Electronic Supplementary Material (ESI) for ChemComm.

Facile synthesis of *α*-aminophosphine oxides from diarylphosphine oxides, arynes and formamides

Wen-Bin Huang, Li-Qi Qiu, Fang-Yu Ren, Liang-Nian He*

State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

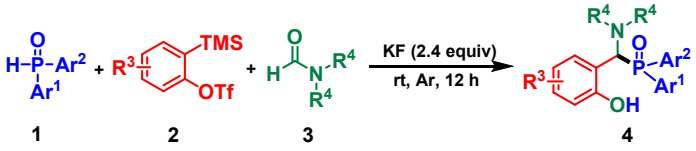
Table of Contents

1. General information

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Diphenylphosphine oxide **1a** was purchased from J&K Chemical Ltd., diarylphosphine oxide **1b-1e**, **1j-1o** were purchased from Energy Chemicalor Adamas-beta®, **1f-1i**, **1p**, **1q** were prepared according to the literature procedures.[1] Aryne precursors **2a**, **2c**, **2d**, **2f** and **2g** were prepared according to the literature procedures.[2] Aryne precursors **2b**, **2e** and **2h** were purchased from Shanghai Xian Ding Biotechnology Co., Ltd®. The products were isolated by column chromatography on silica gel (100-200 mesh) using petroleum ether/ethyl acetate or recrystallization with hexane and ethyl acetate. NMR spectra were obtained on a Bruker 400 MHz spectrometer at 20 °C. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$, DMSO-d_6 and CDCN as the internal reference ($CDCl_3$: δ = 7.26 ppm, DMSO-d_6: δ = 2.49 ppm, CD_3CN: δ = 1.94 ppm). The ^{13}C NMR (101 MHz) chemical shifts were given using $CDCl_3$, DMSO-d_6 and CD_3CN as the internal standard ($CDCl_3$: δ = 77.16 ppm, DMSO-d_6: δ = 39.52 ppm, CD_3CN: δ = 1.32, 118.29 ppm). The ^{31}P NMR (162 MHz) data were recorded with a Bruker 400 MHz spectrometer. FT-IR was recorded on a Bruker Tensor 27 FT-IR spectrophotometer with KBr pellets. High-resolution mass spectra (HR-MS) were obtained with a Waters-Q-TOF-Premier (ESI^+ or ESI^-).

2. General experimental procedure

General procedure for the synthesis of *α*-amino phosphine oxide compounds.

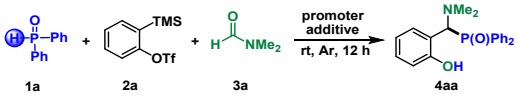


1 **2** **3** **4**

To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with diarylphosphine oxide **1** (0.25 mmol), KF (34.9 mg, 0.6 mmol) and formamide (1 mL) in a glove box. The aryne precursor **2** (0.3 mmol) was added to the reaction mixture, then stirred at room temperature for 12 h. After the reaction, formamide **3** was distilled under reduced pressure. The reaction mixture was concentrated and purified by silica gel column chromatography (silica: 100-200 mesh, petroleum ether/ethyl acetate, from 3:1 to 1:2) to afford the corresponding *α*-amino phosphine oxide products **4**.

3. Optimization of the reaction conditions

Table S1 Optimization of reaction conditions[a]



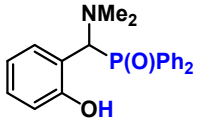
1a 2a 3a 4aa

Entry	**2a** (equiv)	**3a**	promoter (equiv)	additive (equiv)	T (°C)	Yield[b]/%
1	2.0	1 mL	KF (4.0)	18-Crown-6 (2.4 equiv)	25	96
2	2.0	1 mL	CsF (4.0)	18-Crown-6 (2.4 equiv)	25	67
3	2.0	1 mL	TBAF (4.0)	18-Crown-6 (2.4 equiv)	25	62
4	1.2	1 mL	KF (2.4)	18-Crown-6 (2.4 equiv)	25	94
5	1.2	1 mL	KF (2.4)	-	25	95 (91)[c]
6	1.2	1 mL	LiF (2.4)	-	25	n.d.
7	1.2	1 mL	NaF (2.4)	-	25	n.d.
8	1.2	1 mL	Na_2CO_3 (2.4)	-	25	<10
9	1.2	1 mL	K_2CO_3 (2.4)	-	25	68
10	1.2	1 mL	Cs_2CO_3 (2.4)	-	25	44
11	1.2	1 mL	KF (2.4)	-	0	trace
12	1.2	1 mL	KF (2.4)	-	15	71
13	1.2	1 mL	KF (2.4)	-	40	87
14	1.2	1 mL	KF (1.2)	-	25	89
15	1.2	0.5 mL	KF (2.4)	-	25	87
16	1.2	2.0 mL	KF (2.4)	-	25	92
17[d]	1.2	3.0 equiv	KF (2.4)	-	25	n.d.
18[e]	1.2	10 equiv	KF (2.4)	-	25	<10
19[f]	1.2	0.5 mL	KF (2.4)	-	25	65
20[g]	1.2	0.5 mL	KF (2.4)	-	25	56
21[h]	1.2	0.5 mL	KF (2.4)	-	25	53
22[i]	1.2	0.5 mL	KF (2.4)	-	25	22
23	1.2	1 mL	KF (2.4)	4A molecular sieve (25 mol%)	25	trace
24	1.2	1 mL	KF (2.4)	anhydrous Na_2SO_4 (50 mol%)	25	87
25	1.2	1 mL	-	-	25	n.d.

[a] Unless otherwise specified notes, the reactions were performed with **1a** (0.25 mmol, 1.0 equiv), fluoride source (specified equiv), additive (0.6 mmol, 2.4 equiv), DMF (1 mL), rt, 12 h. [b] Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yield was given in parenthesis. [d] 1 mL CH_3CN was used as solvent. [e] 1 mL THF was used as solvent. [f] 0.5 mL THF was used as co-solvent. [g] 0.5 mL CH_3CN was used as co-solvent. [h] 0.5 mL 1,4-dioxane was used as co-solvent. [i] 0.5 mL chlorobenzene was used as co-solvent. n.d. = not detected.

4. Characterization data of the products

((dimethylamino)(2-hydroxyphenyl)methyl)diphenylphosphine oxide (4aa).



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/2, v/v)

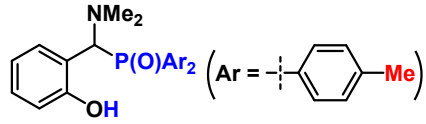
White solid, m. p.: 156-157 °C.

79.8 mg, 91% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.83 (s, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 7.3 Hz, 1H), 7.66-7.57 (m, 2H), 7.53 (s, 3H), 7.38-7.23 (m, 3H), 7.02 (t, J = 7.3 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.69 (t, J = 7.1 Hz, 1H), 5.27 (d, J = 11.6 Hz, 1H), 2.25 (s, 6H). **^{13}C NMR** (101

MHz, DMSO-d_6) δ 156.4 (d, J = 8.5 Hz), 134.0 (d, J = 98.0 Hz), 133.3 (d, J = 92.9 Hz), 132.4 (d, J = 4.6 Hz), 131.2 (dd, J = 5.1, 1.6 Hz), 130.8 (d, J = 8.6 Hz), 130.1 (d, J = 8.3 Hz), 128.9, 128.5 (d, J = 11.1 Hz), 128.2 (d, J = 10.9 Hz), 118.0, 116.8 (d, J = 4.4 Hz), 115.4, 58.1 (d, J = 90.7 Hz), 43.5 (d, J = 7.7 Hz). **^{31}P NMR** (162 MHz, DMSO-d_6) δ 31.49. **IR** (KBr): 3692, 3652, 3631, 3057, 2988, 2947, 2868, 2829, 2784, 1601, 1454, 1438, 1384, 1265, 1150, 1117, 1026, 737, 700, 557, 527 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{21}H_{23}NO_2P]^+$: 352.1466, found: 352.1462.

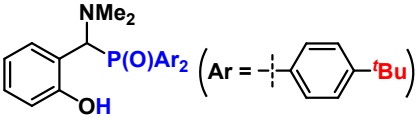
((dimethylamino)(2-hydroxyphenyl)methyl)di-*p*-tolylphosphine oxide (4ba)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/2, v/v)
Pale yellow solid, m. p.: 97-98 °C.
88.2 mg, 93% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 7.81 (dd, J = 10.1, 8.5 Hz, 2H), 7.42 (dd, J = 10.1, 8.6 Hz, 2H), 7.31 (d, J = 6.8 Hz, 2H), 7.11-6.97 (m, 3H), 6.90 (d, J = 8.1 Hz, 1H), 6.78 (d, J = 7.5 Hz, 1H), 6.54 (t, J = 7.3 Hz, 1H), 4.40 (d, J = 9.3 Hz, 1H), 2.40 (s, 3H), 2.39 (s, 6H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.5 (d, J = 4.8 Hz), 142.1 (dd, J = 35.8, 2.8 Hz), 133.1 (d, J = 7.8 Hz), 131.3 (d, J = 8.9 Hz), 130.9 (d, J = 9.1 Hz), 129.5, 129.4 (d, J = 11.1 Hz), 129.0 (d, J = 12.0 Hz), 128.9 (d, J = 102.0 Hz), 128.3 (d, J = 100.0 Hz), 118.7, 117.8, 117.4, 69.1 (d, J = 83.4 Hz), 44.6 (d, J = 7.1 Hz), 21.6 (d, J = 18.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 35.01. **IR** (KBr): 3062, 2940, 2867, 2830, 2785, 2733, 2617, 1914, 1738, 1602, 1501, 1454, 1397, 1379, 1346, 1275, 1240, 1150, 1116, 1099, 1023, 848, 806, 758, 738, 712, 659, 617, 550, 520, 453 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{23}H_{27}NO_2P]^+$: 380.1779, found: 380.1777.

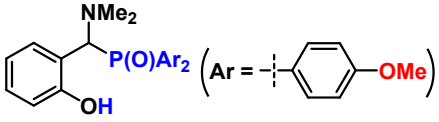
bis(4-(*tert*-butyl)phenyl)((dimethylamino)(2-hydroxyphenyl)methyl)phosphine oxide (4ca)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/2, v/v)
White solid, m. p.: 191-192 °C.
107.7 mg, 93% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 7.92-7.78 (m, 2H), 7.59-7.37 (m, 4H), 7.22 (d, J = 6.3 Hz, 2H), 7.03 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 6.71 (d, J = 7.4 Hz, 1H), 6.48 (t, J = 7.3 Hz, 1H), 4.38 (d, J = 8.9 Hz, 1H), 2.39 (s, 6H), 1.33 (s, 9H), 1.19 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.5 (d, J = 4.4 Hz), 155.1 (dd, J = 31.4, 2.5 Hz), 133.0 (d, J = 7.9 Hz), 131.2 (d, J = 8.9 Hz), 130.8 (d, J = 9.1 Hz), 129.4, 128.4, 128.3 (d, J = 101.0 Hz), 125.59 (d, J = 11.8 Hz), 125.24 (d, J = 11.8 Hz), 118.59, 117.70 (d, J = 20.1 Hz), 69.93 (d, J = 82.0 Hz), 44.75 (d, J = 7.2 Hz), 34.95 (d, J = 20.3 Hz), 31.13 (d, J = 15.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.53. **IR** (KBr): 3064, 2965, 2907, 2869, 2830, 2785, 2735, 1919, 1600, 1455, 1393, 1268, 1170, 1115, 1093, 1024, 828, 757, 745, 613, 593, 566, 515 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{29}H_{39}NO_2P]^+$: 464.2718, found: 464.2708.

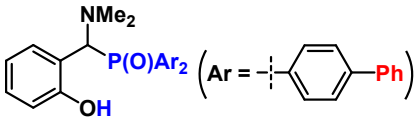
((dimethylamino)(2-hydroxyphenyl)methyl)bis(4-methoxyphenyl)phosphine oxide (4da)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/2, v/v)
White solid, m. p.: 94-95 °C.
92.5 mg, 90% yield;

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.83 (dd, *J* = 10.3, 8.8 Hz, 2H), 7.43 (dd, *J* = 10.3, 8.9 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.99 (dd, *J* = 8.7, 2.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 7.4 Hz, 1H), 6.71 (dd, *J* = 8.7, 2.0 Hz, 2H), 6.55 (t, *J* = 7.3 Hz, 1H), 4.36 (d, *J* = 9.7 Hz, 1H), 3.82 (s, 3H), 3.67 (s, 3H), 2.38 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4 (dd, *J* = 29.9, 2.7 Hz), 157.6 (d, *J* = 4.1 Hz), 133.3 (d, *J* = 10.1 Hz), 133.2 (d, *J* = 8.1 Hz), 132.9 (d, *J* = 10.1 Hz), 129.6, 123.1 (d, *J* = 105.5 Hz), 122.7 (d, *J* = 104.6 Hz), 118.8, 118.2, 117.5, 114.2 (d, *J* = 12.6 Hz), 113.9 (d, *J* = 12.6 Hz), 70.9 (d, *J* = 82.9 Hz), 55.4 (d, *J* = 15.7 Hz), 44.7 (d, *J* = 7.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.77. **IR** (KBr): 3286, 2955, 2920, 2850, 1736, 1646, 1597, 1502, 1458, 1376, 1256, 1119, 1082, 1026, 800, 765, 556, 515, 448 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+Na]^+$ for $[C_{23}H_{26}NO_4PNa]^+$: 434.1497, found: 434.1492.

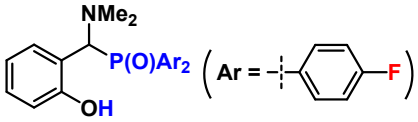
di([1,1'-biphenyl]-4-yl)((dimethylamino)(2-hydroxyphenyl)methyl)phosphine oxide (4ea)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v)
White solid, m. p.: 126-127 °C.
120.7 mg, 96% yield;

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 8.07 (dd, *J* = 10.6, 8.3 Hz, 2H), 7.76 (dd, *J* = 8.2, 2.5 Hz, 2H), 7.71-7.61 (m, 4H), 7.48 (dd, *J* = 8.8, 6.0 Hz, 6H), 7.43-7.30 (m, 4H), 7.10 (t, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.57 (t, *J* = 7.4 Hz, 1H), 4.55 (d, *J* = 8.8 Hz, 1H), 2.47 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.5 (d, *J* = 4.7 Hz), 144.5 (dd, *J* = 41.0, 2.5 Hz), 139.8 (d, *J* = 9.3 Hz), 133.0 (d, *J* = 7.6 Hz), 131.9 (d, *J* = 8.8 Hz), 131.5 (d, *J* = 9.1 Hz), 130.7 (d, *J* = 99.5 Hz), 130.1 (d, *J* = 99.2 Hz), 129.8, 129.0 (d, *J* = 14.6 Hz), 128.2 (d, *J* = 16.0 Hz), 127.4 (d, *J* = 11.7 Hz), 127.3 (d, *J* = 13.3 Hz), 127.0 (d, *J* = 11.8 Hz), 118.9, 117.9, 117.3, 69.2 (d, *J* = 82.6 Hz), 44.8 (d, *J* = 7.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.28. **IR** (KBr): 3703, 3678, 3659, 3631, 3059, 3030, 2941, 2868, 2830, 2785, 1599, 1484, 1454, 1393, 1265, 1169, 1150, 1121, 1007, 834, 758, 697, 670, 660, 570, 525 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{33}H_{31}NO_2P]^+$: 504.2092, found: 504.2089.

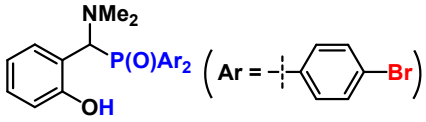
((dimethylamino)(2-hydroxyphenyl)methyl)bis(4-fluorophenyl)phosphine oxide (4fa)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1, v/v)
White solid, m. p.: 171-172 °C.
90.0 mg, 93% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.91 (ddd, *J* = 10.2, 8.8, 5.9 Hz, 2H), 7.50 (ddd, *J* = 10.4, 8.8, 5.8 Hz, 2H), 7.25-7.18 (m, 2H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.99-6.90 (m, 2H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.63 (d, *J* = 7.4 Hz, 1H), 6.54 (t, *J* = 7.3 Hz, 1H), 4.28 (d, *J* = 8.8 Hz, 1H), 2.39 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4 (dd, *J* = 29.8, 3.3 Hz), 163.9 (dd, *J* = 29.5, 3.4 Hz), 157.4 (d, *J* = 4.6 Hz), 134.0 (d, *J* = 18.7 Hz), 133.8 (d, *J* = 37.3 Hz), 133.6 (d, *J* = 19.2 Hz), 132.9 (d, *J* = 8.1 Hz), 130.0, 127.7 (dd, *J* = 101.4, 3.4 Hz), 127.1 (d, *J* = 101.1 Hz), 119.1, 118.1, 117.0, 116.4, 116.2 (d, *J* = 8.7 Hz), 116.1 (d, *J* = 1.5 Hz), 115.9 (d, *J* = 8.7 Hz), 115.7, 70.5 (d, *J* = 83.5 Hz), 44.8 (d, *J* = 7.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.00. **IR** (KBr): 3069, 2949, 2927, 2869, 2832, 2788, 1592, 1500, 1455, 1265, 1236, 1161, 1116, 1026, 829, 748, 549, 457 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{21}H_{21}F_2NO_2P]^+$: 388.1278, found: 388.1276.

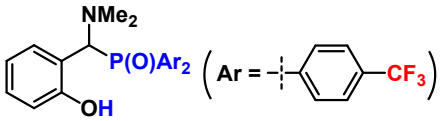
bis(4-bromophenyl)((dimethylamino)(2-hydroxyphenyl)methyl)phosphine oxide (4ga)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1, v/v)
White solid, m. p.: 178-179 °C.
115.3 mg, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.83-7.71 (m, 2H), 7.66 (d, *J* = 6.4 Hz, 2H), 7.41-7.34 (m, 4H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 6.58 (t, *J* = 7.4 Hz, 1H), 4.38 (d, *J* = 8.8 Hz, 1H), 2.39 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.2 (d, *J* = 5.1 Hz), 132.9 (d, *J* = 9.3 Hz), 132.7 (d, *J* = 7.3 Hz), 132.5 (d, *J* = 9.5 Hz), 132.1 (d, *J* = 12.0 Hz), 131.8 (d, *J* = 12.0 Hz), 130.9 (d, *J* = 98.9 Hz), 130.2 (d, *J* = 98.5 Hz), 130.0, 127.5 (d, *J* = 3.2 Hz), 127.2 (d, *J* = 3.4 Hz), 119.2, 117.7, 116.8, 68.3 (d, *J* = 83.8 Hz), 44.7 (d, *J* = 7.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.25. **IR** (KBr): 2955, 2925, 2867, 2786, 1577, 1478, 1455, 1384, 1275, 1262, 1171, 1152, 1116, 1096, 1069, 1010, 812, 744, 706, 564, 531 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+Na]^+$ for $[C_{21}H_{20}Br_2NO_2PNa]^+$: 529.9496, found: 529.9494.

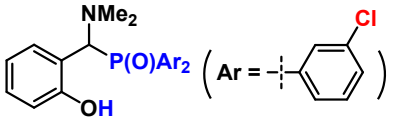
((dimethylamino)(2-hydroxyphenyl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (4ha)



Compound **4ha** is easily decomposed during the isolation process.
^{1}H NMR yield = 51%.

Characteristic peaks of the crude reaction mixture: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.39 (s, 1H), 6.63 (t, *J* = 6.4 Hz, 1H), 4.97 (d, *J* = 8.9 Hz, 1H), 2.38 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.9 (d, *J* = 7.0 Hz), 64.2 (d, *J* = 85.4 Hz), 44.4 (d, *J* = 7.8 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.09. **HR-ESI-MS**: calculated m/z $[M+Na]^+$ for $[C_{23}H_{20}F_6NO_2PNa]^+$: 510.1034, found: 510.1033.

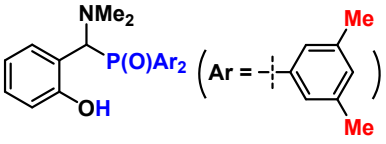
bis(3-chlorophenyl)((dimethylamino)(2-hydroxyphenyl)methyl)phosphine oxide (4ia)



Recrystallization with hexane and ethyl acetate
White solid, m. p.: 177-178 °C.
^{1}H NMR yield = 76%.
48.2 mg, recrystallization yield = 46%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.81 (s, 1H), 7.95 (d, *J* = 10.9 Hz, 1H), 7.92-7.85 (m, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.58 (ddd, *J* = 12.2, 11.2, 5.8 Hz, 4H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.35 (td, *J* = 7.7, 2.9 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 5.31 (d, *J* = 11.8 Hz, 1H), 2.25 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.4 (d, *J* = 9.1 Hz), 136.0 (d, *J* = 96.1 Hz), 135.3 (d, *J* = 90.4 Hz), 133.6 (d, *J* = 14.5 Hz), 133.4 (d, *J* = 14.2 Hz), 132.2 (d, *J* = 4.3 Hz), 131.5, 130.7 (d, *J* = 12.1 Hz), 130.5 (d, *J* = 11.7 Hz), 130.3 (d, *J* = 9.2 Hz), 129.6 (d, *J* = 9.4 Hz), 129.4 (d, *J* = 8.4 Hz), 129.3, 128.7 (d, *J* = 8.1 Hz), 118.1, 116.1 (d, *J* = 4.7 Hz), 115.3, 57.6 (d, *J* = 92.3 Hz), 43.4 (d, *J* = 8.1 Hz). **^{31}P NMR** (162 MHz, DMSO-d_6) δ 29.61. **IR** (KBr): 3197, 3147, 3069, 2947, 2878, 2829, 2735, 2619, 1601, 1564, 1454, 1403, 1347, 1271, 1238, 1172, 1152, 1133, 1073, 1028, 848, 757, 678, 572, 550, 509, 459 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+Na]^+$ for $[C_{21}H_{20}Cl_2NO_2PNa]^+$: 442.0506, found: 442.0497.

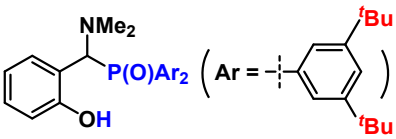
((dimethylamino)(2-hydroxyphenyl)methyl)bis(3,5-dimethylphenyl)phosphine oxide (4ja)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v)
White solid, m. p.: 161-162 °C.
93.6 mg, 92% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.87 (s, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 11.0 Hz, 2H), 7.23 (d, J = 10.7 Hz, 2H), 7.16 (s, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.97 (s, 1H), 6.81 (d, J = 8.1 Hz, 1H), 6.71 (t, J = 7.4 Hz, 1H), 5.22 (d, J = 11.8 Hz, 1H), 2.34 (s, 6H), 2.23 (s, 6H), 2.17 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.5 (d, J = 8.1 Hz), 137.4 (d, J = 27.7 Hz), 137.3 (d, J = 27.3 Hz), 134.0 (d, J = 97.3 Hz), 133.3 (d, J = 92.5 Hz), 132.5 (t, J = 5.0 Hz), 128.8, 128.1 (d, J = 8.5 Hz), 127.6 (d, J = 8.4 Hz), 117.9, 117.0 (d, J = 4.5 Hz), 115.3, 58.0 (d, J = 90.5 Hz), 43.4 (d, J = 7.7 Hz), 20.8 (d, J = 19.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 36.91. **IR** (KBr): 3055, 2940, 2862, 2784, 2307, 1738, 1602, 1455, 1266, 1151, 1125, 1030, 850, 750, 694, 579, 435 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{25}H_{31}NO_2P]^+$: 408.2092, found: 408.2082.

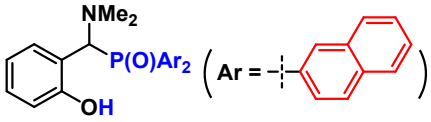
bis(3,5-di-*tert*-butylphenyl)((dimethylamino)(2-hydroxyphenyl)methyl)phosphine oxide (4ka)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v)
White solid, m. p.: 180-181 °C.
135.2 mg, 94% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.76 (s, 1H), 7.77 (dd, J = 11.7, 1.7 Hz, 2H), 7.61 (s, 1H), 7.42-7.35 (m, 3H), 7.02 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 7.9 Hz, 1H), 6.50 (d, J = 7.4 Hz, 1H), 6.44 (t, J = 7.3 Hz, 1H), 4.17 (d, J = 9.3 Hz, 1H), 2.39 (s, 6H), 1.35 (s, 18H), 1.18 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.7 (d, J = 3.7 Hz), 150.9 (d, J = 11.3 Hz), 150.6 (d, J = 11.3 Hz), 132.9 (d, J = 7.7 Hz), 130.8 (d, J = 97.5 Hz), 130.4 (d, J = 96.9 Hz), 129.4, 126.0 (d, J = 2.1 Hz), 125.8 (d, J = 8.8 Hz), 125.8 (overlapped), 125.5 (d, J = 9.3 Hz), 118.5, 118.1 (d, J = 2.3 Hz), 73.6-70.1 (m), 44.96 (d, J = 7.2 Hz), 35.1 (d, J = 21.6 Hz), 31.4 (d, J = 22.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 35.34. **IR** (KBr): 3066, 2964, 2905, 2869, 2830, 2785, 1593, 1477, 1455, 1424, 1363, 1249, 1169, 1149, 1127, 1026, 871, 754, 707, 603, 496 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{37}H_{55}NO_2P]^+$: 576.3970, found: 576.3966.

((dimethylamino)(2-hydroxyphenyl)methyl)di(naphthalen-2-yl)phosphine oxide (4la)

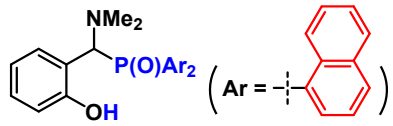


Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1, v/v)
White solid, m. p.: 184-185 °C.
107.2 mg, 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 8.64 (d, J = 13.1 Hz, 1H), 8.24 (d, J = 13.1 Hz, 1H), 7.97 (d, J = 5.6 Hz, 2H), 7.90 (t, J = 8.9 Hz, 2H), 7.71-7.50 (m, 6H), 7.44 (t, J = 7.1 Hz, 1H), 7.37 (t, J = 7.1 Hz, 1H), 7.06-6.96 (m, 2H), 6.93 (d, J = 7.5 Hz, 1H), 6.50 (t, J = 7.0 Hz, 1H), 4.77 (d, J = 8.9 Hz, 1H), 2.47 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.5 (d, J = 5.2 Hz), 134.6 (dd, J = 30.7, 1.9 Hz), 133.5 (d, J = 7.8 Hz), 133.2 (d, J = 8.1 Hz), 133.0 (d, J = 7.4 Hz), 132.7 (d, J = 12.7 Hz), 132.3 (d, J = 12.6 Hz), 129.7, 129.6 (d, J = 98.7 Hz), 129.0 (d, J = 11.7 Hz), 128.8 (d, J = 97.9 Hz), 128.3 (d, J = 23.7 Hz), 127.7 (d, J = 26.4 Hz), 126.8 (d, J = 35.2 Hz), 126.2 (d, J = 9.8 Hz), 125.6 (d, J = 9.8 Hz), 118.9, 117.7, 117.4, 68.0 (d, J =

83.7 Hz), 44.7 (d, J = 7.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.67. **IR** (KBr): 3056, 2940, 2868, 2830, 2785, 2732, 2611, 1601, 1591, 1501, 1454, 1382, 1341, 1271, 1240, 1162, 1150, 1132, 1089, 1043, 1021, 858, 815, 742, 655, 598, 532, 477 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{29}H_{27}NO_2P]^+$: 452.1779, found: 452.1770.

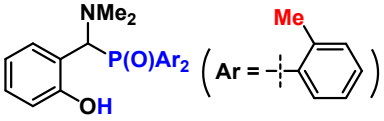
((dimethylamino)(2-hydroxyphenyl)methyl)di(naphthalen-1-yl)phosphine oxide (4ma)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1, v/v)
White solid, m. p.: 176-178 °C.
79.0 mg, 70% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.27 (s, 1H), 8.81 (d, J = 7.5 Hz, 1H), 8.66 (d, J = 8.3 Hz, 1H), 8.31 (dd, J = 13.2, 7.1 Hz, 1H), 8.09 (d, J = 7.7 Hz, 1H), 7.99-7.85 (m, 4H), 7.80 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 6.8 Hz, 1H), 7.50-7.29 (m, 5H), 6.97 (t, J = 7.3 Hz, 1H), 6.75 (d, J = 7.4 Hz, 1H), 6.63 (t, J = 7.0 Hz, 1H), 5.60 (d, J = 11.6 Hz, 1H), 2.29 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.3 (d, J = 10.5 Hz), 133.4 (dd, J = 49.1, 7.8 Hz), 133.2 (dd, J = 49.7, 7.1 Hz), 132.5, 132.3 (d, J = 3.6 Hz), 131.9 (d, J = 9.5 Hz), 131.2, 130.2, 129.4, 128.9 (d, J = 8.5 Hz), 128.8, 126.6, 126.0, 124.9 (d, J = 11.9 Hz), 124.3 (d, J = 13.2 Hz), 117.8, 117.4 (d, J = 5.2 Hz), 115.2, 58.6 (d, J = 84.9 Hz), 43.5 (d, J = 7.4 Hz). **^{31}P NMR** (162 MHz, DMSO-d_6) δ 36.85. **IR** (KBr): 3441, 3354, 3056, 2936, 2862, 2828, 2784, 2253, 2125, 1506, 1455, 1275, 1151, 1052, 1026, 1006, 801, 774, 763, 674, 567, 486, 457 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+Na]^+$ for $[C_{29}H_{26}NO_2PNa]^+$: 474.1599, found: 474.1595.

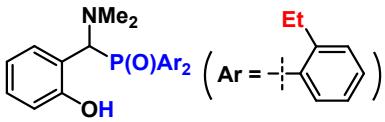
((dimethylamino)(2-hydroxyphenyl)methyl)di-*o*-tolylphosphine oxide (4na)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v)
White solid, m. p.: 169-170 °C.
75.8 mg, 80% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.80 (s, 1H), 8.06 (dd, J = 11.1, 8.0 Hz, 1H), 7.80 (d, J = 7.4 Hz, 1H), 7.54 (dd, J = 11.2, 8.0 Hz, 1H), 7.40 (dt, J = 23.7, 7.0 Hz, 2H), 7.21 (t, J = 7.1 Hz, 2H), 7.11-6.98 (m, 3H), 6.78 (d, J = 8.0 Hz, 1H), 6.70 (t, J = 7.4 Hz, 1H), 5.32 (d, J = 11.9 Hz, 1H), 2.29 (s, 6H), 2.23 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.1 (d, J = 8.9 Hz), 141.4 (d, J = 7.5 Hz), 140.7 (d, J = 7.9 Hz), 132.7 (d, J = 2.8 Hz), 132.6, 132.4 (d, J = 78.0 Hz), 132.4 (d, J = 9.8 Hz) (overlapped), 132.0 (d, J = 8.8 Hz), 131.5 (d, J = 10.0 Hz), 131.4, 131.3, 131.2 (d, J = 1.9 Hz), 131.1, 128.9, 125.41 (d, J = 11.1 Hz), 125.0 (d, J = 11.0 Hz), 118.0, 117.1 (d, J = 5.1 Hz), 115.2, 43.4 (d, J = 7.8 Hz), 20.5 (dd, J = 22.4, 3.4 Hz). **^{31}P NMR** (162 MHz, DMSO-d_6) δ 34.10. **IR** (KBr): 3567, 3503, 3447, 2956, 2925, 2855, 2358, 2342, 2331, 1772, 1457, 1275, 1262, 1174, 1145, 1030, 990, 946, 764, 751, 690, 566, 531, 458 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{23}H_{27}NO_2P]^+$: 380.1779, found: 380.1773.

((dimethylamino)(2-hydroxyphenyl)methyl)bis(2-ethylphenyl)phosphine oxide (4oa)

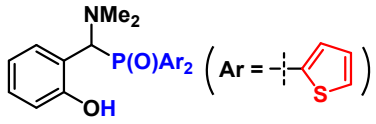


Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1, v/v)
White solid, m. p.: 165-166 °C.
83.5 mg, 82% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.98 (s, 1H), 8.04-7.93 (m, 1H), 7.83 (d, J = 6.0 Hz, 1H), 7.57-7.42 (m, 2H), 7.34 (s, 1H), 7.27 (d, J = 6.0 Hz, 2H), 7.12-6.98 (m, 3H), 6.81 (d, J = 7.5

Hz, 1H), 6.69 (t, J = 6.8 Hz, 1H), 5.30 (d, J = 11.2 Hz, 1H), 2.90-2.69 (m, 3H), 2.66-2.52 (m, 1H), 2.28 (s, 6H), 0.79 (t, J = 6.8 Hz, 3H), 0.66 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.2 (d, J = 8.8 Hz), 148.1 (d, J = 7.7 Hz), 147.4 (d, J = 7.6 Hz), 133.0, 132.6, 132.0 (d, J = 9.9 Hz), 131.7 (d, J = 87.9 Hz), 131.4, 131.3, 131.2, 130.0 (d, J = 10.0 Hz), 129.8 (d, J = 9.9 Hz), 128.8, 125.3 (d, J = 11.2 Hz), 124.8 (d, J = 10.9 Hz), 117.8, 117.3 (d, J = 5.1 Hz), 115.2, 57.5 (d, J = 98.7 Hz), 43.4 (d, J = 7.6 Hz), 25.9 (dd, J = 19.9, 3.1 Hz), 15.2 (d, J = 34.4 Hz). **^{31}P NMR** (162 MHz, DMSO-d_6) δ 34.85. **IR** (KBr): 3648, 3627, 3064, 2966, 2934, 2871, 2830, 2785, 1683, 1594, 1507, 1456, 1375, 1267, 1148, 1087, 1021, 844, 790, 754, 572, 560, 529, 508, 475 cm^{-1}. **HR-ESI-MS**: calculated m/z [M+Na]$^+$ for [$C_{25}H_{30}NO_2PNa$]$^+$: 430.1912, found: 430.1909.

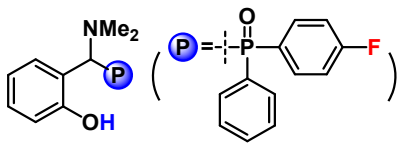
((dimethylamino)(2-hydroxyphenyl)methyl)di(thiophen-2-yl)phosphine oxide (4pa)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1, v/v)
Pale brown solid, m. p.:160-161 °C.
79.9 mg, 88% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.68 (s, 1H), 8.03 (t, J = 3.6 Hz, 1H), 7.85 (t, J = 3.6 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.53 (dd, J = 5.7, 3.4 Hz, 1H), 7.30 (dd, J = 5.2, 3.6 Hz, 1H), 7.25 (s, 1H), 7.06 (d, J = 5.0 Hz, 2H), 6.84-6.66 (m, 2H), 4.91 (d, J = 12.8 Hz, 1H), 2.30 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.5 (d, J = 9.9 Hz), 135.5 (d, J = 9.4 Hz), 135.0, 134.7 (d, J = 9.3 Hz), 134.3 (d, J = 3.4 Hz), 134.2 (d, J = 4.0 Hz), 133.6 (d, J = 72.8 Hz), 131.9 (d, J = 4.6 Hz), 129.2, 128.2 (d, J = 13.4 Hz), 128.0 (d, J = 14.1 Hz), 118.1, 116.8 (d, J = 5.0 Hz), 115.2, 61.5 (d, J = 101.0 Hz), 43.6 (d, J = 8.4 Hz). **^{31}P NMR** (162 MHz, DMSO-d_6) δ 21.67. **IR** (KBr): 3650, 3577, 3420, 2365, 2037, 1718, 1684, 1559, 1457, 1339, 1220, 1156, 1095, 1021, 721, 577, 526 cm^{-1}. **HR-ESI-MS**: calculated m/z [M+Na]$^+$ for [$C_{17}H_{18}NO_2PS_2Na$]$^+$: 386.0414, found: 386.0407.

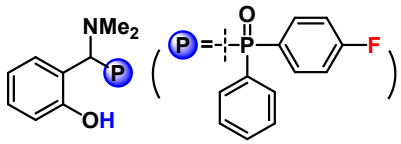
((dimethylamino)(2-hydroxyphenyl)methyl)(4-fluorophenyl)(phenyl)phosphine oxide (4qa-1)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1, v/v)
White solid, m. p.: 164-165 °C.
36.9 mg, 40% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.99-7.90 (m, 2H), 7.59-7.50 (m, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.25-7.14 (m, 4H), 7.04 (t, J = 7.5 Hz, 1H), 6.91 (t, J = 8.1 Hz, 2H), 6.55 (t, J = 7.3 Hz, 1H), 4.55 (d, J = 9.5 Hz, 1H), 2.40 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3 (d, J = 3.1 Hz), 163.8 (d, J = 3.2 Hz), 157.2 (d, J = 5.3 Hz), 134.0 (d, J = 18.7 Hz), 134.0 (overlapped), 132.9 (d, J = 7.3 Hz), 131.8 (d, J = 2.4 Hz), 131.2 (d, J = 98.3 Hz), 130.9 (d, J = 8.9 Hz), 129.7, 128.4 (d, J = 11.5 Hz), 128.1 (dd, J = 100.9, 3.3 Hz), 118.9, 117.3 (d, J = 51.1 Hz), 116.1 (d, J = 21.2 Hz), 115.9 (d, J = 21.3 Hz), 68.1 (d, J = 83.8 Hz), 44.6 (d, J = 7.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.90. **IR** (KBr): 3063, 2942, 2869, 2831, 2787, 1593, 1499, 1455, 1265, 1236, 1161, 1118, 1026, 830, 747, 693, 555, 519 cm^{-1}. **HR-ESI-MS**: calculated m/z [M+Na]$^+$ for [$C_{21}H_{21}FNO_2PNa$]$^+$: 392.1192, found: 392.1181.

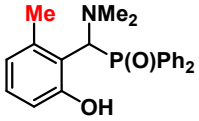
((dimethylamino)(2-hydroxyphenyl)methyl)(4-fluorophenyl)(phenyl)phosphine oxide (4qa-2)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v)
Pale yellow solid, m. p.: 111-112 °C.
39.7 mg, 43% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.94 (dd, *J* = 9.4, 8.7 Hz, 2H), 7.63-7.44 (m, 5H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.91 (dt, *J* = 15.5, 7.6 Hz, 3H), 6.54 (dt, *J* = 14.6, 7.4 Hz, 2H), 4.27 (d, *J* = 7.6 Hz, 1H), 2.40 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1 (d, *J* = 3.2 Hz), 163.6 (d, *J* = 3.3 Hz), 157.5 (d, *J* = 4.4 Hz), 133.6 (d, *J* = 19.0 Hz), 133.6 (overlapped), 132.6 (d, *J* = 7.6 Hz), 132.2 (d, *J* = 2.5 Hz), 132.0 (d, *J* = 97.9 Hz), 131.3 (d, *J* = 8.7 Hz), 129.8 (d, *J* = 1.1 Hz), 128.8 (d, *J* = 11.6 Hz), 127.4 (dd, *J* = 101.2, 3.0 Hz), 119.0, 117.8, 117.4, 115.7 (d, *J* = 21.3 Hz), 115.6 (d, *J* = 21.3 Hz), 69.8 (d, *J* = 82.3 Hz), 44.9 (d, *J* = 7.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.87. **IR** (KBr): 3065, 2941, 2868, 2831, 2786, 2735, 2613, 1907, 1665, 1593, 1500, 1455, 1396, 1276, 1237, 1161, 1118, 1026, 909, 831, 737, 555, 532, 466 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+Na]^+$ for $[C_{21}H_{21}FNO_2PNa]^+$: 392.1192, found: 392.1181.

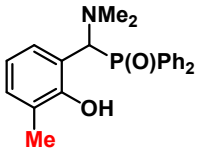
((dimethylamino)(2-hydroxy-6-methylphenyl)methyl)diphenylphosphine oxide (4ab)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v)
White solid, m. p.: 163-164 °C.
57.5 mg, 63% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.94 (ddd, *J* = 10.8, 8.0, 1.4 Hz, 2H), 7.59-7.44 (m, 5H), 7.32 (td, *J* = 7.4, 1.3 Hz, 1H), 7.22 (td, *J* = 7.5, 3.0 Hz, 2H), 6.93 (t, *J* = 4.5 Hz, 1H), 6.37 (d, *J* = 4.8 Hz, 2H), 4.23 (d, *J* = 7.9 Hz, 1H), 2.40 (s, 6H), 2.23 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.9 (d, *J* = 3.9 Hz), 132.3 (d, *J* = 96.8 Hz), 132.0 (d, *J* = 2.4 Hz), 131.7 (d, *J* = 2.5 Hz), 131.4 (d, *J* = 8.5 Hz), 131.4 (d, *J* = 99.0 Hz), 131.2 (d, *J* = 8.8 Hz), 130.8 (d, *J* = 1.3 Hz), 130.3 (d, *J* = 7.7 Hz), 128.7 (d, *J* = 11.4 Hz), 128.2 (d, *J* = 11.5 Hz), 126.7 (d, *J* = 1.2 Hz), 118.3, 117.0, 71.7 (d, *J* = 79.8 Hz), 45.0 (d, *J* = 7.0 Hz), 16.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.31. **IR** (KBr): 3058, 2962, 2924, 2857, 2785, 1592, 1468, 1438, 1261, 1145, 1097, 1025, 800, 747, 697, 660, 550, 537, 507 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{22}H_{25}NO_2P]^+$: 366.1623, found: 366.1620.

((dimethylamino)(2-hydroxy-3-methylphenyl)methyl)diphenylphosphine oxide (4ab')

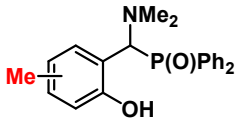


Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/2, v/v)
White solid, m. p.: 95-96 °C.
28.3 mg, 31% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.86 (s, 1H), 7.99-7.91 (m, 2H), 7.60 (dd, *J* = 15.2, 7.5 Hz, 3H), 7.36 (dd, *J* = 10.6, 8.3 Hz, 2H), 7.29 (t, *J* = 7.0 Hz, 1H), 7.13 (dd, *J* = 7.2, 4.9 Hz, 2H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.25 (d, *J* = 7.3 Hz, 1H), 4.42 (d, *J* = 3.0 Hz, 1H), 2.40 (s, 6H), 1.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.5 (d, *J* = 3.6 Hz), 137.2 (d, *J* = 5.6 Hz), 132.6 (d, *J* = 92.1 Hz), 132.1 (d, *J* = 1.7 Hz), 131.6 (d, *J* = 1.8 Hz), 131.5 (d, *J* = 101.0 Hz), 131.5 (d, *J* = 4.6 Hz), 131.4 (d, *J* = 3.1 Hz), 129.3, 128.8 (d, *J* = 11.3 Hz), 127.7 (d, *J* = 11.8 Hz), 121.3, 118.4 (d, *J* = 4.0 Hz), 115.6, 67.3 (d, *J* = 76.9 Hz), 45.6 (d, *J* = 7.0 Hz), 20.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.62. **IR** (KBr): 3728, 3663, 3631, 3056, 2960, 2867, 2831, 2784, 1584, 1467, 1438, 1276, 1225, 1175, 1115, 1005, 953, 864, 749, 696, 572, 545,

502 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{22}H_{25}NO_2P]^+$: 366.1623, found: 366.1619.

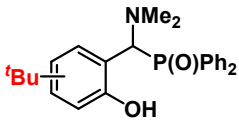
((dimethylamino)(2-hydroxy-4-methylphenyl)methyl)diphenylphosphine oxide (4ac) and ((dimethylamino)(2-hydroxy-5-methylphenyl)methyl)diphenylphosphine oxide (4ac')



Purification via silica gel column chromatography (petroleum ether/ethyl acetate =2/1, v/v)
White solid, m. p.: 161-163 °C.
67.6 mg, 74% yield (**4ac**/**4ac'** = 1:1.4).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.74 (d, 1H), 7.99-7.89 (m, 2H), 7.65 (dd, J = 15.9, 7.9 Hz, 3H), 7.54 (d, J = 2.1 Hz, 4H), 7.40-7.29 (m, 3H), 6.86 (dd, J = 8.2, 1.4 Hz, 0.4H), 6.73 (d, J = 8.1 Hz, 0.5H), 6.65 (s, 0.6H), 6.55 (d, J = 7.8 Hz, 0.6H), 5.27 (dd, 1H), 2.28 (d, 6H), 2.14 (d, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.3 (d, J = 8.5 Hz), 154.1 (d, J = 8.2 Hz), 138.3, 134.1 (d, J = 98.1 Hz), 134.0 (d, J = 98.2 Hz), 133.4 (d, J = 92.7 Hz), 133.3 (d, J = 93.2 Hz), 132.7 (d, J = 4.5 Hz), 132.3 (d, J = 4.2 Hz), 131.2, 130.7 (d, J = 8.5 Hz), 130.2-130.0 (m), 129.5, 128.4 (d, J = 11.0 Hz), 128.3 (d, J = 10.7 Hz), 126.3, 119.0, 116.5 (d, J = 4.2 Hz), 116.0, 115.2, 113.7 (d, J = 4.4 Hz), 58.2 (d, J = 90.3 Hz), 57.9 (d, J = 92.1 Hz), 43.4 (d, J = 4.2 Hz), 20.8 (d, J = 1.5 Hz), 20.4 (d, J = 1.6 Hz). **^{31}P NMR** (162 MHz, DMSO-d_6) δ 31.74, 31.66. **IR** (KBr): 3503, 3447, 3393, 2954, 2924, 2853, 2358, 1653, 1555, 1507, 1458, 1448, 1261, 1025, 998, 825, 764, 750, 699, 537 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+Na]^+$ for $[C_{22}H_{24}NO_2PNa]^+$: 388.1442, found: 388.1432.

((4-(*tert*-butyl)-2-hydroxyphenyl)(dimethylamino)methyl)diphenylphosphine oxide (4ad) and ((5-(*tert*-butyl)-2-hydroxyphenyl)(dimethylamino)methyl)diphenylphosphine oxide (4ad')

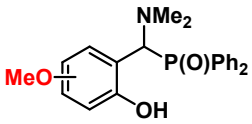


Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1, v/v)
White solid, m. p.: 166-168 °C.
85.5 mg, 84% yield (**4ad**/**4ad'** = 1:4).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 8.14-8.05 (m, 0.4H), 7.98-7.90 (m, 2H), 7.64-7.44 (m, 5.8H), 7.44-7.36 (m, 0.4H), 7.30 (td, J = 7.4, 1.1 Hz, 1H), 7.20 (td, J = 7.6, 2.9 Hz, 2H), 7.11-7.05 (m, 0.4H), 6.90 (d, J = 0.8 Hz, 1H), 6.85 (d, J = 1.7 Hz, 0.2H), 6.62 (d, J = 1.3 Hz, 0.2H), 6.51-6.43 (m, 2H), 4.87 (d, J = 1.9 Hz, 0.2H), 4.23 (d, J = 7.6 Hz, 1H), 2.40 (s, 1.2H), 2.38 (s, 6H), 1.20 (s, 9H), 1.18 (s, 1.8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7 (d, J = 3.7 Hz), 157.2 (d, J = 4.0 Hz), 154.5, 153.4, 133.1, 132.4 (d, J = 7.8 Hz), 132.3 (d, J = 96.7 Hz), 132.3 (d, J = 2.3 Hz), 132.1 (d, J = 2.7 Hz), 131.8 (d, J = 85.8 Hz), 131.6 (d, J = 2.3 Hz), 131.5 (d, J = 8.6 Hz), 131.2, 131.1 (d, J = 8.9 Hz), 129.0 (d, J = 11.5 Hz), 128.8 (d, J = 11.7 Hz), 128.3 (d, J = 11.5 Hz), 127.6 (d, J = 12.0 Hz), 116.2, 115.2, 114.4, 70.7 (d, J = 81.5 Hz), 70.4 (d, J = 76.4 Hz), 45.6 (d, J = 6.7 Hz), 45.0 (d, J = 7.2 Hz), 34.7, 34.6, 31.4, 31.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.01, 32.14. **IR** (KBr): 3079, 3059, 2964, 2867, 2830, 2786, 1610, 1437, 1417, 1242, 1171, 1152, 1118, 1027, 939, 871, 740, 721, 694, 540, 489 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+Na]^+$ for $[C_{25}H_{30}NO_2PNa]^+$: 430.1912, found: 430.1905.

((dimethylamino)(2-hydroxy-4-methoxyphenyl)methyl)diphenylphosphine oxide (4ae)

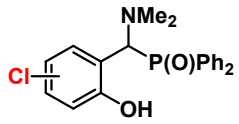
and ((dimethylamino)(2-hydroxy-5-methoxyphenyl)methyl)diphenylphosphine oxide (4ae')



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1, v/v)
Yellow solid, m. p.: 147-149 °C.
81.9 mg, 86% yield (**4ae**/**4ae'** = 1:1.2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.01-7.91 (m, 2H), 7.62-7.47 (m, 5H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.26-7.17 (m, 2H), 6.82 (dd, *J* = 13.2, 8.7 Hz, 1H), 6.66-6.60 (m, 0.6H), 6.51-6.41 (m, 1H), 6.18-6.11 (m, 0.4H), 4.50 (t, 1H), 3.63 (s, 1.3H), 3.52 (s, 1.7H), 2.40 (d, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.8, 158.6 (d, *J* = 4.8 Hz), 151.9, 151.4 (d, *J* = 5.2 Hz), 133.3 (d, *J* = 103.3 Hz), 133.7, 132.2 (d, *J* = 98.1 Hz), 131.7, 131.6, 131.4 (d, *J* = 3.2 Hz), 131.3 (d, *J* = 98.9 Hz), 131.3 (d, *J* = 2.9 Hz), 131.1, 131.0, 130.9, 128.6 (d, *J* = 11.4 Hz), 128.6 (d, *J* = 11.5 Hz), 128.3 (d, *J* = 11.6 Hz), 128.3 (d, *J* = 11.6 Hz), 118.0 (d, *J* = 15.8 Hz), 117.3 (d, *J* = 7.2 Hz), 115.5, 109.3, 105.5, 102.4, 68.9-67.0 (m), 55.7, 55.1, 44.8 (d, *J* = 7.4 Hz), 44.5 (d, *J* = 7.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.73, 33.25. **IR** (KBr): 3054, 2988, 2949, 2830, 2785, 1738, 1615, 1507, 1436, 1375, 1265, 1167, 1149, 1117, 1028, 912, 743, 699, 531 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{22}H_{25}NO_3P]^+$: 382.1572, found: 382.1562.

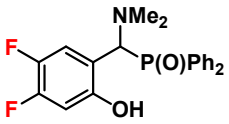
((4-chloro-2-hydroxyphenyl)(dimethylamino)methyl)diphenylphosphine oxide (4af) and ((5-chloro-2-hydroxyphenyl)(dimethylamino)methyl)diphenylphosphine oxide (4af')



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1, v/v)
Green solid, m. p.: 153-155 °C.
89.5 mg, 93% yield (**4af**/**4af'** = 1:4).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.22 (d, 1H), 7.93 (dd, *J* = 9.3, 5.2 Hz, 2H), 7.75 (d, *J* = 9.6 Hz, 1H), 7.67-7.59 (m, 2H), 7.53 (s, 3H), 7.33 (d, *J* = 7.4 Hz, 3H), 7.13-7.01 (m, 1H), 6.81 (d, *J* = 8.7 Hz, 1H), 5.24 (d, *J* = 11.3 Hz, 1H), 2.26 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 157.6 (d, *J* = 8.6 Hz), 155.5 (d, *J* = 8.4 Hz), 133.6 (d, *J* = 3.7 Hz), 133.6 (d, *J* = 98.8 Hz) (overlapped), 133.4 (d, *J* = 99.0 Hz), 133.0, 133.0 (d, *J* = 93.4 Hz) (overlapped), 132.9 (d, *J* = 93.7 Hz), 131.6, 131.5 (d, *J* = 4.2 Hz), 130.9 (d, *J* = 8.6 Hz), 130.2 (d, *J* = 8.5 Hz), 129.3, 128.9, 128.7 (d, *J* = 11.4 Hz), 128.5 (d, *J* = 11.0 Hz), 121.8, 119.1 (d, *J* = 4.3 Hz), 118.2, 117.1, 117.0, 116.3 (d, *J* = 4.5 Hz), 115.2, 57.7 (d, *J* = 90.1 Hz), 57.5 (d, *J* = 88.2 Hz), 43.5 (d, *J* = 4.9 Hz). **^{31}P NMR** (162 MHz, DMSO-d_6) δ 31.88, 31.79. **IR** (KBr): 3736, 3671, 3650, 3057, 2926, 2855, 2831, 2786, 2728, 2361, 1744, 1577, 1497, 1437, 1420, 1271, 1164, 1116, 1027, 820, 721, 693, 648, 553, 532 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+Na]^+$ for $[C_{21}H_{21}ClNO_2PNa]^+$: 408.0896, found: 408.0886.

((4,5-difluoro-2-hydroxyphenyl)(dimethylamino)methyl)diphenylphosphine oxide (4ag)

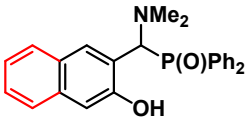


Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/2, v/v)
White solid, m. p.: 154-155 °C.
87.1 mg, 90% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.30 (s, 1H), 7.97-7.86 (m, 2H), 7.75-7.67 (m, 1H), 7.65-7.58 (m, 2H), 7.53 (d, *J* = 12.7 Hz, 3H), 7.41-7.29 (m, 3H), 6.72 (dd, *J* = 12.2, 7.2 Hz, 1H), 5.17 (d, *J* = 11.4 Hz, 1H), 2.25 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 153.3 (t, *J* = 8.6

Hz), 149.9 (d, J = 13.4 Hz), 147.4 (d, J = 13.8 Hz), 142.8 (d, J = 12.3 Hz), 140.5 (d, J = 12.5 Hz), 133.1 (d, J = 99.1 Hz), 132.8 (d, J = 93.6 Hz), 131.5, 130.8 (d, J = 8.7 Hz), 130.1 (d, J = 8.6 Hz), 128.6 (d, J = 11.3 Hz), 128.4 (d, J = 11.0 Hz), 119.7 (dd, J = 18.5, 3.4 Hz), 113.6 (dd, J = 7.8, 3.9 Hz), 103.9 (d, J = 18.8 Hz), 57.3 (d, J = 90.1 Hz), 43.3 (d, J = 7.1 Hz). **^{31}P NMR** (162 MHz, DMSO-d_6) δ 31.66. **IR** (KBr): 3060, 2990, 2944, 2868, 2831, 2787, 1618, 1528, 1437, 1322, 1265, 1225, 1159, 1119, 1098, 1027, 885, 746, 724, 694, 601, 538, 491 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{21}H_{21}F_2NO_2P]^+$: 388.1278, found: 388.1268.

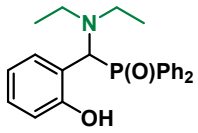
((dimethylamino)(3-hydroxynaphthalen-2-yl)methyl)diphenylphosphine oxide (4ah)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v)
White solid, m. p.: 171-172 °C.
87.2 mg, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 8.01 (dd, J = 9.5, 8.4 Hz, 2H), 7.56 (dd, J = 18.2, 8.5 Hz, 6H), 7.46-7.40 (m, 2H), 7.33-7.27 (m, 2H), 7.21-7.07 (m, 4H), 4.78 (d, J = 8.4 Hz, 1H), 2.46 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.1 (d, J = 4.6 Hz), 134.7, 132.4 (d, J = 7.7 Hz), 132.3 (d, J = 98.0 Hz), 131.3 (d, J = 98.3 Hz), 132.1 (d, J = 2.2 Hz), 131.7 (d, J = 2.7 Hz), 131.5 (d, J = 8.6 Hz), 131.0 (d, J = 8.8 Hz), 128.7 (d, J = 11.7 Hz), 128.3 (d, J = 11.7 Hz), 127.6, 126.4, 126.0, 123.0, 120.7, 111.7, 68.8 (d, J = 80.8 Hz), 44.9 (d, J = 7.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.87. **IR** (KBr): 3737, 3679, 3652, 3058, 2924, 2858, 2831, 2786, 2707, 2613, 1664, 1629, 1599, 1450, 1438, 1398, 1364, 1236, 1168, 1154, 1118, 1027, 913, 871, 745, 722, 693, 645, 589, 552, 535, 478 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{25}H_{25}NO_2P]^+$: 402.1623, found: 402.1613.

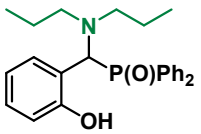
((diethylamino)(2-hydroxyphenyl)methyl)diphenylphosphine oxide (4aab)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1, v/v)
White solid, m. p.: 157-158 °C.
71.1 mg, 75% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.74 (s, 1H), 7.88-7.77 (m, 2H), 7.71 (d, J = 7.6 Hz, 1H), 7.67-7.58 (m, 2H), 7.50 (s, 3H), 7.44-7.26 (m, 3H), 6.99 (t, J = 7.3 Hz, 1H), 6.75 (d, J = 8.1 Hz, 1H), 6.65 (t, J = 7.4 Hz, 1H), 5.30 (d, J = 12.6 Hz, 1H), 2.98 (dq, J = 14.1, 7.1 Hz, 2H), 2.14 (dq, J = 13.1, 6.5 Hz, 2H), 0.79 (t, J = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.2 (d, J = 8.9 Hz), 133.9 (d, J = 98.9 Hz), 133.2 (d, J = 91.7 Hz), 132.0 (d, J = 4.1 Hz), 131.3 (d, J = 1.6 Hz), 131.1, 131.0 (d, J = 8.6 Hz), 130.3 (d, J = 8.1 Hz), 128.8, 128.3 (d, J = 10.7 Hz), 128.1 (d, J = 11.3 Hz), 119.6 (d, J = 5.3 Hz), 118.3, 115.1, 53.7 (d, J = 91.6 Hz), 45.2 (d, J = 7.1 Hz), 13.7. **^{31}P NMR** (162 MHz, DMSO-d_6) δ 32.05. **IR** (KBr): 3060, 2962, 2924, 2869, 2850, 2733, 1601, 1455, 1437, 1383, 1276, 1242, 1152, 1118, 751, 721, 698, 557, 529 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{23}H_{27}NO_2P]^+$: 380.1779, found: 380.1777.

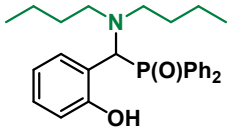
((dipropylamino)(2-hydroxyphenyl)methyl)diphenylphosphine oxide (4aac)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v)
White solid, m. p.: 162-163 °C.
80.4 mg, 79% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.78 (s, 1H), 7.85 (s, 2H), 7.75 (d, J = 7.0 Hz, 1H), 7.69-7.58 (m, 2H), 7.49 (s, 3H), 7.31 (d, J = 6.2 Hz, 3H), 6.99 (t, J = 6.5 Hz, 1H), 6.78 (d, J = 7.5 Hz, 1H), 6.67 (t, J = 6.7 Hz, 1H), 5.35 (d, J = 12.6 Hz, 1H), 2.83 (d, J = 10.2 Hz, 2H), 2.14 (s, 2H), 1.38-1.12 (m, 4H), 0.58 (d, J = 6.3 Hz, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.2 (d, J = 8.8 Hz), 133.8 (d, J = 98.0 Hz), 133.6 (d, J = 92.2 Hz), 132.0, 131.1, 131.0, 130.9, 130.1 (d, J = 8.0 Hz), 128.7, 128.1 (d, J = 24.1 Hz), 128.1 (overlapped), 119.3 (d, J = 4.8 Hz), 118.3, 115.0, 54.2, 53.5 (d, J = 6.0 Hz), 20.8, 11.5. **^{31}P NMR** (162 MHz, DMSO-d_6) δ 31.42. **IR** (KBr): 3057, 2958, 2927, 2870, 2732, 1600, 1454, 1437, 1379, 1266, 1163, 1117, 1052, 1026, 1004, 820, 742, 699, 557, 527, 419 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{25}H_{31}NO_2P]^+$: 408.2092, found: 408.2082.

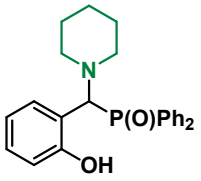
((dibutylamino)(2-hydroxyphenyl)methyl)diphenylphosphine oxide (4aae)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1, v/v)
White solid, m. p.: 169-170 °C.
83.8 mg, 77% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.72 (s, 1H), 7.82 (dd, J = 9.9, 4.3 Hz, 2H), 7.73 (d, J = 7.6 Hz, 1H), 7.68-7.57 (m, 2H), 7.50 (s, 3H), 7.33 (dd, J = 11.9, 6.4 Hz, 3H), 7.06-6.92 (m, 1H), 6.82-6.61 (m, 2H), 5.32 (d, J = 12.7 Hz, 1H), 3.00-2.77 (m, 2H), 2.22-2.00 (m, 2H), 1.20 (d, J = 5.2 Hz, 4H), 0.98 (d, J = 6.9 Hz, 4H), 0.74 (t, J = 6.6 Hz, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.2 (d, J = 6.5 Hz), 134.5-134.3 (m), 134.1-133.9 (m), 133.4 (d, J = 2.9 Hz), 133.1 (d, J = 5.7 Hz), 132.0, 131.1, 131.0, 130.9, 130.2 (d, J = 5.9 Hz), 128.7, 128.2 (d, J = 10.8 Hz), 128.0 (d, J = 10.4 Hz), 119.2, 118.3, 115.0, 53.8 (d, J = 94.1 Hz), 51.3, 30.1, 19.7, 14.1. **^{31}P NMR** (162 MHz, DMSO-d_6) δ 31.50. **IR** (KBr): 3059, 2956, 2930, 2870, 2735, 2615, 1601, 1455, 1438, 1378, 1266, 1163, 1118, 1105, 750, 721, 699, 558, 529 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{27}H_{35}NO_2P]^+$: 436.2405, found: 436.2395.

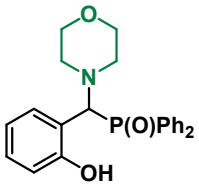
((2-hydroxyphenyl)(piperidin-1-yl)methyl)diphenylphosphine oxide (4aaf)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 3/1, v/v)
White solid, m. p.: 186-188 °C.
50.9 mg, 52% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.70 (s, 1H), 8.12-7.80 (m, 2H), 7.54 (dt, J = 10.9, 7.0 Hz, 5H), 7.34 (t, J = 7.1 Hz, 1H), 7.25 (dt, J = 7.1, 3.9 Hz, 2H), 7.06 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 6.63 (d, J = 7.3 Hz, 1H), 6.49 (t, J = 7.3 Hz, 1H), 4.38 (d, J = 8.9 Hz, 1H), 2.78 (s, 2H), 2.59 (d, J = 4.7 Hz, 2H), 1.47 (d, J = 5.0 Hz, 4H), 1.37-1.19 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.7 (d, J = 4.2 Hz), 132.9 (d, J = 8.2 Hz), 132.7, 132.0 (d, J = 2.7 Hz), 131.7 (d, J = 2.6 Hz), 131.5 (d, J = 8.5 Hz), 131.1 (d, J = 8.9 Hz), 131.0, 129.6, 128.5 (d, J = 11.6 Hz), 128.3 (d, J = 11.5 Hz), 118.8, 118.1, 117.9, 71.0 (d, J = 81.0 Hz), 53.6 (d, J = 6.9 Hz), 26.4, 23.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.30. **IR** (KBr): 3059, 2932, 2852, 2809, 2753, 2607, 1601, 1485, 1454, 1437, 1383, 1266, 1163, 1118, 1096, 1040, 998, 860, 740, 721, 699, 557, 533 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{24}H_{27}NO_2P]^+$: 392.1779, found: 392.1770.

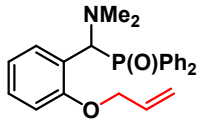
((2-hydroxyphenyl)(morpholino)methyl)diphenylphosphine oxide (4aag)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 3/1, v/v)
White solid, m. p.: 150-151 °C.
61.9 mg, 63% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.95 (dd, *J* = 9.8, 8.4 Hz, 2H), 7.66-7.47 (m, 5H), 7.35 (t, *J* = 7.0 Hz, 1H), 7.30-7.20 (m, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.71 (d, *J* = 7.3 Hz, 1H), 6.55 (t, *J* = 7.3 Hz, 1H), 4.35 (d, *J* = 8.5 Hz, 1H), 3.57 (s, 4H), 2.83 (d, *J* = 3.6 Hz, 2H), 2.64-2.52 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.2 (d, *J* = 4.0 Hz), 133.1 (d, *J* = 8.6 Hz), 132.2 (d, *J* = 2.5 Hz), 132.0 (d, *J* = 2.1 Hz), 131.5 (d, *J* = 8.7 Hz), 131.2, 131.1 (d, *J* = 8.9 Hz), 130.9 (d, *J* = 98.8 Hz), 130.1, 128.7 (d, *J* = 11.8 Hz), 128.5 (d, *J* = 11.5 Hz), 119.2, 118.4, 117.2, 70.4 (d, *J* = 82.4 Hz), 67.2, 52.5 (d, *J* = 6.8 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.22. **IR** (KBr): 3360, 3184, 3057, 2956, 2921, 2850, 1736, 1648, 1602, 1455, 1438, 1378, 1265, 1160, 1117, 1004, 860, 749, 700, 558, 526 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{23}H_{25}NO_3P]^+$: 394.1572, found: 394.1562.

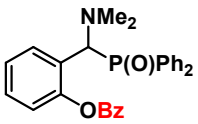
((2-(allyloxy)phenyl)(dimethylamino)methyl)diphenylphosphine oxide (5a)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v)
White solid, m. p.: 105-106 °C.
72.0 mg, 92% yield.

^{1}H NMR (400 MHz, CD_3CN) δ 8.02-7.87 (m, 3H), 7.67-7.49 (m, 5H), 7.38-7.23 (m, 3H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.96-6.82 (m, 2H), 6.25-6.06 (m, 1H), 5.51-5.38 (m, 2H), 5.32 (dd, *J* = 10.6, 1.5 Hz, 1H), 4.64-4.53 (m, 1H), 4.53-4.43 (m, 1H), 2.32 (d, *J* = 1.4 Hz, 6H). **^{13}C NMR** (101 MHz, CD_3CN) δ 158.2 (d, *J* = 8.8 Hz), 135.4 (d, *J* = 98.2 Hz), 134.8, 134.7 (d, *J* = 93.4 Hz), 133.4 (d, *J* = 3.9 Hz), 132.2 (d, *J* = 2.1 Hz), 132.2 (d, *J* = 2.1 Hz), 131.9 (d, *J* = 8.2 Hz), 131.2 (d, *J* = 8.4 Hz), 130.2, 129.5 (d, *J* = 11.4 Hz), 129.2 (d, *J* = 11.0 Hz), 120.6, 120.3 (d, *J* = 5.0 Hz), 117.6, 112.9, 69.9, 58.2 (d, *J* = 91.2 Hz), 44.2 (d, *J* = 8.0 Hz). **^{31}P NMR** (162 MHz, CD_3CN) δ 30.30. **IR** (KBr): 3055, 2924, 2857, 2828, 2784, 1598, 1486, 1451, 1437, 1263, 1237, 1190, 1155, 1116, 1105, 1024, 799, 750, 720, 699, 562, 543, 527 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+Na]^+$ for $[C_{24}H_{26}NO_2PNa]^+$: 414.1599, found: 414.1589.

2-((dimethylamino)(diphenylphosphoryl)methyl)phenyl benzoate (5b)

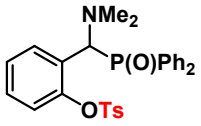


Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v)
White solid, m. p.: 181-182 °C.
86.5 mg, 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 14.6, 7.6 Hz, 3H), 7.89 (dd, *J* = 9.6, 8.2 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.60-7.38 (m, 8H), 7.28 (ddd, *J* = 17.0, 13.8, 7.4 Hz, 5H), 7.08 (d, *J* = 7.8 Hz, 1H), 4.88 (d, *J* = 10.9 Hz, 1H), 2.40 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.4, 149.8 (d, *J* = 9.1 Hz), 134.0, 133.0 (d, *J* = 99.9 Hz), 132.9 (d, *J* = 3.8 Hz), 132.4, 132.2 (d, *J* = 95.5 Hz), 131.6, 131.5 (d, *J* = 8.9 Hz), 131.4, 131.0 (d, *J* = 8.7 Hz), 130.0, 129.3, 129.0, 128.9, 128.4 (d, *J* = 11.3 Hz), 128.2, 128.2 (d, *J* = 11.5 Hz), 125.4, 123.4 (d, *J* = 4.1 Hz), 122.4, 60.2 (d, *J* = 89.3 Hz), 44.0 (d, *J* = 7.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.33. **IR** (KBr): 3059, 2934, 2867, 2831, 2787, 1739, 1601, 1485, 1451, 1438, 1374, 1262, 1201, 1175, 1117, 1090,

1059, 1024, 849, 754, 733, 700, 558, 546, 523, 507 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{28}H_{27}NO_3P]^+$: 456.1729, found: 456.1721.

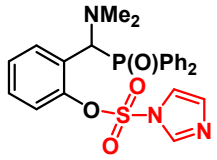
2-((dimethylamino)(diphenylphosphoryl)methyl)phenyl 4-methylbenzenesulfonate (5c)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/1, v/v)
Colorless oil
61.6 mg, 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.4 Hz, 1H), 8.02-7.94 (m, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.66-7.58 (m, 2H), 7.58-7.46 (m, 4H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.1 Hz, 1H), 7.23 (d, *J* = 6.9 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.14-7.07 (m, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.09 (d, *J* = 9.7 Hz, 1H), 2.48 (s, 3H), 2.34 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.3 (d, *J* = 10.0 Hz), 145.8, 133.6, 133.5 (d, *J* = 4.5 Hz), 131.6 (d, *J* = 2.0 Hz), 131.5, 131.4 (d, *J* = 19.4 Hz), 131.3 (d, *J* = 2.4 Hz), 131.2, 130.1, 129.2, 128.9 (d, *J* = 5.2 Hz), 128.8 (d, *J* = 5.1 Hz), 128.6 (d, *J* = 11.5 Hz), 128.2, 128.1 (d, *J* = 11.6 Hz), 126.4, 125.7 (d, *J* = 4.6 Hz), 121.3, 60.5 (d, *J* = 89.5 Hz), 44.3 (d, *J* = 7.2 Hz), 21.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.43. **IR** (KBr): 3658, 3631, 3057, 2928, 2865, 2830, 2785, 1597, 1482, 1438, 1371, 1195, 1178, 1158, 1116, 1079, 1028, 874, 848, 775, 723, 698, 662, 556, 543, 519 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{28}H_{29}NO_4PS]^+$: 506.1555, found: 506.1547.

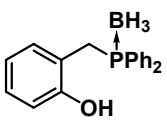
2-((dimethylamino)(diphenylphosphoryl)methyl)phenyl 1*H*-imidazole-1-sulfonate (5d)



Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 1/2, v/v)
Colorless oil
61.3 mg, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.8 Hz, 1H), 7.98 (ddd, *J* = 10.7, 7.5, 1.7 Hz, 2H), 7.67 (s, 1H), 7.55 (td, *J* = 11.4, 6.9 Hz, 5H), 7.30 (dd, *J* = 12.8, 6.3 Hz, 2H), 7.25-7.19 (m, 3H), 7.19-7.10 (m, 2H), 6.38 (d, *J* = 8.2 Hz, 1H), 4.88 (d, *J* = 9.8 Hz, 1H), 2.34 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.8 (d, *J* = 9.7 Hz), 137.4, 134.1 (d, *J* = 4.1 Hz), 132.5 (d, *J* = 101.0 Hz), 132.4, 131.9 (d, *J* = 2.6 Hz), 131.8, 131.5 (d, *J* = 3.4 Hz), 131.5, 131.4, 129.9, 128.7 (d, *J* = 11.5 Hz), 128.1 (d, *J* = 11.4 Hz), 127.9, 125.7 (d, *J* = 4.8 Hz), 119.8, 118.2, 60.6 (d, *J* = 88.3 Hz), 44.1 (d, *J* = 7.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.29. **IR** (KBr): 3518, 3460, 3439, 3401, 2922, 2852, 2831, 2787, 1660, 1645, 1634, 1483, 1437, 1424, 1260, 1207, 1144, 1049, 899, 852, 782, 726, 699, 616, 550, 517 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+H]^+$ for $[C_{24}H_{25}N_3O_4PS]^+$: 482.1303, found: 482.1292.

2-((diphenylphosphanyl)methyl)phenol borane adduct 6

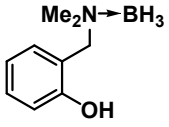


Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 5/1, v/v)
White solid, m. p.: 118-119 °C.
16.0 mg, 21% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 13.8, 5.0 Hz, 4H), 7.56-7.48 (m, 2H), 7.47-7.38 (m, 4H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 5.48 (s, 1H), 3.67 (d, *J* = 12.0 Hz, 2H), 1.14 (dd, *J* = 269.2, 121.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.3 (d, *J* = 4.3 Hz), 132.7 (d, *J* = 8.9 Hz), 131.7 (d, *J* = 4.3 Hz), 131.6 (d, *J* = 2.1 Hz), 128.9 (d, *J* = 9.9 Hz), 128.7 (d, *J* = 3.1 Hz), 128.4 (d, *J* = 55.2 Hz),

121.4 (d, J = 2.3 Hz), 120.4 (d, J = 4.5 Hz), 118.4 (d, J = 2.3 Hz), 28.4 (d, J = 33.9 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.28 (d, J = 73.4 Hz). **^{11}B NMR** (128 MHz, $CDCl_3$) δ -39.16 (dd, J = 85.2, 65.0 Hz). **IR** (KBr): 3524, 3485, 3460, 3433, 3366, 2961, 2923, 2849, 2386, 1651, 1595, 1455, 1436, 1384, 1262, 1108, 1059, 866, 750, 692, 591, 502 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M+Na]^+$ for $[C_{19}H_{20}BOPNa]^+$: 329.1243, found: 329.1242.

2-((dimethylamino)methyl)phenol borane adduct 7

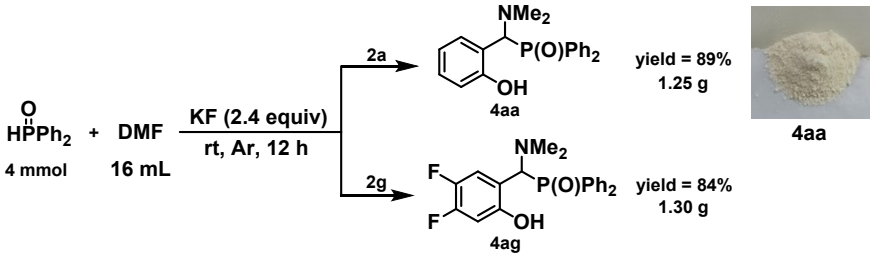


Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 5/1, v/v)
Colorless oil
26.8 mg, 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 1H), 7.15 (d, J = 7.5 Hz, 1H), 7.01-6.89 (m, 2H), 3.91 (s, 2H), 2.64 (s, 6H), 1.76 (dd, J = 171.9, 81.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.4, 134.0, 131.2, 120.8, 119.6, 118.5, 63.7, 51.6. **^{11}B NMR** (128 MHz, $CDCl_3$) δ -10.30 (dd, J = 188.4, 93.1 Hz). **IR** (KBr): 3594, 3527, 3481, 3437, 3330, 2954, 2925, 2869, 2854, 2380, 2319, 2269, 1651, 1610, 1457, 1378, 1288, 1260, 1165, 1111, 1017, 936, 872, 818, 757, 696 cm^{-1}. **HR-ESI-MS**: calculated m/z $[M-H]^+$ for $[C_9H_{15}BNO]^+$: 164.1247, found: 164.1240.

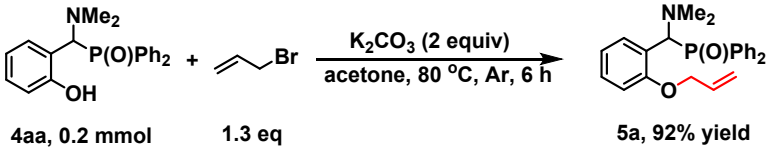
5. Gram-scale syntheses and transformations of 4aa.

5.1 Gram-scale reaction



To an oven-dried flask (50 mL) equipped with a magnetic stir bar was charged successively with diphenylphosphine oxide **1a** (808.8 mg, 4.0 mmol), KF (557.8 mg, 9.6 mmol), and anhydrous DMF (16 mL) in a glove box. The aryne precursor **2** (4.8 mmol) was added to the above mixture. The reaction mixture was allowed to stir at room temperature for 12 h. After the reaction, DMF was distilled under reduced pressure. Then, 30 mL dichloromethane was added to the flask and stir for 5 minutes, and the mixture was filtered through a celite pale to remove the precipitates. The reaction mixture was concentrated and purified by silica gel column chromatography (petroleum ether/EtOAc = 1:2) to afford the desired product **4aa** and **4ag** as white solid.

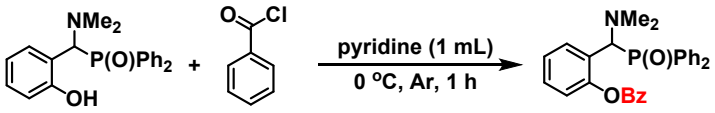
5.2 Synthesis of ((2-(allyloxy)phenyl)(dimethylamino)methyl)diphenylphosphine oxide



To a 25 mL Schlenk tube was charged with **4aa** (0.2 mmol, 70.3 mg), acetone (1 mL), K_2CO_3 (55.3 mg, 2 equiv), and allyl bromide (23 μL, 1.3 equiv) successively under Ar

atmosphere. After the Schlenk tube was sealed, the resulting mixture was refluxed for 6 h. After the reaction completed, the acetone was removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1, v/v) to give compound **5a** as white solid (72.0 mg, 92% yield).

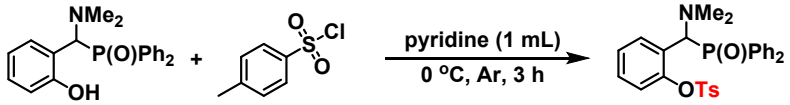
5.3 Synthesis of 2-((dimethylamino)(diphenylphosphoryl)methyl)phenyl benzoate



4aa, 0.2 mmol 1.2 eq 5b, 95% yield

To a solution of **4aa** (0.2 mmol, 70.3 mg) in pyridine (1 mL) cooled in an ice bath was added benzoyl chloride (27.9 μL, 1.2 equiv) dropwise over 3 minutes with stirring. Subsequently, the reaction mixture was kept under stirring for 1 h. After the reaction completed, 5 mL dichloromethane was added to the flask and washed with a solution of 1M HCl (1 mL). The organic phase was dried over anhydrous Na_2SO_4, filtrated and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1, v/v) to give compound **5b** as white solid (86.5 mg, 95% yield).

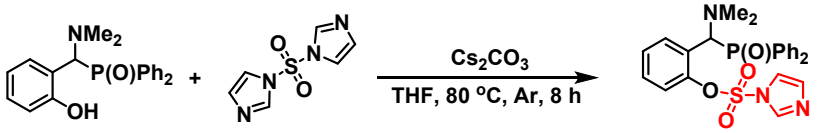
5.4 Synthesis of 2-((dimethylamino)(diphenylphosphoryl)methyl)phenyl 4-methylbenzenesulfonate



4aa, 0.2 mmol 1.2 eq 5c, 61% yield

A solution of **4aa** (0.2 mmol, 70.3 mg), *p*-toluenesulfonyl chloride (45.8 mg, 1.2 equiv), and pyridine (1 mL) was stirred at 0 °C for 3 h. After the reaction, water (5 mL) was added and the reaction mixture was extracted with CH_2Cl_2 (2×10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to give compound **5c** as colorless oil (61.6 mg, 61% yield).

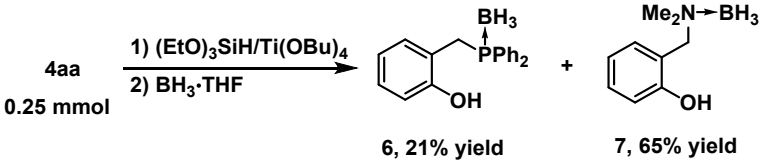
5.5 Synthesis of 2-((dimethylamino)(diphenylphosphoryl)methyl)phenyl 1*H*-imidazole-1-sulfonate



4aa, 0.45 mmol 0.15 mmol 5d, 85% yield

A solution of *N*,*N*′-sulfonyldiimidazole (0.15 mmol, 29.8 mg), **4aa** (0.45 mmol, 158.1 mg) and Cs_2CO_3 (48.9 mg, 1 equiv) in THF (1 mL) was stirred at 80 °C for 8 h. The mixture was cooled to room temperature and then filtered through a celite pale. After concentration of the filtrate, the sulfonate **5d** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1) to give compound **5d** as colorless oil (61.3 mg, 85% yield). The yield reported here was based on *N*,*N*′-sulfonyldiimidazole.

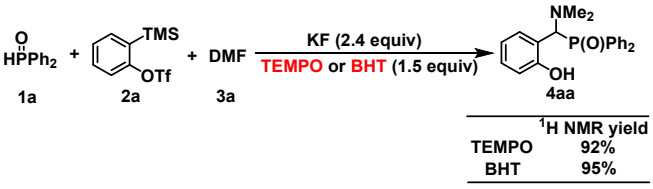
5.6 Reduction of 4aa in the $(EtO)_3SiH/Ti(OBu)_4/BH_3\cdot THF$ system



To a 25 mL Schlenk tube was charged with **4aa** (0.25 mmol, 87.8 mg), degassed toluene (5mL), $(EtO)_3SiH$ (1.5 mmol, 6.0 equiv, 277 μL), and $Ti(OBu)_4$ (0.2 mmol, 0.8 equiv, 68 μL) under Ar atmosphere. After the Schlenk tube was sealed, the resulting mixture was stirred at 120 °C for 30 min. After the reaction completed, the reaction was cooled to room temperature and BH_3 (0.75 mL 1 M in THF, 3.0 equiv) was added via syringe under Ar atmosphere. The resulting reaction mixture was stirred at room temperature for 1 h. The mixture was concentrated in vacuo, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) to give compound **6** as white solid (16.0 mg, 21% yield), compound **7** as colorless oil (26.8 mg, 65% yield).

6. Mechanistic study

6.1 Radical trapping experiment

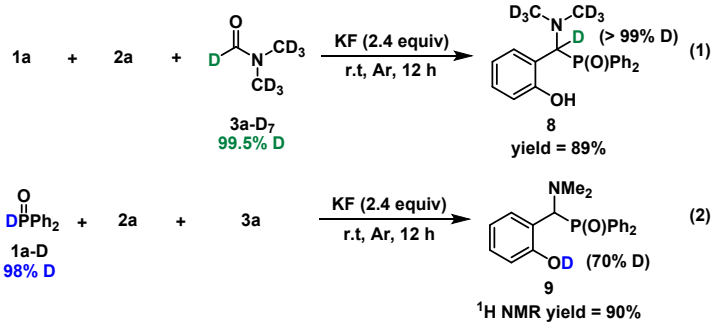


Scheme S1 Radical trapping experiments.

To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with diphenylphosphine oxide **1a** (50.6 mg, 0.25 mmol), KF (34.9 mg, 0.6 mmol), 2,2,6,6-Tetramethyl-1-piperdinyloxy (TEMPO) (58.6 mg, 0.375 mmol) and DMF (1 mL) in a glove box. The aryne precursor **2a** (0.3 mmol, 1.2 equiv) was added into the reaction mixture, then stirred at room temperature for 12 h. After the reaction, DMF was distilled under reduced pressure, and the yield was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Results: when adding 1.5 equiv of TEMPO into the reaction system, 92% ^1H NMR yield of **4aa** was produced; As for BHT, yield was 95%, both of which excluded the radical pathway of this transformation.

6.2 Deuterium experiments



Scheme S2 Deuterium experiments with 3a-D_7 and 1a-D.

According to the general procedure, when **3a-D$_7$** was subjected to the standard reaction conditions, affording the benzyl isotope labeled product **8** with 89% isolated yield, which proved the [2+2] cycloaddition process of benzyne with DMF.

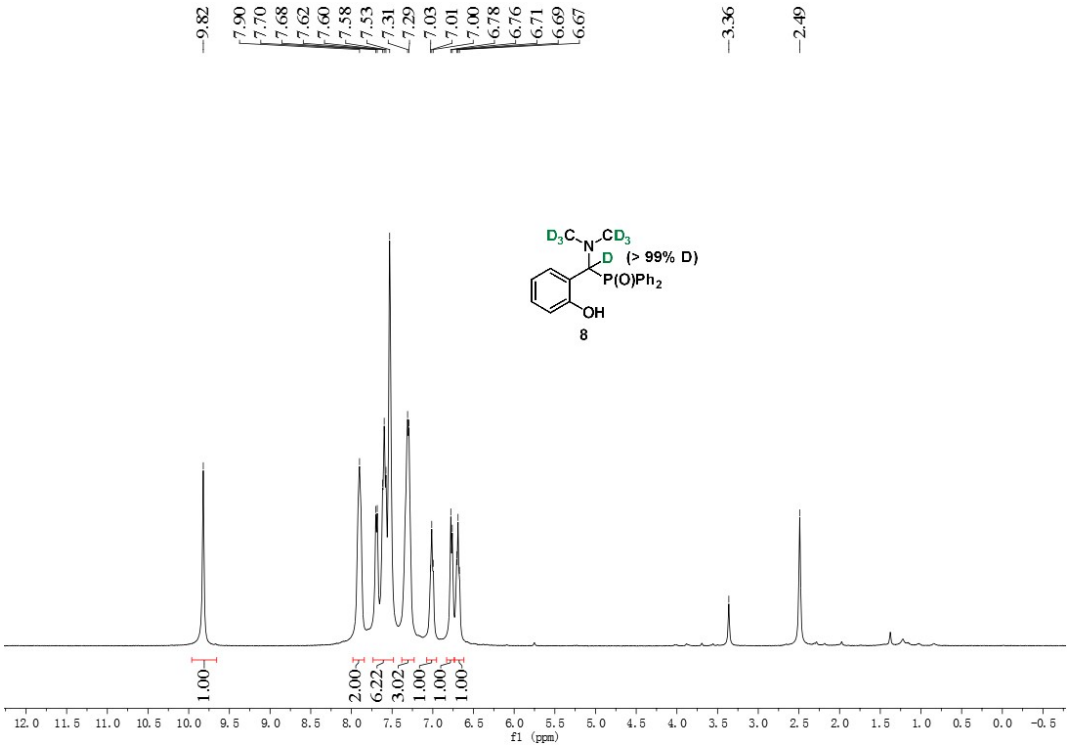


Figure S1. The deuterium labeling experiment with 3a-D$_7$.

Furthermore, the reaction of deuterium-labeled phosphine oxide **1a-D** afforded **9** in 90% yield with 70% deuterium incorporation at the phenolic hydroxyl, which revealed the H-P(O) compound probably underwent 1,4-addition process in the multi-component reaction.

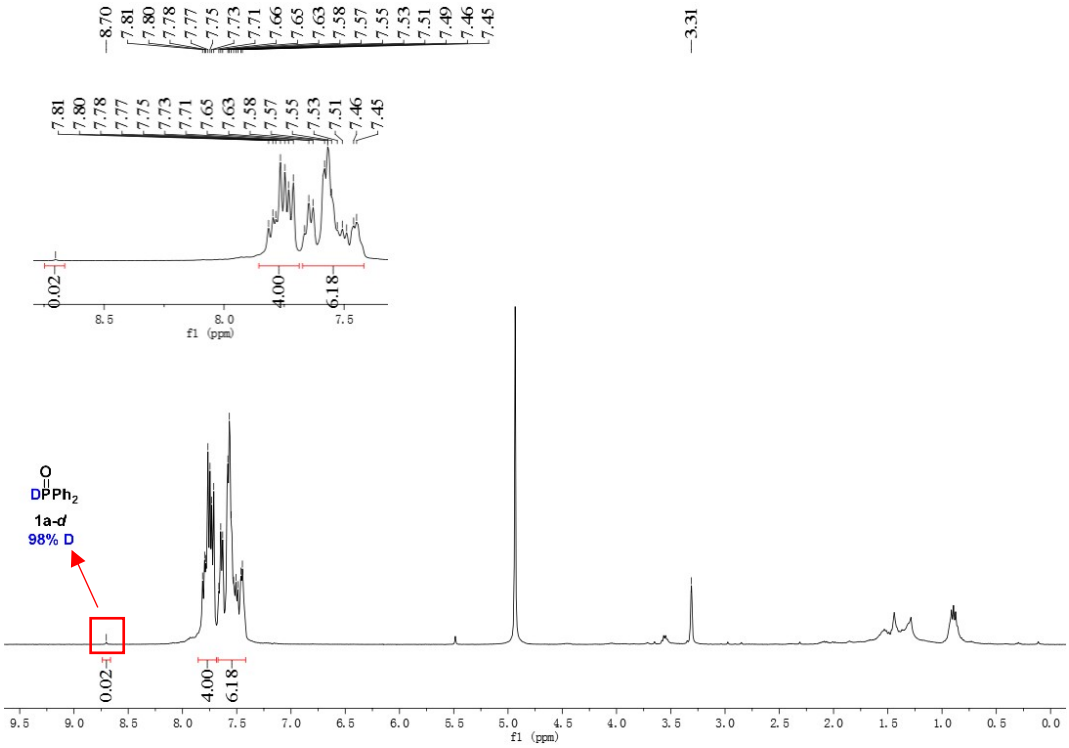


Figure S2. ^{1}H NMR spectrum of 1a-D

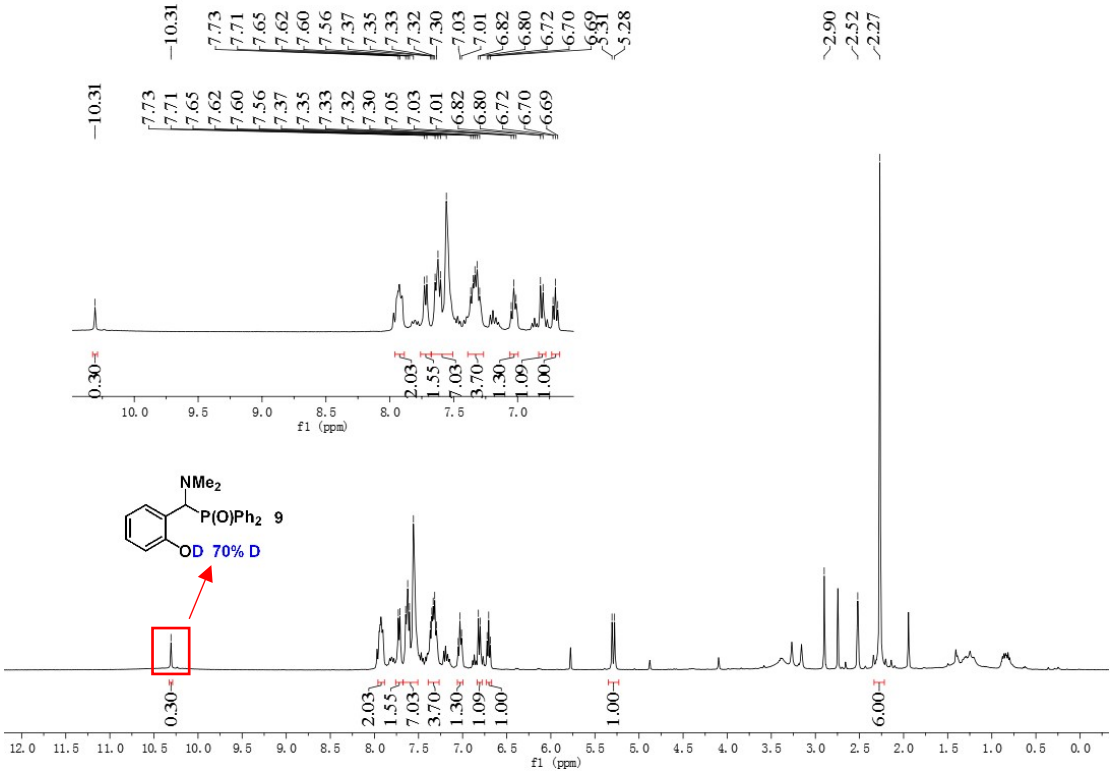
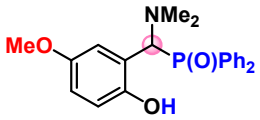


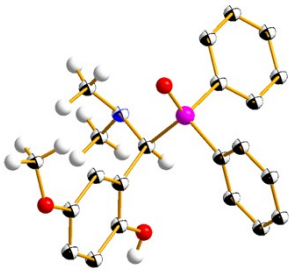
Figure S3. The deuterium labeling experiment of 1a-D, 2a and DMF

7. X-ray crystal structure

Recrystallization of the mixed products **4ae** and **4ae'** from hexane and ethyl acetate (v/v = 1:1) afforded **4ae** with high purity, second recrystallization of **4ae** from $CDCl_3$ afforded crystals suitable for X-ray diffraction analysis. The level set for thermal ellipsoids of all atoms is 50%.



4ae



X-ray of **4ae**

Table S1 Crystal Data and Structure Refinement for 4ae

Identification code	**4ae**
Empirical formula	$C_{22}H_{24}NO_3P$
Formula weight	381.39
Temperature/K	113.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.5354(3)
b/Å	13.7676(5)
c/Å	15.1853(4)
α/°	90
β/°	90.373(3)
γ/°	90
Volume/Å^3	1993.48(11)
Z	4
ρ_{calc}g/cm^3	1.271
μ/mm^{-1}	0.160
F(000)	808.0
Crystal size/mm^3	0.26 × 0.18 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.994 to 57.392
Index ranges	$-12 \le h \le 12$, $-18 \le k \le 18$, $-20 \le l \le 20$
Reflections collected	24933
Independent reflections	5152[R_{int} = 0.0565, R_{sigma} = 0.0392]
Data/restraints/parameters	5152/0/249
Goodness-of-fit on F^2	1.041

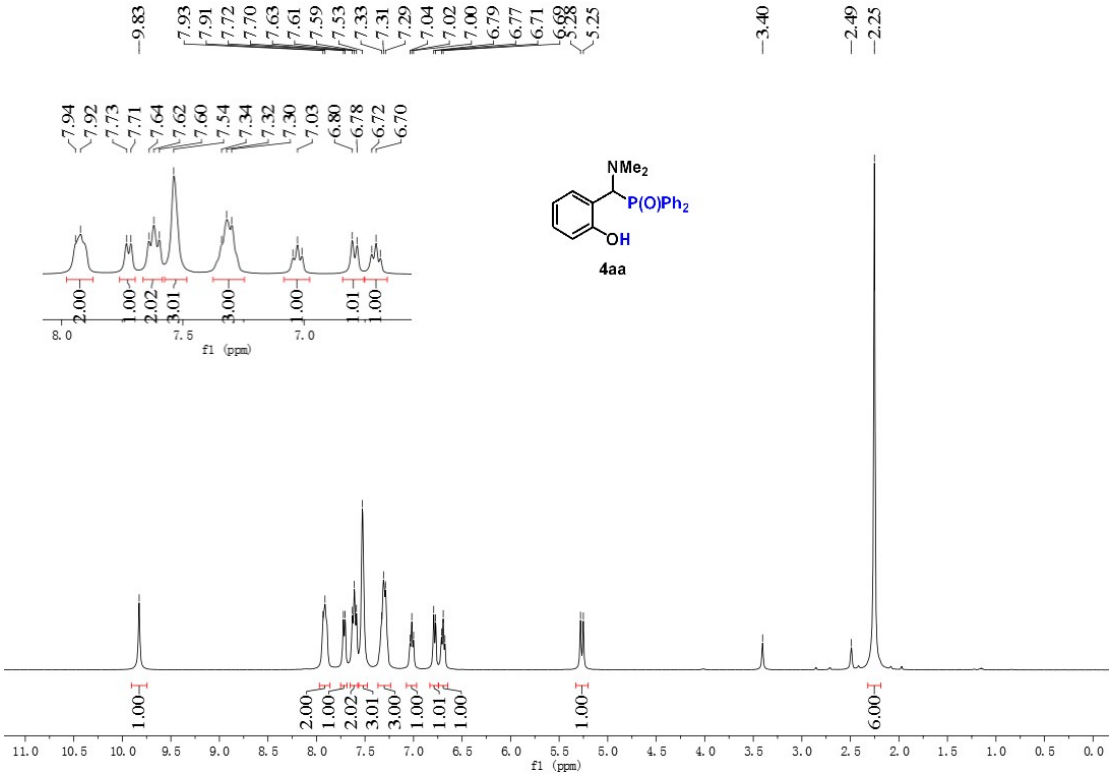
Final R indexes [I>=2σ (I)]	R_1 = 0.0415, wR_2 = 0.0991
Final R indexes [all data]	R_1 = 0.0517, wR_2 = 0.1055
Largest diff. peak/hole / e Å^{-3}	0.37/-0.32

8. References

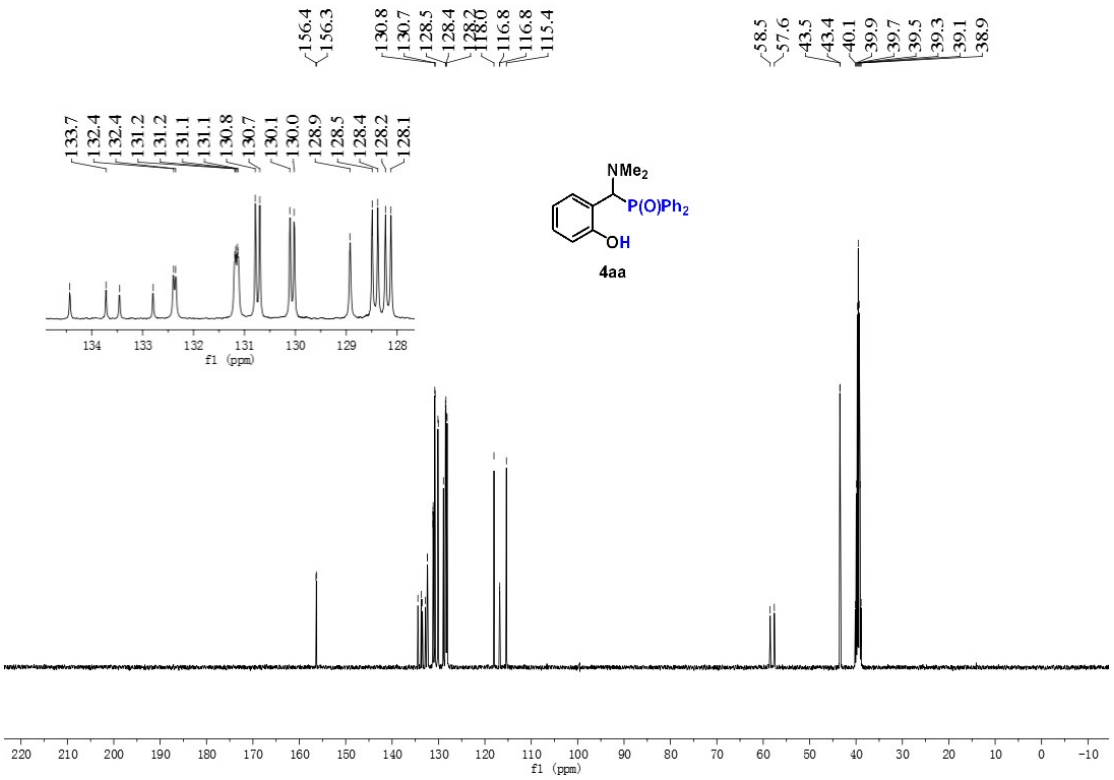
(1) Y.-C. Ou, Y.-T. Huang, Z.-L. He, G.-D. Yu, Y.-P. Huo, X.-W. Li, Y. Gao and Q. Chen. *Chem. Commun*., 2020, **56**, 1357-1360.

(2) X.-J. Li, Y. Sun, X. Huang, L. Zhang, L.-C. Kong and B. Peng, *Org. Lett*. 2017, **19**, 838-841.

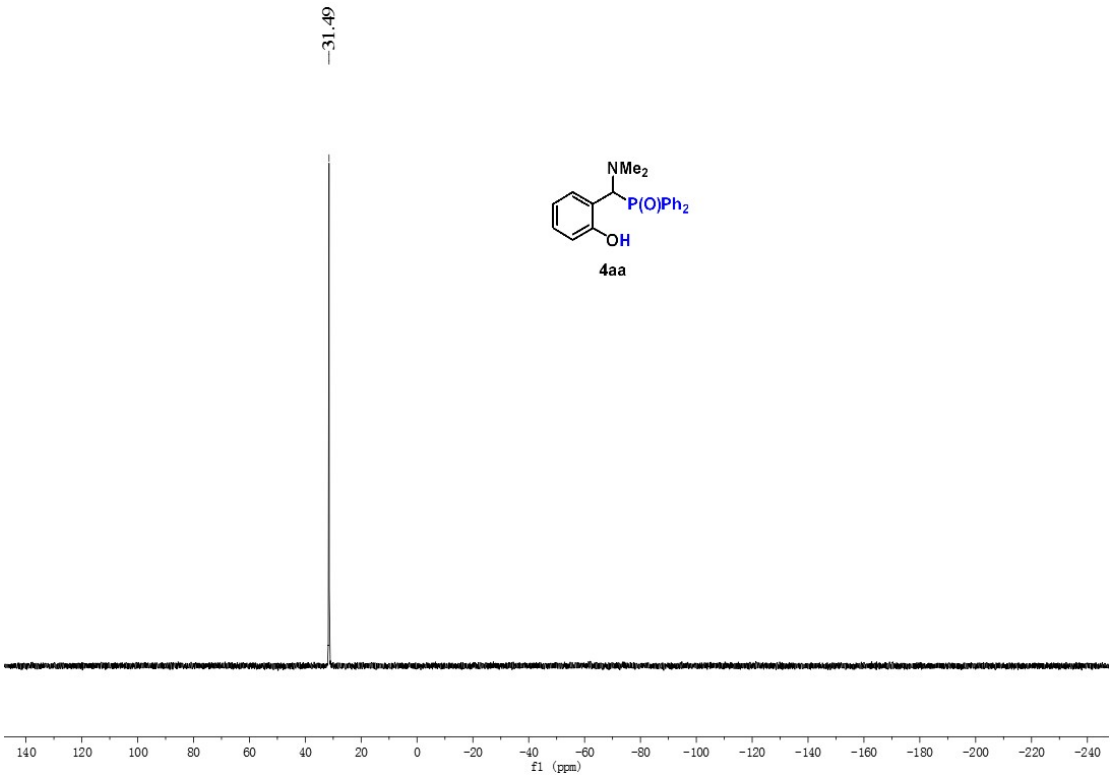
9. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{11}B NMR spectra of the products



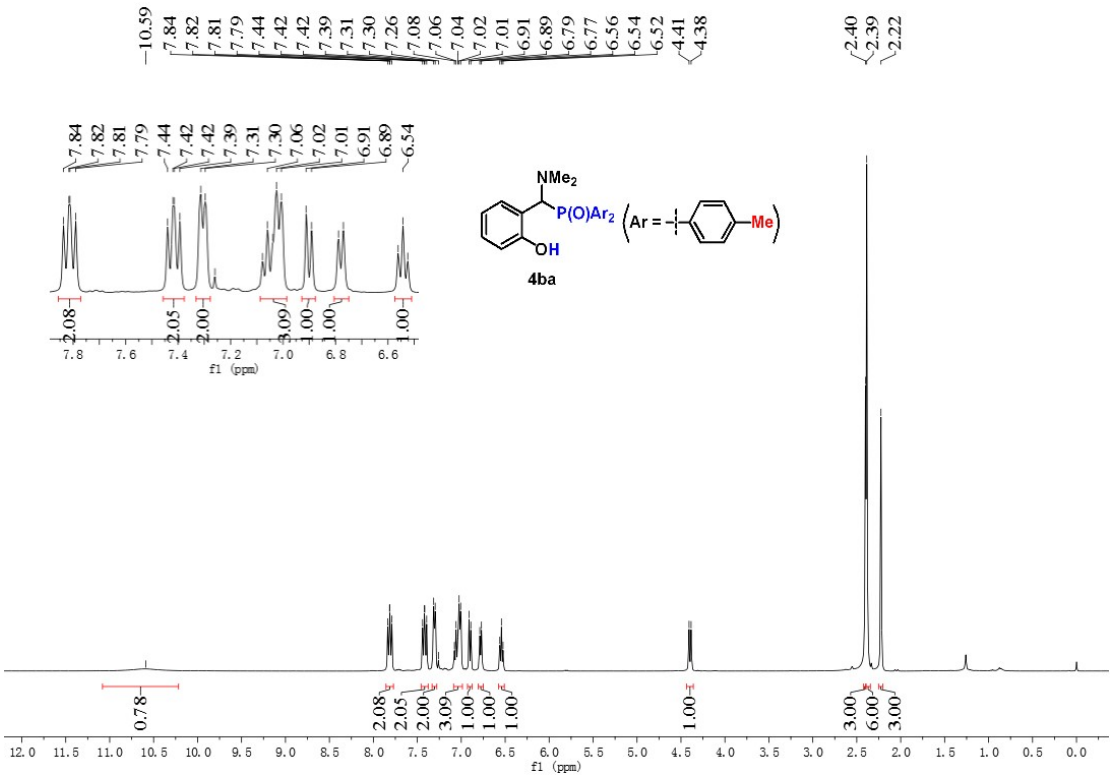
^{1}H NMR (400 MHz, DMSO-d_6)



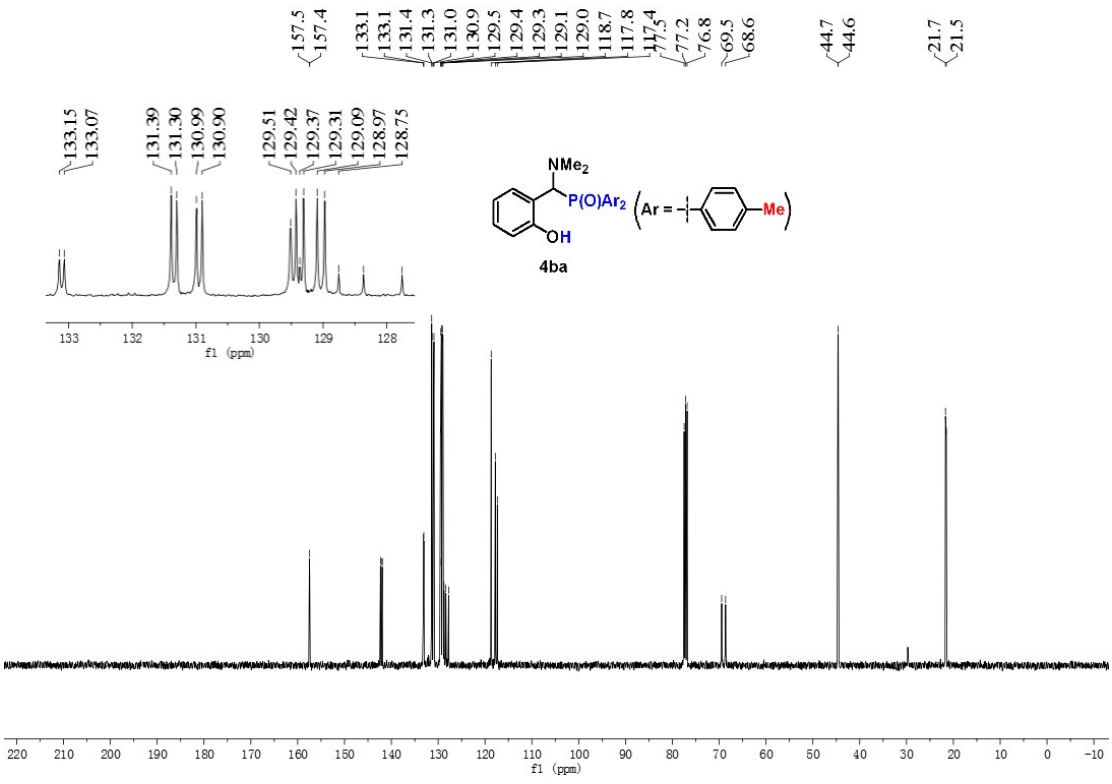
^{13}C NMR (101 MHz, DMSO-d_6)



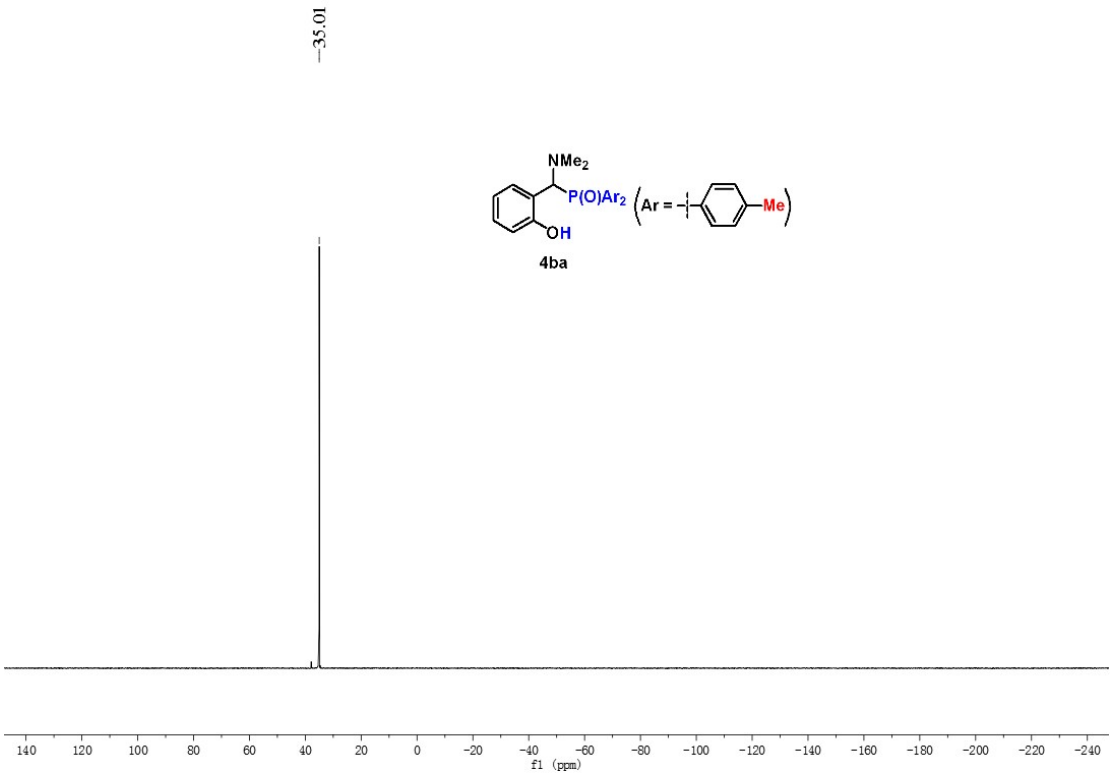
^{31}P NMR (162 MHz, DMSO-d_6)



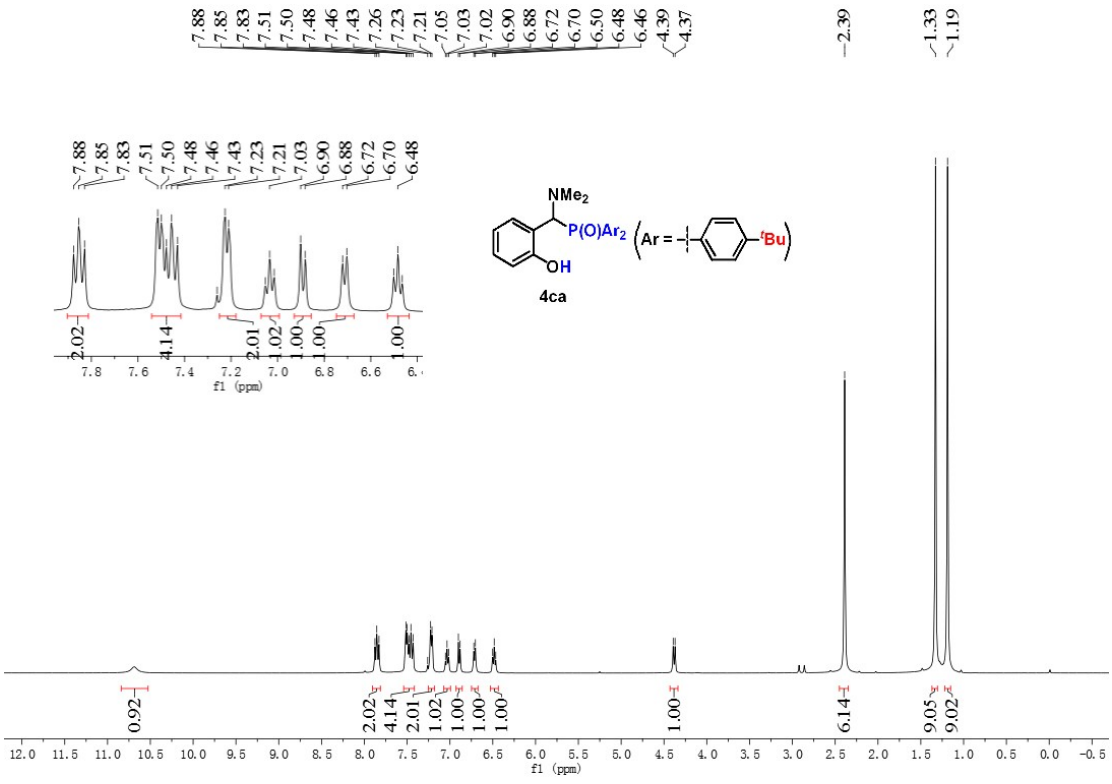
^{1}H NMR (400 MHz, $CDCl_3$)



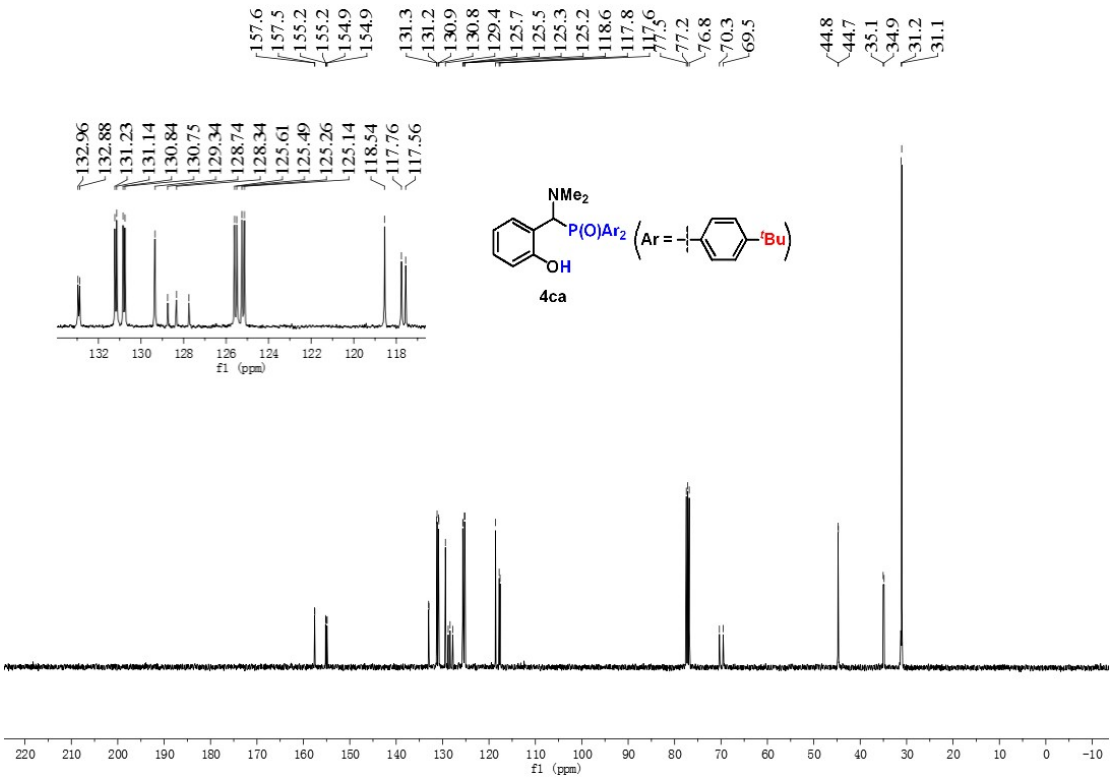
^{13}C NMR (101 MHz, $CDCl_3$)



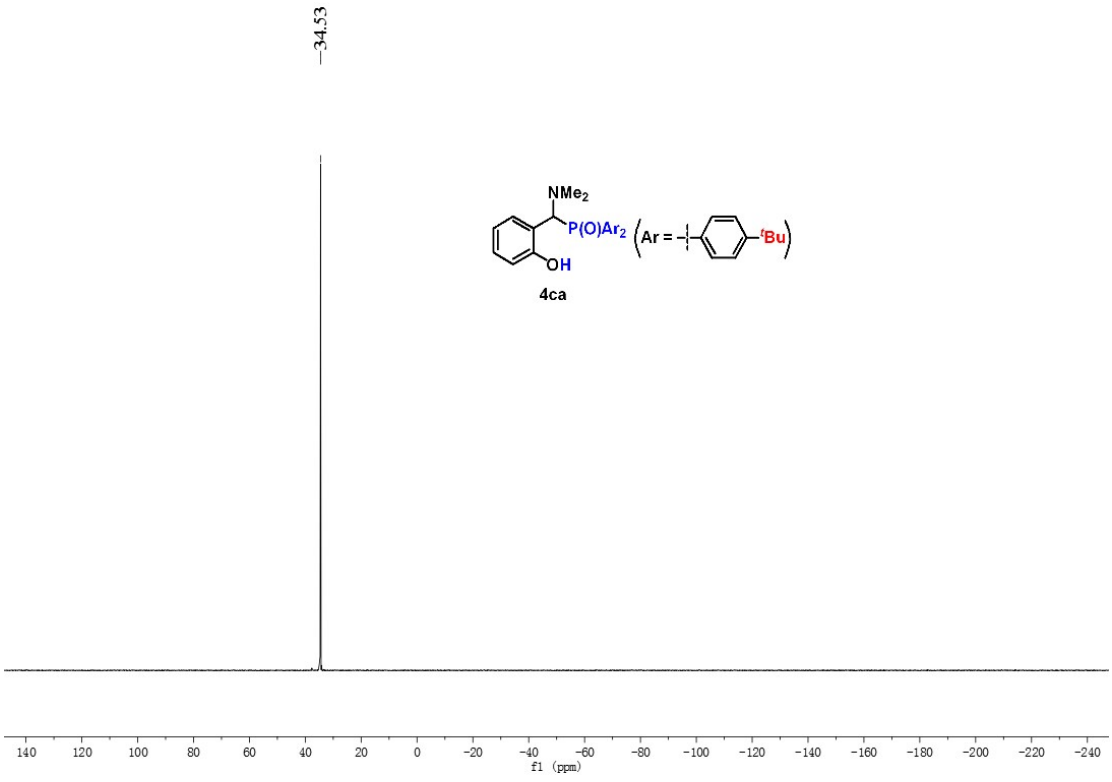
^{31}P NMR (162 MHz, $CDCl_3$)



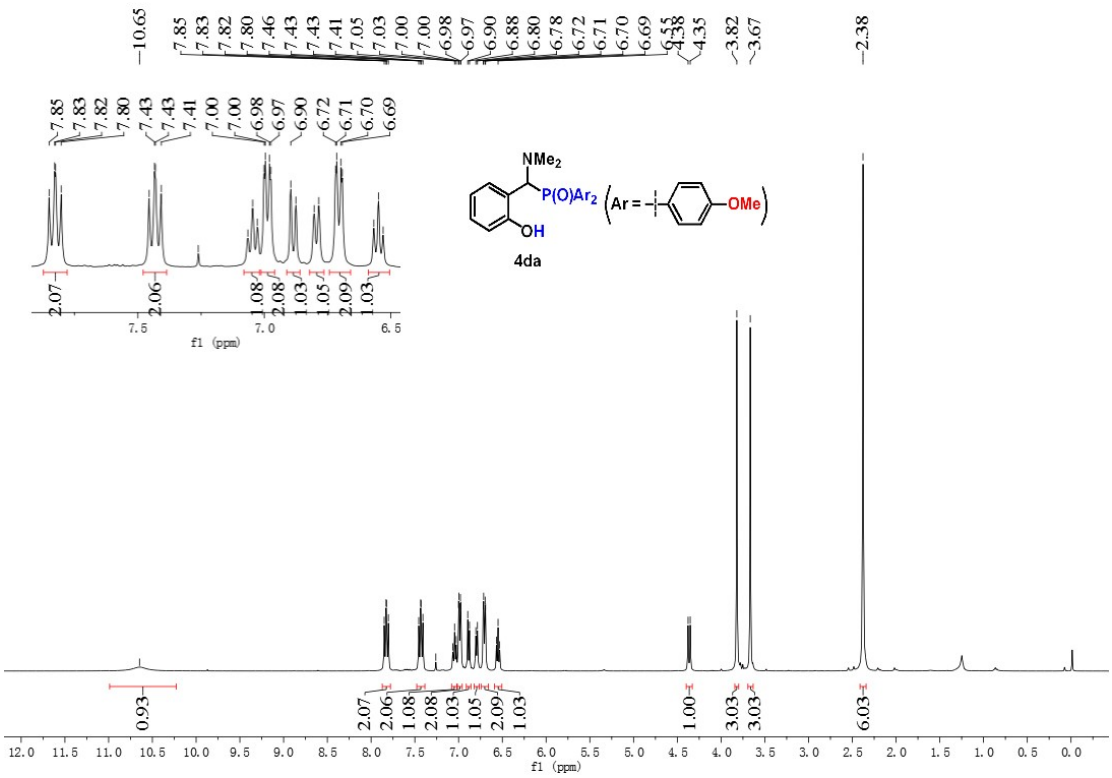
^{1}H NMR (400 MHz, $CDCl_3$)



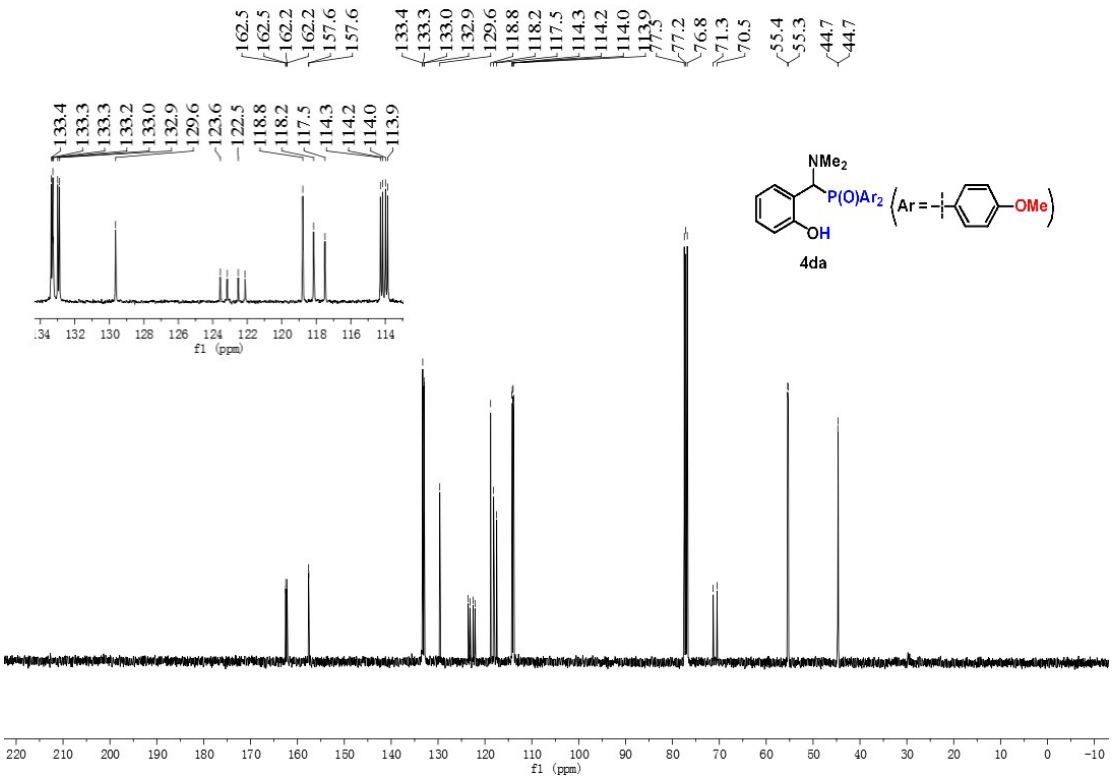
^{13}C NMR (101 MHz, $CDCl_3$)



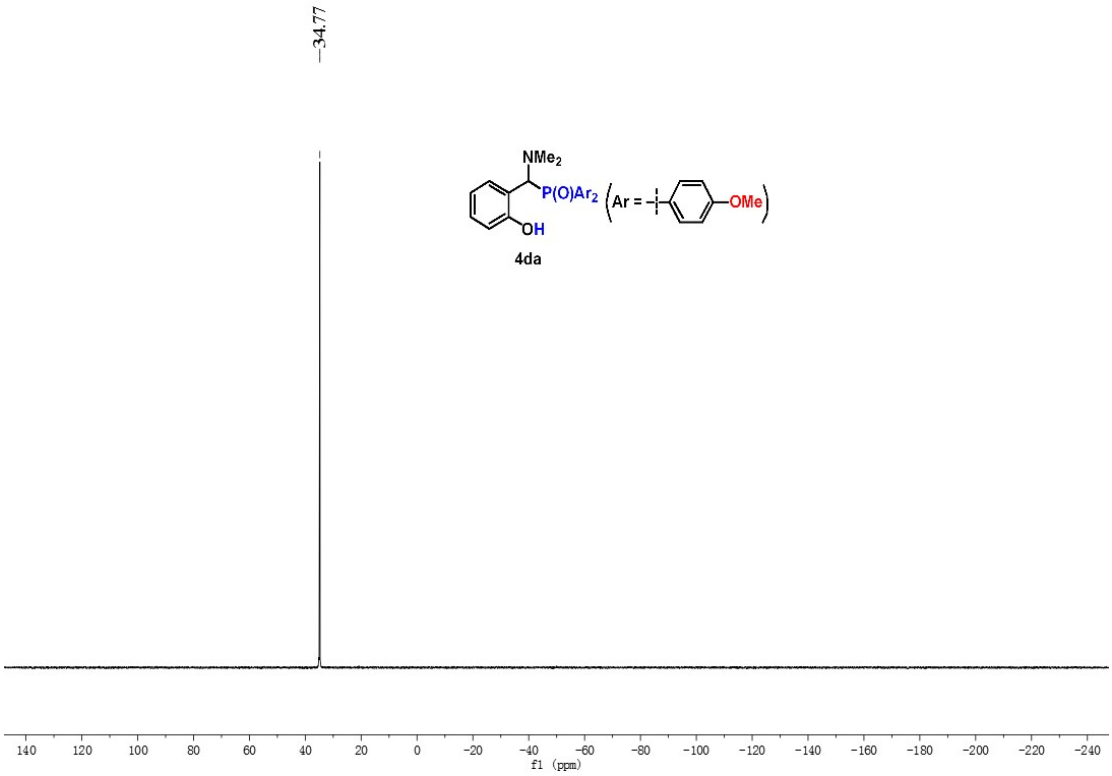
^{31}P NMR (162 MHz, $CDCl_3$)



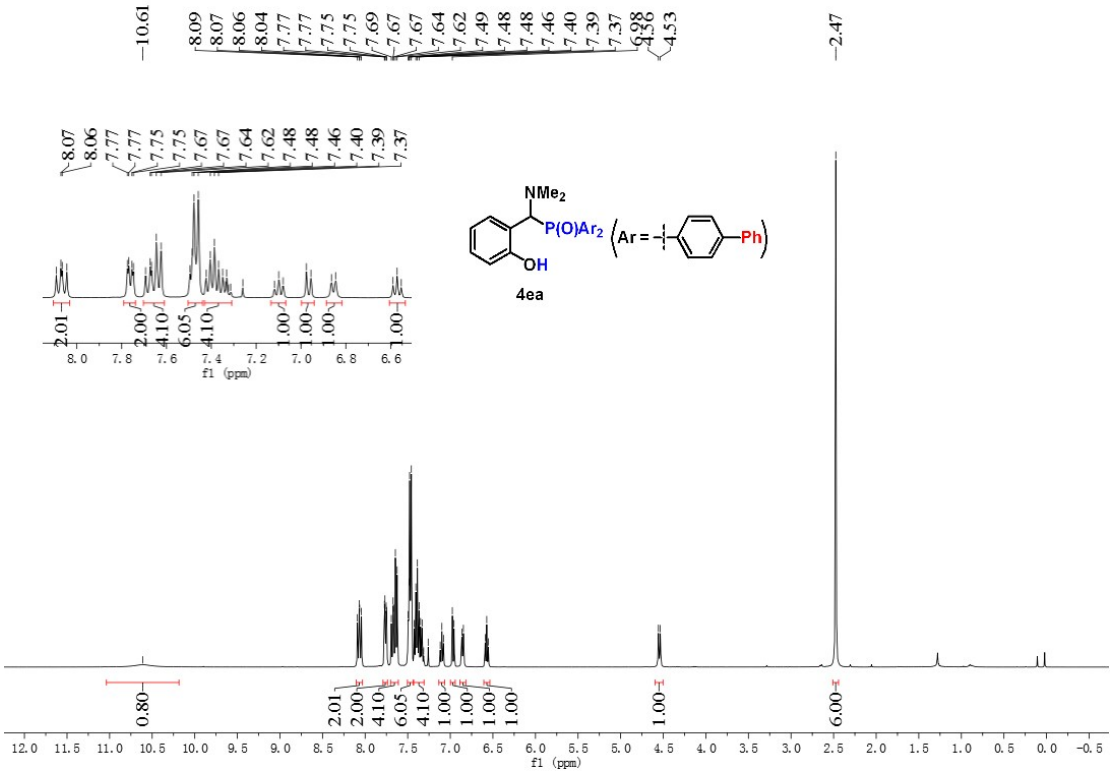
^{1}H NMR (400 MHz, $CDCl_3$)



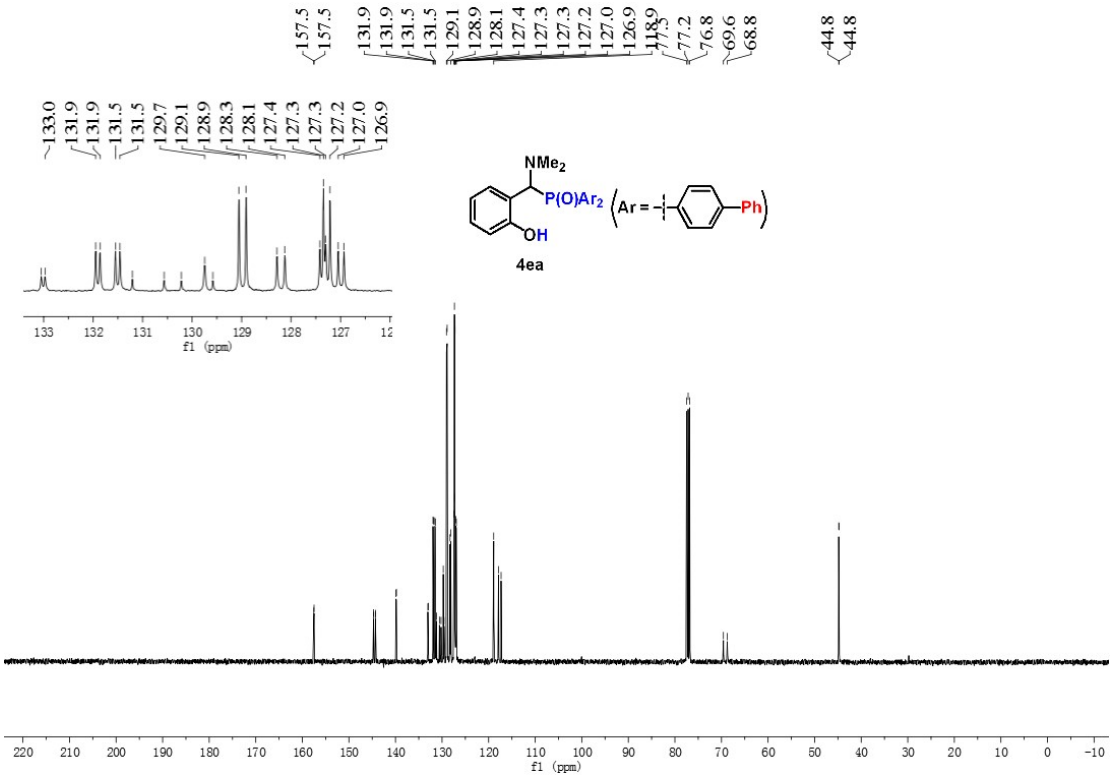
^{13}C NMR (101 MHz, $CDCl_3$)



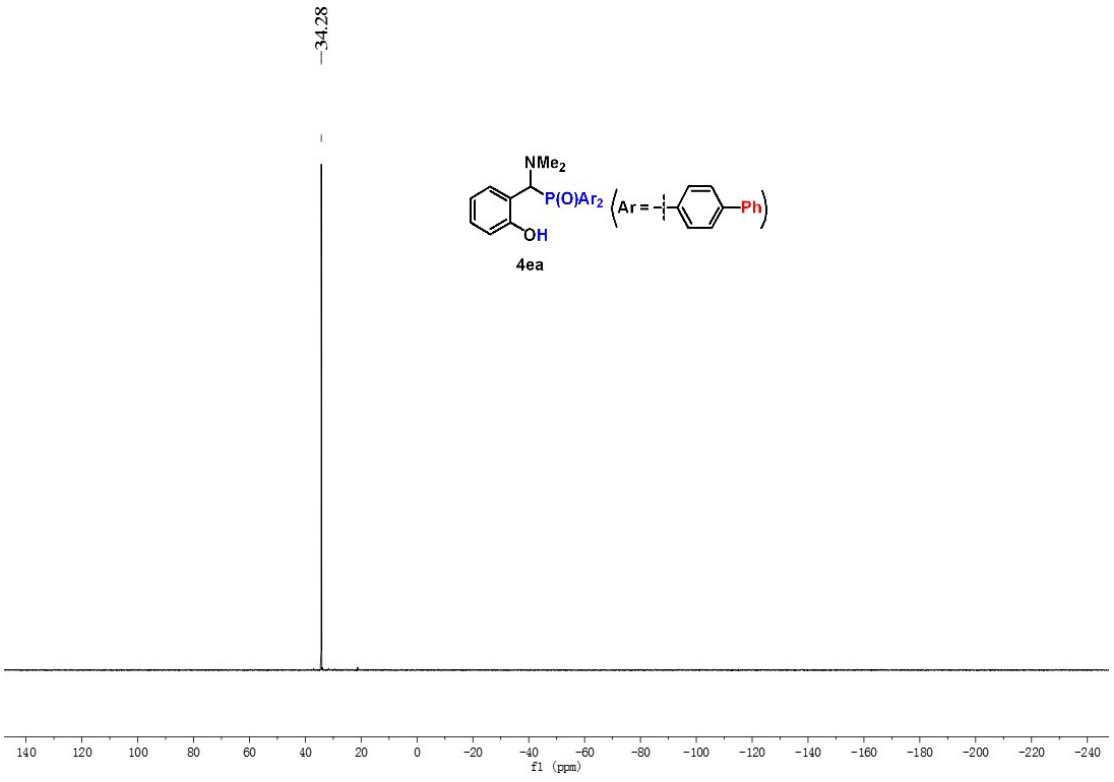
^{31}P NMR (162 MHz, $CDCl_3$)



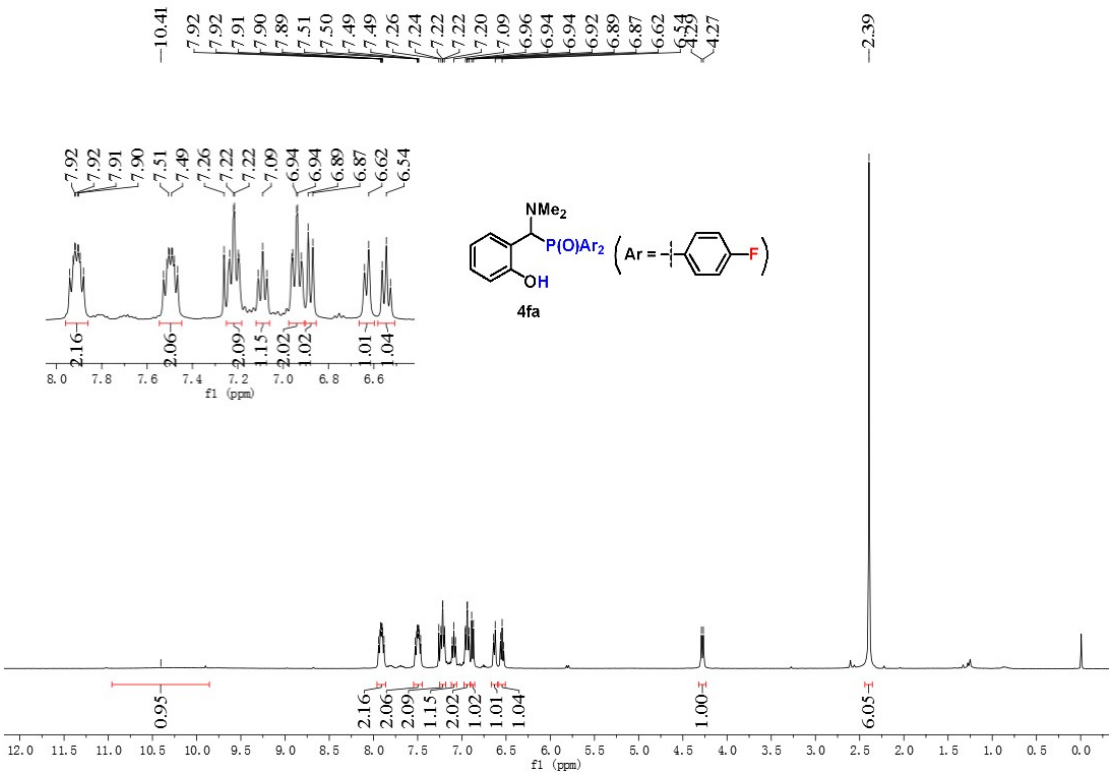
^{1}H NMR (400 MHz, $CDCl_3$)



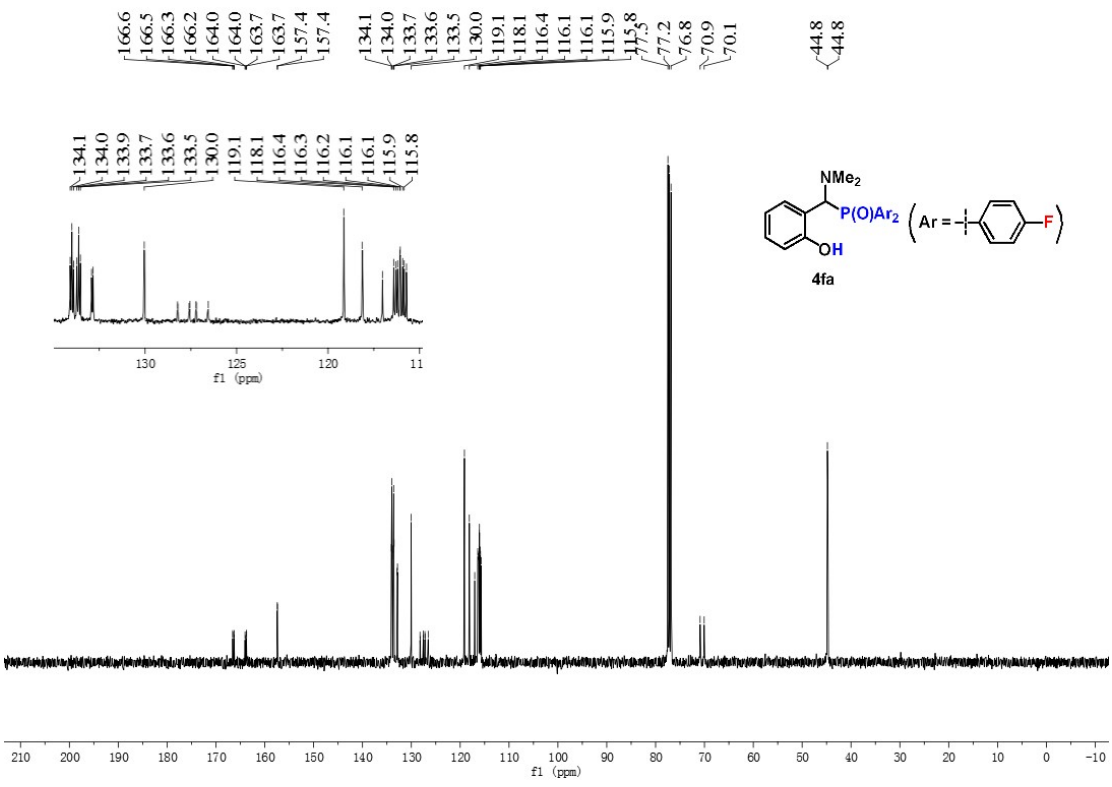
^{13}C NMR (101 MHz, $CDCl_3$)



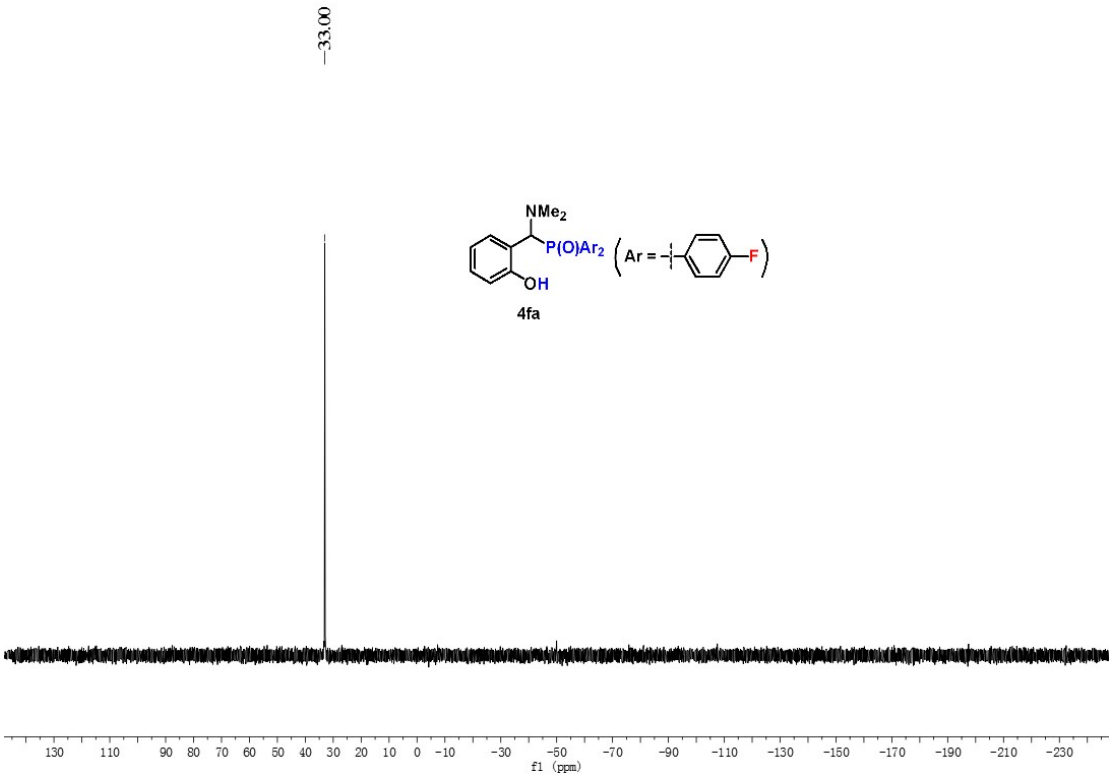
^{31}P NMR (162 MHz, $CDCl_3$)



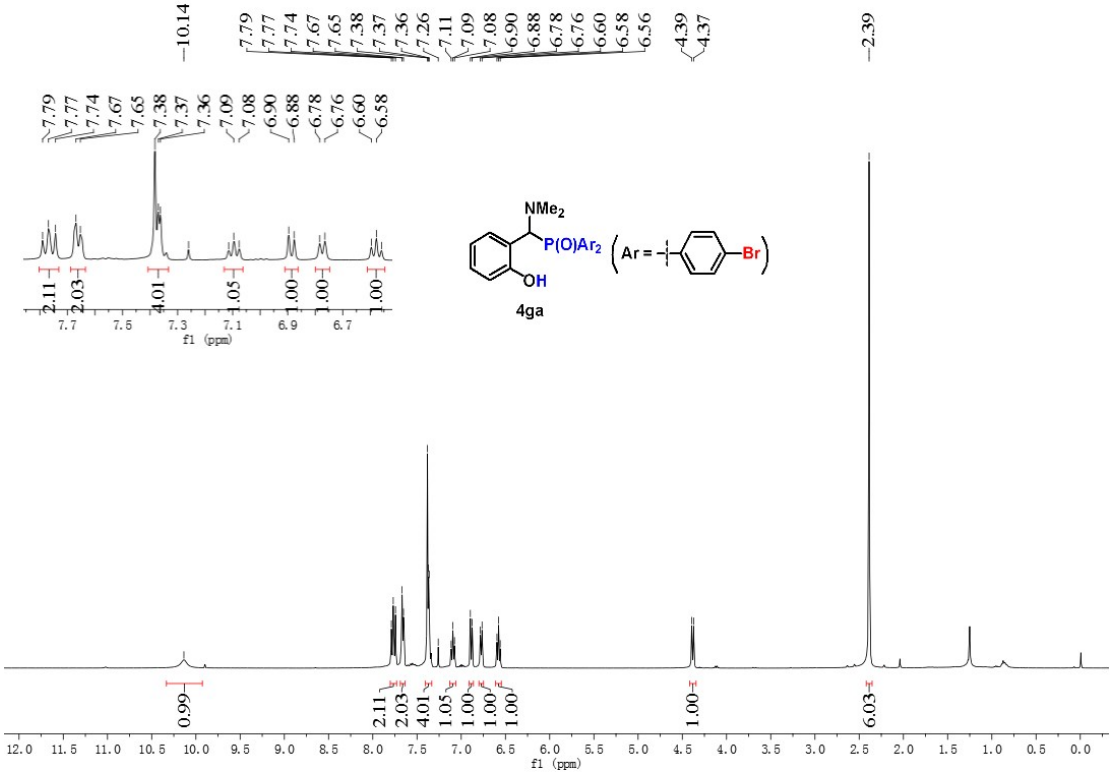
^{1}H NMR (400 MHz, $CDCl_3$)



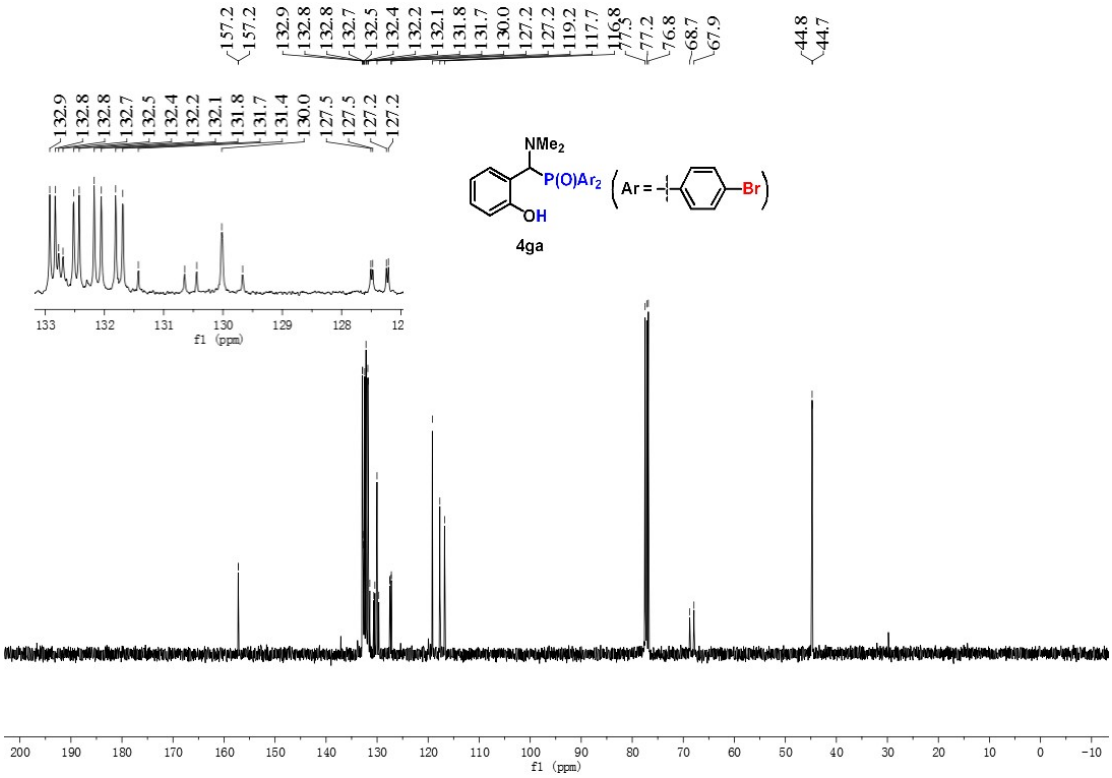
^{13}C NMR (101 MHz, $CDCl_3$)



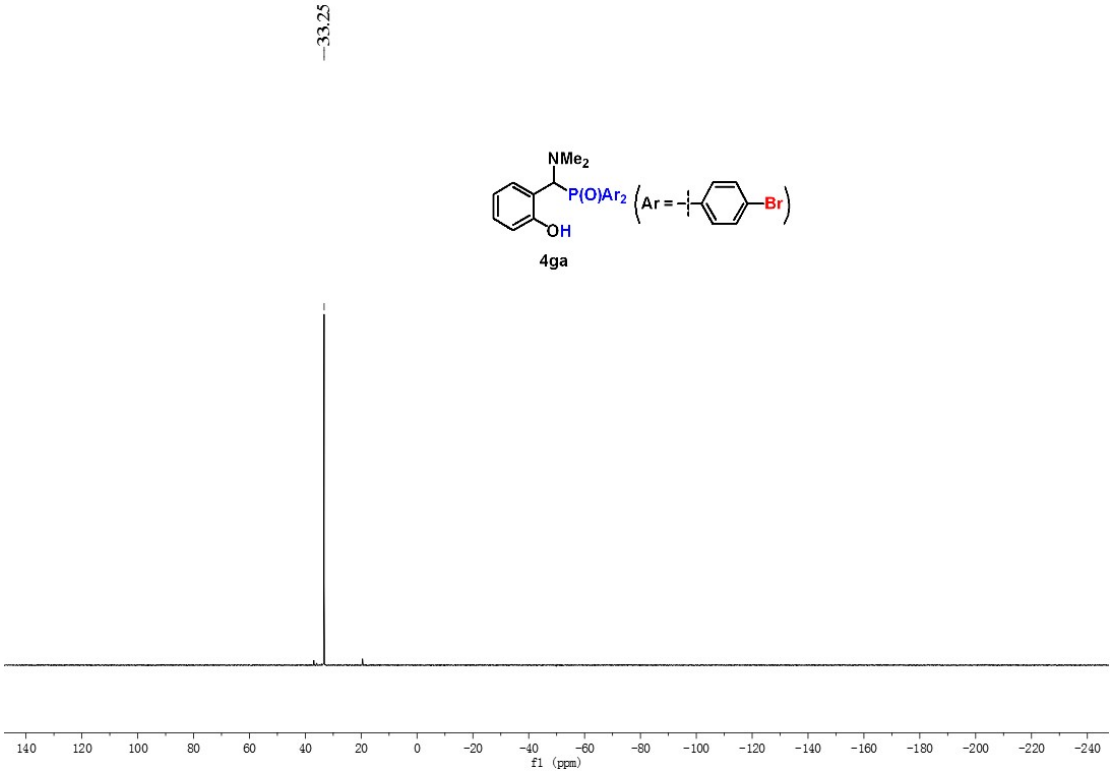
^{31}P NMR (162 MHz, $CDCl_3$)



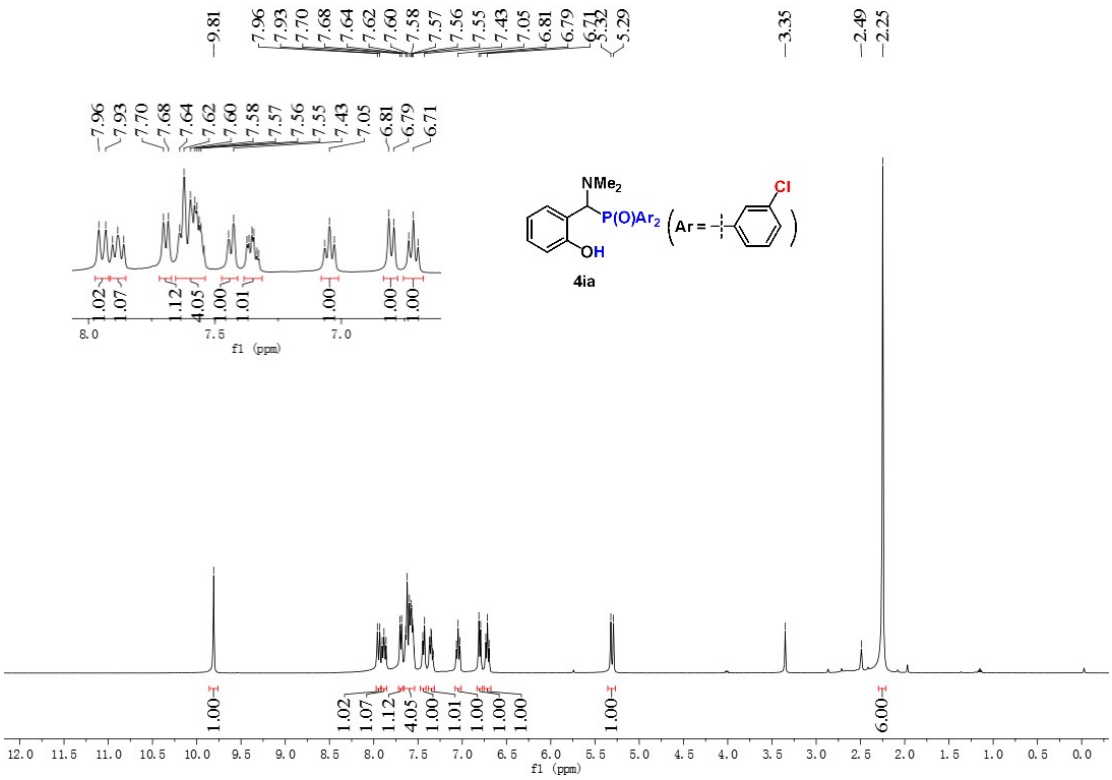
^{1}H NMR (400 MHz, $CDCl_3$)



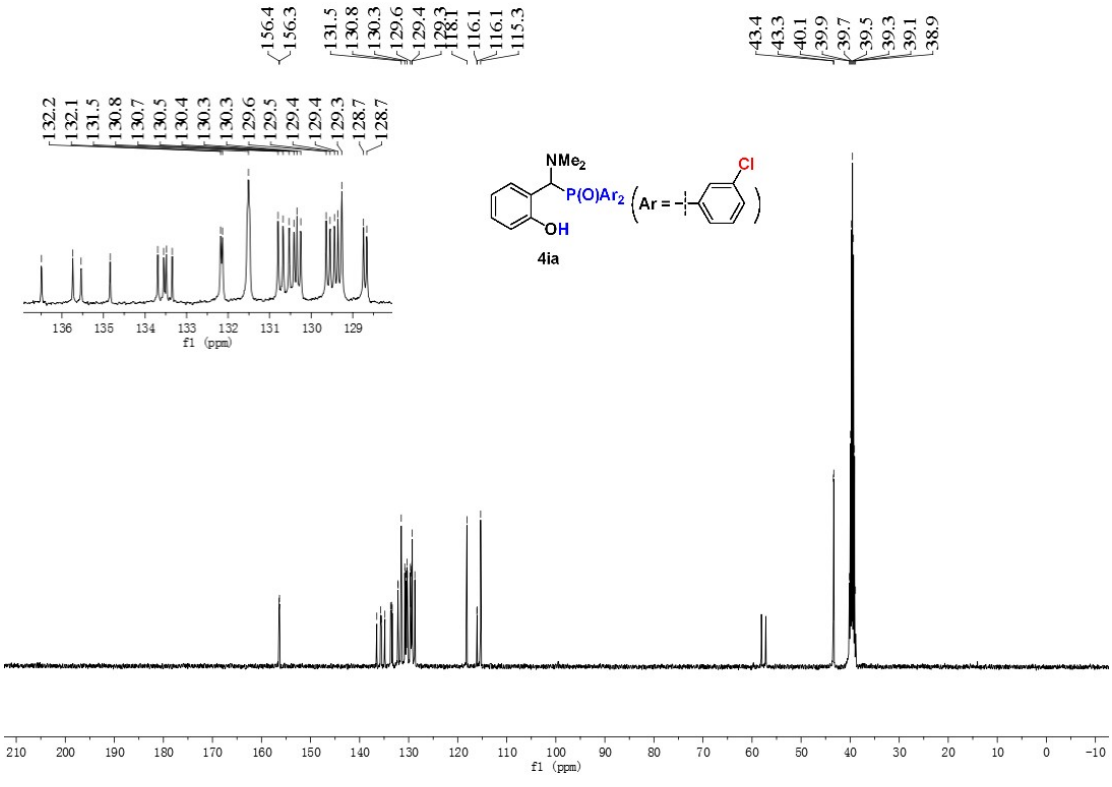
^{13}C NMR (101 MHz, $CDCl_3$)



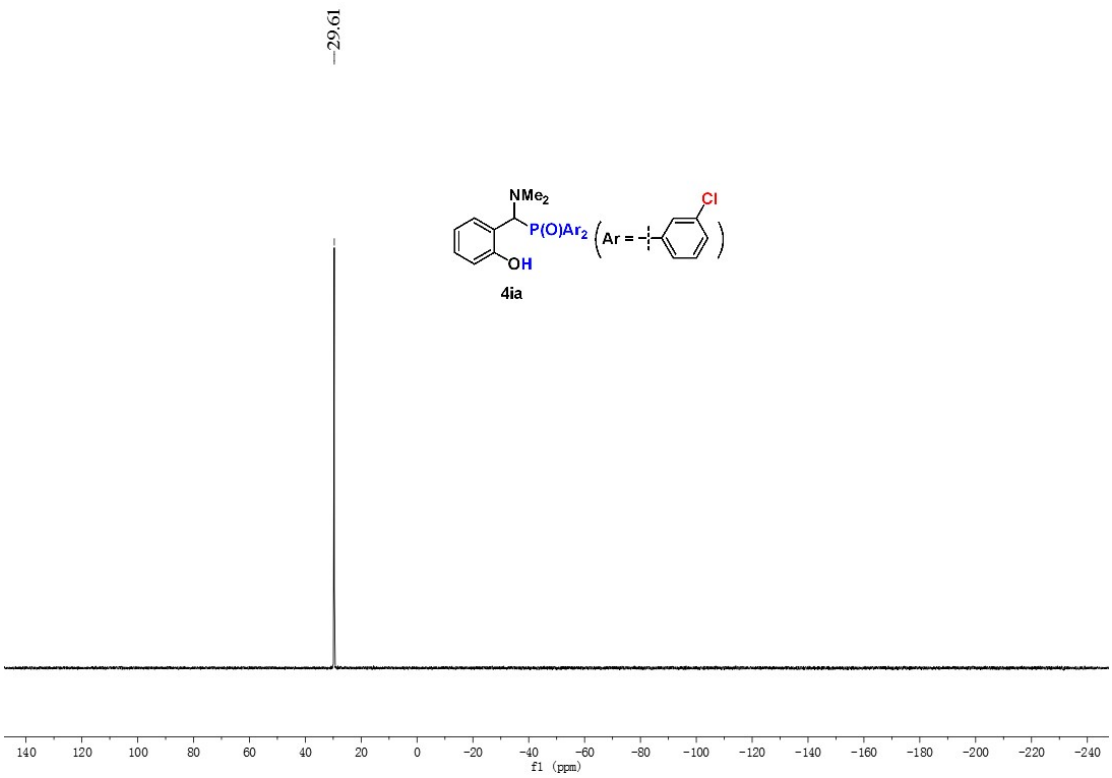
^{31}P NMR (162 MHz, $CDCl_3$)



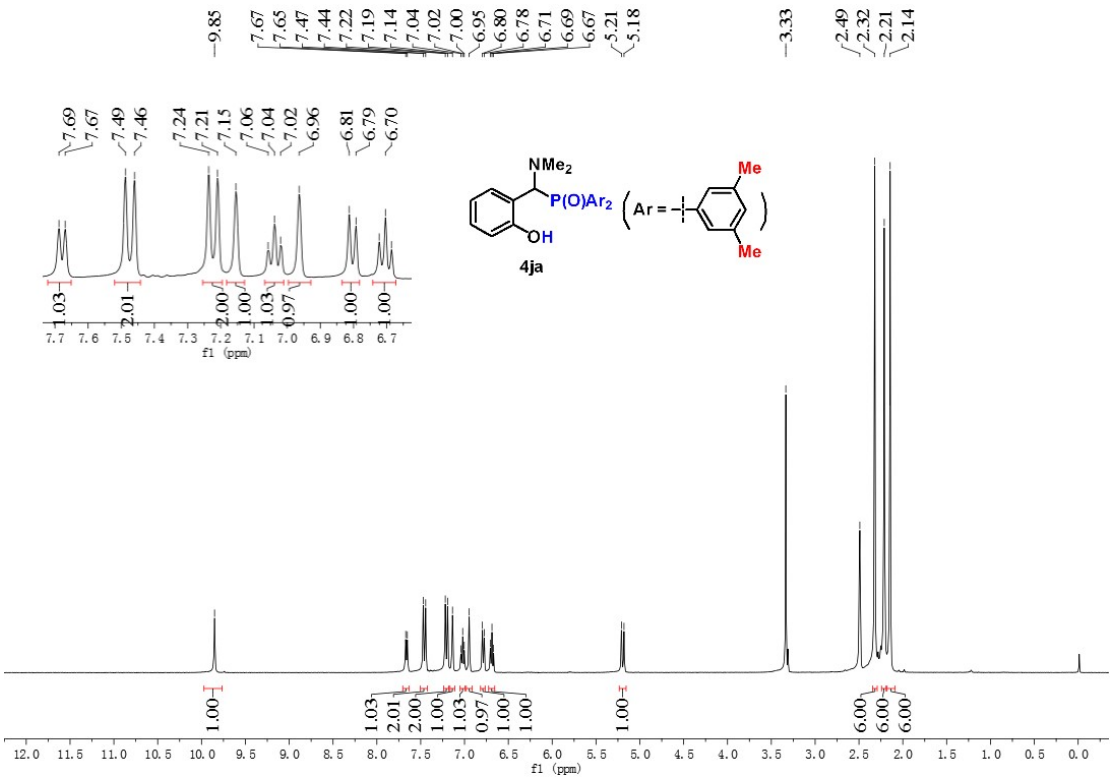
^{1}H NMR (400 MHz, DMSO-d_6)



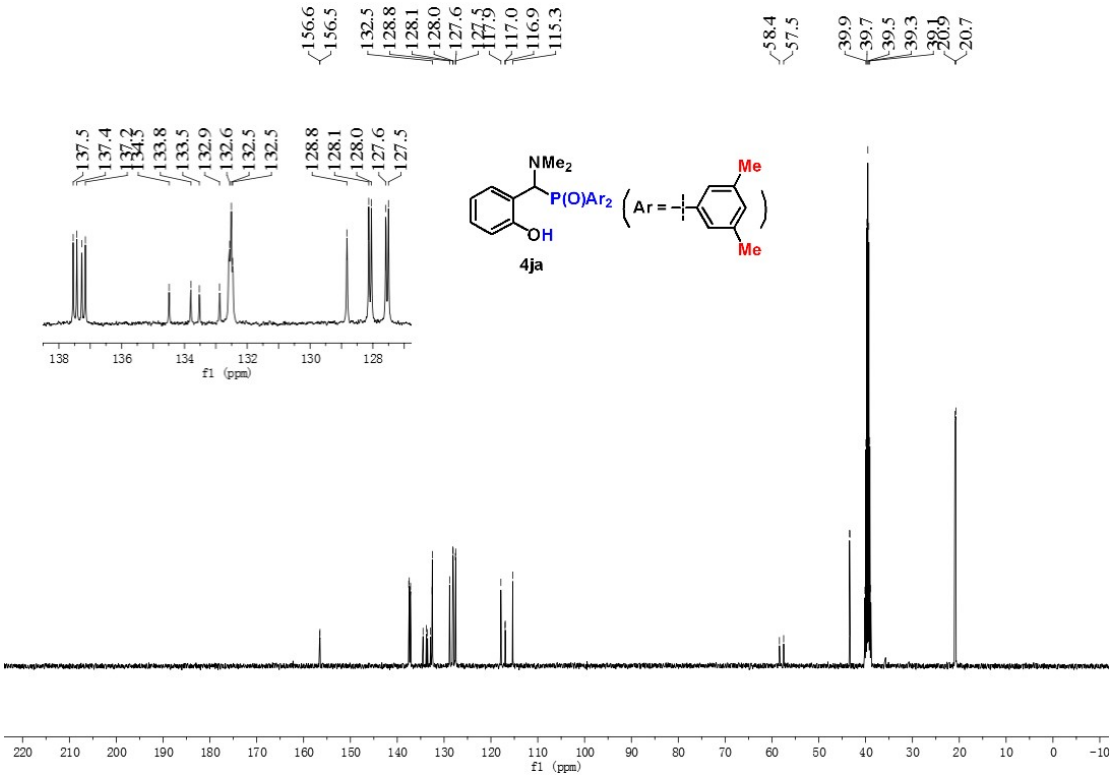
^{13}C NMR (101 MHz, DMSO-d_6)



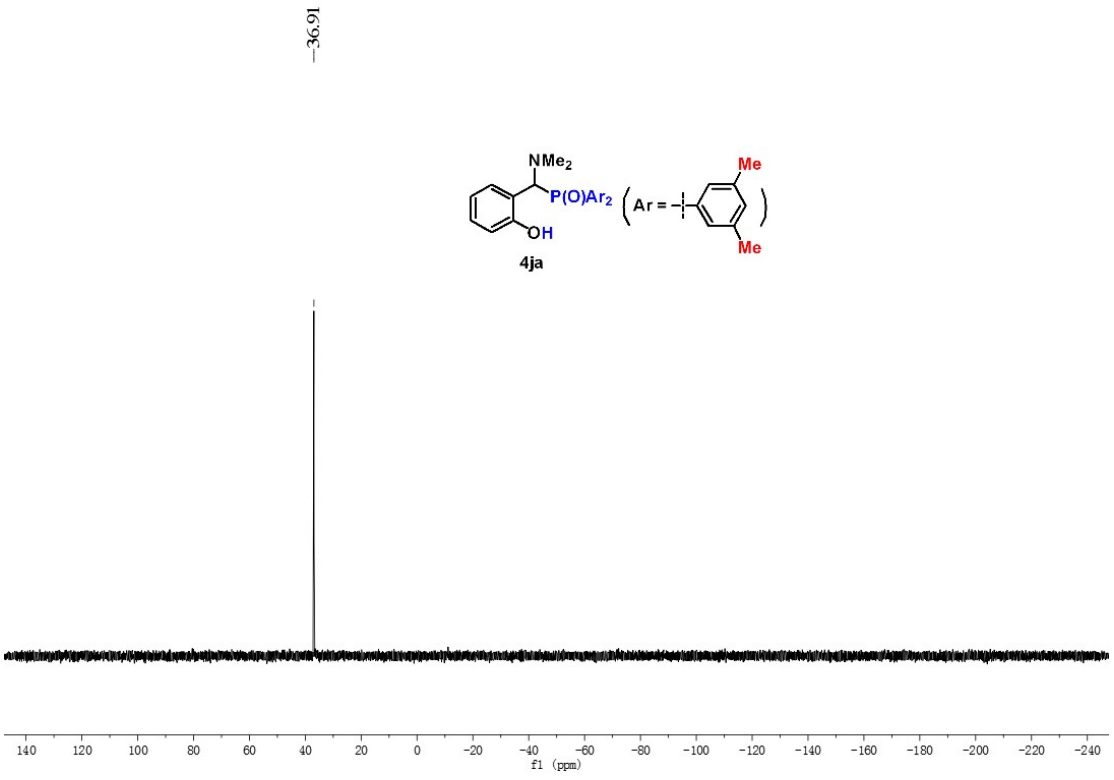
^{31}P NMR (162 MHz, DMSO-d_6)



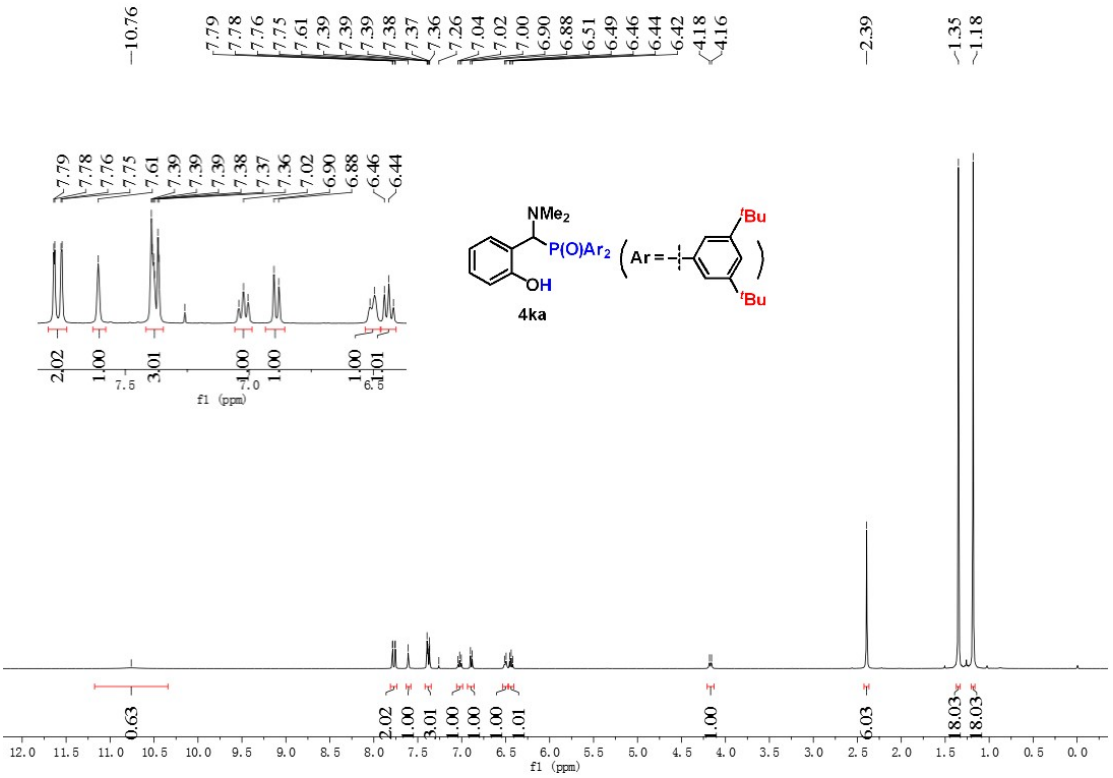
^{1}H NMR (400 MHz, DMSO-d_6)



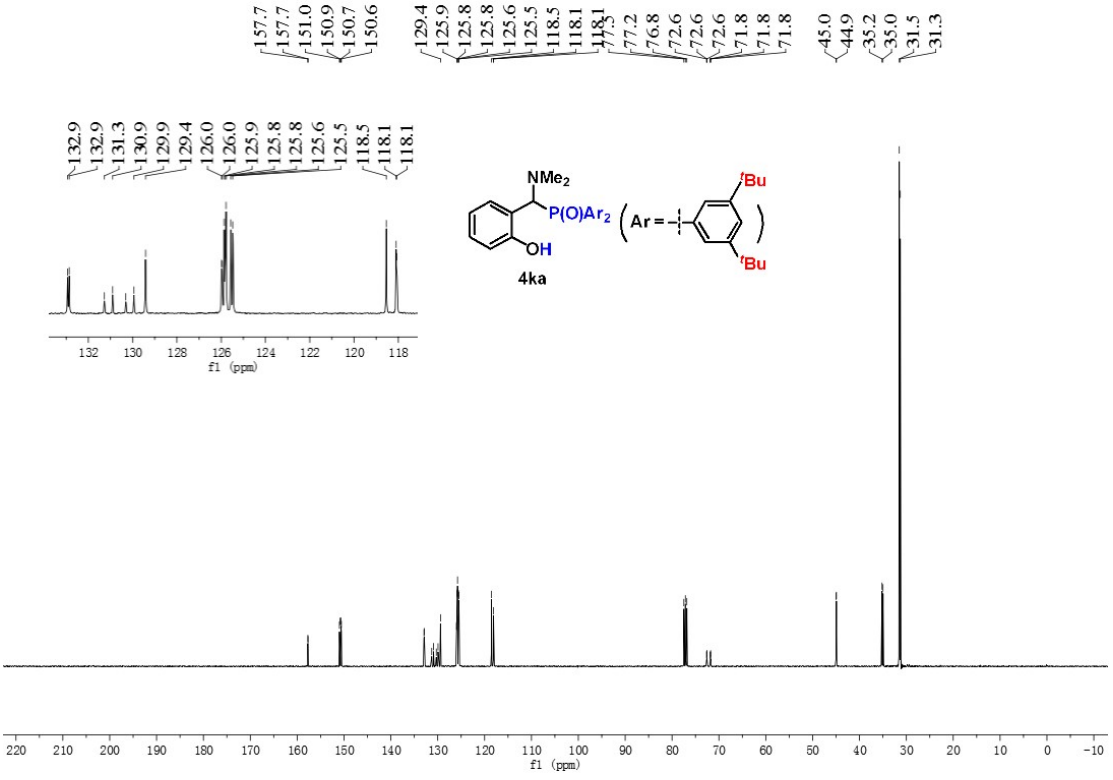
^{13}C NMR (101 MHz, DMSO-d_6)



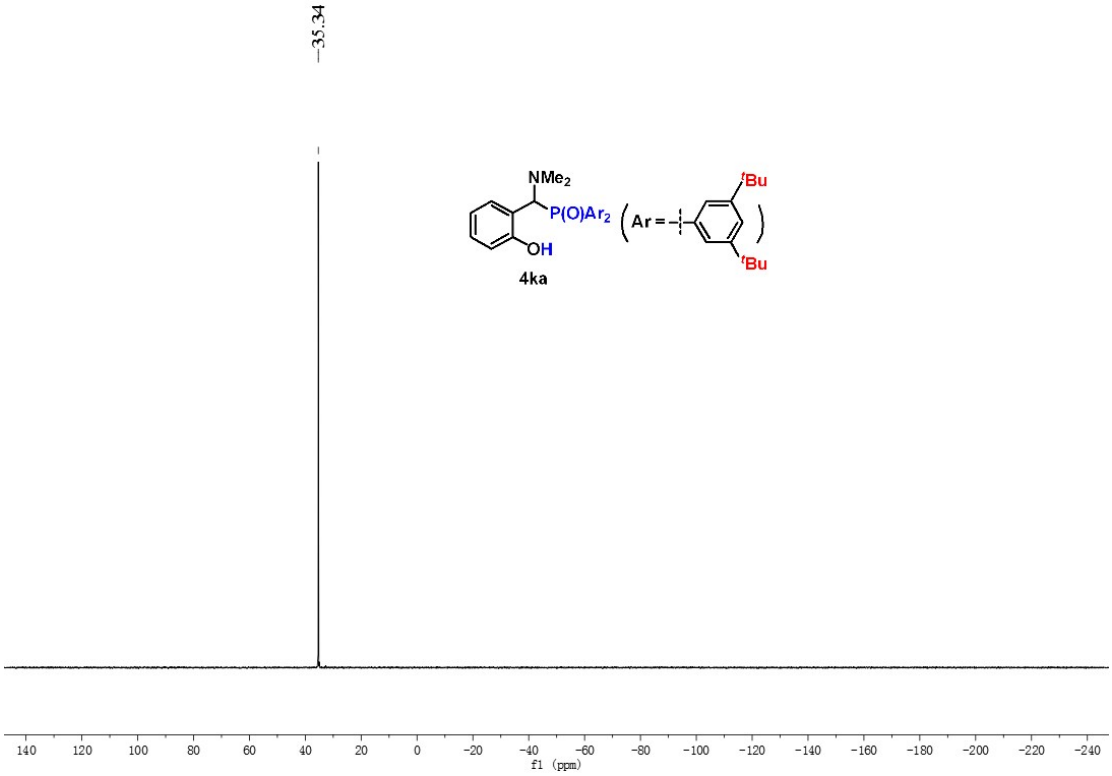
^{31}P NMR (162 MHz, $CDCl_3$)



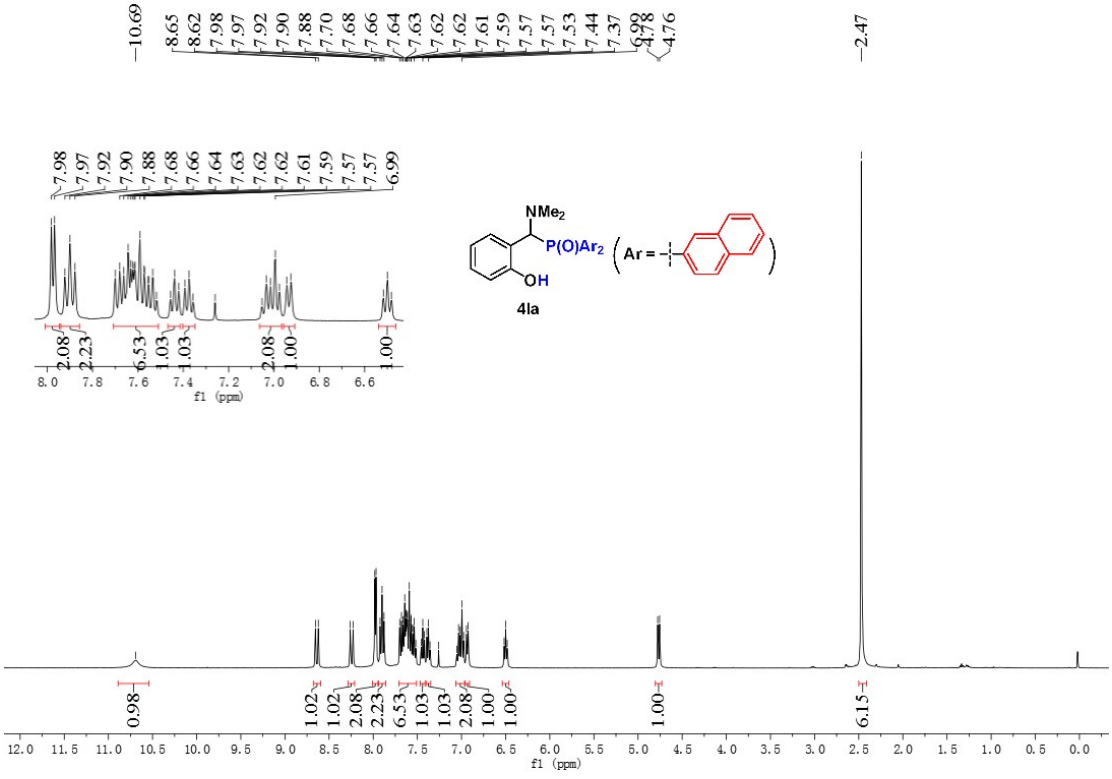
^{1}H NMR (400 MHz, $CDCl_3$)



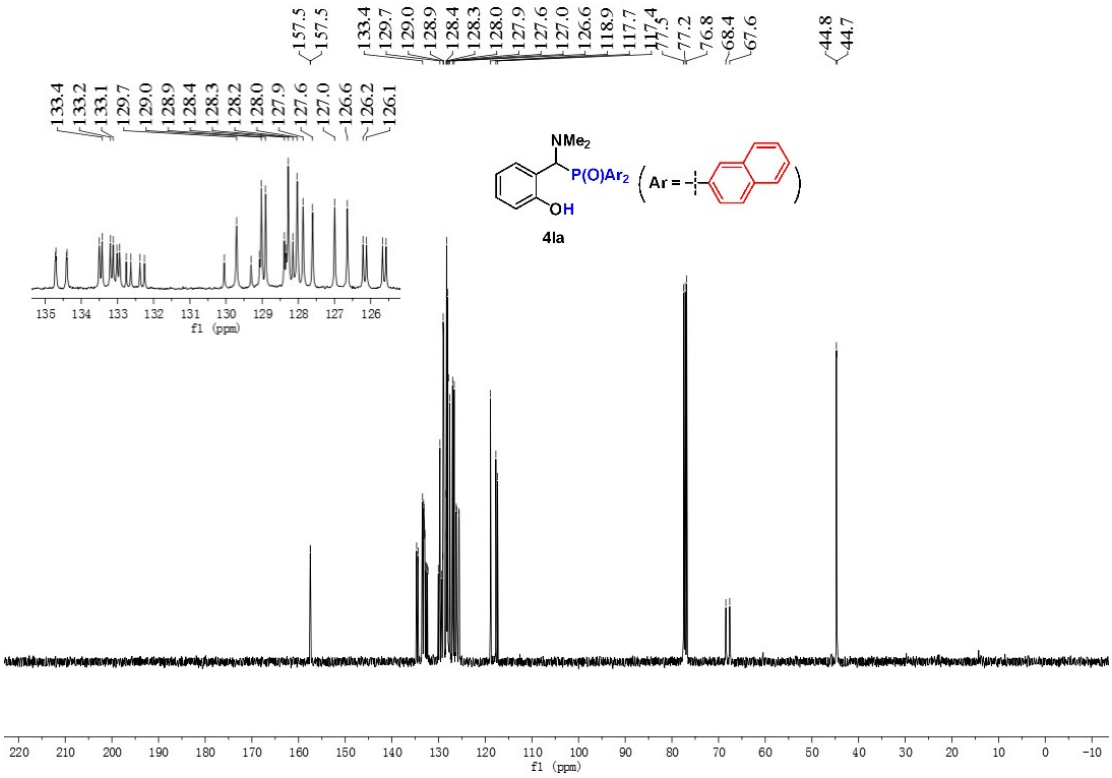
^{13}C NMR (101 MHz, $CDCl_3$)



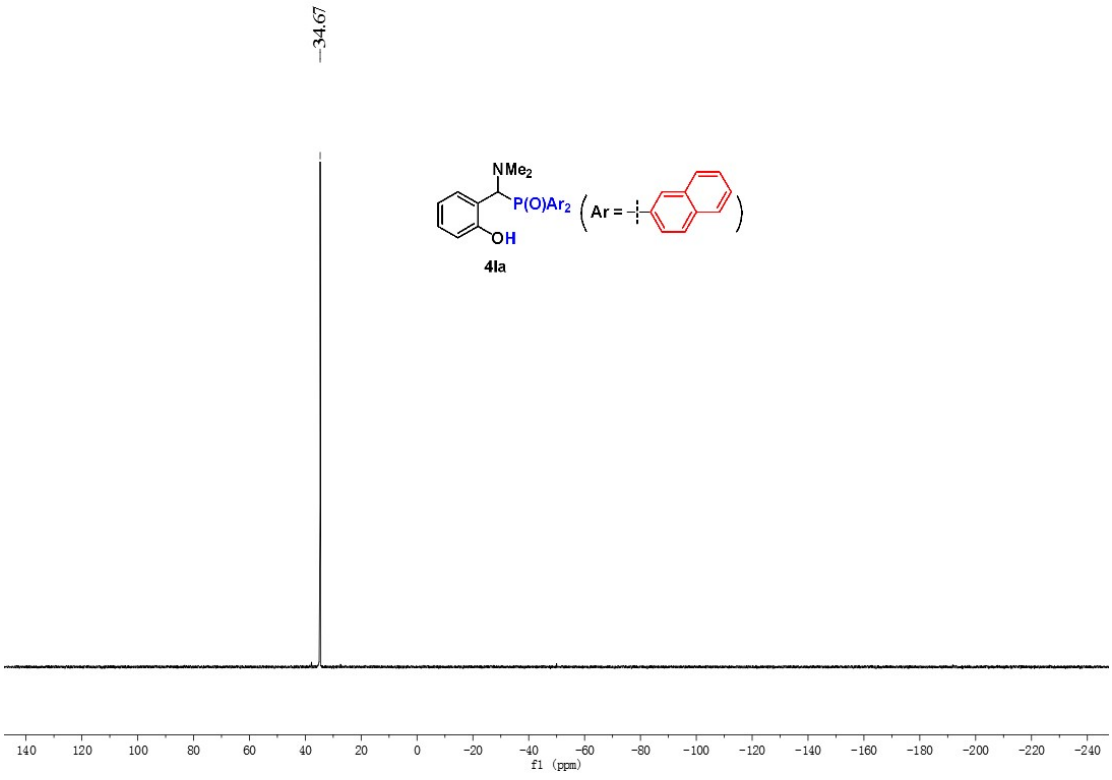
^{31}P NMR (162 MHz, $CDCl_3$)



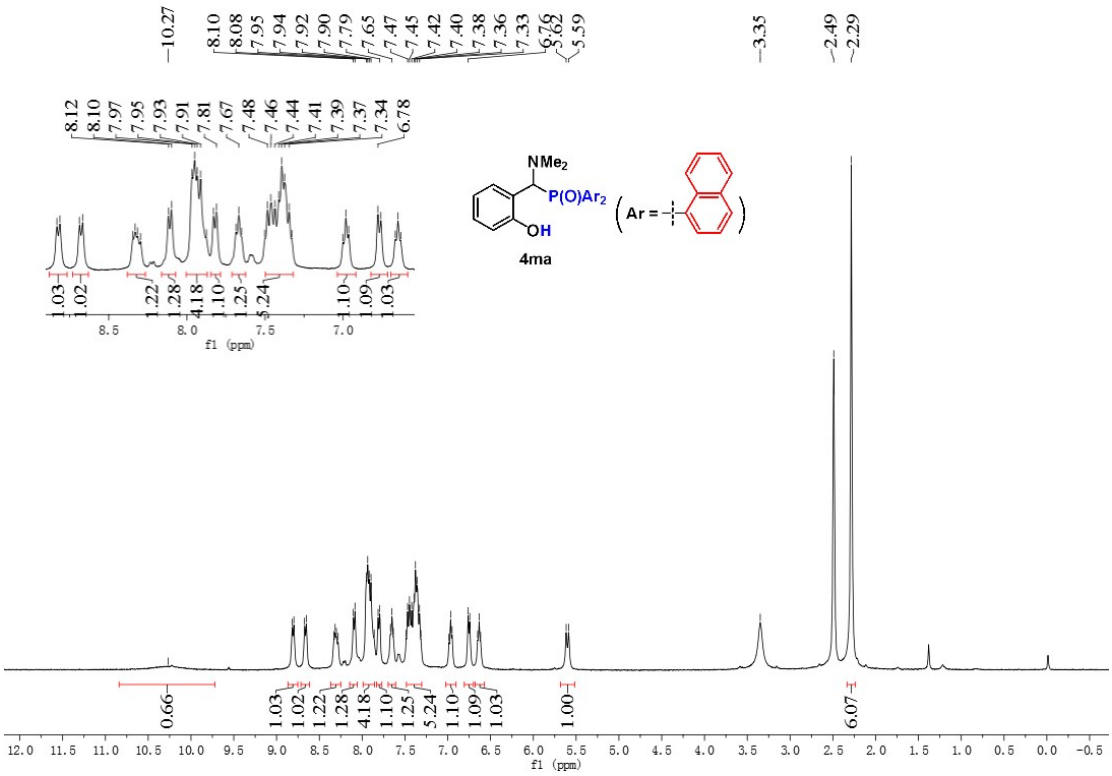
^{1}H NMR (400 MHz, $CDCl_3$)



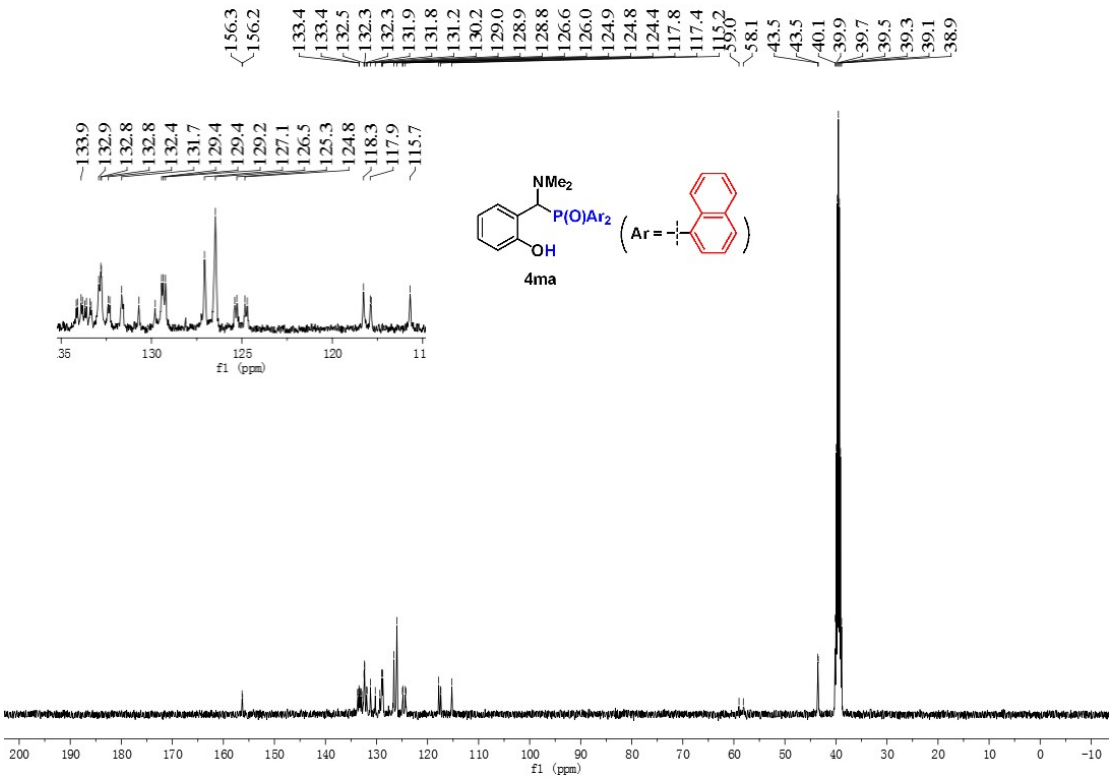
^{13}C NMR (101 MHz, $CDCl_3$)



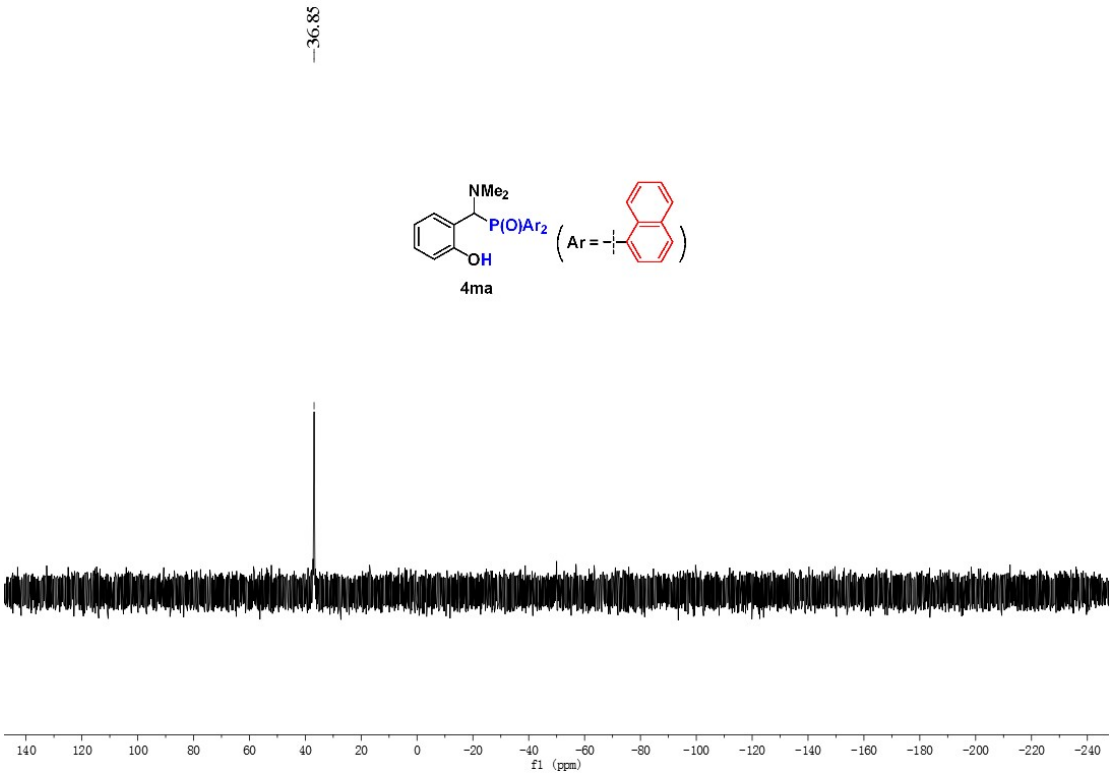
^{31}P NMR (162 MHz, $CDCl_3$)



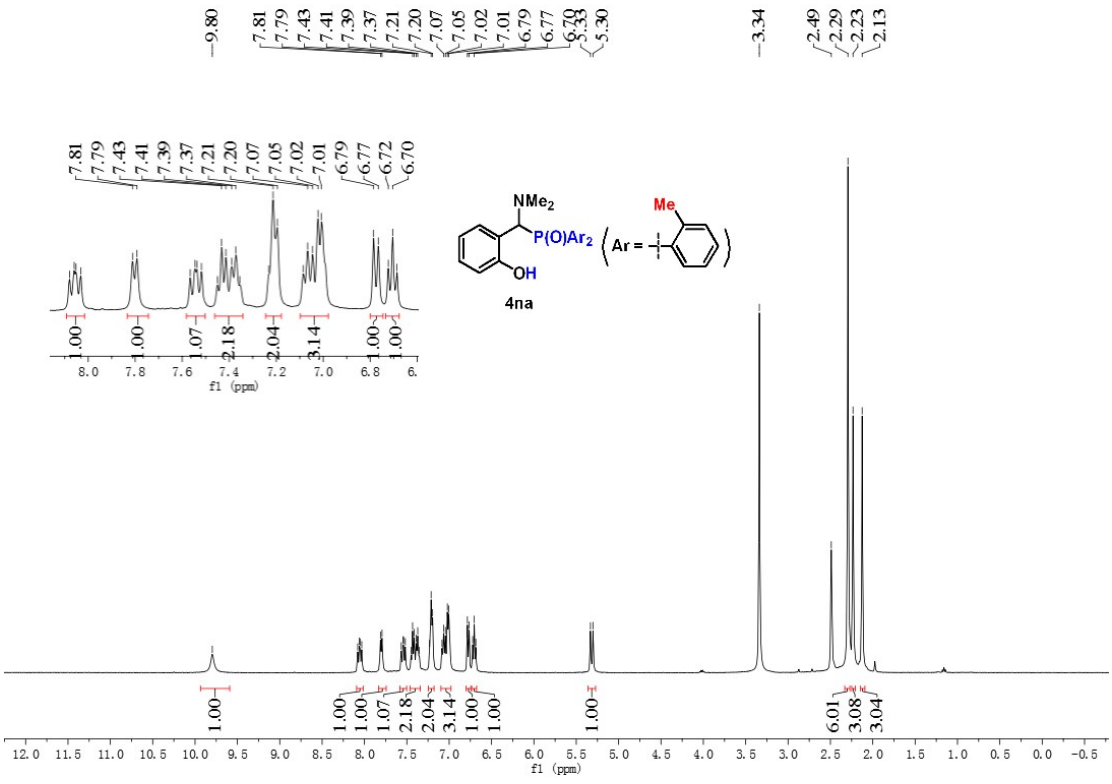
^{1}H NMR (400 MHz, DMSO-d_6)



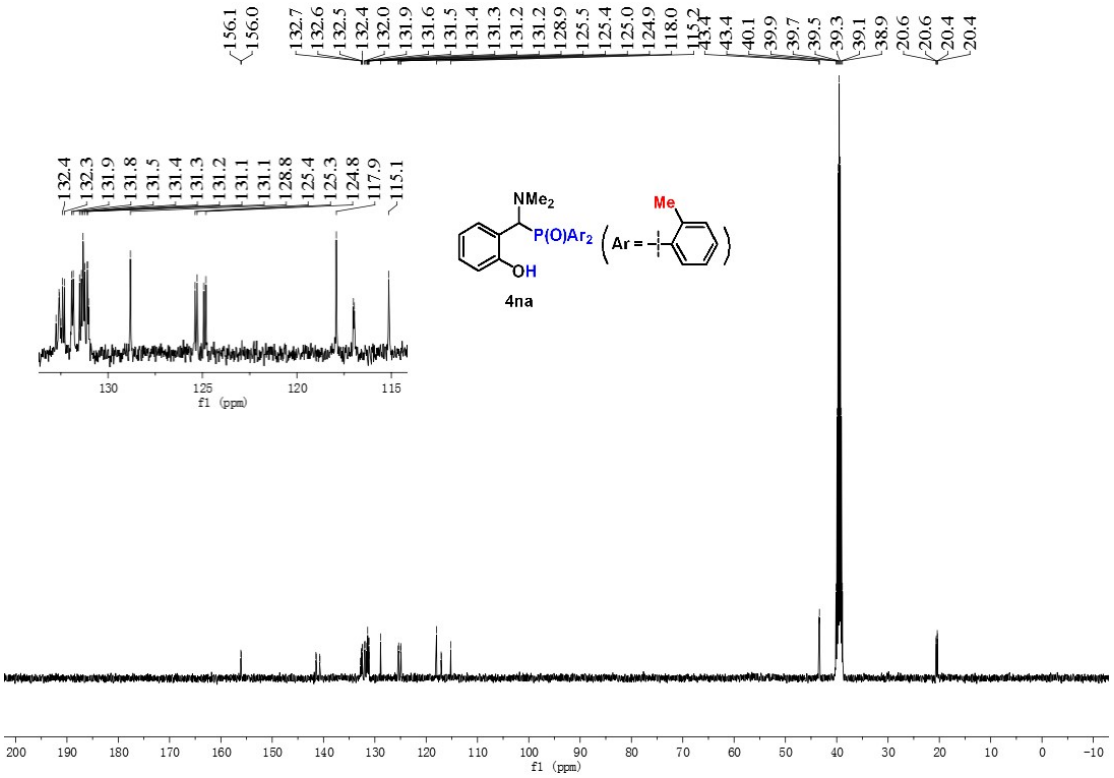
^{13}C NMR (101 MHz, DMSO-d_6)



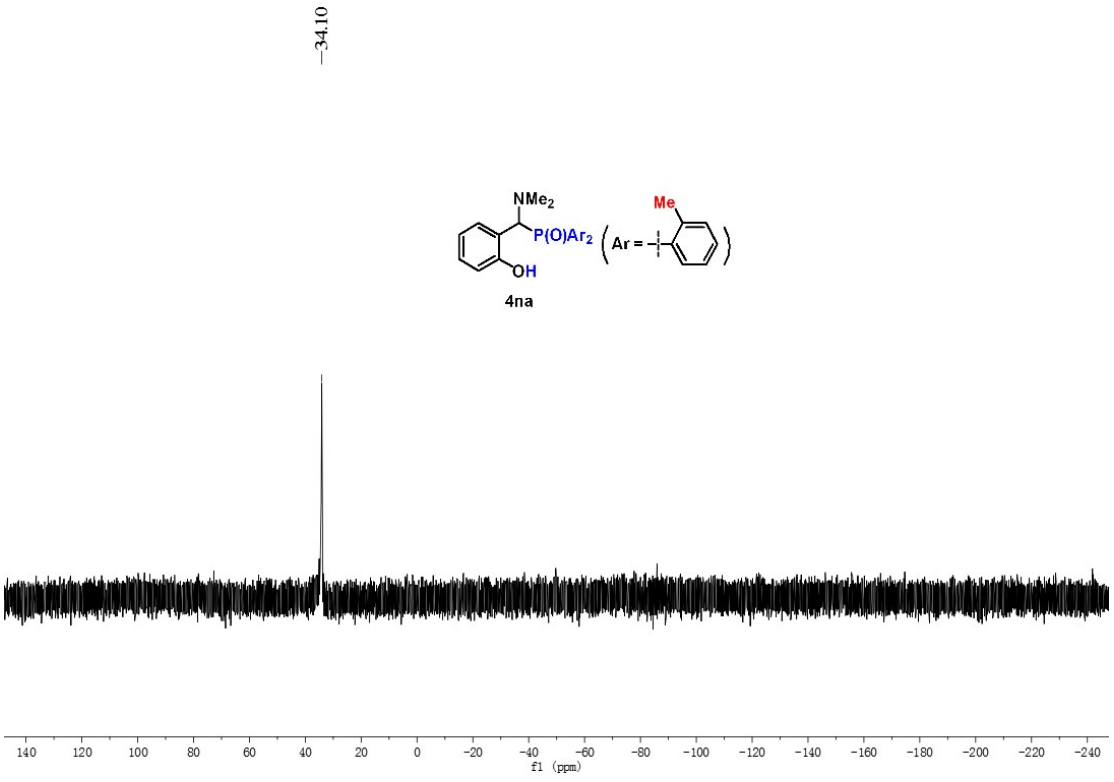
^{31}P NMR (162 MHz, DMSO-d_6)



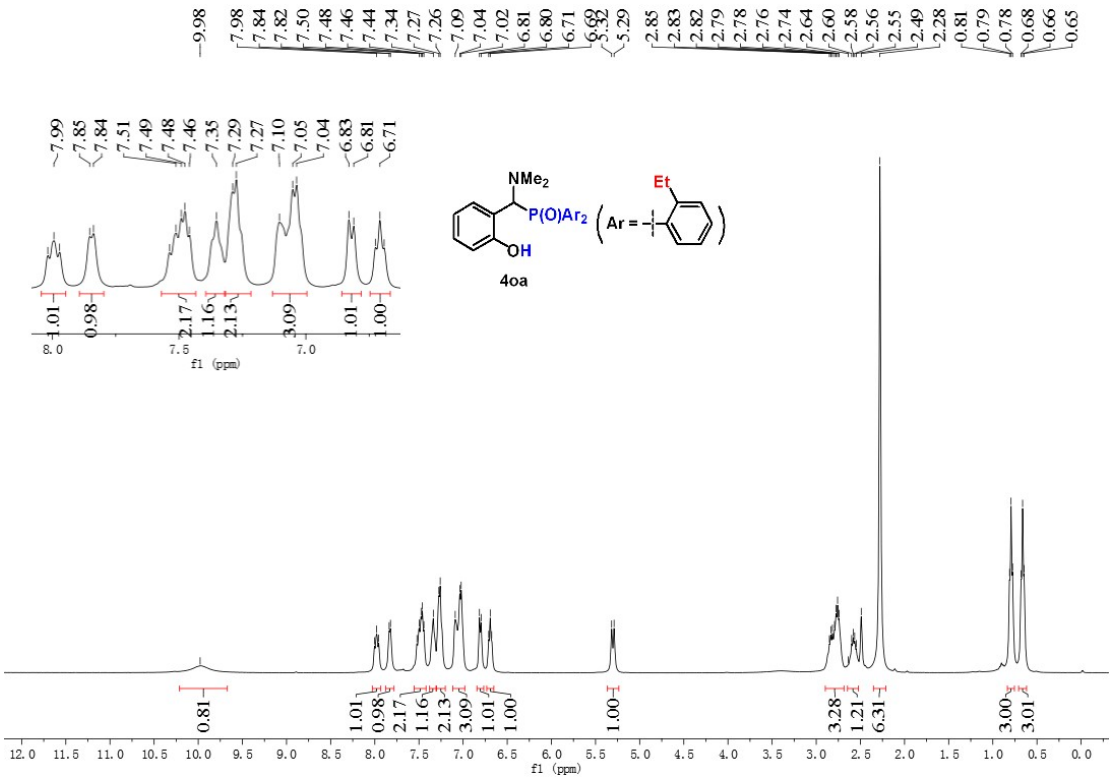
^{1}H NMR (400 MHz, DMSO-d_6)



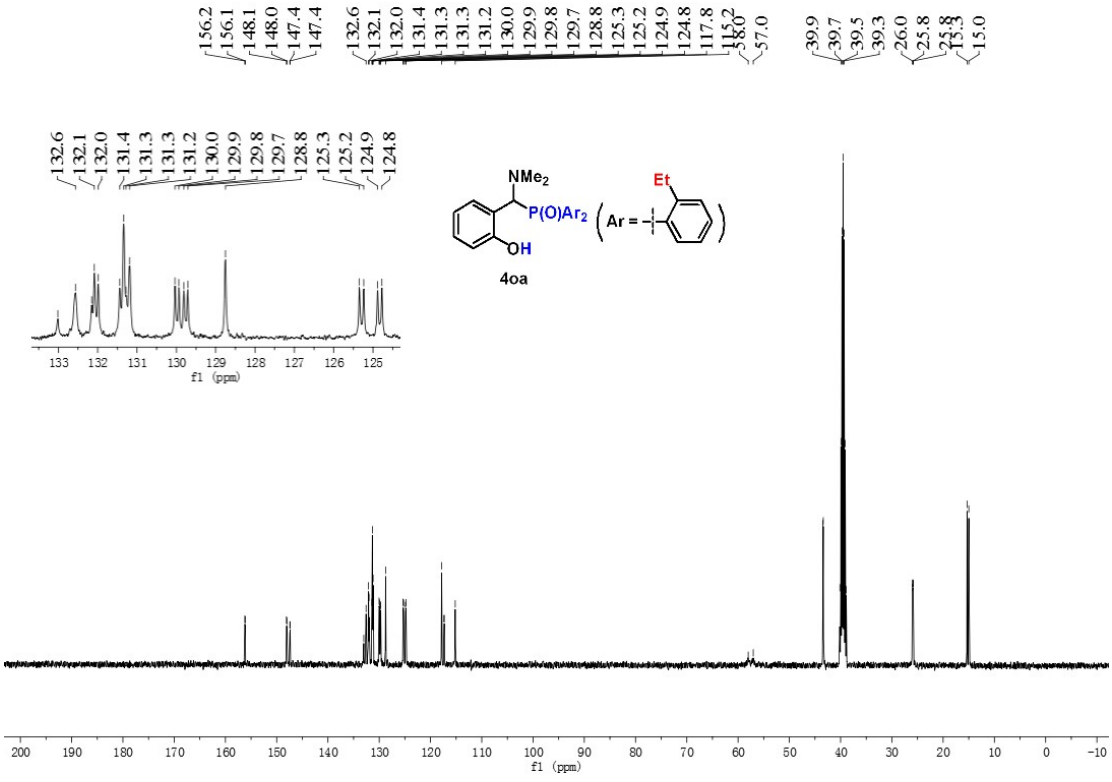
^{13}C NMR (101 MHz, DMSO-d_6)



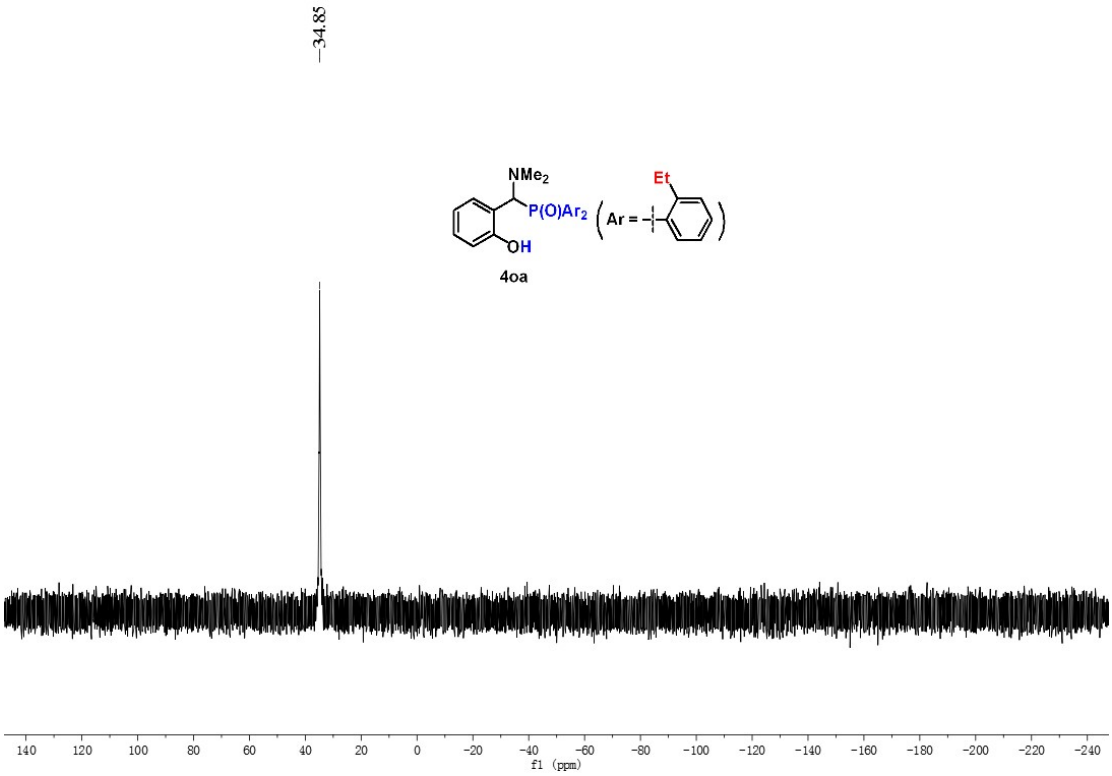
^{31}P NMR (162 MHz, DMSO-d_6)



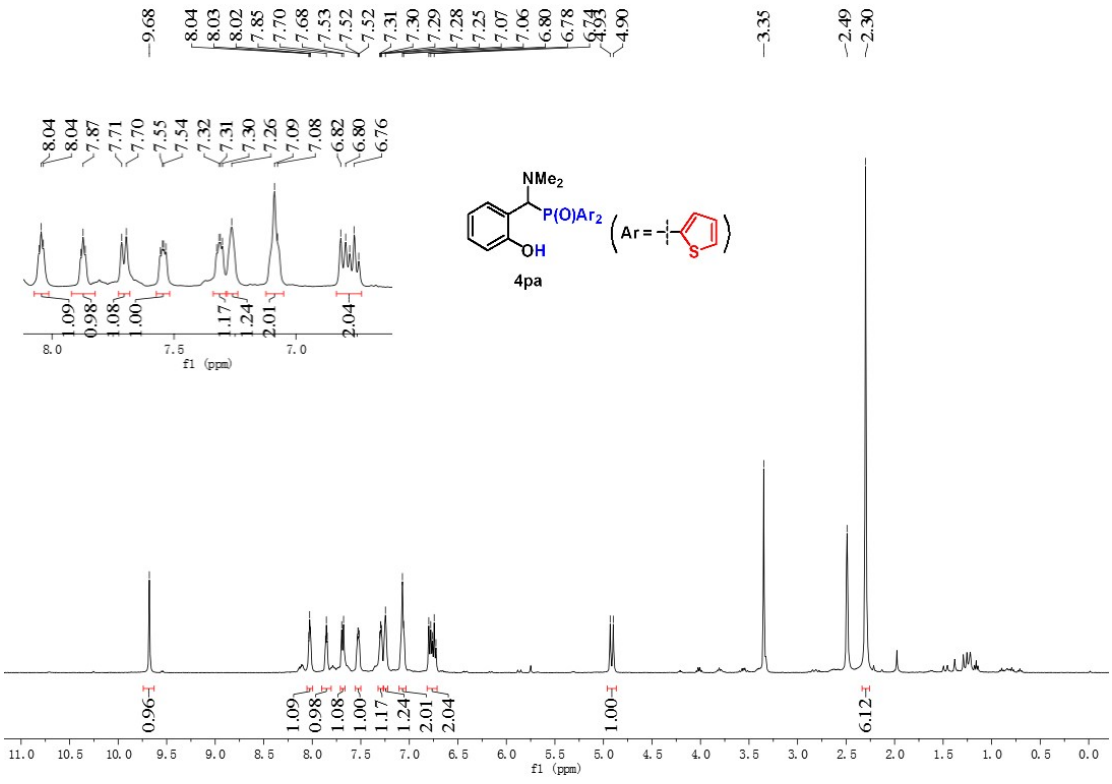
^{1}H NMR (400 MHz, DMSO-d_6)



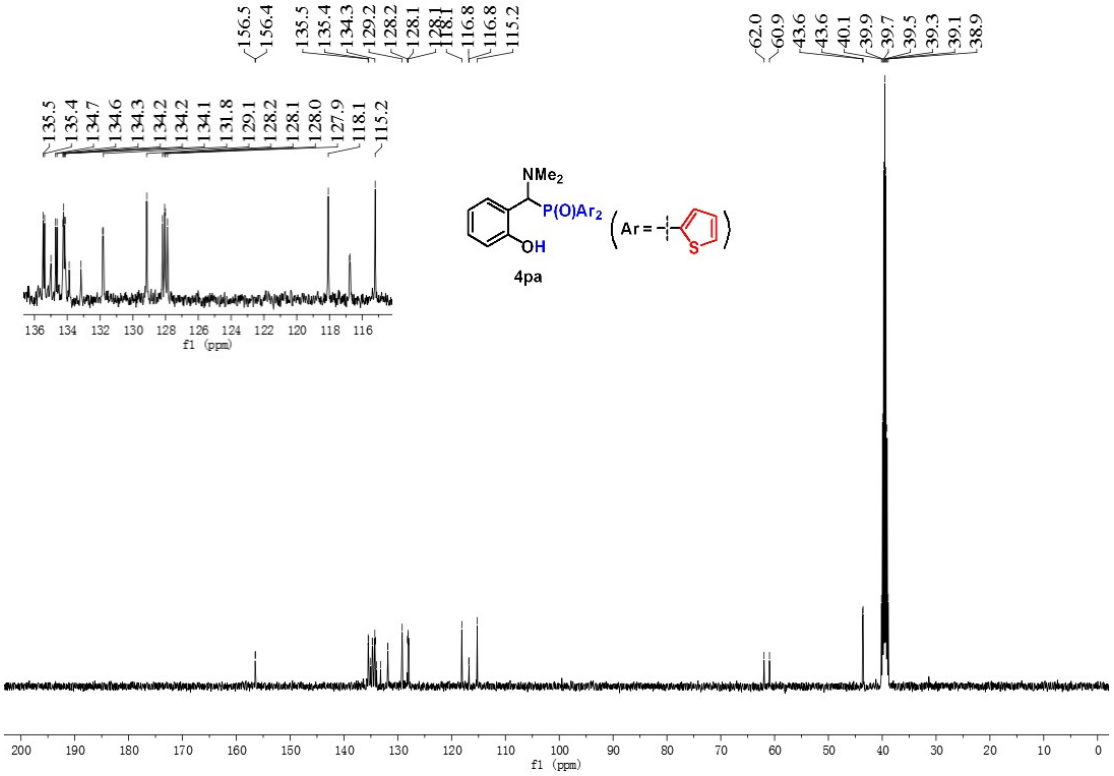
^{13}C NMR (101 MHz, DMSO-d_6)



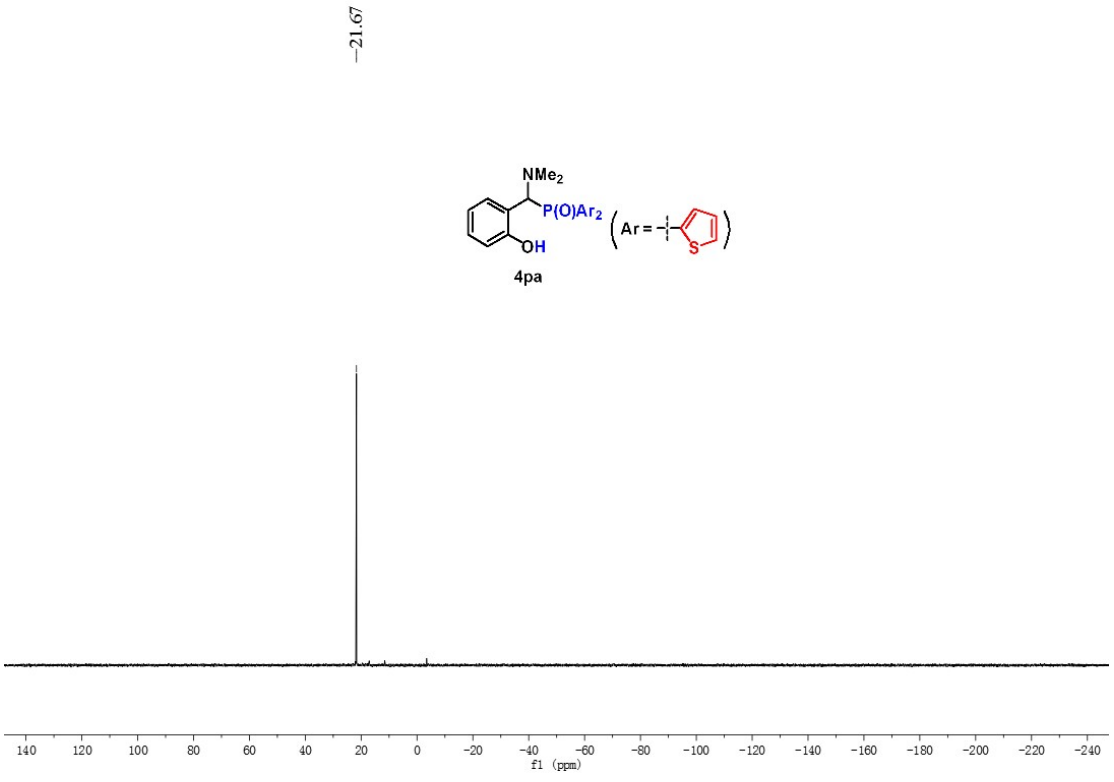
^{31}P NMR (162 MHz, DMSO-d_6)



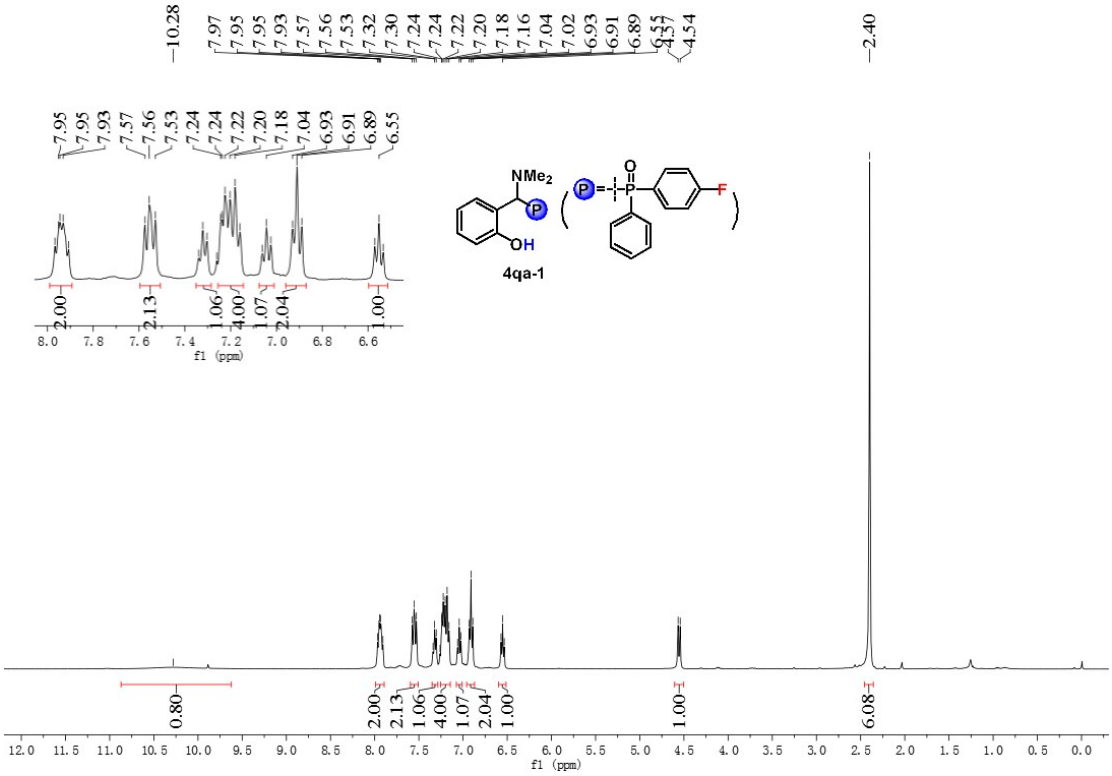
^{1}H NMR (400 MHz, DMSO-d_6)



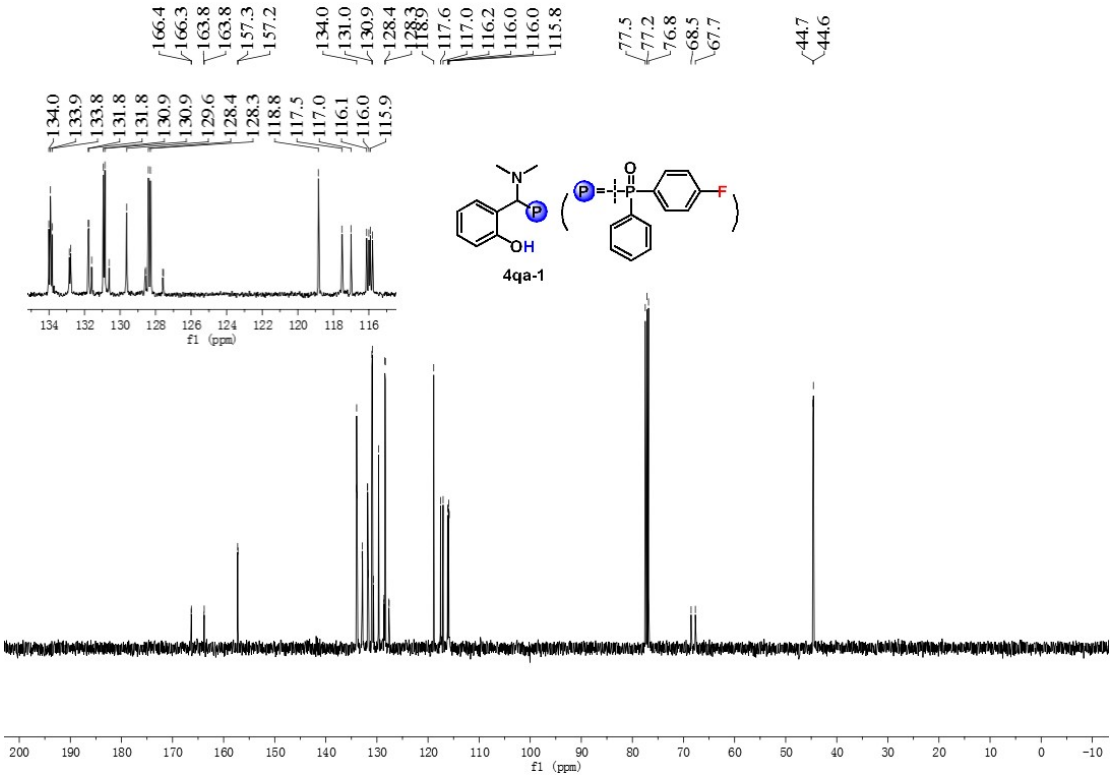
^{13}C NMR (101 MHz, DMSO-d_6)



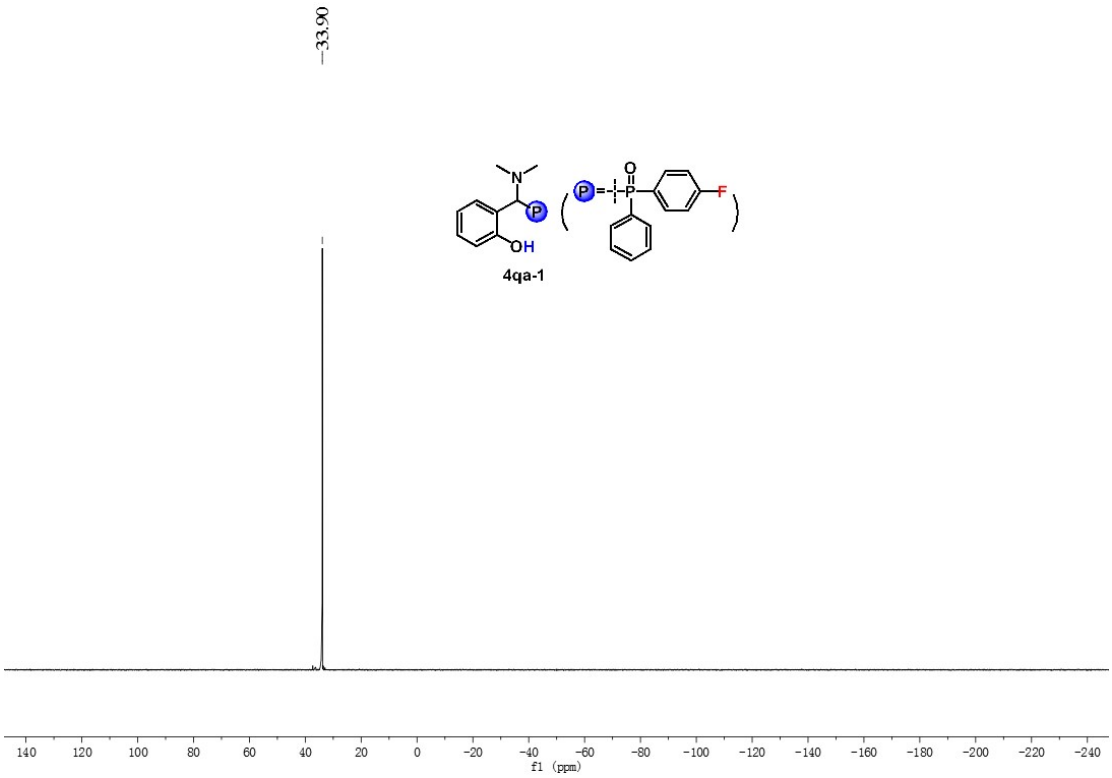
^{31}P NMR (162 MHz, DMSO-d_6)



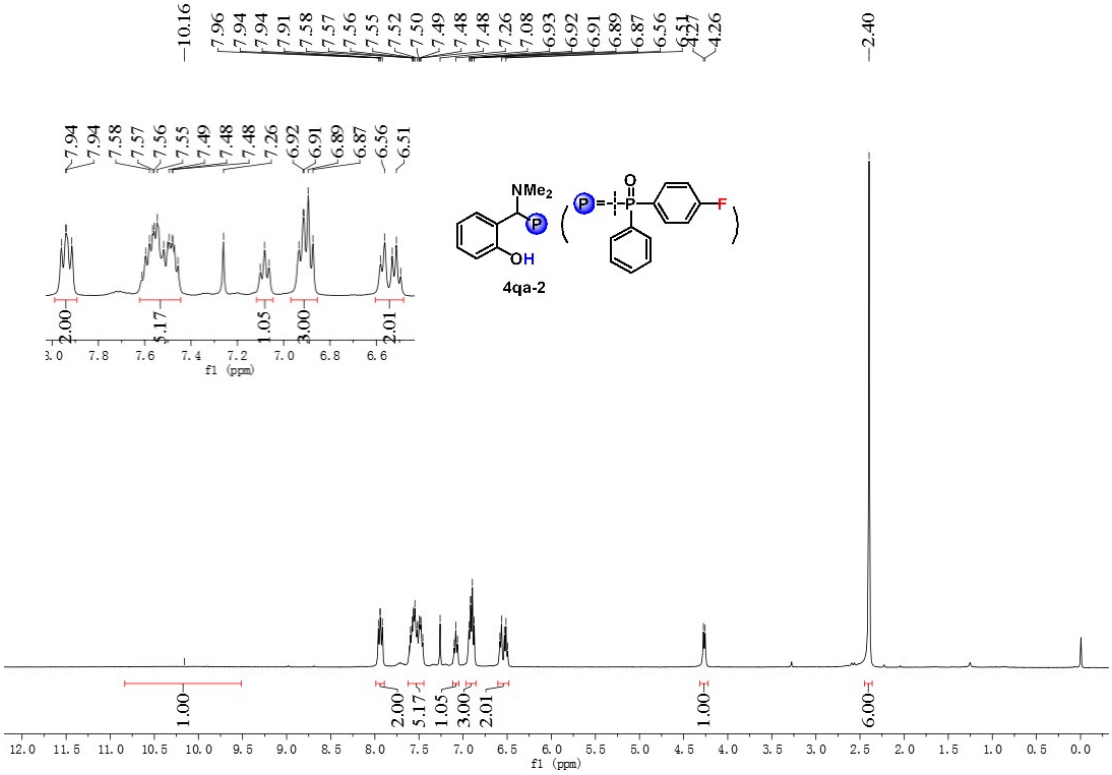
^{1}H NMR (400 MHz, $CDCl_3$)



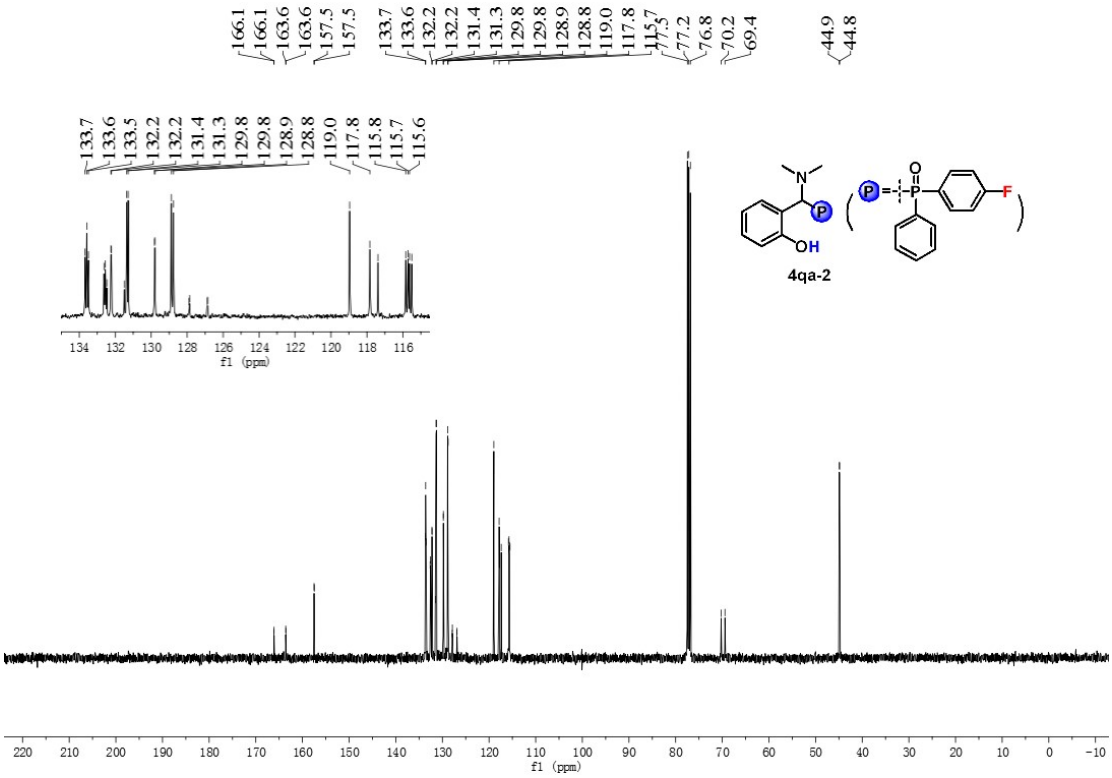
^{13}C NMR (101 MHz, $CDCl_3$)



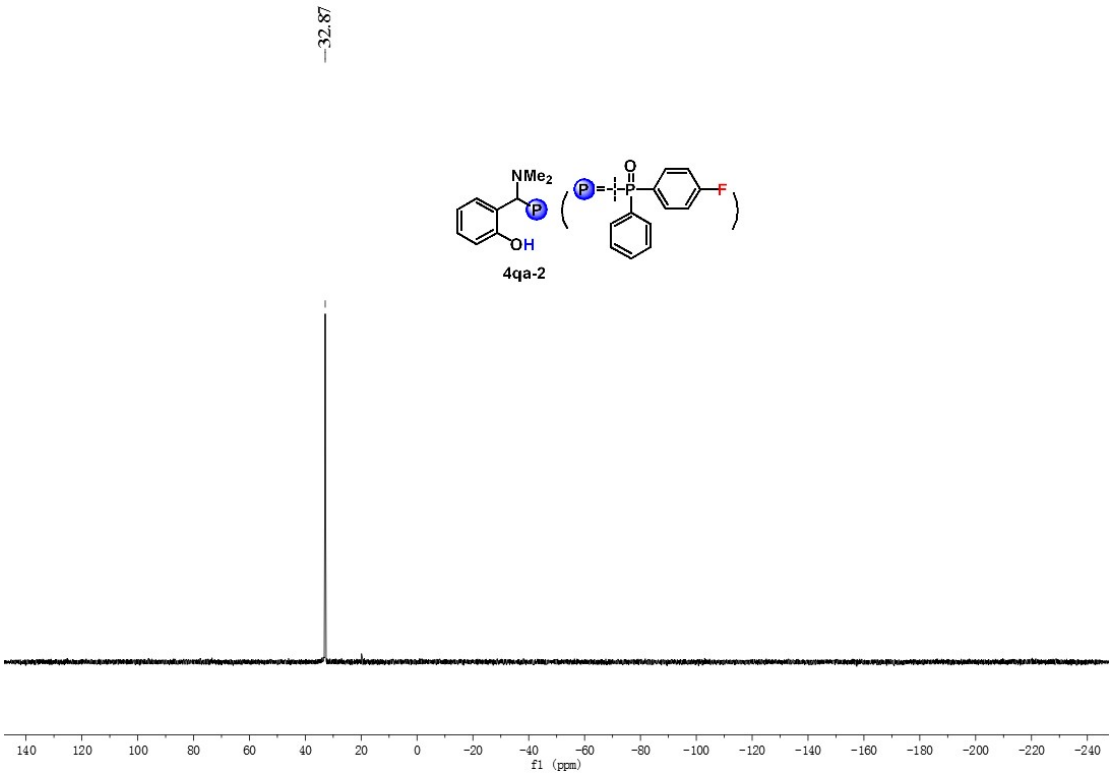
^{31}P NMR (162 MHz, $CDCl_3$)



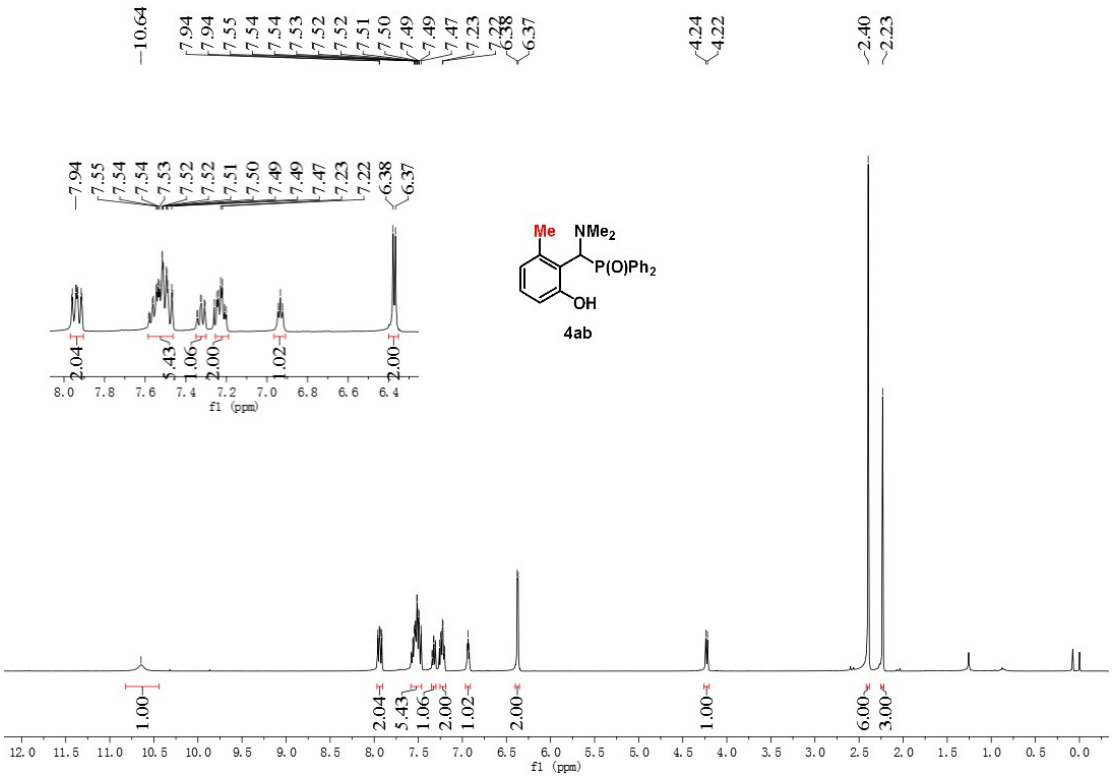
^{1}H NMR (400 MHz, $CDCl_3$)



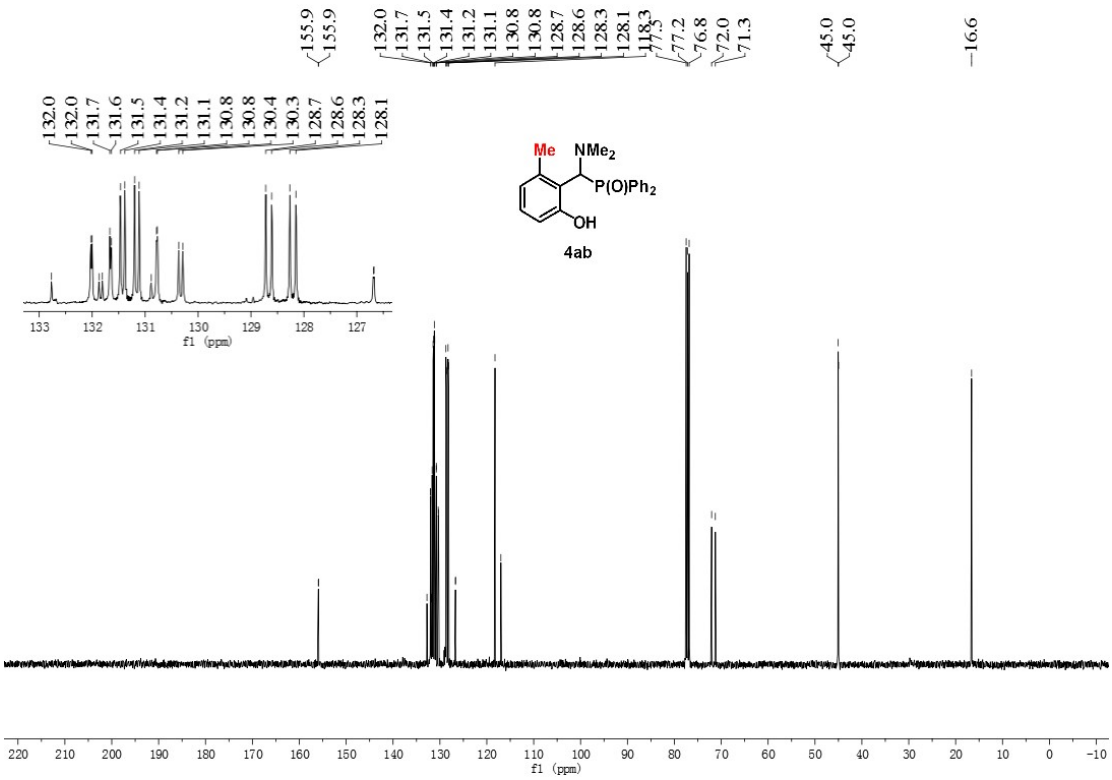
^{13}C NMR (101 MHz, $CDCl_3$)



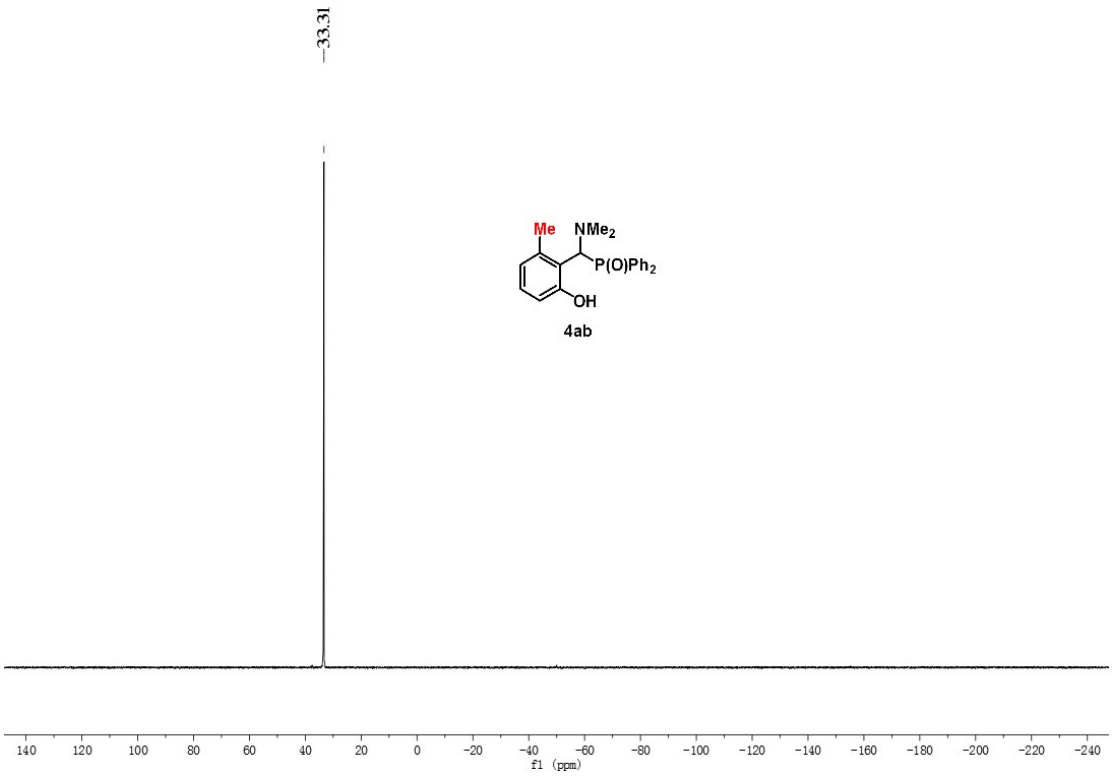
^{31}P NMR (162 MHz, $CDCl_3$)



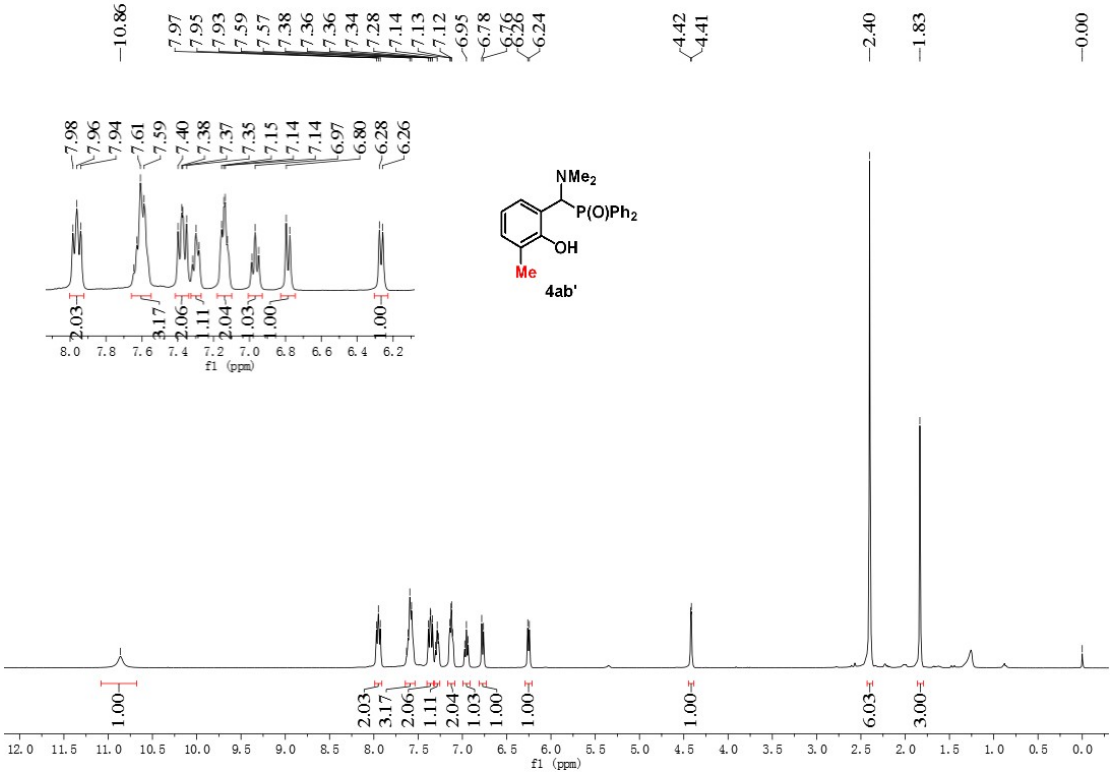
^{1}H NMR (400 MHz, $CDCl_3$)



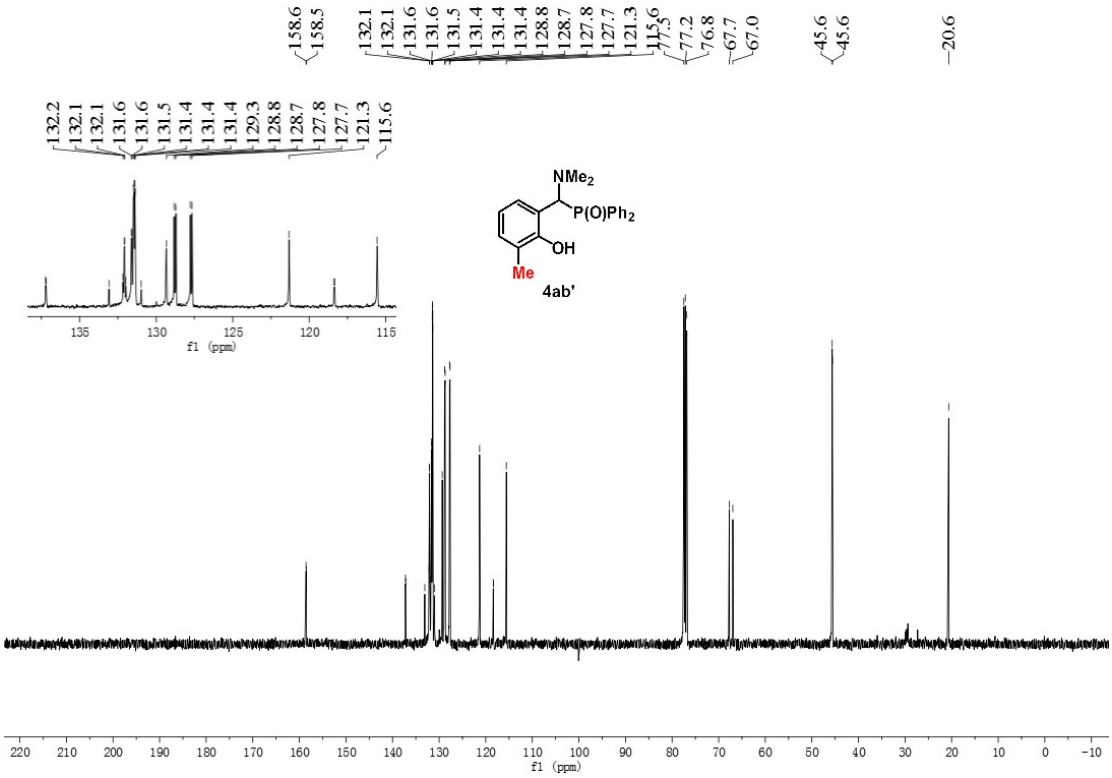
^{13}C NMR (101 MHz, $CDCl_3$)



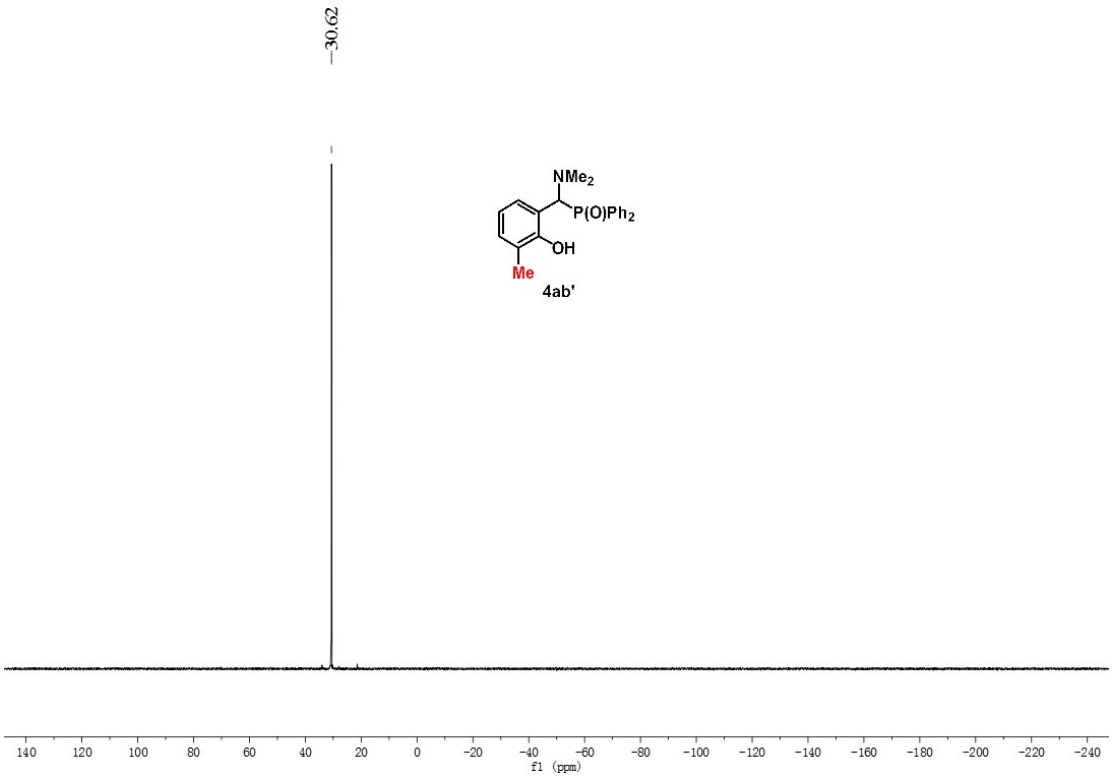
^{31}P NMR (162 MHz, $CDCl_3$)



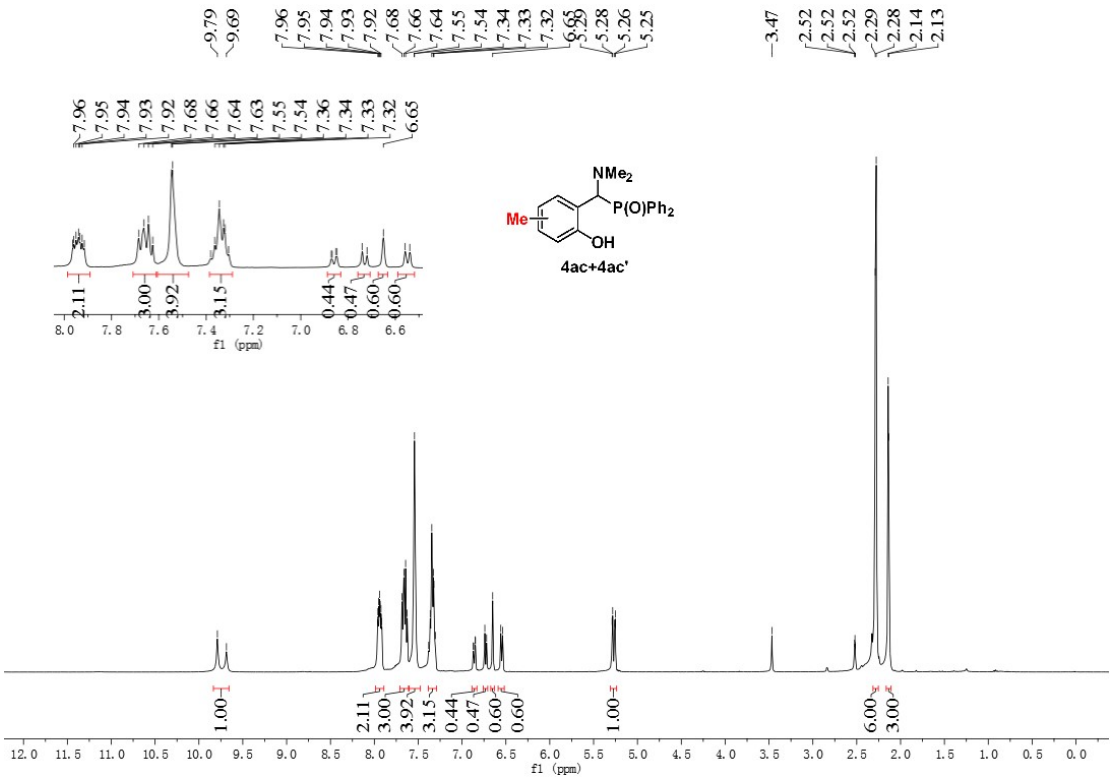
^{1}H NMR (400 MHz, $CDCl_3$)



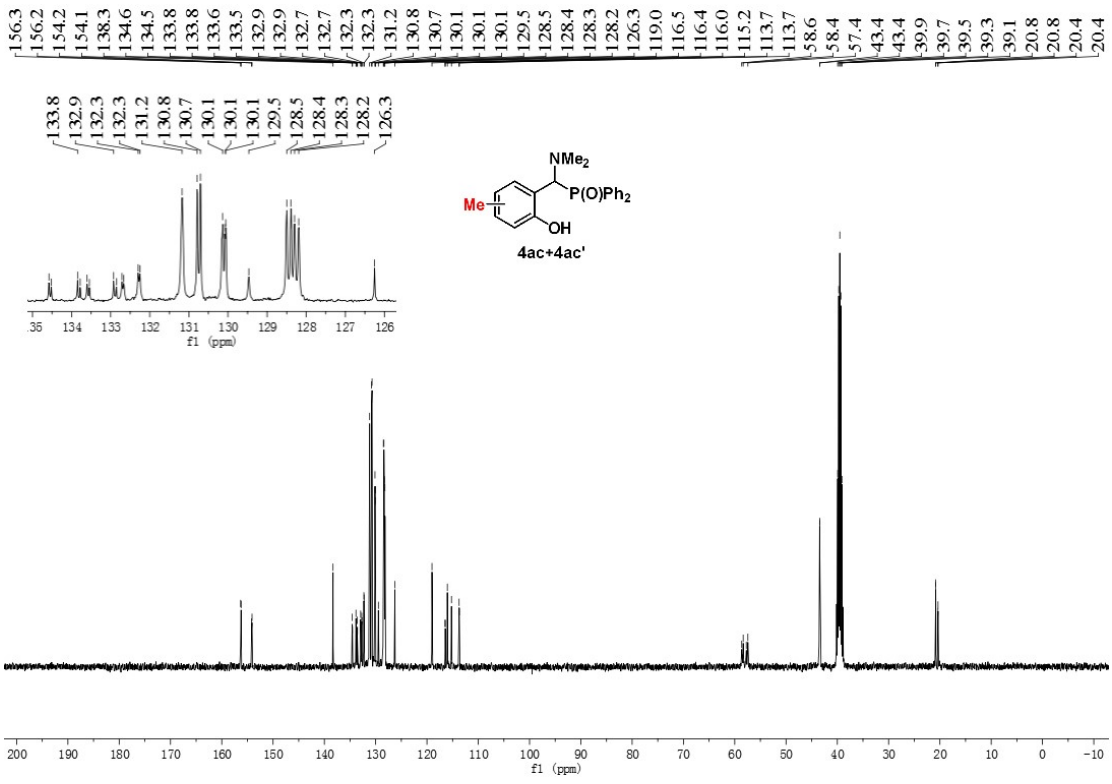
^{13}C NMR (101 MHz, $CDCl_3$)



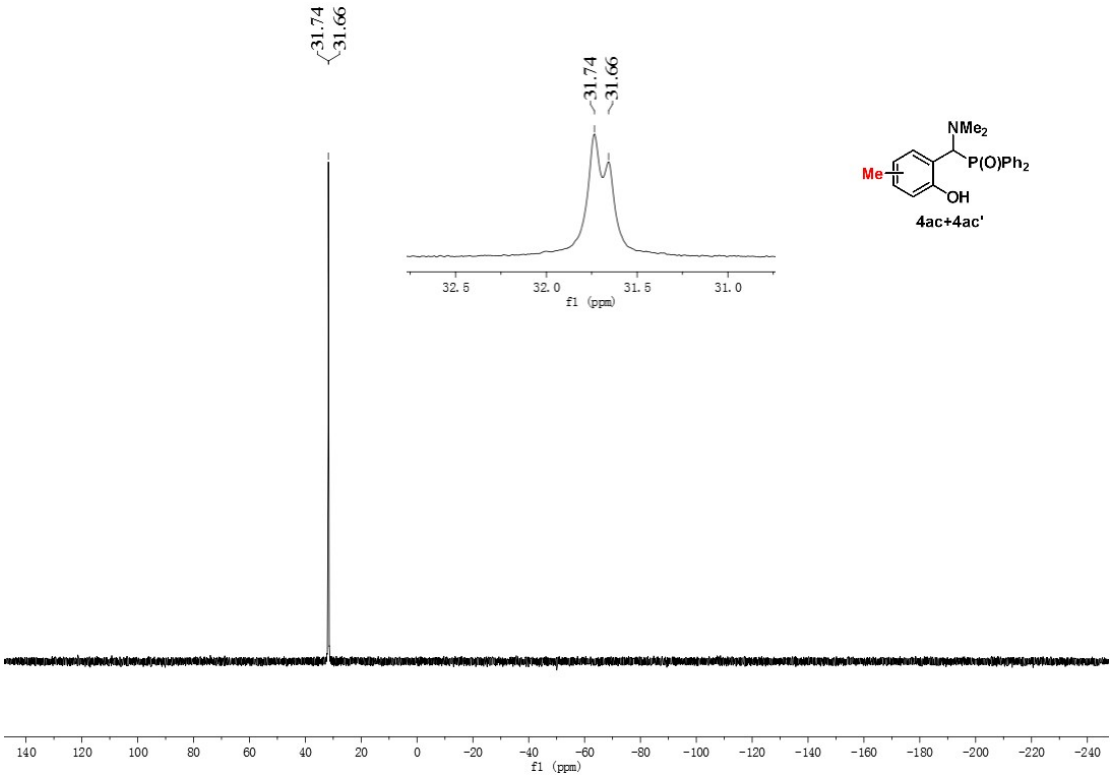
^{31}P NMR (162 MHz, $CDCl_3$)



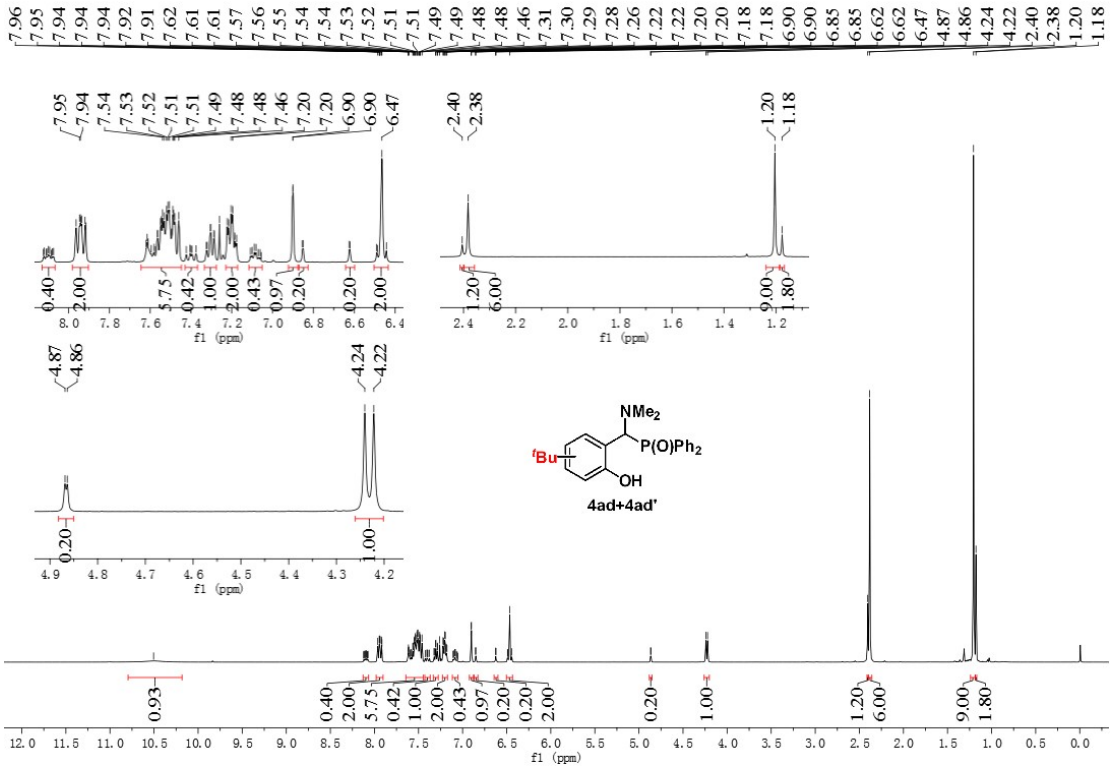
^{1}H NMR (400 MHz, DMSO-d_6)



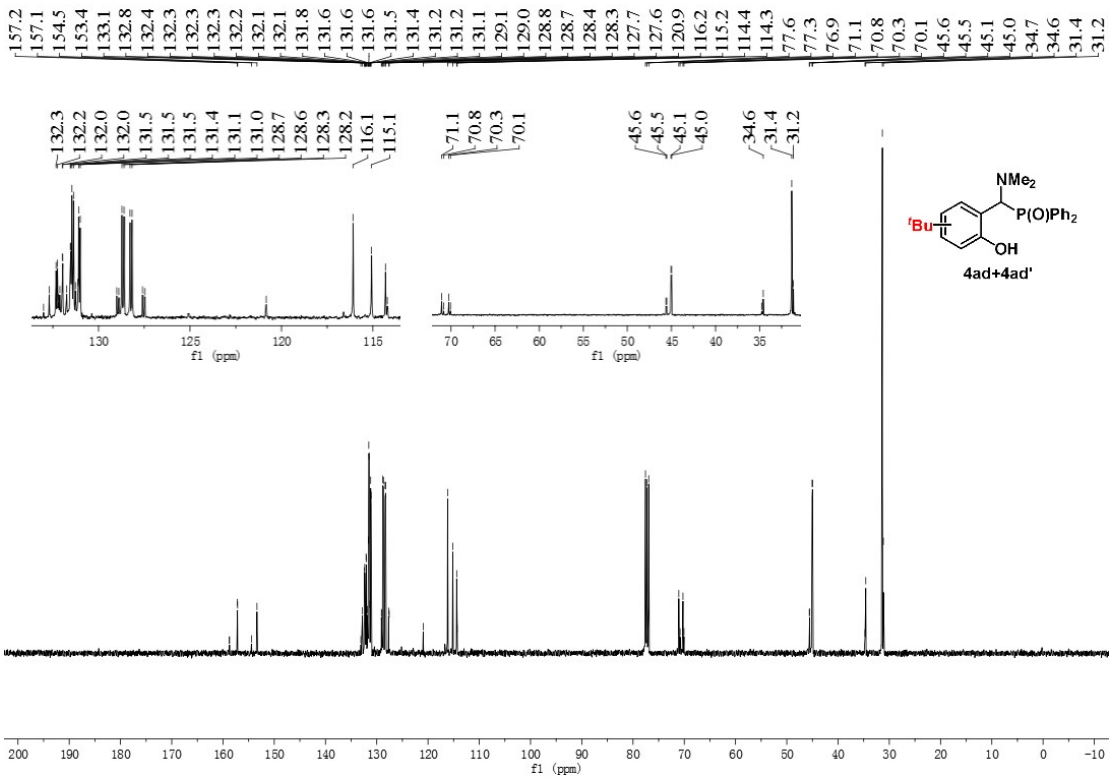
^{13}C NMR (101 MHz, DMSO-d_6)



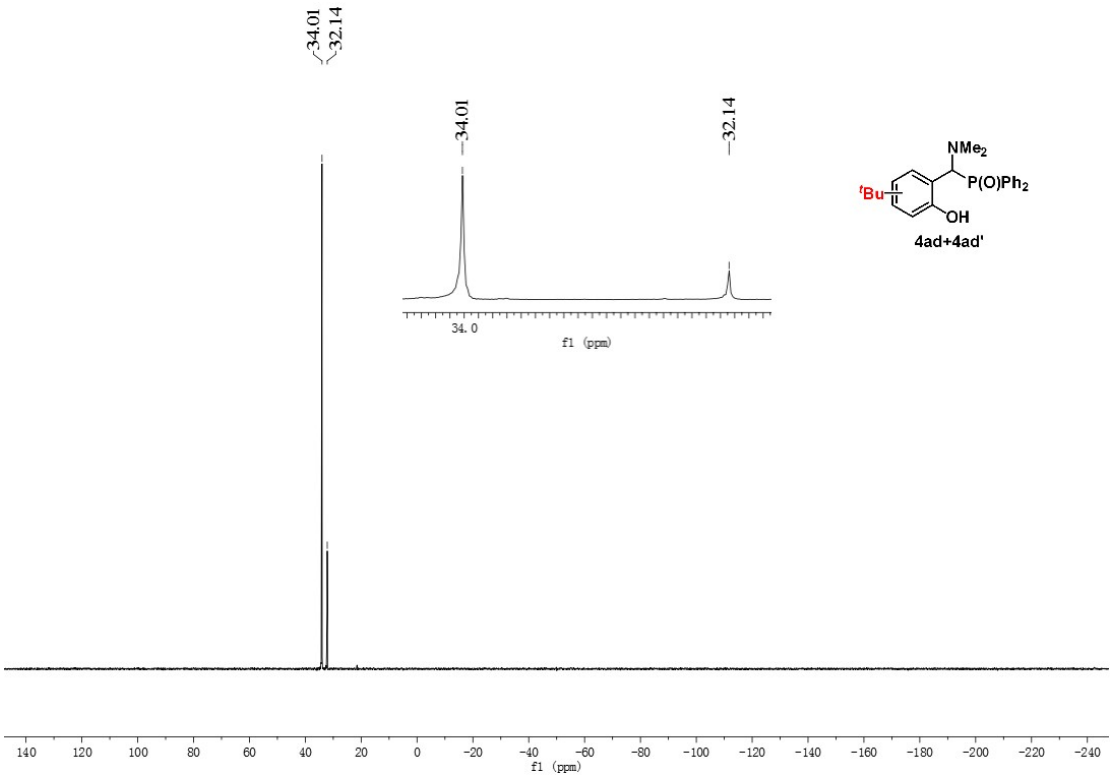
^{31}P NMR (162 MHz, DMSO-d_6)



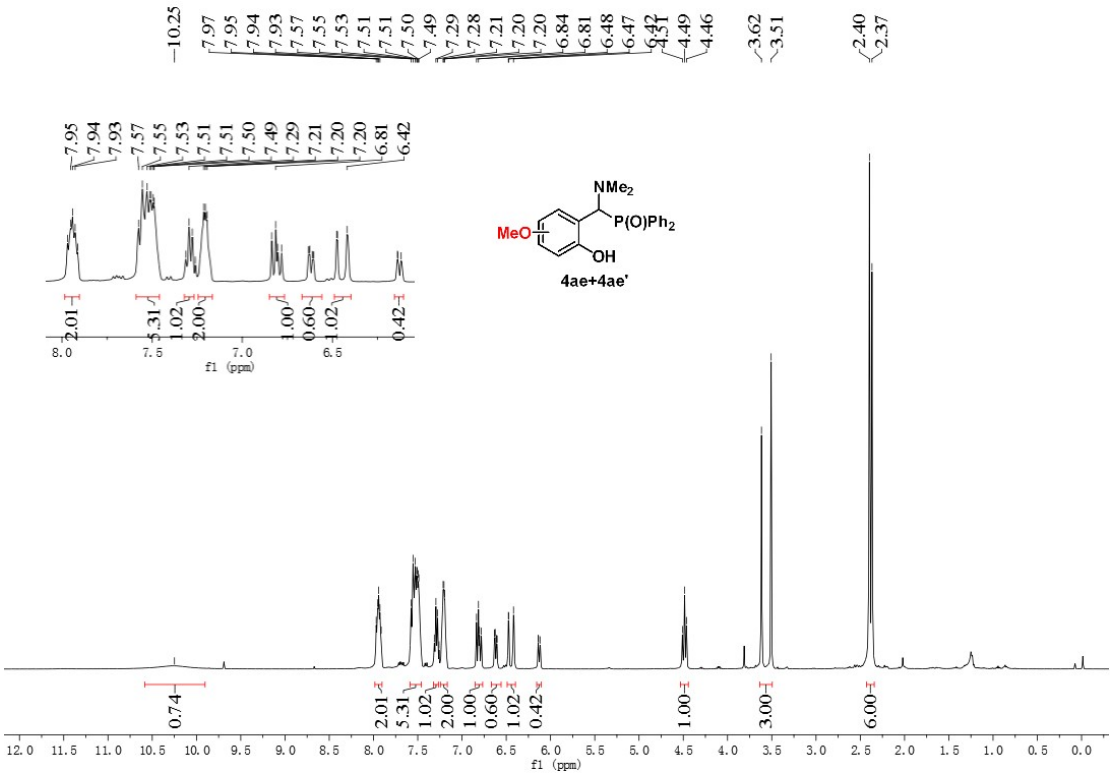
^{1}H NMR (400 MHz, $CDCl_3$)



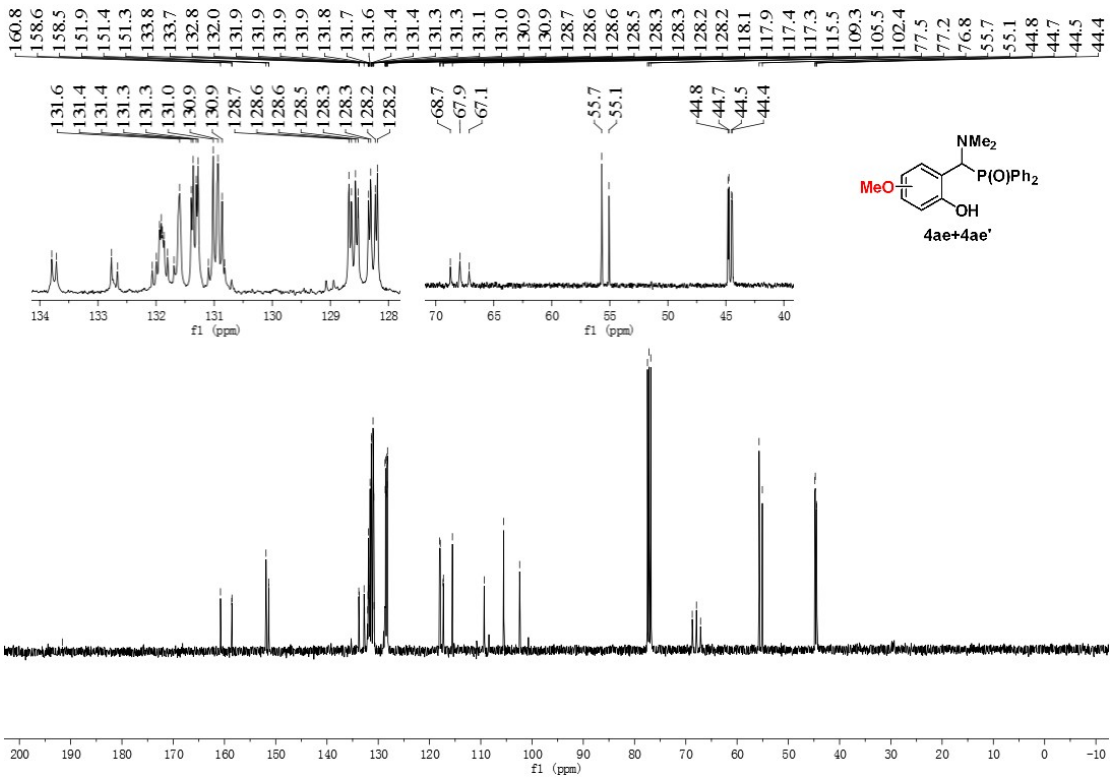
^{13}C NMR (101 MHz, $CDCl_3$)



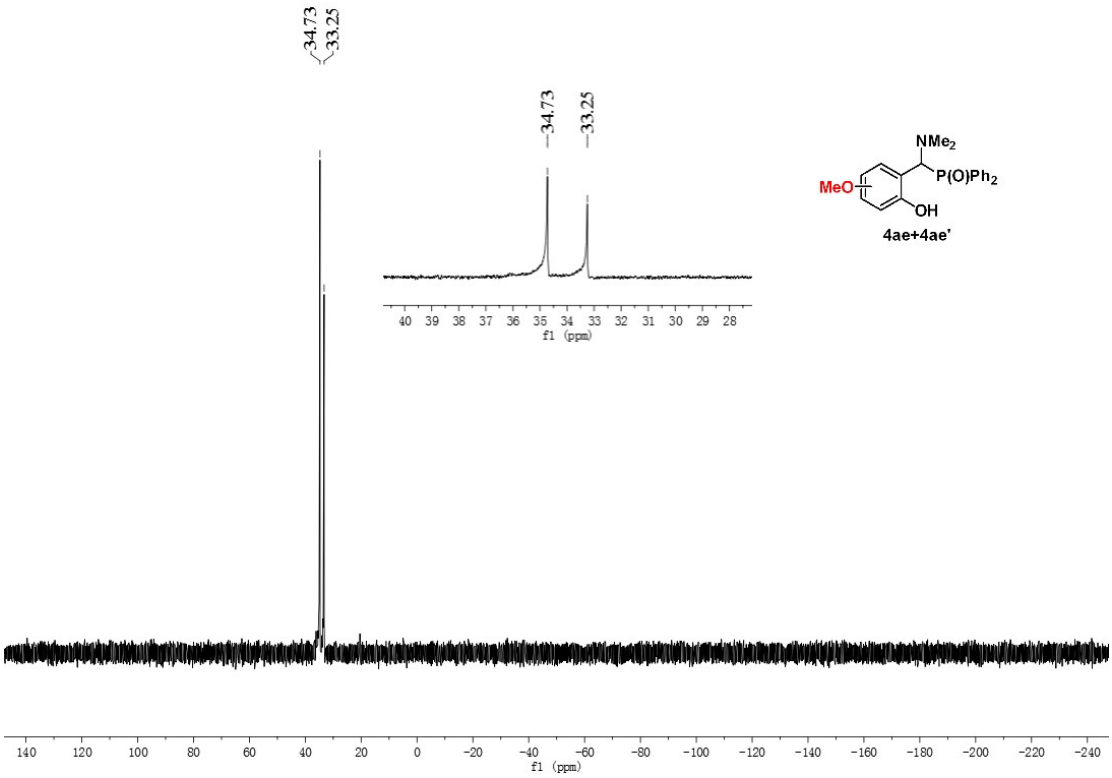
^{31}P NMR (162 MHz, $CDCl_3$)



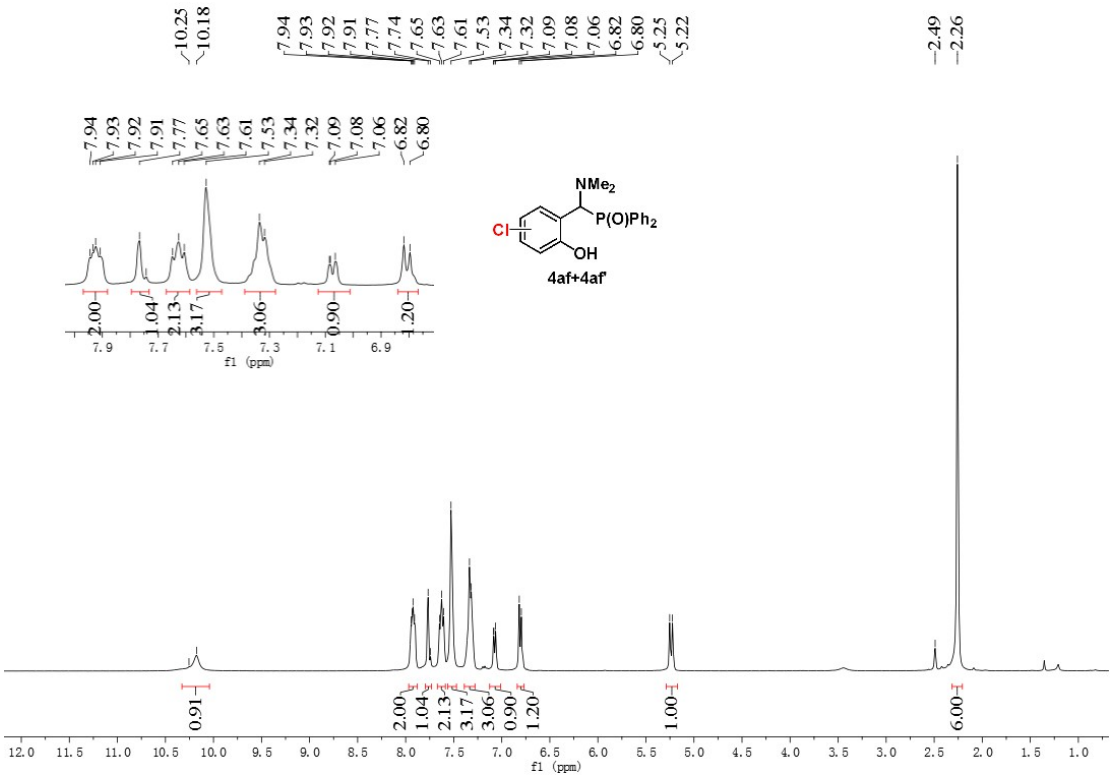
^{1}H NMR (400 MHz, $CDCl_3$)



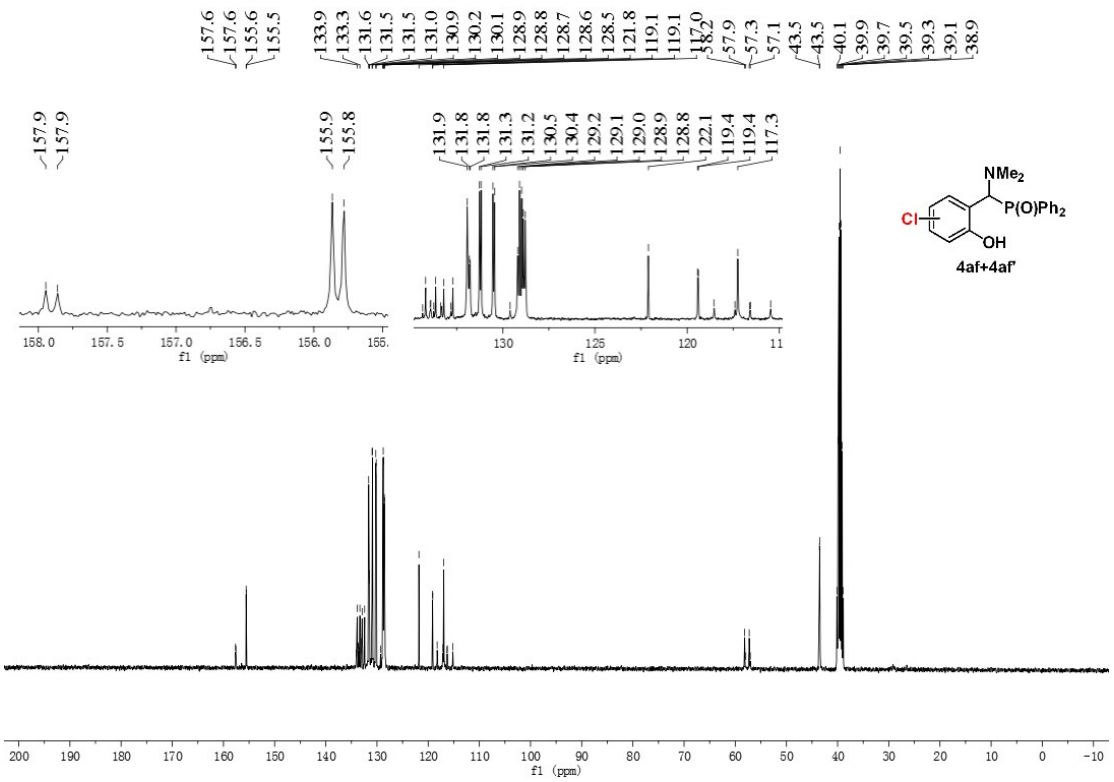
^{13}C NMR (101 MHz, $CDCl_3$)



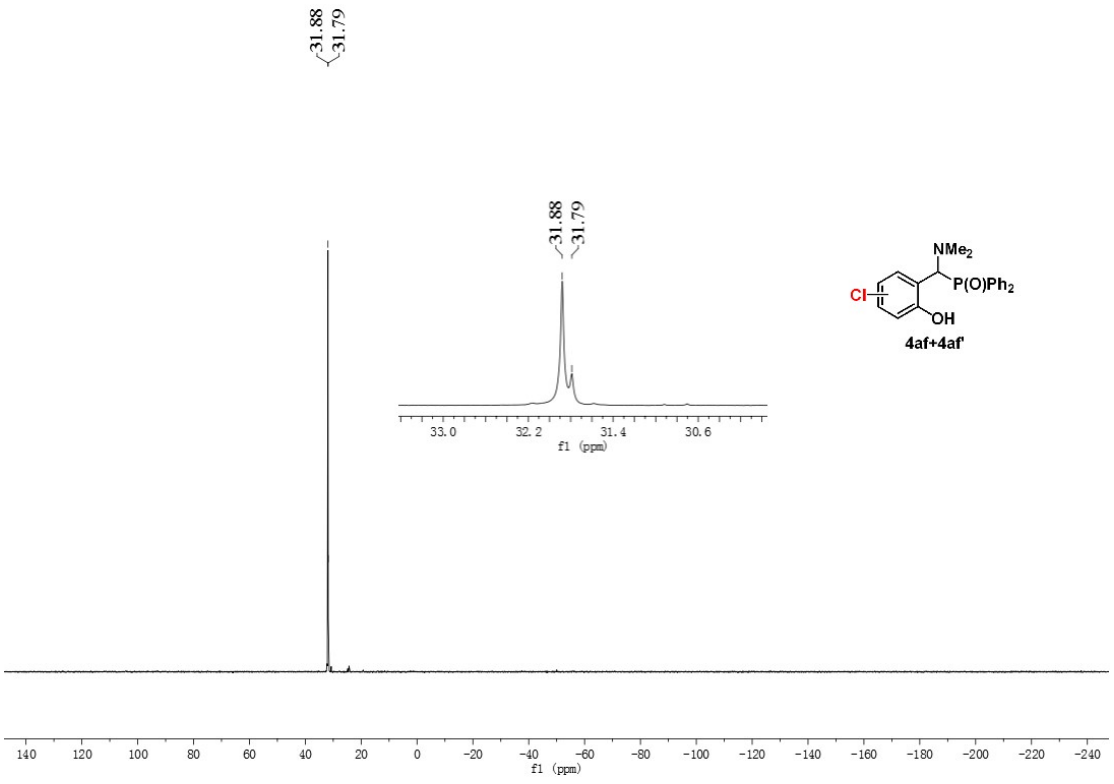
^{31}P NMR (162 MHz, $CDCl_3$)



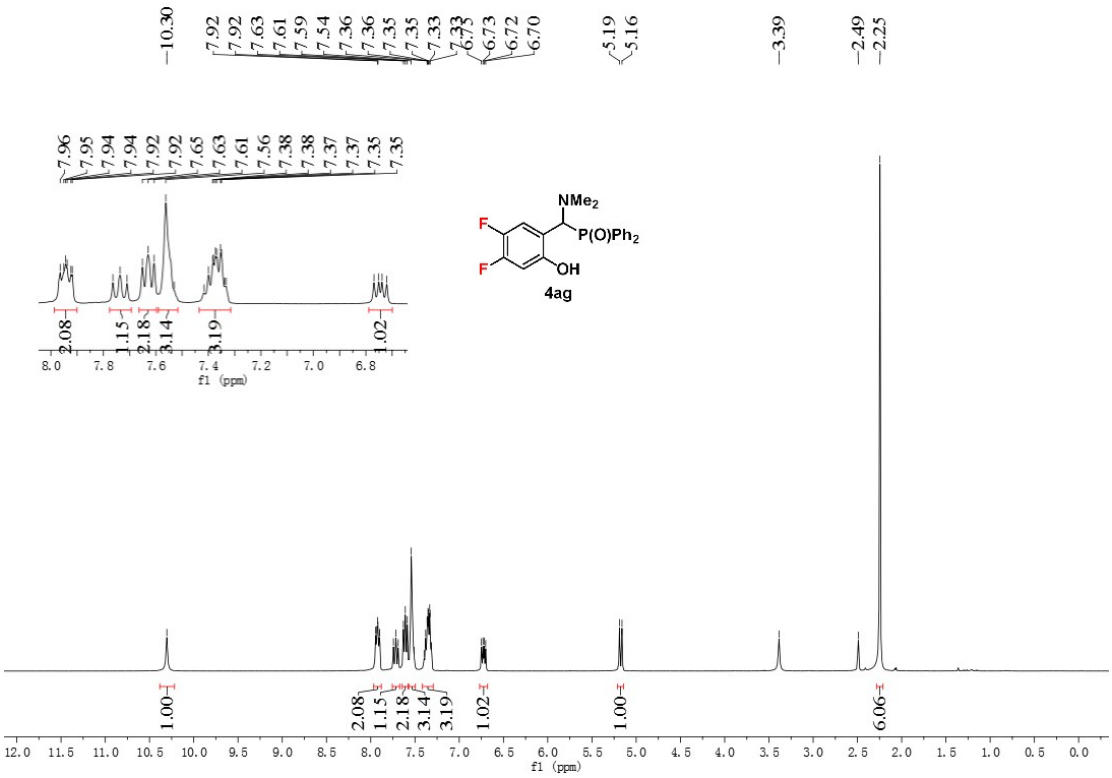
^{1}H NMR (400 MHz, DMSO-d_6)



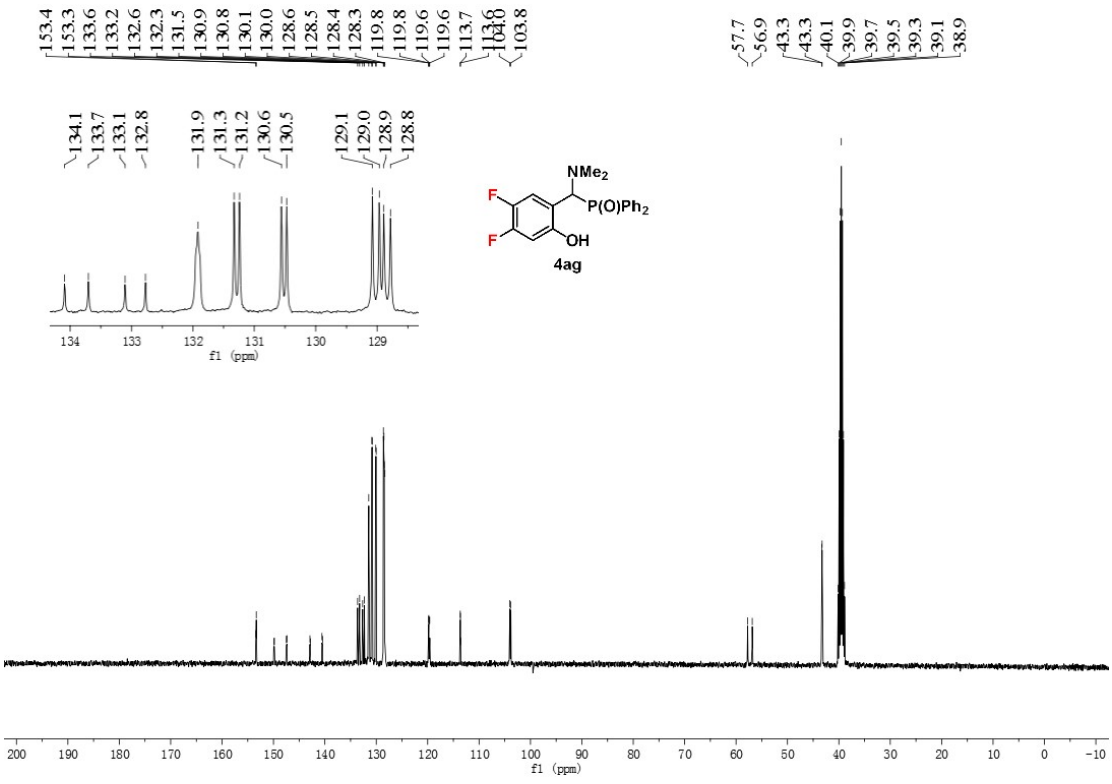
^{13}C NMR (101 MHz, DMSO-d_6)



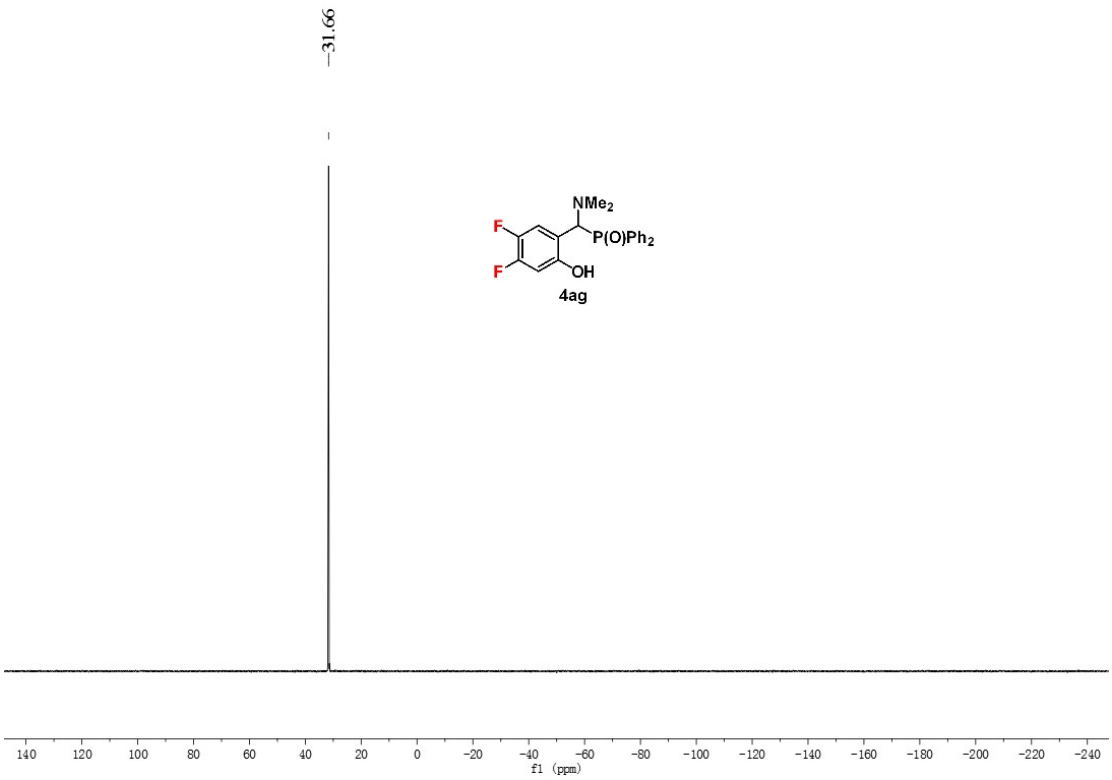
^{31}P NMR (162 MHz, DMSO-d_6)



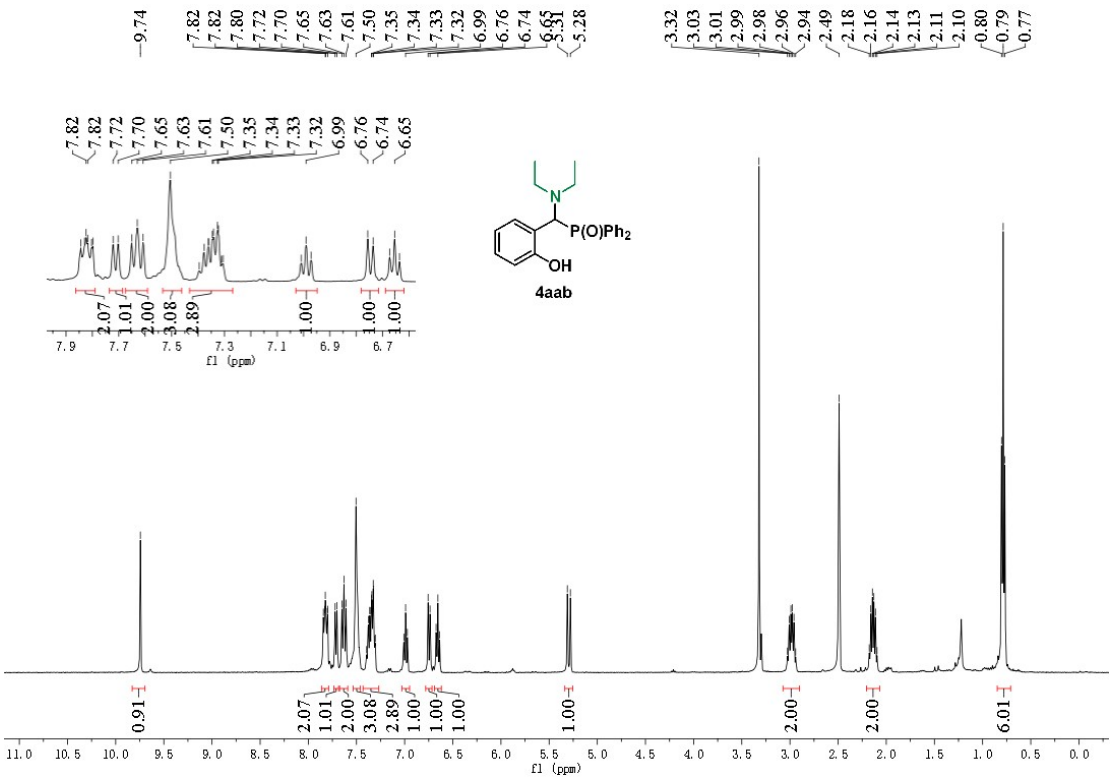
^{1}H NMR (400 MHz, DMSO-d_6)



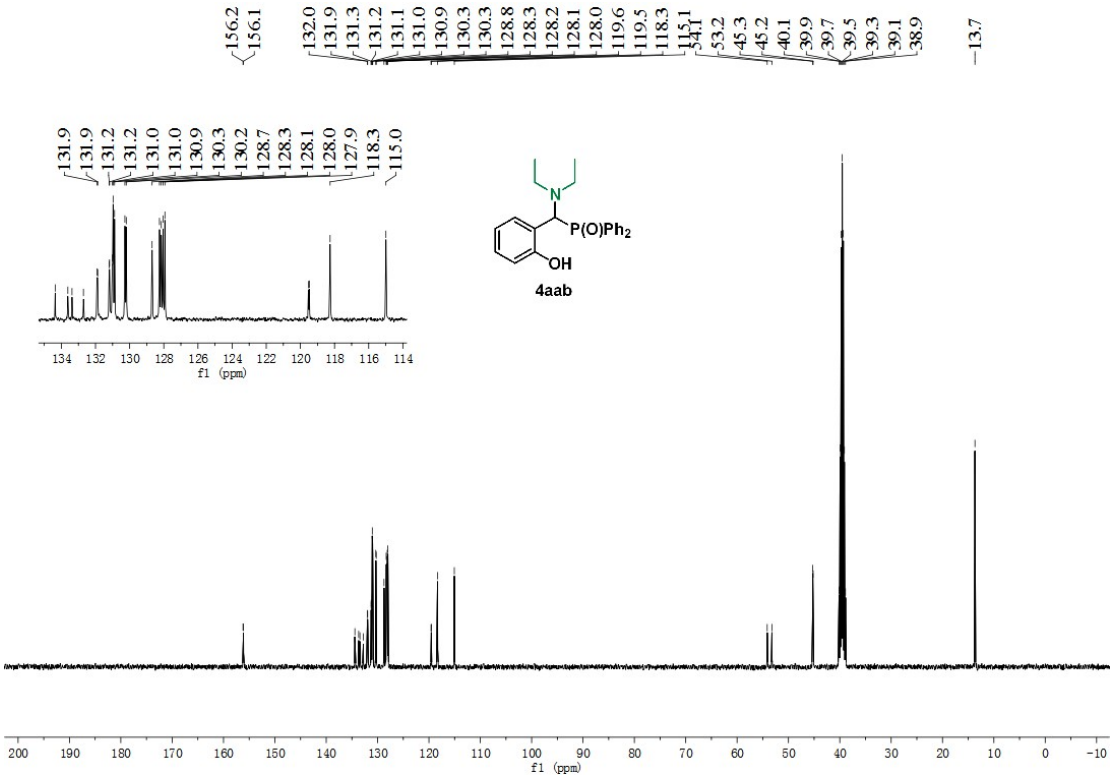
^{13}C NMR (101 MHz, DMSO-d_6)



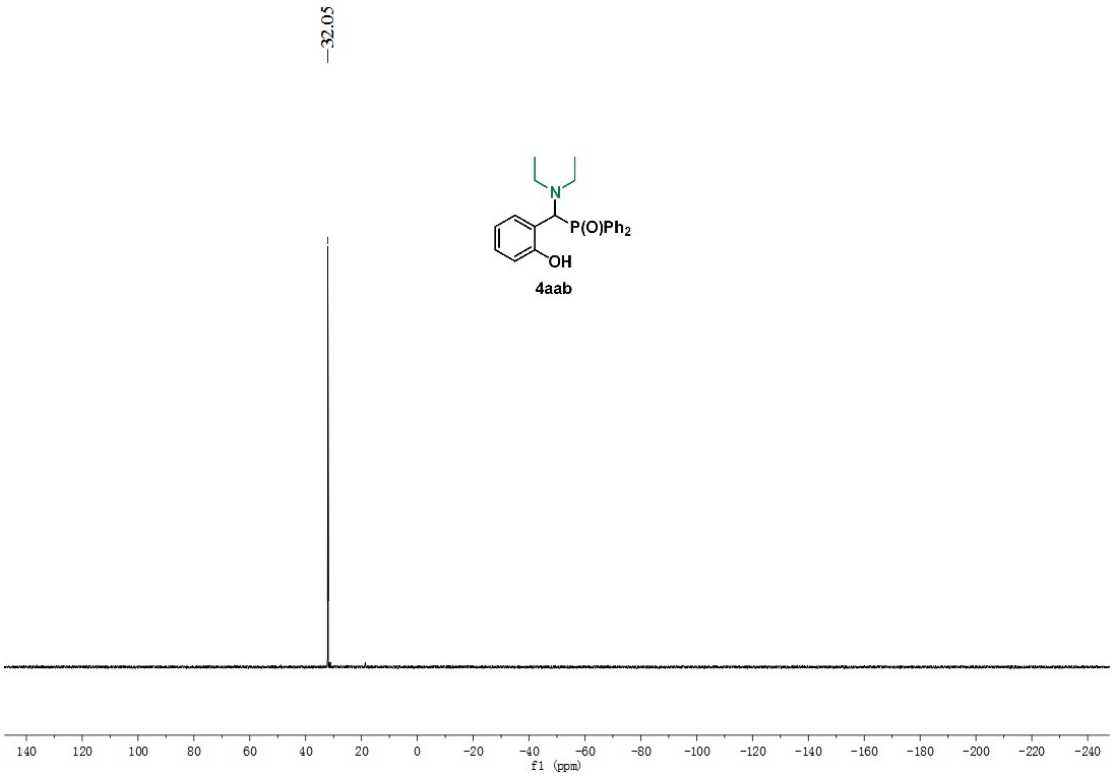
^{31}P NMR (162 MHz, DMSO-d_6)



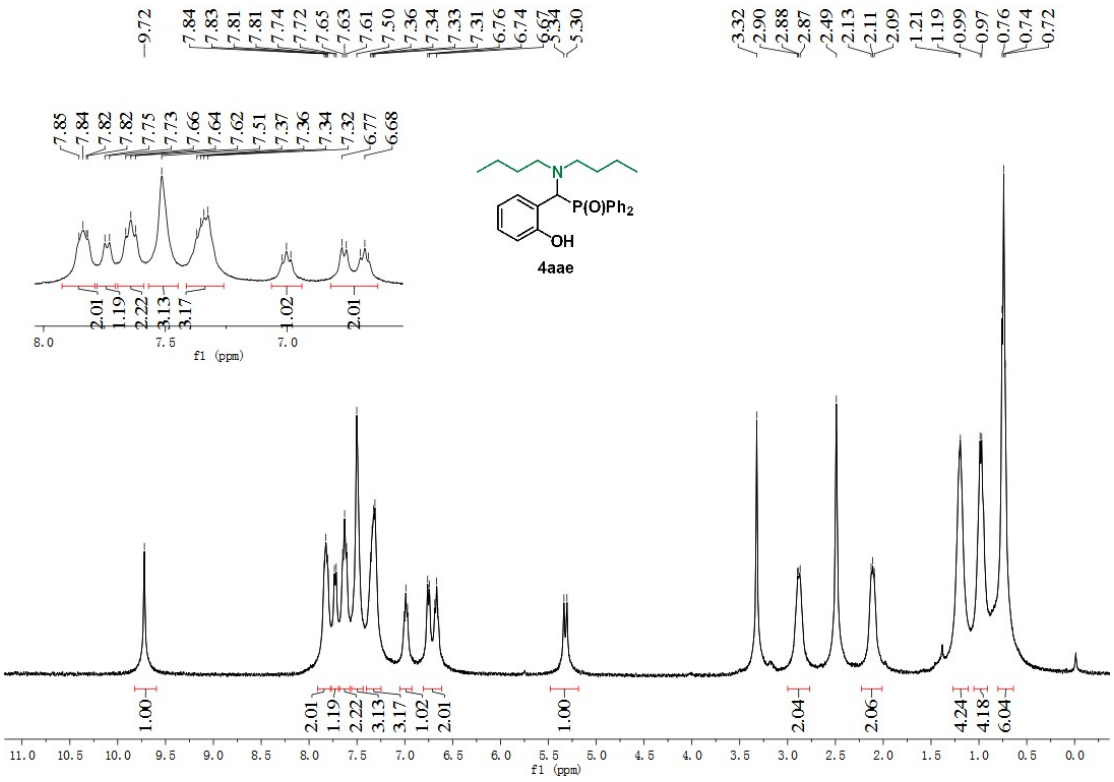
^{1}H NMR (400 MHz, DMSO-d_6)



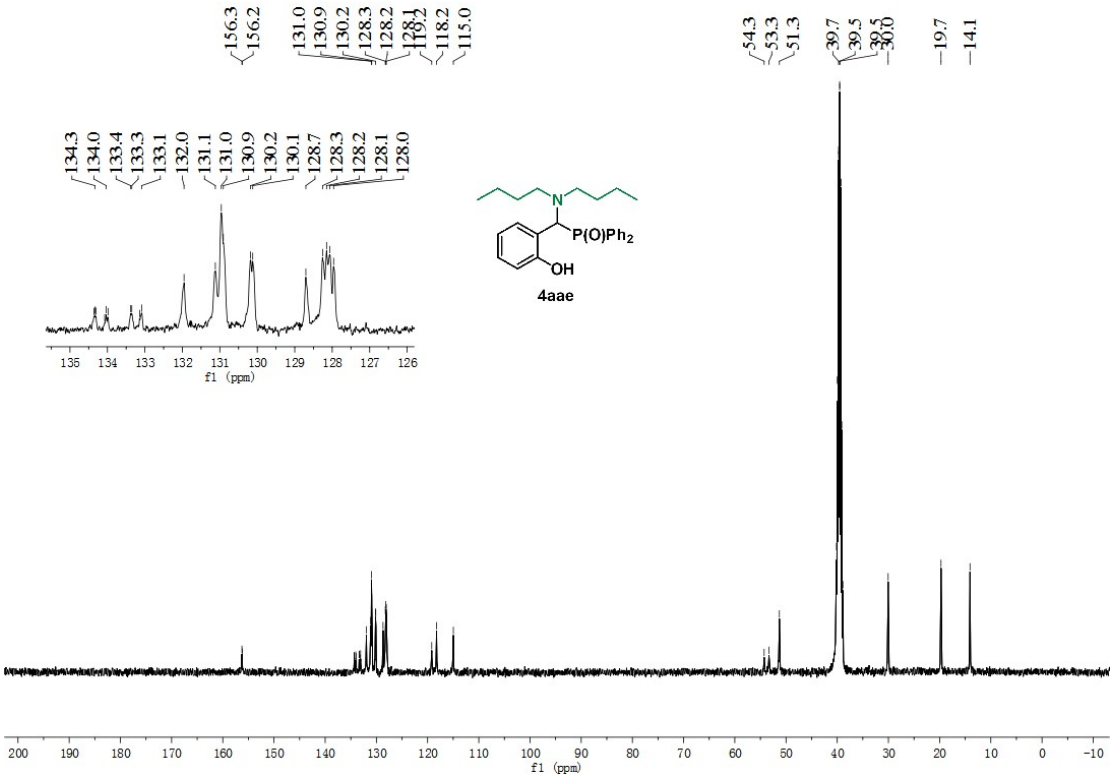
^{13}C NMR (101 MHz, DMSO-d_6)



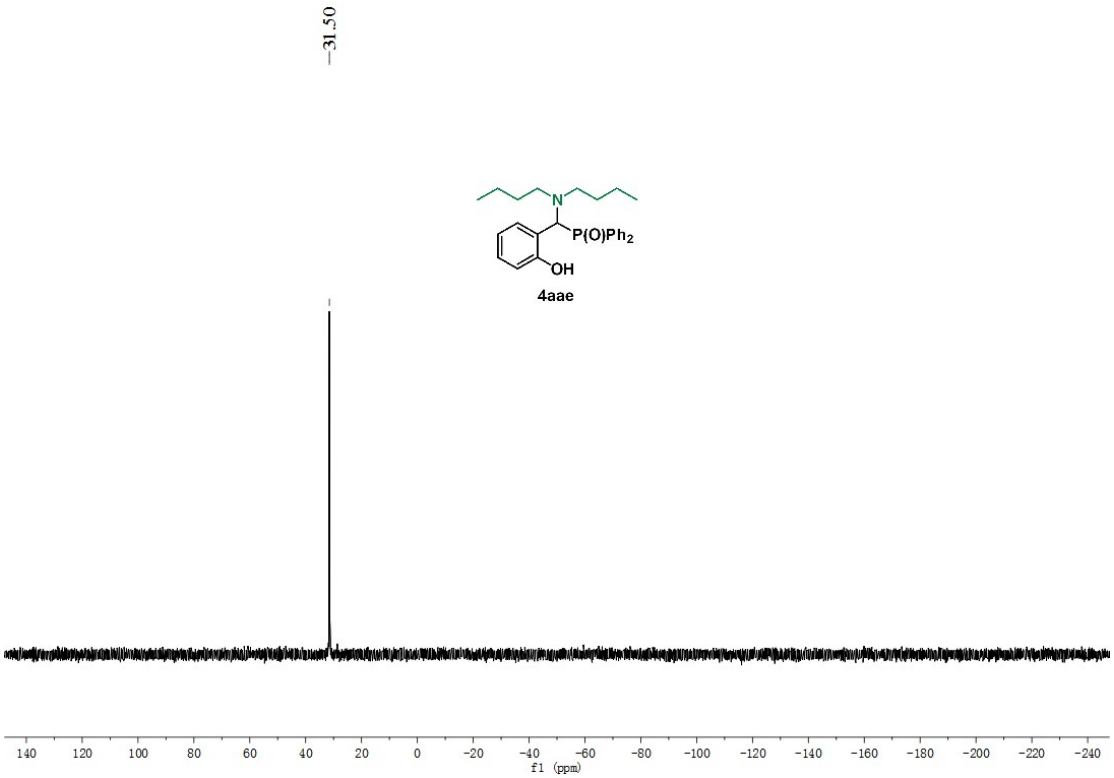
^{31}P NMR (162 MHz, DMSO-d_6)



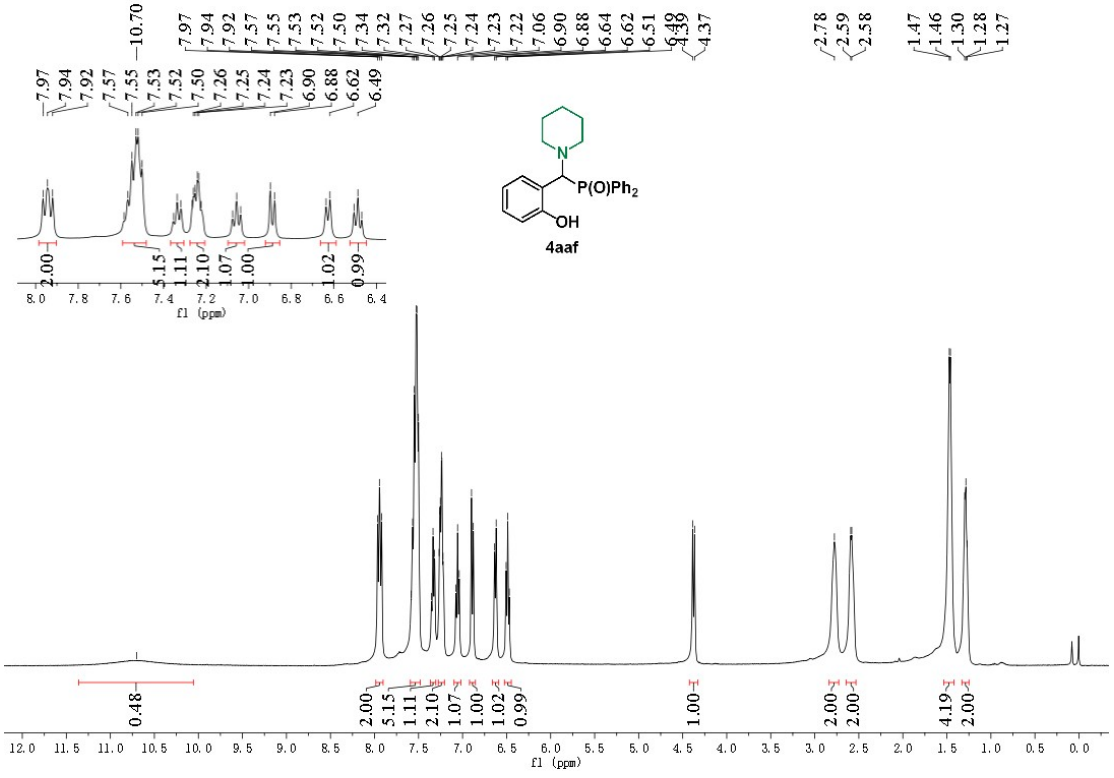
^{1}H NMR (400 MHz, DMSO-d_6)



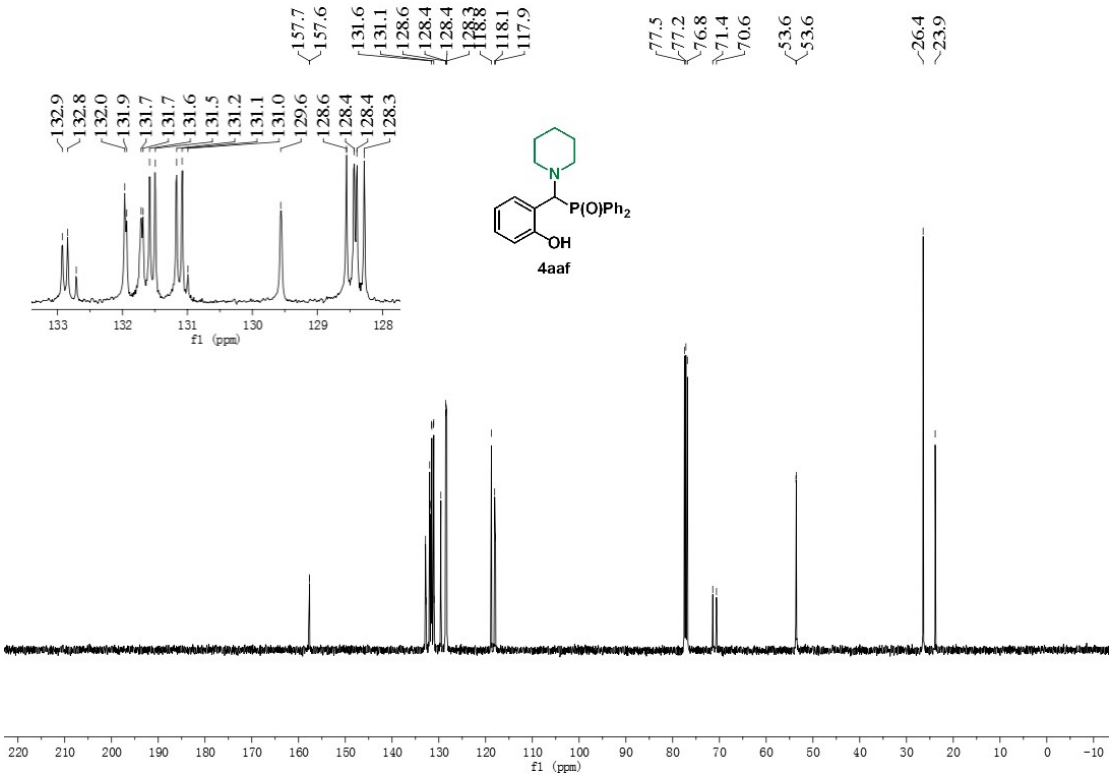
^{13}C NMR (101 MHz, DMSO-d_6)



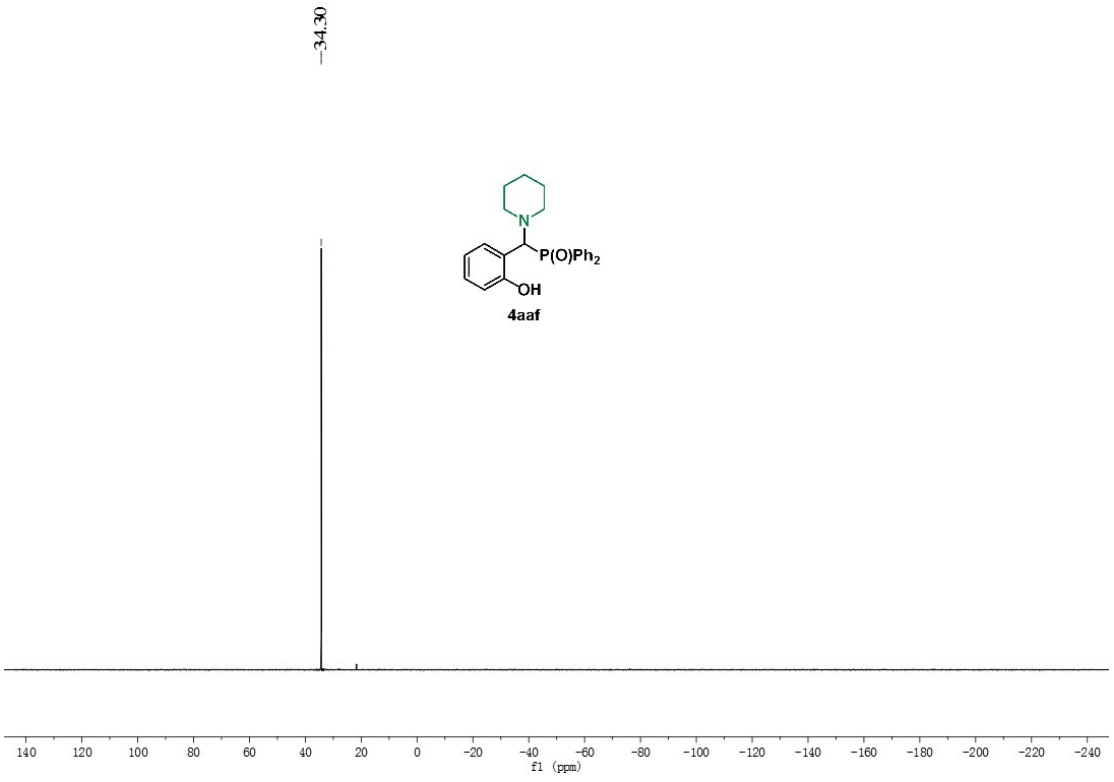
^{31}P NMR (162 MHz, DMSO-d_6)



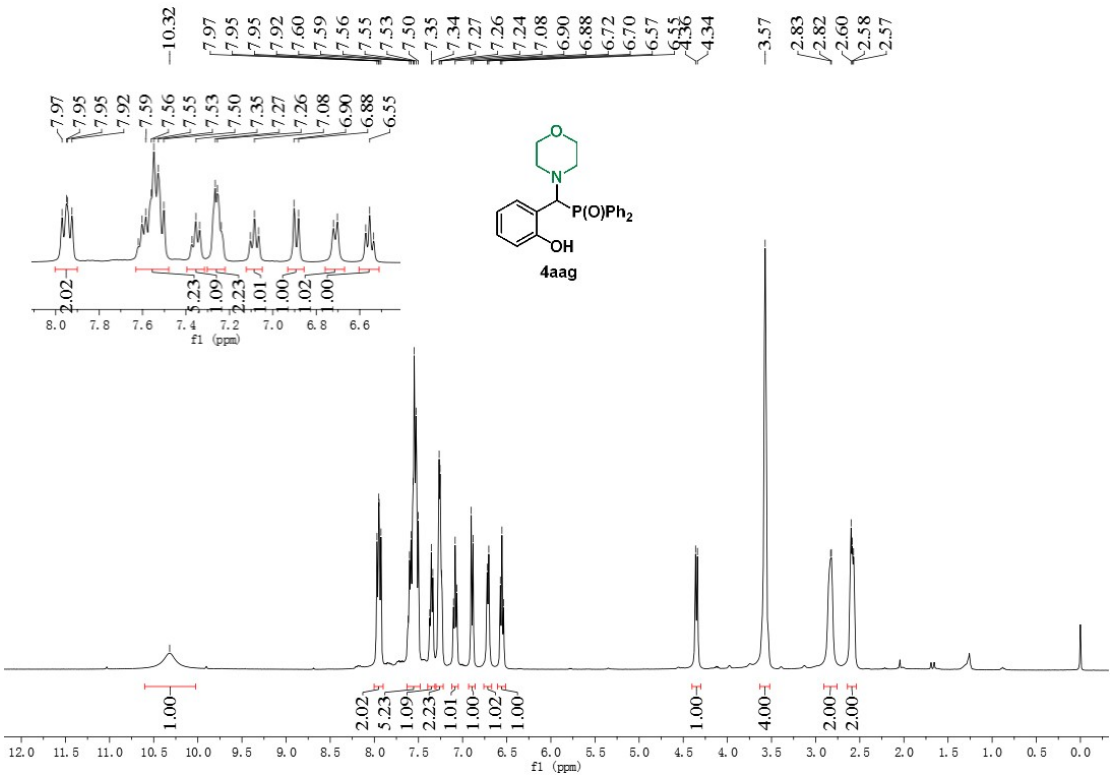
^{1}H NMR (400 MHz, $CDCl_3$)



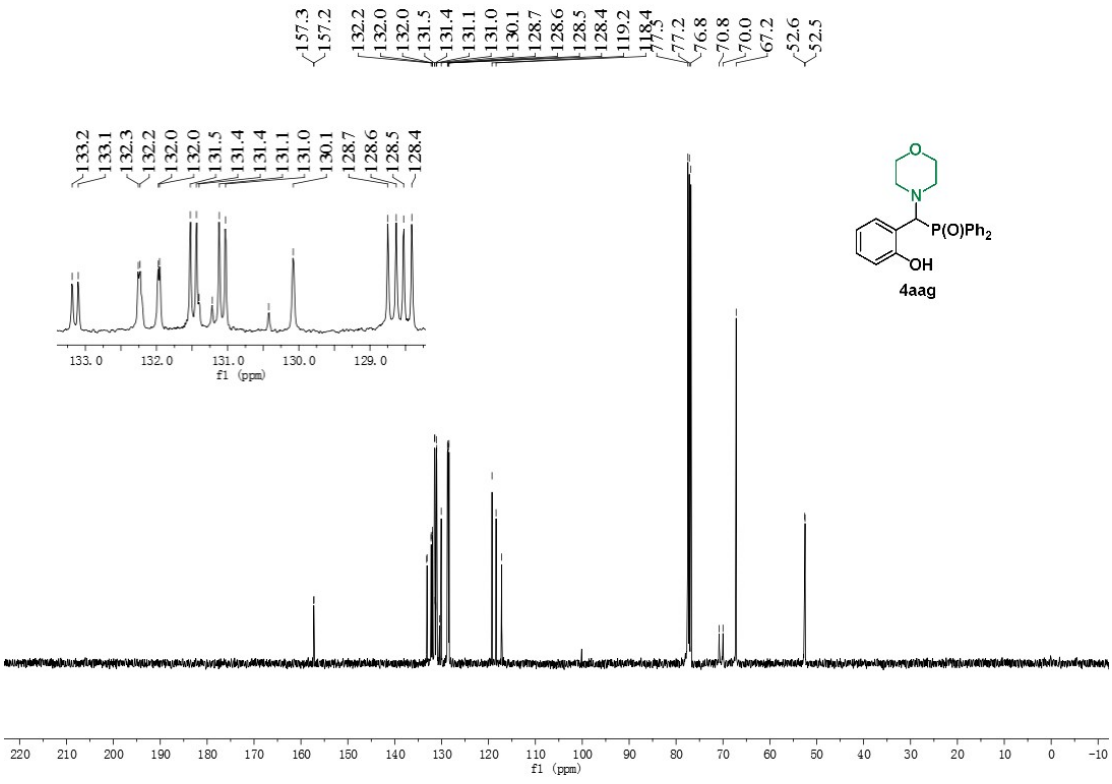
^{13}C NMR (101 MHz, $CDCl_3$)



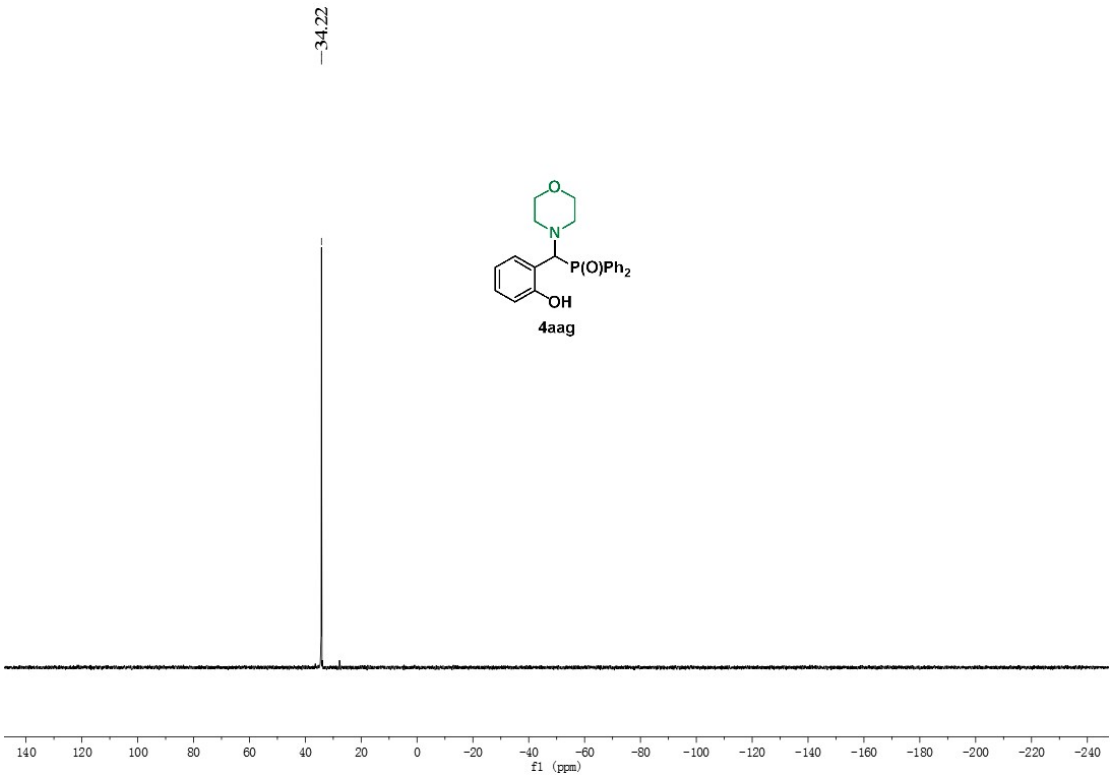
^{31}P NMR (162 MHz, $CDCl_3$)



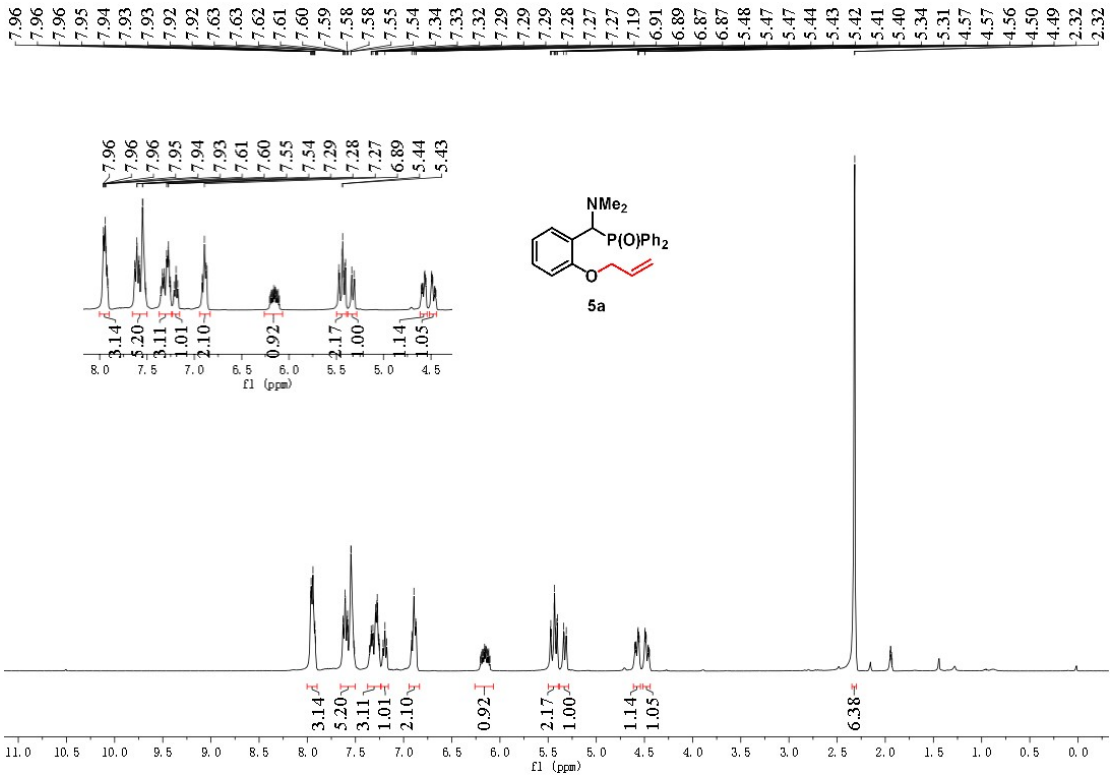
^{1}H NMR (400 MHz, $CDCl_3$)



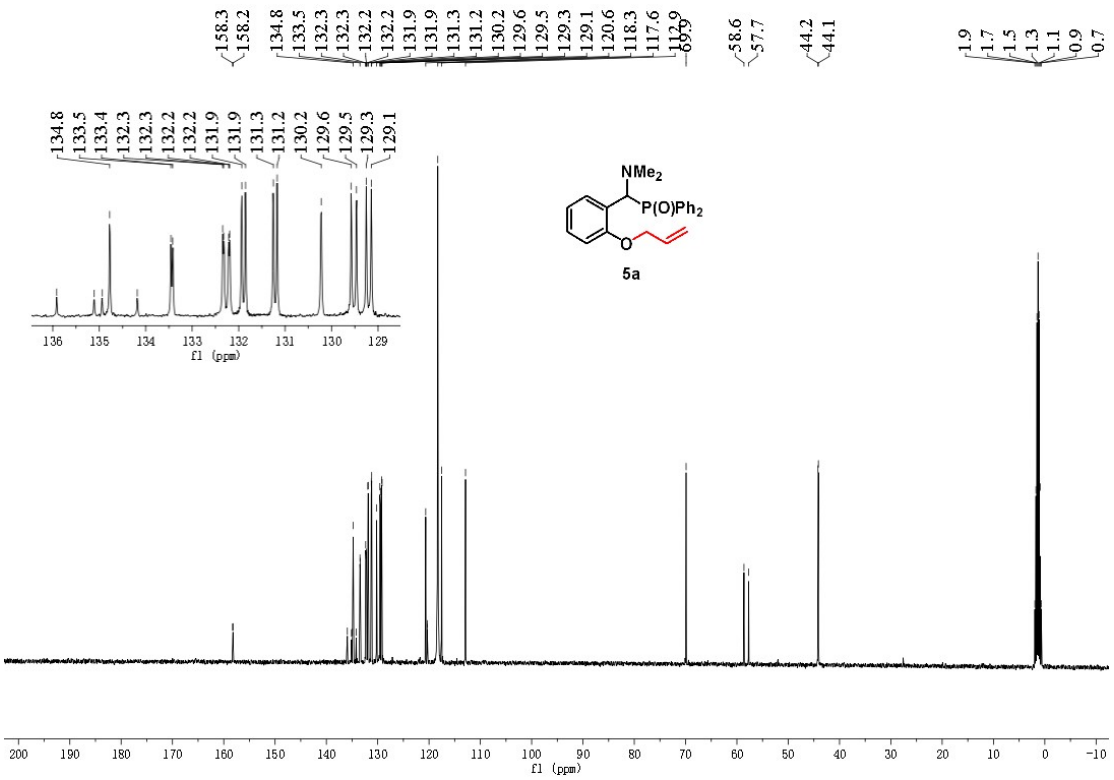
^{13}C NMR (101 MHz, $CDCl_3$)



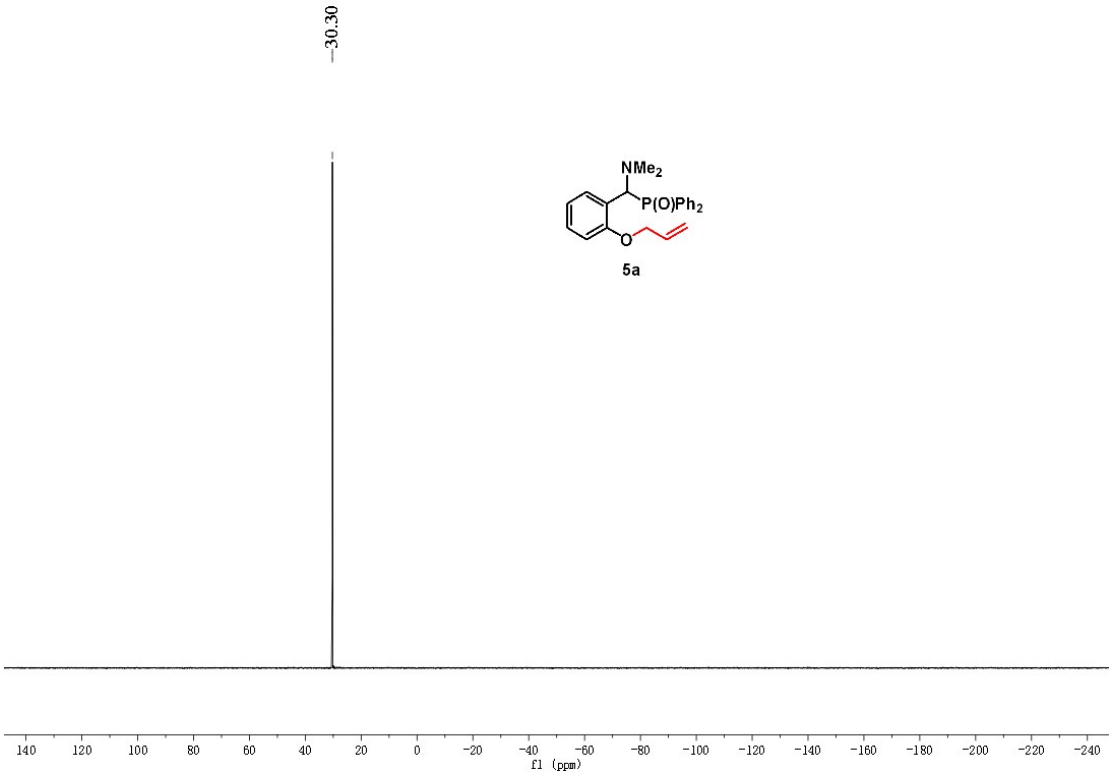
^{31}P NMR (162 MHz, $CDCl_3$)



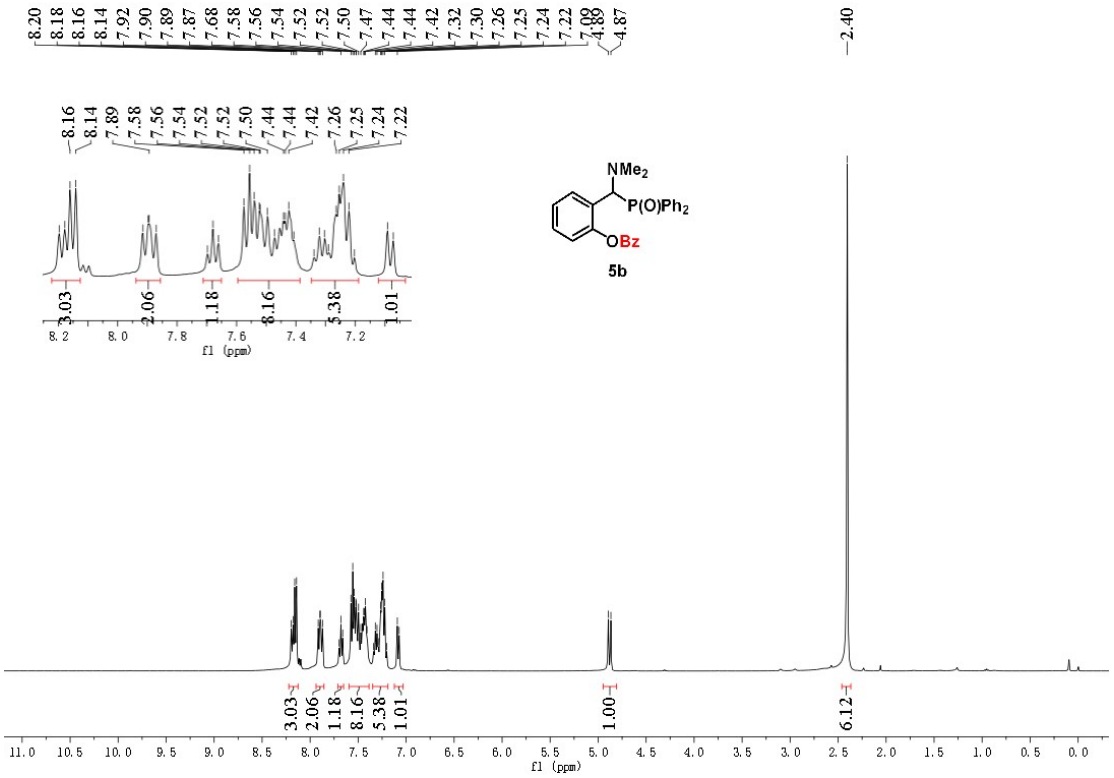
^{1}H NMR (400 MHz, CD_3CN)



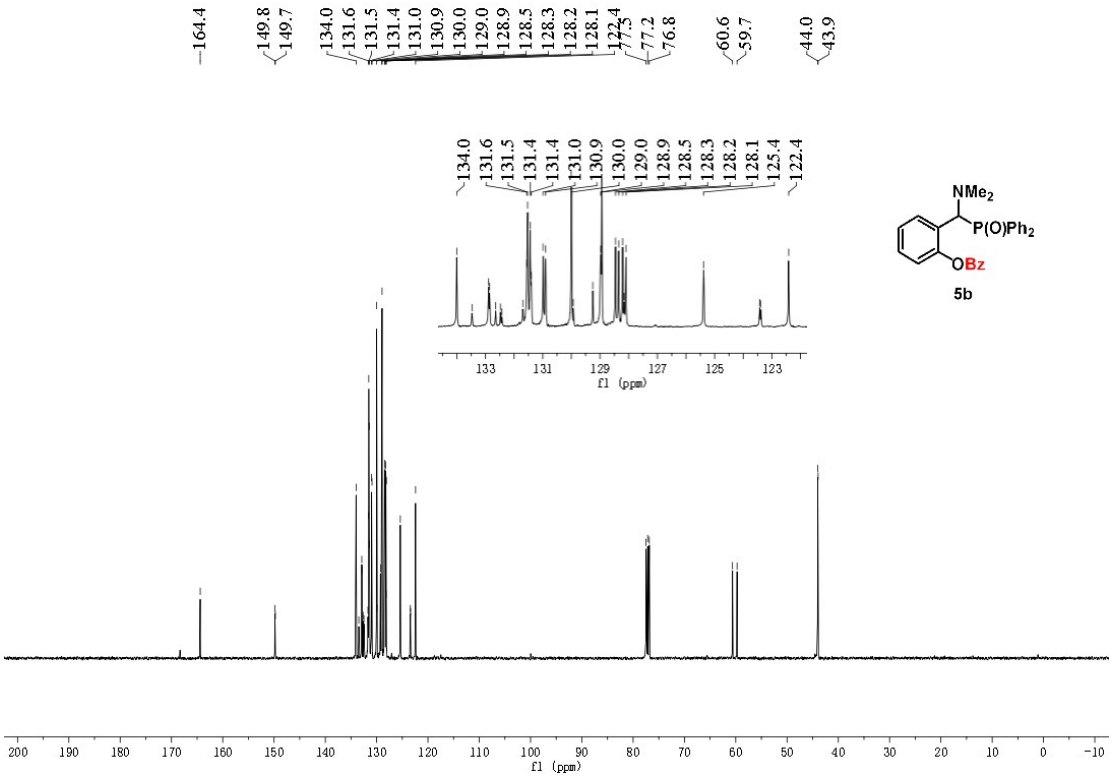
^{13}C NMR (101 MHz, CD_3CN)



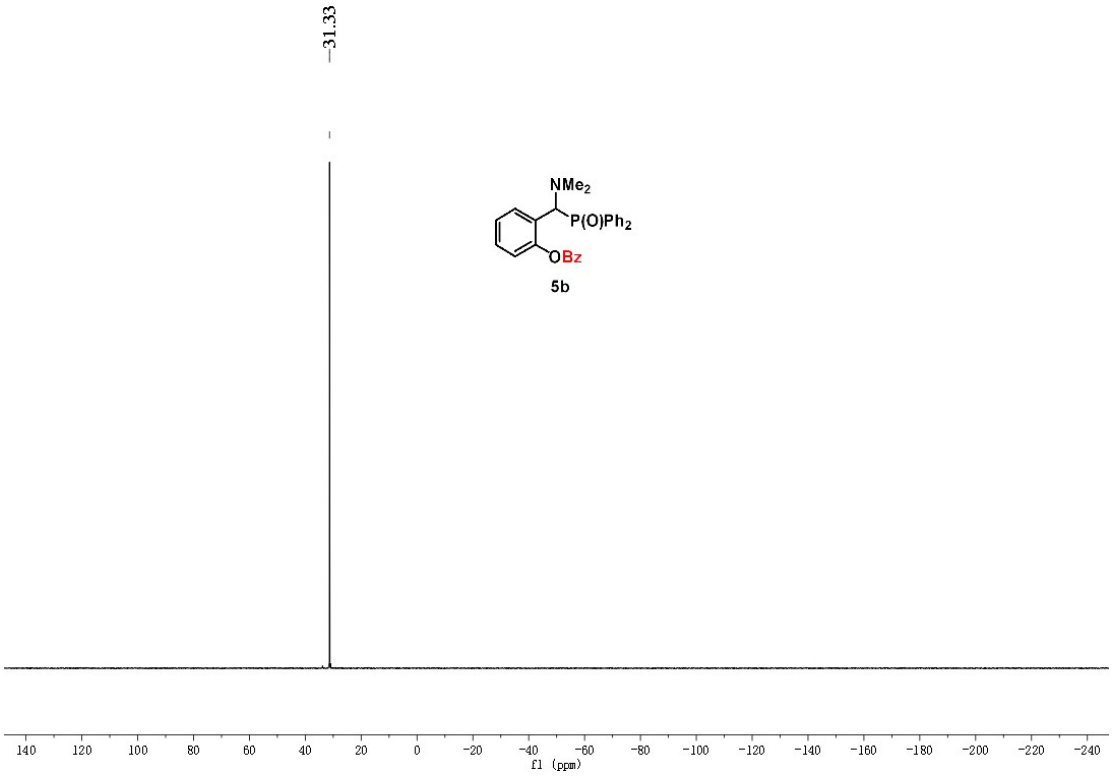
^{31}P NMR (162 MHz, CD_3CN)



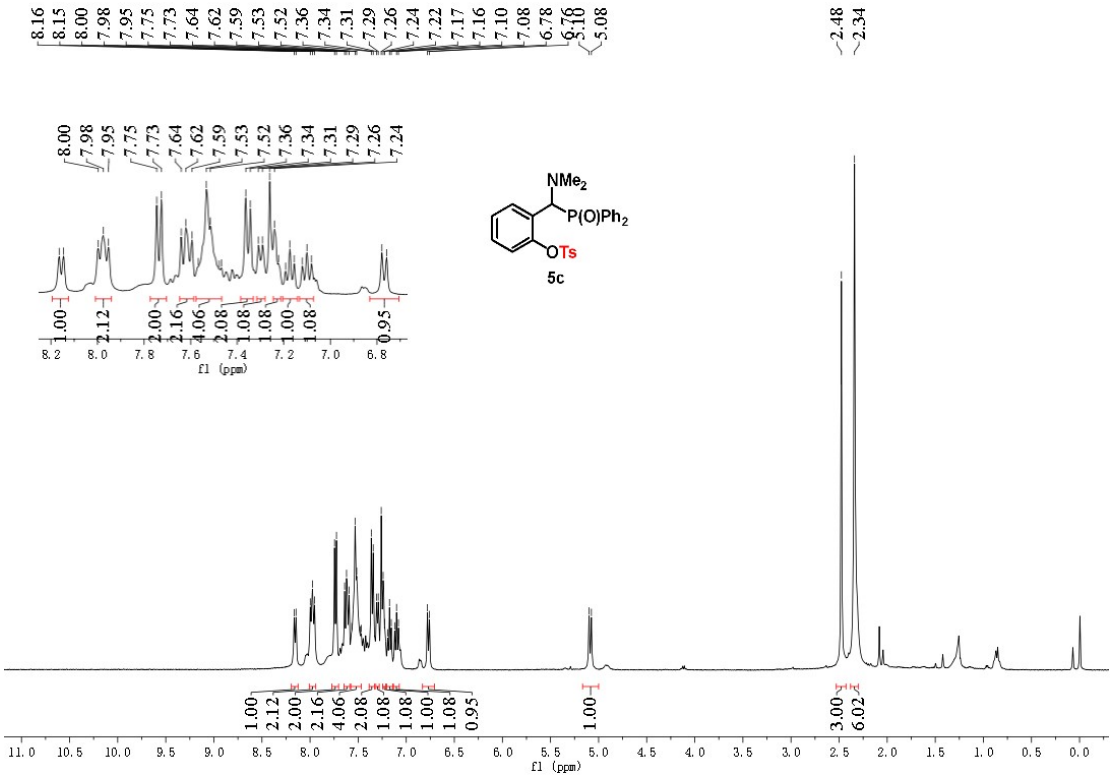
^{1}H NMR (400 MHz, $CDCl_3$)



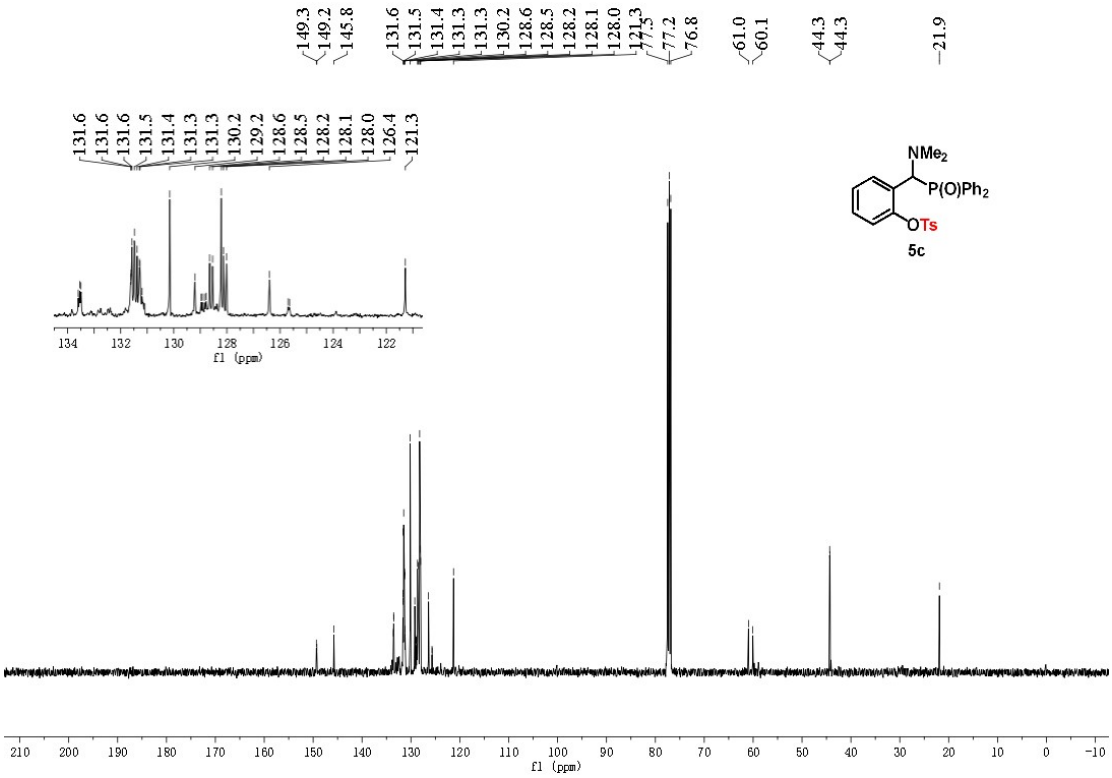
^{13}C NMR (101 MHz, $CDCl_3$)



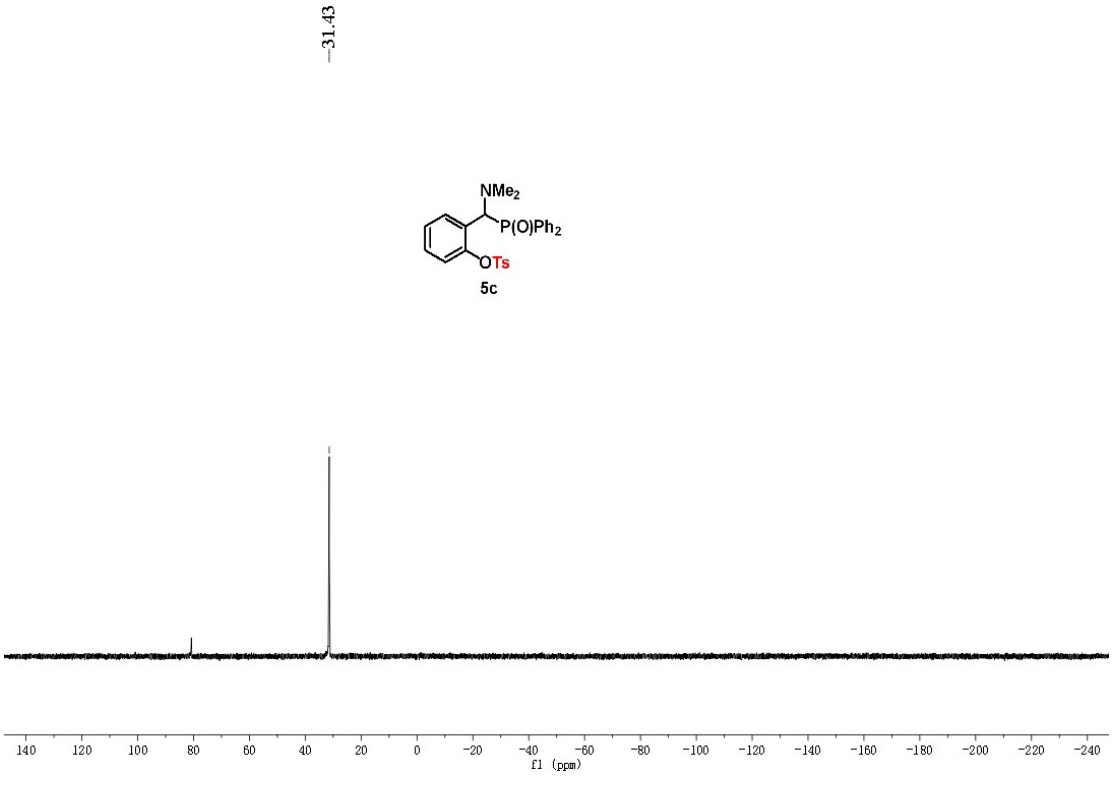
^{31}P NMR (162 MHz, $CDCl_3$)



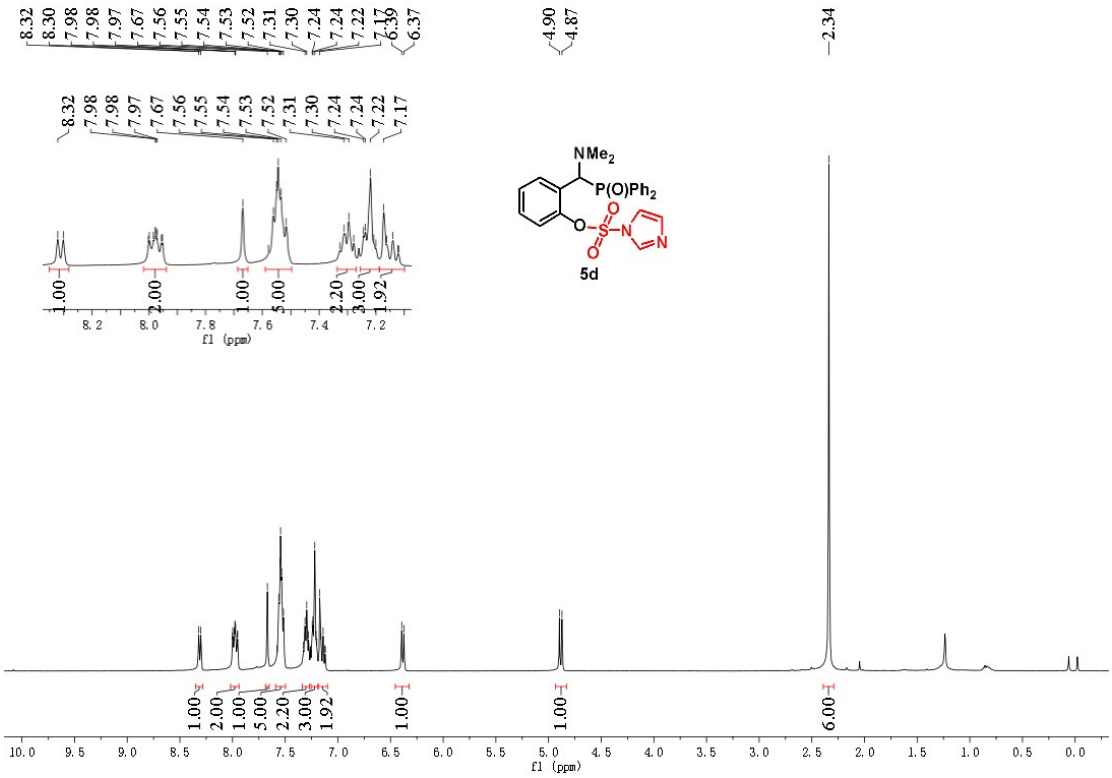
^{1}H NMR (400 MHz, $CDCl_3$)



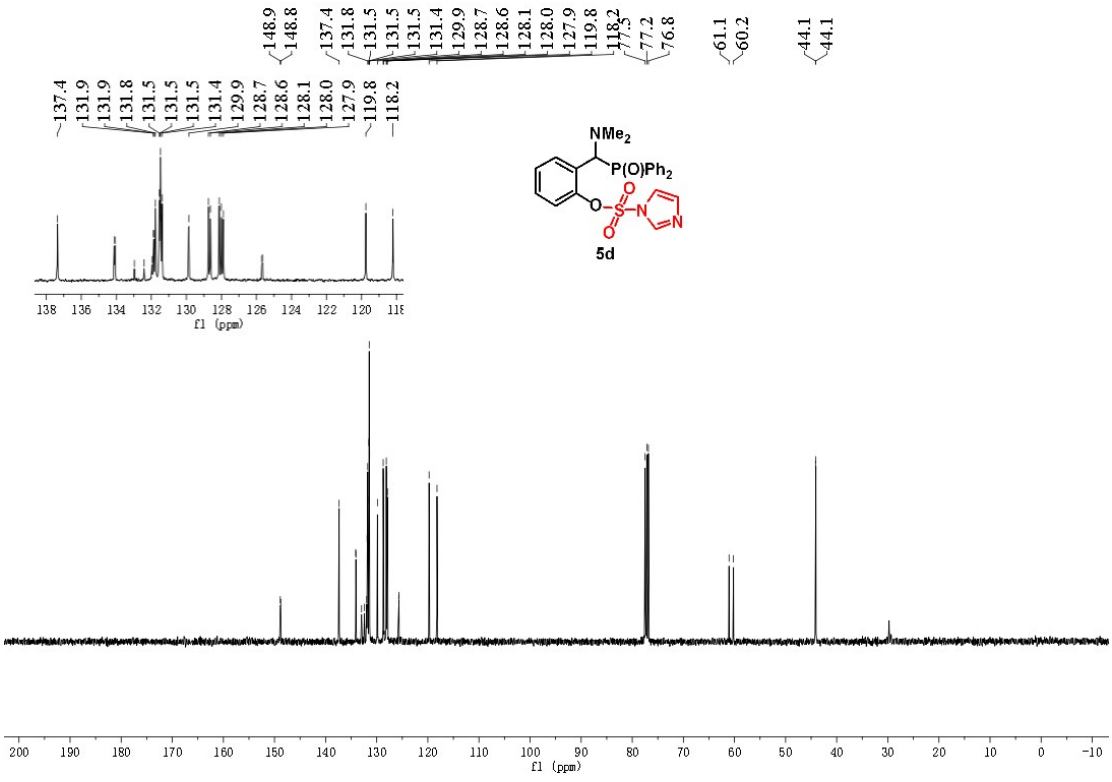
^{13}C NMR (101 MHz, $CDCl_3$)



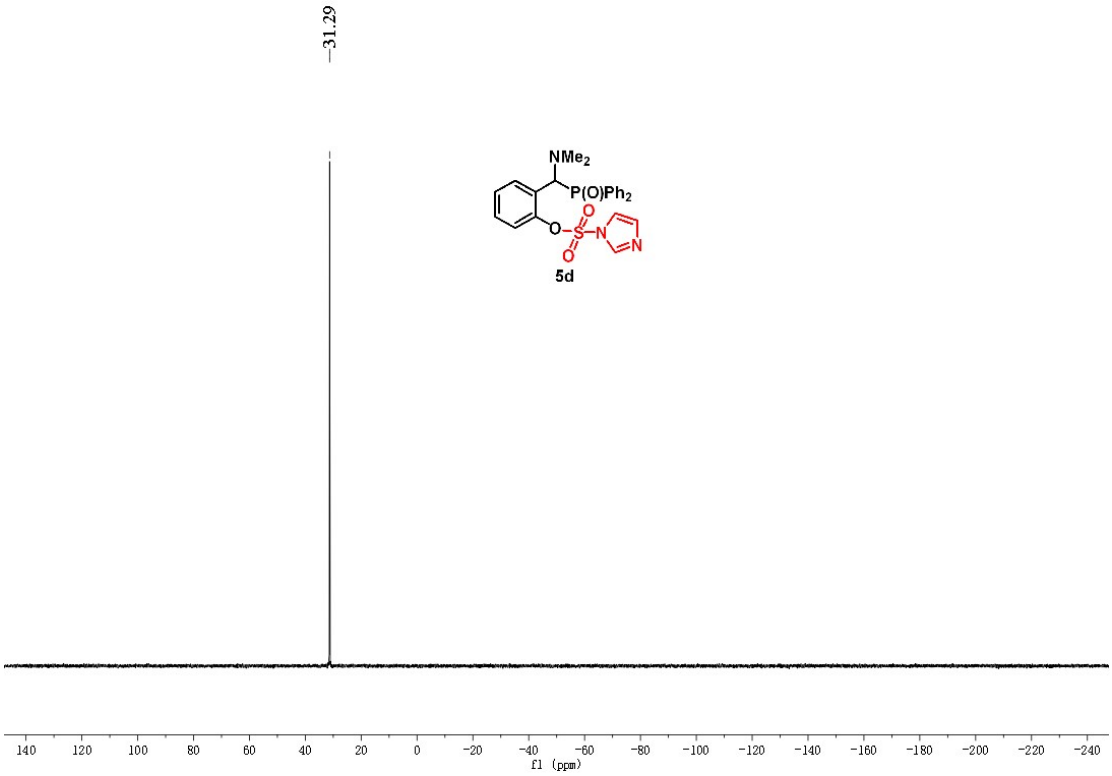
^{31}P NMR (162 MHz, $CDCl_3$)



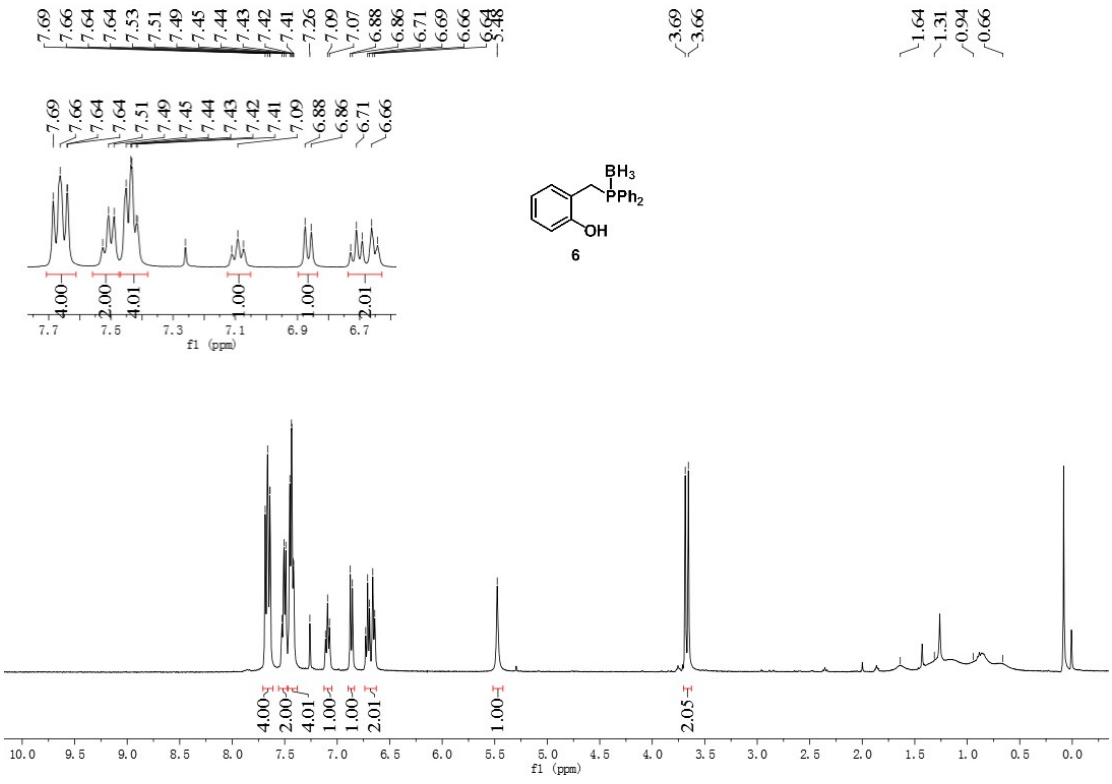
^{1}H NMR (400 MHz, $CDCl_3$)



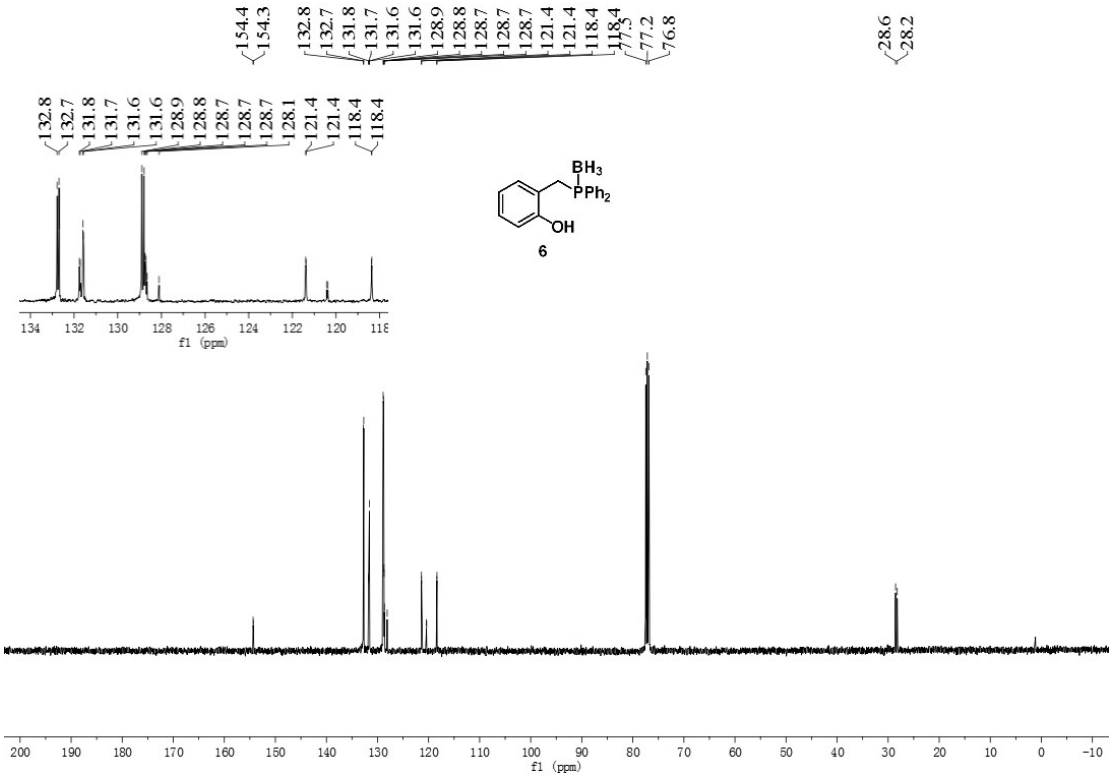
^{13}C NMR (101 MHz, $CDCl_3$)



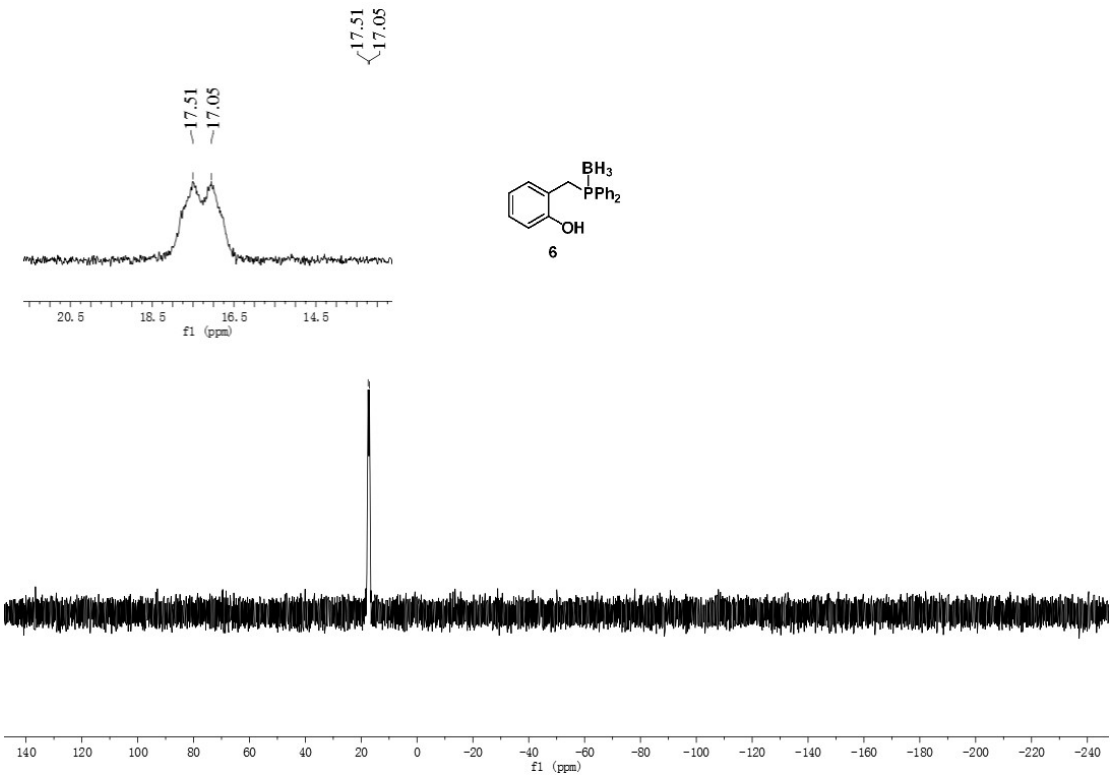
^{31}P NMR (162 MHz, $CDCl_3$)



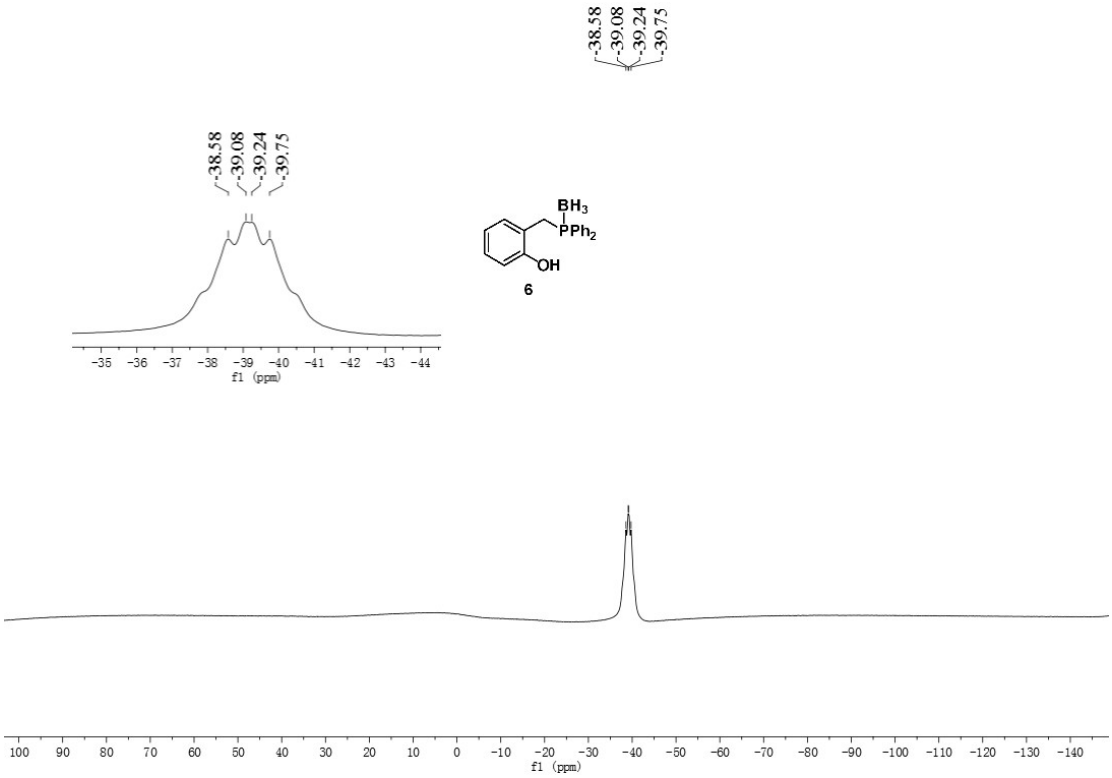
^{1}H NMR (400 MHz, $CDCl_3$)



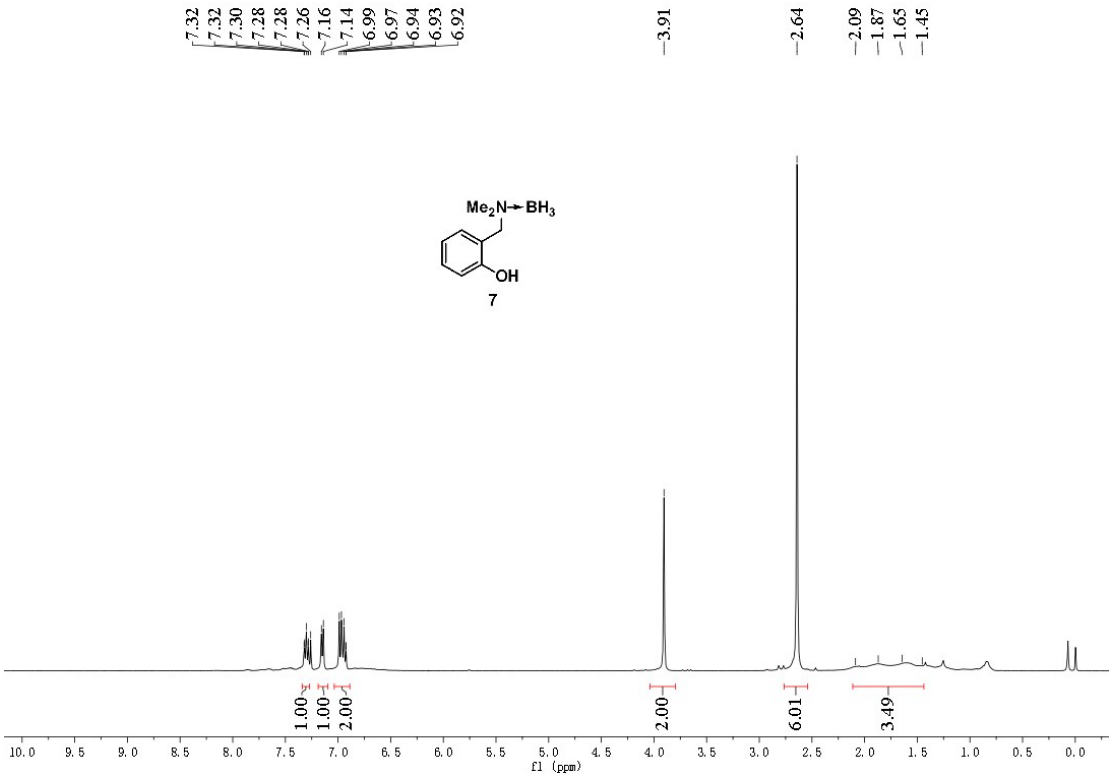
^{13}C NMR (101 MHz, $CDCl_3$)



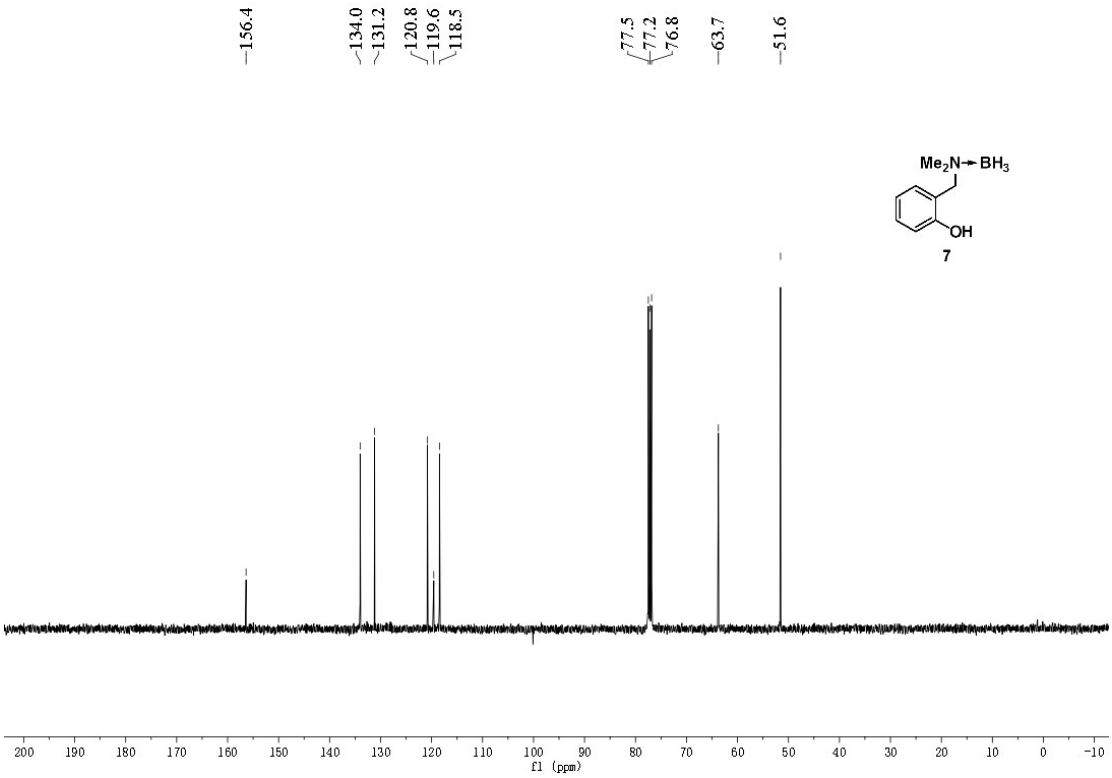
^{31}P NMR (162 MHz, $CDCl_3$)



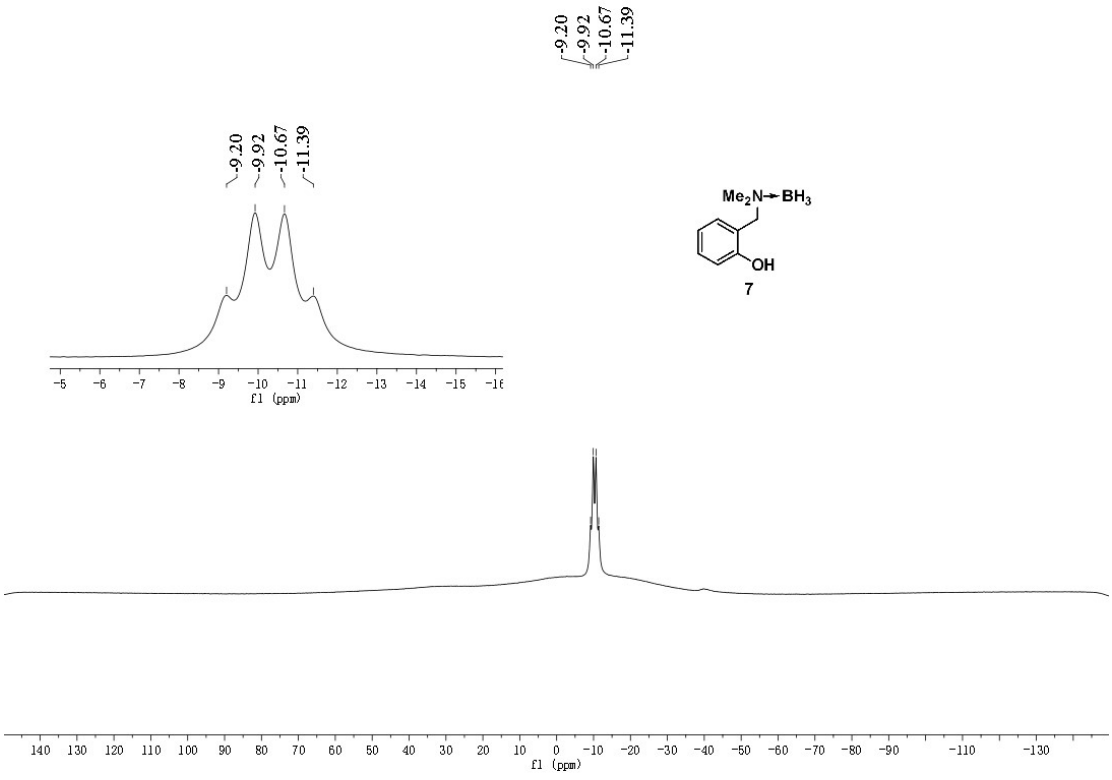
^{11}B NMR (128 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{11}B NMR (128 MHz, $CDCl_3$)