Supporting Information

Synthesis of iridium and rhodium complexes with new chiral phosphine-NHC ligands based on 1,1'-binaphthyl framework and their application in asymmetric hydrogenation

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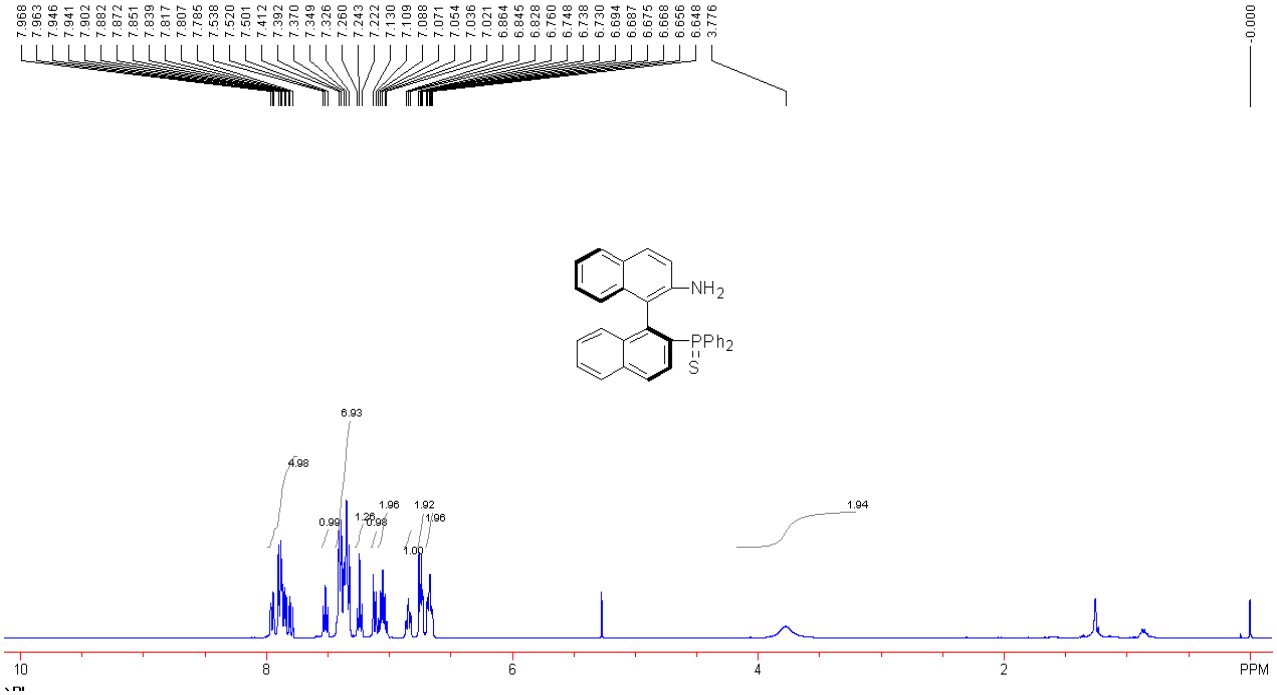
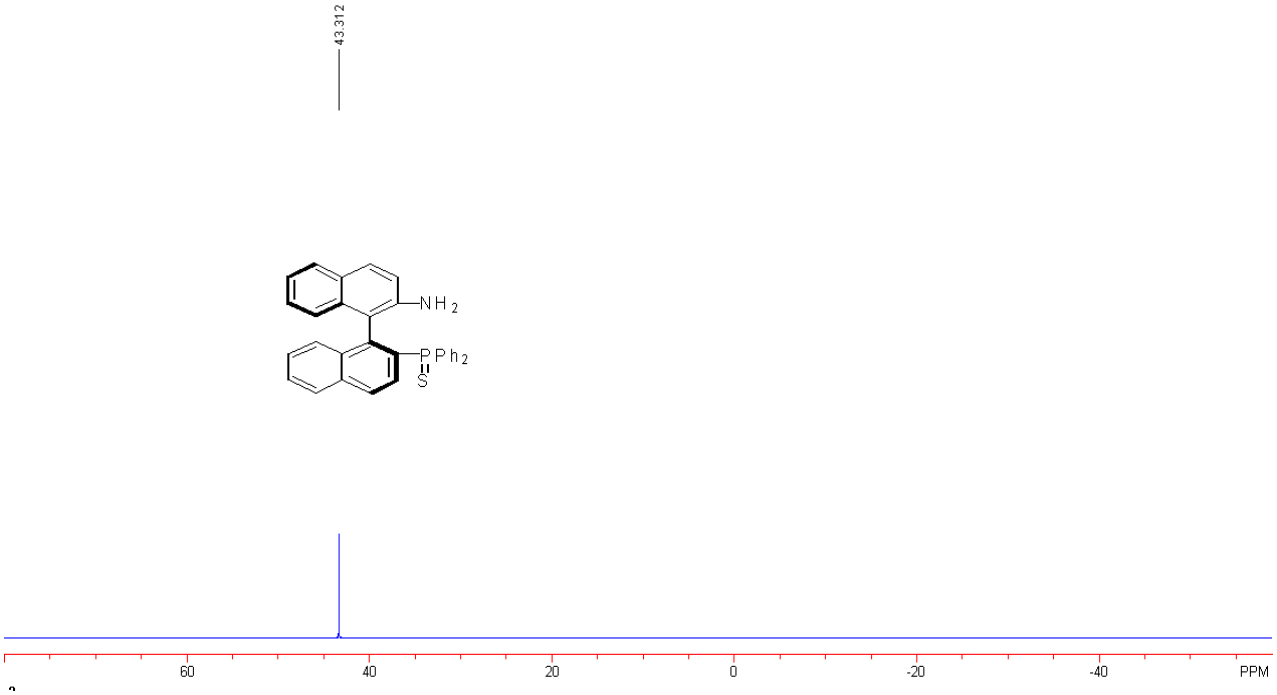
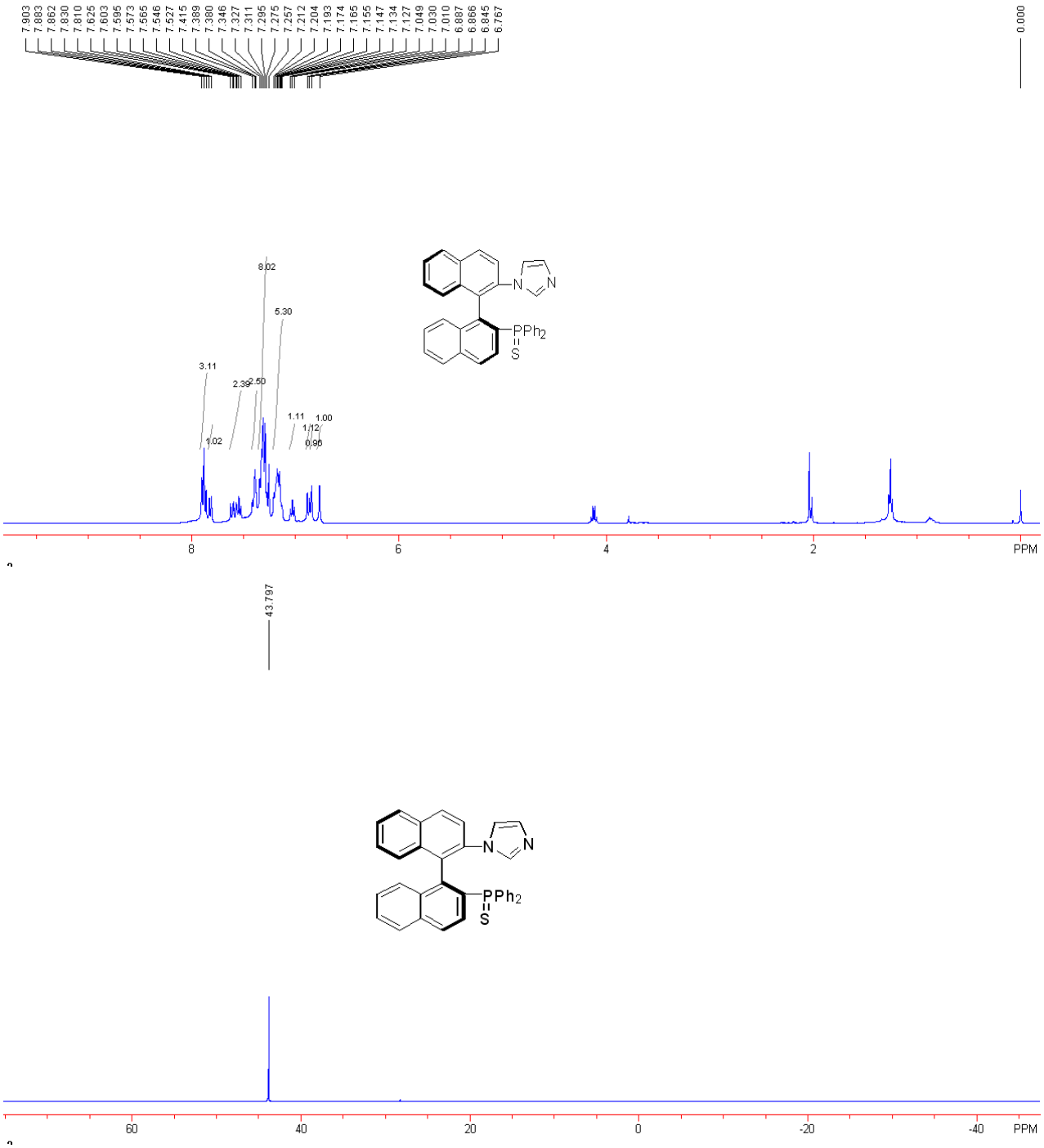
Content

^{1}H NMR and ^{31}P NMR spectra of compound **2**

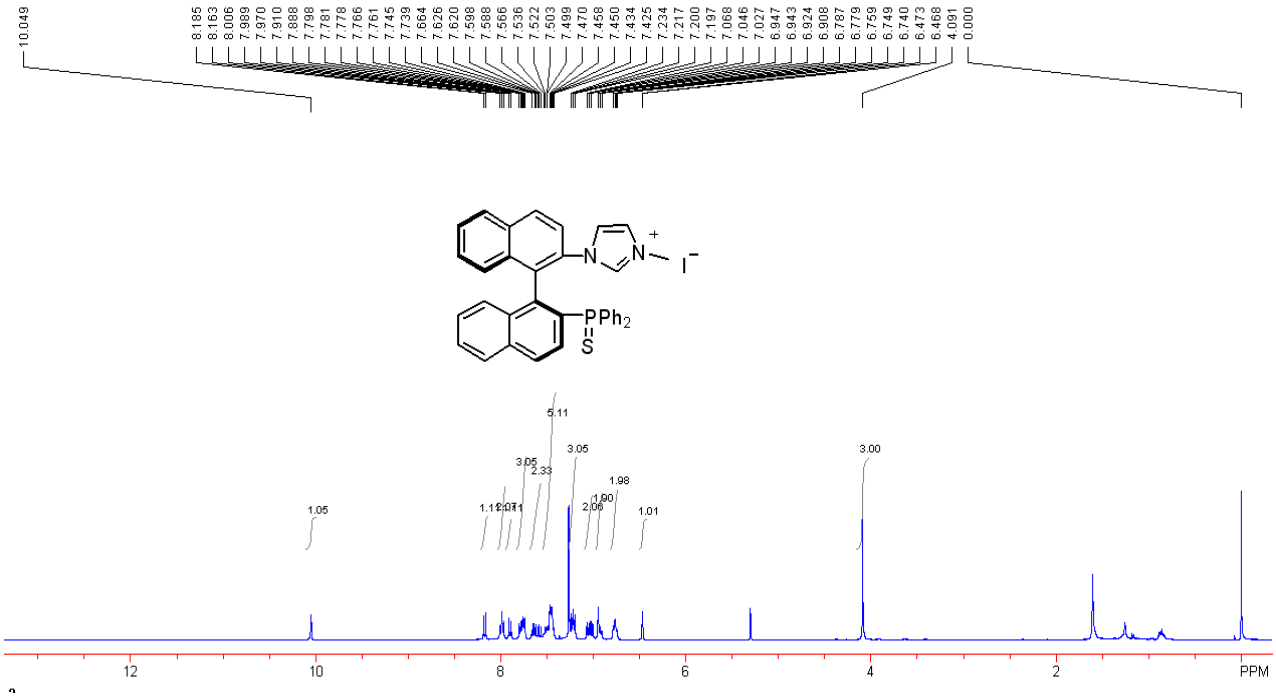


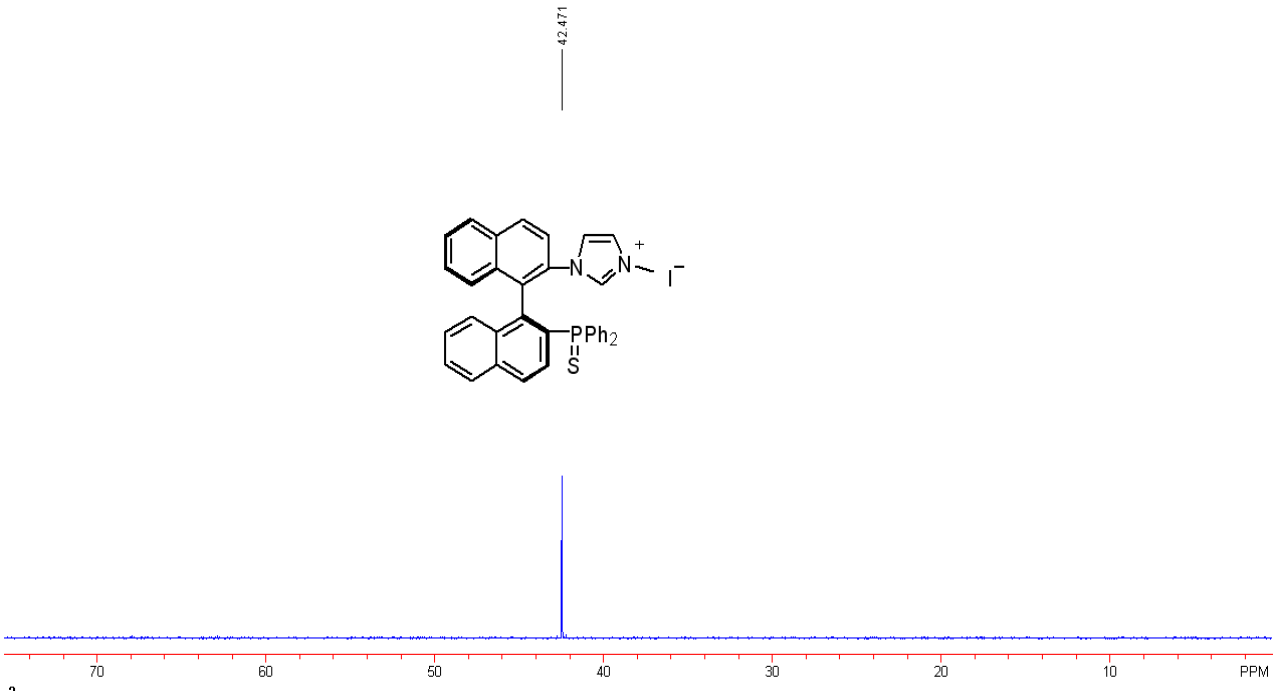


^{1}H NMR and ^{31}P NMR spectra of compound **3**

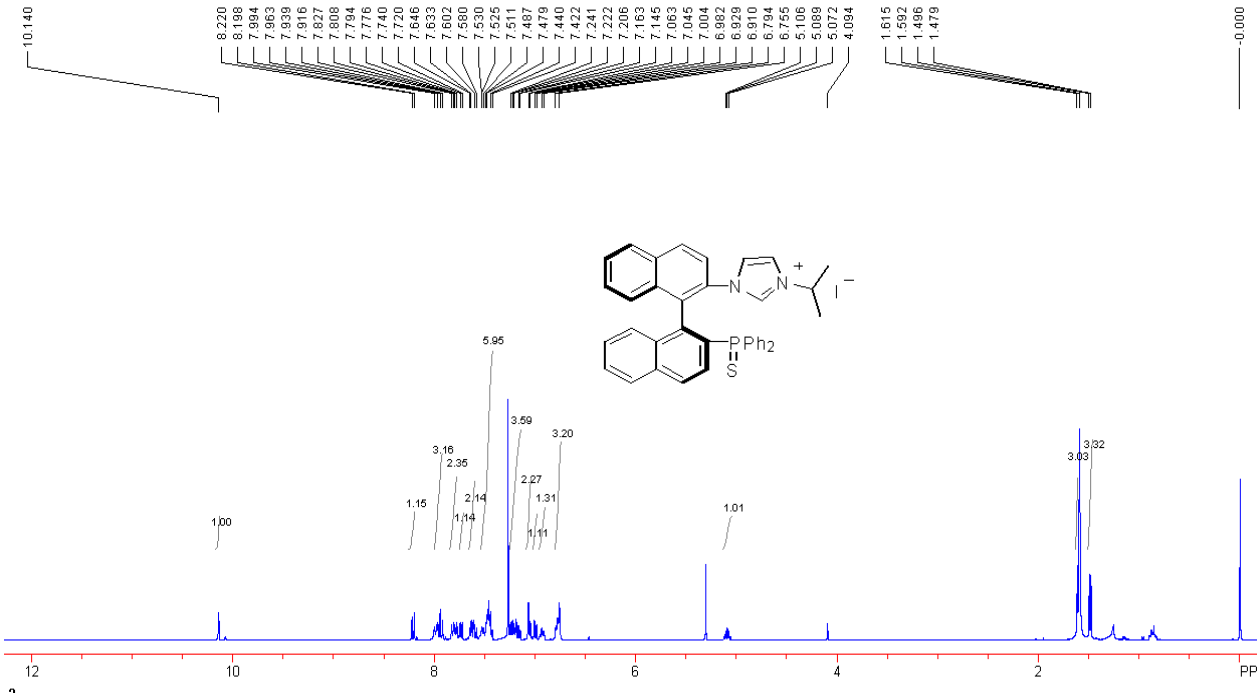


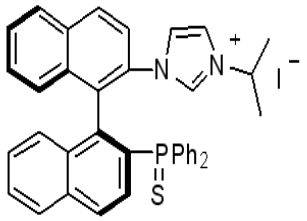
^{1}H NMR and ^{31}P NMR spectra of compound **4a**

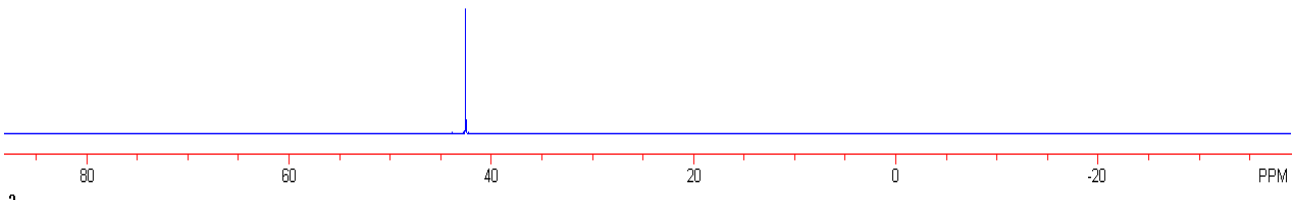




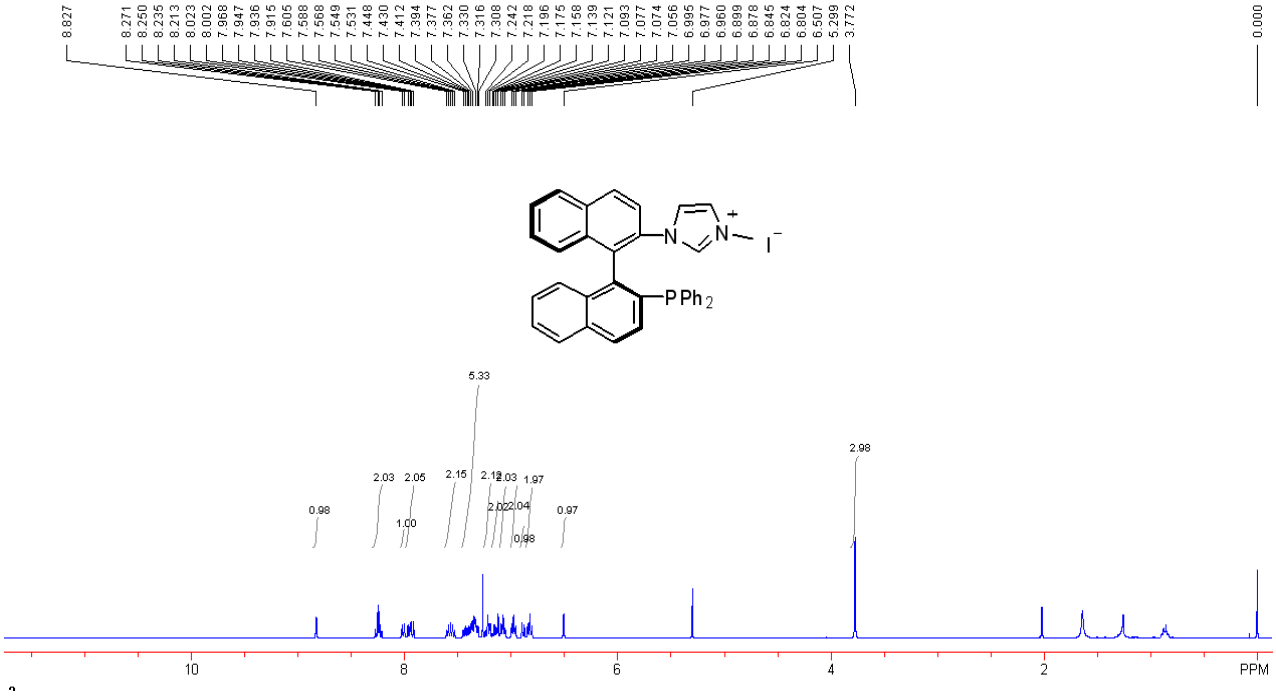
^{1}H NMR and ^{31}P NMR spectra of compound **4b**

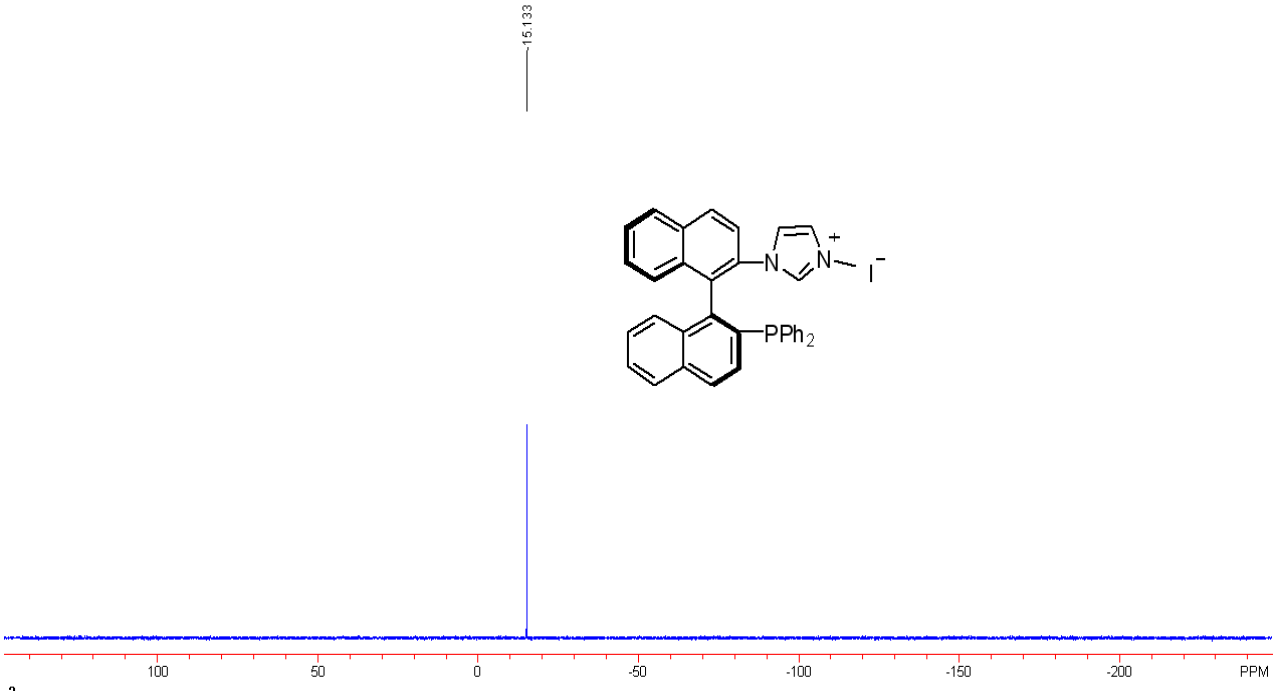




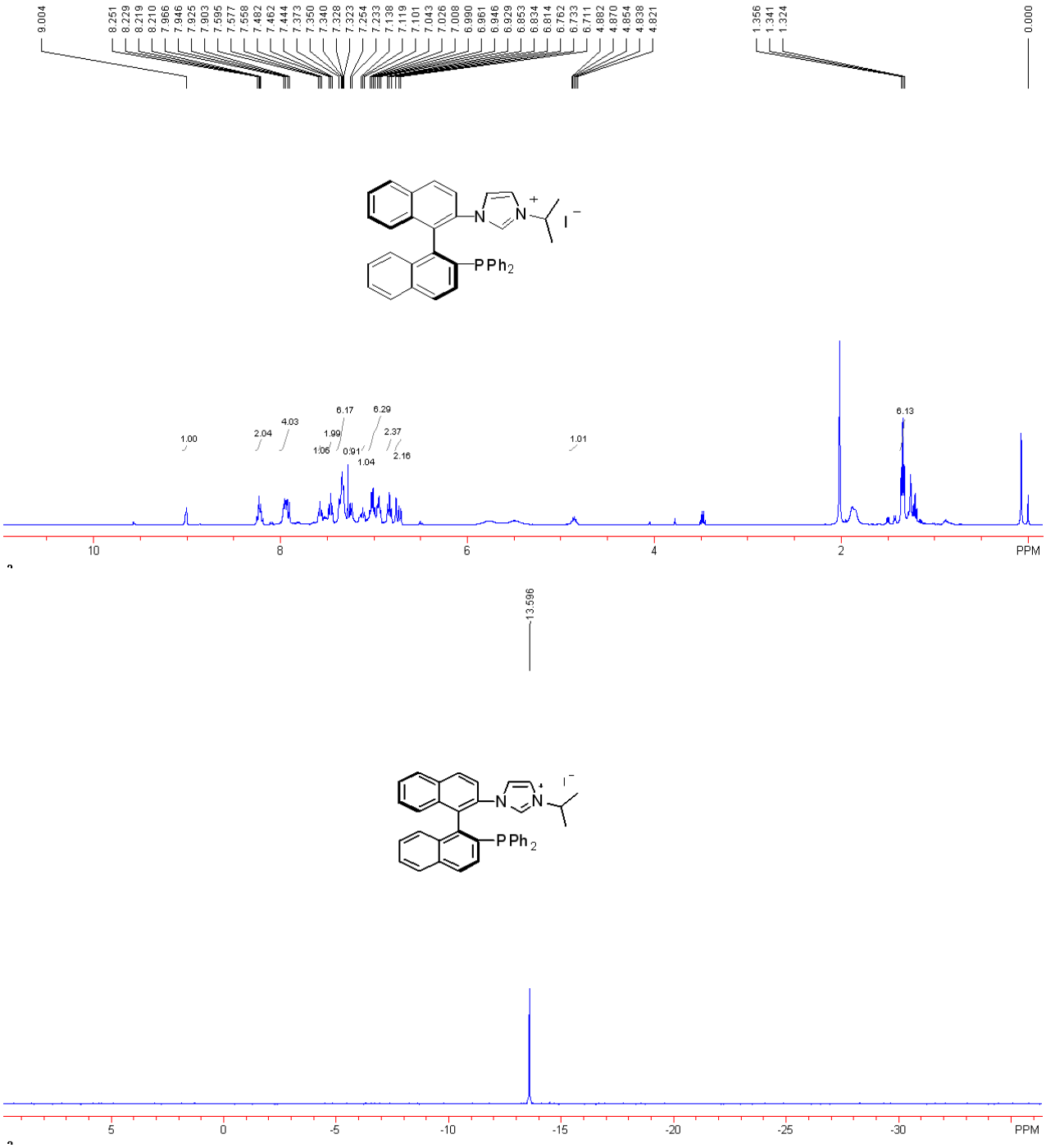


^{1}H NMR and ^{31}P NMR spectra of compound **5a**

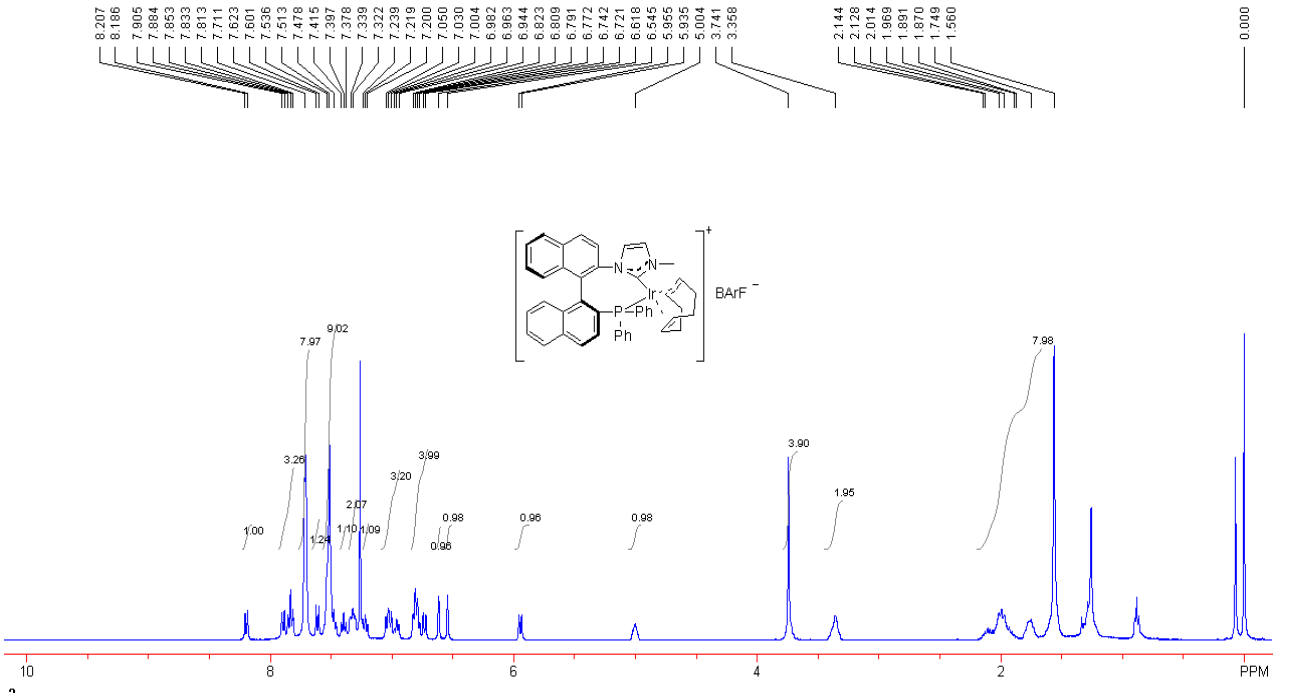


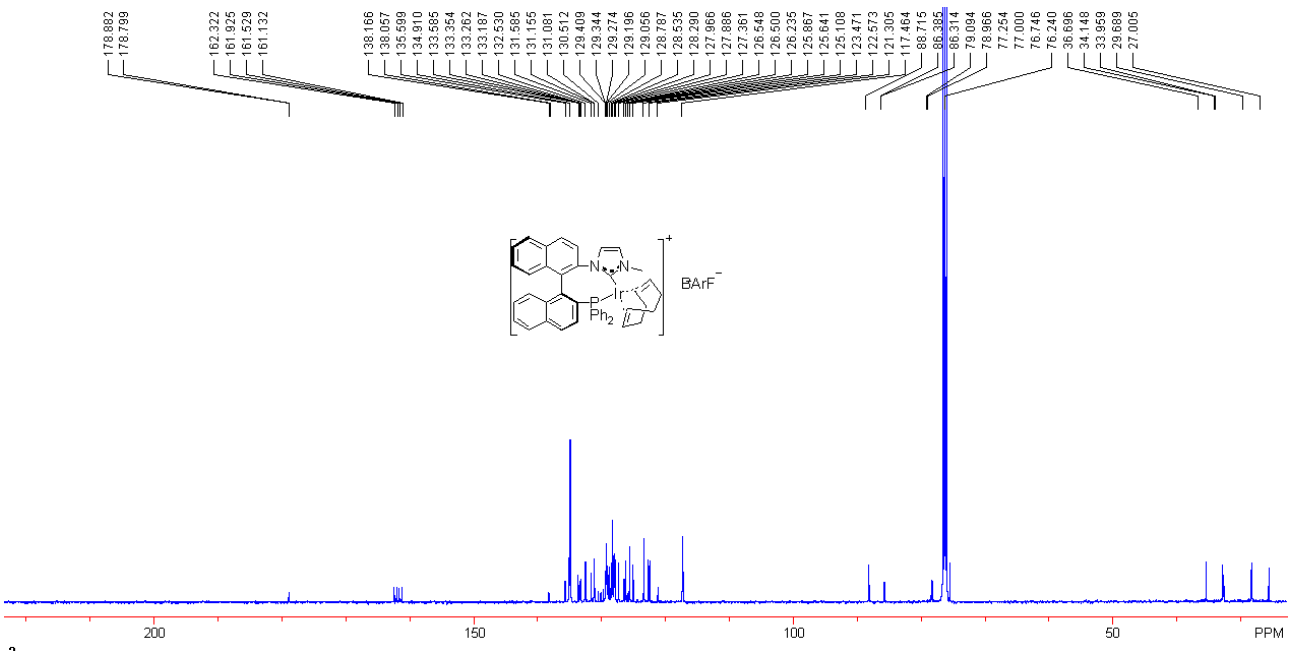


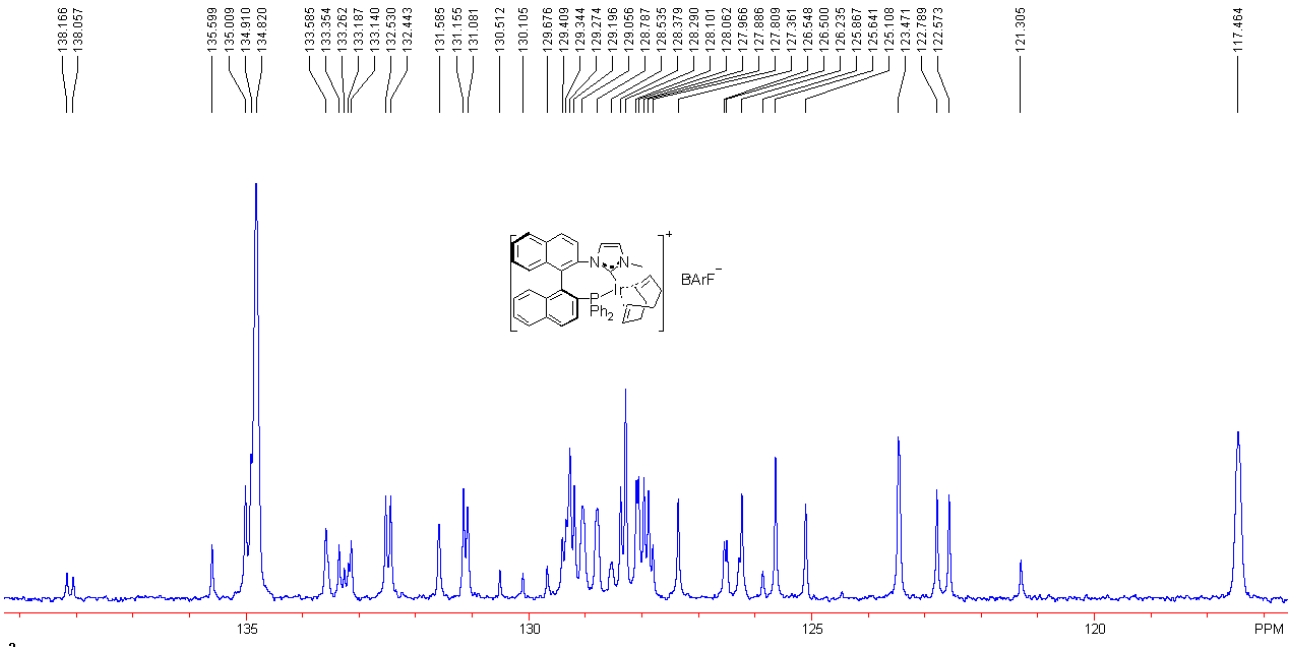
^{1}H NMR and ^{31}P NMR spectra of compound **5b**



^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra of Ir complex **6a**



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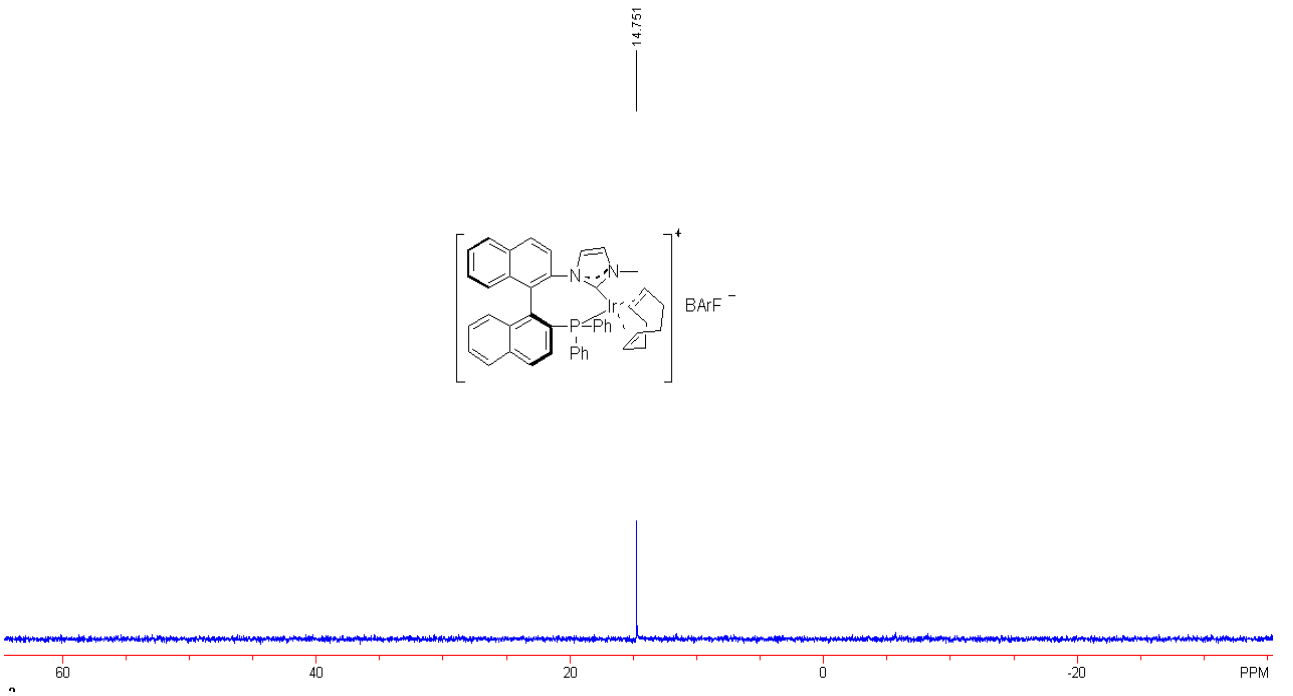
135.599
135.009
134.910
134.820
133.585
133.354
133.262
133.187
133.140
132.530
132.443
131.585
131.155
131.081
130.512
130.105
129.676
129.409
129.344
129.274
129.196
129.056
128.787
128.535
128.379
128.290
128.101
128.062
127.966
127.886
127.809
127.361
126.548
126.500
126.235
125.867
125.641
125.108
123.471
122.789
122.573
121.305
117.464
BArF
135
130
125
120
PPM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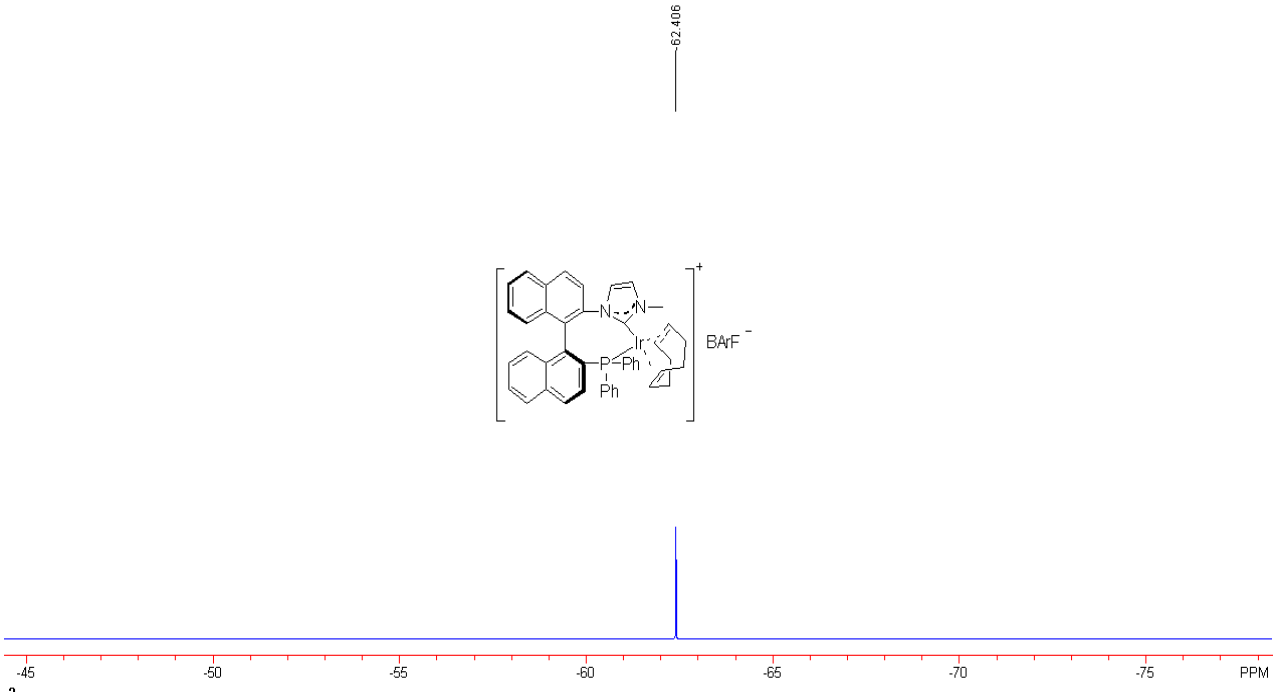
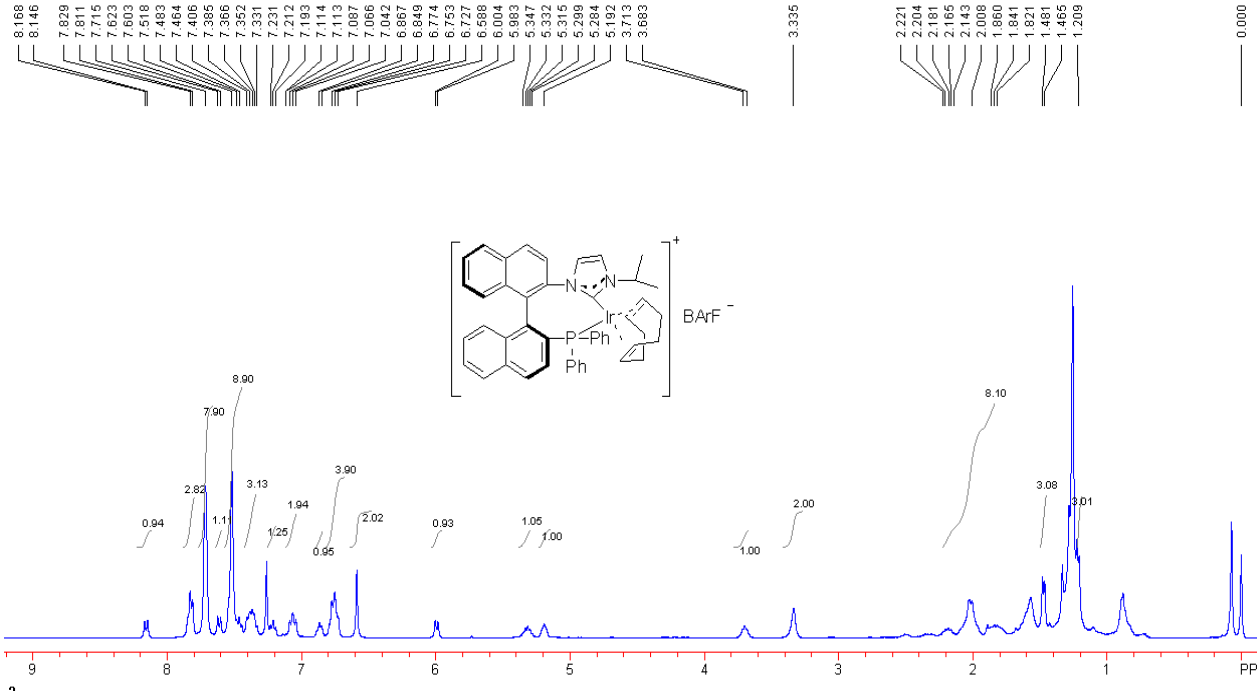
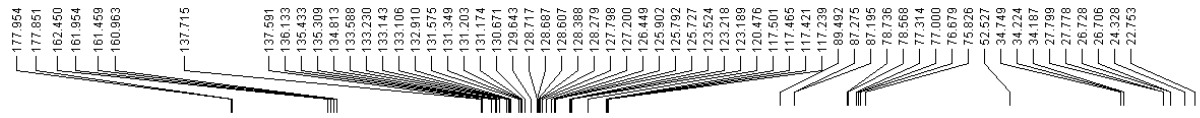
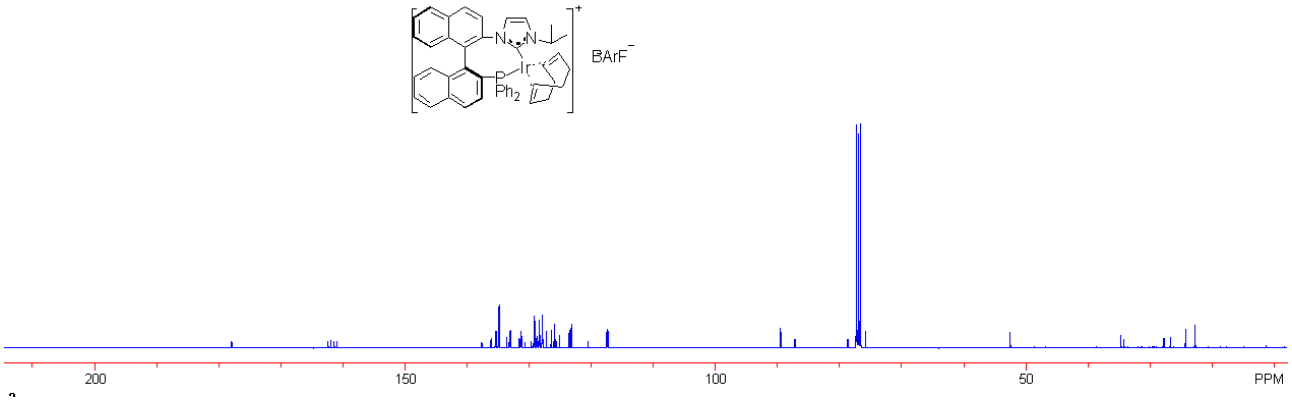
BArF
60
40
20
0
-20
PPM

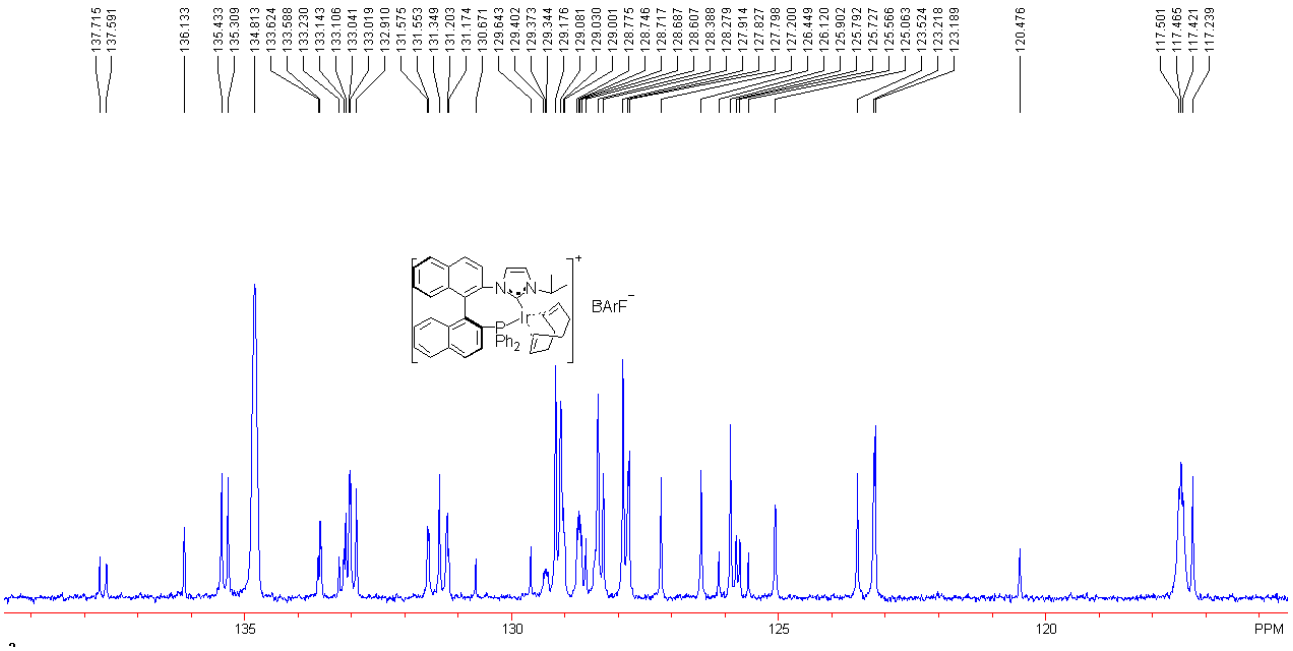

62.406
N
N
Ir
P
Ph
Ph
BArF
+
-
-45
-50
-55
-60
-65
-70
-75
PPM

^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra of Ir complex **6b**





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137.591
136.133
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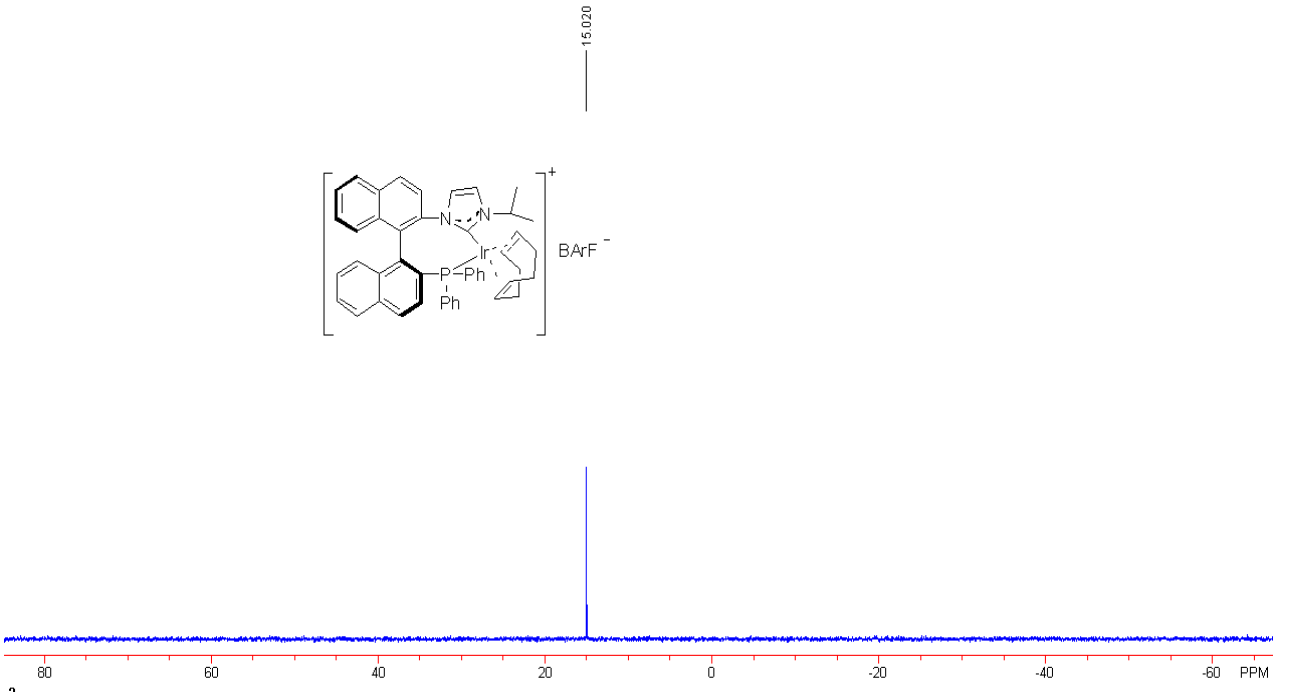
135.309
134.813
133.624
133.588
133.230
133.143
133.106
133.041
133.019
132.910
131.575
131.553
131.349
131.203
131.174
130.671
129.643
129.402
129.373
129.344
129.176
129.081
129.030
129.001
128.775
128.746
128.717
128.687
128.607
128.388
128.279
127.914
127.827
127.798
127.200
126.449
126.120
125.902
125.792
125.727
125.566
125.063
123.524
123.218
123.189
120.476
117.501
117.465
117.421
117.239
BArF
135
130
125
120
PPM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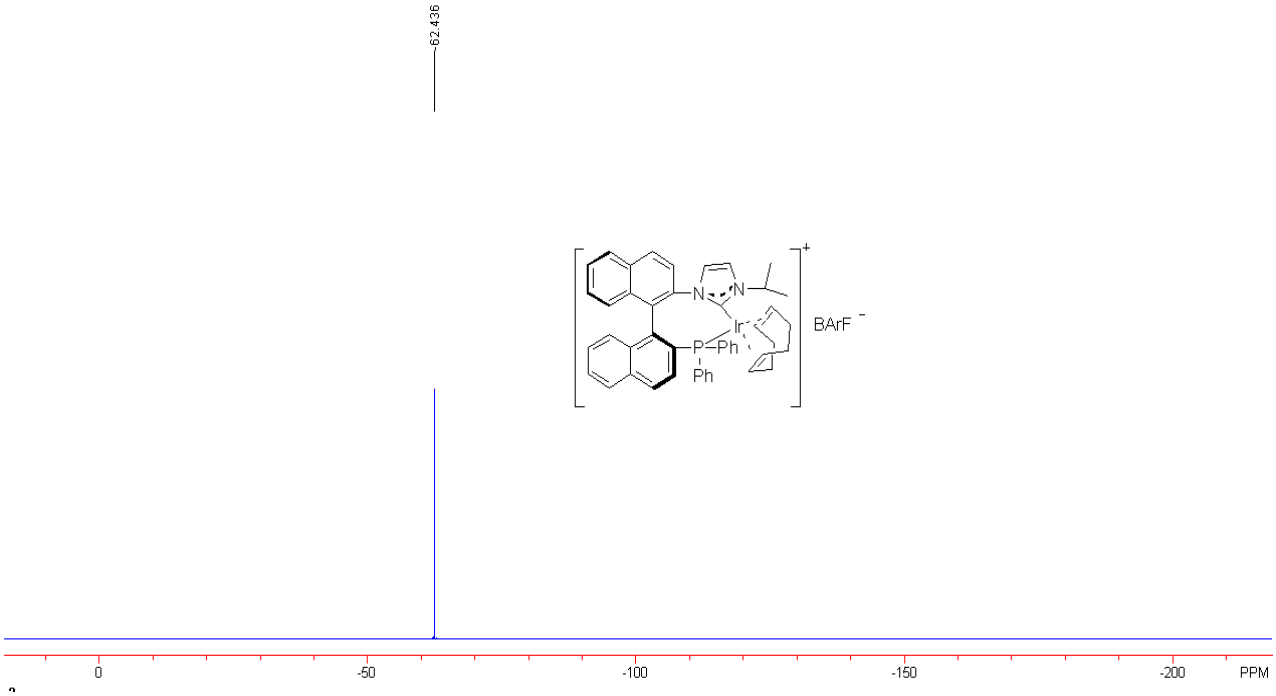
BArF
80
60
40
20
0
-20
-40
-60
PPM


62.436
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N
Ir
P
Ph
Ph
BArF
+
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-150
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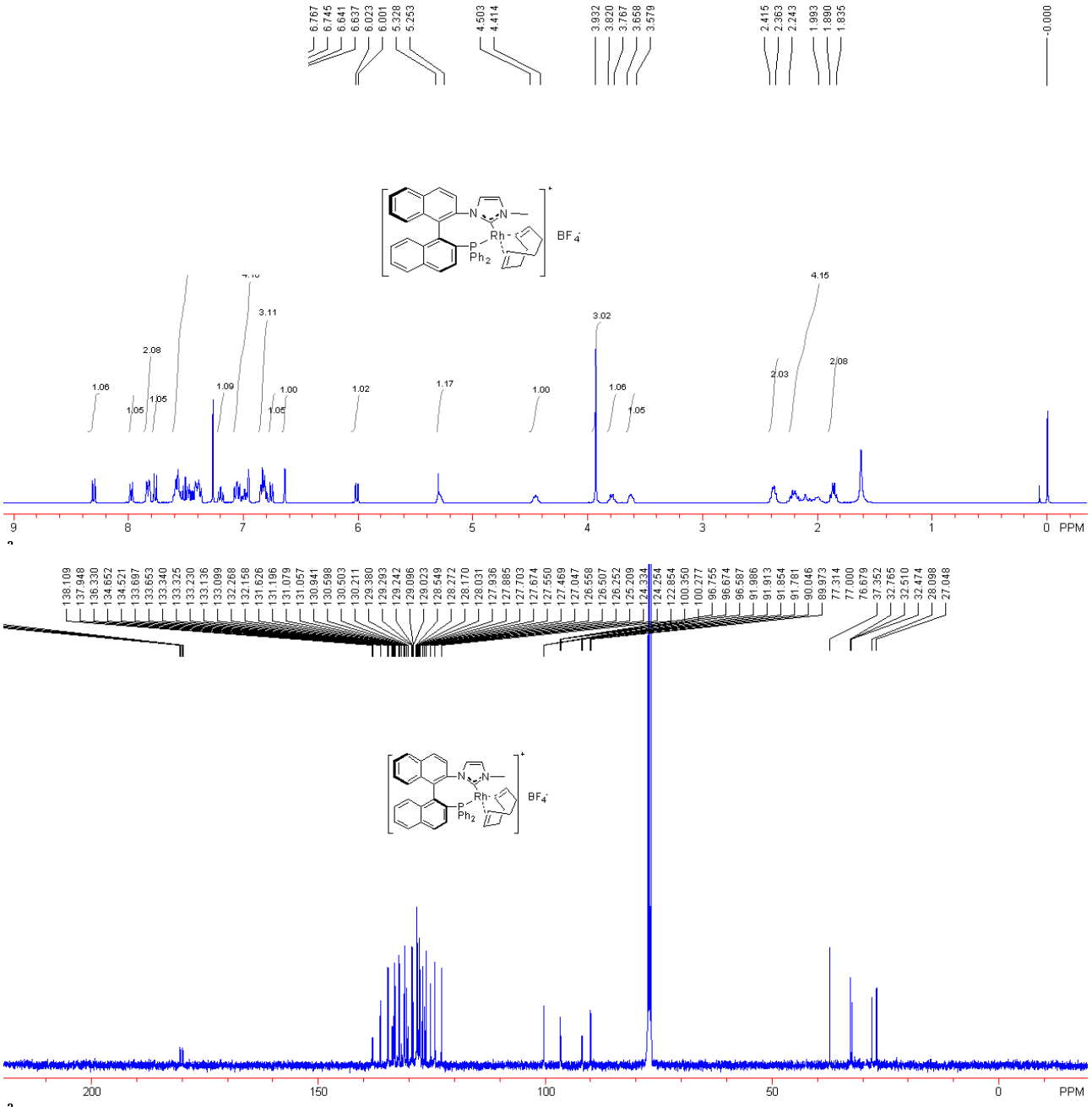
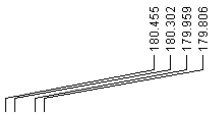
PPM

^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra of Rh complex **6c**

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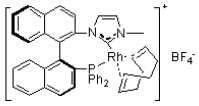
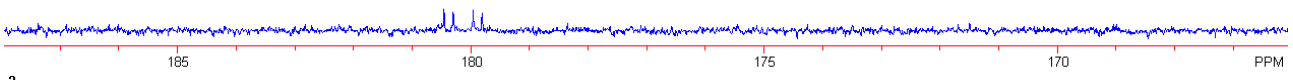
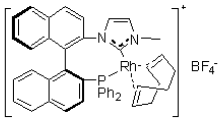
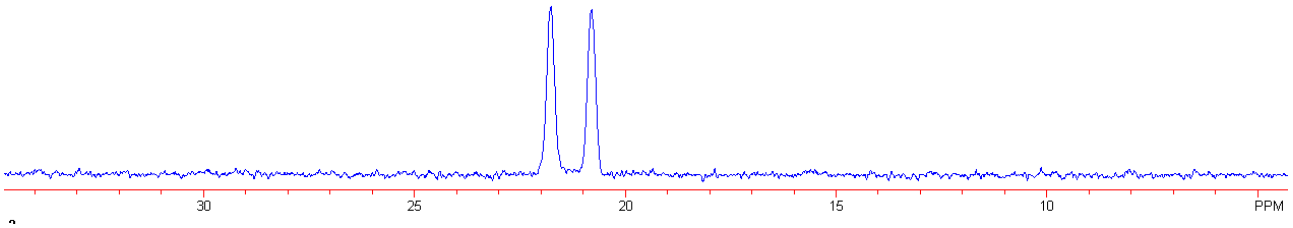
180.302
179.959
179.806

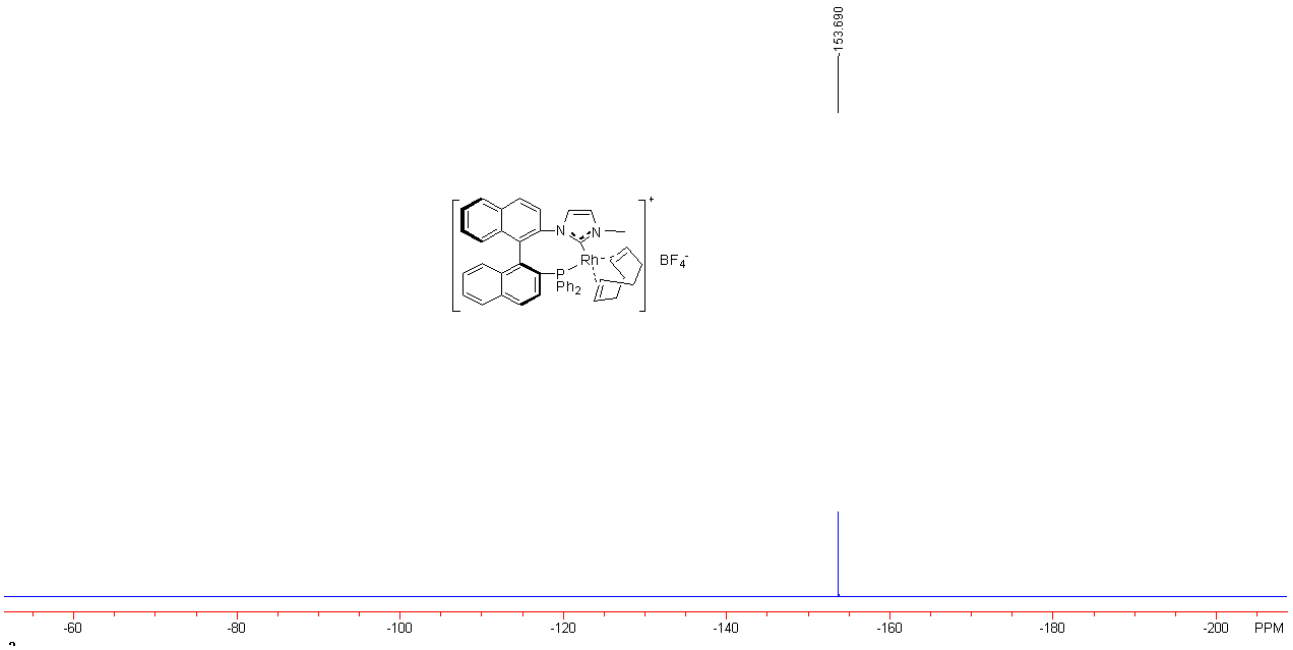

N
N
Rh
P
Ph2
BF4-


185
180
175
170
PPM

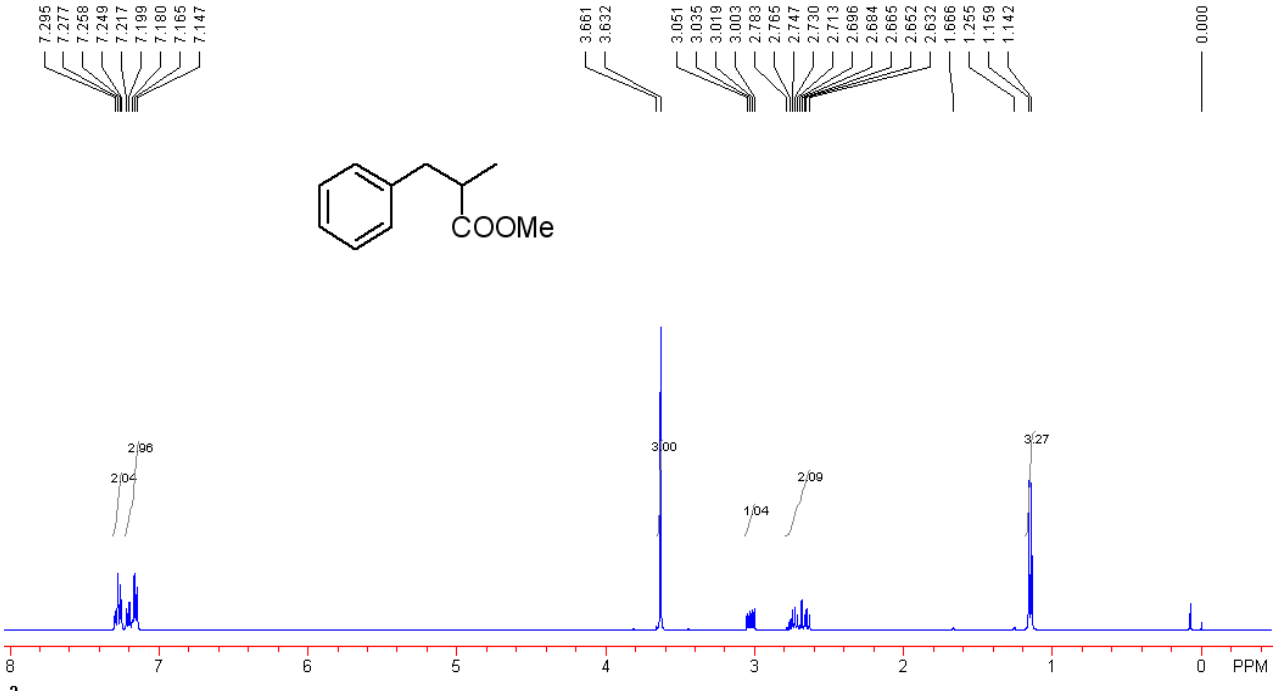

21.754
20.788

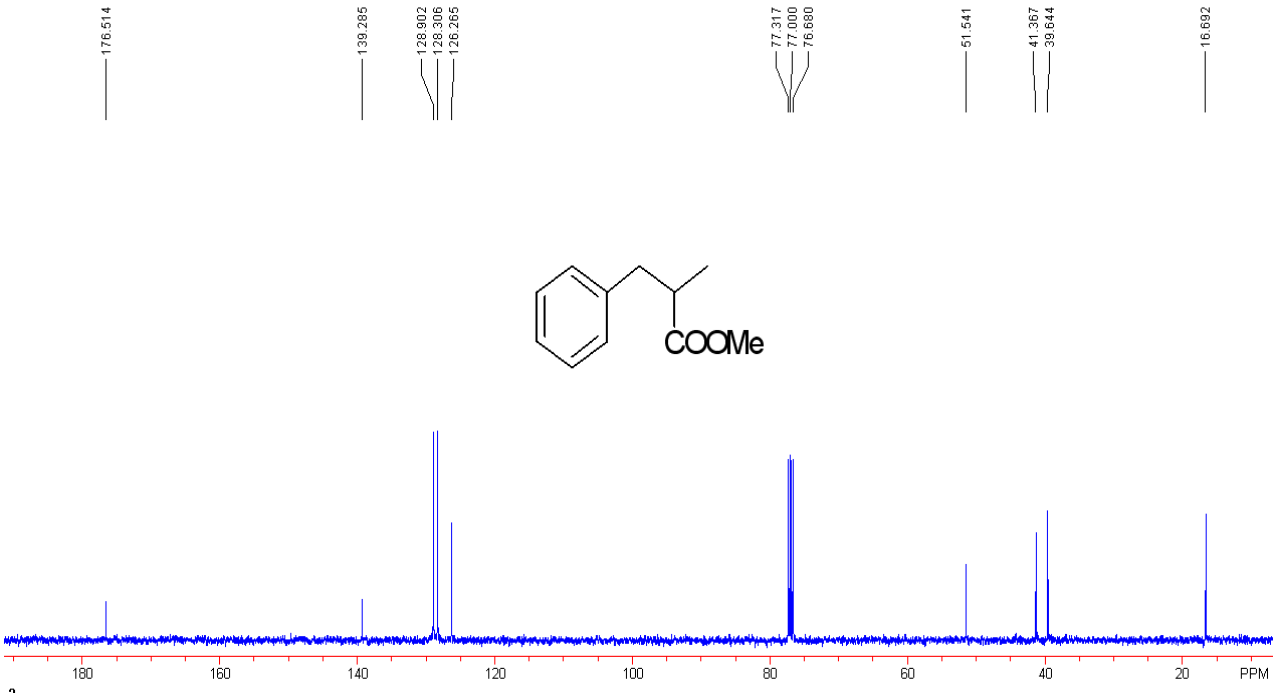

N
N
Rh
P
Ph2
BF4-


30
25
20
15
10
PPM

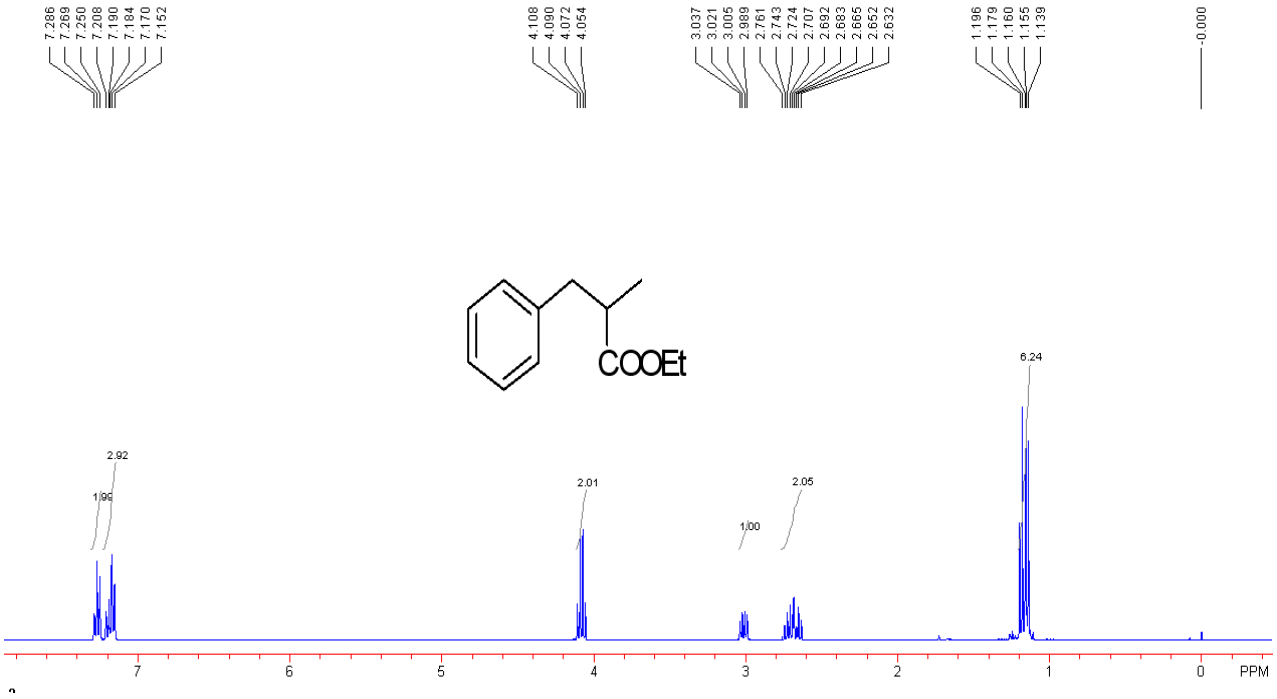

153.690
N
N
Rh
P
Ph2
BF4
-60
-80
-100
-120
-140
-160
-180
-200
PPM

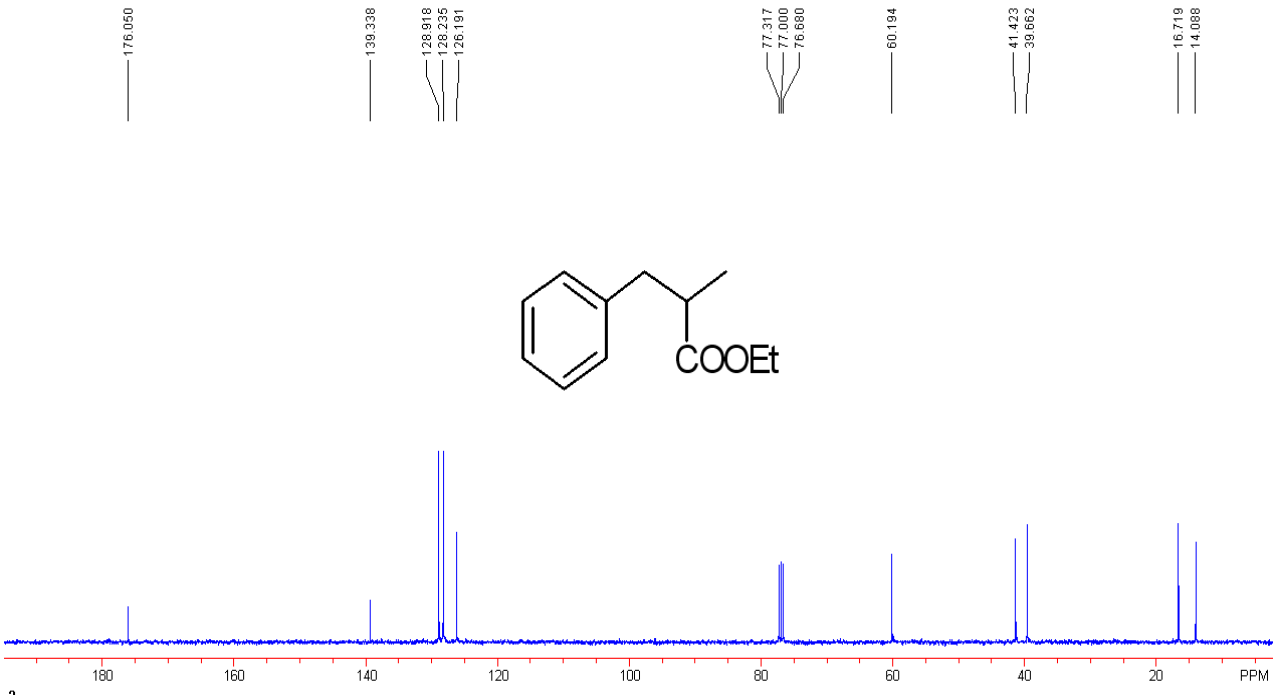
^{1}H NMR and ^{13}C NMR spectra of compound **10**



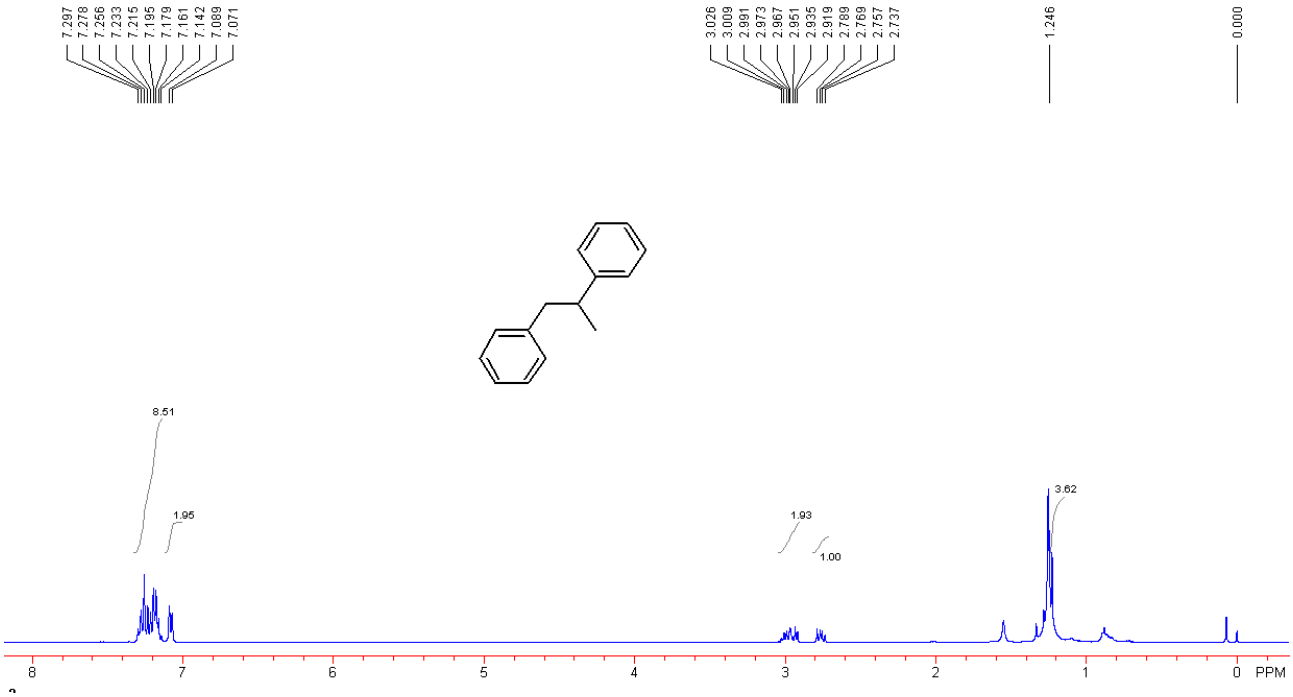


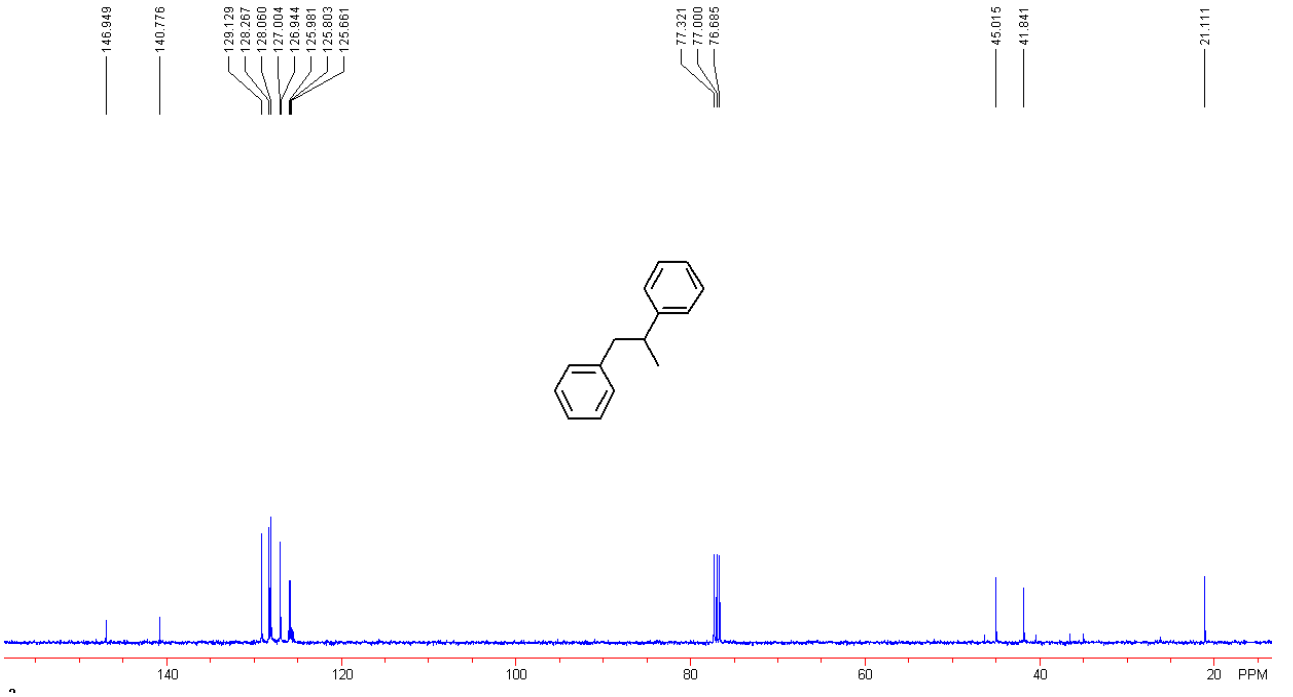
^{1}H NMR and ^{13}C NMR spectra of compound **11**





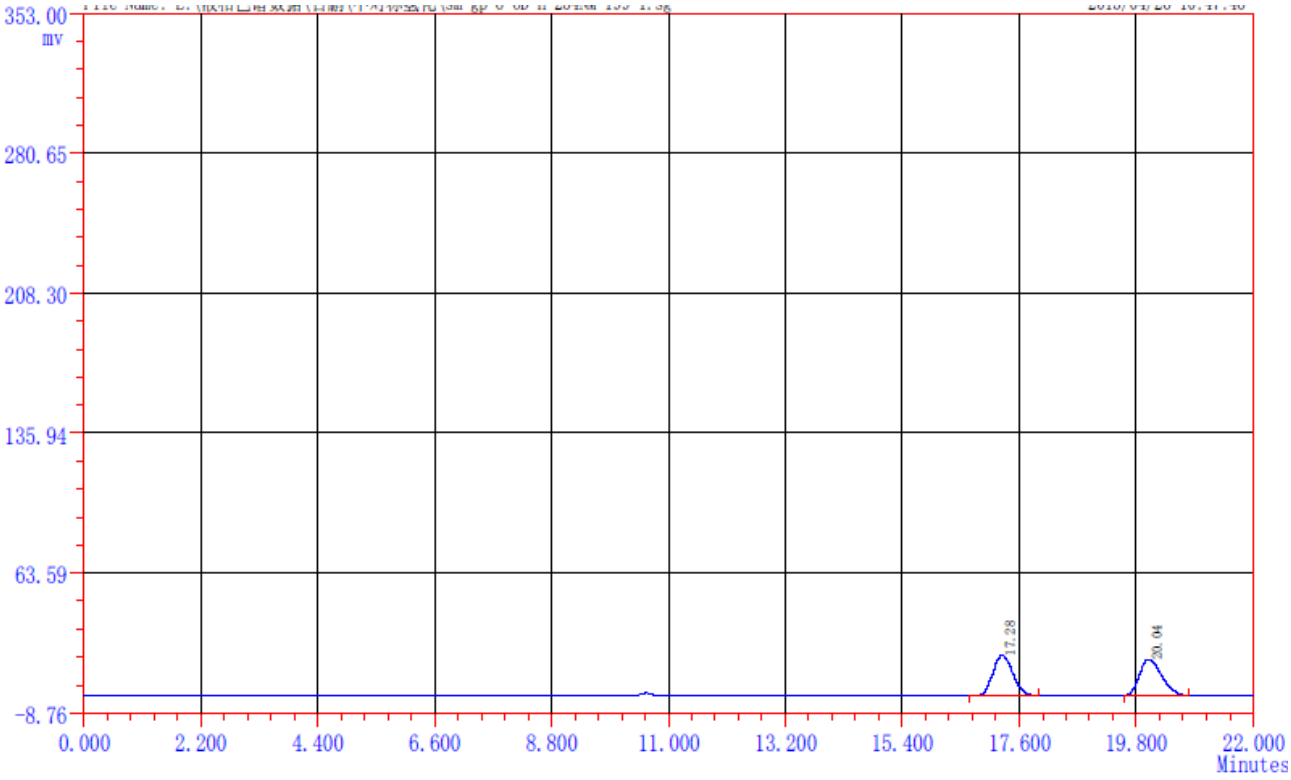
^{1}H NMR and ^{13}C NMR spectra of compound **12**





HPLC Traces

The HPLC results of compound **10**



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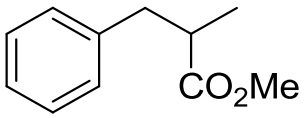
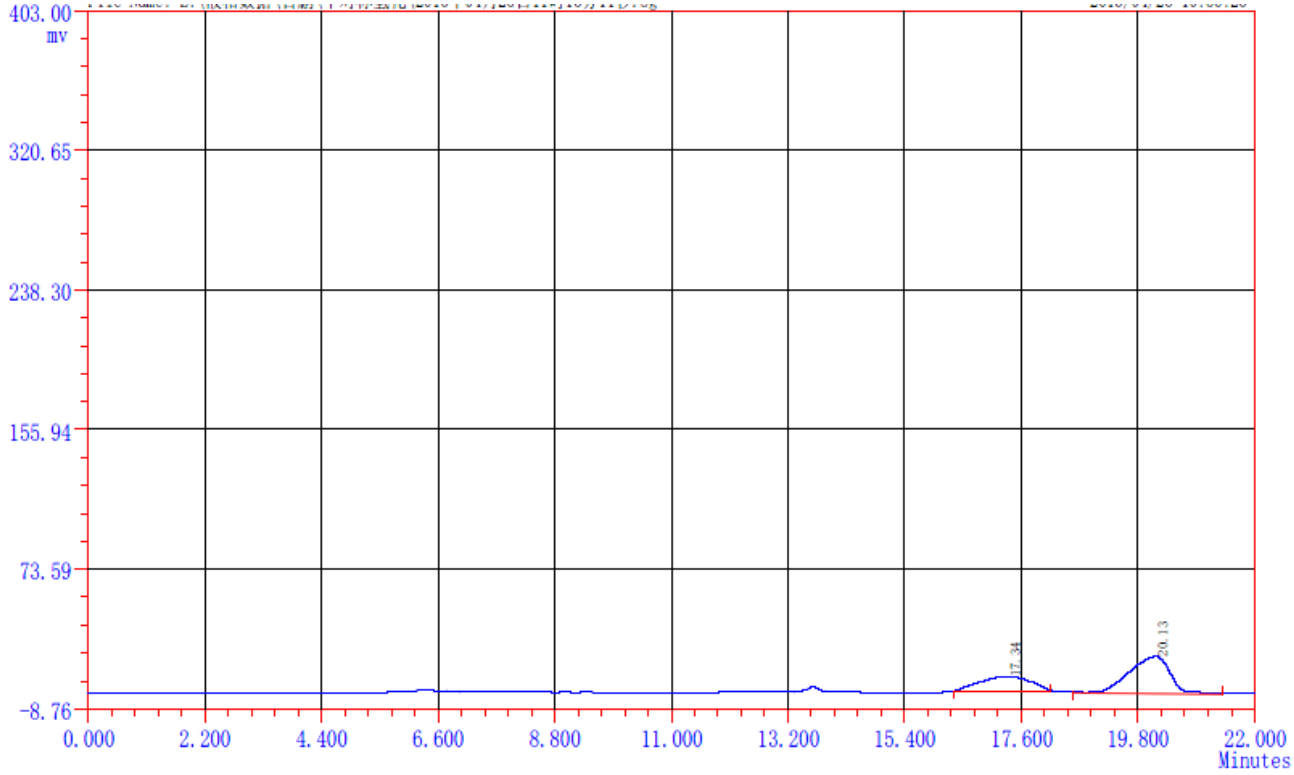
1		17.280	20702	538037.9	49.6766	1.12	8811
2		20.035	18598	545044.2	50.3234	1.30	9315
	Σ:		39300	1083082.0	100.0000		

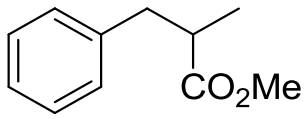


Chiral OD-H, n-hexane-iPrOH = 99.5:0.5, 254 nm, 0.5 mL-min

Table 1, entry 2

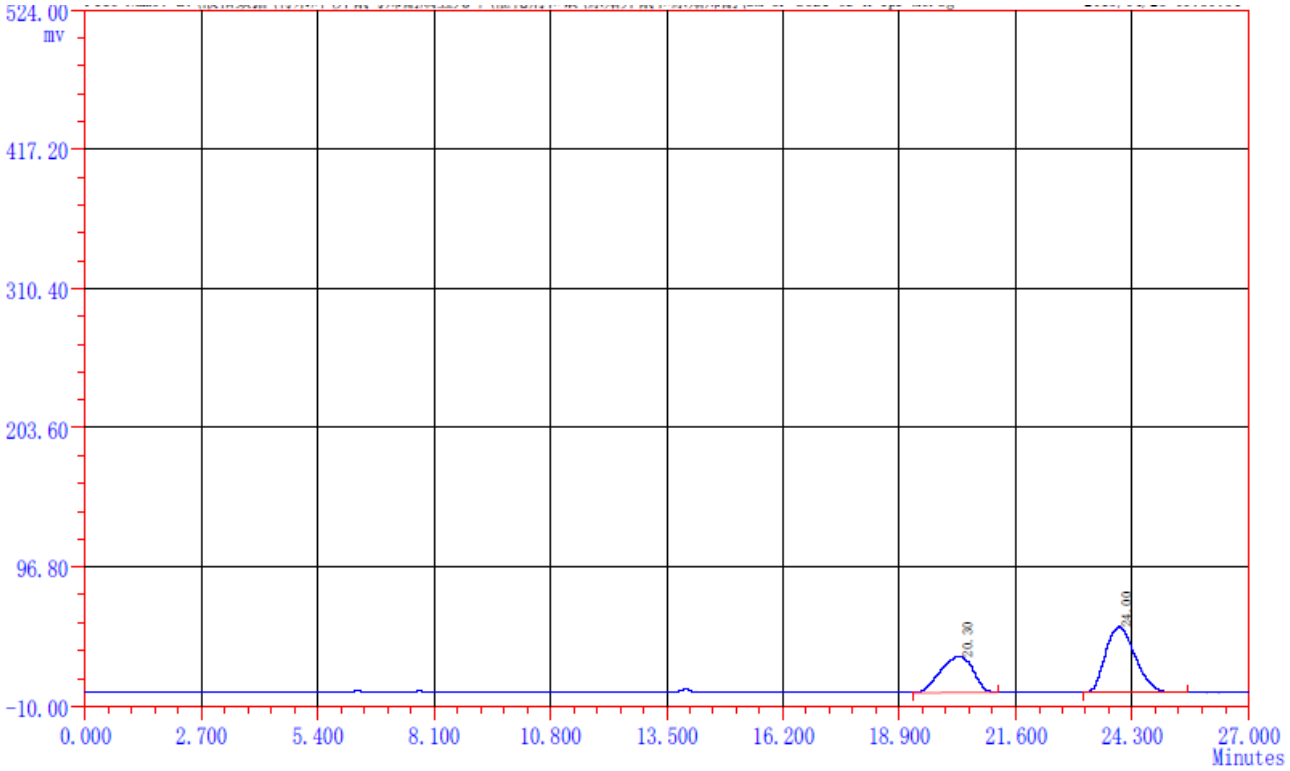


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		17.338	8702	611658.0	34.1012	0.90	1213
2		20.128	21790	1181996.8	65.8988	0.79	2744
	Σ:		30492	1793654.8	100.0000		

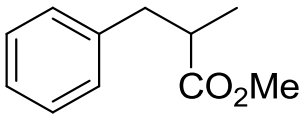


Chiral OD-H, n-hexane-iPrOH = 99.5:0.5, 254 nm, 0.5 mL-min

Table 1, entry 3

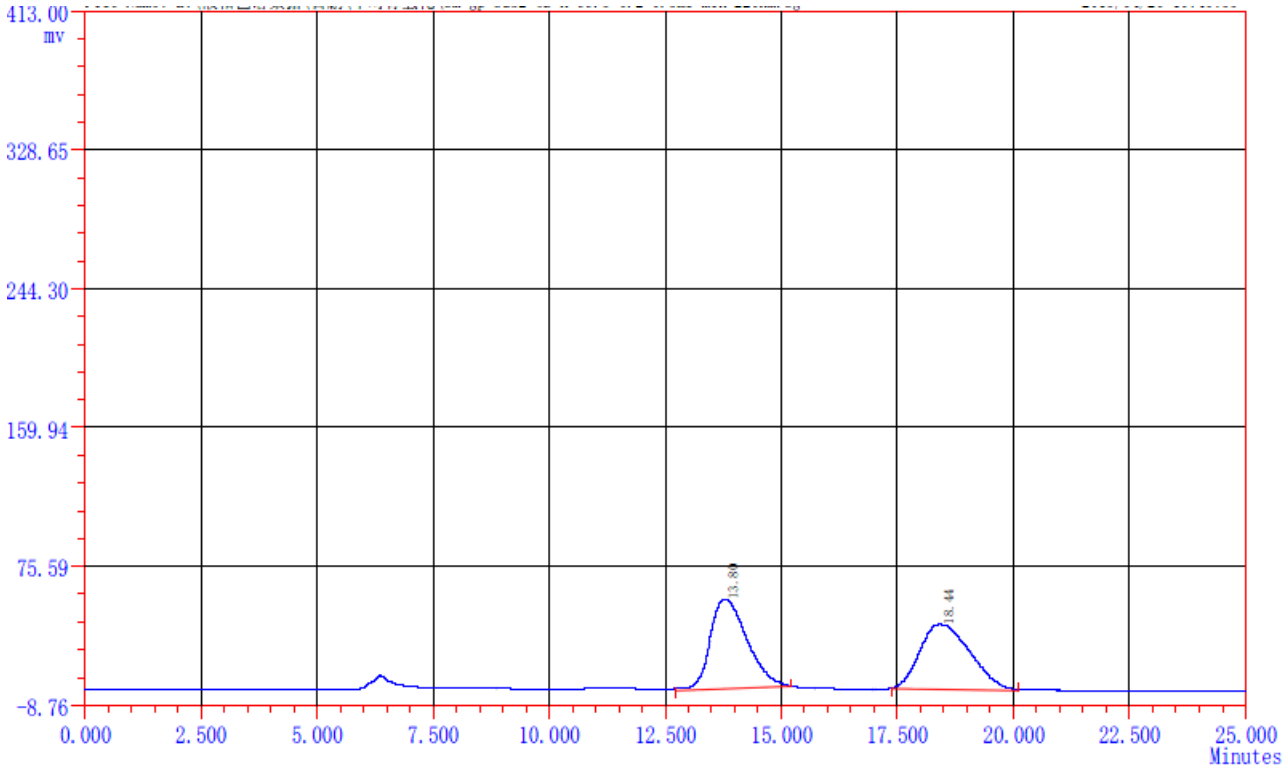


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		20.295	27460	1463705.9	37.3309	0.88	2889
2		23.995	50434	2457185.9	62.6691	1.24	4834
	Σ:		77894	3920891.8	100.0000		

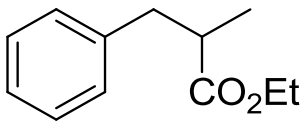


Chiral OD-H, n-hexane-iPrOH = 99.5:0.5, 254 nm, 0.5 mL-min

The HPLC results of compound **11**

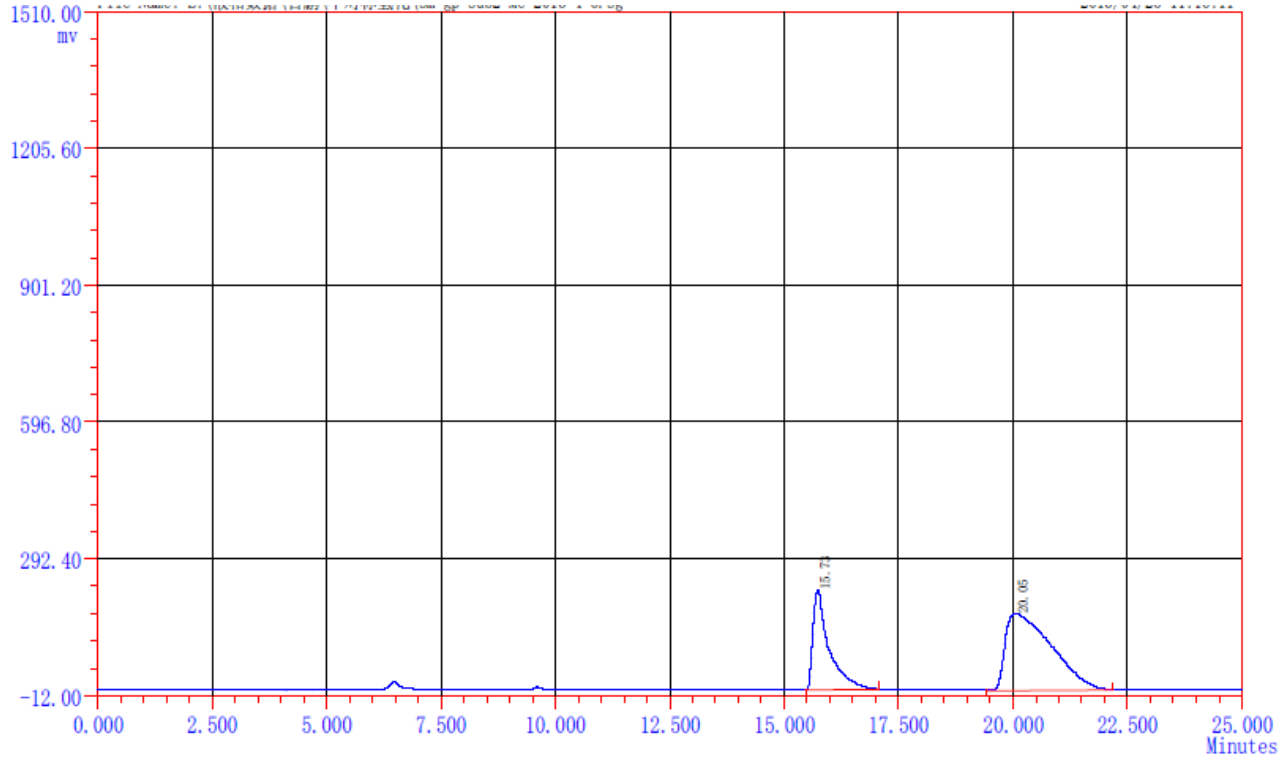


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		13.798	54590	3009924.7	50.2712	1.45	1248
2		18.442	39612	2977443.7	49.7288	1.20	1200
	Σ:		94202	5987368.4	100.0000		

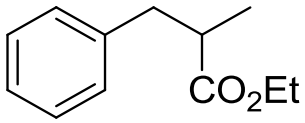


Chiral OB-H, n-hexane-iPrOH = 99.8:0.2, 220 nm, 0.5 mL-min

Table 1, entry 4

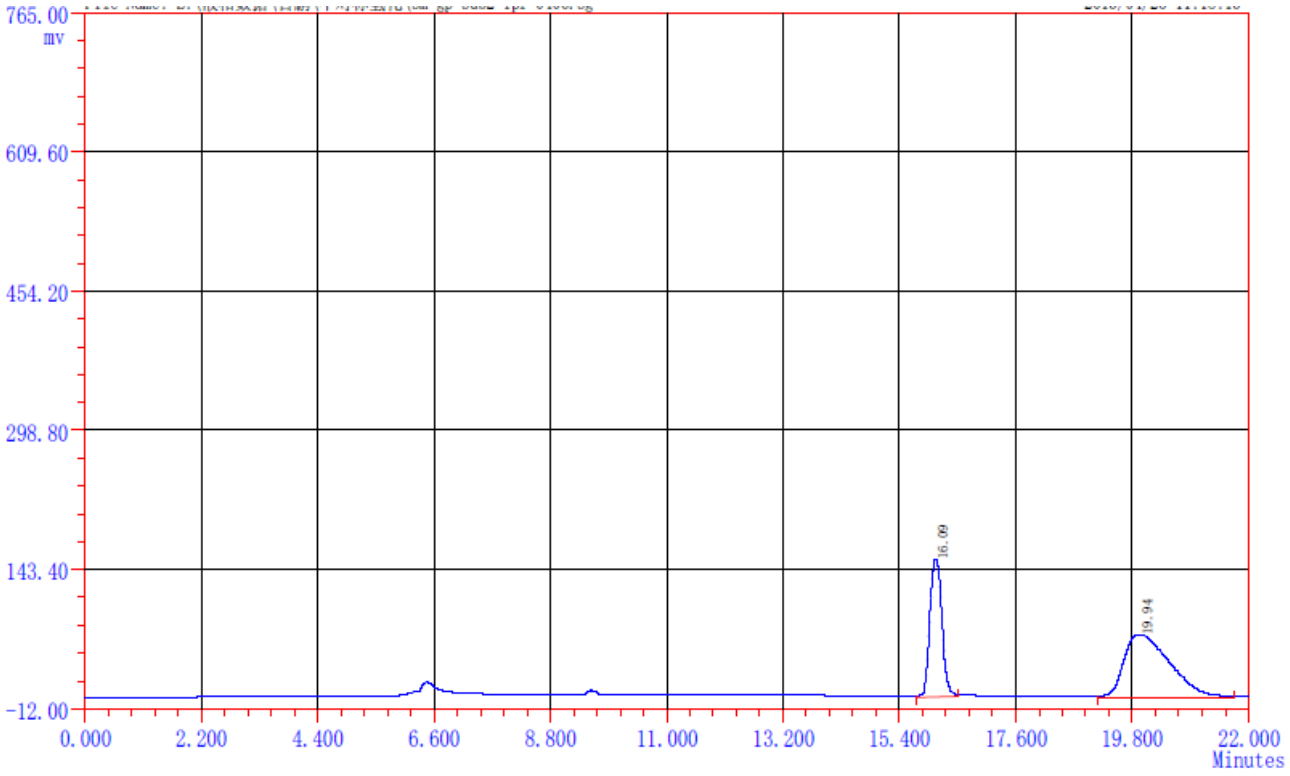


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		15.730	222503	5418659.4	31.1518	2.80	8315
2		20.053	170642	11975706.2	68.8482	2.71	1627
	Σ:		393145	17394365.6	100.0000		

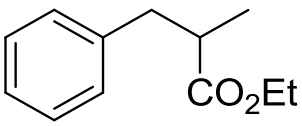


Chiral OB-H, n-hexane-iPrOH = 99.8:0.2, 220 nm, 0.5 mL-min

Table 1, entry 5

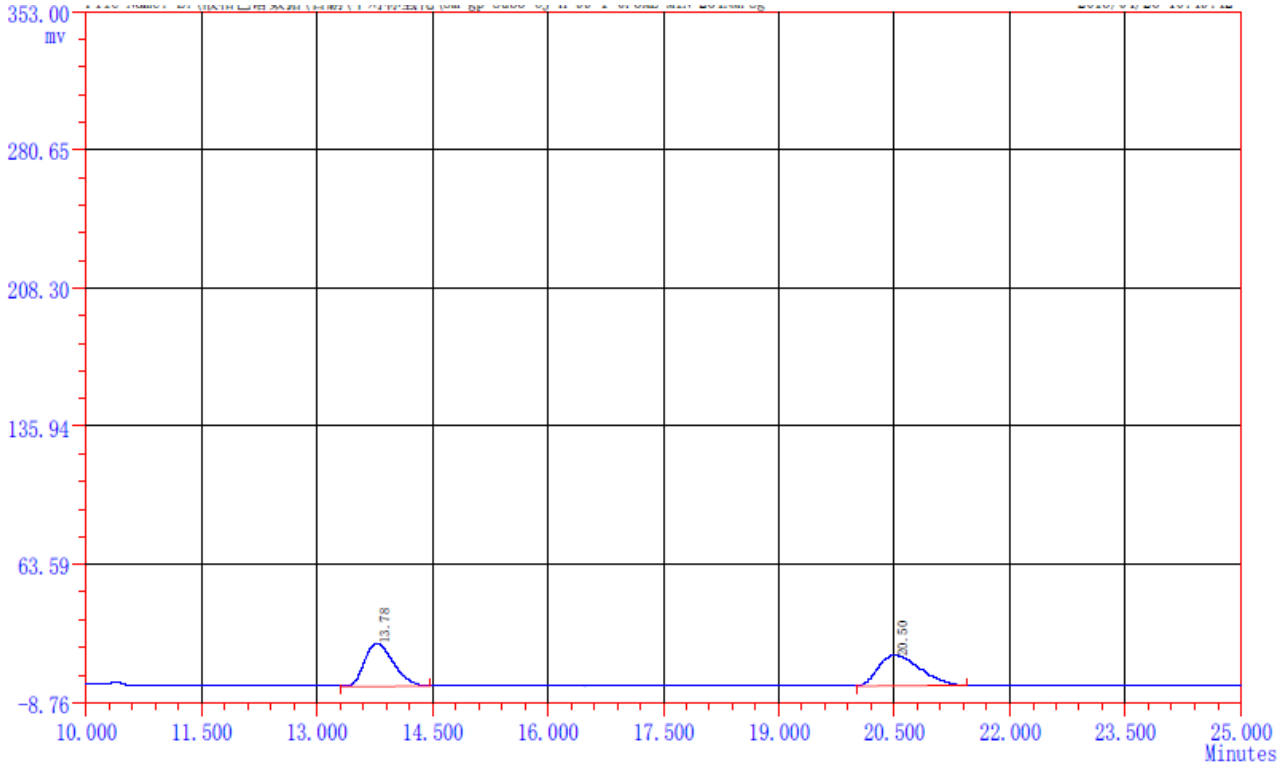


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		16.085	154145	2458881.2	36.6042	1.13	20265
2		19.940	71012	4258602.1	63.3958	1.64	2203
	Σ:		225157	6717483.3	100.0000		

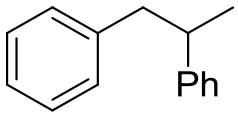


Chiral OB-H, n-hexane-iPrOH = 99.8:0.2, 220 nm, 0.5 mL-min

The HPLC results of compound **12**

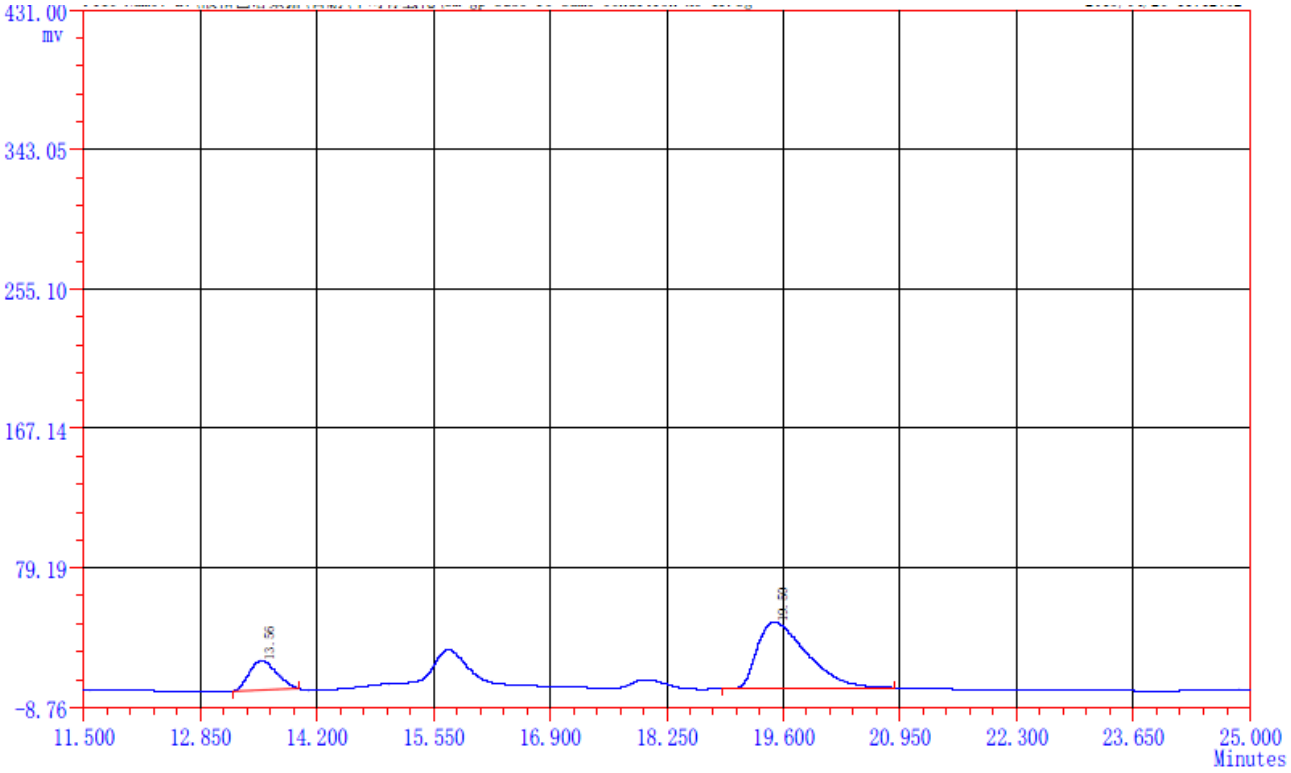


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		13.778	22660	596510.0	49.6086	1.33	5460
2		20.503	15950	605921.4	50.3914	1.47	5806
	Σ:		38610	1202431.4	100.0000		

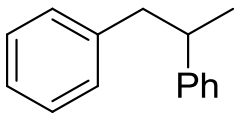


Chiral OJ-H, n-hexane-iPrOH = 99:1, 254 nm, 0.5 mL-min

Table 1, entry 7

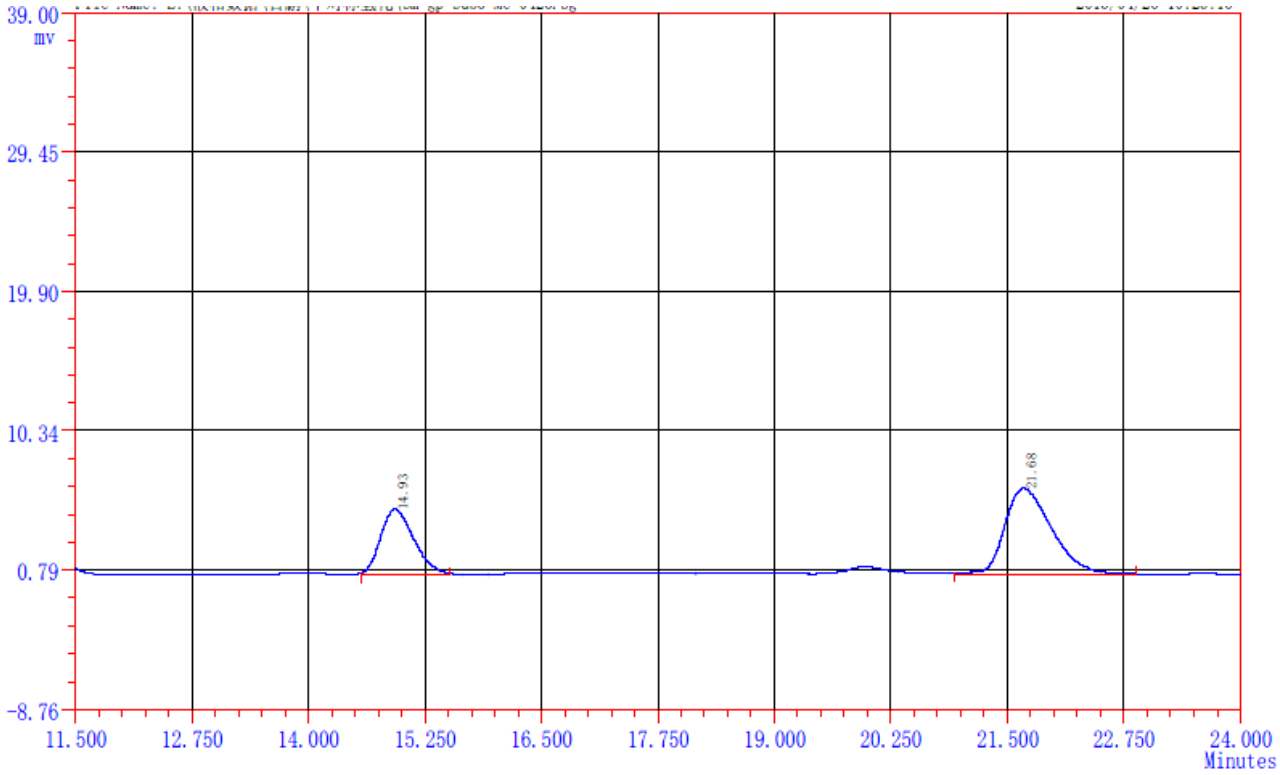


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		13.557	18452	409151.2	19.5165	1.32	7450
2		19.503	41777	1687281.1	80.4835	1.78	4648
	Σ:		60229	2096432.4	100.0000		

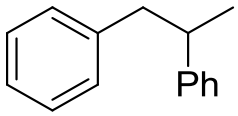


Chiral OJ-H, n-hexane-iPrOH = 99:1, 254 nm, 0.5 mL-min

Table 1, entry 8

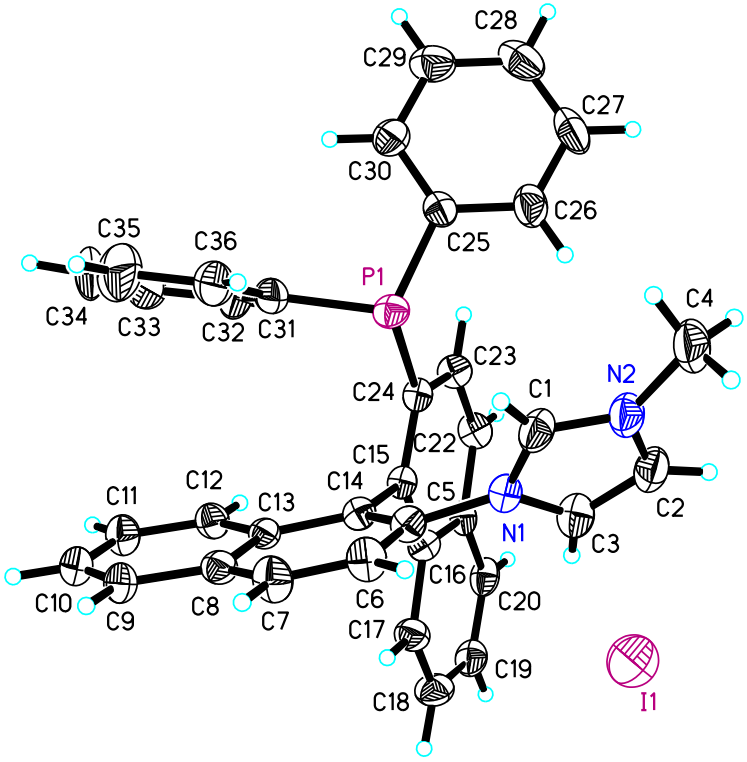


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		14.928	4460	111556.9	34.9207	1.28	7099
2		21.677	5881	207901.0	65.0793	1.37	7494
	Σ:		10341	319457.9	100.0000		



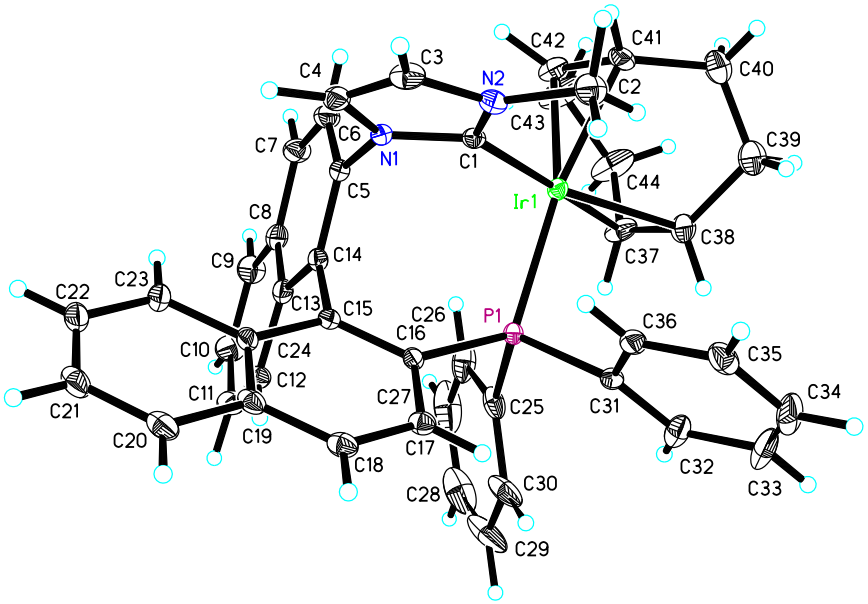
Chiral OJ-H, n-hexane-iPrOH = 99:1, 254 nm, 0.5 mL-min

Crystal structure data for compound **5a**



The crystal data of **5a** have been deposited in CCDC with number 909182. Empirical Formula: $C_{36}H_{30}IN_2OP$; Formula Weight: 664.49; Crystal System: Orthorhombic; Crystal size: 0.212 x 0.165 x 0.121; Lattice Parameters: a = 9.6940(6)Å, b = 16.1252(10)Å, c = 19.7229(12)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 3083.0(3)$Å^3$; Space group: P2(1)2(1)2(1); Z = 4; D_{calc} = 1.432 g/cm^3; F_{000} = 1344; Final R indices [I>2sigma(I)]: R1 = 0.0630; wR2 = 0.1634.

Crystal structure data for complex **6a**



The crystal data of **6a** have been deposited in CCDC with number 884914. Empirical Formula: $C_{76}H_{51}BF_{24}N_2PIr$; Formula Weight: 1682.17; Crystal System: Orthorhombic; Crystal size: 0.30 x 0.20 x 0.12; Lattice Parameters: a = 17.4690(12)Å, b = 19.7716(14)Å, c = 19.8753(14)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 6864.7(8)Å^3; Space group: P2(1)2(1)2(1); Z = 4; D_{calc} = 1.628 g/cm^3; F_{000} = 3336; Final R indices [I>2sigma(I)]: R1 = 0.0287; wR2 = 0.0732.