Synthesis of 1,2,4-Azadiphosphole Derivatives Based on Vanadium-Catalyzed [2+2+1] Cycloaddition Reactions of Azobenzenes with Phosphaalkynes

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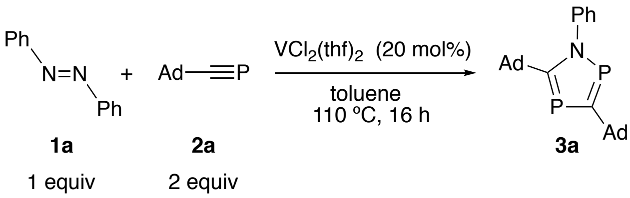
1. General methods

^1H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{31}P NMR (162 MHz) spectra were recorded on a JEOL Excalibur 400 spectrometer, and chemical shifts of ^{31}P NMR were referenced to an external standard of 85% H_3PO_4. Elemental analysis was performed at the Microanalytical Center of The University of Tokyo. Mass spectra were measured on a JEOL JMS-700 mass spectrometer. Gel permeation chromatography (GPC) was performed using a JAI model LC-908-G30 recycling preparative HPLC equipped with JAIGEL-1H and 2H with chloroform as an eluent.

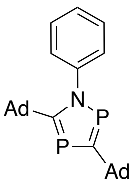
Unless otherwise noted, all reactions were carried out under a dry argon atmosphere. Solvents were dried by the general methods and degassed before use. Azobenzene (**1a**), 3,3'-dimethylazobenzene (**1b**), dimethyl azobenzene-4,4'-dicarboxylate (**1l**), and di-*tert*-butyl azodicarboxylate (**1m**) were purchased from commercial sources. Other azobenzenes (**1**)[S1] and phosphaalkynes (**2**)[S2] were prepared according to the literature procedures. The other reagents were commercially available.

2. Vanadium-Catalyzed [2+2+1] Cycloaddition Reactions of Azobenzenes (1) with Phosphaalkynes (2)



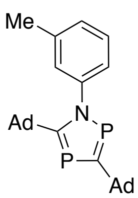
A typical experimental procedure of the preparation of 1,2,4-azadiphosphole **3a** is described below. In a 50 mL sealed vessel were placed azobenzene **1a** (17.8 mg, 0.0978 mmol), $VCl_2(thf)_2$ (5.5 mg, 0.021 mmol), and toluene (2.0 mL) under N_2. Then, 1-adamantylphosphaethyne **2a** (36.6 mg, 0.206 mmol) was added. The reaction resulting mixture was stirred at 110 ºC for 16 h. After cooling to room temperature, toluene was removed under reduced pressure. The reaction mixture was purified by column chromatography on SiO_2 with hexane as an eluent to afford **3a** (27.0 mg, 0.0604 mmol).

Isolated yields and spectroscopic data of 1,2,4-azadiphospholes (**3**) are described as follows:



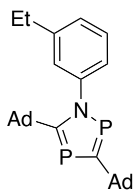
3a

60% Yield. A pale yellow solid, m.p. = 236.4-238.3 ºC. ^{1}H NMR (C_6D_6): δ 7.24-7.22 (m, 2H), 6.95-6.87 (m, 3H) 2.410-2.405 (m, 6H), 2.154-2.148 (m, 6H), 1.99 (brs, 3H), 1.80 (brs, 3H) 1.72-1.64 (m, 6H), 1.50-1.43 (m, 6H). ^{13}C{^{1}H} NMR (C_6D_6): δ 205.9 (dd, $^1J_{P\text{-}C}$ = 62.9 Hz and $^1J_{P\text{-}C}$ = 57.2 Hz), 196.9 (d, $^1J_{P\text{-}C}$ = 60.0 Hz), 144.0 (d, $^2J_{P\text{-}C}$ = 15.3 Hz), 129.8 (d, $^3J_{P\text{-}C}$ = 5.8 Hz), 127.9, 48.5 (dd, $^3J_{P\text{-}C}$ = 11.5 Hz and $^4J_{P\text{-}C}$ = 8.6 Hz), 44.4 (d, $^3J_{P\text{-}C}$ = 14.3 Hz), 43.1 (dd, $^2J_{P\text{-}C}$ = 15.8 Hz and $^3J_{P\text{-}C}$ = 3.4 Hz), 39.9 (t, $^2J_{P\text{-}C}$ = 16.2 Hz), 36.9, 36.6, 29.8, 29.2 (d, $^4J_{P\text{-}C}$ = 1.9 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 261.4 (d, $^2J_{P\text{-}P}$ = 26.2 Hz), 150.9 (d, $^2J_{P\text{-}P}$ = 26.2 Hz). HRMS (FAB) Calcd. for $C_{28}H_{36}NP_2$ $[M+H]^+$: 448.2323. Found: 448.2346.



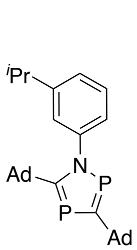
3b

55% Yield. A pale yellow solid, m.p. = 207.2-208.9 ºC. ^{1}H NMR ($CDCl_3$): δ 7.27-7.20 (m, 4H), 2.39 (s, 3H), 2.10-2.08 (m, 9H), 2.04-1.97 (m, 6H), 1.90 (brs, 3H), 1.76 (brs, 6H), 1.61-1.48 (m, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 205.5 (dd, $^{1}J_{P\text{-}C}$ = 62.0 Hz and $^{1}J_{P\text{-}C}$ = 57.1 Hz), 197.0 (d, $^{1}J_{P\text{-}C}$ = 59.1 Hz), 143.4 (d, $^{2}J_{P\text{-}C}$ = 16.2 Hz), 137.9, 130.1 (d, $^{3}J_{P\text{-}C}$ = 5.7 Hz), 129.2, 127.7, 126.5 (d, $^{3}J_{P\text{-}C}$ = 5.7 Hz), 48.0 (dd, $^{3}J_{P\text{-}C}$ = 11.5 Hz and $^{4}J_{P\text{-}C}$ = 8.6 Hz), 44.0 (d, $^{3}J_{P\text{-}C}$ = 14.3 Hz), 42.9 (dd, $^{2}J_{P\text{-}C}$ = 16.2 Hz and $^{3}J_{P\text{-}C}$ = 2.9 Hz), 39.4 (t, $^{2}J_{P\text{-}C}$ = 15.8 Hz), 36.7, 36.4, 29.5 28.9 (d, $^{4}J_{P\text{-}C}$ = 1,9 Hz), 21.4. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 260.9 (d, $^{2}J_{P\text{-}P}$ = 28.3 Hz), 150.6 (d, $^{2}J_{P\text{-}P}$ = 28.3 Hz). HRMS (FAB) Calcd. for $C_{29}H_{38}NP_2$ $[M+H]^+$: 462.2479. Found: 462.2492.



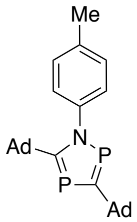
3c

51% Yield. A pale yellow solid, m.p. = 177.8-179.5 ºC.^{1}H NMR ($CDCl_3$): δ 7.30-7.20 (m, 4H), 2.68 (q, J = 7.7 Hz, 2H), 2.11-2.08 (m, 9H), 2.03-1.97 (m, 6H), 1.89 (brs, 3H), 1.77 (brs, 6H), 1.60-1.47 (m, 6H), 1.24 (t, J = 7.7 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 205.5 (dd, $^{1}J_{P\text{-}C}$ = 62.2 Hz and $^{1}J_{P\text{-}C}$ = 57.5 Hz), 197.1 (d, $^{1}J_{P\text{-}C}$ = 59.4 Hz), 144.3, 143.4 (d, $^{2}J_{P\text{-}C}$ = 16.3 Hz), 129.1 (d, $^{3}J_{P\text{-}C}$ = 4.8 Hz), 128.1, 127.8, 126.7 (d, $^{3}J_{P\text{-}C}$ = 4.8 Hz), 48.0 (dd, $^{3}J_{P\text{-}C}$ = 11.5 Hz and $^{4}J_{P\text{-}C}$ = 8.6 Hz), 44.0 (d, $^{3}J_{P\text{-}C}$ = 14.4 Hz), 42.9 (dd, $^{2}J_{P\text{-}C}$ = 16.3 Hz and $^{3}J_{P\text{-}C}$ = 2.9 Hz), 39.5 (t, $^{2}J_{P\text{-}C}$ = 15.8 Hz), 36.8, 36.4, 29.5, 29.0 (d, ^{4}J = 1.9 Hz), 28.7. 15.7 ^{31}P{^{1}H} NMR ($CDCl_3$): δ 260.5 (d, $^{2}J_{P\text{-}P}$ = 28.2 Hz), 150.5 (d, $^{2}J_{P\text{-}P}$ = 28.2 Hz). HRMS (FAB) Calcd. for $C_{30}H_{39}NP_2$ $[M]^+$: 475.2558. Found: 475.2567.



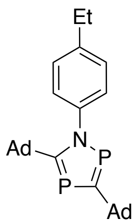
3d

46% Yield. A pale yellow solid, m.p. = 160.1-161.5 ºC. ^{1}H NMR ($CDCl_3$): δ 7.30-7.19 (m, 4H), 2.99-2.89 (m, 1H), 2.11-2.08 (m, 9H), 2.03-1.95 (m, 6H), 1.88 (brs, 3H), 1.77 (brs, 6H), 1.60-1.47 (m, 6H), 1.27 (d, J = 4.4 Hz, 3H), 1.25 (d, J = 4.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 205.5 (dd, $^{1}J_{P\text{-}C}$ = 62.5 Hz and $^{1}J_{P\text{-}C}$ = 57.7 Hz), 197.1 (d, $^{1}J_{P\text{-}C}$ = 60.1 Hz), 148.9, 143.4 (d, $^{2}J_{P\text{-}C}$ = 15.3 Hz), 127.8, 127.7 (d, $^{3}J_{P\text{-}C}$ = 5.7 Hz), 126.8 (d, $^{2}J_{P\text{-}C}$ = 4.7 Hz), 126.7, 48.0 (dd, $^{3}J_{P\text{-}C}$ = 11.4 Hz and $^{4}J_{P\text{-}C}$ = 8.6 Hz), 44.0 (d, $^{3}J_{P\text{-}C}$ = 14.3 Hz), 42.9 (dd, $^{2}J_{P\text{-}C}$ = 16.2 Hz and $^{3}J_{P\text{-}C}$ = 2.9 Hz), 39.5 (t, $^{2}J_{P\text{-}C}$ = 15.8 Hz), 36.8, 36.4, 34.0, 29.5, 29.0 (d, $^{4}J_{P\text{-}C}$ = 1.9 Hz), 24.2, 23.8. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 260.1 (d, $^{2}J_{P\text{-}P}$ = 28.4 Hz), 150.5 (d, $^{2}J_{P\text{-}P}$ = 28.4 Hz). HRMS (FAB) Calcd. for $C_{31}H_{41}NP_2$ $[M]^{+}$: 489.2714. Found: 489.2722.



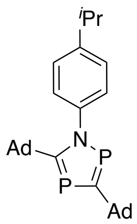
3e

55% Yield. A pale yellow solid, m.p. = 181.5-183.2 ºC. ^{1}H NMR ($CDCl_3$): δ 7.27 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 2.42 (s, 3H), 2.10-2.08(m, 9H), 2.014-2.009 (m, 6H), 1.90 (brs, 3H), 1.77-1.76 (m, 6H), 1.60-1.48 (m, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 205.5 (dd, $^{1}J_{P\text{-}C}$ = 61.0 Hz and $^{1}J_{P\text{-}C}$ = 57.2 Hz), 197.1 (d, $^{1}J_{P\text{-}C}$ = 60.0 Hz), 140.8 (d, $^{2}J_{P\text{-}C}$ = 16.3 Hz), 138.4, 129.3 (d, $^{3}J_{P\text{-}C}$ = 4.8 Hz), 128.6, 48.0 (dd, $^{3}J_{P\text{-}C}$ = 11.5 Hz and $^{4}J_{P\text{-}C}$ = 8.6 Hz), 43.9 (d, $^{3}J_{P\text{-}C}$ = 15.3 Hz), 42.8 (dd, $^{2}J_{P\text{-}C}$ = 15.3 Hz and $^{3}J_{P\text{-}C}$ = 2.9 Hz), 39.4 (t, $^{2}J_{P\text{-}C}$ = 15.7 Hz), 36.8, 36.4, 29.5, 28.9 (d, $^{4}J_{P\text{-}C}$ = 1.9 Hz), 21.4 $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 261.4 (d, $^{2}J_{P\text{-}P}$ = 30.4 Hz), 150.6 (d, $^{2}J_{P\text{-}P}$ = 30.4 Hz). HRMS (FAB) Calcd. for $C_{29}H_{37}NP_2$ $[M]^{+}$: 461.2401. Found: 461.2387.



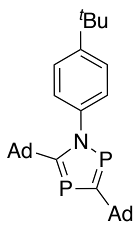
3f

53% Yield. A pale yellow solid, m.p. = 175.5-177.1 ºC. ^{1}H NMR (C_6D_6): δ 7.21 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 8.0 Hz, 2H), 2.423-2.419 (m, 6H), 2.31 (q, J = 7.6 Hz, 2H), 2.205-2.198 (m, 6H), 2.00 (brs, 3H), 1.82 (brs, 3H), 1.73-1.64 (m, 6H), 1.48 (brs, 6H), 0.96 (t, J = 7.6 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 205.9 (dd, $^{1}J_{P\text{-}C}$ = 62.4 Hz and $^{1}J_{P\text{-}C}$ = 56.7 Hz), 196.9 (d, $^{1}J_{P\text{-}C}$ = 59.6 Hz), 144.5, 141.6 (d, $^{2}J_{P\text{-}C}$ = 16.2 Hz), 129.7 (d, $^{3}J_{P\text{-}C}$ = 4.8 Hz), 127.4, 48.5 (dd, $^{3}J_{P\text{-}C}$ = 11.5 Hz and $^{4}J_{P\text{-}C}$ = 8.6 Hz), 44.4 (d, $^{3}J_{P\text{-}C}$ = 15.2 Hz), 43.0 (dd, $^{2}J_{P\text{-}C}$ = 15.7 Hz and $^{3}J_{P\text{-}C}$ = 3.3 Hz), 39.9 (t, $^2J_{P\text{-}C}$ = 15.8 Hz), 36.9, 36.6, 29.8, 29.3 (d, $^4J_{P\text{-}C}$ = 1.9 Hz), 28.6, 15.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 261.2 (d, $^2J_{P\text{-}P}$ = 28.4 Hz), 150.4 (d, $^2J_{P\text{-}P}$ = 28.4 Hz). HRMS (FAB) Calcd. for $C_{30}H_{39}NP_2$ $[M]^+$: 475.2558. Found: 475.2562.



3g

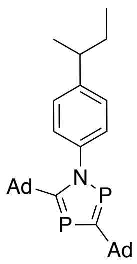
54% Yield. A pale yellow solid, m.p. = 160.9-162.6 ºC.^1H NMR ($CDCl_3$): δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 3.03-2.93 (m, 1H), 2.10-2.08 (m, 9H), 2.00 (s, 6H) 1.89 (brs, 3H), 1.77 (s, 6H), 1.60-1.46 (m, 6H), 1.29 (d, *J* = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 205.5 (dd, $^1J_{P\text{-}C}$ = 62.0 Hz and $^1J_{P\text{-}C}$ = 57.2 Hz), 197.1 (d, $^2J_{P\text{-}C}$ = 59.2 Hz), 149.5, 140.9 (d, $^2J_{P\text{-}C}$ = 16.2 Hz), 129.3 (d, $^3J_{P\text{-}C}$ = 5.7 Hz), 125.8, 48.0 (dd, $^3J_{P\text{-}C}$ =11.4 Hz and $^4J_{P\text{-}C}$ = 8.6 Hz), 43.9 (d, $^3J_{P\text{-}C}$ = 15.3 Hz), 42.8 (dd, $^2J_{P\text{-}C}$ = 15.8 Hz and $^3J_{P\text{-}C}$ = 3.4 Hz), 39.4 (t, $^2J_{P\text{-}C}$ = 15.3 Hz), 36.8, 36.4, 34.0, 29.5, 28.9 (d, $^4J_{P\text{-}C}$ = 1.9 Hz), 24.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 260.9 (d, $^2J_{P\text{-}P}$ = 26.2 Hz), 150.3 (d, $^2J_{P\text{-}P}$ = 26.2 Hz). HRMS (FAB) Calcd. for $C_{31}H_{41}NP_2$ $[M]^+$: 489.2714. Found: 489.2725.



3h

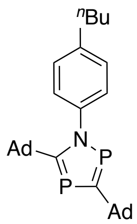
66% Yield. A pale yellow solid, m.p. = 204.5-206.1 ºC. ^1H NMR (C_6D_6): δ 7.28-7.26 (m, 2H), 7.05-7.03 (m, 2H), 2.43-2.42 (m, 6H), 2.210-2.205 (m, 6H), 1.99 (brs, 3H), 1.82 (brs, 3H), 1.72-1.64 (m, 6H), 1.49 (brs, 6H) 1.10 (s, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 205.9 (dd, $^1J_{P\text{-}C}$ = 62.9 Hz and $^1J_{P\text{-}C}$ = 57.2 Hz), 197.0 (d, $^1J_{P\text{-}C}$ = 61.1 Hz), 151.6, 141.4 (d, $^2J_{P\text{-}C}$ = 17.2 Hz), 129.5 (d, $^3J_{P\text{-}C}$ = 4.7 Hz), 124.9, 48.5 (dd, $^3J_{P\text{-}C}$ = 11.0 Hz and $^4J_{P\text{-}C}$ = 8.2 Hz), 44.3 (d, $^3J_{P\text{-}C}$ = 14.3 Hz), 43.0 (dd, $^2J_{P\text{-}C}$ = 16.2 Hz and $^3J_{P\text{-}C}$ = 2.9 Hz), 39.9 (t, $^2J_{P\text{-}C}$ = 15.7 Hz), 36.9, 36.7, 34.6, 31.3, 29.8, 29.3 (d, $^4J_{P\text{-}C}$ = 1.9 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 260.9 (d, $^2J_{P\text{-}P}$ = 30.5 Hz), 150.3 (d, $^2J_{P\text{-}P}$ = 30.5 Hz). HRMS (FAB) Calcd. for $C_{32}H_{43}NP_2$ $[M]^+$: 503.2871. Found:

503.2863.



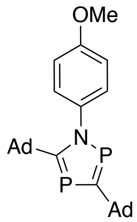
3i

50% Yield. A pale yellow solid, m.p. = 109.6-111.3 ºC. ^{1}H NMR ($CDCl_3$): δ 7.33-7.29 (m, 2H), 7.19-7.15 (m, 2H), 2.72-2.63 (m, 1H), 2.10-2.08 (m, 9H), 2.00-1.99 (m, 6H), 1.89 (brs, 3H), 1.77-1.76 (m, 6H), 1,69-1.46 (m, 8H), 1.28 (d, J = 7.2 Hz, 3H), 0.81 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 205.5 (dd, $^{1}J_{P\text{-}C}$ = 62.3 Hz and $^{1}J_{P\text{-}C}$ = 56.5 Hz), 197.1 (d, $^{1}J_{P\text{-}C}$ = 59.4 Hz), 148.1, 141.0 (d, $^{2}J_{P\text{-}C}$ = 16.3 Hz), 129.4(d, $^{3}J_{P\text{-}C}$ = 4.8 Hz), 129.2 (d, $^{3}J_{P\text{-}C}$ = 4.8 Hz), 127.0, 126.0, 48.0 (dd, $^{3}J_{P\text{-}C}$ = 11.5 Hz and $^{4}J_{P\text{-}C}$ = 8.6 Hz), 43.9 (d, $^{3}J_{P\text{-}C}$ = 14.4 Hz), 42.8 (dd, $^{2}J_{P\text{-}C}$ = 16.3 Hz and $^{3}J_{P\text{-}C}$ = 2.9 Hz), 41.5, 39.5 (t, $^{3}J_{P\text{-}C}$ = 15.3 Hz), 36.8, 36.4, 31.4, 29.5, 28.9 (d, $^{4}J_{P\text{-}C}$ = 1.9 Hz), 22.1, 12.2. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 260.4 (d, $^{2}J_{P\text{-}P}$ = 28.1 Hz), 150.2 (d, $^{2}J_{P\text{-}P}$ = 28.1 Hz). HRMS (FAB) Calcd. for $C_{32}H_{44}NP_2$ $[M+H]^+$:504.2949. Found: 504.2928.



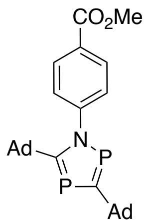
3j

47% Yield. A pale yellow solid, m.p. = 198.2-199.6 ºC. ^{1}H NMR ($CDCl_3$): δ 7.29 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.68 (t, J = 7.4 Hz, 2H), 2.10-2.08 (m, 9H), 2.002-1.996 (m, 6H), 1.89(m, 3H), 1.76 (m, 6H), 1.76-1.47 (m, 8H), 1.41-1.31 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 205.5 (dd, $^{1}J_{P\text{-}C}$ = 62.3 Hz and $^{1}J_{P\text{-}C}$ = 57.5 Hz), 197.1 (d, $^{1}J_{P\text{-}C}$ = 59.4 Hz), 143.4, 140.9 (d. $^{2}J_{P\text{-}C}$ = 15.3 Hz), 129.3 (d, $^{3}J_{P\text{-}C}$ = 4.8 Hz), 127.9, 48.0 (dd, $^{3}J_{P\text{-}C}$ = 11.5 Hz and $^{4}J_{P\text{-}C}$ = 8.7 Hz), 43.9 (d, $^{3}J_{P\text{-}C}$ =14.3 Hz), 42.8 (dd, $^{2}J_{P\text{-}C}$ = 16.3 Hz and $^{3}J_{P\text{-}C}$ = 2.9 Hz), 39.4 (t, $^{2}J_{P\text{-}C}$ = 15.4 Hz), 36.8, 36.4, 35.4, 33.6, 29.5, 29.4 (d, $^{4}J_{P\text{-}C}$ = 1.9 Hz), 22.3, 14.1. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 260.8 (d, $^{2}J_{P\text{-}P}$ = 30.5 Hz), 150.4 (d, $^{2}J_{P\text{-}P}$ = 30.5 Hz). HRMS (FAB) Calcd. for $C_{32}H_{43}NP_2$ $[M]^+$: 503.2871. Found: 503.2847.



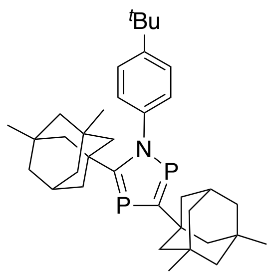
3k

52% Yield. A pale yellow solid, m.p. = 210.5-212.1 ºC. ^{1}H NMR (C_6D_6): δ 7.16-7.15 (m, 2H), 6.52-6.48 (m, 2H), 3.15 (s, 3H), 2.43-2.42 (m, 6H), 2.208-2.201 (m, 6H), 2.00 (brs, 3H), 1.84 (brs, 3H), 1.73-1.64 (m, 6H), 1.49 (brs, 6H). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 205.9 (dd, $^{1}J_{P\text{-}C}$ = 62.9 Hz and $^{1}J_{P\text{-}C}$ = 57.2 Hz), 197.1 (d, $^{1}J_{P\text{-}C}$ = 60.0 Hz), 159.7, 136.5 (d, $^{2}J_{P\text{-}C}$ = 16.2 Hz), 130.8 (d, $^{3}J_{P\text{-}C}$ = 4.7 Hz), 113.1, 54.9, 48.5 (dd, $^{3}J_{P\text{-}C}$ = 11.5 Hz and $^{4}J_{P\text{-}C}$ = 8.6 Hz), 44.4 (d, $^{3}J_{P\text{-}C}$ = 14.3 Hz), 43.0 (dd. $^{2}J_{P\text{-}C}$ = 16.2 Hz and $^{3}J_{P\text{-}C}$ = 2.9 Hz), 39.9 (t, $^{2}J_{P\text{-}C}$ = 15.8 Hz), 36.9, 36.6, 29.8, 29.3 (d, $^{4}J_{P\text{-}C}$ = 1.9 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 261.4 (d, $^{2}J_{P\text{-}P}$ = 28.1 Hz), 150.8 (d, $^{2}J_{P\text{-}P}$ = 28.1 Hz). HRMS (FAB) Calcd. for $C_{29}H_{37}NOP_2$ $[M]^+$: 477.2350. Found: 477.2369.



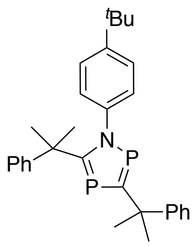
3l

47% Yield. A yellow solid. m.p. 146.5-148.3 ºC. ^{1}H NMR ($CDCl_3$): δ 8.07 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 3.96 (s, 3H), 2.09 (brs, 9H), 1.991-1.985 (m, 6H), 1.89 (brs, 3H), 1.77 (brs, 6H), 1.60-1.46 (m, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 205.9 (dd, $^{1}J_{P\text{-}C}$ = 62.8 Hz and $^{1}J_{P\text{-}C}$ = 57.1 Hz), 197.2 (d, $^{1}J_{P\text{-}C}$ = 59.5 Hz), 166.4, 148.0 (d, $^{2}J_{P\text{-}C}$ = 16.3 Hz), 130.2, 129.7 (d, $^{3}J_{P\text{-}C}$ = 4.8 Hz), 129.4, 52.5, 48.0 (dd, $^{3}J_{P\text{-}C}$ = 11.5 Hz and $^{4}J_{P\text{-}C}$ = 8.6 Hz), 44.2 (d, $^{3}J_{P\text{-}C}$ = 14.4 Hz), 42.9 (dd, $^{2}J_{P\text{-}C}$ = 15.4 Hz and $^{3}J_{P\text{-}C}$ = 2.9 Hz), 39.5 (t, $^{2}J_{P\text{-}C}$ = 15.4 Hz), 36.7, 36.3, 29.5, 28.9 (d, $^{4}J_{P\text{-}C}$ = 2.9 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 261.8 (d, $^{2}J_{P\text{-}P}$ = 30.3 Hz), 152.9 (d, $^{2}J_{P\text{-}P}$ = 30.3 Hz). HRMS (FAB) Calcd. for $C_{30}H_{38}NO_2P_2$ $[M+H]^+$: 506.2378. Found: 506.2397.



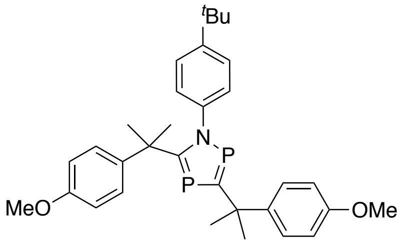
3o

50% Yield. A pale yellow solid, m.p. = 161.8-163.6 ºC. ^{1}H NMR ($CDCl_3$): δ 7.39-7.37 (m, 2H), 7.31-7.29 (m, 2H), 2.18-1.51 (m, 14H), 1.45-1.33 (m, 13H), 1.31-0.89 (m, 8H), 0.86 (s, 6H), 0.70 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 204.7 (dd, $^{1}J_{P\text{-}C}$ = 61.8 Hz and $^{1}J_{P\text{-}C}$ = 57.0 Hz), 196.7 (d, $^{1}J_{P\text{-}C}$ = 58.4 Hz), 152.0, 140.6 (d, $^{2}J_{P\text{-}C}$ = 16.3 Hz), 129.0 (d, $^{3}J_{P\text{-}C}$ = 4.8 Hz), 124.7, 54.3 (dd, $^{3}J_{P\text{-}C}$ = 10.6 Hz and $^{4}J_{P\text{-}C}$ = 8.6 Hz), 50.9, 50.4, 50.1 (d, $^{3}J_{P\text{-}C}$ = 14.4 Hz), 46.4 (dd, $^{3}J_{P\text{-}C}$ = 11.5 Hz and $^{4}J_{P\text{-}C}$ = 7.7 Hz), 44.6 (dd, $^{2}J_{P\text{-}C}$ = 15.4 Hz and $^{3}J_{P\text{-}C}$ = 2.9 Hz), 43.0, 42.6, 42.6-42.5 (m), 41.0 (t, $^{2}J_{P\text{-}C}$ = 15.4 Hz), 34.9, 32.2, 31.5, 30.8, 30.6, 30.0. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 259.5 (d, $^{2}J_{P\text{-}P}$ = 30.3 Hz), 149.6 (d, $^{2}J_{P\text{-}P}$ = 30.3 Hz). HRMS (FAB) Calcd. for $C_{36}H_{51}NP_2$ $[M]^+$: 559.3497. Found: 559.3509.



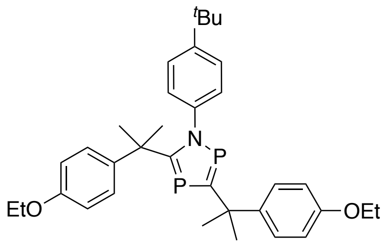
3p

41% Yield. A pale yellow solid, m.p. = 108.0-109.8 ºC. ^{1}H NMR (C_6D_6): δ 7.68-7.66 (m, 2H), 7.25-7.19 (m, 2H), 7.10-7.06 (m, 1H), 6.90-6.82 (m, 5H), 6.71-6.69 (m, 2H), 6.52-6.50 (m, 2H), 2.06 (s, 6H), 1.69 (d, $^{4}J_{P\text{-}H}$ = 2.0 Hz, 6H), 1.07 (s, 9H). ^{13}C{^{1}H} NMR (C_6D_6): δ 204.9 (dd, $^{1}J_{P\text{-}C}$ = 63.0 Hz and $^{1}J_{P\text{-}C}$ = 57.2 Hz), 195.1 (d, $^{1}J_{P\text{-}C}$ = 61.0 Hz), 150.8 (dd, $^{3}J_{P\text{-}C}$ = 5.8 Hz and $^{3}J_{P\text{-}C}$ = 2.9 Hz), 150.4, 148.5 (d, $^{3}J_{P\text{-}C}$ = 1.9 Hz), 139.3 (d, $^{2}J_{P\text{-}C}$ = 15.3 Hz), 129.0 (d, $^{3}J_{P\text{-}C}$ = 4.8 Hz), 128.5, 128.2, 127.0, 126.6, 126.4, 125.8, 124.3, 45.8 (dd, $^{2}J_{p\text{-}C}$ = 17.4 Hz and $^{3}J_{p\text{-}C}$ = 2.9 Hz), 43.9 (t, $^{2}J_{P=C}$ = 17.2 Hz), 34.8 (t, $^{3}J_{P\text{-}C}$ = 9.1 Hz), 34.3, 33.5 (d, $^{3}J_{P\text{-}C}$ = 17.2 Hz), 31.3. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 259.9 (d, $^{2}J_{P\text{-}P}$ = 30.4 Hz), 154.8 (d, $^{2}J_{P\text{-}P}$ = 30.4 Hz). HRMS (FAB) Calcd. for $C_{30}H_{35}NP_2$ $[M]^+$: 471.2245. Found: 471.2246.



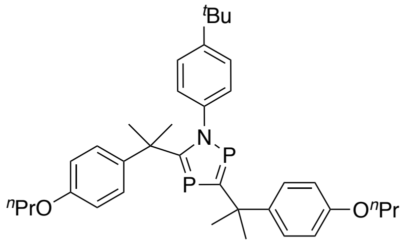
3q

45% Yield. A pale yellow solid, m.p. = 108.0-109.8 ºC. ^{1}H NMR ($CDCl_3$): δ 7.51-7.47 (m, 2H), 6.94-6.92 (m, 2H), 6.87-6.84 (m, 2H), 6.79-6.77 (m, 2H), 6.62-6.60 (m, 2H), 6.52-6.50 (m, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 1.93 (s, 6H), 1.66 (d, $^4J_{P\text{-}H}$ = 2.0 Hz, 6H), 1.25 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 204.7 (dd, $^1J_{P\text{-}C}$ = 63.0 Hz and $^1J_{P\text{-}C}$ = 56.5 Hz), 195.1 (d, $^2J_{P\text{-}C}$ = 61.0 Hz), 157.8, 157.7, 150.5, 142.8 (dd, $^3J_{P\text{-}C}$ = 5.8 Hz and $^3J_{P\text{-}C}$ = 2.9 Hz), 140.4 (d, $^3J_{P\text{-}C}$ = 2.8 Hz), 138.8 (d, $^2J_{P\text{-}C}$ = 16.2 Hz), 128.5 (d, $^3J_{P\text{-}C}$ = 4.8 Hz), 127.7, 127.4, 124.0, 113.32, 113.30, 55.4, 55.3, 45.1 (dd, $^2J_{P\text{-}C}$ = 17.2 Hz and $^3J_{P\text{-}C}$ = 2.9 Hz), 42.9 (t, $^2J_{P\text{-}C}$ = 17.7 Hz), 34.8 (t, $^3J_{P\text{-}C}$ = 9.1 Hz), 34.6, 33.4 (d, $^3J_{P\text{-}C}$ = 17.1 Hz), 31.4. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 259.1 (d, $^2J_{P\text{-}P}$ = 30.5 Hz), 153.7 (d, $^2J_{P\text{-}P}$ = 30.5 Hz). HRMS (FAB) Calcd. for $C_{32}H_{39}NO_2P_2$ $[M]^+$: 531.2456. Found: 531.2480.



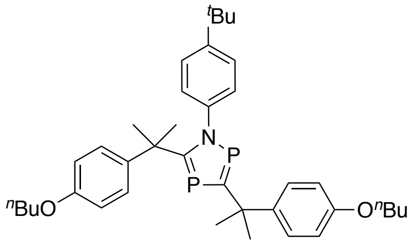
3r

36% Yield. A pale yellow solid, m.p. = 110.1-111.5 ºC. ^{1}H NMR ($CDCl_3$): δ 7.49-7.46 (m, 2H), 6.95-6.92 (m, 2H), 6.85-6.83 (m, 2H), 6.78-6.75 (m, 2H), 6.62-6.58 (m, 2H), 6.52-6.50 (m, 2H), 4.03-3.95 (m, 4H), 1.92 (s, 6H), 1.65 (d, $^4J_{P\text{-}H}$ = 2.0 Hz, 6H), 1.43-1.37 (m, 6H), 1.25 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 204.8 (dd, $^1J_{P\text{-}C}$ = 63.4 Hz and $^1J_{P\text{-}C}$ = 56.5 Hz), 195.1 (d, $^1J_{P\text{-}C}$ = 59.4 Hz), 157.2, 157.0, 150.5, 142.6 (dd, $^3J_{P\text{-}C}$ = 6.3 Hz and $^3J_{P\text{-}C}$ = 2.4 Hz), 140.3, 138.8 (d, $^2J_{P\text{-}C}$ = 15.3 Hz), 128.5 (d, $^3J_{P\text{-}C}$ = 4.8 HZ), 127.7, 127.4, 124.0, 114.0, 113.8, 63.5, 63.4, 45.1 (dd, $^2J_{P\text{-}C}$ = 17.2 Hz and $^3J_{P\text{-}C}$ = 2.9 Hz), 42.9 (t, $^2J_{P\text{-}C}$ = 17.3 Hz), 34.8 (t, $^3J_{P\text{-}C}$ = 8.6 Hz), 34.6, 33.4 (d, $^3J_{P\text{-}C}$ = 17.3 Hz), 31.4, 15.1, 15.0. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 259.2 (d, $^2J_{P\text{-}P}$ = 30.5 Hz), 153.8 (d, $^2J_{P\text{-}P}$ = 30.5 Hz). HRMS (FAB) Calcd. for $C_{34}H_{43}NO_2P_2$ $[M]^+$: 559.2769. Found: 559.2759.



3s

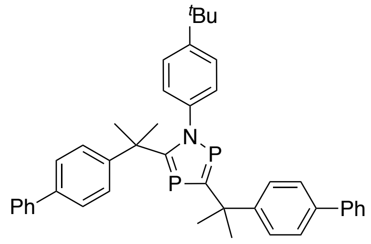
31% Yield. A pale yellow solid, m.p. = 109.5-110.8 ºC. ^{1}H NMR ($CDCl_3$): δ 7.48-7.45 (m, 2H), 6.94-6.92 (m, 2H), 6.86-6.82 (m, 2H), 6.77-6.74 (m, 2H), 6.62-6.58 (m, 2H), 6.52-6.50 (m, 2H), 3.91-3.85 (m, 4H), 1.92 (s, 6H), 1.85-1.74 (m, 4H), 1.65 (d, $^{4}J_{P\text{-}H}$ = 1.6 Hz, 6H), 1.25 (s, 9H), 1.06-1.00 (m, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 204.8 (dd, $^{1}J_{P\text{-}C}$ = 62.8 Hz and $^{1}J_{P\text{-}C}$ = 56.1 Hz), 195.1 (d, $^{1}J_{P\text{-}C}$ = 60.4 Hz), 157.4, 157.2, 150.4, 142.6 (dd, $^{3}J_{P\text{-}C}$ = 6.7 Hz and $^{3}J_{P\text{-}C}$ = 2.9 Hz), 140.2 (d, $^{3}J_{P\text{-}C}$ = 2.9 Hz), 138.8 (d, $^{2}J_{P\text{-}C}$ = 16.3 Hz), 128.5 (d, $^{3}J_{P\text{-}C}$ = 5.7 Hz), 127.7, 127.4, 124.0, 114.0, 113.8, 69.7, 69.4, 45.1 (dd, $^{2}J_{P\text{-}C}$ = 17.2 Hz and $^{3}J_{P\text{-}C}$ = 2.9 Hz), 42.9 (t, $^{2}J_{P\text{-}C}$ = 17.3 Hz), 34.8 (t, $^{3}J_{P\text{-}C}$ = 9.1 Hz), 34.6, 33.4 (d, $^{3}J_{P\text{-}C}$ = 17.2 Hz), 31.4, 22.8, 22.7, 10.74, 10.70. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 259.1 (d, $^{2}J_{P\text{-}P}$ = 30.4 Hz), 153.6 (d, $^{2}J_{P\text{-}P}$ = 30.4 Hz). HRMS (FAB) Calcd. for $C_{36}H_{47}NO_2P_2$ $[M]^+$: 578.3082. Found: 578.3069.



3t

27% Yield. A pale yellow solid, m.p. = 115.3-116.7 ºC. ^{1}H NMR ($CDCl_3$): δ 7.48-7.46 (m, 2H), 6.94-6.92 (m, 2H), 6.85-6.83 (m, 2H), 6.77-6.75 (m, 2H), 6.61-6.59 (m, 2H), 6.52-6.50 (m, 2H), 3.95-3.89 (m, 4H), 1.92 (s, 6H), 1.80-1.71 (m, 4H), 1.65 (d, $^{4}J_{P\text{-}H}$ = 1.6 Hz, 6H), 1.54-1.43 (m, 4H), 1.25 (s, 9H), 1.00-0.94 (m, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 204.8 (dd, $^{1}J_{P\text{-}C}$ = 63.0 Hz and $^{1}J_{P\text{-}C}$ = 56.3 Hz), 195.1 (d, $^{1}J_{P\text{-}C}$ = 60.0 Hz), 157.5, 157.3, 150.4, 142.6 (t, $^{3}J_{P\text{-}C}$ = $^{3}J_{P\text{-}C}$ = 2.9 Hz), 140.2, 138.8 (d, $^{2}J_{P\text{-}C}$ = 15.2 Hz), 128.5 (d, $^{3}J_{P\text{-}C}$ = 4.8 Hz), 127.7, 127.4, 124.0, 114.0, 113.8, 67.8, 67.6, 45.1 (dd, $^{2}J_{P\text{-}C}$ = 17.2 Hz and $^{3}J_{P\text{-}C}$ = 2.9 Hz), 42.9 (t, $^{2}J_{P\text{-}C}$ = 17.7 Hz), 34.9 (t, $^{3}J_{P\text{-}C}$ = 9.1 Hz), 34.6, 33.5, 33.3, 31.5 (d, $^{3}J_{P\text{-}C}$ = 9.5 Hz), 31.4, 19.44, 19.42, 14.0. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 259.2 (d, $^{2}J_{P\text{-}P}$ = 30.5 Hz), 153.6 (d, $^{2}J_{P\text{-}P}$ = 30.5 Hz). HRMS (FAB)

Calcd. for $C_{38}H_{52}NO_2P_2$ $[M+H]^+$: 616.3473. Found: 616.3494.



3u

41% yield. A yellow soild, m.p. = 154.6-156.1 ºC. ^{1}H NMR ($CDCl_3$): δ 7.67-7.55 (m, 9H), 7.46-7.39 (m, 5H), 7.36-7.29 (m, 4H), 6.96-6.89 (m, 3H), 6.57-6.55 (m, 1H), 2.00 (s, 6H), 1.74 (d, $^4J_{P-H}$ = 2.0 Hz, 6H), 1.22 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 203.7 (dd, $^1J_{P-C}$ = 63.5 Hz and $^1J_{P-C}$ = 56.8 Hz), 194.9 (d, $^1J_{P-C}$ = 60.0 Hz), 150.7, 149.7 (dd, $^3J_{P-C}$ = 5.7 Hz and $^3J_{P-C}$ = 1.9 Hz), 147.2 (d, $^3J_{P-C}$ = 2.9 Hz), 141.0, 138.9, 138.7 (d, $^2J_{P-C}$ = 16.2 Hz), 138.5, 128.9, 128.8, 128.6 (d, $^3J_{P-C}$ = 5.7 Hz), 127.24, 127.17, 127.1, 127.0, 126.8, 126.6, 124.1, 45.5 (dd, $^2J_{P-C}$ = 17.2 Hz and $^3J_{P-C}$ = 2.9 Hz), 43.4 (t, $^2J_{P-C}$ = 17.7 Hz), 34.7 (t, $^3J_{P-C}$ = 9.5 Hz), 34.6, 33.3 (d, $^3J_{P-C}$ = 17.1 Hz), 31.4. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 260.2 (d, $^2J_{P-P}$ = 30.5 Hz), 154.9 (d, $^2J_{P-P}$ = 30.5 Hz). HRMS (FAB) Calcd. for $C_{42}H_{44}NP_2$ $[M+H]^+$: 624.2949. Found: 624.2974.

3. X-ray crystallographic analysis of 3a

Crystals suitable for an X-ray analysis was obtained by the vapor-assisted recrystallization from Et_2O (**3a**). Diffraction data were collected for the 2θ range of 5 to 55° at –95 °C on a Rigaku R-AXIS RAPID imaging plate area detector with graphite monochromated Mo-$K\alpha$ (λ = 0.71075 Å) radiation with VariMax optics. Intensity data were corrected for empirical absorptions (ABSCOR), and for Lorentz and polarization effects. Structure solutions and refinements were carried out by using CrystalStructure package.[S3] The positions of non-hydrogen atoms were determined by direct methods (SHELXS Version 2013/1)[S4] and subsequent Fourier synthesis (SHELXL Version 2016/6)[S4], and were refined on F_o^2 using all the unique reflections by full-matrix least squares.

As the molecule is packed in an S_1 symmetry with a mirror plane consisting of a five-membered ring (P(1)–C(1)–P(2)–C(2)–N(1)), C(7)–C(8)–C(9) and C(13) in one of the two 1-adamantyl groups, and C(14) in the other 1-adamantyl group, the asymmetric unit contains only a half of the molecule. Here, the latter 1-adamantyl group (C(14) to C(23)) is heavily disordered among two positions sharing C(14), positions of the nine carbon atoms (C(15) to C(23)) were solved with isotropic thermal parameters, where positions of 15 hydrogen atoms attached to the 1-adamantyl carbon atoms could not be located. In addition, the former 1-adamantyl group (C(7) to C(13)) is also slightly disordered, thus one shared carbon atom (C(13)) was solved isotropically. All the other non-hydrogen atoms were solved with anisotropic thermal parameters, while all the other hydrogen atoms were located at the calculated positions. Anomalous dispersion effects were included in F_c, and neutral atom scattering factors and the values for $\Delta f'$ and$\Delta f''$ were taken from ref. S5. Details of the crystal and data collection parameters are summarized in Table S1.

According to the checkCIF reports, there are three B-level alerts for crystallographic data of **3a**. The first B-level alert of **3a** (PLAT043_ALERT_1_B Calculated and Reported Mol. Weight Differ by .. 15.15 Check) is due to a heavy disorder in one of the two 1-adamantyl groups, where positions of 15 hydrogen atoms could not be located properly. The second B-level alert of **3a** (PLAT201_ALERT_2_B Isotropic non-H Atoms in Main Residue(s) .... 1 Report) is also due to a disorder of the C(13) atom in a mirror plane, which was solved isotropically. The third B-level alert of **3a** (PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds .... 0.01013 Ang) is due to the heavy disorders as mentioned above.

Crystallographic data for the structure of **3a** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1974229. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Data collection parameters.

compound	**3a**
CCDC number	
chemical formula	$C_{28}H_{35}NP_2$
formula weight	447.54
crystal size (mm^3)	0.29 × 0.16 × 0.11
crystal color, habit	colorless, plate
crystal system	orthorhombic
space group	*Pnma* (#62)
a (Å)	14.2420(9)
b (Å)	10.3185(7)
c (Å)	16.3776(9)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	2406.8(3)
Z	4
D_{calcd} (g cm^{-3})	1.235
F(000)	960
μ_{calcd} (cm^{-1})	1.966
radiation	Mo-Kα (λ = 0.71075 Å)
temperature (ºC)	–95.0
transmission factors rage	0.560 – 0.979
no. measured reflections	19428
no. unique reflections	2989 (R_{int} = 0.0812)
no. refined parameters	152
$R1$ ($I > 2\sigma(I)$)[a]	0.1398
$wR2$ (all data)[b]	0.2519
GOF[c]	1.000

[a] $R1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$.
[b] $wR2 = [\Sigma(w(Fo^2 - Fc^2)^2)/ \Sigma w(Fo^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + 17.65P]$, where $P = (F_o^2 + 2F_c^2)/3$.
[c] GOF = $[\Sigma w(Fo^2 - Fc^2)^2/(N_{obs} - N_{params})]^{1/2}$.

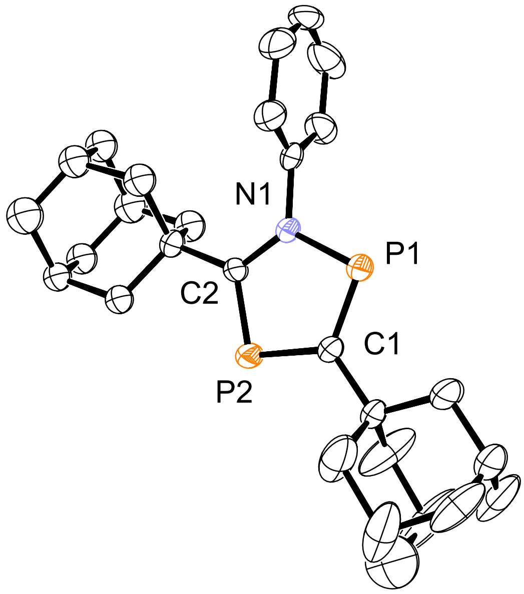


Figure S1. ORTEP drawing of **3a**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (º): P1–C1, 1.696(7); P1–N1, 1.710(5); P2–C2, 1.737(7); P2–C1, 1.755(7); N1–C2, 1.383(8); C1–P1–N1, 95.5(3); C2–P2–C1, 95.9(3); C2–N1–C3, 127.1(5); C2–N1–P1, 119.2(4); C3–N1–P1, 113.7(4).

4. References

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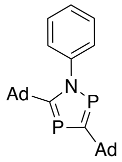
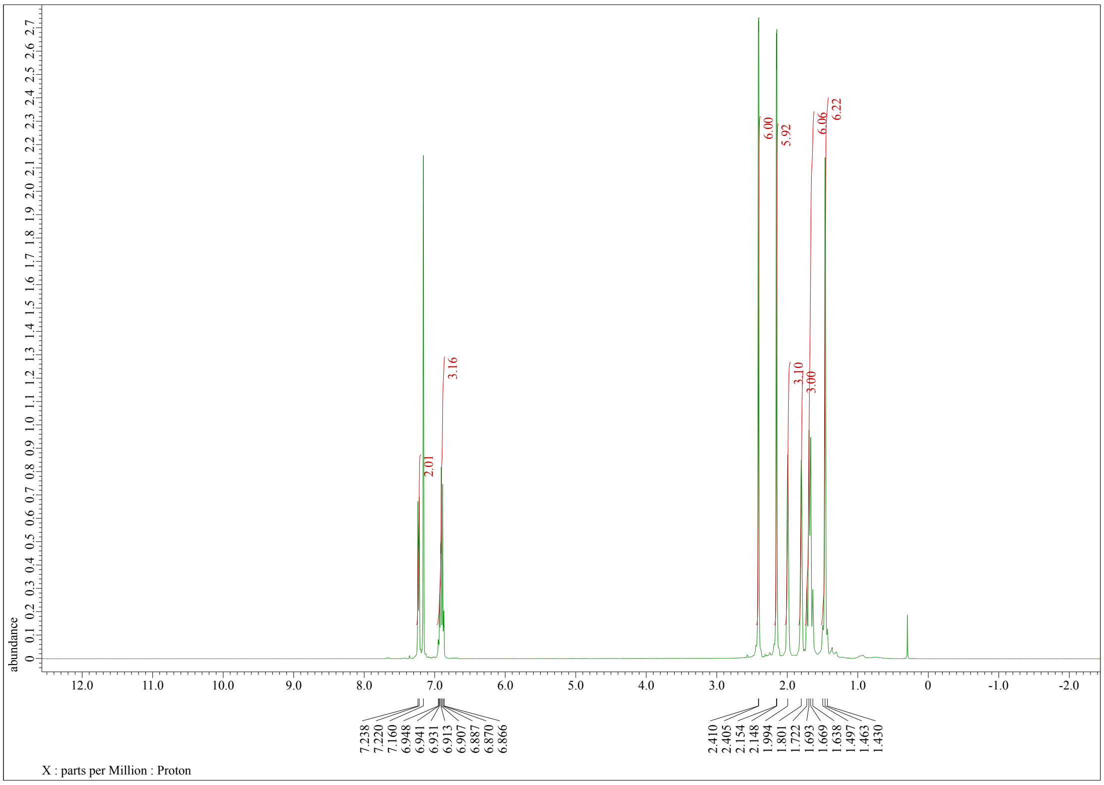
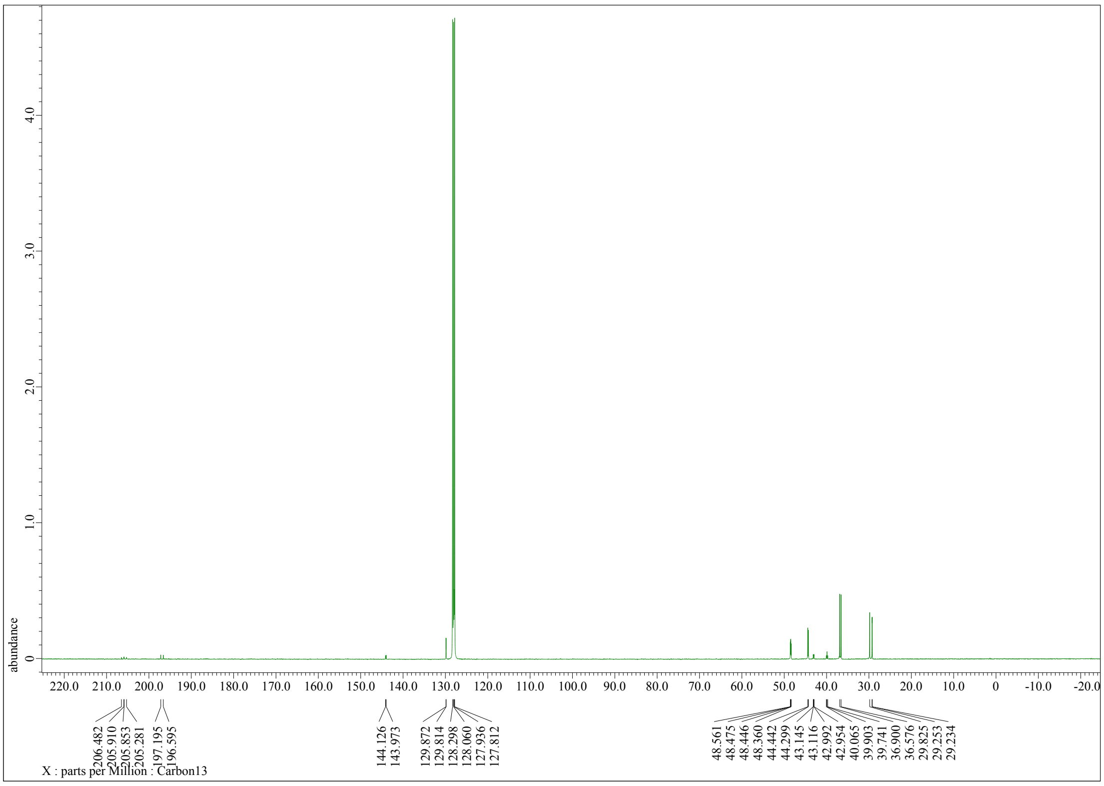
S5. (a) International Tables for Crystallography, Vol. C (1992), Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, Netherlands, Table 6.1.1.4, pp. 572. (b) J. A. Ibers, W. C. Hamilton, Acta Crystallogr., 1964, **17**, 781. (c) D. C. Creagh, W. J. McAuley, "International Tables for Crystallography," Vol C (1992), Ed. A. J. C. Wilson, Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222.

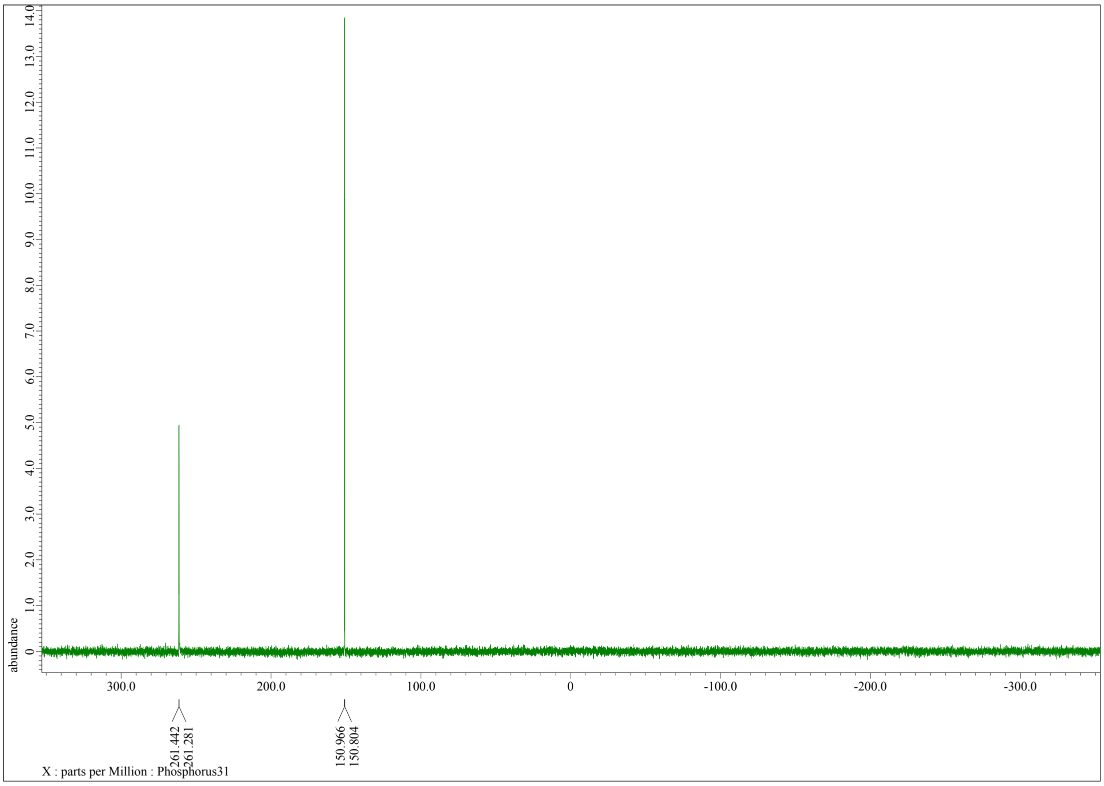
5. ^{1}H, ^{13}C and ^{31}P NMR spectra.



3a



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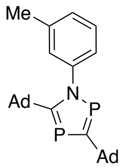
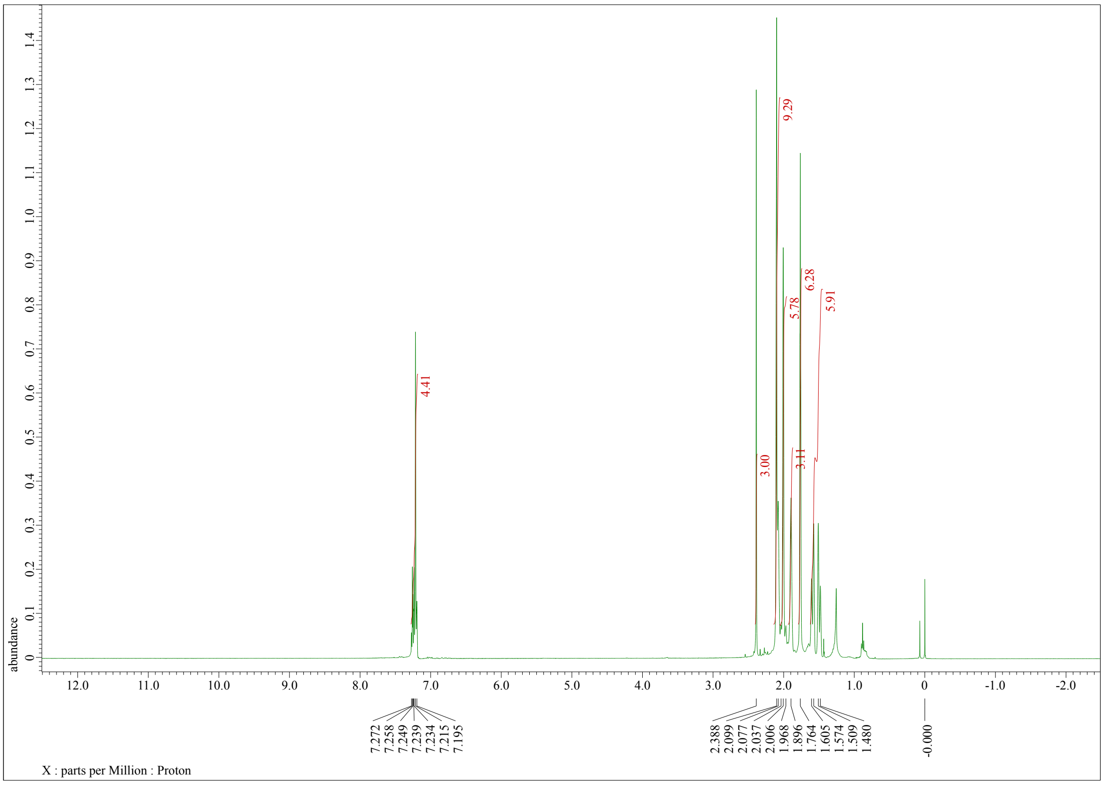
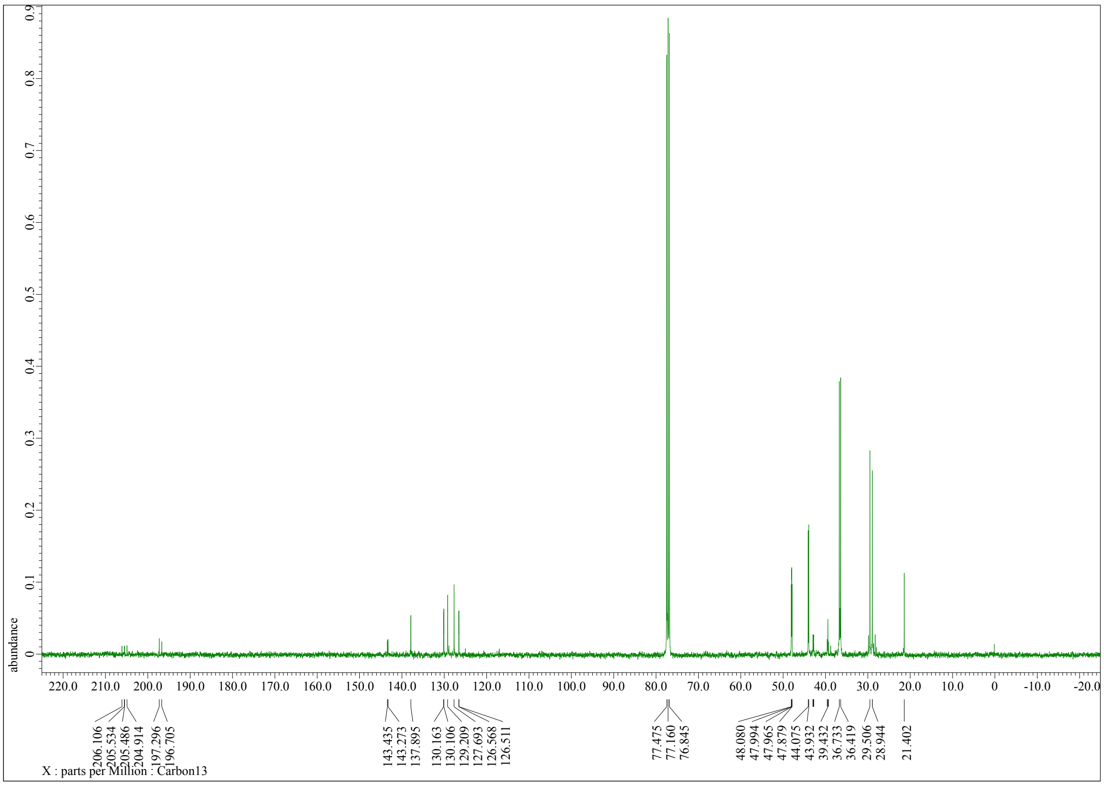
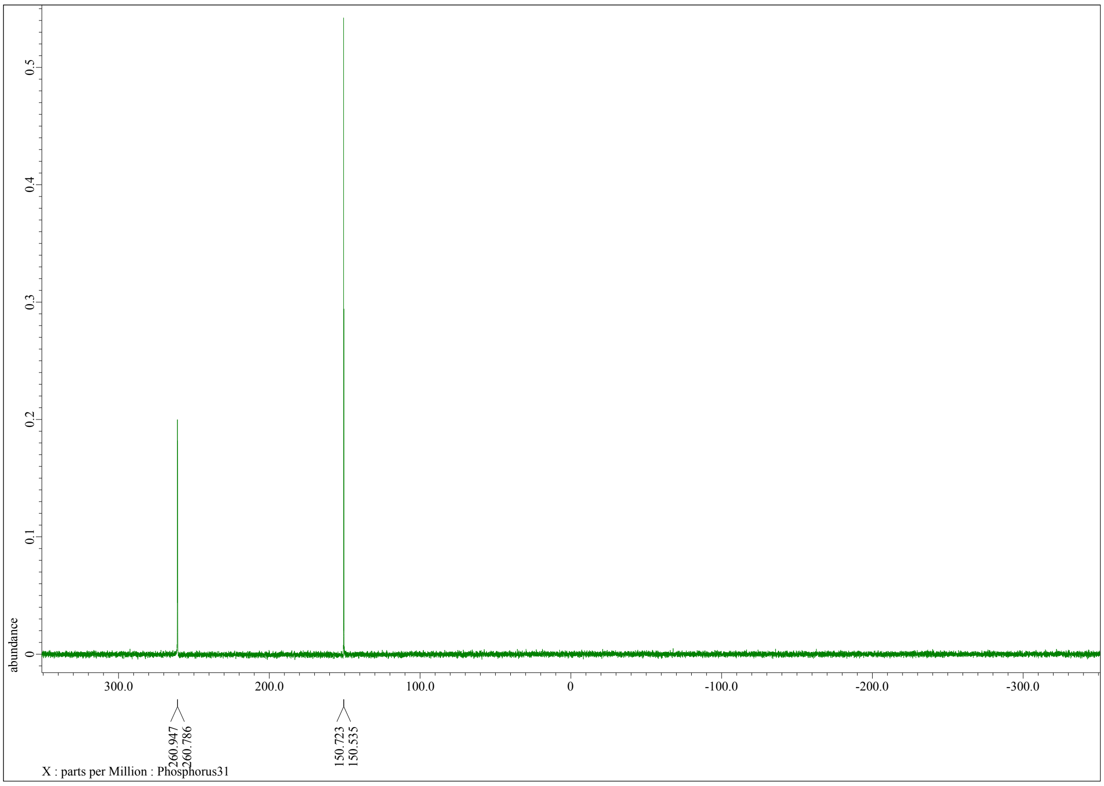
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
261.442
261.281
150.966
150.804
X : parts per Million : Phosphorus31



3b



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0.1
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260.786
150.723
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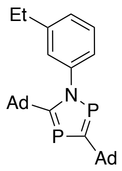
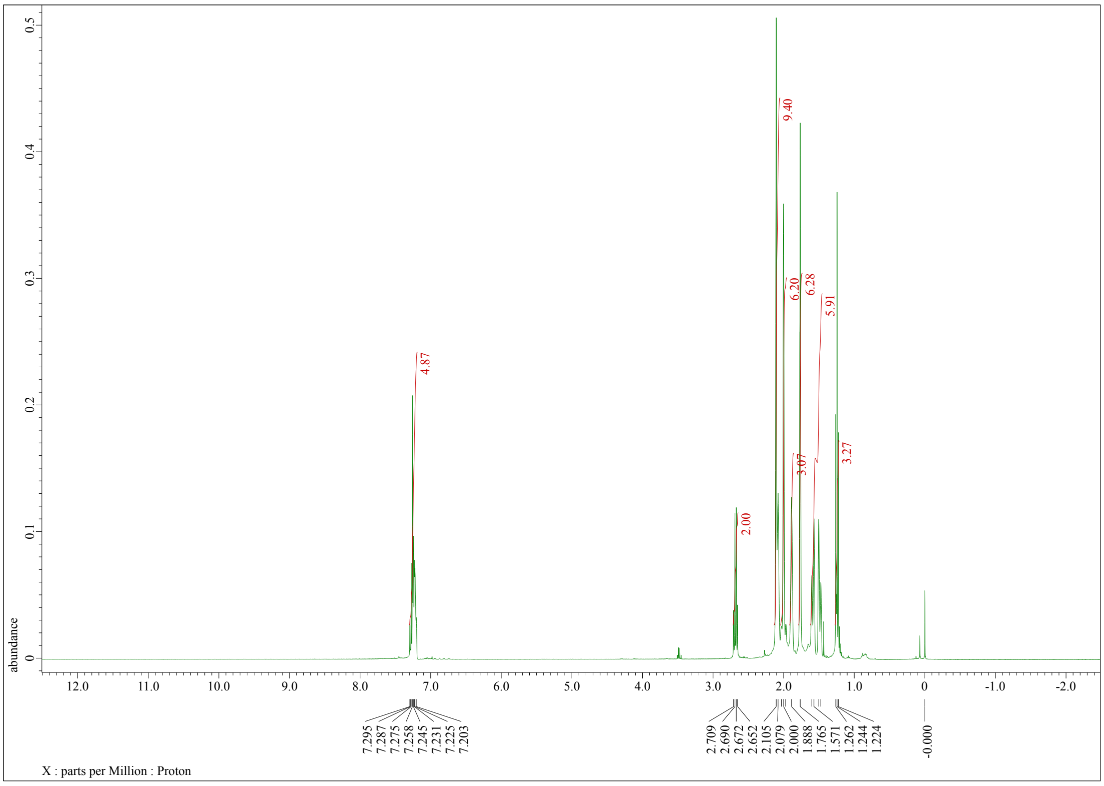
X : parts per Million : Phosphorus31



Et
N
P
Ad
P
Ad

3c



abundance
X : parts per Million : Proton
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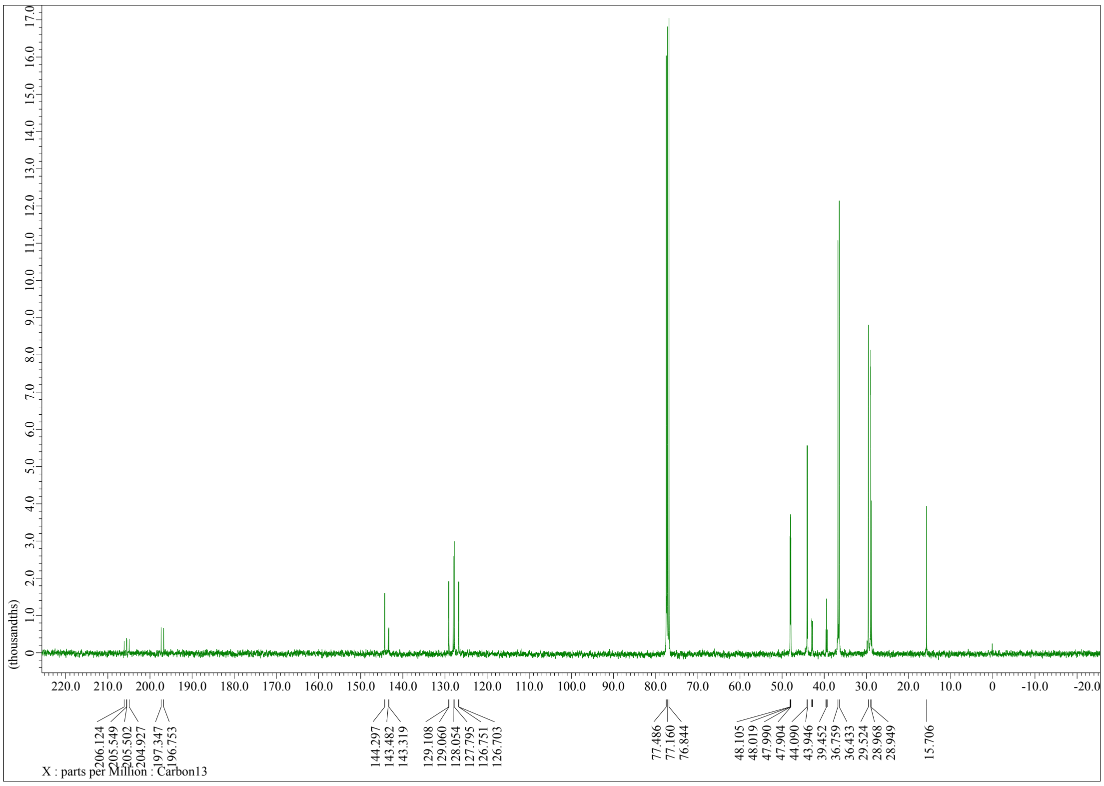
6.28
5.91
3.07
3.27
7.295
7.287
7.275
7.258
7.245
7.231
7.225
7.203
2.709
2.690
2.672
2.652
2.105
2.079
2.000
1.888
1.765
1.571
1.262
1.244
1.224
-0.000



(thousandths)
X : parts per Million : Carbon13
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205.549
205.502
204.927
197.347
196.753
144.297
143.482
143.319
129.108
129.060
128.054
127.795
126.751
126.703
77.486
77.160
76.844
48.105
48.019
47.990
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29.524
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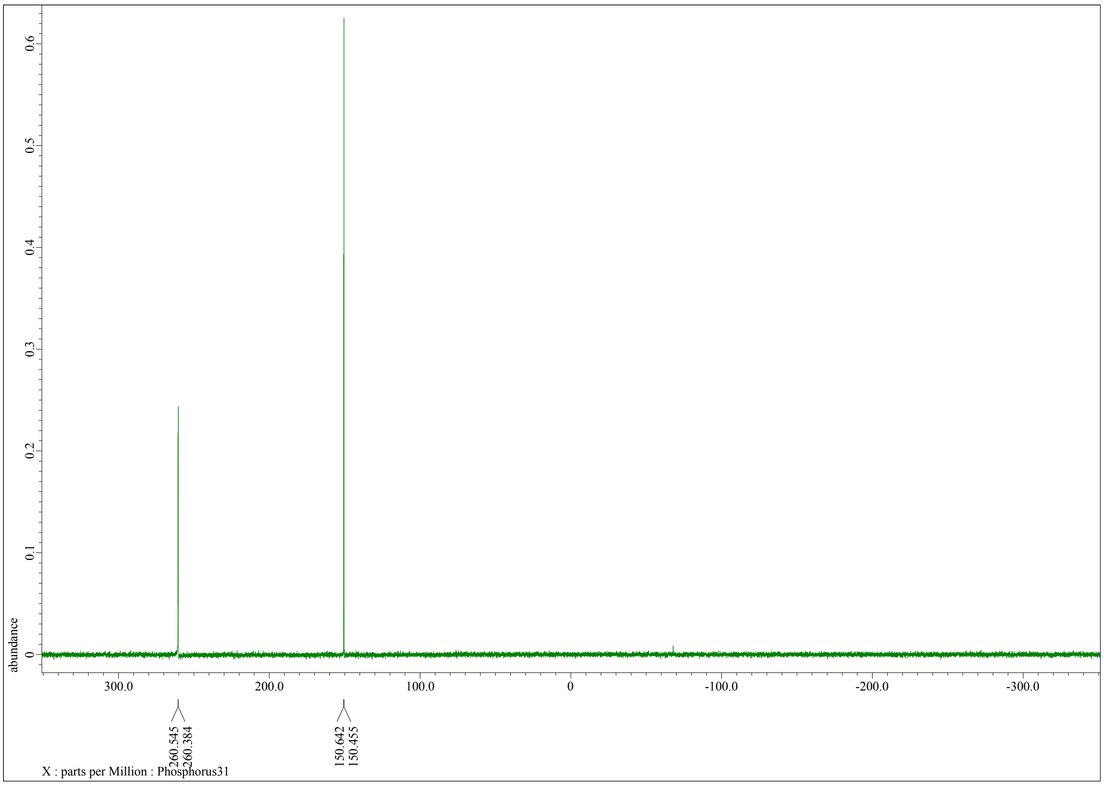
28.949
15.706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0.2
0.1
0
abundance
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-200.0
-300.0
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260.384
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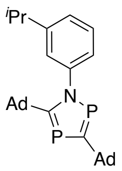
150.455
X : parts per Million : Phosphorus31



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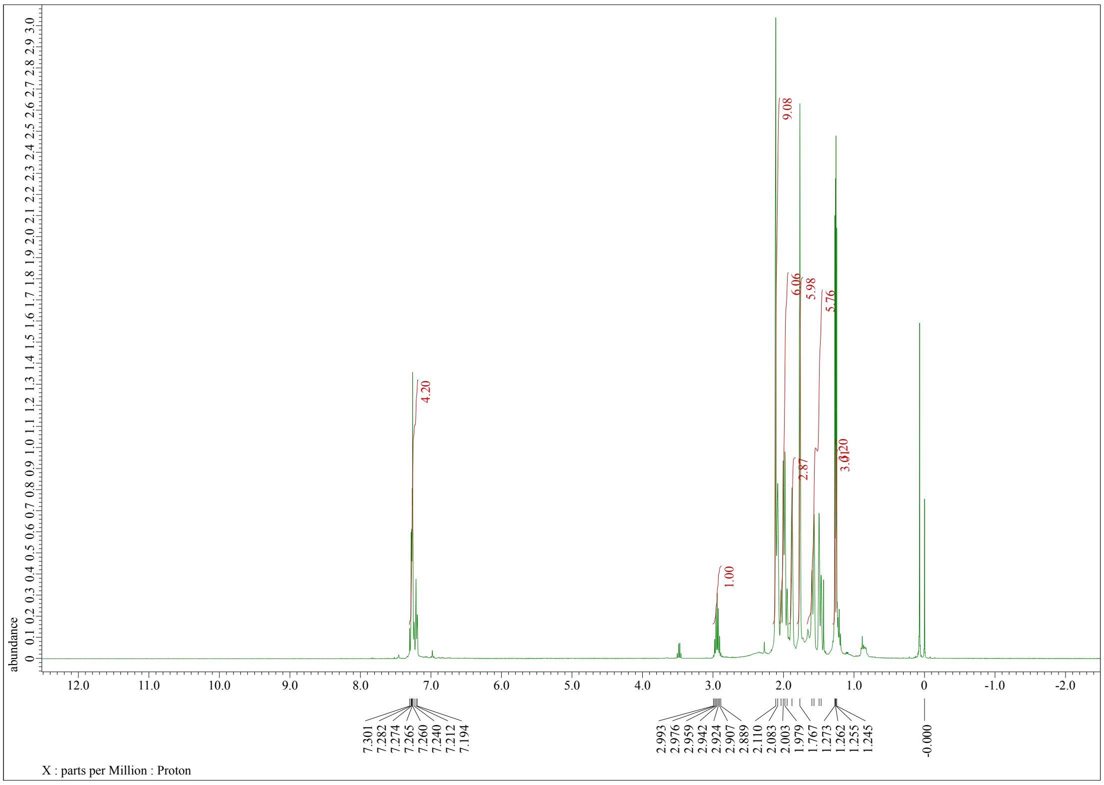

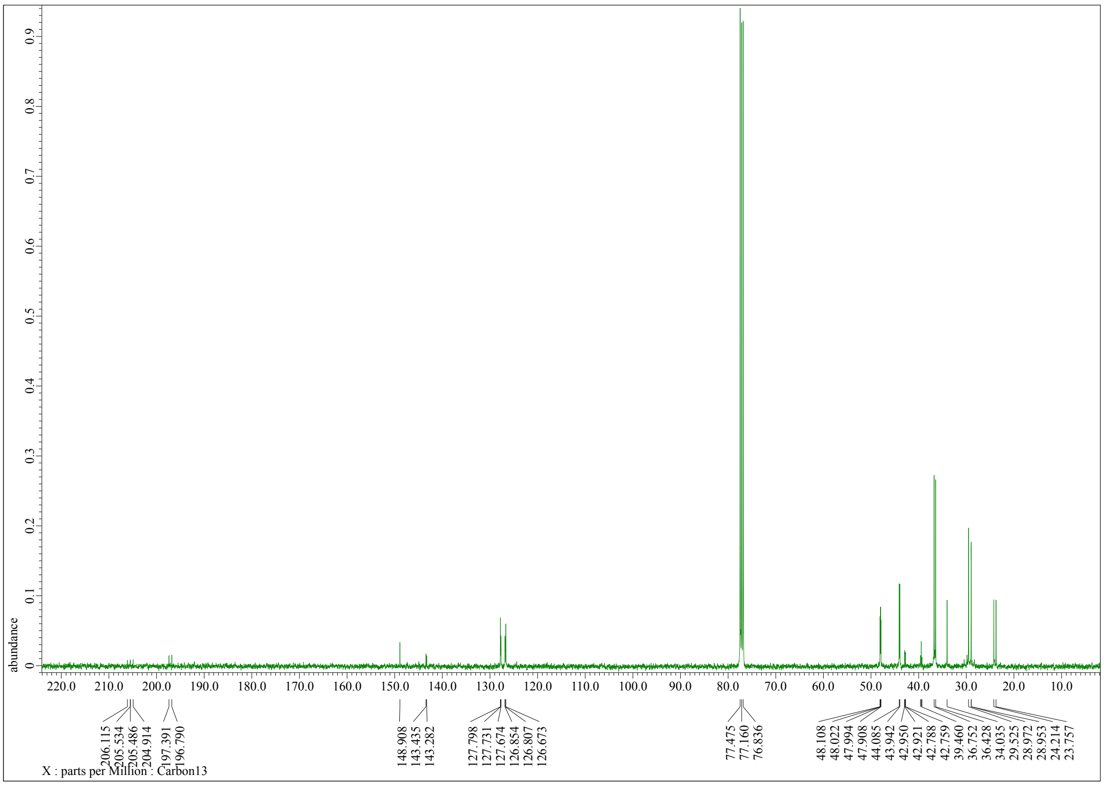

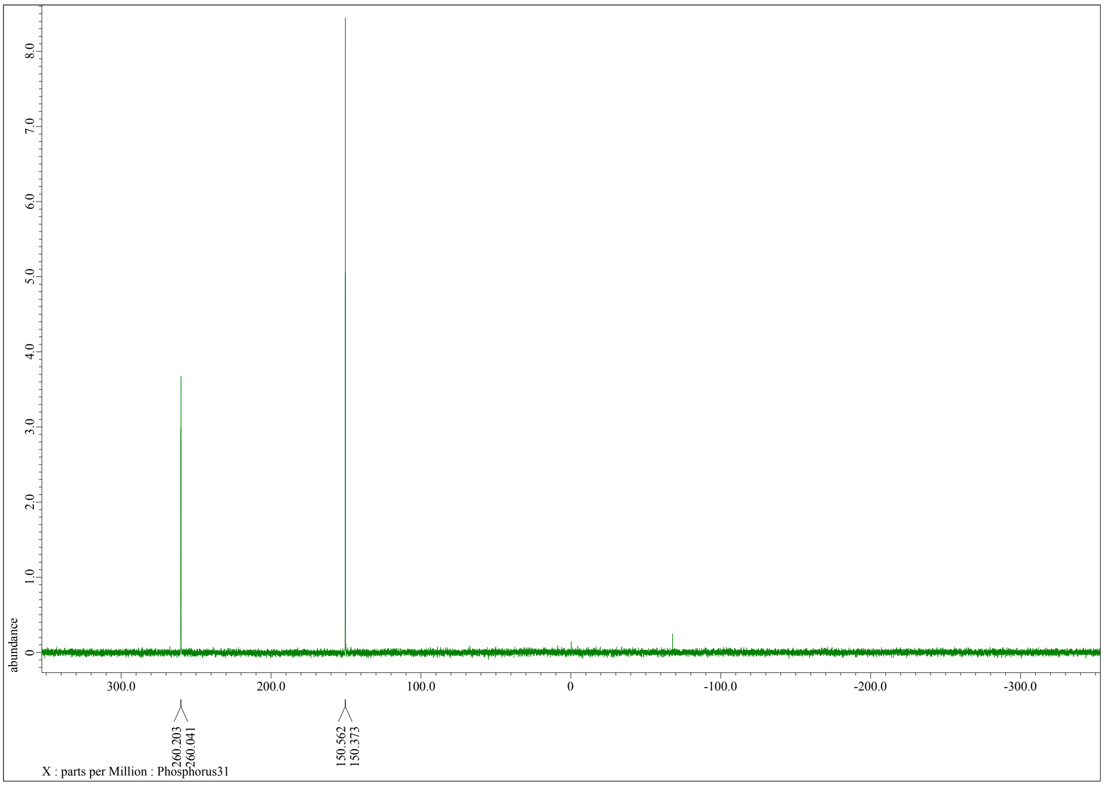

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7.0
6.0
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4.0
3.0
2.0
1.0
0
300.0
200.0
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0
-100.0
-200.0
-300.0
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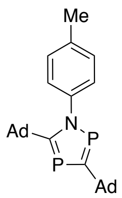
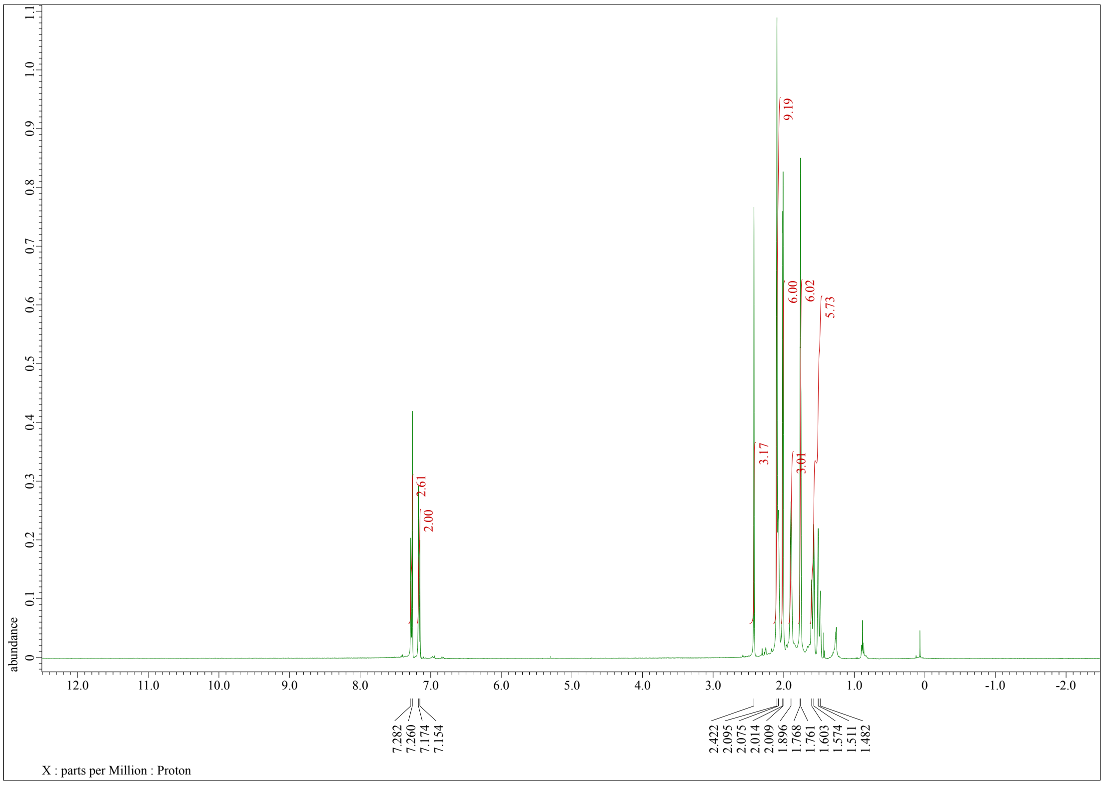
260.041
150.562
150.373
X : parts per Million : Phosphorus31


Me
N
P
Ad
P
Ad

3e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3.01
2.61
2.00
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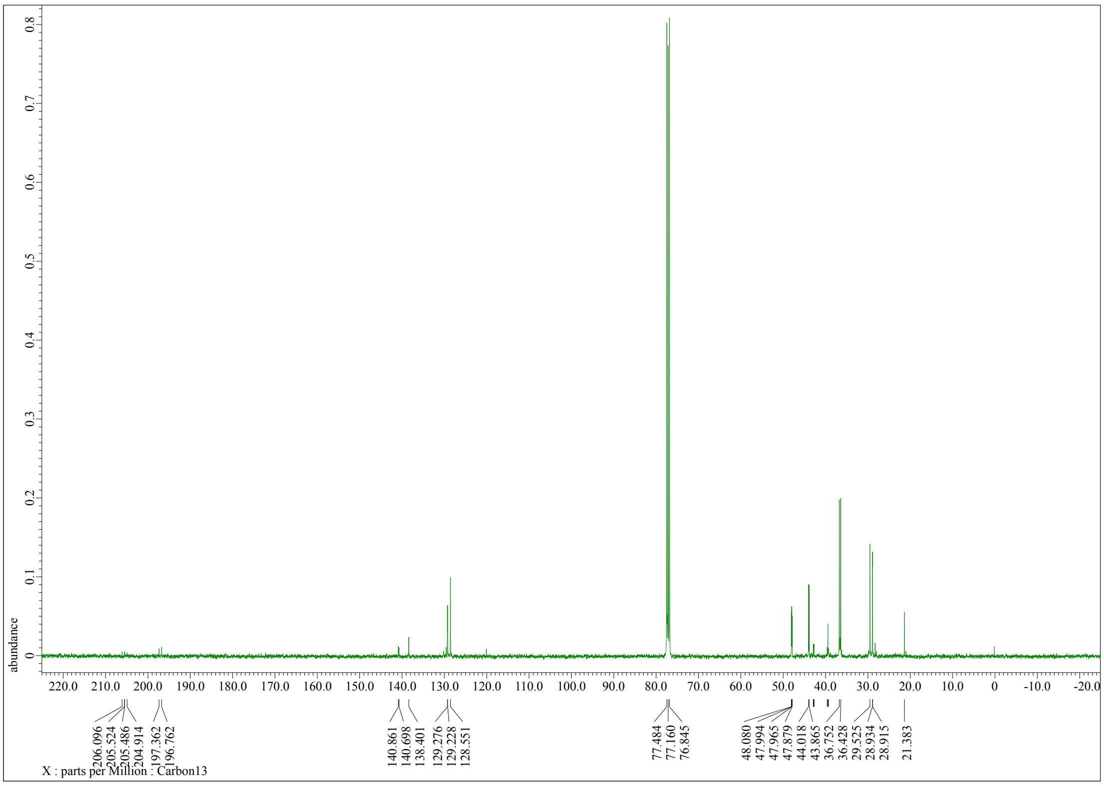
7.260
7.174
7.154
2.422
2.095
2.075
2.014
2.009
1.896
1.768
1.761
1.603
1.574
1.511
1.482
X : parts per Million : Proton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205.486
204.914
197.362
196.762
140.861
140.698
138.401
129.276
129.228
128.551
77.484
77.160
76.845
48.080
47.994
47.965
47.879
44.018
43.865
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36.428
29.525
28.934
28.915
21.383
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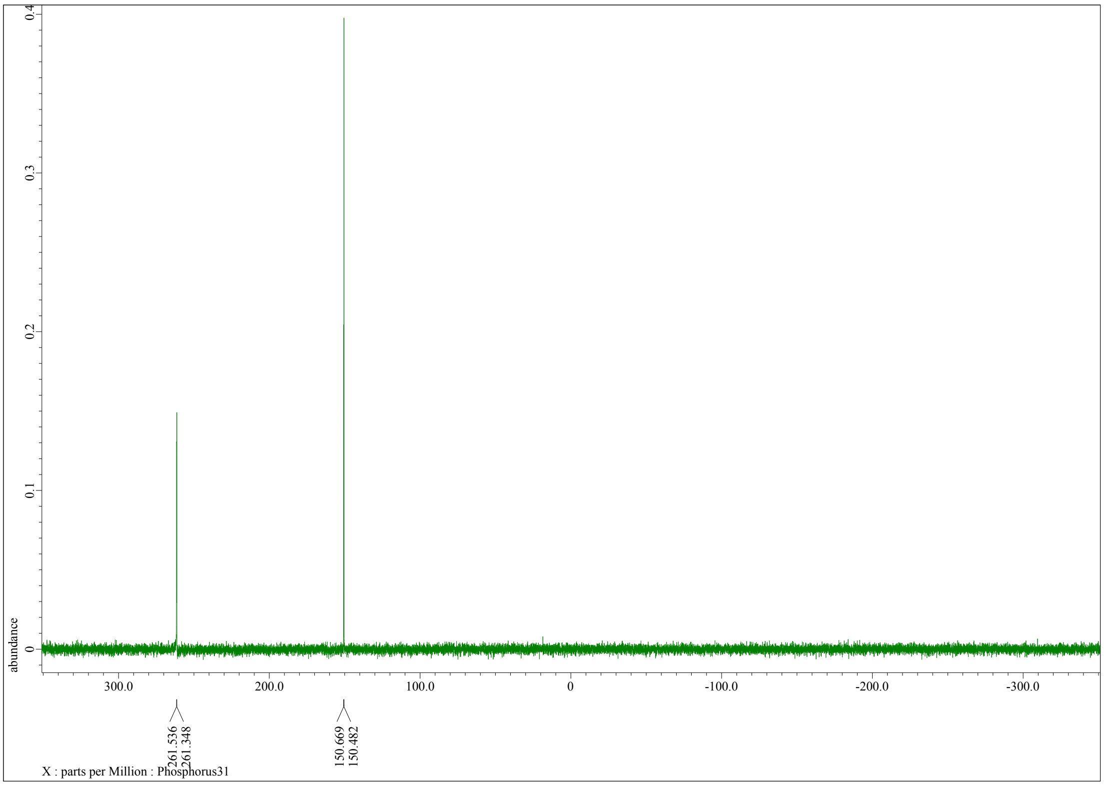
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0.3
0.2
0.1
0
abundance
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200.0
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0
-100.0
-200.0
-300.0
261.536
261.348
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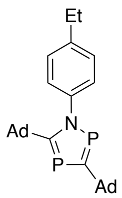
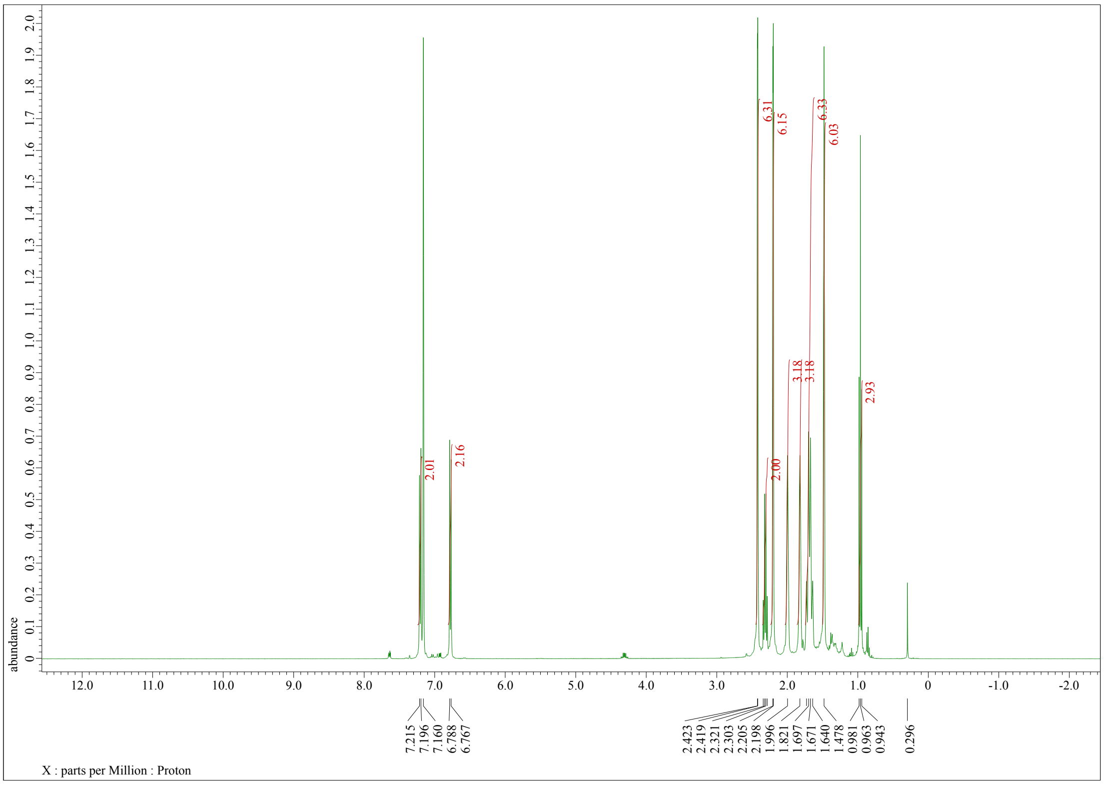
150.482
X : parts per Million : Phosphorus31


Et
N
P
Ad
P
Ad

3f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2.16
6.31
6.15
2.00
3.18
3.18
6.33
6.03
2.93
7.215
7.196
7.160
6.788
6.767
2.423
2.419
2.321
2.303
2.205
2.198
1.996
1.821
1.697
1.671
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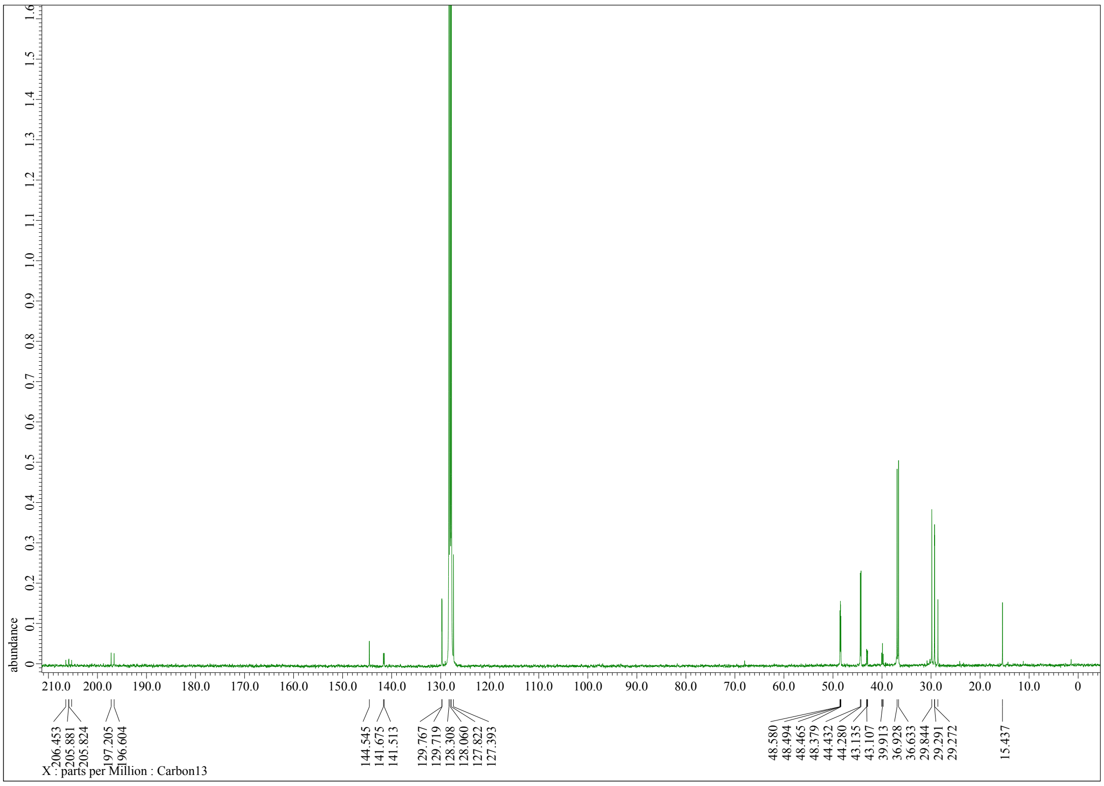
0.963
0.943
0.296
X : parts per Million : Proton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141.675
141.513
129.767
129.719
128.308
128.060
127.822
127.393
48.580
48.494
48.465
48.379
44.432
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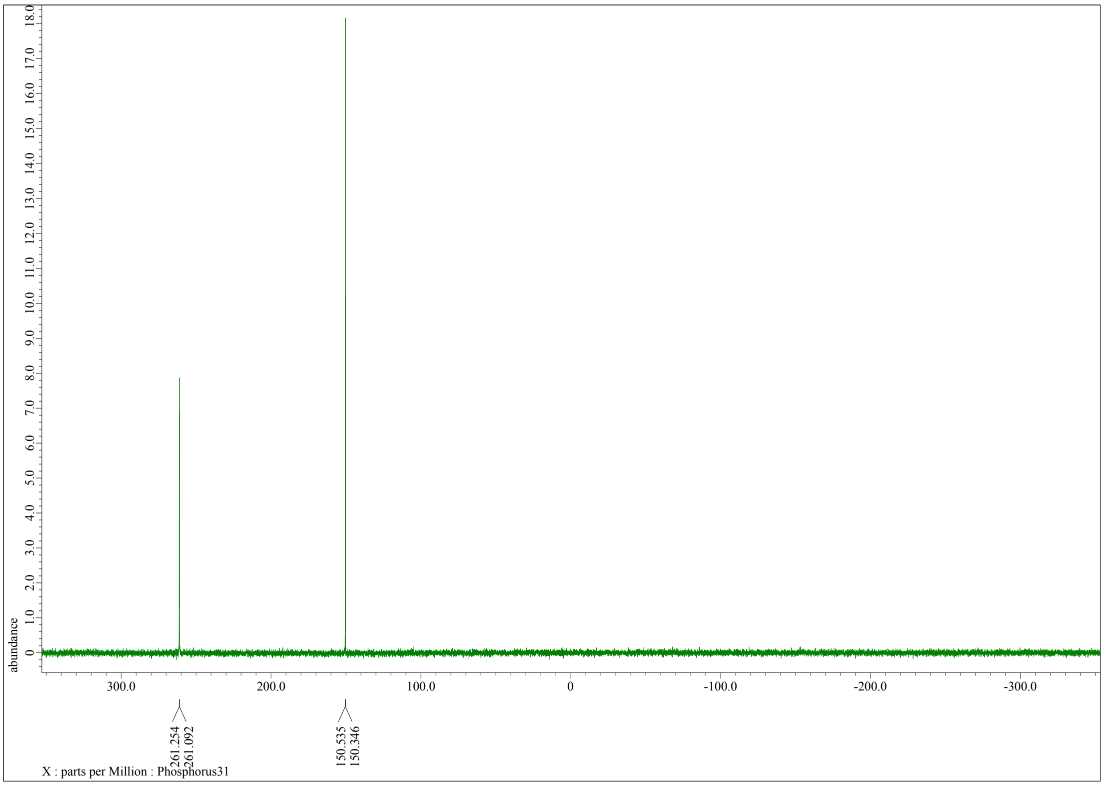

abundance
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15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
261.254
261.092
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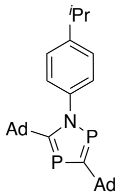
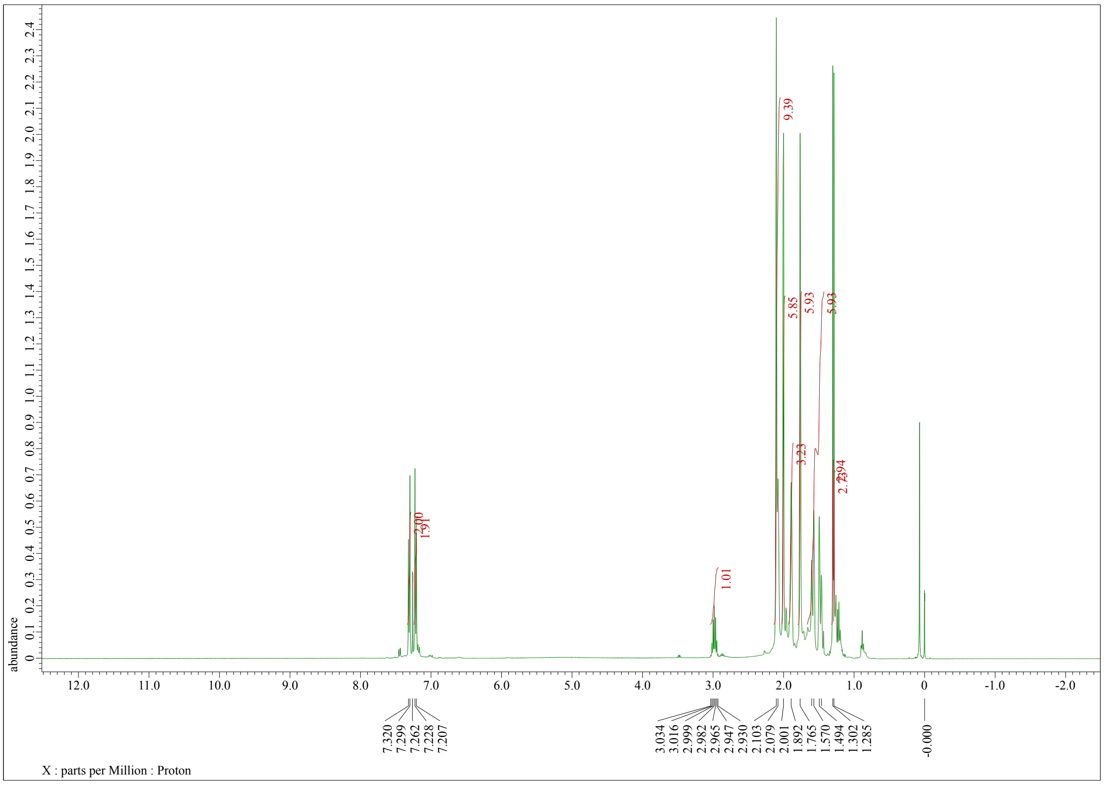
150.346
X : parts per Million : Phosphorus31



iPr
N
P
Ad
P
Ad

3g



abundance
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5.93
3.23
2.94
2.00
1.91
1.01
7.320
7.299
7.262
7.228
7.207
3.034
3.016
2.999
2.982
2.965
2.947
2.930
2.103
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1.302
1.285
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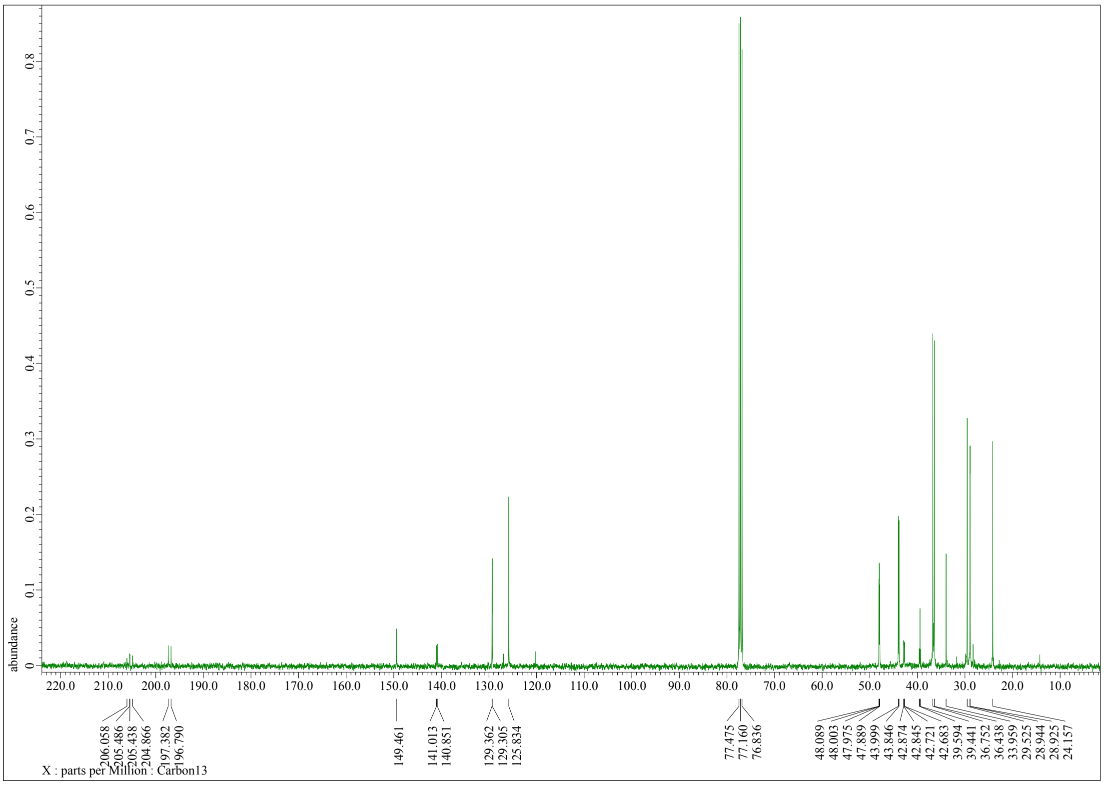

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196.790
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140.851
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129.305
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77.475
77.160
76.836
48.089
48.003
47.975
47.889
43.999
43.846
42.874
42.845
42.721
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24.157
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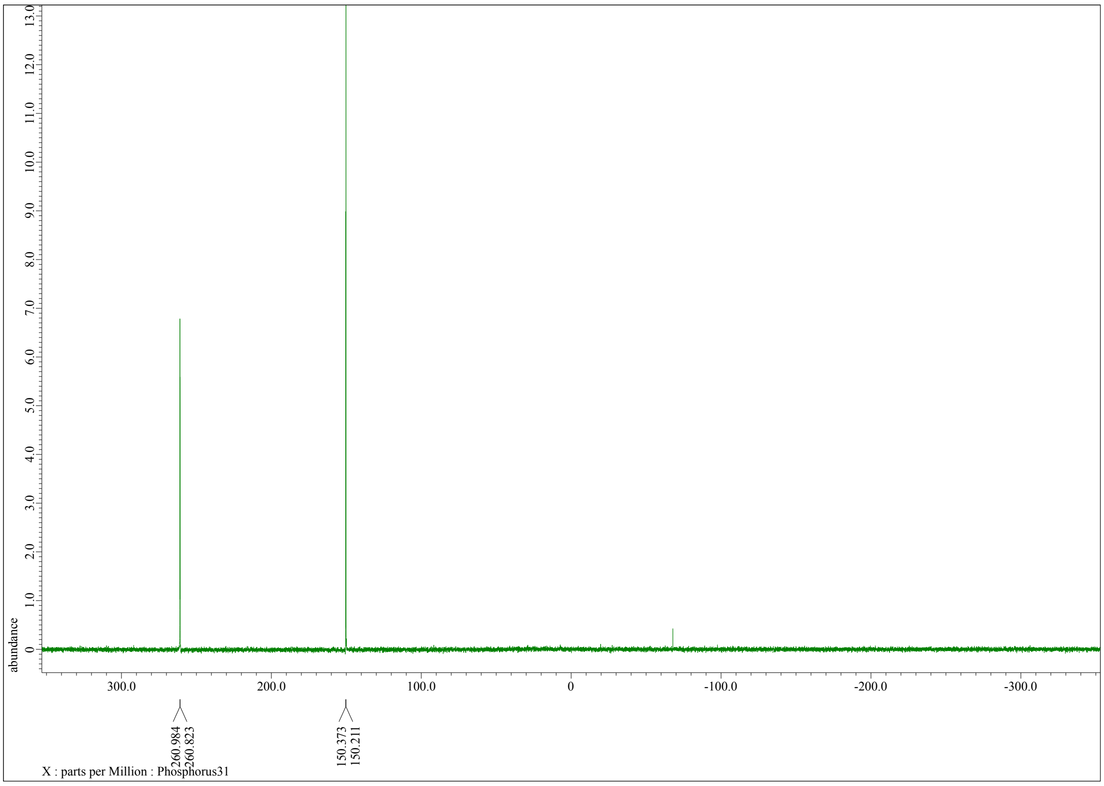
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3.0
4.0
5.0
6.0
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9.0
10.0
11.0
12.0
13.0
300.0
200.0
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-200.0
-300.0
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150.373
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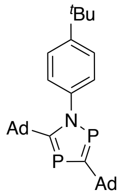
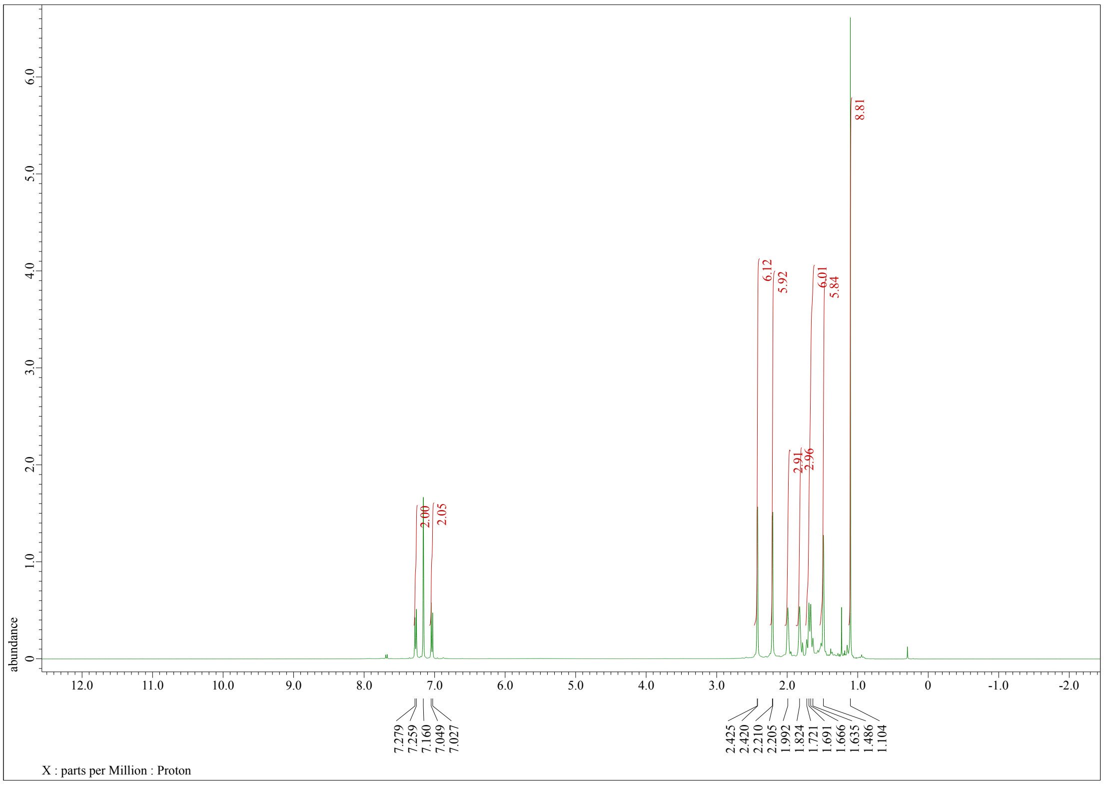

tBu
N
P
P
Ad
Ad

3h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2.96
2.00
2.05
7.279
7.259
7.160
7.049
7.027
2.425
2.420
2.210
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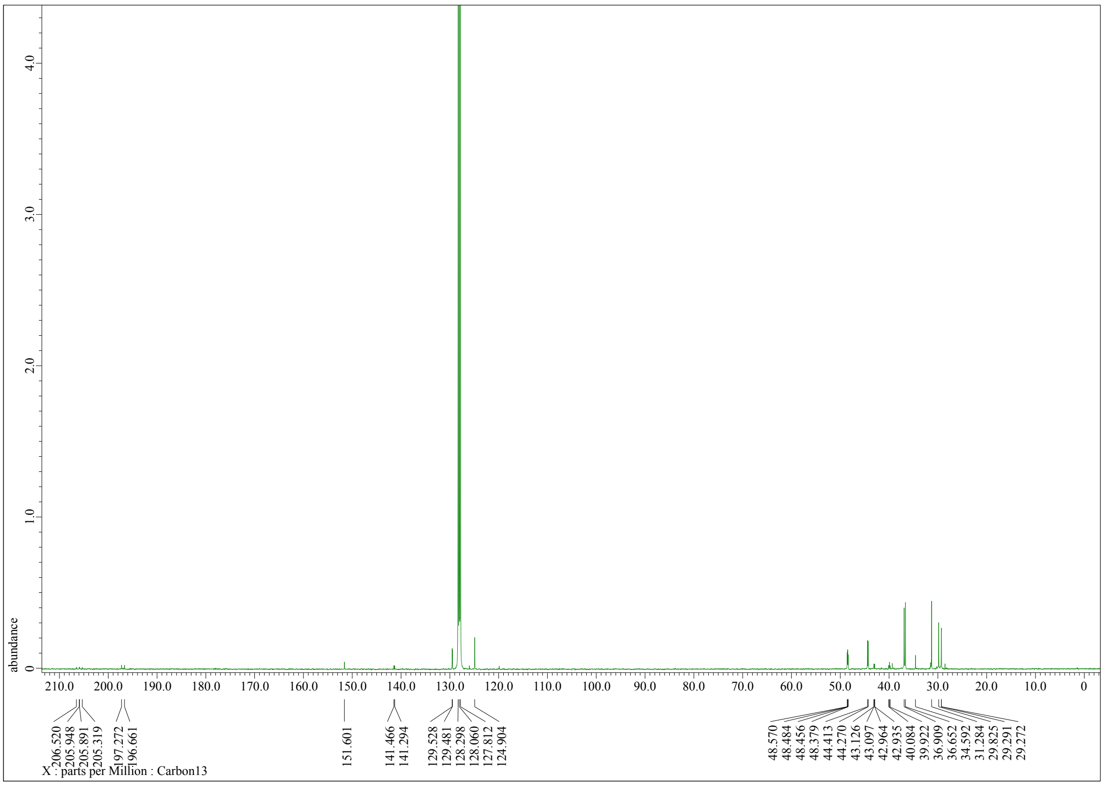
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128.298
128.060
127.812
124.904
48.570
48.484
48.456
48.379
44.413
44.270
43.126
43.097
42.964
42.935
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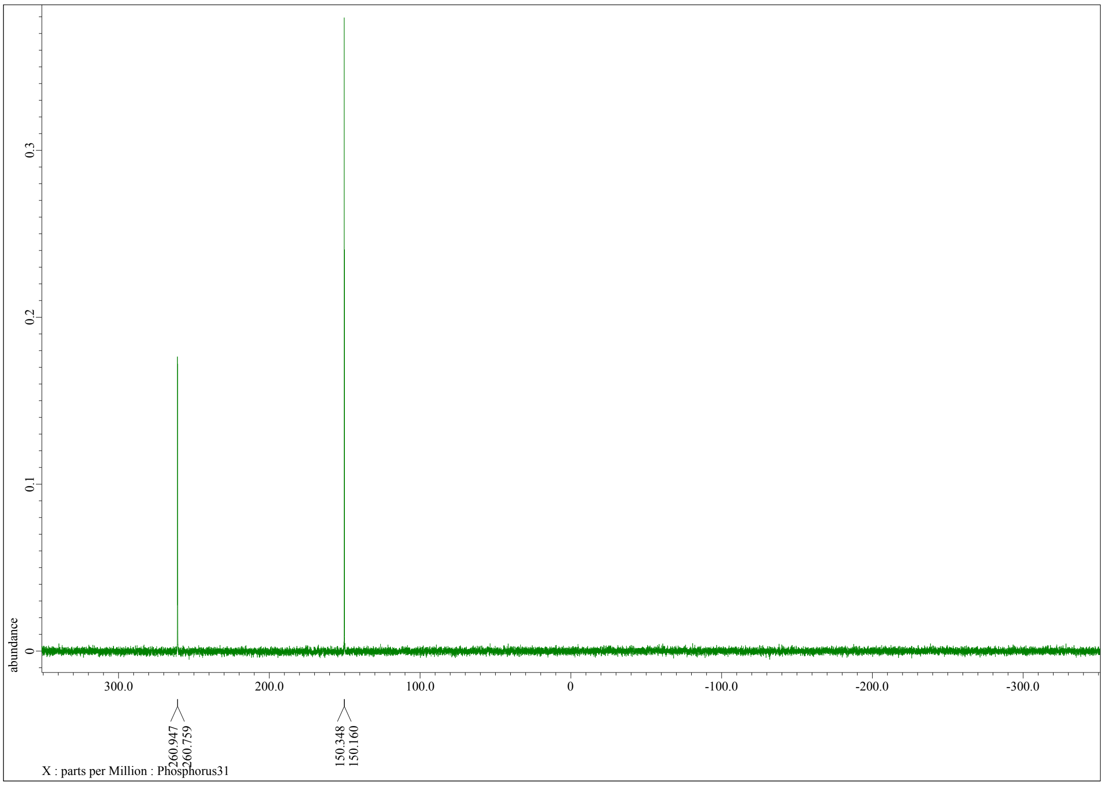
X : parts per Million : Carbon13



abundance
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0.2
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300.0
200.0
100.0
0
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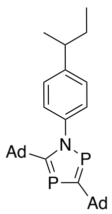
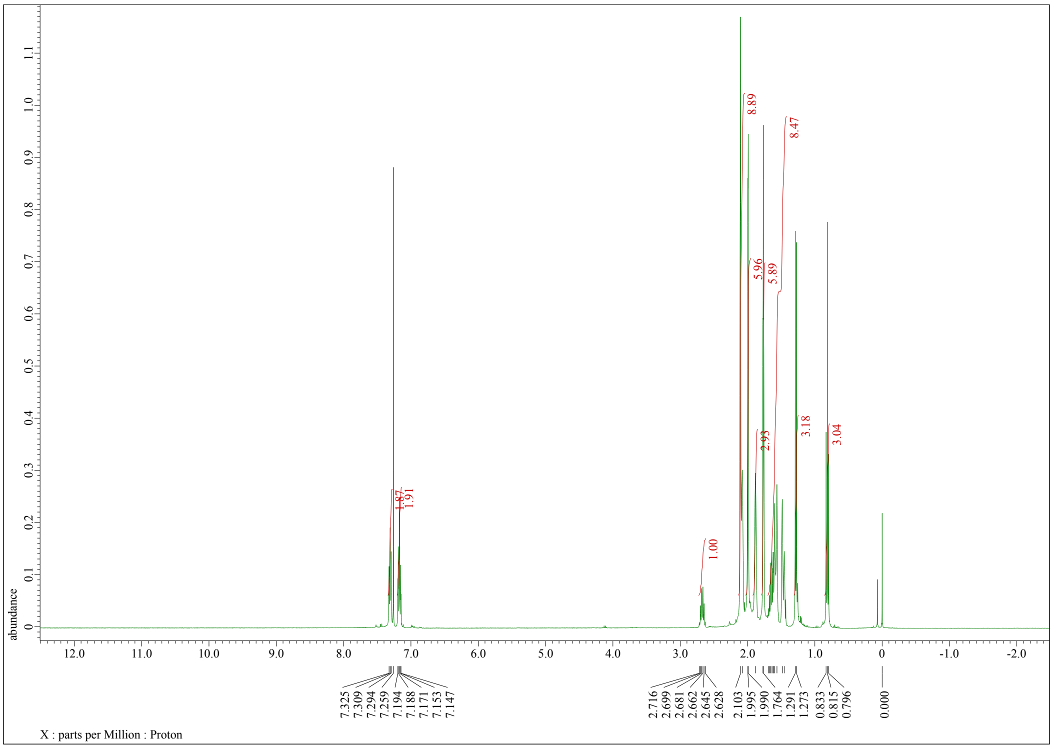
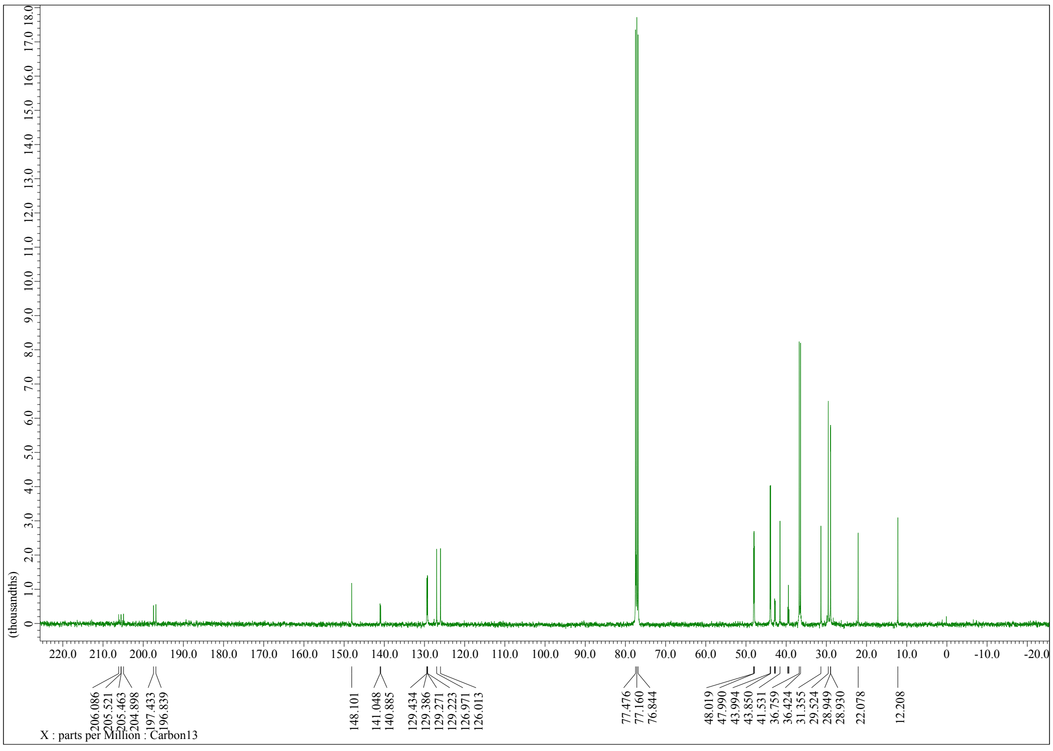
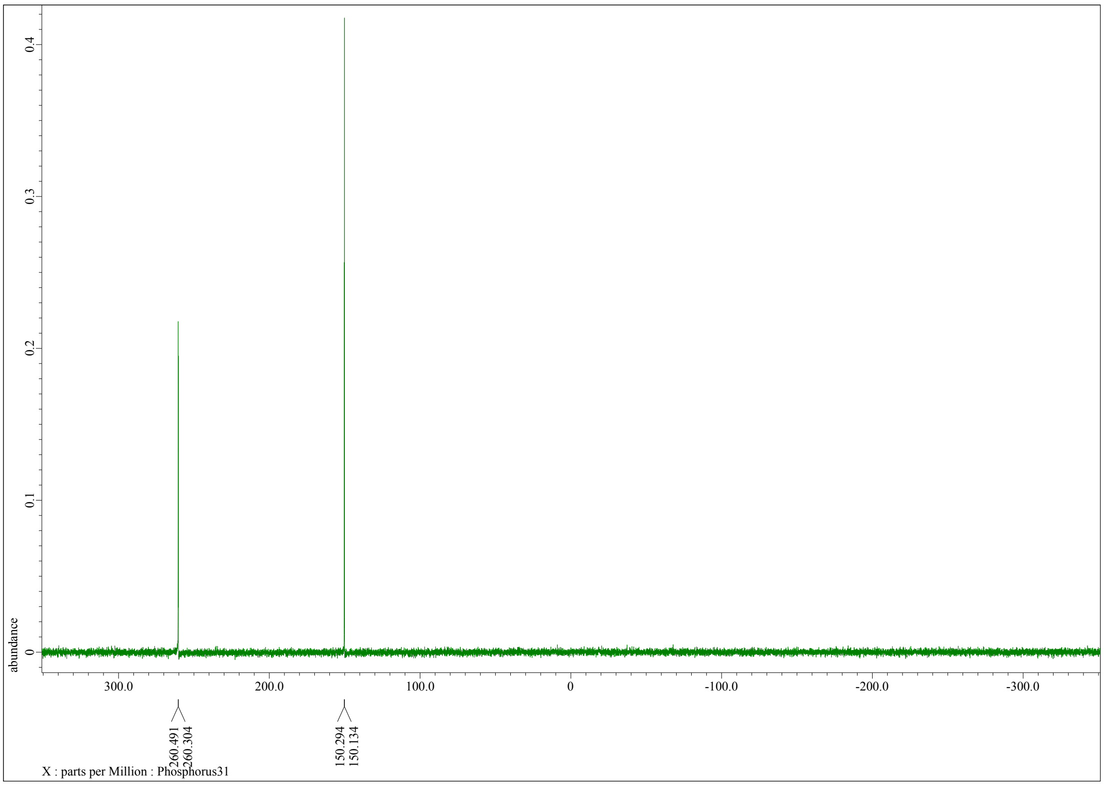
-200.0
-300.0
260.947
260.759
150.348
150.160
X : parts per Million : Phosphorus31



3i







abundance
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0.2
0.1
0
300.0
200.0
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0
-100.0
-200.0
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150.134
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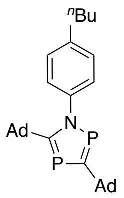
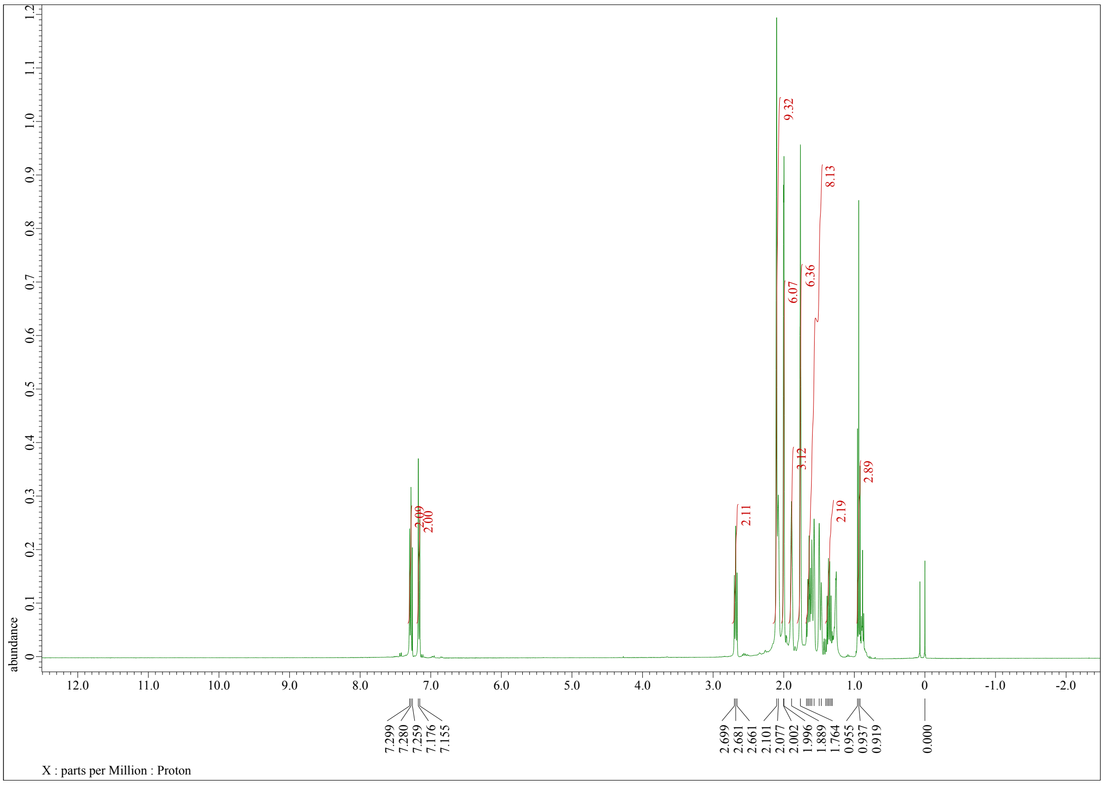


^{n}Bu
N
P
P
Ad
Ad

3j



abundance
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6.36
3.12
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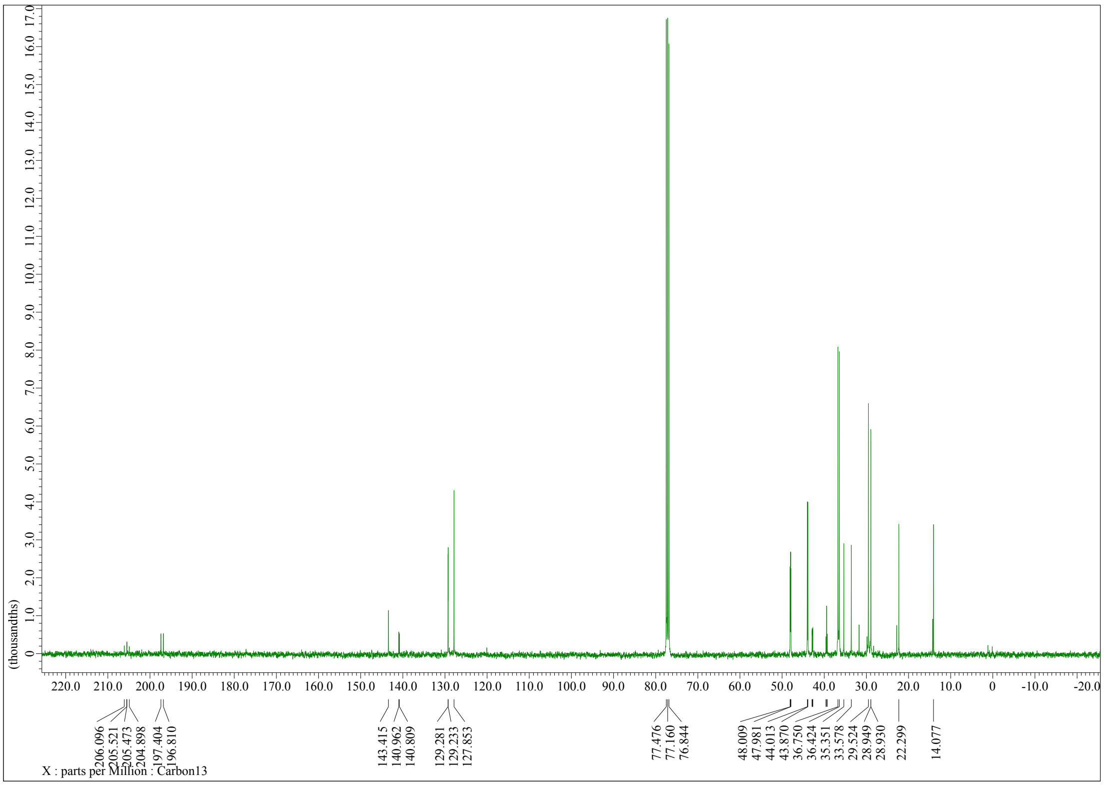
2.19
2.11
2.09
2.00
7.299
7.280
7.259
7.176
7.155
2.699
2.681
2.661
2.101
2.077
2.002
1.996
1.889
1.764
0.955
0.937
0.919
0.000
X : parts per Million : Proton



(thousandths)
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205.521
205.473
204.898
197.404
196.810
143.415
140.962
140.809
129.281
129.233
127.853
77.476
77.160
76.844
48.009
47.981
44.013
43.870
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29.524
28.949
28.930
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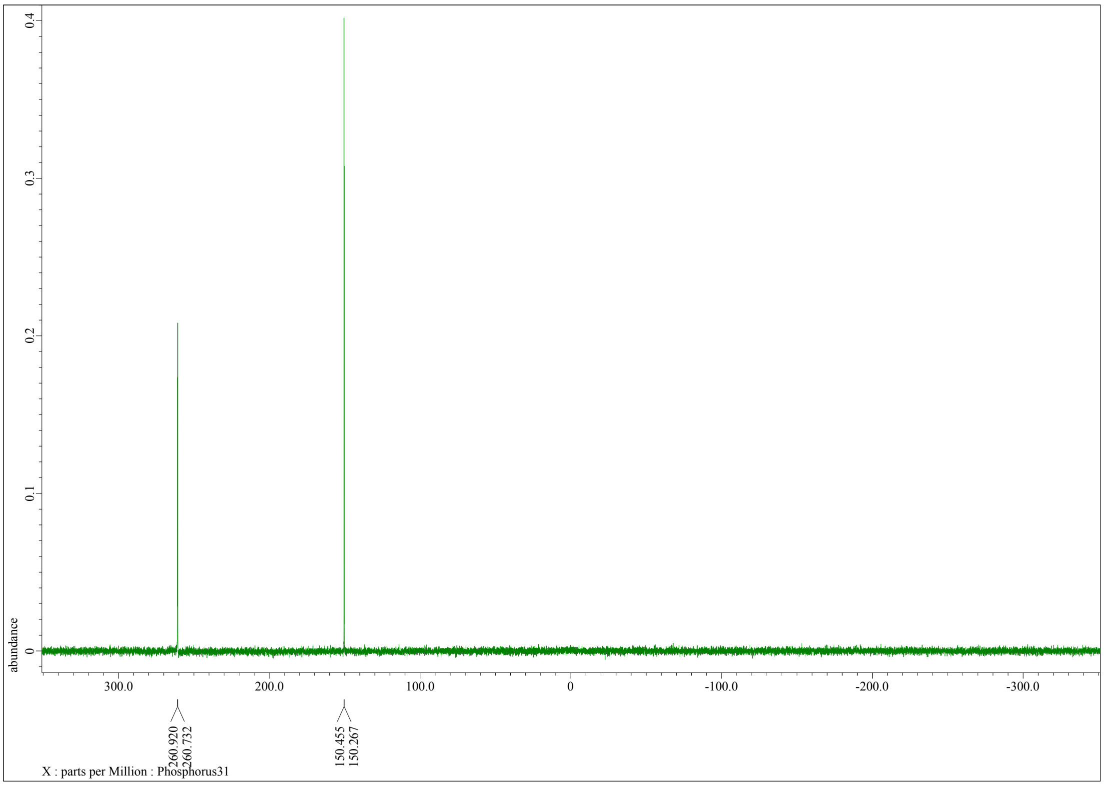
14.077
X : parts per Million : Carbon13



0.4
0.3
0.2
0.1
0
abundance
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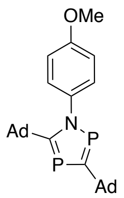
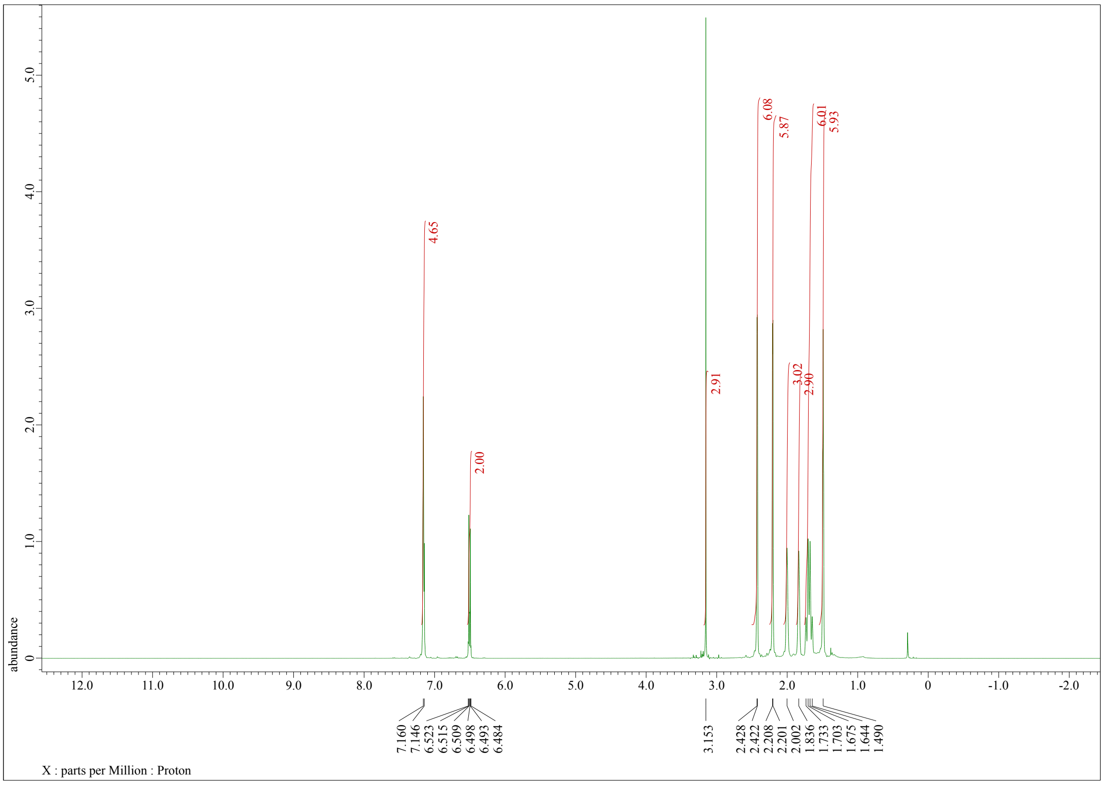
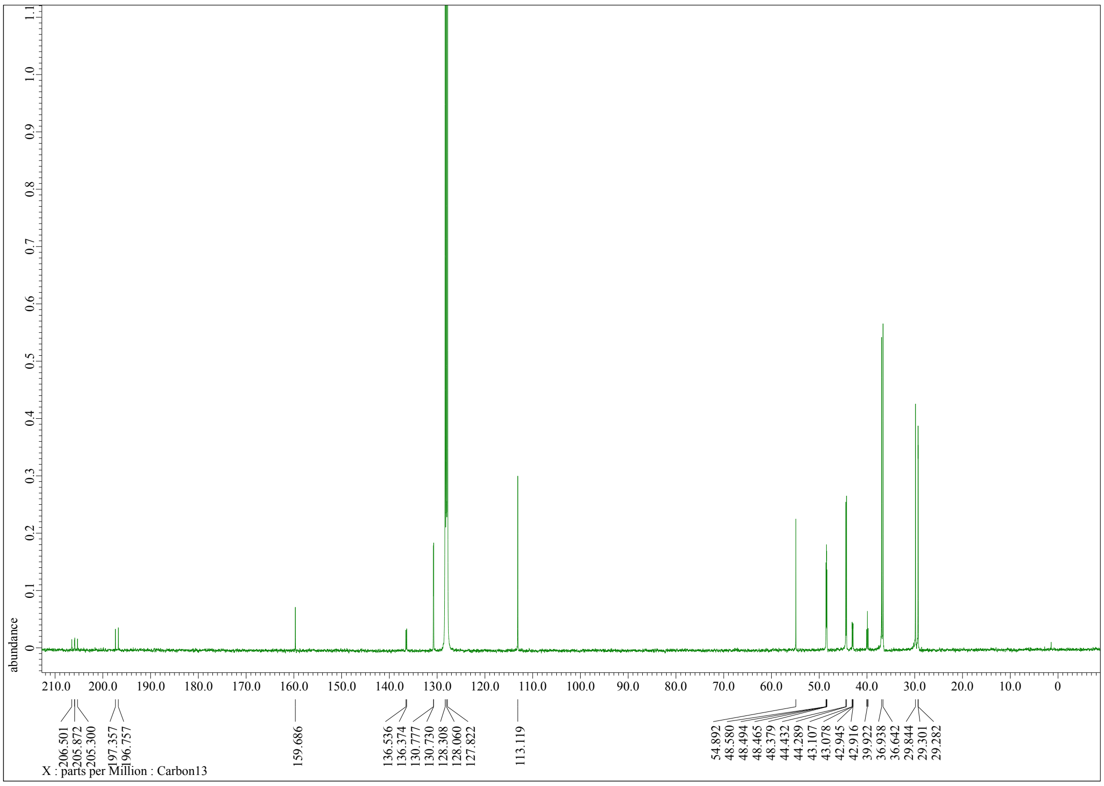
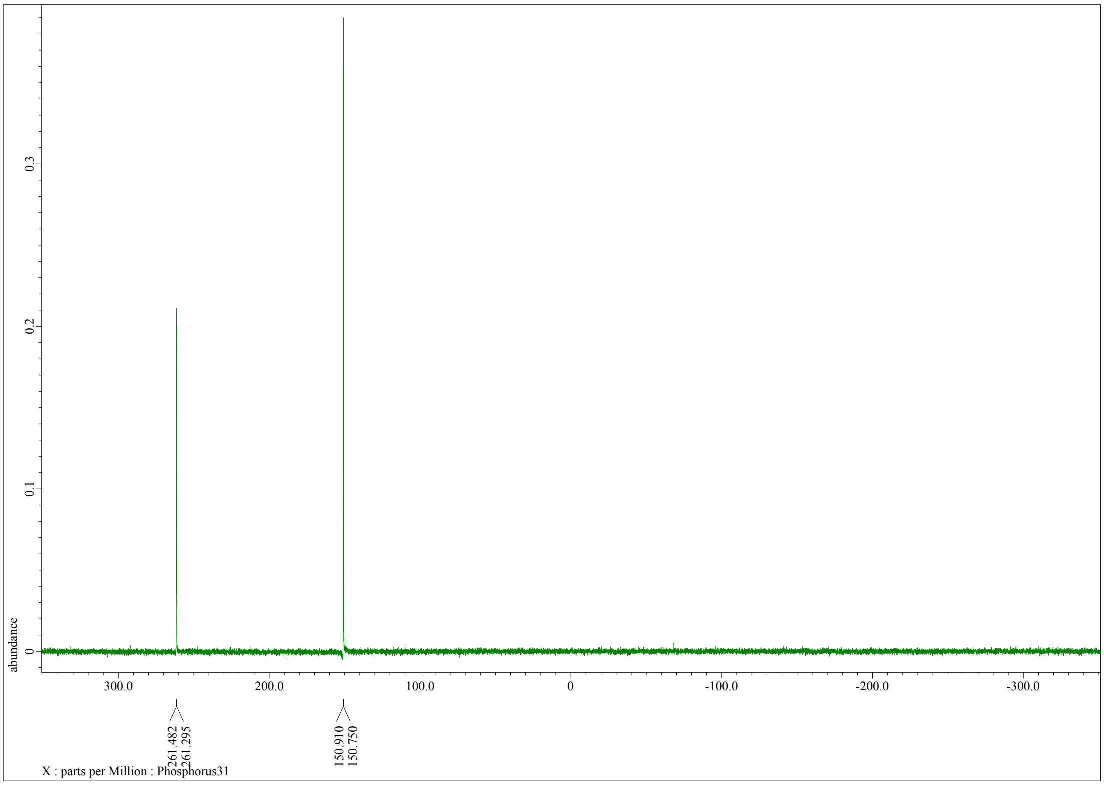
100.0
0
-100.0
-200.0
-300.0
260.920
260.732
150.455
150.267
X : parts per Million : Phosphorus31


OMe
N
P
P
Ad
Ad

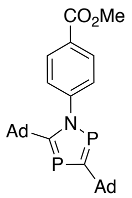
3k


4.65
2.00
2.91
6.08
5.87
3.02
2.90
6.01
5.93
7.160
7.146
6.523
6.515
6.509
6.498
6.493
6.484
3.153
2.428
2.422
2.208
2.201
2.002
1.836
1.733
1.703
1.675
1.644
1.490
abundance
X : parts per Million : Proton

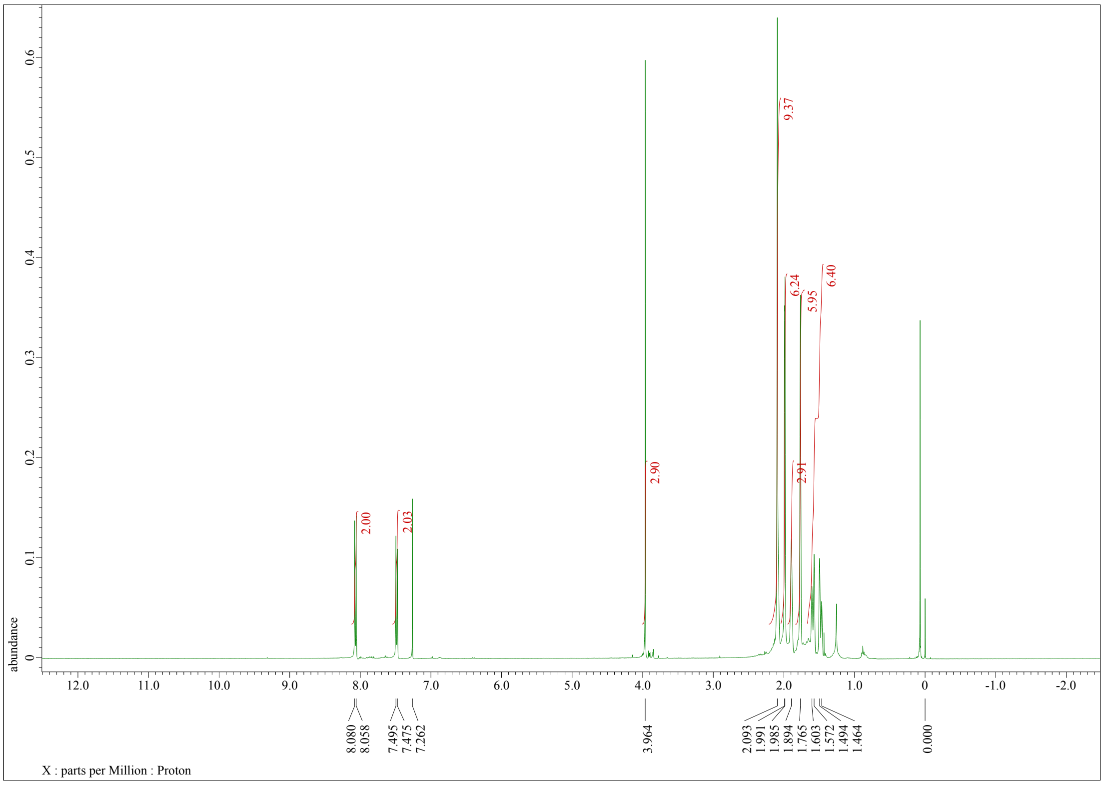

206.501
205.872
205.300
197.357
196.757
159.686
136.536
136.374
130.777
130.730
128.308
128.060
127.822
113.119
54.892
48.580
48.494
48.465
48.379
44.432
44.289
43.107
43.078
42.945
42.916
39.922
36.938
36.642
29.844
29.301
29.282
abundance
X : parts per Million : Carbon13

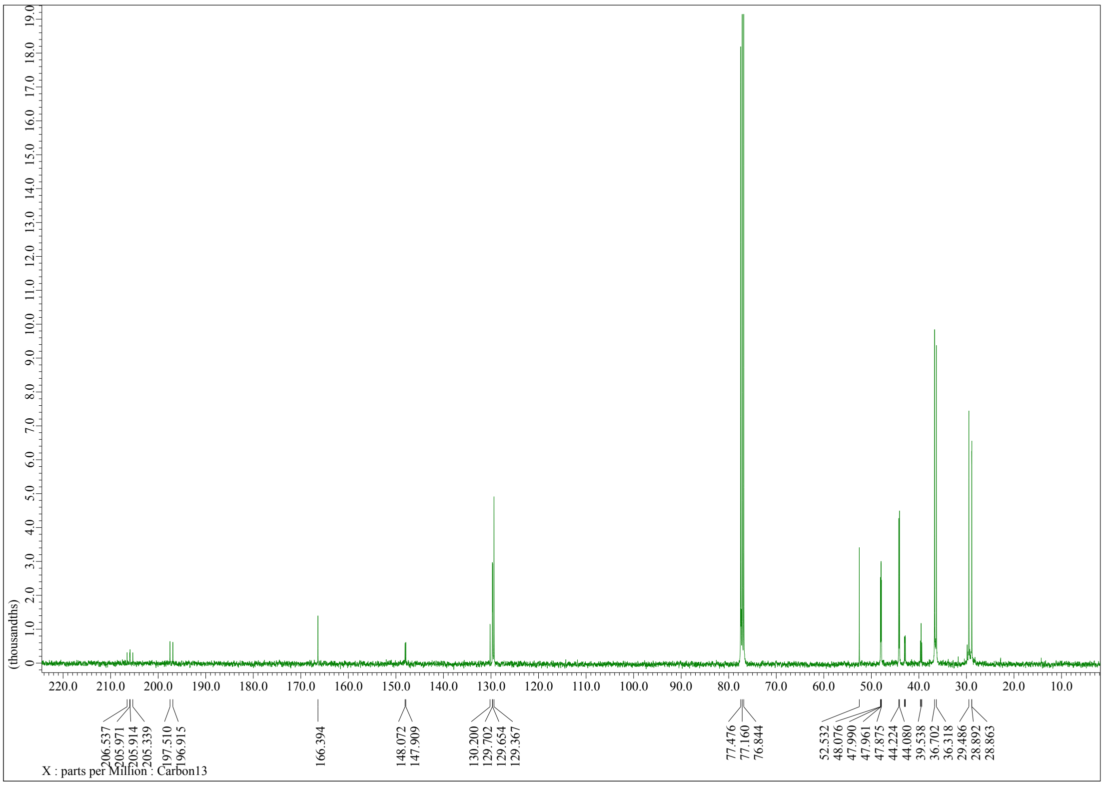


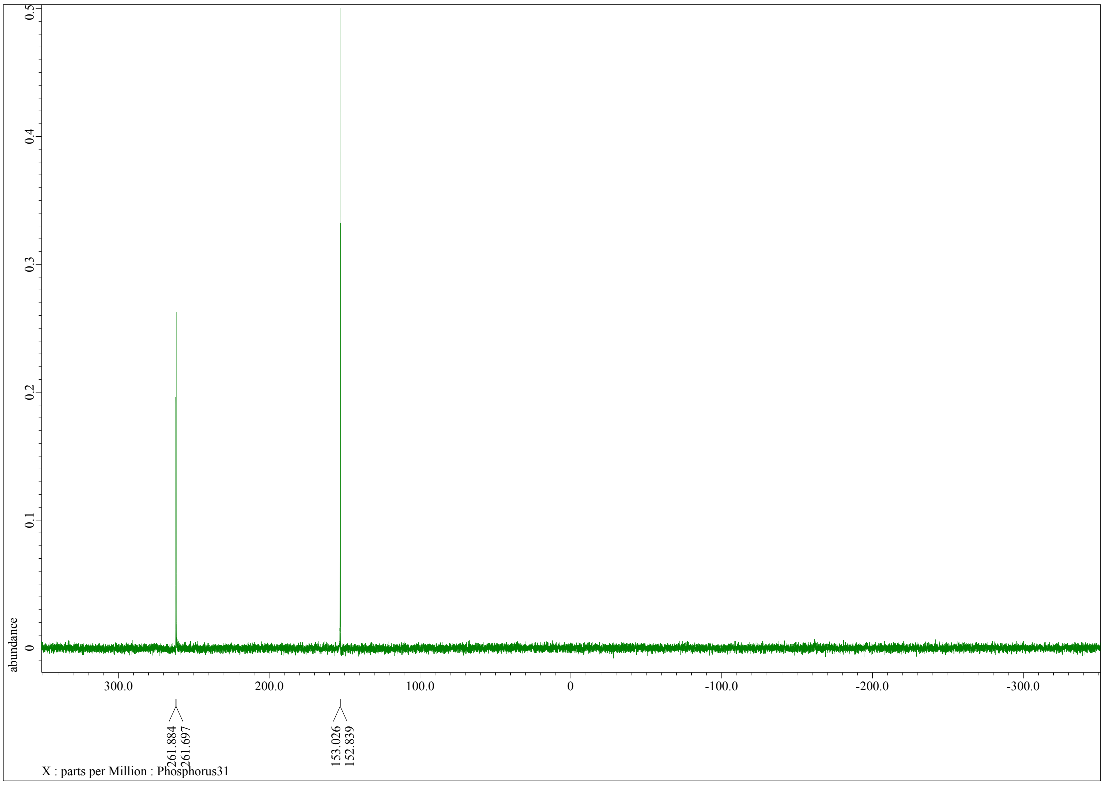
abundance
0
0.1
0.2
0.3
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
261.482
261.295
150.910
150.750
X : parts per Million : Phosphorus31



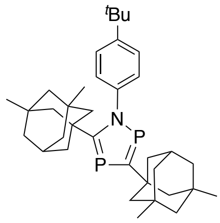
3l





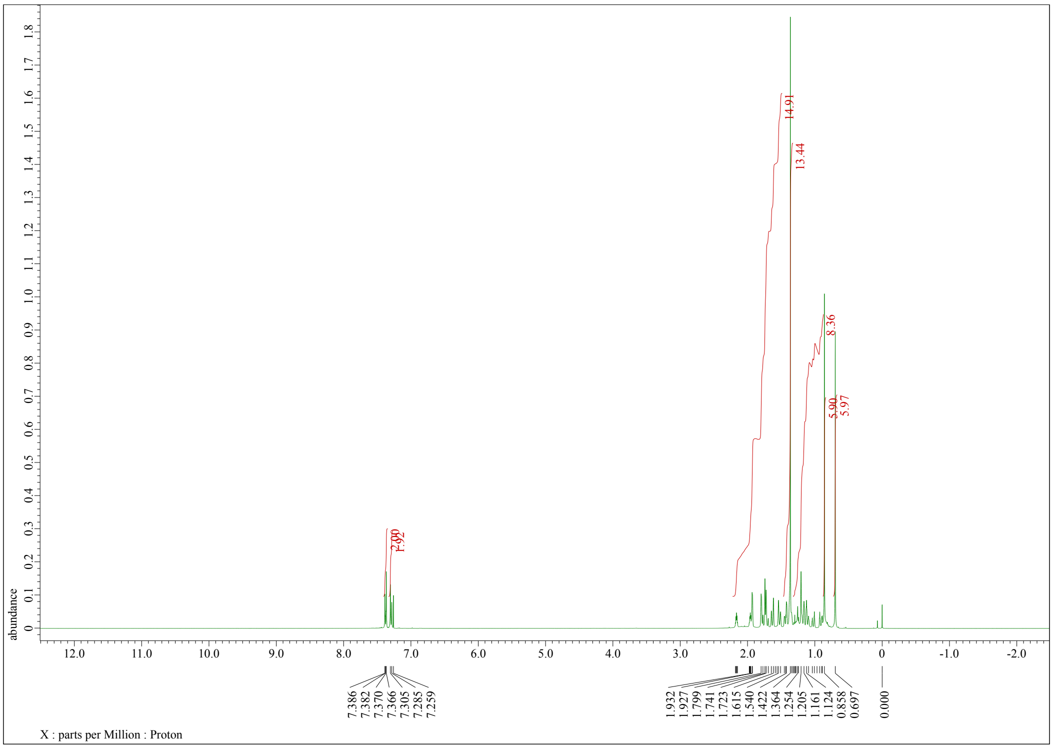


abundance
0
0.1
0.2
0.3
0.4
0.5
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
261.884
261.697
153.026
152.839
X : parts per Million : Phosphorus31

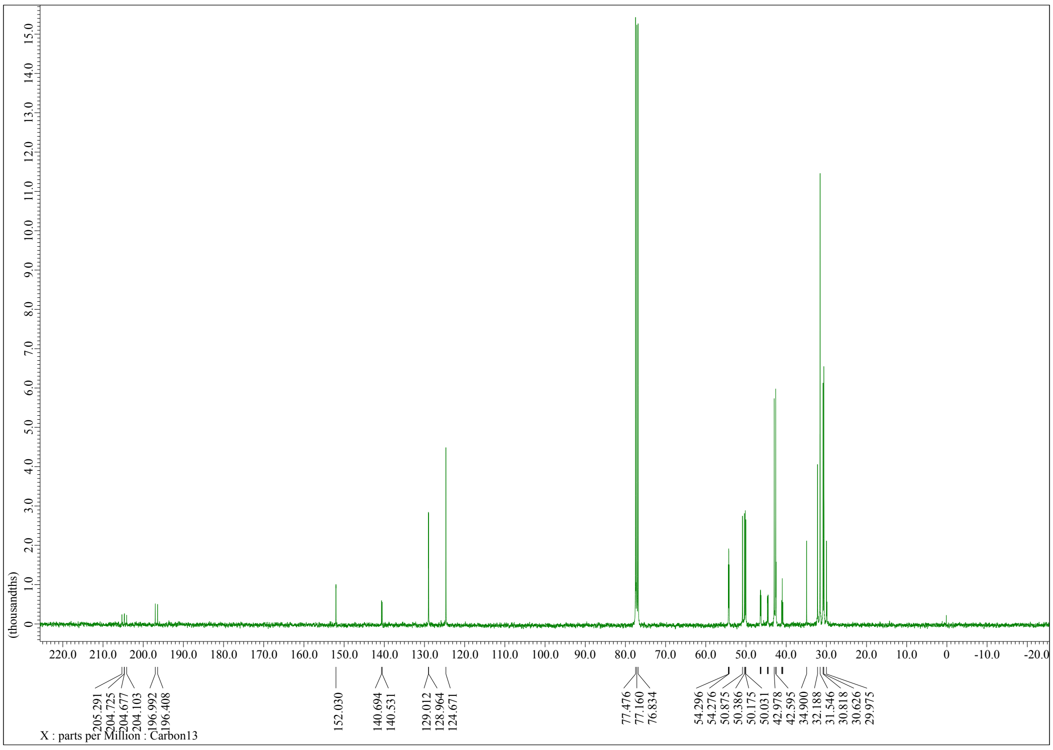


tBu
N
P
P

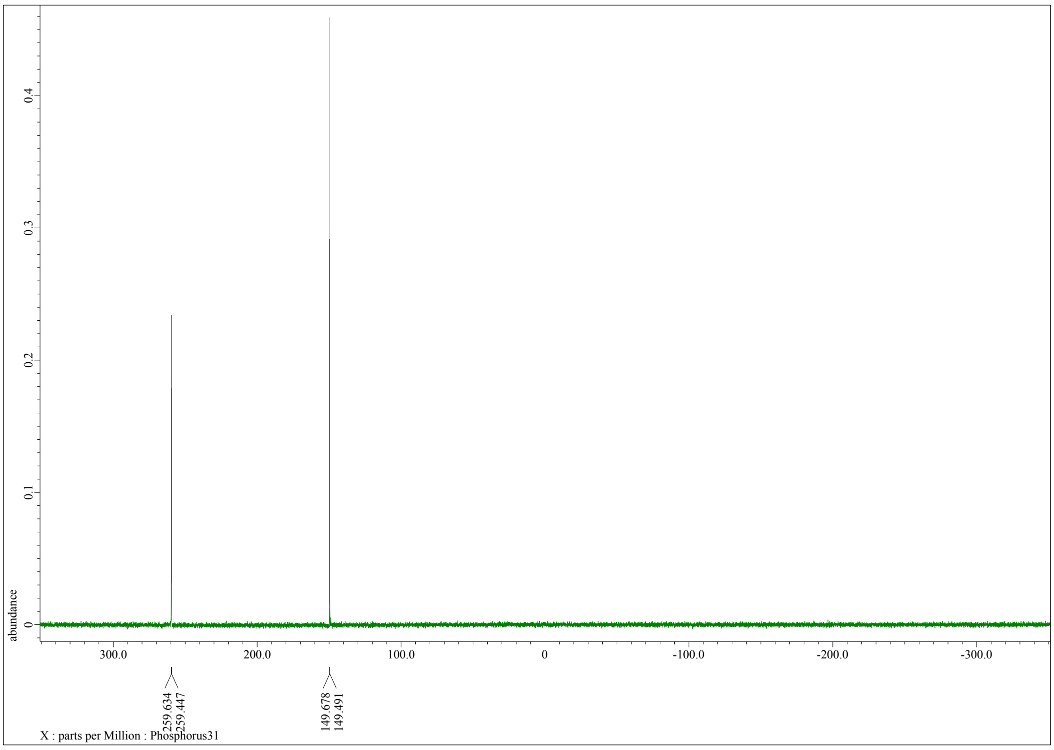
3o

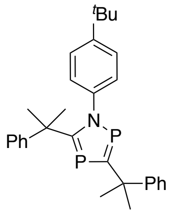


abundance
X : parts per Million : Proton
14.91
13.44
8.36
5.90
5.97
2.00
1.92
7.386
7.382
7.370
7.366
7.305
7.285
7.259
1.932
1.927
1.799
1.741
1.723
1.615
1.540
1.422
1.364
1.254
1.205
1.161
1.124
0.858
0.697
0.000

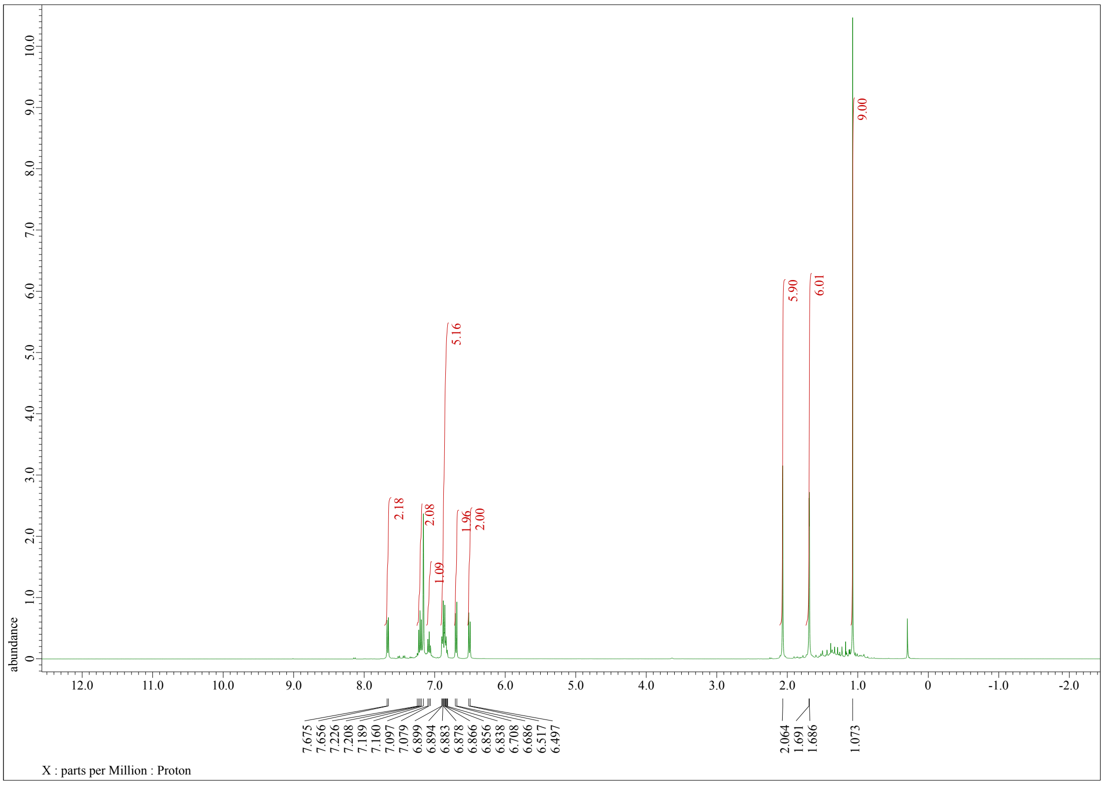


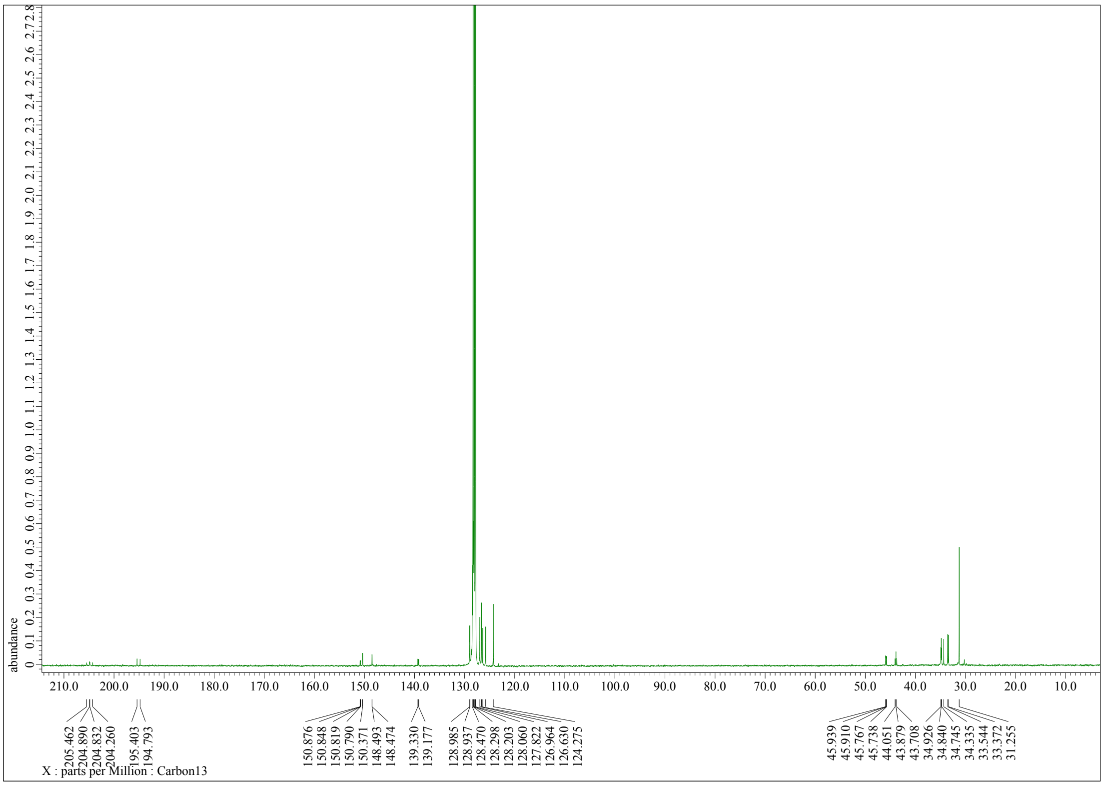
(thousandths)
X : parts per Million : Carbon13
205.291
204.725
204.677
204.103
196.992
196.408
152.030
140.694
140.531
129.012
128.964
124.671
77.476
77.160
76.834
54.296
54.276
50.875
50.386
50.175
50.031
42.978
42.595
34.900
32.188
31.546
30.818
30.626
29.975

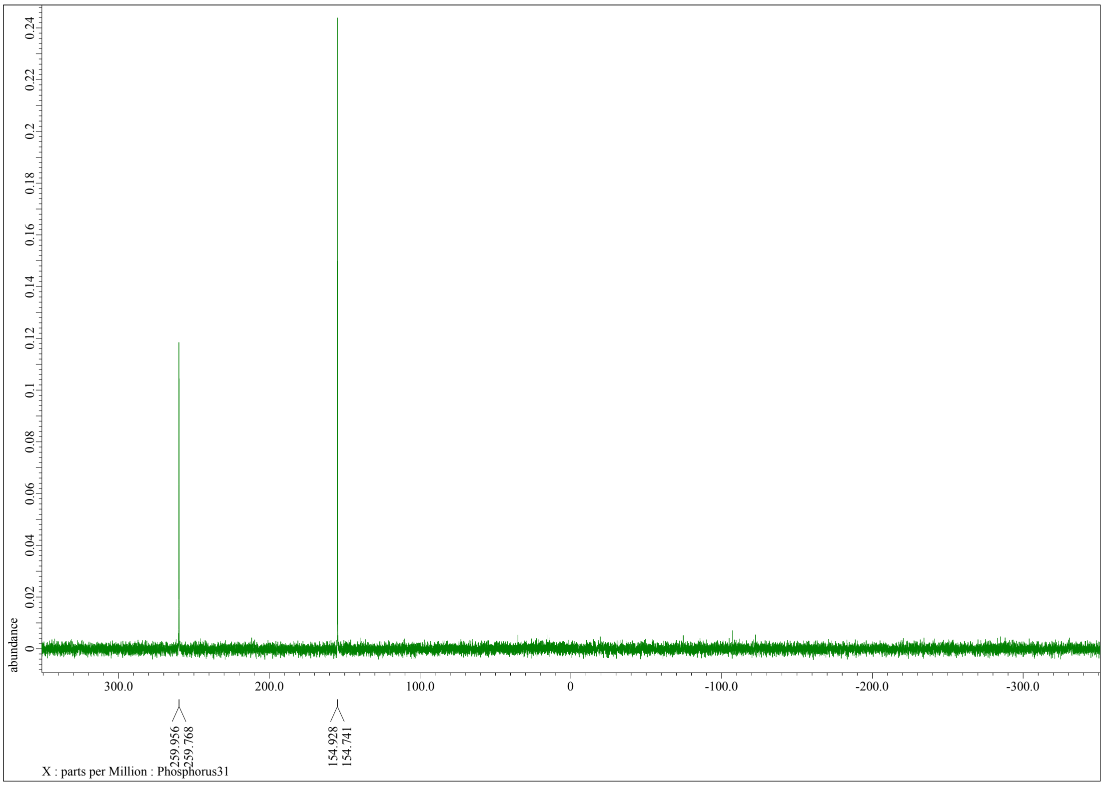

abundance
0.4
0.3
0.2
0.1
0
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
259.634
259.447
149.678
149.491
X : parts per Million : Phosphorus31

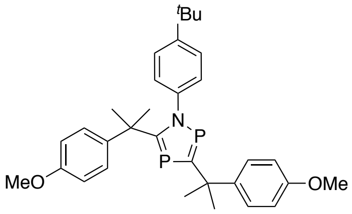


3p

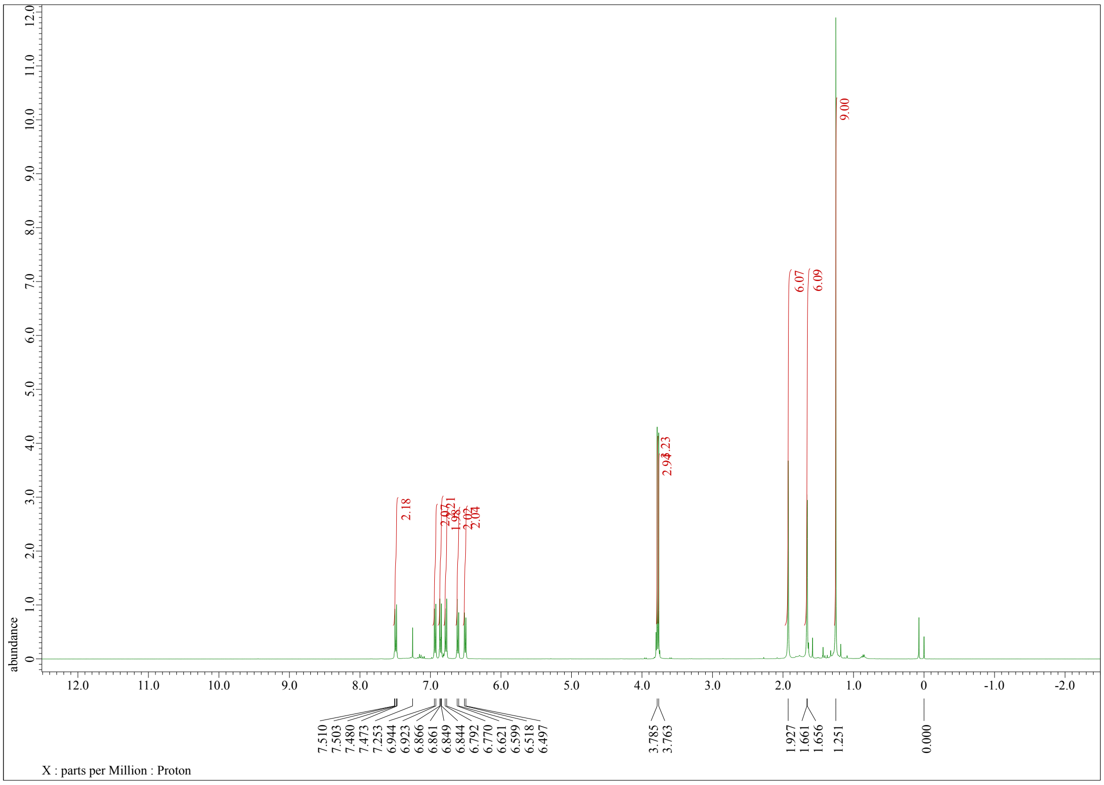


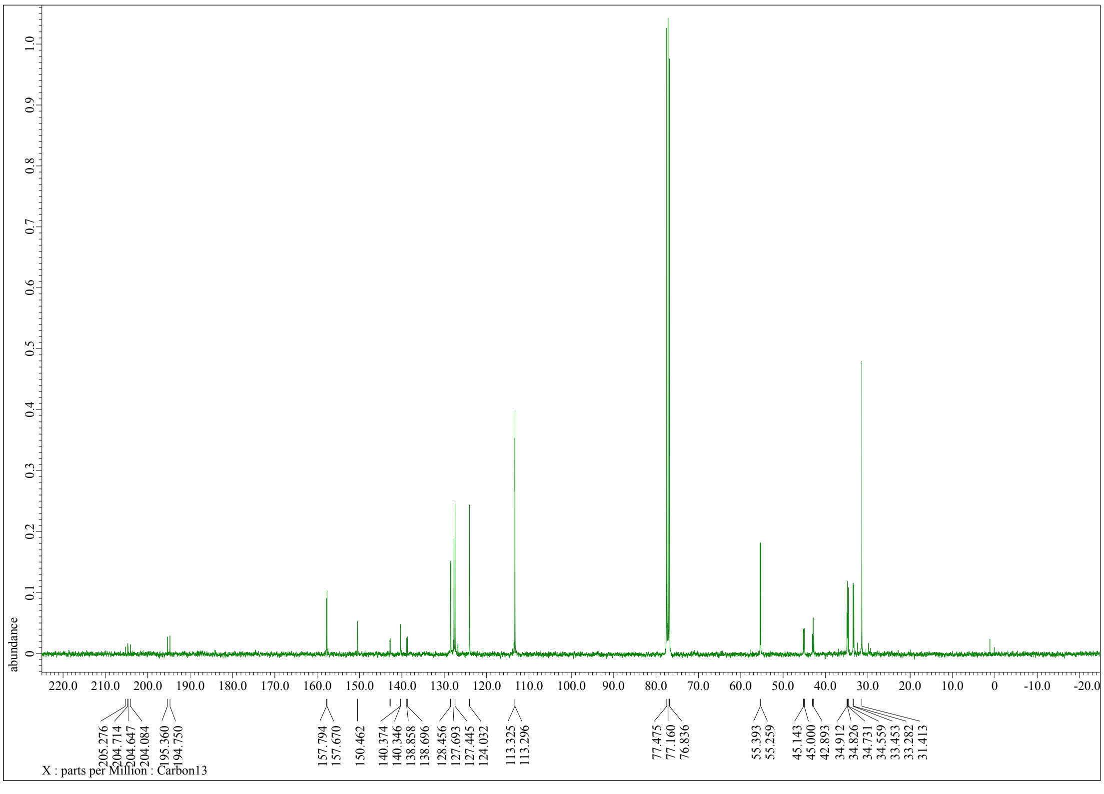


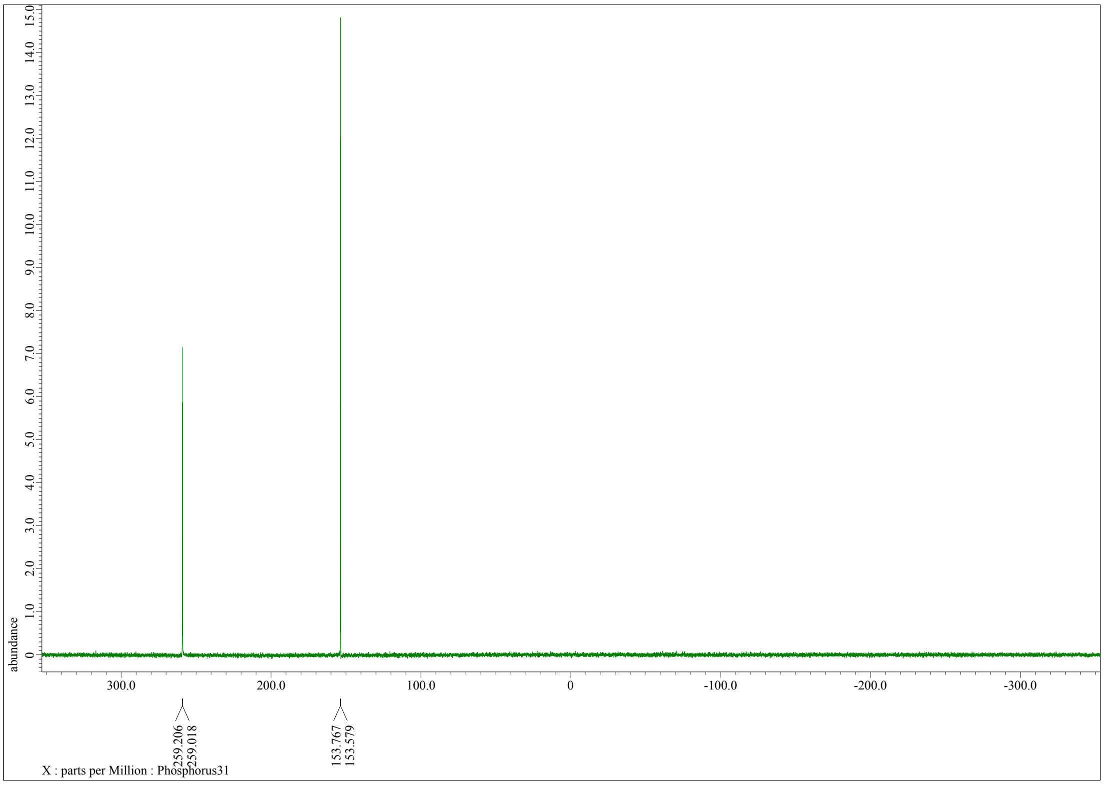

abundance
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
259.956
259.768
154.928
154.741
X : parts per Million : Phosphorus31


tBu
N
P
P
MeO
OMe

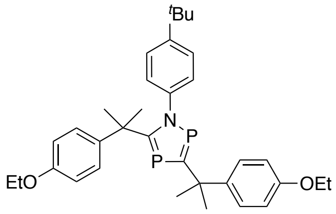
3q


abundance
2.18
2.07
2.21
1.98
2.02
2.04
2.94
3.23
6.07
6.09
9.00
7.510
7.503
7.480
7.473
7.253
6.944
6.923
6.866
6.861
6.849
6.844
6.792
6.770
6.621
6.599
6.518
6.497
3.785
3.763
1.927
1.661
1.656
1.251
0.000
X : parts per Million : Proton

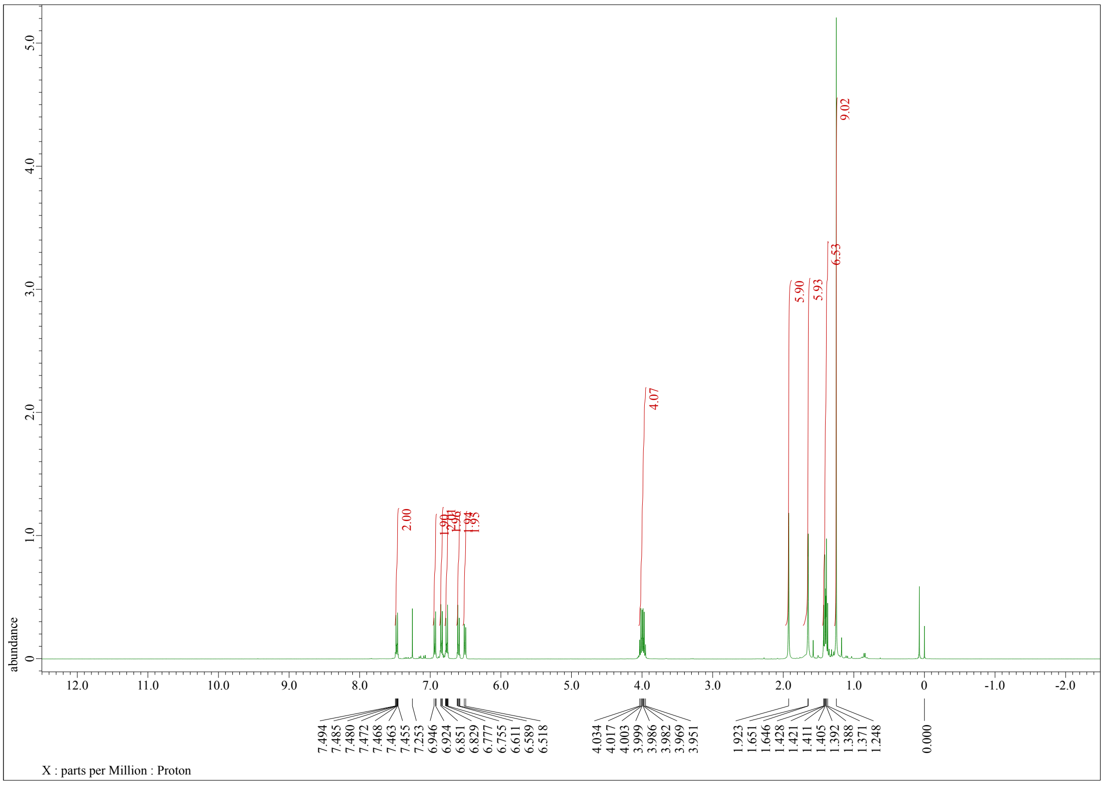

abundance
205.276
204.714
204.647
204.084
195.360
194.750
157.794
157.670
150.462
140.374
140.346
138.858
138.696
128.456
127.693
127.445
124.032
113.325
113.296
77.475
77.160
76.836
55.393
55.259
45.143
45.000
42.893
34.912
34.826
34.731
34.559
33.453
33.282
31.413
X : parts per Million : Carbon13

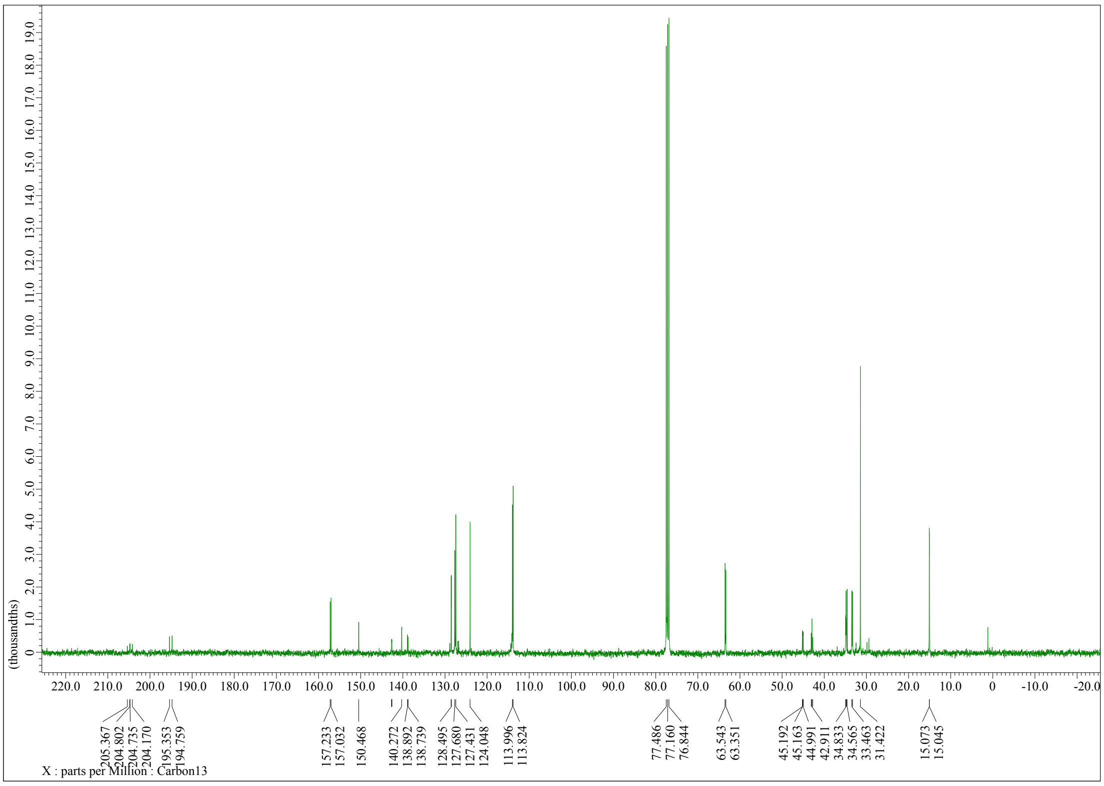


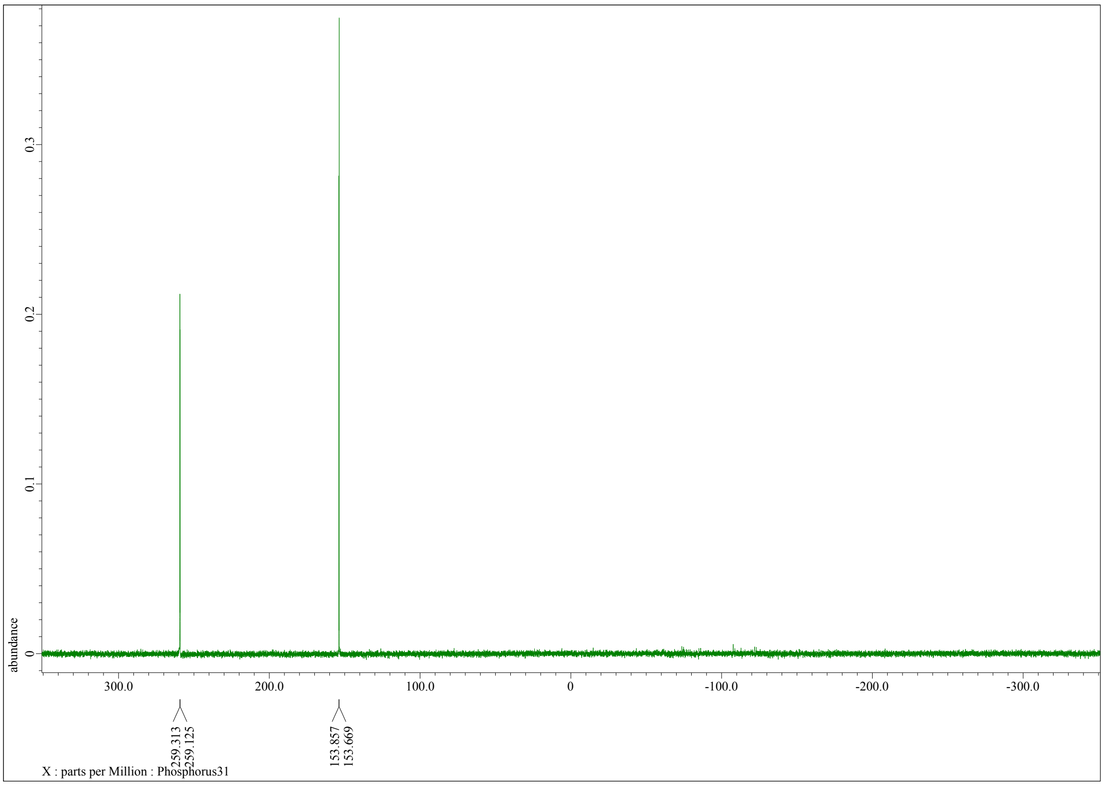
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
259.206
259.018
153.767
153.579
X : parts per Million : Phosphorus31



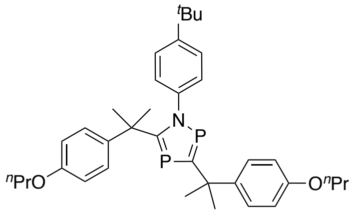
3r



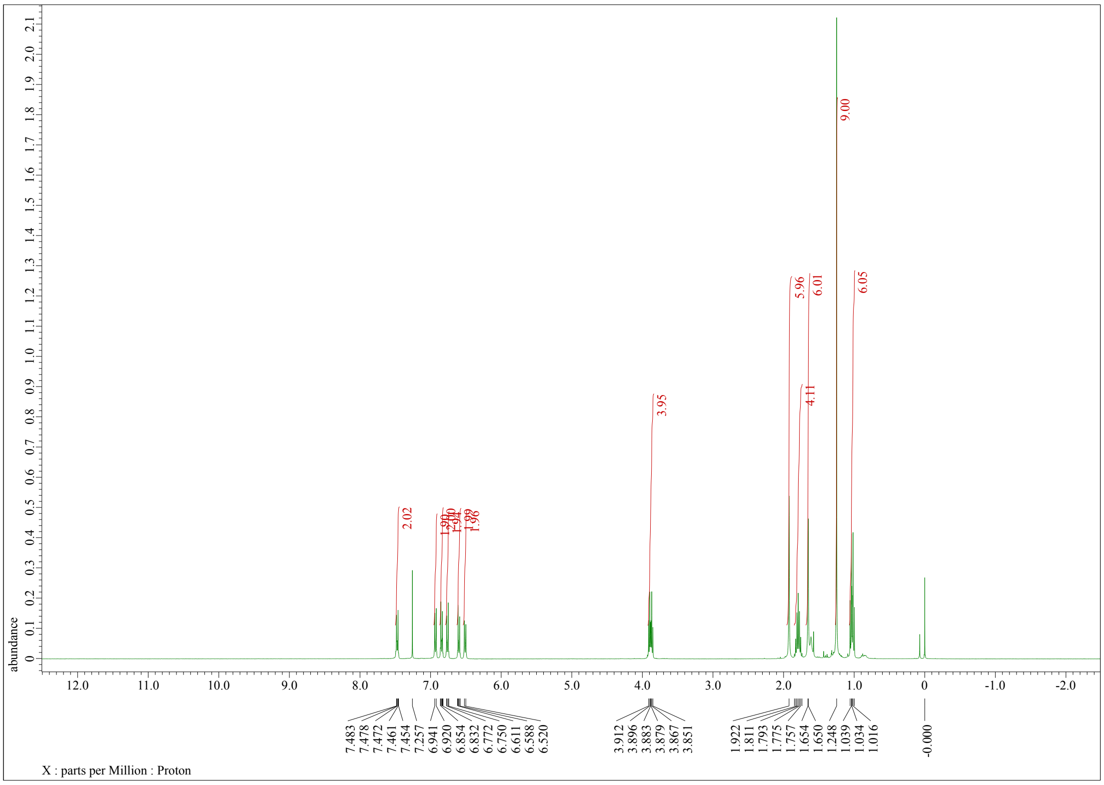


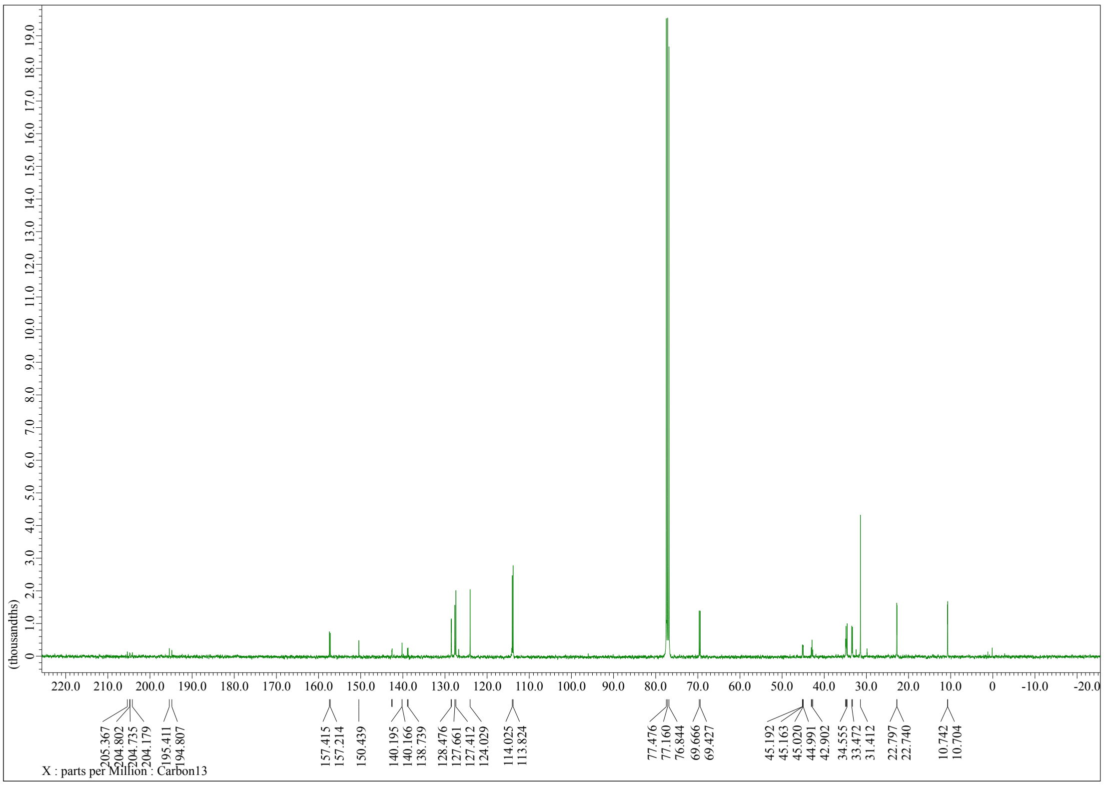


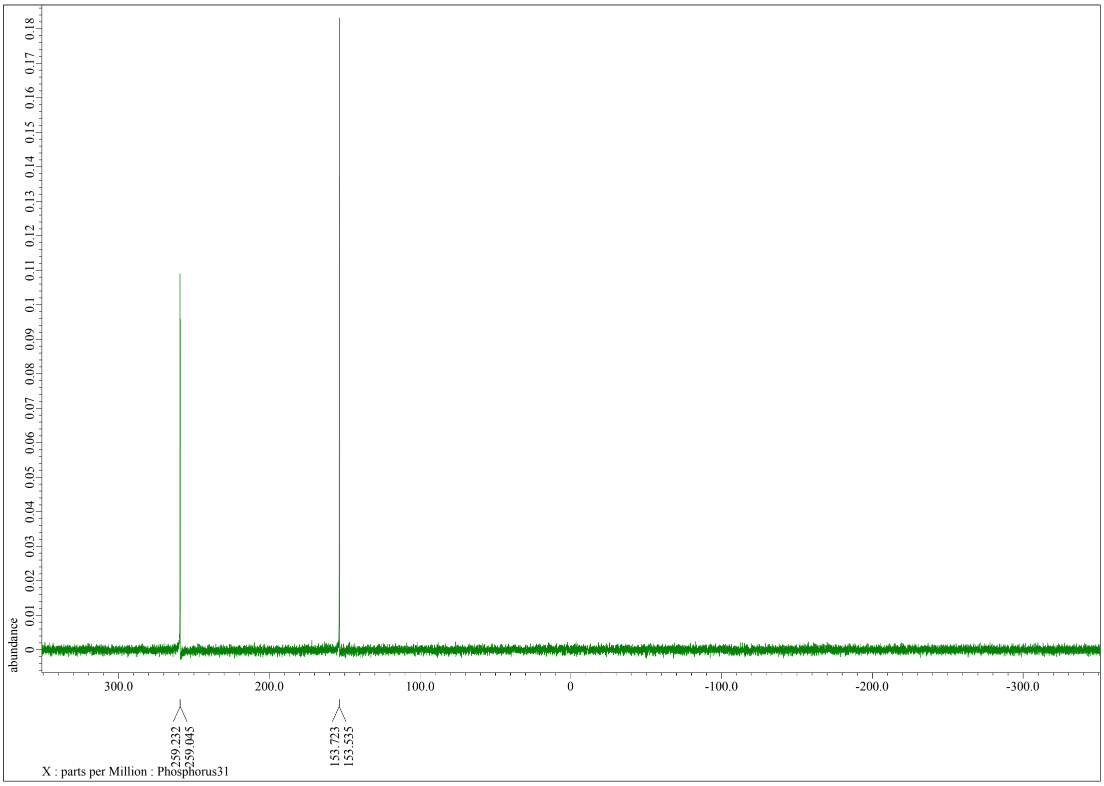
abundance
0.3
0.2
0.1
0
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
259.313
259.125
153.857
153.669
X : parts per Million : Phosphorus31

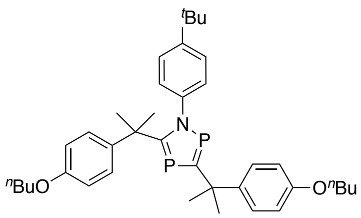


3s

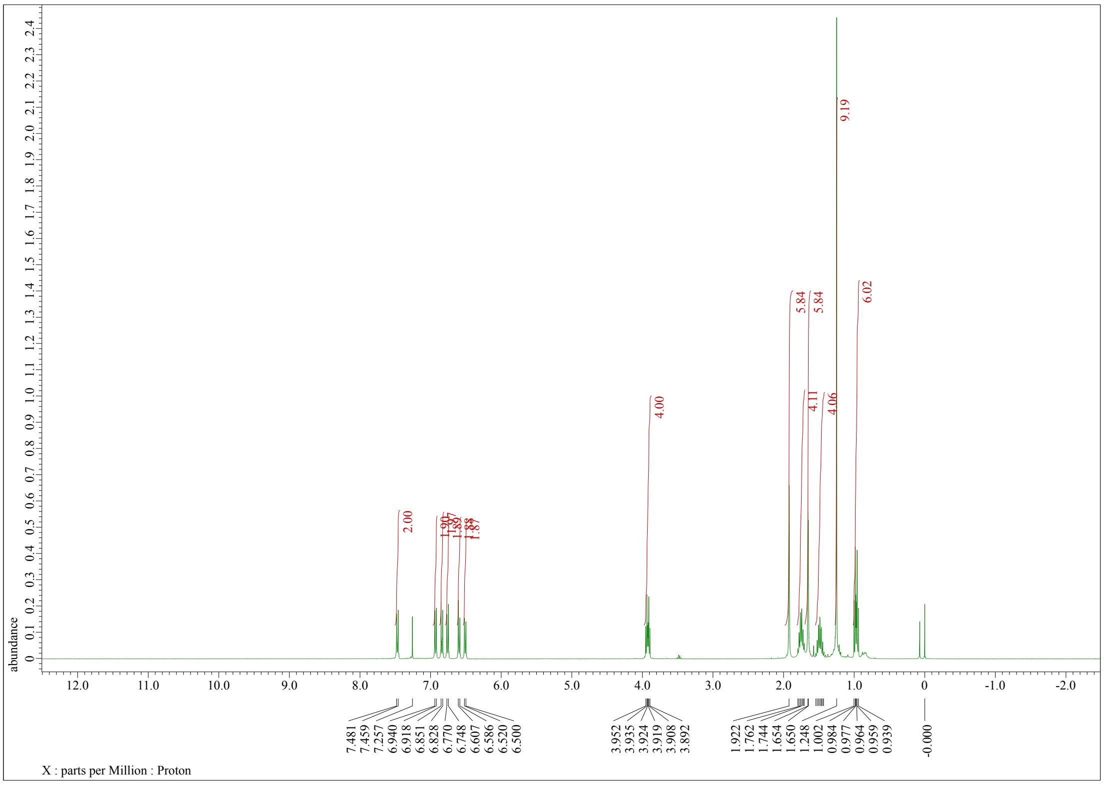




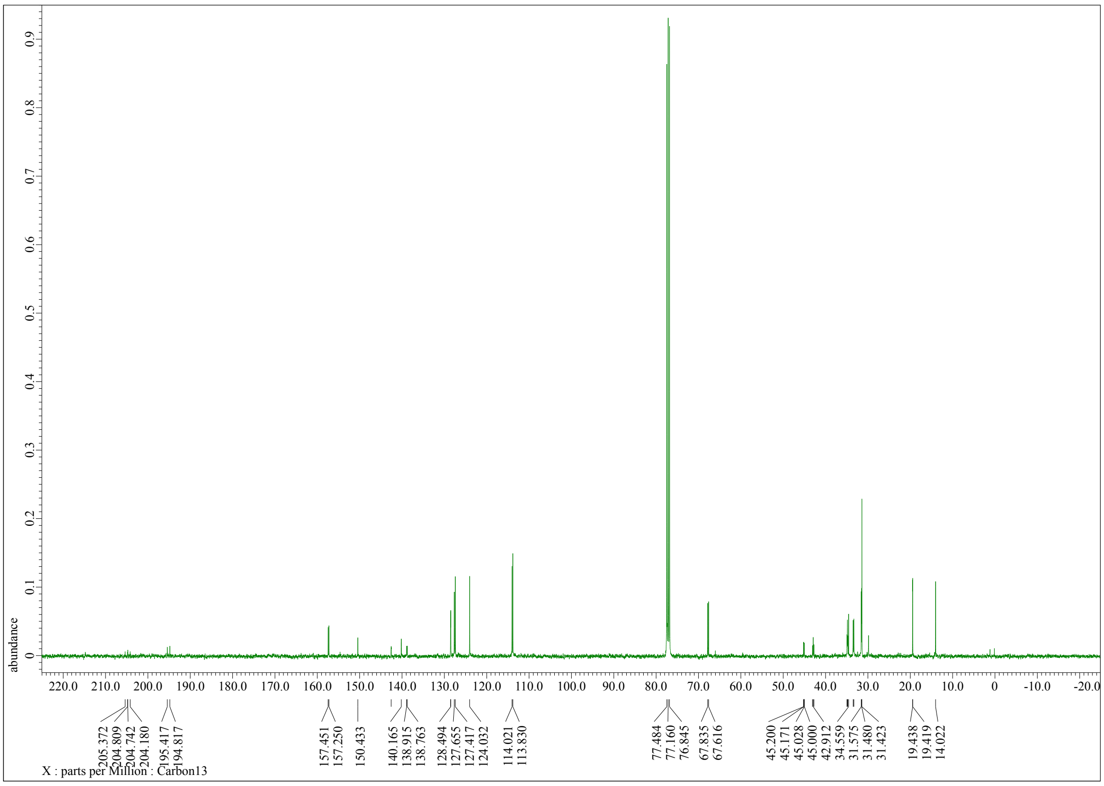

abundance
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
259.232
259.045
153.723
153.535
X : parts per Million : Phosphorus31



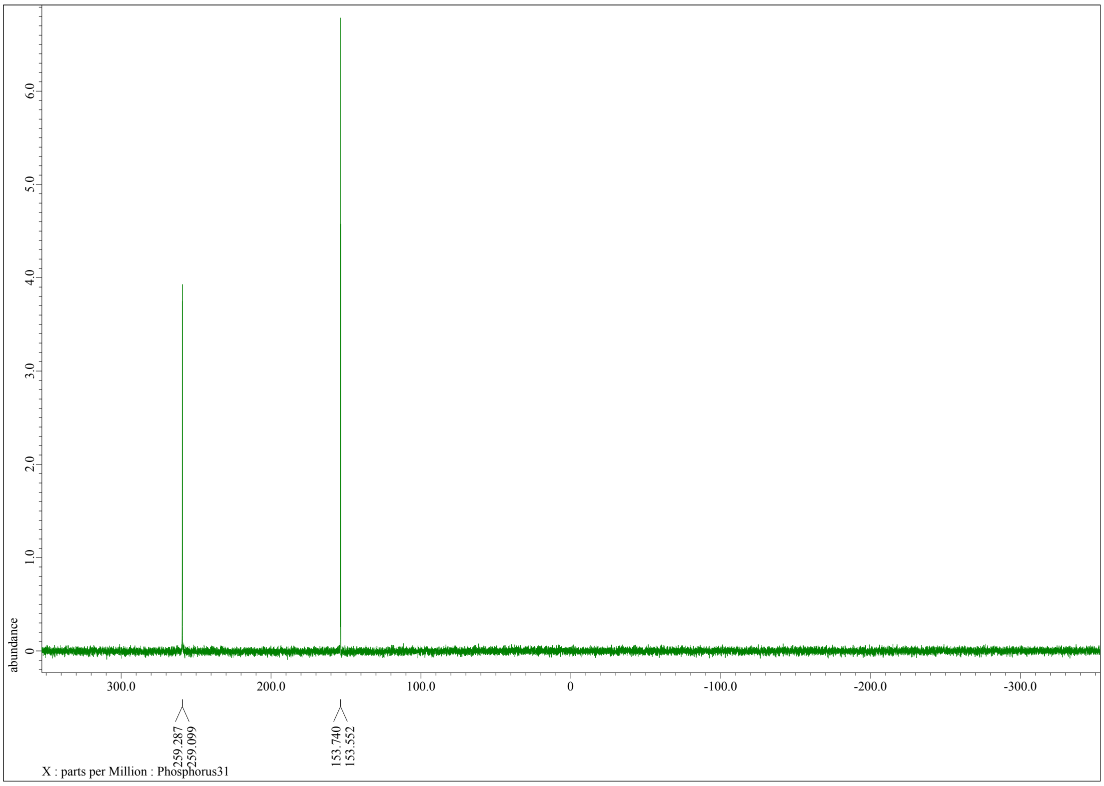
3t



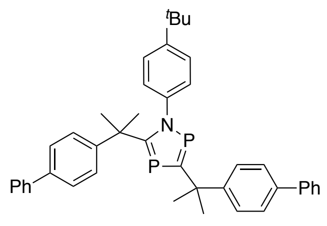
X : parts per Million : Proton
abundance



X : parts per Million : Carbon13
abundance

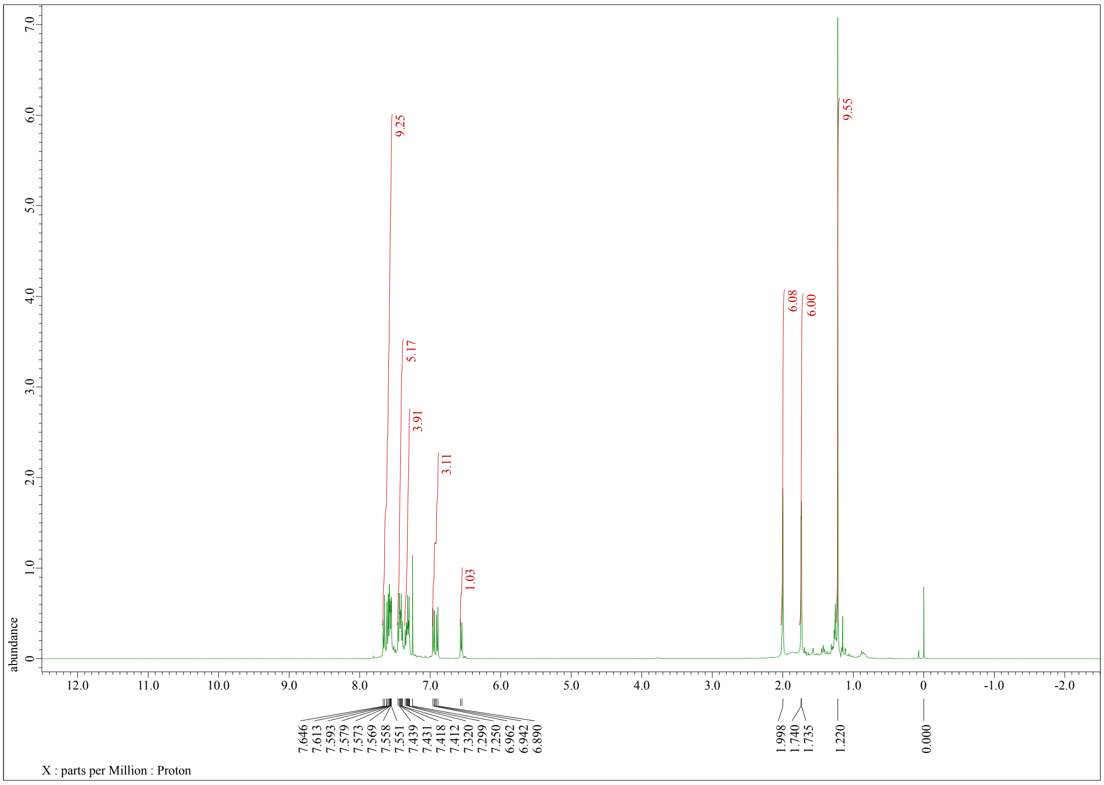


abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
259.287
259.099
153.740
153.552
X : parts per Million : Phosphorus31

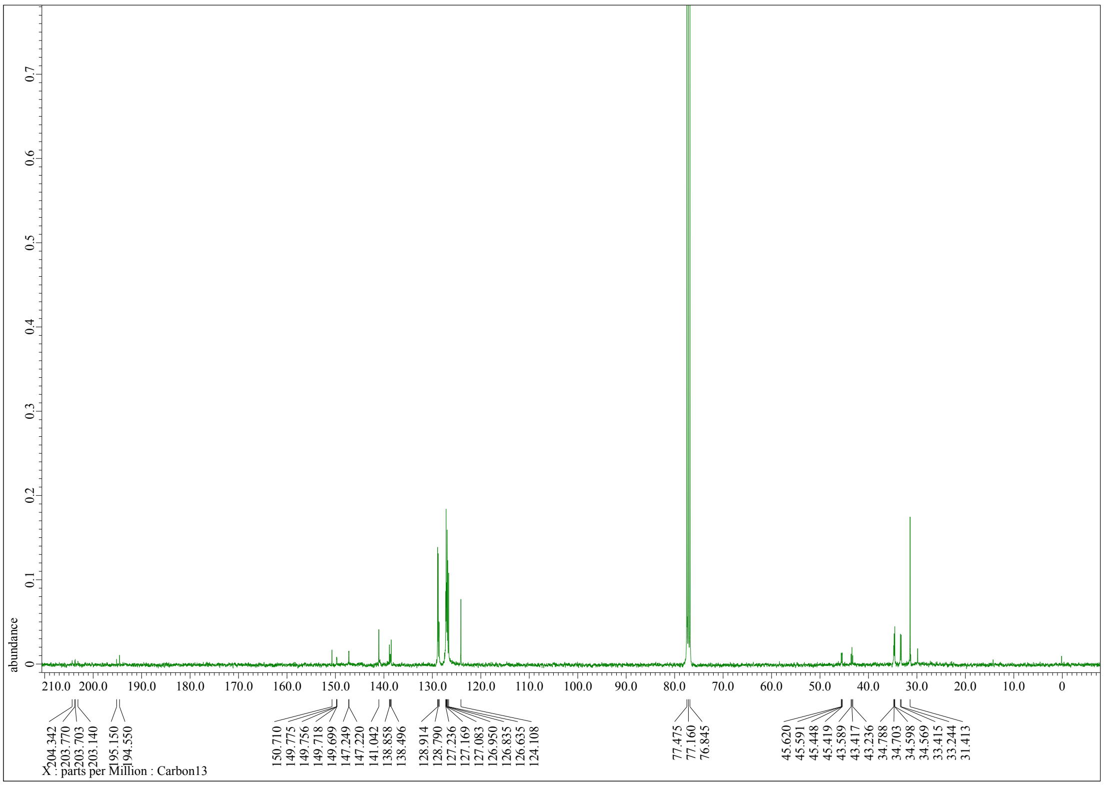


tBu
N
P
P
Ph
Ph

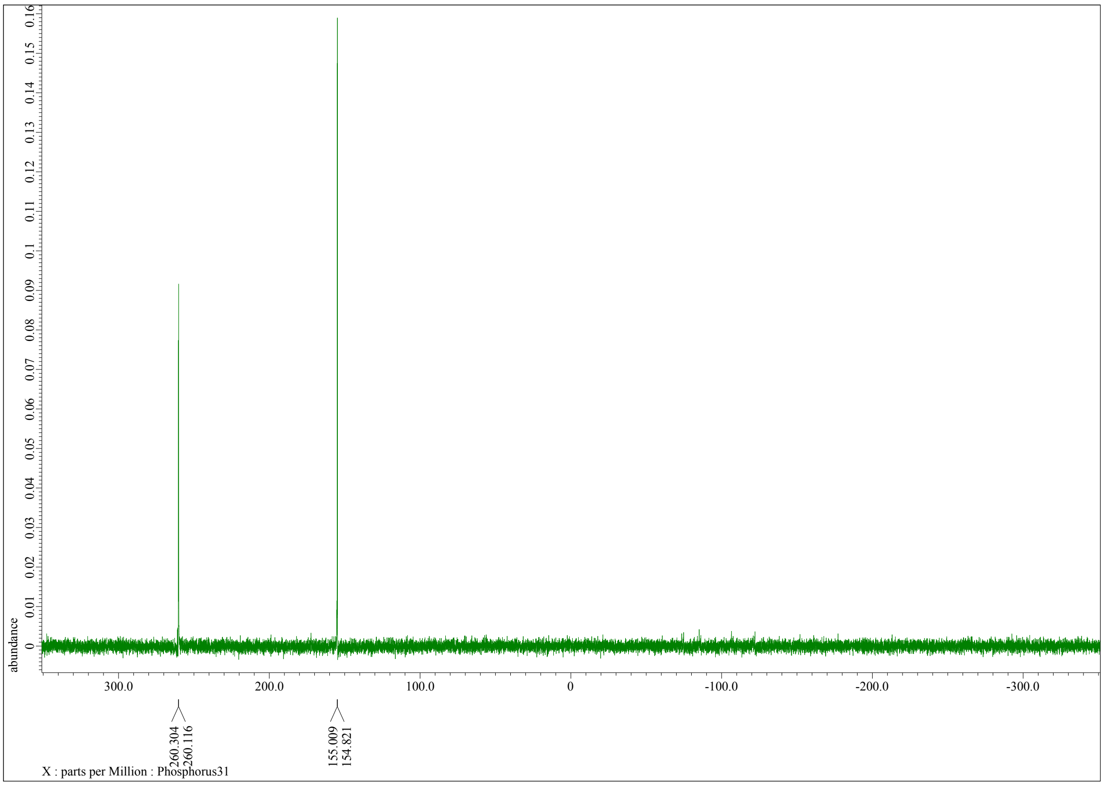
3u



abundance
9.25
5.17
3.91
3.11
1.03
6.08
6.00
9.55
7.646
7.613
7.593
7.579
7.573
7.569
7.558
7.551
7.439
7.431
7.418
7.412
7.320
7.299
7.250
6.962
6.942
6.890
1.998
1.740
1.735
1.220
0.000
X : parts per Million : Proton



abundance
204.342
203.770
203.703
203.140
195.150
194.550
150.710
149.775
149.756
149.718
149.699
147.249
147.220
141.042
138.858
138.496
128.914
128.790
127.236
127.169
127.083
126.950
126.835
126.635
124.108
77.475
77.160
76.845
45.620
45.591
45.448
45.419
43.589
43.417
43.236
34.788
34.703
34.598
34.569
33.415
33.244
31.413
X : parts per Million : Carbon13



abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
0.15
0.16
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
260.304
260.116
155.009
154.821
X : parts per Million : Phosphorus31