catalysts

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Supporting Information: Hydrotalcite-Supported Ag/Pd Bimetallic Nanoclusters Catalyzed Oxidation and One-pot Aldol Reaction in Water

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1. Preparation of Hydrotalcite (HT)

Mg/Al hydrotalcite (HT) was prepared as described in previous methods. Briefly, a 100 ml solution containing 30 mmol of $Mg(NO_3)_2.6H_2O$ and 10 mmol of $Al(NO_3)_3.9H_2O$ (Mg/Al=3/1) was slowly dropped over 100 ml of 0.3M Na_2CO_3. The solution was kept under vigorous stirring for 1h. During precipitation, the pH of the solution was kept constant at 10 at 60 ^{0}C by using 1M aq. NaOH. The suspension was continued to stir at 60 ^{0}C for more 1 h and the solid was obtained after centrifugation. It was washed with water 3 times and dried at 100 ^{0}C for 24h.

2. Preparation of Silver; Palladium or Silver/Palladium bimetallic nanoclusters:

0.025 mmol 12.5 mM aq. $Pd(OAc)_2$ or AgOAc solution was mixed with 300 mg of HT. Then, 2.5 mmol, 0.27 mM aq. $NaBH_4$ was added and stirred at room temperature for 1 h. The catalyst after washing several times by deionized water and drying under vacuum was directly used for reaction.

0.0125 mmol 12.5 mM aq. $Pd(OAc)_2$ solution and 0.0125 mmol AgOAc was mixed with 300 mg of HT. Then, 2.5 mmol, 0.27 mM aq. $NaBH_4$ was added and stirred at 15 ^{0}C for 1 h. The catalyst after washing several times by deionized water and drying under vacuum was directly used for reaction.

3. Procedure for time profile and hot filtration test

For the time profile, several parallel reactions for one-pot oxidation and aldol reaction were carried out taking 1-indanol (0.1 mmol), 4-methoxybenzaldehyde (0.3 mmol), Cs_2CO_3 (150 mol%) and Ag/Pd catalysts 5 atom% in 13-mm test tubes. The oxygen gas was supplied from the balloon. 1 ml solvent (dioxane/H_2O, 1:3) was added and stirred at 1200 rpm at 70 °C for the desired time. The reactions were stopped at different intervals, centrifuged and washed at least 3 times with acetone. The acetone layer were collected, evaporated and filtered through a celite. The NMR spectra were recorded to check the ratio of product and the starting material at different time intervals.

For hot filtration test, two parallel sets of reactions were conducted under the optimized reaction condition in test tubes (13 mm) using an organic synthesizer as follows. 1-indanol (0.1 mmol), 4-methoxybenzaldehyde (0.3 mmol), Cs_2CO_3 (150 mol%) and Ag/Pd catalysts 5 atom% were placed in test tubes. The oxygen gas was supplied from the balloon. 1 ml solvent (dioxane/H_2O, 1:3) was added and stirred at 1200 rpm at 70 °C for 3h. Both reactions were stopped at 3h and the catalyst

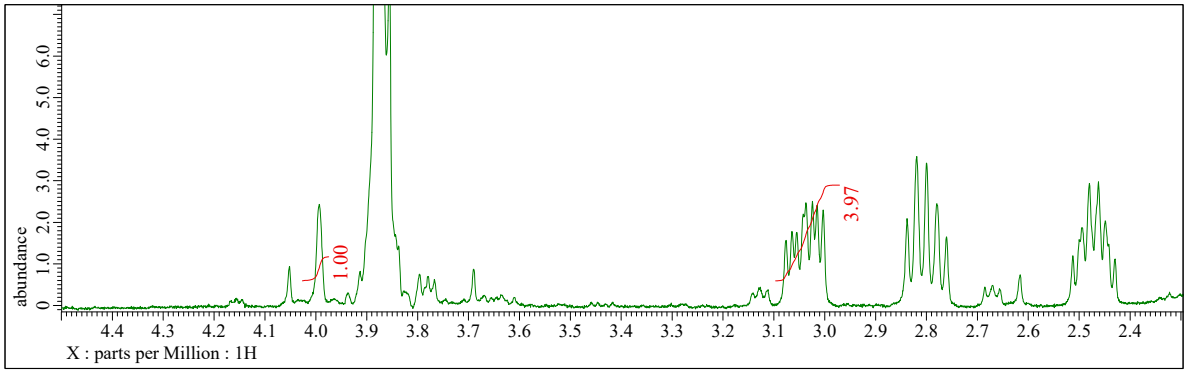
was removed by centrifugation and filtration. One of the reaction mixture, after evaporation, immediately analyzed by NMR (entry 1), while another reaction mixture was continued for another 4 h without catalyst (entry 2). Then it was evaporated and analyzed by NMR.

Table S1. Time course study.

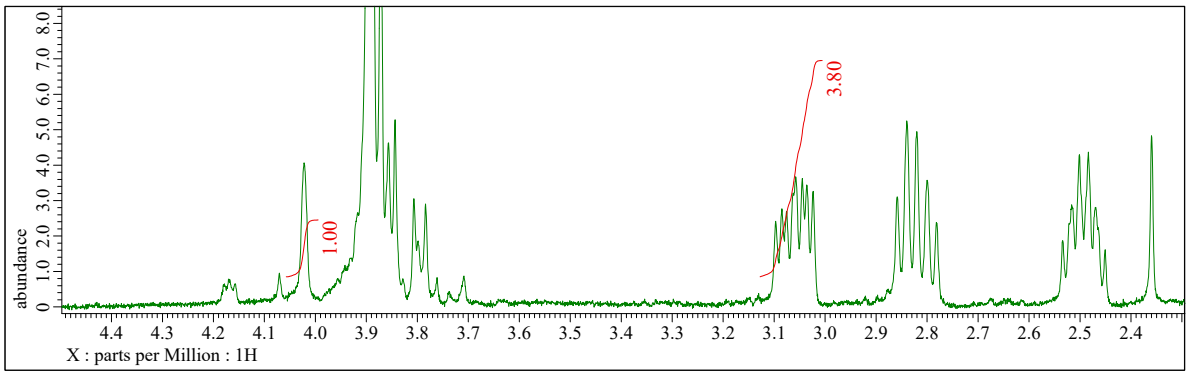
Time (h)	NMR ratio (P:SM)
1	0.22
3	0.25
5	0.56
7	1.06
14	2.22

Table S2. Hot filtration test for one-pot oxidation and aldol reaction of 1-indanol and 4-methoxybenzaldehyde.

Entry	NMR ratio (P:SM)
1	1:3.97
2	1:3.80



(a)



(b)

Figure S1. NMR of reaction mixture at 3 h and 7 h (removed catalyst at 3 h) (**a**) NMR of reaction at 3h before filtration. (**b**) NMR of reaction after 7 h (catalyst removed after 3 h).

4. Reusability test

The oxidation reaction of 1-indanol and one pot aldol reaction with 4-methoxybenzaldehyde was performed following the general reaction procedure in a test tube (30 mm) using an organic synthesizer. After completion of the reaction, the reaction mixture was transferred to a centrifuged tube and acetone was added. It was centrifuged and washed three times with acetone (45 ml each) and finally with water. The acetone was collected, evaporated and purified to get isolated yield of

the product in each cycle. The catalyst was dried after the first catalytic cycle and used for the next run.

Table S3. Result of Reusability test of (1:1)Ag/Pd-HT in oxidative coupling of 1-indanol with 4-methoxybenzaldehyde (upto 5 cycles)

Entry*	amount of catalyst (mg)		Yield %
	used	recovered	
1	156	140	77
2	130	112	81
3	104	82	71
4	82	71	85
5	52	47	87

Table S4. Reusability tests of different batches (1:1)Ag/Pd-HT catalysts in oxidative coupling of 1-indanol with 4-methoxybenzaldehyde

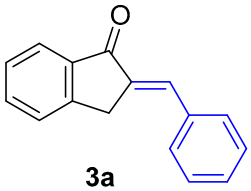
cycle	Yield %	
	1st time	2nd time
1	77	84
2	81	85
3	71	70
4	85	67

*Each successive runs were conducted 0.05 mmol smaller scale than the previous one due to the loss of 5-20% catalyst during centrifuging and washing process.

The products were confirmed by ^{1}H NMR, ^{13}C NMR, IR and mass comparing with the reported NMR in the literature which exactly matched with the reported values.

The ^{1}H NMR, ^{13}C NMR and IR spectral data were in accordance with those reported in the literature [1−6].

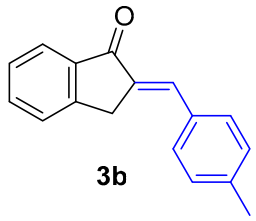
2-benzylidene-indan-1-one1,4



3a

^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.06 (s, 2H), 7.40-7.69 (m, 9H), 7.91 (d, *J*. = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 194.5, 149.8, 138.1, 135.5, 134.9, 134.8, 134.8 134.1, 130.8, 130.8 129.8, 129.1, 127.8, 126.3, 124.6, 32.6; IR (KBr, cm^{-1}): 3021, 2913, 1694, 1604, 1581, 1492, 1448, 1421, 1325, 1294, 1267, 1209, 1186, 1114, 1092, 1073, 1030.

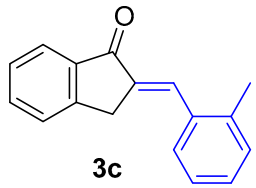
2-(4-Methylbenzylidene)-indan-1-one1,4



3b

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.40 (s, 3H), 4.03 (s, 2H), 7.26-7.67 (m, 8H), 7.91 (d, *J*. = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 194.5, 149.7, 140.3, 138.3, 134.6, 134.1, 133.9, 132.8, 130.9, 130.9, 129.8, 129.8, 127.7, 126.3, 124.5, 32.6, 21.6; IR (KBr, cm^{-1}): 3021, 2916, 1687, 1621, 1602, 1581, 1511, 1465, 1328, 1296, 1271, 1199, 1184, 1087.

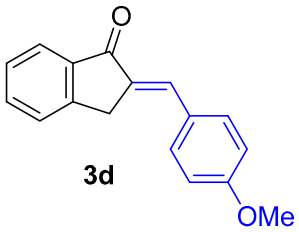
2-(2-methylbenzylidene)- indan-1-one5



3c

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.48 (s, 3H), 3.98 (s, 2H), 7.26-7.30 (m, 3H), 7.43 (t, *J*. = 7.2 Hz, 1H), 7.52-7.65 (m, 3H), 7.91-7.93 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): 194.6, 150.3, 139.6, 138.5, 135.9, 134.9, 134.6, 131.9, 131.2, 129.8, 128.9, 127.9, 126.5, 126.4, 124.8, 32.5, 20.5;
IR (KBr, cm^{-1}): 3059, 2955, 1698, 1618, 1583, 1542, 1482, 1465, 1368, 1327, 1295, 1184, 1086.

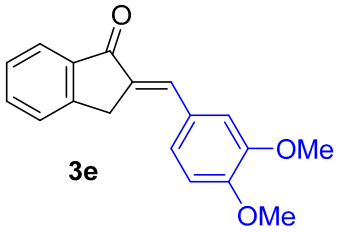
2-(4-Methoxybenzylidene)-indan-1-one1,4



3d

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.87 (s, 3H), 4.02 (s, 2H), 6.99 (d, *J*. = 8.8 Hz, 2H), 7.43 (t, *J*. = 7.6 Hz, 1H), 7.55-7.66 (m, 5H), 7. 91 (d, *J*. = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 194.7, 161.2, 149.9, 138.6, 134.7, 134.2, 132.9, 132.9, 132.8, 128.5, 127.9, 126.5, 126.5, 124.7, 114.8, 55.8, 32.8; IR (KBr, cm^{-1}): 3021, 2950, 2916, 2887, 1687, 162, 1581, 1561, 1465, 1445, 1361, 1328, 1296, 1271, 1184, 1087.

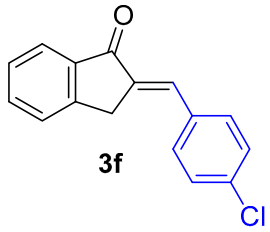
2-(3,4-Dimethoxybenzylidene)-indan-1-one3,4



3e

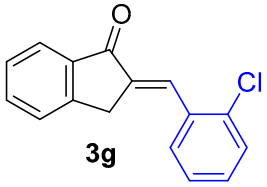
^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.94 (s, 3H), 3.96 (s, 3H), 4.01 (s, 2H), 6.94 (d, *J*. = 8.4 Hz, 1H), 7.18 (s, 1H), 7.30 (d, *J*. = 7.6 Hz, 1H), 7.42 (t, *J*. = 7.2 Hz, 1H), 7.54-7.62 (m, 3H), 7.90 (d, *J*. = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 194.3, 150.7, 149.5, 149.2, 138.3, 134.5, 134.2, 132.7, 128.5, 127.7, 126.2, 124.7, 124.4, 113.6, 111.4, 56.1,56.1, 32.5; IR (KBr, cm^{-1}): 3043, 3015, 2957, 2936, 2833, 1807, 1678, 1583, 1468, 1442, 1331, 1247, 1023.

2-(4-Chlorobenzylidene)-indan-1-one1



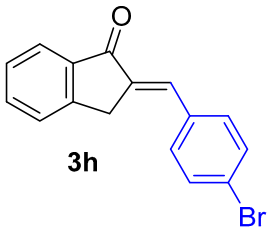
^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.01 (d, *J*. = 1.6 Hz, 1H), 7.41-7.43 (m, 3H), 7.56-7.62 (m, 5H), 7.90 (d, *J*. = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 194.2, 149.6, 138.0, 135.8, 135.3, 134.9, 134.0, 132.6, 131.9, 131.9, 129.3, 129.3, 127.9, 126.3, 124.6, 32.5; IR (KBr, cm^{-1}): 3068, 2924, 1697, 1625, 1585, 1561, 1490, 1468, 1326, 1297, 1093.

2-(2-Chlorobenzylidene)-indan-1-one



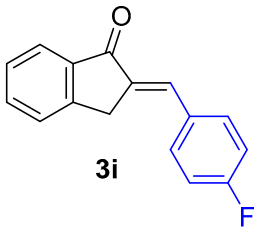
^{1}H NMR ($CDCl_3$, 400 MHz) (isomeric mixture): δ 3.98 (s, 2H), 7.26-7.62 (m, 7H), 7.93 (d, *J*. = 7.6 Hz, 1H), 8.05 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 193.9, 149.8, 138.1, 137.1, 136.3, 134.9, 133.7, 130.5, 130.4, 130.0, 129.9, 127.8, 126.9, 126.2, 124.7, 32.0; IR (KBr, cm^{-1}): 3077, 3046, 2928, 1696, 1630, 1586, 1560, 1492, 1467, 1338, 1267, 1093.

2-(4-Bromobenzylidene)-indan-1-one2,4



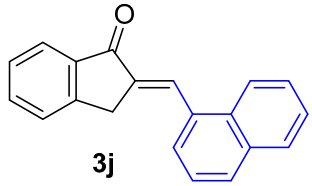
^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.01 (s, 2H), 7.15 (t, *J*. = 8.4 Hz, 2H), 7.43 (t, *J*. = 7.6 Hz, 1H), 7.55 (d, *J*. = 7.6 Hz, 1H), 7.56-7.68 (m, 4H), 7.90 (d, *J*. = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 194.5, 149.8, 138.3, 135.7, 135.2, 134.7, 132.9, 132.6, 132.6, 132.4, 132.4, 128.2, 126.6, 124.9, 124.4, 32.8; IR (KBr, cm^{-1}): 3028, 2961, 2930, 1723, 1698, 1625, 1582, 1560, 1465, 1420, 1351, 1326, 1273, 1072.

2-(4-Fluorobenzylidene)-indan-1-one2,4



^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.01 (s, 2H), 7.44 (t, *J*. = 7.6 Hz, 1H), 7.52-7.65 (m, 7H), 7.91 (d, *J*. = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 194.3, 164.4, 162.4, 149.6, 138.1, 134.8, 134.4, 132.8, 131.8, 131.7, 127.9, 126.3, 124.6, 116.3, 116.2, 32.4; IR (KBr, cm^{-1}): 3071, 2925, 1697, 1633, 1549, 1466, 1354, 1328, 1298, 1184, 1096.

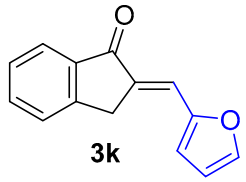
2-Naphthalen-1-ylmethylene-indan-1-one1



3j

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.99 (s, 2H), 7.42-7.61 (m, 6H), 7.79 (d, *J*. = 7.2 Hz, 1H), 7.89-7.97 (m, 3H), 8.23 (d, *J*. =8.0 Hz, 1H), 8.46 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 194.0, 150.3, 139.6, 138.5, 135.9, 134.9, 134.6, 131.9, 131.2, 129.8, 128.9, 127.9, 126.5, 126.4, 124.8, 32.5, 20.5; IR (KBr, cm^{-1}): 3047, 2924, 1827, 1697, 1616, 1583, 1569, 1466, 1387, 1296, 1187, 1089.

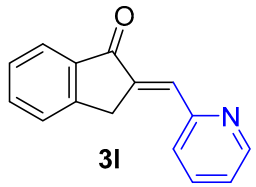
2-furan-2-ylmethylene-indan-1-one4



3k

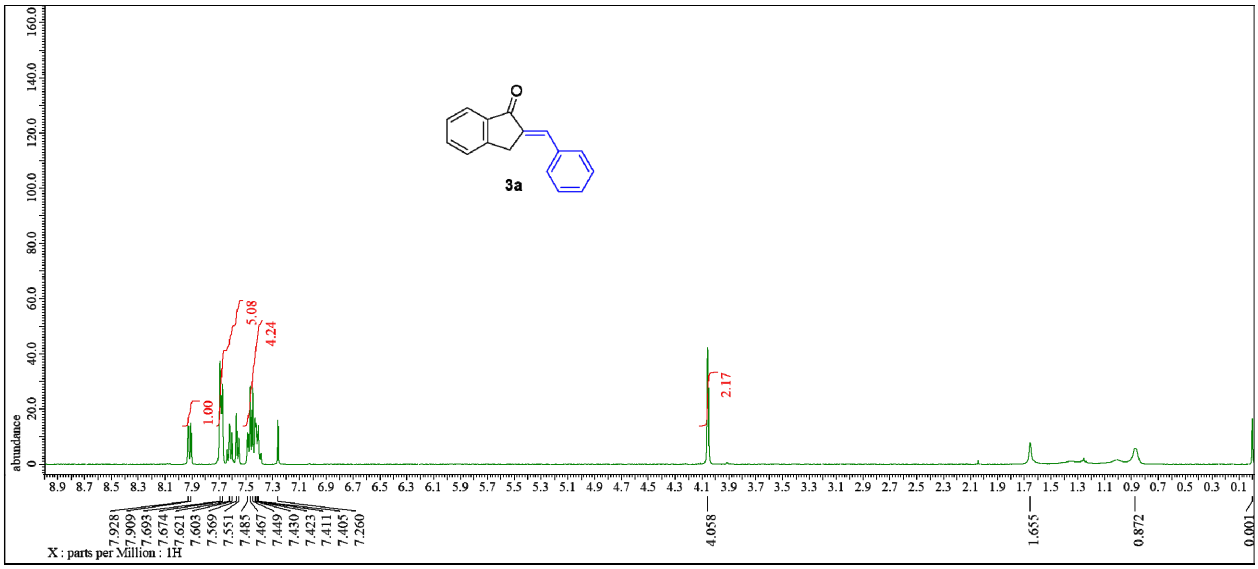
^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.04 (s, 2H), 6.55 (s, 1H), 6.77 (d, *J*. = 3.2 Hz, 1H), 7.39-7.46 (m, 2H), 7.59-7.63 (m, 3H), 7.88 (d, *J*. = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 194.1, 152.4, 149.9, 145.5, 138.6, 134.6, 132.7, 127.6, 126.3, 124.3, 120.2, 116.8, 112.8, 32.5; IR (KBr, cm^{-1}): 3043, 2962, 2911, 2854, 1685, 1625, 1580, 1477, 1466, 1392, 1327, 1297, 1152, 1080.

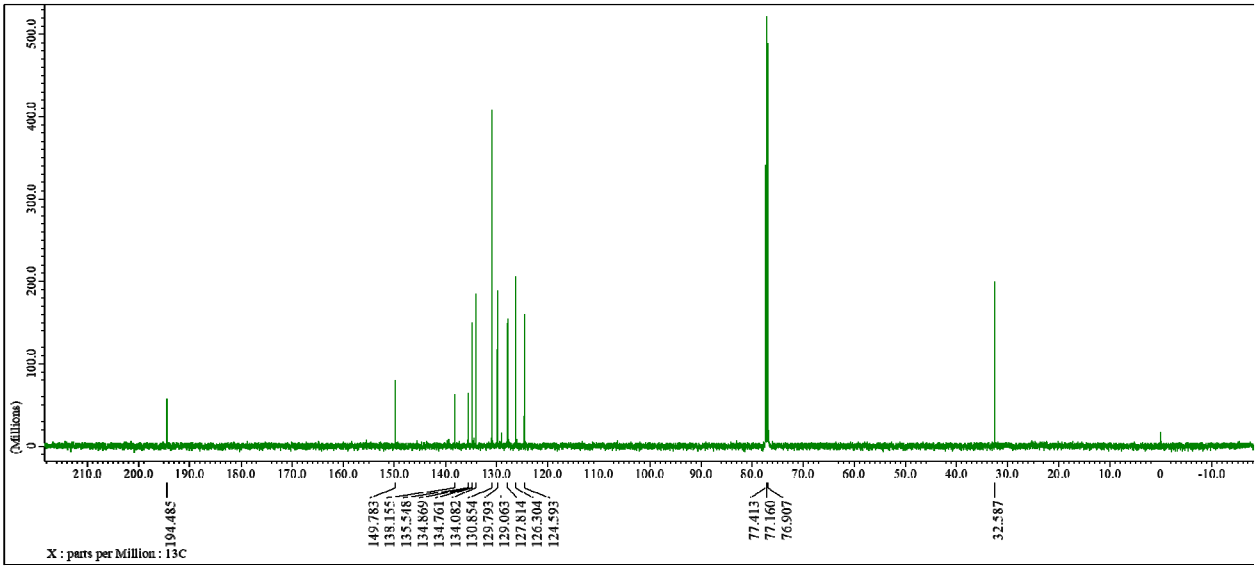
2-pyridine-2-ylmethylene-indan-1-one6

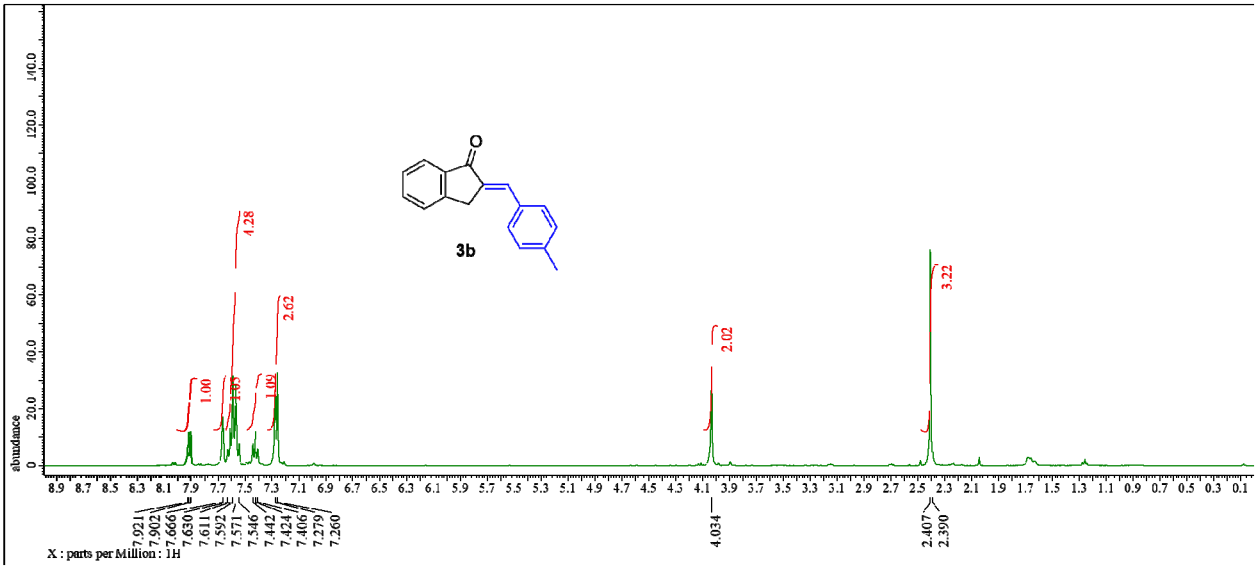


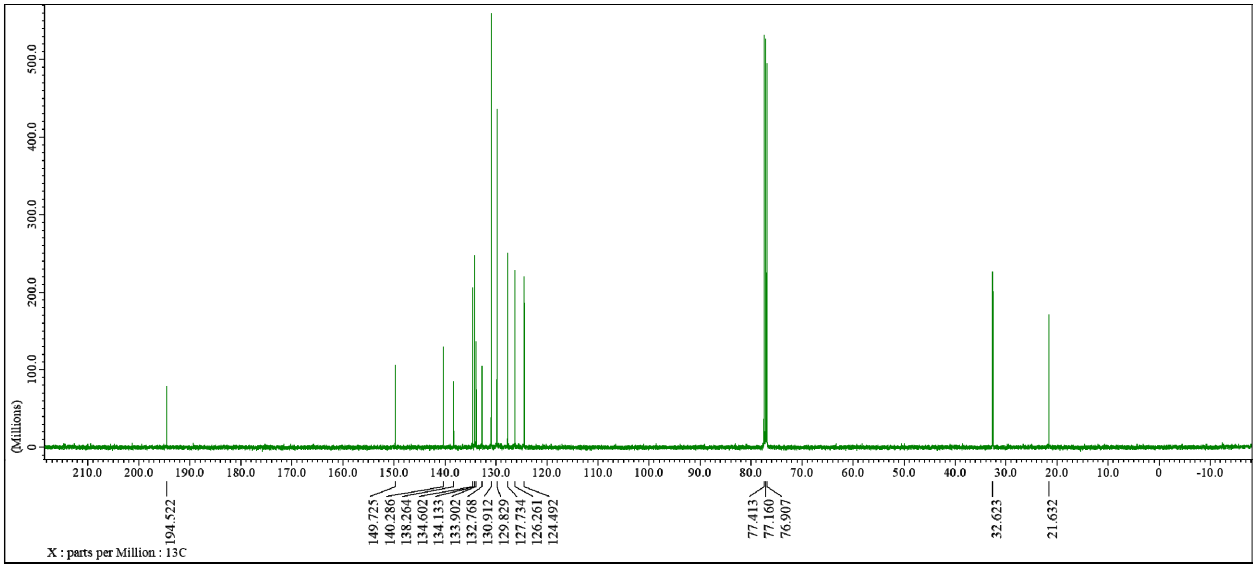
3l

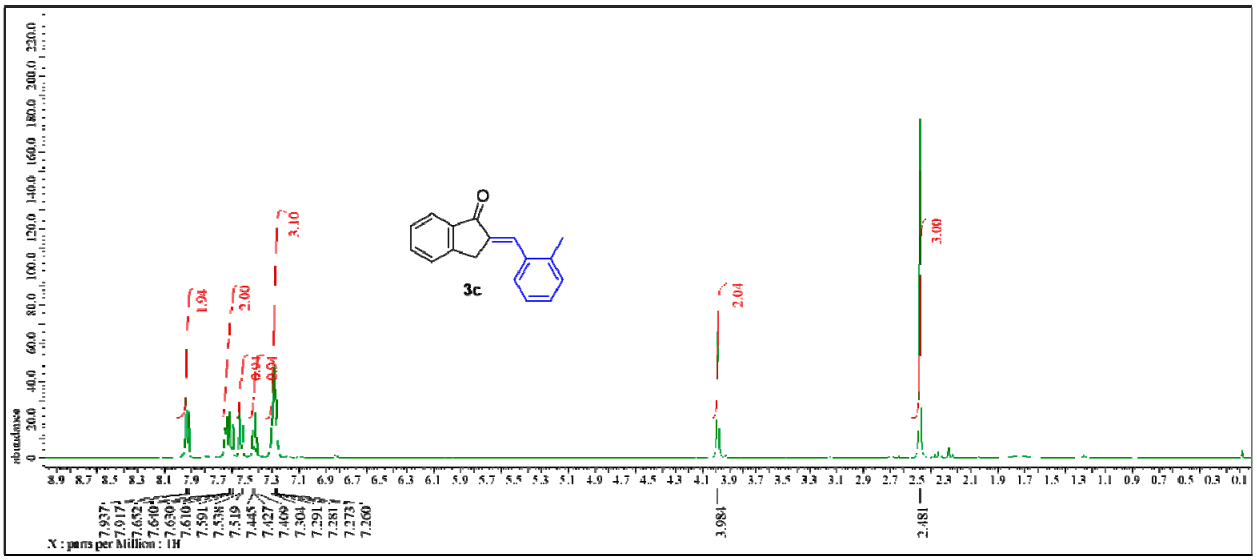
^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.30 (s, 2H), 7.23-7.26 (m, 1H), 7.41 (t, *J*. = 7.5 Hz, 1H), 7.53-7.62 (m, 4H), 7.73 (m, 1H), 7.90 (d, *J*. = 7.6 Hz, 1H), 8.75 (d, *J*. = 4.4, 1H); ^{13}C-NMR ($CDCl_3$, 125 MHz): 195.1, 154.9, 151.4, 150.2, 139.2, 138.0, 136.5, 134.9, 131.1, 127.5, 127.5, 126.5, 124.5, 123.1, 33.5; IR (KBr, cm^{-1}): 3384, 3323, 3087, 3058, 3028, 3011, 2915, 1825, 1786, 1638, 1606, 1560, 1542, 1465, 1428, 1348, 1294, 1180, 1091.

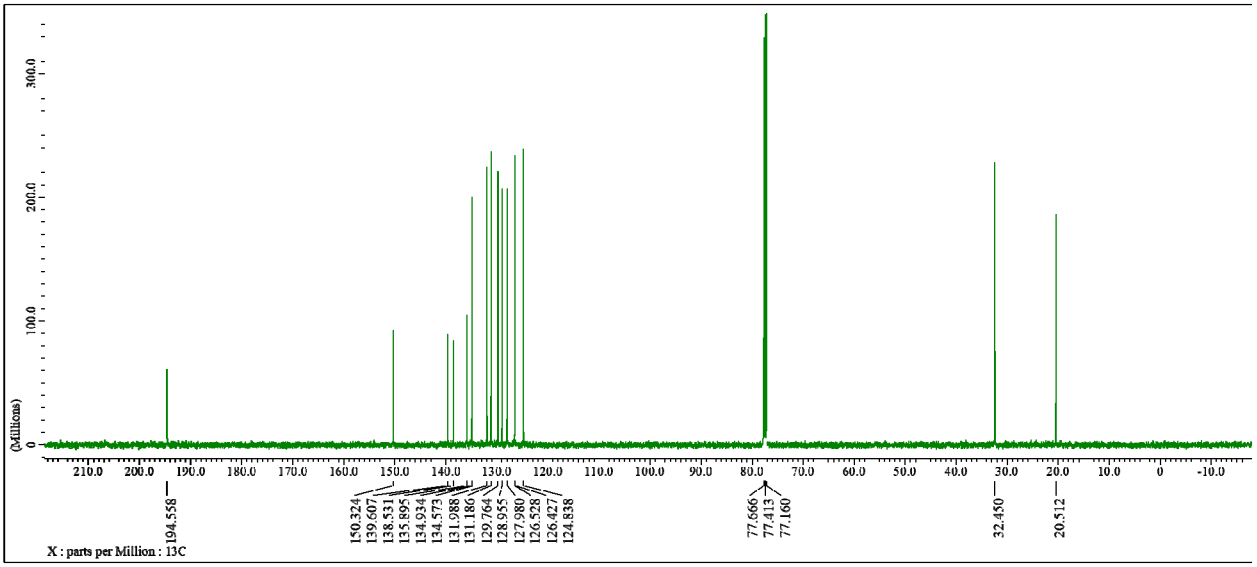

3a
abundance
X : parts per Million : 1H
7.928
7.909
7.693
7.674
7.621
7.603
7.569
7.551
7.485
7.467
7.449
7.430
7.423
7.411
7.405
7.260
4.058
1.655
0.872
0.001
1.00
5.08
4.24
2.17

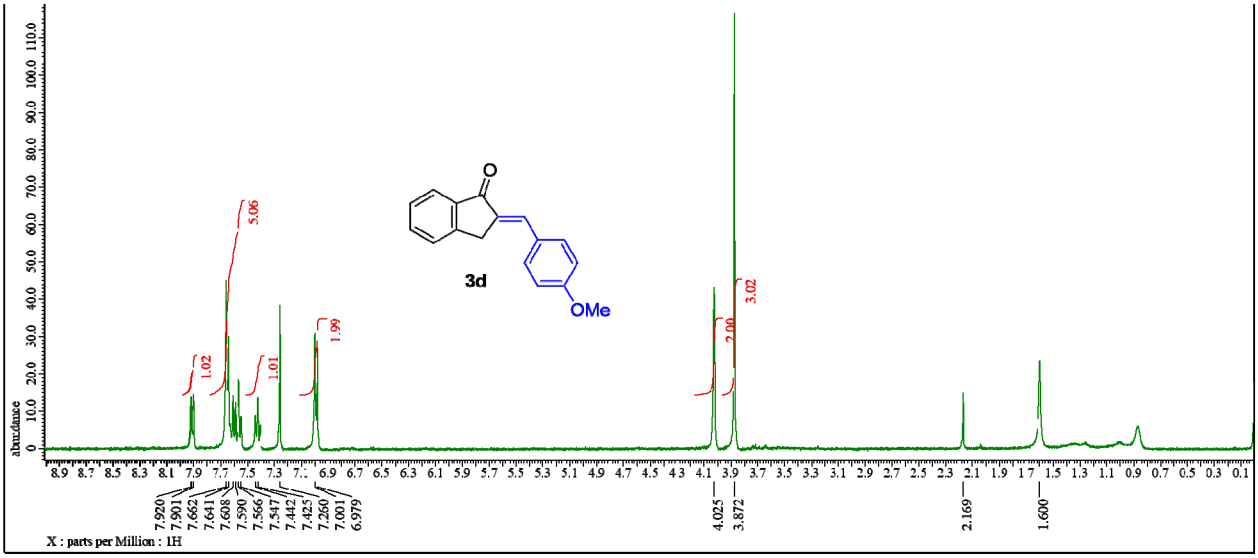

(Millions)
X : parts per Million : 13C
194.485
149.783
138.155
135.548
134.869
134.761
134.082
130.854
129.793
129.063
127.814
126.304
124.593
77.413
77.160
76.907
32.587

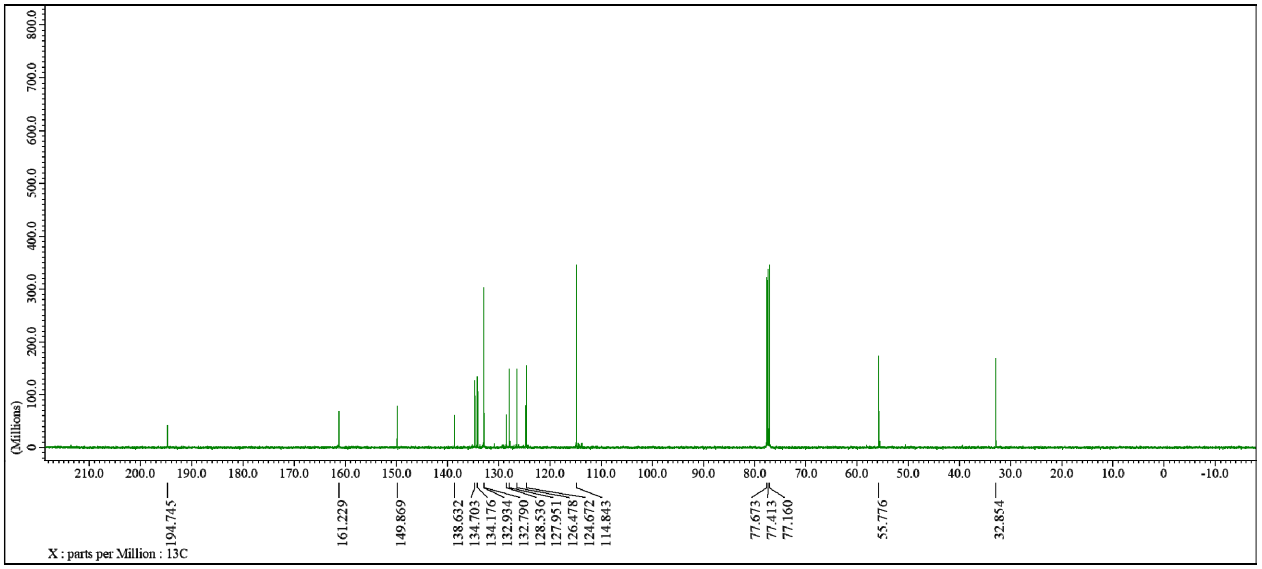

3b
abundance
X : parts per Million : 1H
7.921
7.902
7.666
7.630
7.611
7.592
7.571
7.546
7.442
7.424
7.406
7.279
7.260
4.034
2.407
2.390
1.00
4.28
2.62
1.09
2.02
3.22

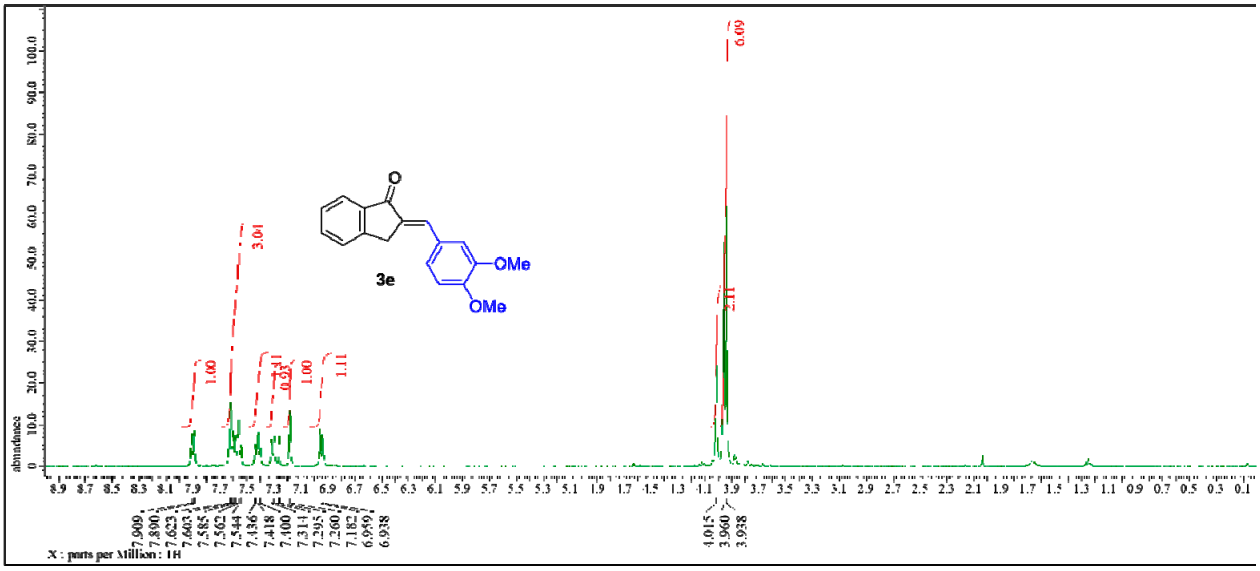

(Millions)
194.522
149.725
140.286
138.264
134.602
134.133
133.902
132.768
130.912
129.829
127.734
126.261
124.492
77.413
77.160
76.907
32.623
21.632
X : parts per Million : 13C

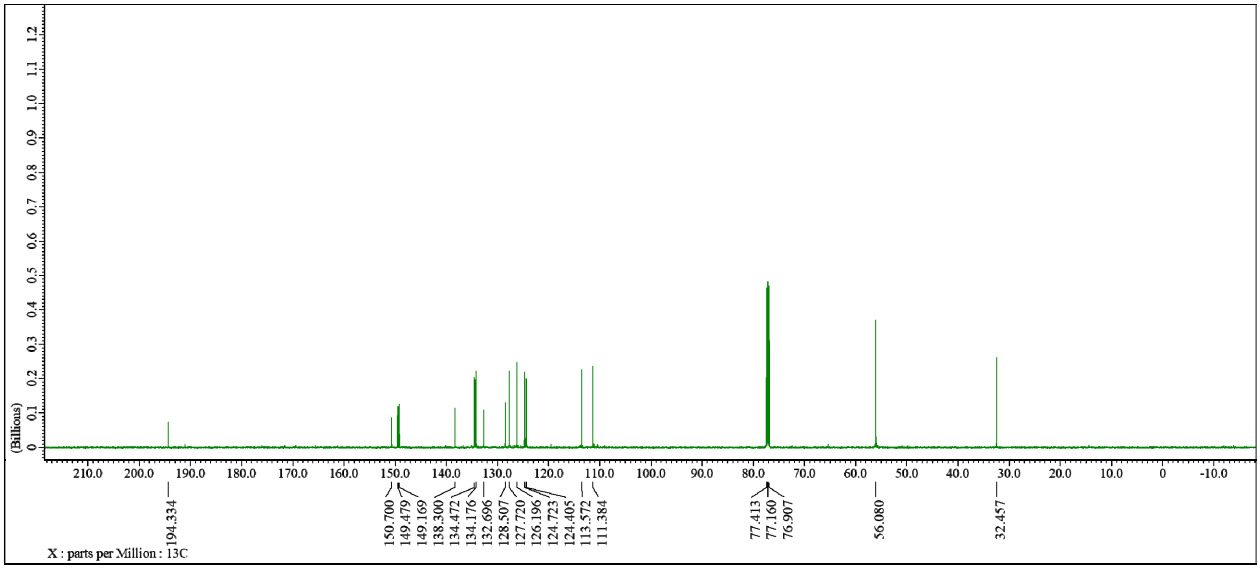

1.94
2.00
6.94
3.10
2.04
3.00
3c
3.984
2.481
X : parts per Million : 1H

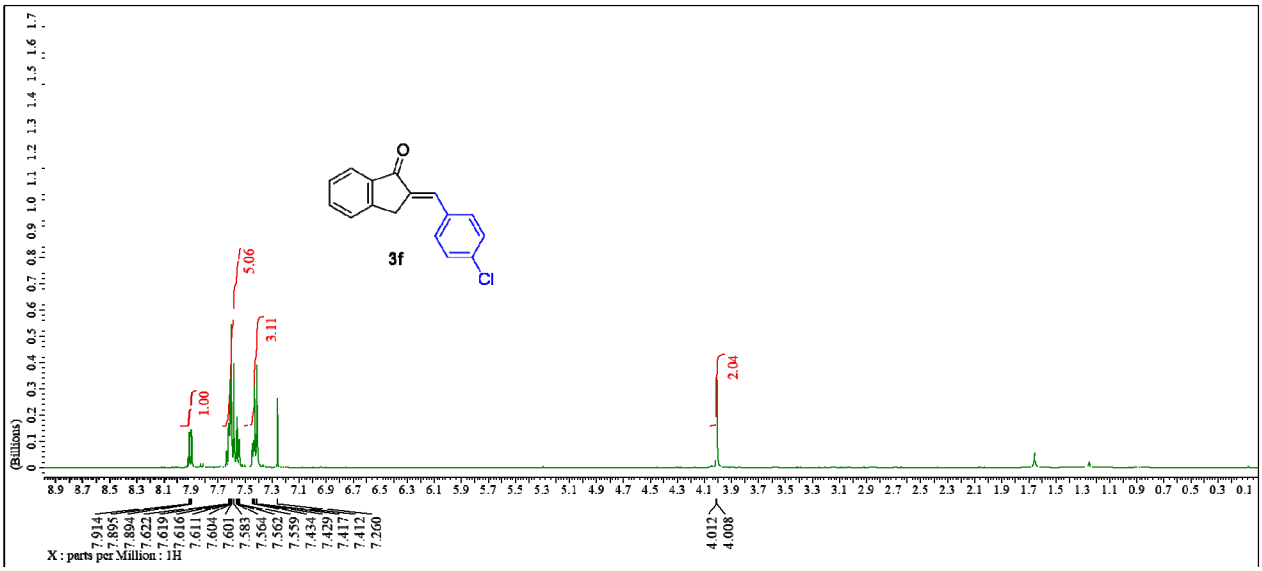

(Millions)
194.558
150.324
139.607
138.531
135.895
134.934
134.573
131.988
131.186
129.764
128.955
127.980
126.528
126.427
124.838
77.666
77.413
77.160
32.450
20.512
X : parts per Million : 13C

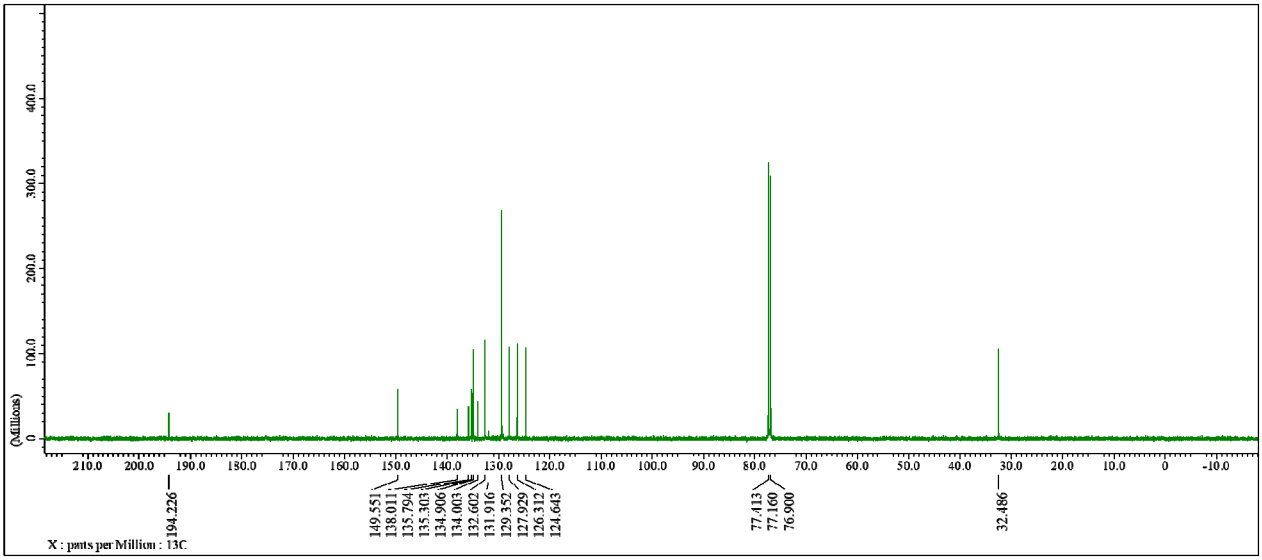

3d
OMe
5.06
1.02
1.01
1.99
2.00
3.02
abundance
7.920
7.901
7.662
7.641
7.608
7.590
7.566
7.547
7.442
7.425
7.260
7.001
6.979
4.025
3.872
2.169
1.600
X : parts per Million : 1H

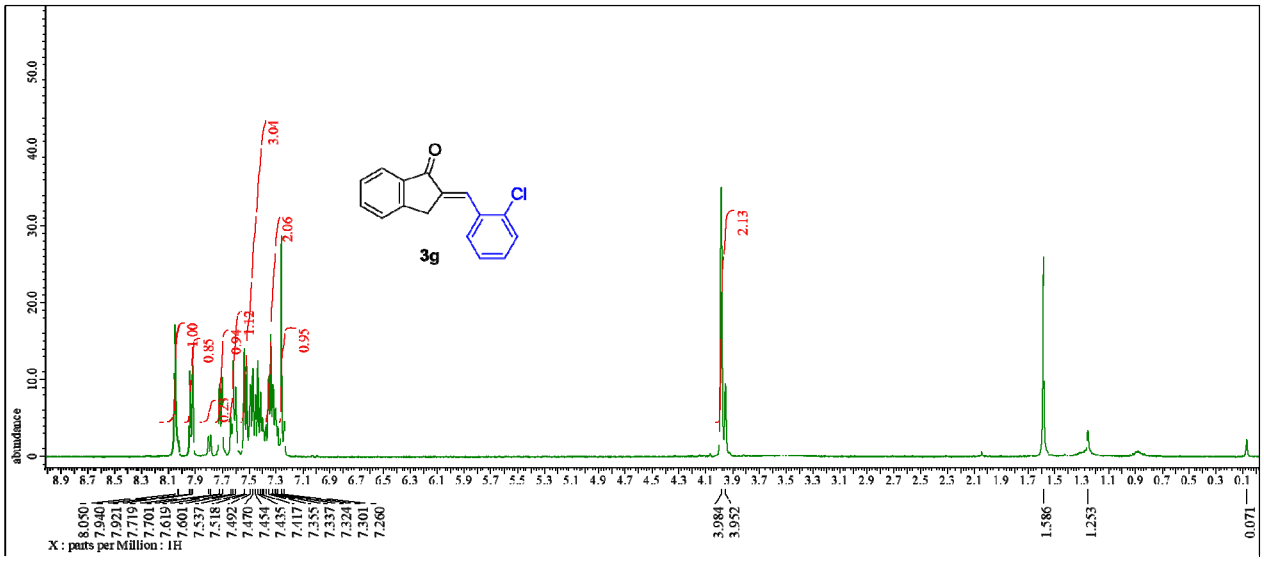

(Millions)
194.745
161.229
149.869
138.632
134.703
134.176
132.934
132.790
128.536
127.951
126.478
124.672
114.843
77.673
77.413
77.160
55.776
32.854
X : parts per Million : 13C

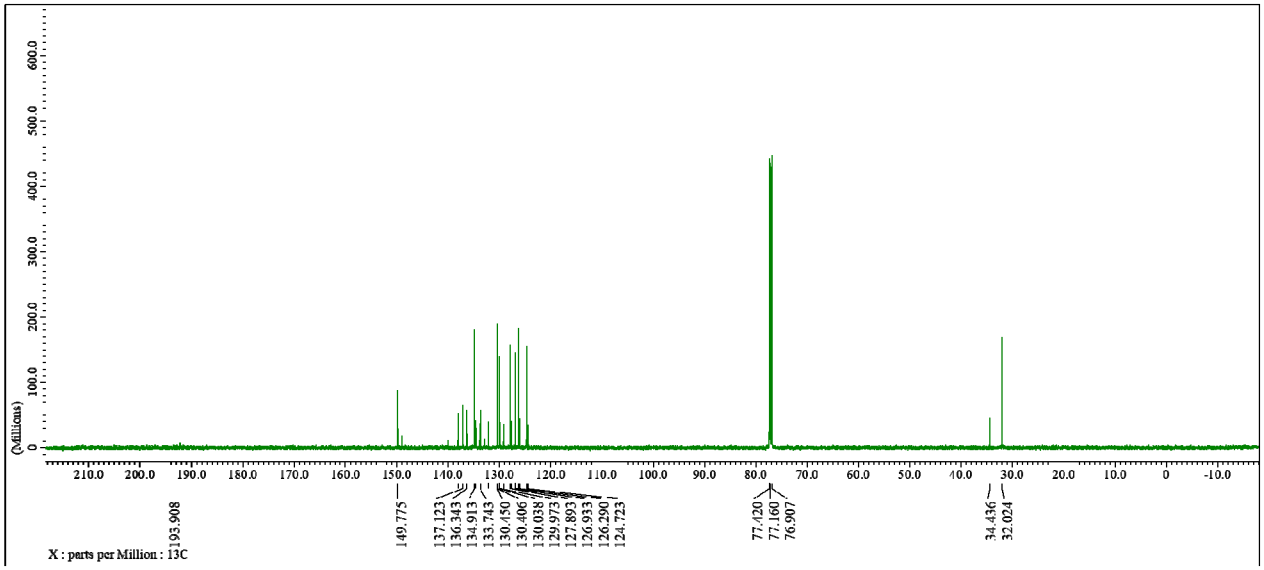

O
OMe
OMe
3e
abundance
X : parts per Million : 1H

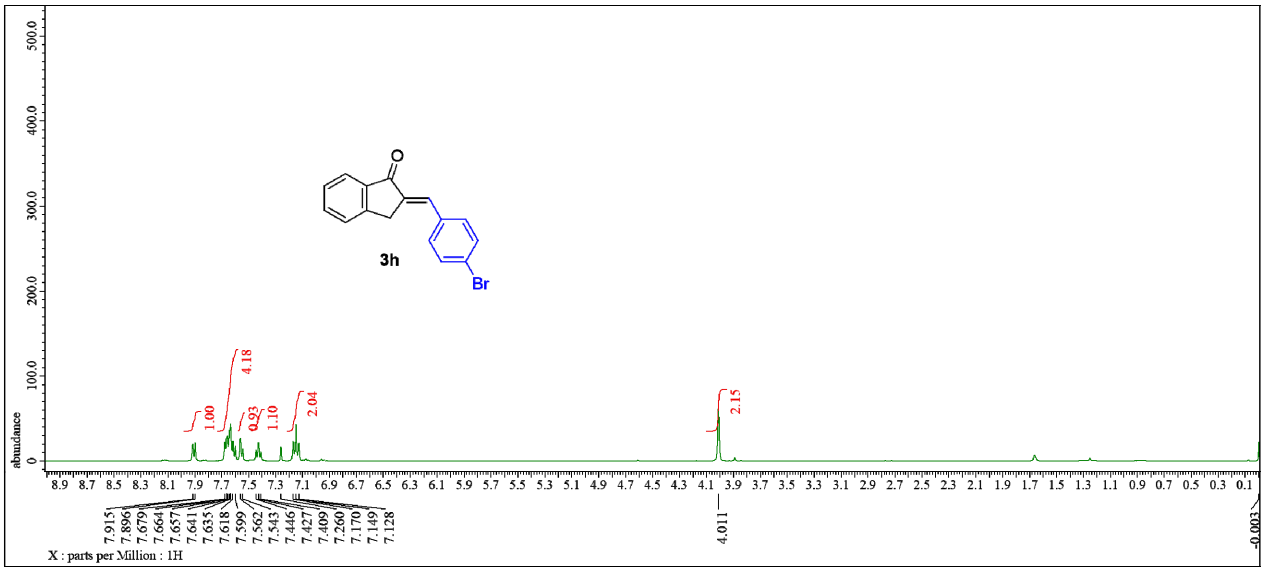

(Billions)
X : parts per Million : 13C

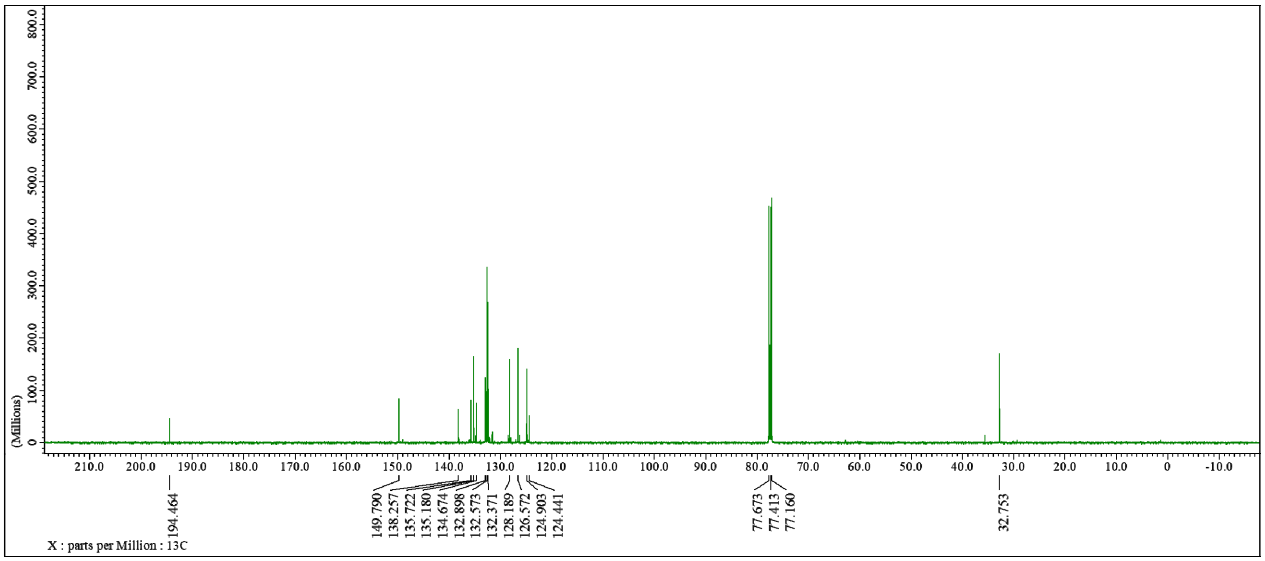

O
Cl
3f
5.06
3.11
1.00
2.04
(Billions)
7.914
7.895
7.894
7.622
7.619
7.616
7.611
7.604
7.601
7.583
7.564
7.562
7.559
7.434
7.429
7.417
7.412
7.260
4.012
4.008
X : parts per Million : 1H

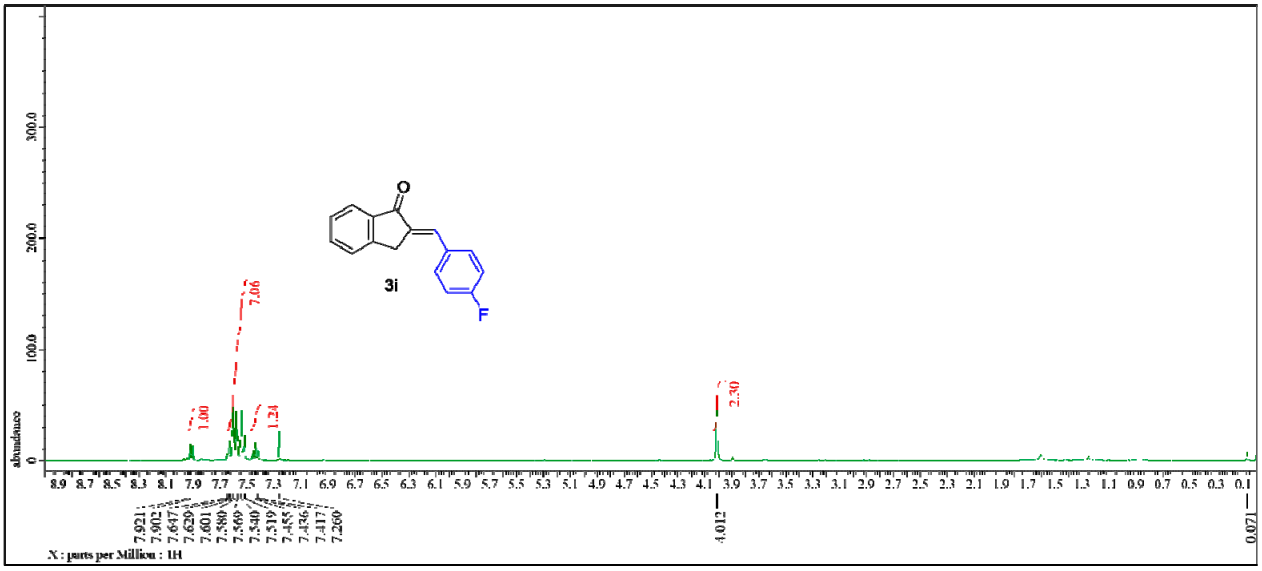

(Millions)
194.226
149.551
138.011
135.794
135.303
134.906
134.003
132.602
131.916
129.352
127.929
126.312
124.643
77.413
77.160
76.900
32.486
X : parts per Million : 13C

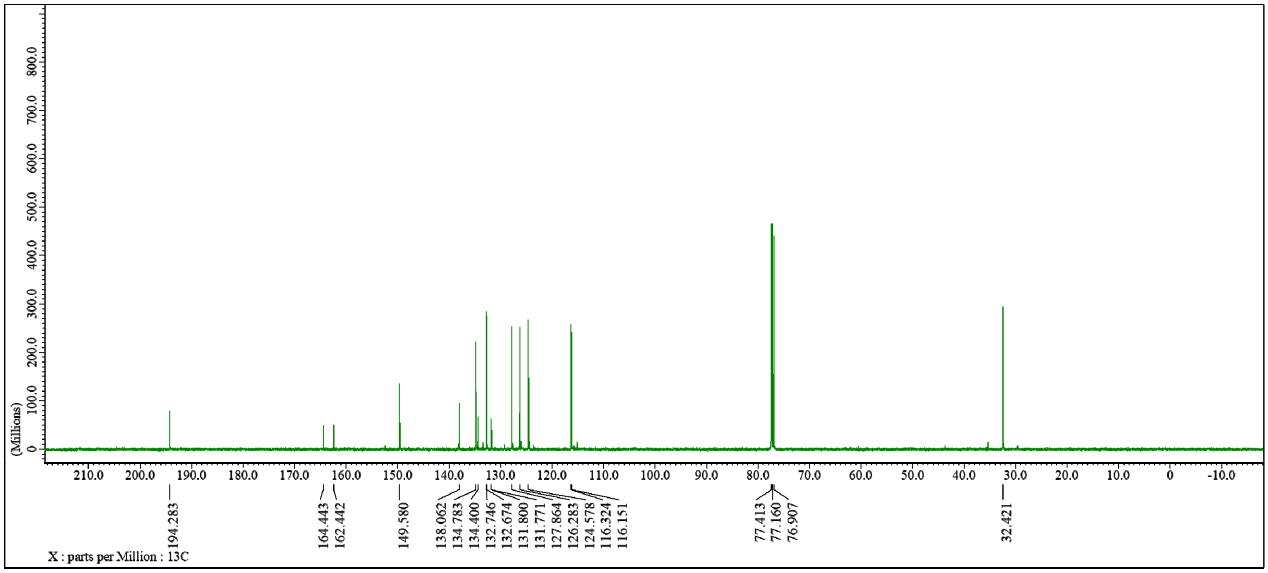

O
Cl
3g
3.01
2.06
2.13
1.00
0.85
0.94
1.19
0.95
0.25
abundance
X : parts per Million : 1H

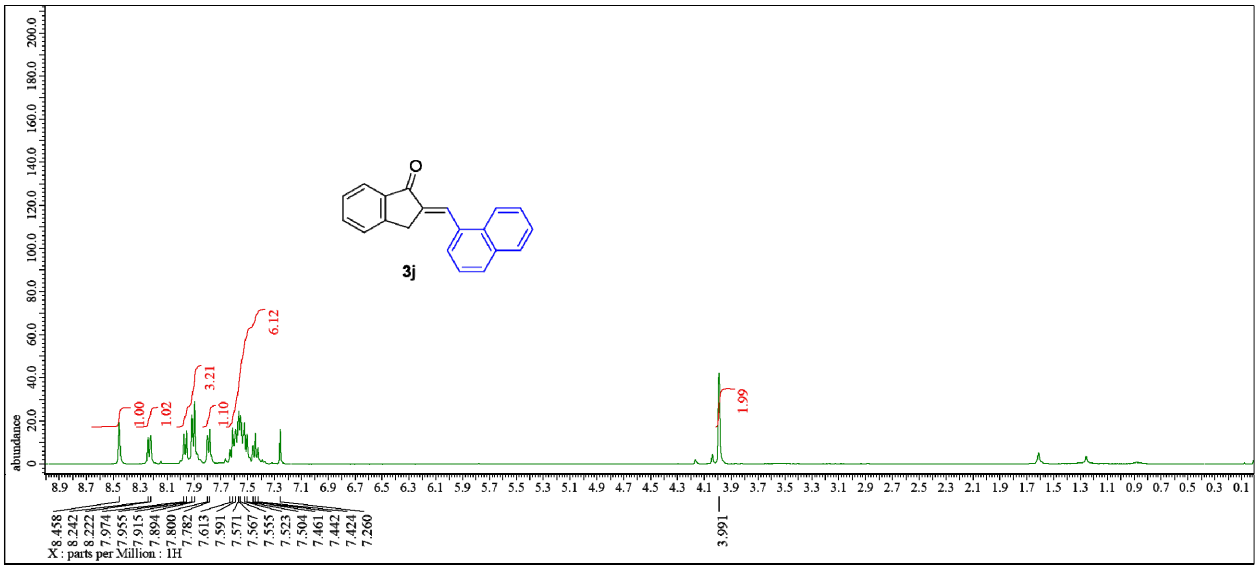

(Millions)
X : parts per Million : 13C

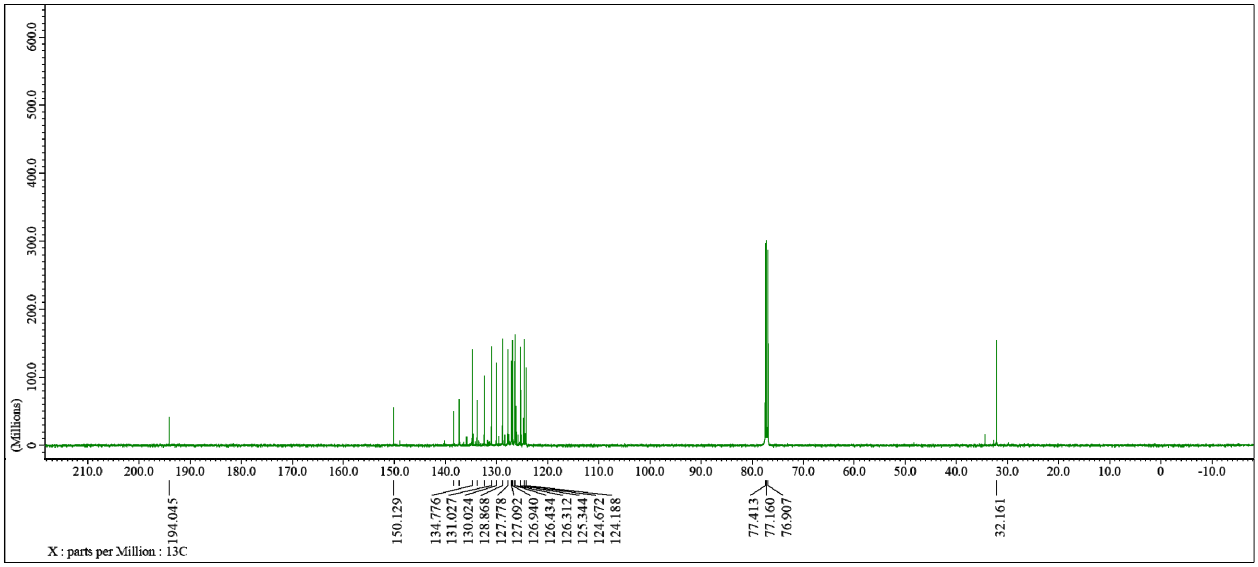

3h
Br
abundance
1.00
4.18
0.93
1.10
2.04
2.15
7.915
7.896
7.679
7.664
7.657
7.641
7.635
7.618
7.599
7.562
7.543
7.446
7.427
7.409
7.260
7.170
7.149
7.128
4.011
-0.003
X : parts per Million : 1H

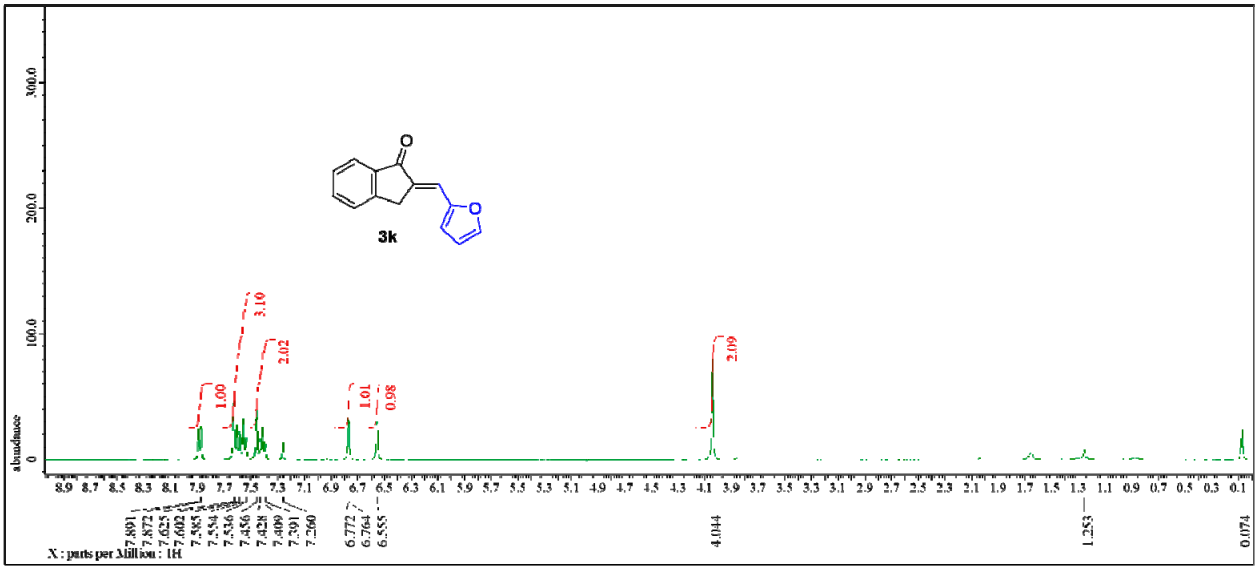

(Millions)
194.464
149.790
138.257
135.722
135.180
134.674
132.898
132.573
132.371
128.189
126.572
124.905
124.441
77.673
77.413
77.160
32.753
X : parts per Million : 13C

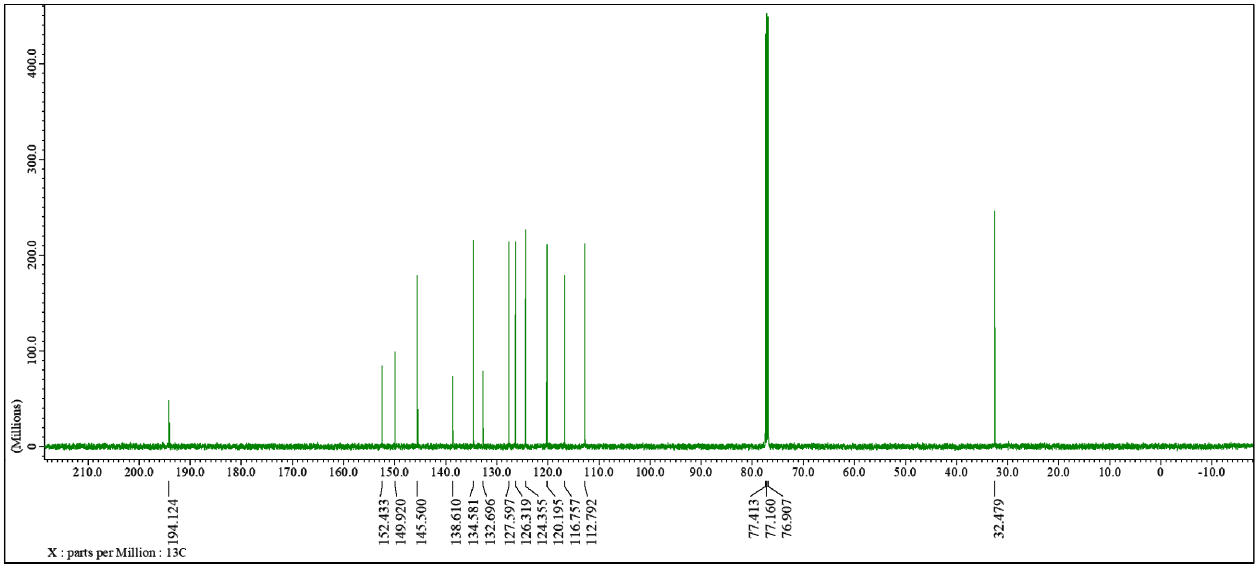

O
3i
F
7.06
1.00
1.24
2.30
abundance
X : parts per Million : 1H

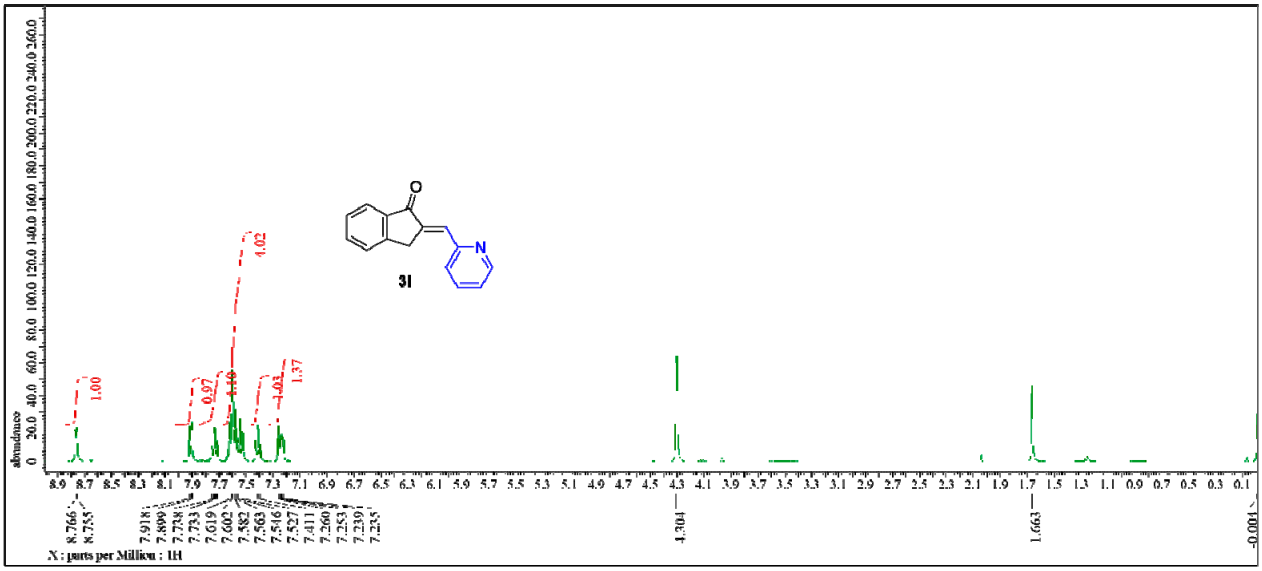

(Millions)
194.283
164.443
162.442
149.580
138.062
134.783
134.400
132.746
132.674
131.800
131.771
127.864
126.283
124.578
116.324
116.151
77.413
77.160
76.907
32.421
X : parts per Million : 13C

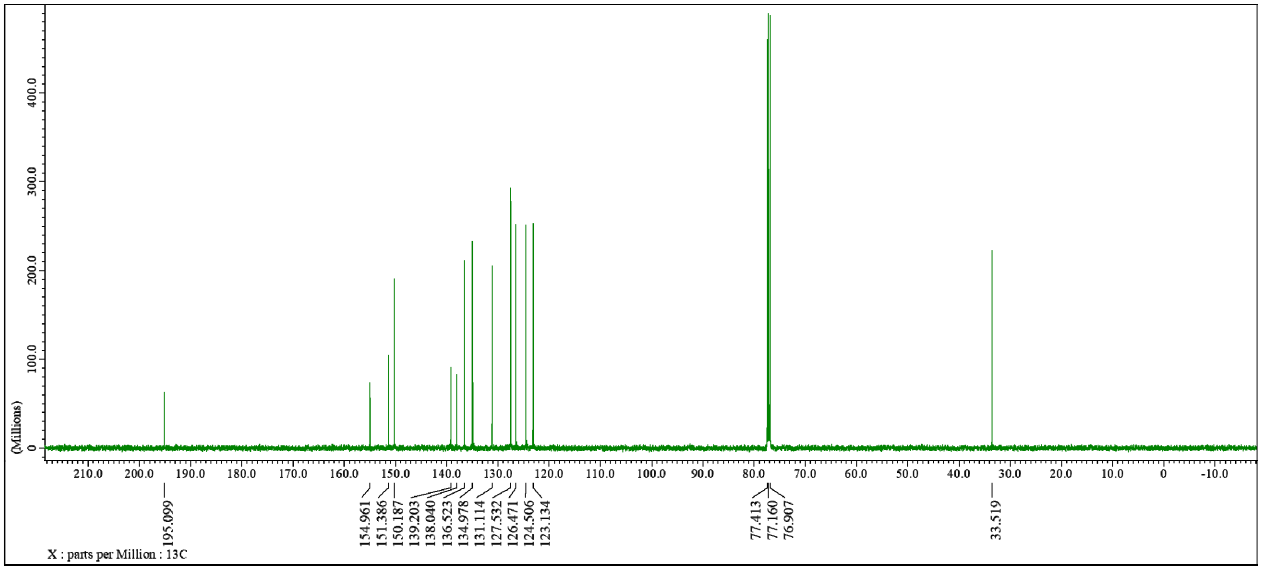

3j
abundance
1.00
1.02
3.21
1.10
6.12
1.99
8.458
8.242
8.222
7.974
7.955
7.915
7.894
7.800
7.782
7.613
7.591
7.571
7.567
7.555
7.523
7.504
7.461
7.442
7.424
7.260
3.991
X : parts per Million : 1H


(Millions)
194.045
150.129
134.776
131.027
130.024
128.868
127.778
127.092
126.940
126.434
126.312
125.344
124.672
124.188
77.413
77.160
76.907
32.161
X : parts per Million : 13C


3k
1.00
3.10
2.02
1.01
0.98
2.09
X : parts per Million : 1H


(Millions)
194.124
152.433
149.920
145.500
138.610
134.581
132.696
127.597
126.319
124.355
120.195
116.757
112.792
77.413
77.160
76.907
32.479
X : parts per Million : 13C


O
N
3l
abundance
X : parts per Million : 1H


(Millions)
X : parts per Million : 13C

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