Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Base catalysed intermolecular cyclisation of *N*-protected *o*-amino benzaldehyde/ acetophenone with phosphorus/ sulphur based allenes: Facile synthesis of substituted quinolines

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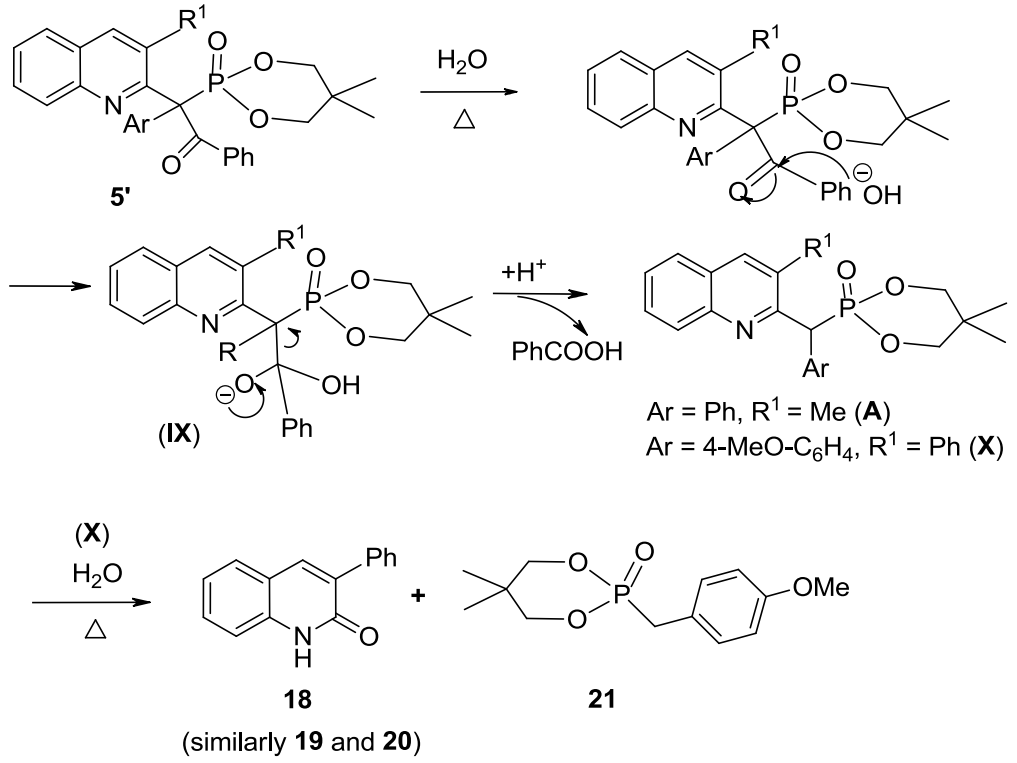
1. Plausible pathway for the formation of phosphorus-free quinolinones 18-20, anisyl phosphonate 21, and phosphono-quinoline A

Formation of compound **A** can be explained *via* compound **5'** (R = Ph, R^1 = Me; Scheme S1) similar to **5** (cf. Scheme 5) may be involved. In the presence of liberated H_2O, **5'** leads to **X** after benzoic acid elimination followed by abstraction of proton , which may to lead to product **A**.[15] Formation of phosphorus-free quinolinone **18** and anisyl phosphonate **21** looks odd, but we presume that intermediate **X** that is analogous to compound **A** may be involved. Compounds **19** and **20** are formed in a similar manner. As mentioned in the main text, we concentrated upon quinolones and hence did not investigate this part further.

Scheme S1. Possible pathway for the formation of compounds A, X and 18-21



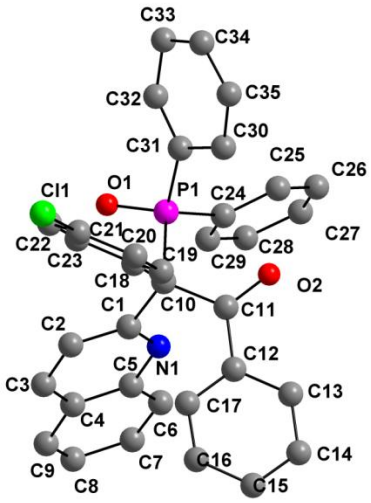


Figure S1. Molecular structure of compound **26**. Hydrogen atoms are omitted for clarity. Selected bond parameters: N1-C1 1.31(5), C1-C10 1.54(6), C10-C11 1.53(6), C18-C10 1.55(6), P1-C10 1.91(4), C1-C2 1.40(6), O2-C11 1.22(5) (Å).

X-ray Data.

X-ray data for compounds **5, 18, 19, 26, 31** and **33** were collected using Mo K_α (λ = 0.71073 Å) and for compound **9,** by Cu K_α radiation. The structures were solved and refined by standard methods as mentioned in the main text. The CCDC numbers are 1447739-1447745.

Compound 5.

Colorless block, $C_{28}H_{26}NO_4P$, M = 471.47, Monoclinic, Space group $P2(1)/n$, a = 12.282(3), b = 8.9370(18), c = 22.179(4) Å, β = 92.60(3), V = 2431.9(8) $Å^3$, Z = 4, μ = 0.148 mm^{-1}, data/restraints/parameters: 4288/0/309, R indices (I> 2σ(I)): R1 = 0.0573, *w*R2 (all data) = 0.1337. CCDC No. 1447739.

Compound 9.

Colorless block, $C_{29}H_{28}NO_4P$, M = 485.49, Triclinic, Space group *P-1*, a = 10.4790(9), b = 10.8907(9), c = 12.8985(9) Å, α = 68.115(7), β = 68.507(7), γ = 89.099(7)°, V = 1258.45(17) $Å^3$,

Z = 2, μ = 1.255 mm^{-1}, data/restraints/parameters: 4810/0/319, R indices (I> 2σ(I)): R1 = 0.0463, *w*R2 (all data) = 0.1358. CCDC No. 1447740.

Compound 18.

Colorless block, $C_{15}H_{11}NO$, M = 221.25, Monoclinic, Space group C2/c, a = 17.8590(16), b = 5.8124(4), c = 21.742(2) Å, β = 106.101(10), V = 2168.3(3) $Å^3$, Z = 8, μ = 0.085 mm^{-1}, data/restraints/parameters: 1902/0/158, R indices (I> 2σ(I)): R1 = 0.0409, *w*R2 (all data) = 0.1139. CCDC No. 1447741.

Compound 19.

Colorless block, $C_{15}H_{10}ClNO$, M = 255.69, Monoclinic, Space group C2/c, a = 17.482(4), b = 5.9043(13), c = 23.251(5) Å, β = 100.505(3)°, V = 2359.7(9) $Å^3$, Z = 8, μ = 0.308 mm^{-1}, data/restraints/parameters: 2057/0/167, R indices (I> 2σ(I)): R1 = 0.0479, *w*R2 (all data) = 0.1272. CCDC No. 1447742.

Compound 26.

Colorless block, $C_{35}H_{25}ClNO_2P$, M = 557.98, Monoclinic, Space group *P*2(1)/c, a = 9.6939(19), b = 21.405(4), c = 27.668(6) Å, β = 80.83(3)°, V = 5668(2) $Å^3$, Z = 8, μ = 0.225 mm^{-1}, data/restraints/parameters: 9976/26/721, R indices (I> 2σ(I)): R1 = 0.1094, *w*R2 (all data) = 0.2583. The quality of data was only moderate, and disorder was found at two carbon atoms (C41 and C42), However, the structure could be readily discerned. CCDC No. 1447743.

Compound 31.

Colorless block, $C_{30}H_{22}ClNO_3S$, M = 512.01, Triclinic, Space group *P-1*, a = 10.626(2), b = 11.358(2), c = 21.635(4) Å, α = 104.76(3), β = 91.46(3), γ = 90.01(3)°, V = 2524.1(9) $Å^3$, Z = 4, μ = 0.267 mm^{-1}, data/restraints/parameters: 5334/0/651, R indices (I> 2σ(I)): R1 = 0.0836, *w*R2 (all data) = 0.2541. CCDC No. 1447744.

Compound 33

Colorless block, $C_{29}H_{32}NO_6PS$, M = 553.59, Monoclinic, Space group C2/c, a = 34.280(3), b = 17.618(13), c = 25.486(4) Å, β = 131.39(3)^o, V = 11548(2) Å^3, Z = 16, μ = 0.209 mm^{-1}, data/restraints/parameters: 9448/0/696, R indices (I> 2σ(I)): R1 = 0.0617, *w*R2 (all data) = 0.1823. CCDC No. 1447745.

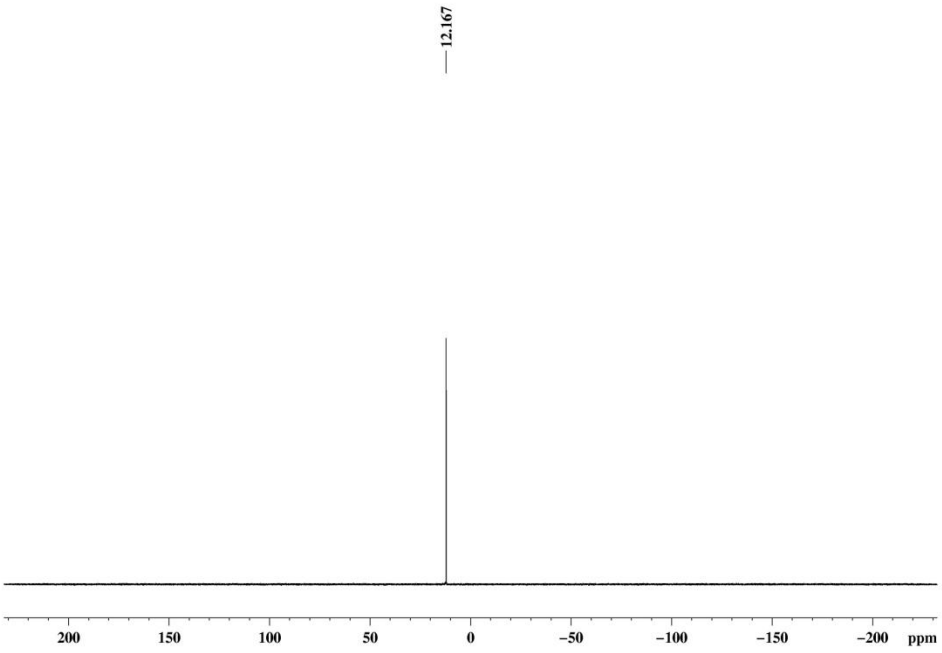


Figure S2. ^{31}P NMR spectrum of compound **5**

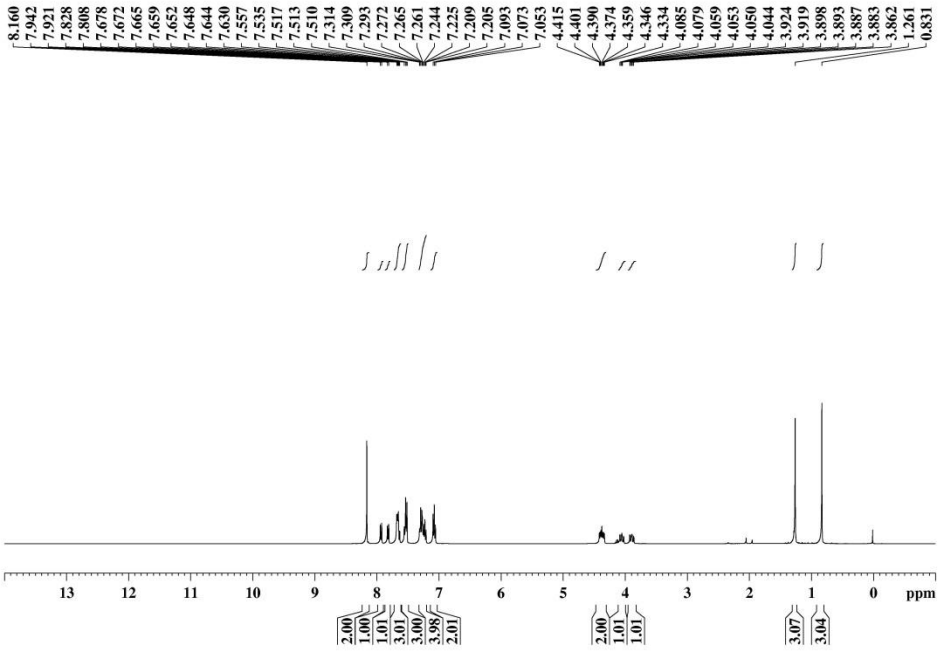


Figure S3. ^{1}H NMR spectrum of compound **5**

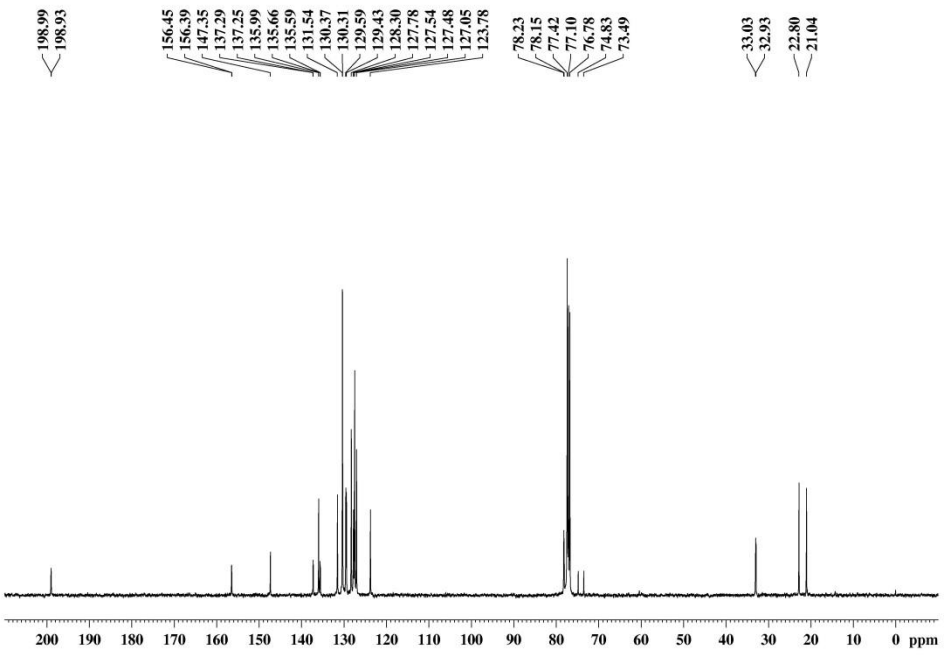


Figure S4. ^{13}C NMR spectrum of compound **5**

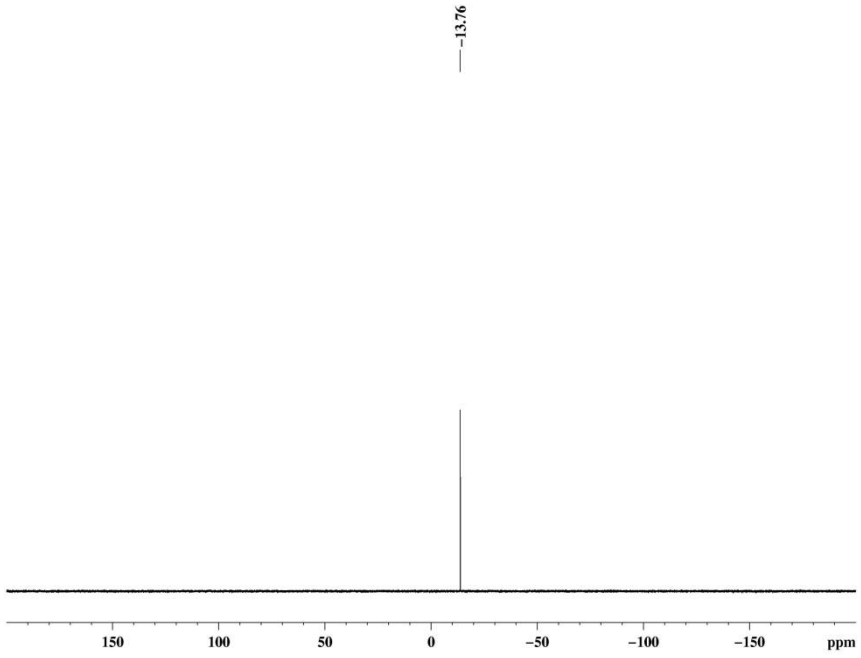


Figure S5. ^{31}P NMR spectrum of compound **6**

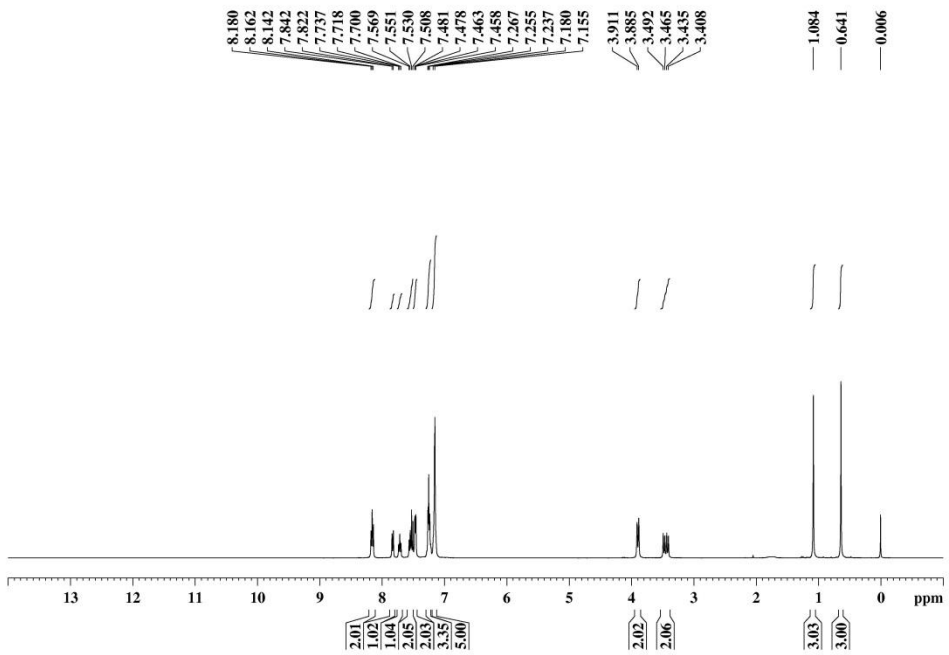


Figure S6. ^{1}H NMR spectrum of compound **6**

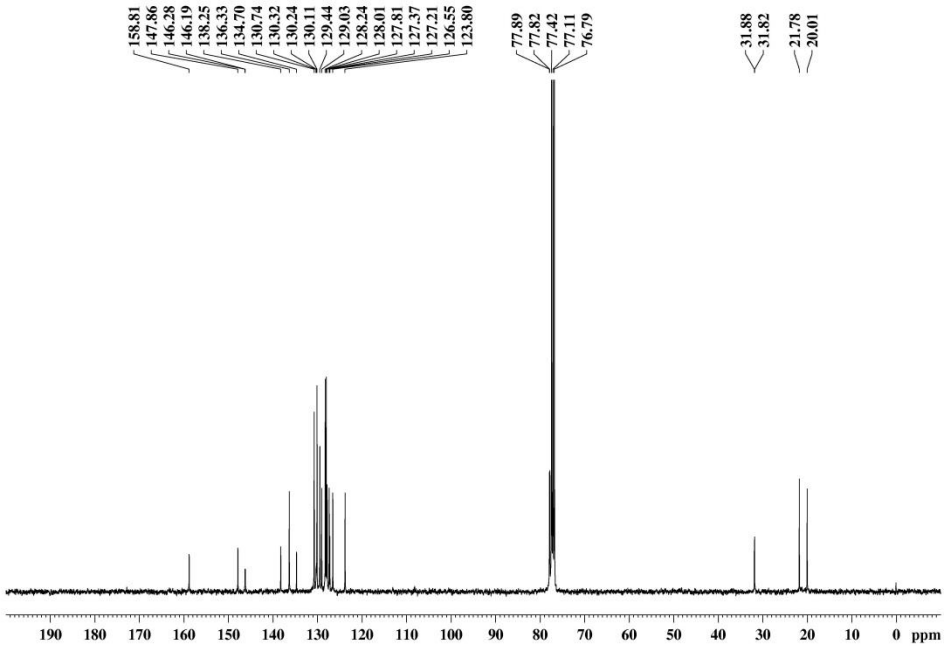


Figure S7. ^{13}C NMR spectrum of compound **6**

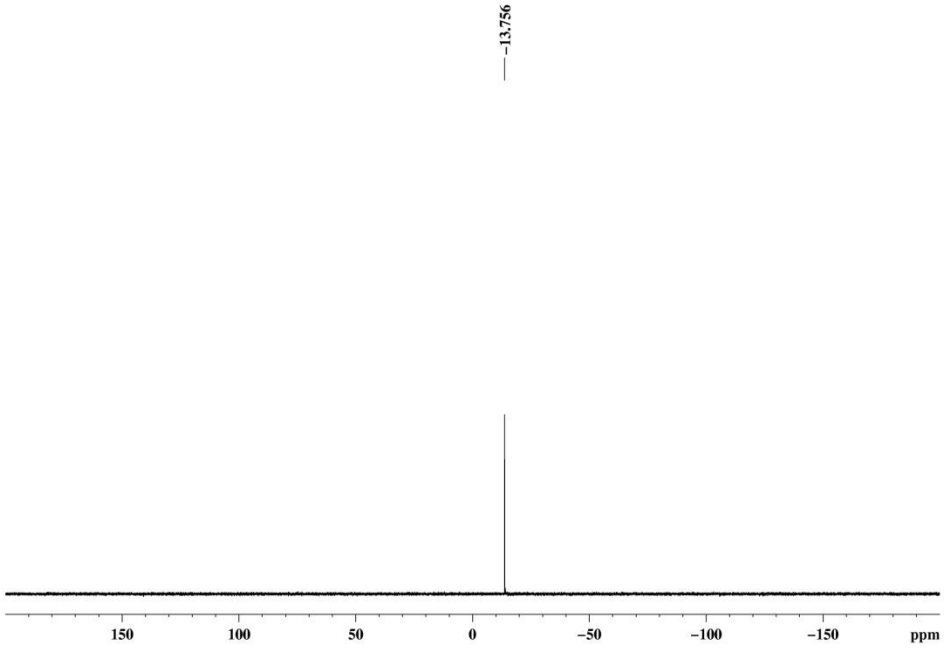


Figure S8. ^{31}P NMR spectrum of compound **7**

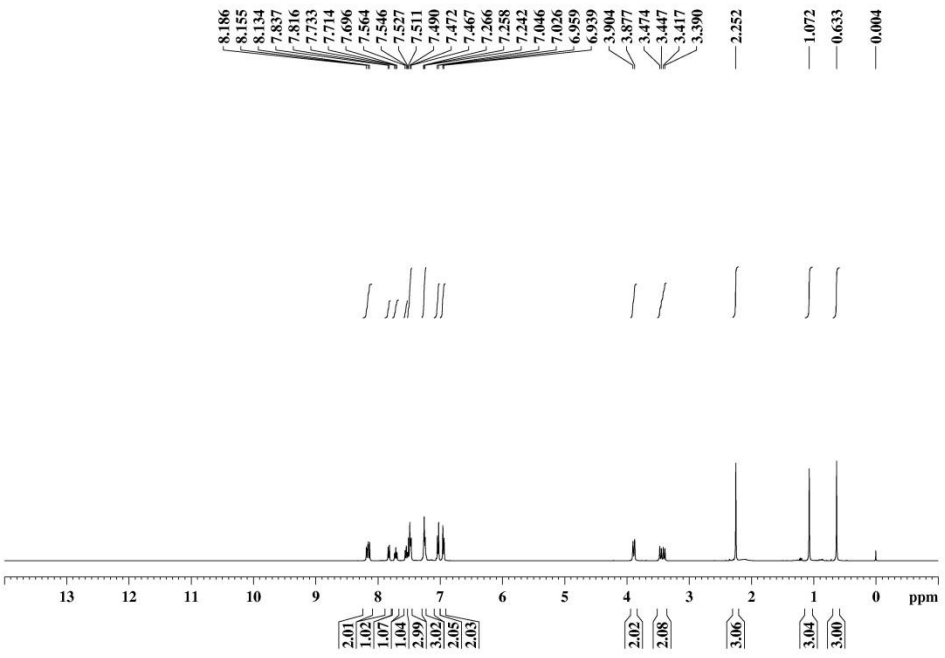


Figure S9. ^{1}H NMR spectrum of compound 7

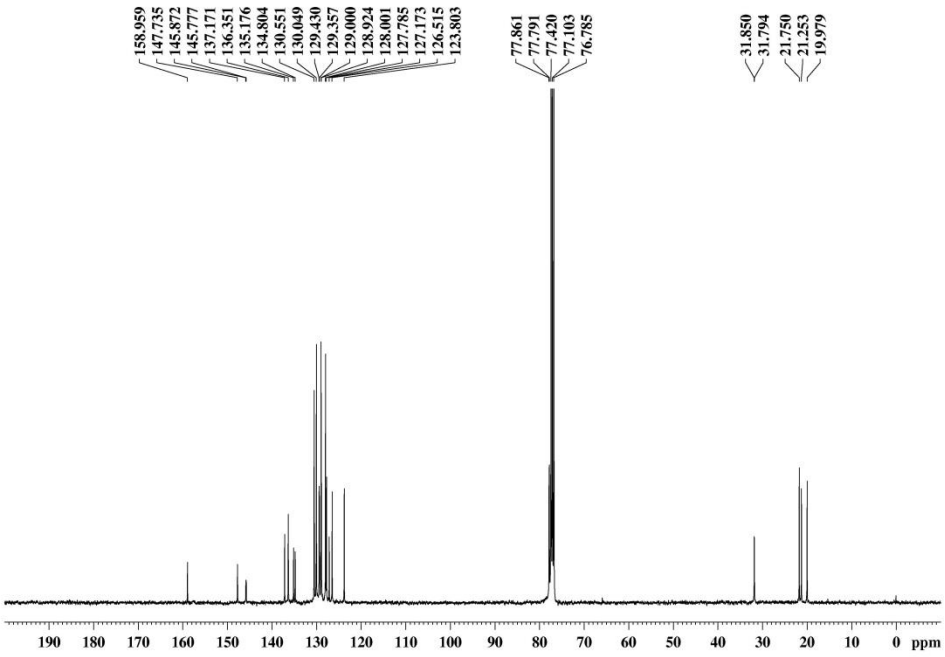


Figure S10. ^{13}C NMR spectrum of compound **7**

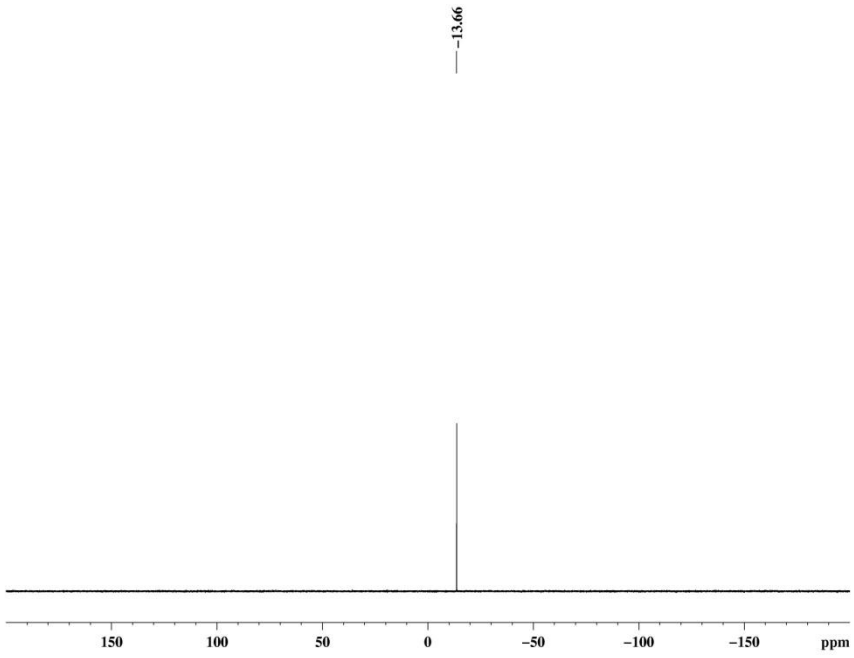


Figure S11. ^{31}P NMR spectrum of compound **8**

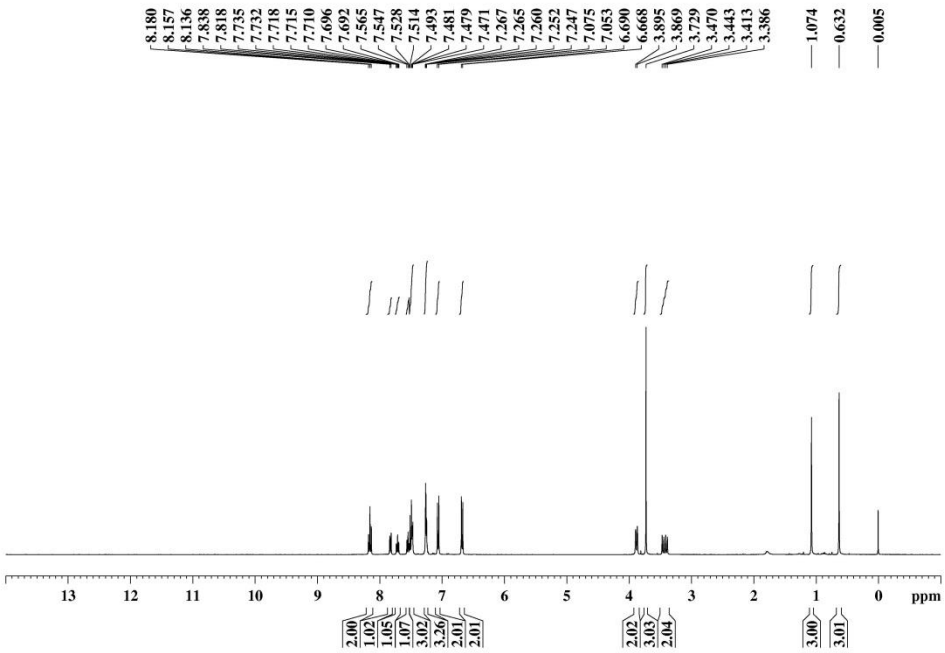


Figure S12. ^{1}H NMR spectrum of compound **8**

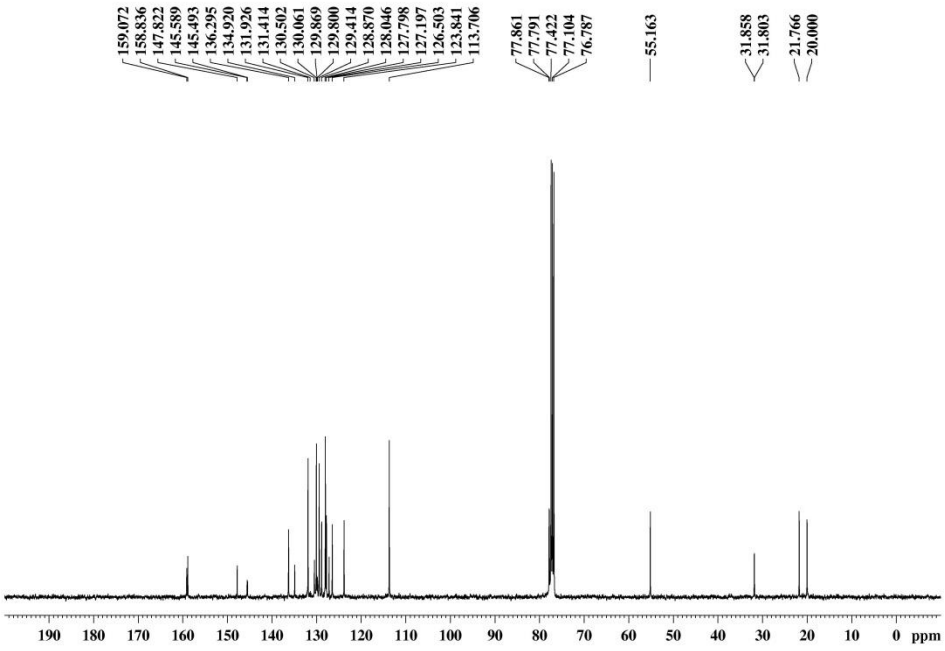


Figure S13. ^{13}C NMR spectrum of compound **8**

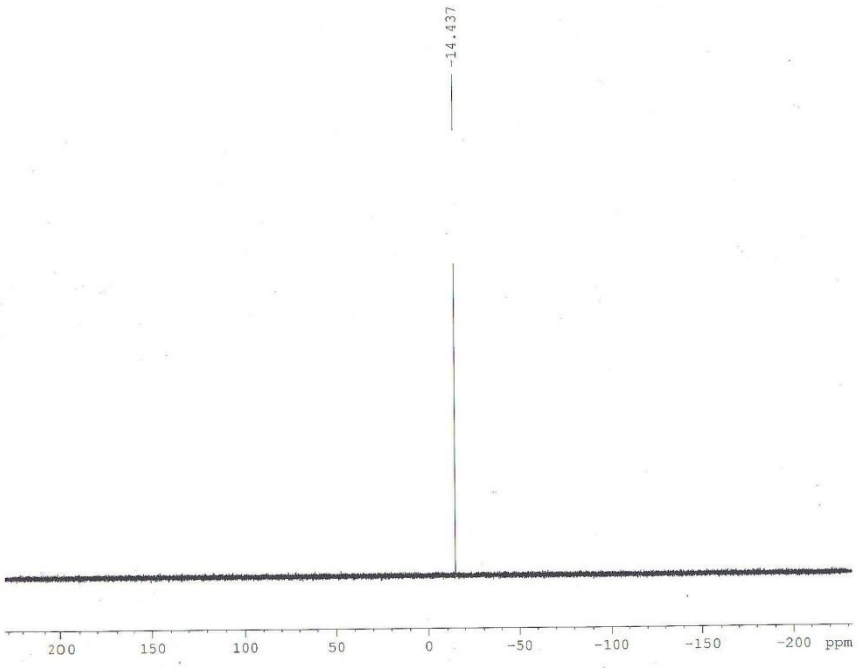


Figure S14. ^{31}P NMR spectrum of compound **9**

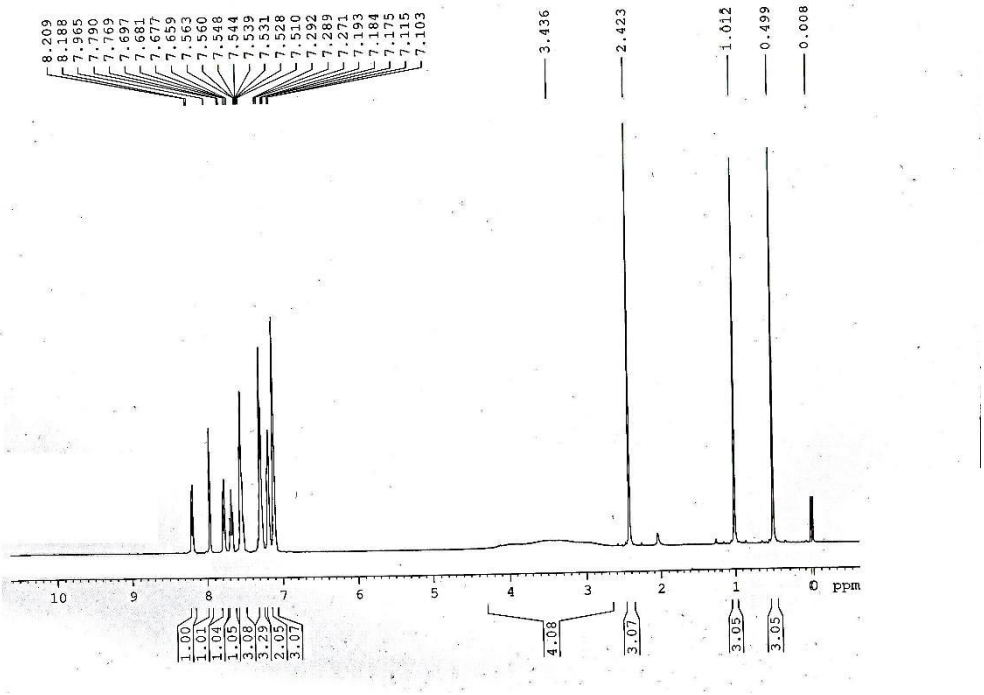


Figure S15. ^{1}H NMR spectrum of compound **9**

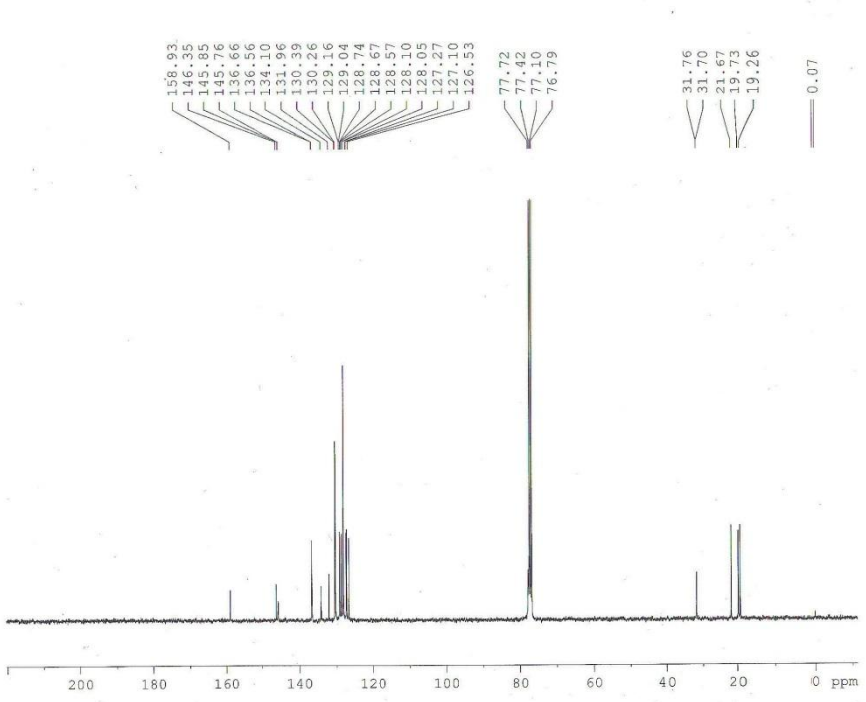


Figure S16. ^{13}C NMR spectrum of compound **9**

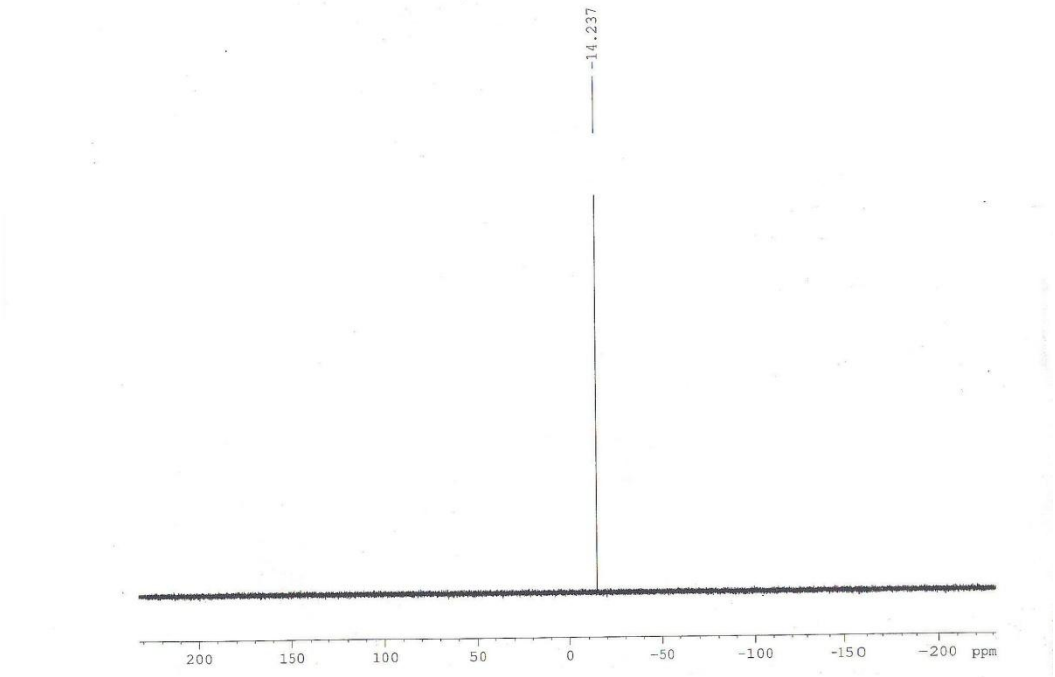


Figure S17. ^{31}P NMR spectrum of compound **10**

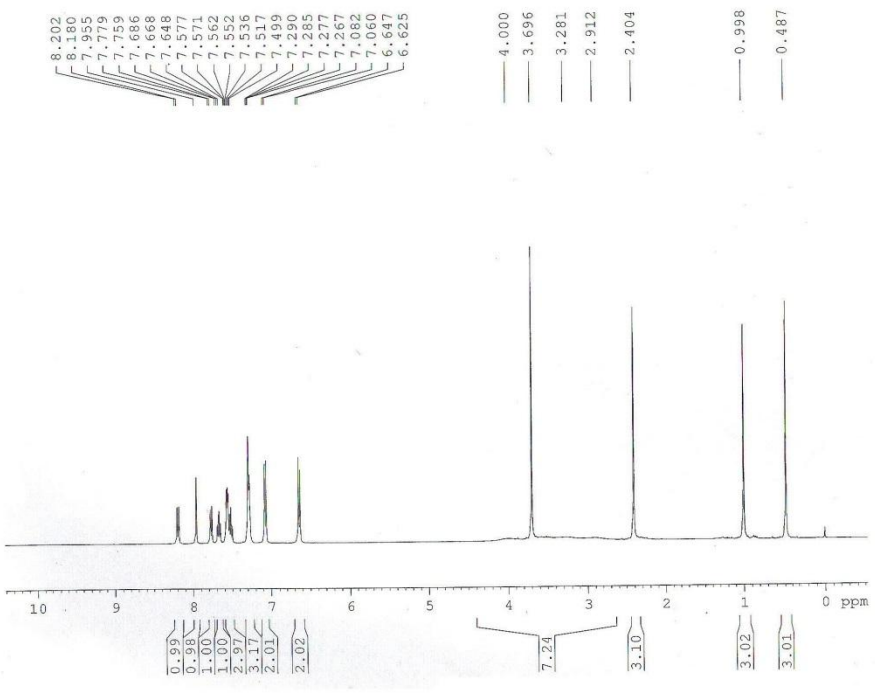


Figure S18. ^{1}H NMR spectrum of compound **10**

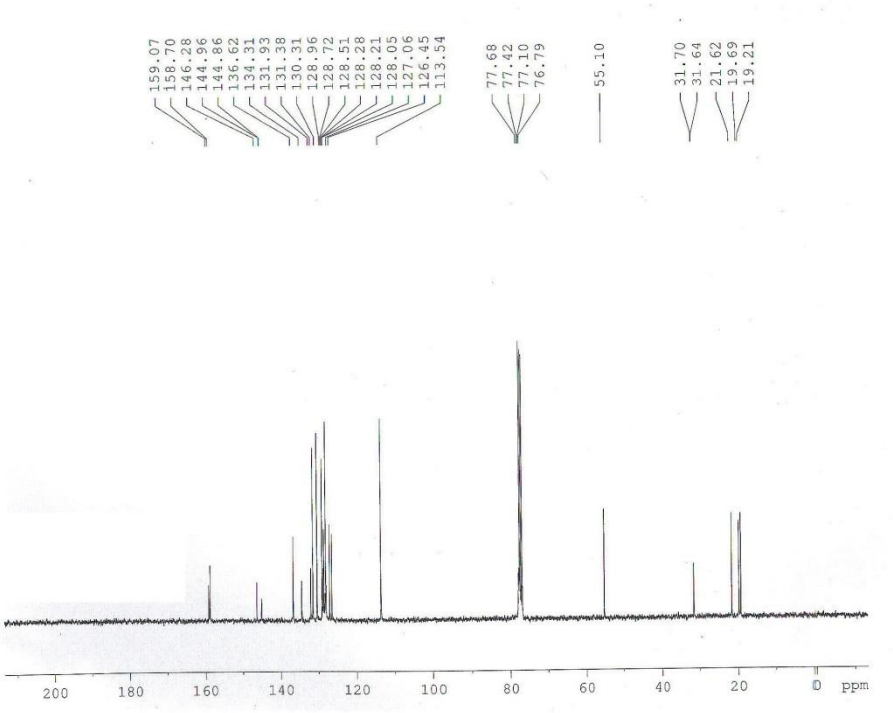


Figure S19. ^{13}C NMR spectrum of compound **10**

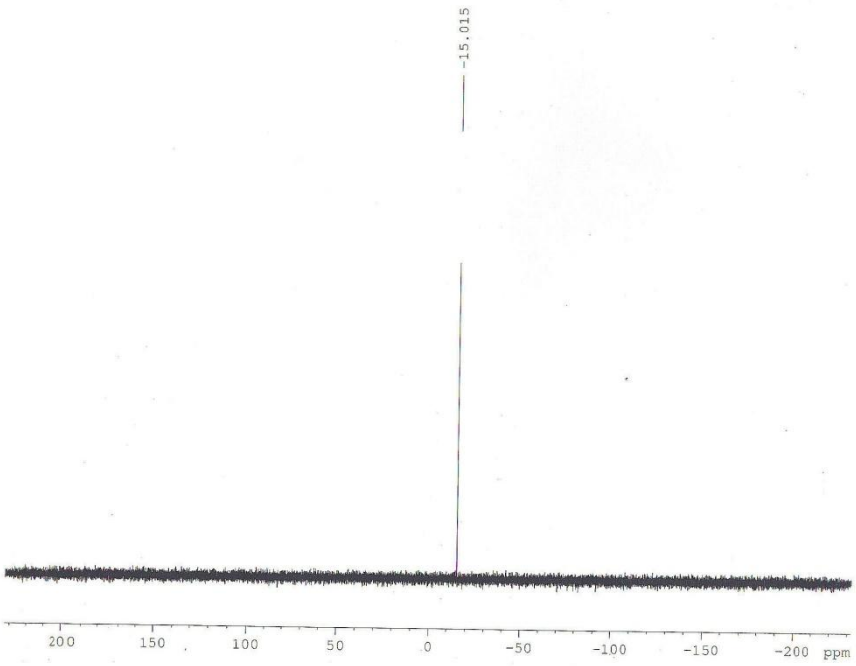


Figure S20. ^{31}P NMR spectrum of compound **11**

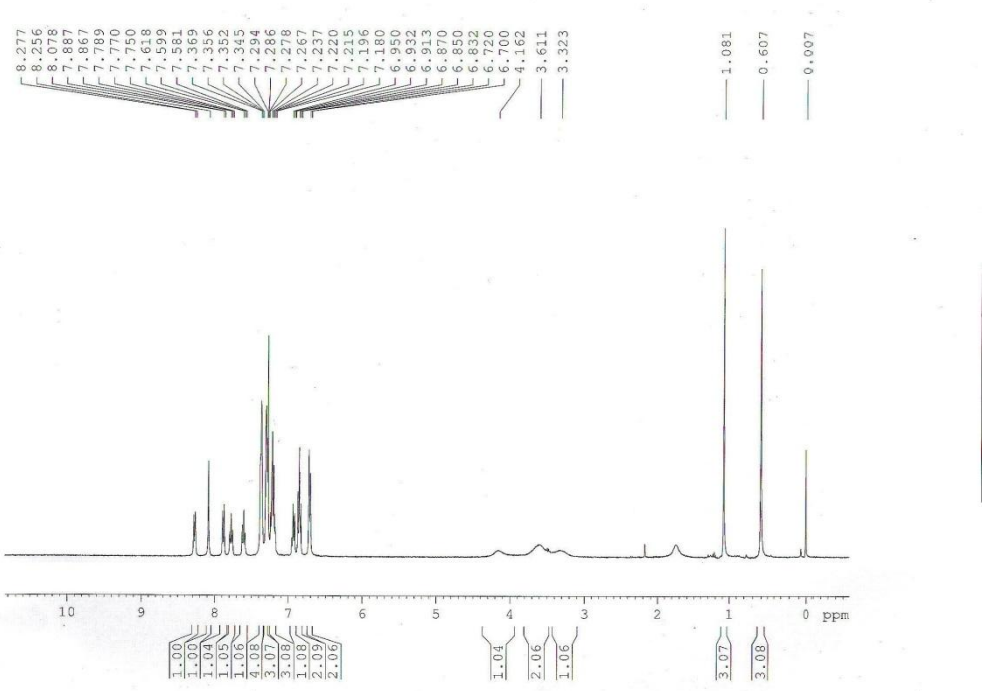


Figure S21. ^{1}H NMR spectrum of compound **11**

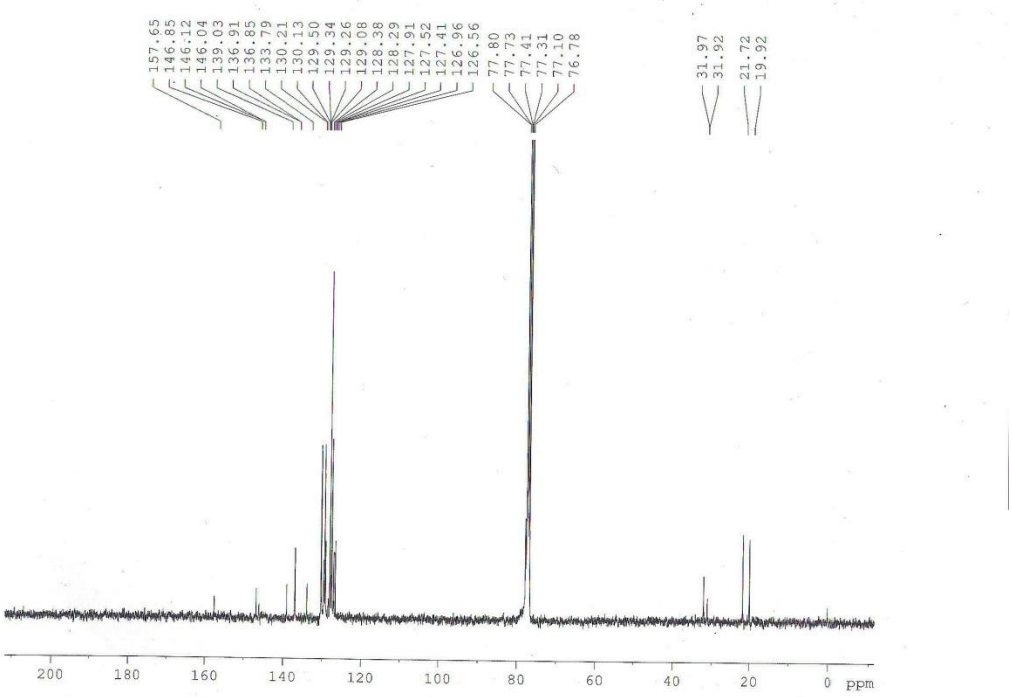


Figure S22. ^{13}C NMR spectrum of compound **11**

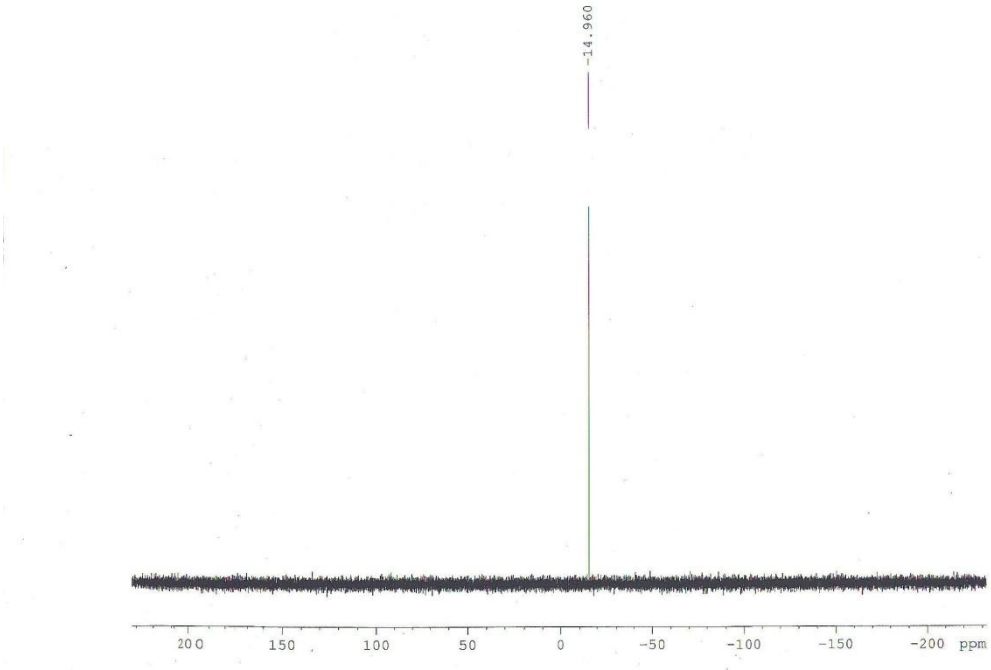


Figure S23. ^{31}P NMR spectrum of compound **12**

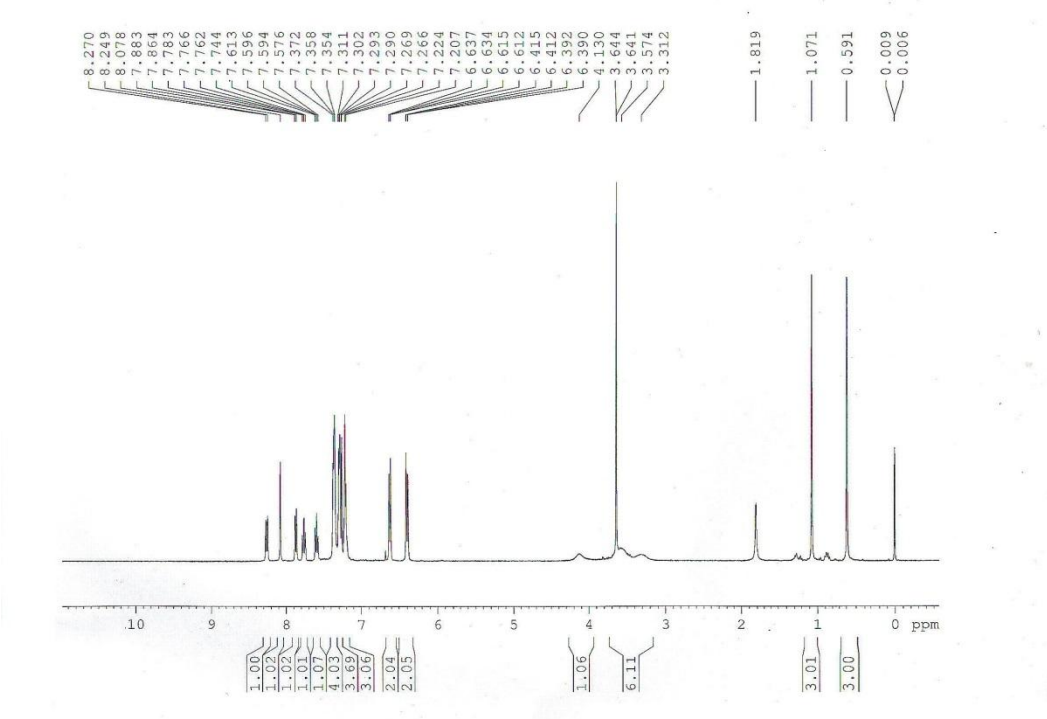


Figure S24. ^{1}H NMR spectrum of compound **12**

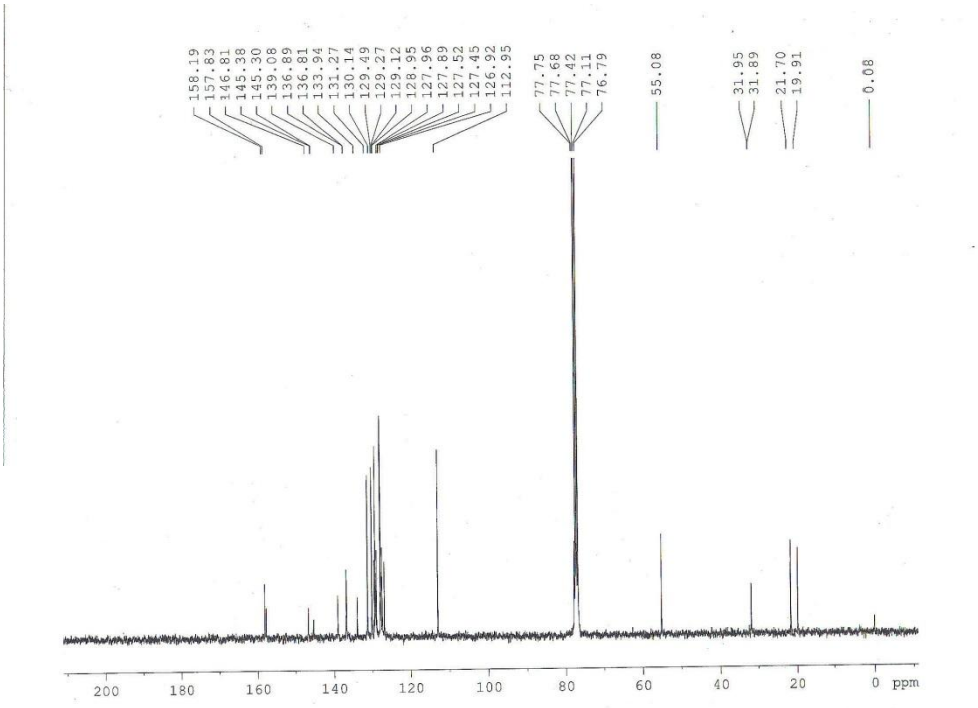


Figure S25. ^{13}C NMR spectrum of compound **12**

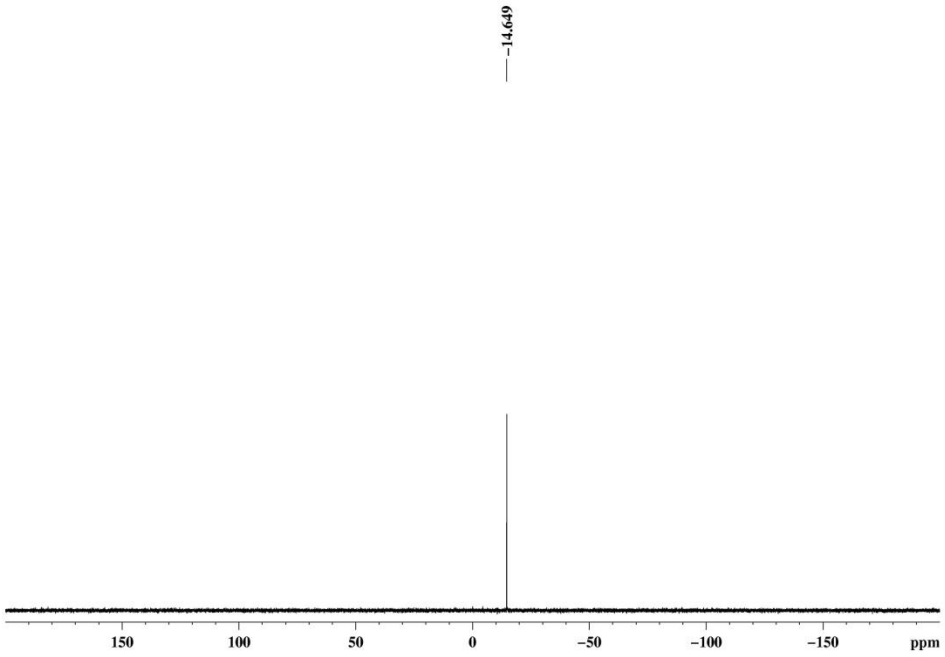


Figure S26. ^{31}P NMR spectrum of compound **13**

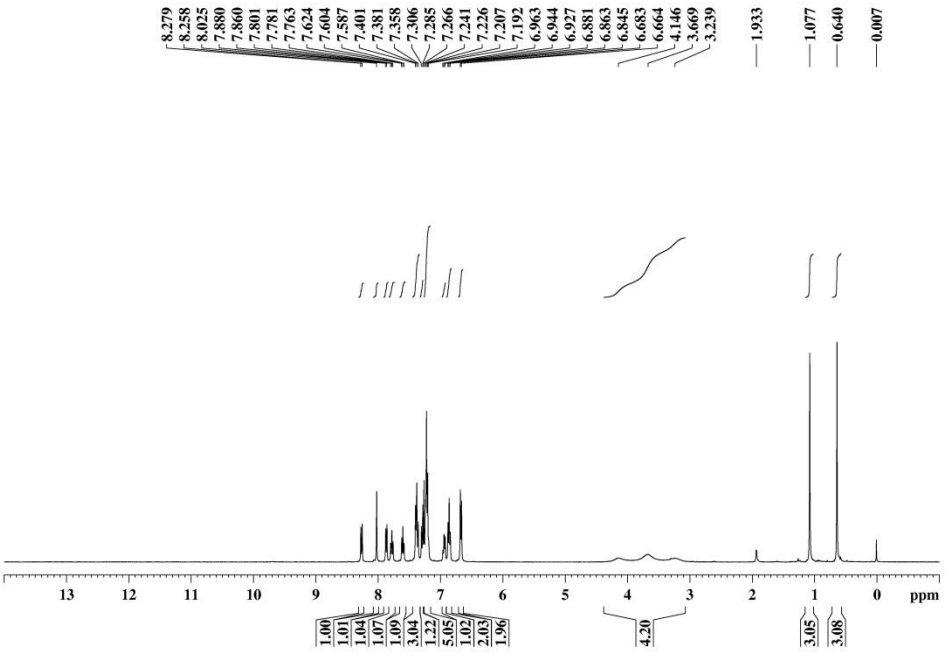


Figure S27. ^{1}H NMR spectrum of compound **13**

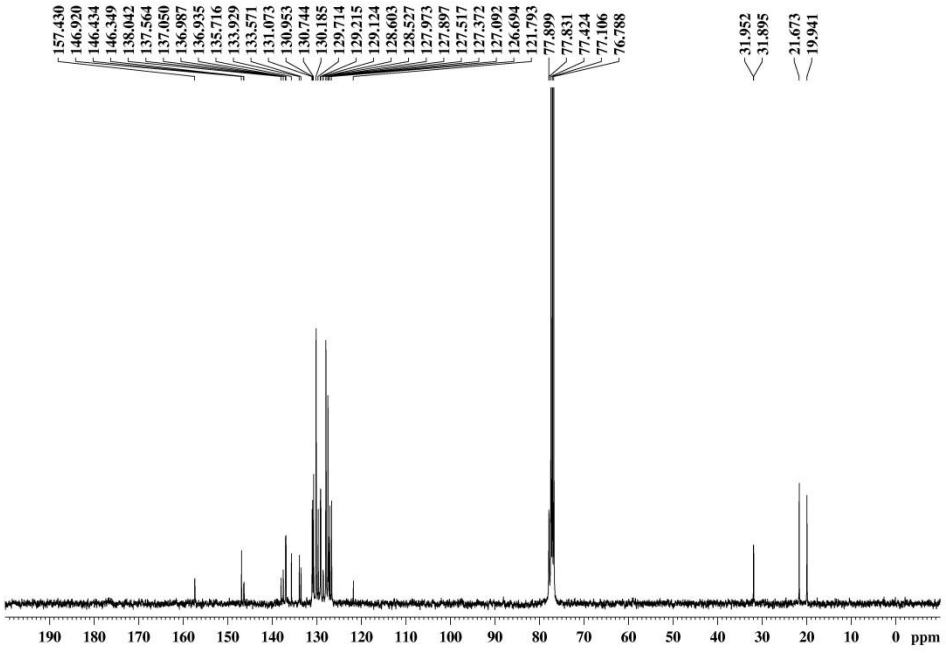


Figure S28. ^{13}C NMR spectrum of compound **13**

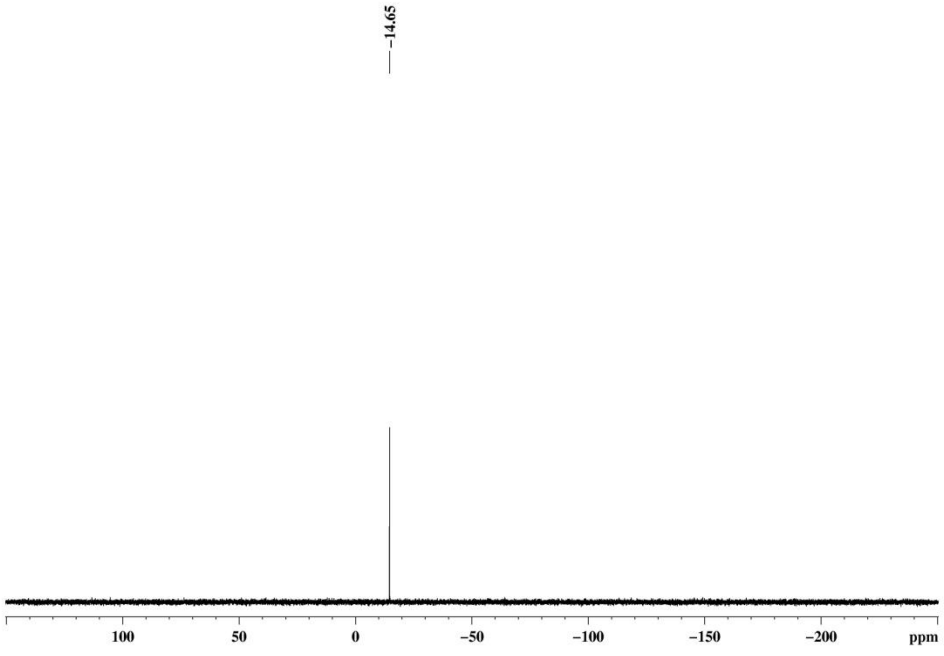


Figure S29. ^{31}P NMR spectrum of compound **14**

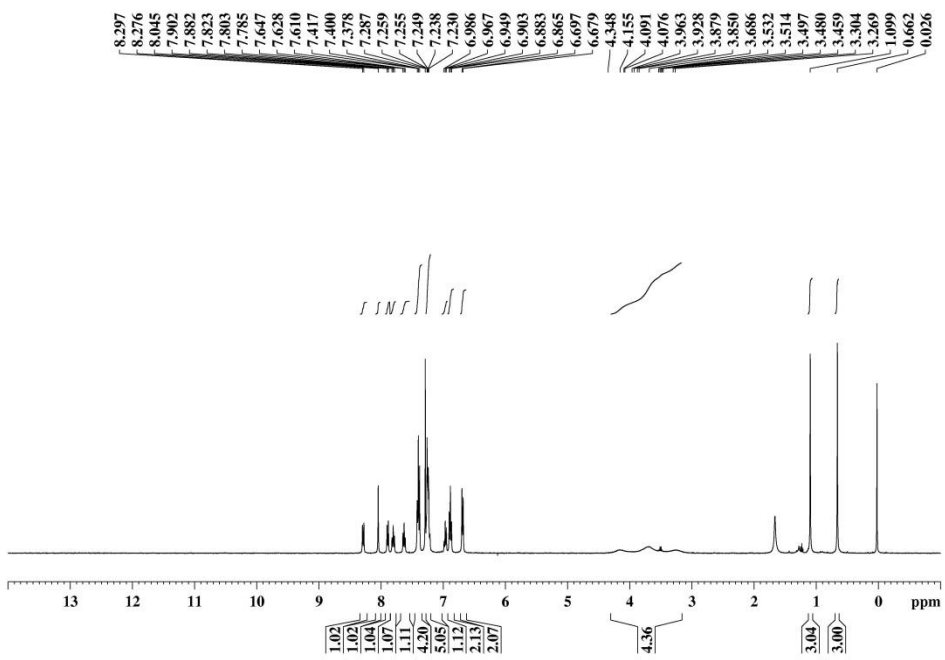


Figure S30. ^{1}H NMR spectrum of compound **14**

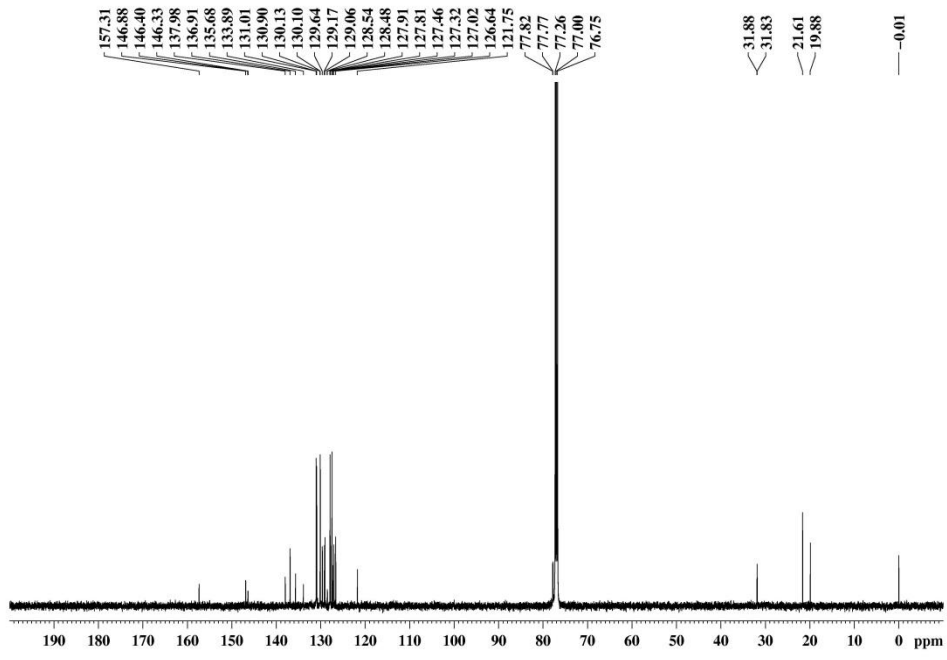


Figure S31. ^{13}C NMR spectrum of compound **14**

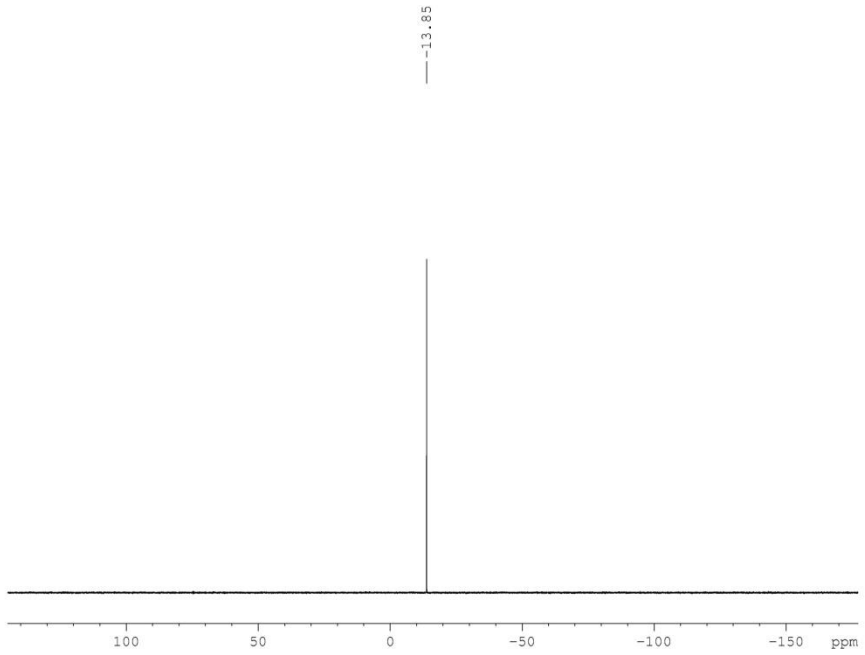


Figure S32. ^{31}P NMR spectrum of compound **15**

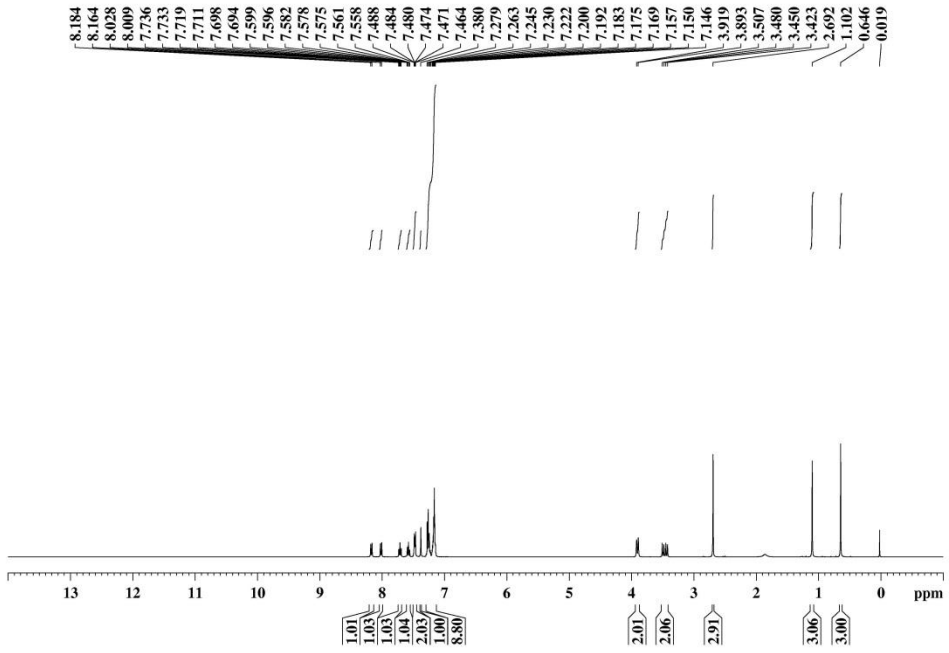


Figure S33. ^{1}H NMR spectrum of compound **15**

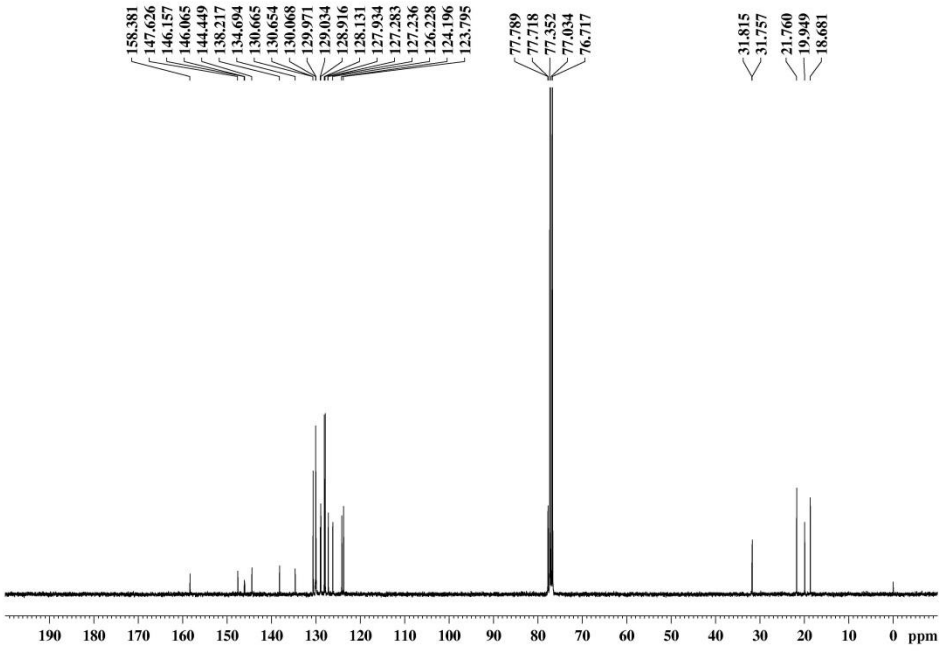


Figure S34. ^{13}C NMR spectrum of compound **15**

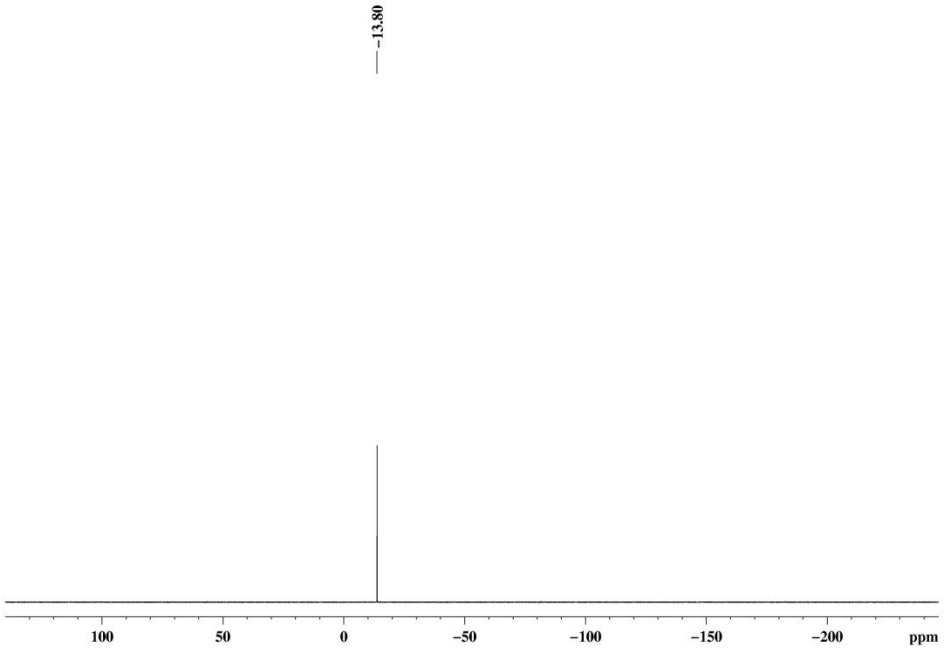


Figure S35. ^{31}P NMR spectrum of compound **16**

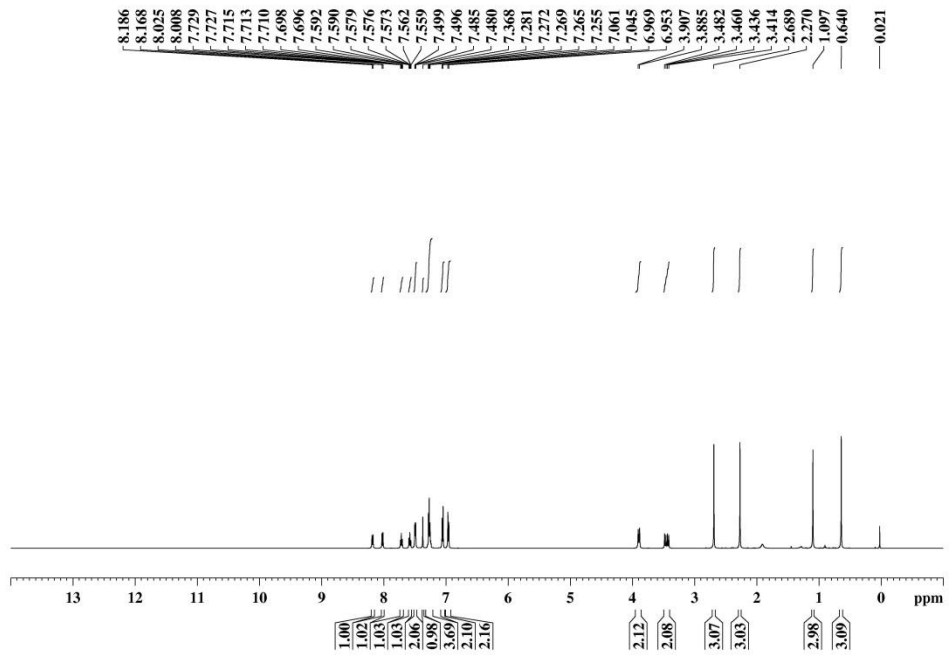


Figure S36. ^{1}H NMR spectrum of compound **16**

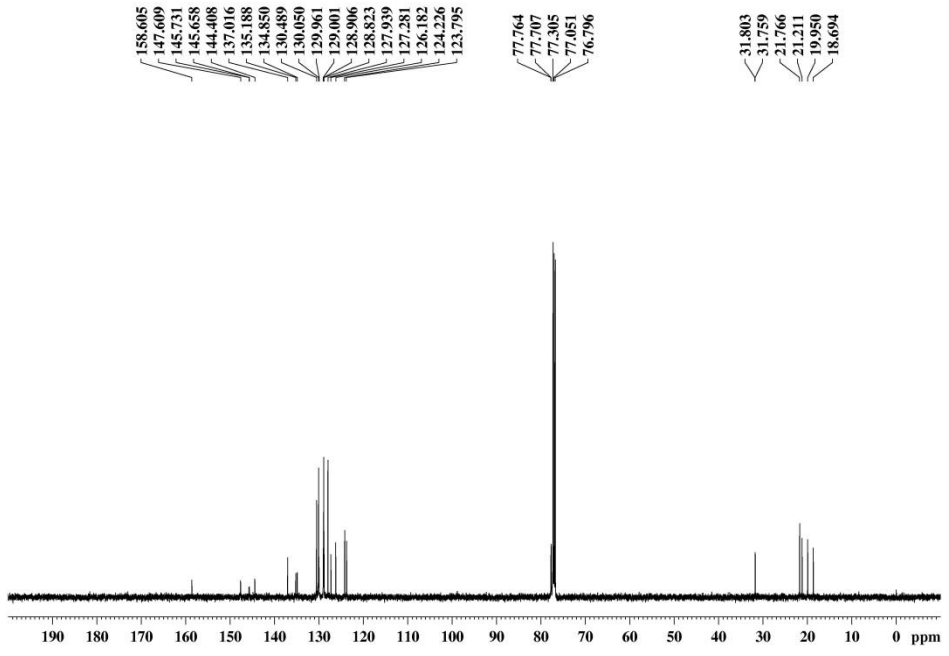


Figure S37. ^{13}C NMR spectrum of compound **16**

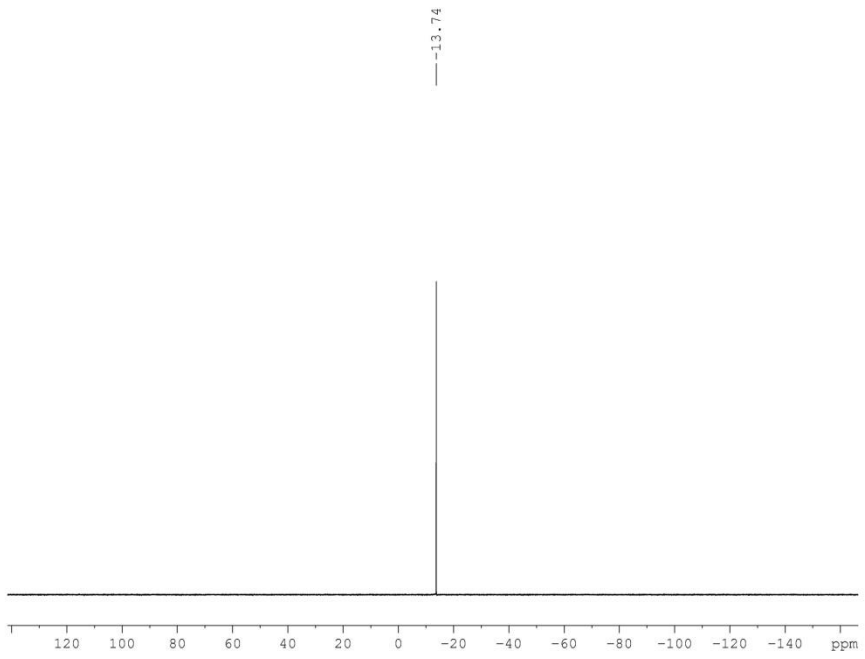


Figure S38. ^{31}P NMR spectrum of compound **17**

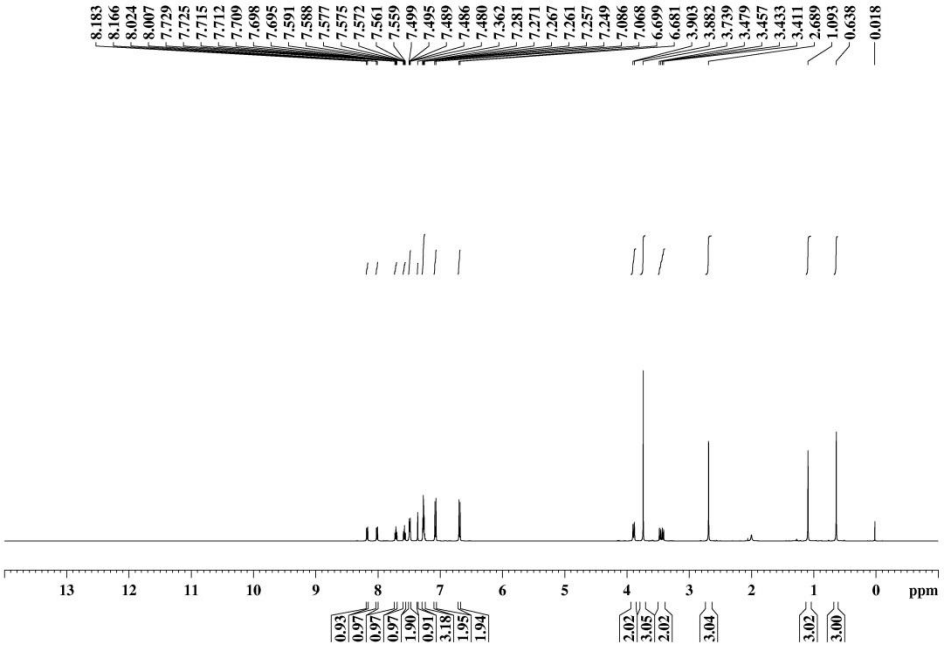


Figure S39. ^{1}H NMR spectrum of compound **17**

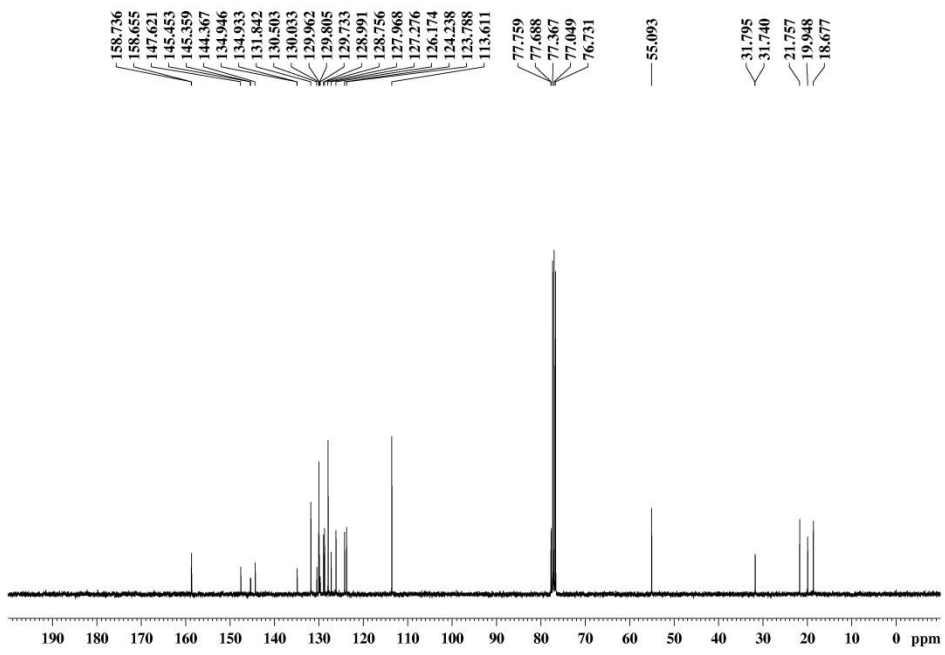


Figure S40. ^{13}C NMR spectrum of compound **17**

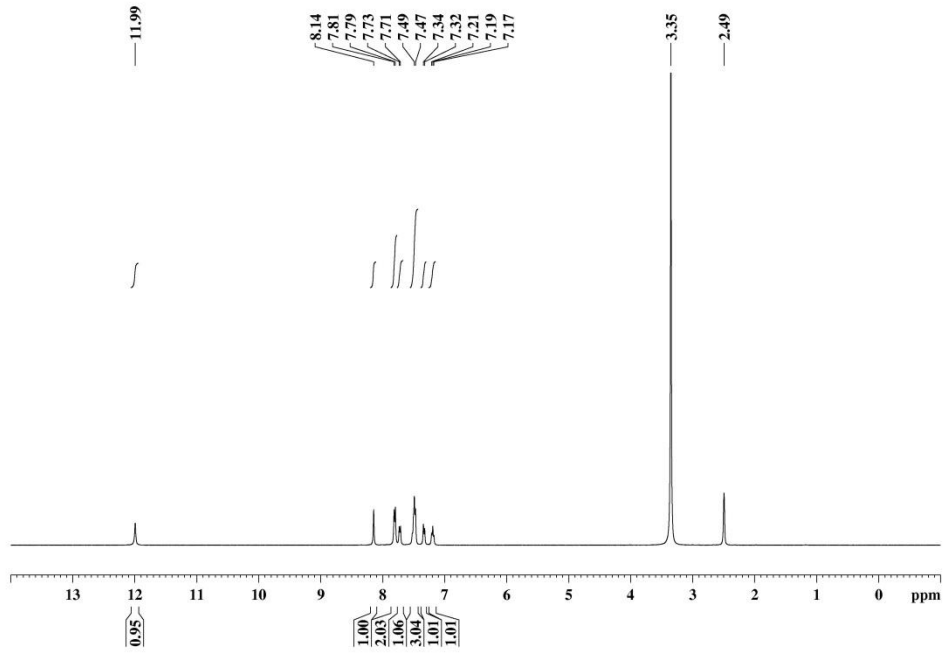


Figure S41. ^{1}H NMR spectrum of compound **19**

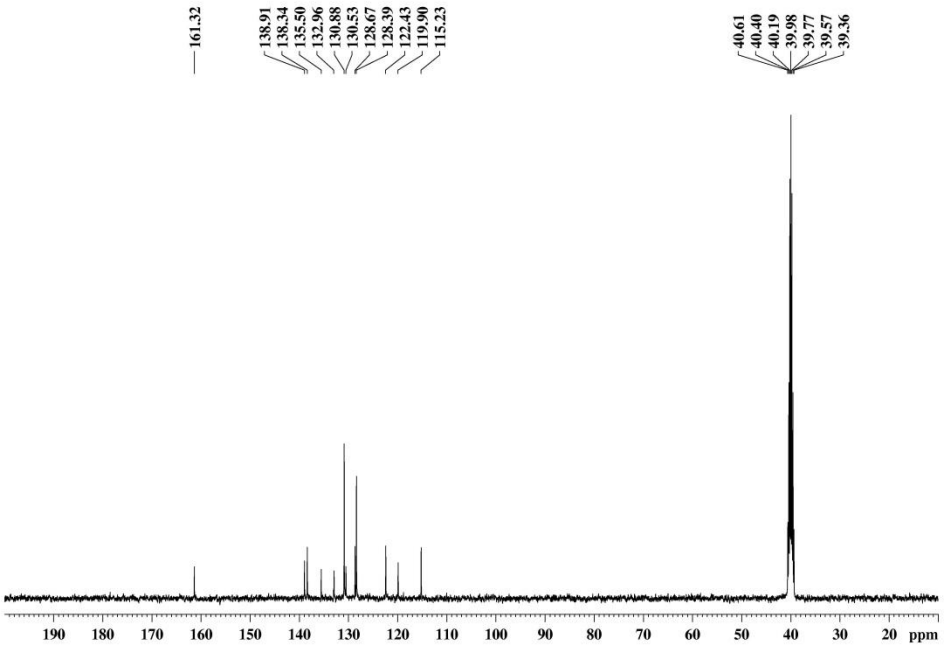


Figure S42. ^{13}C NMR spectrum of compound **19**

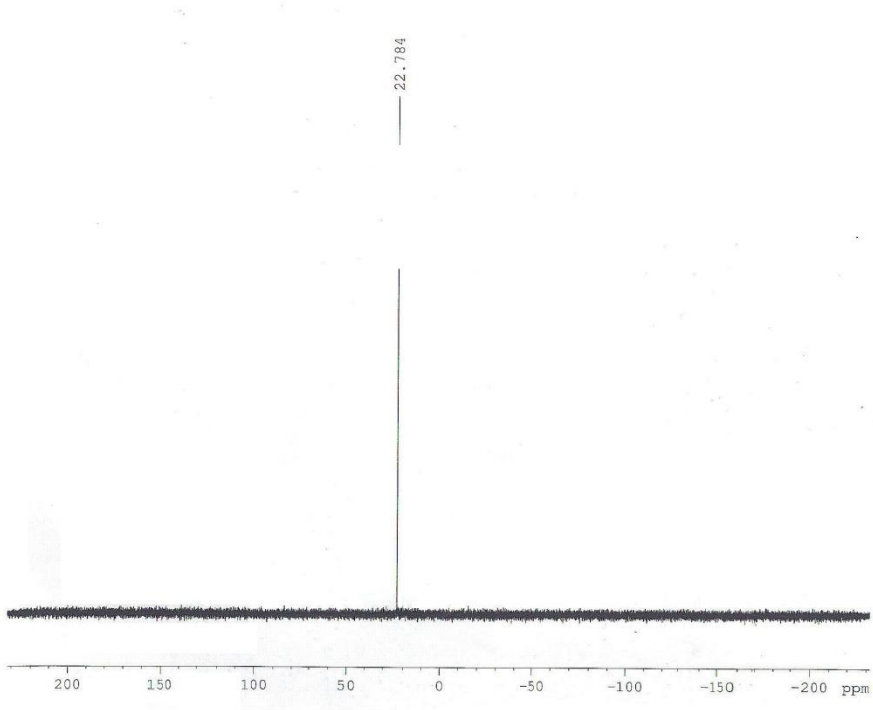


Figure S43. ^{31}P NMR spectrum of compound **21**

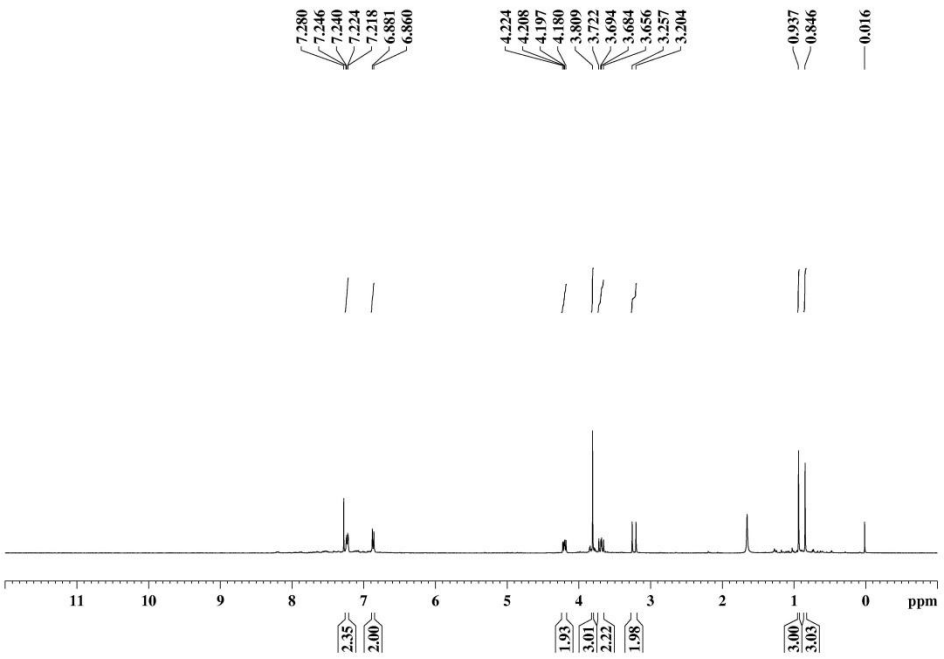


Figure S44. ^{1}H NMR spectrum of compound **21**

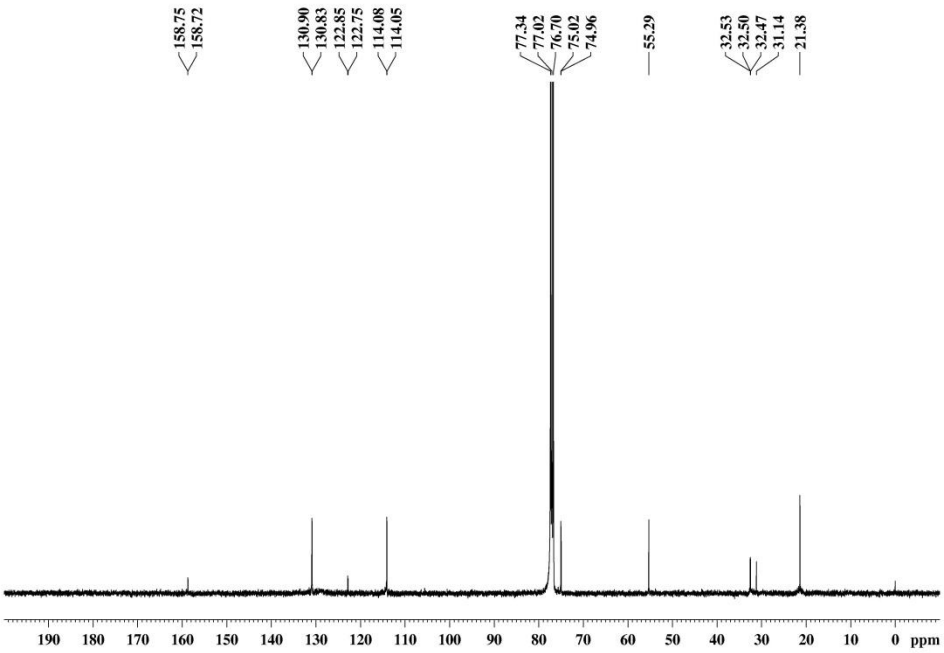


Figure S45. ^{13}C NMR spectrum of compound **21**

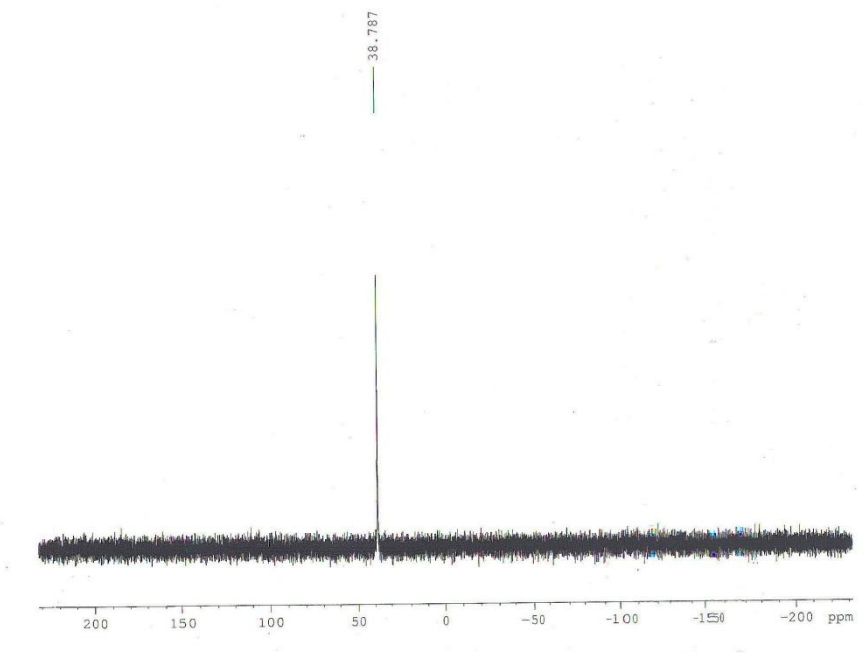


Figure S46. ^{31}P NMR spectrum of compound **22**

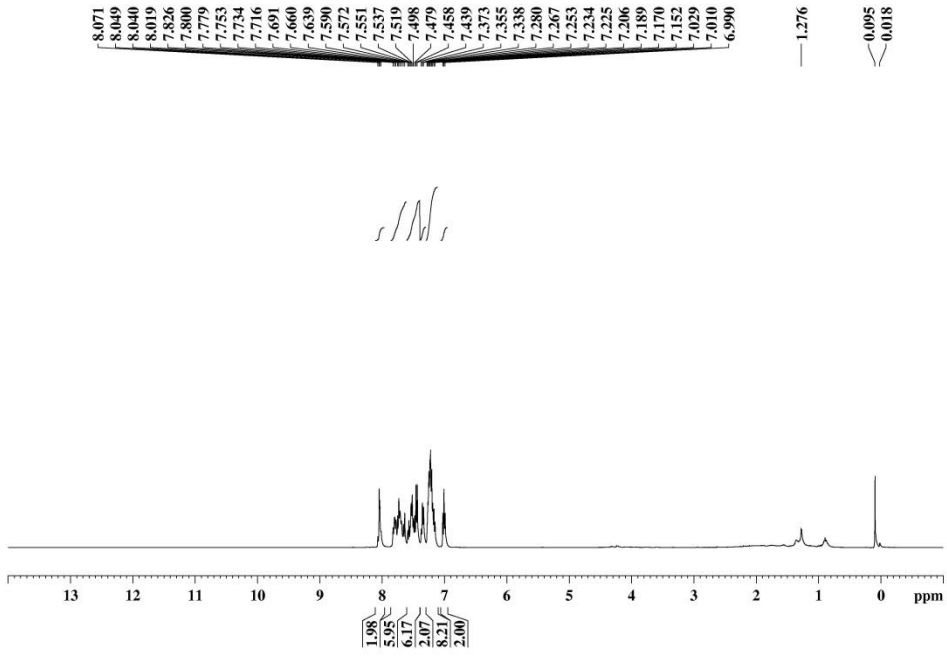


Figure S47. ^{1}H NMR spectrum of compound **22**

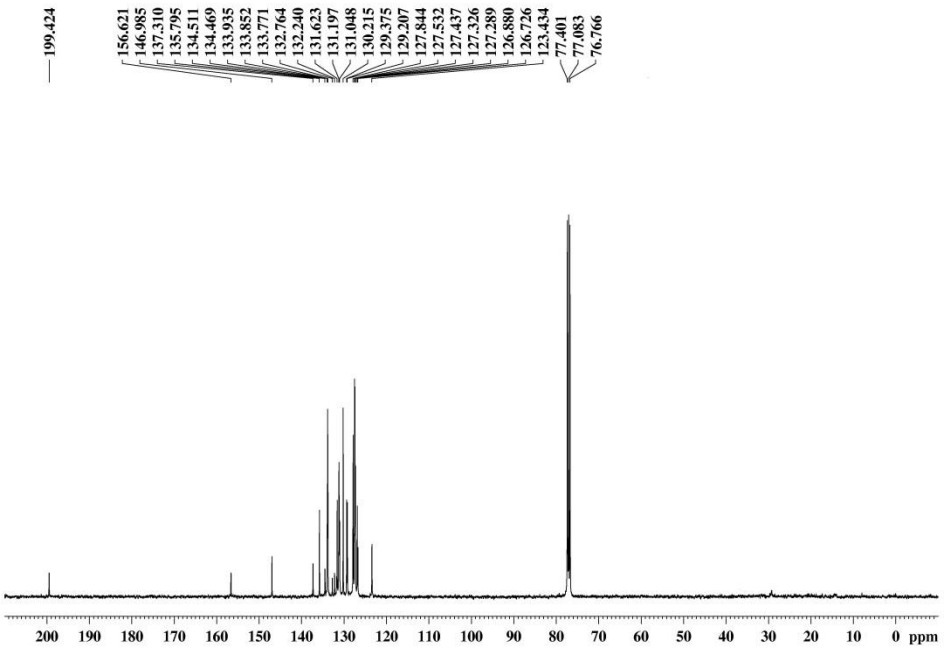


Figure S48. ^{13}C NMR spectrum of compound **22**

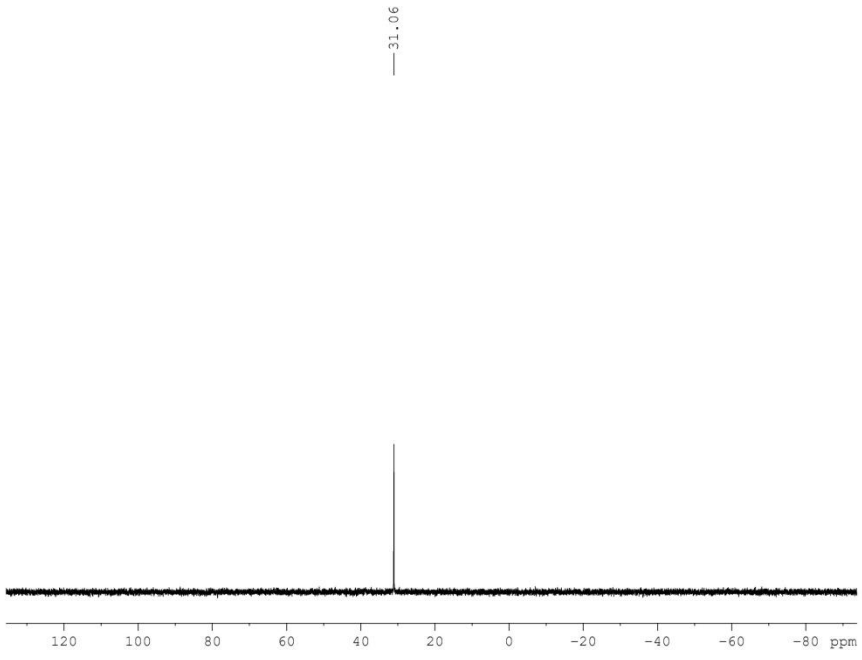


Figure S49. ^{31}P NMR spectrum of compound **23**

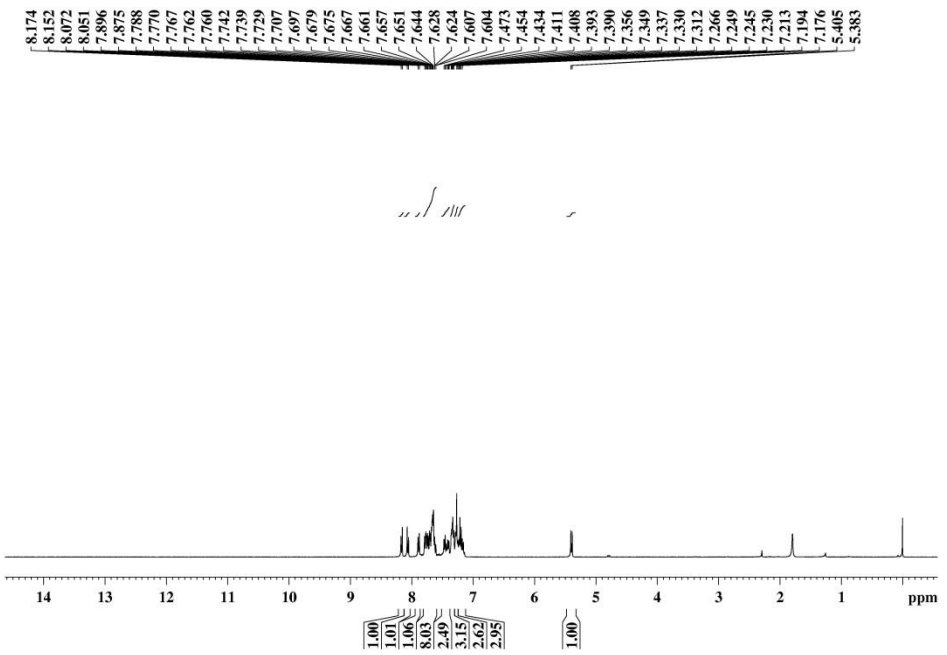


Figure S50. ^{1}H NMR spectrum of compound **23**

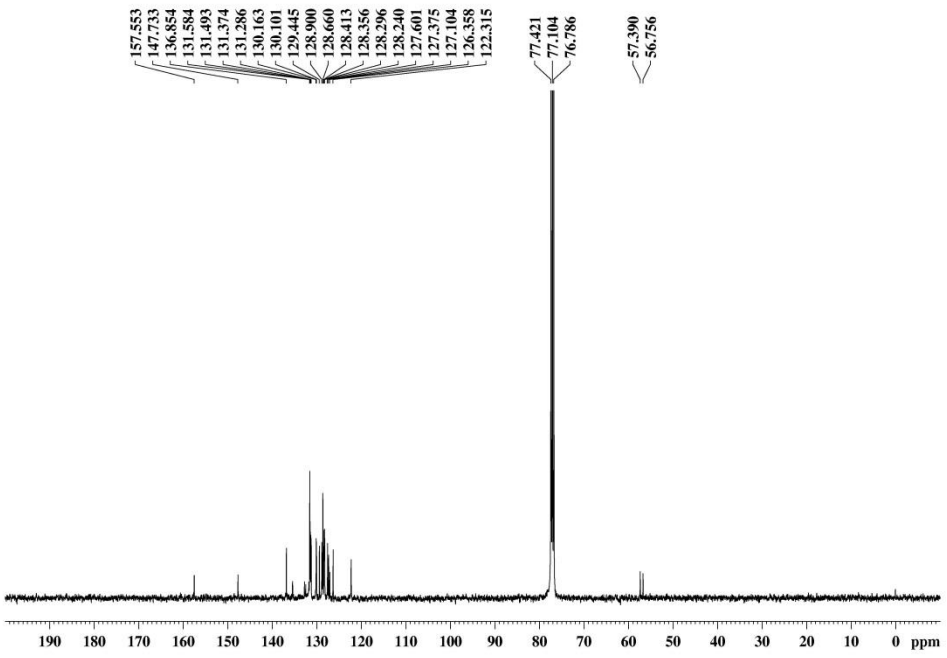


Figure S51. ^{13}C NMR spectrum of compound **23**

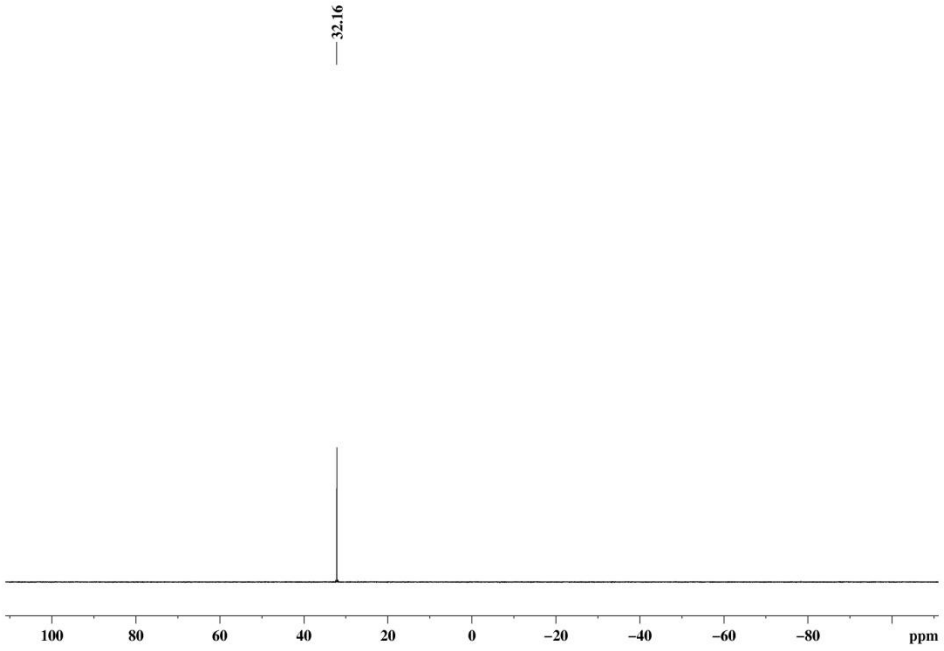


Figure S52. ^{31}P NMR spectrum of compound **24**

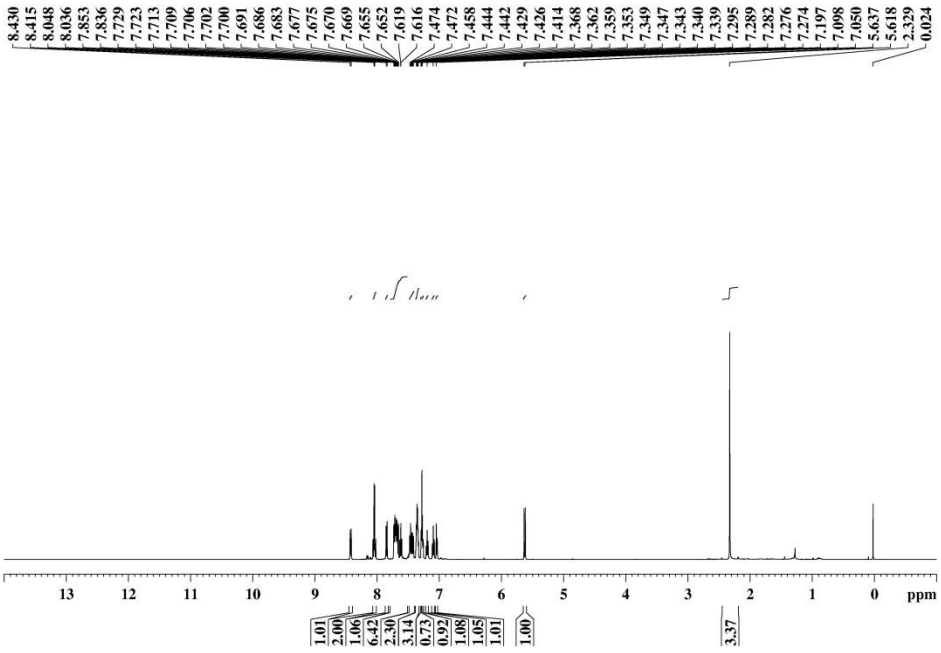


Figure S53. ^{1}H NMR spectrum of compound **24**

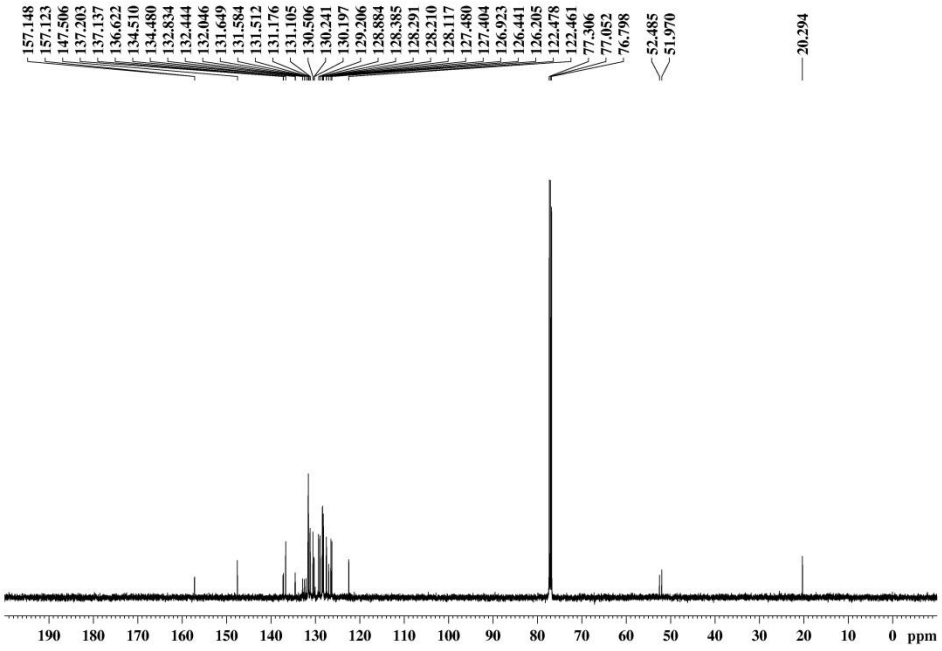


Figure S54. ^{13}C NMR spectrum of compound **24**

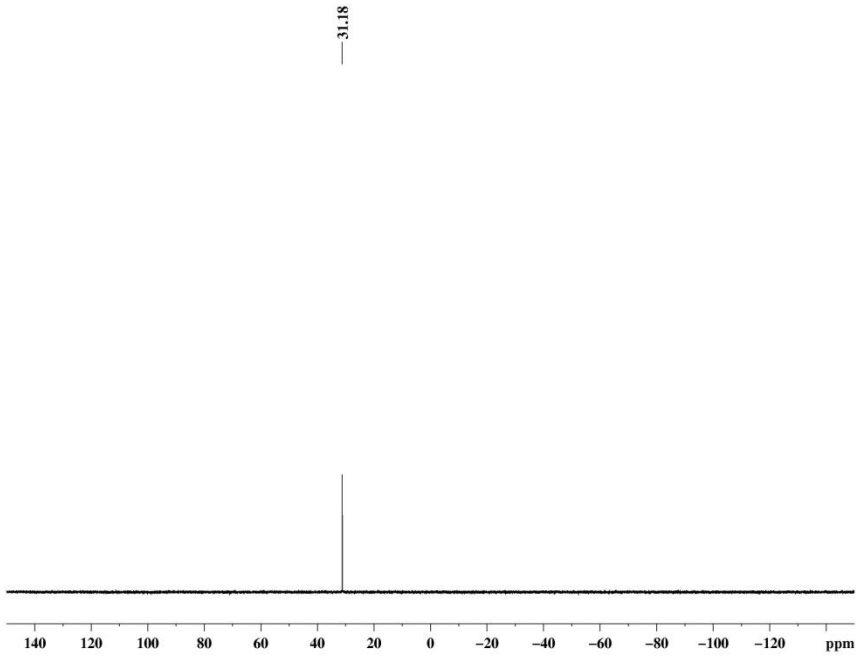


Figure S55. ^{31}P NMR spectrum of compound **25**

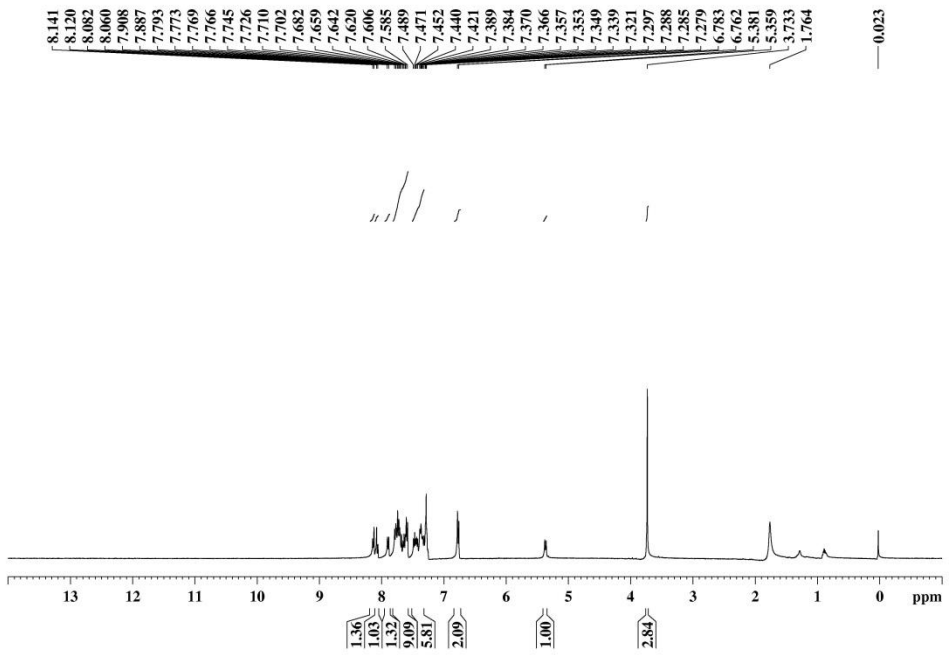


Figure S56. ^{1}H NMR spectrum of compound **25**

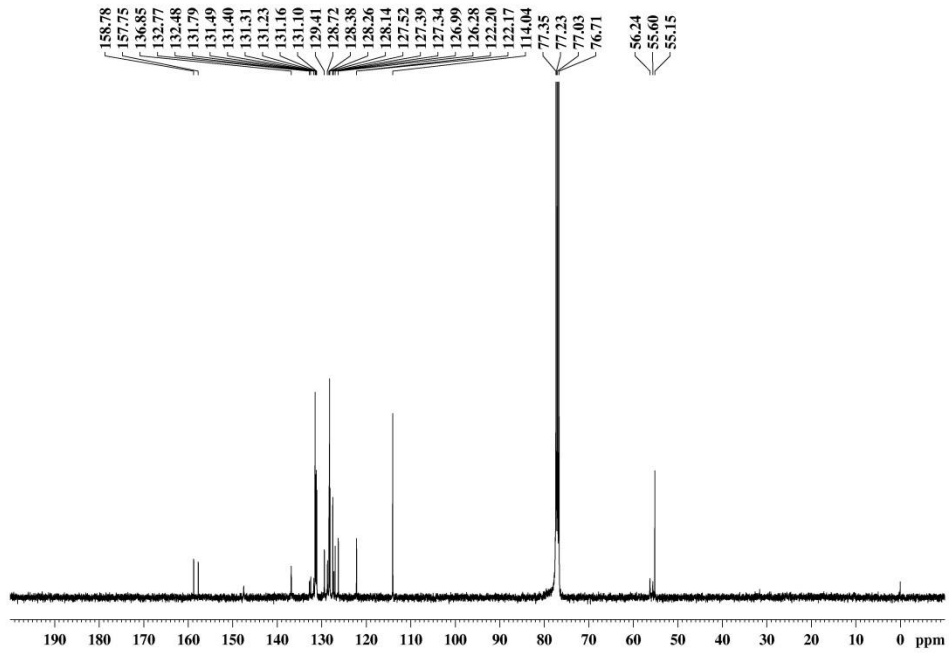


Figure S57. ^{13}C NMR spectrum of compound **25**

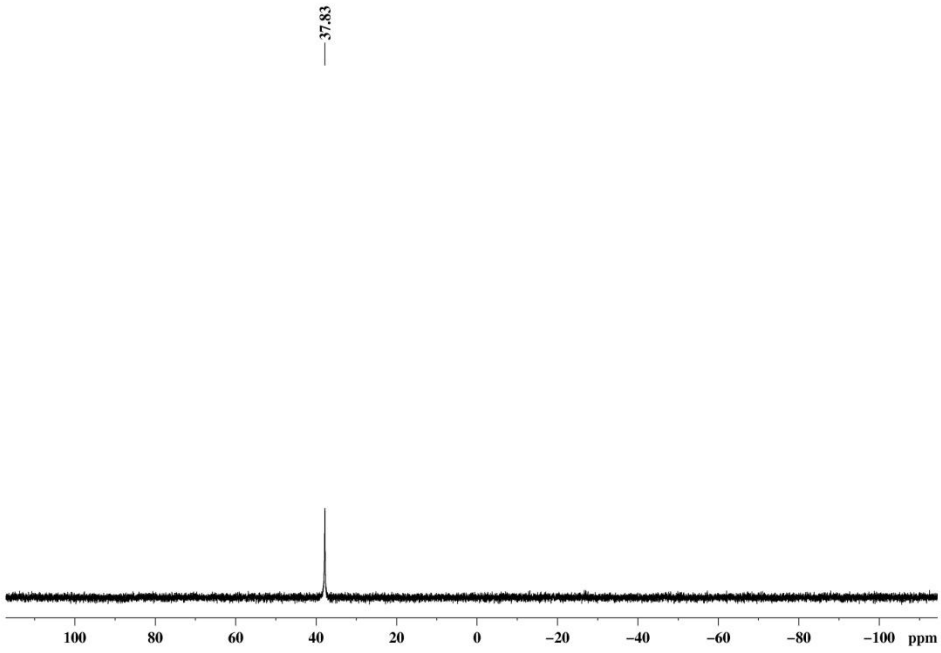


Figure S58. ^{31}P NMR spectrum of compound **26**

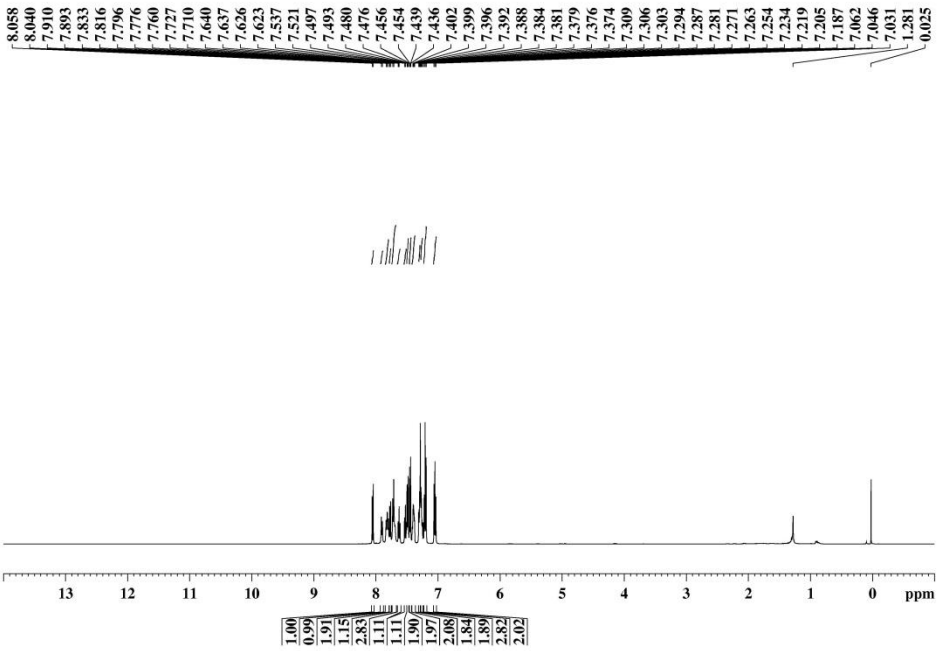


Figure S59. ^{1}H NMR spectrum of compound **26**

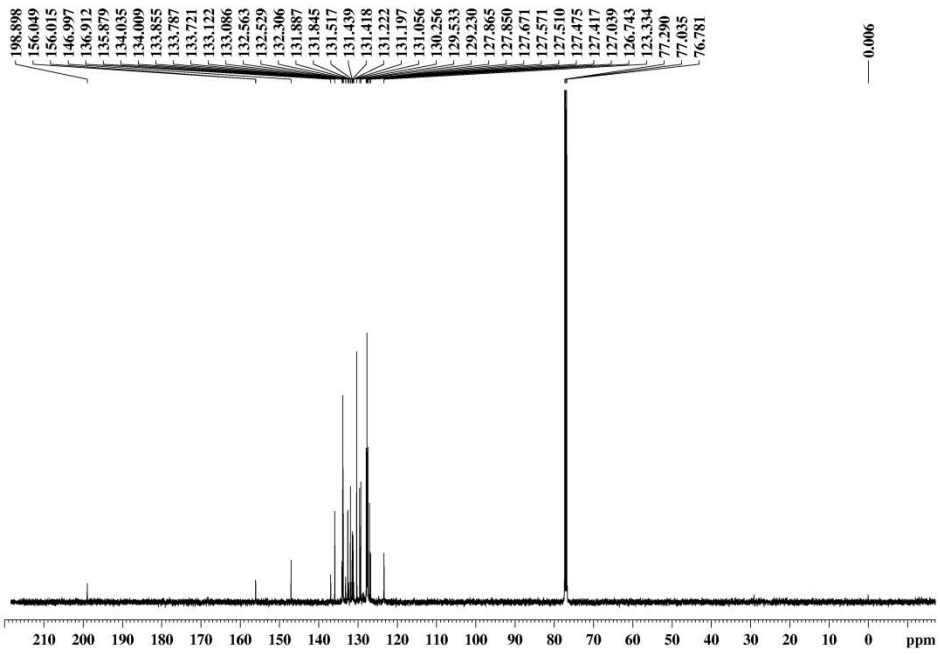


Figure S60. ^{13}C NMR spectrum of compound **26**

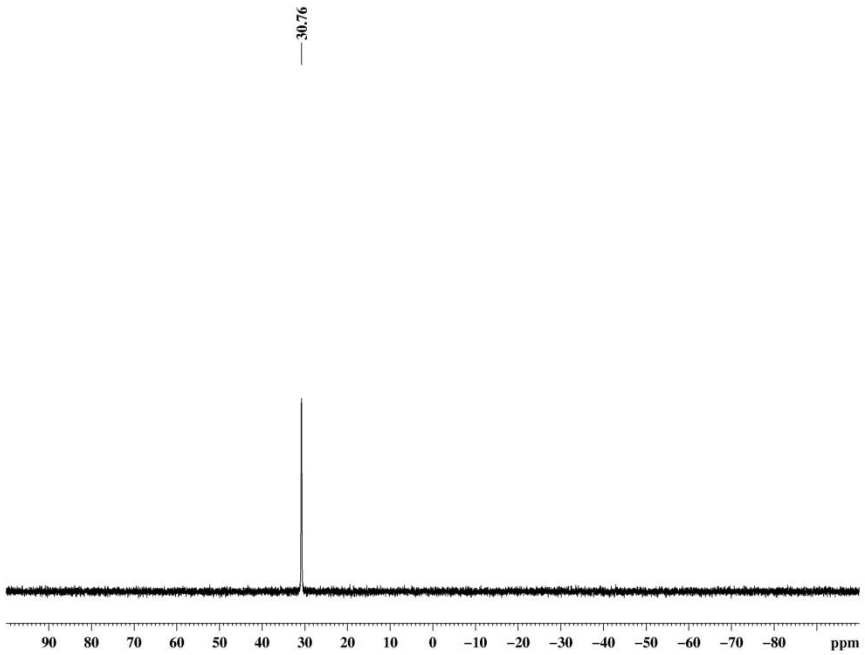


Figure S61. ^{31}P NMR spectrum of compound **27**

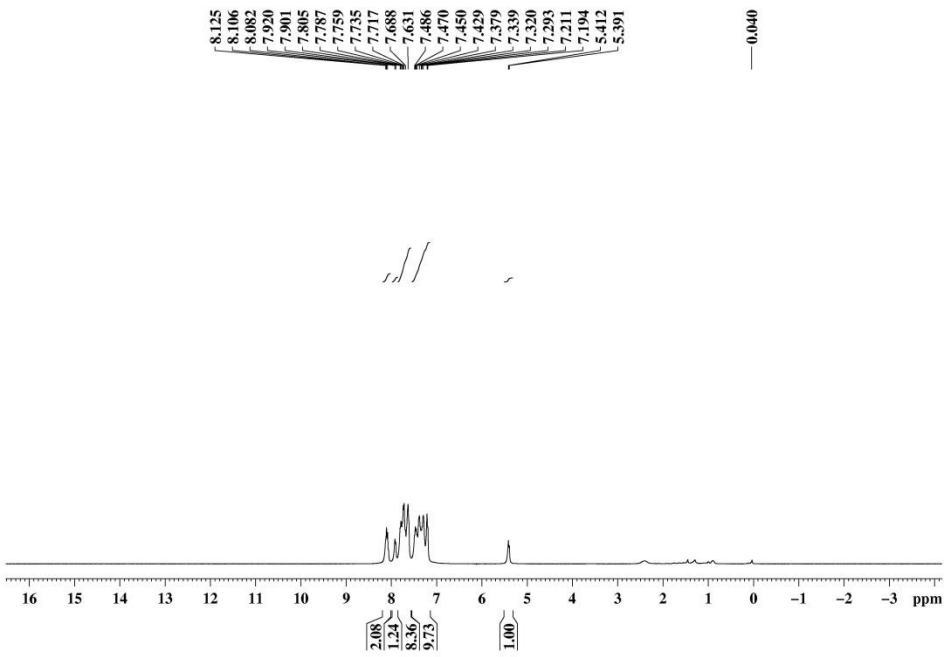


Figure S62. ^{1}H NMR spectrum of compound **27**

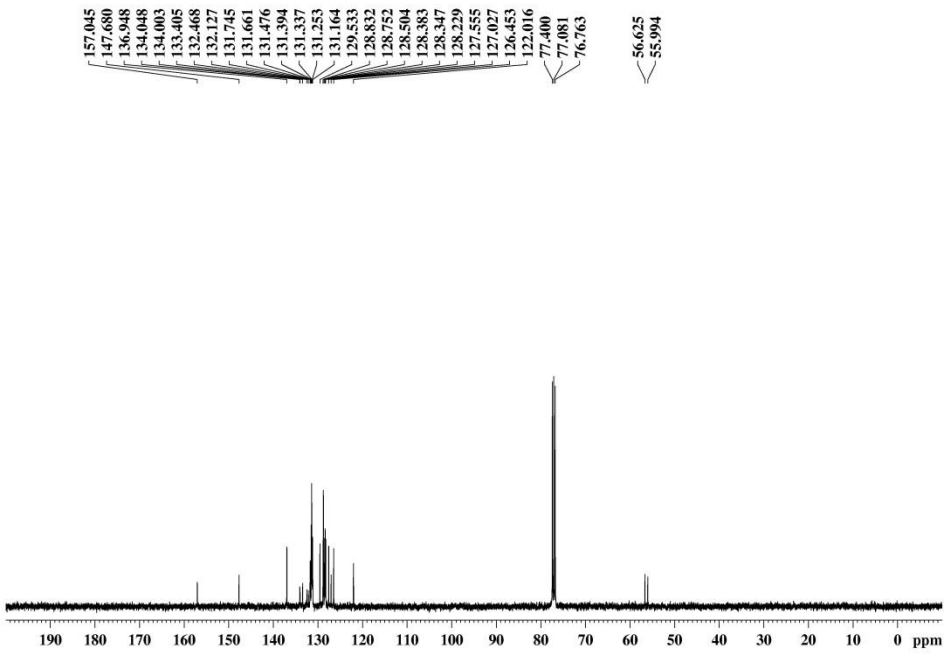


Figure S63. ^{13}C NMR spectrum of compound **27**

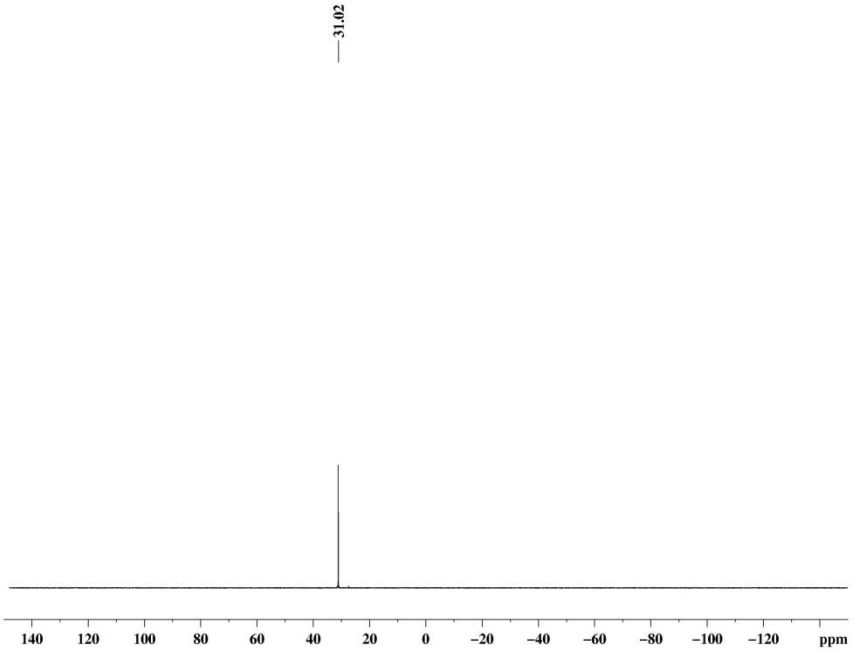


Figure S64. ^{31}P NMR spectrum of compound **28**

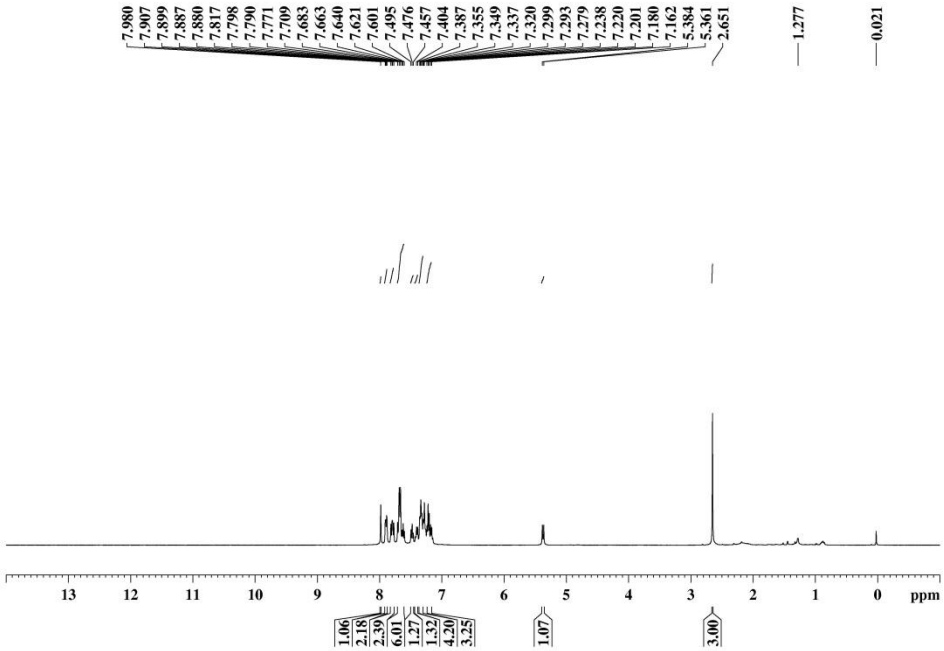


Figure S65. ^{1}H NMR spectrum of compound **28**

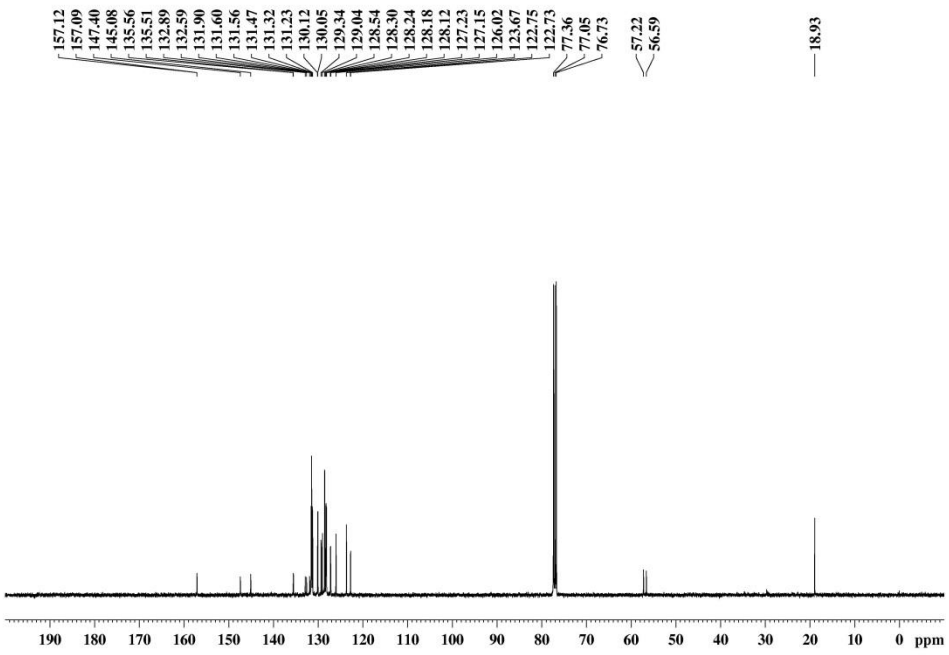


Figure S66. ^{13}C NMR spectrum of compound **28**

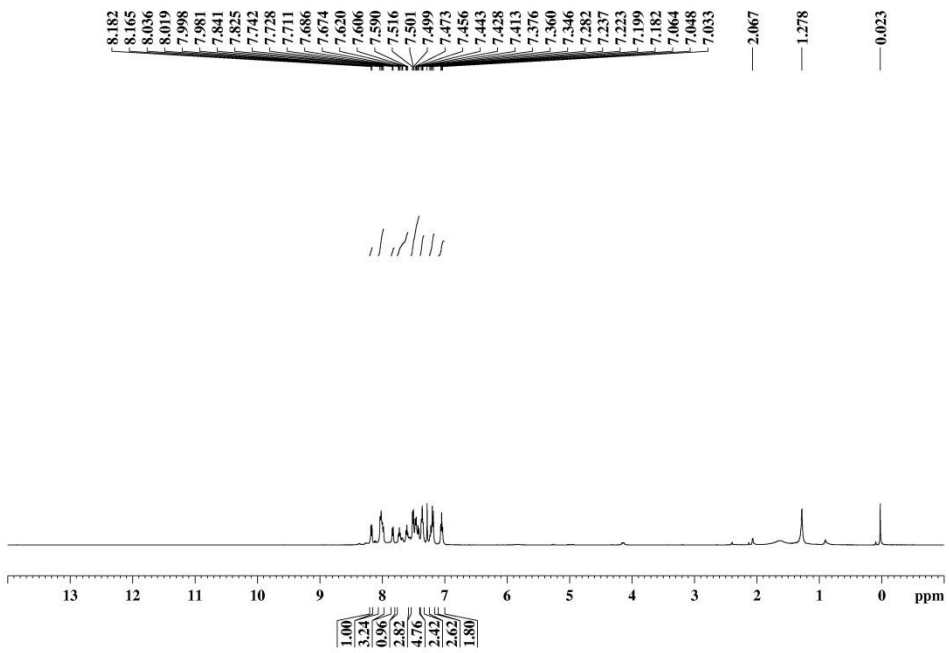


Figure S67. ^{1}H NMR spectrum of compound **29**

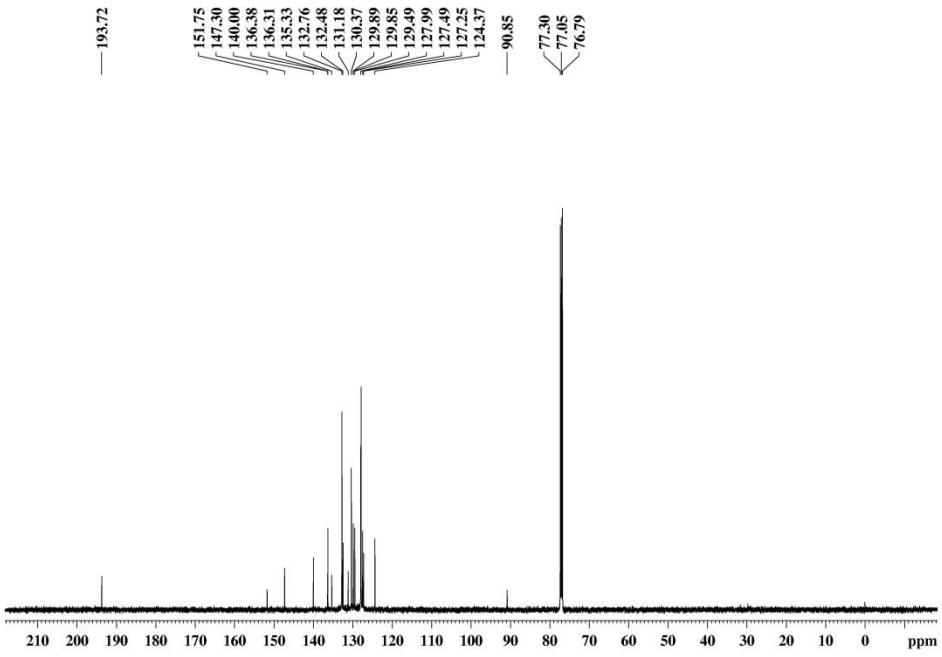


Figure S68. ^{13}C NMR spectrum of compound **29**

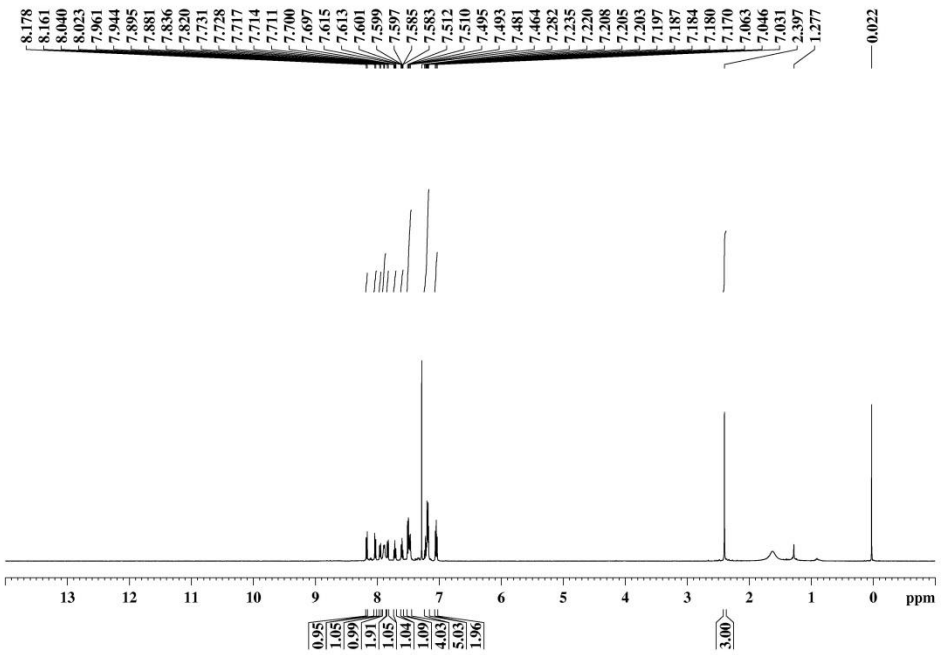


Figure S69. ^{1}H NMR spectrum of compound **30**

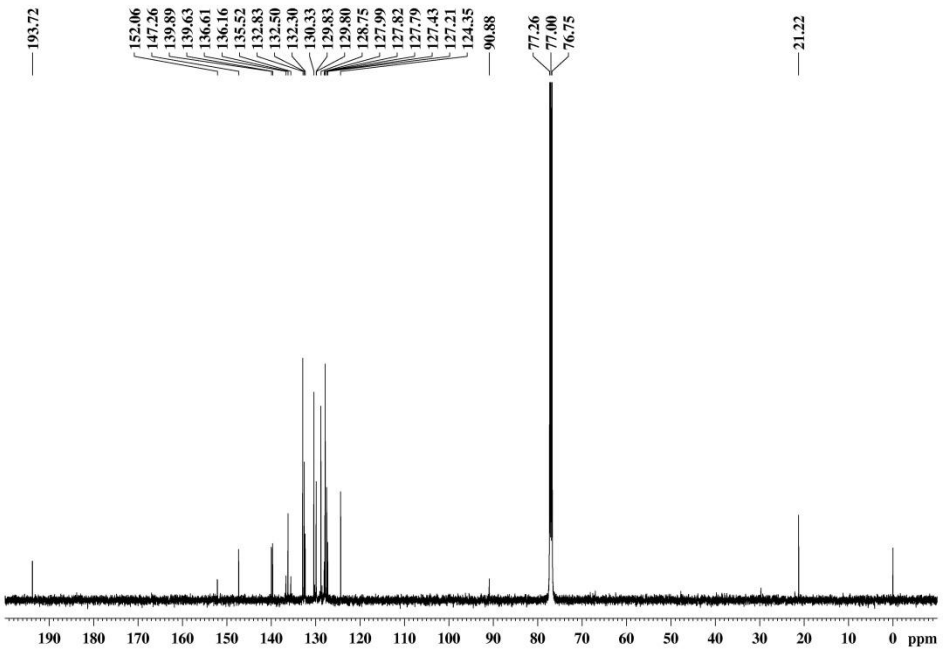


Figure S70. ^{13}C NMR spectrum of compound **30**

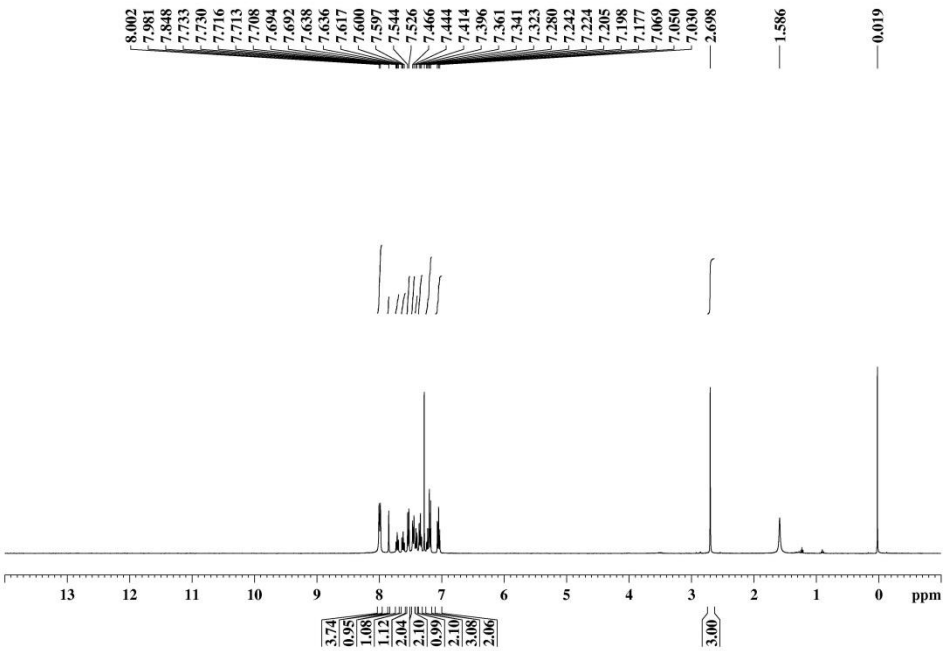


Figure S71. ^{1}H NMR spectrum of compound **31**

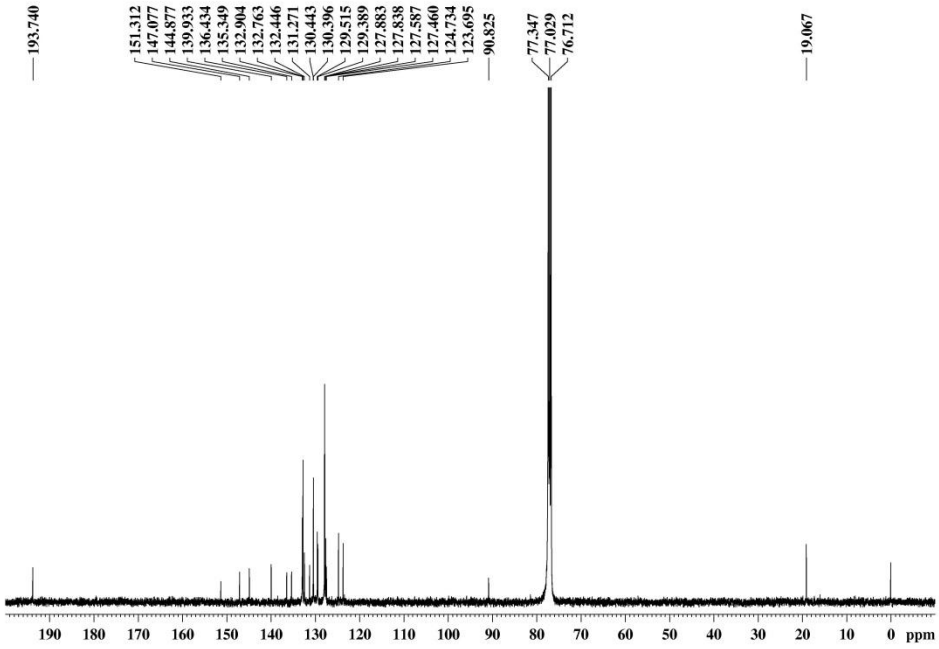


Figure S72. ^{13}C NMR spectrum of compound **31**

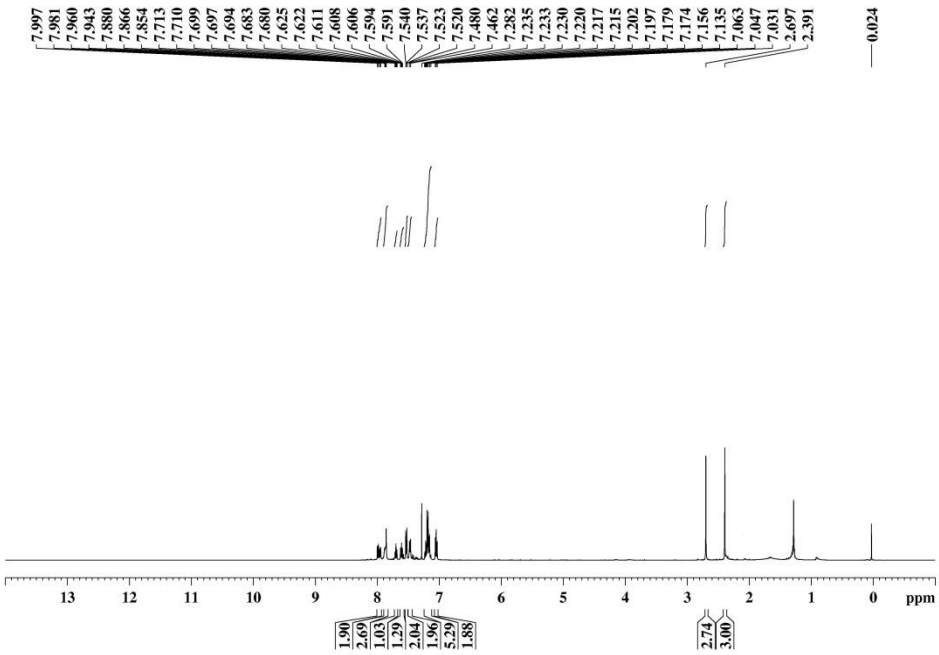


Figure S73. ^{1}H NMR spectrum of compound **32**

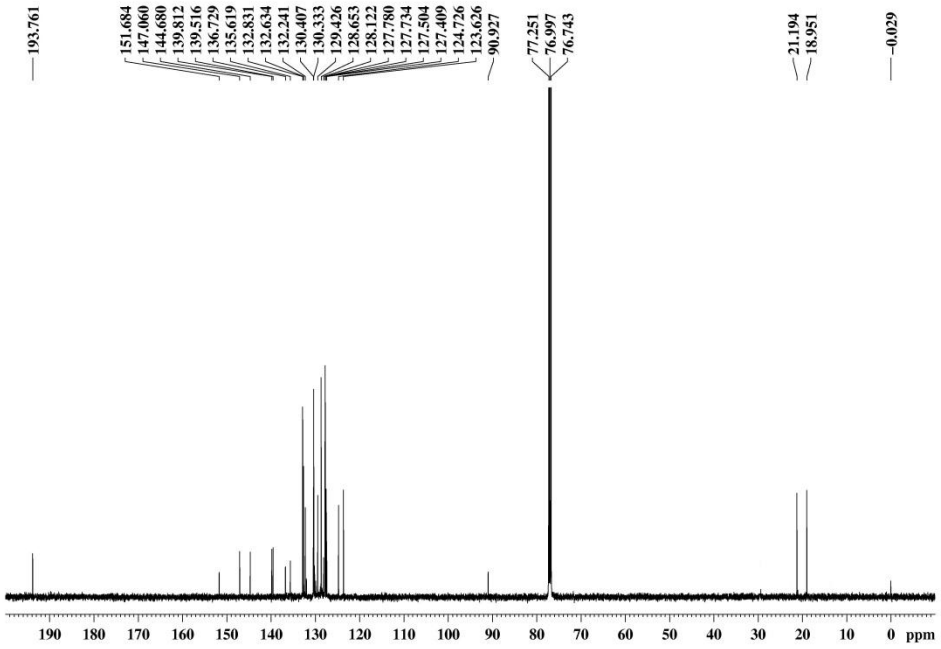


Figure S74. ^{13}C NMR spectrum of compound **32**

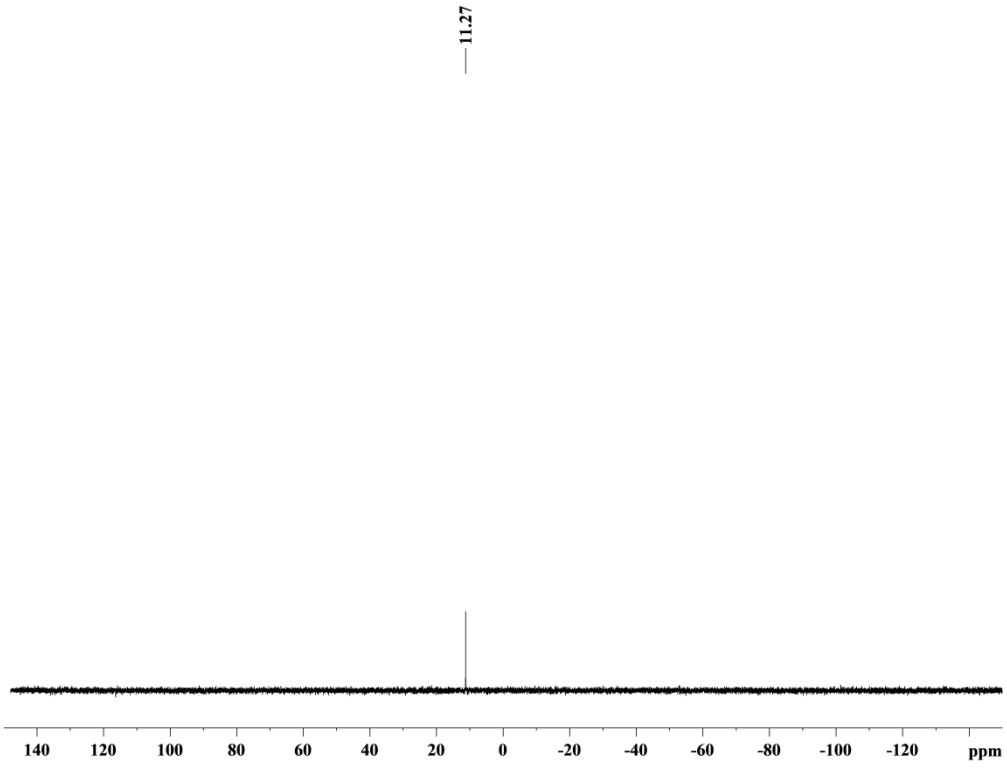


Figure S75. ^{31}P NMR spectrum of compound **33**

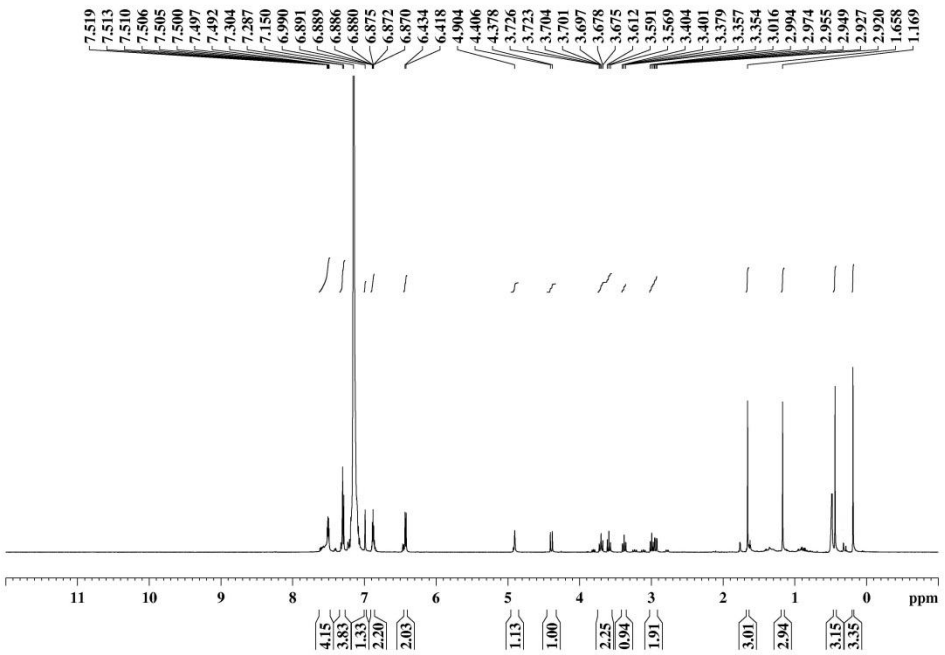


Figure S76. ^{1}H NMR spectrum of compound **33** in C_6D_6 (see text)

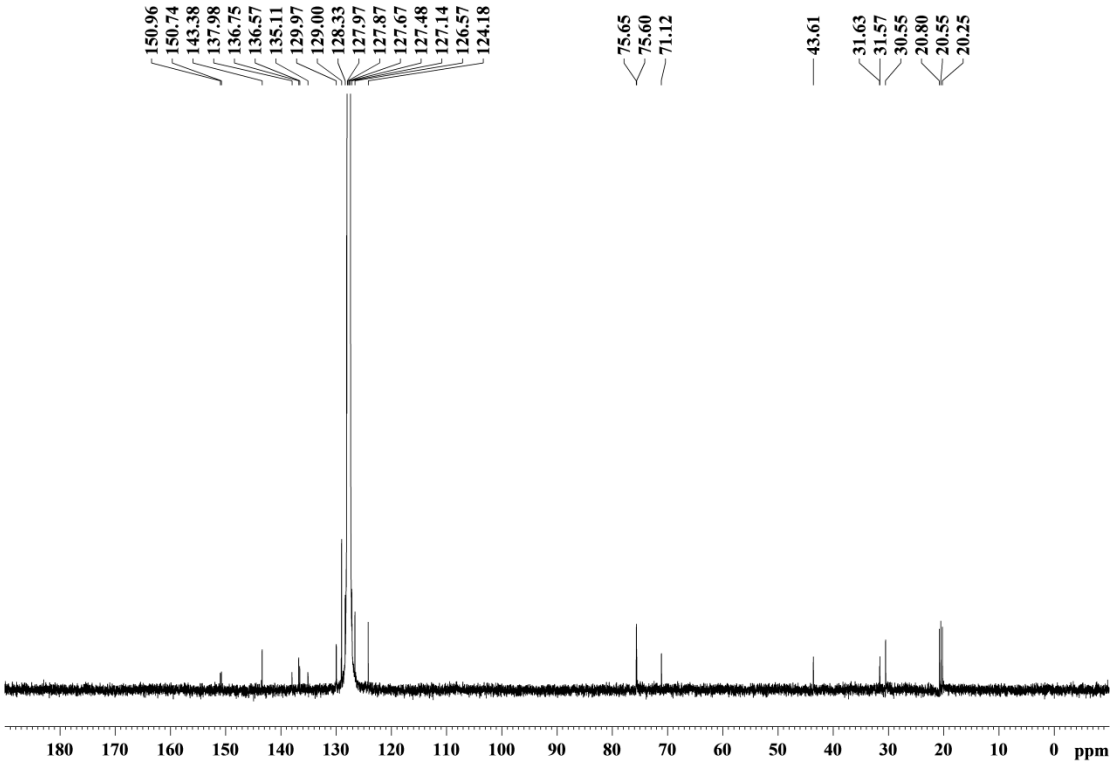


Figure S77. ^{13}C NMR spectrum of compound **33** in C_6D_6 (see text)