Electronic Supplementary Material (ESI) for RSC Advances.

A novel coupling reaction of α-halo ketones promoted by SmI_3/CuI

Yongjun Liu,* Hengmin Zhao, Guang Tian, Feng Du, Yan Qi, Yonghong Wen

Experimental

General

All NMR spectra were measured in $CDCl_3$ and recorded on Bruker Avance-500 (500 MHz) spectrometer with TMS as the internal standard. Chemical shifts are expressed in ppm and *J* values are given in Hz. IR spectra were recorded on a Bruker Tensor-27 spectrometer. Melting points are uncorrected. All the reactions in this paper were performed under nitrogen atmosphere. Before use, DMF was pre-dried over molecule sieve, and THF was refluxed and redistilled over sodium.

Typical procedure for the preparation of 2-hydroxy-1,4-diphenylbutane-1,4- dione (2a)

To a mixture of Sm powder (0.3 g, 2 mmol) in anhydrous DMF (10 mL) under a nitrogen atmosphere, I_2 (0.8 g, 3.2 mmol) was added at room temperature with magnetic stirring, and a dark brown solution of triiodide samarium was afforded in 2 h. Cuprous iodide (0.02 g, 0.1 mmol) and 2-bromoacetophenone (0.4 g, 2 mmol) were added and the mixture was then heated to 105 ºC. After completion of the reaction (about 2 h, monitored by TLC), dilute hydrochloric acid (2 M, 5 mL) was added and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine and saturated sodium thiosulfate solution, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified with flash chromatography (silica/hexane - ethyl acetate 5 : 1 v/v) to afford 0.18 g of **2a** with 71% yield.

Typical procedure for the preparation of 1,4-diphenylbutane-1,4-dione(3a)

To a mixture of Sm powder (0.3 g, 2 mmol) in anhydrous THF (10 mL) under a nitrogen

atmosphere, I_2 (0.8 g, 3.2 mmol) was added at room temperature with magnetic stirring, and a yellow solution of triiodide samarium was afforded in 2 h. Cuprous iodide (0.02 g, 0.1 mmol) and 2-bromoacetophenone (0.4 g, 2 mmol) were added and the mixture was refluxed. After completion of the reaction (about 2.5 h, monitored by TLC), dilute hydrochloric acid (2 M, 5 mL) was added and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine and saturated sodium thiosulfate solution, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified with flash chromatography (silica/hexane - ethyl acetate 5 : 1 v/v) to afford 0.17 g of **3a** with 73% yield.

2-Hydroxy-1,4-diphenylbutane-1,4-dione (2a):[19a] White solid: 0.19 g, 77% of yield; m.p. 90-92 °C (lit. 98°C)[19a] ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.37 (m, 2 H), 3.99 (s, 1 H), 5.66 (m, 1 H), 7.46 (m, 4 H) , 7.57 (m, 2 H), 7.98 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.7, 197.2, 136.8, 133.9, 133.7, 133.6, 128.9, 128.8, 128.7, 128.3, 70.2, 43.6; IR (KBr) ν 3432, 3055, 2900, 1678, 1596, 1580, 1446 cm^{-1}; HRMS m/z calcd for $C_{16}H_{14}O_3$ $[M + H]^+$ 255.1021, found 255.1029.

2-Hydroxy-1,4-di-p-tolyl-butane-1,4-dione (2b): White solid: 0.17 g, 62% of yield.;m.p. 112-114 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (s, 3 H), 2.45 (s, 3 H), 3.34 (m, 2 H), 3.99 (d, 1 H, J = 6.0 Hz) , 5.67 (m, 1 H), 7.26 (m, 2 H), 7.30 (m, 2 H), 7.85 (m, 2 H), 7.90 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.4, 196.8, 129.6, 129.4, 128.9, 128.5, 70.0, 43.7, 21.8, 21.7; IR (KBr) ν 3424, 2920, 2856, 1674, 1643, 1587, 1487 cm^{-1}; HRMS m/z calcd for $C_{18}H_{18}O_3$ $[M + H]^+$ 283.1334, found 283.1342.

1,4-Bis-(4-chloro-phenyl)-2-hydroxy-butane-1,4-dione (2c): White solid: 0.23 g, 72% of yield; m.p. 156-158 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.35 (m, 2 H), 3.98 (s, 1 H), 5.54 (m, 1 H), 7.42 (m, 2 H), 7.46 (m, 2 H), 7.86 (m, 2 H), 7.93 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.3, 196.3, 140.5, 140.3, 134.8, 132.0, 130.2, 129.8, 129.3, 129.1, 70.3, 43.1; IR (KBr) ν 3423, 2921, 2852, 1650, 1587, 1486, 1462 cm^{-1}; HRMS m/z calcd for $C_{16}H_{12}Cl_2O_3$ $[M + H]^+$ 323.0242, found 323.0251.

1,4-Bis(4-bromo-phenyl)-2-hydroxy-butane-1,4-dione (2d): White solid: 0.28 g, 67% of yield; m.p. 186-188 °C.; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.38 (m, 2 H), 3.97 (d,1 H, J = 6.5 Hz), 5.56 (m, 1 H,), 7.63 (m, 2 H), 7.67 (m, 2 H), 7.82 (m, 2 H) 7.89 (m, 2 H);^{13}C NMR (125 MHz, $CDCl_3$) δ 200.4, 196.8, 145.0, 144.5, 134.4, 131.1, 129.6, 129.4, 128.9, 128.5, 70.0, 43.7; IR (KBr) ν 3420, 2977, 2925, 1674, 1648, 1586, 1541 cm^{-1}; HRMS m/z calcd for $C_{16}H_{12}Br_2O_3$ $[M + H]^+$ 410.9231, found 410.9231.

1,4-Bis(4-fluoro-phenyl)-2-hydroxy-butane-1,4-dione (2e): White solid: 0.21 g, 71% of yield; m.p. 140-142 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.38 (m, 2 H), 4.01 (d, 1 H, J = 6.5 Hz), 5.59 (m, 1 H), 7.18 (m, 4 H), 7.99 (m, 2 H), 8.07 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.9, 196.0, 167.2, 165.1, 133.1, 131.7, 131.6, 131.1, 130.1, 125.9, 116.3, 116.1, 116.0, 115.8, 70.4, 43.1; IR (KBr) ν 3409, 2974, 2924, 1677, 1599, 1510, 1454 cm^{-1} HRMS m/z calcd for $C_{16}H_{12}F_2O_3$ $[M + H]^+$ 291.0833, found 291.0839.

1,4-Bis(4-methoxy-phenyl)-2-hydroxy--butan-1,4-dione (2f): White solid: 0.19 g, 61% of yield; m.p. 122-124 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.32 (m, 2 H), 3.87 (s, 3 H), 3.89 (s, 3 H), 4.06 (d, 1 H, J = 6.0 Hz), 5.66 (m,1 H), 6.94 (m, 2 H), 6.99 (m, 2 H), 7.95 (m, 2 H), 8.00 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.2, 195.9, 164.2, 163.9, 131.2, 130.7, 130.0, 126.4, 114.2, 113.8, 69.9, 55.5, 43.6; IR (KBr) ν 3434, 2962, 2920, 1673, 1603, 1587, 1511, 1456 cm^{-1}; HRMS m/z calcd for $C_{18}H_{18}O_5$ $[M + H]^+$ 315.1232, found 315.1238.

1,4-Bis-(3,4-dimethyl-phenyl)-2-hydroxy-butane-1,4-dione (2g): White solid: 0.24 g, 78% of yield; m.p. 110-111 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31 (m, 12 H), 3.33 (m, 2 H), 4.00 (d, 1 H, J = 6.0 Hz), 5.66 (m, 1 H), 7.23 (m, 2 H), 7.69 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.7, 197.0, 143.7, 143.1, 137.4, 137.0, 134.7, 131.4, 130.1, 129.9, 129.8, 129.5, 126.4, 126.1, 69.9, 43.8, 20.0, 19.7; IR (KBr) ν 3432, 2915, 1664, 1604, 1568, 1506, 1449,1401cm^{-1}; HRMS m/z calcd for $C_{20}H_{22}O_3$ $[M + H]^+$ 311.1647, found 311.1640.

1,4-Bis-(4-ethyl-phenyl)-2-hydroxy-butane-1,4-dione (2h): White solid: 0.22 g, 72% of yield; m.p. 62-63 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (m, 6 H), 2.71 (m, 4 H), 3.35 (m, 2 H), 4.00 (d, 1 H, J = 6.0 Hz), 5.67 (m, 1 H), 7.27 (m, 2 H), 7.32 (m, 2 H), 7.87 (m, 2 H),

7.92 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$). δ 200.4, 196.8, 151.2, 150.6, 134.5, 131.1, 129.0, 128.6, 128.5, 128.2, 70.0, 43.7, 29.0, 15.1; IR (KBr) ν 3441, 2967, 2930, 1676, 1607, 1570, 1411 cm^{-1}; HRMS m/z calcd for $C_{20}H_{22}O_3$ $[M + H]^+$ 311.1647, found 311.1652.

1,4-Bis-(4-isopropyl-phenyl)-2-hydroxy-butane-1,4-dione (2i): White solid: 0.25 g, 75% of yield; m.p. 68-69°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (s, 3 H), 1.26 (s, 6 H), 1.27 (s, 3 H), 2.96 (m, 2 H), 3.36 (m, 2 H), 4.02 (s, 1 H), 5.67 (m, 1 H), 7.29 (m, 2 H), 7.33 (m, 2 H), 7.88 (m, 2 H), 7.92 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$). δ 200.4, 196.7, 155.7, 155.2, 134.5, 131.2, 129.0, 128.6, 127.0, 126.7, 70.0, 43.7, 34.3, 23.6; IR (KBr) ν 3446, 2956, 2918, 2869, 1670, 1605, 1569, 1418 cm^{-1}; HRMS m/z calcd for $C_{22}H_{26}O_3$ $[M + H]^+$ 339.1960, found 339.1965.

2-Hydroxy-1,4-bis(5,6,7,8-tetrahydronaphthalen-2-yl)butane-1,4-dione (2j): White solid: 0.27 g, 76% of yield; m.p. 86-87°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.80 (m, 8 H), 2.80 (m, 8 H), 3.33 (m, 2 H), 4.00 (d, 1 H, J = 6 Hz), 5.65 (m, 1 H), 7.14 (m, 2 H), 7.65 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ .200.8, 197.0, 144.4, 143.8, 138.0, 137.5, 134.2, 130.8, 129.6, 129.4, 129.3, 125.7, 125.4, 69.8, 43.8, 29.7, 29.3, 22.7; IR (KBr) ν 456, 2934, 2857, 2833, 1726, 1663, 1601, 1571, 1419 cm^{-1}; HRMS m/z calcd for $C_{24}H_{26}O_3$ $[M + H]^+$ 363.1960, found 363.1965.

1,4-Diphenyl-butane-1,4-dione (3a):[19b] Straw yellow solid: 0.17 g, 73% of yield; m.p. 145-146°C (lit. 144-145°C);[19b] ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.48 (s, 4 H), 7.49 (m, 4 H), 7.58 (m, 2 H), 8.05 (m, 4 H); IR (KBr) ν 3441, 2881, 2827, 2675, 2631cm^{-1}.

1,4-Bis(4-chloro-phenyl)butane-1,4-dione (3b):[19c] Red solid: 0.22 g, 71% of yield; m.p. 149-151 °C (lit. 151-152°C);[19c] ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.43 (s, 4 H), 7.46 (d, 4 H, J = 8.5 Hz), 7.98 (d, 4 H, J = 8.5 Hz); IR (KBr) 3409, 3091, 1727, 1676 cm^{-1}.

1,4-Di*p*-tolybutane-1,4-dione (3c):[19d] Red solid: 0.18 g, 66% of yield; m.p. 160-162 °C. (lit. 161°C);[19d] ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.40 (s, 6 H), 3.40 (s, 4 H), 7.25 (d, 4 H, J = 8.0 Hz), 7.91 (d, 4 H, J = 8.0 Hz).

1,4-Bis(4-ethylphenyl)-butane-1,4-dione (3d):[19e] White solid: 0.21 g, 70% of yield; m.p.

123-125 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (t, 6 H, J = 7.6 Hz), 2.72 (q, 4 H, J = 7.6 Hz), 3.44 (s, 4 H), 7.30 (d, 4 H, J = 8.0 Hz), 7.96 (d, 4 H, J = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 150.1, 134.6, 128.4, 128.1, 32.6, 29.0, 15.2.

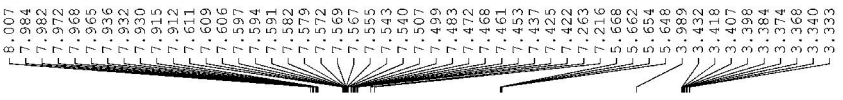
1,4-Bis(3,4-xylene)-butan-1,4-dione (3e):[19f] Red solid: 0.22 g, 74% of yield; m.p. 158-160 °C (lit. 157 °C);[19f] ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.33 (s, 6 H), 2.35 (s, 6 H), 3.42 (s, 4 H), 7.24 (m, 2 H), 7.79 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 142.6, 136.9, 134.8, 129.8, 129.3, 125.9, 32.6, 20.0, 19.8.

[2,3-Bis-(4-methyl-benzoyl)-cyclopropyl]-p-tolyl-methanone (4a):[19g] White solid: 83 mg, 21% of yield; m.p. 151-153°C(lit. 147-148 °C);[19g] ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 6 H), 2.44 (s, 3 H), 3.71 (d, 2 H, J = 6.0 Hz), 4.20 (t, 1 H, J = 6.0 Hz), 7.21 (d, 2 H, J = 8.0 Hz), 7.31 (d, 2 H, J = 8.0 Hz), 7.91 (d, 4 H, J = 8.0 Hz), 8.09 (d, 2 H, J = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.8, 192.6, 144.8, 144.3, 134.2, 129.5, 129.3, 128.9, 128.6, 36.3, 30.2, 21.7.

(*E*)-1,4-bis(4-methoxyphenyl)but-2-ene-1,4-dione (5a):[19h] Yellow solid: 0.14 g, 46% of yield; m.p. 160-162°C (167-168.5°C);[19h] ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.90 (s, 6 H), 7.00 (m, 4 H), 8.02 (s, 2 H), 8.08 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.1, 164.2, 134.6, 131.3, 130.1, 114.1, 55.5; IR (KBr): 3779, 3428, 2976, 2891, 2830, 1641, 1601cm^{-1}.

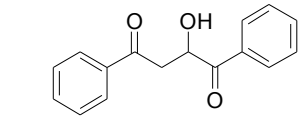
Referneces

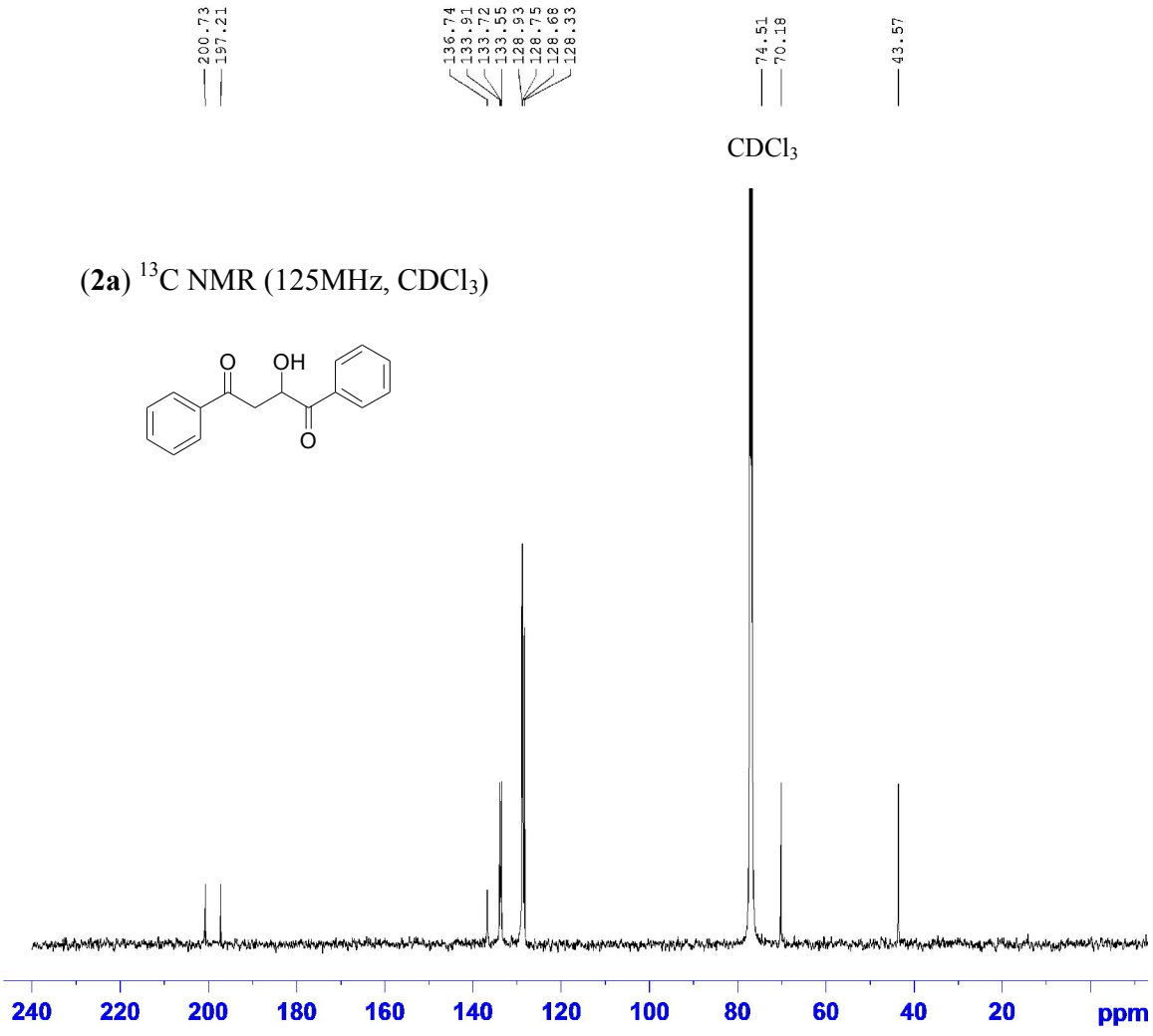
(19) (a) S. Sayama, *Synth. Commun*. 2005, **35**, 2115-2124. (b) D. C. Magri, *Chem. Eur. J.* 2008, **14**, 1698-1709. (c) A. Bhunia, S. R. Yetra, S. S. Bhojgude, A. T. Biju, *Org. Lett*. 2012, **14**, 2830−2833. (d) C. Peppe, *Synlett*. 2004, **7**, 1187-1190. (e) G. X. Hua, J. B. Henry, Y. Li, A. R. Mount, *Org. Biomol. Chem.* 2010, **8**, 1655–1660. (f) H.-D. Becker, *J. Org. Chem.* 1967, **32**, 2140-2144. (g) H.-W. Hu, W.-X. Chen, M. Tao, J.-Y. Gao, *Acta Chim. Sinica* 1987, **45**, 204-207 (in Chinese). (h) K. Xu, Y. Fang, Z. C. Yan, Z. U. Wang, *Org. Lett*. 2013, **15**, 2148−2151.



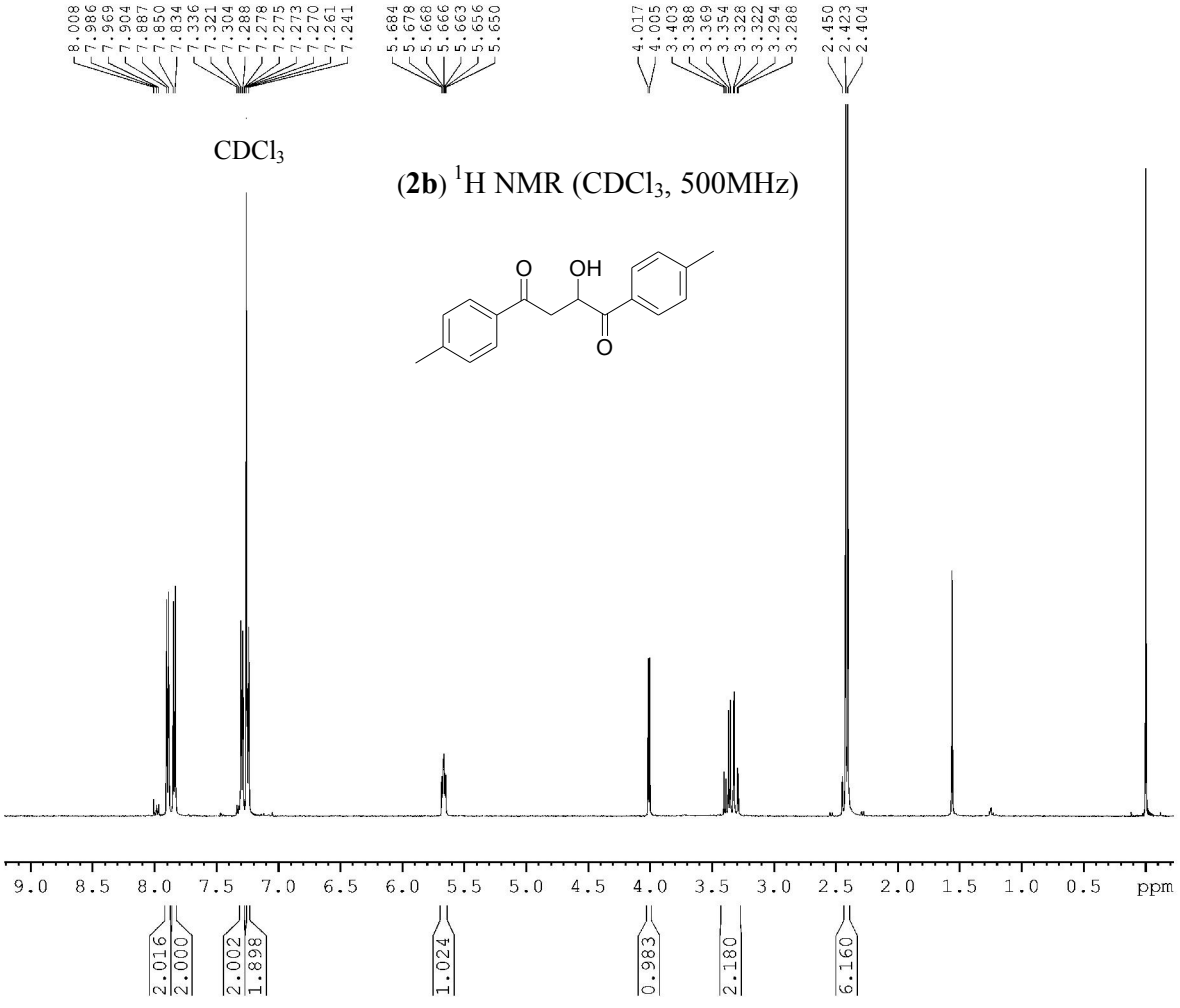
$CDCl_3$

(**2a**) ^{1}H NMR ($CDCl_3$, 500MHz)

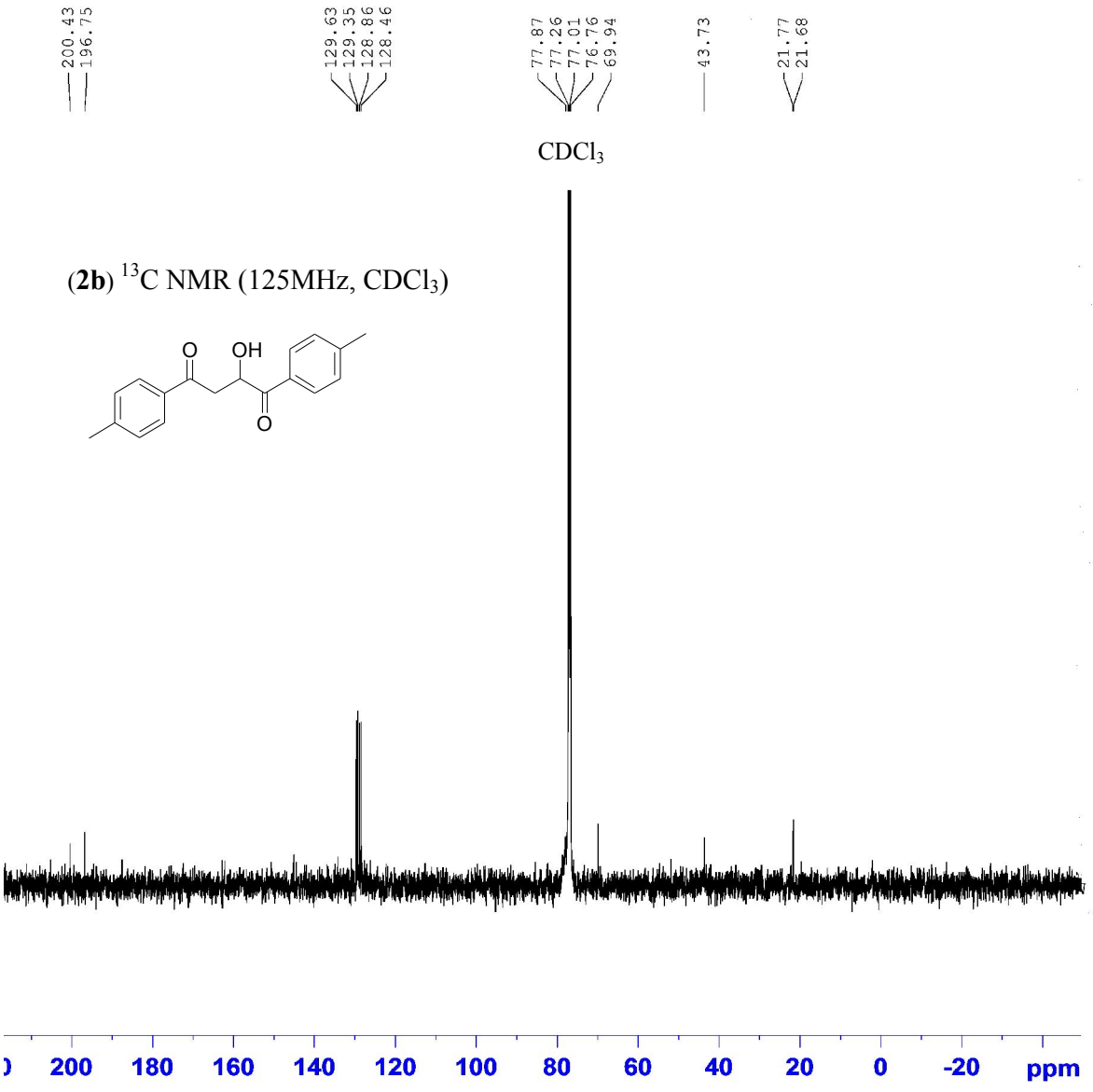




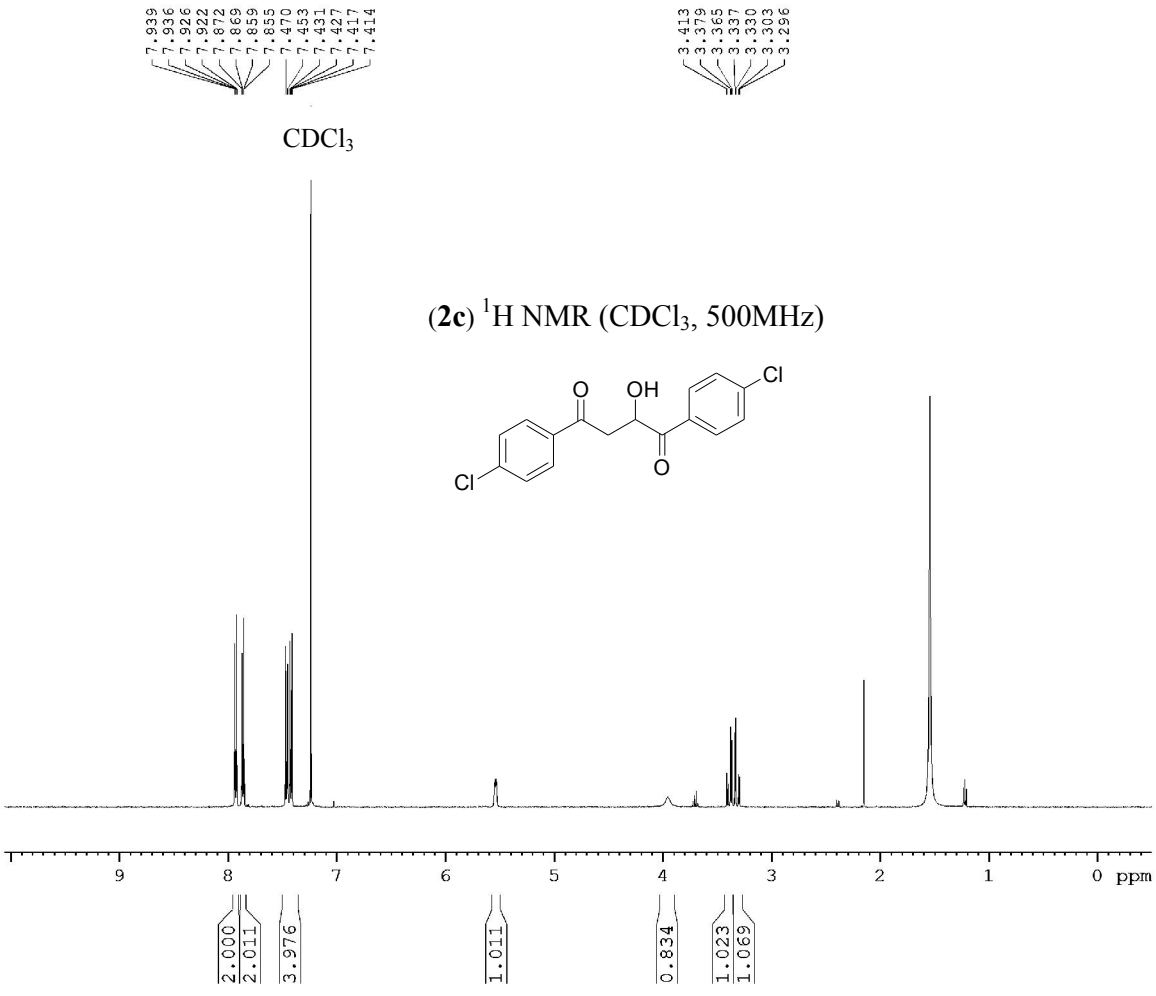
(**2a**) ^{13}C NMR (125MHz, $CDCl_3$)



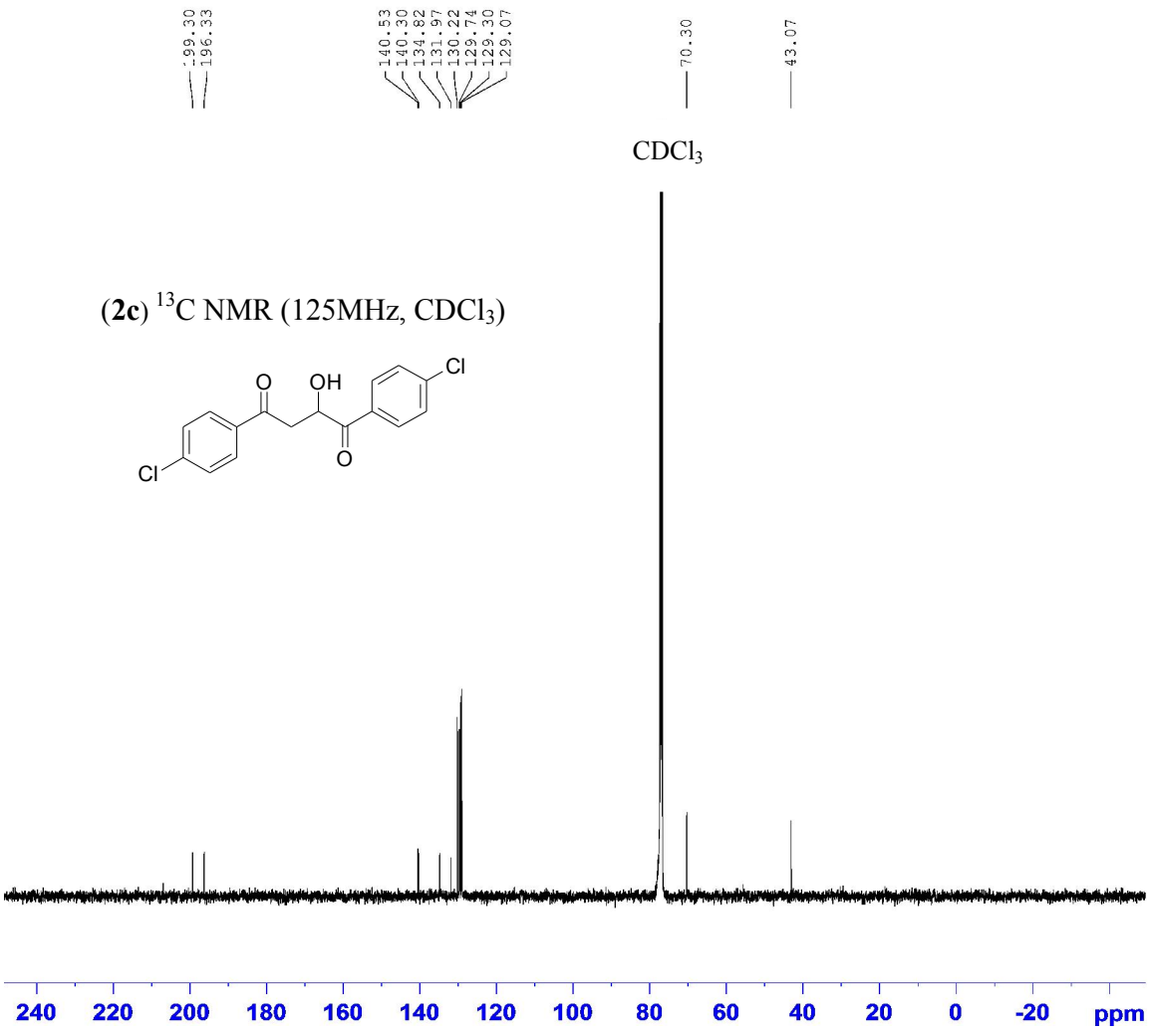
(**2b**) ^{1}H NMR ($CDCl_3$, 500MHz)

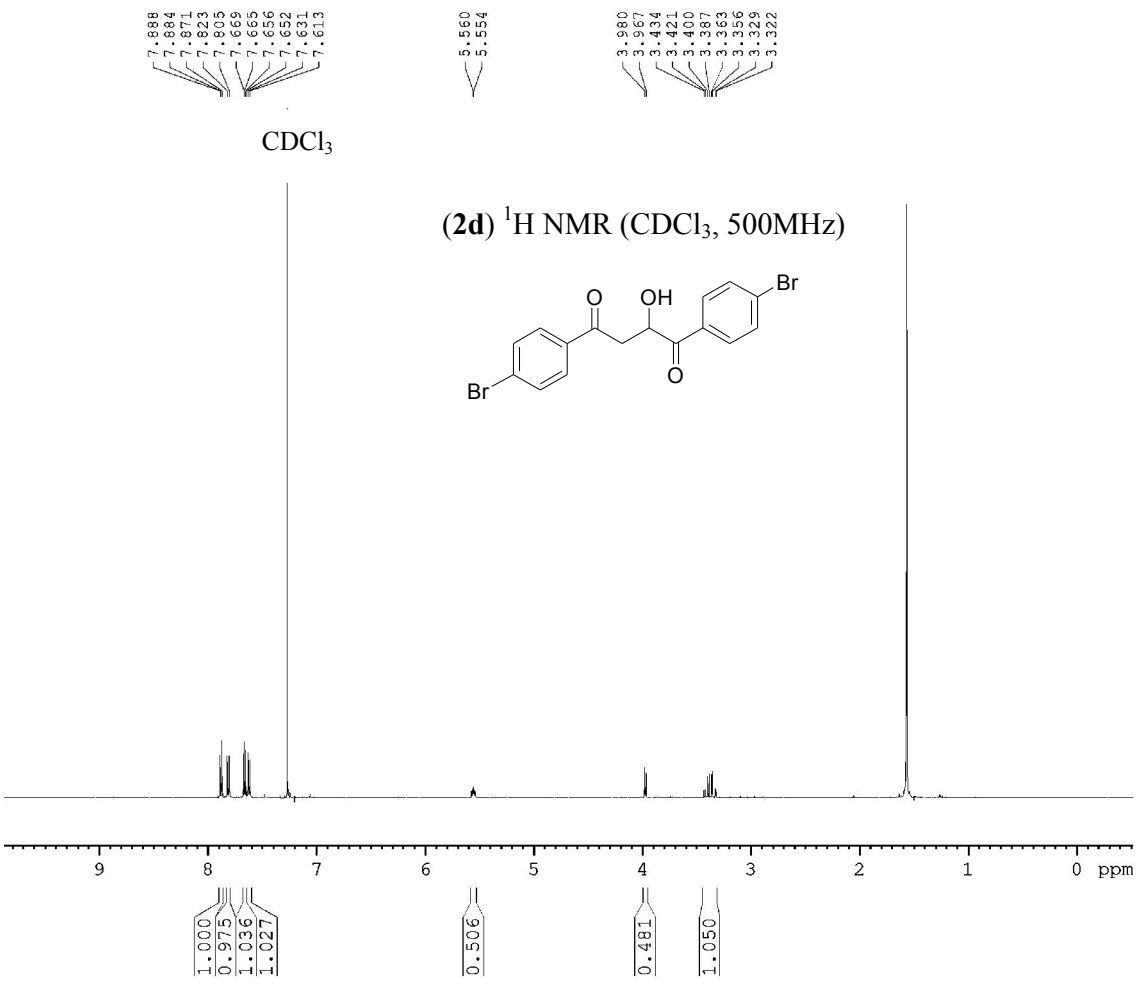


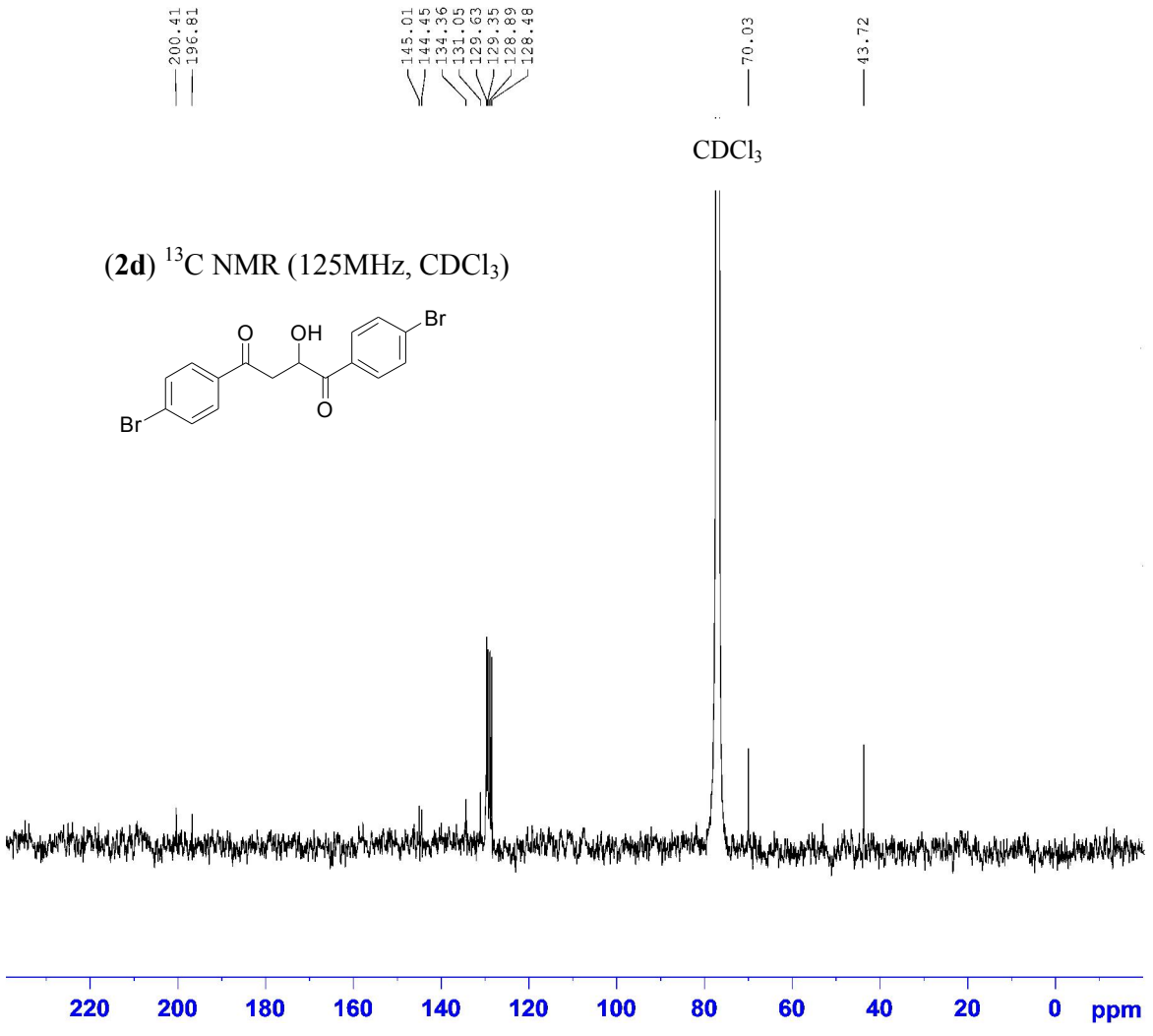
(**2b**) ^{13}C NMR (125MHz, $CDCl_3$)

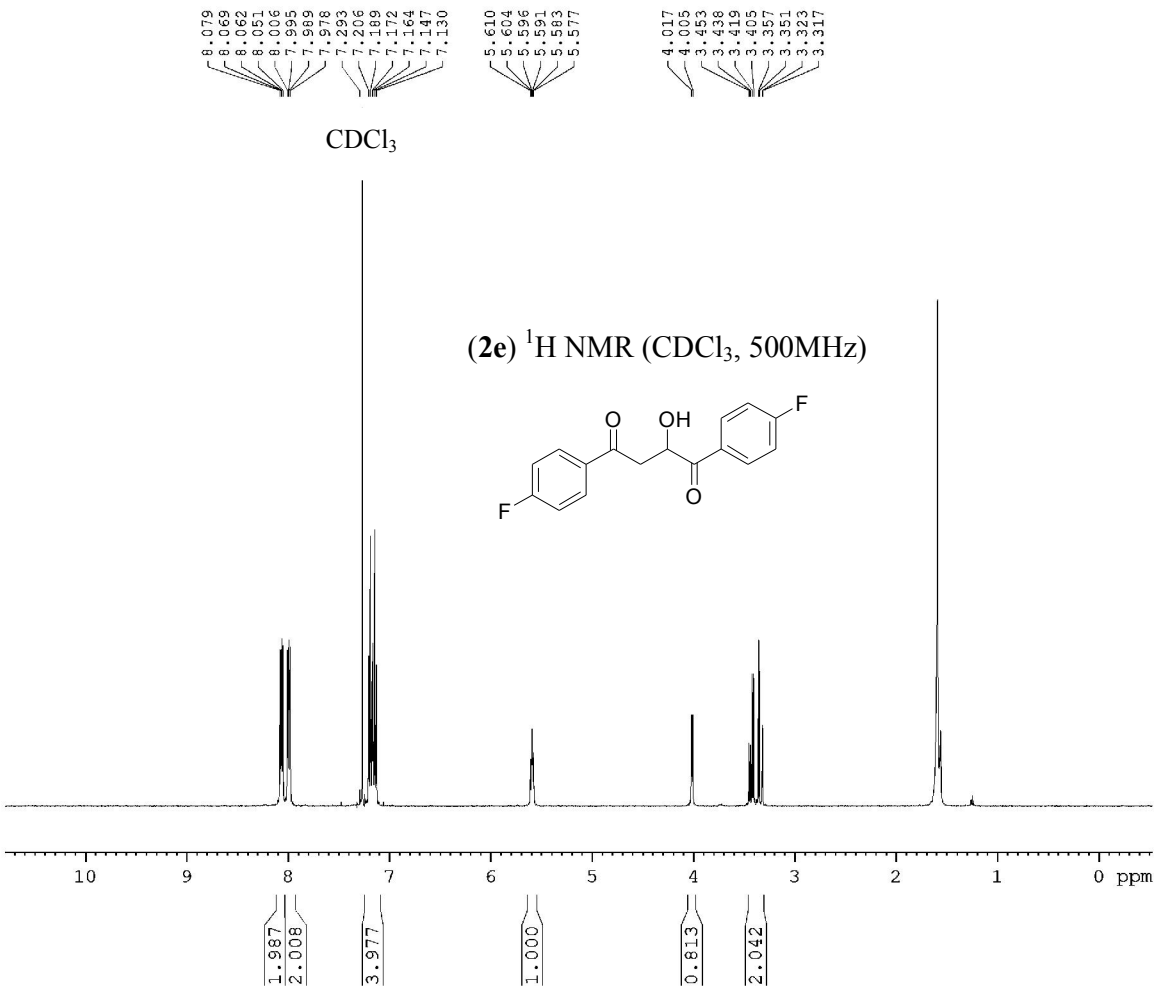


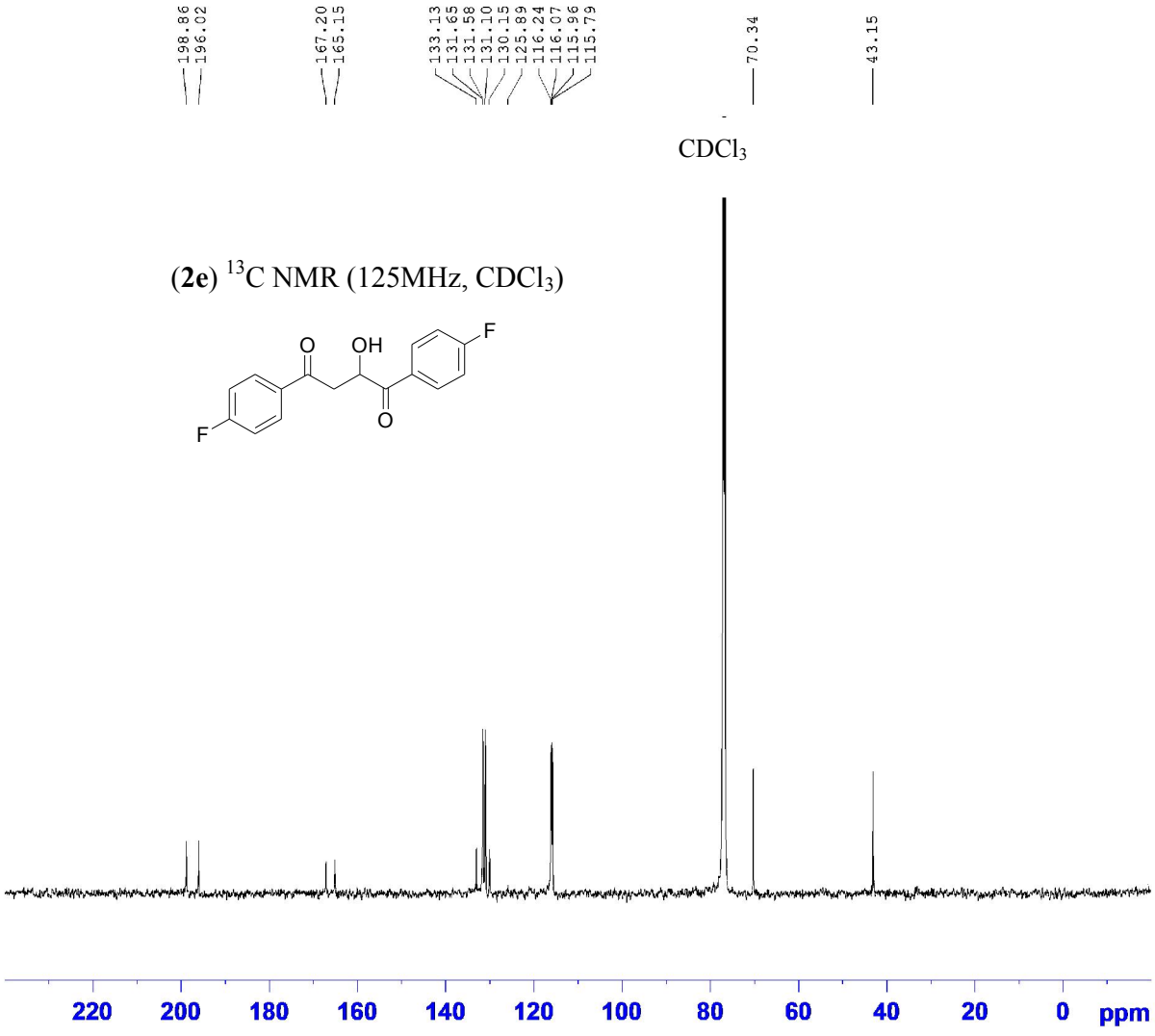
(**2c**) ^{1}H NMR ($CDCl_3$, 500MHz)

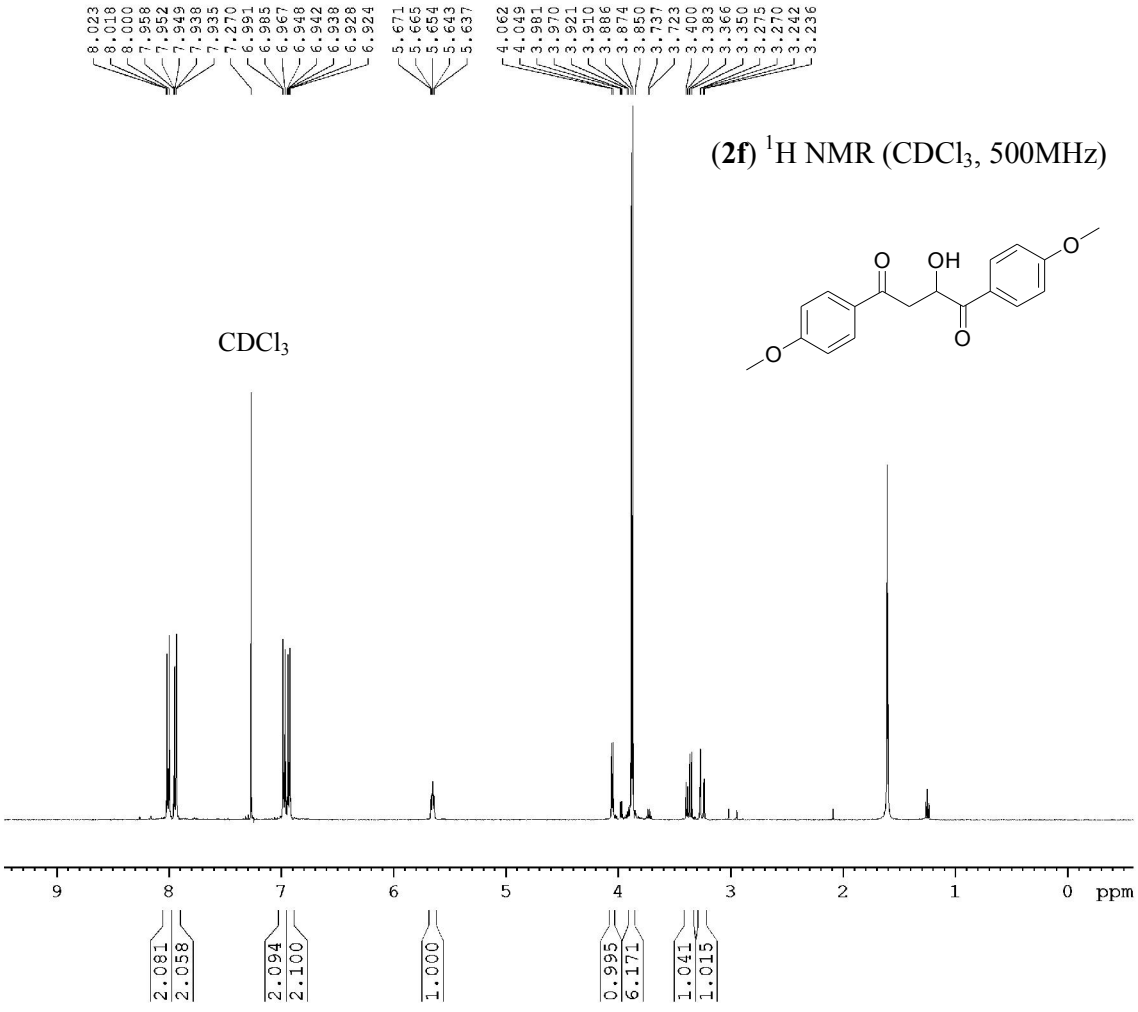

199.30
196.33
140.53
140.30
134.82
131.97
130.22
129.74
129.30
129.07
70.30
43.07
CDCl3
(2c) 13C NMR (125MHz, CDCl3)
O
OH
Cl
Cl
O
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

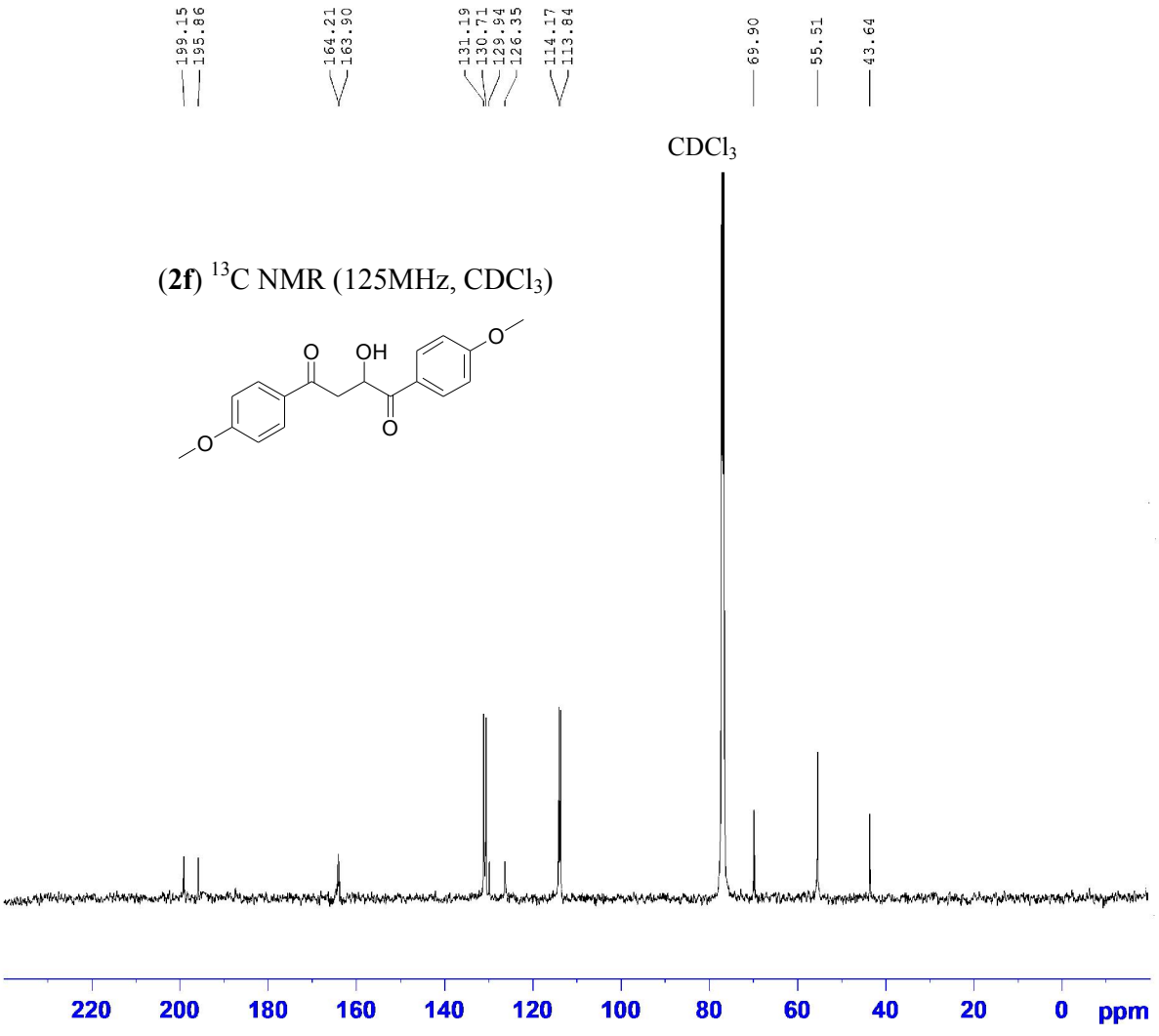

7.888
7.884
7.871
7.823
7.805
7.669
7.665
7.656
7.652
7.631
7.613
5.560
5.554
3.980
3.967
3.434
3.421
3.400
3.387
3.363
3.356
3.329
3.322
CDCl3
(2d) 1H NMR (CDCl3, 500MHz)
O
OH
Br
Br
O
9
8
7
6
5
4
3
2
1
0 ppm
1.000
0.975
1.036
1.027
0.506
0.481
1.050

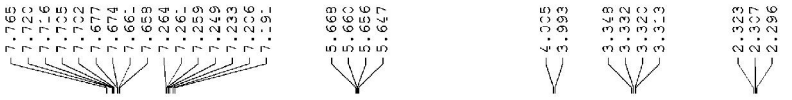

200.41
196.81
145.01
144.45
134.36
131.05
129.63
129.35
128.89
128.48
70.03
43.72
CDCl3
(2d) 13C NMR (125MHz, CDCl3)
O
OH
Br
O
Br
220
200
180
160
140
120
100
80
60
40
20
0
ppm


8.079
8.069
8.062
8.051
8.006
7.995
7.989
7.978
7.293
7.206
7.189
7.172
7.164
7.147
7.130
5.610
5.604
5.596
5.591
5.583
5.577
4.017
4.005
3.453
3.438
3.419
3.405
3.357
3.351
3.323
3.317
CDCl3
(2e) 1H NMR (CDCl3, 500MHz)
O
OH
O
F
F
10
9
8
7
6
5
4
3
2
1
0 ppm
1.987
2.008
3.977
1.000
0.813
2.042

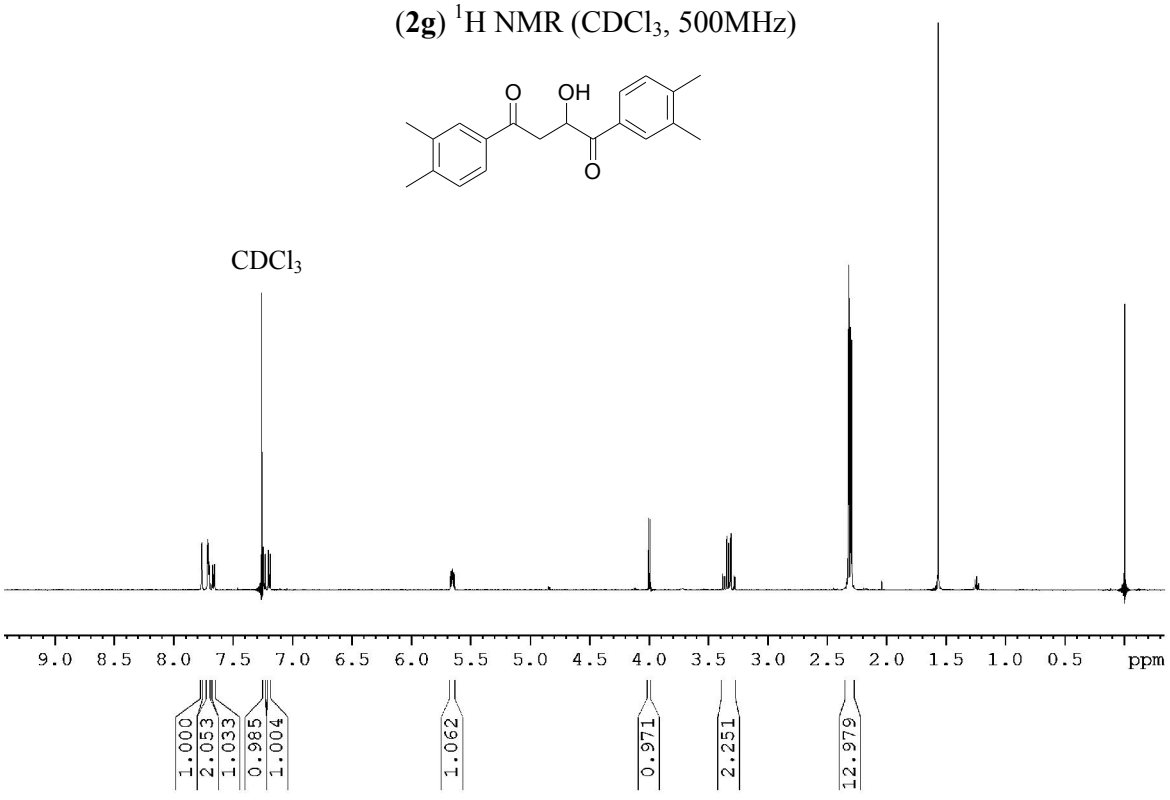

198.86
196.02
167.20
165.15
133.13
131.65
131.58
131.10
130.15
125.89
116.24
116.07
115.96
115.79
70.34
43.15
CDCl3
(2e) 13C NMR (125MHz, CDCl3)
O
OH
F
O
F
220
200
180
160
140
120
100
80
60
40
20
0
ppm

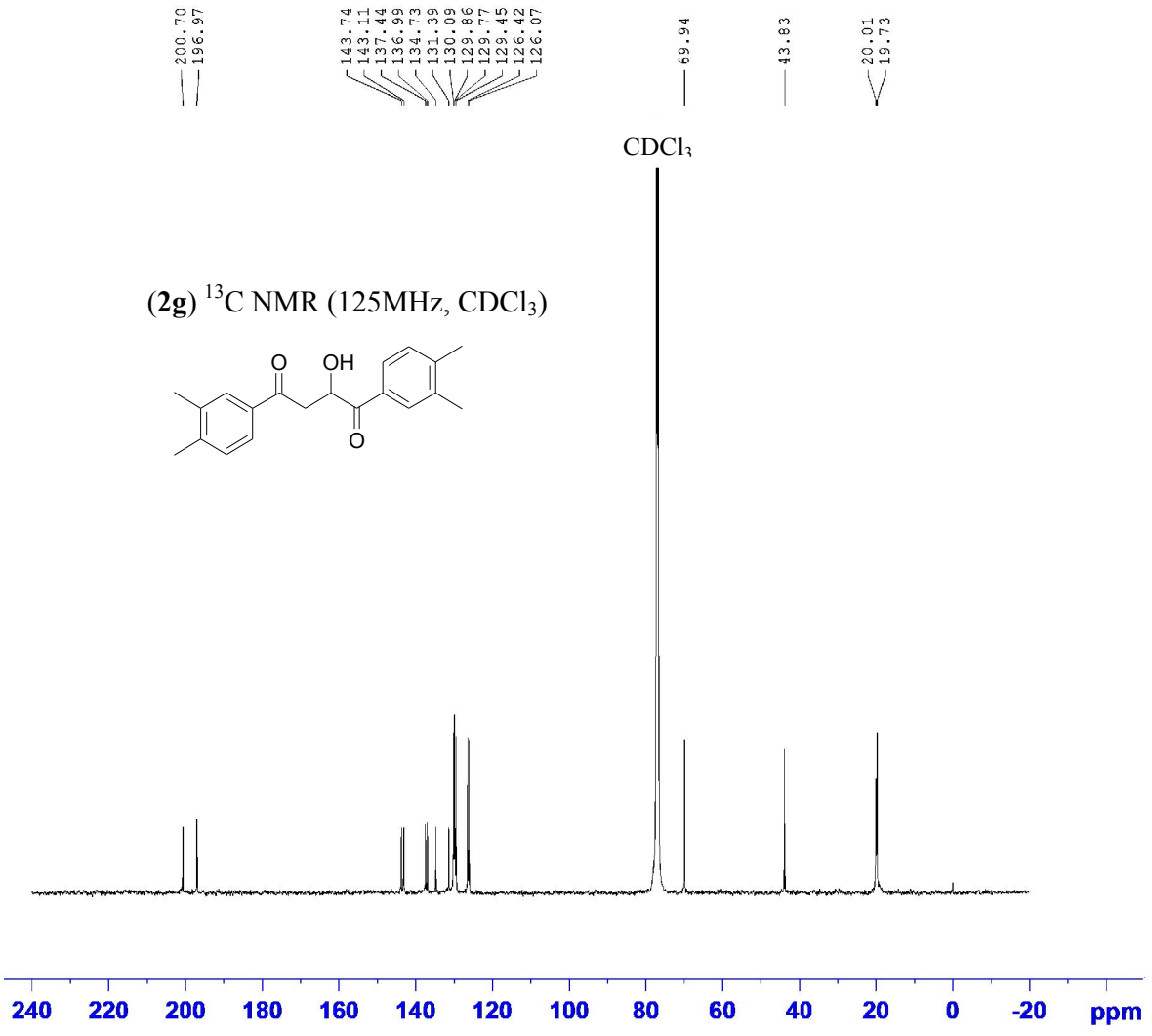

8.023
8.018
8.000
7.958
7.952
7.949
7.938
7.935
7.270
6.991
6.985
6.967
6.948
6.942
6.938
6.928
6.924
5.671
5.665
5.654
5.643
5.637
4.062
4.049
3.981
3.970
3.921
3.910
3.886
3.874
3.850
3.737
3.723
3.400
3.383
3.366
3.350
3.275
3.270
3.242
3.236
(2f) 1H NMR (CDCl3, 500MHz)
CDCl3
O
OH
O
O
O
9
8
7
6
5
4
3
2
1
0
ppm
2.081
2.058
2.094
2.100
1.000
0.995
6.171
1.041
1.015


199.15
195.86
164.21
163.90
131.19
130.71
129.94
126.35
114.17
113.84
69.90
55.51
43.64
CDCl3
(2f) 13C NMR (125MHz, CDCl3)
O
OH
O
O
O
220
200
180
160
140
120
100
80
60
40
20
0
ppm

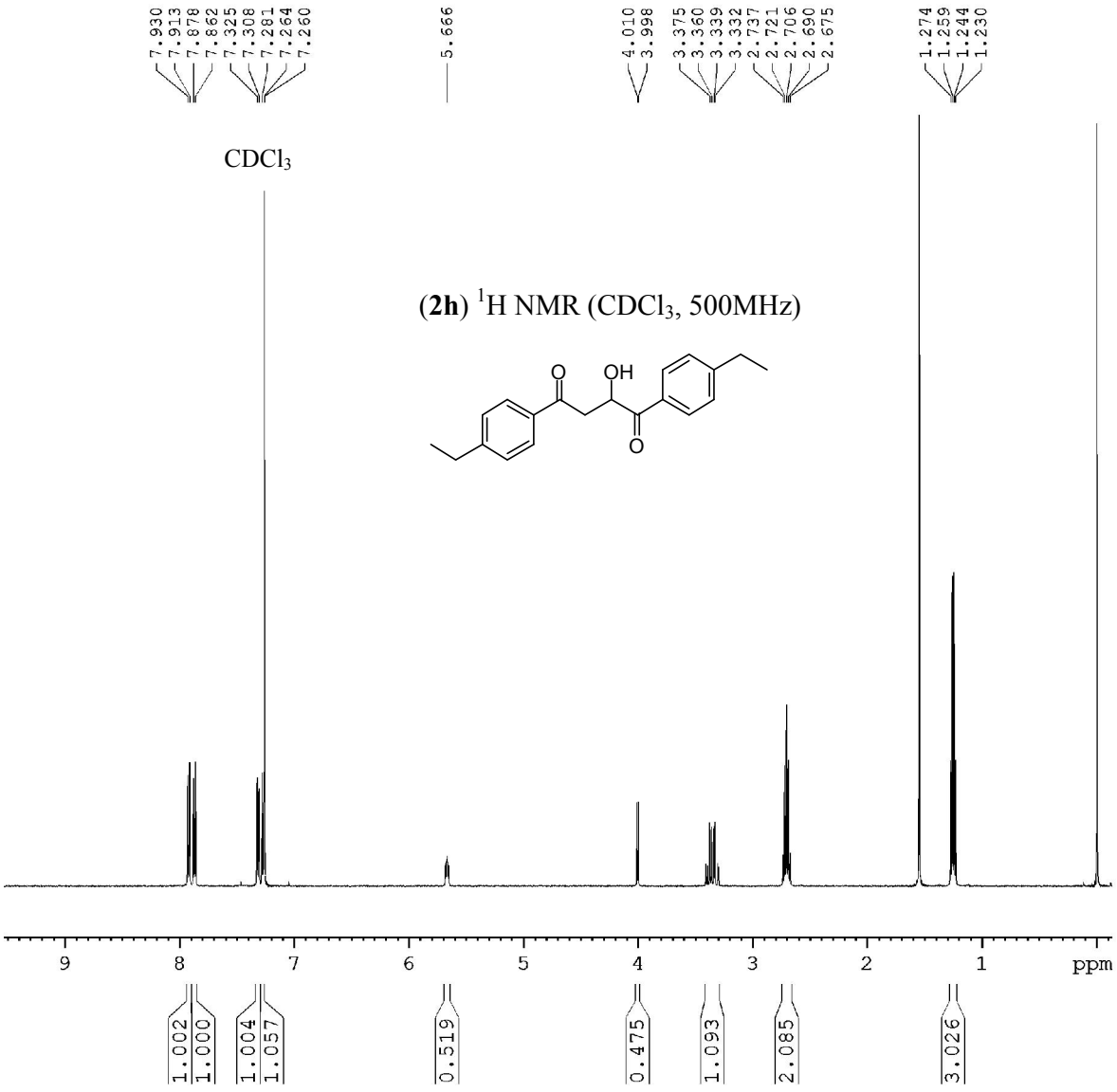


(**2g**) ^{1}H NMR ($CDCl_3$, 500MHz)

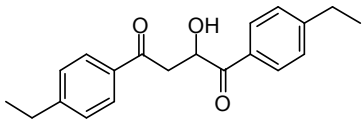


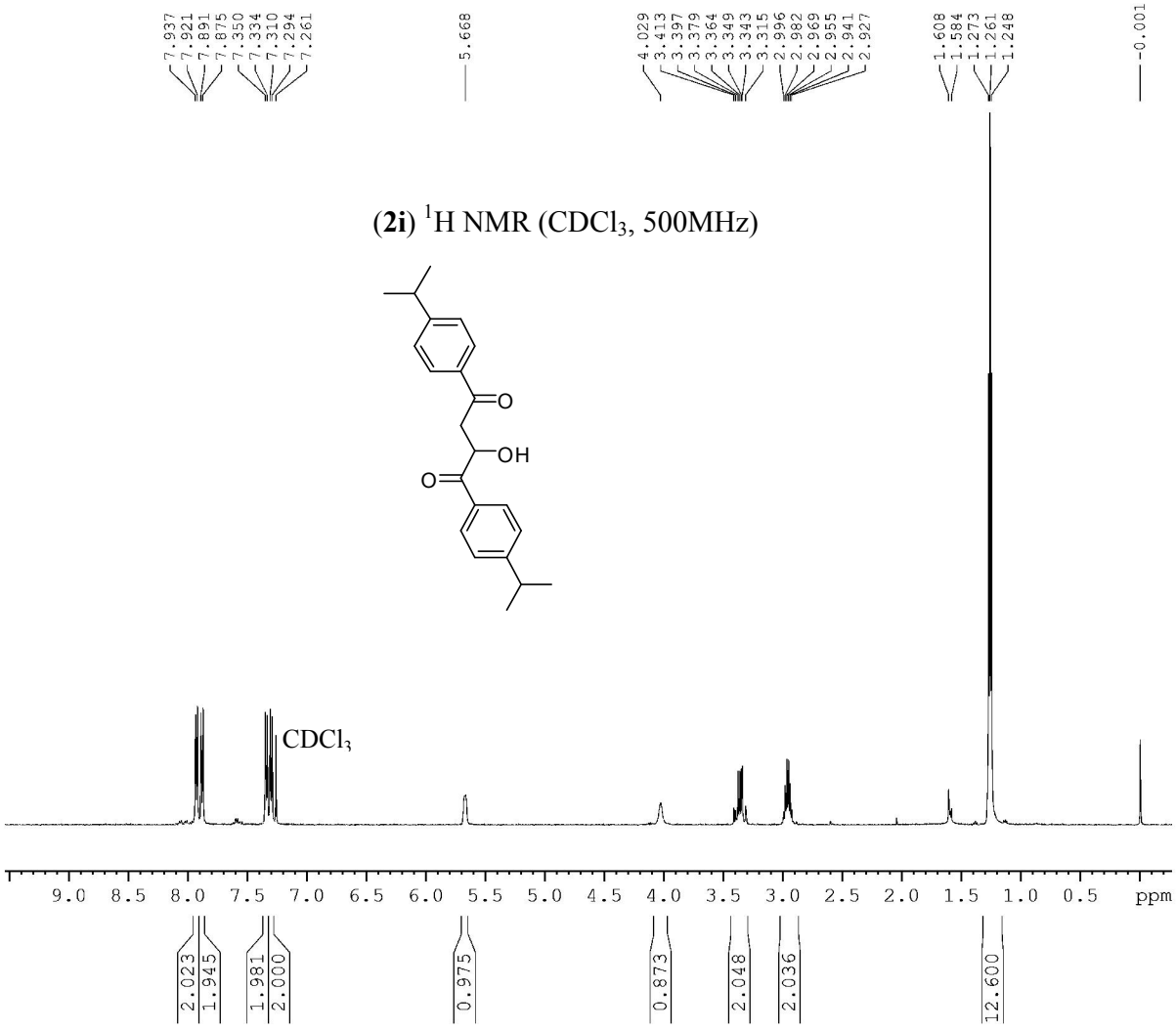


(**2g**) ^{13}C NMR (125MHz, $CDCl_3$)


7.930
7.913
7.878
7.862
7.325
7.308
7.281
7.264
7.260
5.666
4.010
3.998
3.375
3.360
3.339
3.332
2.737
2.721
2.706
2.690
2.675
1.274
1.259
1.244
1.230
CDCl3
(2h) 1H NMR (CDCl3, 500MHz)
O
OH
O
9
8
7
6
5
4
3
2
1
ppm
1.002
1.000
1.004
1.057
0.519
0.475
1.093
2.085
3.026

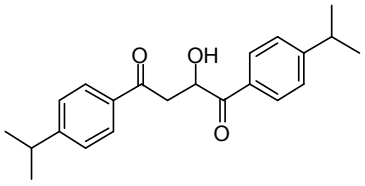
(**2h**) ^{13}C NMR (125MHz, $CDCl_3$)

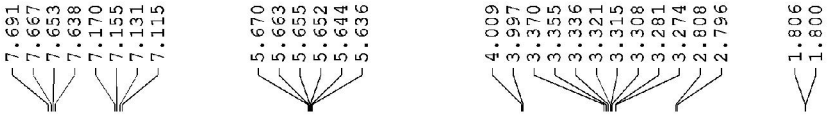




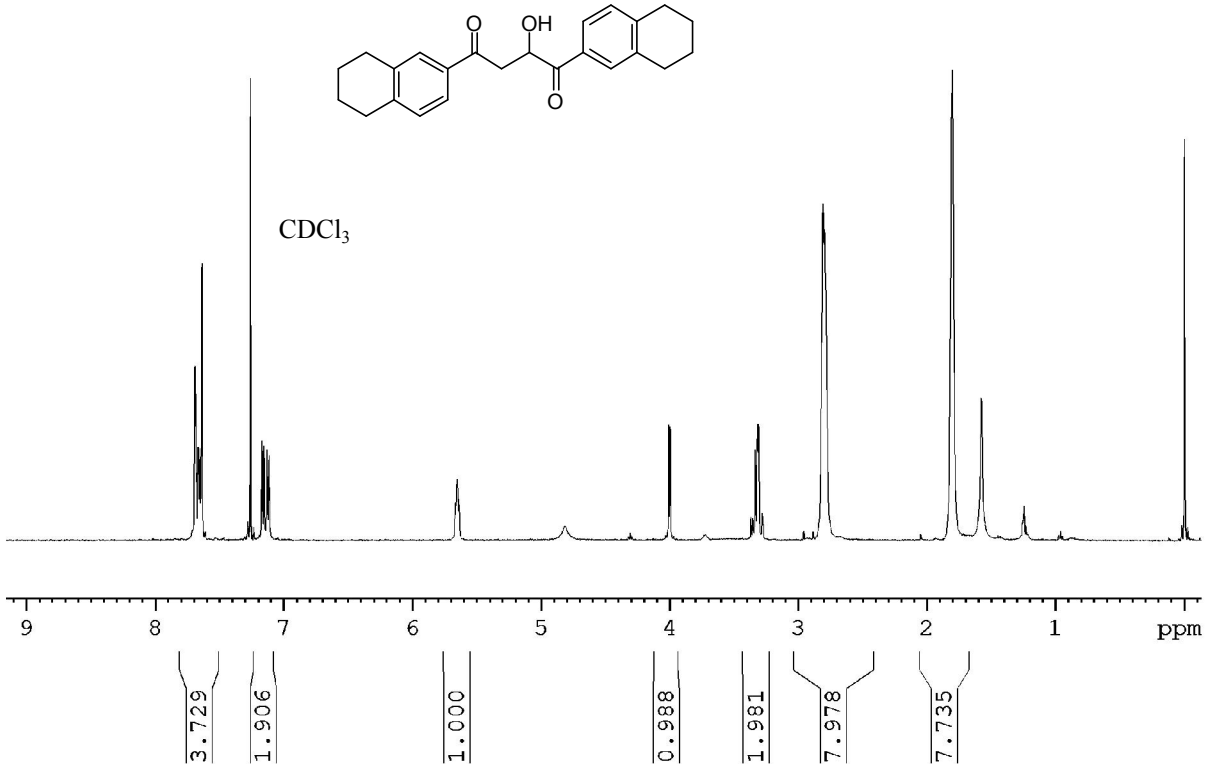
(**2i**) ^{1}H NMR ($CDCl_3$, 500MHz)

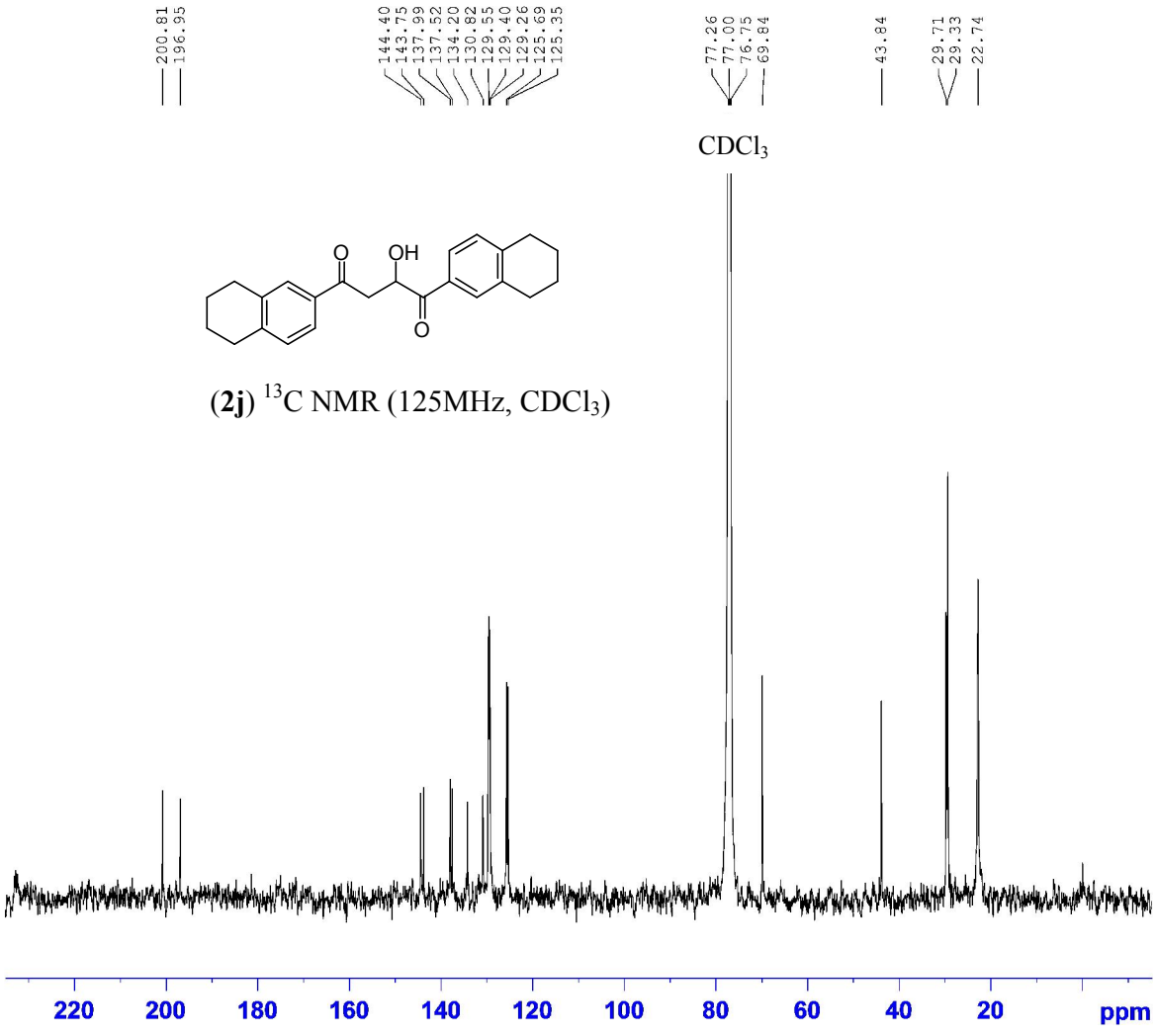
(**2i**) ^{13}C NMR (125MHz, $CDCl_3$)



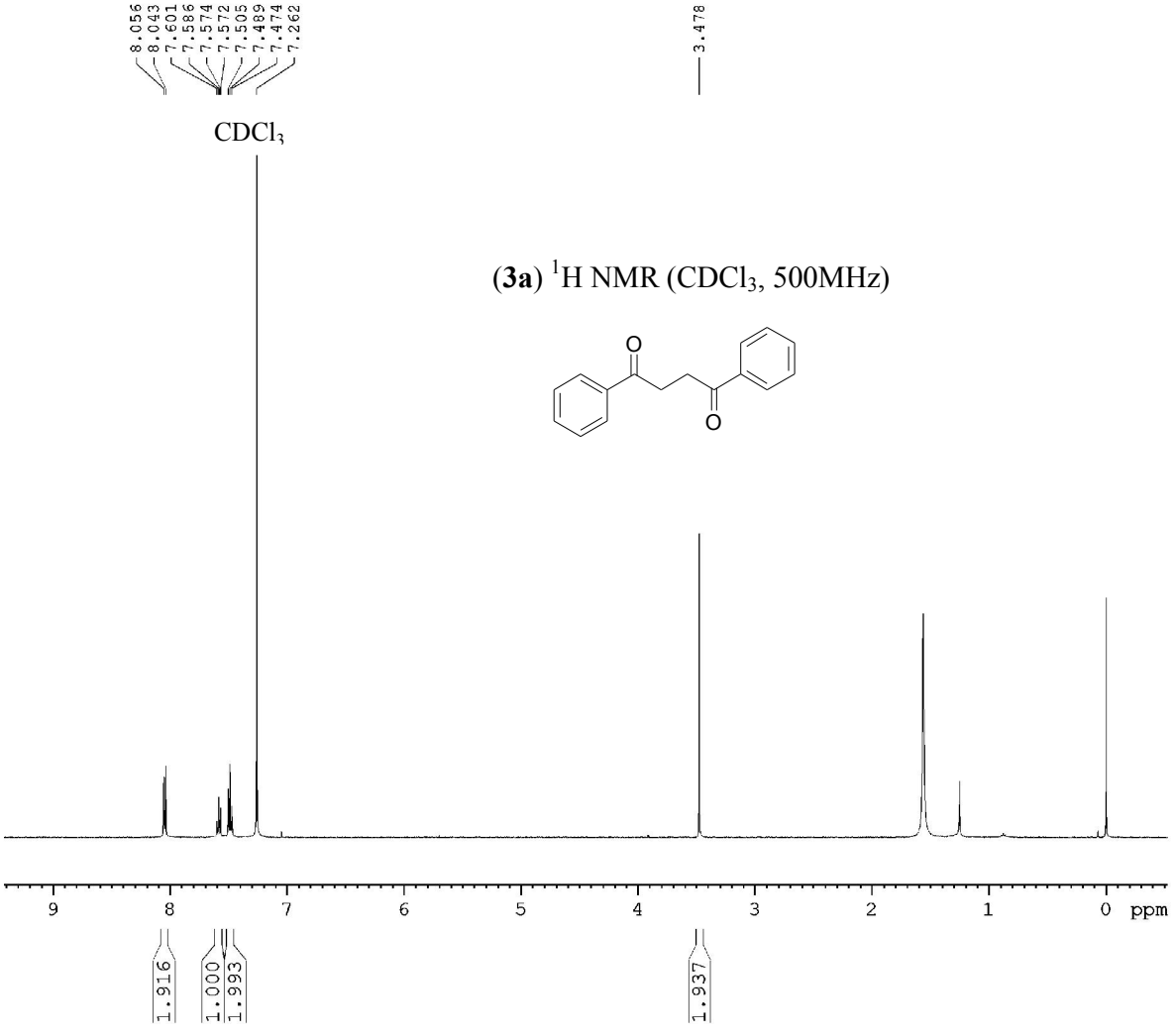


(**2j**) ^{1}H NMR ($CDCl_3$, 500MHz)

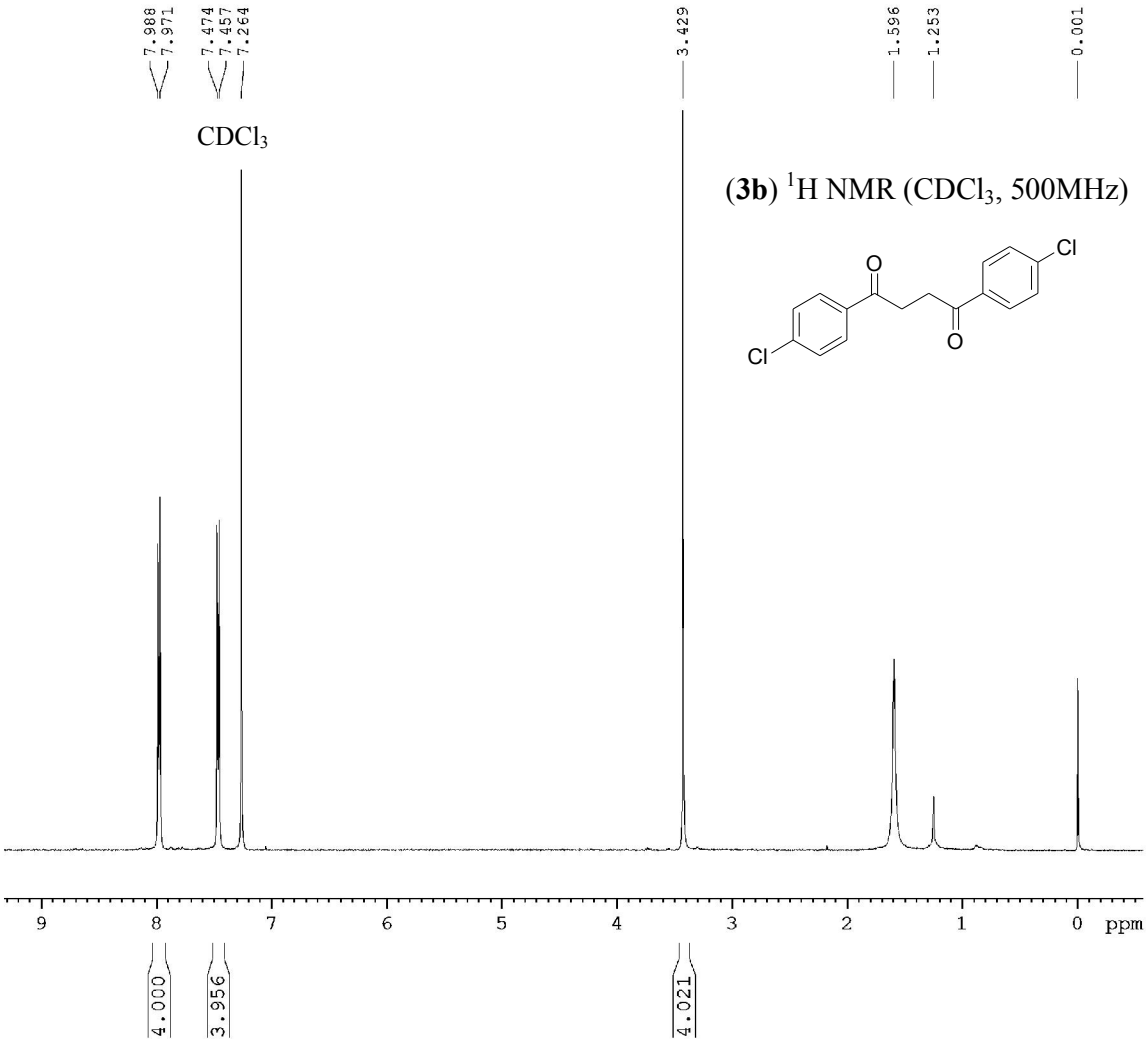




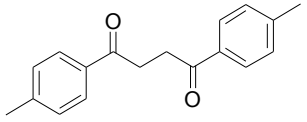
(**2j**) ^{13}C NMR (125MHz, $CDCl_3$)



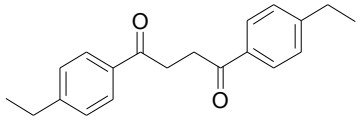
(**3a**) ^{1}H NMR ($CDCl_3$, 500MHz)


7.988
7.971
7.474
7.457
7.264
3.429
1.596
1.253
0.001
CDCl3
(3b) 1H NMR (CDCl3, 500MHz)
Cl
O
O
Cl
9
8
7
6
5
4
3
2
1
0
ppm
4.000
3.956
4.021

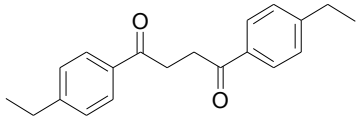
(**3c**) ^{1}H NMR ($CDCl_3$, 500MHz)



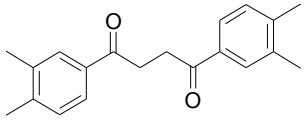
(**3d**) ^{1}H NMR ($CDCl_3$, 500MHz)



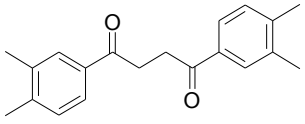
(**3d**) ^{13}C NMR (125MHz, $CDCl_3$)

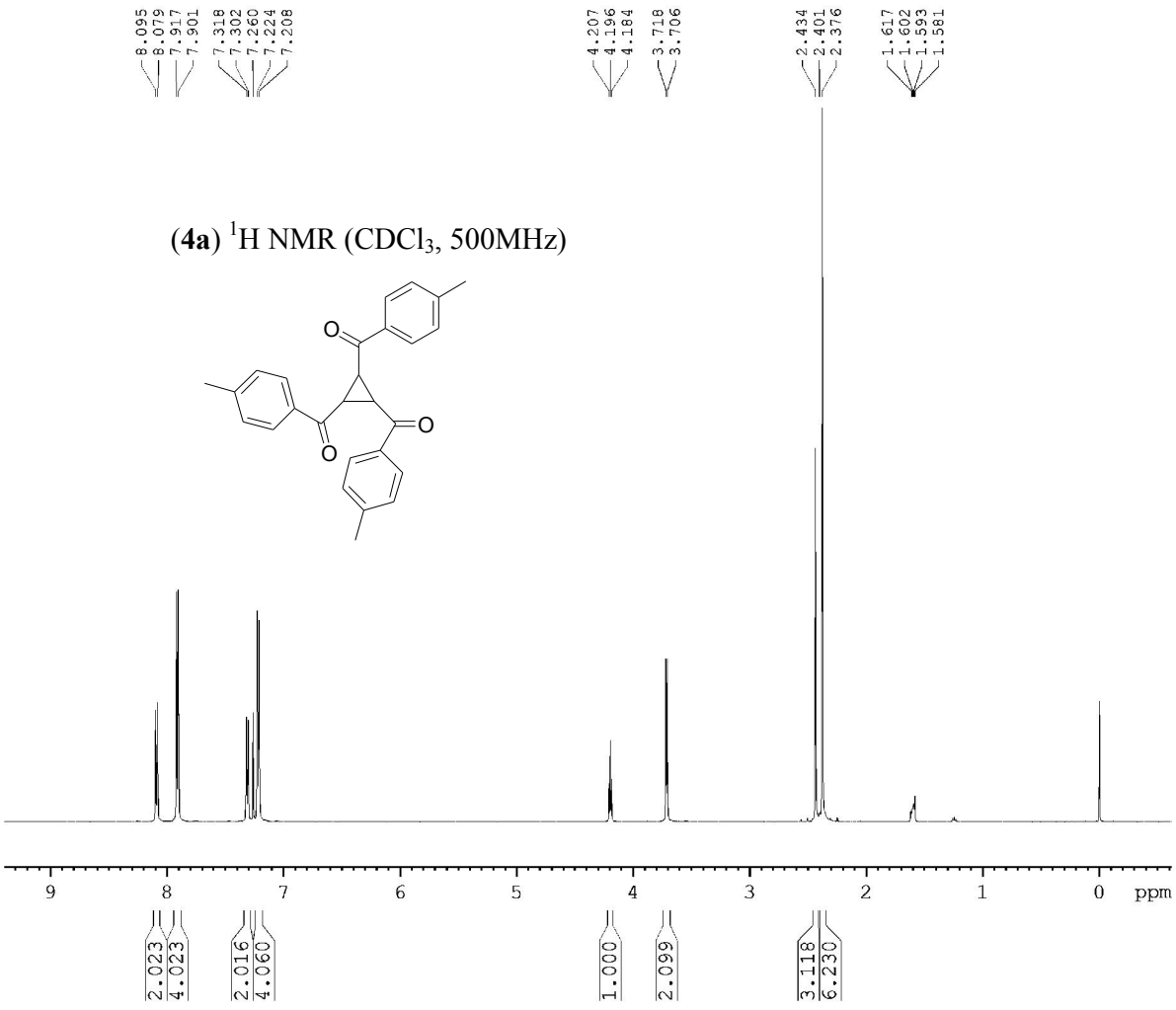


(**3e**) ^{1}H NMR ($CDCl_3$, 500MHz)

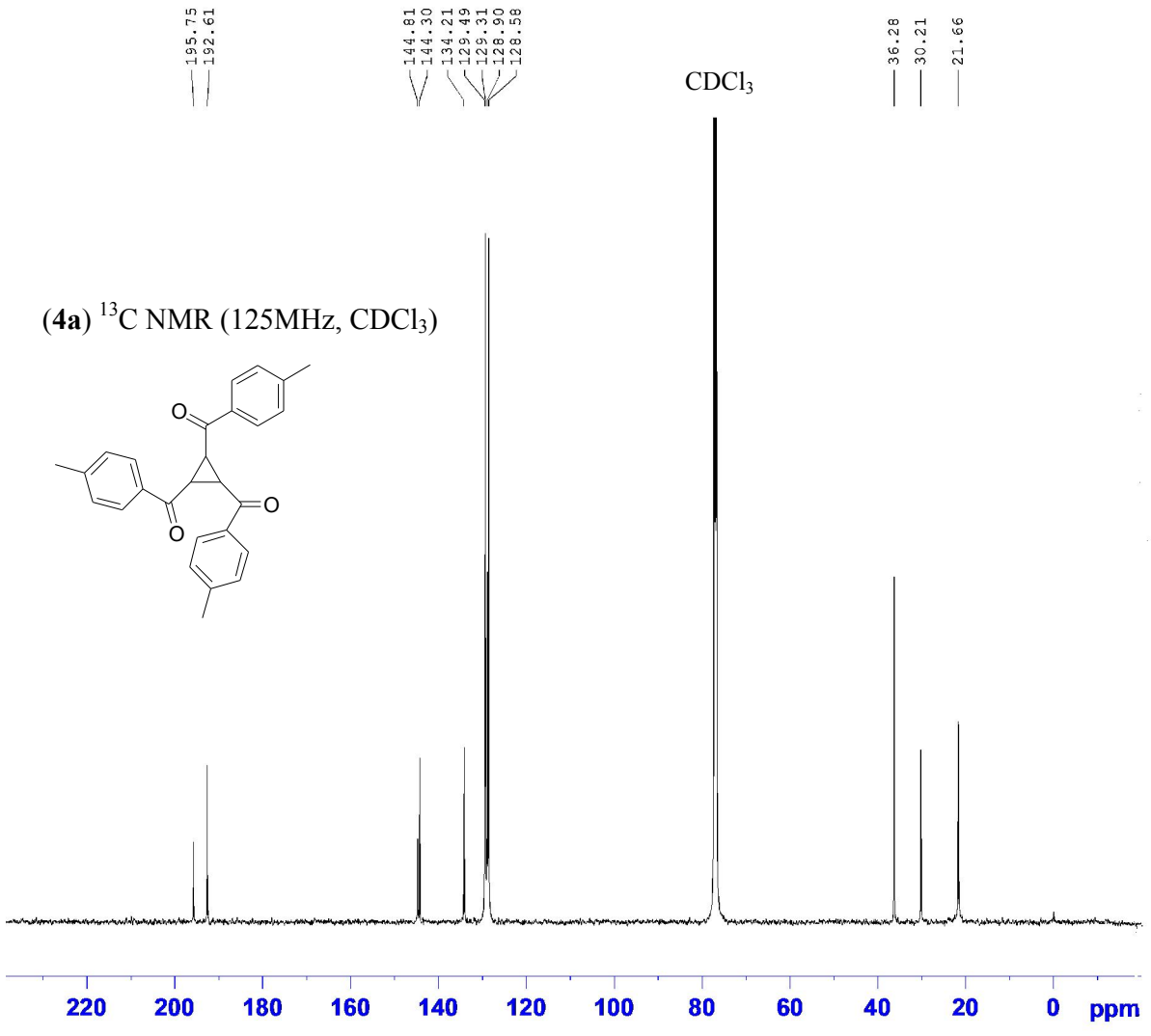


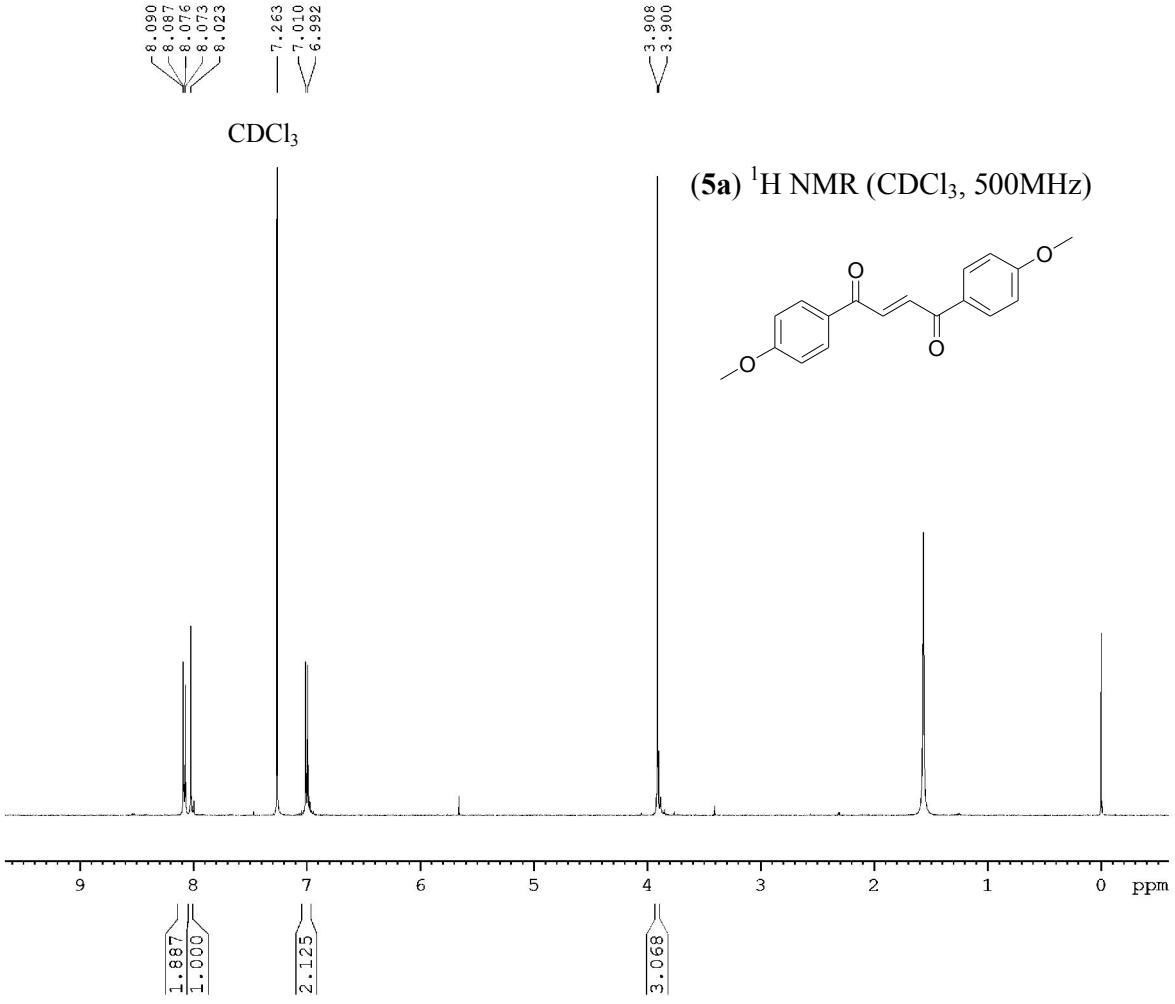
(**3e**) ^{13}C NMR (125MHz, $CDCl_3$)

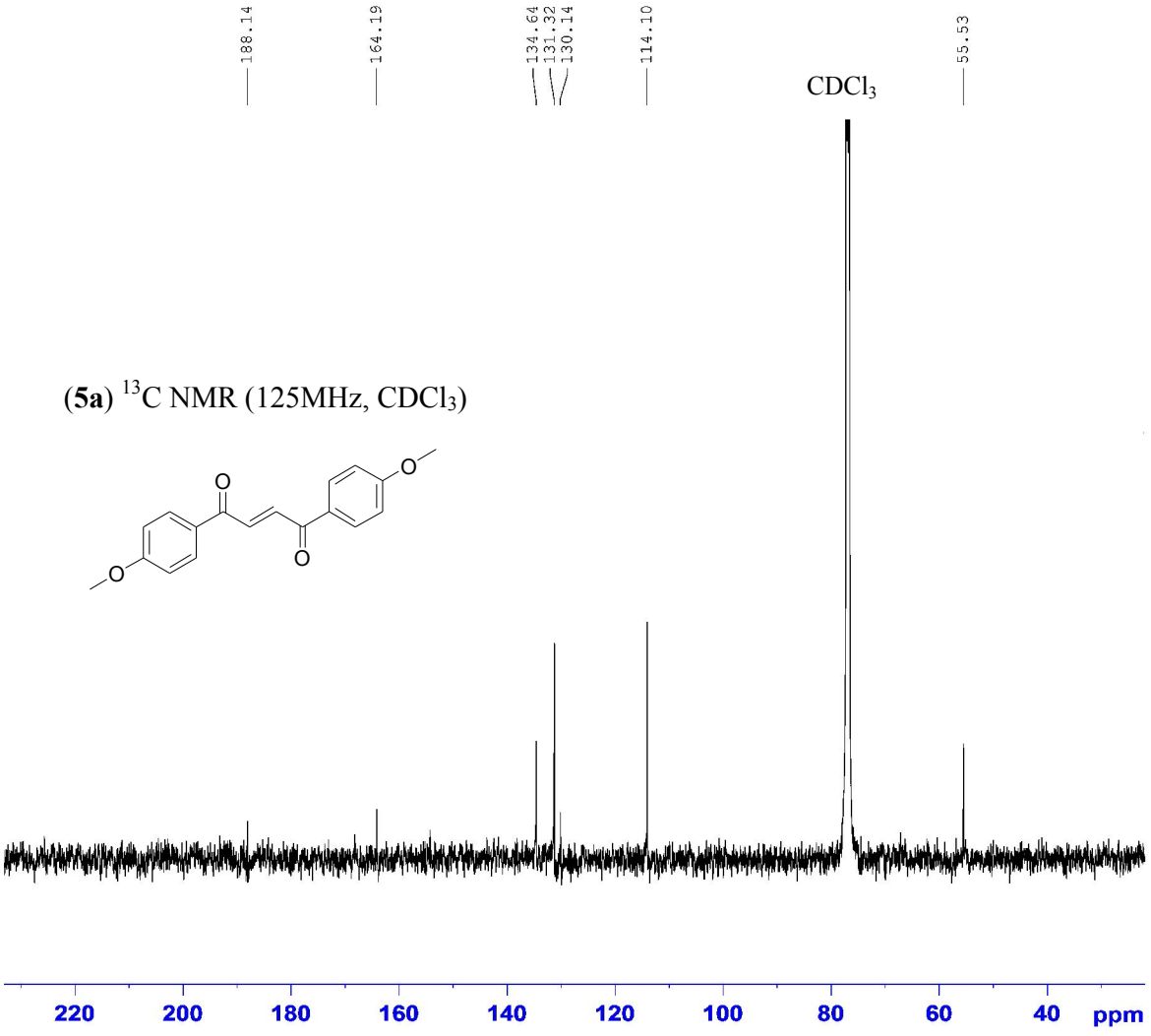




(**4a**) ^{1}H NMR ($CDCl_3$, 500MHz)


195.75
192.61
144.81
144.30
134.21
129.49
129.31
128.90
128.58
CDCl3
36.28
30.21
21.66
(4a) 13C NMR (125MHz, CDCl3)
O
O
O
220
200
180
160
140
120
100
80
60
40
20
0
ppm


8.090
8.087
8.076
8.073
8.023
7.263
7.010
6.992
3.908
3.900
CDCl3
(5a) 1H NMR (CDCl3, 500MHz)
O
O
O
O
9
8
7
6
5
4
3
2
1
0
ppm
1.887
1.000
2.125
3.068



(**5a**) ^{13}C NMR (125MHz, $CDCl_3$)