**** Supporting information ****

Trifunctional Organocatalyst-Promoted Counterion Catalysis for Fast and Enantioselective aza-Morita-Baylis-Hillman Reactions at Ambient Temperature

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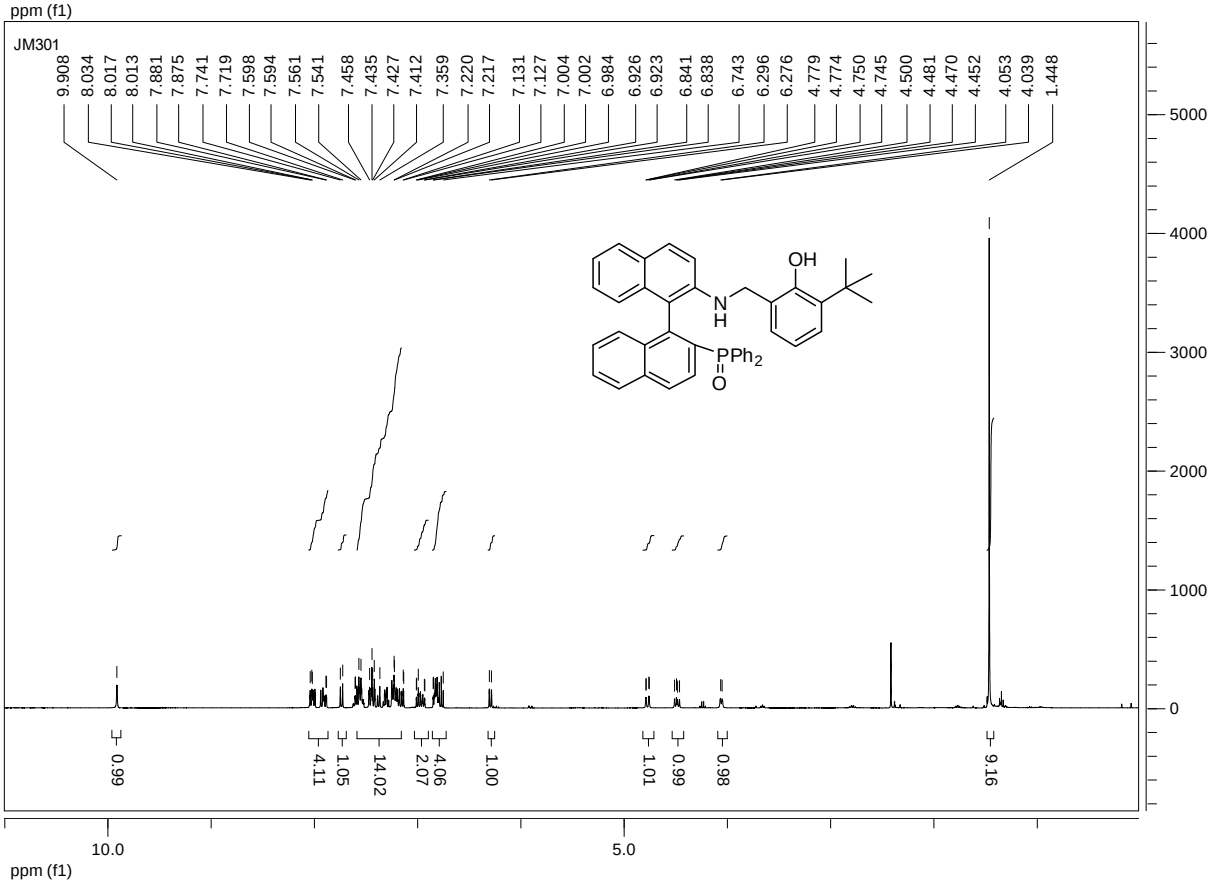
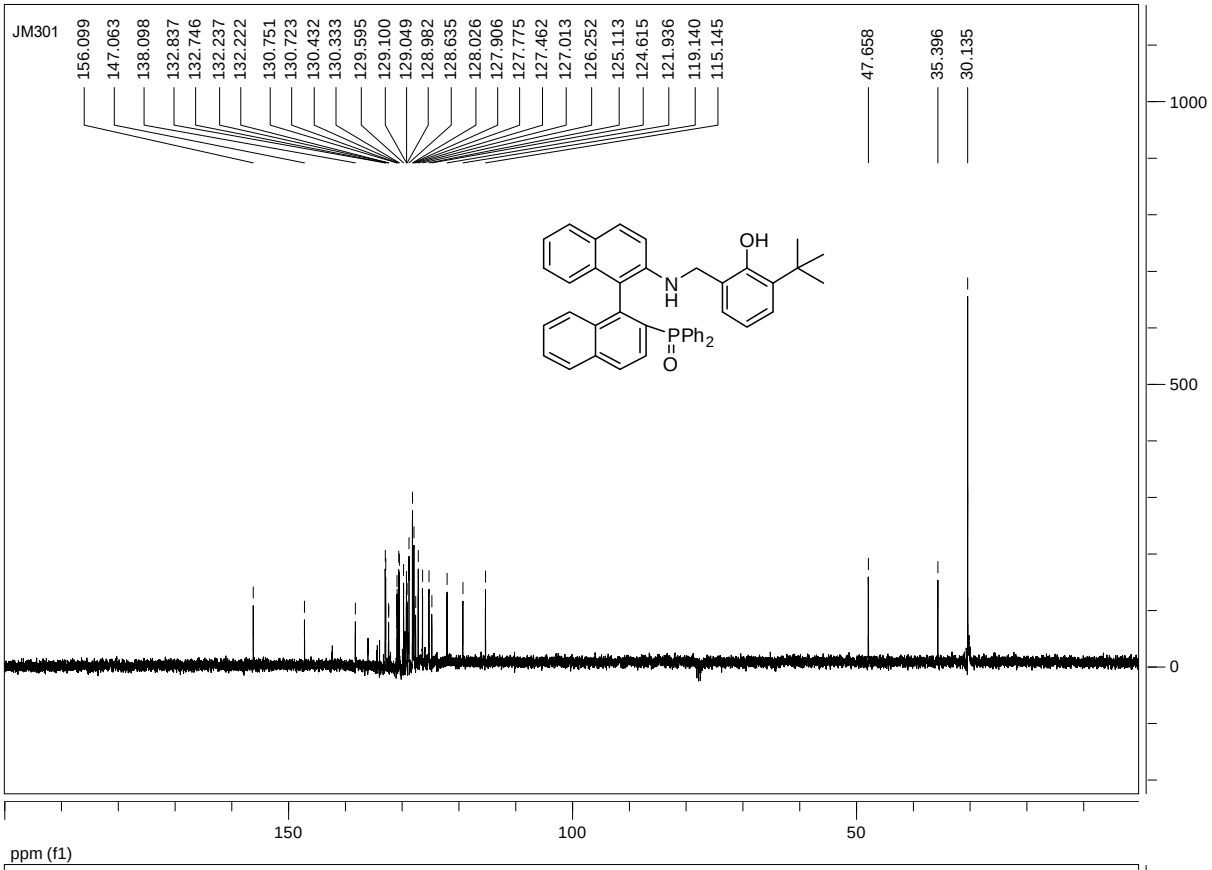
I- General information:

Unless otherwise stated, all chemicals and reagents were received from Sigma Aldrich, Castle Hill, NSW, Australia and used without further purification. Reactions were performed under a nitrogen atmosphere. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using silica gel 60 F254 aluminium pre-coated plates from Merck (0.25mm). Flash column chromatography was performed on silica gel (60 Å 0.06-0.2 mm, 400 mesh from Scharlau).

^{1}H NMR and ^{13}C NMR spectra were obtained in dry $CDCl_3$ on Bruker Avance DPX 400 MHz spectrometer. Chemical shifts were reported in ppm (parts per millions) using chloroform as the internal reference (^{1}H, 7.26 ppm, ^{13}C, 77.5 ppm). All spectra were acquired and processed using Bruker XWinNMR (2.5), Bruker TOPSPIN (1.3) and MestRec 4.9.9.6. Infrared spectra were taken on a Perkin Elmer paragon 1000PC FTIR spectrometer. Optical rotations were measured at 23°C on a P1010 digital polarimeter (Jasco, Japan). High resolution mass analysis was provided by Macquarie University and by University of Illinois, US.

II- Copies of NMR spectra:

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129.100
129.049
128.982
128.635
128.026
127.906
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127.462
127.013
126.252
125.113
124.615
121.936
119.140
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H
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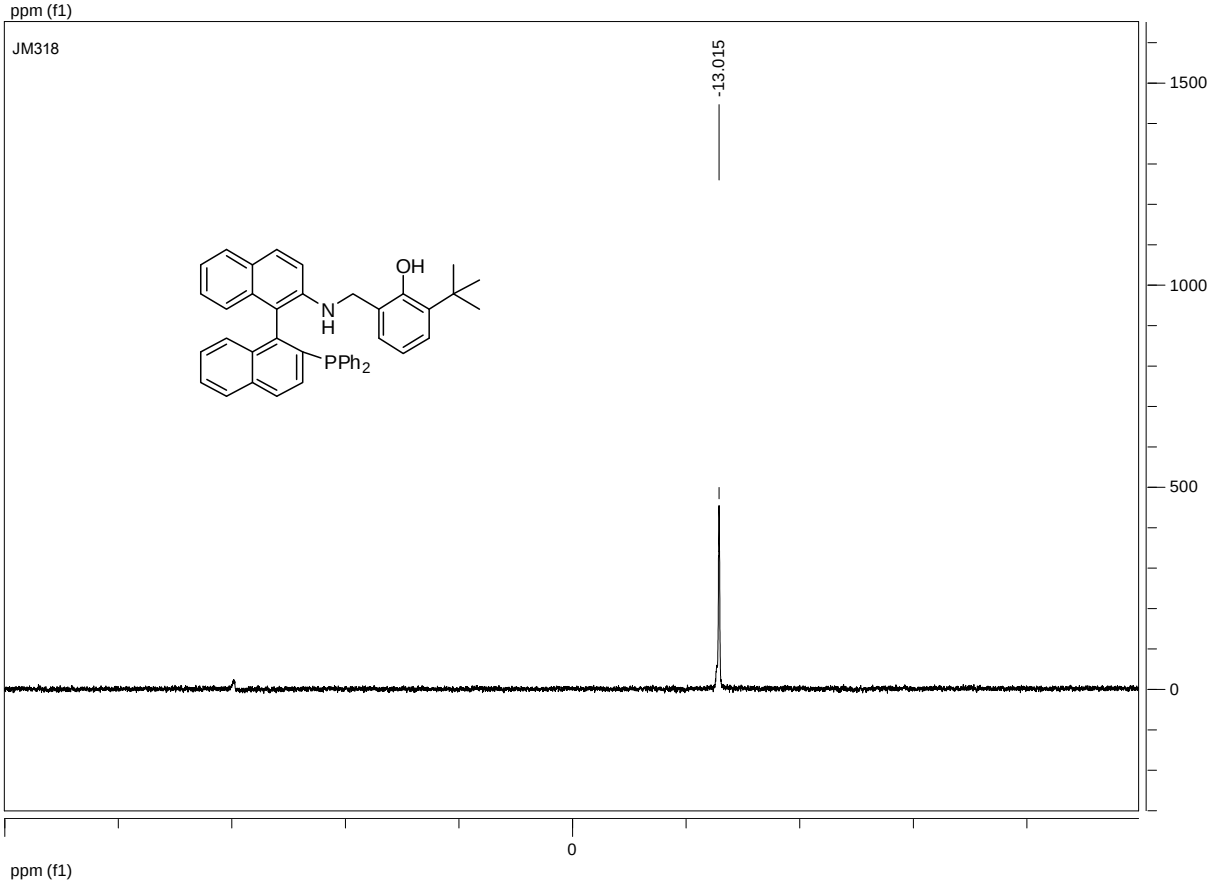
150
100
50
ppm (f1)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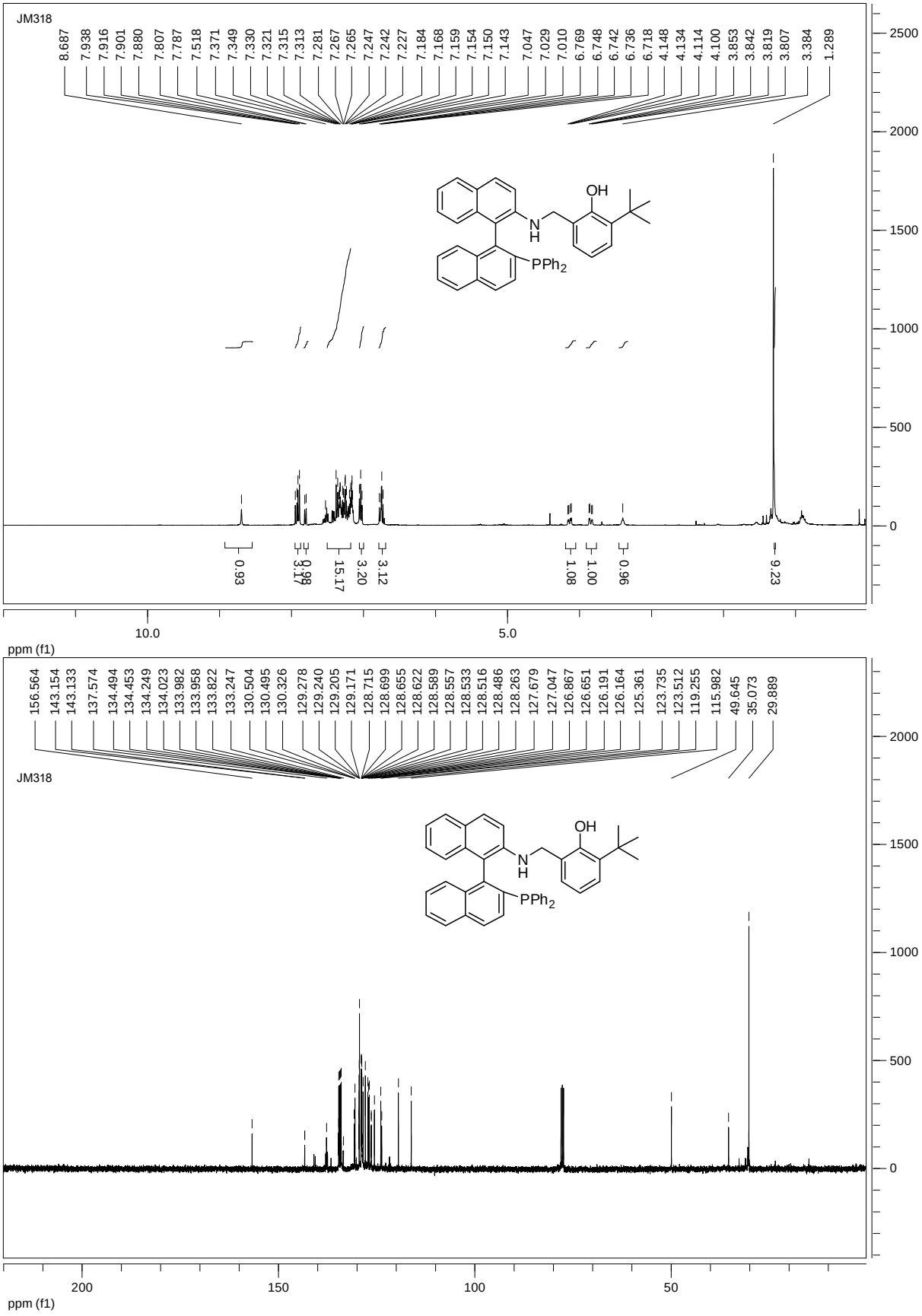
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7.321
7.315
7.313
7.281
7.267
7.265
7.247
7.242
7.227
7.184
7.168
7.159
7.154
7.150
7.143
7.047
7.029
7.010
6.769
6.748
6.742
6.736
6.718
4.148
4.134
4.114
4.100
3.853
3.842
3.819
3.807
3.384
1.289
OH
N
H
PPh2
0.93
3.17
0.98
1.17
3.20
3.12
1.08
1.00
0.96
9.23
2500
2000
1500
1000
500
0
10.0
5.0
ppm (f1)
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143.133
137.574
134.494
134.453
134.249
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133.822
133.247
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130.326
129.278
129.240
129.205
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128.655
128.622
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128.516
128.486
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126.867
126.651
126.191
126.164
125.361
123.735
123.512
119.255
115.982
49.645
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H
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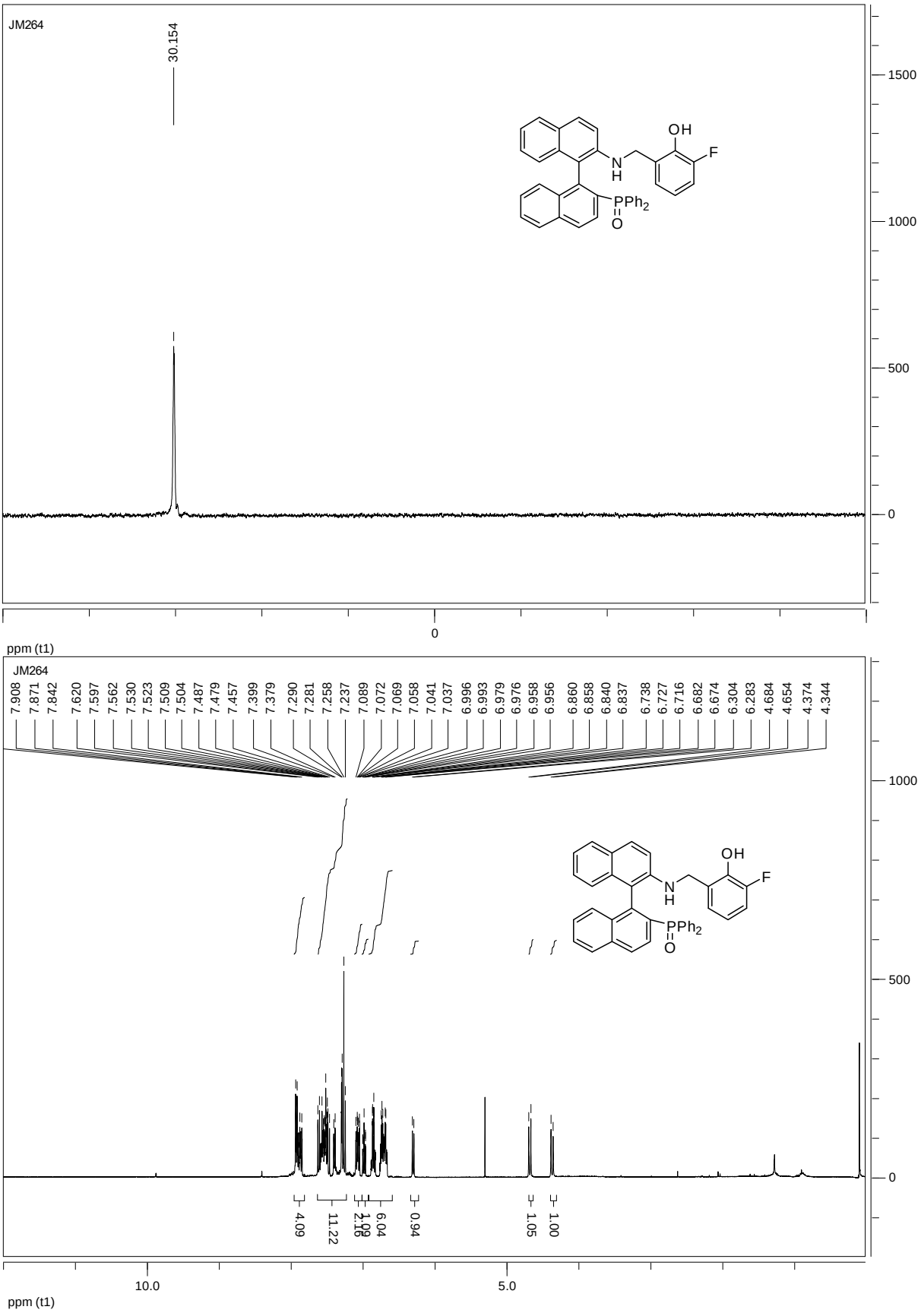
200
150
100
50
ppm (f1)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7.842
7.620
7.597
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7.530
7.523
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7.487
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7.037
6.996
6.993
6.979
6.976
6.958
6.956
6.860
6.858
6.840
6.837
6.738
6.727
6.716
6.682
6.674
6.304
6.283
4.684
4.654
4.374
4.344
1000
500
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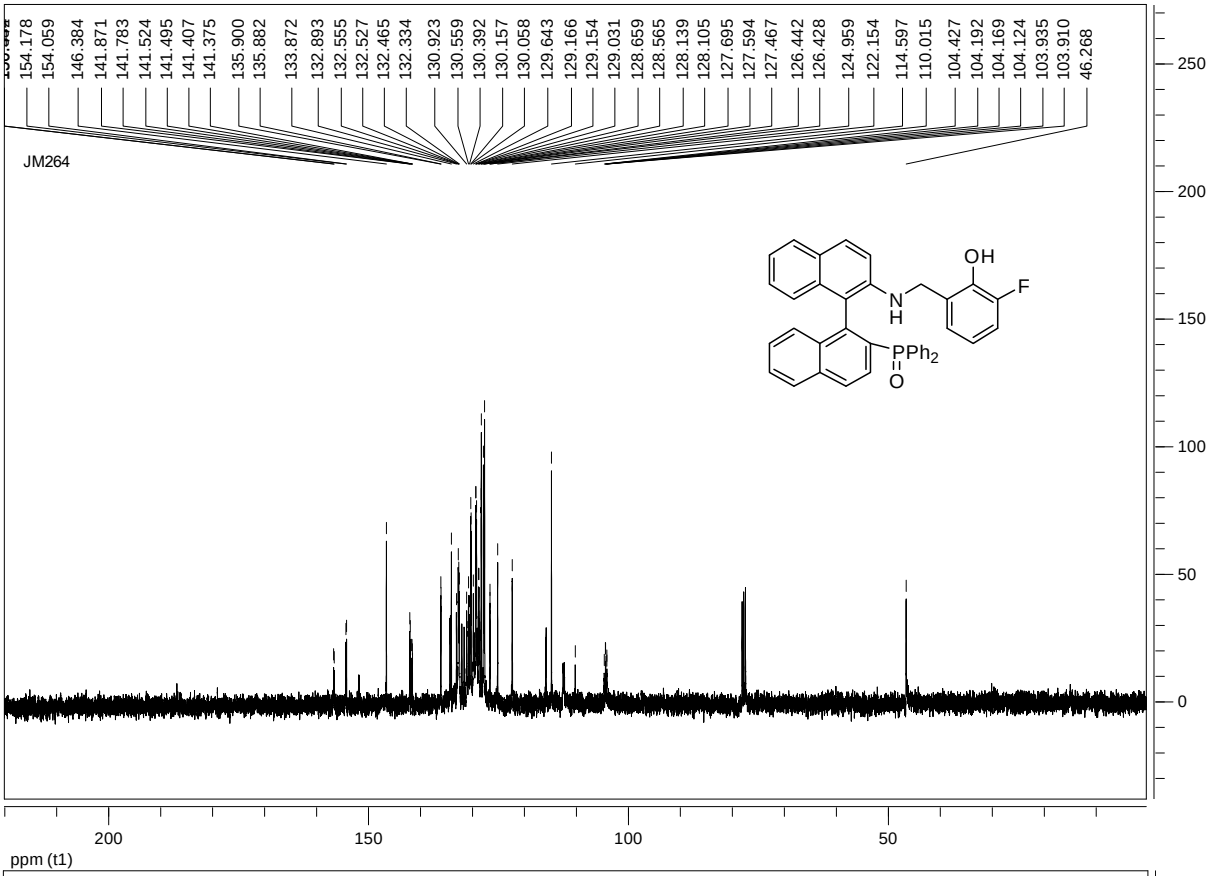
ppm (t1)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132.555
132.527
132.465
132.334
130.923
130.559
130.392
130.157
130.058
129.643
129.166
129.154
129.031
128.659
128.565
128.139
128.105
127.695
127.594
127.467
126.442
126.428
124.959
122.154
114.597
110.015
104.427
104.192
104.169
104.124
103.935
103.910
46.268
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H
PPh2
O
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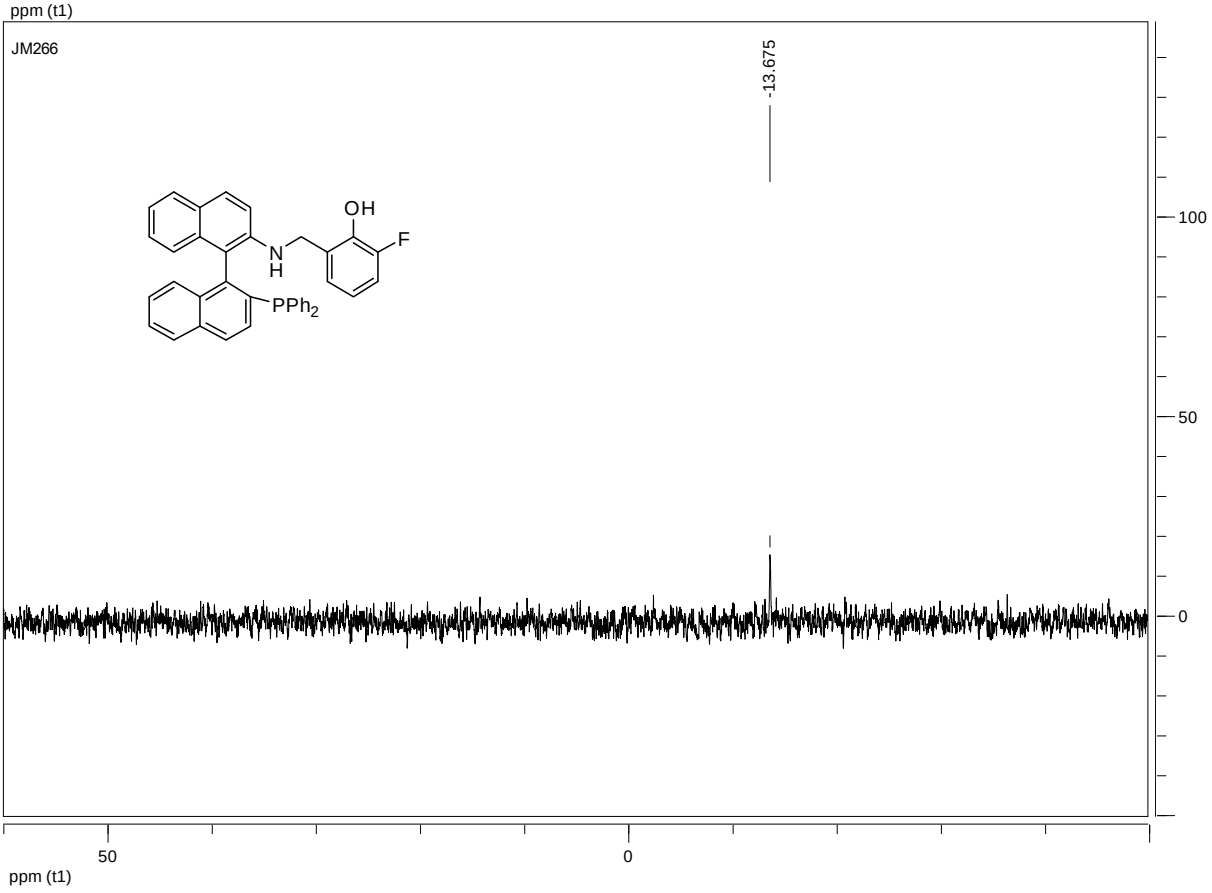
200
150
100
50
0
200
150
100
50
ppm (t1)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N
H
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0
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0
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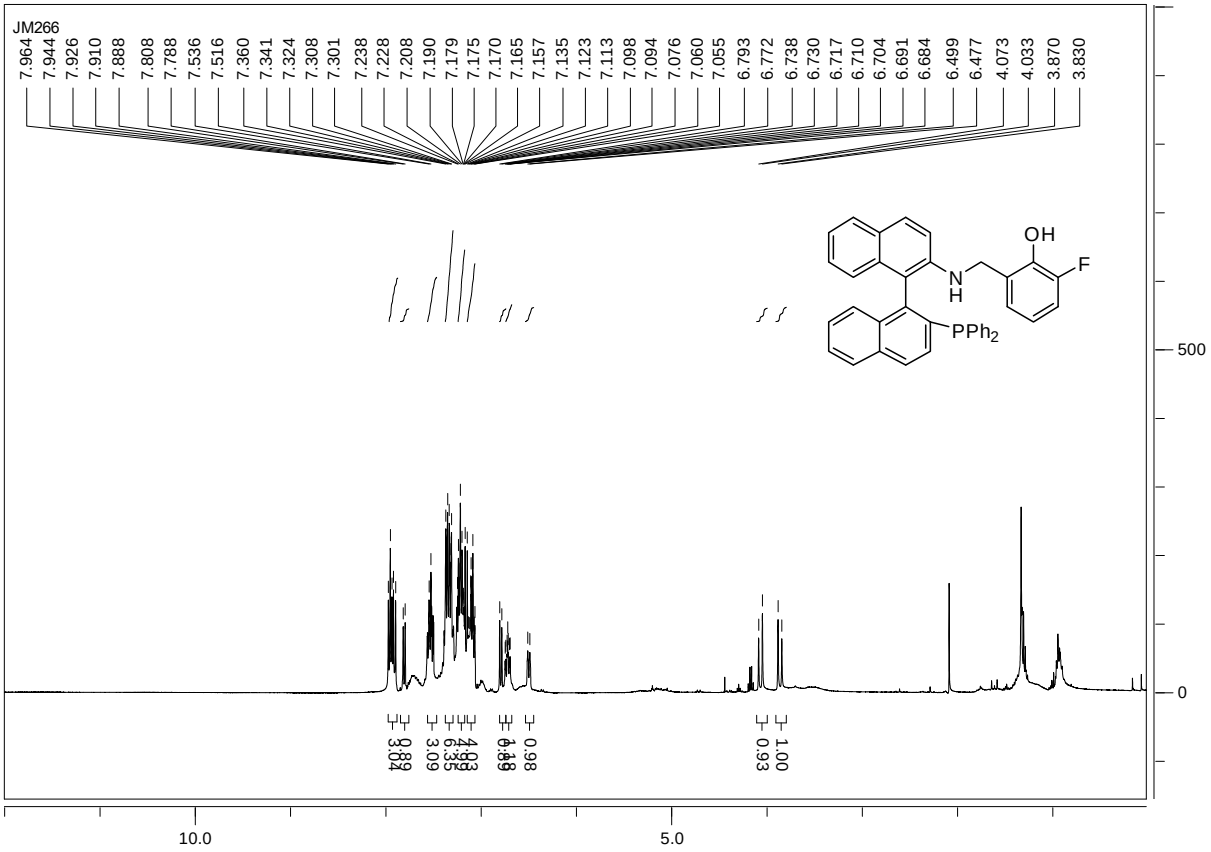
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7.910
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7.341
7.324
7.308
7.301
7.238
7.228
7.208
7.190
7.179
7.175
7.170
7.165
7.157
7.135
7.123
7.113
7.098
7.094
7.076
7.060
7.055
6.793
6.772
6.738
6.730
6.717
6.710
6.704
6.691
6.684
6.499
6.477
4.073
4.033
3.870
3.830
OH
F
N
H
PPh2
500
0
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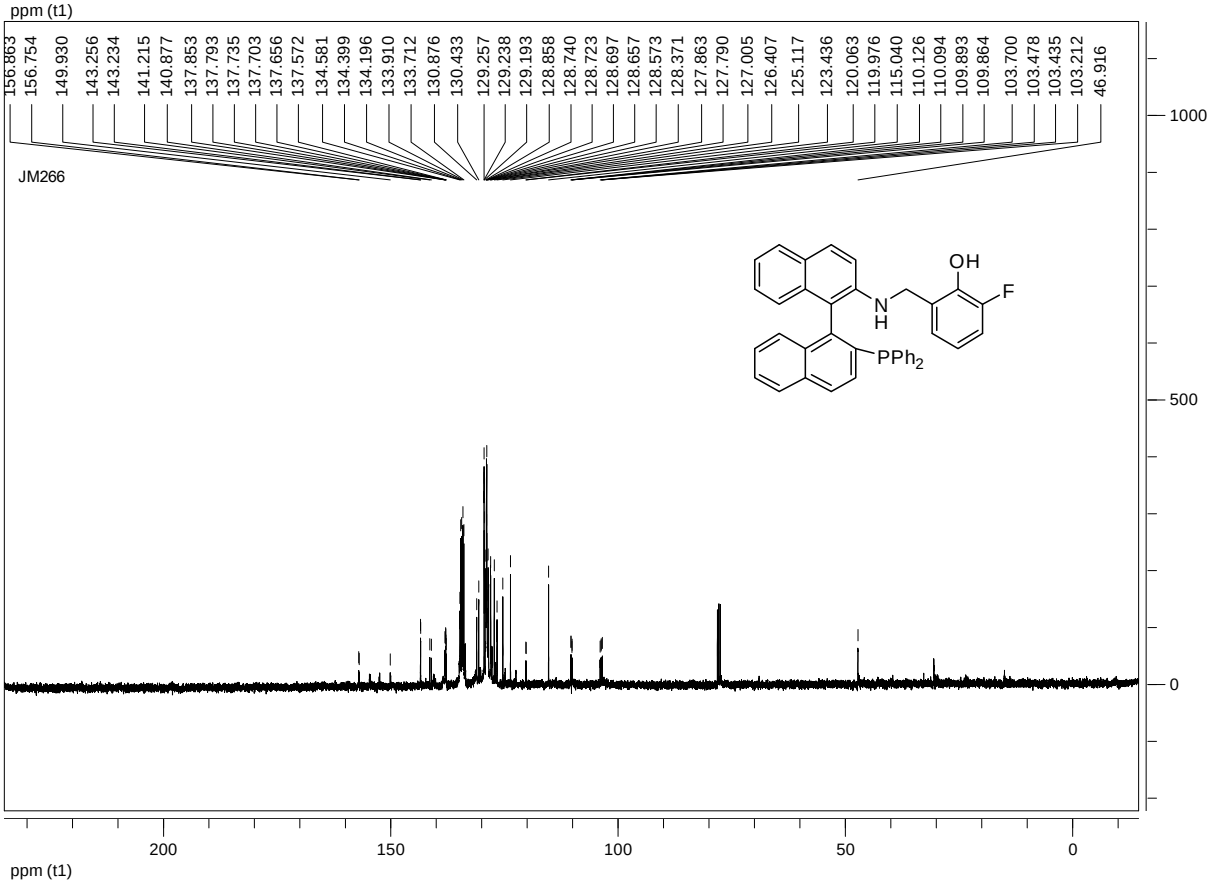
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129.238
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123.436
120.063
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110.094
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109.864
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103.478
103.435
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50
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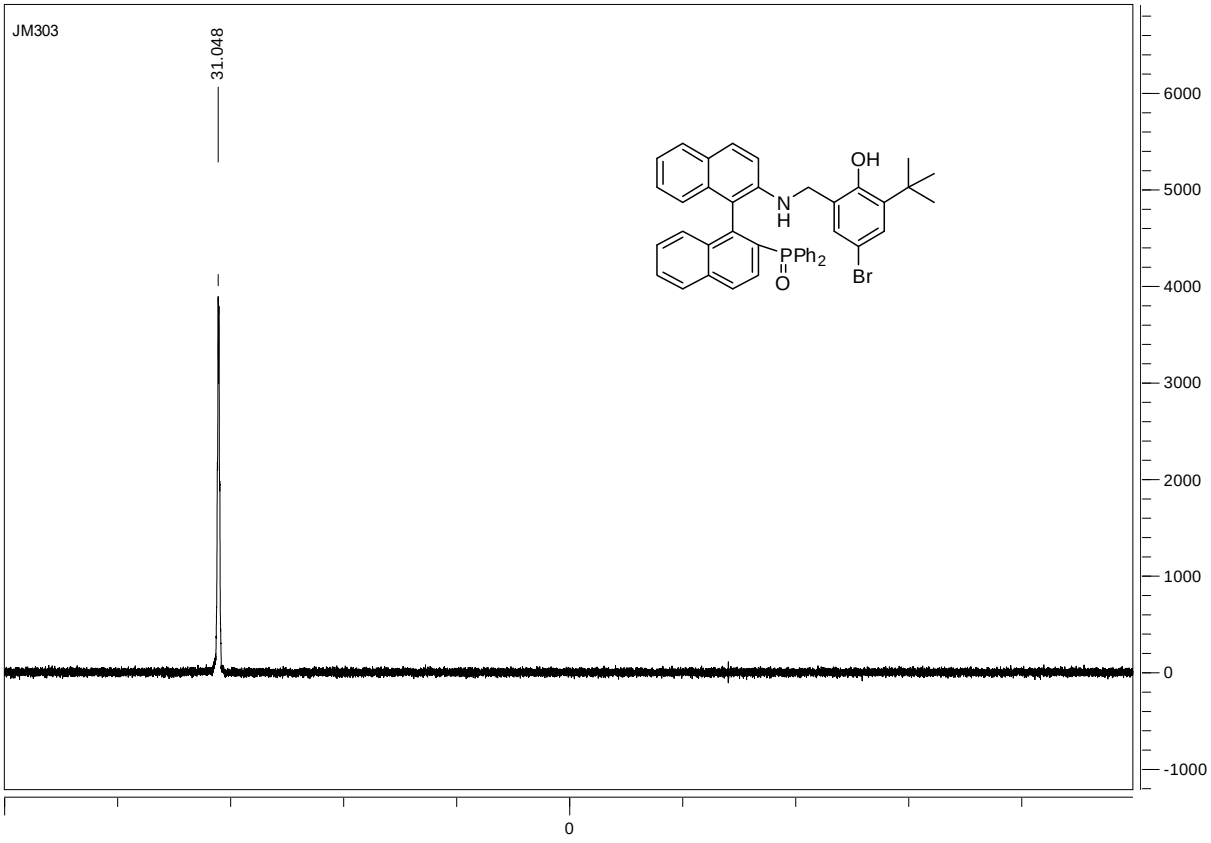
ppm (t1)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-1000
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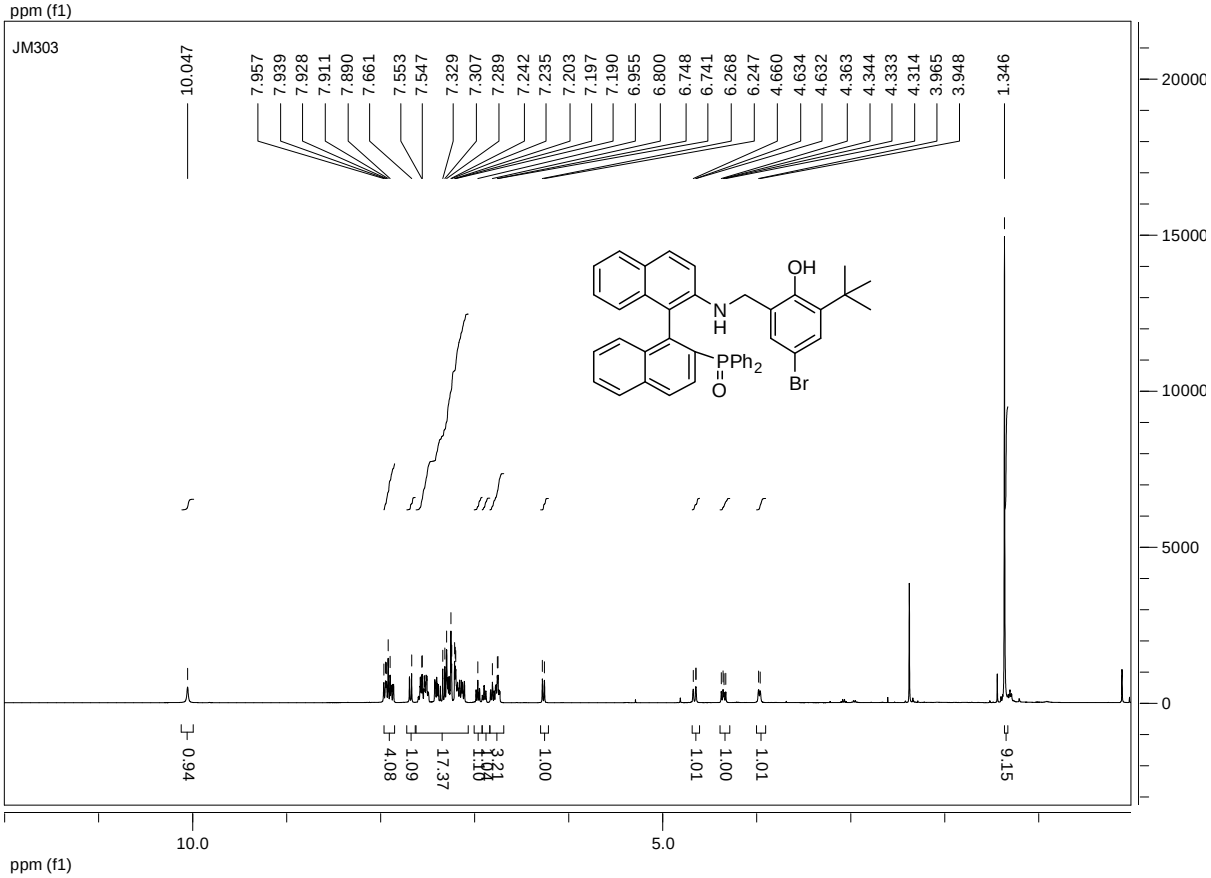
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7.911
7.890
7.661
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7.307
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7.242
7.235
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6.955
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6.748
6.741
6.268
6.247
4.660
4.634
4.632
4.363
4.344
4.333
4.314
3.965
3.948
1.346
OH
N
H
PPh2
O
Br
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15000
10000
5000
0
0.94
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1.00
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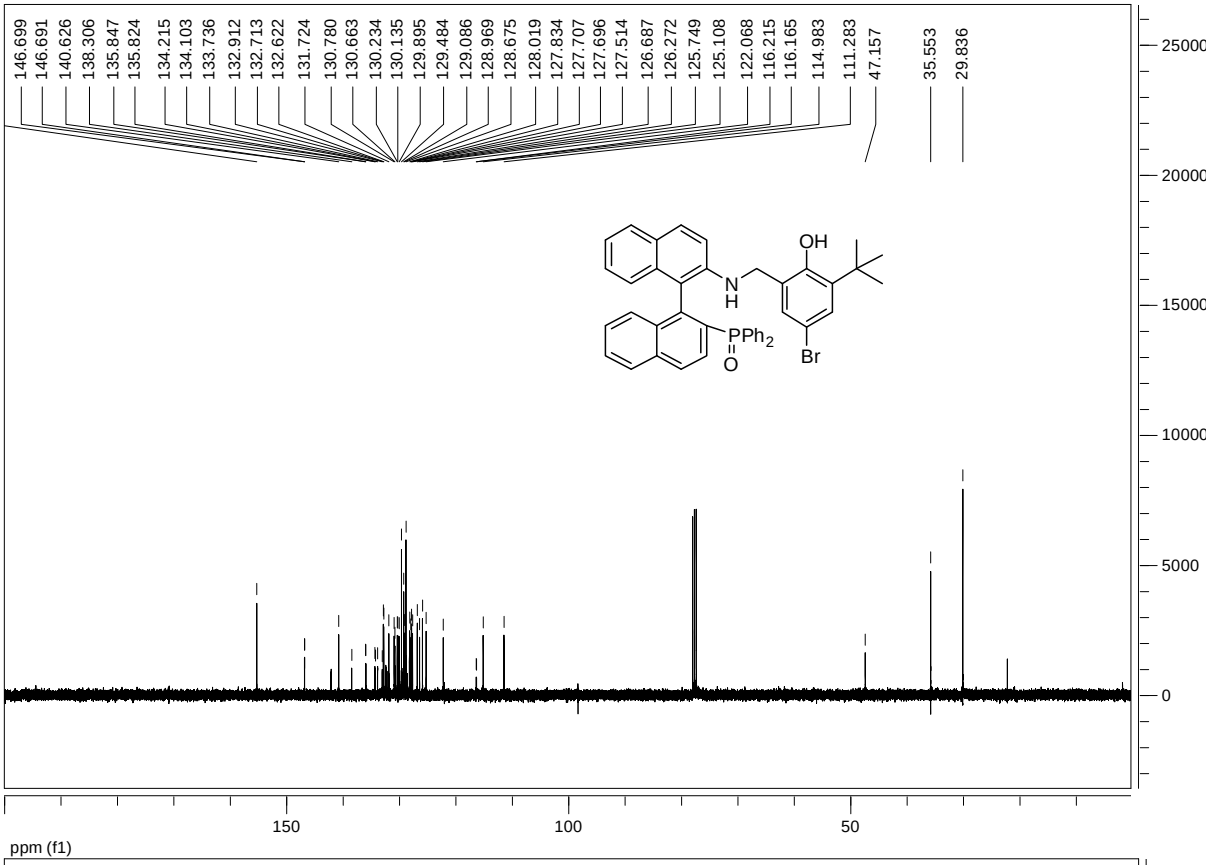
5.0
ppm (f1)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132.622
131.724
130.780
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130.234
130.135
129.895
129.484
129.086
128.969
128.675
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127.834
127.707
127.696
127.514
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126.272
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122.068
116.215
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114.983
111.283
47.157
35.553
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OH
N
H
PPh2
O
Br
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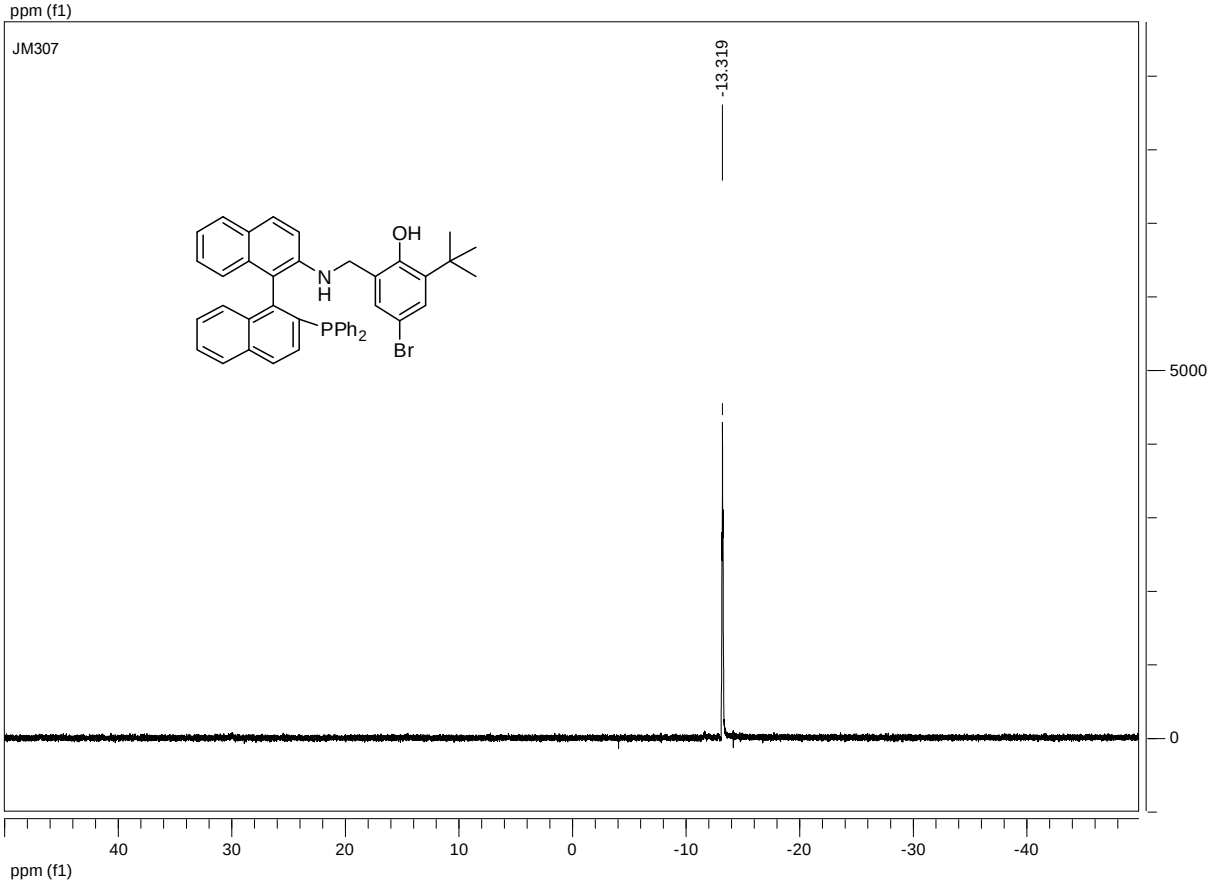
150
100
50
ppm (f1)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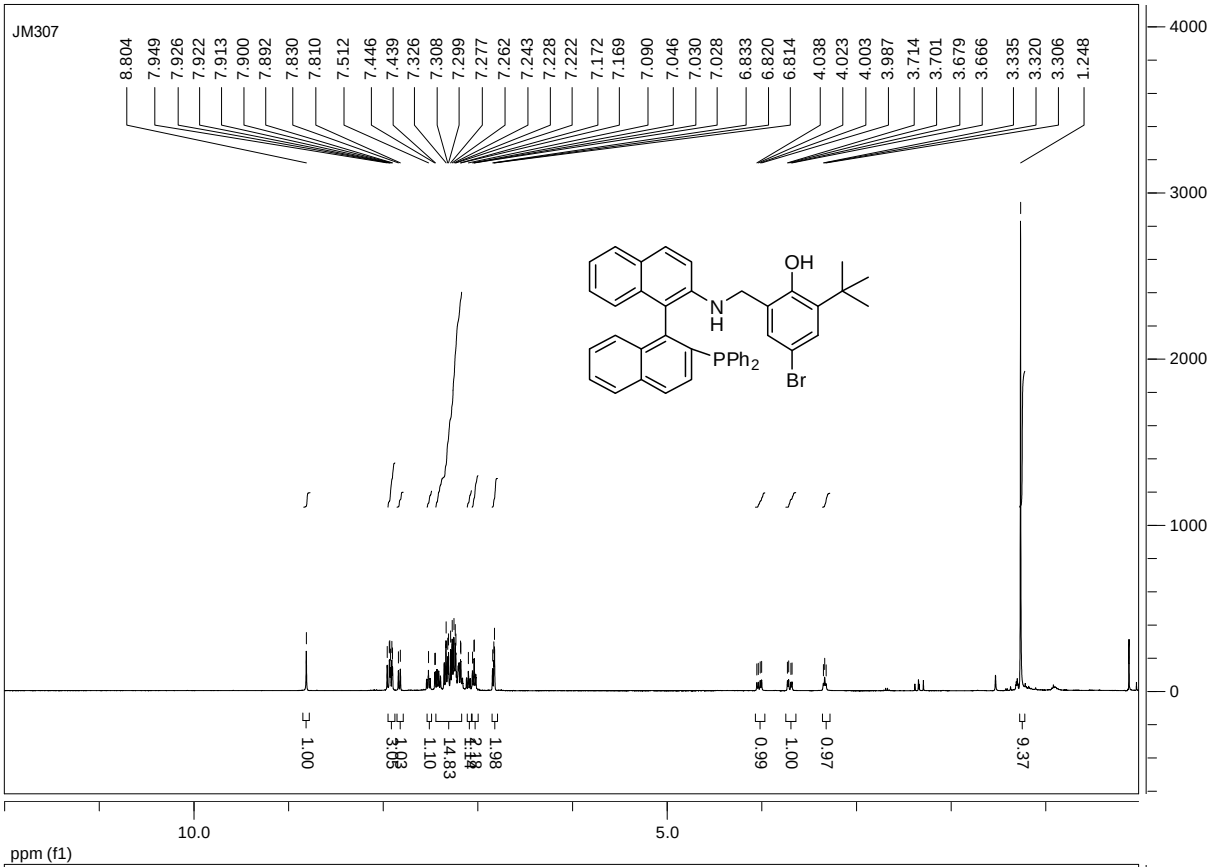
ppm (f1)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7.922
7.913
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7.892
7.830
7.810
7.512
7.446
7.439
7.326
7.308
7.299
7.277
7.262
7.243
7.228
7.222
7.172
7.169
7.090
7.046
7.030
7.028
6.833
6.820
6.814
4.038
4.023
4.003
3.987
3.714
3.701
3.679
3.666
3.335
3.320
3.306
1.248
OH
N
H
PPh2
Br
1.00
3.03
1.10
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1000
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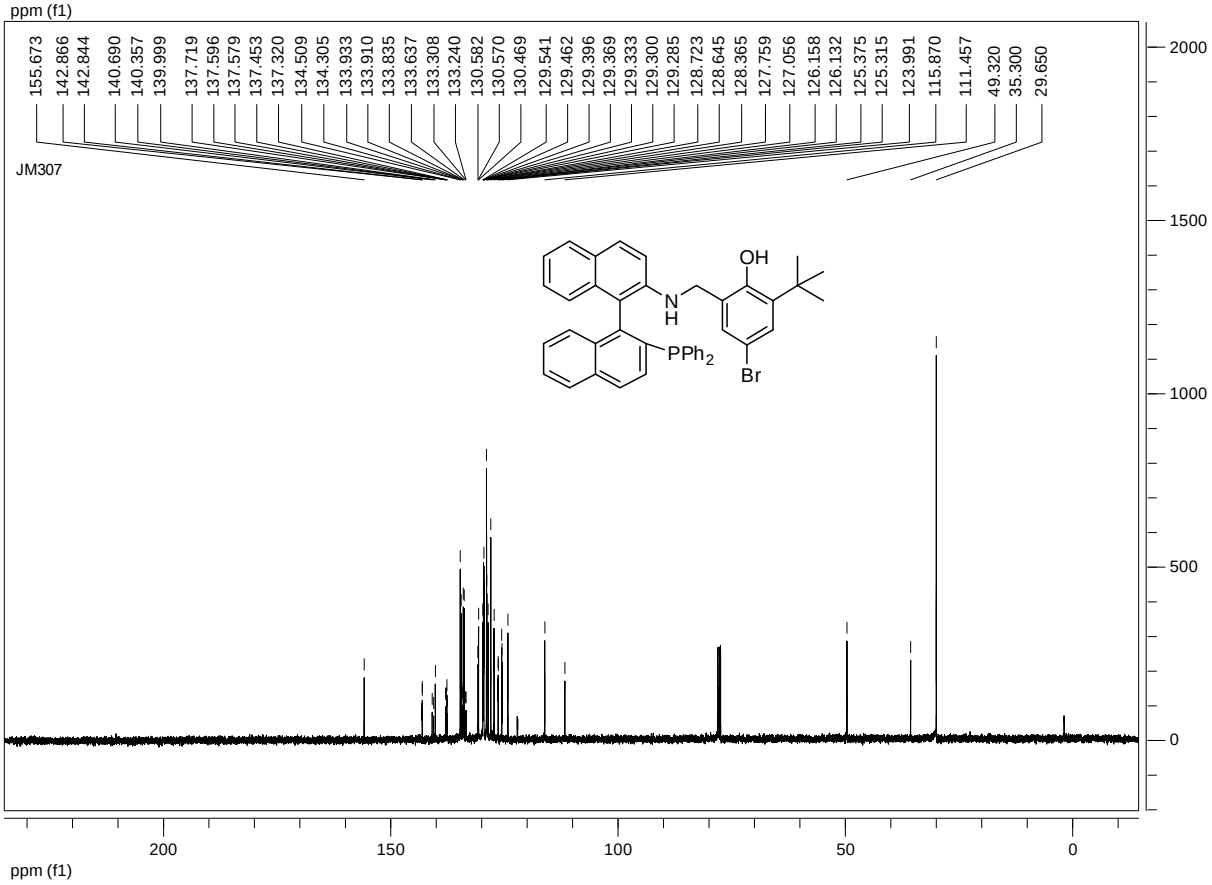
10.0
5.0
ppm (f1)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134.305
133.933
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125.315
123.991
115.870
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200
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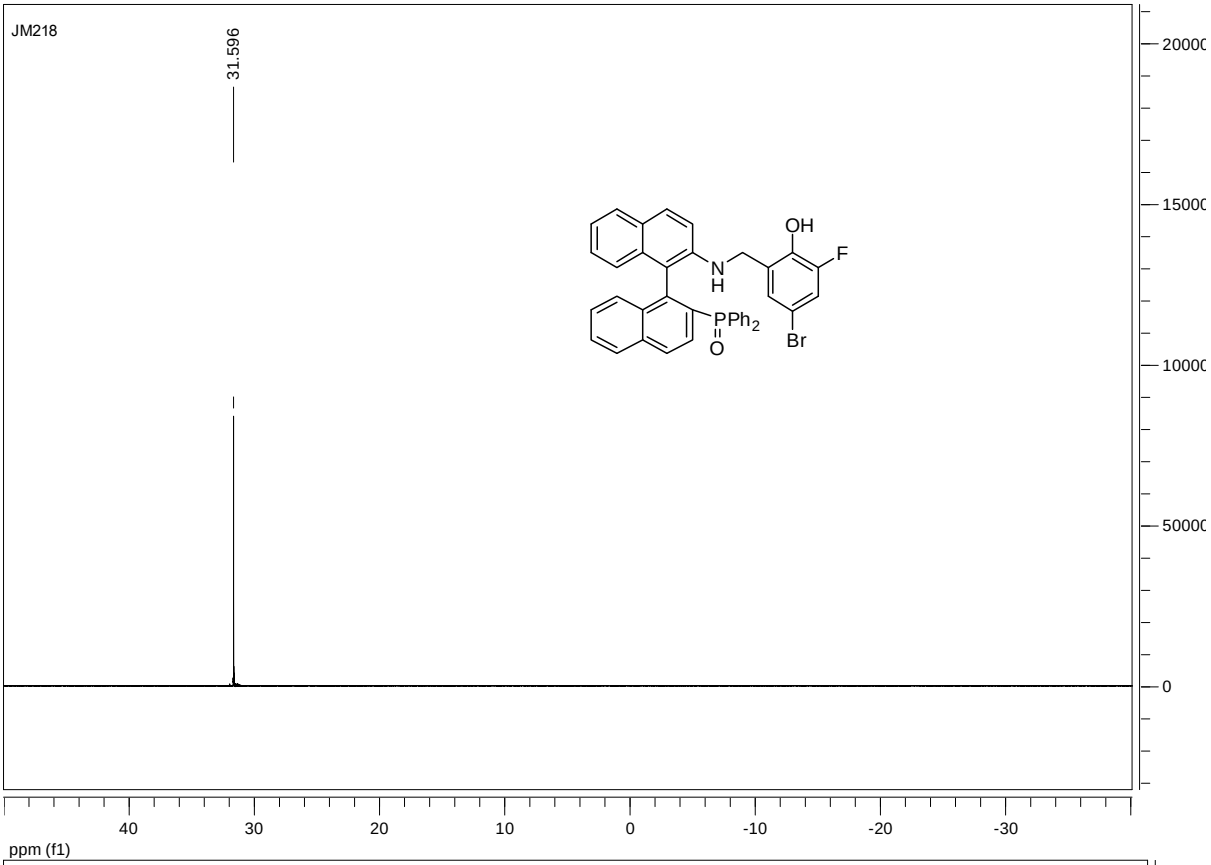
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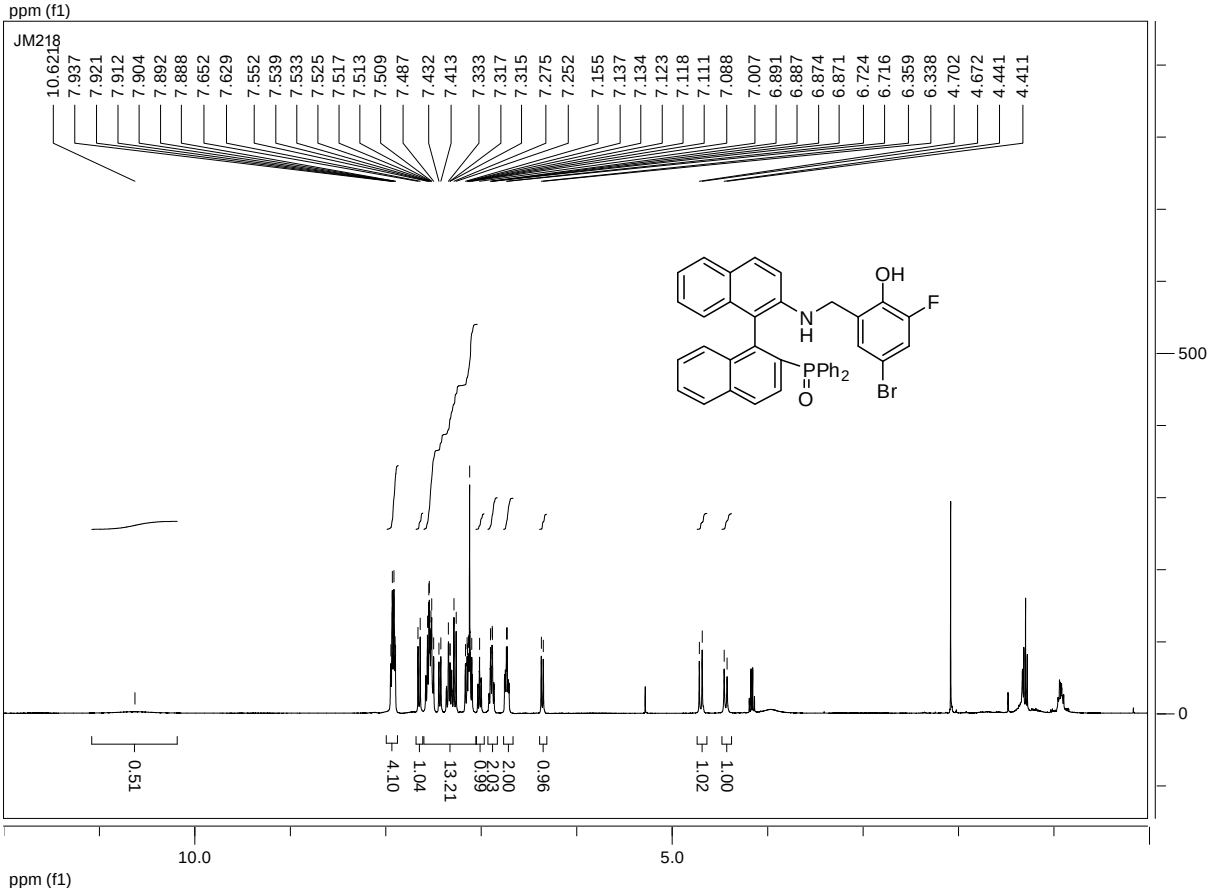
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7.888
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7.552
7.539
7.533
7.525
7.517
7.513
7.509
7.487
7.432
7.413
7.333
7.317
7.315
7.275
7.252
7.155
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7.134
7.123
7.118
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7.088
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6.891
6.887
6.874
6.871
6.724
6.716
6.359
6.338
4.702
4.672
4.441
4.411
OH
F
N
H
PPh2
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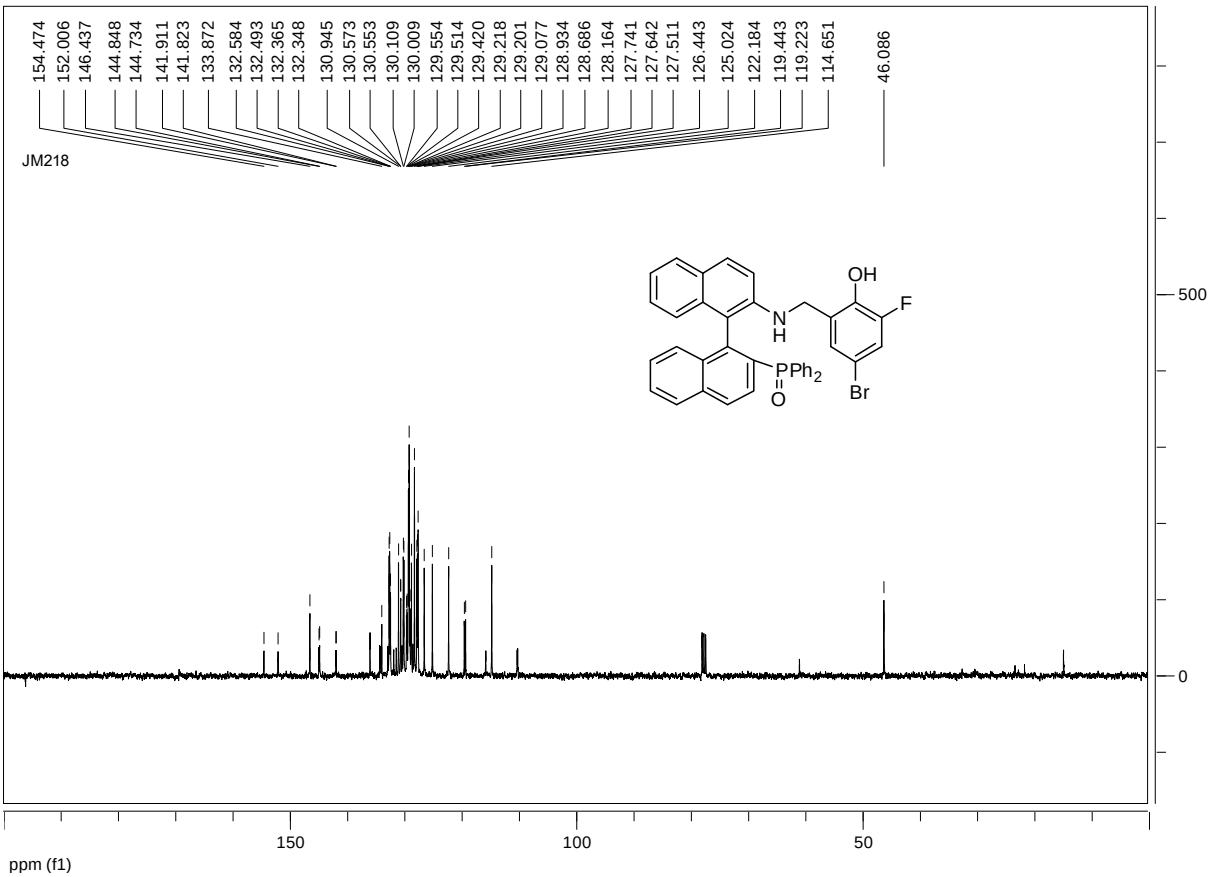
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126.443
125.024
122.184
119.443
119.223
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Br
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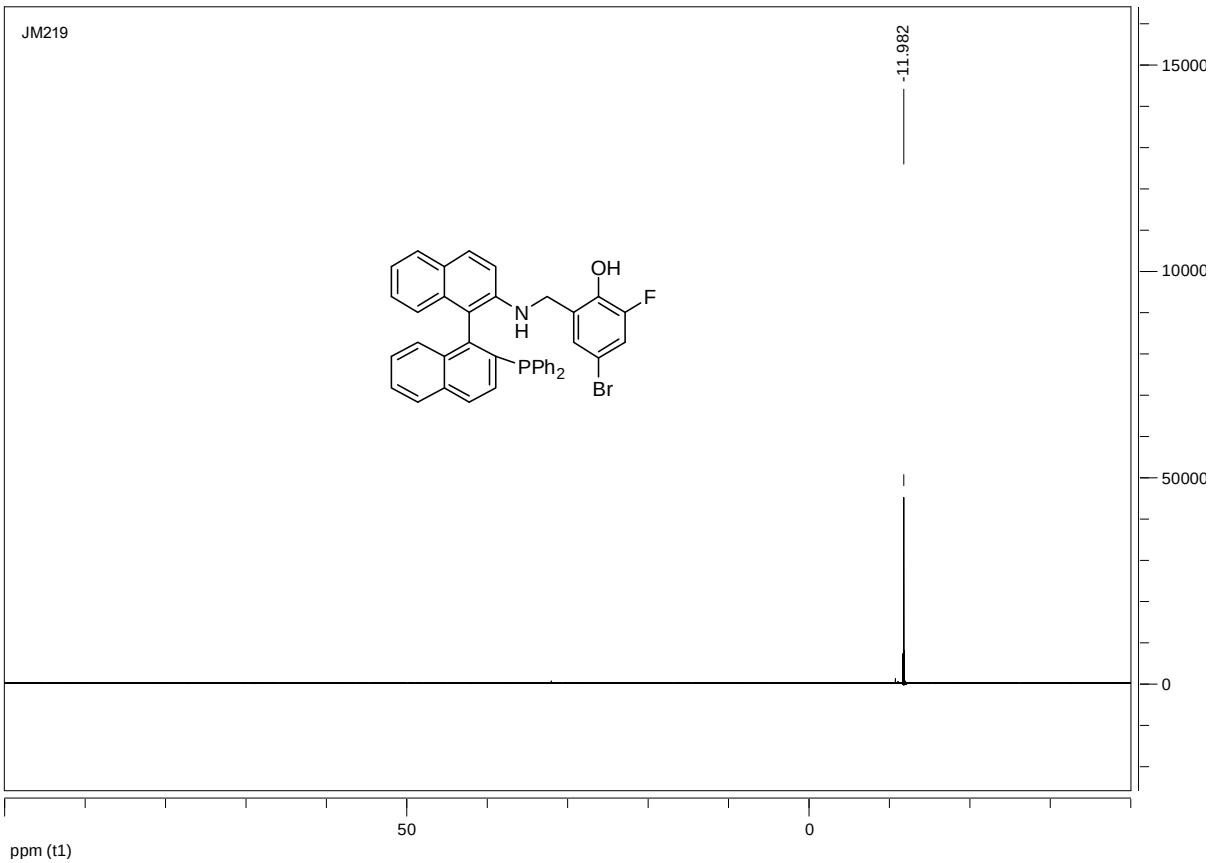
150
100
50
ppm (f1)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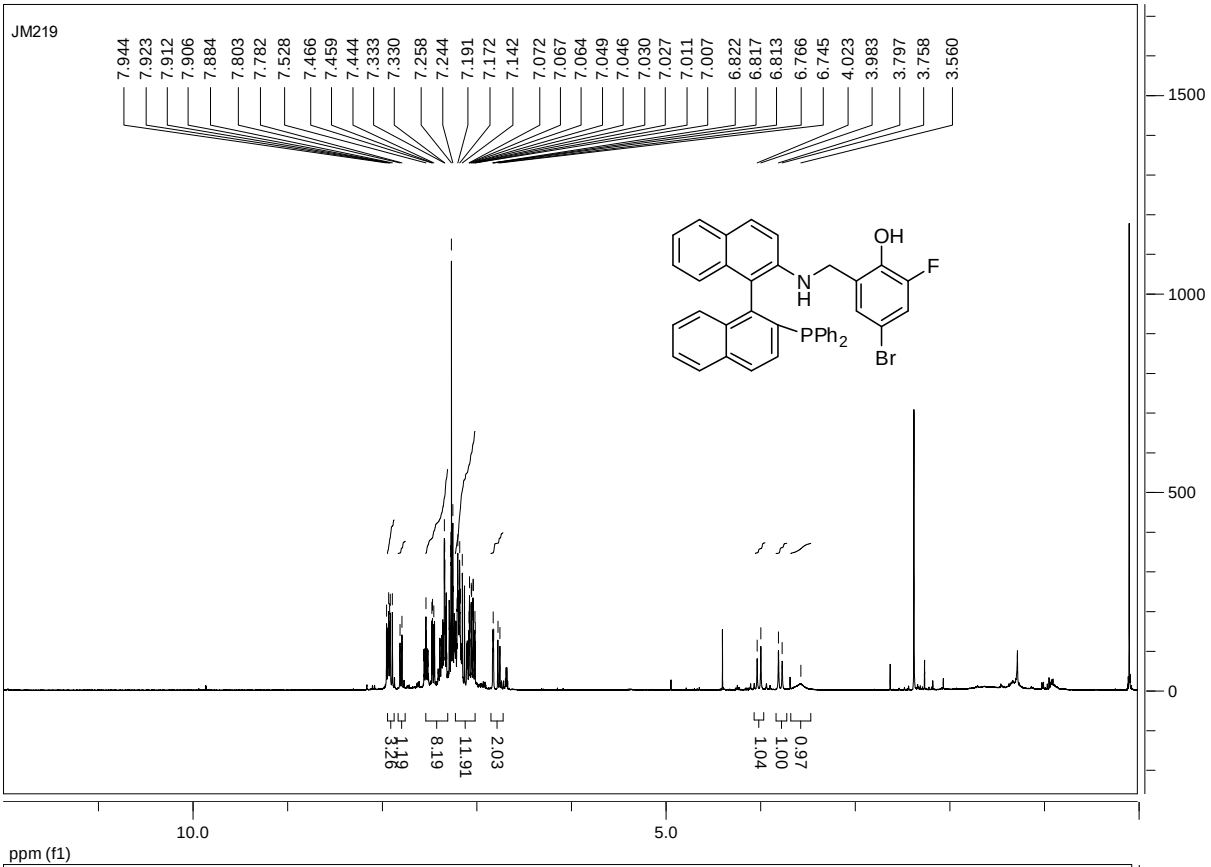
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7.333
7.330
7.258
7.244
7.191
7.172
7.142
7.072
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7.064
7.049
7.046
7.030
7.027
7.011
7.007
6.822
6.817
6.813
6.766
6.745
4.023
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OH
F
N
H
PPh2
Br
3.26
1.19
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2.03
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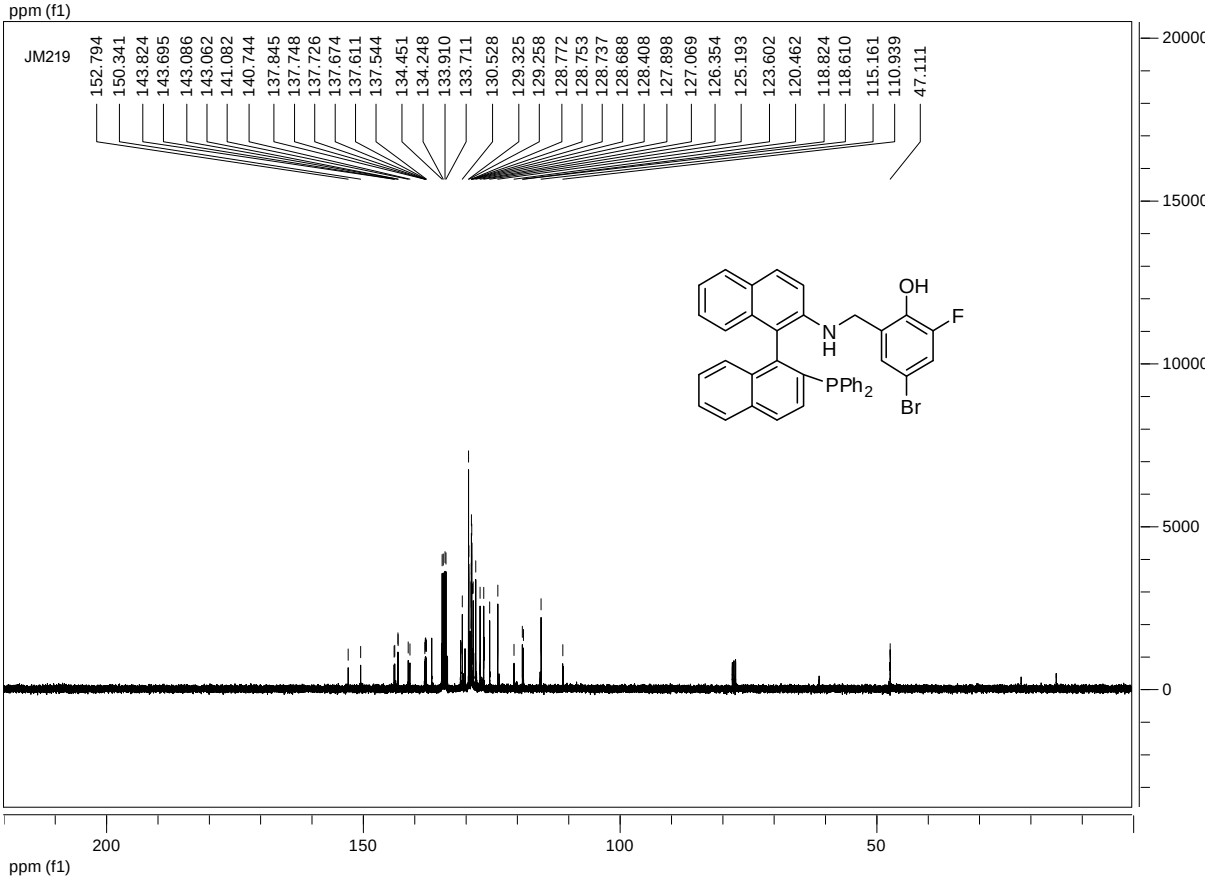
1000
500
0
10.0
5.0
ppm (f1)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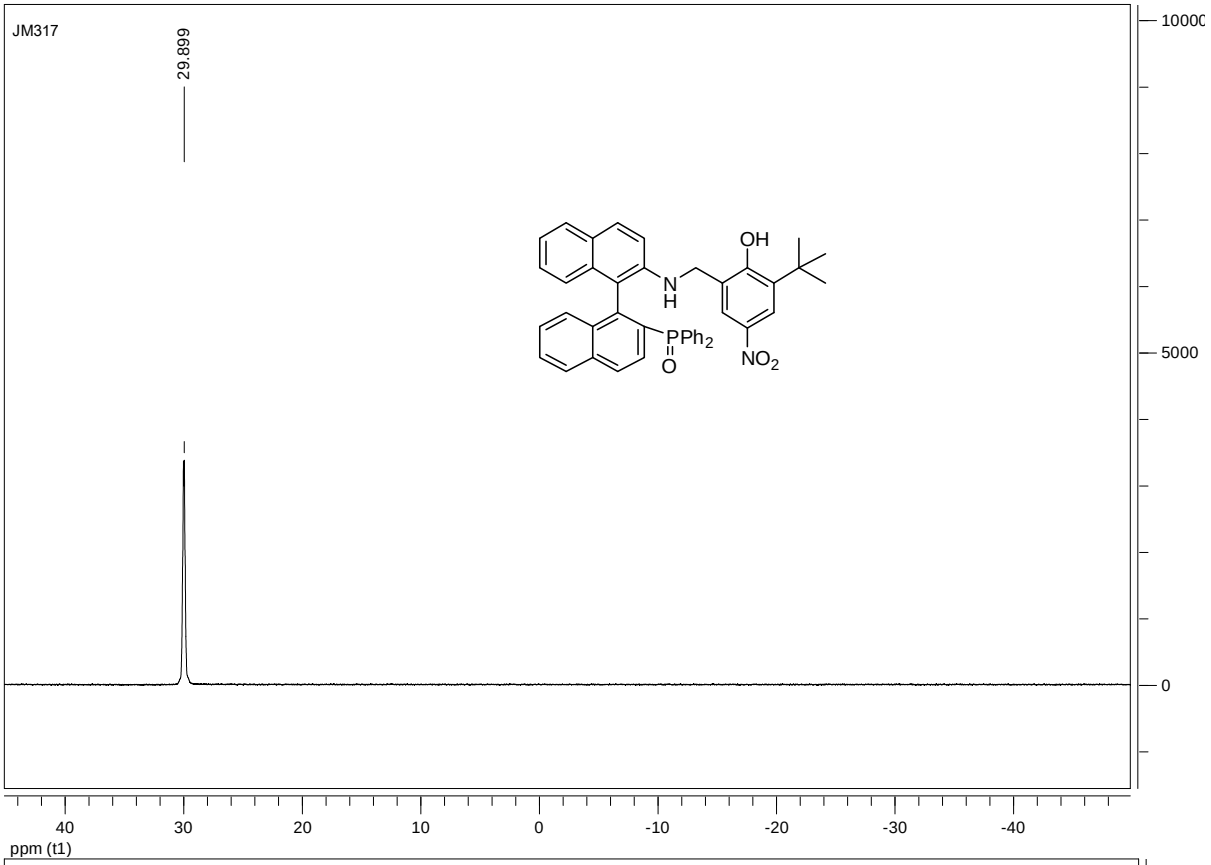
143.695
143.086
143.062
141.082
140.744
137.845
137.748
137.726
137.674
137.611
137.544
134.451
134.248
133.910
133.711
130.528
129.325
129.258
128.772
128.753
128.737
128.688
128.408
127.898
127.069
126.354
125.193
123.602
120.462
118.824
118.610
115.161
110.939
47.111
OH
F
N
H
PPh2
Br
20000
15000
10000
5000
0
200
150
100
50
ppm (f1)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10
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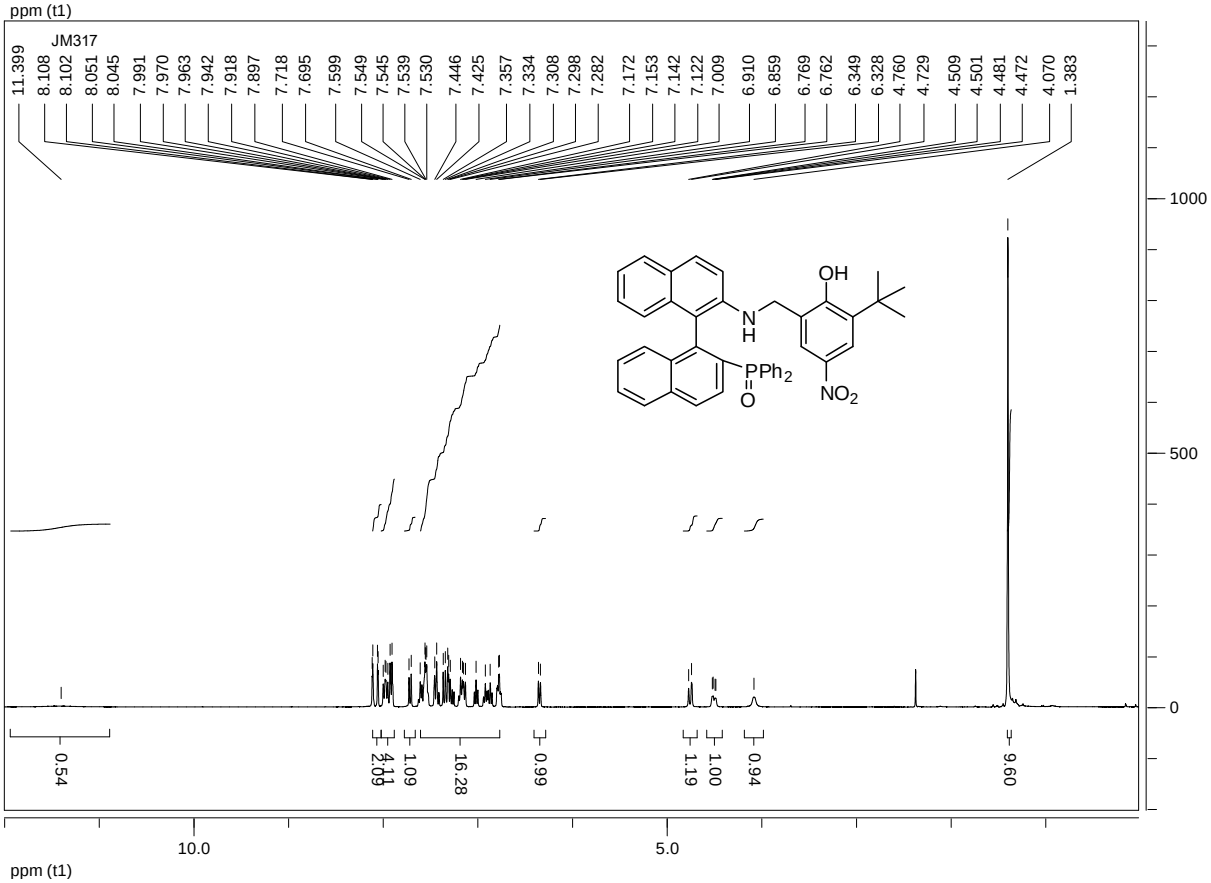
-10
-20
-30
-40
ppm (t1)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11.399
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8.102
8.051
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7.718
7.695
7.599
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7.539
7.530
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7.425
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7.308
7.298
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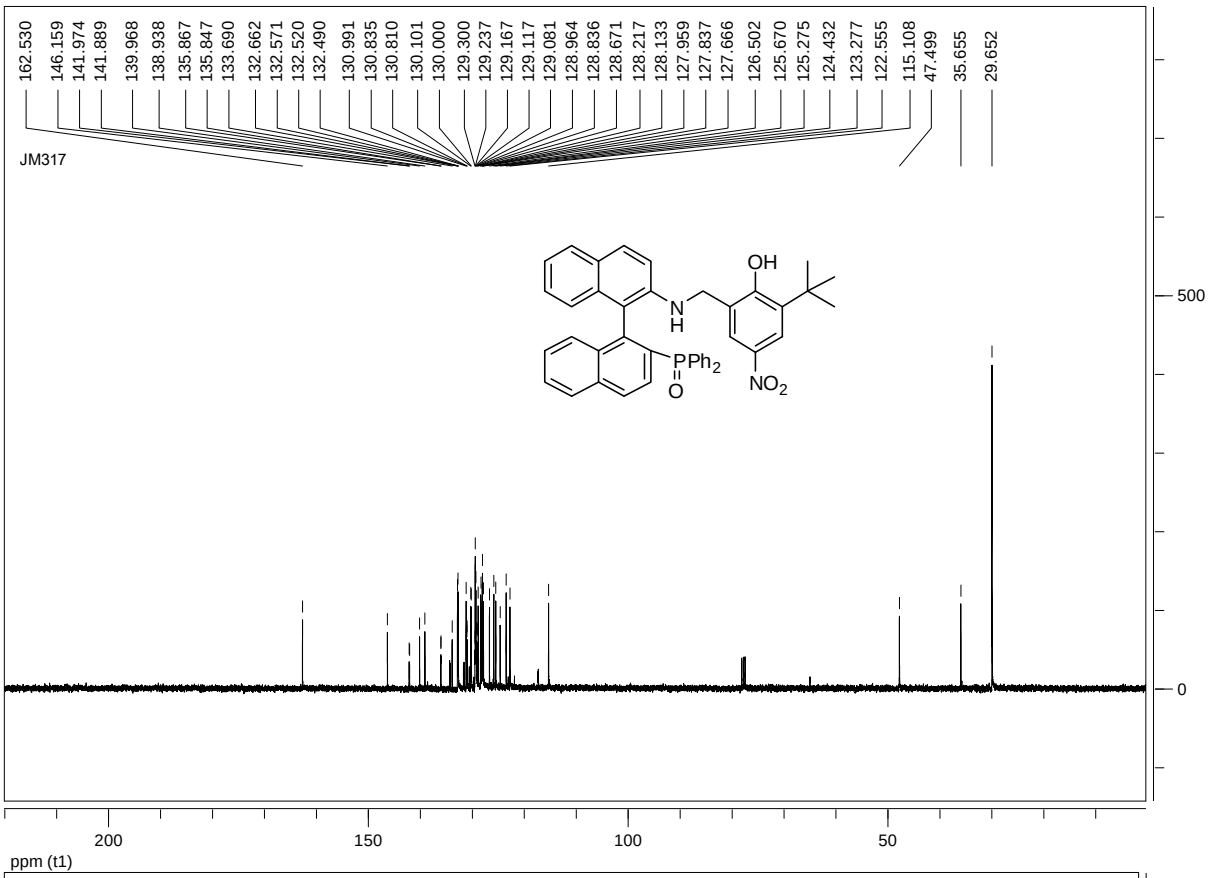
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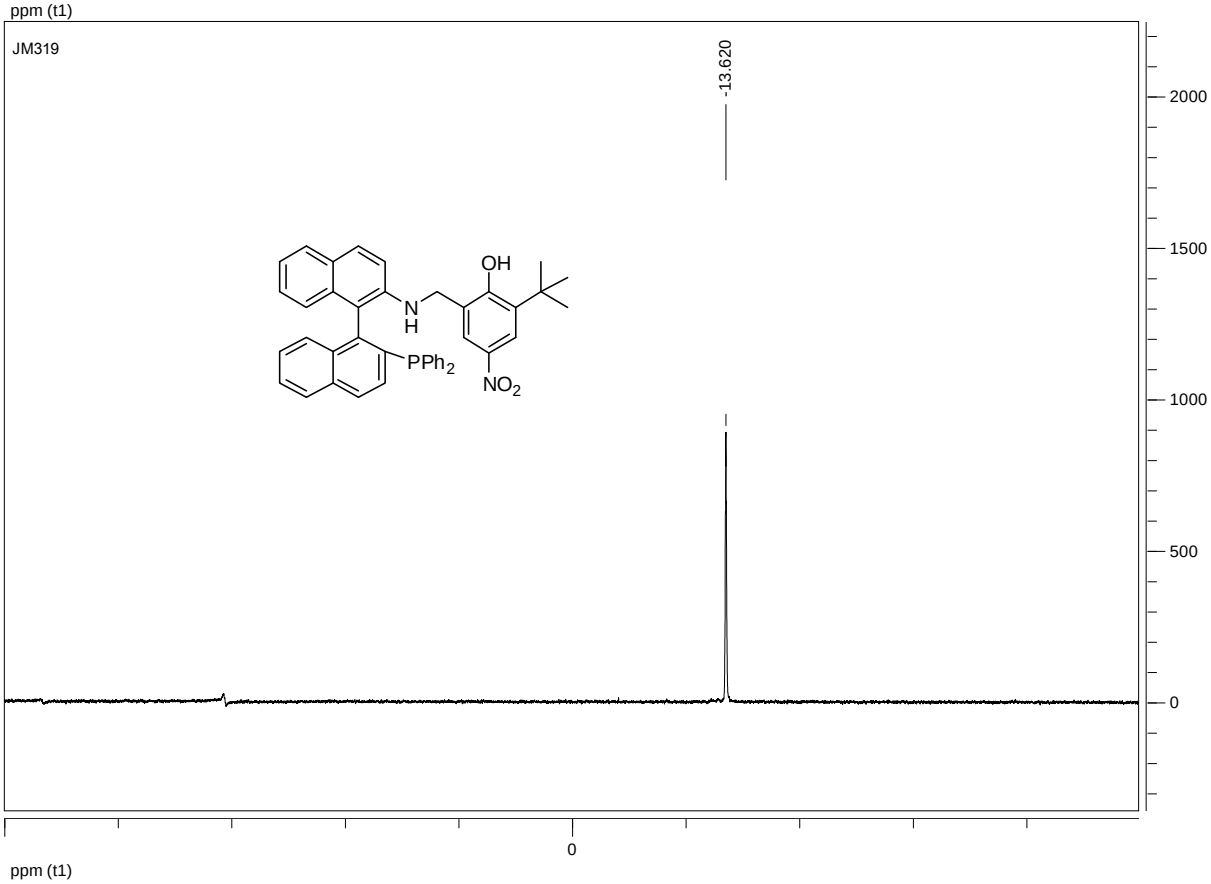
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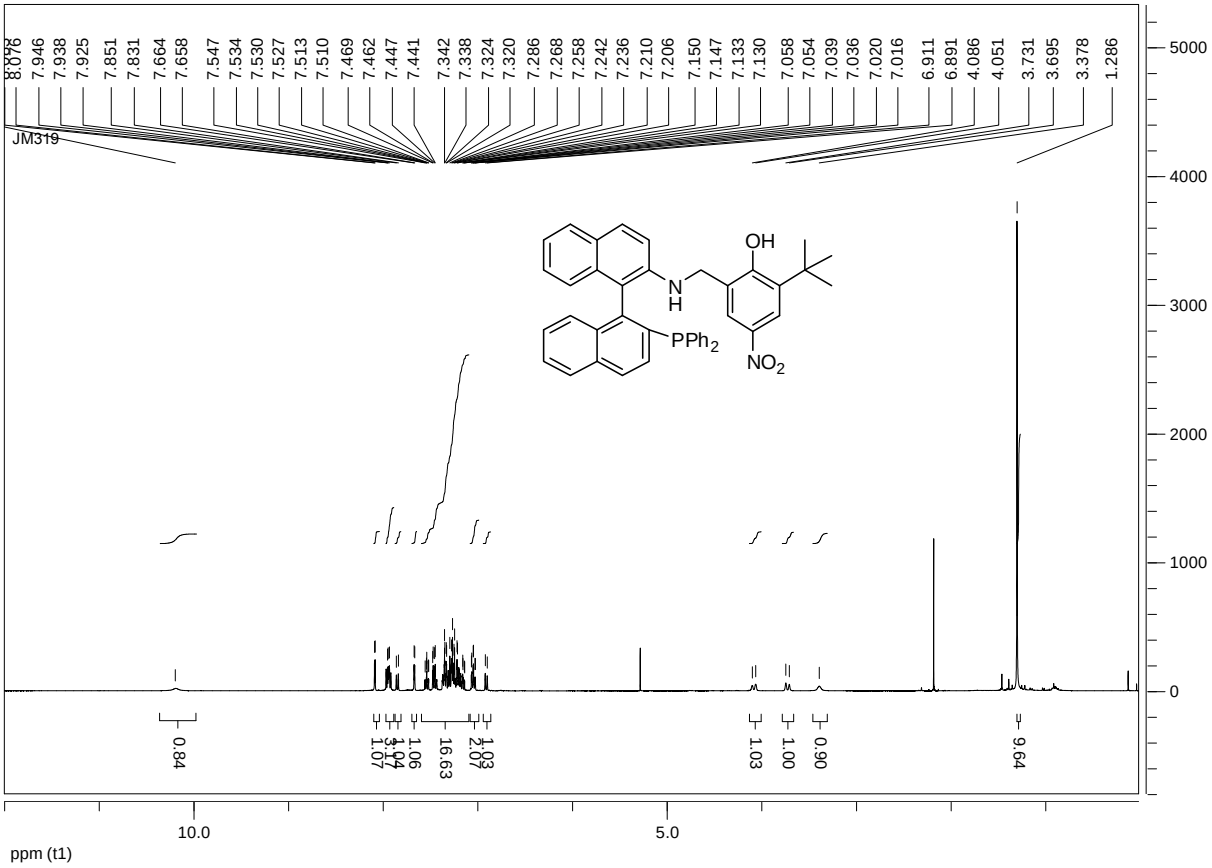
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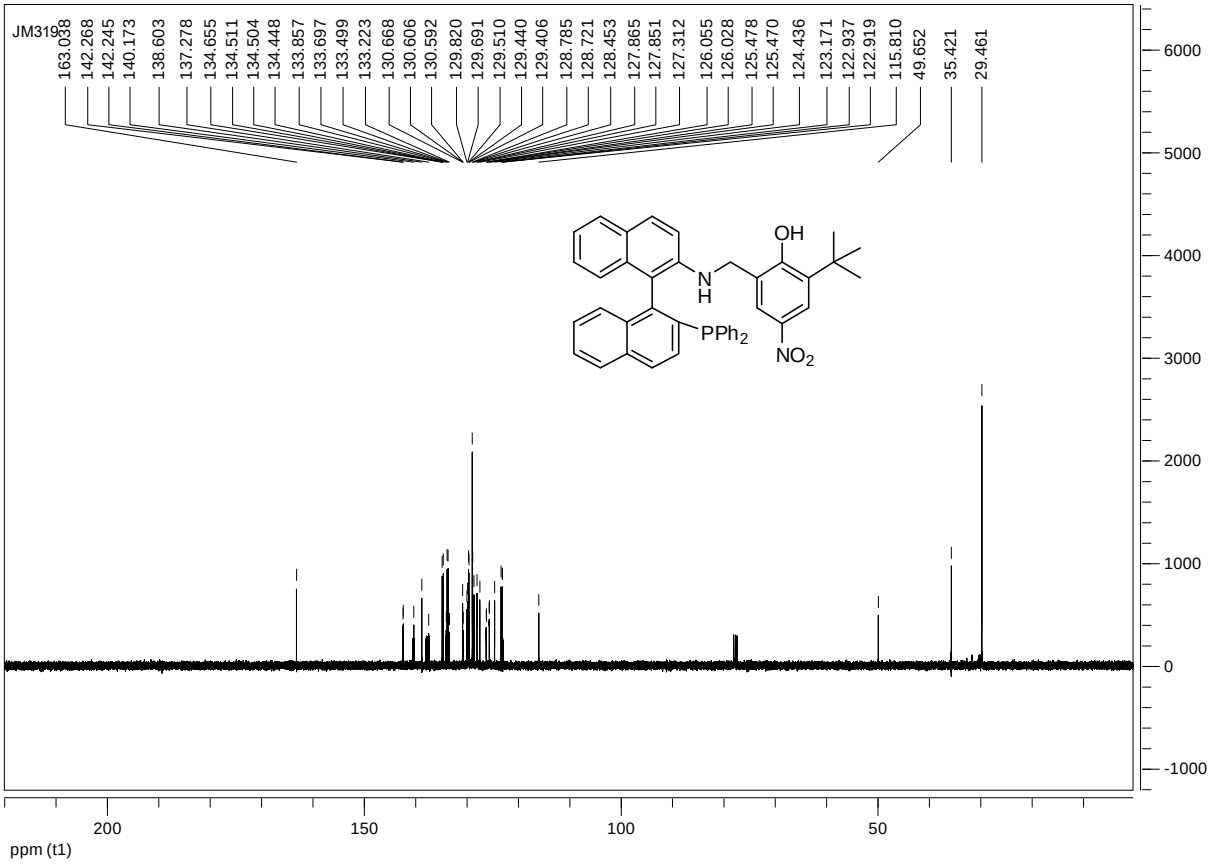
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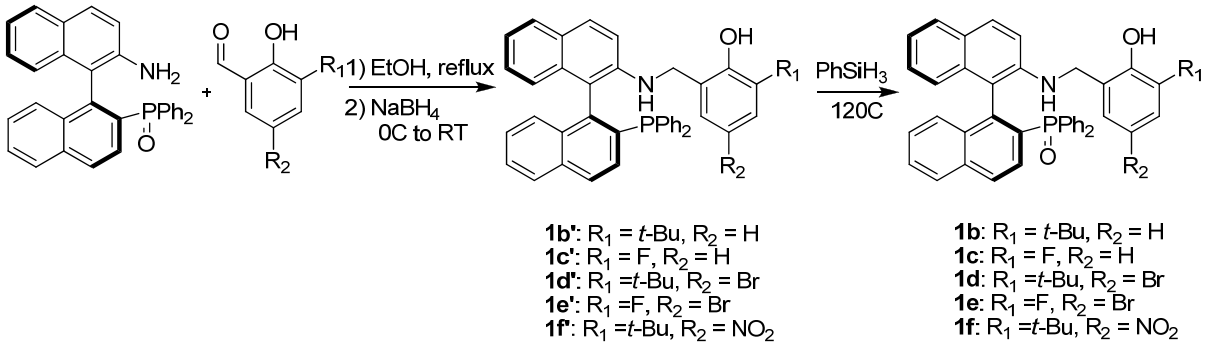
III- NMR data of catalysts 1b'1b-1f'1f



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1f': R_1 =*t*-Bu, R_2 = NO_2

1b: R_1 = *t*-Bu, R_2 = H
1c: R_1 = F, R_2 = H
1d: R_1 =*t*-Bu, R_2 = Br
1e: R_1 =F, R_2 = Br
1f: R_1 =*t*-Bu, R_2 = NO_2

(*S*)-2-tert-butyl-6-((2'-(diphenylphosphoryl)-1,1'-binaphthyl-2-ylamino)methyl)phenol (1b')

Yield: 76%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.45 (s, 9H); 4.04 (d, *J* = 5.6 Hz, 1H); 4.48 (dd, *J1* = 12.0 Hz, *J2* = 7.6 Hz, 1H); 4.76 (d, *J* = 11.6 Hz, 1H); 6.28 (d, *J* = 8.0 Hz, 1H); 6.74-7.60 (m, 19H); 7.73 (d, *J* = 8.8 Hz, 1H); 7.87-8.03 (m, 4H); 9.90 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 30.1, 35.4, 47.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ +29.86; **ESI** [M+H^+]: 632.2663, calcd for $(C_{43}H_{39}NO_2P)^+$: 632.2718; $[\alpha]_D$ = +31.1 (c 2.00; CH_2Cl_2).°

(*S*)-2-tert-butyl-6-((2'-(diphenylphosphino)-1,1'-binaphthyl-2-ylamino)methyl)phenol (1b)

Yield: 67%; off-white solid; **mp** 117-119°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.29 (s, 9H); 3.38 (m, 1H); 3.82 (dd, *J1* = 13.6 Hz, *J2* = 4.4 Hz, 1H); 4.12 (dd, *J1* = 13.6 Hz, *J2* = 5.6 Hz, 1H); 6.73 (m, 3H); 7.03 (t, *J* = 7.2 Hz, 3H); 7.14-7.52 (m, 15H); 7.79 (d, *J* = 8.0 Hz, 1H); 7.88-7.94 (m, 3H); 8.69 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 29.9, 35.1, 49.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -13.01; **ESI** [M+H^+]: 616.2780, calcd for $(C_{43}H_{39}NOP)^+$: 616.2769; $[\alpha]_D$ = +6.6 (c 1.22; CH_2Cl_2).

(*S*)- 2-((2'-(diphenylphosphoryl)-1,1'-binaphthyl-2-ylamino)methyl)-6-fluorophenol (1c')

Yield: 81%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.36 (d, *J* = 12.0 Hz, 1H); 4.67 (d, *J* = 12.0 Hz, 1H); 6.29 (d, *J* = 8.4 Hz, 1H); 6.66-6.76 (m, 4H); 6.82-6.88 (m, 2H); 6.98 (t, *J* = 6.8 Hz, 1H); 7.03-7.09 (m, 2H); 7.24-7.62 (m, 11H); 7.84-7.92 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 46.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ +30.16; $[\alpha]_D$ = +61.2 (c 2.00; CH_2Cl_2).

(*S*)- 2-((2'-(diphenylphosphino)-1,1'-binaphthyl-2-ylamino)methyl)-6-fluorophenol (1c)

Yield: 61%; off-white solid; **mp** 124-126°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.85 (d, *J* = 16.0 Hz, 1H); 4.05 (d, *J* = 16.0 Hz, 1H); 6.48 (d, *J* = 8.8 Hz, 1H); 6.71 (t, *J* = 9.4 Hz, 1H); 6.78 (d, *J* = 8.4 Hz, 1H); 7.05-7.54 (m, 18H); 7.79 (d, *J* = 8.0 Hz, 1H); 7.89-7.96 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 46.9; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -13.67; **ESI** [M+H$^+$]: 578.2056, calcd for $(C_{39}H_{30}NOFP)^+$: 578.2049; $[\alpha]_D$ = +16.9 (c 1.05; CH_2Cl_2).

(*S*)-4-bromo-2-tert-butyl-6-((2'-(diphenylphosphoryl)-1,1'-binaphthyl-2-ylamino)methyl)phenol (1d')

Yield: 95%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.35 (s, 9H); 3.95 (d, *J* = 6.8 Hz, 1H); 4.34 (dd, *J1* = 13.2 Hz, *J2* = 7.6 Hz, 1H); 4.63 (d, *J* = 11.2 Hz, 1H); 6.25 (d, *J* = 8.4 Hz, 1H); 6.72-6.82 (m, 3H); 6.89 (t, *J* = 7.6 Hz, 1H); 6.96 (t, *J* = 7.6 Hz, 1H); 7.10-7.59 (m, 13H); 7.67 (d, *J* = 8.8 Hz, 1H); 7.85-7.96 (m, 4H); 10.04 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 29.8, 35.5, 47.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ +31.05; **ESI** [M+H$^+$]: 710.1700, calcd for $(C_{43}H_{38}NO_2PBr)^+$: 710.1823; $[\alpha]_D$ = +84.2 (c 1.00; CH_2Cl_2).

(*S*)-4-bromo-2-tert-butyl-6-((2'-(diphenylphosphino)-1,1'-binaphthyl-2-ylamino)methyl)phenol (1d)

Yield: 67%; off-white solid; **mp** 126-128°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.25 (s, 9H); 3.32 (t, *J* = 6.0 Hz, 1H); 3.69 (dd, *J1* = 14.0 Hz, *J2* = 5.2 Hz, 1H); 4.01 (dd, *J1* = 14.0 Hz, *J2* = 6.0 Hz, 1H); 6.82 (m, 2H); 7.03 (t, *J* = 6.8 Hz, 2H); 7.09 (t, *J* = 7.6 Hz, 1H); 7.16-7.44 (m, 14H); 7.51 (t, *J* = 7.4 Hz, 1H); 7.82 (d, *J* = 8.0 Hz, 1H); 7.89-7.95 (m, 3H); 8.80 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 29.6, 35.3, 49.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -13.32; **ESI** [M+H$^+$]: 694.1850, calcd for $(C_{43}H_{38}NOPBr)^+$: 694.1874; $[\alpha]_D$ = +16.6 (c 1.01; CH_2Cl_2).

(*S*)-4-bromo-2-((2'-(diphenylphosphoryl)-1,1'-binaphthyl-2-ylamino)methyl)-6-fluorophenol (1e')

Yield: 83%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.95 (br s, 1H); 4.42 (d, *J* = 12.0 Hz, 1H); 4.69 (d, *J* = 12.0 Hz, 1H); 6.34 (d, *J* = 8.4 Hz, 1H); 6.72 (m, 2H); 6.88 (m, 2H); 7.00 (t, *J* = 7.4 Hz, 1H); 7.08-7.52 (m, 13H); 7.64 (d, *J* = 9.2 Hz, 1H); 7.89-7.94 (m, 4H); 10.62 (br s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 46.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ +31.59; **ESI** [M+H$^+$]: 672.1038, calcd for $(C_{39}H_{29}NO_2PBrF)^+$: 672.1103; $[\alpha]_D$ = +129.8 (c 1.96; CH_2Cl_2).

(*S*)-4-bromo-2-((2'-(diphenylphosphino)-1,1'-binaphthyl-2-ylamino)methyl)-6-fluorophenol (1e)

Yield: 89%; off-white solid; **mp** 133-135°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.56 (br s, 1H); 3.77 (d, *J* = 15.6 Hz, 1H); 4.00 (d, *J* = 16.0 Hz, 1H); 6.80 (m, 2H); 7.01-7.53 (m, 18H); 7.79 (d, *J* = 8.4 Hz, 1H); 7.88-7.95 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 47.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -11.98; **ESI** [M+H$^+$]: 656.1133, calcd for $(C_{39}H_{29}NOPBrF)^+$: 656.1154; $[\alpha]_D$ = +28.1 (c 1.02; CH_2Cl_2).

(*S*)-2-tert-butyl-6-((2'-(diphenylphosphoryl)-1,1'-binaphthyl-2-ylamino)methyl)-4-nitrophenol (1f')

Yield: 82%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.07 (br s, 1H); 4.49 (d, *J* = 11.2 Hz, 1H); 4.74 (d, *J* = 12.4 Hz, 1H); 6.33 (d, *J* = 8.4 Hz, 1H); 6.76 (m, 2H); 6.89 (m, 2H); 7.01 (t, *J* = 7.2 Hz, 1H); 7.12-7.60 (m, 12H); 7.70 (d, *J* = 9.2 Hz, 1H); 7.90-8.11 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 29.6, 35.7, 47.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ +29.90; **ESI** [M+H$^+$]: 677.2582, calcd for $(C_{43}H_{38}N_2O_4P)^+$: 677.2569; $[\alpha]_D$ = +118.7 (c 2.00; CH_2Cl_2).

(*S*)-2-tert-butyl-6-((2'-(diphenylphosphino)-1,1'-binaphthyl-2-ylamino)methyl)-4-nitrophenol (1f)

Yield: 73%; off-white solid; **mp** 125-127°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.38 (br s, 1H); 3.71 (d, *J* = 14.4 Hz, 1H); 4.07 (d, *J* = 14.0 Hz, 1H); 6.90 (d, *J* = 8.0 Hz, 1H); 7.03 (dt, *J1* = 7.6 Hz, *J2* = 1.6 Hz, 2H); 7.13-7.36 (m, 12H); 7.42-7.47 (m, 2H); 7.53 (t, *J* = 7.2 Hz, 1H); 7.66 (d, *J* = 2.4 Hz, 1H); 7.84 (d, *J* = 8.0 Hz, 1H); 7.91-7.96 (m, 3H); 8.08 (d, *J* = 2.6 Hz, 1H); 10.19 (br s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 29.5, 35.4, 49.7; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -13.62; **ESI** [M+H$^+$]: 661.2601, calcd for $(C_{43}H_{38}N_2O_3P)^+$: 661.2620; $[\alpha]_D$ = +18.9 (c 1.06; CH_2Cl_2).

IV-NMR data of MBH adducts

3-((3-nitrophenyl)(tosylamino)methyl)but-3-en-2-one (3a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16 (s, 3H); 2.39 (s, 3H); 5.30 (d, *J* = 9.4 Hz, 1H); 5.89 (d, *J* = 9.4 Hz, 1H); 6.12 (s, 1H); 6.18 (s, 1H); 7.25 (d, *J* = 8.6 Hz, 2H); 7.44 (dd, *J*1 = 8.2 Hz, *J*2 = 7.8 Hz, 1H); 7.61 (d, *J* = 7.8 Hz, 1H); 7.65 (d, *J* = 8.6 Hz, 2H); 7.89 (s, 1H); 8.05 (d, *J* = 8.2 Hz, 1H). HPLC: Whelk-O1 column; λ = 254 nm; eluent: hexane/isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{minor} = 32.0 min, t_{major} = 36.0 min.

3-((4-bromophenyl)(tosylamino)methyl)but-3-en-2-one (3b). ^{1}H NMR (400 MHz, $CDCl_3$) 2.15 (s, 3H); 2.41 (s, 3H); 5.19 (d, *J* = 9.1 Hz, 1H); 5.71 (d, *J* = 9.1 Hz, 1H); 6.06 (s, 1H); 6.09 (s, 1H); 6.96 (d, *J* = 8.1 Hz, 2H); 7.25 (d, *J* = 8.1Hz, 2H); 7.25 (d, *J* = 8.6 Hz, 2H); 7.60 (d, *J* = 8.0 Hz, 2H). HPLC: AD column; λ = 254 nm; eluent: hexane/isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{minor} = 23.1 min, t_{major} = 27.5 min.

3-((4-chlorophenyl)(tosylamino)methyl)but-3-en-2-one (3c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 3H); 2.40 (s, 3H); 5.21 (d, *J* = 8.6 Hz, 1H); 5.78 (d, *J* = 8.6 Hz, 1H); 6.03 (s, 1H); 6.05 (s, 1H); 7.03 (d, *J* = 8.3 Hz, 2H); 7.15 (d, *J* = 8.3 Hz, 2H); 7.25 (d, *J* = 8.2 Hz, 2H); 7.62 (d, *J* = 8.2 Hz, 2H). HPLC: AD column; λ = 254 nm; eluent: hexane/isopropanol = 80/20; Flow rate: 0.3 mL/min; t_{minor} = 43.5 min, t_{major} = 48.0 min.

3-((2-chlorophenyl)(tosylamino)methyl)but-3-en-2-one (3d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (s, 3H); 2.37 (s, 3H); 5.69 (d, *J* = 8.0 Hz, 1H); 5.90 (d, *J* = 8.0 Hz, 1H); 6.16 (s, 1H); 6.17 (s, 1H); 7.06-7.15 (m, 2H); 7.20 (d, *J* = 8.4Hz, 2H); 7.21-7.24 (m, 1H); 7.30-7.33 (m, 1H); 7.63 (d, *J* = 8.4 Hz, 2H). HPLC: AD column; λ = 254 nm; eluent: hexane/isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{minor} = 22.1 min, t_{major} = 24.5 min.

3-((4-fluorophenyl)(tosylamino)methyl)but-3-en-2-one (3e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 3H); 2.41 (s, 3H); 5.23 (d, *J* = 8.7 Hz, 1H); 5.73 (d, *J* = 8.7 Hz, 1H); 6.06 (s, 1H); 6.09 (s, 1H); 6.89 (d, *J* = 8.6 Hz, 2H); 7.05 (d, *J* = 8.6 Hz, 2H); 7.24 (d, *J* = 8.3 Hz, 2H); 7.63 (d, *J* = 8.3 Hz, 2H). HPLC: AD column; λ = 254 nm; eluent: hexane/isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{minor} = 15.5 min, t_{major} = 16.5 min.

3-((4-nitrophenyl)(tosylamino)methyl)but-3-en-2-one (3f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 3H); 2.44 (s, 3H); 5.29 (d, *J* = 9.4 Hz, 1H); 5.90 (d, *J* = 9.4 Hz, 1H); 6.07 (s, 1H); 6.13 (s, 1H); 7.25 (d, *J* = 8.5 Hz, 2H); 7.33 (d, *J* = 8.8 Hz, 2H); 7.64 (d, *J* = 8.5 Hz, 2H); 8.06 (d, *J* = 8.8 Hz, 2H). HPLC: AD column; λ = 254 nm; eluent: hexane/isopropanol = 80/20; Flow rate: 0.5 mL/min; t_{minor} = 53.0 min, t_{major} = 68.0 min.

3-((2-nitrophenyl)(tosylamino)methyl)but-3-en-2-one (3g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3H); 2.46 (s, 3H); 5.03 (d, *J* = 9.8 Hz, 1H); 6.08 (s, 1H); 6.26 (s, 1H); 6.93 (m, 2H); 7.15 (m, 3H); 7.37 (d, *J* = 8.0 Hz, 2H); 7.73 (d, *J* = 9.2 Hz, 2H). HPLC: AD column; λ = 254 nm; eluent: hexane/isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{minor} = 35.3 min, t_{major} = 37.6 min.

3-(p-tolyl(tosylamino)methyl)but-3-en-2-one (3h). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16 (s, 3H); 2.27 (s, 3H); 2.42 (s, 3H); 5.23 (d, *J* = 8.4 Hz, 1H); 5.56 (d, *J* = 8.4 Hz, 1H); 6.10 (s, 2H); 6.95 (d, *J* = 8.2 Hz, 2H); 7.00 (d, *J* = 8.2 Hz, 2H); 7.24 (d, *J* = 8.2 Hz, 2H); 7.65 (d, *J* = 8.2 Hz, 2H). HPLC: AD column; λ = 254 nm; eluent: hexane/isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{minor} = 16.0 min, t_{major} = 18.0 min.

3-((2-methoxyphenyl)(tosylamino)methyl)but-3-en-2-one (3i). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16 (s, 3H); 2.33 (s, 3H); 3.64 (s, 3H); 5.59 (d, *J* = 9.4 Hz, 1H); 5.95 (d, *J* = 9.4 Hz, 1H); 6.07 (s, 1H); 6.11 (s, 1H); 6.66 (d, *J* = 8.0 Hz, 1H); 6.72 (dd, *J*1 = 8.0 Hz, *J*2 = 8.0 Hz, 1H); 7.21 (m, 4H); 7.57 (d, *J* = 8.4 Hz, 2H). HPLC: (*S*, *S*)-Whelk-O1 column; λ = 254 nm; eluent: hexane/isopropanol = 80/20; flow rate: 0.7 mL/min; t_{minor} = 50.0 min, t_{major} = 53.0 min.

3-((3-methoxyphenyl)(tosylamino)methyl)but-3-en-2-one (3j). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 3H); 2.39 (s, 3H); 3.67 (s, 3H); 5.24 (d, *J* = 8.8 Hz, 1H); 5.74 (d, *J* = 8.8 Hz, 1H); 6.07 (s, 1H); 6.08 (s, 1H); 6.60 (s, 1H); 6.64 (d, *J* = 8.0 Hz, 1H); 6.69 (d, *J* = 8.0 Hz, 1H); 7.09 (dd, *J*1 = 8.0 Hz, *J*2 = 8.0 Hz, 1H); 7.21 (d, *J* = 8.4Hz, 2H); 7.63 (d, *J* = 8.4 Hz, 2H). HPLC: AD column; λ = 254 nm; eluent: hexane/isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{minor} = 23.2 min, t_{major} = 25.8 min.

3-(hydroxy(4-nitrophenyl)methyl)but-3-en-2-one (6a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H); 5.67 (s, 1H); 6.03 (s, 1H); 6.25 (s, 1H); 7.54 (d, *J* = 8.6 Hz, 2H); 8.17 (d, *J* = 8.6 Hz, 2H). HPLC: AD column; λ = 254 nm; eluent: hexane/isopropanol = 80/20; Flow rate: 0.5 mL/min; t_{minor} = 47.1 min, t_{major} = 58.5 min.

Phenyl 2-((4-methylphenylsulfonamido)(4-nitrophenyl)methyl)acrylate (6b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H); 5.48 (d, *J* = 9.0 Hz, 1H); 5.87 (d, *J* = 9.0 Hz, 1H); 6.06 (s, 1H); 6.53 (s, 1H); 6.88 (m, 2H); 7.23-7.37 (m, 5H); 7.43 (d, *J* = 8.7 Hz, 2H); 7.70 (d, *J* = 8.7 Hz, 2H); 8.12 (m, 2H). HPLC: AD column; λ = 254 nm; eluent: hexane/isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{minor} = 30.3 min, t_{major} = 35.2 min.

Phenyl 2-((4-bromophenyl)(4-methylphenylsulfonamido)methyl)acrylate (6c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H); 5.35 (d, *J* = 8.8 Hz, 1H); 5.59 (d, *J* = 8.8 Hz, 1H); 6.04 (s, 1H); 6.50 (s, 1H); 6.87 (m, 2H); 7.06 (m, 2H); 7.22-7.26 (m, 3H); 7.31-7.39 (m, 4H); 7.68 (m, 2H). HPLC: AD column; λ = 254 nm; eluent: hexane/isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{minor} = 17.9 min, t_{major} = 20.1 min.

Phenyl 2-((4-chlorophenyl)(4-methylphenylsulfonamido)methyl)acrylate (6d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H); 5.38 (d, *J* = 8.8 Hz, 1H); 5.64 (d, *J* = 8.8 Hz, 1H); 6.05 (s, 1H); 6.50 (s, 1H); 6.88 (m, 2H); 7.14 (m, 2H); 7.20-7.28 (m, 5H); 7.33-7.38 (m, 2H); 7.70 (m, 2H). HPLC: AD column; λ = 254 nm; eluent: hexane/isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{minor} = 16.8 min, t_{major} = 19.7 min.