_3$, 75 MHz) NMR of **5b**



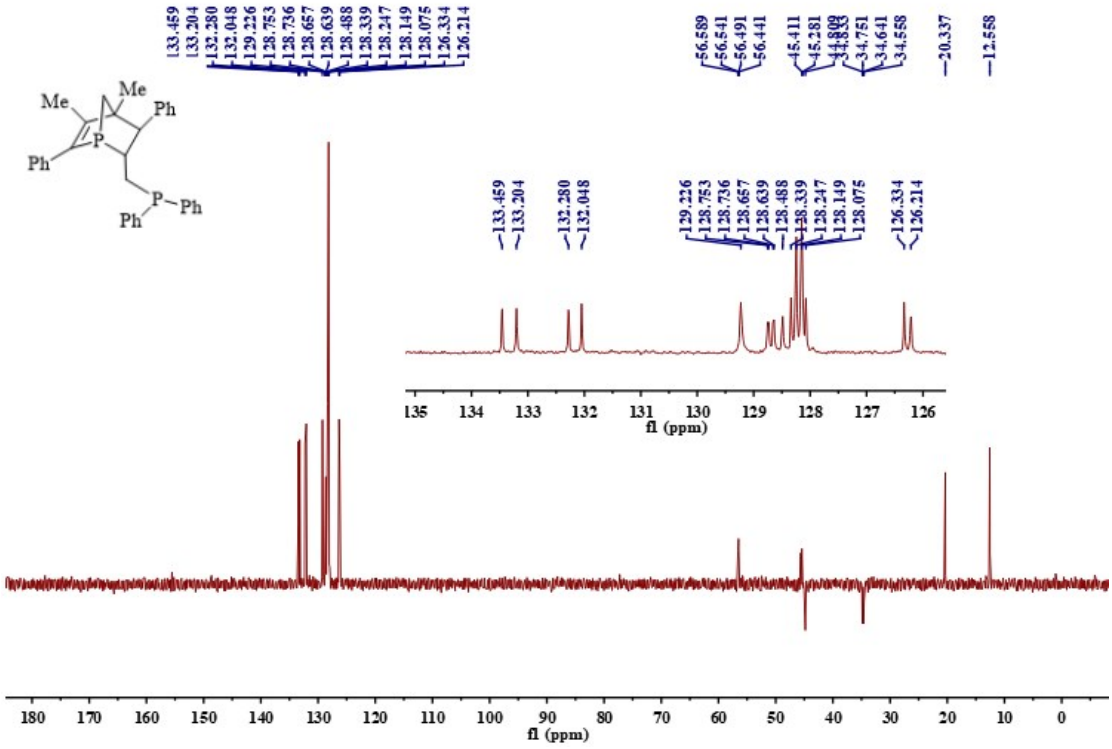
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of **5b**



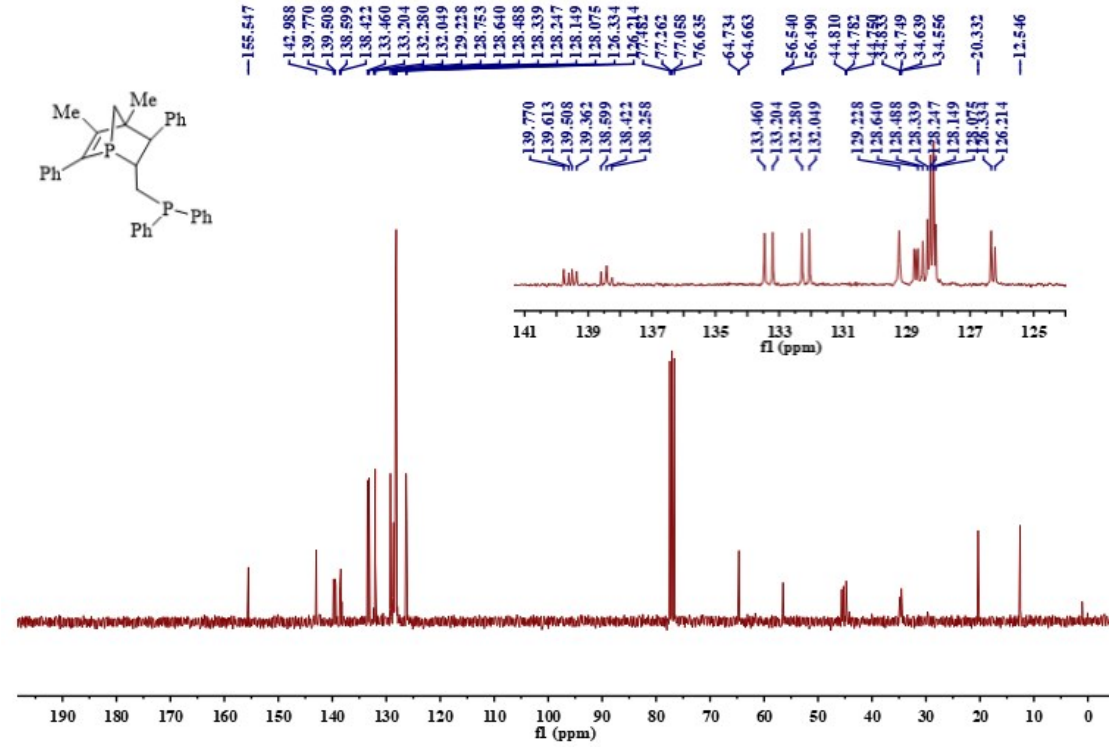
^{31}P ($CDCl_3$, 121 MHz) NMR of **6a**



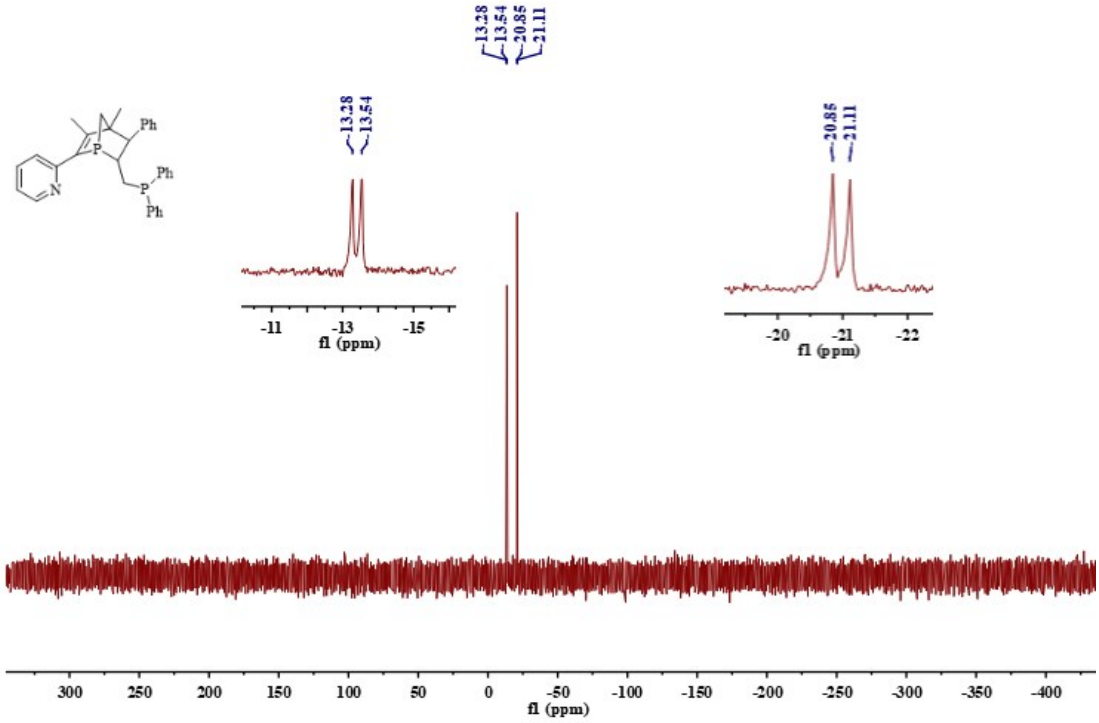
^{1}H ($CDCl_3$, 300 MHz) NMR of **6a**



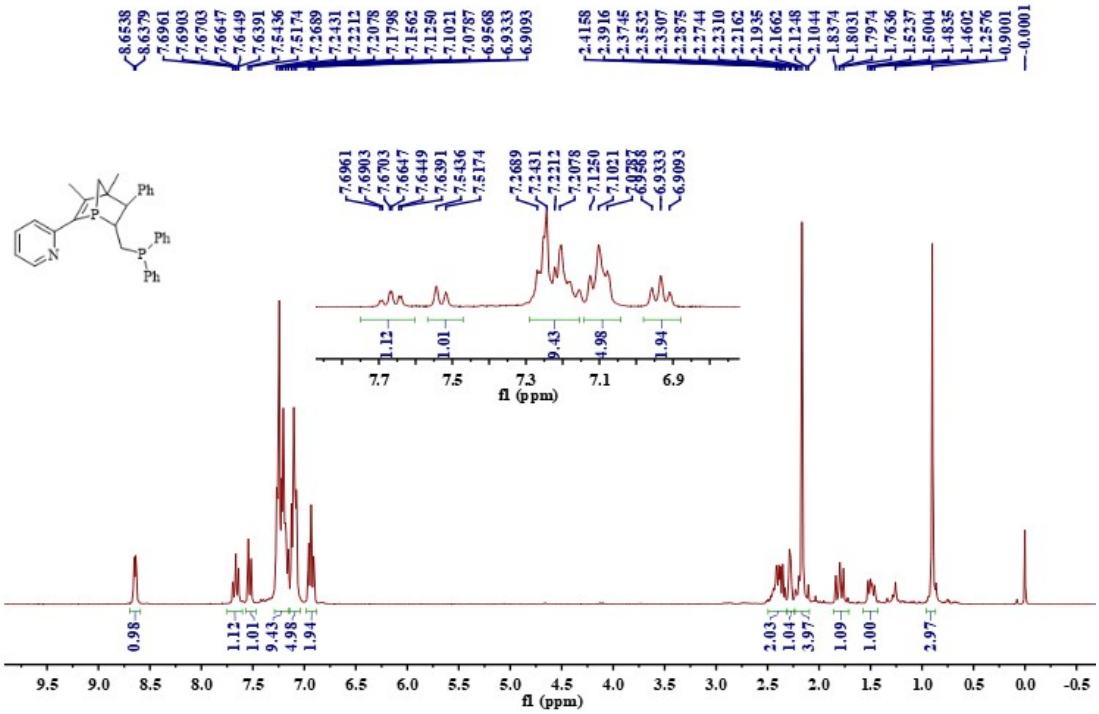
Dept135 ($CDCl_3$, 75 MHz) NMR of **6a**



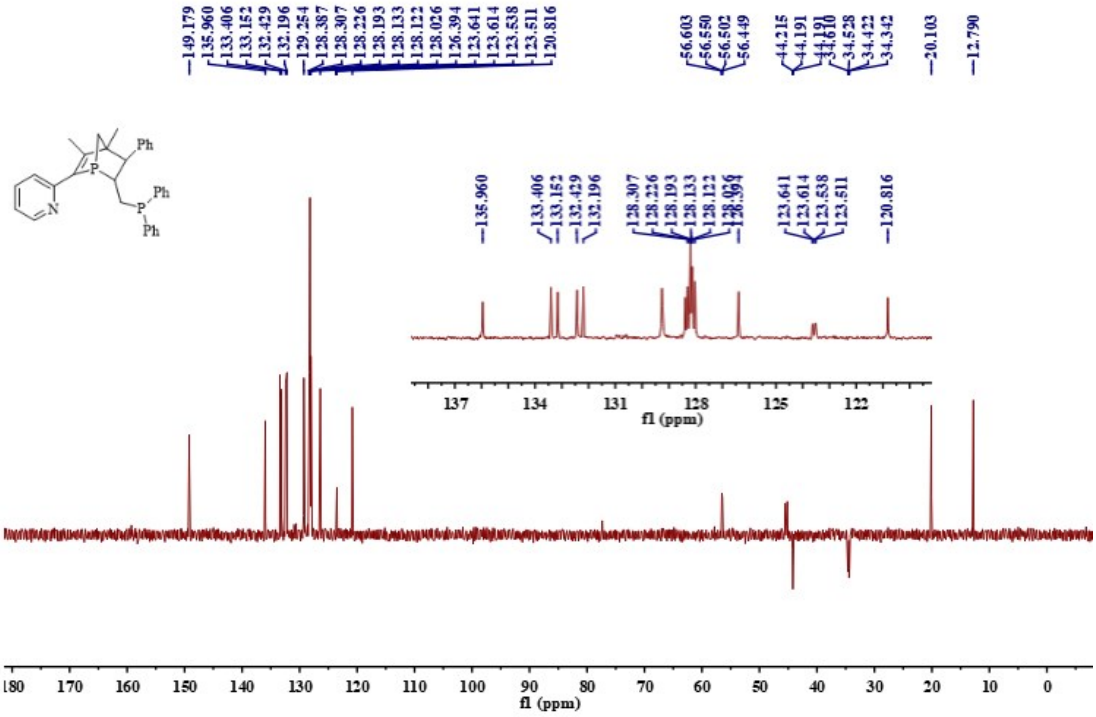
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of **6a**



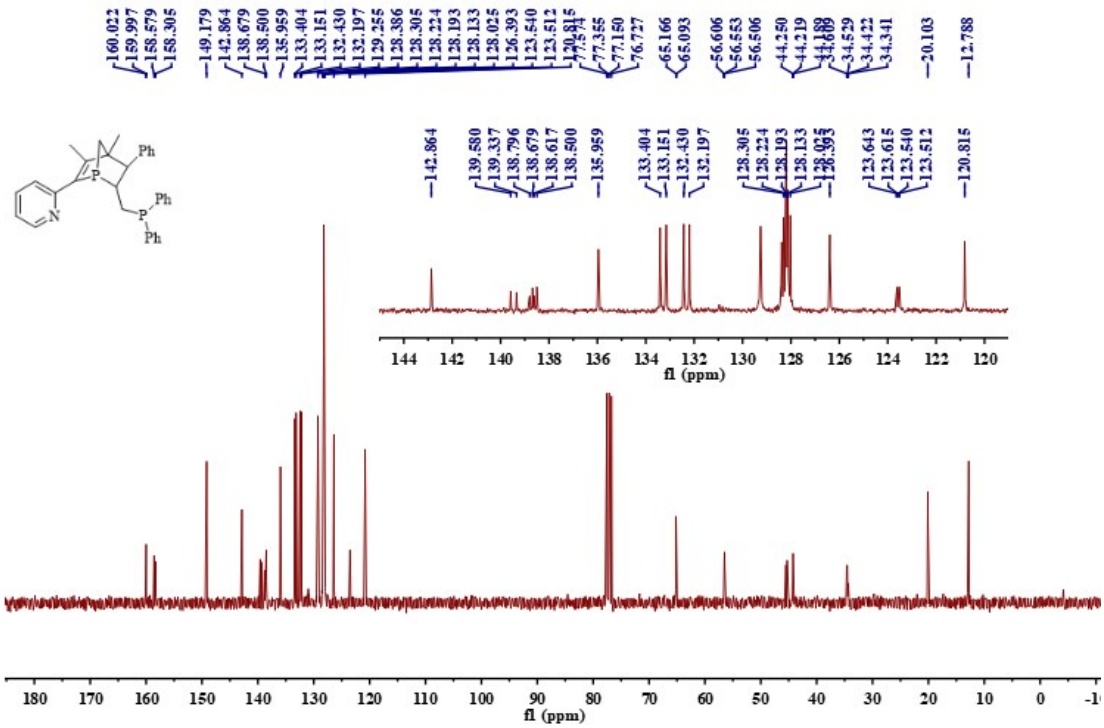
^{31}P ($CDCl_3$, 121 MHz) NMR of **6b**



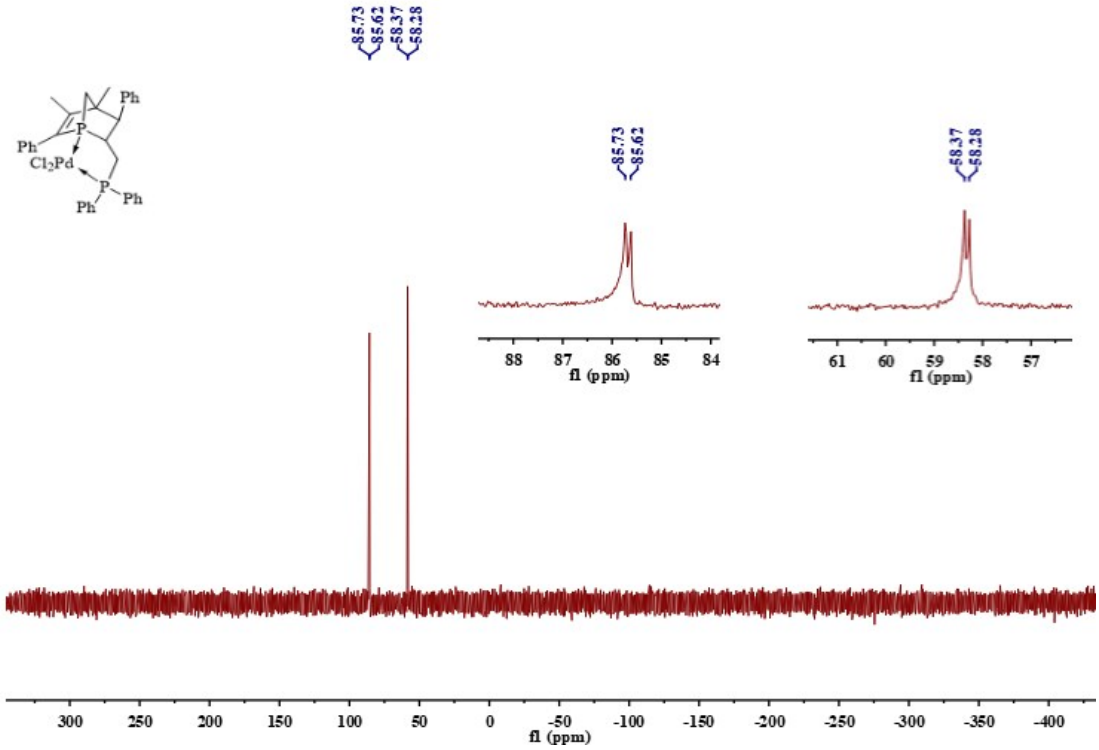
^{1}H ($CDCl_3$, 300 MHz) NMR of **6b**



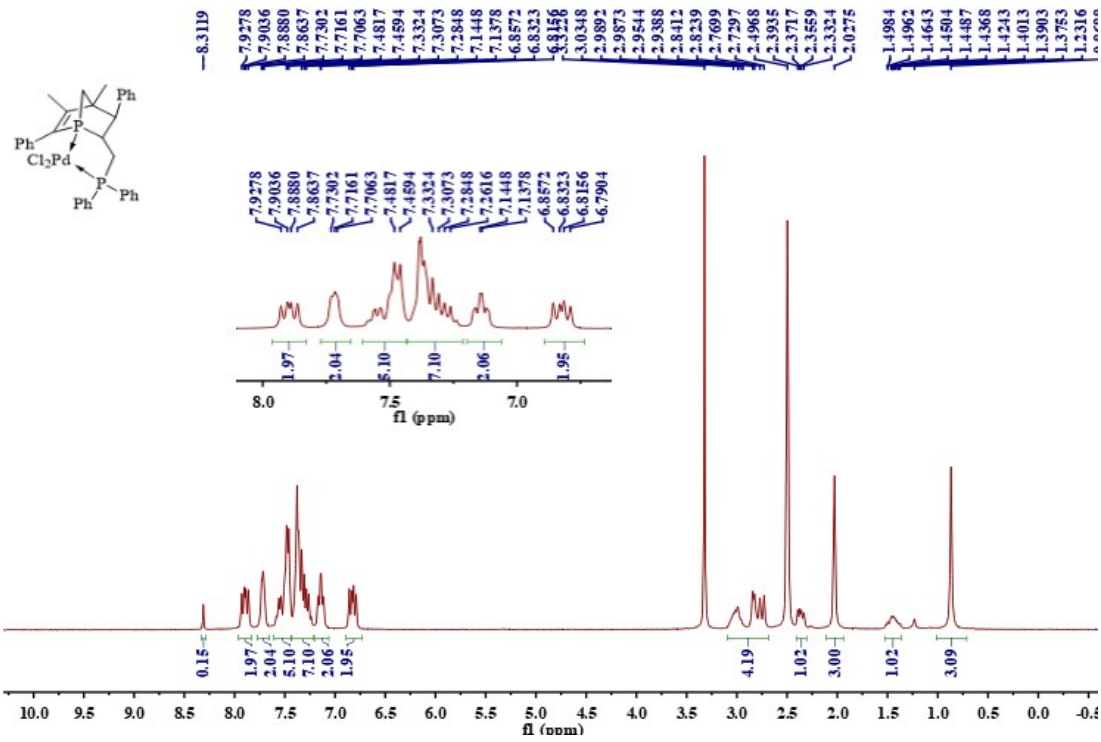
Dept135 ($CDCl_3$, 75 MHz) NMR of **6b**



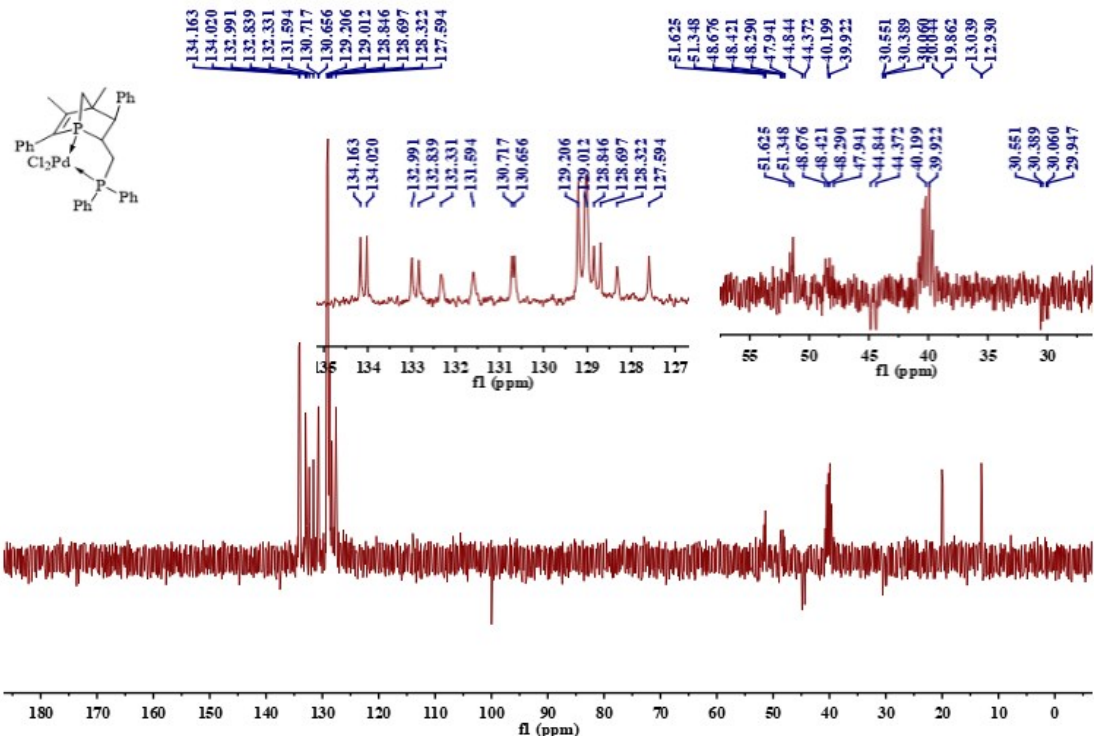
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of **6b**



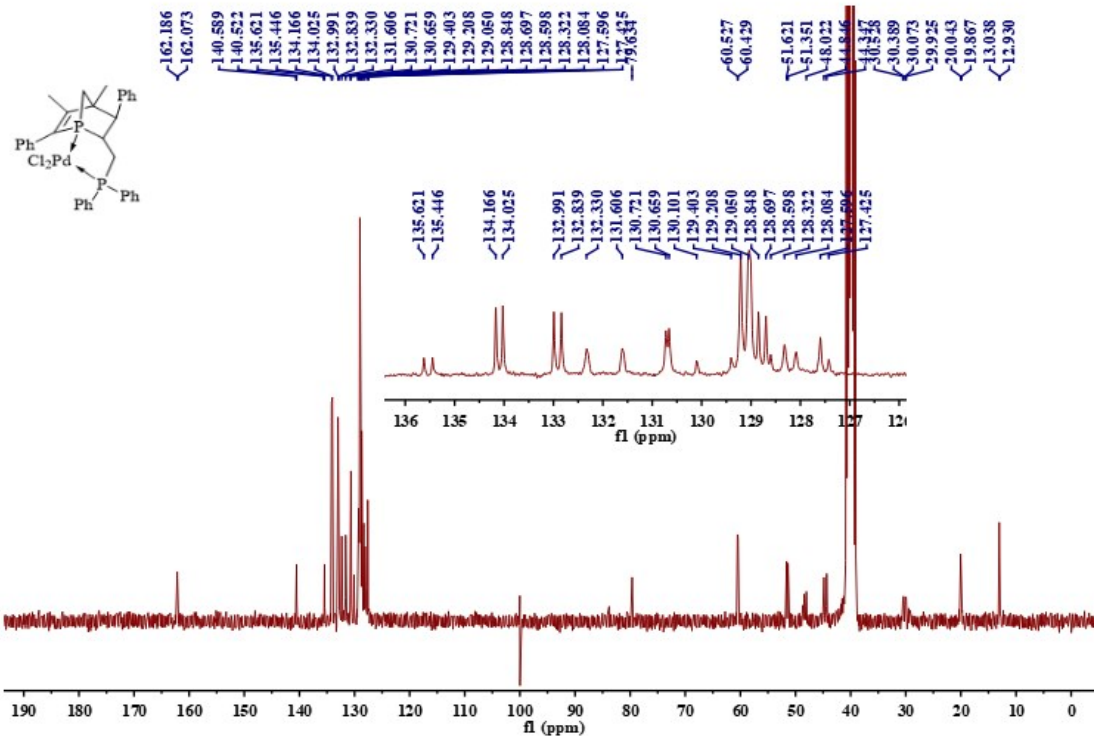
^{31}P ($(CD_3)_2SO$, 121 MHz) NMR of **7**



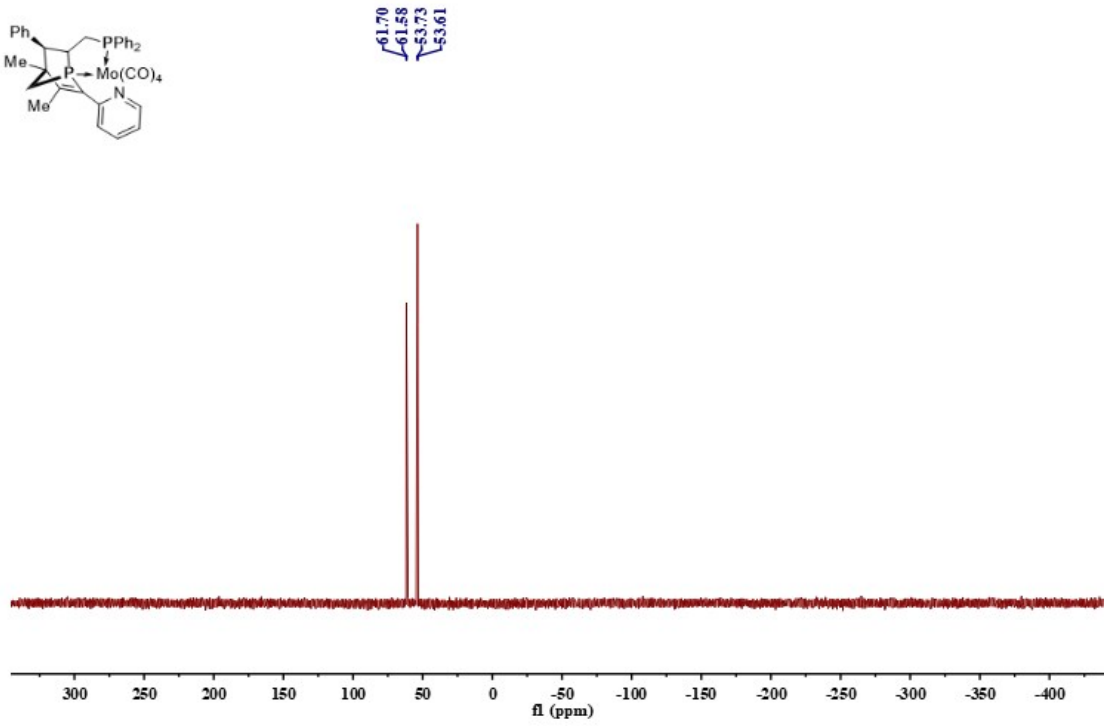
^{1}H ($(CD_3)_2SO$, 300 MHz) NMR of **7**



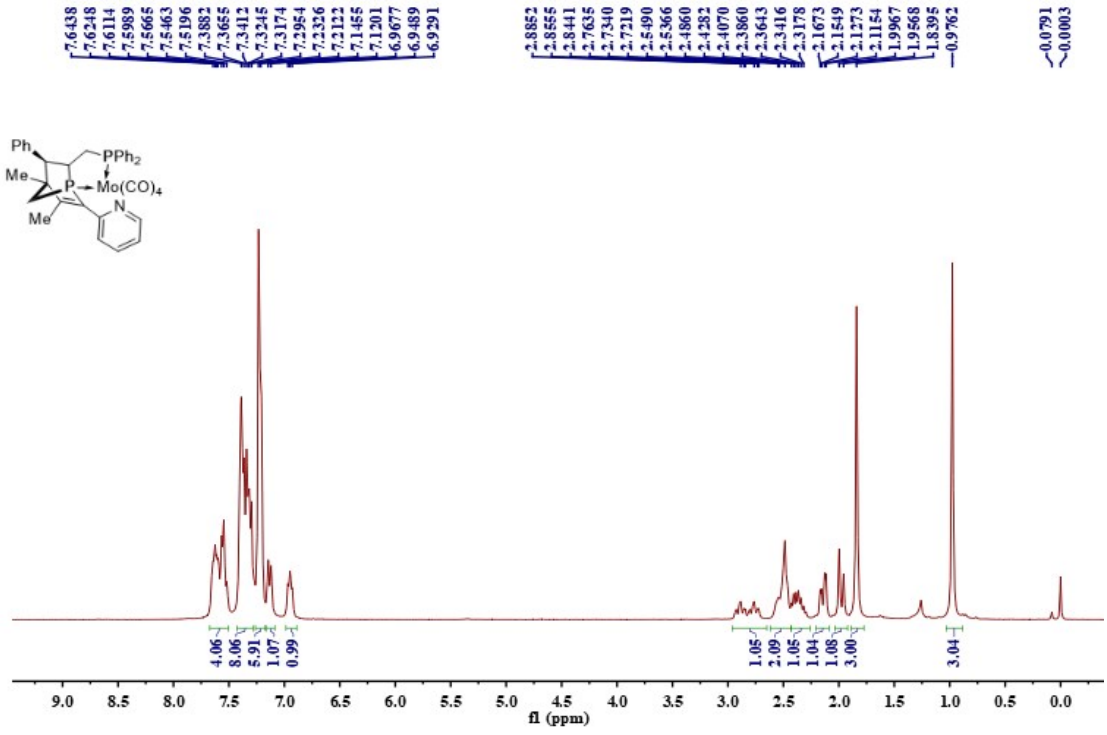
Dept135 ($(CD_3)_2SO$, 75 MHz) NMR of **7**



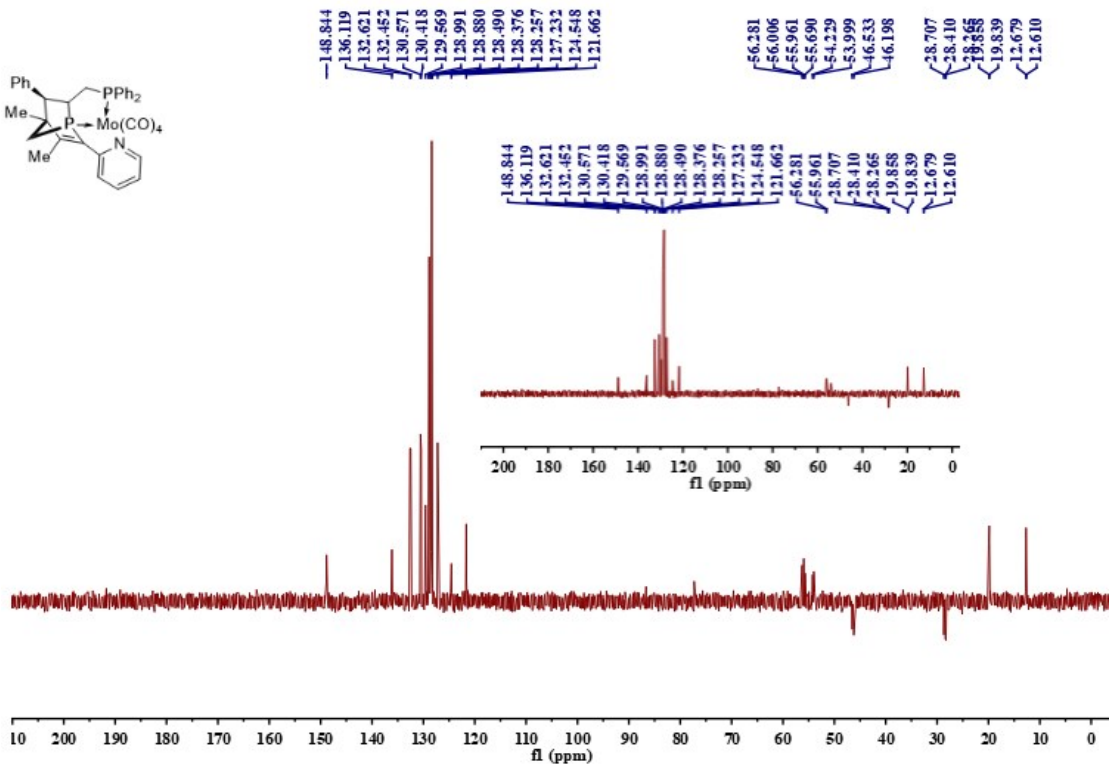
^{13}C {^{1}H} ($(CD_3)_2SO$, 75 MHz) NMR of **7**



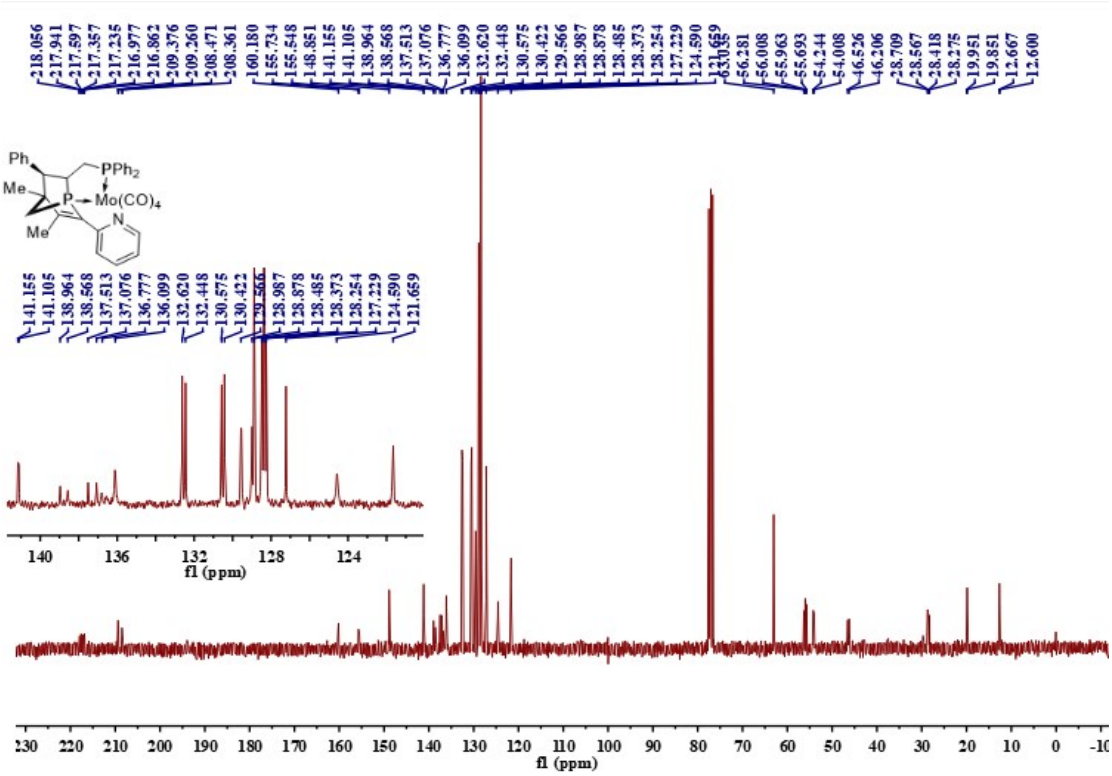
^{31}P ($CDCl_3$, 121 MHz) NMR of **8**



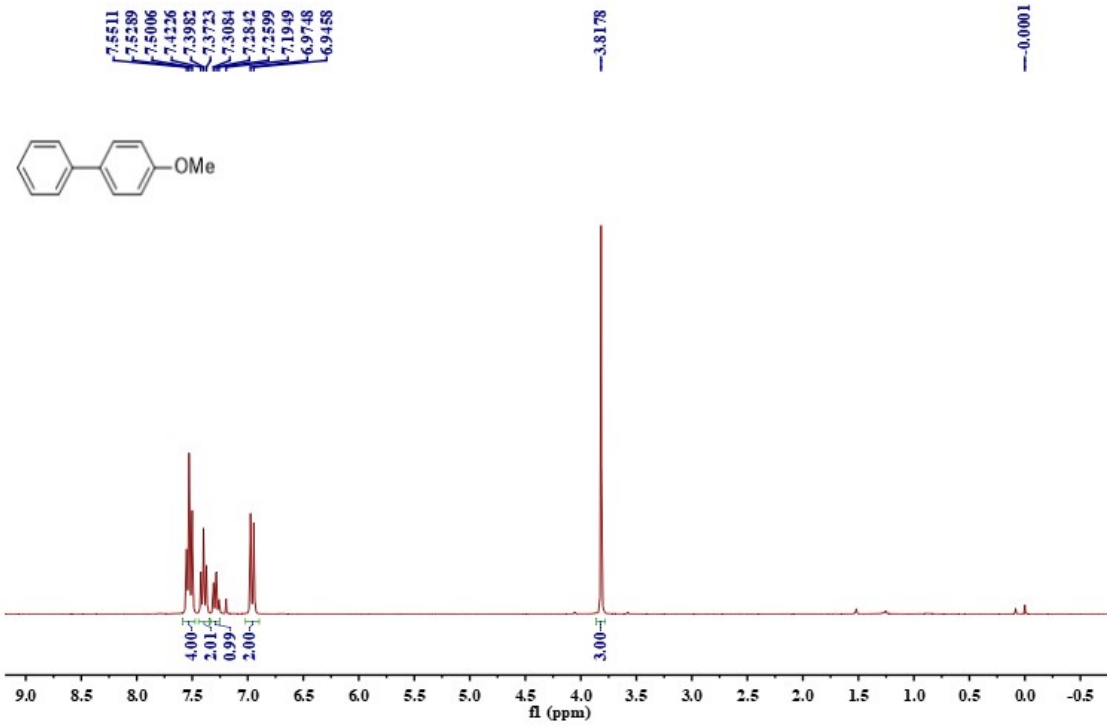
^{1}H ($CDCl_3$, 300 MHz) NMR of **8**



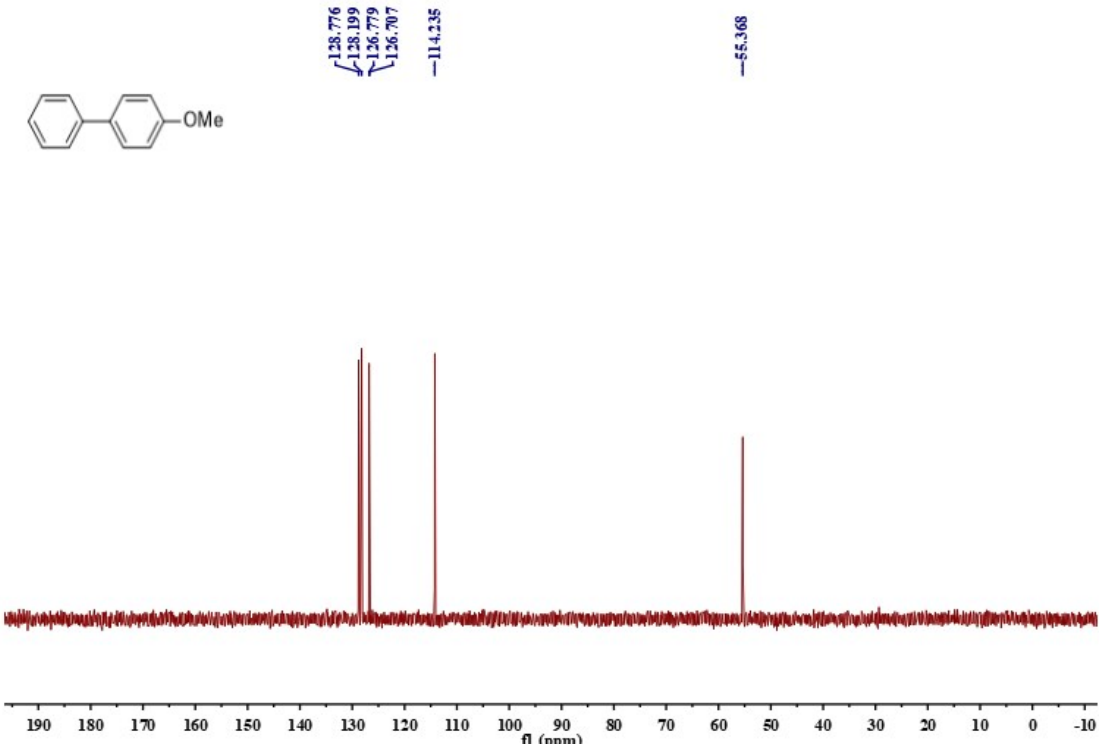
Dept135 ($CDCl_3$, 75 MHz) NMR of **8**



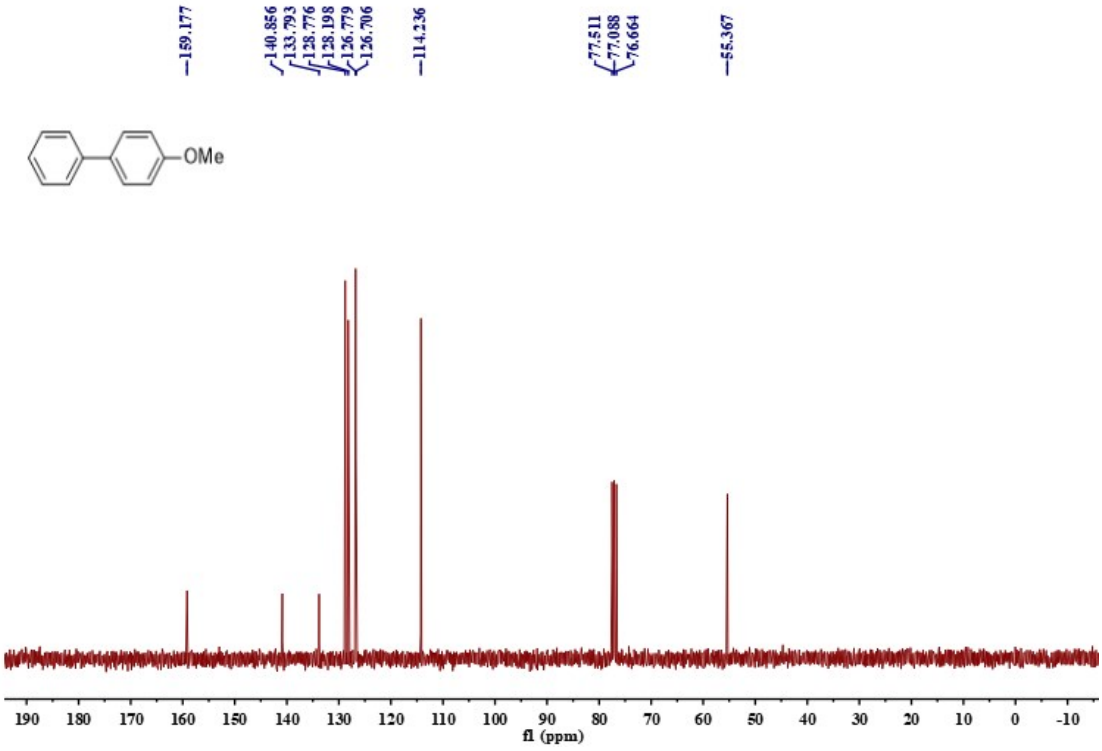
^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of **8**



^{1}H ($CDCl_3$, 300 MHz) NMR of **9**



Dept135 ($CDCl_3$, 75 MHz) NMR of **9**



^{13}C {^{1}H} ($CDCl_3$, 75 MHz) NMR of **9**