Rhodium(I)-Catalysed Conjugate Phosphination of Cyclic α,β-Unsaturated Ketones with Silylphosphines as Masked Phosphinides

Verena T. Trepohl and Martin Oestreich*

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster,
Corrensstrasse 40, D-48149 Münster, Germany
martin.oestreich@uni-muenster.de

Electronic Supplementary Information

Contents

1 General Information

Reagents obtained from commercial suppliers were used without further purification unless otherwise noted. All reactions were performed in flame-dried glassware under a static pressure of argon. Liquids and solutions were transferred with syringes or double-ended needles. Solvents were dried prior to use following standard procedures (THF). Technical grade solvents for extraction or chromatography (cyclohexane, *t*-butyl methyl ether and ethyl acetate) were distilled before use. Et_3N and the α,β-unsaturated cyclic ketones **6–8** were dried over CaH_2 and distilled prior to use. Silylphosphines **1a**, **2a** and **3b** were prepared according to the reported procedure.[1] Analytical thin layer chromatography was performed on silica gel SIL G-25 glass plates by Macherey-Nagel/Germany and flash chromatography on silica gel 60 (40-63 μm, 230-400 mesh, ASTM) by Merck/Germany using the indicated solvents. ^1H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ on Bruker AM 300, AM 400 and DRX 500 instruments.

2 Characterisation data for Compounds **3b**, **4b** and **5c** as well as **12**–**14**

(Triisopropylsilyl)dicyclohexylphosphine (3b): 280 °C/5·10^{-2} mbar. IR ($CHCl_3$/cuvette): 1449 (s), 1229 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.86–1.41 (m, 32H), 1.58–1.76 (m, 6H), 1.80–2.02 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9 (d, J_{C-P} = 8.2 Hz), 19.8 (d, J_{C-P} = 3.9 Hz), 26.1 (d, J_{C-P} = 0.5 Hz), 27.9 (d, J_{C-P} = 9.1 Hz), 30.1 (d, J_{C-P} = 14.1 Hz), 34.3 ppm. ^{31}P {^1H} NMR (162 MHz, $CDCl_3$) δ –50.6 ppm. Anal. Calcd for $C_{21}H_{43}PSi$ (354.63): C, 71.12; H, 12.22; Found: C, 70.73; H, 11.94.

(Dimethylphenylsilyl)dicyclohexylphosphine (4b): 275 °C/5·10^{-2} mbar. IR ($CHCl_3$/cuvette): 1446 (s), 1247 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 0.51 (s, 3H), 0.53 (s, 3H), 1.03–1.36 (m, 10H), 1.54–1.90 (m, 12H), 7.28–7.45 (m, 3H), 7.51–7.67 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.6 (d, J_{C-P} = 10.6 Hz), 26.2, 27.5 (d, J_{C-P} = 10.0 Hz), 27.7 (d, J_{C-P} = 9.6 Hz), 30.9 (d, J_{C-P} = 14.0 Hz), 32.6 (d, J_{C-P} = 10.5 Hz), 33.5 (d, J_{C-P} = 10.6 Hz), 127.6, 128.8, 134.1 (d, J_{C-P} = 3.4 Hz), 139.2 (d, J_{C-P} = 10.1 Hz) ppm. ^{31}P {^1H} NMR (162 MHz, $CDCl_3$) δ –52.9 ppm.

Di-*tert*-butyl(dimethylphenylsilyl)phosphine (5c): 220 °C/5·10^{-2} mbar. IR ($CHCl_3$/cuvette): 1473 (s), 1250 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 0.61 (s, 3H), 0.62 (s, 3H), 1.20 (s, 9H), 1.24 (s, 9H), 7.30–7.37 (m, 3H), 7.60–7.68 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 1.7 (d, J_{C-P} = 9.8 Hz), 32.8, 33.1 (d, J_{C-P} = 11.5 Hz), 127.7, 128.7, 134.4 (d, J_{C-P} = 3.5 Hz), 140.8 (d, J_{C-P} = 11.9 Hz) ppm. ^{31}P {^1H} NMR (162 MHz, $CDCl_3$) δ –3.2 ppm. Anal. Calcd for $C_{16}H_{29}PSi$ (280.46): C, 68.52; H, 10.42; Found: C, 68.40; H, 9.97.

3-(Diphenylphosphinoxy)cyclopentanone (12a): R_f = 0.18 (cyclohexane–ethyl acetate 1:9). Mp 86 °C. IR ($CHCl_3$/cuvette): 1744 (s) (C=O) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.03–2.11 (m, 1H), 2.18–2.37 (m, 3H), 2.45 (m, 1H), 2.62 (m, 1H), 3.06 (m, 1H), 7.46–7.58 (m, 6H), 7.74–7.84 (m, 4H)

[1] M. Hayashi, Y. Matsuura and Y. Watanabe, *Tetrahedron Lett.*, 2004, **45**, 1409–1411.

ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.5 (d, J_{C-P} = 2.3 Hz), 35.0, 35.6, 37.9 (d, J_{C-P} = 2.1 Hz), 128.8 (d, J_{C-P} = 2.0 Hz), 128.9 (d, J_{C-P} = 2.0 Hz), 130.7 (d, J_{C-P} = 9.1 Hz), 130.9 (d, J_{C-P} = 9.1 Hz), 132.0 (d, J_{C-P} = 2.7 Hz), 132.1 (d, J_{C-P} = 2.7 Hz), 216.0 (d, J_{C-P} = 12.7 Hz) ppm. ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) δ 32.8 ppm. Anal. Calcd for $C_{17}H_{17}O_2P$ (284.29): C, 71.82; H, 6.03; Found: C, 71.43; H, 5.83.

3-(Diphenylphosphinoxy)cyclohexanone (13a): R_f = 0.22 (cyclohexane–ethyl acetate 1:9). Mp 154°C. IR ($CHCl_3$/cuvette): 1712 (s) (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70 (m, 1H), 1.85 (m, 1H), 1.97 (m, 1H), 2.19 (m, 1H), 2.30 (m, 1H), 2.38 (m, 2H), 2.67 (m, 2H), 7.45–7.56 (m, 6H), 7.73–7.83 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.4 (d, J_{C-P} = 3.0 Hz), 26.4 (d, J_{C-P} = 15.5 Hz), 37.9 (d, J_{C-P} = 17.6 Hz), 39.4 (d, J_{C-P} = 3.2 Hz), 41.1, 128.8 (d, J_{C-P} = 3.5 Hz), 128.9 (d, J_{C-P} = 3.5 Hz), 130.8 (d, J_{C-P} = 2.5 Hz), 130.9 (d, J_{C-P} = 2.5 Hz), 131.9 (d, J_{C-P} = 2.8 Hz), 132.0 (d, J_{C-P} = 2.8 Hz), 209.7 (d, J_{C-P} = 14.0 Hz) ppm. ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) δ 31.8 ppm. Anal. Calcd for $C_{18}H_{19}O_2P$ (298.32): C, 72.47; H, 6.42; Found: C, 72.09; H, 6.47.

3-(Diphenylphosphinoxy)cycloheptanone (14a): R_f = 0.15 (cyclohexane–ethyl acetate 1:9). Mp 198°C. IR ($CHCl_3$/cuvette): 1709 (s) (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (m, 1H), 1.65 (m, 2H), 1.87–2.13 (m, 3H), 2.44–2.64 (m, 4H), 2.79 (m, 1H), 7.44–7.57 (m, 6H), 7.73–7.84 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.6, 28.9, 29.2 (d, J_{C-P} = 15.3 Hz), 35.4 (d, J_{C-P} = 14.0 Hz), 41.8, 43.7, 128.8 (d, J_{C-P} = 11.5 Hz), 129.9 (d, J_{C-P} = 11.5 Hz), 130.9 (d, J_{C-P} = 8.0 Hz), 131.0 (d, J_{C-P} = 7.9 Hz), 131.8 (d, J_{C-P} = 2.8 Hz), 131.9 (d, J_{C-P} = 2.7 Hz), 212.1 (d, J_{C-P} = 17.8 Hz) ppm. ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) δ 36.1 ppm. Anal. Calcd for $C_{19}H_{21}O_2P$ (312.34): C, 73.06; H, 6.78; Found: C, 72.71; H, 6.59.

3-(Dicyclohexylphosphinoxy)cyclopentanone (12b): R_f = 0.06 (cyclohexane–ethyl acetate 1:9). Mp 154°C. IR ($CHCl_3$/cuvette): 1742 (s) (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19–1.44 (m, 10H), 1.69–2.01 (m, 12H), 2.06 (m, 1H), 2.18 (m, 2H), 2.29 (m, 1H), 2.65–2.35 (m, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.1 (d, J_{C-P} = 2.9 Hz), 26.0 (d, J_{C-P} = 1.4 Hz), 26.1 (d, J_{C-P} = 1.5 Hz), 26.5 (d, J_{C-P} = 2.8 Hz), 26.7 (d, J_{C-P} = 5.9 Hz), 26.8 (d, J_{C-P} = 3.2 Hz), 26.9 (d, J_{C-P} = 10.9 Hz), 27.0 (d, J_{C-P} = 11.0 Hz), 31.5, 32.0, 36.7, 37.0, 37.2, 37.5, 37.6 (d, J_{C-P} = 5.9 Hz), 38.6 (d, J_{C-P} = 2.5 Hz), 216.41 (d, J_{C-P} = 12.4 Hz) ppm. ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) δ 49.9 ppm. Anal. Calcd for $C_{17}H_{29}O_2P$ (296.39): C, 68.89; H, 9.86; Found: C, 69.01; H, 10.06.

3-(Dicyclohexylphosphinoxy)cyclohexanone (13b): R_f = 0.03 (cyclohexane–ethyl acetate 1:9). Mp 155°C. IR ($CHCl_3$/cuvette): 1712 (s) (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.18–1.30 (m, 6H), 1.31–1.45 (m, 4H), 1.67–1.77 (m, 3H), 1.78–2.01 (m, 11H), 2.06 (m, 1H), 2.24 (m, 2H), 2.34 (dt, J = 13.7, 6.1 Hz, 1H), 2.45 (m, 2H), 2.61 (dt, J = 13.7, 8.3 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.5 (d, J_{C-P} = 3.5 Hz), 25.9 (d, J_{C-P} = 1.4 Hz), 26.0 (d, J_{C-P} = 1.5 Hz), 26.4 (d, J_{C-P} = 3.0 Hz), 26.5 (d, J_{C-P} = 2.9 Hz), 26.6 (d, J_{C-P} = 2.7 Hz), 26.7 (d, J_{C-P} = 5.5 Hz), 26.8 (d, J_{C-P} = 4.8 Hz), 26.8 (d, J_{C-P} = 2.8 Hz), 26.9 (d, J_{C-P} = 2.8 Hz), 30.0 (d, J_{C-P} = 2.8 Hz), 34.5, 34.9, 35.9 (d, J_{C-P} = 10.0 Hz), 36.4 (d,

J_{C-P} = 10.4 Hz), 40.7 (d, J_{C-P} = 3.4 Hz), 41.2, 209.7 (d, J_{C-P} = 11.9 Hz) ppm. ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) δ 48.6 ppm. Anal. Calcd for $C_{18}H_{31}O_2P$ (310.41): C, 69.65; H, 10.07; Found: C, 69.35; H, 10.07.

3-(Dicyclohexylphosphinoxy)cycloheptanone (14b): R_f = 0.10 (cyclohexane–ethyl acetate 1:9). Mp 122°C. IR ($CHCl_3$/cuvette): 1700 (s) (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.20–1.32 (m, 6H), 1.35–1.52 (m, 6H), 1.59 (m, 1H), 1.74 (m, 2H), 1.79–2.01 (m, 11H), 2.15 (m, 2H), 2.31 (m, 1H), 2.54 (m, 2H), 2.63 (m, 1H), 2.73 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.3, 25.8 (d, J_{C-P} = 1.4 Hz), 25.9 (d, J_{C-P} = 1.4 Hz), 26.0 (d, J_{C-P} = 3.2 Hz), 26.1 (d, J_{C-P} = 3.1 Hz), 26.2 (d, J_{C-P} = 3.2 Hz), 26.4 (d, J_{C-P} = 3.1 Hz), 26.7 (d, J_{C-P} = 11.7 Hz), 26.8 (d, J_{C-P} = 11.7 Hz), 26.9 (d, J_{C-P} = 11.8 Hz), 29.9 (d, J_{C-P} = 2.1 Hz), 30.4 (d, J_{C-P} = 12.6 Hz), 32.9, 33.4, 35.0 (d, J_{C-P} = 24.0 Hz), 35.5 (d, J_{C-P} = 23.7 Hz), 43.1 (d, J_{C-P} = 0.9 Hz), 43.2, 212.1 (d, J_{C-P} = 16.0 Hz) ppm. ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) δ 52.1 ppm. HRMS (ESI) calculated for $C_{19}H_{33}O_2PNa$ ($[M+Na]^+$): 295.1797; Found: 295.1795.

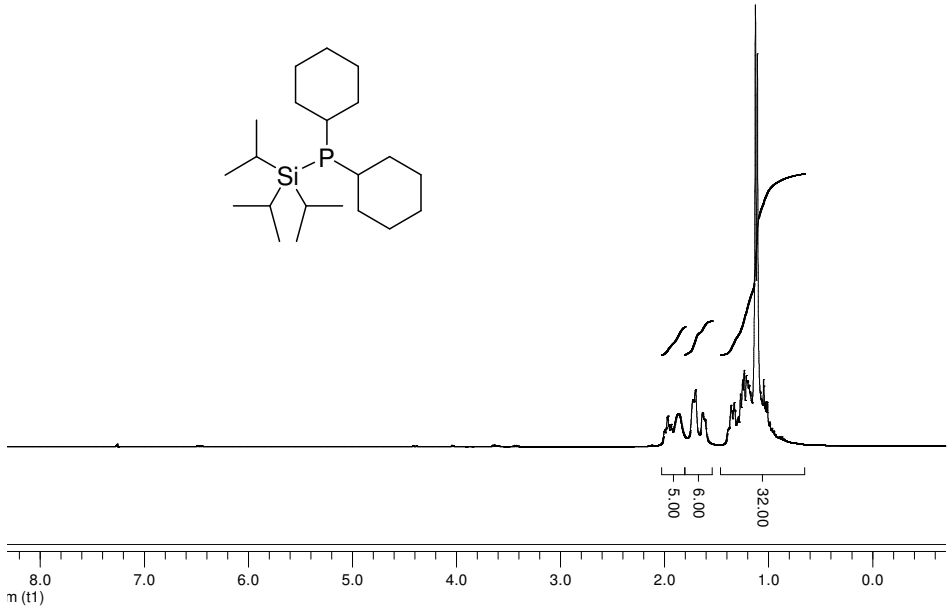
3-(Di-*tert*-butylphosphinoxy)cyclopentanone (12c): R_f = 0.04 (cyclohexane–ethyl acetate 1:9). Mp 61°C. IR ($CHCl_3$/cuvette): 1743 (s) (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 9H), 1.29 (s, 9H), 2.13 (m, 1H), 2.21–2.36 (m, 2H), 2.37–2.72 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.1 (d, J_{C-P} = 2.9 Hz), 27.3, 27.5, 33.9, 34.4, 36.6 (d, J_{C-P} = 18.6 Hz), 37.1 (d, J_{C-P} = 18.4 Hz), 38.0 (d, J_{C-P} = 5.8 Hz), 216.4 (d, J_{C-P} = 12.2 Hz) ppm. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ 59.6 ppm. HRMS (ESI) calculated for $C_{13}H_{25}O_2PNa$ ($[M+Na]^+$): 267.1484; Found: 267.1483.

3-(Di-*tert*-butylphosphinoxy)cyclohexanone (13c): R_f = 0.05 (cyclohexane–ethyl acetate 1:9). Mp 120°C. IR ($CHCl_3$/cuvette): 1712 (s) (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (s, 9H), 1.30 (s, 9H), 1.62 (m, 1H), 1.85 (m, 1H), 2.17 (m, 1H), 2.25–2.47 (m, 4H), 2.55 (td, J = 14.0, 5.0 Hz, 1H), 2.83 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.1, 27.2, 27.4, 37.1 (d, J_{C-P} = 2.4 Hz), 37.6, 37.7 (d, J_{C-P} = 2.1 Hz), 38.1, 41.5, 43.6 (d, J_{C-P} = 2.9 Hz), 208.8 (d, J_{C-P} = 11.5 Hz) ppm. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ 56.2 ppm. Anal. Calcd for $C_{14}H_{27}O_2P$ (258.34): C, 65.09; H, 10.53; Found: C, 65.09; H, 10.64.

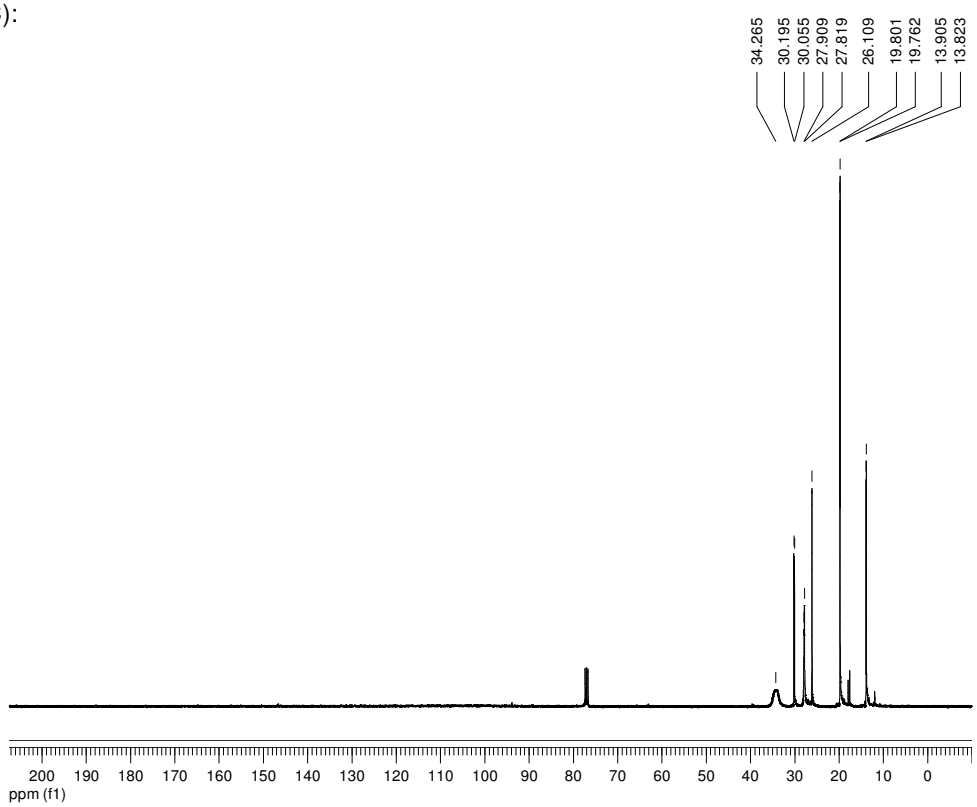
3-(Di-*tert*-butylphosphinoxy)cycloheptanone (14c): R_f = 0.07 (cyclohexane–ethyl acetate 1:9). Mp 81°C. IR ($CHCl_3$/cuvette): 1700 (s) (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (s, 3H), 1.26 (s, 3H), 1.28 (s, 3H), 1.29 (s, 3H), 1.31 (s, 3H), 1.32 (s, 3H), 1.35–1.63 (m, 3H), 1.96 (m, 1H), 2.10 (m, 1H), 2.33 (m, 1H), 2.46–2.65 (m, 3H), 2.70 (m, 1H), 3.06 (ddt, J = 15.4, 8.7, 2.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.5, 25.7 (d, J_{C-P} = 1.5 Hz), 27.7, 31.3 (d, J_{C-P} = 11.7 Hz), 35.3 (d, J_{C-P} = 18.9 Hz), 37.4 (d, J_{C-P} = 18.9 Hz), 43.0, 44.7 (d, J_{C-P} = 1.0 Hz), 212.3 (d, J_{C-P} = 14.6 Hz) ppm. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ 59.8 ppm. HRMS (ESI) calculated for $C_{15}H_{29}O_2PNa$ ($[M+Na]^+$): 295.1797; Found: 295.1795.

3 ^{1}H, ^{13}C and ^{31}P NMR Spectra for Compounds **3b**, **4b** and **5c** as well as **12**–**14**

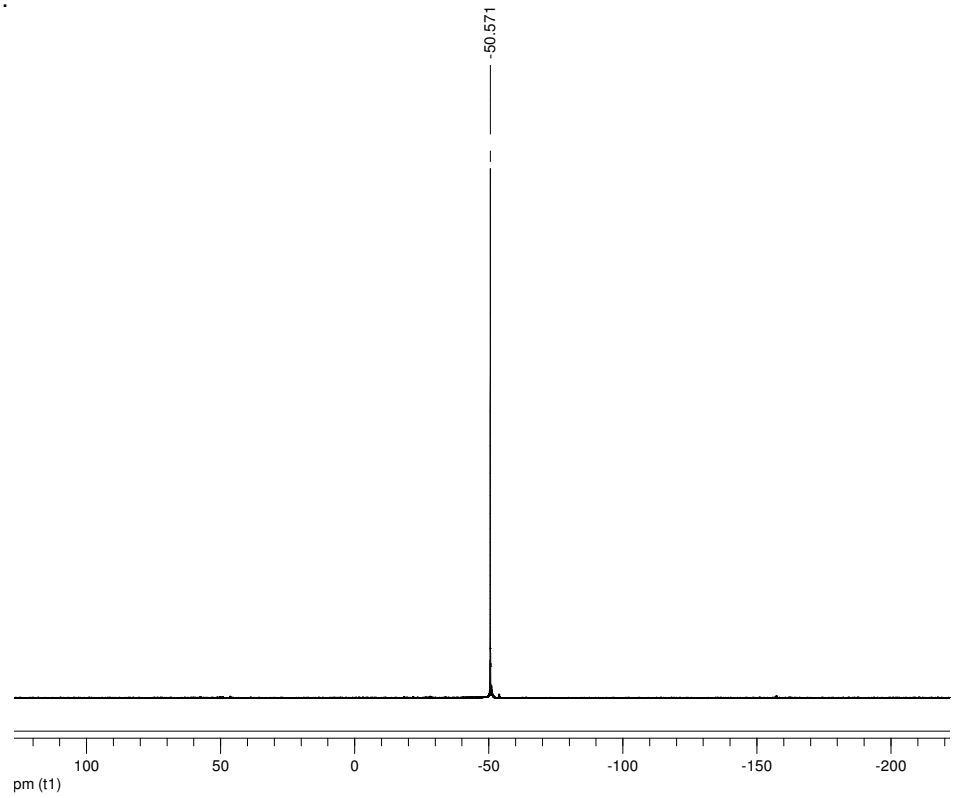
3b (^{1}H):



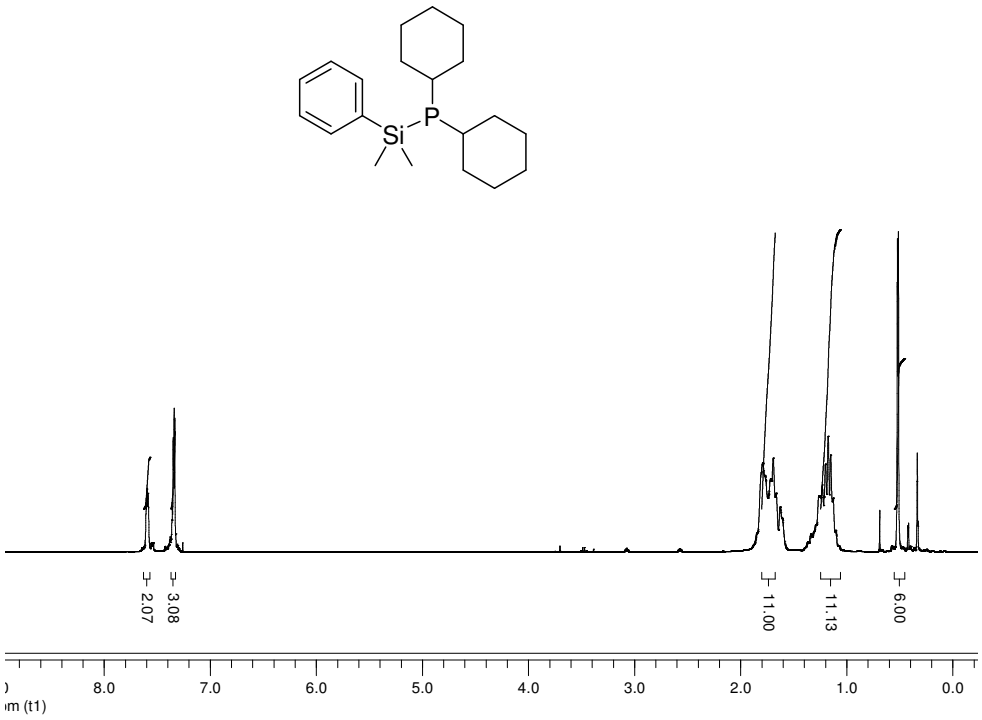
3b (^{13}C):



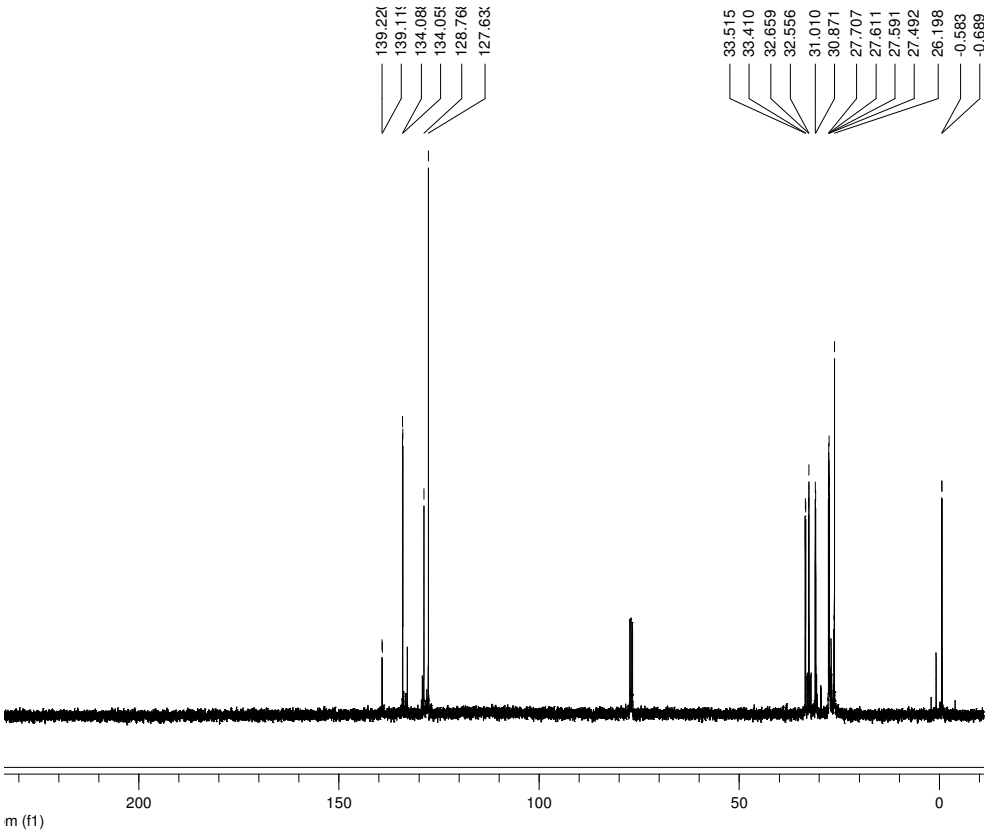
3b (^{31}P):


-50.571
100
50
0
-50
-100
-150
-200
pm (t1)

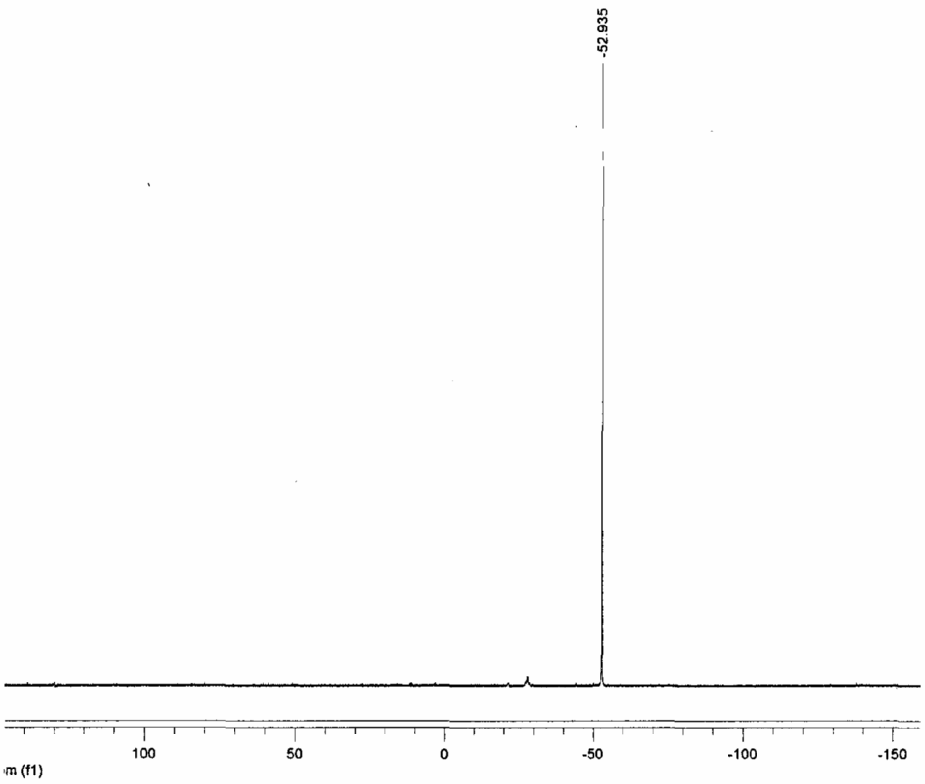
4b (^{1}H):


Si
P
2.07
3.08
11.00
11.13
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

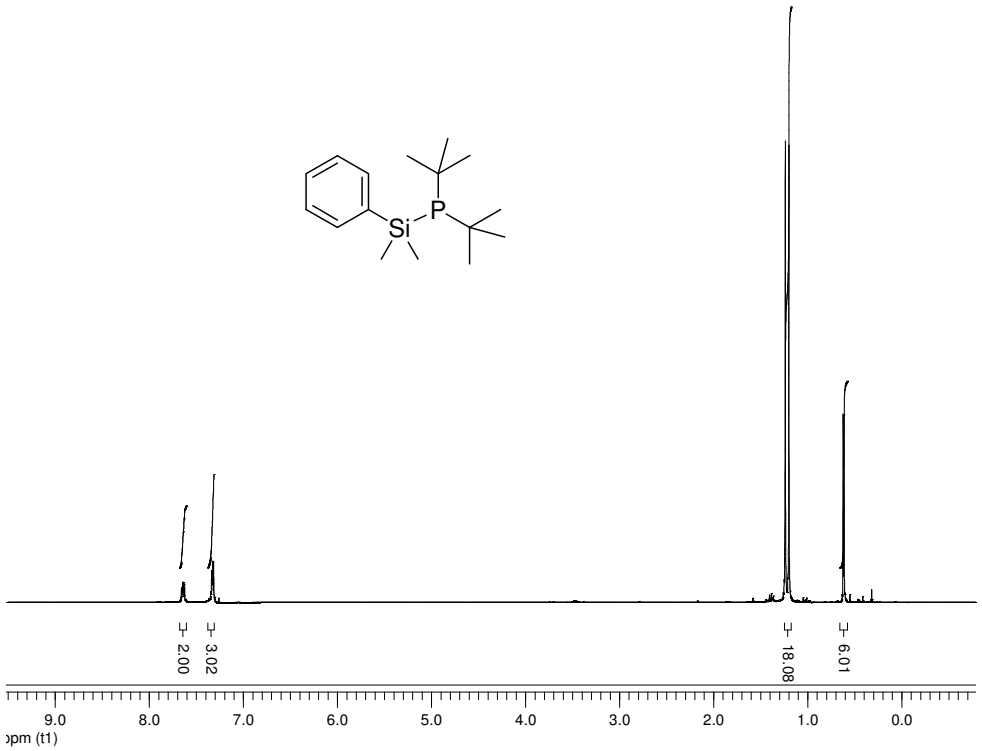
4b (^{13}C):


139.22
139.11
134.08
134.05
128.76
127.63
33.515
33.410
32.659
32.556
31.010
30.871
27.707
27.611
27.591
27.492
26.198
-0.583
-0.689
200
150
100
50
0
m (f1)

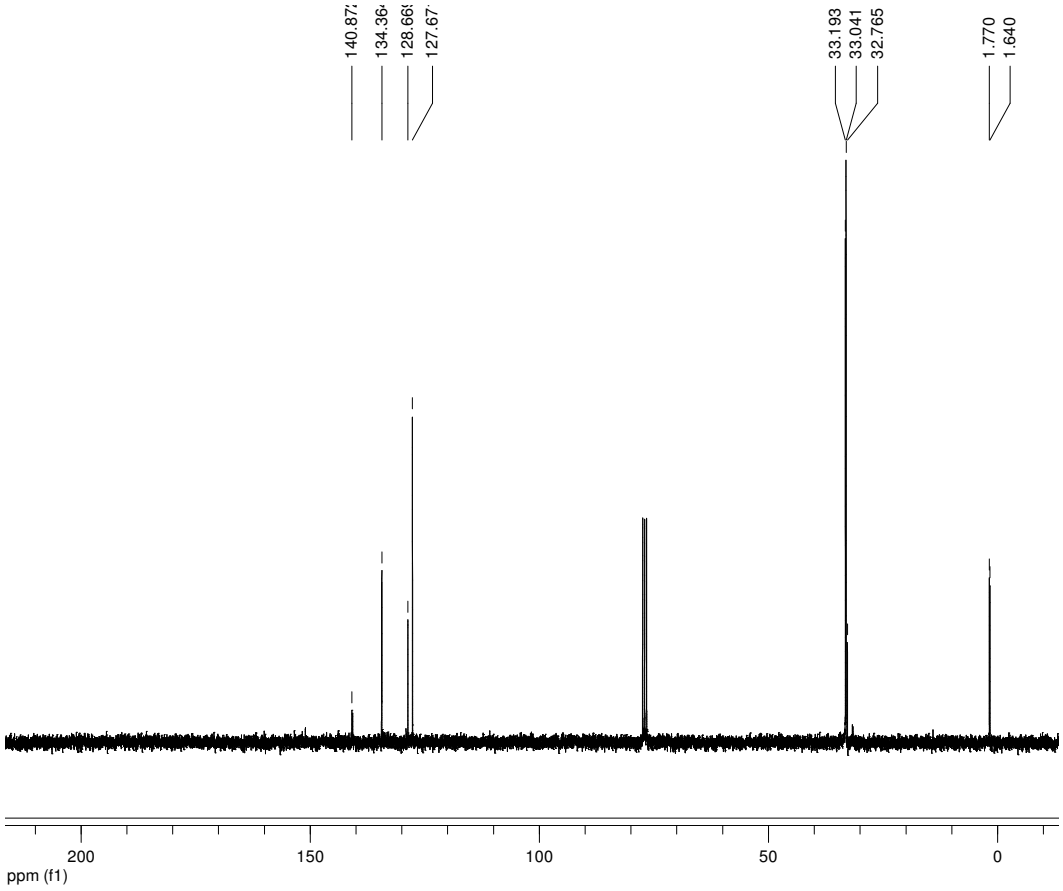
4b (^{31}P):


-52.935
100
50
0
-50
-100
-150
m (f1)

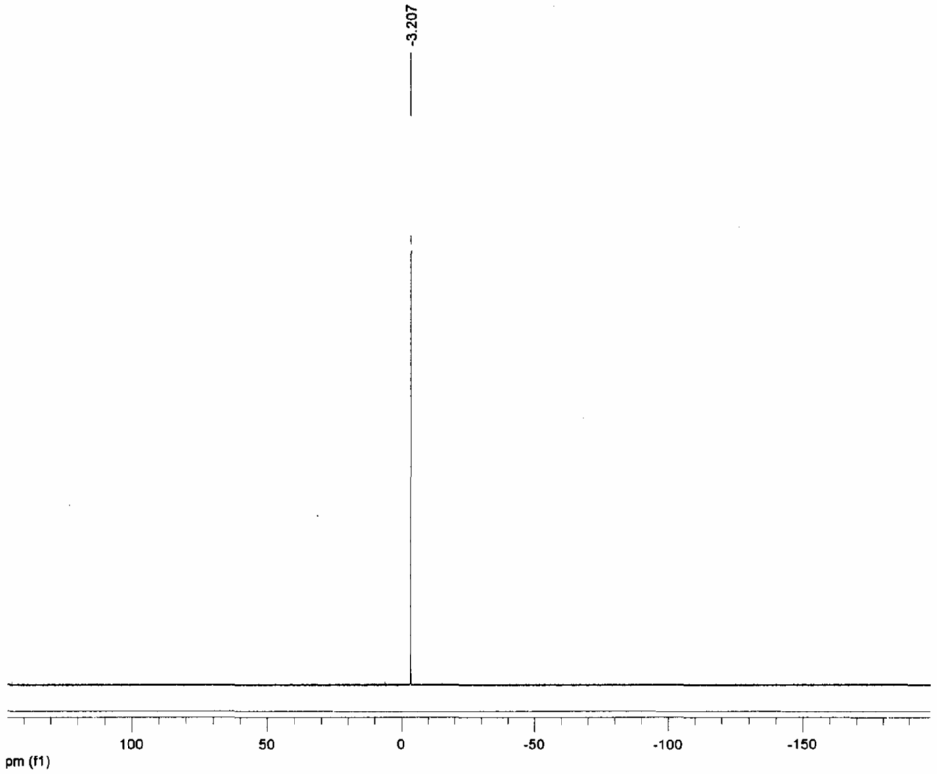
5c (^{1}H):


Si
P
2.00
3.02
18.08
6.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

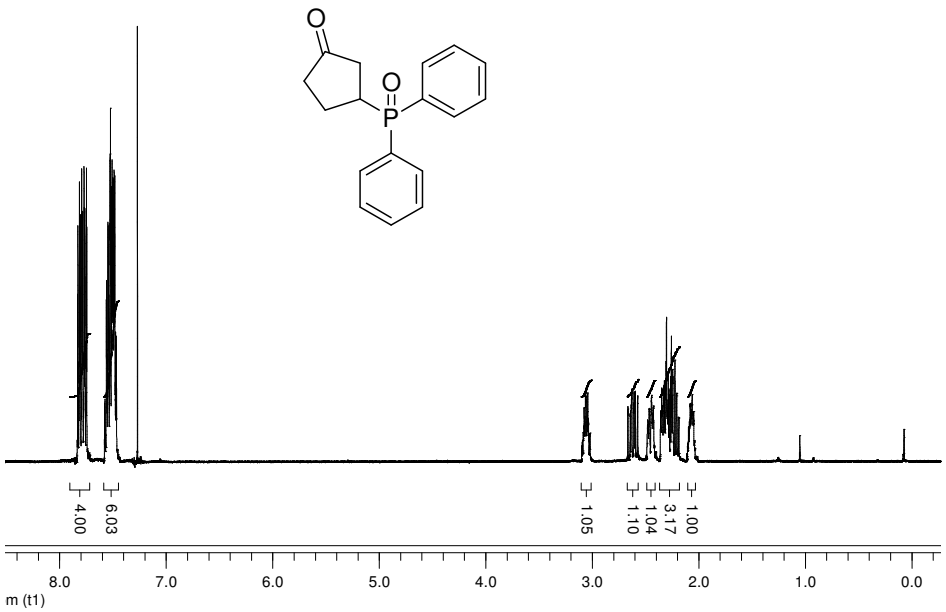
5c (^{13}C):


140.87
134.36
128.66
127.67
33.193
33.041
32.765
1.770
1.640
200
150
100
50
0
ppm (f1)

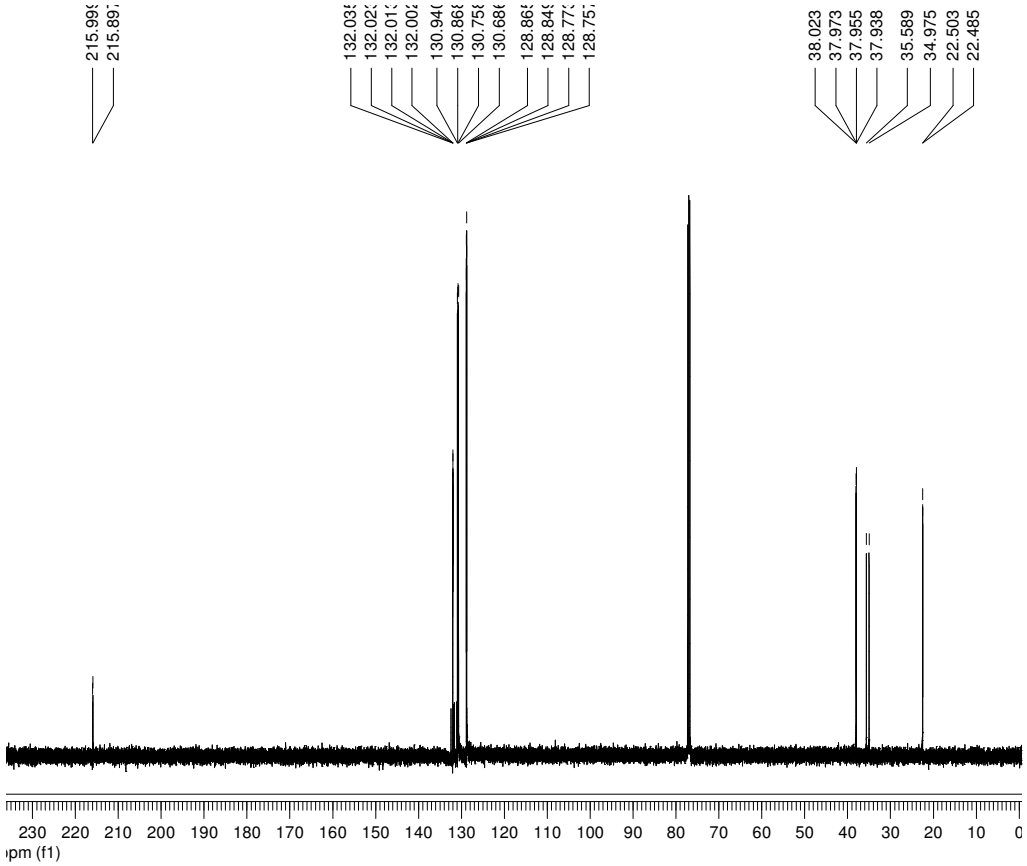
5c (^{31}P):


-3.207
100
50
0
-50
-100
-150
ppm (f1)

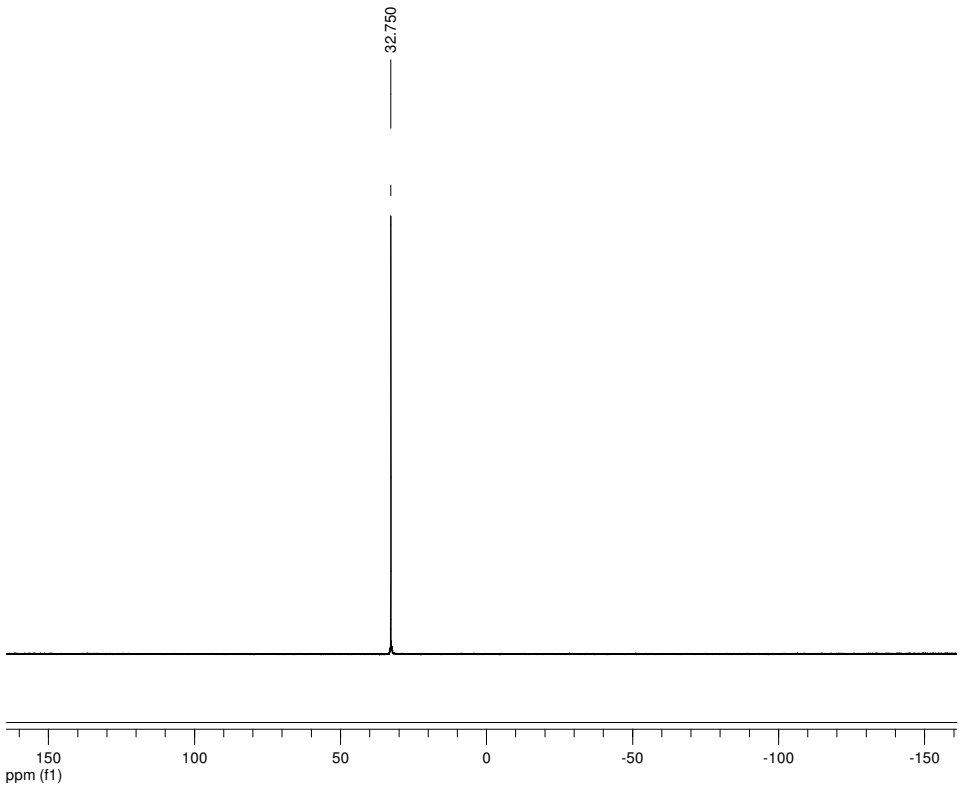
12a (^{1}H):


O
O
P
4.00
6.03
1.05
1.10
1.04
3.17
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
m (t1)

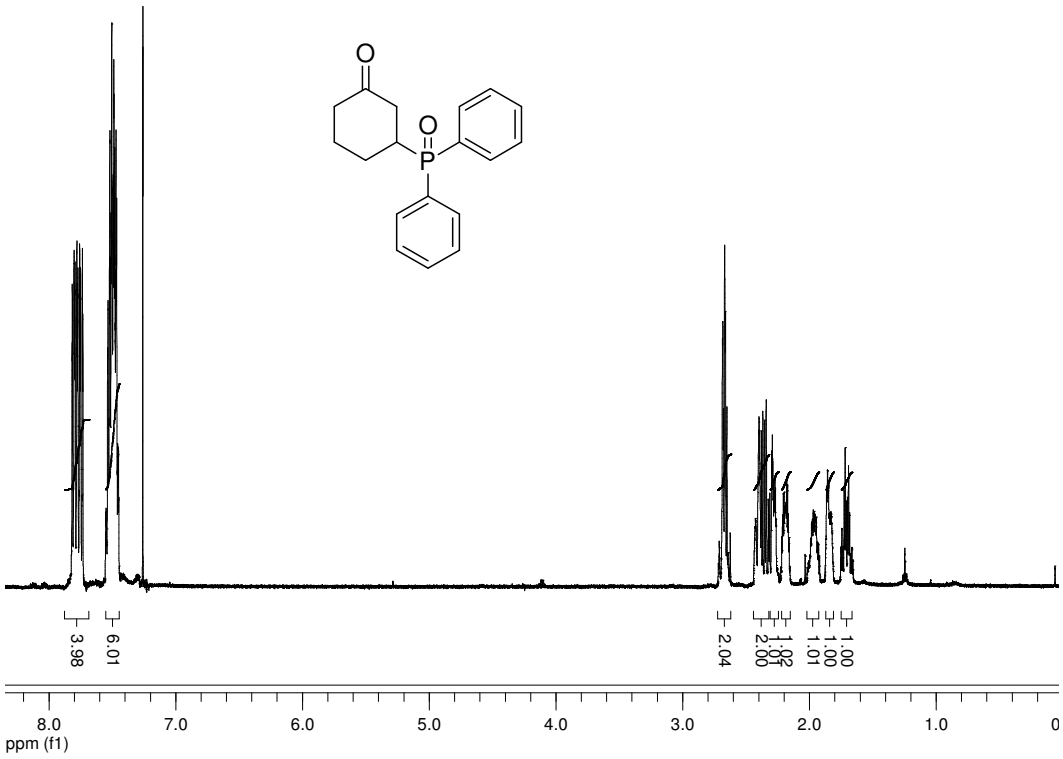
12a (^{13}C):



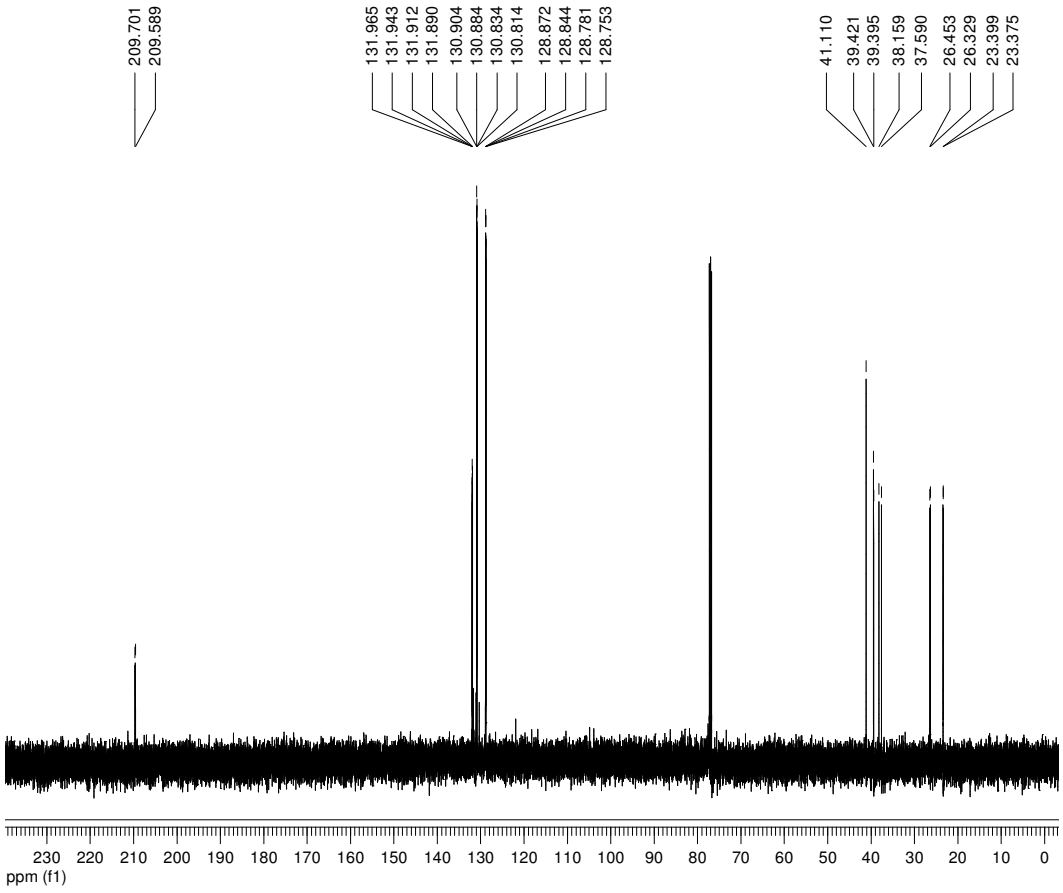
12a (^{31}P):



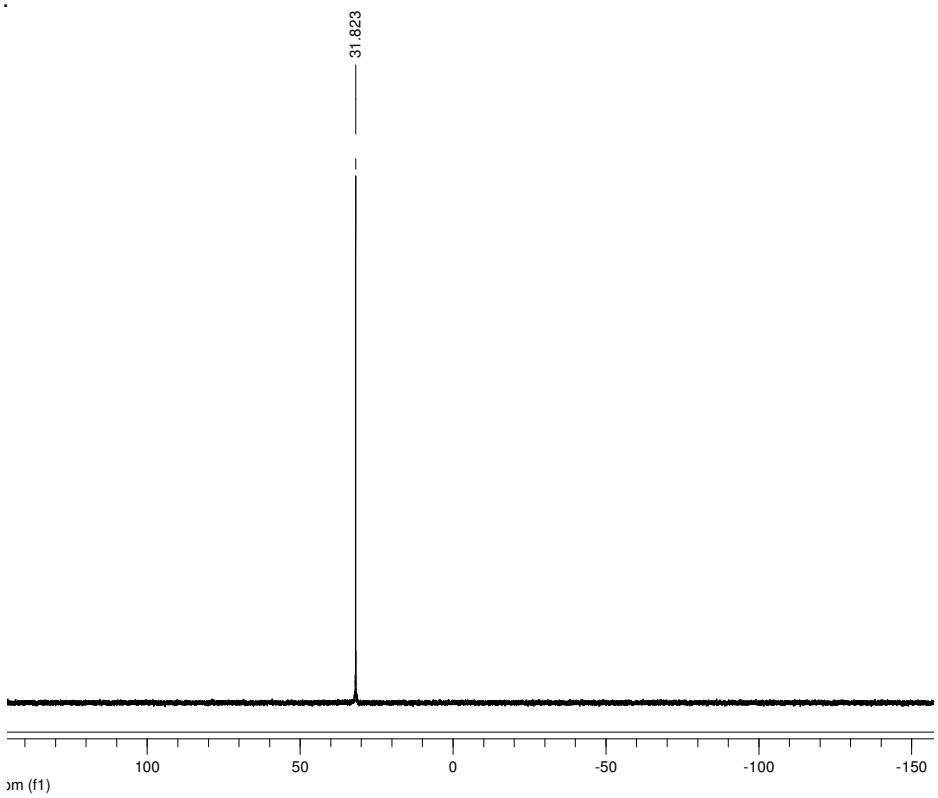
13a (^{1}H):



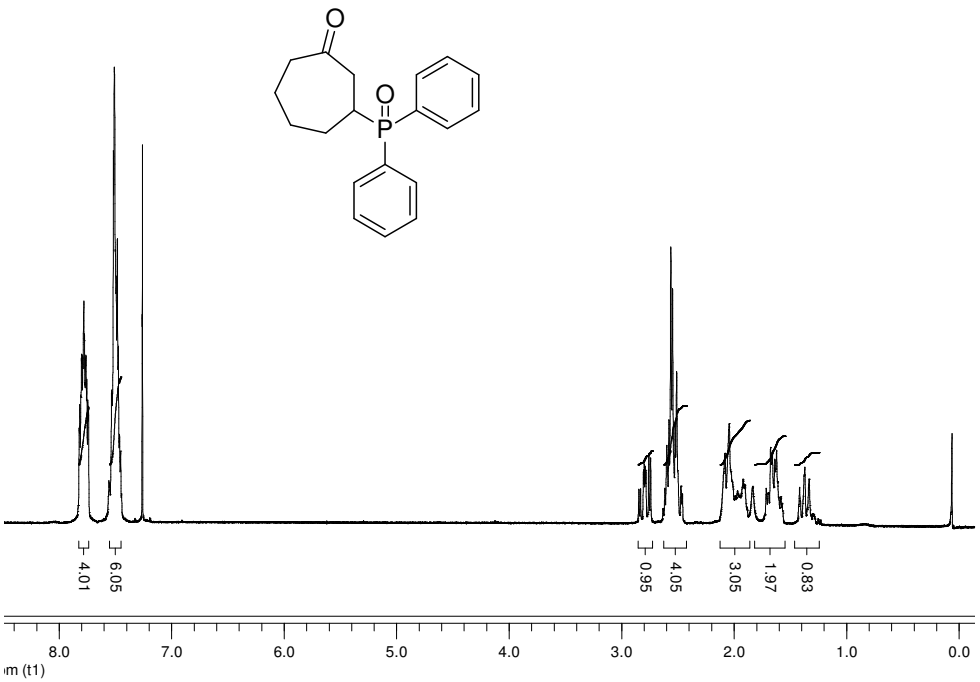
13a (^{13}C):



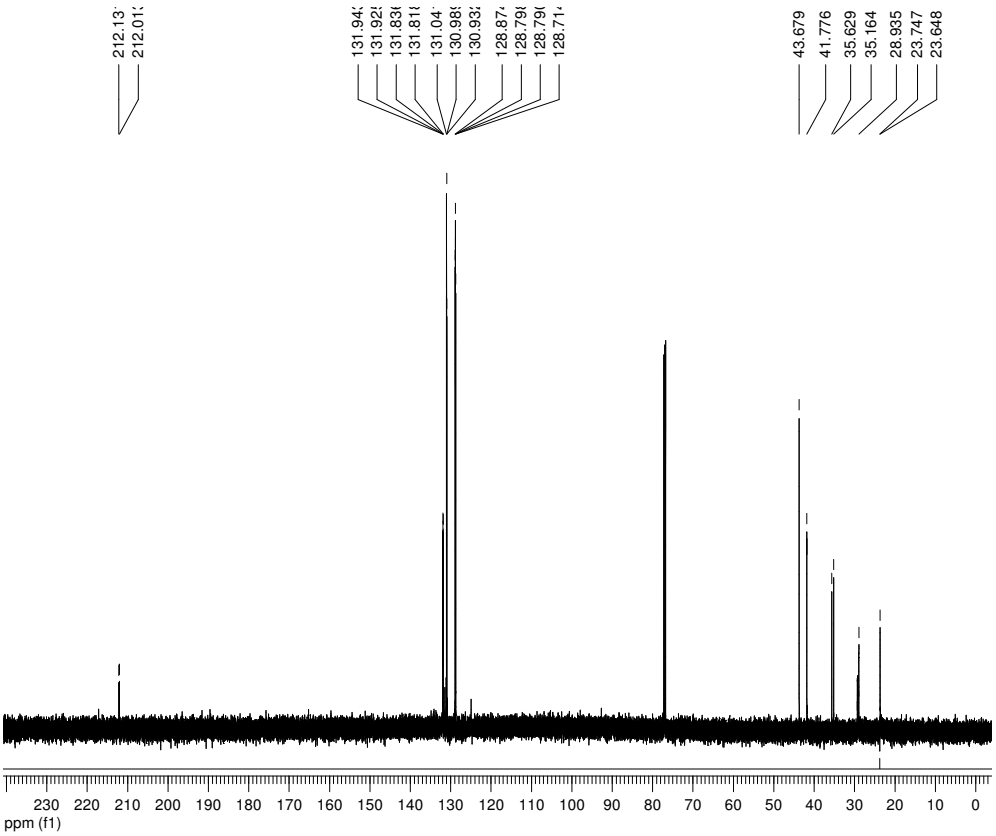
13a (^{31}P):



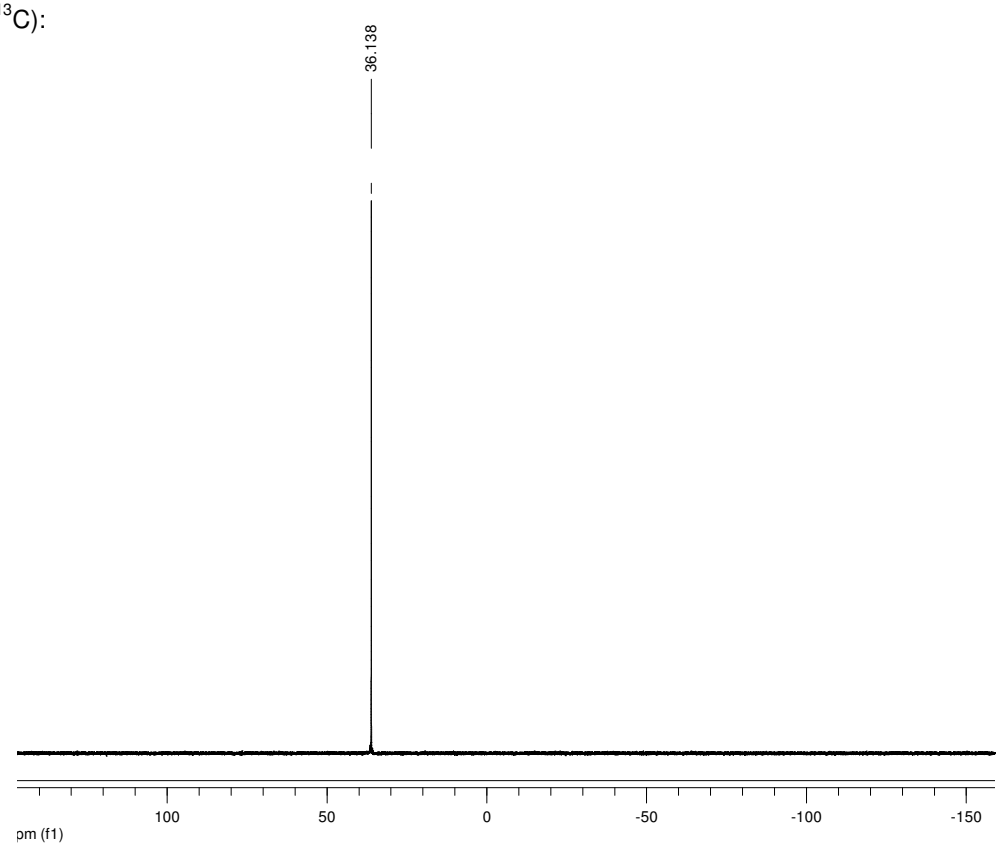
14a (^{1}H):



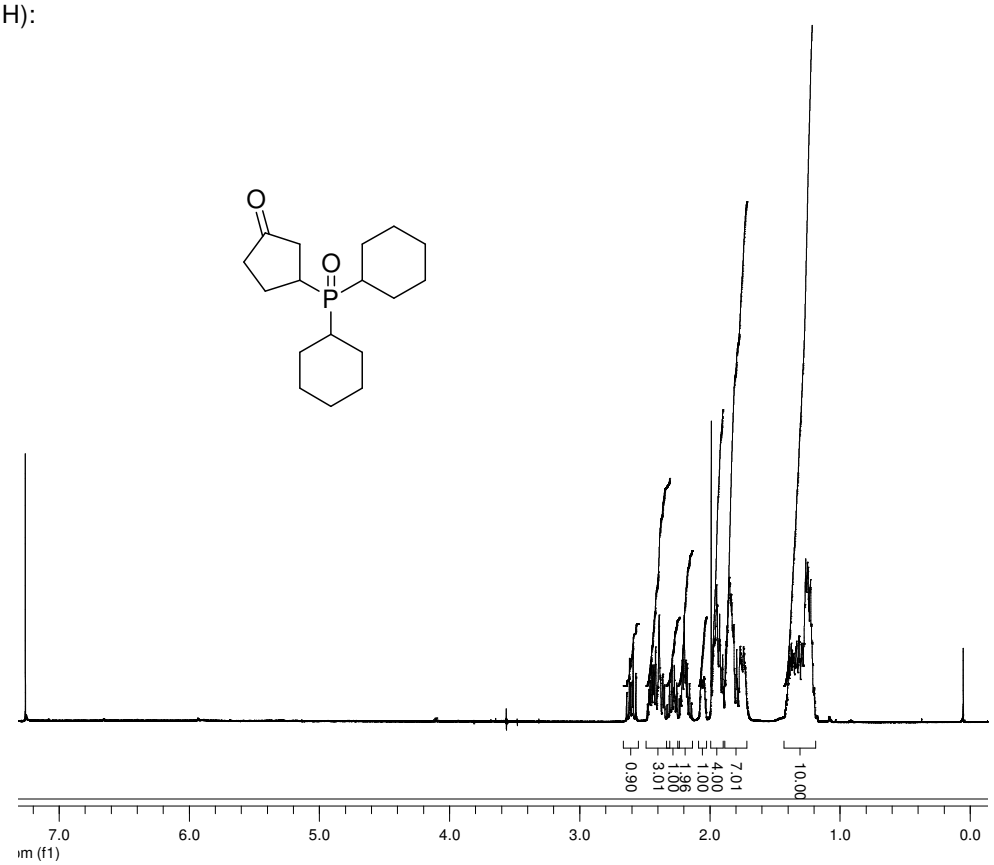
14a (^{13}C):



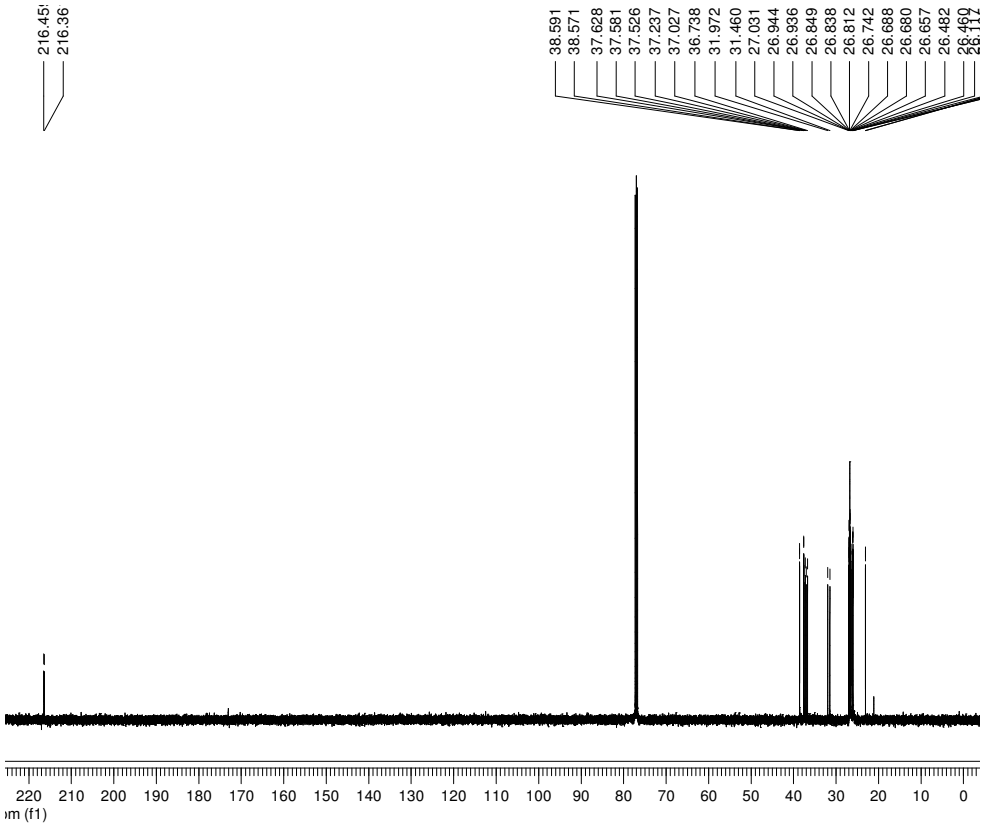
14a (^{13}C):



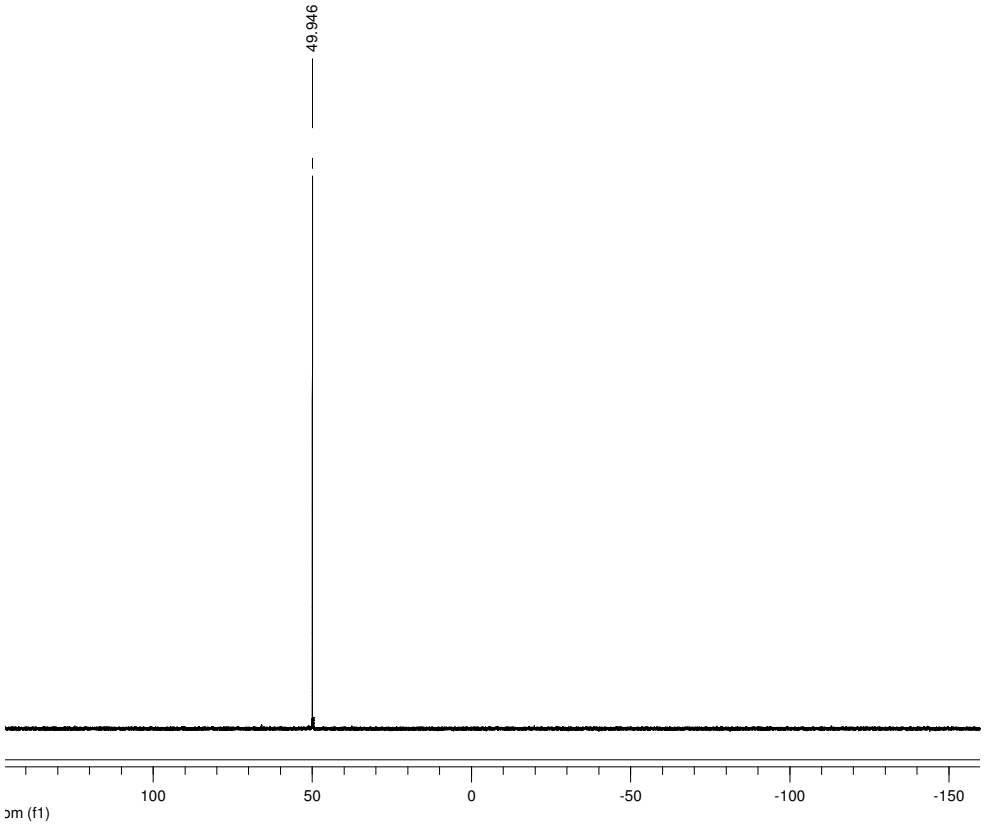
12b (^{1}H):



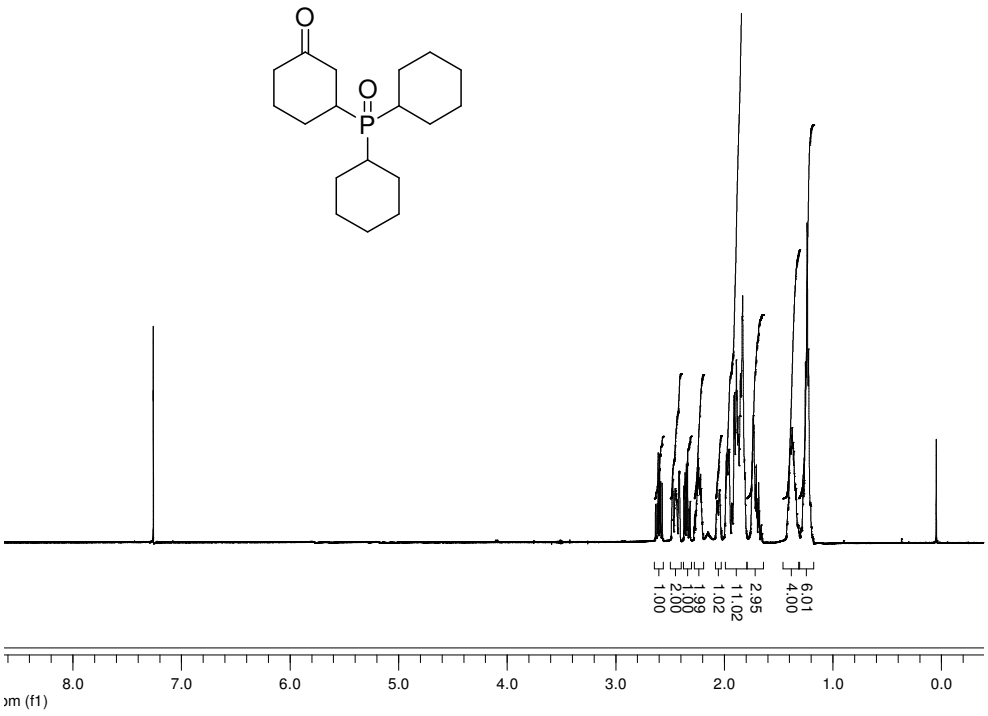
12b (^{13}C):



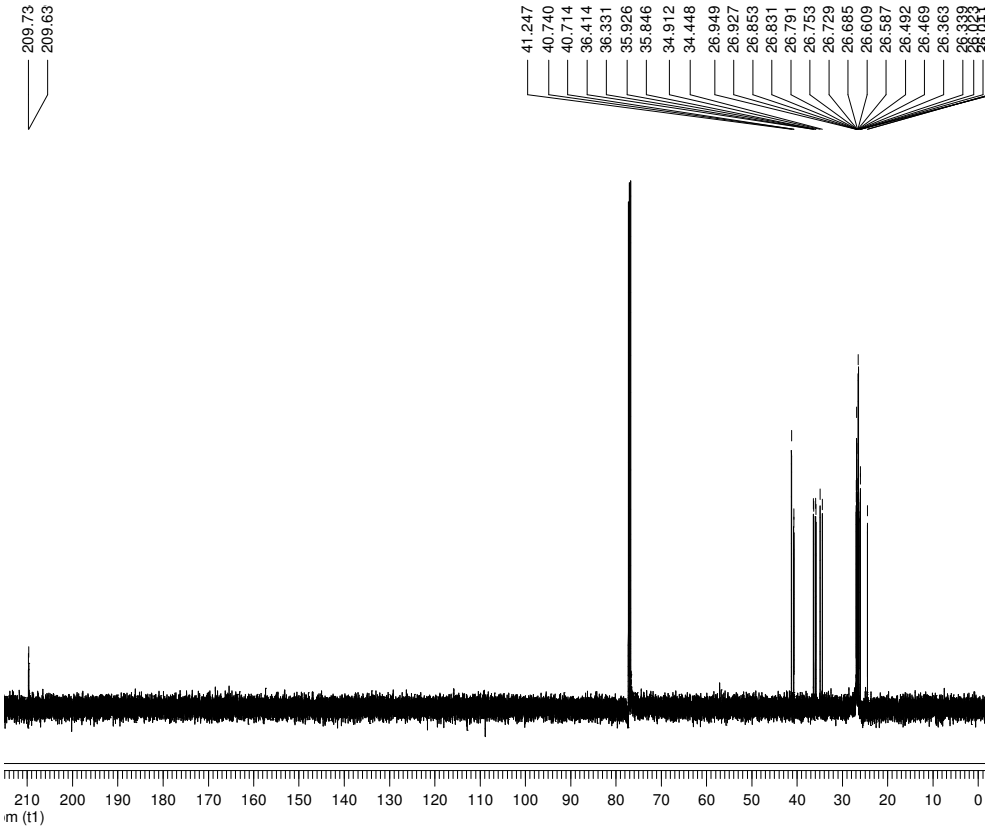
12b (^{31}P):



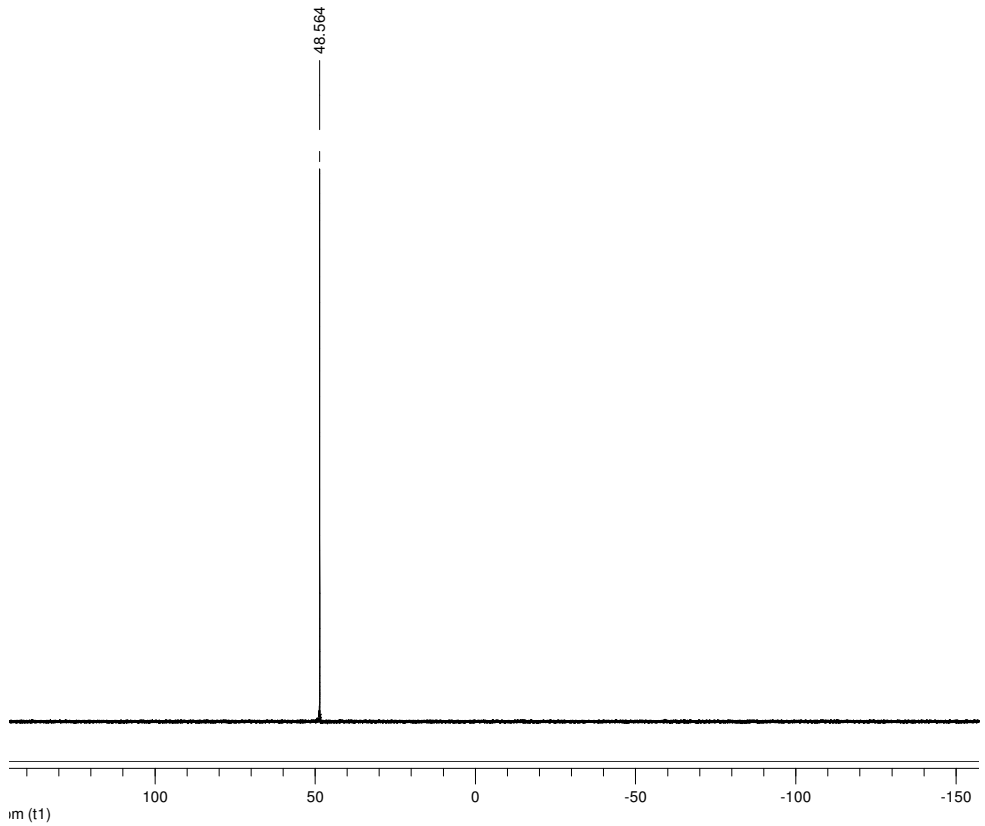
13b (^{1}H):



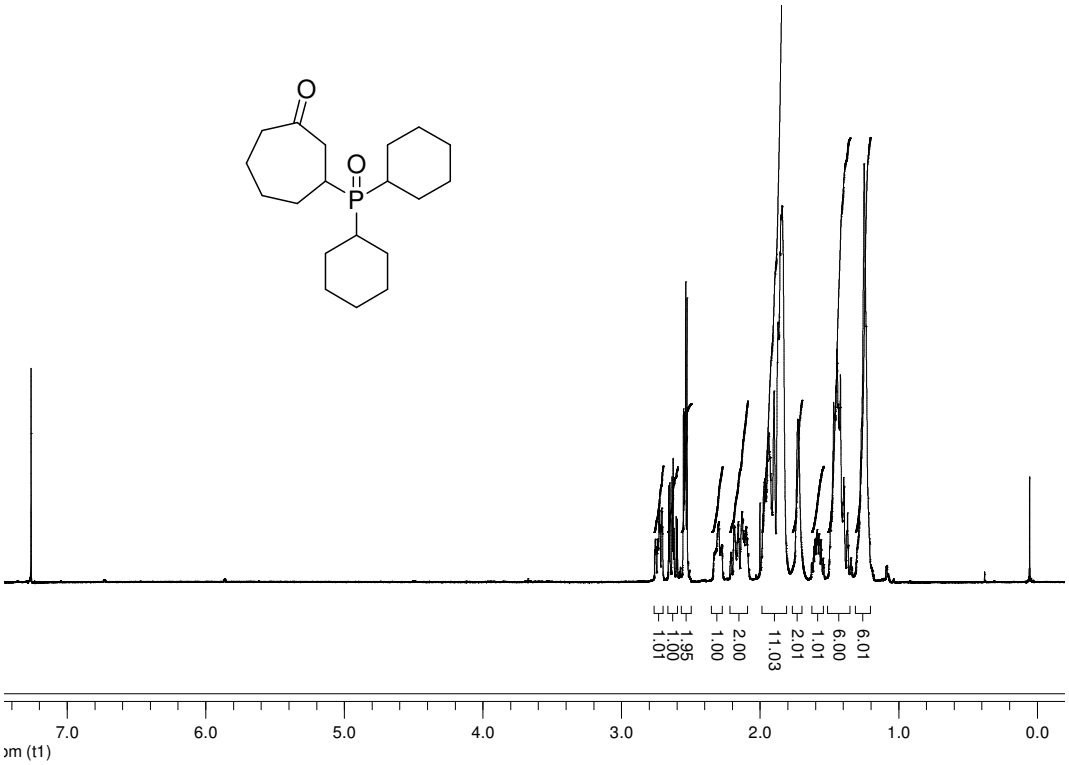
13b (^{13}C):



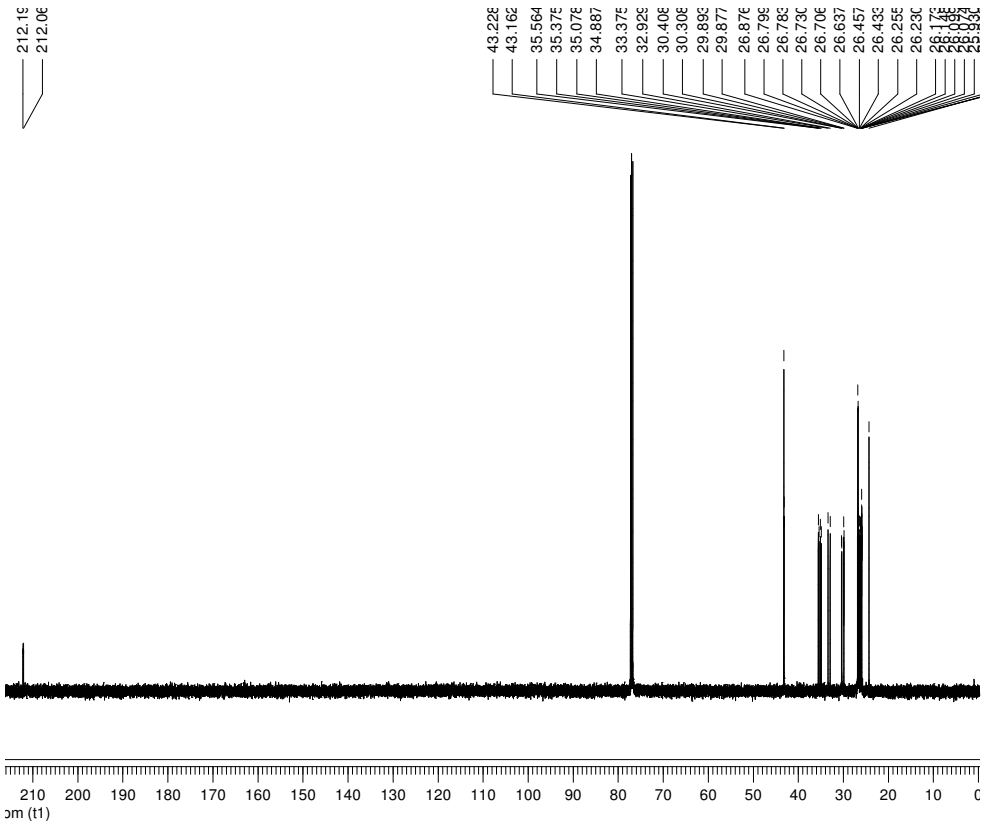
13b (^{31}P):



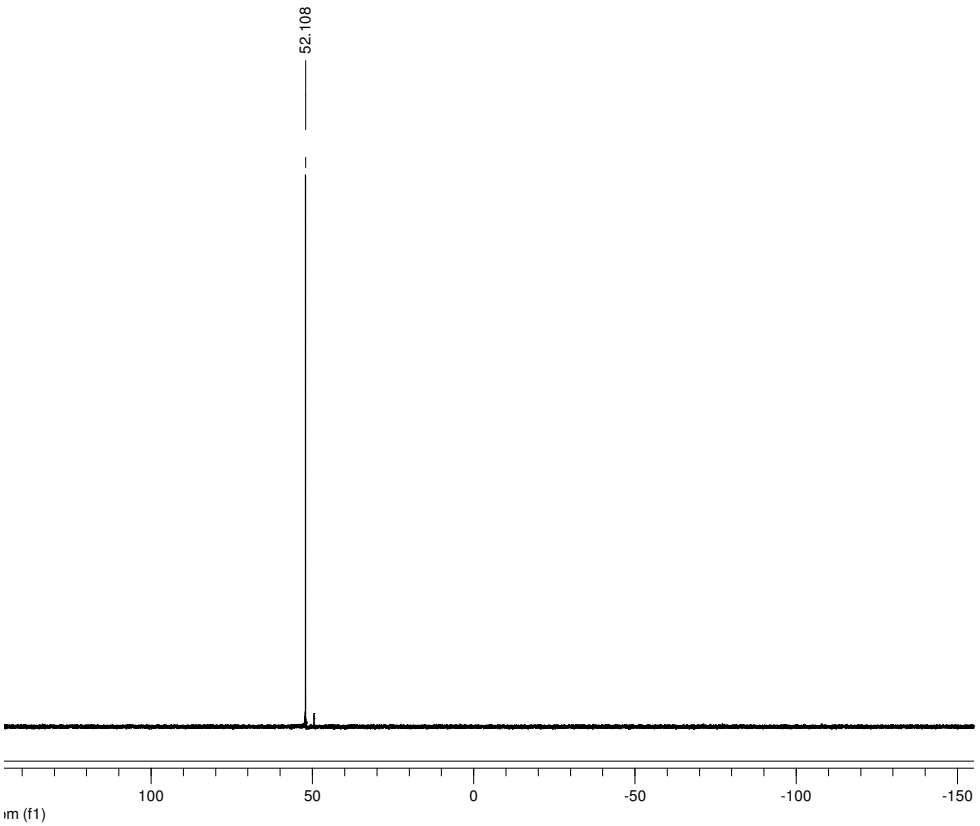
14b (^{1}H):



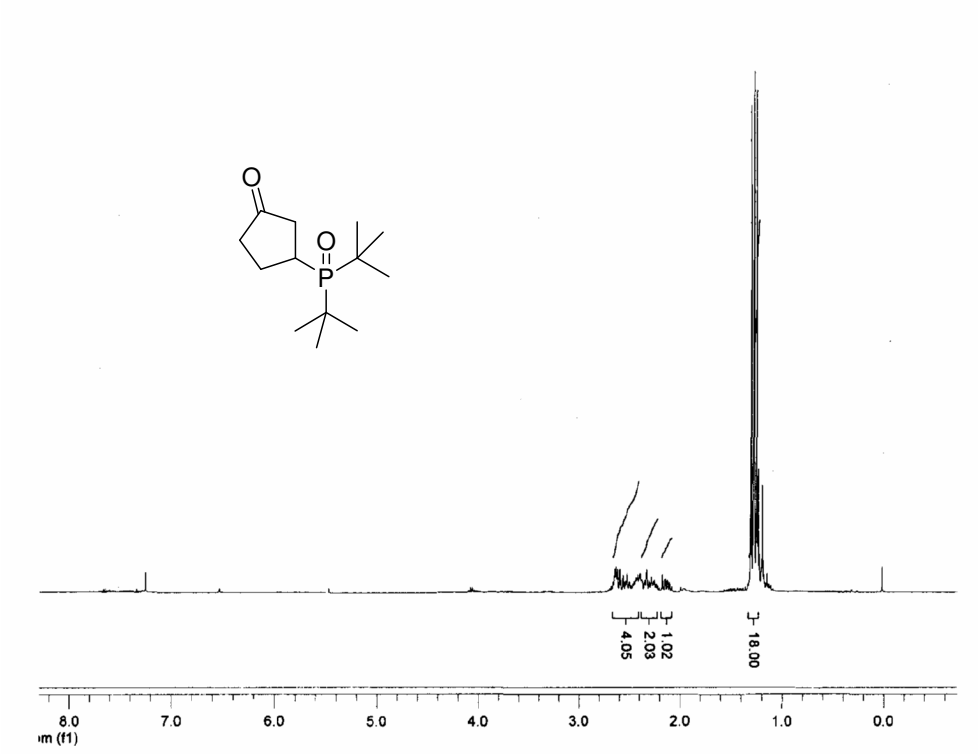
14b (^{13}C):



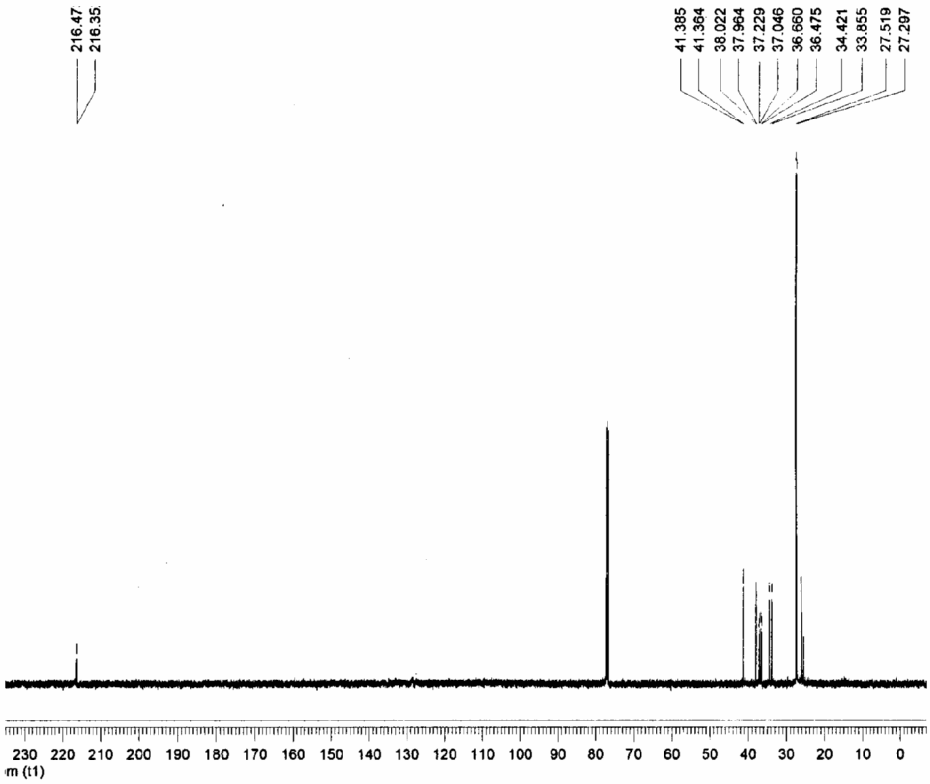
14b (^{31}P):



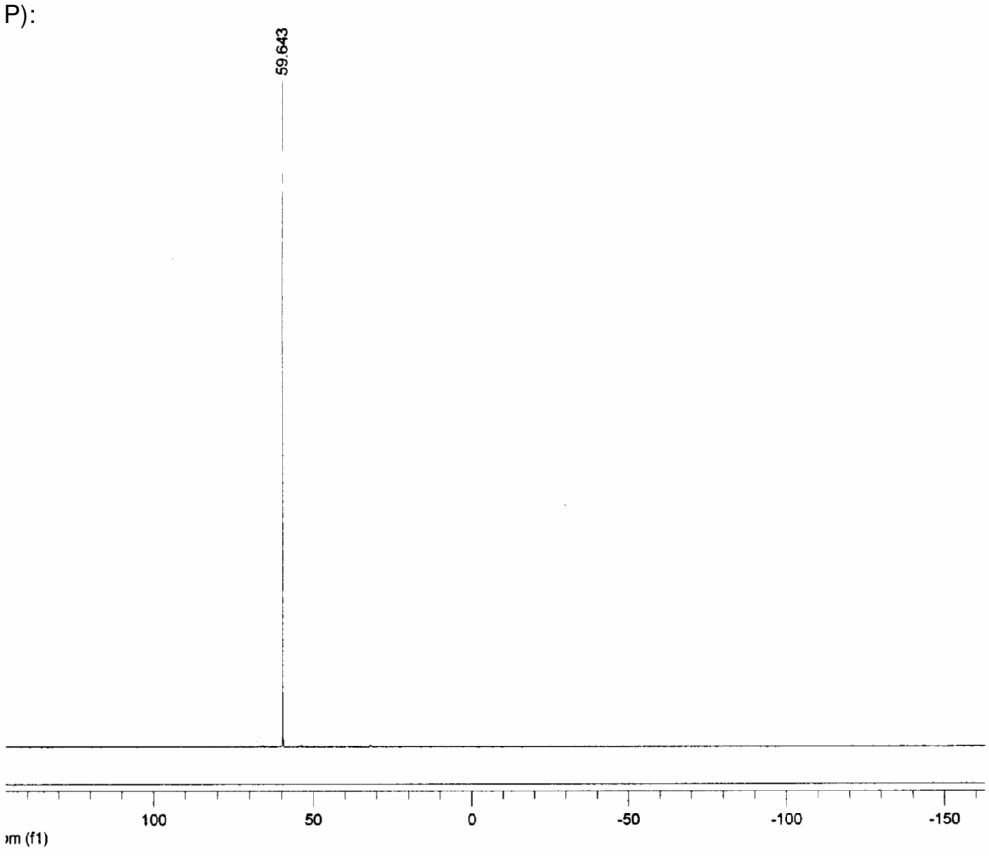
12c (^{1}H):



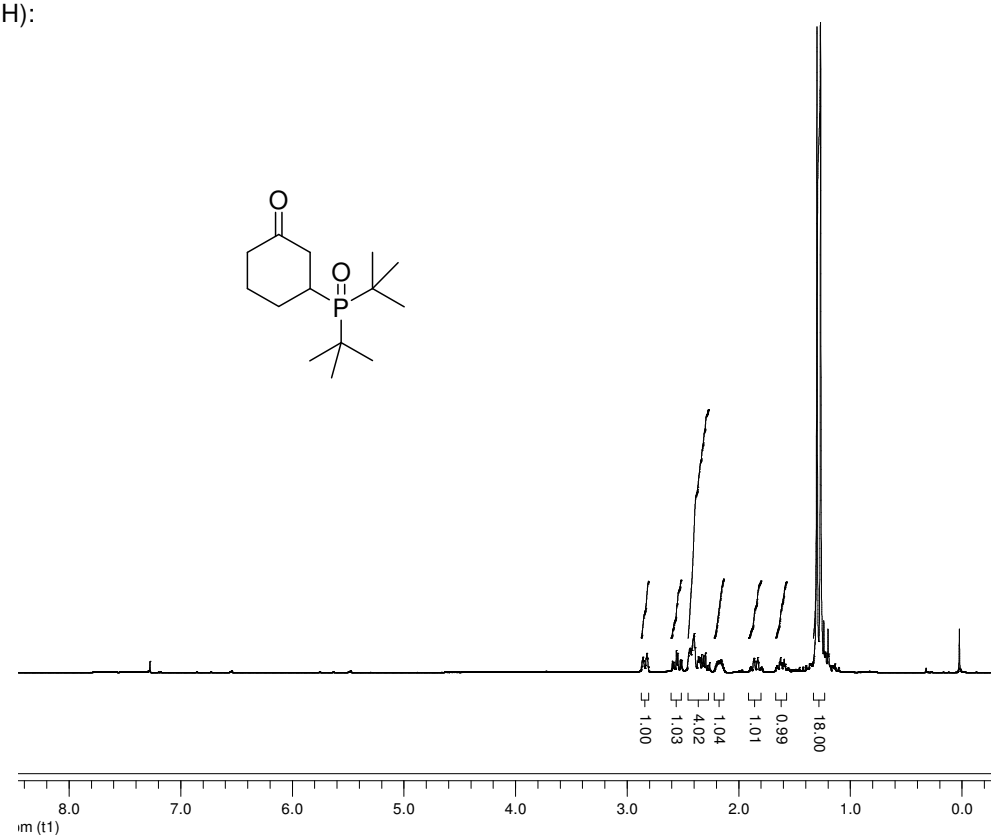
12c (^{13}C):



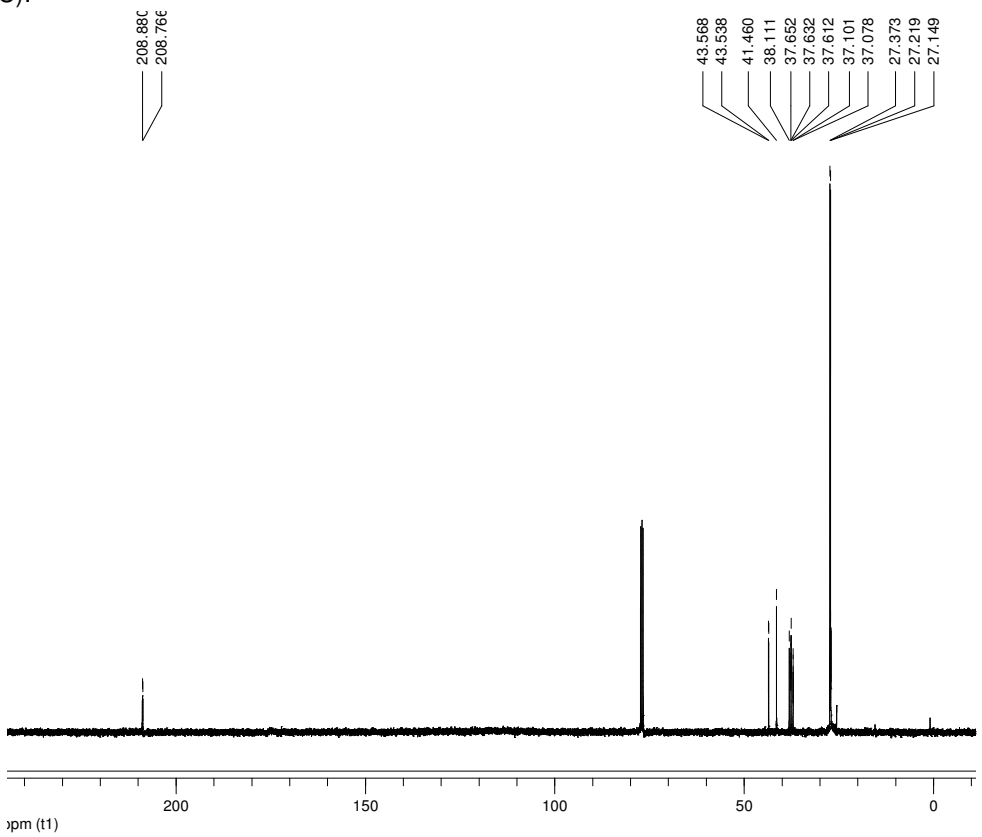
12c (^{31}P):



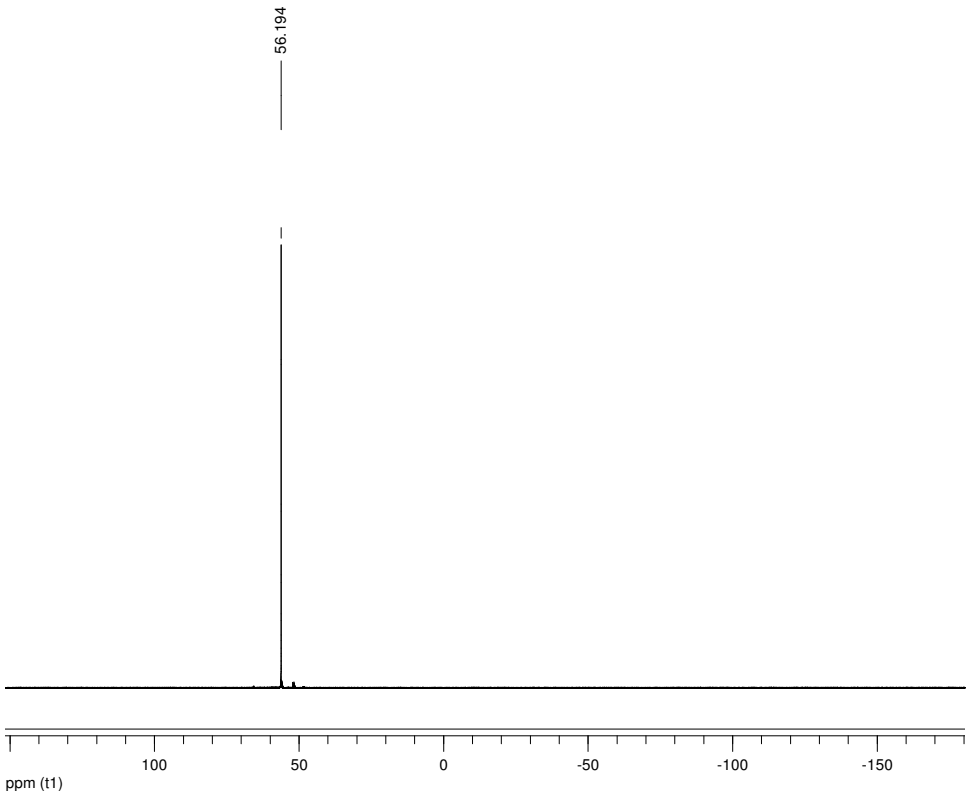
13c (^{1}H):



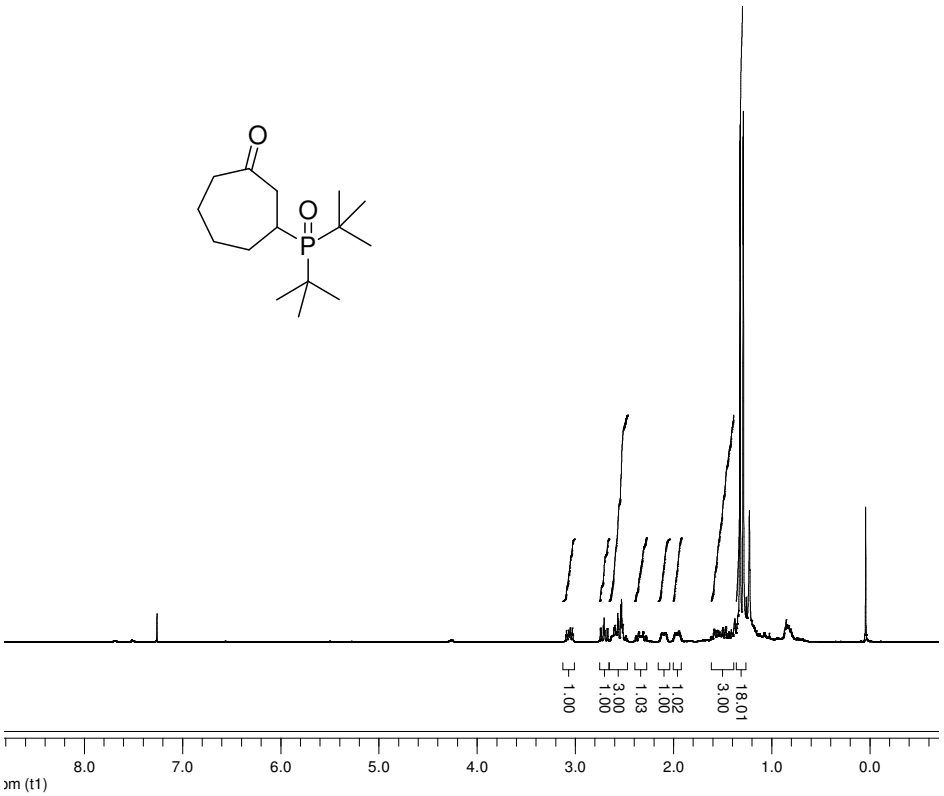
13c (^{13}C):



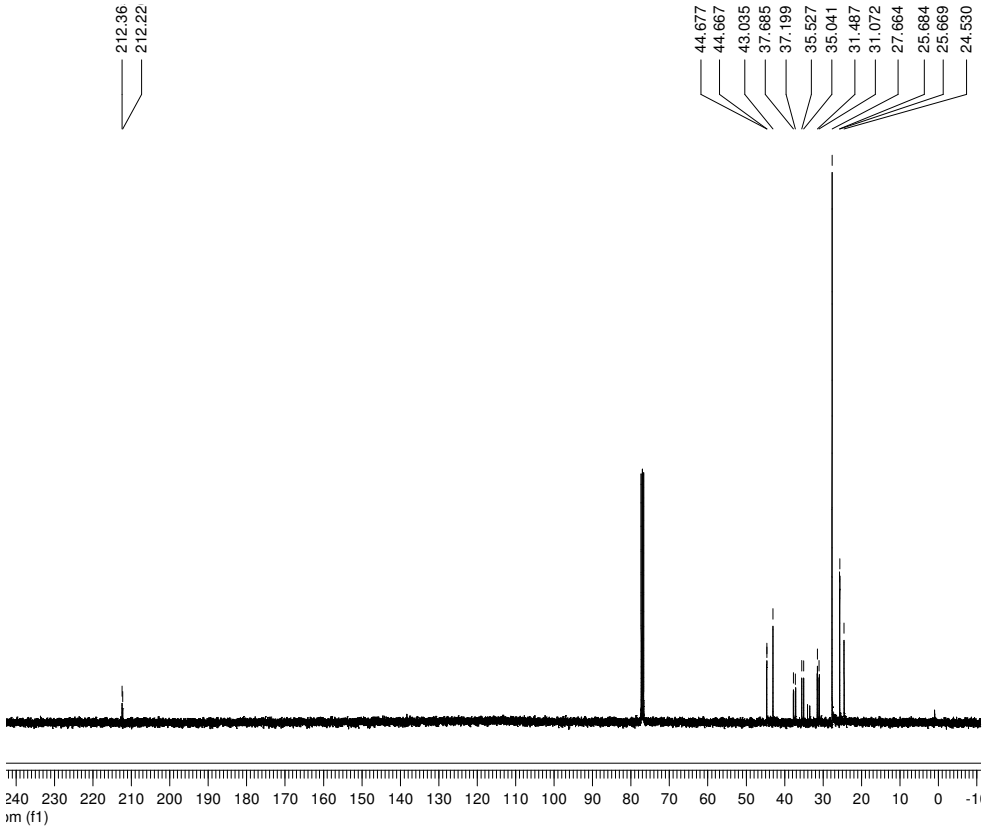
13c (^{31}P):



14c (^{1}H):



14c (^{13}C):



14c (^{31}P):