Electronic Supplementary information

N, *N*-Dimethylformamide-stabilized palladium nanoclusters as catalyst for Larock indole synthesis

Kaito Onishi,[a] Kei Oikawa,[a] Hiroki Yano,[a] Takeyuki Suzuki,[b] and Yasushi Obora *[a]

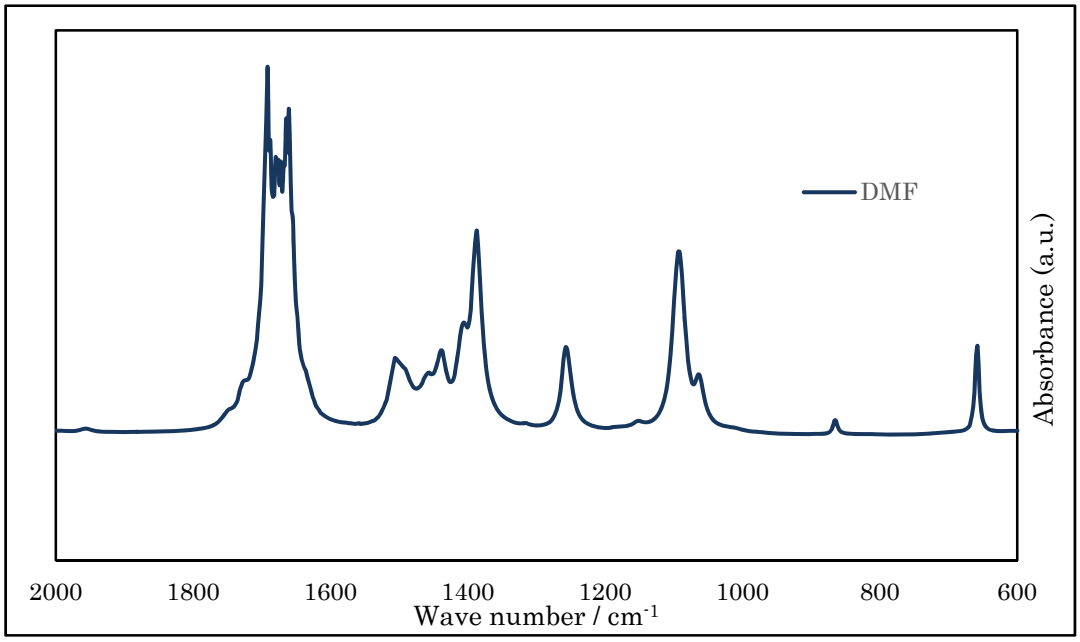
[a] *Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan*

[b] *Comprehensive Analysis Center, The Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0057, Japan*

E-mail: obora@kansai-u.ac.jp

Table of Contents

(a)



(b)

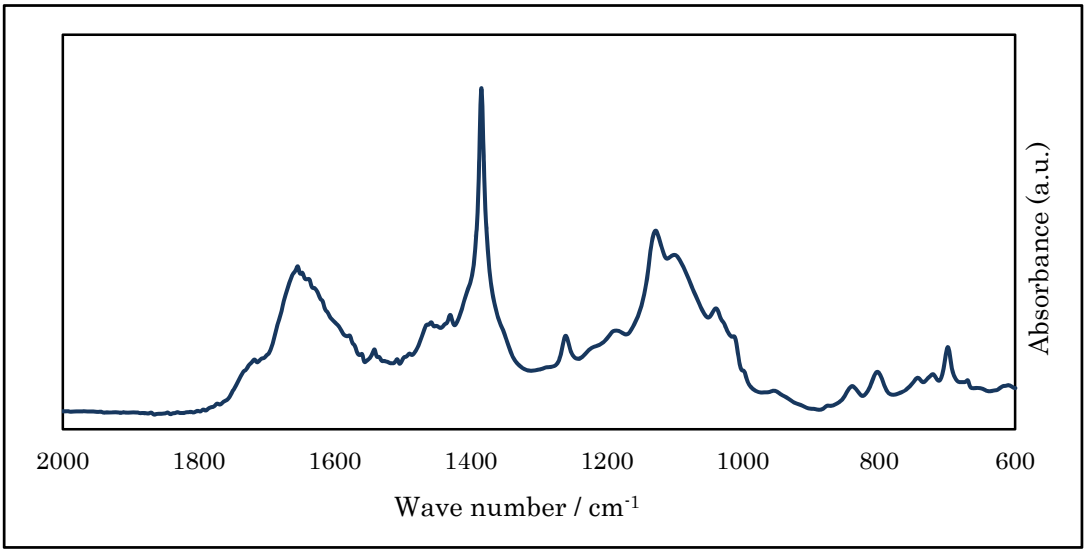


Fig. S1. IR spectra of DMF molecules (a) and Pd NCs (b)

Table S1. Concentration of Na, K, and Pd analyzed by ICP

<intensity>			
element	Na	K	Pd
wave number	589.592 nm	766.491 nm	340.458 nm
Run 1	0.105796	0.000007	0.632416
Run 2	0.105259	−1.6E−05	0.626861
Run 3	0.10616	0.000037	0.636318
average	0.105738	.000009R	0.631865
R	0.000901	0.000053	0.009456
SD	0.000453	0.000026	0.004752
RSD	0.428757	281.036	0.752102
<concentration>			
element	Na	K	Pd
wave number	589.592 nm	766.491 nm	340.458 nm
unit	ppm	ppm	Ppm
Run 1	2.7186	0	3.38199
Run 2	2.70314	0	3.34839
Run 3	2.72911	0.004297	3.40559
average	2.71695	0.001432	3.37866
R	0.025975	0.004297	0.057195
SD	0.013066	0.002481	0.028743
RSD	0.480909	173.205	0.850715

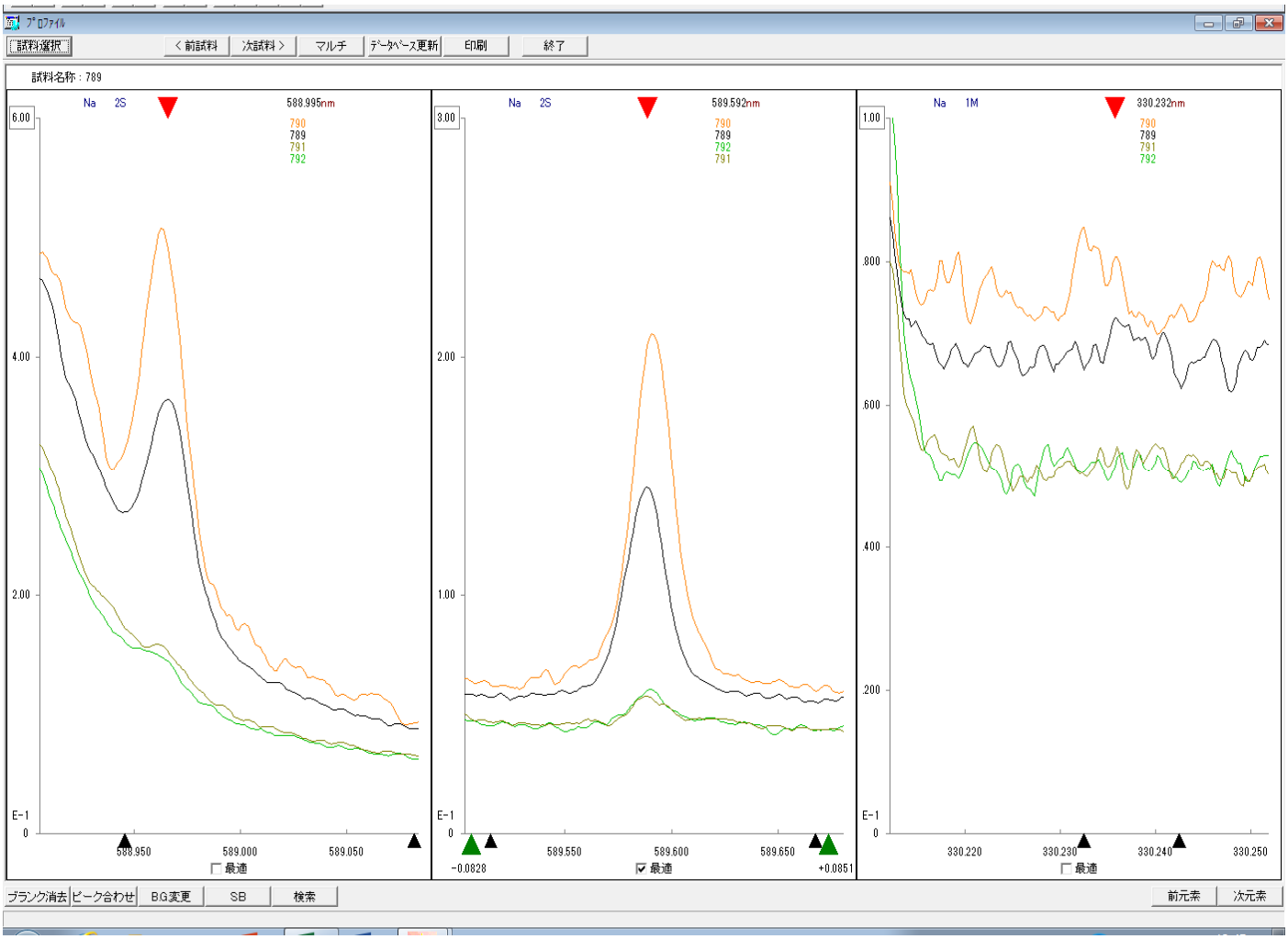


Fig. S2. Peak profile of Na (black curve)

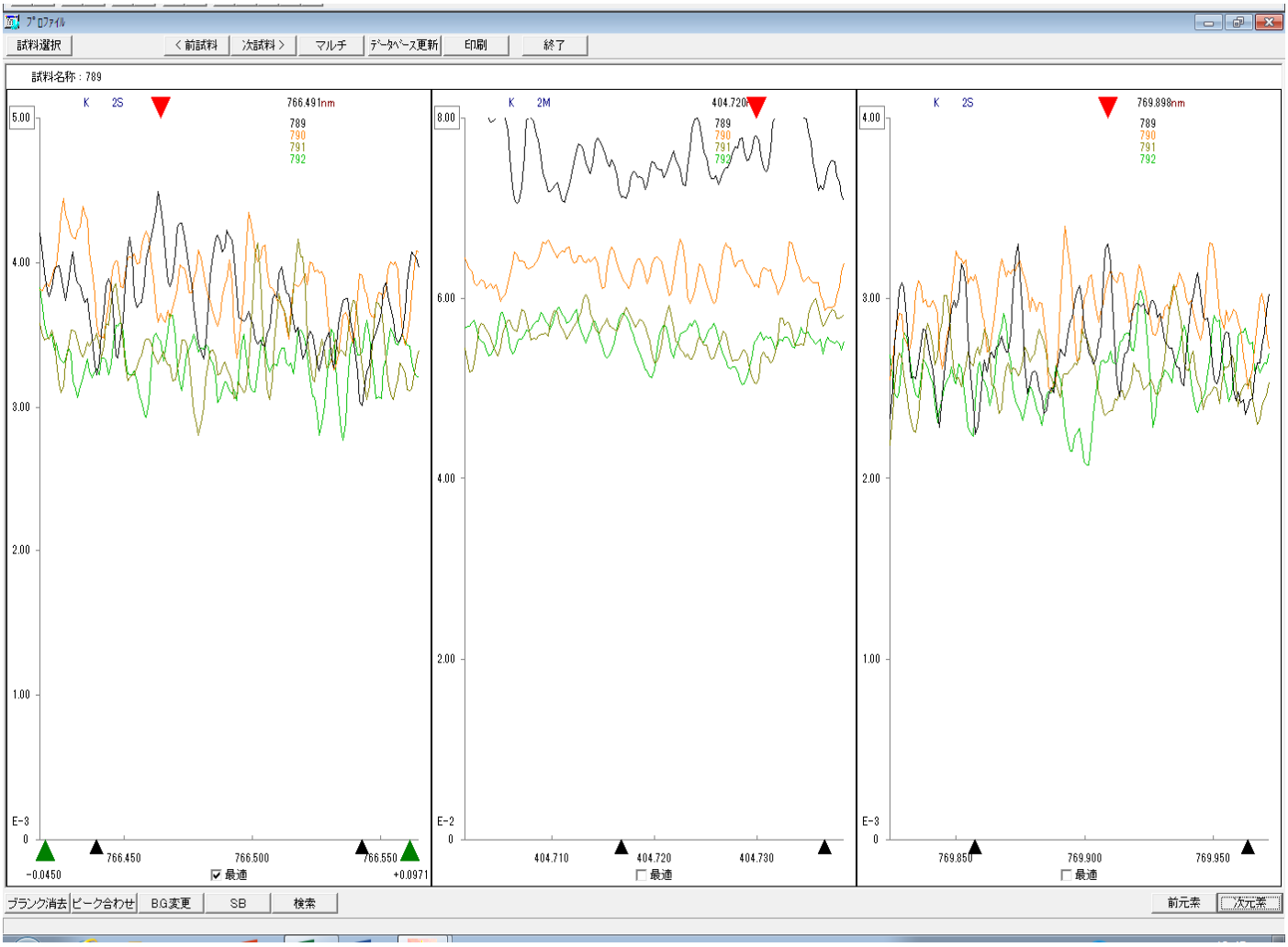


Fig. S3. Peak profile of K (black curve)

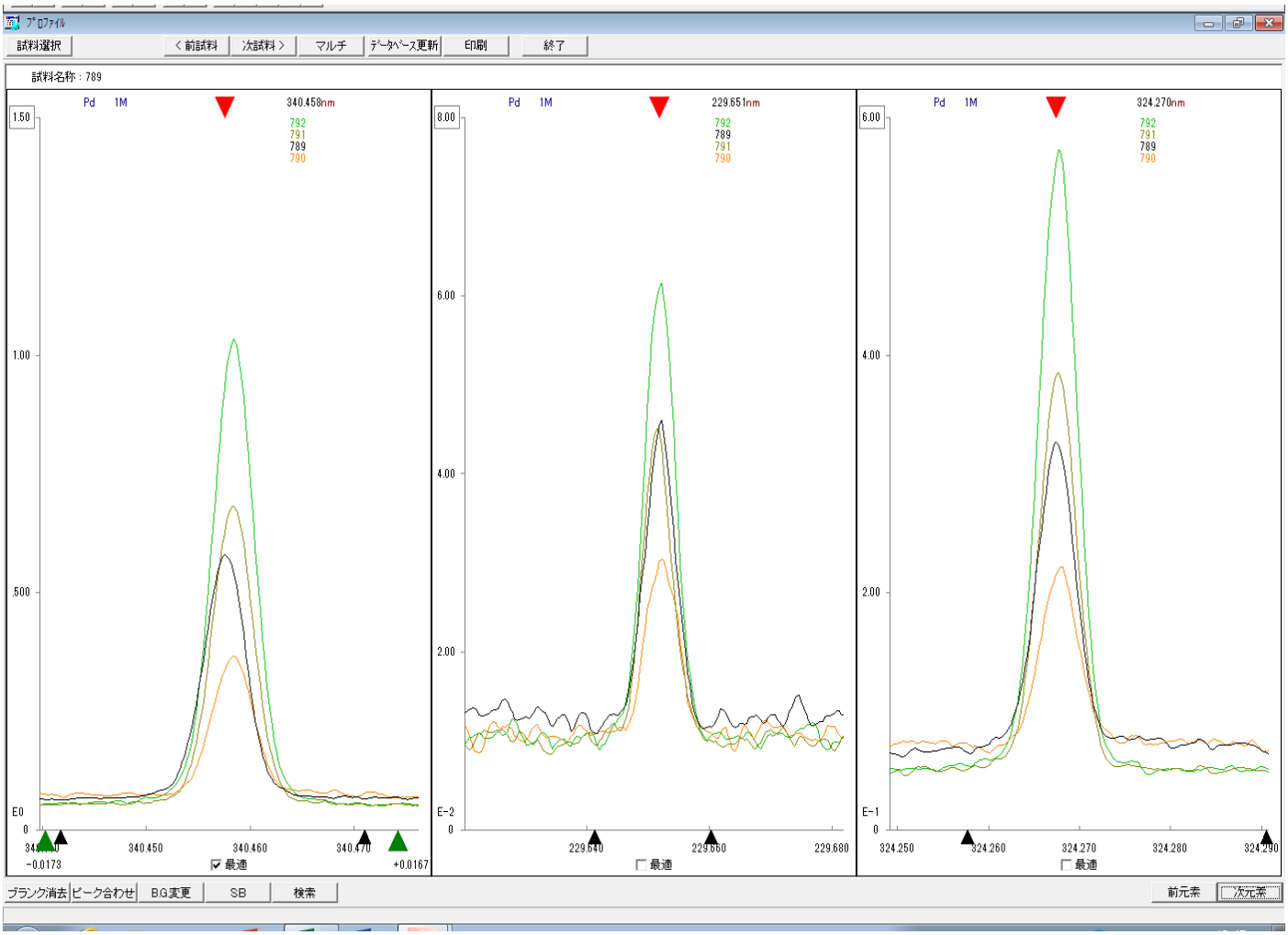


Fig. S4. Peak profile of Pd (black curve)

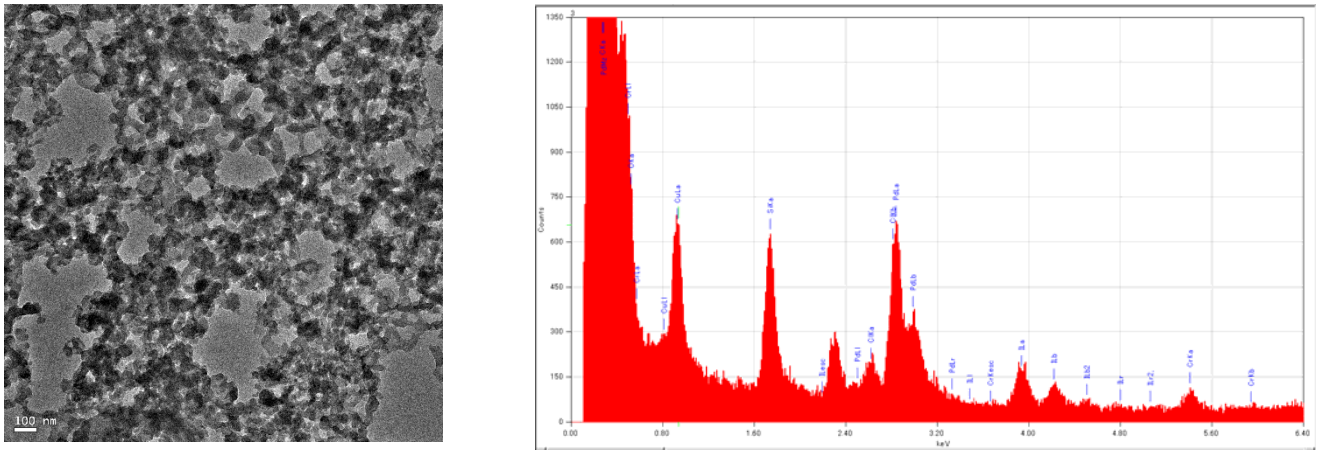


Fig. S5. (a) Aggregated Pd NCs in TEM image (scale bar = 100 nm), (b) Pd peak analyzed by EDS

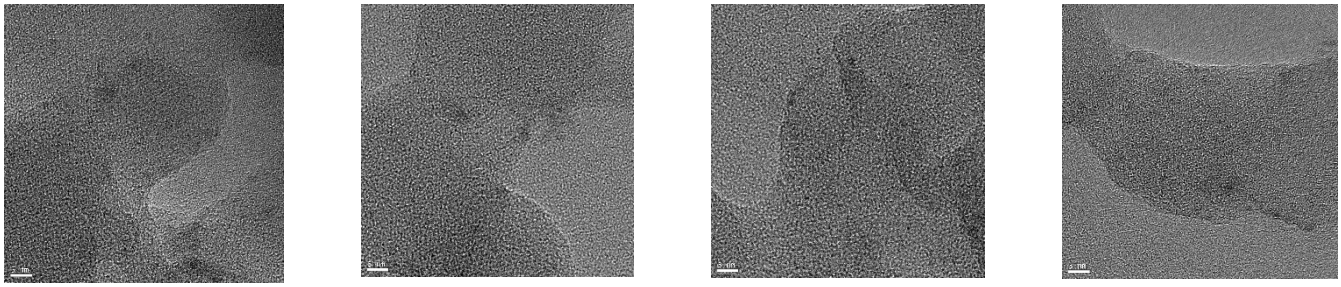


Fig. S6. Transmission electron microscopy images (TEM image) of Pd NCs after the reaction under the conditions entry 14 of Table 1 (scale bar = 5 nm). Particle size distribution of the nanoparticles after the reaction under the conditions entry 14 of Table 1 (Fig. 3. (b)) was used TEM images of Fig. S6 and Fig.3.

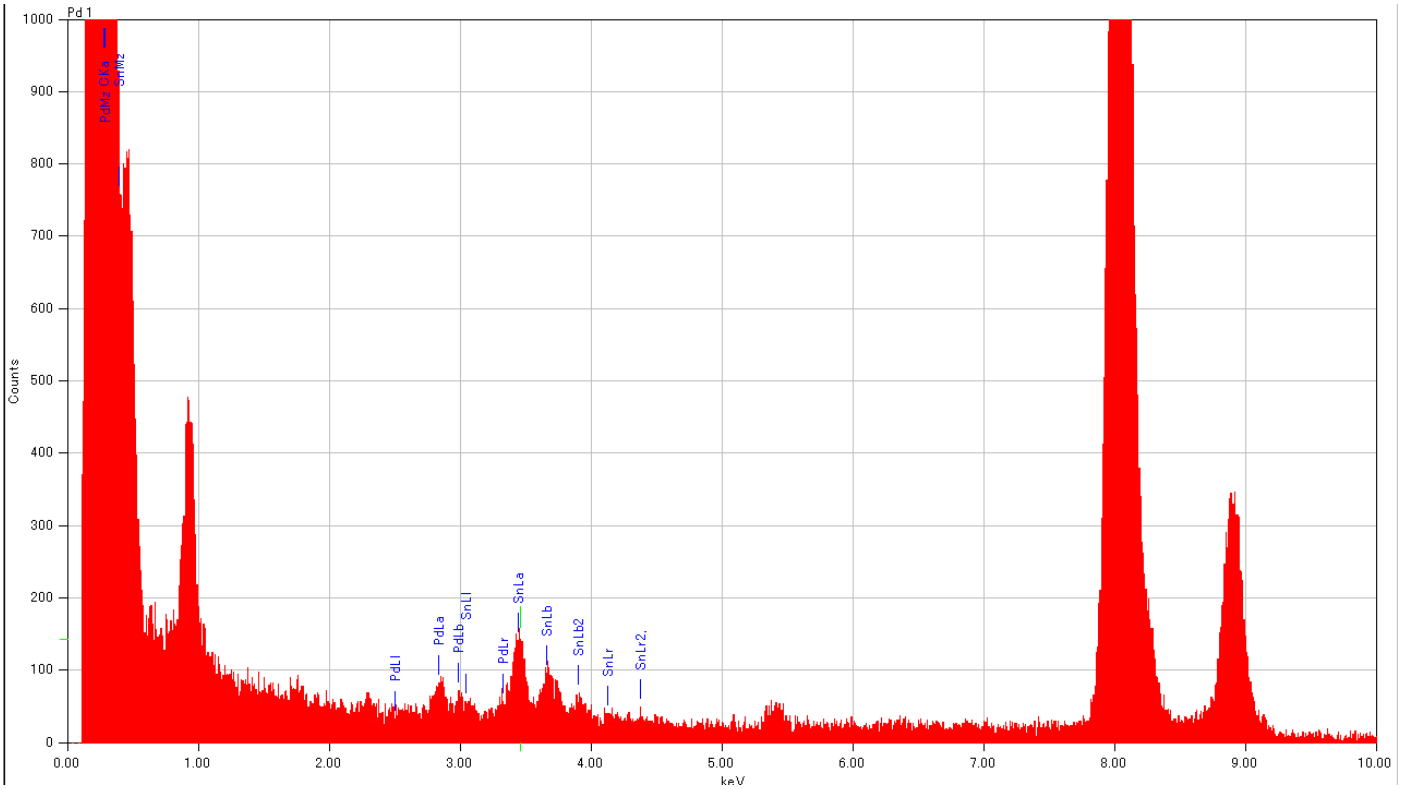


Fig. S7. EDS spectral of Figs. 3(a) and S6

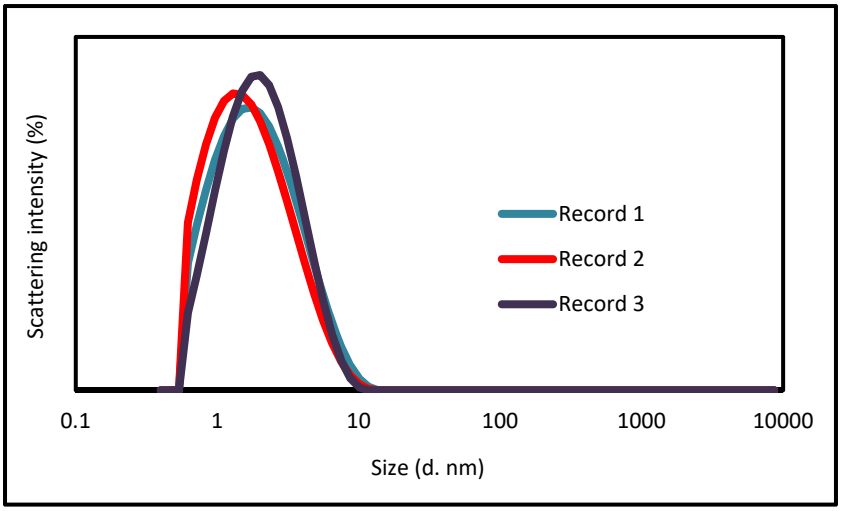


Fig. S8. Dynamic light scattering intensity of Pd NCs. Average Pd NCs size was 2.3 nm.

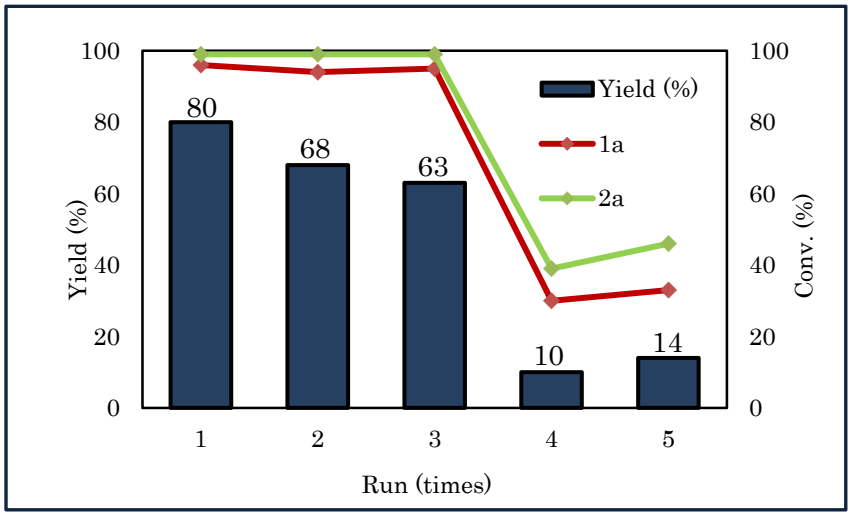


Fig. S9. Catalyst-recycling. Conditions as given in entry 14, Table 1

Table S2. Concentration of Pd analyzed by ICP in the hexane/ ethyl acetate phase

〈Intensity〉

Element	Pd
Wavenumber	340.458nm
Run 1	1.44989
Run 2	1.43035
Run 3	1.44245
Average	1.4409
R	0.019542
SD	0.009863
RSD	0.684483

〈concentration〉

Element	Pd
Wavenumber	340.458nm
Unit	ppm
Run 1	6.24719
Run 2	6.15821
Run 3	6.21328
Average	6.20623
R	0.088986
SD	0.044911
RSD	0.723636

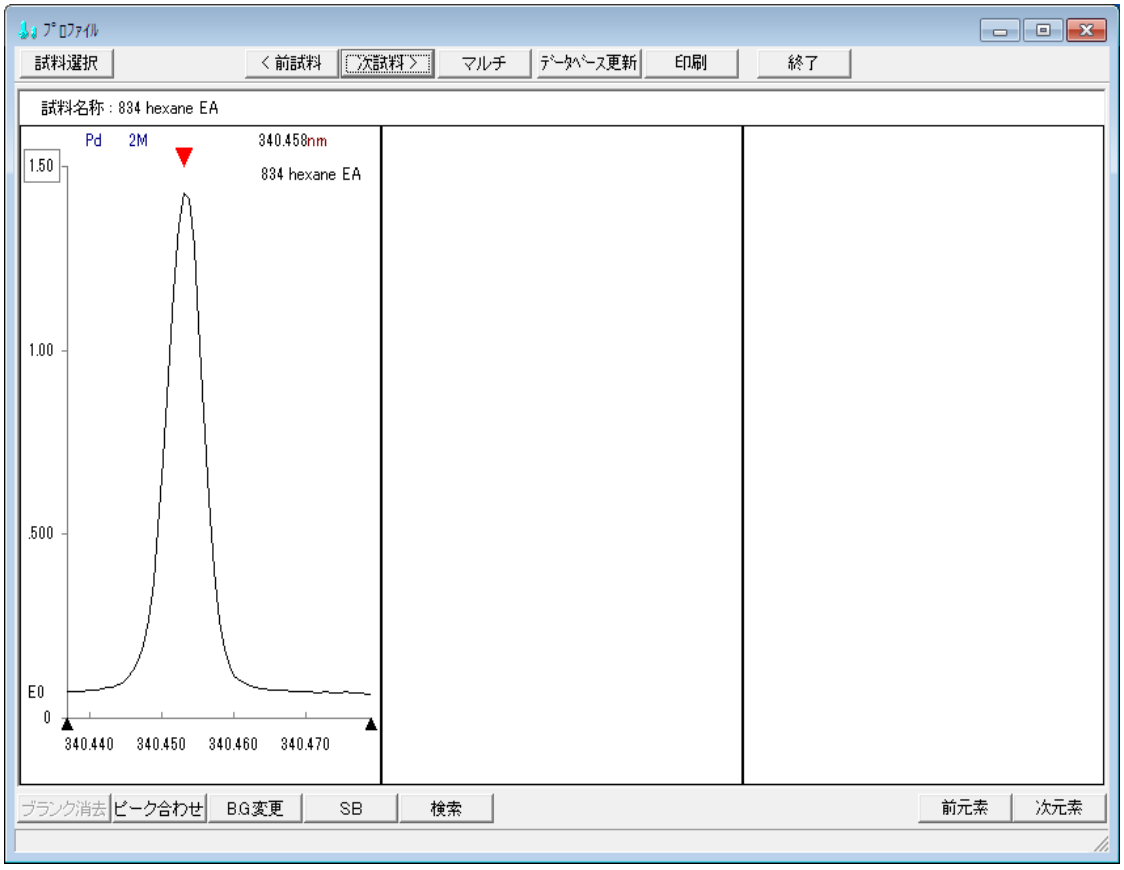


Fig. S10. Peak profile of Pd in the hexane/ ethyl acetate phase

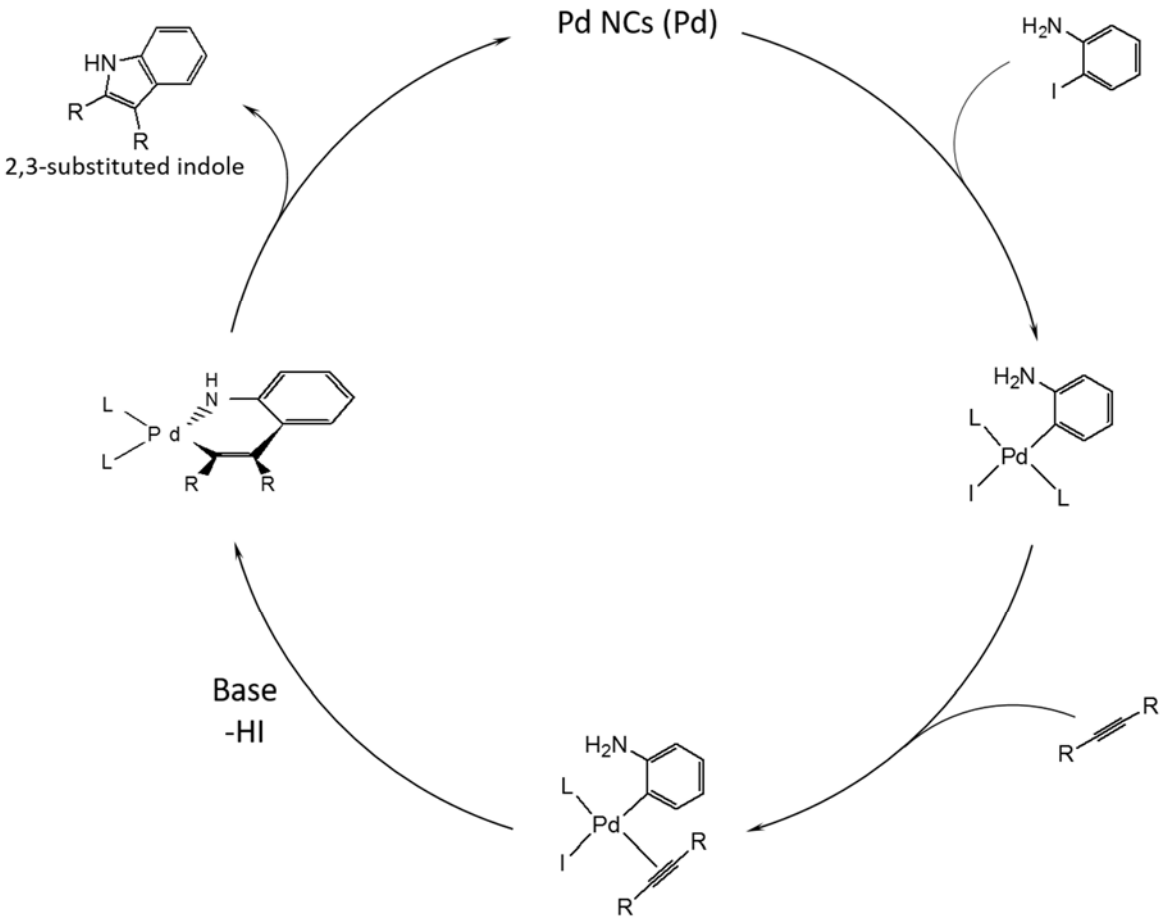


Fig. S11. A Plausible Catalytic Cycle of Larock Indole Synthesis Catalyzed by Pd NCs[1]

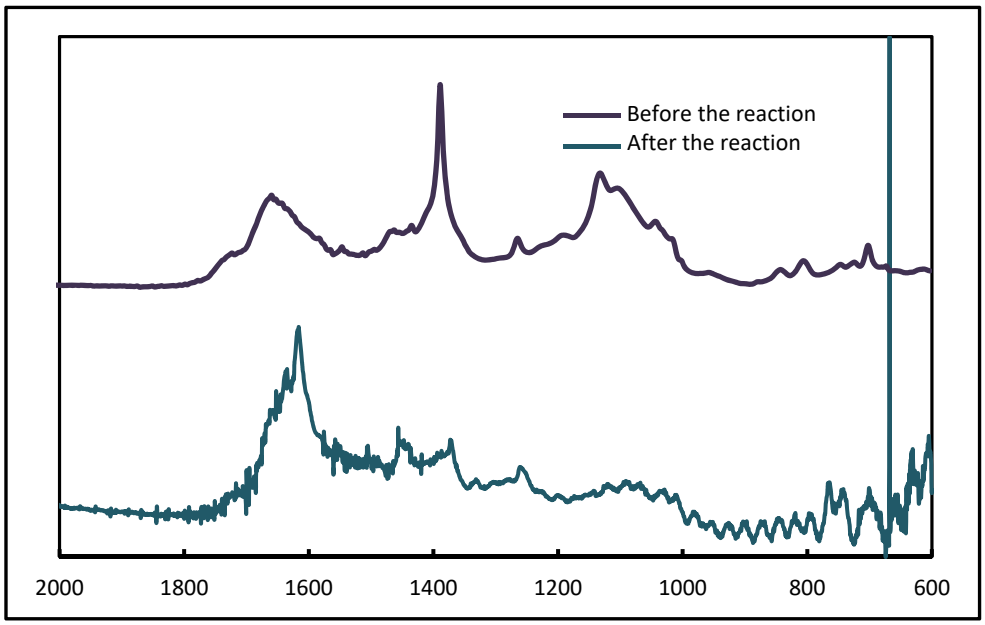


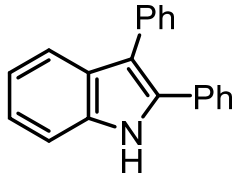
Fig. S12. IR spectrum of (a) Pd NCs before the raction; (b) Pd NCs after the reaction.

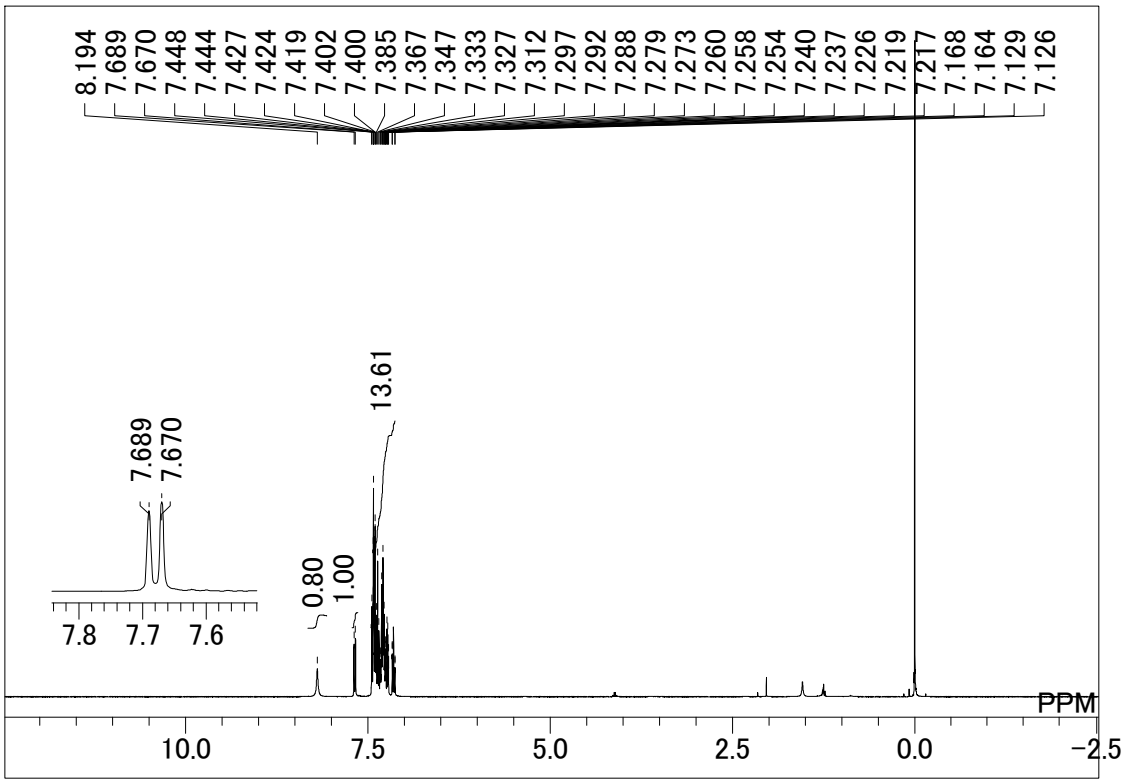
Reference

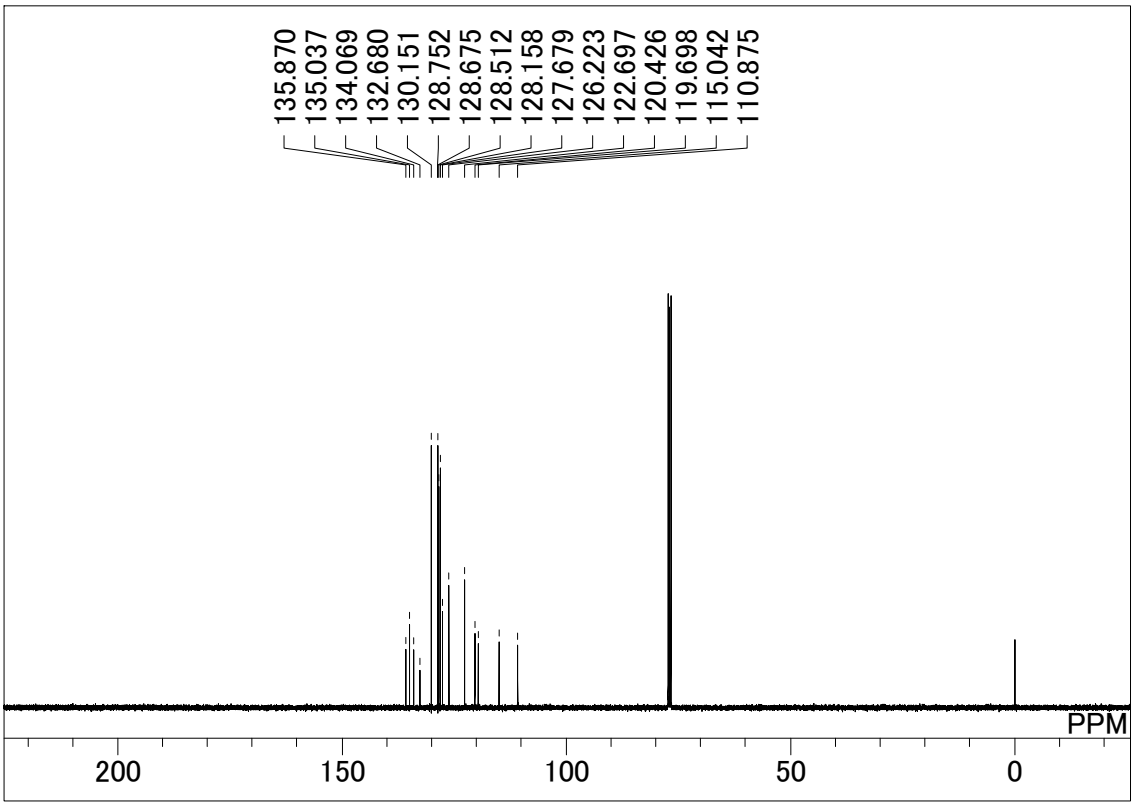
(1) R. C. Larock, E. K. Yum and M. D. Refvik, *J. Org. Chem.,* 1998, **63**, 7652-7662.

^{1}H-NMR and ^{13}C-NMR Spectra of the products

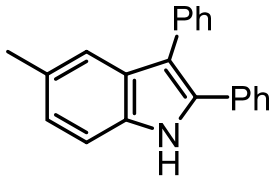
3a

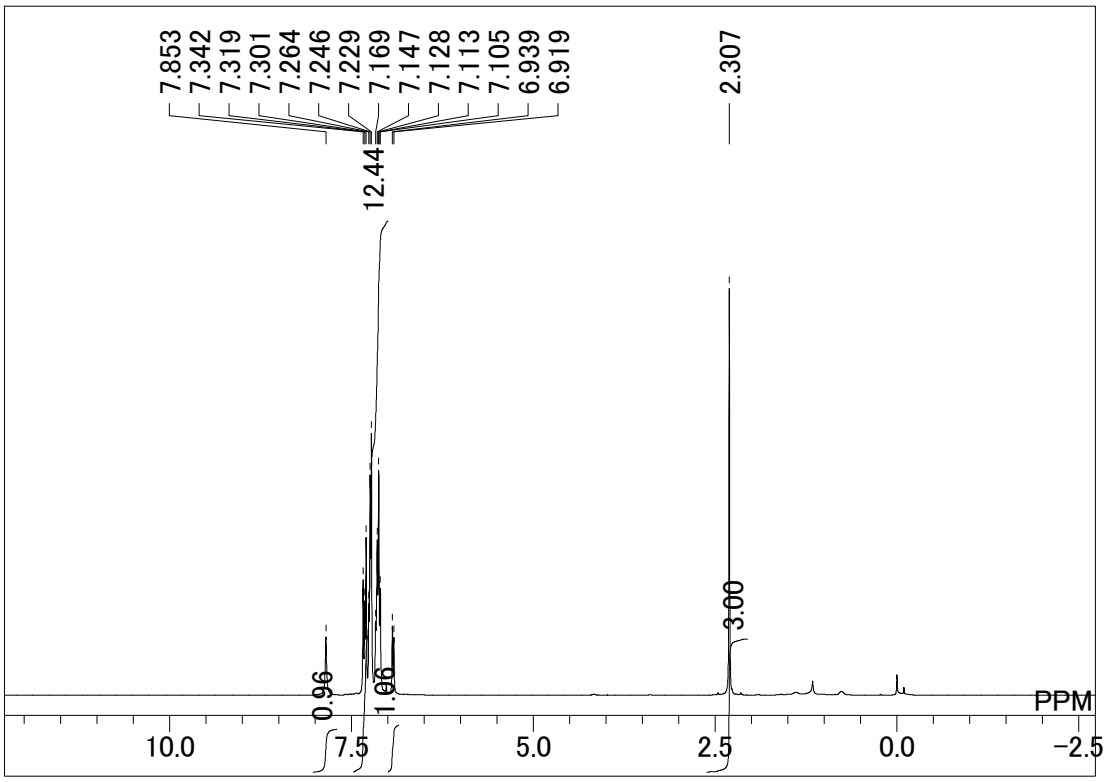


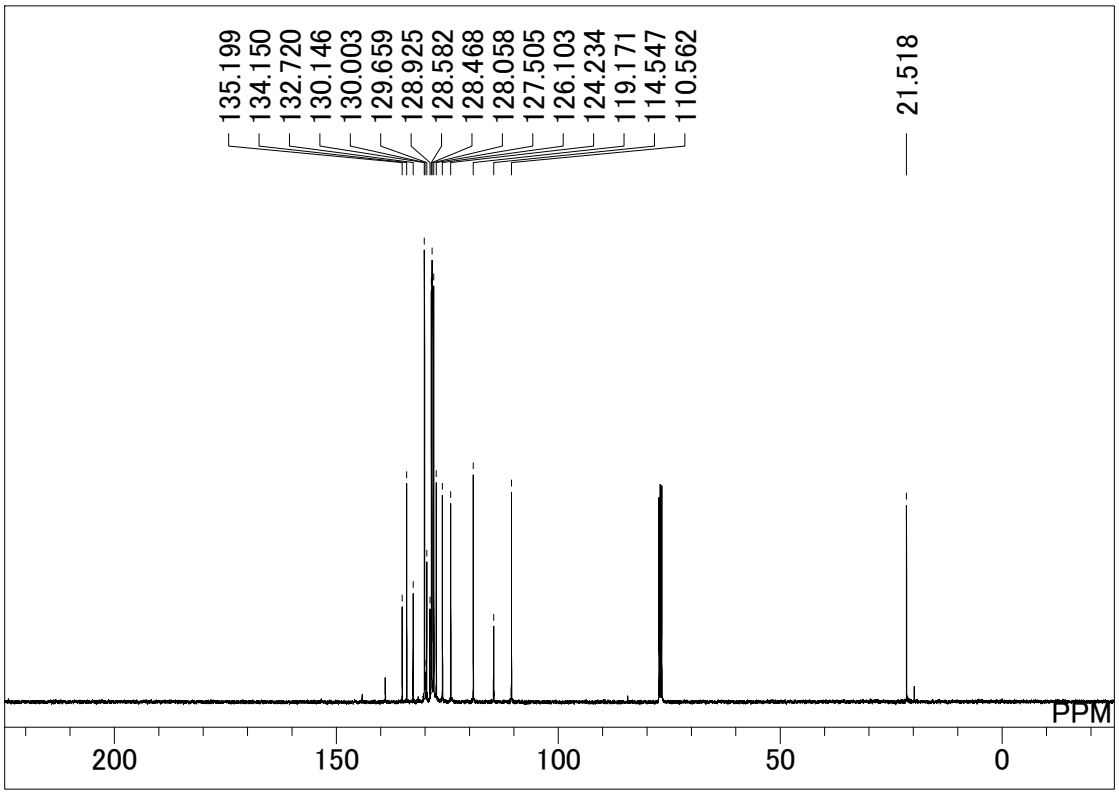




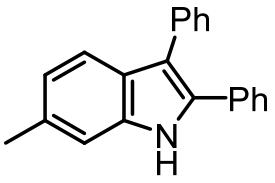
3b

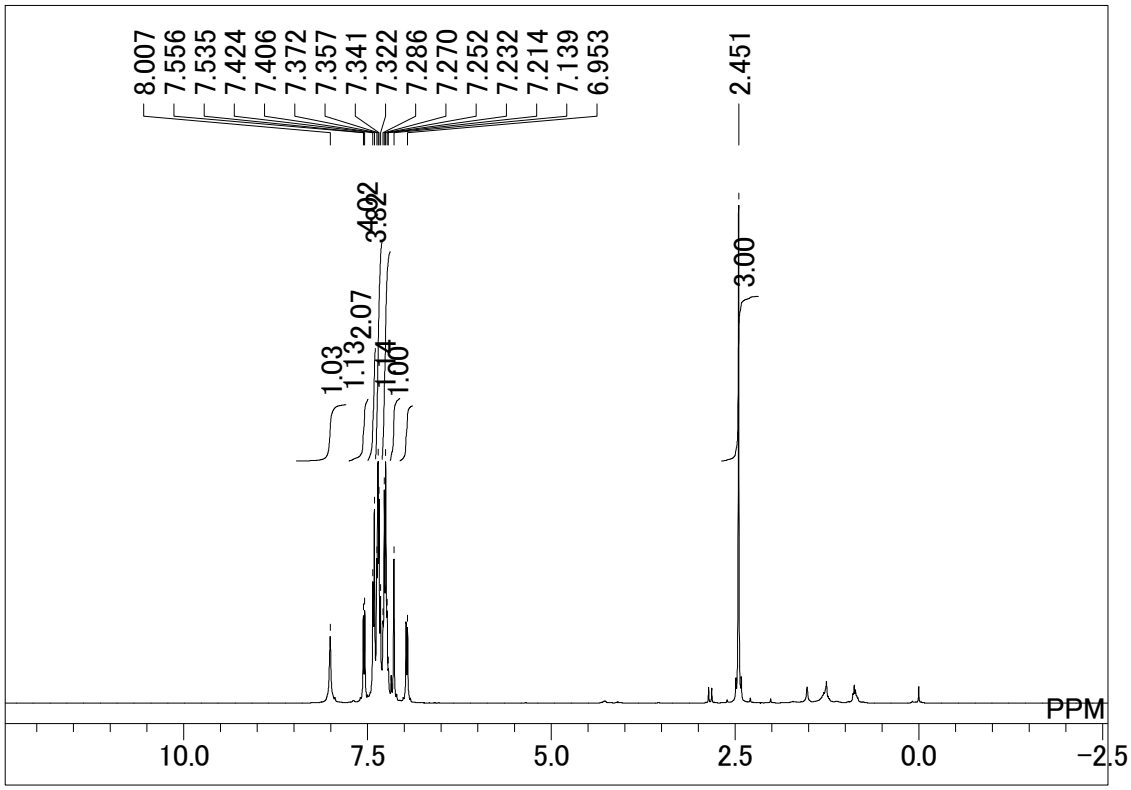

Ph
Ph
N
H

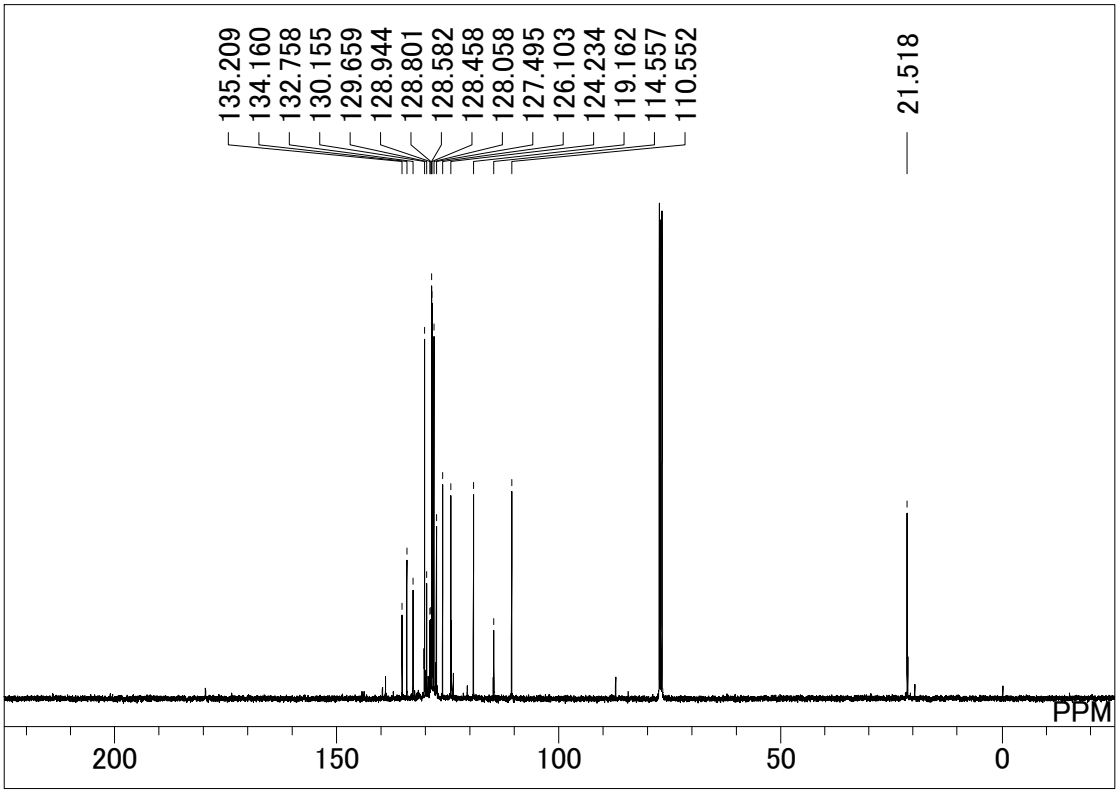

7.853
7.342
7.319
7.301
7.264
7.246
7.229
7.169
7.147
7.128
7.113
7.105
6.939
6.919
2.307
12.44
3.00
0.96
1.06
PPM
10.0
7.5
5.0
2.5
0.0
−2.5


135.199
134.150
132.720
130.146
130.003
129.659
128.925
128.582
128.468
128.058
127.505
126.103
124.234
119.171
114.547
110.562
21.518
PPM
200
150
100
50
0

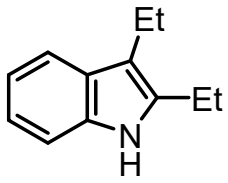
3c

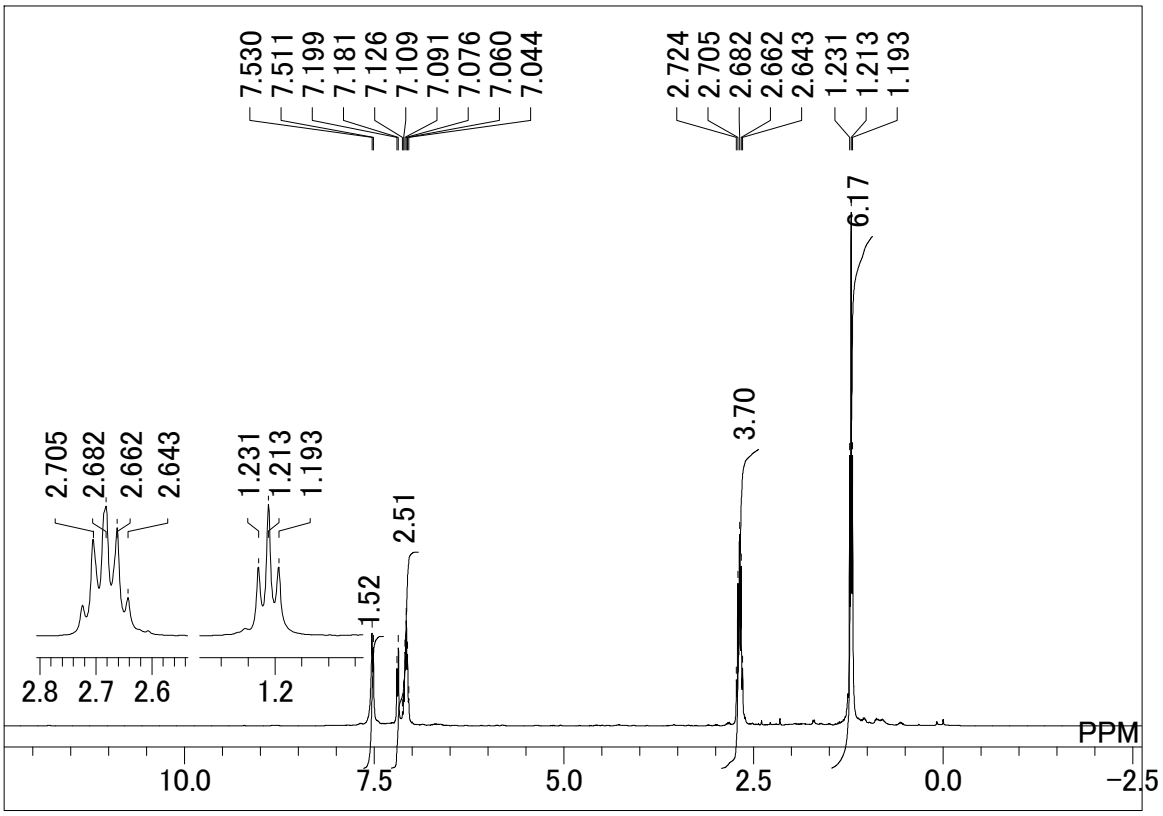

Ph
Ph
N
H

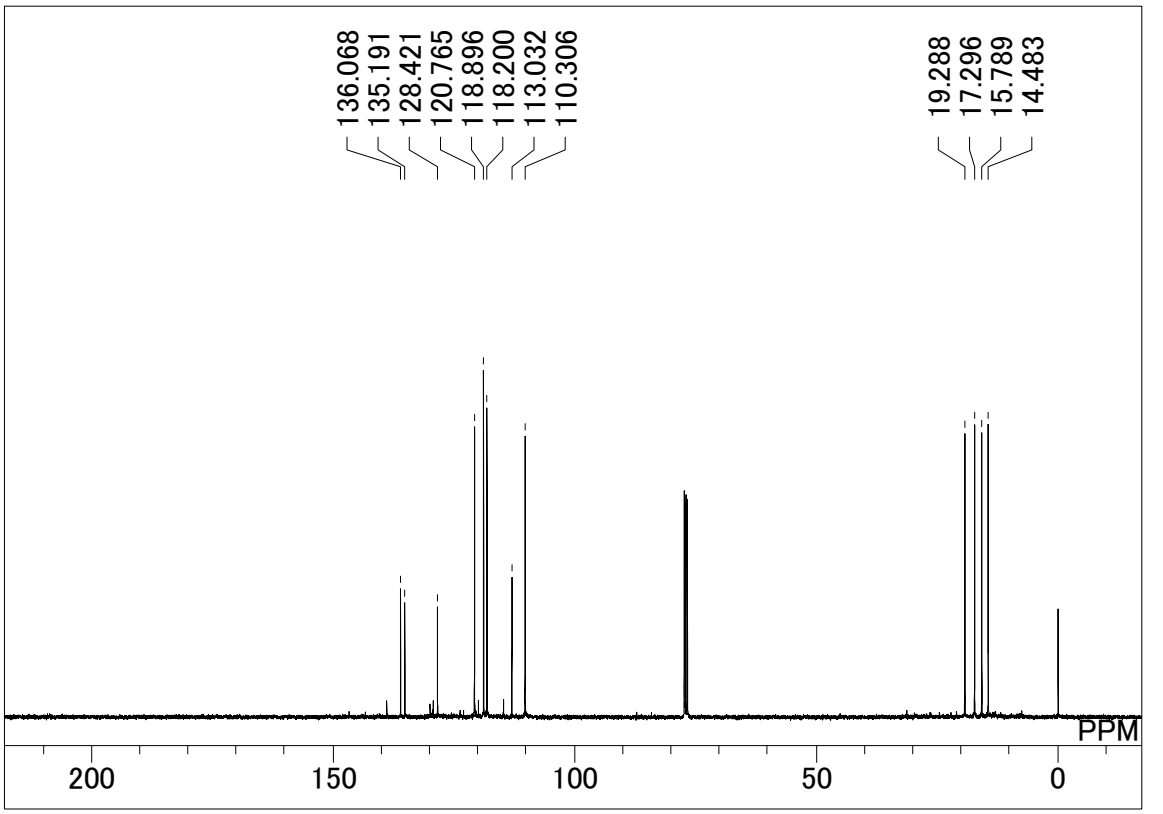

8.007
7.556
7.535
7.424
7.406
7.372
7.357
7.341
7.322
7.286
7.270
7.252
7.232
7.214
7.139
6.953
2.451
4.02
3.92
3.00
2.07
1.13
1.03
1.00
PPM
10.0
7.5
5.0
2.5
0.0
-2.5


135.209
134.160
132.758
130.155
129.659
128.944
128.801
128.582
128.458
128.058
127.495
126.103
124.234
119.162
114.557
110.552
21.518
PPM
200
150
100
50
0

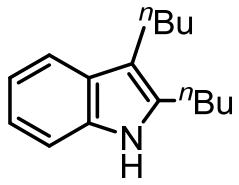
3d

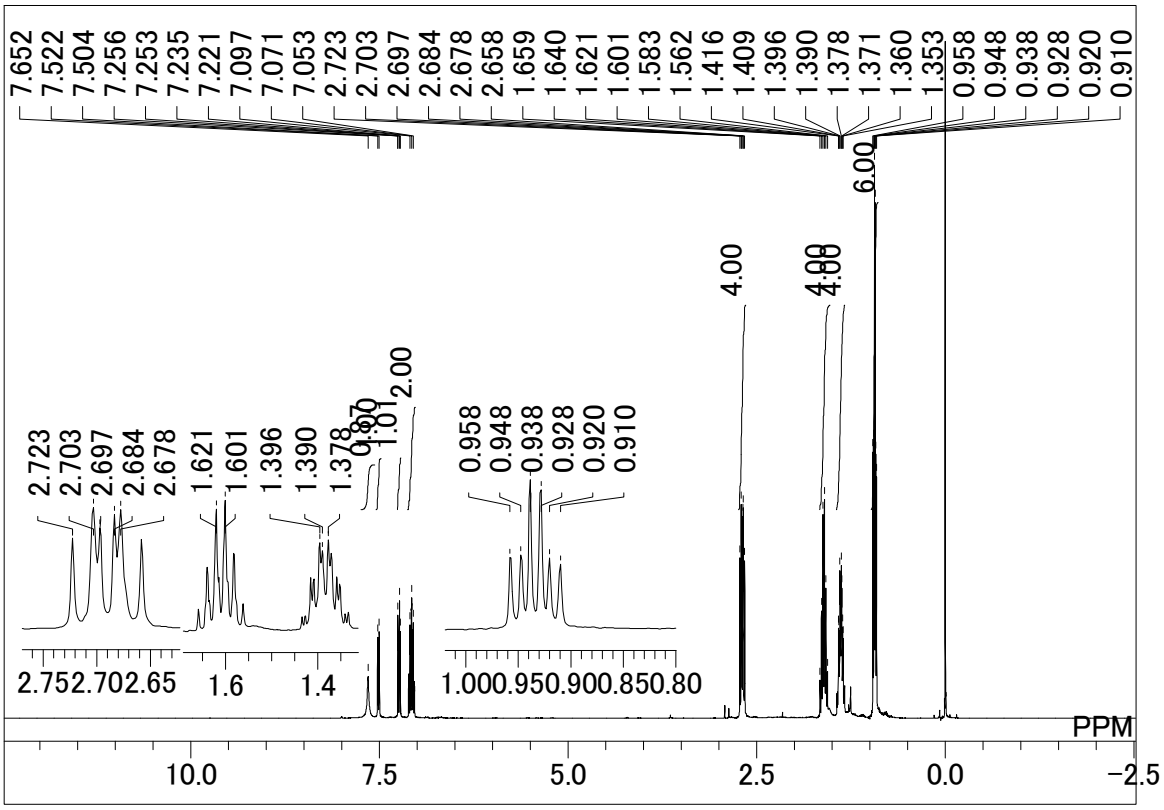

Et
Et
N
H

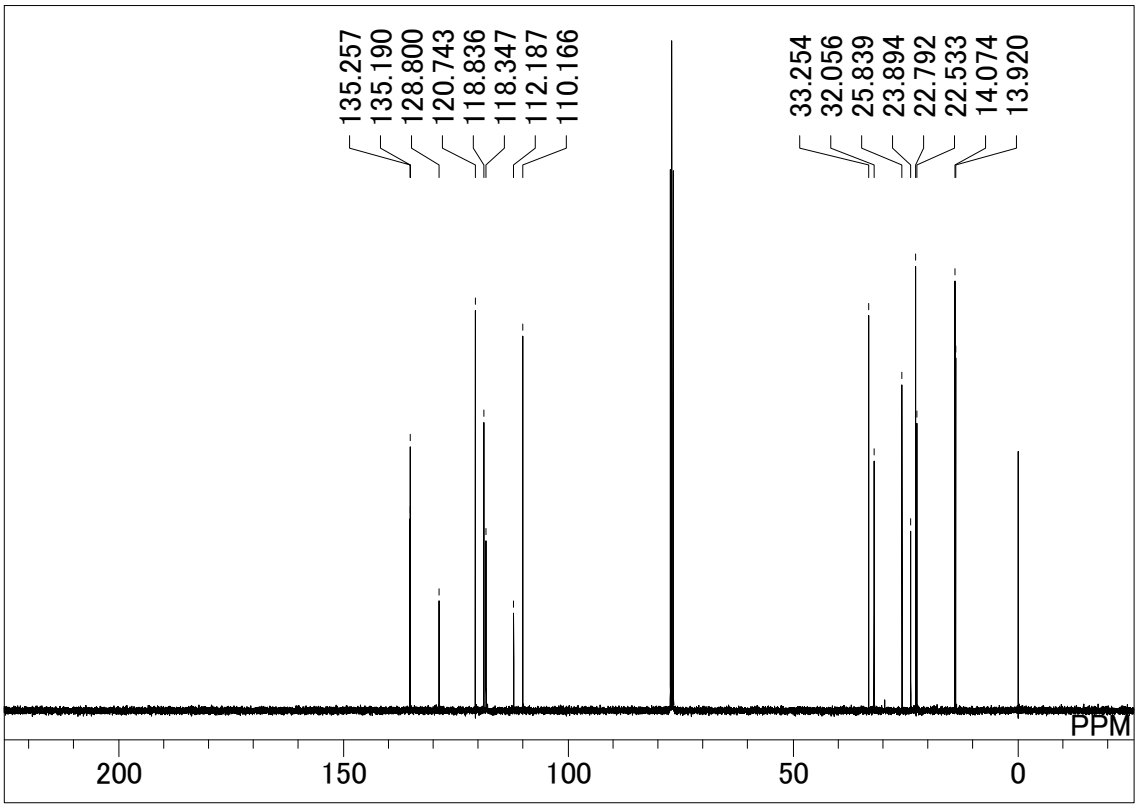

7.530
7.511
7.199
7.181
7.126
7.109
7.091
7.076
7.060
7.044
2.724
2.705
2.682
2.662
2.643
1.231
1.213
1.193
6.17
3.70
2.51
1.52
2.705
2.682
2.662
2.643
1.231
1.213
1.193
2.8 2.7 2.6
1.2
PPM
10.0
7.5
5.0
2.5
0.0
−2.5


136.068
135.191
128.421
120.765
118.896
118.200
113.032
110.306
19.288
17.296
15.789
14.483
PPM
200
150
100
50
0

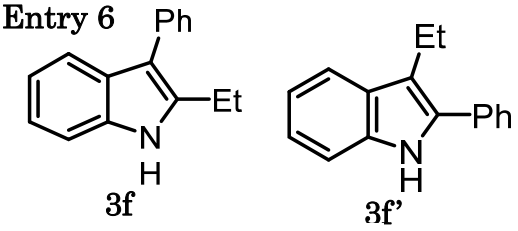
3e


nBu
nBu
N
H

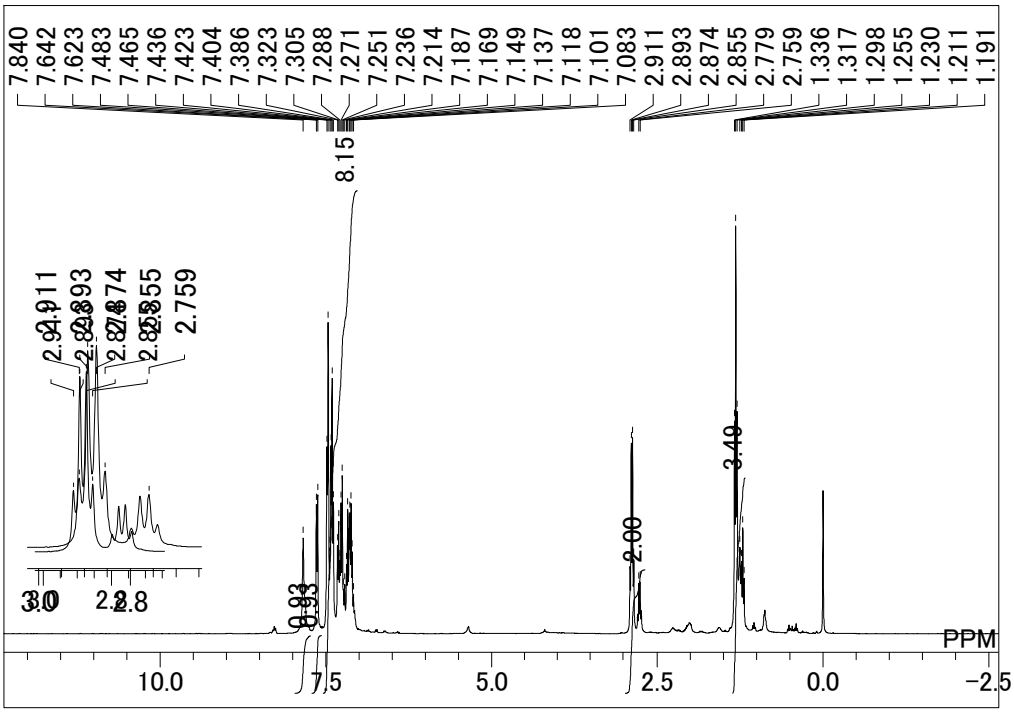

7.652
7.522
7.504
7.256
7.253
7.235
7.221
7.097
7.071
7.053
2.723
2.703
2.697
2.684
2.678
2.658
1.659
1.640
1.621
1.601
1.583
1.562
1.416
1.409
1.396
1.390
1.378
1.371
1.360
1.353
0.958
0.948
0.938
0.928
0.920
0.910
6.00
4.00
4.00
4.00
2.00
1.01
0.97
0.90
2.752.702.65
1.6
1.4
1.000.950.900.850.80
PPM
10.0
7.5
5.0
2.5
0.0
−2.5

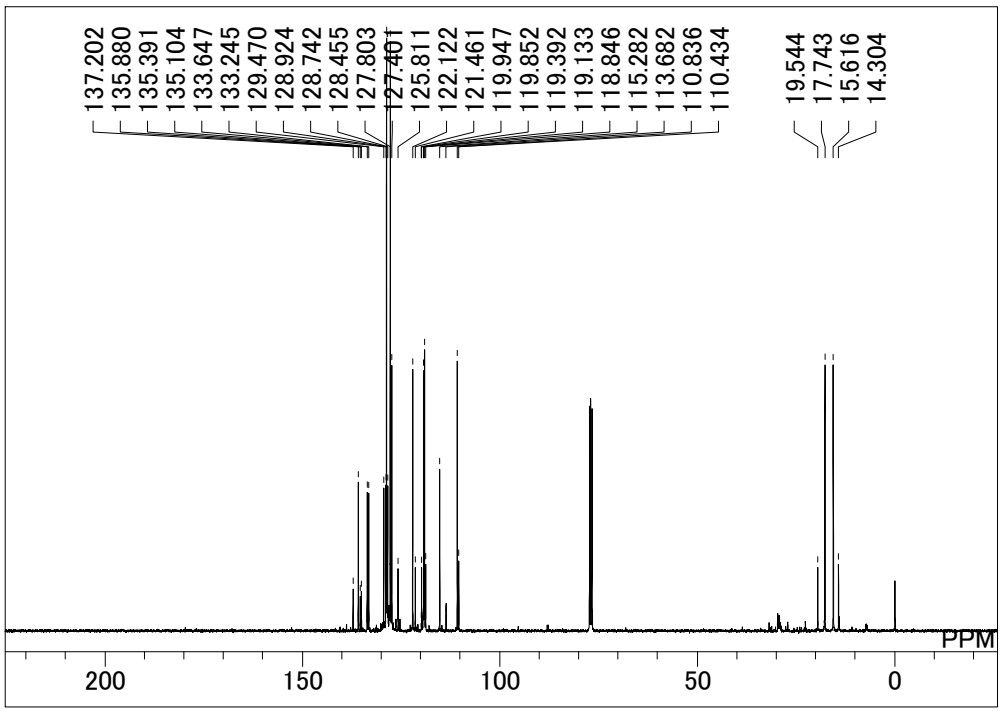

135.257
135.190
128.800
120.743
118.836
118.347
112.187
110.166
33.254
32.056
25.839
23.894
22.792
22.533
14.074
13.920
PPM
200
150
100
50
0

Entry 6

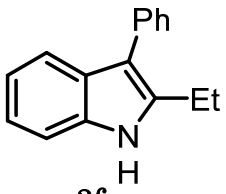


3f : 3f' = 4 : 1

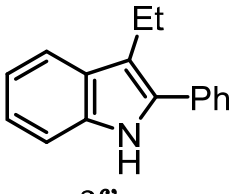




Entry 9

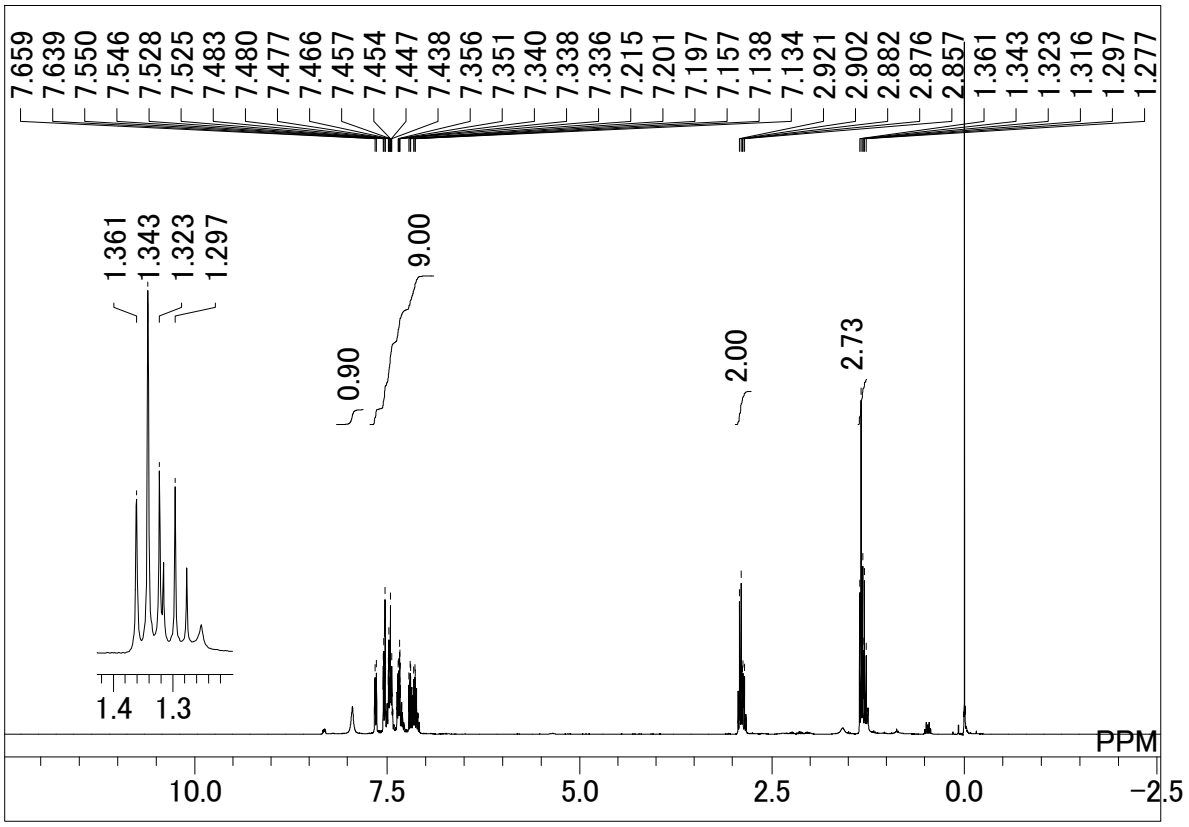


3f

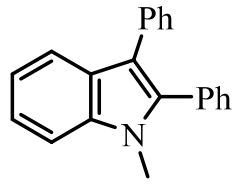


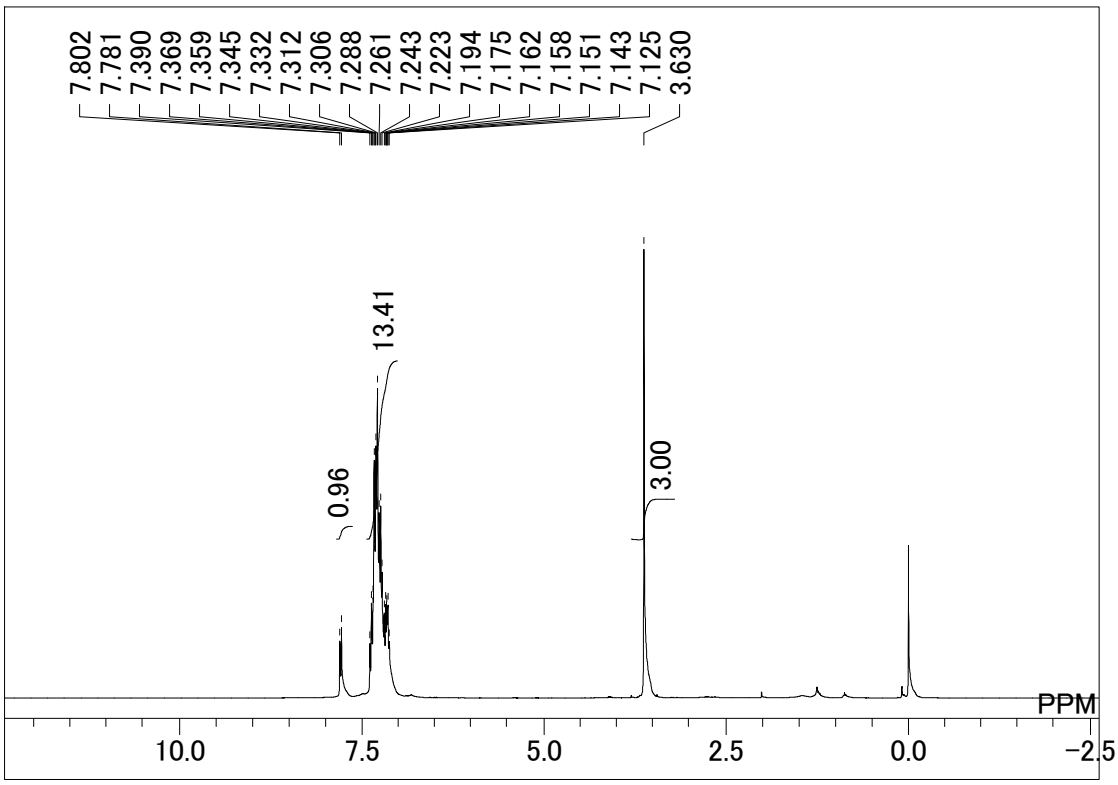
3f'

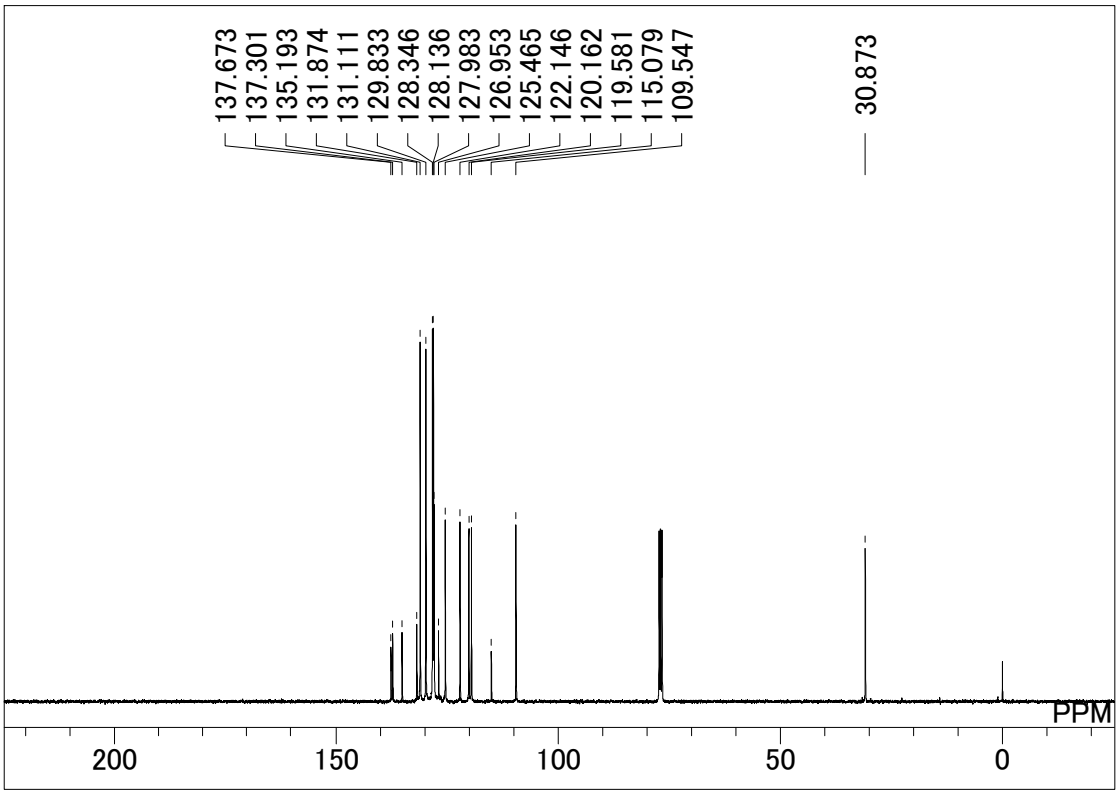
3f : 3f' = 2 : 1



3g


Ph
Ph
N


7.802
7.781
7.390
7.369
7.359
7.345
7.332
7.312
7.306
7.288
7.261
7.243
7.223
7.194
7.175
7.162
7.158
7.151
7.143
7.125
3.630
13.41
0.96
3.00
PPM
10.0
7.5
5.0
2.5
0.0
-2.5


137.673
137.301
135.193
131.874
131.111
129.833
128.346
128.136
127.983
126.953
125.465
122.146
120.162
119.581
115.079
109.547
30.873
PPM
200
150
100
50
0