Supporting Information for

Metal-free photocatalytic homo- and cross dimerization of α-hydroxy ketones via dual C(sp^3)-H functionalization: synthesis of 2,3-dihydroxy-1,4-butanediones

Zhouying Wang,[a] Enrong Tang,[a] Quan-Quan Zhou, [a,]* Jie-Ping Wan[a,]*

[a]College of Chemistry and Chemical Engineering, Institute of Advanced Materials, Jiangxi Normal University, Nanchang 330022, China

***Email**: quanquan.zhou@jxnu.edu.cn; wanjieping@jxnu.edu.cn

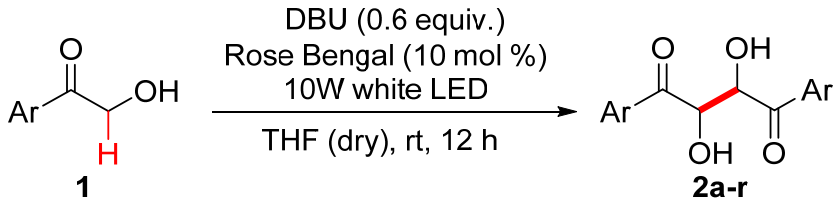
Table of Contents

1. General Information

α-Hydroxy ketone **1b-1r** were synthesized following literature procedures.[1] Other chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further treatment. The ^{1}H NMR and ^{13}C NMR spectra were recorded in a 400 MHz apparatus in DMSO-d_6 or $CDCl_3$. The frequencies for ^{1}H NMR and ^{13}C NMR tests are 400 and 100 MHz, respectively. The chemical shifts were reported in ppm, with TMS as the internal standard. Melting points were tested in an X-4A instrument without correcting temperature, and the HRMS data for all new products were obtained under the ESI model with the TOF analyzer. The EPR spectra were obtained using a Bruker EMXplus-9.5/12 spectrometer.

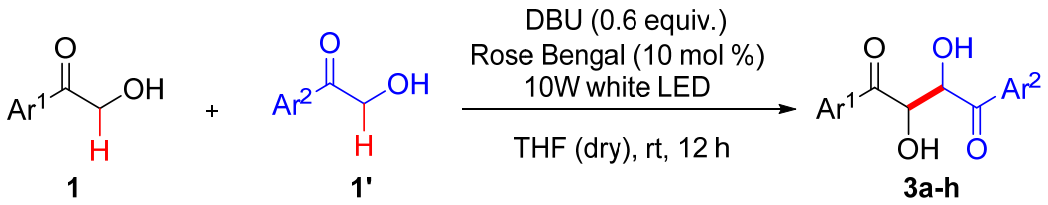
2. General Procedure and Spectral Data of the Products

2.1 General procedure for homo-dimerization of α-hydroxy ketones



Procedure: In a 25 mL round bottom flask, α-hydroxy ketone **1** (0.3 mmol), Rose Bengal (0.03 mmol), DBU (0.09 mmol), dry THF (1 mL), stirred for 12 h at ambient temperature under air with 10 W white LEDs. Subsequently, the mixture was directly employed to reduced pressure to remove the solvent, and the resulting residue was purified by flash column chromatography to give pure product by using mixed ethyl acetate and petroleum ether as eluent (v/v = 3:1~1:10).

2.2 General procedure for cross-dimerization of α-hydroxy ketones



In a 25 mL round bottom flask, α-hydroxyketome **1** (0.15 mmol), α-hydroxyketome **1'** (0.15 mmol), Rose Bengal (0.015 mmol), DBU (0.09 mmol), dry THF (1 mL), stirred for 12 h at ambient temperature under air with 10 W white LEDs. Subsequently, the mixture was directly employed to reduced pressure to remove the solvent, and the resulting residue was purified by flash column chromatography to give pure product by using mixed ethyl acetate and petroleum ether as eluent (v/v = 1:1~1:5).

We have performed 3 representative examples in our condition to detect the homo-coupling products, the present reaction show a good selectivity between two different α-hydroxyl ketones, the homo-dimerization product also detected in the reaction mixture, the results were show below:

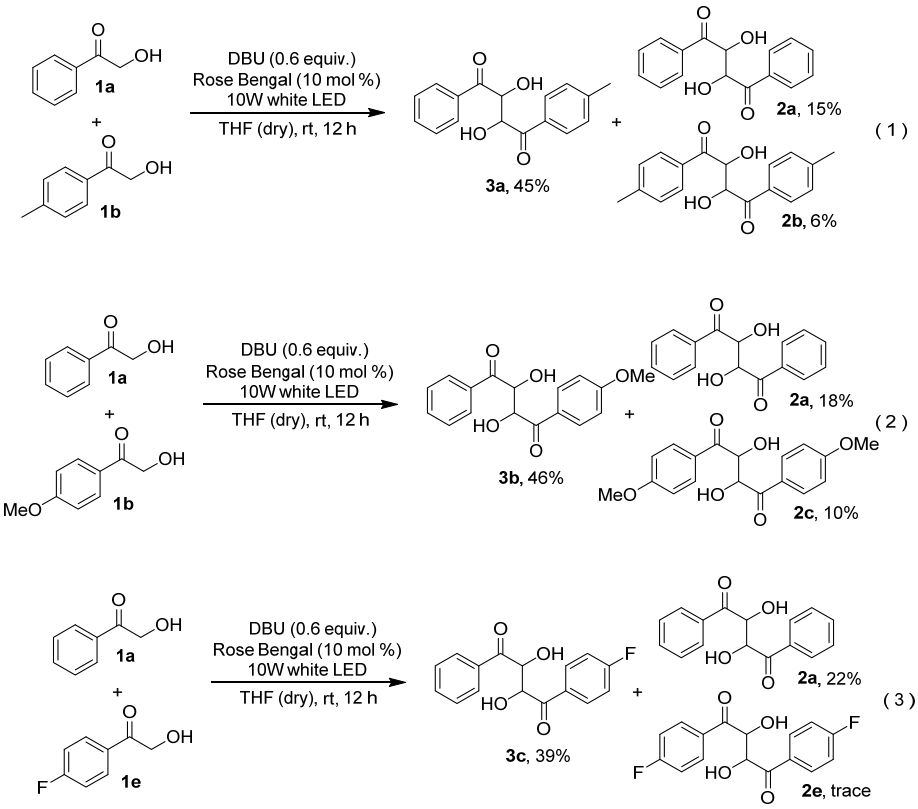


Figure S1 Isolation of homo-coupling products in cross dimerization reaction

2.3 EPR experiments

To a 15 mL Schlenk tube were charged with **1a** (0.30 mmol, 1.0 equiv), Rose Bengal (0.015 mmol, 0.05 equiv), DBU (0.09 mmol, 0.3 equiv), DMPO (5,5-Dimethyl-1-pyrroline *N*-oxide, 0.4 mmol, 2.0 equiv), and dry THF (1 mL). The mixture was

stirred for 10 minutes at ambient temperature under air with sunlight. The solution from the reaction at this stage was located in a small quartz tube and analyzed by the EPR. The spectrum showing signals of carbon-centered free radical was give as Figure S1.

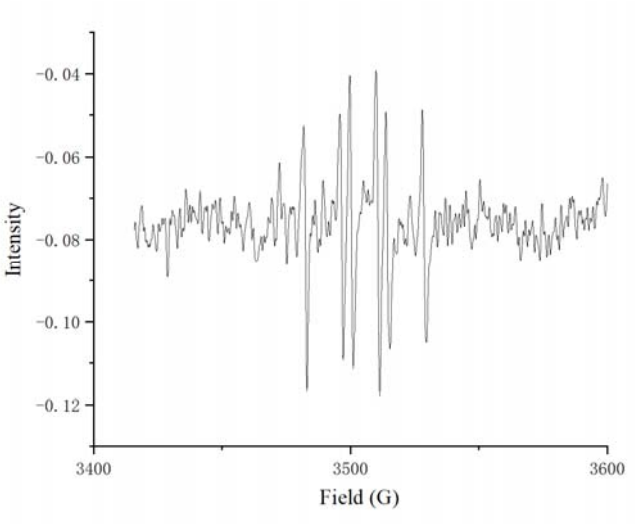


Figure S2 The EPR spectra

2.3 Test 2-oxo-2-phenylacetaldehyde under the optimal conditions

we set up a reaction of 2-oxo-2-phenylacetaldehyde under the optimal conditions, only trace product was observed after 12 hours (**Figure S3)**. On the other hand, we test our model reaction system from time to time with GC-MS analysis, no 2-oxo-2-phenylacetaldehyde was observed in the crude reaction mixture after 30 minutes, 1 hour and 3 hours. These results implicates the 1,2-diketone was not a key intermediate.

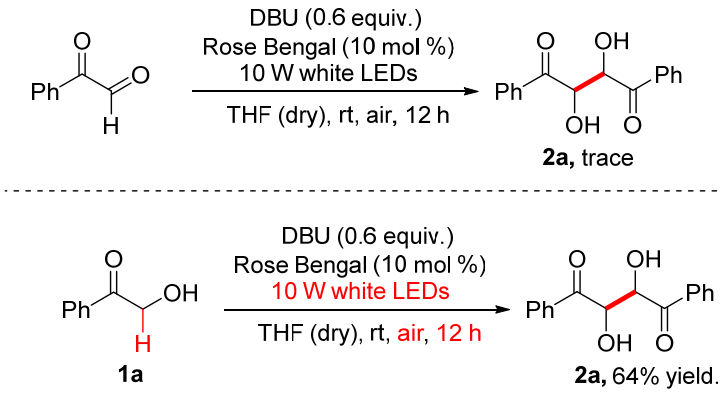
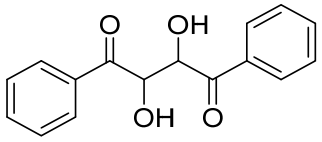


Figure S3 Test 2-oxo-2-phenylacetaldehyde under the optimal conditions

Characterization data of all products



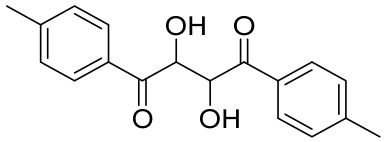
2,3-Dihydroxy-1,4-diphenylbutane-1,4-dione (**2a**).[2]

Eluent: V_{PE}/V_{EA}= 5:1; mp 58-60 ºC.

Yield: 64% (White solid, 26.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.99 (d, *J* = 7.4 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 4H), 5.38 (d, *J* = 4.8 Hz, 2H), 3.94 (d, *J* = 5.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =197.7, 134.2, 134.0, 129.2, 128.3, 74.7.



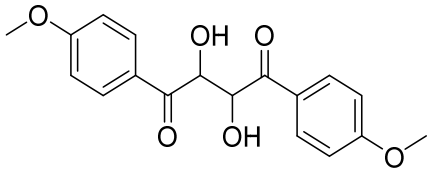
2,3-Dihydroxy-1,4-di-p-tolylbutane-1,4-dione (**2b**).[2]

Eluent: V_{PE}/V_{EA}= 3:1; mp 65-67 ºC.

Yield: 70% (White solid, 31.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.89 (d, *J* = 8.0 Hz, 4H), 7.39 (d, *J* = 7.8 Hz, 4H), 5.33 (d, *J* = 5.4 Hz, 2H), 3.92 (d, *J* = 7.0 Hz, 2H), 2.48 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =197.2, 145.3, 131.4, 129.9, 128.4, 74.7, 21.8.



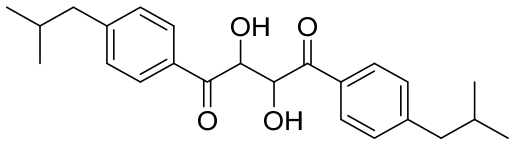
2,3-Dihydroxy-1,4-bis(4-methoxyphenyl)butane-1,4-dione (**2c**).[2]

Eluent: V_{PE}/V_{EA}= 1:2; mp 88-90 ºC.

Yield:71% (White solid, 35.2 mg).

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) =8.00 (d, *J* = 9.0 Hz, 4H), 7.09 (d, *J* = 9.0 Hz, 4H), 5.41 (d, *J* = 6.8 Hz, 2H), 5.20 (d, *J* = 6.2 Hz, 2H), 3.87 (s, 6H).

^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) =202.5, 168.4, 136.2, 133.1, 119.2, 79.6, 60.8.



2,3-Dihydroxy-1,4-bis(4-isobutylphenyl)butane-1,4-dione (**2d**).

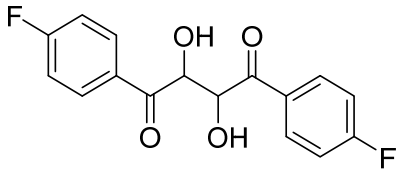
Eluent: V_{PE}/V_{EA}= 4:1; mp 96-98 ºC.

Yield: 54% (White solid, 30.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.93 (d, *J* = 8.0 Hz, 4H), 7.37 (d, *J* = 8.0 Hz, 4H), 5.38 (s, 2H), 3.96 (s, 2H), 2.59 (d, *J* = 7.2 Hz, 4H), 1.98 - 1.91 (m, 2H), 0.95 (dd, *J* = 6.6, 2.2 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =197.2, 149.1, 131.5, 123.0, 128.4, 74.7, 45.5, 30.1, 22.4, 22.3.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{30}O_4Na$ 405.2036; Found 405.2033.



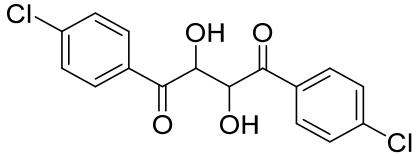
1,4-Bis(4-fluorophenyl)-2,3-dihydroxybutane-1,4-dione (**2e**).[2]

Eluent: V_{PE}/V_{EA}= 4:1; mp 67-69 ºC.

Yield: 49% (White solid, 22.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =8.02 (dd, *J* = 8.6, 5.4 Hz, 4H), 7.29 – 7.23 (m, 4H), 5.33 (d, *J* = 5.0 Hz, 2H), 3.88 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =191.4, 161.6 (d, $J_{C\text{-}F}$ = 255 Hz), 126.4 (d, $J_{C\text{-}F}$ = 9 Hz), 125.5 (d, $J_{C\text{-}F}$ = 2 Hz), 111.8 (d, $J_{C\text{-}F}$ = 22 Hz), 69.9.



1,4-Bis(4-chlorophenyl)-2,3-dihydroxybutane-1,4-dione (**2f**).

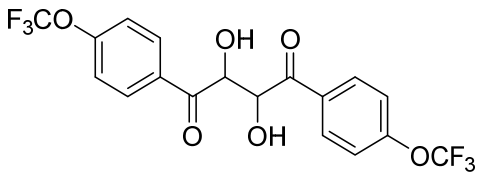
Eluent: V_{PE}/V_{EA}= 5:1; mp 78-80 ºC.

Yield: 44% (White solid 22.3 mg).

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) =8.01 (d, J = 8.6 Hz, 4H), 7.63 (d, J = 8.6 Hz, 4H), 5.69 (d, J = 7.0 Hz, 2H), 5.21 (d, J = 6.0 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) =198.9, 138.5, 134.5, 131.1, 129.3, 75.4.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{12}Cl_2O_4Na$ 361.0005; Found 361.0001.



2,3-Dihydroxy-1,4-bis(4-(trifluoromethoxy)phenyl)butane-1,4-dione (**2g**).

Eluent: V_{PE}/V_{EA}=3:1; mp 51-53 ºC.

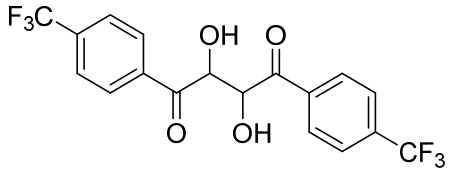
Yield: 41% (White solid, 27.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =8.04 (d, J = 8.8 Hz, 4H), 7.42 (d, J = 8.6 Hz, 4H), 5.35 (s, 2H), 3.86 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =196.3, 153.5, 132.1, 130.5, 120.9, 120.3, (d, $J_{C\text{-}F}$ = 258 Hz) 74.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) =-57.6.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{12}F_6O_6Na$ 461.0430; Found 461.0433.



2,3-Dihydroxy-1,4-bis(4-(trifluoromethyl)phenyl)butane-1,4-dione (**2h**).

Eluent: V_{PE}/V_{EA}=10:1; mp 49-51 ºC.

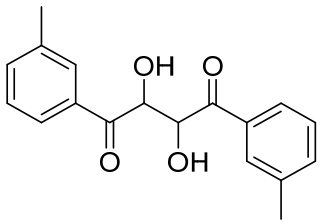
Yield: 26% (White solid, 15.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =8.07 (d, J = 8.2 Hz, 4H), 7.87 (d, J = 8.2 Hz, 4H), 5.36 (s, 2H), 3.86 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =197.0, 136.8, 135.6 (d, J_{C-F} = 33 Hz), 128.7, 126.3 (d, J_{C-F} = 3 Hz), 123.3 (d, J_{C-F} = 272 Hz), 75.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) =-63.3.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{12}F_6O_4Na$ 429.0532; Found 429.0537.



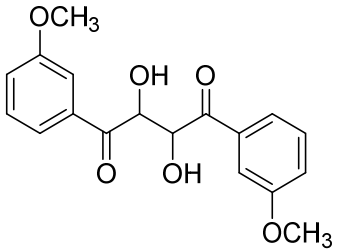
2,3-Dihydroxy-1,4-di-m-tolylbutane-1,4-dione (**2i**).[2]

Eluent: V_{PE}/V_{EA}=5:1; mp 48-50 °C.

Yield: 55% (White solid, 24.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.79 (s, 2H), 7.76 (d, *J* = 7.0 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 4H), 5.33 (d, *J* = 7.0 Hz, 2H), 3.89 (d, *J* = 7.4 Hz, 2H), 2.48 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =197.9, 139.3, 135.0, 133.9, 129.0, 129.0, 125.4, 74.7, 21.4.



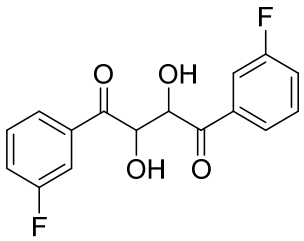
2,3-Dihydroxy-1,4-bis(4-methoxyphenyl)butane-1,4-dione (**2j**).[2]

Eluent: V_{PE}/V_{EA}=1:1; mp 71-73 °C.

Yield: 62% (White solid , 30.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.56 – 7.48 (m, 6H), 7.23 (dd, *J* = 7.8, 2.5 Hz, 2H), 5.35 (d, *J* = 3.9 Hz, 2H), 3.91 (s, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =197.5, 160.3, 135.2, 130.2, 120.7, 120.4, 112.9, 74.8, 55.6.



1,4-Bis(3-fluorophenyl)-2,3-dihydroxybutane-1,4-dione (**2k**).

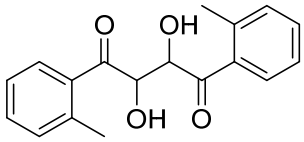
Eluent: V_{PE}/V_{EA}=5:1; mp 57-59 ºC.

Yield: 43% (White solid, 19.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.76 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 9.0 Hz, 2H), 7.62 - 7.56 (m, 2H), 7.42-7.38 (m, 2H), 5.3 (s, 2H), 3.9 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =196.5, 163.2 (d, J_{C-F} = 248 Hz), 135.8 (d, J_{C-F} = 6 Hz), 131.0 (d, J_{C-F} = 8 Hz), 123.9 (d, J_{C-F} = 3 Hz), 121.4 (d, J_{C-F} = 21 Hz), 115.4 (d, J_{C-F} = 23 Hz), 74.8.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{12}F_2O_4Na$ 329.0596; Found 329.0598.



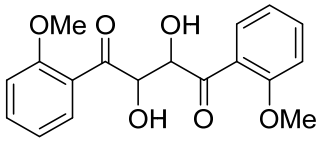
2,3-Dihydroxy-1,4-di-o-tolylbutane-1,4-dione (**2l**).[2]

Eluent: V_{PE}/V_{EA}=4:1; mp 99-100 ºC.

Yield: 39% (White solid, 17.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.46 (dd, *J* = 17.5, 7.7 Hz, 4H), 7.37 – 7.30 (m, 4H), 5.08 (d, *J* = 6.7 Hz, 2H), 3.85 (d, *J* = 6.8 Hz, 2H), 2.52 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =200.8, 139.5, 134.3, 132.5, 132.2, 127.3, 125.8, 75.9, 20.4.



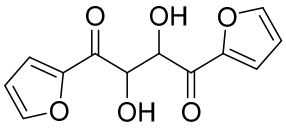
2,3-Dihydroxy-1,4-bis(2-methoxyphenyl)butane-1,4-dione (**2m**).[2]

Eluent: V_{PE}/V_{EA}=1:1; mp 64-66 ºC.

Yield: 43% (White solid, 21.3 mg).

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) =7.57 – 7.52 (m, 4H), 7.13 (d, J = 8.2 Hz, 2H), 7.02 (t, J = 7.5 Hz, 2H), 6.95 (s, 2H), 3.8 (s, 6H).

^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) =193.1, 159.2, 136.7, 134.8, 130.6, 127.1, 121.0, 113.1, 56.3.



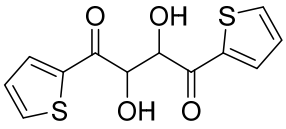
1,4-Di(furan-2-yl)-2,3-dihydroxybutane-1,4-dione (**2n**).[2]

Eluent: V_{PE}/V_{EA}=5:1; mp 51-53 ºC.

Yield: 49% (White solid, 18.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.74 (s, 2H), 7.51 (d, J = 3.3 Hz, 2H), 6.69 – 6.68 (m, 2H), 5.45 (s, 2H), 3.85 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =185.3, 150.2, 147.3, 119.5, 113.0, 75.0.



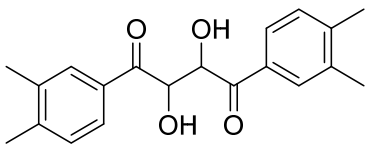
2,3-Dihydroxy-1,4-di(thiophen-2-yl)butane-1,4-dione (**2o**).[2]

Eluent: V_{PE}/V_{EA}=1:1; mp 67-69 ºC.

Yield: 43% (White solid, 18.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =8.02 (d, J = 3.8 Hz, 2H), 7.81 (d, J = 4.9 Hz, 2H), 7.28 (s, 2H), 5.31 (s, 2H), 3.88 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =189.8, 139.2, 135.2, 133.5, 128.6, 76.4.



1,4-Bis(3,4-dimethylphenyl)-2,3-dihydroxybutane-1,4-dione (**2p**).

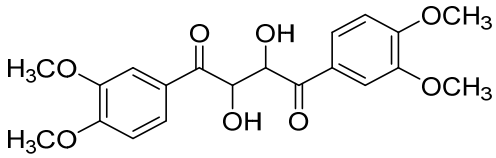
Eluent: V_{PE}/V_{EA}=2:1; ; mp 94-96 ºC.

Yield: 66% (White solid, 32.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.78 (s, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 5.32 (d, *J* = 5.6 Hz, 2H), 3.91 (d, *J* = 6.6 Hz, 2H), 2.39 (d, *J* = 3.7 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =197.5, 144.1, 137.8, 131.6, 130.3, 129.6, 125.9, 74.6, 20.2, 19.9.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{22}O_4Na$ 349.1410; Found 349.1411.



1,4-Bis(3,4-dimethoxyphenyl)-2,3-dihydroxybutane-1,4-dione (**2q**).

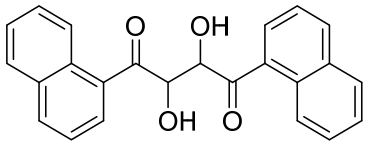
Eluent: V_{PE}/V_{EA}=1:3; mp 119-121 ºC.

Yield: 63% (White solid, 36.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.64 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.62 (s, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 5.37 (d, *J* = 5.2 Hz, 2H), 4.01 (s, 6H), 3.99 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =196.0, 154.4, 149.8, 126.8, 122.5, 111.1, 110.3, 74.7, 56.2, 56.1.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{22}O_8Na$ 413.1207; Found 413.1205.



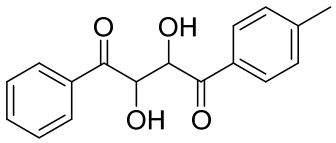
2,3-Dihydroxy-1,4-di(naphthalen-1-yl)butane-1,4-dione (**2r**).

Eluent: V_{PE}/V_{EA}=5:1; mp 92-94 ºC.

Yield: 41% (White solid, 22.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =8.48 (d, *J* = 8.3 Hz, 2H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.68 – 7.63 (m, 4H), 7.62 – 7.58 (m, 2H), 7.56 – 7.52 (m, 2H), 5.31 (d, *J* = 5.5 Hz, 2H), 4.03 (d, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =200.7, 134.2, 133.6, 132.5, 130.5, 130.1, 128.5, 127.2, 126.7, 125.7, 124.2, 76.4.



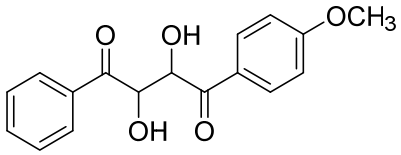
2,3-Dihydroxy-1-phenyl-4-(p-tolyl)butane-1,4-dione (**3a**).[2]

Eluent: V_{PE}/V_{EA}=5:1; mp 67-69 °C.

Yield: 45% (White solid, 19.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.98 (d, *J* = 7.7 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 5.36 (d, *J* = 10.0 Hz, 2H), 3.95 (d, *J* = 12.1 Hz, 2H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =197.8, 197.1, 145.4, 134.2, 134.0, 131.2, 129.9, 129.2, 128.4, 128.3, 74.9, 74.5, 21.8.



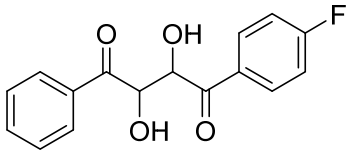
2,3-Dihydroxy-1-(4-methoxyphenyl)-4-phenylbutane-1,4-dione (**3b**).

Eluent: V_{PE}/V_{EA}=3:1; mp 78-80 °C.

Yield: 47% (White solid, 21.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =8.01 (d, *J* = 8.4 Hz, 4H), 7.72 (t, *J* = 7.3 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 5.35 (d, *J* = 24.7 Hz, 2H), 4.00 (s, 1H), 3.93 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =197.9, 195.7, 164.5, 134.2, 134.1, 130.8, 129.2, 128.3, 126.4, 114.5, 75.1, 74.2, 55.7.



1-(4-Fluorophenyl)-2,3-dihydroxy-4-phenylbutane-1,4-dione (**3c**).

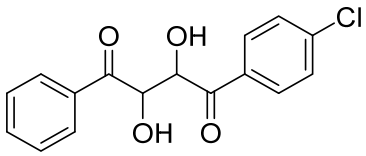
Eluent: V_{PE}/V_{EA}=5:1; mp 67-69 ºC.

Yield: 39% (White solid, 16.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =8.03 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 5.35 (d, *J* = 13.4 Hz, 2H), 3.95 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =197.6, 196.1, 166.3 (d, $J_{C\text{-}F}$ = 256 Hz), 134.3, 133.9, 131.2 (d, $J_{C\text{-}F}$ = 9 Hz), 130.3 (d, $J_{C\text{-}F}$ = 3 Hz), 129.3, 128.3, 116.5 (d, $J_{C\text{-}F}$ = 22 Hz), 74.72, 74.70; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) =-102.4.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{13}FO_4Na$ 311.0690; Found 311.0689.



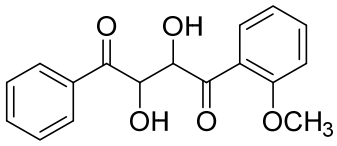
1-(4-Chlorophenyl)-2,3-dihydroxy-4-phenylbutane-1,4-dione (**3d**).

Eluent: V_{PE}/V_{EA}=5:1; mp 71-73 ºC.

Yield: 34% (White solid, 15.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.97 (d, *J* = 7.4 Hz, 4H), 7.93 (d, *J* = 8.5 Hz, 4H),7.70 (t, *J* = 7.4 Hz, 1H), 7.60 (dd, *J* = 12.9, 8.1 Hz, 4H), 5.34 (dd, *J* = 12.7, 6.3 Hz, 2H), 3.95 (d, *J* = 6.9 Hz, 1H), 3.87 (d, *J* = 7.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =197.6, 196.7, 140.8, 134.3, 133.9, 132.3, 129.8, 129.6, 129.3, 128.3, 74.8, 74.6.



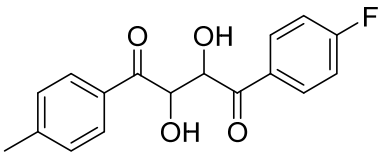
2,3-Dihydroxy-1-(2-methoxyphenyl)-4-phenylbutane-1,4-dione (**3e**).

Eluent: V_{PE}/V_{EA}=1:1; mp 98-100 ºC.

Yield: 41% (White solid, 18.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =8.03 (d, *J* = 7.3 Hz, 2H), 7.89 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.57 (dt, *J* = 15.3, 7.1 Hz, 3H), 7.15 – 7.08 (m, 2H), 5.58 (s, 1H), 5.41 (s, 1H), 4.03 (s, 4H), 3.88 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =198.7, 197.8, 158.2, 135.0, 134.1, 133.9, 131.9, 128.9, 128.5, 124.3, 122.0, 111.8, 78.3, 74.0, 56.0.



1-(4-Fluorophenyl)-2,3-dihydroxy-4-(p-tolyl)butane-1,4-dione (**3f**).

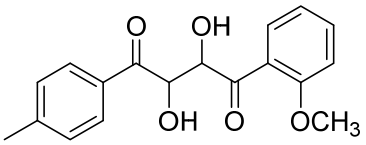
Eluent: V_{PE}/V_{EA}=5:1; mp 77-79 ºC.

Yield: 51% (White solid, 23.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =8.03 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.26 (s, 2H), 5.33 (s, 2H), 3.99 (s, 1H), 3.89 (s, 1H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =197.1, 196.3, 166.3 (d, $J_{C\text{-}F}$ = 255 Hz), 145.5, 131.2 (d, $J_{C\text{-}F}$ = 5 Hz), 131.1, 130.3 (d, $J_{C\text{-}F}$ = 3 Hz), 130.0, 128.4, 116.5 (d, $J_{C\text{-}F}$ = 22 Hz), 74.9, 74.5, 21.8.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{15}FO_4Na$ 325.0847; Found 325.0849.



2,3-Dihydroxy-1-(2-methoxyphenyl)-4-(p-tolyl)butane-1,4-dione (**3g**).

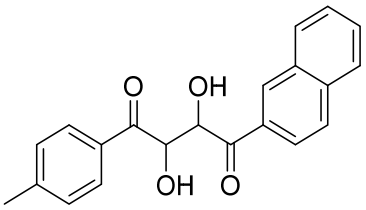
Eluent: V_{PE}/V_{EA}=2:1; mp 82-84 ºC.

Yield: 48% (White solid, 22.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.93 (d, *J* = 7.8 Hz, 2H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 5.56 (s, 1H), 5.36 (s, 1H), 4.04 (s, 3H), 3.99 (d, *J* = 5.3 Hz, 1H), 3.90 (d, *J* = 6.5 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =198.8, 197.2, 158.2, 145.0, 134.8, 131.9, 131.3, 129.5, 128.7, 124.6, 122.0, 111.8, 78.5, 73.8, 56.0, 21.8..

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{18}O_5Na$ 337.1046; Found 337.1048.



2,3-Dihydroxy-1-(naphthalen-2-yl)-4-(p-tolyl)butane-1,4-dione (**3h**).

Eluent: V_{PE}/V_{EA}=4:1; mp 93-95 °C.

Yield: 33% (White solid, 16.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =8.50 (s, 1H), 8.02 (d, *J* = 5.5 Hz, 3H), 7.93 (t, *J* = 6.8 Hz, 3H), 7.69 – 7.61 (m, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 5.49 (d, *J* = 6.6 Hz, 1H), 5.39 (d, *J* = 6.5 Hz, 1H), 3.94 (d, *J* = 7.1 Hz, 2H), 2.50 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =197.8, 197.3, 145.4, 136.1, 132.5, 131.4, 131.3, 130.2, 129.9, 129.5, 129.3, 129.2, 128.5, 128.0, 127.4, 123.8, 74.9, 74.6, 21.8.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{18}O_4Na$ 357.1097; Found 357.1099.

References

1. R. Mato, R. Manzano, E. Reyes, L. Carrillo, U. Uria and J. L. Vicario, *J. Am. Chem. Soc.,* 2019, **141**, 9495-9499.

2. J. Wang, P.-L. Shao, X. Lin, B. Mao, J. Wen and Zhang, *Angew. Chem., Int. Ed.,* 2020, **59**, 18166-18171.

NMR Spectra of the Synthesized Compounds

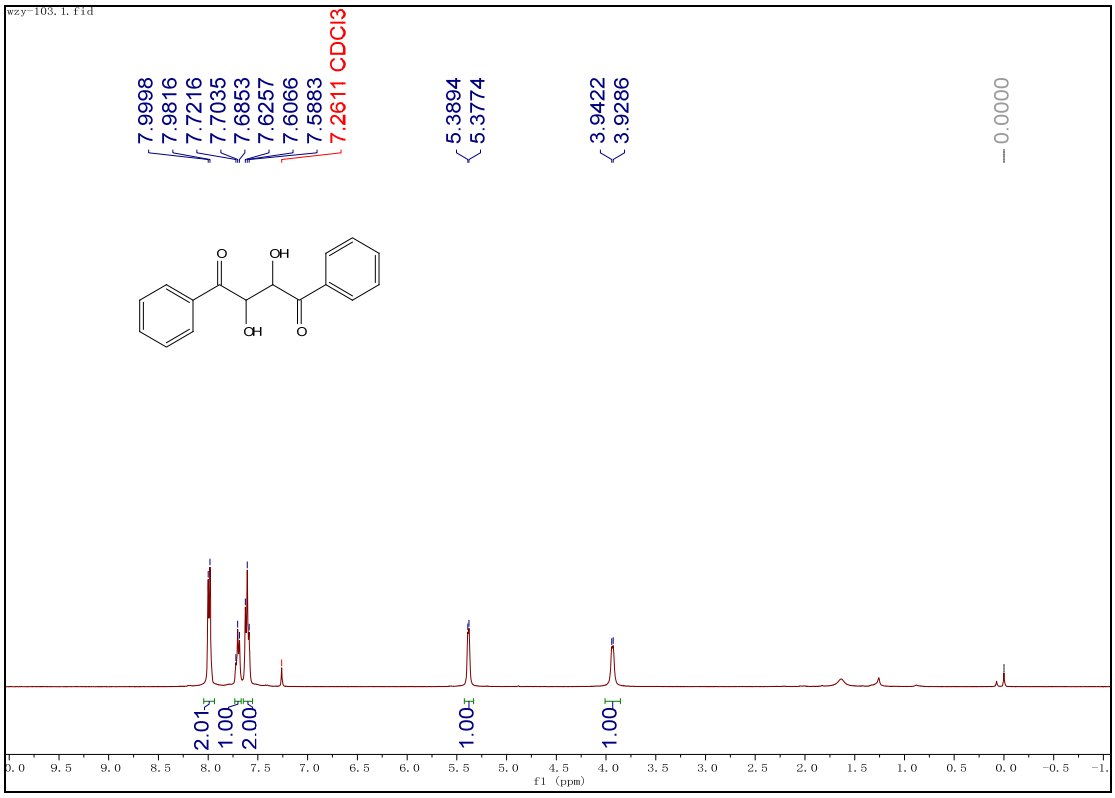


Figure S4. ^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$)

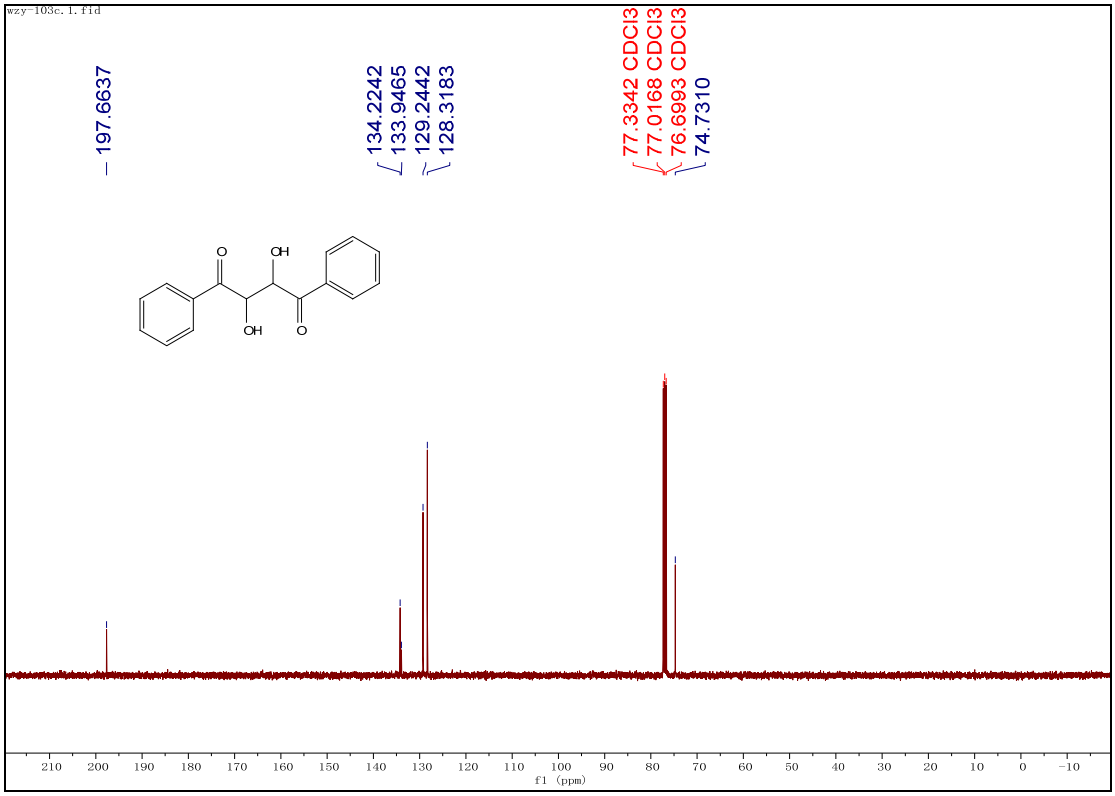


Figure S5. ^{13}C NMR spectrum of **2a** (100 MHz, $CDCl_3$)

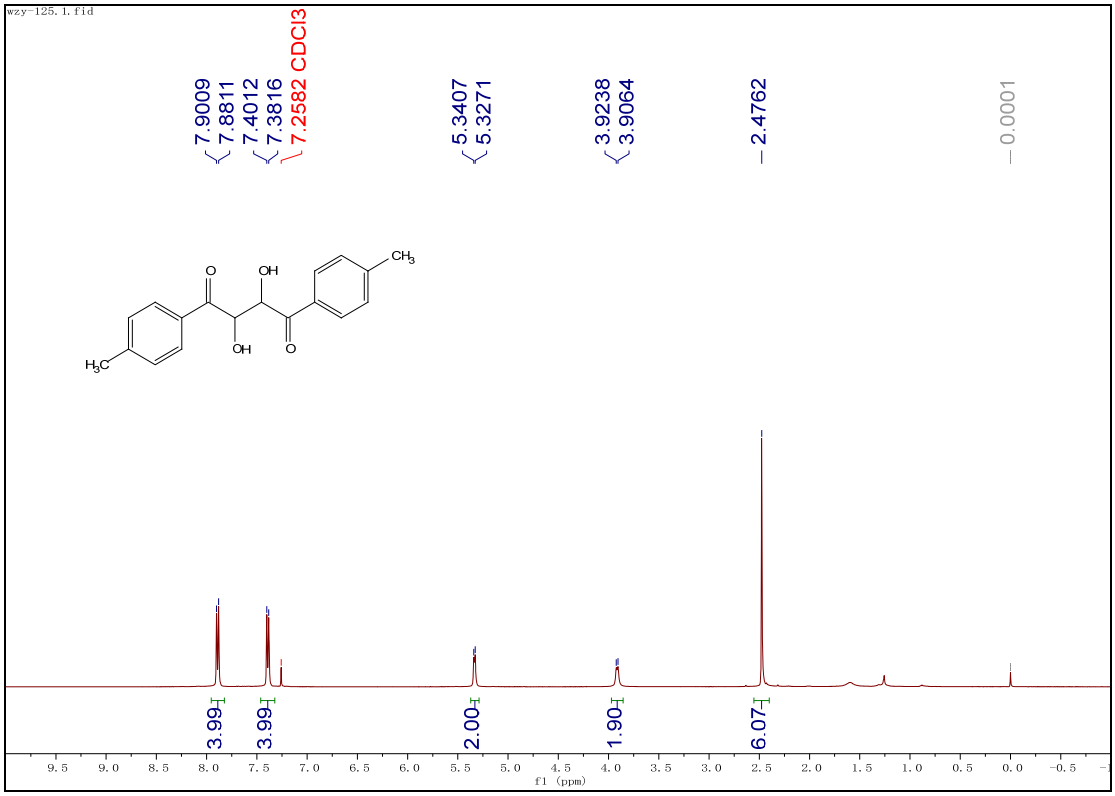


Figure S6. ^{1}H NMR spectrum of **2b** (400 MHz, $CDCl_3$)

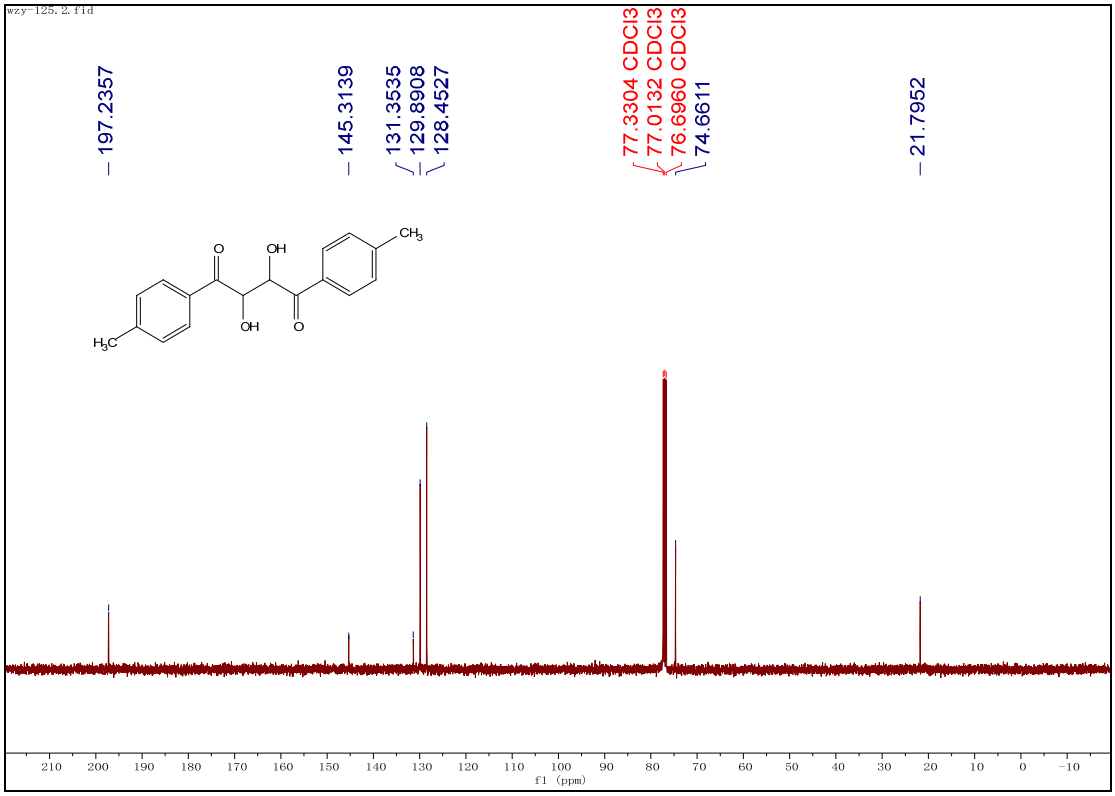


Figure S7. ^{13}C NMR spectrum of **2b** (100 MHz, $CDCl_3$)

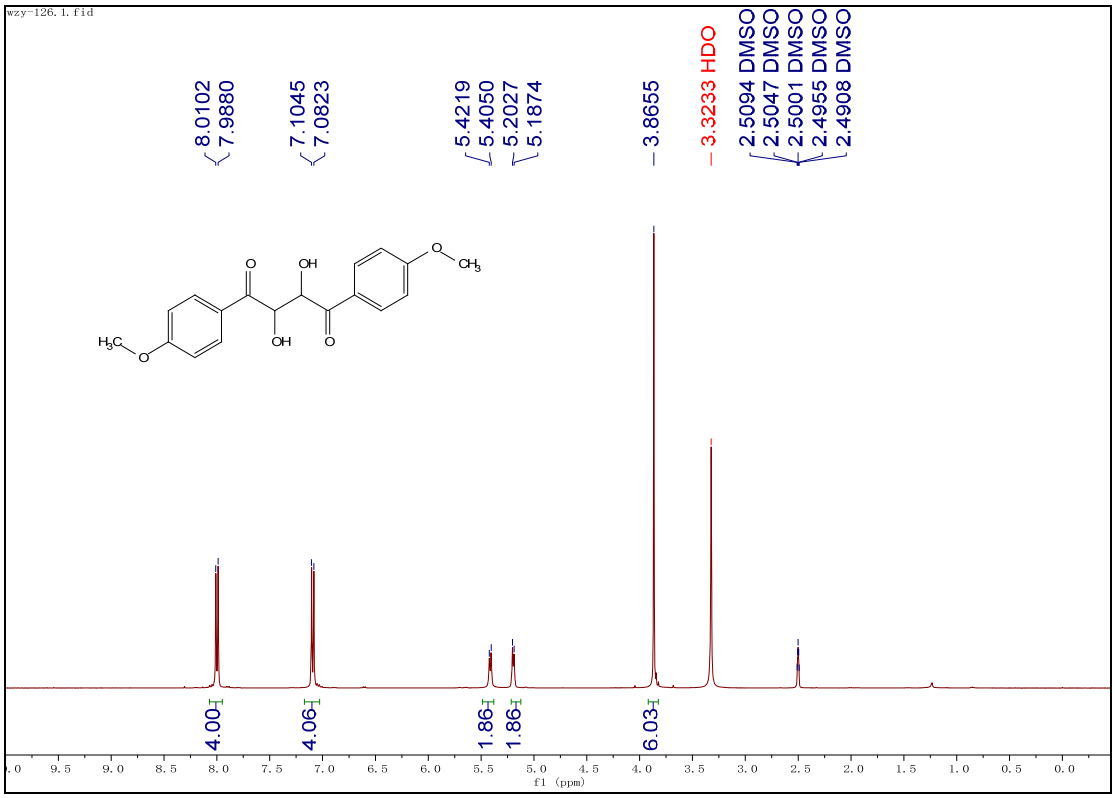


Figure S8. ^{1}H NMR spectrum of **2c** (400 MHz, $CDCl_3$)

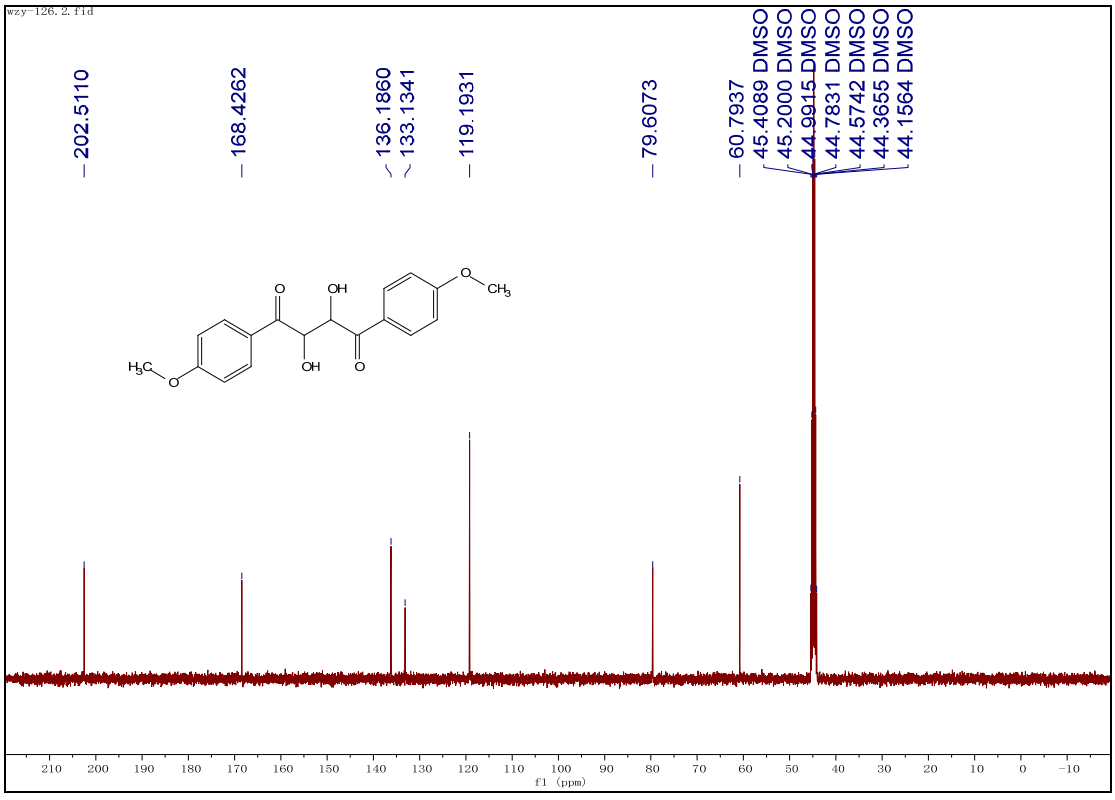


Figure S9. ^{13}C NMR spectrum of **2c** (100 MHz, $CDCl_3$)

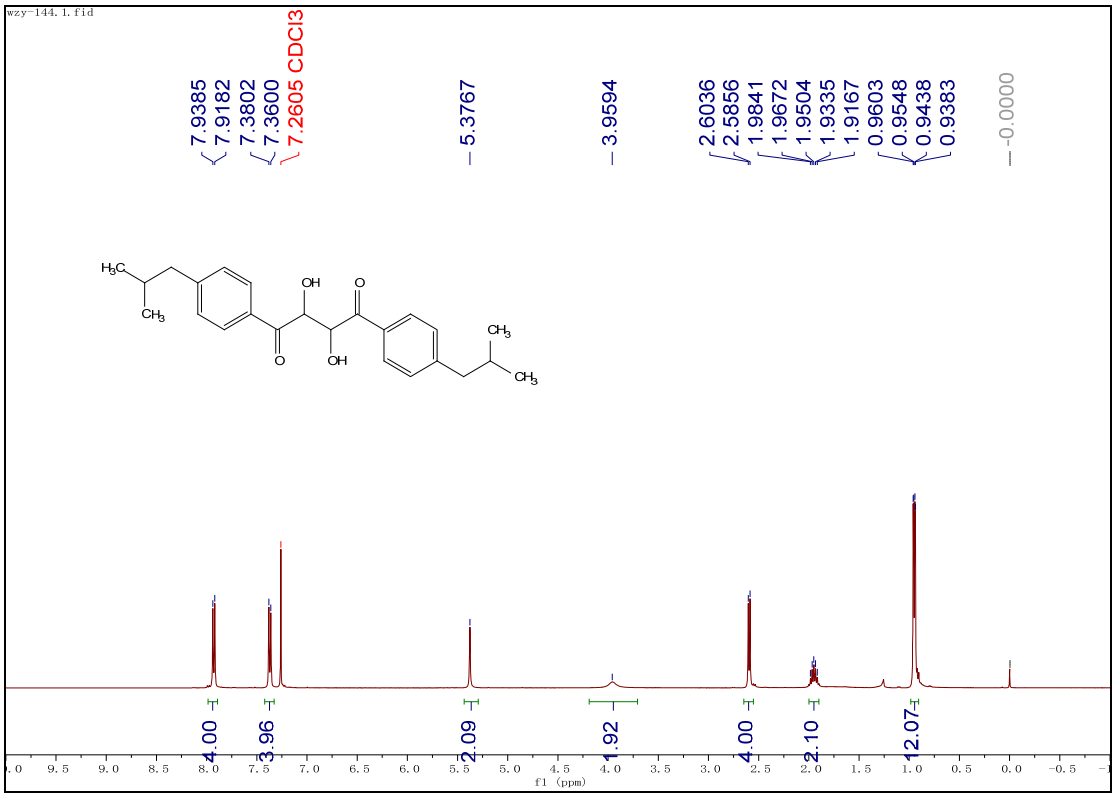


Figure S10. ^{1}H NMR spectrum of **2d** (400 MHz, $CDCl_3$)

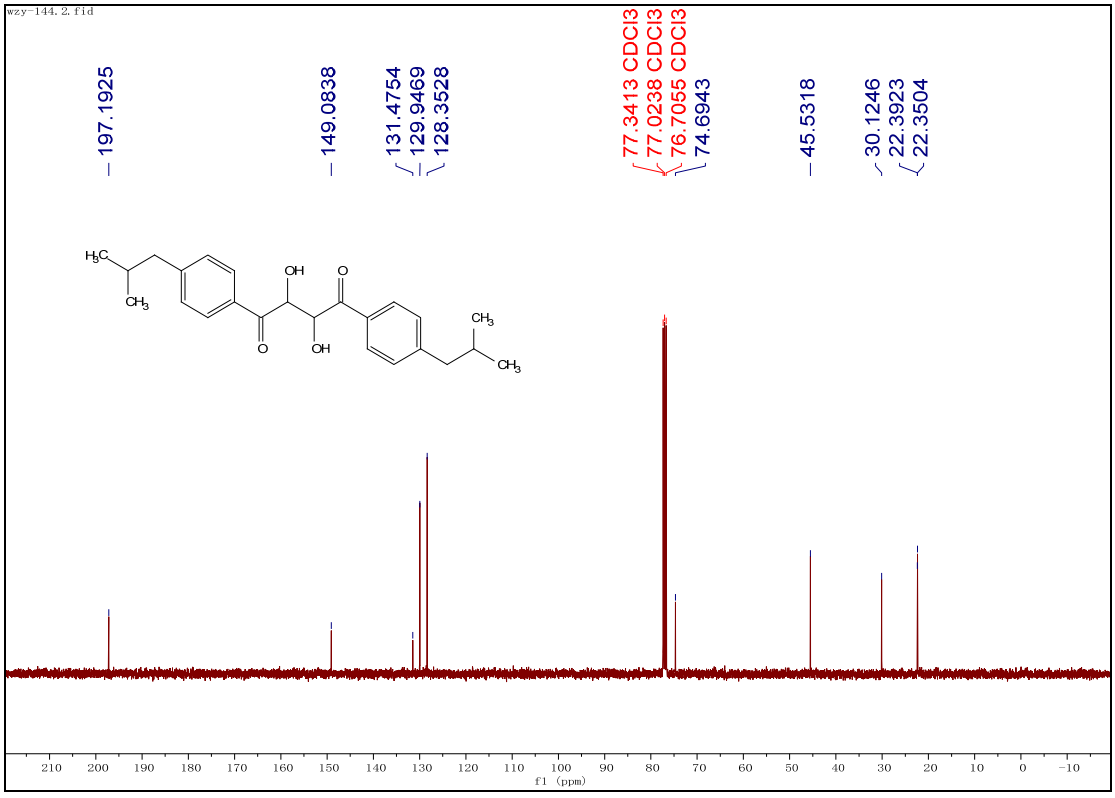


Figure S11. ^{13}C NMR spectrum of **2d** (100 MHz, $CDCl_3$)

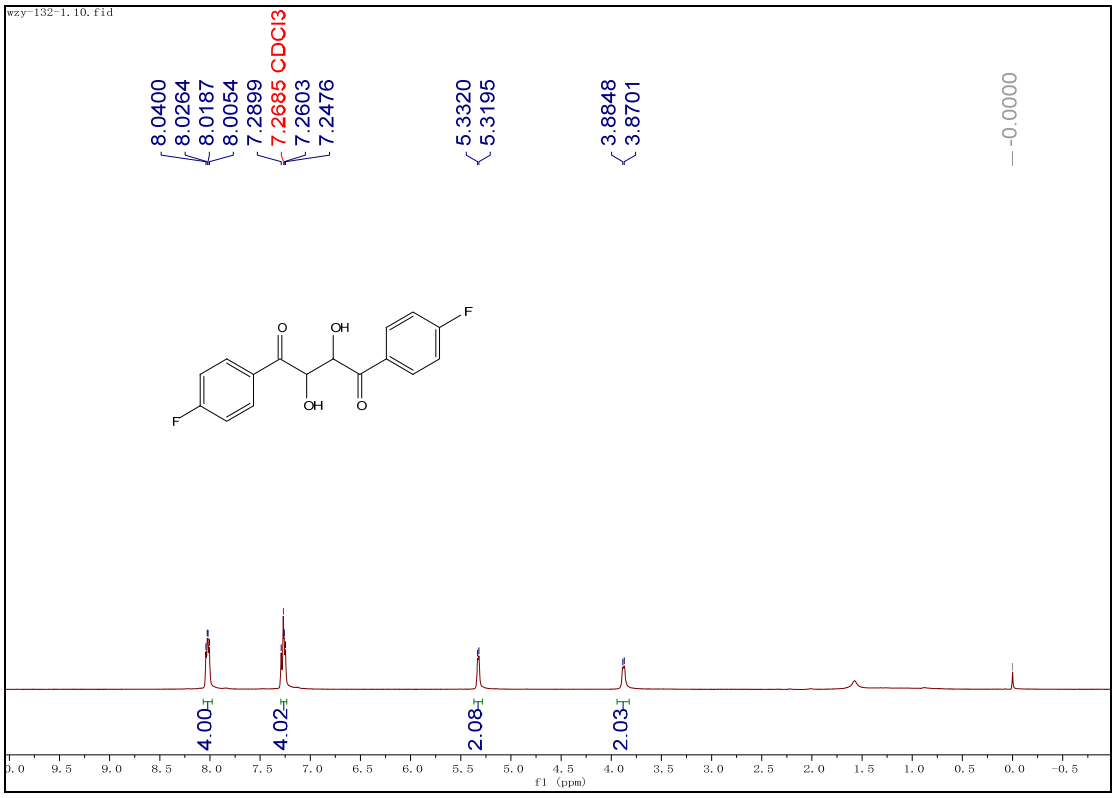


Figure S12. ^{1}H NMR spectrum of **2e** (400 MHz, $CDCl_3$)

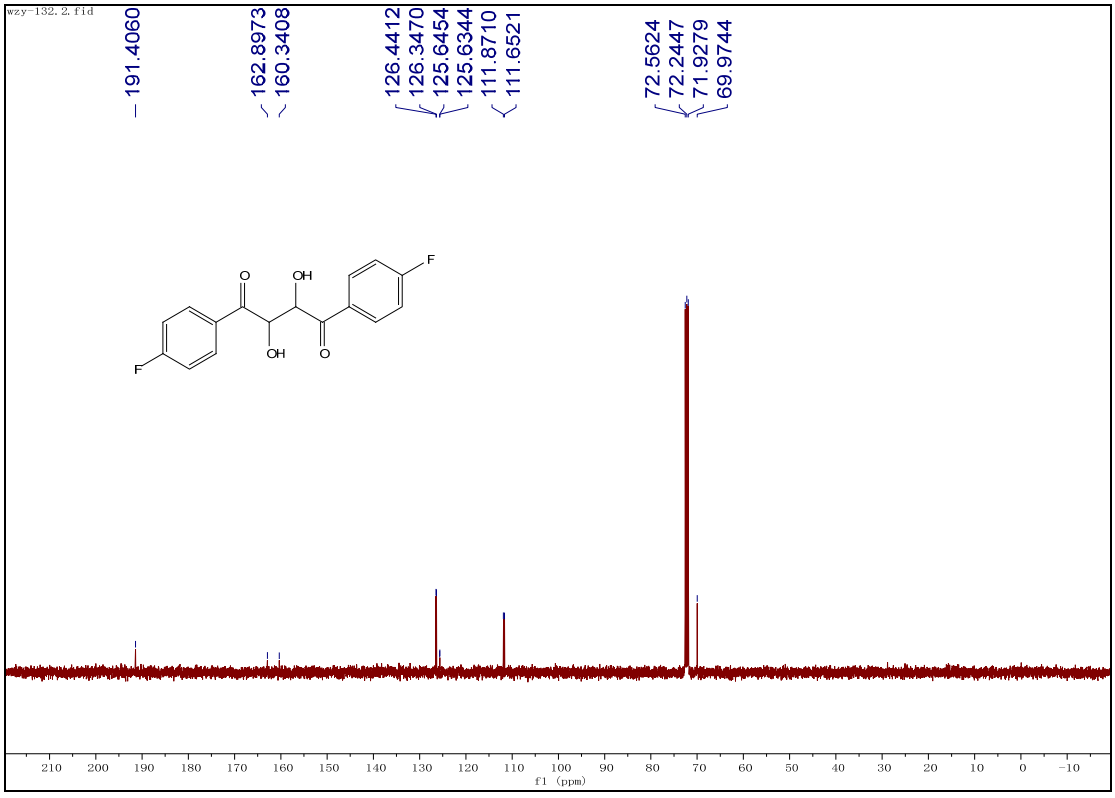


Figure S13. ^{13}C NMR spectrum of **2e** (100 MHz, $CDCl_3$)

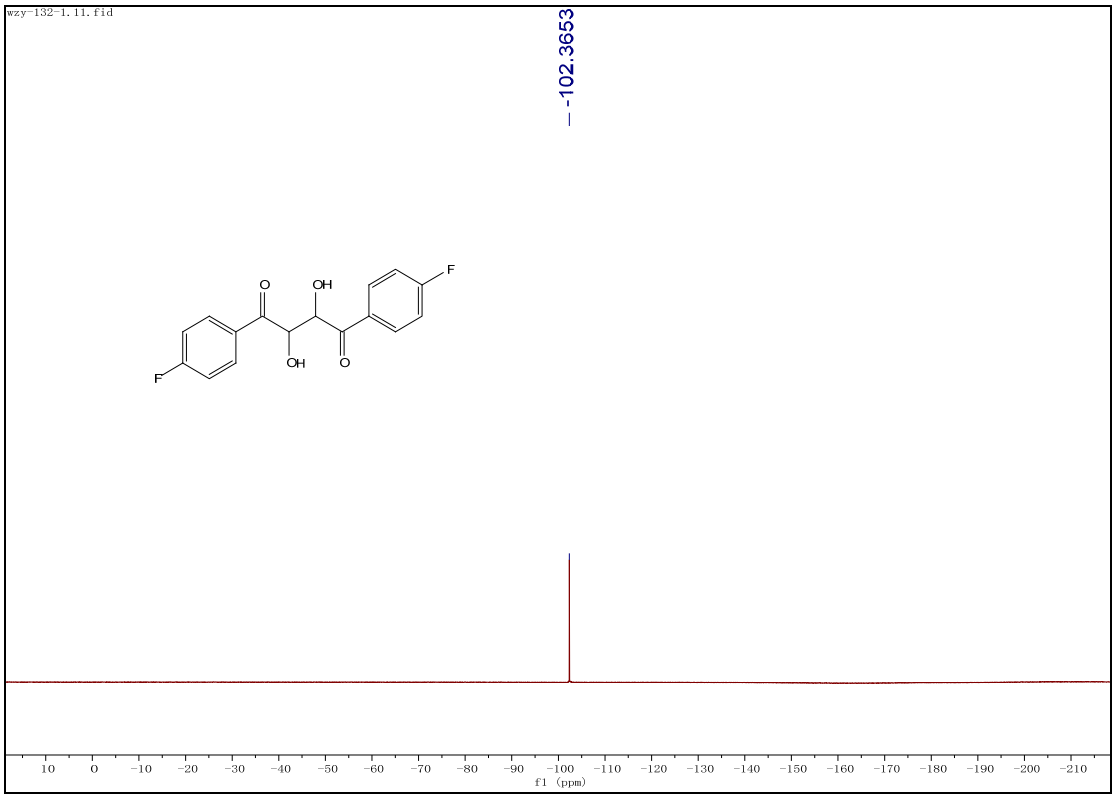


Figure S14. ^{19}F NMR spectrum of **2e** (376 MHz, $CDCl_3$)

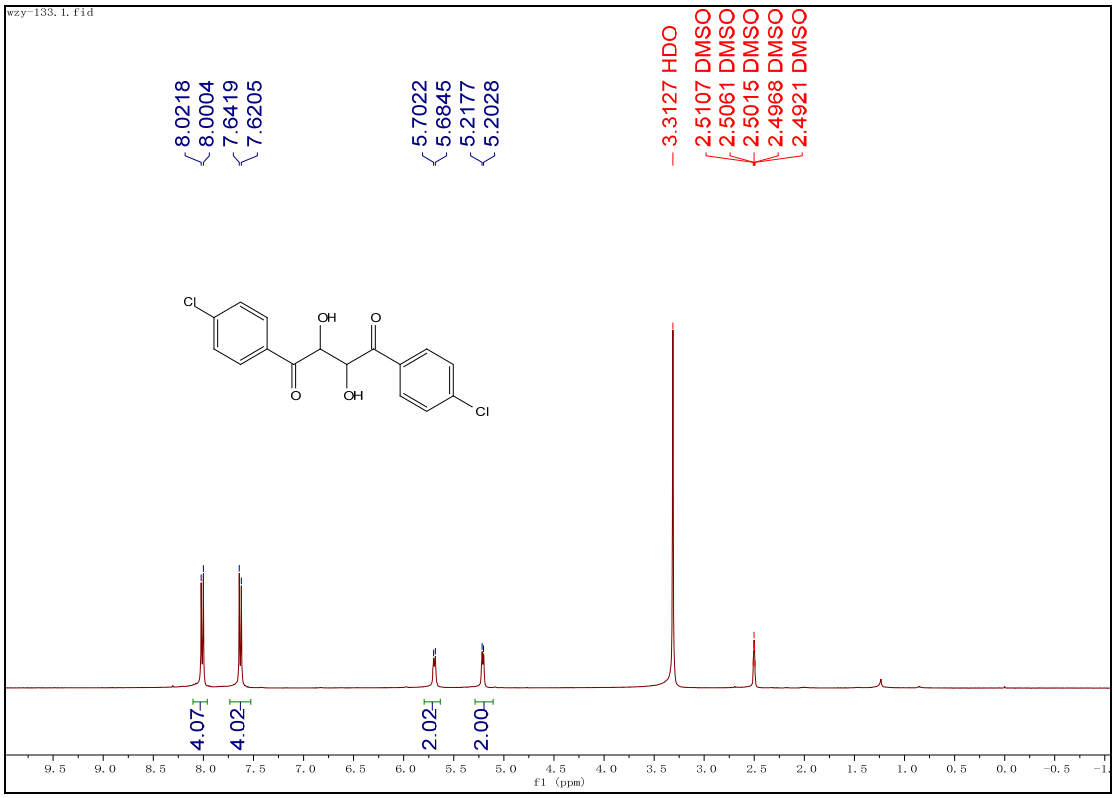


Figure S15. ^{1}H NMR spectrum of **2f** (400 MHz, DMSO-d_6)

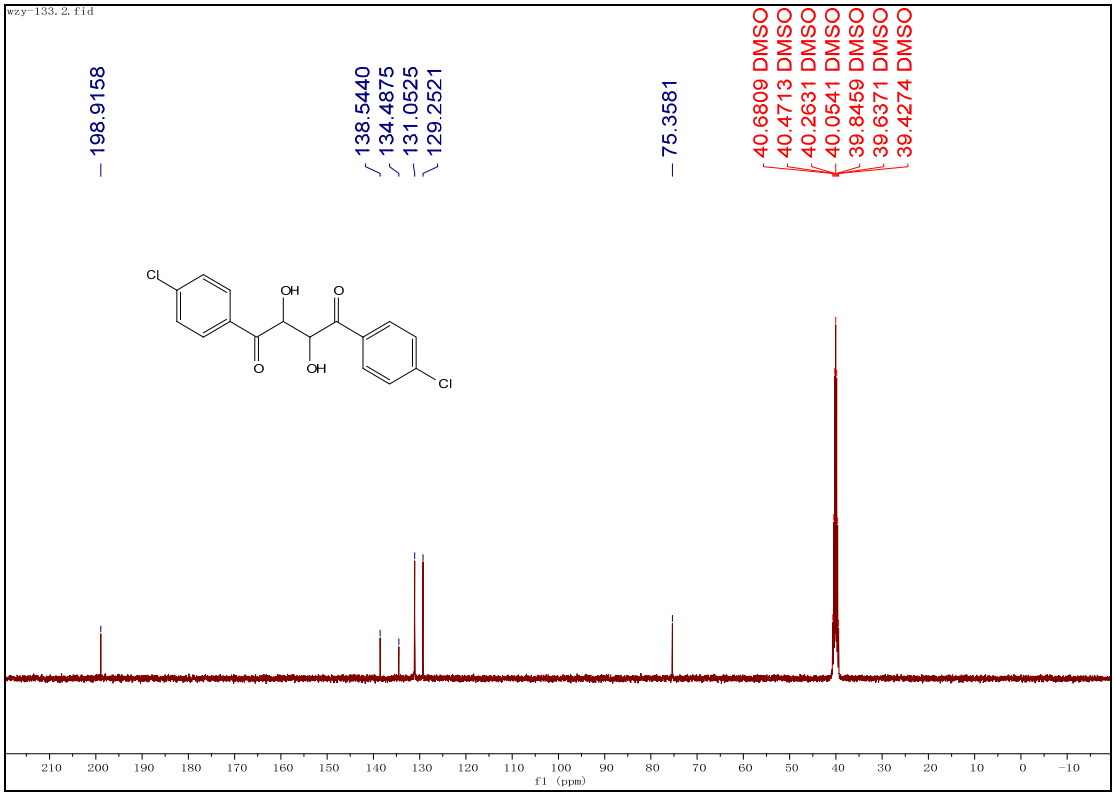


Figure S16. ^{13}C NMR spectrum of **2f** (100 MHz, DMSO-d_6)

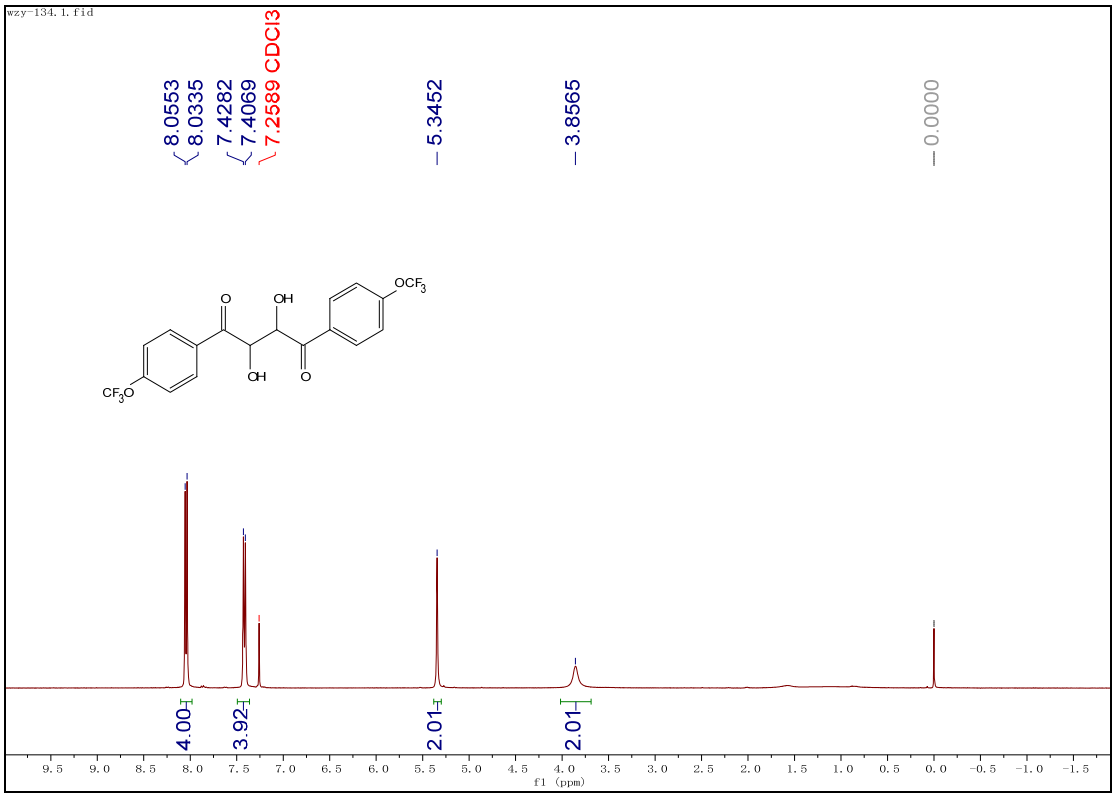


Figure S17 ^{1}H NMR spectrum of **2g** (400 MHz, $CDCl_3$)

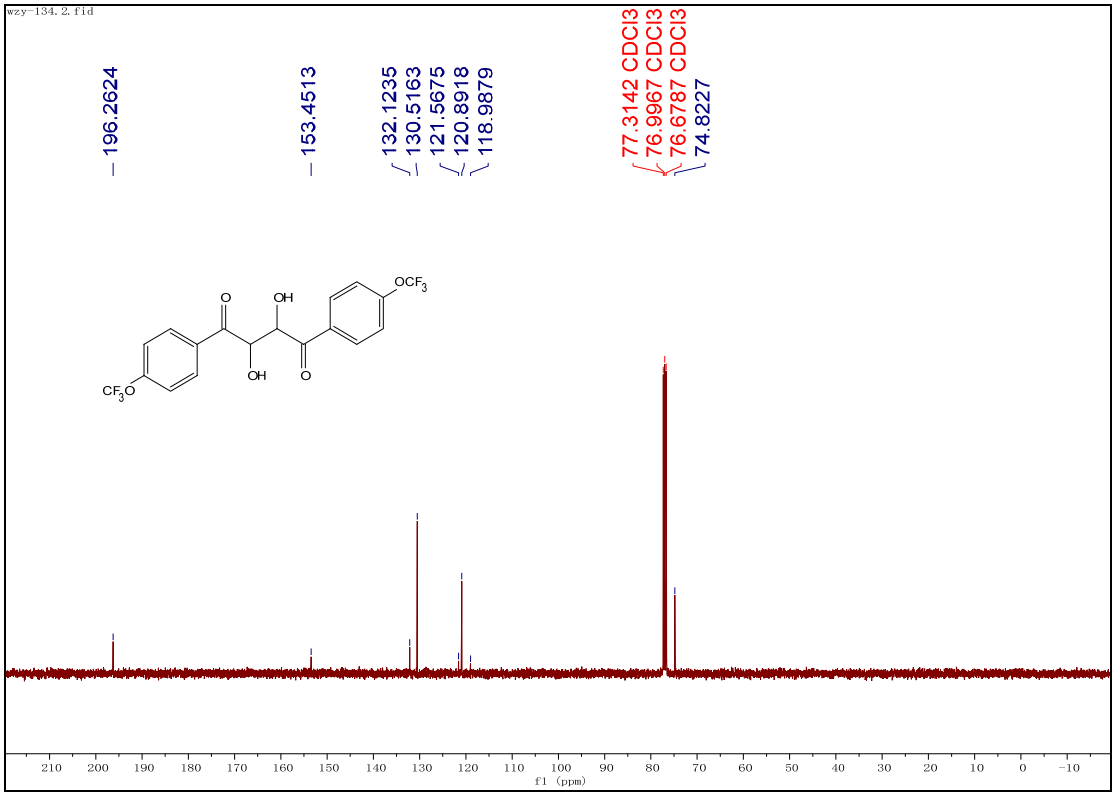


Figure S18. ^{13}C NMR spectrum of **2g** (100 MHz, $CDCl_3$)

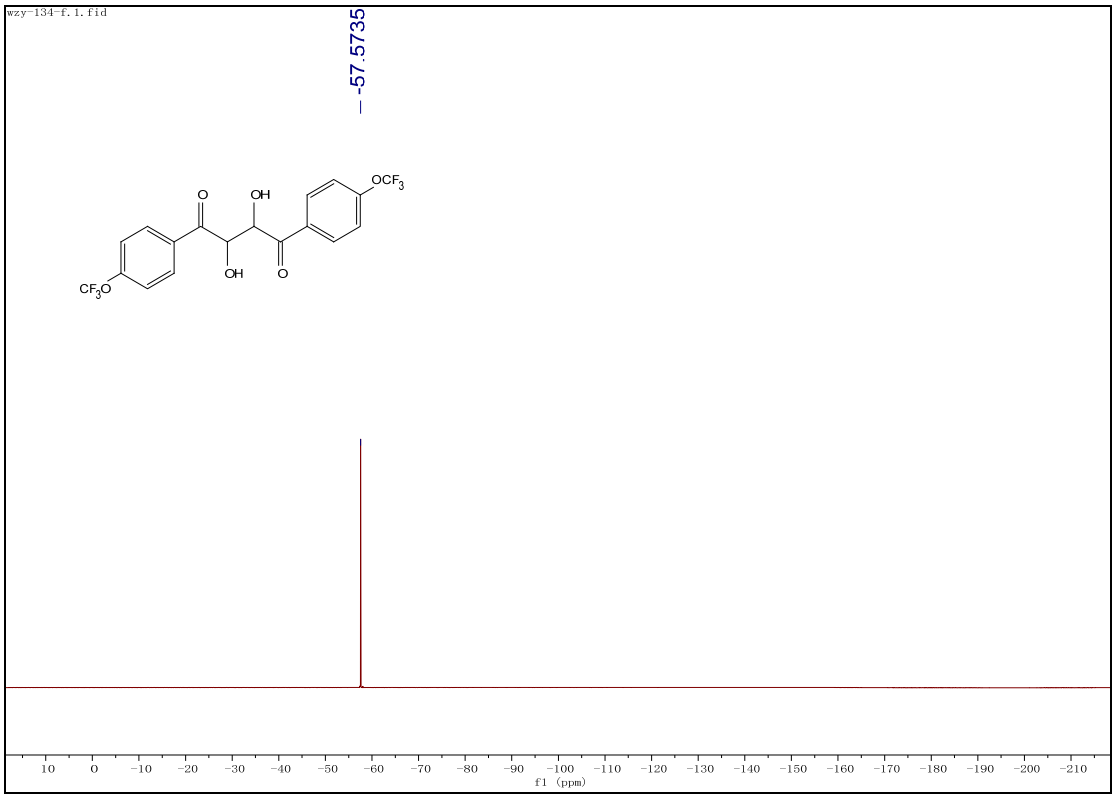


Figure S19. ^{19}F NMR spectrum of **2g** (376 MHz, $CDCl_3$)

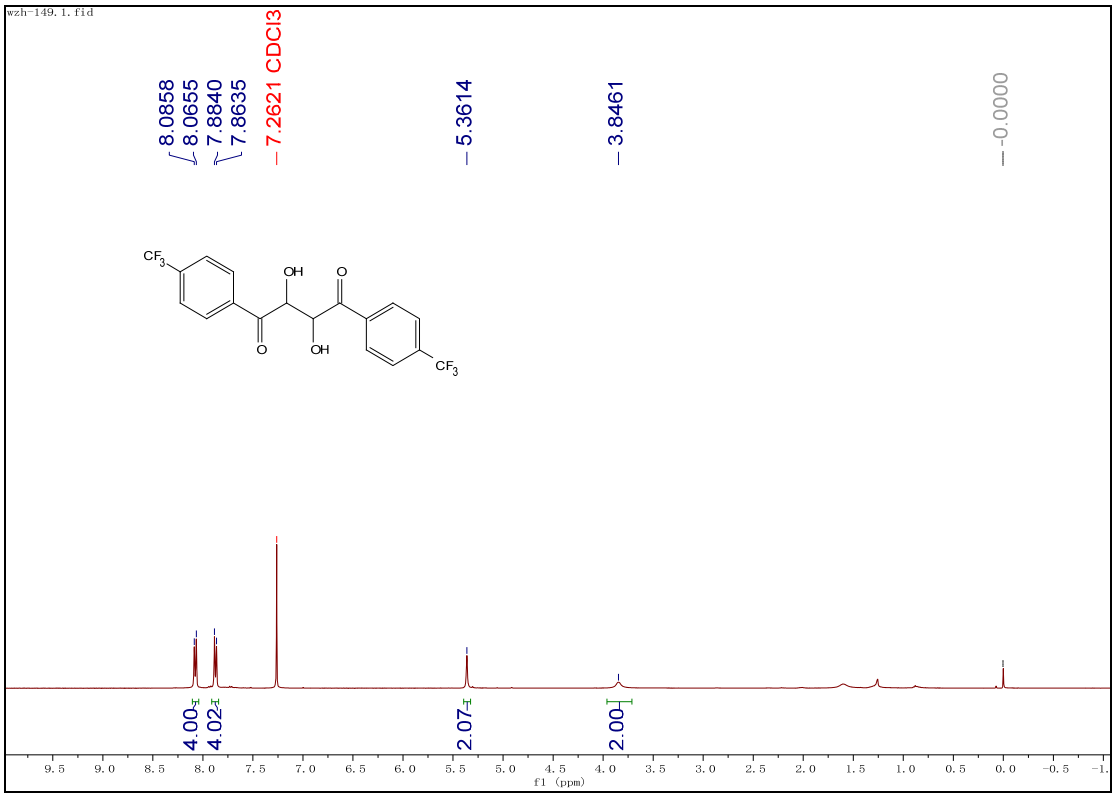


Figure S20. ^{1}H NMR spectrum of **2h** (400 MHz, $CDCl_3$)

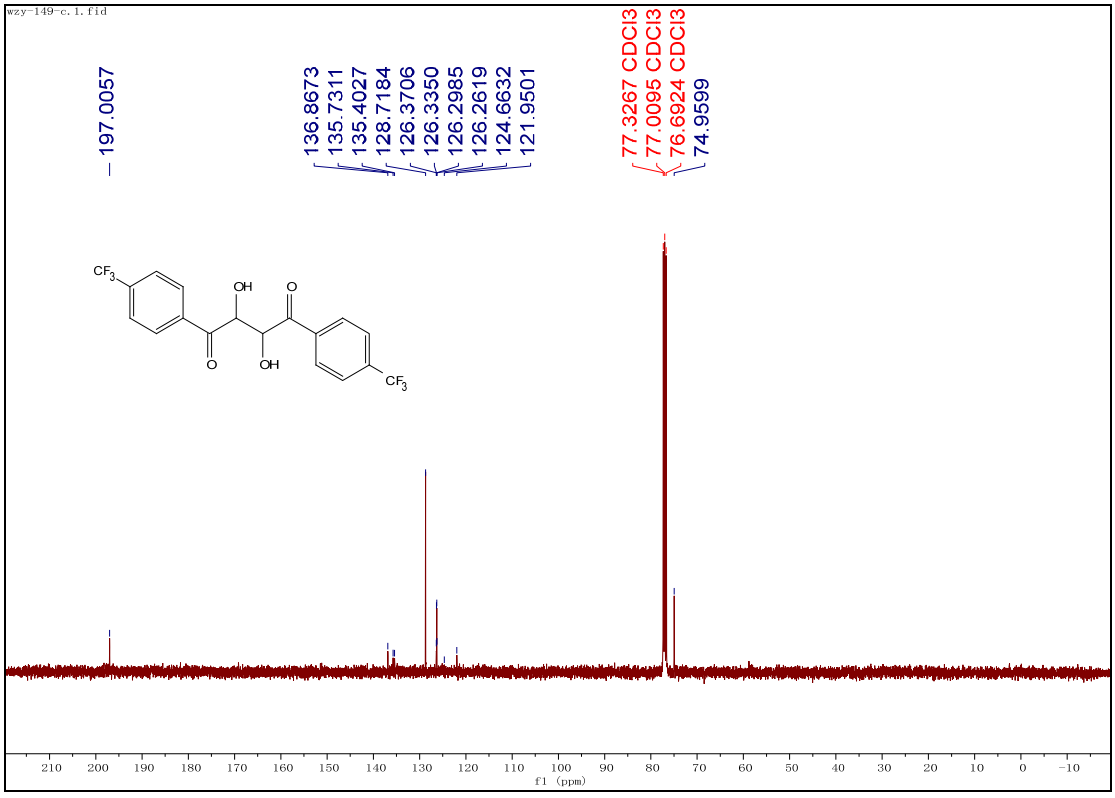


Figure S21. ^{13}C NMR spectrum of **2h** (100 MHz, $CDCl_3$)

Figure S22. ^{19}F NMR spectrum of **2h** (376 MHz, $CDCl_3$)

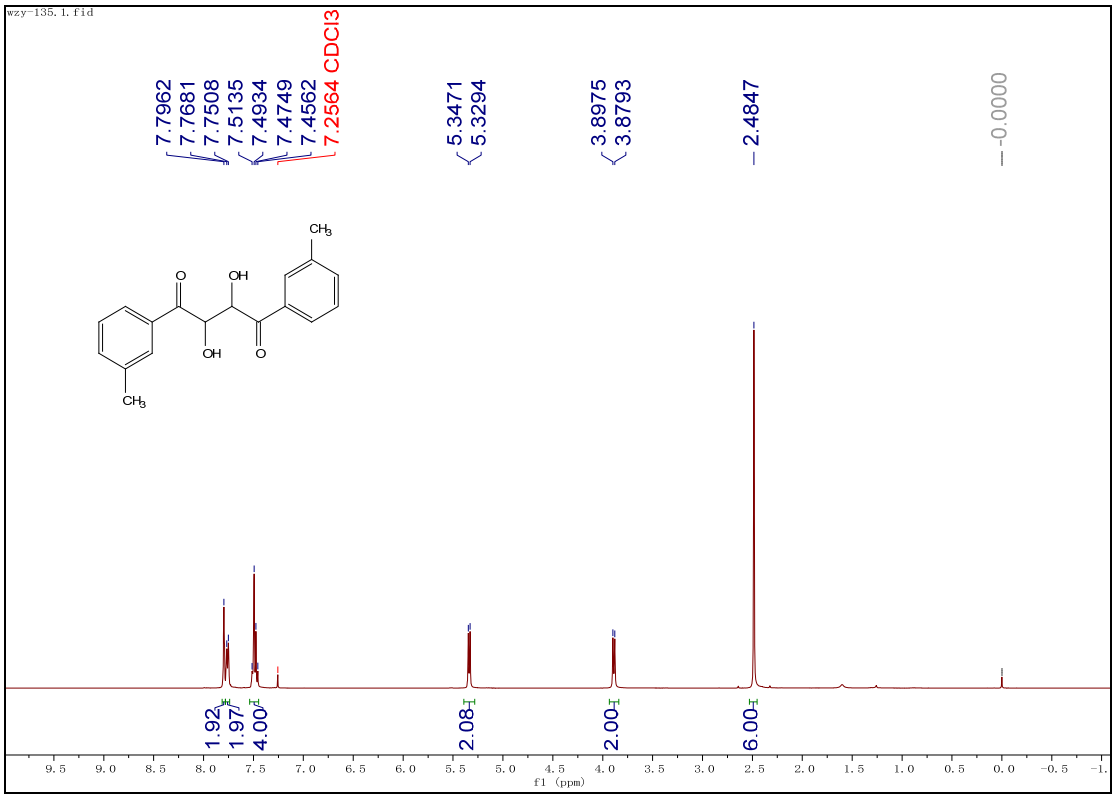


Figure S23. ^{1}H NMR spectrum of **2i** (400 MHz, $CDCl_3$)

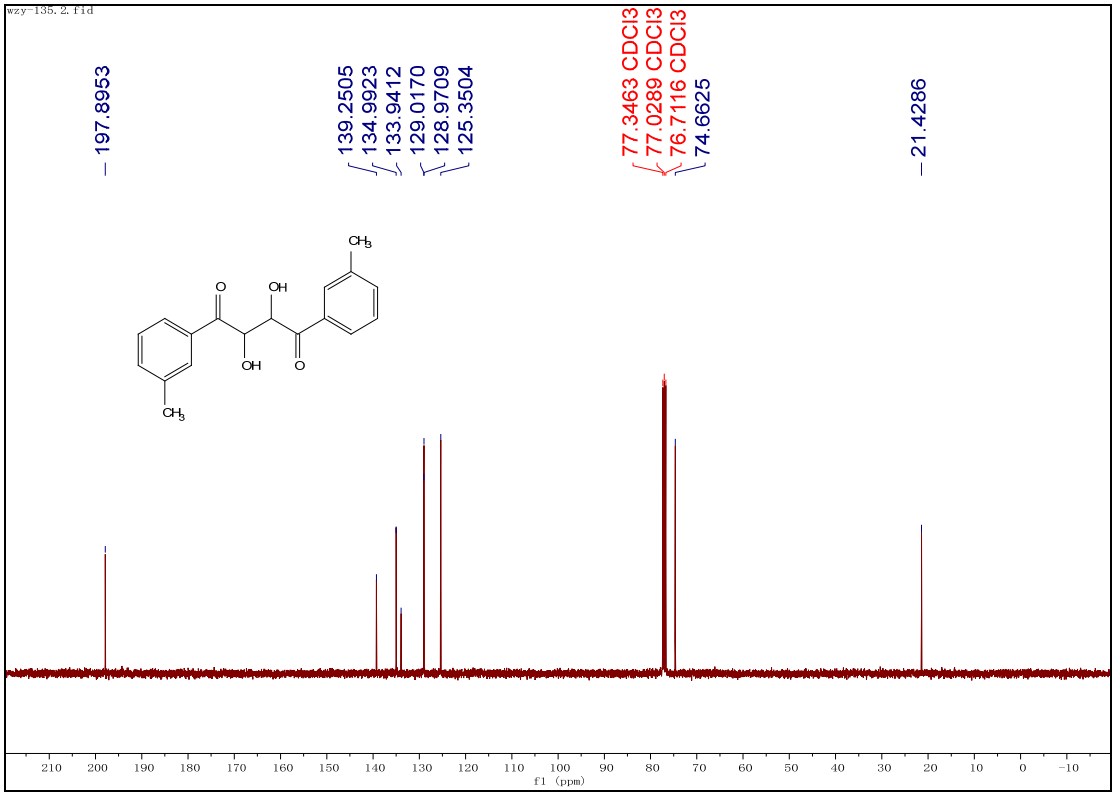


Figure S24. ^{13}C NMR spectrum of **2i** (100 MHz, $CDCl_3$)

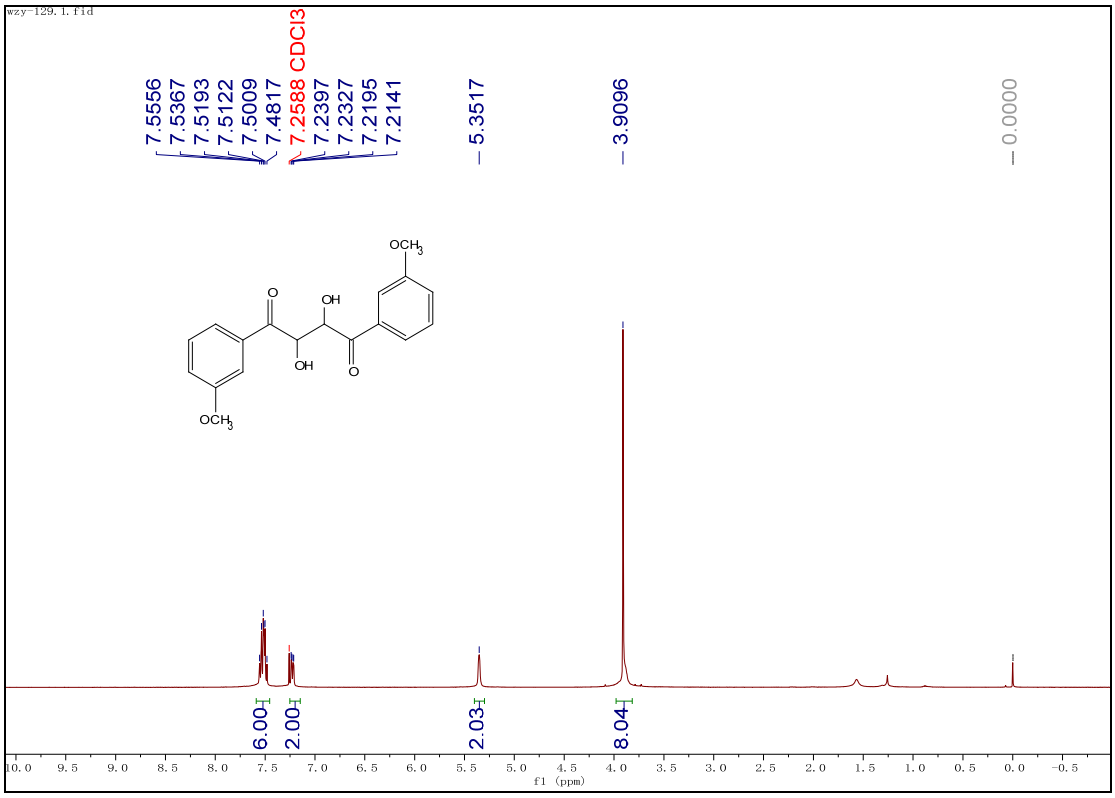


Figure S25. ^{1}H NMR spectrum of **2j** (400 MHz, $CDCl_3$)

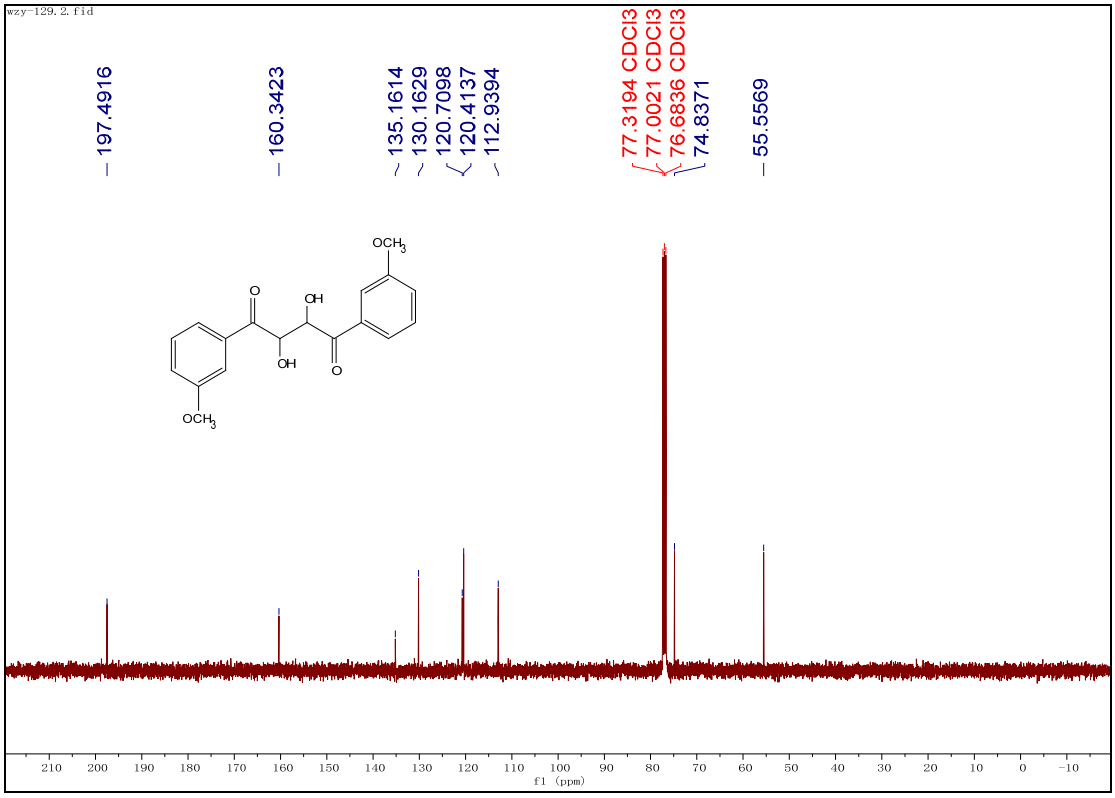


Figure S26. ^{13}C NMR spectrum of **2j** (100 MHz, $CDCl_3$)

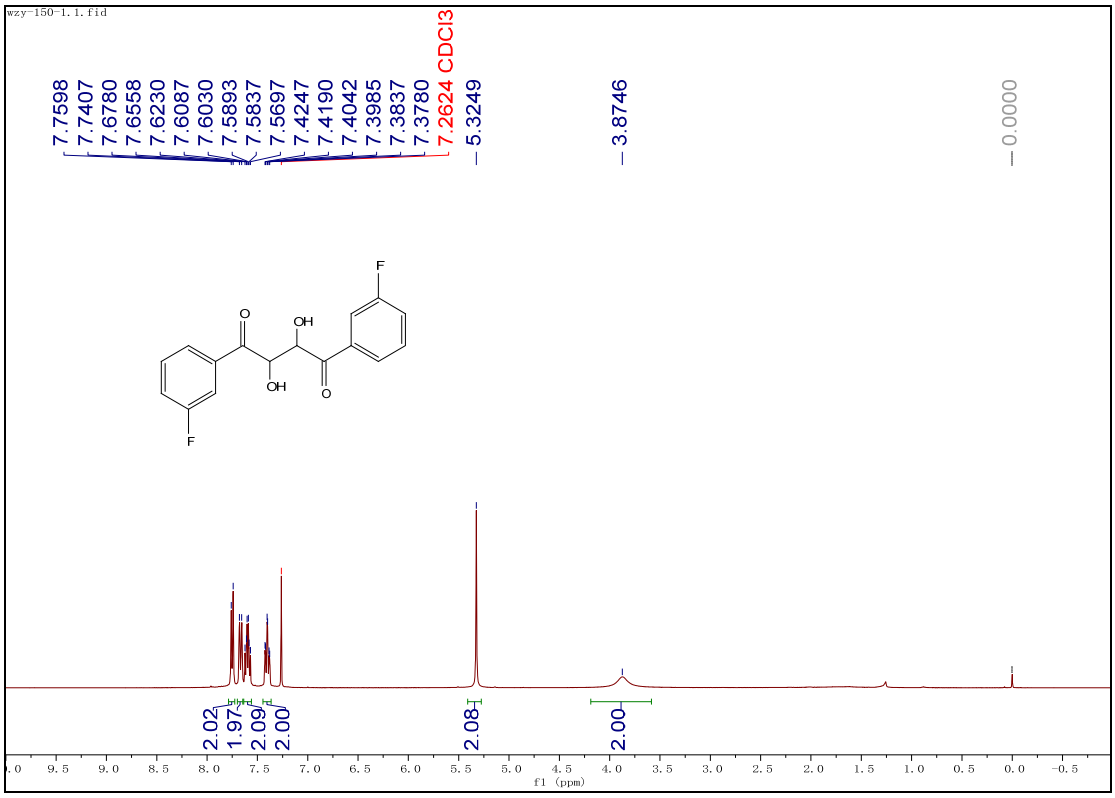


Figure S27. ^{1}H NMR spectrum of **2k** (400 MHz, $CDCl_3$)

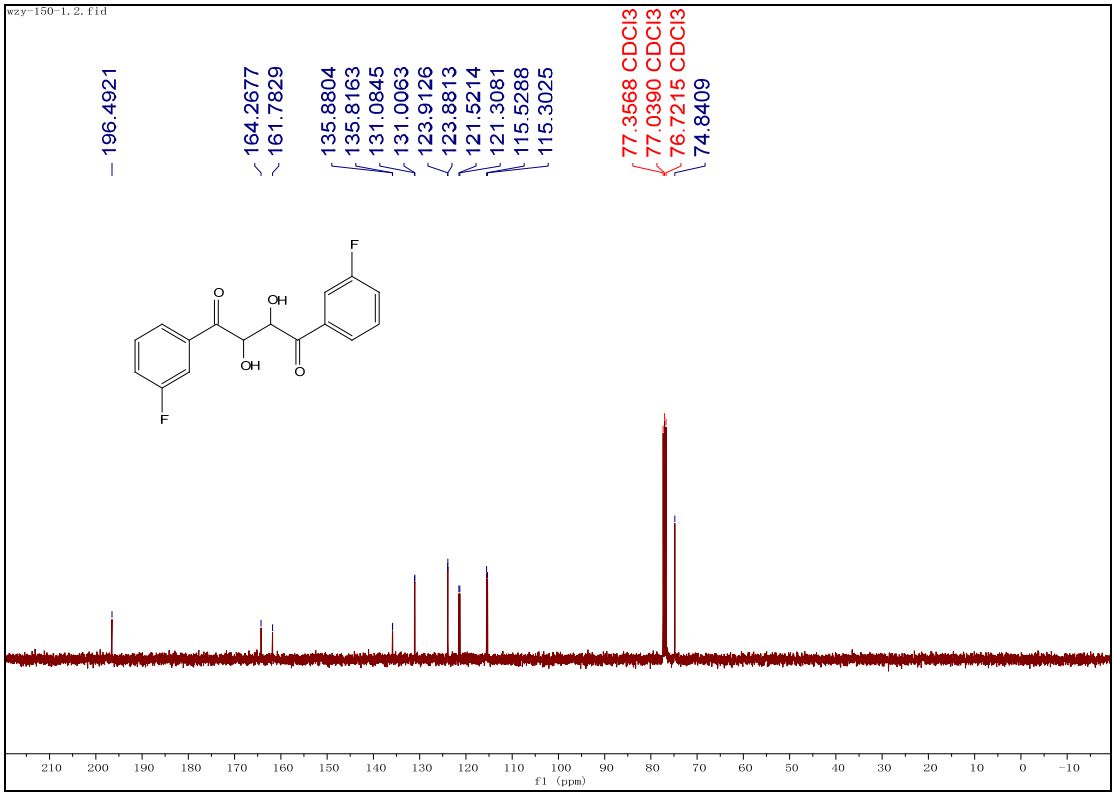


Figure S28. ^{13}C NMR spectrum of **2k** (100 MHz, $CDCl_3$)

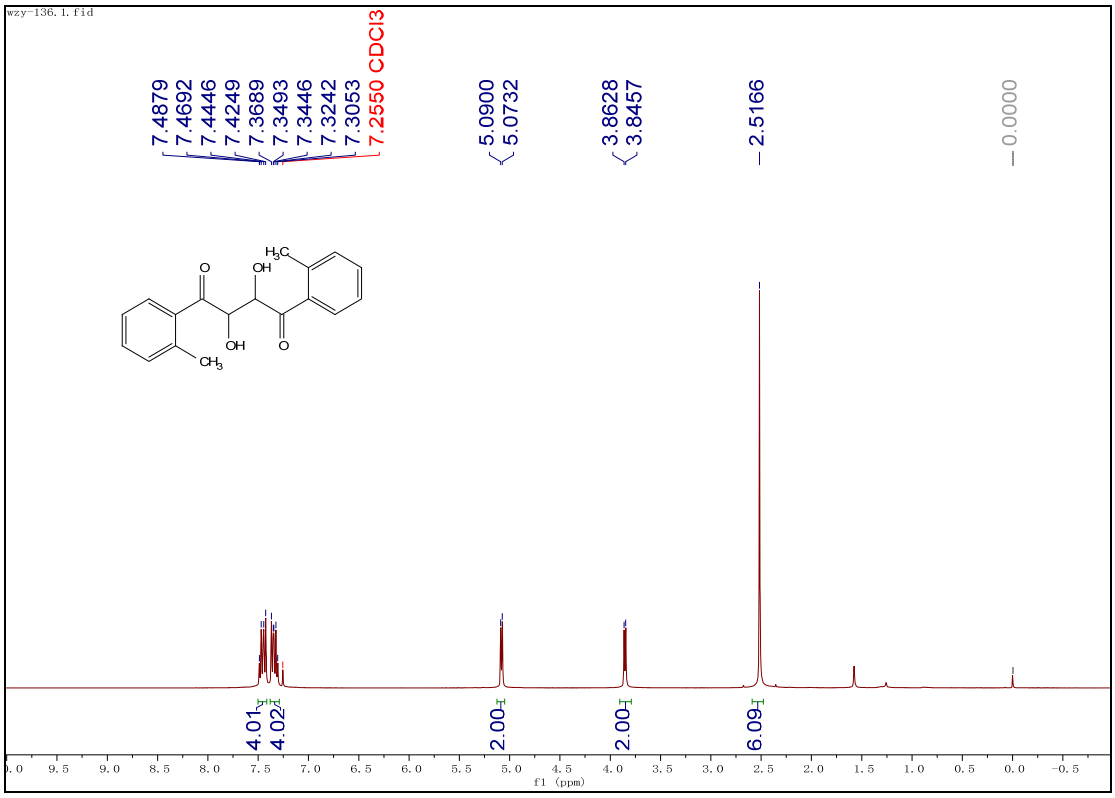


Figure S29. ^{1}H NMR spectrum of **2l** (400 MHz, $CDCl_3$)

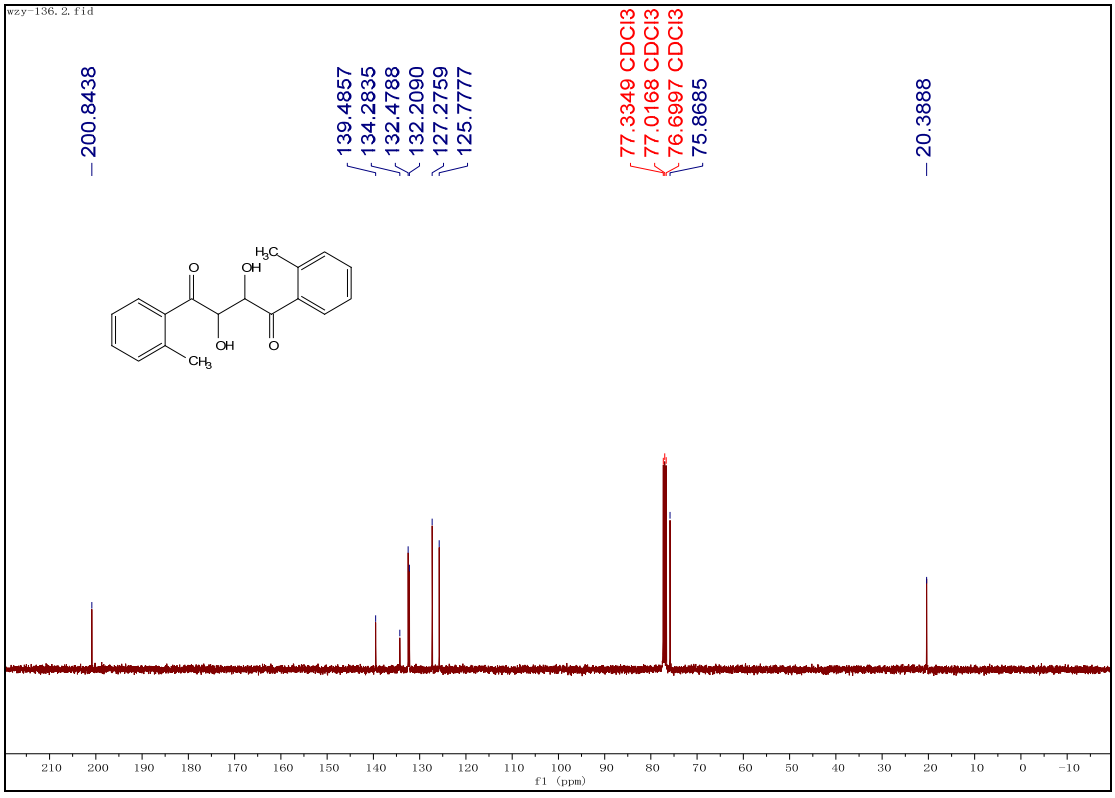


Figure S30. ^{13}C NMR spectrum of **2l** (100 MHz, $CDCl_3$)

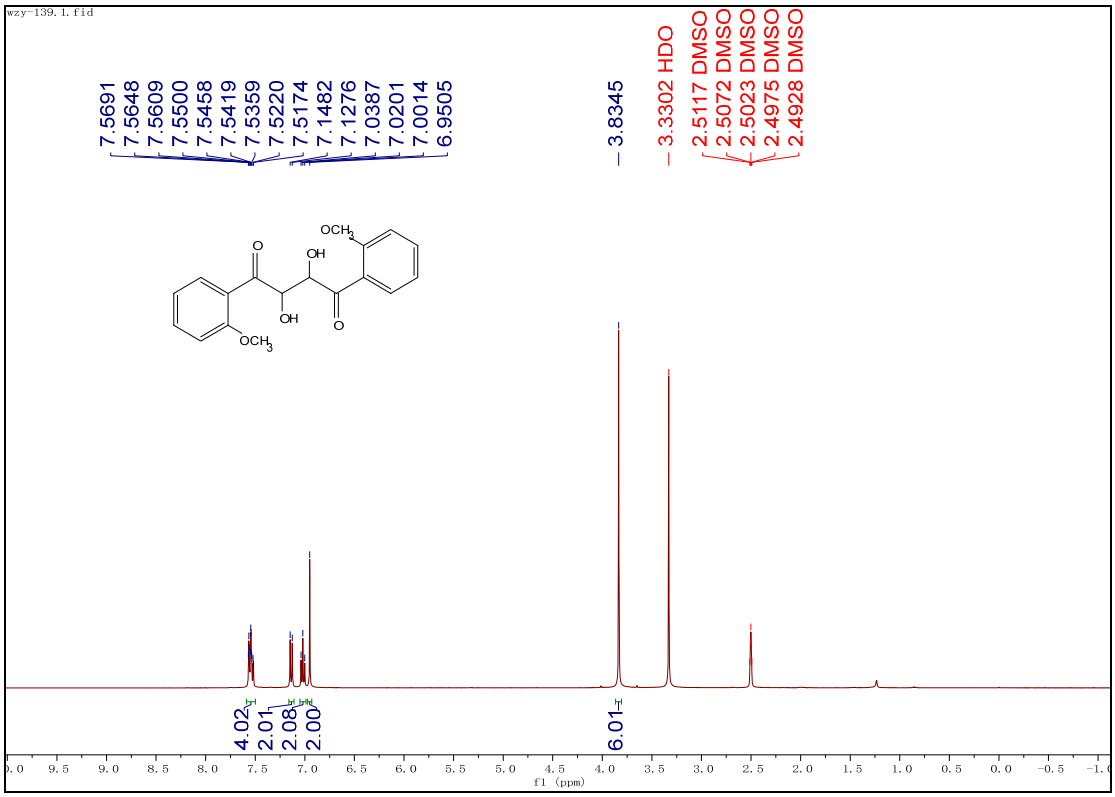


Figure S31. ^{1}H NMR spectrum of **2m** (400 MHz, DMSO-d_6)

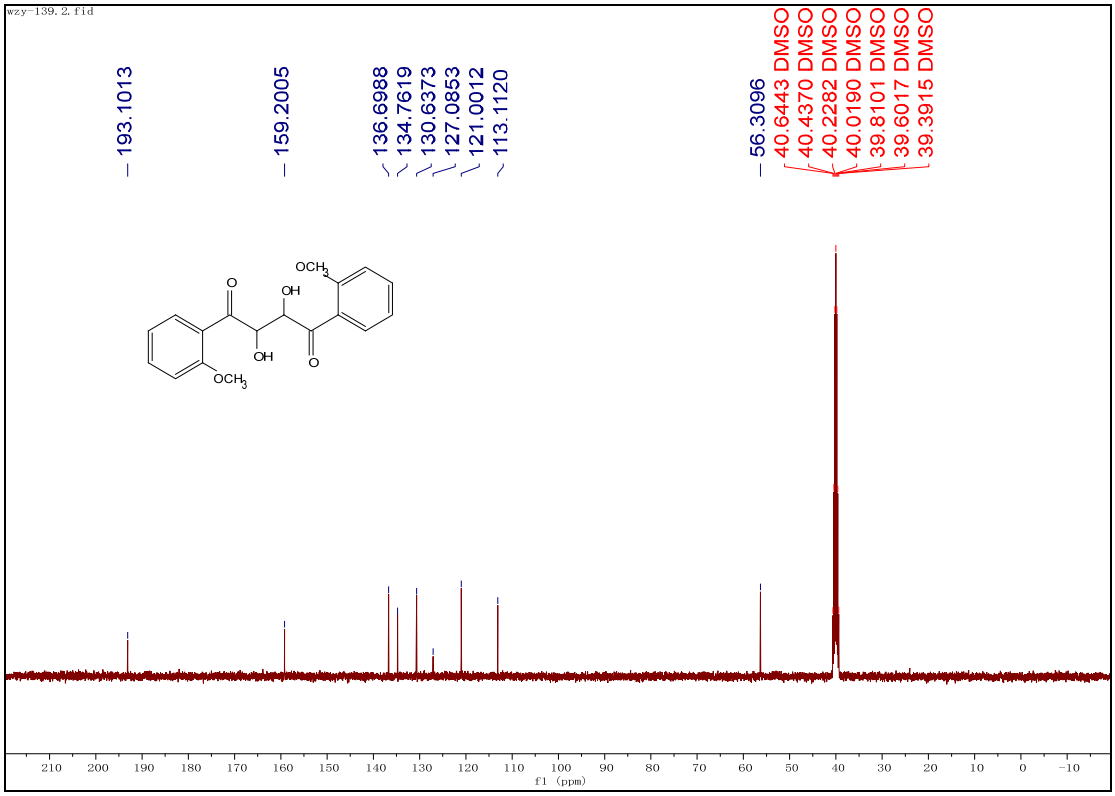


Figure S32. ^{13}C NMR spectrum of **2m** (100 MHz, DMSO-d_6)

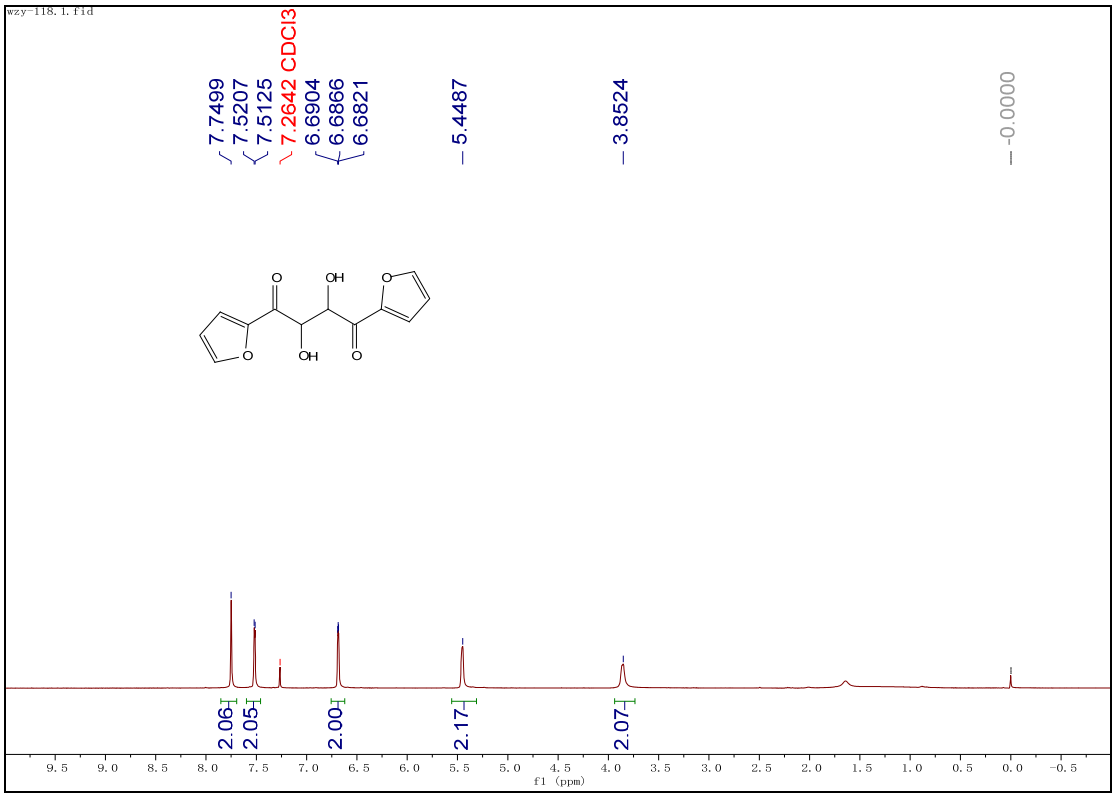


Figure S33. ^{1}H NMR spectrum of **2n** (400 MHz, $CDCl_3$)

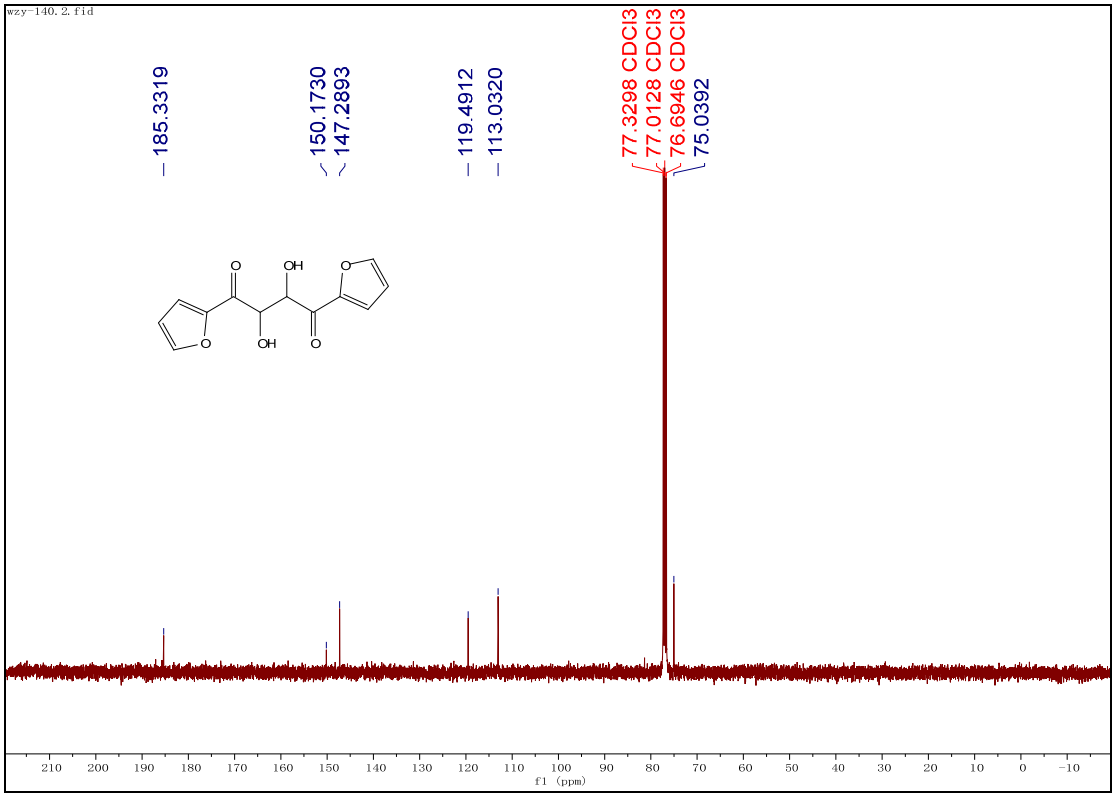


Figure S34. ^{13}C NMR spectrum of **2n** (100 MHz, $CDCl_3$)

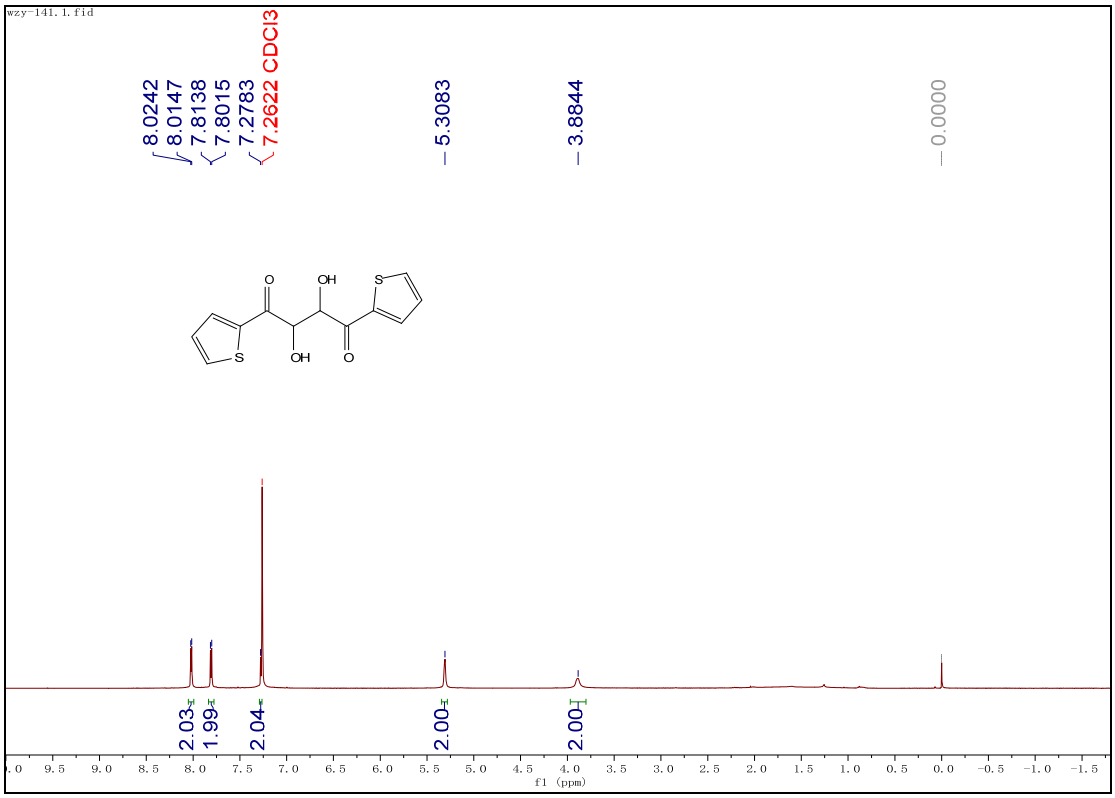


Figure S35. ^{1}H NMR spectrum of **2o** (400 MHz, $CDCl_3$)

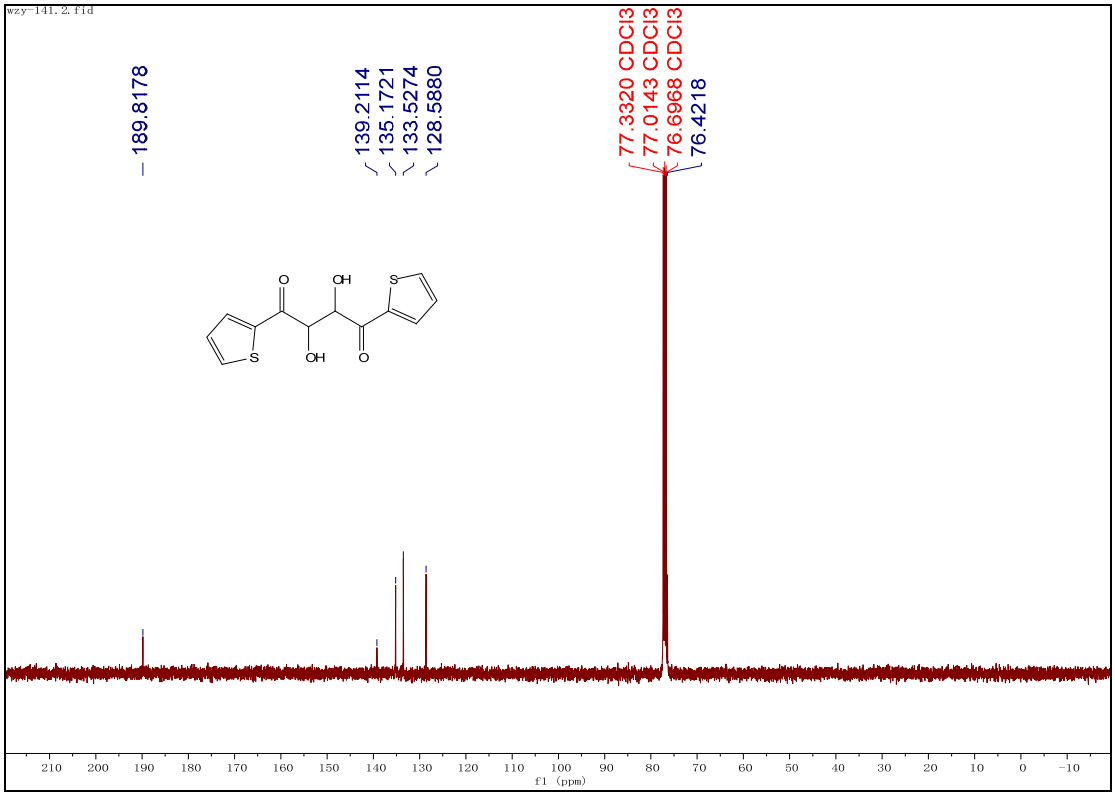


Figure S36. ^{13}C NMR spectrum of **2o** (100 MHz, $CDCl_3$)

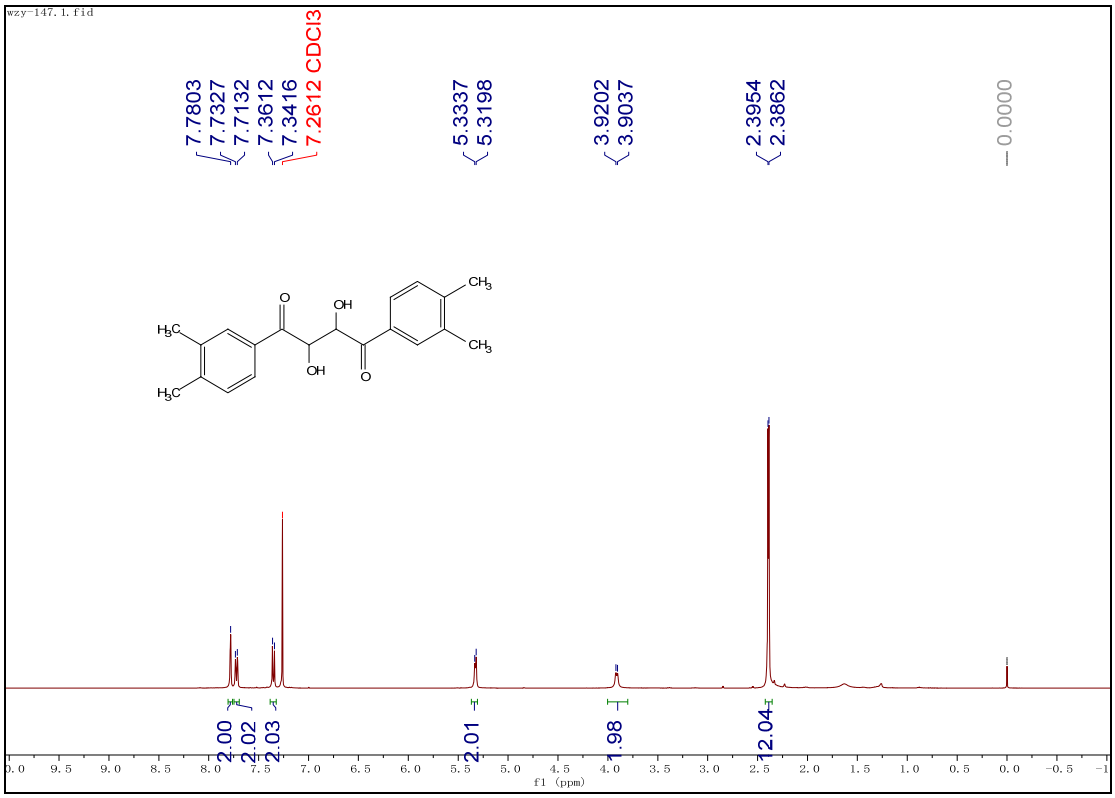


Figure S37. ^{1}H NMR spectrum of **2p** (400 MHz, $CDCl_3$)

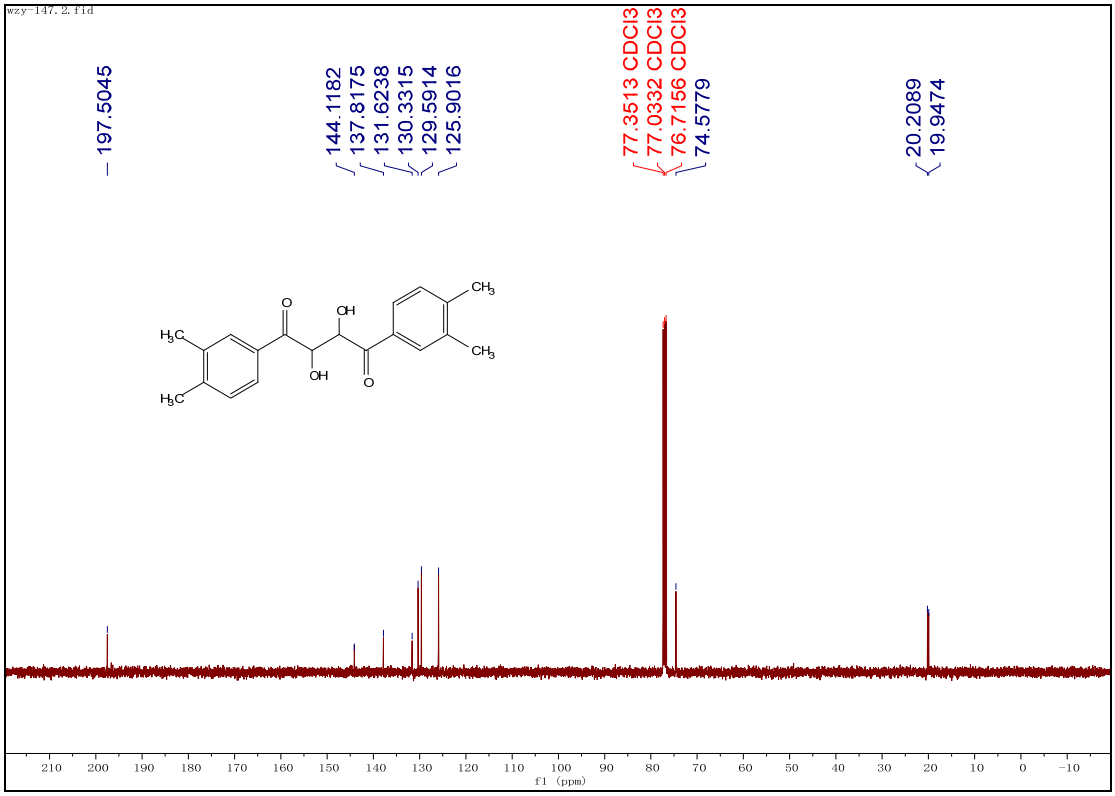


Figure S38. ^{13}C NMR spectrum of **2p** (100 MHz, $CDCl_3$)

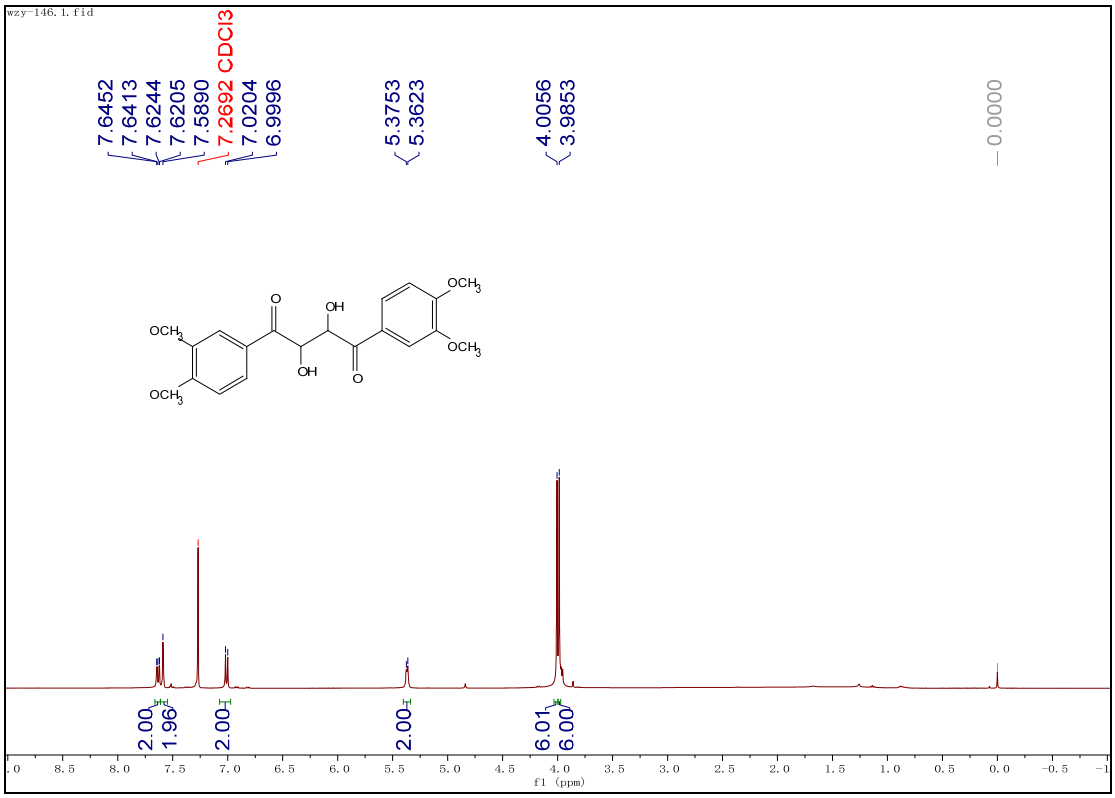


Figure S39. ^{1}H NMR spectrum of **2q** (400 MHz, $CDCl_3$)

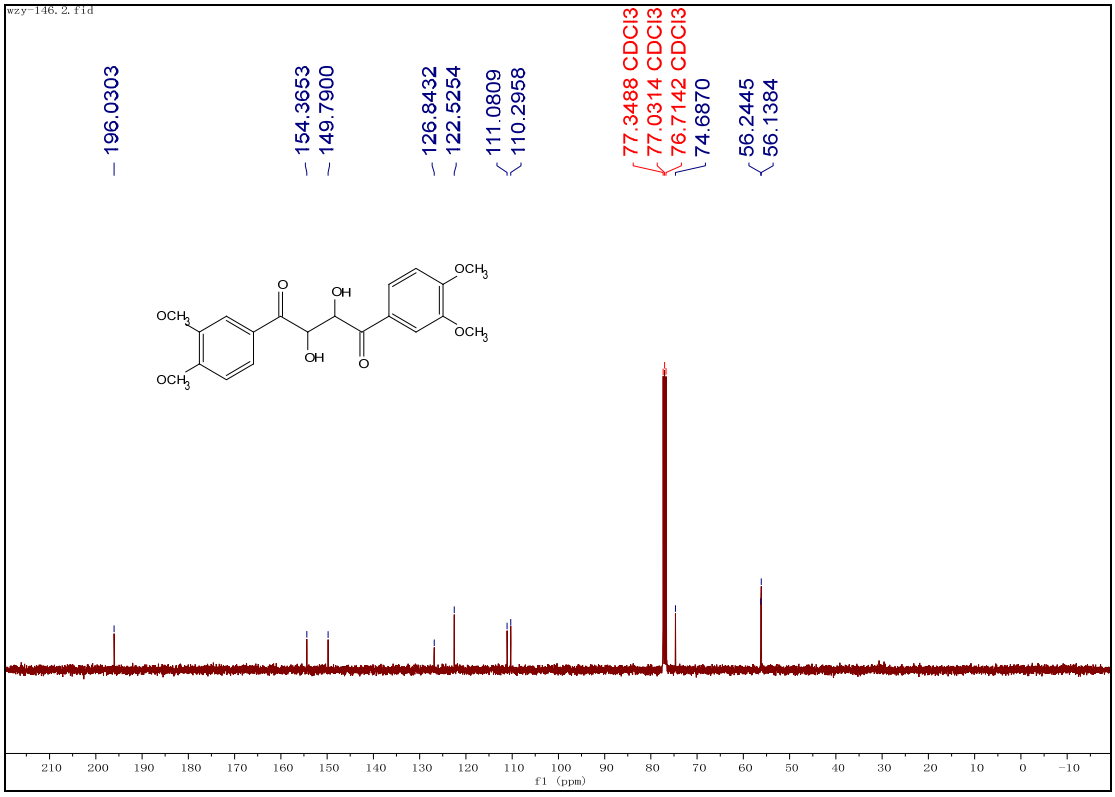


Figure S40. ^{13}C NMR spectrum of **2q** (100 MHz, $CDCl_3$)

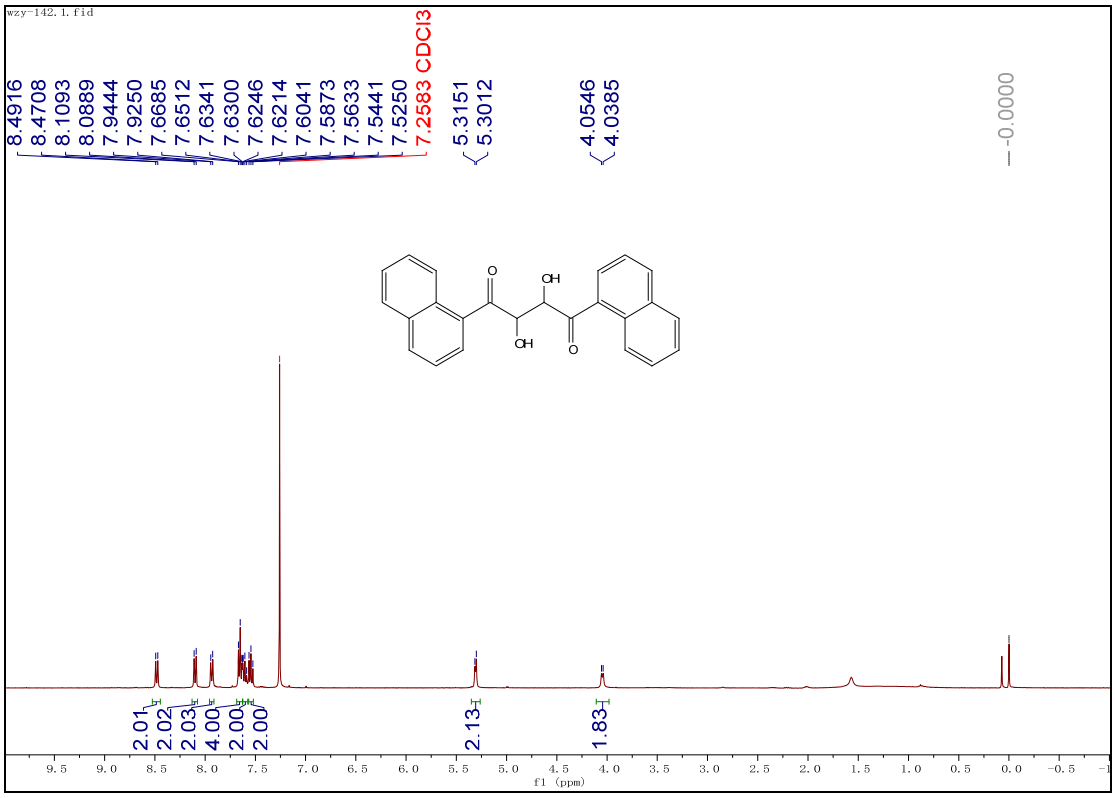


Figure S41. ^{1}H NMR spectrum of **2r** (400 MHz, $CDCl_3$)

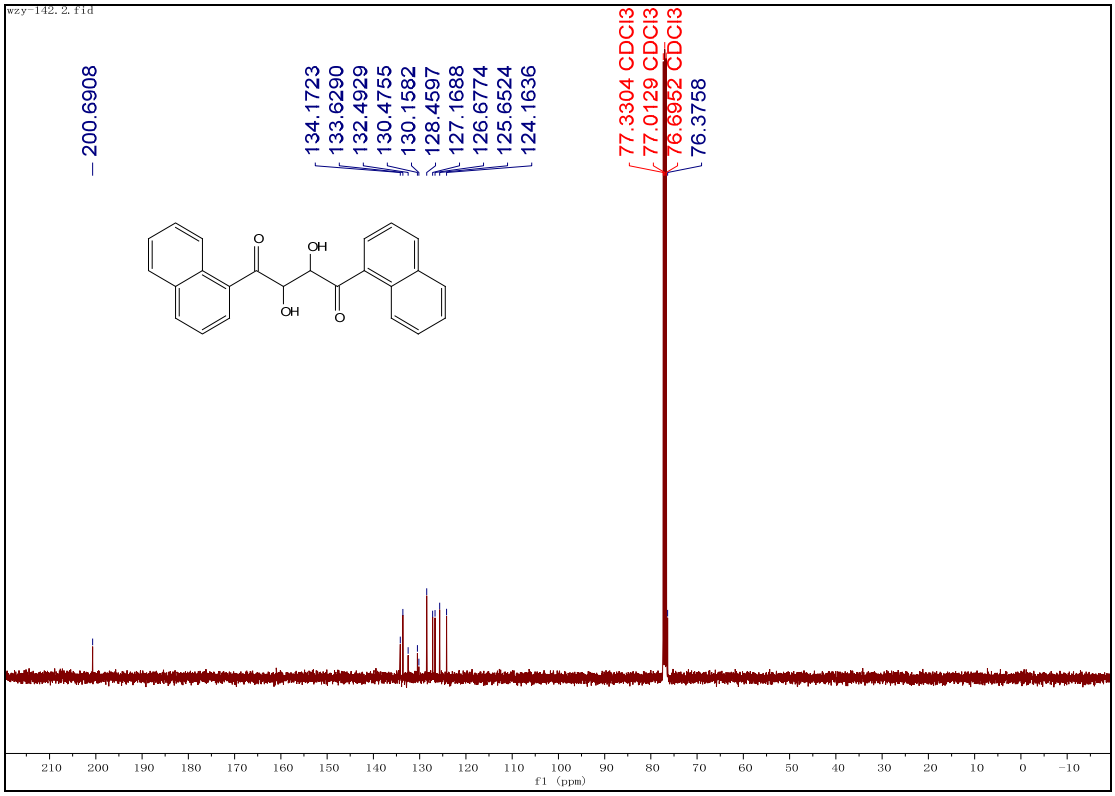


Figure S42. ^{13}C NMR spectrum of **2r** (100 MHz, $CDCl_3$)

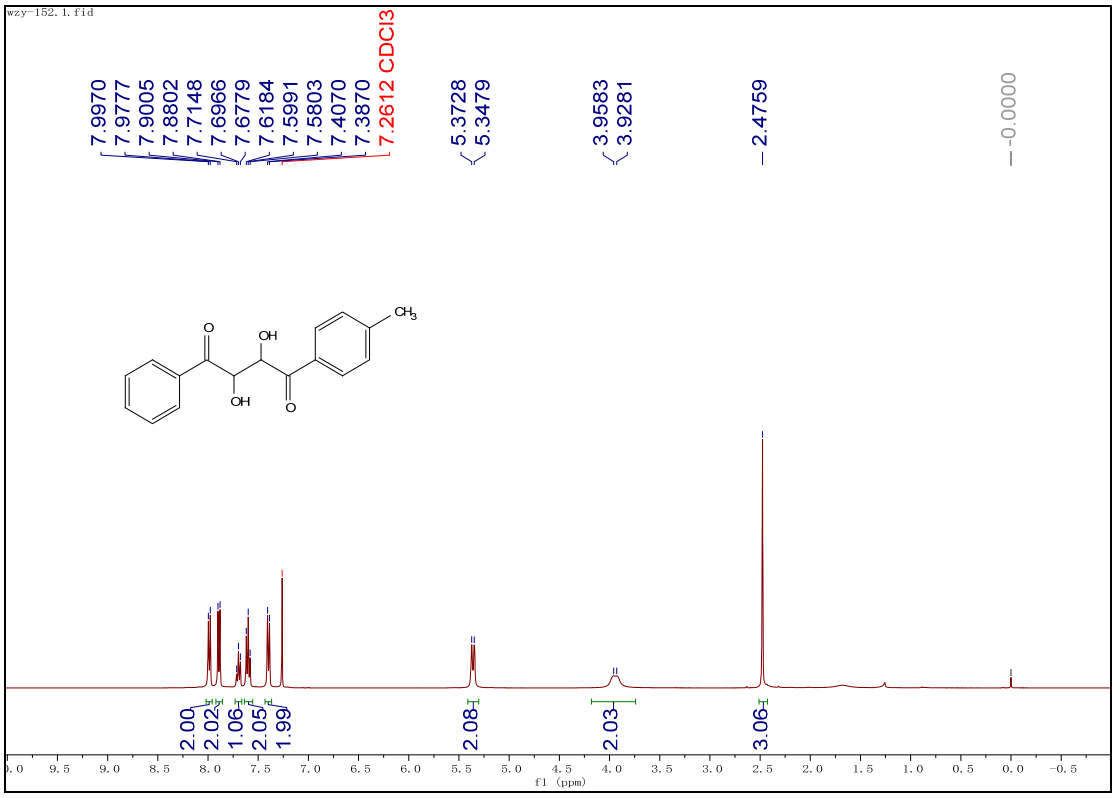


Figure S43. ^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)

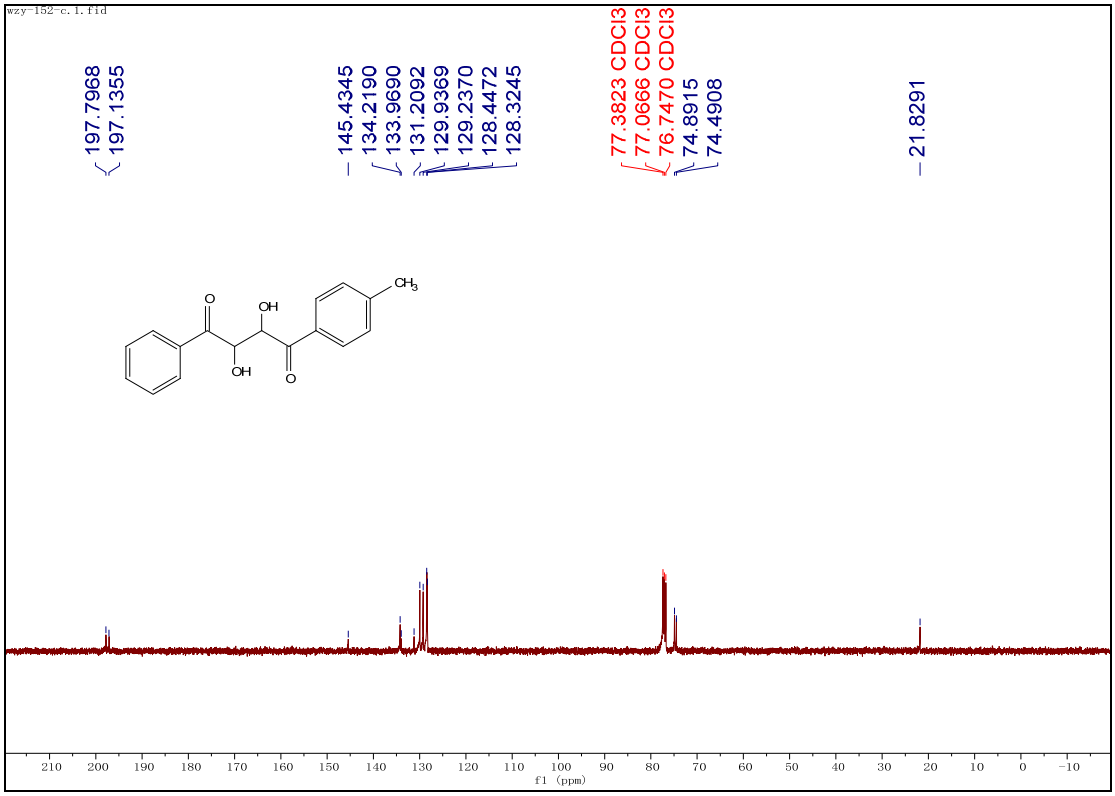


Figure S44. ^{13}C NMR spectrum of **3a** (100 MHz, $CDCl_3$)

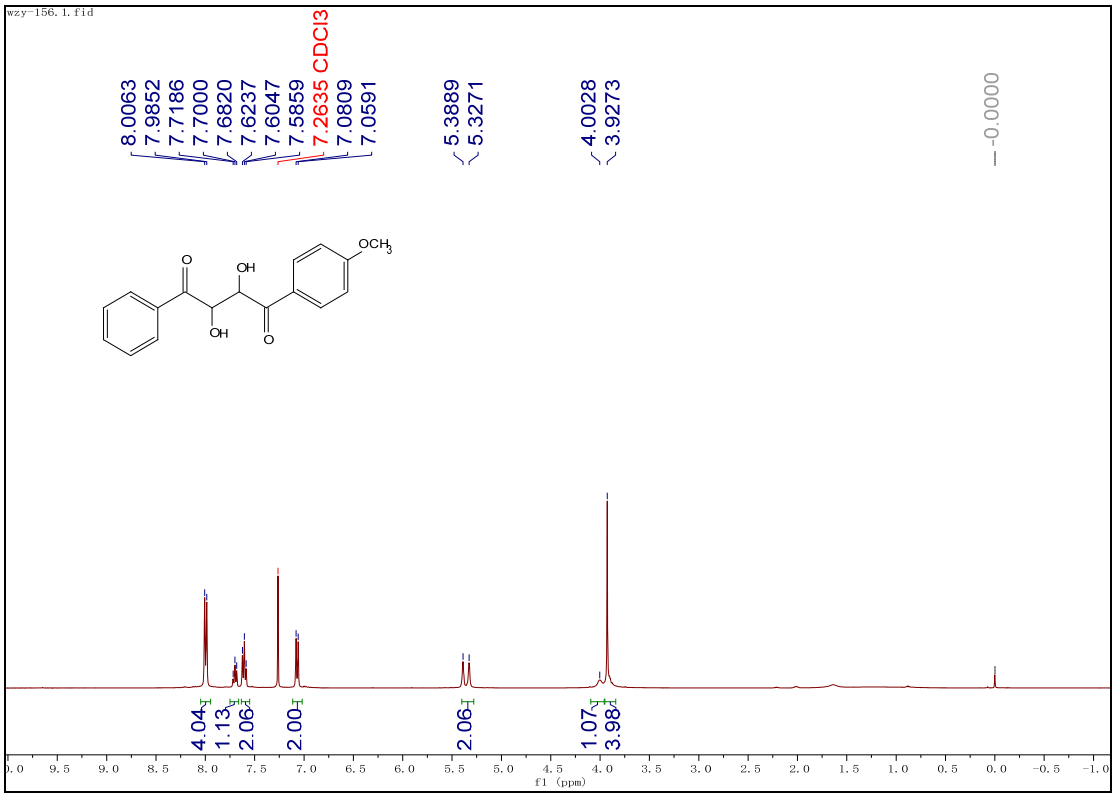


Figure S45. ^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)

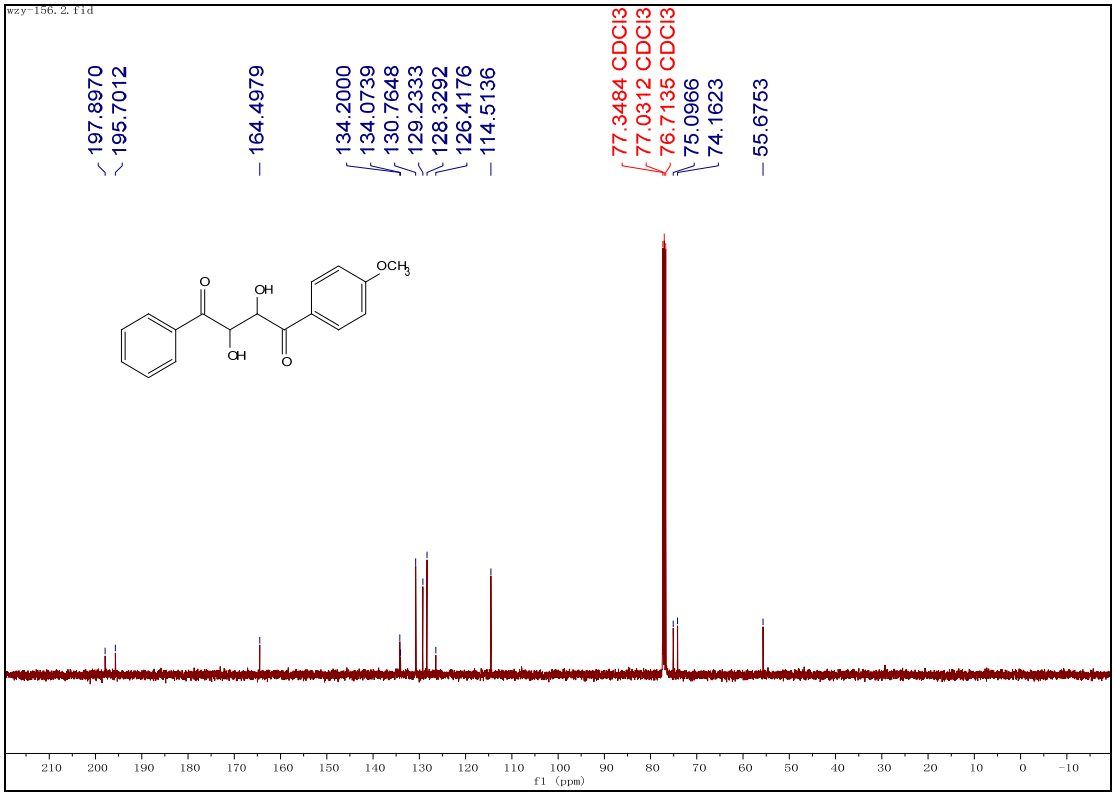


Figure S46. ^{13}C NMR spectrum of **3b** (100 MHz, $CDCl_3$)

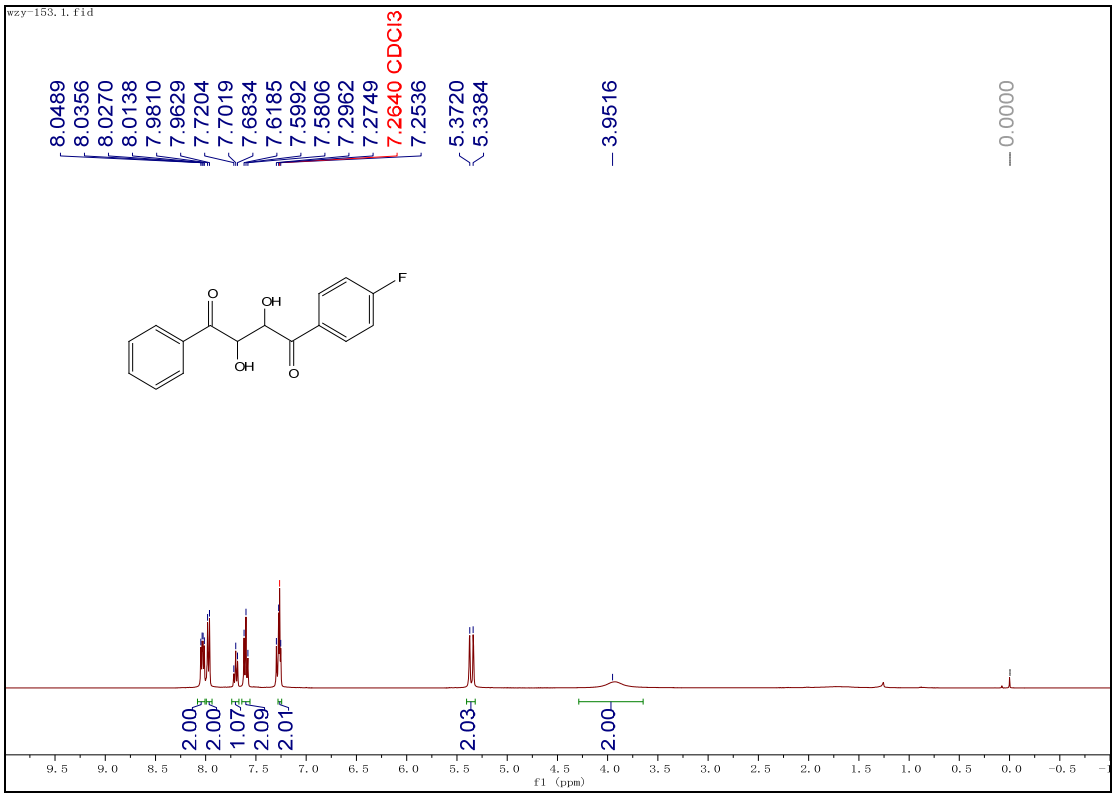


Figure S47. ^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$)

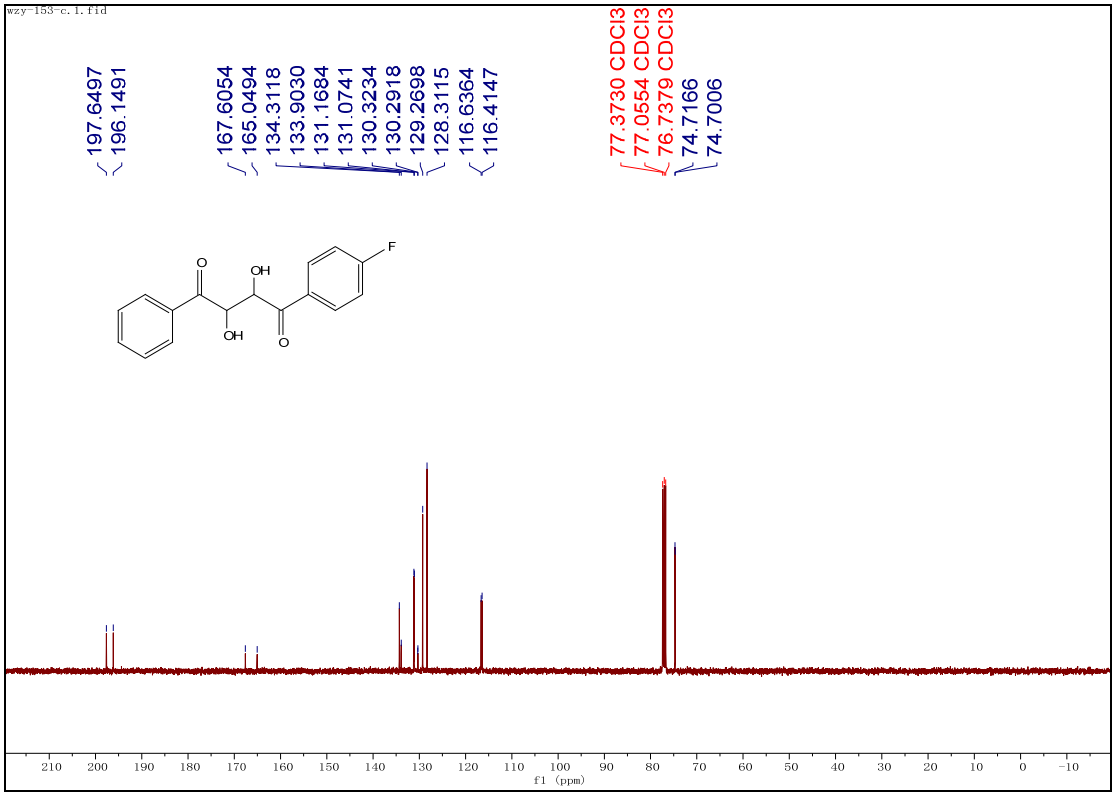


Figure S48. ^{13}C NMR spectrum of **3c** (100 MHz, $CDCl_3$)

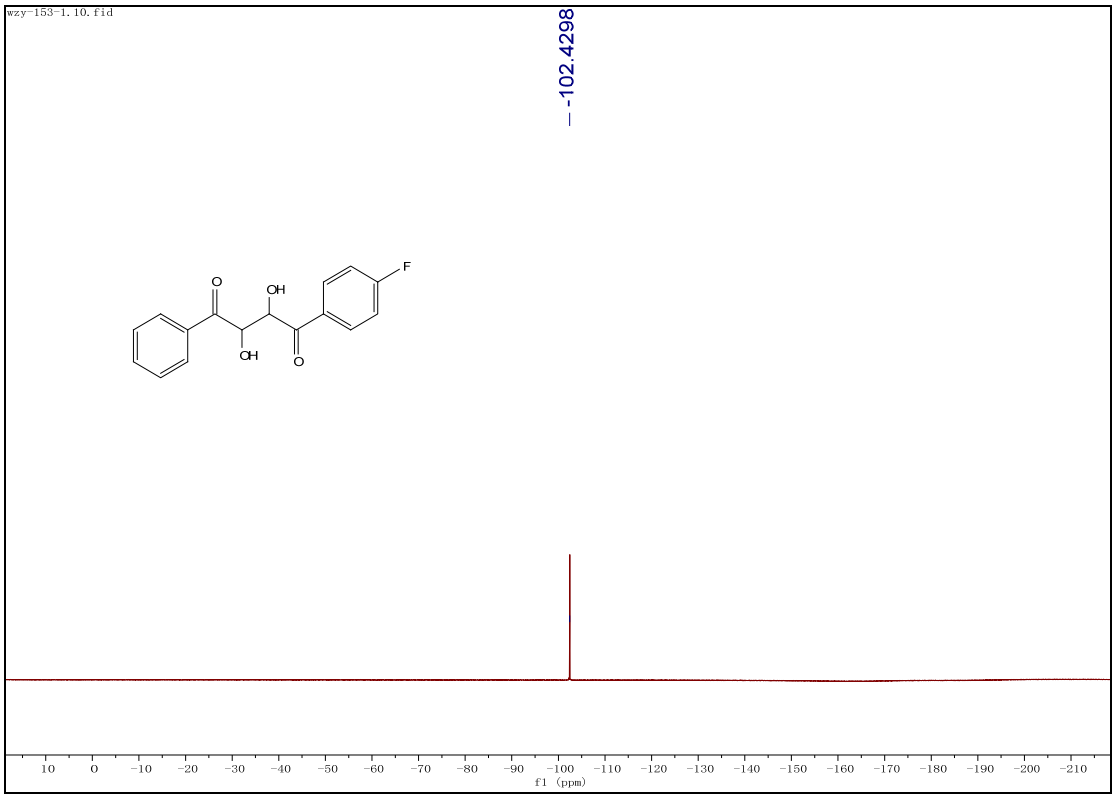


Figure S49. ^{19}F NMR spectrum of **3c** (376 MHz, $CDCl_3$)

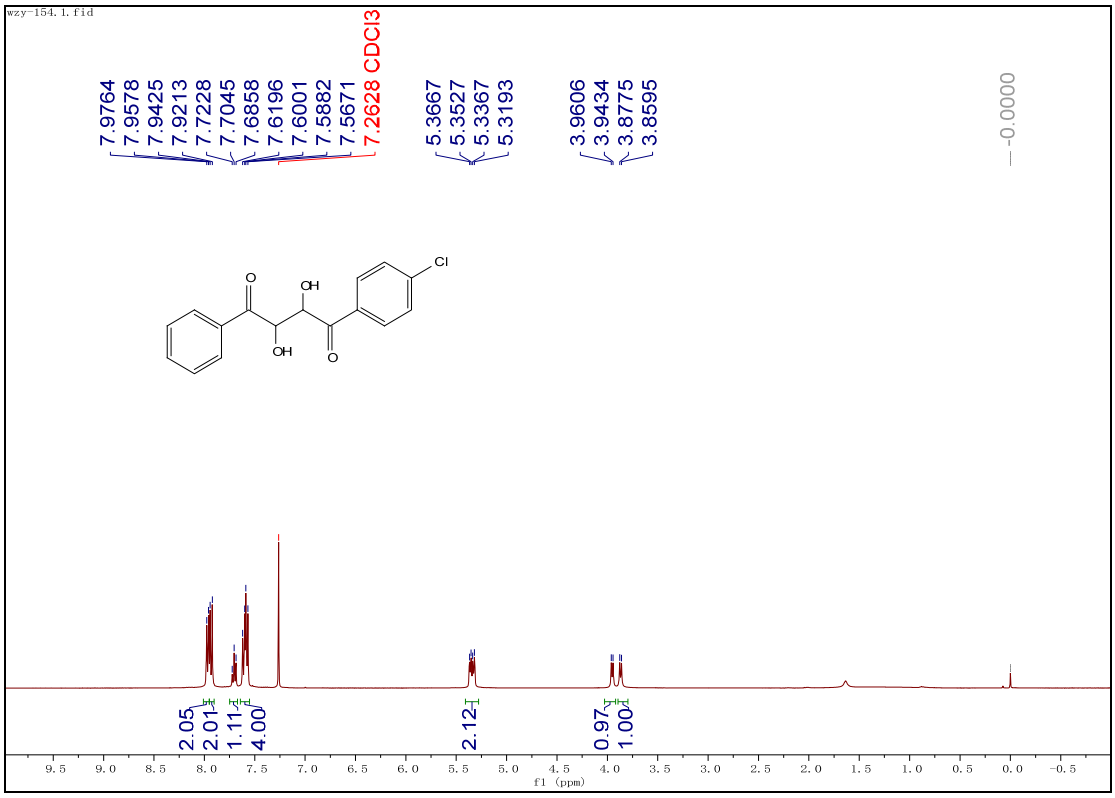


Figure S50 ^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$)

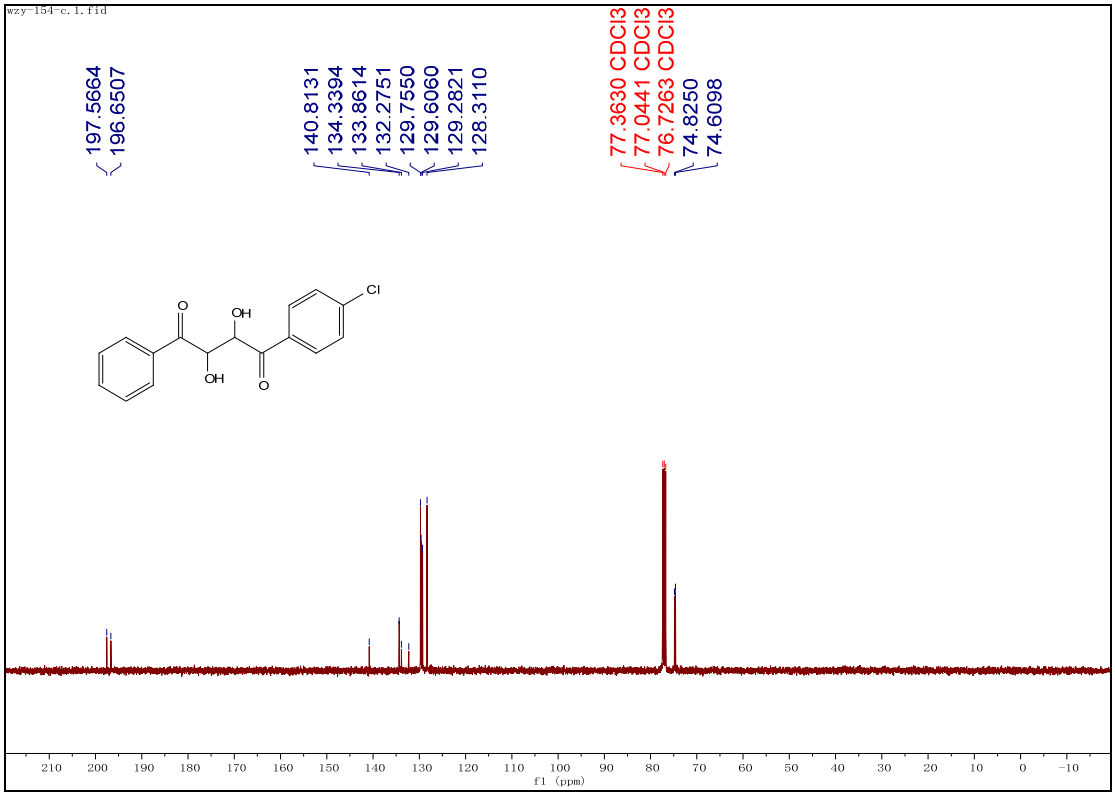


Figure S51. ^{13}C NMR spectrum of **3d** (100 MHz, $CDCl_3$)

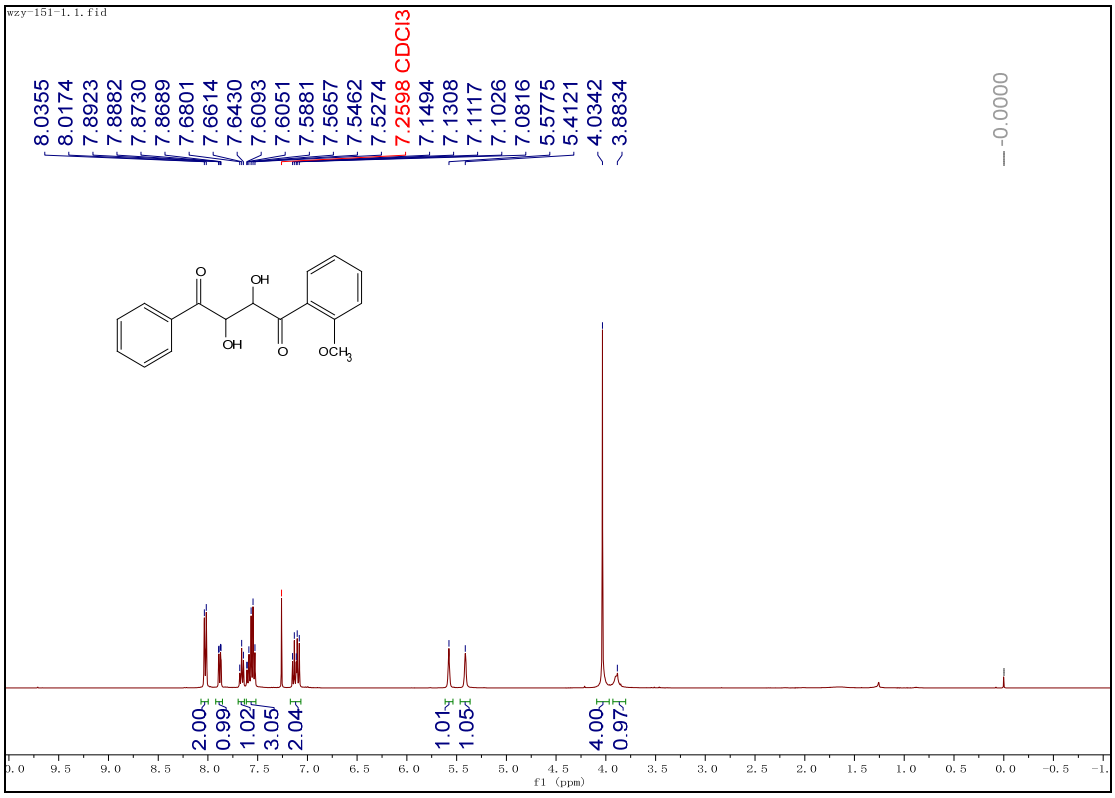


Figure S52. ^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$)

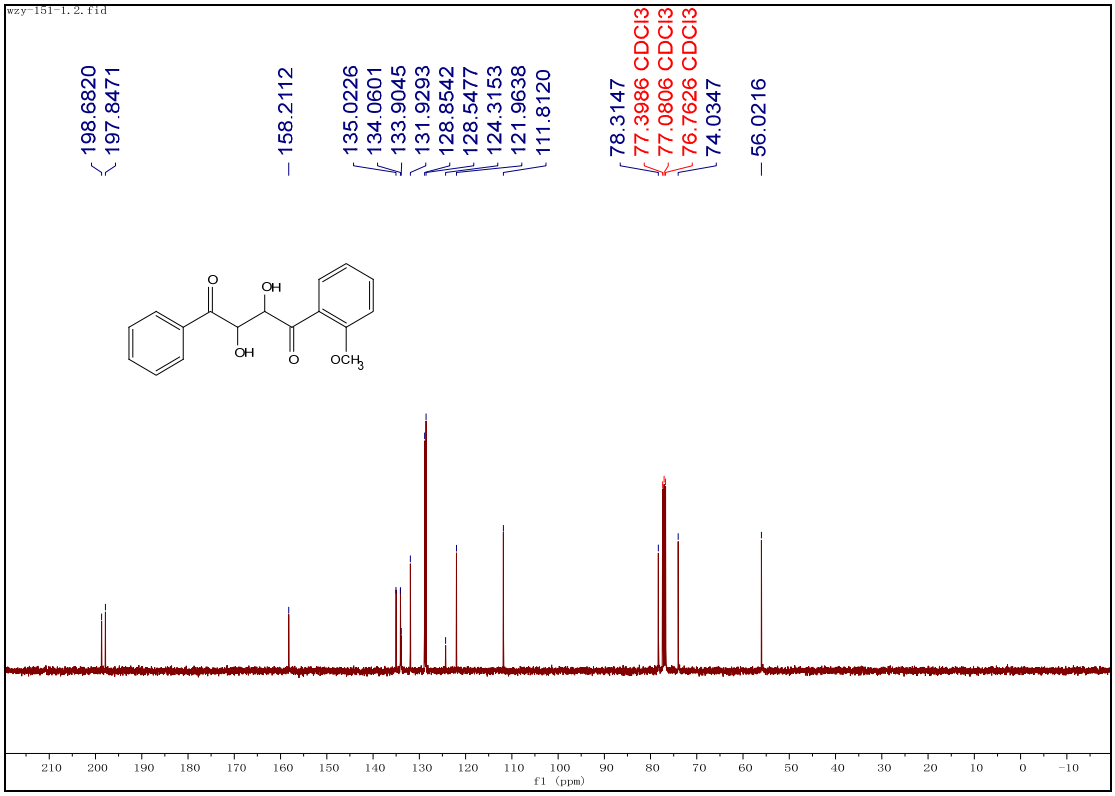


Figure S53. ^{13}C NMR spectrum of **3e** (100 MHz, $CDCl_3$)

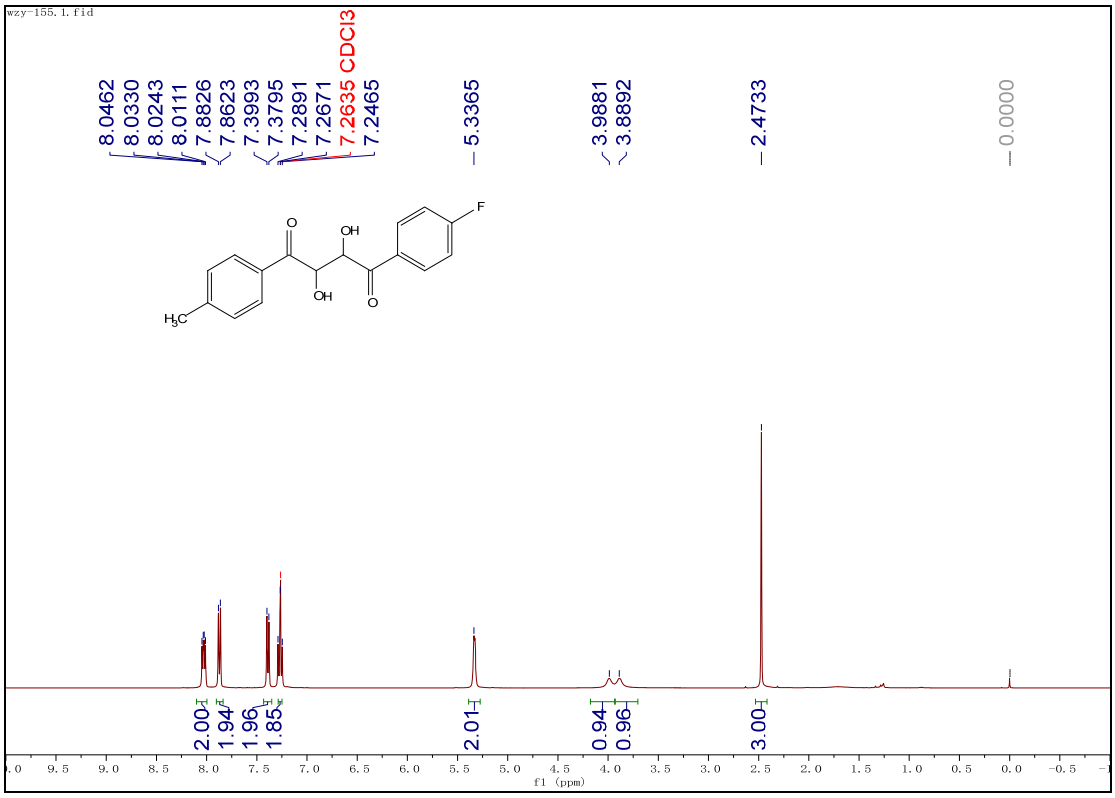


Figure S54. ^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)

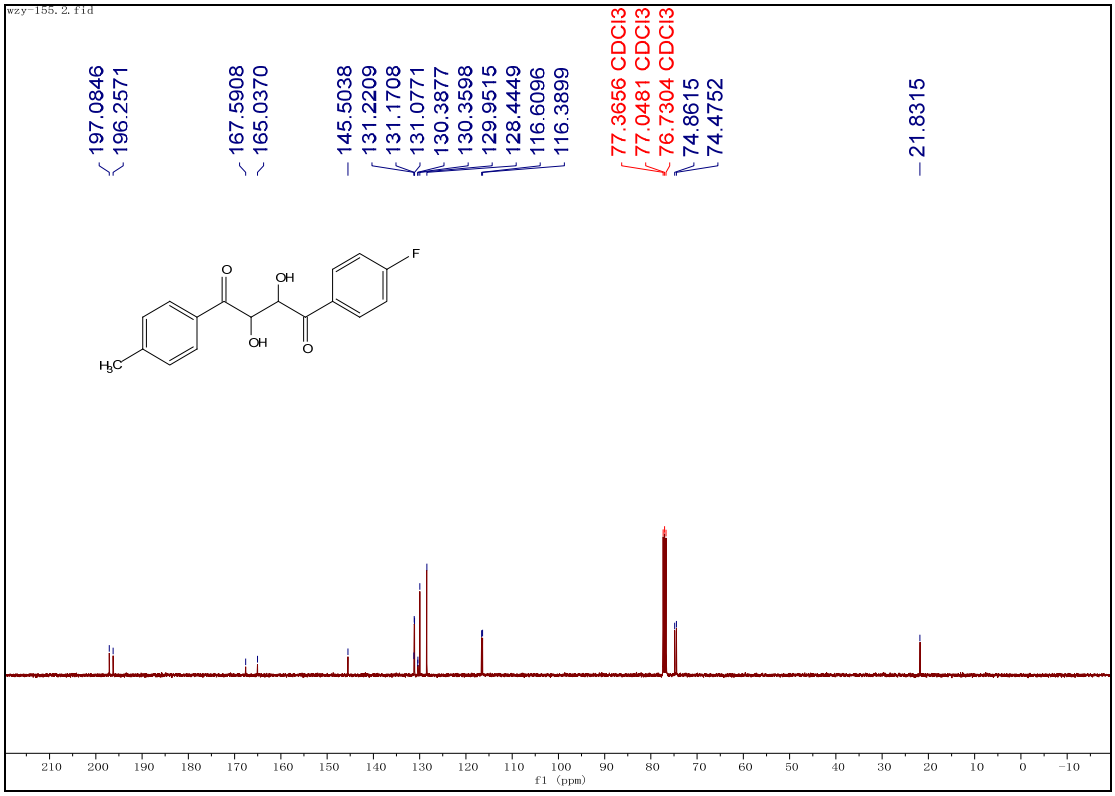


Figure S55. ^{13}C NMR spectrum of **3f** (100 MHz, $CDCl_3$)

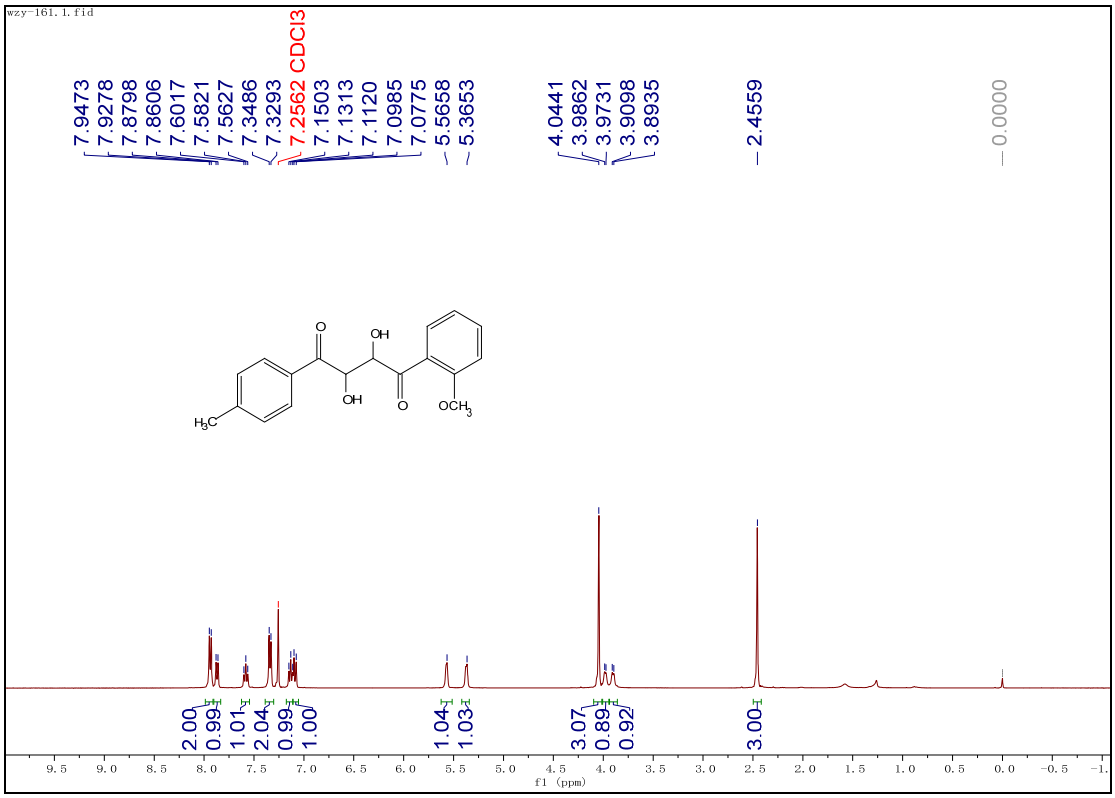


Figure S56. ^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)

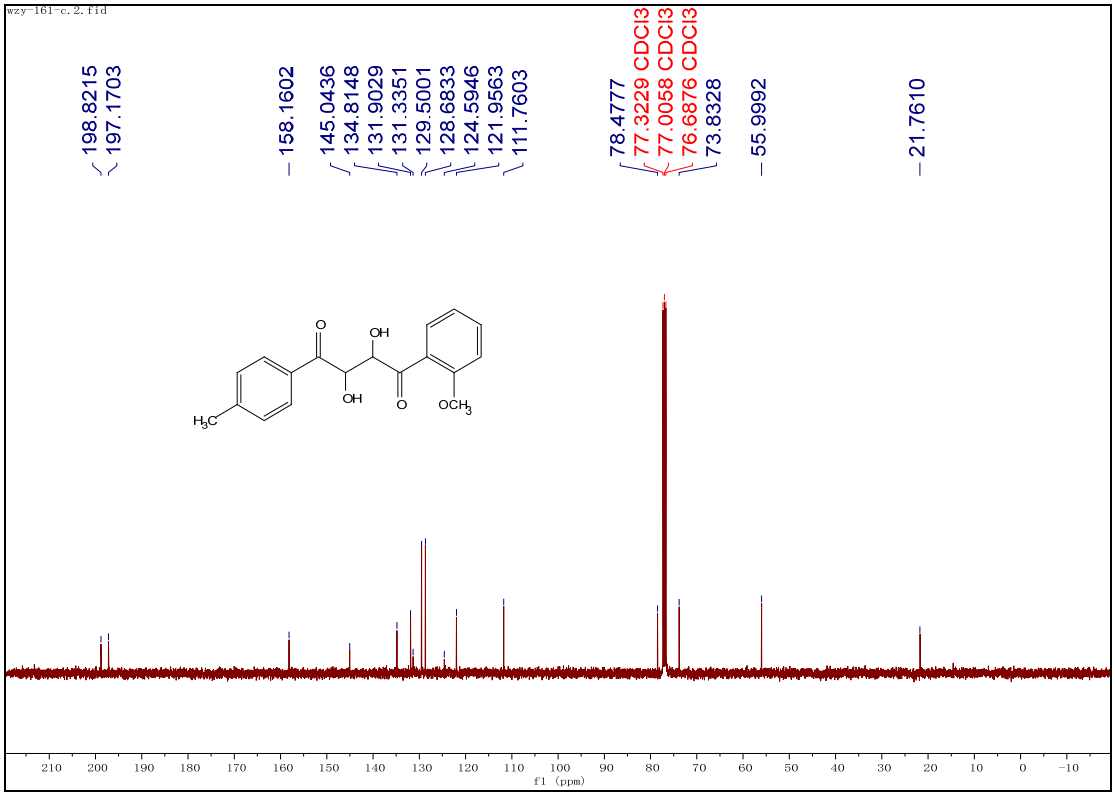


Figure S57. ^{13}C NMR spectrum of **3g** (100 MHz, $CDCl_3$)

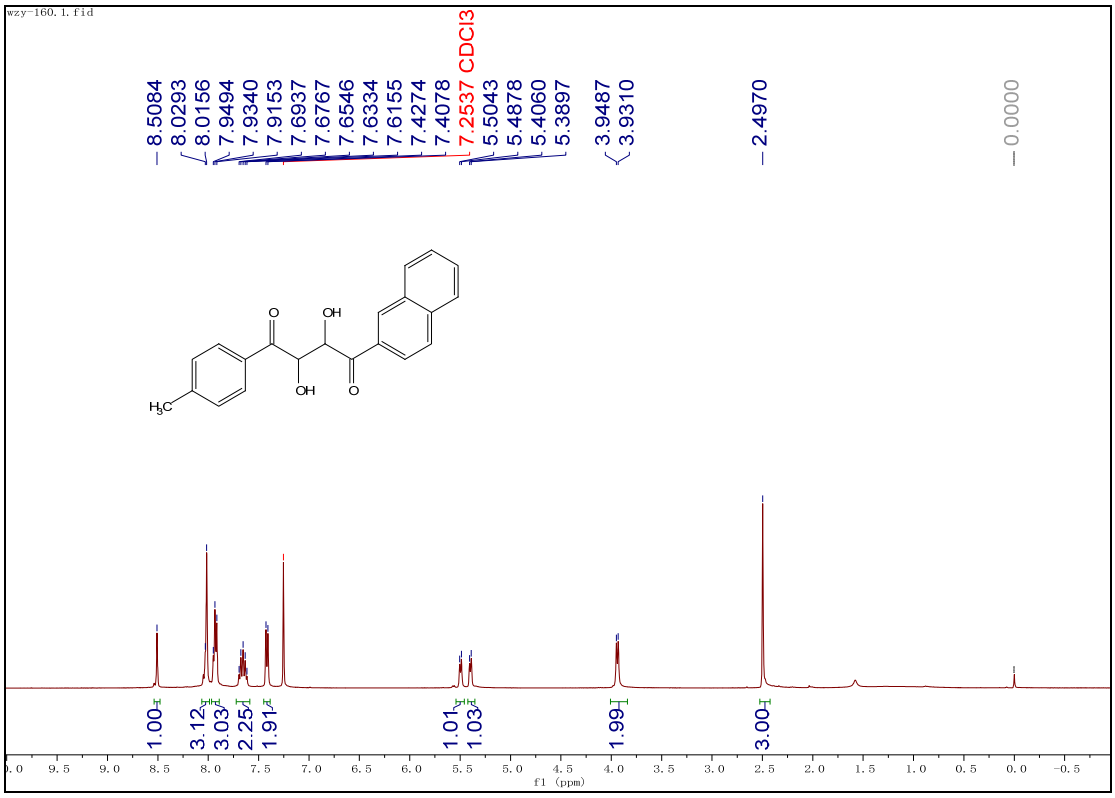


Figure S58. ^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)

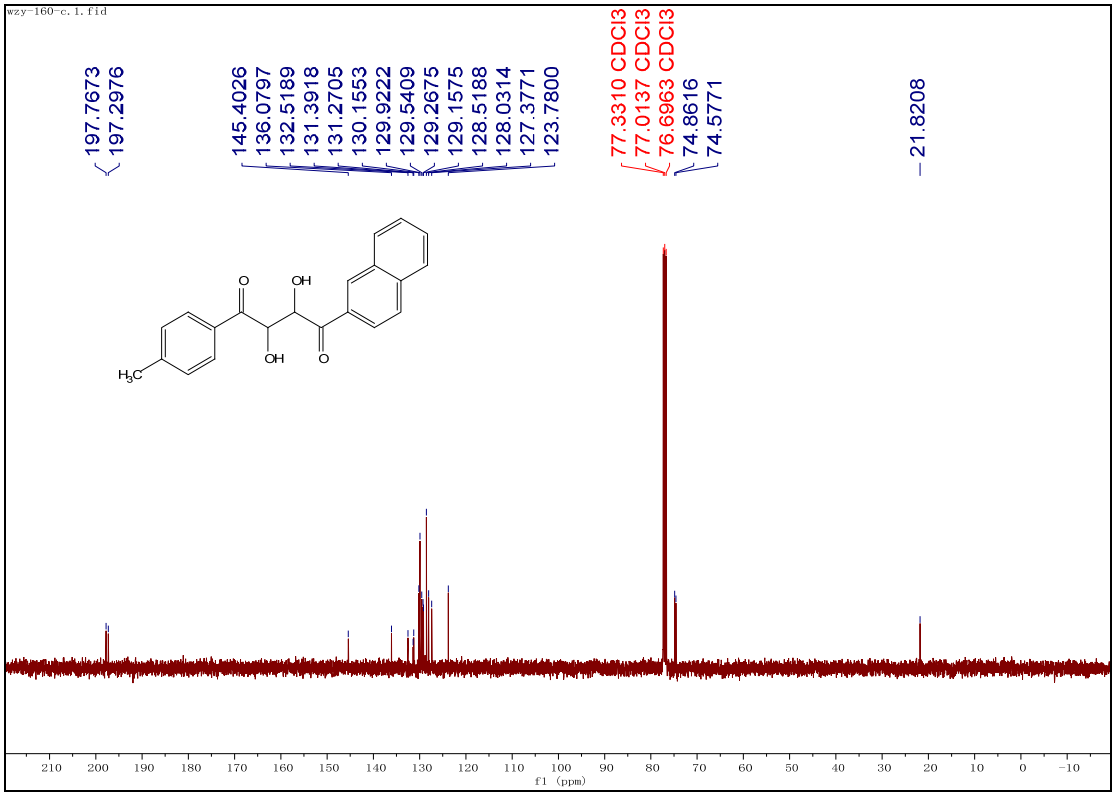


Figure S59. ^{13}C NMR spectrum of **3h** (100 MHz, $CDCl_3$)