Electronic Supplementary Information (ESI)

Facile formation of tetrazole-thiolato Pd(II) and -Pt(II) complexes through deprotonation or oxidative addition using organic tetrazole-thiones

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Figure S95. ^{1}H-NMR spectra of methyl signal of 6-membered complexes, **18** (the below is normal ^{1}H-NMR. The above is phosphorus decoupled spectrum)

Figure S96 The Pt(II) Hydride region in the variable ^{1}H-NMR (400 MHz) spectra of complex **16.**

Table - SM1 X-ray data collection and structure refinements

	4	**10·(CH_2Cl_2)**	**12**	**16**	**18·(CH_2Cl_2)**
formula	$C_{15}H_{28}N_4P_2PdS$	$C_{29}H_{44}Cl_2N_8P_2PdS_2$	$C_{18}H_{34}N_8P_2PdS_2$	$C_{15}H_{28}N_4P_2PtS$	$C_{11}H_{26}Cl_2N_4P_2PtS$
fw	464.81	808.08	594.99	553.50	574.35
temperature, K	296(2)	223(2)	223(2)	223(2)	223(2)
crystal size (mm^3)	0.68 × 0.48 × 0.36	0.15×0.10×0.07	0.13×0.12×0.10	0.20×0.11×0.08	0.15×0.10×0.07
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C222_1$	$P2_1/c$	$P2_1/n$	$P\text{-}1$
a, Å	11.2692(4)	12.1391(7)	10.481(2)	9.802(2)	11.205(7)
b, Å	10.0561(4)	19.4487(11)	14.414(4)	19.264(4)	11.285(7)
c, Å	18.5744(6)	15.6956(8)	18.274(5)	12.273(3)	17.208(13)
□, deg	94.113(2)	90	106.241(7)	113.057(7)	99.31(2)
V, $Å^3$	2099.51(13)	3705.6(4)	2650.6(11)	2132.3(7)	2027(2)
Z	4	4	4	4	4
d_{cal}, g cm^{-3}	1.471	1.448	1.491	1.724	1.881
□, mm^{-1}	1.139	0.876	1.000	6.832	7.439
F(000)	952	1664	1224	1080	1112
T_{min}	0.5113	0.880	0.6681	0.340	0.400
T_{max}	0.6845	0.941	0.810	0.611	0.616
No. of reflns Measured	45218	70396	57571	79387	78215
No. of reflns Unique	5271	4619	5200	4178	7953
No. of reflns with $I > 2\sigma(I)$	4906	4004	4310	3722	7054
No. of params Refined	209	204	320	212	379
Max., in Δρ (e $Å^{-3}$)	0.317	0.550	0.856	1.096	1.859
Min., in Δρ (e $Å^{-3}$)	–0.298	–0.312	–0.613	–0.800	–0.631
GOF onF^2	1.068	1.053	1.021	1.068	1.042
$R1$[a]	0.0190	0.0313	0.0303	0.0202	0.0312
$wR2$[b]	0.0496	0.0568	0.0818	0.0449	0.0781
R (all data)	0.0216	0.0451	0.0411	0.0255	0.0370
wR_2[a] (all data)	0.0524	0.0606	0.0927	0.0470	0.0813

[a]$R1 = \Sigma||F_o| - |F||/\Sigma|F_o|$, [b]$wR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

	20	**23**	**31**
formula	$C_{20}H_{28}N_4P_2PtS$	$C_{11}H_{26}N_4P_2PtS$	$C_{17}H_{16}N_4OS$
fw	613.55	503.45	324.40
temperature, K	223(2)	223(2)	223(2)
crystal size (mm^3)	0.16×0.14×0.09	0.12×0.07×0.07	0.27×0.11×0.08
crystal system	monoclinic	triclinic	monoclinic
space group	*P2₁/c*	*P-1*	*P2₁/n*
a, Å	10.6808(11)	6.5317(9)	12.572(5)
b, Å	12.6140(13)	9.9539(15)	8.002(2)
c, Å	20.6847(16)	14.2527(19)	16.371(5)
β, deg	102.441(3)	94.011(4)	101.725(11)
V, $Å^3$	2321.4(4)	922.9(2)	1612.5(9)
Z	4	2	4
d_{cal}, g cm^{-3}	1.756	1.812	1.336
μ, mm^{-1}	6.285	7.882	0.210
F(000)	1200	488	680
T_{min}	0.442	0.451	0.946
T_{max}	0.602	0.608	0.984
No. of reflns Measured	43785	32917	20093
No. of reflns Unique	5850	4599	3172
No. of reflns with $I > 2\sigma(I)$	4452	4204	2484
No. of params Refined	253	182	208
Max., in Δρ (e $Å^{-3}$)	1.809	0.718	0.713
Min., in Δρ (e $Å^{-3}$)	–1.616	–0.551	–0.779
GOF on F^2	1.057	1.092	1.109
*R*1[a]	0.0449	0.0223	0.0547
*wR*2[b]	0.0924	0.0497	0.1650
R (all data)	0.0662	0.0270	0.0814
wR_2[a] (all data)	0.0997	0.0513	0.2001

[a] $R1 = \Sigma||F_o| - |F||/\Sigma|F_o|$, [b] $wR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

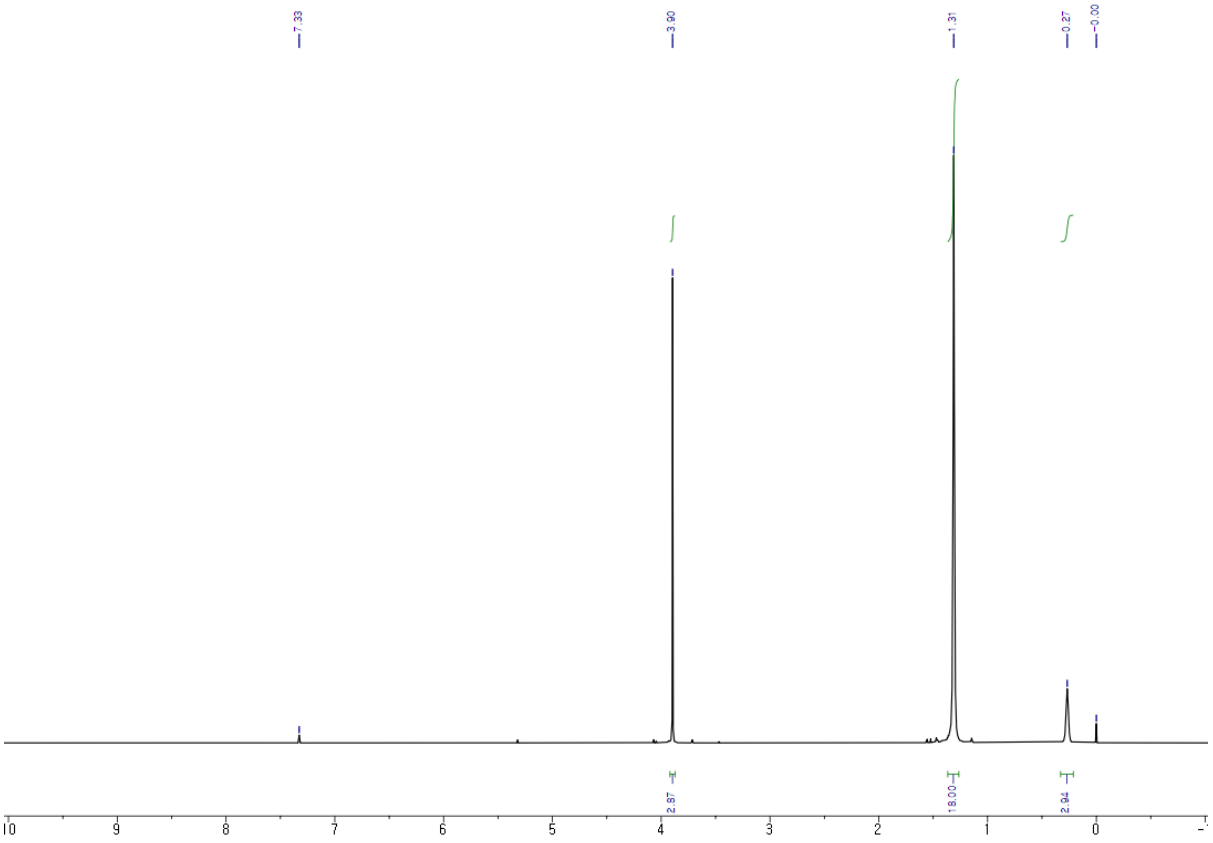

Figure S1. ^{1}H NMR spectrum of **1** (400 MHz, $CDCl_3$, 300 K)

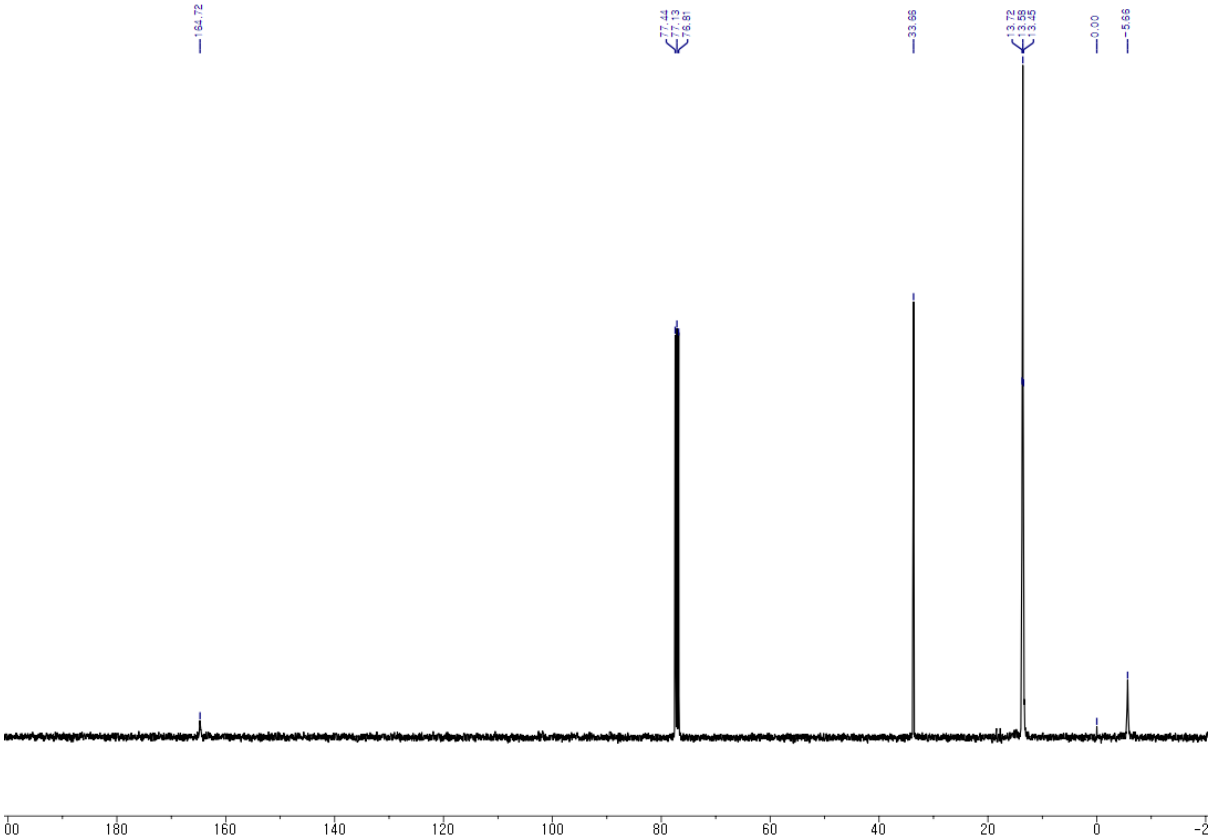

Figure S2. ^{13}C NMR spectrum of **1** (101 MHz, $CDCl_3$, 300 K)

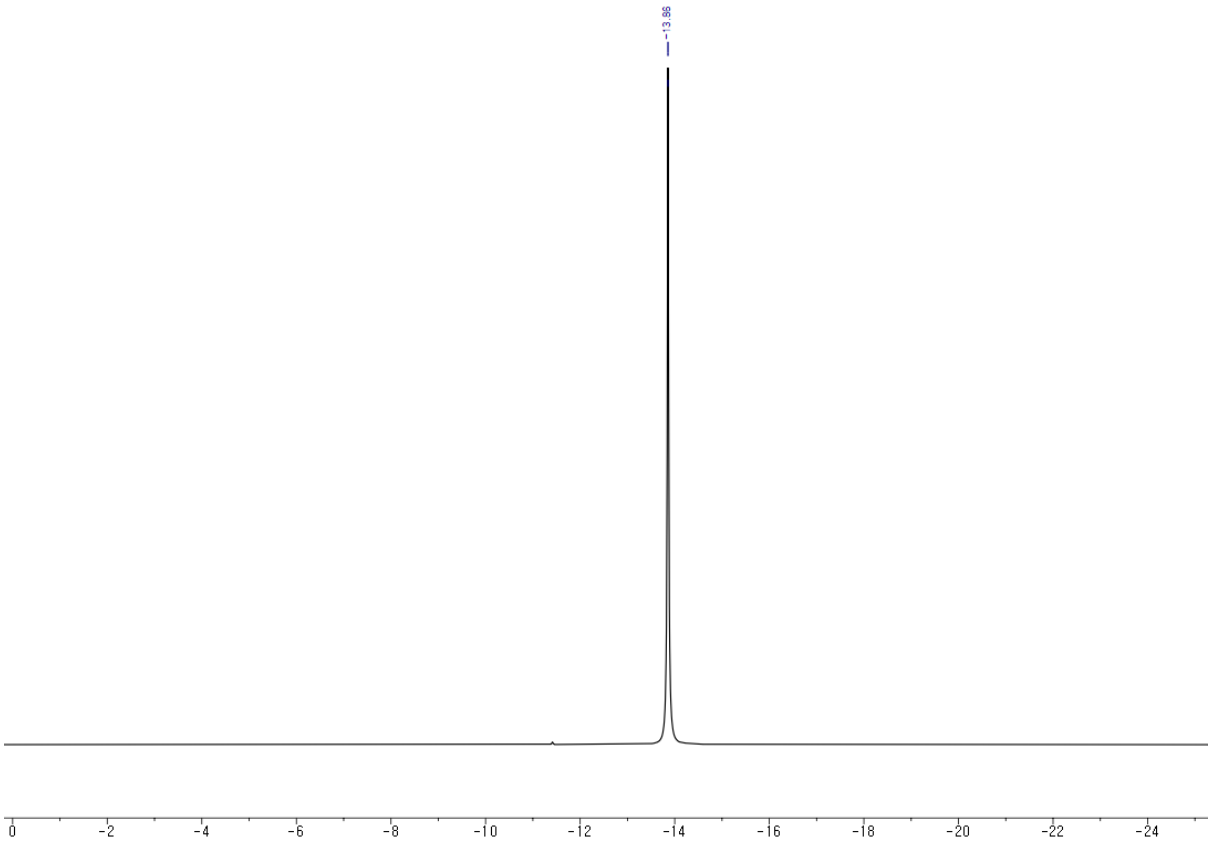

Figure S3. ^{31}P NMR spectrum of **1** (162 MHz, $CDCl_3$, 300 K)

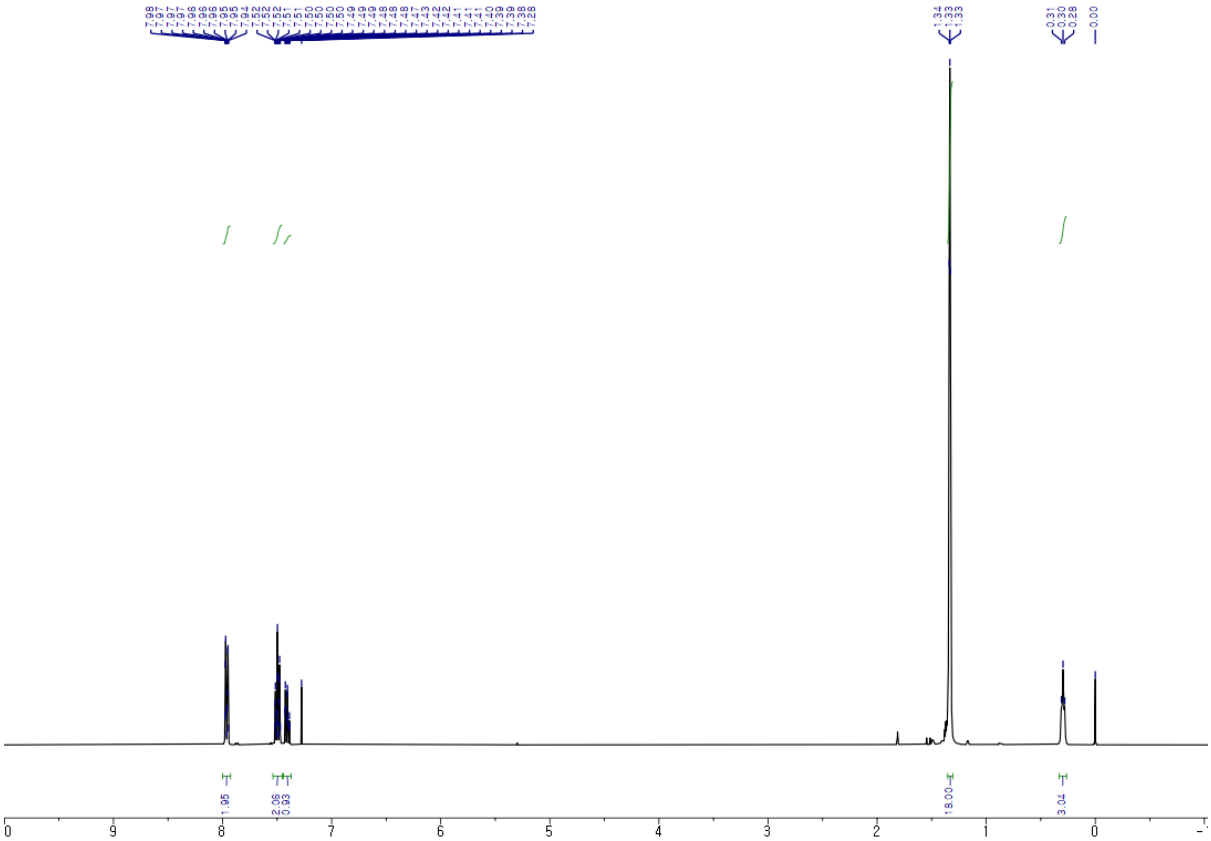

Figure S4. ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$, 300 K)

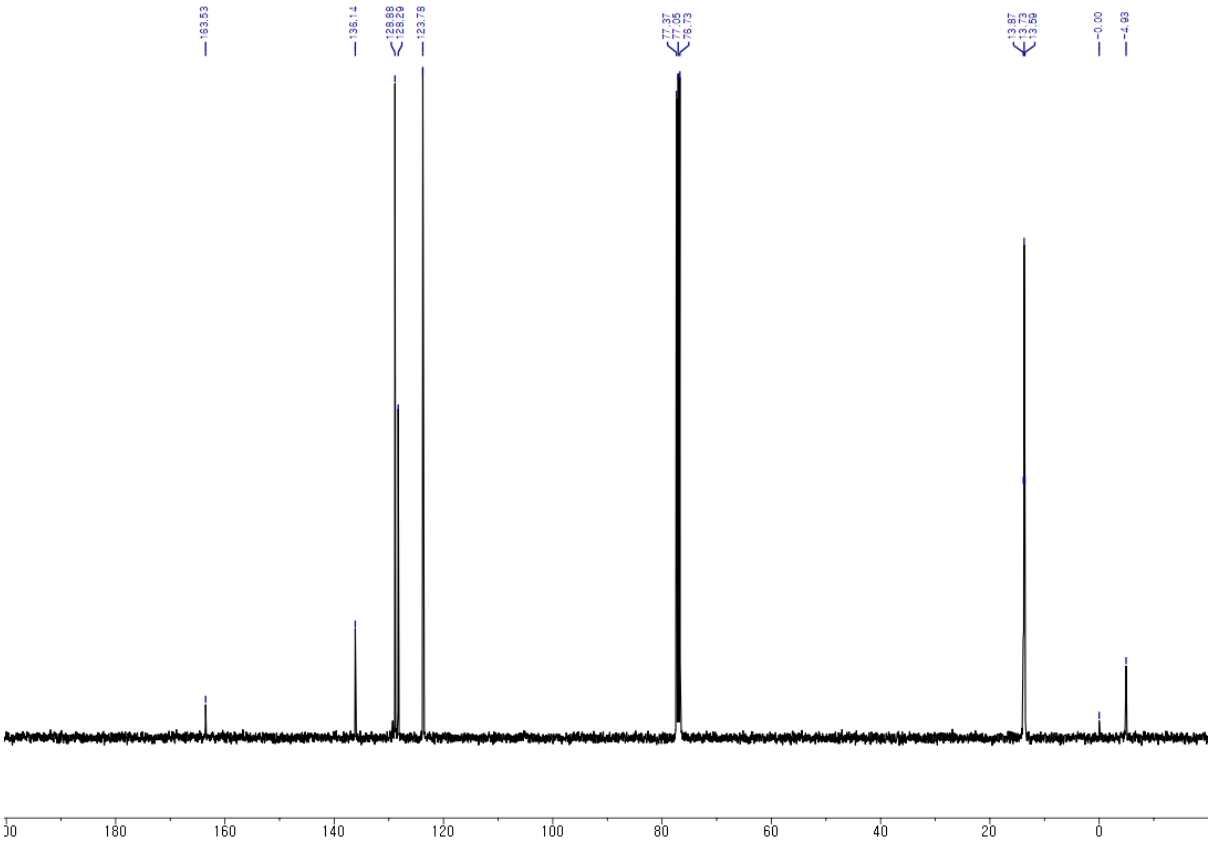

Figure S5. ^{13}C NMR spectrum of **2** (101 MHz, $CDCl_3$, 300 K)

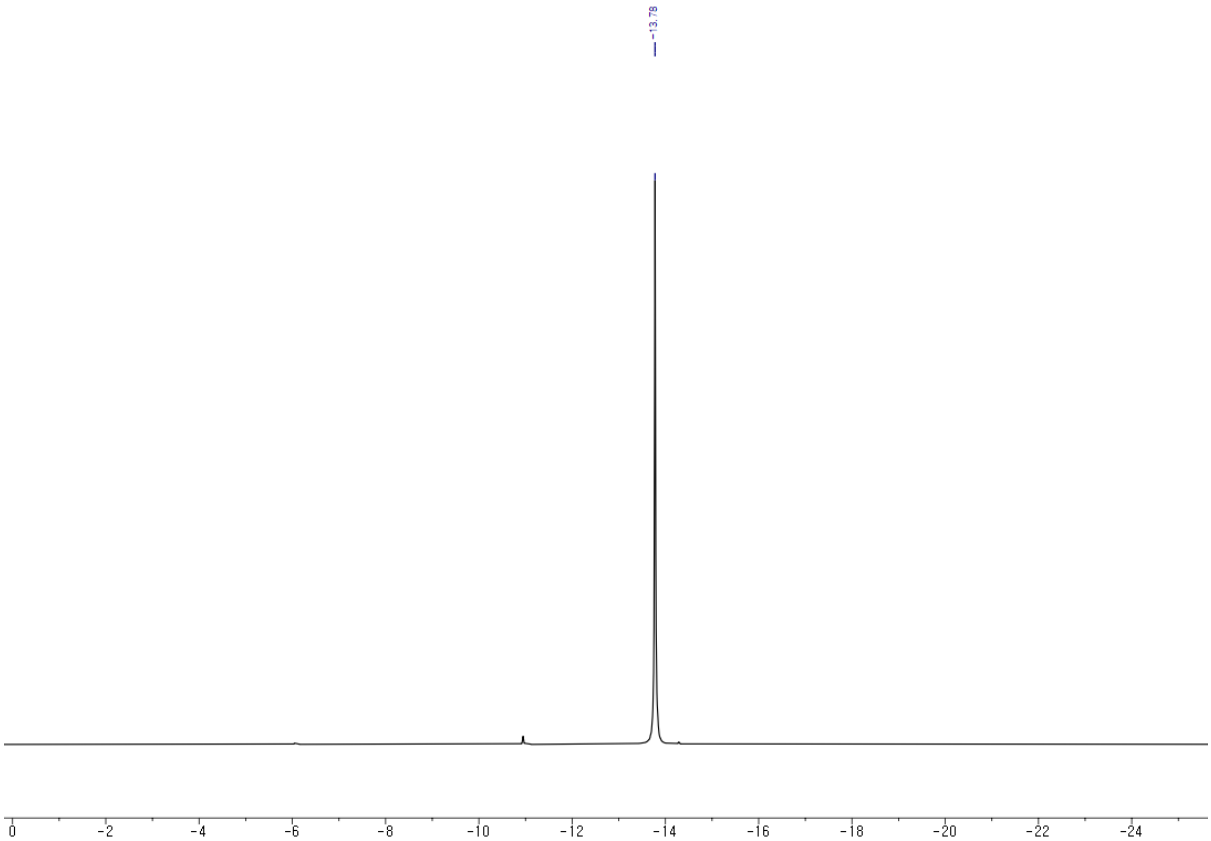

Figure S6. ^{31}P NMR spectrum of **2** (162 MHz, $CDCl_3$, 300 K)

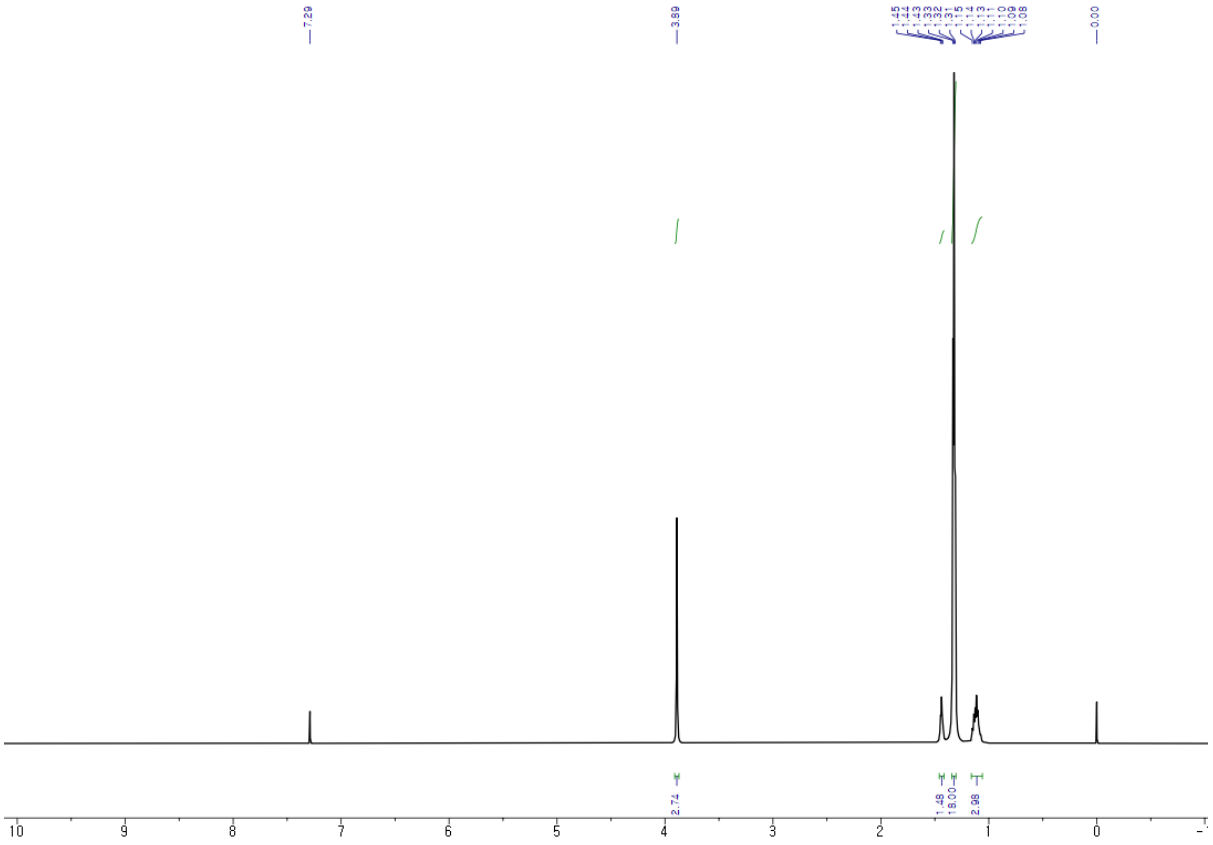

Figure S7. ^{1}H NMR spectrum of **3** (300 MHz, $CDCl_3$, 300 K)

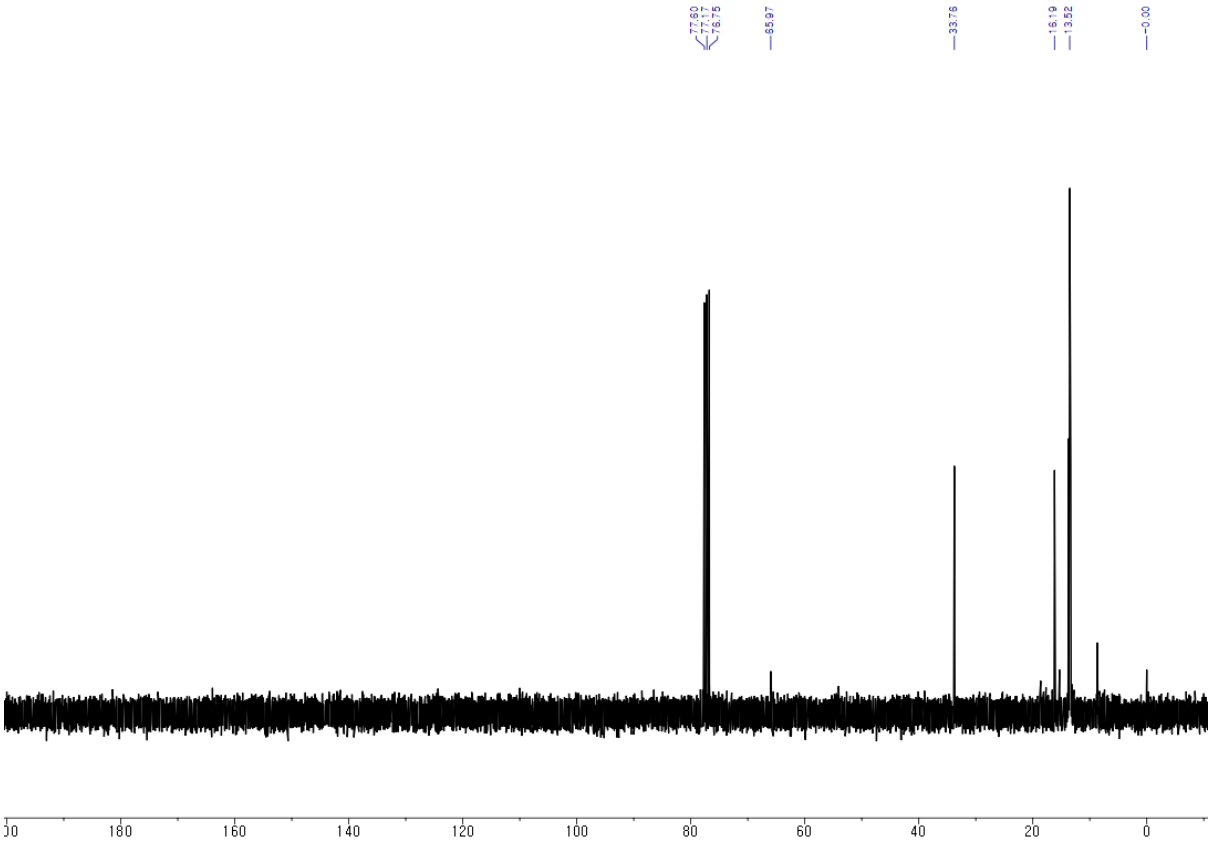

Figure S8. ^{13}C NMR spectrum of **3** (75 MHz, $CDCl_3$, 300 K)

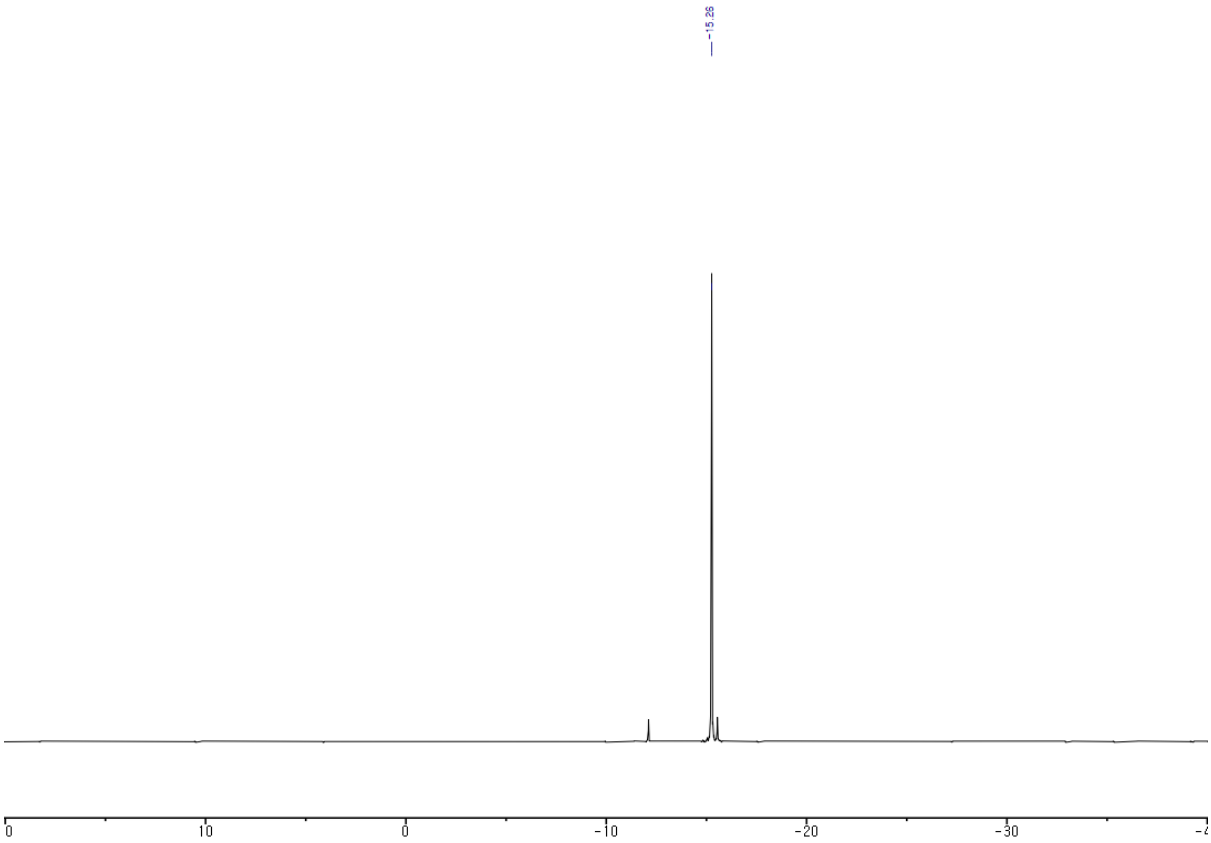

Figure S9. ^{31}P NMR spectrum of **3** (122 MHz, $CDCl_3$, 300 K)

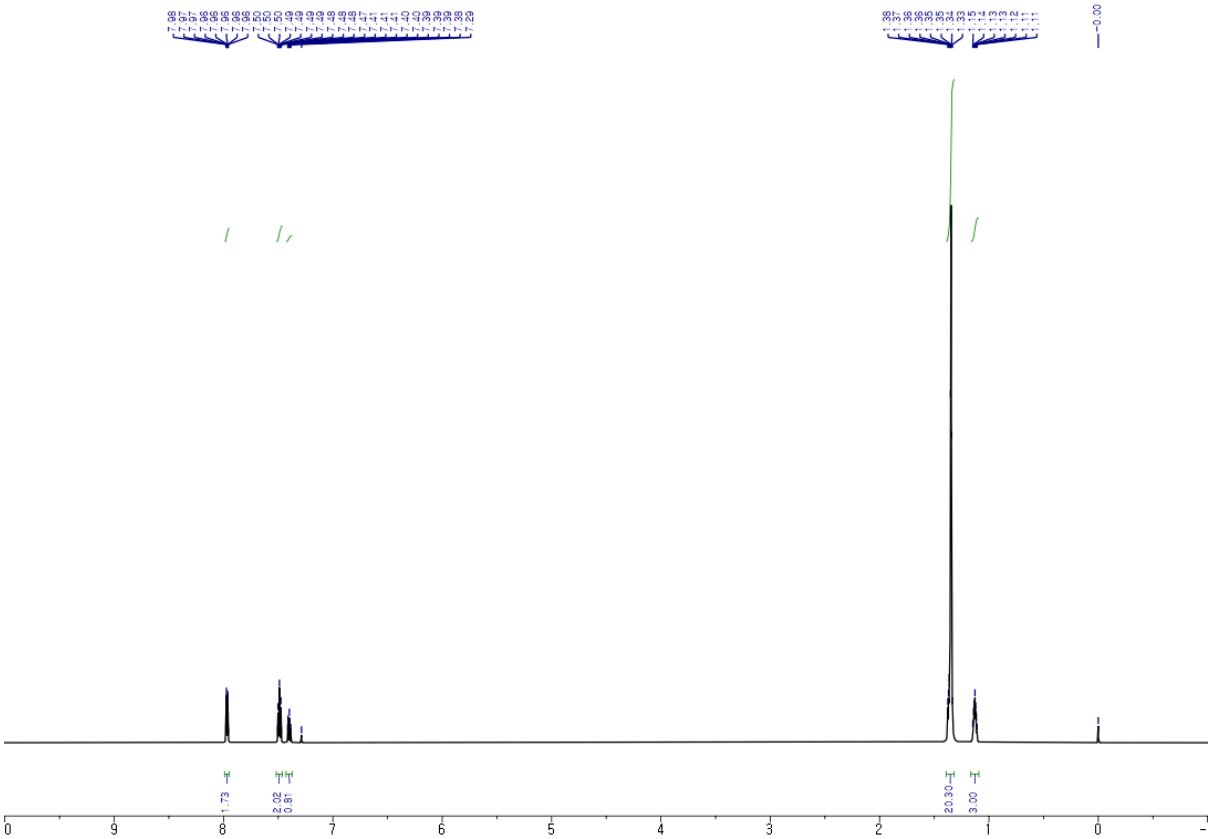

Figure S10. ^{1}H NMR spectrum of **4** (600 MHz, $CDCl_3$, 300 K)

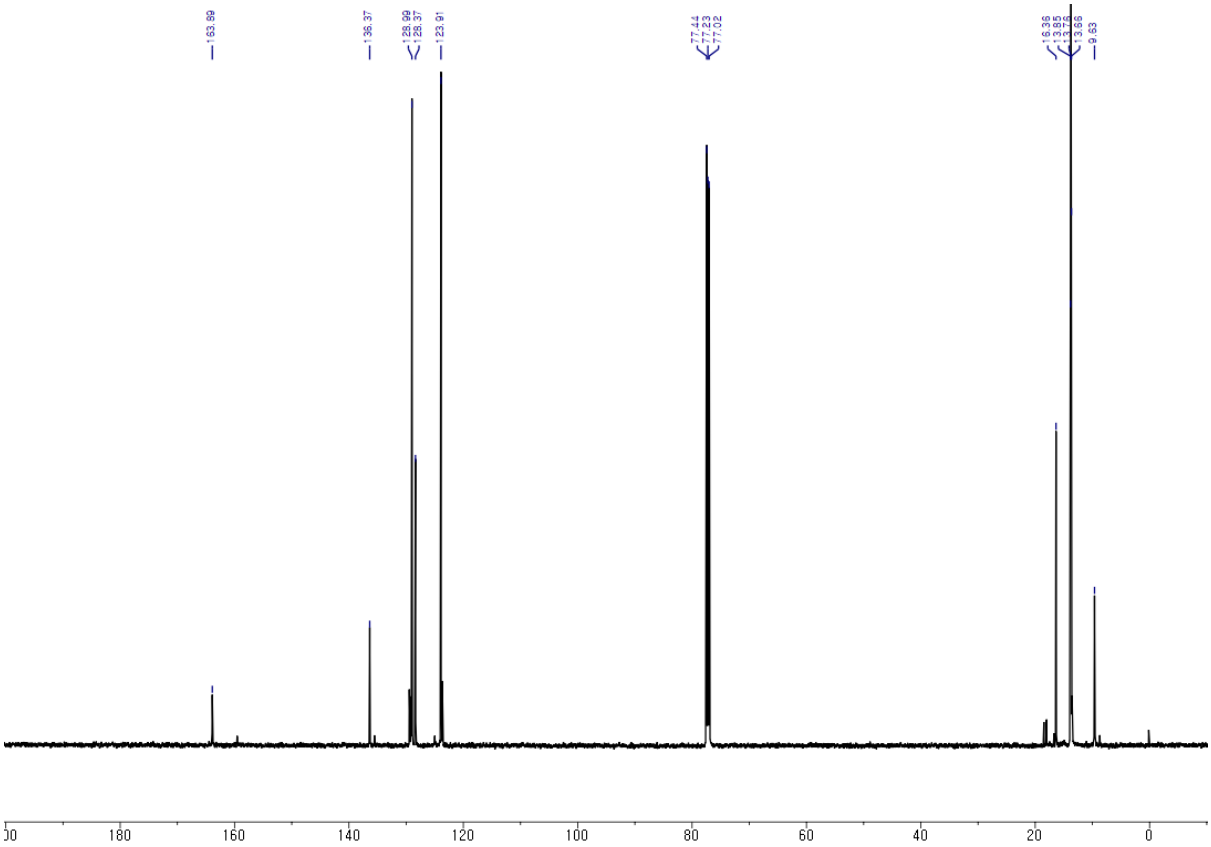

Figure S11. ^{13}C NMR spectrum of **4** (151 MHz, $CDCl_3$, 300 K)

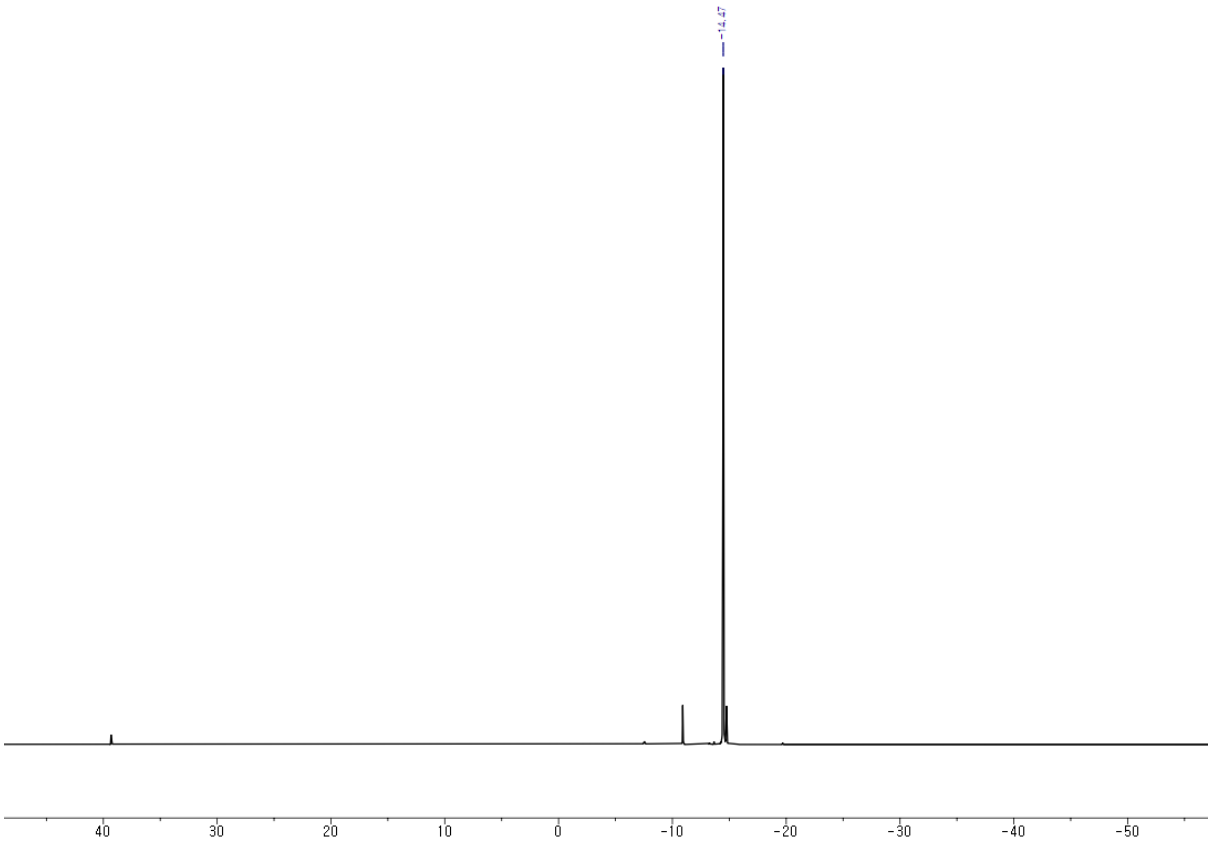

Figure S12. ^{31}P NMR spectrum of **4** (243 MHz, $CDCl_3$, 300 K)

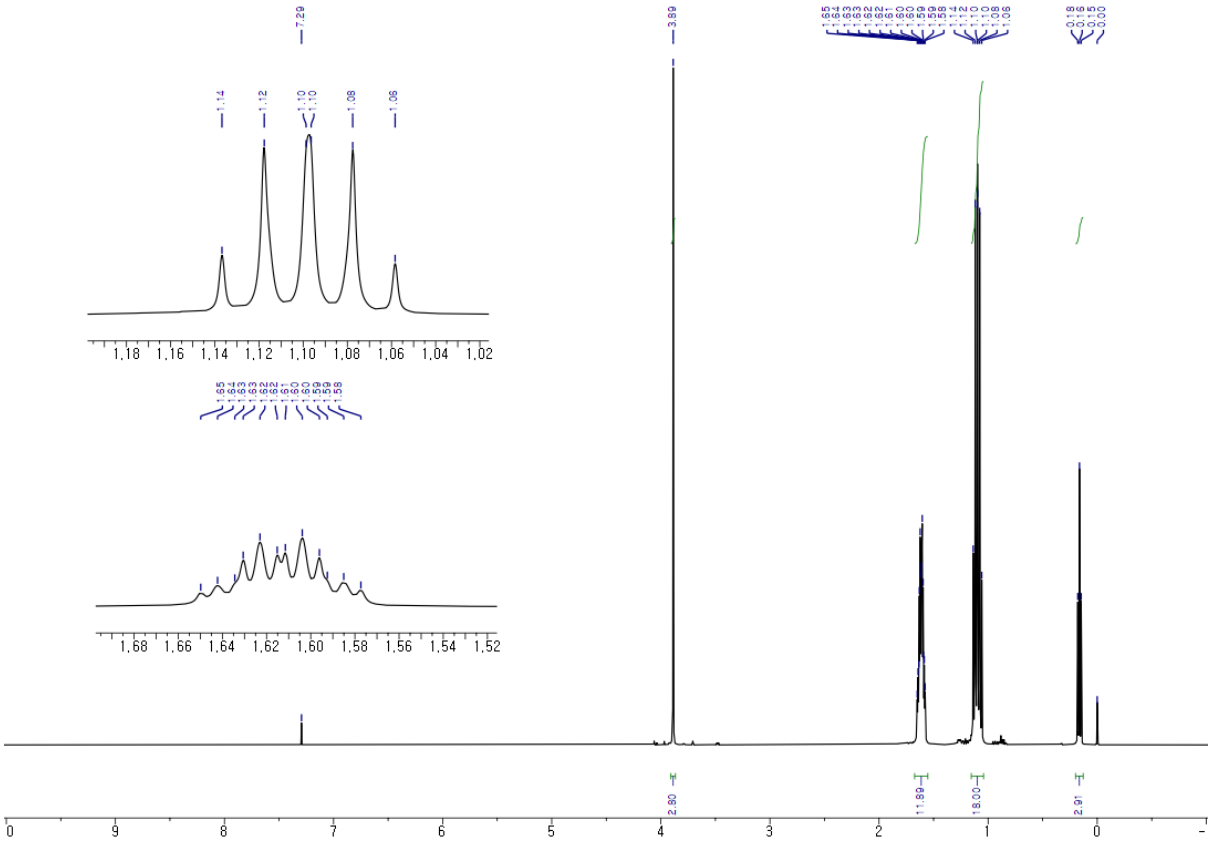

Figure S13. ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$, 300 K)

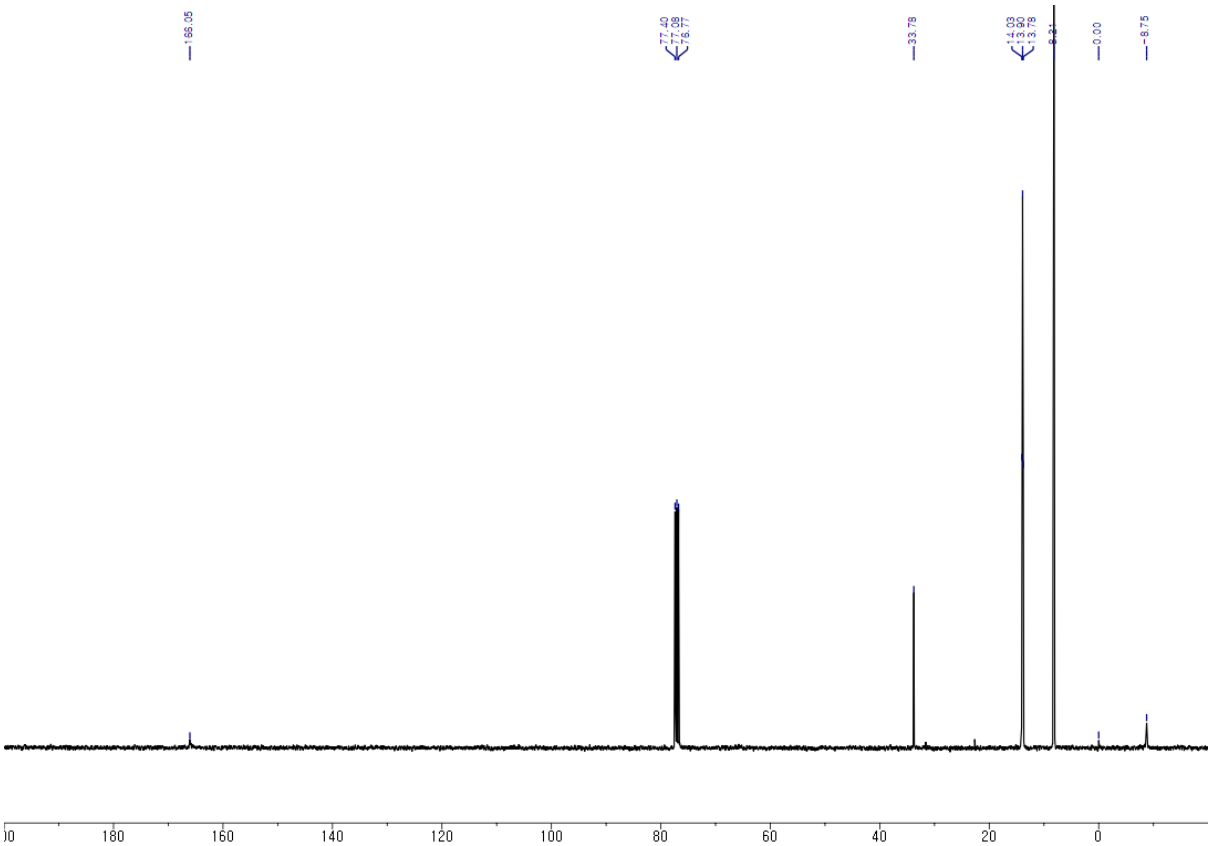

Figure S14. ^{13}C NMR spectrum of **5** (101 MHz, $CDCl_3$, 300 K)

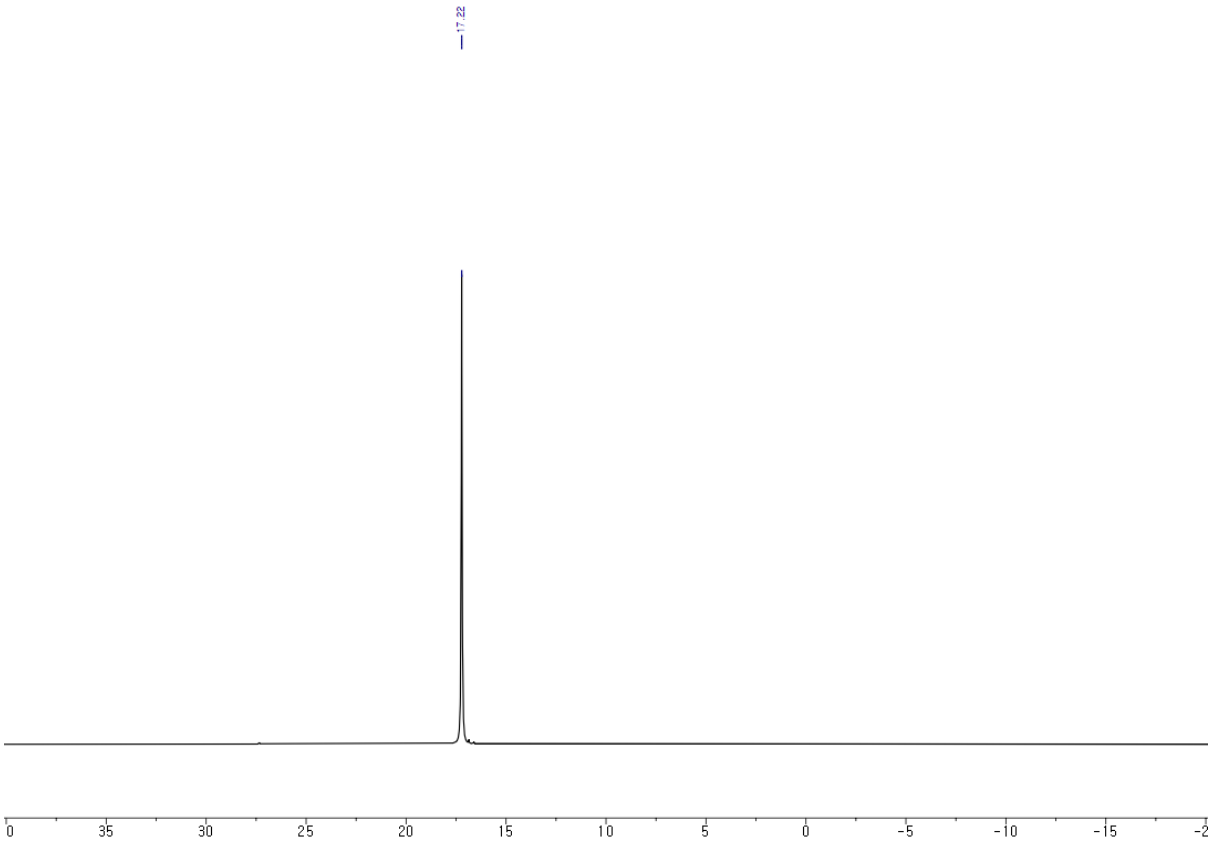

Figure S15. ^{31}P NMR spectrum of **5** (162 MHz, $CDCl_3$, 300 K)

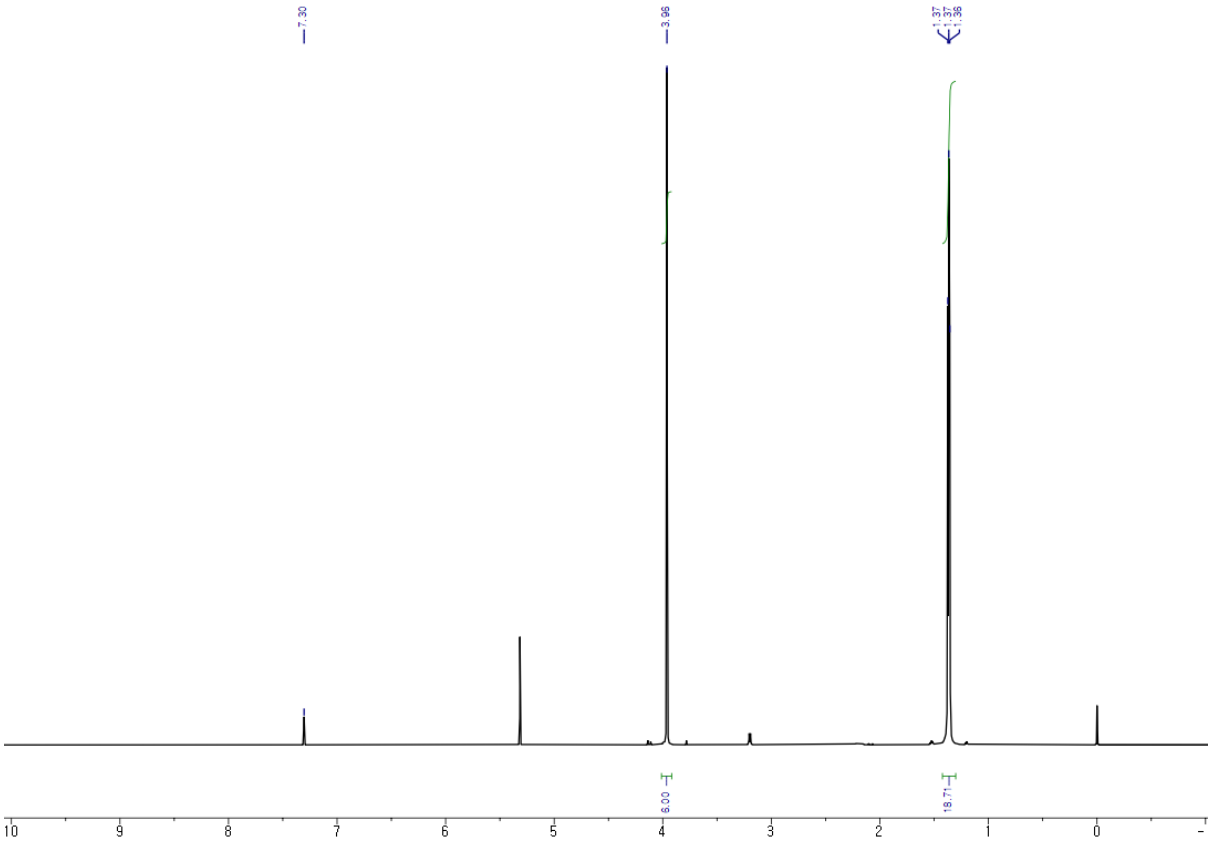

Figure S16. ^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$, 300 K)

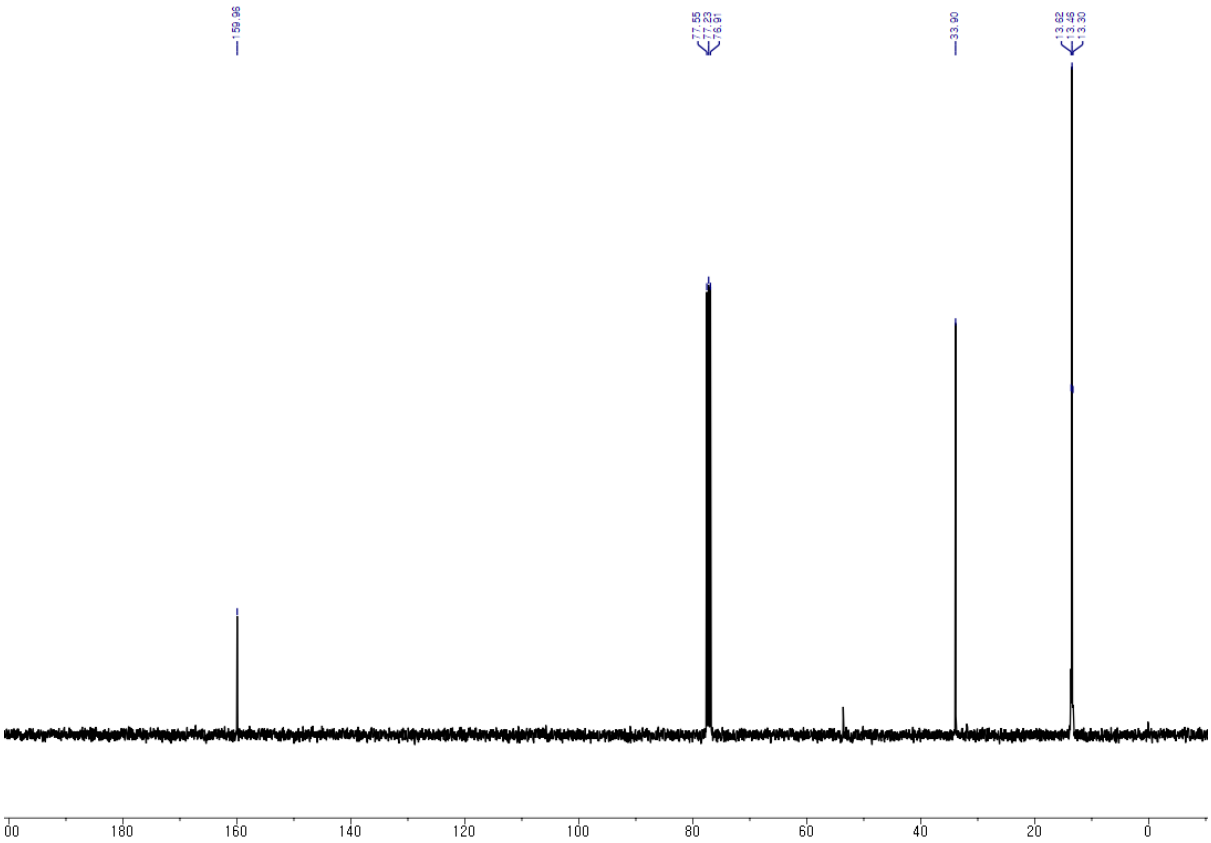

Figure S17. ^{13}C NMR spectrum of **6** (101 MHz, $CDCl_3$, 300 K)

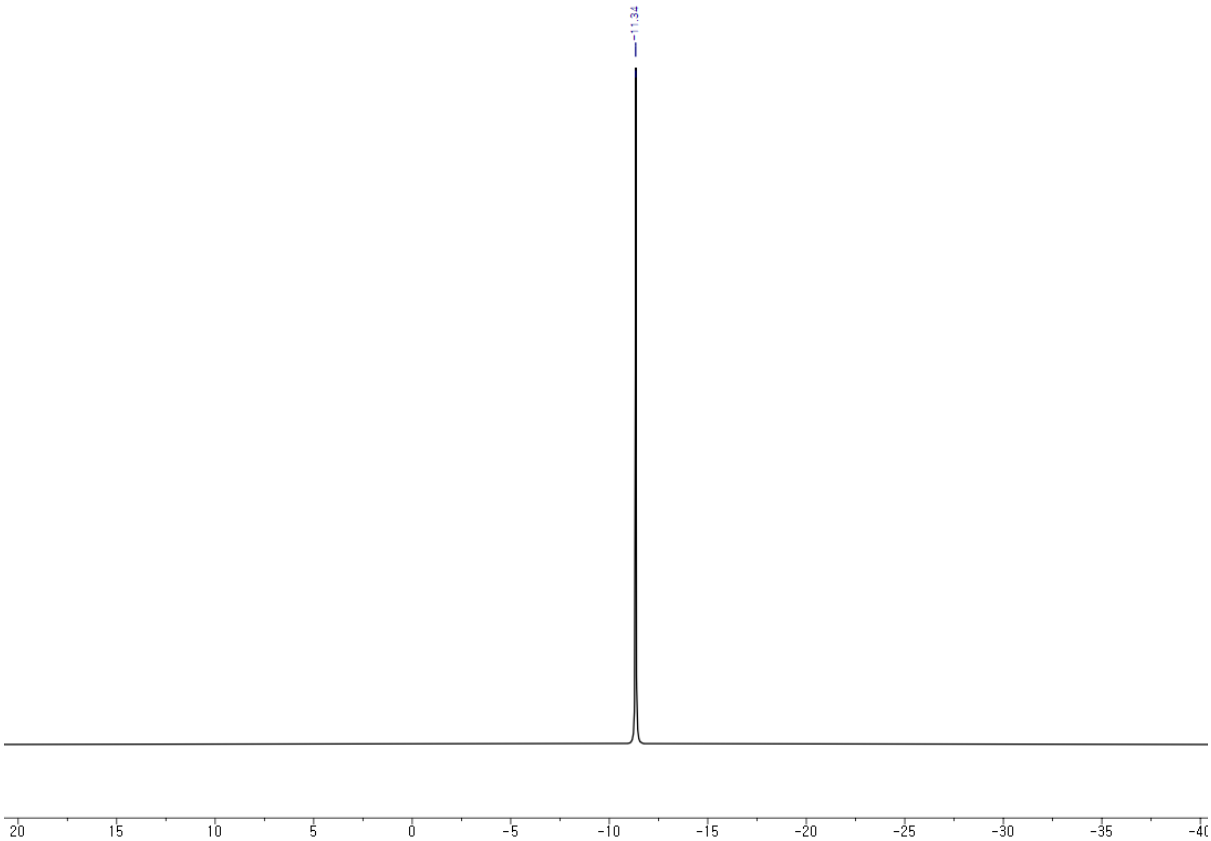

Figure S18. ^{31}P NMR spectrum of **6** (162 MHz, $CDCl_3$, 300 K)

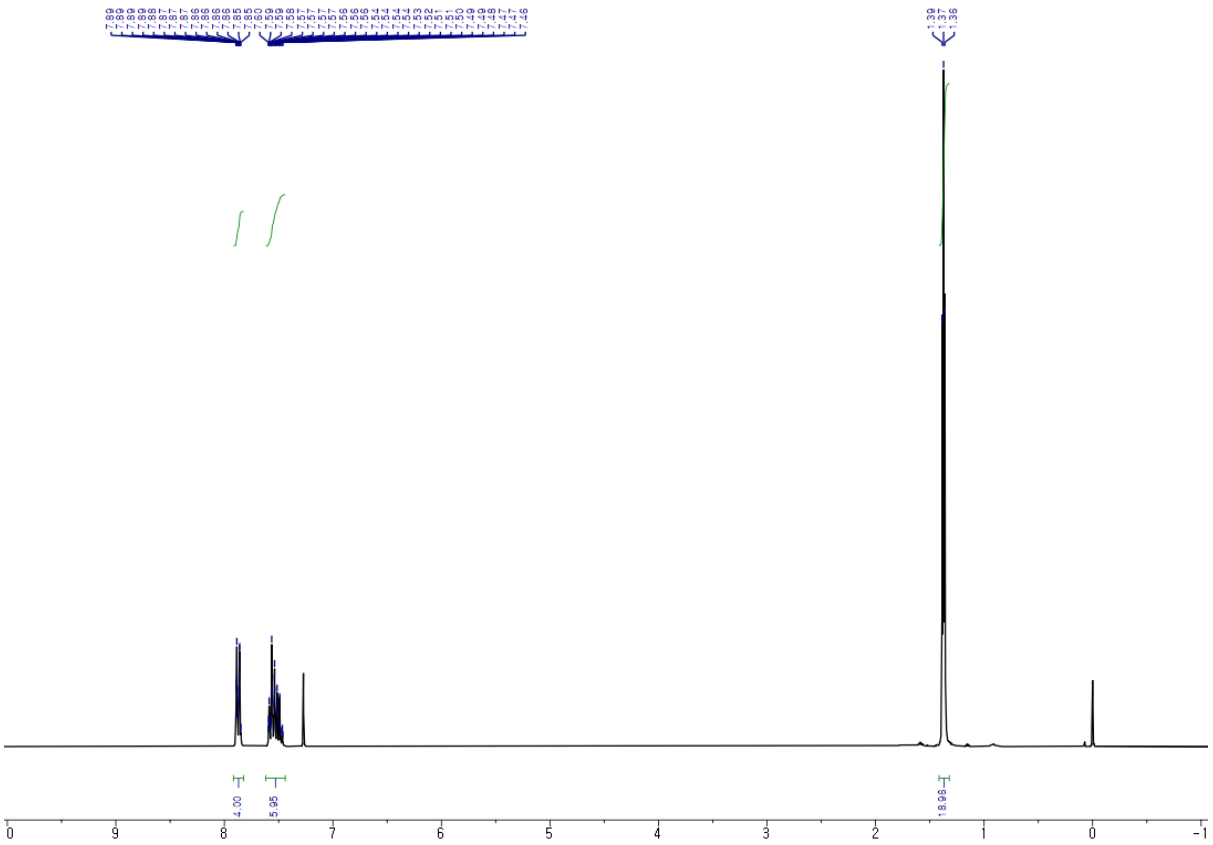

Figure S19. ^{1}H NMR spectrum of **7** (300 MHz, $CDCl_3$, 300 K)

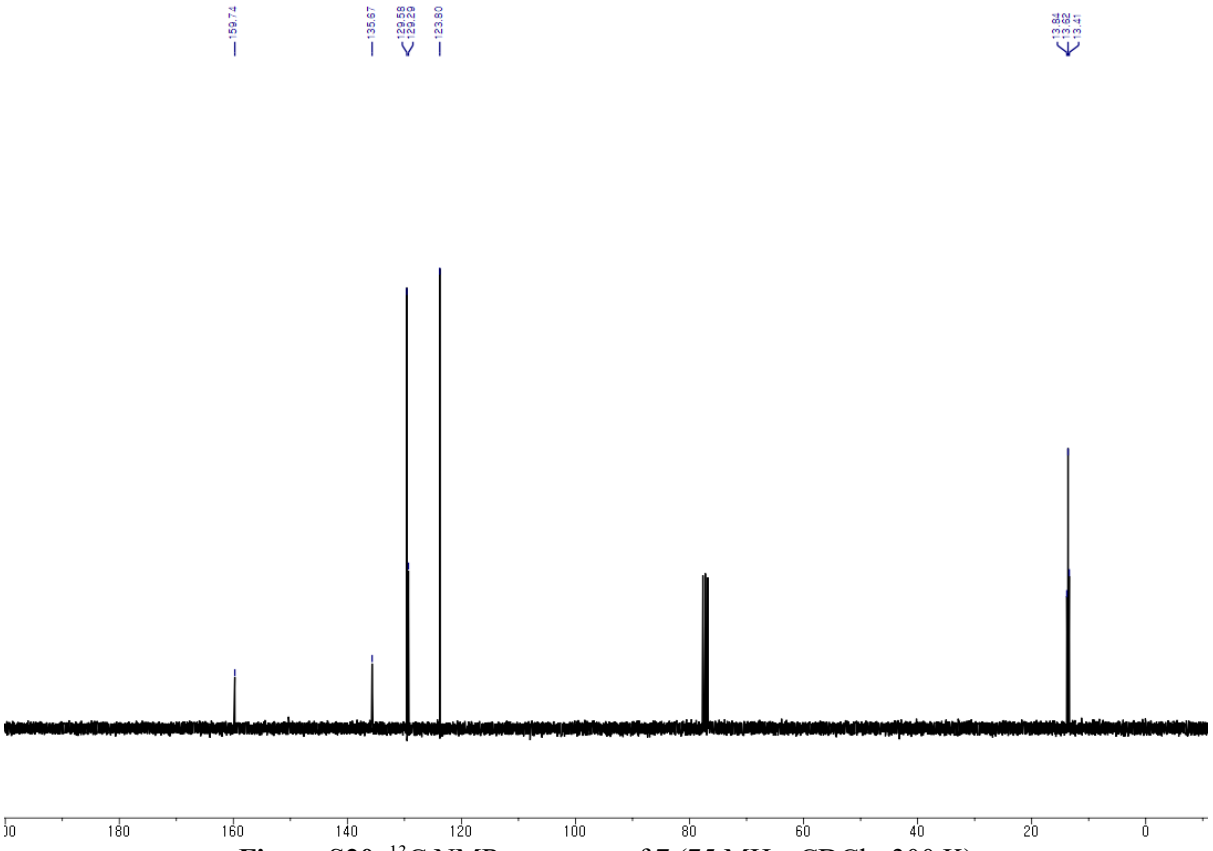

Figure S20. ^{13}C NMR spectrum of **7** (75 MHz, $CDCl_3$, 300 K)

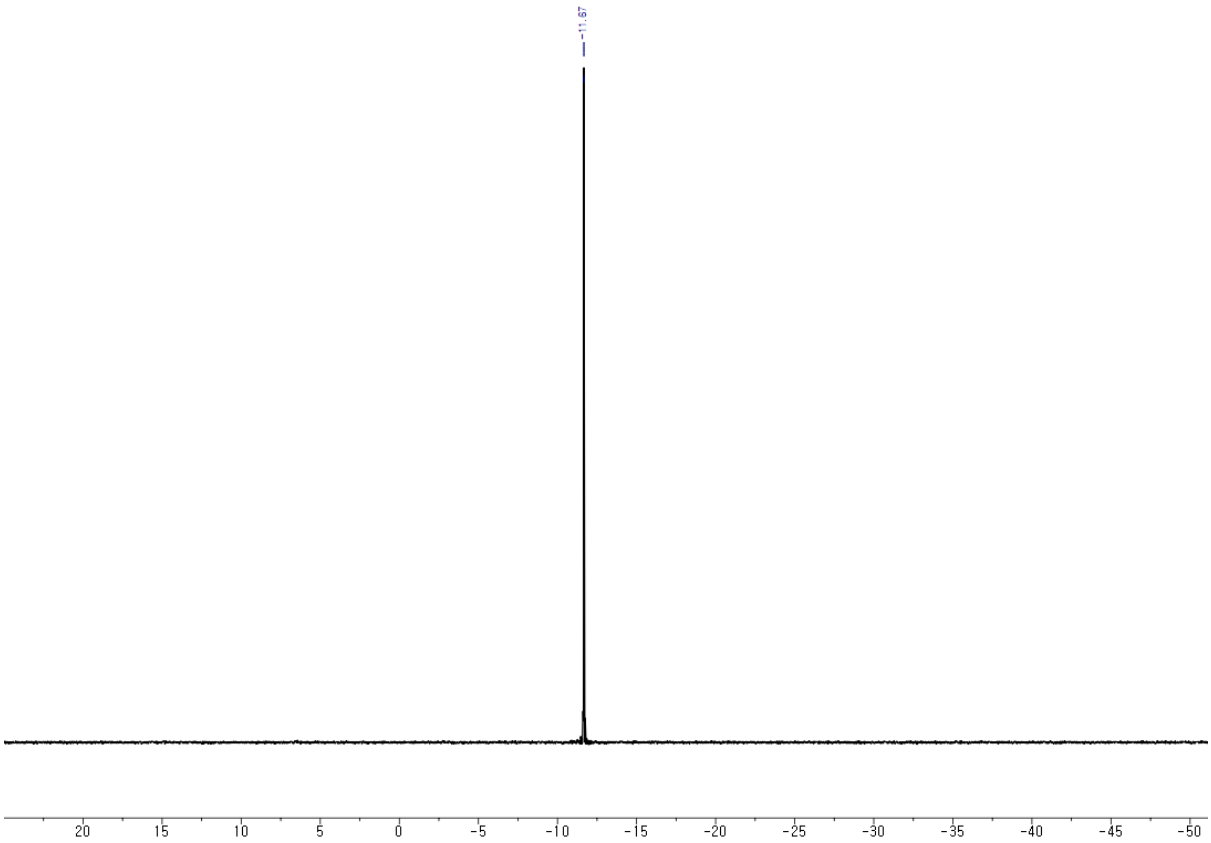

Figure S21. ^{31}P NMR spectrum of **7** (122 MHz, $CDCl_3$, 300 K)

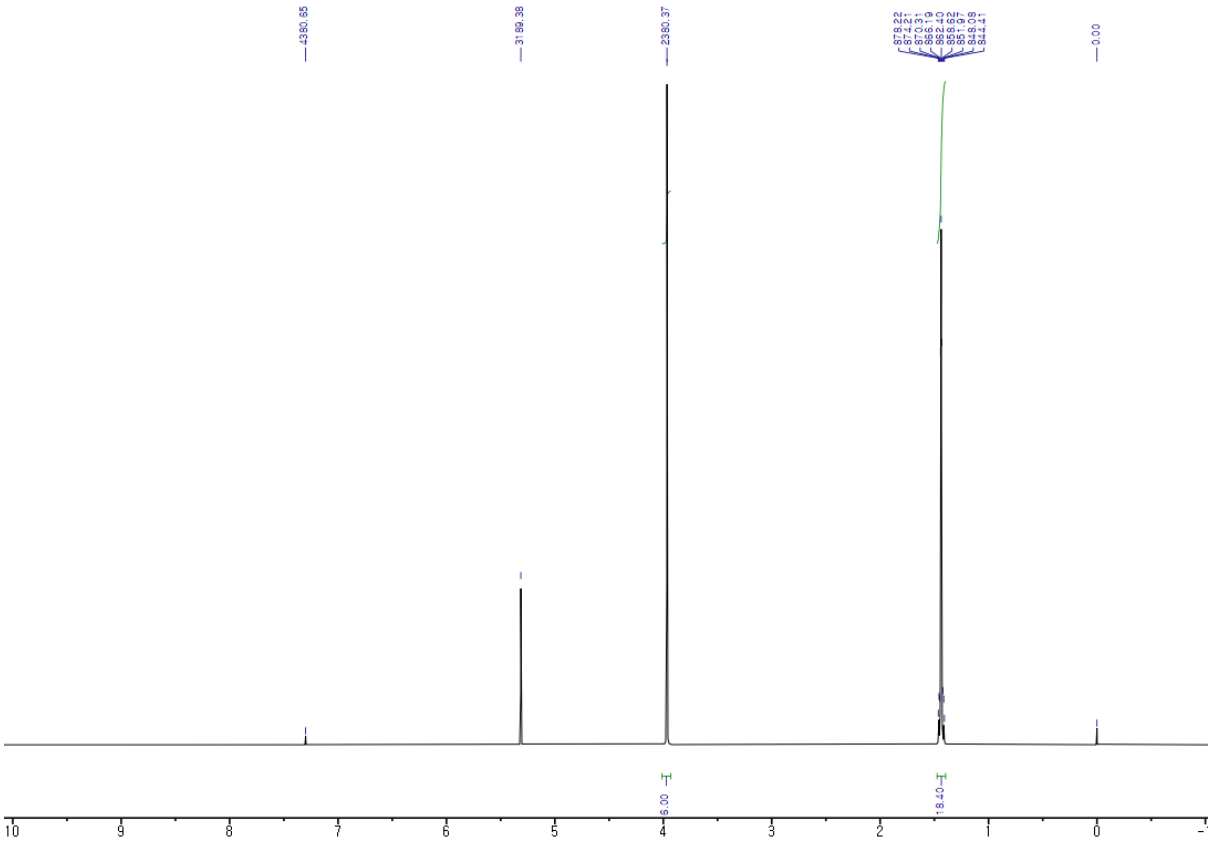

Figure S22. ^{1}H NMR spectrum of **8** (600 MHz, $CDCl_3$, 300 K)

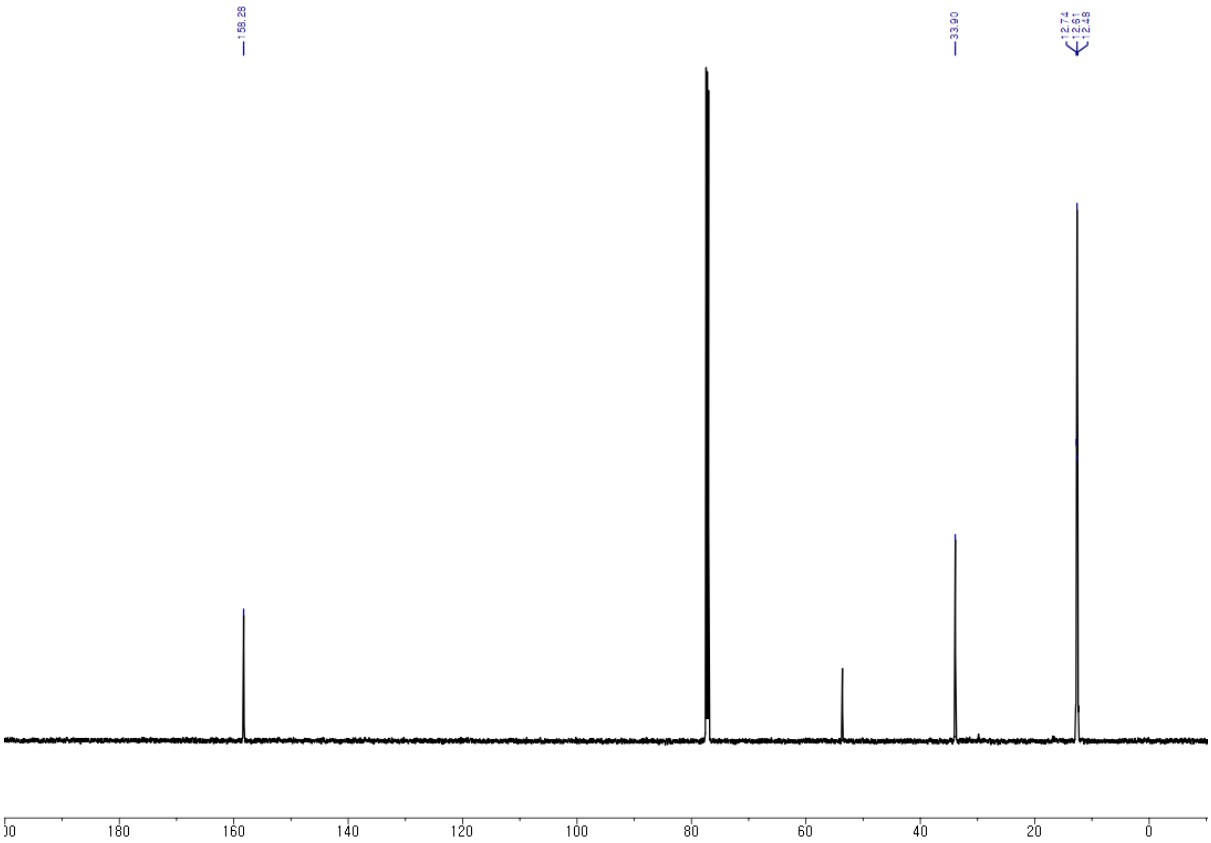

Figure S23. ^{1}C NMR spectrum of **8** (151 MHz, $CDCl_3$, 300 K)

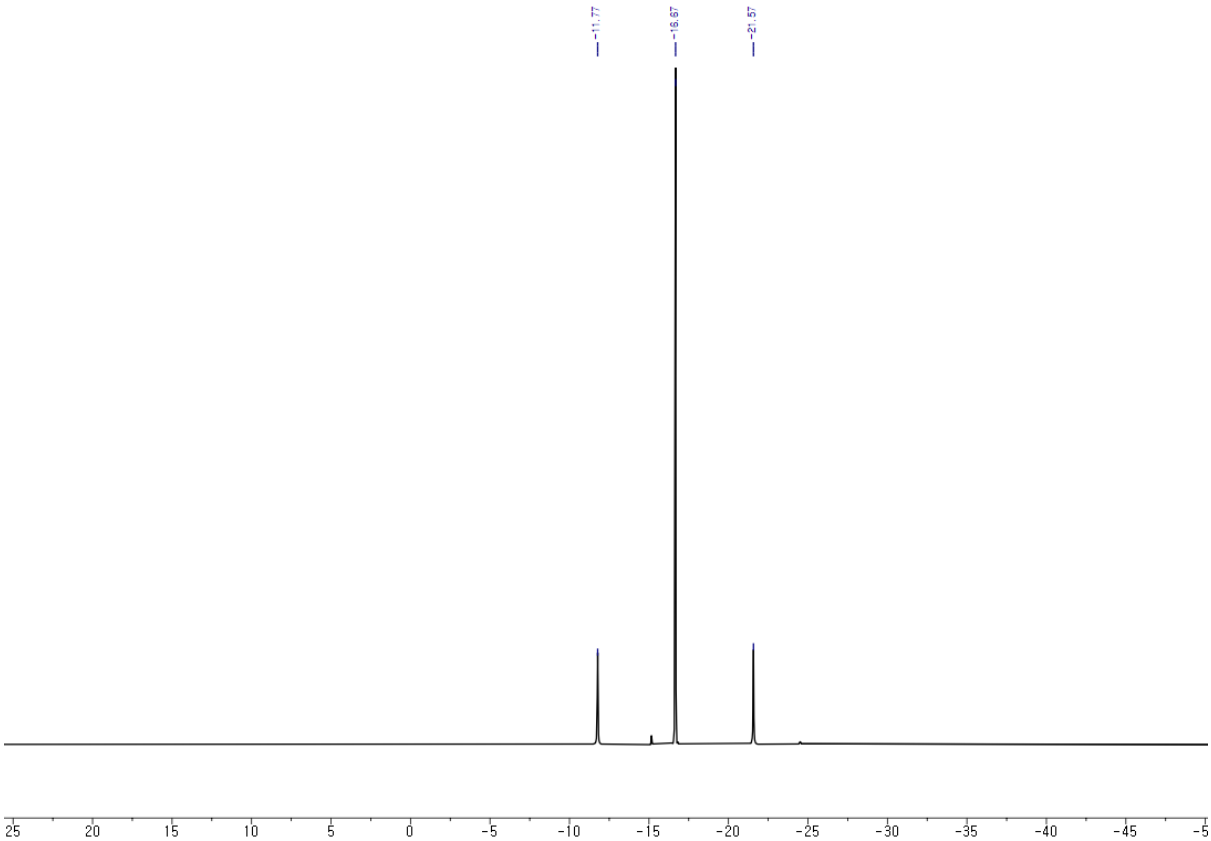

Figure S24. ^{31}P NMR spectrum of **8** (243 MHz, $CDCl_3$, 300 K)

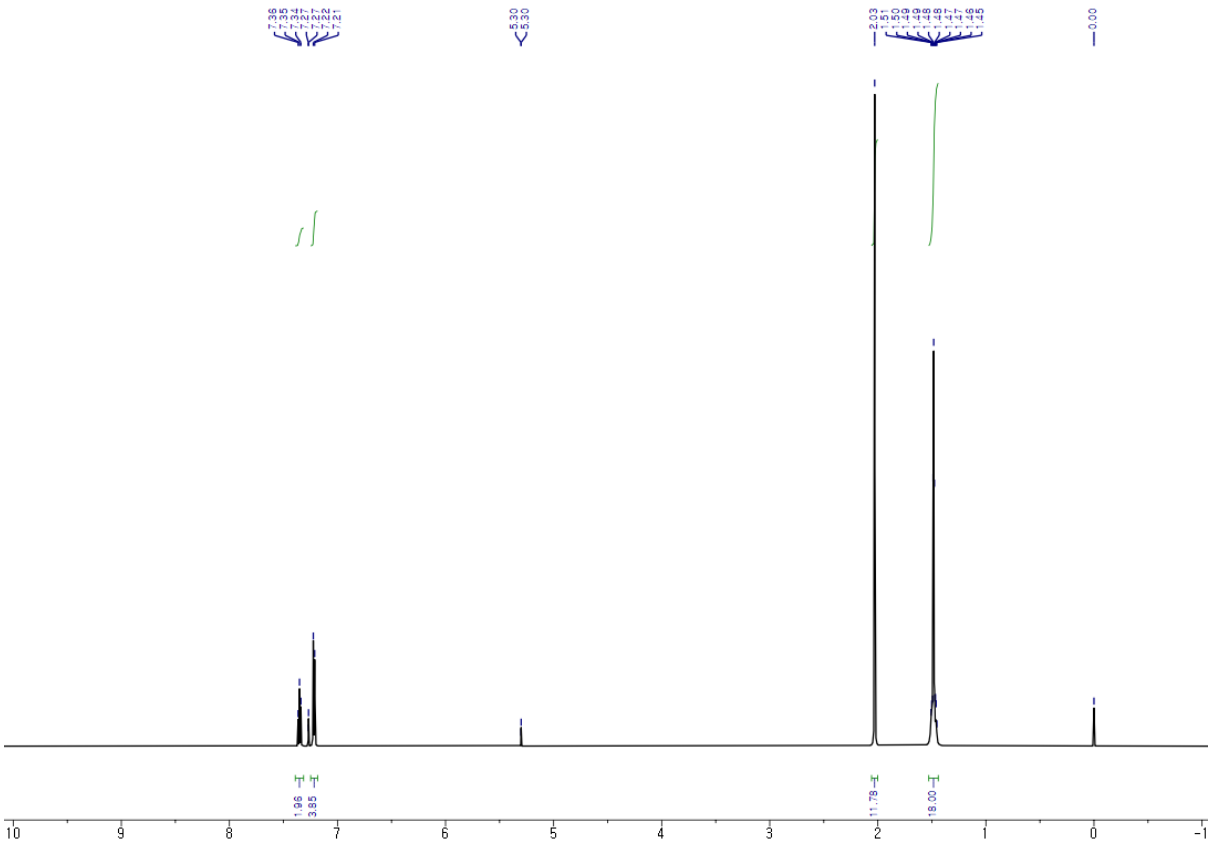

Figure S25. ^{1}H NMR spectrum of **9** (600 MHz, $CDCl_3$, 300 K)

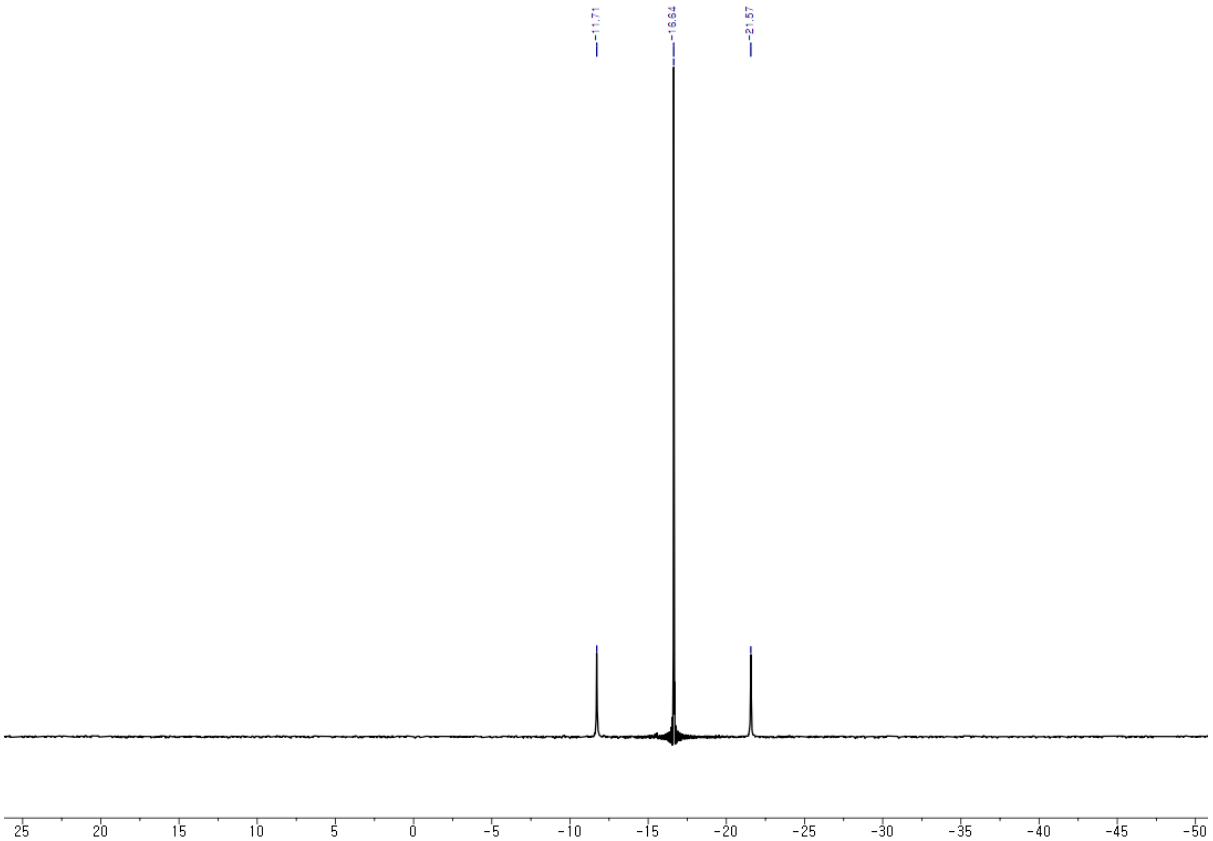

Figure S26. ^{31}P NMR spectrum of **9** (243 MHz, $CDCl_3$, 300 K)

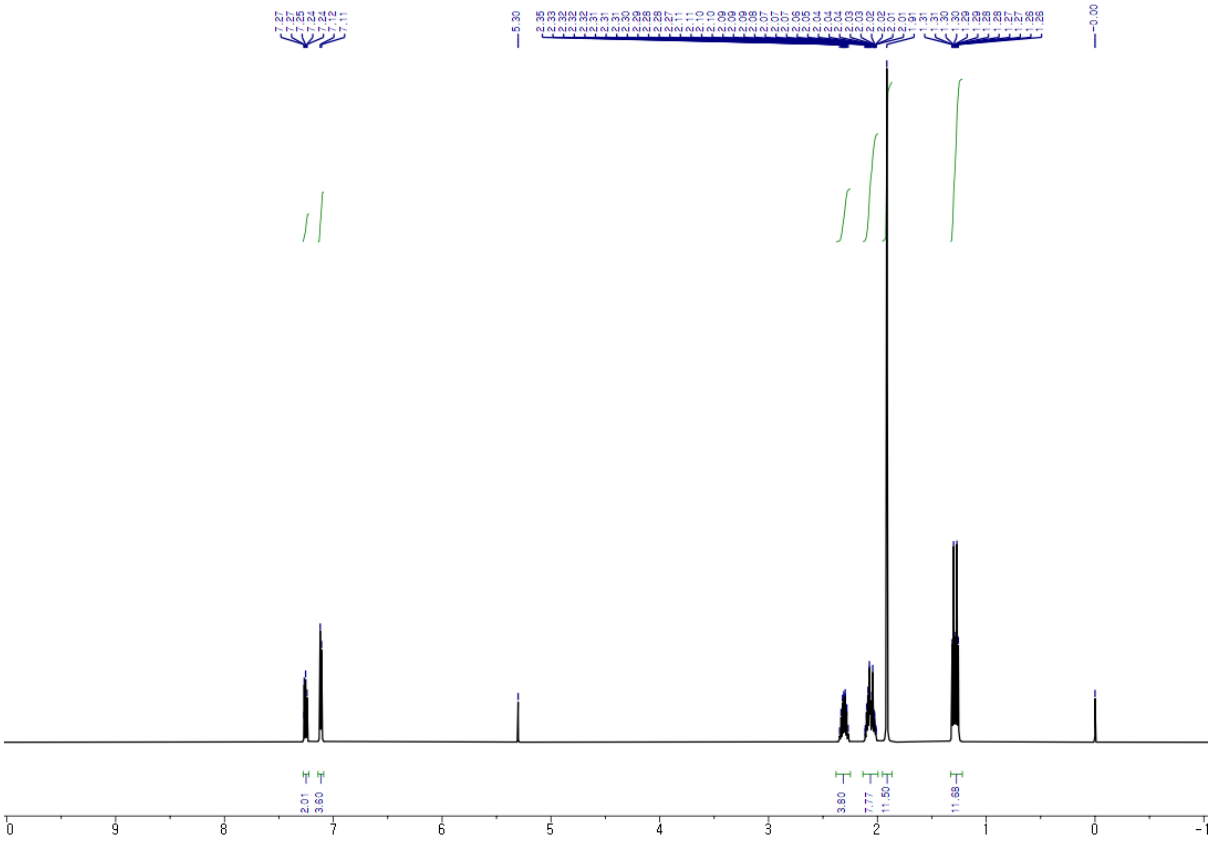

Figure S27. ^{1}H NMR spectrum of **10** (600 MHz, $CDCl_3$, 300 K)

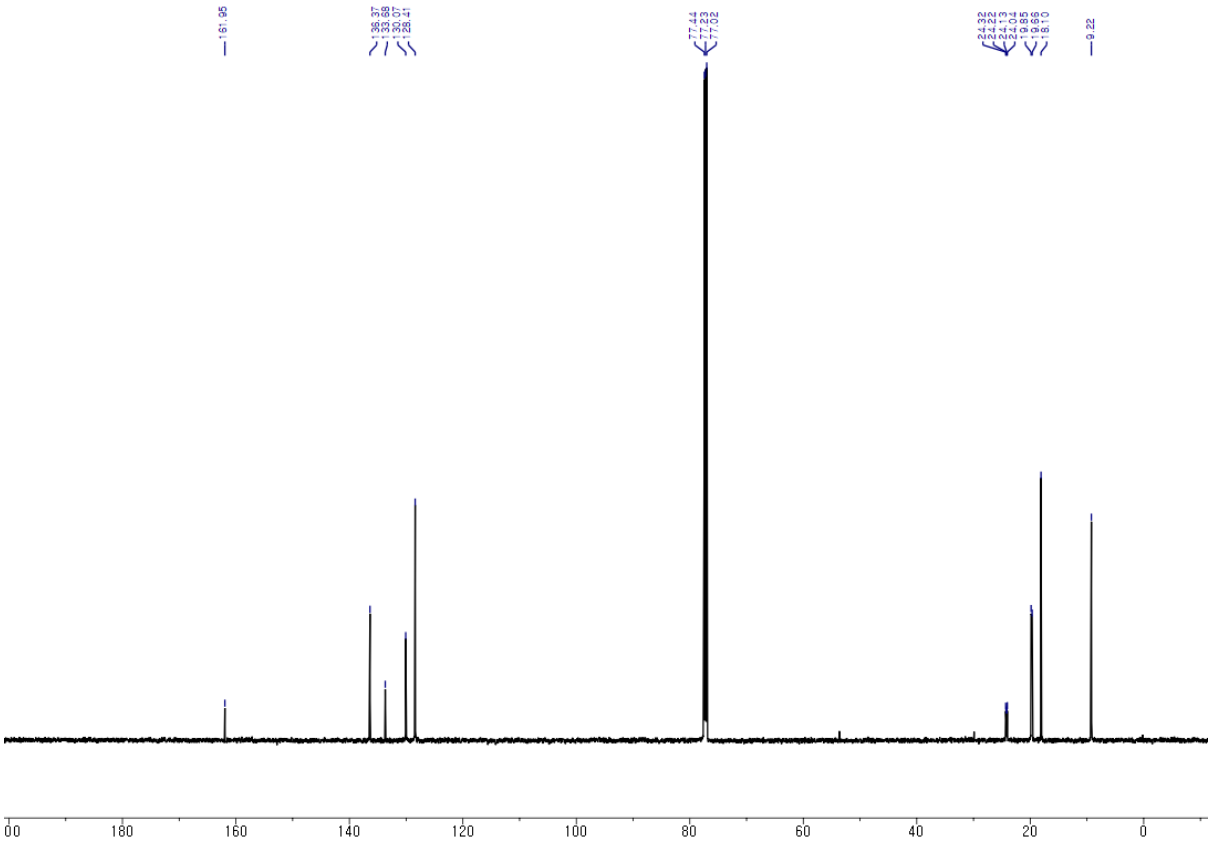

Figure S28. ^{13}C NMR spectrum of **10** (151 MHz, $CDCl_3$, 300 K)

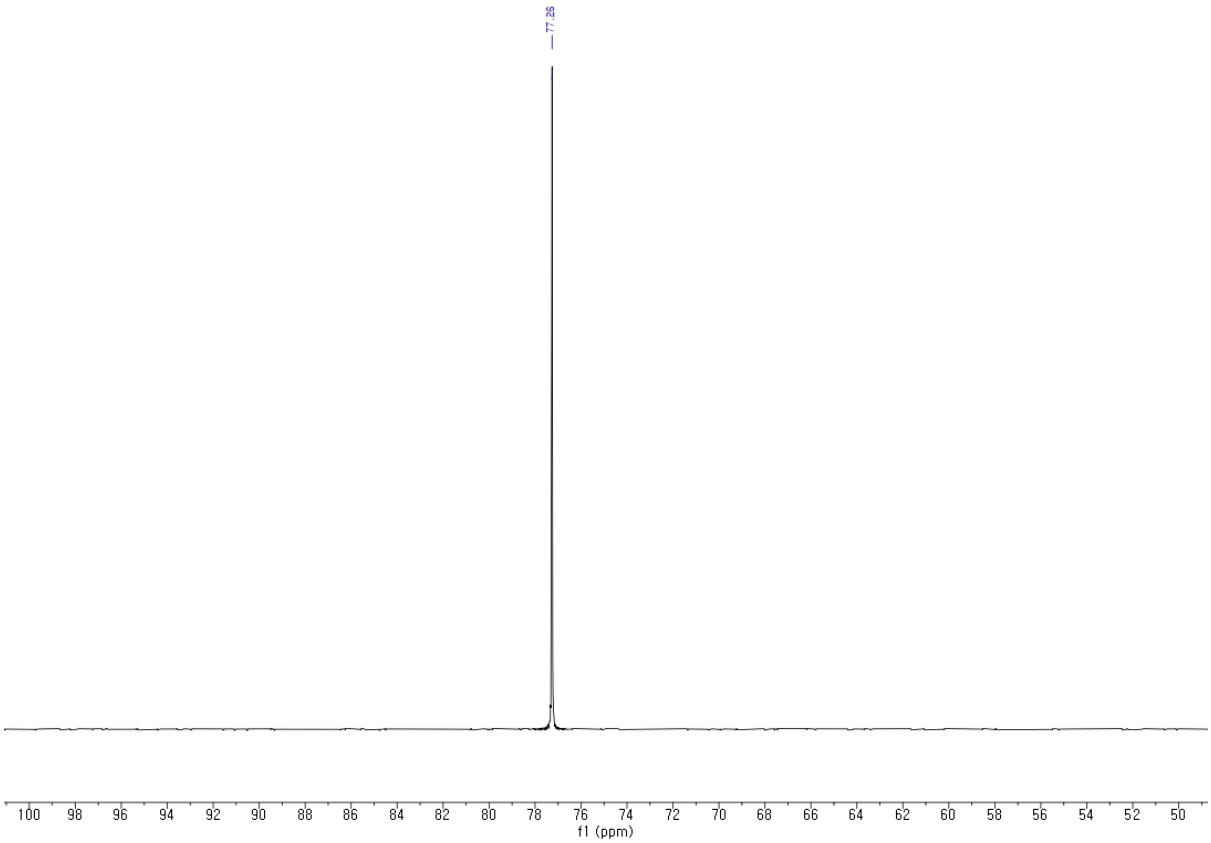

Figure S29. ^{31}P NMR spectrum of **10** (243 MHz, $CDCl_3$, 300 K)

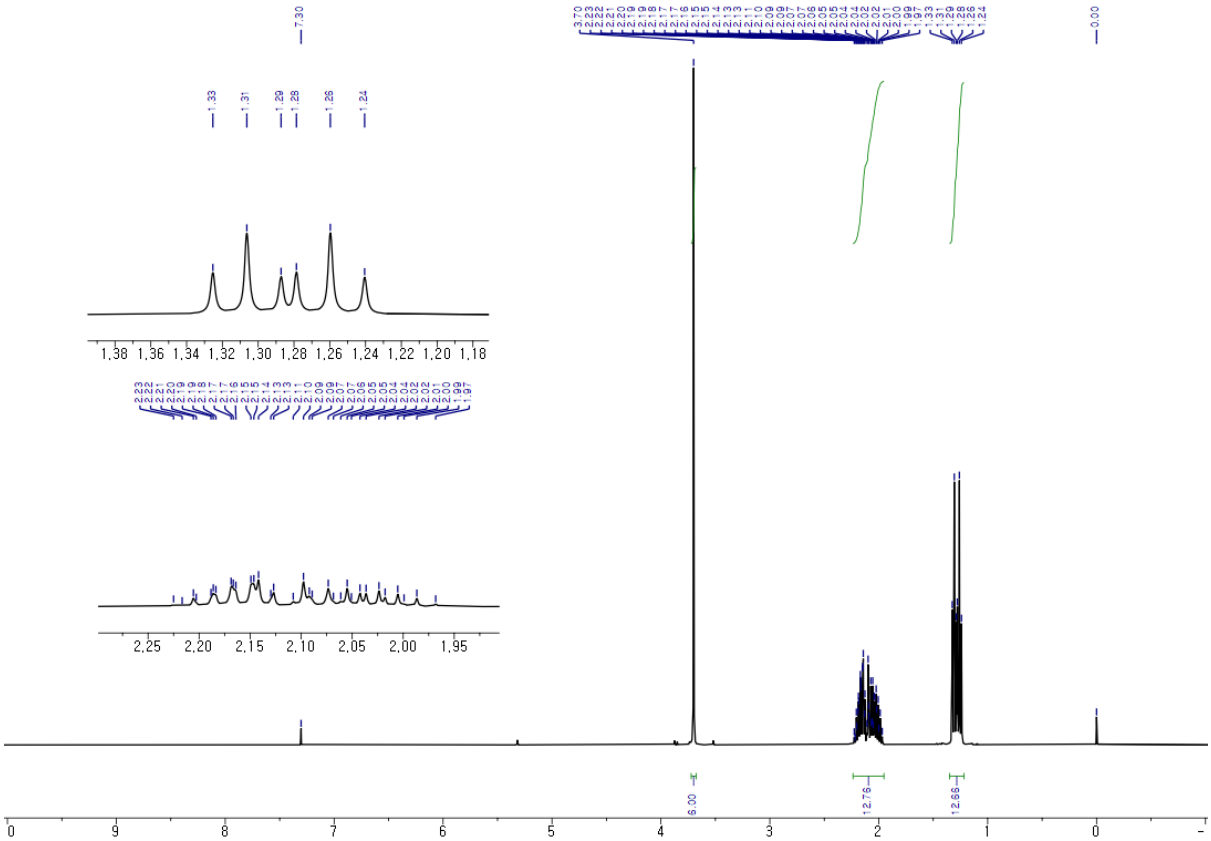

Figure S30. ^{1}H NMR spectrum of **11** (400 MHz, $CDCl_3$, 300 K)

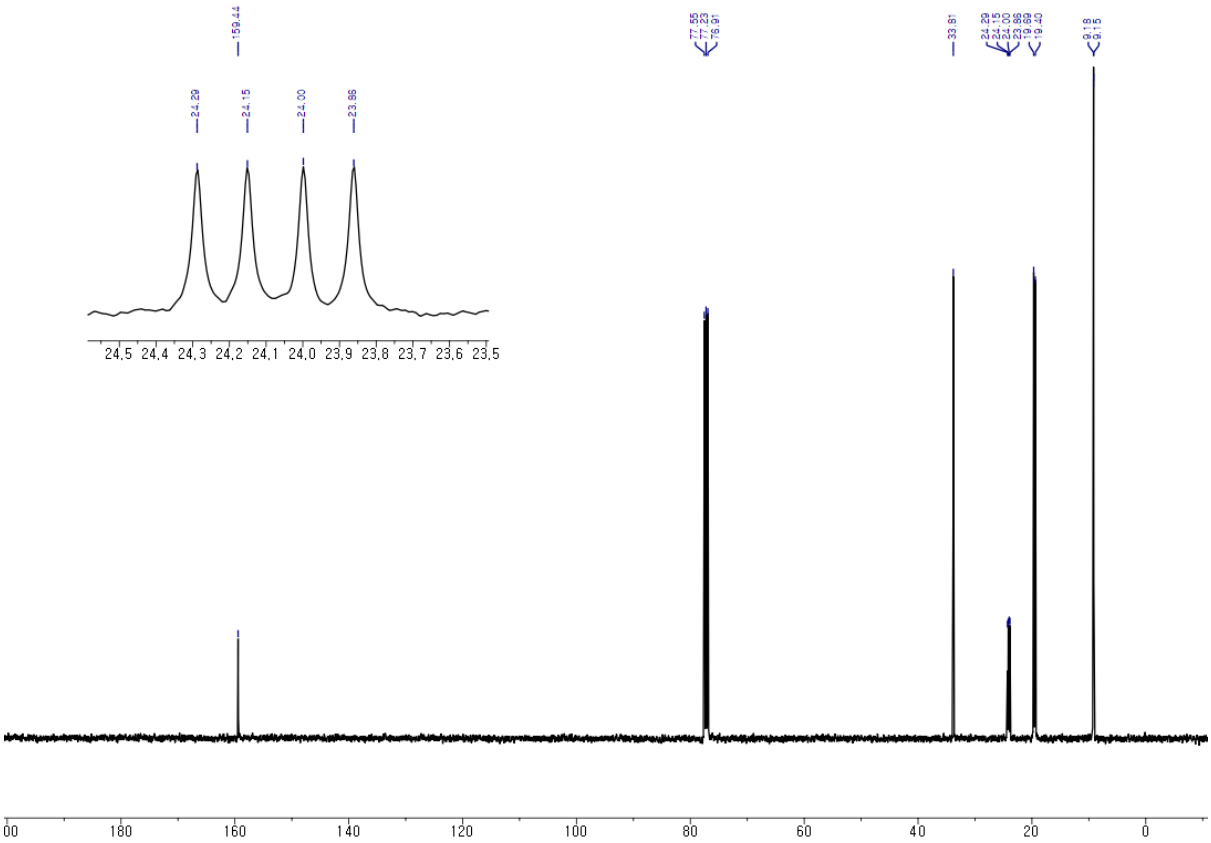

Figure S31. ^{13}C NMR spectrum of **11** (101 MHz, $CDCl_3$, 300 K)

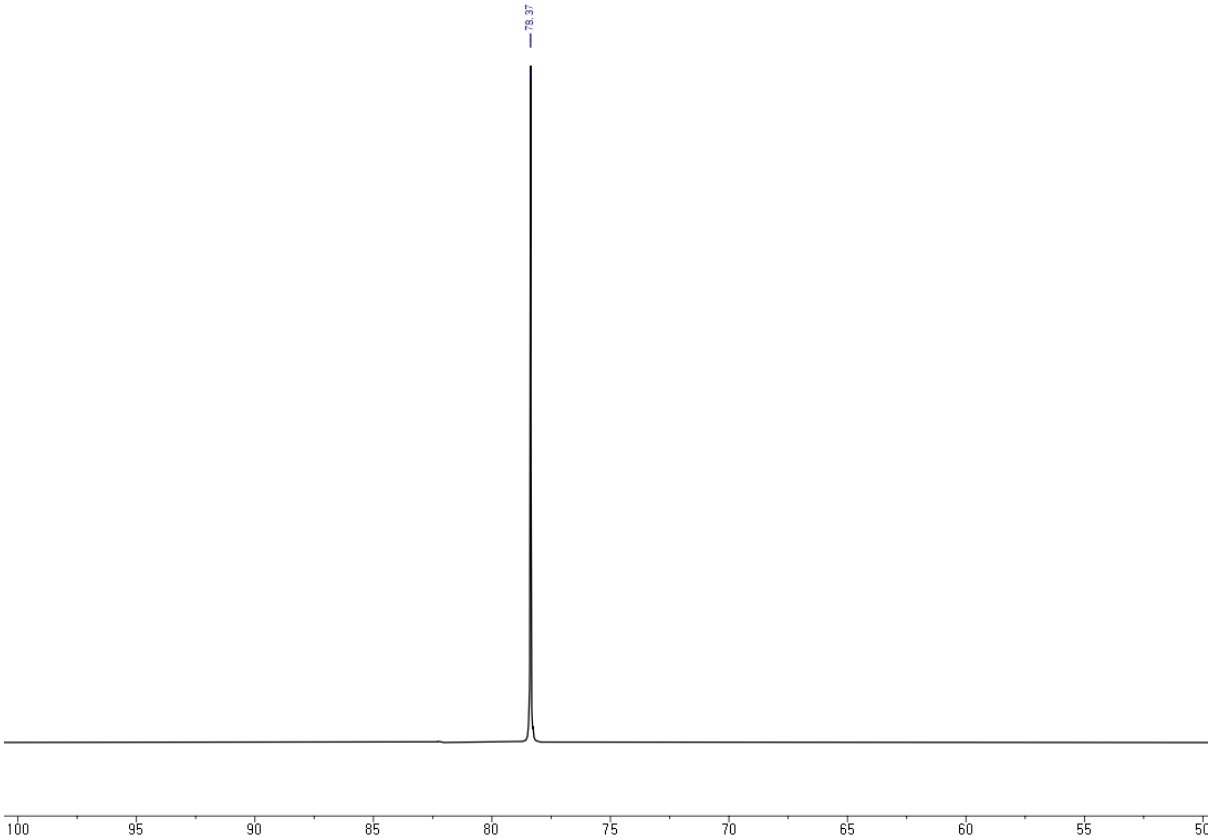

Figure S32. ^{31}P NMR spectrum of **11** (162 MHz, $CDCl_3$, 300 K)

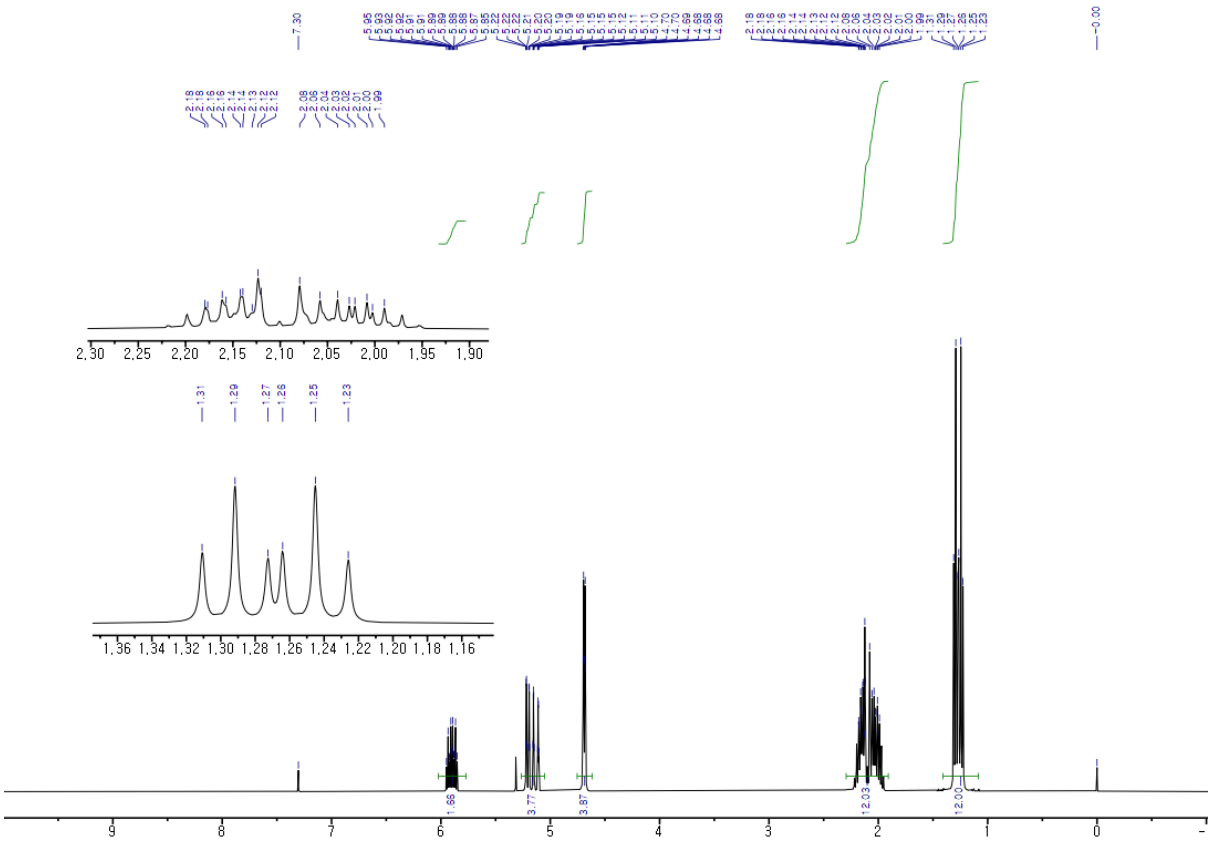

Figure S33. ^{1}H NMR spectrum of **12** (400 MHz, $CDCl_3$, 300 K)

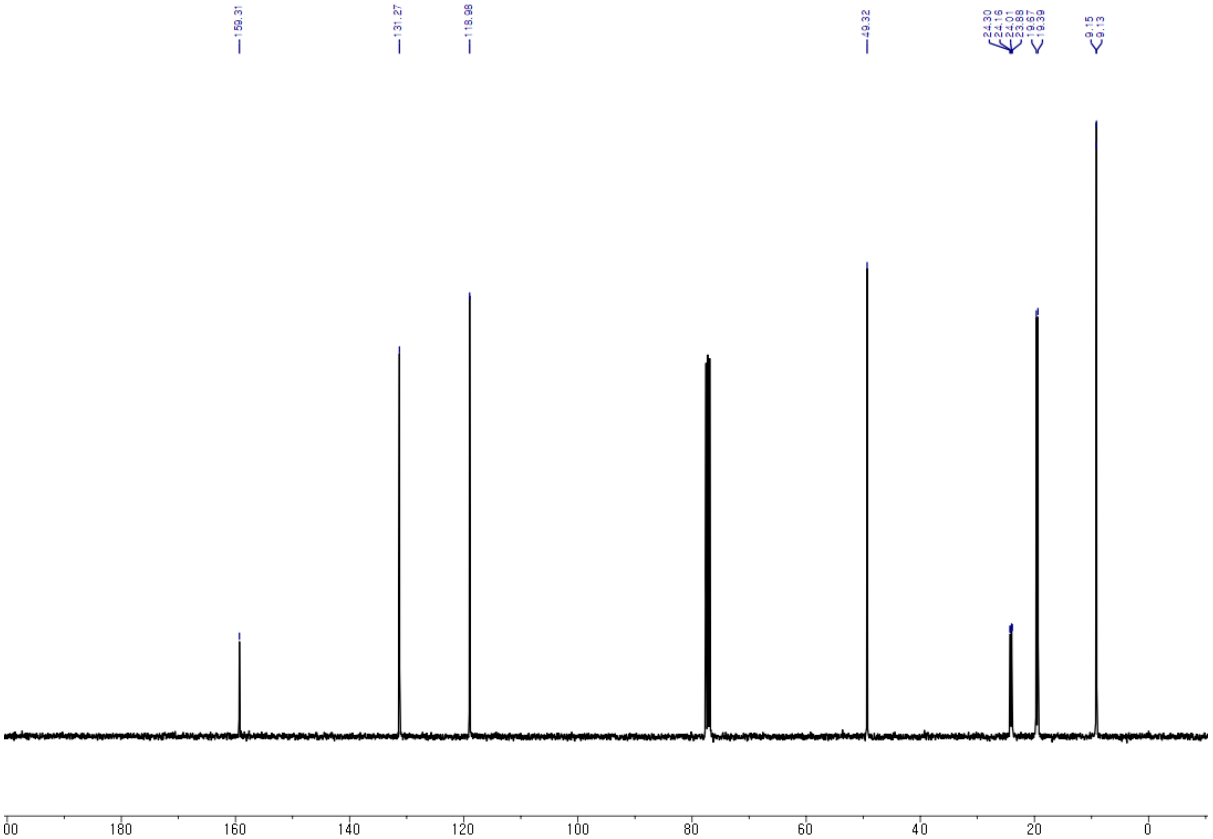

Figure S34. ^{13}C NMR spectrum of **12** (101 MHz, $CDCl_3$, 300 K)

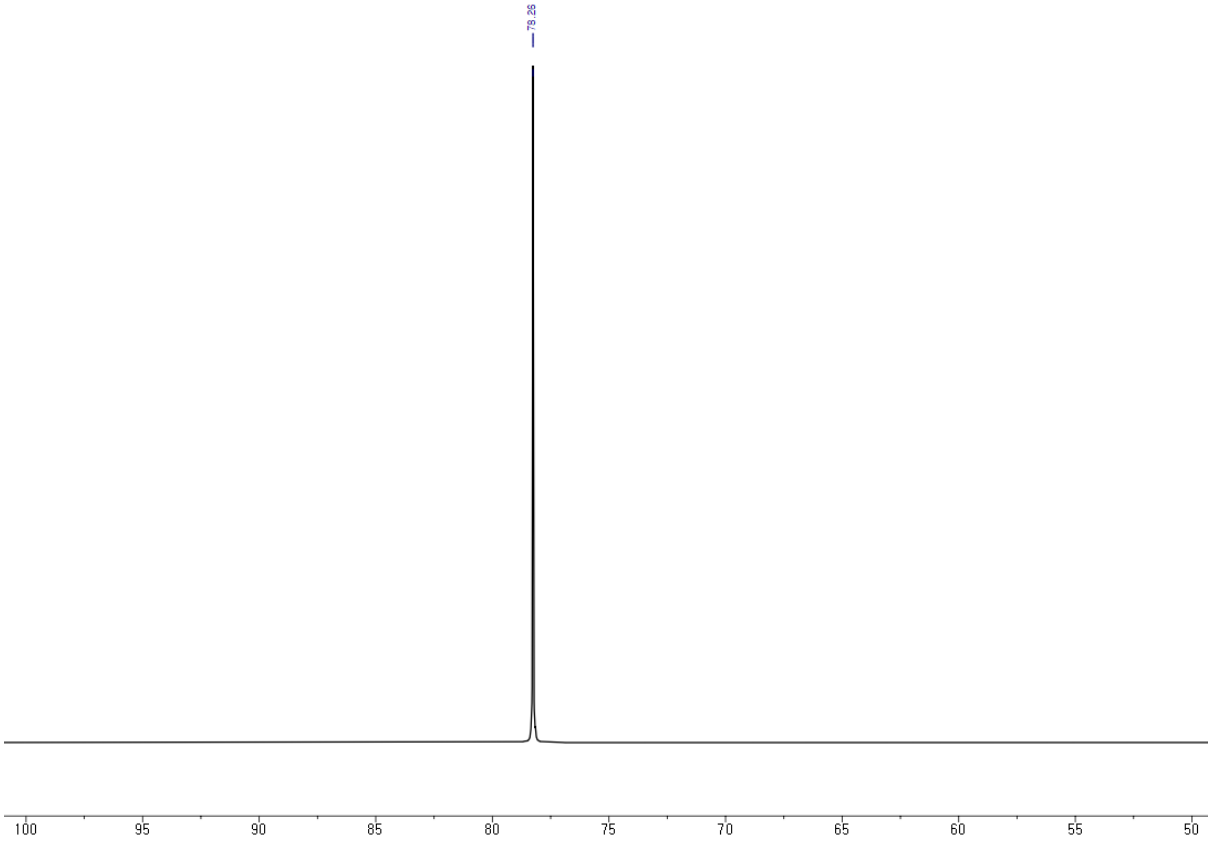

Figure S35. ^{31}P NMR spectrum of **12** (162 MHz, $CDCl_3$, 300 K)

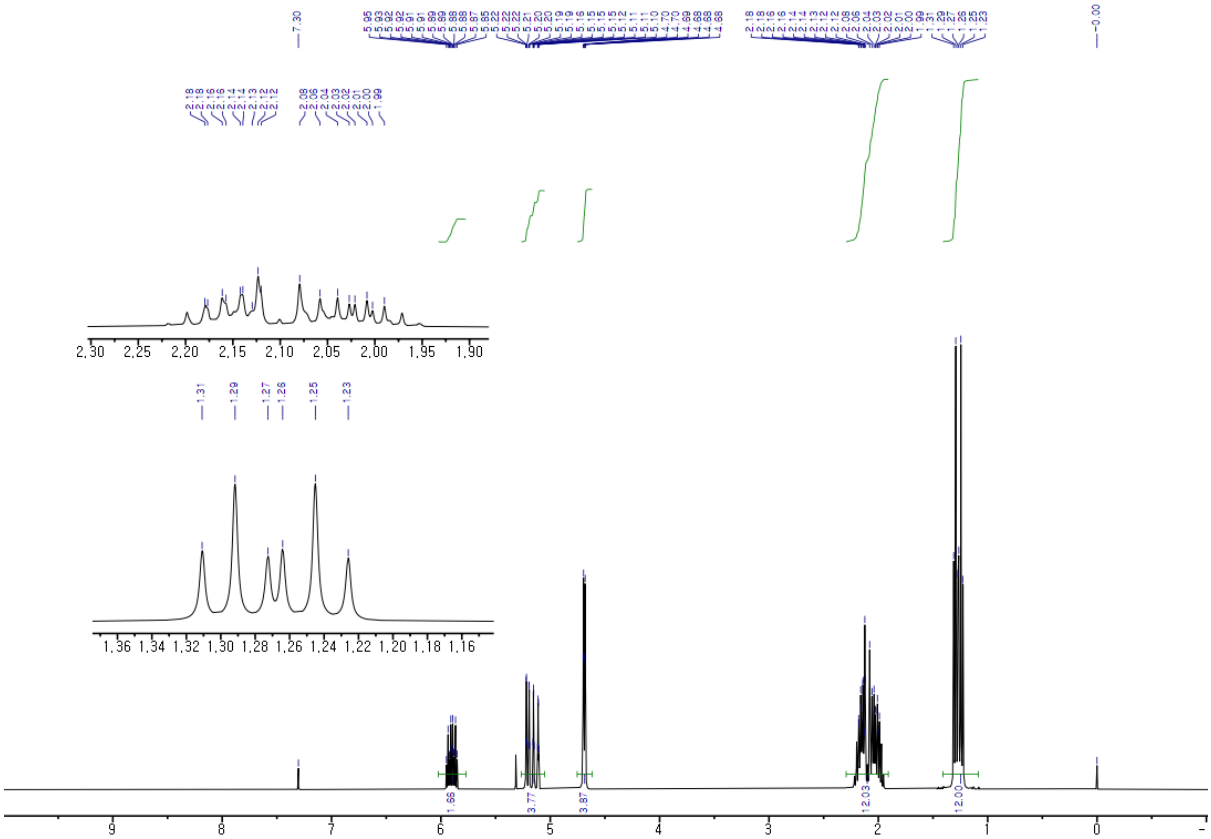

Figure S36. ^{1}H NMR spectrum of **13** (600 MHz, $CDCl_3$, 300 K)

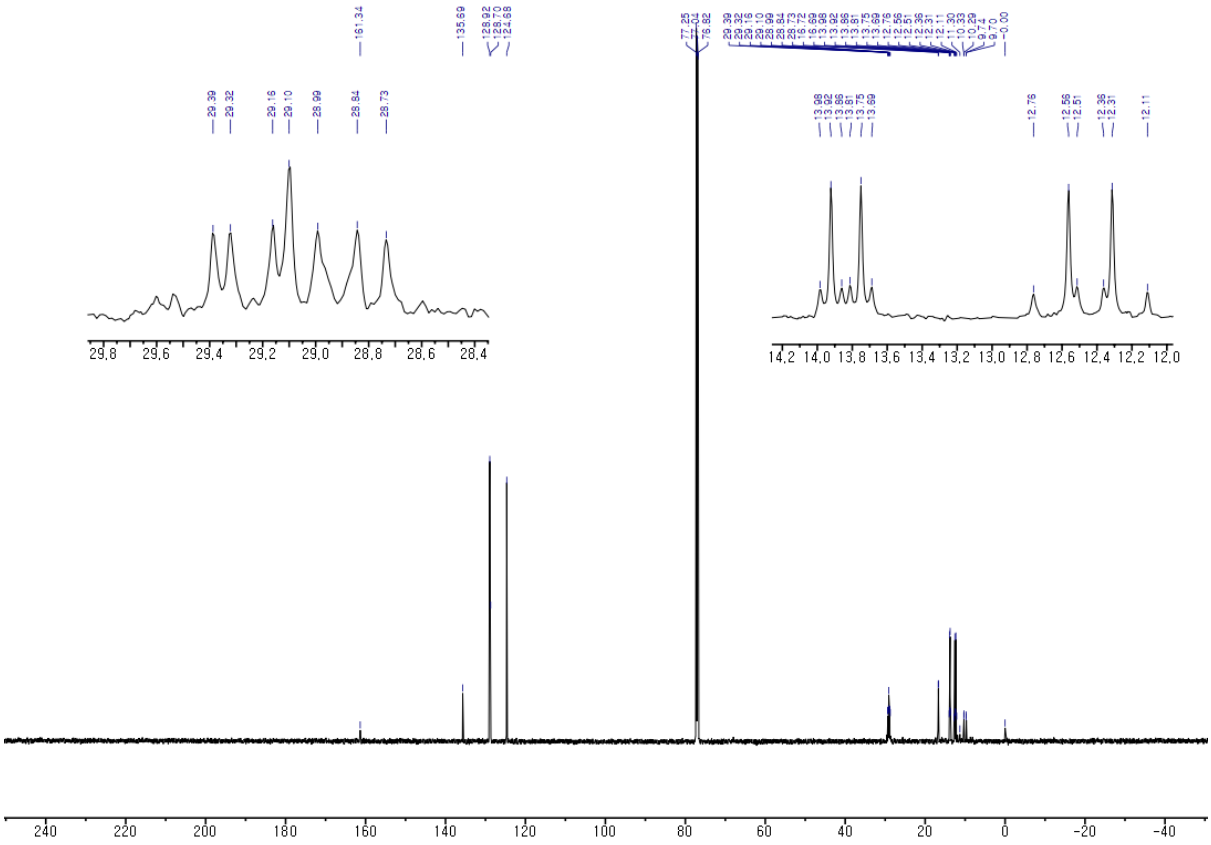

Figure S37. ^{13}C NMR spectrum of **13** (151 MHz, $CDCl_3$, 300 K)

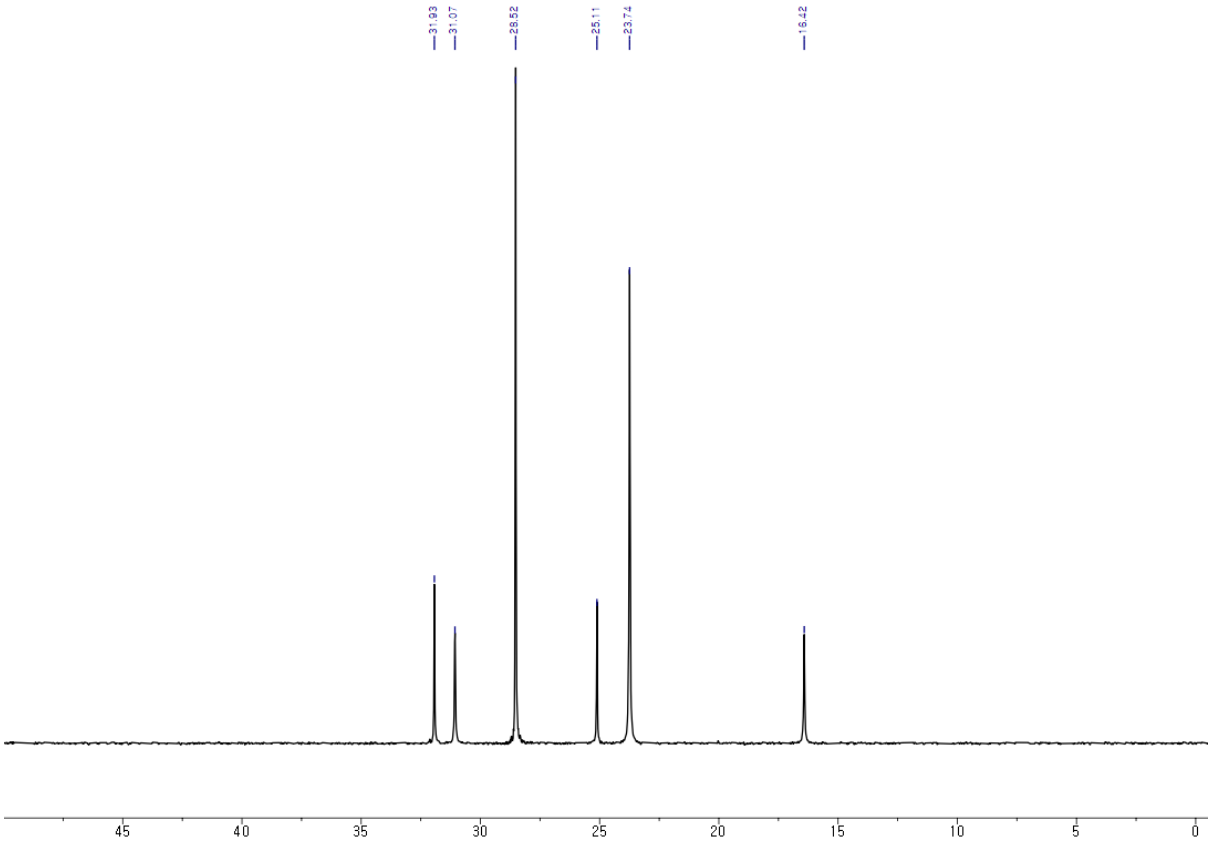

Figure S38. ^{31}P NMR spectrum of **13** (243 MHz, $CDCl_3$, 300 K)

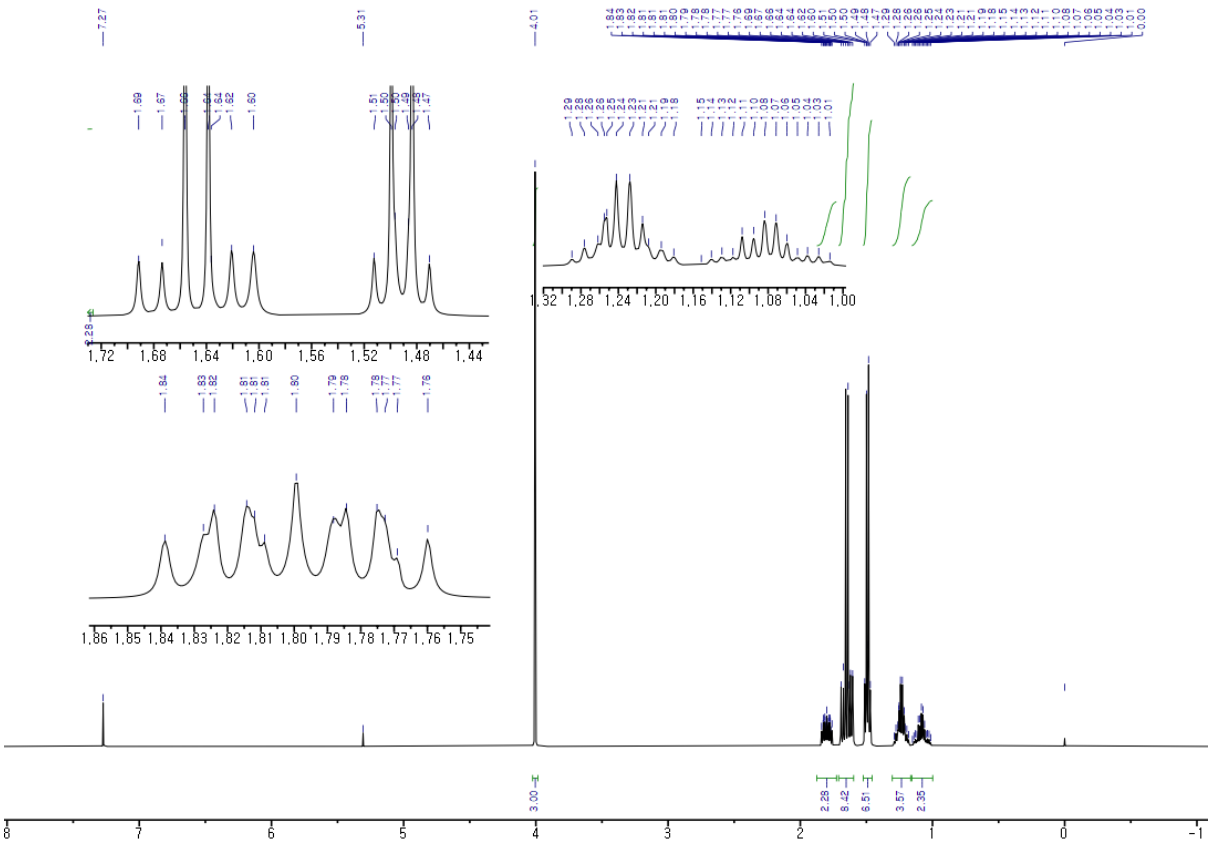

Figure S39. ^{1}H NMR spectrum of **14** (600 MHz, $CDCl_3$, 300 K)

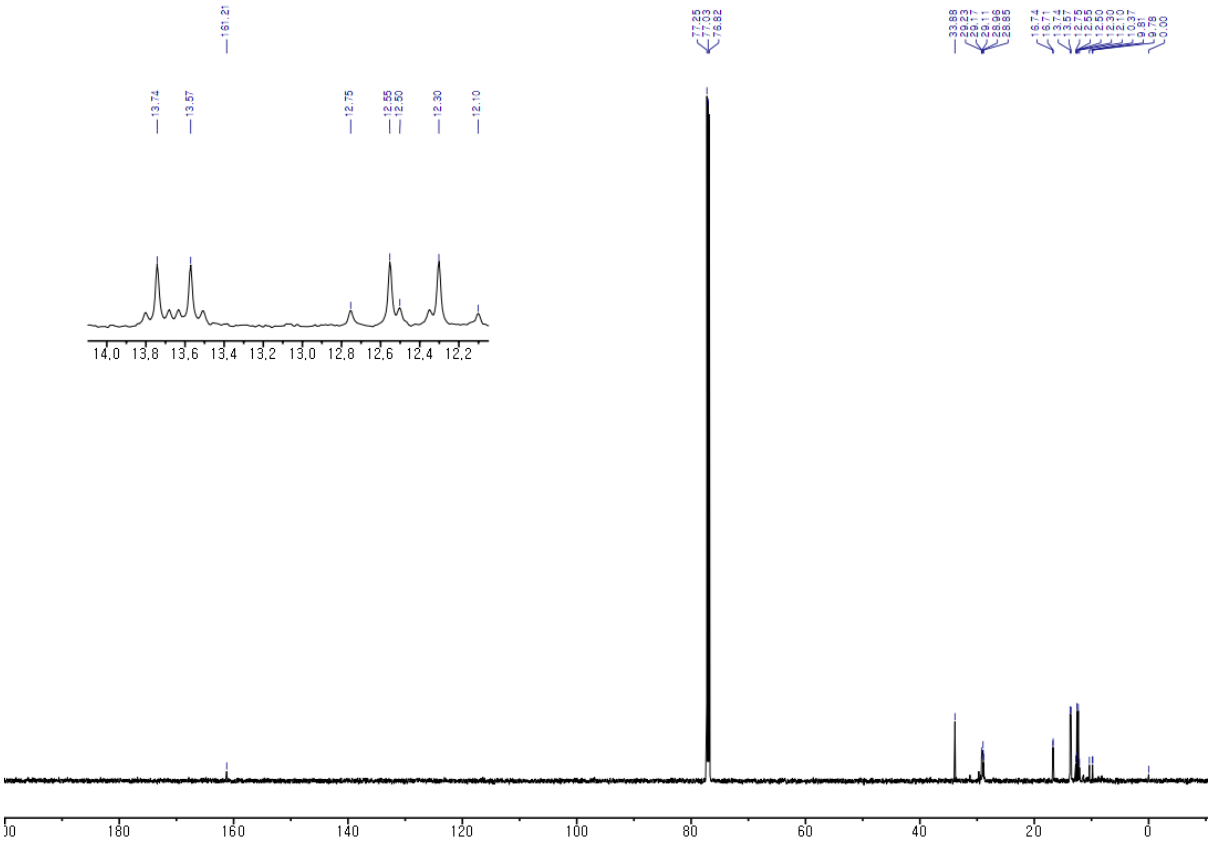

Figure S40. ^{13}C NMR spectrum of **14** (151 MHz, $CDCl_3$, 300 K)

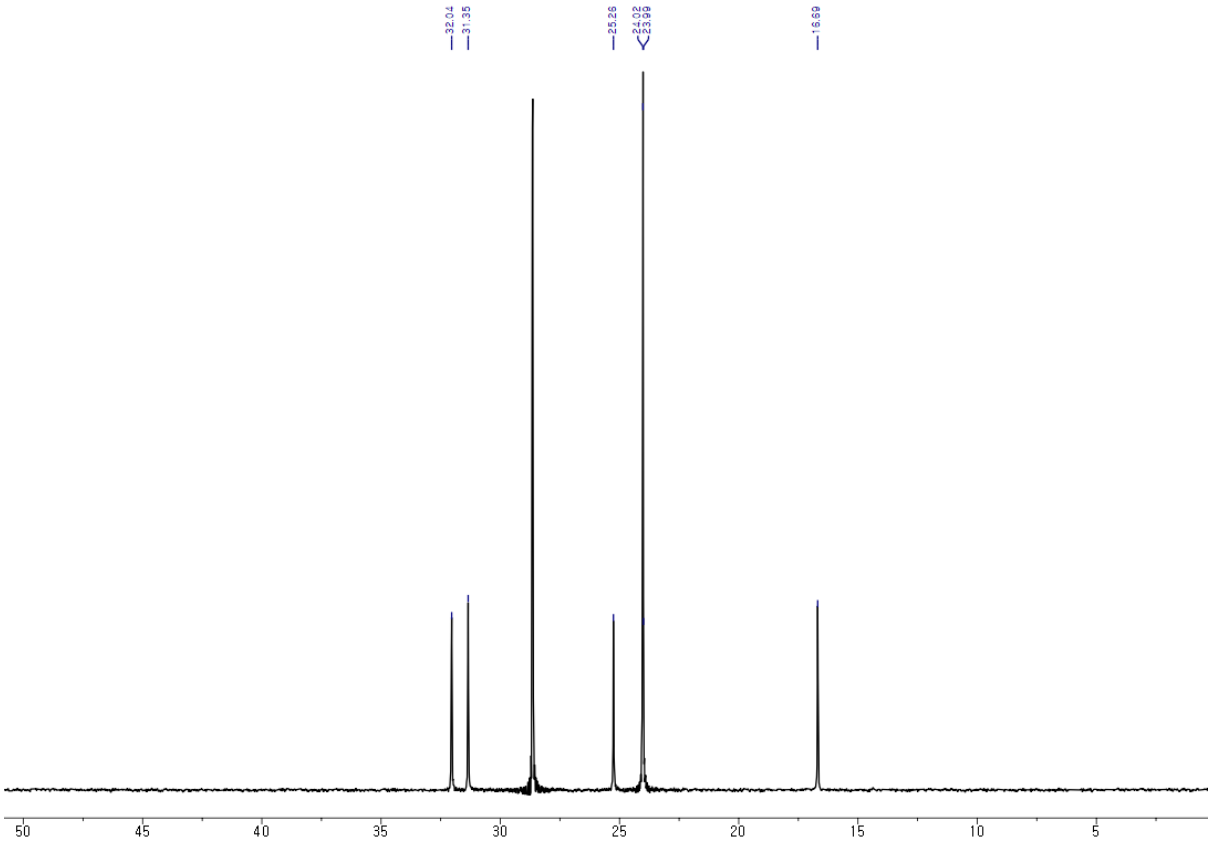

Figure S41. ^{31}P NMR spectrum of **14** (243 MHz, $CDCl_3$, 300 K)

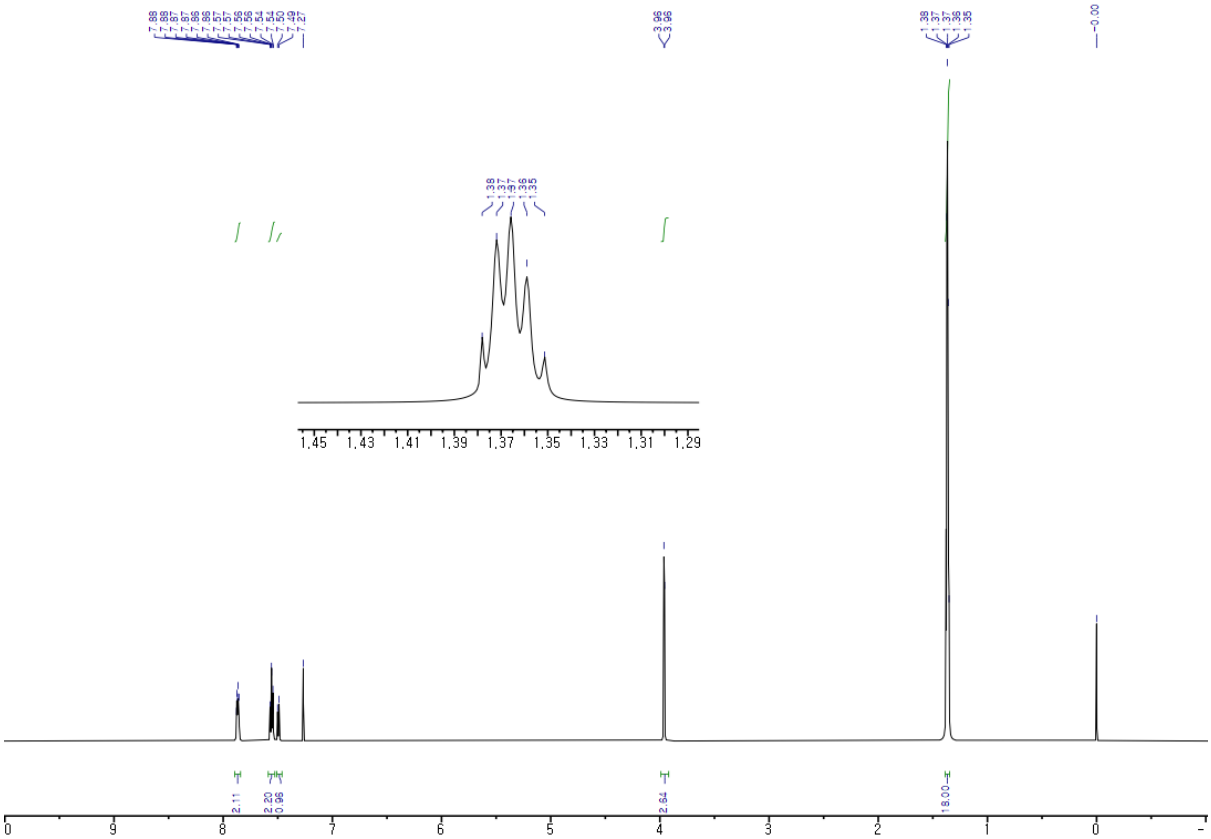

Figure S42. ^{1}H NMR spectrum of **15** (600 MHz, $CDCl_3$, 300 K)

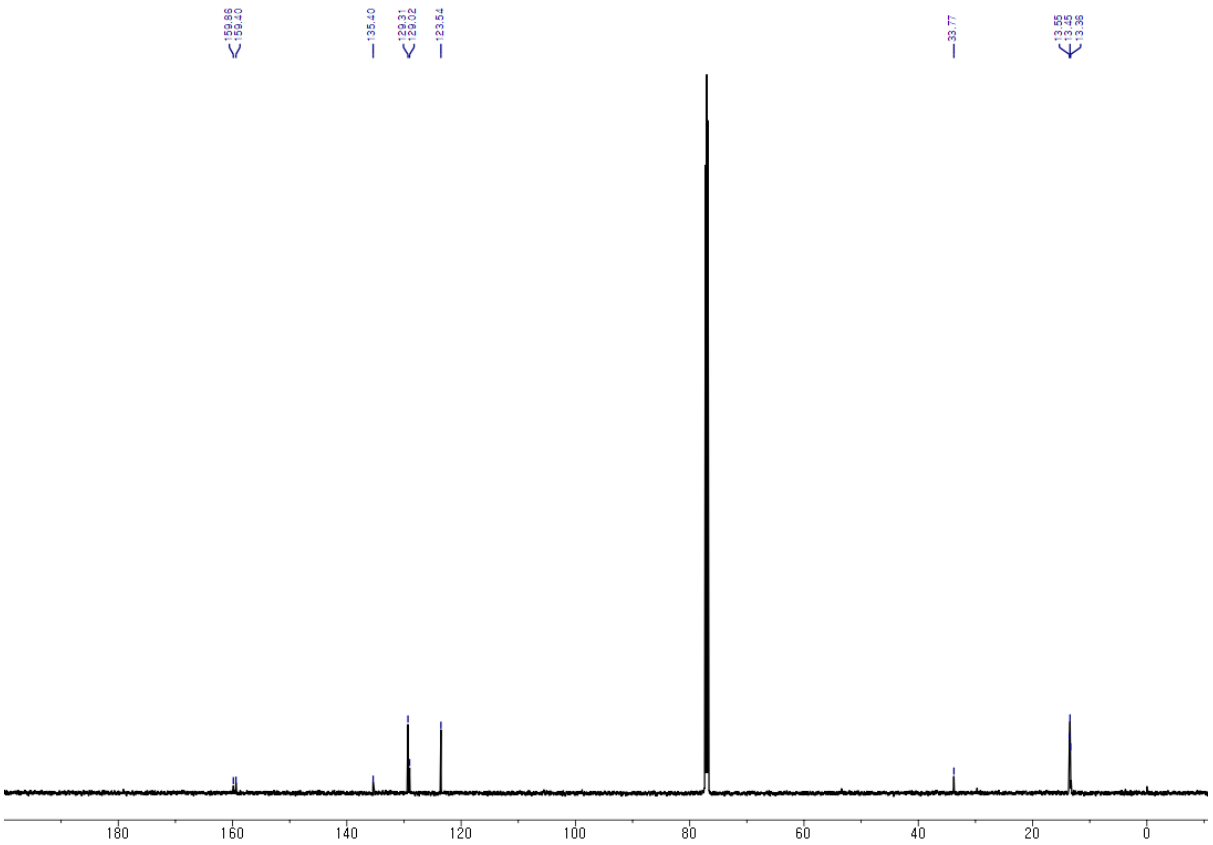

Figure S43. ^{13}C NMR spectrum of **15** (151 MHz, $CDCl_3$, 300 K)

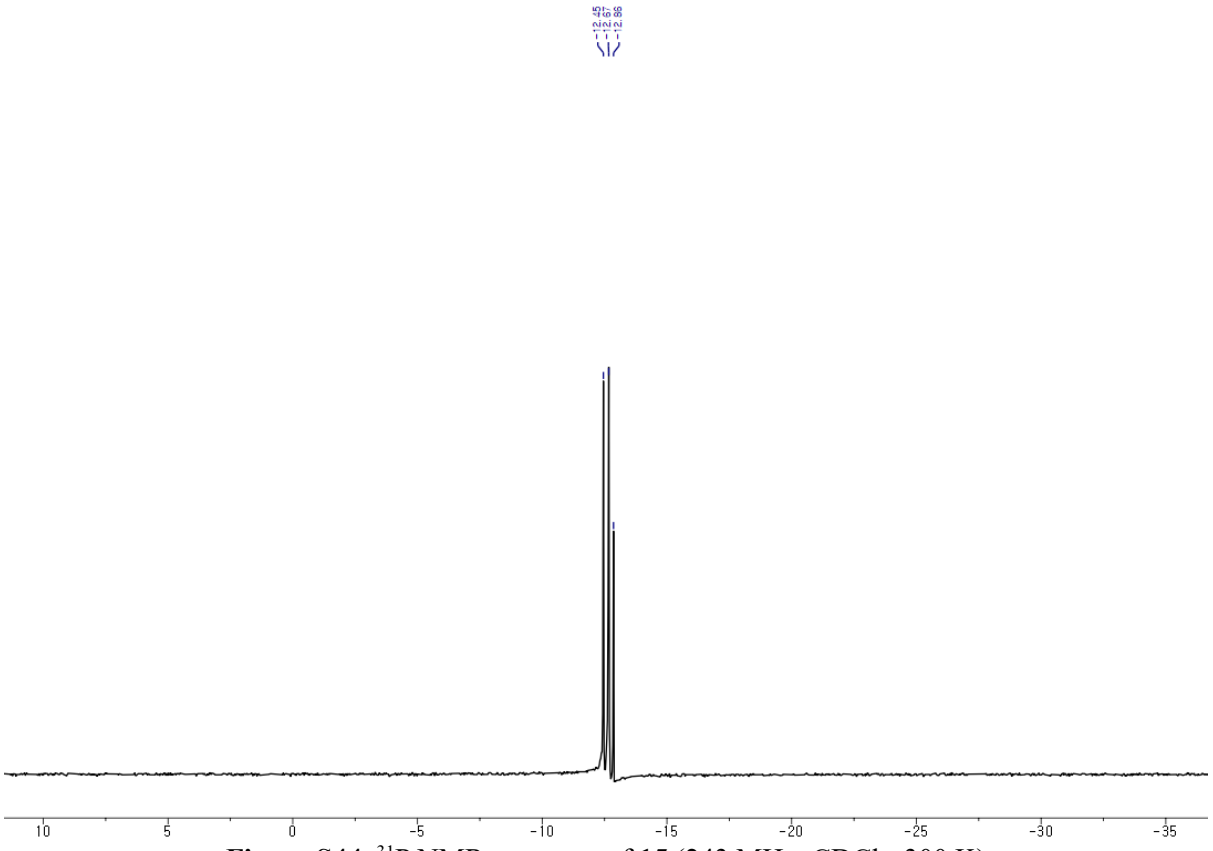

Figure S44. ^{31}P NMR spectrum of **15** (243 MHz, $CDCl_3$, 300 K)

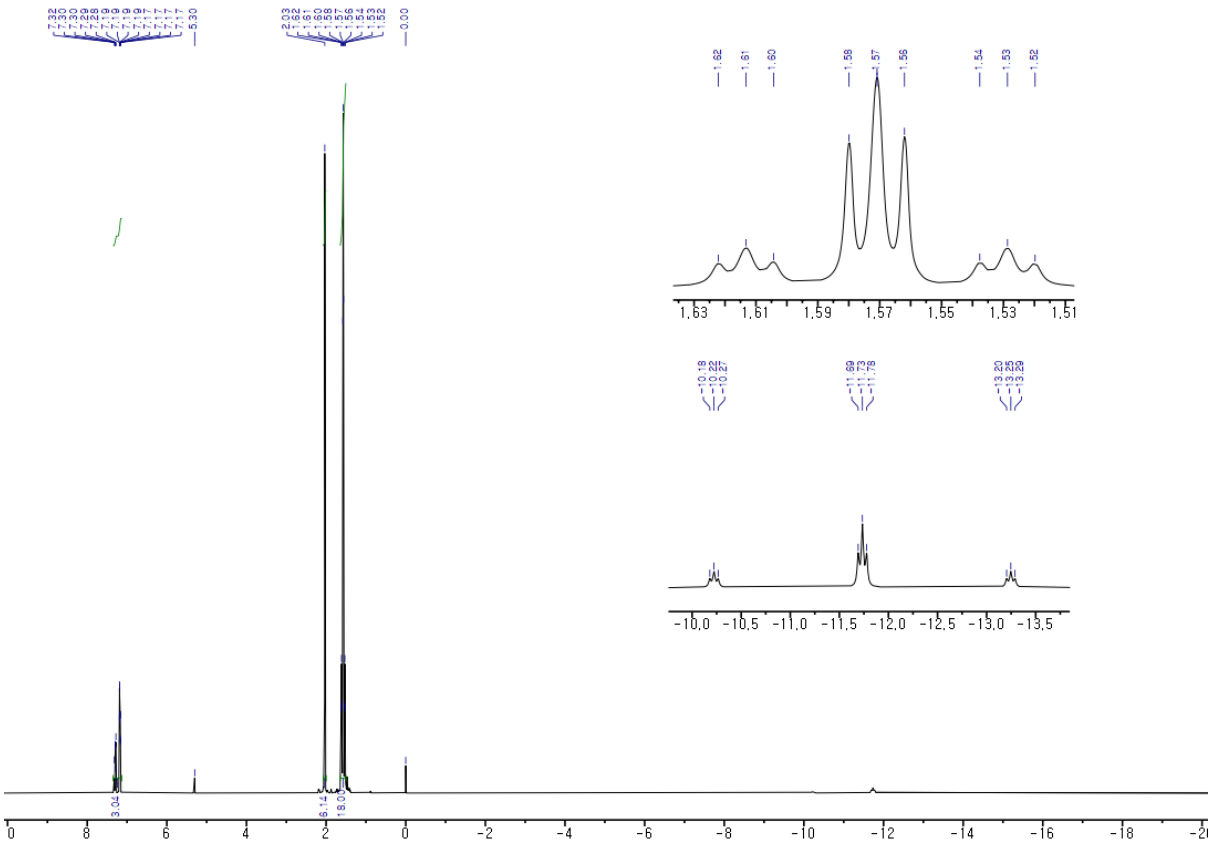

Figure S45. ^{1}H NMR spectrum of **16** (400 MHz, $CDCl_3$, 300 K)

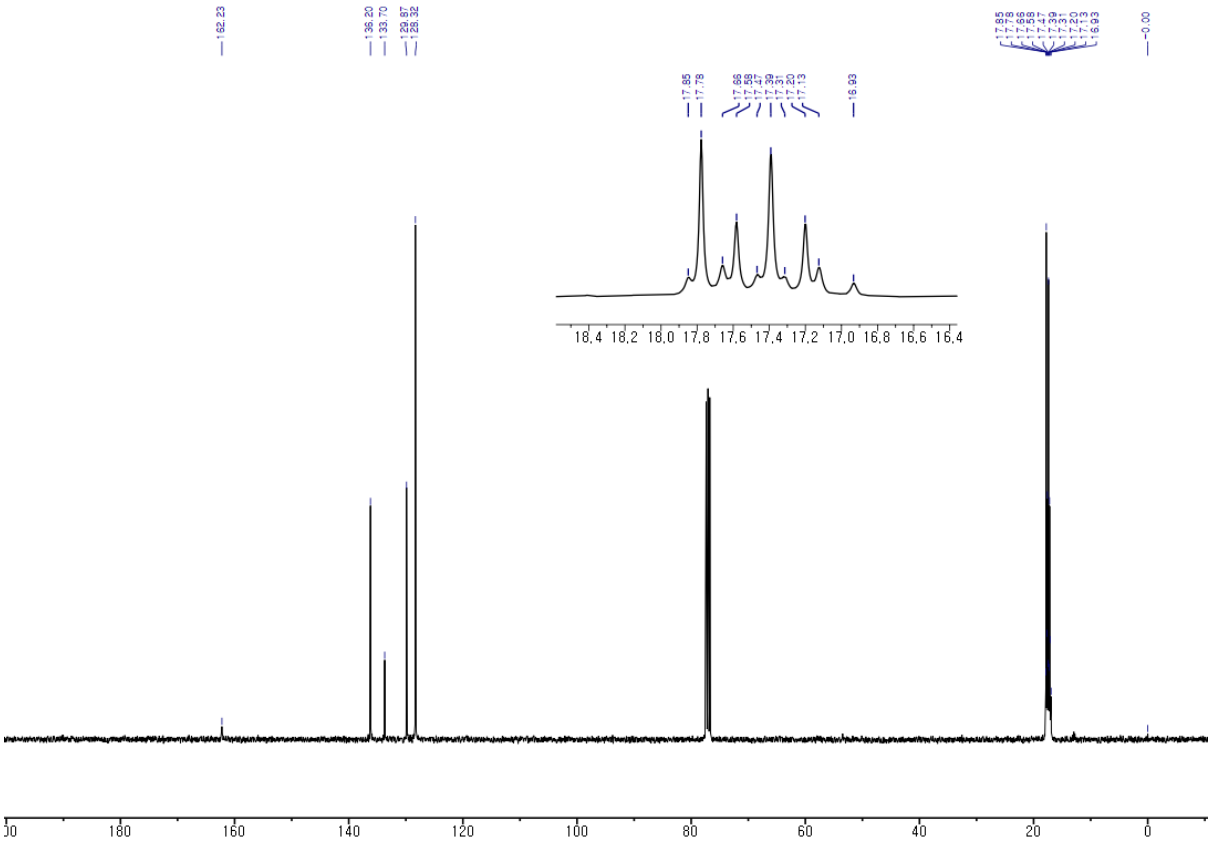

Figure S46. ^{1}H NMR spectrum of **16** (101 MHz, $CDCl_3$, 300 K)

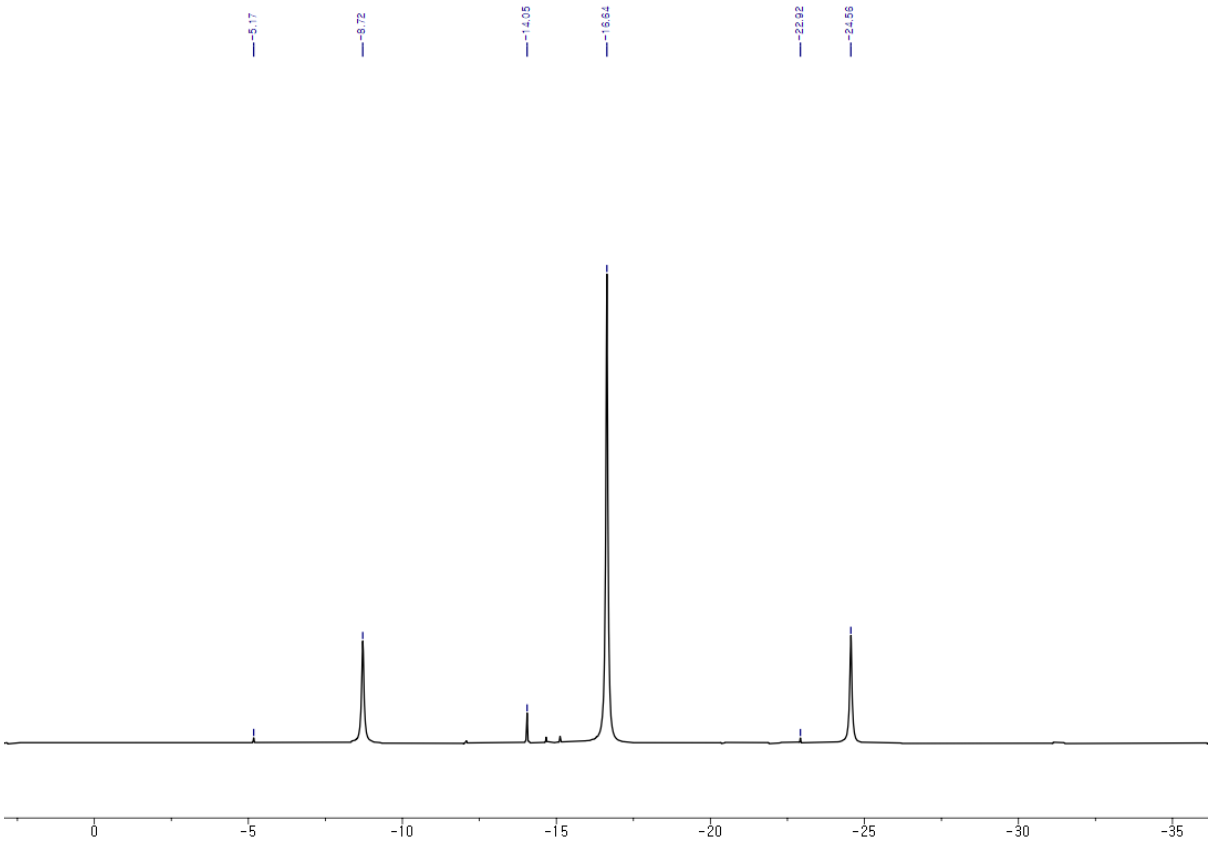

Figure S47. ^{31}P NMR spectrum of **16** (162 MHz, $CDCl_3$, 300 K)

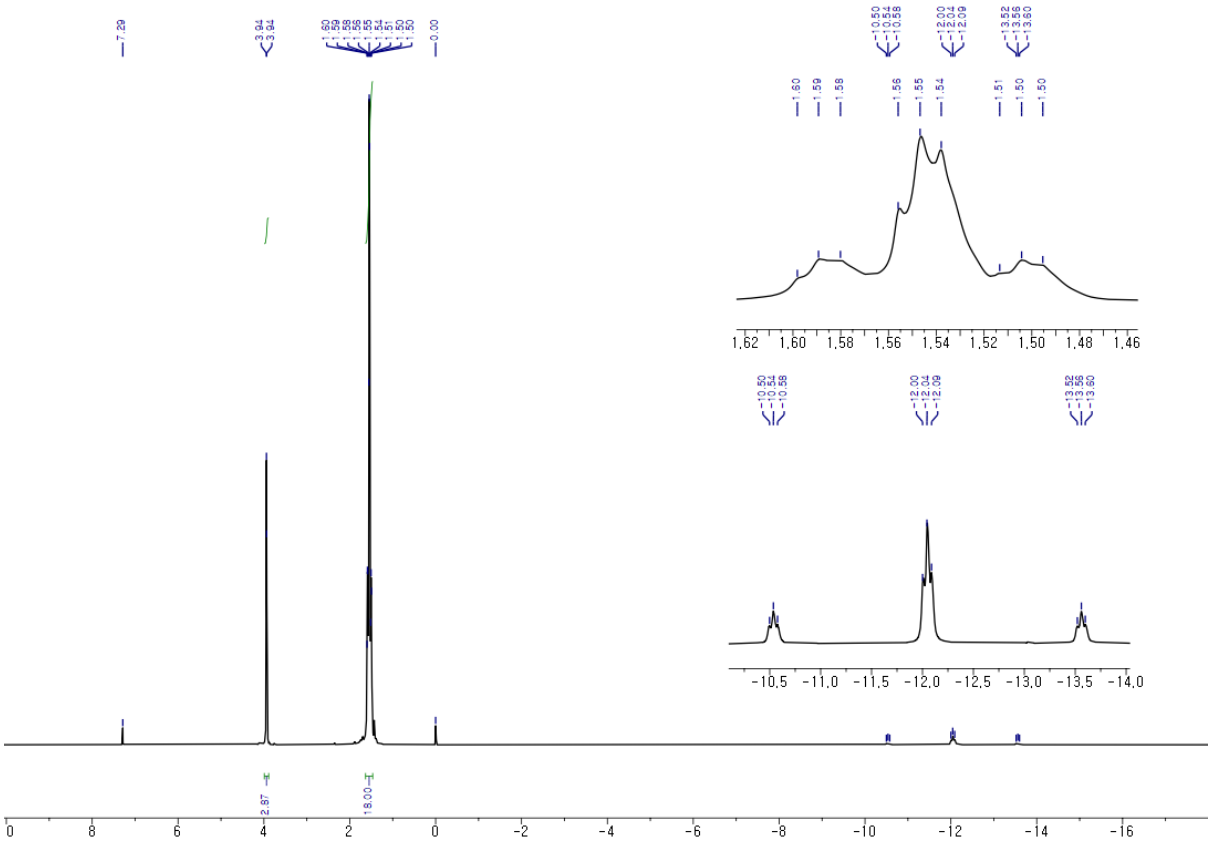

Figure S48. ^{1}H NMR spectrum of **17** (400 MHz, $CDCl_3$, 300 K)

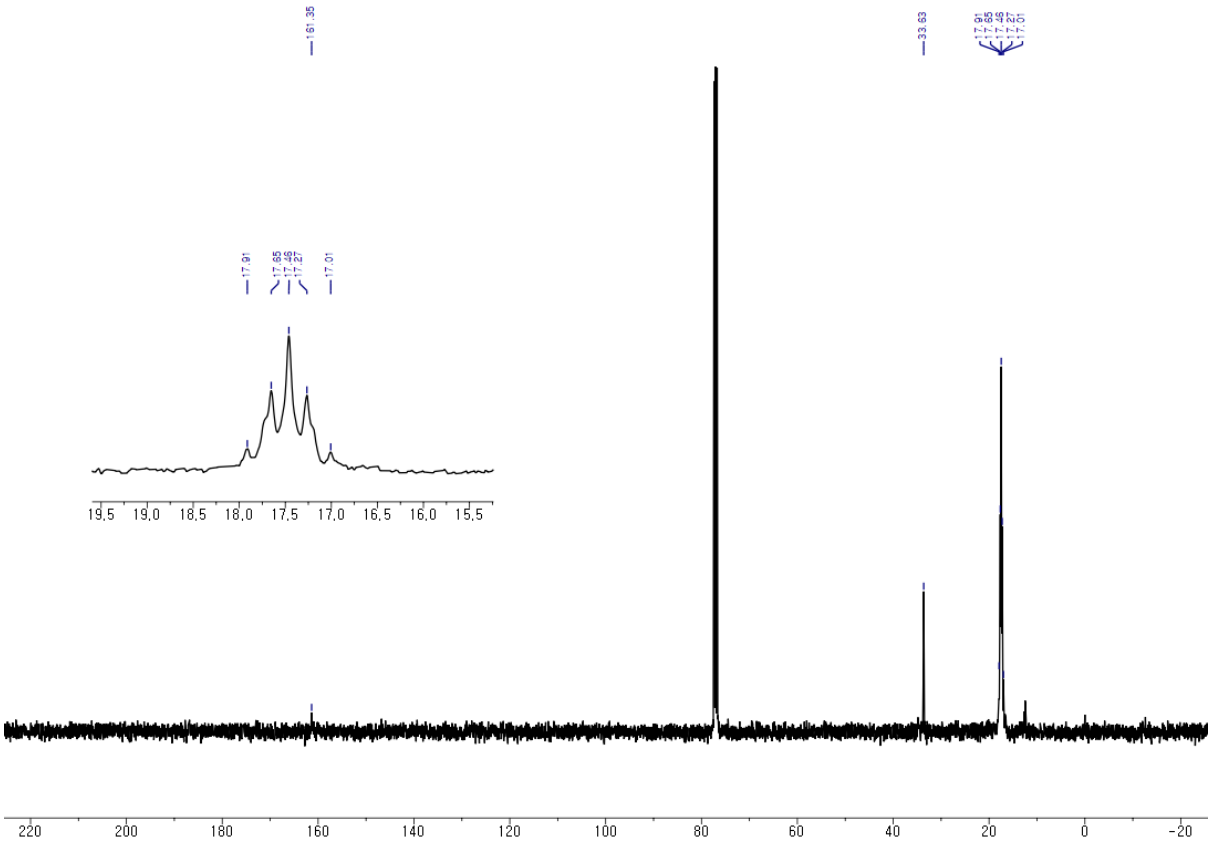

Figure S49. ^{13}C NMR spectrum of **17** (101 MHz, $CDCl_3$, 300 K)

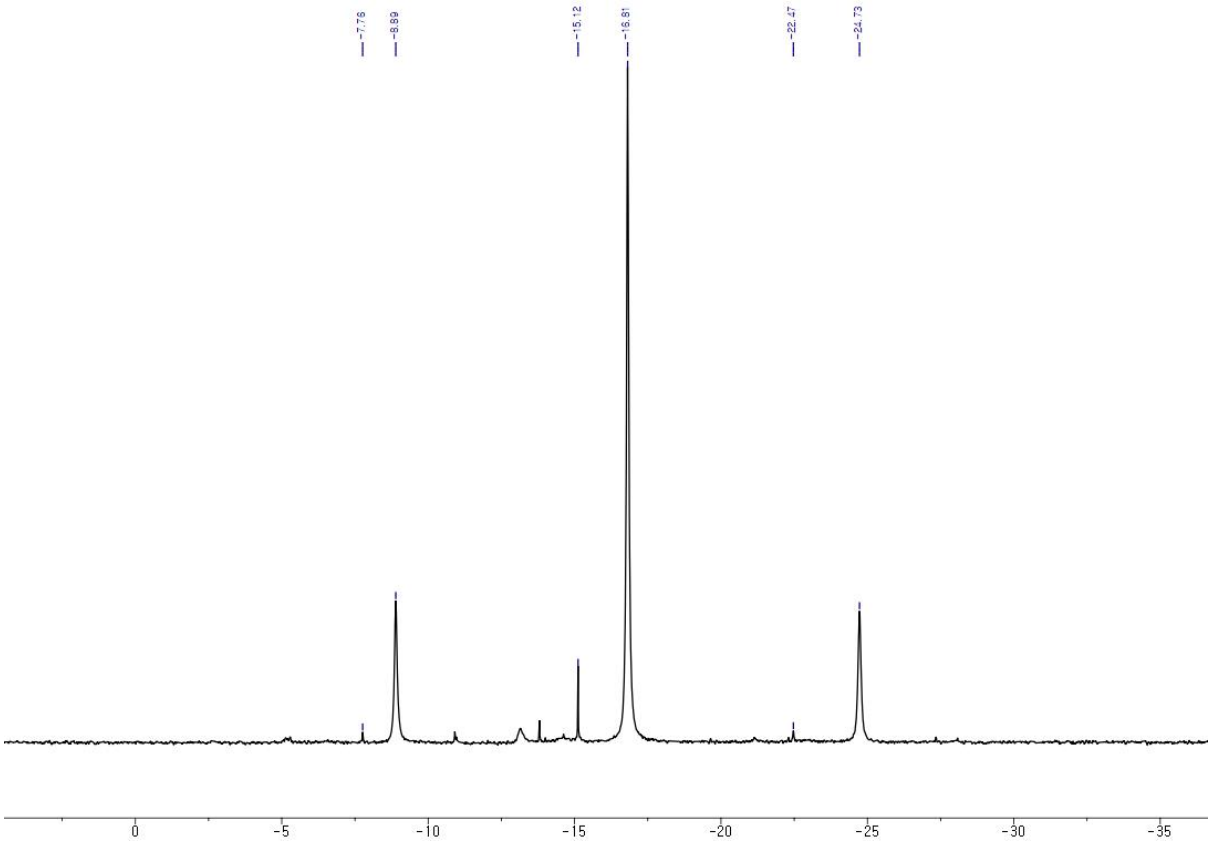

Figure S50. ^{31}P NMR spectrum of **17** (162 MHz, $CDCl_3$, 300 K)

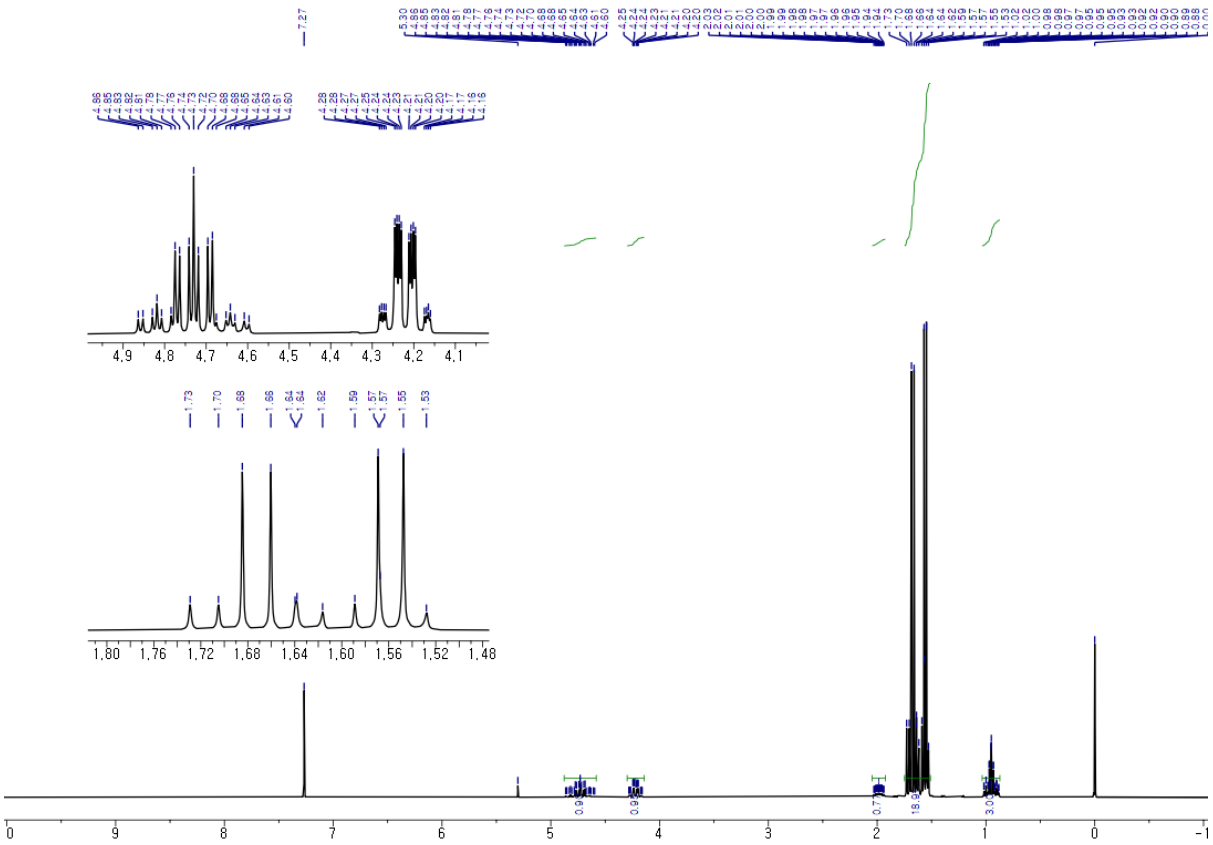

Figure S51. ^{1}H NMR spectrum of **18** (400 MHz, $CDCl_3$, 300 K)

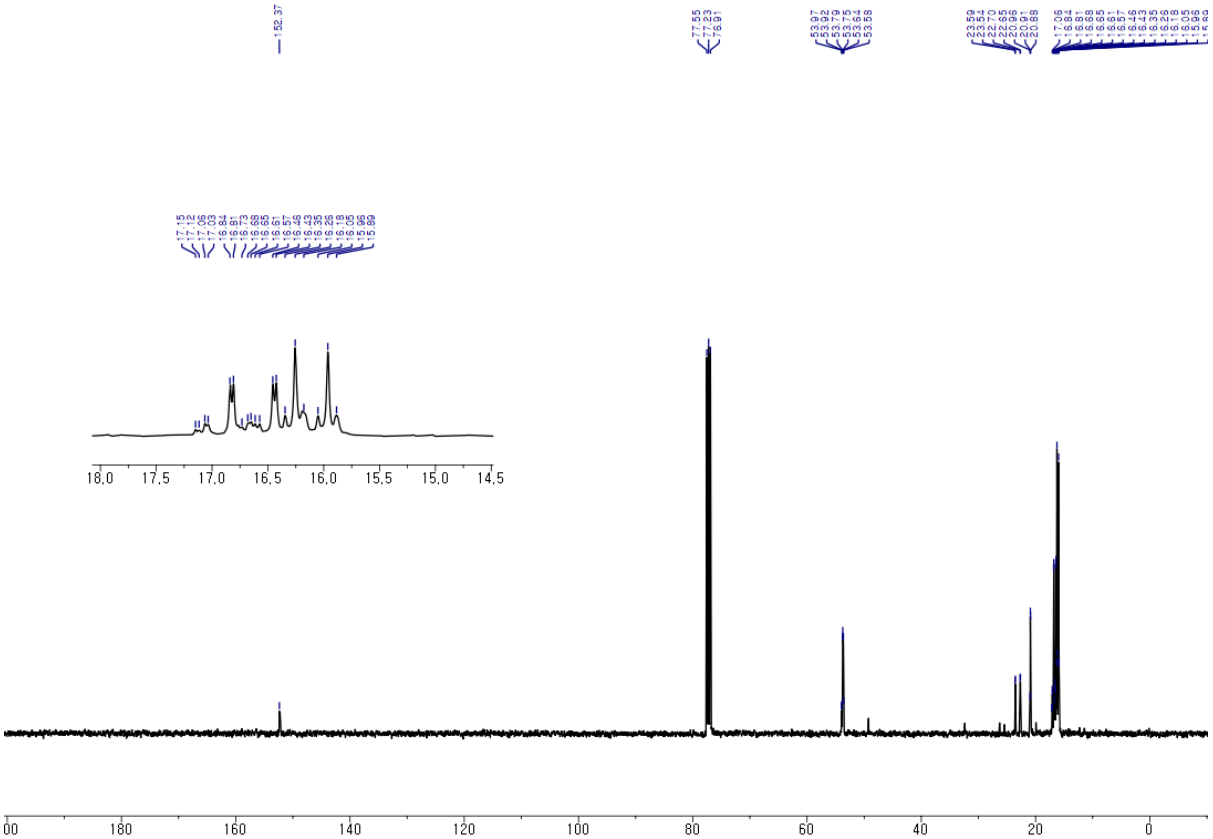

Figure S52. ^{13}C NMR spectrum of **18** (101 MHz, $CDCl_3$, 300 K)

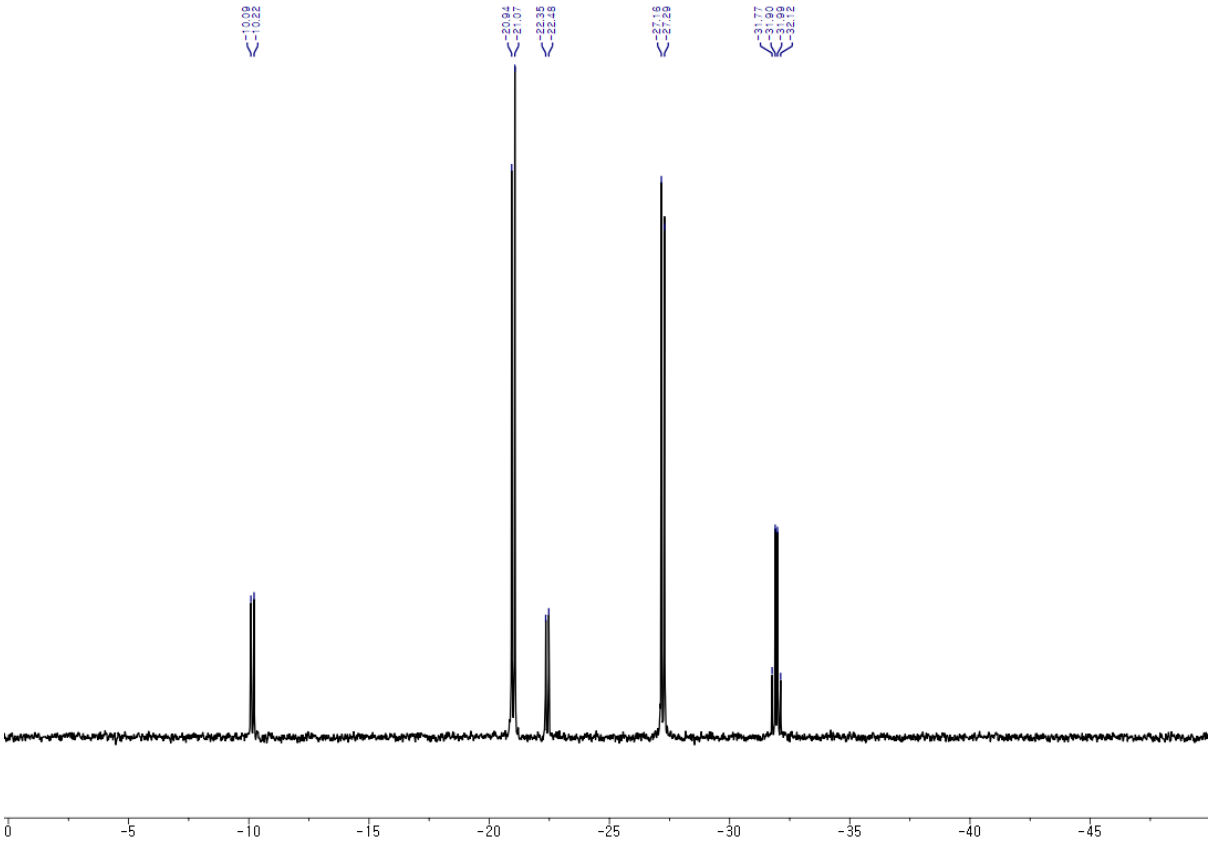

Figure S53. ^{31}P NMR spectrum of **18** (162 MHz, $CDCl_3$, 300 K)

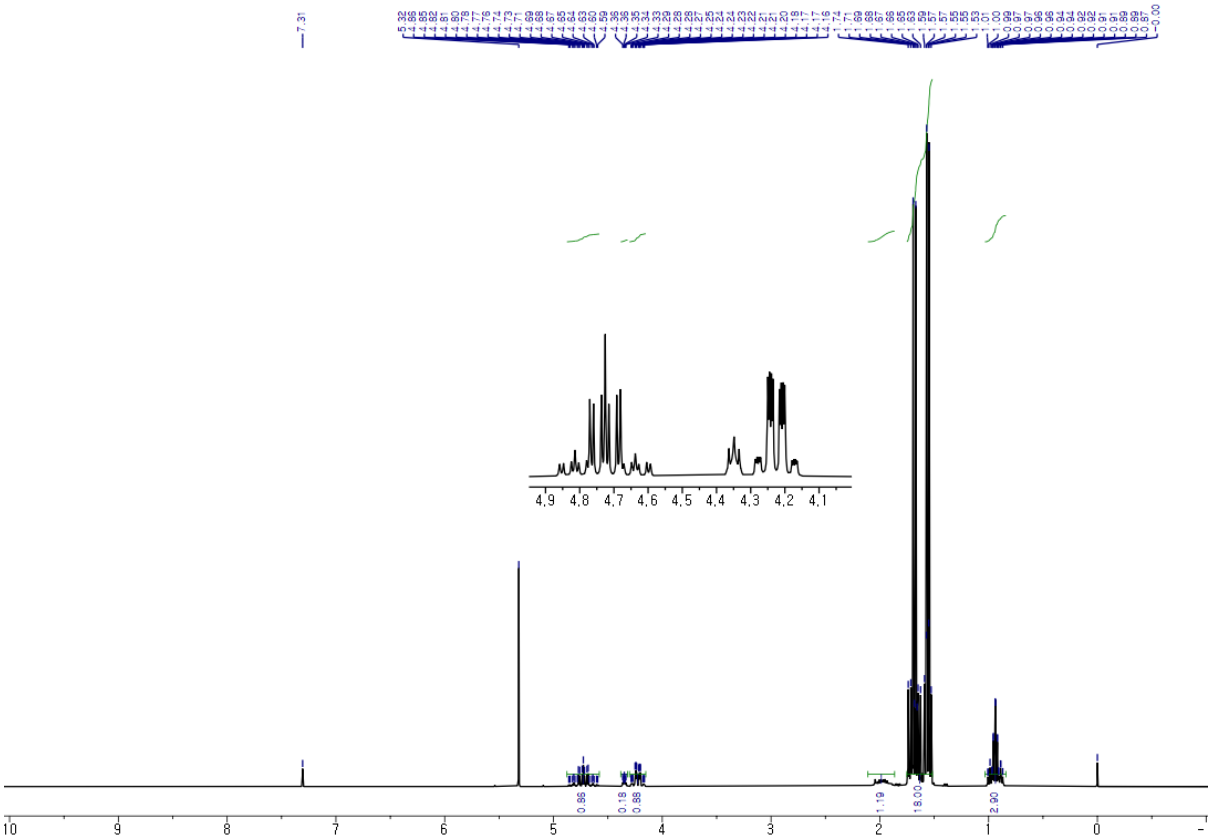

Figure S54. ^{1}H NMR spectrum of **18, 19 Mix** (400 MHz, $CDCl_3$, 300 K)

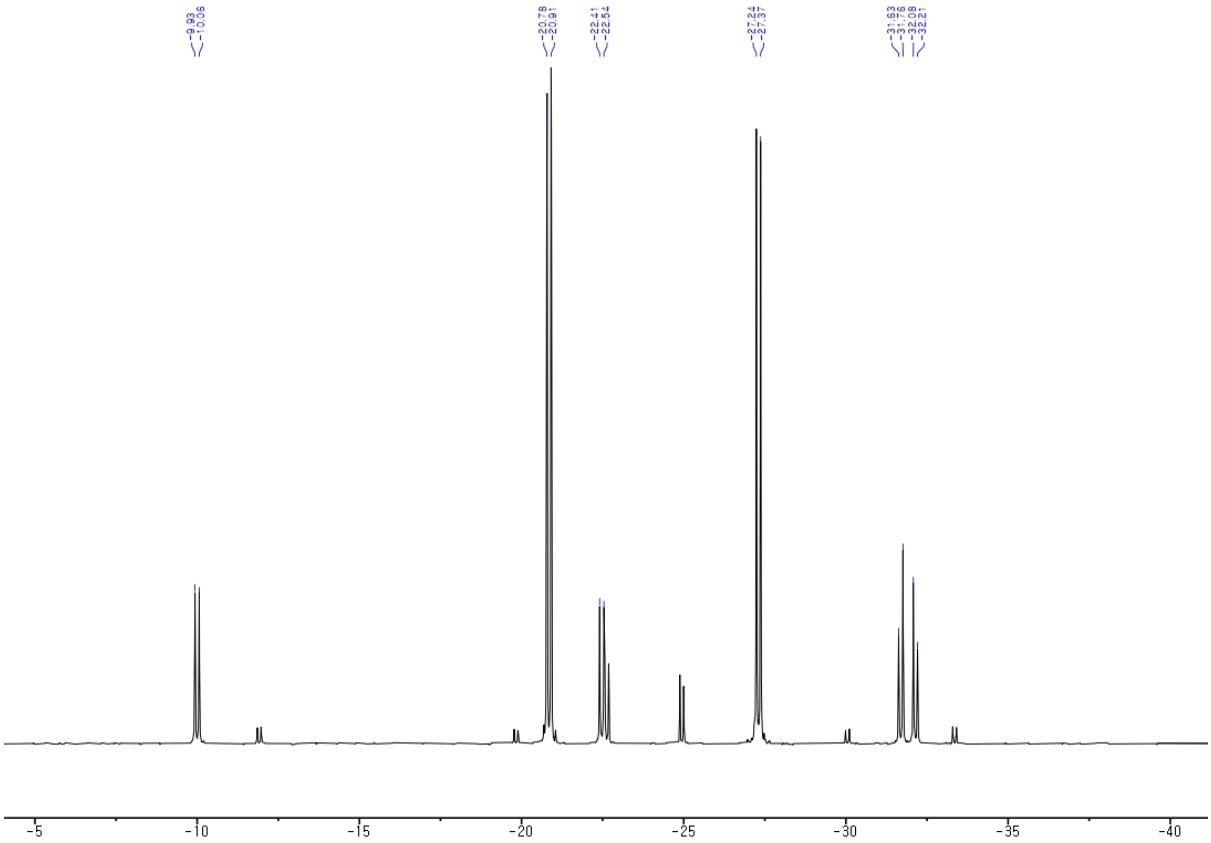

Figure S55. ^{31}P NMR spectrum of **18, 19 Mix** (162 MHz, $CDCl_3$, 300 K)

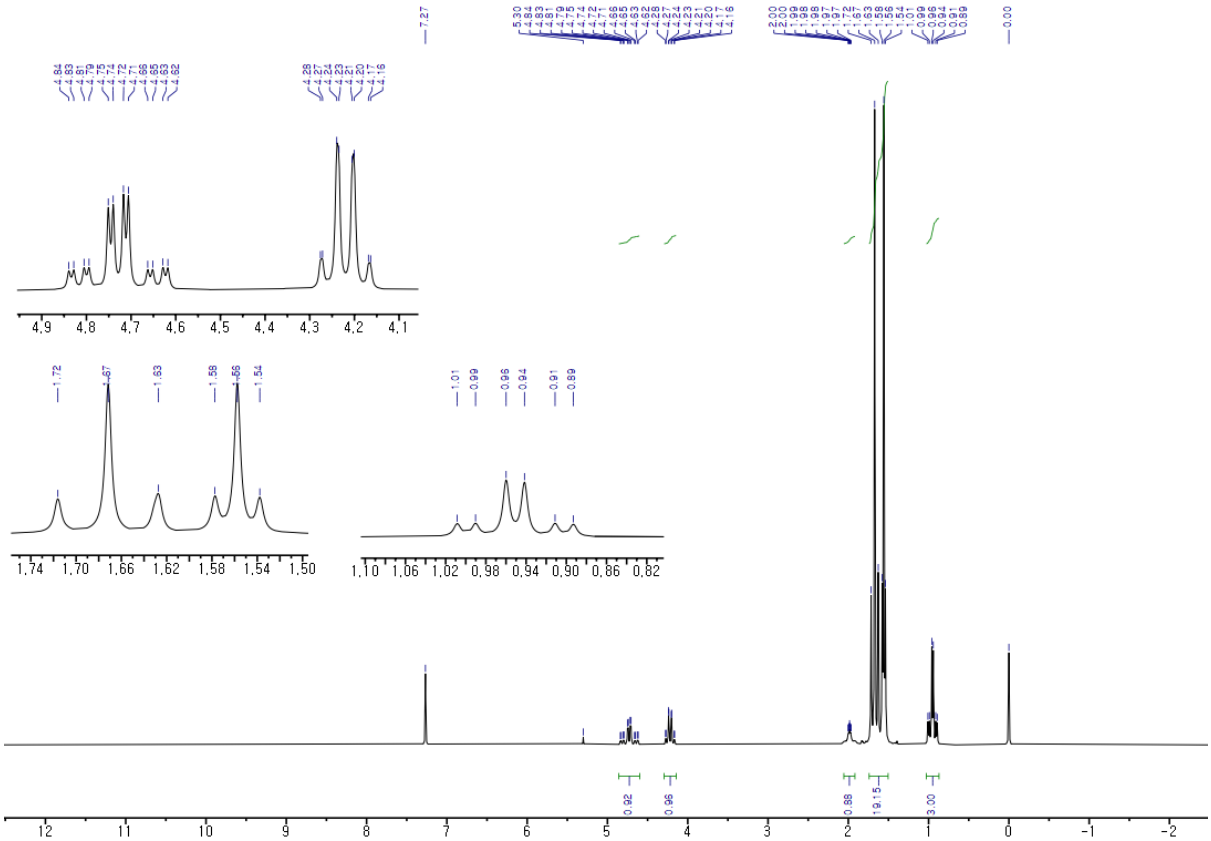

Figure S56. $^{1}H\{^{31}P\}$ NMR spectrum of **18** (400 MHz, $CDCl_3$, 300 K)

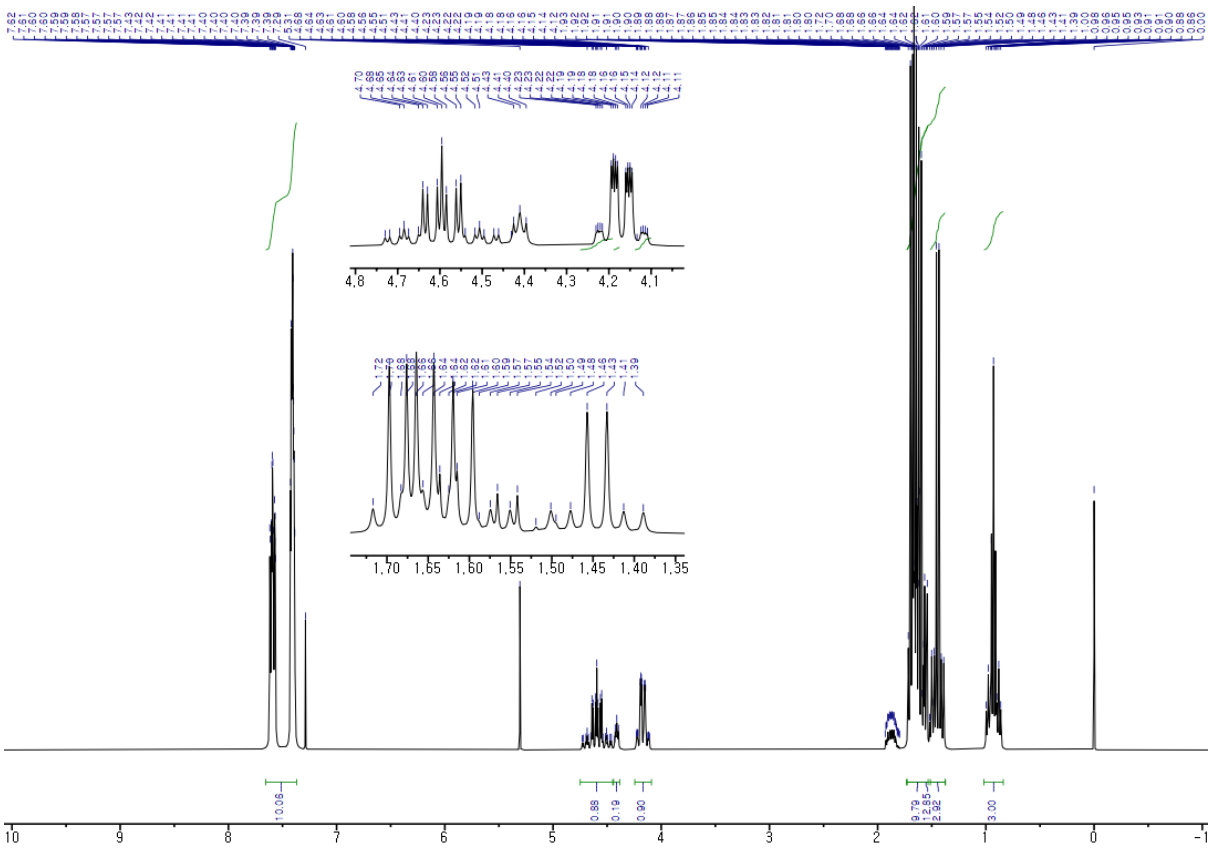

Figure S57. ^{1}H NMR spectrum of **20, 21 Mix** (400 MHz, $CDCl_3$, 300 K)

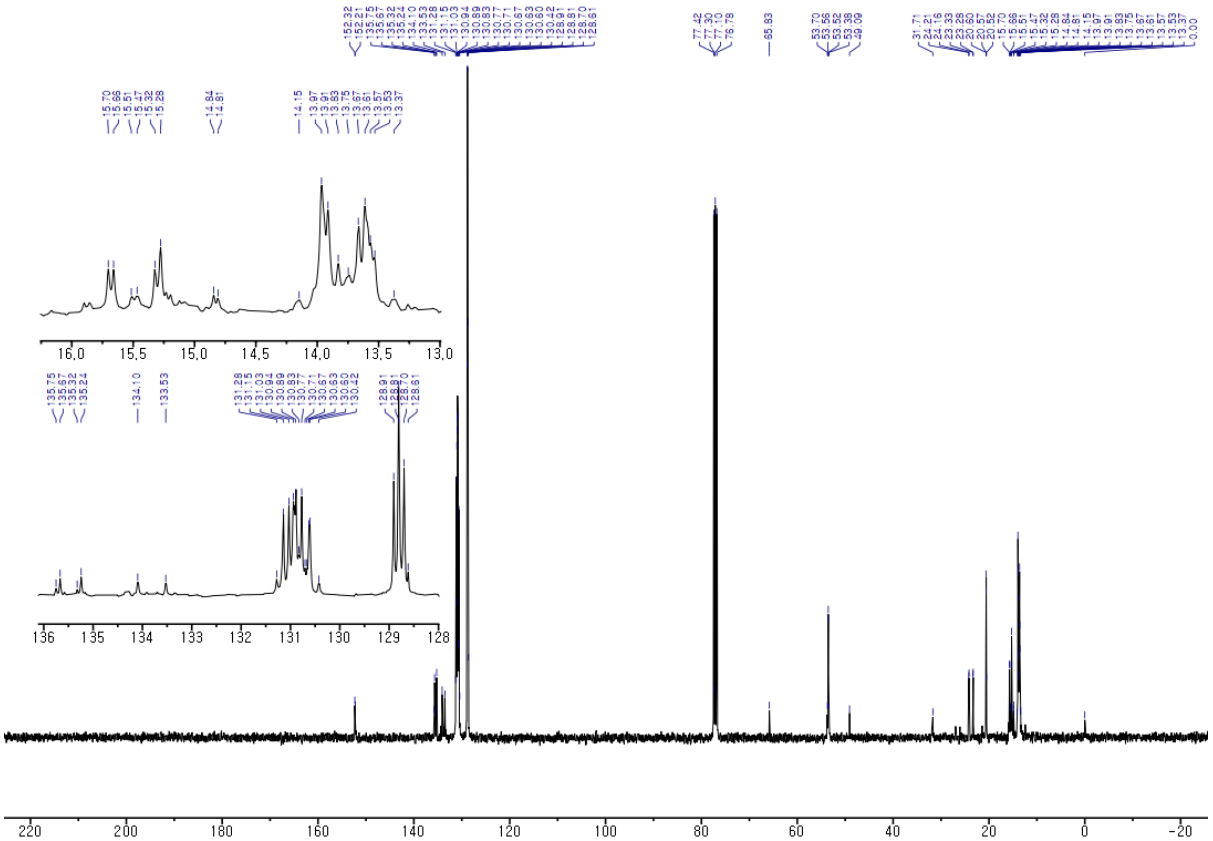

Figure S58. ^{13}C NMR spectrum of **20, 21 Mix** (101 MHz, $CDCl_3$, 300 K)

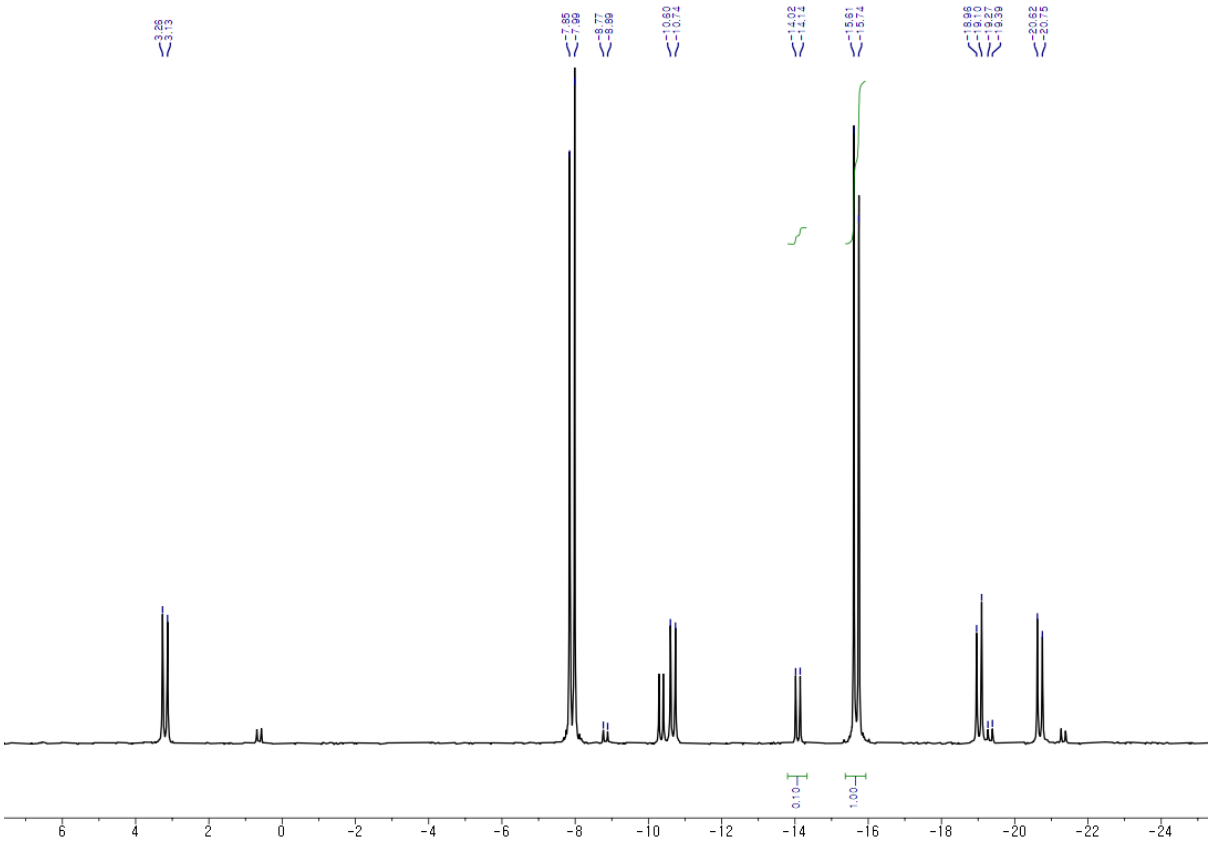

Figure S59. ^{31}P NMR spectrum of **20, 21 Mix** (162 MHz, $CDCl_3$, 300 K)

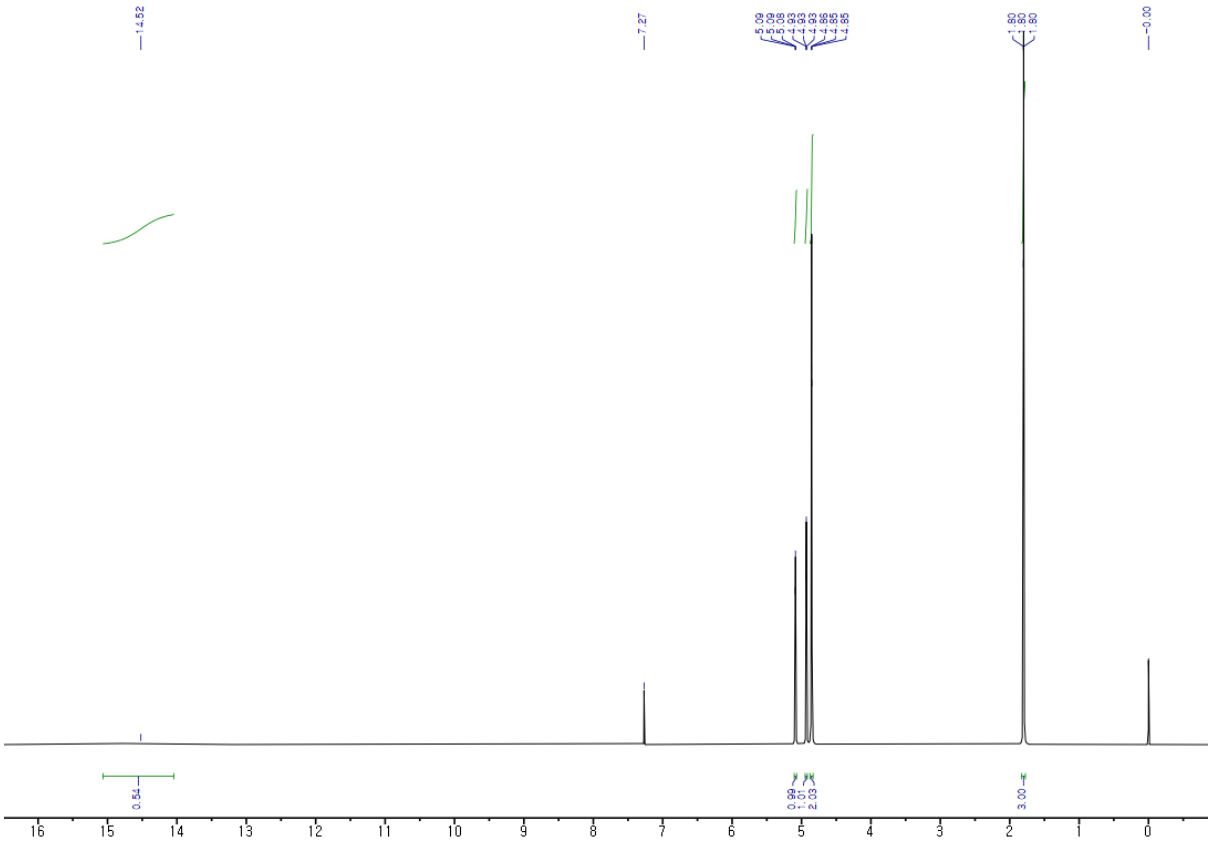

Figure S60. ^{1}H NMR spectrum of **22** (400 MHz, $CDCl_3$, 300 K)

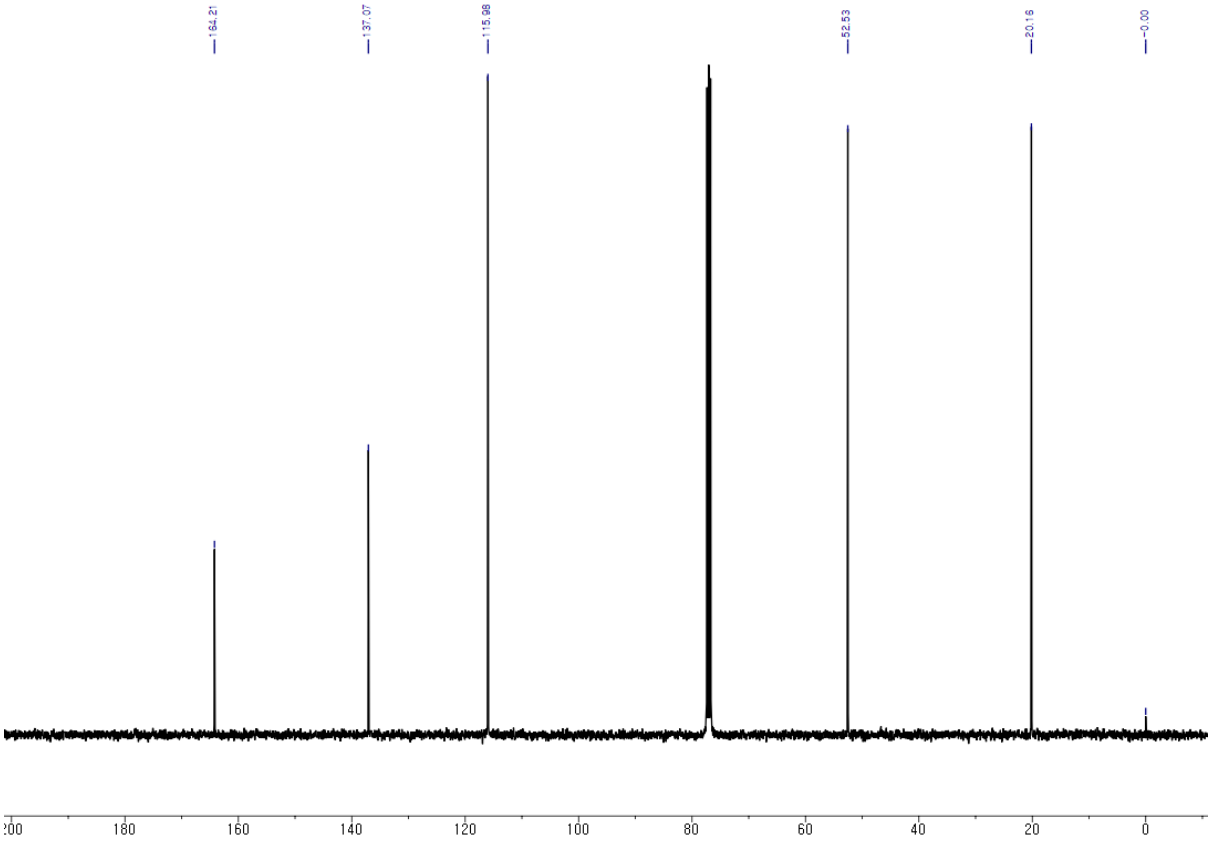

Figure S61. ^{13}C NMR spectrum of **22** (101 MHz, $CDCl_3$, 300 K)

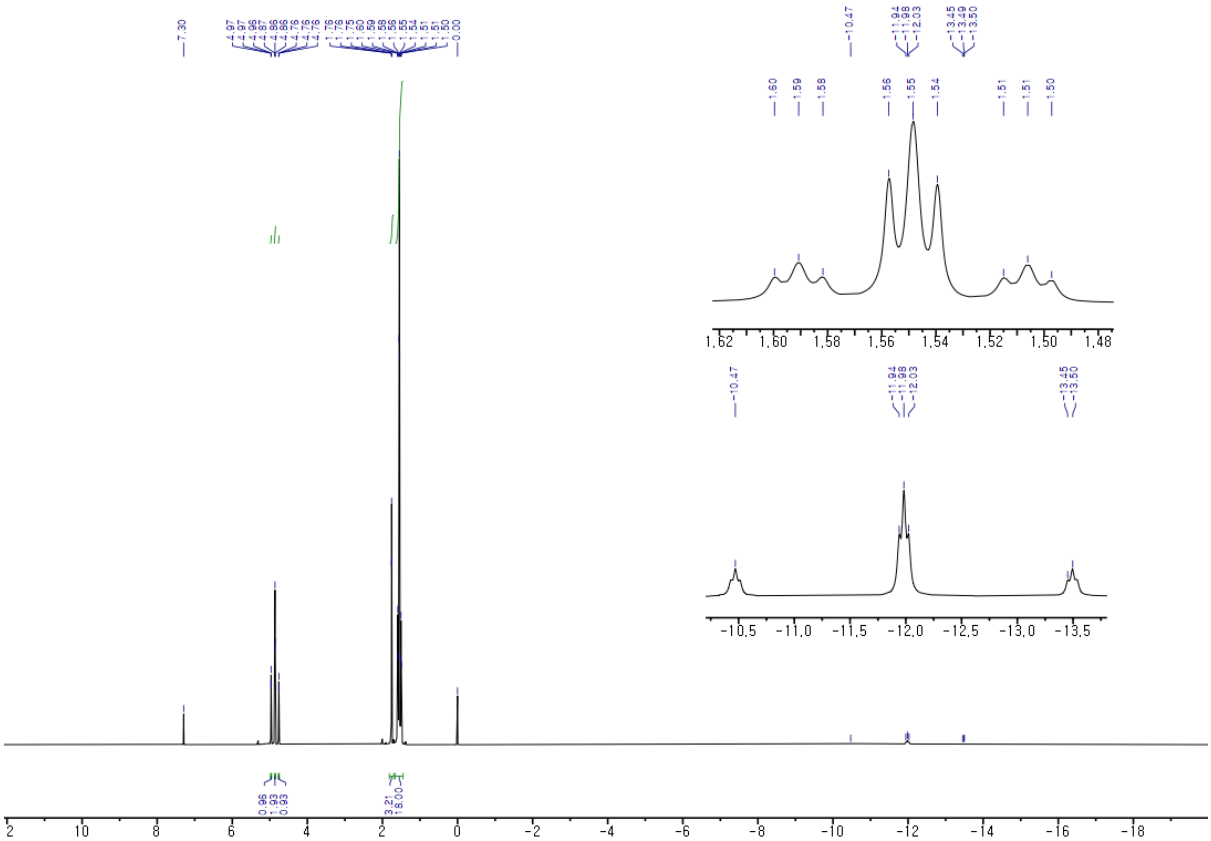

Figure S62. ^{1}H NMR spectrum of **23** (400 MHz, $CDCl_3$, 300 K)

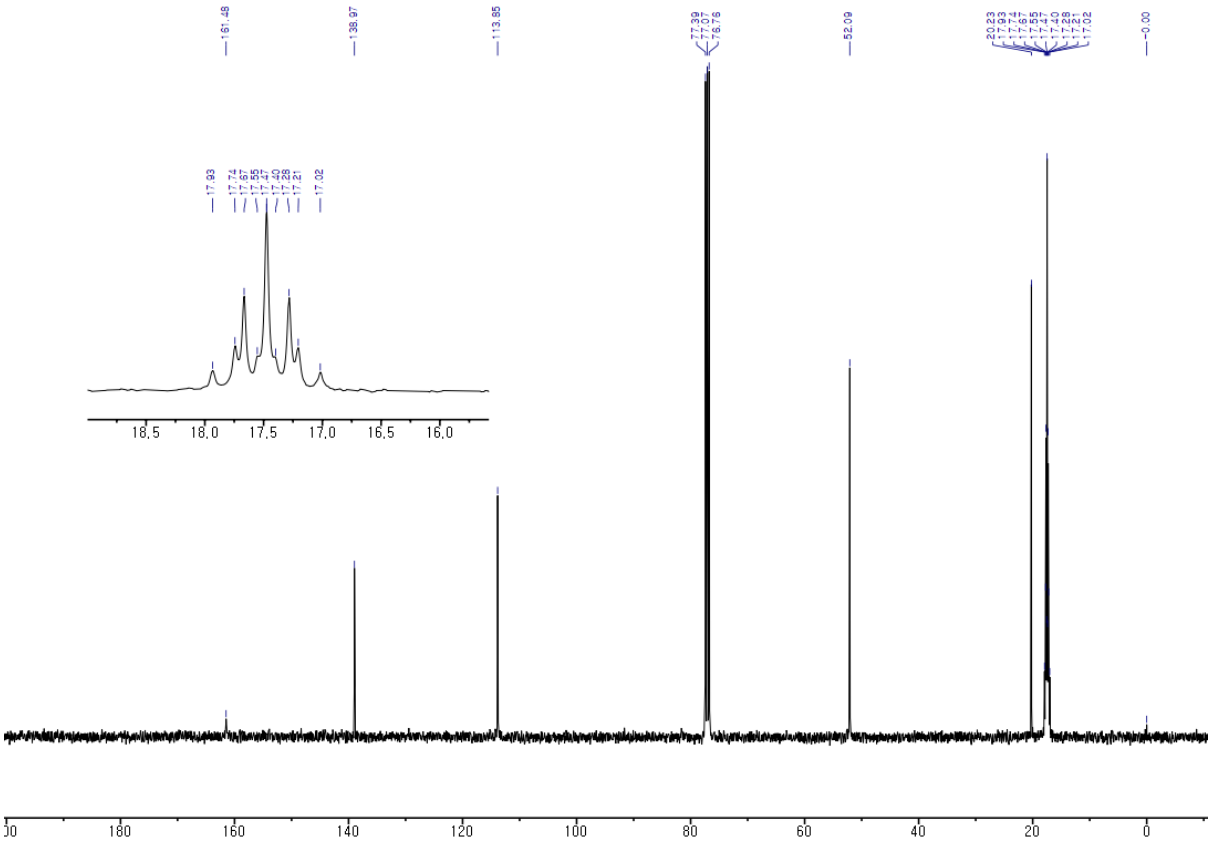

Figure S63. ^{13}C NMR spectrum of **23** (101 MHz, $CDCl_3$, 300 K)

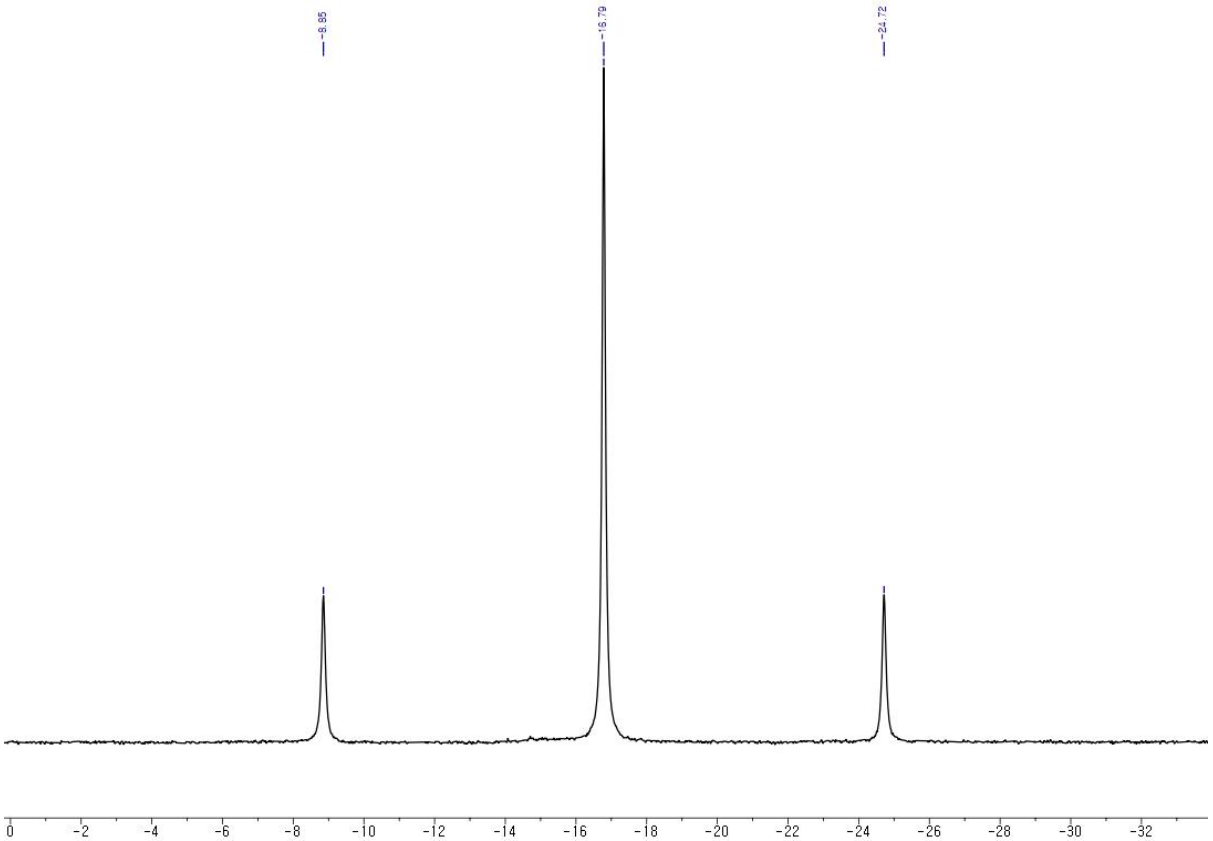

Figure S64. ^{31}P NMR spectrum of **23** (162 MHz, $CDCl_3$, 300 K)

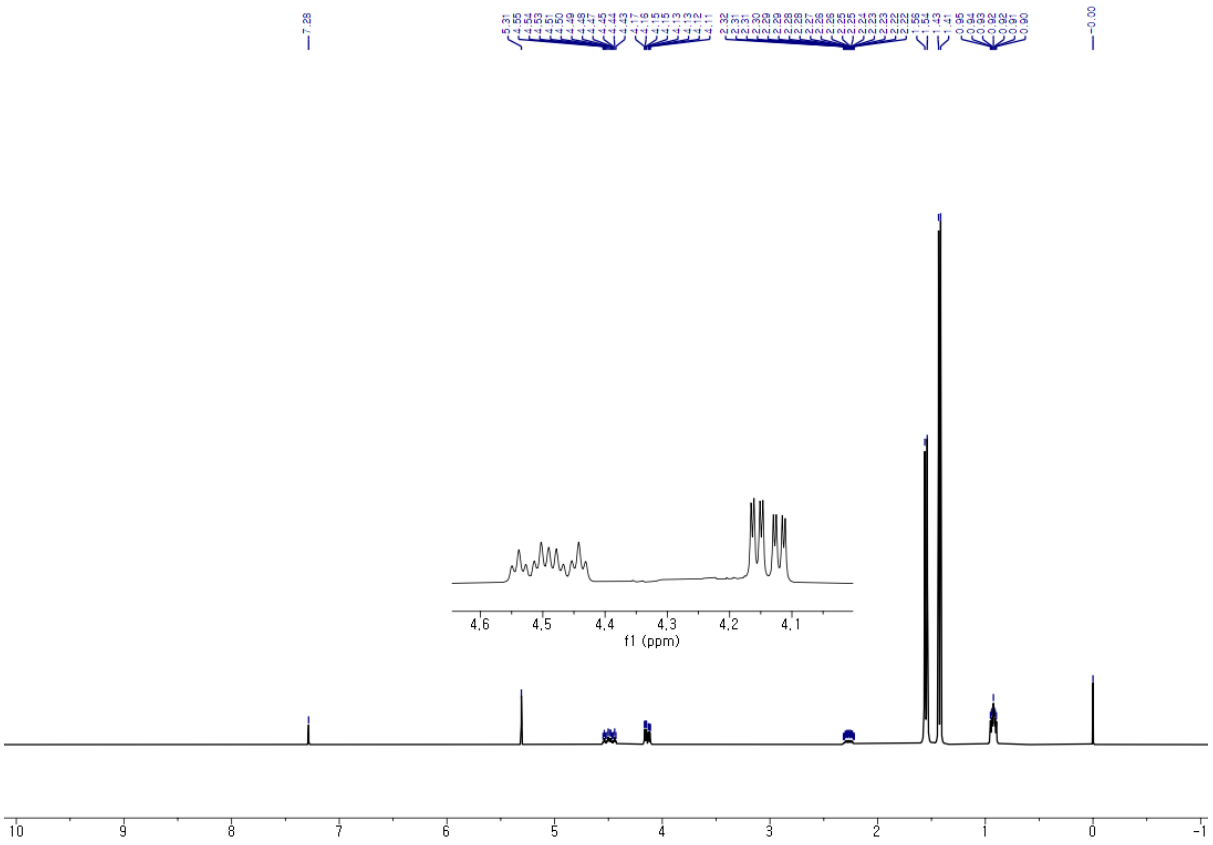

Figure S65. ^{1}H NMR spectrum of **24** (400 MHz, $CDCl_3$, 300 K)

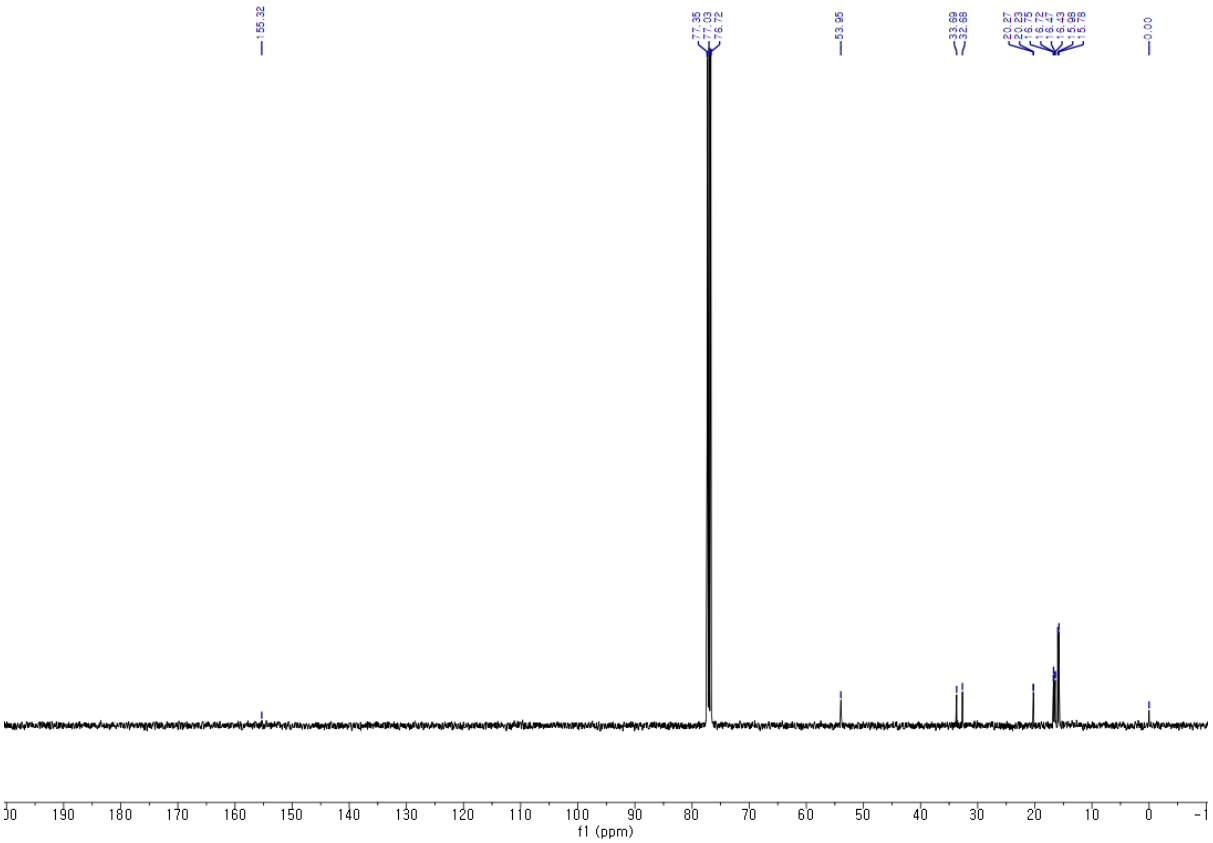

Figure S66. ^{13}C NMR spectrum of **24** (151 MHz, $CDCl_3$, 300 K)

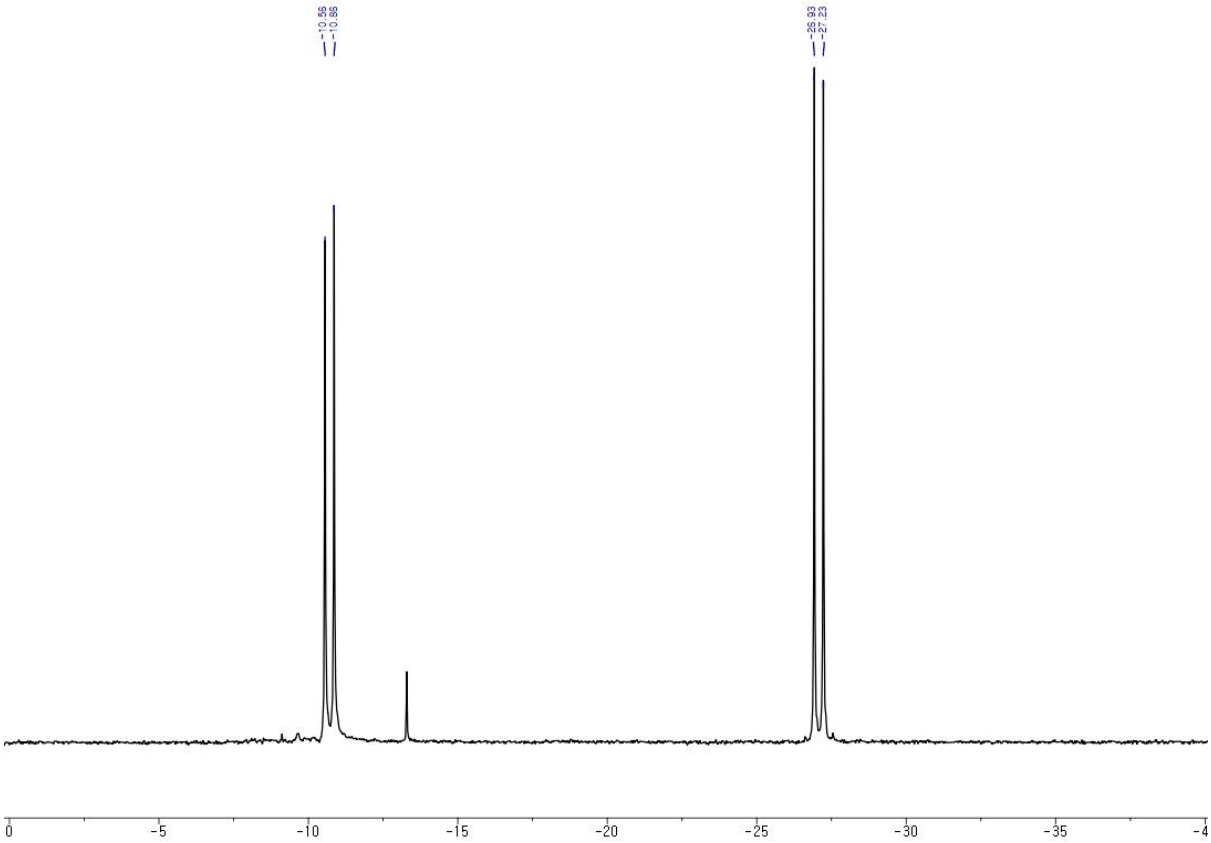

Figure S67. ^{31}P NMR spectrum of **24** (162 MHz, $CDCl_3$, 300 K)

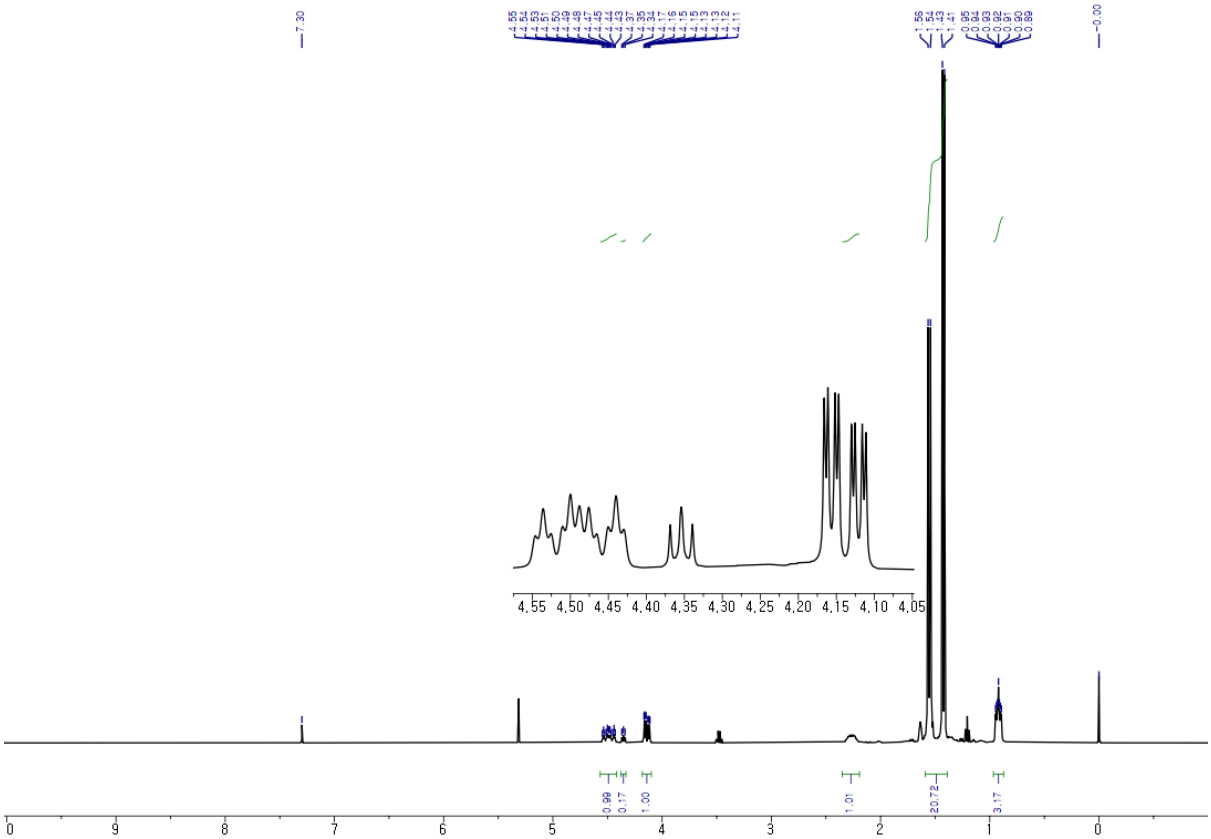

Figure S68. ^{1}H NMR spectrum of **24, 25 Mix** (400 MHz, $CDCl_3$, 300 K)

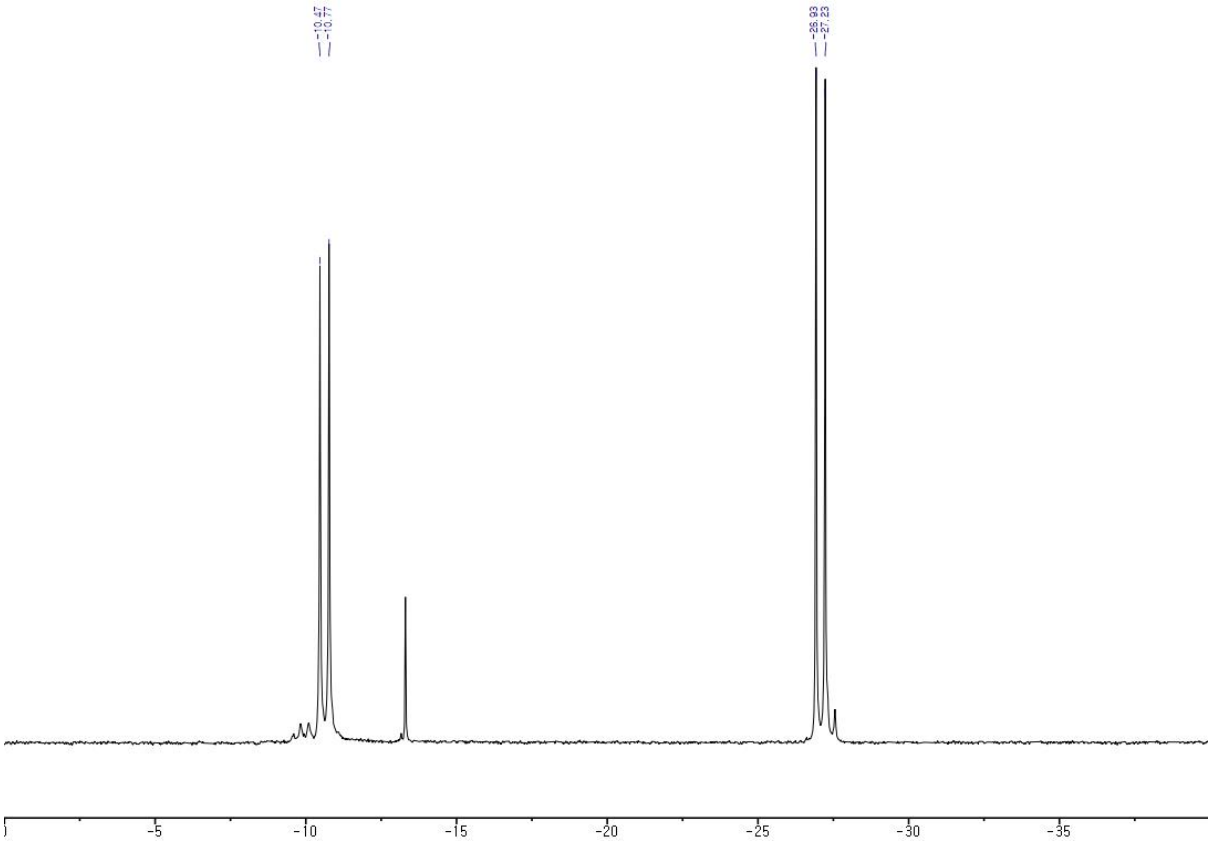

Figure S69. ^{31}P NMR spectrum of **24, 25 Mix** (162 MHz, $CDCl_3$, 300 K)

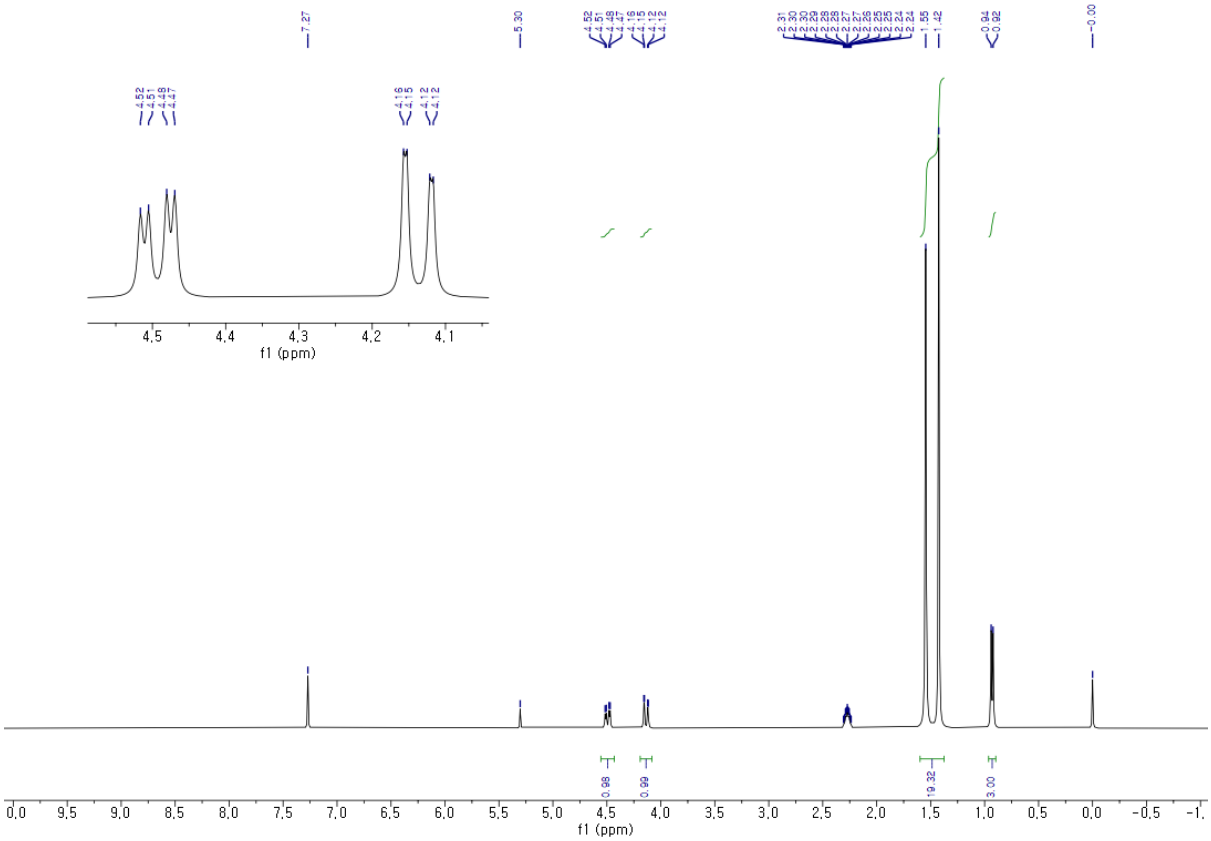

Figure S70. $^{1}H\{^{31}P\}$ NMR spectrum of **24** (400 MHz, $CDCl_3$, 300 K)

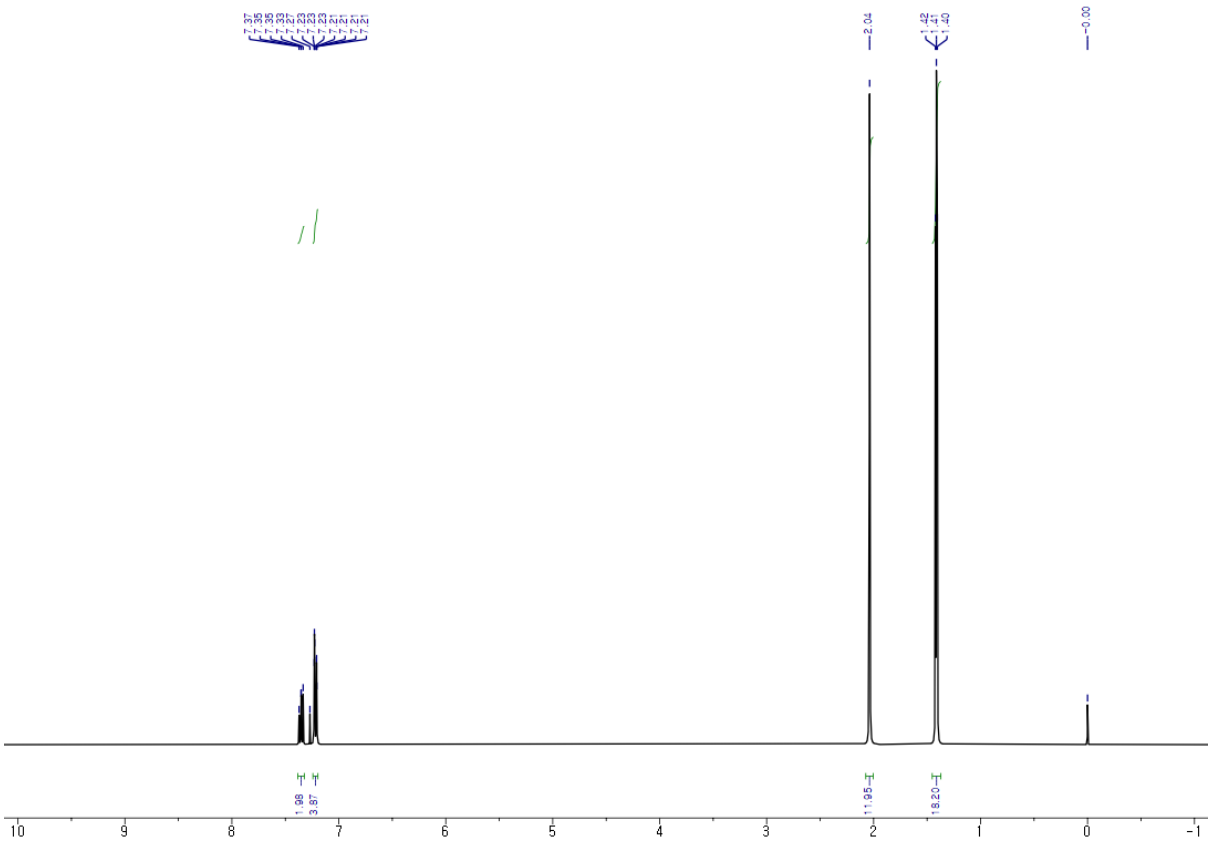

Figure S71. ^{1}H NMR spectrum of **26** (400 MHz, $CDCl_3$, 300 K)

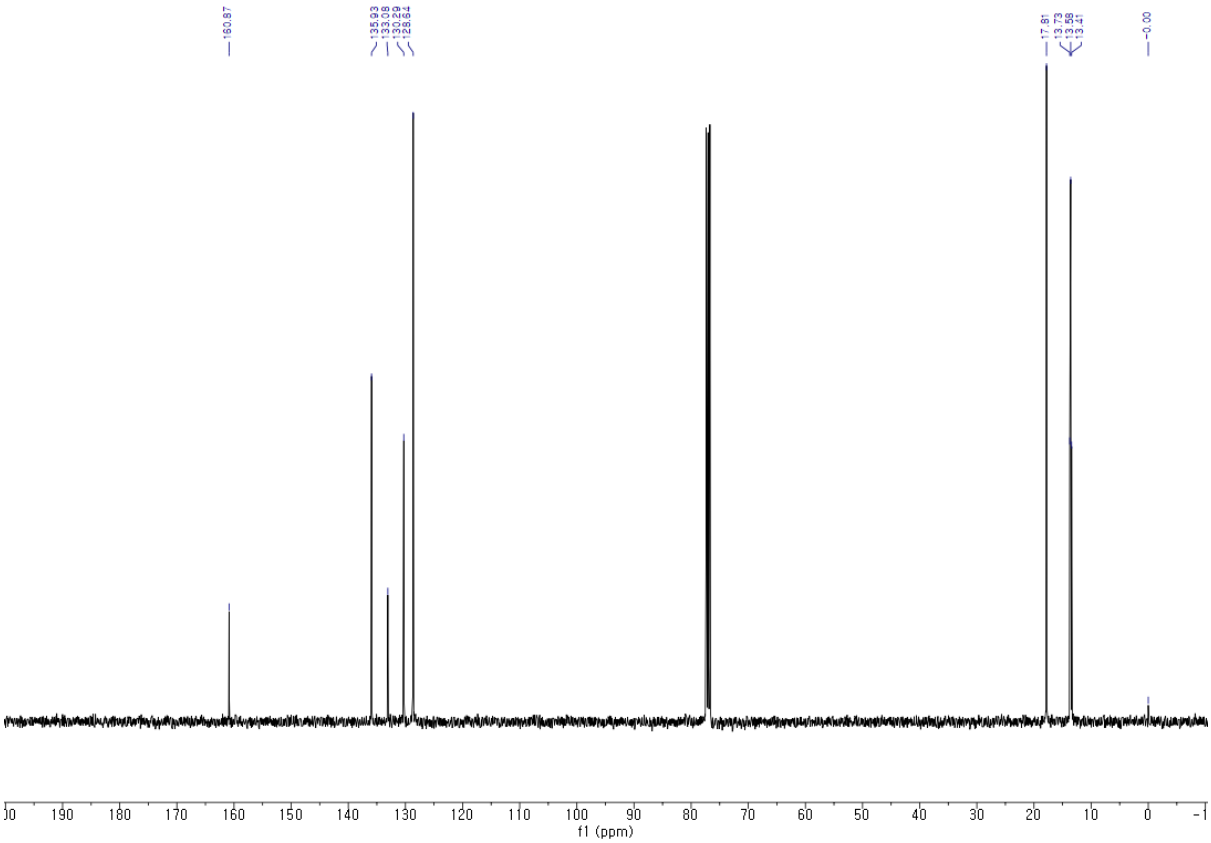

Figure S72. ^{13}C NMR spectrum of **26** (101 MHz, $CDCl_3$, 300 K)

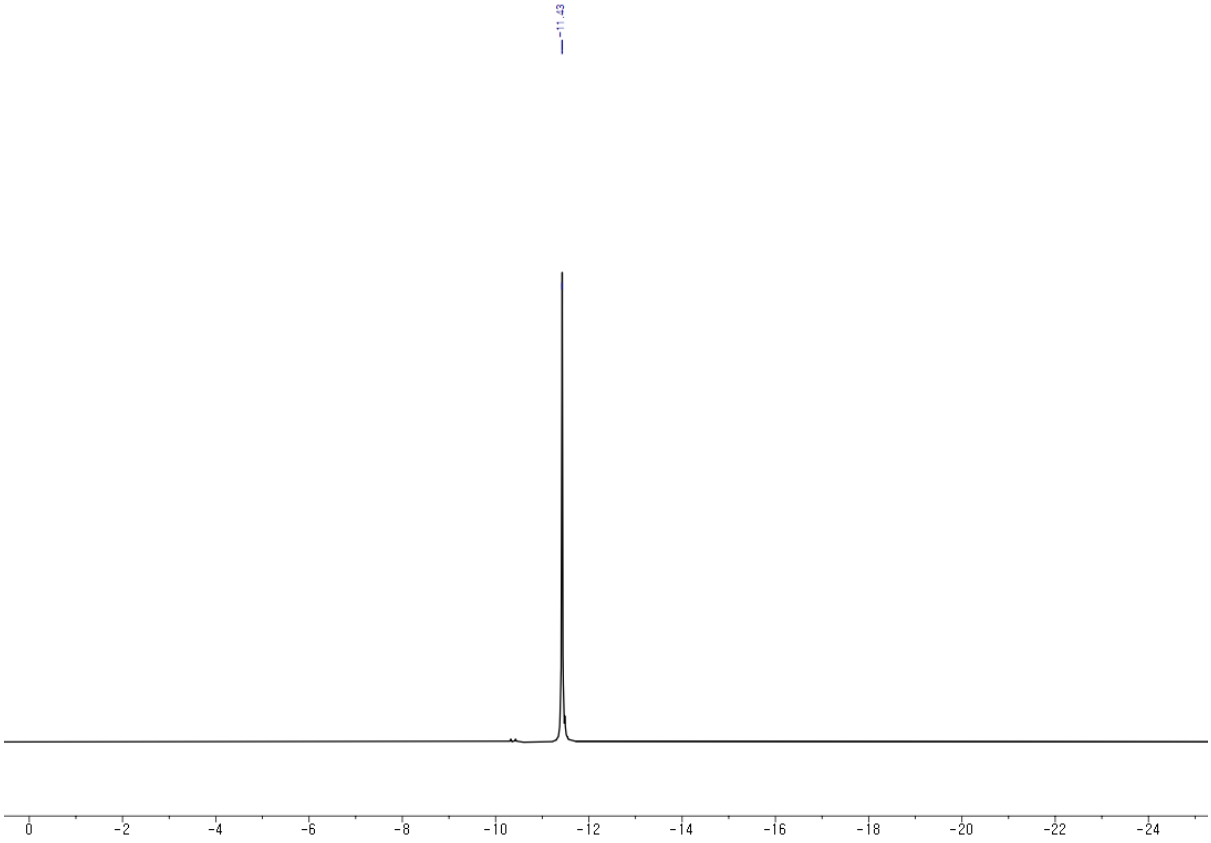

Figure S73. ^{31}P NMR spectrum of **26** (162 MHz, $CDCl_3$, 300 K)

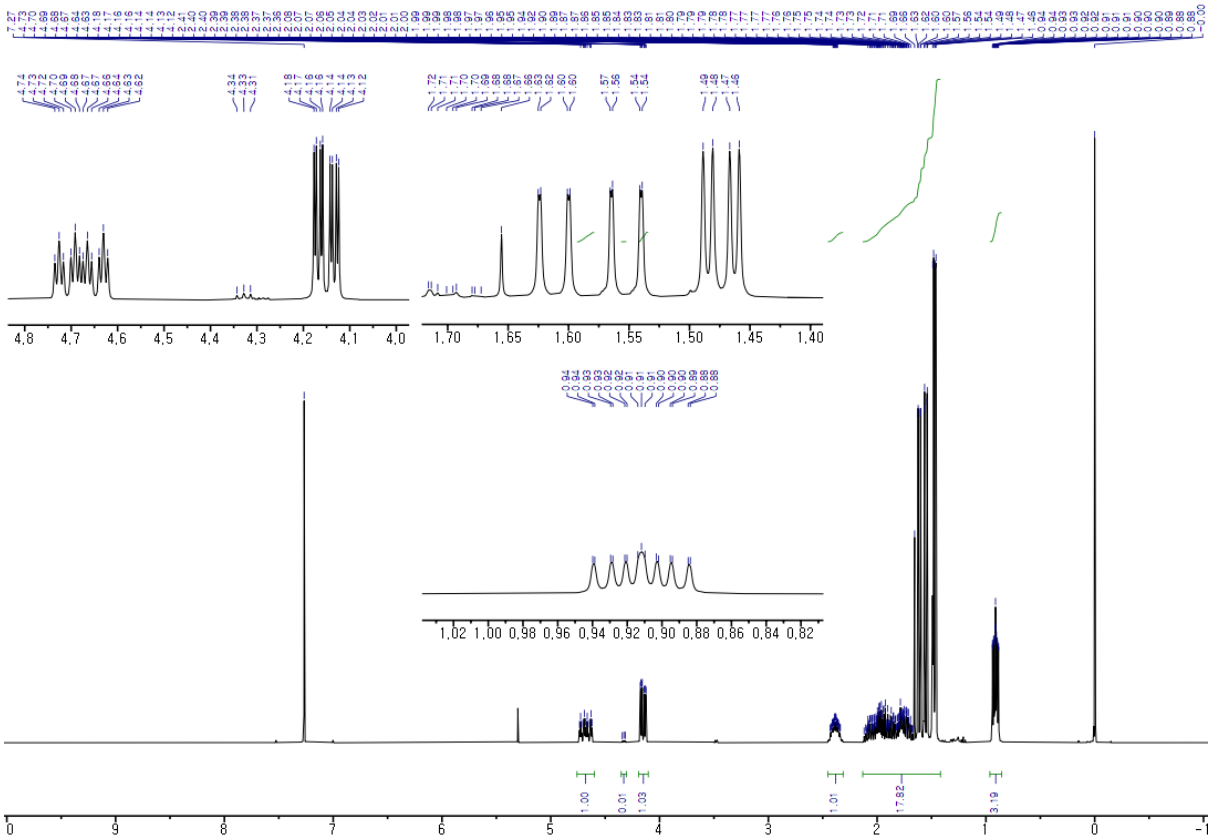

Figure S74. ^{1}H NMR spectrum of **27** (400 MHz, $CDCl_3$, 300 K)

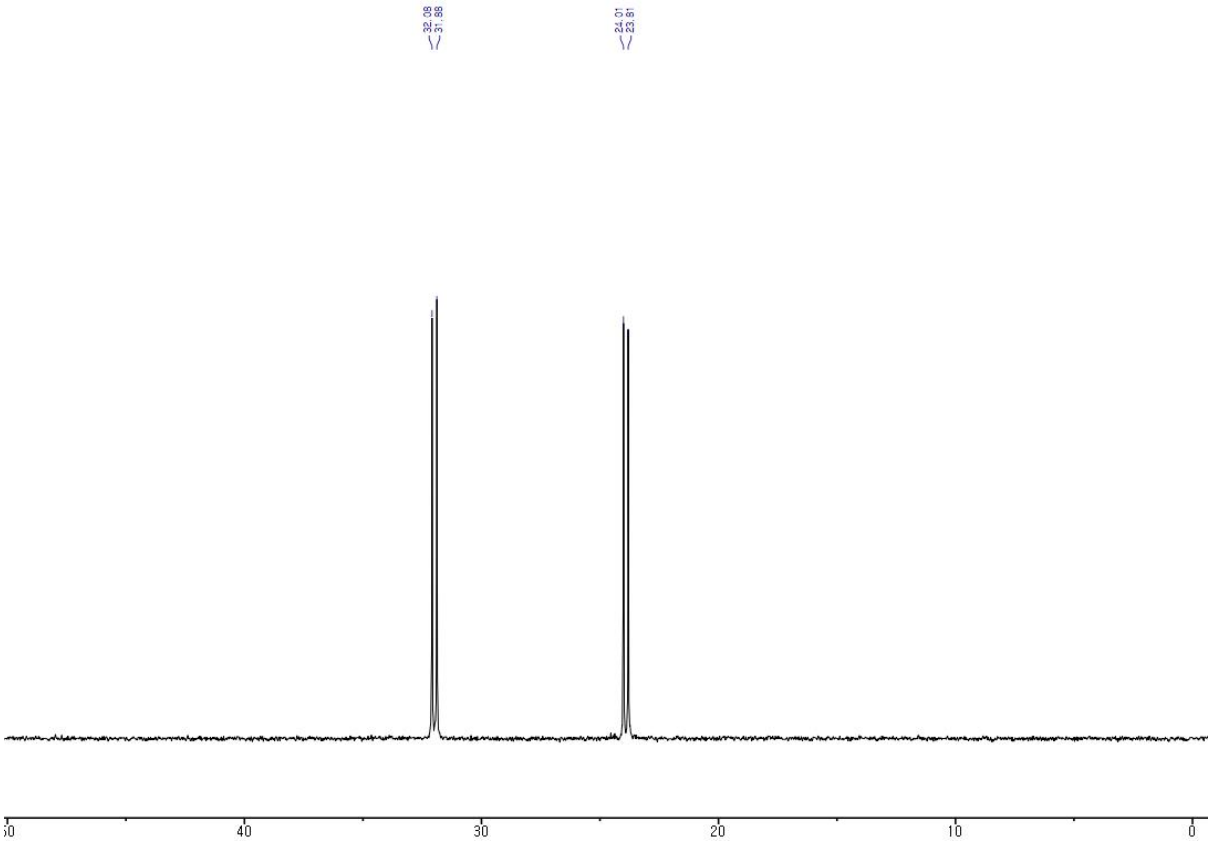

Figure S75. ^{31}P NMR spectrum of **27** (162 MHz, $CDCl_3$, 300 K)

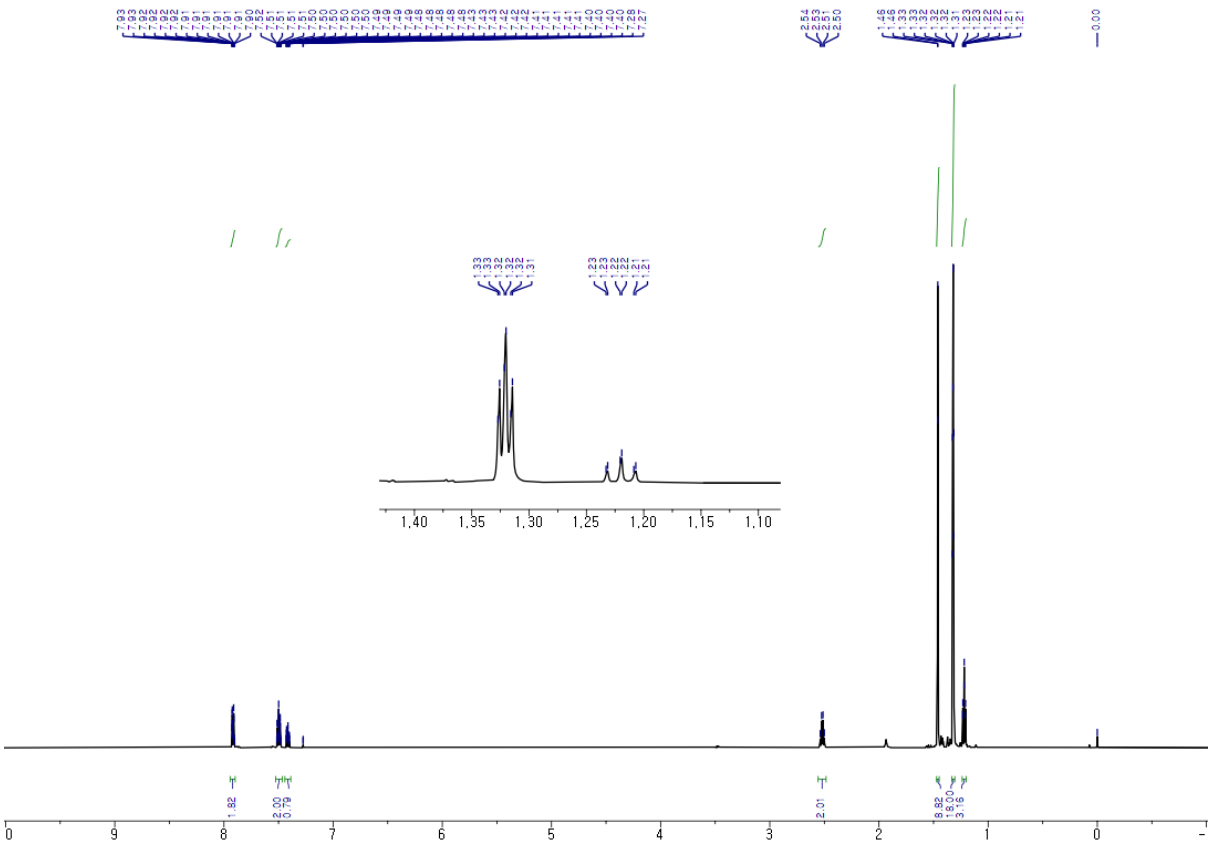

Figure S76. ^{1}H NMR spectrum of **28** (600 MHz, $CDCl_3$, 300 K)

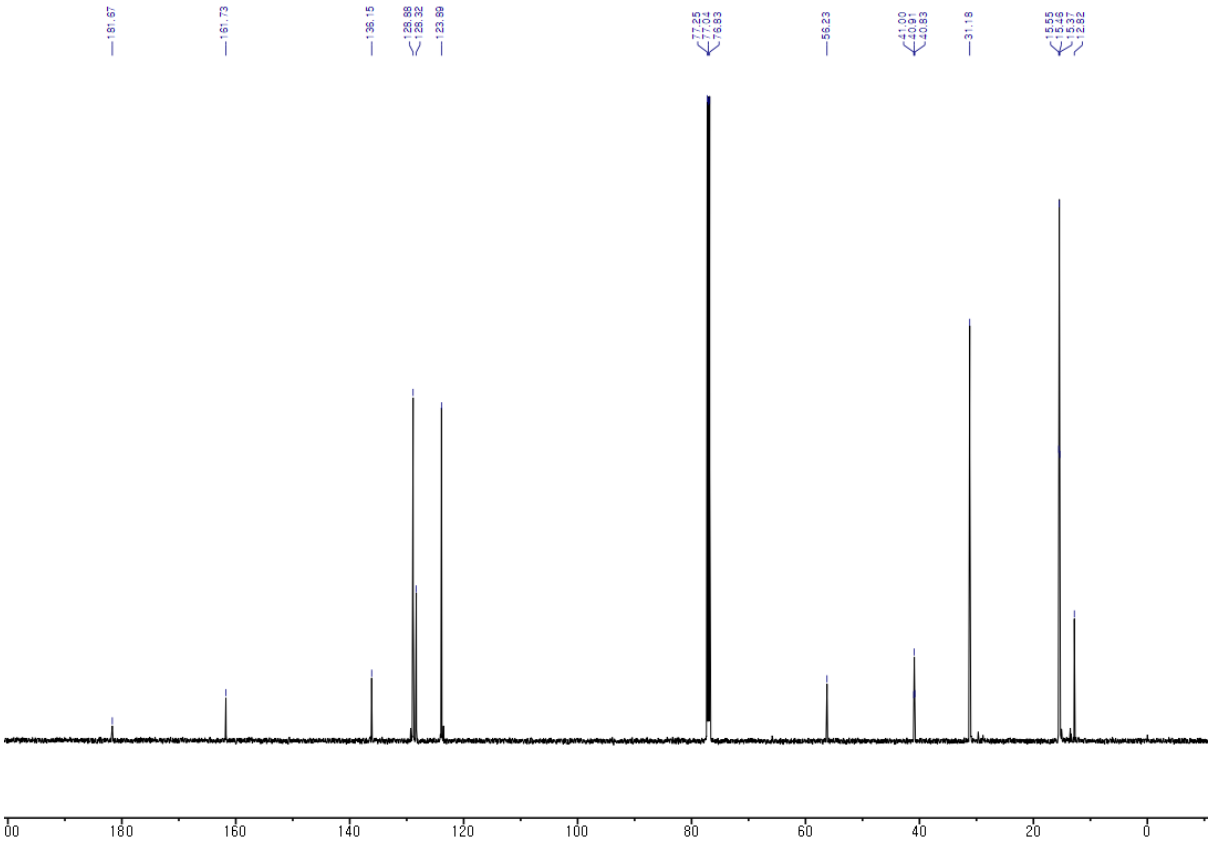

Figure S77. ^{13}C NMR spectrum of **28** (151 MHz, $CDCl_3$, 300 K)

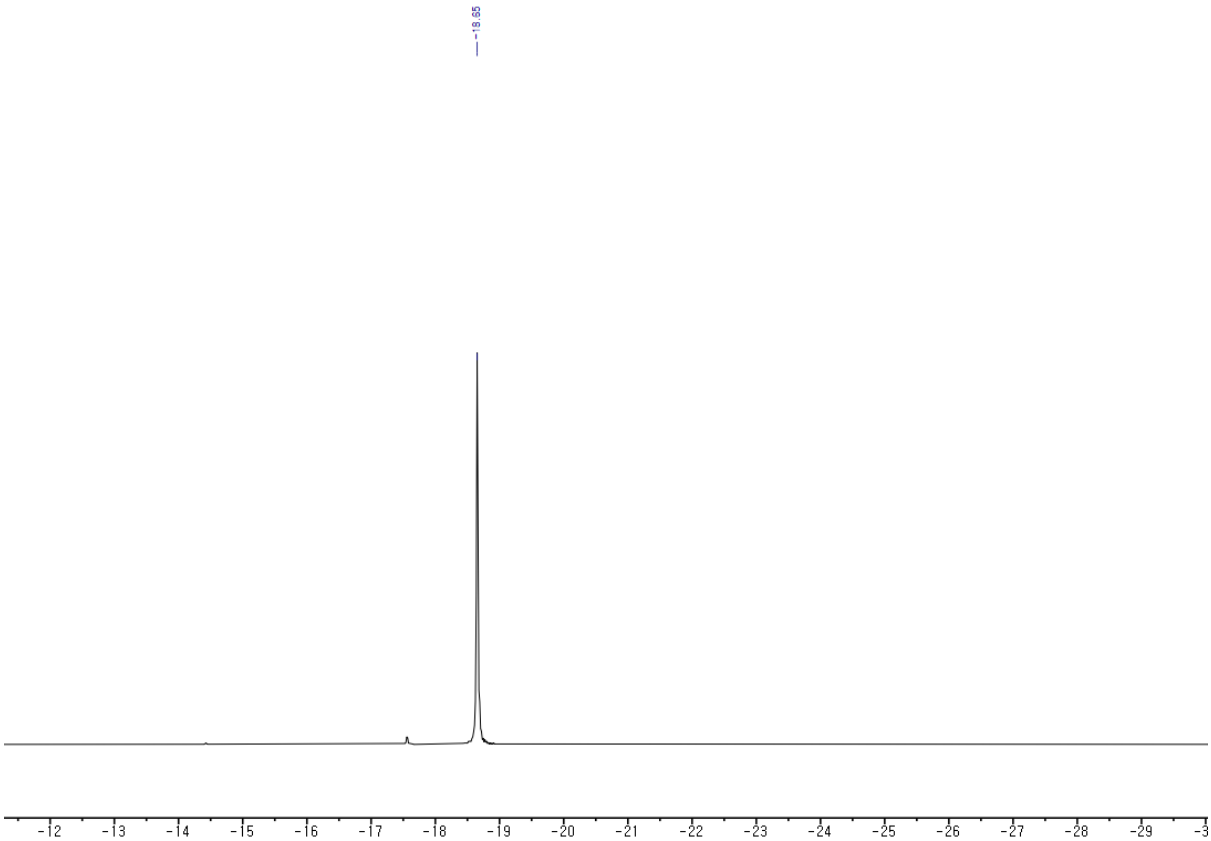

Figure S78. ^{31}P NMR spectrum of **28** (243 MHz, $CDCl_3$, 300 K)

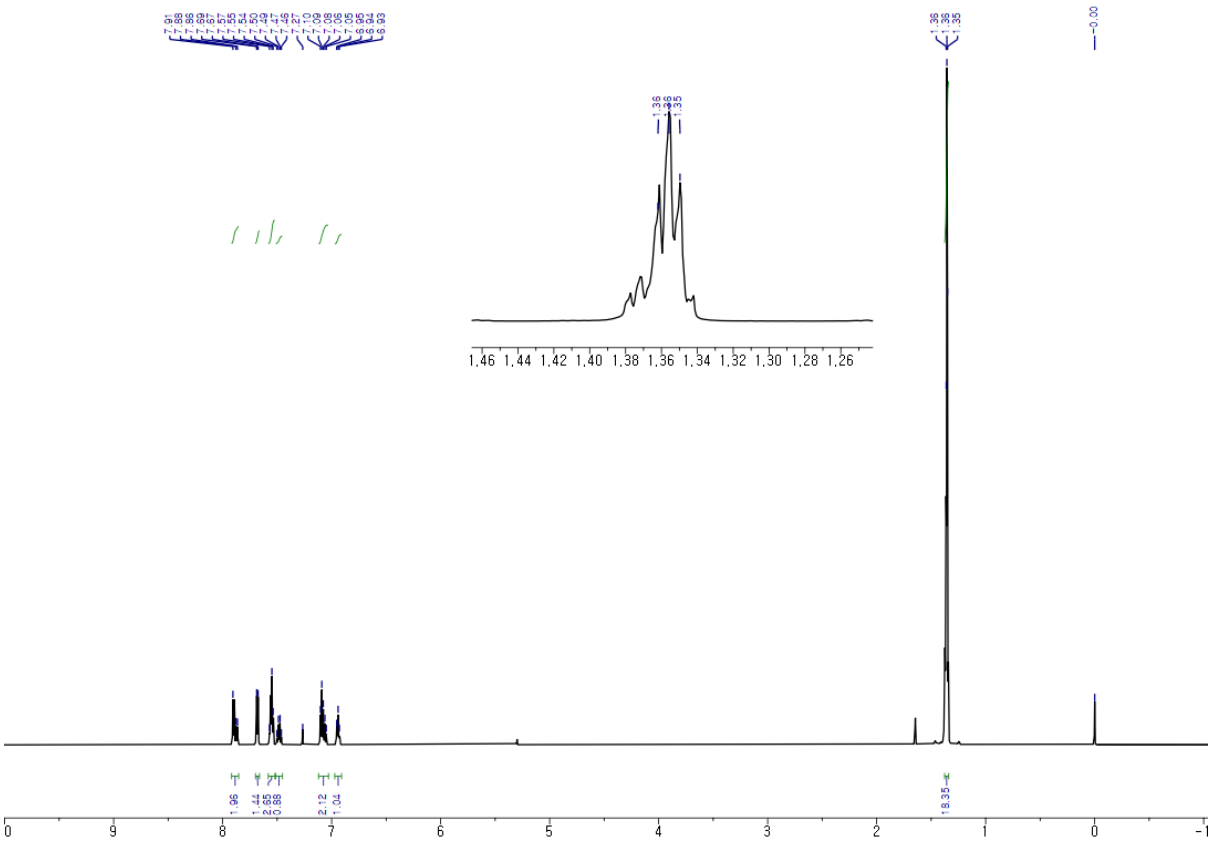

Figure S79. ^{1}H NMR spectrum of **29** (600 MHz, $CDCl_3$, 300 K)

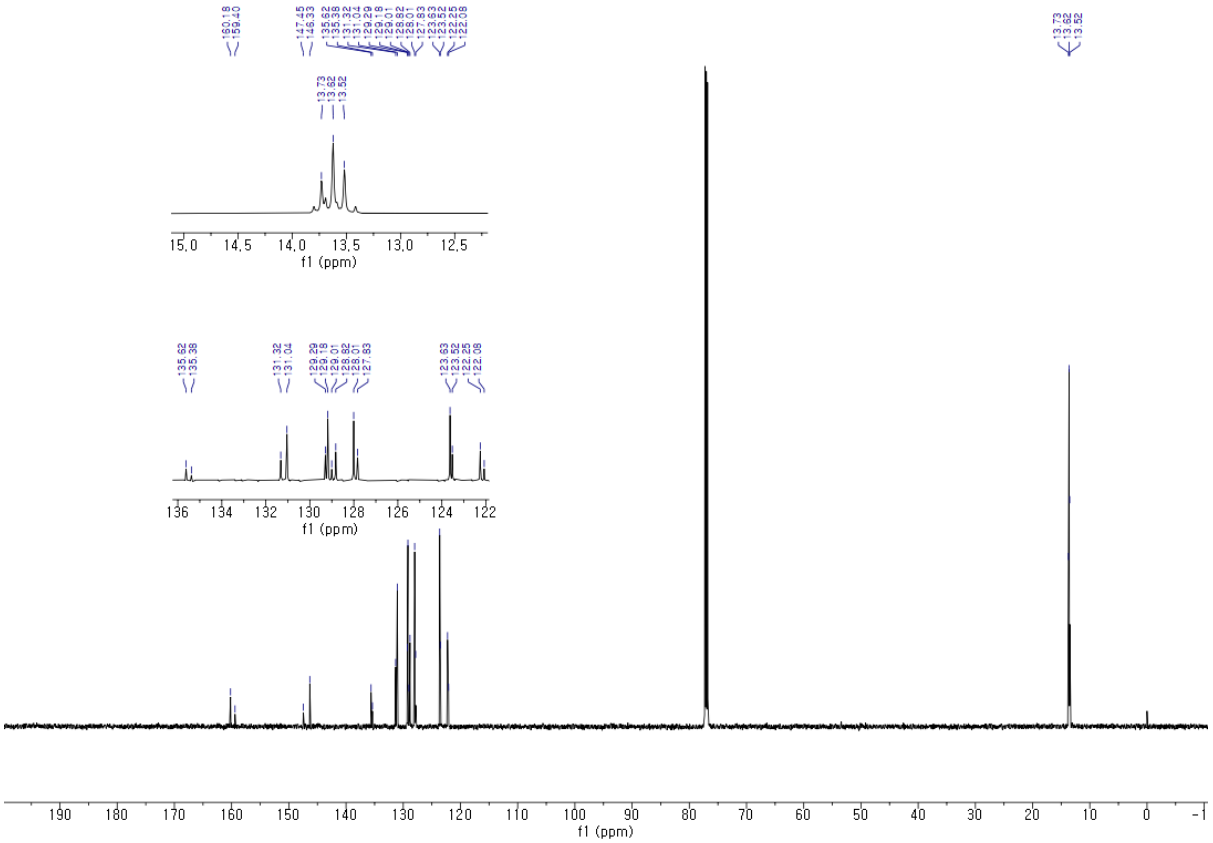

Figure S80. ^{13}C NMR spectrum of **29** (151 MHz, $CDCl_3$, 300 K)

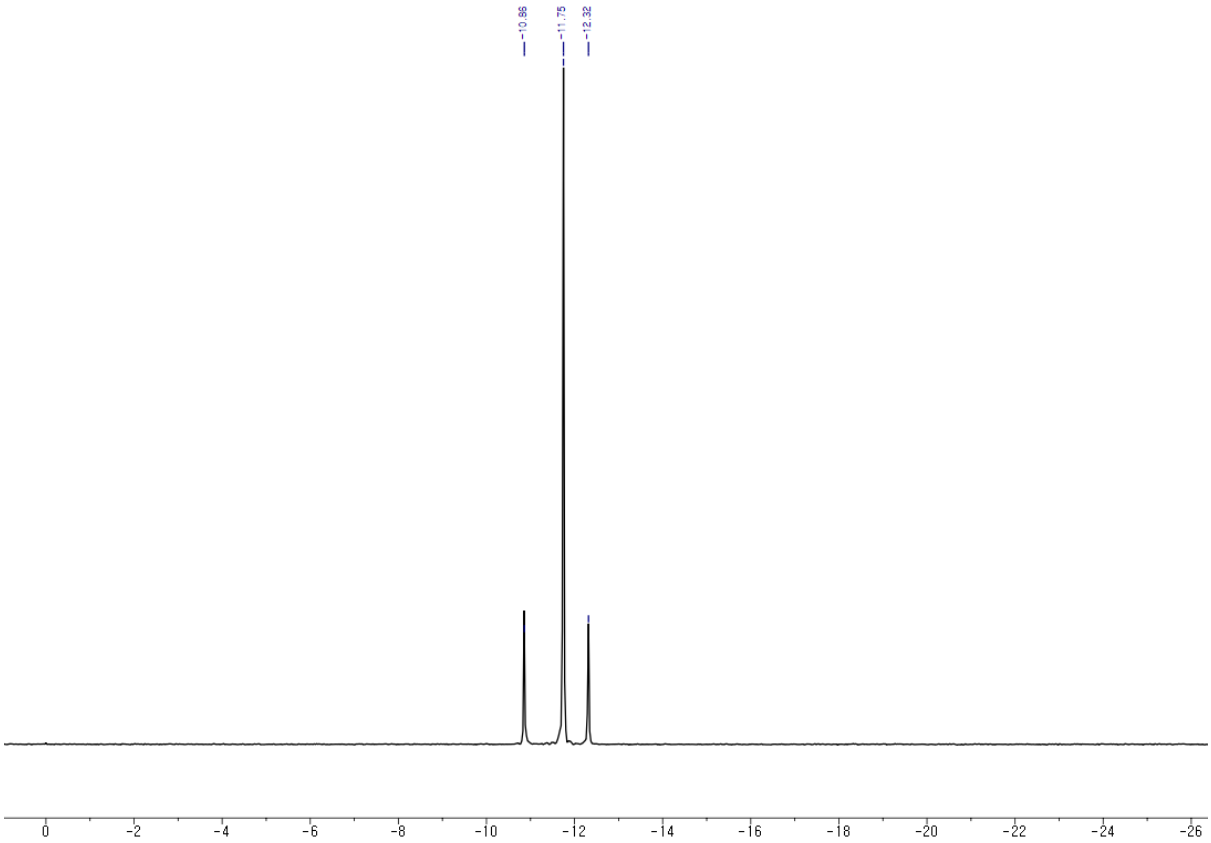

Figure S81. ^{31}P NMR spectrum of **29** (243 MHz, $CDCl_3$, 300 K)

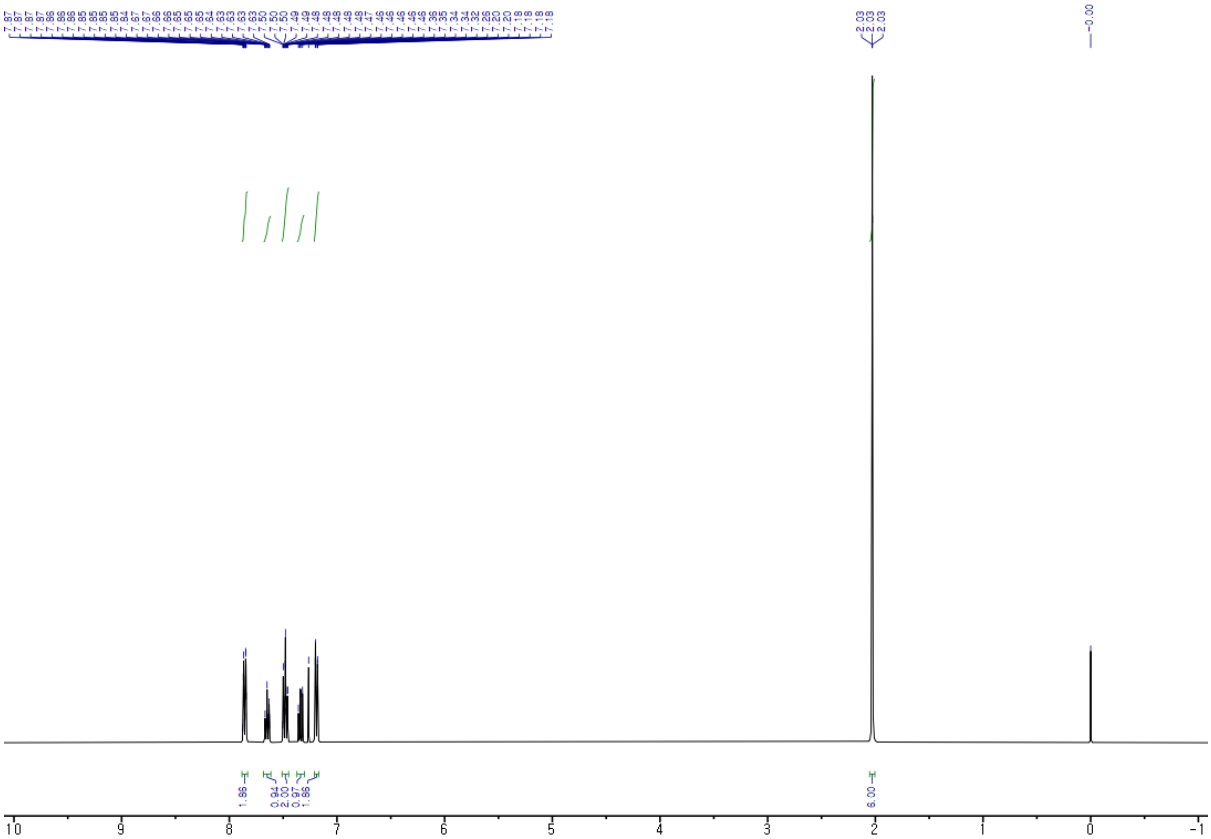

Figure S82. ^{1}H NMR spectrum of **30** (400 MHz, $CDCl_3$, 300 K)

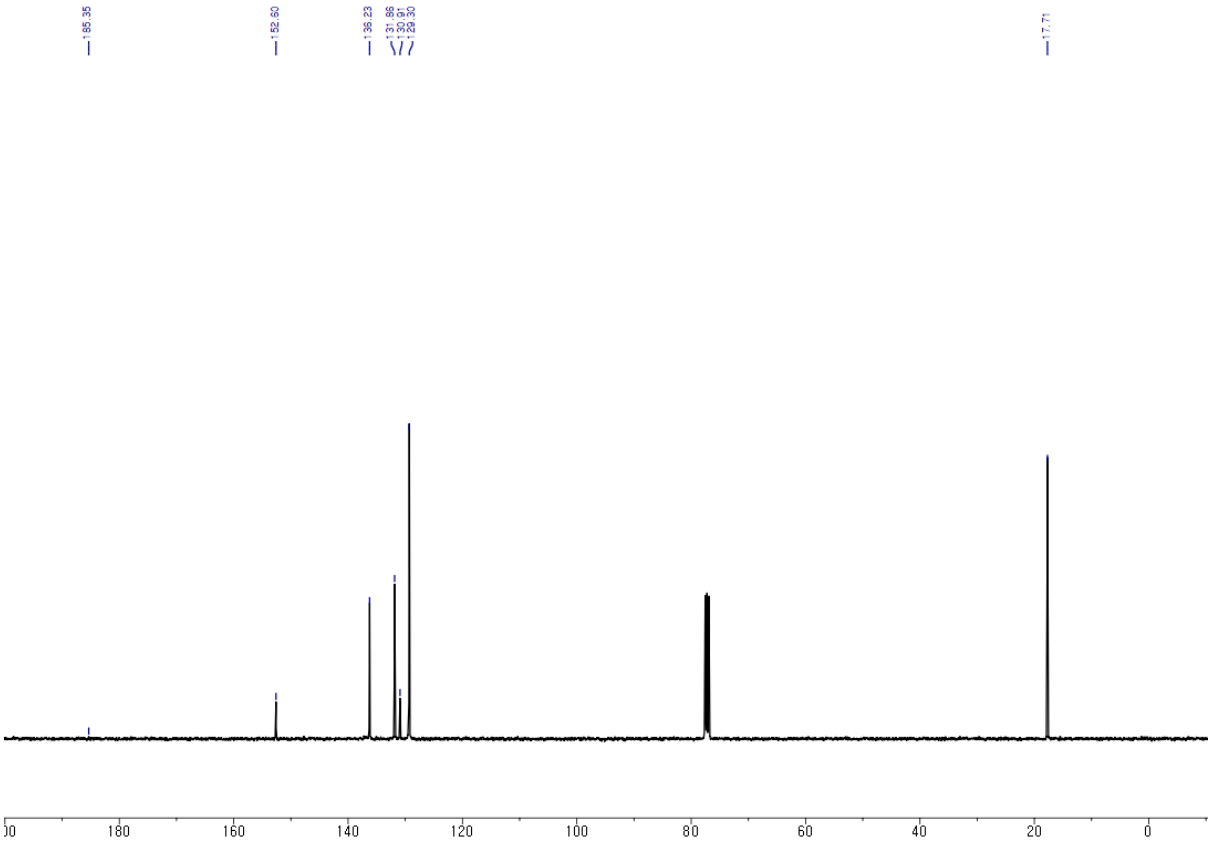

Figure S83. ^{13}C NMR spectrum of **30** (101 MHz, $CDCl_3$, 300 K)

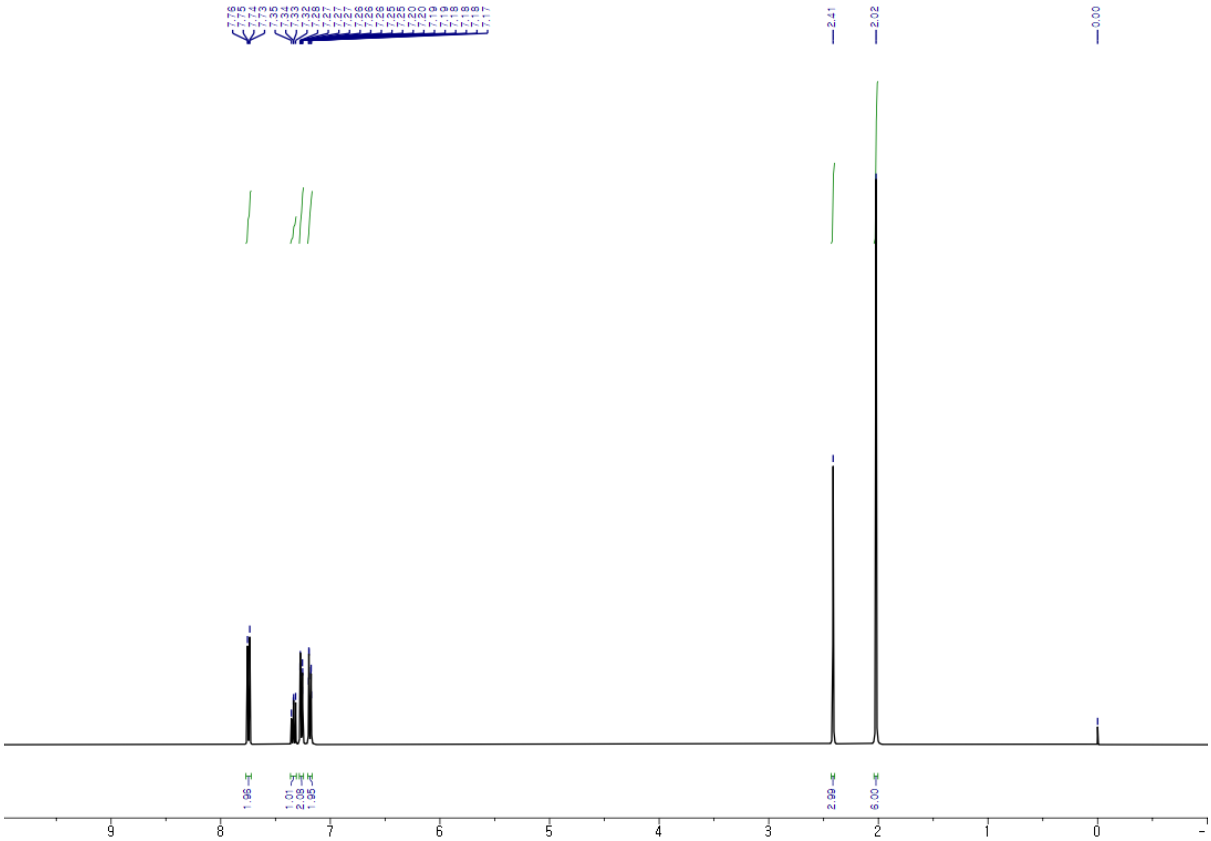

Figure S84. ^{1}H NMR spectrum of **31** (400 MHz, $CDCl_3$, 300 K)

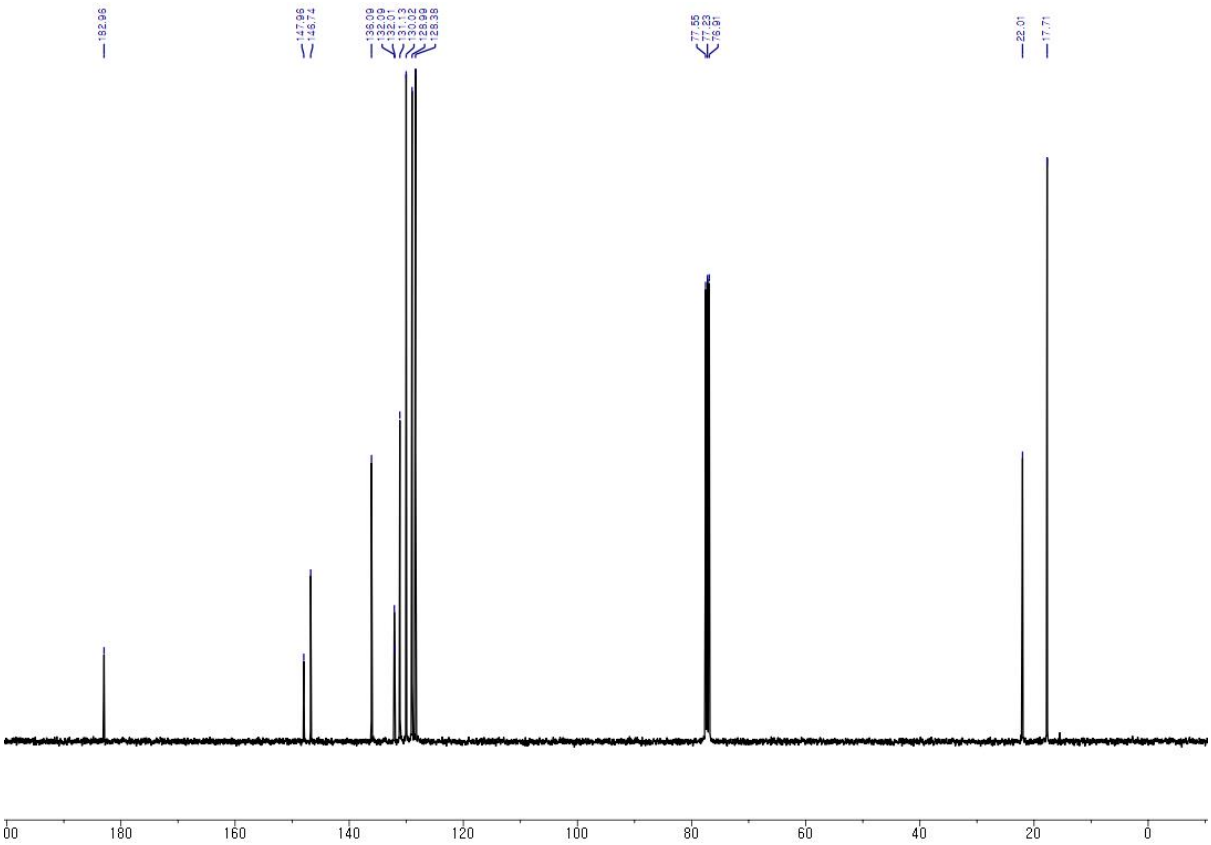

Figure S85. ^{13}C NMR spectrum of **31** (101 MHz, $CDCl_3$, 300 K)

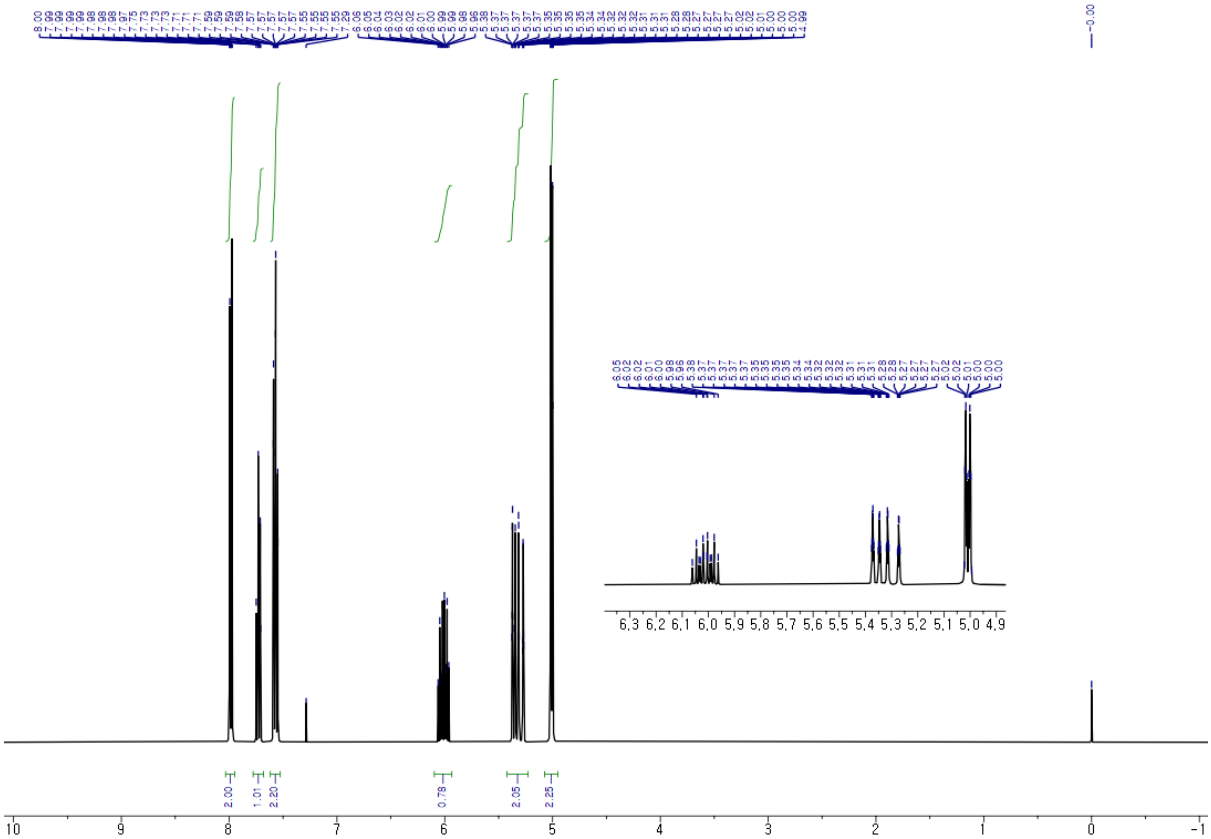

Figure S86. ^{1}H NMR spectrum of **32** (400 MHz, $CDCl_3$, 300 K)

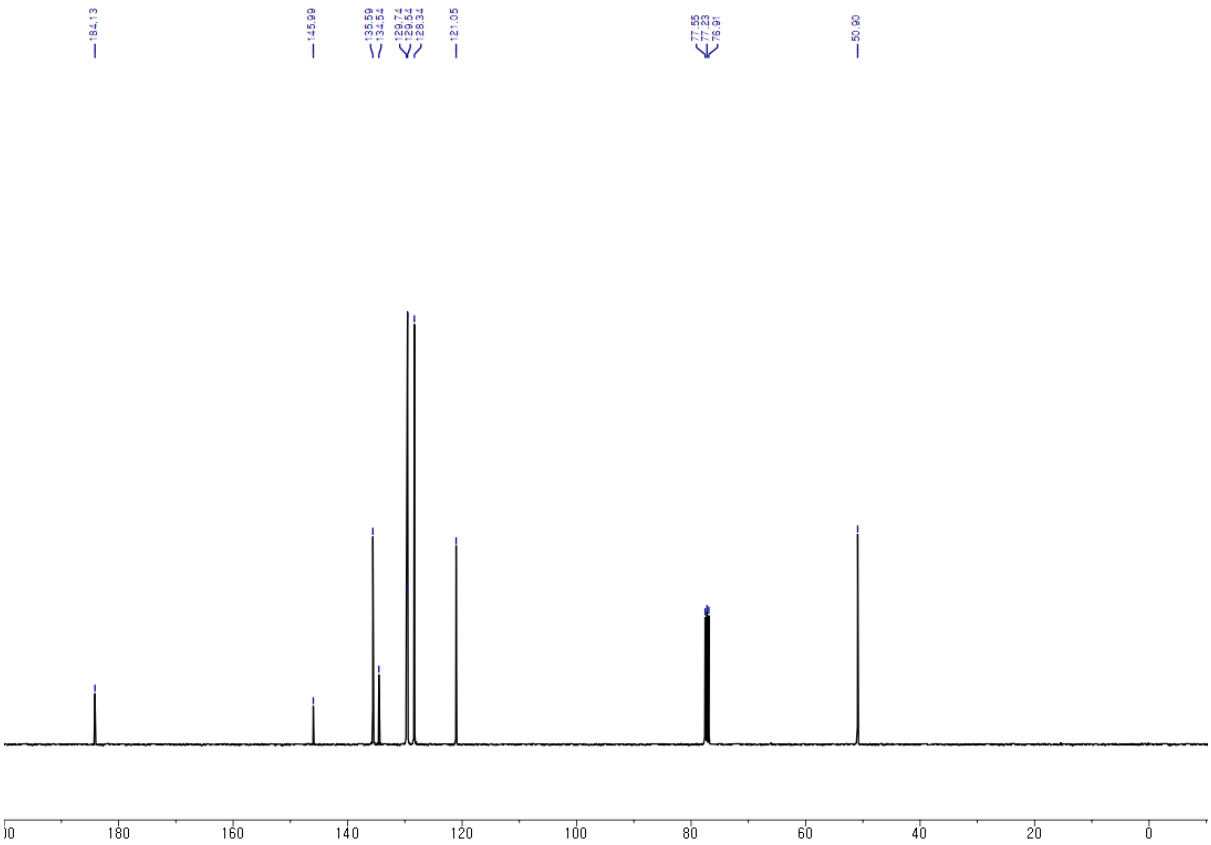

Figure S87. ^{13}C NMR spectrum of **32** (101 MHz, $CDCl_3$, 300 K)

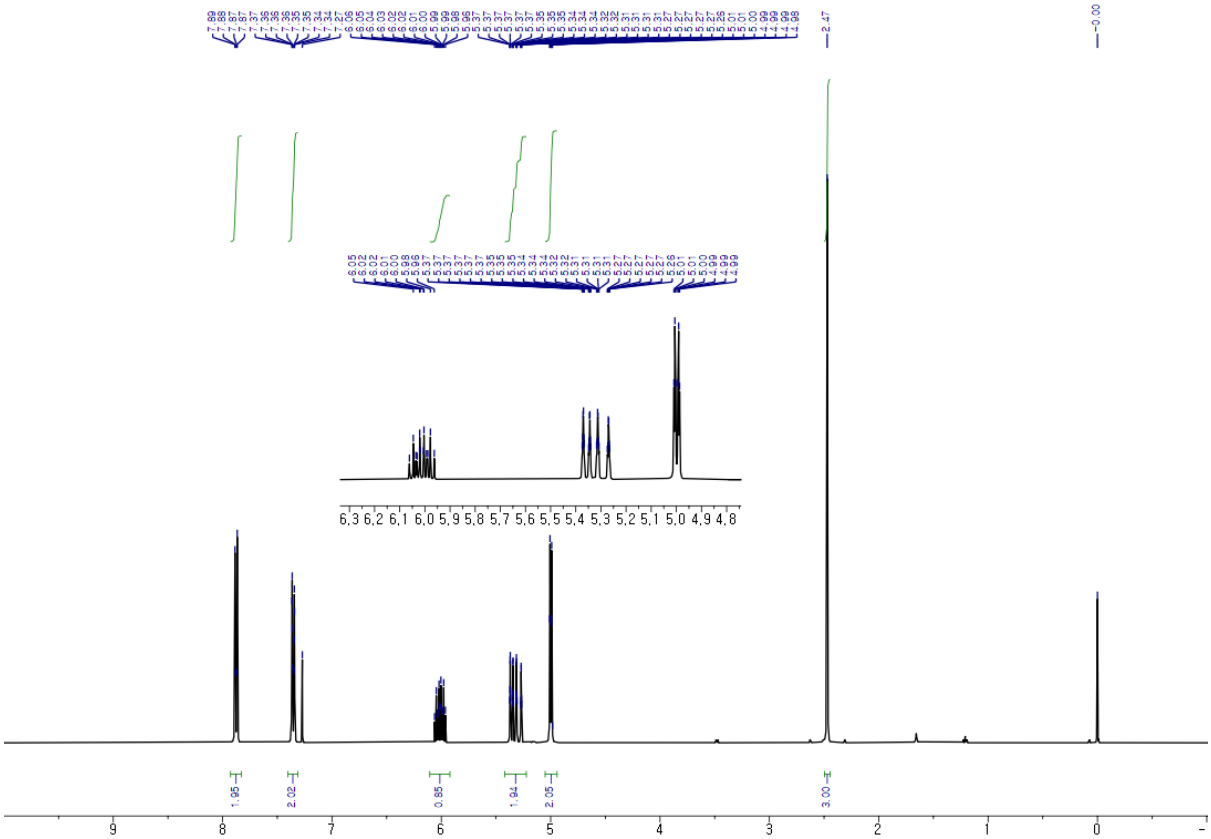

Figure S88. ^{1}H NMR spectrum of **33** (400 MHz, $CDCl_3$, 300 K)

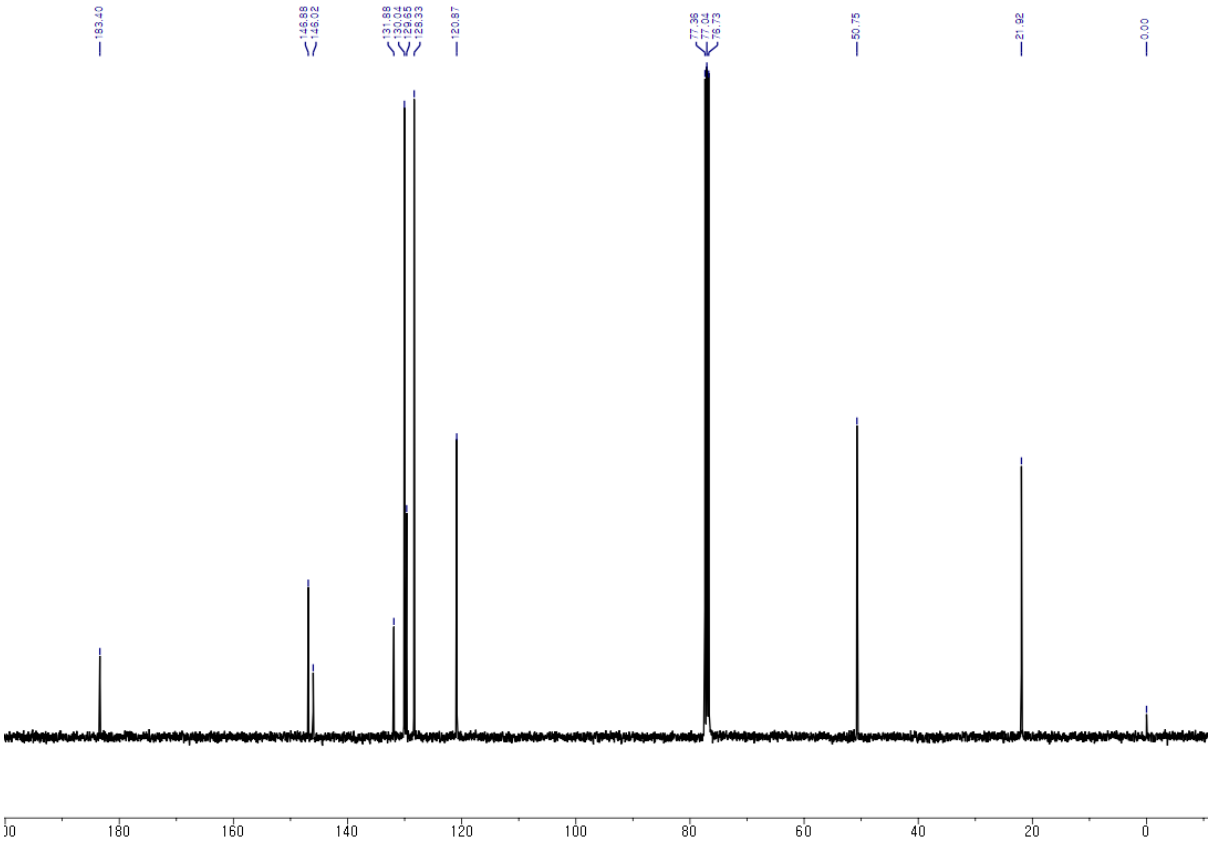

Figure S89. ^{13}C NMR spectrum of **33** (101 MHz, $CDCl_3$, 300 K)

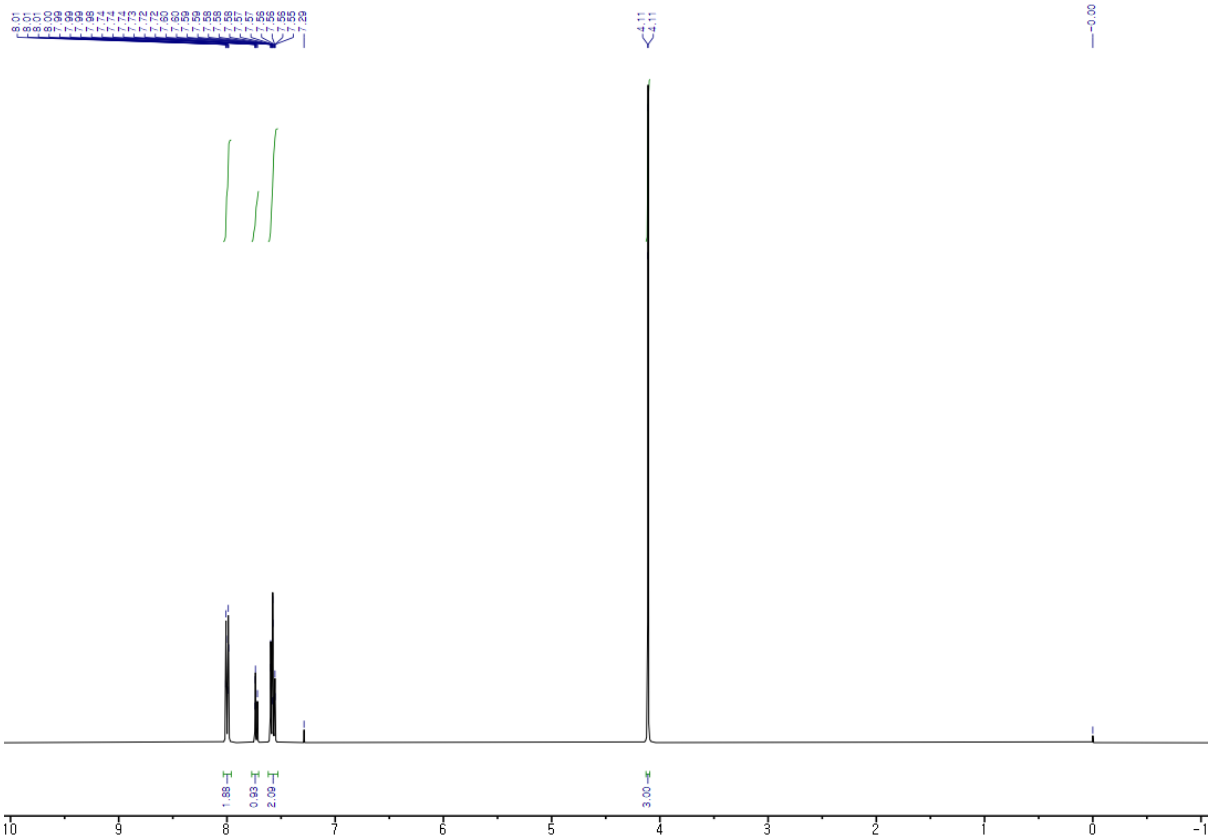

Figure S90. ^{1}H NMR spectrum of **34** (400 MHz, $CDCl_3$, 300 K)

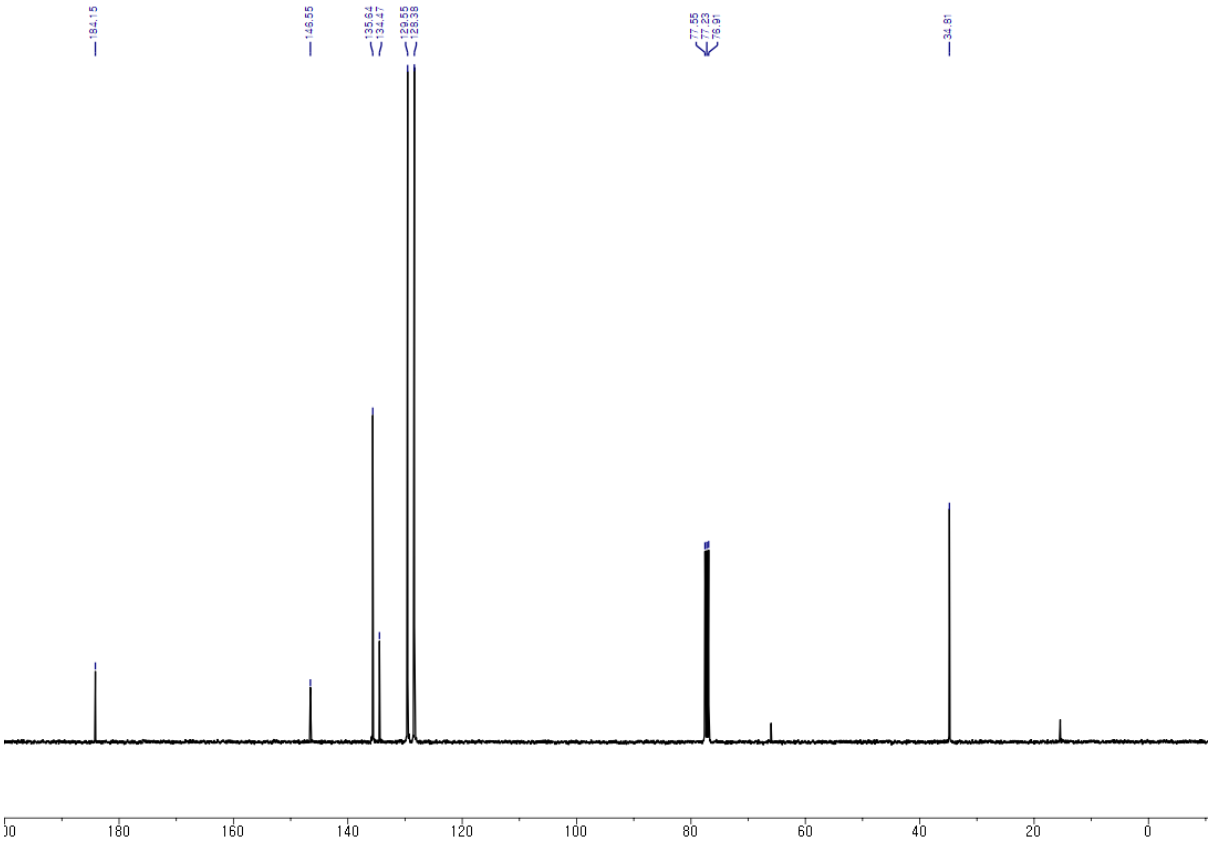

Figure S91. ^{13}C NMR spectrum of **34** (101 MHz, $CDCl_3$, 300 K)

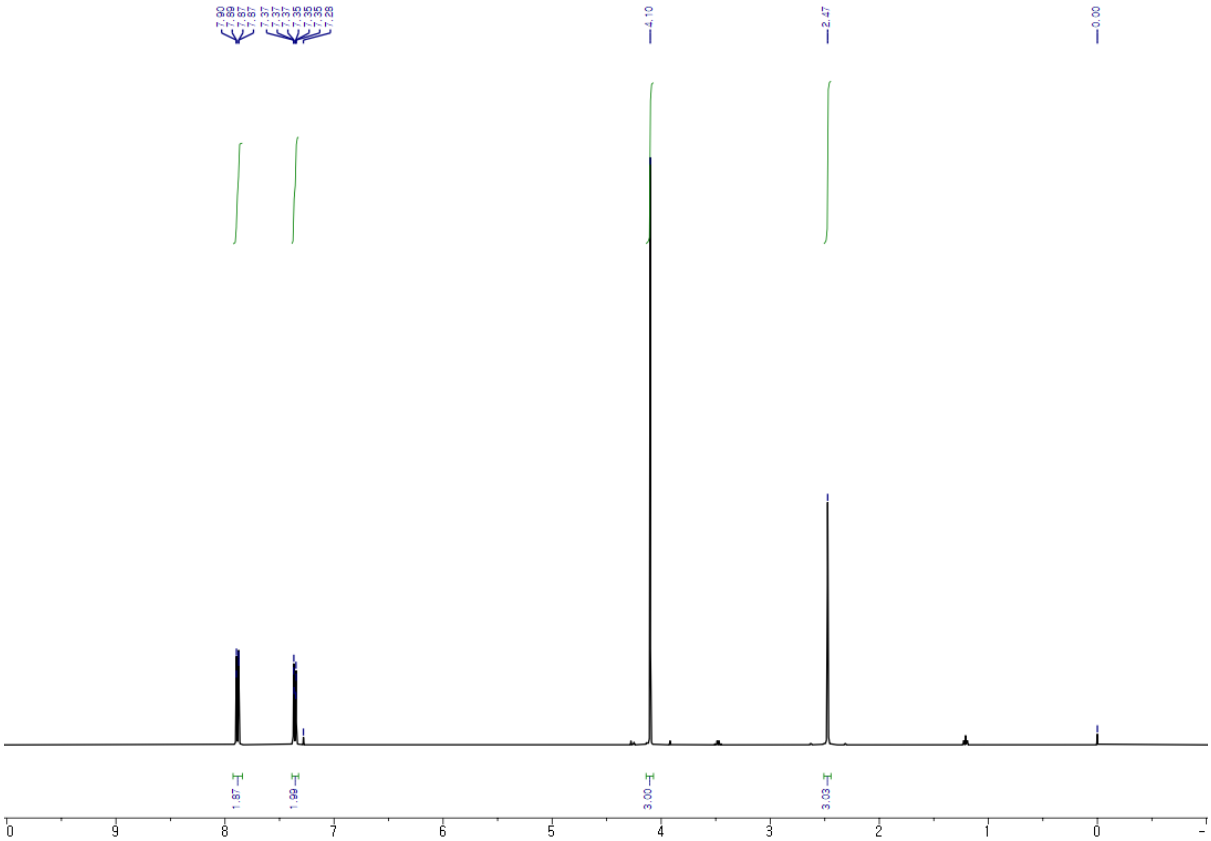

Figure S92. ^{1}H NMR spectrum of **35** (400 MHz, $CDCl_3$, 300 K)

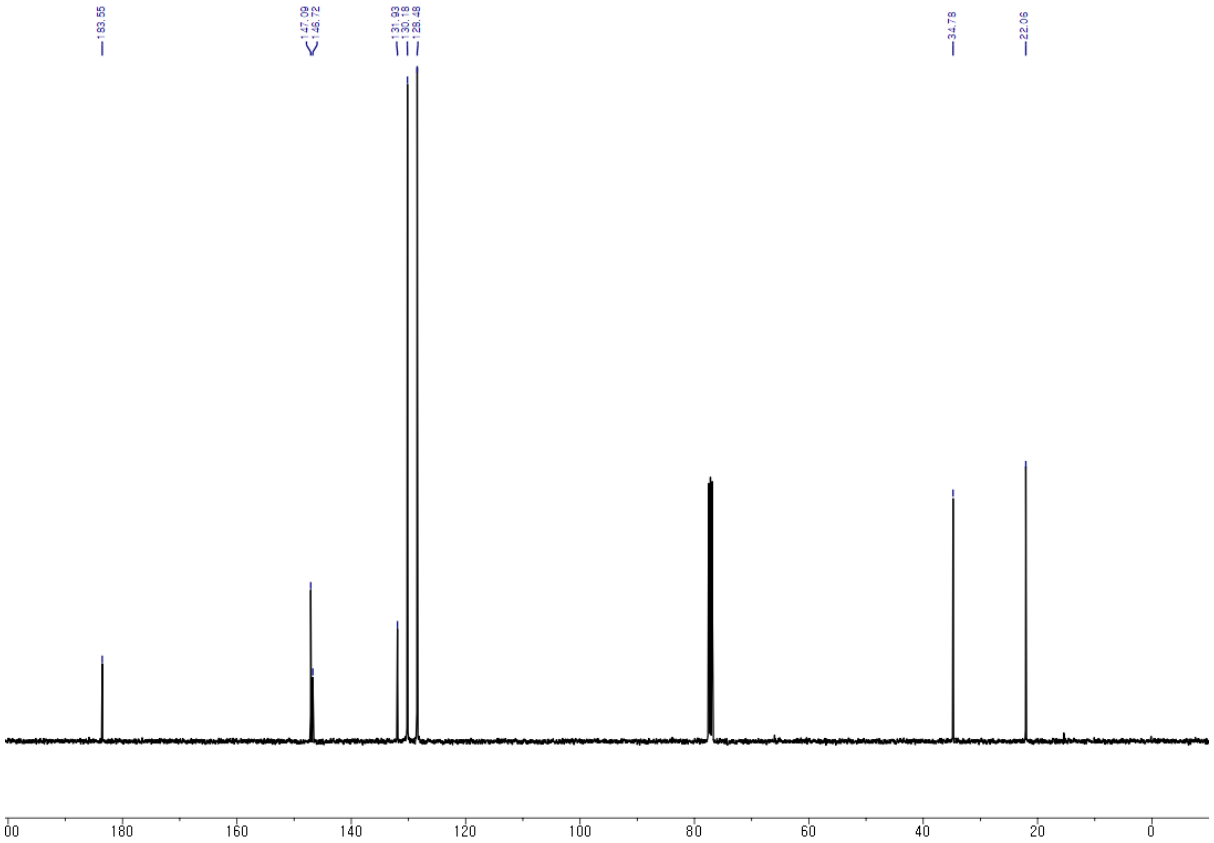

Figure S93. ^{13}C NMR spectrum of **35** (101 MHz, $CDCl_3$, 300 K)

Figure S94. [1]H-NMR spectrum of *N*-methylene proton regions (germinal coupling) of 6-membered complex, **18**

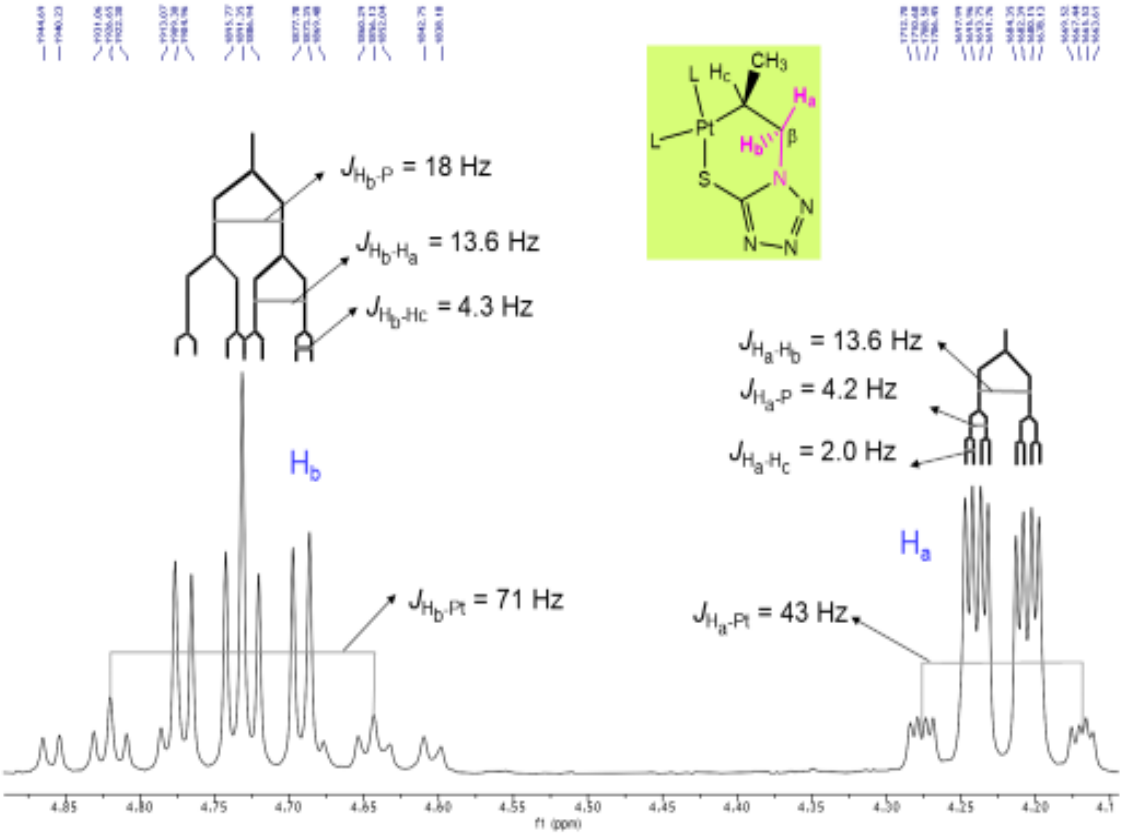

Figure S95. ^{1}H-NMR spectra of methyl signal of 6-membered complexes, **18** (the below, A is a normal ^{1}H-NMR. The above, B is a phosphorus decoupled spectrum)

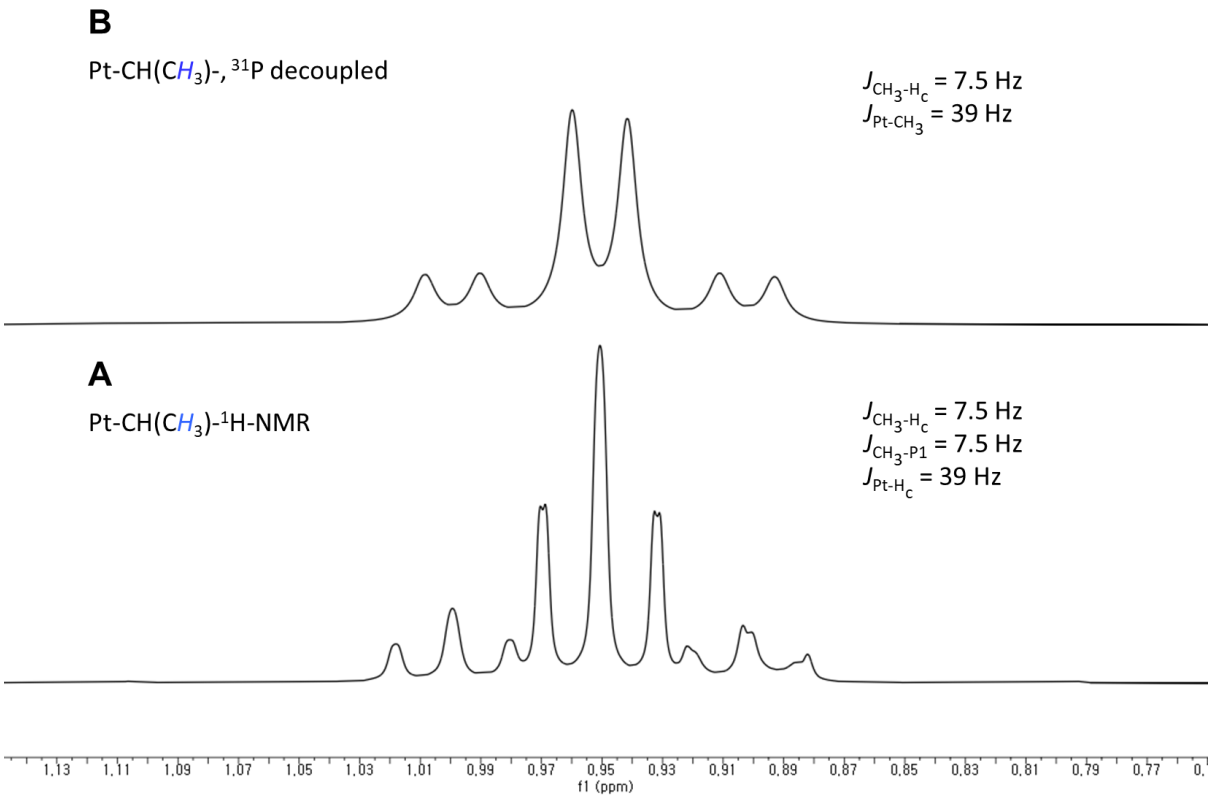

Figure S96 The Pt(II) Hydride region in the variable ^{1}H-NMR (400 MHz) spectra of complex **16.**