Supporting Information

The Effectiveness and Mechanism of Ene(amido) Group in Activating Iron for Catalytic Asymmetric Transfer Hydrogenation of Ketones

Qingquan Xue[⊥], *Rongliang Wu*[⊥], *Di Wang, Meifang Zhu*, Weiwei Zuo**

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, P. R. China.

*E-mail: zhumf@dhu.edu.cn, zuoweiwei@dhu.edu.cn

1. Scheme for the syntheses of the new tridentate (*R, R*)-P-NH-NH_2 ligand

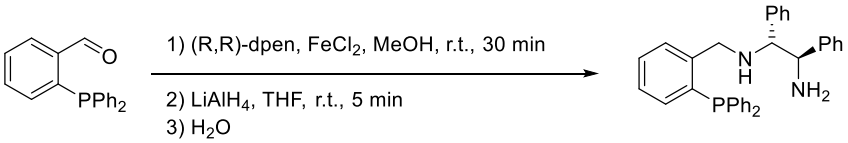


Figure S1 Scheme of synthesis of *N^1-[[2-(diphenylphosphino)phenyl]methyl]-1,2-diphenyl-(1R,2R)-1,2-ethanediamine*

2. The setup for the synthesis of *1-(diphenylphosphino)-propanone*.

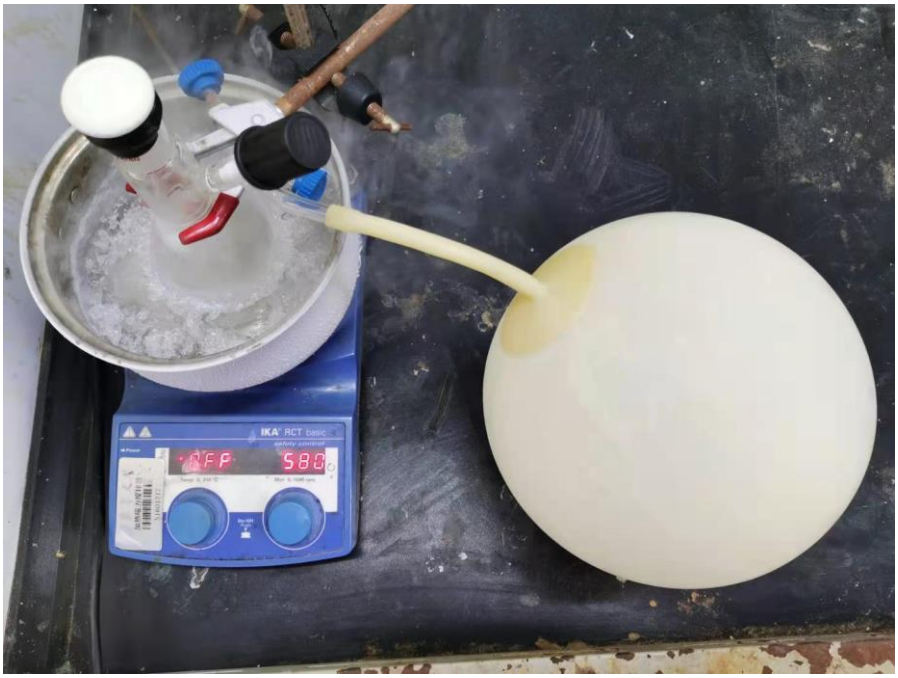


Figure S2 The setup for the synthesis of *1-(diphenylphosphino)-propanone.*

3. The FTIR spectra of 1b and 2a

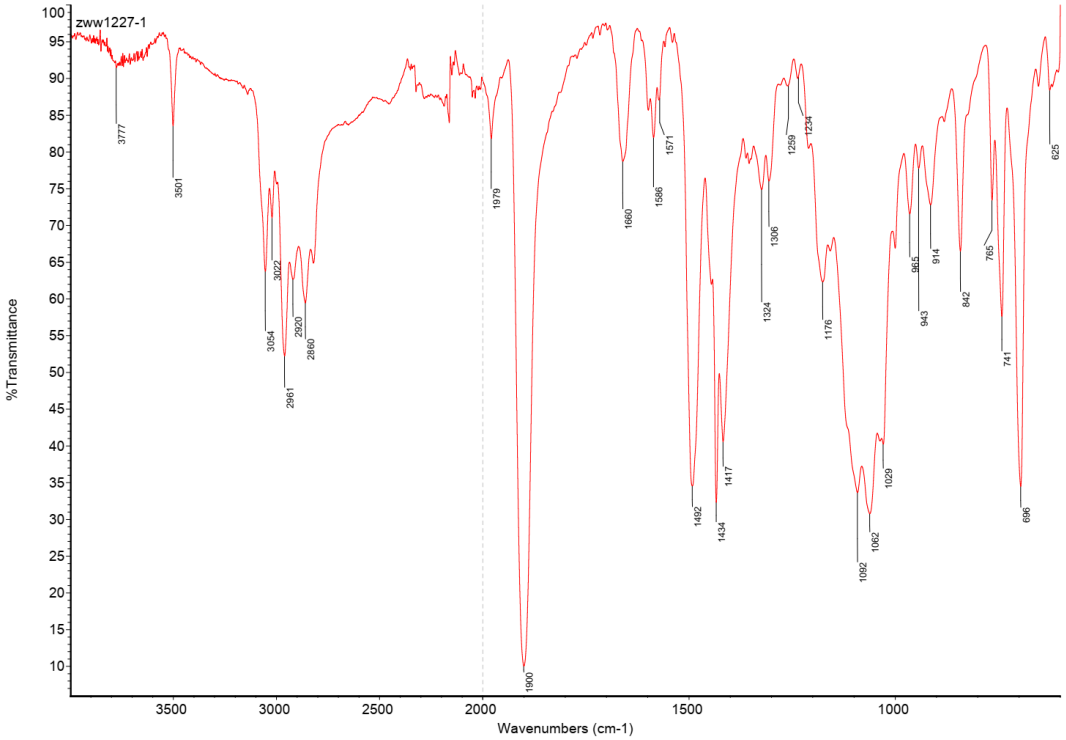


Figure S3 The FTIR spectrum of **1b.**

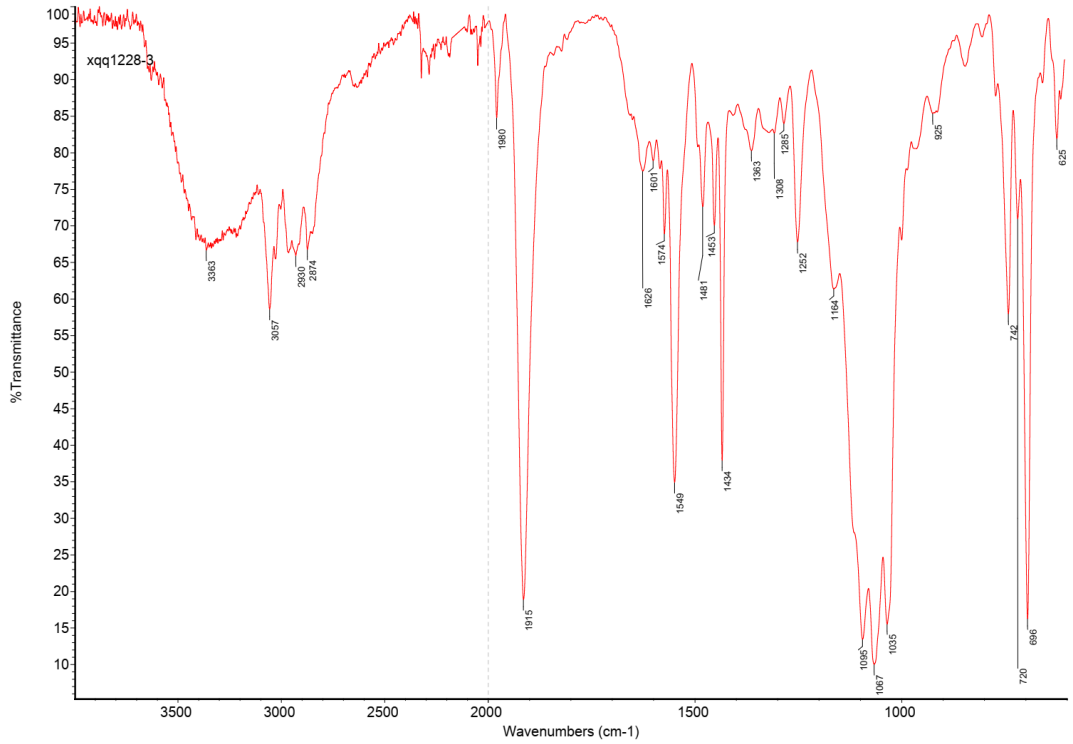


Figure S4 The FTIR spectrum of **2a**.

4. The ^{1}H NMR chemical shifts of 1a

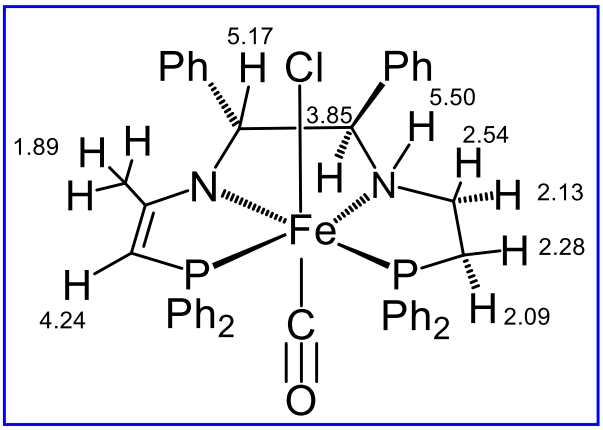


Figure S5 ^{1}H NMR chemical shifts of **1a**

5. Qualitative molecular orbital diagrams of 1b

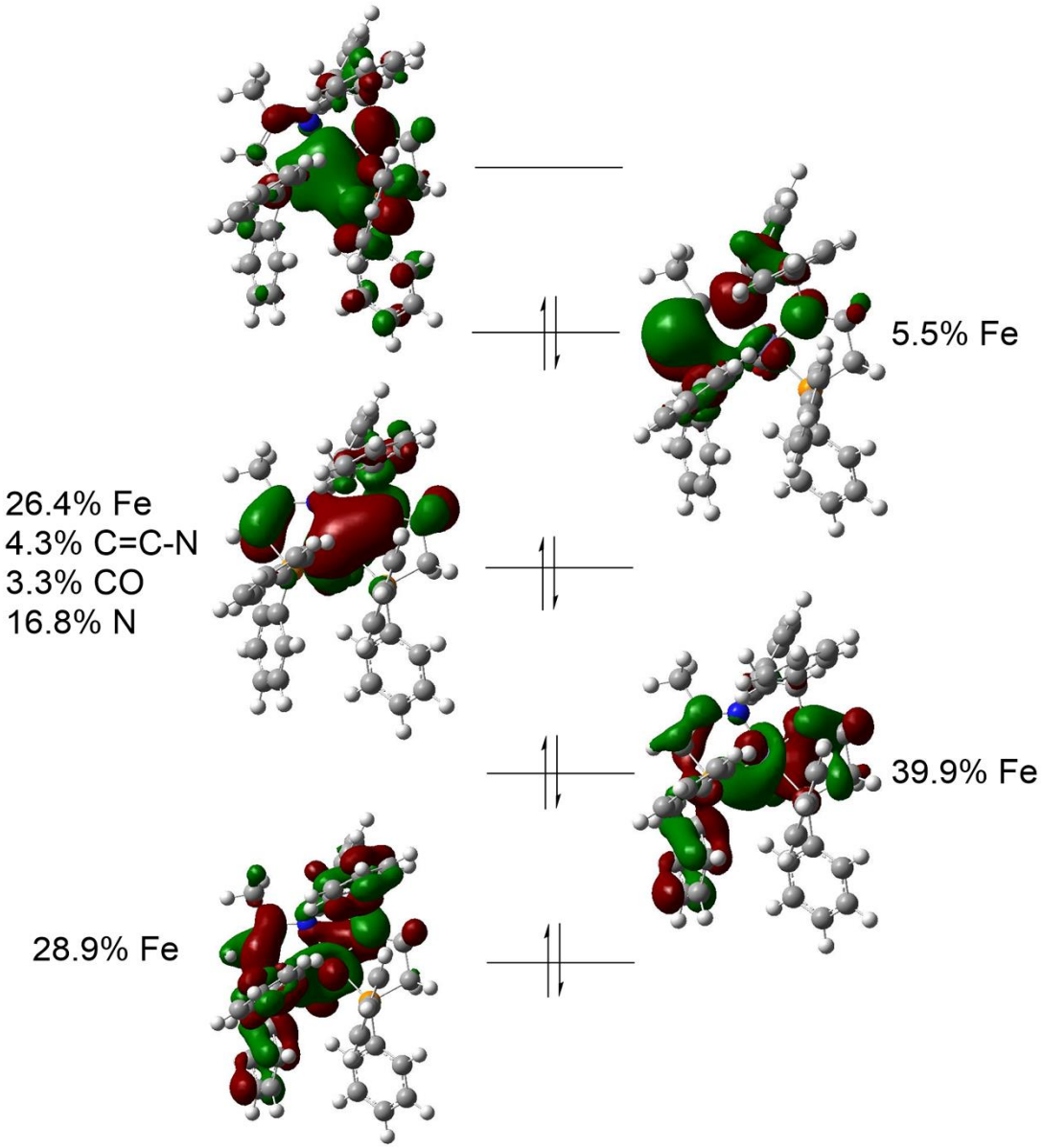


Figure S6 Qualitative molecular orbital diagrams of **1b**

Table S1. Crystal data and Structure refinement for complexes **1** and **3**

Compound reference	**1**	**3**
Empirical formula	$C_{44}H_{42}BClF_4FeN_2OP_2$	$C_{43}H_{38}BClF_5FeN_2OP_2$
Formula weight	854.84	857.80
Temperature/K	296 (2)	173 (2)
Crystal system	monoclinic	Orthorhombic
Space group	P 21	P 21 21 2
a/Å	14.0962(9)	19.6543(3)
b/Å	10.1694(6)	23.2544(7)
c/Å	14.1863(8)	18.1244(5)
α/°	90	90
β/°	93.626(2)	90
γ/°	90	90
Volume/$Å^3$	2029.5(2)	8283.7(4)
Z	2	8
$\rho_{calc}g/cm^3$	1.399	1.376
μ/mm^{-1}	0.572	0.564
F (000)	884	3528
Crystal size/mm^3	0.16 × 0.13 × 0.1	0.170 x 0.140 x 0.060
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.466 to 25.998	1.424 to 25.497
Index ranges	$-17 \le h \le 17$, $-12 \le k \le 12$, $-17 \le l \le 17$	$-23 \le h \le 18$, $-28 \le k \le 28$, $-21 \le l \le 21$
Reflections collected	38726	40369
Independent reflections	7986 [R_{int} = 0.0437]	15154 [R_{int} = 0.0559]
Data/restraints/parameters	7986/1/511	15154/81/1021
Goodness-of-fit on F^2	1.050	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.038, wR_2 = 0.0918	R_1 = 0.0602, wR_2 = 0.1534
Final R indexes [all data]	R_1 = 0.0433, wR_2 = 0.0966	R_1 = 0.0739, wR_2 = 0.1649
Largest diff. peak/hole / e $Å^{-3}$	0.387/-0.294	0.795/-0.507

6. General procedure for ATH:

The quantity of the precatalyst was measured via a stock solution method. A concentrated stock solution was made by dissolving the precatalysts (1.97 x 10^{-2} mmol) in 6.08 g cold dichloromethane. After all the solid was dissolved, the solution was immediately sucked into a syringe. The solution was then divided into equal portions into several 20 mL vials such that each portion has 0.2 g of the stock solution, and then dichloromethane was removed under vacuum. These operations led to a precatalyst quantity of 6.48 x 10^{-4} mmol in each vial. The base was prepared by dissolving KO^{t}Bu (10 mg, 0.089 mmol) in ^{i}PrOH (1.02 g, 1.30 mL). ^{i}PrOH (6.63 g, 8.44 mL), substrate (3.95 mmol) and a clean stirring bar were added to the vial that contains the precatalyst and the solution was stirred for 5 minutes, or until it was dissolved. 0.015 g of the base stock solution was added into a vial that contains 0.546 g of ^{i}PrOH and the mixed solution was then added into the catalyst solution to start the catalytic reaction. 0.1 mL samples were taken via syringe and injected into Teflon-sealed GC vials prepared with wet, aerated ^{i}PrOH to quench catalysis.

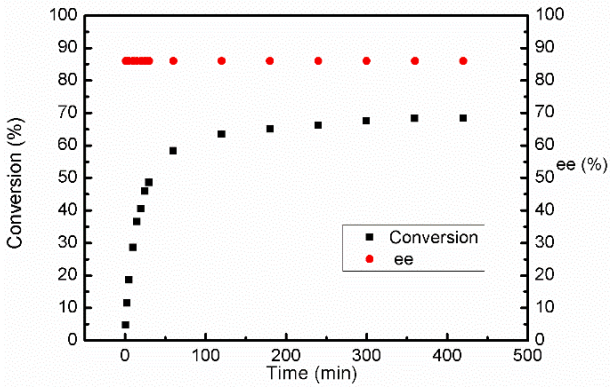


Figure S7 Reaction profile and ee of catalytic reduction of acetophenone using complex **1**. Reaction conditions: [**1**] = 6.73 × 10^{-5} M, [KO^{t}Bu] = 5.45 × 10^{-4} M, [substrate] = 0.412 M, [^{i}PrOH] = 12.4 M, 28°C.

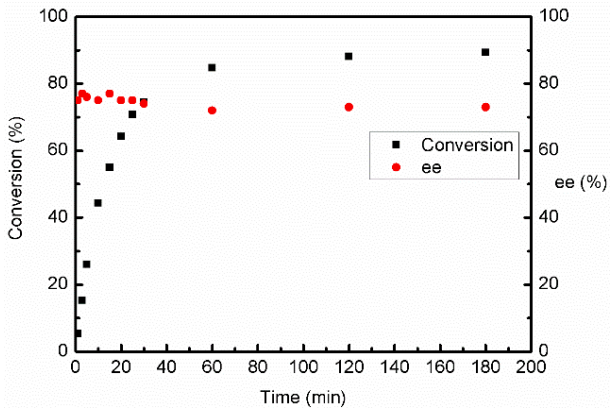


Figure S8 Reaction profile and ee of catalytic reduction of acetophenone using complex **2**. Reaction conditions: [**2**] = 6.73 × 10^{-5} M, [KO^{t}Bu] = 5.45 × 10^{-4} M, [substrate] = 0.412 M, [^{i}PrOH] = 12.4 M, 28°C.

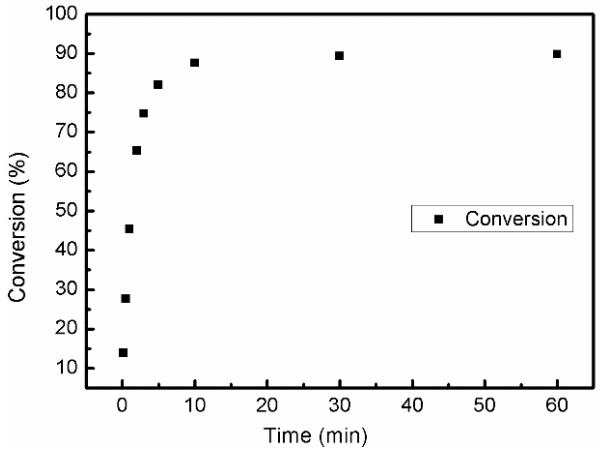


Figure S9 Reaction profile and ee of catalytic reduction of acetophenone using complex **4**. Reaction conditions: [**4**] = 6.73 × 10^{-5} M, [KO^{t}Bu] = 5.45 × 10^{-4} M, [substrate] = 0.412 M, [^{i}PrOH] = 12.4 M, 28^{o}C.

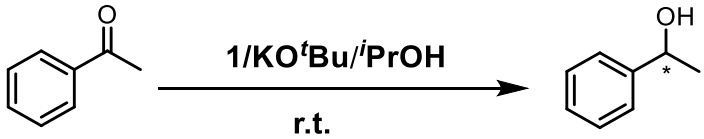


Figure S10 Gas chromatographs. Reaction conditions: [Cat] = 6.73 × 10^{-5} M, [KO^{t}Bu] = 5.45 × 10^{-4}M, [substrate] = 0.412 M, [^{i}PrOH] = 12.4 M, 28 ^{o}C. GC analysis conditions: Oven temperature (130 ^{o}C). Retention time: product minor isomer = 7.2 min, product major isomer (*S*) = 7.5 min, starting material = 4.7 min.

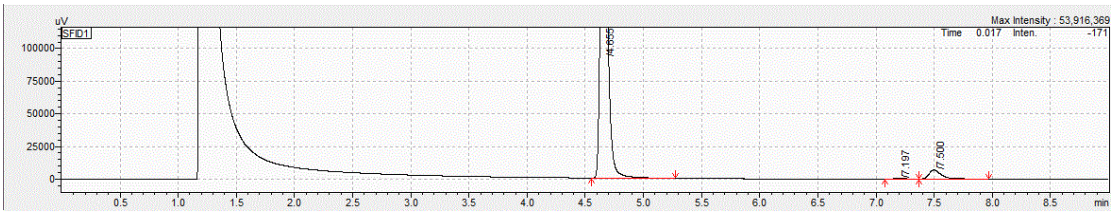


Figure S10.1 1 minute 4.7 % conversion 86% ee

The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	4.655	1147946	275023			95.289
2	7.197	4002	599			0.332
3	7.500	52753	6839			4.379
Total		1204702	282461			100.000

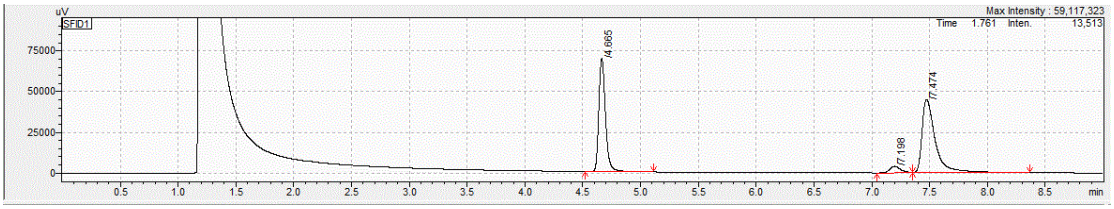


Figure S10.2 60 minutes 58.3 % conversion 86% ee

The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	4.665	279760	69712			41.694
2	7.198	27163	4061			4.048
3	7.474	364068	45079			54.258
Total		670991	118852			100.000

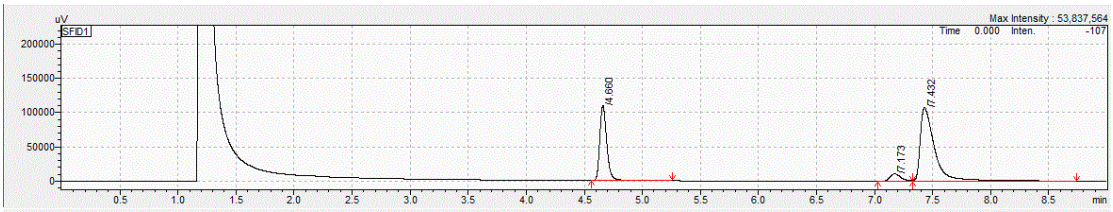


Figure S10.3 420 minutes 68.3 % conversion 86% ee

The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	4.660	459701	109098			31.681
2	7.173	68314	10698			4.708
3	7.432	922996	107537			63.611
Total		1451010	227332			100.000

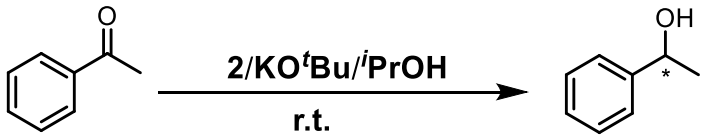


Figure S11 Gas chromatographs. Reaction conditions: [Cat] = 6.73 × 10^{-5} M, [KO^{t}Bu] = 5.45 × 10^{-4}M, [substrate] = 0.412 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (130 °C). Retention time: product minor isomer = 7.2 min, product major isomer (*S*) = 7.5 min, starting material = 4.7 min.

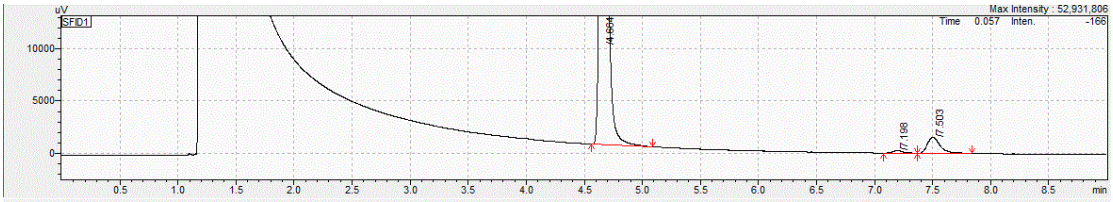


Figure S11.1 1 minute 5.4% conversion 75% ee

The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	4.664	237960	55895			94.605
2	7.198	1618	229			0.643
3	7.503	11952	1558			4.752
Total		251530	57682			100.000

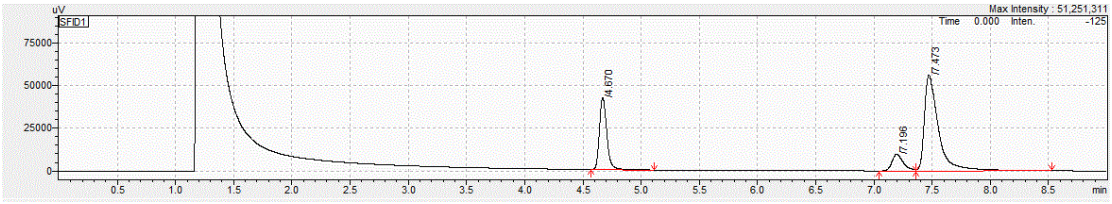


Figure S11.2 30 minutes 74.4 % conversion 74% ee

The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	4.670	186078	42247			25.583
2	7.196	66819	9973			9.187
3	7.473	474462	56072			65.231
Total		727359	108291			100.000

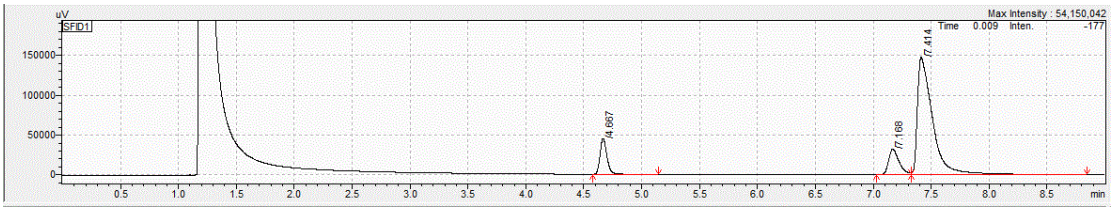


Figure S11.3 180 minutes 89.3 % conversion 73% ee

The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	4.667	188444	44880			10.733
2	7.168	205651	32380			11.714
3	7.414	1361579	147716			77.553
Total		1755674	224976			100.000

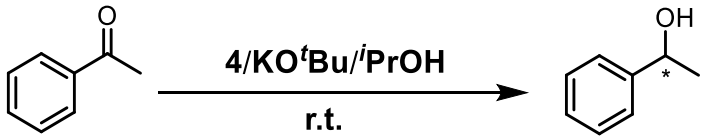


Figure S12 Gas chromatographs. Reaction conditions: [Cat] = 6.73 × 10^{-5} M, [KO^{t}Bu] = 5.45 × 10^{-4} M, [substrate] = 0.412 M, [^{i}PrOH] = 12.4 M, 28 ºC. GC analysis conditions: Oven temperature (130 ºC). Retention time: product isomer (*R*) = 7.2 min, product isomer (*S*) = 7.5 min, starting material = 4.7 min.

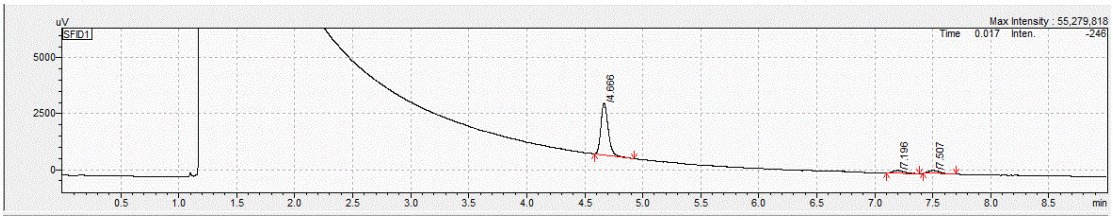


Figure S12.1 10 seconds 13.9 % conversion

The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	4.666	10119	2318			86.077
2	7.196	776	122			6.599
3	7.507	861	140			7.323
Total		11756	2580			100.000

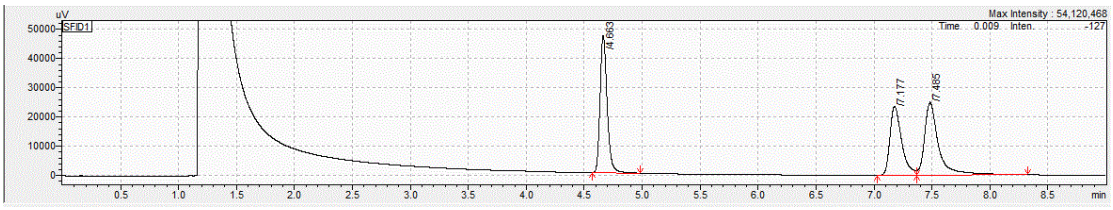


Figure S12.2 2 minutes 65.3 % conversion

The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	4.663	199851	46694			34.702
2	7.177	165279	23608			28.699
3	7.485	210769	24954			36.598
Total		575898	95256			100.000

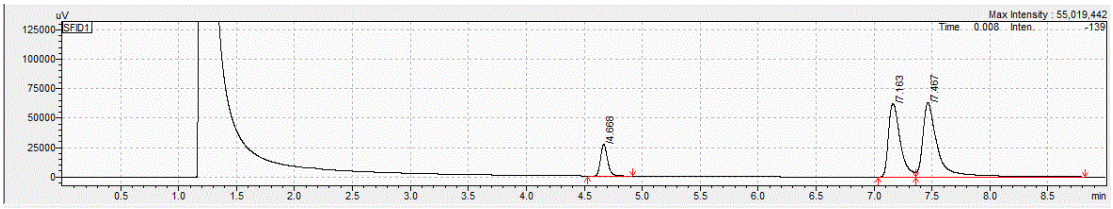


Figure S12.3 60 minutes 89.8 % conversion

The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	4.668	113189	27022			10.170
2	7.163	438963	62373			39.442
3	7.467	560778	63280			50.388
Total		1112930	152675			100.000

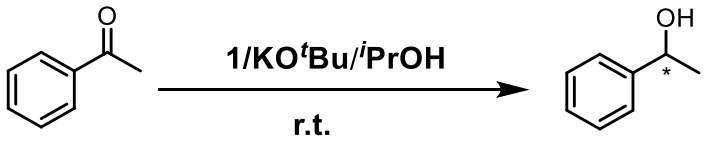
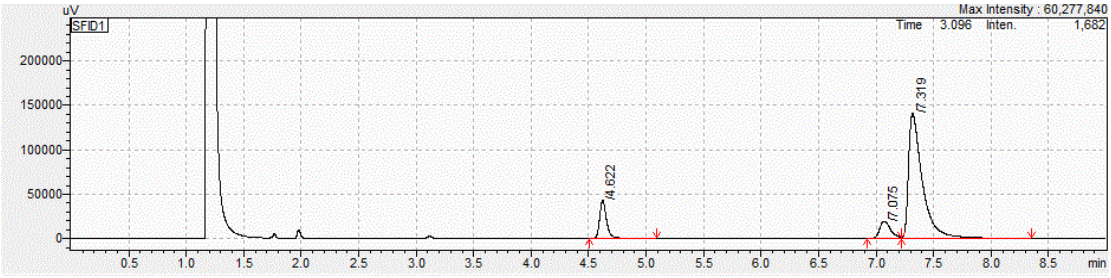


Figure S13 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (130 °C). Retention time: product minor isomer = 7.1 min, product major isomer (*S*) = 7.3 min, starting material = 4.6 min, 88 % conversion 80 % ee**.**



The analysis result is as follow:

Peaks number	**Retention time**	**Area**	**Height of peaks**	**Mark**	**Name of compounds**	**Area percentage**
1	4.622	184191	43188			12.194
2	7.075	130988	19670			8.672
3	7.319	1195269	140916			79.133
Total		1510447	203774			100.000

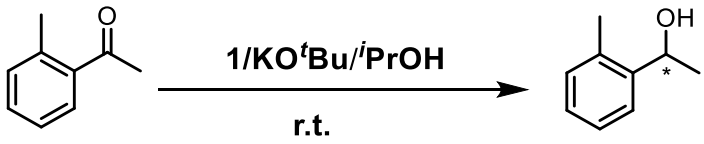
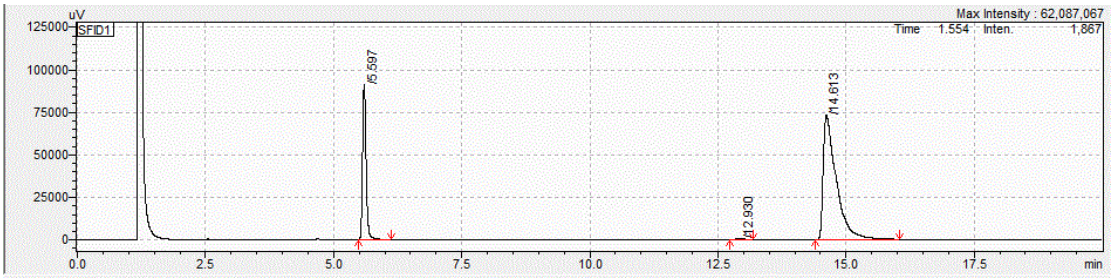


Figure S14 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (130 °C). Retention time: product minor isomer = 12.9 min, product major isomer (*S*) = 14.6 min, starting material = 5.6 min, 75 % conversion 98 % ee**.**



The analysis result is as follow:

Peaks number	**Retention time**	**Area**	**Height of peaks**	**Mark**	**Name of compounds**	**Area percentage**
1	5.597	445293	91362			25.298
2	12.930	10175	853			0.578
3	14.613	1304717	73510			74.124
Total		1760185	165724			100.000

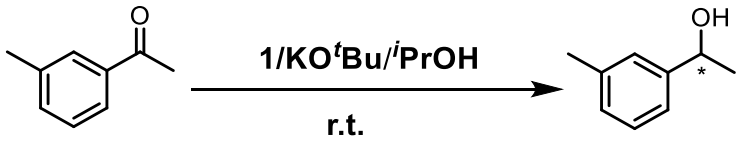
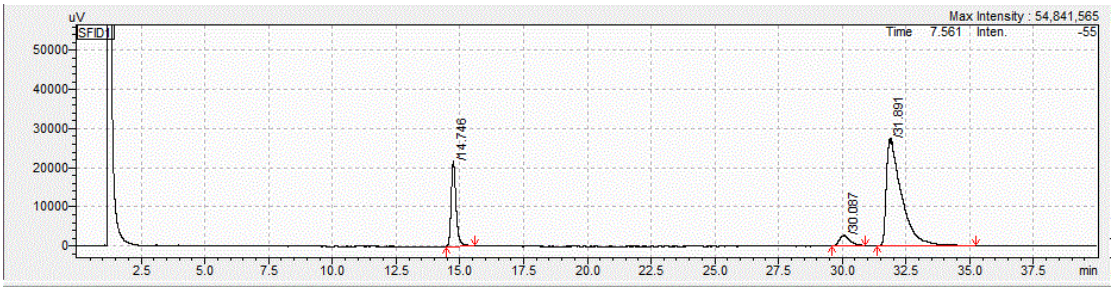


Figure S15 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (110 °C). Retention time: product minor isomer = 30.1 min, product major isomer (*S*) = 31.9 min, starting material = 14.7 min, 81 % conversion 87 % ee**.**



The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	14.746	289717	21844			19.258
2	30.087	78522	2651			5.220
3	31.891	1136148	27548			75.522
Total		1504387	52043			100.000

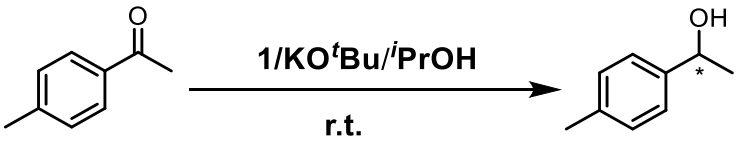
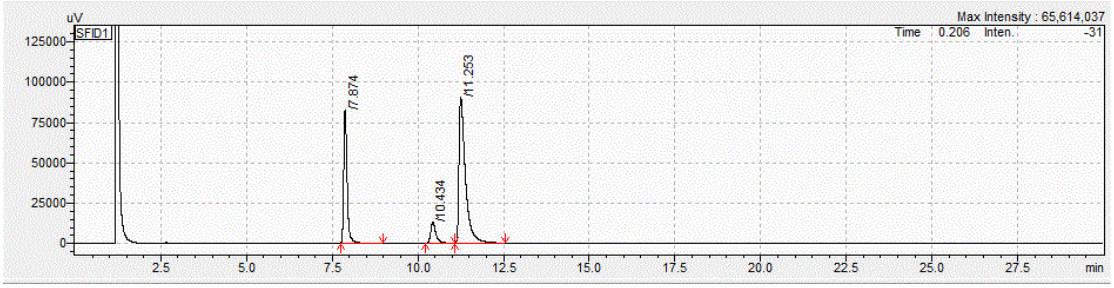


Figure S16 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (130 °C). Retention time: product minor isomer = 10.4 min, product major isomer (*S*) = 11.3 min, starting material = 7.9 min, 70 % conversion 78 % ee.



The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	7.874	581484	82171			30.323
2	10.434	145063	13337			7.565
3	11.253	1191063	90481			62.112
Total		1917610	185988			100.000

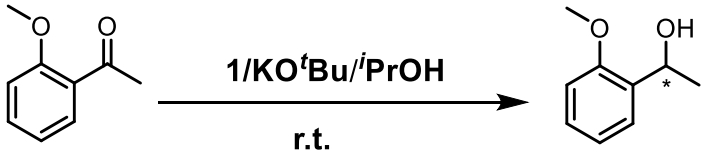
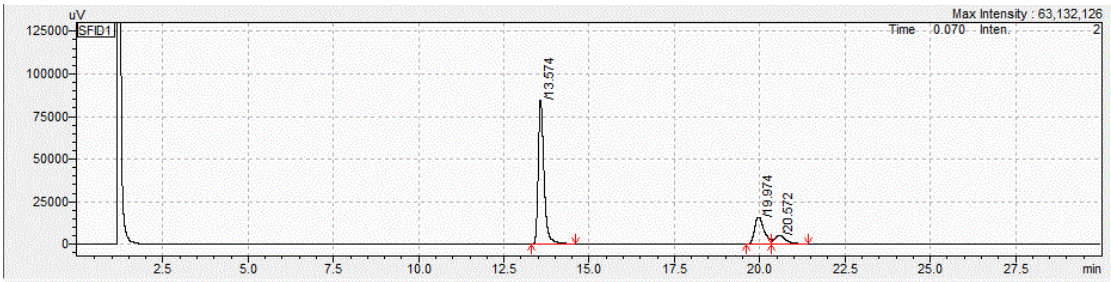


Figure S17 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (130 °C). Retention time: product major isomer (*S*) = 20.0 min, product minor isomer = 20.6 min, starting material = 13.6 min, 30 % conversion 44 % ee**.**



The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	13.574	999002	84546			69.930
2	19.974	308499	15855			21.595
3	20.572	121076	5280			8.475
Total		1428577	105681			100.000

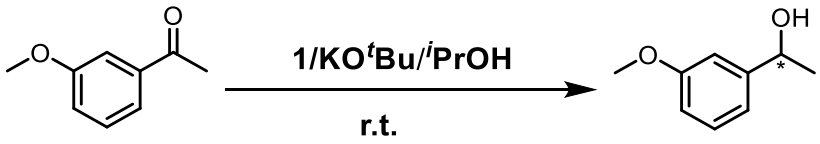
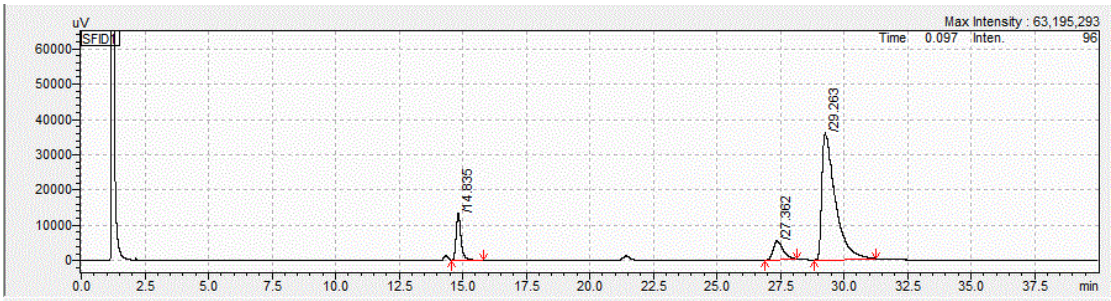


Figure S18 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (130 °C). Retention time: product minor isomer = 27.4 min, product major isomer (*S*) = 29.3 min, starting material = 14.8 min, 89 % conversion 80 % ee**.**



The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	14.835	175304	13360			10.741
2	27.362	143936	5321			8.819
3	29.263	1312852	35993			80.440
Total		1632092	54675			100.000

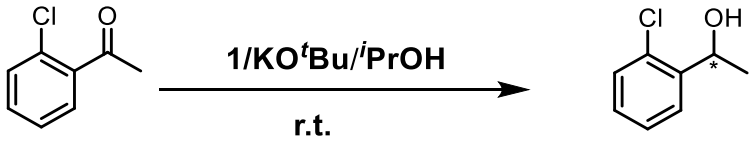
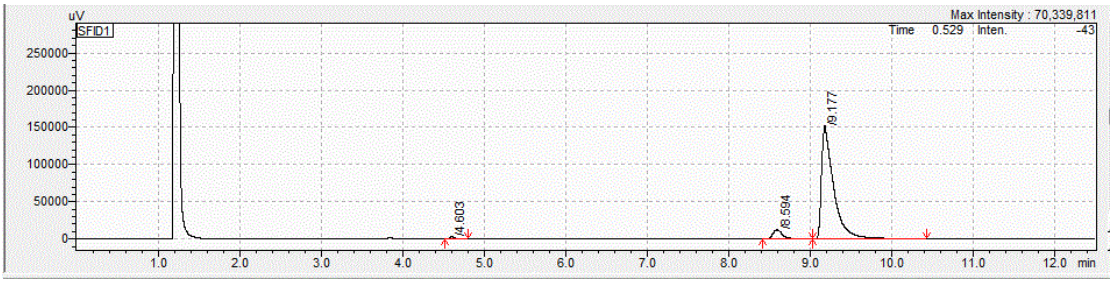


Figure S19 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (150 °C). Retention time: product minor isomer = 8.6 min, product major isomer (*S*) = 9.2 min, starting material = 4.6 min, 99 % conversion 87 % ee**.**



The analysis result is as follow:

Peaks number	**Retention time**	**Area**	**Height of peaks**	**Mark**	**Name of compounds**	**Area percentage**
1	4.603	13557	3344			0.802
2	8.594	106824	12548			6.318
3	9.177	1570314	152784			92.880
Total		1690695	168677			100.000

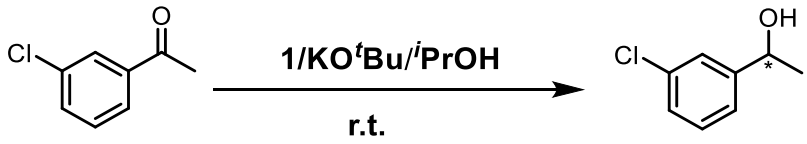
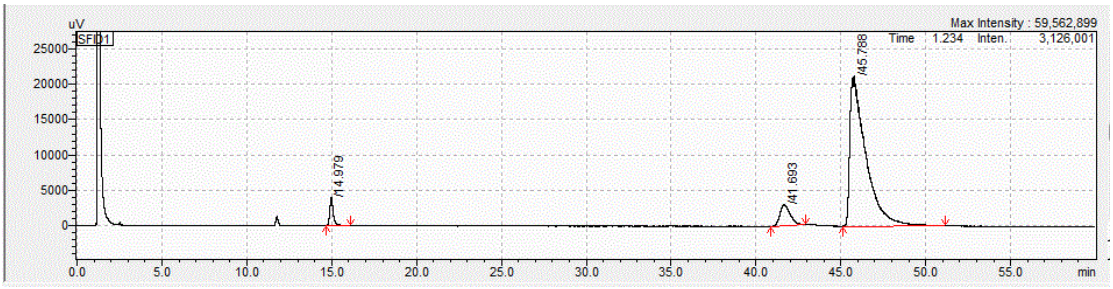


Figure S20 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (120 °C). Retention time: product minor isomer = 41.7 min, product major isomer (*S*) = 45.8 min, starting material = 15.0 min, 96 % conversion 84 % ee.



The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	14.979	57867	4020			3.674
2	41.693	122112	3025			7.753
3	45.788	1395049	21298			88.573
Total		1575027	28343			100.000

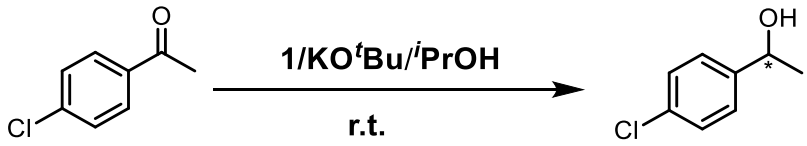
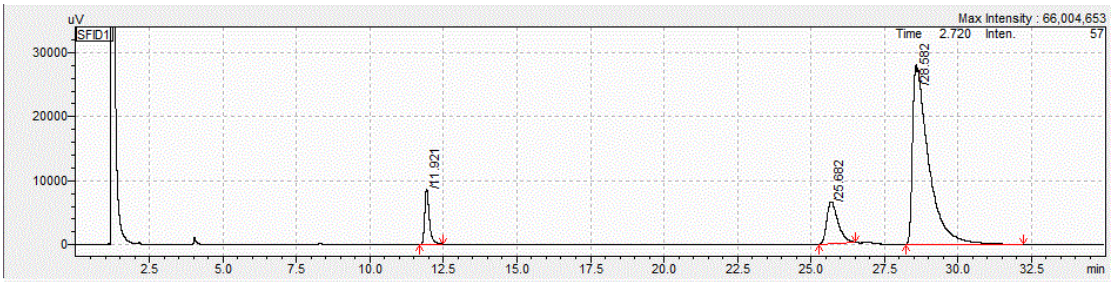


Figure S21 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (130 °C). Retention time: product minor isomer = 25.7 min, product major isomer (*S*) = 28.6 min, starting material = 11.9 min, 93 % conversion 72 % ee.



The analysis result is as follow:

Peaks number	**Retention time**	**Area**	**Height of peaks**	**Mark**	**Name of compounds**	**Area percentage**
1	11.921	95840	8621			7.205
2	25.682	174046	6525			13.085
3	28.582	1060273	27949			79.710
Total		1330159	43095			100.000

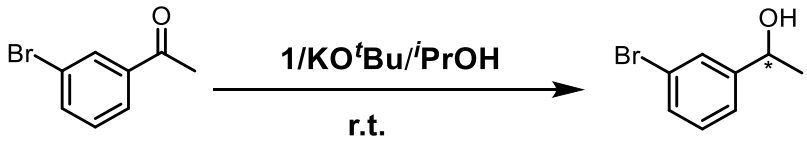
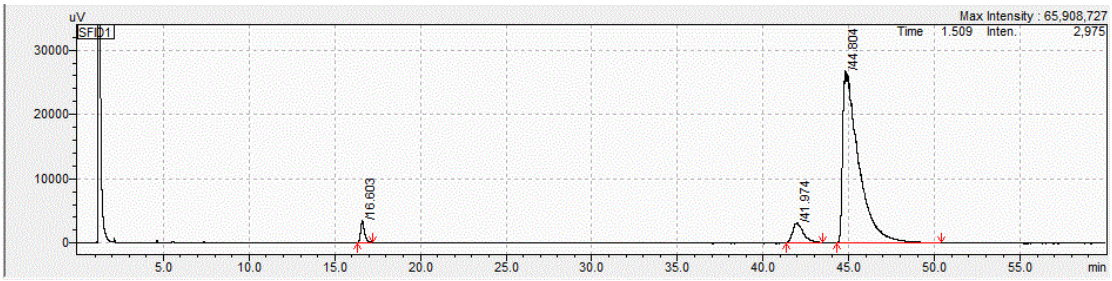


Figure S22 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (130 °C). Retention time: product minor isomer = 42.0 min, product major isomer (*S*) = 44.8 min, starting material = 4.6 min, 93 % conversion 72 % ee.



The analysis result is as follow:

Peaks number	**Retention time**	**Area**	**Height of peaks**	**Mark**	**Name of compounds**	**Area percentage**
1	16.603	52866	3434			2.765
2	41.974	134902	3114			7.057
3	44.804	1723882	26775			90.178
Total		1911650	33323			100.000

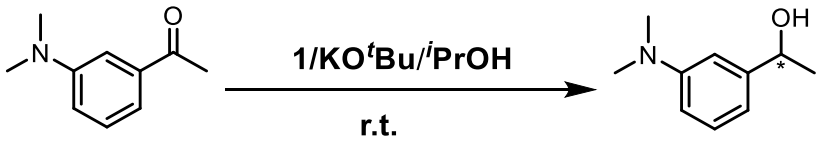
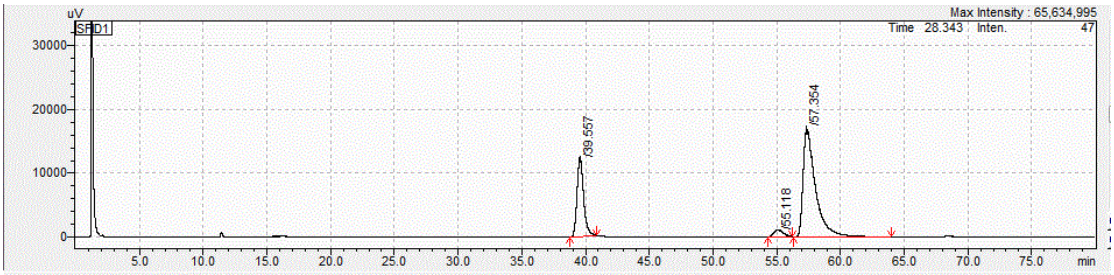


Figure S23 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (130 °C). Retention time: product minor isomer = 55.1 min, product major isomer (*S*) = 57.4 min, starting material = 39.6 min, 73 % conversion 90% ee.



The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	39.557	441429	12422			26.882
2	55.118	57853	1147			3.523
3	57.354	1142816	17291			69.595
Total		1642098	30859			100.000

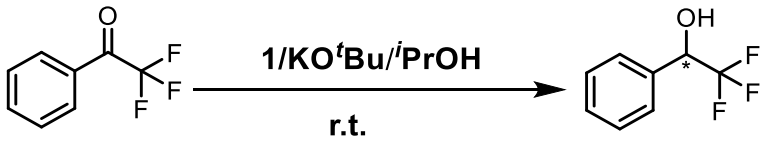
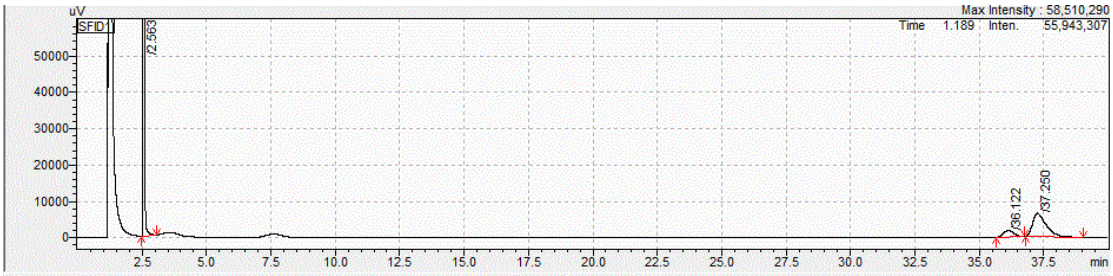


Figure S24 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (110 °C). Retention time: product minor isomer = 36.1 min, product major isomer (*S*) = 37.3 min, starting material = 2.6 min, 26 % conversion 64 % ee.



The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	2.563	822132	302954			74.088
2	36.122	52200	1822			4.704
3	37.250	235339	6460			21.208
Total		1109671	311236			100.000

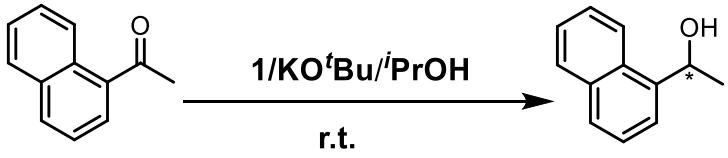
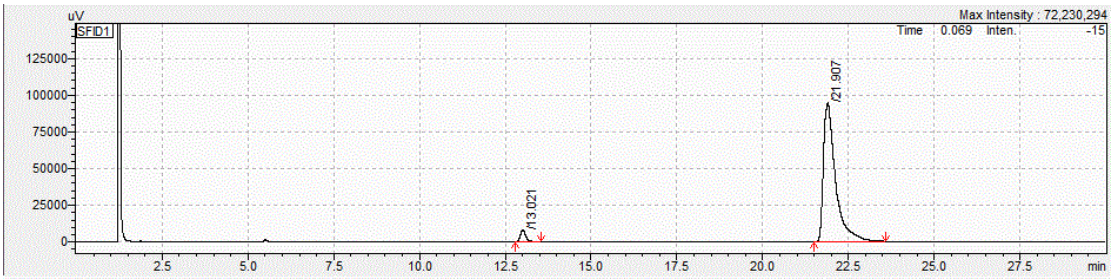


Figure S25 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (170 °C). Retention time: product major isomer (*S*) = 21.9 min, starting material = 13.0 min, 96 % conversion 99 % ee.



The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	13.021	94011	8434			3.868
2	21.907	2336496	95106			96.12
Total		2430507	103540			100.000

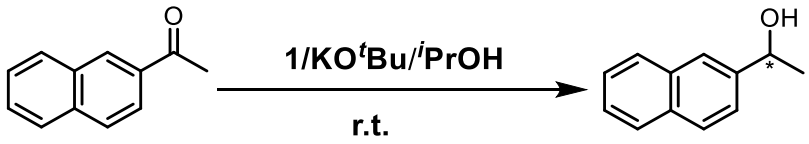
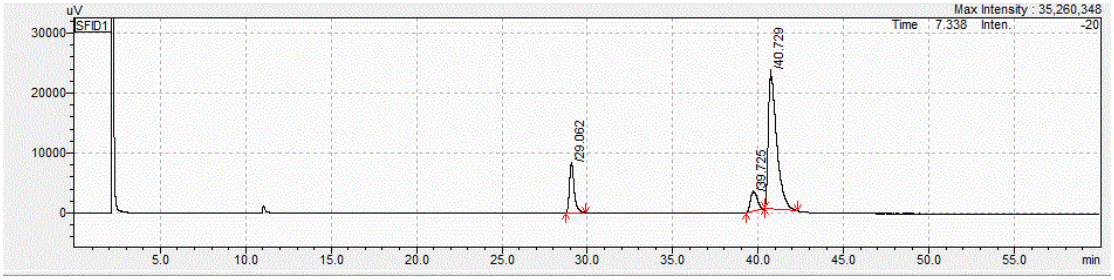


Figure S26 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 °C. GC analysis conditions: Oven temperature (170 °C). Retention time: product minor isomer = 39.7 min, product major isomer (*S*) = 40.7 min, starting material = 29.1 min, 85 % conversion 80 % ee.



The analysis result is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	29.062	161110	8436			15.492
2	39.725	89071	3316			8.560
3	40.729	789805	23267			75.948
Total		1039932	35019			100.000

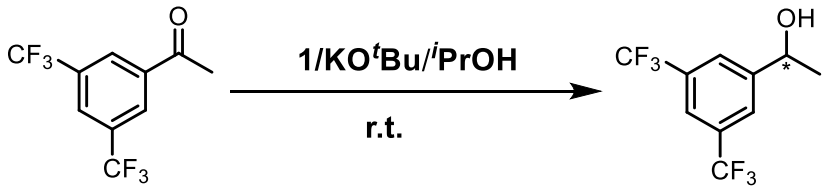
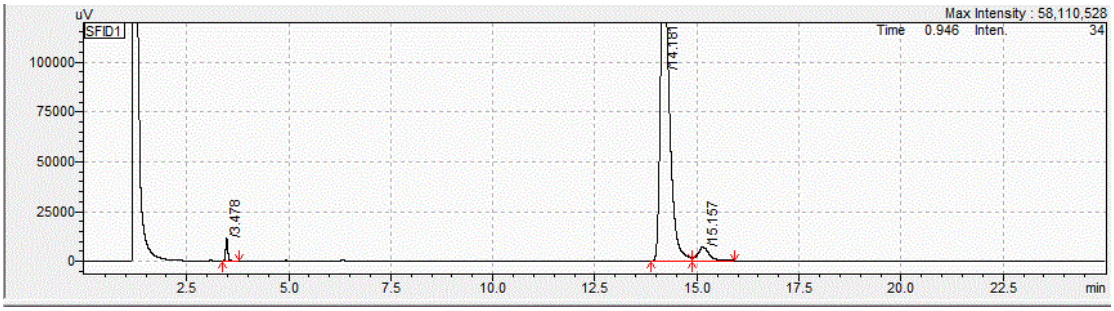


Figure S27 Gas chromatograph. Reaction conditions: [Cat] = 6.48 × 10^{-4} M, [KO^{t}Bu] = 5.24 × 10^{-3} M, [substrate] = 0.397 M, [^{i}PrOH] = 12.4 M, 28 ºC. GC analysis conditions: Oven temperature (110 ºC). Retention time: product major isomer (*S*) = 14.2 min, product minor isomer = 15.2 min, starting material = 3.5 min, 98 % conversion 89% ee.



The analysis result is as follow:

Peaks number	**Retention time**	**Area**	**Height of peaks**	**Mark**	**Name of compounds**	**Area percentage**
1	3.478	42455	11289			15.492
2	14.181	2339845	152818			8.560
3	15.157	135030	6977			75.948
Total		2517330	35019			100.000

7. Copies of ^{1}H NMR, $^{19}F\{^{1}H\}$ NMR, $^{13}C\{^{1}H\}$ NMR and $^{31}P\{^{1}H\}$ NMR spectra

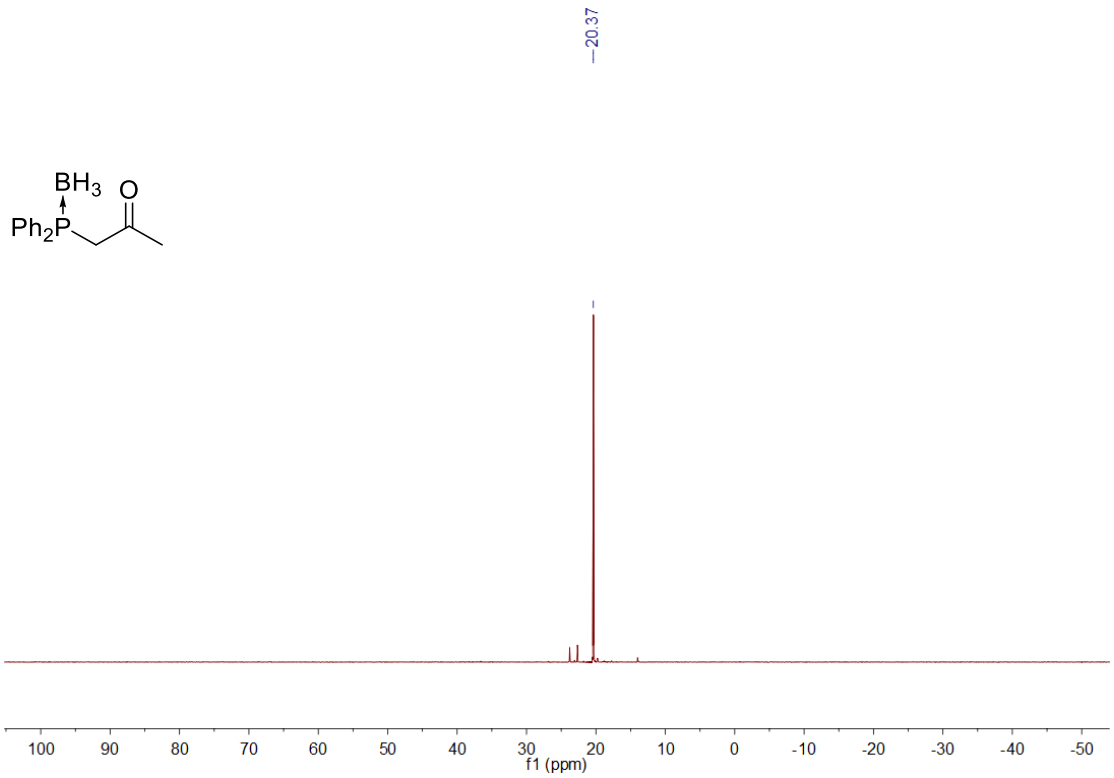


Figure S28 $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$) spectrum of borane adduct of *1-(diphenylphosphino)-propanone*

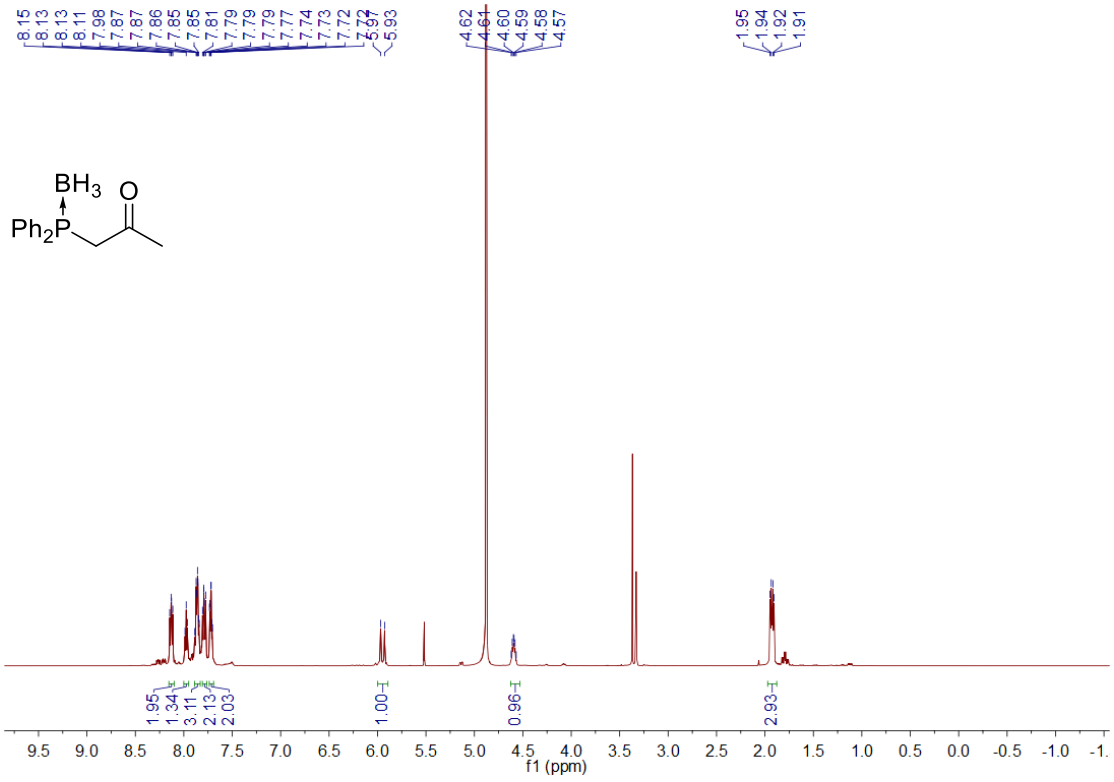


Figure S29 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of borane adduct of *1-(diphenylphosphino)-propanone*

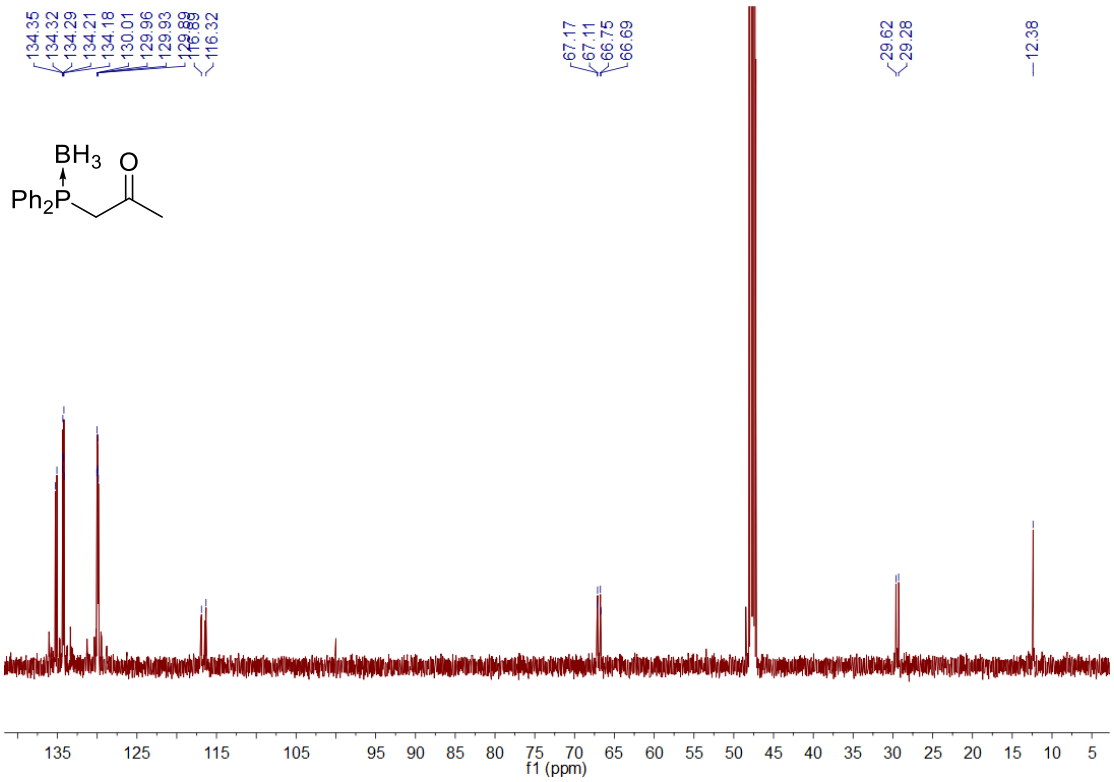


Figure S30 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of borane adduct of *1-(diphenylphosphino)-propanone*

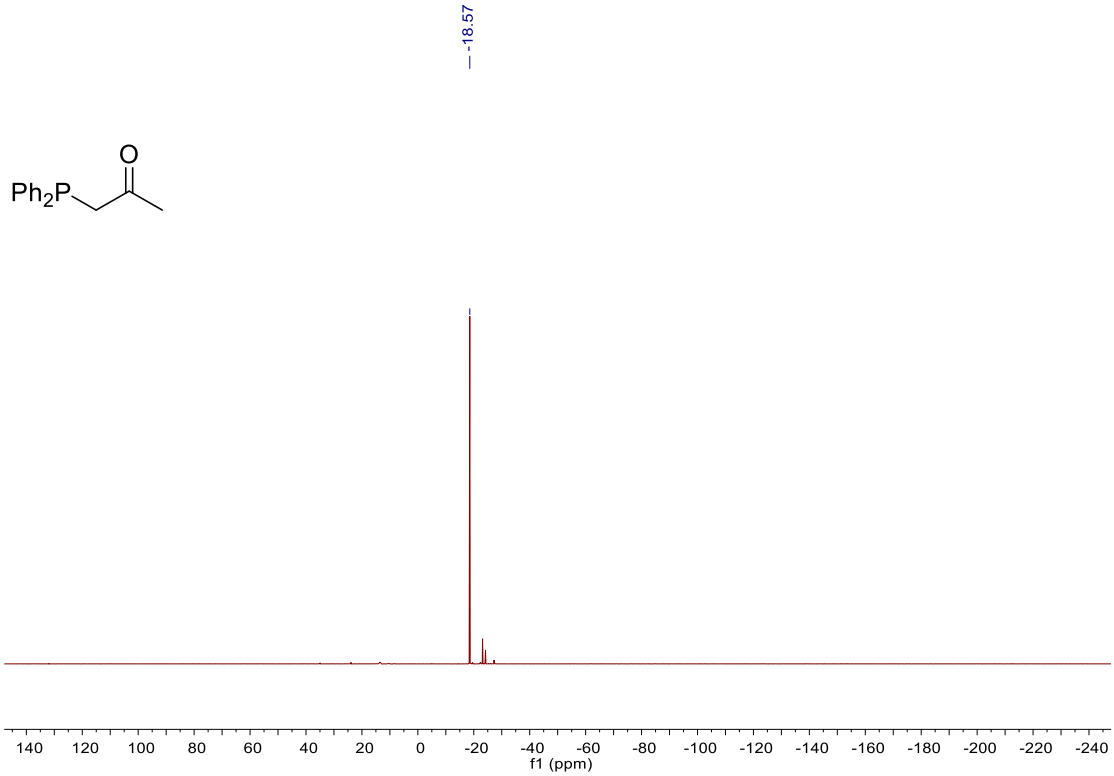


Figure S31 $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6) spectrum of *1-(diphenylphosphino)-propanone*

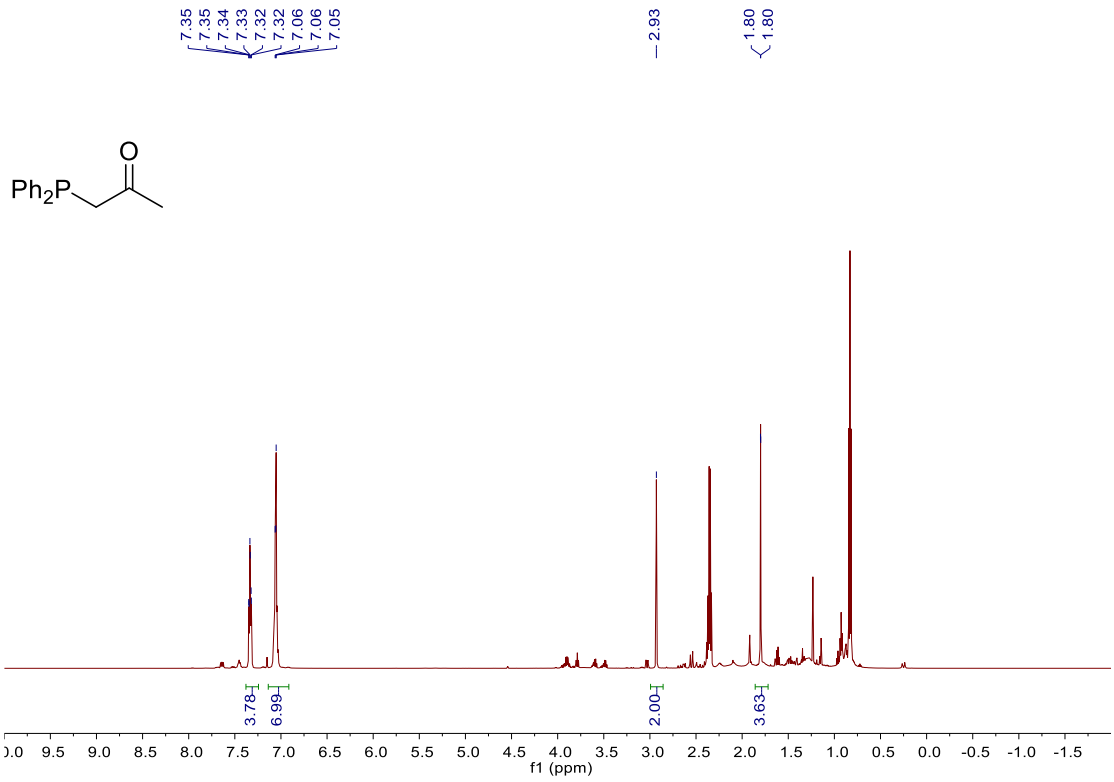


Figure S32 ^{1}H NMR (600 MHz, C_6D_6) spectrum of *1-(diphenylphosphino)-propanone*

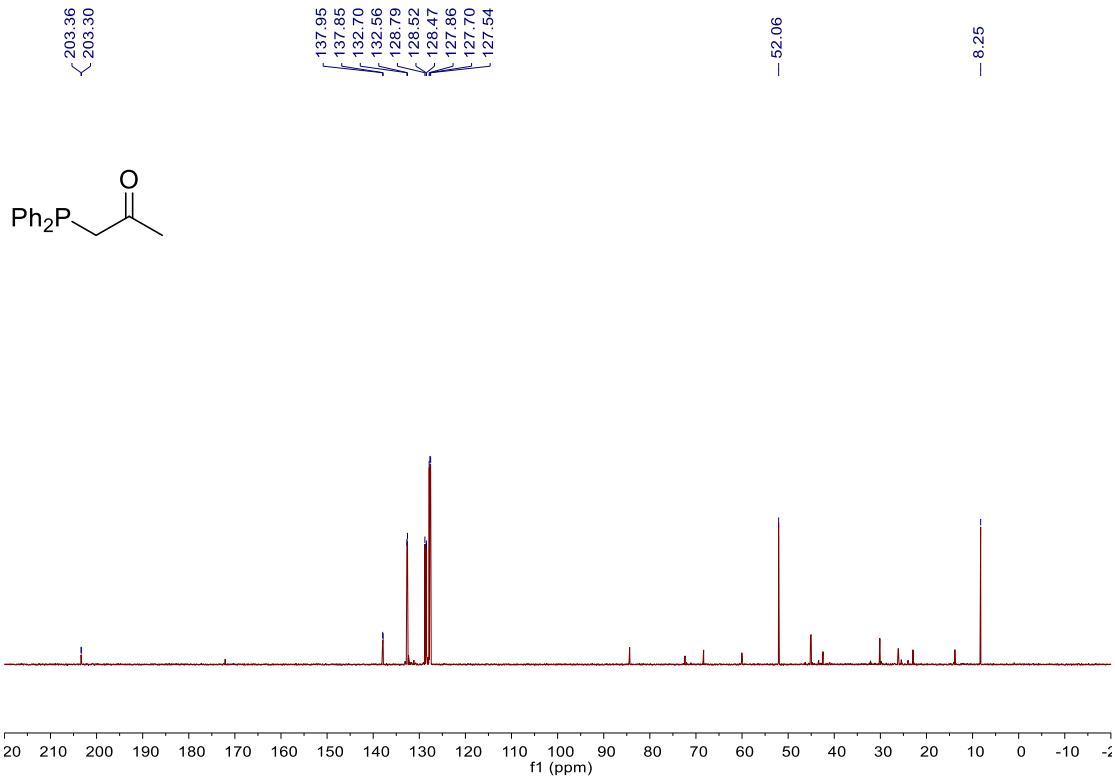


Figure S33 ^{13}C{^{1}H} NMR (151 MHz, C_6D_6) spectrum of *1-(diphenylphosphino)-propanone*

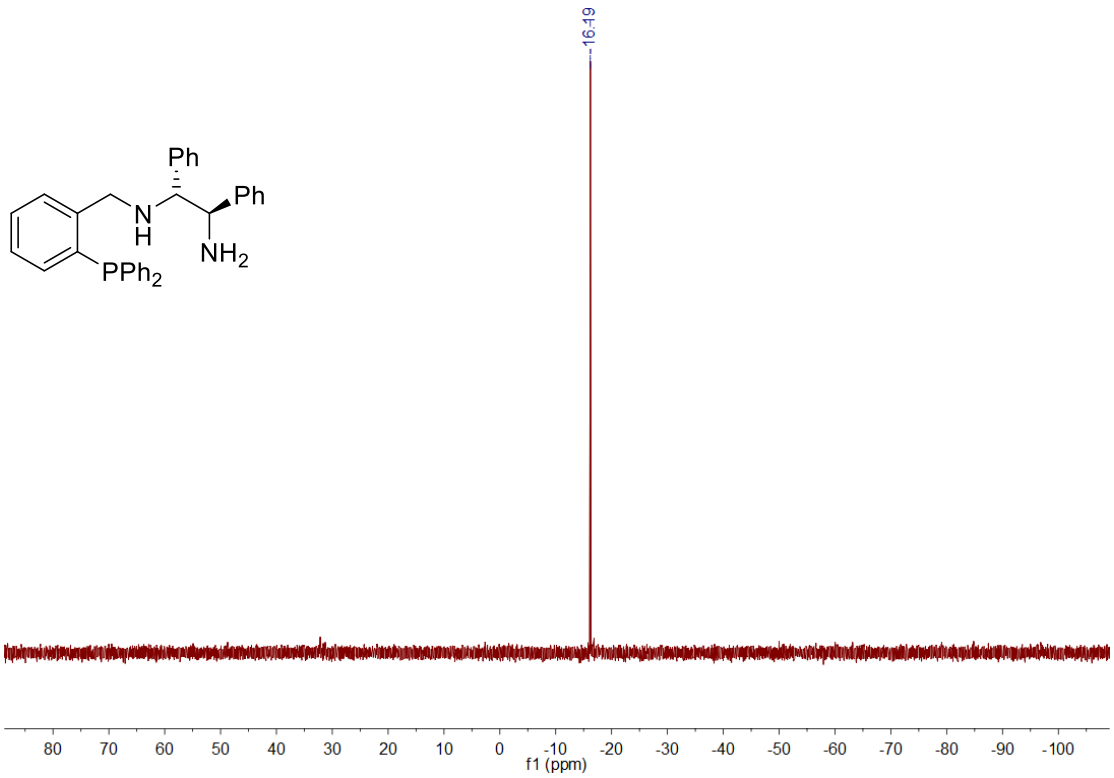


Figure S34 $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$) spectrum of *N^1-[[2-(diphenylphosphino)phenyl]methyl]-1,2-diphenyl-(1R,2R)-1,2-ethanediamine*

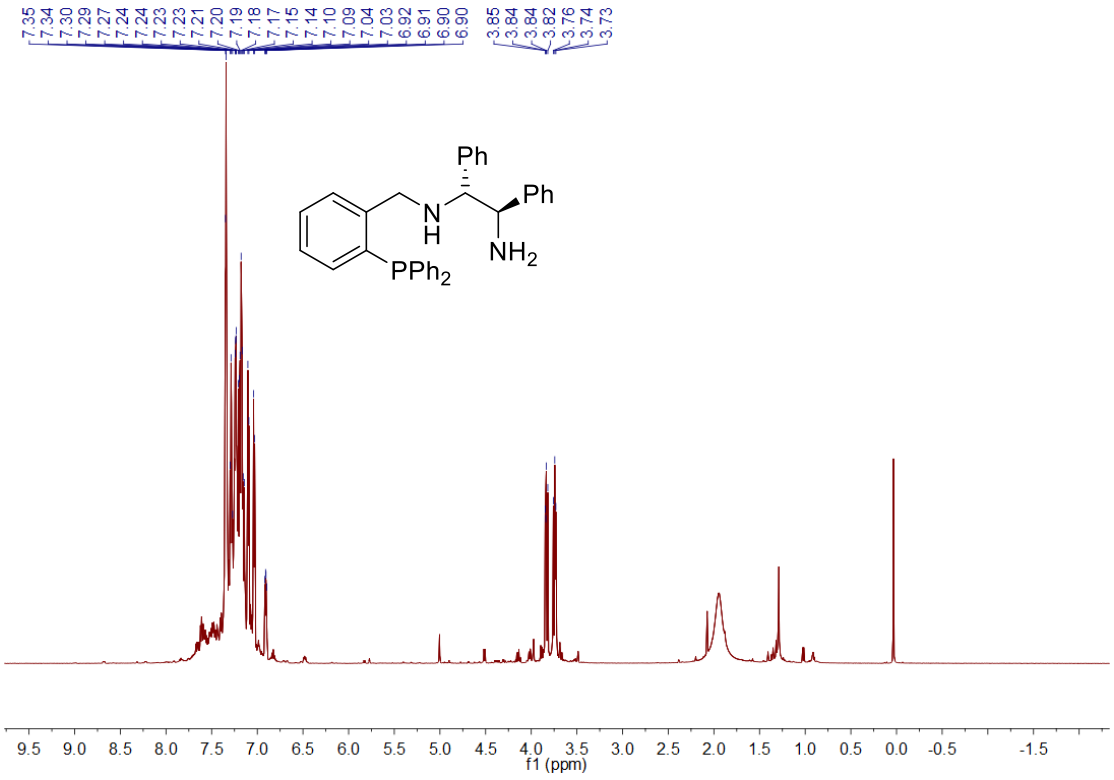


Figure S35 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of *N^1-[[2-(diphenylphosphino)phenyl]methyl]-1,2-diphenyl-(1R,2R)-1,2-ethanediamine*

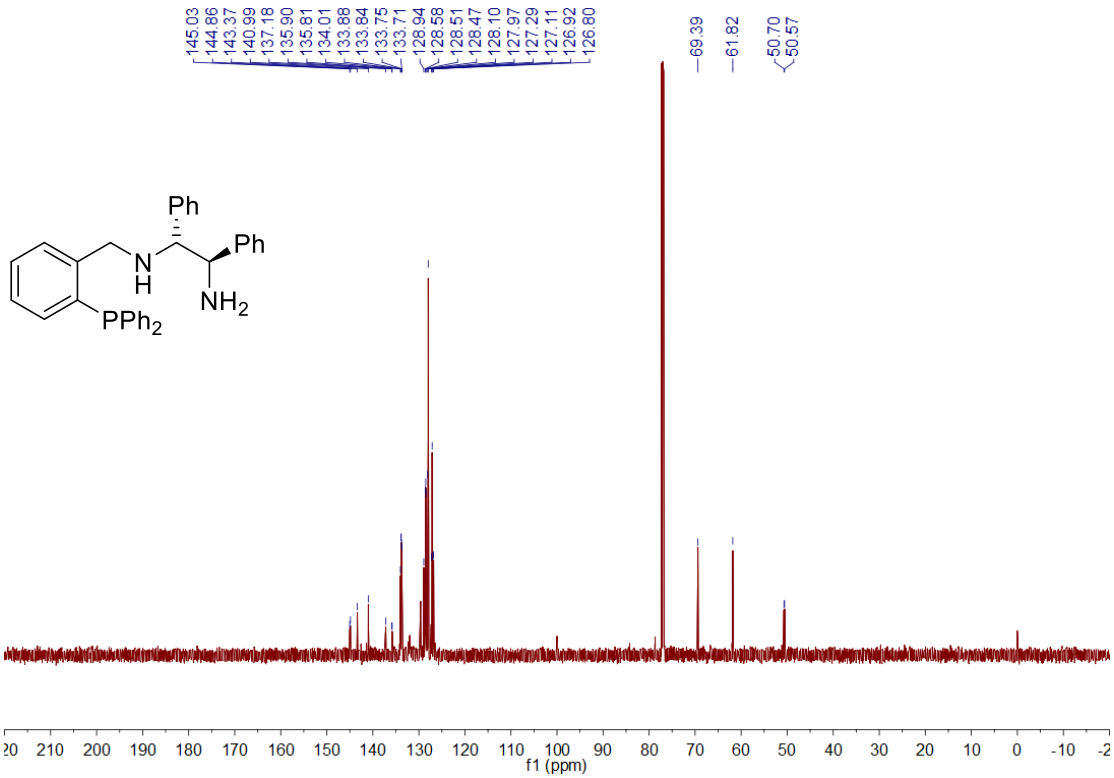


Figure S36 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of *N^1-[[2-(diphenylphosphino)phenyl]methyl]-1,2-diphenyl-(1R,2R)-1,2-ethanediamine*

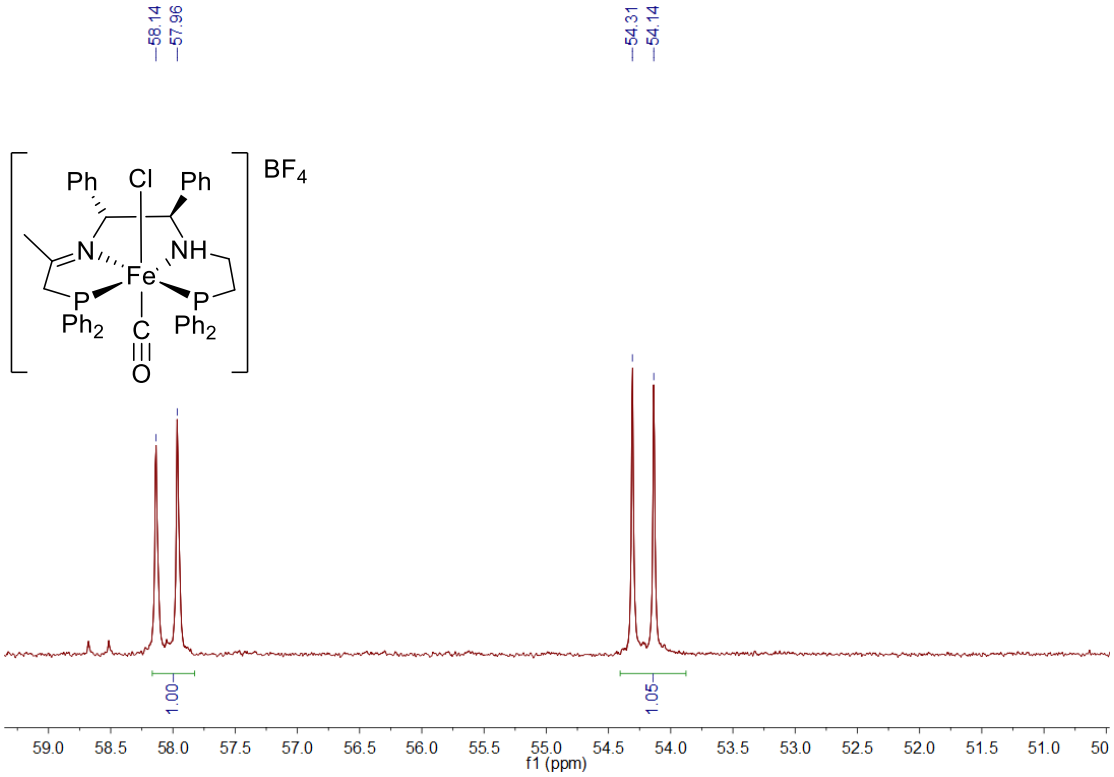


Figure S37 $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$) spectrum of **1**.

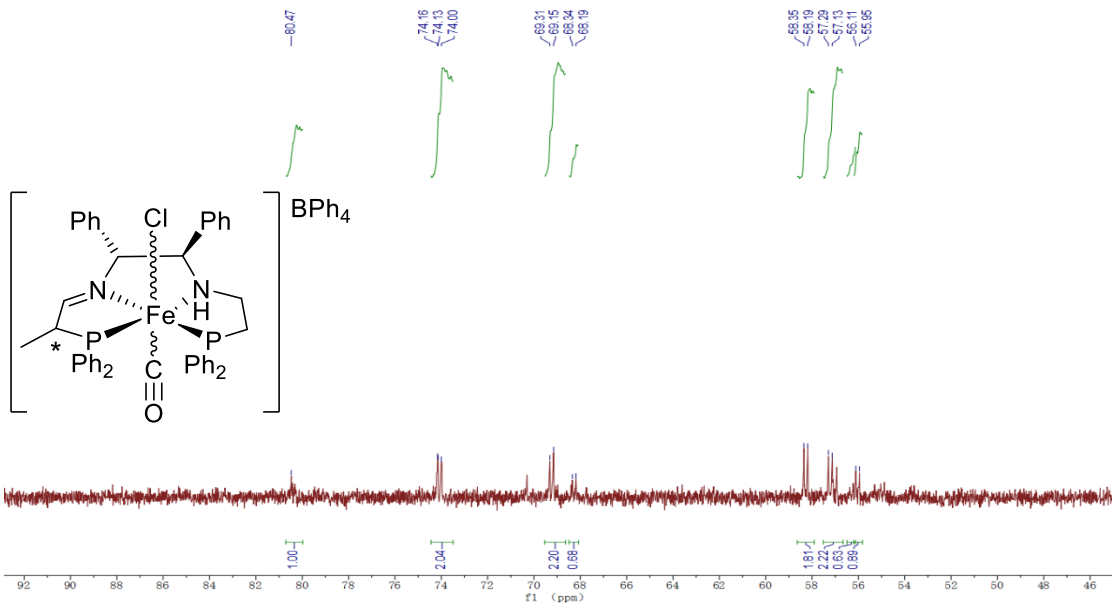


Figure S38 $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$) spectrum of **2**.

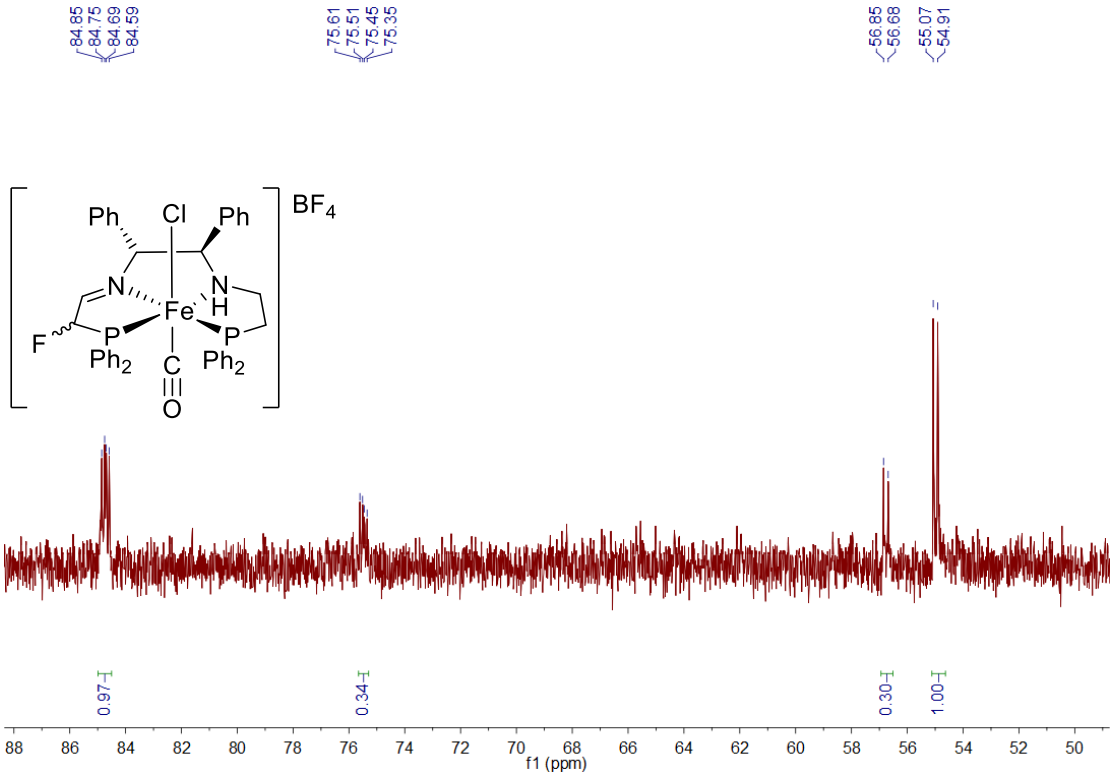


Figure S39 $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$) spectrum of **3**.

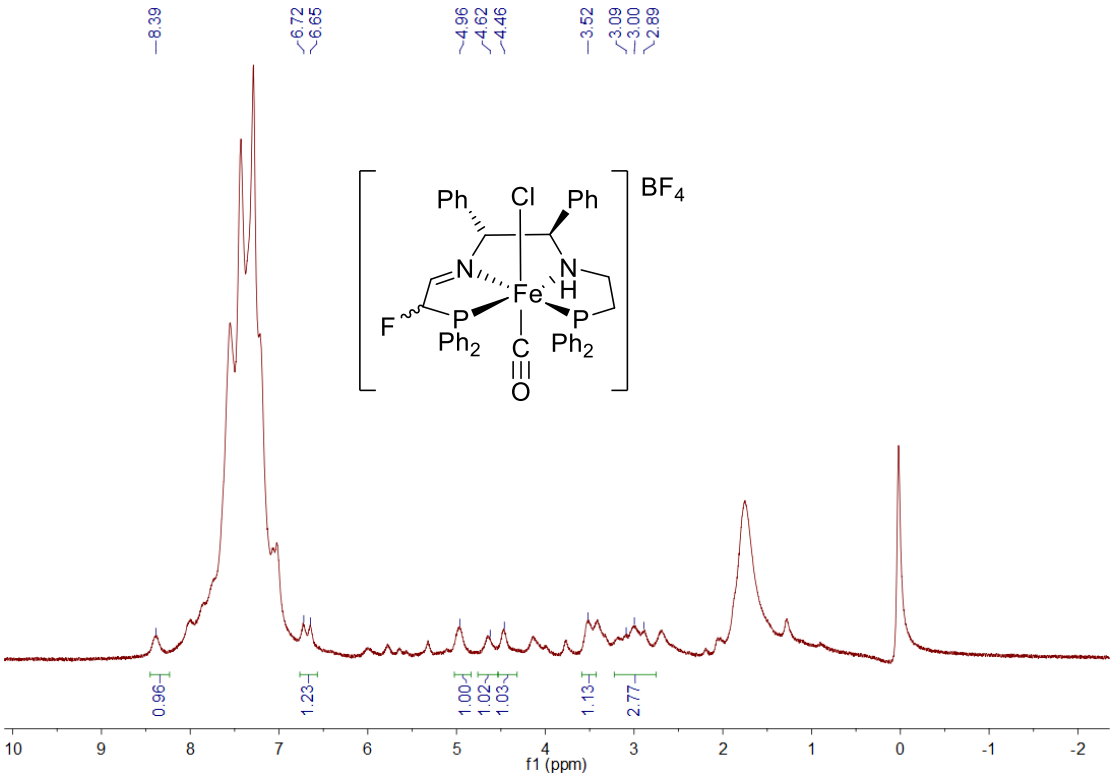


Figure S40 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3**.

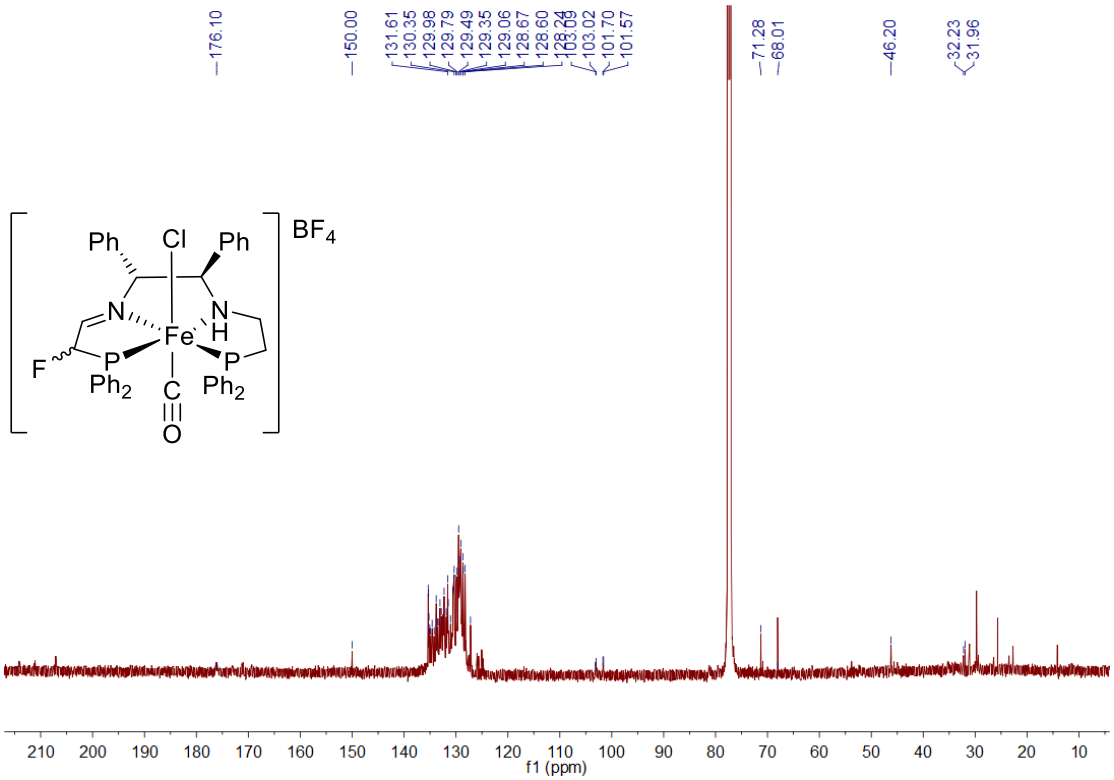


Figure S41 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **3**.

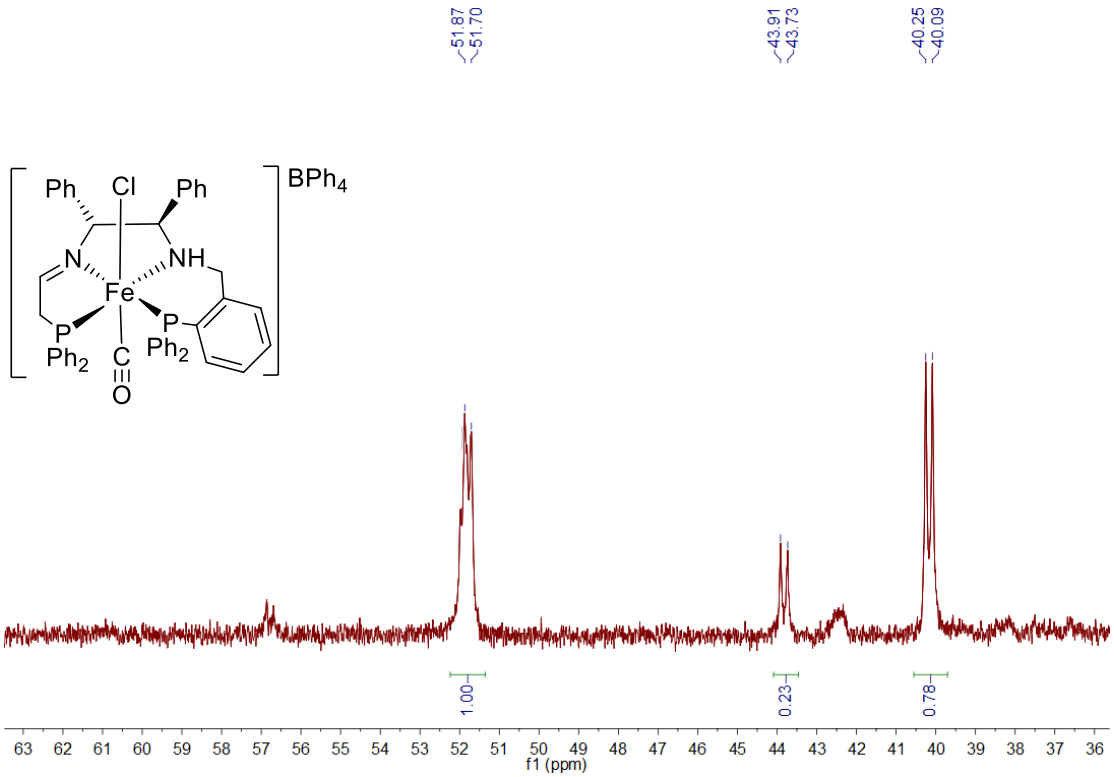


Figure S42 $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$) spectrum of **4**.

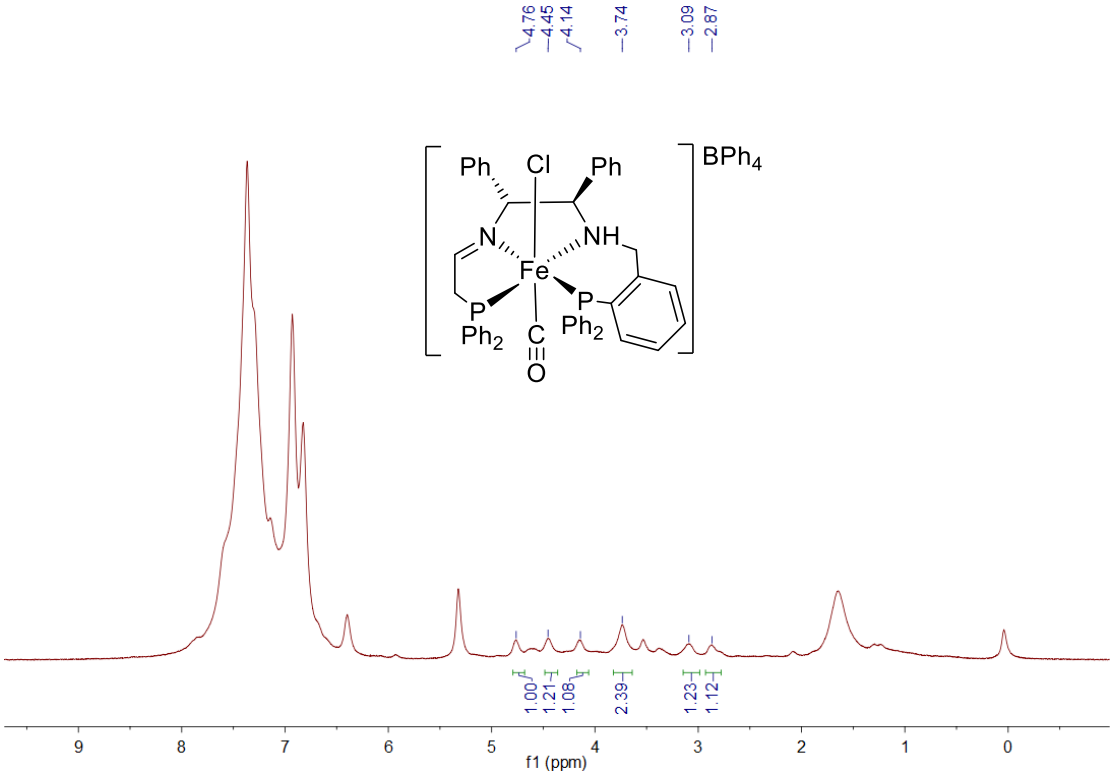


Figure S43 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4**.

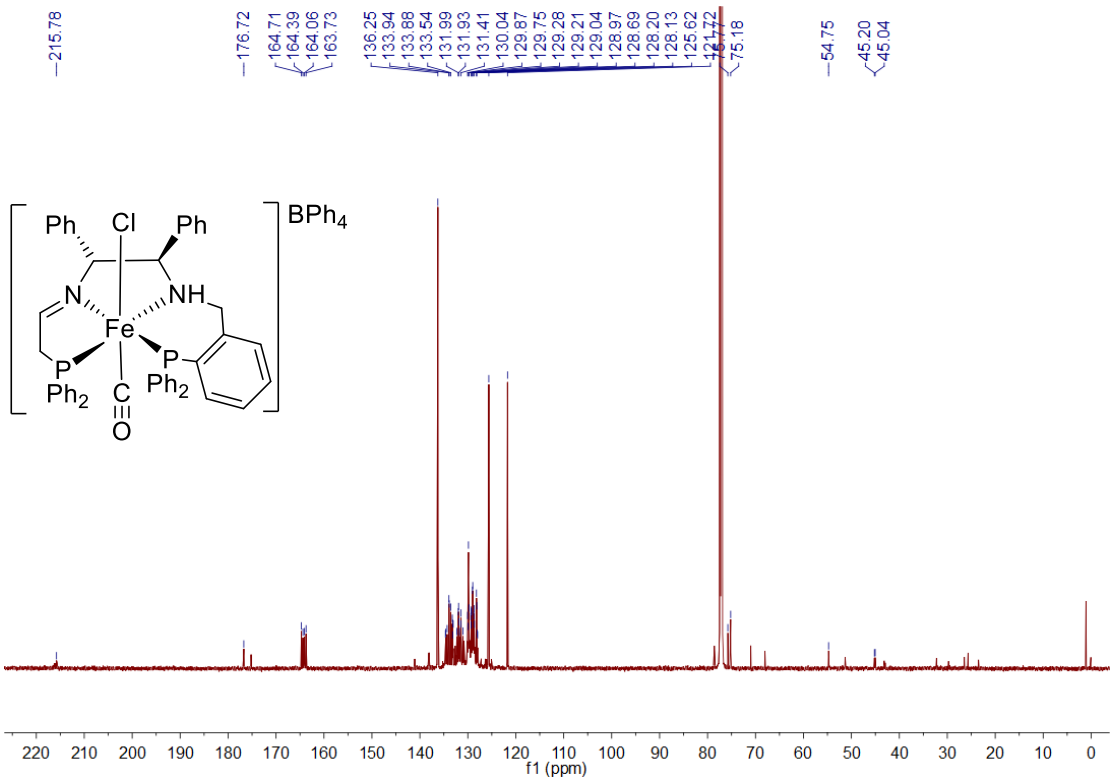


Figure S44 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **4**.

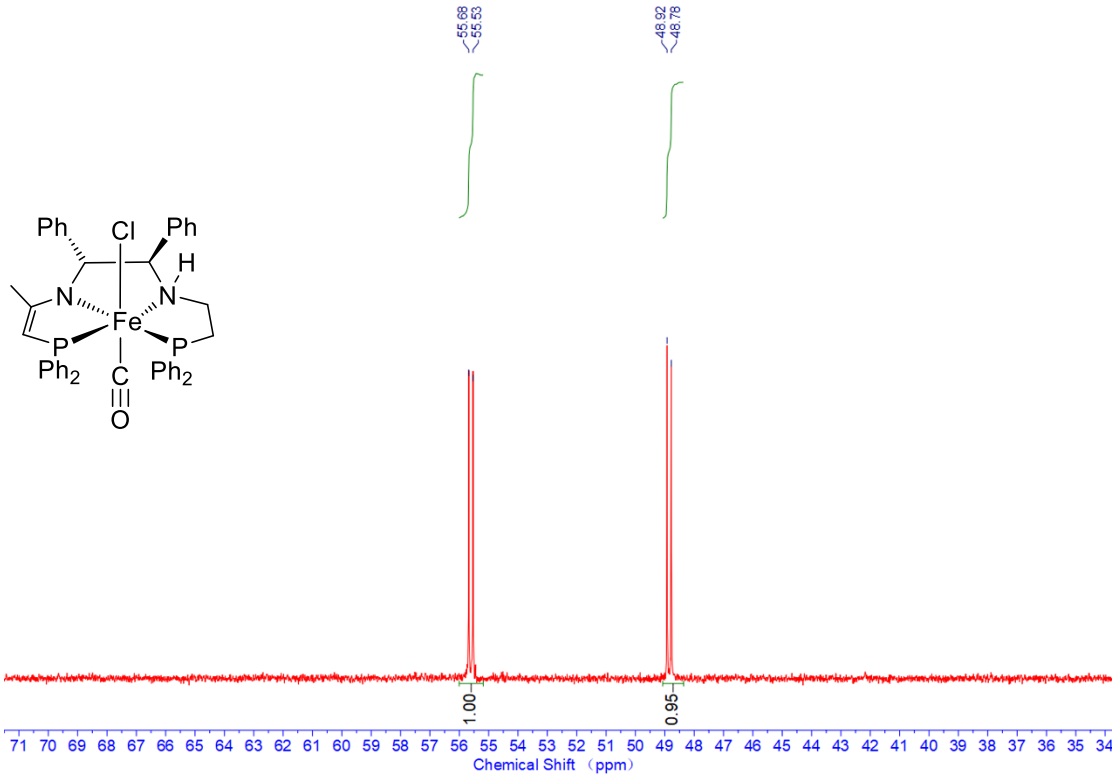


Figure S45 $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6) spectrum of **1a**.

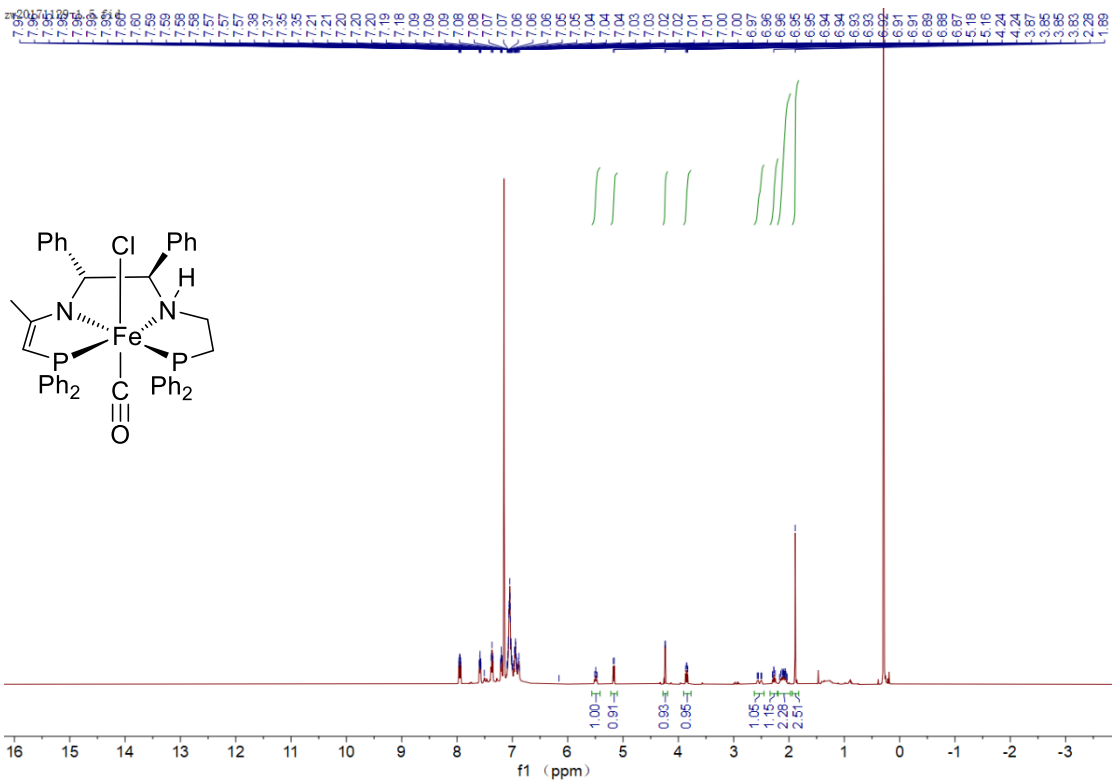


Figure S46 ^{1}H NMR (600 MHz, C_6D_6) spectrum of **1a**.

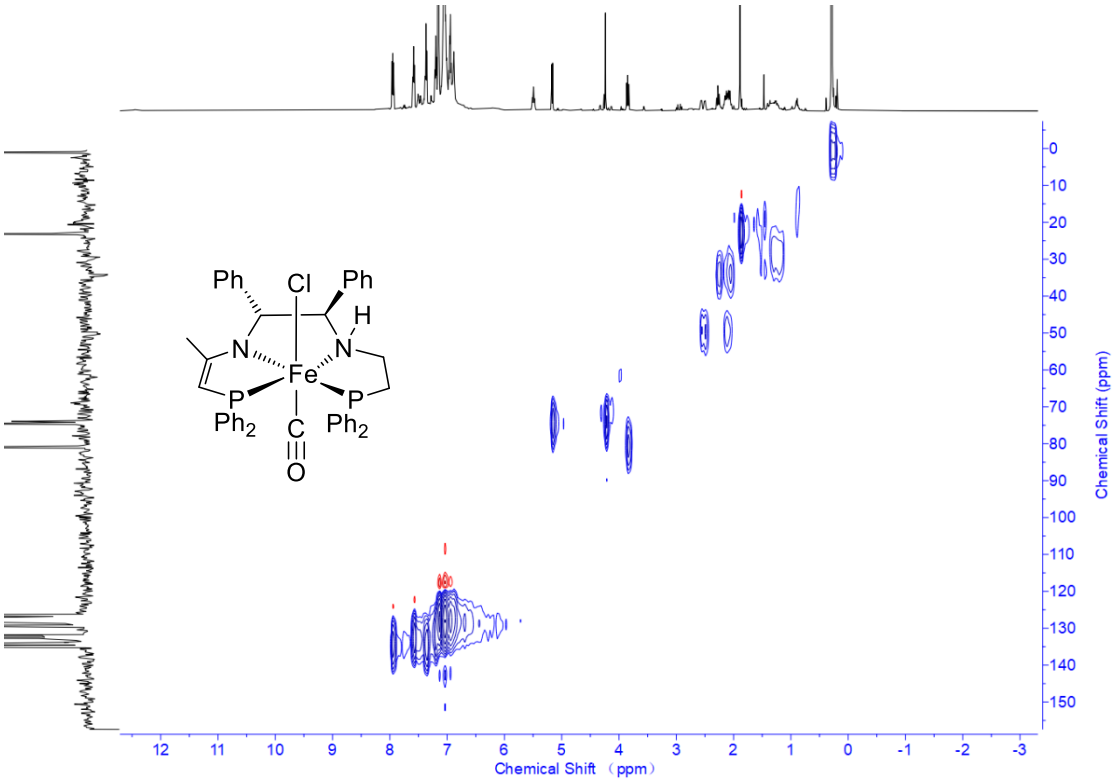


Figure S47 ^{1}H-^{13}C HSQC NMR (600 MHz, C_6D_6) spectrum of **1a**.

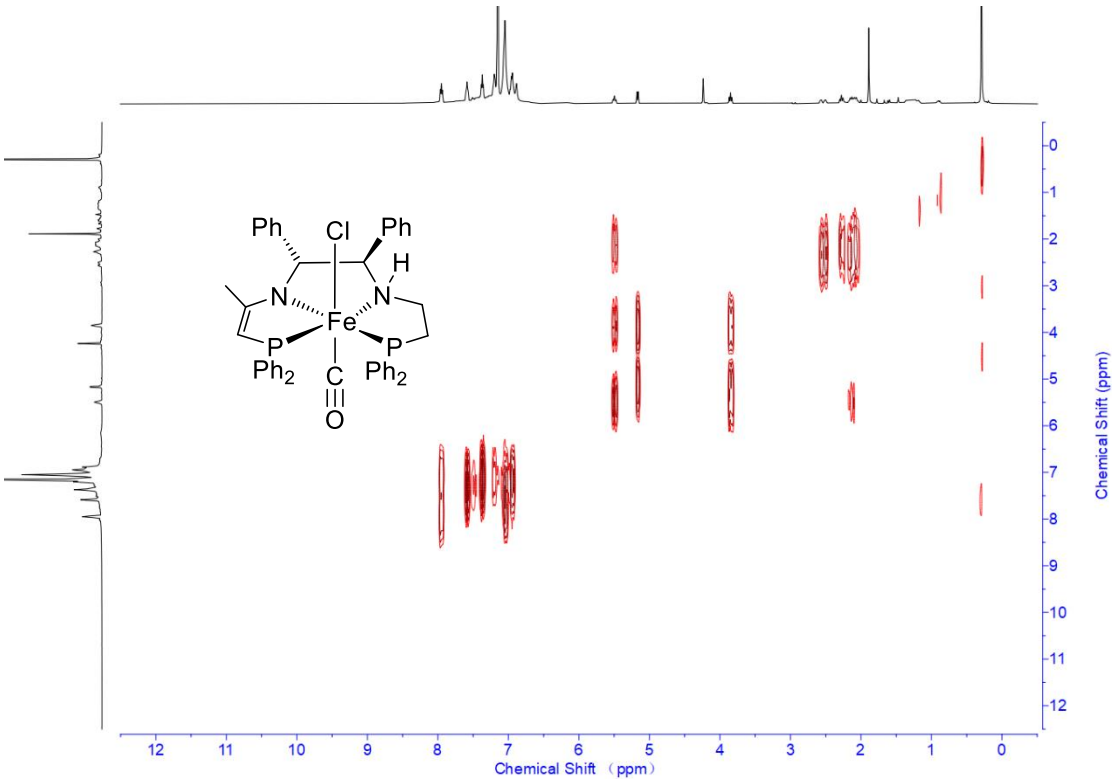


Figure S48 ^{1}H-^{1}H COSY NMR (600 MHz, C_6D_6) spectrum of **1a**.

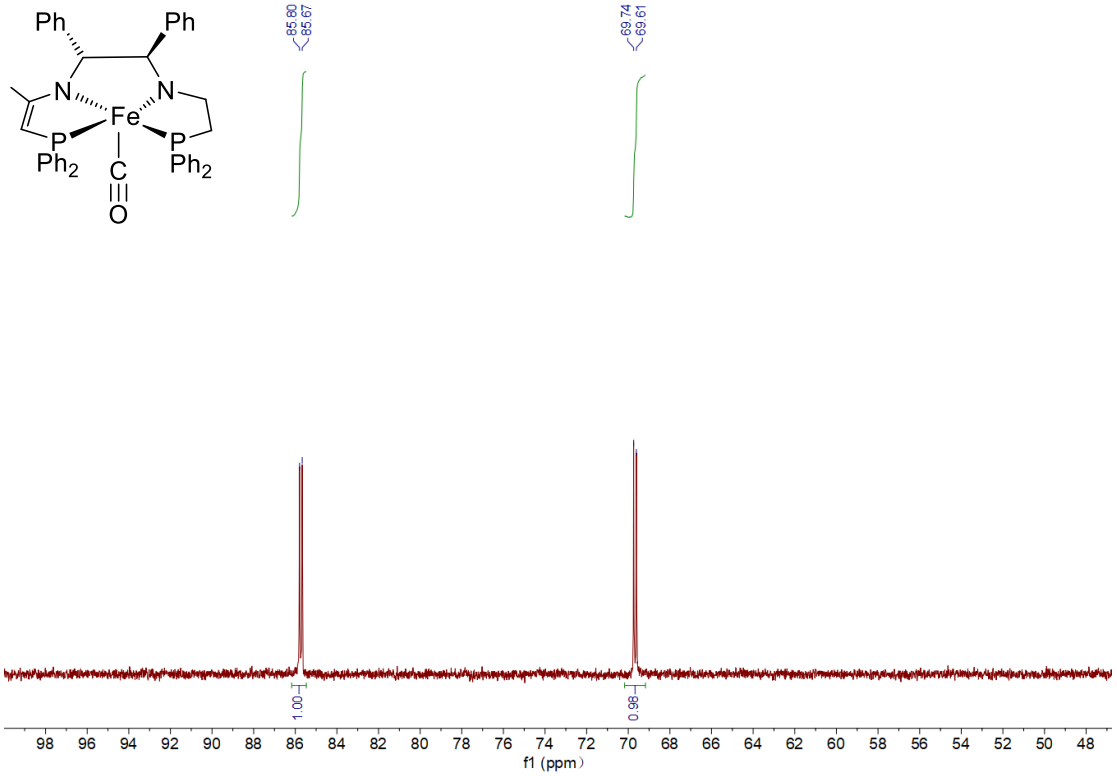


Figure S49 ^{31}P{^{1}H} NMR (243 MHz, C_6D_6) spectrum of **1b**.

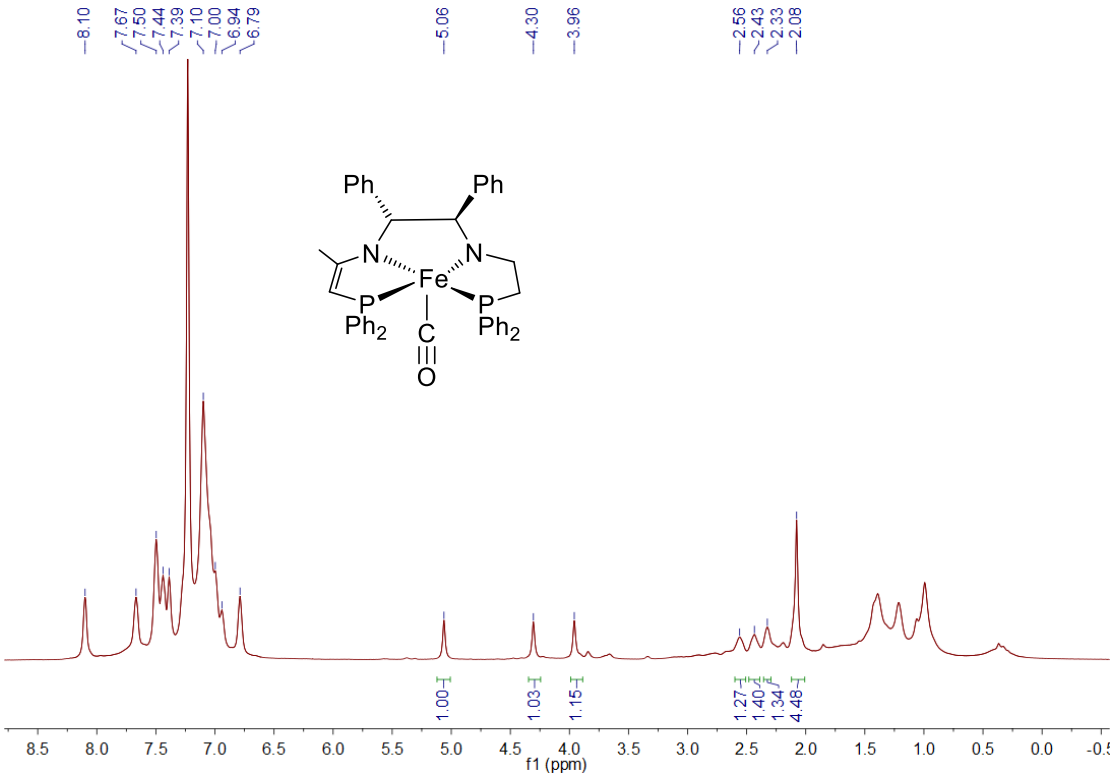


Figure S50 ^{1}H NMR (600 MHz, C_6D_6) spectrum of **1b**.

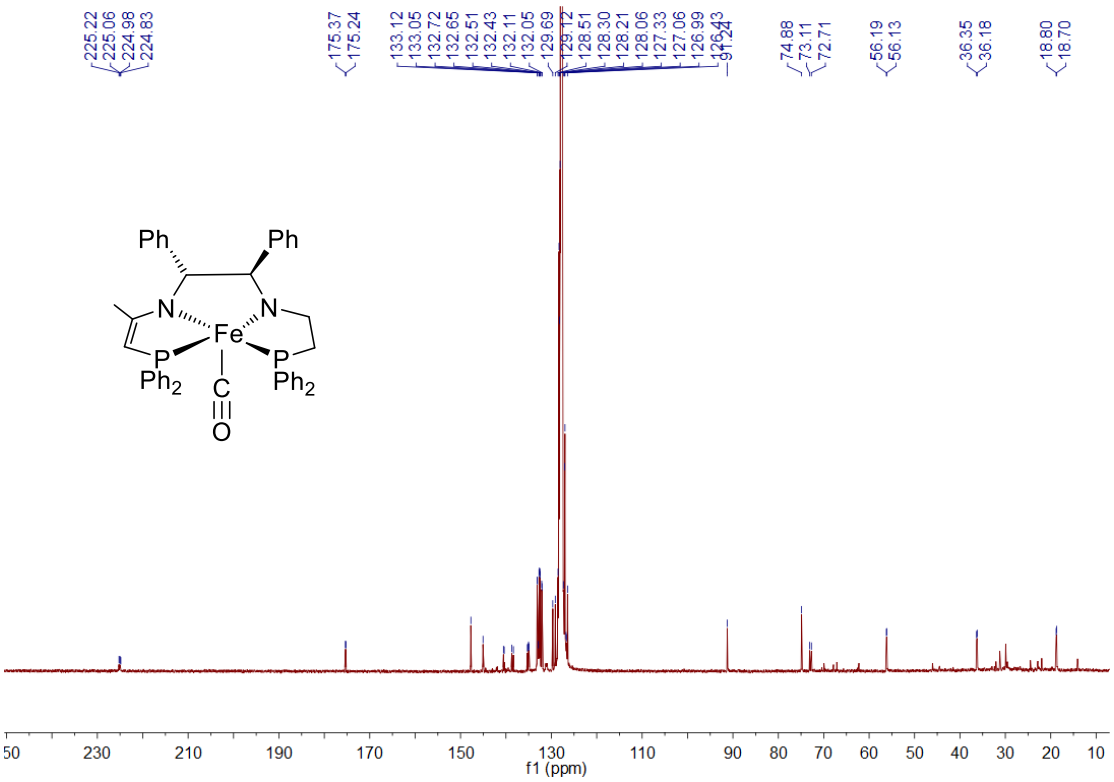


Figure S51 ^{13}C{^{1}H} NMR (151 MHz, C_6D_6) spectrum of **1b**.

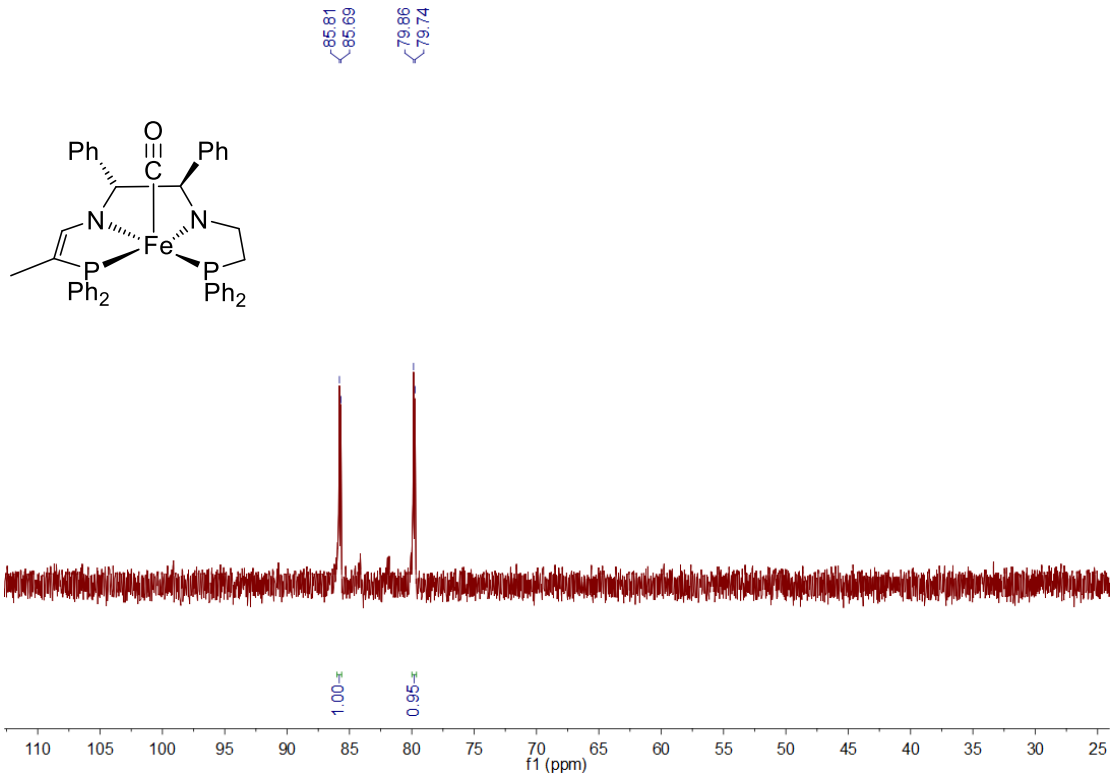


Figure S52 $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6) spectrum of **2a'**.

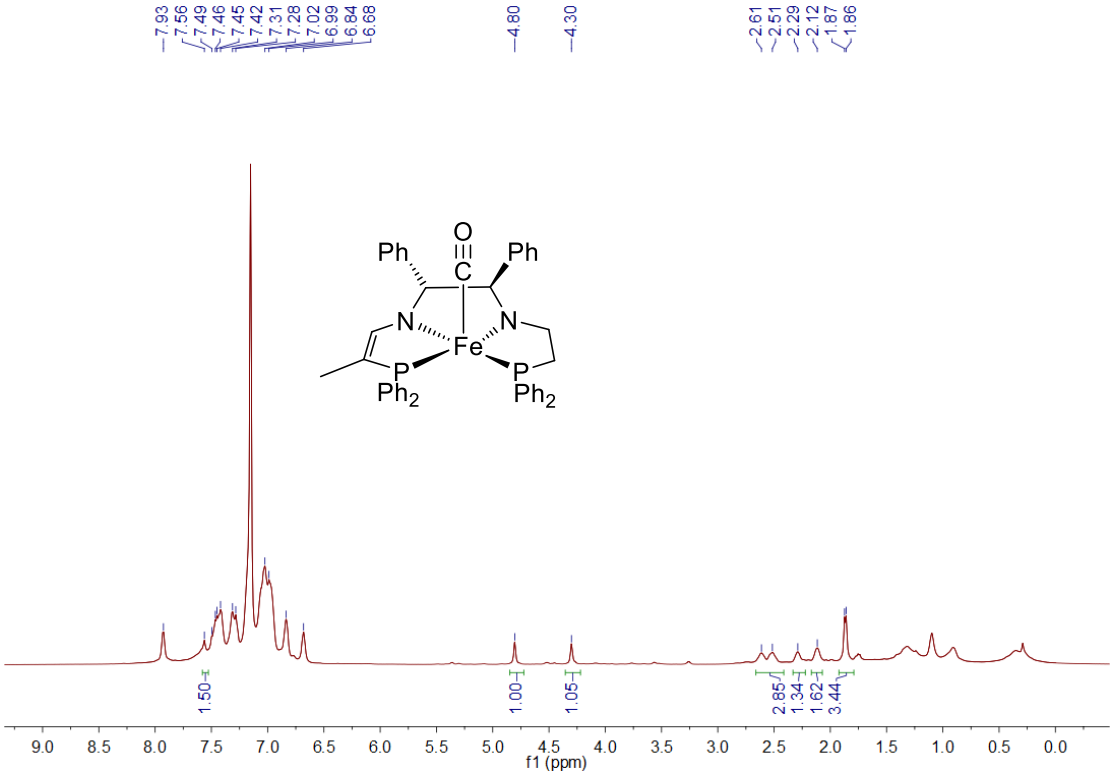


Figure S53 ^{1}H NMR (600 MHz, C_6D_6) spectrum of **2a'**.

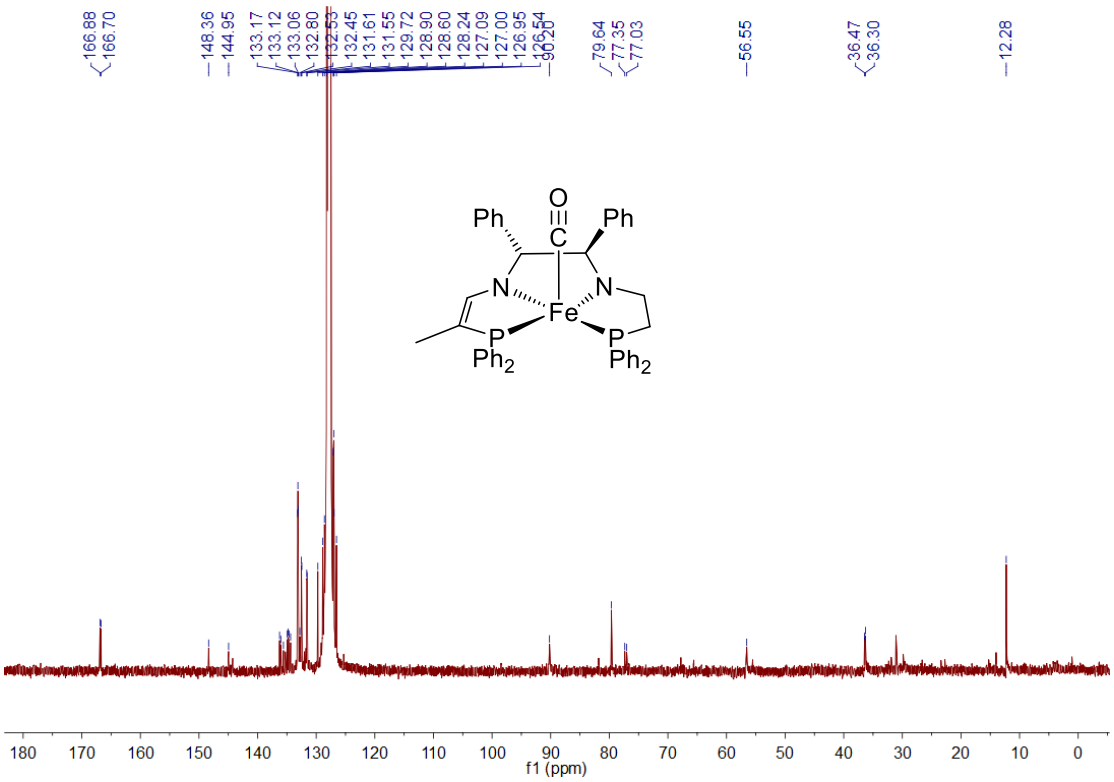


Figure S54 $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6) spectrum of **2a'**.

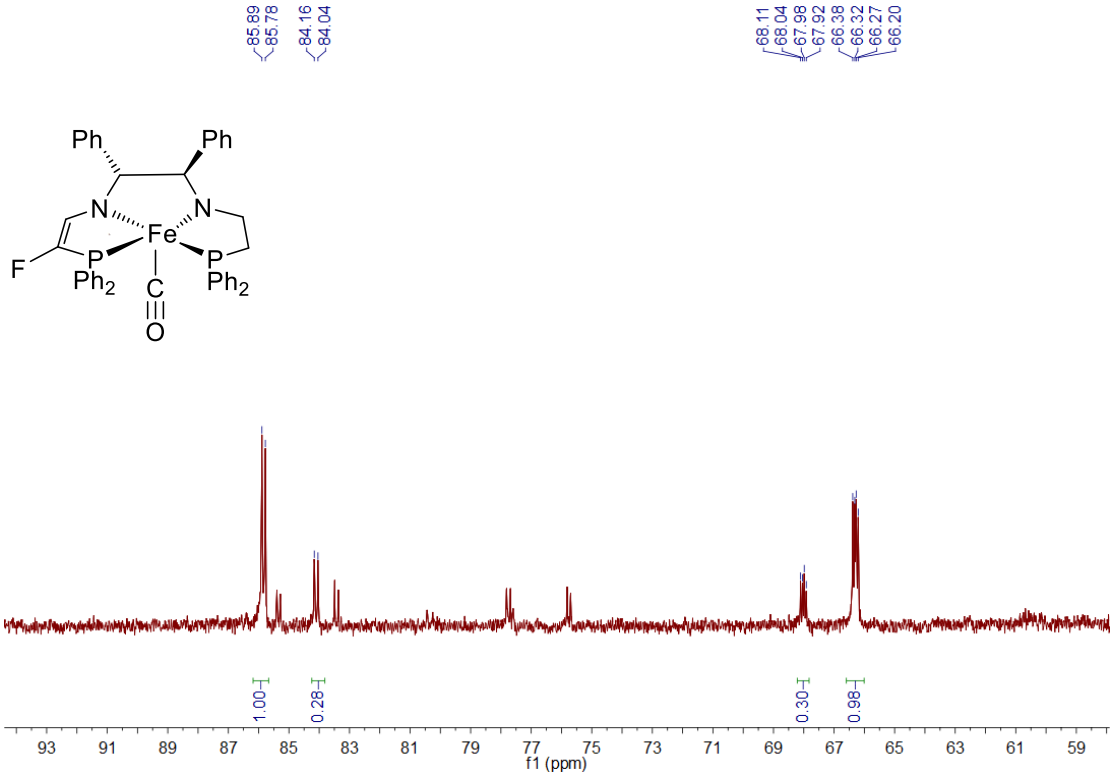


Figure S55 $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6) spectrum of **3a**.

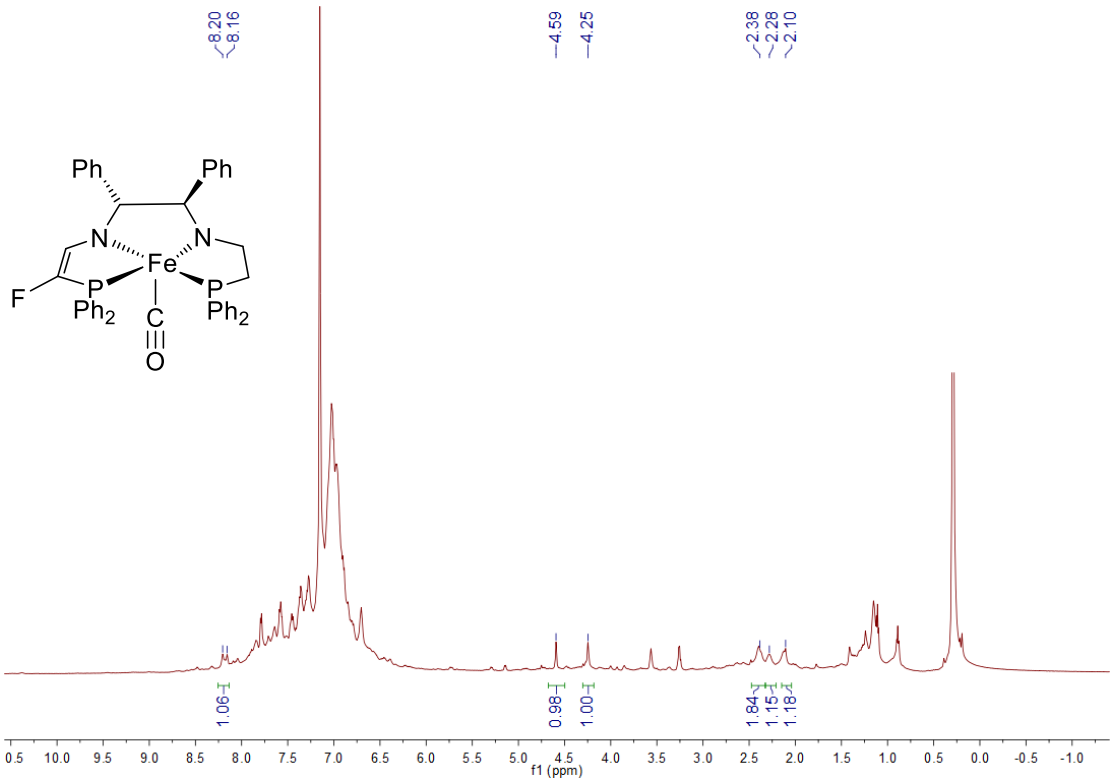


Figure S56 ^{1}H NMR (600 MHz, C_6D_6) spectrum of **3a**.

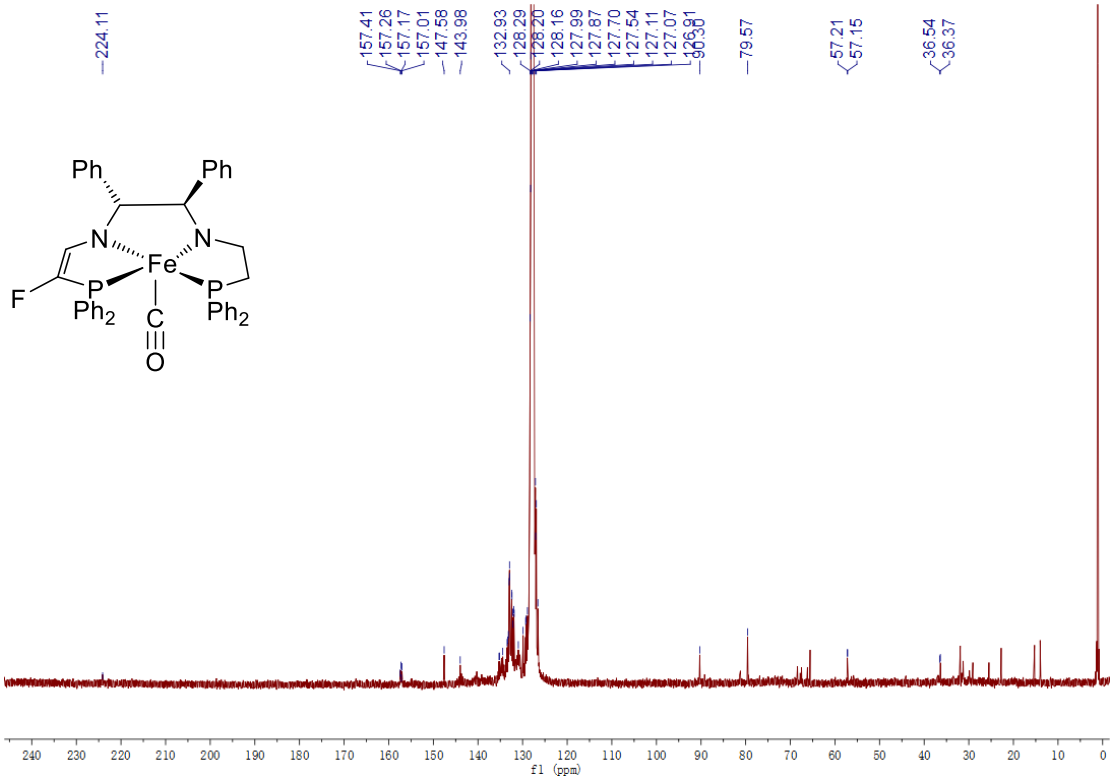


Figure S57 $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6) spectrum of **3a**.

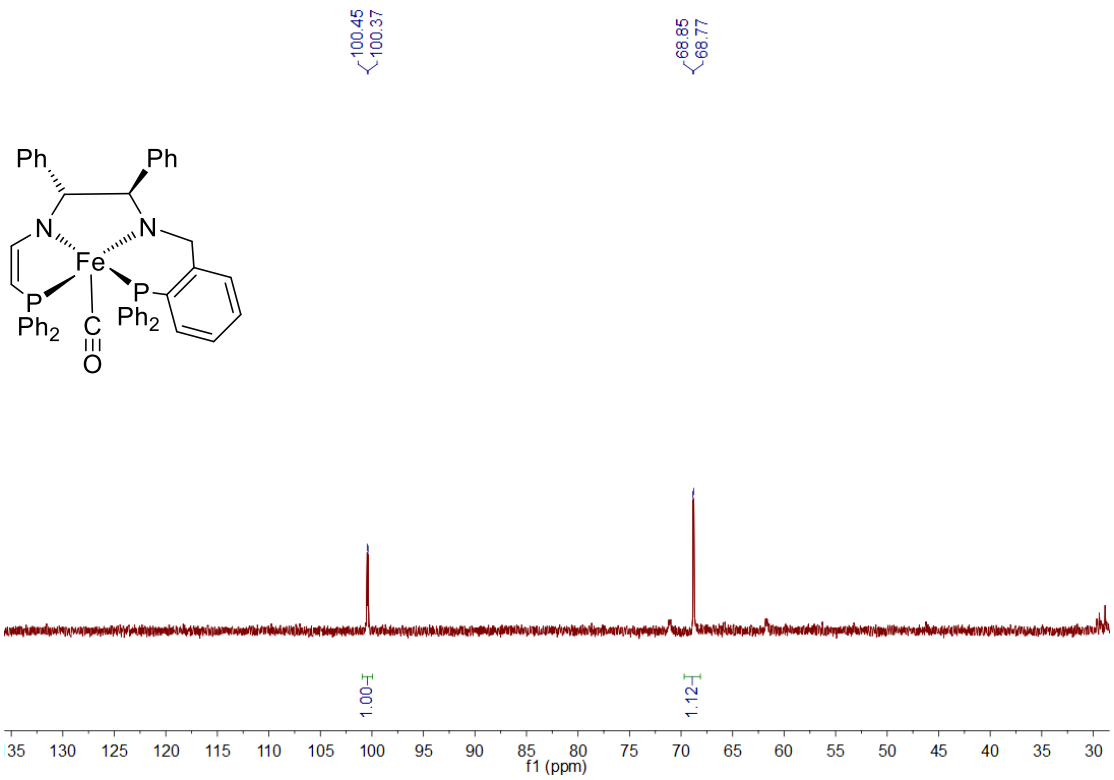


Figure S58 $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6) spectrum of **4a**.

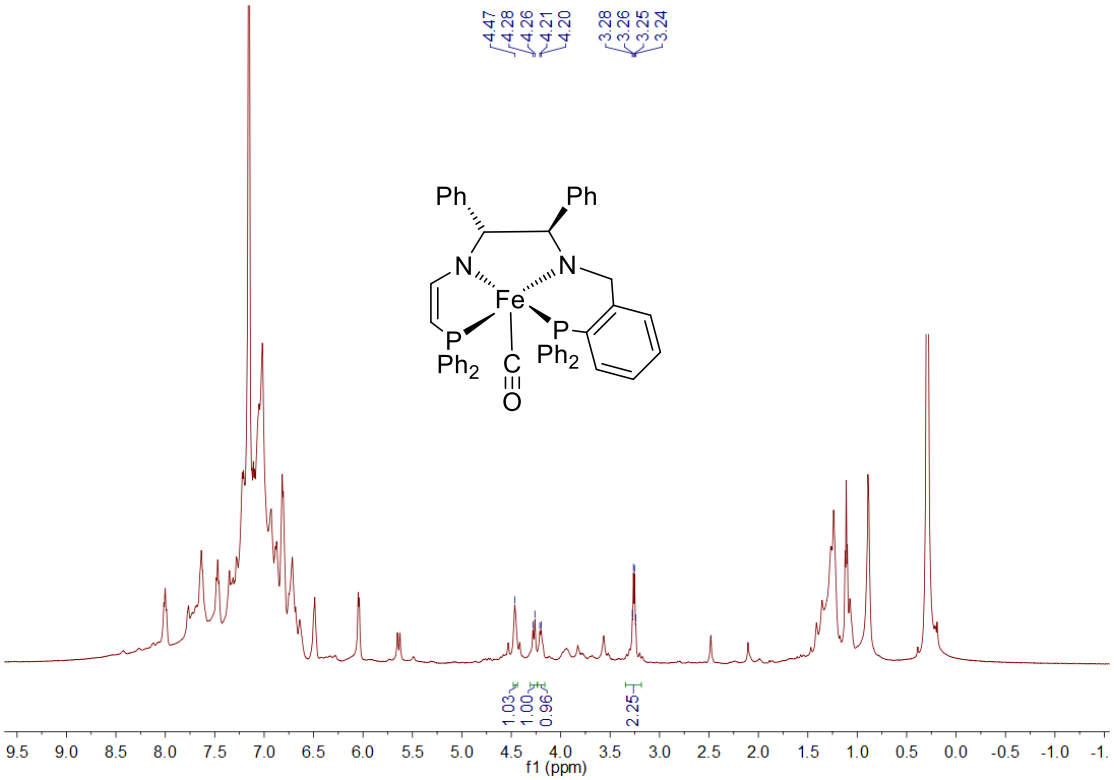


Figure S59 ^{1}H NMR (600 MHz, C_6D_6) spectrum of **4a**.

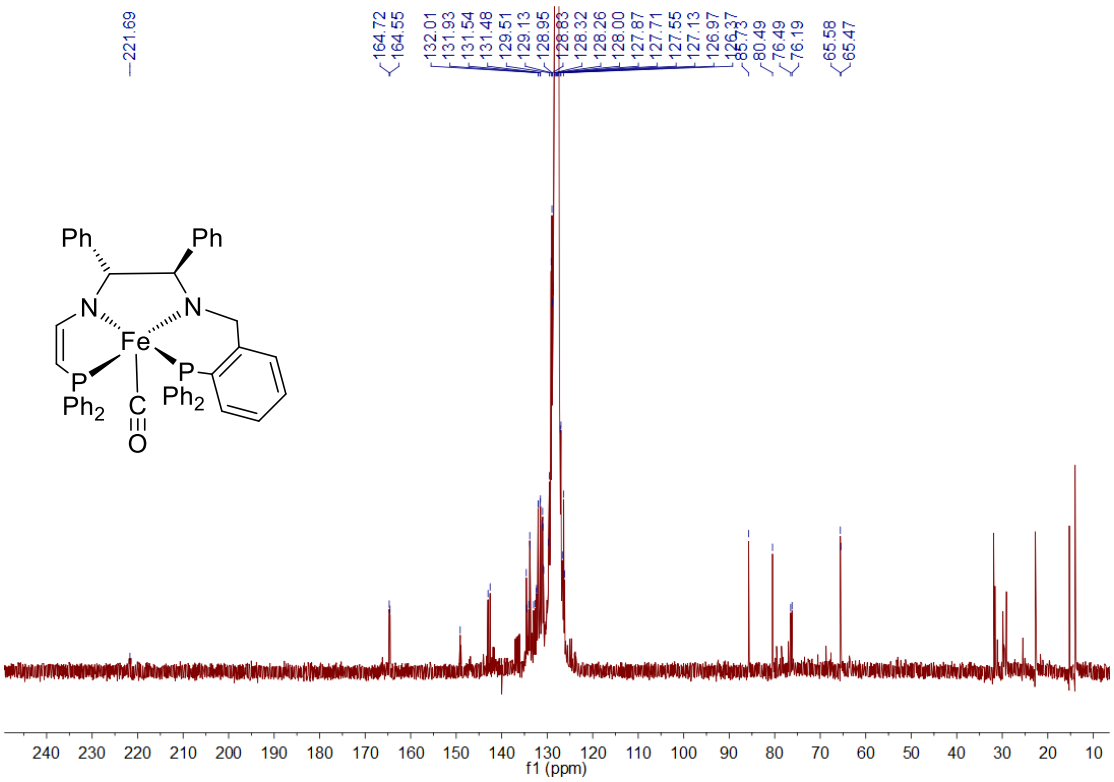


Figure S60 $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6) spectrum of **4a**.

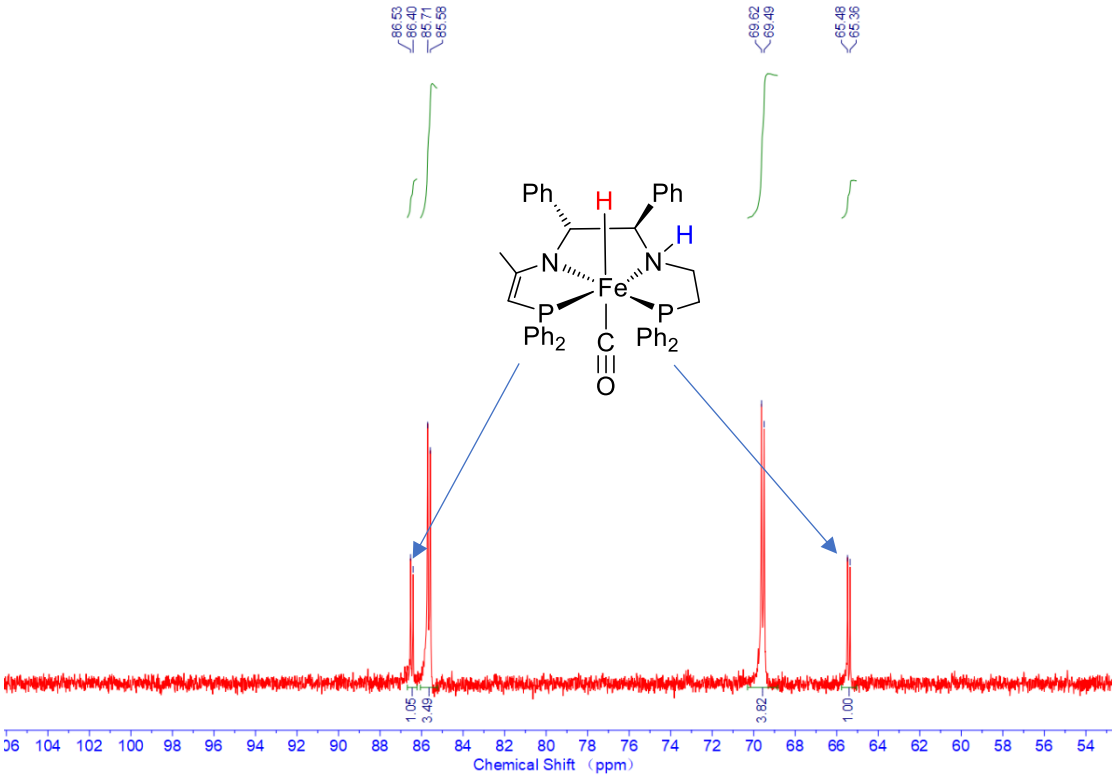


Figure S61 $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6) spectrum of the mixture of **1b** with isopropanol.

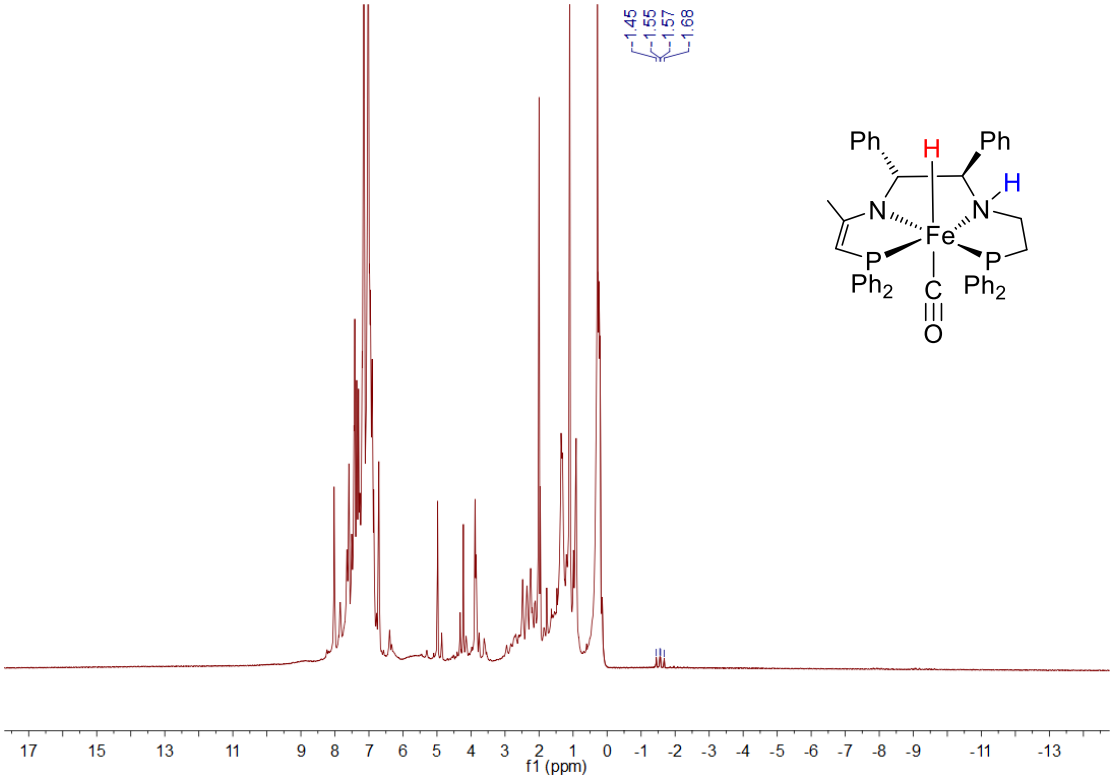


Figure S62 ^{1}H NMR (600 MHz, C_6D_6) spectrum of the mixture of **1b** with isopropanol.

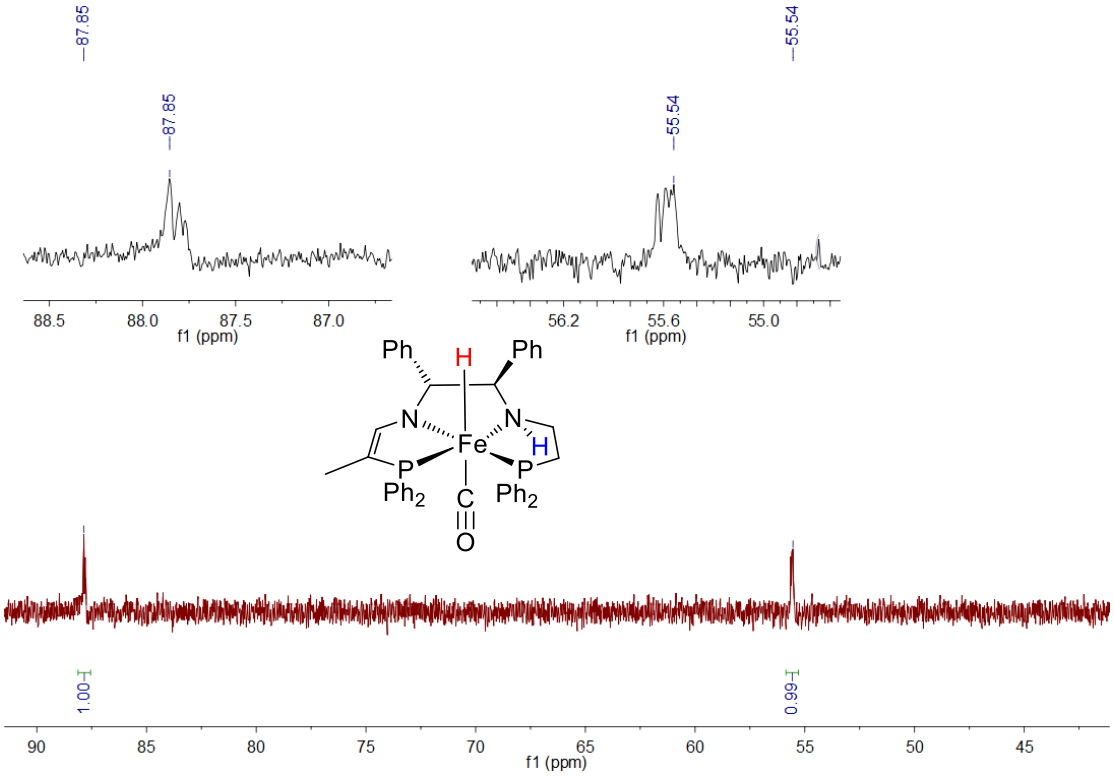


Figure S63 $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6) spectrum of **2b'**.

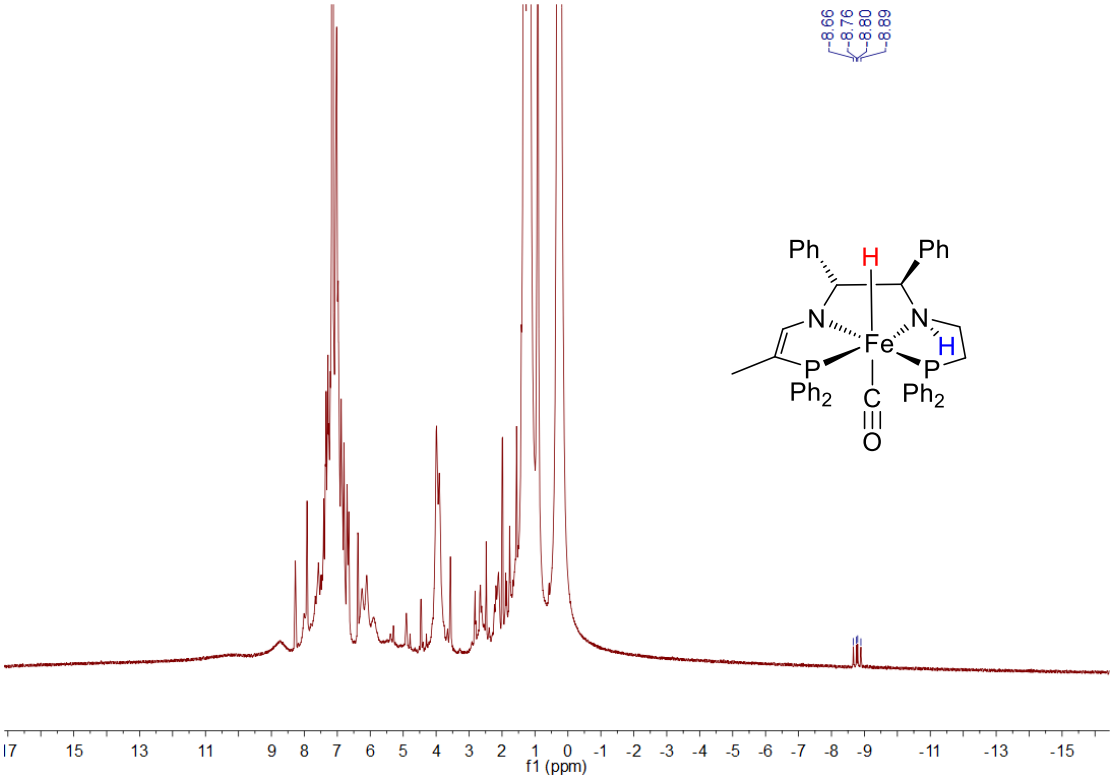


Figure S64 ^{1}H NMR (600 MHz, C_6D_6) spectrum of **2b'**.

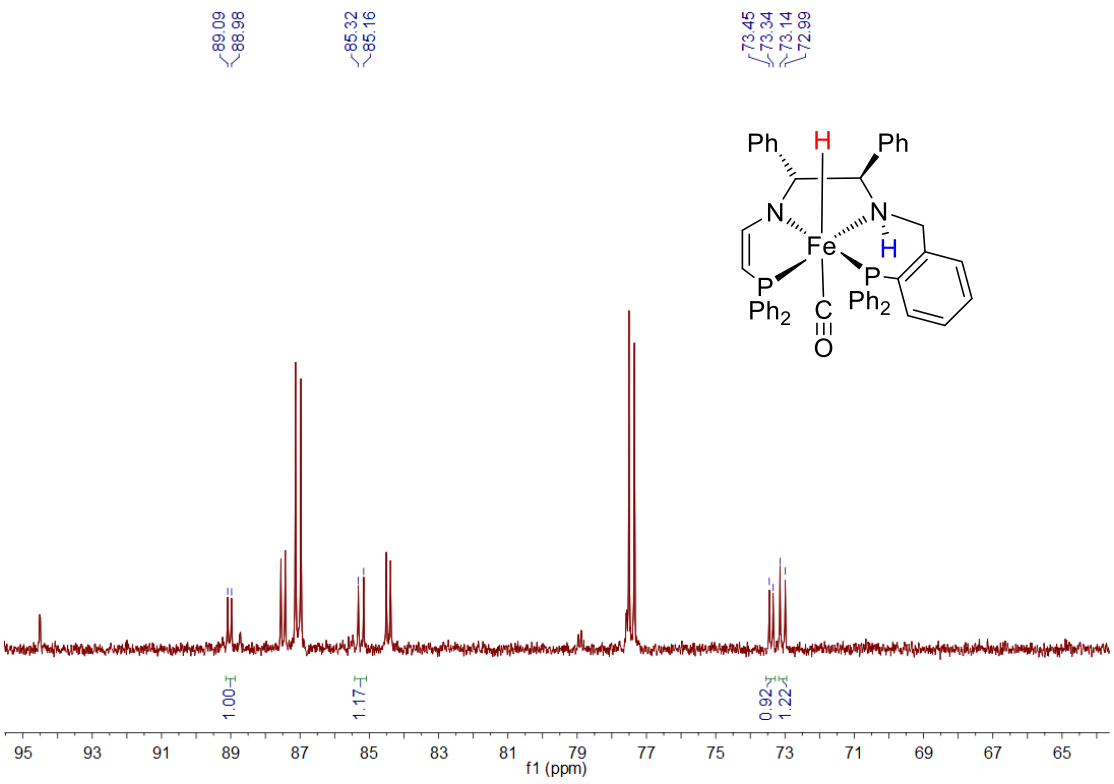


Figure S65 $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6) spectrum of **4b'**.

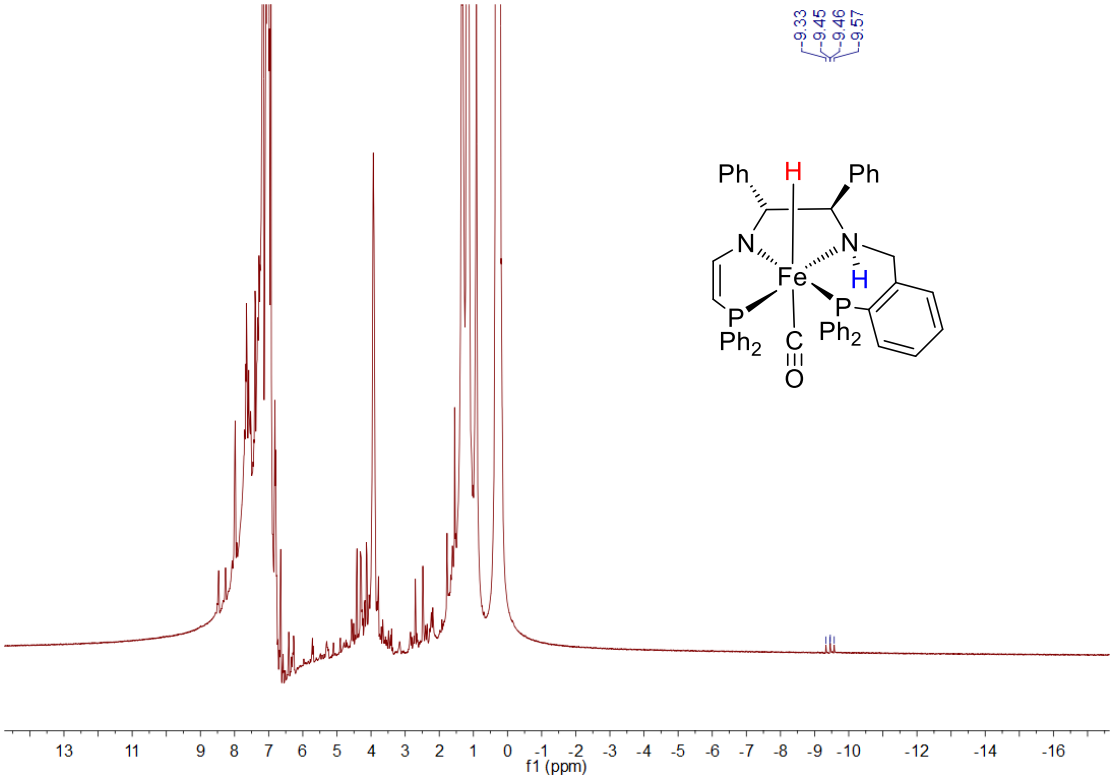


Figure S66 ^{1}H NMR (600 MHz, C_6D_6) spectrum of **4b'**.