Supporting Information

Copper-Catalyzed *Ortho*-Acylation of Phenols with Aryl Aldehydes and Its Application in One-Step Preparation of Xanthones

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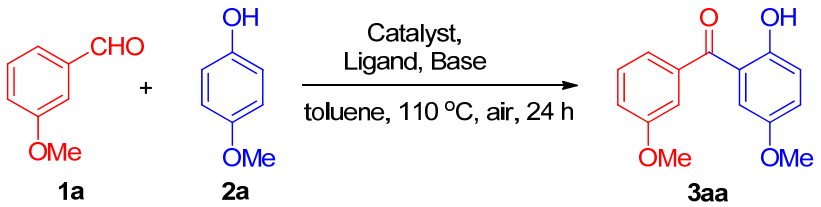
1. Table S1 Optimization of the reaction conditions for *ortho*-acylation of 4-methoxyphenol with 3-methoxybenzaldehyde

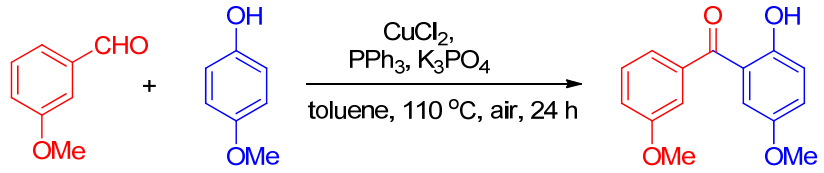


1a **2a** **3aa**

Entry [a]	Catalyst	Ligand	Base	Yield (%) [b]
1	$Pd(OAc)_2$	PPh_3	K_2CO_3	77
2	$Pd(OAc)_2$	PPh_3	K_3PO_4	75
3	$Pd(OAc)_2$	PPh_3	Na_2CO_3	<5
4	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	<5
5	$CuCl_2$	PPh_3	K_3PO_4	91
6	$CuCl_2$	PPh_3	K_2CO_3	76
7	$CuCl_2$	PPh_3	Na_2CO_3	<5
8	$CuCl_2$	PPh_3	Cs_2CO_3	<5
9	$CuCl_2$	*t*-ButylXPhos	K_3PO_4	63
10	$CuCl_2$	*t*-ButylXPhos	K_2CO3	50
11	$CuCl_2$	*t*-ButylXPhos	Na_2CO_3	<5
12	$CuCl_2$	*t*-ButylXPhos	Cs_2CO_3	<5
13	$Pd(OAc)_2$	*t*-ButylXPhos	K_3PO_4	73
14	$Pd(OAc)_2$	*t*-ButylXPhos	K_2CO_3	66
15	$Pd(OAc)_2$	*t*-ButylXPhos	Na_2CO_3	<5
16	$Pd(OAc)_2$	*t*-ButylXPhos	Cs_2CO_3	<5
17		PPh_3	K_3PO_4	-
18	$CuCl_2$		K_3PO_4	trace

[a] Reaction condition: **1a** (1 equiv), **2a** (1.3 equiv.), base (2.2 equiv.), catalyst (5 mol%) and ligand (7.5 mol%); [b] ^1H NMR yield. The reaction time was not optimized.

2. **Table S2** Optimization of ratio ($CuCl_2$ and PPh_3) for *ortho*-acylation of 4-methoxyphenol with 3-methoxybenzaldehyde[a]



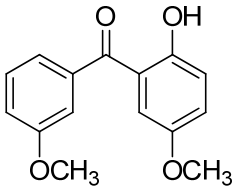
$CuCl_2$/PPh_3	Yields %[b]
1:1	65
2:3	91
1:2	90

[a] K_3PO_4 (2.2 equiv.), $CuCl_2$ (5 mol%); [b] ^{1}H-NMR yield.

3. **General Procedures for Ortho-Acylation of Phenols with Aldehydes**: Phenols (1.3 equiv), aryl aldehydes (1 equiv.), K_3PO_4 (2.2 equiv.), $CuCl_2$ (5 mol%) and PPh_3 (7.5 mol%) were added in 3 mL toluene, and then the reaction solution was stirred at 110 °C for 24 h. The mixture was extracted with DCM, washed by water, brine, and then the combined organic layer was dried by anhydrous Na_2SO_4. After evaporation of solvents, the crude product was purified by flash chromatography to afford the products.

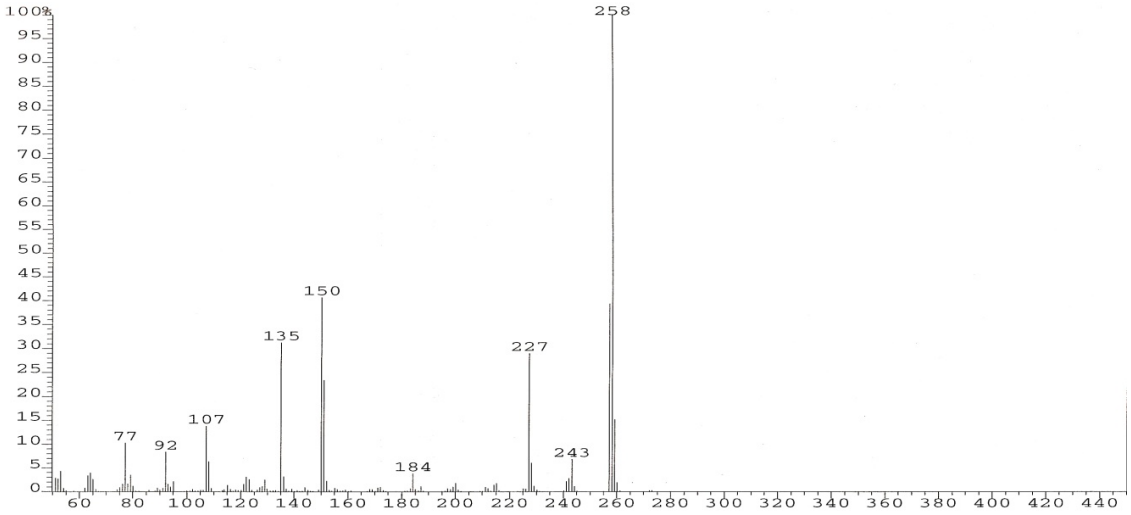
4. **General Procedure for One-step Preparation of Xanthones:** Phenols (1.3 equiv), 2-nitrobenzaldehydes (1 equiv.), K_3PO_4 (2.2 equiv.), $CuCl_2$ (5 mol%) and PPh_3 (7.5 mol%) were added in 3 mL toluene, and then the reaction solutions was stirred at 110 °C for 24 h. The mixture was extracted with DCM, washed by water, brine, and then the combined organic layer was dried by anhydrous Na_2SO_4. After evaporation of solvents, the crude product was purified by flash chromatography to afford the products.

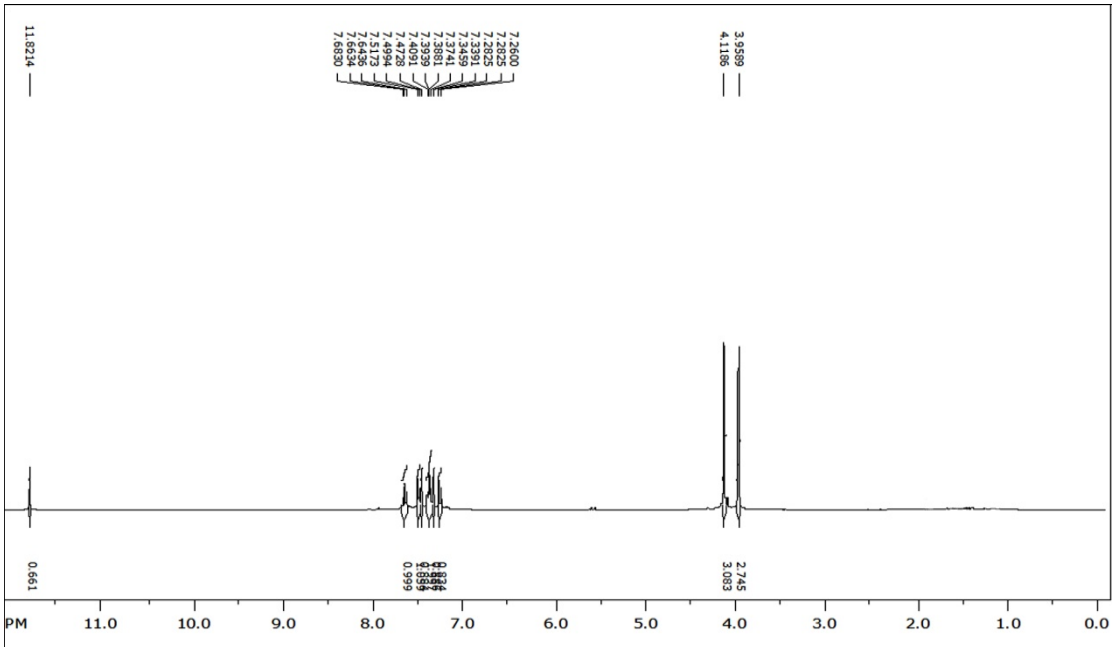
5. **Data and MS, ^{1}H NMR, ^{13}C NMR spectra**

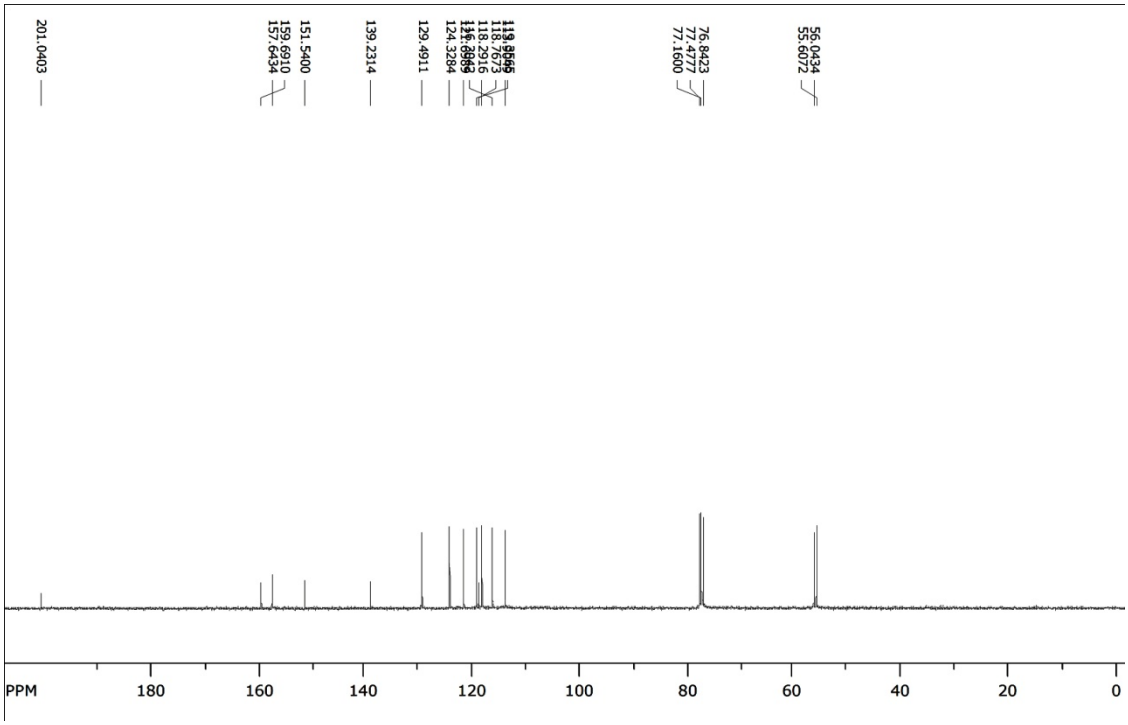


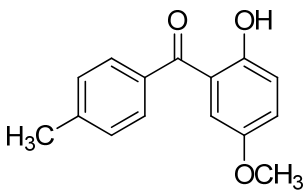
3aa

V(hexane):V(EtOAc)=10:1 as the mobile phase; yellow solid, mp. 40-41°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.82 (s, 1H, OH), 7.28-7.68 (m, 7H, Ph-H), 3.95, 4.11 (2*s, 2*3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ 201.04, 159.69, 157.64, 151.54, 139.23, 129.49, 124.32, 121.69, 119.35, 118.76, 118.29, 116.30, 113.90, 56.04, 55.60; MS-EI(m/z) = 258. [1]



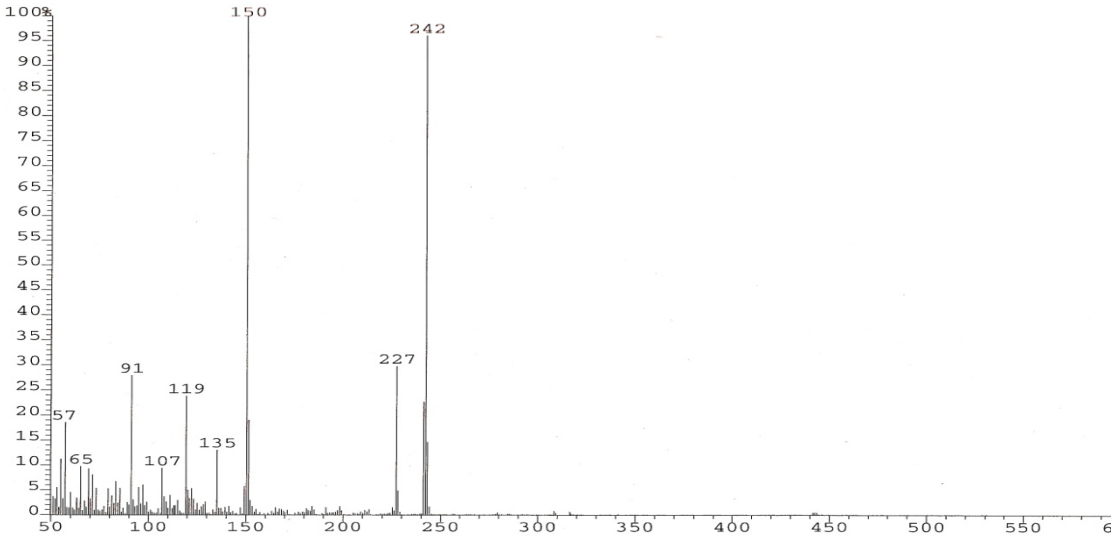


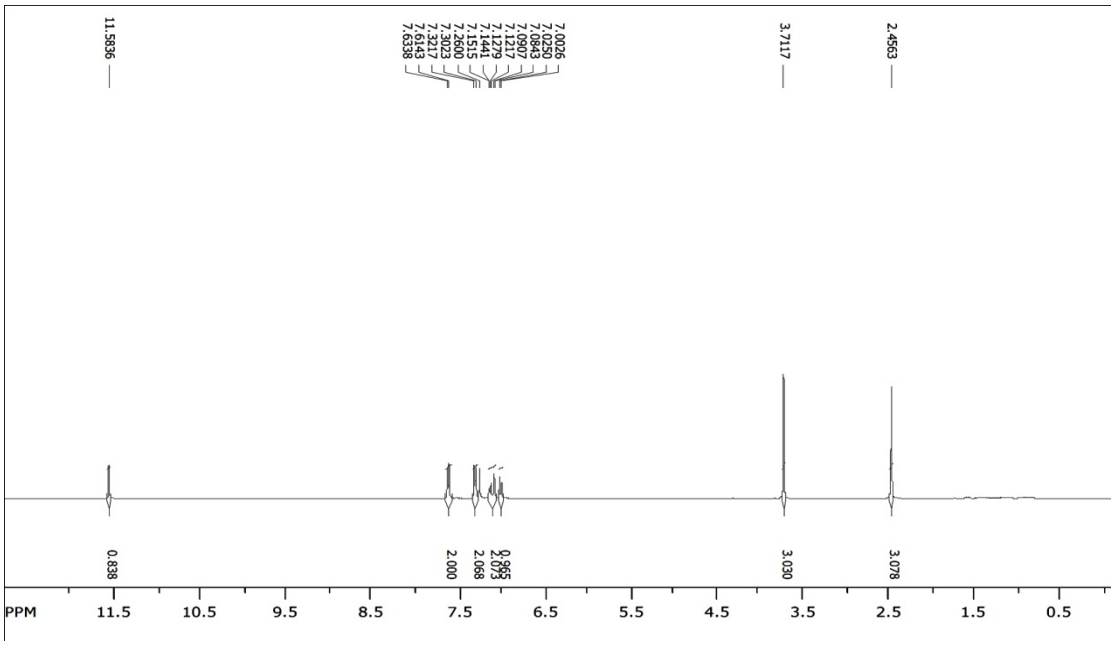


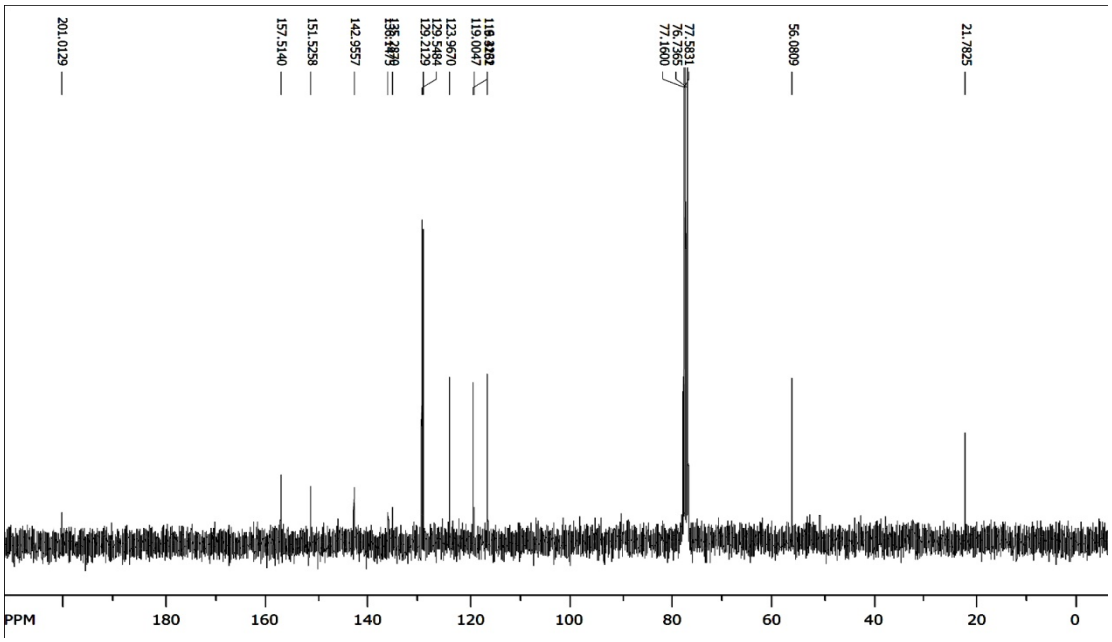


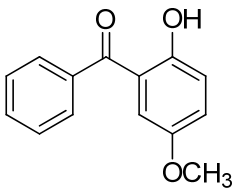
3ba

V(hexane):V(EtOAc)=10:1 as the mobile phase; white solid, mp. 92-95^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHZ): δ 11.58 (s, 1H, OH), 7.00-7.63 (m, 7H, Ph-H), 3.71 (s, 3H, OCH_3), 2.45 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ201.01, 157.51, 151.52, 142.95, 136.14, 135.29, 135.21, 129.54, 129.21, 119.00, 118.82, 116.32, 56.08, 21.78; MS-EI(m/z) = 242. [2]



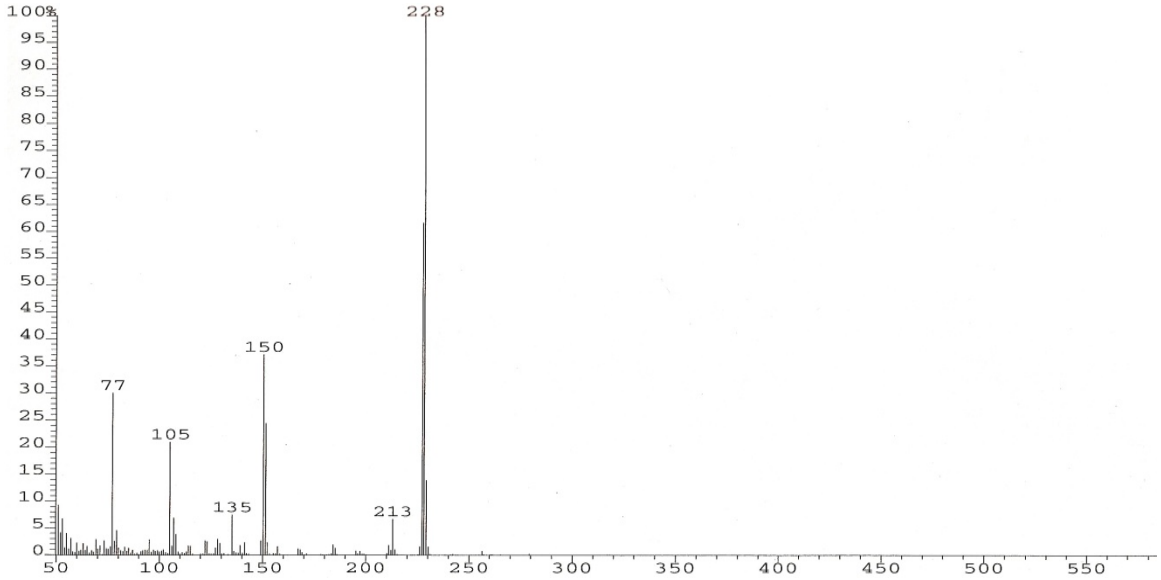






3ca

V(hexane):V(EtOAc)=8:1 as the mobile phase; white solid, mp. 82-84^{o}C [84-85.5 °C[3]]; ^{1}H NMR ($CDCl_3$, 400 MHZ): δ 11.60 (s, 1H, OH), 7.05-7.70 (m, 8H, Ph-H), 3.69 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ200.26, 156.59, 150.51, 136.96, 131.11, 128.20, 127.50, 123.15, 118.33, 117.79, 115.20, 55.00; MS-EI (m/z) = 228.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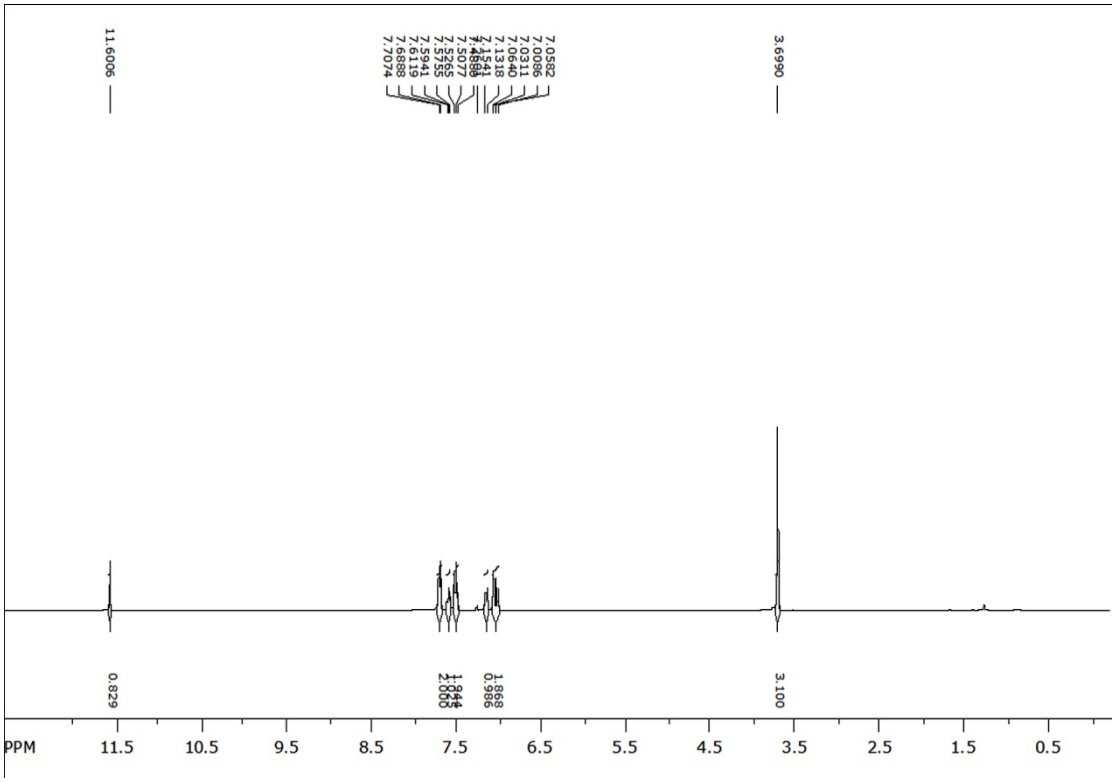
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7.0582
3.6990
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2.000
0.986
3.100
PPM
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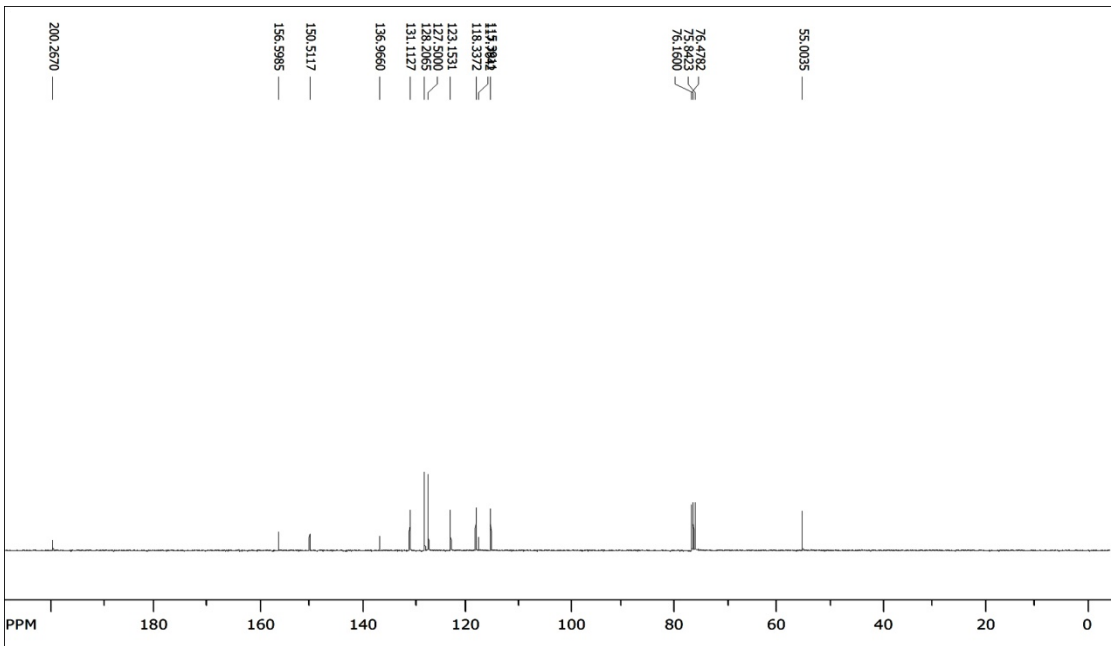
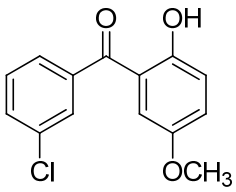
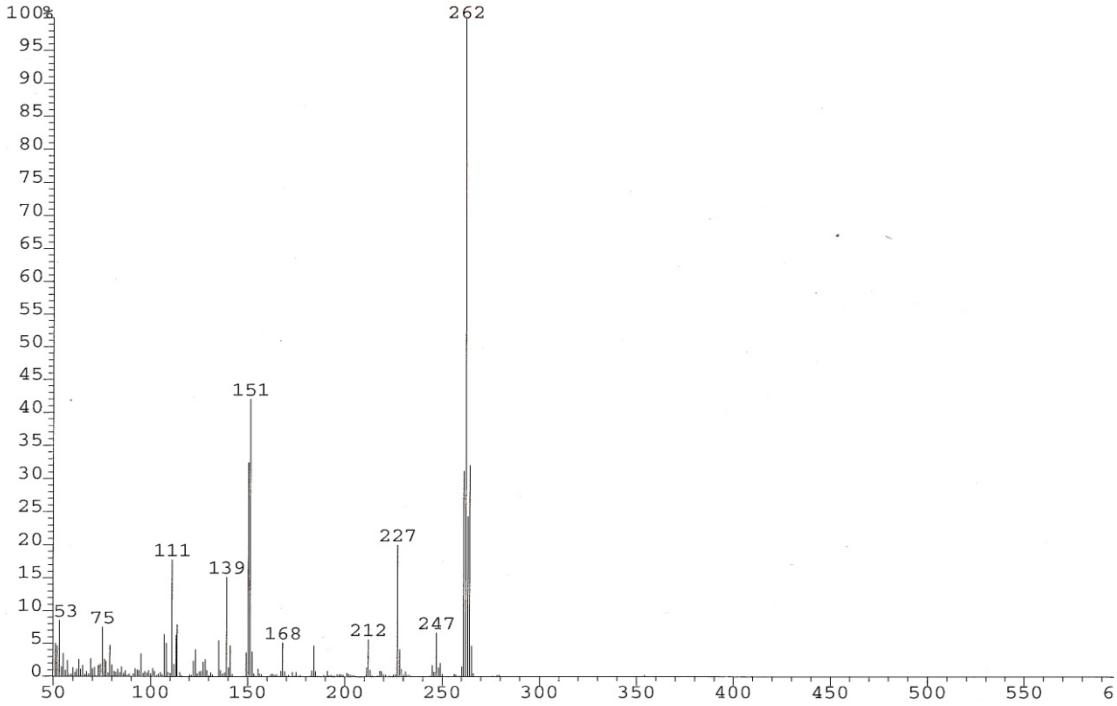
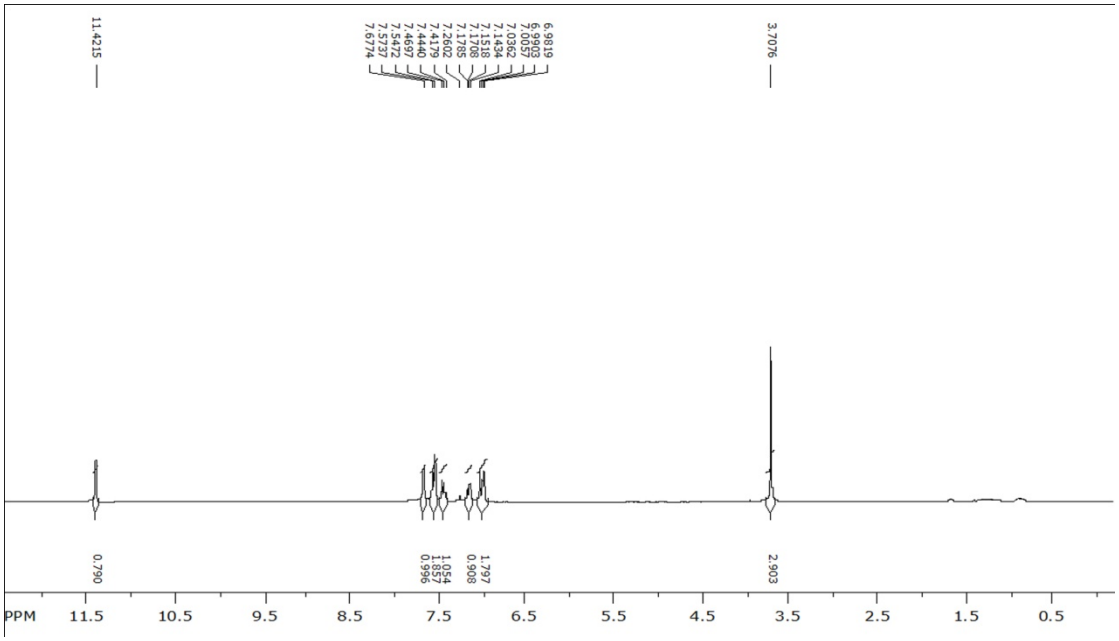


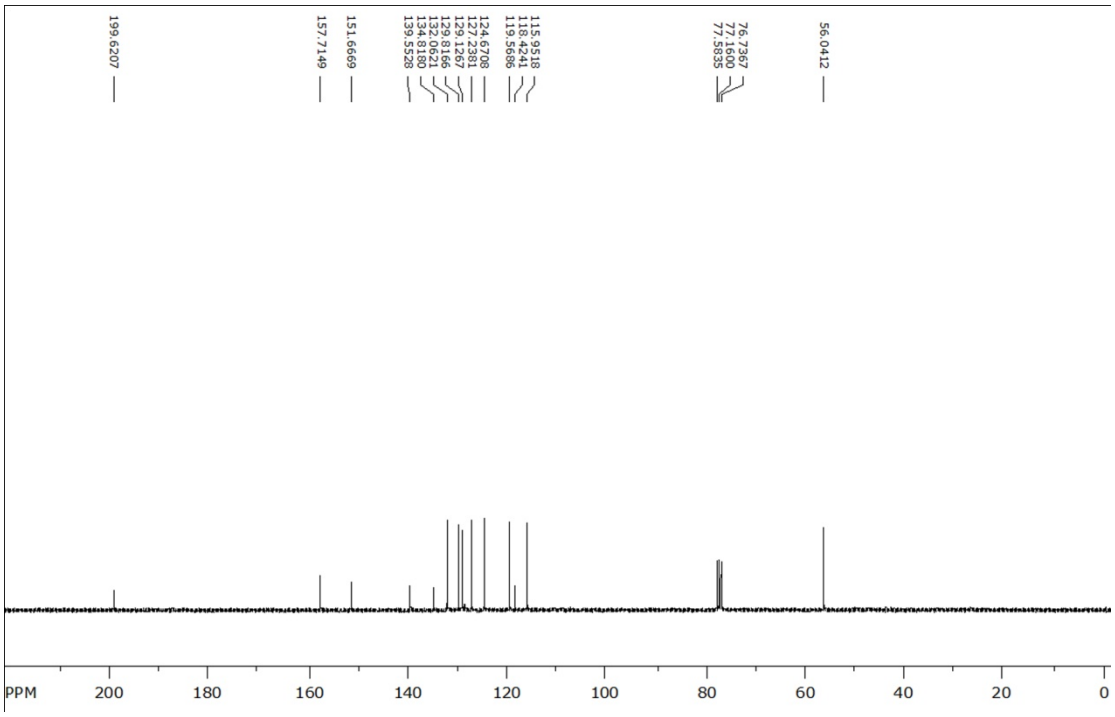


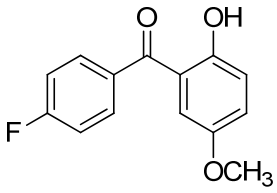
3da

V(hexane):V(EtOAc)=8:1 as the mobile phase; yellow solid, mp. 56-59^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHZ): δ 11.42 (s, 1H, OH), 6.98-7.67 (m, 7H, Ph-H), 3.70 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 199.62, 157.71, 151.66, 139.55, 134.81, 132.06, 129.81, 129.12, 127.23, 124.67, 119.56, 118.42, 115.95, 56.04; MS-EI (m/z) = 262; HRMS(EI): m/z calcd for C14H11ClO3: 262.0397; found: 262.0392.



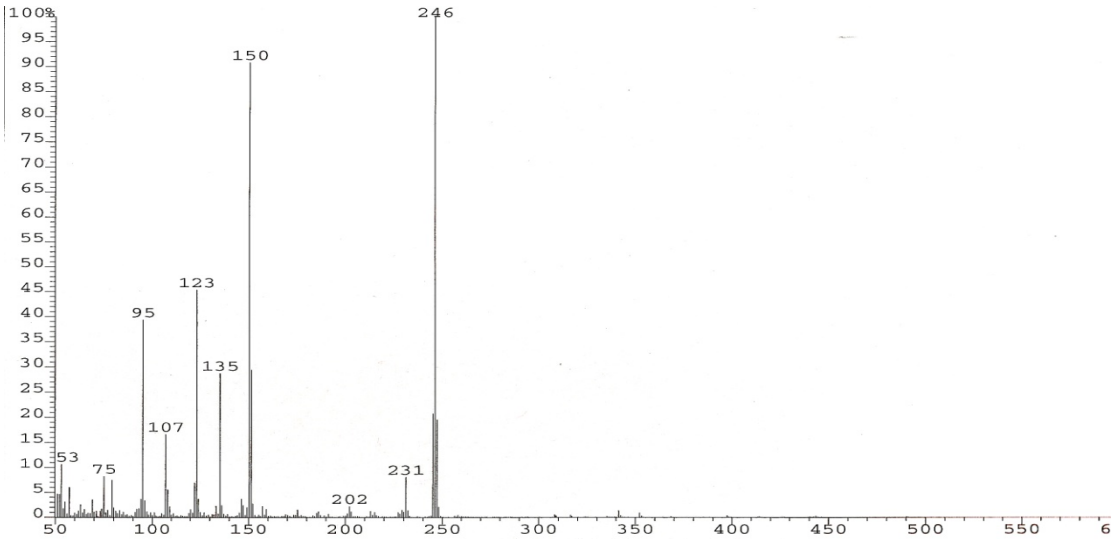






3ea

V(hexane):V(EtOAc)=8:1 as the mobile phase; white solid, mp. 76-78^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHZ): δ 11.42 (s, 1H, OH), 7.00-7.76 (m, 7H, Ph-H), 3.71 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 199.67, 166.82, 163.46, 157.51, 151.61, 131.92, 131.80, 124.16, 119.48, 118.71, 116.16, 115.90, 115.61, 56.05; MS-EI (m/z) = 246.[4]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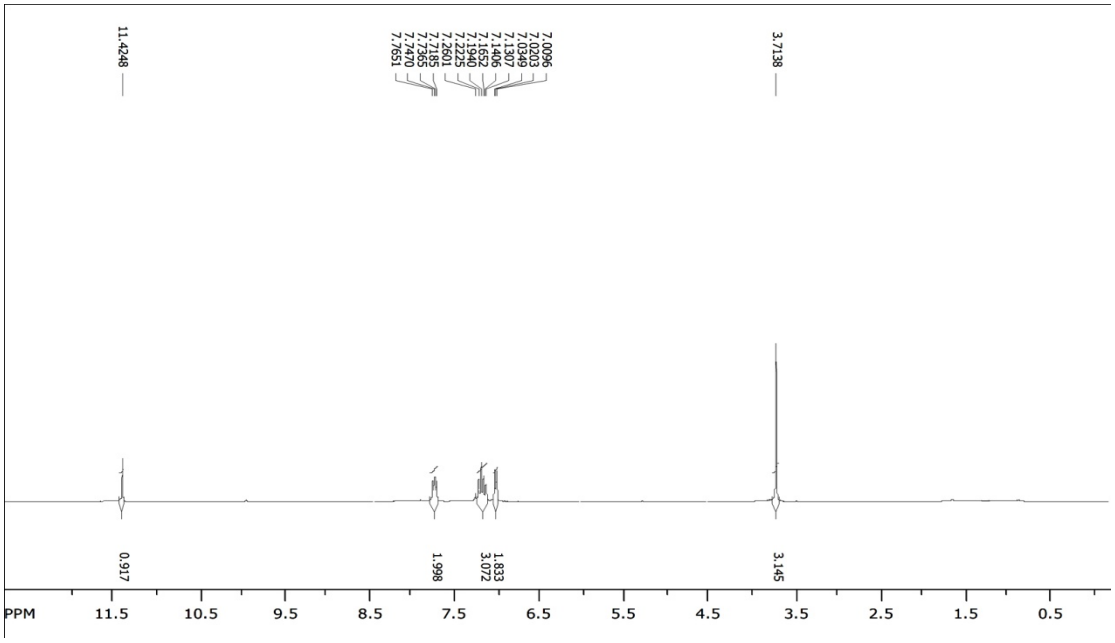
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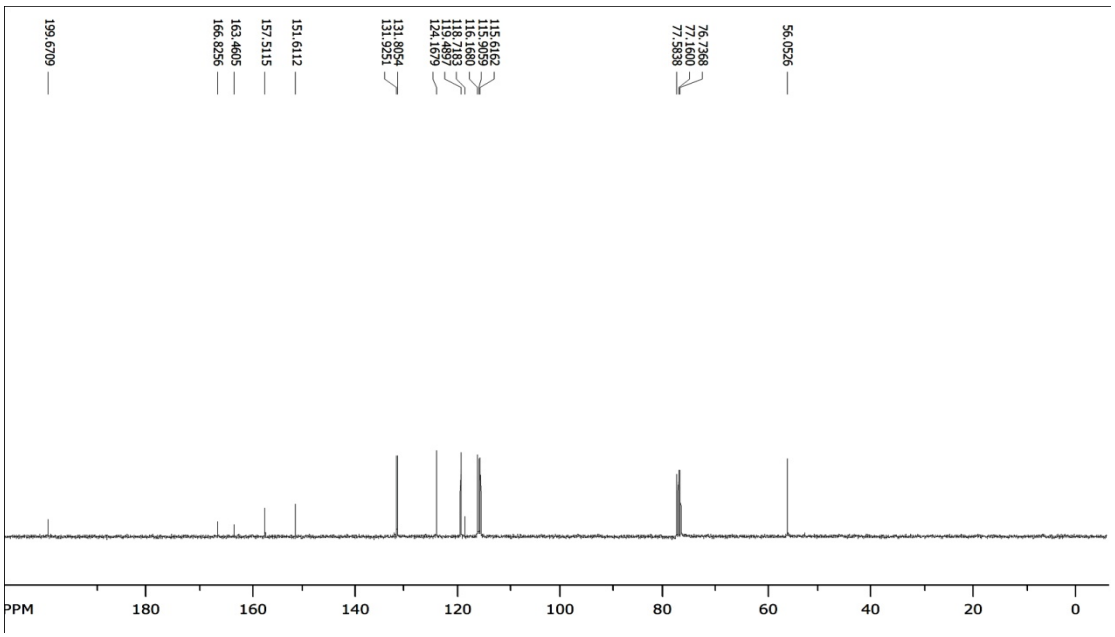
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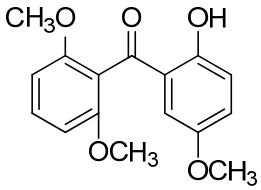
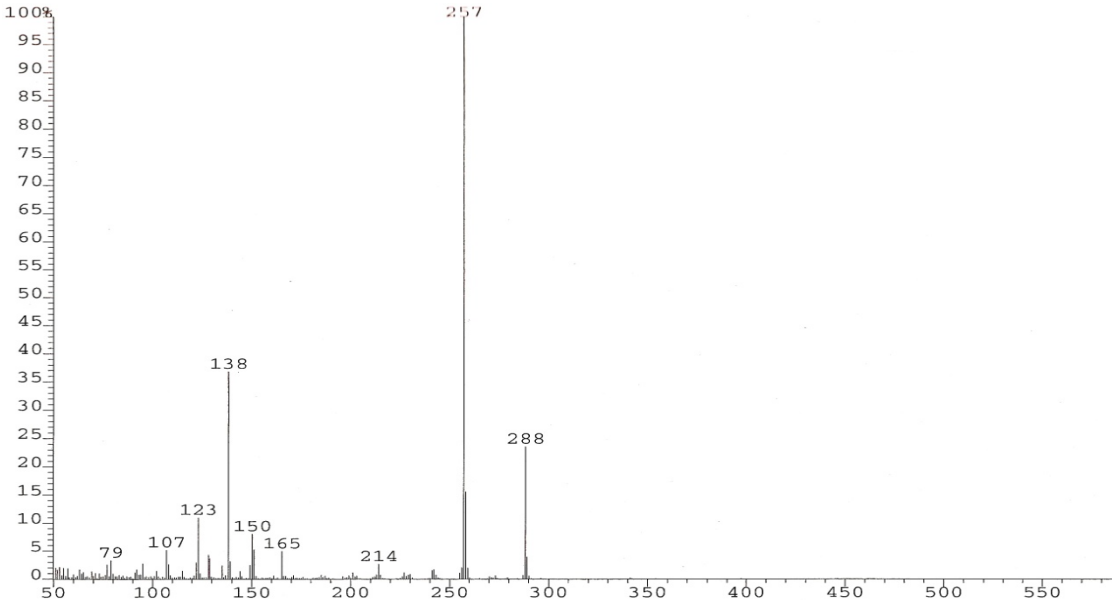
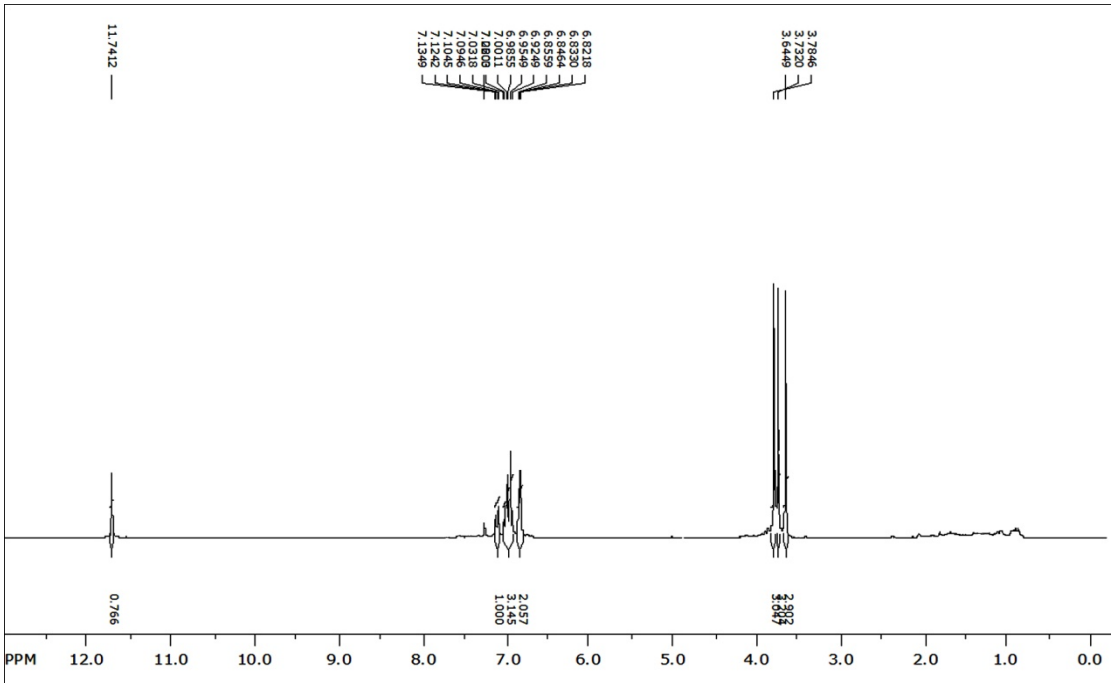
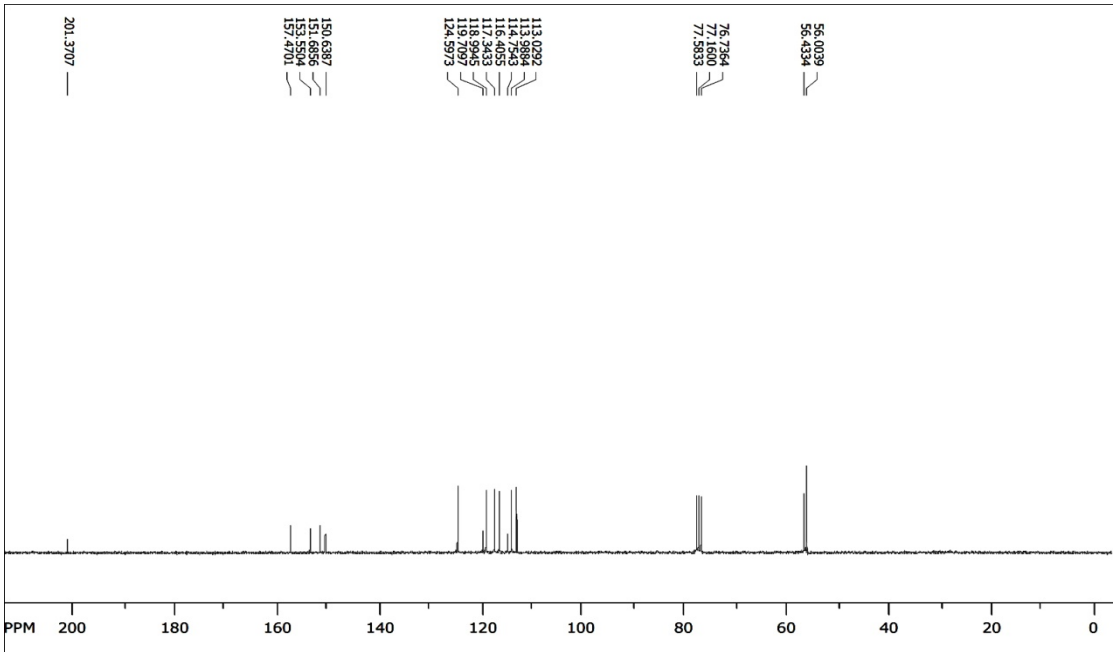


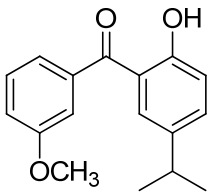
3fa

V(hexane):V(EtOAc)=10:1 as the mobile phase; white solid, mp. 67-70°C; ^{1}H NMR ($CDCl_3$, 300 MHZ): δ 11.74 (s, 1H, OH), 6.82-7.13 (m, 6H, Ph-H), 3.64, 3.73, 3.78 (3*s, 3*3H, OCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 201.37, 157.47, 153.55, 151.68, 150.63, 124.59, 119.70, 118.99, 117.34, 116.40, 114.75, 113.98, 113.02, 56.43, 56.00; MS-EI (m/z) = 288; HRMS(EI): m/z calcd for C16H16O5: 288.0998; found: 288.0994.



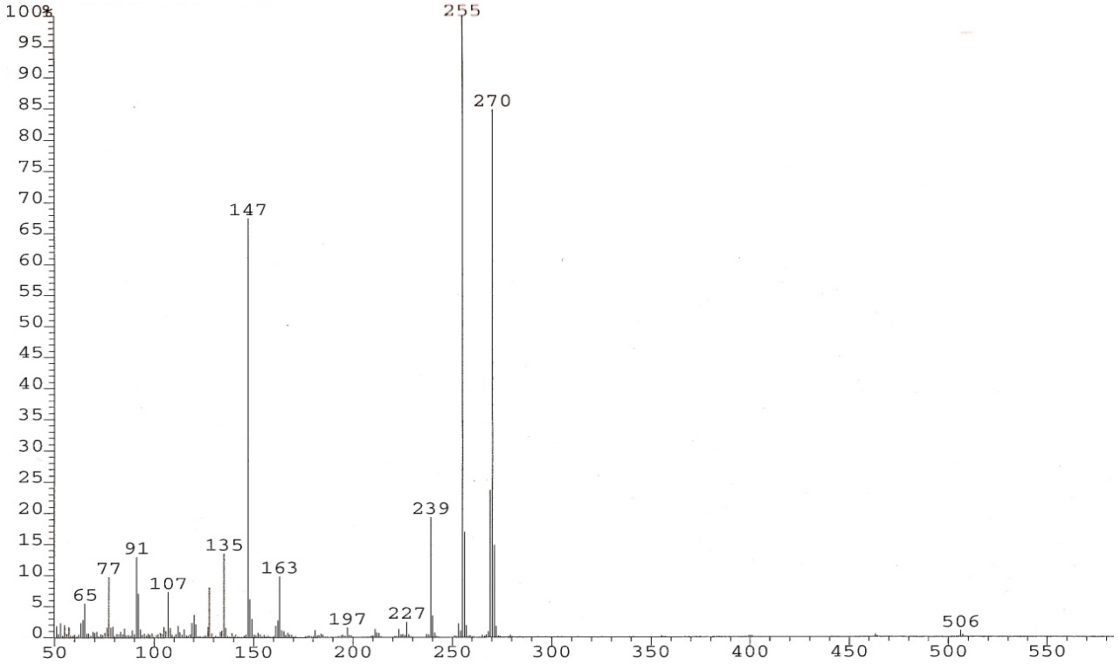


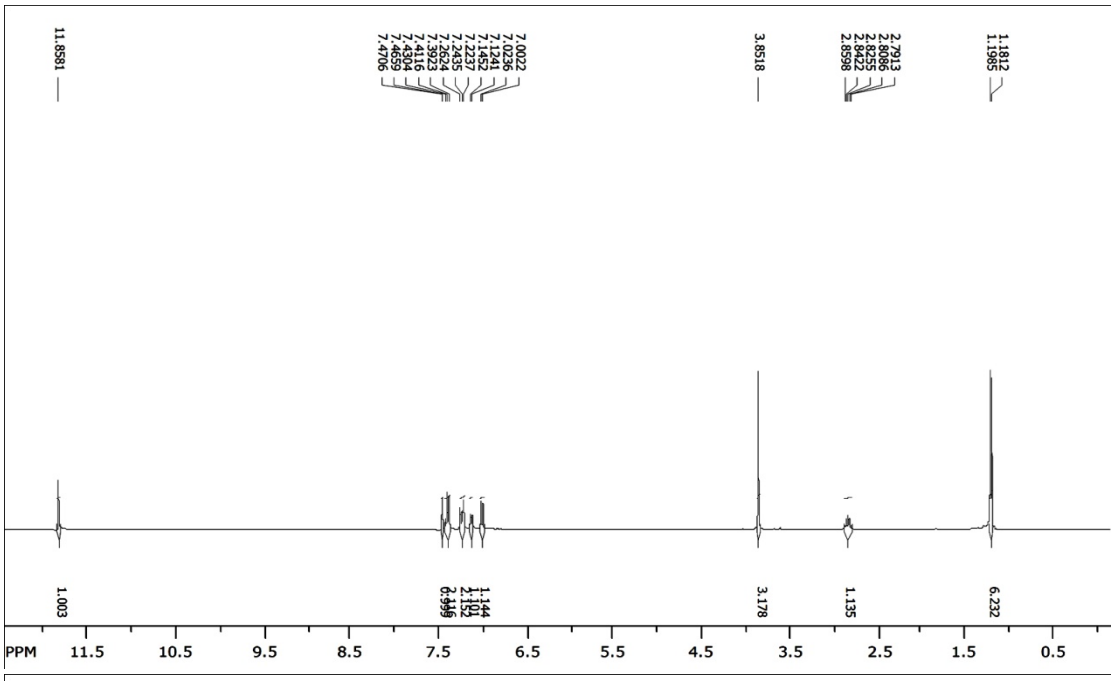


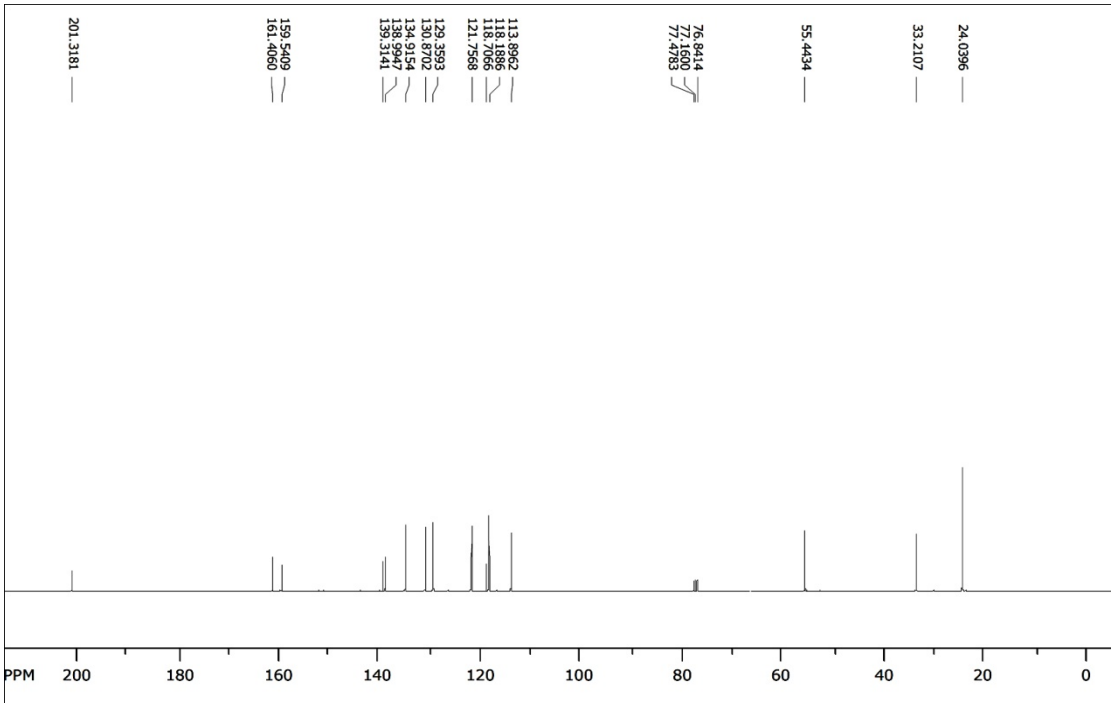


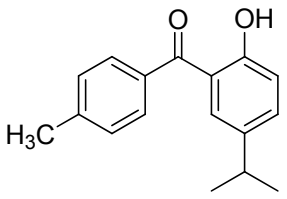
3ab

V(hexane):V(EtOAc)=8:1 as the mobile phase; yellow solid, mp. 71-72°C; ^{1}H NMR ($CDCl_3$, 400 MHZ): δ 11.85 (s, 1H, OH), 7.00-7.47 (m, 7H, Ph-H), 3.85 (s, 3H, OCH_3), 2.85 (m, 1H, C<u>H</u>$(CH_3)_2$), 1.18 (d, 2*3H, J= 6.92Hz, CH(C<u>H</u>$_3)_2$); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ 201.31, 161.40, 159.54, 139.31, 138.99, 134.91, 130.87, 129.35, 121.75, 118.70, 118.18, 113.89, 55.44, 33.21, 24.03; MS-EI (m/z) = 270; HRMS(EI): m/z calcd for C17H18O3: 270.1256; found: 270.1259.



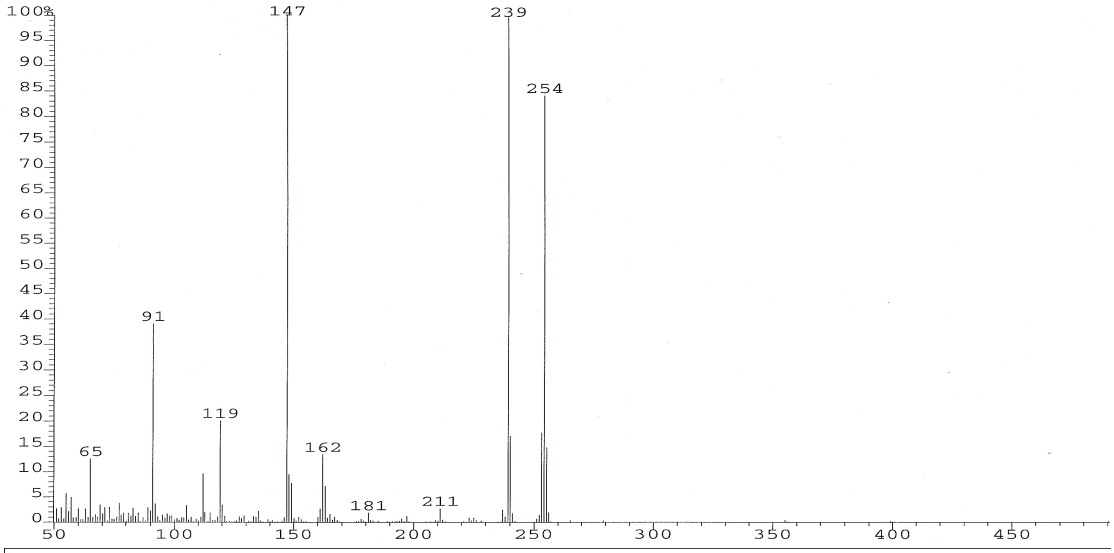






3bb

V(hexane):V(EtOAc)=8:1 as the mobile phase; white solid, mp. 64-66^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHZ): δ 11.88 (s, 1H, OH), 7.00-7.62 (m, 7H, Ph-H), 2.84 (m, 1H, C<u>H</u>$(CH_3)_2$), 2.46 (s, 3H, CH_3), 1.19 (d, 2*3H, J= 6.88 Hz, CH(C<u>H</u>$_3)_2$); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ 201.40, 161.25, 142.78, 138.96, 135.40, 134.65, 130.90, 129.60, 129.10, 118.98, 118.21, 33.30, 24.09, 21.72; MS-EI (m/z) = 254; HRMS(EI): m/z calcd for C17H18O2: 254.1307; found: 254.1308..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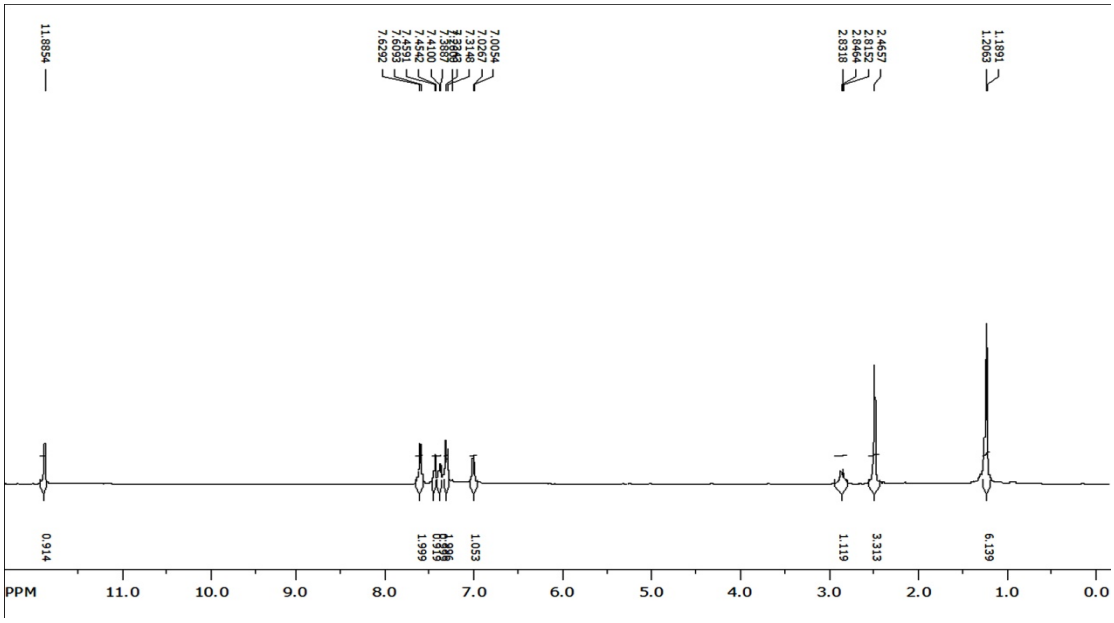
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PPM
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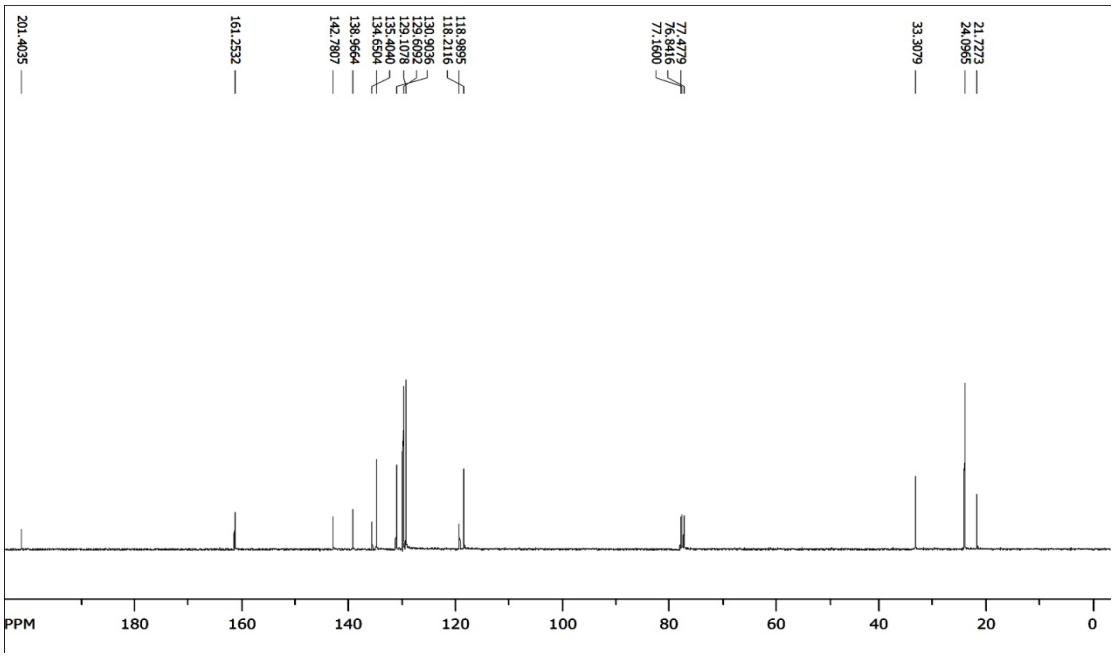
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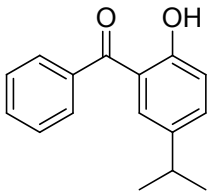
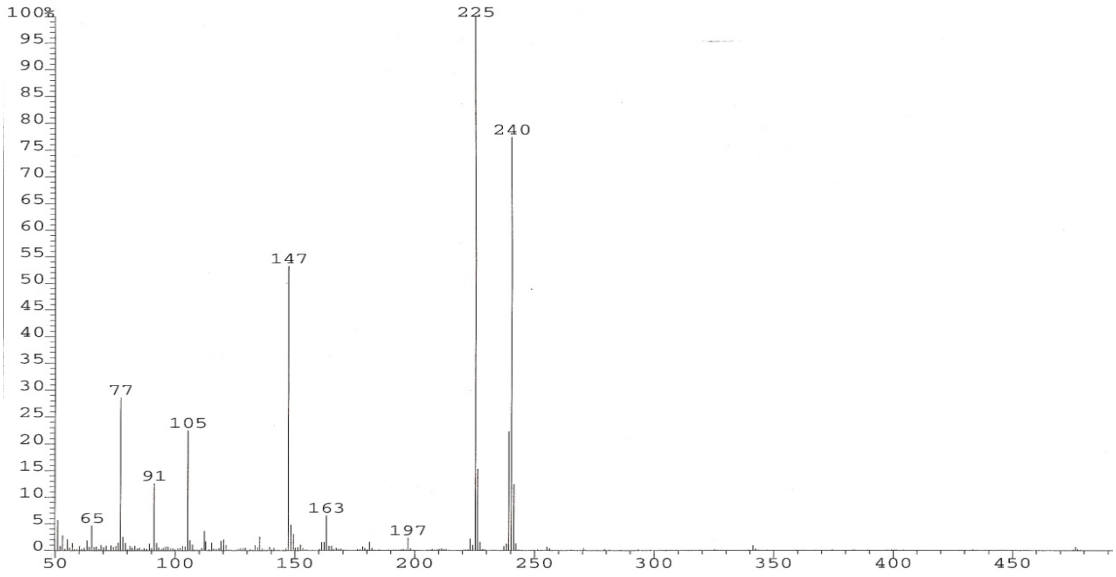
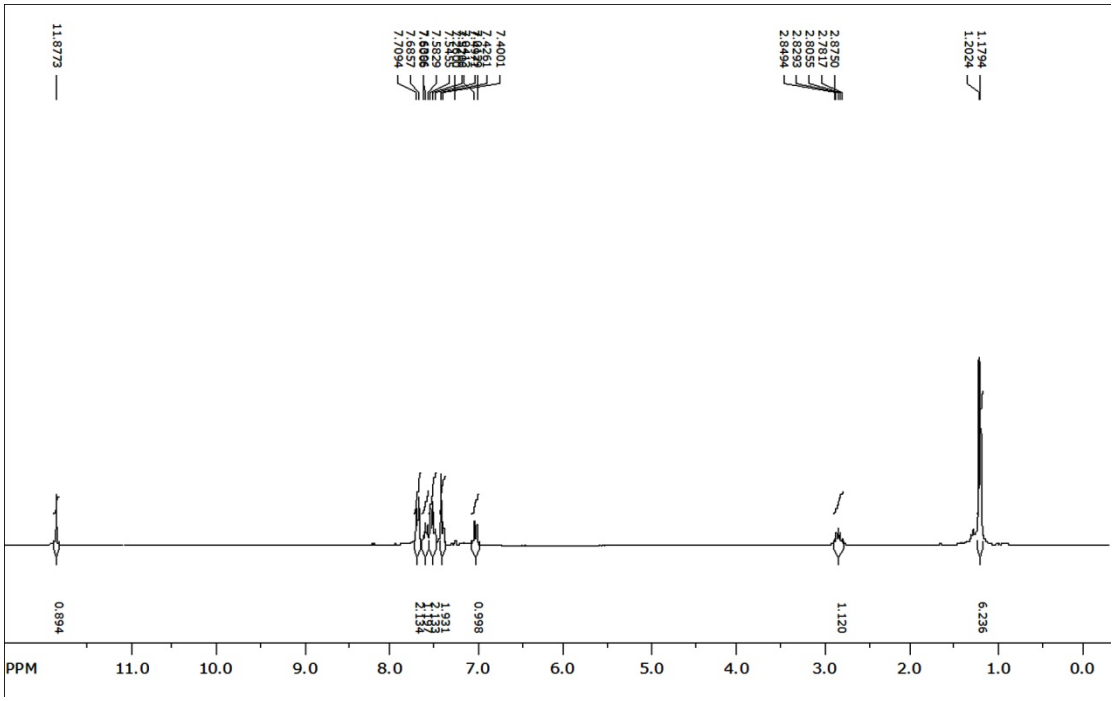
160
140
120
100
80
60
40
20
0

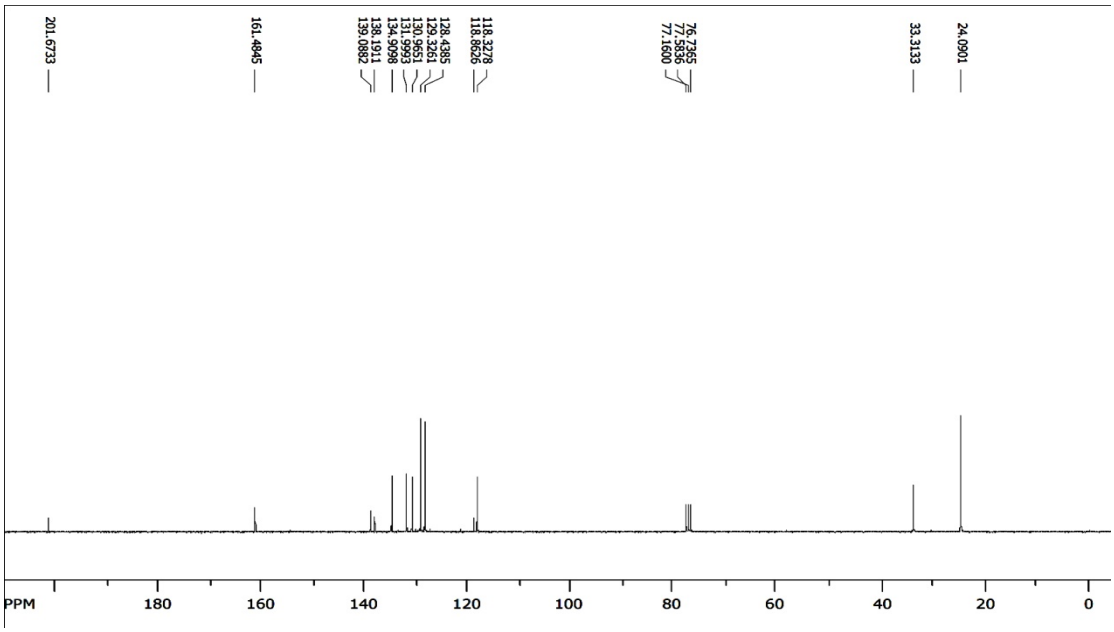


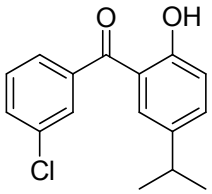
3cb

V(hexane):V(EtOAc)=8:1 as the mobile phase; yellow solid, mp. 70-73°C; ^{1}H NMR ($CDCl_3$, 300 MHZ): δ 11.87 (s, 1H, OH), 7.00-7.70 (m, 8H, Ph-H), 2.85 (m, 1H, C<u>H</u>$(CH_3)_2$),1.19 (d, 2*3H, J= 6.90 Hz, CH(C<u>H</u>$_3)_2$); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 201.67, 161.48, 139.08, 138.19, 134.90, 131.99, 130.96, 129.32, 128.43, 118.86, 118.32, 33.31, 24.09; MS-EI (m/z) = 240. [5]



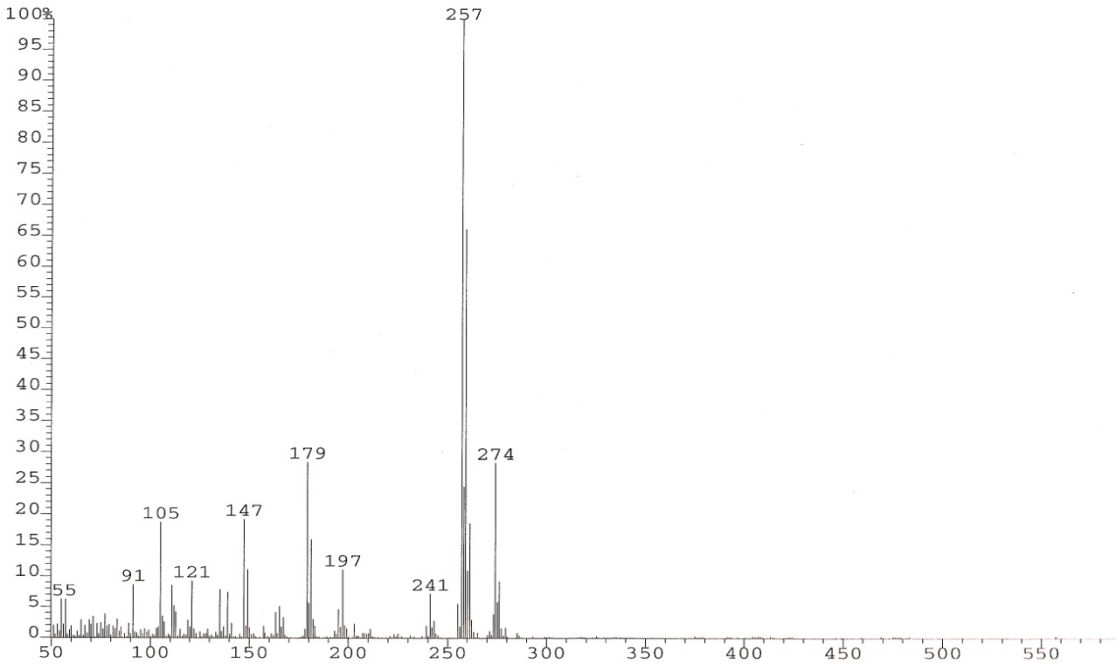


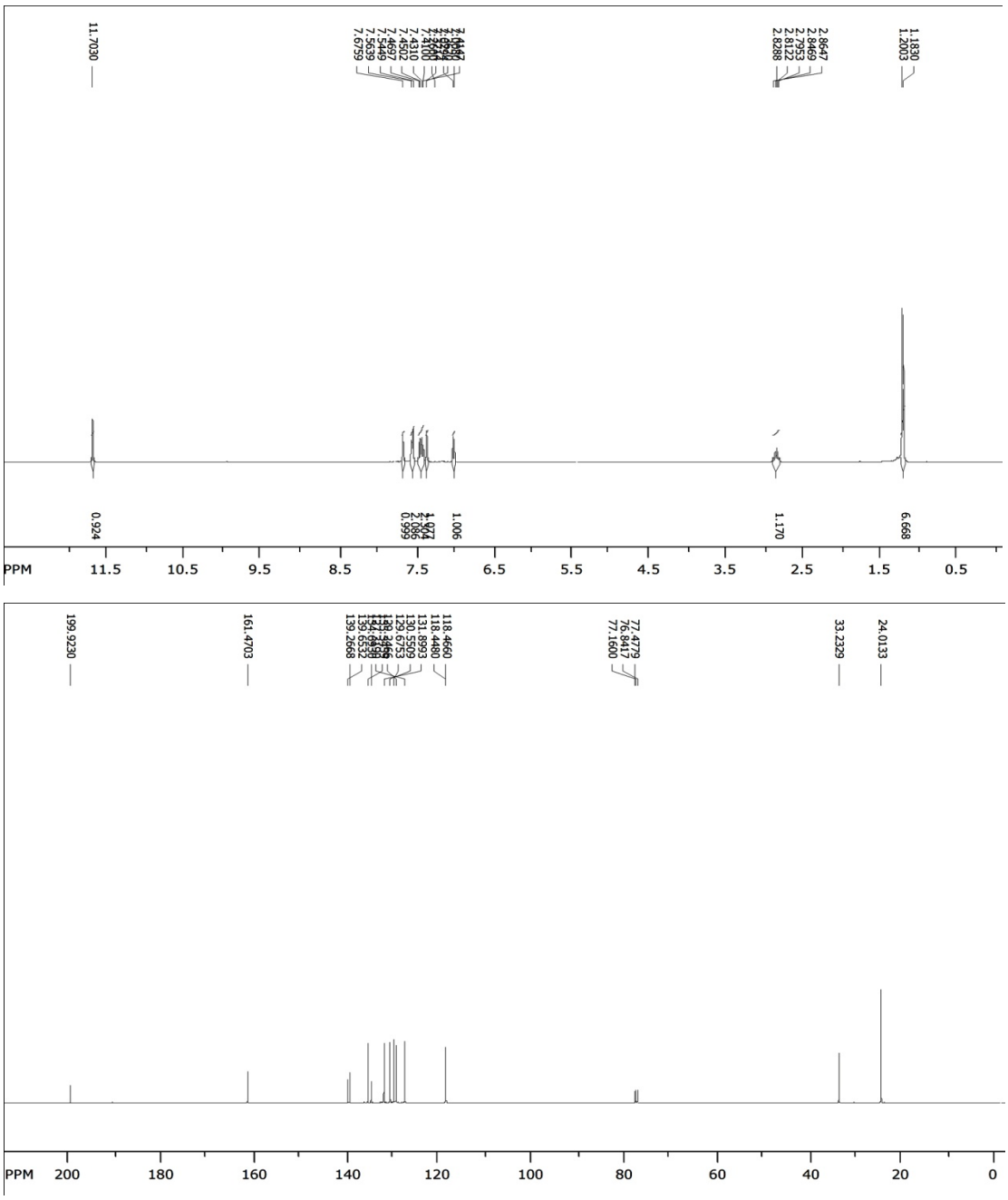


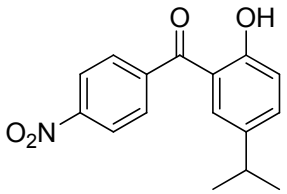


3db

V(hexane):V(EtOAc)=8:1 as the mobile phase; yellow solid, mp. 44-46^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.70 (s, 1H, OH), 7.02-7.67 (m, 7H, Ph-H), 2.83 (m, 1H, C<u>H</u>$(CH_3)_2$), 1.19 (d, 2*3H, J= 6.92 Hz, CH(C<u>H</u>$_3)_2$); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ 199.92, 161.47, 139.65, 139.26, 135.34, 134.69, 131.89, 130.55, 129.67, 129.24, 127.31, 118.46, 118.44, 33.23, 24.01; MS-EI (m/z) = 274; HRMS(EI): m/z calcd for C16H15ClO2: 274.0761; found: 274.0762.

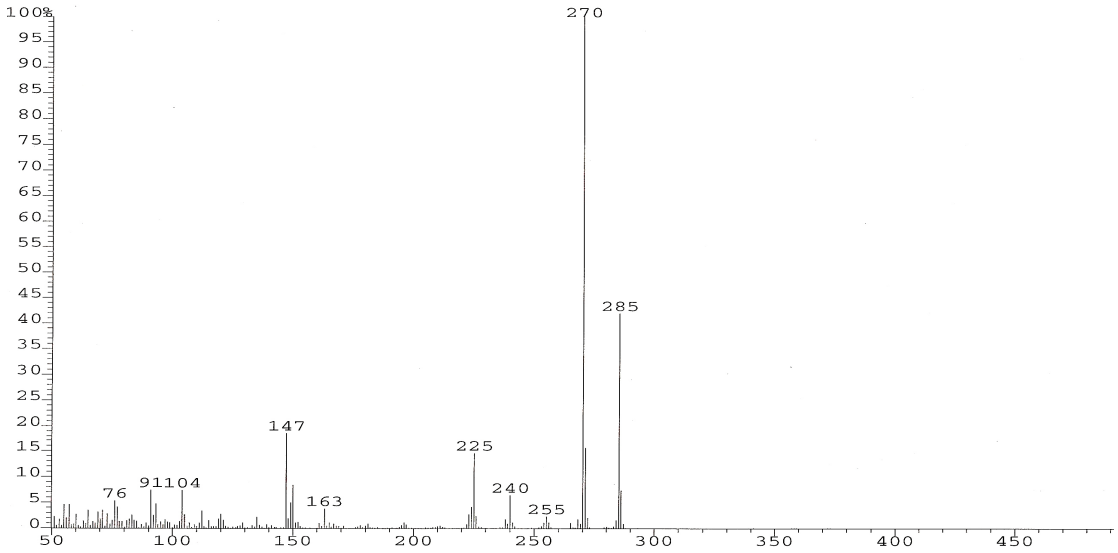


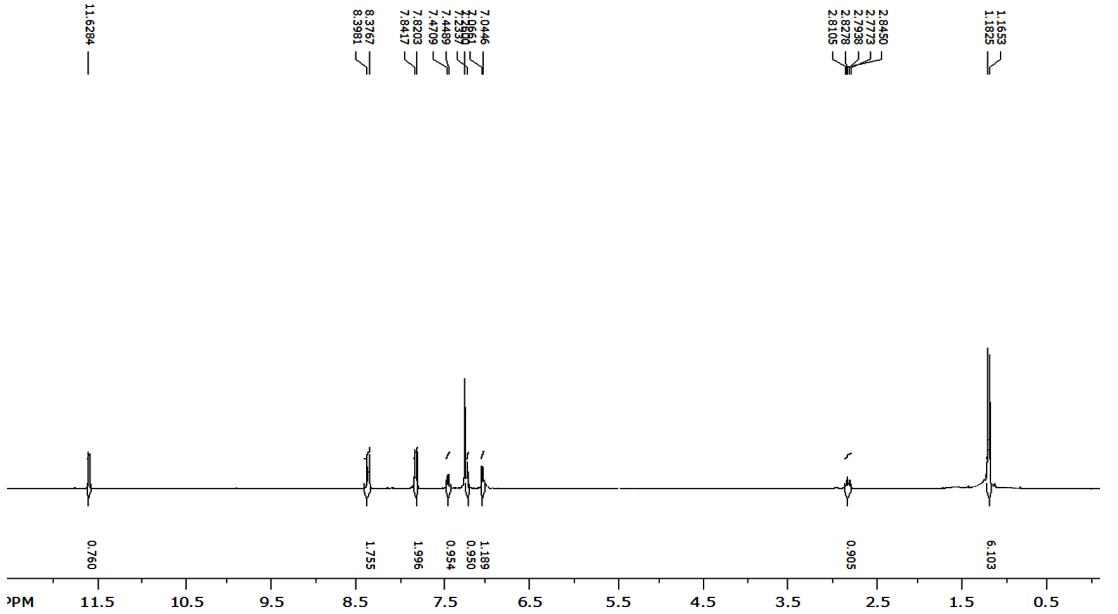


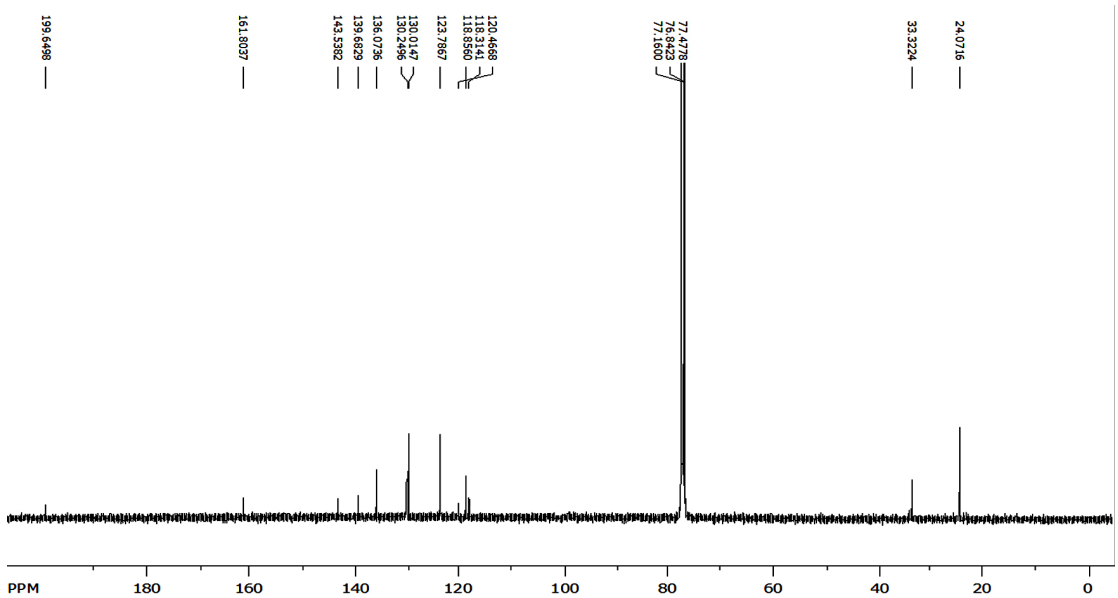


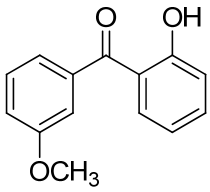
3gb

V(hexane):V(EtOAc)=7:1 as the mobile phase; yellow solid, mp. 53-55^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.62 (s, 1H, OH), 8.38 (d, 2H, J= 8.56Hz, Ph-H), 7.83 (d, 2H, J=8.56Hz, Ph-H), 7.04-7.47 (m, 3H, Ph-H), 2.83 (m, 1H, C<u>H</u>$(CH_3)_2$), 1.17 (d, 2*3H, J= 6.88Hz, CH(C<u>H</u>$_3)_2$); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ 199.64, 161.80, 143.53, 139.68, 136.07, 130.24, 130.01, 123.78, 120.46, 118.85, 118.31, 33.32, 24.07; MS-EI (m/z) = 285; HRMS(EI): m/z calcd for C16H15NO4: 285.1001; found: 285.1000.


270
285
147
225
240
255
163
91104
76

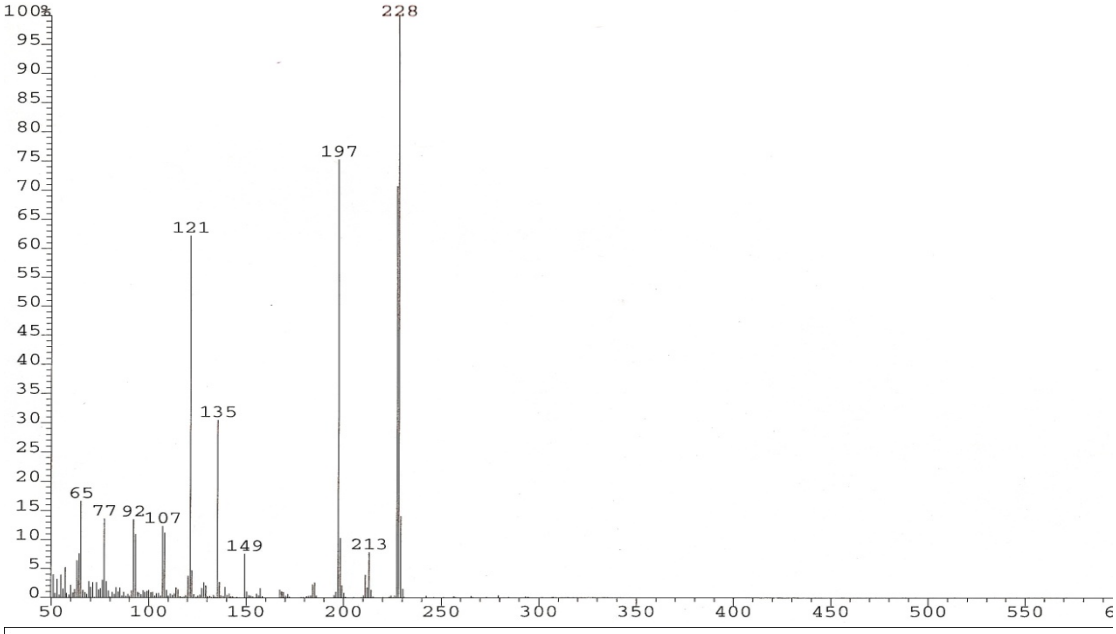

11.6284
8.3767
8.3981
7.8203
7.8417
7.4489
7.4709
7.0446
2.8450
2.8105
1.1653
1.1825
0.760
1.755
1.996
0.954
0.950
1.189
0.905
6.103
PPM

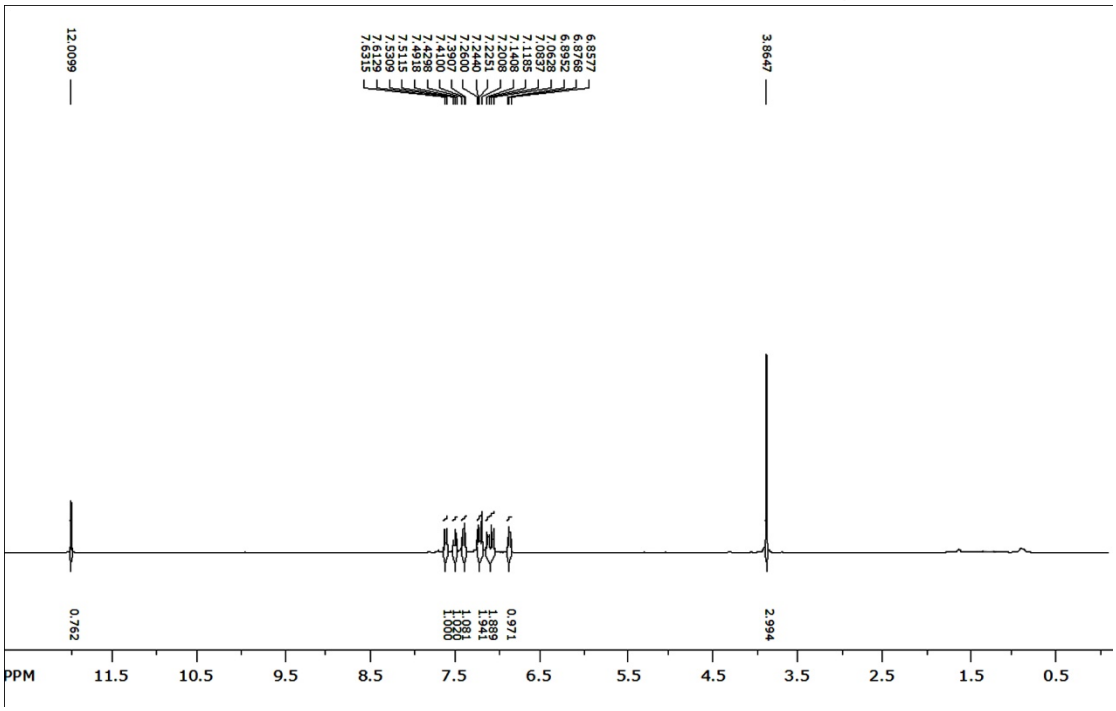

199.6498
161.8037
143.5382
139.6829
136.0736
130.0147
130.2496
123.7867
120.4668
118.8561
118.8560
77.4778
77.1600
76.8423
33.3224
24.0716
PPM

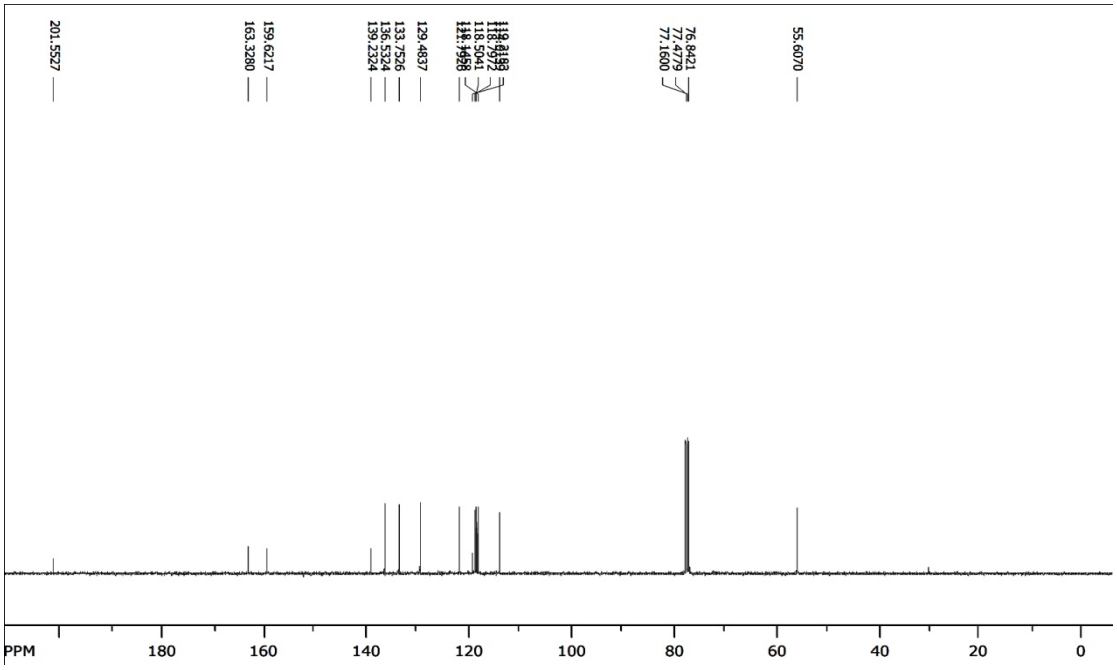


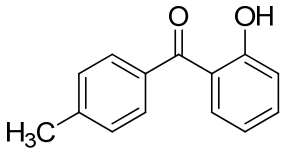
3ac

V(hexane):V(EtOAc)=8:1 as the mobile phase; white solid, mp. 60-62°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 12.00 (s, 1H, OH), 6.85-7.63 (m, 8H, Ph-H), 3.86 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ 201.55, 163.32, 159.62, 139.23, 136.53, 133.75, 129.48, 121.79, 119.21, 118.79, 118.50, 118.14, 114.00, 55.60; MS-EI (m/z) = 228. [6]



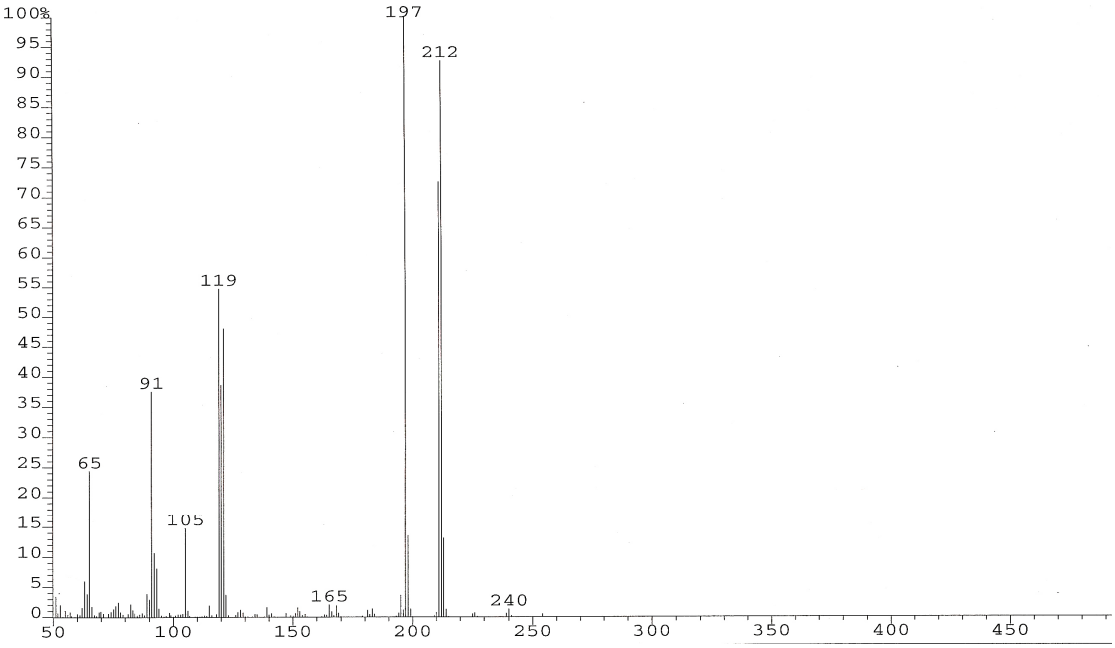


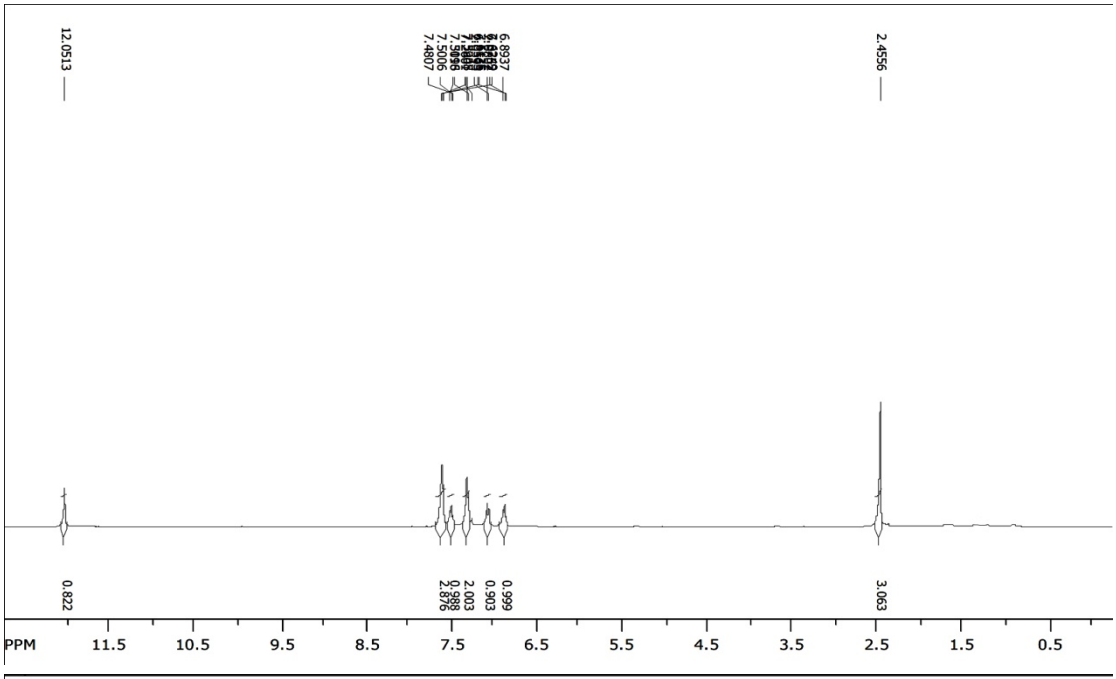


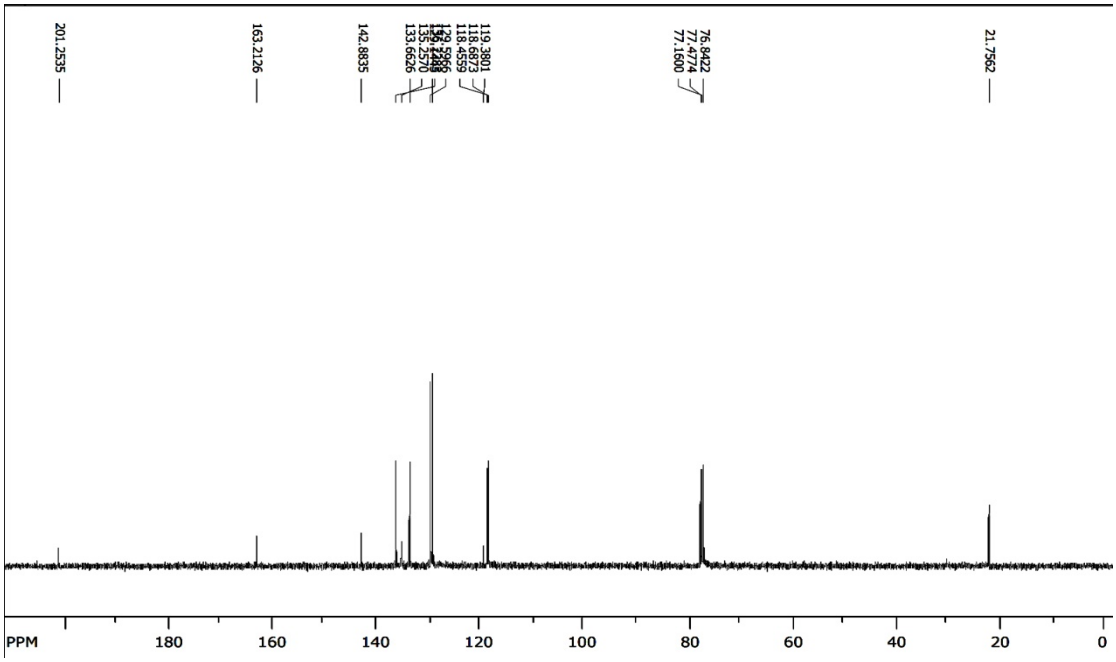


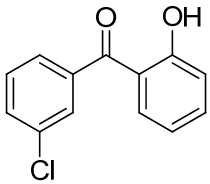
3bc

V(hexane):V(EtOAc)=8:1 as the mobile phase; white solid, mp. 60-62°C [61-62°C[7]]; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 12.05 (s, 1H, OH), 6.89-7.48 (m, 8H, Ph-H), 2.45 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 201.25, 163.21, 142.88, 136.24, 135.25, 133.66, 129.59, 128.00, 119.38, 118.68, 118.45, 21.75; MS-EI (m/z) = 212.



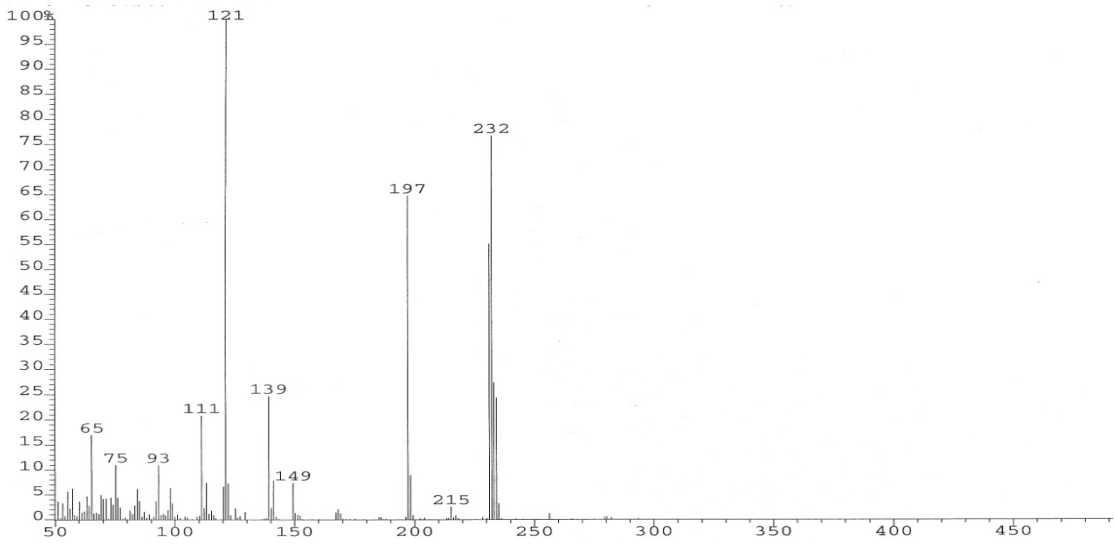


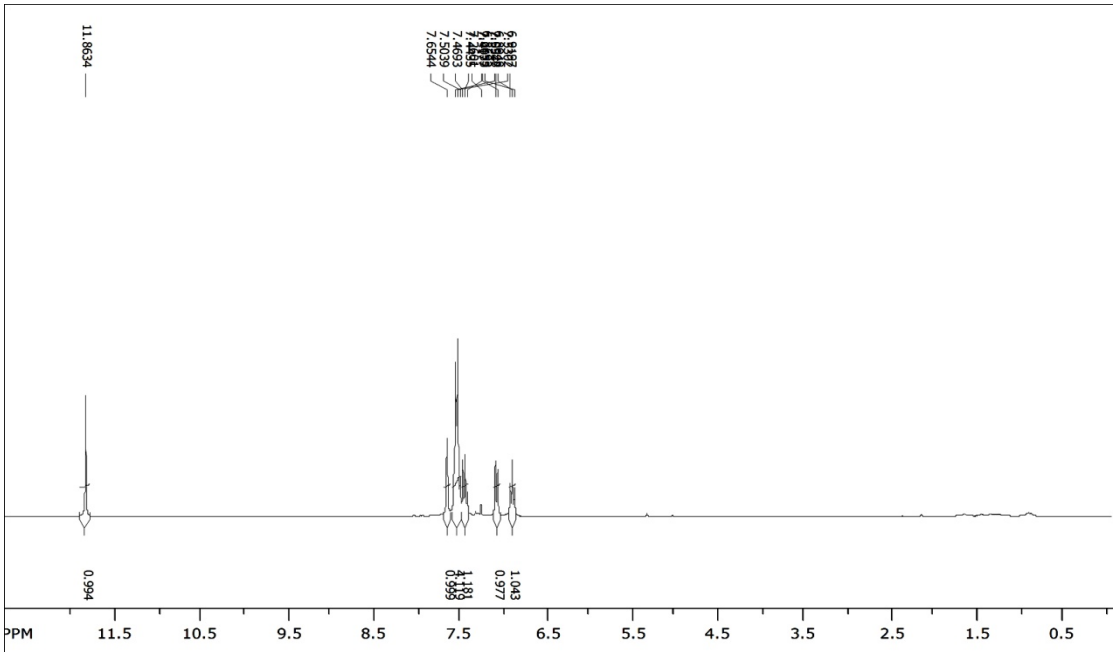


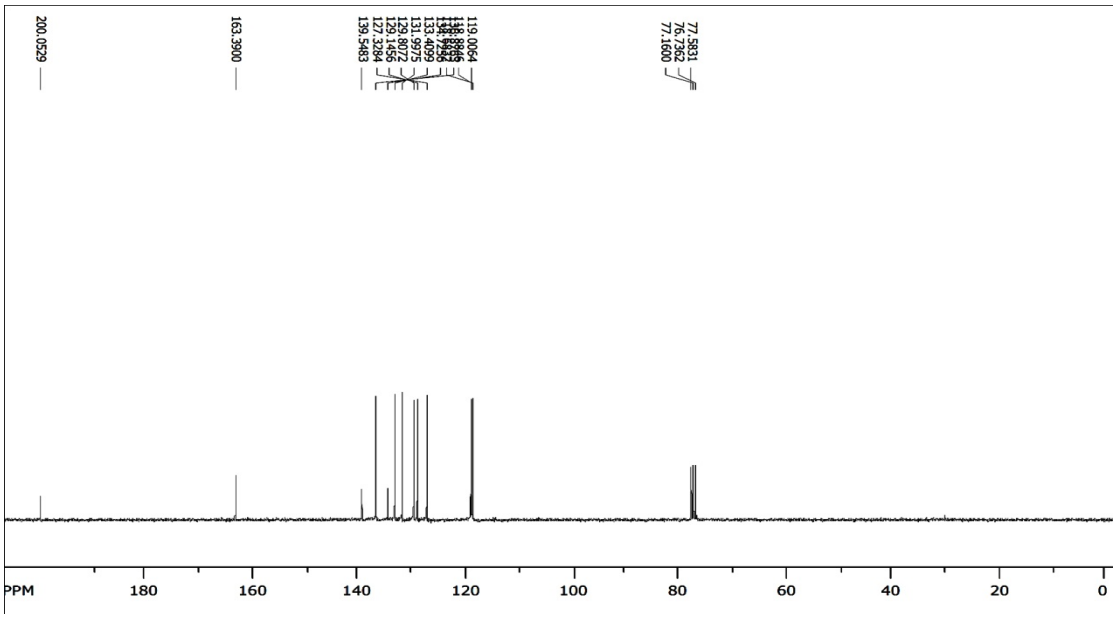


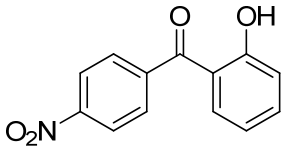
3dc

V(hexane):V(EtOAc)=7:1 as the mobile phase; white solid, mp. 74-75^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 11.86 (s, 1H, OH), 6.80-7.65 (m, 8H, Ph-H); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 200.05, 163.39, 139.54, 138.00, 134.79, 133.40, 131.99, 129.80, 129.14, 127.32, 120.02, 119.00, 118.80; MS-EI (m/z) = 232. [8]


121
232
197
139
111
65
75
93
149
215

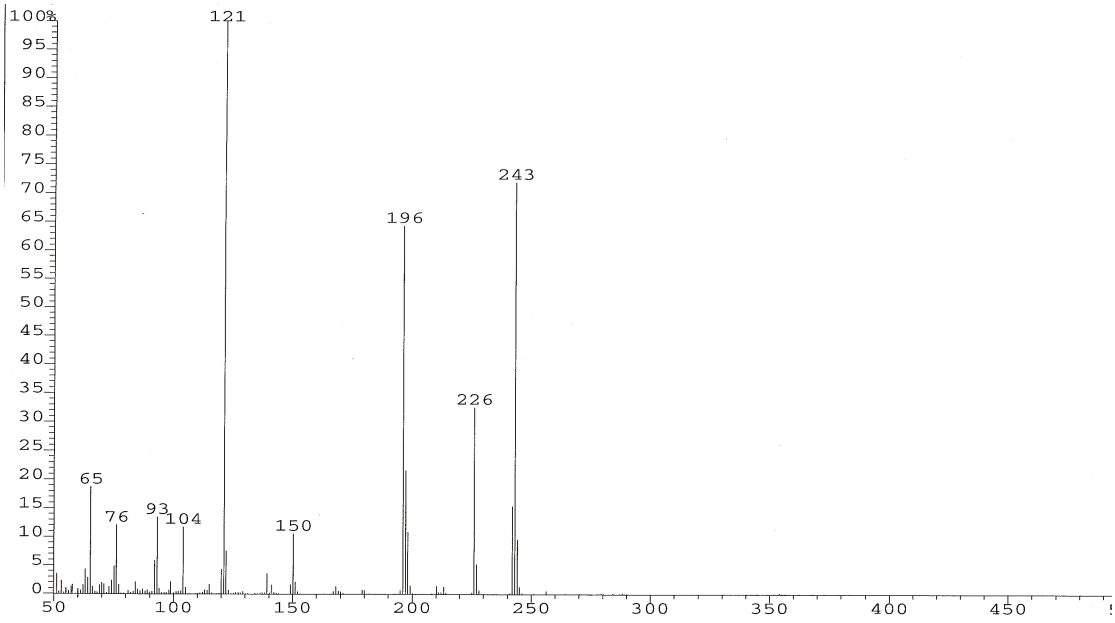

11.8634
7.6544
7.5039
7.4693
0.994
1.181
0.999
0.977
1.043
PPM

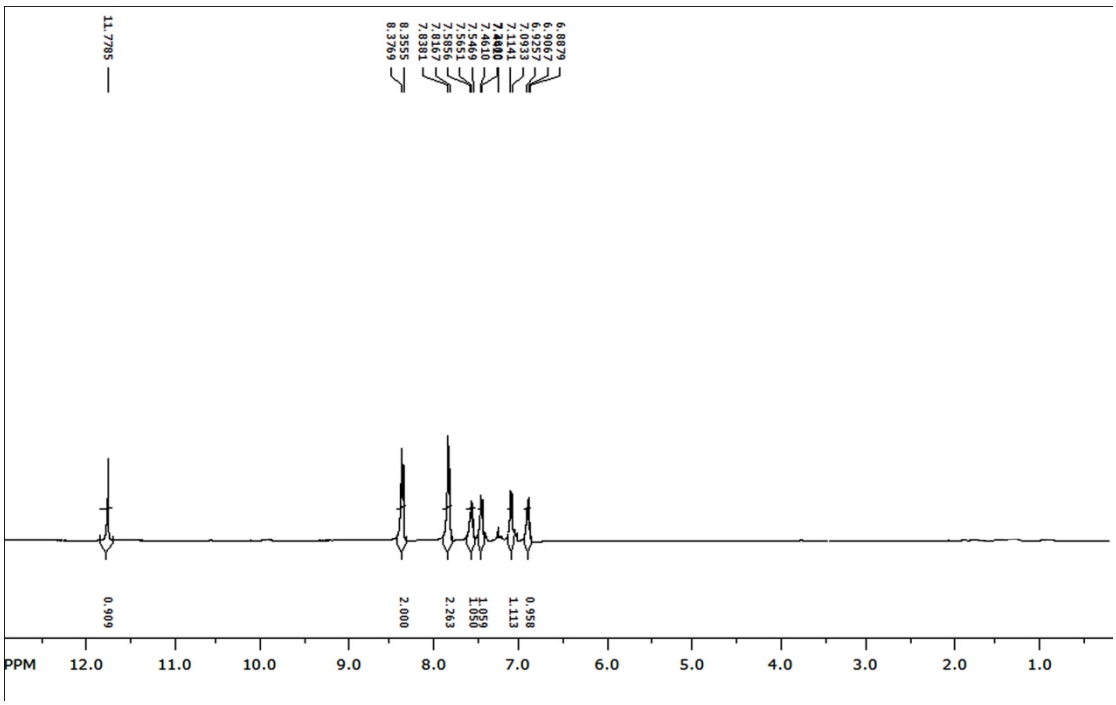

200.0529
163.3900
139.5483
127.3284
129.1456
129.8072
131.9975
133.4099
119.0064
77.5831
76.7362
77.1600
PPM

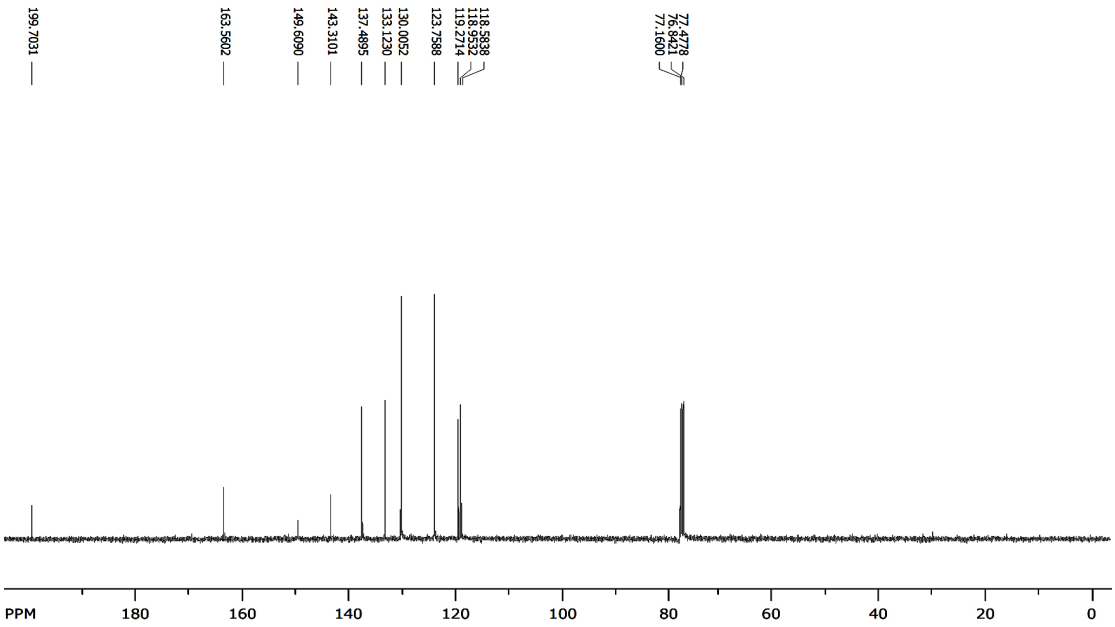


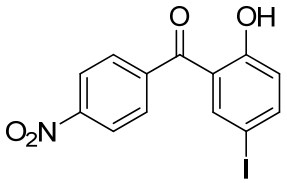
3gc

V(hexane):V(EtOAc)=7:1 as the mobile phase; white solid, mp. 90-93°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.77 (s, 1H, OH), 6.88-8.37 (m, 8H, Ph-H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ199.70, 163.56, 149.60, 143.31, 137.48, 133.12, 130.00, 123.75, 120.54, 119.27, 118.95, 118.58; MS-EI (m/z) = 243. [9]



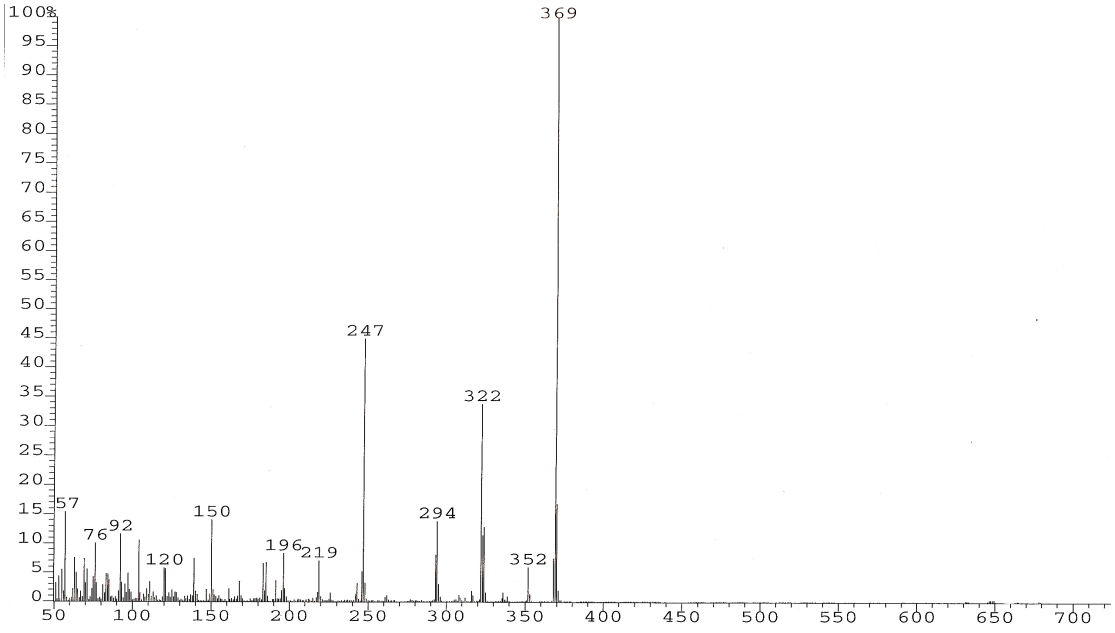


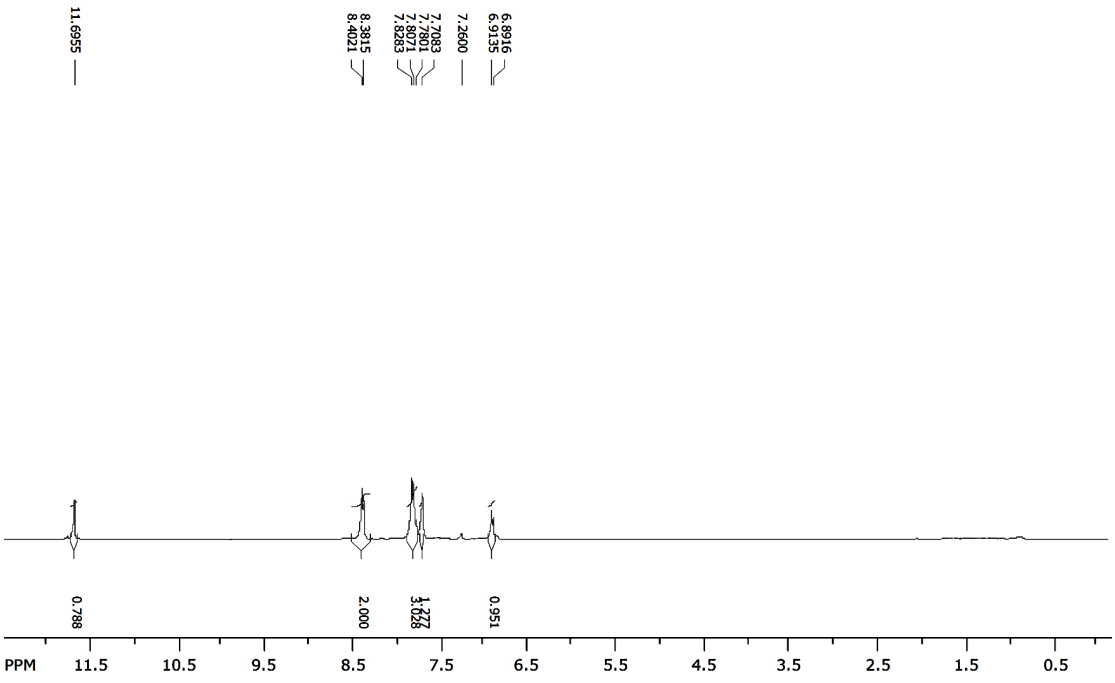


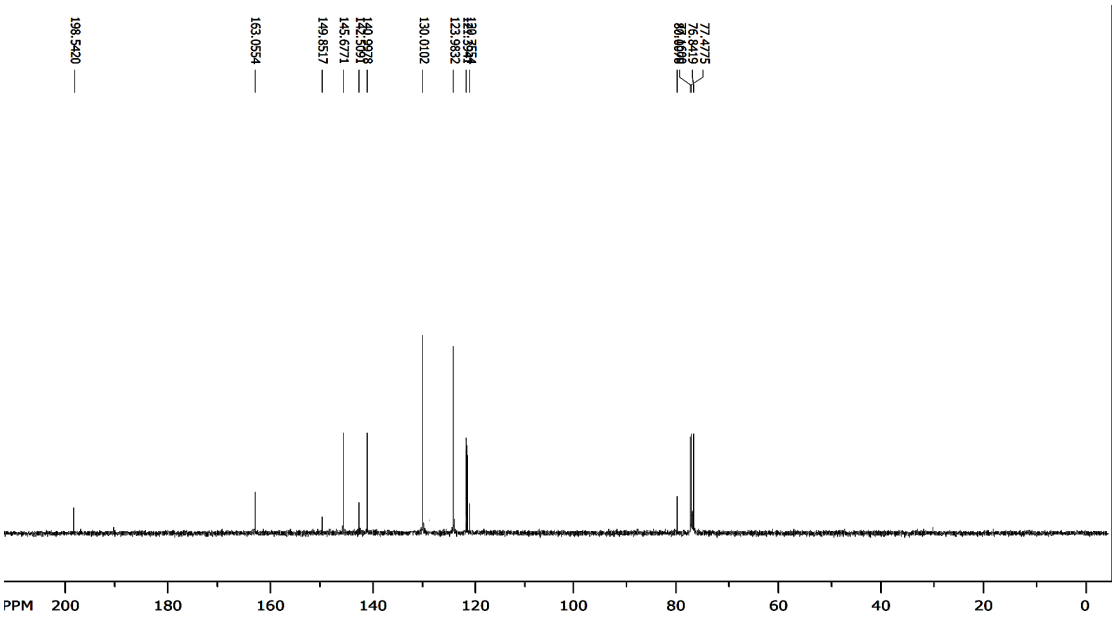


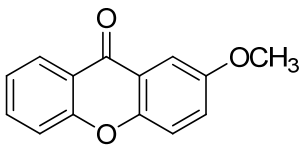
3gd

V(hexane):V(EtOAc)=7:1 as the mobile phase; white solid, mp. 82-84^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.69 (s, 1H, OH), 8.39 (d, 2H, J=8.24 Hz, Ph-H), 7.80 (m, 3H, ph-H), 7.70 (m, 1H, ph-H), 6.90 (m, 1H, Ph-H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ 198.54, 163.05, 149.85, 145.67, 142.50, 140.99, 130.01, 123.98, 121.39, 120.75, 80.06; MS-EI (m/z) = 369; HRMS(EI): m/z calcd for C13H8INO4: 368.9498; found: 368.9498.



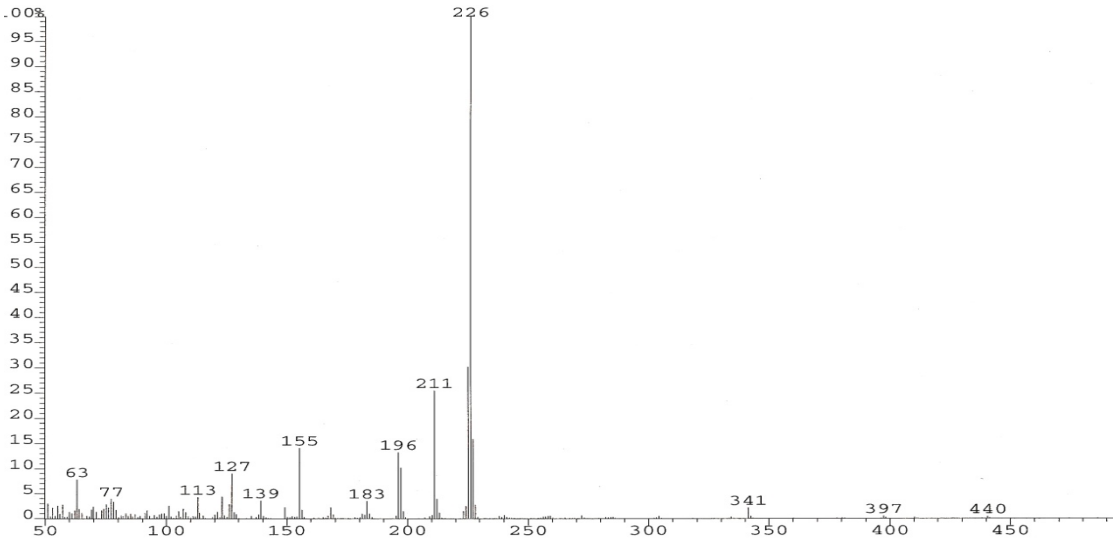


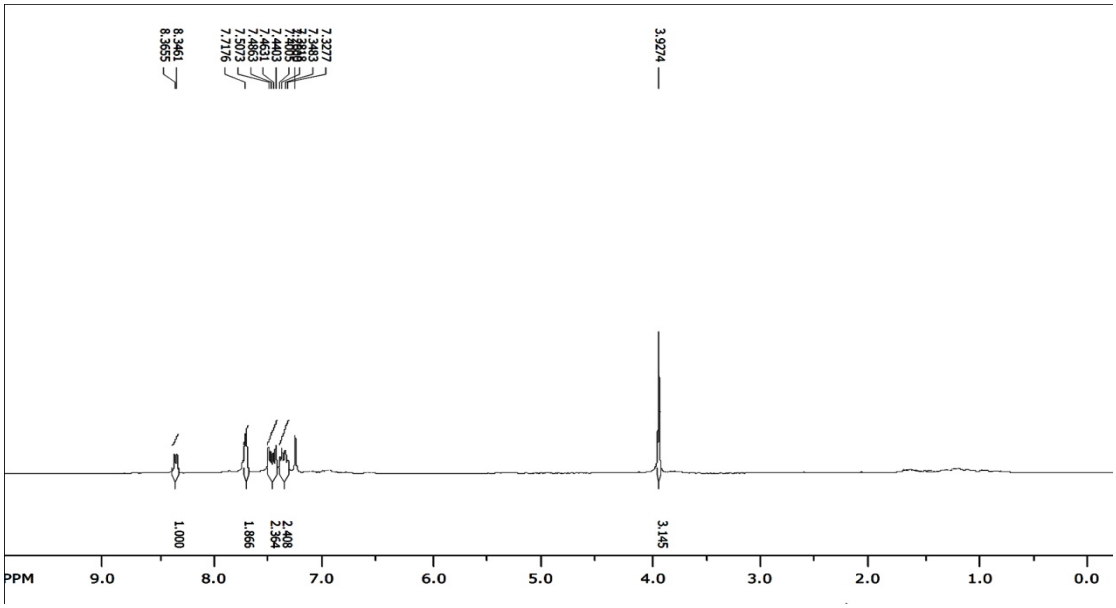




4a

V(hexane):V(EtOAc)=12:1 as the mobile phase; white solid, mp. 132-134^{o}C [130-131^{o}C[10]]; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.35 (d, 1H, J=7.76 Hz, ph-H), 7.71 (m, 2H, ph-H), 7.50-7.32 (m, 4H, ph-H), 3.92 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ 177.27, 156.25, 156.11, 151.14, 134.74, 126.82, 125.09, 123.87, 122.24, 121.37, 119.57, 118.12, 105.91, 56.08; MS-EI (m/z) = 226.


226
211
155
196
127
63
77
113
139
183
341
397
440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7.7176
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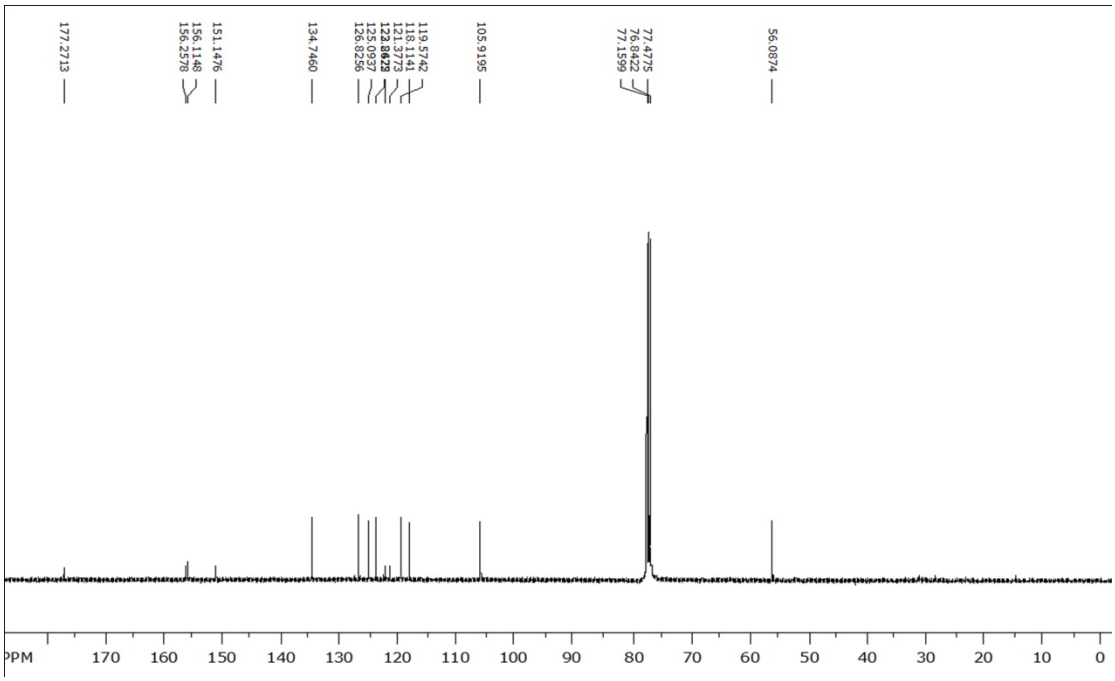
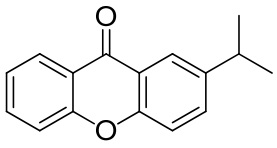
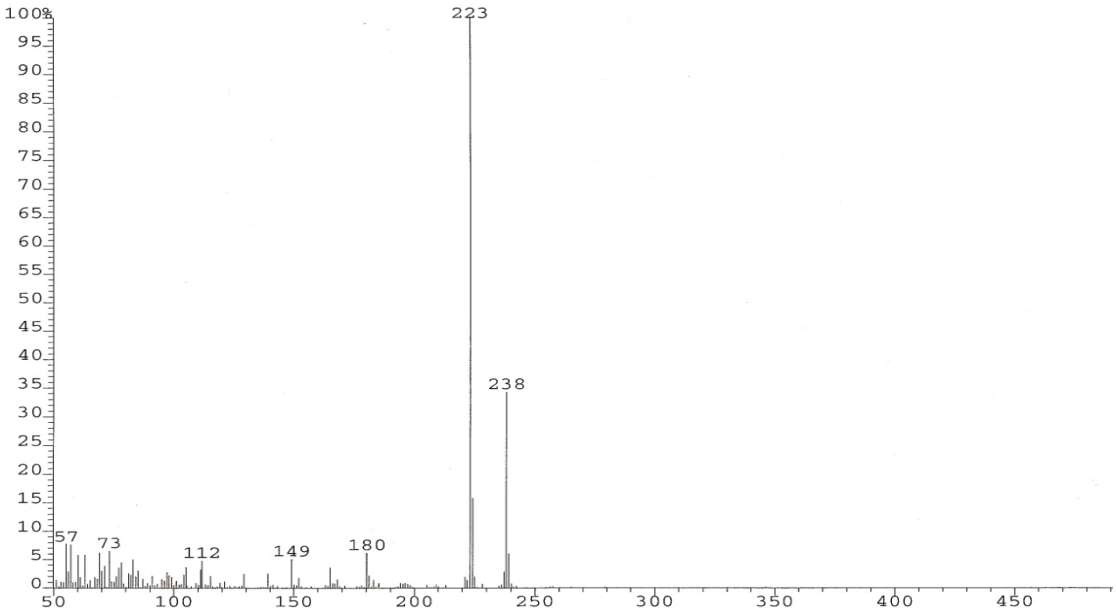
1.000
1.866
2.408
2.364
3.145
PPM

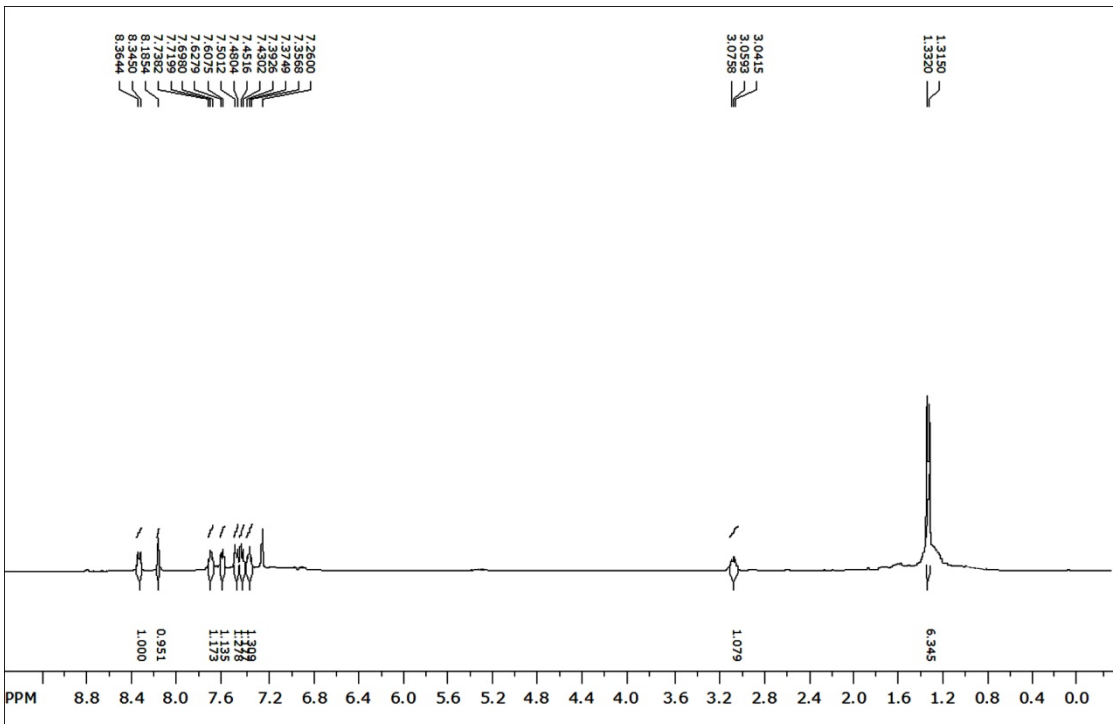

177.2713
156.2578
156.1148
151.1476
134.7460
126.8256
125.0937
123.8629
121.3773
118.1141
119.5742
105.9195
77.4775
76.8422
77.1599
56.0874
PPM

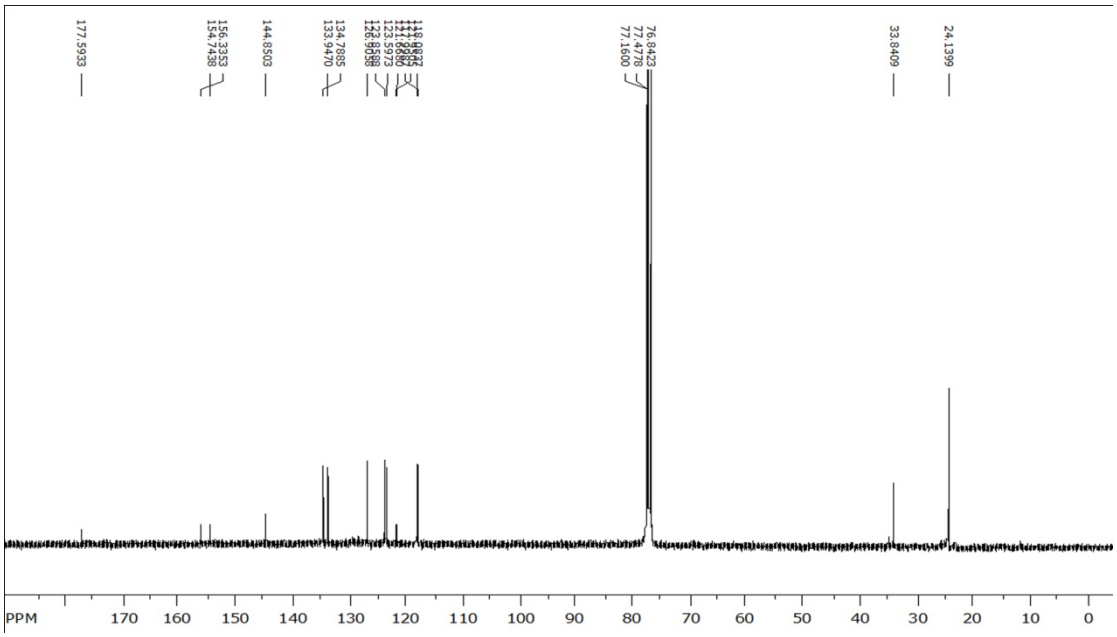


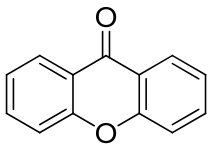
4b

V(hexane):V(EtOAc)=12:1 as the mobile phase; white solid, 100-103°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.36 (d, 1H, J=7.76 Hz, ph-H), 8.18 (m, 1H, ph-H), 7.35-7.73 (m, 5H, ph-H), 3.05 (m, 1H, -C<u>H</u>$(CH_3)_2$), 1.32 (d, 2*3H, J = 6.8 Hz, CH($C\underline{H}_3$)$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.59, 156.33, 154.74, 144.85, 134.78, 133.94, 126.90, 123.85, 123.59, 121.66, 121.37, 121.05, 111.08, 33.84, 24.13; MS-EI (m/z) = 238. [11]



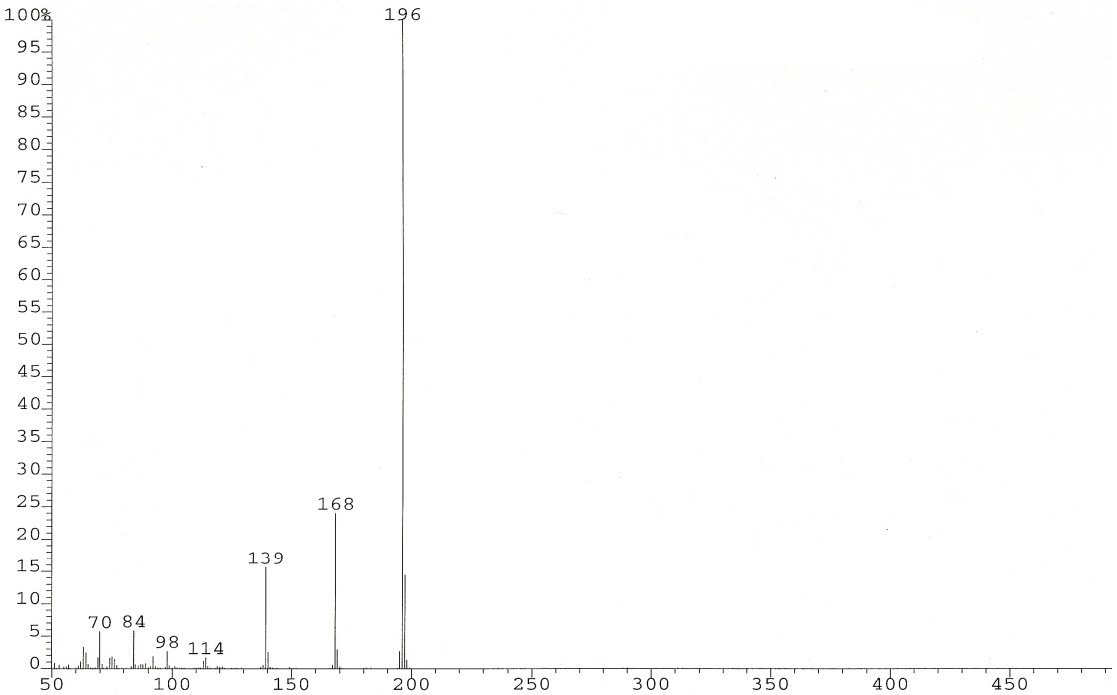


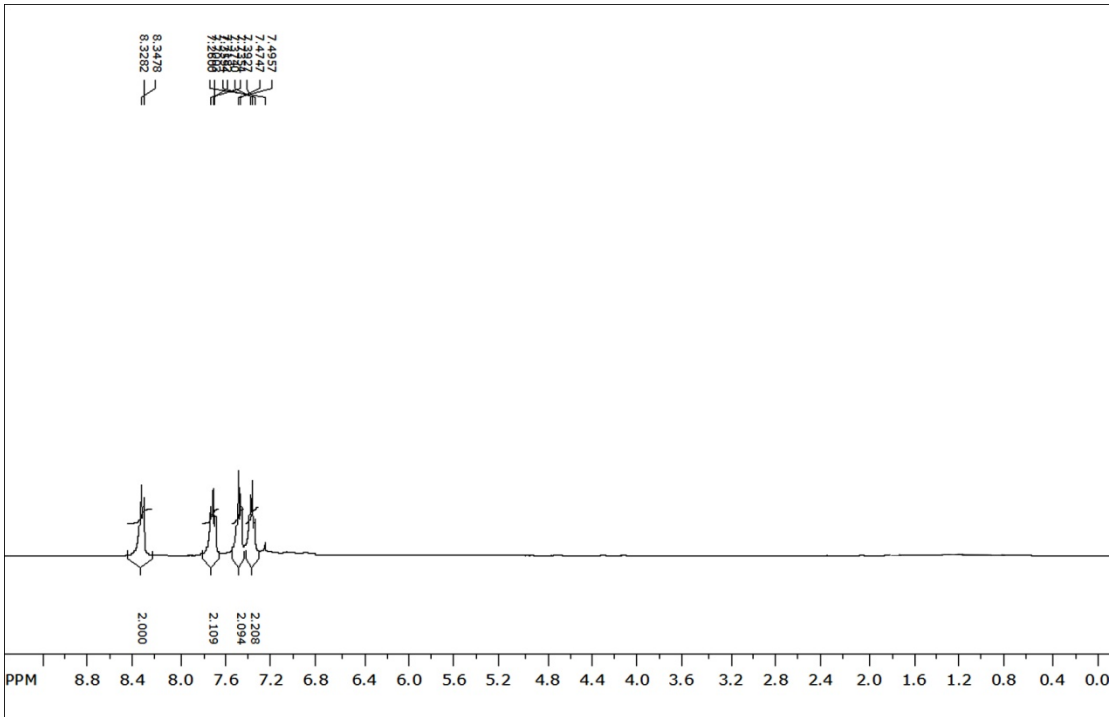


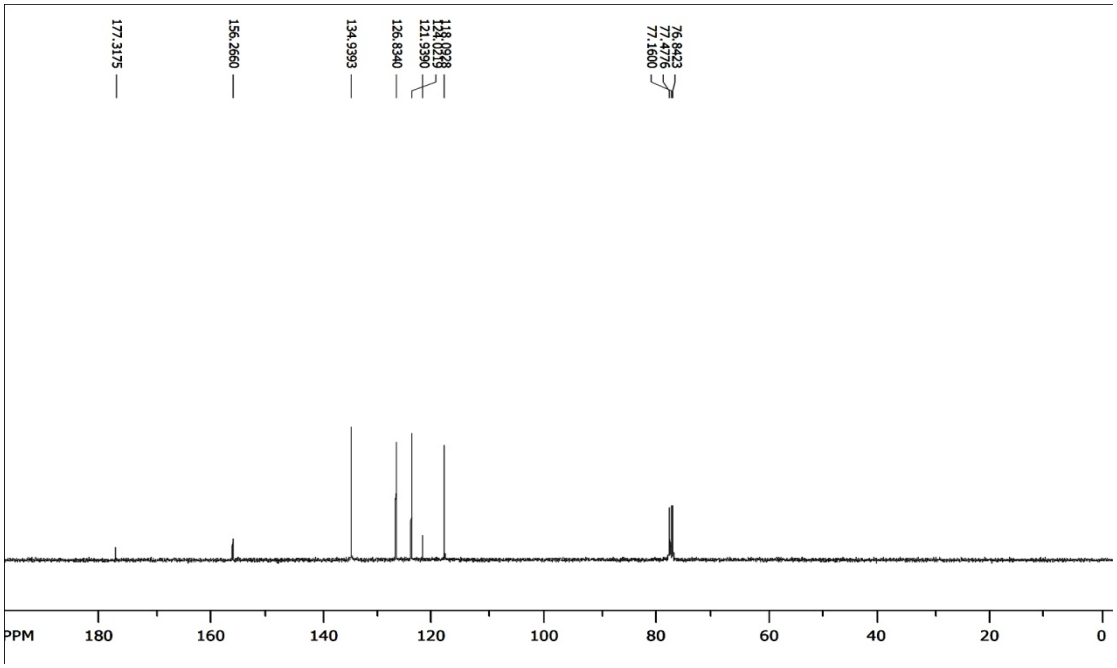


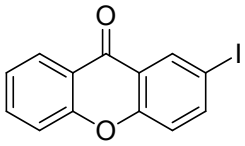
4c

V(hexane):V(EtOAc)=12:1 as the mobile phase; white solid, mp.172-174^{o}C [175-176^{o}C[12]]; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.33 (d, 2H, J=7.84 Hz, ph-H), 7.72 (m, 2H, ph-H), 7.48 (m, 2H, ph-H), 7.38 (m, 2H, ph-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.31, 156.26, 134.93, 126.83, 124.02, 121.93, 118.09; MS-EI (m/z) = 196.



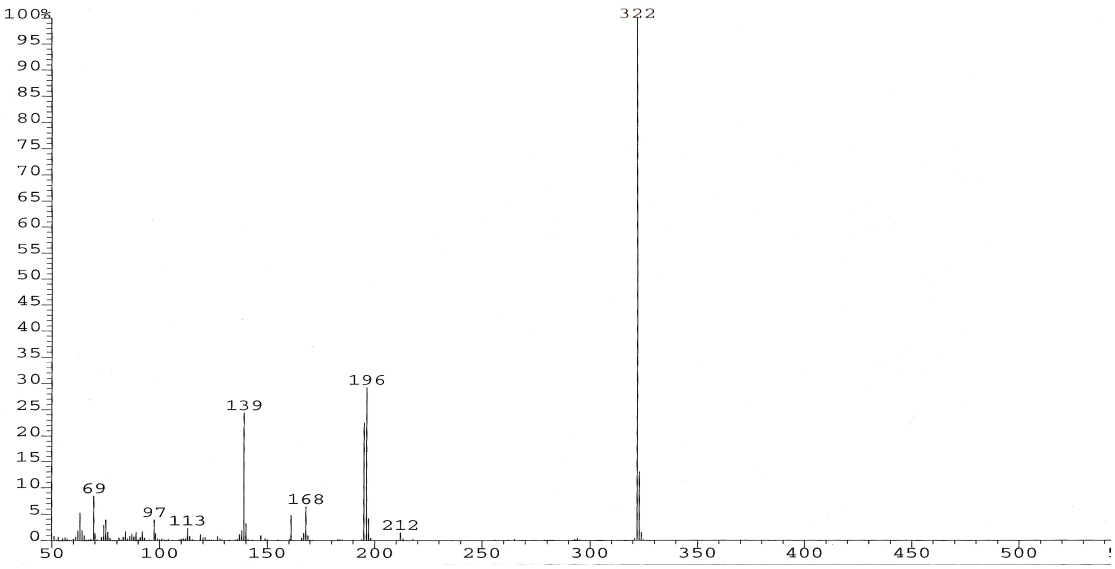


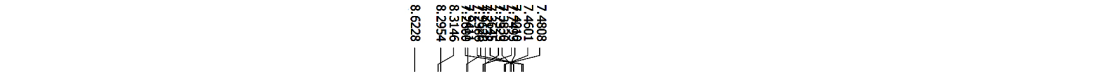


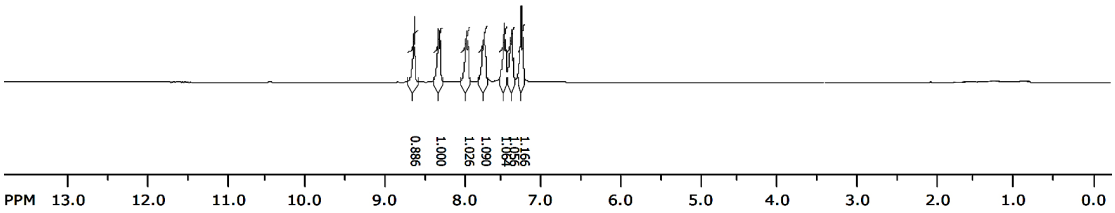


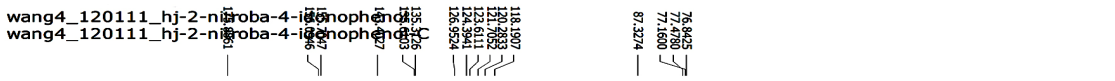
4d

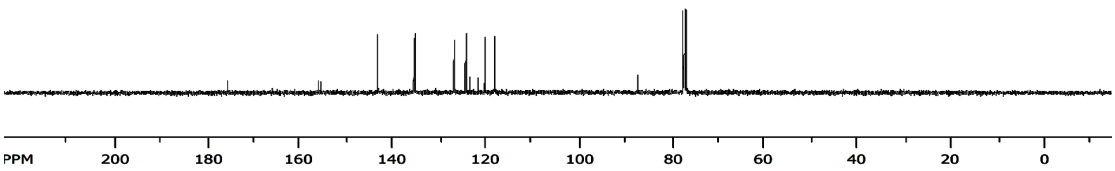
V(hexane):V(EtOAc)=12:1 as the mobile phase; white solid, mp. 171-174^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.62 (s, 1H, ph-H), 8.30 (d, 1H, J=7.68 Hz, ph-H), 7.95 (d, 1H, J=8.56 Hz, Ph-H), 7.73 (m, 1H, Ph-H), 7.47 (d, 1H, J=8.24Hz, Ph-H), 7.38 (m, 1H, Ph-H), 7.25 (d, 1H, J=8.52Hz, Ph-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.88, 156.09, 155.70, 143.40, 135.61, 135.31, 126.95, 124.39, 123.61, 121.70, 120.28, 118.19, 87.32; MS-EI (m/z) = 322. [13]

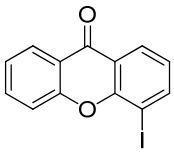

322
196
139
69
97
113
168
212




PPM

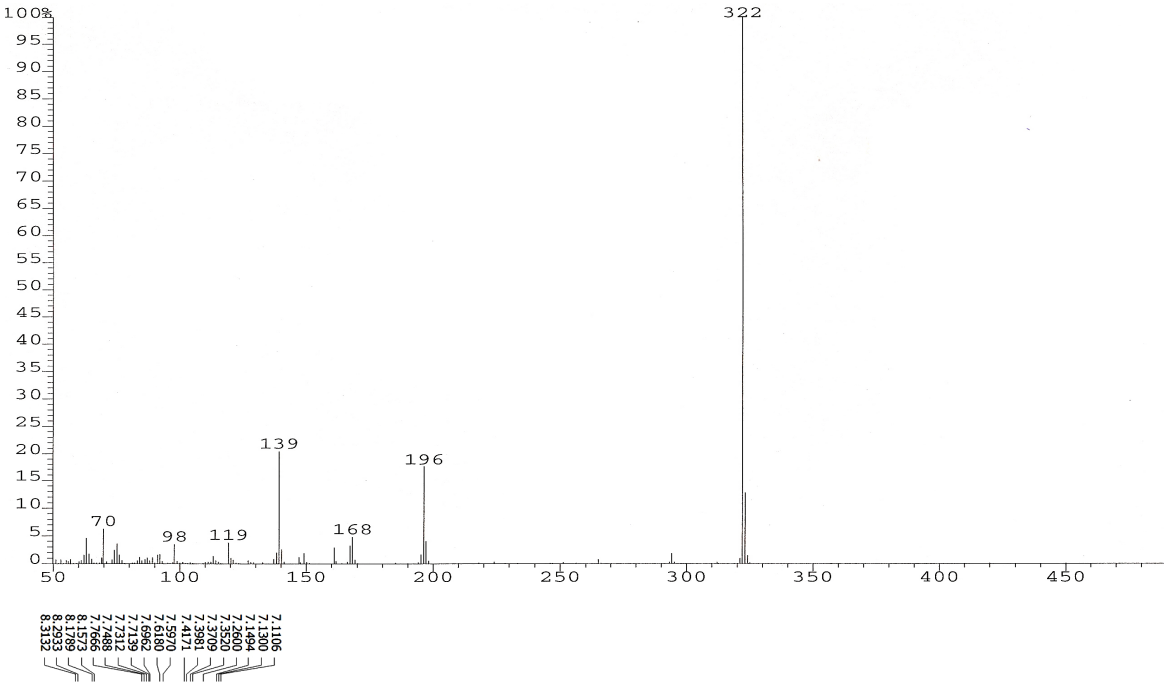


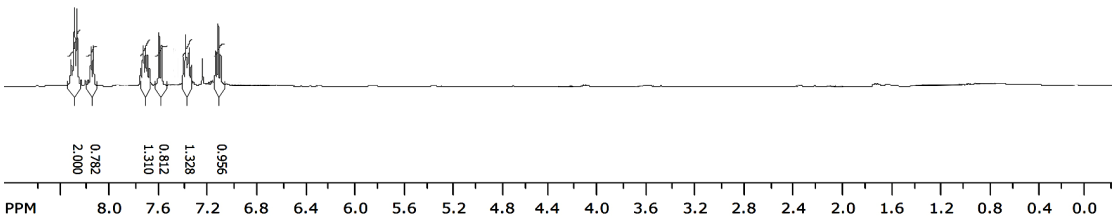

PPM

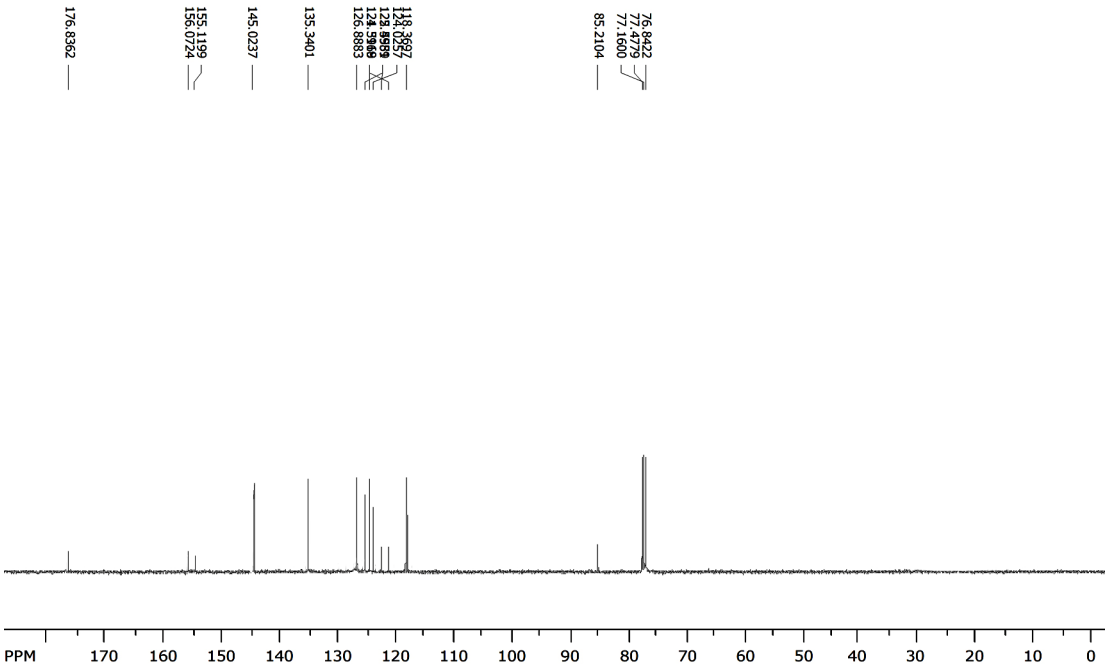


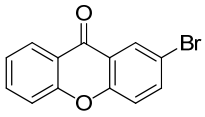
4e

V(hexane):V(EtOAc)=15:1 as the mobile phase; white solid, mp. 172-173°C [172-173.5°C[14]]; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.30 (m, 2H, ph-H), 8.16 (d, 1H, J=8.64 Hz, ph-H), 7.73 (m, 1H, Ph-H), 7.60 (d, 1H, J=8.40 Hz, ph-H), 7.38 (m, 1H, ph-H), 7.13 (t, 1H, J=7.76Hz, Ph-H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 176.83, 156.07, 155.11, 145.02, 135.34, 126.88, 125.00, 124.59, 124.02, 123.00, 121.12, 118.36.; MS-EI (m/z) = 322.



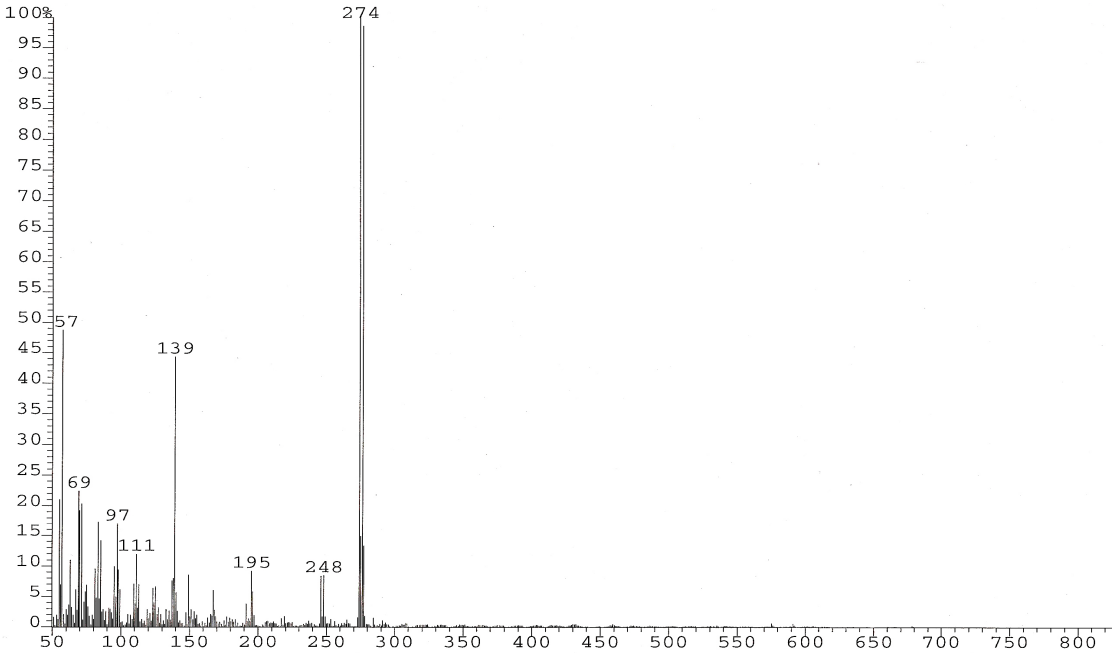


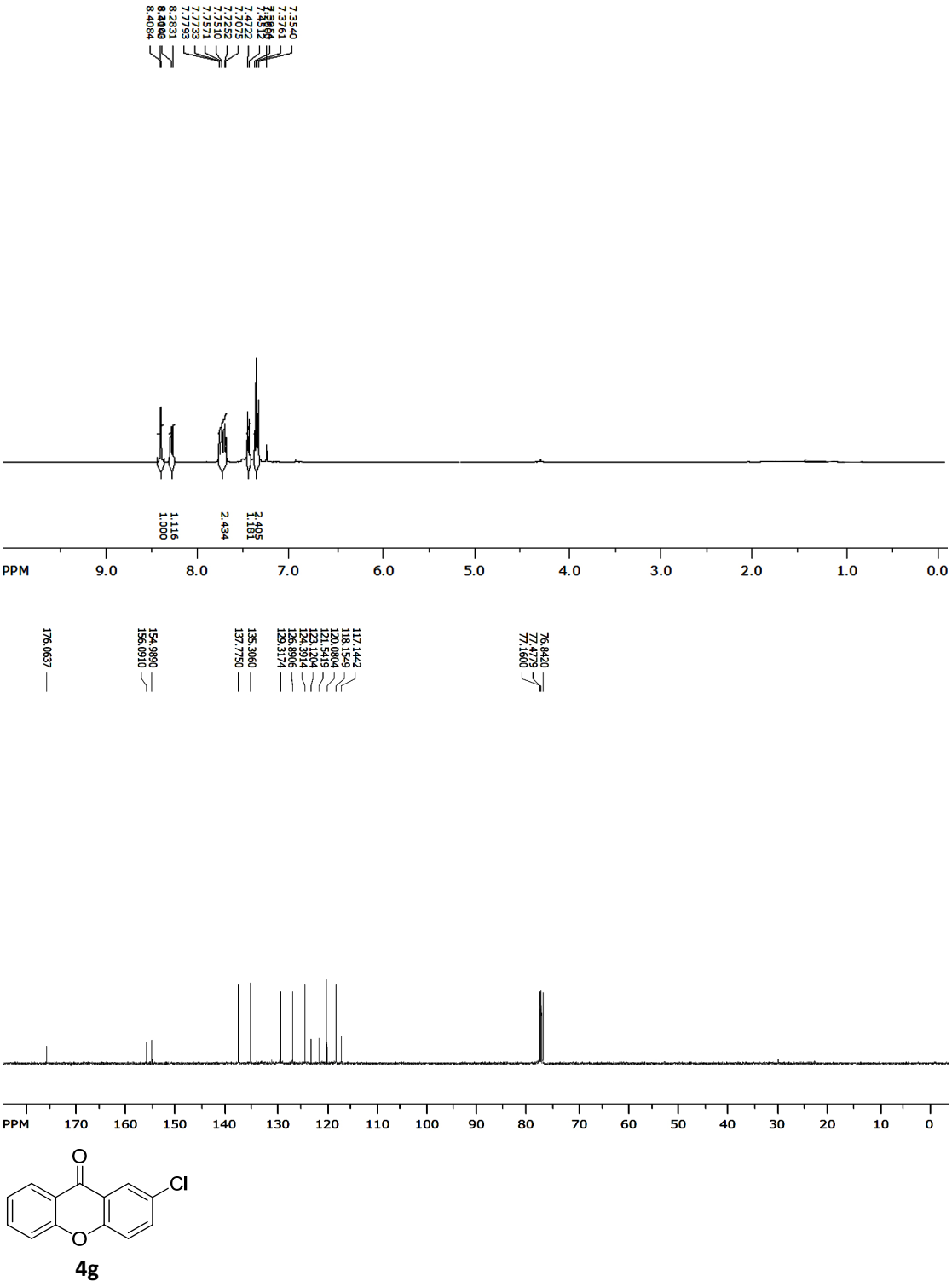




4f

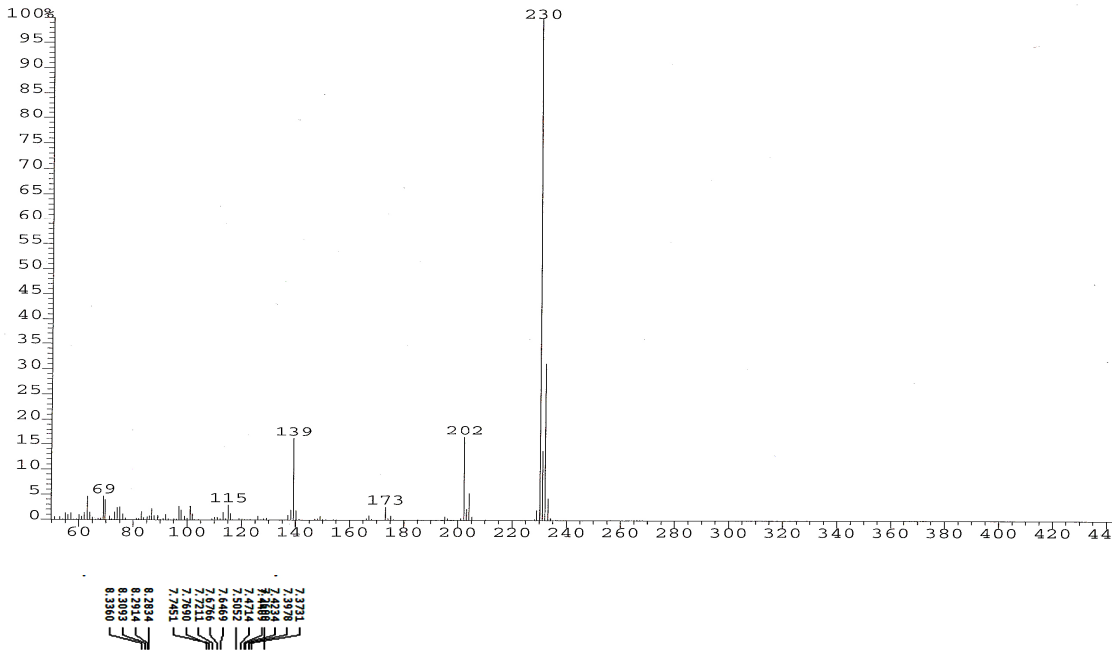
V(hexane):V(EtOAc)=15:1 as the mobile phase; white solid, mp.175-177°C [176°C[15]]; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.40 (d, 1H, J=1.76 Hz, ph-H), 8.29 (d, 1H, J=10.76 Hz, ph-H), 7.70-7.77 (m, 2H, ph-H), 7.46 (d, 1H, J=8.40 Hz, ph-H), 7.37 (m, 2H, ph-H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 176.06, 156.09, 154.98, 137.77, 135.30, 129.31, 126.89, 124.39, 123.12, 121.54, 120.08, 118.15, 117.14; MS-EI (m/z) = 274.

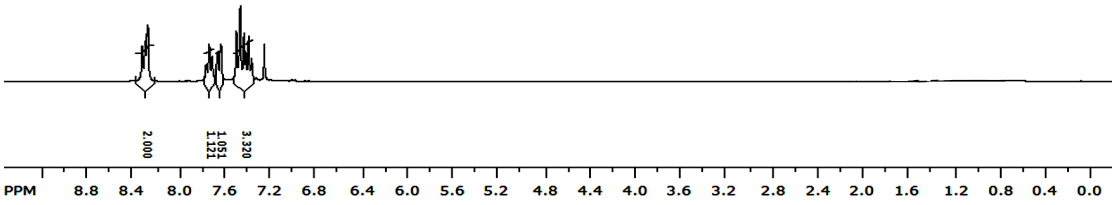




4g

V(hexane):V(EtOAc)=15:1 as the mobile phase; white solid, mp. 169-171°C [174-175°C[16]]; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.30 (m, 2H, ph-H), 7.74 (t, 1H, J=9.56Hz, ph-H), 7.65 (d, 1H, J=10.8Hz, ph-H), 7.37-7.50 (m, 3H, ph-H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.10, 155.92, 136.68, 134.50, 129.72, 128.28, 127.06, 126.75, 124.62, 124.20, 123.07, 121.68, 118.21; MS-EI (m/z) = 230.


230
139
202
69
115
173
8.3360
8.3093
8.2914
8.2834
7.7451
7.7690
7.6469
7.5052
7.4714
7.3978
7.3731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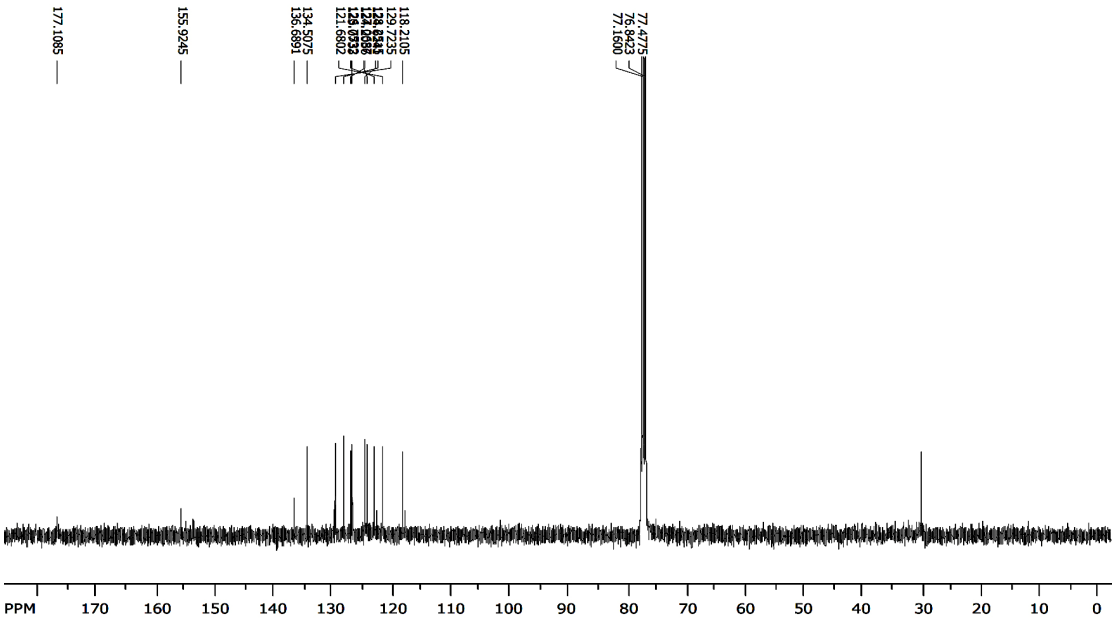
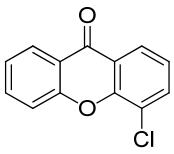
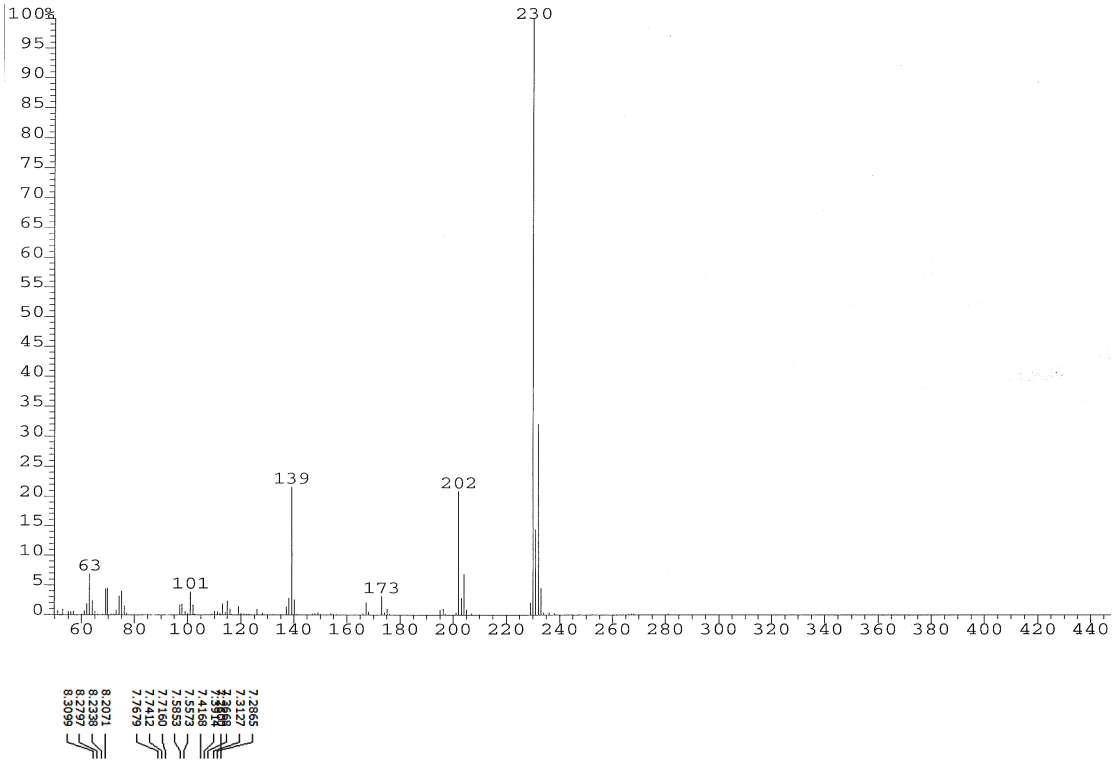
1.051
1.121
3.320
PPM

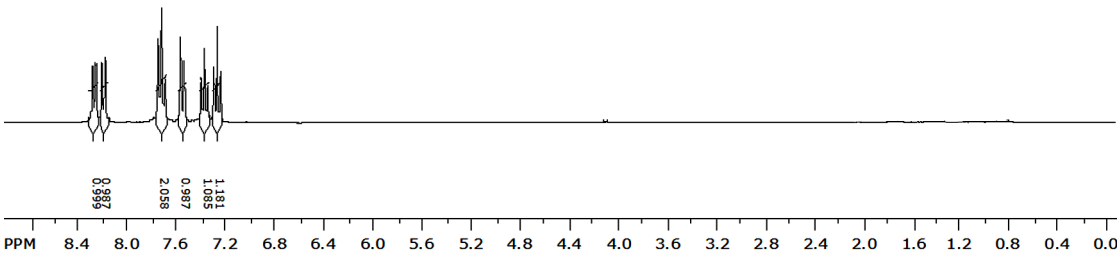

177.1085
155.9245
136.6891
134.5075
121.6802
118.2105
77.4775
77.1600
PPM

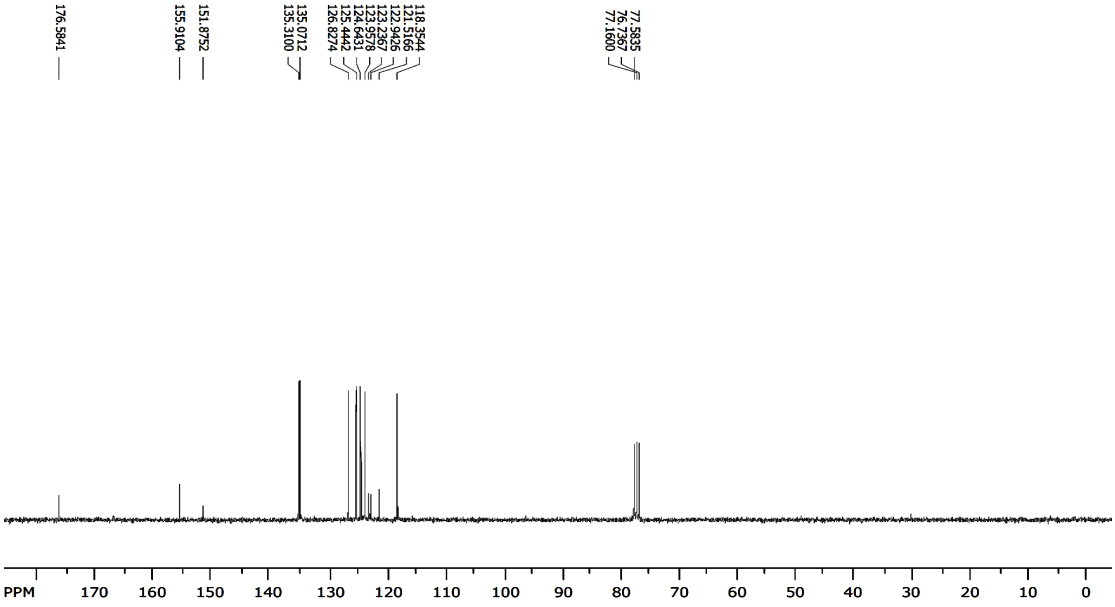


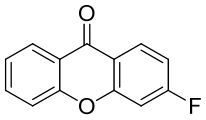
4h

V(hexane):V(EtOAc)=13:1 as the mobile phase; white solid, mp. 131-134°C [135-136°C[17]]; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.28 (d, 1H, J=9.06Hz, ph-H), 8.21 (d, 1H, J=8.01Hz, ph-H), 7.74 (t, 2H, J=8.01Hz, ph-H), 7.56 (d, 1H, J=8.40Hz, ph-H), 7.39 (t, 1H,J=7.62Hz, ph-H), 7.30 (m, 1H, ph-H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 176.58, 155.91, 151.87, 135.31, 135.07, 126.82, 125.44, 124.64, 123.95, 123.23, 122.94, 121.51, 118.35. MS-EI (m/z) = 230.



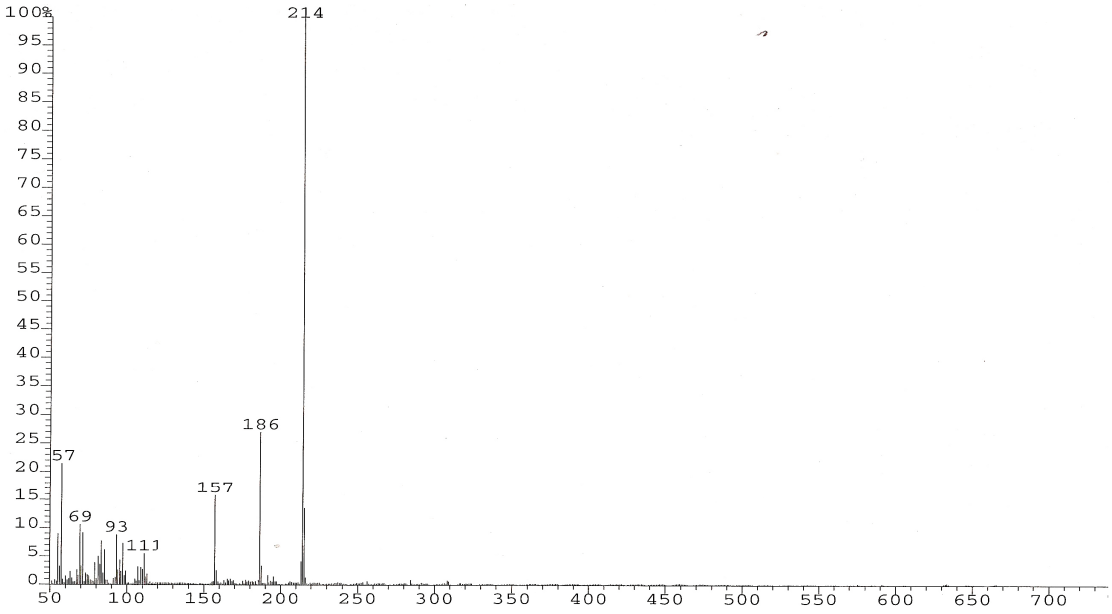


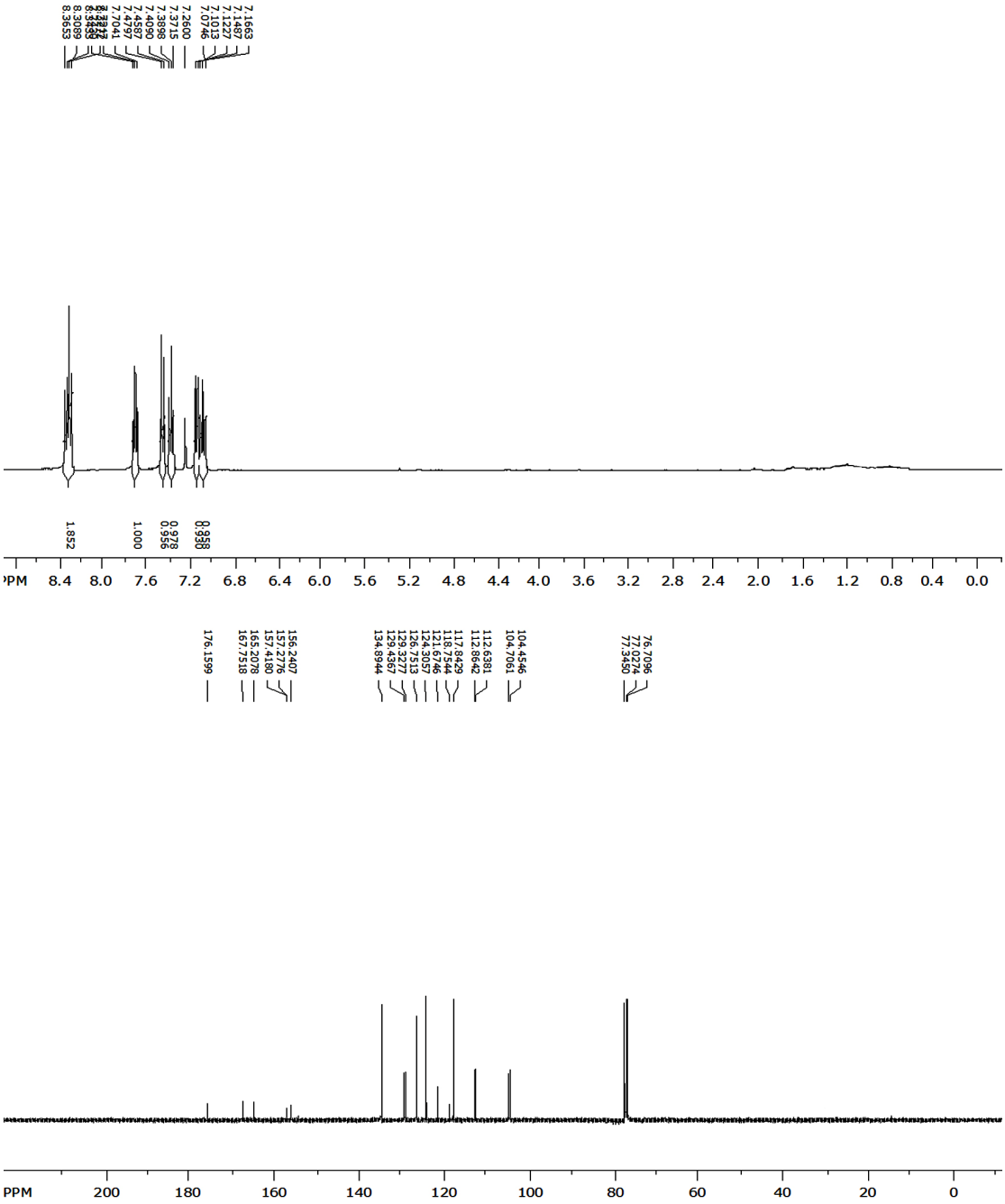


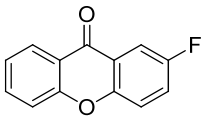


4i

V(hexane):V(EtOAc)=15:1 as the mobile phase; white solid, mp. 163-165^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.33 (m, 2H, ph-H), 7.72 (t, 1H, J=7.00Hz, ph-H), 7.46 (d, 1H, J=8.4Hz, ph-H), 7.38 (t, 1H, J= 7.68Hz, ph-H), 7.07-7.16 (m, 2H, ph-H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 176.15, 167.75, 165.20 (d, J_{C-F}=255Hz), 157.41, 157.27 (d, J_{C-F}=17Hz), 156.24, 134.89, 129.43, 129.32 (d, J_{C-F}=11Hz), 126.75, 124.30, 121.67, 118.75, 117.84, 112.86, 112.63 (d, J_{C-F}=23Hz), 104.70, 104.45 (d, J_{C-F}=25Hz); MS-EI (m/z) = 214. [18]

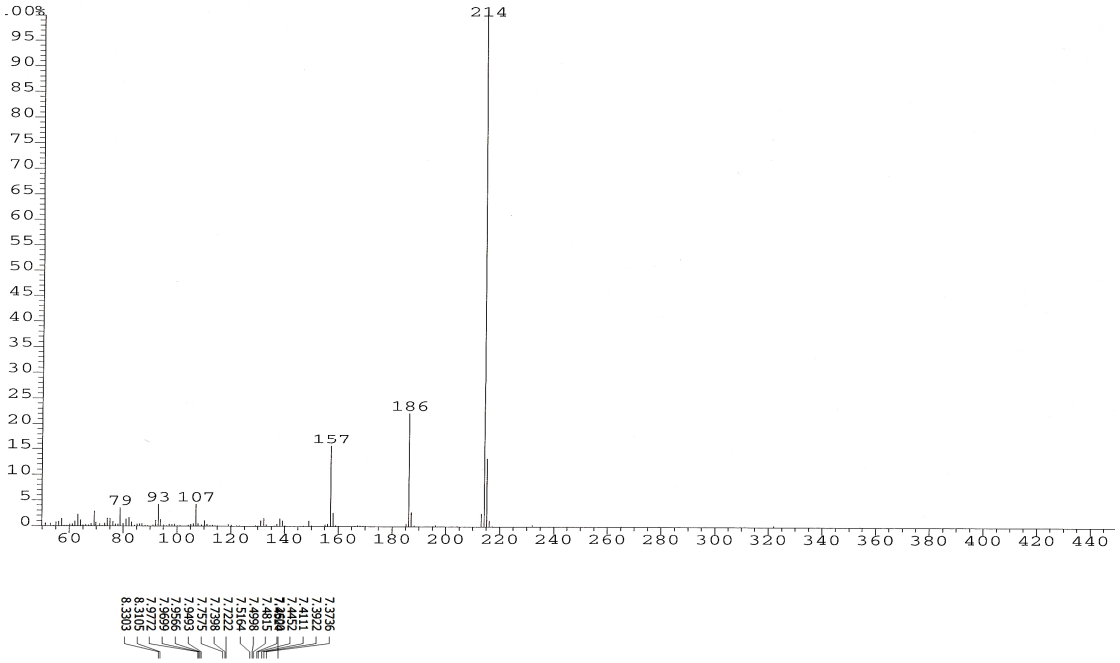


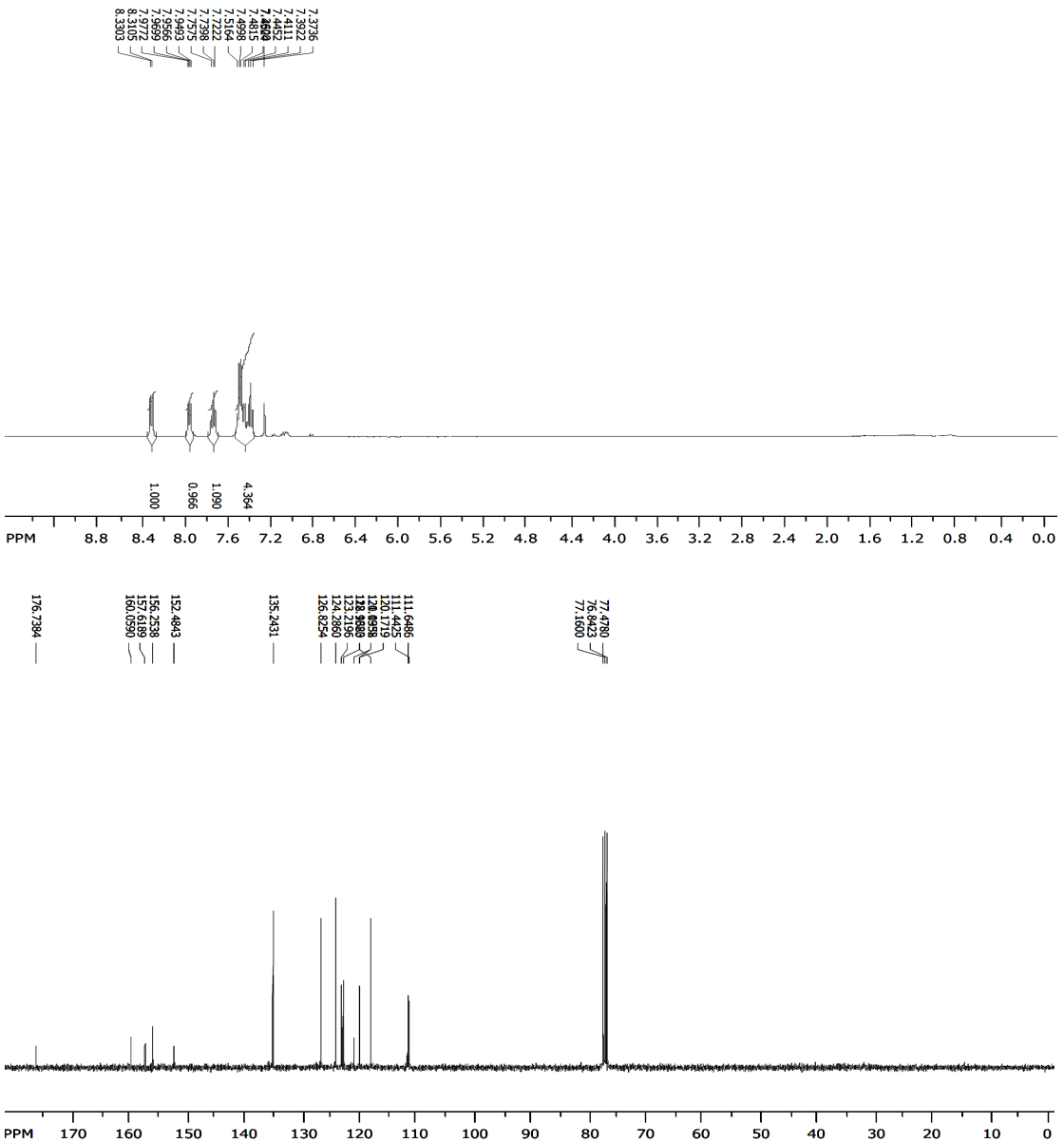




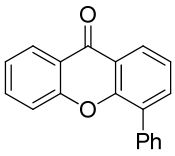
4j

V(hexane):V(EtOAc)=13:1 as the mobile phase; white solid, mp. 148-150^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.32 (d, 1H, J=7.92 Hz, ph-H), 7.96 (m, 1H, ph-H), 7.73 (m, 1H, ph-H), 7.37-7.51 (m, 4H, ph-H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 176.73, 176.67 (d, J_{C-F}=6Hz), 160.05, 157.61 (d, J_{C-F}=244Hz), 156.25, 152.50, 152.48 (d, J_{C-F}=2Hz), 135.24, 126.82, 124.28, 123.21, 122.96 d, J_{C-F}=25Hz), 121.13, 120.17, 120.09 (d, J_{C-F}=8Hz), 118.13, 111.64, 111.44 (d, J_{C-F}=20Hz); MS-EI (m/z) = 214. [19]


214
186
157
79
93
107

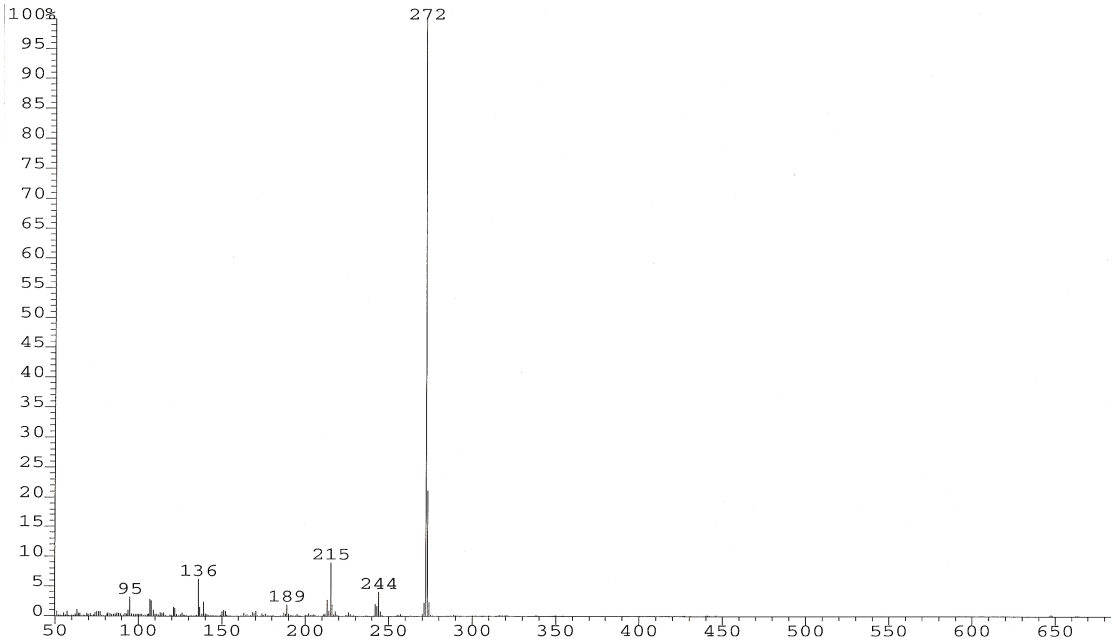

1.000
0.966
1.090
4.364
PPM

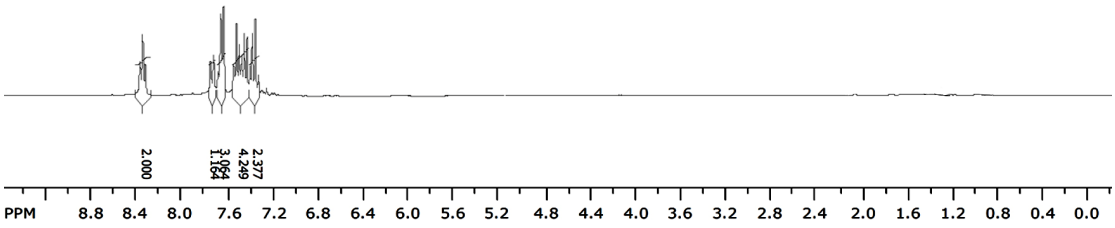
PPM

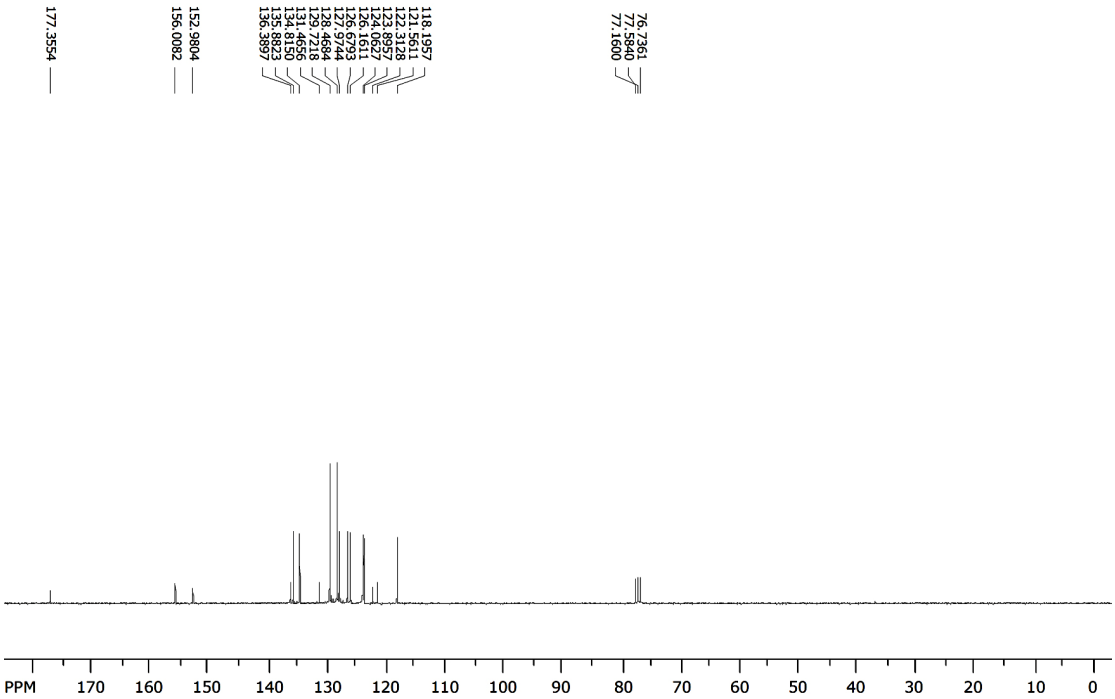


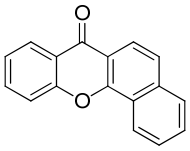
4k

V(hexane):V(EtOAc)=15:1 as the mobile phase; white solid, mp. 130-132°C [131-132°C[20]]; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.33 (t, 2H, J=6.57 Hz, ph-H), 7.64-7.75 (m, 4H, ph-H), 7.33-7.547 (m, 6H, ph-H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 177.35, 156.00, 152.98, 136.38, 135.88, 134.81, 131.46, 129.72, 128.46, 127.97, 126.67, 126.67, 124.06, 123.89, 122.31, 121.56, 118.19; MS-EI (m/z) = 272.



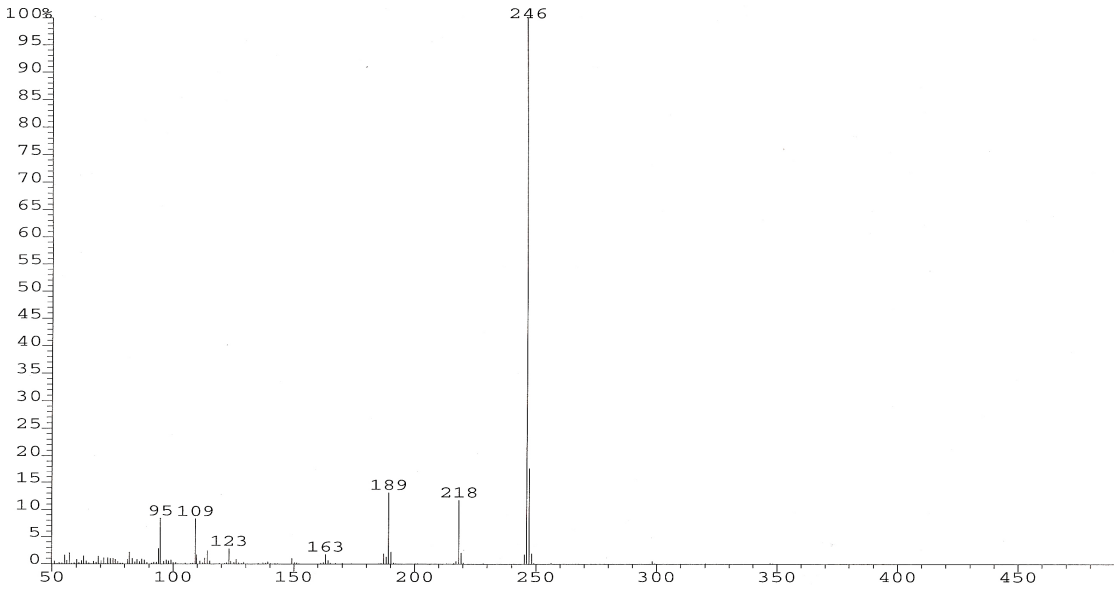


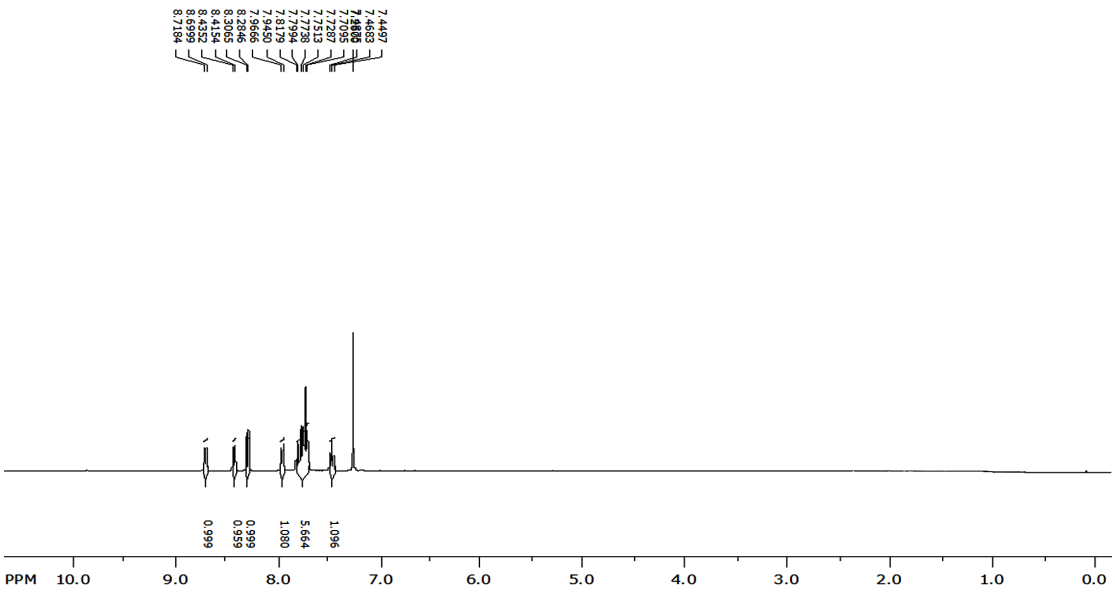


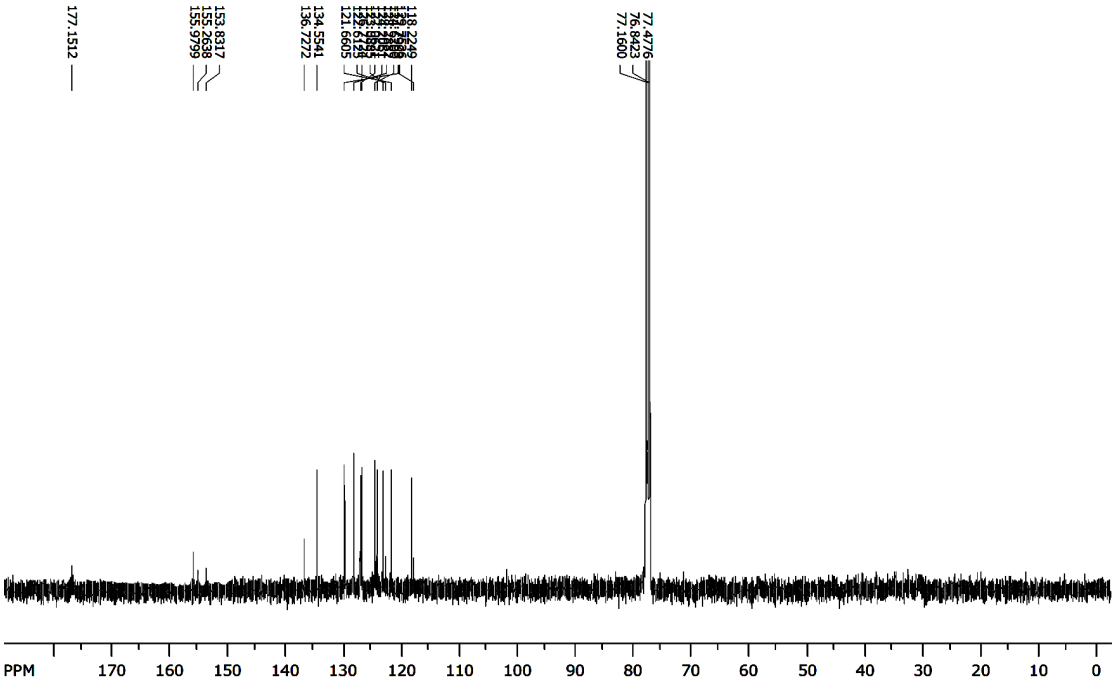


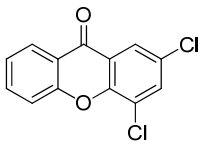
4l

V(hexane):V(EtOAc)=10:1 as the mobile phase; white solid, mp. 156-158^{o}C [159-160^{o}C[12]]; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.70 (d, 1H, J=7.40 Hz, ph-H), 8.42 (d, 1H, J=7.92Hz, ph-H), 8.29 (d, 1H, J=8.76Hz, ph-H), 7.95 (d, 1H, J=8.64Hz, ph-H), 7.70-7.81 (m, 5H, ph-H), 7.46 (t, 1H, J=7.44Hz, ph-H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 177.15, 155.97, 155.26, 153.83, 136.72, 134.55, 129.70, 128.30, 127.10, 126.76, 124.60, 124.21, 123.11, 122.60, 121.67, 118.22, 117.79; MS-EI (m/z) = 246.



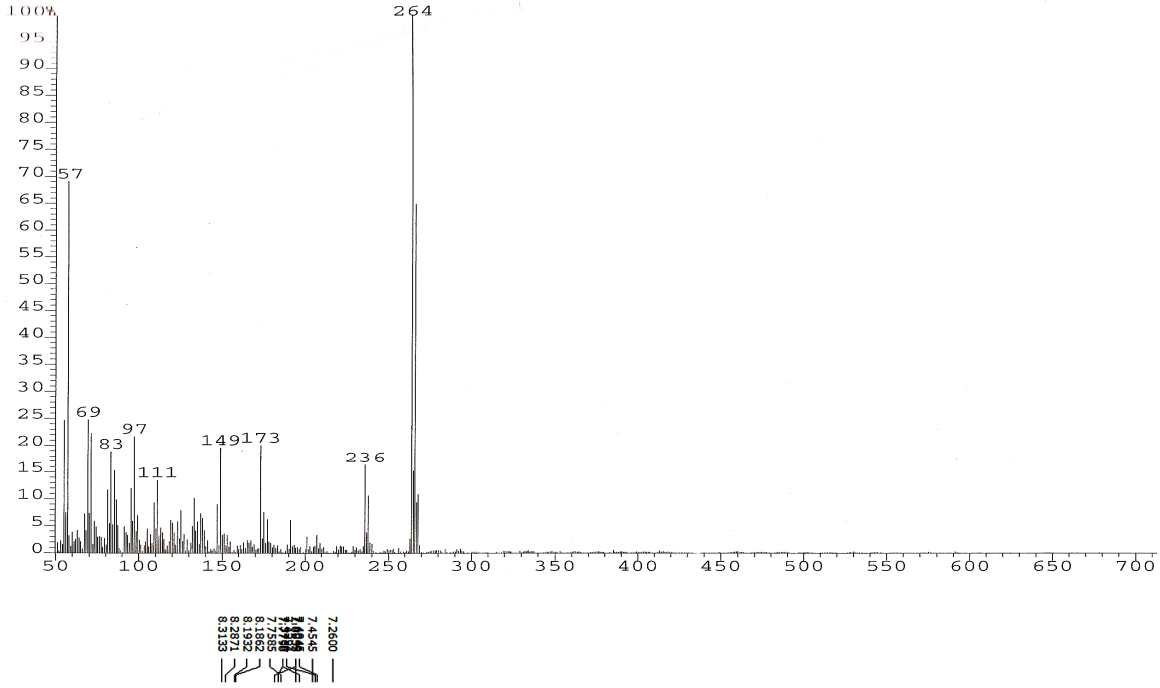






4m

V(hexane):V(EtOAc)=14:1 as the mobile phase; white solid, mp.155-157^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.30 (m, 1H, ph-H), 8.18 (d, 1H, J=2.1Hz, ph-H), 7.76 (m, 2H, ph-H), 7.58 (m, 1H, ph-H), 7.46 (t, 1H, J=7.44Hz, ph-H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 175.63, 155.85, 150.56, 135.69, 134.83, 129.46, 126.95, 125.01, 124.91, 124.19, 123.60, 121.23, 118.44; MS-EI (m/z) = 264. [19]


264
57
69
83
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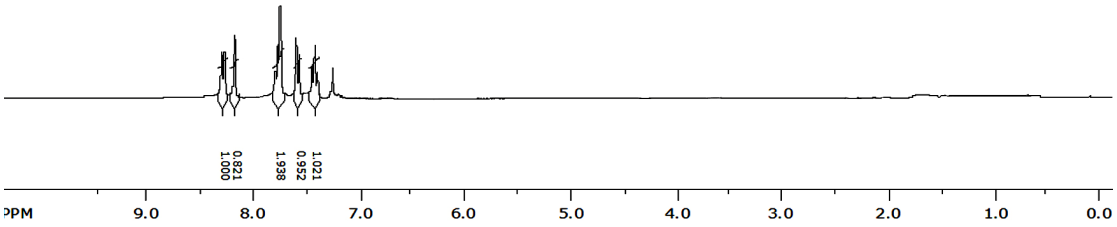
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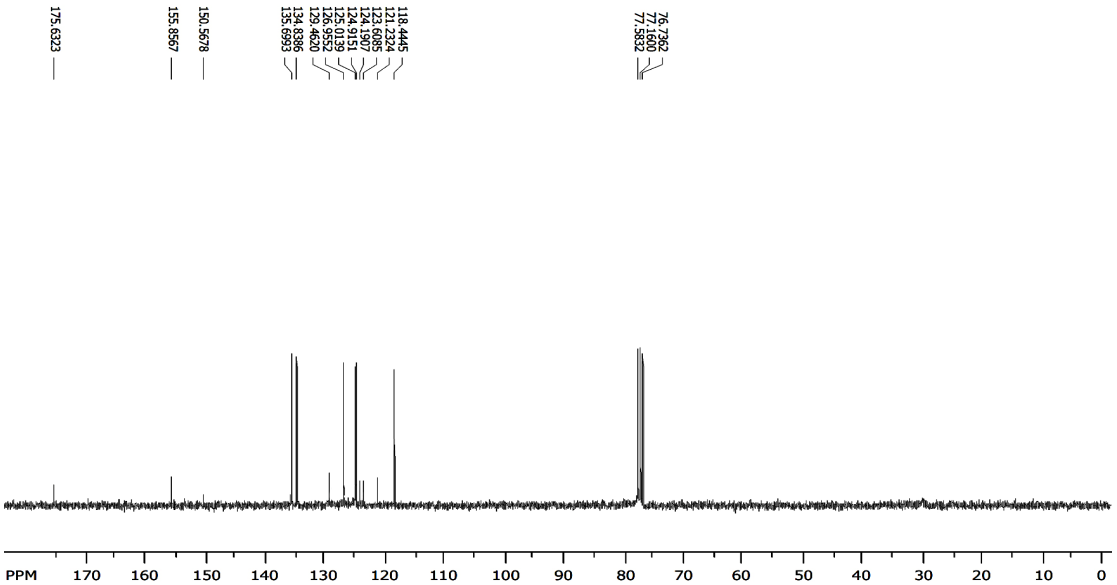
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77.1600
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PPM
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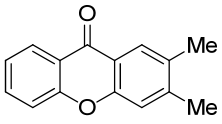
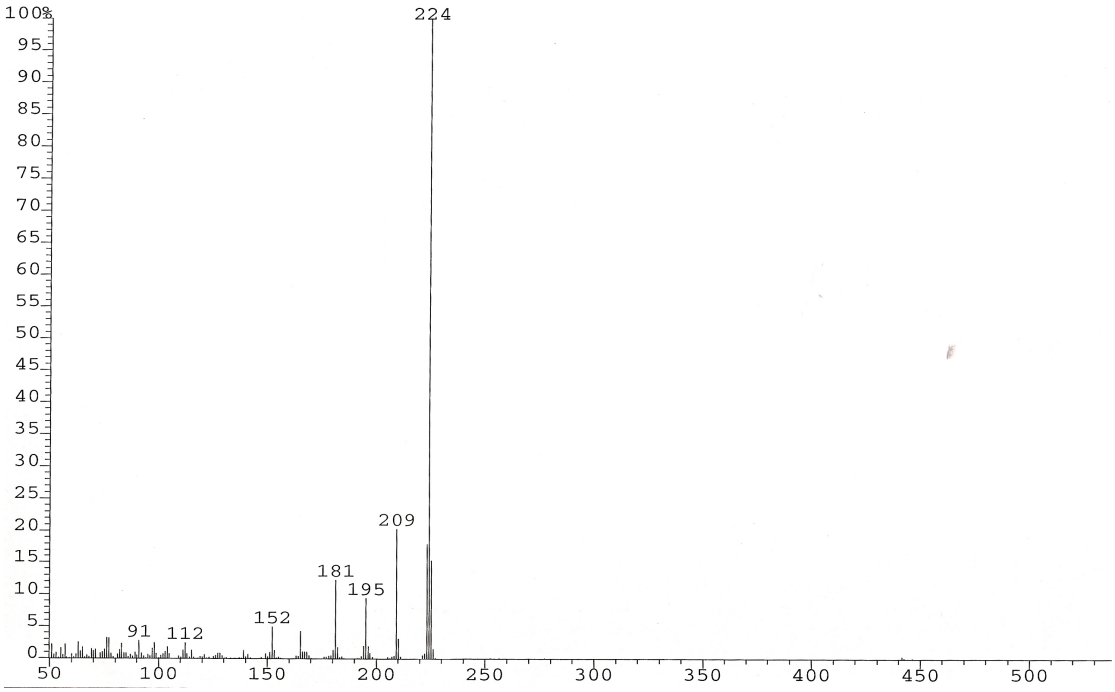
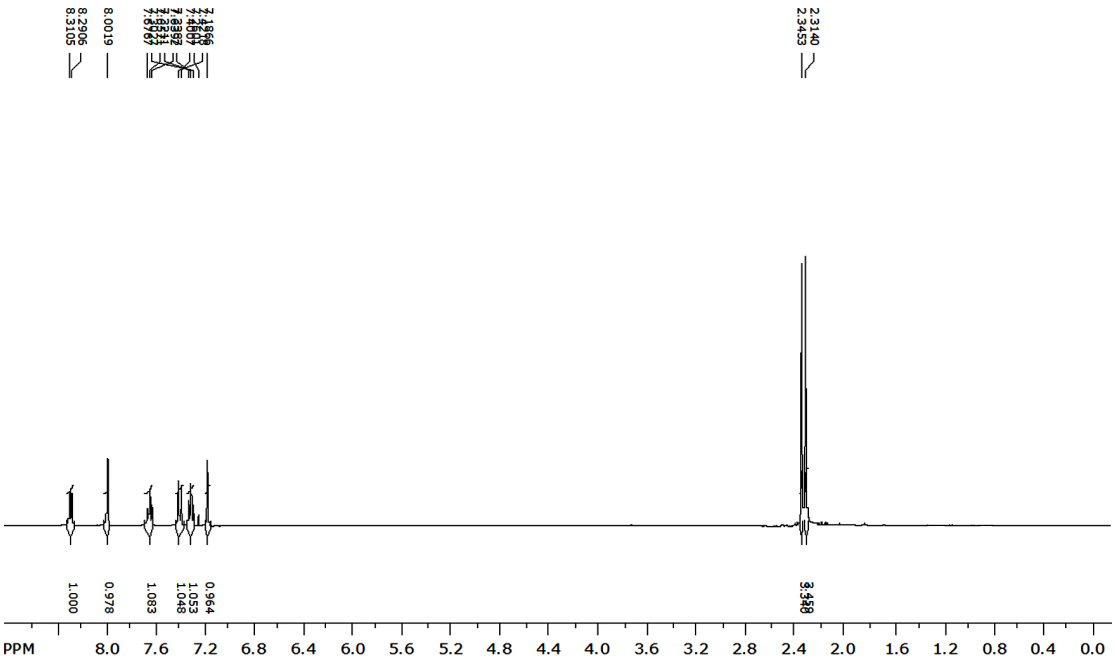
0

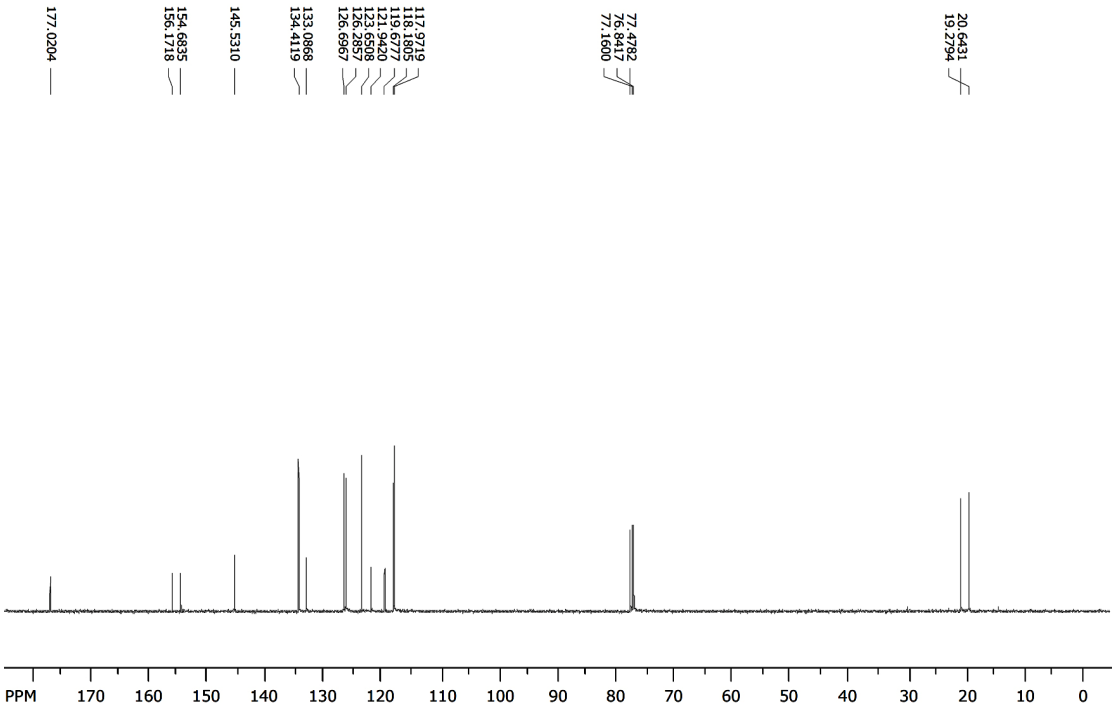


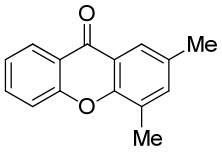
4n

V(hexane):V(EtOAc)=10:1 as the mobile phase; white solid, mp. 152-154^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.20 (d, 1H, J=7.92Hz, ph-H), 8.00 (s, 1H, ph-H), 7.76 (t, 1H, J=7.84Hz, ph-H), 7.41 (d, 1H, J=8.44Hz, ph-H), 7.32 (t, 1H, J=7.04Hz, ph-H), 7.18 (s, 1H, ph-H), 2.34 (s, 3H, CH_3), 2.31 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 177.02, 156.17, 154.68, 145.53, 134.41, 133.08, 126.69, 126.28, 123.65, 121.94, 119.67, 118.18, 117.97, 20.64, 19.27; MS-EI (m/z) = 224. [21]



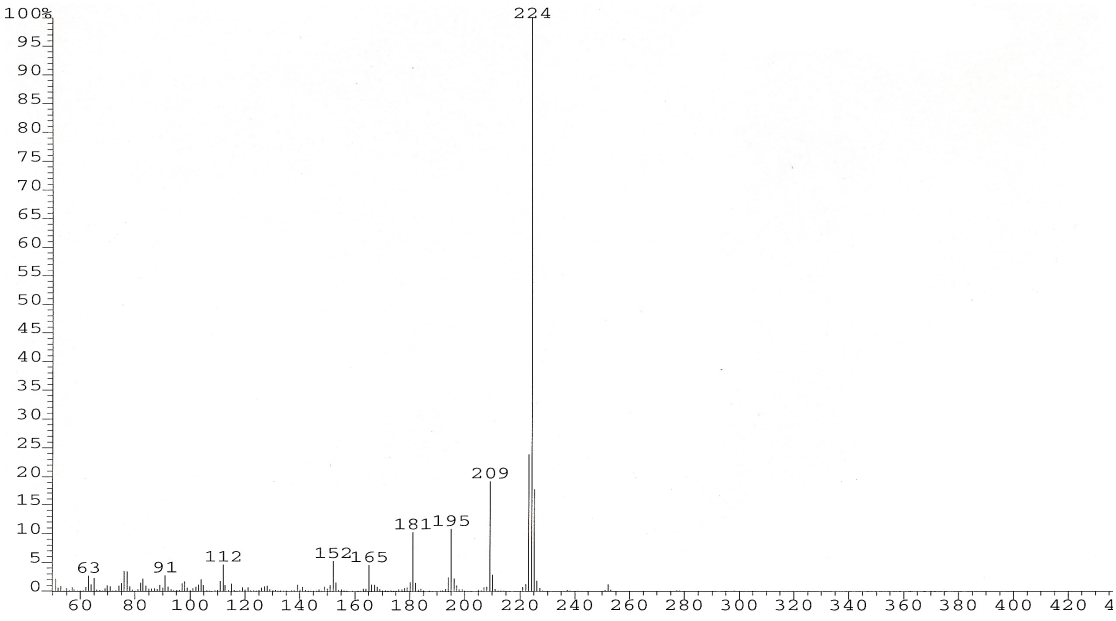


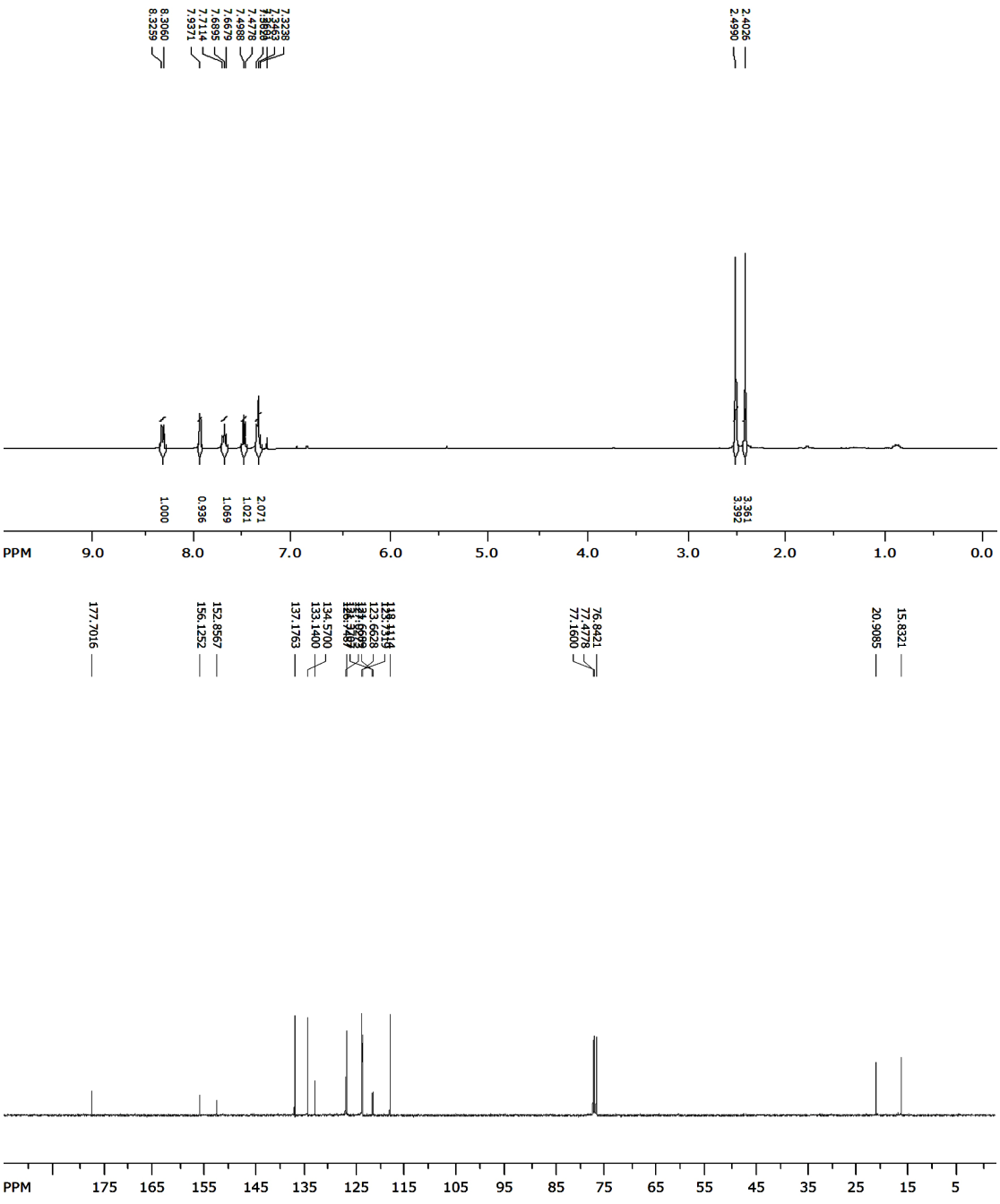


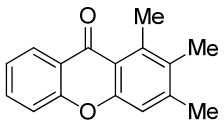


4o

V(hexane):V(EtOAc)=10:1 as the mobile phase; white solid, mp. 159-161^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.31 (d, 1H, J=7.96Hz, ph-H), 7.93 (s, 1H, ph-H), 7.68 (t, 1H, J=8.76Hz, ph-H), 7.48 (d, 1H, J=8.40Hz, ph-H), 7.34 (m, 2H, ph-H), 2.49 (s, 3H, CH_3), 2.40 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 177.70, 156.12, 152.85, 137.17, 134.57, 133.14, 127.02, 126.74, 123.73, 123.66, 121.66, 121.37, 118.11, 20.90, 15.83; MS-EI (m/z) = 224. [19]

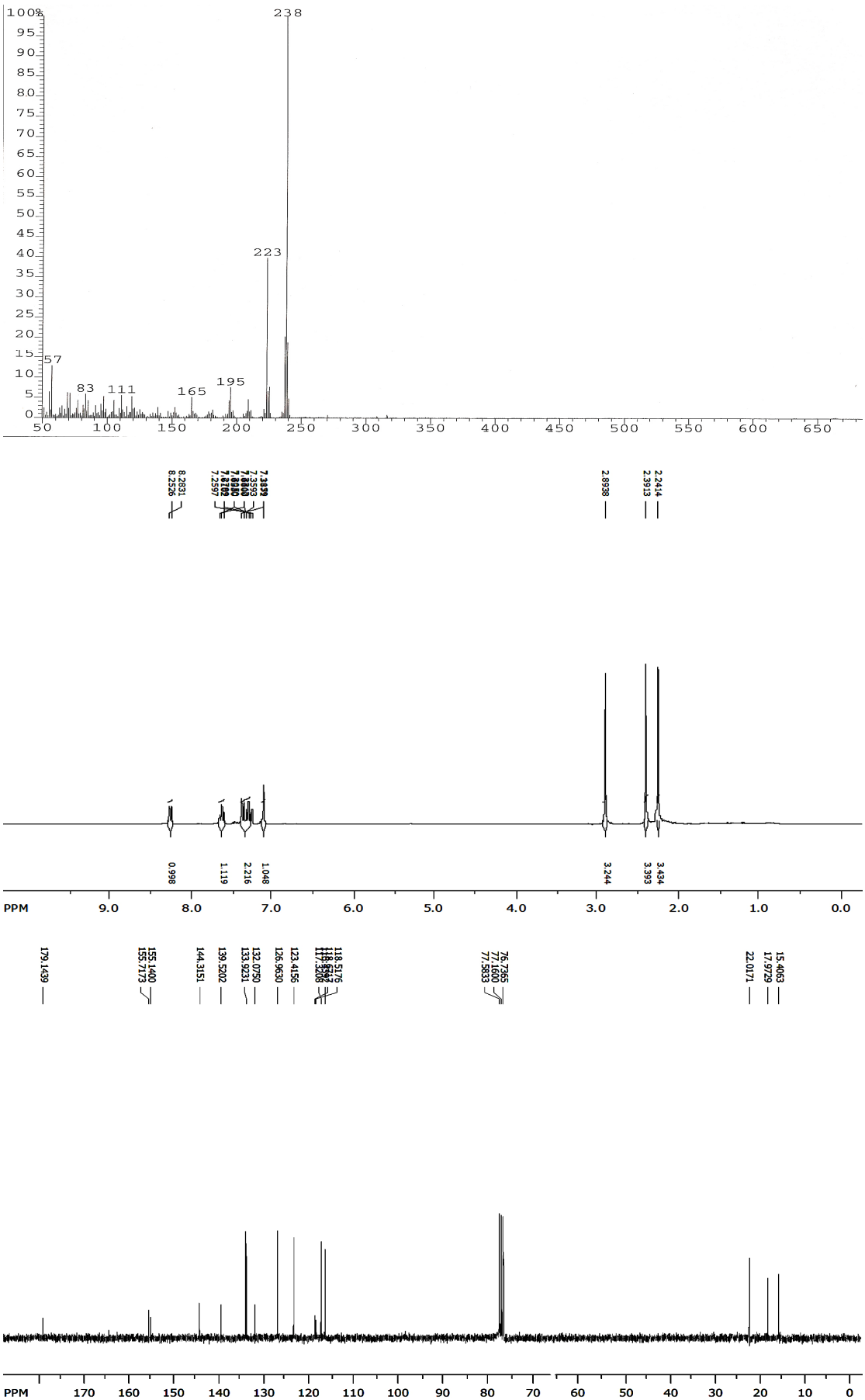


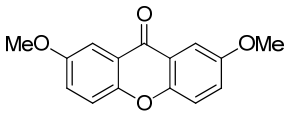




4p

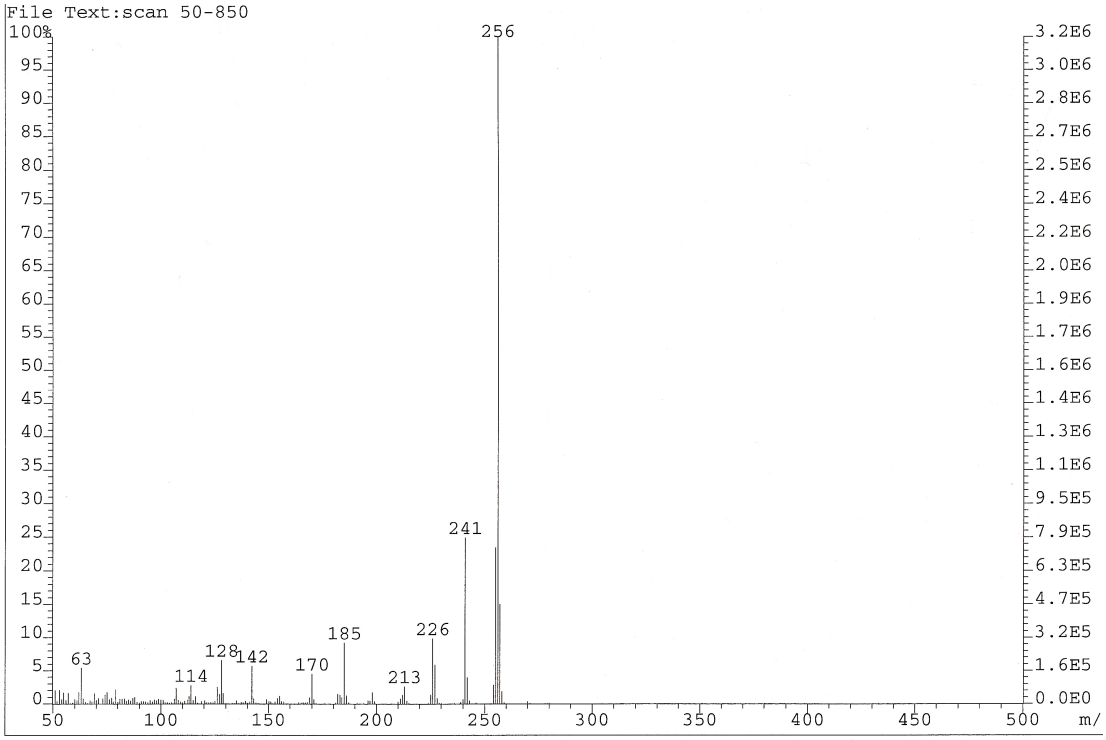
V(hexane):V(EtOAc)=10:1 as the mobile phase; white solid, mp. 125-126°C [124-126°C[22]]; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.26 (d, 1H, J=9.15Hz, ph-H), 7.63 (t, 1H, J=7.14Hz, ph-H), 7.36 (d, 1H, J=8.34Hz, ph-H), 7.30 (t, 1H, J=7.80Hz, ph-H), 7.11 (s, 1H, ph-H), 2.89 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.24 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 179.14, 155.71, 155.14, 144.31, 139.52, 133.92, 132.07, 126.96, 123.41, 118.51, 118.18, 117.32, 116.43, 22.01, 17.97, 15.40; MS-EI (m/z) = 238.

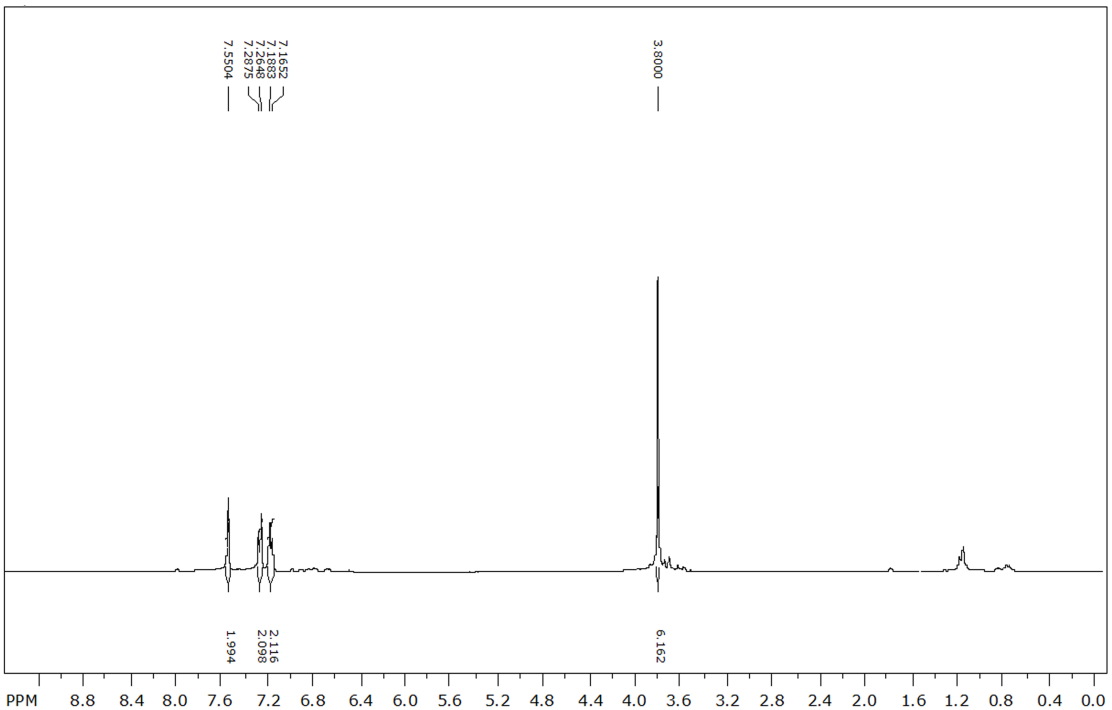

238
223
57
83
111
165
195
PPM

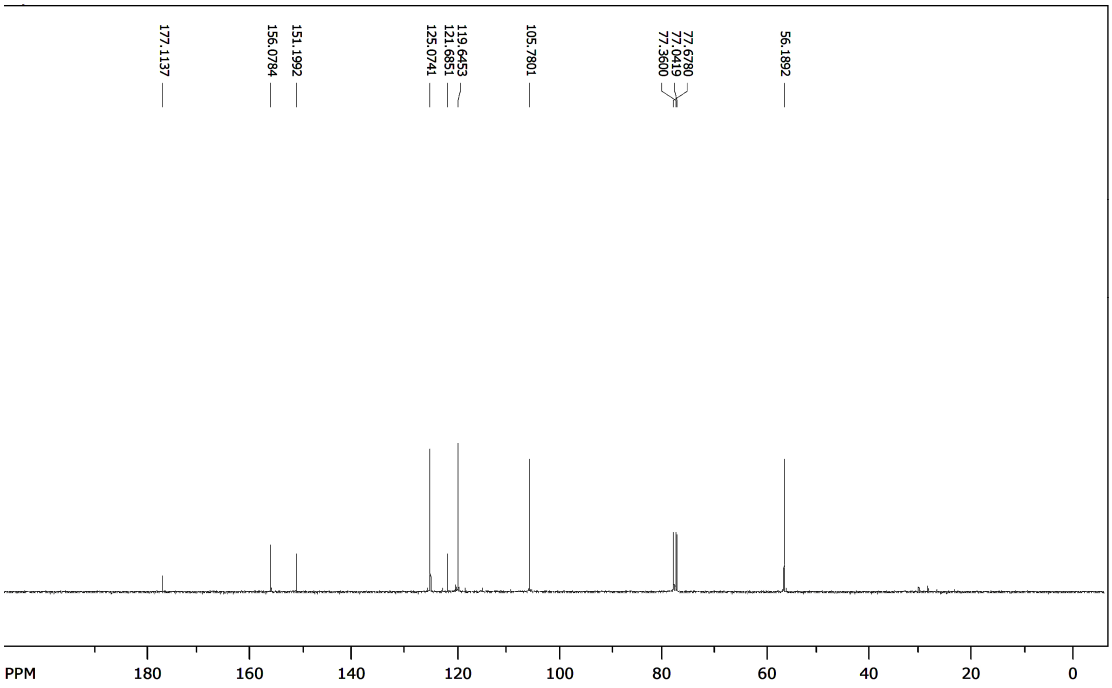


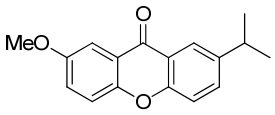
4q

V(hexane):V(EtOAc)=15:1 as the mobile phase; white solid, mp. 165-167°C [174-176°C[23]]; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.55 (s, 2×1H, ph-H), 7.27 (d, 2×1H, J = 9.1 Hz, ph-H), 7.17 (d, 2×1H, 9.2 Hz), 3.80 (s, 2×3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 177.11, 156.07, 151.19, 125.07, 121.68, 119.64, 105.78, 56.18; MS-EI (m/z) = 256.



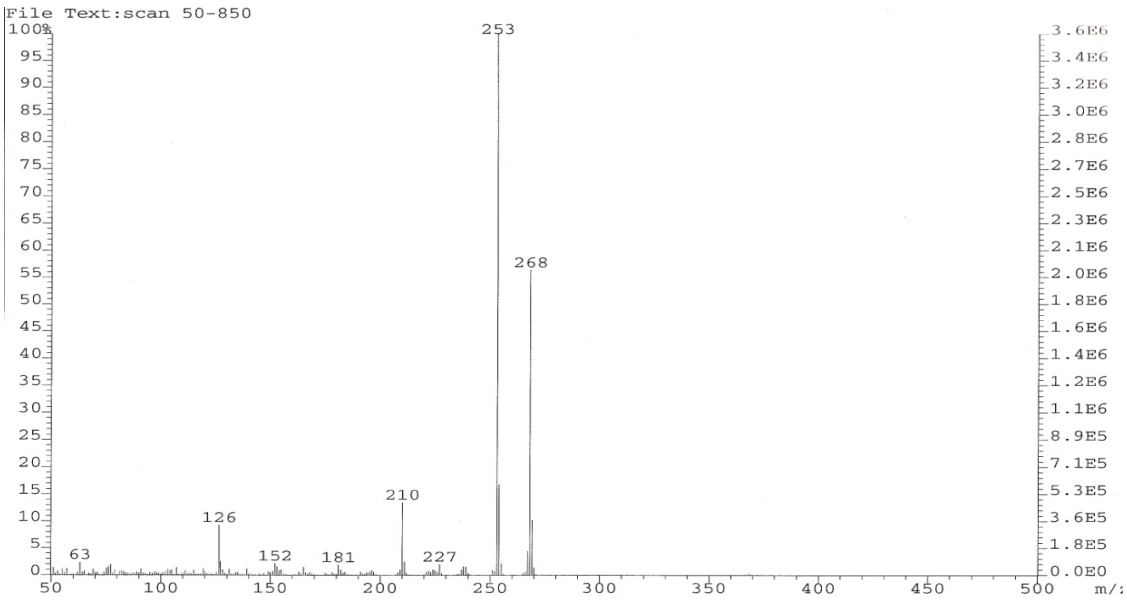


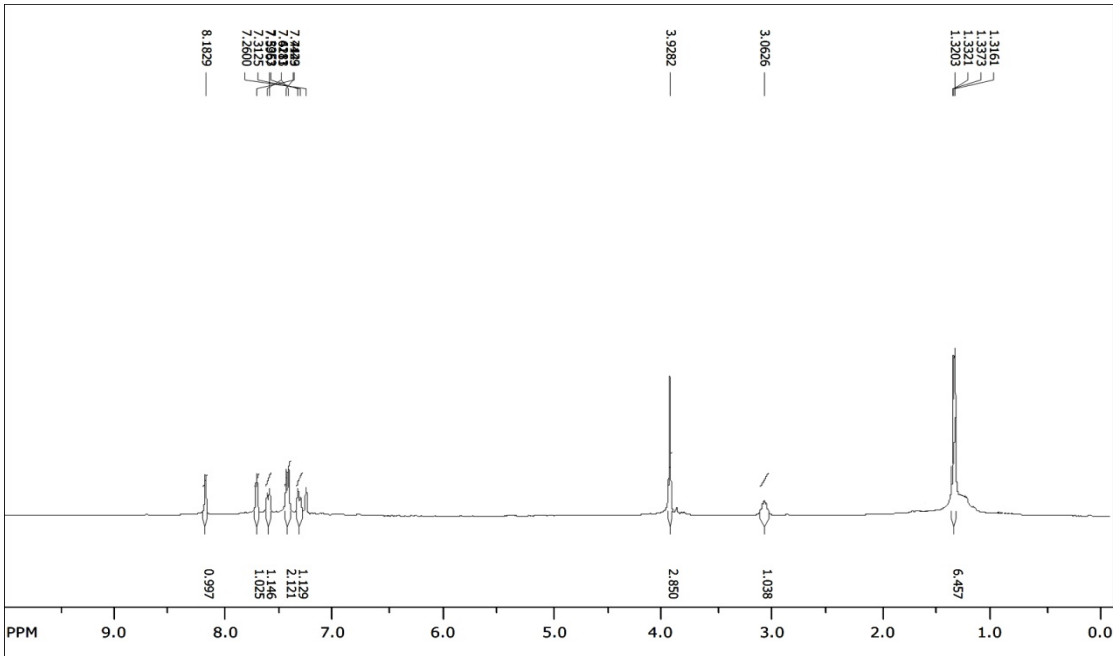


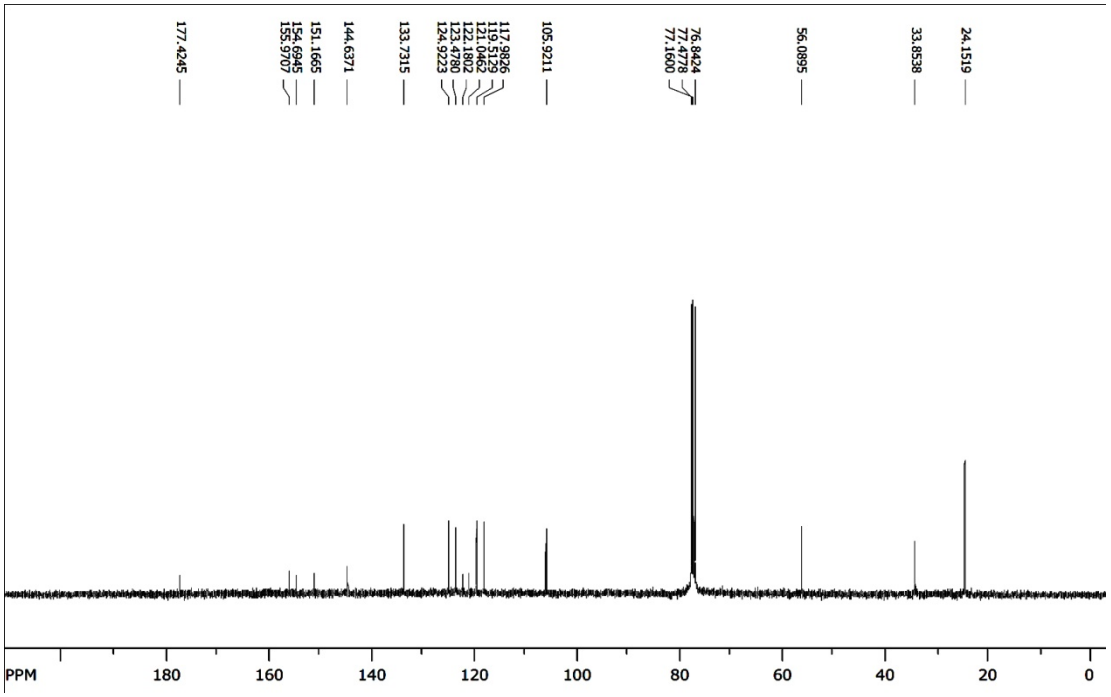


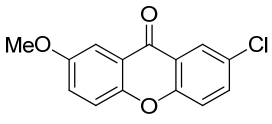
4r

V(hexane):V(EtOAc)=14:1 as the mobile phase; white solid, mp. 102-104°C; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.18 (s, 1H, ph-H), 7.71 (s, 1H, ph-H), 7.60 (d, 1H, J= 8.56 Hz, ph-H), 7.43 (d, 2H, J = 8.64 Hz ph-H), 7.32 (d, 1H, J=9.12Hz, ph-H), 3.92 (s, 3H, OCH_3), 3.06 (m, 1H, C<u>H</u>$(CH_3)_2$), 1.32 (d, 2×3H, J=6.36 Hz, CH(C<u>H</u>$_3)_2$; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 177.42, 154.97, 154.69, 151.16, 144.63, 133.73, 124.92, 123.47, 122.18, 121.04, 119.51, 117.98, 105.92, 56.08, 33.85, 24.15; MS-EI (m/z) = 268. HRMS(EI): m/z calcd for C17H16O3: 268.1099; found: 268.1090



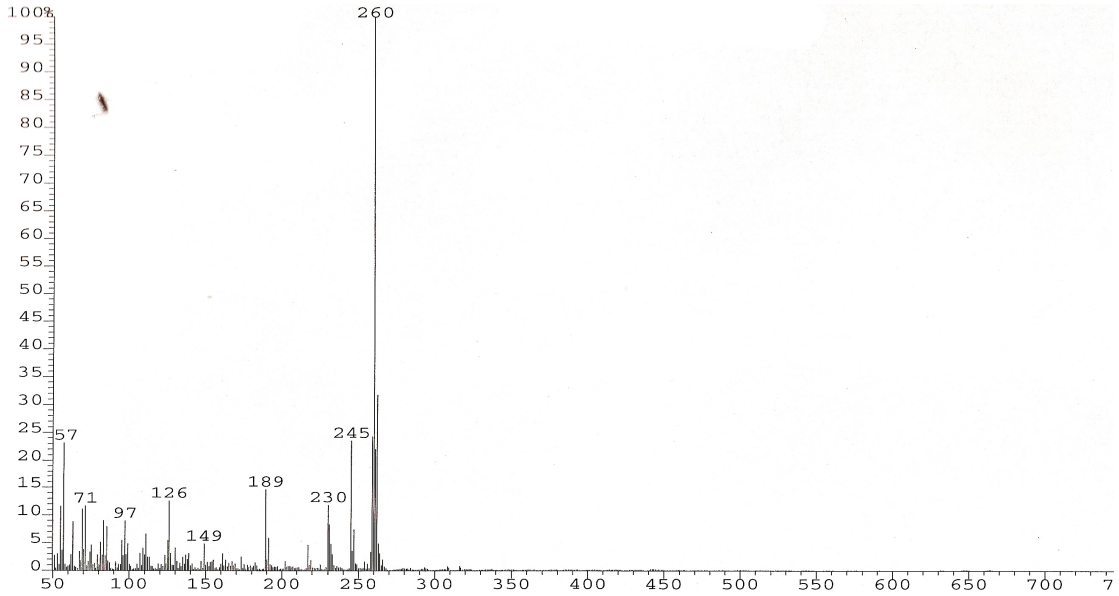






4s

V(hexane):V(EtOAc)=12:1 as the mobile phase; white solid, mp. 130-133°C [130-133°C[24]]; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.29 (d, 1H, J=2.36Hz, ph-H), 7.66 (m, 2H, ph-H), 7.43 (m, 2H, ph-H), 7.34 (m, 1H, ph-H), 3.66 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 176.15, 156.34, 154.54, 151.01, 134.84, 129.62, 126.06, 125.50, 122.16, 121.87, 119.87, 119.61, 105.84, 56.09; MS-EI (m/z) = 260.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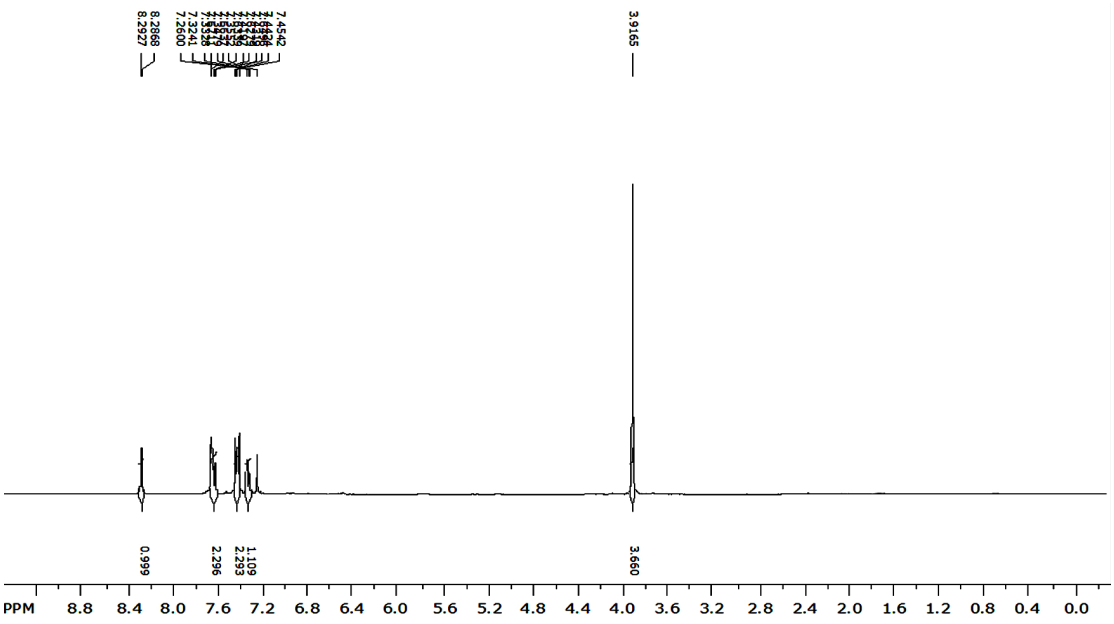
230
126
97
71
57
149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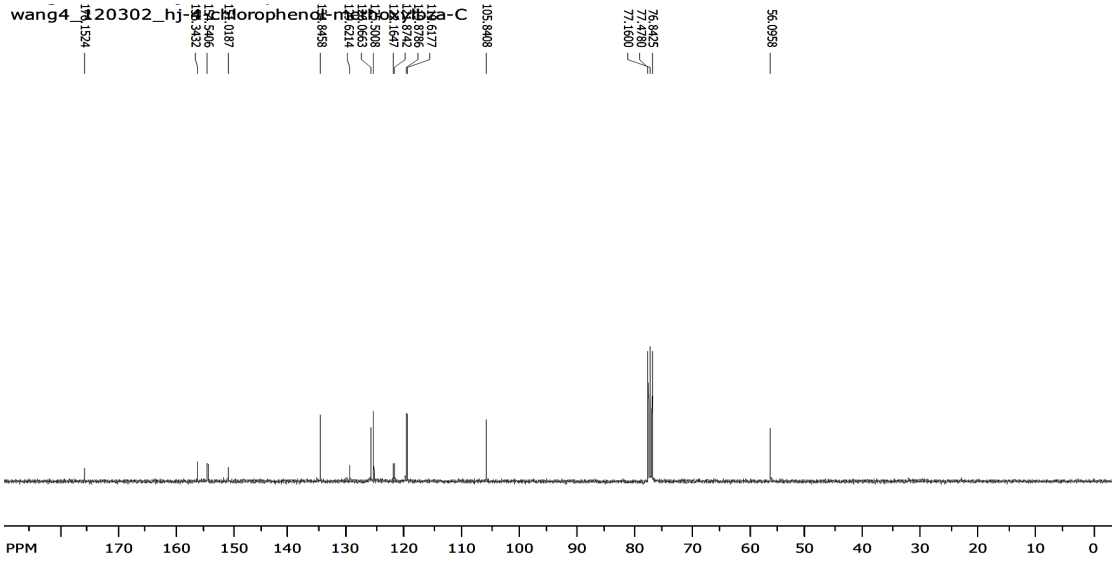
PPM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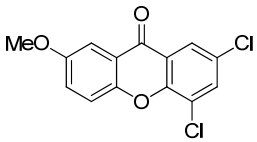
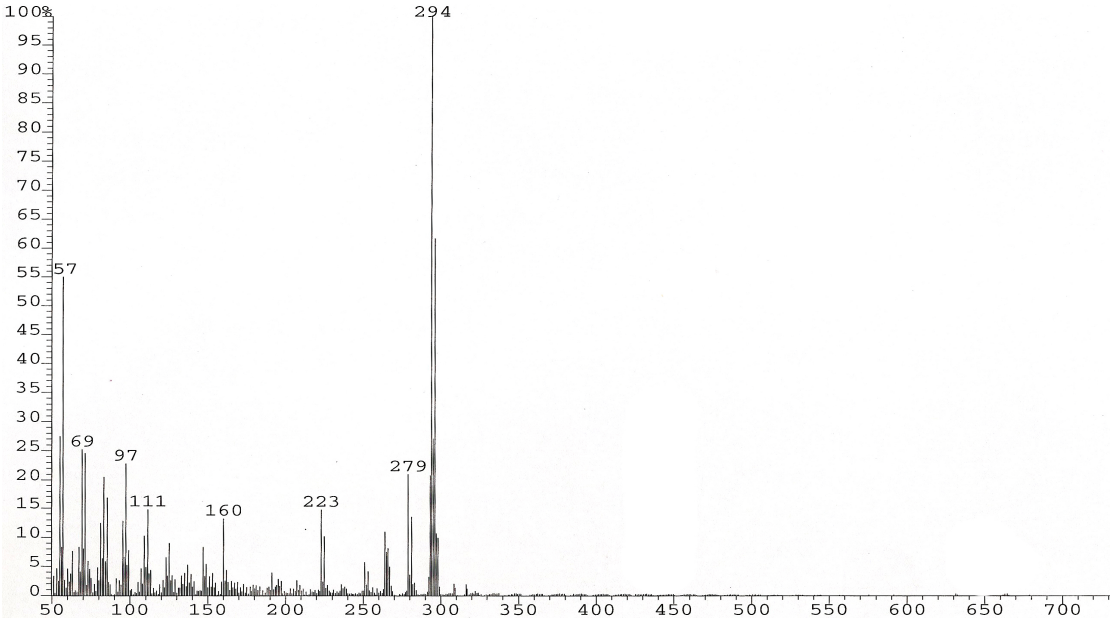
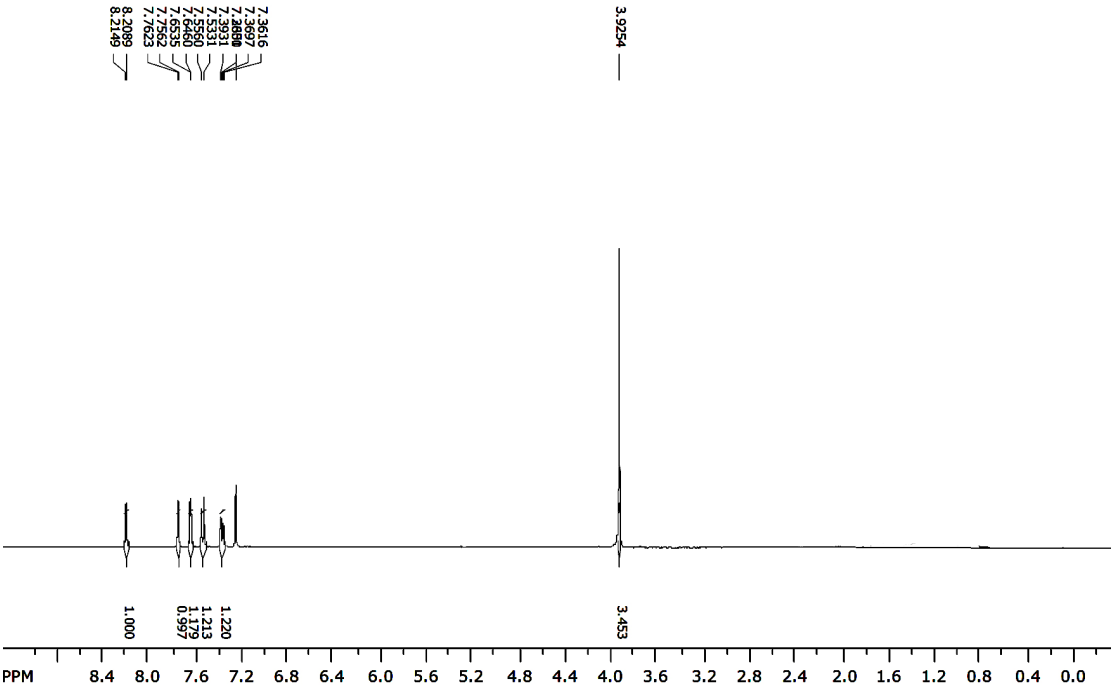
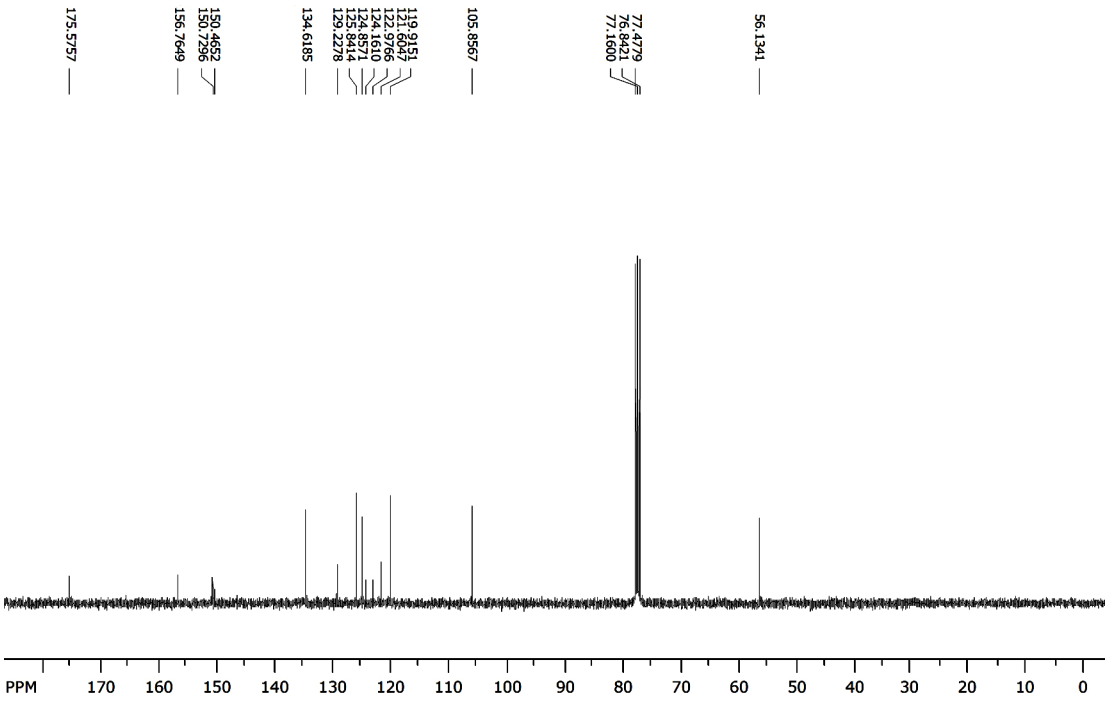


4t

V(hexane):V(EtOAc)=15:1 as the mobile phase; white solid, mp. 176-179^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.20 (d, 1H, J=2.40Hz, ph-H), 7.75 (d, 2H, J=2.44Hz, ph-H), 7.64 (d, 1H, J=3.00Hz, ph-H), 7.54 (m, 1H, ph-H), 7.37 (m, 1H, ph-H), 3.45 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 175.57, 156.76, 150.72, 150.46, 134.61, 129.22, 125.84, 124.85, 124.16, 122.97, 121.60, 119.91, 105.85, 56.13; MS-EI (m/z) = 294; HRMS(EI): m/z calcd for C14H8Cl2O3: 293.9850; found: 293.9841



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PPM
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