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Supporting Information

DABCO Catalyzed Unusual Formal [4+2] Cycloaddition of 3-acyl (or alkoxycarbonyl)-1,4-enediones with 2,3-butadienoates: An Effective Access to Construct Highly Functionalized Pyrans

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1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel, and reactions were monitored by thin layer chromatography (TLC). Melting points were determined with a WRS-1B digital melting point apparatus, and the thermometer was uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury PLUS 400 or a Varian Mercury PLUS 600 spectrometer in $CDCl_3$ or DMSO-d_6. Chemical shifts (δ) are reported in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, and m = multiplet), and coupling constants, *J*, are reported in hertz. ^{13}C NMR chemical shifts are reported in ppm from $CDCl_3$ (taken as 77.0 ppm). Mass spectra were measured on a Finnigan TRACEMS 2000 (EI-MS) spectrometer. Elementary analysis was taken on a Vario EL III elementary analysis instrument.

3-Acyl(or alkoxycarbonyl)-1,4-enediones **1** were prepared according to the literature [1], and 2,3-butadienoates **2** were synthesized according to the reported method.[2]

References

[1] Gao, M.; Yang, Y.; Wu, Y. D.; Deng, C.; Cao, L. P.; Meng, X. G.; Wu, A. X. *Org. Lett.* **2010,** *12*, 1856-1859.

[2] (a) Anderson, J. C.; Cubbon, R. j.; Harling, J. D. *Tetrahedron: Asymmetry*, **2001**, *12*, 923; (b) Jansch, H.; Kannenberg, S.; Boche, G. *Eur. J. Org. Chem*., **2001**, 2923.

2. Optimization study

Table 1 Reaction conditions screening[a]

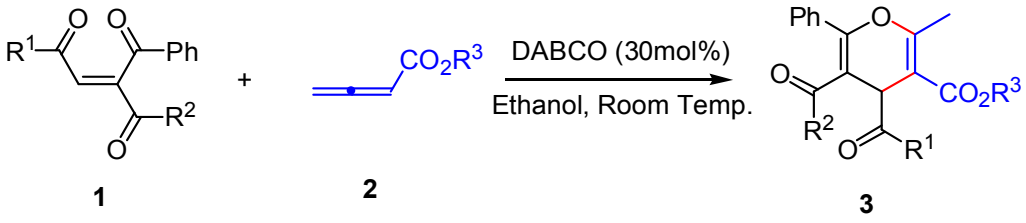
Entry	Catalyst (mol%)	Solvent	Temp(°C)	Time(h)	Yield[b](%)
1	DABCO (20)	toluene	Room Temp.	24	57
2	DMAP (20)	toluene	Room Temp.	24	trace
3	DBU (20)	toluene	Room Temp.	24	trace
4	TMEDA (20)	toluene	Room Temp.	24	40
5	Et_3N (20)	toluene	Room Temp.	24	35
6	Ph_3P (20)	toluene	Room Temp.	36	trace
7	*n*-Bu_3P (20)	toluene	Room Temp.	24	trace
8	Me_3P (20)	toluene	Room Temp.	24	trace
9	DABCO (20)	CH_2Cl_2	Room Temp.	24	50
10	DABCO (20)	CH_3CN	Room Temp.	24	73
11	DABCO (20)	THF	Room Temp.	24	60
12	DABCO (20)	C_2H_5OH	Room Temp.	12	87
13	DABCO (20)	DMF	Room Temp.	24	63
14	DABCO (20)	DMSO	Room Temp.	24	71
15	DABCO (20)	C_2H_5OH	-5	40	75
16	DABCO (20)	C_2H_5OH	0	36	85
17	DABCO (20)	C_2H_5OH	40	12	79
18	DABCO (20)	C_2H_5OH	50	12	81
19	DABCO (30)	C_2H_5OH	Room Temp.	10	90

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), catalyst in solvent (4.0 mL) , under N_2 atmosphere .

[b] Isolated yield.

3. Experimental Procedure

3.1 General procedure for the synthesis of the target compounds 3



Under a N_2 atmosphere, a mixture of 3-acyl(or alkoxycarbonyl)-1,4-enedione **1** (0.5 mmol), 2,3-butadienoate **2** (0.75 mmol), DABCO (0.15 mmol) in anhydrous ethanol (3.0 mL) was stirred at room temperature. After the reaction completed (monitored by TLC), the reaction mixture was diluted with water (5 mL) and extracted with EtOAc. The organic layers were combined, and dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified by flash column chromatography on silica gel (petroleum ether/EtOAc =15:1) to afford the corresponding **3** in 68-96% yields.

3.2 Spectral Data of Products 3

Ethyl 4,5-dibenzoyl-2-methyl-6-phenyl-4H-pyran-3-carboxylate(3a): White solid; 203 mg, yield 90%; m.p. 135.5-136.9°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, J = 7.2 Hz, 2H), 7.47 (t, J = 7.8 Hz, 3H), 7.39 (t, J = 8.0 Hz, 3H), 7.28 (s, 1H), 7.16 (d, J = 7.2 Hz, 1H), 7.01-7.12 (m, 5H), 5.68 (s, 1H), 4.01 (q, J = 7.2 Hz, 2H), 2.55 (s, 3H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ= 200.5, 196.3, 165.9, 161.9, 155.6, 137.2, 136.4, 132.9, 132.5, 132.2, 130.0, 129.2, 129.1, 129.0, 128.2, 127.8, 127.7, 112.2, 103.8, 60.5, 42.4, 18.9, 13.6; EI-MS (70 eV): m/z (%) = 452 (M^+, 1.8), 347 (100), 319 (6.3), 105 (54.7), 77 (32.6). Anal. calcd for $C_{29}H_{24}O_5$: C 76.98, H 5.35; found: C 77.14, H 5.41.

Ethyl 5-benzoyl-2-methyl-4-(4-methylbenzoyl)-6-phenyl-4H-pyran-3-carboxylate(3b): White solid; 202 mg, yield 87%; m.p. 139.8-140.5°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 7.6 Hz, 2H), 7.18 (d, J = 8.0 Hz, 3H), 7.01 – 7.11 (m, 5H), 5.67 (s, 1H), 4.03 (q, J = 7.2 Hz, 2H), 2.54 (s, 3H), 2.36 (s, 3H), 0.99 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.1, 196.5, 166.1, 161.9, 155.5, 143.8, 137.3, 133.8, 132.6, 132.2, 130.0, 129.5, 129.2, 129.1, 129.0, 127.9, 127.8, 112.4, 103.9, 60.6, 42.4, 21.7, 19.0, 13.8; EI-MS (70 eV): m/z (%) = 466 (M^+, 1.2), 349 (1.9), 348 (23.4), 347 (100), 319 (2.9), 119 (2.9), 105 (37.3). Anal. calcd for $C_{30}H_{26}O_5$: C 77.24, H 5.62; found: C 77.02, H 5.53.

Ethyl 5-benzoyl-4-(4-methoxybenzoyl)-2-methyl-6-phenyl-4H-pyran-3-carboxylate(3c): White solid; 193 mg, yield 80%; m.p. 121.2-122.9°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.24 – 7.29 (m, 2H), 7.17 (t, J = 7.6 Hz, 1H), 7.01-7.09 (m, 5H), 6.86 (d, J = 8.8 Hz, 2H), 5.66 (s, 1H), 4.04 (q, J = 7.6 Hz, 2H), 3.82 (s, 3H), 2.54 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.8, 196.6, 166.1, 163.5, 161.9, 155.3, 137.4, 132.6, 132.2, 131.7, 129.9, 129.2, 129.1, 129.0, 127.8, 127.7, 113.5, 112.5, 103.9, 60.6, 55.3, 42.2, 19.0, 13.8; EI-MS (70 eV): m/z (%) = 482 (M^+, 1.5), 349 (3.2), 348 (23.5), 347 (100), 319 (4.8), 135 (11.9), 106 (3.9), 105 (52.1). Anal. calcd for $C_{30}H_{26}O_6$: C 74.67, H 5.43; found: C 74.71, H 5.29.

Ethyl 4-([1,1'-biphenyl]-4-carbonyl)-5-benzoyl-2-methyl-6-phenyl-4H-pyran-3-carboxylate(3d): White solid; 214 mg, yield 81%; m.p. 61.8-62.7°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.16 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 7.2 Hz, 2H), 7.49 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.2 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.29 (d, J = 7.2 Hz, 2H), 7.18 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 7.06 (d, J = 7.2 Hz, 2H), 7.05 (t, J = 7.8 Hz 2H), 5.72 (s, 1H), 4.06 (q, J = 7.2 Hz, 2H), 2.57 (s, 3H), 1.00 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.3, 196.5, 166.1, 162.0, 155.9, 145.5, 140.0, 137.3, 135.2, 132.6, 132.3, 130.1, 129.9, 129.3, 129.2, 128.9, 128.1, 127.9, 127.8, 127.3, 127.0, 112.4, 104.0, 60.7, 42.5, 19.1, 13.8; EI-MS (70 eV): m/z (%) = 528.5 (M^+, 0.8), 349 (2.6), 348 (23.4), 347 (100), 319 (3.3), 152 (10.0), 105 (50.8).Anal. calcd for $C_{35}H_{28}O_5$: C 79.53, H 5.34; found: C 79.70, H 5.17.

Ethyl 5-benzoyl-4-(4-fluorobenzoyl)-2-methyl-6-phenyl-4H-pyran-3-carboxylate(3e): White solid; 223 mg, yield 95%; m.p. 141.9-142.8°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (dd, J = 8.4, 5.6 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.25 (d, J = 7.2 Hz, 2H), 7.18 (t, J = 7.2 Hz, 1H), 7.01-7.09 (m, 7H), 5.62 (s, 1H), 4.04 (q, J = 7.2 Hz, 2H), 2.55 (s, 3H), 1.00 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 199.1, 196.4, 185.5, 166.0, 165.6 ($^1J_{CF}$ = 250 Hz), 162.0, 156.0, 137.3, 132.9, 132.4 ($^2J_{CF}$ = 20 Hz), 132.0, 131.9, 130.1, 129.2 ($^4J_{CF}$ = 3.5 Hz), 127.8 ($^3J_{CF}$ = 8.0 Hz), 115.4, 115.2, 112.1, 103.8, 60.7, 42.4, 19.0, 13.8; EI-MS (70 eV): m/z (%) = 470 (M^+, 0.8), 349 (2.1), 348 (23.5), 347 (100), 319 (6.1), 123 (7.2), 106 (4.6), 105 (65.0). Anal. calcd for $C_{29}H_{23}FO_5$: C 74.03, H 4.93; found: C 73.85, H 4.78.

Ethyl 5-benzoyl-4-(2-fluorobenzoyl)-2-methyl-6-phenyl-4H-pyran-3-carboxylate (3f): White solid; 200 mg, yield 85%; m.p. 108.1-109.9°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.89 (dd, J = 7.2, 6.0 Hz, 1H), 7.50 (d, J = 7.2 Hz, 2H), 7.44 (dd, J = 12.0, 6.6 Hz, 1H), 7.26 (d, J = 7.8 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 7.15 (t, J = 7.8 Hz, 1H), 7.13 (d, J = 7.2 Hz, 1H), 7.04-7.08 (m, 5H), 5.56 (d, J = 2.4 Hz, 1H), 4.02 (q, J = 7.2 Hz, 2H), 2.54 (s, 3H), 0.99 (t, J =

7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 198.3, 196.0, 166.0, 161.9, 155.7, 137.1, 134.2, 134.1, 132.4 ($^2J_{CF}$ = 21 Hz), 131.2, 130.1, 129.2, 129.1, 127.8 ($^2J_{CF}$ = 20 Hz), 125.9, 125.0 ($^1J_{CF}$ = 240 Hz), 116.7, 116.5, 112.1, 110.0, 103.7, 60.6, 46.0, 18.9, 13.7; EI-MS (70 eV): m/z (%) = 470 (M^+, 1.5), 349 (2.0), 348 (23.4), 347 (100), 319 (5.2), 123 (6.3), 105 (53.7). Anal. calcd for $C_{29}H_{23}FO_5$: C 74.03, H 4.93; found: C 74.21, H 4.99.

Ethyl 5-benzoyl-4-(2-chlorobenzoyl)-2-methyl-6-phenyl-4H-pyran-3-carboxylate (3g): White solid; 197 mg, yield 81%; m.p. 147.5-148.2°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.03 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 7.2 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 7.2 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 7.11 (t, J = 7.2 Hz, 1H), 7.03-7.08 (m, 4H), 5.60 (s, 1H), 4.04 (q, J = 7.8 Hz, 2H), 2.55 (s, 3H), 1.00 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 199.7, 196.4, 166.0, 162.0, 156.2, 139.4, 137.2, 136.9, 134.9, 132.4, 132.3, 130.7, 130.2, 129.2, 128.6, 127.9, 127.8, 116.8, 112.1, 103.9, 60.8, 42.3, 19.1, 13.9; EI-MS (70 eV): m/z (%) = 486 (M^+, 0.6), 441 (1.9), 349 (0.6), 348 (4.5), 347 (100), 105 (16.8). Anal. calcd for $C_{29}H_{23}ClO_5$: C 71.53, H 4.76; found: C 71.37, H 4.87.

Ethyl 5-benzoyl-2-methyl-4-(4-nitrobenzoyl)-6-phenyl-4H-pyran-3-carboxylate (3h): White solid; 194 mg, yield 78%; m.p. 168.5-170.2°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.29 (s, 4H), 7.45 (d, J = 7.8 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 7.8 Hz, 1H), 7.04-7.09 (m, 4H), 5.57 (s, 1H), 4.04 (q, J = 7.2 Hz, 2H), 2.57 (s, 3H), 1.00 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.0, 196.3, 166.0, 162.1, 157.2, 150.0, 141.6, 137.1, 132.5, 132.2, 130.5, 130.2, 129.4, 129.2, 128.0, 127.9, 123.5, 111.9, 104.0, 61.0, 42.7, 19.1, 13.9; EI-MS (70 eV): m/z (%) = 497 (M^+, 1.6), 349 (1.9), 348 (24.7), 347 (100), 319 (2.7), 105 (46.4), 77 (21.7). Anal. calcd for $C_{29}H_{23}NO_7$: C 70.01, H 4.66, N 2.82; found: C 69.87, H 4.74, N 3.01.

Ethyl 5-benzoyl-4-(3,4-dimethoxybenzoyl)-2-methyl-6-phenyl-4H-pyran-3-carboxylate (3i): White solid; 202 mg, yield 79%; m.p. 122.3-124.8°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.78 (d, J = 7.8 Hz, 1H), 7.51 (s, 1H), 7.45 (d, J = 7.2 Hz, 2H), 7.25 (d, J = 7.2 Hz, 2H), 7.16 (t, J = 7.2 Hz, 1H), 7.08 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 7.8 Hz, 2H), 7.02 (t, J = 7.8 Hz, 2H), 6.84 (d, J = 8.4 Hz, 1H), 5.66 (s, 1H), 4.05 (q, J = 7.2 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 2.53 (s, 3H), 1.02 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 198.8, 196.6, 166.2, 161.9, 155.2, 153.3, 148.6, 137.3, 132.6, 132.3, 129.9, 129.2, 129.0, 127.9 127.8, 124.6, 112.4, 111.1, 110.0, 109.9, 103.8, 60.6, 56.0, 55.8, 42.2, 19.1, 14.0; EI-MS (70 eV): m/z (%) = 512 (M^+, 1.6), 349 (1.7), 348 (21.4), 347 (100), 319 (2.9), 105 (36.3). Anal. calcd for $C_{31}H_{28}O_7$: C 72.64, H 5.51; found: C 72.51, H 5.62.

Ethyl 5-benzoyl-4-(2,4-dichlorobenzoyl)-2-methyl-6-phenyl-4H-pyran-3-carboxylate(3j): White solid; 236 mg, yield 91%; m.p. 113.2-114.9°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 6.8 Hz, 2H), 7.34 (s, 1H), 7.25 (d, J = 6.8 Hz, 3H), 7.17 (s, 1H), 7.03-7.10 (m, 5H), 5.37 (s, 1H), 4.03 (q, J = 7.2 Hz, 2H), 2.54 (s, 3H), 1.07 (t, J = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 198.7, 195.9, 165.8, 162.5, 158.2, 137.3, 137.0, 136.9, 132.8, 132.3, 132.2, 130.5, 130.4, 130.2, 129.5, 129.3, 127.9, 127.8, 126.7, 110.7, 102.9, 60.8, 46.8, 19.1, 13.9; EI-MS (70 eV): m/z (%) = 520 (M^+, 2.6), 349 (1.3), 348 (20.5), 347 (100), 319 (2.5), 105 (50.6), 77 (21.7). Anal. calcd for $C_{29}H_{22}Cl_2O_5$: C 66.80, H 4.25; found: C 66.94, H 4.14.

Ethyl 5-benzoyl-4-(furan-2-carbonyl)-2-methyl-6-phenyl-4H-pyran-3-carboxylate (3k): White solid; 166 mg, yield 75%; m.p. 184.7-185.6°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 (s, 1H), 7.50 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 3.6 Hz, 1H), 7.21 (d, J = 7.6 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.04-7.10 (m, 5H), 6.50 (s, 1H), 5.40 (s, 1H), 4.09 (q, J = 6.8 Hz, 2H), 2.54 (s, 3H), 1.07 (t, J = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 195.9, 187.8, 165.6, 161.7, 154.9, 151.5, 146.6, 136.8, 132.1, 132.0, 129.7, 128.8, 128.7, 127.5, 127.4, 119.1, 112.0, 111.4, 102.8, 60.3, 43.0, 18.6, 13.4; EI-MS (70 eV): m/z (%) = 442 (M^+, 1.5), 349 (2.2), 348 (22.5), 347 (100), 319 (3.8), 105 (47.3), 77 (23.1). Anal. calcd for $C_{27}H_{22}O_6$: C 73.29, H 5.01; found: C 73.13, H 5.15.

Ethyl 5-benzoyl-2-methyl-6-phenyl-4-(thiophene-2-carbonyl)-4H-pyran-3-carboxylate (3l): White solid; 163 mg, yield 71%; m.p. 133.5-134.8°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, J = 3.6 Hz, 1H), 7.58 (d, J = 4.8 Hz, 1H), 7.48 (d, J = 7.6 Hz, 2H), 7.27 (d, J = 6.8 Hz, 2H), 7.10 (t, J = 6.8 Hz, 1H), 7.02-7.08 (m, 6H), 5.49 (s, 1H), 4.09 (q, J = 7.2 Hz, 2H), 2.54 (s, 3H), 1.05 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.4, 192.5, 185.4, 166.0, 162.1, 155.2, 137.3, 134.6, 134.2, 132.5, 132.3, 130.0, 129.2, 129.0, 128.1, 127.9, 127.8, 112.0, 103.4, 60.7, 44.6, 19.0, 13.8; EI-MS (70 eV): m/z (%) = 458.5 (M^+, 2.4), 349 (3.1), 348 (22.4), 347 (100), 319

(5.5), 111 (5.4), 106 (4.0), 105 (55.0). Anal. calcd for $C_{27}H_{22}O_5S$: C 70.72, H 4.84; found: C 70.53, H 4.91.

Diethyl 4-benzoyl-2-methyl-6-phenyl-4H-pyran-3,5-dicarboxylate (3m): White solid; 178 mg, yield 85%; m.p. 127.9-128.5°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 8.0 Hz, 2H), 7.37-7.42 (m, 5H), 5.58 (s, 1H), 4.02 (q, J = 7.2 Hz, 2H), 3.81 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.00 (t, J = 7.2 Hz, 3H), 0.77 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.8, 166.4, 166.0, 161.6, 158.9, 136.6, 133.7, 133.0, 129.8, 129.4, 128.7, 128.2, 127.8, 105.5, 104.2, 60.6, 40.7, 18.9, 13.8, 13.3; EI-MS (70 eV): m/z (%) = 420 (M^+, 1.8), 375 (2.5), 316 (20.0), 315 (100), 259 (13.6), 105 (12.1). Anal. calcd for $C_{25}H_{24}O_6$: C 71.41, H 5.75; found: C 71.60, H 5.59.

Diethyl 4-(furan-2-carbonyl)-2-methyl-6-phenyl-4H-pyran-3,5-dicarboxylate(3n): White solid; 139 mg, yield 68%; m.p. 100.3-101.8°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 (s, 1H), 7.37−7. 46 (m, 6H), 6.58 (s, 1H), 5.31 (s, 1H), 4.09 (q, J = 4.8 Hz, 2H), 3.87 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H), 0.81 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 188.8, 166.3, 166.0, 161.7, 159.0, 152.0, 146.8, 133.7, 129.9, 128.7, 127.8, 119.3, 112.4, 105.0, 103.8, 60.7, 41.6, 18.9, 13.9, 13.4; EI-MS (70 eV): m/z (%) = 410 (M^+, 3.6), 316 (18.4), 315 (100), 259 (12.5), 105 (8.2). Anal. calcd for $C_{23}H_{22}O_7$: C 67.31, H 5.40; found: C 67.15, H 5.48.

3-Ethyl 5-methyl 4-benzoyl-6-methyl-2-phenyl-4H-pyran-3,5-dicarboxylate (3o): White solid; 174 mg, yield 86%; m.p. 105.4-107.0°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.16 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.43 (t, J = 7.8 Hz, 3H), 7.38 (t, J = 7.2 Hz, 2H), 5.59 (s, 1H), 3.83 (q, J = 7.2 Hz, 2H), 3.54 (s, 3H), 2.44 (s, 3H), 0.77 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.7, 166.5, 166.3, 161.8, 159.0, 136.5, 133.6, 133.0, 129.9, 129.3, 128.8, 128.2, 127.8, 105.5, 104.1, 60.7, 51.4, 40.8, 18.9, 13.4; EI-MS (70 eV): m/z (%) = 406 (M^+, 1.3), 302 (18.2), 301 (100), 273 (17.9), 105 (15.2). Anal. calcd for $C_{24}H_{22}O_6$: C 70.92, H 5.46; found: C 70.77, H 5.32.

Methyl 4,5-dibenzoyl-2-methyl-6-phenyl-4H-pyran-3-carboxylate (3p): White solid; 204 mg, yield 93%; m.p. 151.8-153.1°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.04 (d, J = 7.2 Hz, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.45 (d, J = 7.8 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 7.27 (d, J = 7.2 Hz, 2H), 7.16 (t, J = 7.2 Hz, 1H), 7.11 (t, J = 7.2 Hz, 1H), 7.06 (t, J = 7.2 Hz, 2H), 7.03 (t, J = 7.8 Hz, 2H), 5.68 (s, 1H), 3.53 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.4, 196.3, 166.5, 162.1, 155.7, 137.2, 136.4, 133.0, 132.5, 132.3, 130.1, 129.3, 129.2, 129.1, 128.3, 127.9, 127.8, 112.3, 103.7, 51.4, 42.6, 19.0; EI-MS (70 eV): m/z (%) = 438 (M^+, 0.8), 334 (22.5), 333 (100), 105 (64.1), 77 (35.7). Anal. calcd for $C_{28}H_{22}O_5$: C 76.70, H 5.06; found: C 76.83, H 5.20.

Benzyl 4,5-dibenzoyl-2-methyl-6-phenyl-4H-pyran-3-carboxylate (3q): White solid; 247 mg, yield 96%; m.p. 127.8-129.1°C; ^{1}H NMR (400 MHz, DMSO-d6) δ = 7.94 (d, J = 7.6 Hz, 2H), 7.44 (d, J = 7.6 Hz, 3H), 7.24-7.27 (m, 7H), 7.16 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.6 Hz, 3H), 7.06 (d, J = 7.6 Hz, 2H), 7.03 (d, J =7.6 Hz, 2H), 5.67 (s, 1H), 5.08 (d, J = 12.4 Hz, 1H), 4.88 (d, J = 12.4 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.3, 196.2, 165.8, 162.5, 155.4, 137.2, 136.1, 135.3, 132.9, 132.5, 132.2, 130.0, 129.3, 129.2, 129.1, 128.5, 128.4, 128.2, 128.1, 127.8, 127.7, 112.3, 103.5, 66.5, 42.5, 19.1; EI-MS (70 eV): m/z (%) = 514 (M^+, 0.6), 410 (26.0), 409 (100), 105 (53.8), 91 (31.5), 77 (23.2). Anal. calcd for $C_{34}H_{26}O_5$: C 79.36, H 5.09; found: C 79.14, H 5.03.

4,5-Dibenzoyl-cyclopent-2-enecarboxylic acid methyl ester (3r): Light yellow crystal; 127 mg, yield 76%; m.p. 140-141 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (d, J = 7.2 Hz, 2H), 7.94 (d, J = 7.2 Hz, 2H), 7.50-7.55 (m, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 7.2 Hz, 2H), 5.12-5.18 (m, 3H), 3.70-3.76 (m, 4H), 3.36 (2d, J = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 213.9, 197.6, 197.0, 166.1, 136.3, 135.8, 133.1, 133.0, 128.6, 128.5, 128.4, 128.0, 99.4, 81.7, 52.7, 41.2, 40.5; MS (ESI): m/z (%) = 357.2 (M+Na), 334 (M^+). Anal. calcd for $C_{21}H_{18}O_4$: C 75.43, H 5.43; found: C 75.20, H 5.38.

4. Copies of ^{1}H NMR and ^{13}C NMR Spectra

Figure 1. The ^{1}H NMR (400M Hz, $CDCl_3$) of **3a**.

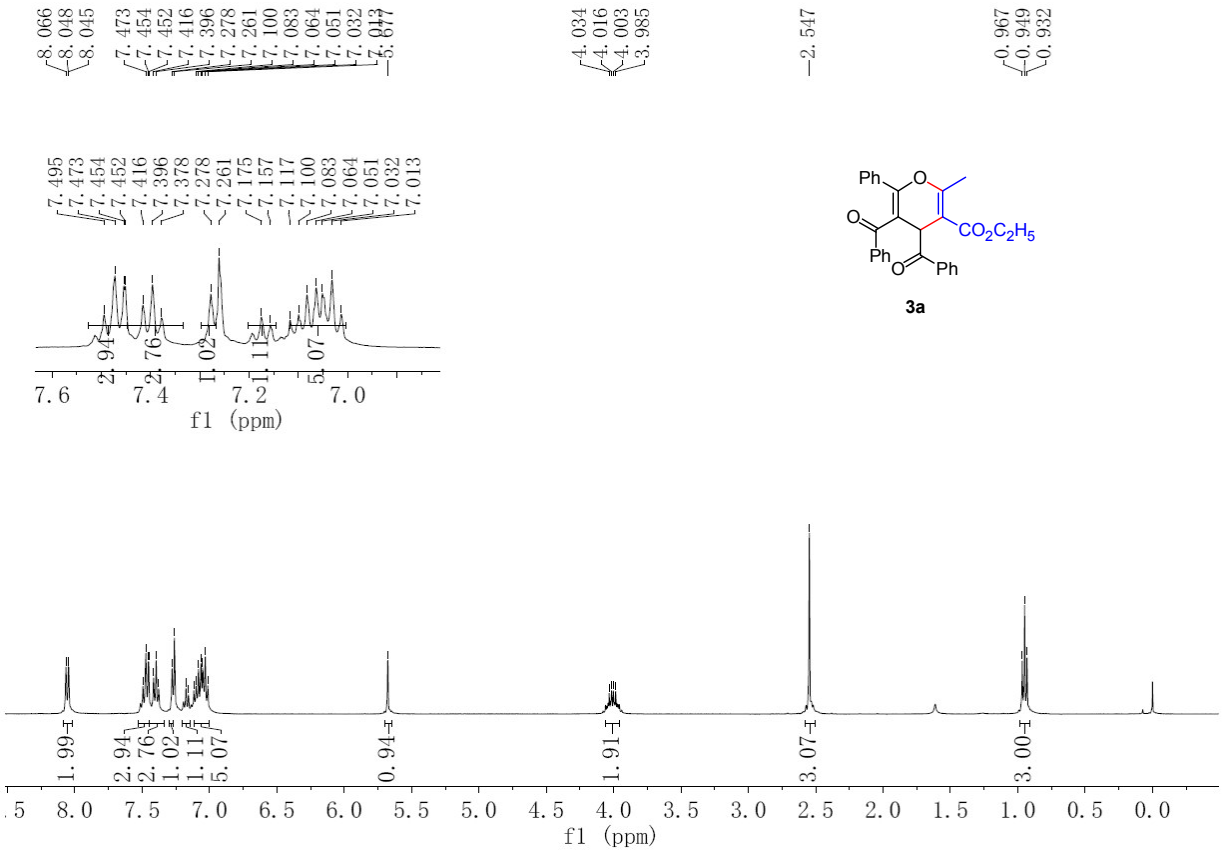


Figure 2. The ^{13}C NMR (100MHz, $CDCl_3$) of **3a**.

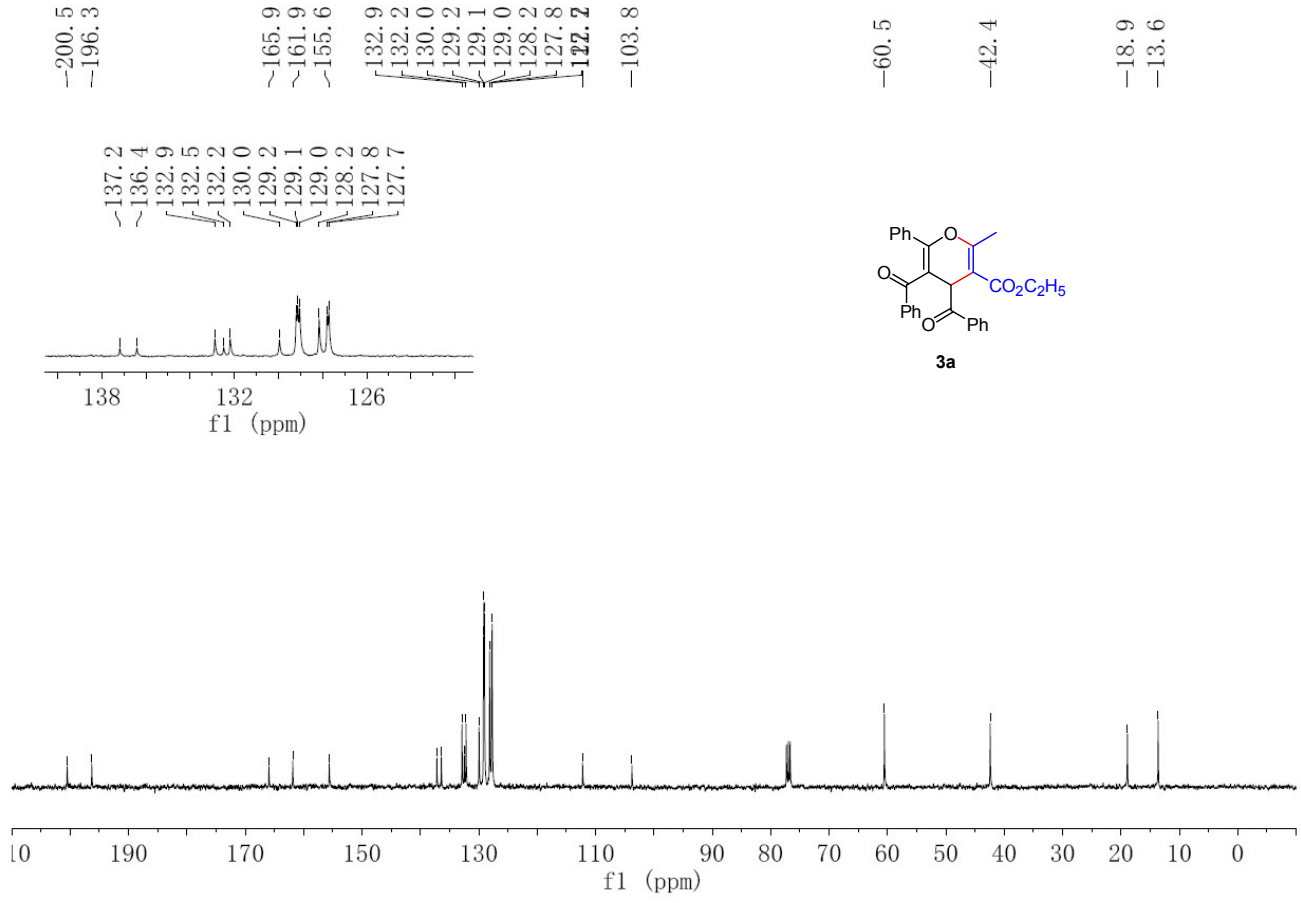


Figure 3. The ^{1}H NMR (400M Hz, $CDCl_3$) of **3b**.

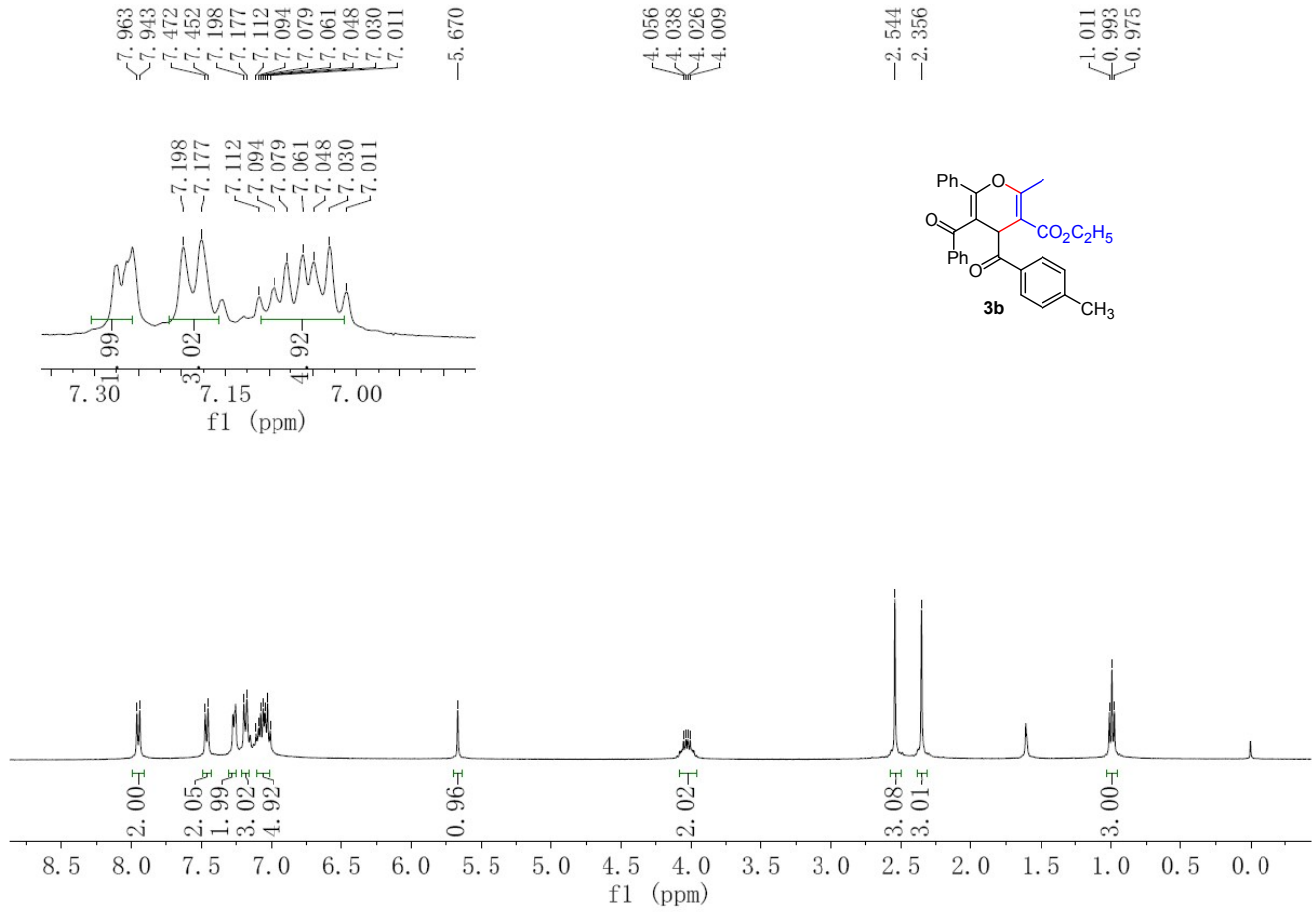


Figure 4. The ^{13}C NMR (150MHz, $CDCl_3$) of **3b**.

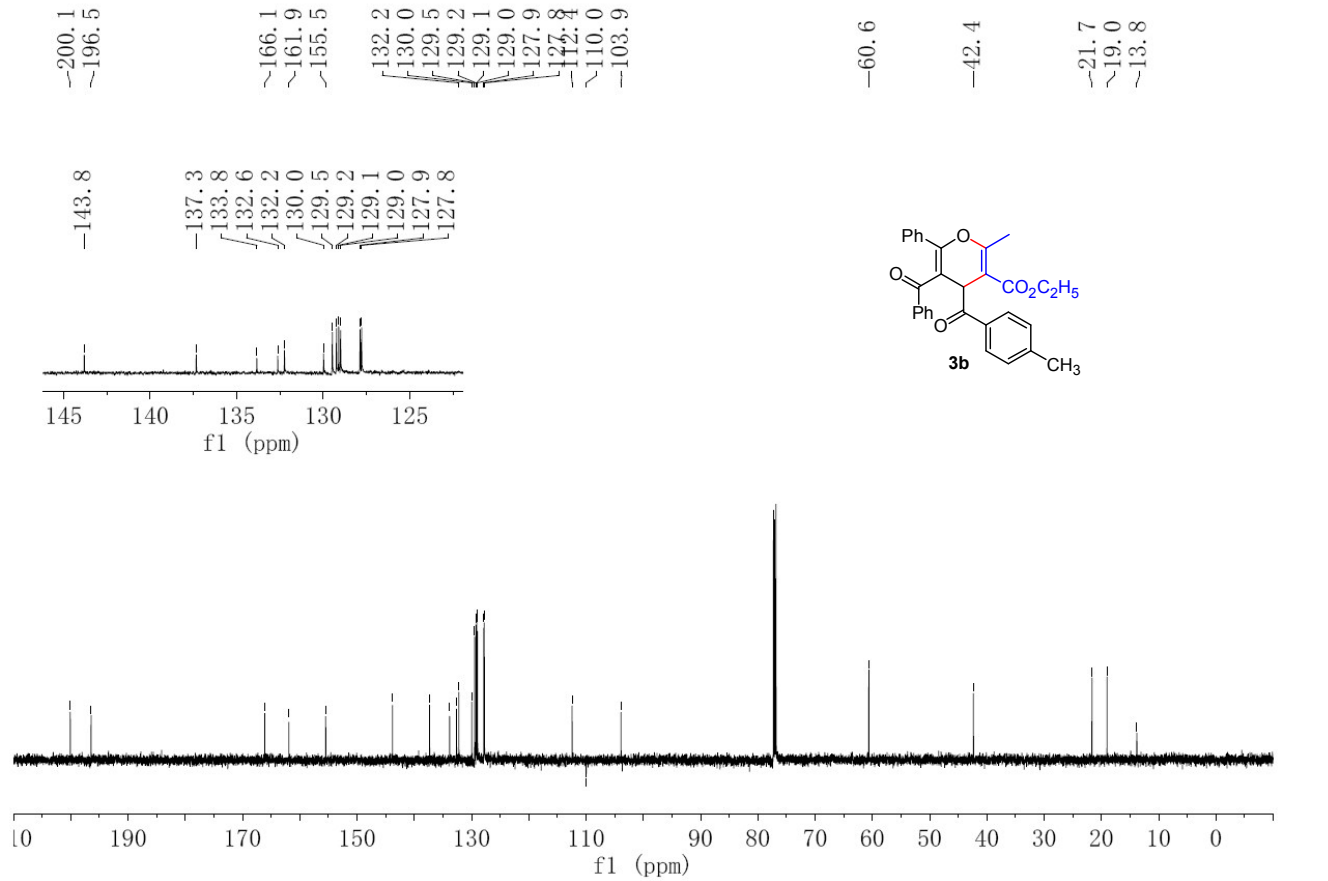


Figure 5. The ^{1}H NMR (400M Hz, $CDCl_3$) of **3c**.

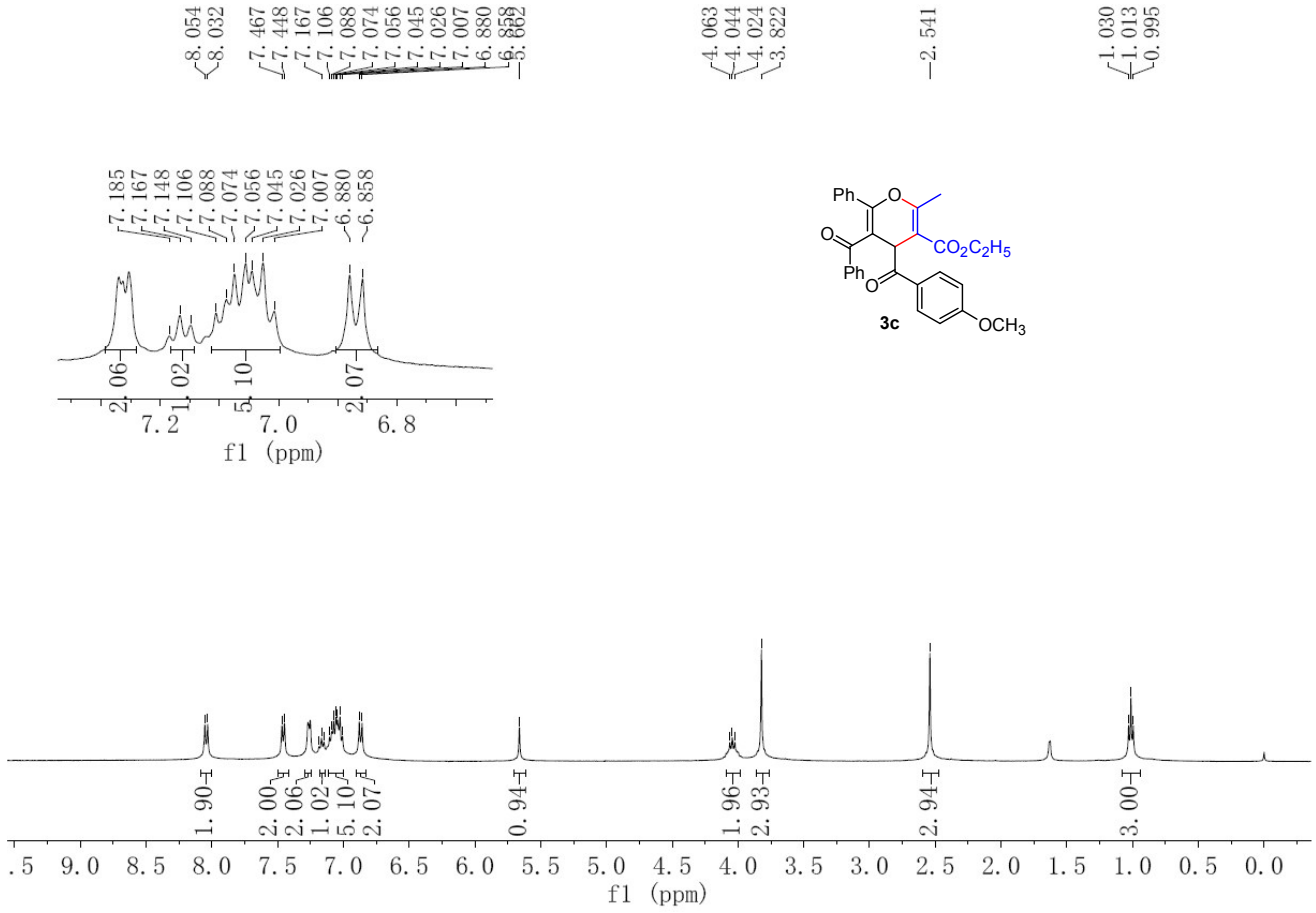


Figure 6. The ^{13}C NMR (100MHz, $CDCl_3$) of **3c**.

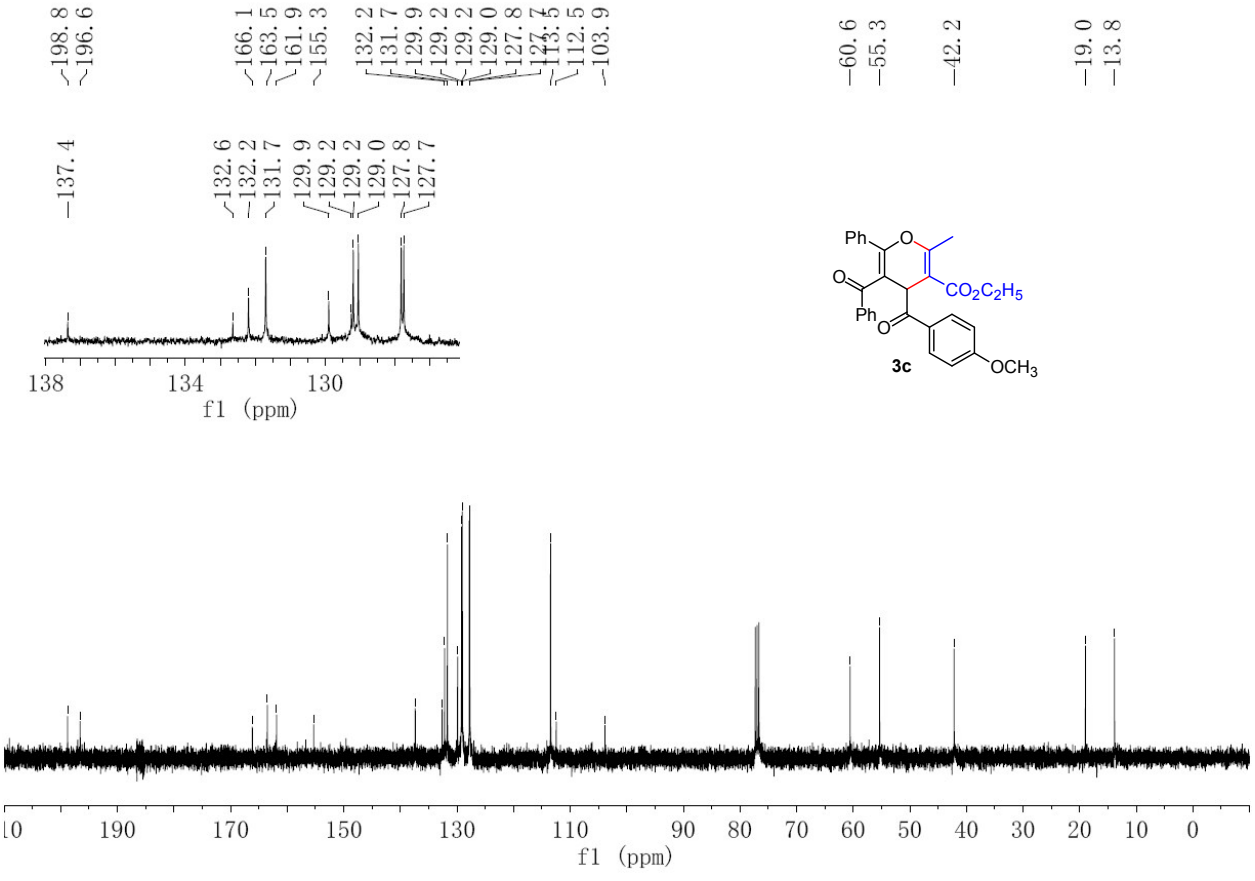


Figure 7. The ^{1}H NMR (600M Hz, $CDCl_3$) of **3d**.

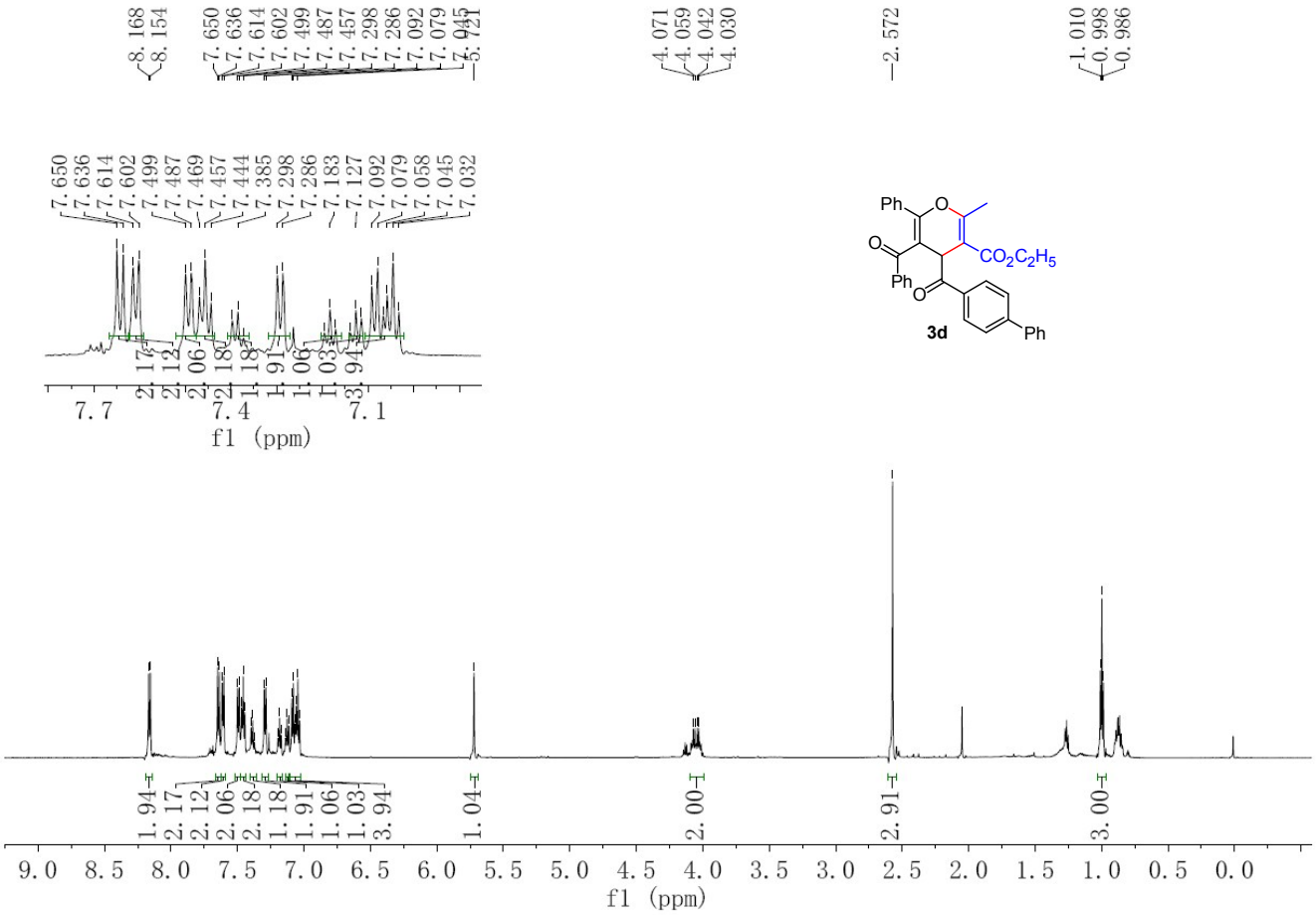


Figure 8. The ^{13}C NMR (150MHz, $CDCl_3$) of **3d**.

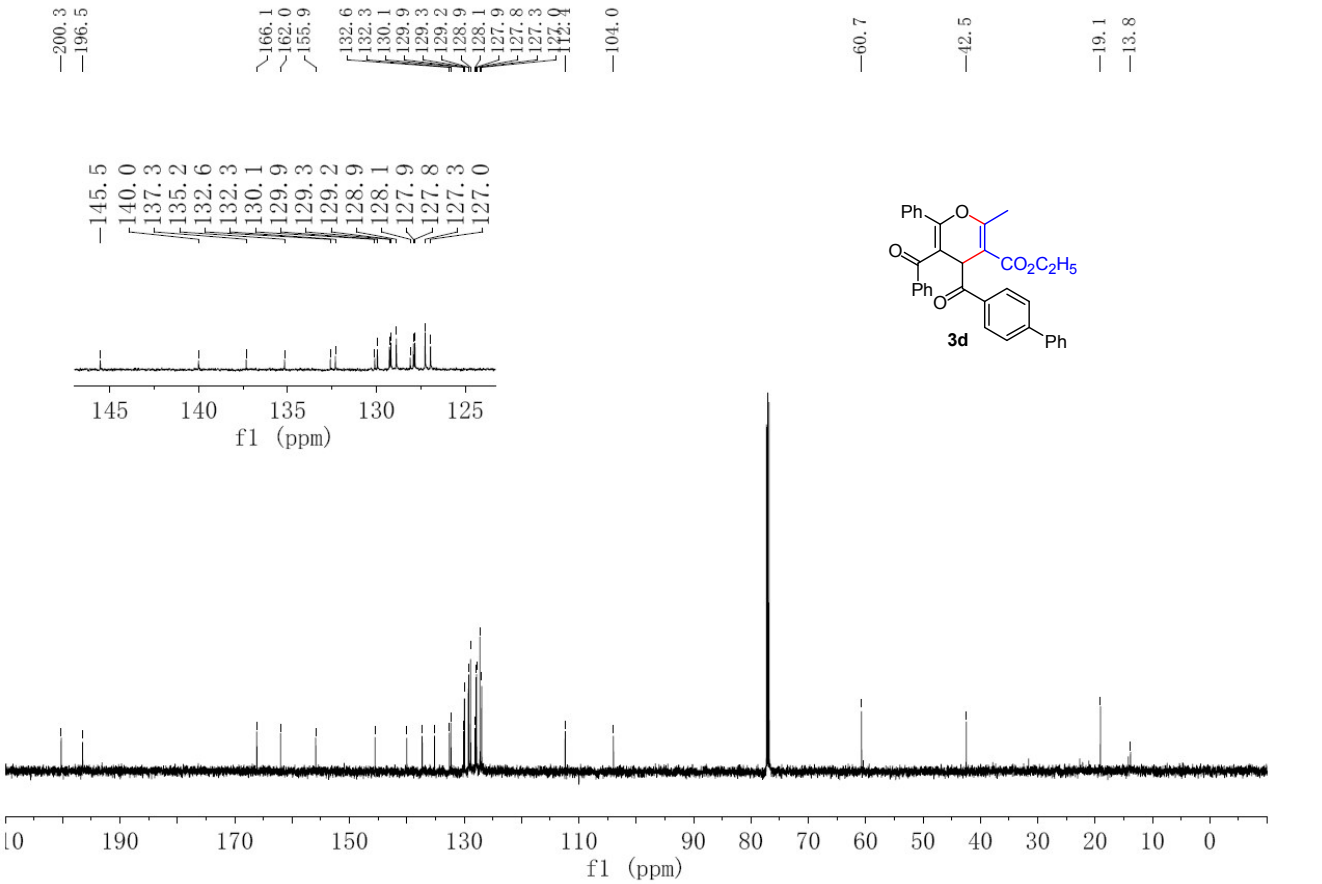


Figure 9. The ^{1}H NMR (400M Hz, $CDCl_3$) of **3e**.

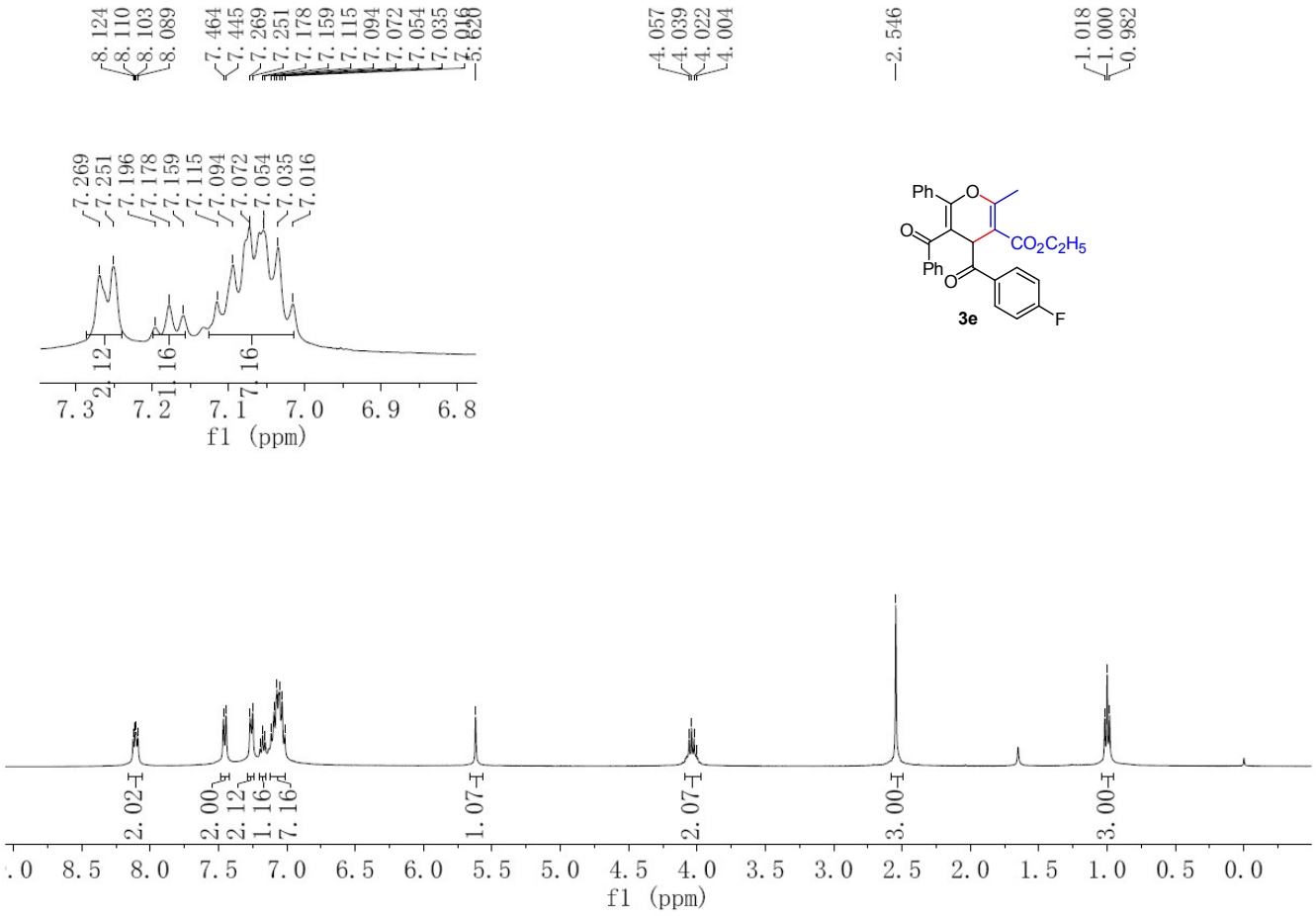


Figure 10. The ^{13}C NMR (100MHz, $CDCl_3$) of **3e**.

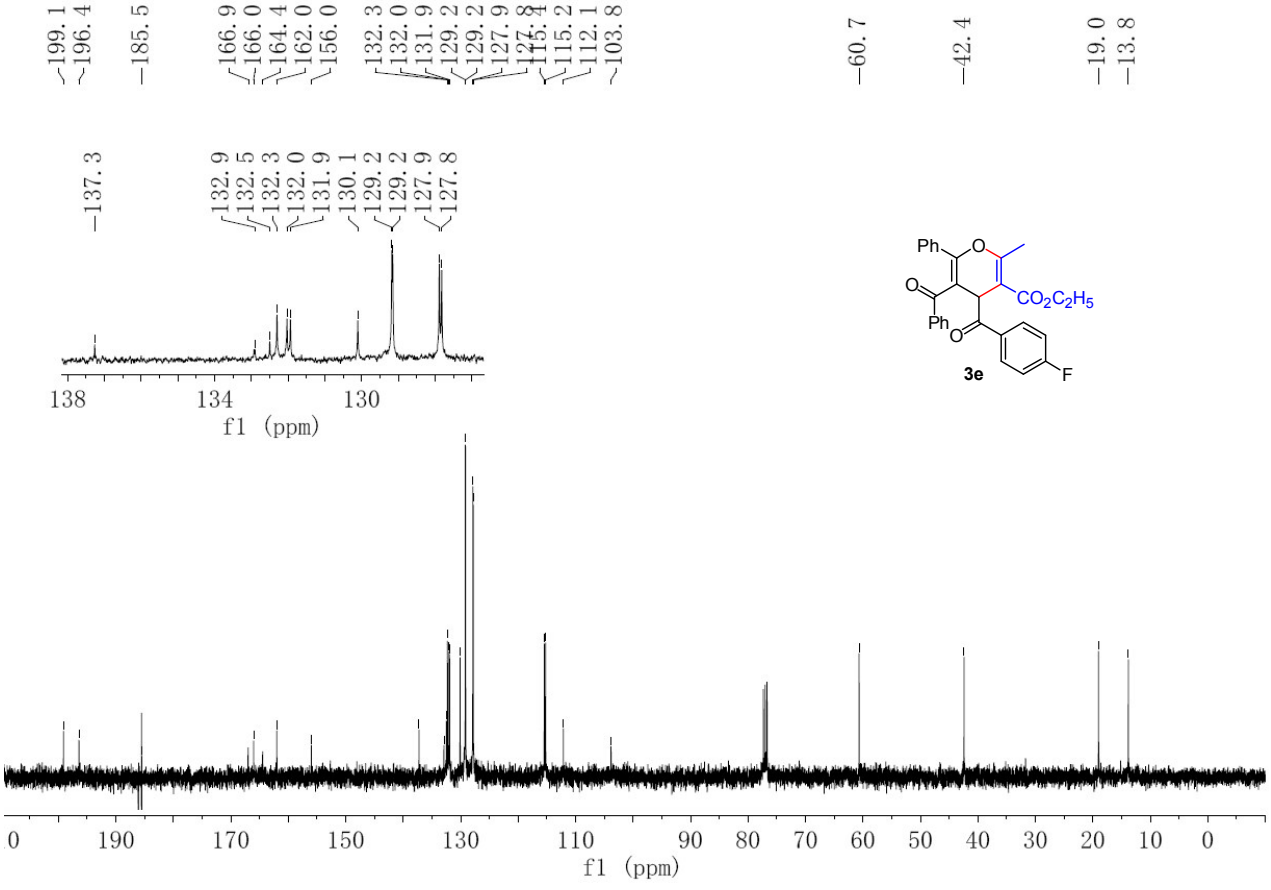


Figure 11. The ^{1}H NMR (600M Hz, $CDCl_3$) of **3f**.

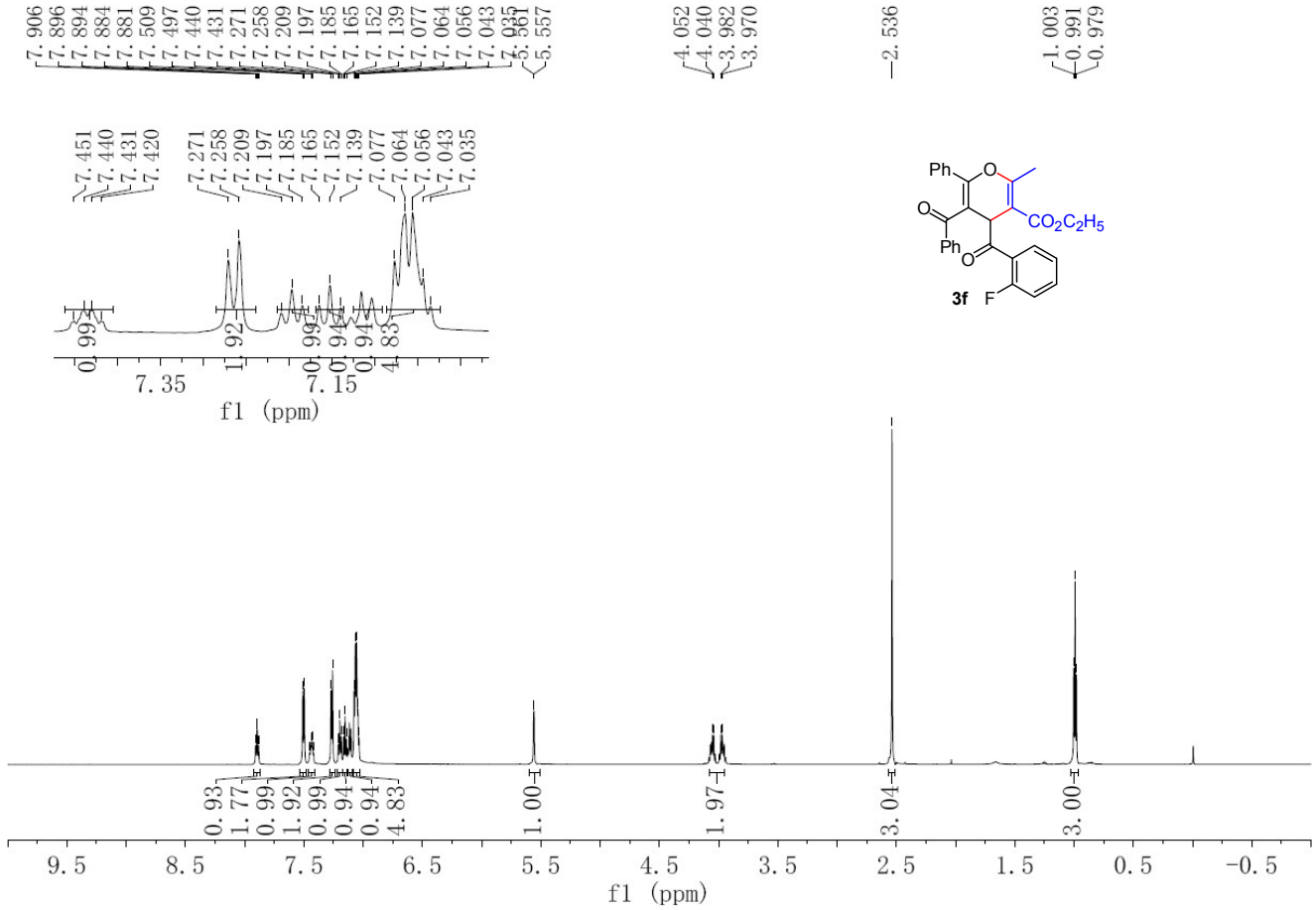


Figure 12. The ^{13}C NMR (150MHz, $CDCl_3$) of **3f**.

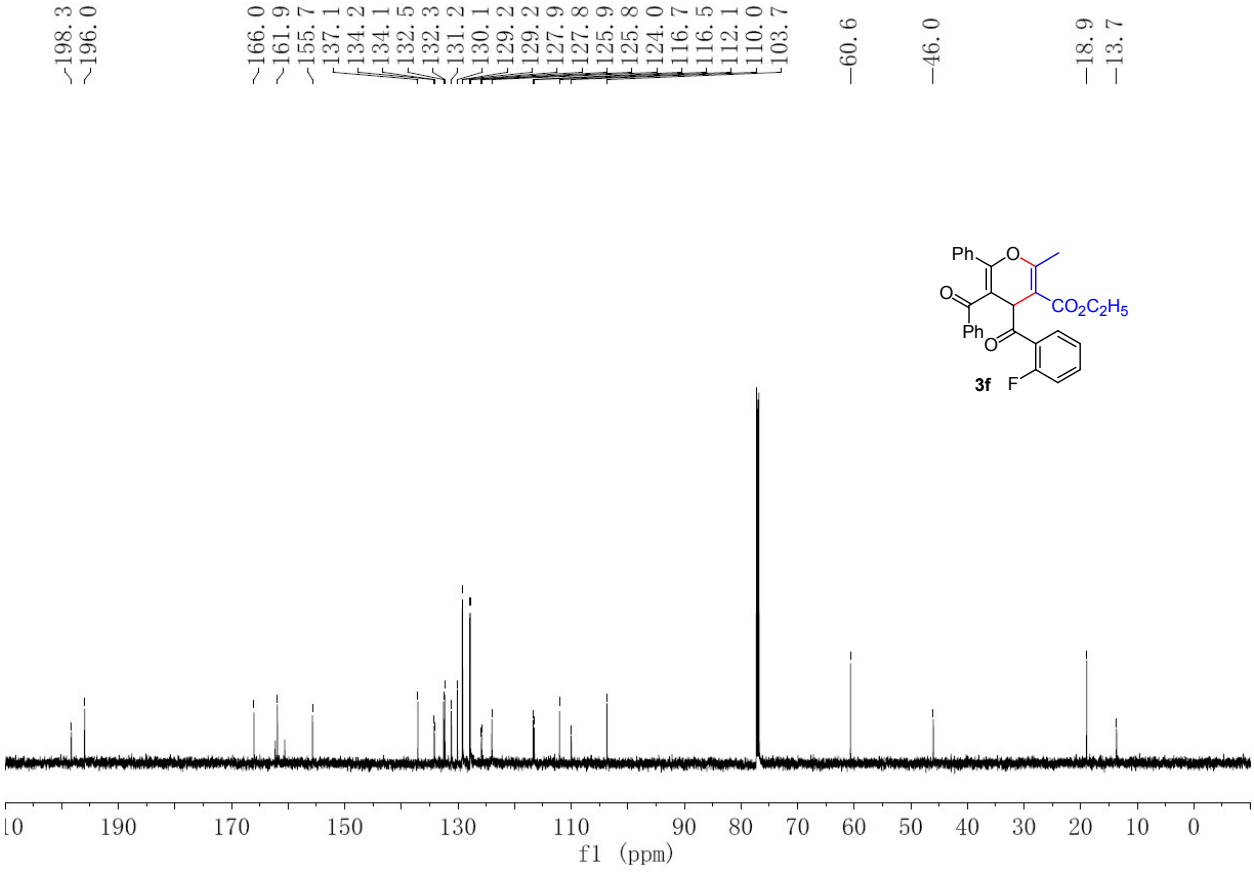


Figure 13. The ^{1}H NMR (600M Hz, $CDCl_3$) of **3g**.

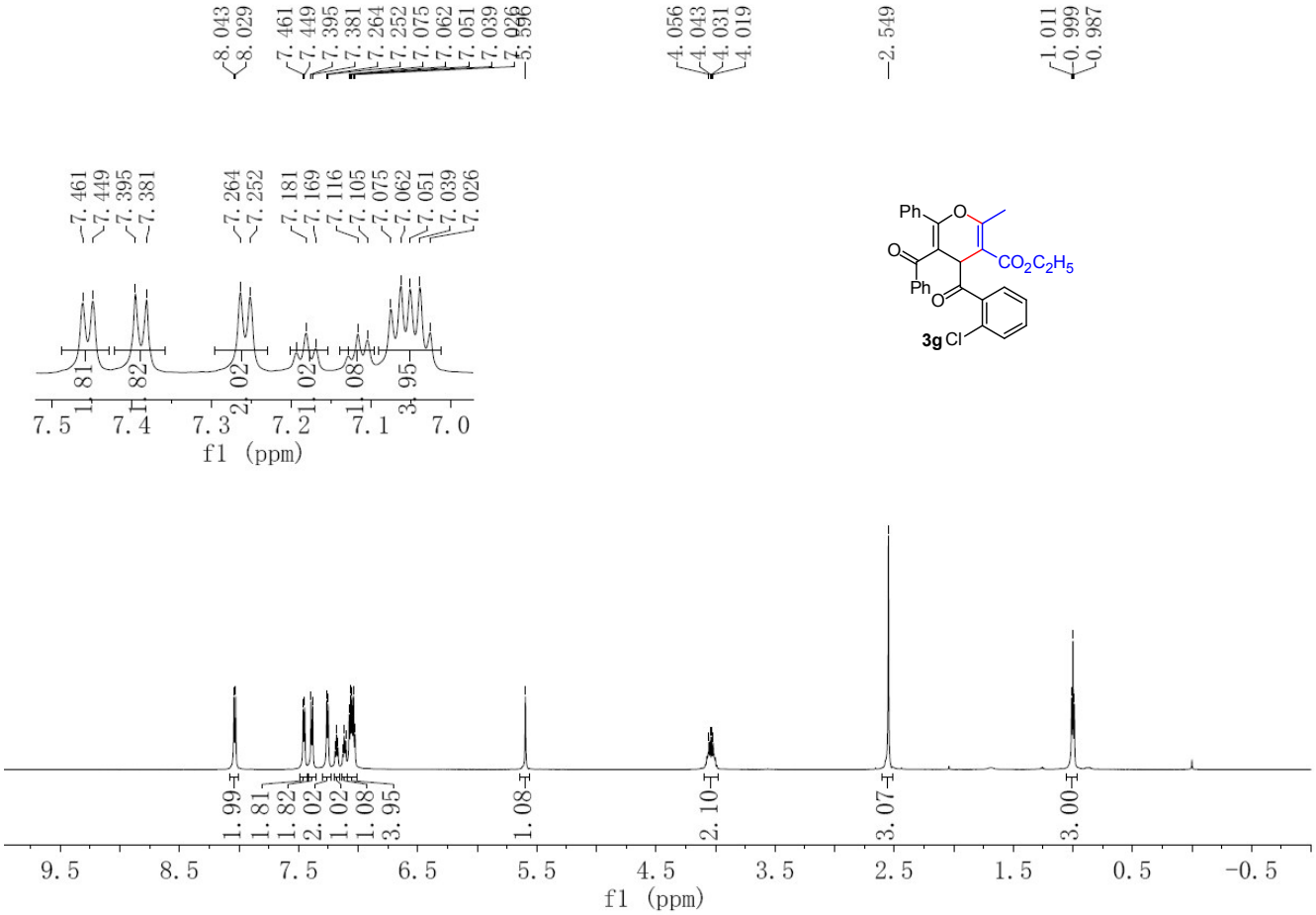


Figure 14. The ^{13}C NMR (150MHz, $CDCl_3$) of **3g**.

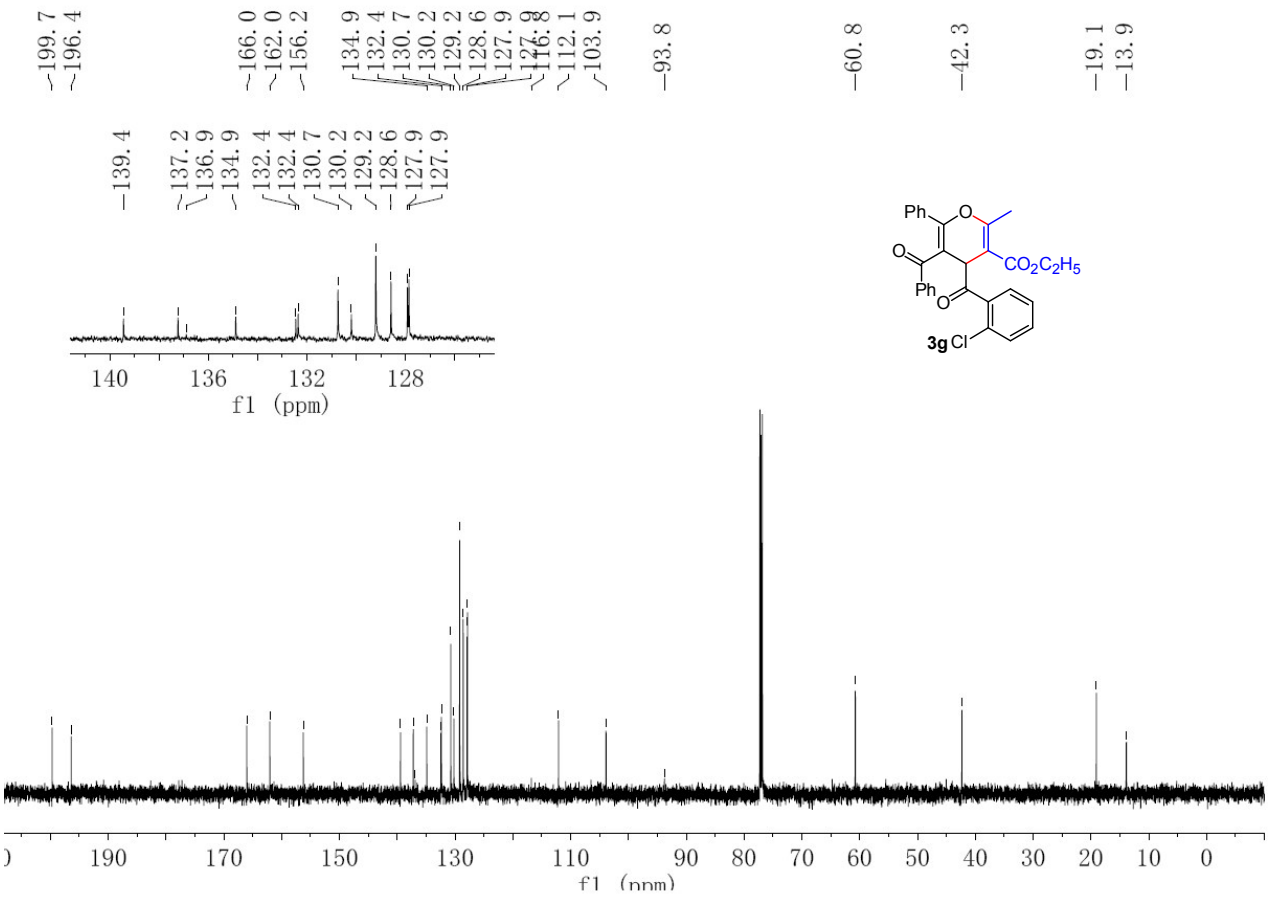


Figure 15. The ^{1}H NMR (600M Hz, $CDCl_3$) of **3h**.

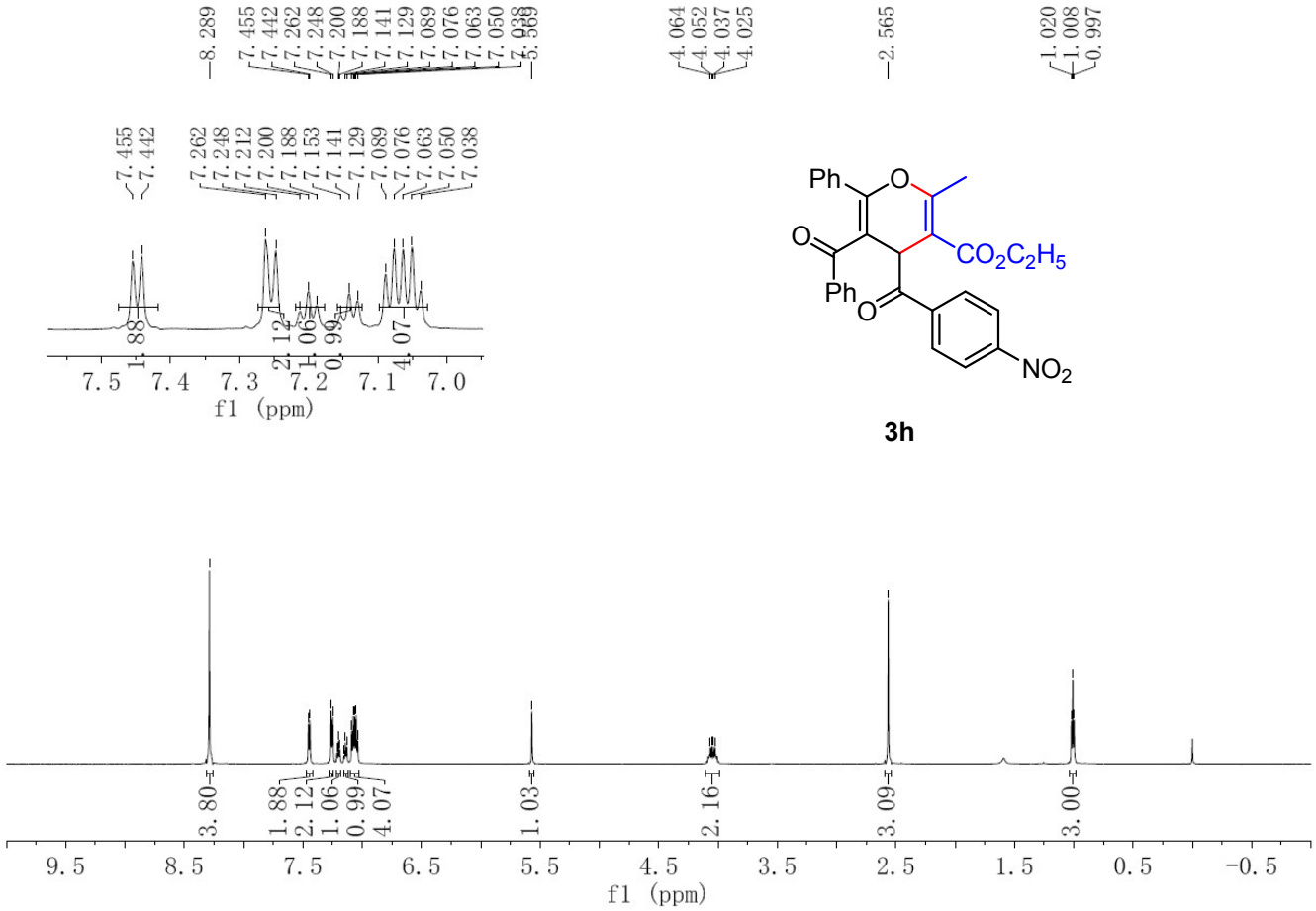


Figure 16. The ^{13}C NMR (150MHz, $CDCl_3$) of **3h**.

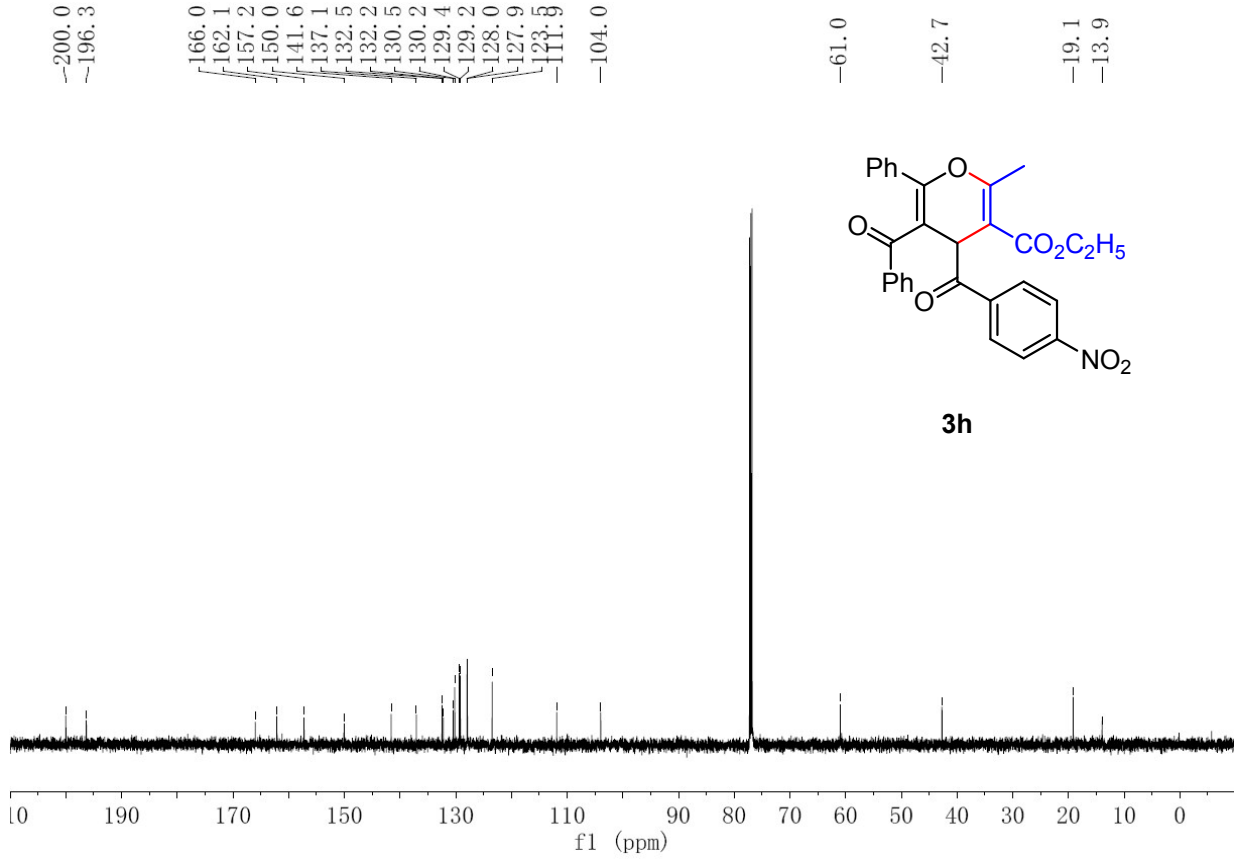


Figure 17. The ^{1}H NMR (600M Hz, $CDCl_3$) of **3i**.

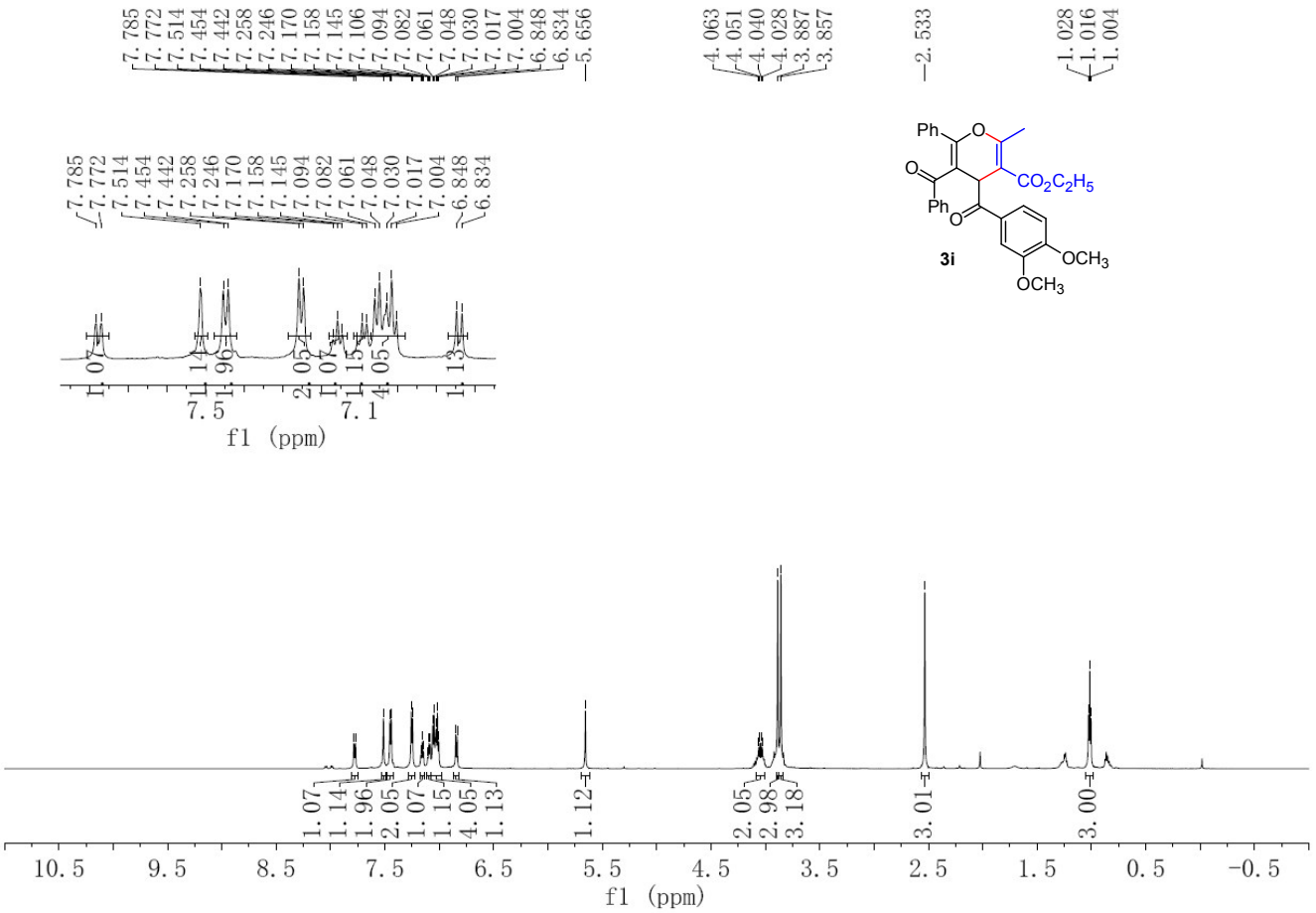


Figure 18. The ^{13}C NMR (150MHz, $CDCl_3$) of **3i**.

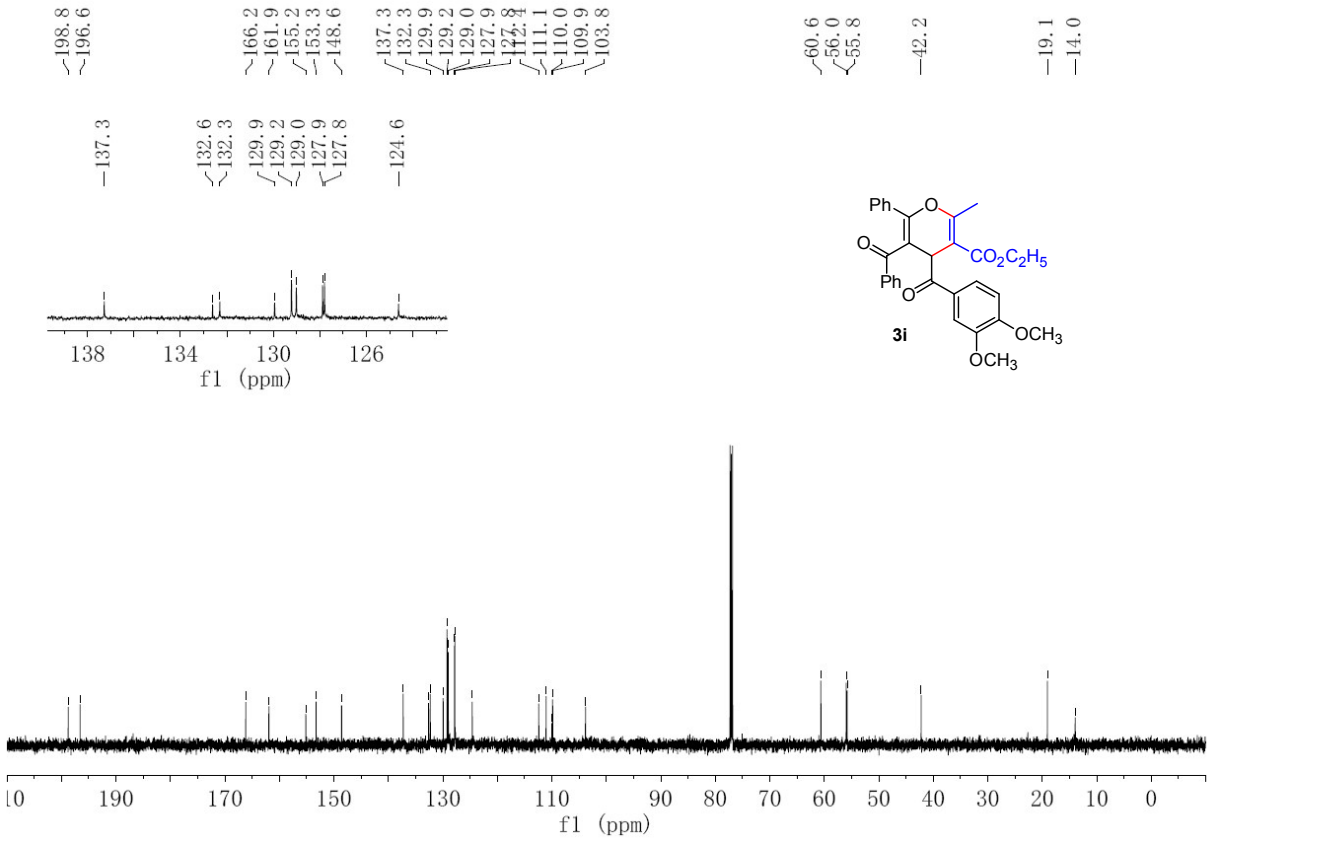


Figure 19. The ^{1}H NMR (400M Hz, $CDCl_3$) of **3j**.

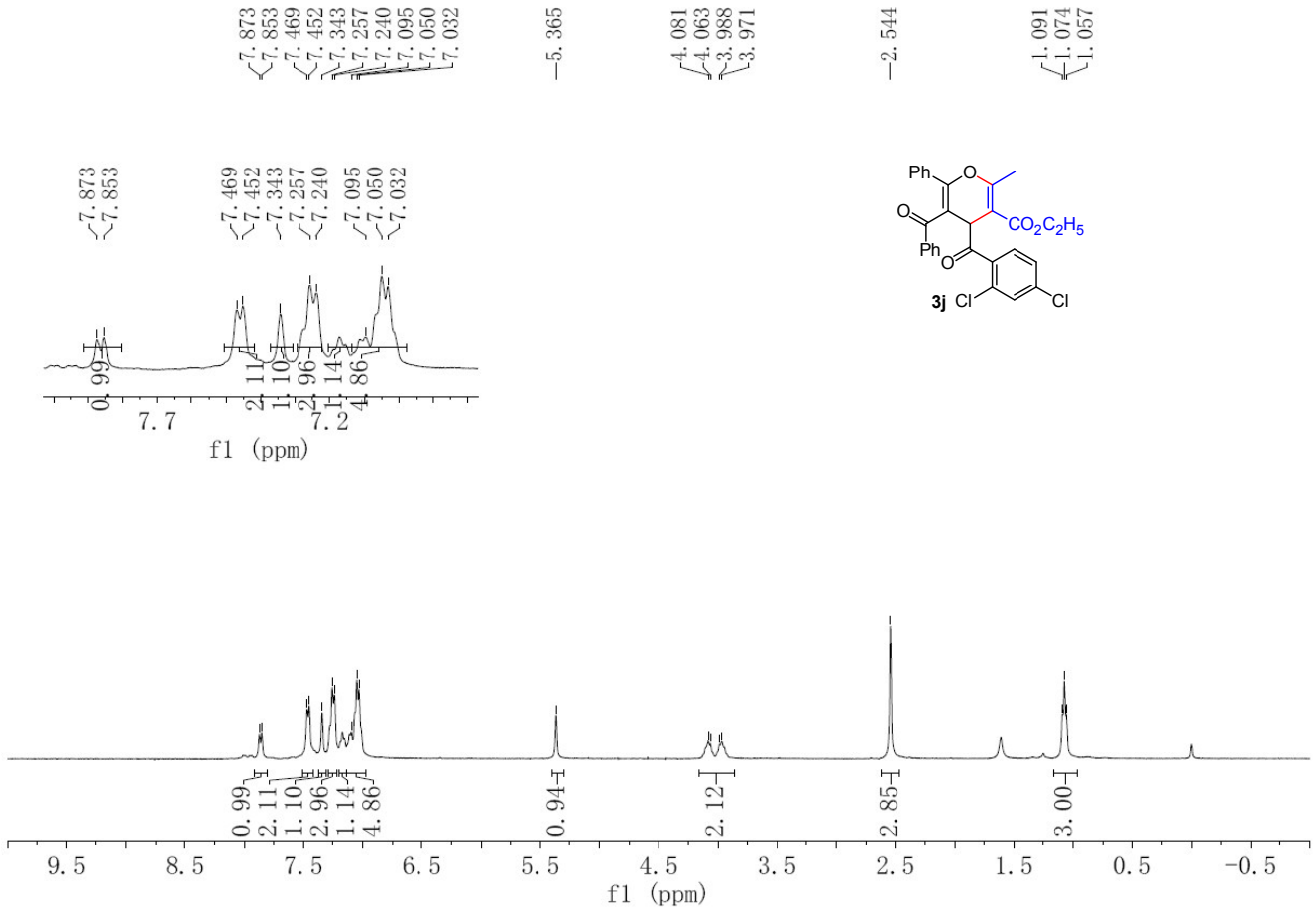


Figure 20. The ^{13}C NMR (150MHz, $CDCl_3$) of **3j**.

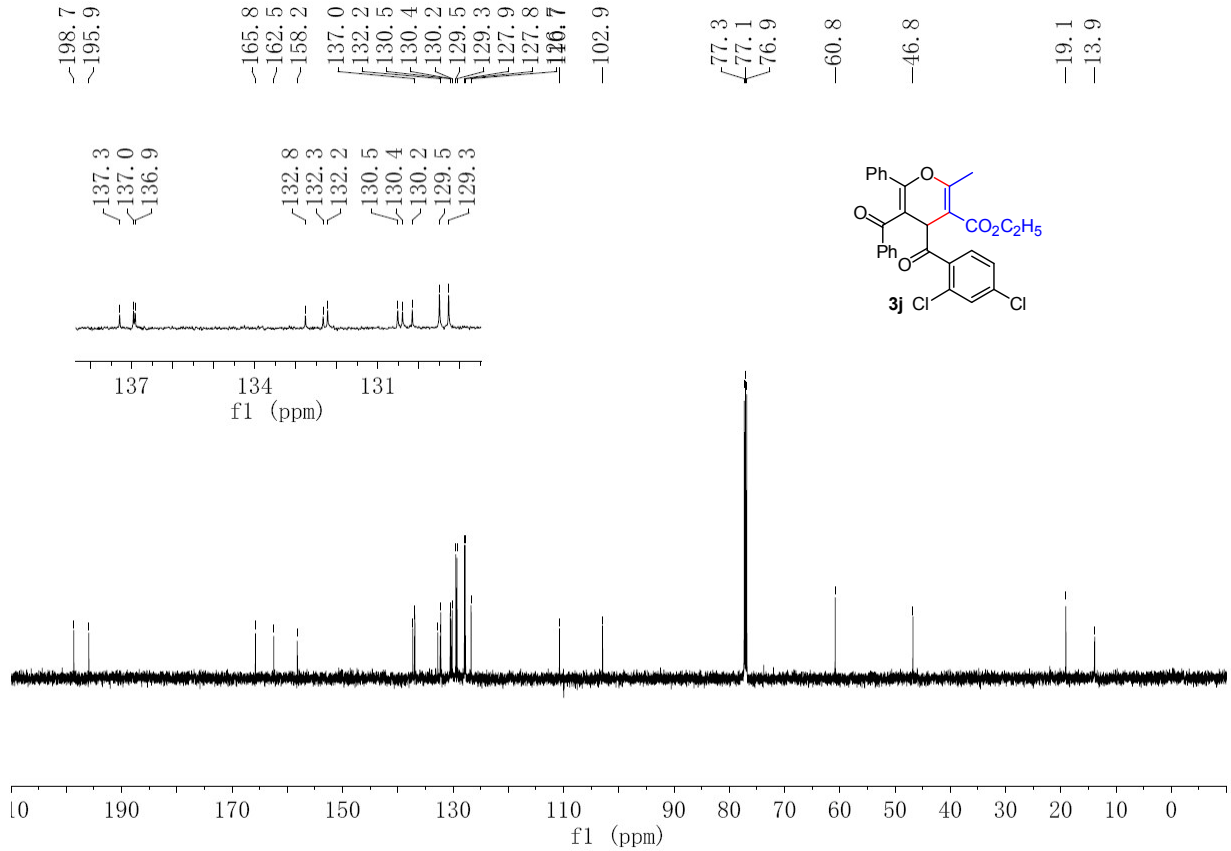


Figure 21. The ^{1}H NMR (400M Hz, $CDCl_3$) of **3k**.

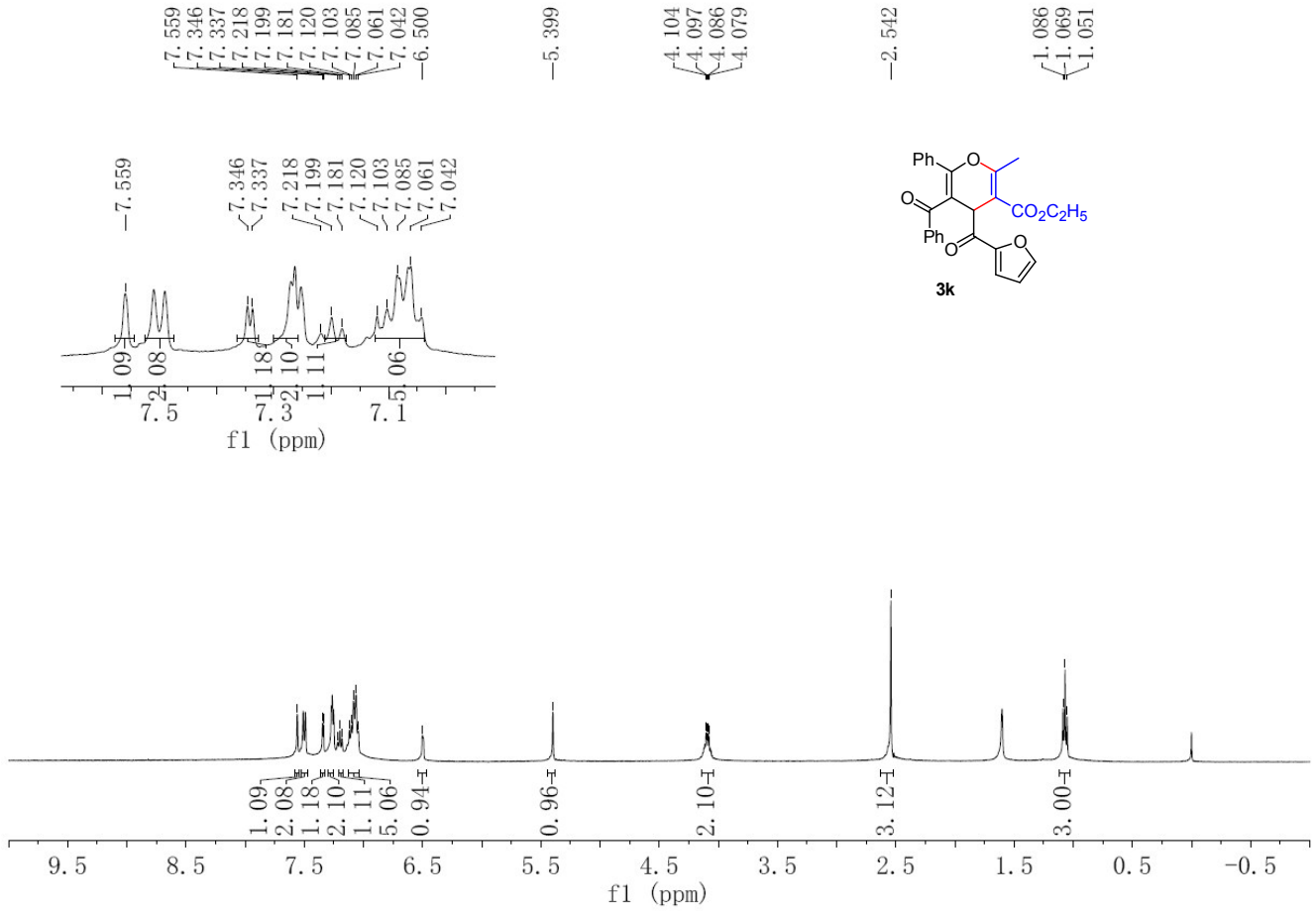


Figure 22. The ^{13}C NMR (150MHz, $CDCl_3$) of **3k**.

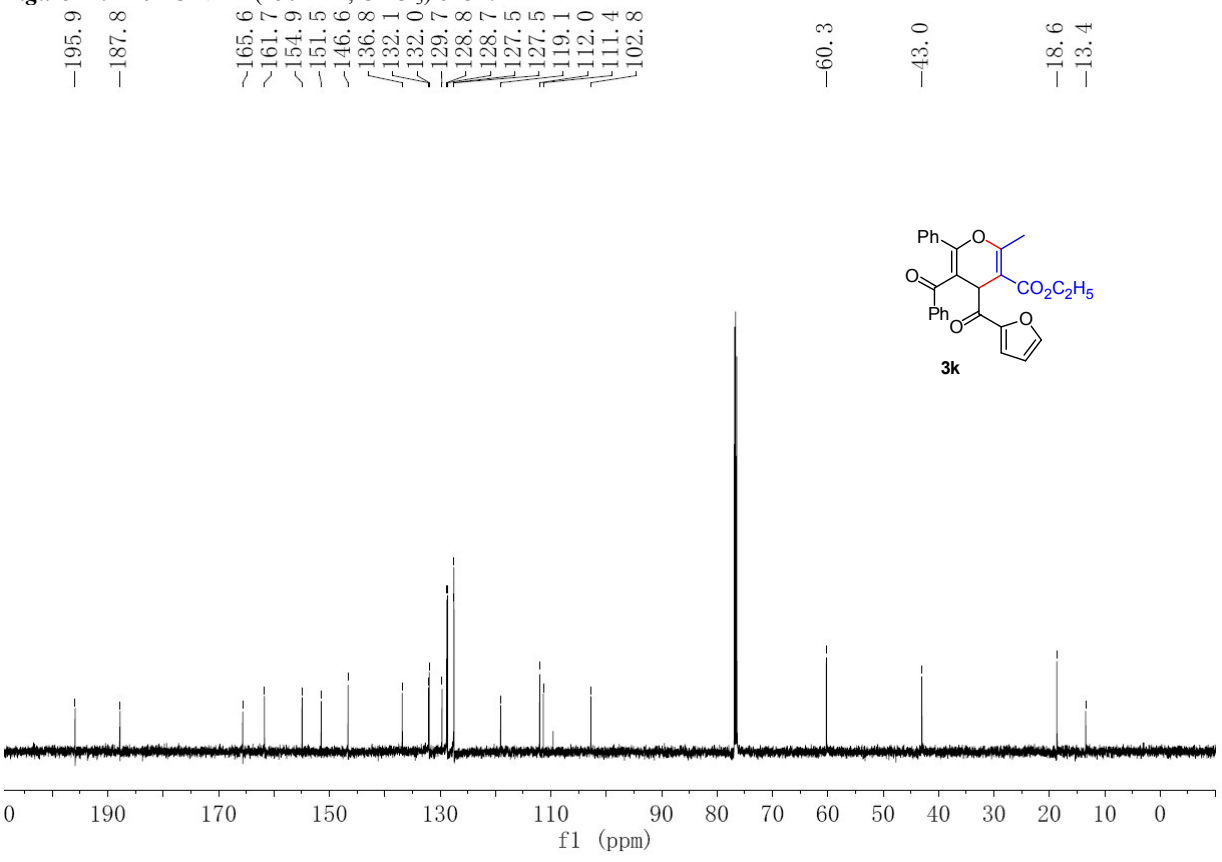


Figure 23. The ^{1}H NMR (400M Hz, $CDCl_3$) of **3l**.

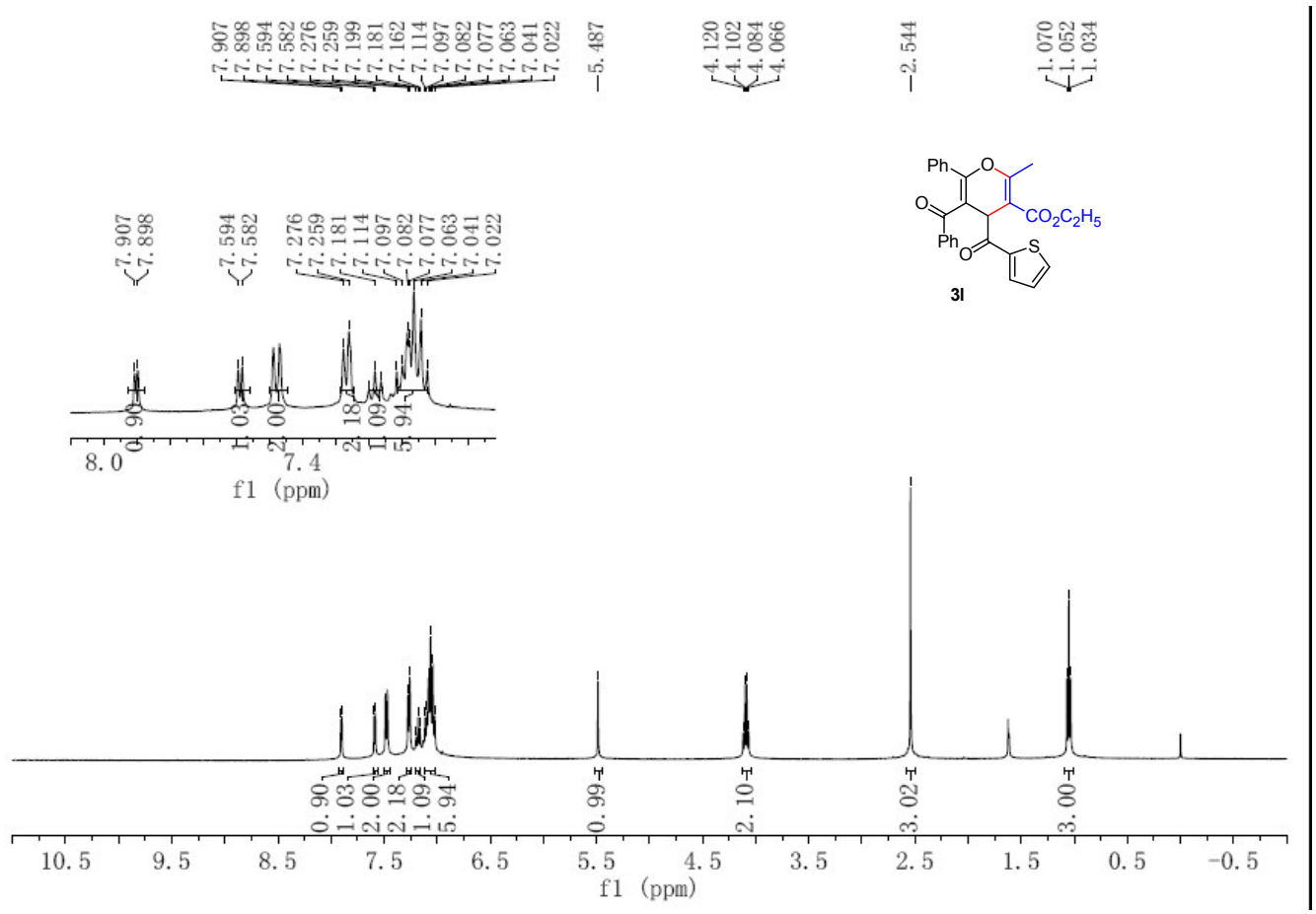


Figure 24. The ^{13}C NMR (100M Hz, $CDCl_3$) of **3l**.

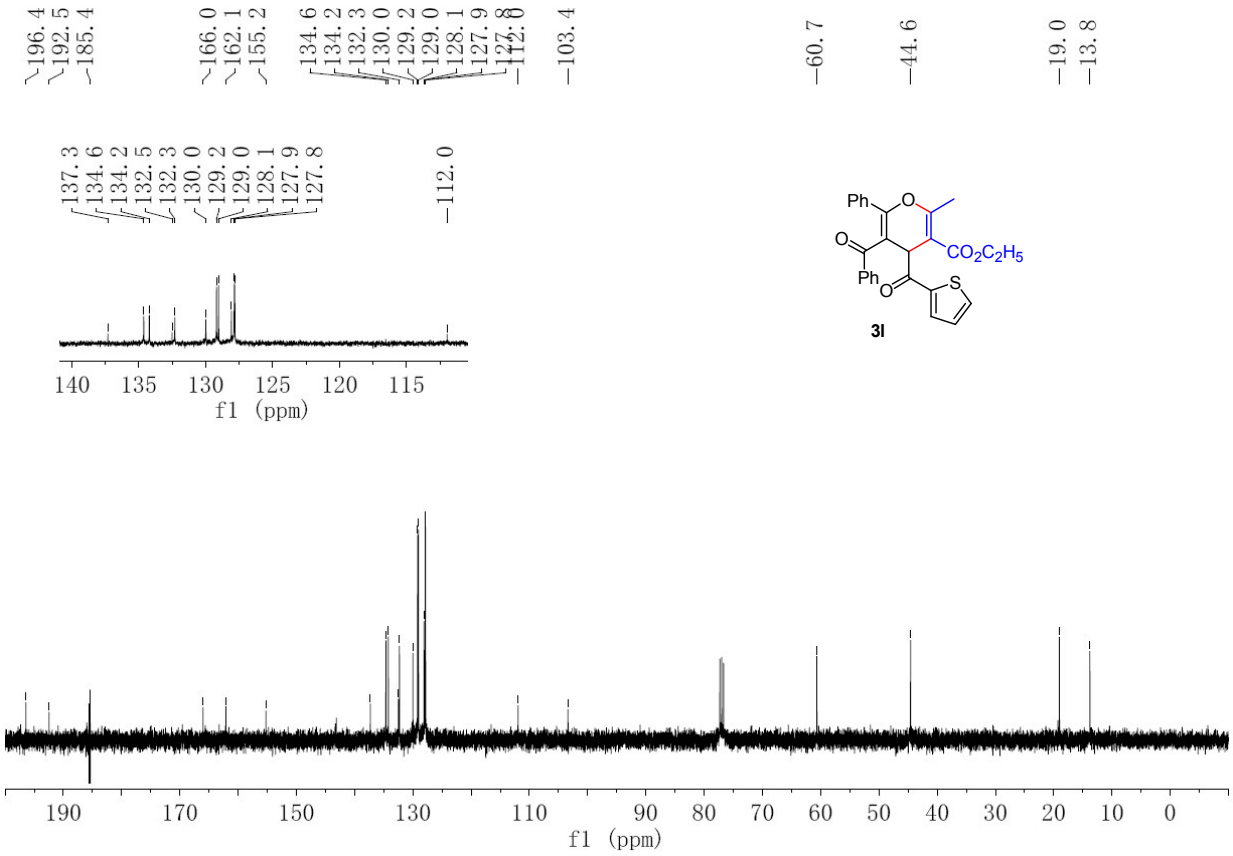


Figure 25. The ^{1}H NMR (400M Hz, $CDCl_3$) of **3m**.

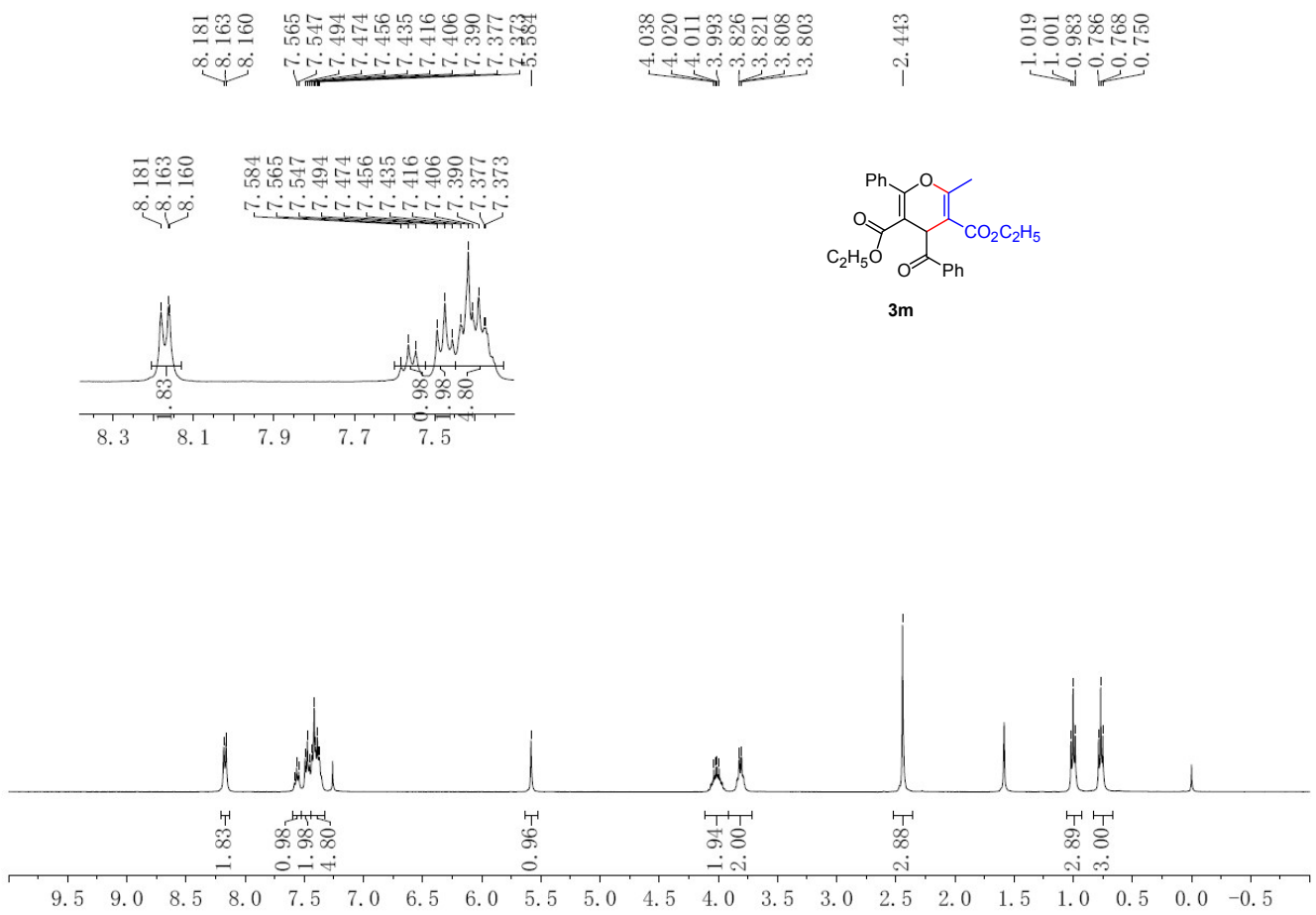


Figure 26. The ^{13}C NMR (100M Hz, $CDCl_3$) of **3m**.

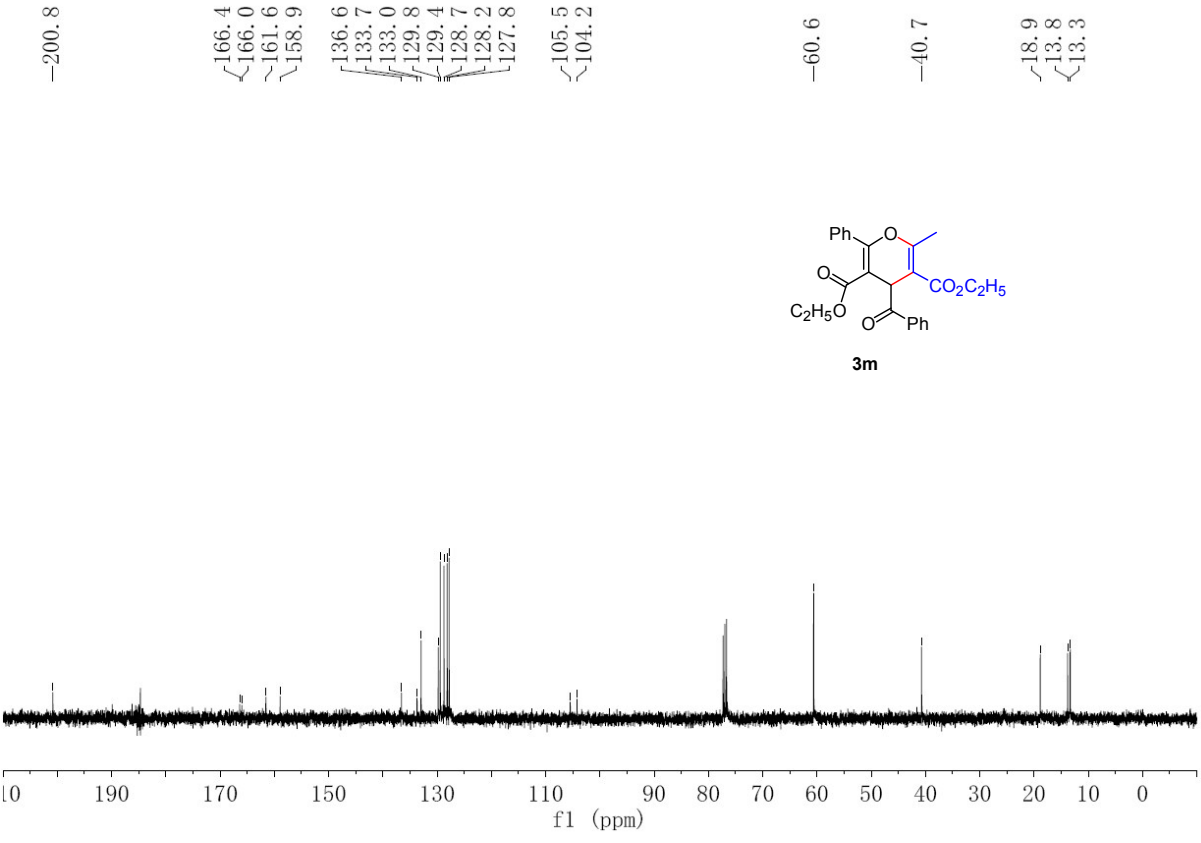


Figure 27. The ^{1}H NMR (400M Hz, $CDCl_3$) of **3n**.

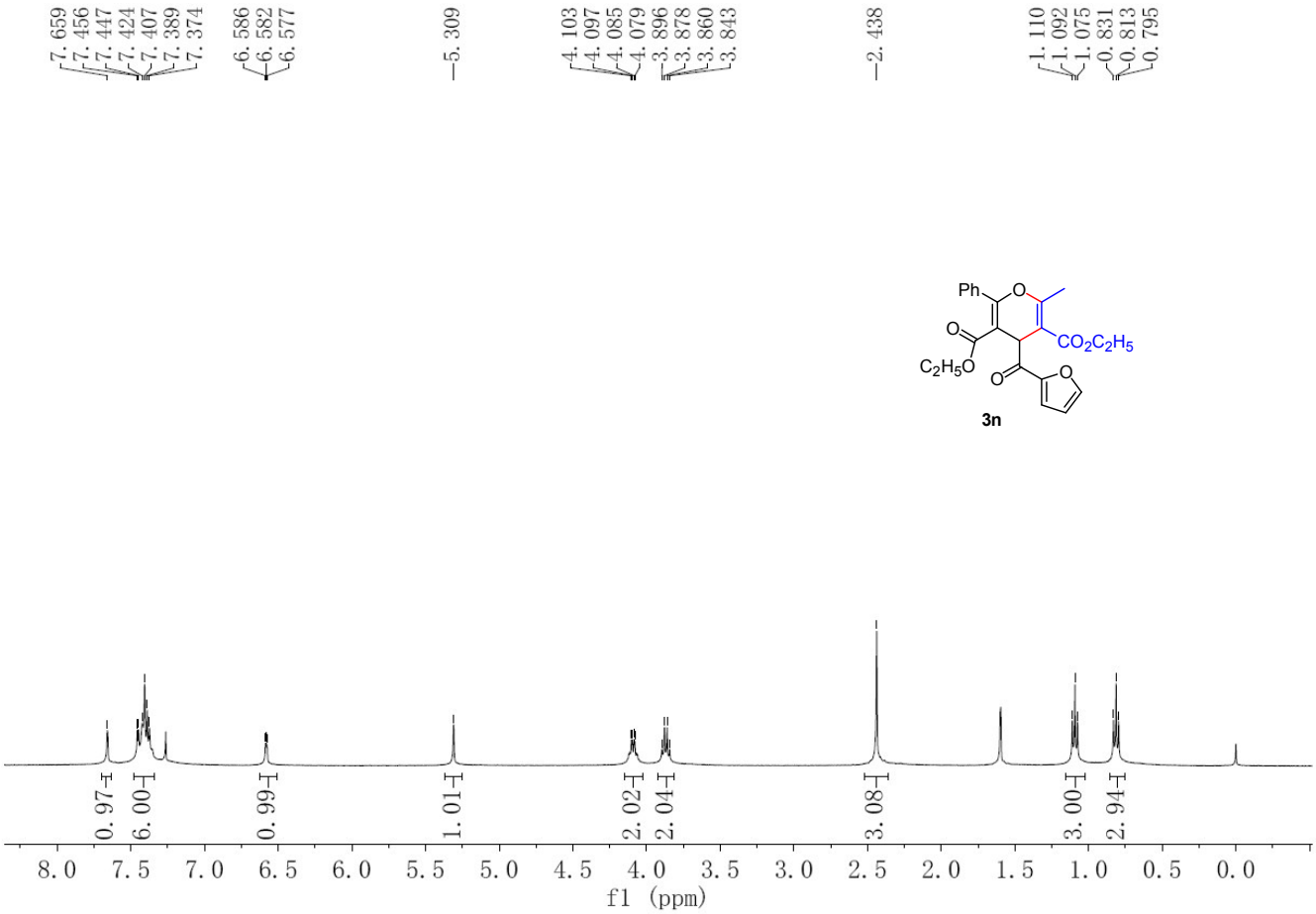


Figure 28. The ^{13}C NMR (150M Hz, $CDCl_3$) of **3n**.

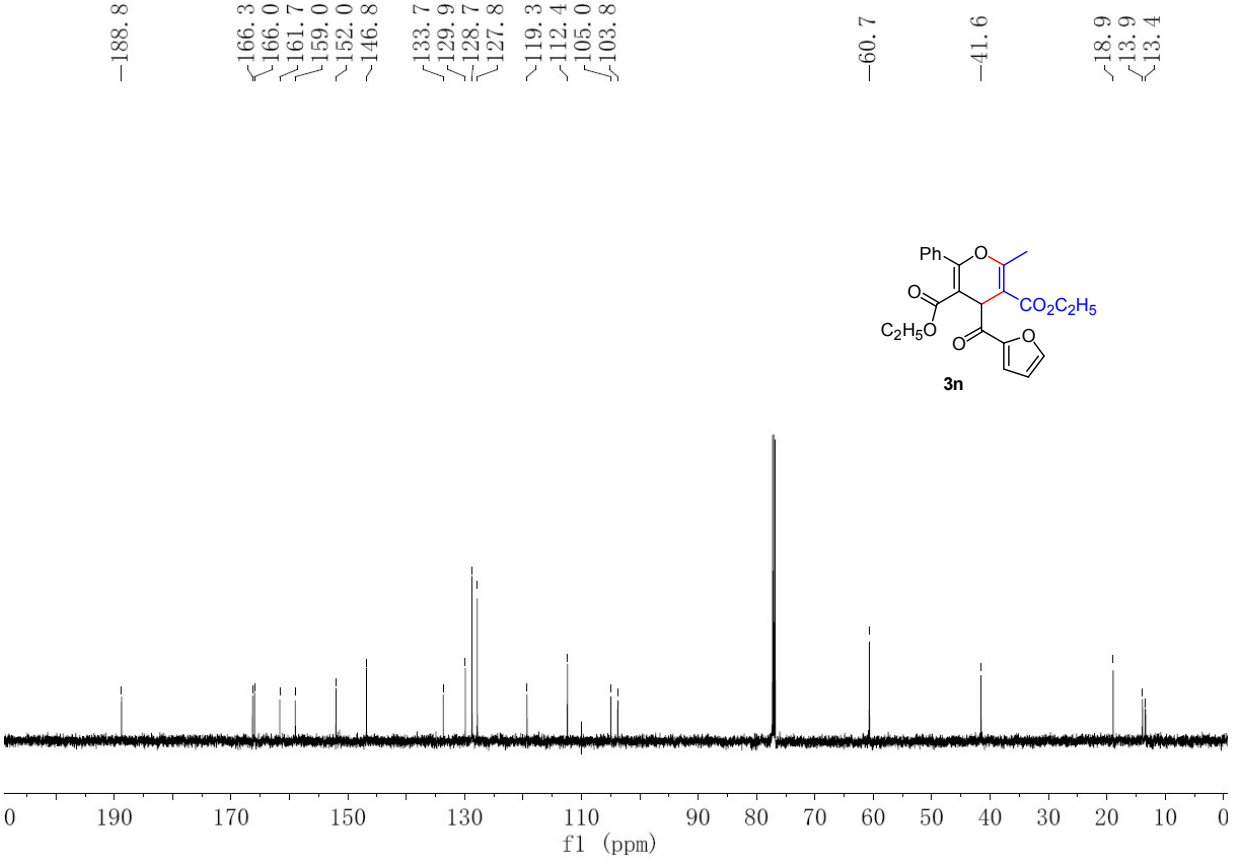


Figure 29. The ^{1}H NMR (600M Hz, $CDCl_3$) of **3o**.

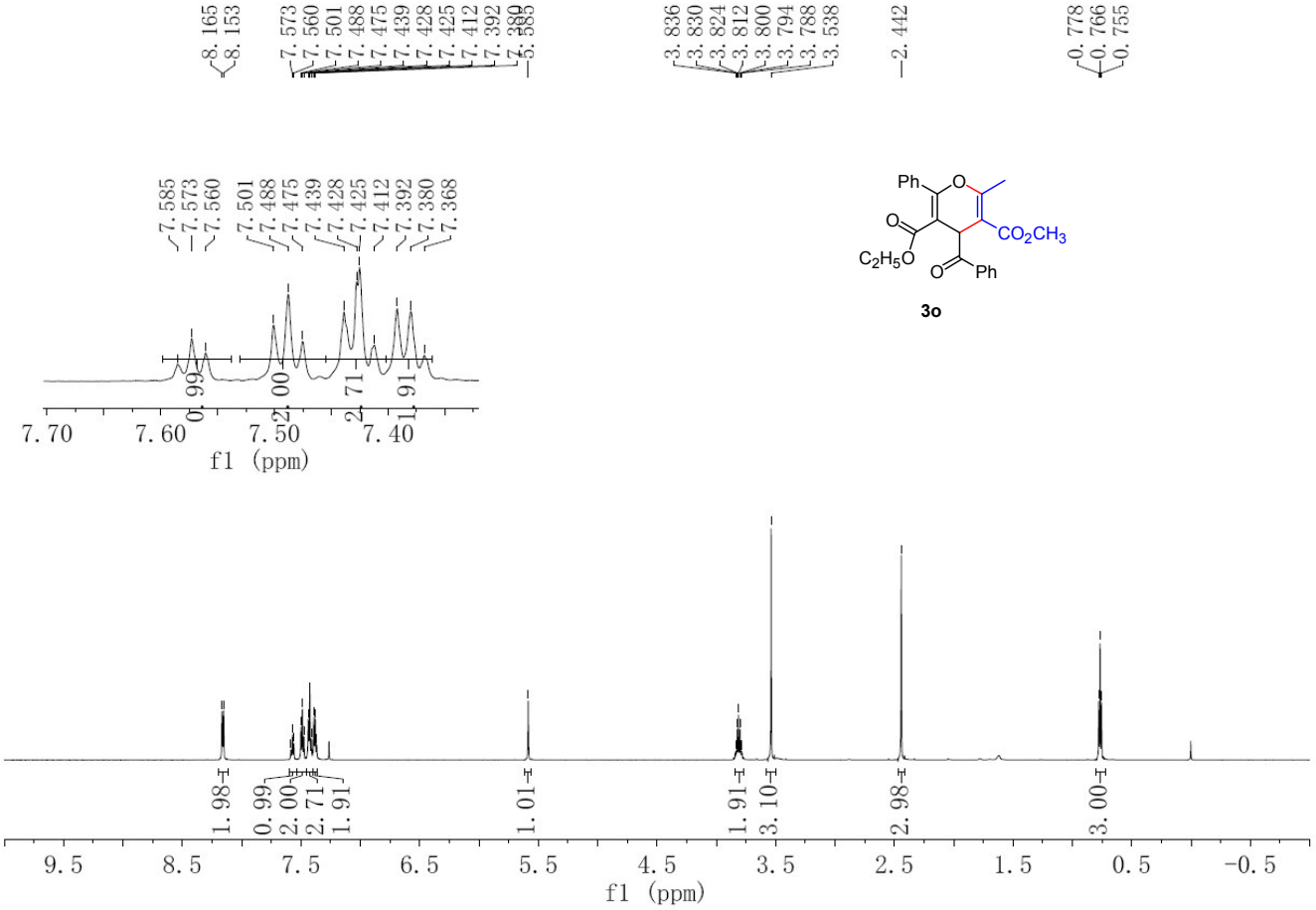


Figure 30. The ^{13}C NMR (150M Hz, $CDCl_3$) of **3o**.

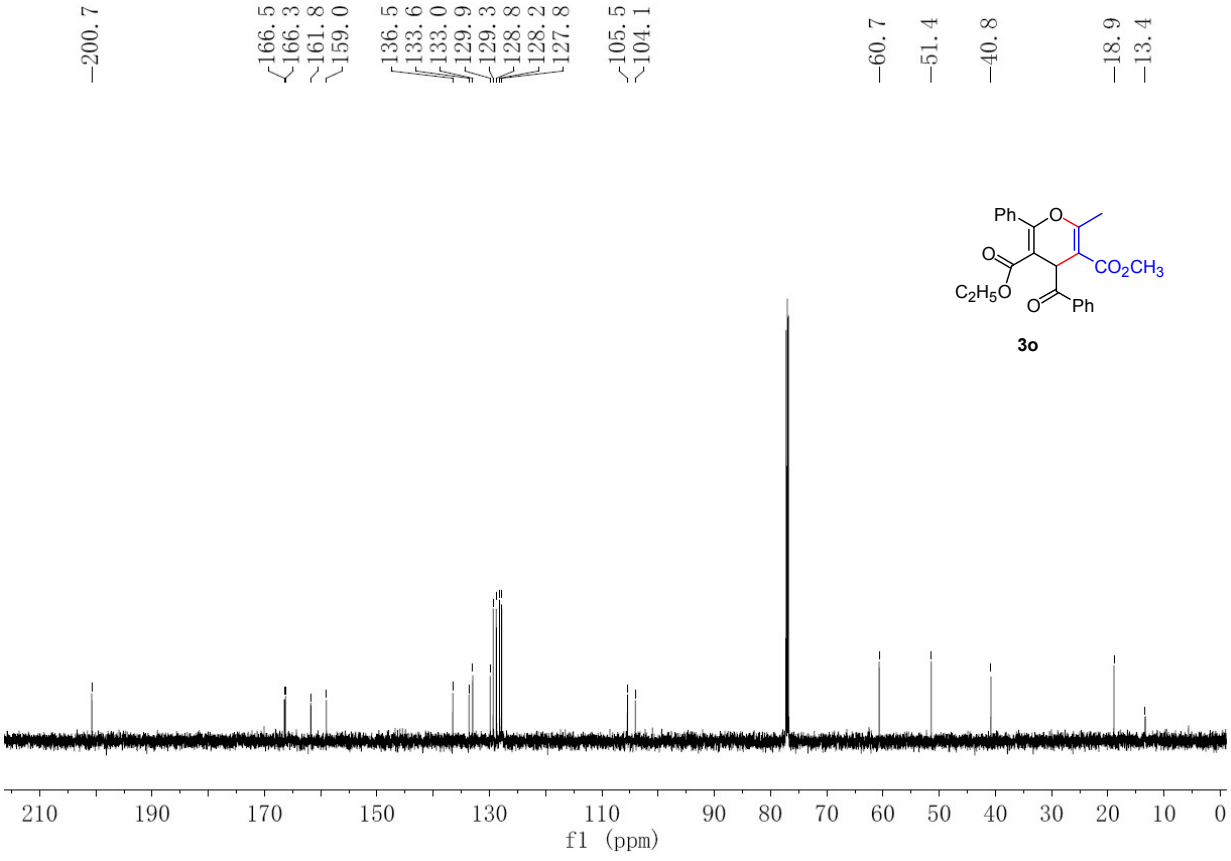


Figure 31. The ^{1}H NMR (600M Hz, $CDCl_3$) of **3p**.

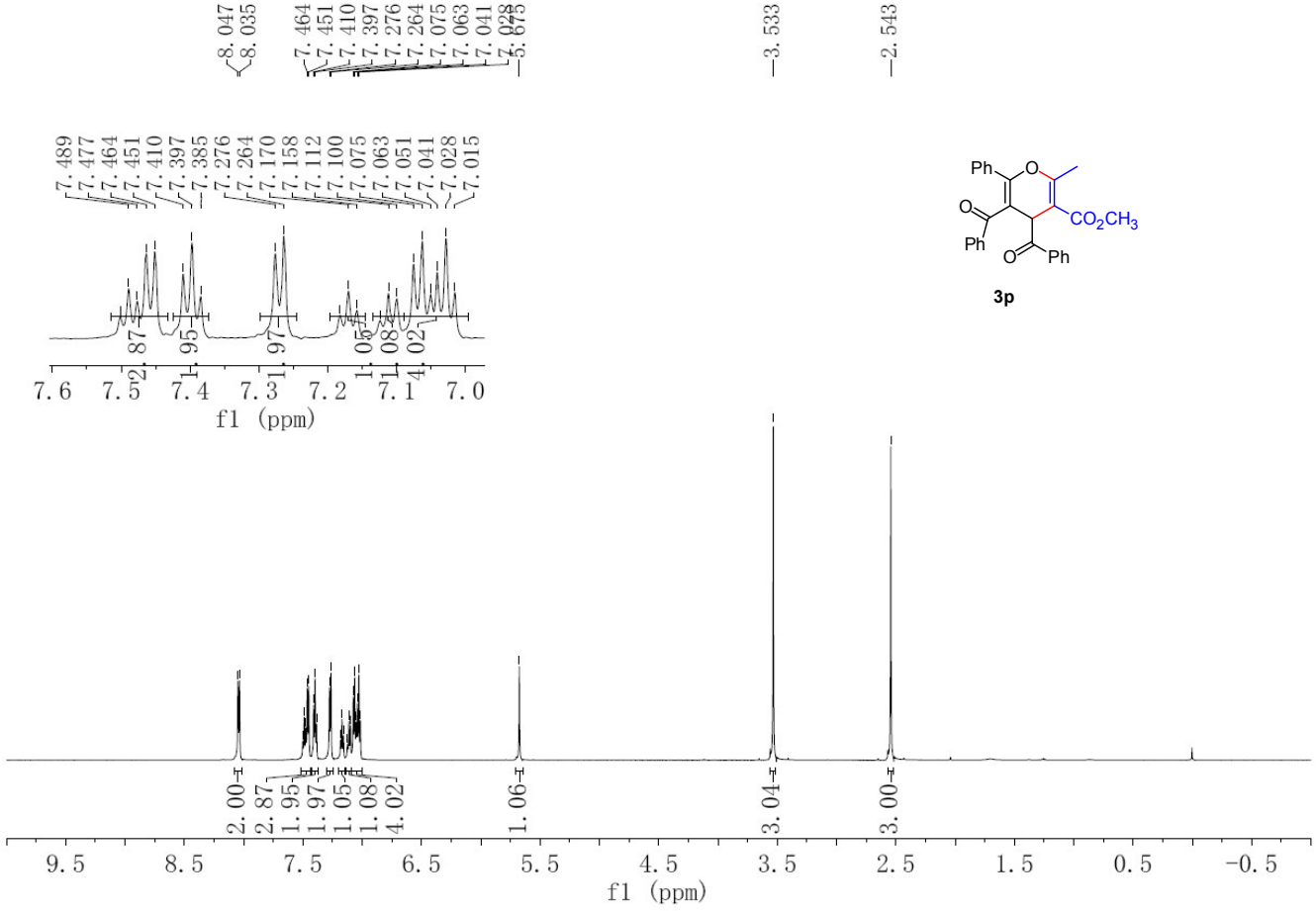


Figure 32. The ^{13}C NMR (150M Hz, $CDCl_3$) of **3p**.

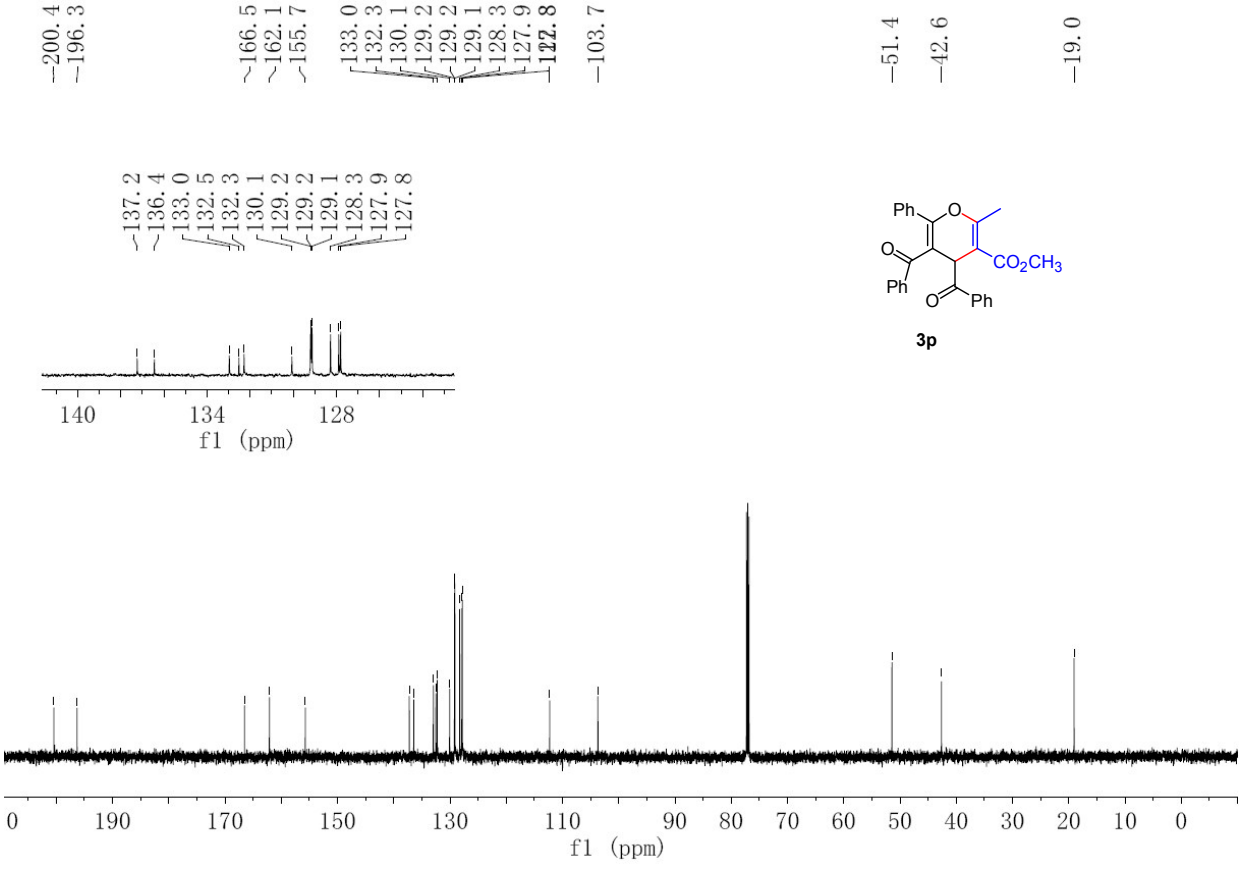


Figure 33. The ^{1}H NMR (400M Hz, DMSO-d6) of **3q**.

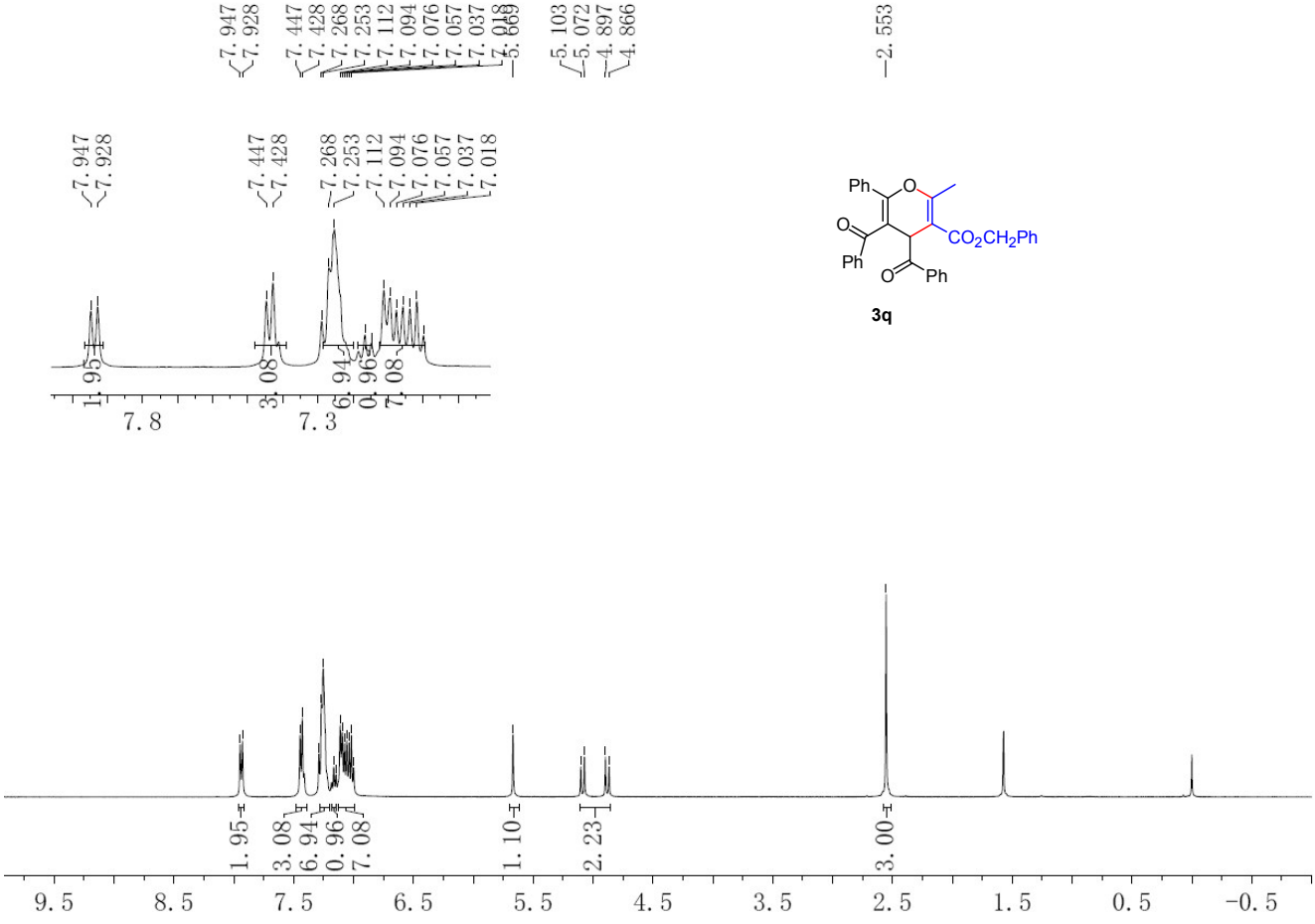


Figure 34. The ^{13}C NMR (100M Hz, $CDCl_3$) of **3q**.

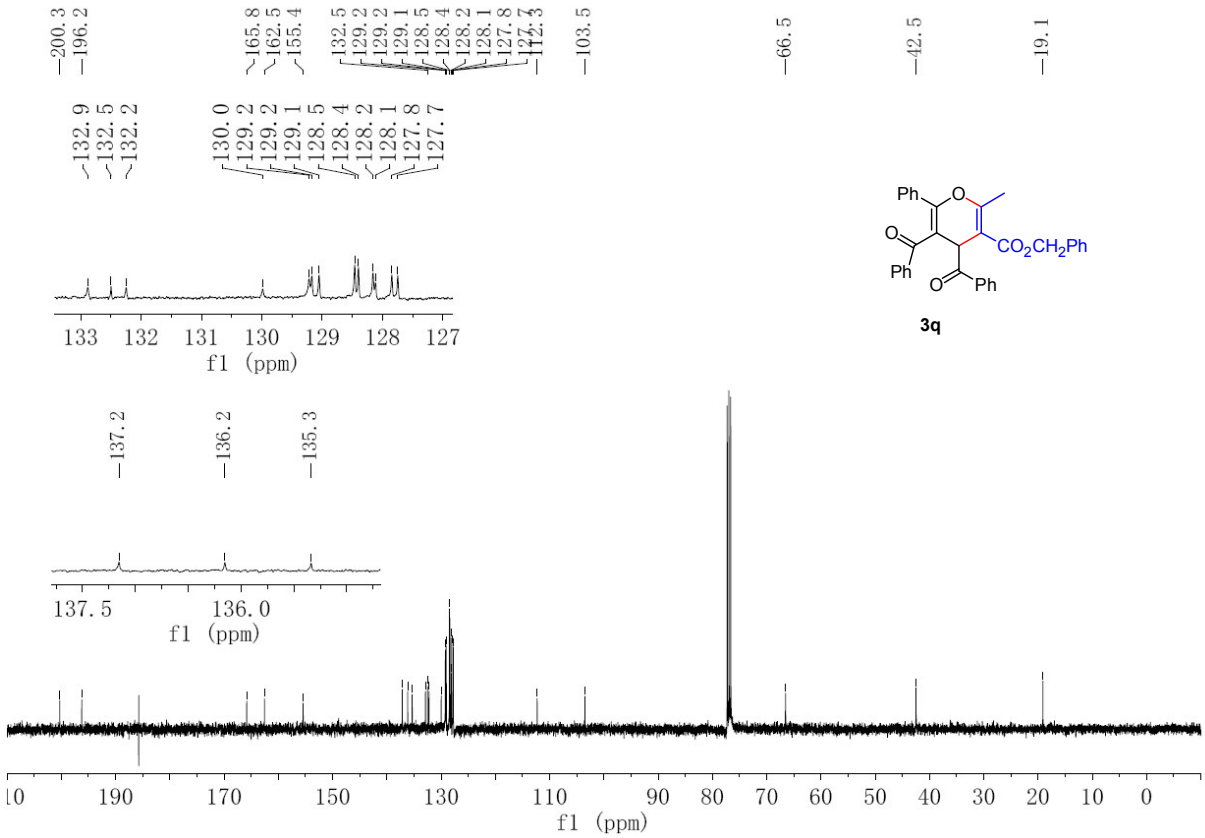


Figure 35. The ^{1}H NMR (400M Hz, CDCl3) of **3r**.

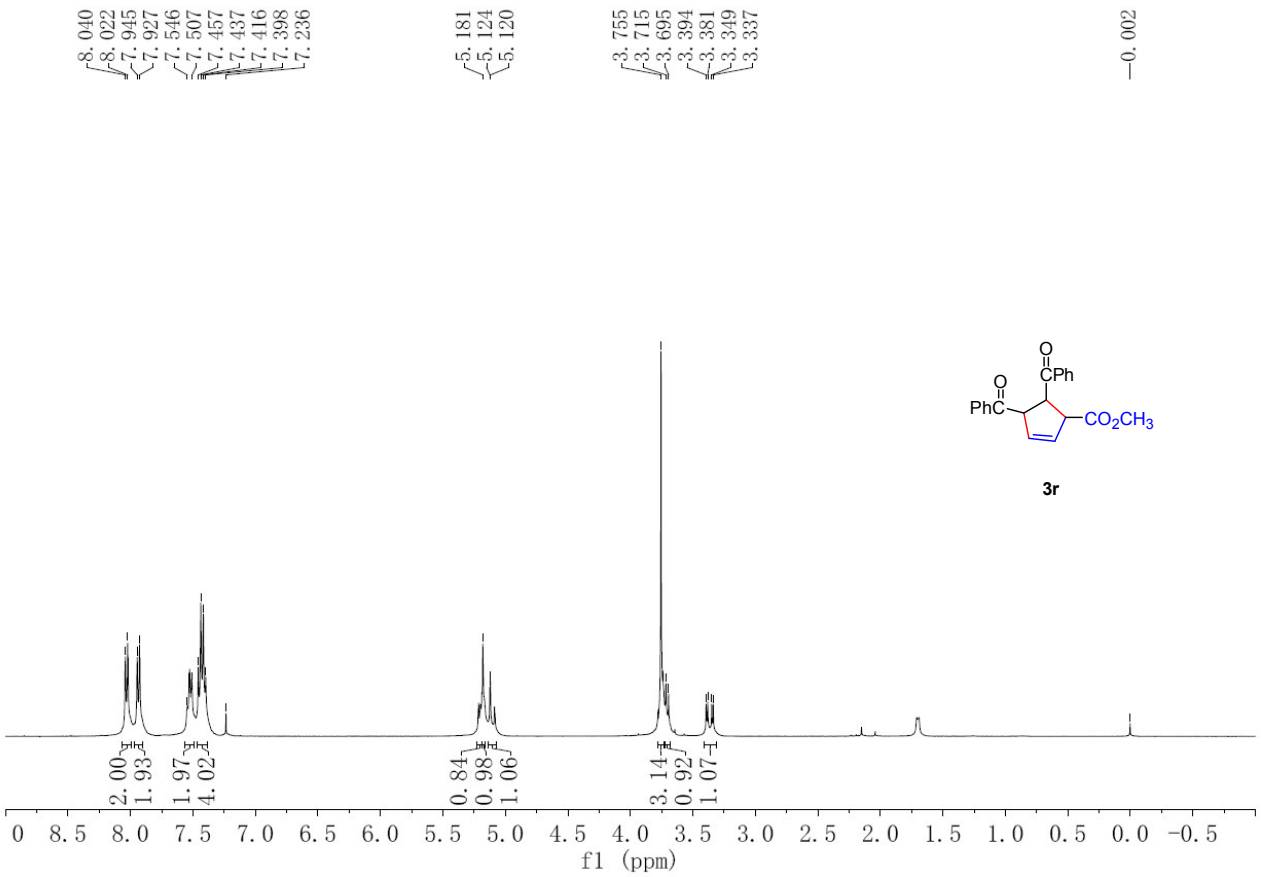
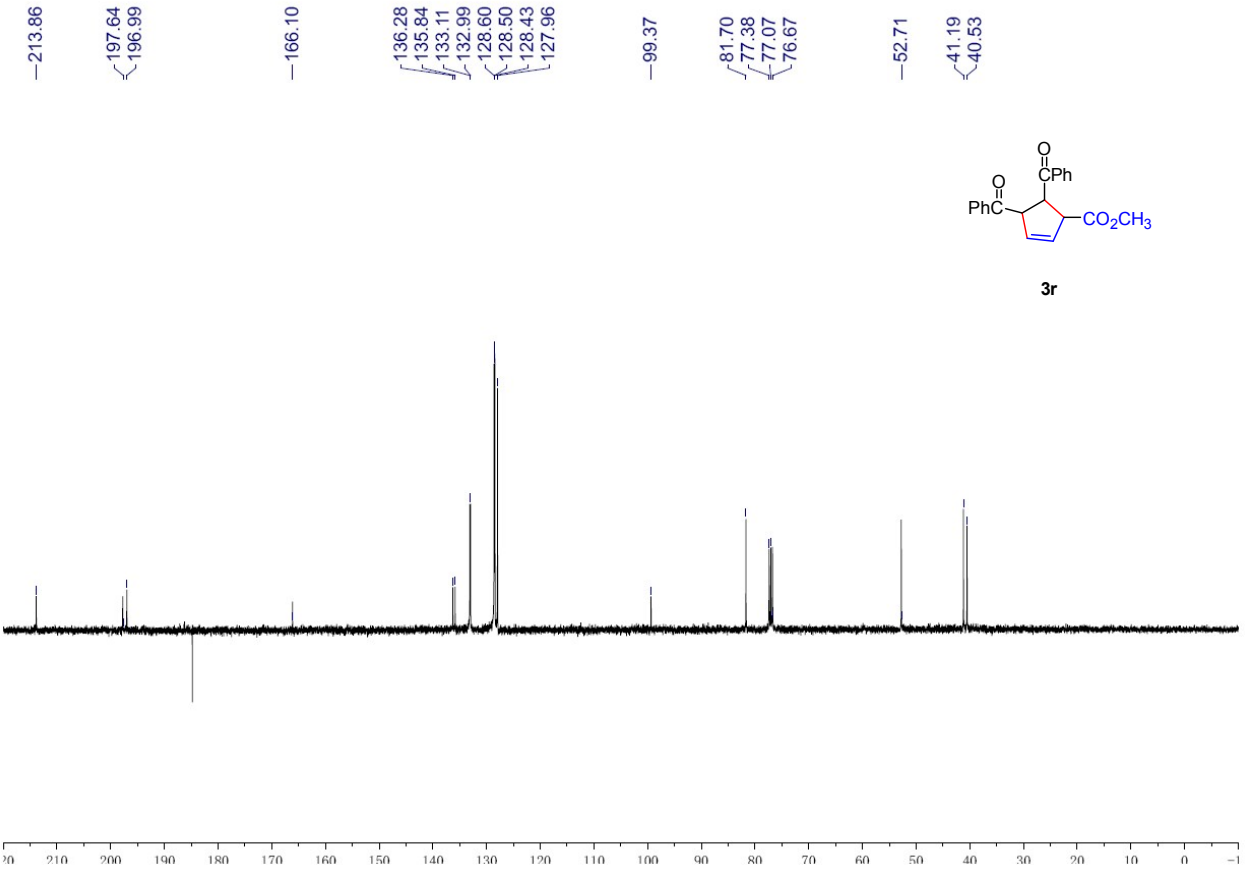


Figure 36. The ^{13}C NMR (100M Hz, $CDCl_3$) of **3r**.



5. X-ray crystal structure of 3q

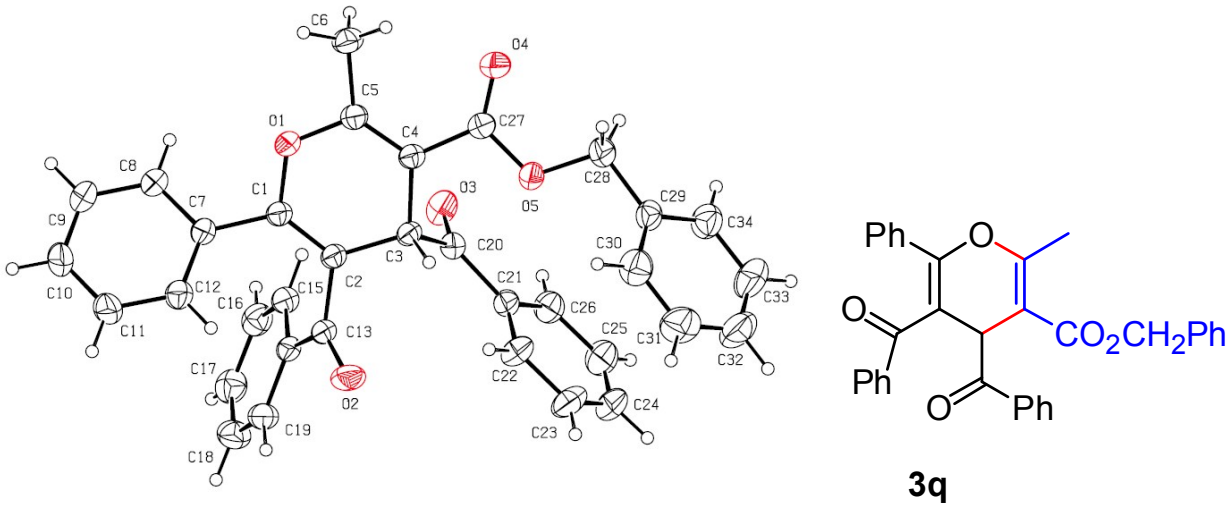


Figure 37. X-ray crystal structure of compound **3q**.

Single crystal of compound **3q** was obtained from the mixed solvents of dicholomethane and n-hexane. CCDC: 1483768 contains the supplementary crystallographic data which can be obtained free of charge from The Cambrige Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Crystal data. C_{34} H_{26} O_5, M = 514.55, triclinic, a = 10.122(1) Å, b = 11.360(2) Å, c = 12.485(2) Å, V = 1316.4(3) Å^3.