Synthesis of functionalized fulvenes: [3+2] annulation of ethyl 2-aroylcyclopropeneformate with 1, 3-dicarbonyl compounds

Yuequan Zhu, Min Zhang, Hongling Yuan, and Yuefa Gong*

School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, People's Republic of China

Supporting information

Experimental section

General information

Solvents and reagents were employed without further purification as commercially available unless otherwise noted. Progress of reactions was monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates. Flash column chromatography was performed on silica gel 60 Å, 10−40 μm. Melting points were measured on a Melt-Temp apparatus and uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AM-400 spectrometer (400 MHz) with TMS as internal standard. ^{1}H NMR splitting patterns are indicated as follows: a, apparent; br, broad; s, singlet; d, doublet; t, triplet; q, quartet; doublet of doublets (dd); m, multiplet. ^{13}C NMR spectra were taken on a Bruker AM-400 (101 MHz) spectrometer. IR spectra were recorded with a Bruker FTIR spectrophotometer as film on KBr plate. HRMS was measured on a TOF-Q mass spectrometer equipped with an EI source.

General procedure for fulvene synthesis

1, 3-Dicarbonyl compound **2** (0.4 mmol for **2a**, 0.3 mmol for others) was added to a solution of ethyl *α*-chlorocyclopropanecarboxylate **1** (0.2 mmol), Cs_2CO_3 (0.4 mmol) in DMF (2.0 mL). The solution was then stirred at 80 ^{o}C. After completion of reaction as indicated by TLC, the reaction solution was cooled to room temperature. Then, 1 mol/L HCl (aq) solution was added to neutralize reaction solution. The mixture was extracted with CH_2Cl_2 three times, and the combined extract was washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired products **3**, **4**, **5**, or **6**. Unless otherwise specified, all the other products were obtained according to this typical procedure.

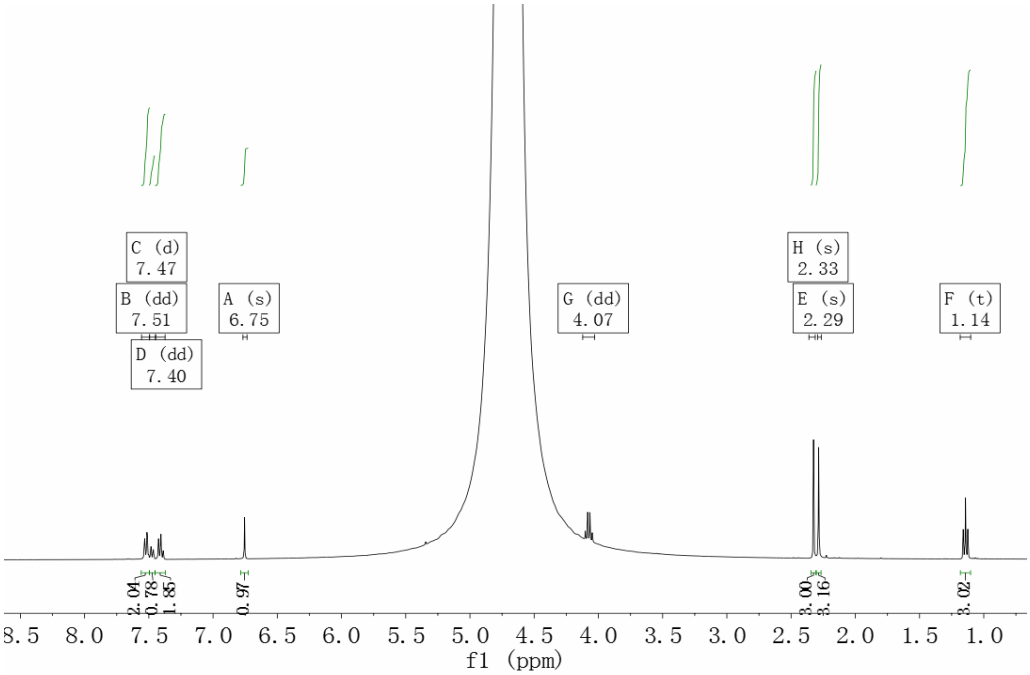
General procedure for azo dye synthesis

Under ice bath, hydrochloric acid (120 μl) was added to a solution of aromatic amine **7** (0.3 mmol) in ethanol (2.0 ml). Then, sodium nitrite (0.3 mmol) solution was dropped into it. Keeping the solution at 0-5 ^{o}C and stirred. After completion of reaction as indicated by TLC, 10% NaOH (aq) solution was slowly added to the reaction solution until pH becomes 9-10. Subsequently, the solution of fulvene **3aa** in ethanol (pH 9-10) was added to the diazo salt solution and stirred at room temperature. After completion of **3aa** as indicated by TLC, removing ethanol under reduced pressure. The mixture was extracted with CH_2Cl_2 three times,

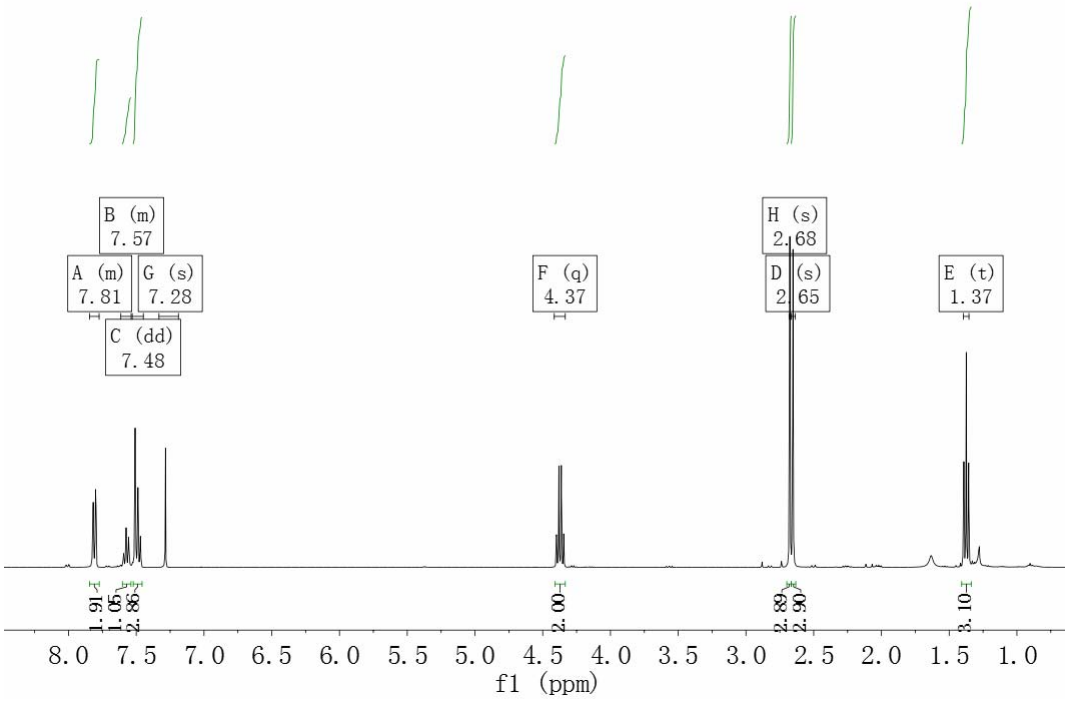
and the extract combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired products **8**.

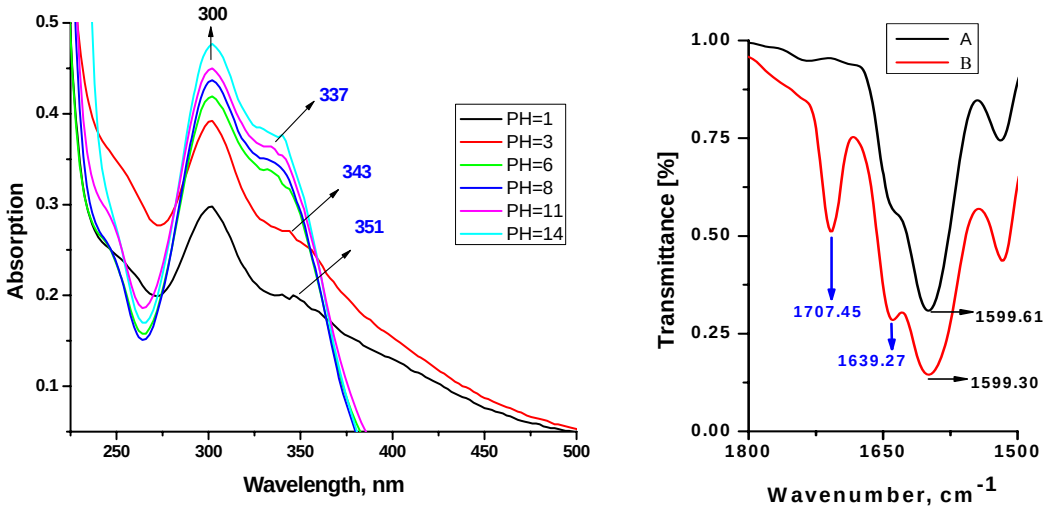
Effect of pH on the chemical shifts of protons of 3aa

^{1}H NMR spectrum for **3aa** in alkaline aqueous solution recorded in D_2O



^{1}H NMR spectrum for **3aa** recorded in $CDCl_3$





a b

Fig. 1 a: pH-dependent changes in the ultraviolet absorption spectra of **3aa** (1μM) in C_2H_5OH:H_2O (v/v = 4:1). b: characteristic IR absorption for the salt of **3aa** (A) and itself (B) (in KBr film).

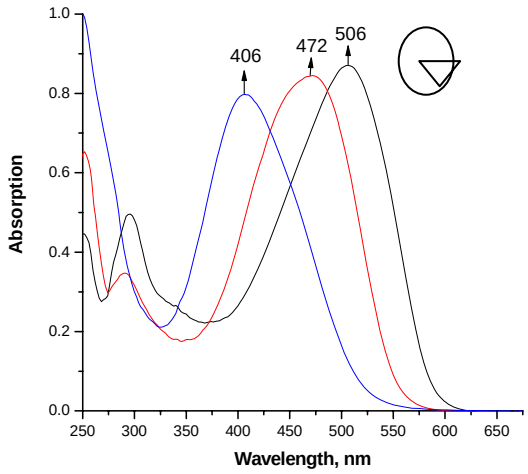
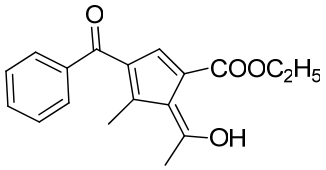


Fig. 2 The ultraviolet absorption spectra of **8a** , **8b**, **8c**(1μM) in CH_2Cl_2.

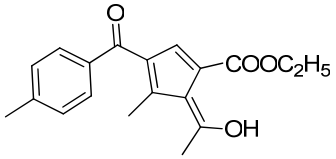
Characterization data for compounds

1. (Z)-ethyl 3-benzoyl-5-(1-hydroxyethylidene)-4-methylcyclopenta-1,3-dienecarbo -xylate (**3aa**)



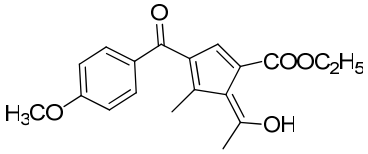
Bright yellow solid, mp 93.6-95.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.60 – 7.54 (m, 1H), 7.51 (s, 1H), 7.49 (s, 1H), 7.47 (d, *J* = 1.5 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.68 (s, 3H), 2.65 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 193.61, 183.62, 170.22, 148.34, 139.97, 137.06, 131.85, 129.47, 128.19, 120.58, 115.70, 62.24, 24.8, 17.28, 14.21. IR (KBr): ν 2983, 2930, 1708, 1639, 1599, 1517, 1446, 1412, 1379, 1333, 1243, 1174, 1028, 1007, 938, 912, 840, 724, 697 cm^{-1}. HRMS-EI (m/z): calcd for $C_{18}H_{18}O_4$ $[M+H]^+$: 299.3331, found: 299.3325.

2. (Z)-ethyl 5-(1-hydroxyethylidene)-4-methyl-3-(4-methylbenzoyl)cyclopenta-1,3-dienecarboxylate (**3ba**)



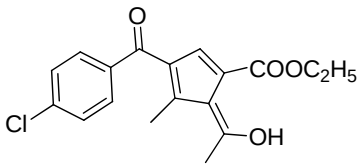
Bright yellow solid, mp 94.6-96.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.51 (s, 1H), 7.29 (s, 1H), 7.27 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.64 (s, 3H), 2.63 (s, 3H), 2.45 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 193.40, 183.22, 170.19, 147.92, 142.59, 137.20, 137.05, 132.16, 129.71, 128.90, 120.46, 115.64, 62.19, 24.73, 21.61, 17.29, 14.23. IR (KBr): ν 2984, 2928, 1716, 1605, 1523, 1446, 1414, 1383, 1335, 1248, 1180, 1058, 1035, 1022, 943, 917, 760 cm^{-1}. HRMS-EI (m/z): calcd for $C_{19}H_{20}O_4$ $[M+H]^+$: 313.3597, found: 313.3589.

3. (Z)-ethyl 5-(1-hydroxyethylidene)-3-(4-methoxybenzoyl)-4-methylcyclopenta-1,3-dienecarboxylate (**3ca**)



Bright yellow solid, mp 73.1-74.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.50 (s, 1H), 6.99 – 6.93 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.89 (d, *J* = 6.1 Hz, 3H), 2.62 (s, 3H), 2.61 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 192.53, 182.85, 170.16, 162.84, 147.35, 136.85, 132.48, 132.43, 131.85, 120.35, 115.67, 113.44, 62.17, 55.43, 24.64, 17.28, 14.22. IR (KBr): ν 2961, 2929, 2852, 1716, 1601, 1513, 1444, 1416, 1332, 1247, 1170, 1133, 1108, 941, 915, 844, 767 cm^{-1}. HRMS-EI (m/z): calcd for $C_{19}H_{20}O_5$ $[M+H]^+$: 329.3591, found: 329.3579.

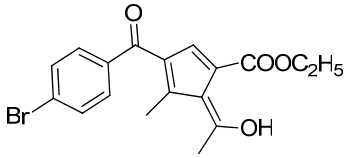
4. (Z)-ethyl 3-(4-chlorobenzoyl)-5-(1-hydroxyethylidene)-4-methylcyclopenta-1,3-dienecarboxylate (**3da**)



Bright yellow solid, mp 99.3-100.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 1H), 7.60 – 7.54 (m, 1H), 7.51 (s, 1H), 7.49 (s, 1H), 7.47 (d, *J* = 1.5 Hz, 1H), 4.37 (q, *J* = 7.1 Hz,

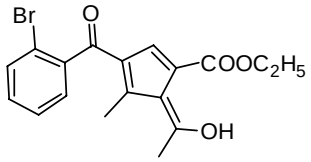
2H), 2.67 (s, 3H), 2.65 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 192.28, 184.21, 170.20, 148.56, 138.30, 138.16, 136.63, 131.27, 130.88, 128.49, 120.66, 115.78, 62.36, 24.94, 17.27, 14.23. IR (KBr): ν 2962, 2925, 2853, 1715, 1596, 1520, 1467, 1442, 1412, 1380, 1333, 1245, 1172, 1134, 1089, 1056, 1032, 1014, 941, 913, 841, 802, 761 cm^{-1}. HRMS-EI (m/z): calcd for $C_{18}H_{17}ClO_4$ $[M+H]^+$: 333.7782, found: 333.7780.

5. (Z)-ethyl 3-(4-bromobenzoyl)-5-(1-hydroxyethylidene)-4-methylcyclopenta-1,3-dienecarboxylate (**3ea**)



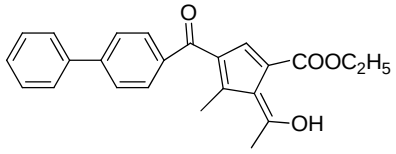
Bright yellow solid, mp 99.8-101.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 2.0 Hz, 1H), 7.67 – 7.65 (m, 1H), 7.63 (d, J = 2.1 Hz, 1H), 7.61 (d, J = 2.0 Hz, 1H), 7.45 (s, 1H), 4.38 (q, J = 7.1 Hz, 2H), 2.68 (s, 3H), 2.66 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 192.41, 184.27, 170.21, 148.63, 138.75, 136.63, 131.47, 131.20, 131.04, 126.75, 120.68, 115.79, 62.37, 24.96, 17.27, 14.23. IR (KBr): ν 2981, 2962, 2926, 2854, 1724, 1596, 1519, 1467, 1442, 1413, 1381, 1334, 1244, 1174, 1134, 1101, 1056, 1069, 1056, 1011, 941, 913, 840, 760 cm^{-1}. HRMS-EI (m/z): calcd for $C_{18}H_{17}BrO_4$ $[M+H]^+$: 378.2292, found: 378.2297.

6. (Z)-ethyl 3-(2-bromobenzoyl)-5-(1-hydroxyethylidene)-4-methylcyclopenta-1,3-dienecarboxylate (**3fa**)



Bright yellow solid, mp 96.7-98.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 17.24 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.40 (t, J = 7.1 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.25 (s, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.82 (s, 3H), 2.66 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 192.68, 185.65, 170.29, 150.35, 142.95, 137.35, 133.14, 130.57, 130.35, 128.63, 127.22, 121.33, 119.30, 116.01, 62.45, 25.33, 17.21, 14.21. IR (KBr): ν 3446, 2964, 2926, 1643, 1600, 1512, 1469, 1417, 1379, 1334, 1261, 1236, 1176, 1097, 1025, 940, 913, 867, 803, 755, cm^{-1}. HRMS-EI (m/z): calcd for $C_{18}H_{17}BrO_4$ $[M+H]^+$: 378.2292, found: 378.2285.

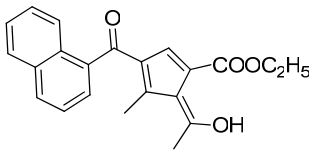
7. (Z)-ethyl 3-([1,1'-biphenyl]-4-carbonyl)-5-(1-hydroxyethylidene)-4-methylcyclo-penta-1,3-dienecarboxylate (**3ga**)



Bright yellow solid, mp 105.1-106.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (t, J = 8.5 Hz, 2H), 7.76 – 7.63 (m, 4H), 7.57 (s, 1H), 7.54 – 7.46 (m, 2H), 7.42 (t, J = 7.3 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 2.70 (s, 3H), 2.66 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H).^{13}C NMR (101 MHz,

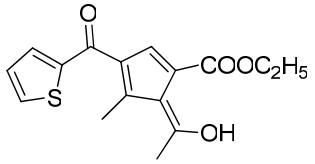
$CDCl_3$) δ 193.16, 183.64, 170.23, 148.28, 144.64, 140.13, 138.61, 137.00, 131.94, 130.15, 128.93, 128.04, 127.25, 126.89, 120.59, 115.73, 62.28, 24.85, 17.34, 14.25. IR (KBr): ν 2983, 2926, 1716, 1597, 1519, 1444, 1410, 1379, 1332, 1245, 1175, 1107, 1032, 1008, 941, 914, 854, 840, 749 cm^{-1}.HRMS-EI (m/z): calcd for $C_{24}H_{22}O_4$ $[M+H]^+$: 375.4291, found: 375.4286.

8. (Z)-ethyl 3-(1-naphthoyl)-5-(1-hydroxyethylidene)-4-methylcyclopenta-1,3-dienecarboxylate (**3ha**)



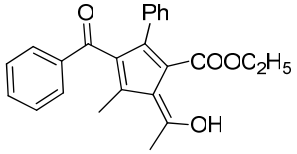
Bright yellow solid, mp 92.5-93.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.15 (m, 1H), 8.00 (t, *J* = 11.0 Hz, 1H), 7.96 – 7.89 (m, 1H), 7.64 – 7.57 (m, 1H), 7.57 – 7.49 (m, 3H), 7.38 (d, *J* = 12.8 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.79 (s, 3H), 2.67 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 195.06, 184.73, 170.27, 149.48, 138.90, 137.74, 133.82, 132.76, 130.72, 130.66, 128.28, 127.05, 127.02, 126.27, 125.79, 124.56, 121.05, 115.80, 62.31, 25.13, 17.34, 14.16. IR (KBr): ν 3057, 2982, 2929, 2855, 1709, 1599, 1516, 1466, 1443, 1381, 1334, 1271, 1237, 1192, 1173, 1131, 1094, 1057, 1032, 1011, 940, 791, 771, 736 cm^{-1}. HRMS-EI (m/z): calcd for $C_{22}H_{20}O_4$ $[M+H]^+$: 349.3918, found: 349.3919.

9. (Z)-ethyl 5-(1-hydroxyethylidene)-4-methyl-3-(thiophene-2-carbonyl)cyclopenta-1,3-dienecarboxylate (**3ia**)



Bright yellow solid, mp 96.7-98.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.64 (ddd, *J* = 4.8, 4.3, 1.1 Hz, 2H), 7.16 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.66 (s, 3H), 2.63 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 184.79, 183.79, 170.20, 147.64, 146.23, 135.98, 133.14, 131.71, 127.73, 120.51, 115.79, 62.29, 24.79, 17.05, 14.25. IR (KBr): ν 3100, 2981, 2962, 2926, 2855, 1710, 1560, 1518, 1441, 1414, 1381, 1333, 1246, 1172, 1134, 1095, 1055, 1033, 1010, 941, 858, 815, 756, 727 cm^{-1}. HRMS-EI (m/z): calcd for $C_{16}H_{16}O_4S$ $[M+H]^+$: 305.3608, found: 305.3600.

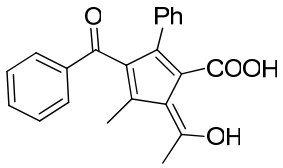
10. (Z)-ethyl 3-benzoyl-5-(1-hydroxyethylidene)-4-methyl-2-phenylcyclopenta-1,3-dienecarb oxylate (**3ja**)



Bright yellow solid, mp 140.2-143.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.54 (s, 1H), 7.84 – 7.77 (m, 2H), 7.48 (q, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.15 (m, 3H), 7.14 – 7.07 (m, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.66 (s, 3H), 2.35 (s, 3H), 0.80 (t, *J* = 7.1 Hz, 3H). ^{13}C

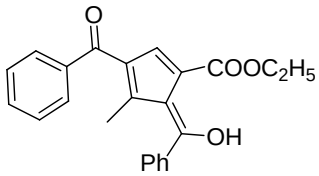
NMR (101 MHz, $CDCl_3$) δ 196.99, 180.98, 170.73, 148.81, 141.13, 139.04, 137.66, 136.93, 132.48, 129.40, 129.00, 128.00, 126.97, 126.51, 119.19, 112.87, 61.69, 24.89, 17.63, 13.11. IR (KBr): ν 3057, 2959, 2920, 2851, 1733, 1678, 1617, 1595, 1469, 1444, 1376, 1327, 1263, 1235, 1151, 1102, 1073, 1006, 977, 939, 858, 795, 748 cm^{-1}. HRMS-EI (m/z): calcd for $C_{24}H_{22}O_4$ $[M+H]^+$: 375.4291, found: 375.4286.

11. (Z)-3-benzoyl-5-(1-hydroxyethylidene)-4-methyl-2-phenylcyclopenta-1,3-dienecarboxylic acid (**3ja'**)



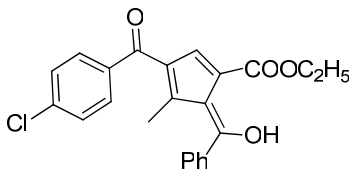
Bright yellow solid, mp 147.8-149.3 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 16.76 (s, 1H), 7.94 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.52 (dd, *J* = 6.5, 3.8 Hz, 3H), 7.49 – 7.40 (m, 3H), 7.36 – 7.30 (m, 2H), 6.86 (s, 1H), 1.96 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.58, 162.74, 159.46, 155.51, 137.32, 131.18, 130.99, 129.60, 129.07, 128.89, 127.66, 125.66, 118.12, 106.92, 104.17, 23.73. IR (KBr): ν 3445, 2959, 2920, 2851, 1702, 1629, 1528, 1496, 1451, 1409, 1375, 1262, 1209, 1085, 1024, 904, 803, 764 cm^{-1}. HRMS-EI (m/z): calcd for $C_{22}H_{18}O_4$ $[M+H]^+$: 347.3759, found: 347.3751.

12. (Z)-ethyl 3-benzoyl-5-(hydroxy(phenyl)methylene)-4-methylcyclopenta-1,3-dienecarboxylate (**3ab**)



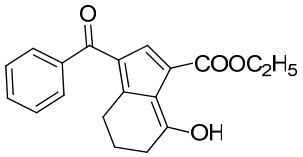
Orange oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.61 (s, 1H), 7.56 (dd, *J* = 3.3, 1.7 Hz, 1H), 7.55 (d, *J* = 2.3 Hz, 2H), 7.53 (s, 1H), 7.52 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.50 (d, *J* = 1.3 Hz, 1H), 7.48 (d, *J* = 1.3 Hz, 1H), 7.46 (s, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.88 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.65, 181.05, 170.10, 150.06, 139.87, 138.34, 137.06, 133.63, 132.80, 131.87, 130.97, 130.16, 129.35, 128.67, 128.46, 128.23, 121.09, 117.00, 62.41, 17.24, 14.27. IR (KBr): ν 3447, 3059, 2957, 2925, 2853, 1722, 1592, 1455, 1416, 1375, 1339, 1259, 1247, 1201, 1177, 1113, 1097, 1068, 1025, 801, 701 cm^{-1}. HRMS-EI (m/z): calcd for $C_{23}H_{20}O_4$ $[M+H]^+$: 361.4025, found: 361.4015.

13. (Z)-ethyl 3-(4-chlorobenzoyl)-5-(hydroxy(phenyl)methylene)-4-methylcyclopenta -1,3- dienecarboxylate (**3db**)



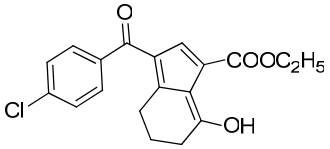
Orange oil; ^{1}H NMR (400 MHz, CDCl3) δ 17.06 (s, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.52 (m, 4H), 7.50 (d, *J* = 4.5 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.88 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.05, 181.61, 170.10, 150.27, 138.25, 138.14, 137.87, 136.98, 132.28, 131.10, 130.76, 128.71, 128.54, 128.48, 120.60, 117.11, 62.53, 17.27, 14.28. IR (KBr): ν 3445, 3060, 2963, 2927, 2854, 1714, 1642,1589, 1449, 1419, 1372, 1338, 1252, 1202, 1173, 1150, 1112, 1092, 1018, 836, 798,701 cm^{-1}. HRMS-EI (m/z): calcd for $C_{23}H_{19}ClO_4$ $[M+H]^+$: 395.8476, found: 395.8470.

14. Ethyl 3-benzoyl-7-hydroxy-5,6-dihydro-4H-indene-1-carboxylate (**3ac**)



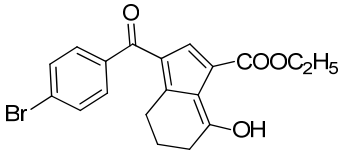
Bright yellow solid, mp 92.8-94.1 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.02 (s, 1H), 7.81 – 7.75 (m, 2H), 7.59 – 7.53 (m, 2H), 7.52 – 7.46 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.17 – 3.05 (m, 2H), 2.72 (t, *J* = 6.3 Hz, 2H), 2.10 (p, *J* = 6.4 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 192.50, 184.52, 169.63, 154.10, 140.21, 136.50, 131.46, 128.98, 128.20, 127.91, 118.44, 114.91, 62.03, 31.57, 25.07, 24.58, 14.28. IR (KBr): ν 3057, 2980, 2944, 2871, 2489, 1779, 1731, 1644, 1607, 1520, 1447, 1430, 1393, 1375, 1344, 1297, 1248, 1176, 1130, 1095, 1029, 965, 870, 734, 703 cm^{-1}. HRMS-EI (m/z): calcd for $C_{19}H_{18}O_4$ $[M+H]^+$: 311.3438, found: 311.3435.

15. Ethyl 3-(4-chlorobenzoyl)-7-hydroxy-5,6-dihydro-4H-indene-1-carboxylate (**3dc**)



Bright yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.05 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.40 (m, 3H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.11 (t, *J* = 6.3 Hz, 2H), 2.73 (t, *J* = 6.3 Hz, 2H), 2.14 – 2.06 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.03, 184.92, 169.60, 154.19, 138.55, 137.69, 136.01, 130.38, 128.48, 127.49, 118.48, 115.05, 62.08, 31.59, 25.03, 24.54, 14.25. IR (KBr): ν 3056, 2963, 2872, 2499, 2354, 1732, 1608, 1522, 1432, 1395, 1375, 1344, 1298, 1254, 1175, 1130, 1089, 1029, 966, 871, 838, 801, 761 cm^{-1}. HRMS-EI (m/z): calcd for $C_{19}H_{17}ClO_4$ $[M+H]^+$: 345.7889, found: 345.7881.

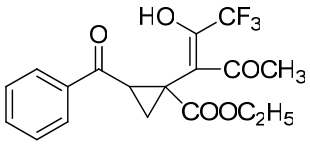
16. Ethyl 3-(4-bromobenzoyl)-7-hydroxy-5,6-dihydro-4H-indene-1-carboxylate (**3ec**)



Bright yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.08 (s, 1H), 7.68 – 7.59 (m, 4H), 7.43 (s, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.11 (t, *J* = 6.3 Hz, 2H), 2.73 (t, *J* = 6.3 Hz, 2H), 2.16 – 2.05 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.22, 185.06, 169.61, 154.34,

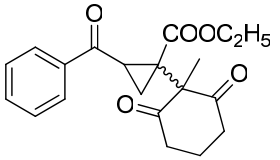
138.95, 136.01, 131.47, 130.56, 127.39, 126.25, 118.50, 115.04, 62.13, 31.61, 25.05, 24.54, 14.28. IR (KBr): ν 3054, 2946, 2871, 2567, 2253, 1731, 1604, 1521, 1431, 1393, 1374, 1344, 1298, 1249, 1235, 1174, 1131, 1096, 1068, 1043, 1028, 965, 870, 837, 759 cm^{-1}. HRMS-EI (m/z): calcd for $C_{19}H_{17}BrO_4$ $[M+H]^+$: 390.2399, found: 390.2391.

17. 3-(2-Benzoyl-1-(ethylperoxymethyl)cyclopropyl)-5,5,5-trifluoro-4-hydroxypent-3-en-2-one (**4**)



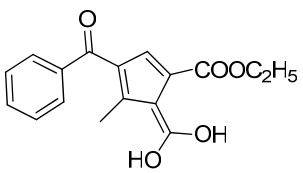
Bright yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.12 (m, 2H), 7.63 – 7.57 (m, 1H), 7.55 – 7.48 (m, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.03 (dt, *J* = 10.0, 6.7 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.22 (s, 3H), 1.68 – 1.62 (m, 1H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.95, 195.67, 171.54, 150.37 (q, *J* = 31.5 Hz), 137.04, 132.74, 129.15, 128.61, 119.29 (q, *J* = 268.1 Hz), 89.46 (q, *J* = 3.7 Hz), 62.41, 30.42, 27.64, 26.53, 18.86, 14.68. IR (KBr): ν 3472, 3064, 2962, 2926, 2854, 1739, 1685, 1597, 1451, 1372, 1328, 1372, 1328, 1261, 1213, 1148, 1097, 1021, 952, 863, 737, 696 cm^{-1}. HRMS-EI (m/z): calcd for $C_{18}H_{17}F_3O_5$ $[M+H]^+$: 371.3198, found: 371.3199.

18. Ethyl 2-benzoyl-1-(1-methyl-2,6-dioxocyclohexyl)cyclopropanecarboxylate (**5**)



Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 – 8.18 (m, 2H), 7.62 – 7.54 (m, 1H), 7.54 – 7.44 (m, 2H), 3.95 – 3.80 (m, 2H), 3.77 – 3.48 (m, 2H), 2.97 – 2.69 (m, 4H), 2.29 – 2.20 (m, 1H), 2.10 (ddd, *J* = 16.0, 9.9, 3.9 Hz, 1H), 1.57 (dd, *J* = 9.1, 6.2 Hz, 1H), 1.15 (s, 3H), 1.00 – 0.94 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 210.25, 209.60, 194.12, 172.25, 137.11, 133.06, 129.11, 128.38, 72.49, 70.19, 61.51, 38.20, 37.95, 28.86, 18.77, 17.40, 14.17, 13.61. IR (KBr): ν 3064, 2959, 2931, 2873, 1727, 1701, 1598, 1450, 1372, 1319, 1258, 1227, 1178, 1100, 1073, 1021, 936, 910, 860, 797, 766, 737 cm^{-1} . HRMS-EI (m/z): calcd for $C_{20}H_{22}O_5$ $[M+H]^+$: 343.3857, found: 343.3850.

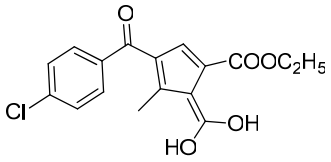
19. Ethyl 3-benzoyl-5-dihydroxymethylene-4-methylcyclopenta-1,3- dienecarboxylate (**6a**)



Yellow green solid, mp 85.6-86.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.79 (s, 1H), 7.87 – 7.79 (m, 2H), 7.59 – 7.50 (m, 4H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.69 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 190.48, 180.51, 179.08, 169.82, 137.70, 132.69, 131.79, 128.56, 128.42, 111.91, 111.72, 108.40, 62.11, 22.15, 14.30. IR (KBr): ν 3465, 3061, 2963,

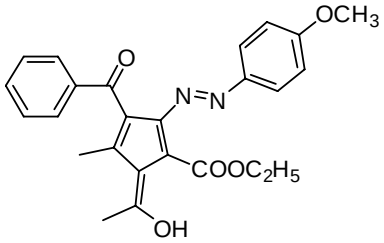
2926, 2854, 1717, 1617, 1450, 1376, 1261, 1226, 1194, 1177, 1095, 1023, 941, 865, 800,701 cm^{-1}. HRMS-EI (m/z): calcd for $C_{17}H_{16}O_5$ $[M+H]^+$: 301.3509, found: 301.3510.

20. Ethyl 3-(4-chlorobenzoyl)-5-dihydroxymethylene-4-methylcyclopenta-1,3-diene-carboxylate (**6d**)



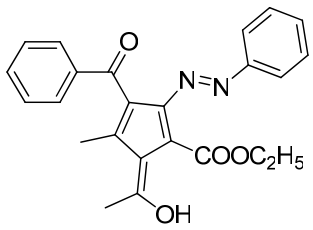
Green solid, mp 156.3-158.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.85 (s, 1H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.47 (s, 1H), 4.38 (dd, *J* = 13.5, 6.6 Hz, 2H), 2.68 (s, 3H), 1.40 (t, *J* = 6.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 189.37, 181.09, 178.66, 169.79, 138.10, 136.12, 132.06, 129.80, 128.90, 111.81, 111.75, 108.29, 62.22, 22.26, 13.68. IR (KBr): ν 3441, 2965, 1632, 1594, 1545, 1404, 1376, 1337, 1296, 1264, 1201, 1178, 1092, 1021, 942, 869, 838, 804, 749 cm^{-1}. HRMS-EI (m/z): calcd for $C_{17}H_{15}ClO_5$ $[M+H]^+$: 335.7510, found: 335.7502.

21. (Z)-ethyl 3-benzoyl-5-(1-hydroxyethylidene)-2-((E)-(4-methoxyphenyl)diazenyl)-4-methylcyclopenta-1,3-dienecarboxylate (**8a**)



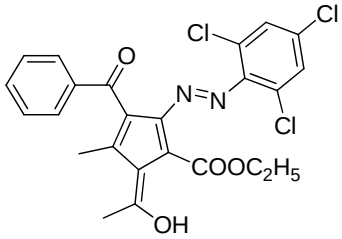
Rose red solid, mp ＞300 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 14.58 (s, 1H), 7.83 (dd, *J* = 20.5, 7.9 Hz, 2H), 7.52 – 7.49 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 4.38 (q, 7.1 Hz, 2H), 3.79 (s, 3H), 2.54 (s, 3H), 2.11 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.56, 183.84, 164.25, 163.61, 149.47, 147.51, 142.67, 138.06, 136.86, 132.79, 130.15, 128.60, 125.35, 121.68, 115.13, 105.69, 61.44, 56.08, 21.71, 15.26, 14.68. IR (KBr): ν 3060, 3029, 2958, 2924, 2853, 1729, 1699, 1643, 1598, 1565, 1510, 1438, 1379, 1338, 1302, 1246, 1185, 1115, 1029, 967, 863, 829, 803, 730 cm^{-1}. HRMS-EI (m/z): calcd for $C_{25}H_{25}N_2O_5$ $[M+H]^+$: 433.4764, found: 433.4751.

22. (Z)-ethyl3-benzoyl-5-(1-hydroxyethylidene)-4-methyl-2-((E)-phenyldiazenyl)cyclopenta-1,3-dienecarboxylate (**8b**)



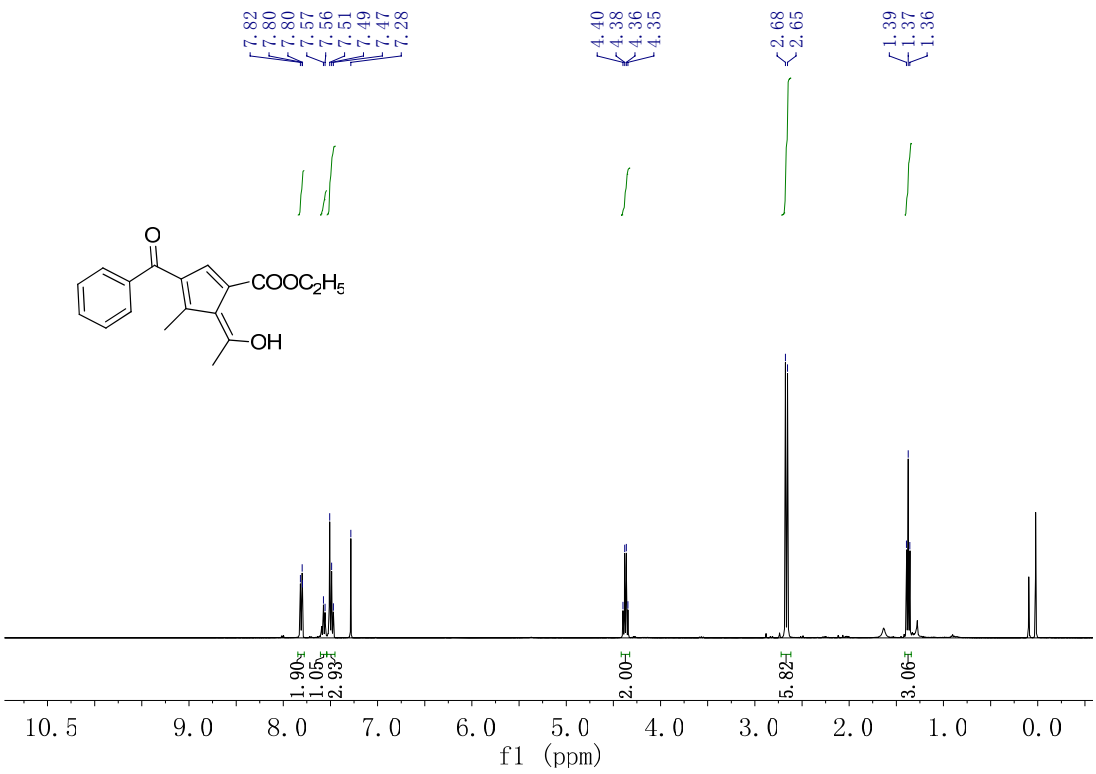
Reddish orange, mp ＞300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.39 (s, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.61 – 7.54 (m, 1H), 7.47 (dd, *J* = 13.4, 5.7 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.55 (s, 3H), 2.10 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.28, 194.28, 165.95, 153.74, 141.89, 140.16, 139.06, 137.27, 135.49, 132.62, 129.98, 129.34, 128.02, 125.33, 116.11, 108.19, 62.51, 32.05, 13.80, 11.88. IR (KBr): ν 3060, 3029, 2981, 2926, 2856, 1700, 1646, 1596, 1561, 1493, 1440, 1381, 1341, 1260, 1231, 1186, 1116, 1043, 1021, 1002, 967, 860, 805, 756, 737 cm^{-1}. HRMS-EI (m/z): calcd for $C_{24}H_{23}N_2O_4$ $[M+H]^+$: 403.4504, found: 403.4513.

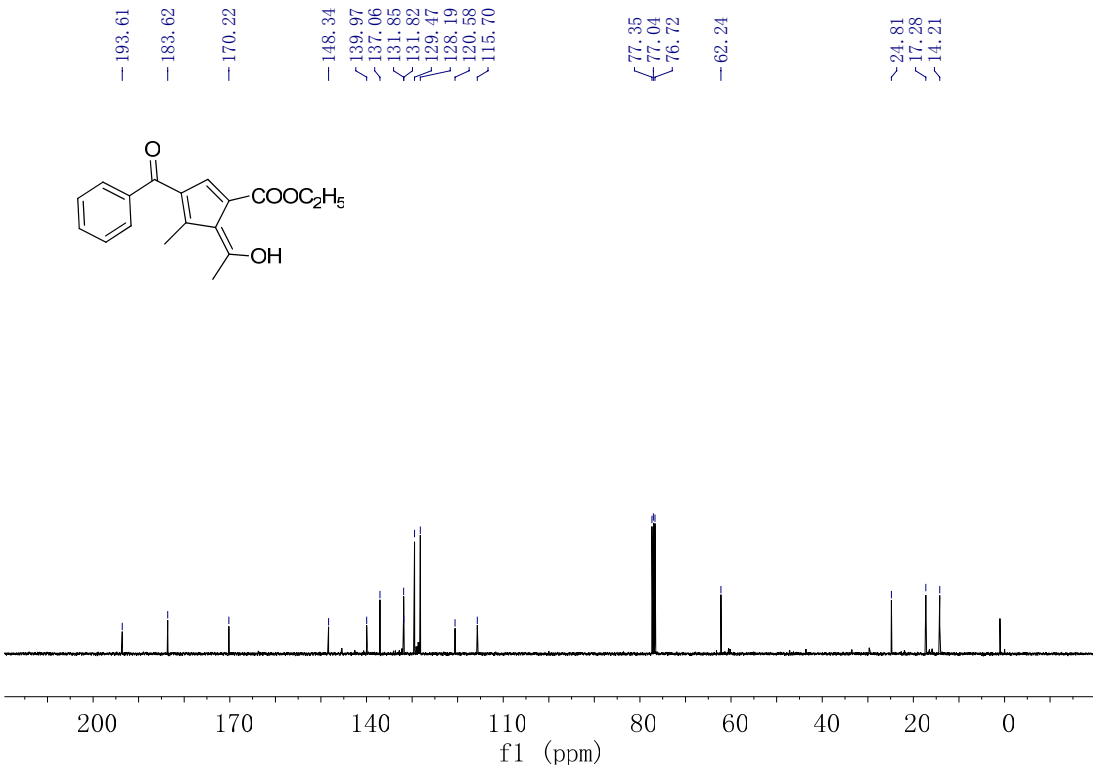
23. (Z)-ethyl 3-benzoyl-5-(1-hydroxyethylidene)-4-methyl-2-((E)-(2,4,6-trichlorophenyl) diazenyl)cyclopenta-1,3-dienecarboxylate (**8c**)

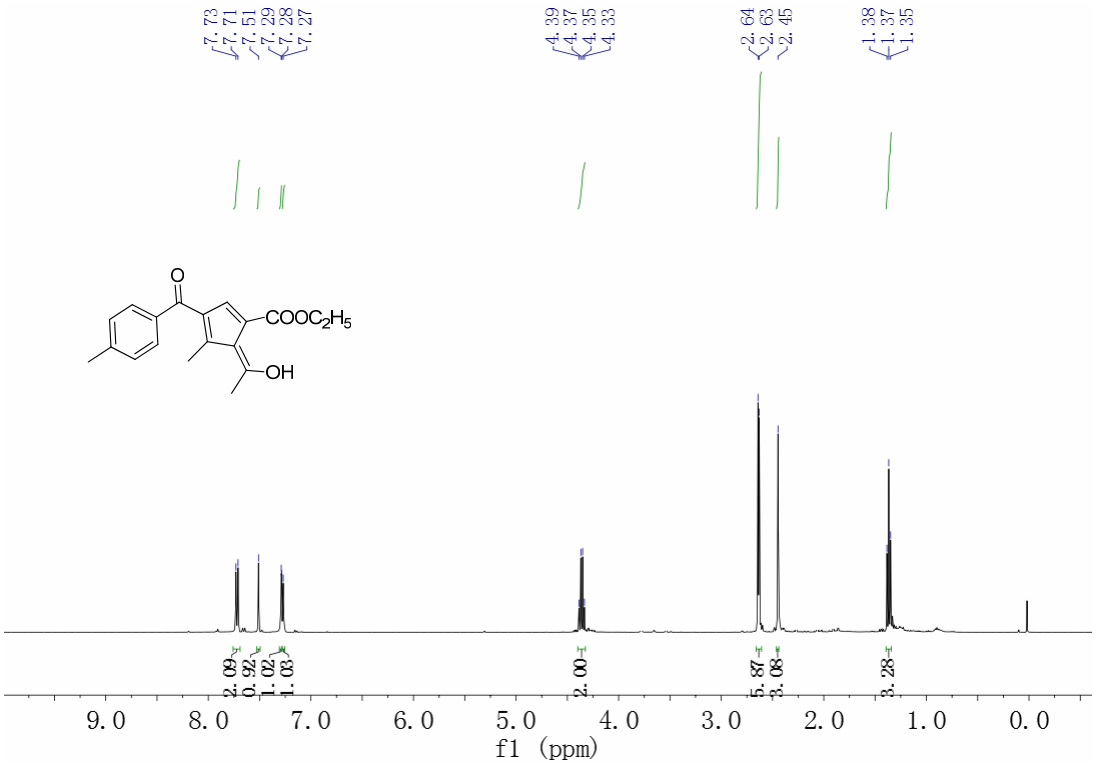


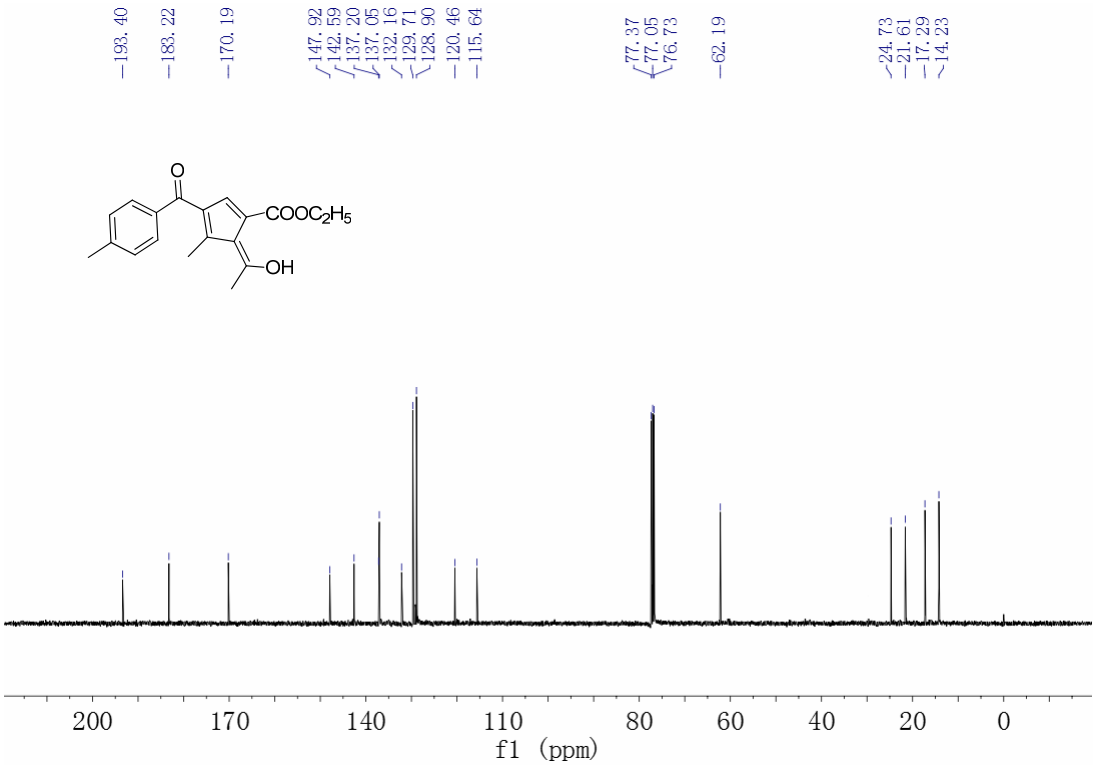
Orange yellow, mp ＞300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.84 (s, 1H), 7.84 (dd, *J* = 9.7, 8.5 Hz, 2H), 7.54 (dd, *J* = 9.5, 5.3 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.28 (s, 1H), 7.23 (s, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.54 (s, 3H), 1.95 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.53, 194.27, 165.27, 156.12, 141.02, 138.93, 138.42, 135.18, 134.36, 133.37, 130.89, 129.91, 129.12, 128.44, 128.33, 109.46, 62.63, 31.82, 13.78, 11.69. IR (KBr): ν2958, 2924, 2855, 1701, 1660, 1566, 1550, 1508, 1463, 1433, 1397, 1380, 1338, 1316, 1253, 1232, 1187, 1040, 1107, 1080, 1040, 998, 966, 859, 788, 732 cm^{-1}. HRMS-EI (m/z): calcd for $C_{24}H_{20}Cl_3N_2O_4$ $[M+H]^+$: 506.7856, found: 506.7851.

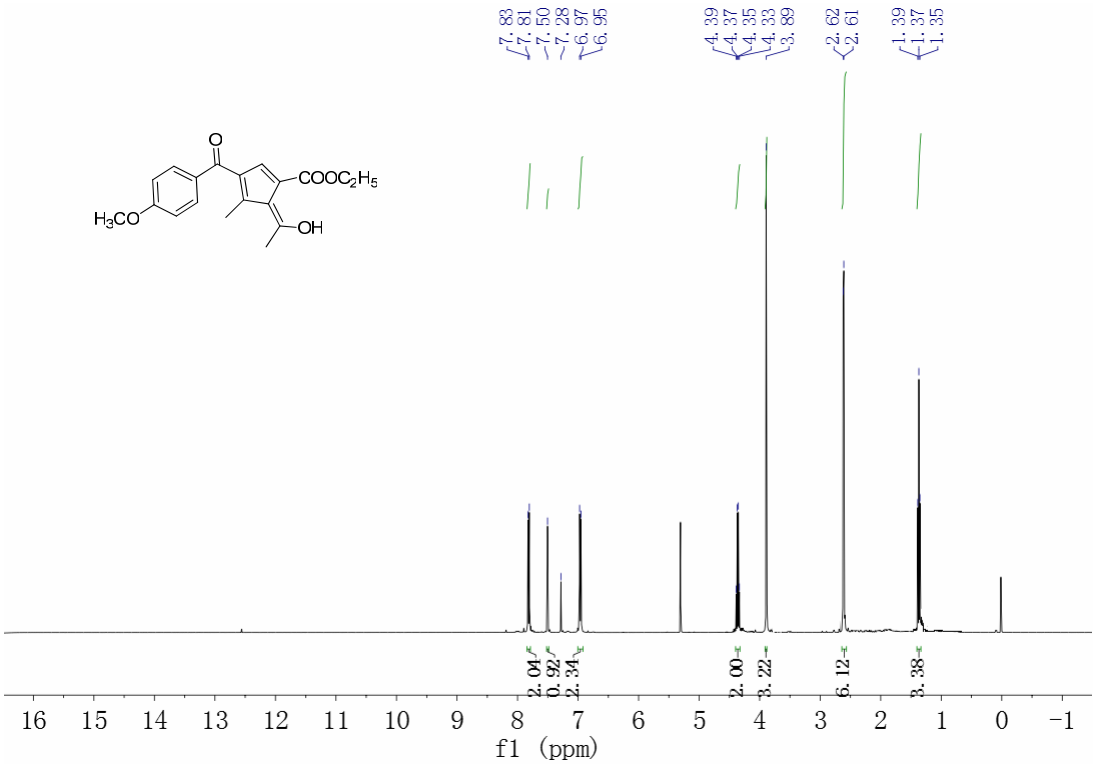
Copies of ^{1}H NMR and ^{13}C NMR spectra for compounds

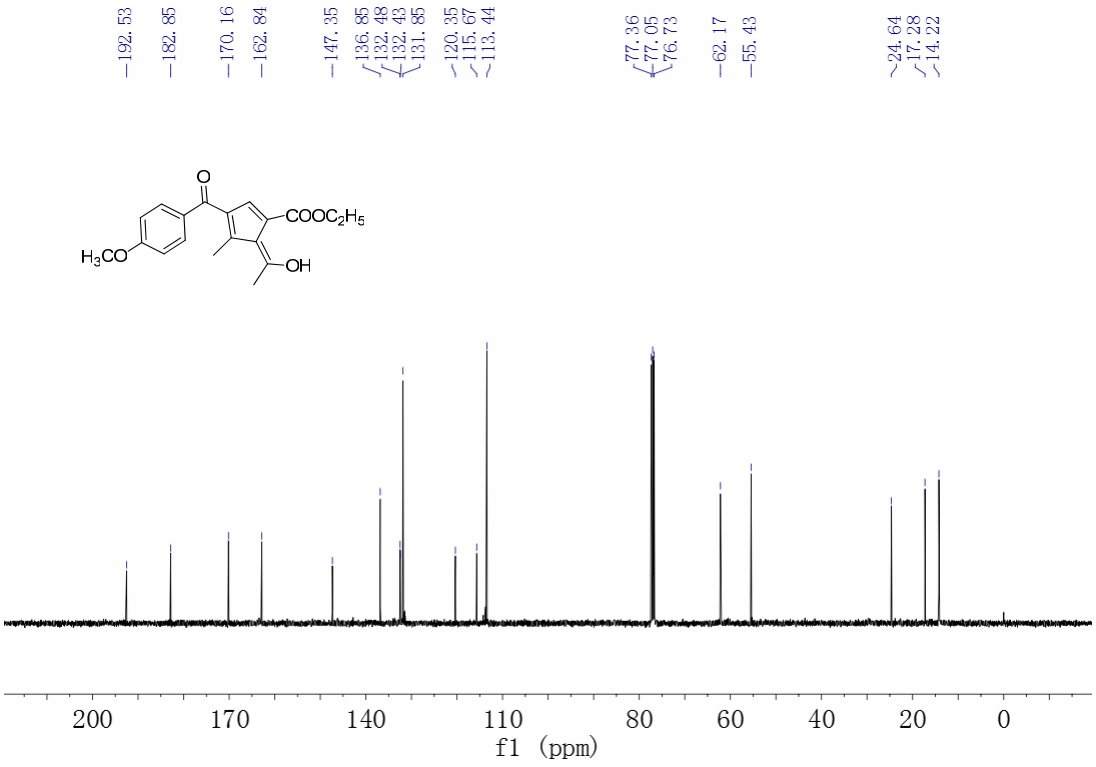

7.82
7.80
7.80
7.57
7.56
7.51
7.49
7.47
7.28
4.40
4.38
4.36
4.35
2.68
2.65
1.39
1.37
1.36
O
COOC2H5
OH
1.90
1.05
2.93
2.00
5.82
3.06
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

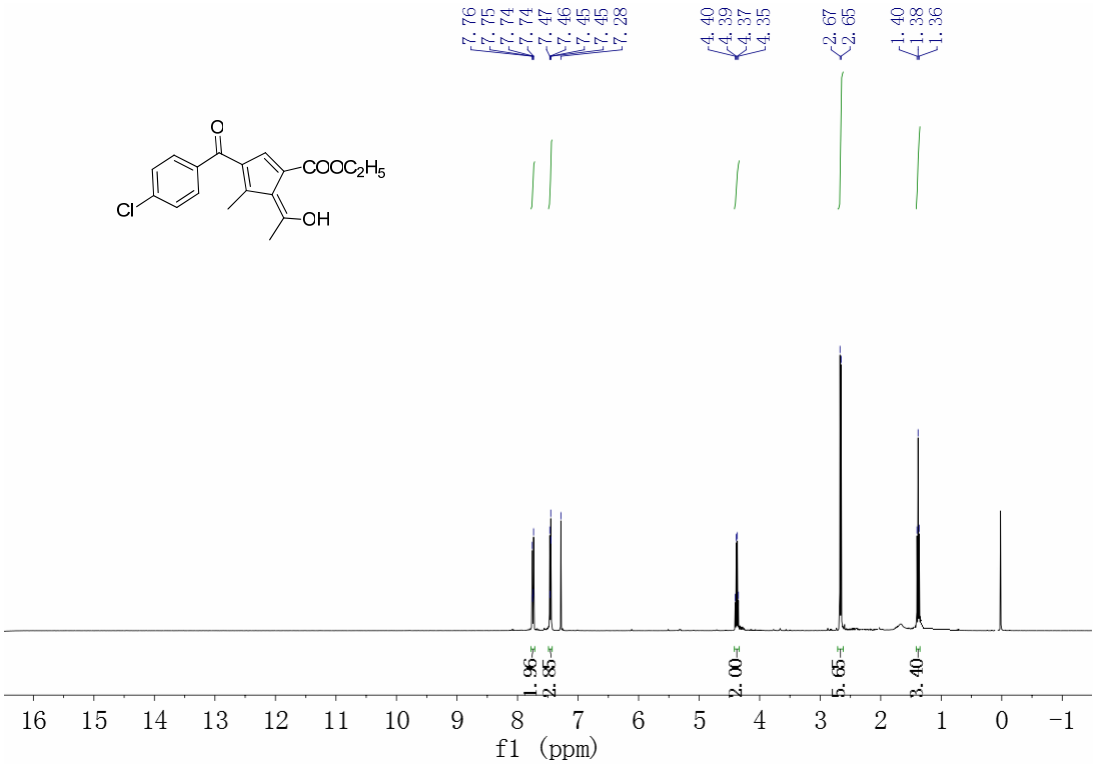

193.61
183.62
170.22
148.34
139.97
137.06
131.85
131.82
129.47
128.19
120.58
115.70
77.35
77.04
76.72
62.24
24.81
17.28
14.21
O
COOC2H5
OH
200
170
140
110
80
60
40
20
0
f1 (ppm)

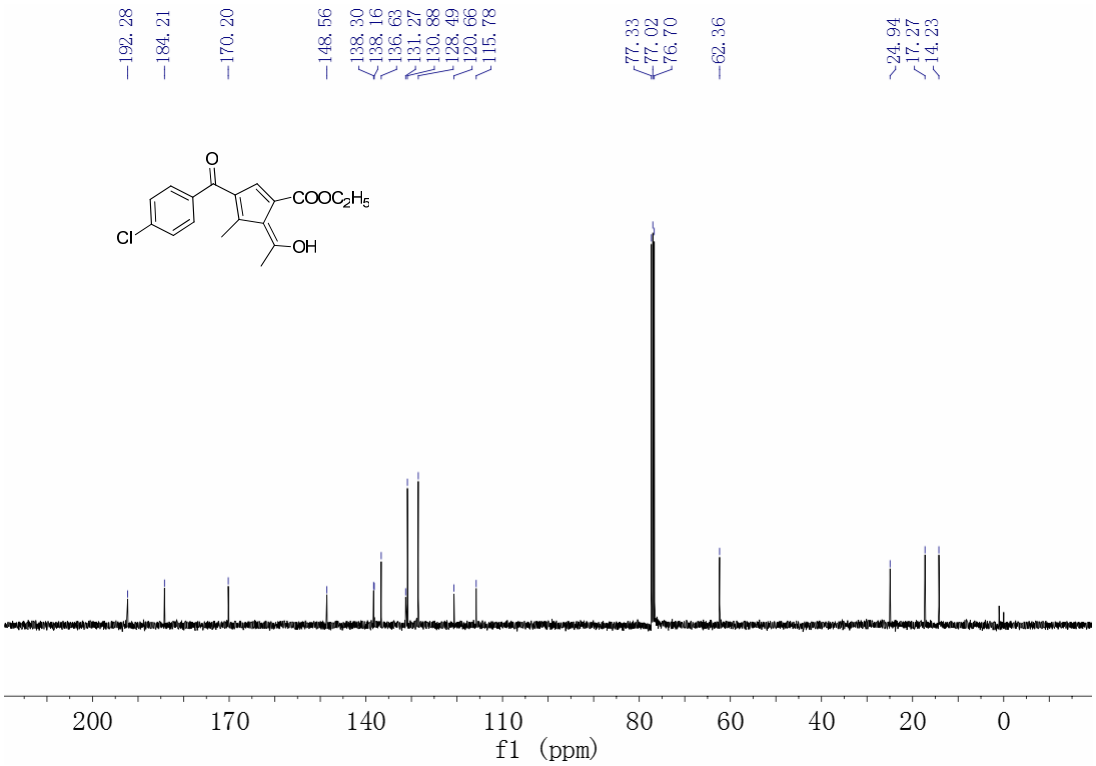

7.73
7.71
7.51
7.29
7.28
7.27
4.39
4.37
4.35
4.33
2.64
2.63
2.45
1.38
1.37
1.35
O
COOC2H5
OH
2.09
0.92
1.02
1.03
2.00
5.87
3.08
3.28
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

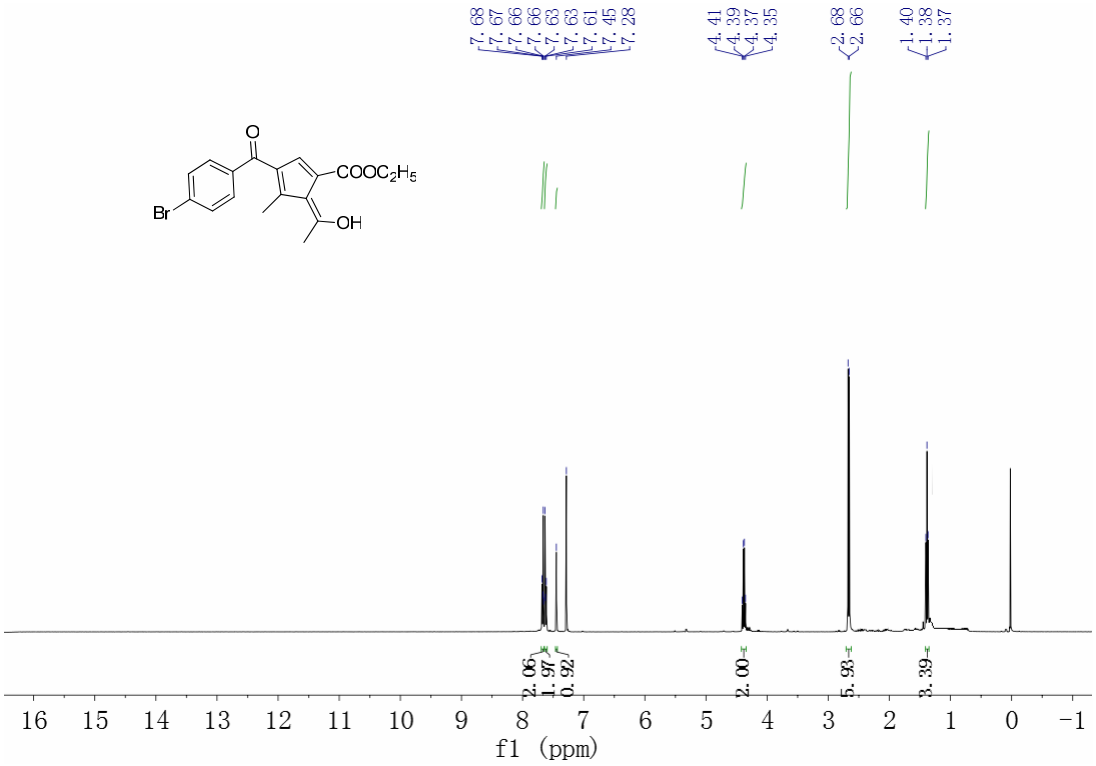

193.40
183.22
170.19
147.92
142.59
137.20
137.05
132.16
129.71
128.90
120.46
115.64
77.37
77.05
76.73
62.19
24.73
21.61
17.29
14.23
O
COOC2H5
OH
200
170
140
110
80
60
40
20
0
f1 (ppm)

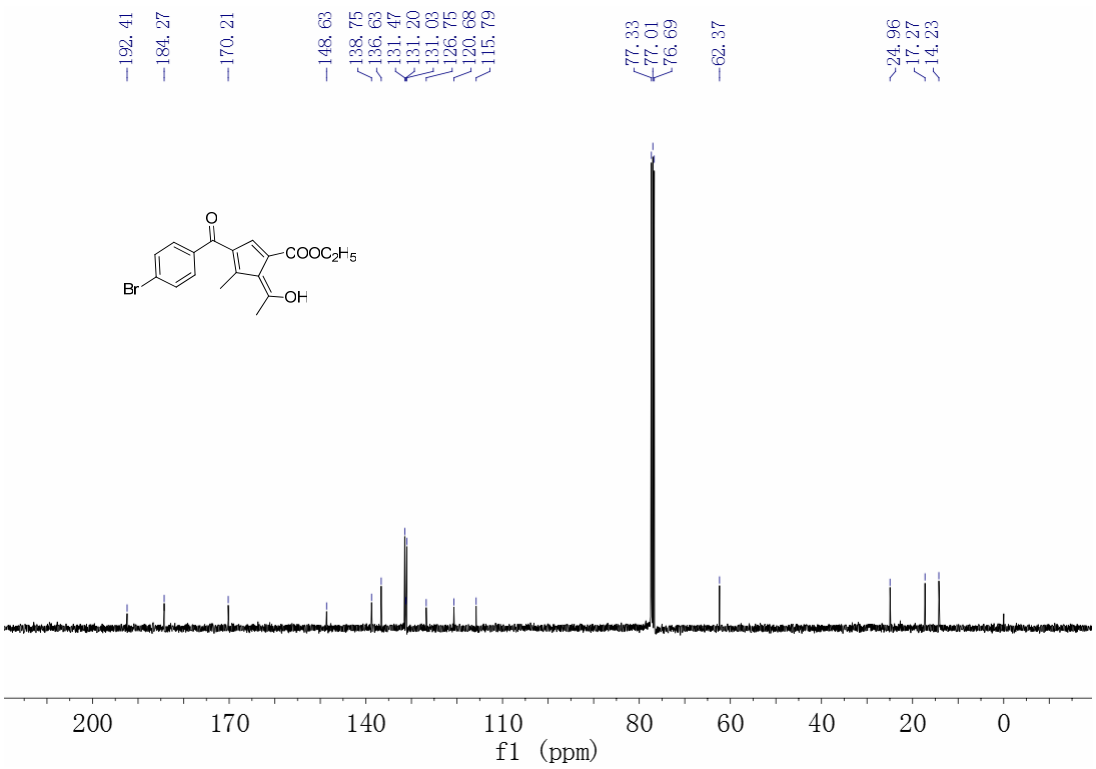

7.83
7.81
7.50
7.28
6.97
6.95
4.39
4.37
4.35
4.33
3.89
2.62
2.61
1.39
1.37
1.35
O
COOC2H5
H3CO
OH
2.04
0.92
2.34
2.00
3.22
6.12
3.38
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

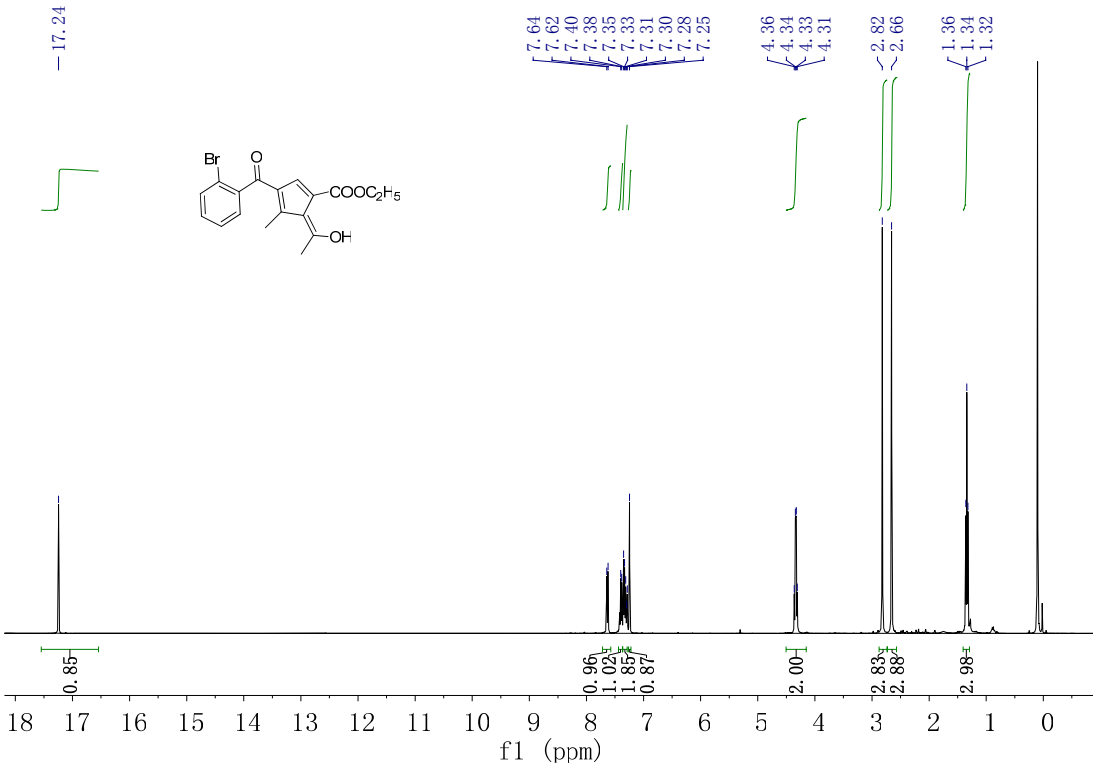

192.53
182.85
170.16
162.84
147.35
136.85
132.48
132.43
131.85
120.35
115.67
113.44
77.36
77.05
76.73
62.17
55.43
24.64
17.28
14.22
O
COOC2H5
H3CO
OH
200 170 140 110 80 60 40 20 0
f1 (ppm)

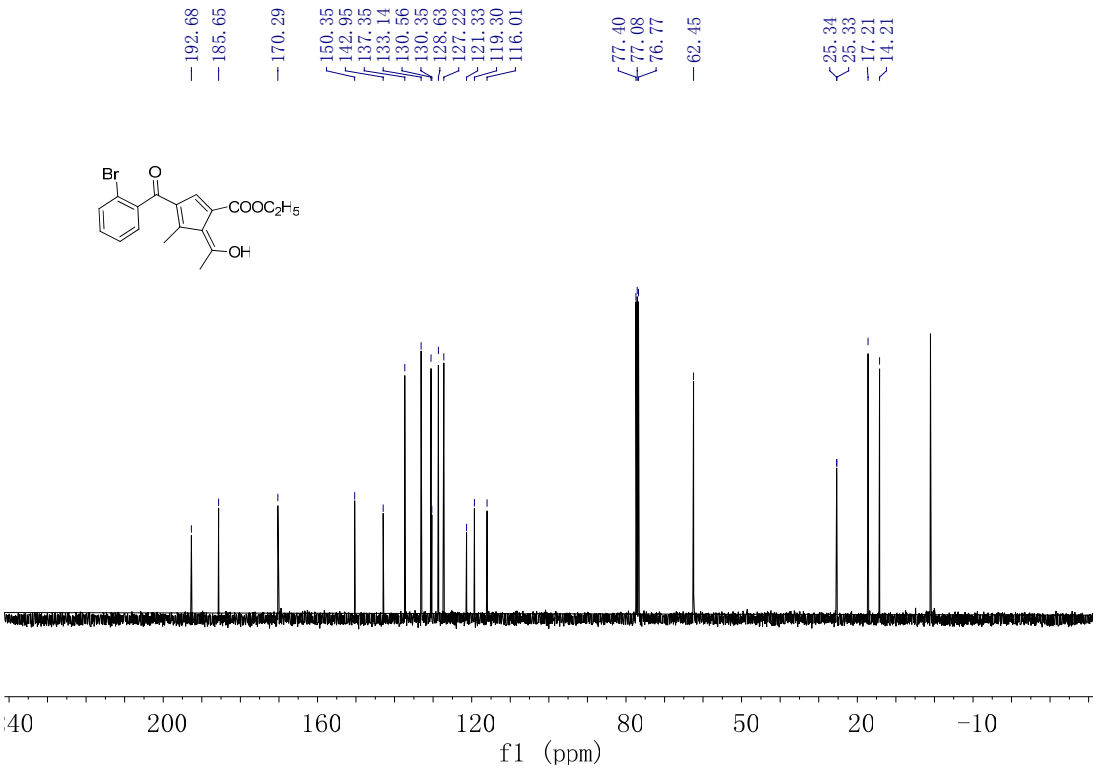

7.76
7.75
7.74
7.74
7.47
7.46
7.45
7.45
7.28
4.40
4.39
4.37
4.35
2.67
2.65
1.40
1.38
1.36
O
COOC2H5
Cl
OH
1.96
2.85
2.00
5.65
3.40
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

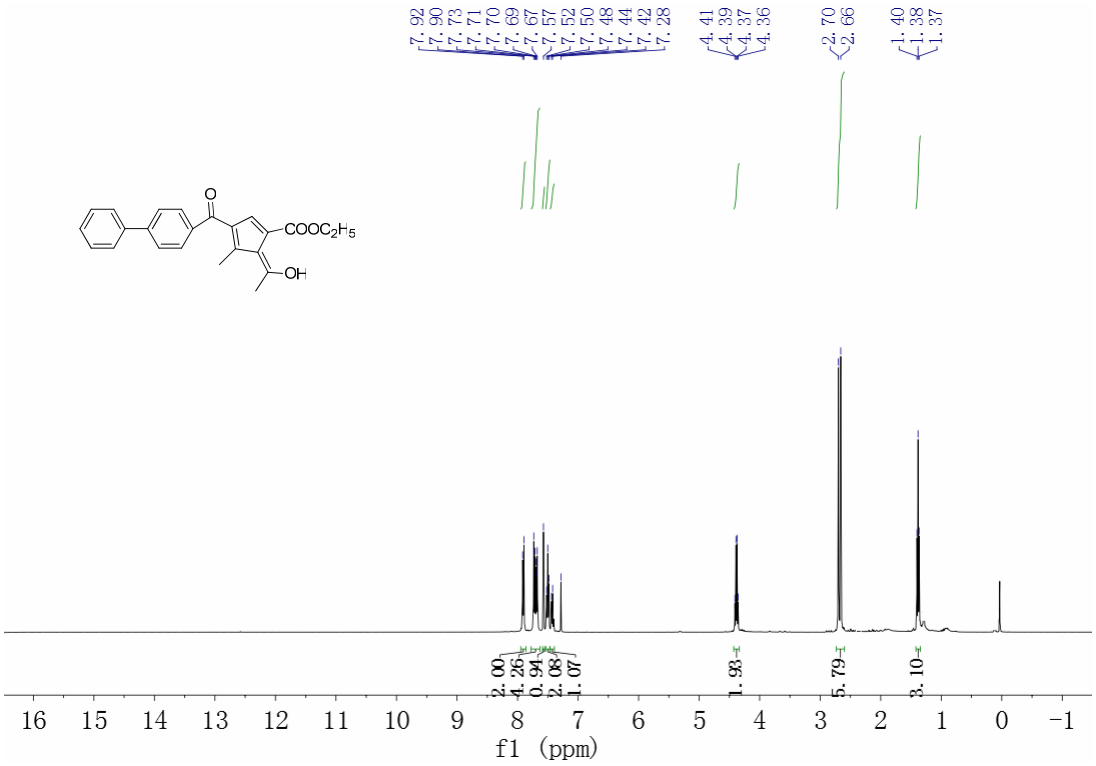

192.28
184.21
170.20
148.56
138.30
138.16
136.63
131.27
130.88
128.49
120.66
115.78
77.33
77.02
76.70
62.36
24.94
17.27
14.23
O
COOC2H5
Cl
OH
200 170 140 110 80 60 40 20 0
f1 (ppm)

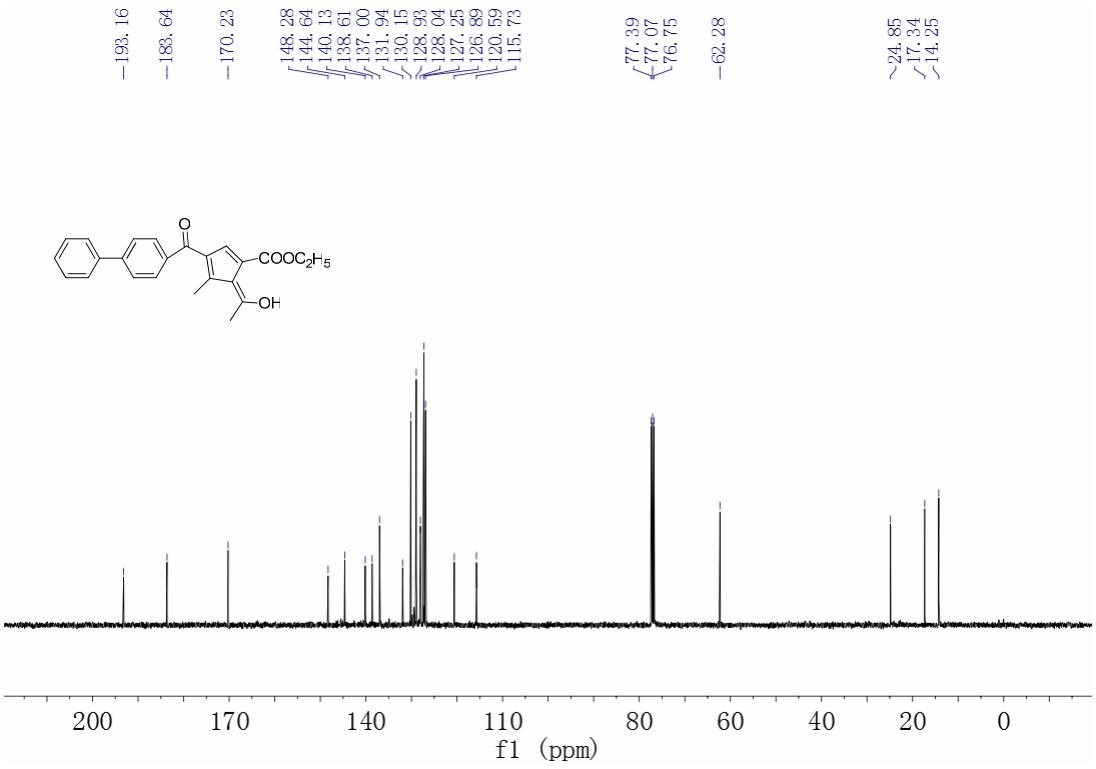

7.68
7.67
7.66
7.66
7.63
7.63
7.61
7.45
7.28
4.41
4.39
4.37
4.35
2.68
2.66
1.40
1.38
1.37
O
COOC2H5
Br
OH
2.06
1.97
0.92
2.00
5.93
3.39
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

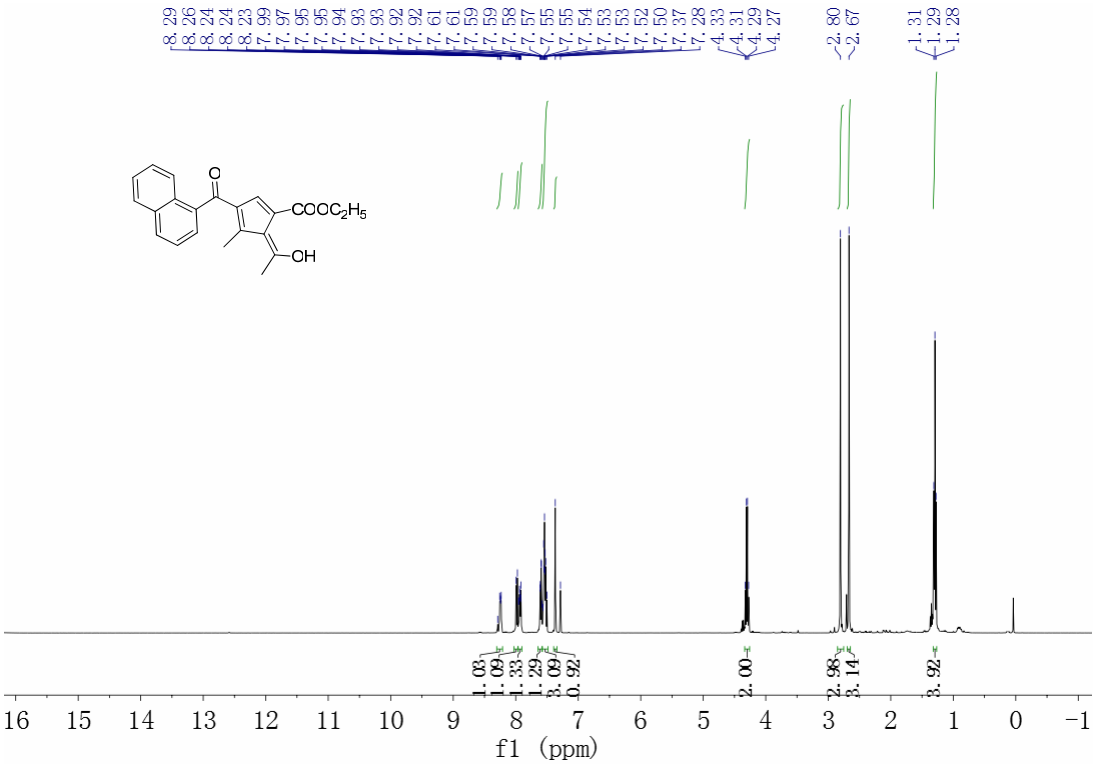

192.41
184.27
170.21
148.63
138.75
136.63
131.47
131.20
131.03
126.75
120.68
115.79
77.33
77.01
76.69
62.37
24.96
17.27
14.23
O
COOC2H5
Br
OH
200 170 140 110 80 60 40 20 0
f1 (ppm)

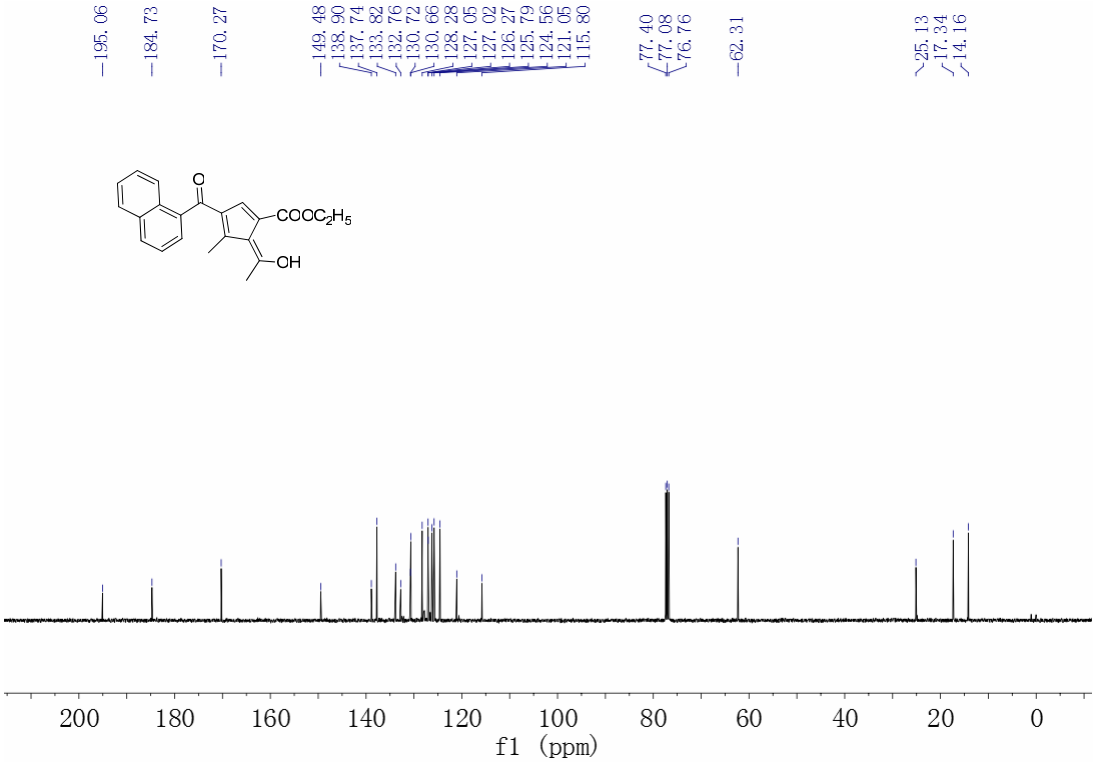

17.24
7.64
7.62
7.40
7.38
7.35
7.33
7.31
7.30
7.28
7.25
4.36
4.34
4.33
4.31
2.82
2.66
1.36
1.34
1.32
Br
O
COOC2H5
OH
0.85
0.96
1.02
1.85
0.87
2.00
2.83
2.88
2.98
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

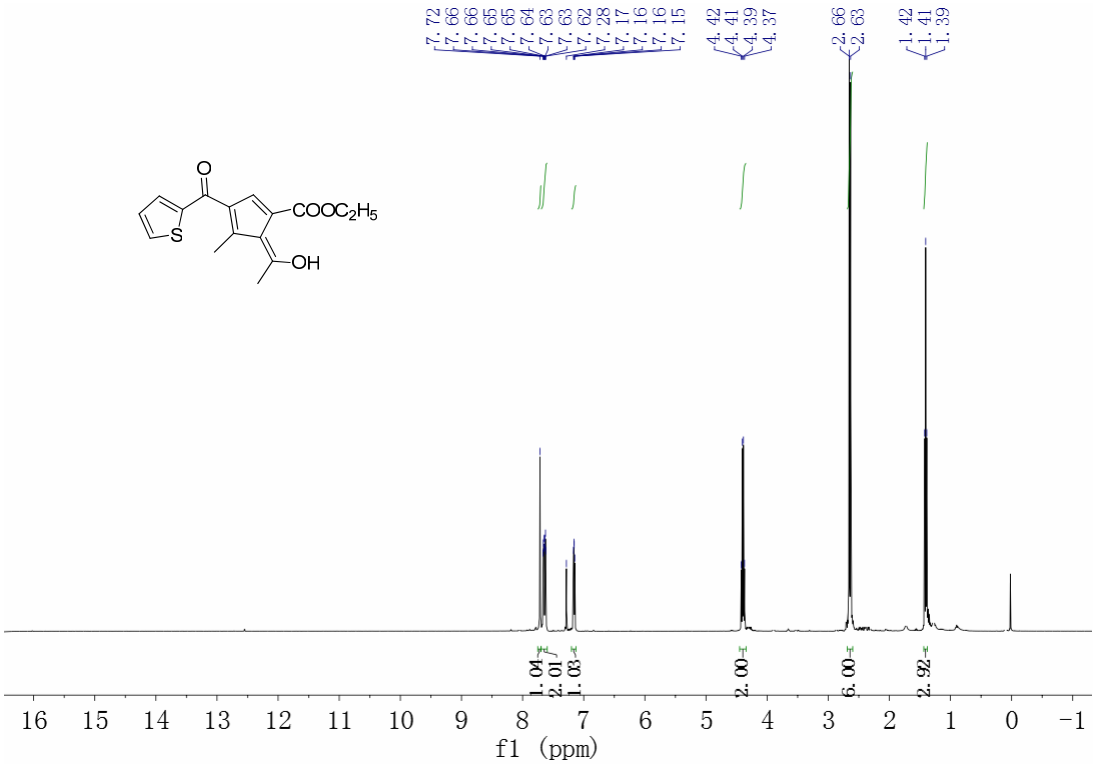

192.68
185.65
170.29
150.35
142.95
137.35
133.14
130.56
130.35
128.63
127.22
121.33
119.30
116.01
77.40
77.08
76.77
62.45
25.34
25.33
17.21
14.21
Br
O
COOC2H5
OH
40 200 160 120 80 50 20 -10
f1 (ppm)

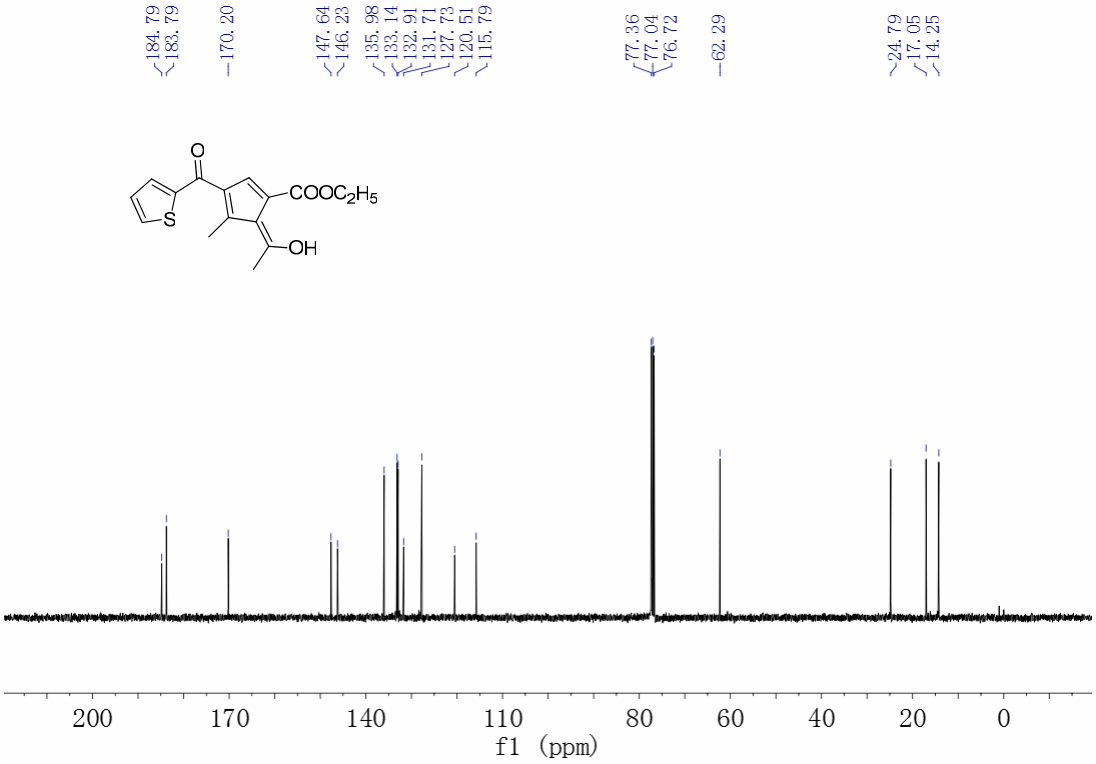

7.92
7.90
7.73
7.71
7.70
7.69
7.67
7.57
7.52
7.50
7.48
7.44
7.42
7.28
4.41
4.39
4.37
4.36
2.70
2.66
1.40
1.38
1.37
O
COOC2H5
OH
2.00
4.26
0.94
2.08
1.07
1.93
5.79
3.10
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

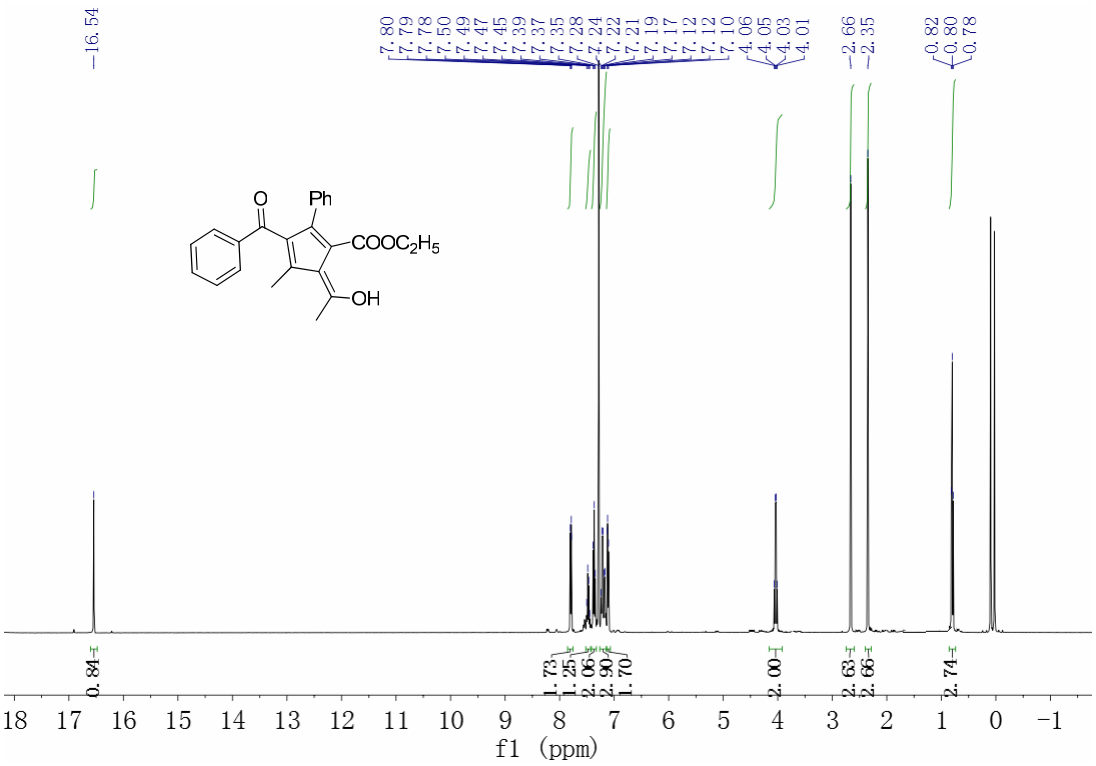

193.16
183.64
170.23
148.28
144.64
140.13
138.61
137.00
131.94
130.15
128.93
128.04
127.25
126.89
120.59
115.73
77.39
77.07
76.75
62.28
24.85
17.34
14.25
O
COOC2H5
OH
200 170 140 110 80 60 40 20 0
f1 (ppm)

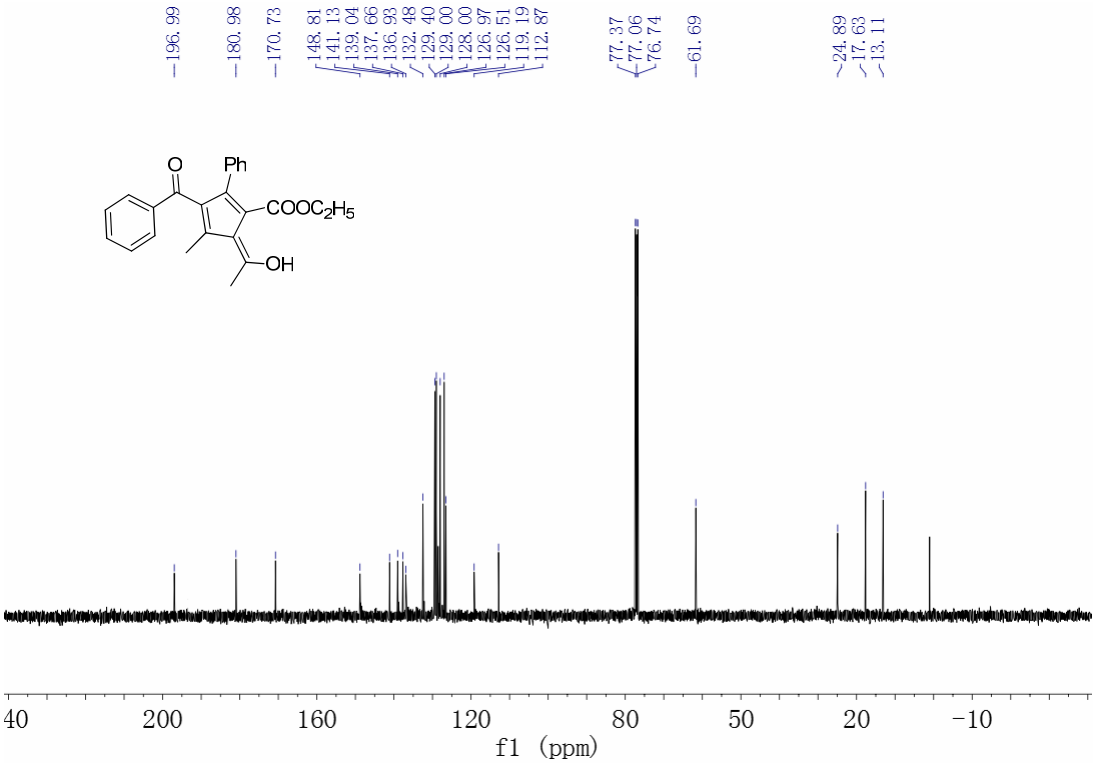

8.29
8.26
8.24
8.24
8.23
7.99
7.97
7.95
7.95
7.94
7.93
7.93
7.92
7.92
7.61
7.61
7.59
7.59
7.58
7.57
7.55
7.55
7.54
7.53
7.53
7.52
7.50
7.37
7.28
4.33
4.31
4.29
4.27
2.80
2.67
1.31
1.29
1.28
O
COOC2H5
OH
1.03
1.09
1.33
1.29
3.09
0.92
2.00
2.98
3.14
3.92
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

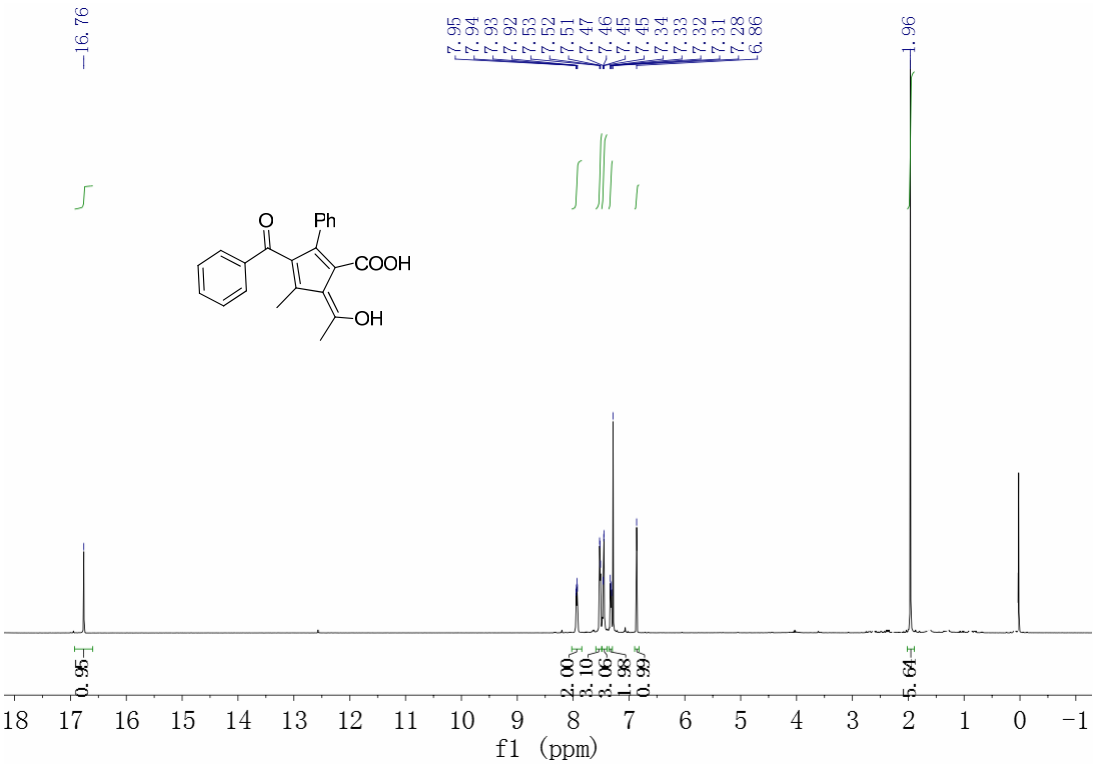

195.06
184.73
170.27
149.48
138.90
137.74
133.82
132.76
130.72
130.66
128.28
127.05
127.02
126.27
125.79
124.56
121.05
115.80
77.40
77.08
76.76
62.31
25.13
17.34
14.16
O
COOC2H5
OH
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

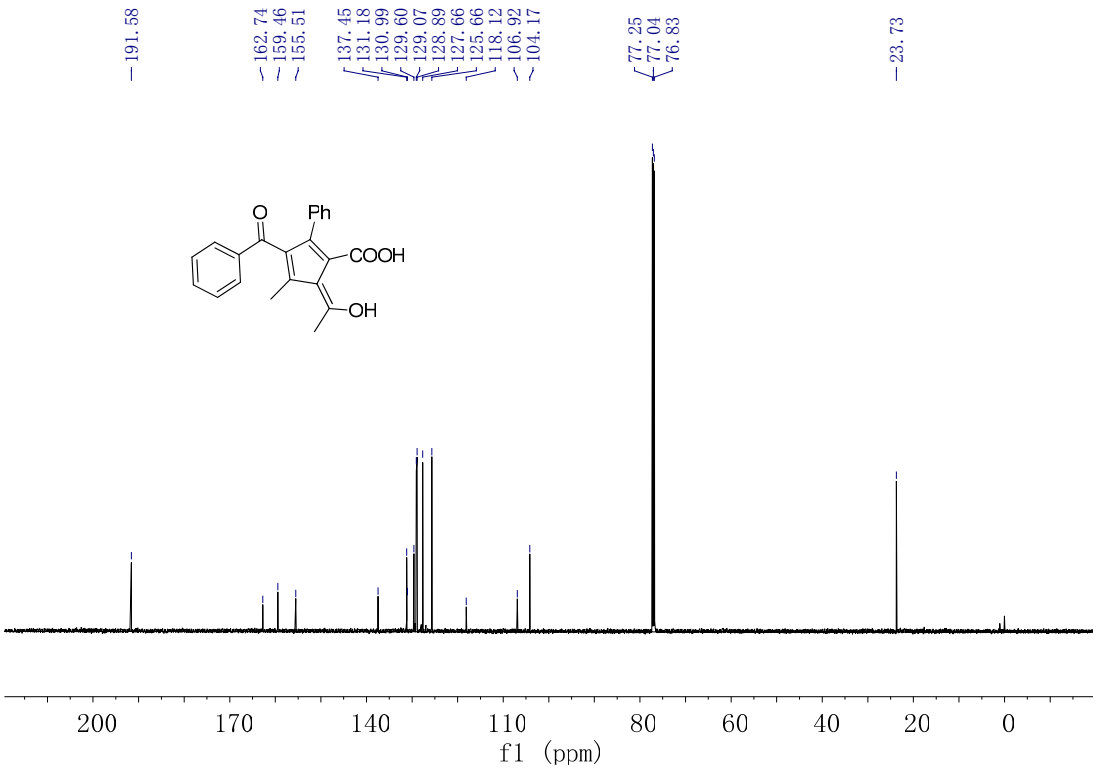

7.72
7.66
7.66
7.65
7.65
7.64
7.63
7.63
7.62
7.28
7.17
7.16
7.15
4.42
4.41
4.39
4.37
2.66
2.63
1.42
1.41
1.39
O
S
COOC2H5
OH
1.04
2.01
1.03
2.00
6.00
2.92
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

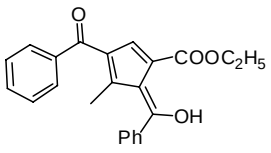

184.79
183.79
170.20
147.64
146.23
135.98
133.14
132.91
131.71
127.73
120.51
115.79
77.36
77.04
76.72
62.29
24.79
17.05
14.25
O
S
COOC2H5
OH
200 170 140 110 80 60 40 20 0
f1 (ppm)

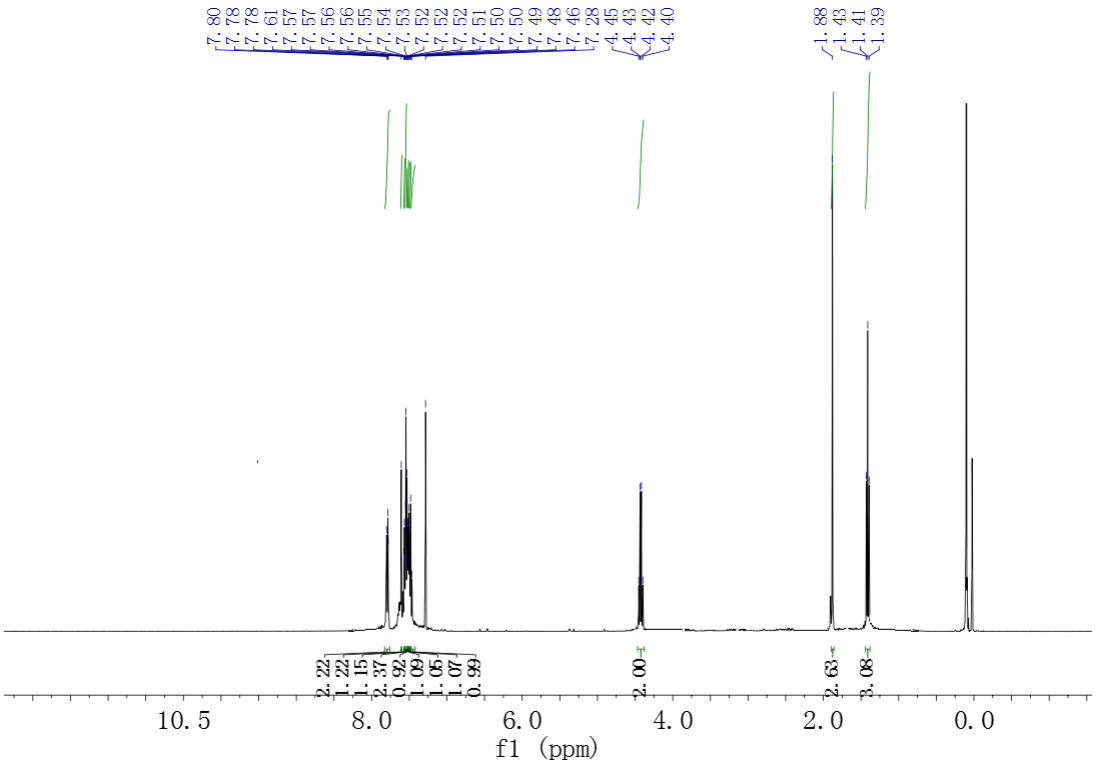

16.54
7.80
7.79
7.78
7.50
7.49
7.47
7.45
7.39
7.37
7.35
7.28
7.24
7.22
7.21
7.19
7.17
7.12
7.12
7.10
4.06
4.05
4.03
4.01
2.66
2.35
0.82
0.80
0.78
O
Ph
COOC2H5
OH
0.84
1.73
1.25
2.06
2.90
1.70
2.00
2.63
2.66
2.74
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

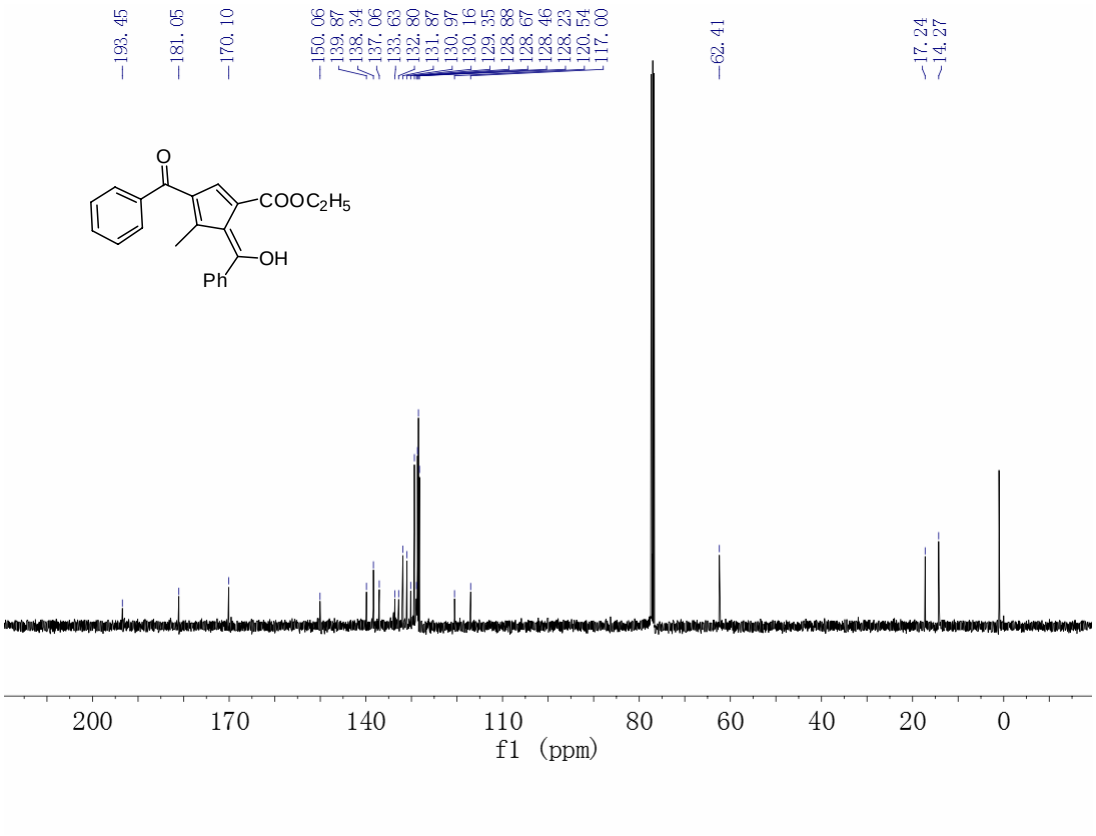

196.99
180.98
170.73
148.81
141.13
139.04
137.66
136.93
132.48
129.40
129.00
128.00
126.97
126.51
119.19
112.87
77.37
77.06
76.74
61.69
24.89
17.63
13.11
O
Ph
COOC2H5
OH
40 200 160 120 80 50 20 −10
f1 (ppm)

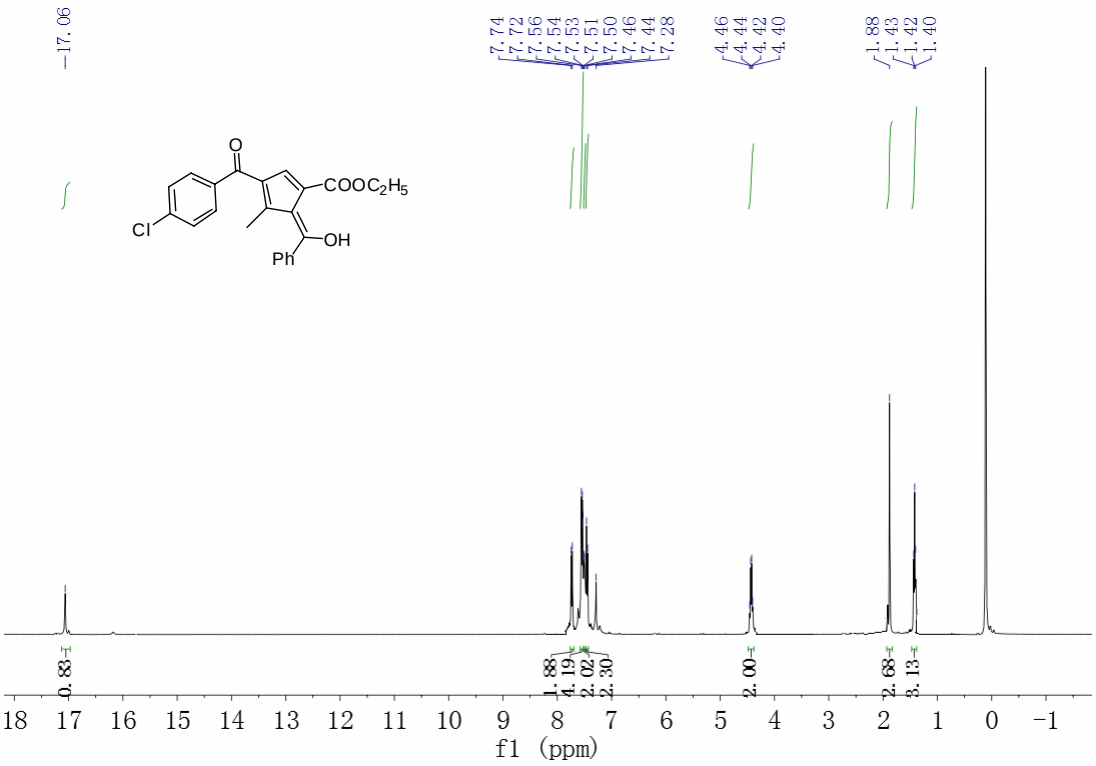

16.76
7.95
7.94
7.93
7.92
7.53
7.52
7.51
7.47
7.46
7.45
7.45
7.34
7.33
7.32
7.31
7.28
6.86
1.96
O
Ph
COOH
OH
0.95
2.00
3.10
3.06
1.98
0.99
5.64
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

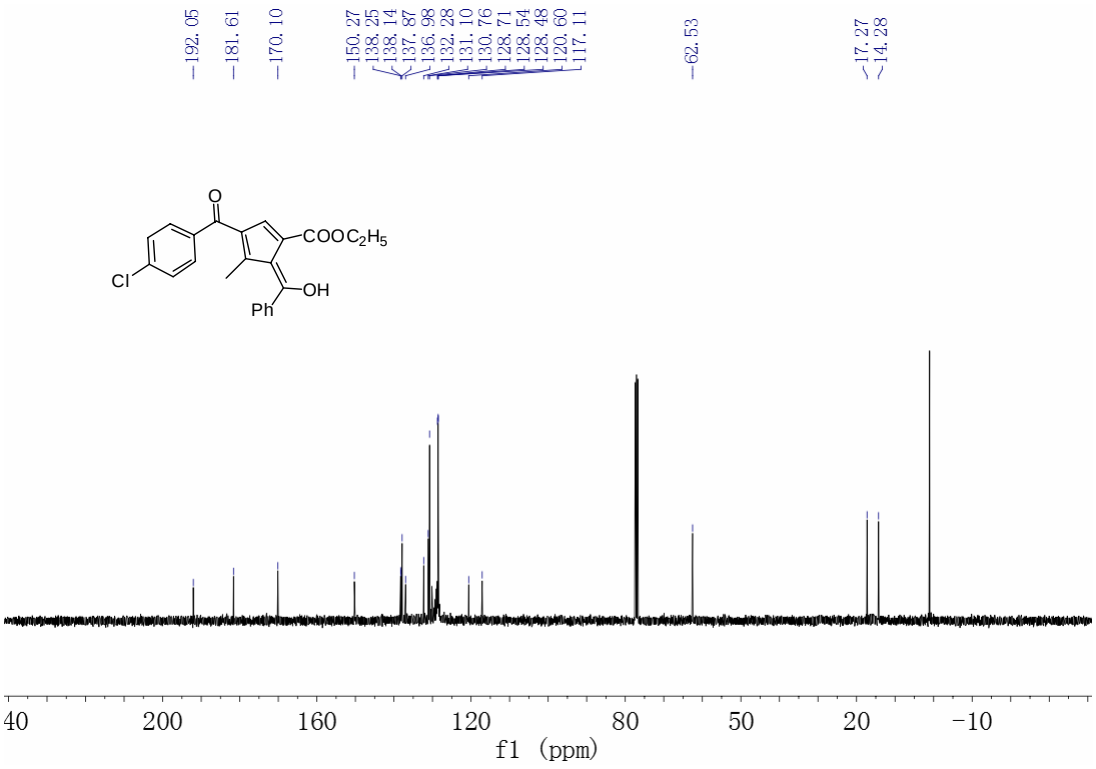

191.58
162.74
159.46
155.51
137.45
131.18
130.99
129.60
129.07
128.89
127.66
125.66
118.12
106.92
104.17
77.25
77.04
76.83
23.73
O
Ph
COOH
OH
200 170 140 110 80 60 40 20 0
f1 (ppm)

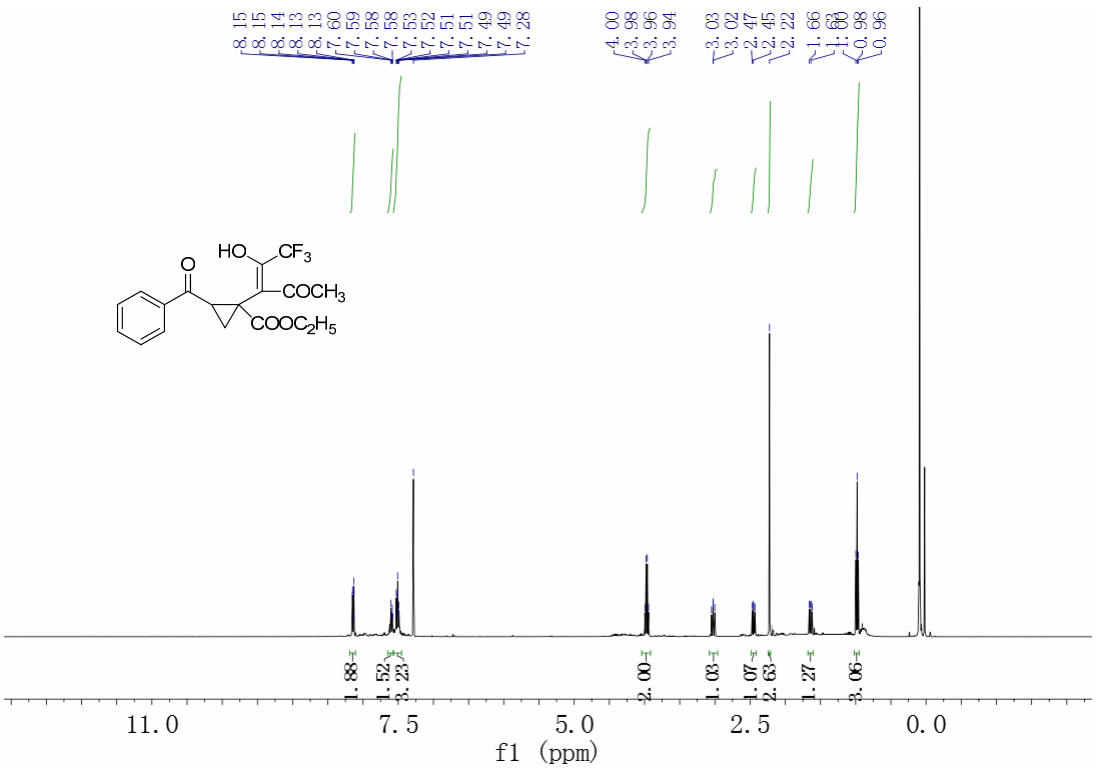

O
COOC2H5
OH
Ph

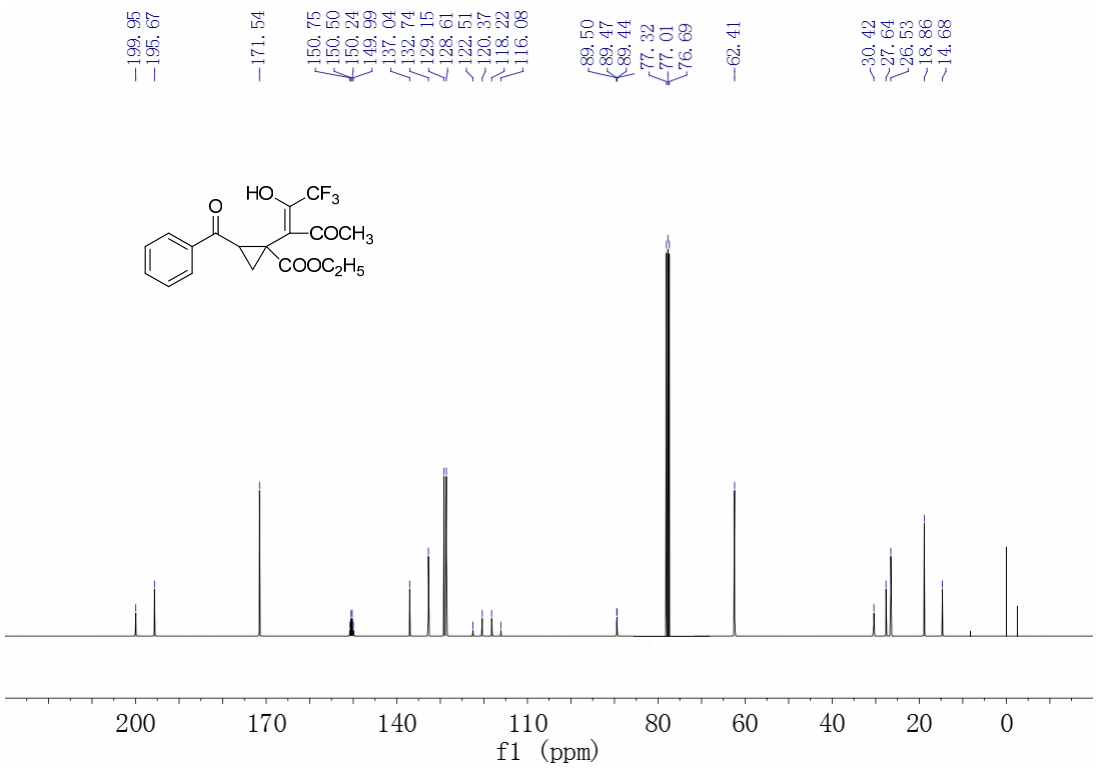

7.80
7.78
7.78
7.61
7.57
7.57
7.56
7.56
7.55
7.54
7.53
7.52
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.46
7.28
4.45
4.43
4.42
4.40
1.88
1.43
1.41
1.39
2.22
1.22
1.15
2.37
0.92
1.09
1.05
1.07
0.99
2.00
2.63
3.08
10.5
8.0
6.0
4.0
2.0
0.0
f1 (ppm)

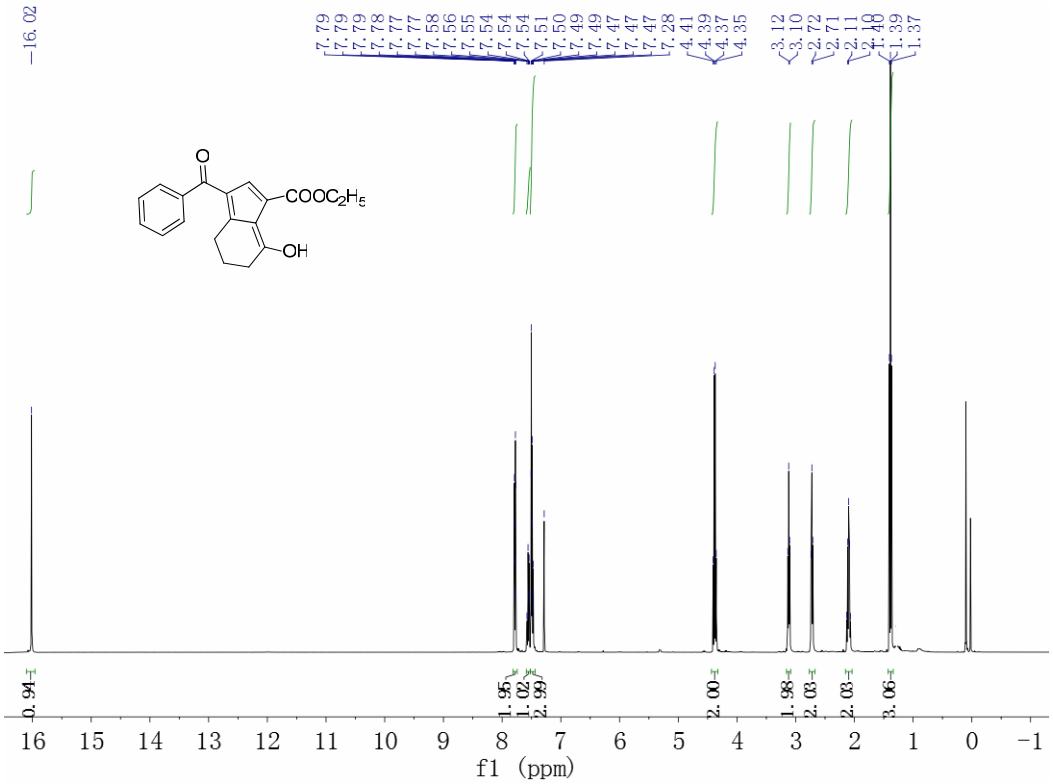

193.45
181.05
170.10
150.06
139.87
138.34
137.06
133.63
132.80
131.87
130.97
130.16
129.35
128.88
128.67
128.46
128.23
120.54
117.00
62.41
17.24
14.27
O
COOC2H5
OH
Ph
200
170
140
110
80
60
40
20
0
f1 (ppm)

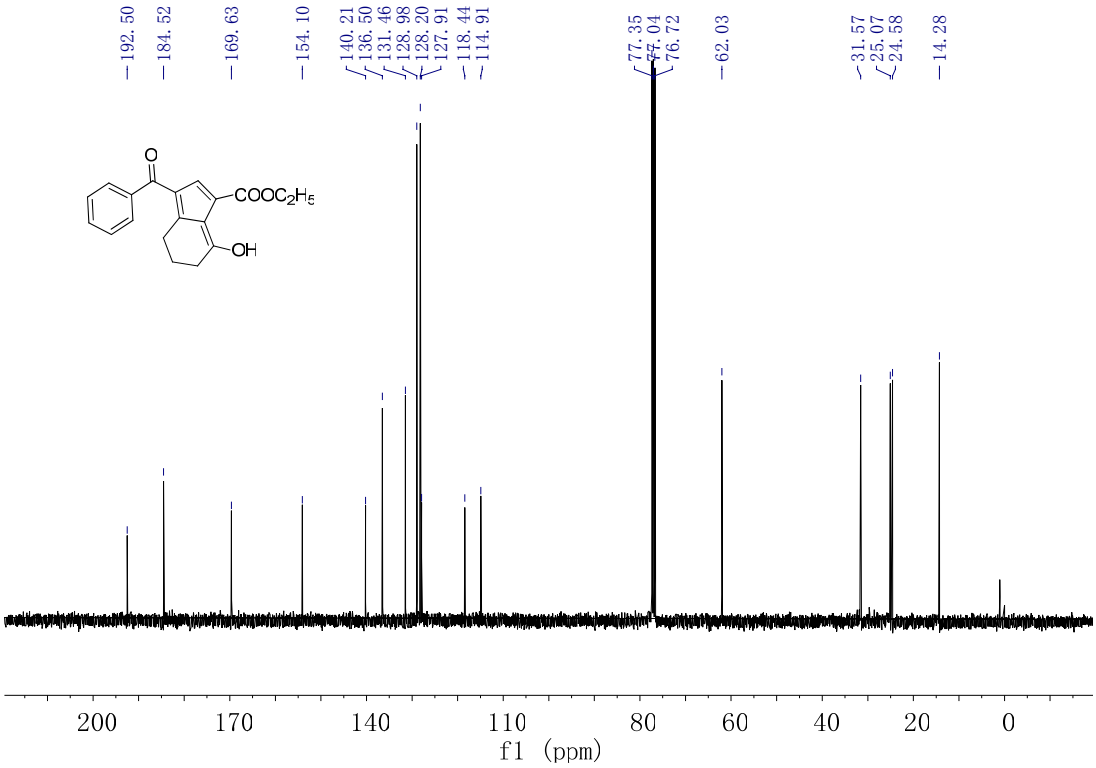

17.06
7.74
7.72
7.56
7.54
7.53
7.51
7.50
7.46
7.44
7.28
4.46
4.44
4.42
4.40
1.88
1.43
1.42
1.40
O
COOC2H5
Cl
OH
Ph
0.83
1.88
4.19
2.02
2.30
2.00
2.68
3.13
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

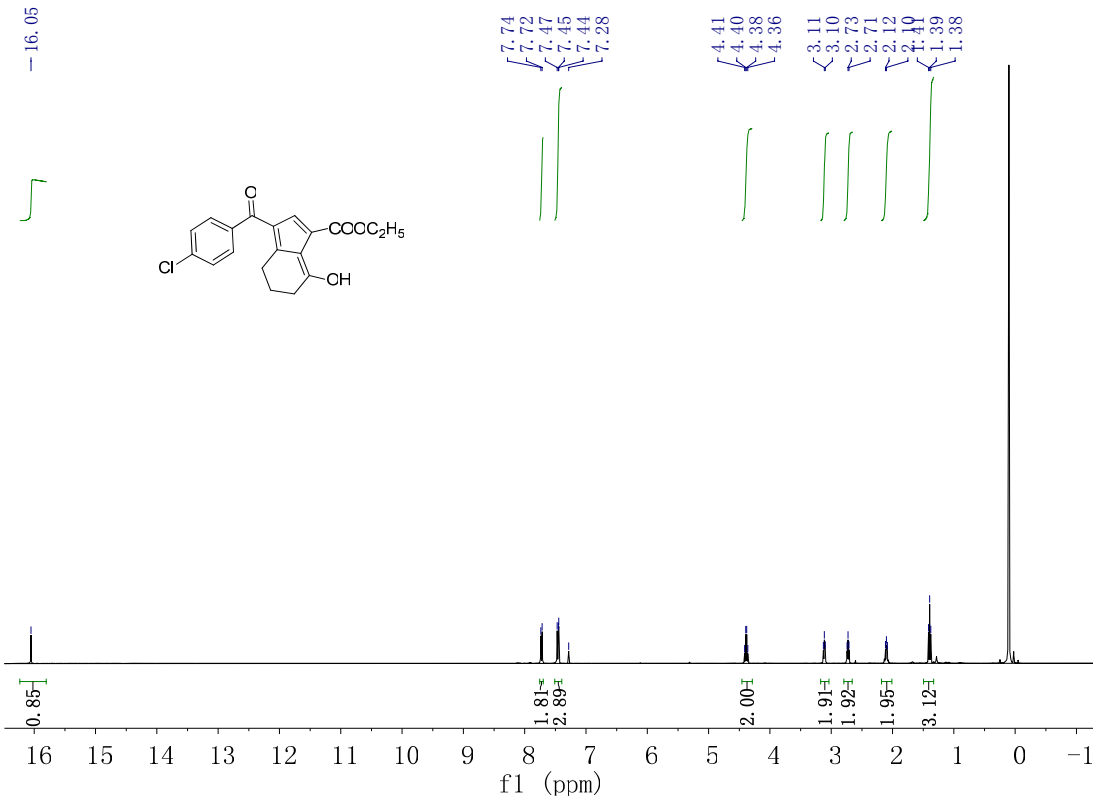

192.05
181.61
170.10
150.27
138.25
138.14
137.87
136.98
132.28
131.10
130.76
128.71
128.54
128.48
120.60
117.11
62.53
17.27
14.28
O
COOC2H5
Cl
OH
Ph
40 200 160 120 80 50 20 -10
f1 (ppm)

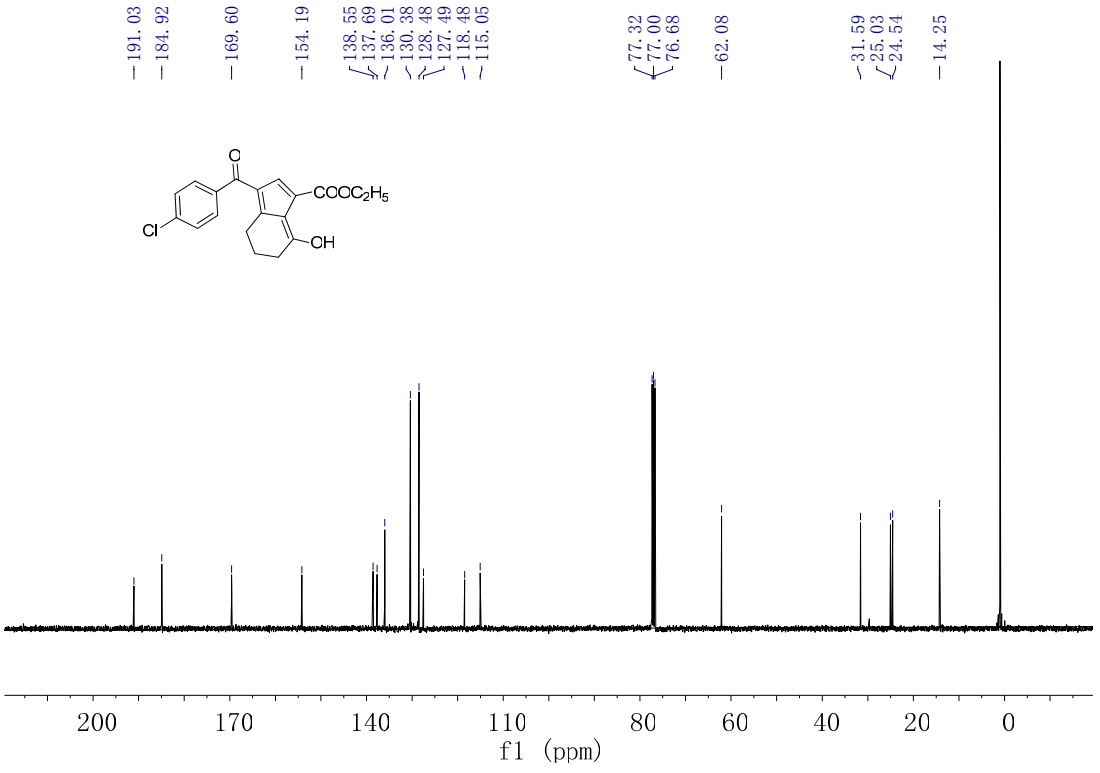

8.15
8.15
8.14
8.13
8.13
7.60
7.59
7.58
7.58
7.53
7.52
7.51
7.51
7.49
7.49
7.28
4.00
3.98
3.96
3.94
3.03
3.02
2.47
2.45
2.22
1.66
1.63
1.60
0.98
0.96
HO
CF3
O
COCH3
COOC2H5
1.88
1.52
3.23
2.00
1.03
1.07
2.63
1.27
3.06
11.0
7.5
5.0
2.5
0.0
f1 (ppm)

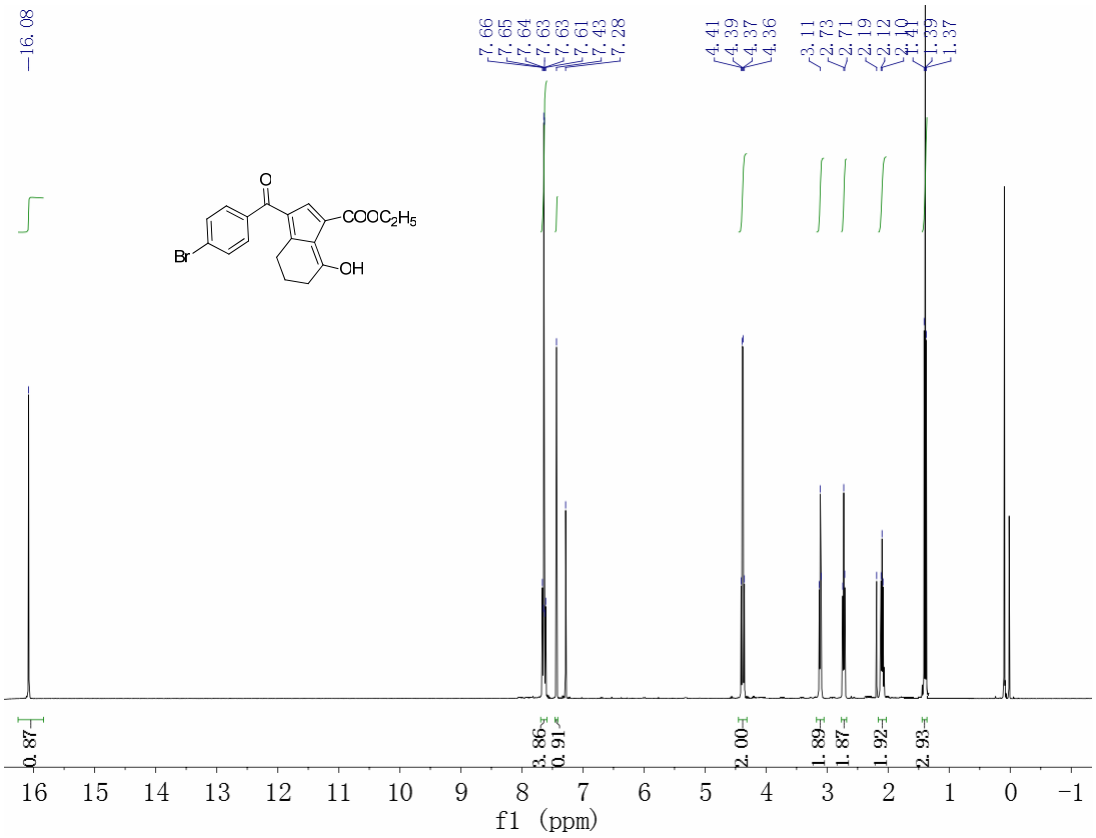

199.95
195.67
171.54
150.75
150.50
150.24
149.99
137.04
132.74
129.15
128.61
122.51
120.37
118.22
116.08
89.50
89.47
89.44
77.32
77.01
76.69
62.41
30.42
27.64
26.53
18.86
14.68
HO
CF3
O
COCH3
COOC2H5
200
170
140
110
80
60
40
20
0
f1 (ppm)

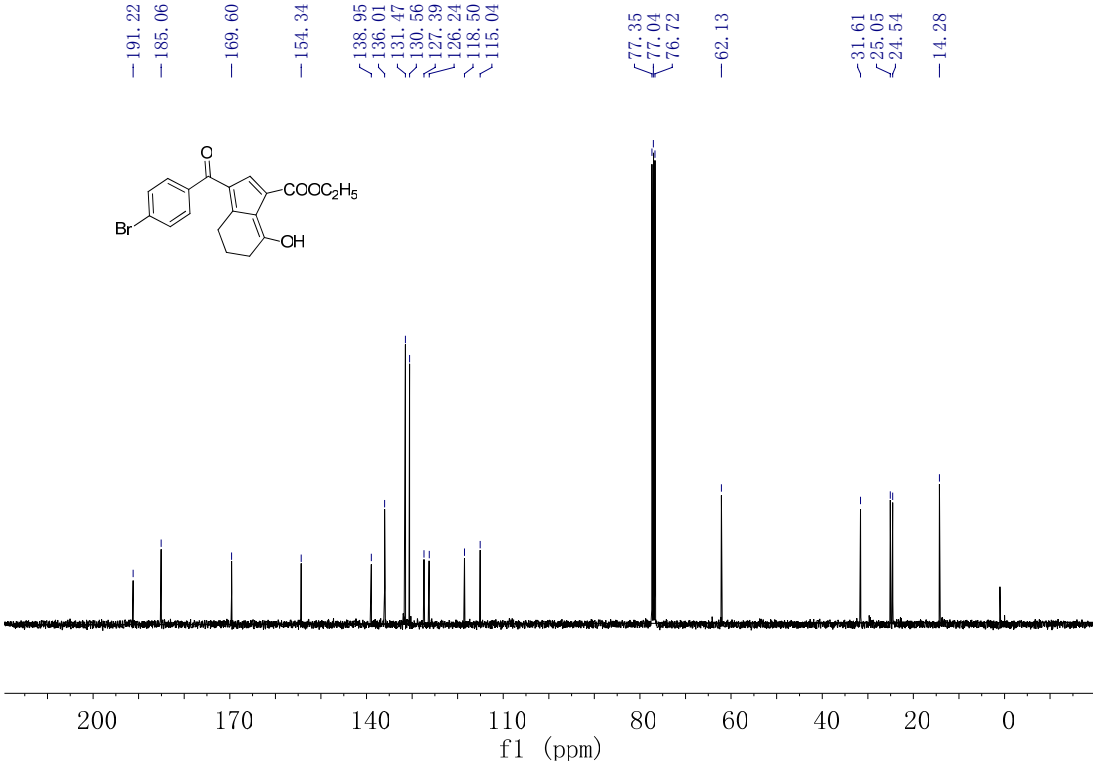

16.02
7.79
7.79
7.79
7.78
7.77
7.77
7.58
7.56
7.55
7.54
7.54
7.54
7.51
7.50
7.49
7.49
7.47
7.47
7.47
7.28
4.41
4.39
4.37
4.35
3.12
3.10
2.72
2.71
2.11
1.39
1.37
O
COOC2H5
OH
0.94
1.95
1.02
2.99
2.00
1.98
2.03
2.03
3.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

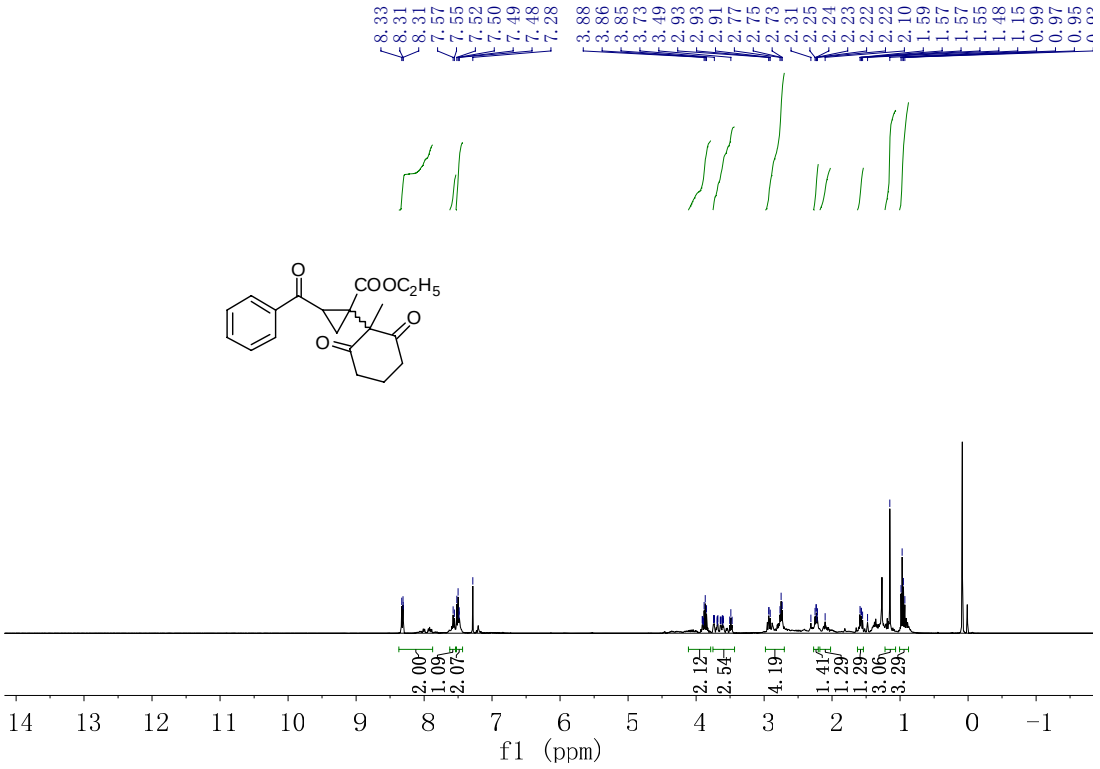

192.50
184.52
169.63
154.10
140.21
136.50
131.46
128.98
128.20
127.91
118.44
114.91
77.35
77.04
76.72
62.03
31.57
25.07
24.58
14.28
O
COOC2H5
OH
200 170 140 110 80 60 40 20 0
f1 (ppm)

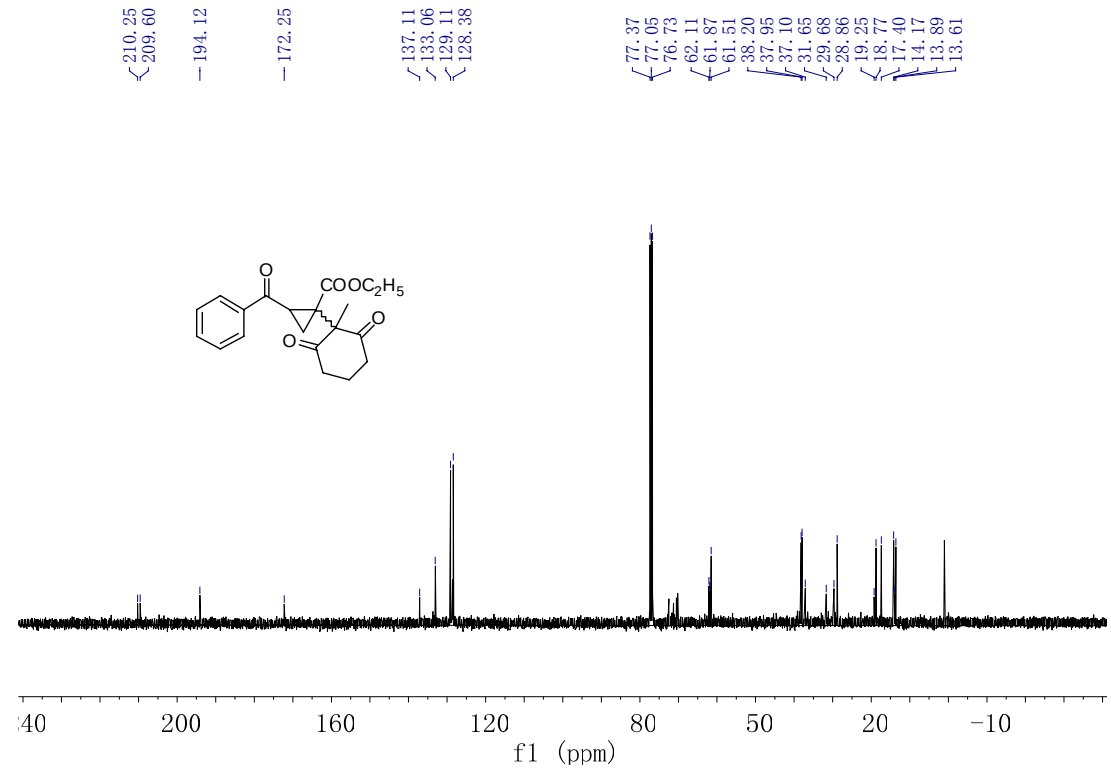

16.05
7.74
7.72
7.47
7.45
7.44
7.28
4.41
4.40
4.38
4.36
3.11
3.10
2.73
2.71
2.12
2.10
1.41
1.39
1.38
O
CCOC2H5
Cl
OH
0.85
1.81
2.89
2.00
1.91
1.92
1.95
3.12
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

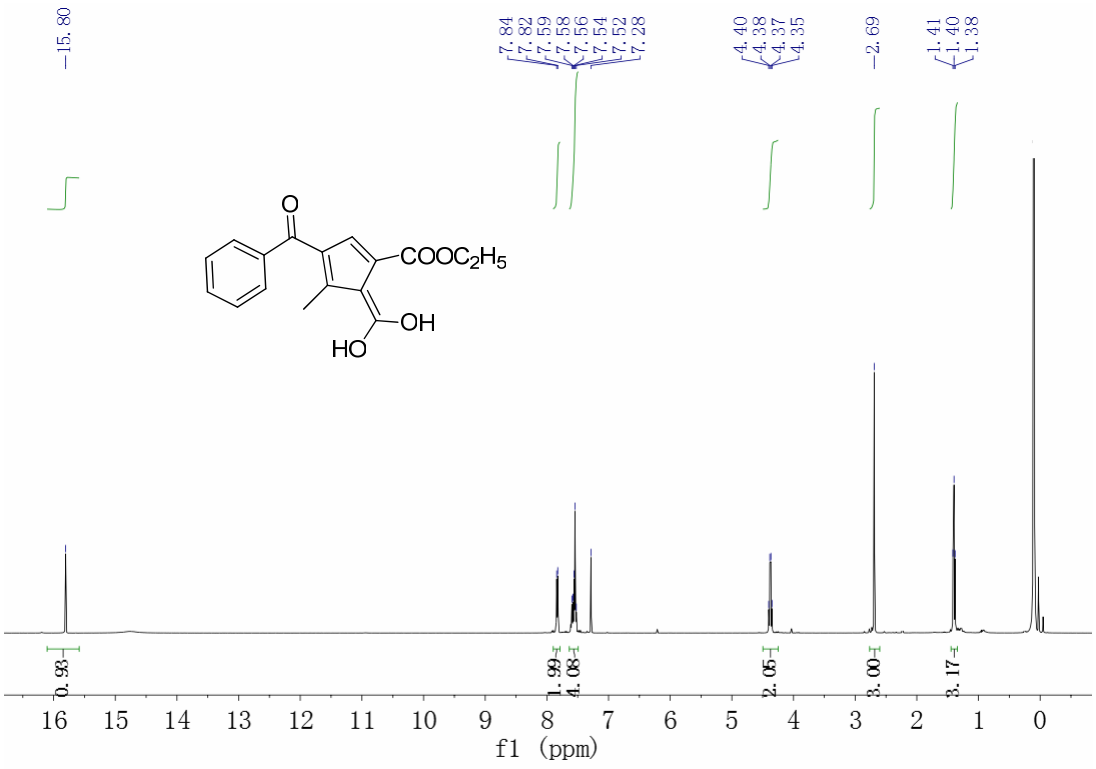

191.03
184.92
169.60
154.19
138.55
137.69
136.01
130.38
128.48
127.49
118.48
115.05
77.32
77.00
76.68
62.08
31.59
25.03
24.54
14.25
O
CCOC2H5
Cl
OH
200 170 140 110 80 60 40 20 0
f1 (ppm)

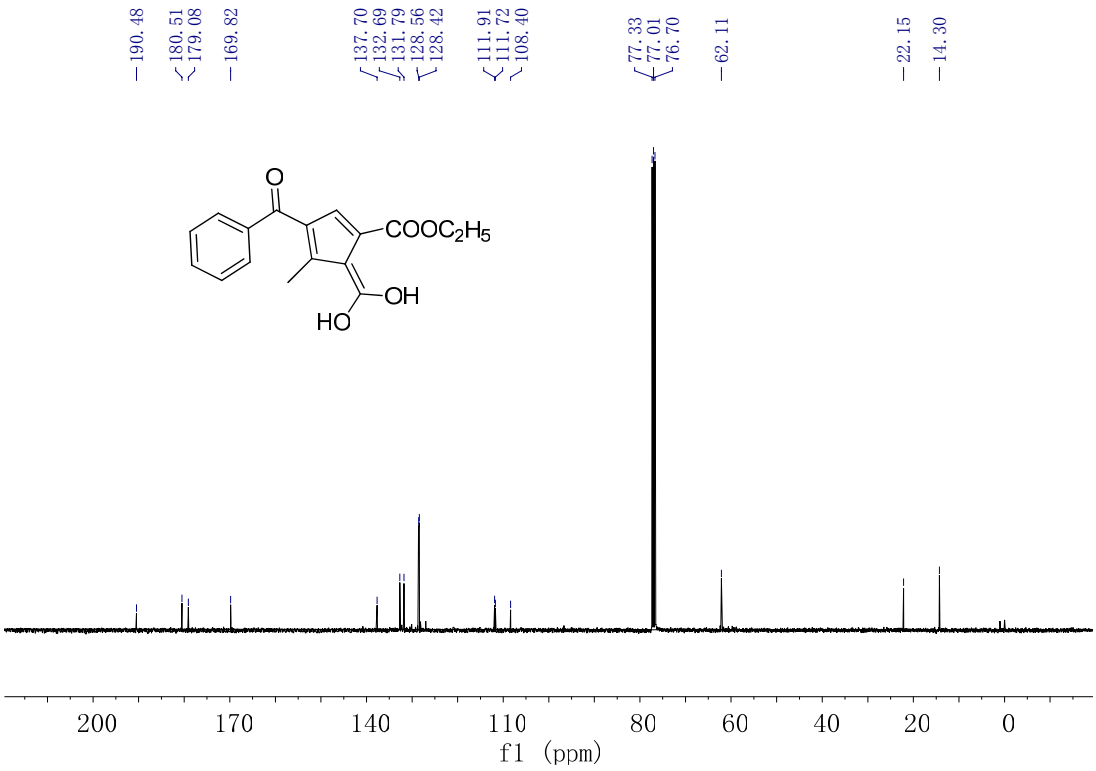

16.08
7.66
7.65
7.64
7.63
7.63
7.61
7.43
7.28
4.41
4.39
4.37
4.36
3.11
2.73
2.71
2.19
2.12
2.10
1.41
1.39
1.37
O
COOC2H5
Br
OH
0.87
3.86
0.91
2.00
1.89
1.87
1.92
2.93
f1 (ppm)

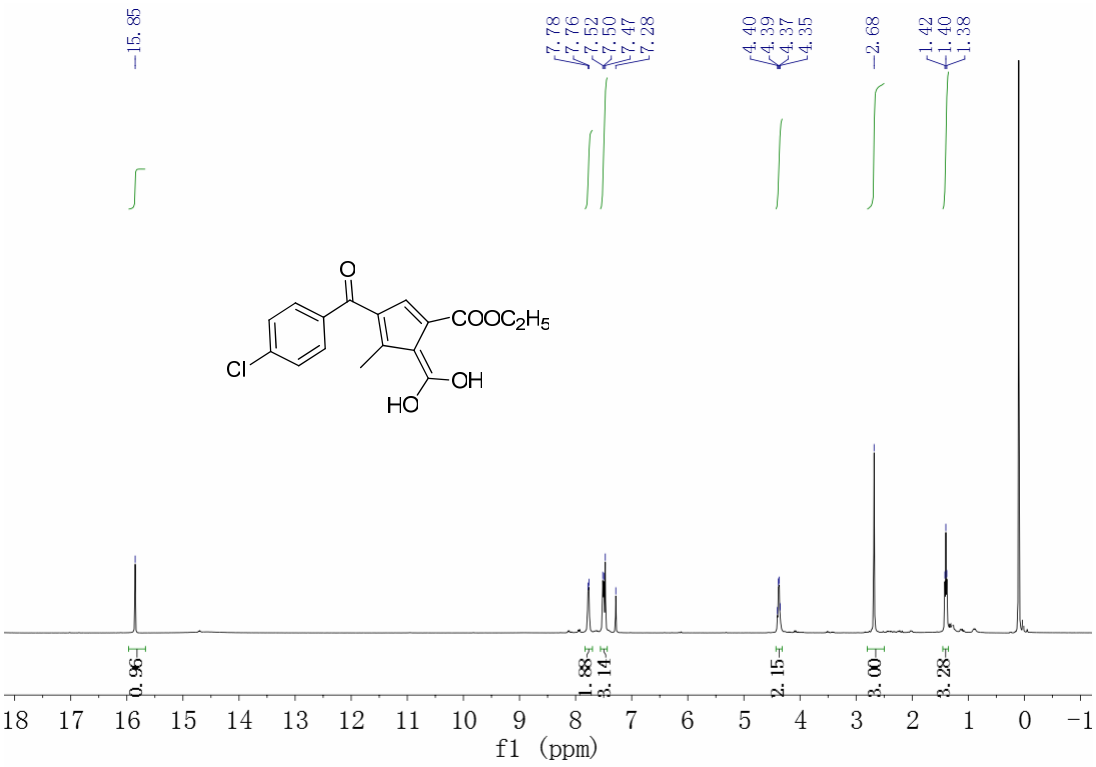

191.22
185.06
169.60
154.34
138.95
136.01
131.47
130.56
127.39
126.24
118.50
115.04
77.35
77.04
76.72
62.13
31.61
25.05
24.54
14.28
O
COOC2H5
Br
OH
f1 (ppm)

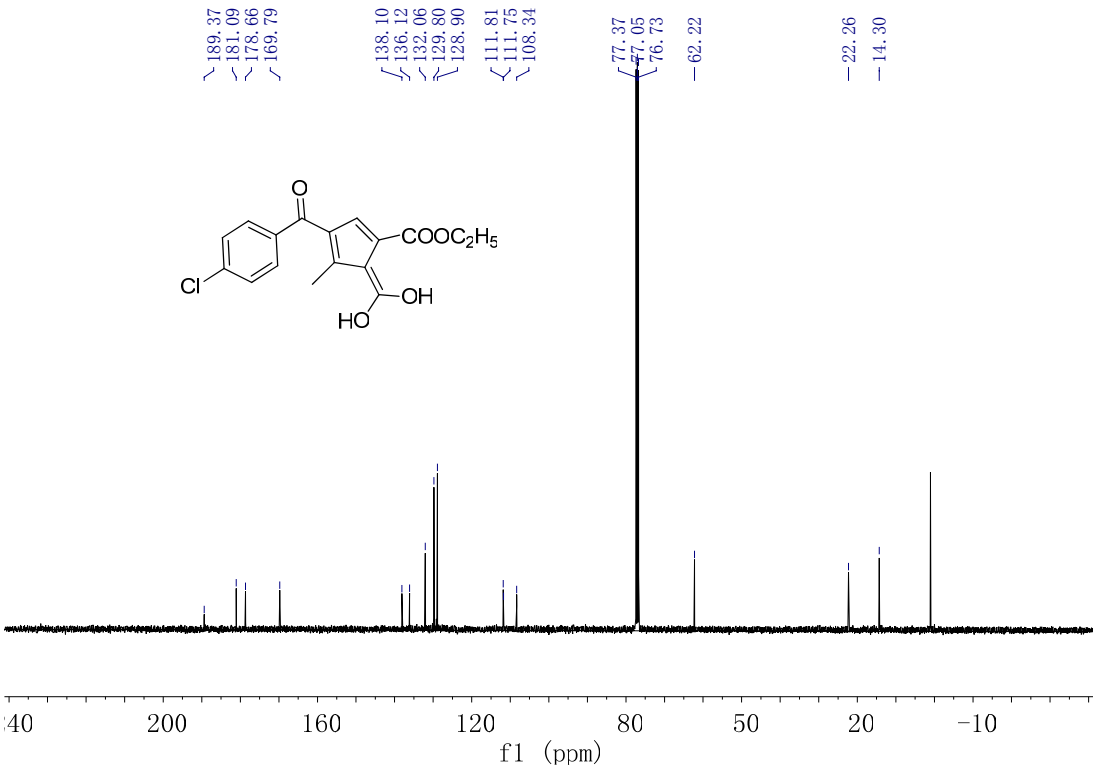

8.33
8.31
8.31
7.57
7.55
7.52
7.50
7.49
7.48
7.28
3.88
3.86
3.85
3.73
3.49
2.93
2.91
2.77
2.75
2.73
2.31
2.25
2.24
2.23
2.22
2.22
2.10
1.59
1.57
1.57
1.55
1.48
1.15
0.99
0.97
0.95
COOC2H5
O
O
O
2.00
1.09
2.07
2.12
2.54
4.19
1.41
1.29
1.29
3.06
3.29
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

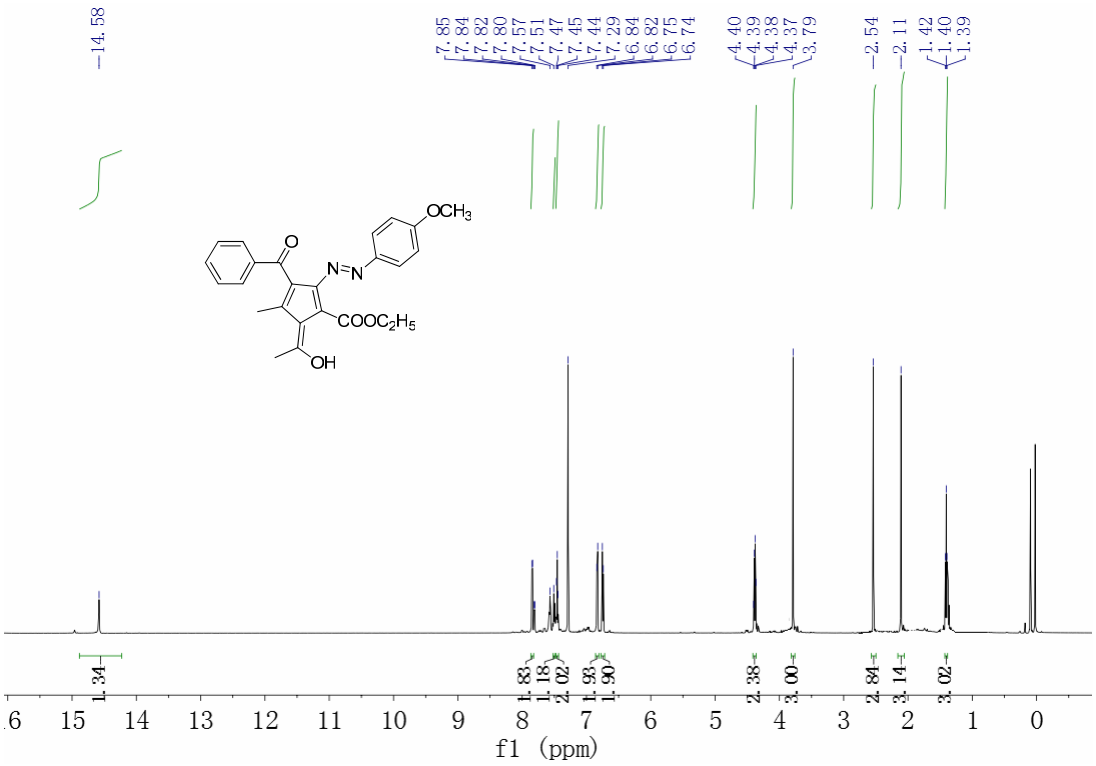

210.25
209.60
194.12
172.25
137.11
133.06
129.11
128.38
77.37
77.05
76.73
62.11
61.87
61.51
38.20
37.95
37.10
31.65
29.68
28.86
19.25
18.77
17.40
14.17
13.89
13.61
COOC2H5
O
O
O
200
160
120
80
50
20
−10
f1 (ppm)

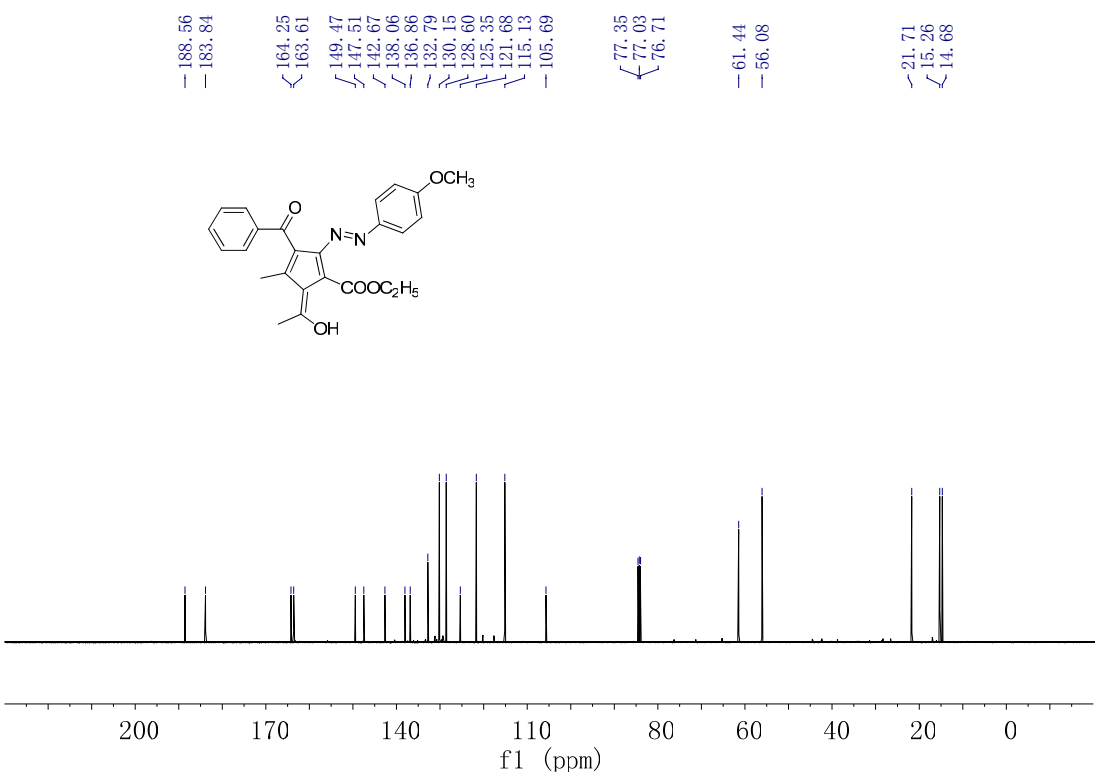

15.80
7.84
7.82
7.59
7.58
7.56
7.54
7.52
7.28
4.40
4.38
4.37
4.35
2.69
1.41
1.40
1.38
O
COOC2H5
OH
HO
0.93
1.99
4.08
2.05
3.00
3.17
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

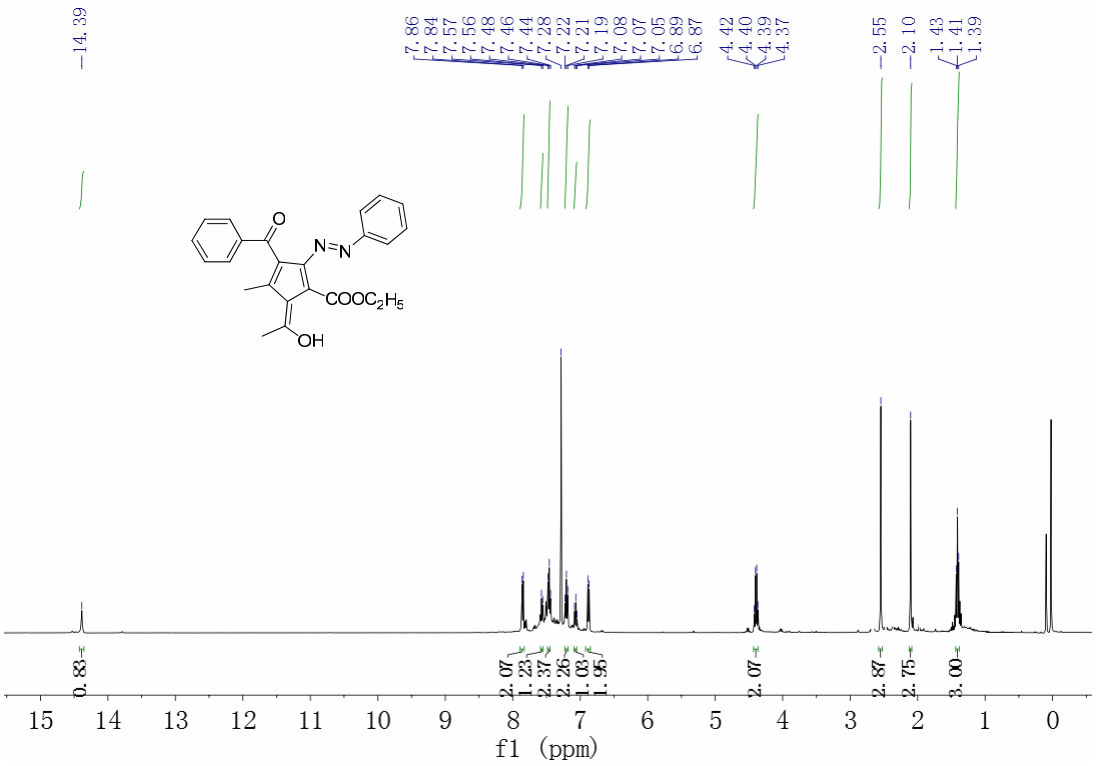

190.48
180.51
179.08
169.82
137.70
132.69
131.79
128.56
128.42
111.91
111.72
108.40
77.33
77.01
76.70
62.11
22.15
14.30
O
COOC2H5
OH
HO
200 170 140 110 80 60 40 20 0
f1 (ppm)

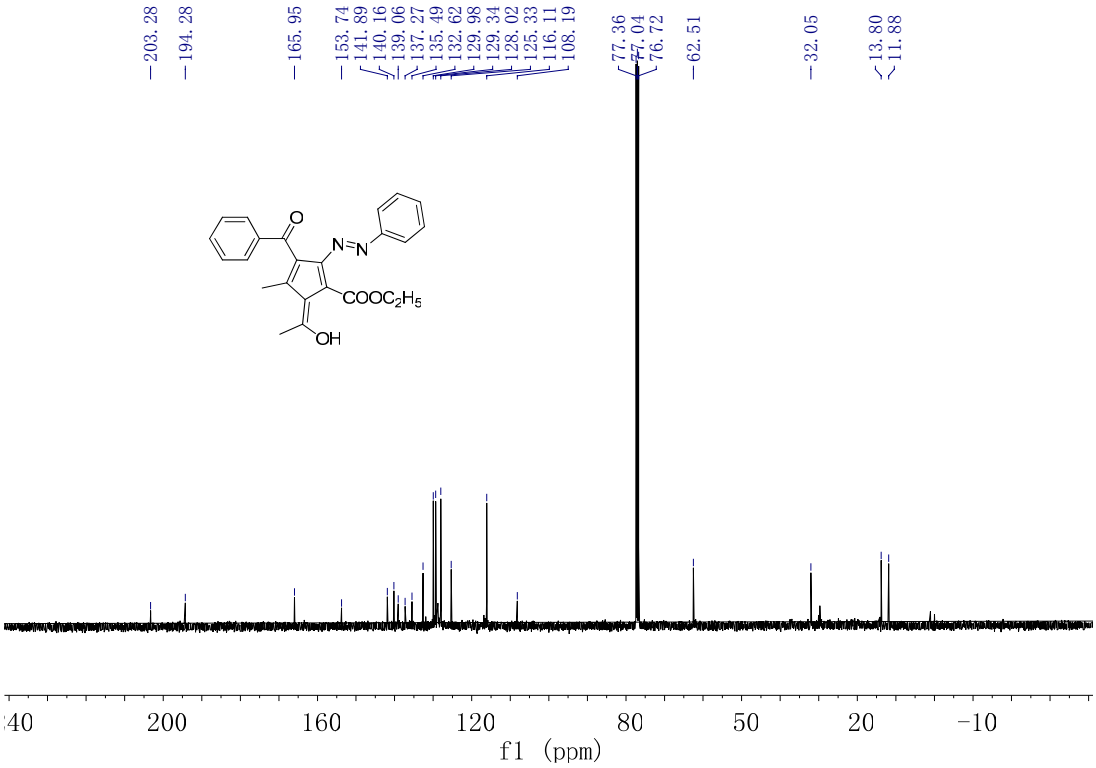

15.85
7.78
7.76
7.52
7.50
7.47
7.28
4.40
4.39
4.37
4.35
2.68
1.42
1.40
1.38
O
COOC2H5
Cl
OH
HO
0.96
1.88
3.14
2.15
3.00
3.28
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

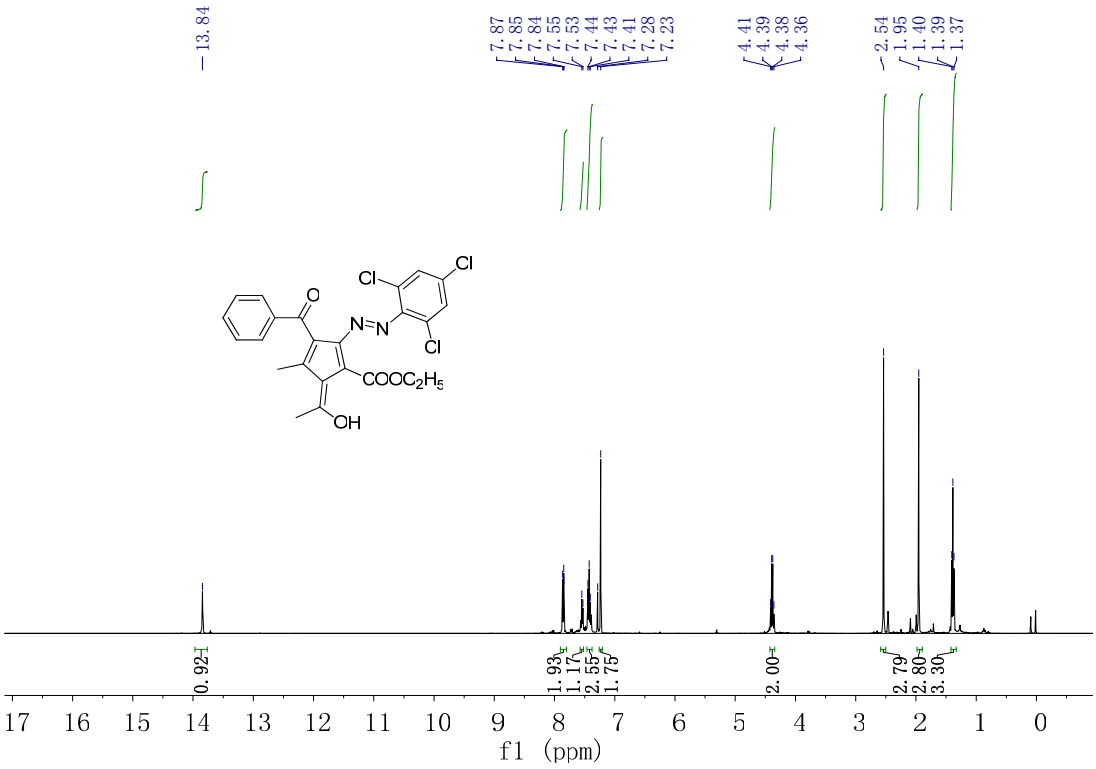

189.37
181.09
178.66
169.79
138.10
136.12
132.06
129.80
128.90
111.81
111.75
108.34
77.37
77.05
76.73
62.22
22.26
14.30
O
COOC2H5
Cl
OH
HO
40 200 160 120 80 50 20 −10
f1 (ppm)

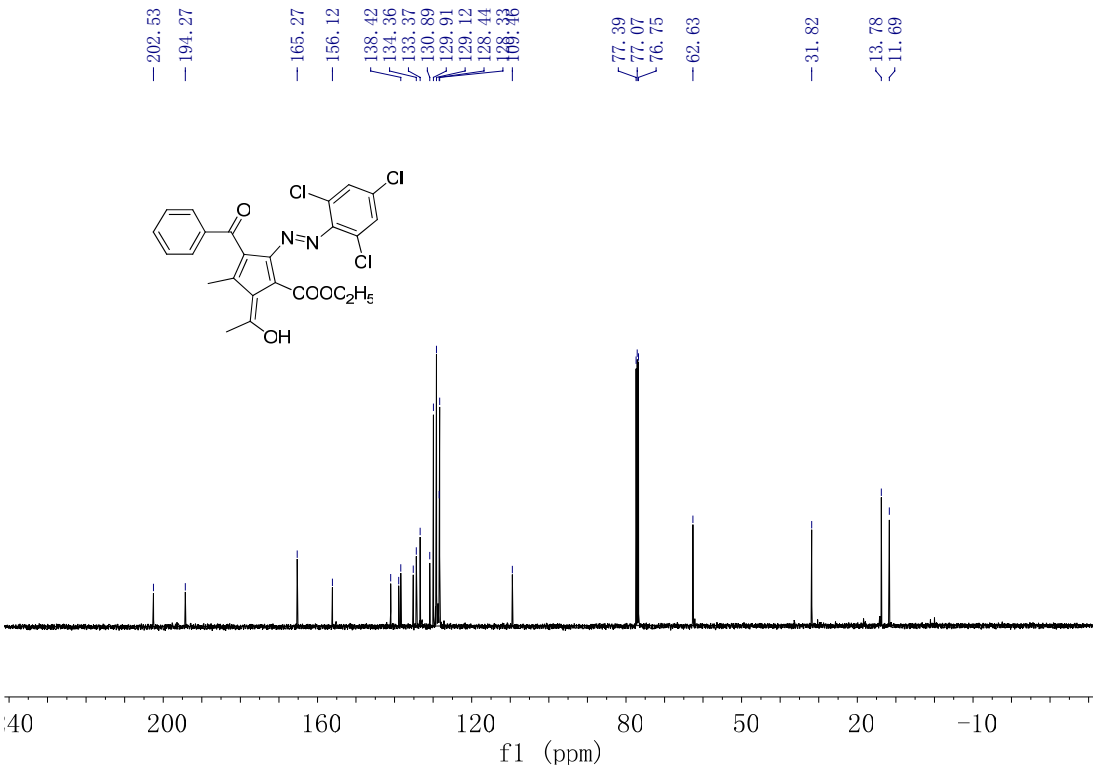

14.58
7.85
7.84
7.82
7.80
7.57
7.51
7.47
7.45
7.44
7.29
6.84
6.82
6.75
6.74
4.40
4.39
4.38
4.37
3.79
2.54
2.11
1.42
1.40
1.39
OCH3
O
N=N
COOC2H5
OH
1.34
1.83
1.18
2.02
1.93
1.90
2.38
3.00
2.84
3.14
3.02
f1 (ppm)


188.56
183.84
164.25
163.61
149.47
147.51
142.67
138.06
136.86
132.79
130.15
128.60
125.35
121.68
115.13
105.69
77.35
77.03
76.71
61.44
56.08
21.71
15.26
14.68
OCH3
O
N=N
COOC2H5
OH
f1 (ppm)


14.39
7.86
7.84
7.57
7.56
7.48
7.46
7.44
7.28
7.22
7.21
7.19
7.08
7.07
7.05
6.89
6.87
4.42
4.40
4.39
4.37
2.55
2.10
1.43
1.41
1.39
O
N=N
COOC2H5
OH
0.83
2.07
1.23
2.37
2.26
1.03
1.95
2.07
2.87
2.75
3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


203.28
194.28
165.95
153.74
141.89
140.16
139.06
137.27
135.49
132.62
129.98
129.34
128.02
125.33
116.11
108.19
77.36
77.04
76.72
62.51
32.05
13.80
11.88
O
N=N
COOC2H5
OH
40 200 160 120 80 50 20 -10
f1 (ppm)


13.84
7.87
7.85
7.84
7.55
7.53
7.44
7.43
7.41
7.28
7.23
4.41
4.39
4.38
4.36
2.54
1.95
1.40
1.39
1.37
Cl
Cl
O
N=N
Cl
COOC2H5
OH
0.92
1.93
1.17
2.55
1.75
2.00
2.79
2.80
3.30
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


202.53
194.27
165.27
156.12
138.42
134.36
133.37
130.89
129.91
129.12
128.44
77.39
77.07
76.75
62.63
31.82
13.78
11.69
Cl
Cl
O
N=N
Cl
COOC2H5
OH
40 200 160 120 80 50 20 -10
f1 (ppm)

X-ray structure of compound 3aa: