Supporting information

Synthesis of xanthones from the one-pot reaction of 2-nitrobenzyl alcohol with phenol catalyzed by $Cu(OTf)_2$-1,10-phenanthroline complex

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Contents

General remarks

Unless otherwise indicated, all commercially reagents and solvents were used directly without further purification. ^1H NMR and ^{13}C NMR were recorded at ambient temperature in $CDCl_3$. Chemical shift values are expressed as parts per million (ppm) and J values are in Hertz. Splitting patterns are indicated as s: singlet, d: doublet, t: triplet, q: quartet or combination, br. s broad singlet orm: multiplet. HRMS were recorded on the TOF-HRMS-EI at the Instruments' Center for Physical Science, University of Ji Nan.

General experimental procedure

2-Nitrobenzyl alcohol (76.2 mg, 0.5 mmol) and phenol (47 mg, 0.5 mmol) were placed into a 10 ml dry round-bottom flask. To this, 1 ml of redistilled toluene was added as the solvent. Anhydrous $Cu(OTf)_2$ (36.4 mg, 0.1 mmol) catalyst, 1,10-phenanthroline (18 mg, 0.1 mmol) ligand, and potassium phosphate (212 mg, 1 mmol) were subsequently introduced. The reaction mixture was heated and refluxed with rapid stirring for 12 hours. The reaction can proceed effectively both in the presence of O_2 and under the exclusion of oxygen. The progress of the reaction was monitored by thin-layer chromatography (TLC). After the reaction was completed, it was cooled to

room temperature, extracted by (15mL×3) EtOAc, washed with saturated saline, the organic phases were combined, dried with anhydrous sodium sulfate for more than 30 min, rotary evaporation of solvent, and the target product was obtained by column chromatography separation of 20/1=petroleum ether:EtOAc, a light-yellow solid of 110.8 mg, and the structure was determined by solvent NMR detection done with $CDCl_3$.

Liquid chromatogram

Figure 1 The chromatogram of 2-nitrobenzyl alcohol

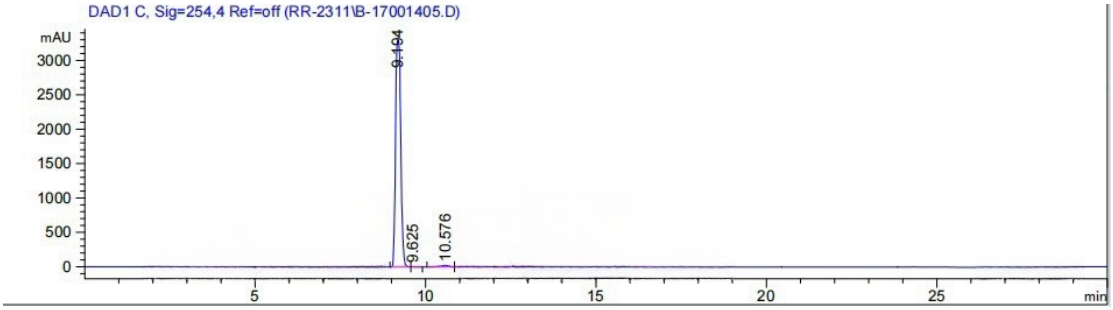


Figure 2 The chromatogram of 2-nitrobenzaldehyde

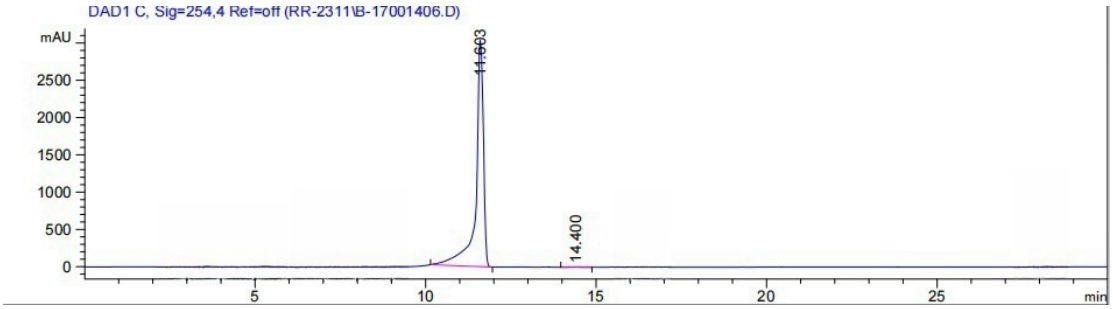


Figure 3 The chromatogram of the xanthone product 3aa generated from the reaction under O_2 conditions

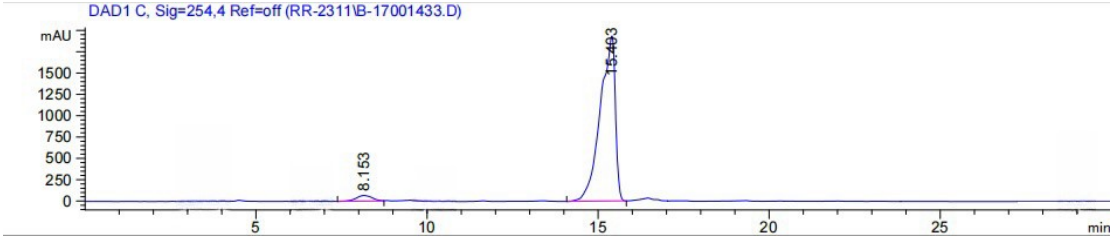
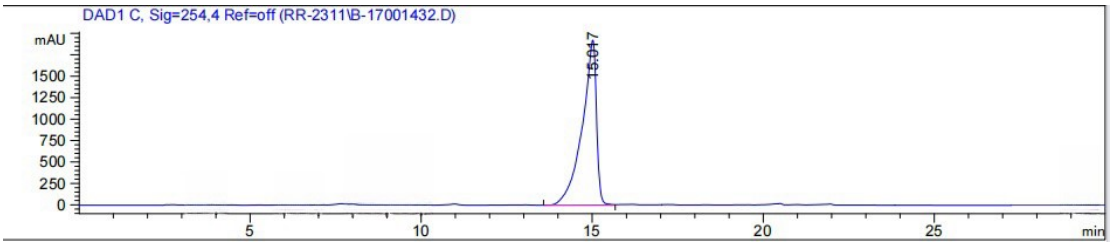
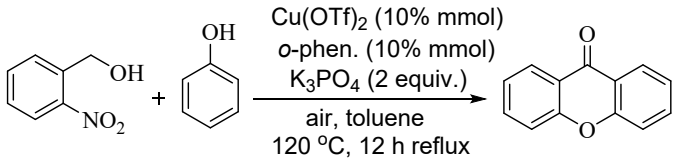


Figure 4 The chromatogram of the xanthone product 3aa generated from the reaction under N_2 conditions



Synthesis reactions with different substrates

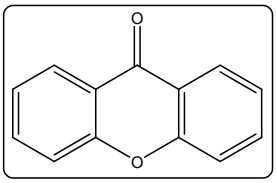


1a **2a** **3aa**

Entry	1a	2a	T/°C	Product	Yield(%)[a,b]
1	5-H	H	120	3aa	88
2	5-H	2-CH_3	120	3ab	69
3	5-H	4-CH_3	120	3ac	82
4	5-H	2-CH_2CH_3	120	3ad	75
5	5-H	2-$CH(CH_3)_2$	120	3ae	68
6	5-H	4-OCH_3	120	3af	77
7	5-H	2-$C(CH_3)_3$	120	3ag	85
8	5-H	4-$C(CH_3)_3$	120	3ah	88
9	5-H	2-Naphthol	120	3ai	73
10	5-H	2-Cl	120	3aj	36
11	5-H	4-Cl	120	3ak	21
12	5-H	4-Br	120	3al	17
13	5-H	4-I	120	3am	trace
14	5-CH_3	H	120	3ba	79
15	5-OCH_3	H	120	3ca	72
16	5-Cl	H	120	3da	28

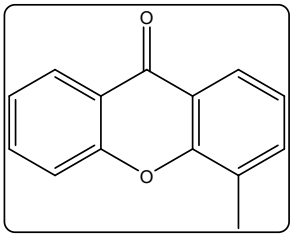
[a] 2-Nitrobenzyl alcohol (0.5 mmol), phenol (0.5 mmol), toluene (1 ml), $Cu(OTf)_2$ (36.4 mg, 0.1 mmol), 1,10-phenanthroline (10 mol%), K_3PO_4 (212 mg, 1 mmol), 120 °C. [b] GC-yields.

Characterization data of all substances



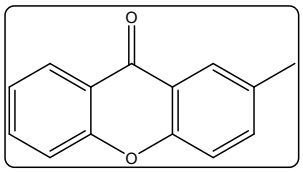
3aa 9H-Xanthen-9-one

Compound **3aa** was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc= 10:1) to give a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) =7.39 (td, *J*= 8 Hz, 2H), 7.50 (q, *J*= 4 Hz, 2H), 7.73 (td, *J*= 4 Hz, 2H), 8.35 (dd, *J*= 8 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) =117.6, 117.7, 118.2, 118.7, 121.8, 123.2, 124.3, 126.5, 126.8, 134.2, 134.9, 156.1, 177.2.



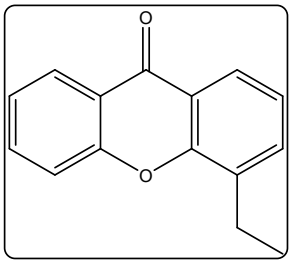
3ab 4-Methyl-9H-xanthen-9-one

Compound **3ab** was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc= 10:1) to give a pale yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) =2.58 (s, 3H), 7.28 (t, *J*= 8 Hz, 1H), 7.39 (t, *J*= 8 Hz, 1H), 7.56 (t, *J*= 8 Hz, 2H), 7.73 (t, *J*= 12 Hz, 1H), 8.20 (dd, *J*= 12 Hz, 1H), 8.35 (dd, *J*= 8 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) =16.0, 118.3, 121.9, 121.9, 123.6, 124.1, 124.5, 126.9, 127.5, 134.9, 135.9, 154.8, 156.3, 177.8.



3ac(3ba) 2-Methyl-4aH-xanthen-9(9aH)-one

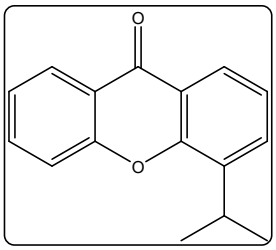
Compound **3ac** was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc= 10:1) to give a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) =2.44 (s, 3H), 7.35 (d, *J* = 8 Hz, 2H), 7.44 (d, *J* = 8 Hz, 1H), 7.49 (dd, *J* = 8 Hz, 1H), 7.68 (t, *J* = 8 Hz, 1H), 8.09 (s, 1H), 8.32 (dd, *J* = 8 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) =21.0, 117.9, 118.1, 121.6, 121.9, 123.8, 126.1, 126.8, 133.8, 134.8, 136.2, 154.5, 156.3, 177.4.



3ad 4-Ethyl-4aH-xanthen-9(9aH)-one

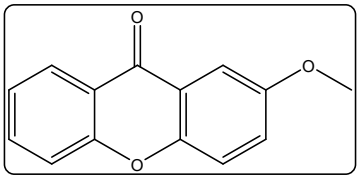
Compound **3ad** was prepared according to the general procedure and purified by column

chromatography (Petroleum Ether: EtOAc= 10:1) to give a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) =1.36 (t, *J* = 8 Hz, 3H), 3.00 (q, *J* = 4 Hz, 2H), 7.30 (t, *J* = 8 Hz, 1H), 7.37 (t, *J* = 8 Hz, 1H), 7.53(d, *J* = 8 Hz, 1H), 7.58(d, *J* = 8 Hz, 1H), 7.72 (t, *J* = 8 Hz, 1H), 8.20 (dd, *J* = 8 Hz, 1H), 8.34 (dd, *J* = 8 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.3, 23.1, 118.2, 121.8, 121.9, 123.8, 124.0, 124.5, 126.9, 133.3, 134.3, 134.8, 154.4, 156.2, 177.8.



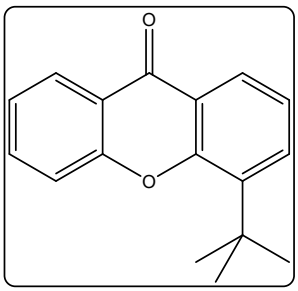
3ae 4-Isopropyl-4aH-xanthen-9(9aH)-one

Compound **3ae** was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc= 10:1) to give a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.38 (d, *J*= 8 Hz, 6H), 3.71 (quint, *J*= 8 Hz, 1H), 7.35 (quint, *J*= 8 Hz, 2H), 7.52 (dd, *J*= 8 Hz, 1H), 7.64 (dd, *J*= 8 Hz, 1H), 7.71 (t, *J* = 8 Hz, 1H), 8.20 (dd, *J* = 8 Hz, 1H), 8.34 (dd, *J* = 8 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.9, 27.3, 118.1, 121.7, 122.0, 122.2, 123.8, 124.0, 124.3, 126.8, 131.7, 134.8, 137.7, 153.8, 156.2, 177.8.



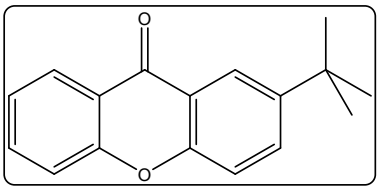
3af(3ca) 2-Methoxy-9H-xanthen-9-one

Compound **3af** was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc= 10:1) to give a white solid. H-NMR (400 MHz, $CDCl_3$): δ (ppm) =3.92 (s, 3H), 7.35 (m, 2H), 7.46 (q, *J*= 8 Hz, 2H), 7.70(t, *J*= 8 Hz, 2H), 8.34(dd,*J*= 8 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 56.0, 105.9, 118.0, 119.5, 121.3, 122.2, 123.8, 125.0, 126.7, 134.6, 151.1, 156.1, 156.2, 177.2.



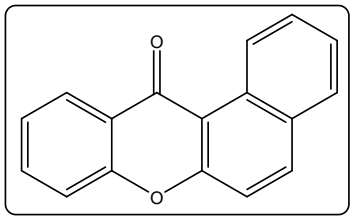
3ag 4-Tert-butyl-4aH-xanthen-9(9aH)-one

Compound **3ag** was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc= 10:1) to give a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) =1.58 (s, 9H), 7.32 (t, *J* = 8 Hz, 1H), 7.40 (t, *J* = 8 Hz, 1H), 7.56 (d, *J* = 8 Hz, 2H), 7.73 (m, 1H), 8.26 (dd, *J* = 8 Hz, 1H), 8.35 (dd, *J* = 8 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) =30.2, 30.3, 35.4, 118.1, 121.6, 122.7, 123.7, 123.9, 124.1, 125.1, 126.9, 132.2, 134.9, 139.0, 155.2, 155.8, 177.9.



3ah 2-Tert-butyl-4aH-xanthen-9(9aH)-one

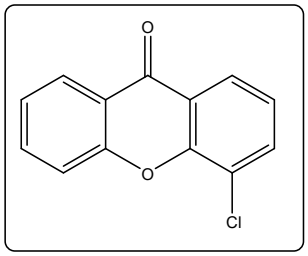
Compound **3ah** was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc= 10:1) to give a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) =1.39 (s, 9H), 7.40 (m, 3H), 7.69 (t, *J* = 12 Hz, 1H), 7.77 (dd, *J* = 12 Hz, 1H), 8.34 (d, *J* = 8 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) =31.5, 31.7, 34.9, 117.8, 118.1, 121.3, 122.0, 122.6, 123.9, 126.0, 126.9, 132.9, 134.8, 147.3, 154.5, 156.4, 177.6.



3ai 12H-Benzo[a]xanthen-12-one

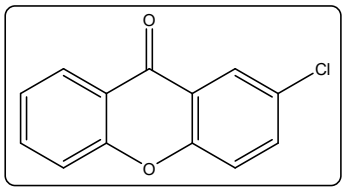
Compound **3ai** was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc= 10:1) to give a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) =7.24 – 7.41 (m, 2H), 7.53 (d, J = 6.3 Hz, 1H), 7.58 (d, J = 5.5 Hz, 1H), 7.69 –

7.76 (m, 2H), 7.83 (d, J = 6.0 Hz, 1H), 8.20 (d, J = 6.0 Hz, 1H), 8.34 (d, J = 6.0 Hz, 1H), 8.72 (d, J = 6.0 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) =118.0, 121.6, 121.7, 123.6, 123.8, 124.3, 126.1, 126.3, 126.8, 126.9, 129.4, 131.0, 134.6, 137.0, 154.1, 156.0, 177.6.



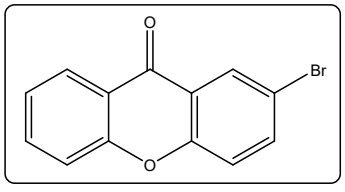
3aj 4-Chloro-9H-xanthen-9-one

Compound **3aj** was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc= 10:1) to give a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) =7.40 – 7.46 (m, 2H), 7.62 (d, J = 6.3 Hz, 1H), 7.74 – 7.85 (m, 2H), 8.05 (d, J = 6.1 Hz, 1H), 8.48 (d, *J* = 8 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) =118.2, 118.3, 121.8, 121.9, 123.5, 124.3, 125.2, 126.5, 126.8, 134.7, 134.9, 156.1, 177.2.



3ak 2-Chloro-9H-xanthen-9-one

Compound **3ak** was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc= 10:1) to give a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) =7.24 – 7.46 (m, 2H), 7.52 (d, J = 6.3 Hz, 2H), 7.75 (t, J = 5.8 Hz, 2H), 8.36 (d, J = 6.0 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) =118.3, 121.1, 121.8, 123.5, 124.3, 124.8, 125.3, 126.8, 134.2, 134.8, 151.1, 156.1, 177.2.

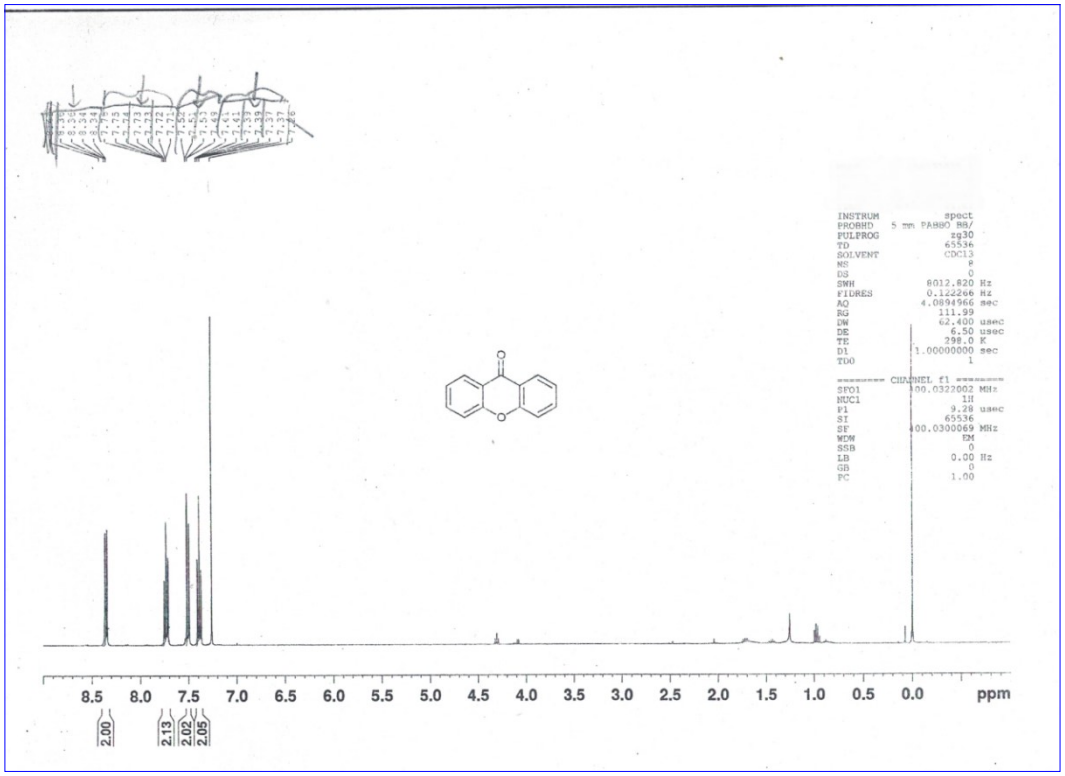


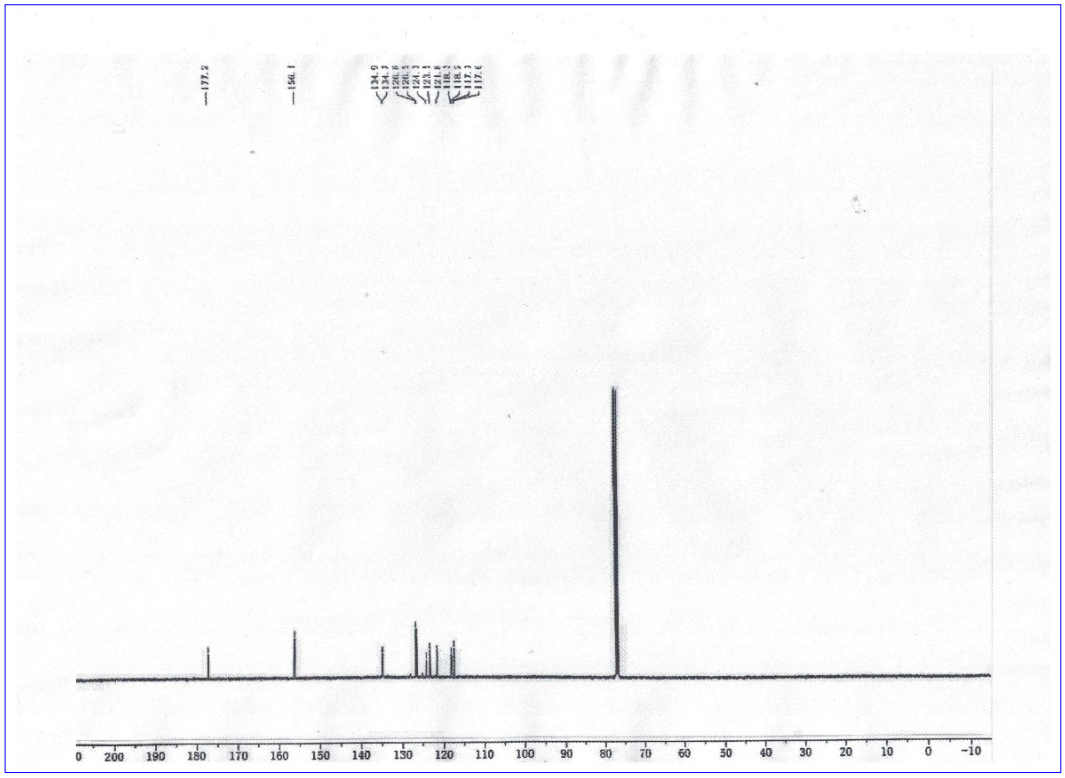
3al 2-Bromo-9H-xanthen-9-one

Compound **3al** was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc= 10:1) to give a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) =7.43 (dt, J = 7.7, 3.2 Hz, 2H), 7.52 (d, J = 8.5 Hz, 1H), 7.73 – 7.86 (m, 2H), 8.35 (d, J = 8.1 Hz, 1H), 8.48 (d, J = 2.5 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) =117.0, 117.7, 119.6, 121.4, 123.0, 126.9, 129.0, 129.3, 135.2, 137.6, 154.8, 155.9, 175.9.

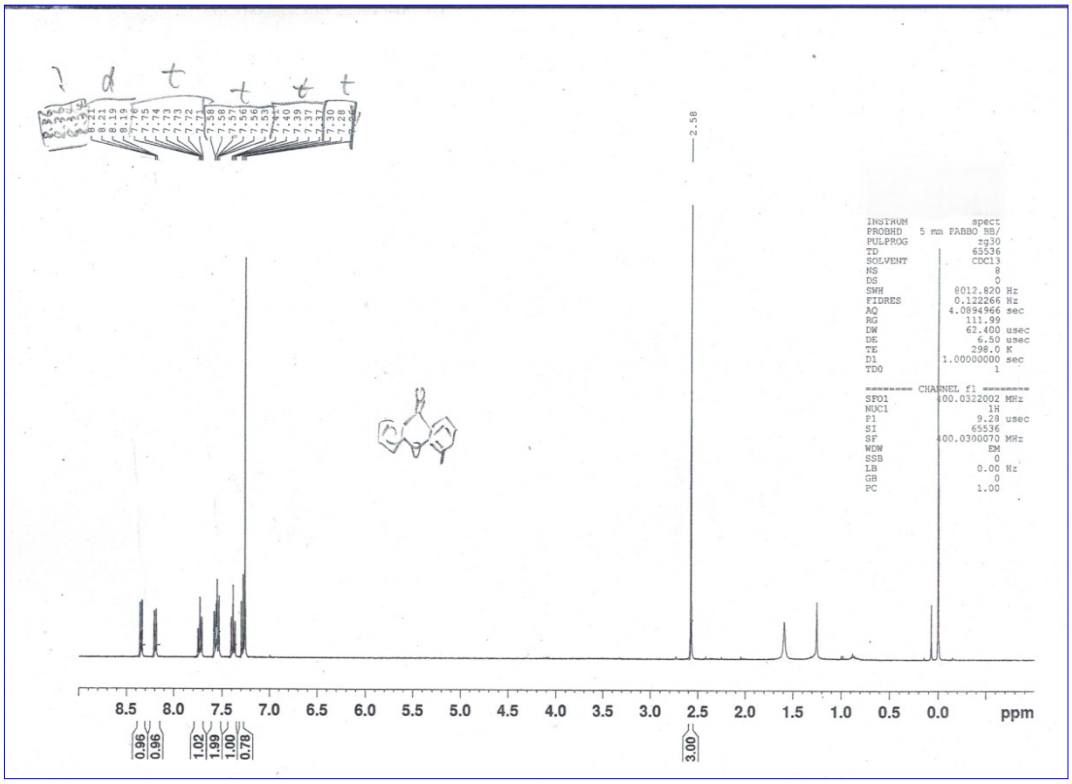
NMR Spectra of all compounds

3aa 9H-Xanthen-9-one





3ab 4-Methyl-9H-xanthen-9-one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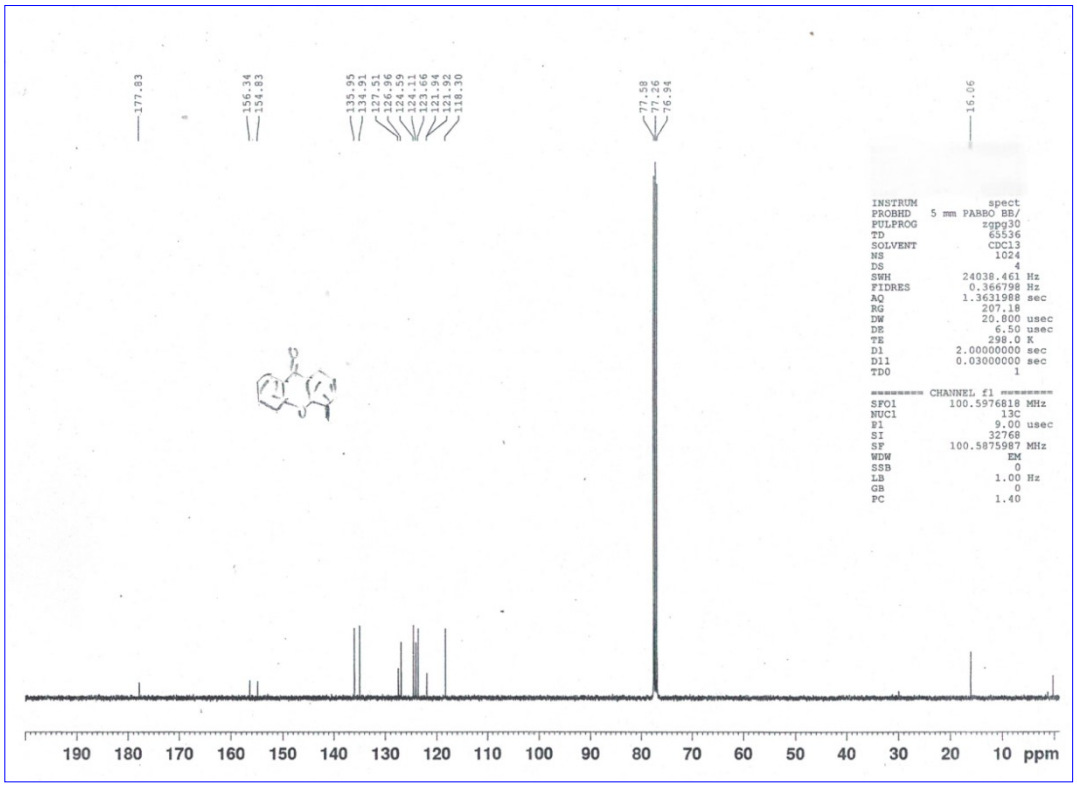
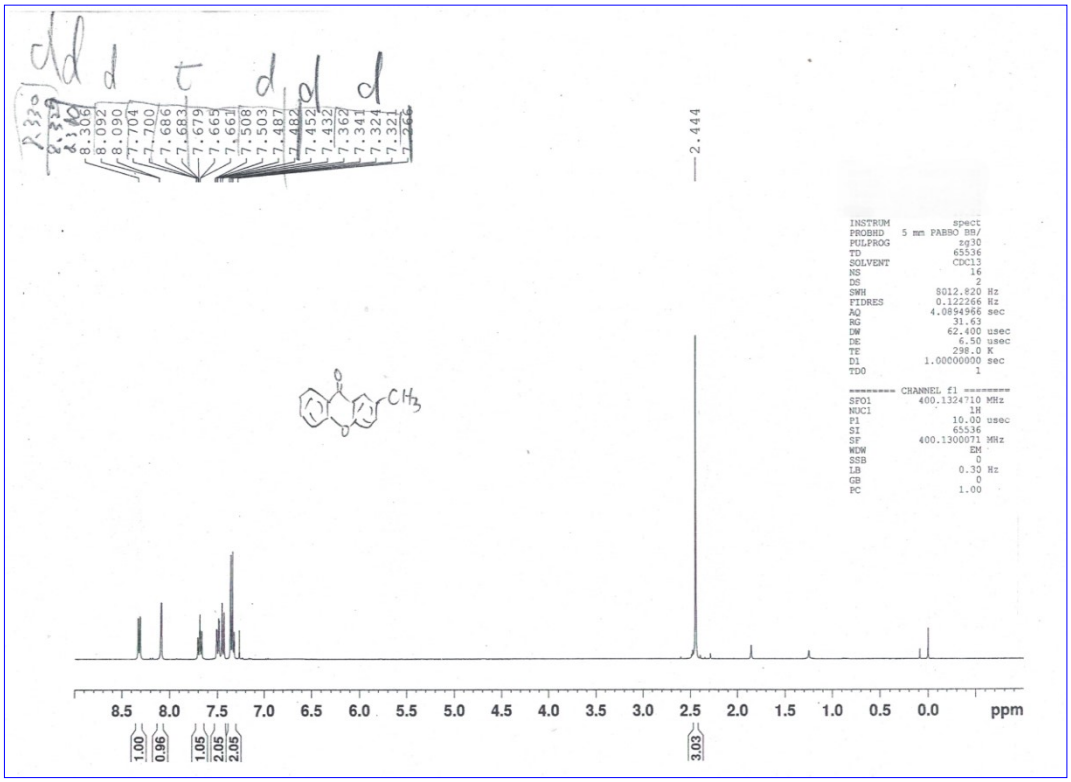


3ac 2-Methyl-4aH-xanthen-9(9aH)-one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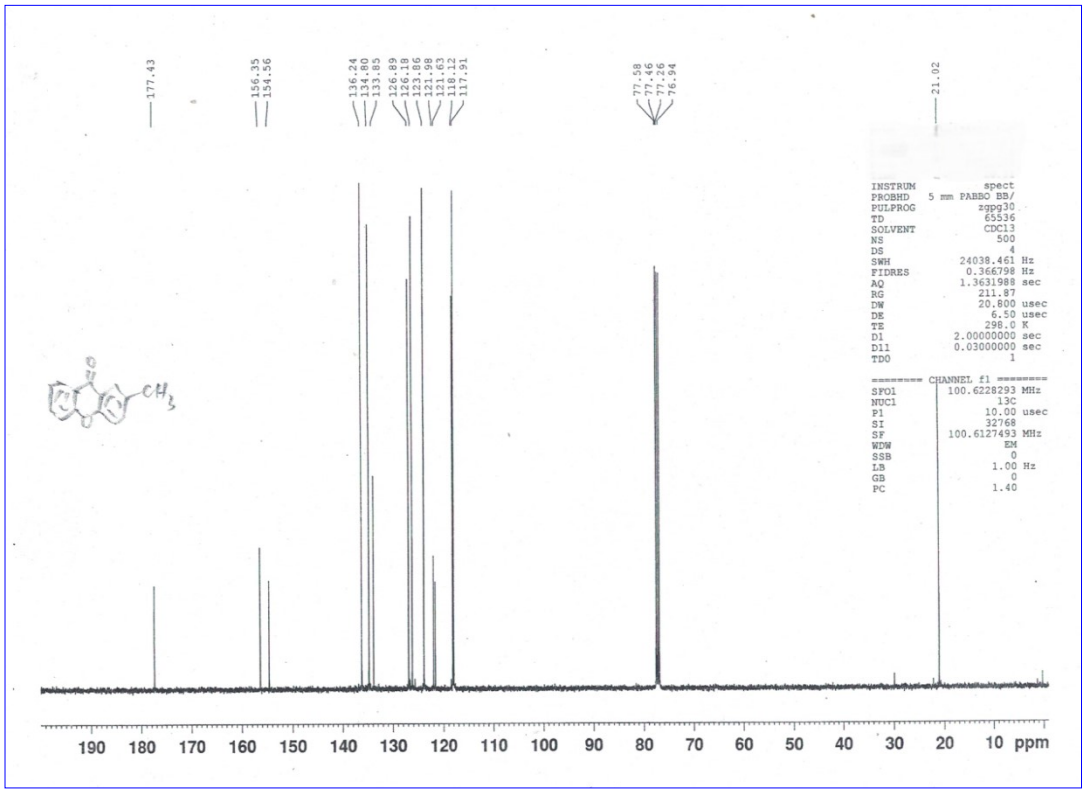
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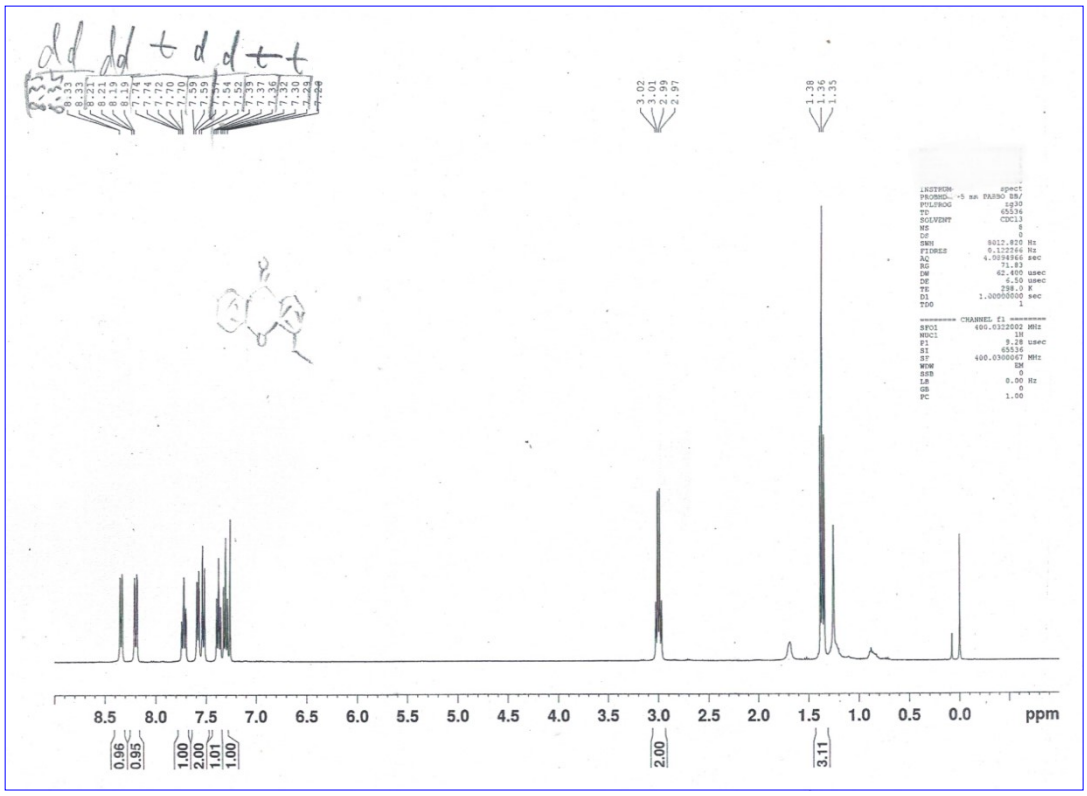
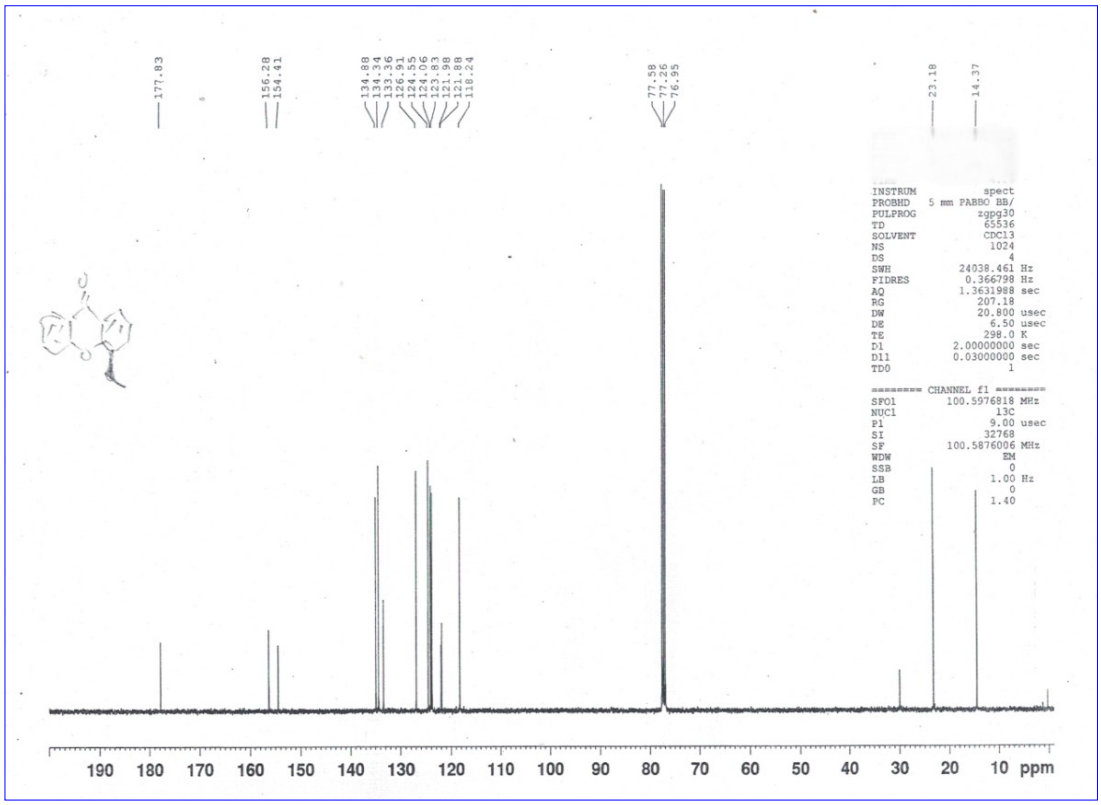
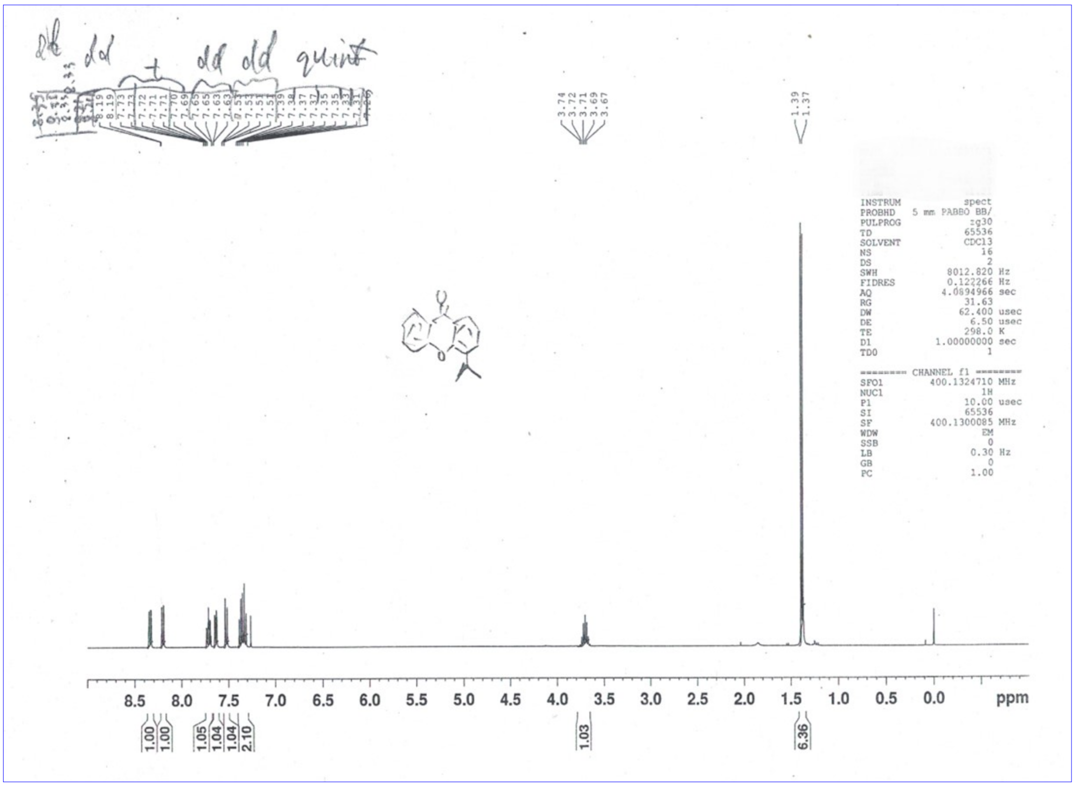
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127493 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

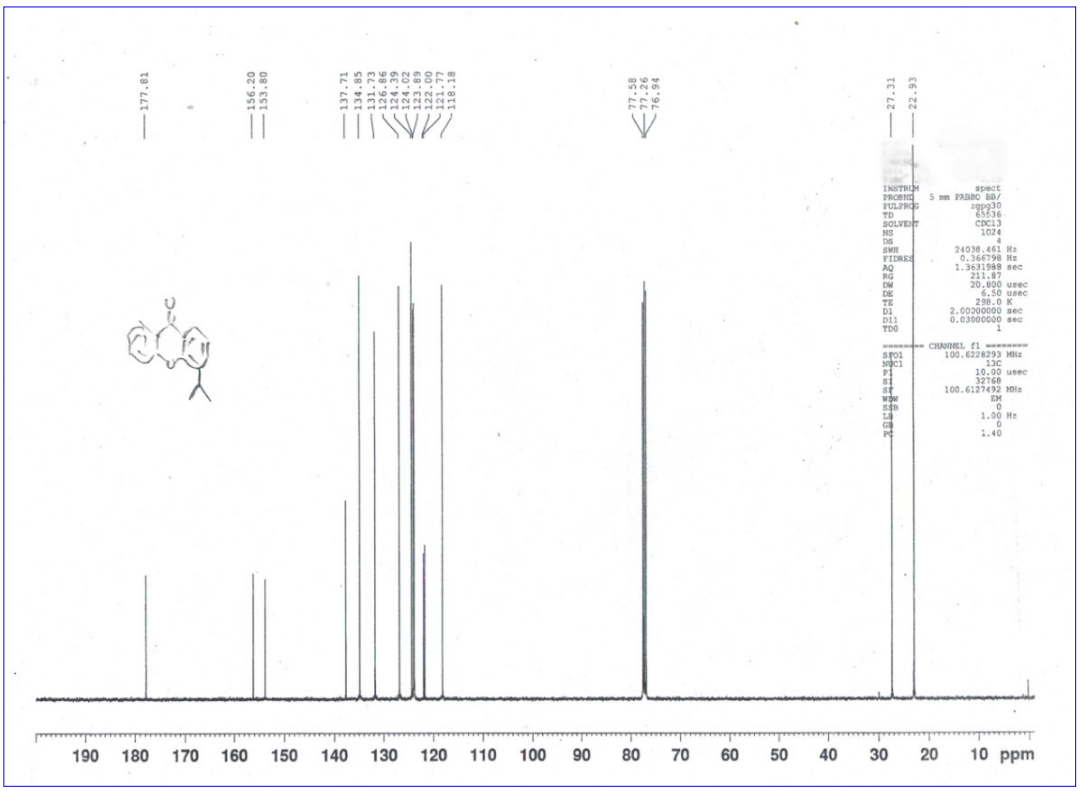
3ad 4-Ethyl-4aH-xanthen-9(9aH)-one



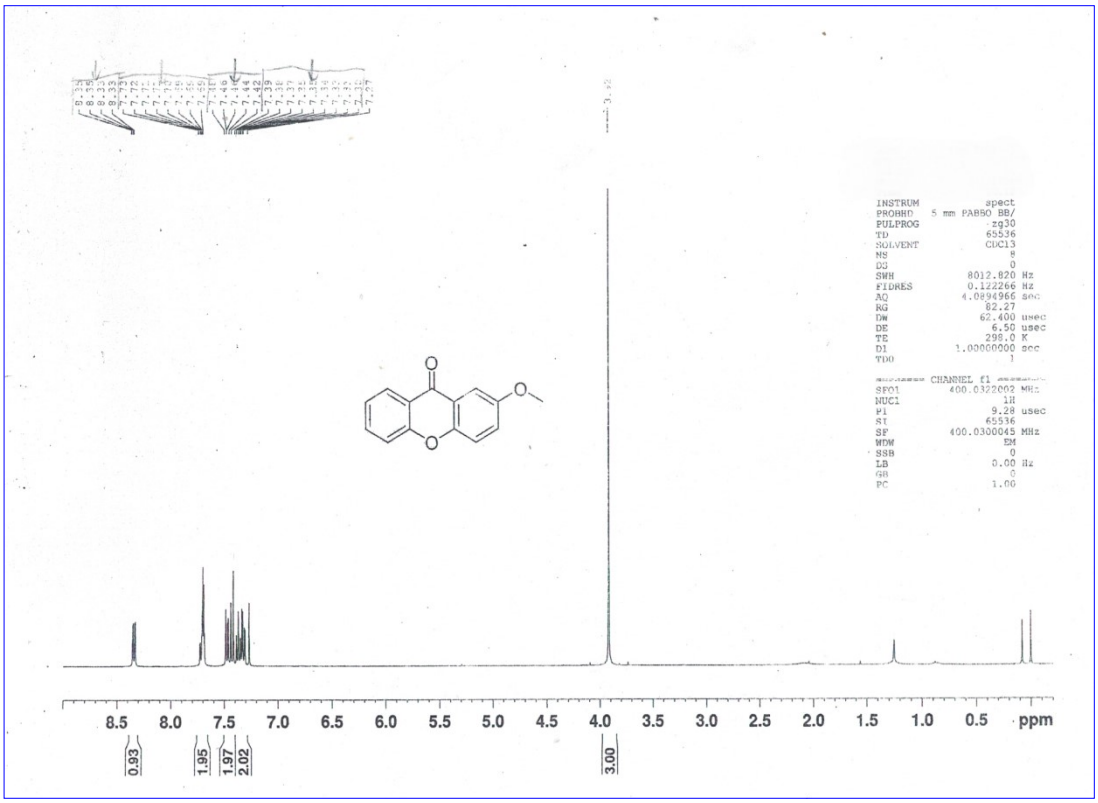


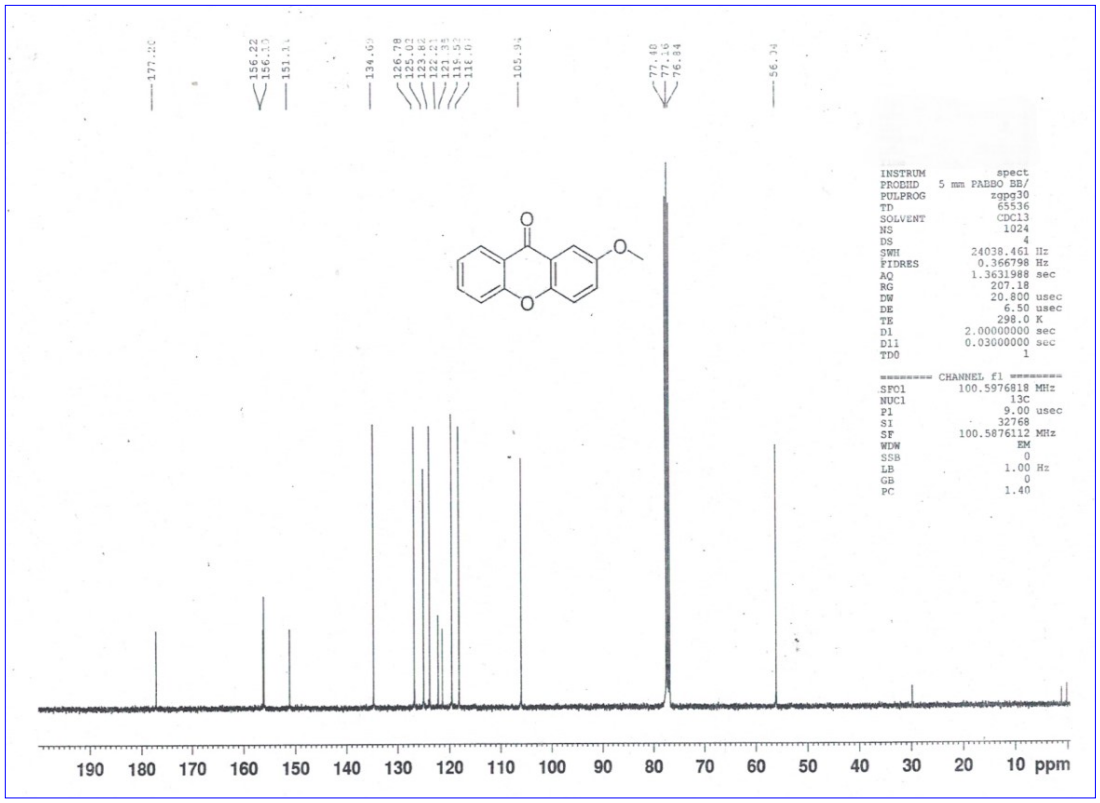
3ae 4-Isopropyl-4aH-xanthen-9(9aH)-one


INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 31.63
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300085 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

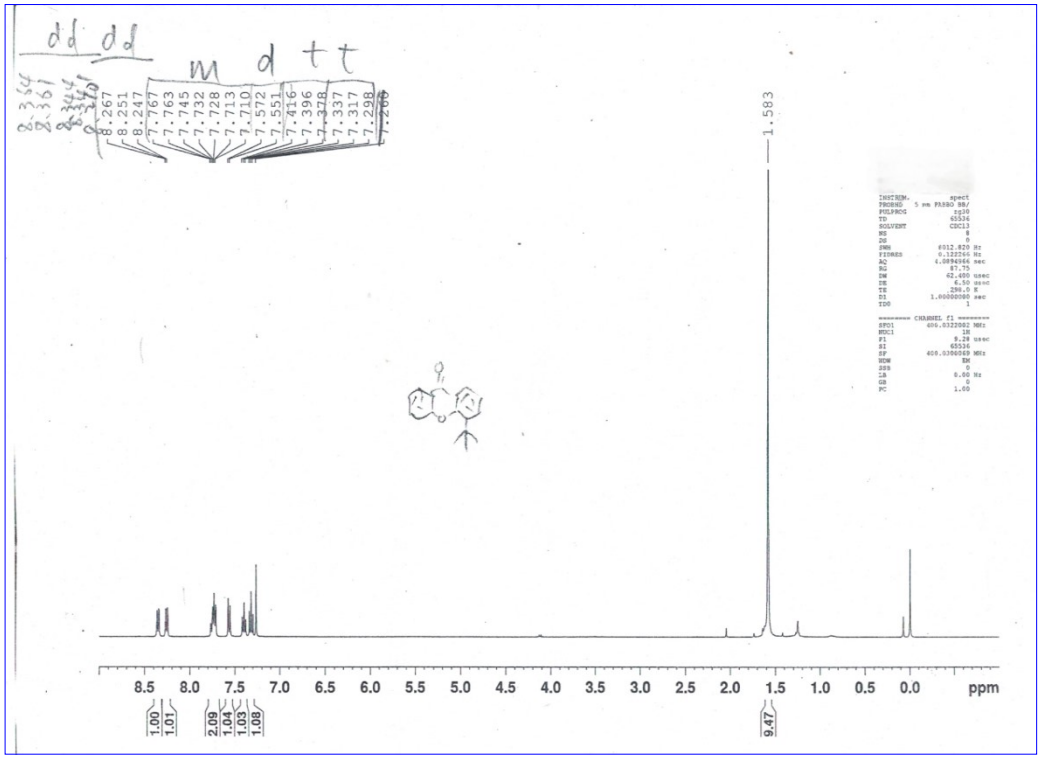


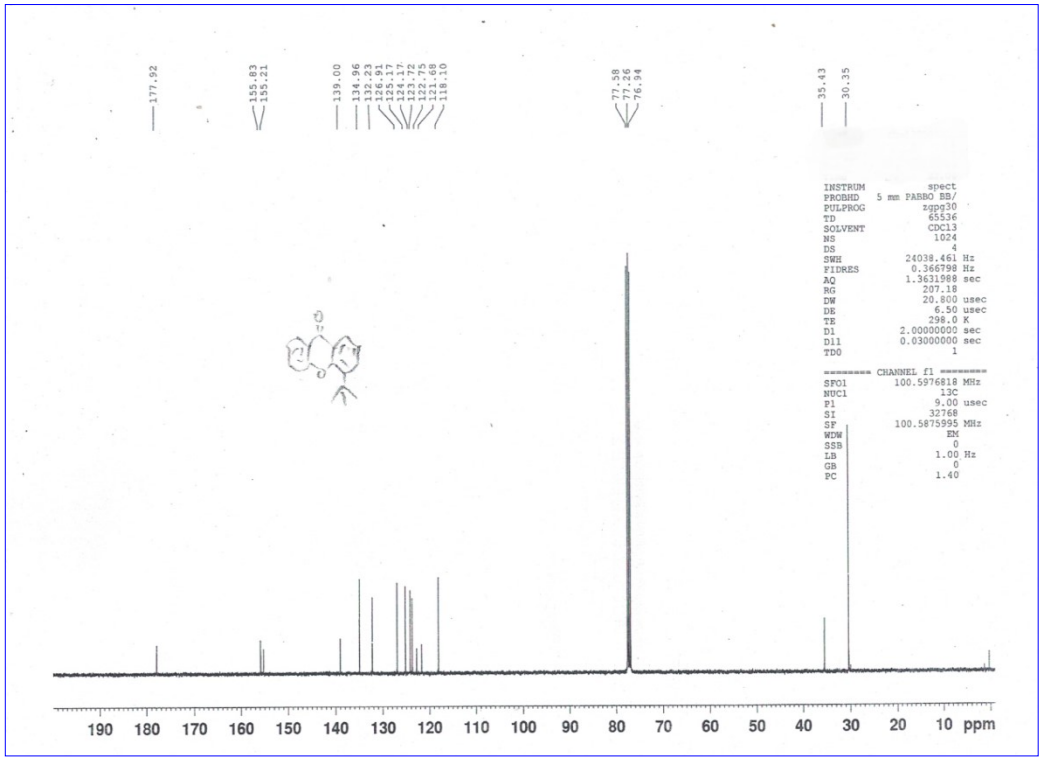
3af 2-Methoxy-9H-xanthen-9-one


INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 82.27
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
SFO1 400.0322002 MHz
NUC1 1H
P1 9.28 usec
SI 65536
SF 400.0300045 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.93
1.95
1.97
2.02
3.00

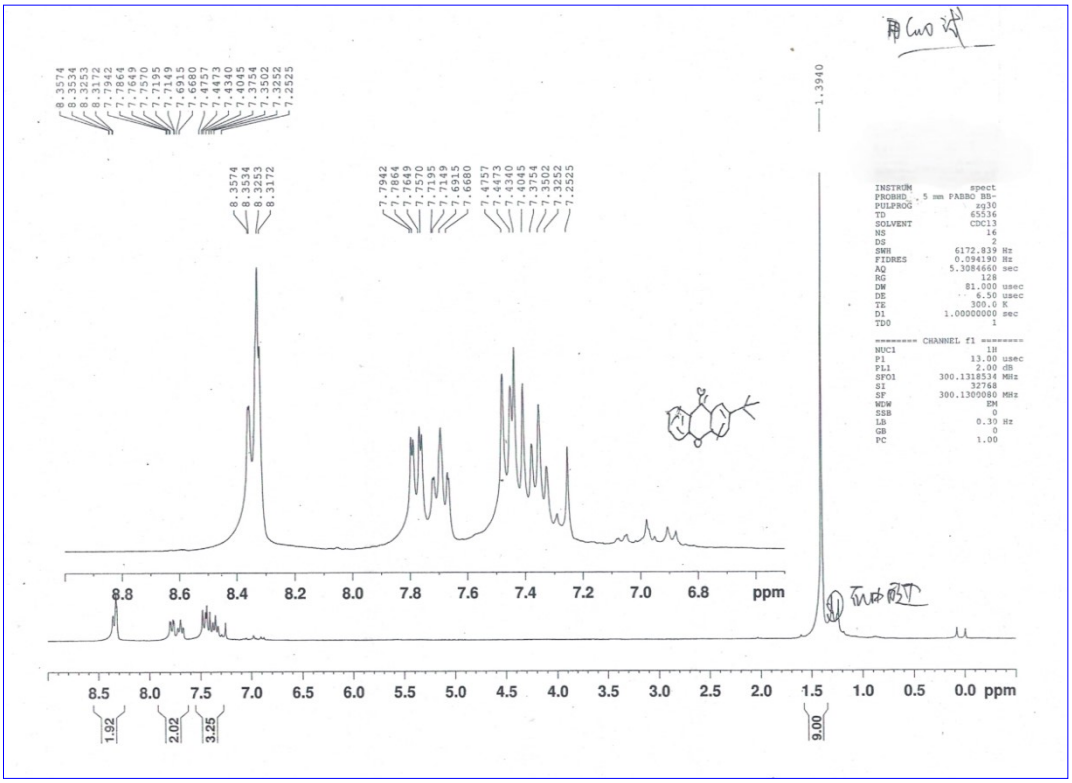


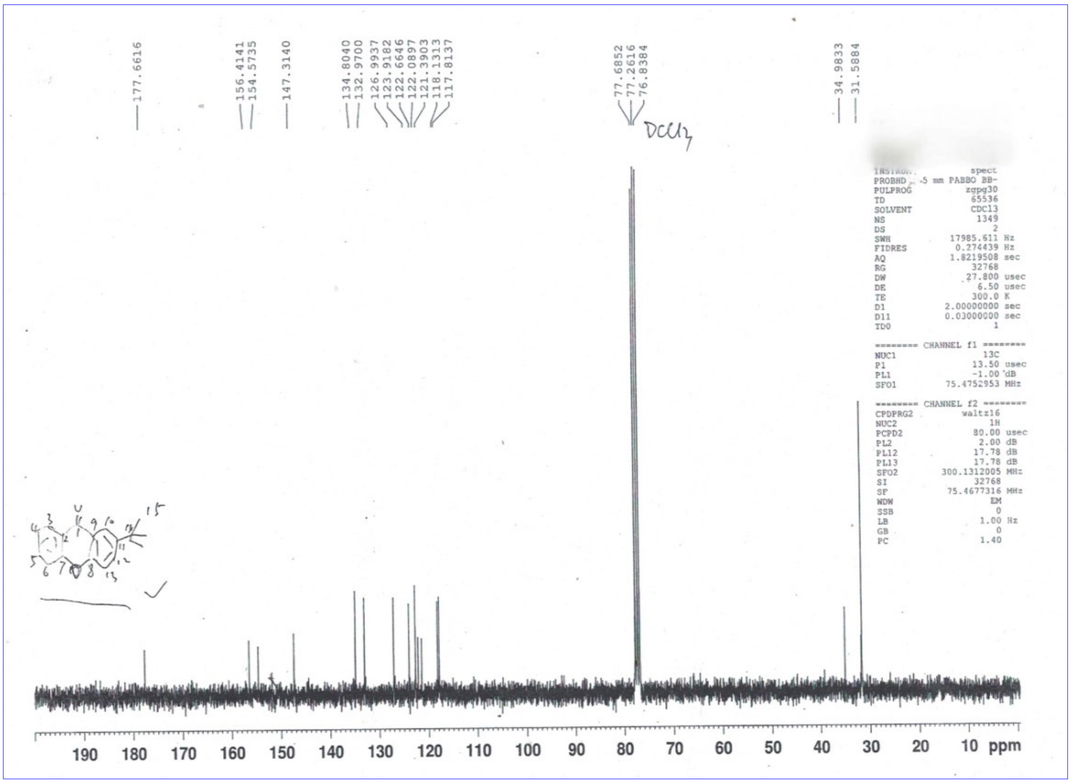
3ag 4-Tert-butyl-4aH-xanthen-9(9aH)-one


dd dd
m d t t
8.267
8.251
8.247
7.767
7.763
7.745
7.732
7.728
7.713
7.710
7.572
7.551
7.416
7.396
7.378
7.337
7.317
7.298
7.266
1.583
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.01
2.09
1.04
1.03
1.08
9.47

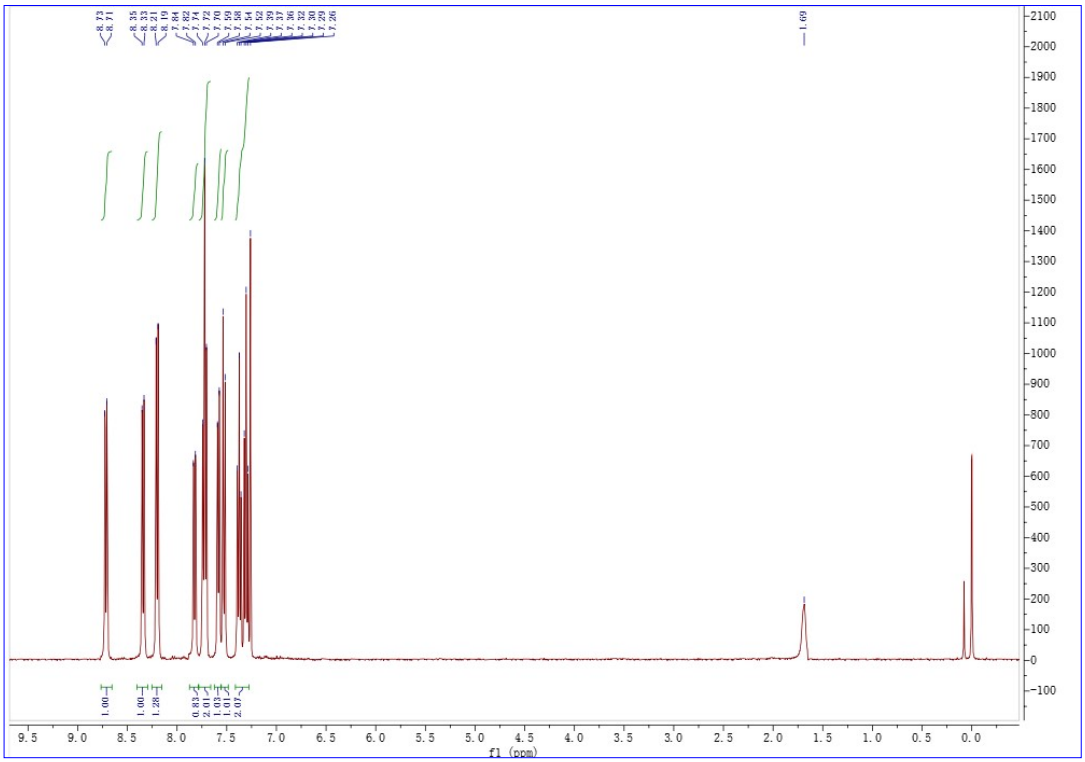


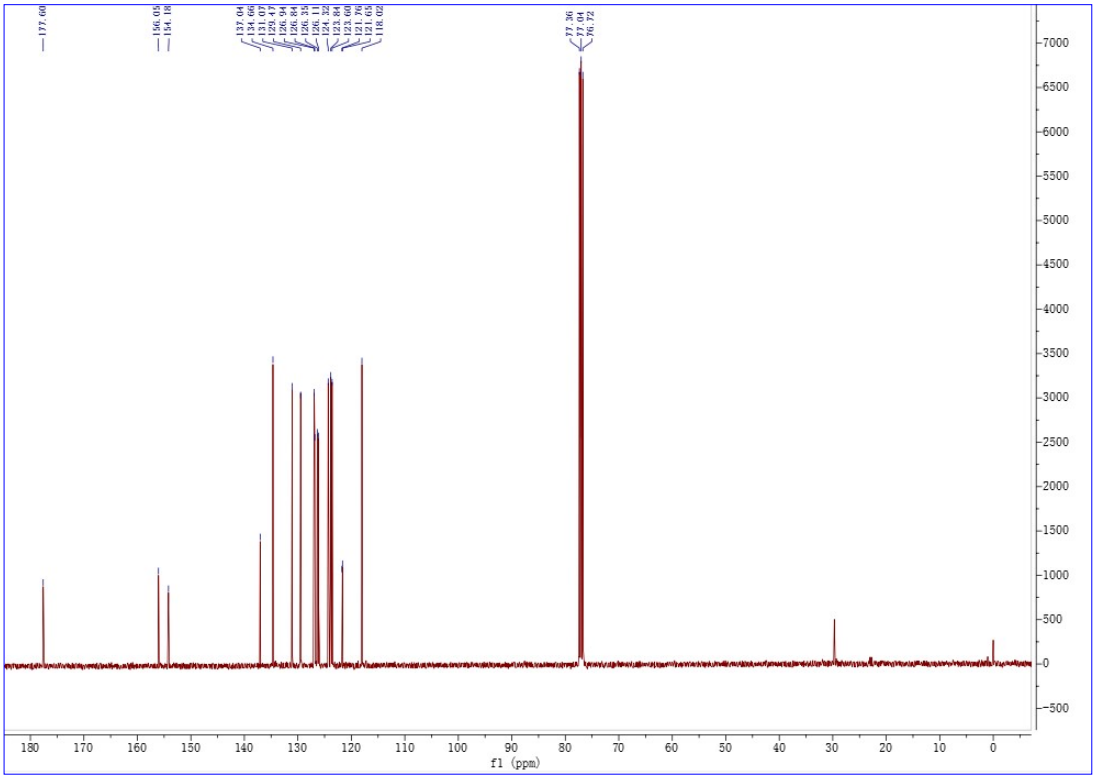
3ah 2-Tert-butyl-4aH-xanthen-9(9aH)-one


8.3574
8.3534
8.3253
8.3172
7.7942
7.7864
7.7669
7.7570
7.7195
7.7149
7.6915
7.6680
7.4757
7.4473
7.4340
7.4045
7.3754
7.3502
7.3252
7.2525
1.3940
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300080 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.92
2.02
3.25
9.00

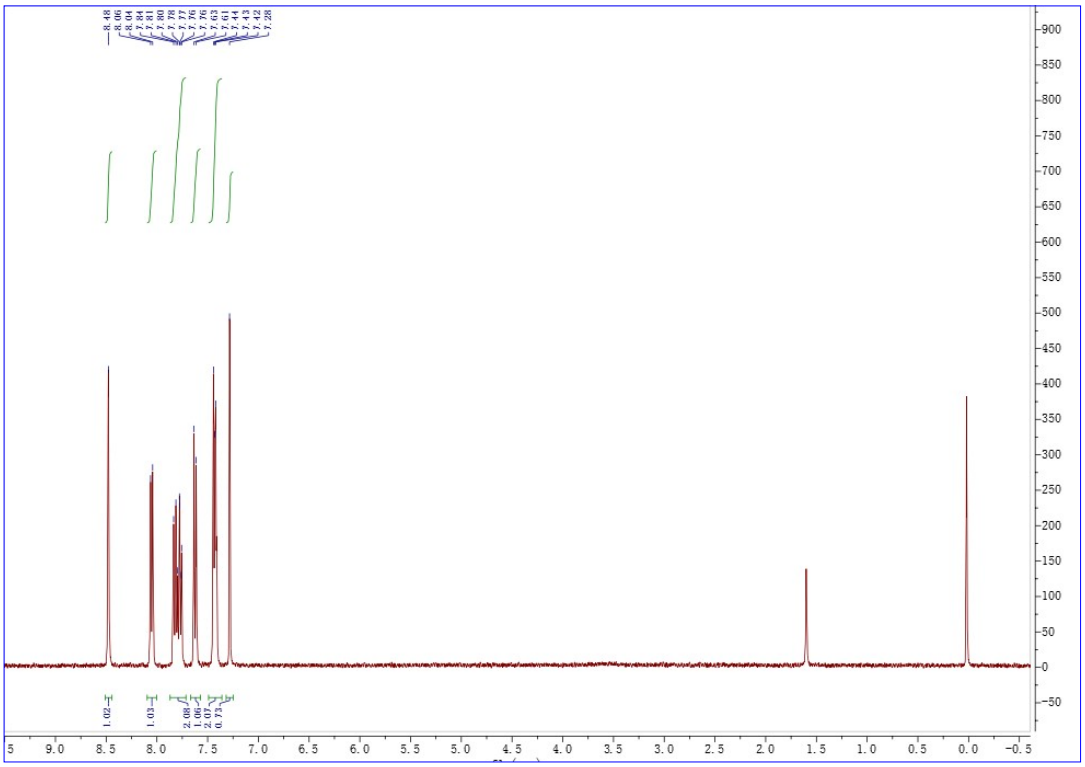

177.6616
156.4141
154.5735
147.3140
134.8040
132.9700
126.9937
123.9182
122.6646
122.0897
121.3903
118.1313
117.8137
77.6852
77.2616
76.8384
34.9833
31.5884
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

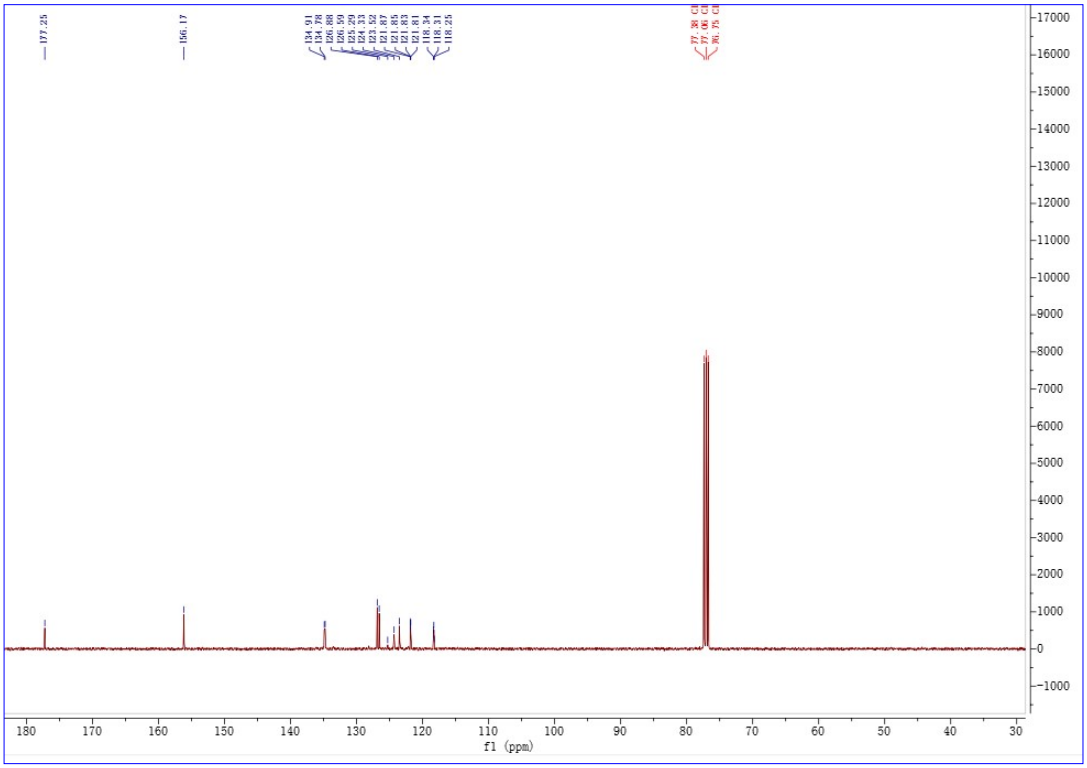
3ai 12H-Benzo[a]xanthen-12-one



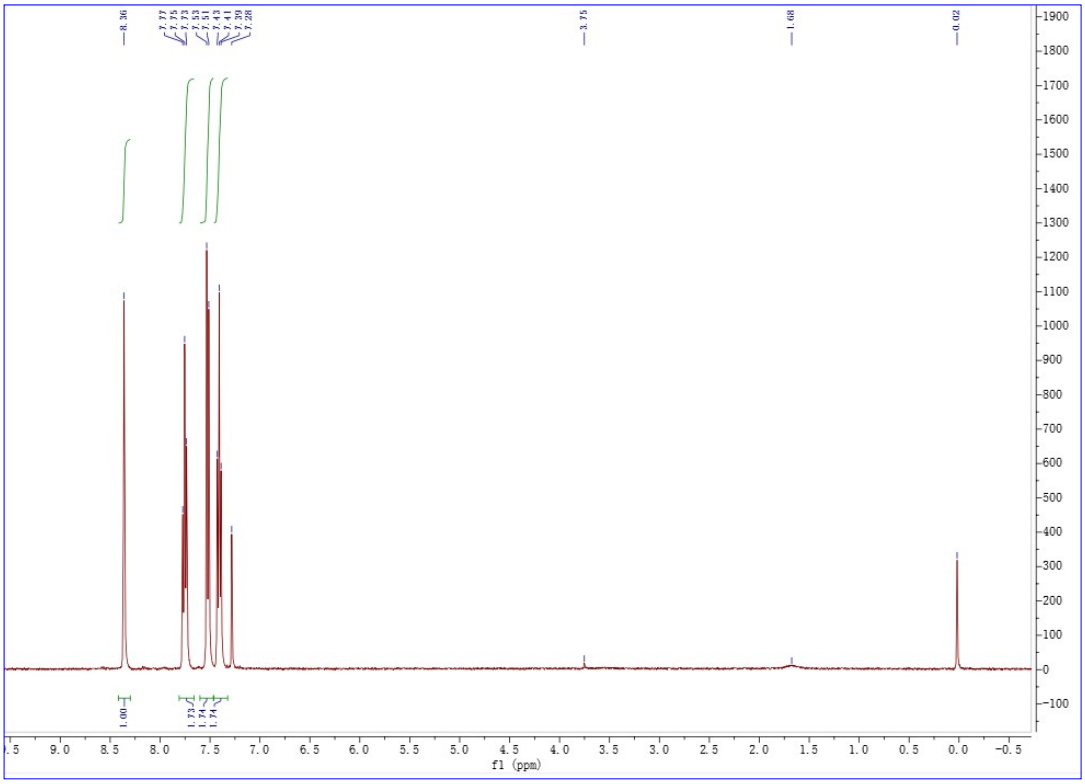


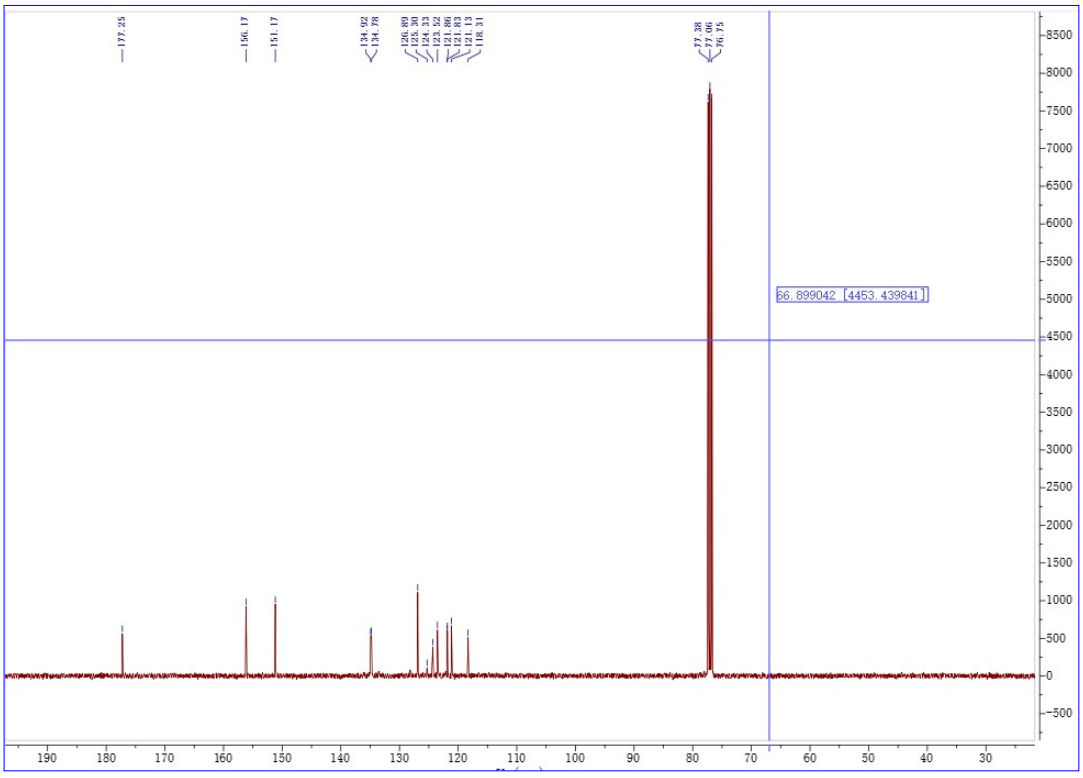
3aj 2-Chloro-9H-xanthen-9-one



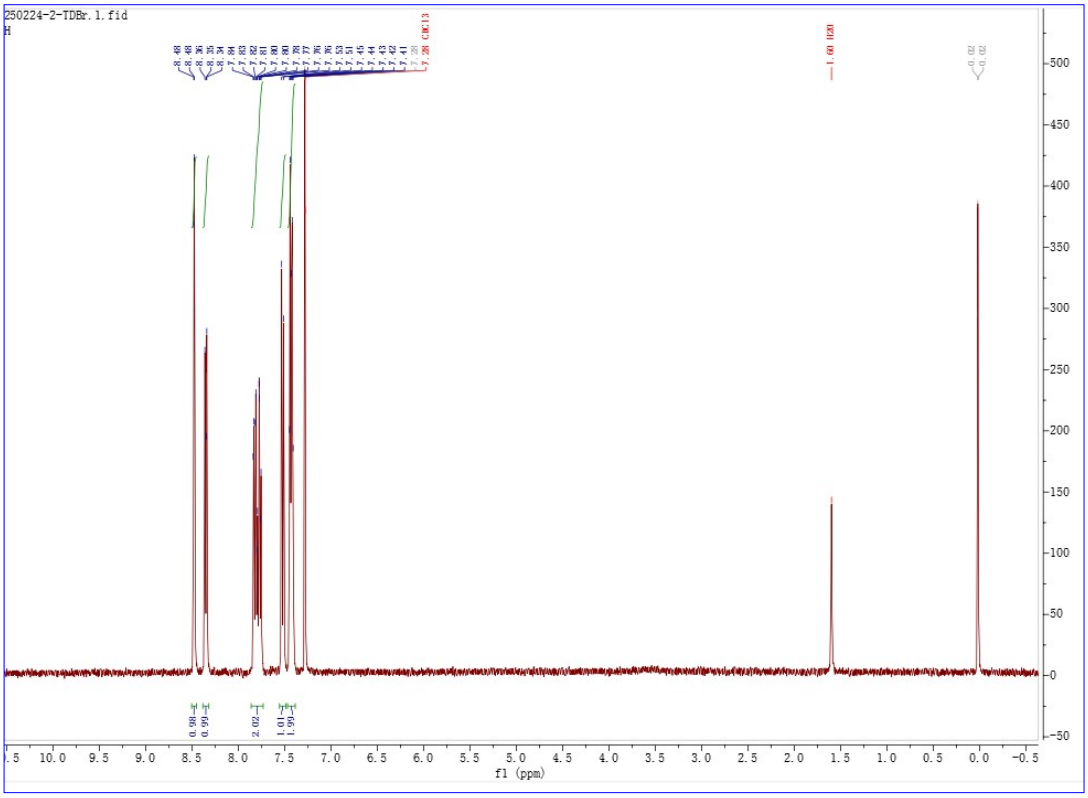


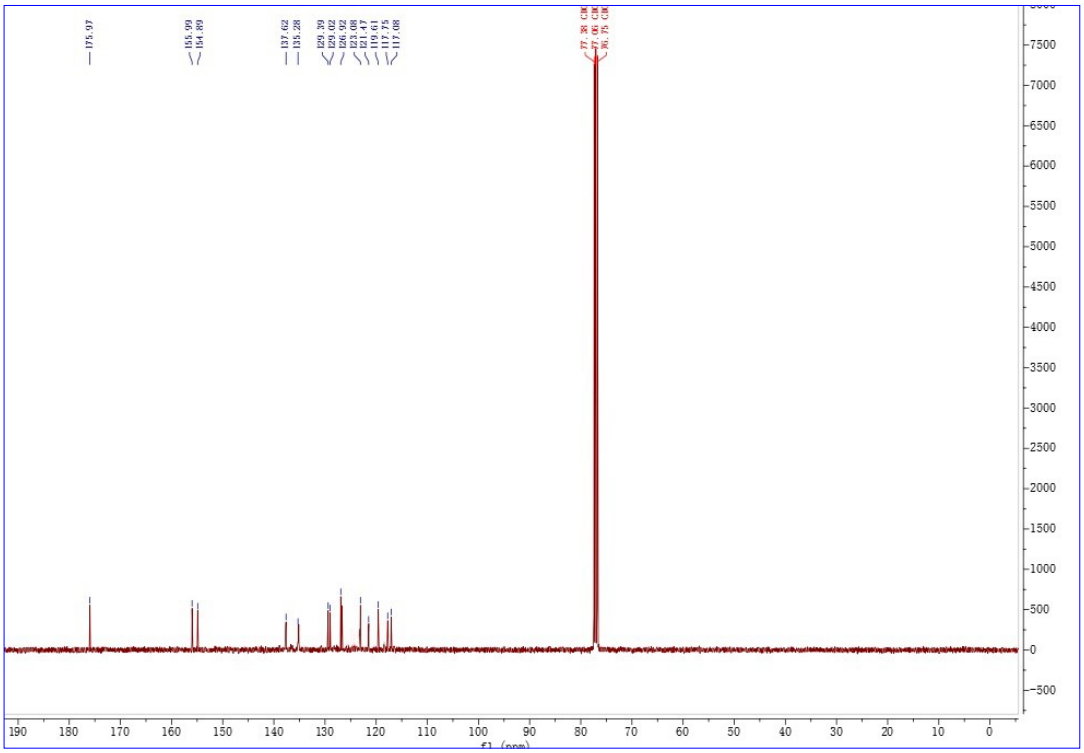
3ak 4-Chloro-9H-xanthen-9-one



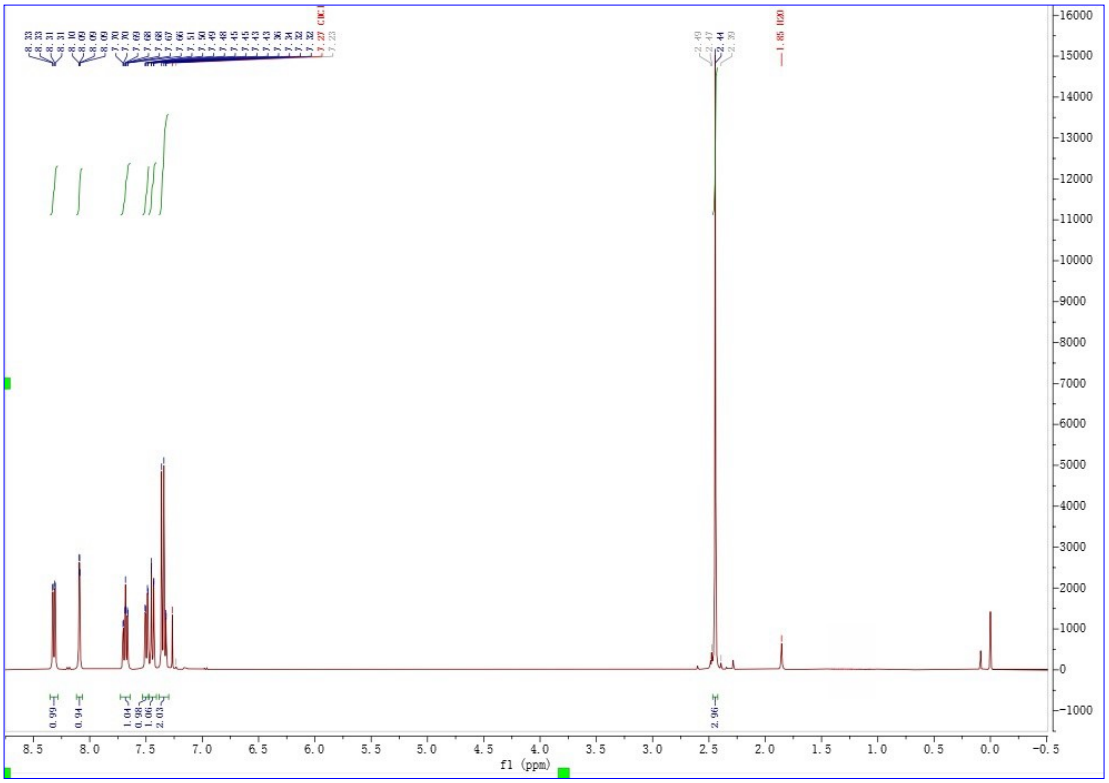


3al 2-Bromo-9H-xanthen-9-one

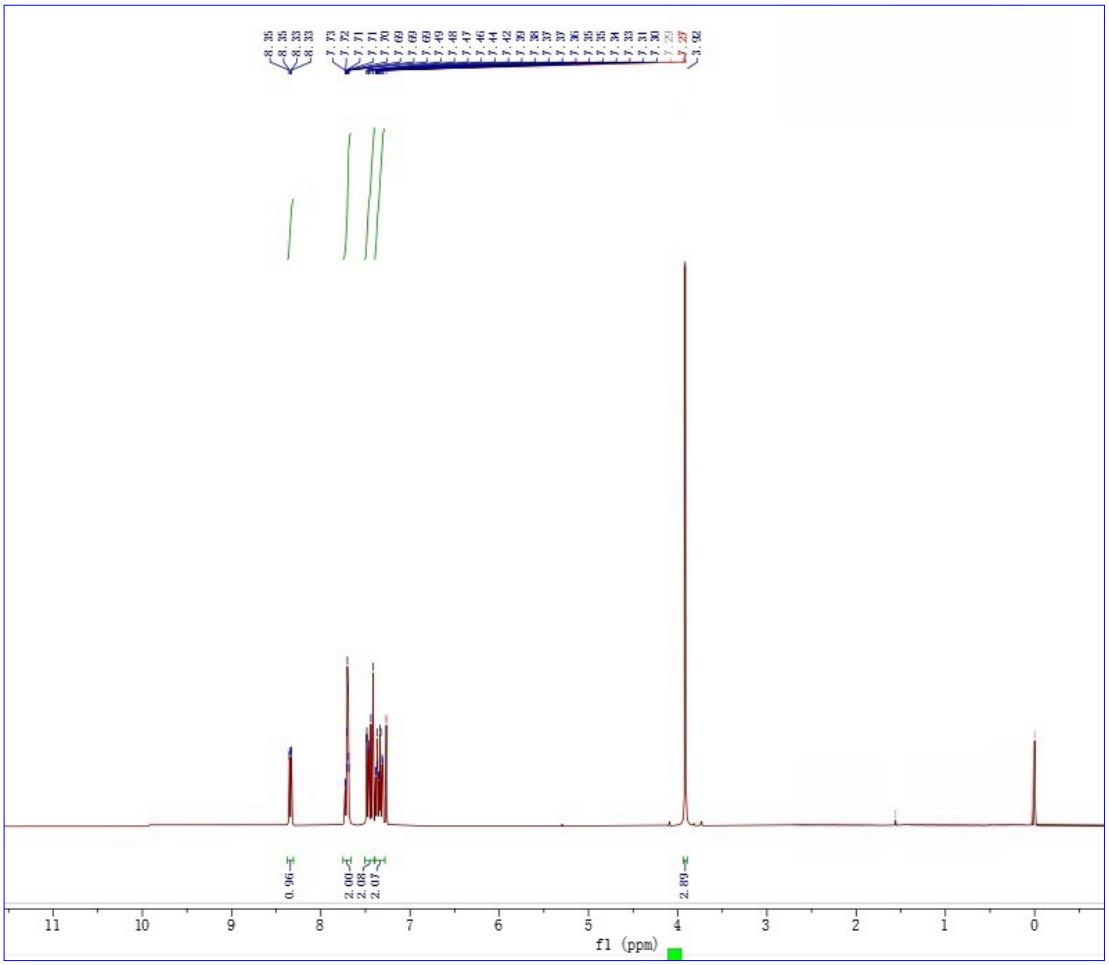




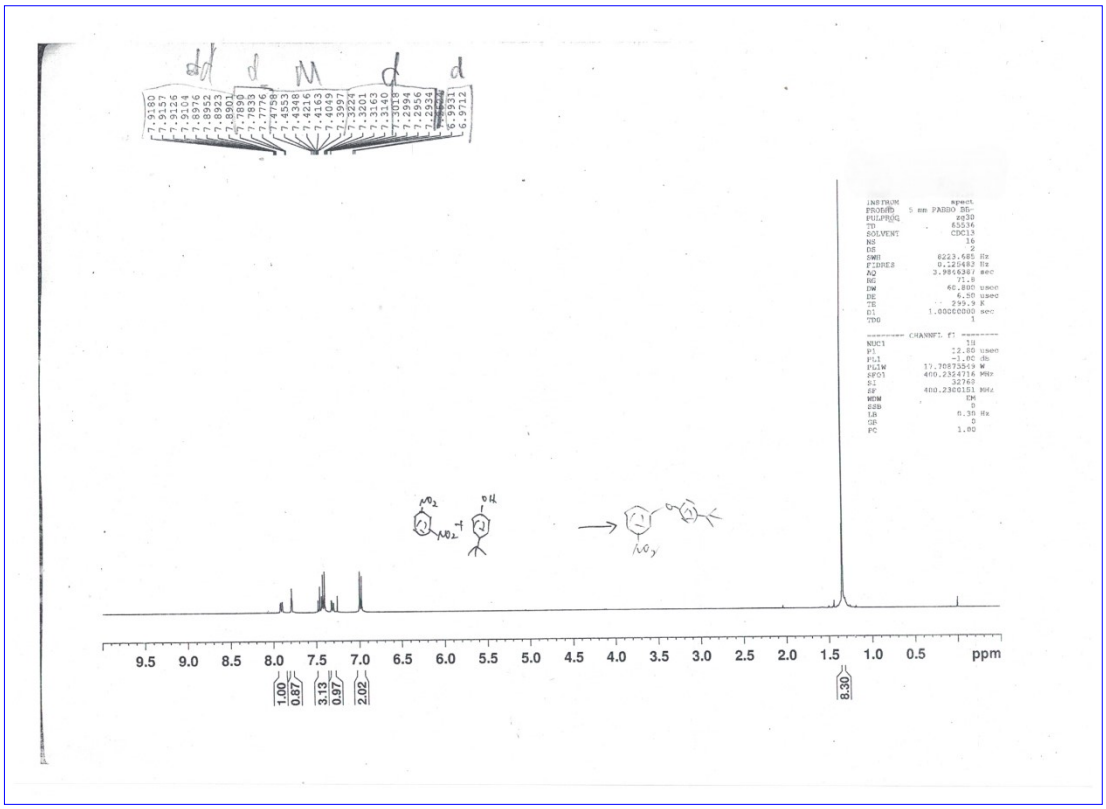
3ba 2-Methyl-4aH-xanthen-9(9aH)-one

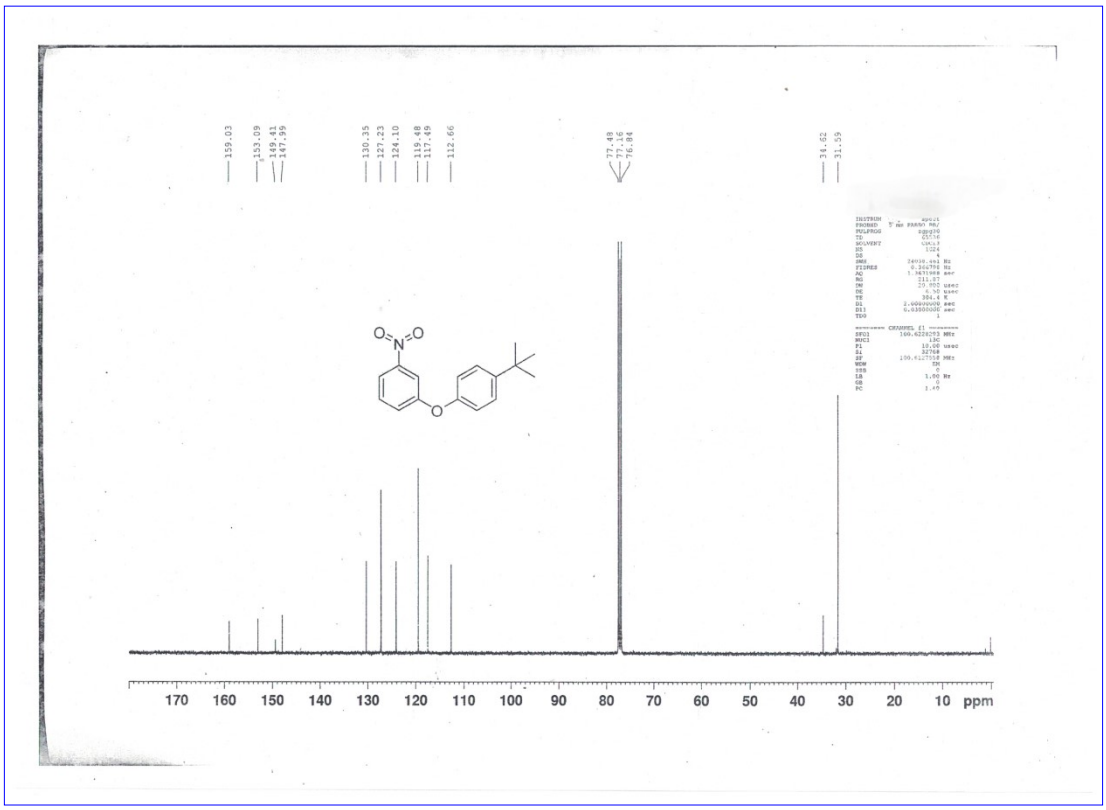


3ca 2-Methoxy-9H-xanthen-9-one



1-[4-(1,1-Dimethylethyl)phenoxy]-3-nitrobenzene




159.03
153.09
149.41
147.99
130.35
127.23
124.10
119.48
117.48
112.66
77.48
77.16
76.84
34.62
31.59
O
N
O
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm