Electronic Supplementary Information for

Novel Bidentate N-coordinated Aluminum Complexes: Synthesis, Characterization, and Efficient Catalysis for Hydrophosphonylation

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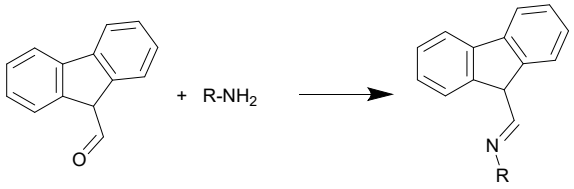
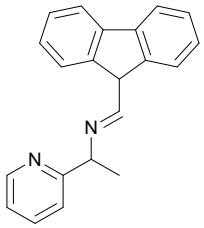
I. Synthesis and characterization data of proligands L^1 – L^3

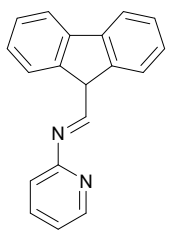


R= 2-Pyridyl-CH(CH_3) (L^1)
R= 2-Pyridyl (L^2)
R=N(CH_3)$_2$-Cy, (Cy=2-cyclohexyl) (L^3)

Scheme 1 Preparation of L^1-L^3

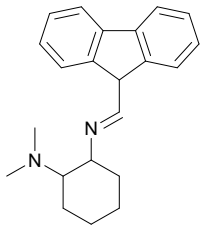


L^1 : Add 9-fluorenecarboxaldehyde (4.8517 g, 25 mmol) and 1-(2-pyridyl)ethylamine (3.0520 g, 25 mmol) to a 250 mL single-necked flask containing 50 mL of ethanol. Heat the mixture under reflux and monitor the reaction progress using thin-layer chromatography (TLC). After the reaction is complete, remove the ethanol under reduced pressure. The residue is then recrystallized in a mixture of ethyl acetate and petroleum ether, resulting in the precipitation of a white solid **L^1**, white powder, 6.6339 g, yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.76 – 8.67 (m, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 7.4 Hz, 1H), 7.84 (d, J = 7.7 Hz, 1H), 7.72 (td, J = 7.7, 1.8 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.57–7.46 (m, 2H), 7.41–7.32 (m, 3H), 7.30–7.25 (m, 2H), 6.51 (dd, J = 13.4, 6.9 Hz, 1H), 4.75 (p, J = 6.8 Hz, 1H), 1.73 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 161.5, 149.5, 140.1, 137.3, 137.1, 136.4, 135.3, 135.0, 126.2, 125.9, 124.0, 123.3, 122.6, 121.3, 120.8, 120.0, 119.7, 116.8, 107.0, 58.6, 24.4.



L^2 : By reacting 9-fluorenecarboxaldehyde (4.8517 g, 25 mmol) with 2-aminopyridine

(2.3528 g, 25 mmol) using the same method as the synthesis of **L[1]**, a yellow-green solid compound named **L[2]** is obtained, yellow-green powder, 6.1452 g, yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.31 (dd, J = 4.9, 1.0 Hz, 1H), 8.24 (d, J = 12.2 Hz, 1H), 7.90–7.86 (m, 1H), 7.84–7.80 (m, 1H), 7.79–7.75 (m, 1H), 7.74–7.70 (m, 1H), 7.59–7.52 (m, 2H), 7.41–7.36 (m, 2H), 7.33 (td, J = 6.9, 1.4 Hz, 2H), 6.87 (ddd, J = 7.3, 5.0, 0.9 Hz, 1H), 6.77 (dt, J = 8.4, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 298K) δ 152.8, 148.5, 139.6, 138.8, 138.2, 136.5, 135.8, 126.5, 125.8, 125.1, 124.6, 122.1, 120.2, 119.7, 118.4, 117.2, 112.8, 108.9.



L[3] : Synthesize white solid **L[3]** by reacting 9-fluorenecarboxaldehyde (4.8517 g, 25 mmol) with (1R,2R)-1-amino-2-(dimethylamino)cyclohexane (3.5550 g, 25 mmol) using the same method as the synthesis of **L[1]**, white powder, 7.3140g, yield: 92%.^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.99 (dd, J = 7.6, 1.1 Hz, 1H), 7.92 (dd, J = 7.6, 1.1 Hz, 1H), 7.72–7.66 (m, 2H), 7.59 (d, J = 14.2 Hz, 1H), 7.46–7.40 (m, 1H), 7.37–7.31 (m, 2H), 7.28–7.22 (m, 1H), 7.00 (d, J = 14.1 Hz, 1H), 3.12 (dt, J = 10.3, 5.1 Hz, 1H), 2.47–2.39 (m, 2H), 2.39–2.34 (m, 6H), 1.95–1.82 (m, 3H), 1.39–1.23 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 140.3, 136.8, 136.5, 134.5, 134.4, 126.0, 125.6, 123.3, 122.5, 120.7, 119.8, 119.6, 116.5, 105.6, 67.6, 55.2, 40.1, 31.9, 25.1, 24.3, 20.7.

II.The ^{1}H NMR, ^{13}C NMR spectra of proligands L^1 – L^3

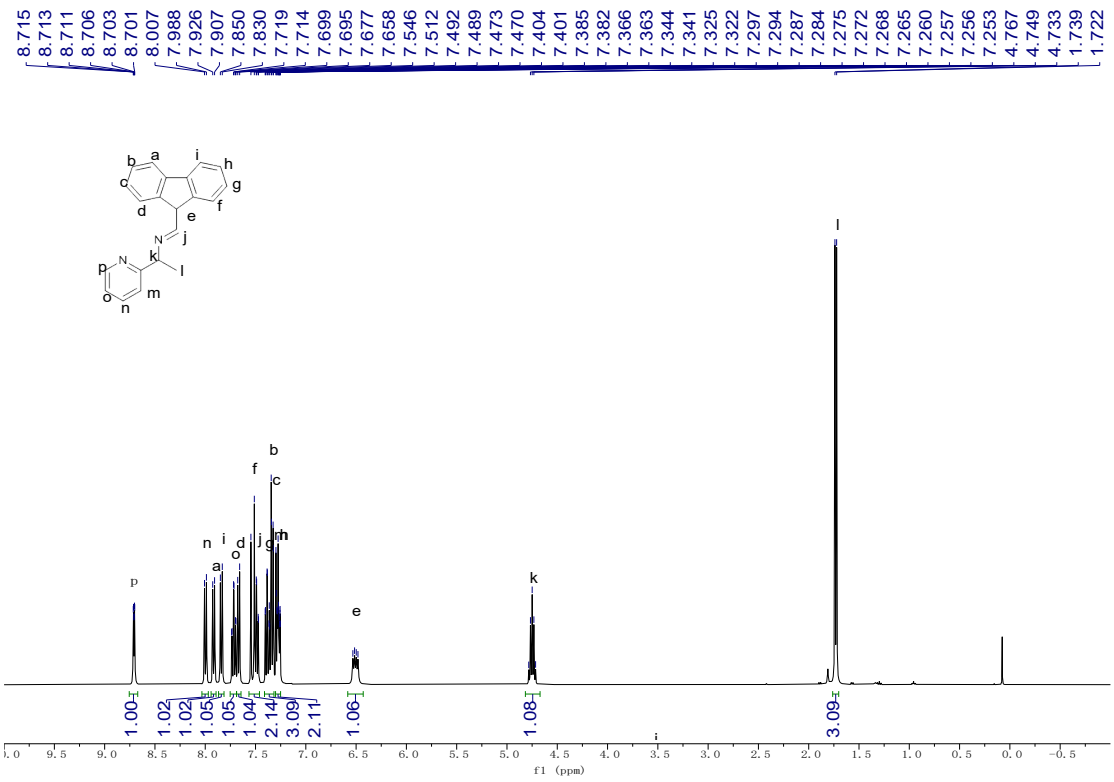


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **L^1**

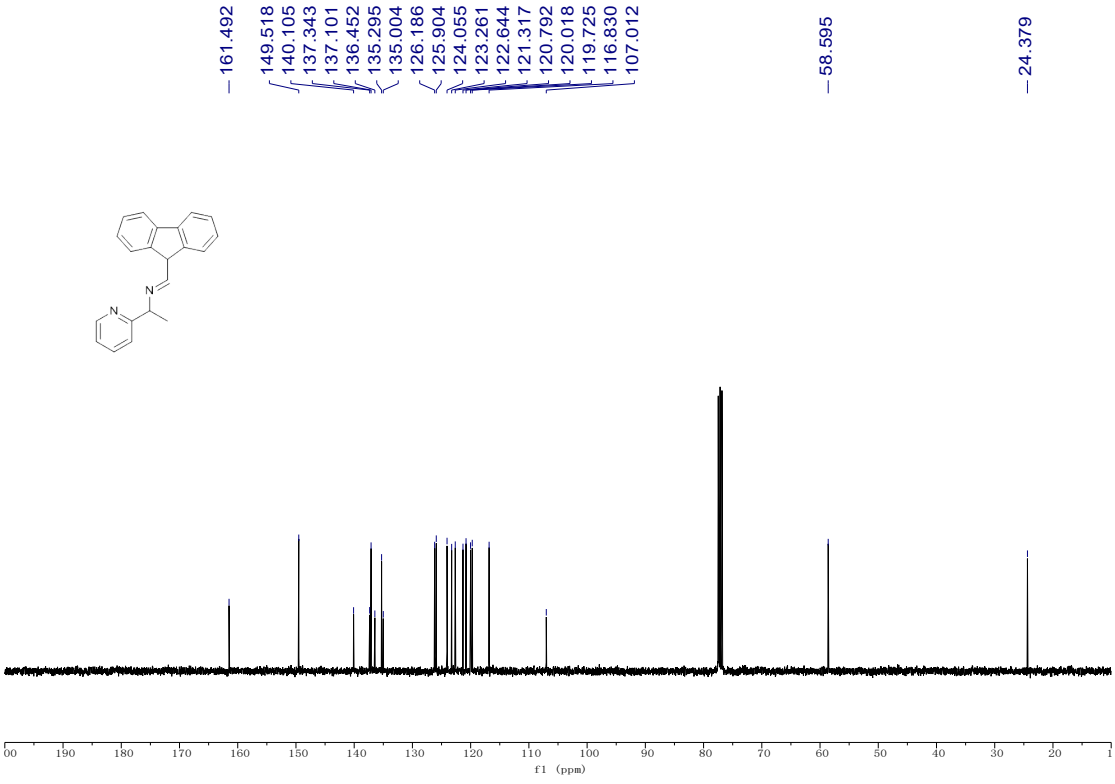


Figure S2. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **L^1**

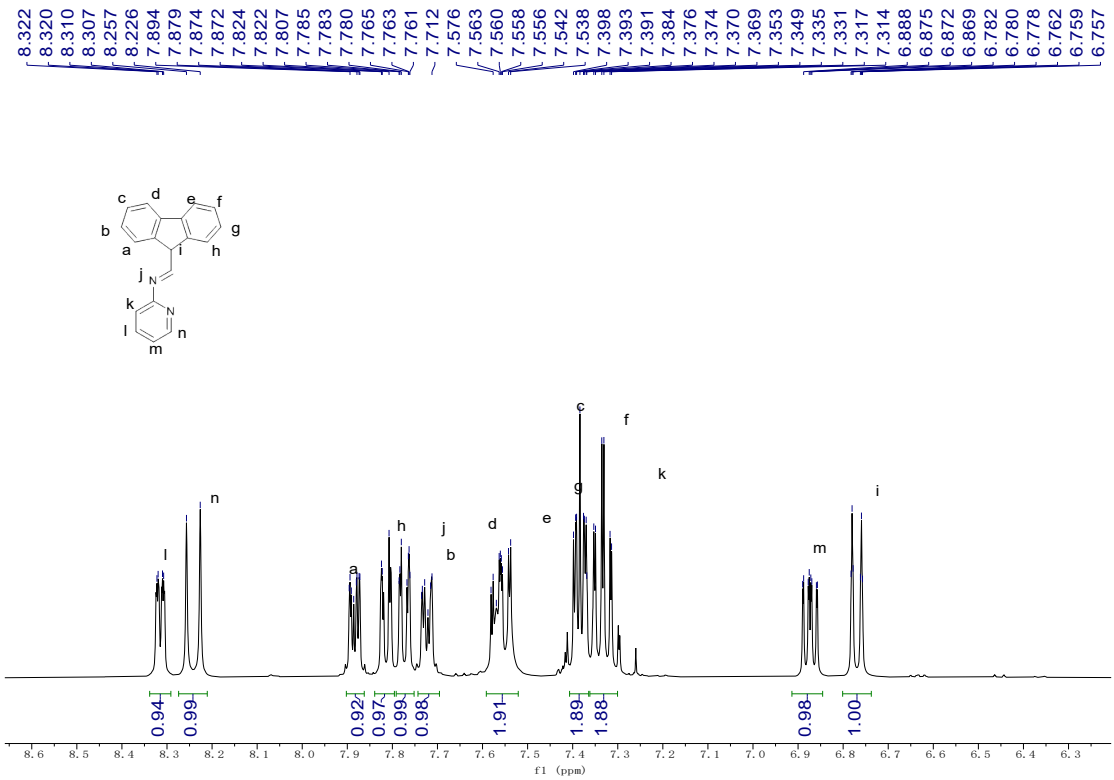


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **L²**

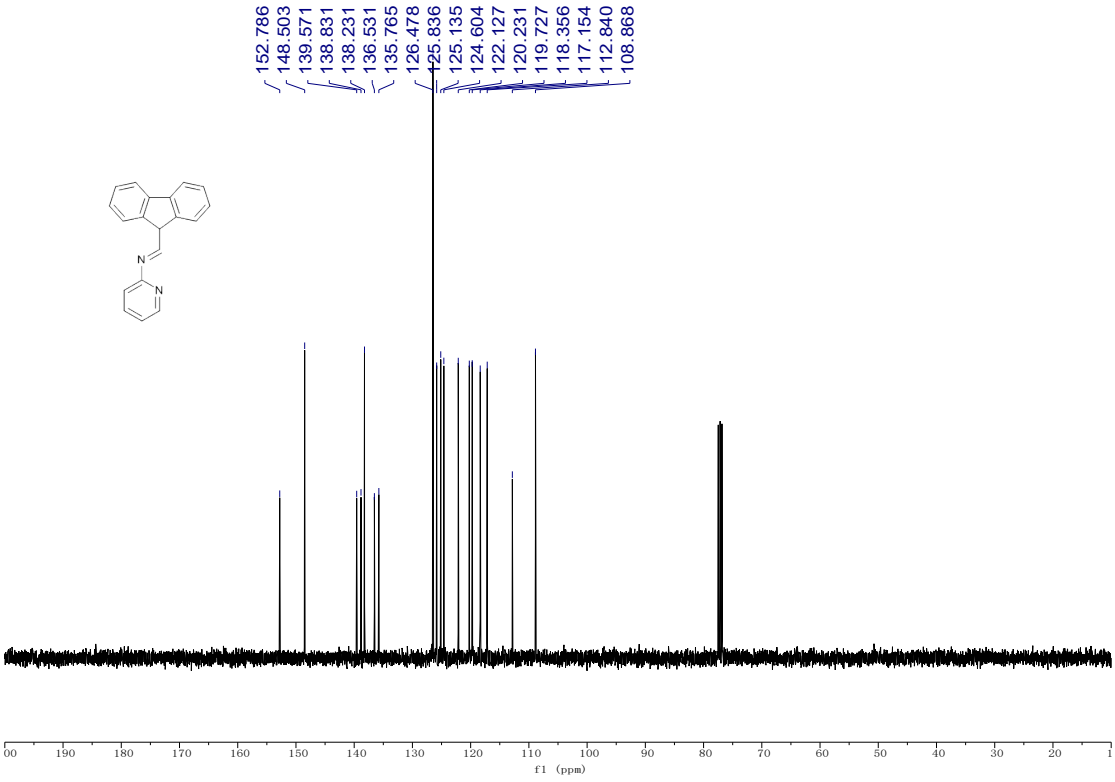


Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **L²**

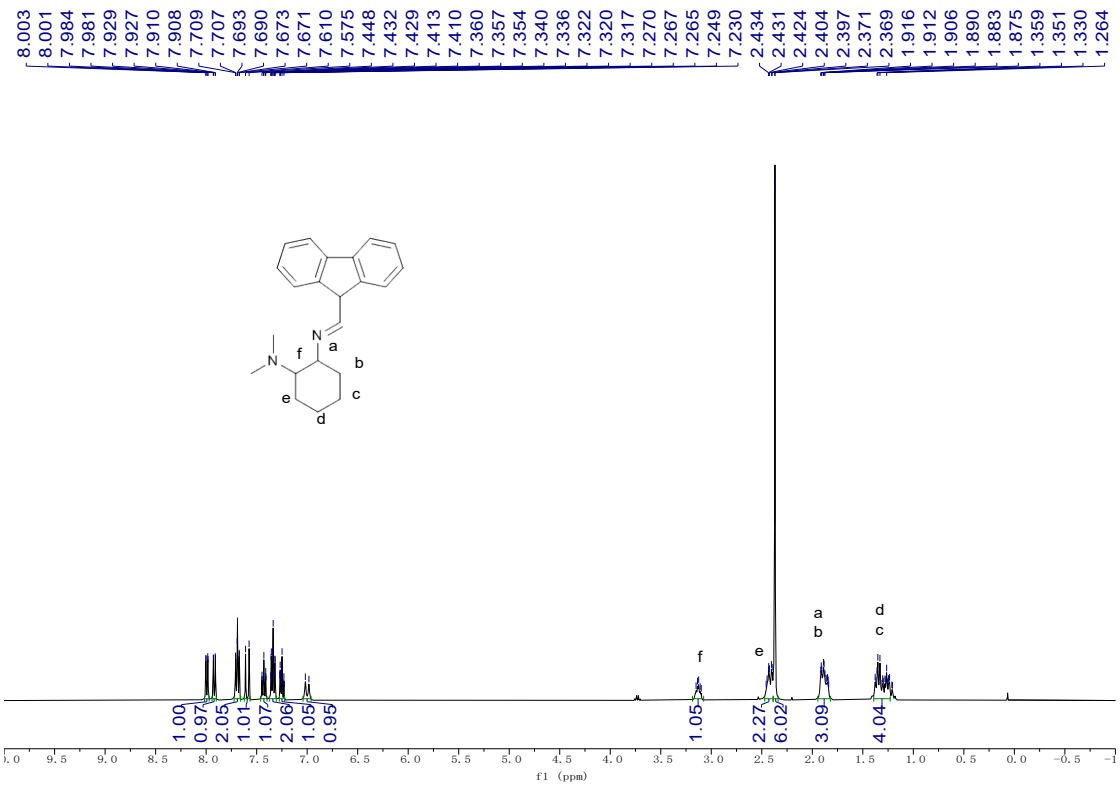


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **L³**

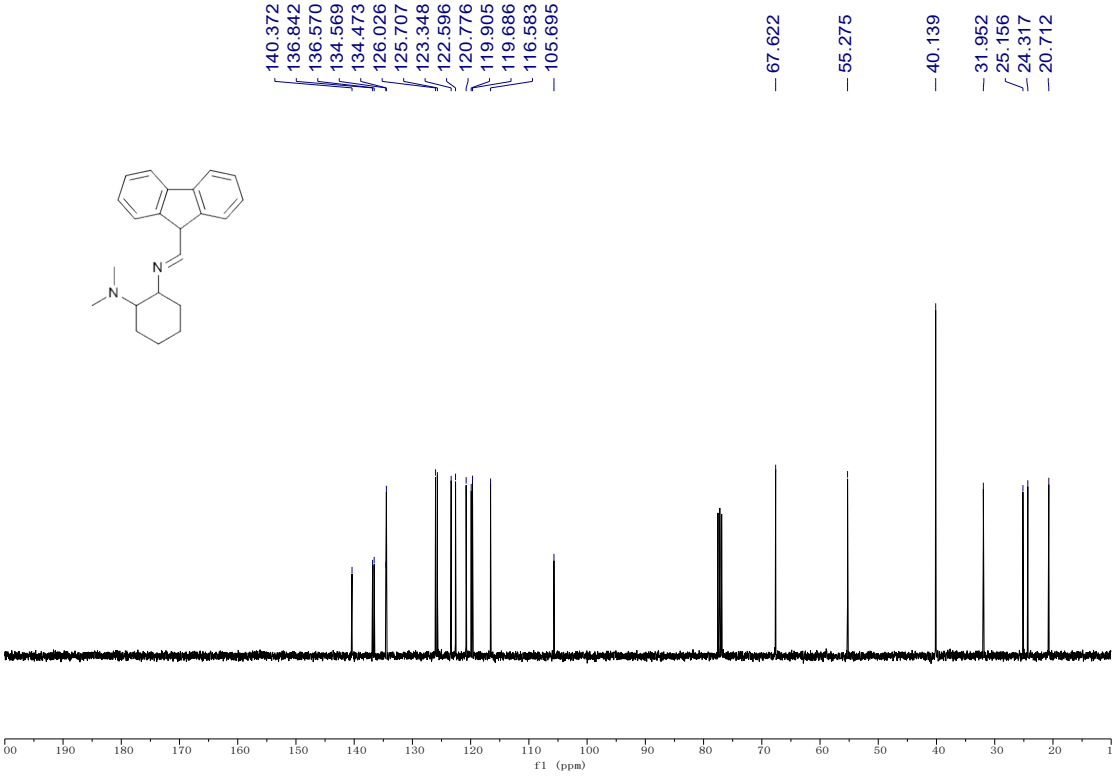


Figure S6. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **L³**

III. The ^{1}H NMR, ^{13}C NMR spectra of Complexes 1-5

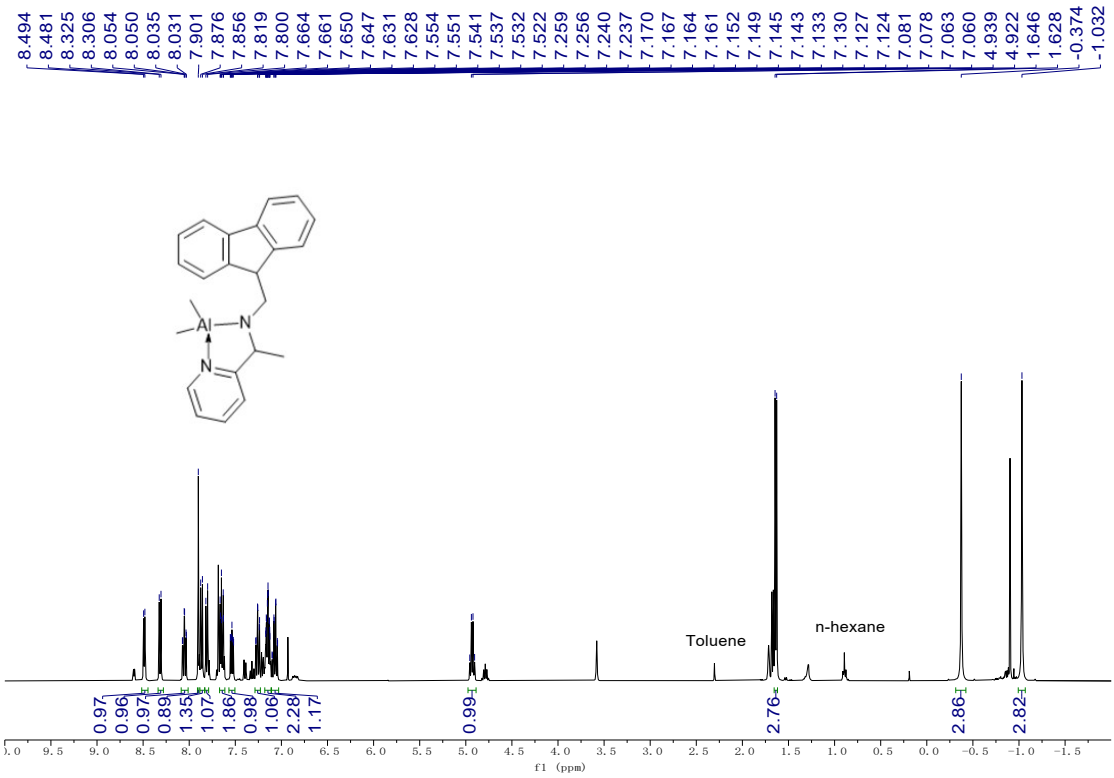


Figure S7. ^{1}H NMR (400 MHz, THF-d_8) spectra of Complex **1**

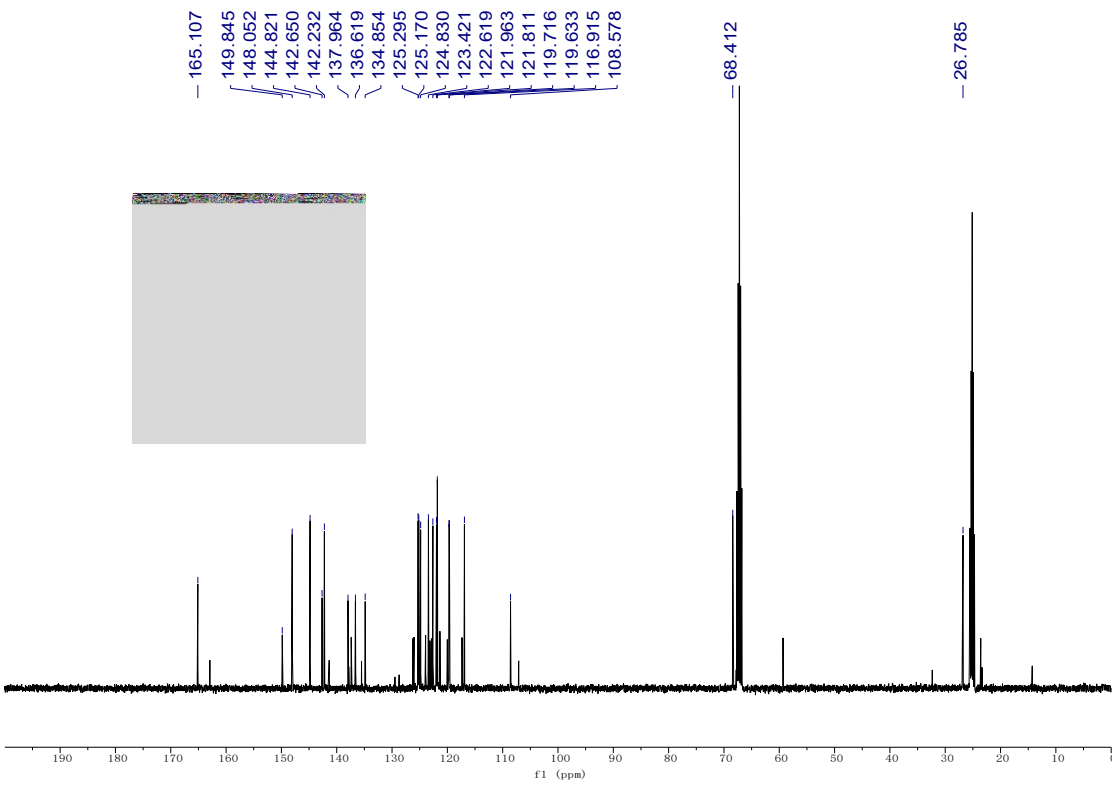


Figure S8. ^{13}C NMR (101 MHz, THF-d_8) spectra of Complex **1**

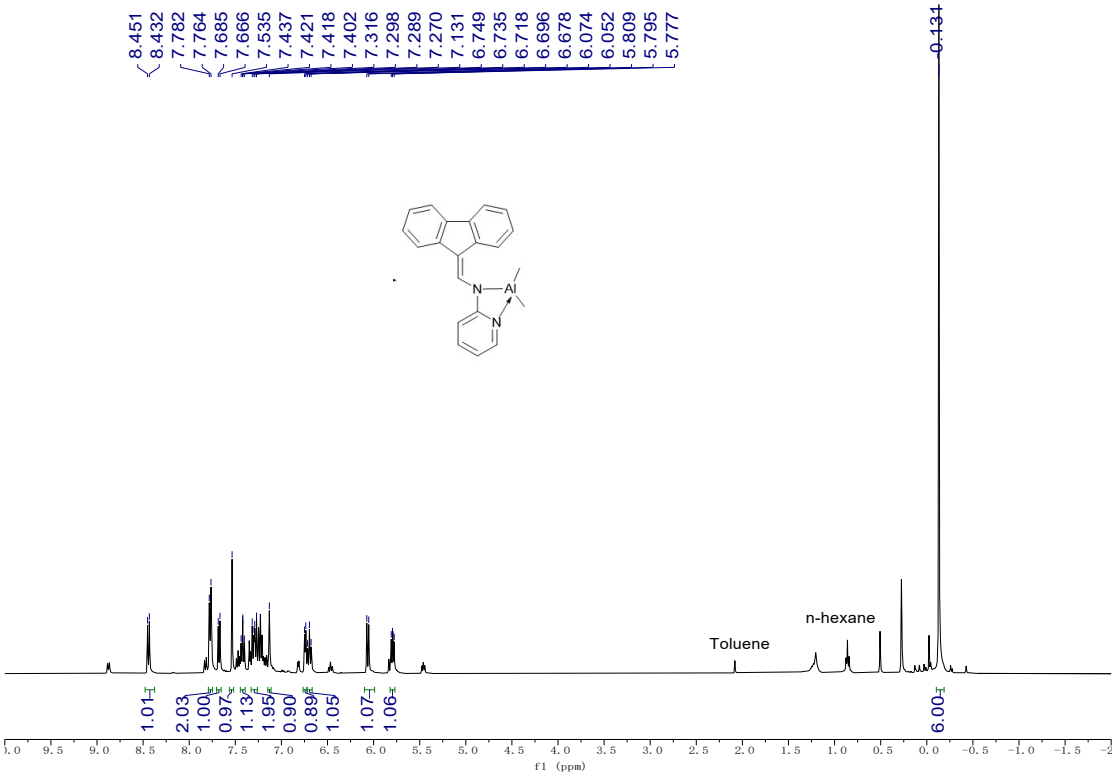


Figure S9. ^{1}H NMR (400 MHz, C_6D_6) spectra of Complex **2**

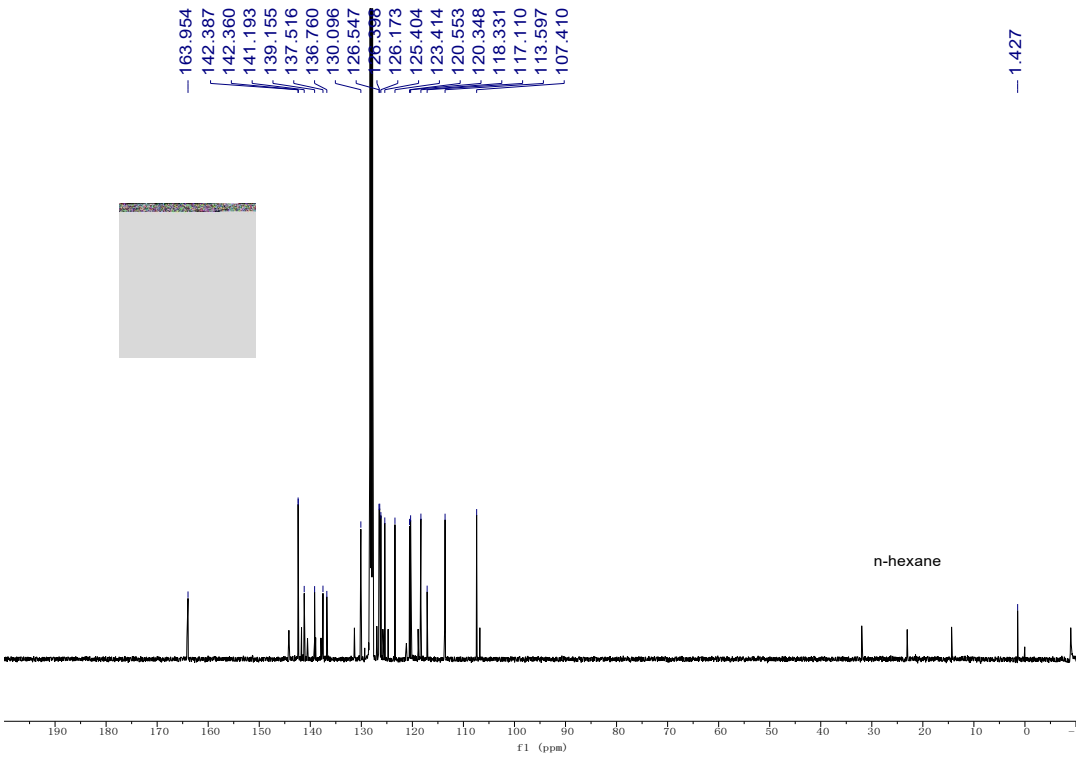


Figure S10. ^{13}C NMR (101 MHz, C_6D_6) spectra of Complex **2**

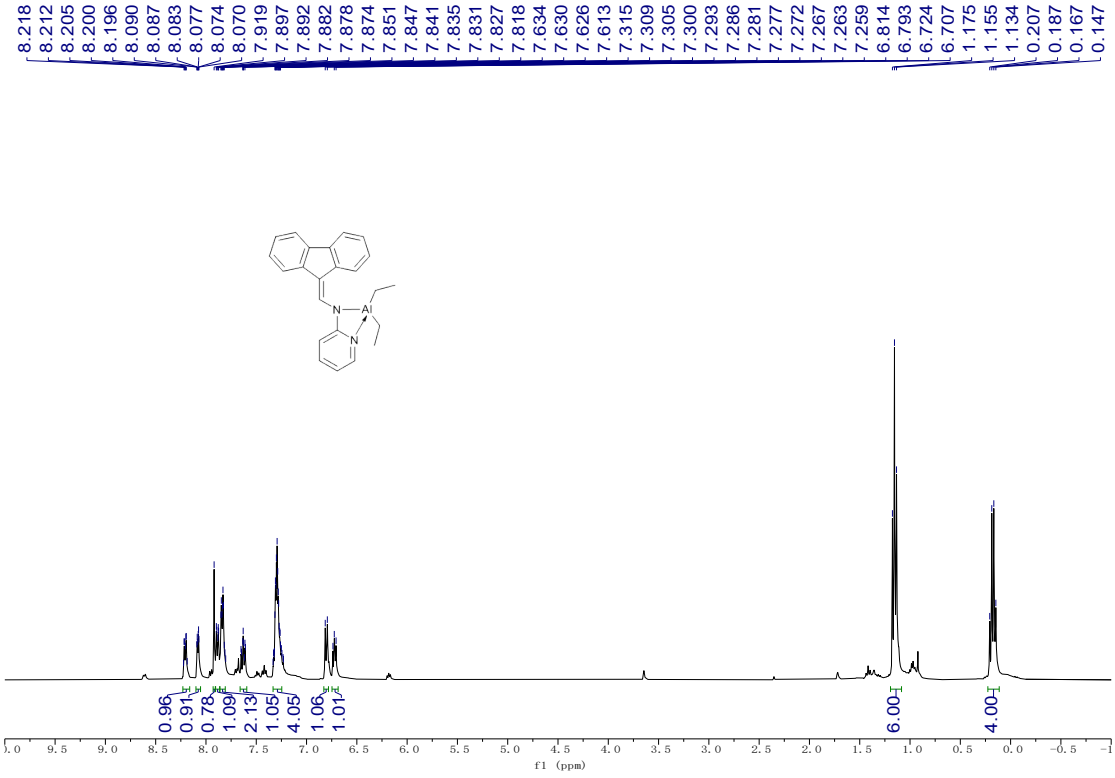


Figure S11. ^{1}H NMR (400 MHz, THF-d_8) spectra of Complex **3**

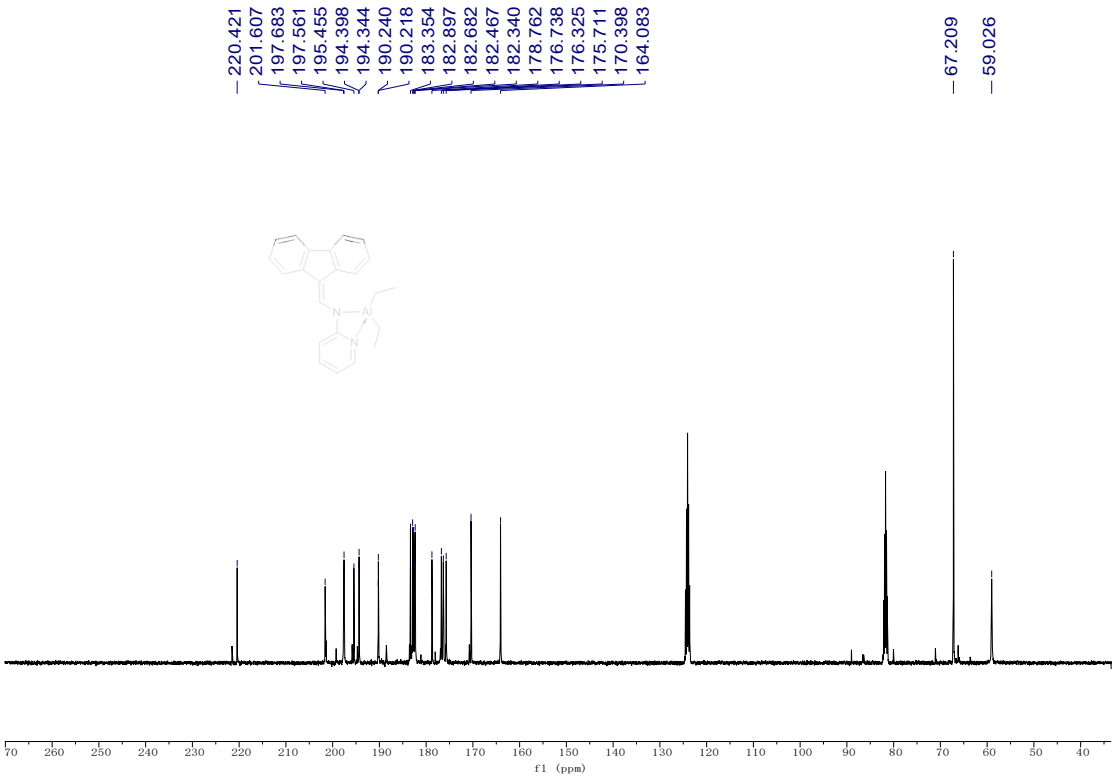


Figure S12. ^{13}C NMR (101 MHz, THF-d_8) spectra of Complex **3**

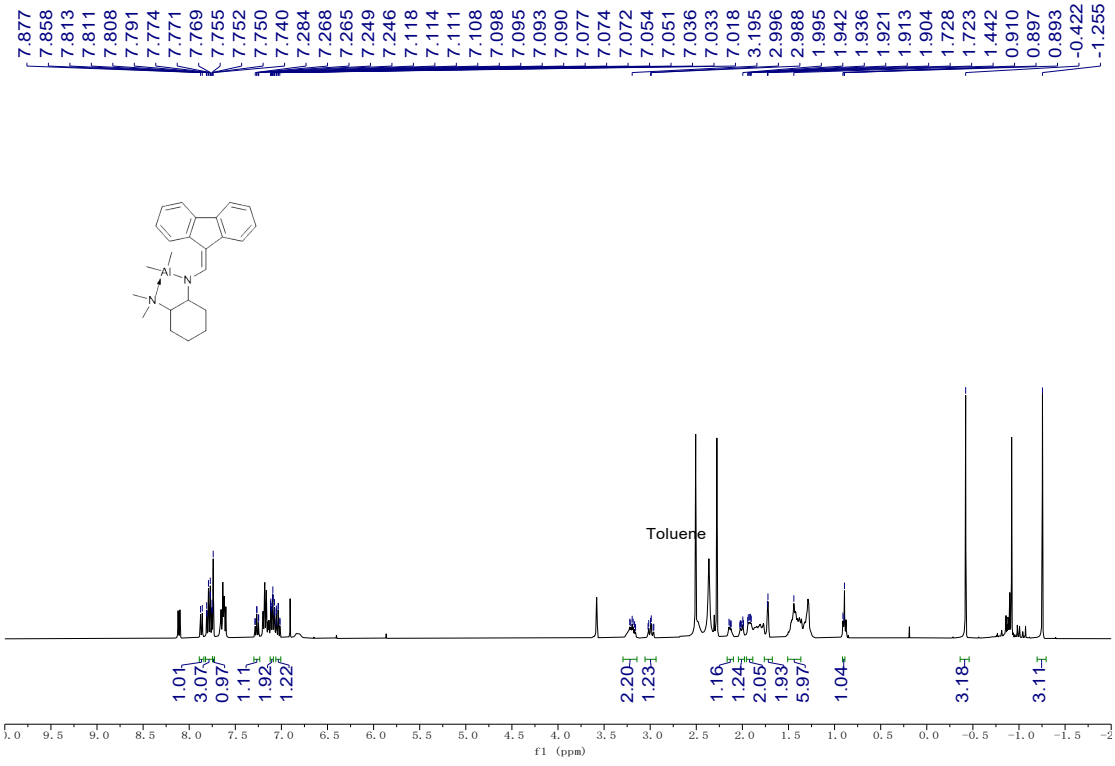


Figure S13. ^{1}H NMR (400 MHz, THF-d_8) spectra of Complex **4**

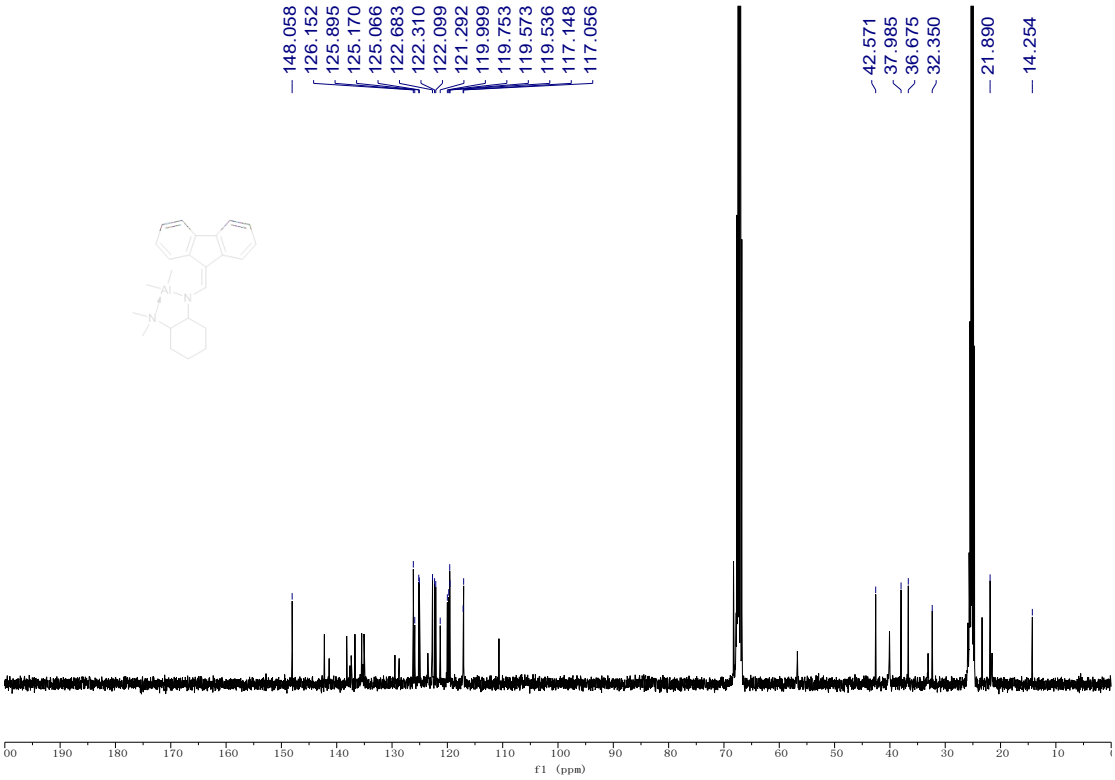


Figure S14. ^{13}C NMR (101 MHz, THF-d_8) spectra of Complex **4**

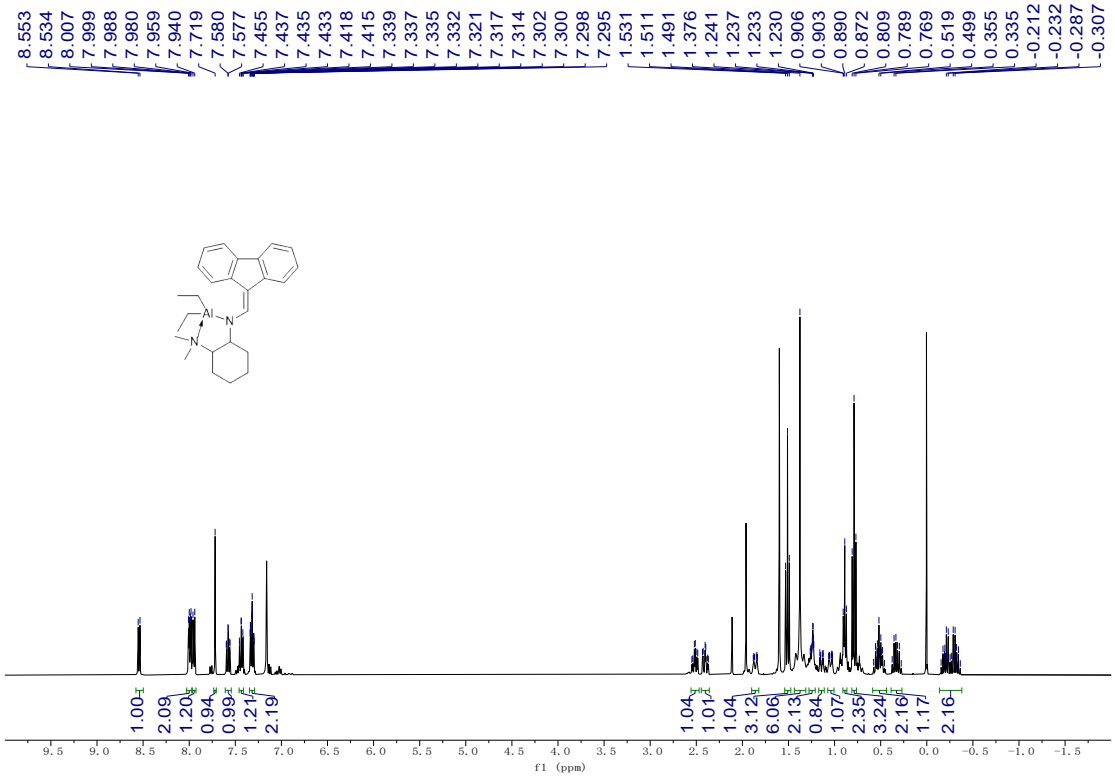


Figure S15. ^{1}H NMR (400 MHz, C_6D_6) spectra of Complex **5**

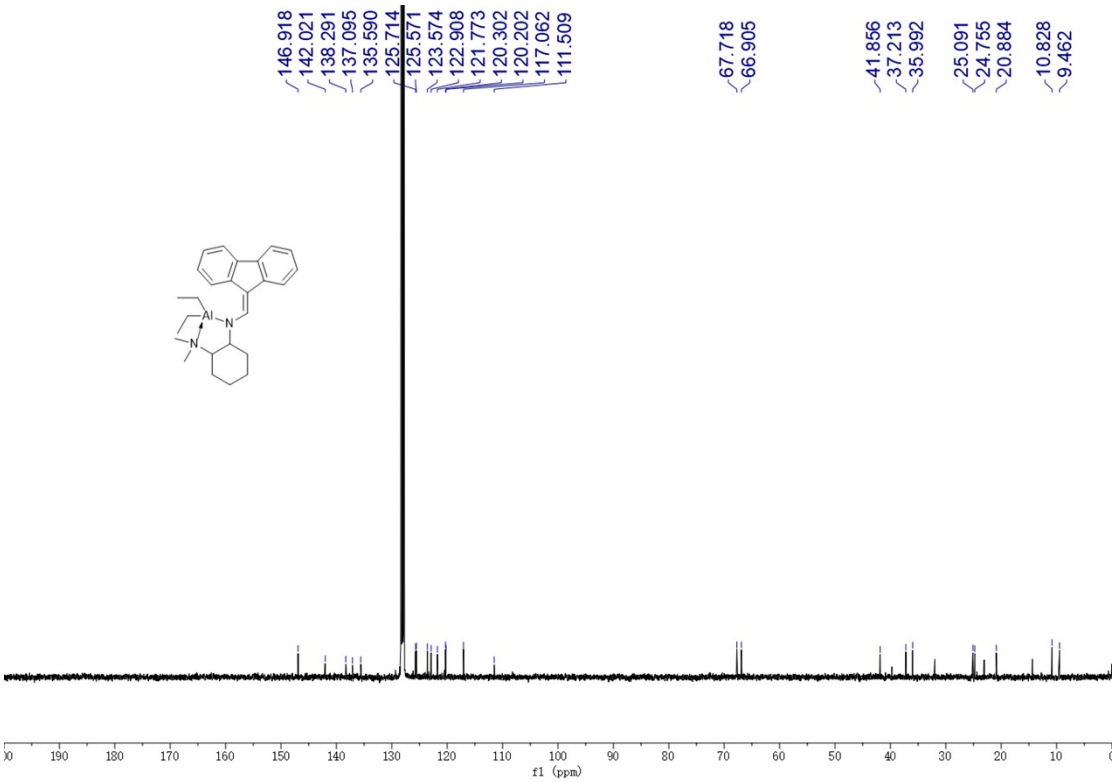


Figure S16. ^{13}C NMR (101 MHz, C_6D_6) spectra of Complex **5**

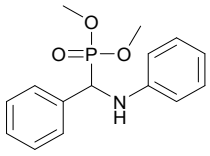
V. Crystallographic data of Complexes 1-5

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{23}H_{23}AlN_2$	$C_{21}H_{19}AlN_2$	$C_{23}H_{23}AlN_2$	$C_{24}H_{31}AlN_2$	$C_{26}H_{35}AlN_2$
Formula weight	354.41	326.36	354.41	374.49	402.54
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
λ(Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*I2/a*	$P2_1/n$	$P2_1/c$	*C2/c*	*C2/c*
a (Å)	16.7984(9)	12.9752(7)	8.9561(5)	23.8578(15)	23.2371(14)
b (Å)	11.7252(5)	7.9387(4)	14.6783(8)	11.8686(6)	13.1513(6)
c (Å)	20.9895(9)	17.5169(9)	14.9503(8)	15.7892(7)	15.8236(7)
α(°)	90	90	90	90	90
β (°)	104.505(5)	94.684(5)	90.965(4)	100.681(5)	100.535(5)
γ (°)	90	90	90	90	90
V (Å^3)	4002.4(3)	1798.32(16)	1965.09(19)	4393.4(4)	4754.1(4)
Z	8	4	4	8	8
D_{calcd} (mg m^{-3})	1.176	1.205	1.198	1.132	1.125
μ (mm^{-1})	0.109	0.116	0.111	0.103	0.099
F (000)	1504.0	688.0	752.0	1616.0	1744.0
θ range (°)	4.008 to 59.342	4.07 to 59.278	3.888 to 59.132	4.472 to 59.564	4.234 to 59.21
Reflections collected	24471	10961	12566	24600	29338
Data/restraints/parameters	5057/0/238	4378/0/219	4758/0/237	5576/0/248	6114/15/266
Goodness-of-fit on F^2	0.972	1.074	0.976	0.969	1.053
R_1wR_2 ($I > 2\sigma(I)$)	0.0579, 0.1510	0.0478, 0.1312	0.0620, 0.1758	0.0584, 0.1714	0.0574, 0.1627
Largest diff peak/hole / e Å^{-3}	0.37/-0.22	0.21/-0.31	0.53/-0.49	0.28/-0.37	0.28/-0.21

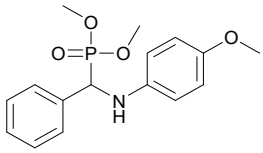
VI. Selected Bond Distances (Å) and Angles (deg) for Complexes 1−5

	1	2	3	4	5
Al(1)-N(1)	1.9040(17)	1.9548(14)	1.963(2)	1.9088(16)	1.9109(15)
Al(1)-N(2)	1.9853(18)	1.9686(15)	1.968(2)	2.0218(17)	2.0377(16)
N(1)-C(1)	1.360(2)			1.359(2)	1.355(2)
N(1)-C(6)		1.365(2)	1.364(3)		
Al(1)-C(22)	1.947(2)				
Al(1)-C(23)	1.963(2)			1.952(3)	1.964(2)
Al(1)-C(24)				1.981(3)	1.990(2)
Al(1)-C(20)		1.942(2)	1.942(3)		
Al(1)-C(21)		1.948(2)	1.952(3)		
N(1)-Al(1)-N(2)	84.18(7)	68.40(6)	68.37(9)	86.50(7)	85.68(6)
C(20)-Al(1)-C(21)		120.74(11)	125.23(14)		
N(1)-Al(1) -C(20)		114.46(8)	110.25(12)		
N(1)-Al(1) -C(21)		118.04(9)	117.38(13)		
N(2)-Al(1) -C(20)		114.65(9)	113.71(13)		
N(2)-Al(1) -C(21)		108.65(8)	107.87(12)		
C(22)-Al(1)-C(23)	118.54(10)				
N(1)-Al(1) -C(22)	114.22(9)				
N(1)-Al(1) -C(23)	119.62(10)			113.68(10)	115.57(10)
N(2)-Al(1) -C(22)	109.41(10)				
N(2)-Al(1) -C(23)	103.45(9)			111.28(10)	107.76(9)
N(2)-Al(1) -C(24)				103.36(10)	104.05(8)
C(23)-Al(1)-C(24)				118.36(13)	120.85(11)
N(1)-Al(1) -C(24)				117.91(10)	115.36(9)

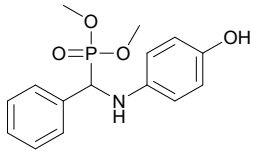
VII. Spectral data of the hydrophosphination products a-u



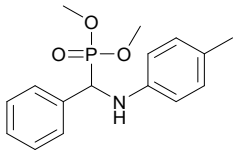
Dimethyl (phenyl(phenylamino)methyl)phosphonate (a)[1] **:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.49 (d, J = 7.3 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.31–7.25 (m, 1H), 7.16–7.06 (m, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 8.0 Hz, 2H), 4.92–4.77 (m, 2H), 3.77 (d, J = 10.7 Hz, 3H), 3.48 (d, J = 10.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 146.0, 135.6, 129.2, 128.8, 128.1, 127.9, 118.6, 113.9, 56.4, 54.9, 53.9.



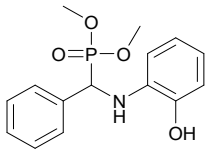
Dimethyl (((4-methoxyphenyl)amino)(phenyl)methyl)phosphonate (b)[1] **:** Light gray solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 (dd, *J* = 7.3, 1.9 Hz, 1H), 6.68 (d, *J* = 8.9 Hz, 2H), 6.55 (d, *J* = 8.9 Hz, 2H), 4.80–4.68 (m, 1H), 4.68–4.54 (m, 1H), 3.75 (d, *J* = 10.7 Hz, 3H), 3.65 (s, 3H), 3.46 (d, *J* = 10.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 152.8, 140.2, 135.8, 128.7, 128.0, 127.9, 115.3, 114.8, 57.4, 55.8, 55.6, 53.8.



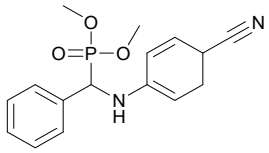
Dimethyl (((4-hydroxyphenyl)amino)(phenyl)methyl)phosphonate (c)[2] **:** Light brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.45–7.36 (m, 2H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.21 (dd, *J* = 7.2, 1.8 Hz, 1H), 6.63 (d, *J* = 8.8 Hz, 2H), 6.46 (d, *J* = 8.8 Hz, 2H), 4.78–4.66 (m, 1H), 4.55 (s, 1H), 3.69 (d, *J* = 10.7 Hz, 3H), 3.43 (d, *J* = 10.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 149.7, 138.8, 135.4, 128.4, 127.7, 127.6, 115.8, 57.1, 55.6, 53.8, 53.5.



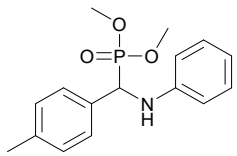
Dimethyl (phenyl(p-tolylamino)methyl)phosphonate (d)[3] **:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.47 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 7.7 Hz, 2H), 7.27 (t, J = 6.6 Hz, 1H), 6.91 (d, J = 8.4 Hz, 2H), 6.52 (d, J = 8.4 Hz, 2H), 4.85–4.74 (m, 1H), 4.41 (s, 1H), 3.76 (d, J = 10.6 Hz, 3H), 3.47 (d, J = 10.6 Hz, 3H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 143.7, 135.7, 129.7, 128.8, 128.0, 127.8, 114.0, 56.7, 55.2, 53.7, 20.4.



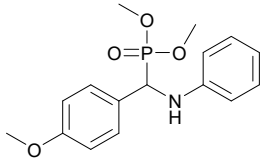
Dimethyl (((2-hydroxyphenyl)amino)(phenyl)methyl)phosphonate (e)[4] **:** Light brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.09 (s, 1H), 7.45 (dd, J = 5.2, 2.3 Hz, 2H), 7.18 (dd, J = 5.3, 1.8 Hz, 3H), 6.80 (d, J = 6.3 Hz, 1H), 6.66 (t, J = 7.0 Hz, 1H), 6.56 (t, J = 6.8 Hz, 1H), 6.52 (d, J = 8.1 Hz, 1H), 5.80–5.66 (m, 1H), 5.03–4.88 (m, 1H), 3.89 (d, J = 10.7 Hz, 3H), 3.46 (d, J = 10.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 145.3, 135.5, 134.9, 128.7, 128.1, 120.0, 118.5, 114.5, 112.1, 56.6, 55.0, 54.8, 54.1.



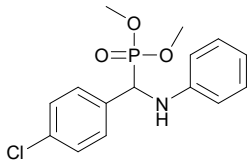
Dimethyl (((4-cyanophenyl)amino)(phenyl)methyl)phosphonate (f)[3] **:** Yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.45 (d, J = 7.7 Hz, 2H), 7.33 (dd, J = 8.3, 2.9 Hz, 5H), 6.60 (d, J = 8.8 Hz, 2H), 5.78 (s, 1H), 4.89–4.72 (m, 1H), 3.76 (d, J = 10.9 Hz, 3H), 3.44 (d, J = 10.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 149.8, 134.6, 133.6, 129.0, 128.6, 127.8, 120.1, 113.5, 100.2, 55.7, 54.2, 53.8.



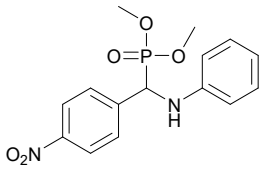
Dimethyl ((phenylamino)(p-tolyl)methyl)phosphonate (g)[1] **:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.37 (d, J = 5.9 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 15.8 Hz, 2H), 6.70 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 8.0 Hz, 2H), 4.95–4.69 (m, 2H), 3.77 (d, J = 10.7 Hz, 3H), 3.49 (d, J = 10.6 Hz, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 146.2, 137.8, 132.5, 132.4, 129.5, 129.2, 127.7, 118.5, 113.9, 56.1, 54.6, 53.8, 21.2.



Dimethyl ((4-methoxyphenyl)(phenylamino)methyl)phosphonate (h)[1] **:** Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.39 (d, J = 6.5 Hz, 2H), 7.11 (t, J = 7.7 Hz, 2H), 6.88 (d, J = 8.3 Hz, 2H), 6.70 (t, J = 7.4 Hz, 1H), 6.60 (d, J = 8.0 Hz, 2H), 4.83–4.67 (m, 2H), 3.76 (d, J = 10.0 Hz, 6H), 3.49 (d, J = 10.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 159.5, 146.3, 129.3, 129.0, 127.4, 118.6, 114.3, 114.0, 55.8, 55.3, 54.3, 53.9.

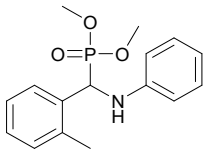


Dimethyl ((4-chlorophenyl)(phenylamino)methyl)phosphonate (i)[2] **:** Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.42 (d, J = 6.2 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.20–7.05 (m, 2H), 6.72 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 7.7 Hz, 2H), 5.00–4.69 (m, 2H), 3.77 (d, J = 10.7 Hz, 3H), 3.55 (d, J = 10.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 145.9, 134.3, 133.9, 129.3, 129.2, 129.0, 118.9, 113.9, 55.9, 54.4, 54.0.

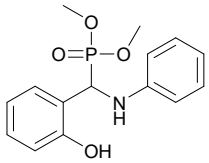


Dimethyl ((4-nitrophenyl)(phenylamino)methyl)phosphonate (j)[1] **:** Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.20 (d, J = 7.9 Hz, 2H), 7.66 (dd, J = 8.9, 2.4 Hz, 2H), 7.19–7.04 (m, 2H), 6.73 (t, J = 7.4 Hz, 1H), 6.54 (d, J = 7.5 Hz, 2H), 5.10–4.82 (m, 2H), 3.80 (d, J = 10.7 Hz, 3H), 3.62 (d, J = 10.8 Hz, 3H). ^{13}C NMR (101 MHz,

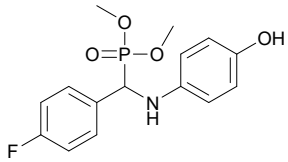
$CDCl_3$, 298 K) δ 147.7, 145.4, 143.8, 129.5, 128.7, 124.0, 119.3, 113.9, 56.3, 54.8, 54.3, 54.0.



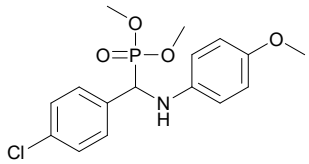
Dimethyl ((phenylamino)(o-tolyl)methyl)phosphonate (k)[1] **:** Light brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.55–7.48 (m, 1H), 7.21–7.12 (m, 3H), 7.09 (d, J = 7.3 Hz, 2H), 6.69 (t, J = 7.3 Hz, 1H), 6.54 (d, J = 7.6 Hz, 2H), 5.09–4.98 (m, 1H), 4.88 (t, J = 8.8 Hz, 1H), 3.78 (d, J = 10.8 Hz, 3H), 3.38 (d, J = 10.5 Hz, 3H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 146.0, 136.3, 133.9, 130.7, 129.3, 128.0, 127.2, 126.7, 118.5, 113.6, 53.9, 52.5, 51.0, 19.8.



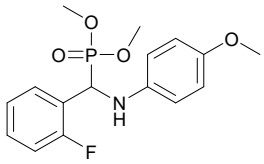
Dimethyl ((2-hydroxyphenyl)(phenylamino)methyl)phosphonate (l)[1] **:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.98 (s, 1H), 7.27 (d, J = 7.2 Hz, 1H), 7.13 (t, J = 7.6 Hz, 3H), 6.95 (d, J = 8.1 Hz, 1H), 6.88 (d, J = 7.5 Hz, 1H), 6.75 (d, J = 7.4 Hz, 1H), 6.69 (d, J = 7.9 Hz, 2H), 5.20–5.01 (m, 1H), 4.79 (t, J = 7.7 Hz, 1H), 3.76 (d, J = 10.5 Hz, 3H), 3.65 (d, J = 10.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 155.7, 146.1, 129.6, 129.4, 129.0, 121.4, 120.8, 119.5, 118.2, 114.5, 54.6, 54.0, 52.4.



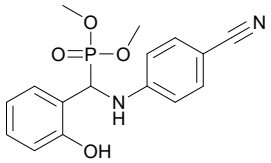
Dimethyl ((4-fluorophenyl)((4-hydroxyphenyl)amino)methyl)phosphonate (m) : Yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.21 (d, J = 6.3 Hz, 2H), 6.77 (t, J = 8.3 Hz, 4H), 6.60–6.52 (m, 2H), 6.46 (s, 3H), 4.79–4.56 (m, 1H), 3.74 (d, J = 10.7 Hz, 3H), 3.67 (d, J = 12.2 Hz, 1H), 3.48 (d, J = 10.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 157.7, 157.1, 155.3, 142.3, 142.1, 129.0, 125.3, 116.1, 115.8, 115.3, 56.5, 54.9, 54.2.



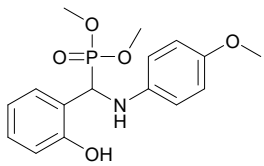
Dimethyl ((4-chlorophenyl)((4-methoxyphenyl)amino)methyl)phosphonate (n) : Gray solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.40 (dd, J = 8.6, 2.4 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 6.68 (d, J = 9.0 Hz, 2H), 6.52 (d, J = 9.0 Hz, 2H), 4.84–4.49 (m, 2H), 3.76 (d, J = 10.7 Hz, 3H), 3.67 (s, 3H), 3.54 (d, J = 10.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 152.9, 139.8, 134.5, 133.8, 129.2, 128.9, 115.3, 114.8, 56.8, 55.6, 55.3, 54.0, 53.8.



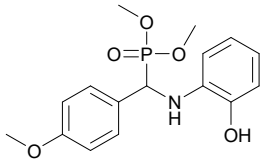
Dimethyl ((2-fluorophenyl)((4-methoxyphenyl)amino)methyl)phosphonate (o) : White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.56 (t, J = 7.6 Hz, 1H), 7.33–7.22 (m, 1H), 7.21–7.03 (m, 2H), 6.73 (d, J = 9.0 Hz, 2H), 6.62 (d, J = 9.0 Hz, 2H), 5.36–5.04 (m, 1H), 4.67 (s, 1H), 3.87 (d, J = 10.7 Hz, 3H), 3.70 (s, 3H), 3.55 (d, J = 10.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 152.9, 139.7, 129.7, 128.9, 124.7, 123.3, 115.2, 115.1, 114.8, 55.6, 54.0, 53.8, 49.4, 47.8.



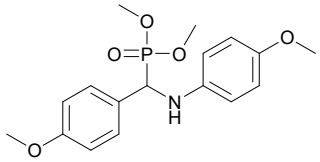
Dimethyl (((4-cyanophenyl)amino)(2-hydroxyphenyl)methyl)phosphonate (p) : White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.52 (s, 1H), 7.37 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 7.6 Hz, 1H), 7.15 (t, J = 7.7 Hz, 1H), 6.99–6.78 (m, 2H), 6.63 (d, J = 8.4 Hz, 2H), 5.42 (t, J = 7.2 Hz, 1H), 5.29–5.07 (m, 1H), 3.78 (d, J = 10.6 Hz, 3H), 3.65 (d, J = 10.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 155.2, 149.7, 133.8, 130.1, 128.8, 121.0, 120.9, 120.1, 118.0, 113.5, 100.6, 54.5, 54.2, 29.8.



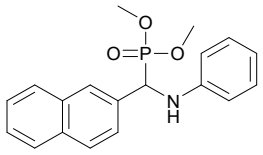
Dimethyl ((2-hydroxyphenyl)((4-methoxyphenyl)amino)methyl)phosphonate (q) : White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.15 (s, 1H), 7.20 (d, J = 7.6 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 6.90 (d, J = 8.1 Hz, 1H), 6.86 (t, J = 7.7 Hz, 1H), 6.69 (q, J = 9.1 Hz, 4H), 4.96–4.83 (m, 1H), 4.53 (s, 1H), 3.75 (d, J = 10.6 Hz, 3H), 3.68 (d, J = 10.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 156.2, 156.2, 153.9, 139.9, 129.7, 129.2, 120.6, 118.2, 116.8, 114.8, 55.7, 54.5, 54.0.



Dimethyl (((2-hydroxyphenyl)amino)(4-methoxyphenyl)methyl)phosphonate (r)[4] : Light gray solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.29 (s, 1H), 7.35 (d, J = 5.8 Hz, 2H), 7.01 (d, J = 7.8 Hz, 2H), 6.83 (d, J = 6.2 Hz, 1H), 6.68 (t, J = 6.9 Hz, 1H), 6.62–6.52 (m, 2H), 5.76 (s, 1H), 5.02–4.88 (m, 1H), 3.91 (d, J = 10.7 Hz, 3H), 3.50 (d, J = 10.5 Hz, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 145.3, 137.8, 134.9, 132.3, 129.4, 127.9, 119.9, 118.4, 114.4, 111.9, 56.2, 54.8, 54.1, 21.2.

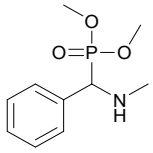


Dimethyl ((4-methoxyphenyl)((4-methoxyphenyl)amino)methyl)phosphonate (s)[5] : White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.06 (d, J = 6.3 Hz, 2H), 6.51 (d, J = 8.2 Hz, 2H), 6.38–6.19 (m, 4H), 4.48 (t, J = 8.3 Hz, 1H), 4.44–4.33 (m, 1H), 3.37 (s, 6H), 3.29 (d, J = 2.5 Hz, 3H), 3.15 (d, J = 10.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 159.2, 152.5, 140.2, 128.9, 127.5, 115.2, 114.5, 113.9, 56.4, 55.3, 55.0, 53.5.



Dimethyl (naphthalen-2-yl(phenylamino)methyl)phosphonate (t)[1] : White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.25 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 9.8 Hz, 1H), 7.86–7.77 (m, 2H), 7.64 (t, J = 6.9 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.11–6.91 (m, 2H), 6.67 (t, J = 7.3 Hz, 1H), 6.57 (d, J = 7.6 Hz, 2H), 5.84–5.59 (m, 1H), 5.15 (t, J = 8.8 Hz, 1H), 3.83 (d, J = 10.8 Hz, 3H), 3.16 (d, J = 10.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 146.0, 133.9, 131.4, 129.3, 129.2, 128.7, 126.6, 125.8, 125.7, 125.6, 122.6, 118.5, 113.6, 53.7, 51.9, 50.4.



Dimethyl ((methylamino)(phenyl)methyl)phosphonate (u) : White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.42–7.33 (m, 4H), 7.31 (d, J = 7.5 Hz, 1H), 4.00–3.88 (m, 1H), 3.71 (d, J = 10.6 Hz, 3H), 3.54 (d, J = 10.4 Hz, 3H), 2.32 (s, 3H), 1.99 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 128.7, 128.5, 128.2, 63.4, 61.8, 53.5, 35.1.

VIII. The ^{1}H NMR, ^{13}C NMR spectra of a-u

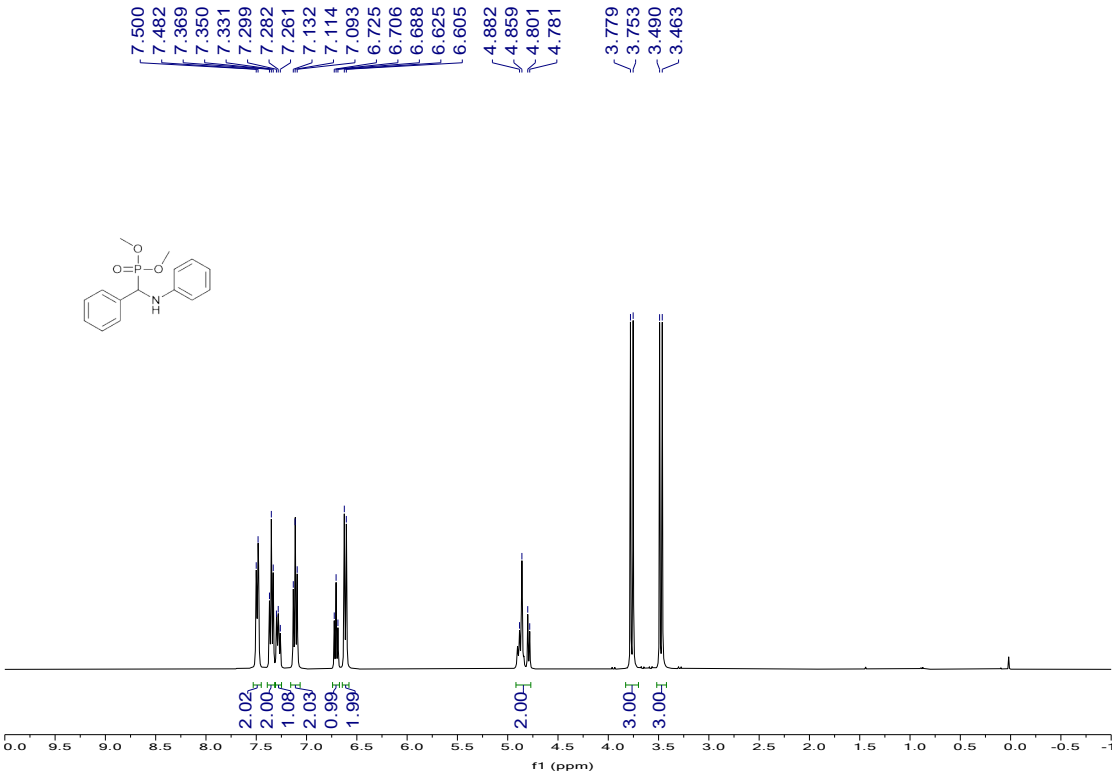


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **a**

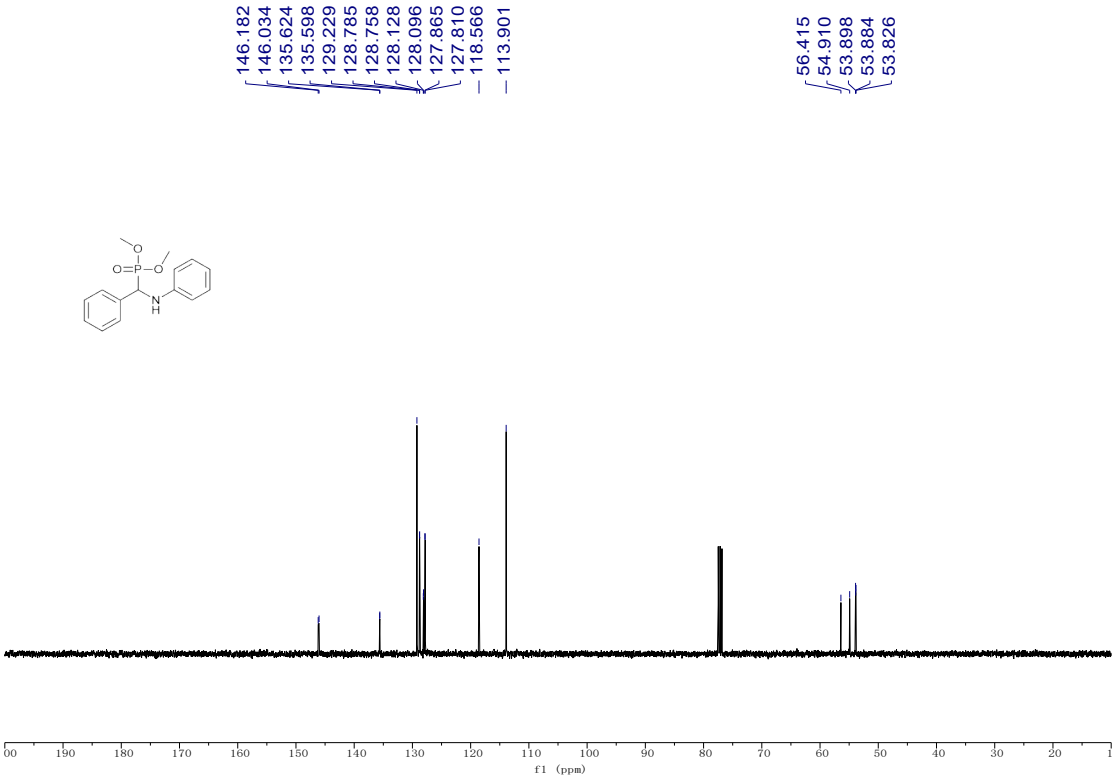


Figure S18. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **a**

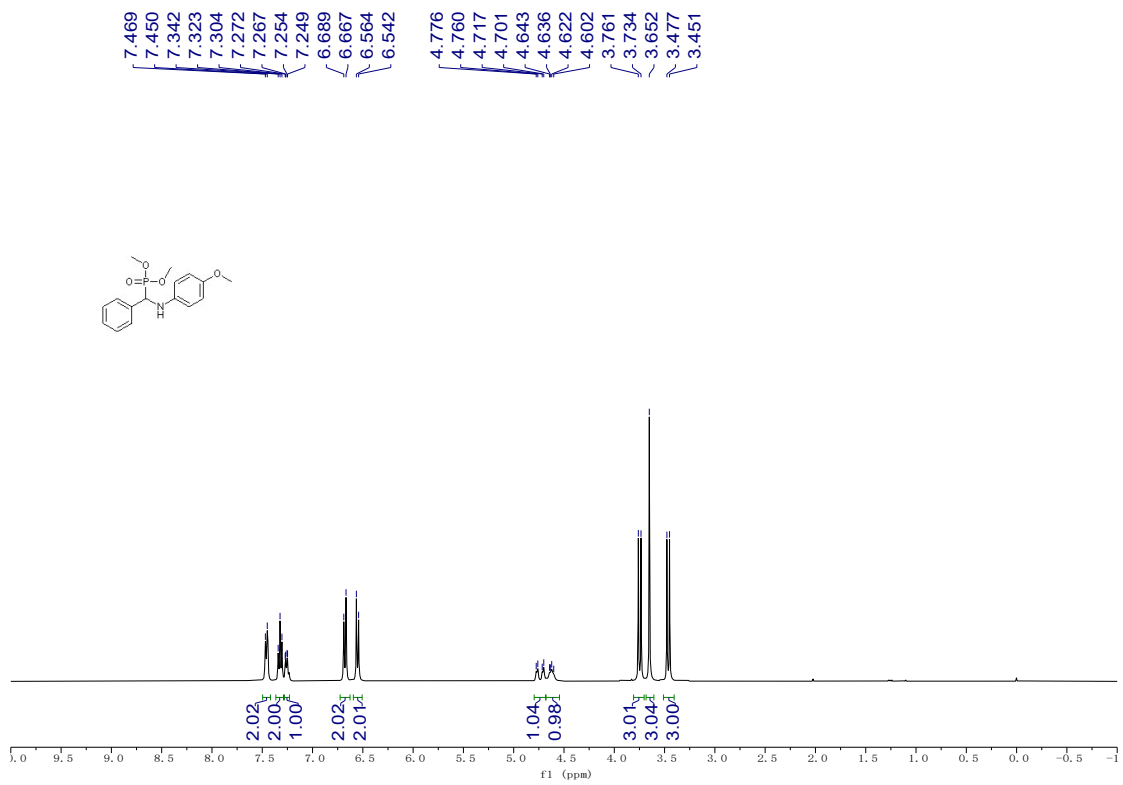


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **b**

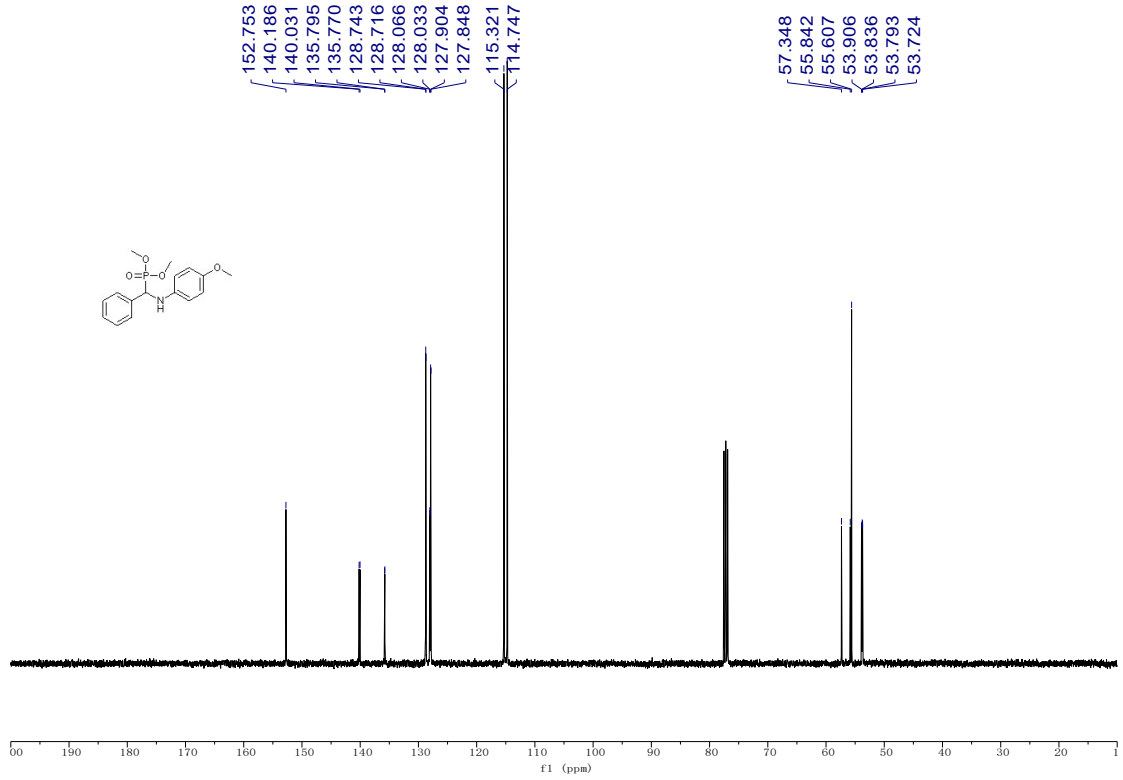


Figure S20. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **b**

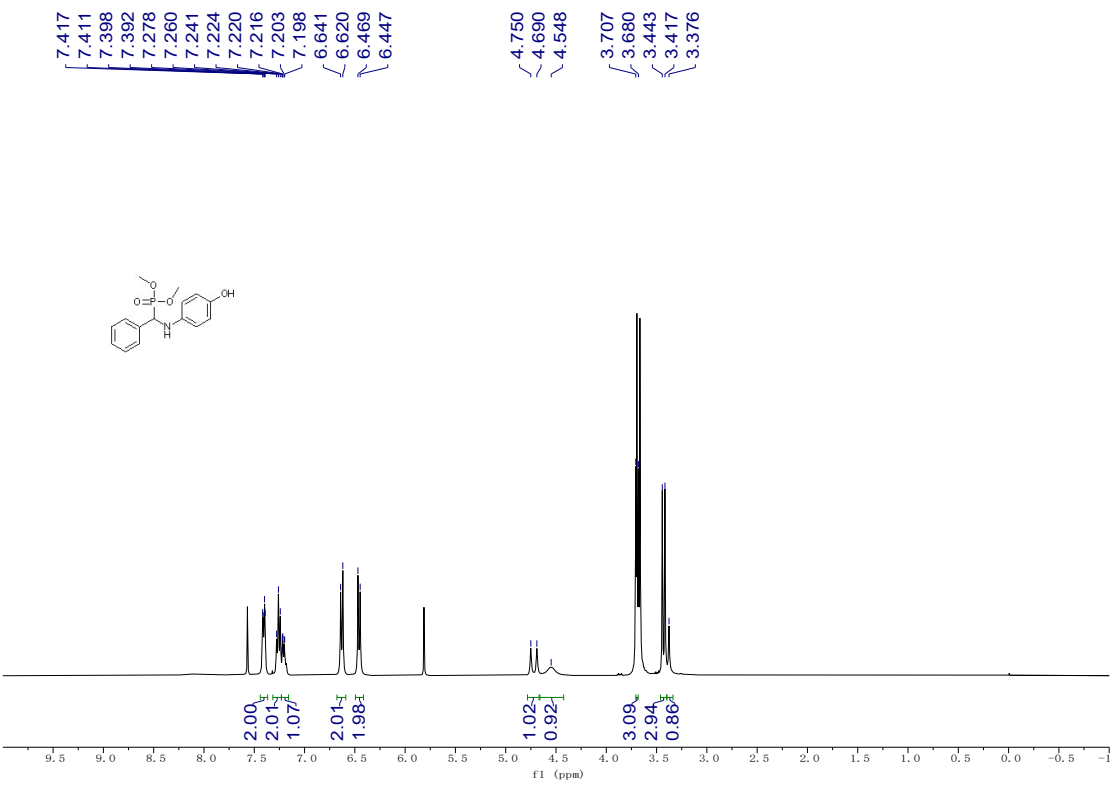


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **c**

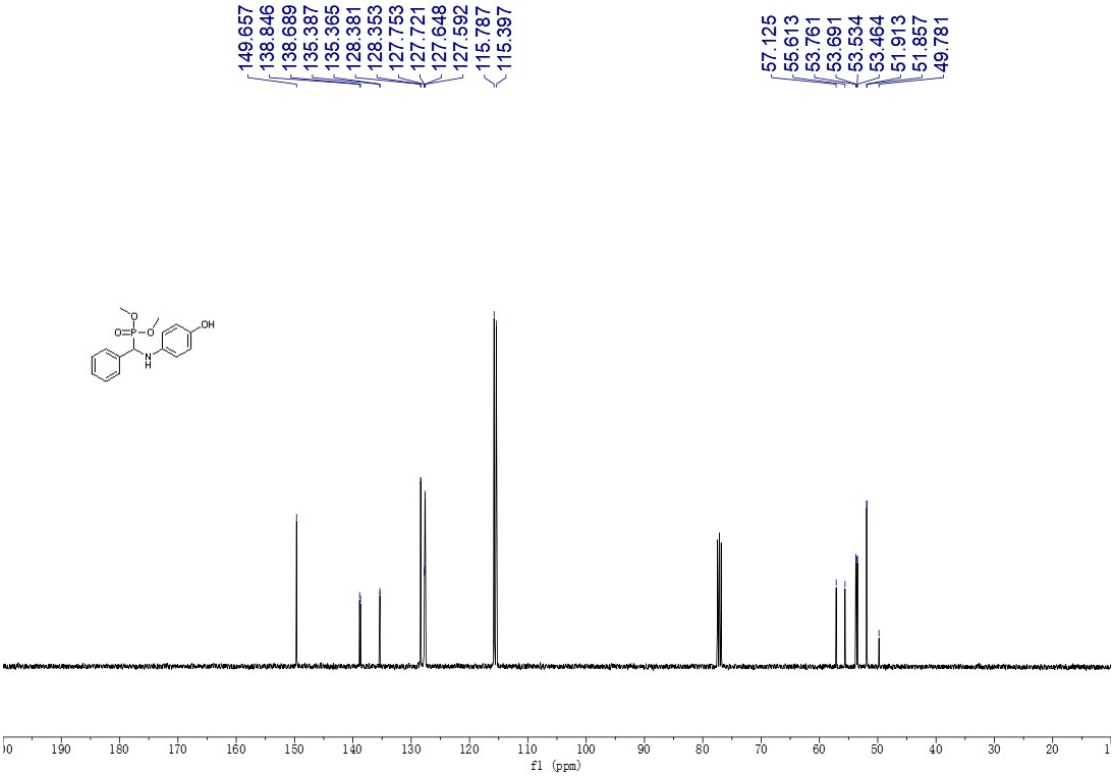


Figure S22. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **c**

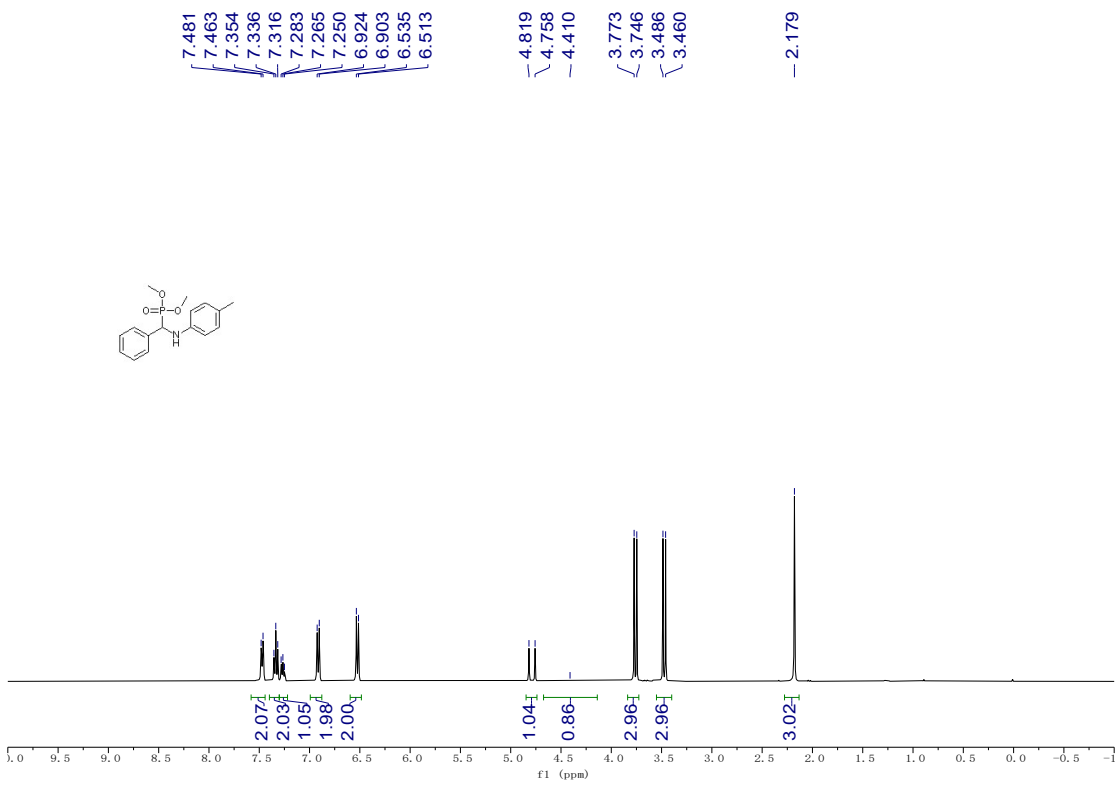


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **d**

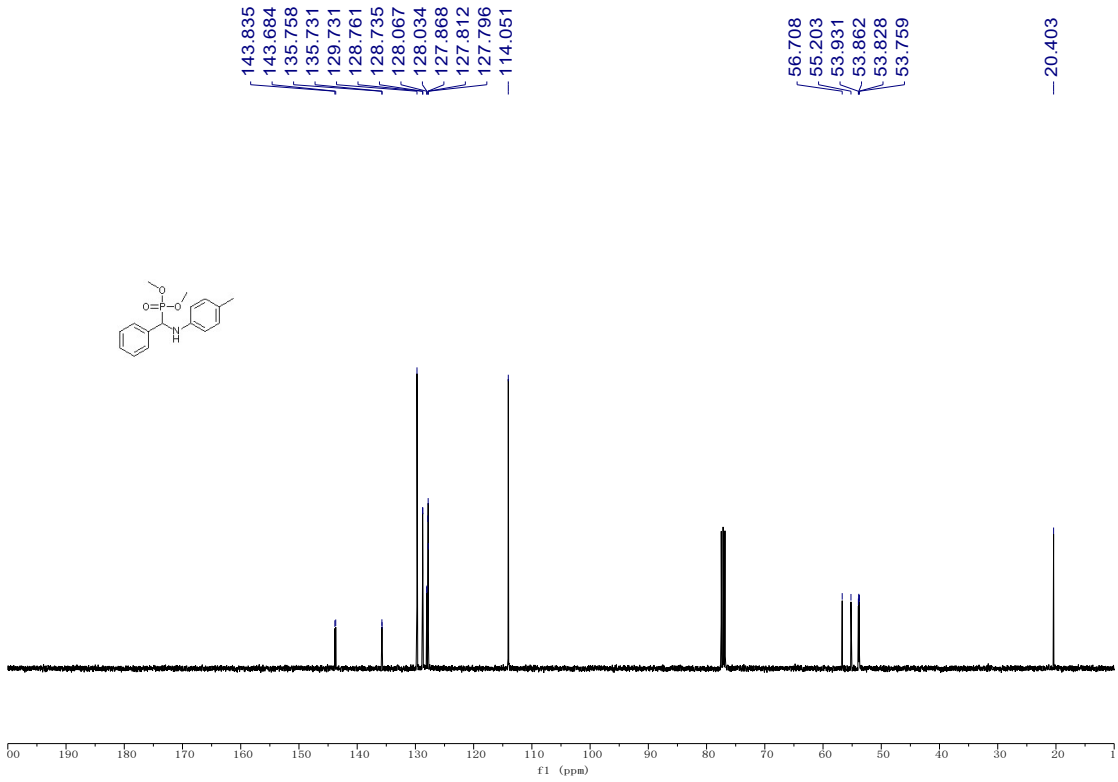


Figure S24. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **d**

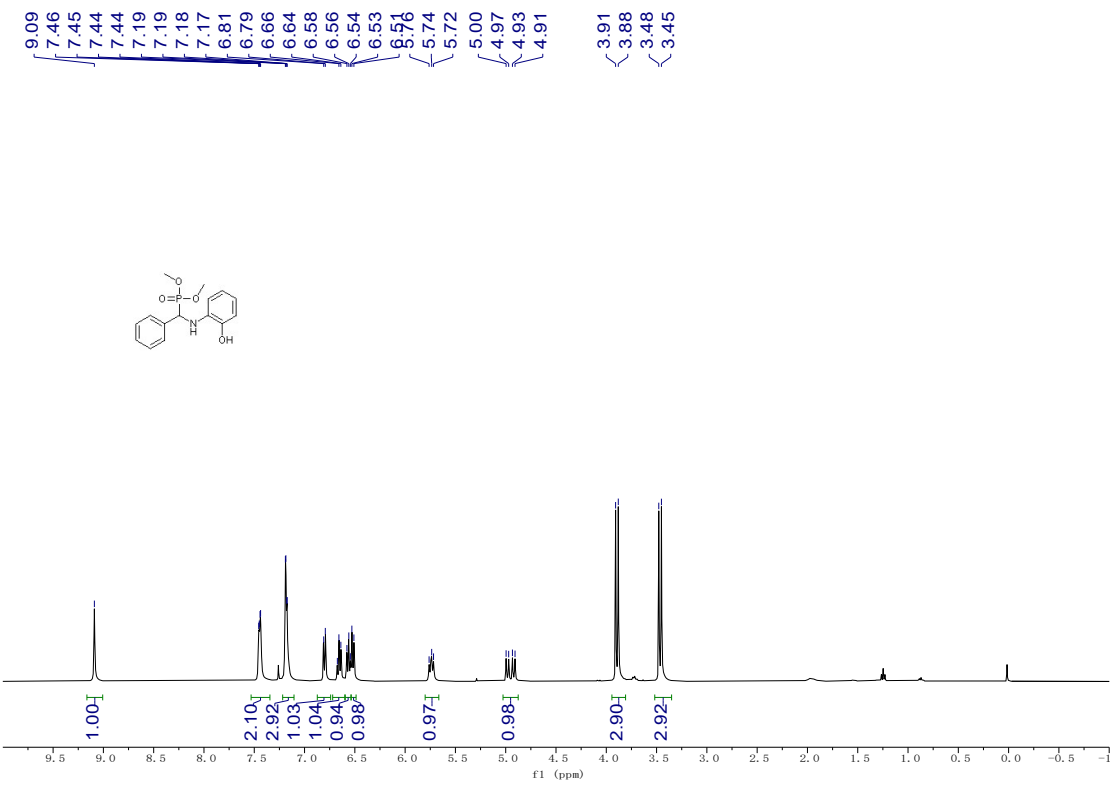


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **e**

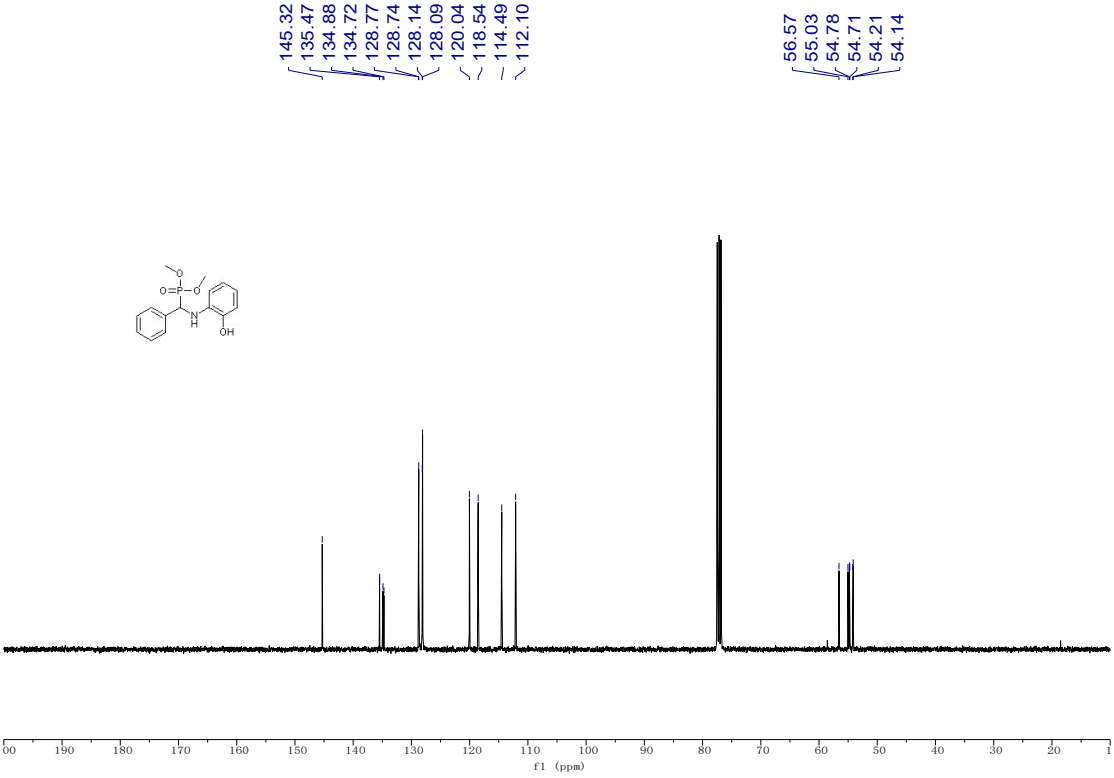


Figure S26. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **e**

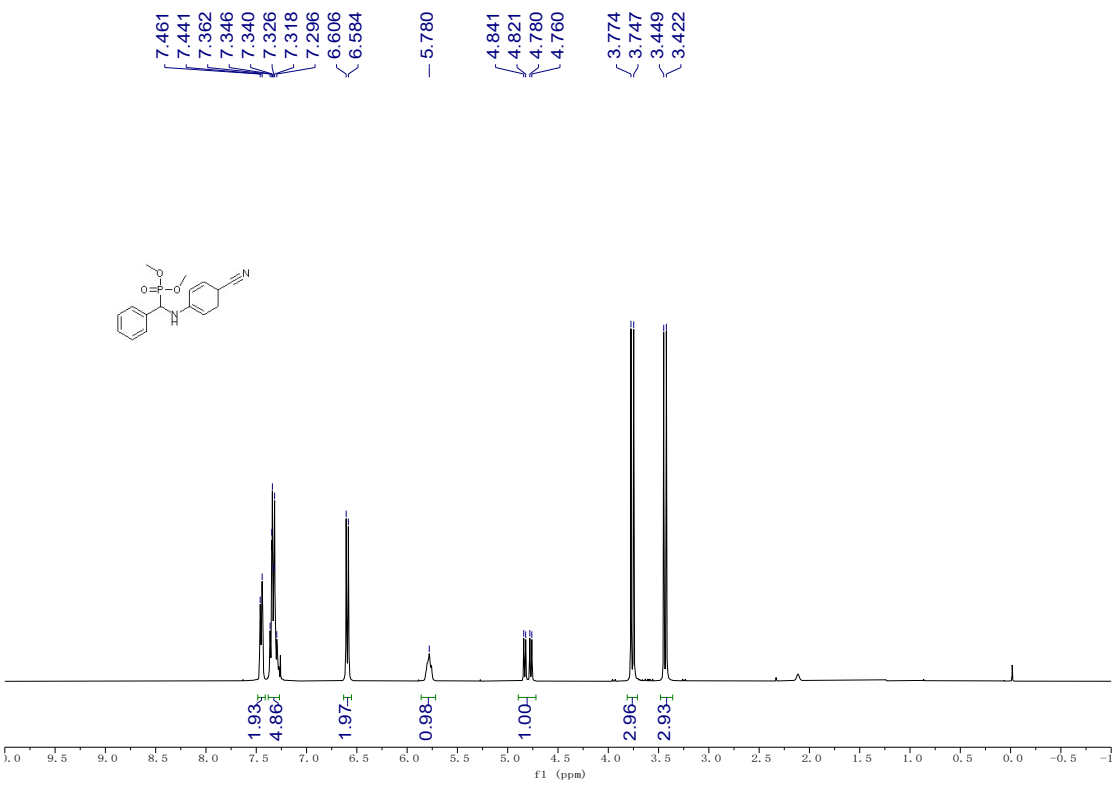


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **f**

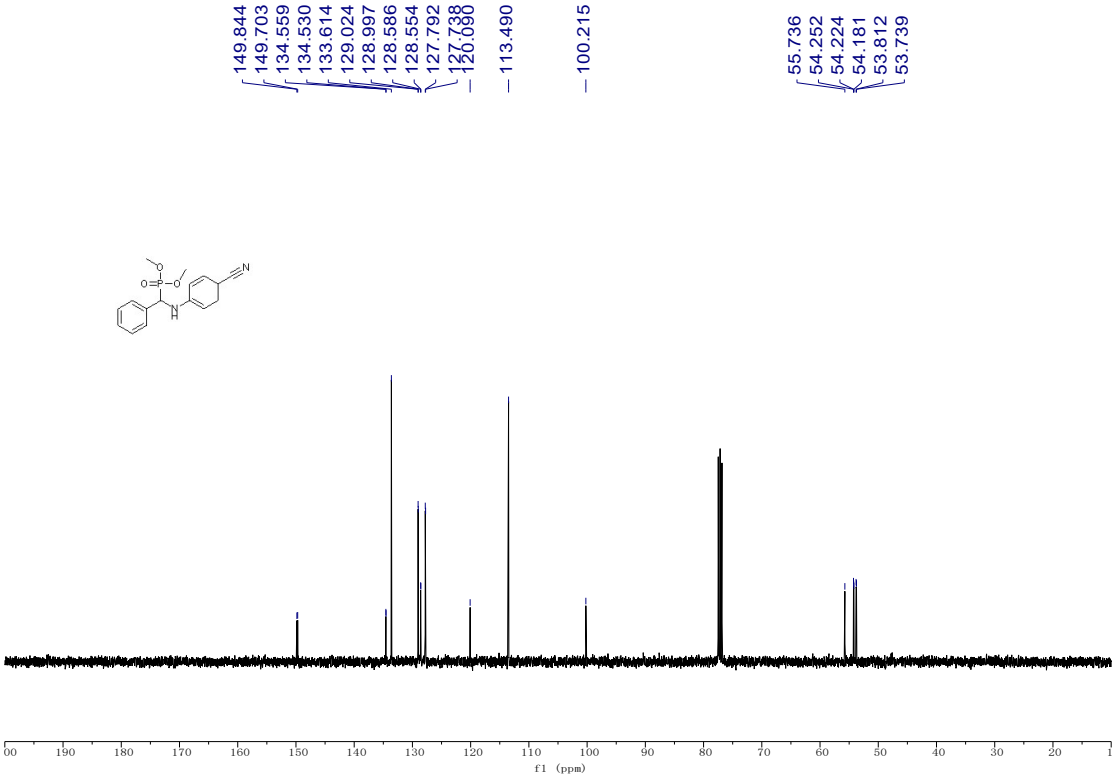


Figure S28. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **f**

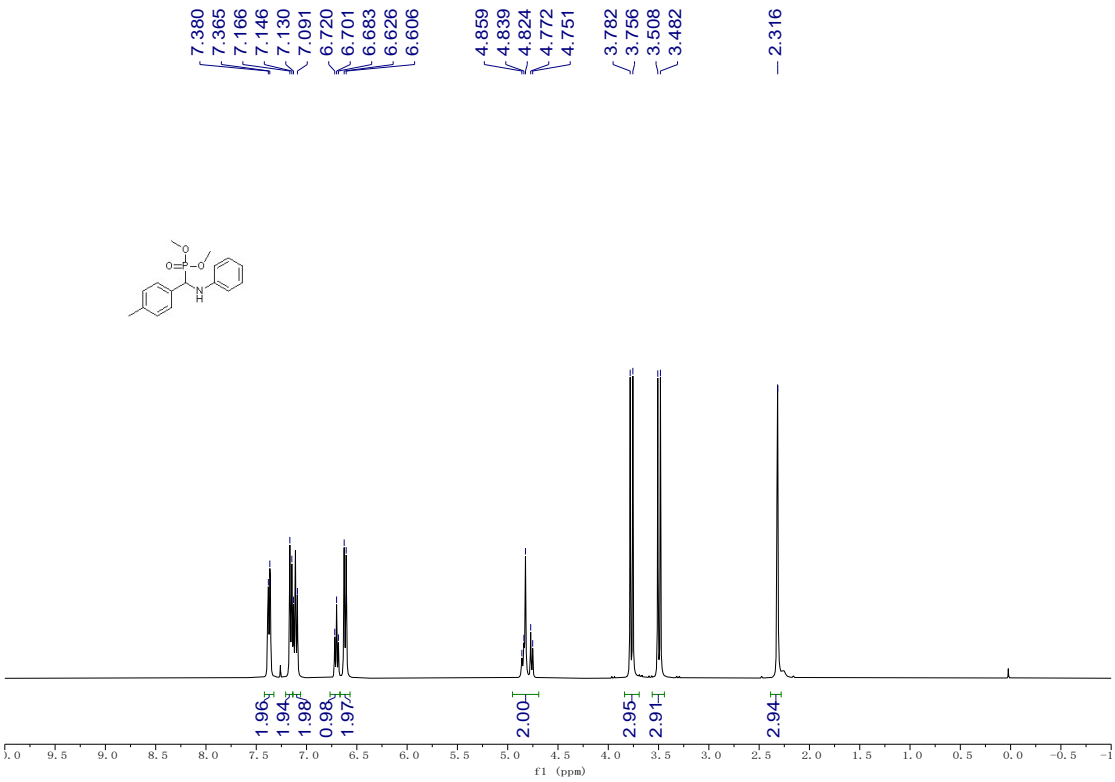


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **g**

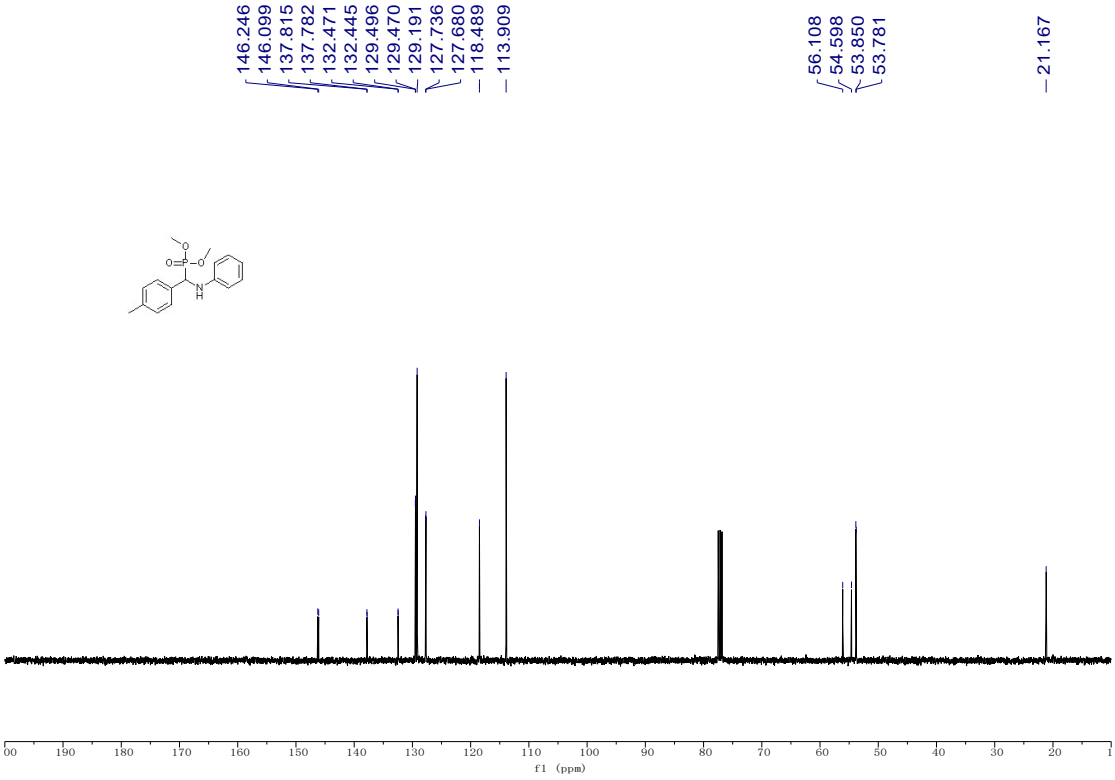


Figure S30. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **g**

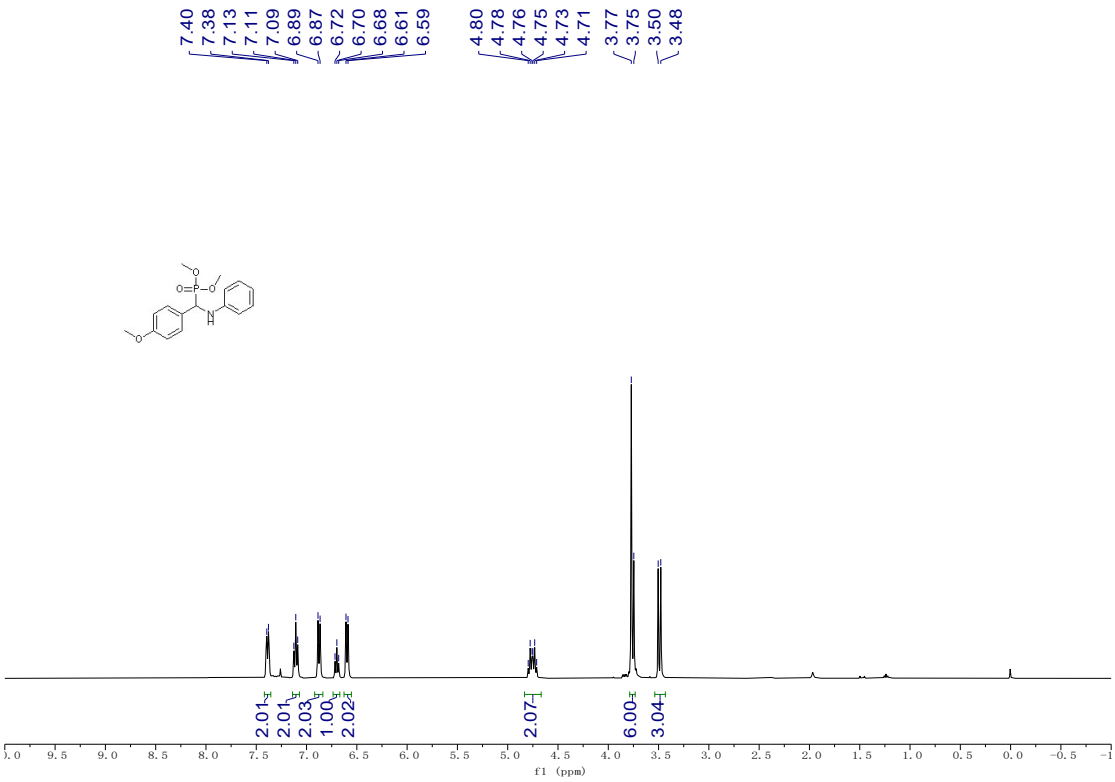


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **h**

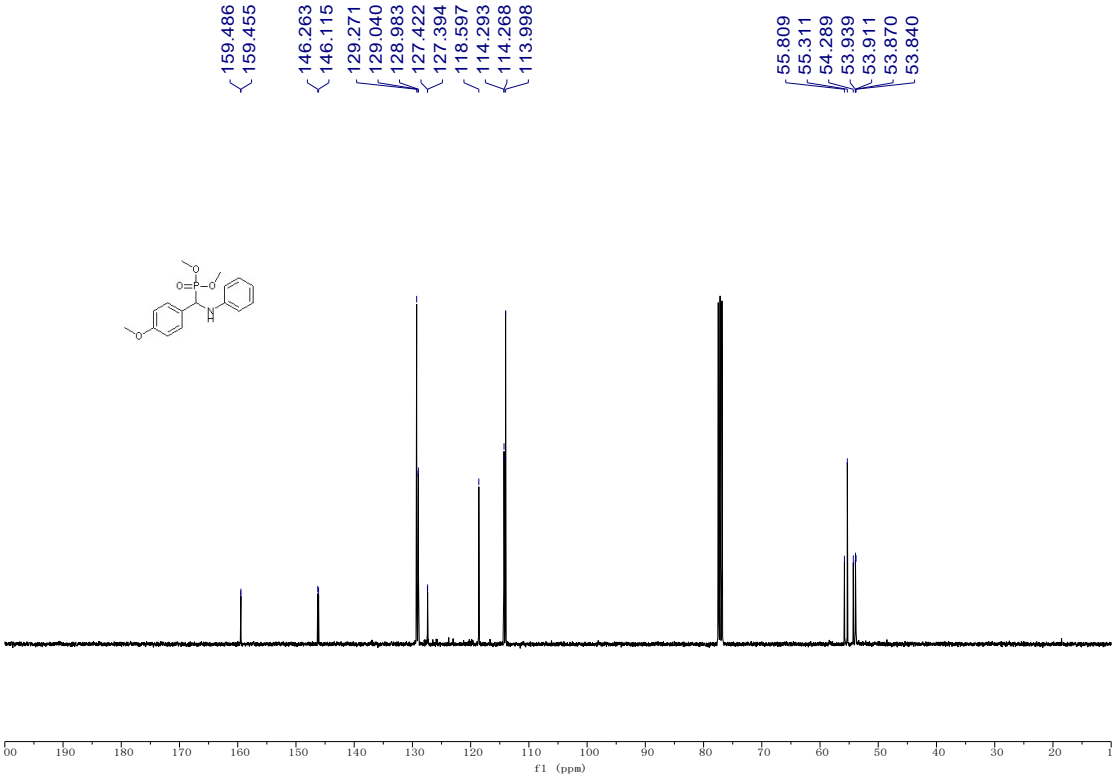


Figure S32. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **h**

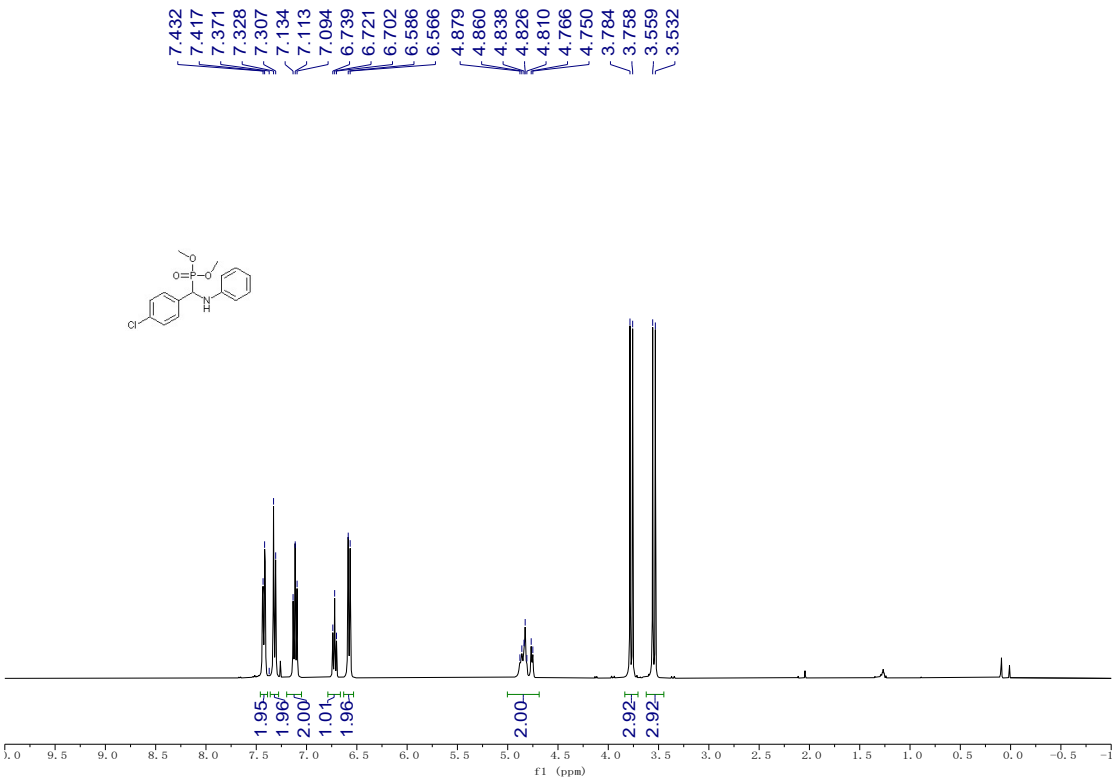


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **i**

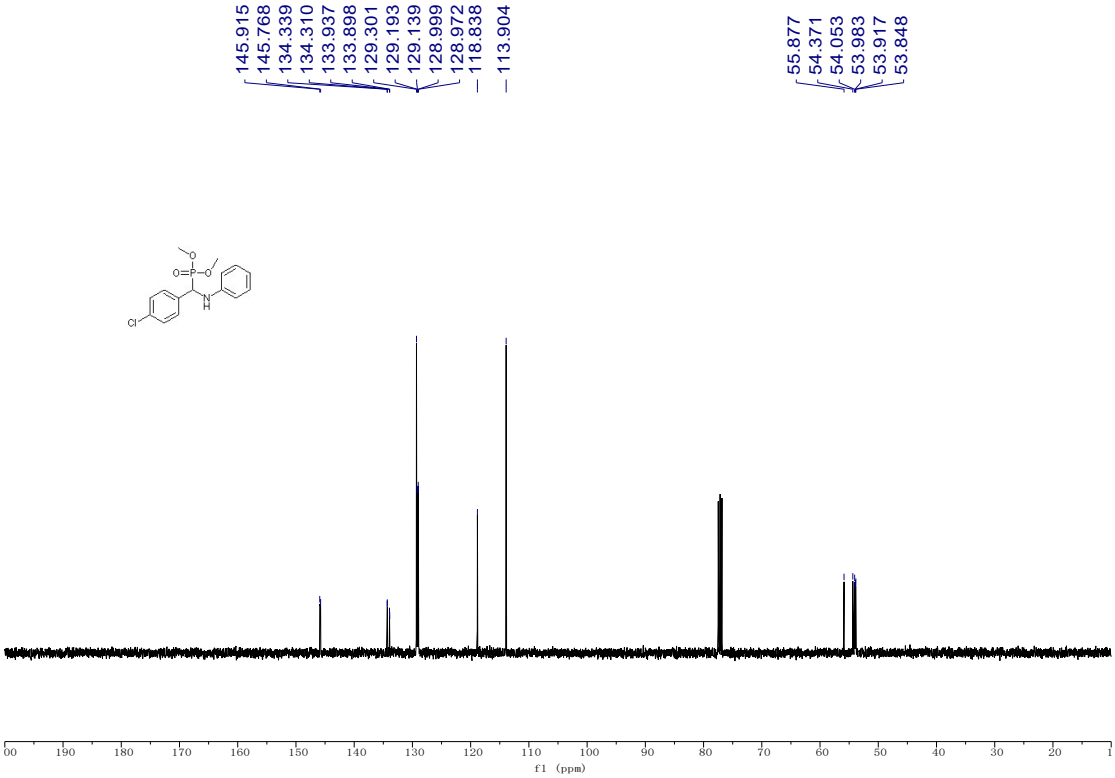


Figure S34. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **i**

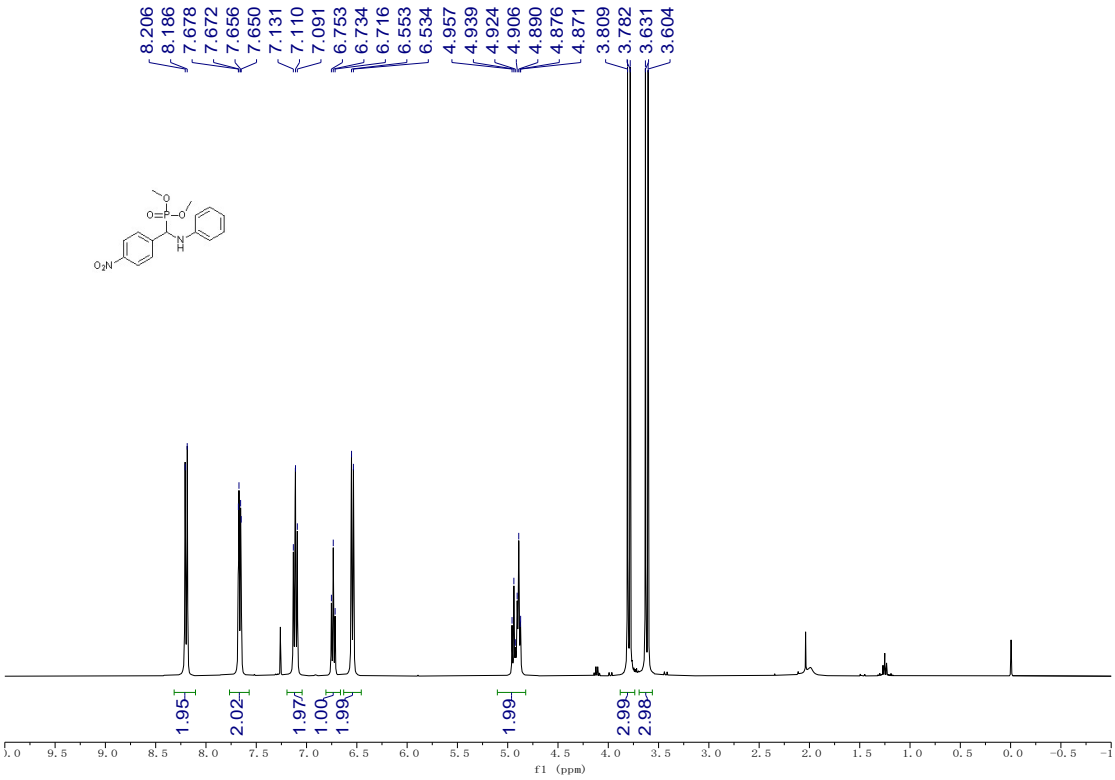


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **j**

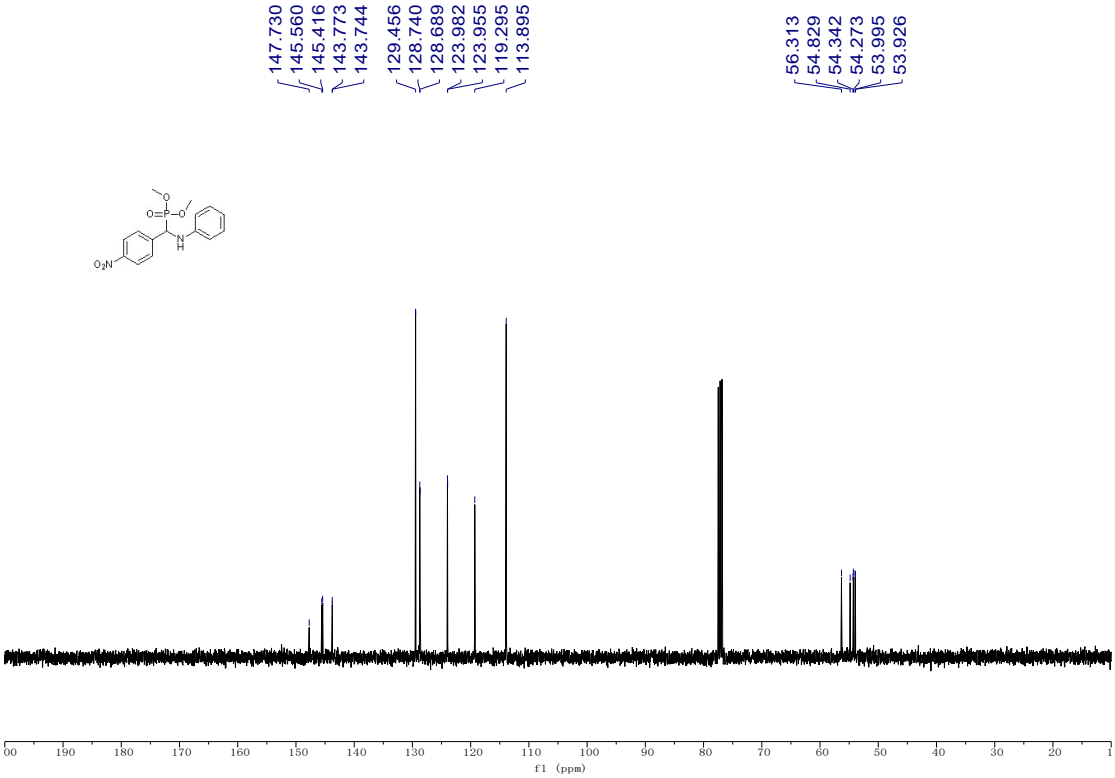


Figure S36. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **j**

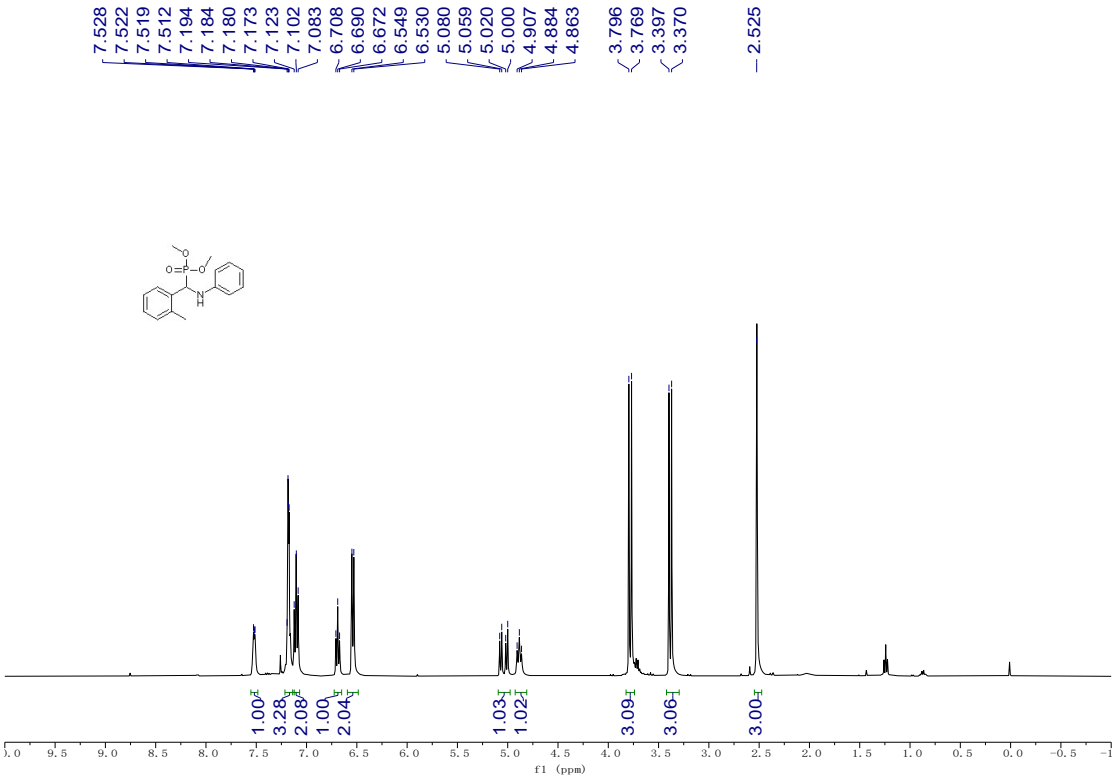


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **k**

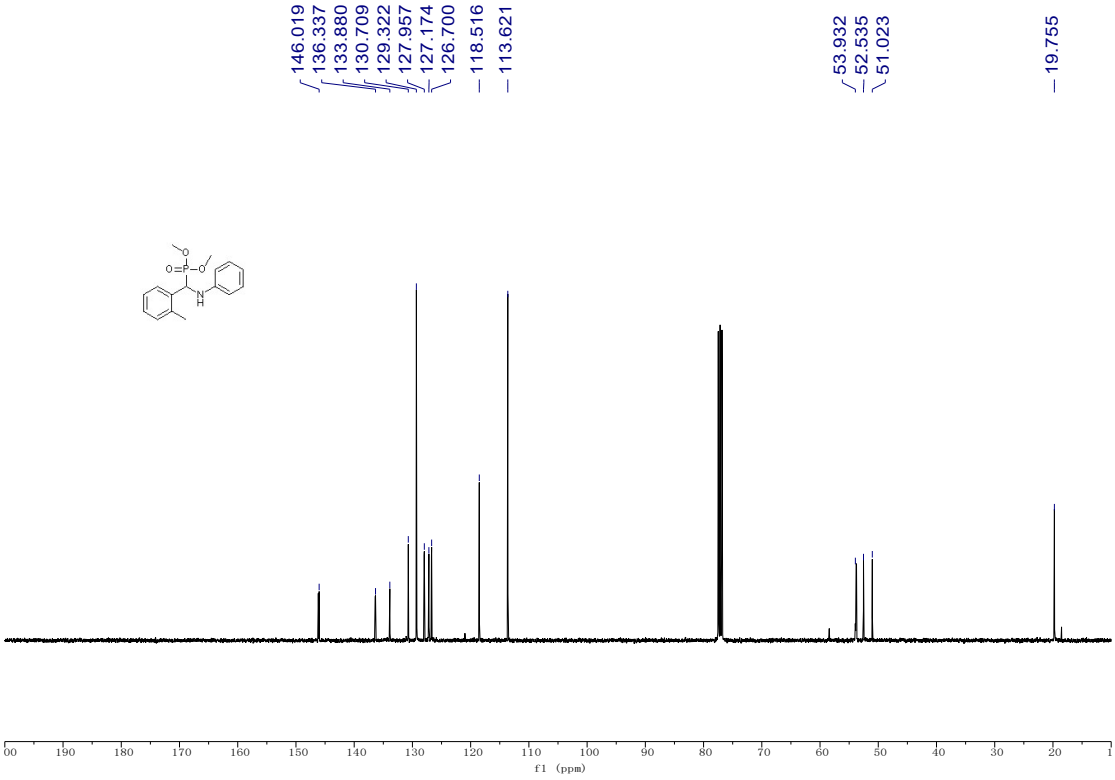


Figure S38. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **k**

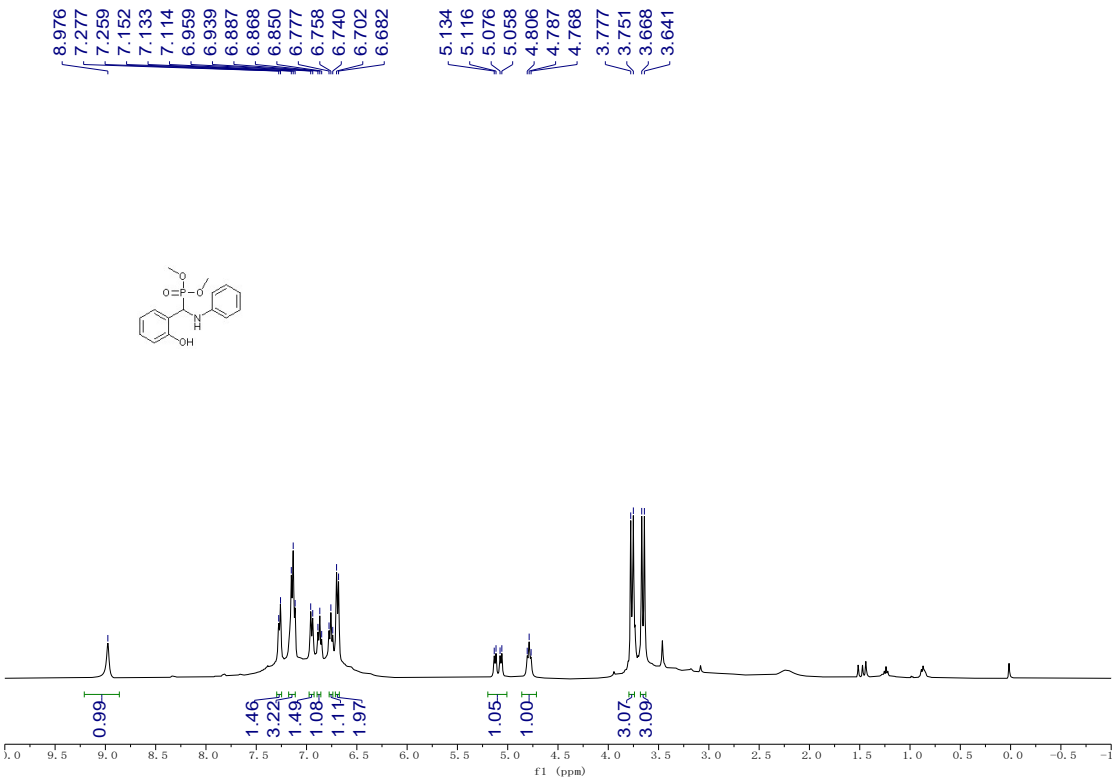


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **l**

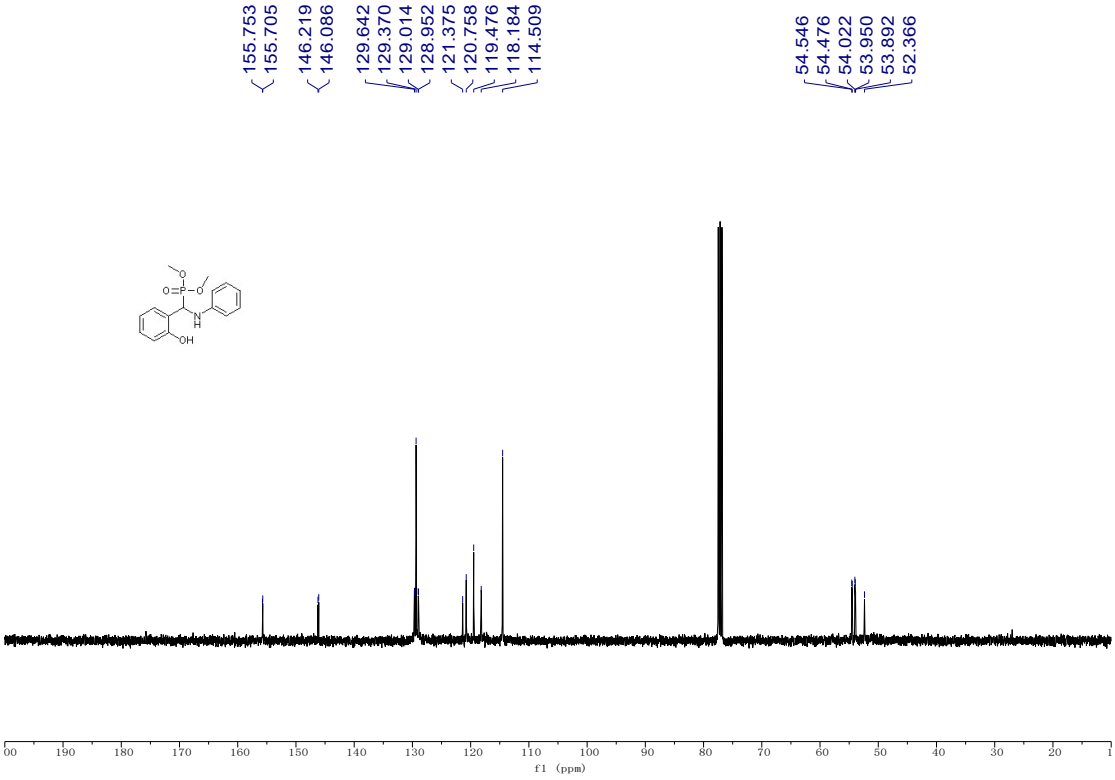


Figure S40. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **l**

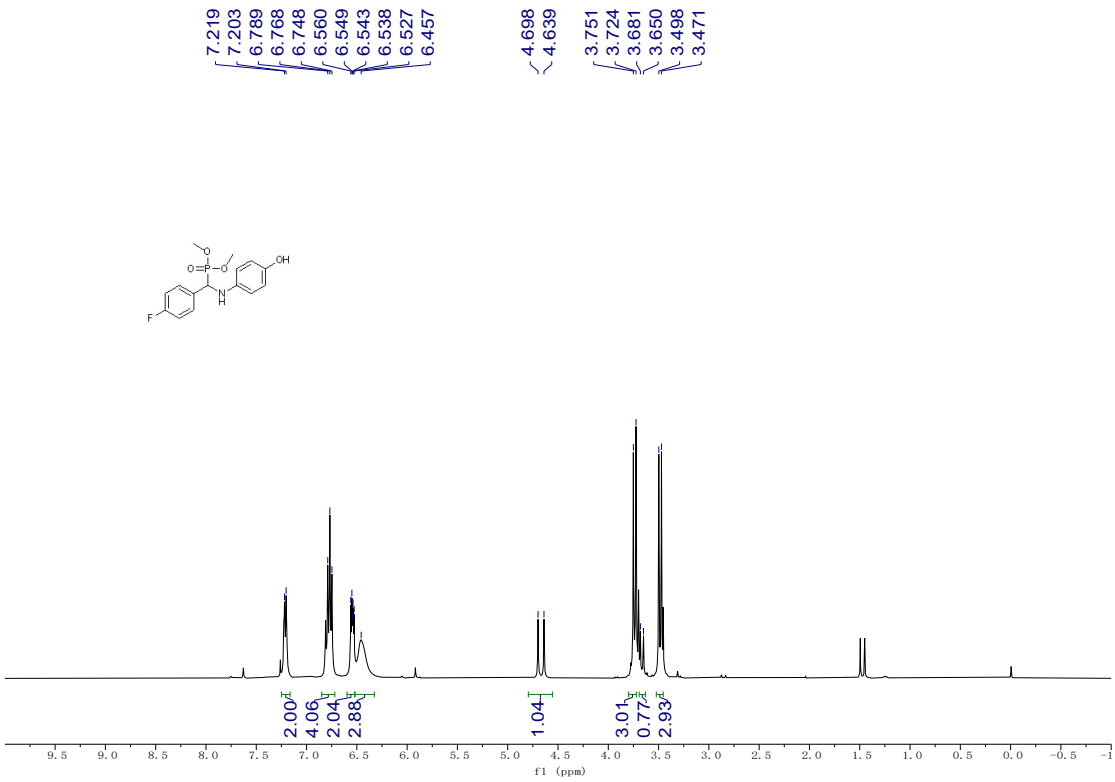


Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **m**

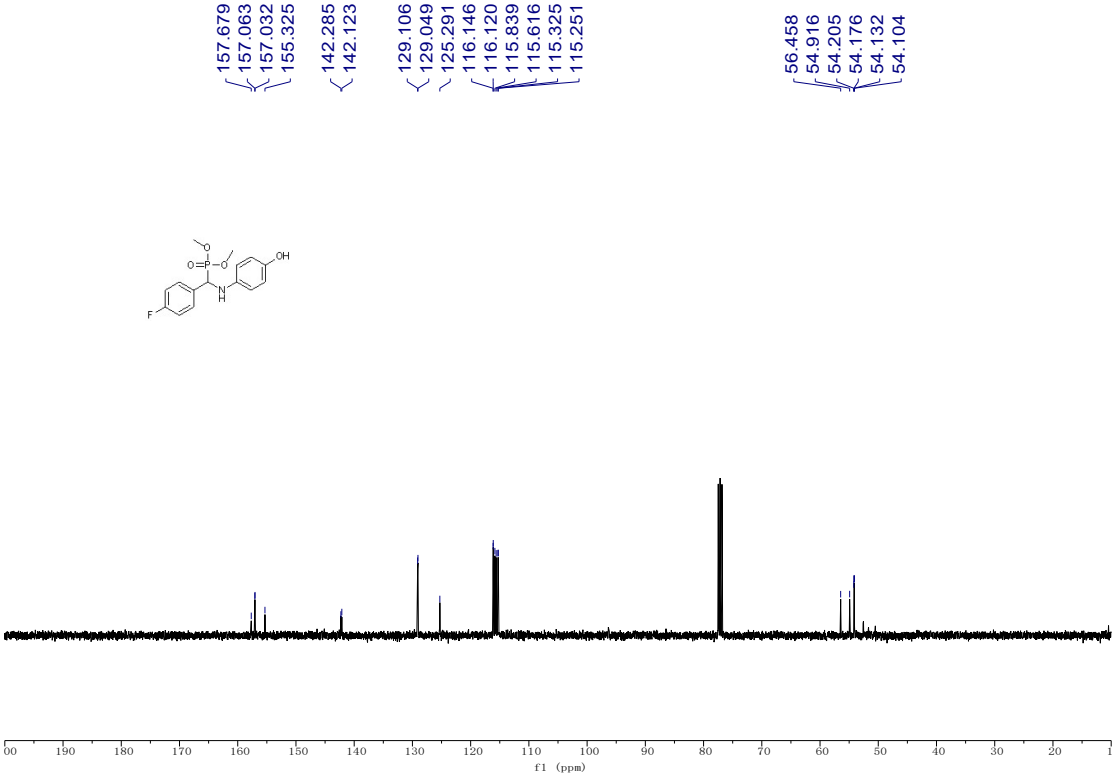


Figure S42. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **m**

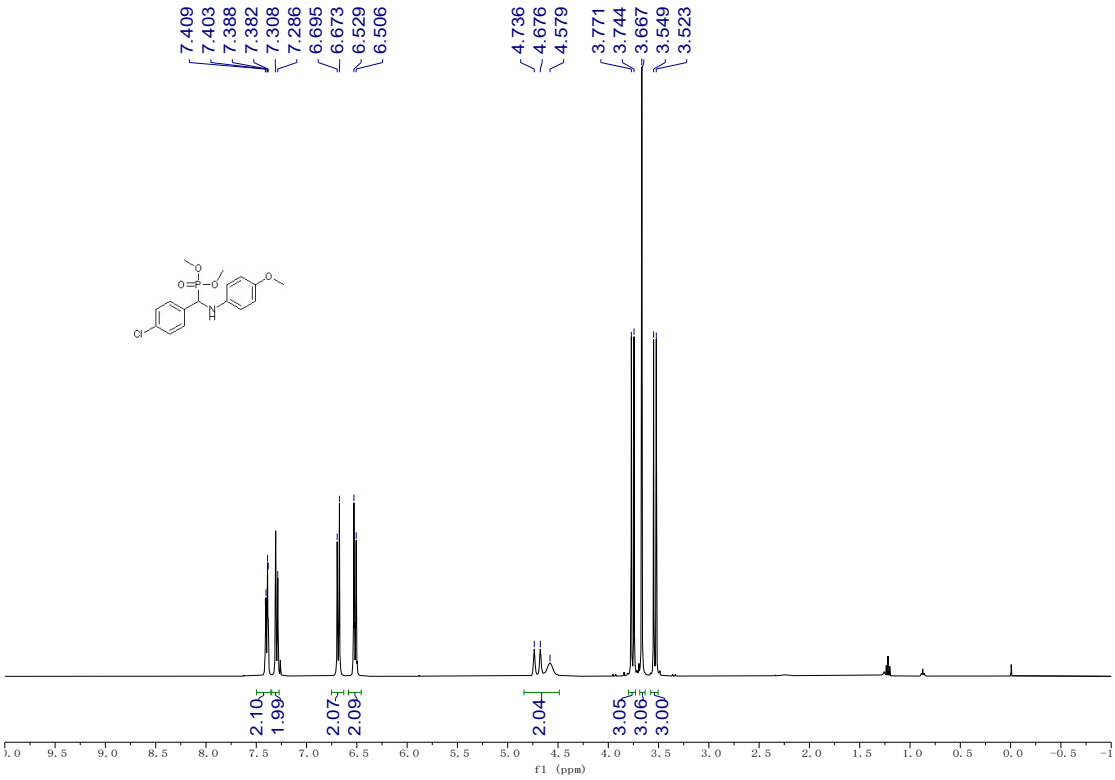


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **n**

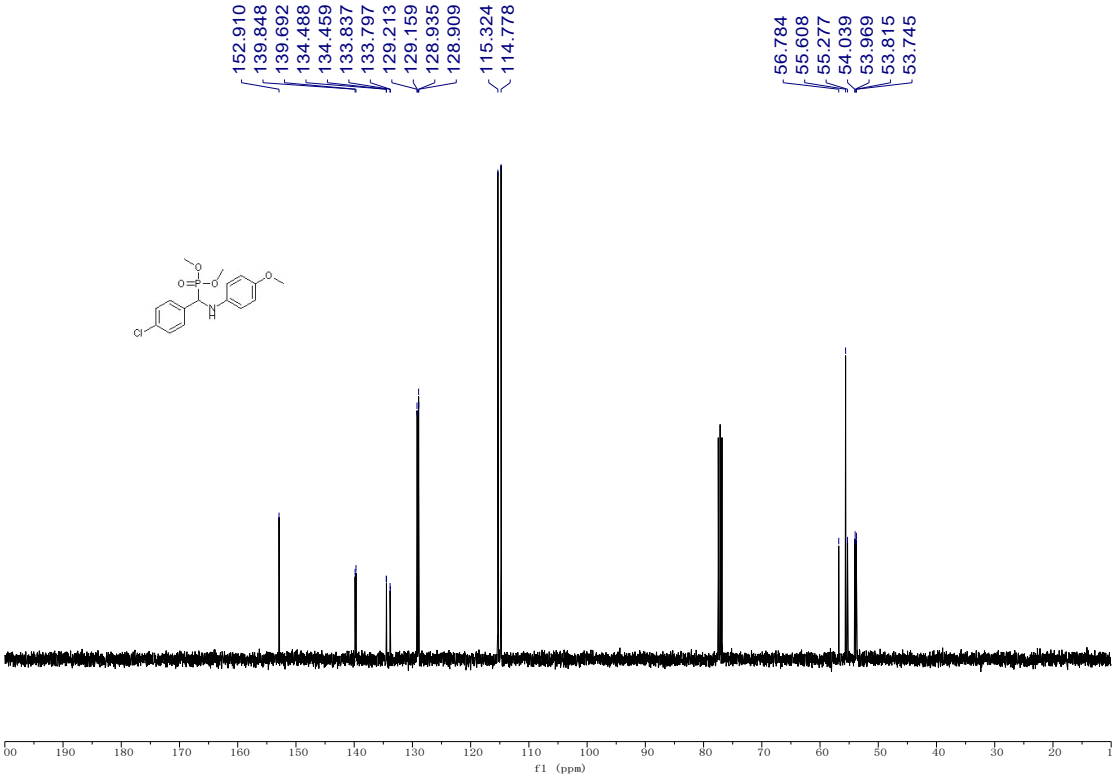


Figure S44. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **n**

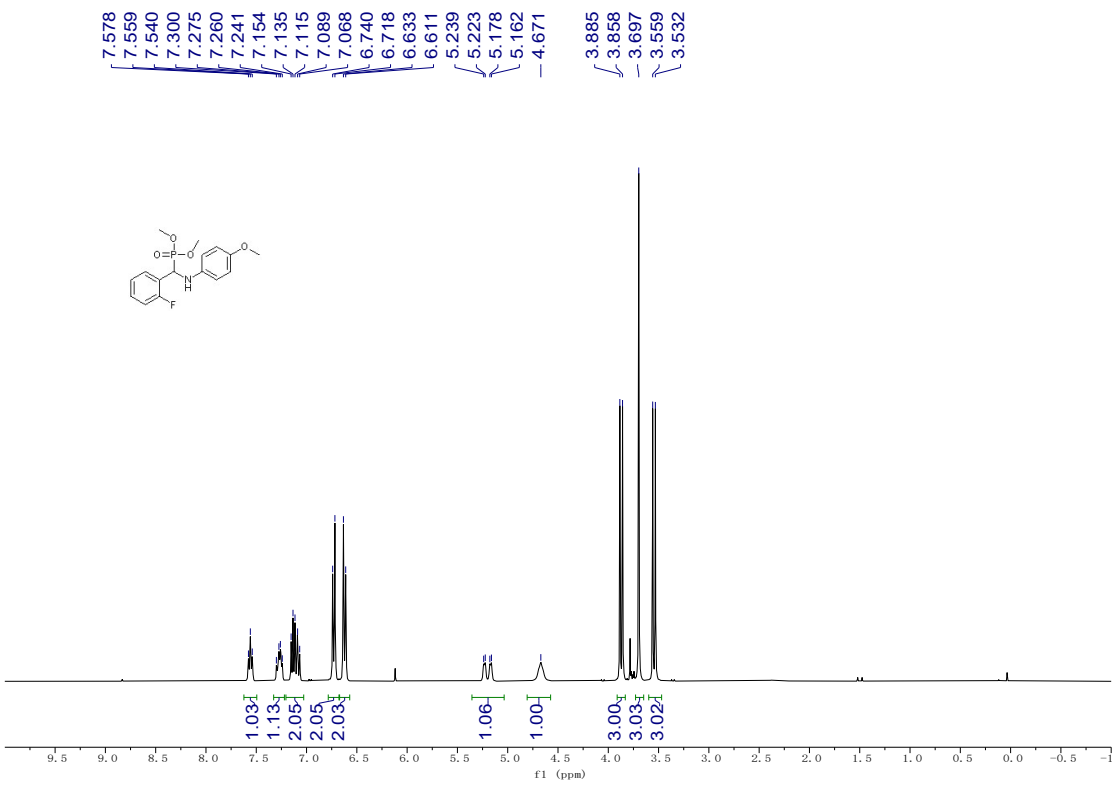


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **o**

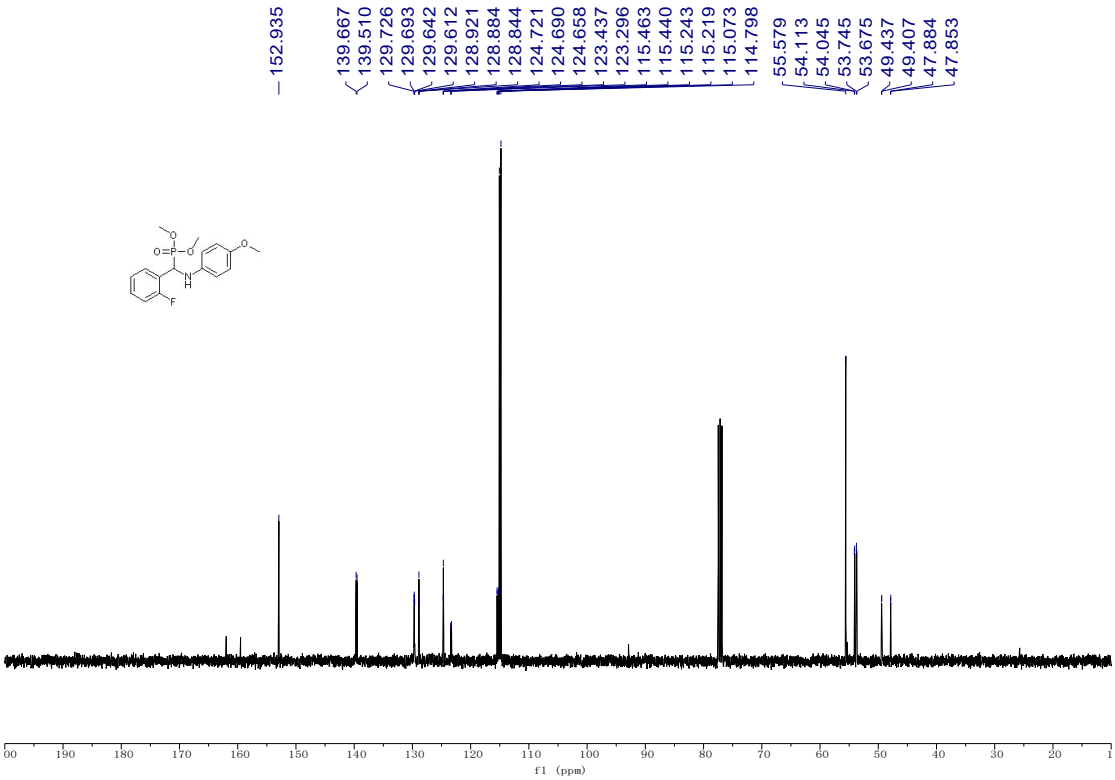


Figure S46. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **n**

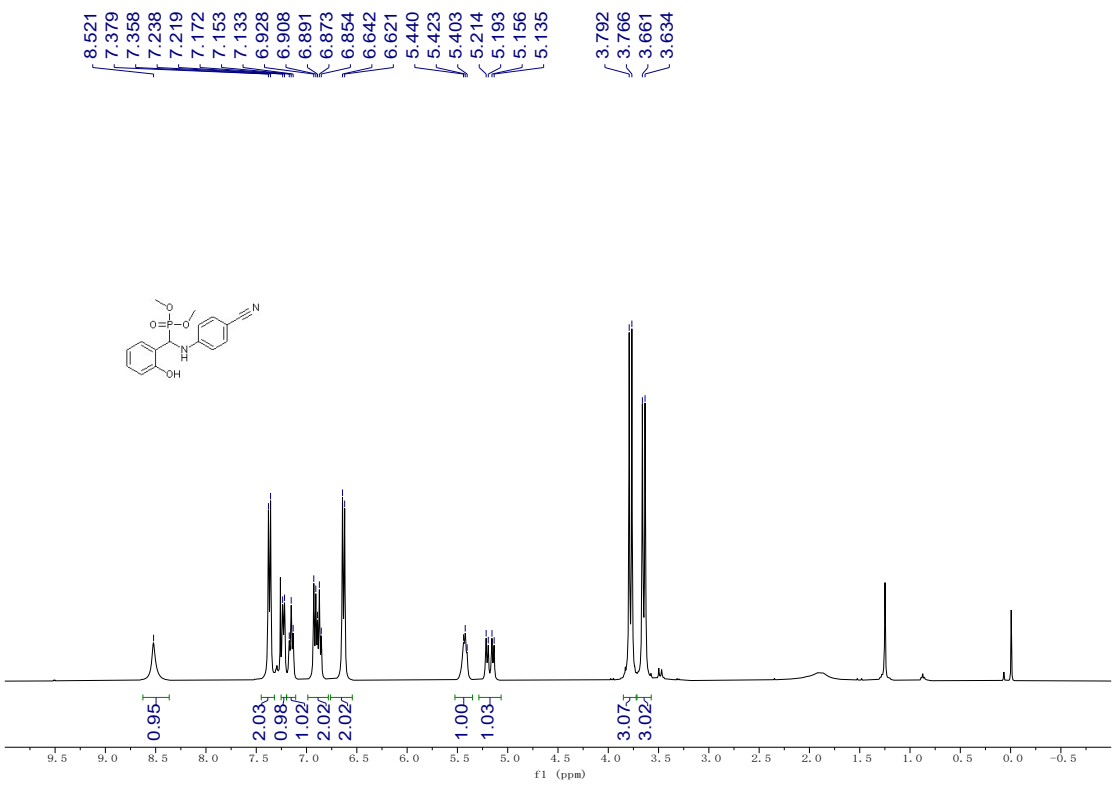


Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **p**

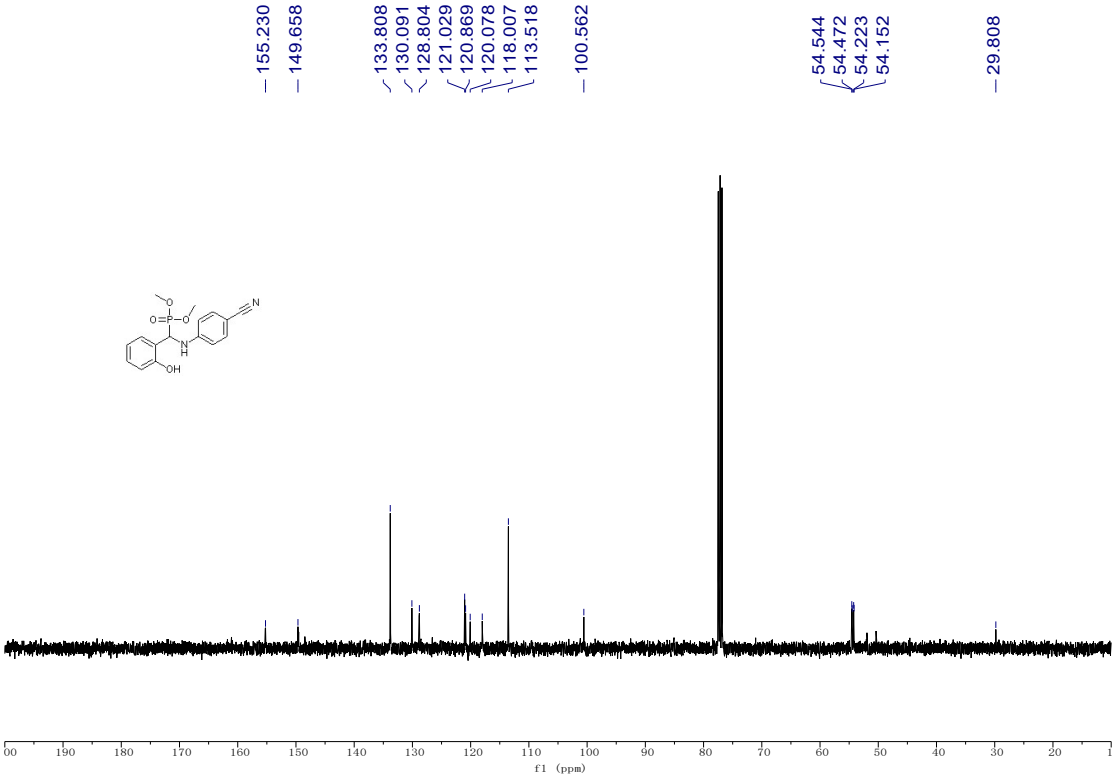


Figure S48. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **p**

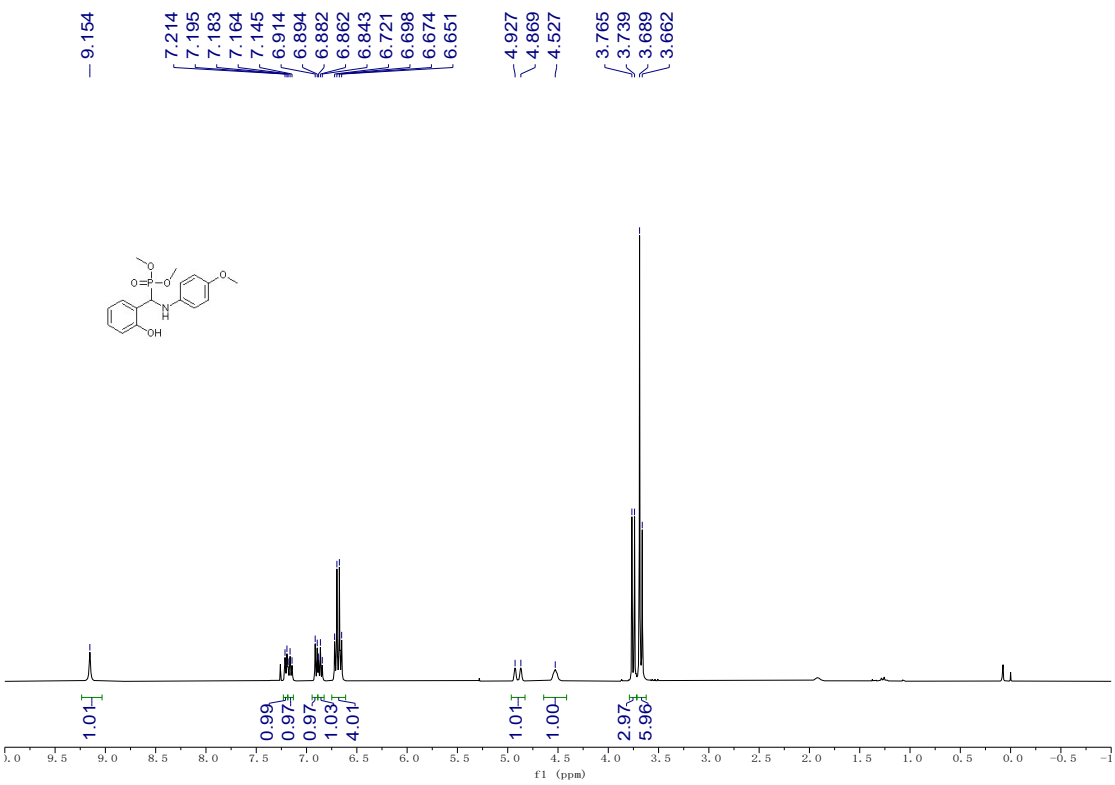


Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **q**

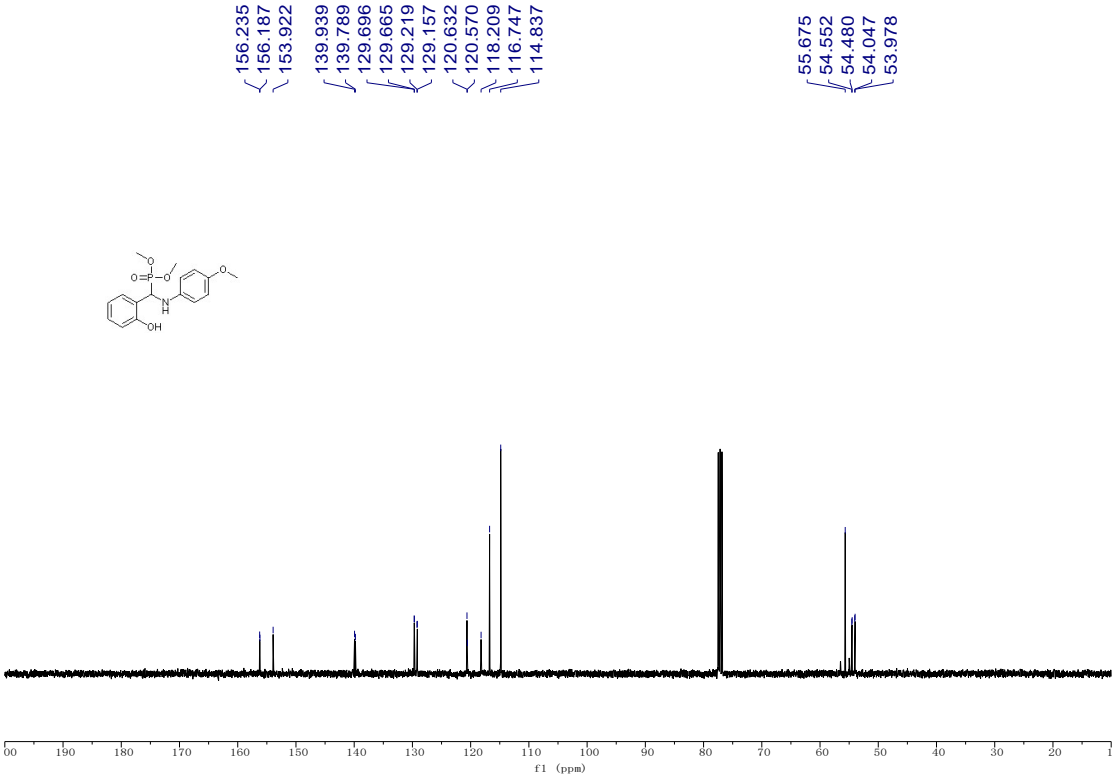


Figure S50. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **q**

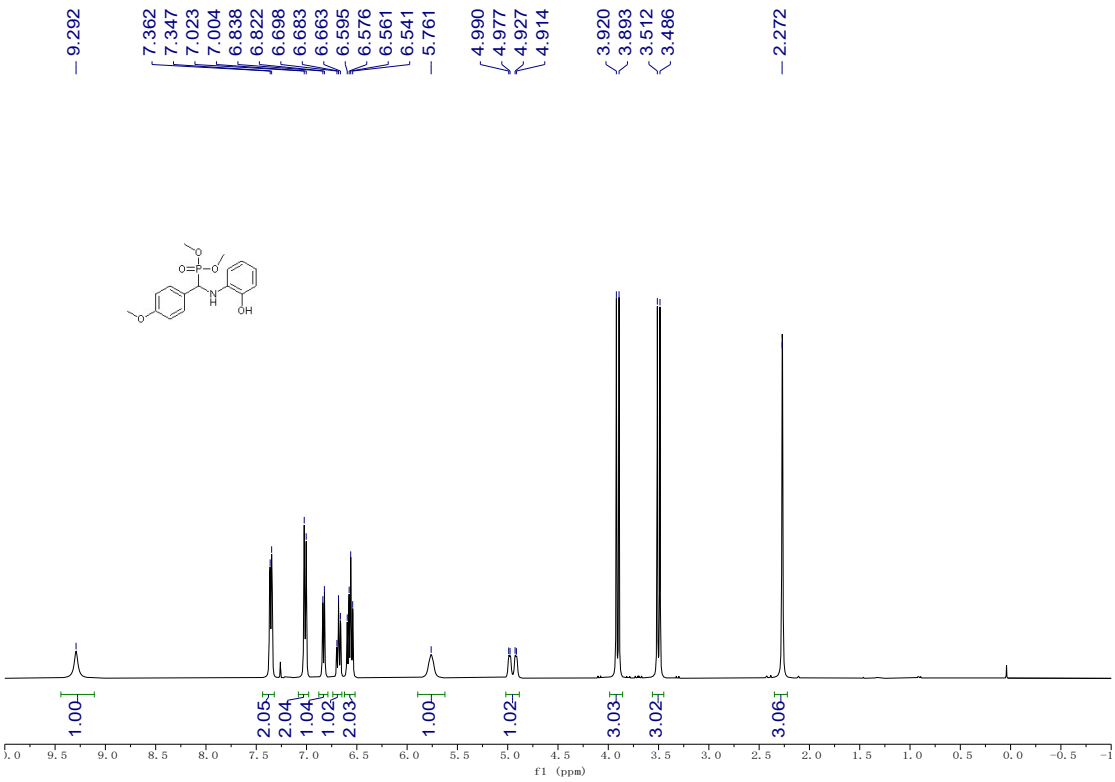


Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **r**

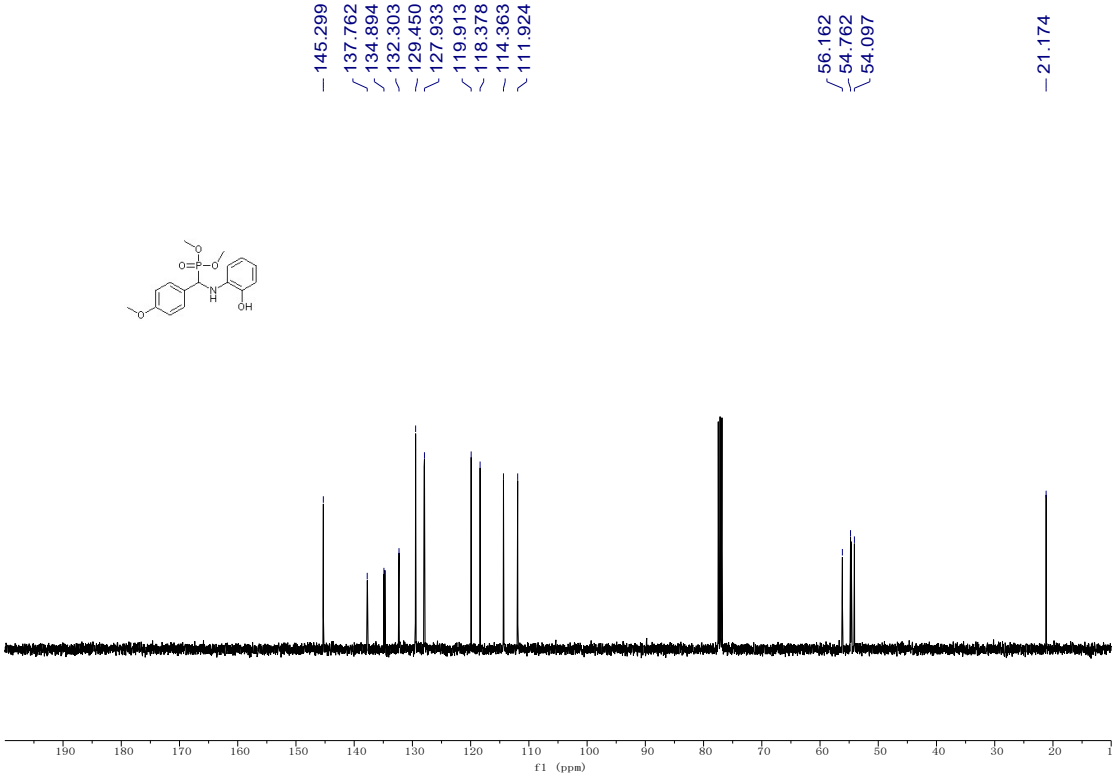


Figure S52. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **r**

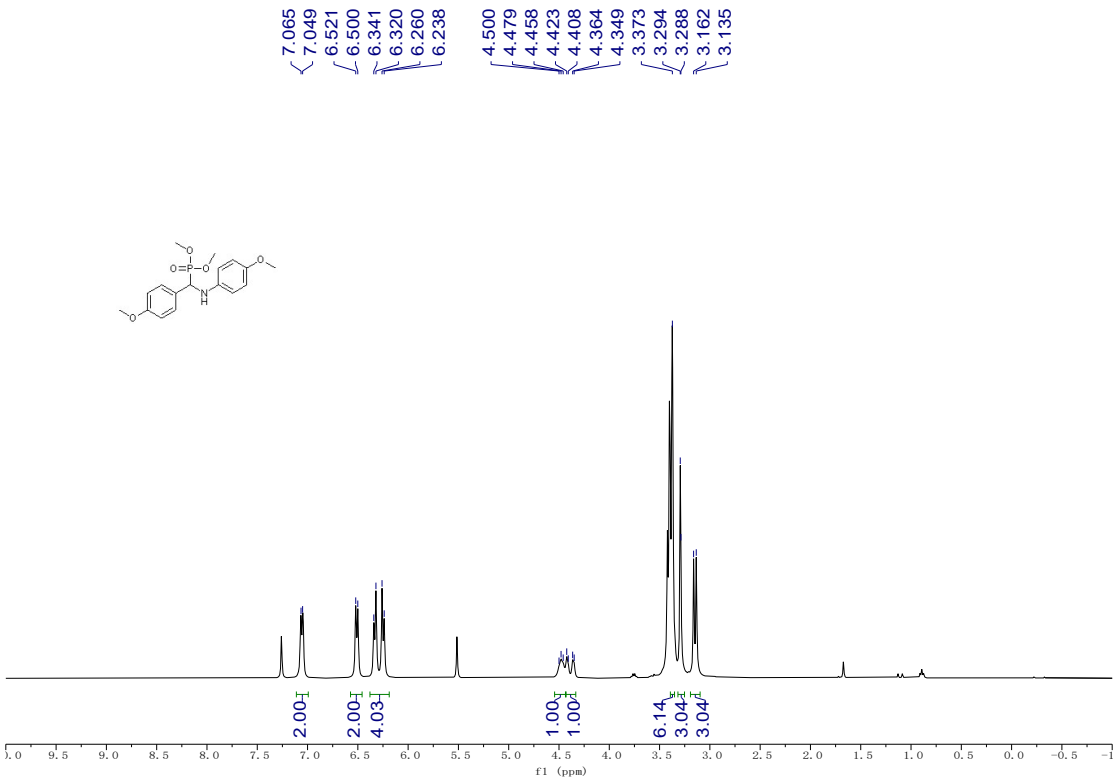


Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **s**

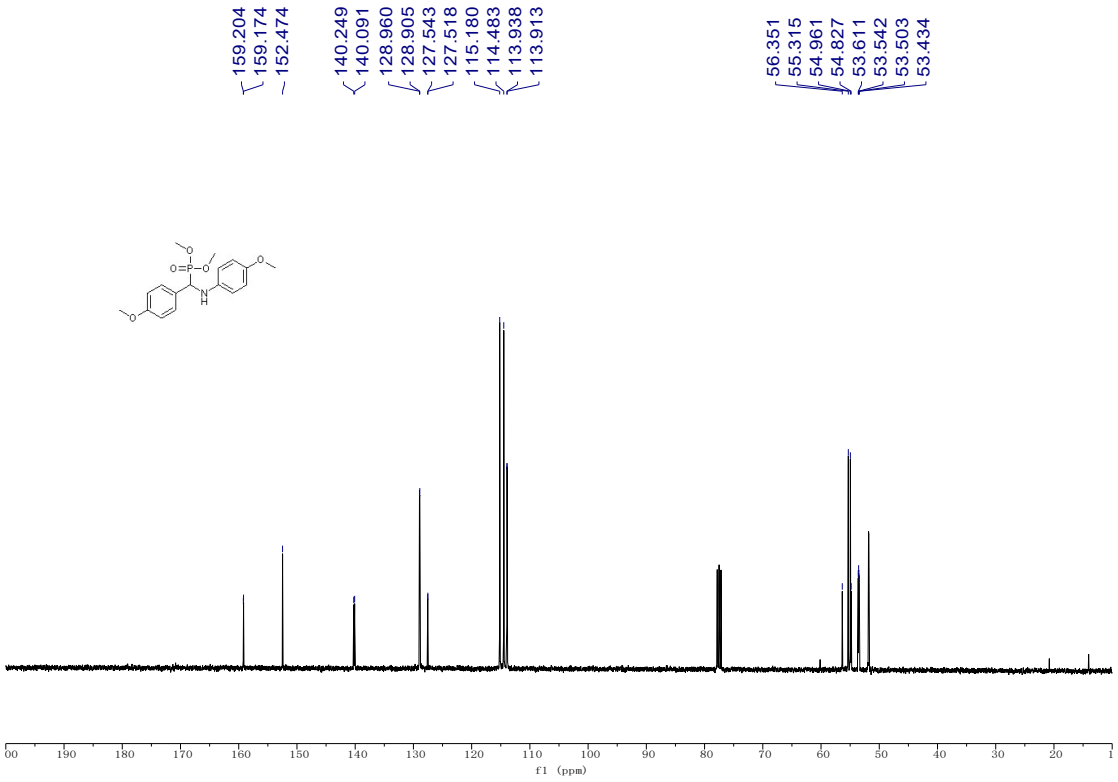


Figure S54. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **s**

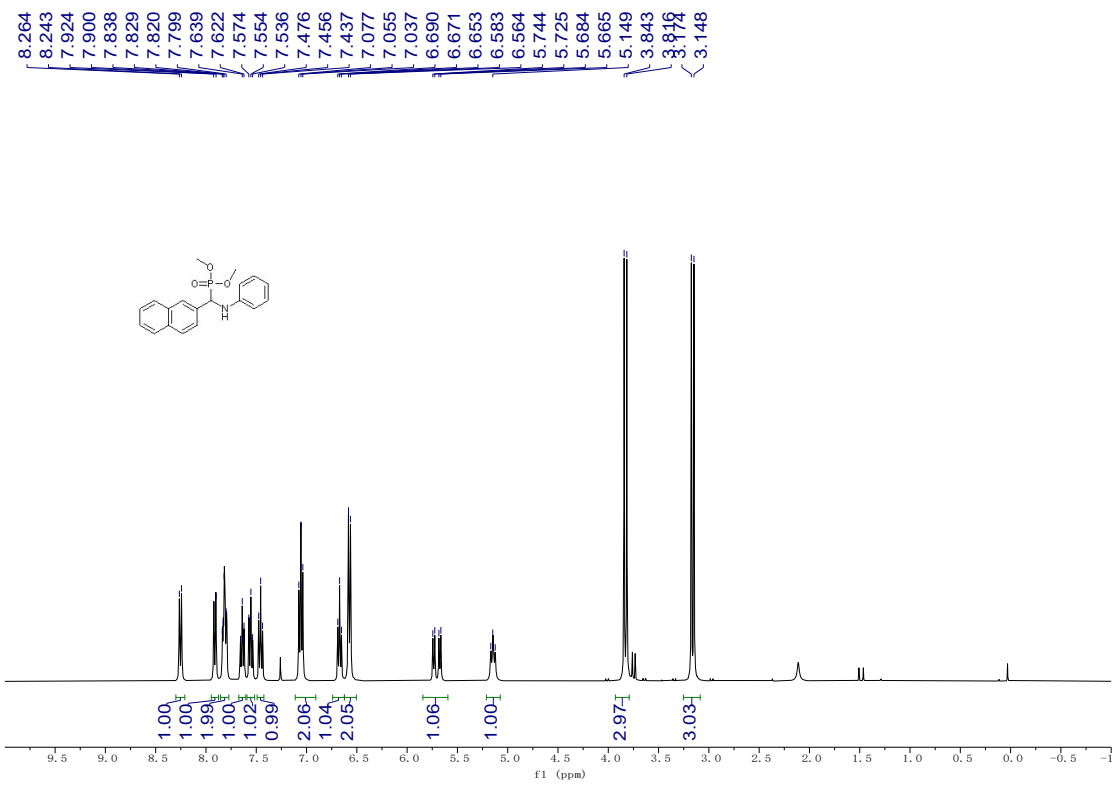


Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **t**

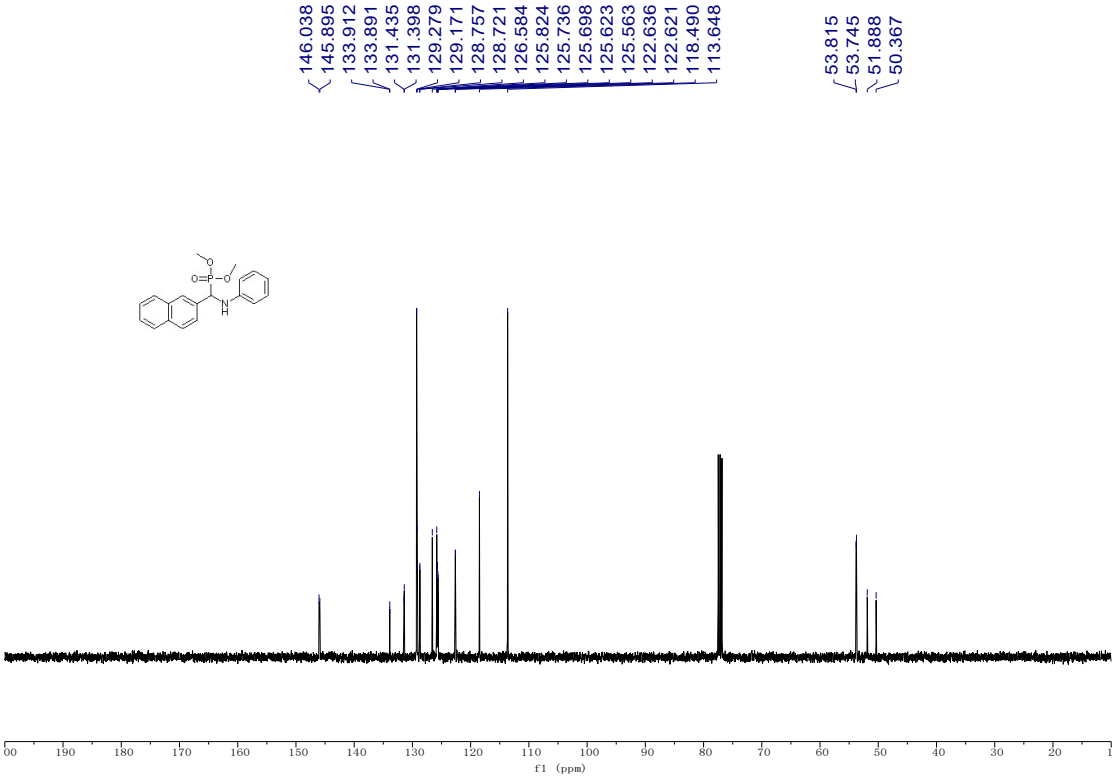


Figure S56. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **t**

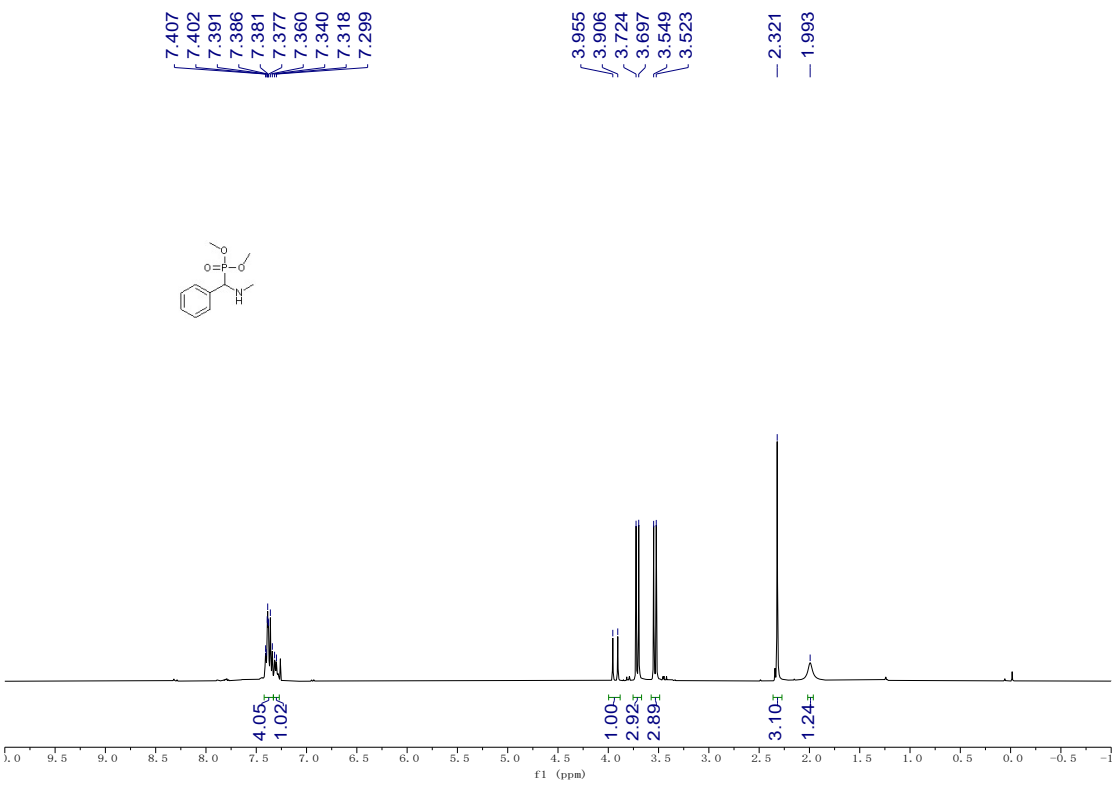


Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **u**

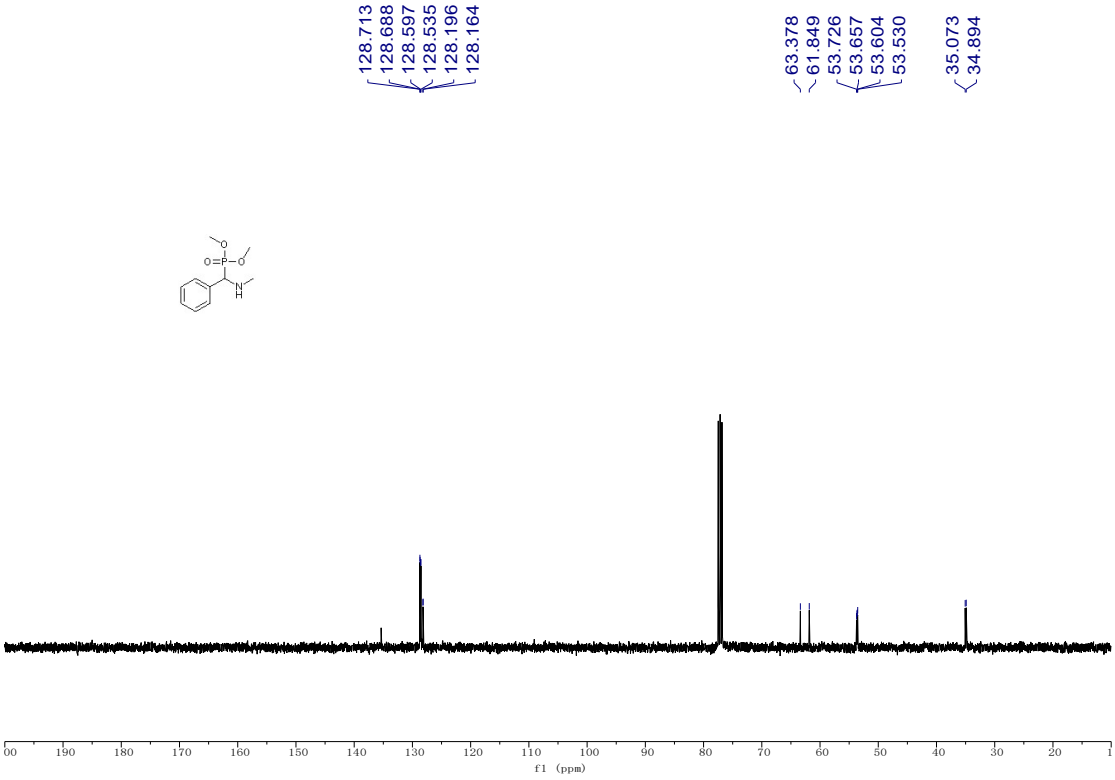


Figure S58. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **u**

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