Supporting Information

Reactivity differences between 2,4- and 2,5-disubstituted zirconacyclopentadienes: a highly selective and general approach to 2,4-disubstituted phospholes.

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Content

I. Spectroscopic data of compounds **3a-m**

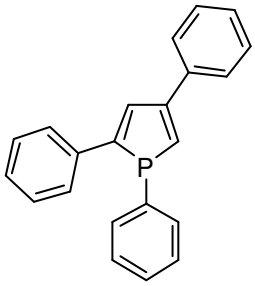
General procedure for the optimized preparation of phospholes **3**.

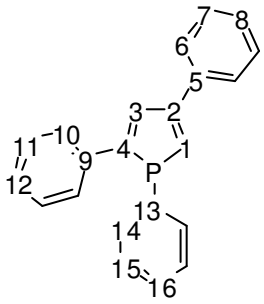
A Schlenk tube was loaded with dichlorozirconocene (Cp_2ZrCl_2) (584 mg, 2.0 mmol), lanthanum (186 mg, 1.32 mmol) and THF (10 mL) under an atmosphere of argon. The resulting mixture was stirred vigorously at room temperature until a deep red color appeared. At this stage, the alkyne (4 mmol) was added to the reaction mixture and the stirring was continued until complete disappearance of the alkyne as shown by TLC. Then the optimized amount of dichlorophenylphosphine (1.05 - 1.70 mmol) was added at -78°C. After slow warming to room temperature, the reaction mixture was stirred for 18 h. After that time, petroleum ether (20 mL) was added to the brown solution and the solution was filtered over a short column of basic aluminum oxide using petroleum ether/ethyl acetate 8:2 as eluent. The solvent was evaporated and the crude residue was purified by flash column chromatography on silica gel using petroleum ether to yield phospholes **3**. Alternatively, solid phospholes were obtained by recrystallisation from the crude residue using diethyl ether.

Procedure for determining the ratio **3/4**

The above reaction was carried out with 1.0 equivalent of dichlorophosphine. Before quenching the reaction mixture, a sample (2 mL) of the solution of phospholes was taken, quenched with water and extracted with diethyl ether. The solvent was evaporated and the residue was analyzed by ^{1}H NMR to determine the ratio **3/4** based on the protons of the phosphole and butadiene backbones.

1,2,4-triphenylphosphole (3a)





According to the general procedure using phenylacetylene (0.42 mL, 4.0 mmol) and dichlorophenylphosphine (0.14 mL, 1.0 mmol), **3a** was obtained as a light yellow solid in 70.0 % yield (0.70 mmol, 218 mg).

^{1}H (500 MHz, $CDCl_3$)
7.08 (dd, J_{P-H} = 40.0 Hz, J_{H-H} = 1.5 Hz, 1H, H1), 7.22-7.29 (m, 3H, H12, H15), 7.31 (d, J_{H-H} = 8.0 Hz, 2H, H11), 7.34-7.38 (m, 3H, H8, H16), 7.43 (d, J_{H-H} = 7.0 Hz, 2H, H7), 7.46 (d, J_{P-H} = 7.5 Hz, 2H, H14), 7.61 (d, J_{H-H} = 8.0 Hz, 2H, H10), 7.66 (dd, J_{P-H} = 12.5 Hz, J_{H-H} = 1.5 Hz, 1H, H3), 7.73 (d, J_{H-H} = 7.0 Hz, 2H, H6).

^{13}C (125 MHz, $CDCl_3$)
126.6 (d, J_{P-C} = 1.3 Hz, CH, C6), 126.8 (d, J_{P-C} = 9.5 Hz, CH, C10), 127.5 (CH, C12), 128.0 (CH, C1), 128.2 (CH, C8), 128.8 (CH, C7), 128.8 (d, J_{P-C} = 6.6 Hz, CH, C15), 128.9 (CH, C11), 129.7 (d, J_{P-C} = 1.5 Hz, CH, C16), 130.8 (d, J_{P-C} = 9.9 Hz, C, C13), 131.9 (d, J_{P-C} = 10.3

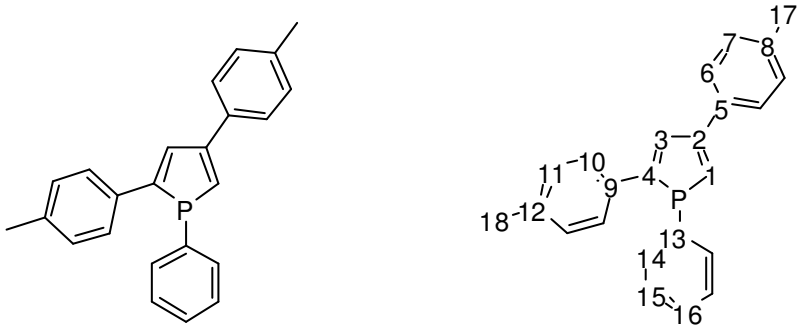
Hz, CH, C3), 134.0 (d, J_{P-C} = 19.5 Hz, CH, C14), 136.5 (d, J_{P-C} = 15.9 Hz, C, C9), 137.0 (d, J_{P-C} = 3.0 Hz, C, C5), 150.4 (d, J_{P-C} = 7.8 Hz, C, C2), 153.8 (d, J_{P-C} = 2.0 Hz, C, C4).

^{31}P (200 MHz, $CDCl_3$)
11.3.

HRMS (EI) for $C_{22}H_{17}P$: calc. (m/z) 312.1068 ; found (m/z) 312.1068.

Melting point: 124°C

2,4-bis(4-methylphenyl)-1-phenylphosphole (3b)



According to the general procedure using 4-methylphenylacetylene (464 mg, 4.0 mmol) and dichlorophenylphosphine (0.14 mL, 1.0 mmol), **3b** was obtained as a yellow solid in 60.9 % yield (0.61 mmol, 207 mg).

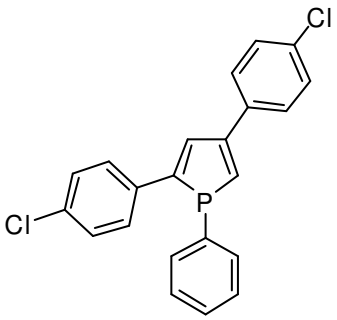
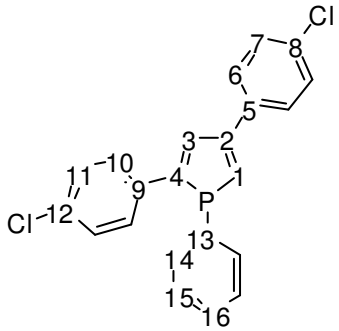
^{1}H (500 MHz, $CDCl_3$)
2.36 (s, 3H, H18), 2.44 (s, 3H, H17), 7.03 (dd, J_{P-H} = 40.0 Hz, J_{H-H} = 1.5 Hz, 1H, H1), 7.15 (d, J_{H-H} = 8.0 Hz, 2H, H11), 7.28 (m, 5H, H7, H15, H16), 7.47 (ddd, J_{P-H} = 8.5 Hz, J_{H-H} = 8.5 Hz, J_{H-H} = 1.5 Hz, 2H, H14), 7.55 (d, J_{H-H} = 7.5 Hz, 2H, H10), 7.64 (dd, J_{P-H} = 13.0 Hz, J_{H-H} = 1.5 Hz, 1H, H3), 7.71 (d, J_{H-H} = 8.0 Hz, 2H, H6).

^{13}C (125 MHz, $CDCl_3$)
21.3 (CH_3, C17), 21.3 (CH_3, C18), 126.3 (CH, C1), 126.4 (d, J_{P-C} = 0.9 Hz, CH, C6), 126.6 (d, J_{P-C} = 9.4 Hz, CH, C10), 128.7 (d, J_{P-C} = 8.4 Hz, CH, C15), 129.5 (CH, 2C, C7, C11), 129.5 (d, J_{P-C} = 1.3 Hz, CH, C16), 131.2 (d, J_{P-C} = 10.1 Hz, CH, C3), 131.2 (d, J_{P-C} = 10.3 Hz, C, C13), 133.7 (d, J_{P-C} = 16.0 Hz, C, C9), 134.0 (d, J_{P-C} = 19.4 Hz, CH, C14), 134.2 (d, J_{P-C} = 3.1 Hz, C, C5), 137.3 (C, C12), 137.9 (C, C8), 150.3 (d, J_{P-C} = 7.9 Hz, C, C2), 153.6 (d, J_{P-C} = 1.6 Hz, C, C4).

^{31}P (200 MHz, $CDCl_3$)
10.8.

HRMS (EI) for $C_{24}H_{21}P$: calc. (m/z) 340.1381 ; found (m/z) 340.1381.

2,4-bis(4-chlorophenyl)-1-phenylphosphole (3c)

According to the general procedure using 4-chlorophenylacetylene (476 mg, 4.0 mmol) and dichlorophenylphosphine (0.24 mL, 1.7 mmol), **3c** was obtained as a light yellow solid in 45.7 % yield (0.78 mmol, 295 mg).

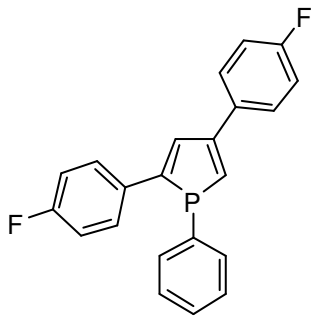
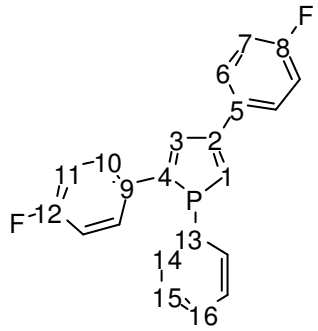
^{1}H (500 MHz, $CDCl_3$)
7.09 (d, J_{P-H} = 38.0 Hz, 1H, H1), 7.29-7.32 (m, 3H, H11, H16), 7.34-7.35 (m, 2H, H15), 7.38-7.44 (m, 4H, H7, H14), 7.53 (d, J_{H-H} = 8.5 Hz, 2H, H10), 7.57 (d, J_{P-H} = 12.5 Hz, 1H, H3), 7.64 (d, J_{H-H} = 8.0 Hz, 2H, H6).

^{13}C (125 MHz, $CDCl_3$)
127.7 (CH, C11), 127.8 (d, J_{P-C} = 1.3 Hz, CH, C6), 127.9 (d, J_{P-C} = 9.4 Hz, CH, C10), 128.6 (d, J_{P-C} = 1.0 Hz, CH, C1), 128.9 (d, J_{P-C} = 3.3 Hz, CH, C15), 129.0 (d, J_{P-C} = 2.0 Hz, CH, C7), 130.0 (d, J_{P-C} = 1.5 Hz, CH, C16), 131.7 (d, J_{P-C} = 10.4 Hz, CH, C3), 133.4 (d, J_{P-C} = 0.9 Hz, C, C5), 134.0 (d, J_{P-C} = 19.6 Hz, CH, C14), 134.0 (C, C8), 134.8 (d, J_{P-C} = 16.4 Hz, C, C9), 135.2 (d, J_{P-C} = 3.0 Hz, C, C13), 135.8 (C, C12), 149.0 (d, J_{P-C} = 7.8 Hz, C, C2), 152.9 (d, J_{P-C} = 2.1 Hz, C, C4).

^{31}P (200 MHz, $CDCl_3$)
12.3.

HRMS (EI) for $C_{22}H_{15}Cl_2P$: calc. (m/z) 380.0288 ; found (m/z) 380.0288.

2,4-bis(4-fluorophenyl)-1-phenylphosphole (3d)

According to the general procedure using 4-fluorophenylacetylene (480 mg, 4.0 mmol) and dichlorophenylphosphine (0.20 mL, 1.4 mmol), **3d** was obtained as a light yellow oil in 48.0 % yield (0.67 mmol, 234 mg).

^{1}H (500 MHz, $CDCl_3$)
6.97 (dd, J_{P-H} = 39.0 Hz, J_{H-H} = 1.5 Hz, 1H, H1), 6.98 (dd, J_{H-H} = 8.0 Hz, J_{F-H} = 8.0 Hz, 2H, H11), 7.11 (dd, J_{H-H} = 8.5 Hz, J_{F-H} = 8.5 Hz, 2H, H7), 7.24-7.30 (m, 3H, H15, H16), 7.38 (ddd, J_{P-H} = 8.5 Hz, J_{H-H} = 8.5 Hz, J_{H-H} = 1.5 Hz, 2H, H14), 7.48 (dd, J_{P-H} = 12.5 Hz, J_{H-H} = 1.5 Hz, 1H, H3), 7.52 (dd, J_{H-H} = 7.5 Hz, J_{F-H} = 5.5 Hz, 2H, H10), 7.67 (dd, J_{H-H} = 8.5 Hz, J_{F-H} = 5.0 Hz, 2H, H6).

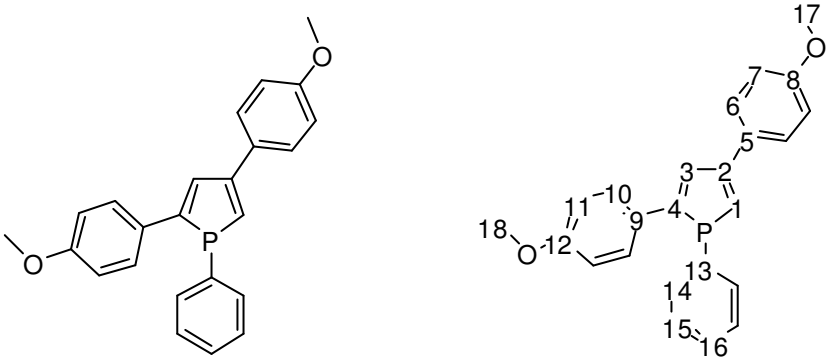
^{13}C (125 MHz, $CDCl_3$)
115.7 (d, J_{P-C} = 2.9 Hz, CH, C11), 115.9 (d, J_{P-C} = 3.0 Hz, CH, C7), 127.4 (CH, C1), 128.2 (dd, J_{P-C} = 9.1 Hz, J_{F-C} = 8.1 Hz, CH, C10), 128.2 (dd, J_{P-C} = 3.8 Hz, J_{F-C} = 10.4 Hz, CH, C6), 128.9 (d, J_{P-C} = 8.5 Hz, CH, C15), 129.9 (d, J_{P-C} = 1.4 Hz, CH, C16), 130.4 (d, J_{P-C} = 9.6 Hz, C, C13), 131.5 (dd, J_{P-C} = 10.1 Hz, CH, C3), 132.6 (dd, J_{P-C} = 16.3 Hz, J_{F-C} = 3.5 Hz, C, C9), 133.1 (dd, J_{P-C} = 3.3 Hz, J_{F-C} = 3.3 Hz, C, C5), 134.0 (d, J_{P-C} = 19.5 Hz, CH, C14), 149.3 (d, J_{P-C} = 7.6 Hz, C, C2), 153.1 (d, J_{P-C} = 1.8 Hz, C, C4), 161.6 (d, J_{F-C} = 33.1 Hz, C, C12), 163.6 (d, J_{F-C} = 33.8 Hz, C, C8).

^{19}F (470 MHz, $CDCl_3$)
-113.7, -114.6.

^{31}P (200 MHz, $CDCl_3$)
11.9.

HRMS (EI) for $C_{22}H_{15}F_2P$: calc. (m/z) 348.0879 ; found (m/z) 348.0879.

2,4-bis(4-methoxyphenyl)-1-phenylphosphole (3e)



According to the general procedure using 4-methoxyphenylacetylene (0.46 mL, 4.0 mmol) and dichlorophenylphosphine (0.20 mL, 1.4 mmol), **3e** was obtained as a yellow solid in 36.5 % yield (0.51 mmol, 190 mg).

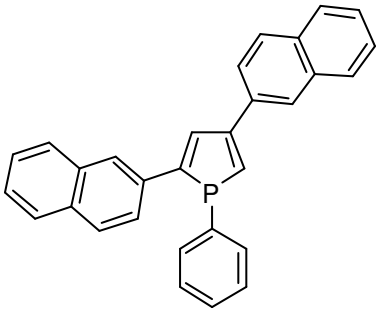
^{1}H (500 MHz, $CDCl_3$)
3.81 (s, 3H, H18), 3.88 (s, 3H, H17), 6.88 (d, J_{H-H} = 8.0 Hz, 2H, H11), 6.91 (d, J_{P-H} = 38.0 Hz, 1H, H1), 7.00 (d, J_{H-H} = 8.0 Hz, 2H, H7), 7.30 (m, 3H, H15, H16), 7.47 (ddd, J_{P-H} = 8.0 Hz, J_{H-H} = 8.0 Hz, J_{H-H} = 1.5 Hz, 2H, H14), 7.56 (d, J_{P-H} = 11.0 Hz, 1H, H3), 7.58 (d, J_{H-H} = 7.0 Hz, 2H, H10), 7.70 (d, J_{H-H} = 8.0 Hz, 2H, H6).

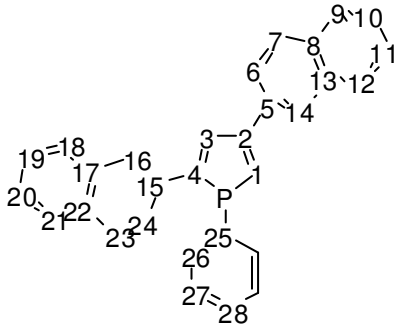
^{13}C (125 MHz, $CDCl_3$)
55.3 (CH_3, C18), 55.4 (CH_3, C17), 114.1 (CH, C11), 114.2 (CH, C7), 124.5 (CH, C1), 127.7 (CH, C6), 127.8 (d, J_{P-C} = 9.4 Hz, CH, C10), 128.7 (d, J_{P-C} = 8.4 Hz, CH, C15), 129.4 (d, J_{P-C} = 16.4 Hz, C, C9), 129.5 (d, J_{P-C} = 1.0 Hz, CH, C16), 129.8 (d, J_{P-C} = 3.3 Hz, C, C5), 130.2 (d, J_{P-C} = 10.0 Hz, CH, C3), 131.5 (d, J_{P-C} = 10.9 Hz, C, C13), 133.9 (d, J_{P-C} = 19.4 Hz, CH, C14), 150.0 (d, J_{P-C} = 7.6 Hz, C, C2), 153.3 (d, J_{P-C} = 1.8 Hz, C, C4), 159.2 (C, C12), 159.6 (C, C8).

^{31}P (200 MHz, $CDCl_3$)
10.6.

HRMS (EI) for $C_{24}H_{21}O_2P$: calc. (m/z) 372.1279 ; found (m/z) 372.1279.

2,4-bis(2-naphtyl)-1-phenylphosphole (3f)





According to the general procedure using 2-naphtylacetylene (304 mg, 4.0 mmol) and dichlorophenylphosphine (0.20 mL, 1.4 mmol), **3f** was obtained as a yellow solid in 24.3 % yield (0.34 mmol, 140 mg).

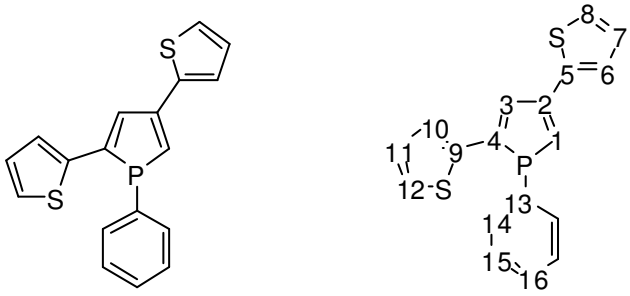
^{1}H (500 MHz, $CDCl_3$)
7.27 (d, J_{P-H} = 38.0 Hz, 1H, H1), 7.29 (d, J_{H-H} = 6.0 Hz, 3H, H27, H28), 7.45-7.49 (m, 3H, H19, H20, H23), 7.51-7.58 (m, 3H, H7, H26), 7.53 (d, J_{H-H} = 8.5 Hz, 1H, H10), 7.82-7.85 (m, 3H, H18, H21, H24), 7.90 (d, J_{H-H} = 4.0 Hz, 2H, H6, H11), 7.93-7.97 (m, 2H, H12), 7.95 (d, J_{P-H} = 13.5 Hz, 1H, H3), 8.10 (s, 1H, H16), 8.24 (s, 1H, H14).

^{13}C (125 MHz, $CDCl_3$)
124.7 (CH, C6), 125.0 (d, J_{P-C} = 8.3 Hz, CH, C24), 125.4 (d, J_{P-C} = 1.6 Hz, CH, C14), 125.6 (d, J_{P-C} = 10.8 Hz, CH, C16), 125.9 (CH, C7), 126.3 (CH, C23), 126.4 (CH, C19), 126.4 (CH, C20), 127.8 (CH, C10), 127.8 (CH, C11), 128.2 (CH, C18), 128.4 (CH, C9), 128.4 (CH, C21), 128.5 (CH, C12), 128.6 (CH, C1), 128.8 (d, J_{P-C} = 8.8 Hz, CH, C27), 129.7 (d, J_{P-C} = 1.2 Hz, CH, C28), 130.8 (d, J_{P-C} = 10.0 Hz, C, C25), 132.3 (d, J_{P-C} = 10.3 Hz, CH, C3), 132.9 (C, C17), 133.1 (C, C13), 133.6 (d, J_{P-C} = 11.9 Hz, C, C15), 133.9 (d, J_{P-C} = 19.3 Hz, CH, C26), 134.0 (C, C17), 134.1 (C, C13), 134.2 (d, J_{P-C} = 2.9 Hz, C, C5), 150.3 (d, J_{P-C} = 7.7 Hz, C, C2), 153.8 (d, J_{P-C} = 1.8 Hz, C, C4).

^{31}P (200 MHz, $CDCl_3$)
11.7.

HRMS (EI) for $C_{30}H_{21}P$: calc. (m/z) 412.1381 ; found (m/z) 412.1381.

1-phenyl-2,4-bis(2-thienyl)phosphole (3g)



According to the general procedure using 2-thienylacetylene (0.38 mL, 4.0 mmol) and dichlorophenylphosphine (0.14 mL, 1.0 mmol), **3g** was obtained as a yellow solid in 57.1 % yield (0.57 mmol, 185 mg).

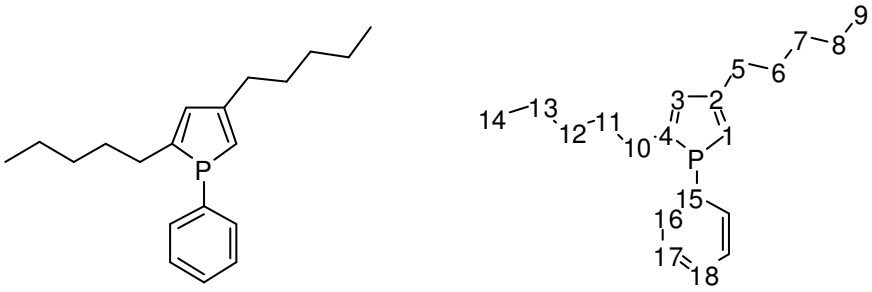
^{1}H (500 MHz, $CDCl_3$)
6.88 (dd, J_{P-H} = 38.5 Hz, J_{H-H} = 1.5 Hz, 1H, H1), 6.94 (dd, J_{H-H} = 5.0 Hz, J_{H-H} = 3.5 Hz, 1H, H11), 7.08 (d, J_{H-H} = 3.5 Hz, 1H, H10), 7.10 (dd, J_{H-H} = 5.0 Hz, J_{H-H} = 3.5 Hz, 1H, H7), 7.17 (d, J_{H-H} = 5.0 Hz, 1H, H12), 7.30-7.33 (m, 4H, H8, H15, H16), 7.37 (d, J_{H-H} = 3.5 Hz, 2H, H6), 7.43 (dd, J_{P-H} = 11.5 Hz, J_{H-H} = 1.5 Hz, 1H, H3), 7.50 (ddd, J_{P-H} = 8.0 Hz, J_{H-H} = 8.0 Hz, J_{H-H} = 1.5 Hz, 2H, H14).

^{13}C (125 MHz, $CDCl_3$)
124.7 (d, J_{P-C} = 3.5 Hz, CH, C12), 124.8 (d, J_{P-C} = 1.6 Hz, CH, C6), 124.9 (J_{P-C} = 0.5 Hz CH, C1), 125.1 (d, J_{P-C} = 7.3 Hz, CH, C10), 125.5 (d, J_{P-C} = 0.6 Hz, CH, C8), 127.9 (CH, C7), 127.9 (CH, C11), 128.9 (d, J_{P-C} = 8.6 Hz, CH, C15), 130.0 (d, J_{P-C} = 1.5 Hz, CH, C16), 130.5 (d, J_{P-C} = 9.1 Hz, CH, C3), 130.8 (d, J_{P-C} = 11.8 Hz, C, C13), 134.2 (d, J_{P-C} = 20.4 Hz, CH, C14), 139.9 (d, J_{P-C} = 20.1 Hz, C, C9), 140.8 (d, J_{P-C} = 2.9 Hz, C, C5), 143.8 (d, J_{P-C} = 7.8 Hz, C, C2), 147.0 (d, J_{P-C} = 4.4 Hz, C, C4).

^{31}P (200 MHz, $CDCl_3$)
13.4.

HRMS (EI) for $C_{18}H_{13}PS_2$: calc. (m/z) 324.0196 ; found (m/z) 324.0196.

2,4-bis(1-pentyl)-1-phenylphosphole (3h)



According to the general procedure using 1-heptyne (0.52 mL, 4.0 mmol) and dichlorophenylphosphine (0.14 mL, 1.0 mmol), **3h** was obtained as a colourless oil in 63.3 % yield (0.63 mmol, 190 mg).

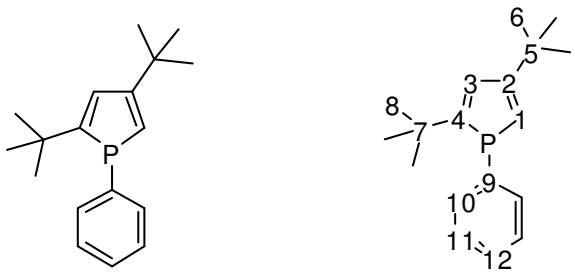
^{1}H (500 MHz, $CDCl_3$)
0.84 (t, J_{H-H} = 7.0 Hz, 3H, H9), 0.91 (t, J_{H-H} = 7.0 Hz, 3H, H14), 1.23-1.26 (m, 4H, H8, H13), 1.35 (dd, J_{H-H} = 7.5 Hz, J_{H-H} = 3.5 Hz, 4H, H7, H12), 1.43-1.50 (m, 2H, H11), 1.58-1.63 (m, 2H, H6), 2.37 (t, J_{H-H} = 8.5 Hz, 2H, H10), 2.45 (t, J_{H-H} = 7.5 Hz, 2H, H5), 6.23 (dd, J_{P-H} = 40.5 Hz, J_{H-H} = 1.5 Hz, 1H, H1), 6.48 (dd, J_{P-H} = 14.5 Hz, J_{H-H} = 1.5 Hz, 1H, H3), 7.27-7.32 (m, 5H, H16, H17, H18).

^{13}C (125 MHz, $CDCl_3$)
14.1 (CH_3, C14), 14.2 (CH_3, C9), 22.6 (CH_2, C8), 22.7 (CH_2, C13), 28.7 (d, J_{P-C} = 2.1 Hz, CH_2, C6), 30.5 (CH_2, C7), 30.6 (CH_2, C12), 30.8 (d, J_{P-C} = 6.6 Hz, CH_2, C11), 31.7 (d, J_{P-C} = 9.0 Hz, CH_2, C10), 33.5 (d, J_{P-C} = 3.4 Hz, CH_2, C5), 124.1 (CH, C1), 128.6 (d, J_{P-C} = 8.1 Hz, CH, C17), 129.2 (d, J_{P-C} = 1.1 Hz, CH, C18), 130.7 (d, J_{P-C} = 10.4 Hz, C, C15), 133.7 (d, J_{P-C} = 19.0 Hz, CH, C16), 134.3 (d, J_{P-C} = 10.9 Hz, CH, C3), 154.4 (d, J_{P-C} = 7.8 Hz, C, C2), 156.3 (d, J_{P-C} = 4.6 Hz, C, C4).

^{31}P (200 MHz, $CDCl_3$)
8.1.

HRMS (ESI) for $C_{20}H_{29}P$ [M+H]: calc. (m/z) 301.2007 ; found (m/z) 301.2079.

2,4-bis(tert-butyl)-1-phenylphosphole (3i)



According to the general procedure using tert-butylacetylene (0.48 mL, 4.0 mmol) and dichlorophenylphosphine (0.20 mL, 1.4 mmol), **3i** was obtained as a colourless oil in 47.3 % yield (0.66 mmol, 180 mg).

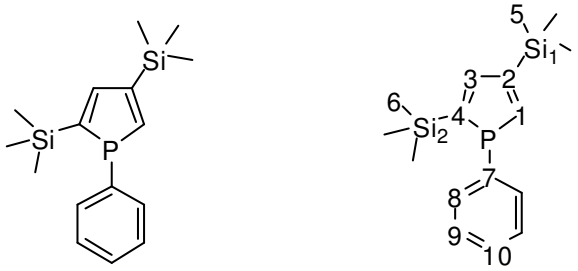
^{1}H (500 MHz, $CDCl_3$)
1.10 (s, 9H, H8), 1.24 (s, 9H, H6), 6.24 (dd, J_{P-H} = 41.0 Hz, J_{H-H} = 1.5 Hz, 1H, H1), 6.75 (dd, J_{P-H} = 15.0 Hz, J_{H-H} = 1.5 Hz, 1H, H3), 7.23 (m, 2H, H10), 7.30 (m, 3H, H11, H12).

^{13}C (125 MHz, $CDCl_3$)
29.8 (d, J_{P-C} = 1.9 Hz, CH_3, C6), 32.4 (d, J_{P-C} = 5.9 Hz, CH_3, C8), 34.7 (d, J_{P-C} = 2.8 Hz, C, C5), 35.7 (d, J_{P-C} = 13.9 Hz, C, C7), 122.7 (d, J_{P-C} = 1.3 Hz, CH, C1), 128.2 (d, J_{P-C} = 8.6 Hz, CH, C11), 129.3 (d, J_{P-C} = 1.6 Hz, CH, C12), 130.9 (d, J_{P-C} = 10.8 Hz, CH, C3), 132.2 (d, J_{P-C} = 10.8 Hz, C, C9), 134.2 (d, J_{P-C} = 20.1 Hz, CH, C10), 161.8 (d, J_{P-C} = 7.1 Hz, C, C4), 165.8 (d, J_{P-C} = 9.1 Hz, C, C2).

^{31}P (200 MHz, $CDCl_3$)
1.4.

HRMS (EI) for $C_{18}H_{25}P$: calc. (m/z) 272.1694 ; found (m/z) 272.1694.

1-phenyl-2,4-bis(trimethylsilyl)phosphole (3j)



According to the general procedure using trimethysilylacetylene (0.56 mL, 4.0 mmol) and dichlorophenylphosphine (0.14 mL, 1.0 mmol), **3j** was obtained as a colourless oil in 72.4 % yield (0.72 mmol, 220 mg).

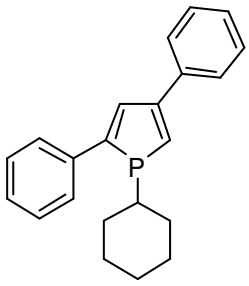
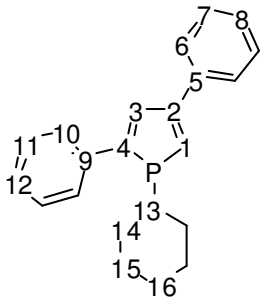
^{1}H (500 MHz, $CDCl_3$)
0.07 (s, 9H, H5), 0.27 (s, 9H, H6), 7.24-7.27 (m, 4H, H8, H9), 7.29 (dd, J_{P-H} = 18.5 Hz, J_{H-H} = 1.0 Hz, 1H, H3), 7.31-7.32 (m, 1H, H10), 7.43 (dd, J_{P-H} = 40.5 Hz, J_{H-H} = 1.0 Hz, 1H, H1).
^{13}C (125 MHz, $CDCl_3$)
-0.9 (CH_3, C5), 0.2 (d, J_{P-C} = 2.7 Hz, CH_3, C6), 128.4 (d, J_{P-C} = 8.8 Hz, CH, C9), 129.6 (d, J_{P-C} = 1.8 Hz, CH, C10), 130.3 (d, J_{P-C} = 9.0 Hz, C, C7), 134.5 (d, J_{P-C} =19.4 Hz, CH, C8), 147.4 (d, J_{P-C} = 10.1 Hz, CH, C3), 149.4 (d, J_{P-C} = 10.8 Hz, CH, C1), 150.3 (d, J_{P-C} = 26.1 Hz, C, C4), 154.8 (d, J_{P-C} = 5.5 Hz, C, C2).

^{29}Si (100 MHz)
-7.04 (d, J_{P-Si} = 25.8 Hz, Si2), -8.17 (d, J_{P-Si} =8.0 Hz, Si1)

^{31}P (200 MHz, $CDCl_3$)
31.9.

HRMS (EI) for $C_{16}H_{25}PSi_2$: calc. (m/z) 304.1232 ; found (m/z) 304.1232.

1-cyclohexyl-2,4-diphenylphosphole (3k)

According to the general procedure using phenylacetylene (0.42 mL, 4.0 mmol) and dichlorocyclohexylphosphine (0.15 mL, 1.0 mmol), **3k** was obtained as a light yellow solid in 40.3 % yield (0.40 mmol, 128 mg).

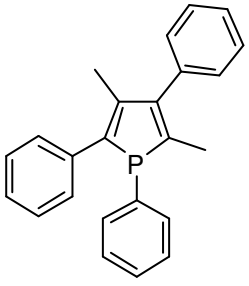
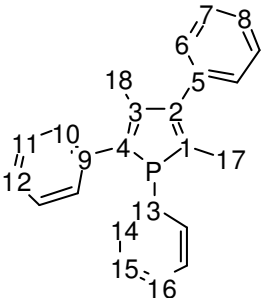
^{1}H (500 MHz, $CDCl_3$)
1.10-1.30 (m, 6H, H15, H16), 1.60-1.68 (m, 4H, H14), 2.09-2.14 (m, 1H, H13), 6.96 (dd, $J_{P\text{-}H}$ = 36.5 Hz, $J_{H\text{-}H}$ = 1.0 Hz, 1H, H1), 7.30-7.36 (m, 2H, H8, H12), 7.40-7.46 (m, 4H, H7, H11), 7.52 (dd, $J_{P\text{-}H}$ = 11.5 Hz, $J_{H\text{-}H}$ = 1.0 Hz, 1H, H3), 7.62 (d, $J_{H\text{-}H}$ = 8.0 Hz, 2H, H10), 7.70 (d, $J_{H\text{-}H}$ = 7.5 Hz, 2H, H6).

^{13}C (125 MHz, $CDCl_3$)
26.1 (CH_2, 2C, C15, C16), 27.5 (d, $J_{P\text{-}C}$ = 10.0 Hz, CH_2, C14), 37.5 (d, $J_{P\text{-}C}$ = 12.6 Hz, CH, C13), 125.1 (d, $J_{P\text{-}C}$ = 4.1 Hz, CH, C1), 126.4 (CH, C11), 127.0 (d, $J_{P\text{-}C}$ = 9.1 Hz, CH, C6), 127.3 (CH, C8), 127.8 (CH, C12), 128.8 (d, $J_{P\text{-}C}$ = 9.3 Hz, CH, C10), 131.9 (d, $J_{P\text{-}C}$ = 8.8 Hz, CH, C3), 132.9 (CH, C7), 137.4 (d, $J_{P\text{-}C}$ = 2.8 Hz, C, C5), 137.9 (d, $J_{P\text{-}C}$ = 15.8 Hz, C, C9), 150.4 (d, $J_{P\text{-}C}$ = 6.6 Hz, C, C2), 152.3 (d, $J_{P\text{-}C}$ = 4.6 Hz, C, C4).

^{31}P (200 MHz, $CDCl_3$)
26.3.

HRMS (EI) for $C_{22}H_{23}P$: calc. (m/z) 318.1537 ; found (m/z) 318.1537.

3,5-dimethyl-2,4-diphenyl-phenylphosphole (3l)

According to the general procedure using phenylpropyne (0.50 mL, 4.0 mmol) and dichlorophenylphosphine (0.28 mL, 2.0 mmol), **3l** was obtained as a colourless oil in 25 % yield (0.50 mmol, 169 mg). In addition a non-separable mixture of **3l** and **3m** (1 : 1) was obtained in 13 % yield (0.26 mmol, 89 mg).

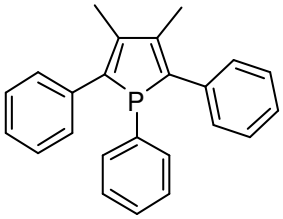
^{1}H (500 MHz, $CDCl_3$)
1.92 (d, J_{P-H} = 11.0 Hz, 3H, H17), 1.98 (d, J_{P-H} = 3.0 Hz, 3H, H18), 7.13-7.16 (m, 1H, H12), 7.23-7.24 (m, 3H, H15, H16), 7.25-7.29 (m, 4H, H7, H11), 7.30-7.35 (m, 3H, H8, H14), 7.36 (d, J_{H-H} = 7.5 Hz, 2H, H10), 7.43 (dd, J_{H-H} = 7.5 Hz, J_{P-H} = 1.5 Hz, 2H, H6).

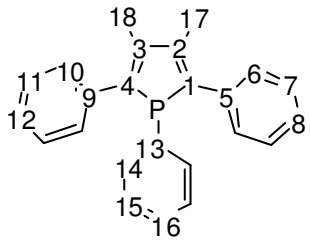
^{13}C (125 MHz, $CDCl_3$)
14.0 (d, J_{P-C} = 20.4 Hz, CH_3, C17), 16.8 (d, J_{P-C} = 1.8 Hz, CH_3, C18), 126.1 (CH, C12), 127.1 (CH, C8), 128.3 (d, J_{P-C} = 2.3 Hz, CH, 2C, C6, C7), 128.7 (d, J_{P-C} = 8.0 Hz, CH, C15), 129.3 (d, J_{P-C} = 8.5 Hz, CH, C10), 129.3 (CH, C16), 129.6 (d, J_{P-C} = 1.3 Hz, CH, C11), 132.2 (d, J_{P-C} = 11.9 Hz, C, C13), 133.6 (d, J_{P-C} = 18.6 Hz, CH, C14), 137.8 (d, J_{P-C} = 17.9 Hz, C, C9), 138.1 (d, J_{P-C} = 3.5 Hz, C, C5), 142.2 (C, C4), 142.7 (C, C1), 143.1 (d, J_{P-C} = 11.8 Hz, C, C3), 149.5 (d, J_{P-C} = 10.6 Hz, C, C2).

^{31}P (200 MHz, $CDCl_3$)
15.8

HRMS (EI) for $C_{24}H_{21}P$: calc. (m/z) 340.1381 ; found (m/z) 340.1381.

3,4-dimethyl-2,5-diphenyl-phenylphosphole (3m)





^{1}H (500 MHz, $CDCl_3$)
2.10 (d, J_{P-H} = 2.5 Hz, 6H, H17, H18), 6.91-6.97 (m, 2H, H8, H12), 7.01-7.07 (m, 2H, H14), 7.12-7.20 (m, 7H, H7, H11, H15, H16), 7.22-7.28 (m, 4H, H6, H10).

^{13}C (125 MHz, $CDCl_3$)
15.4 (d, J_{P-C} = 1.3 Hz, CH_3, 2C, C17, C18), 126.3 (CH, C8, C12), 128.3 (d, J_{P-C} = 12.4 Hz, CH, C7, C11), 128.4 (d, J_{P-C} = 6.8 Hz, CH, C6, C10), 128.9 (CH, C16), 129.4 (d, J_{P-C} = 8.4 Hz, CH, C15), 131.9 (d, J_{P-C} = 12.3 Hz, CH, C13), 133.1 (d, J_{P-C} = 18.0 Hz, CH, C14), 137.6 (d, J_{P-C} = 17.6 Hz, C, C5, C9), 143.5 (d, J_{P-C} = 11.8 Hz, C, C2, C3), 144.9 (d, J_{P-C} = 1.5 Hz, C, C1, C4).

^{31}P (200 MHz, $CDCl_3$)
13.9

II. Crystallographic data for **1b**, **3a, 5a**

Crystal data for **1b**

Compound	bg237
Molecular formula	$C_{26}H_{22}Zr,1/2(C_4H_8O)$
Molecular weight	461.71
Crystal habit	Orange Block
Crystal dimensions(mm)	0.40x0.16x0.10
Crystal system	triclinic
Space group	P-1
a(Å)	13.136(1)
b(Å)	13.406(1)
c(Å)	13.761(1)
α(°)	115.669(1)
β(°)	95.441(1)
γ(°)	95.918(1)
V(Å^3)	2146.1(3)
Z	4
d(g-cm^{-3})	1.429
F(000)	952
μ(cm^{-1})	0.526
Absorption corrections	multi-scan ; 0.8170 min, 0.9492 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-18 17 ; -17 18 ; -19 19
Reflections measured	23820
Unique data	12382
Rint	0.0348
Reflections used	10938
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	532
Reflections / parameter	20
wR2	0.0789
R1	0.0375
Weights a, b	0.0000 ; 3.0712
GoF	1.082
difference peak / hole (e Å^{-3})	0.568(0.075) / -0.613(0.075)

Crystal data for **3a**

Compound	fj373
Molecular formula	'C_{22} H_{17} P'
Molecular weight	312.33
Crystal habit	Yellow Block
Crystal dimensions(mm)	0.30x0.20x0.15
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	5.884(1)
b(Å)	8.898(1)
c(Å)	30.968(1)
α(°)	90.00
β(°)	96.658(2)
γ(°)	90.00
V(Å^3)	1610.4(3)
Z	4
d(g-cm^{-3})	1.288
F(000)	656
μ(cm^{-1})	0.167
Absorption corrections	multi-scan ; 0.9515 min, 0.9753 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	28.70
HKL ranges	-6 7 ; -12 10 ; -38 41
Reflections measured	8866
Unique data	4031
Rint	0.0329
Reflections used	3582
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	208
Reflections / parameter	17
wR2	0.1149
R1	0.0462
Weights a, b	0.0483 ; 0.8203
GoF	1.055
difference peak / hole (e Å^{-3})	0.362(0.047) / -0.306(0.047)

Crystal data for **5a**

Compound	fj_triphenylphosphol
Molecular formula	'C_{22} H_{17} P'
Molecular weight	312.33
Crystal habit	Yellow Block
Crystal dimensions(mm)	0.22x0.18x0.10
Crystal system	monoclinic
Space group	$P2_1$
a(Å)	12.079(1)
b(Å)	5.832(1)
c(Å)	12.562(1)
α(°)	90.000(1)
β(°)	115.528(1)
γ(°)	90.000(1)
V(Å^3)	798.54(16)
Z	2
d(g-cm^{-3})	1.299
F(000)	328
μ(cm^{-1})	0.169
Absorption corrections	multi-scan ; 0.9638 min, 0.9833 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-10 16 ; -8 7 ; -17 17
Reflections measured	5707
Unique data	3917
Rint	0.0256
Reflections used	3795
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	209
Reflections / parameter	18
wR2	0.0788
R1	0.0359
Flack's parameter	0.17(8)
Weights a, b	0.0000 ; 0.3882
GoF	1.064
difference peak / hole (e Å^{-3})	0.219(0.041) / -0.188(0.041)

III. Details on DFT calculations of compounds **1a**, **1b**, **1d** and **1e**

Geometry, three lowest frequencies and thermochemistry of **1a**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	40	0	0.839773	-1.156427	0.035012
2	6	0	-1.385991	-1.262938	0.180932
3	6	0	-1.917983	-0.002141	0.062898
4	6	0	-1.013893	1.164438	-0.064460
5	6	0	0.349917	1.058601	-0.129762
6	6	0	1.217637	2.254032	-0.124287
7	6	0	0.857818	3.438519	0.563535
8	6	0	1.693068	4.557935	0.567742
9	6	0	2.919313	4.530701	-0.109268
10	6	0	3.302142	3.366268	-0.785238
11	6	0	2.467542	2.244989	-0.785036
12	6	0	2.064135	-2.850044	-1.526514
13	6	0	2.419655	-1.539145	-1.968705
14	6	0	1.247844	-0.924542	-2.510722
15	6	0	0.170938	-1.852456	-2.387263
16	6	0	0.676577	-3.040978	-1.780169
17	6	0	0.598090	-1.626769	2.563201
18	6	0	1.226220	-0.348035	2.473533
19	6	0	2.533423	-0.532510	1.929269
20	6	0	2.710874	-1.920745	1.672514
21	6	0	1.511067	-2.599980	2.053742
22	1	0	-1.492497	2.147629	-0.070798
23	1	0	-0.077701	3.466343	1.113246
24	1	0	1.391546	5.450950	1.107554
25	1	0	3.569259	5.399995	-0.102133
26	1	0	4.251468	3.331274	-1.311918
27	1	0	2.773258	1.349652	-1.317366
28	1	0	2.736186	-3.576348	-1.092971
29	1	0	3.411100	-1.109266	-1.940895
30	1	0	1.189247	0.057003	-2.954762
31	1	0	-0.846762	-1.687322	-2.704137
32	1	0	0.105107	-3.931543	-1.559776
33	1	0	-0.386914	-1.822612	2.956670
34	1	0	0.797462	0.594002	2.777036
35	1	0	3.255083	0.250173	1.744480
36	1	0	3.602884	-2.384036	1.276345
37	1	0	1.343788	-3.667022	2.008259
38	1	0	-2.068615	-2.114772	0.216679
39	6	0	-3.390216	0.250352	0.024716
40	6	0	-3.939809	1.256193	-0.796889
41	6	0	-4.275088	-0.523655	0.802972
42	6	0	-5.320761	1.472299	-0.844454
43	1	0	-3.284052	1.856319	-1.419495
44	6	0	-5.654307	-0.307472	0.757343
45	1	0	-3.868757	-1.285819	1.460393
46	6	0	-6.184800	0.692737	-0.067354
47	1	0	-5.721395	2.246685	-1.491828
48	1	0	-6.314808	-0.911756	1.372095
49	1	0	-7.256261	0.863659	-0.100823

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering activities (A**4/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

	1	2	3
	A	A	A
Frequencies --	27.4444	31.4898	34.8488
Red. masses --	3.9262	3.5015	4.7318
Frc consts --	0.0017	0.0020	0.0034
IR Inten --	0.0898	0.0210	0.1548

Sum of electronic and zero-point Energies= -1049.969302
Sum of electronic and thermal Energies= -1049.945737

```
 Sum of electronic and thermal Enthalpies=           -1049.944792
 Sum of electronic and thermal Free Energies=        -1050.024931

HF=-1050.3666336
```

Geometry, three lowest frequencies and thermochemistry of **1b (monomer)**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	40	0	-0.000288	-0.662840	0.000235
2	6	0	3.742734	0.026978	-0.649235
3	6	0	5.139925	0.058320	-0.655201
4	6	0	5.822999	1.142589	-0.092455
5	6	0	5.090176	2.191272	0.479440
6	6	0	3.694532	2.160536	0.481514
7	6	0	2.980203	1.081796	-0.095881
8	6	0	1.507661	1.025313	-0.101155
9	6	0	0.730755	2.156436	-0.044565
10	6	0	-0.731114	2.156521	0.041945
11	6	0	-1.508005	1.025478	0.100020
12	6	0	-2.980552	1.081813	0.094876
13	6	0	-3.695005	2.159834	-0.483699
14	6	0	-5.090653	2.190430	-0.481613
15	6	0	-5.823335	1.142302	0.091478
16	6	0	-5.140128	0.058736	0.655422
17	6	0	-3.742936	0.027533	0.649445
18	6	0	0.558659	-2.630461	1.601020
19	6	0	-0.750454	-2.166726	1.943762
20	6	0	-0.620708	-0.859153	2.505009
21	6	0	0.763093	-0.511856	2.485647
22	6	0	1.490854	-1.609253	1.934867
23	6	0	0.620127	-0.861544	-2.504499
24	6	0	-0.764232	-0.516798	-2.485204
25	6	0	-1.489867	-1.614829	-1.932725
26	6	0	-0.555643	-2.633959	-1.597942
27	6	0	0.752457	-2.168264	-1.941736
28	1	0	3.223431	-0.818182	-1.089794
29	1	0	5.695597	-0.763479	-1.097527
30	1	0	6.908120	1.166623	-0.090073
31	1	0	5.609411	3.030617	0.932935
32	1	0	3.144525	2.968944	0.952421
33	1	0	1.193849	3.147976	-0.061748
34	1	0	-1.194188	3.148093	0.058021
35	1	0	-3.145060	2.967745	-0.955534
36	1	0	-5.609998	3.029211	-0.936024
37	1	0	-6.908459	1.166193	0.089082
38	1	0	-5.695709	-0.762619	1.098690
39	1	0	-3.223509	-0.817065	1.090935
40	1	0	0.797713	-3.596997	1.181461
41	1	0	-1.667038	-2.731118	1.844916
42	1	0	-1.422564	-0.246891	2.887217
43	1	0	1.189963	0.415262	2.835117
44	1	0	2.560500	-1.645521	1.787501
45	1	0	1.420829	-0.248429	-2.887774
46	1	0	-1.193041	0.408995	-2.835829
47	1	0	-2.559473	-1.653066	-1.785581
48	1	0	-0.792843	-3.600362	-1.177015
49	1	0	1.670212	-2.730595	-1.842005

```
 Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering
 activities (A**4/AMU), depolarization ratios for plane and unpolarized
 incident light, reduced masses (AMU), force constants (mDyne/A),
 and normal coordinates:
                      1                      2                      3
                      A                      A                      A
 Frequencies --    21.5373                31.5347                38.4799
 Red. masses --     3.8242                 4.7774                 4.2532
 Frc consts  --     0.0010                 0.0028                 0.0037
 IR Inten    --     0.2220                 0.1606                 0.0238
```

```
 Sum of electronic and zero-point Energies=          -1049.973364
 Sum of electronic and thermal Energies=             -1049.949773
 Sum of electronic and thermal Enthalpies=           -1049.948829
 Sum of electronic and thermal Free Energies=        -1050.028604

HF=-1050.3710451
```

Geometry, three lowest frequencies and thermochemistry of **1d**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	40	0	-0.922081	-1.137827	0.066493
2	6	0	1.329895	-1.139703	0.180404
3	6	0	1.806921	0.131934	-0.010312
4	6	0	0.863936	1.284408	-0.199041
5	6	0	-0.492057	1.061044	-0.209544
6	6	0	-1.517095	2.129692	-0.233010
7	6	0	-1.554642	3.133878	0.765703
8	6	0	-2.560548	4.104098	0.788114
9	6	0	-3.565235	4.105775	-0.187458
10	6	0	-3.549158	3.123699	-1.184877
11	6	0	-2.546589	2.148954	-1.202781
12	6	0	-2.514048	-2.189400	1.848255
13	6	0	-2.669912	-0.775399	1.948850
14	6	0	-1.440911	-0.230003	2.429943
15	6	0	-0.524786	-1.308532	2.621229
16	6	0	-1.187932	-2.519585	2.256540
17	6	0	-0.205347	-2.096184	-2.249213
18	6	0	-1.166453	-1.073746	-2.511237
19	6	0	-2.428586	-1.519783	-2.010333
20	6	0	-2.245037	-2.817255	-1.447672
21	6	0	-0.872165	-3.171973	-1.590023
22	1	0	-0.781084	3.142270	1.527734
23	1	0	-2.559848	4.860228	1.568046
24	1	0	-4.346340	4.859207	-0.170504
25	1	0	-4.317795	3.117446	-1.952569
26	1	0	-2.543707	1.400600	-1.987952
27	1	0	-3.274908	-2.890225	1.537461
28	1	0	-3.565757	-0.214539	1.721825
29	1	0	-1.250953	0.812087	2.630378
30	1	0	0.484489	-1.224950	2.992675
31	1	0	-0.767109	-3.514325	2.304615
32	1	0	0.838328	-2.067408	-2.519849
33	1	0	-0.973629	-0.142971	-3.020918
34	1	0	-3.364330	-0.981626	-2.067749
35	1	0	-3.017320	-3.432535	-1.009950
36	1	0	-0.420420	-4.101705	-1.273759
37	6	0	3.287057	0.424130	-0.029583
38	6	0	3.976463	0.744648	1.155044
39	6	0	4.018981	0.370210	-1.230922
40	6	0	5.351294	1.006545	1.139977
41	1	0	3.427605	0.785390	2.091512
42	6	0	5.393769	0.631582	-1.249084
43	1	0	3.503104	0.121510	-2.153962
44	6	0	6.064617	0.952231	-0.063094
45	1	0	5.864084	1.251082	2.065559
46	1	0	5.939700	0.584195	-2.186711
47	1	0	7.130950	1.155453	-0.076019
48	6	0	1.486040	2.660688	-0.381912
49	1	0	2.041129	2.979342	0.510577
50	1	0	2.211952	2.653041	-1.204286
51	1	0	0.728115	3.415075	-0.599822
52	6	0	2.221173	-2.342096	0.396183
53	1	0	2.037463	-3.114985	-0.364977
54	1	0	3.290770	-2.100508	0.371854
55	1	0	2.010895	-2.817225	1.366223

```
 Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering
 activities (A**4/AMU), depolarization ratios for plane and unpolarized
 incident light, reduced masses (AMU), force constants (mDyne/A),
 and normal coordinates:
                      1                      2                      3
                      A                      A                      A
 Frequencies --    20.9000                24.2791                34.1129
 Red. masses --     3.7776                 3.6593                 4.6868
 Frc consts  --     0.0010                 0.0013                 0.0032
 IR Inten    --     0.0163                 0.0037                 0.0487

HF=-1128.9703575
```

Geometry, three lowest frequencies and thermochemistry of **1e**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	40	0	0.002098	-0.844994	0.075088
2	6	0	3.754788	-0.004102	-0.961290
3	6	0	5.135315	-0.067928	-0.745157
4	6	0	5.726702	0.666633	0.289124
5	6	0	4.919760	1.473649	1.100547
6	6	0	3.540993	1.543233	0.879648
7	6	0	2.920463	0.807001	-0.159158
8	6	0	1.447910	0.845287	-0.332055
9	6	0	0.743260	1.979890	-0.650172
10	6	0	-0.759991	1.976113	-0.642633
11	6	0	-1.456649	0.840214	-0.311735
12	6	0	-2.929191	0.798016	-0.135787
13	6	0	-3.544510	1.509200	0.923279
14	6	0	-4.923334	1.440512	1.144429
15	6	0	-5.735245	0.659182	0.313222
16	6	0	-5.148985	-0.049701	-0.741654
17	6	0	-3.768511	0.013822	-0.958805
18	6	0	0.702480	-2.209648	2.147670
19	6	0	-0.728838	-2.136173	2.175216
20	6	0	-1.093468	-0.784149	2.440126
21	6	0	0.105767	-0.021384	2.556670
22	6	0	1.214158	-0.903575	2.391531
23	6	0	0.701946	-1.473338	-2.355103
24	6	0	-0.724603	-1.455073	-2.352731
25	6	0	-1.178346	-2.530859	-1.530599
26	6	0	-0.032351	-3.215187	-1.031317
27	6	0	1.130051	-2.559889	-1.533347
28	1	0	3.316788	-0.576853	-1.770888
29	1	0	5.750165	-0.691670	-1.387791
30	1	0	6.797229	0.612287	0.459503
31	1	0	5.364323	2.051625	1.905710
32	1	0	2.923286	2.171760	1.514337
33	1	0	-2.922792	2.119585	1.571806
34	1	0	-5.364031	1.999625	1.964881
35	1	0	-6.805801	0.605464	0.483592
36	1	0	-5.767841	-0.652325	-1.400411
37	1	0	-3.335214	-0.536902	-1.786024
38	1	0	1.289366	-3.105126	2.002055
39	1	0	-1.410184	-2.966717	2.058397
40	1	0	-2.099534	-0.400327	2.519708
41	1	0	0.164509	1.040892	2.739339
42	1	0	2.256230	-0.621985	2.424947
43	1	0	1.336323	-0.795793	-2.903866
44	1	0	-1.343029	-0.760907	-2.898861
45	1	0	-2.208772	-2.788521	-1.330839
46	1	0	-0.042764	-4.087578	-0.394251
47	1	0	2.153932	-2.846062	-1.338554
48	6	0	-1.455105	3.278438	-1.017351
49	1	0	-2.540235	3.165345	-1.003935
50	1	0	-1.192905	4.096536	-0.333212
51	1	0	-1.164358	3.606942	-2.023911
52	6	0	1.427883	3.288904	-1.020616
53	1	0	1.174929	4.097940	-0.322147
54	1	0	2.513407	3.179225	-1.027004

55	1	0	1.118929	3.628759	-2.017817

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering activities (A**4/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

	1	2	3
	A	A	A
Frequencies --	20.1136	24.4941	35.2801
Red. masses --	3.8339	3.5997	4.7998
Frc consts --	0.0009	0.0013	0.0035
IR Inten --	0.0361	0.0309	0.0024

HF=-1128.9741671

NBO analysis of **1a**

Summary of Natural Population Analysis:

Atom No	Natural Charge	Natural Population			
		Core	Valence	Rydberg	Total
Zr 1	1.65141	35.97814	2.27740	0.09305	38.34859
C 2	-0.63201	1.99868	4.61760	0.01572	6.63201
C 3	-0.06900	1.99883	4.05613	0.01405	6.06900
C 4	-0.24217	1.99884	4.23251	0.01083	6.24217
C 5	-0.40529	1.99868	4.38545	0.02116	6.40529
C 6	-0.06047	1.99889	4.04746	0.01411	6.06047
C 7	-0.23130	1.99896	4.22189	0.01046	6.23130
C 8	-0.23748	1.99899	4.22699	0.01150	6.23748
C 9	-0.24956	1.99899	4.23914	0.01143	6.24956
C 10	-0.24048	1.99899	4.22996	0.01153	6.24048
C 11	-0.22950	1.99896	4.21985	0.01069	6.22950
C 12	-0.34454	1.99882	4.32860	0.01712	6.34454
C 13	-0.37345	1.99880	4.35806	0.01659	6.37345
C 14	-0.34287	1.99875	4.32790	0.01622	6.34287
C 15	-0.31852	1.99876	4.30331	0.01645	6.31852
C 16	-0.34932	1.99878	4.33440	0.01613	6.34932
C 17	-0.33398	1.99875	4.31909	0.01614	6.33398
C 18	-0.32554	1.99876	4.31013	0.01665	6.32554
C 19	-0.34516	1.99877	4.33017	0.01621	6.34516
C 20	-0.34717	1.99883	4.33139	0.01695	6.34717
C 21	-0.37385	1.99880	4.35831	0.01673	6.37385
H 22	0.22748	0.00000	0.77013	0.00239	0.77252
H 23	0.24208	0.00000	0.75652	0.00140	0.75792
H 24	0.24203	0.00000	0.75684	0.00113	0.75797
H 25	0.24108	0.00000	0.75789	0.00103	0.75892
H 26	0.24066	0.00000	0.75826	0.00108	0.75934
H 27	0.23208	0.00000	0.76642	0.00150	0.76792
H 28	0.27012	0.00000	0.72895	0.00092	0.72988
H 29	0.27128	0.00000	0.72784	0.00087	0.72872
H 30	0.28235	0.00000	0.71665	0.00100	0.71765
H 31	0.28315	0.00000	0.71587	0.00098	0.71685
H 32	0.27264	0.00000	0.72650	0.00086	0.72736
H 33	0.28078	0.00000	0.71826	0.00096	0.71922
H 34	0.28279	0.00000	0.71616	0.00105	0.71721
H 35	0.27849	0.00000	0.72050	0.00101	0.72151
H 36	0.26991	0.00000	0.72918	0.00091	0.73009
H 37	0.27186	0.00000	0.72720	0.00094	0.72814
H 38	0.22732	0.00000	0.77146	0.00121	0.77268
C 39	-0.04663	1.99890	4.03491	0.01282	6.04663
C 40	-0.23229	1.99895	4.22319	0.01014	6.23229
C 41	-0.22520	1.99895	4.21590	0.01034	6.22520
C 42	-0.23772	1.99899	4.22718	0.01155	6.23772
H 43	0.24435	0.00000	0.75439	0.00126	0.75565
C 44	-0.23902	1.99899	4.22857	0.01145	6.23902
H 45	0.24181	0.00000	0.75678	0.00141	0.75819
C 46	-0.24573	1.99899	4.23544	0.01130	6.24573
H 47	0.24200	0.00000	0.75692	0.00108	0.75800
H 48	0.24145	0.00000	0.75747	0.00109	0.75855
H 49	0.24113	0.00000	0.75783	0.00104	0.75887

* Total *	0.00000	87.94857	129.56899	0.48244	218.00000

NBO analysis of **1b**

Summary of Natural Population Analysis:

Atom No	Natural Charge	Natural Population Core	Valence	Rydberg	Total
Zr 1	1.62533	35.97745	2.29605	0.10116	38.37467
C 2	-0.22729	1.99897	4.21780	0.01052	6.22729
C 3	-0.24104	1.99899	4.23049	0.01157	6.24104
C 4	-0.24886	1.99899	4.23842	0.01145	6.24886
C 5	-0.23852	1.99899	4.22805	0.01148	6.23852
C 6	-0.22642	1.99896	4.21710	0.01036	6.22642
C 7	-0.06325	1.99889	4.05037	0.01399	6.06325
C 8	-0.40753	1.99864	4.38821	0.02068	6.40753
C 9	-0.25030	1.99885	4.23948	0.01197	6.25030
C 10	-0.25029	1.99885	4.23947	0.01197	6.25029
C 11	-0.40756	1.99864	4.38824	0.02068	6.40756
C 12	-0.06320	1.99889	4.05032	0.01399	6.06320
C 13	-0.22641	1.99896	4.21709	0.01036	6.22641
C 14	-0.23854	1.99899	4.22806	0.01148	6.23854
C 15	-0.24888	1.99899	4.23843	0.01145	6.24888
C 16	-0.24105	1.99899	4.23050	0.01157	6.24105
C 17	-0.22726	1.99897	4.21777	0.01052	6.22726
C 18	-0.34699	1.99880	4.33113	0.01705	6.34699
C 19	-0.37512	1.99879	4.35960	0.01673	6.37512
C 20	-0.33739	1.99874	4.32253	0.01612	6.33739
C 21	-0.32233	1.99874	4.30688	0.01672	6.32233
C 22	-0.33879	1.99876	4.32377	0.01626	6.33879
C 23	-0.33741	1.99874	4.32255	0.01612	6.33741
C 24	-0.32245	1.99874	4.30700	0.01671	6.32245
C 25	-0.33896	1.99876	4.32393	0.01627	6.33896
C 26	-0.34692	1.99880	4.33107	0.01705	6.34692
C 27	-0.37495	1.99879	4.35944	0.01672	6.37495
H 28	0.23210	0.00000	0.76639	0.00151	0.76790
H 29	0.24102	0.00000	0.75791	0.00108	0.75898
H 30	0.24146	0.00000	0.75751	0.00103	0.75854
H 31	0.24212	0.00000	0.75675	0.00113	0.75788
H 32	0.24001	0.00000	0.75857	0.00141	0.75999
H 33	0.22819	0.00000	0.76944	0.00237	0.77181
H 34	0.22820	0.00000	0.76943	0.00237	0.77180
H 35	0.24000	0.00000	0.75858	0.00141	0.76000
H 36	0.24212	0.00000	0.75675	0.00113	0.75788
H 37	0.24146	0.00000	0.75751	0.00103	0.75854
H 38	0.24101	0.00000	0.75791	0.00108	0.75899
H 39	0.23209	0.00000	0.76639	0.00151	0.76791
H 40	0.27062	0.00000	0.72846	0.00093	0.72938
H 41	0.27110	0.00000	0.72795	0.00095	0.72890
H 42	0.28292	0.00000	0.71606	0.00102	0.71708
H 43	0.28252	0.00000	0.71644	0.00104	0.71748
H 44	0.27916	0.00000	0.71976	0.00108	0.72084
H 45	0.28293	0.00000	0.71605	0.00102	0.71707
H 46	0.28253	0.00000	0.71644	0.00104	0.71747
H 47	0.27913	0.00000	0.71978	0.00108	0.72087
H 48	0.27061	0.00000	0.72847	0.00093	0.72939
H 49	0.27107	0.00000	0.72798	0.00095	0.72893
* Total *	0.00000	87.94766	129.55426	0.49808	218.00000

NBO analysis of **1d**

Atom No	Natural Charge	Natural Population Core	Valence	Rydberg	Total
Zr 1	1.68663	35.97695	2.23732	0.09910	38.31337
C 2	-0.37831	1.99862	4.36050	0.01919	6.37831
C 3	-0.07962	1.99871	4.06516	0.01574	6.07962
C 4	-0.00424	1.99874	3.99285	0.01265	6.00424

C 5	-0.43883	1.99860	4.42097	0.01926	6.43883
C 6	-0.05210	1.99888	4.03891	0.01430	6.05210
C 7	-0.24530	1.99894	4.23536	0.01100	6.24530
C 8	-0.23727	1.99898	4.22673	0.01156	6.23727
C 9	-0.25623	1.99899	4.24573	0.01151	6.25623
C 10	-0.23891	1.99899	4.22848	0.01145	6.23891
C 11	-0.23472	1.99894	4.22466	0.01113	6.23472
C 12	-0.34410	1.99883	4.32854	0.01674	6.34410
C 13	-0.36014	1.99877	4.34475	0.01661	6.36014
C 14	-0.33208	1.99874	4.31673	0.01660	6.33208
C 15	-0.33248	1.99874	4.31737	0.01636	6.33248
C 16	-0.36392	1.99878	4.34877	0.01636	6.36392
C 17	-0.32541	1.99875	4.31021	0.01646	6.32541
C 18	-0.34371	1.99874	4.32887	0.01610	6.34371
C 19	-0.36574	1.99878	4.35083	0.01613	6.36574
C 20	-0.34185	1.99882	4.32619	0.01683	6.34185
C 21	-0.36052	1.99878	4.34548	0.01626	6.36052
H 22	0.24201	0.00000	0.75682	0.00117	0.75799
H 23	0.24144	0.00000	0.75742	0.00113	0.75856
H 24	0.24050	0.00000	0.75847	0.00104	0.75950
H 25	0.24014	0.00000	0.75876	0.00110	0.75986
H 26	0.23304	0.00000	0.76554	0.00142	0.76696
H 27	0.26921	0.00000	0.72993	0.00086	0.73079
H 28	0.27703	0.00000	0.72201	0.00096	0.72297
H 29	0.28055	0.00000	0.71827	0.00117	0.71945
H 30	0.27899	0.00000	0.72009	0.00092	0.72101
H 31	0.27126	0.00000	0.72786	0.00088	0.72874
H 32	0.27913	0.00000	0.71993	0.00093	0.72087
H 33	0.28029	0.00000	0.71874	0.00097	0.71971
H 34	0.27263	0.00000	0.72643	0.00094	0.72737
H 35	0.26933	0.00000	0.72982	0.00085	0.73067
H 36	0.27099	0.00000	0.72816	0.00085	0.72901
C 37	-0.04934	1.99890	4.03476	0.01568	6.04934
C 38	-0.23065	1.99890	4.22120	0.01055	6.23065
C 39	-0.23173	1.99890	4.22229	0.01055	6.23173
C 40	-0.23851	1.99899	4.22795	0.01157	6.23851
H 41	0.24333	0.00000	0.75542	0.00126	0.75667
C 42	-0.23847	1.99899	4.22790	0.01158	6.23847
H 43	0.24352	0.00000	0.75523	0.00125	0.75648
C 44	-0.24874	1.99899	4.23847	0.01128	6.24874
H 45	0.24189	0.00000	0.75700	0.00111	0.75811
H 46	0.24203	0.00000	0.75686	0.00111	0.75797
H 47	0.24156	0.00000	0.75739	0.00105	0.75844
C 48	-0.72185	1.99923	4.71804	0.00459	6.72185
H 49	0.24656	0.00000	0.75198	0.00147	0.75344
H 50	0.25072	0.00000	0.74787	0.00141	0.74928
H 51	0.25168	0.00000	0.74718	0.00114	0.74832
C 52	-0.72156	1.99923	4.71704	0.00530	6.72156
H 53	0.23634	0.00000	0.76210	0.00156	0.76366
H 54	0.24800	0.00000	0.75008	0.00192	0.75200
H 55	0.23752	0.00000	0.76083	0.00165	0.76248
* Total *	0.00000	91.94522	141.54223	0.51255	234.00000

NBO analysis of **1e**

		Natural Population			
Atom No	Natural Charge	Core	Valence	Rydberg	Total
Zr 1	1.68547	35.97707	2.23933	0.09813	38.31453
C 2	-0.23528	1.99893	4.22548	0.01086	6.23528
C 3	-0.23800	1.99899	4.22755	0.01146	6.23800
C 4	-0.25648	1.99899	4.24598	0.01151	6.25648
C 5	-0.23824	1.99898	4.22769	0.01157	6.23824
C 6	-0.24725	1.99893	4.23717	0.01115	6.24725
C 7	-0.05543	1.99889	4.04204	0.01450	6.05543
C 8	-0.42279	1.99859	4.40484	0.01937	6.42279
C 9	-0.01911	1.99875	4.00777	0.01260	6.01911
C 10	-0.01904	1.99875	4.00768	0.01262	6.01904

C 11	-0.42331	1.99859	4.40539	0.01933	6.42331
C 12	-0.05487	1.99889	4.04145	0.01453	6.05487
C 13	-0.24885	1.99893	4.23873	0.01119	6.24885
C 14	-0.23755	1.99898	4.22700	0.01157	6.23755
C 15	-0.25643	1.99899	4.24593	0.01151	6.25643
C 16	-0.23772	1.99899	4.22726	0.01147	6.23772
C 17	-0.23604	1.99893	4.22626	0.01085	6.23604
C 18	-0.36686	1.99881	4.35104	0.01701	6.36686
C 19	-0.37245	1.99880	4.35654	0.01710	6.37245
C 20	-0.33191	1.99875	4.31708	0.01608	6.33191
C 21	-0.32468	1.99875	4.30933	0.01660	6.32468
C 22	-0.33201	1.99875	4.31726	0.01600	6.33201
C 23	-0.33446	1.99875	4.31960	0.01611	6.33446
C 24	-0.33341	1.99875	4.31856	0.01609	6.33341
C 25	-0.36046	1.99878	4.34561	0.01607	6.36046
C 26	-0.34354	1.99881	4.32748	0.01725	6.34354
C 27	-0.36192	1.99878	4.34700	0.01614	6.36192
H 28	0.23361	0.00000	0.76499	0.00140	0.76639
H 29	0.24098	0.00000	0.75793	0.00109	0.75902
H 30	0.24114	0.00000	0.75782	0.00103	0.75886
H 31	0.24213	0.00000	0.75674	0.00113	0.75787
H 32	0.24386	0.00000	0.75492	0.00122	0.75614
H 33	0.24418	0.00000	0.75459	0.00123	0.75582
H 34	0.24207	0.00000	0.75680	0.00113	0.75793
H 35	0.24111	0.00000	0.75786	0.00103	0.75889
H 36	0.24099	0.00000	0.75792	0.00109	0.75901
H 37	0.23362	0.00000	0.76498	0.00141	0.76638
H 38	0.27154	0.00000	0.72745	0.00101	0.72846
H 39	0.27222	0.00000	0.72675	0.00103	0.72778
H 40	0.28149	0.00000	0.71731	0.00120	0.71851
H 41	0.27698	0.00000	0.72200	0.00102	0.72302
H 42	0.28173	0.00000	0.71715	0.00112	0.71827
H 43	0.27785	0.00000	0.72120	0.00095	0.72215
H 44	0.27778	0.00000	0.72127	0.00095	0.72222
H 45	0.27394	0.00000	0.72501	0.00104	0.72606
H 46	0.27056	0.00000	0.72850	0.00093	0.72944
H 47	0.27362	0.00000	0.72535	0.00102	0.72638
C 48	-0.71937	1.99924	4.71518	0.00495	6.71937
H 49	0.25493	0.00000	0.74397	0.00110	0.74507
H 50	0.24169	0.00000	0.75699	0.00132	0.75831
H 51	0.24342	0.00000	0.75529	0.00129	0.75658
C 52	-0.71956	1.99924	4.71537	0.00495	6.71956
H 53	0.24147	0.00000	0.75720	0.00133	0.75853
H 54	0.25494	0.00000	0.74396	0.00110	0.74506
H 55	0.24367	0.00000	0.75505	0.00129	0.75633
* Total *	0.00000	91.94537	141.54658	0.50805	234.00000

Geometry, three lowest frequencies and thermochemistry of **1b (tetramer)**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.550742	-3.130631	-2.379764
2	6	0	5.238097	-3.222696	-0.985279
3	6	0	3.819602	-3.090684	-0.836226
4	6	0	3.248562	-2.927652	-2.145973
5	6	0	4.321308	-2.949619	-3.097755
6	40	0	4.609378	-0.782765	-1.729913
7	6	0	6.829384	0.552775	-1.575483
8	6	0	6.830700	-0.102397	-2.849684
9	6	0	5.770522	0.460125	-3.640751
10	6	0	5.120760	1.471051	-2.856331
11	6	0	5.772852	1.522522	-1.578305
12	6	0	4.163154	-0.146631	0.394913
13	6	0	2.883190	0.382266	0.332809
14	6	0	2.099535	0.460745	-0.897211
15	6	0	2.550993	0.040574	-2.136703
16	6	0	1.765723	0.186345	-3.367958
17	6	0	0.535078	0.907795	-3.441897
18	6	0	-0.154708	1.049226	-4.655536
19	6	0	0.350966	0.464484	-5.835563

20	6	0	1.558200	-0.260204	-5.787500
21	6	0	2.254400	-0.388397	-4.574633
22	6	0	4.959450	-0.174575	1.627048
23	6	0	6.159388	-0.938221	1.660992
24	6	0	6.947813	-1.022684	2.820042
25	6	0	6.564541	-0.329414	3.984676
26	6	0	5.390906	0.454399	3.968533
27	6	0	4.601243	0.535341	2.812130
28	6	0	3.118623	3.763508	-0.631981
29	6	0	3.406252	5.154207	-0.424398
30	6	0	2.829280	5.896162	-1.509791
31	6	0	2.187385	4.966380	-2.389108
32	6	0	2.360224	3.651266	-1.847242
33	40	0	0.862944	4.879035	-0.137753
34	6	0	-1.225192	6.401223	-0.017445
35	6	0	-0.084650	7.227846	-0.282533
36	6	0	0.759094	7.208038	0.887461
37	6	0	0.138499	6.365788	1.864687
38	6	0	-1.075789	5.854994	1.299068
39	6	0	-0.679761	3.536961	-1.077678
40	6	0	-0.738374	2.478613	-0.185202
41	6	0	0.035162	2.372959	1.052129
42	6	0	0.933213	3.326898	1.498058
43	6	0	1.666153	3.206484	2.761738
44	6	0	1.326595	2.263770	3.777528
45	6	0	2.067885	2.182724	4.965484
46	6	0	3.166263	3.041002	5.185070
47	6	0	3.514010	3.985692	4.199460
48	6	0	2.769484	4.069075	3.011577
49	6	0	-1.524867	3.620860	-2.274253
50	6	0	-1.354608	4.711859	-3.171338
51	6	0	-2.146258	4.846755	-4.323938
52	6	0	-3.148464	3.897940	-4.609287
53	6	0	-3.346503	2.811814	-3.730129
54	6	0	-2.545056	2.672169	-2.587201
55	6	0	-3.819599	3.090691	0.836235
56	6	0	-5.238083	3.222731	0.985390
57	6	0	-5.550633	3.130652	2.379896
58	6	0	-4.321155	2.949600	3.097798
59	6	0	-3.248475	2.927620	2.145942
60	40	0	-4.609362	0.782777	1.729922
61	6	0	-6.829374	-0.552752	1.575379
62	6	0	-6.830752	0.102431	2.849574
63	6	0	-5.770617	-0.460092	3.640701
64	6	0	-5.120823	-1.471031	2.856323
65	6	0	-5.772848	-1.522505	1.578264
66	6	0	-4.163127	0.146675	-0.394913
67	6	0	-2.883176	-0.382252	-0.332808
68	6	0	-2.099533	-0.460772	0.897215
69	6	0	-2.550996	-0.040616	2.136710
70	6	0	-1.765735	-0.186414	3.367969
71	6	0	-0.535058	-0.907810	3.441888
72	6	0	0.154724	-1.049263	4.655525
73	6	0	-0.350988	-0.464600	5.835575
74	6	0	-1.558258	0.260032	5.787534
75	6	0	-2.254452	0.388249	4.574666
76	6	0	-4.959418	0.174637	-1.627050
77	6	0	-6.159321	0.938336	-1.661012
78	6	0	-6.947746	1.022802	-2.820061
79	6	0	-6.564508	0.329484	-3.984678
80	6	0	-5.390903	-0.454376	-3.968519
81	6	0	-4.601241	-0.535321	-2.812116
82	6	0	-3.118626	-3.763481	0.631990
83	6	0	-3.406280	-5.154171	0.424384
84	6	0	-2.829327	-5.896154	1.509768
85	6	0	-2.187419	-4.966397	2.389102
86	6	0	-2.360232	-3.651271	1.847257
87	40	0	-0.862959	-4.879034	0.137764
88	6	0	1.225194	-6.401193	0.017440
89	6	0	0.084672	-7.227827	0.282582
90	6	0	-0.759103	-7.208066	-0.887390
91	6	0	-0.138549	-6.365834	-1.864656
92	6	0	1.075745	-5.855003	-1.299084
93	6	0	0.679757	-3.536957	1.077667
94	6	0	0.738377	-2.478626	0.185171

95	6	0	-0.035156	-2.372985	-1.052163
96	6	0	-0.933219	-3.326922	-1.498075
97	6	0	-1.666167	-3.206517	-2.761751
98	6	0	-1.326644	-2.263784	-3.777536
99	6	0	-2.067947	-2.182745	-4.965484
100	6	0	-3.166305	-3.041049	-5.185069
101	6	0	-3.514018	-3.985758	-4.199466
102	6	0	-2.769478	-4.069135	-3.011591
103	6	0	1.524869	-3.620839	2.274239
104	6	0	1.354589	-4.711802	3.171362
105	6	0	2.146247	-4.846679	4.323960
106	6	0	3.148483	-3.897883	4.609266
107	6	0	3.346544	-2.811794	3.730068
108	6	0	2.545087	-2.672167	2.587144
109	1	0	-6.456513	1.472303	-0.758381
110	1	0	-7.857682	1.625280	-2.816431
111	1	0	-7.174808	0.389018	-4.886793
112	1	0	-5.088531	-1.011744	-4.855004
113	1	0	-3.709578	-1.159725	-2.828364
114	1	0	-2.384661	-0.780008	-1.225559
115	1	0	-1.099704	-0.888136	0.778905
116	1	0	-0.122006	-1.375884	2.550470
117	1	0	1.084255	-1.617061	4.674806
118	1	0	0.184707	-0.579964	6.778791
119	1	0	-1.957950	0.717260	6.694259
120	1	0	-3.196007	0.935584	4.540351
121	1	0	-7.512866	0.885243	3.163736
122	1	0	-5.513657	-0.181305	4.657454
123	1	0	-4.287099	-2.087178	3.167920
124	1	0	-5.507887	-2.177098	0.758123
125	1	0	-7.485903	-0.336917	0.738698
126	1	0	-5.946524	3.374311	0.178578
127	1	0	-3.271201	3.131445	-0.094985
128	1	0	-2.195458	2.806311	2.366625
129	1	0	-4.221422	2.864739	4.174835
130	1	0	-6.540428	3.199553	2.818624
131	1	0	0.587095	-5.452506	2.942581
132	1	0	1.987379	-5.691976	4.995805
133	1	0	3.770427	-4.005366	5.498858
134	1	0	4.120873	-2.071029	3.929301
135	1	0	2.718232	-1.820685	1.932634
136	1	0	1.407042	-1.632381	0.364932
137	1	0	0.145133	-1.453346	-1.622088
138	1	0	-0.475605	-1.599640	-3.641879
139	1	0	-1.780649	-1.449081	-5.718670
140	1	0	-3.735840	-2.980012	-6.113458
141	1	0	-4.361012	-4.655006	-4.358660
142	1	0	-3.031466	-4.802622	-2.249471
143	1	0	-0.103695	-7.787627	1.193112
144	1	0	-1.694914	-7.744761	-1.005289
145	1	0	-0.540662	-6.111769	-2.839196
146	1	0	1.754842	-5.155143	-1.771857
147	1	0	2.035020	-6.187989	0.705398
148	1	0	-3.410198	-2.939521	-0.006692
149	1	0	-3.973798	-5.574970	-0.399235
150	1	0	-2.873797	-6.973063	1.637673
151	1	0	-1.650579	-5.206311	3.300275
152	1	0	-1.988312	-2.733053	2.279298
153	1	0	-0.587136	5.452576	-2.942522
154	1	0	-1.987407	5.692080	-4.995752
155	1	0	-3.770402	4.005436	-5.498882
156	1	0	-4.120808	2.071035	-3.929403
157	1	0	-2.718183	1.820659	-1.932725
158	1	0	-1.407029	1.632364	-0.364983
159	1	0	-0.145119	1.453310	1.622041
160	1	0	0.475540	1.599648	3.641868
161	1	0	1.780562	1.449074	5.718675
162	1	0	3.735787	2.979961	6.113466
163	1	0	4.361021	4.654918	4.358655
164	1	0	3.031498	4.802545	2.249450
165	1	0	0.103750	7.787669	-1.193042
166	1	0	1.694910	7.744714	1.005399
167	1	0	0.540581	6.111693	2.839232
168	1	0	-1.754913	5.155135	1.771802
169	1	0	-2.035002	6.188049	-0.705432

170	1	0	3.410215	2.939562	0.006710
171	1	0	3.973764	5.575030	0.399212
172	1	0	2.873731	6.973070	-1.637713
173	1	0	1.650533	5.206270	-3.300280
174	1	0	1.988316	2.733035	-2.279265
175	1	0	6.456609	-1.472148	0.758346
176	1	0	7.857775	-1.625122	2.816398
177	1	0	7.174839	-0.388950	4.886792
178	1	0	5.088508	1.011732	4.855030
179	1	0	3.709557	1.159711	2.828392
180	1	0	2.384671	0.780018	1.225559
181	1	0	1.099695	0.888085	-0.778900
182	1	0	0.122055	1.375929	-2.550498
183	1	0	-1.084208	1.617072	-4.674837
184	1	0	-0.184732	0.579832	-6.778780
185	1	0	1.957861	-0.717494	-6.694207
186	1	0	3.195932	-0.935771	-4.540304
187	1	0	7.512802	-0.885203	-3.163888
188	1	0	5.513506	0.181342	-4.657491
189	1	0	4.287013	2.087193	-3.167878
190	1	0	5.507929	2.177109	-0.758147
191	1	0	7.485960	0.336940	-0.738839
192	1	0	5.946484	-3.374240	-0.178412
193	1	0	3.271137	-3.131434	0.094954
194	1	0	2.195557	-2.806365	-2.366727
195	1	0	4.221652	-2.864783	-4.174801
196	1	0	6.540569	-3.199517	-2.818422

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering activities (A**4/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

	1	2	3
	A	A	A
Frequencies --	2.8891	13.2848	16.1131
Red. masses --	5.6773	4.9788	4.7489
Frc consts --	0.0000	0.0005	0.0007
IR Inten --	0.0439	0.0000	0.0000

Sum of electronic and zero-point Energies= -4197.510818
Sum of electronic and thermal Energies= -4197.409820
Sum of electronic and thermal Enthalpies= -4197.408876
Sum of electronic and thermal Free Energies= -4197.658097

HF=-4199.0707572

IV. References for Gaussian

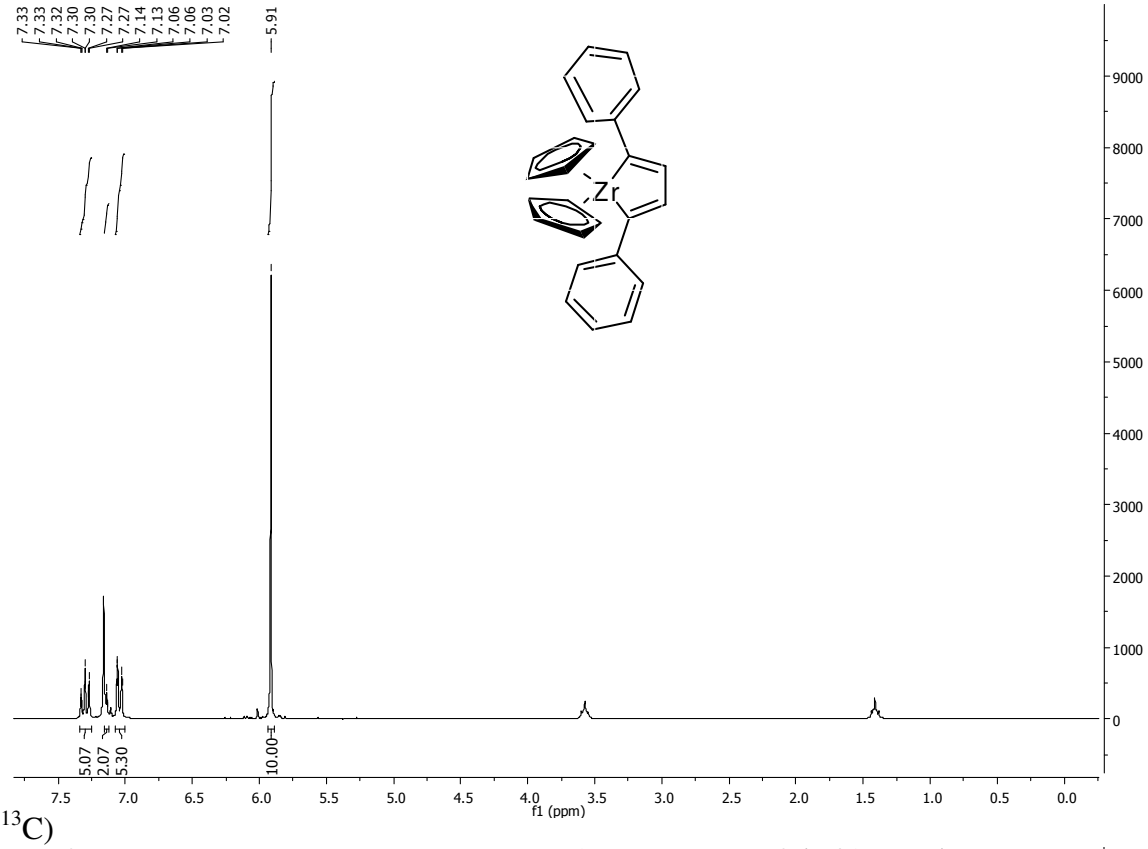
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J.C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03, Revision C.02*, 2004.

M. J. Frisch, G .W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J .C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision B.01*, 2010.

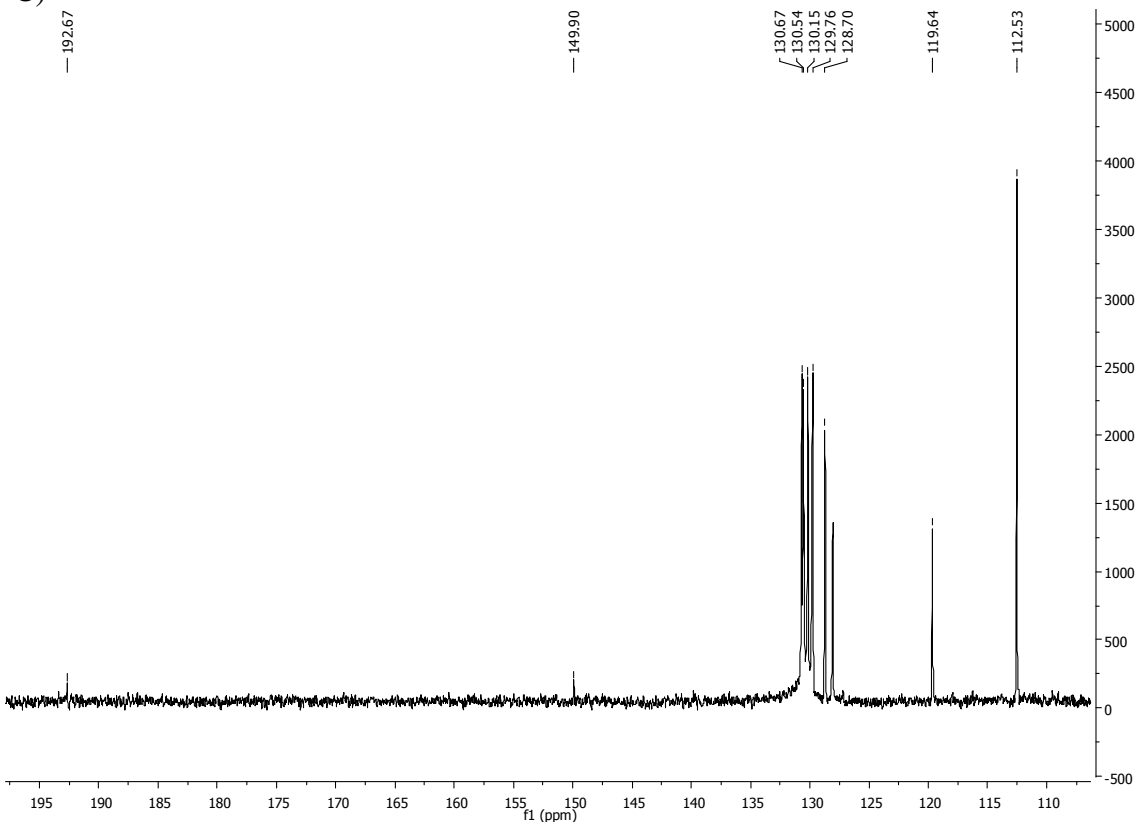
V. ^{1}H, ^{13}C and ^{31}P NMR spectra for compounds **1b**, **3a-m**

(1b)

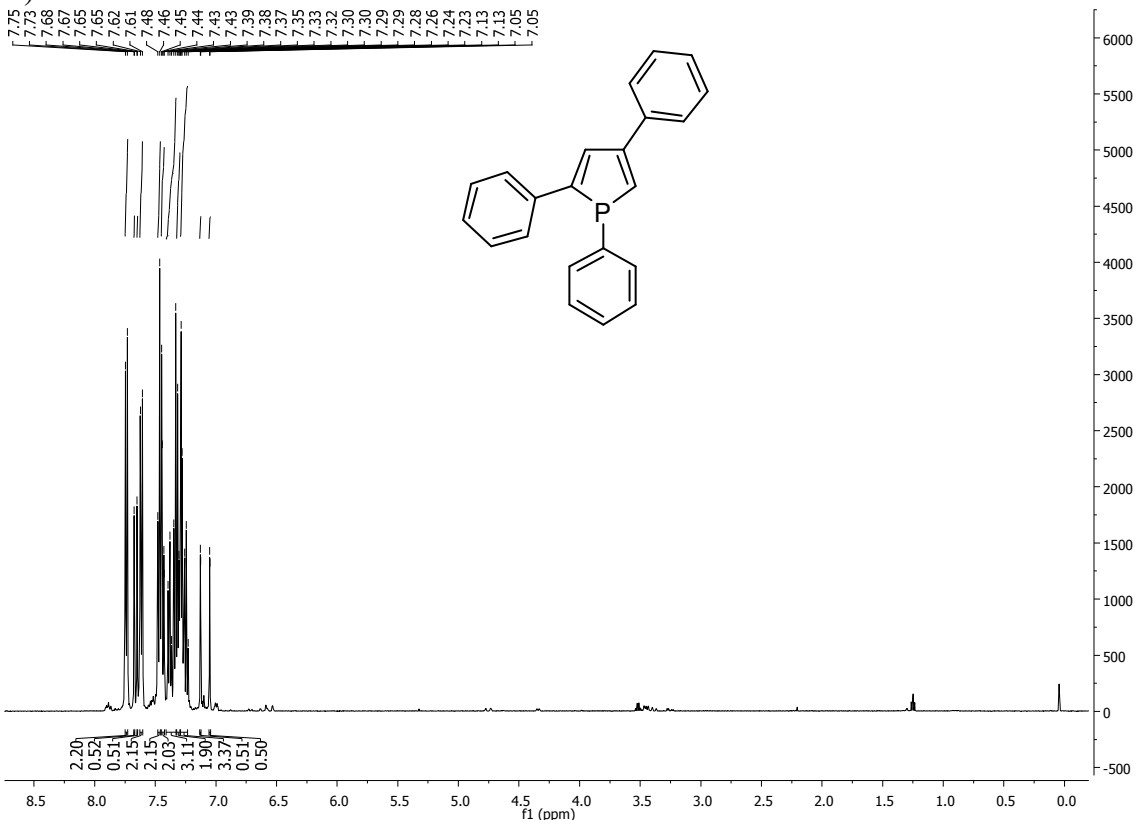
(^{1}H)



(^{13}C)



(3a)
(^{1}H)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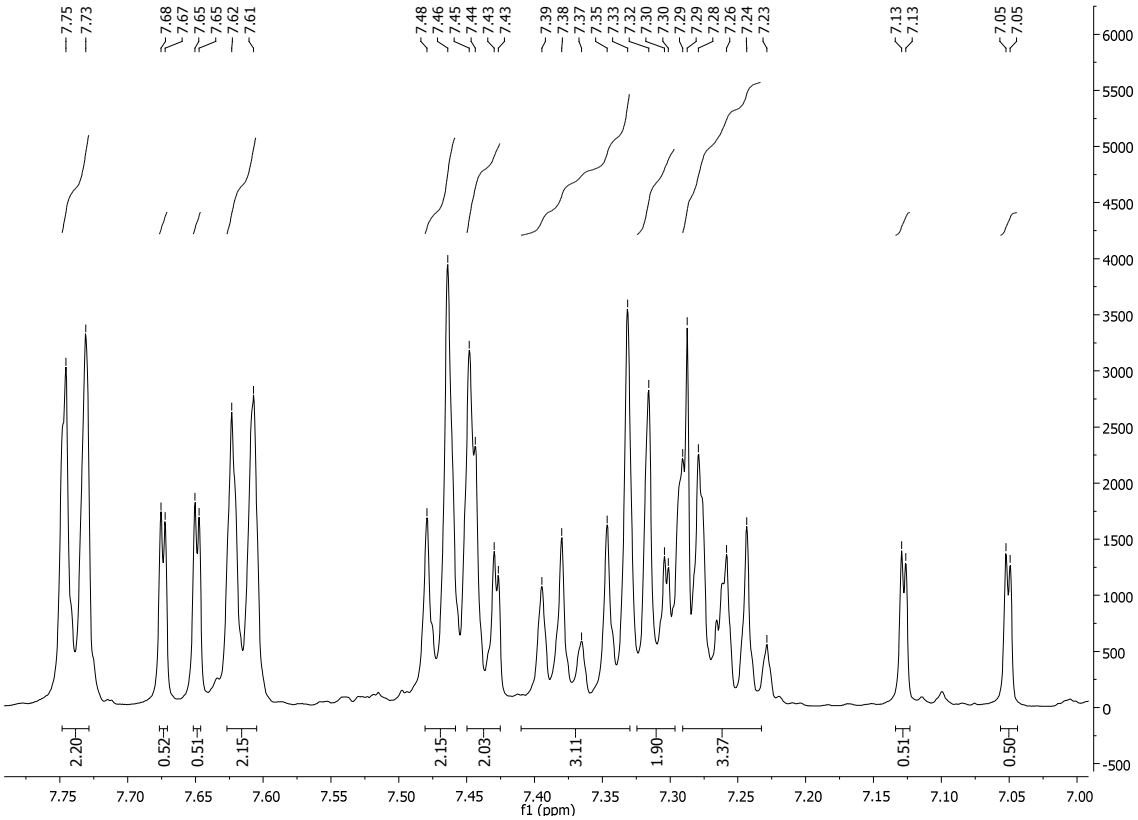
P
2.20 0.52 0.51 2.15 2.03 3.11 1.90 3.37 0.51 0.50
f1 (ppm)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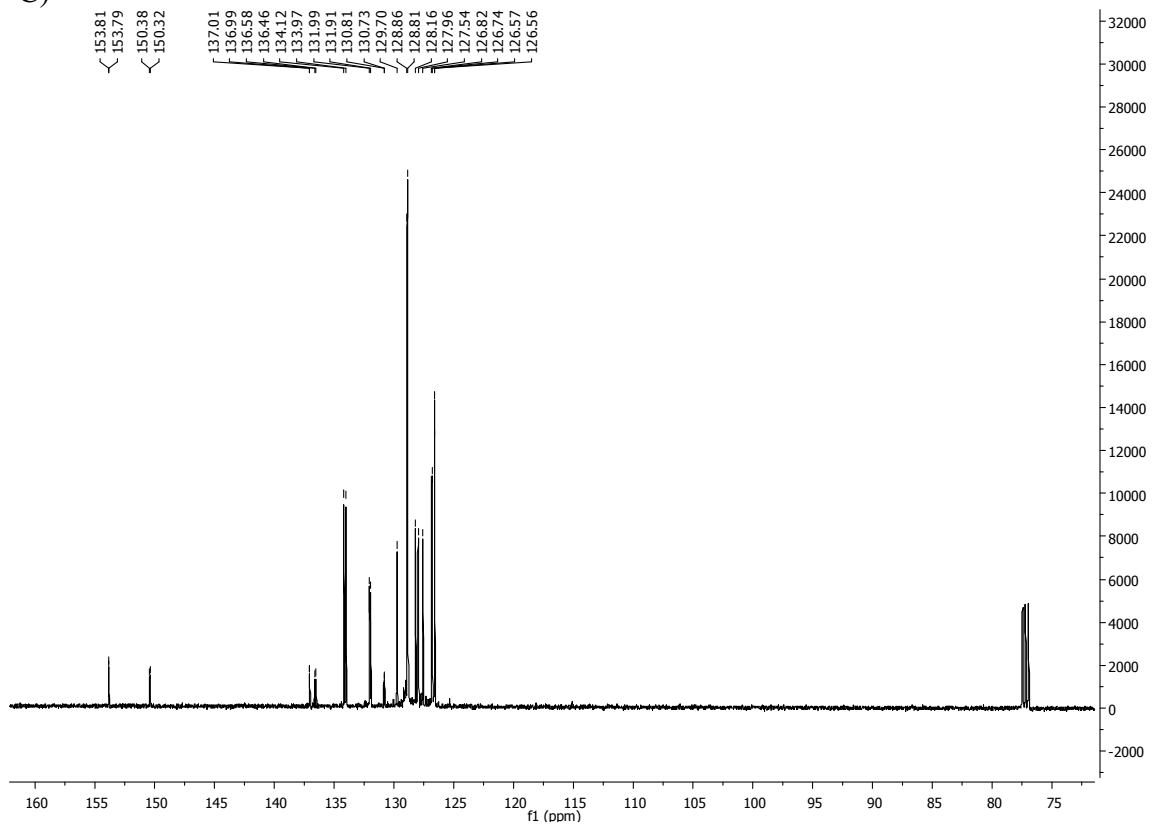
2.20 0.52 0.51 2.15 2.15 2.03 3.11 1.90 3.37 0.51 0.50
f1 (ppm)

(^{13}C)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130.81
130.73
129.70
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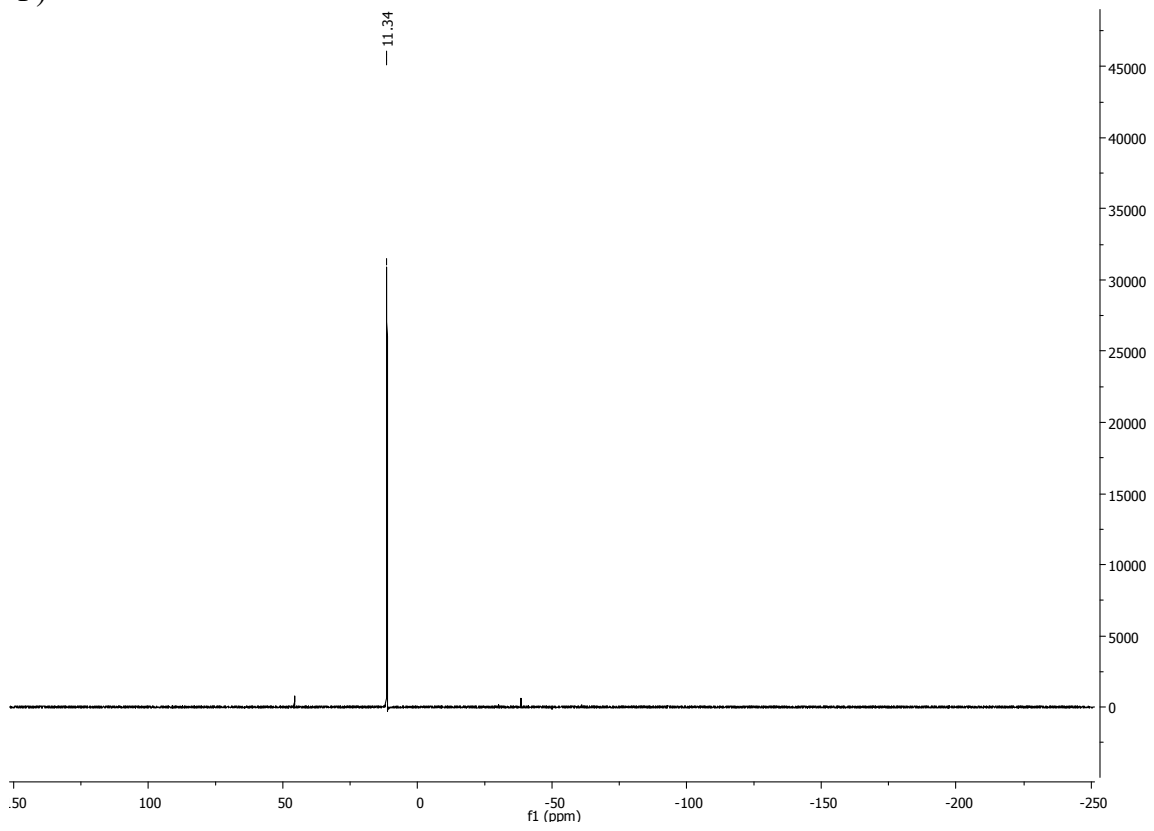
126.57
126.56
f1 (ppm)

(^{31}P)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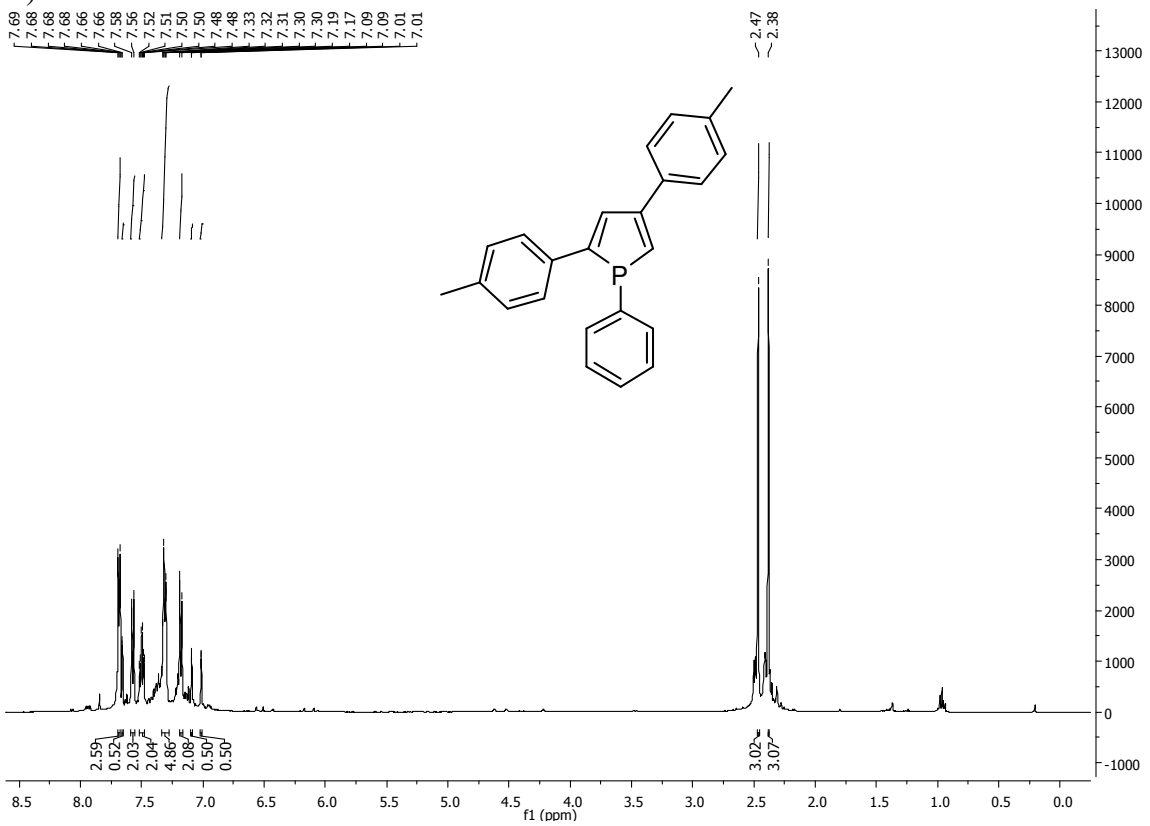
f1 (ppm)

(3b)
(^{1}H)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7.68
7.68
7.68
7.66
7.66
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7.56
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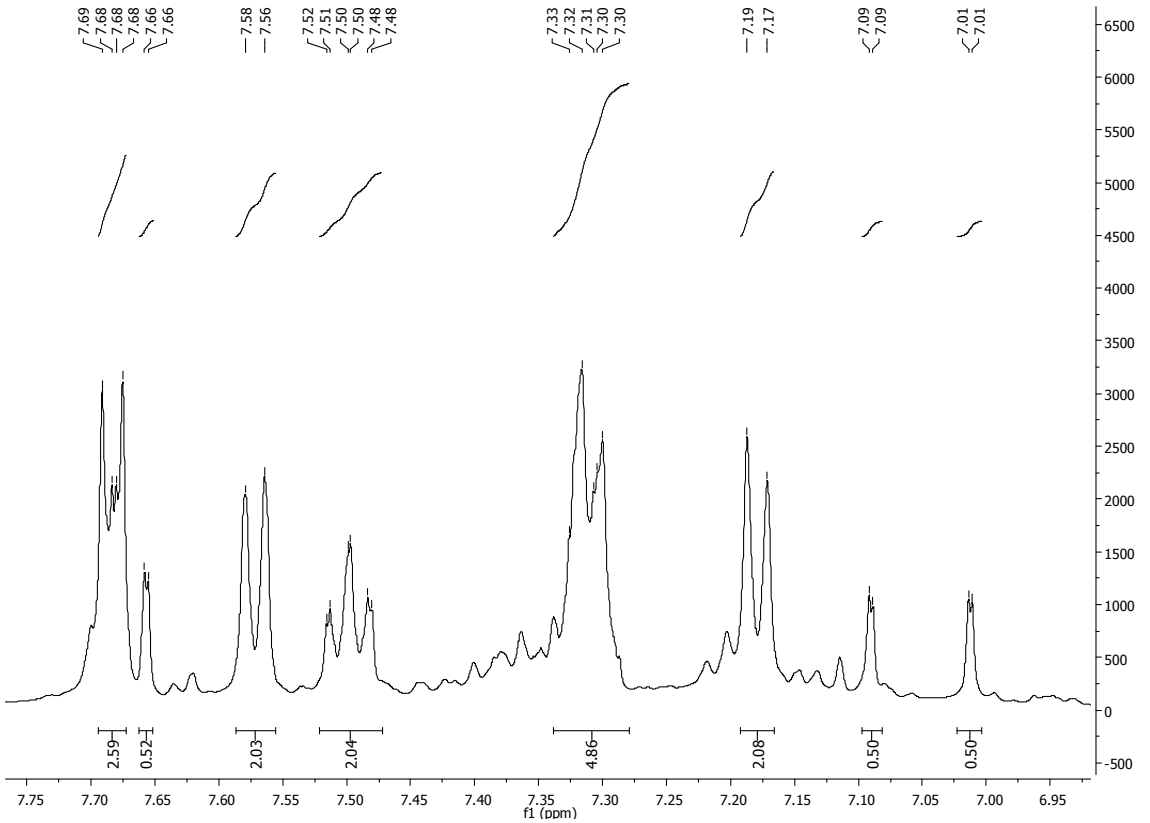
7.50
7.50
7.48
7.48
7.33
7.32
7.31
7.30
7.30
7.19
7.17
7.09
7.09
7.01
7.01
2.47
2.38
P
2.59
0.52
2.03
2.04
4.86
2.08
0.50
0.50
3.02
3.07
f1 (ppm)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7.48
7.33
7.32
7.31
7.30
7.30
7.19
7.17
7.09
7.09
7.01
7.01
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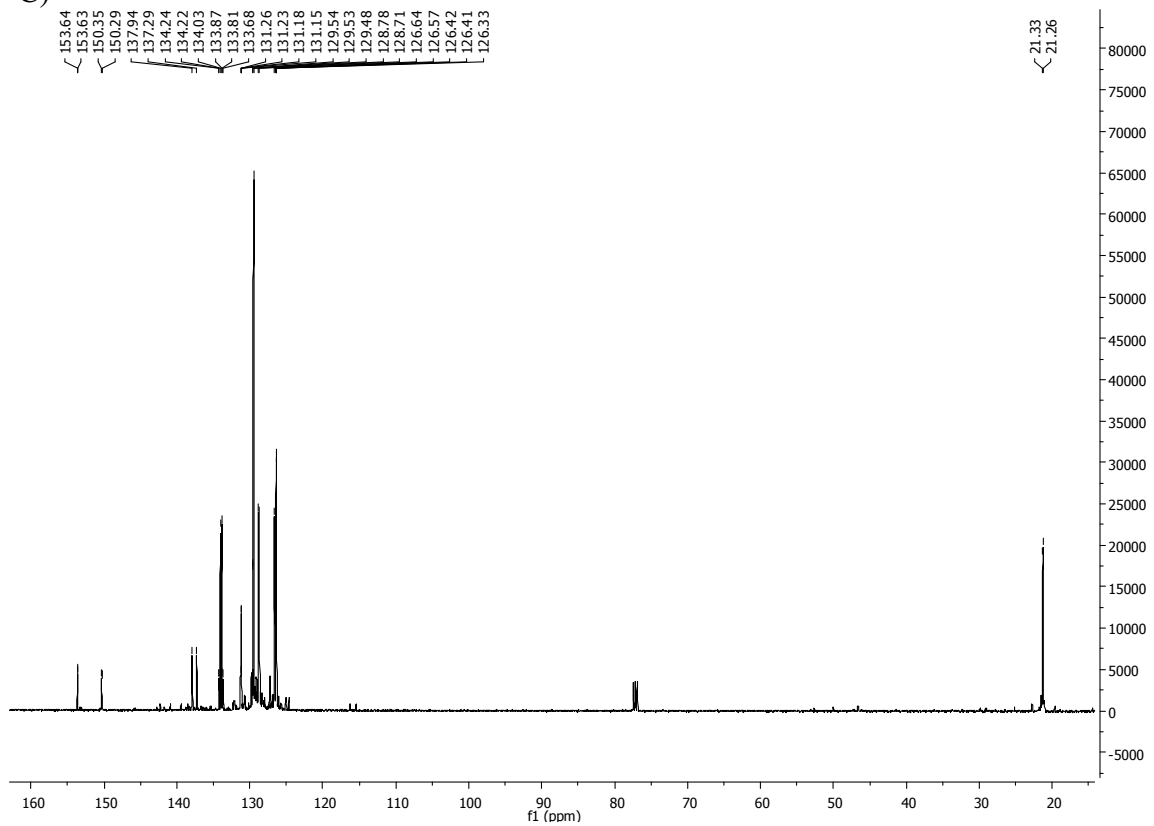
0.52
2.03
2.04
4.86
2.08
0.50
0.50
f1 (ppm)

(^{13}C)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131.26
131.23
131.18
131.15
129.54
129.53
129.48
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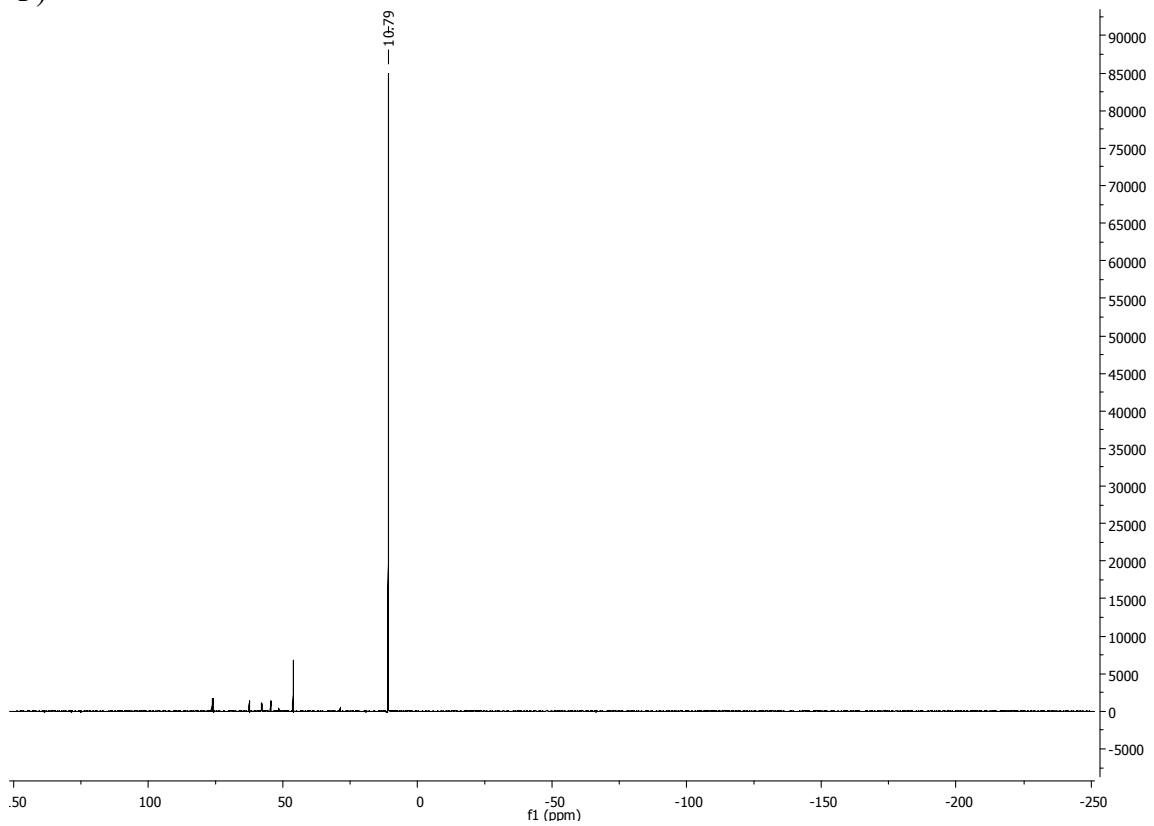
126.57
126.42
126.41
126.33
21.33
21.26
f1 (ppm)

(^{31}P)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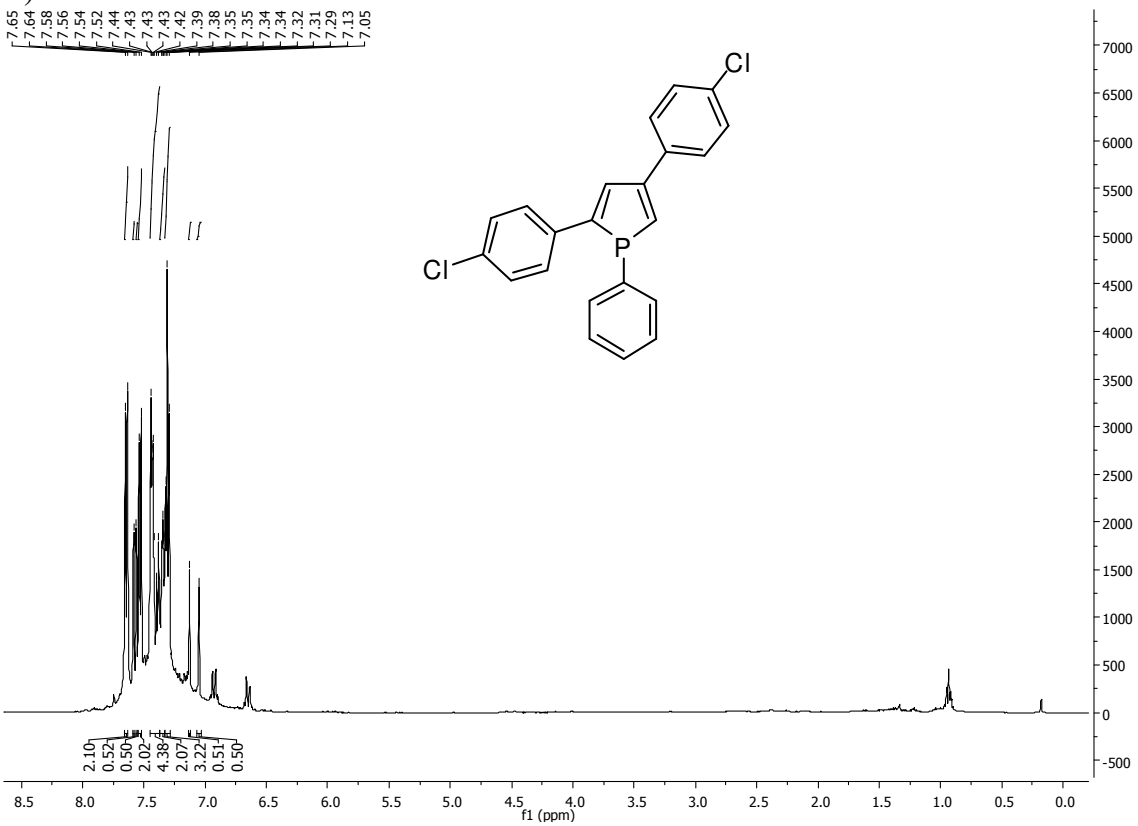
f1 (ppm)

(3c)
(^{1}H)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7.43
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7.39
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7.35
7.35
7.34
7.34
7.32
7.31
7.29
7.13
7.05
Cl
Cl
P
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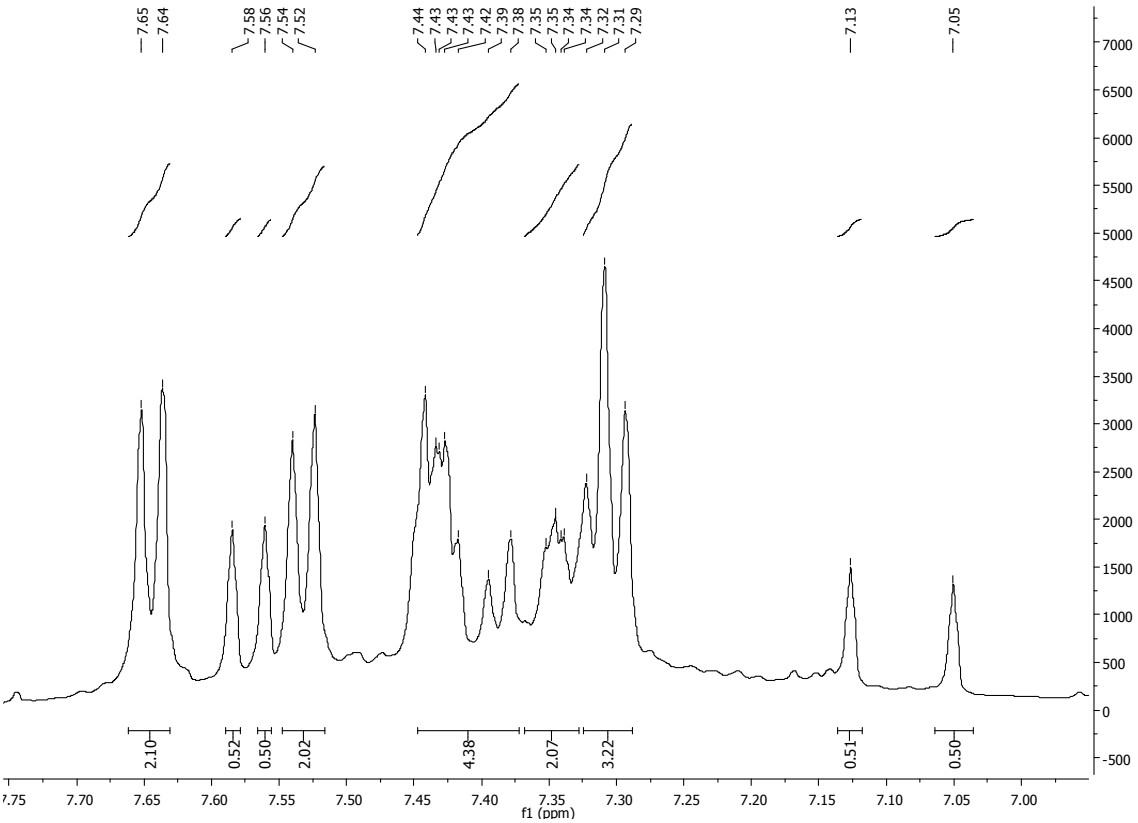
0.52
0.50
2.02
4.38
2.07
3.22
0.51
0.50
f1 (ppm)

.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7.38
7.35
7.35
7.34
7.34
7.32
7.31
7.29
7.13
7.05
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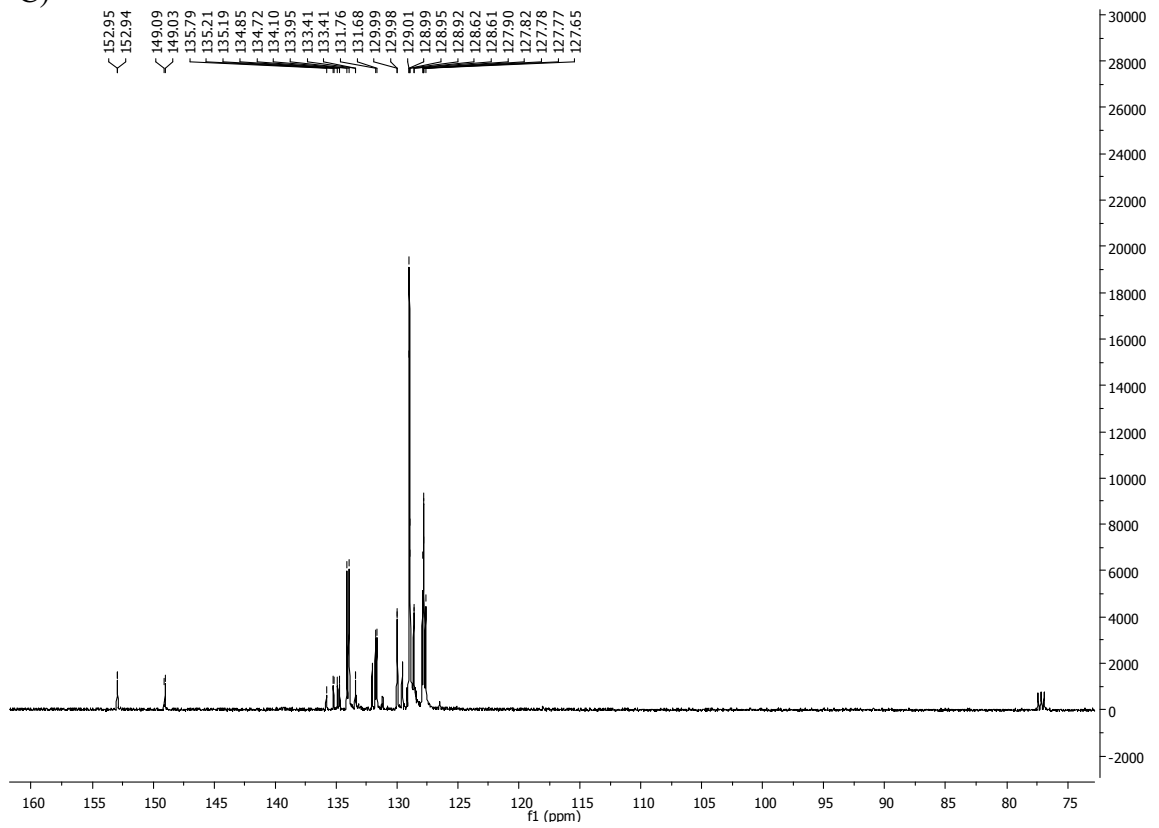
0.52
0.50
2.02
4.38
2.07
3.22
0.51
0.50
f1 (ppm)

(^{13}C)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133.41
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131.76
131.68
129.99
129.98
129.01
128.99
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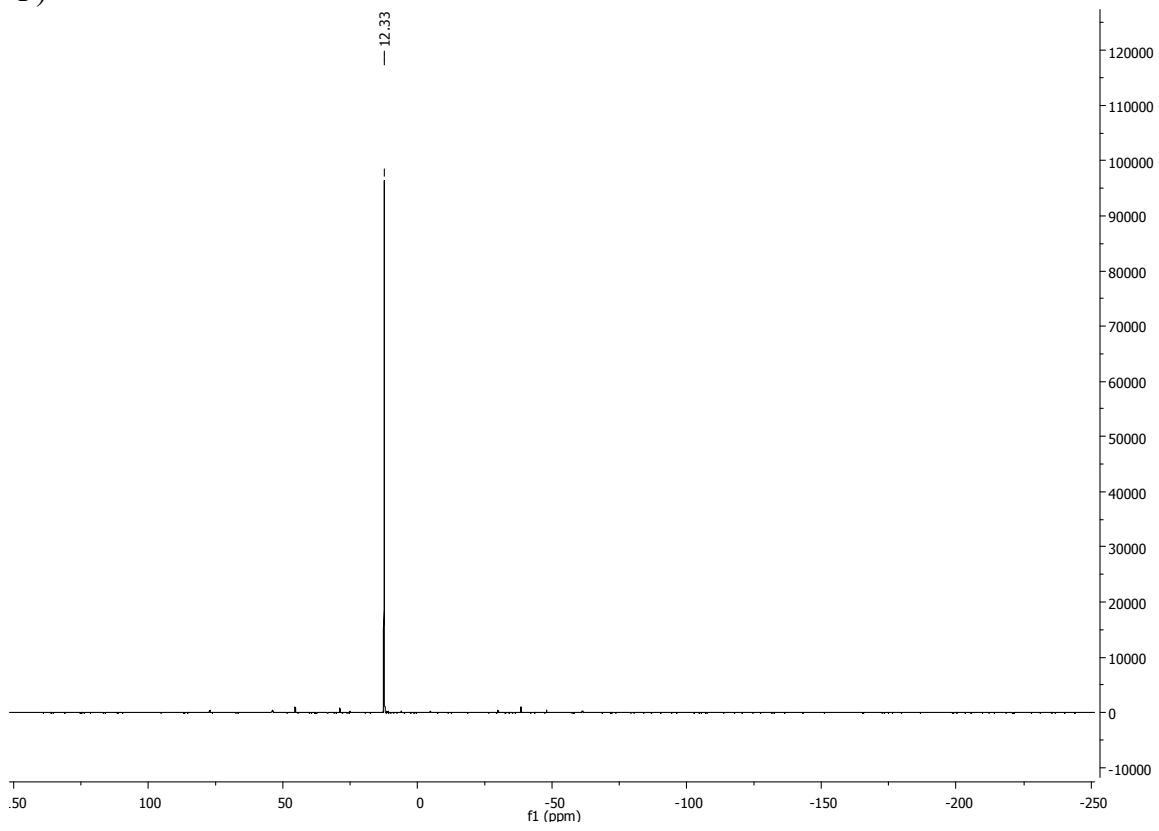
127.77
127.65
f1 (ppm)

(^{31}P)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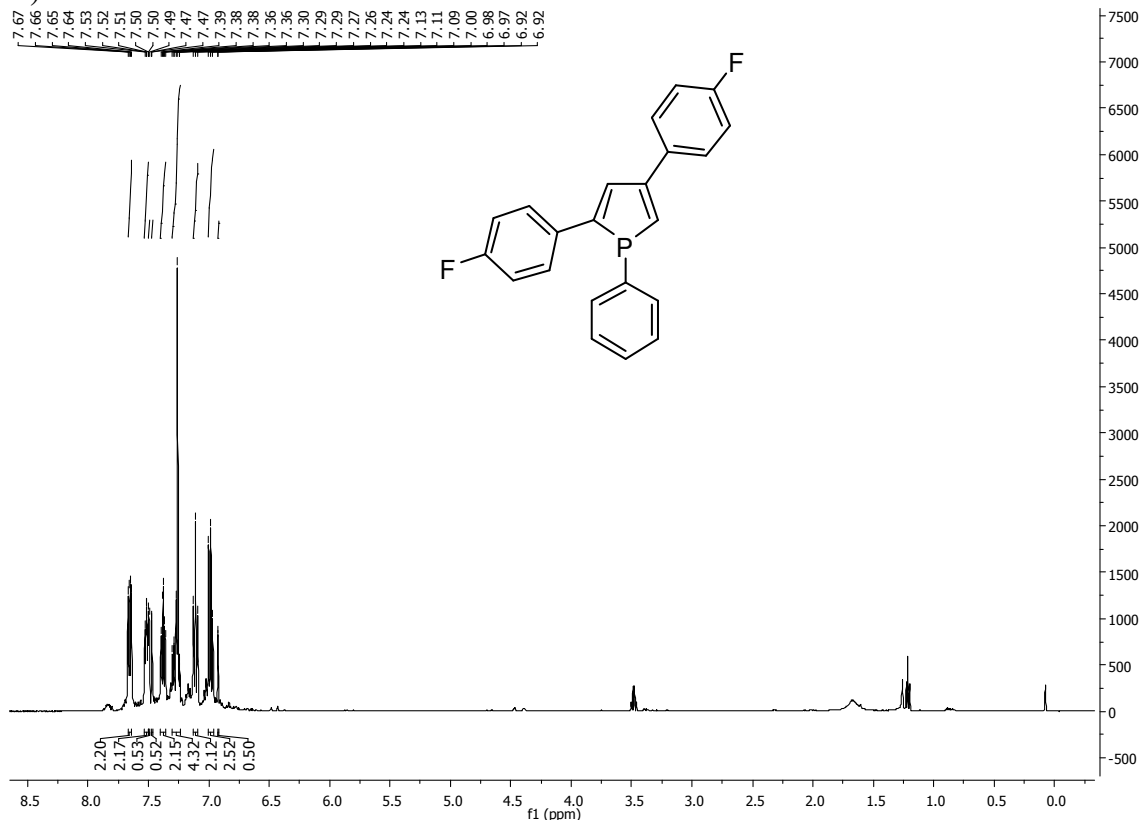
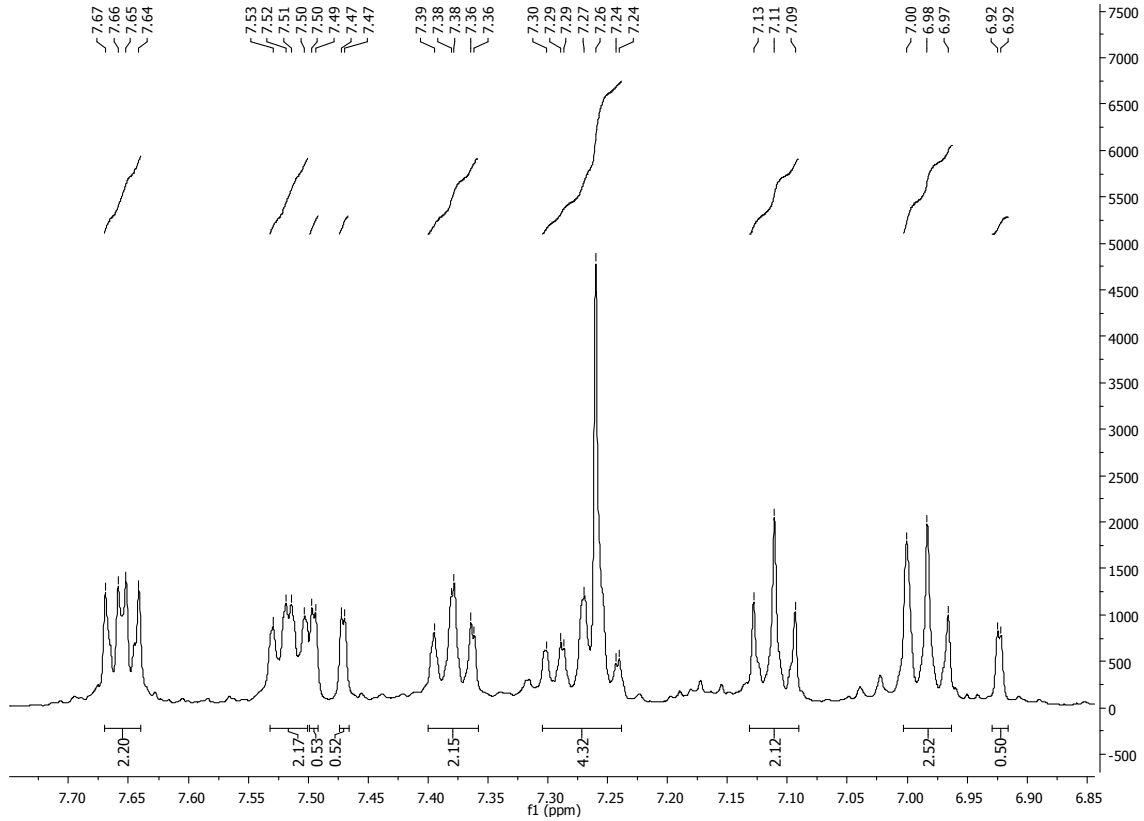
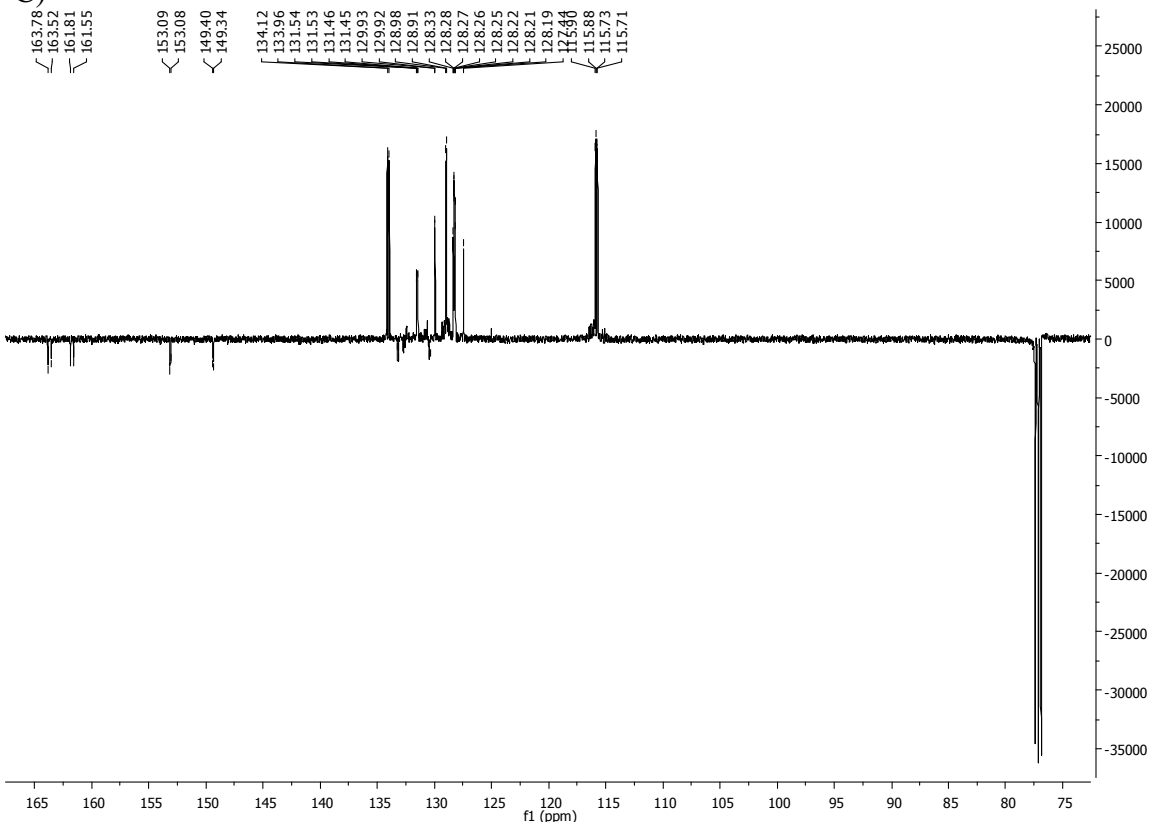
f1 (ppm)

(3d)
(^{1}H)





(^{13}C)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131.46
131.45
129.93
129.92
128.98
128.91
128.33
128.28
128.27
128.26
128.25
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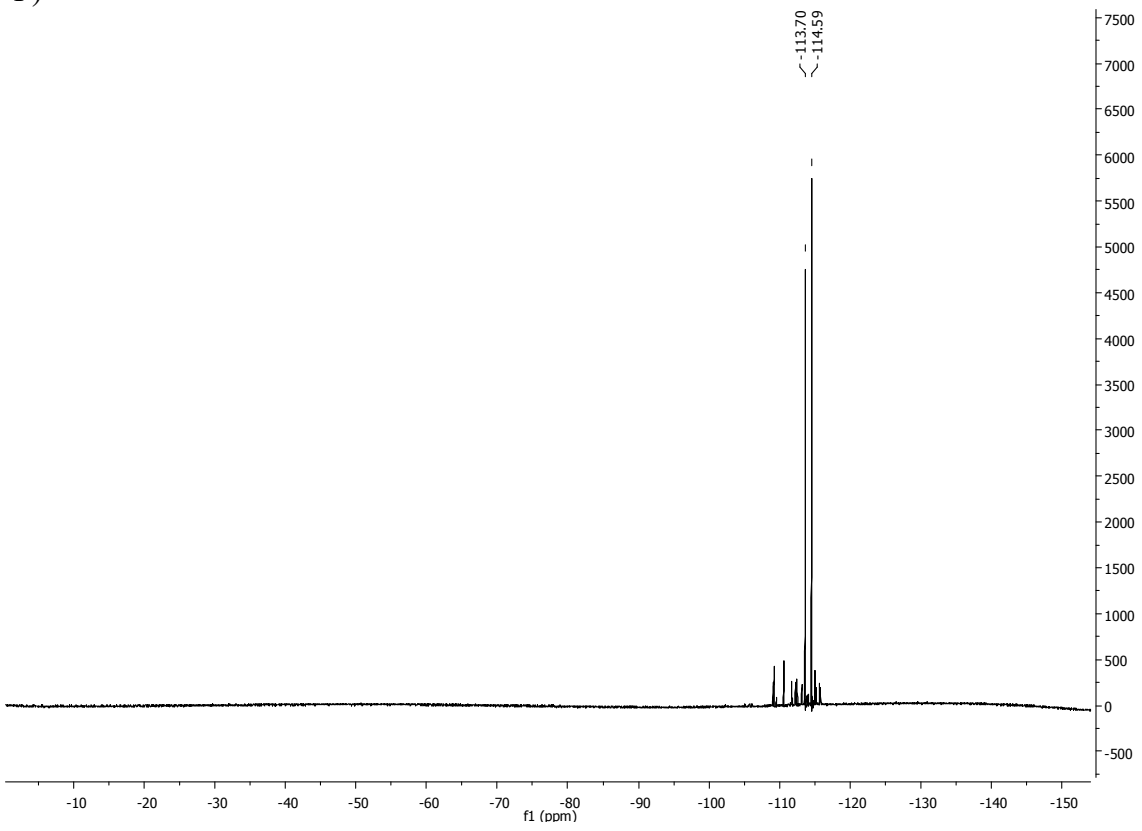
128.21
128.19
127.44
127.40
115.88
115.73
115.71
f1 (ppm)

(^{19}F)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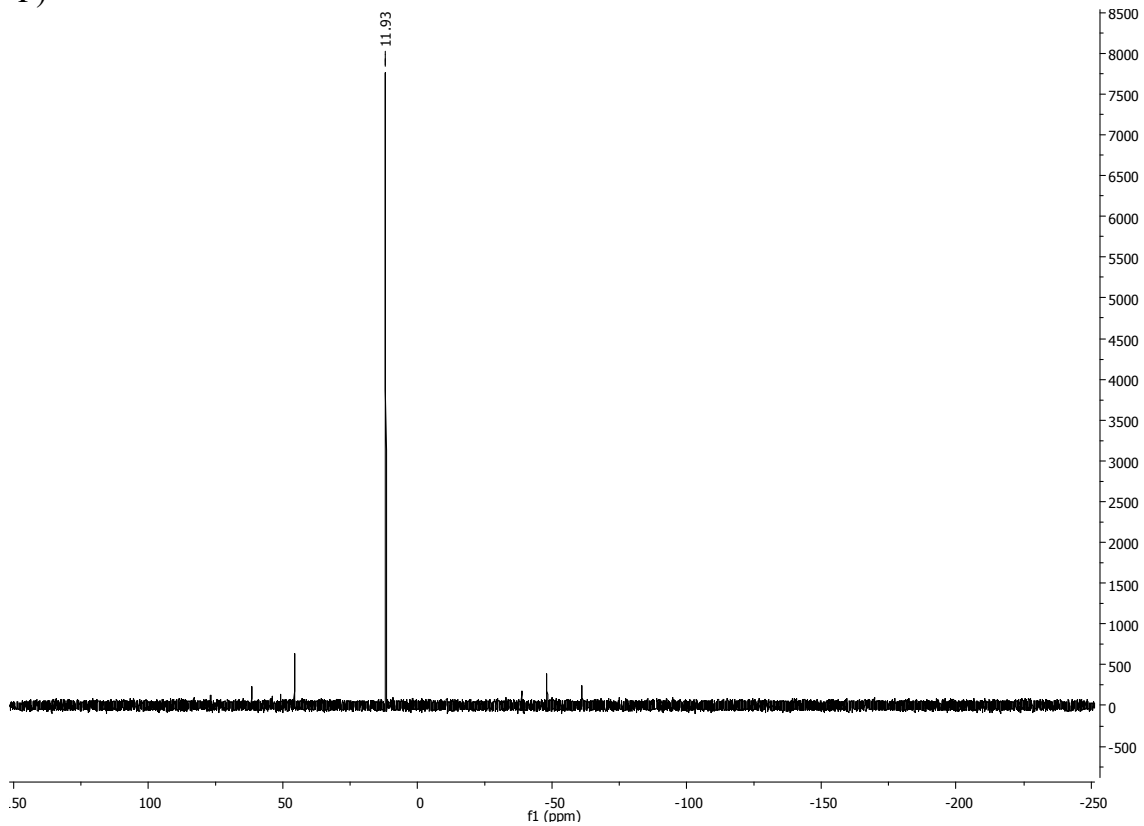
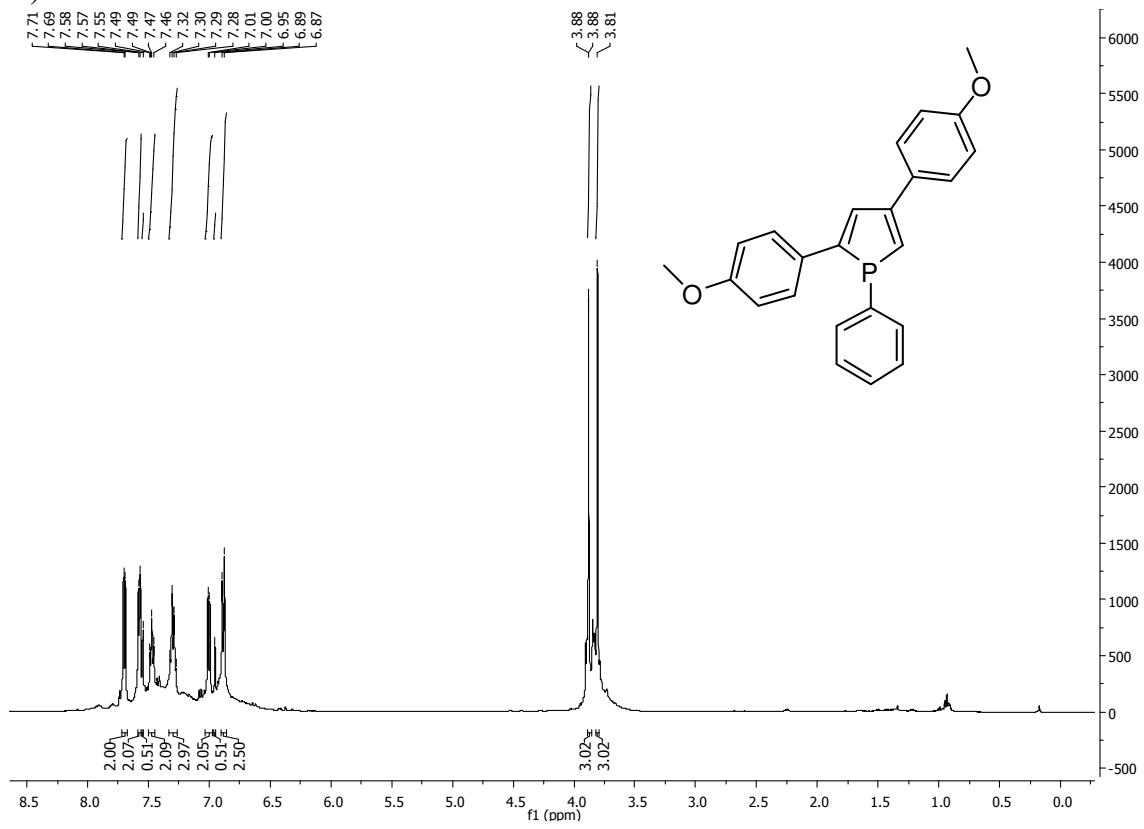
-114.59
f1 (ppm)

(^{31}P)


11.93
f1 (ppm)

(3e)
(^{1}H)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7.47
7.46
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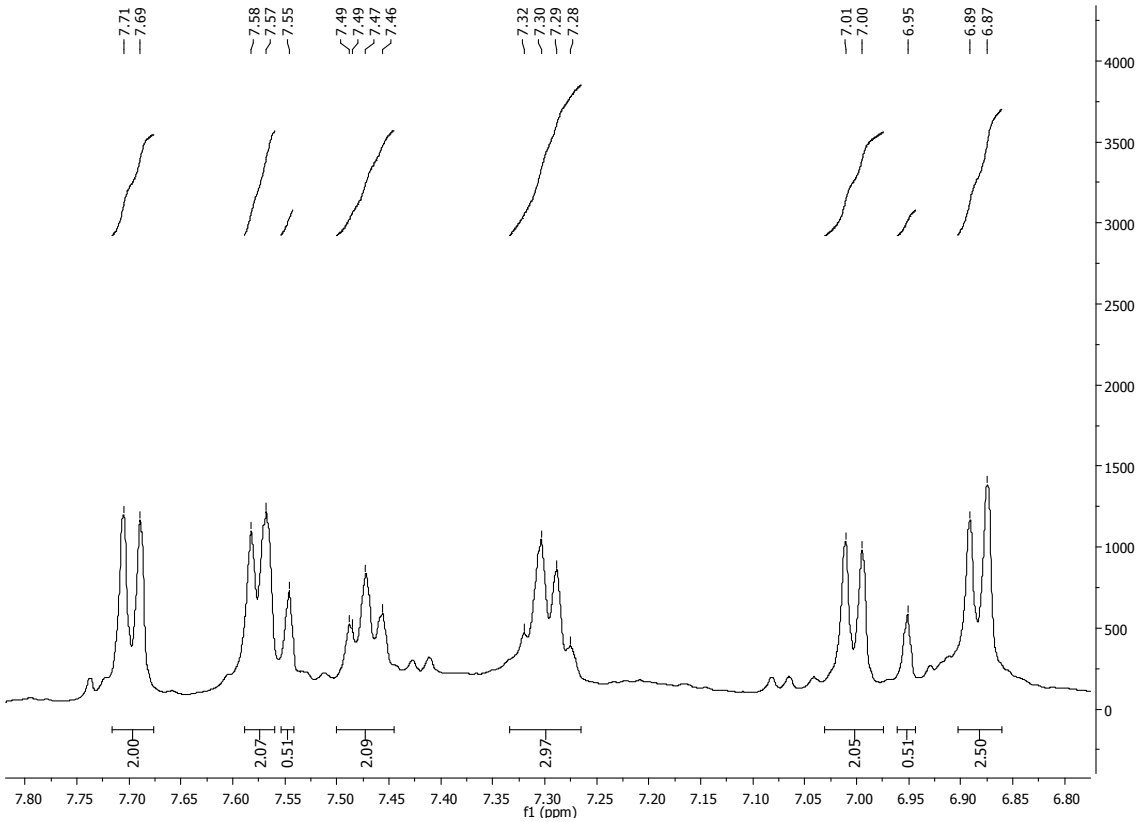
7.29
7.28
7.01
7.00
6.95
6.89
6.87
3.88
3.88
3.81
O
O
P
2.00
2.07
0.51
2.09
2.97
2.05
0.51
2.50
3.02
3.02
f1 (ppm)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7.49
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7.46
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7.30
7.29
7.28
7.01
7.00
6.95
6.89
6.87
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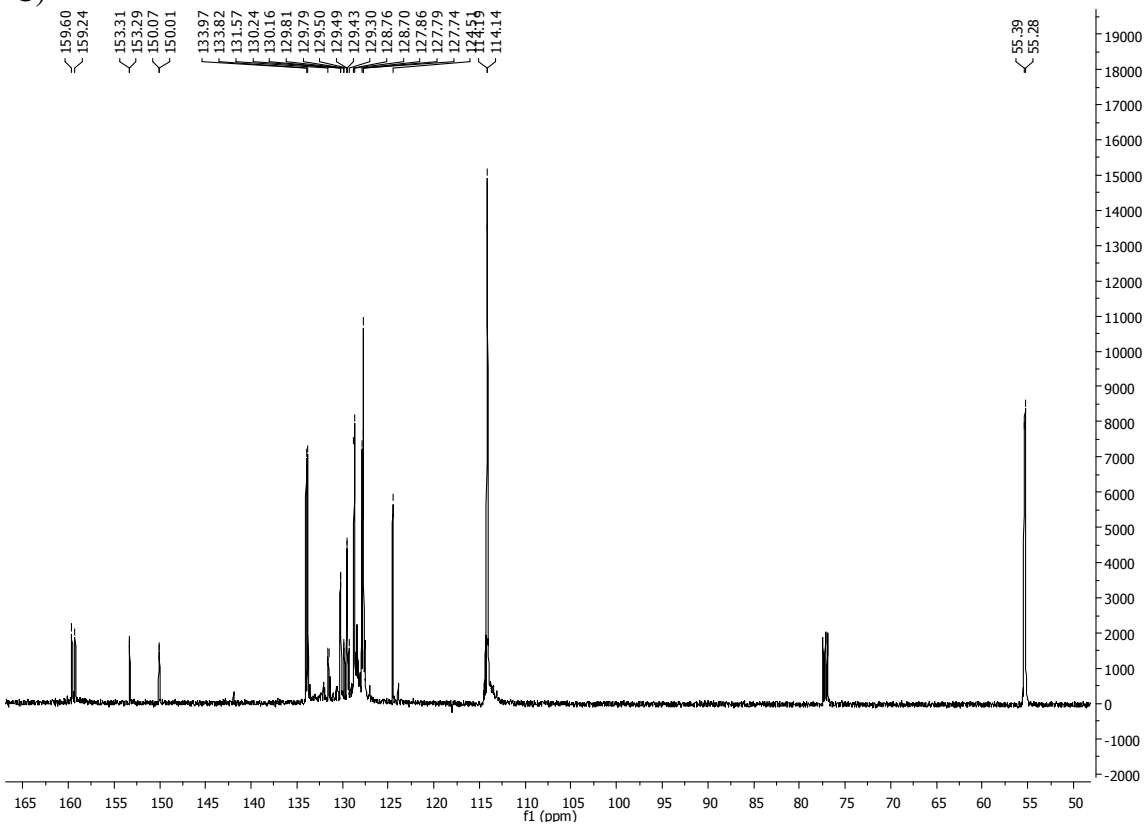
2.07
0.51
2.09
2.97
2.05
0.51
2.50
f1 (ppm)

(^{13}C)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129.79
129.50
129.49
129.43
129.30
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127.86
127.79
127.74
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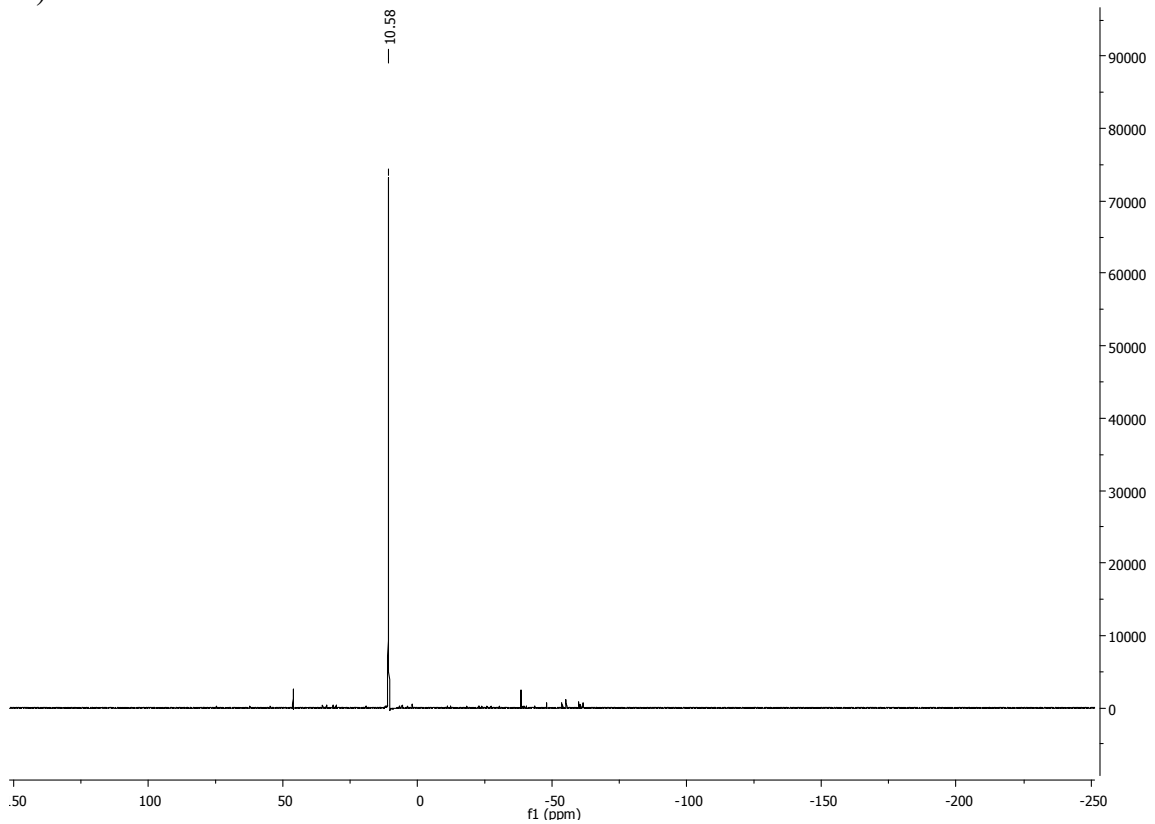
114.14
55.39
55.28
f1 (ppm)

(^{31}P)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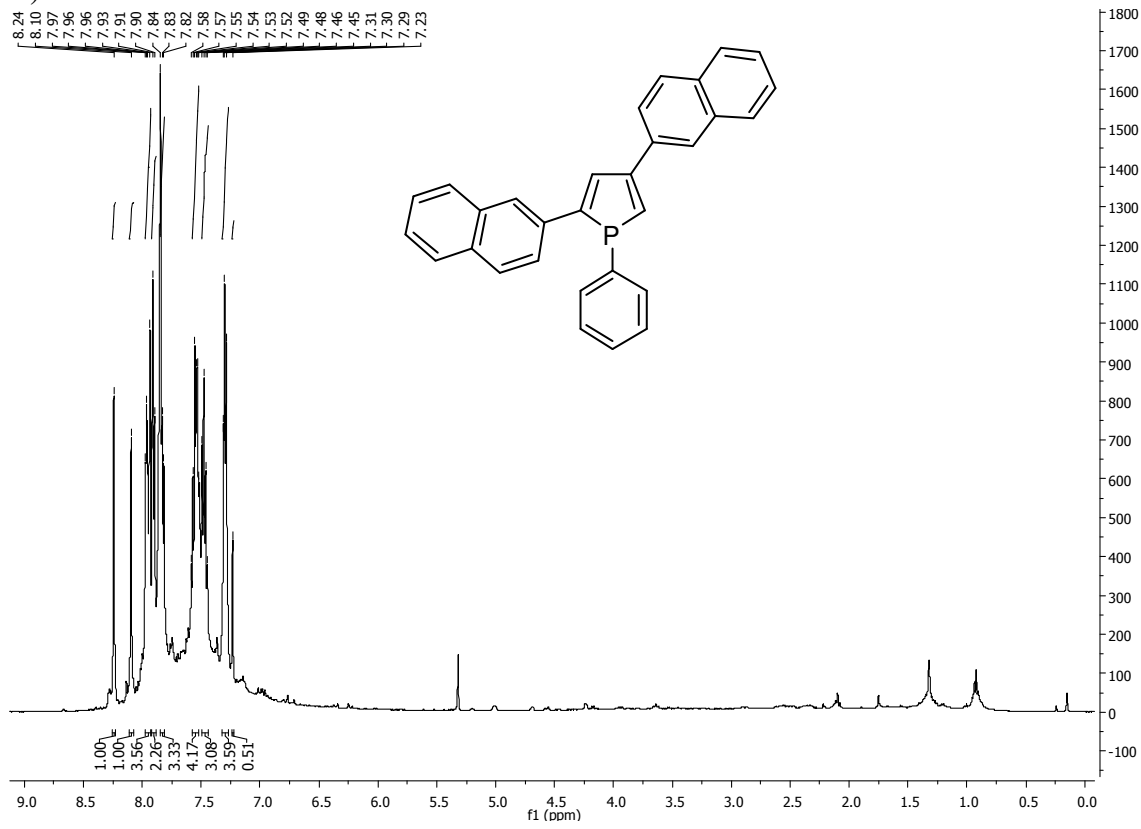
(3f)
(^{1}H)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7.54
7.53
7.52
7.49
7.48
7.46
7.45
7.31
7.30
7.29
7.23
P
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1.00
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2.26
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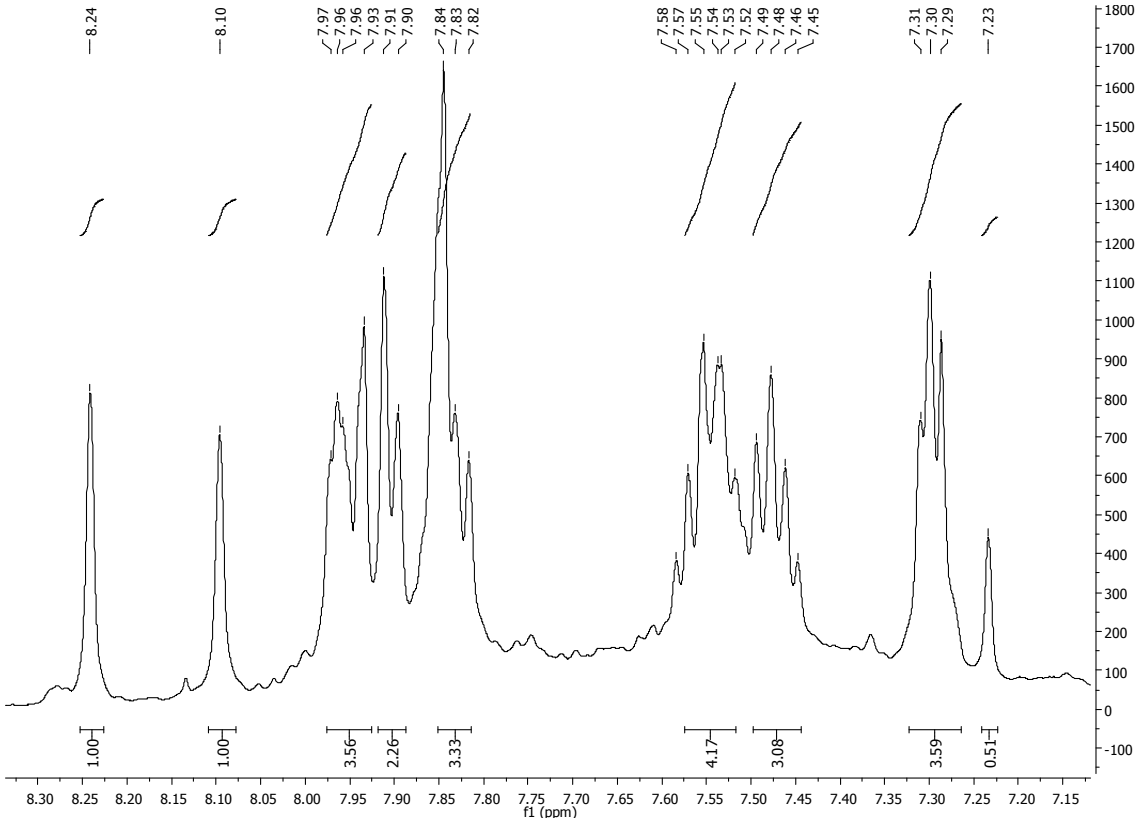
4.17
3.08
3.59
0.51
f1 (ppm)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7.57
7.55
7.54
7.53
7.52
7.49
7.48
7.46
7.45
7.31
7.30
7.29
7.23
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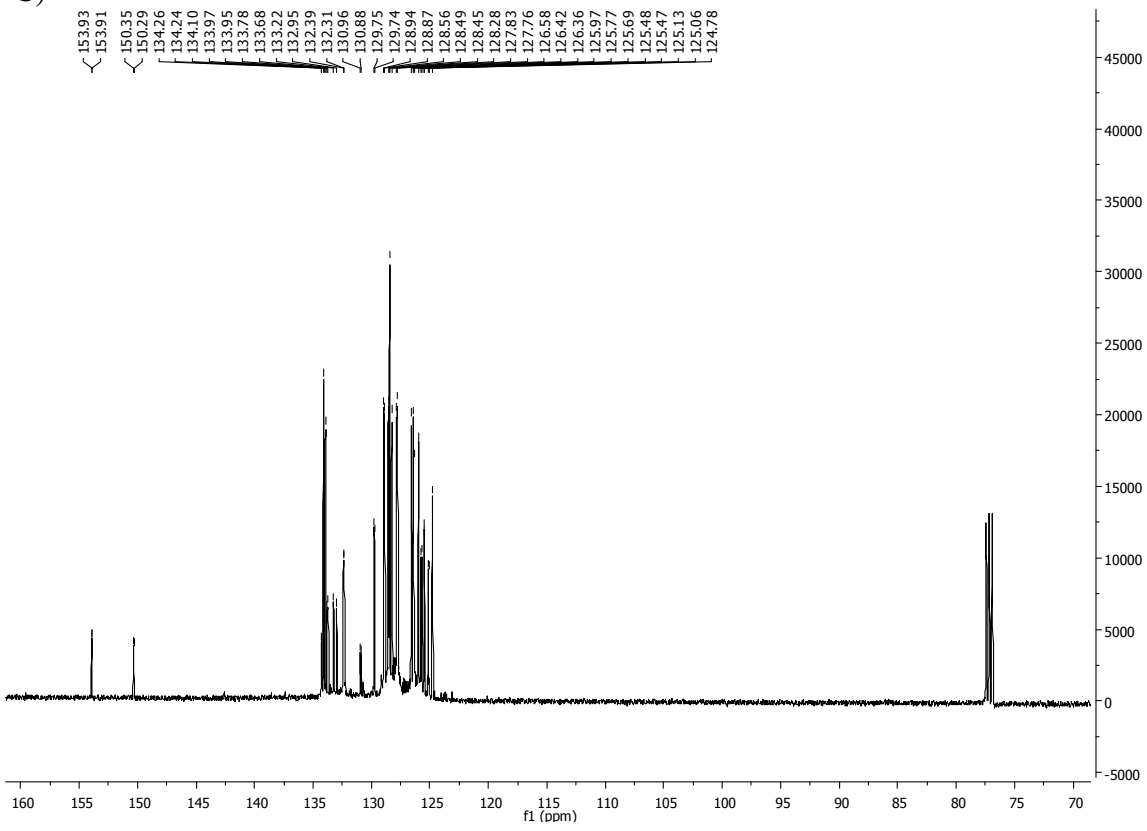
1.00
3.56
2.26
3.33
4.17
3.08
3.59
0.51
f1 (ppm)

(^{13}C)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128.28
127.83
127.76
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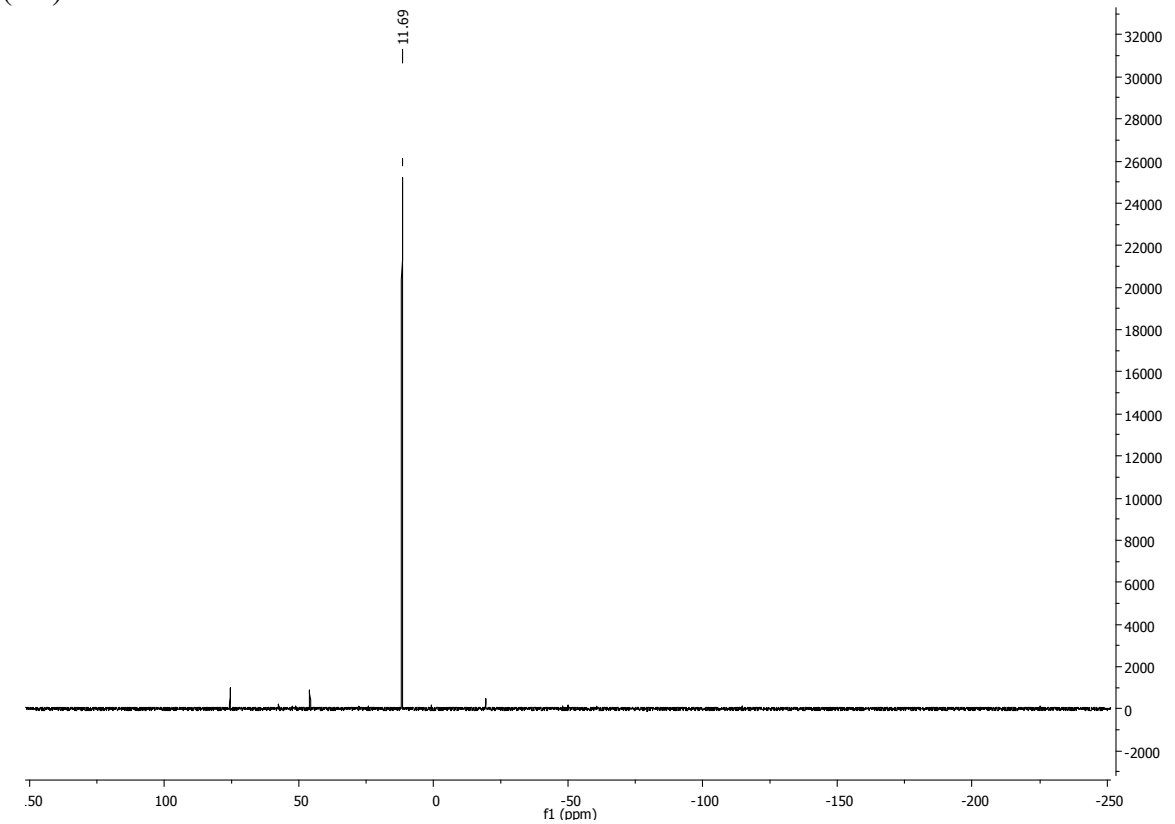
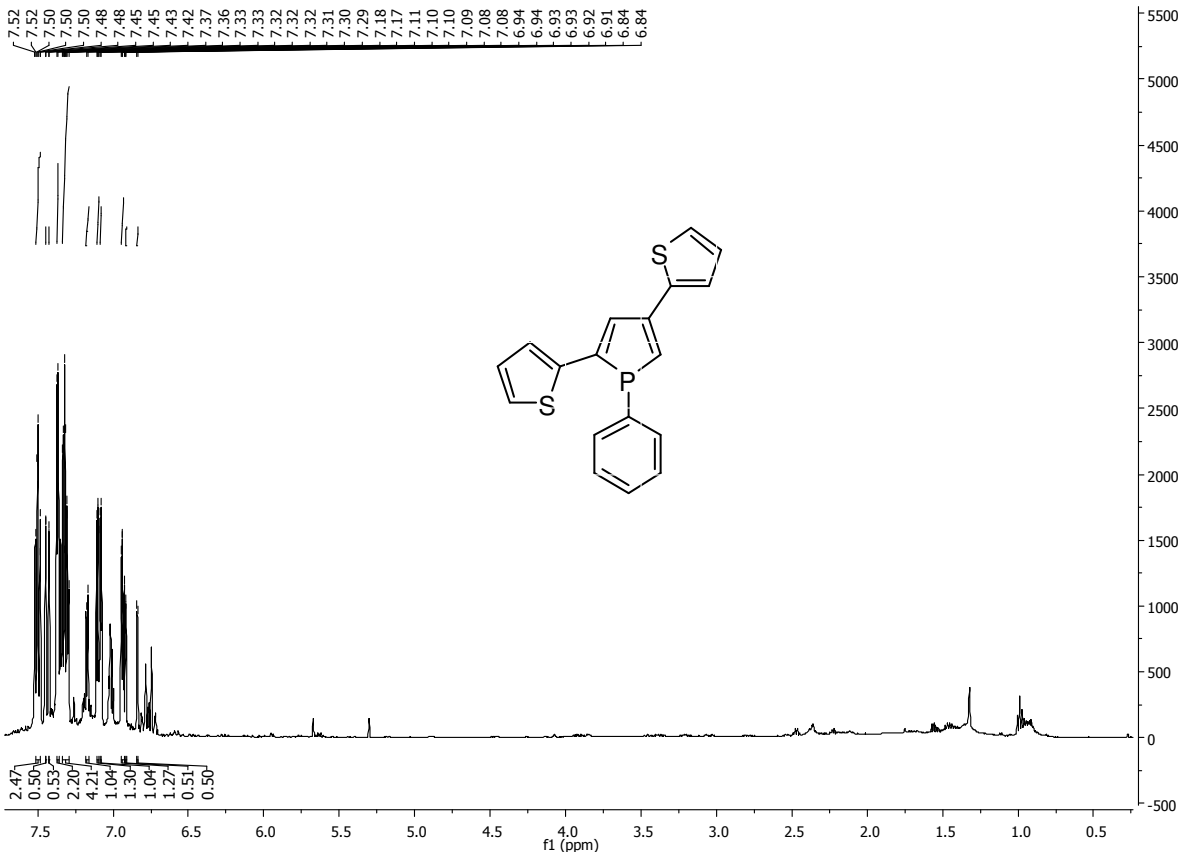
125.06
124.78
f1 (ppm)

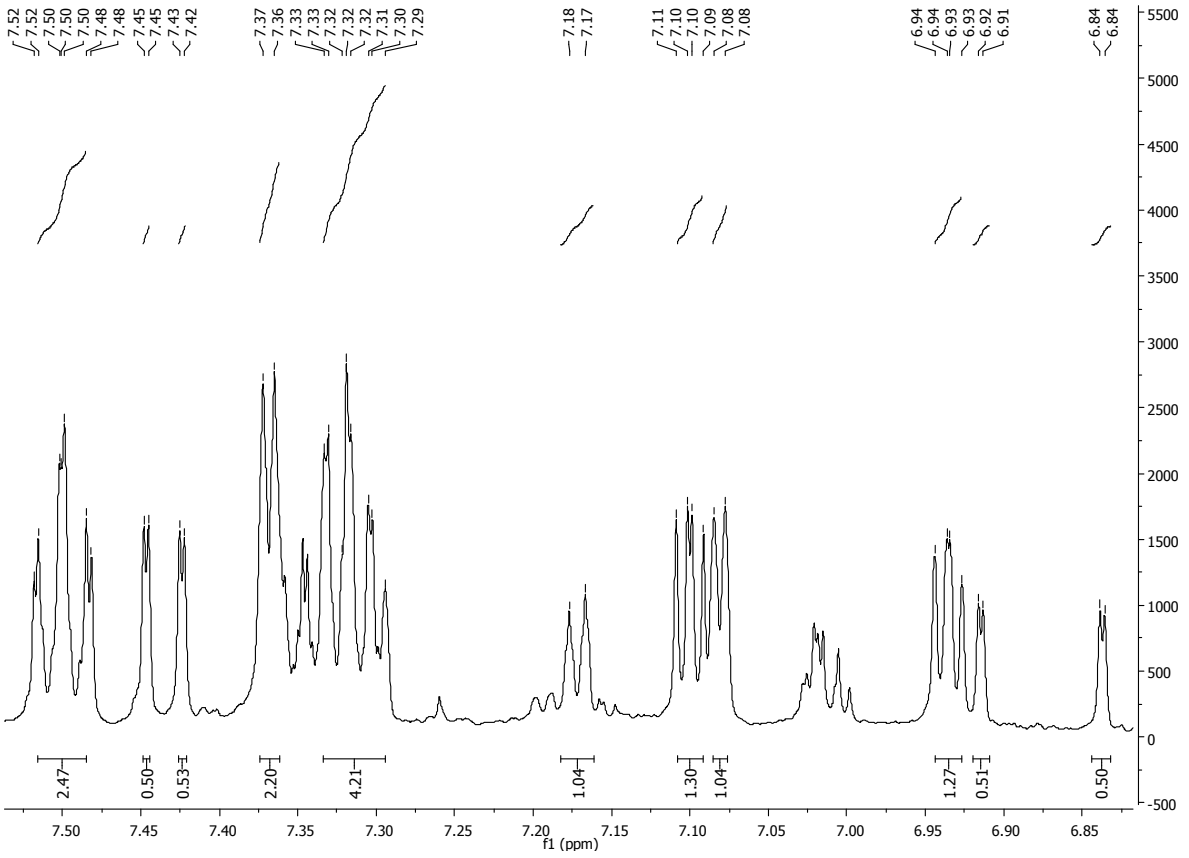
(^{31}P)



(3g)

(^{1}H)

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7.08
6.94
6.94
6.93
6.93
6.92
6.91
6.84
6.84
2.47
0.50
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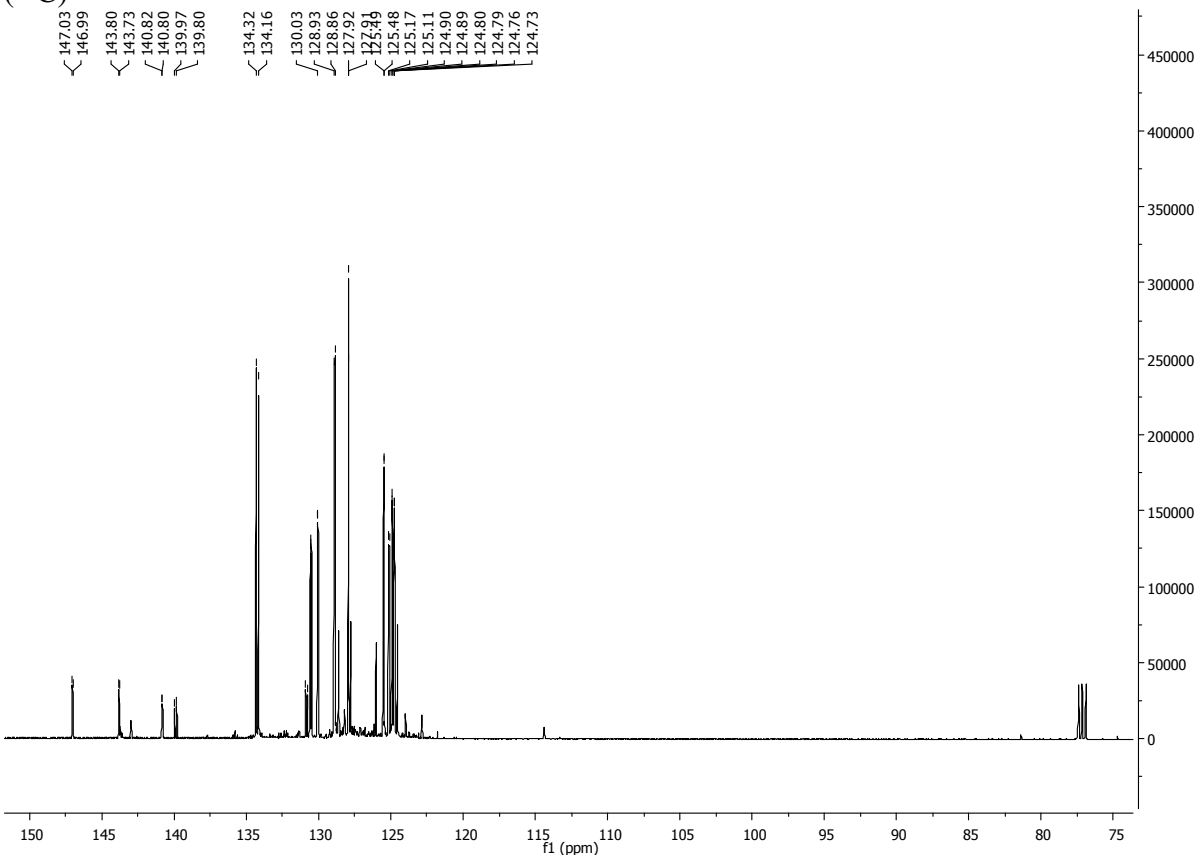
4.21
1.04
1.30
1.04
1.27
0.51
0.50
f1 (ppm)

(^{13}C)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140.82
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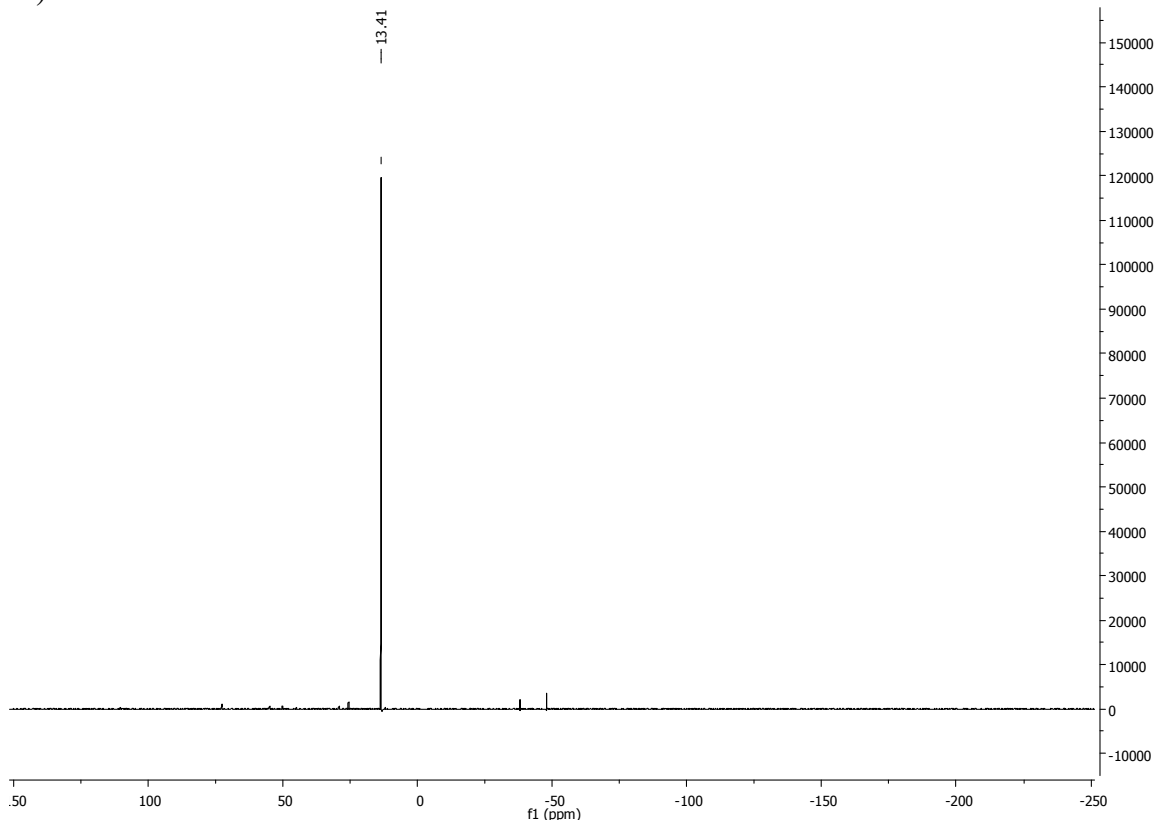
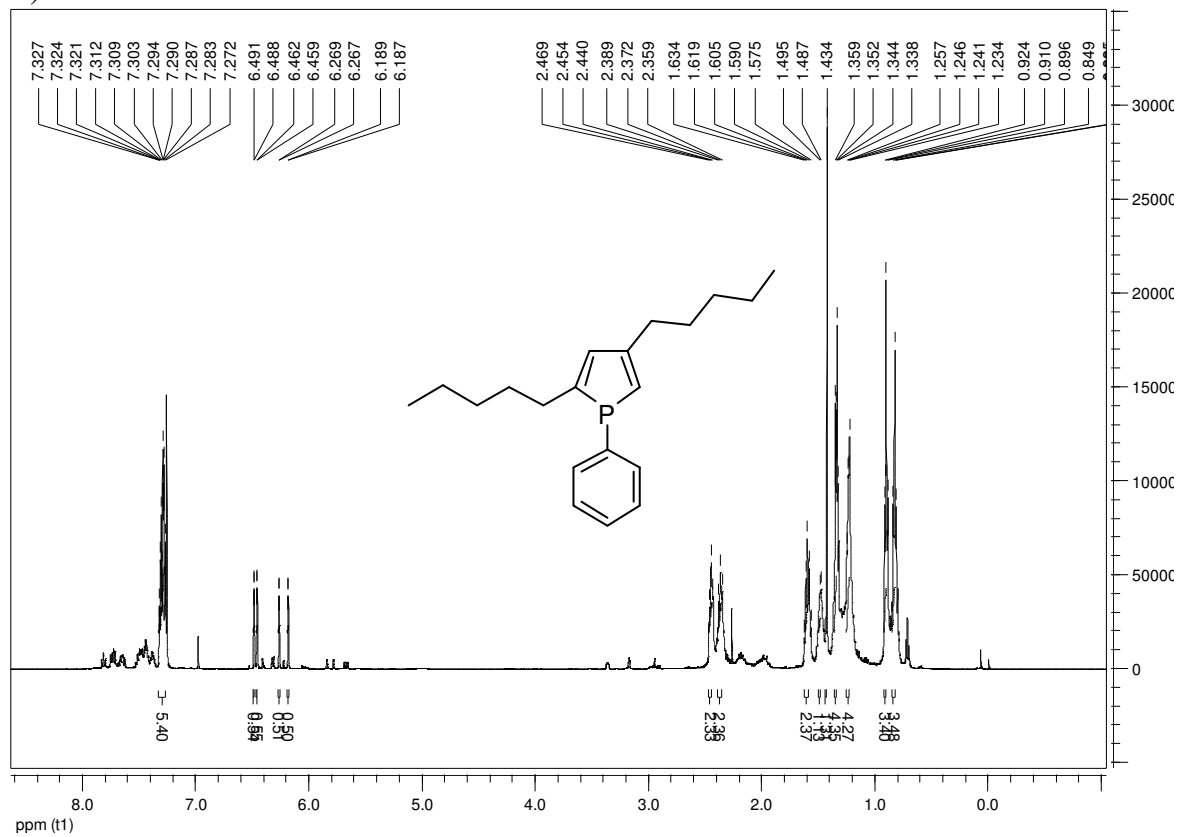
127.92
125.48
125.17
125.11
124.90
124.89
124.80
124.79
124.76
124.73
f1 (ppm)

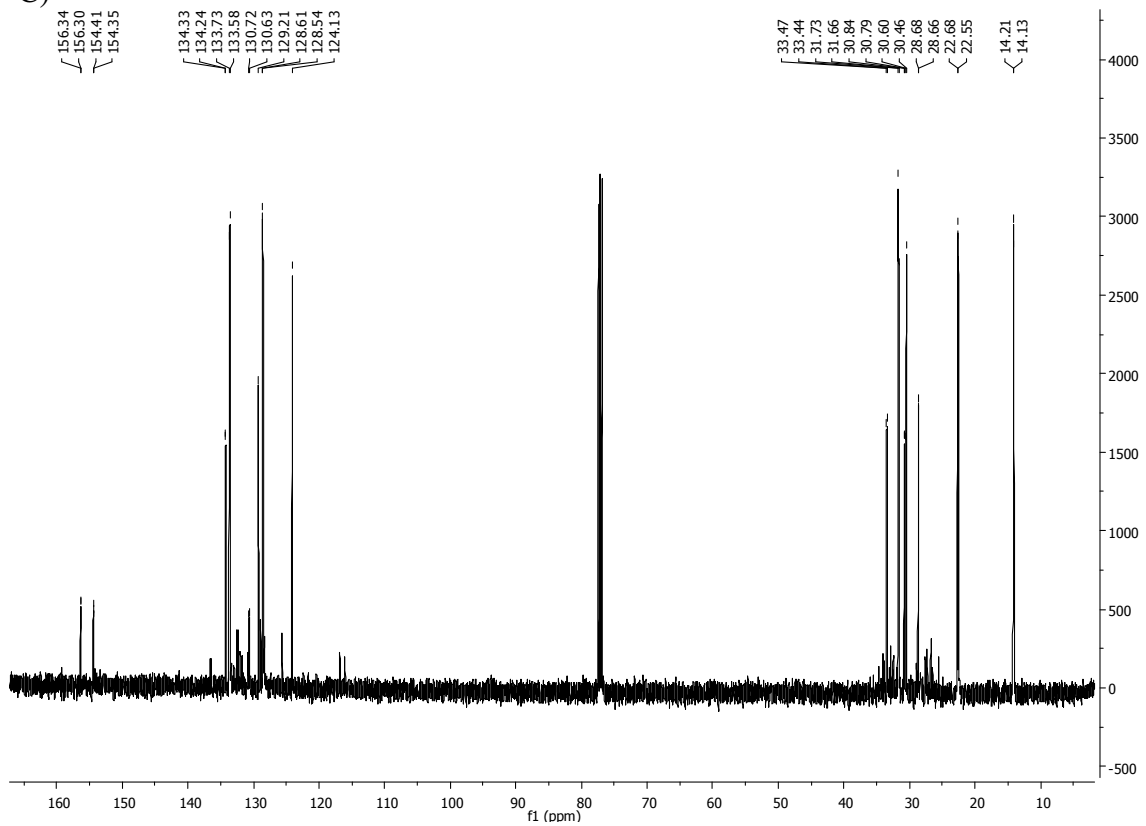
(^{31}P)


13.41
f1 (ppm)

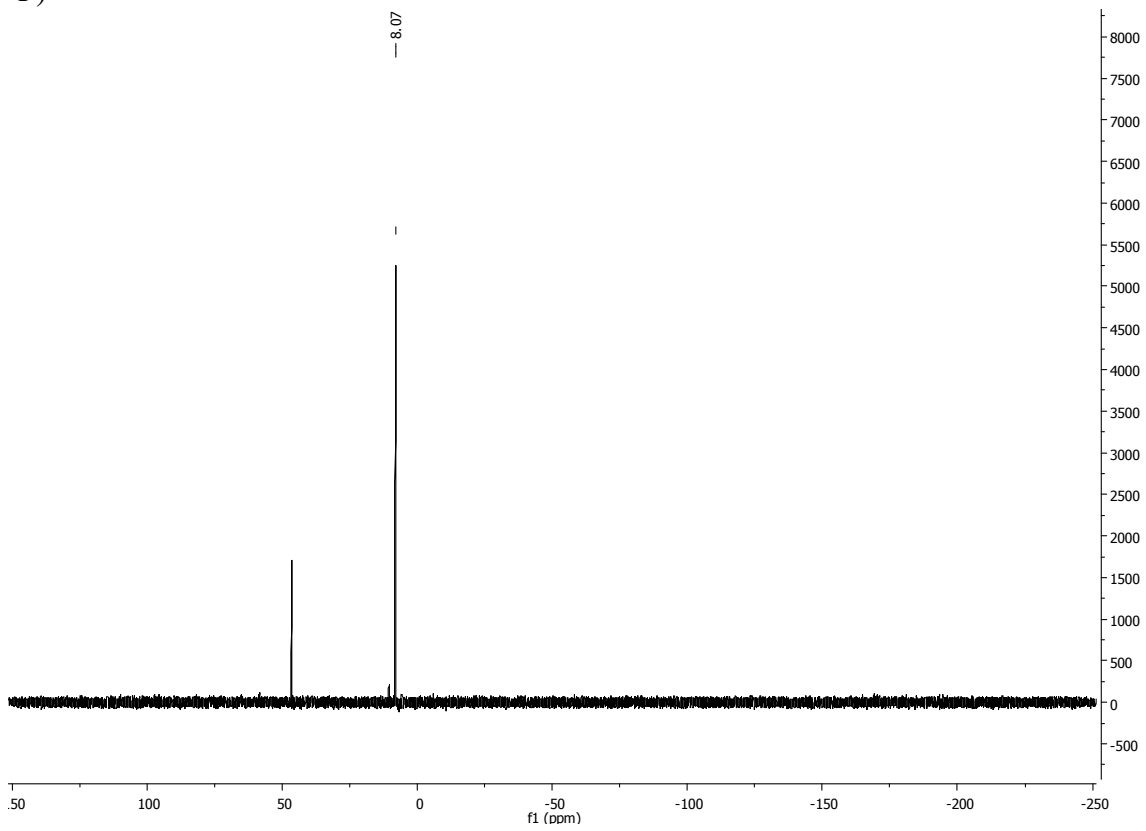
(3h)
(^{1}H)


7.327
7.324
7.321
7.312
7.309
7.303
7.294
7.290
7.287
7.283
7.272
6.491
6.488
6.462
6.459
6.269
6.267
6.189
6.187
2.469
2.454
2.440
2.389
2.372
2.359
1.634
1.619
1.605
1.590
1.575
1.495
1.487
1.434
1.359
1.352
1.344
1.338
1.257
1.246
1.241
1.234
0.924
0.910
0.896
0.849
P
ppm (t1)

(^{13}C)

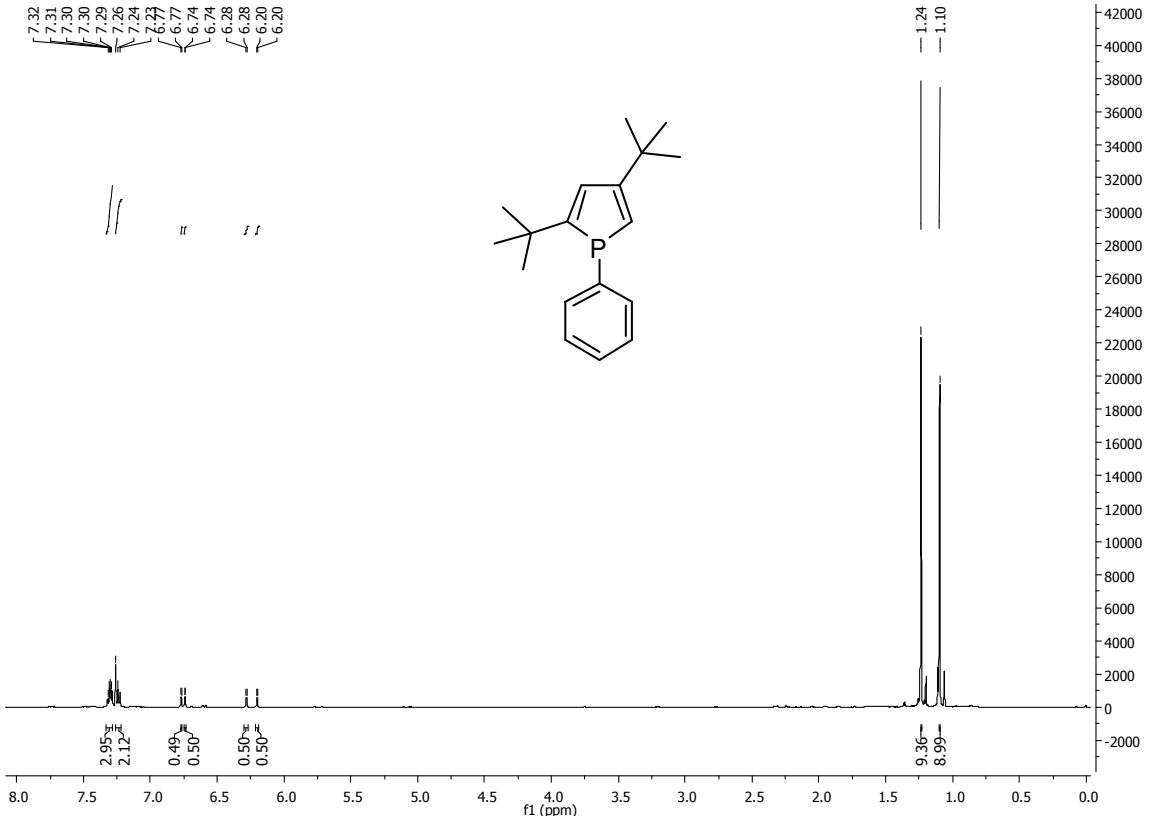

156.34
156.30
154.41
154.35
134.33
134.24
133.73
133.58
130.72
130.63
129.21
128.61
128.54
124.13
33.47
33.44
31.73
31.66
30.84
30.79
30.60
30.46
28.68
28.66
22.68
22.55
14.21
14.13
f1 (ppm)

(^{31}P)

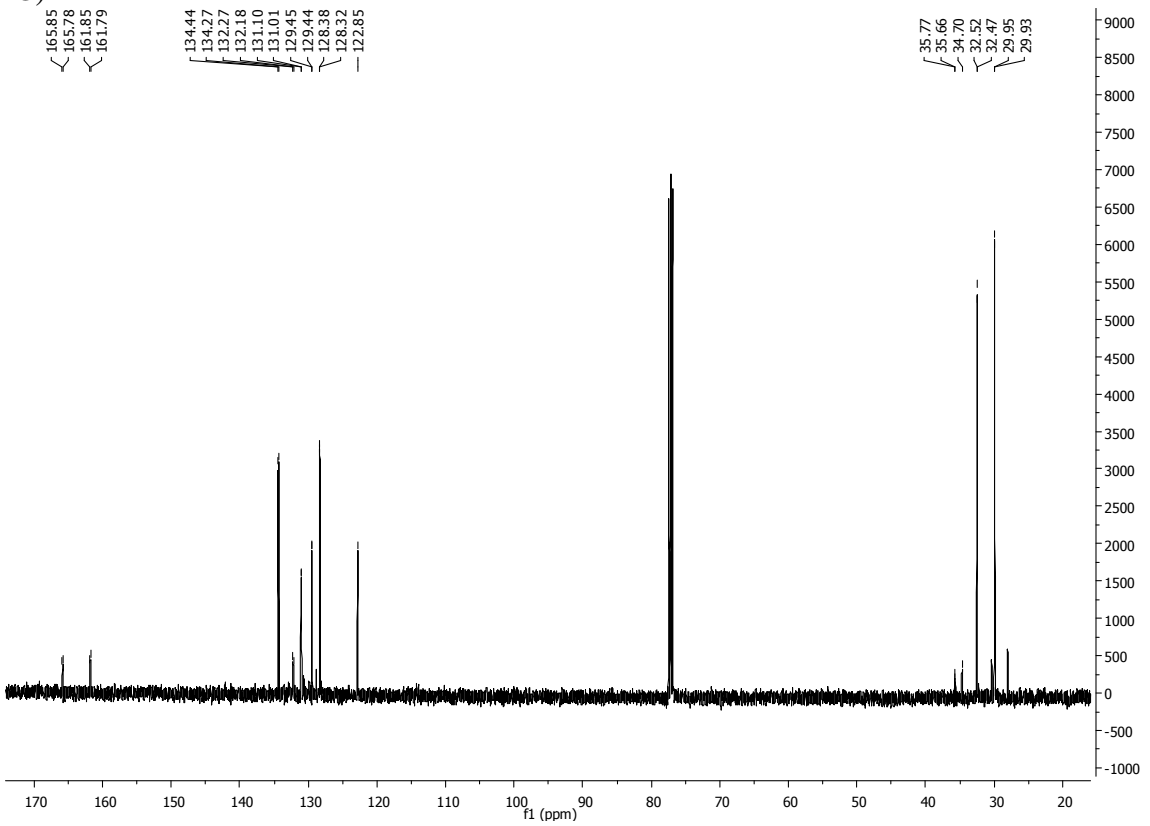

8.07
f1 (ppm)

(3i)

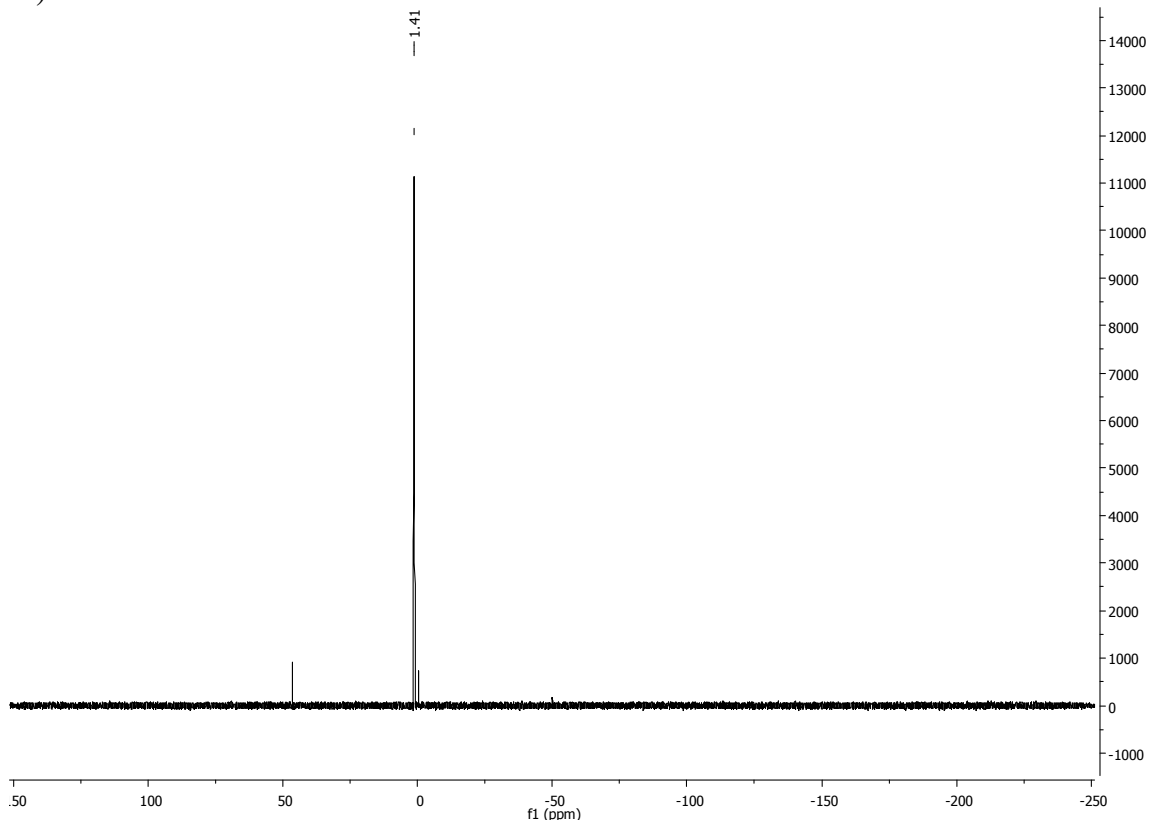
(^{1}H)


7.32
7.31
7.30
7.30
7.29
7.26
7.24
7.23
6.77
6.74
6.74
6.28
6.28
6.20
6.20
1.24
1.10
P
2.95
2.12
0.49
0.50
0.50
0.50
9.36
8.99
f1 (ppm)

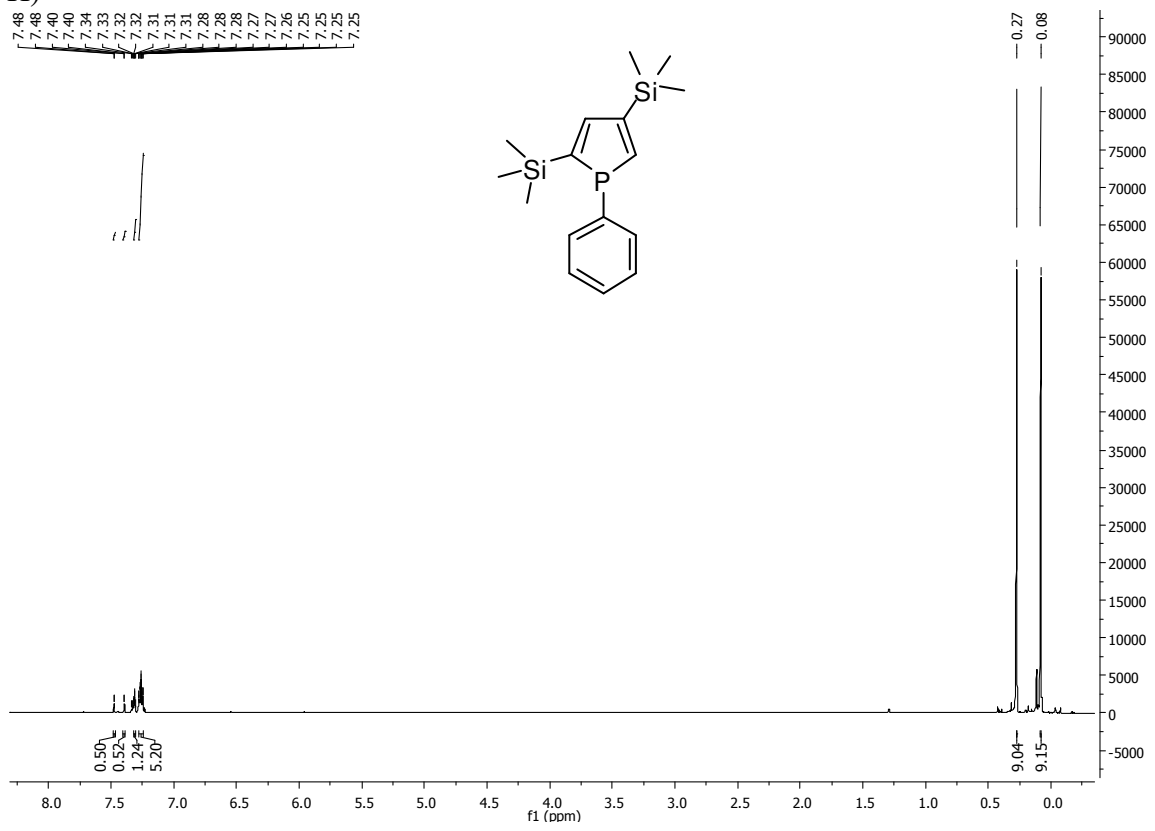
(^{13}C)


165.85
165.78
161.85
161.79
134.44
134.27
132.27
132.18
131.10
131.01
129.45
129.44
128.38
128.32
122.85
35.77
35.66
34.70
32.52
32.47
29.95
29.93
f1 (ppm)

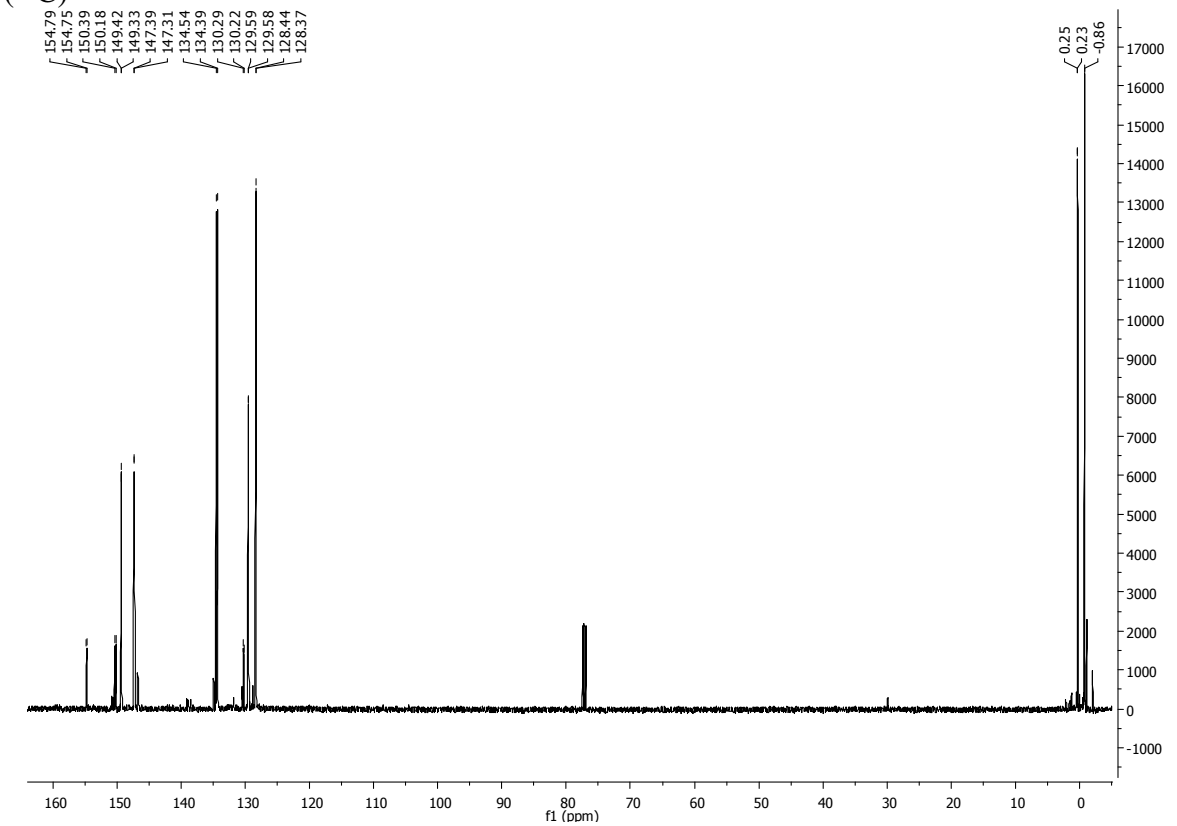
(^{31}P)


1.41
f1 (ppm)

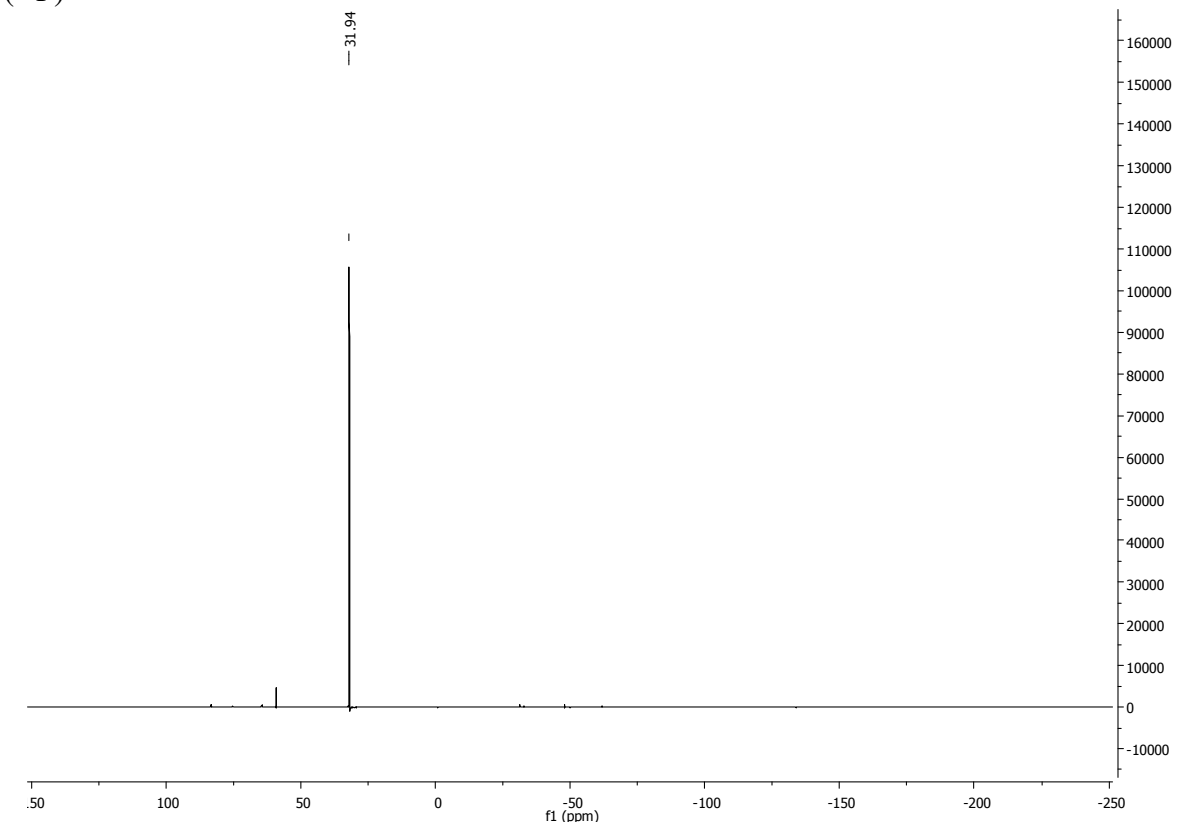
(3j)
(^{1}H)


7.48
7.48
7.40
7.40
7.34
7.33
7.32
7.32
7.31
7.31
7.31
7.28
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.25
7.25
0.27
0.08
Si
Si
P
0.50
0.52
1.24
5.20
9.04
9.15
f1 (ppm)

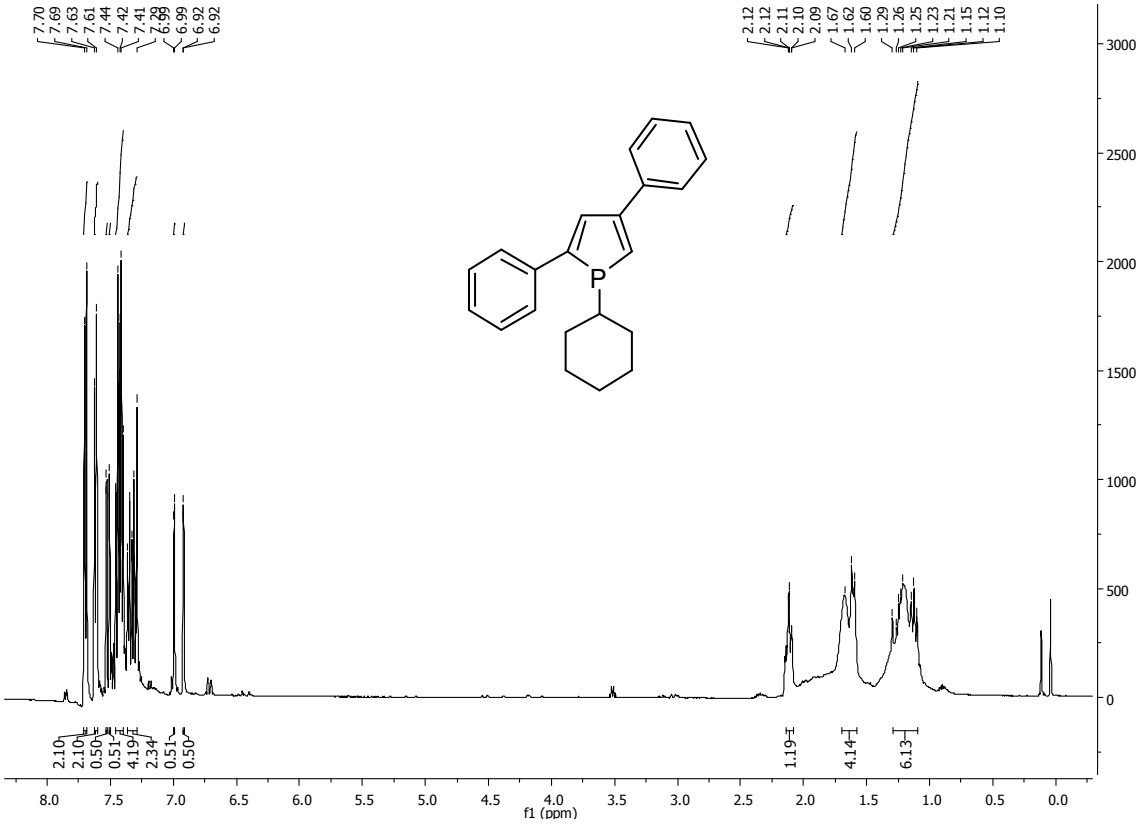
(^{13}C)

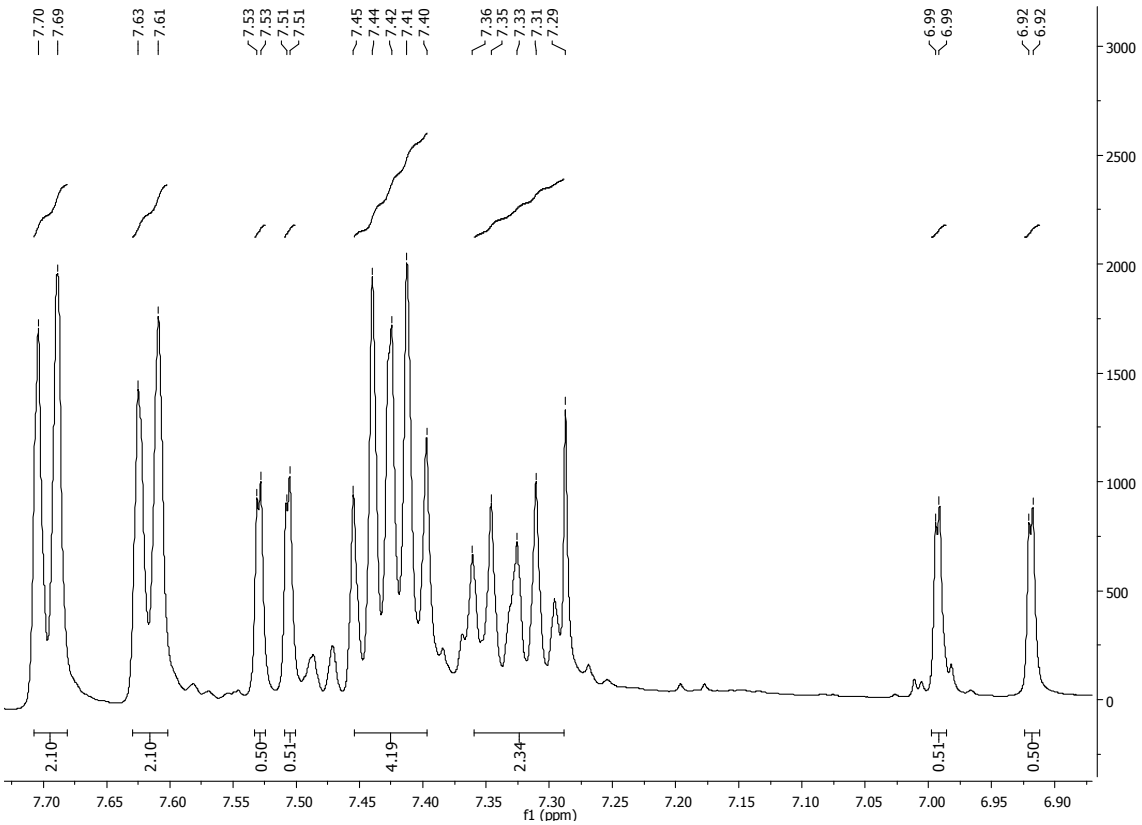

154.79
154.75
150.39
150.18
149.42
149.33
147.39
147.31
134.54
134.39
130.29
130.22
129.59
129.58
128.44
128.37
0.25
0.23
-0.86
f1 (ppm)

(^{31}P)

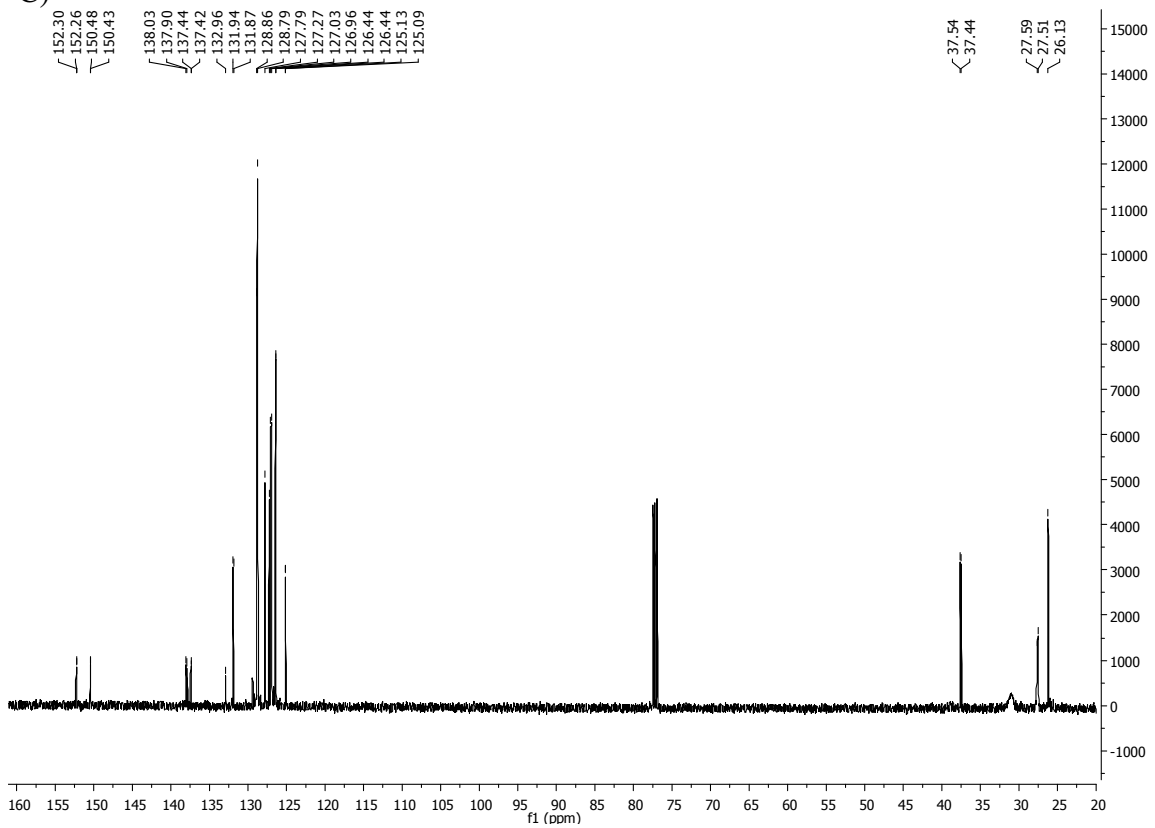

31.94
f1 (ppm)

(3k)
(^{1}H)

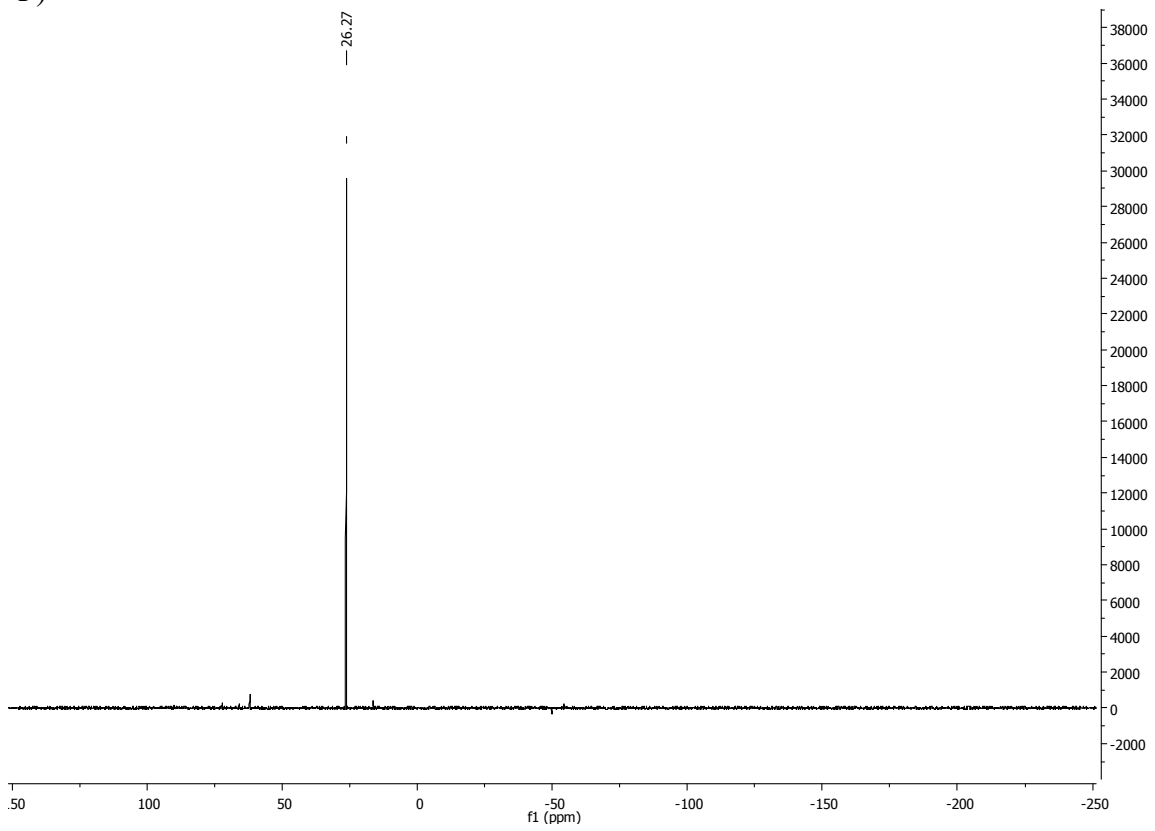

7.70
7.69
7.63
7.61
7.44
7.42
7.41
7.29
6.99
6.92
6.92
2.12
2.12
2.11
2.10
2.09
1.67
1.62
1.60
1.29
1.26
1.25
1.23
1.21
1.15
1.12
1.10
P
2.10
2.10
0.50
0.51
4.19
2.34
0.51
0.50
1.19
4.14
6.13
f1 (ppm)


7.70
7.69
7.63
7.61
7.53
7.53
7.51
7.51
7.45
7.44
7.42
7.41
7.40
7.36
7.35
7.33
7.31
7.29
6.99
6.99
6.92
6.92
2.10
2.10
0.50
0.51
4.19
2.34
0.51
0.50
f1 (ppm)

(^{13}C)


152.30
152.26
150.48
150.43
138.03
137.90
137.44
137.42
132.96
131.94
131.87
128.86
128.79
127.79
127.27
127.03
126.96
126.44
126.44
125.13
125.09
37.54
37.44
27.59
27.51
26.13
f1 (ppm)

(^{31}P)

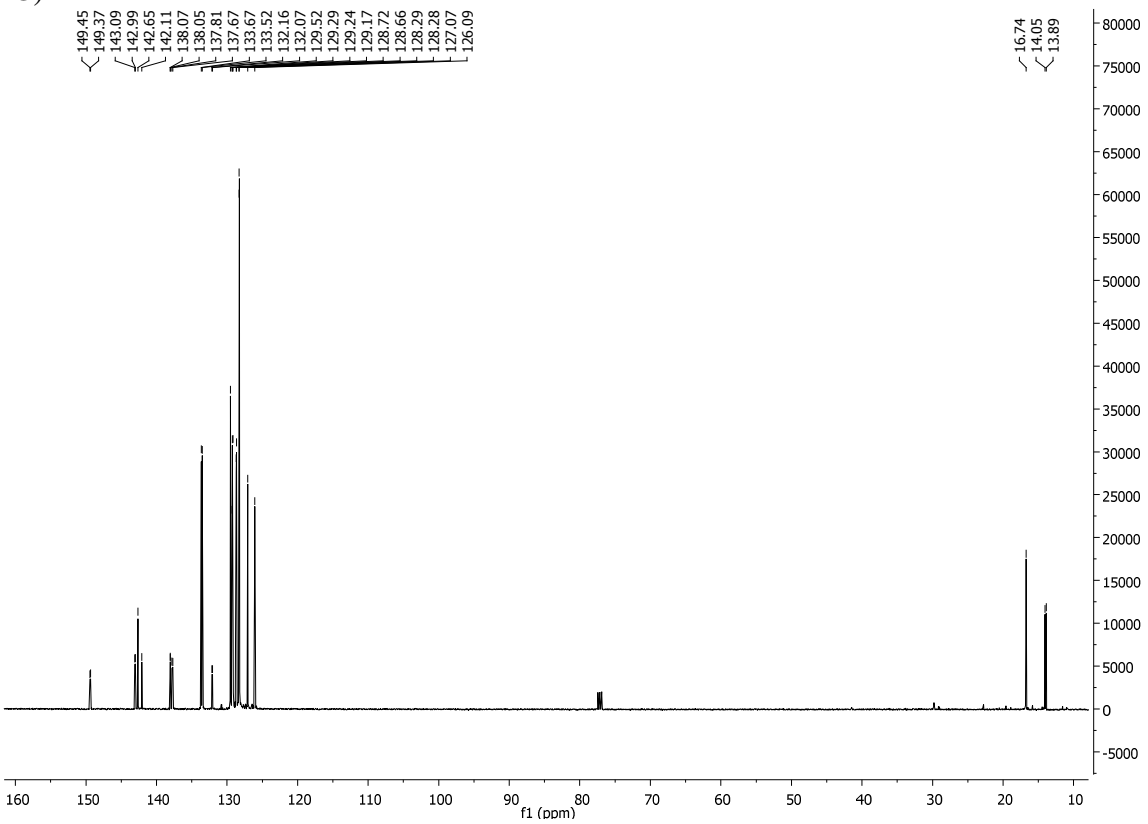

26.27
f1 (ppm)

3l

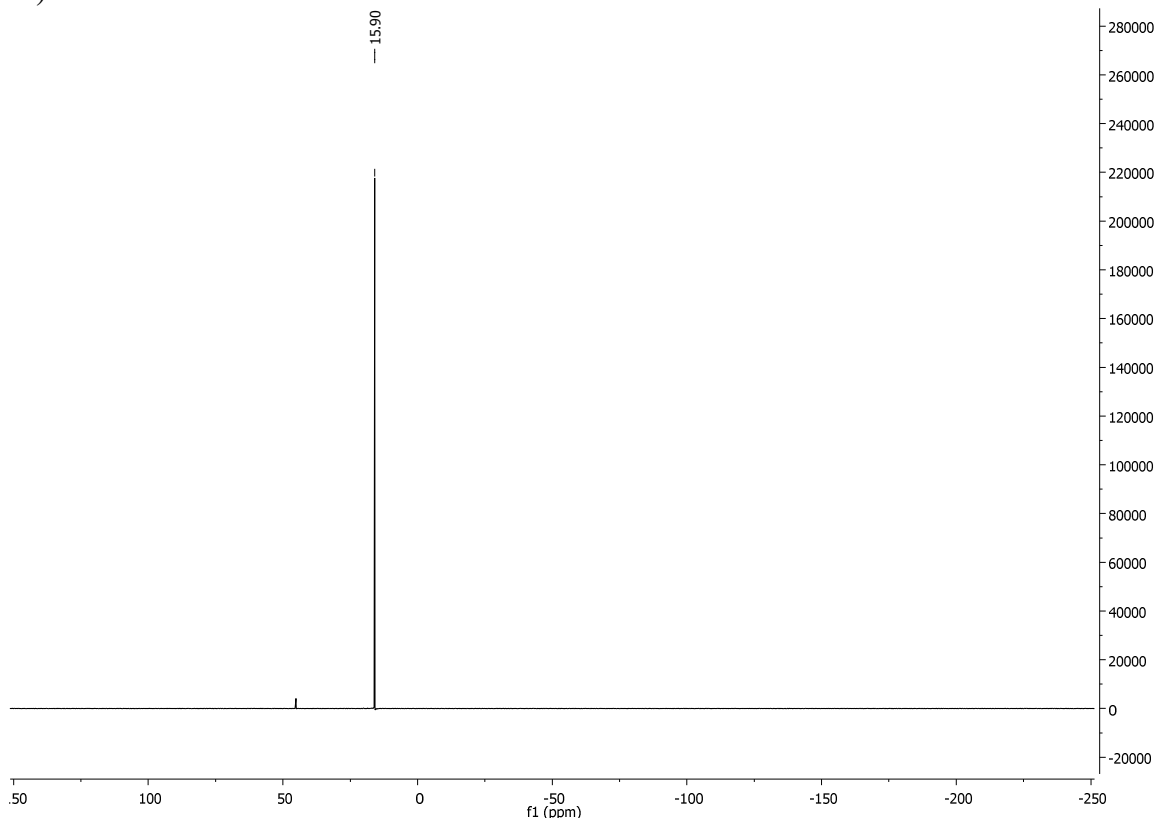
(^{1}H)


7.44 7.42 7.41 7.37 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.30 7.29 7.27 7.26 7.26 7.25 7.24 7.24 7.24 7.23 7.16 7.16 7.15 7.14 7.13 7.13 7.13
1.98 1.97 1.93 1.91
P
2.08 2.04 3.03 3.92 3.09 1.00
3.05 3.10
f1 (ppm)

(^{13}C)


149.45 149.37 143.09 142.99 142.65 142.11 138.07 138.05 137.81 137.67 133.67 133.52 132.16 132.07 129.52 129.29 129.24 129.17 128.72 128.66 128.29 128.28 127.07 126.09
16.74 14.05 13.89
f1 (ppm)

(^{31}P)


15.90
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
.50
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)