Supplementary Information

Are Imidazoles Versatile or Promiscuous in Reactions with Organophosphates? Insights from the Case of Parathion

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Parathion NMR spectrum

^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 1.39 (td, J_{HH} 7.09, J_{HP} 0.96 Hz, 6H), 4.27 (dq, J_{HP} 9.99, J_{HH} 7.09 Hz, 4H), 7.34 and 8.35 (AA'BB', aromatic, 4H).

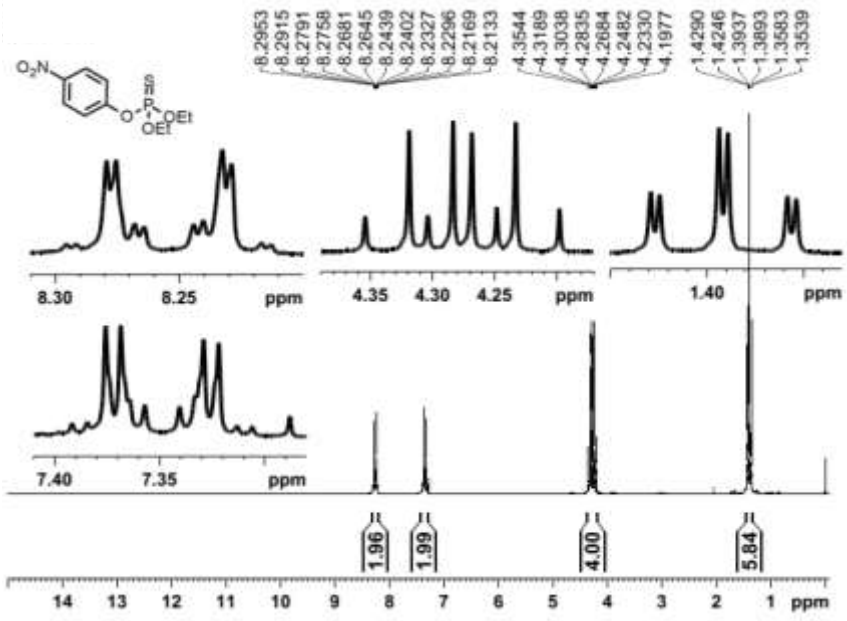


Figure S1. ^{1}H NMR spectrum (200 MHz) of parathion in $CDCl_3$, TMS reference.

^{31}P NMR (80 MHz, $CDCl_3$, H_3PO_4) δ 61.9 (quint, J_{PH} 9.9 Hz).

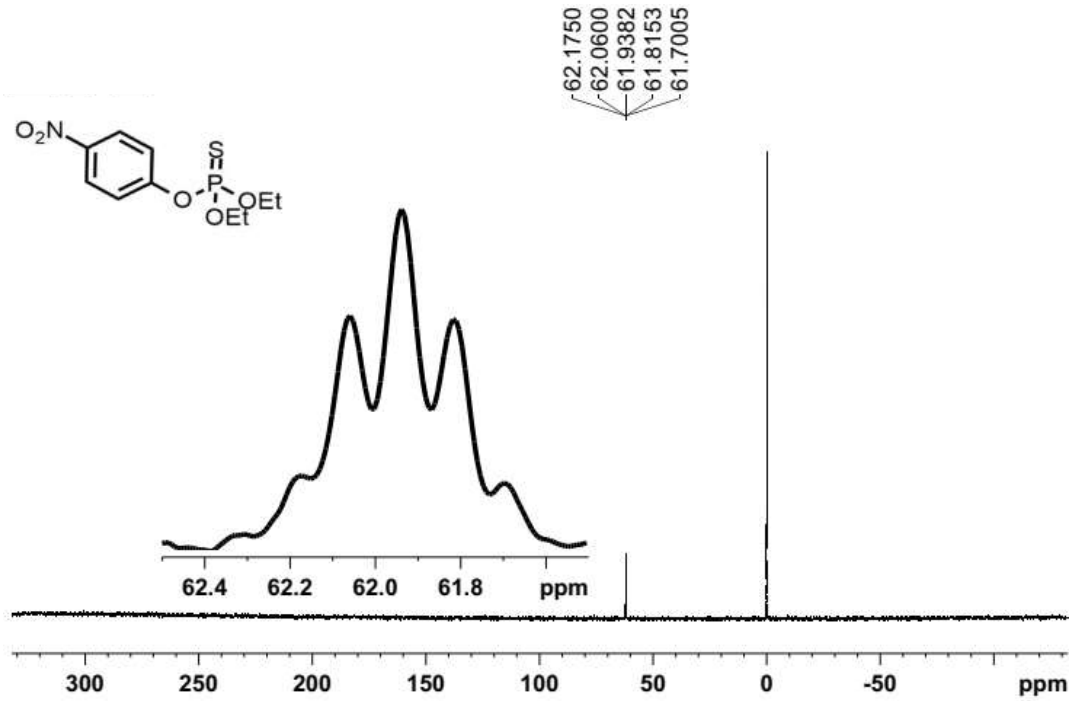


Figure S2. ^{31}P NMR spectrum (80 MHz) of parathion in $CDCl_3$, capillary with H_3PO_4 reference.

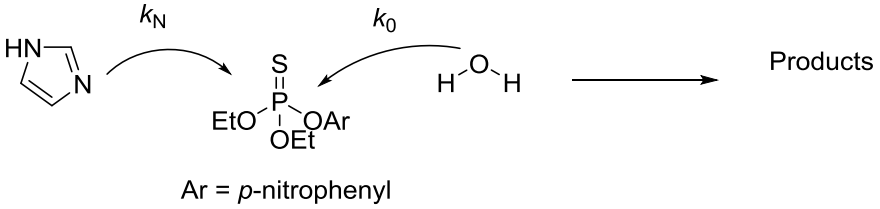
Kinetic profile of imidazole with parathion

Kinetic profiles recorded at 270 nm were fitted with equation S1 for reagents typical for pseudo-1st order reactions.

$$A_t = A_I + \left(e^{-kobs*T}\right) * (A_0 - A_I) \quad \text{(S1)}$$

where A_t: absorbance at time "t", A_0: initial absorbance, A_I: absorbance at "infinite" time, k_{obs}: observed rate constant, t: time.

The pH rate profile (Figure 6, main article) was fitted with equation S2, that consider a solvolysis reaction (k_0) and a nucleophilic reaction (k_N).



Ar = *p*-nitrophenyl

$$k_{obs} = k_0 + k_N[\text{IMIDAZOLE}]f \quad \text{(S2)}$$

where, k_{obs}: observed rate constant, k_0: rate constant of reaction between parathion and water, k_N: rate constant of reaction between imidazole and parathion, [IMIDAZOLE]: imidazole concentration and f: molar fraction of imidazole.

NMR ^{1}H and ^{31}P product analysis

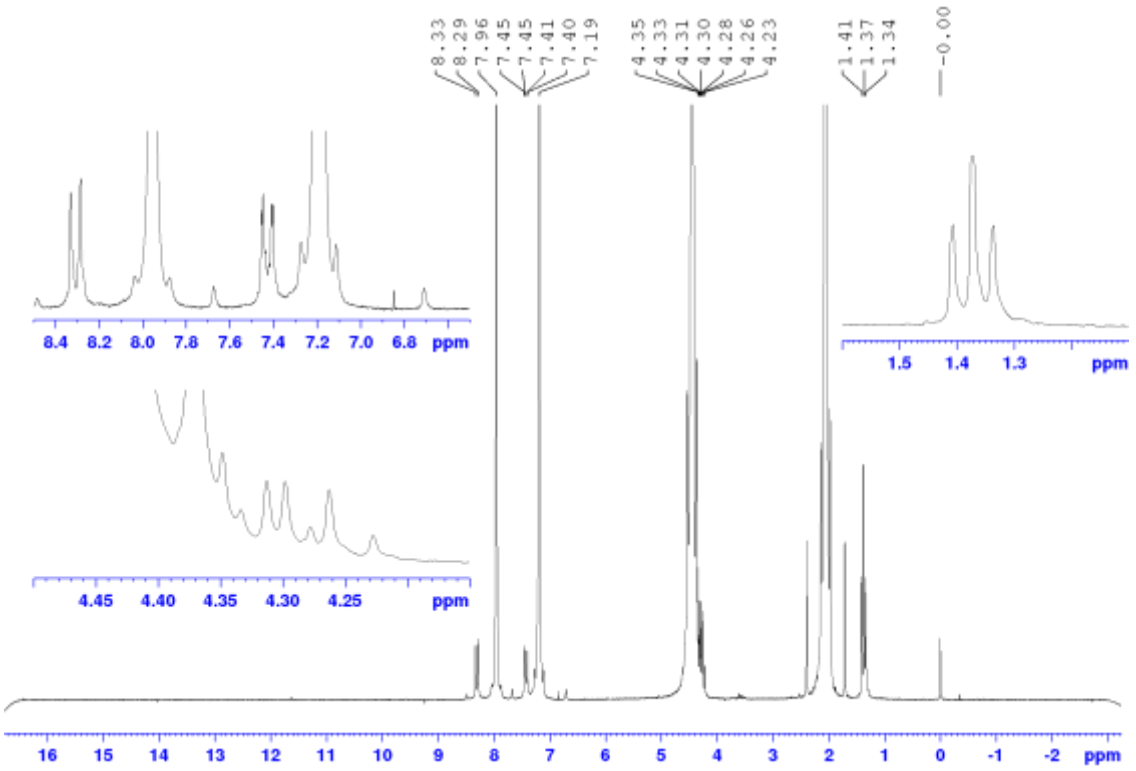


Figure S3. ^{1}H NMR spectrum (200 MHz) at reaction start (day 1), imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.2) at 80 °C.

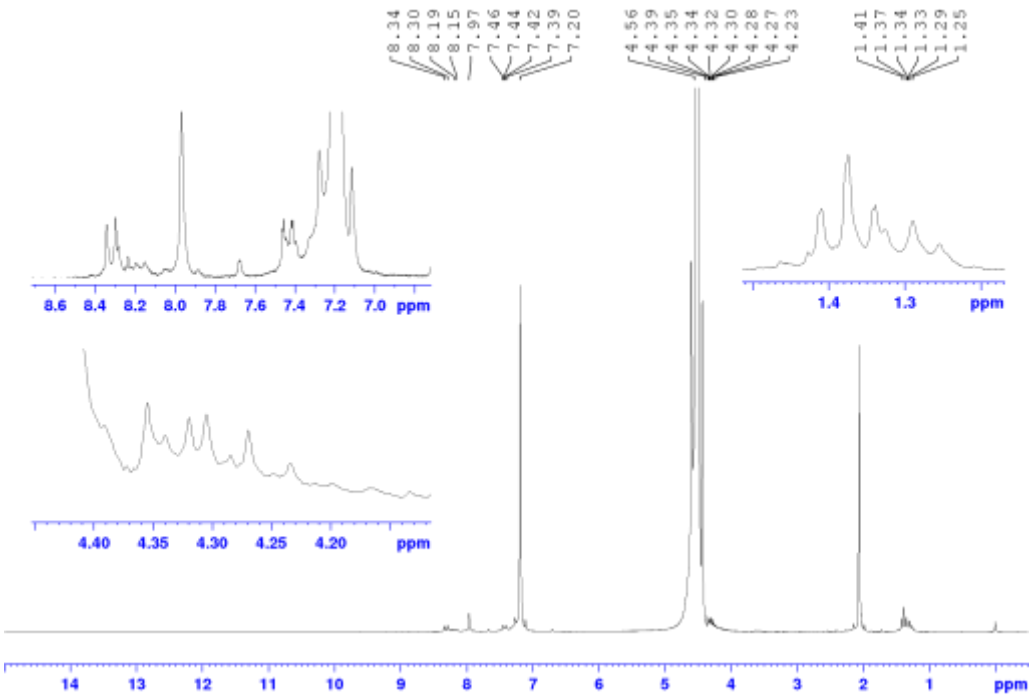


Figure S4. ^{1}H NMR spectrum (200 MHz) at day 2, imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.2) at 80 °C.

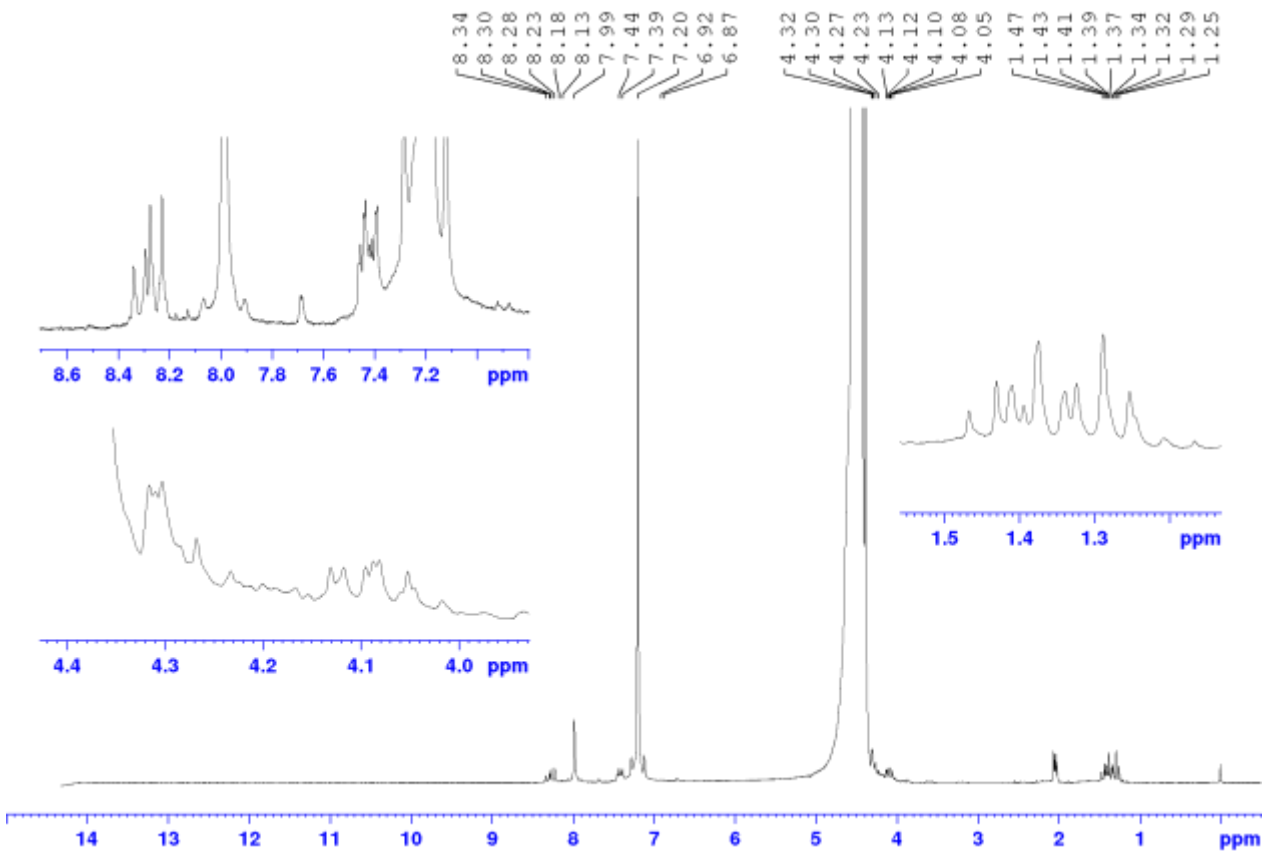


Figure S5. ^{1}H NMR spectrum (200 MHz) at day 3, imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.2) at 80 °C.

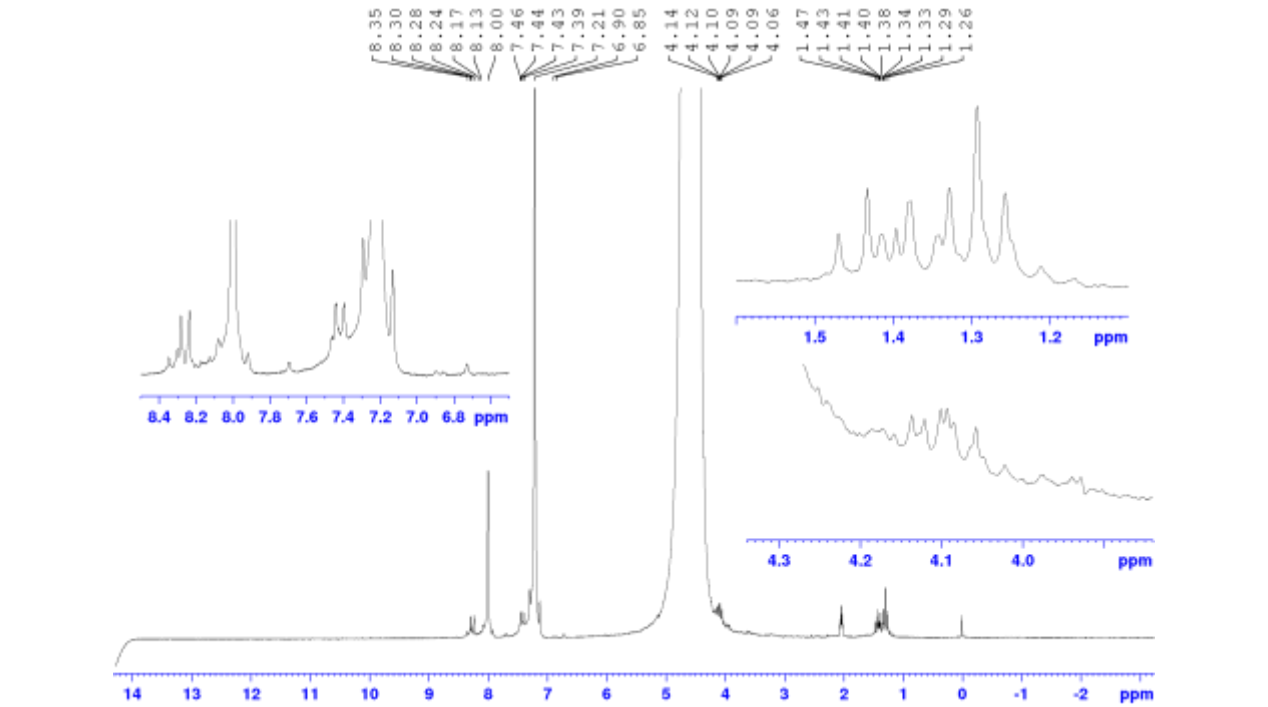


Figure S6. ^{1}H NMR spectrum (200 MHz) at day 4, imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.2) at 80 °C.

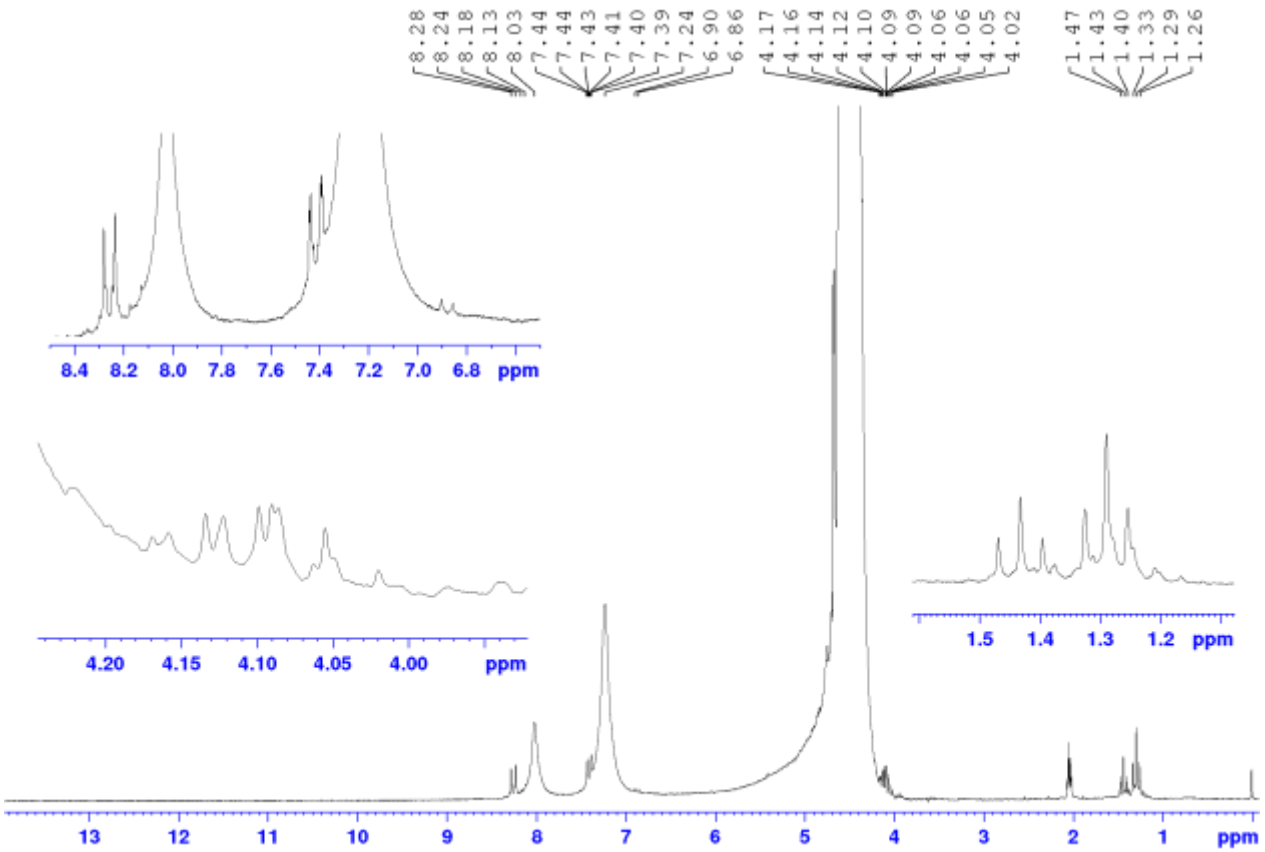


Figure S7. ^{1}H NMR spectrum (200 MHz) at day 5, imidazole (0.17 mol.L^{-1}) + parathion (8.5 × 10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.2) at 80 °C.

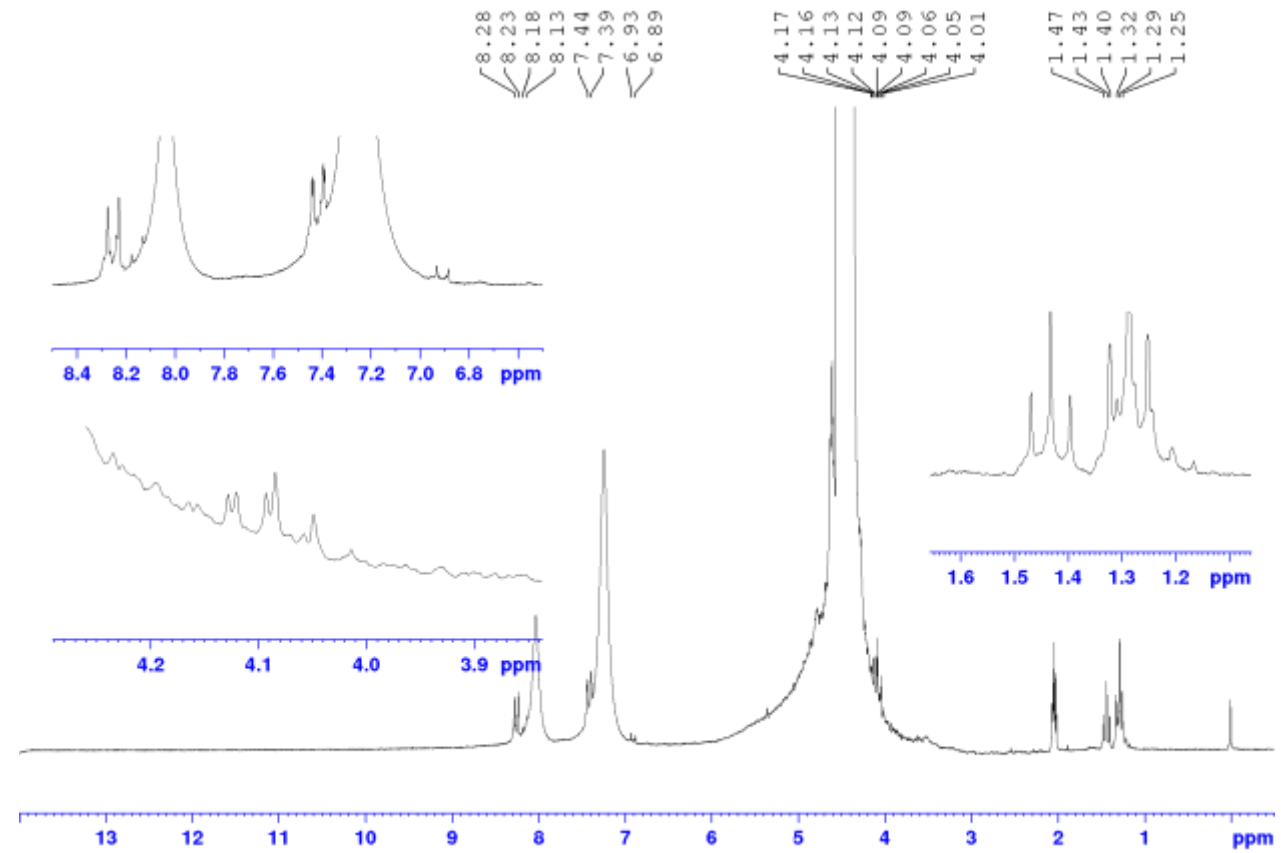


Figure S8. ^{1}H NMR spectrum (200 MHz) at day 6, imidazole (0.17 mol L^{-1}) + parathion (8.5 × 10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.2) at 80 °C.

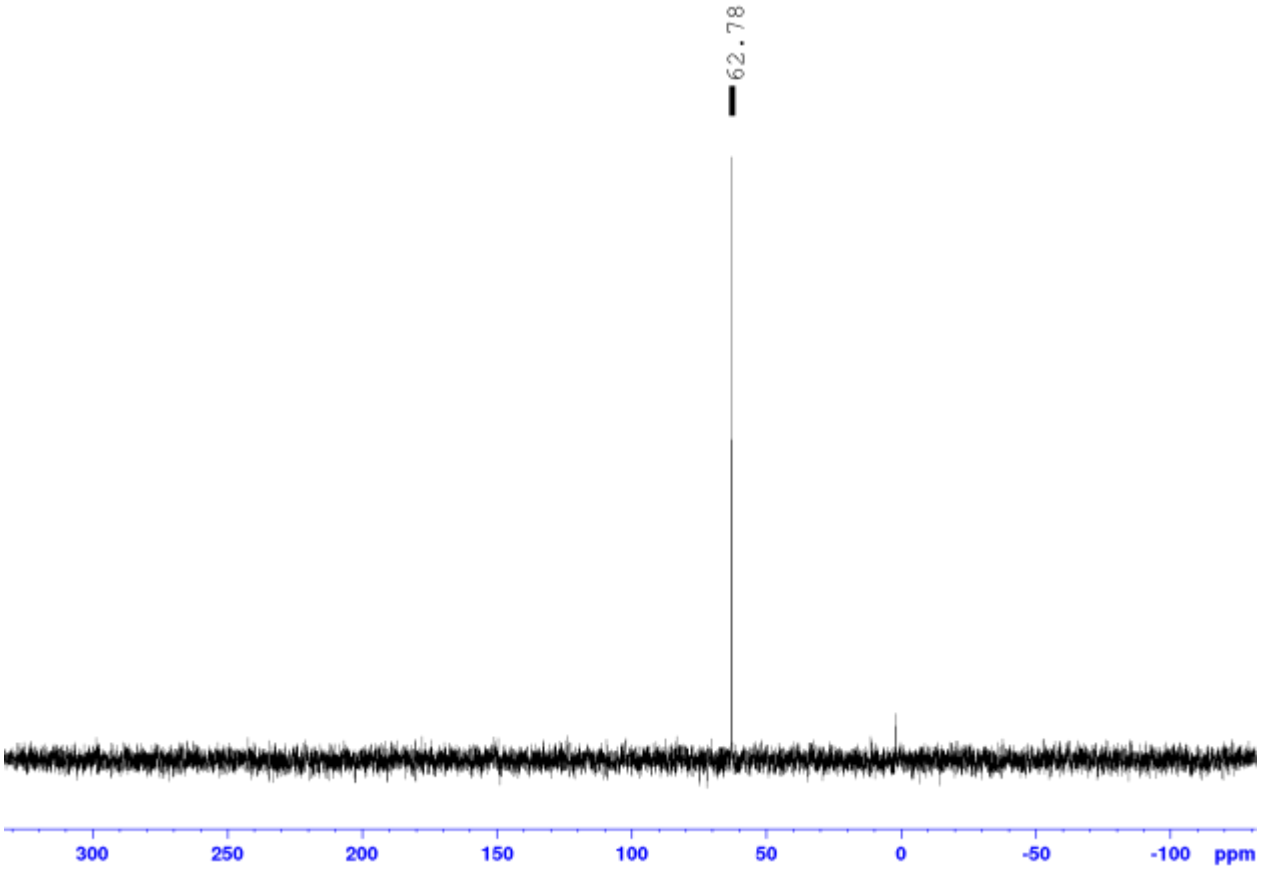


Figure S9. ^{31}P NMR spectrum (80 MHz) at reaction beginning (day 1), imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.2) at 80 °C.

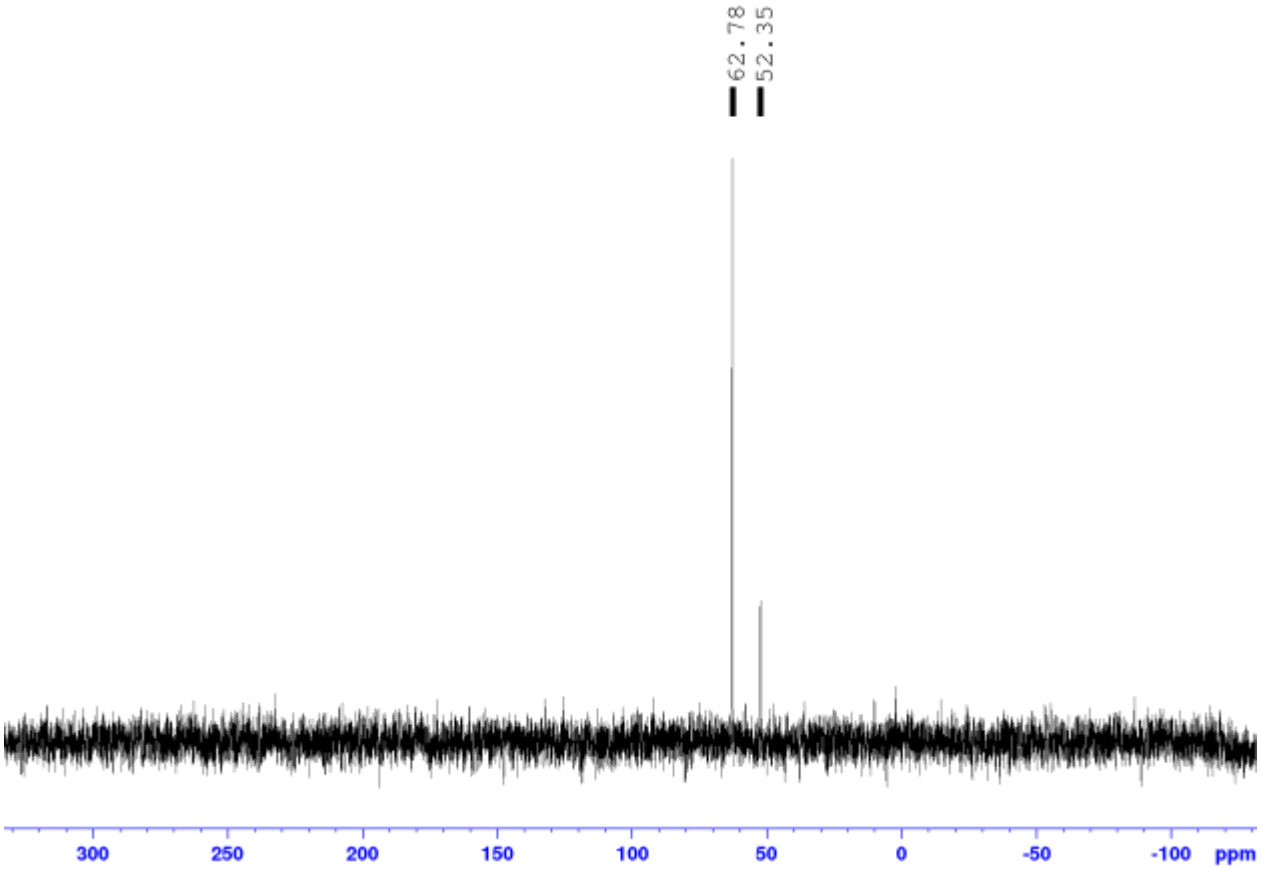


Figure S10. ^{31}P NMR spectrum (80 MHz) at day 2, imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.2) at 80 °C.

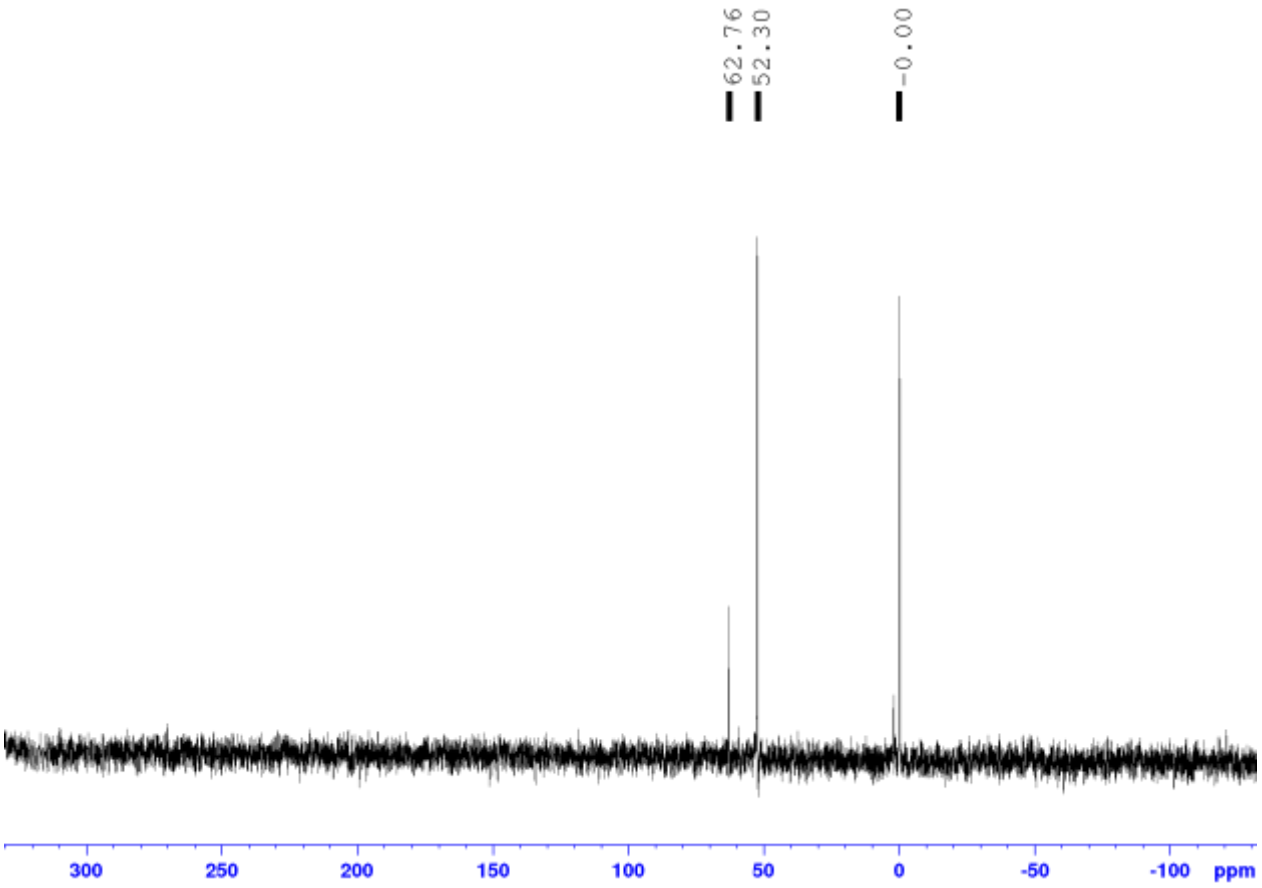


Figure S11. ^{31}P NMR spectrum (80 MHz) at reaction day 4, imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.2) at 80 °C.

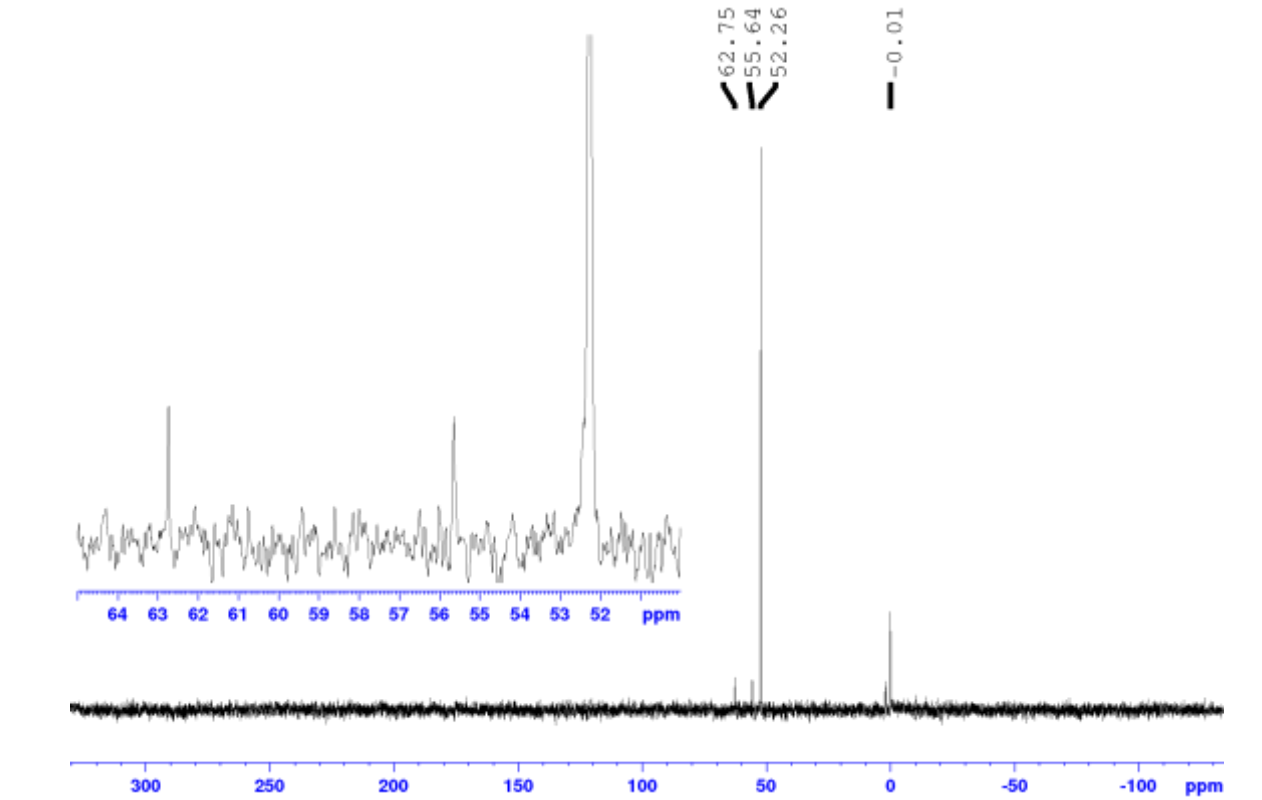


Figure S12. ^{31}P NMR spectrum (80 MHz) at reaction day 5, imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.2) at 80 °C.

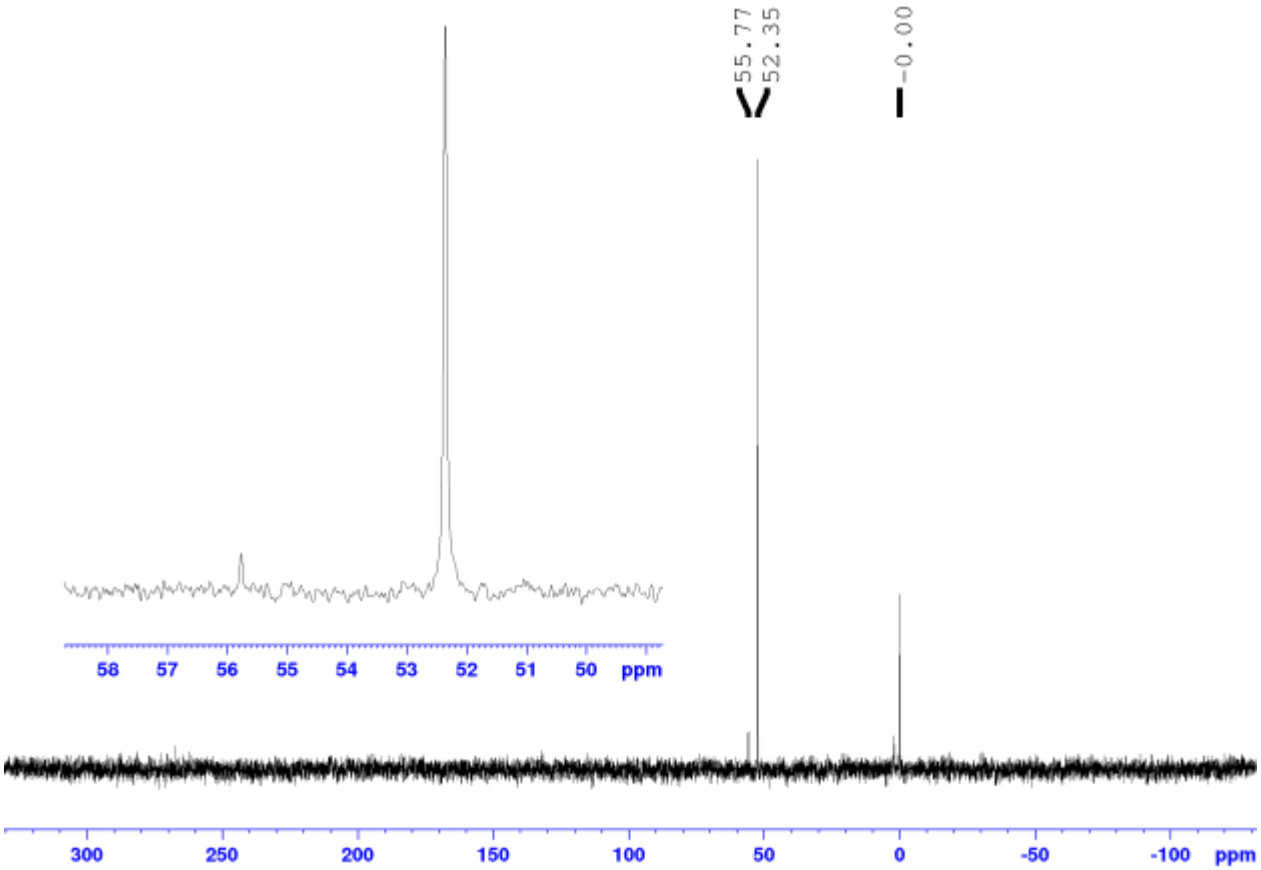


Figure S13. ^{31}P NMR spectrum (80 MHz) at reaction start (day 6), imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.2) at 80 °C.

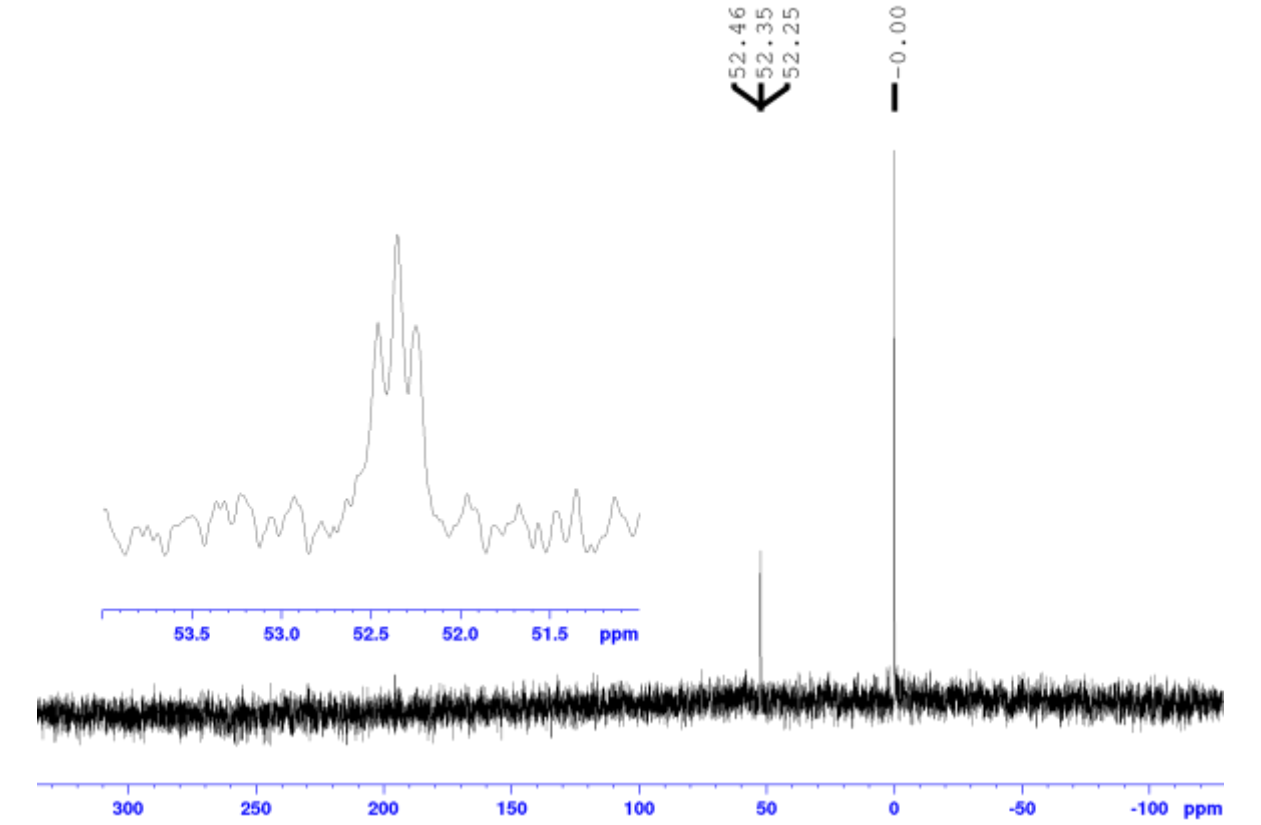


Figure S14. ^{31}P NMR coupled spectrum (80 MHz) at reaction start (day 6), imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.2) at 80 °C.

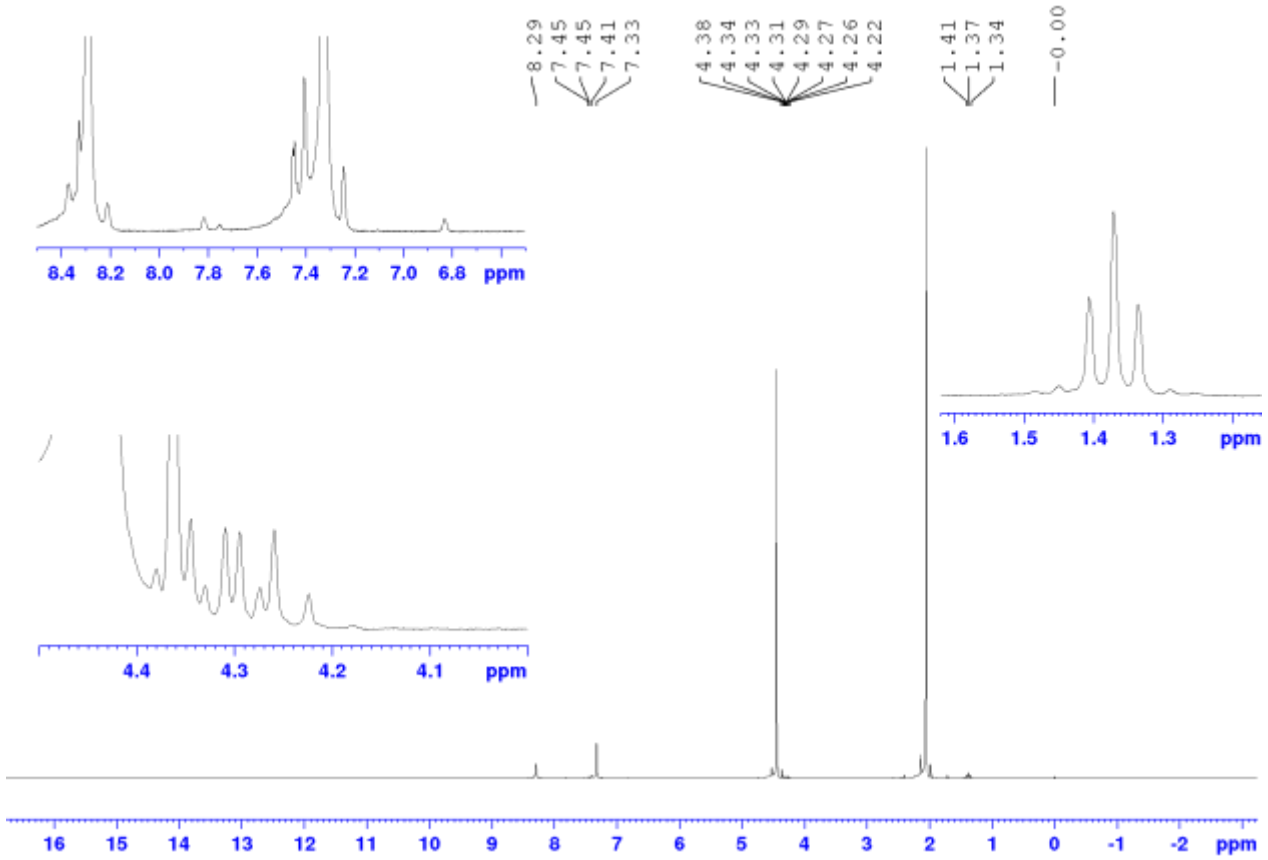


Figure S15. ^{1}H NMR spectrum (200 MHz) at reaction start (day 1), imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 7.2) at 80 °C.

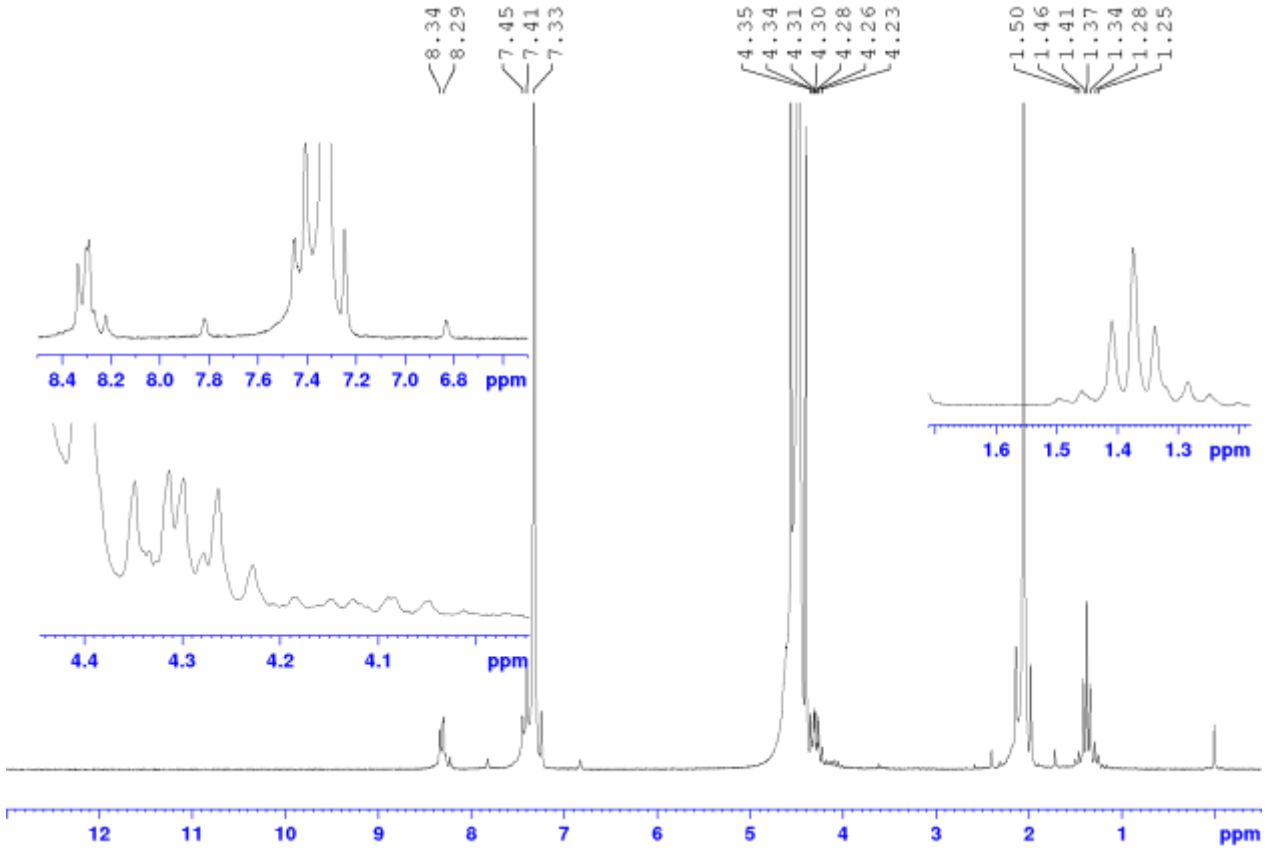


Figure S16. ^{1}H NMR spectrum (200 MHz) at day 2, imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 7.2) at 80 °C.

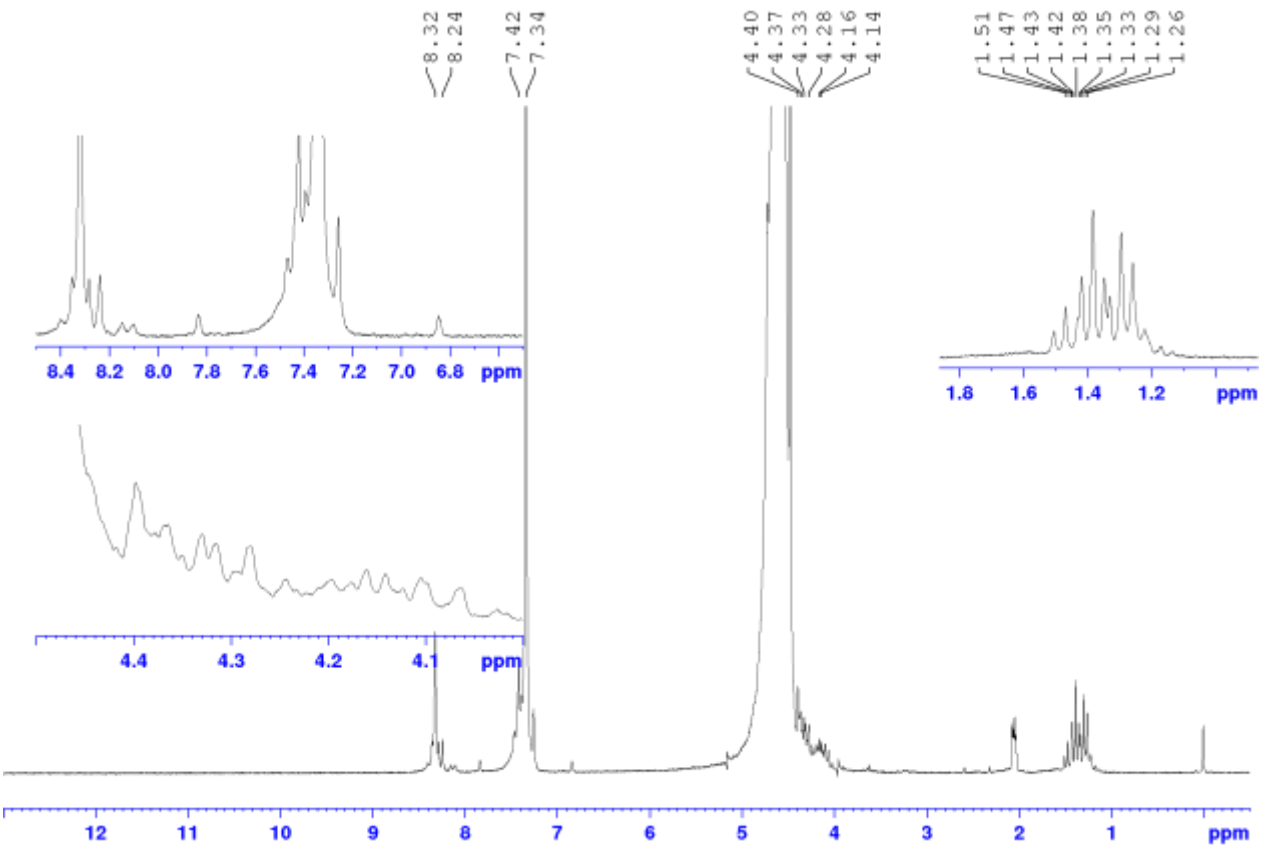


Figure S17. ^{1}H NMR spectrum (200 MHz) at day 3, imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 7.2) at 80 °C.

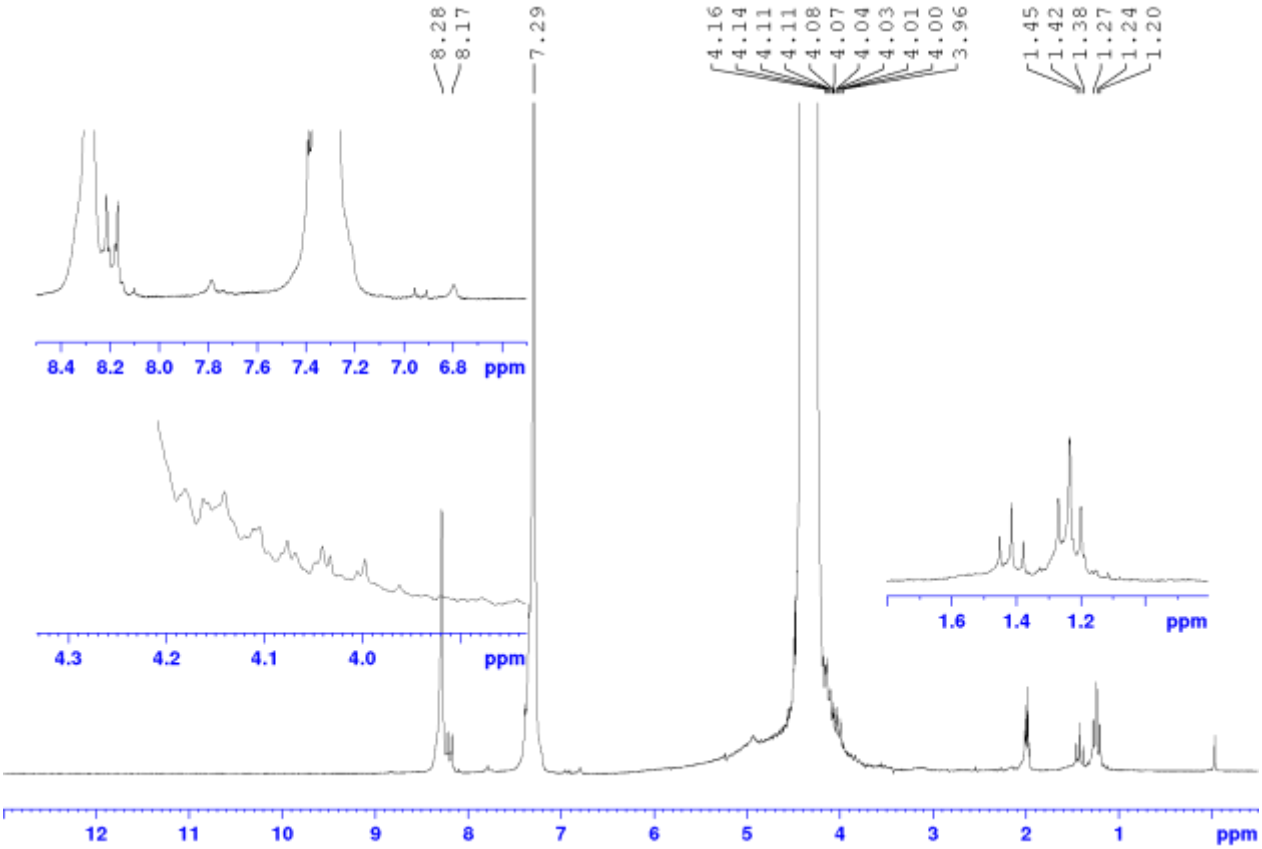


Figure S18. ^{1}H NMR spectrum (200 MHz) at day 6, imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 7.2) at 80 °C.

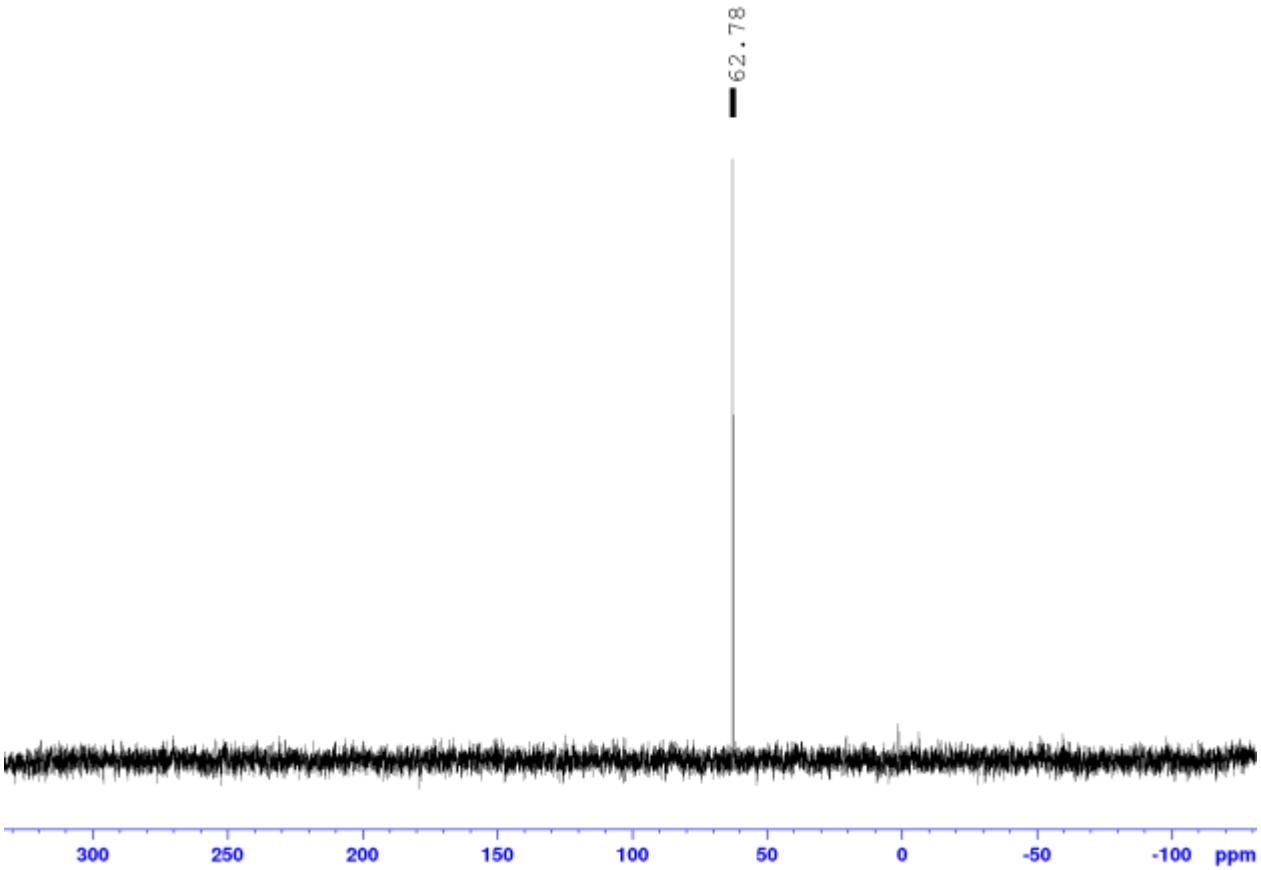


Figure S19. ^{31}P NMR spectrum (80 MHz) at reaction start (day 1), imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 7.2) at 80 °C.

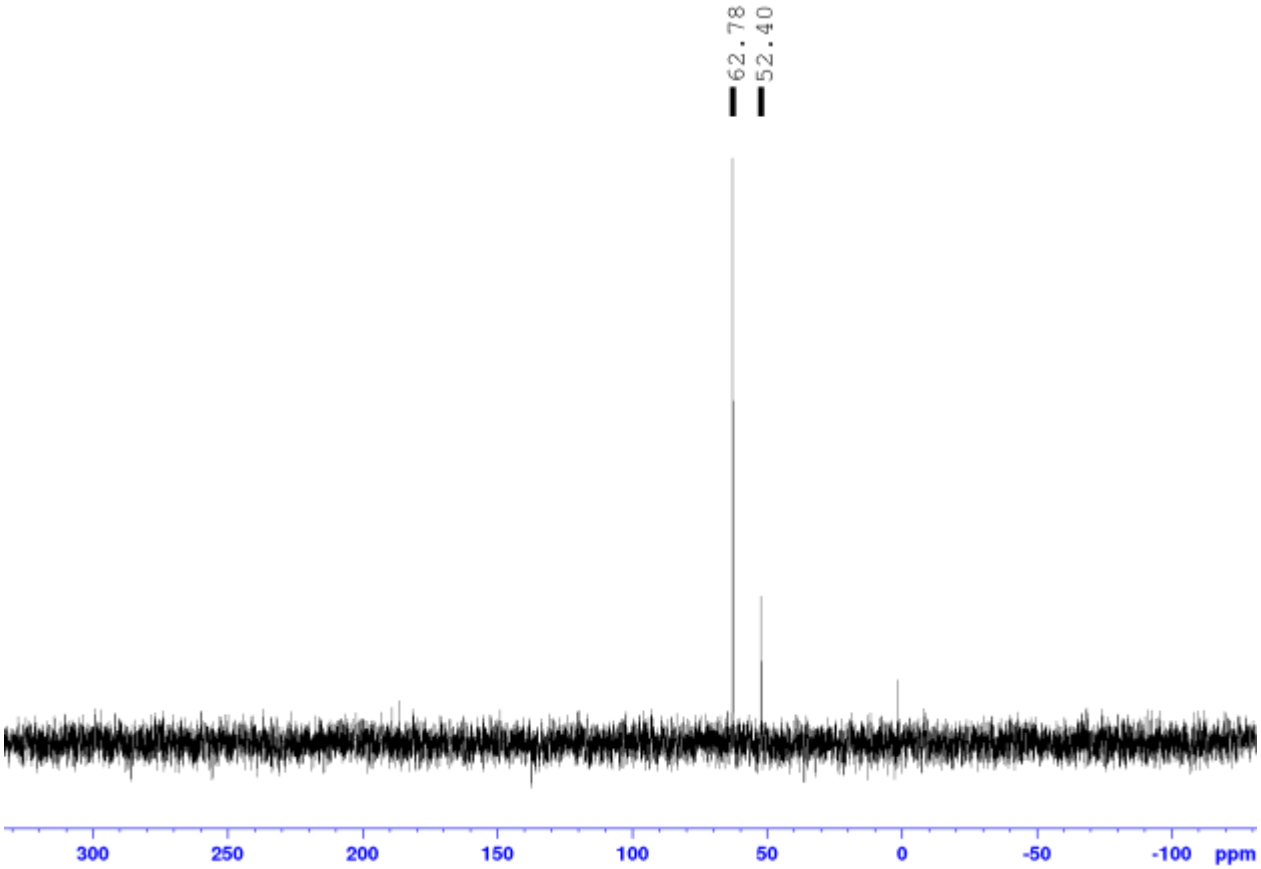


Figure S20. ^{31}P NMR spectrum (80 MHz) at day 2, imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 7.2) at 80 °C.

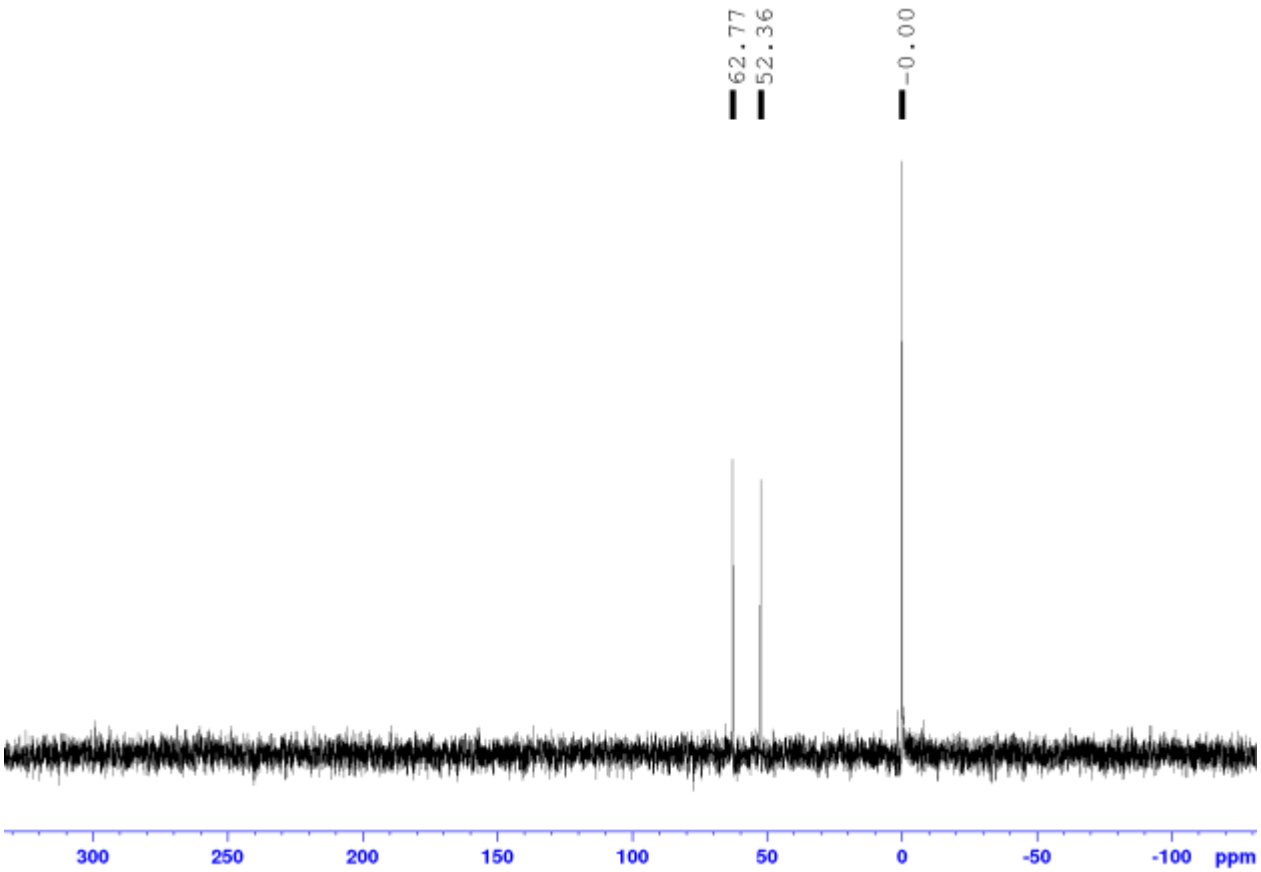


Figure S21. ^{31}P NMR spectrum (80 MHz) at day 3, imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 7.2) at 80 °C.

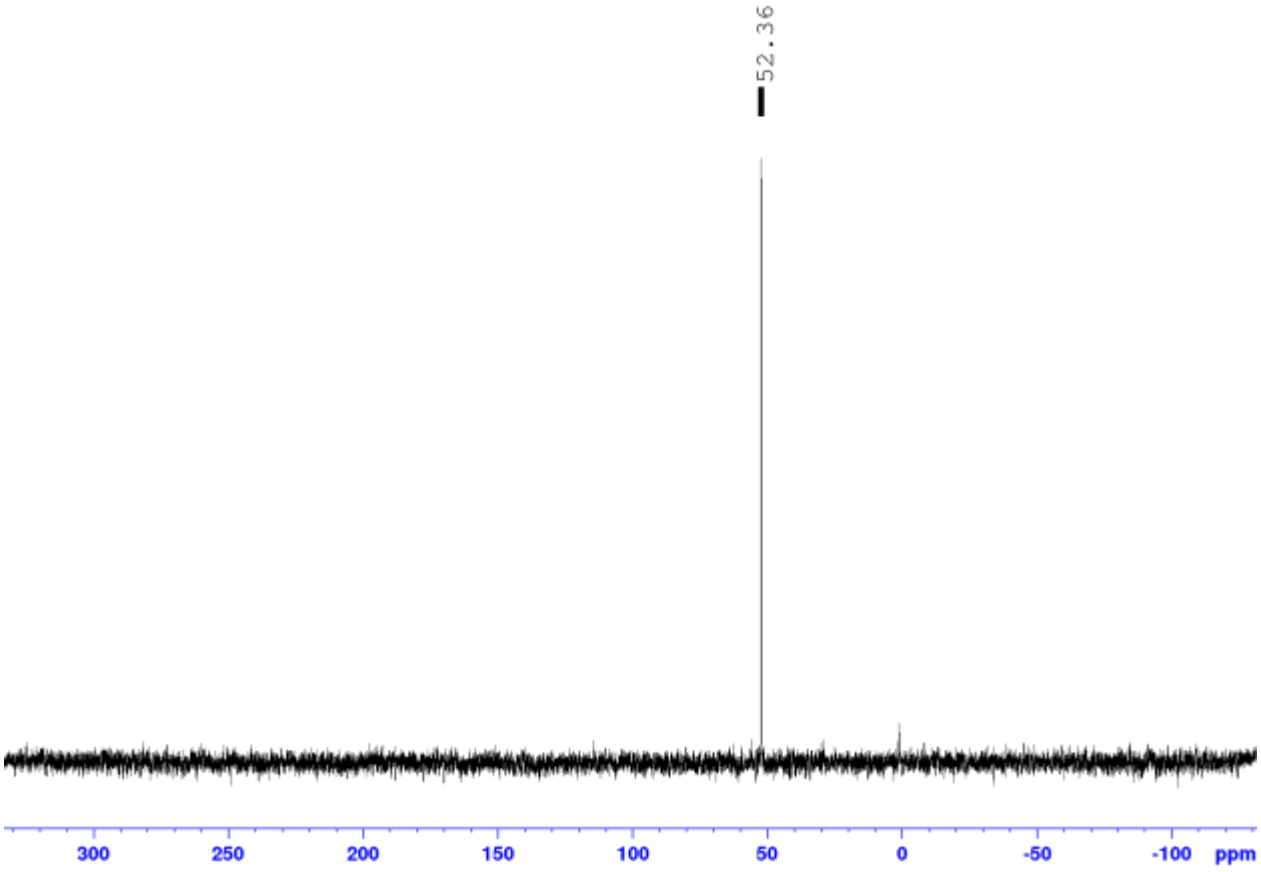


Figure S22. ^{31}P NMR spectrum (80 MHz) at day 6, imidazole (0.17 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 7.2) at 80 °C.

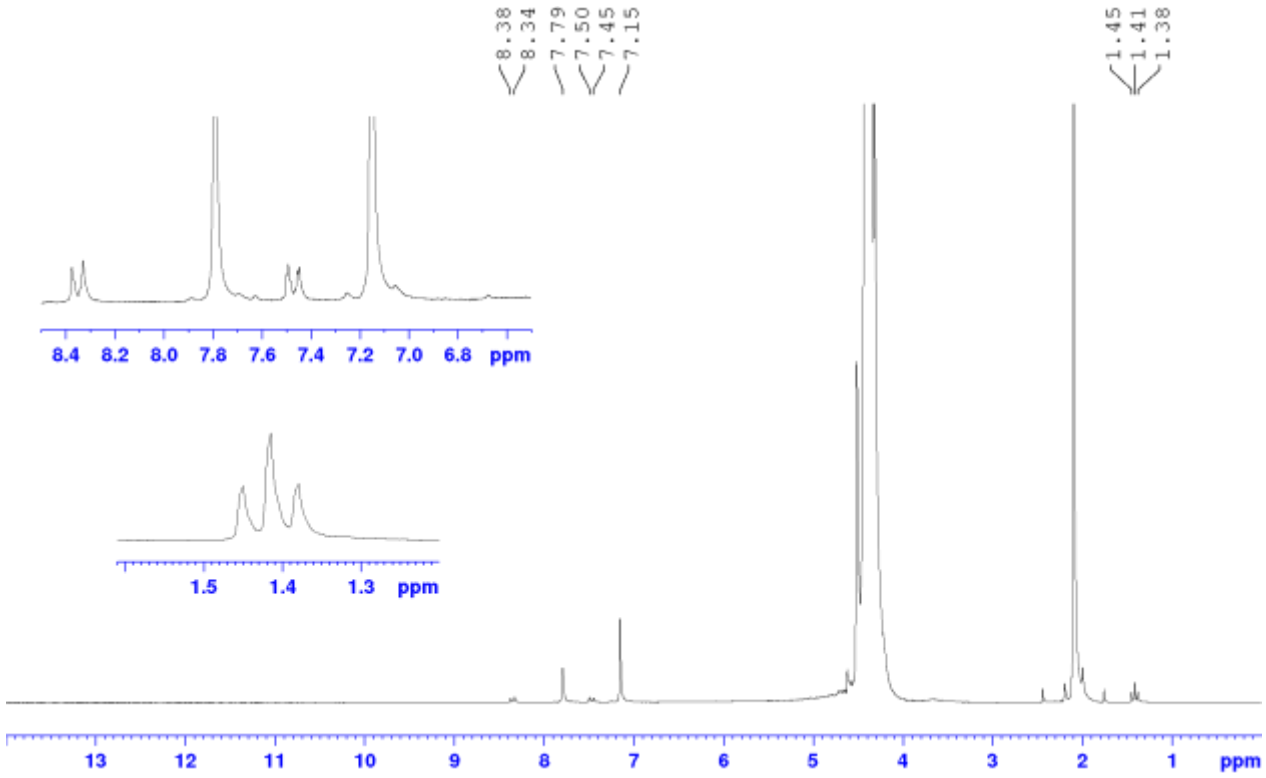


Figure S23. ^{1}H NMR spectrum (200 MHz) at reaction beginning (day 1), imidazole (0.1 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.8) at 60 °C.

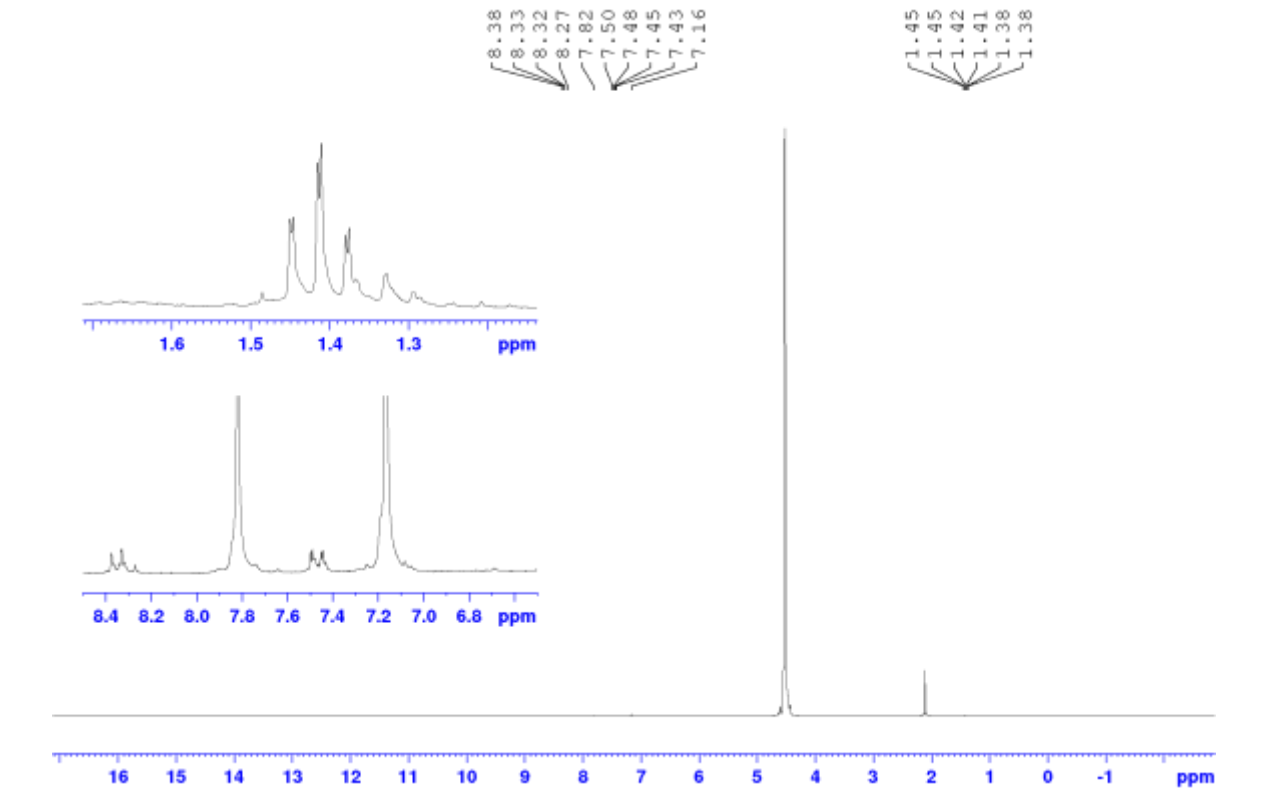


Figure S24. ^{1}H NMR spectrum (200 MHz) at day 5 imidazole (0.1 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.8) at 60 °C.

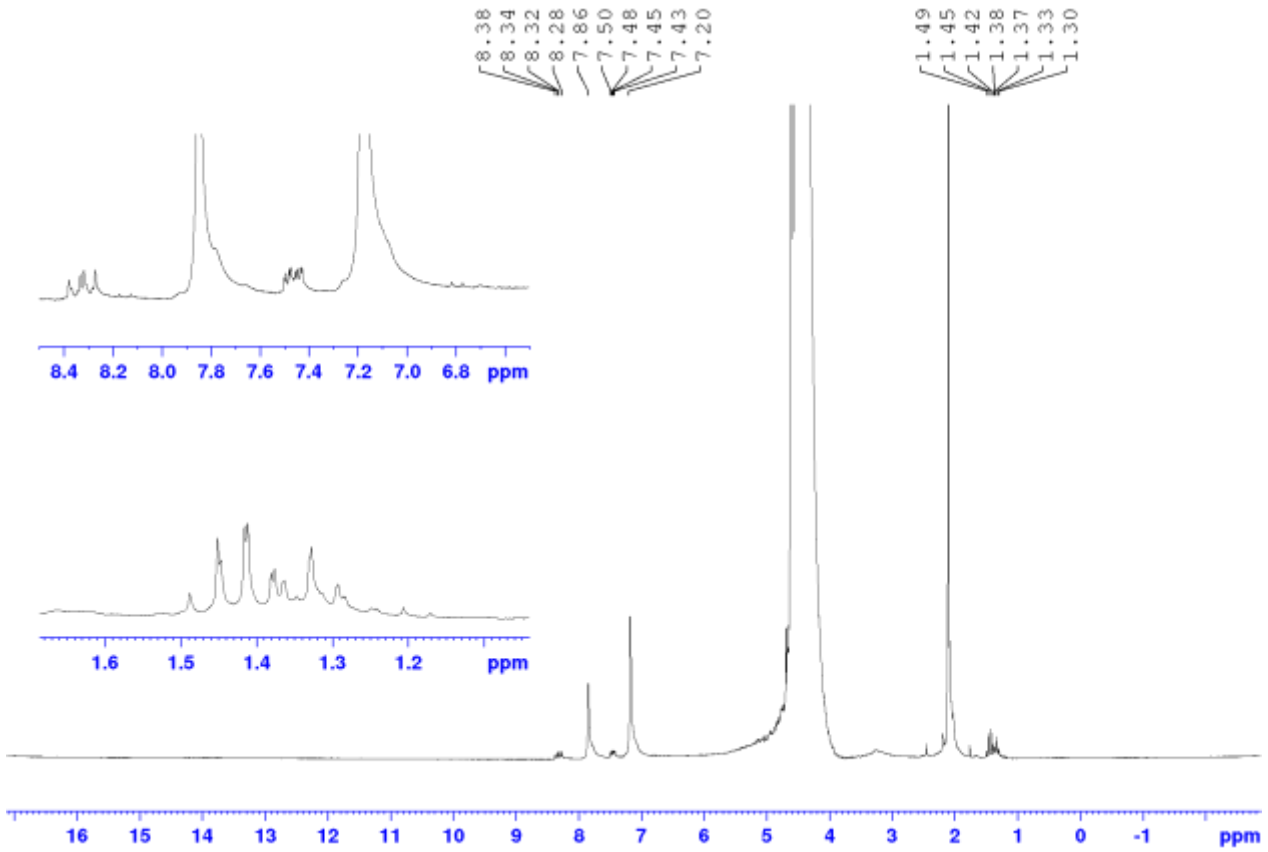


Figure S25. ^{1}H NMR spectrum (200 MHz) at day 10 imidazole (0.1 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.8) at 60 °C.

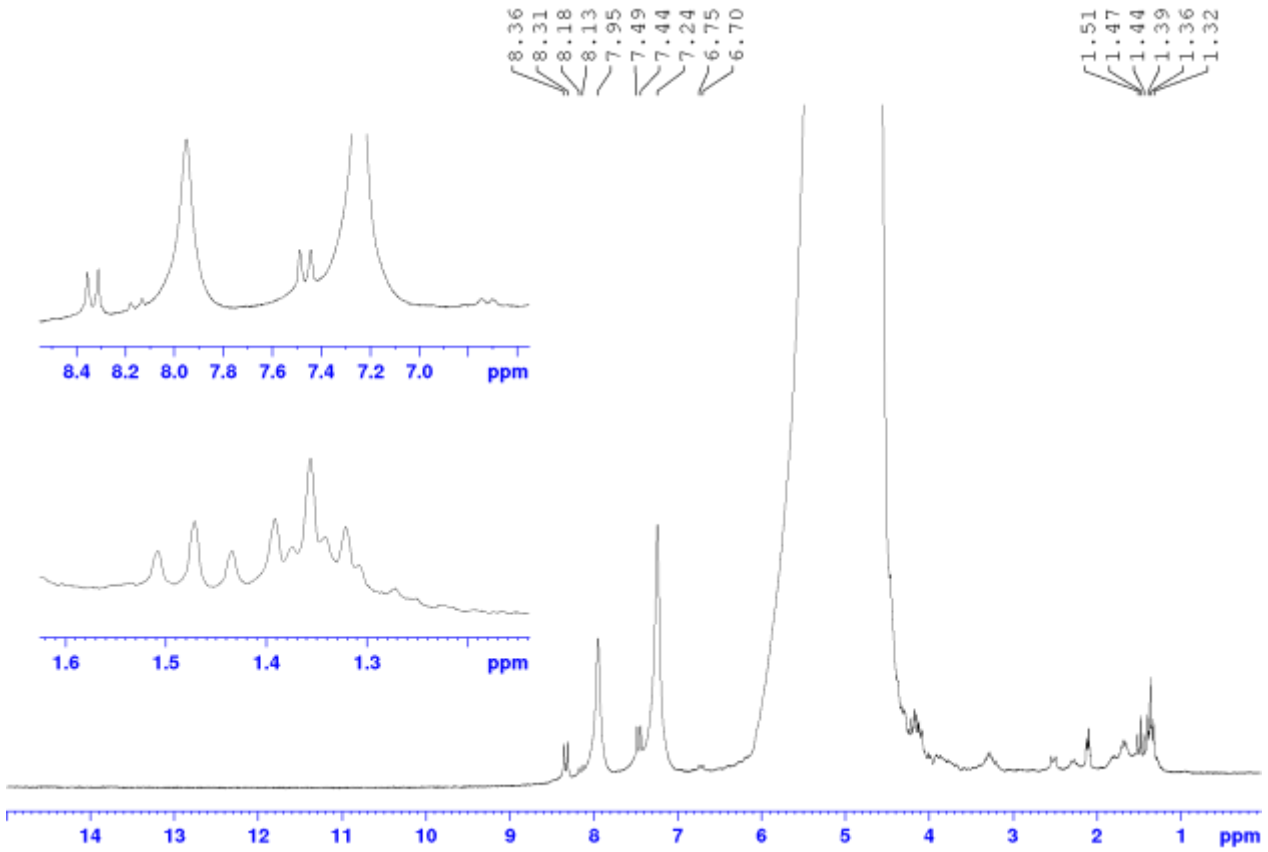


Figure S26. ^{1}H NMR spectrum (200 MHz) at day 20 imidazole (0.1 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.8) at 60 °C.

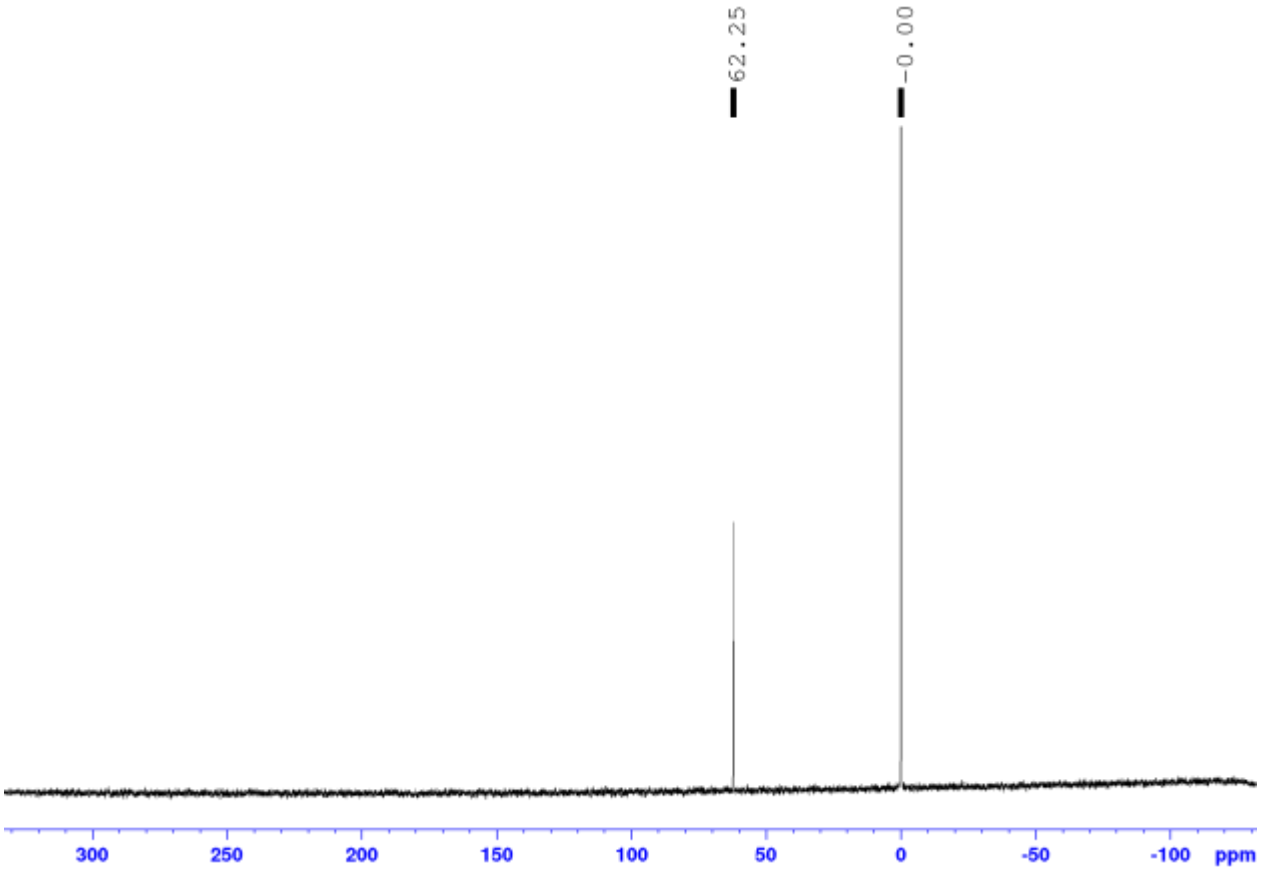


Figure S27. ^{31}P NMR spectrum (80 MHz) at reaction start (day 1) imidazole (0.1 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.8) at 60 °C.

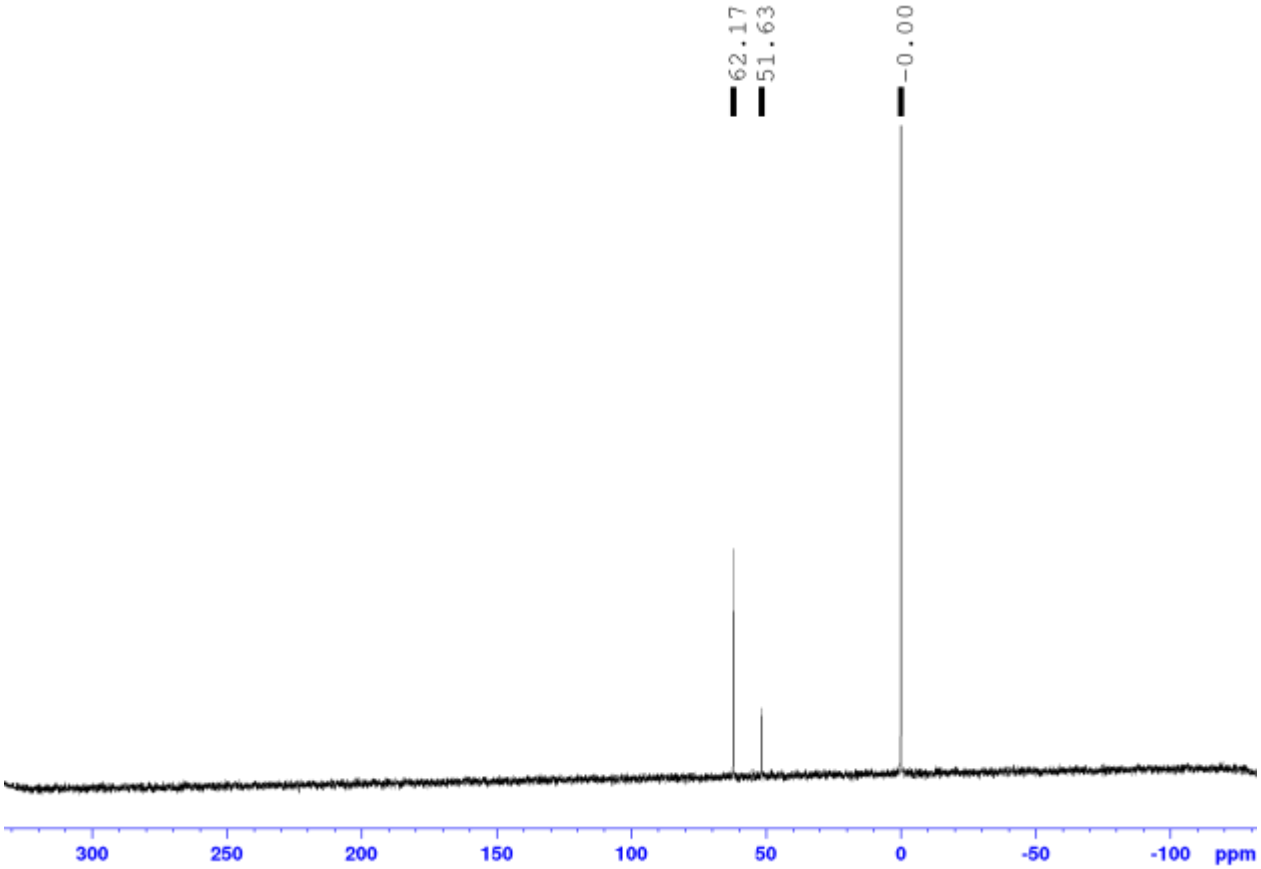


Figure S28. ^{31}P NMR spectrum (80 MHz) at day 5, imidazole (0.1 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.8) at 60 °C.

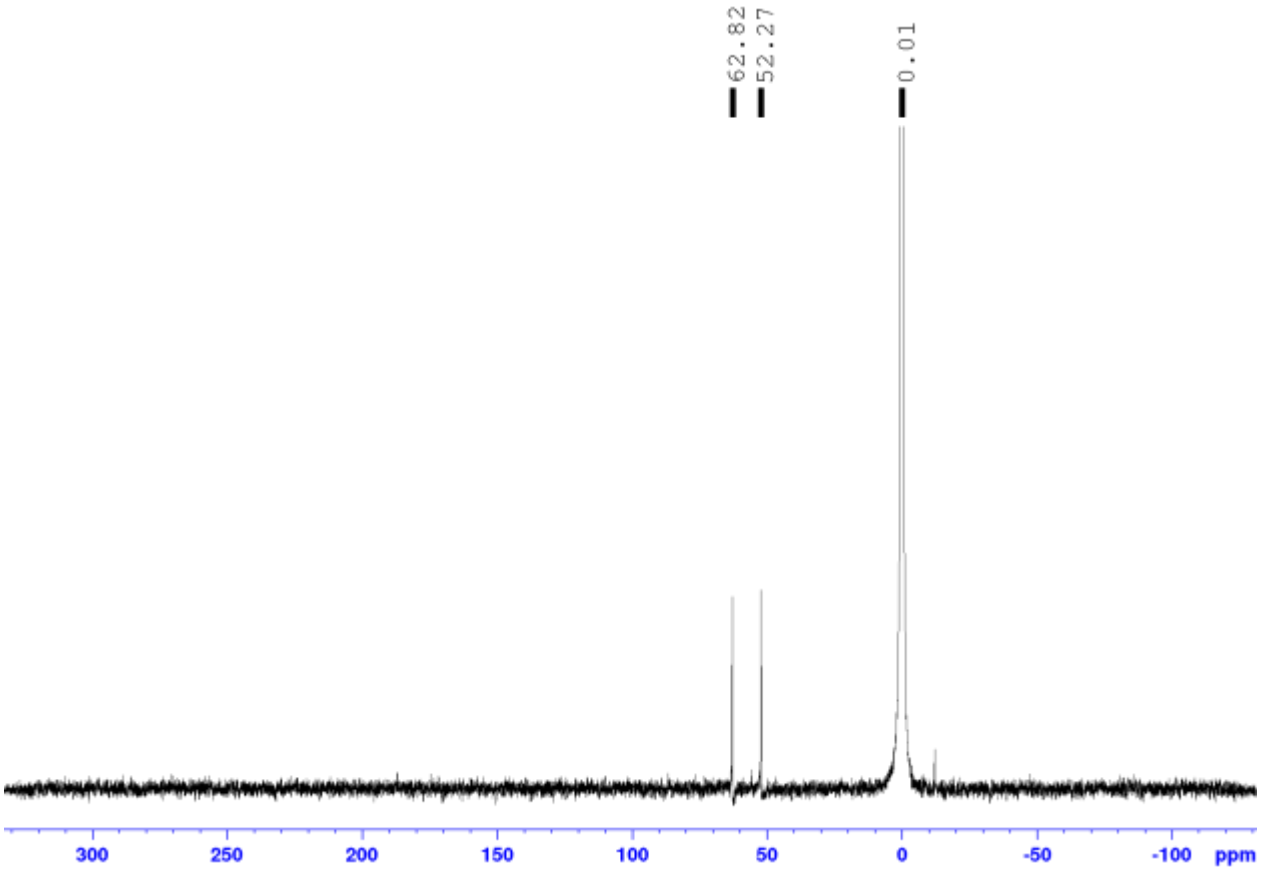


Figure S29. ^{31}P NMR spectrum (80 MHz) at day 10, imidazole (0.1 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.8) at 60 °C.

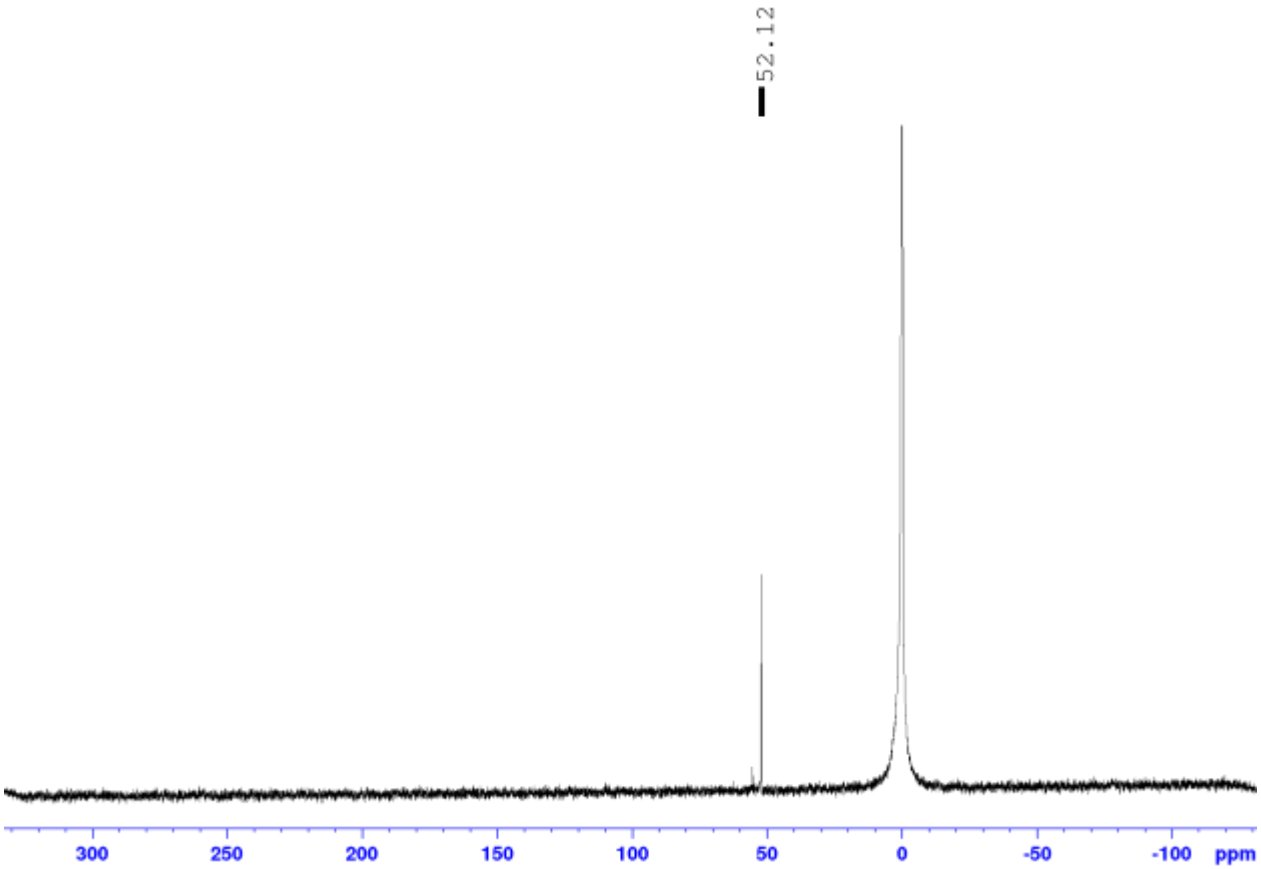


Figure S30. ^{31}P NMR spectrum (80 MHz) at day 20 (day 1) imidazole (0.1 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.8) at 60 °C.

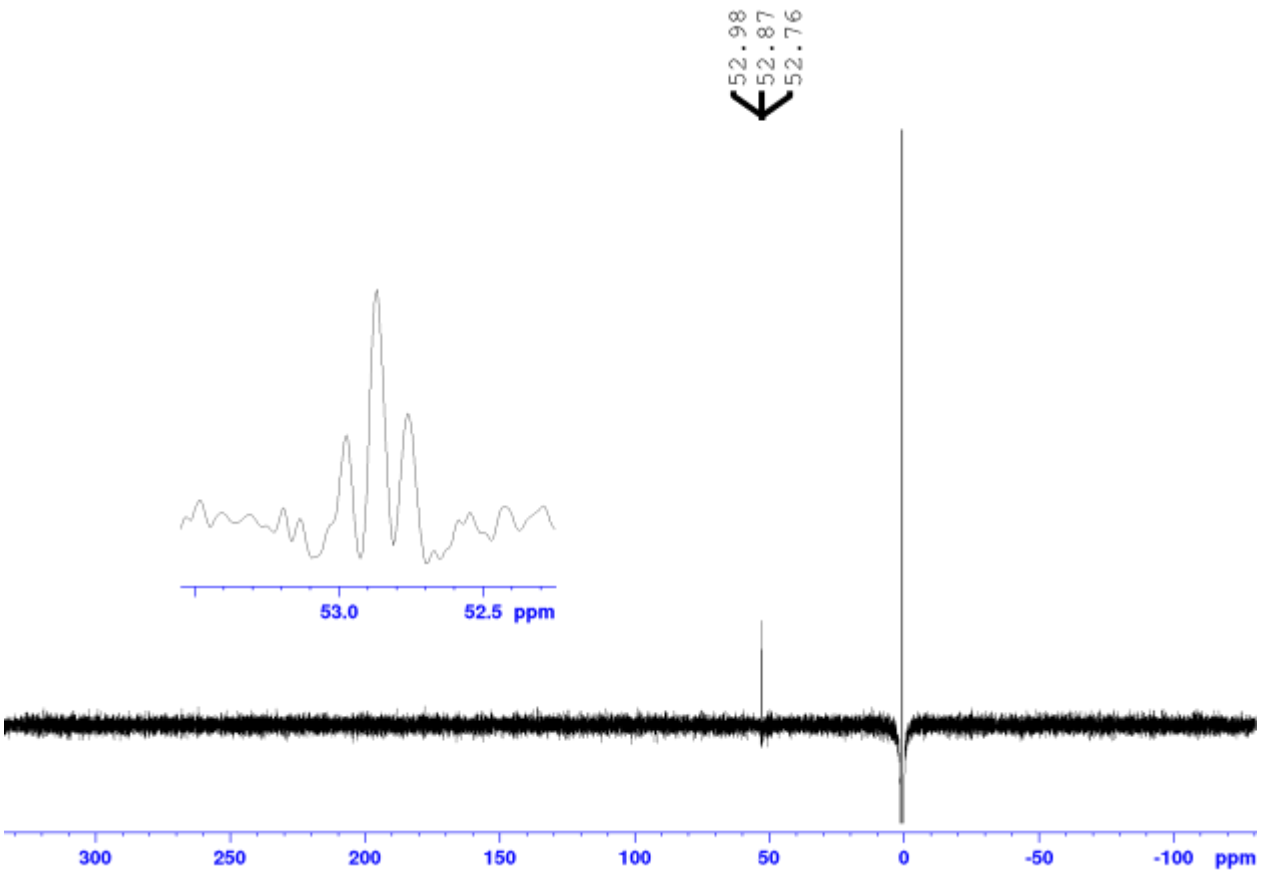


Figure S31. ^{31}P NMR spectrum (80 MHz) coupled at day 20 (day 1) imidazole (0.1 mol L^{-1}) + parathion (8.5×10^{-3} mol L^{-1}) (CD_3CN/D_2O 40:60 pD 8.8) at 60 °C.