SUPPORTING INFORMATION

Phosphine-mediated Domino Sequence of Salicylaldehyde with But-3-yn-2-one: Rapid Access to Chromanone

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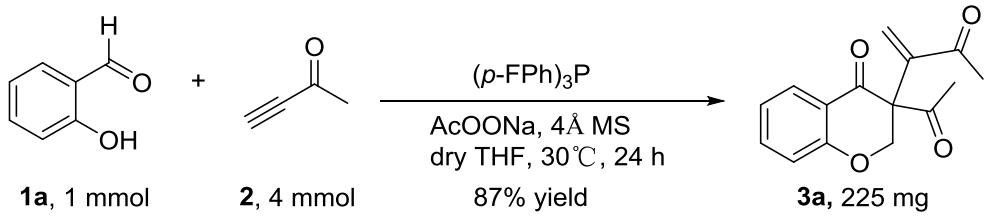
Table of Contents

1. General Information

Unless otherwise noted, all solvents and reagents were purchased from commercial suppliers and used without further purification. Flash chromatography was carried out on silic gel (200-300 mesh, Petroleum Ether/EtOAc solvent systems). ^{1}H NMR spectra were recorded at 400 MHZ. The chemical shifts were recorded in ppm relative to teramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s, single; d, doublet; t, triplet; m, multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHZ with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as an internal standard. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES+ Mass spectrometer and acetonitrile was used to dissolve the sample.

2. Scale-up Experiment



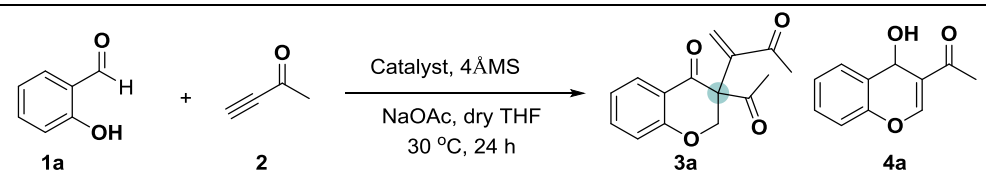
1a, 1 mmol **2**, 4 mmol 87% yield **3a,** 225 mg

Sodium acetate (0.5 mmol, 41 mg, 0.5 equiv.) and 4Å MS (250 mg) were added to a solution of salicylic aldehydes **1a** (1.0 mmol, 122 mg, 1.0 equiv.) and (p-FPh)$_3$P (0.5 mmol, 158 mg, 0.5 equiv.) in anhydrous THF (5.0 mL). After well-mixed, but-3-yn-2-one **2** (2.5 mmol, 170 mg, 2.5 equiv.) was added and the resulting mixture was stirred at 30 ℃ for 12 h. Subsequently, another portion of **2** (1.5 mmol, 102 mg, 1.5 equiv.) and (p-FPh)$_3$P (0.2 mmol, 63 mg, 0.2 equiv.) were added and reacted for an additional 12 h. Following, the solvent was concentrated under reduced pressure and the residue was purified by flash chromatography using silica gel (EtOAc/PE =1:9) to obtain the product **3a**.

3. Table S1. Investigation of asymmetric synthesis

Several chiral phosphine catalyst including (*S*)-(-)-BINAP, (*S*)-(-)-TolBINAP and (-)-DIOP were also investigated, but only giving 4-hydroxy-4*H*-chromene **4a** as product. The results are summarized in Table **S1** (entries 1-3). Additionally, we also tried to

test the ee value of the obtained 4-hydroxy-4*H*-chromene **4a**. However, at current stage, the enantiomers of 4-hydroxy-4*H*-chromene **4a** could not be separated by a set of chiral column including IG, IA, OD-H, OJ-H, AD-H.

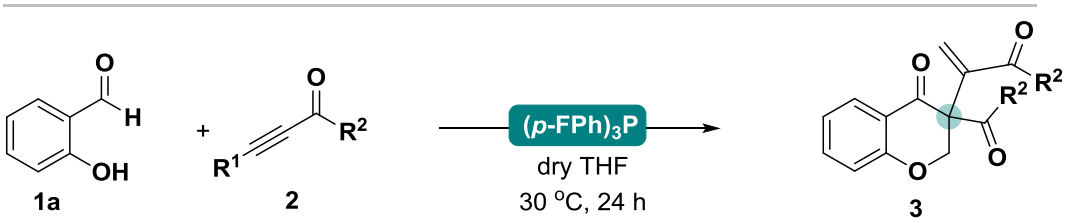


1a 2 3a 4a

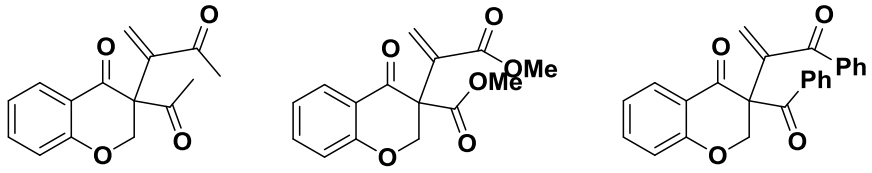
Entry	Solvent	Catalyst	Additive	T (℃)	Yield (4/3a)	ee
1	Dry THF	(*S*)-(-)-BINAP	4Å MS, NaOAc	30	65/0	--
2	Dry THF	(*S*)-(-)-TolBINAP	4Å MS, NaOAc	30	70/0	--
3	Dry THF	(-)-DIOP	4Å MS, NaOAc	30	61/0	--

[a]Unless otherwise noted, reaction were performed with : **1a** (1.0 equiv, 0.2 mmol), **2** (2.5 equiv, 0.5 mmol), 4Å MS (50 mg), NaOAc (0.5 equiv, 0.1 mmol) and Catalyst (0.2 equiv, 0.04 mmol) in anhydrous THF (1.0 ml) at 30 ℃ for 12 h, and then another portion of **2** (1.5 equiv, 0.3 mmol) and catalyst (15 mmol%, 0.03 mmol) were added and stirred at 30 ℃ for an additional 12 h, isolated yield.

4. Scheme S1. Investigation of the substrate scope for yones.



1a 2 3



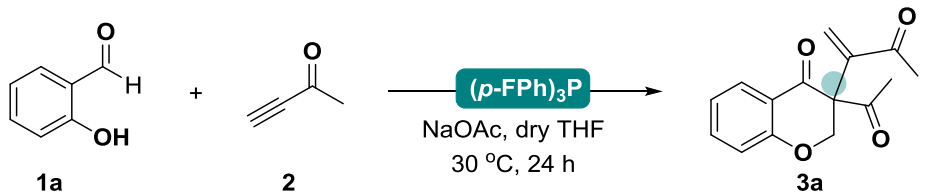
R¹ = TMS; **R²** = Me
62%

R¹ = H; **R²** = CO_2Me
nr.

R¹ = H; **R²** = Ph
nd.

5. Mechanistic studies

In situ ^{31}P *NMR*



1a 2 3a

One designated reaction were set up parallelly according to the following conditions: Sodium acetate (0.2 mmol, 0.5 equiv) was added to a solution of salicylaldehyde **1a** (0.4 mmol, 1.0 equiv) and (p-FPh)$_3$P (0.2 mmol, 0.5 equiv) in anhydrous THF (2.0 mL). But-3-yn-2-one **2** (1.0 mmol, 2.5 equiv) was then added and the resulting mixture was stirred at 30 ℃. The reaction was stopped over time interval of 5 min, 30 min, 1 h, 2 h, 6 h, 18 h. The reaction solution was analyzed by ^{31}P NMR in $CDCl_3$.

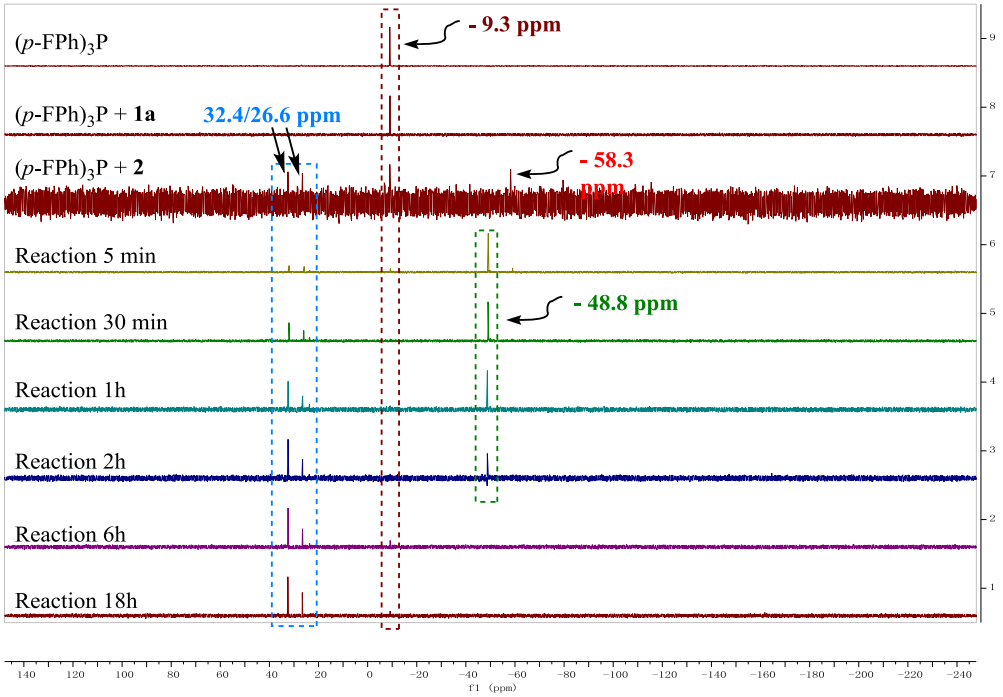
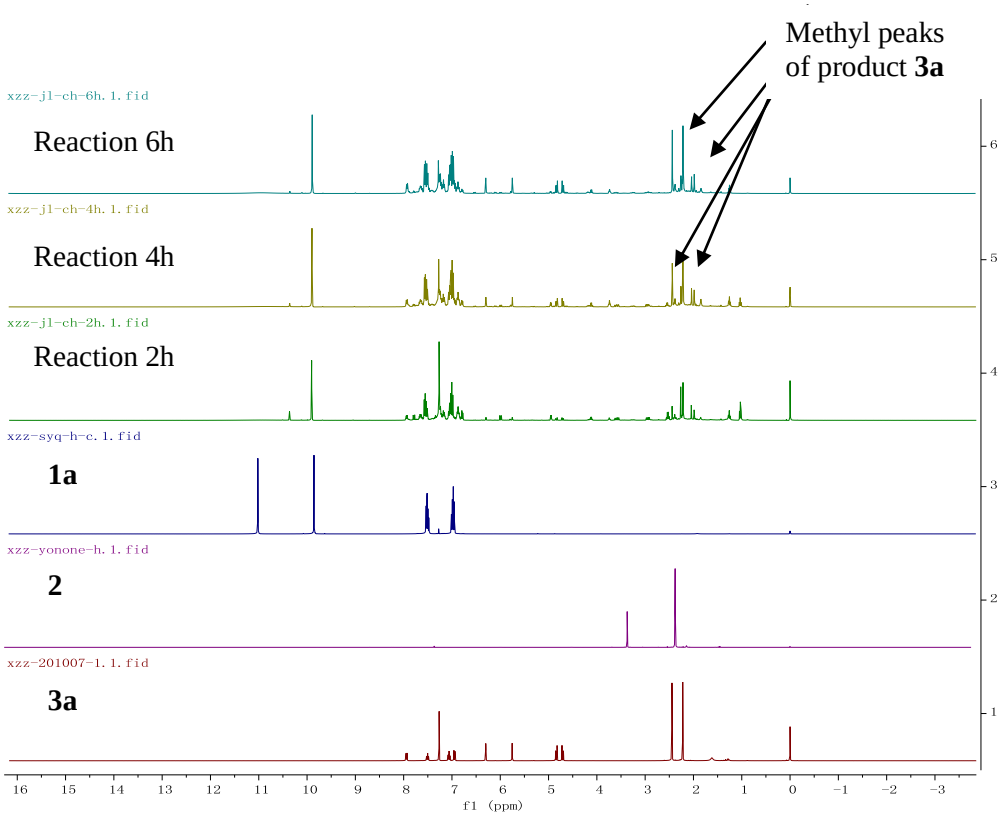


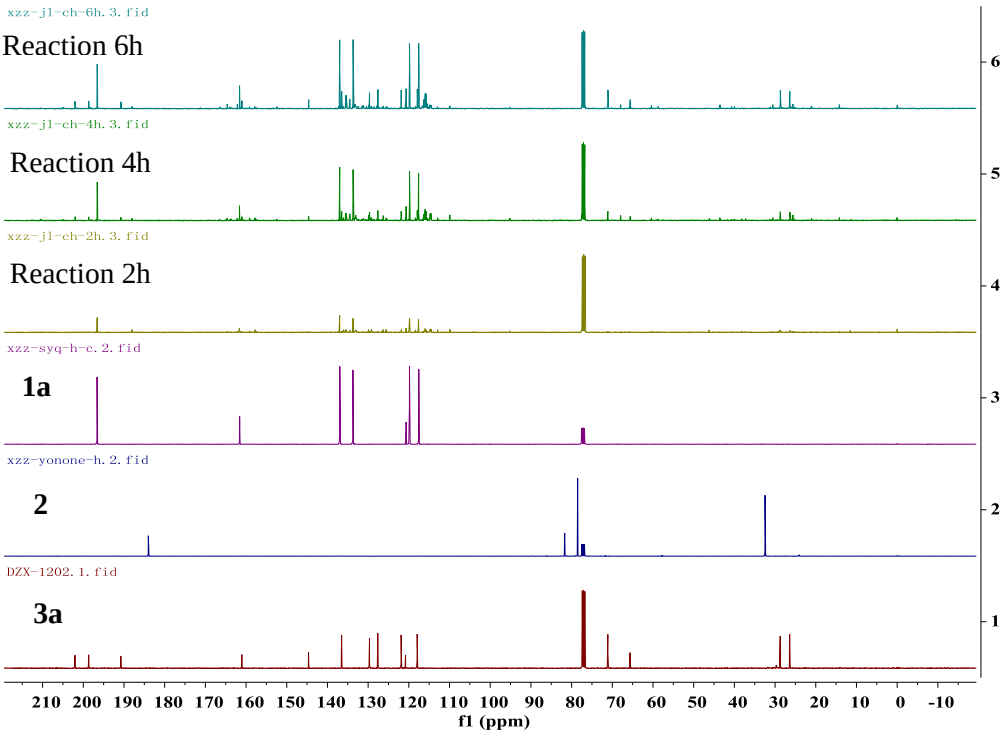
Figure S1. *In situ* ^{31}P NMR studies

In situ NMR monitoring:

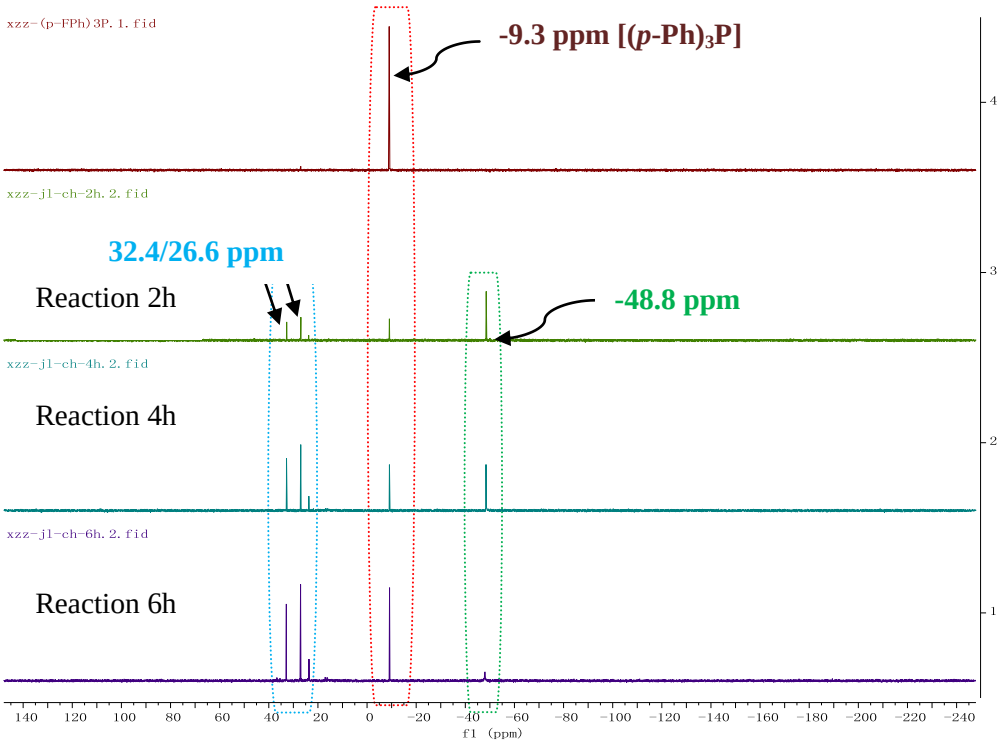
^{1}H NMR:



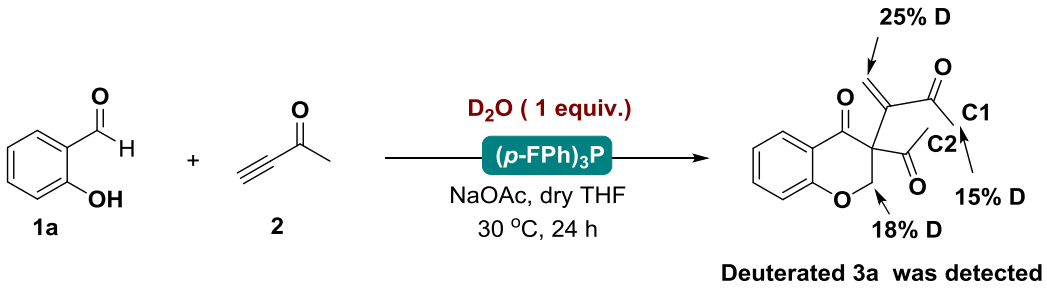
^{13}C NMR:



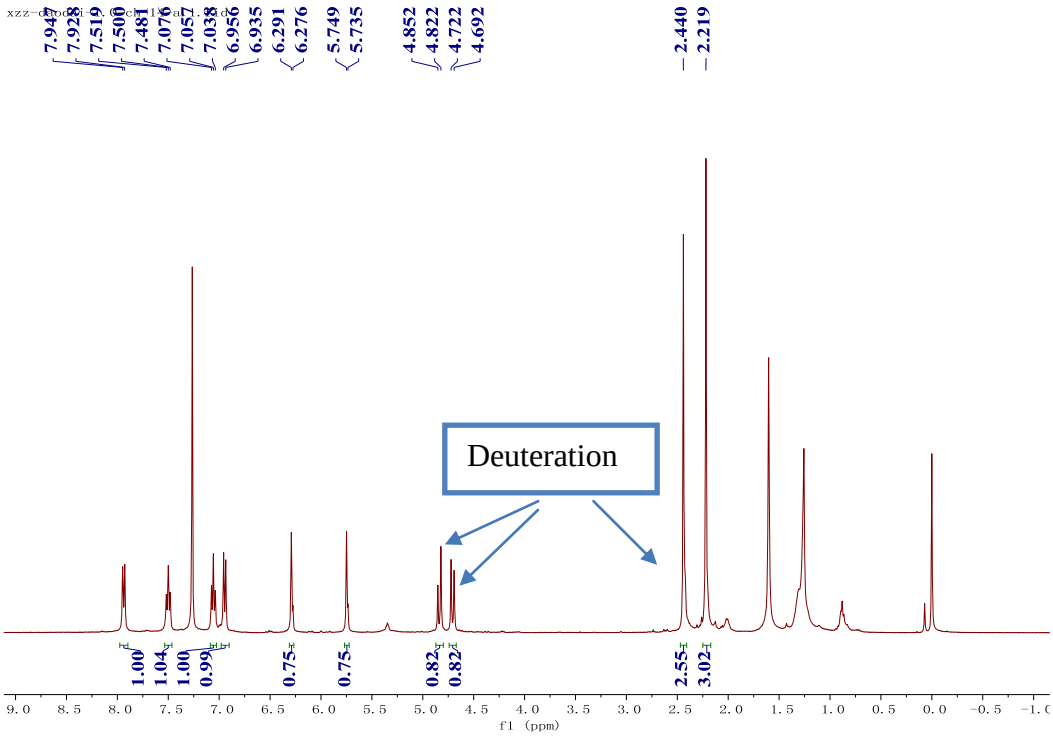
^{31}P NMR:

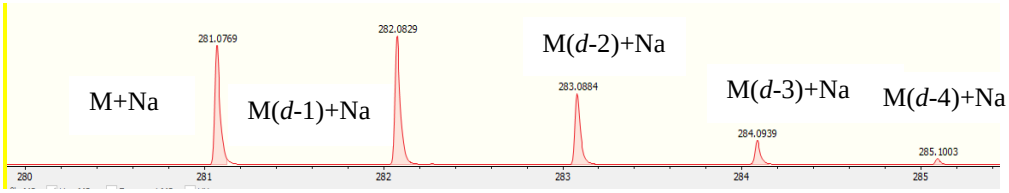


Labelling Experiments

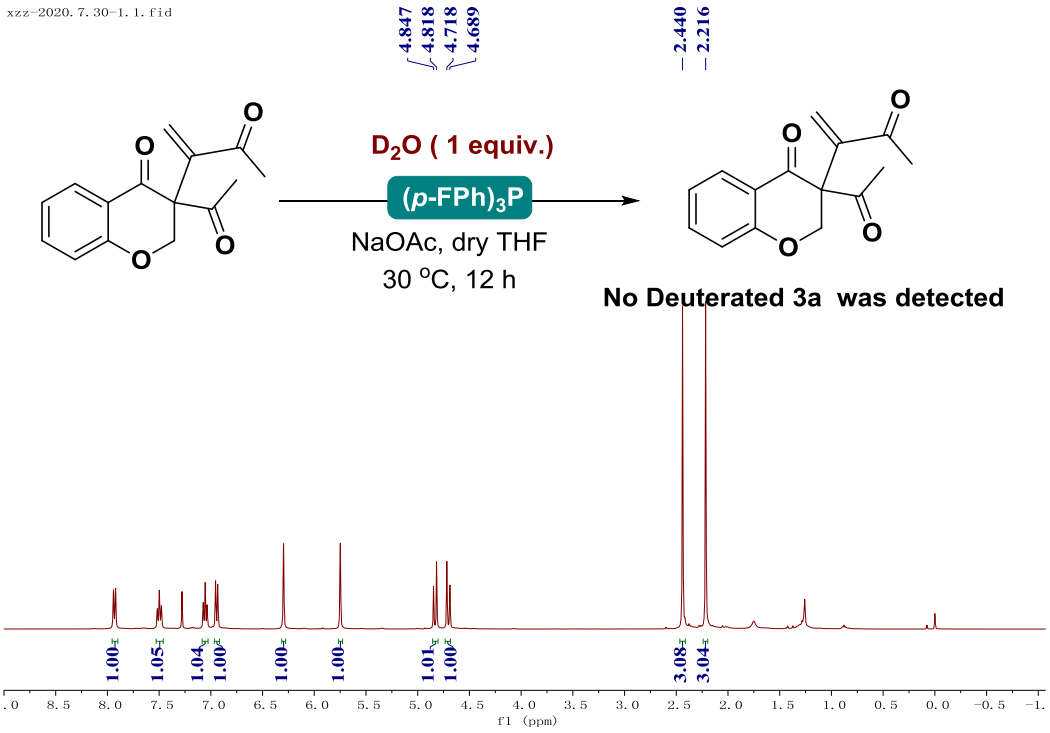


One designated reaction was set up according to the general procedure, but replacing 4Å MS with 1.0 equiv of D_2O. And the corresponding deuterated product was detected by ^1H NMR and HRMS.

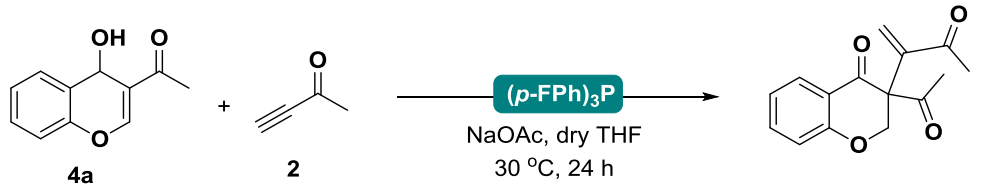




Another designated reaction was set up parallelly according to the following conditions: $(p\text{-FPh})_3P$ (0.1 mmol, 0.5 equiv) was added to a solution of product **3a** (0.2 mmol, 1.0 equiv), D_2O (0.2 mmol, 1.0 equiv), sodium acetate (0.1 mmol, 0.5 equiv) in anhydrous THF (1.0 mL). The resulting mixture was stirred at 30 ℃ for 12 h. the solvent was concentrated under reduced pressure and the residue was purified by flash chromatography using silica gel (EtOAc/PE =1:9). No deuteraed on product **of 3a** was detected by ^{1}H NMR**.**



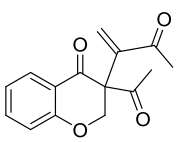
Verification of intermediate



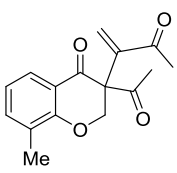
Entry	Solvent	Catalyst	Additive	Time (h)	Yield
1	Dry THF	(p-FPh)$_3$P	--	24	Nd.
2	Dry THF	(p-FPh)$_3$P	NaOAc	24	Nd.

[a]Reaction conditions: **4a** (1.0 equiv, 0.05 mmol), **2** (2.0 equiv, 0.1 mmol), catalyst (0.4 equiv,0.02 mmol), additive (0.5 equiv, 0.025 mmol) and dry THF (0.2 M, 0.25 mL), 24 h, monitored by TLC

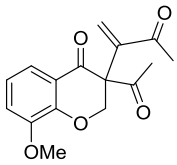
6. Characterization data of compounds (3)



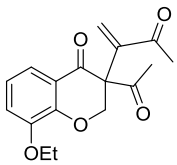
3a: yellow solid; yield 46.5 mg (90%) from 24.4 mg of **1a**; m.p. 115-117 ℃; **IR** (neat) ν 3360, 2940, 2074, 1710, 1175, 956, 759 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.94 (dd, J = 7.9, 1.5 Hz, 1H), 7.61-7.43 (m, 1H), 7.06 (t, J = 7.1 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.30 (d, J = 1.2 Hz, 1H), 5.75 (d, J = 1.3 Hz, 1H), 4.84 (d, J = 11.8 Hz, 1H), 4.70 (d, J = 11.8 Hz, 1H), 2.45 (s, 3H), 2.22 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 202.0, 198.7, 190.8, 161.0, 144.6, 136.5, 129.7, 127.6, 121.9, 120.8, 118.0, 71.1, 65.6, 28.7, 26.4; **HRMS** (ESI): $C_{15}H_{14}NaO_4^+$, [M+Na] $^+$ Calcd 281.0784, Found 281.0781.



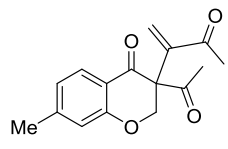
3b: yellow solid; yield 36.5 mg (67%) from 27.2 mg of **1b**; m.p. 164-166 ℃; **IR** (neat) *v* 3391, 2928, 1997, 1691, 1186, 953, 762 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.30 (s, 1H), 5.75 (s, 1H), 4.84 (d, *J* = 11.6 Hz, 1H), 4.73 (d, *J* = 11.6 Hz, 1H), 2.45 (s, 3H), 2.22 (s, 3H), 2.20 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 202.3, 198.8, 191.2, 159.3, 144.7, 137.4, 129.6, 127.3, 125.2, 121.3, 120.5, 71.0, 65.4, 28.8, 26.4, 15.5; **HRMS** (ESI): $C_{16}H_{16}NaO_4^+$, [M+Na] $^+$ Calcd 295.0941, Found 295.0981.



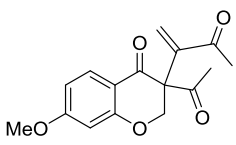
3c; yellow solid; yield 37.5 mg (65%) from 30.4 mg of **1c**; m.p. 140-142 ℃; **IR** (neat) *v* 3388, 2933, 1948, 1690, 1185, 946, 748 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) *δz* 7.53 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 5.76 (s, 1H), 4.90 (d, *J* = 12.0 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 3.89 (s, 3H), 2.43 (s, 3H), 2.22 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 201.9, 198.6, 190.8, 151.0, 148.7, 144.5, 121.5, 121.4, 118.6, 117.1, 71.7, 65.3, 56.2, 28.8, 26.3; **HRMS** (ESI):$C_{16}H_{16}NaO_5^+$, [M+Na] $^+$ Calcd 311.0890, Found 311.0910.



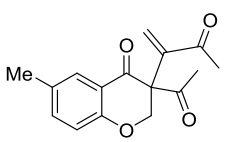
3d: yellow solid; yield 31.4 mg (52%) from 33.2 mg of **1d**; m.p. 151-153 ℃; **IR** (neat) *v* 3343, 2989, 1937, 1770, 1032, 879, 757 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 8.0 Hz, 1H), 6.23 (s, 1H), 5.68 (s, 1H), 4.82 (d, *J* = 12.0 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.05-4.00 (m, 2H), 2.36 (s, 3H), 2.14 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 201.0, 197.5, 189.9, 150.4, 147.1, 143.5, 128.8, 120.7, 120.3, 117.6, 117.5, 70.6, 64.2, 63.9, 27.8, 25.3, 13.7; **HRMS** (ESI): $C_{17}H_{18}NaO_5^+$, [M+Na] $^+$ Calcd 325.1046, Found 325.1024.



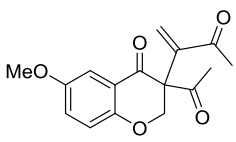
3e: yellow solid; yield 30.5 mg (56%) from 27.2 mg of **1e**; m.p. 176-178 ℃; **IR** (neat) *v* 3365, 2941, 1808, 1571, 1131, 898, 656 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.82 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.74 (s, 1H), 6.28 (d, *J* = 1.2 Hz, 1H), 5.75 (d, *J* = 1.2 Hz, 1H), 4.81 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 2.43 (s, 3H), 2.36 (s, 3H), 2.21 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 202.2, 198.7, 190.4, 161.1, 148.3, 144.8, 129.5, 127.5, 123.3, 118.6, 117.9, 71.1, 65.6, 28.7, 26.4, 22.0; **HRMS** (ESI): $C_{16}H_{16}NaO_4^+$, [M+Na] $^+$ Calcd 295.0941, Found 295.0912.



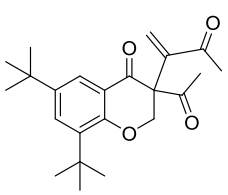
3f: yellow solid; yield 36.9 mg (64%) from 30.4 mg of **1f**; m.p. 139-141 ℃; **IR** (neat) *v* 3396, 2930, 2131, 1686, 1165, 1035, 822 cm^{-1}; **^{1}H NMR** (d_6-DMSO, 400 MHz) δ 7.74 (d, *J* = 8.8 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 6.56 (s, 1H), 6.50 (s, 1H), 5.77 (s, 1H), 4.83 (d, *J* = 11.6 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 3.83 (s, 3H), 2.42 (s, 3H), 2.11 (s, 3H); **^{13}C {^{1}H} NMR** (d_6-DMSO, 100 MHz) δ 202.6, 199.9, 189.2, 166.4, 163.0, 144.2, 130.4, 129.2, 114.7, 111.1, 101.1, 71.4, 65.1, 56.4, 28.4, 26.9; **HRMS** (ESI): $C_{16}H_{16}NaO_5^+$, $[M+Na]^+$ Calcd 311.0890, Found 311.0867.



3g: yellow solid; yield 32.7 mg (60%) from 27.2 mg of **1g**; m.p. 157-159 ℃; **IR** (neat) *v* 3364, 2919, 2071, 1694, 1167, 959, 838 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.71 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.28 (s, 1H), 5.75 (s, 1H), 4.80 (d, *J* = 11.8 Hz, 1H), 4.67 (d, *J* = 11.8 Hz, 1H), 2.43 (s, 3H), 2.32 (s, 3H), 2.21 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 202.1, 198.7, 190.9, 159.1, 144.8, 137.6, 131.4, 129.4, 127.1, 120.4, 117.7, 71.2, 65.7, 28.7, 26.4, 20.4; **HRMS** (ESI): $C_{16}H_{16}NaO_4^+$, $[M+Na]^+$ Calcd 295.0941, Found 295.0922.

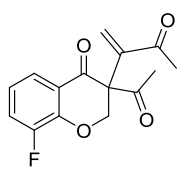


3h: yellow solid; yield 35.8 mg (62%) from 30.4 mg of **1h**; m.p. 173-175 ℃; **IR** (neat) *v* 3378, 2938, 2007, 1693, 1172, 824, 727 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.34 (d, *J* = 2.8 Hz, 1H), 7.11 (dd, *J* = 9.0, 2.8 Hz, 1H), 6.88 (d, *J* = 9.0, 1.2 Hz, 1H), 6.29 (s, *J* = 1.5 Hz, 1H), 5.75 (*J* = 1.6 Hz, 1H), 4.79 (d, *J* = 11.8 Hz, 1H), 4.66 (d, *J* = 11.8 Hz, 1H), 3.81 (s, 3H), 2.44 (s, 3H), 2.22 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 202.0, 198.6, 190.8, 155.8, 154.4, 144.9, 129.4, 125.8, 120.6, 119.2, 107.7, 71.4, 65.7, 55.8, 28.7, 26.4; **HRMS** (ESI): $C_{16}H_{16}NaO_5^+$, $[M+Na]^+$ Calcd 311.0890, Found 311.0871.

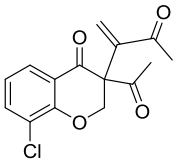


3i: yellow solid; yield 37.0 mg (50%) from 46.9 mg of **1i**; m.p. 181-183 ℃; **IR** (neat) *v* 3345, 2976, 1745, 1508, 1054, 987, 723 cm^{-1}; **^{1}H NMR** (d_6-DMSO, 400 MHz) δ 7.66 (d, *J* = 2.3 Hz, 1H), 7.53 (d, *J* = 2.3 Hz, 1H), 6.46 (d, *J* = 1.2 Hz, 1H), 5.77 (d, *J* = 1.2 Hz, 1H), 4.87 (d, *J* = 11.8 Hz, 1H), 4.71 (d, *J* = 11.8 Hz, 1H), 2.40 (s, 3H), 2.12 (s, 3H), 1.33 (s, 9H), 1.28 (s, 9H); **^{13}C {^{1}H} NMR** (d_6-DMSO, 100 MHz) δ 202.6, 200.0, 191.3, 158.1, 144.2, 143.6, 138.2, 130.8 129.7, 121.1, 120.9, 70.8, 65.3, 35.1, 34.6,

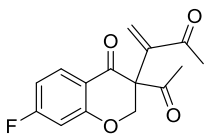
31.5, 29.8, 28.2, 26.9; **HRMS** (ESI): $C_{23}H_{30}NaO_4^+$, [M+Na] $^+$ Calcd 393.2036, Found 393.2012.



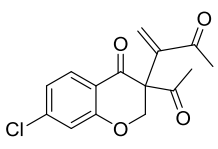
3j: yellow solid; yield 42.0 mg (76%) from 28.0 mg of **1j**; m.p. 170-172 ℃; **IR** (neat) *v* 3387, 2923, 2015, 1701, 1180, 1031, 772 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.64 (d, J = 8.0 Hz, 1H), 7.23-7.20 (m, 1H), 6.94-6.89 (m, 1H), 6.25 (d, J = 7.2 Hz, 1H), 5.68 (d, J = 0.8 Hz, 1H), 4.83 (d, J = 12.0 Hz, 1H), 4.73 (d, J = 12.0 Hz, 1H), 2.37 (s, 3H), 2.14 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 200.4, 197.4, 188.9 (d, $J_{C\text{-}F}$ = 3.3 Hz), 150.4 (d, $J_{C\text{-}F}$ = 249.6 Hz), 148.4 (d, $J_{C\text{-}F}$ = 11.9 Hz), 143.3, 128.8, 121.9, 121.6 (d, $J_{C\text{-}F}$ = 3.9 Hz), 121.3 (d, $J_{C\text{-}F}$ = 17.4 Hz), 120.3 (d, $J_{C\text{-}F}$ = 6.4 Hz), 70.7, 64.7, 27.6, 25.3; **HRMS** (ESI): $C_{15}H_{13}FNaO_4^+$, [M+Na] $^+$ Calcd 299.0690, Found 299.0674.



3k: yellow solid; yield 42.7 mg (73%) from 31.3 mg of **1k**; m.p. 160-162 ℃; **IR** (neat) *v* 3405, 2937, 2292, 1719, 1190, 1048, 742 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.87 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.02 (t, J = 8.0 Hz, 1H), 6.34 (s, 1H), 5.75(s, 1H), 4.93 (d, J = 12.0 Hz, 1H), 4.82 (d, J = 12.0 Hz, 1H), 2.45 (s, 3H), 2.22 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 201.4, 198.5, 190.1, 156.6, 144.2, 136.5, 129.9, 126.2, 122.8, 122.1, 122.0, 71.6, 65.3, 28.6, 26.4; **HRMS** (ESI): $C_{15}H_{13}ClNaO_4^+$, [M+Na] $^+$ Calcd 315.0395, Found 315.0415.

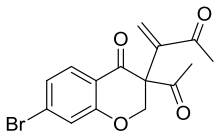


3l: yellow solid; yield 40.3 mg (73%) from 28.0 mg of **1l**; m.p. 155-157 ℃; **IR** (neat) *v* 3391, 2924, 2056, 1681, 1132, 952, 805 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.96 (dd, J = 8.8, 6.5 Hz, 1H), 6.81-6.76 (m, 1H), 6.64 (dd, J = 9.7, 2.4 Hz, 1H), 6.32 (d, J = 1.5 Hz, 1H), 5.76 (d, J = 1.5 Hz, 1H), 4.85 (d, J = 11.9 Hz, 1H), 4.72 (d, J = 11.9 Hz, 1H), 2.45 (s, 3H), 2.21 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 201.7, 198.6, 189.4, 167.7 (d, $J_{C\text{-}F}$ = 257.6 Hz), 162.8 (d, $J_{C\text{-}F}$ = 13.8 Hz), 144.4, 130.2 (d, $J_{C\text{-}F}$ = 11.5 Hz), 129.8, 117.7 (d, $J_{C\text{-}F}$ = 2.4 Hz), 110.5 (d, $J_{C\text{-}F}$ = 22.9 Hz), 104.8 (d, $J_{C\text{-}F}$ = 24.6 Hz), 71.5, 65.5, 28.6, 26.4; **HRMS** (ESI): $C_{15}H_{13}FNaO_4^+$, [M+Na] $^+$ Calcd 299.0690, Found 299.0712.

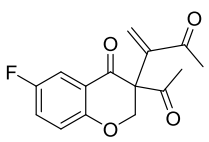


3m: yellow solid; yield 42.2 mg (72%) from 31.3 mg of **1m**; m.p. 133-135 ℃; **IR** (neat) *v* 3389, 2926, 2062, 1674, 1183, 1050, 804 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.80 (d, J = 8.5 Hz, 1H), 6.96

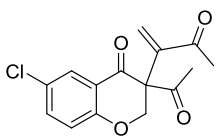
(dd, *J* = 8.5, 1.8 Hz, 1H), 6.90 (d, *J* = 1.8 Hz, 1H), 6.23 (d, *J* = 1.2 Hz, 1H), 5.66 (d, *J* = 1.2 Hz, 1H), 4.76 (d, *J* = 11.9 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 2.36 (s, 3H), 2.13 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) *δ* 200.5, 197.5, 188.7, 160.3, 143.5 141.5, 128.6, 127.8, 121.7, 118.4, 117.1, 70.4, 64.7, 27.5, 25.4; **HRMS** (ESI): $C_{15}H_{13}ClNaO_4^+$, $[M+Na]^+$ Calcd 315.0395, Found 315.0377.



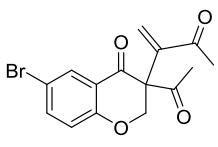
3n: yellow solid; yield 43.8 mg (65%) from 40.2 mg of **1n**; m.p. 185-187 ℃; **IR** (neat) *ν* 3393, 2930, 2056, 1665, 1178, 1041, 864 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) *δ* 7.73 (d, *J* = 8.4 Hz, 1H), 7.13 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.09 (d, *J* = 1.8 Hz, 1H), 6.24 (d, *J* = 1.5 Hz, 1H), 5.67 (d, *J* = 1.5 Hz, 1H), 4.76 (d, *J* = 11.9 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 2.37 (s, 3H), 2.14 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) *δ* 200.5, 197.5, 188.9, 160.2, 143.4, 130.1, 128.8, 127.8, 124.6, 120.2, 118.7, 70.3, 64.6, 27.6, 25.4; **HRMS** (ESI): $C_{15}H_{13}BrNaO_4^+$, $[M+Na]^+$ Calcd 358.9889, Found 358.9864.



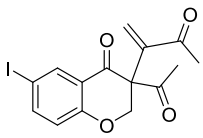
3o: yellow solid; yield 39.2 mg (71%) from 28.0 mg of **1o**; m.p. 144-146 ℃; **IR** (neat) *ν* 3386, 2928, 1701, 1445, 1154, 814, 733 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) *δ* 7.50 (dd, *J* = 8.2, 3.1 Hz, 1H), 7.18-7.13 (m, 1H), 6.86 (dd, *J* = 9.1, 4.2 Hz, 1H), 6.24 (d, *J* = 1.2 Hz, 1H), 5.67 (d, *J* = 1.2 Hz, 1H), 4.74 (d, *J* = 11.9 Hz, 1H), 4.61 (d, *J* = 11.9 Hz, 1H), 2.37 (s, 3H), 2.14 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) *δ* 200.5, 197.4, 189.0 (d, J_{C-F} = 1.8 Hz), 156.4 (d, J_{C-F} = 242.8 Hz), 156.3 (d, J_{C-F} = 1.5 Hz), 143.6, 128.5, 123.1 (d, J_{C-F} = 24.7 Hz), 120.2 (d, J_{C-F} = 6.6 Hz), 118.7 (d, *J* = 7.4 Hz), 111.5 (d, J_{C-F} = 23.6 Hz), 70.4, 64.6, 27.5, 25.3; **HRMS** (ESI): $C_{15}H_{13}FNaO_4^+$, $[M+Na]^+$ Calcd 299.0690, Found 299.0673.



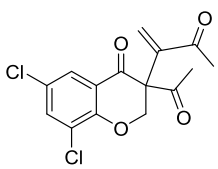
3p: yellow solid; yield 48.6 mg (83%) from 31.3 mg of **1p**; m.p. 167-169 ℃; **IR** (neat) *ν* 3390, 2931, 1696, 1517, 1250, 802, 651 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) *δ* 7.81 (d, *J* = 2.6 Hz, 1H), 7.36 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.84 (d, *J* = 8.9 Hz, 1H), 6.23 (d, *J* = 1.4 Hz, 1H), 5.67 (d, *J* = 1.4 Hz, 1H), 4.74 (d, *J* = 11.9 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 2.36 (s, 3H), 2.13 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) *δ* 200.4, 197.4, 188.7, 158.5, 143.5, 135.3, 128.6, 126.4, 125.8, 120.6, 118.7, 70.3, 64.6, 27.5, 25.3; **HRMS** (ESI): $C_{15}H_{13}ClNaO_4^+$, $[M+Na]^+$ Calcd 315.0395, Found 315.0383.



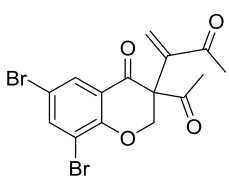
3q: yellow solid; yield 41.1 mg (61%) from 40.2 mg of **1q**; m.p. 191-193 ℃; **IR** (neat) *v* 3389, 2939, 1697, 1446, 1228, 802, 641 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) *δ* 8.04 (d, *J* = 2.4 Hz, 1H), 7.57 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 6.32 (d, *J* = 1.3 Hz, 1H), 5.75 (d, *J* = 1.3 Hz, 1H), 4.82 (d, *J* = 11.9 Hz, 1H), 4.70 (d, *J* = 11.9 Hz, 1H), 2.44 (s, 3H), 2.21 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) *δ* 201.4, 198.4, 189.6, 159.9, 144.4, 139.1, 130.0, 129.8, 122.0, 120.0, 114.6, 71.2, 65.6, 28.6, 26.4; **HRMS** (ESI): $C_{15}H_{13}BrNaO_4^+$, $[M+Na]^+$ Calcd 358.9889, Found 358.9865.



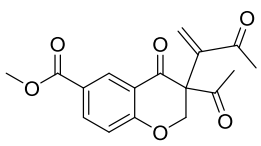
3r: yellow solid; yield 43.8 mg (57%) from 49.6 mg of **1r**; m.p. 177-179 ℃; **IR** (neat) *v* 3339, 2930, 1683, 1391, 1196, 814, 550 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) *δ* 8.22 (d, *J* = 2.2 Hz, 1H), 7.74 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 6.33 (d, *J* = 1.3 Hz, 1H), 5.75 (d, *J* = 1.4 Hz, 1H), 4.81 (d, *J* = 11.9 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 2.44 (s, 3H), 2.21 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) *δ* 201.5, 198.5, 189.4, 160.6, 144.7, 144.3, 136.1, 129.9, 122.6, 120.3, 84.2, 71.1, 65.5, 28.6, 26.4; **HRMS** (ESI): $C_{15}H_{13}INaO_4^+$, $[M+Na]^+$ Calcd 406.9751, Found 406.9794.



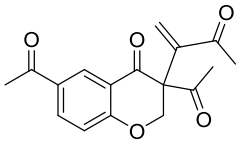
3s: yellow solid; yield 41.9 mg (64%) from 38.2 mg of **1s**; m.p. 183-185 ℃; **IR** (neat) *v* 3347, 2926, 1679, 1366, 1042, 848, 636 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) *δ* 7.82 (d, *J* = 1.6 Hz, 1H), 7.56 (d, *J* = 1.6 Hz, 1H), 6.34 (s, 1H), 5.75 (s, 1H), 4.91 (d, *J* = 11.9 Hz, 1H), 4.80 (d, *J* = 11.9 Hz, 1H), 2.44 (s, 3H), 2.21 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) *δ* 200.8, 198.2, 189.1, 155.3, 144.1, 136.0, 129.9, 127.2, 125.6, 124.0, 122.4, 71.8, 65.5, 28.4, 26.3; **HRMS** (ESI): $C_{15}H_{12}Cl_2NaO_4^+$, $[M+Na]^+$ Calcd 349.0005, Found 348.9983.



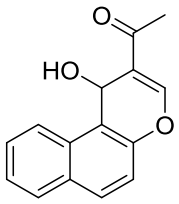
3t: yellow solid; yield 50 mg (60%) from 56 mg of **1t**; m.p. 167-169 ℃; **IR** (neat) *v* 2920, 1706, 1356, 1188, 938 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) *δ* 8.01 (d, *J* = 2.4 Hz, 1H), 7.86 (d, *J* = 2.4 Hz, 1H), 6.34 (s, 1H), 5.75 (s, 1H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 2.44 (s, 3H), 2.21 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) *δ* 200.8, 198.2, 189.0, 156.6, 144.1, 141.5, 130.0, 129.4, 122.7, 114.4, 112.8, 71.8, 65.3, 28.4, 26.3; **HRMS** (ESI): $C_{15}H_{12}Br_2NaO_4^+$, $[M+Na]^+$ Calcd 436.8995, Found 436.9012.



3u: yellow oil; yield 31 mg (49%) from 36.0 mg of **1u**; **IR** (neat) *v* 2936, 1706, 1230, 972, 761 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.63 (d, *J* = 1.6 Hz, 1H), 8.15 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.32 (s, 1H), 5.75 (s, 1H), 4.89 (d, *J* = 12.0 Hz, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 3.92 (s, 3H), 2.45 (s, 3H), 2.22 (s. 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 201.4, 198.4, 189.8, 165.8, 164.0, 144.3, 137.1, 130.1, 129.8, 124.2, 120.3, 118.3, 71.2, 65.7, 52.2, 28.5, 26.4; **HRMS** (ESI): $C_{17}H_{16}NaO_6^+$, [M+Na] $^+$ Calcd 339.0839, Found 339.0853.



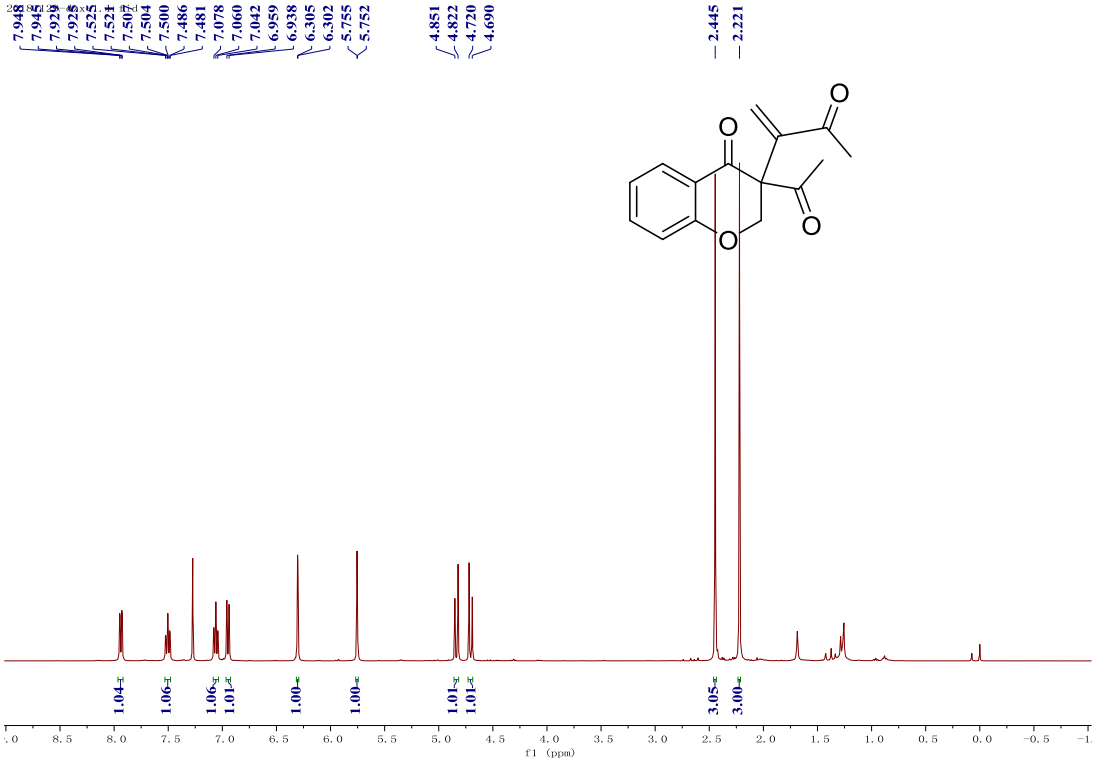
3v: yellow oil; yield 34 mg (57%) from 33 mg of **1v**; **IR** (neat) *v* 3362, 2918, 1678, 1220, 975 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.44 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.26 (s, 1H), 5.69 (s, 1H), 4.83 (d, *J* = 11.9 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 2.53 (s, 3H), 2.38 (s, 3H), 2.15 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 201.2, 198.4, 196.0, 190.0, 164.2, 144.3, 135.7, 131.3, 129.8, 129.0, 120.0, 118.7, 71.3, 65.8, 29.7, 28.4, 26.4; **HRMS** (ESI): $C_{17}H_{16}NaO_5^+$, [M+Na] $^+$ Calcd 323.0890, Found 323.0903.



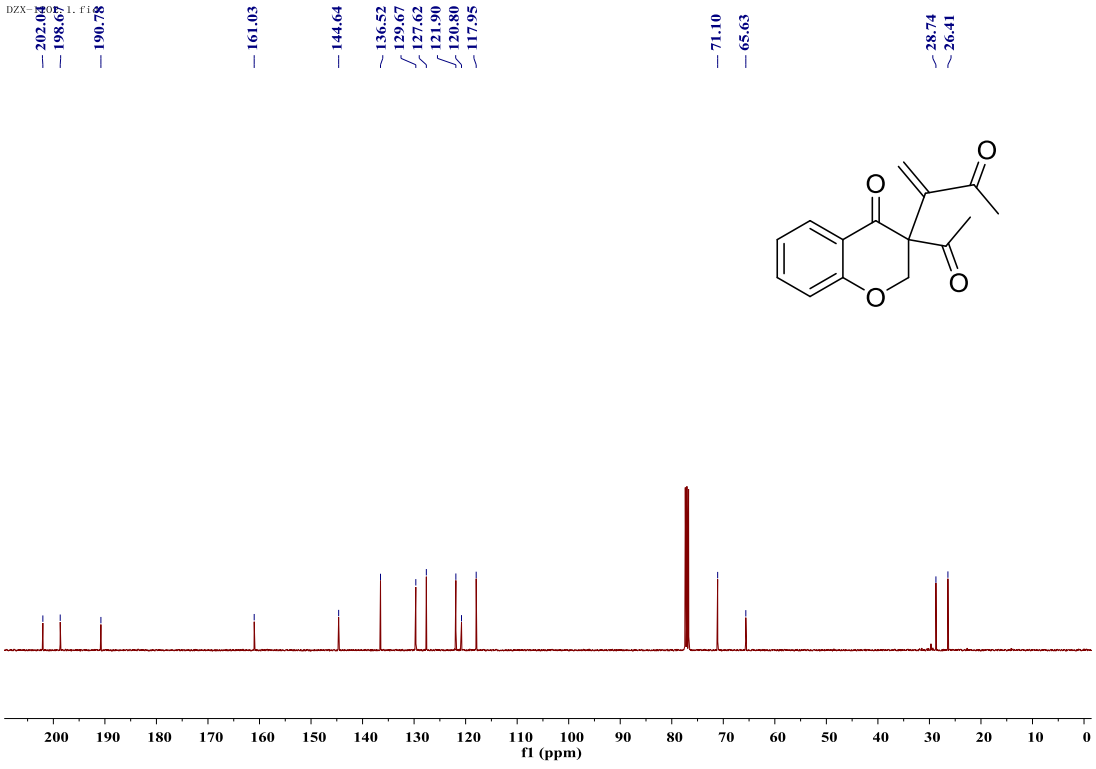
3w: yellow solid; 15 mg (31%) from 34 mg of **3w**; m.p. 191-193 ℃; **IR** (neat) *v* 3368, 2924, 1008, 746, 596 cm^{-1}; **^{1}H NMR (**d_6-DMSO, 400 MHz) δ 8.50-8.47 (m, 2H), 8.01 (d, *J* =8.9 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.33-7.28 (m, 2H), 6.36 (d, *J* = 6.4 Hz, 1H), 2.56 (s, 3H); **^{13}C {^{1}H} NMR** (*d6*-DMSO, 100 MHz) δ 196.7, 152.0, 133.3, 130.9, 129.6, 129.43, 129.36, 129.1, 128.1, 124.9, 122.4, 118.8, 113.0, 88.2, 26.2; **HRMS** (ESI): $C_{15}H_{12}NaO_3^+$, [M+Na] $^+$ Calcd 263.0679, Found 263.0681.

7. ^{1}H NMR, ^{13}C NMR of compounds (3)

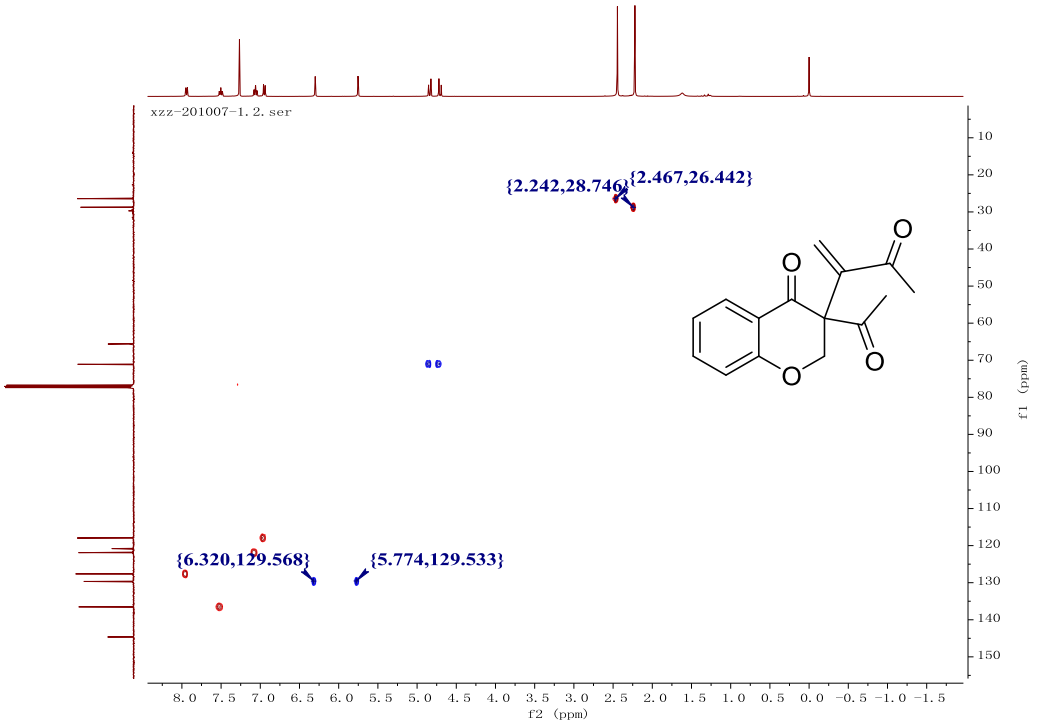
Product 3a: ^{1}H NMR



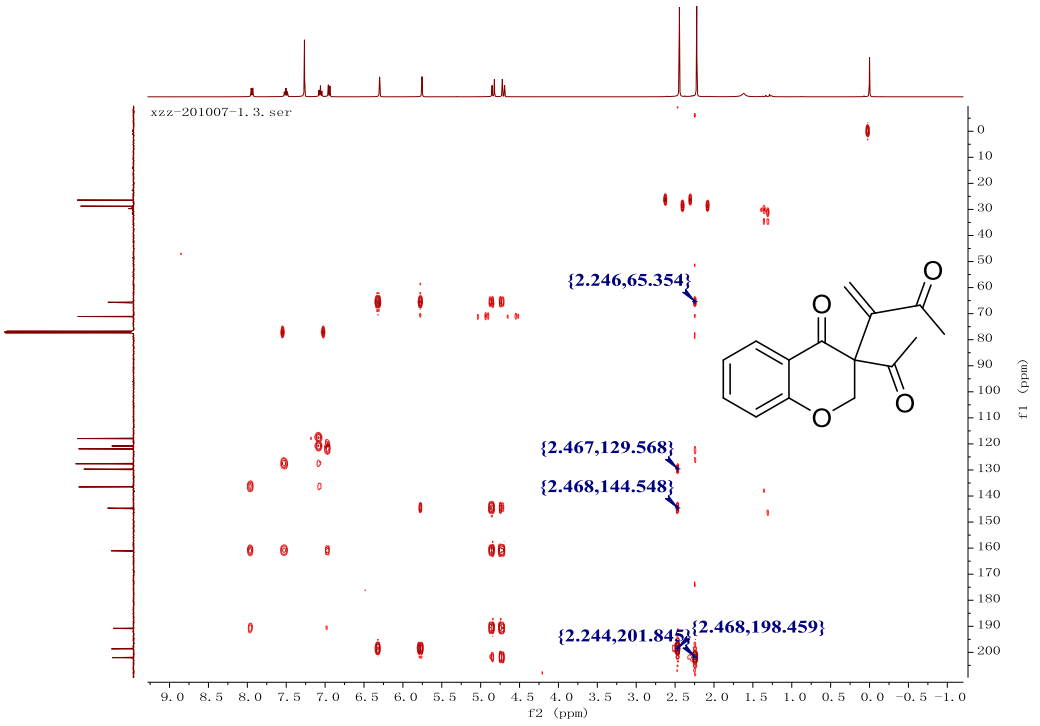
Product 3a: ^{13}C NMR



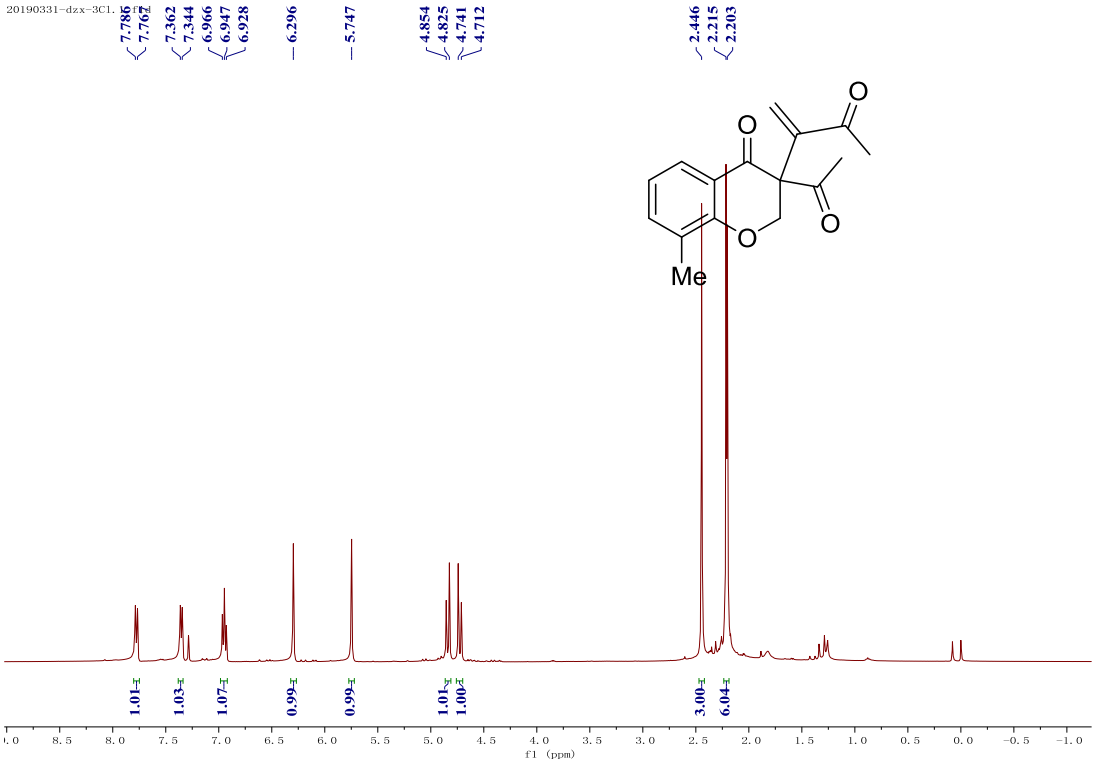
HSQC NMR:



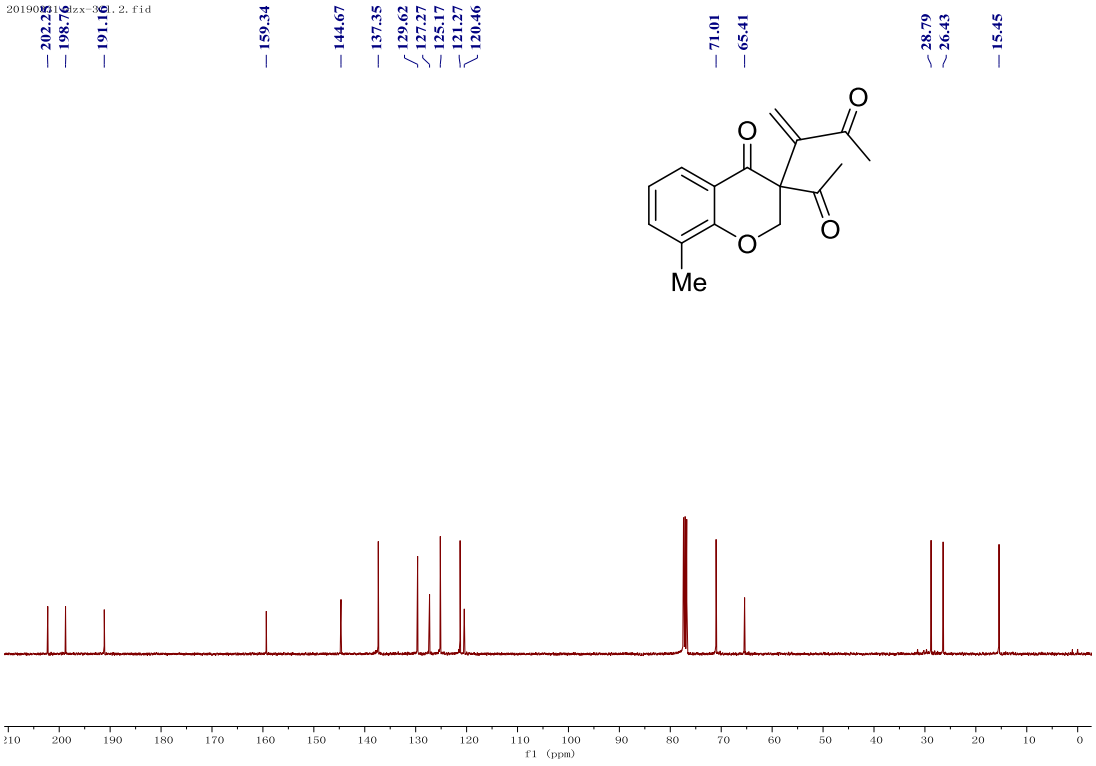
HMBC NMR:



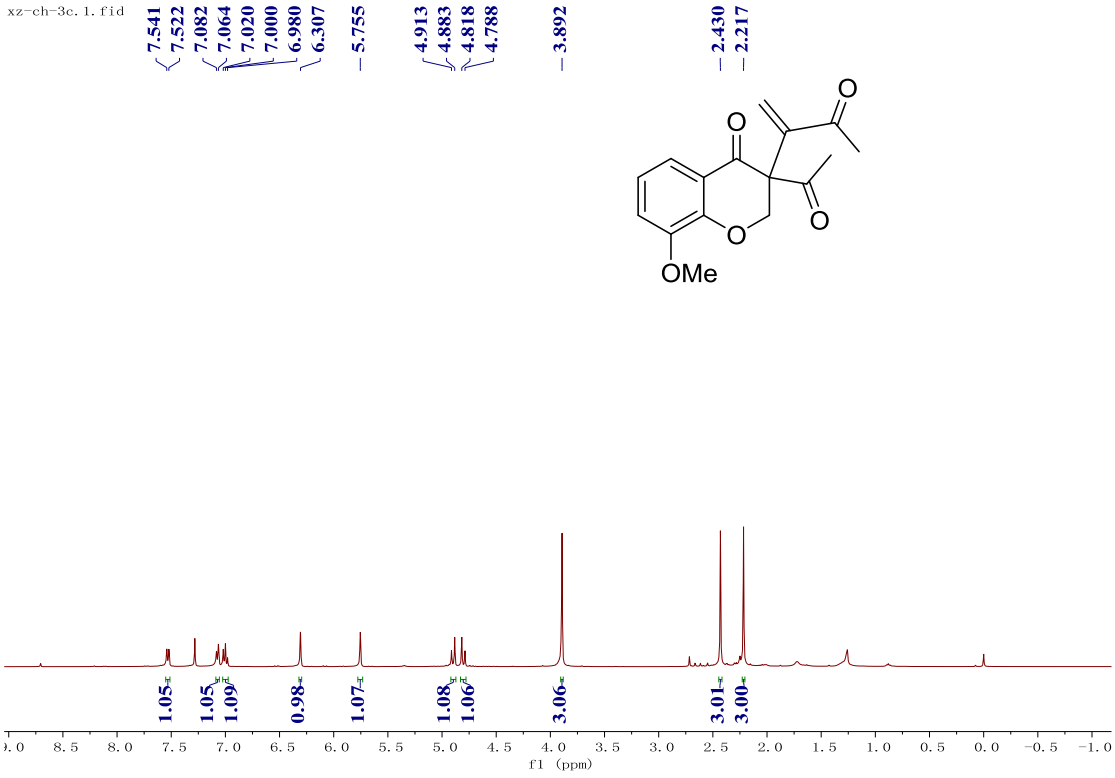
Product 3b: ^{1}H NMR



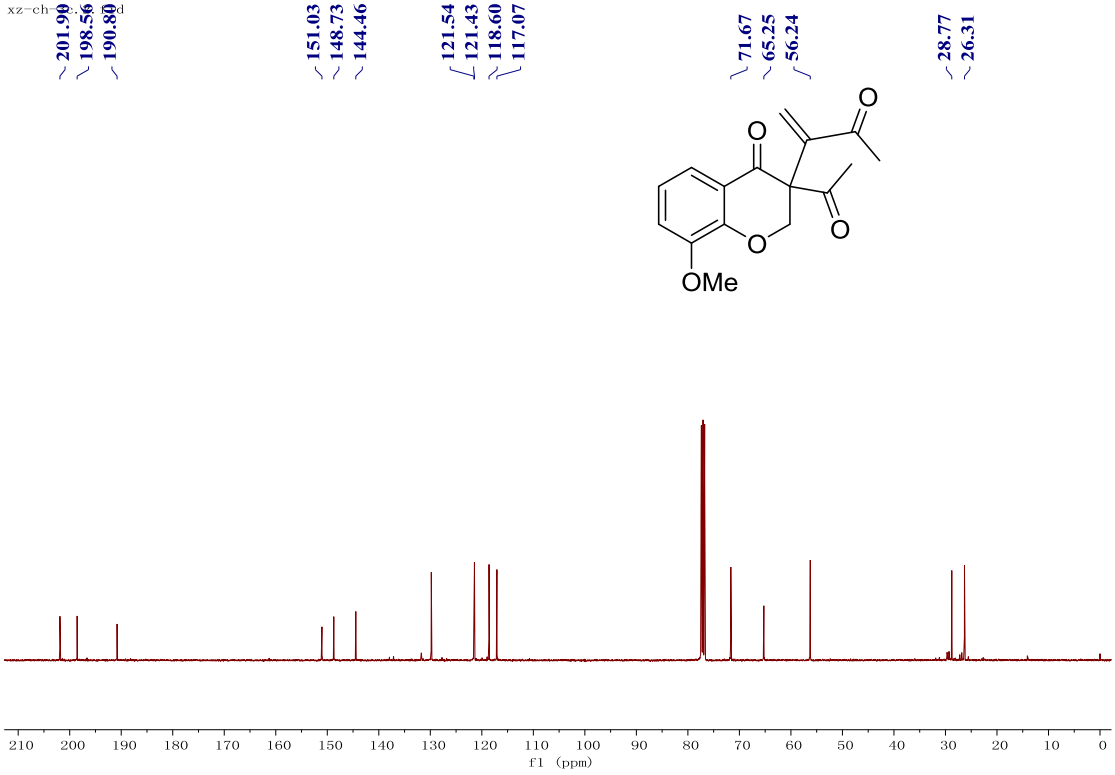
Product 3b: ^{13}C NMR



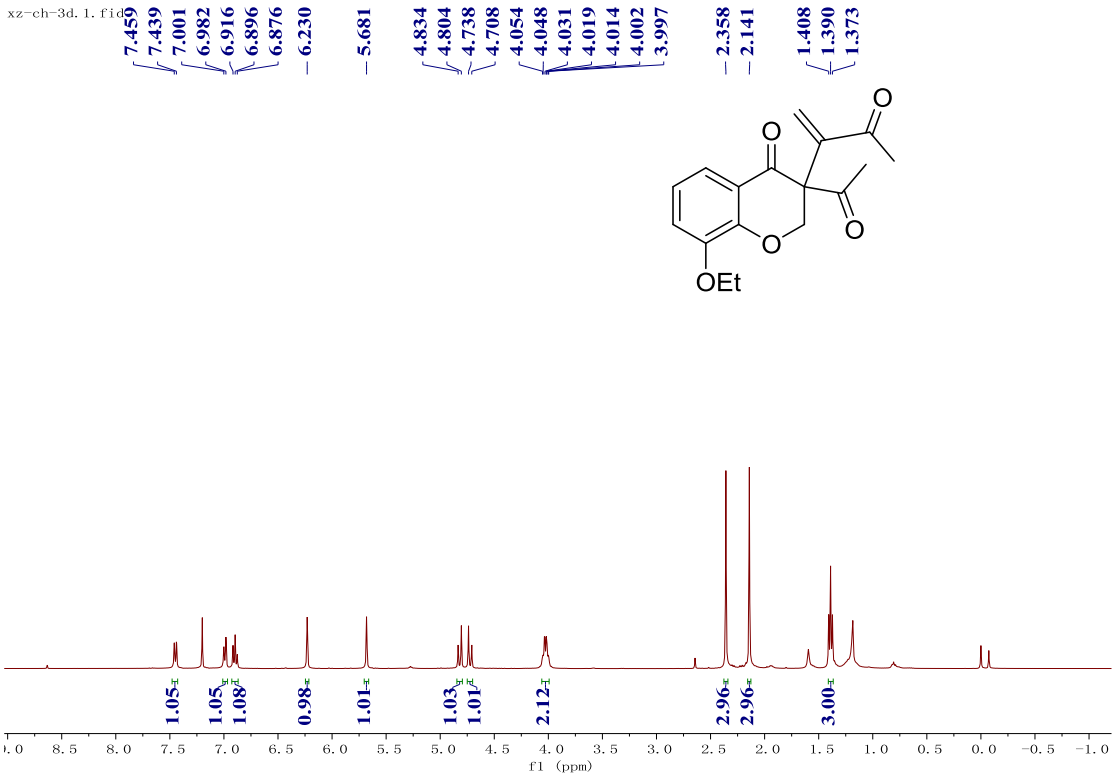
Product 3c: ^{1}H NMR



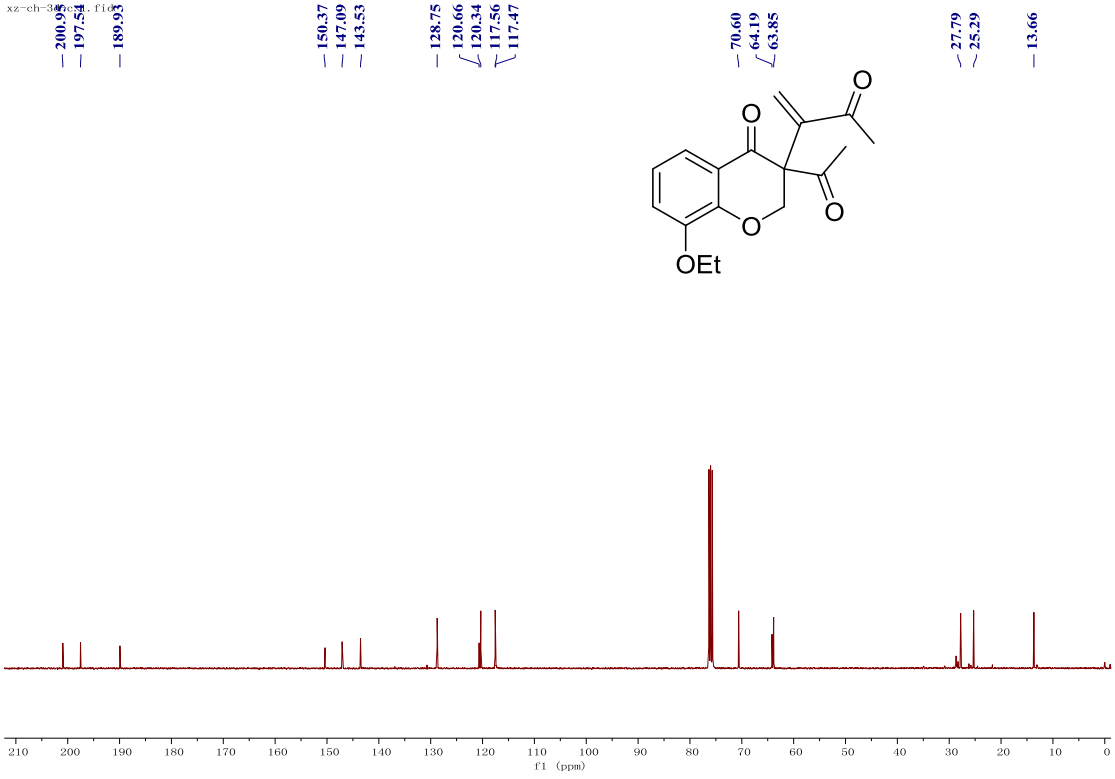
Product 3c: ^{13}C NMR



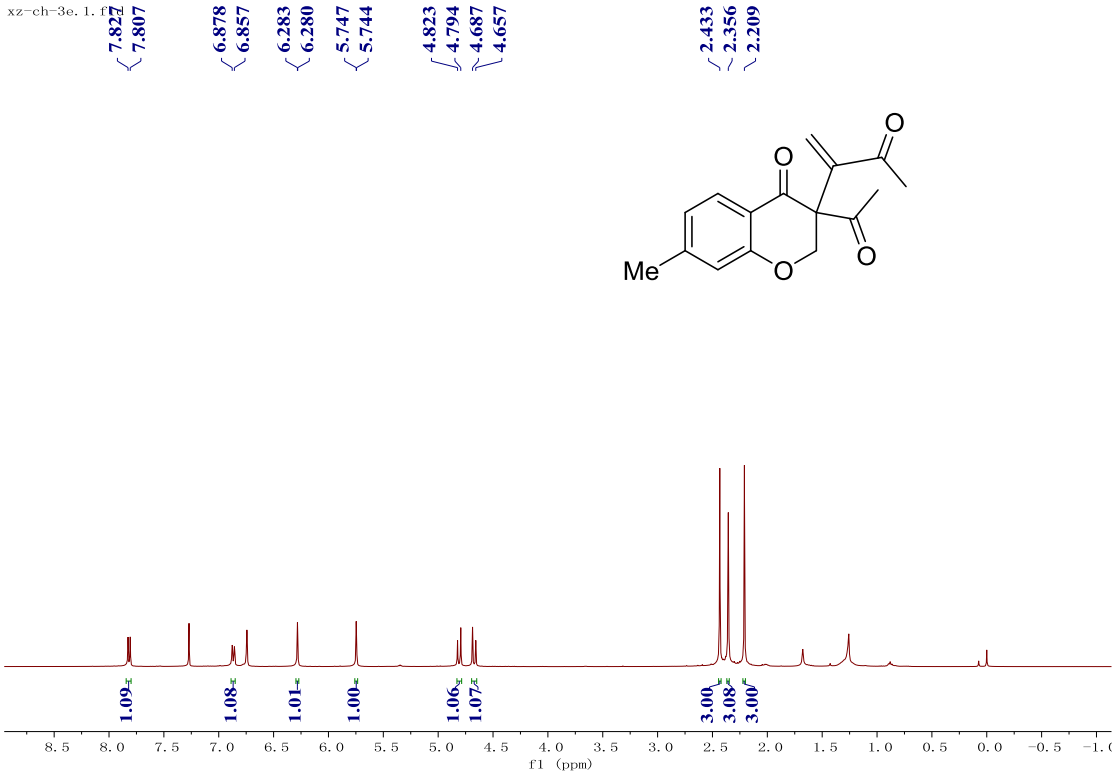
Product 3d: ^{1}H NMR



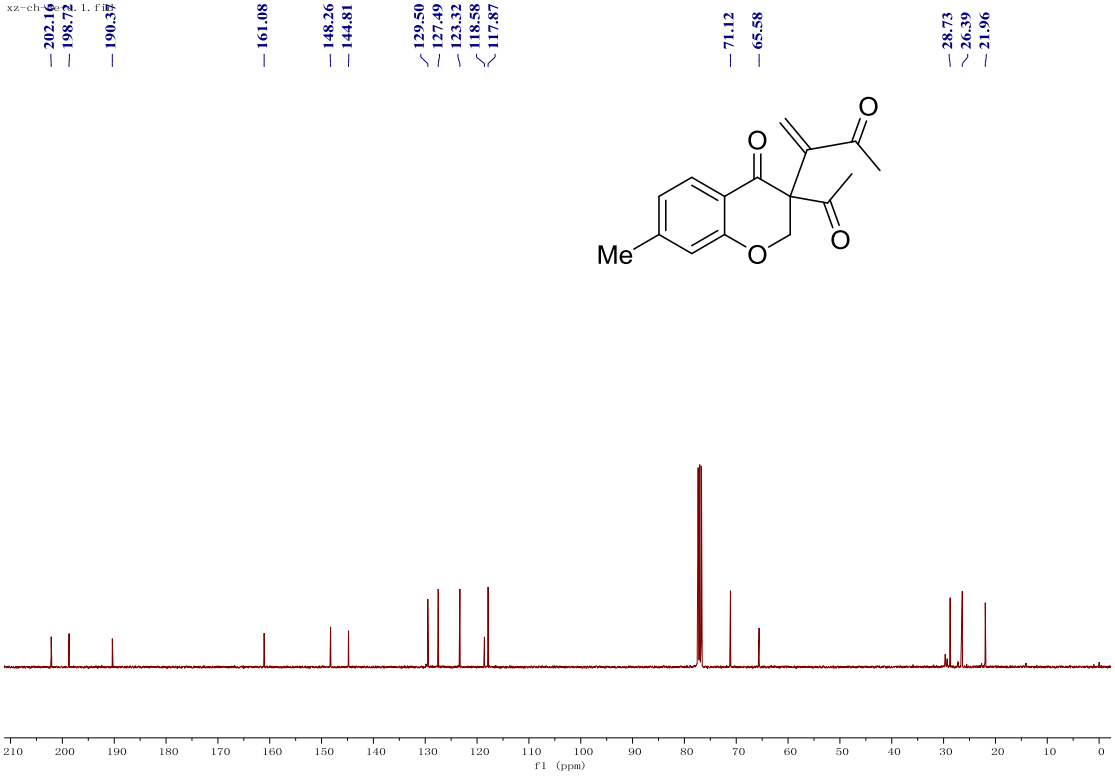
Product 3d: ^{13}C NMR



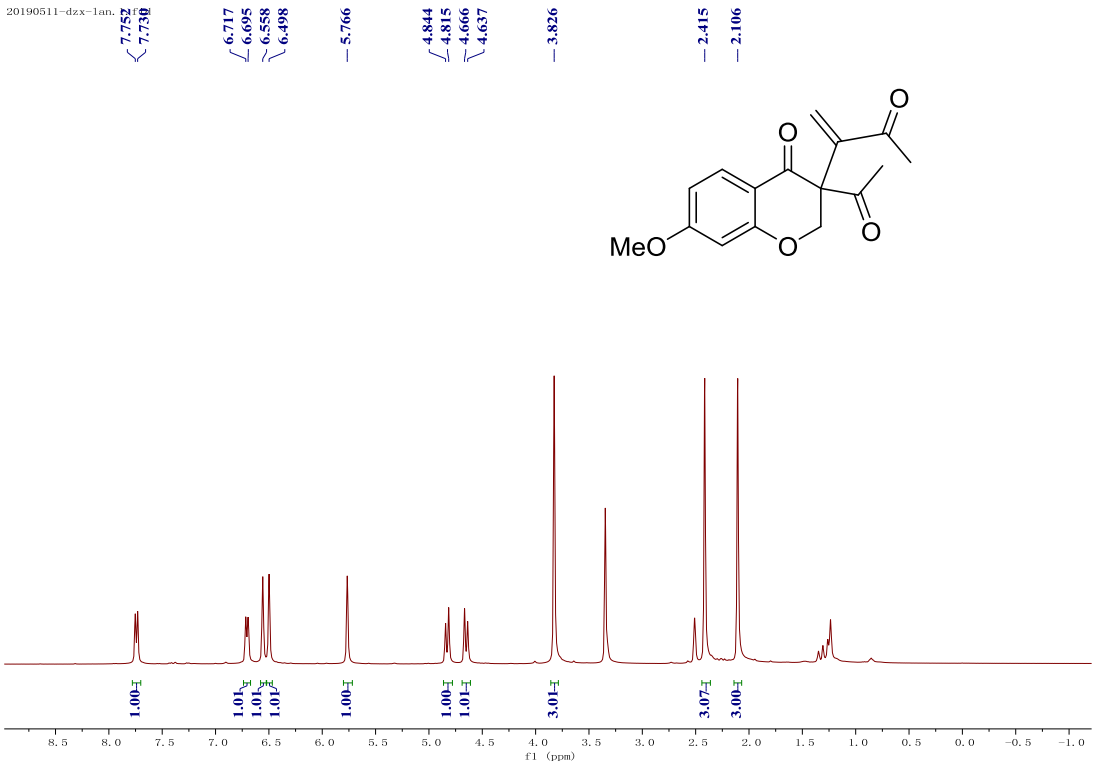
Product 3e: ^{1}H NMR



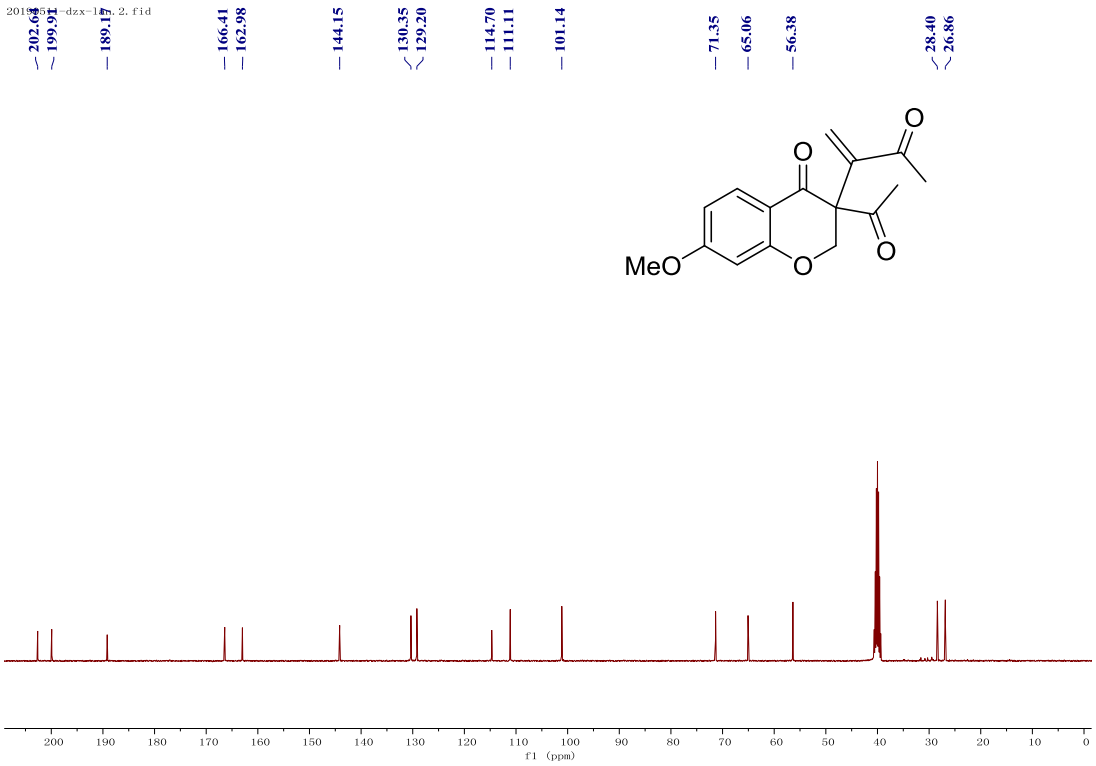
Product 3e: ^{13}C NMR



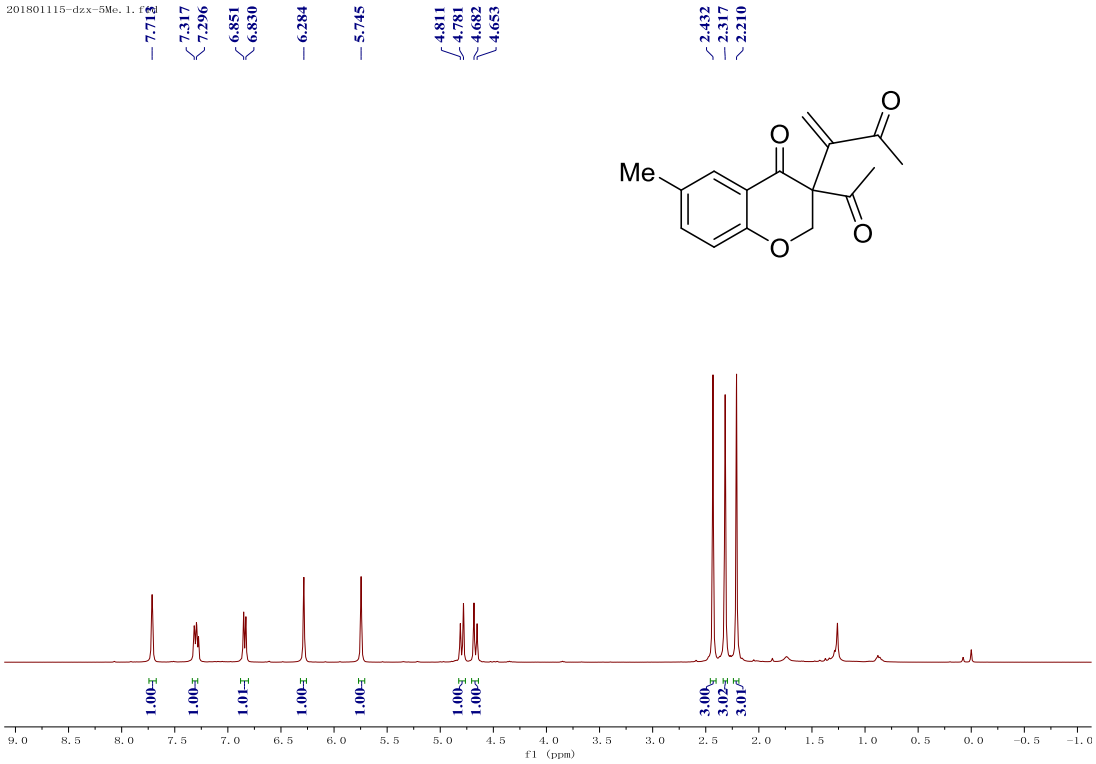
Product 3f: ^{1}H NMR



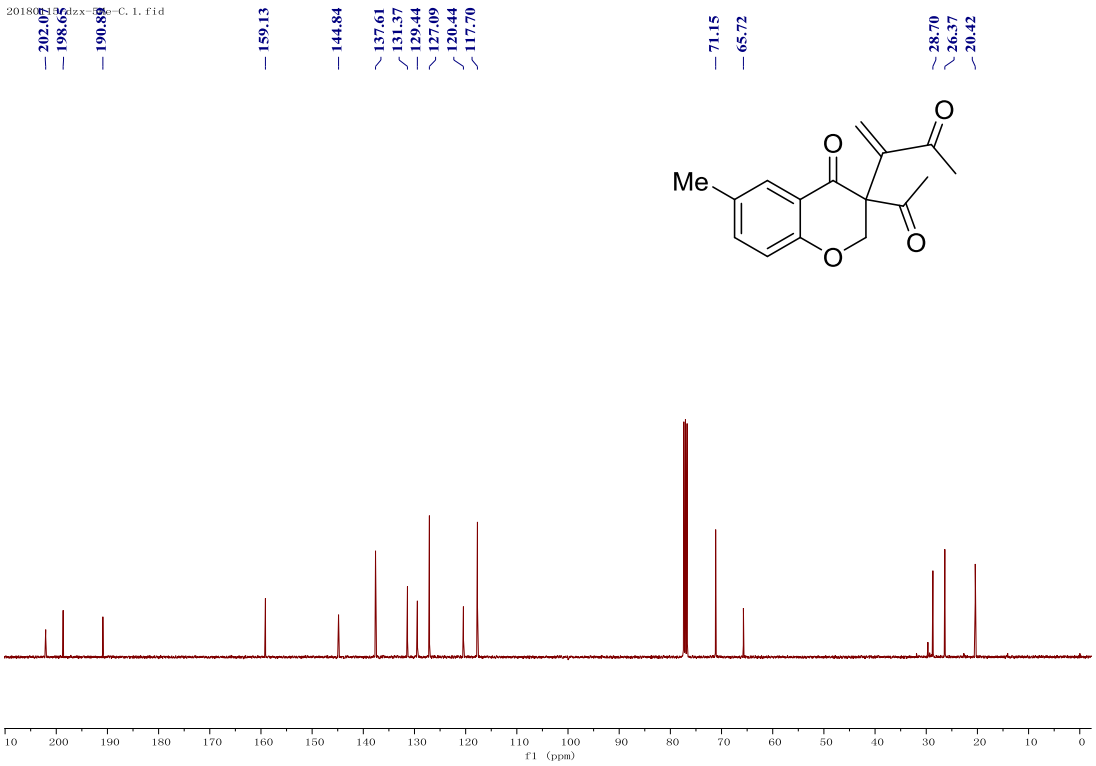
Product 3f: ^{13}C NMR



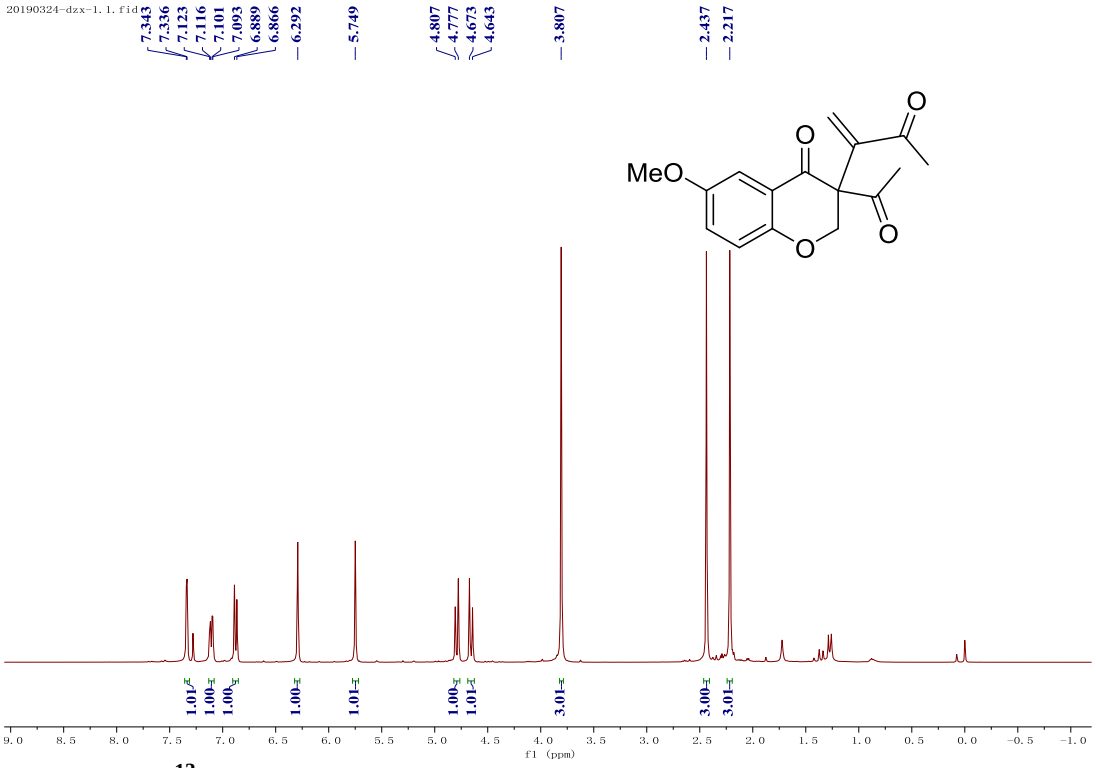
Product 3g: ^{1}H NMR



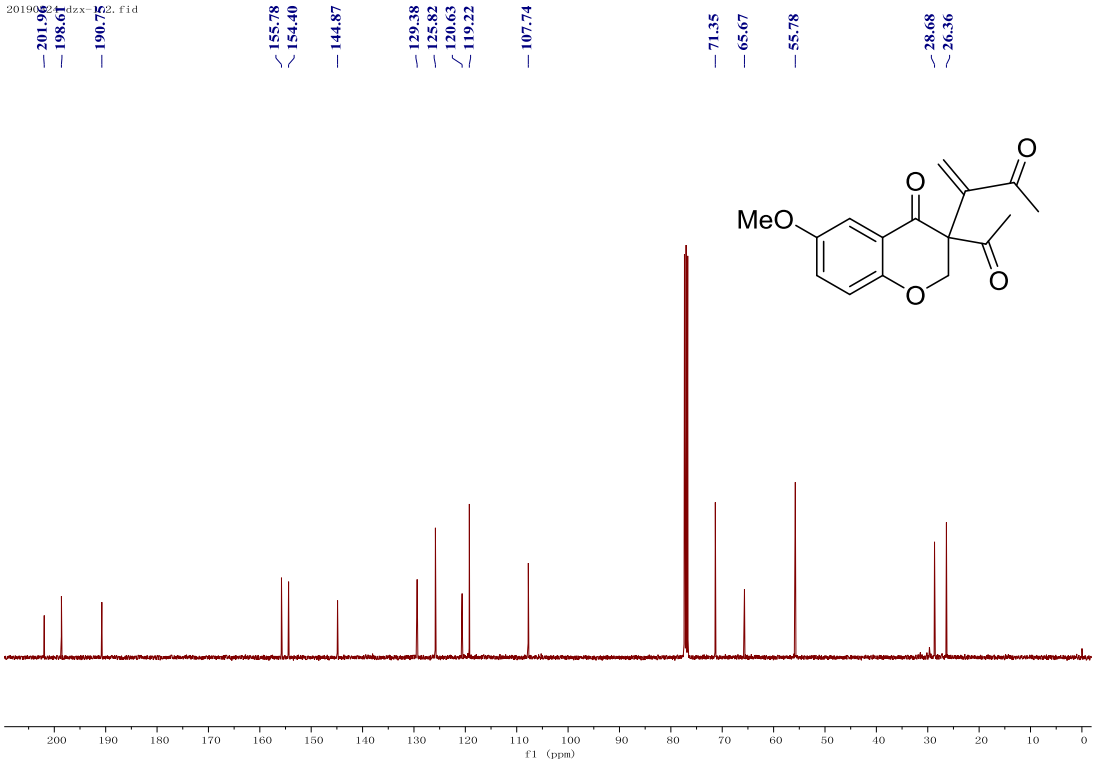
Product 3g: ^{13}C NMR



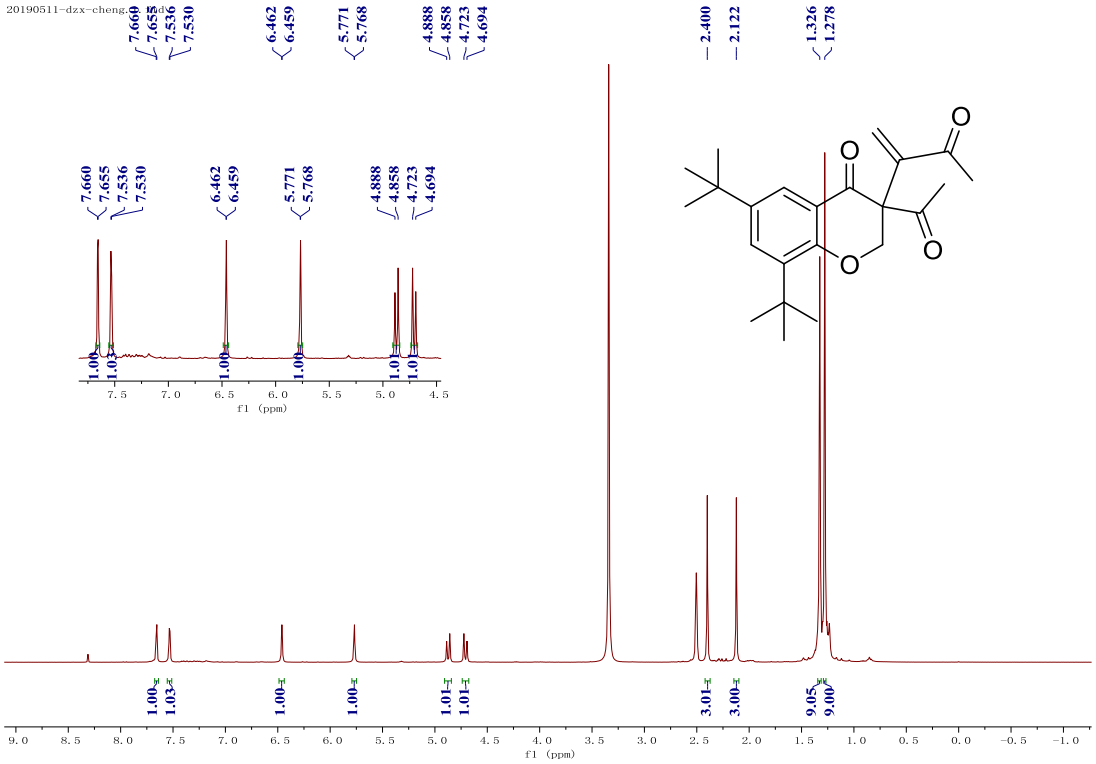
Product 3h: ^{1}H NMR



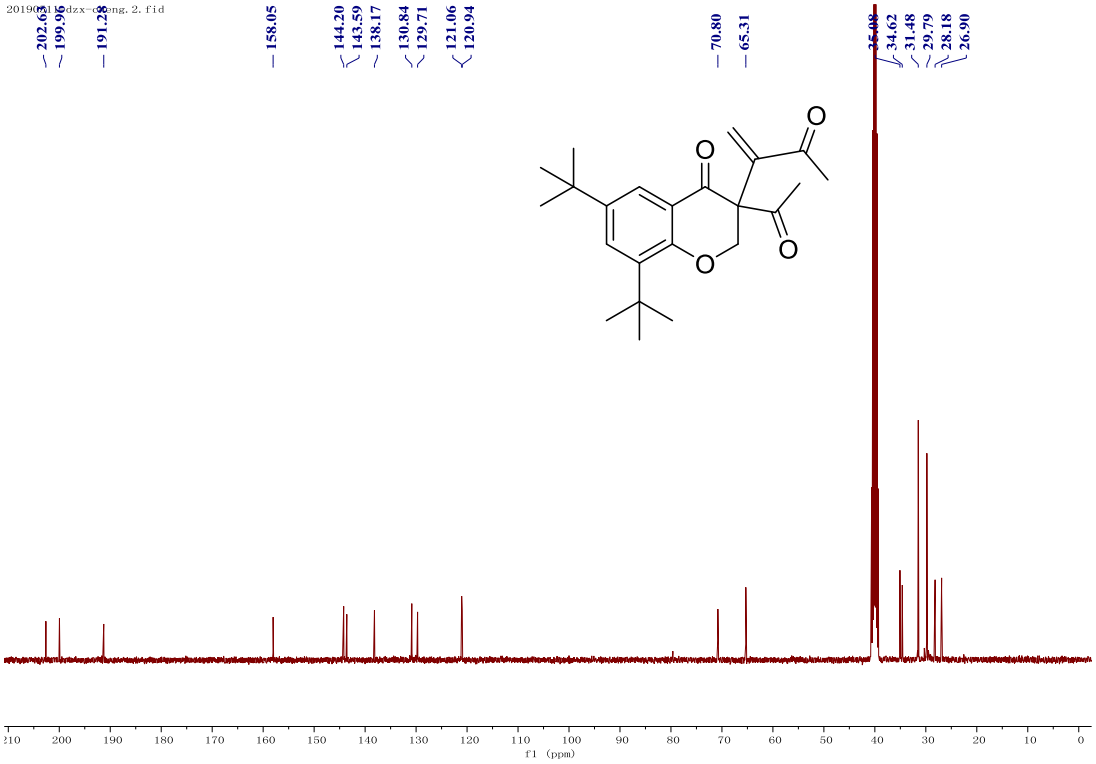
Product 3h: ^{13}C NMR



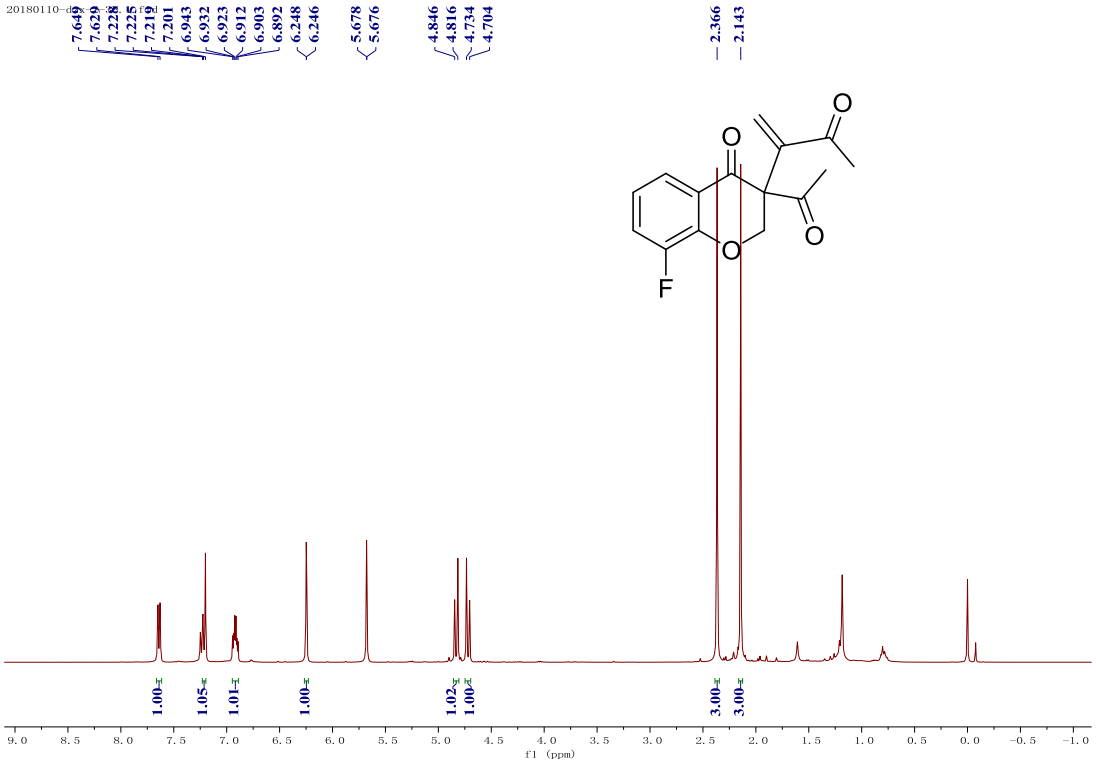
Product 3i: ^{1}H NMR



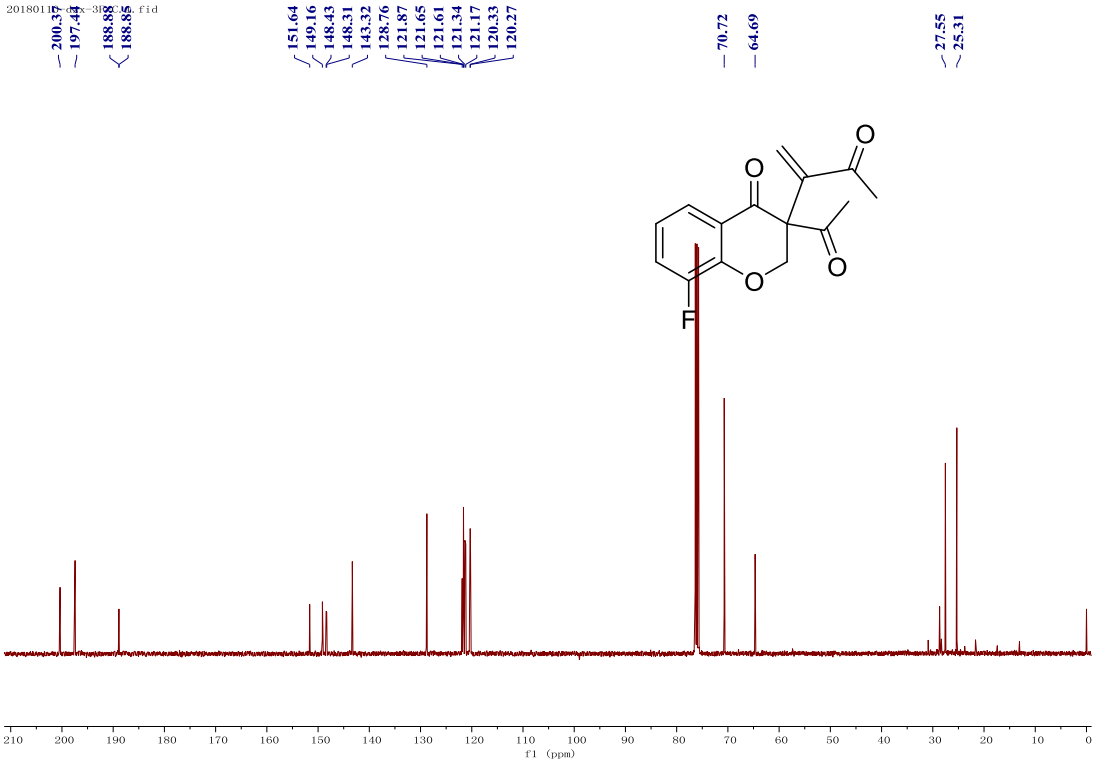
Product 3i: ^{13}C NMR



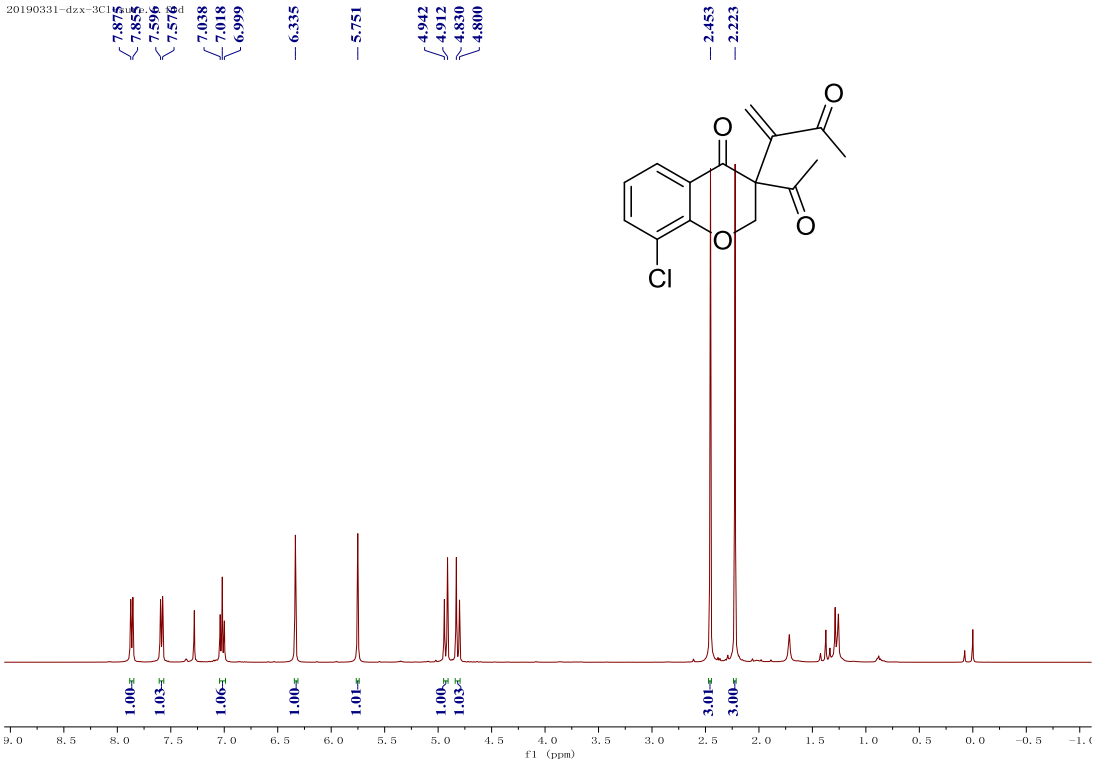
Product 3j: ^{1}H NMR



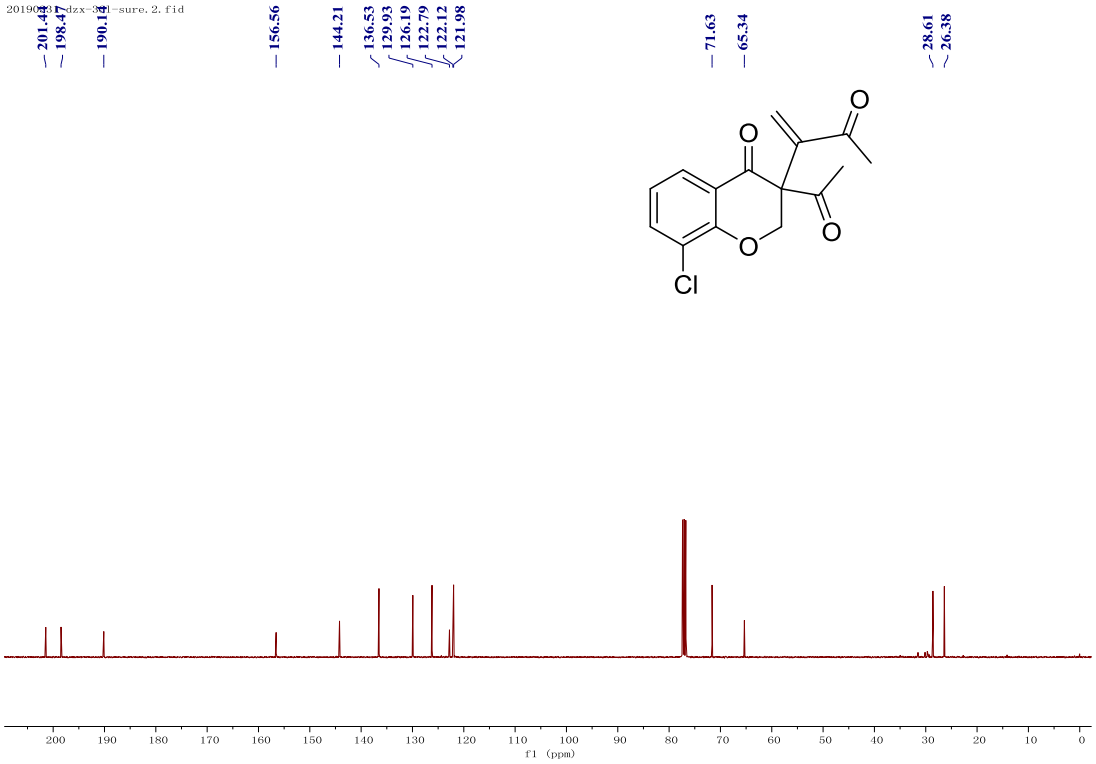
Product 3j: ^{13}C NMR



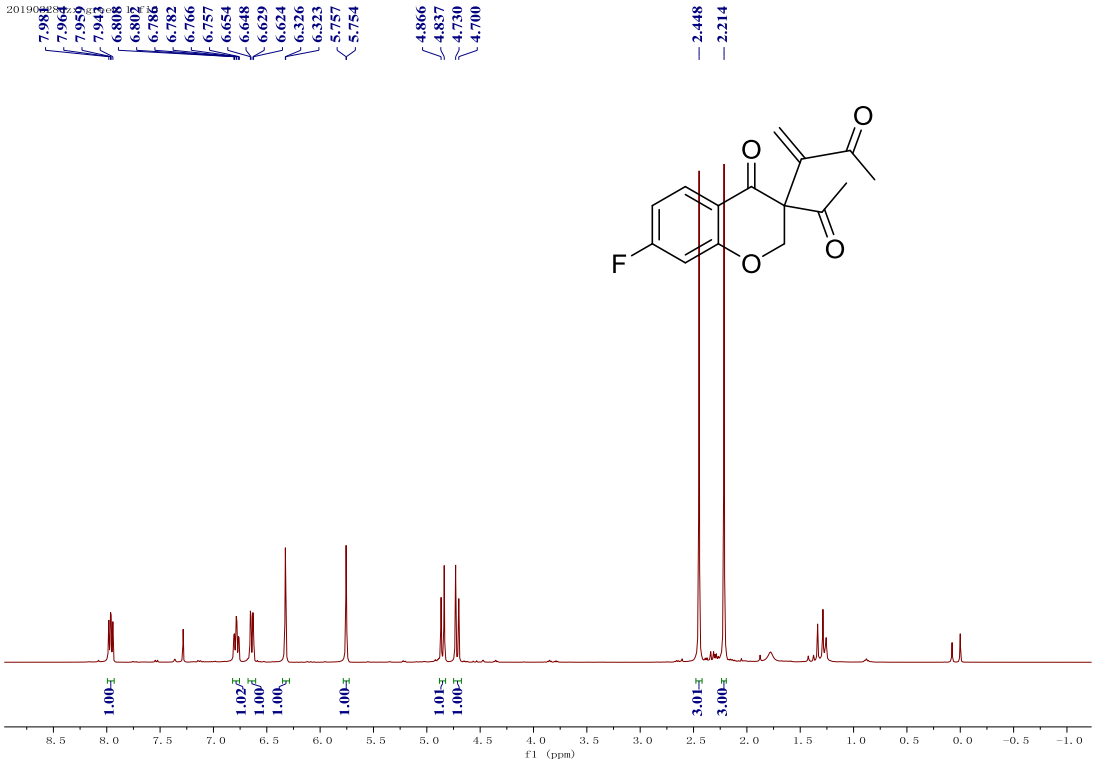
Product 3k: ^{1}H NMR



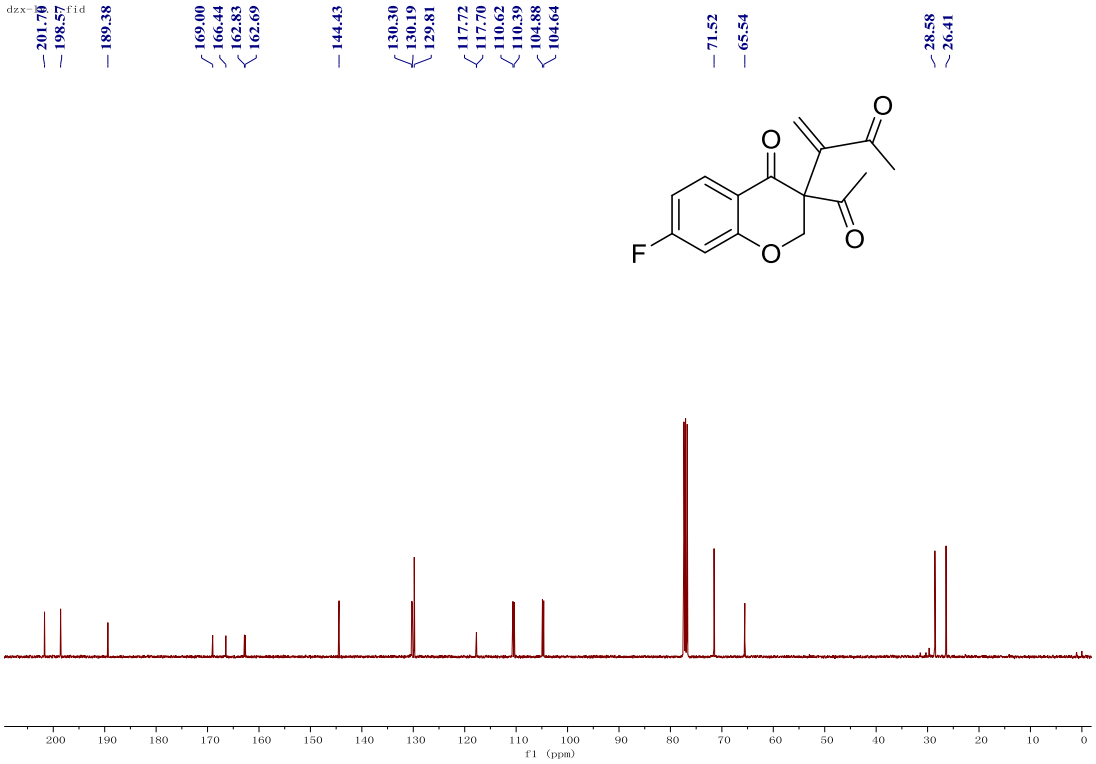
Product 3k: ^{13}C NMR



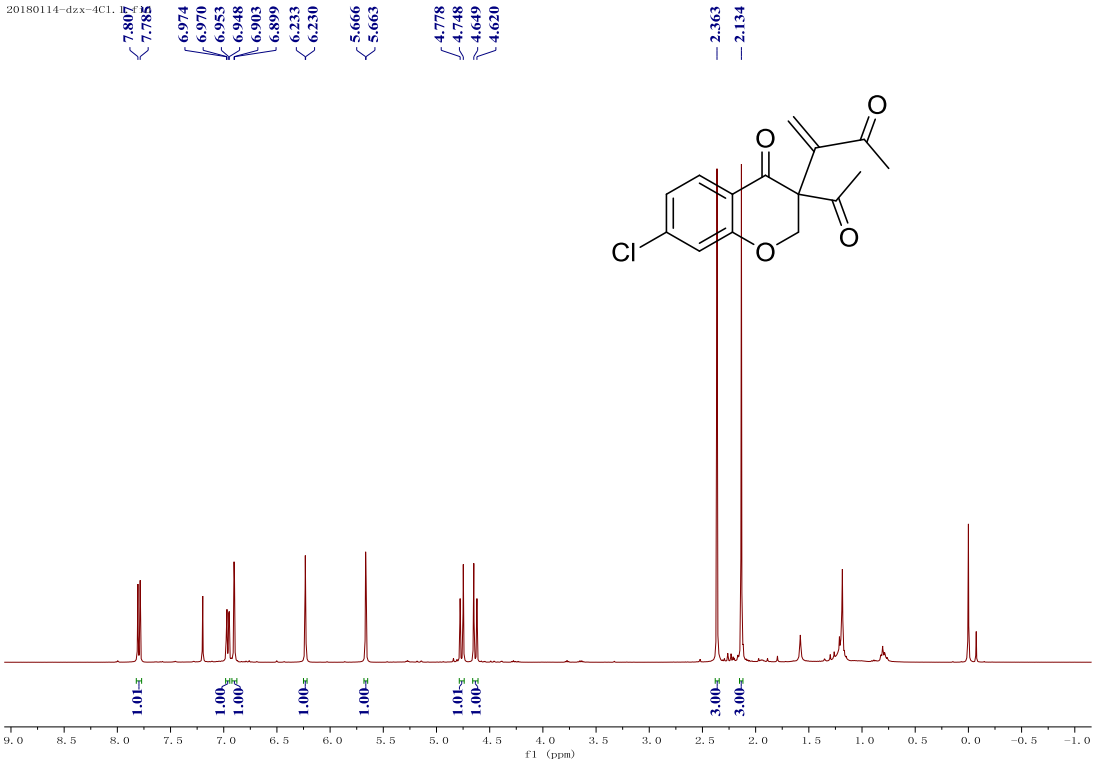
Product 3l: ^{1}H NMR



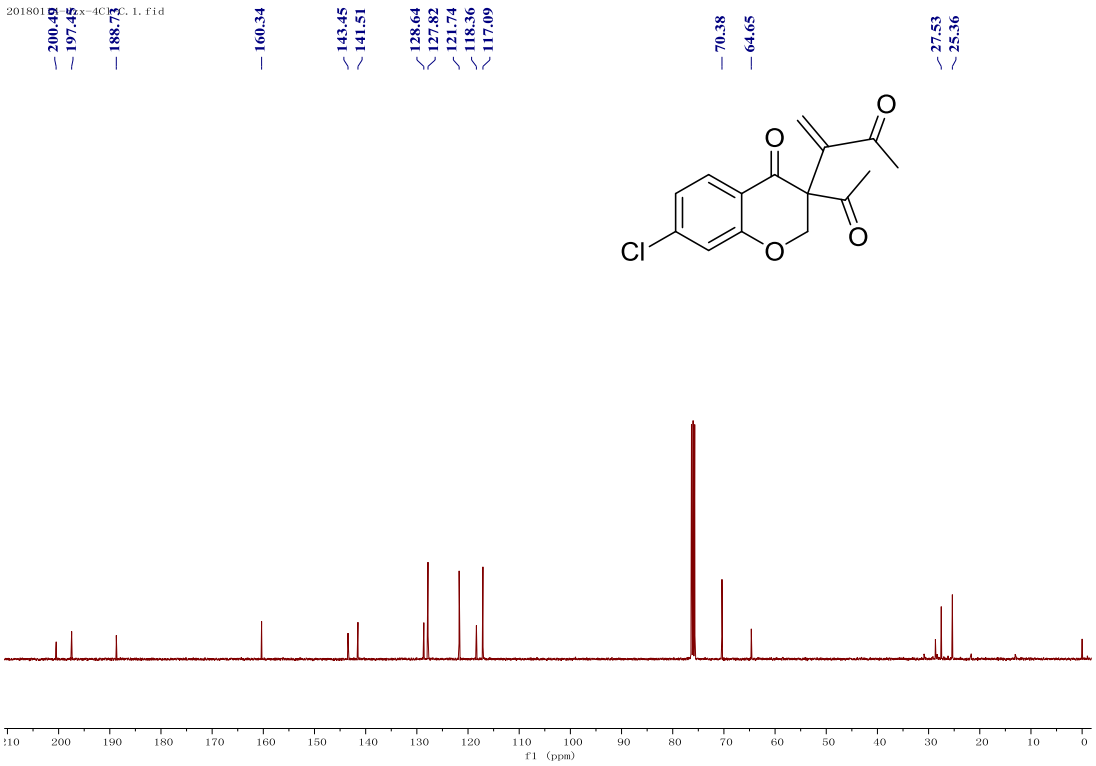
Product 3l: ^{13}C NMR



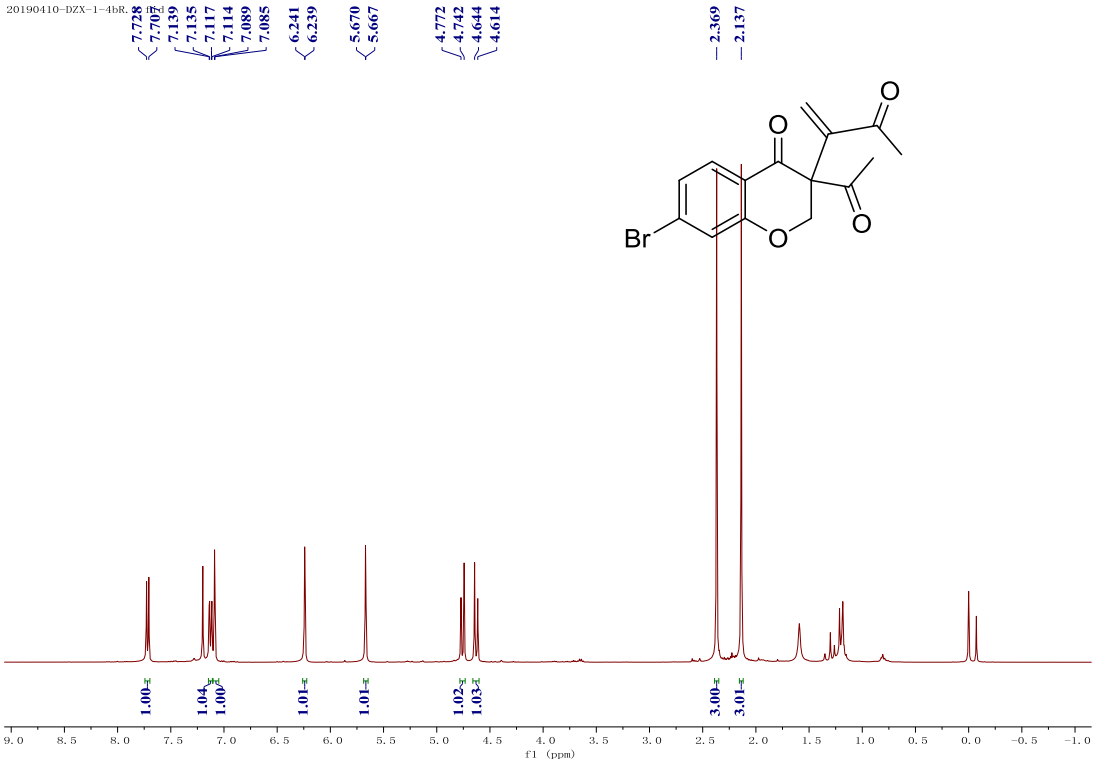
Product 3m: ^{1}H NMR



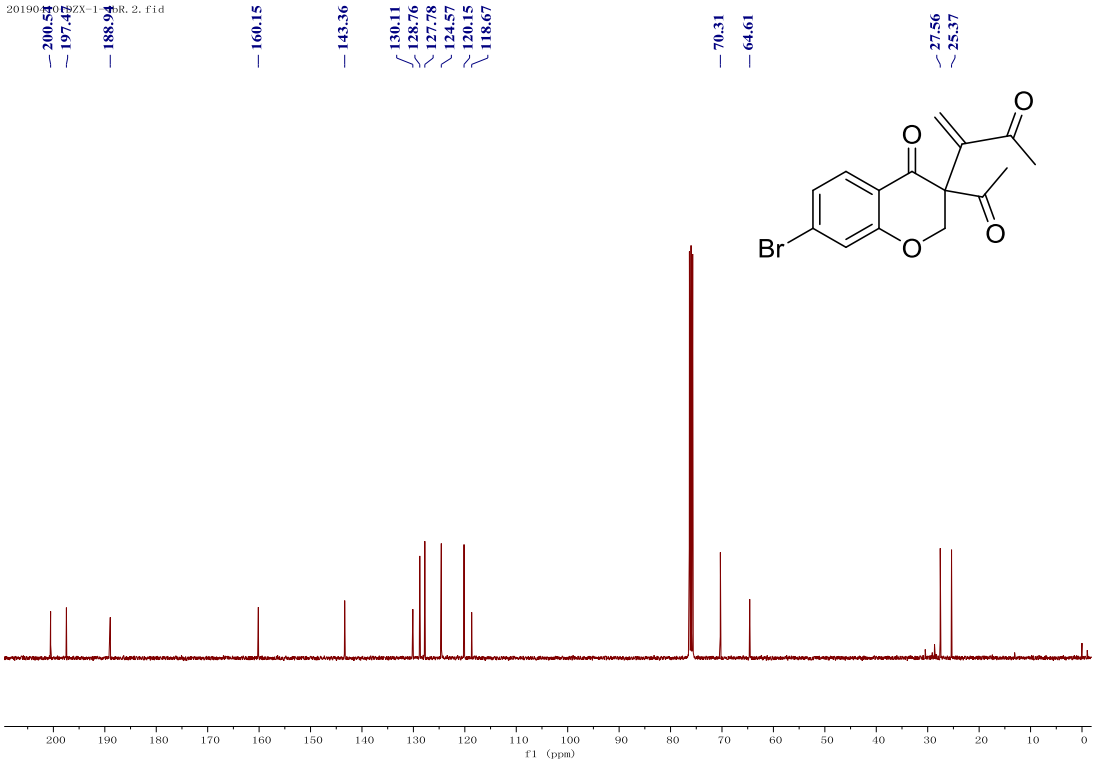
Product 3m: ^{13}C NMR



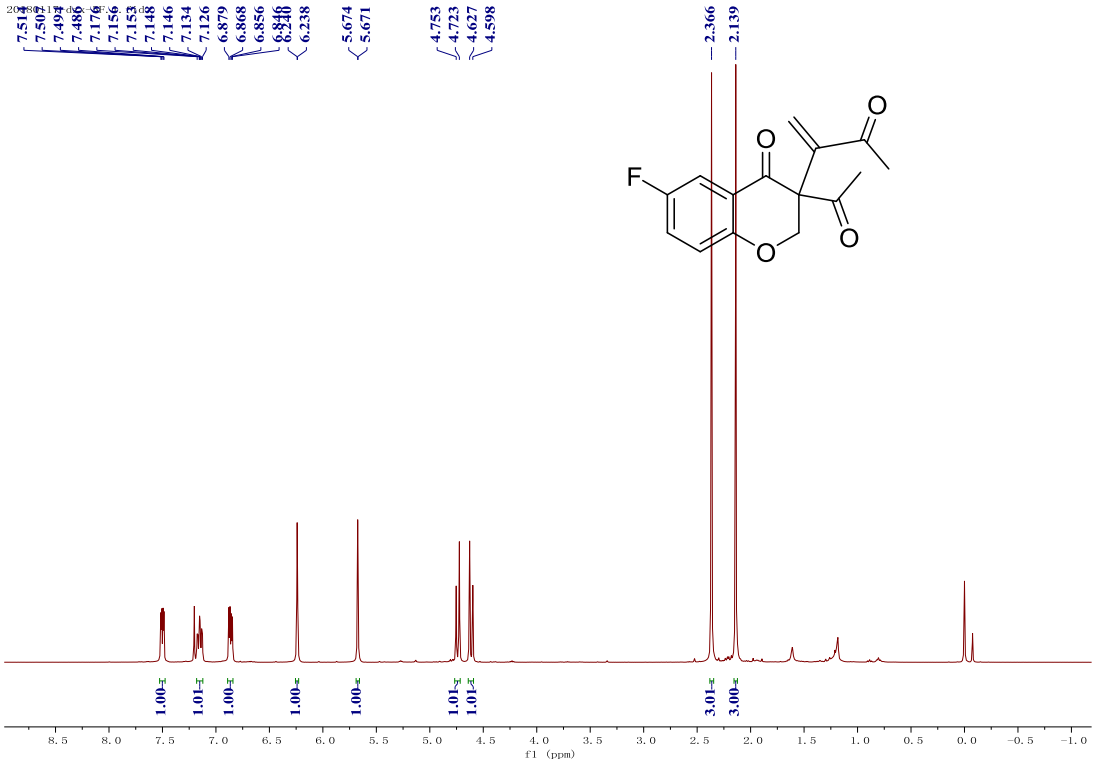
Product 3n: ^{1}H NMR



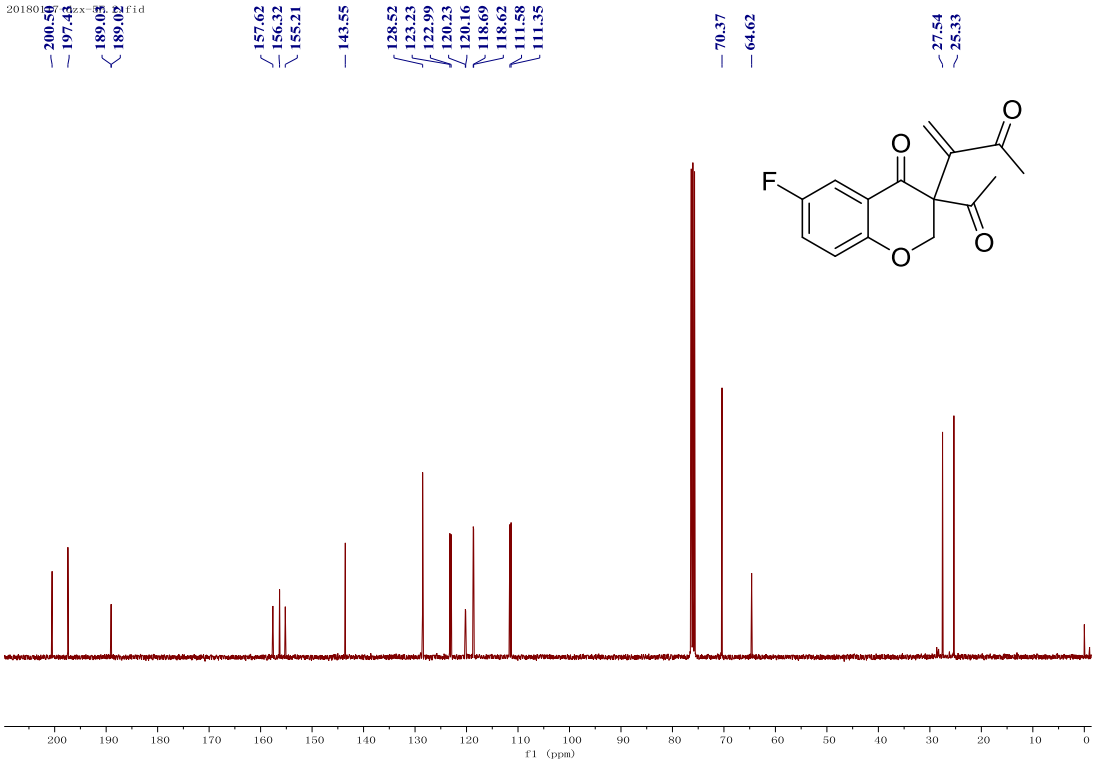
Product 3n: ^{13}C NMR



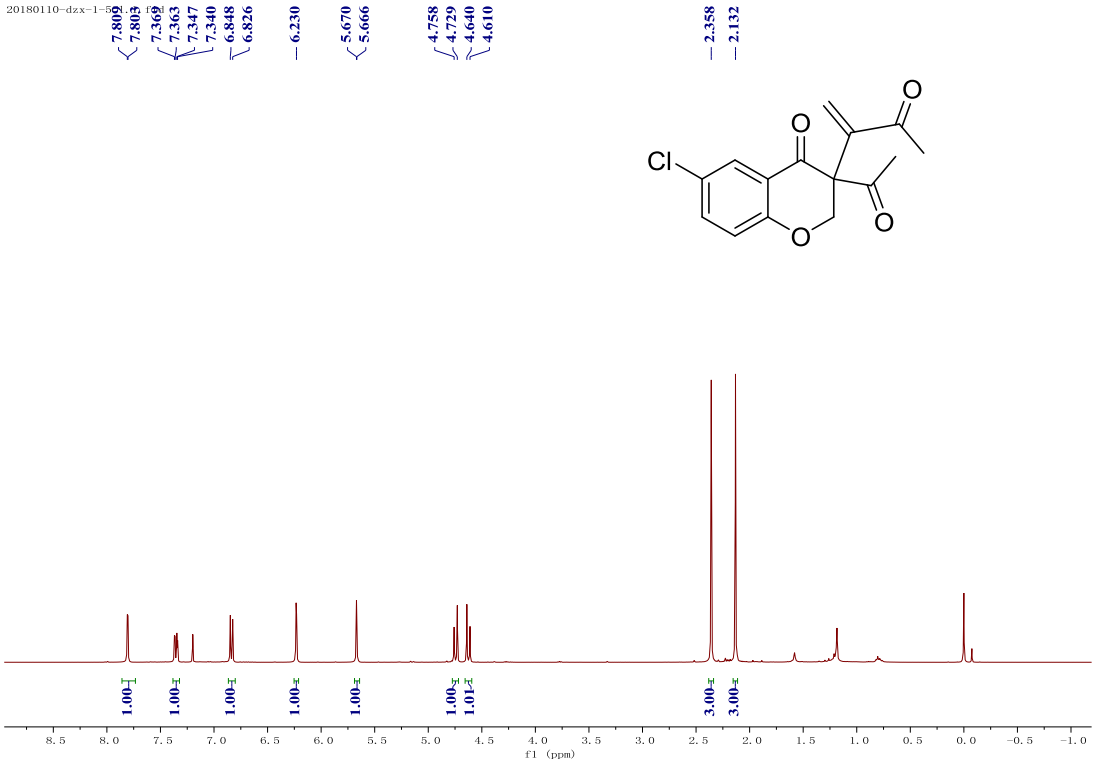
Product 3o: ^{1}H NMR



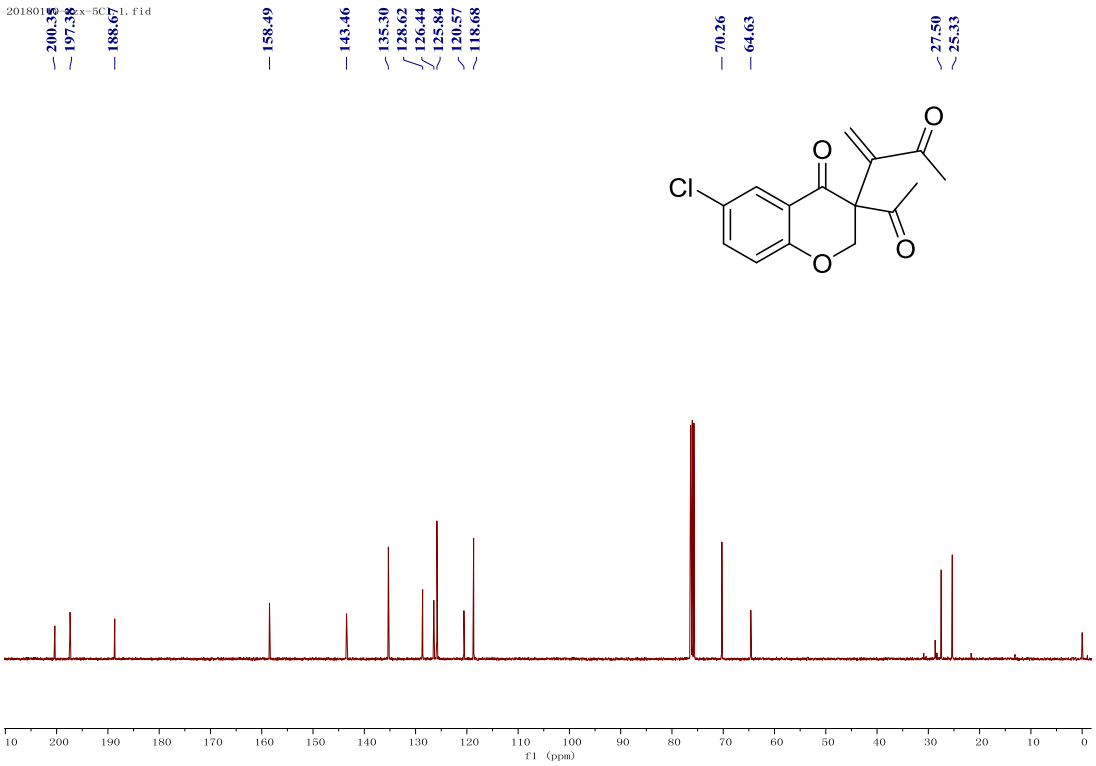
Product 3o: ^{13}C NMR



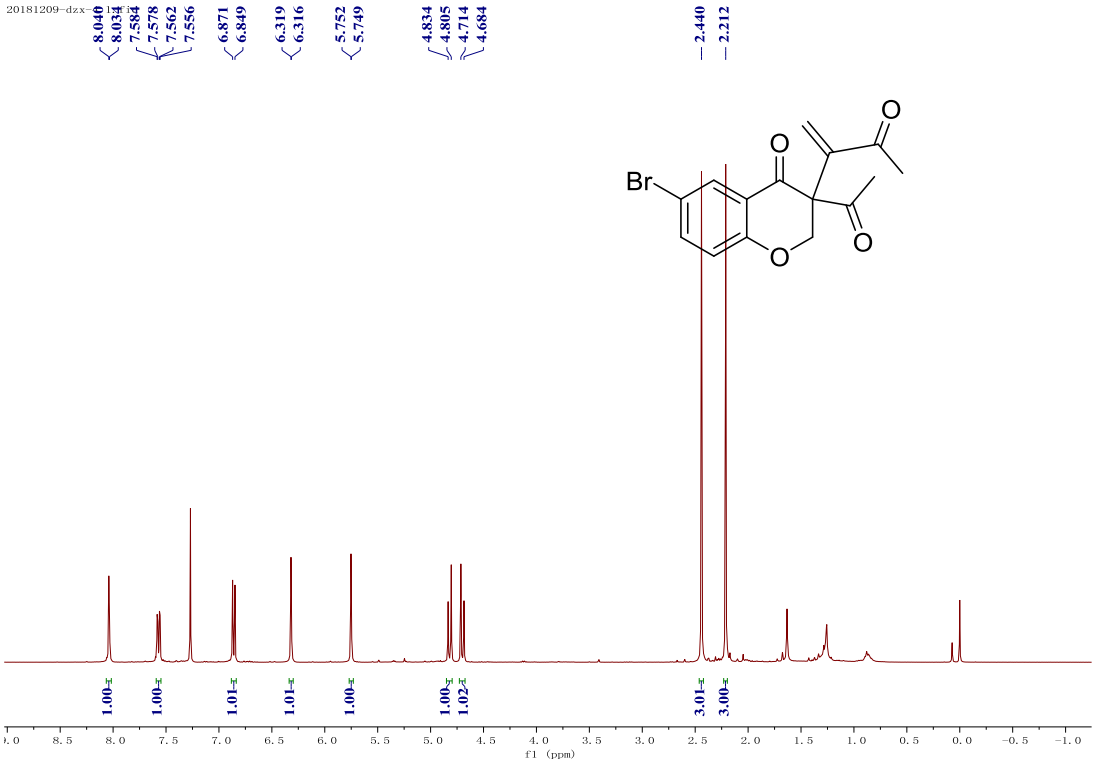
Product 3p: ^{1}H NMR



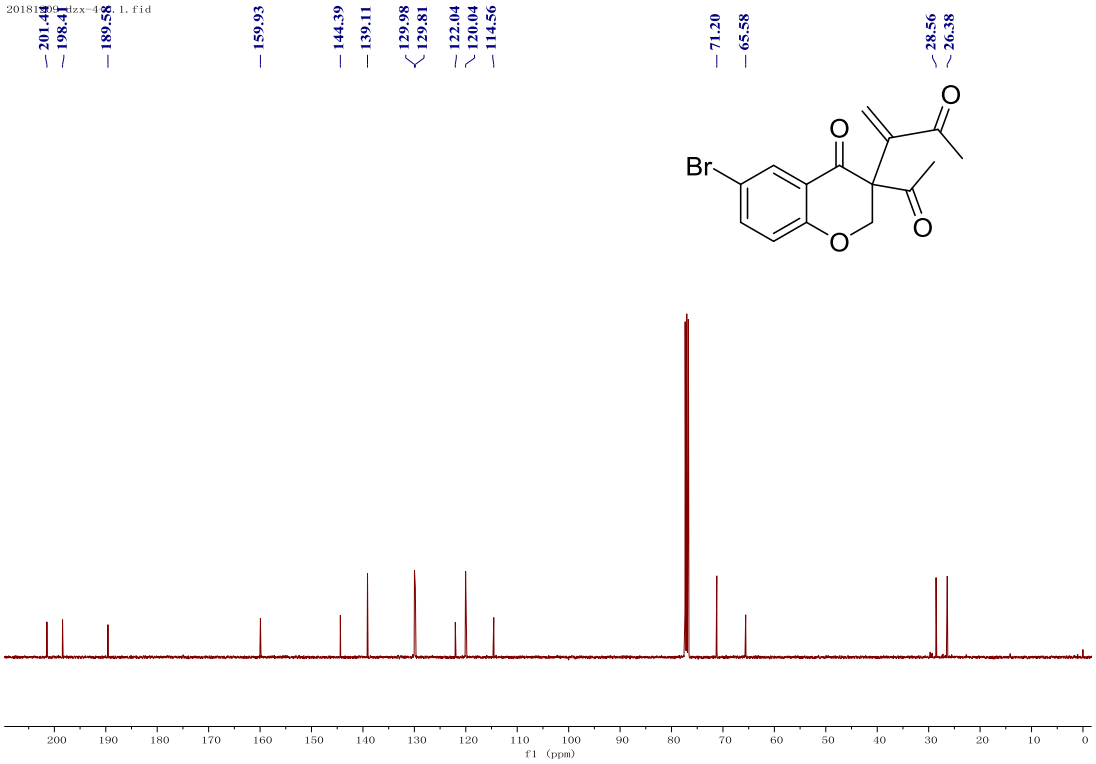
Product 3p: ^{13}C NMR



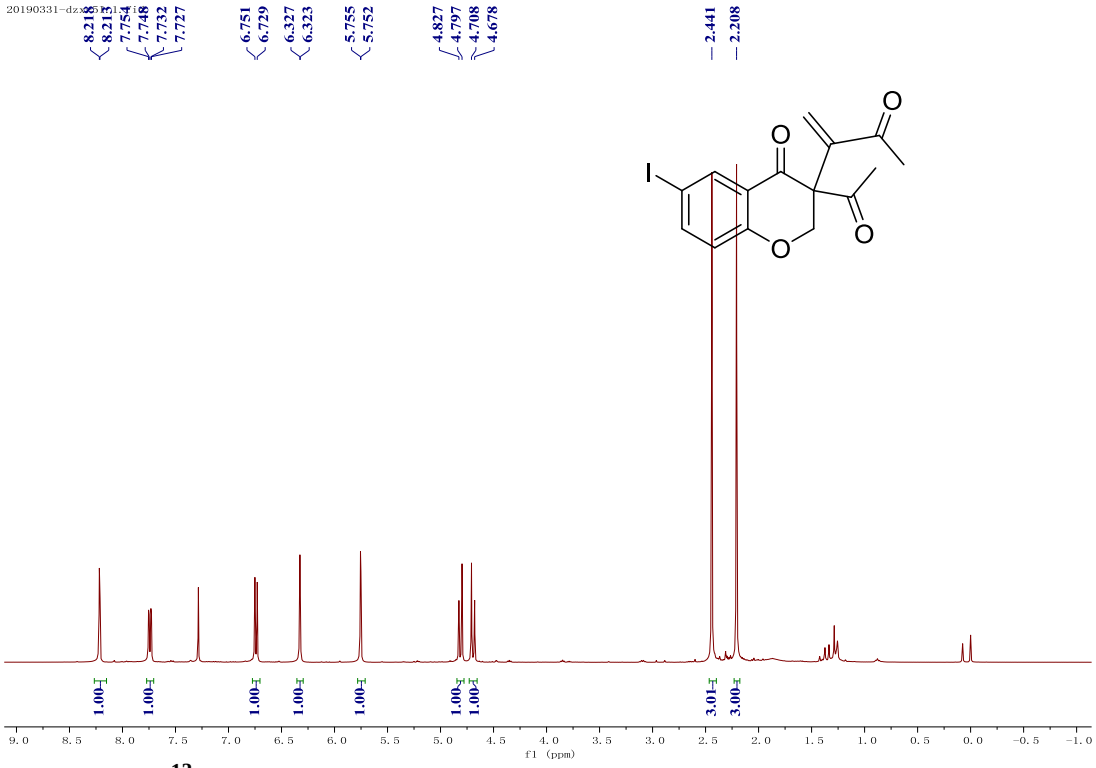
Product 3q: ^{1}H NMR



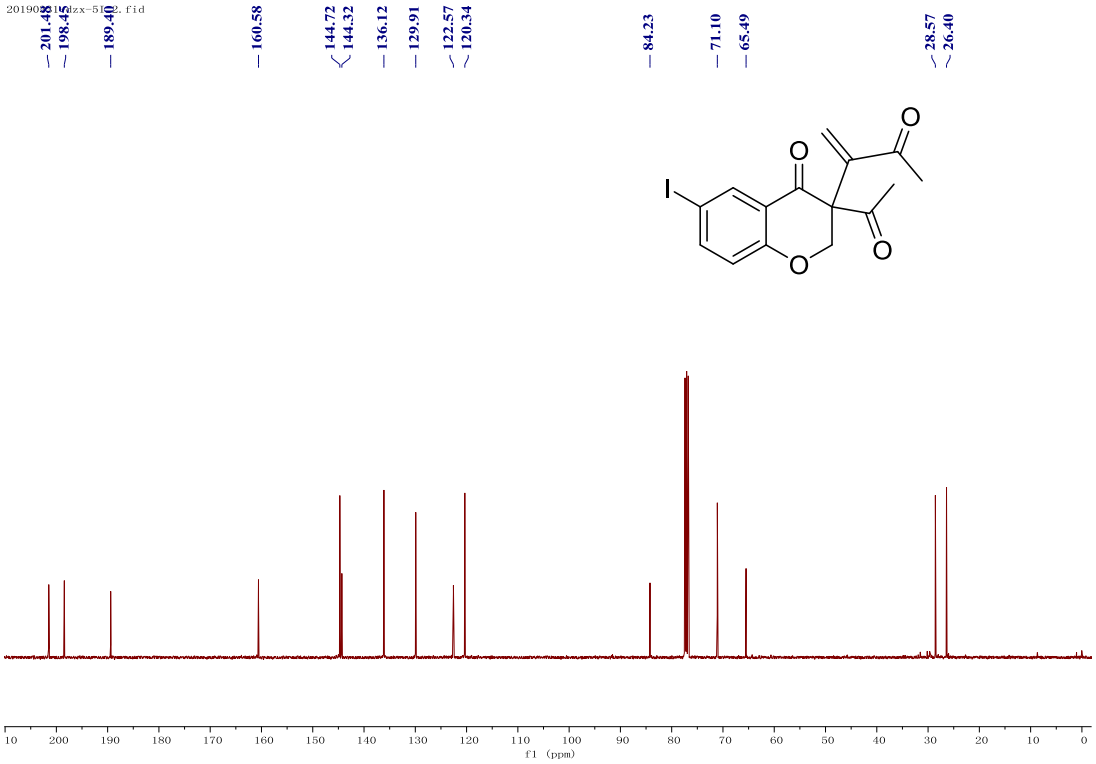
Product 3q: ^{13}C NMR



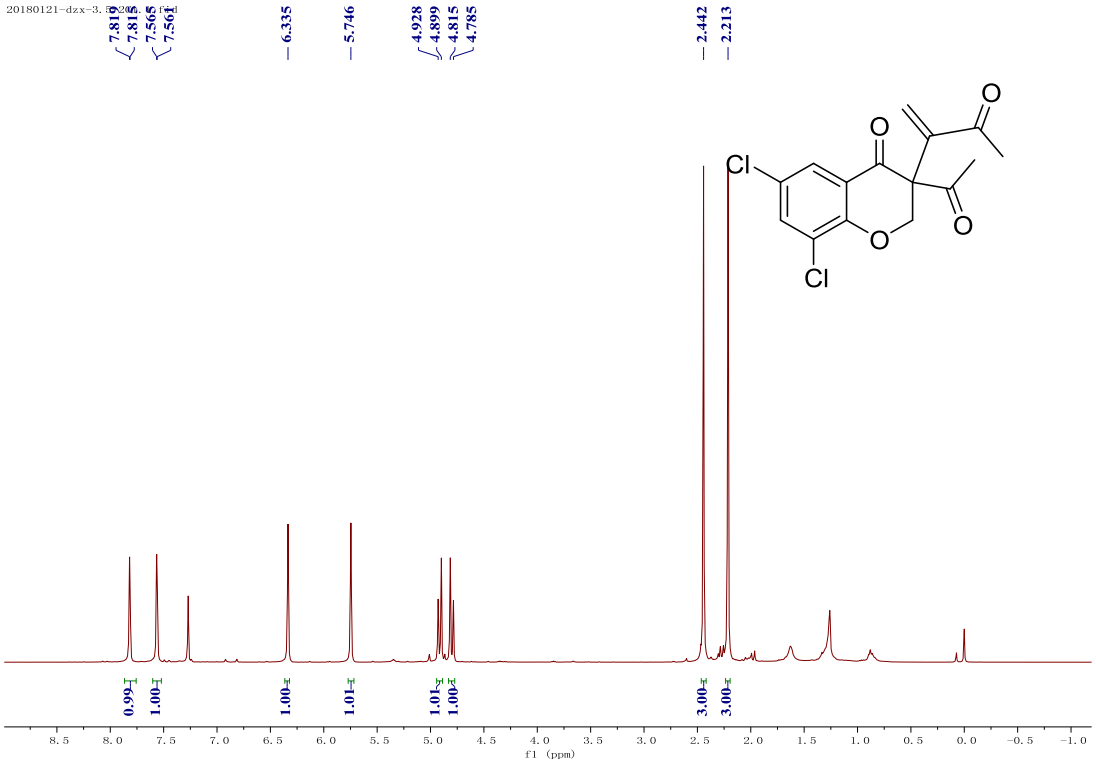
Product 3r: ^{1}H NMR



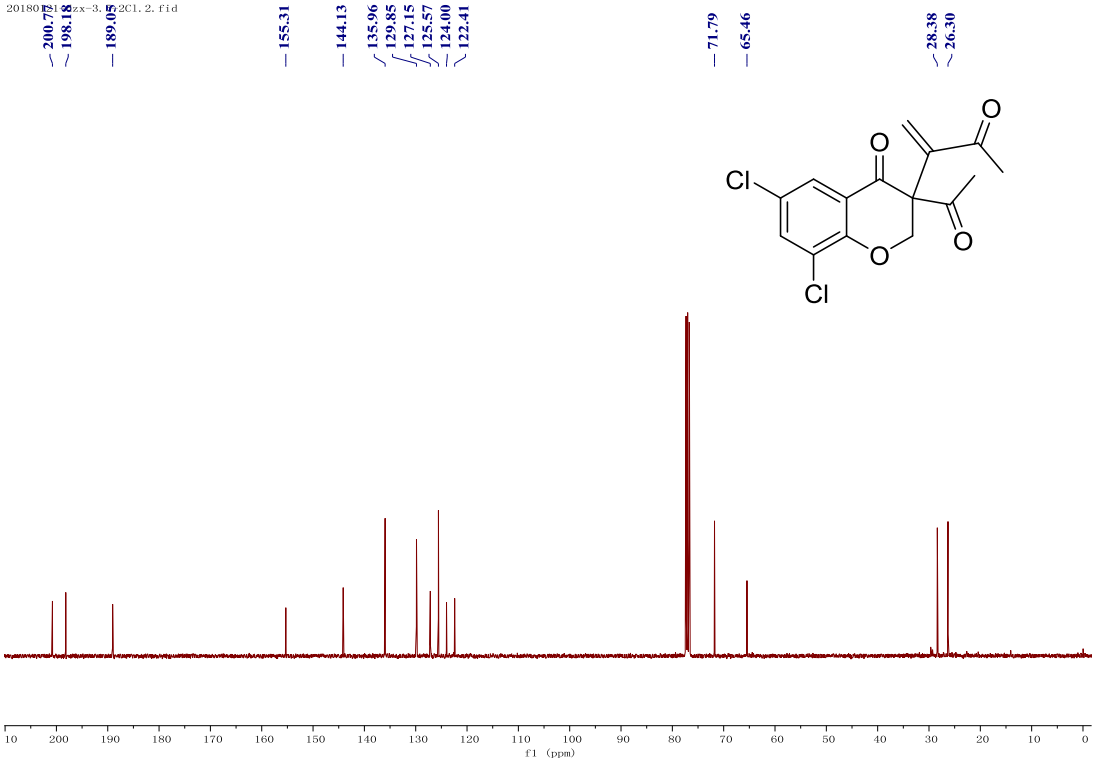
Product 3r: ^{13}C NMR



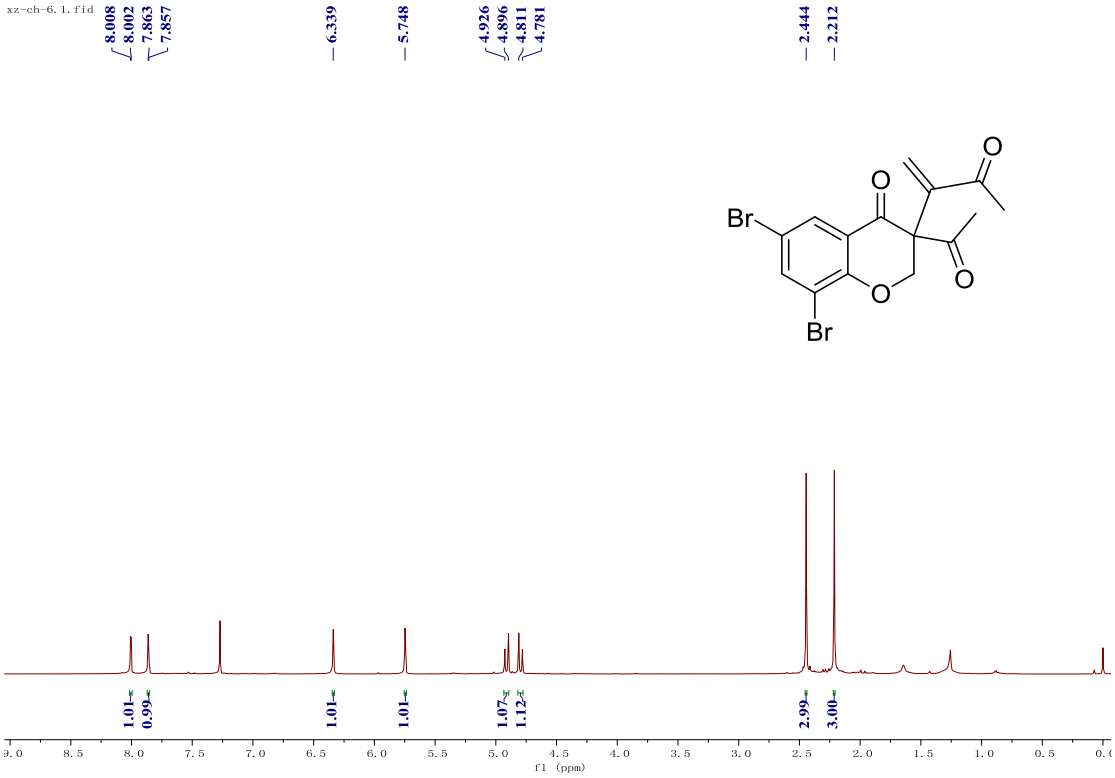
Product 3s: ^{1}H NMR



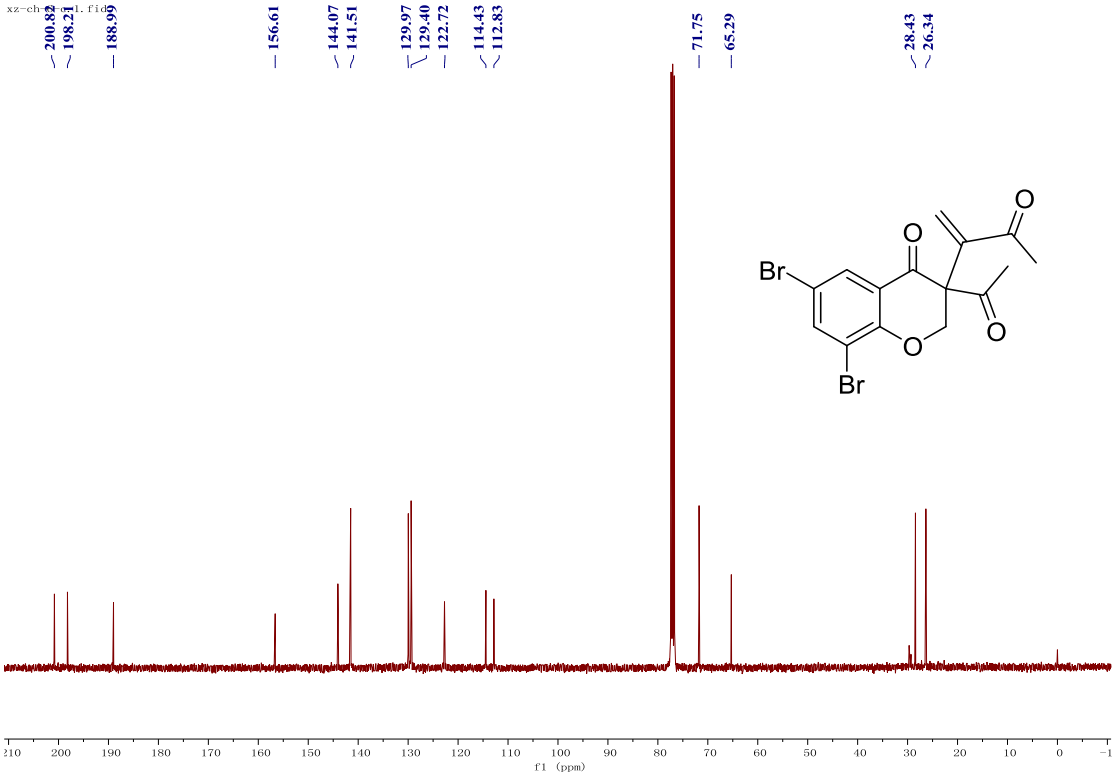
Product 3s: ^{13}C NMR



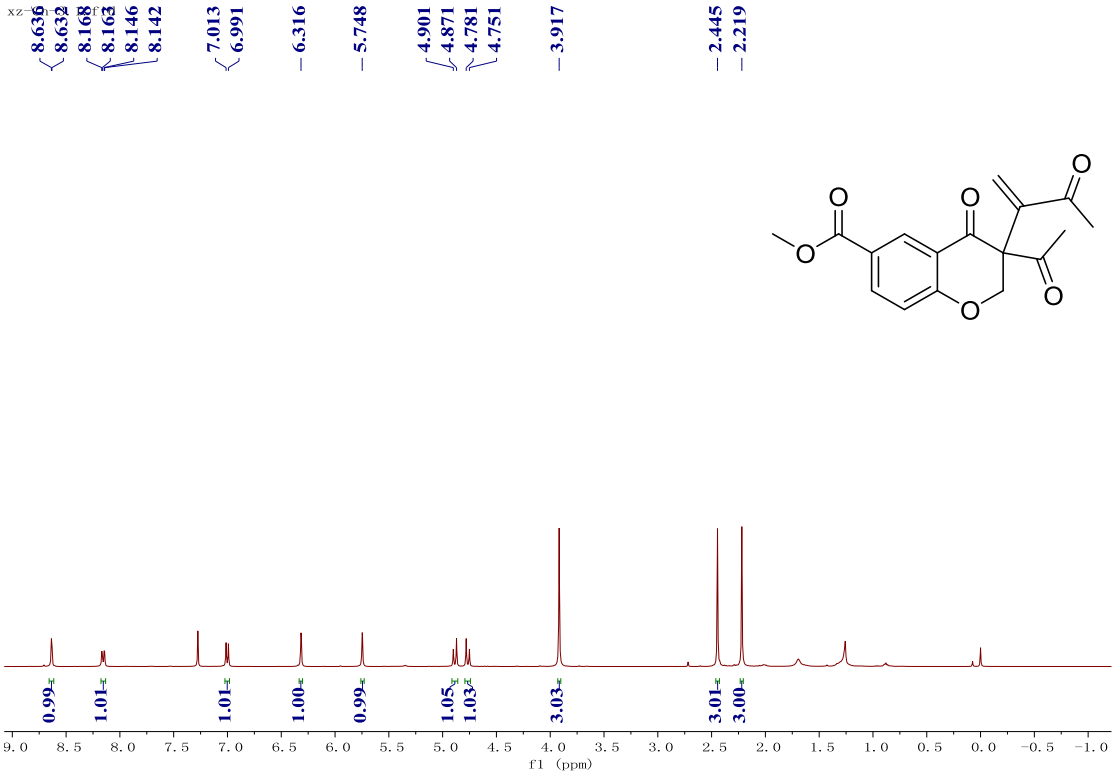
Product 3t: ^{1}H NMR



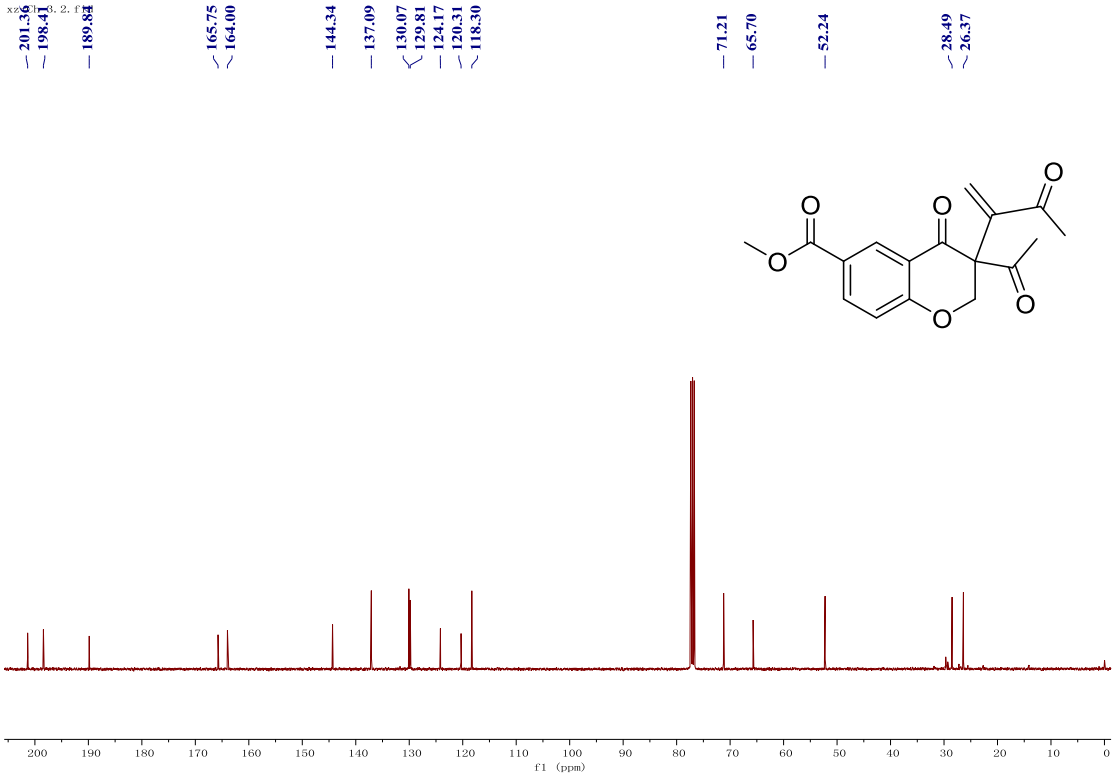
Product 3t: ^{13}C NMR



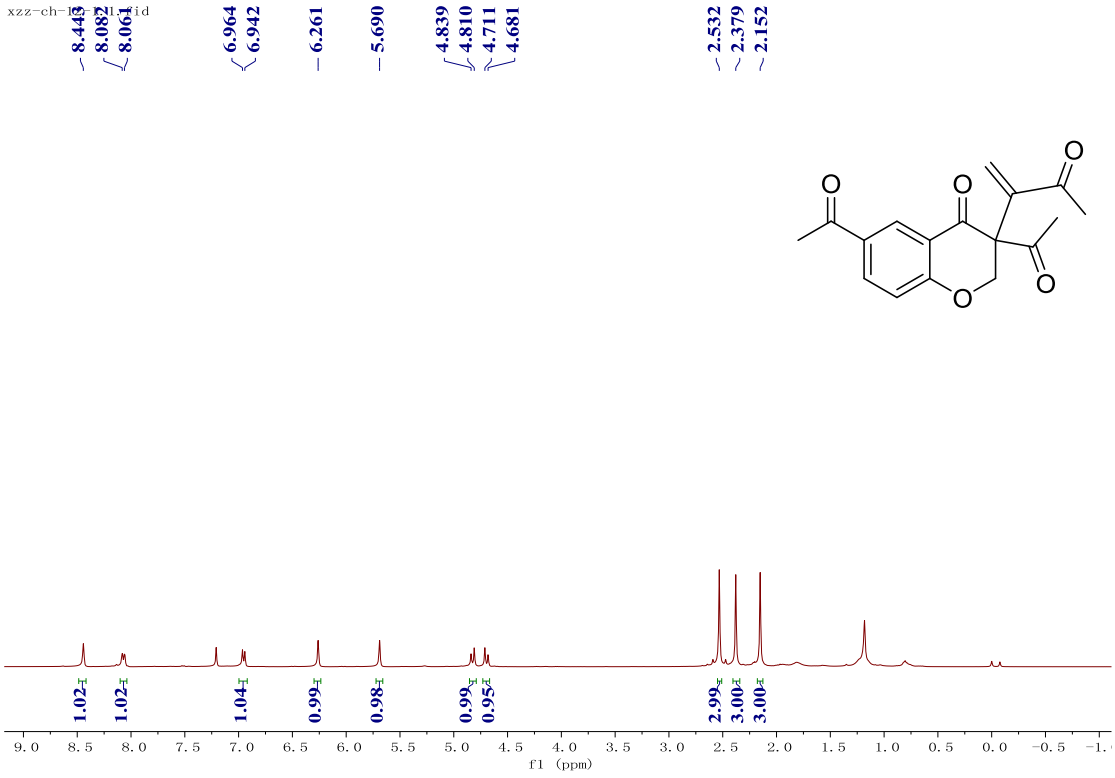
Product 3u: ^{1}H NMR



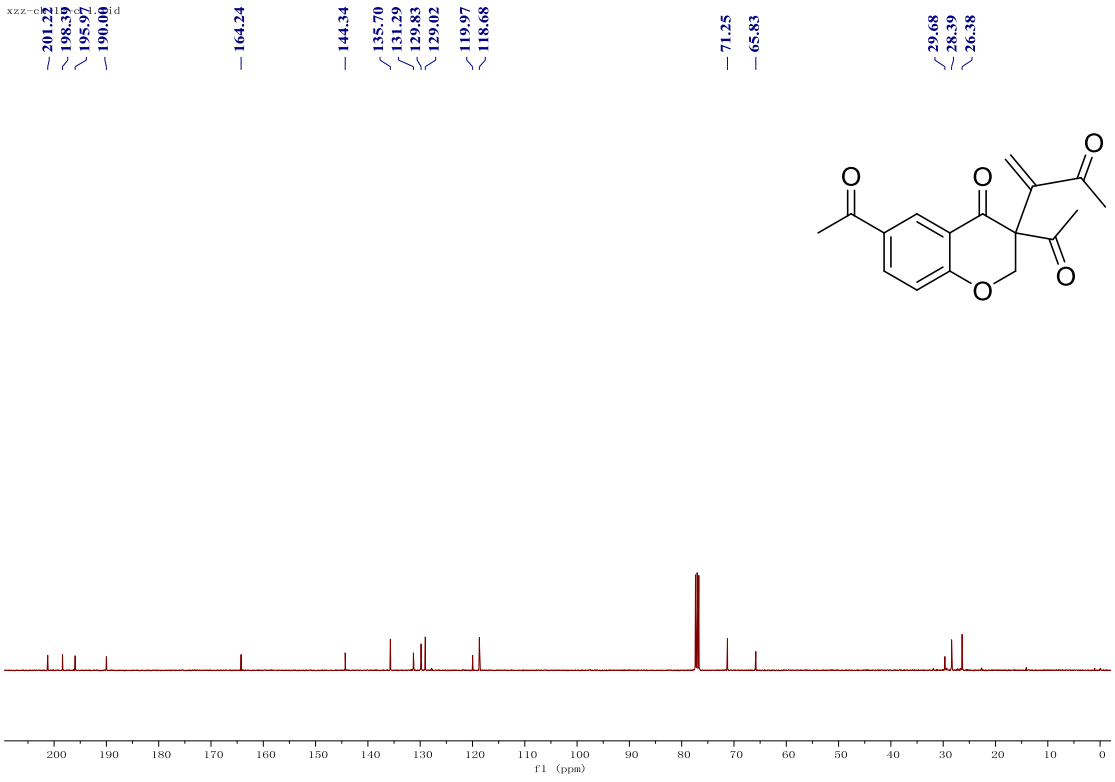
Product 3u: ^{13}C NMR



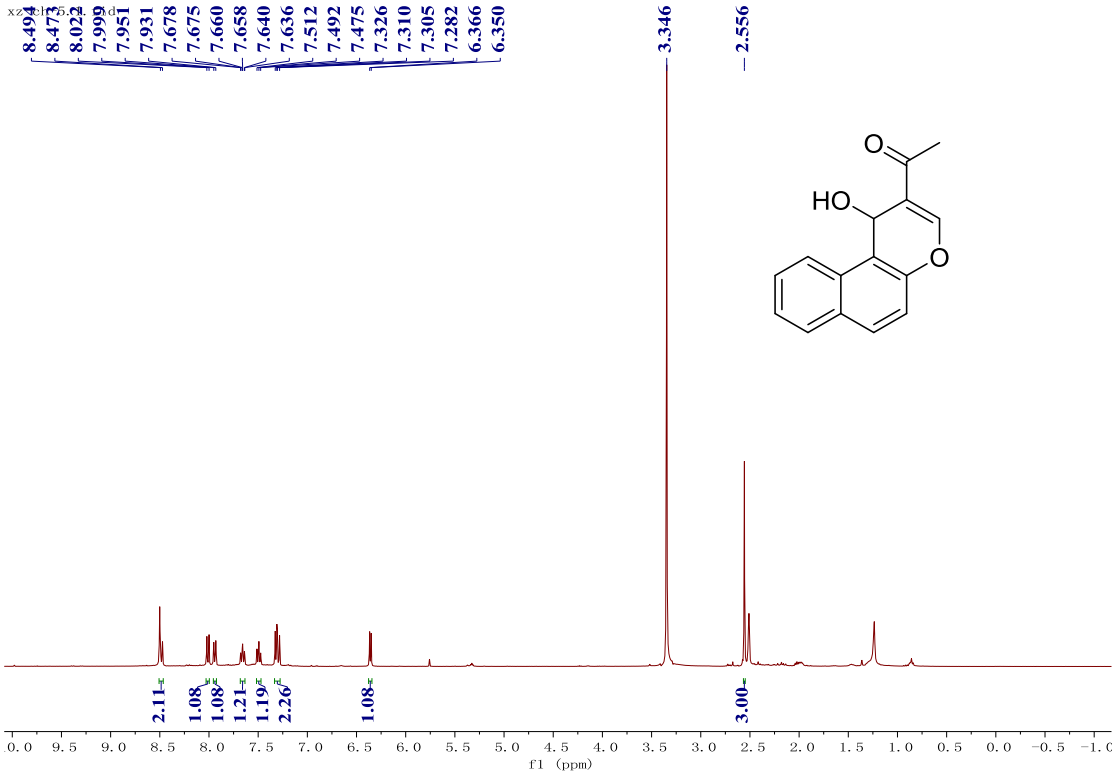
Product 3v: ^{1}H NMR



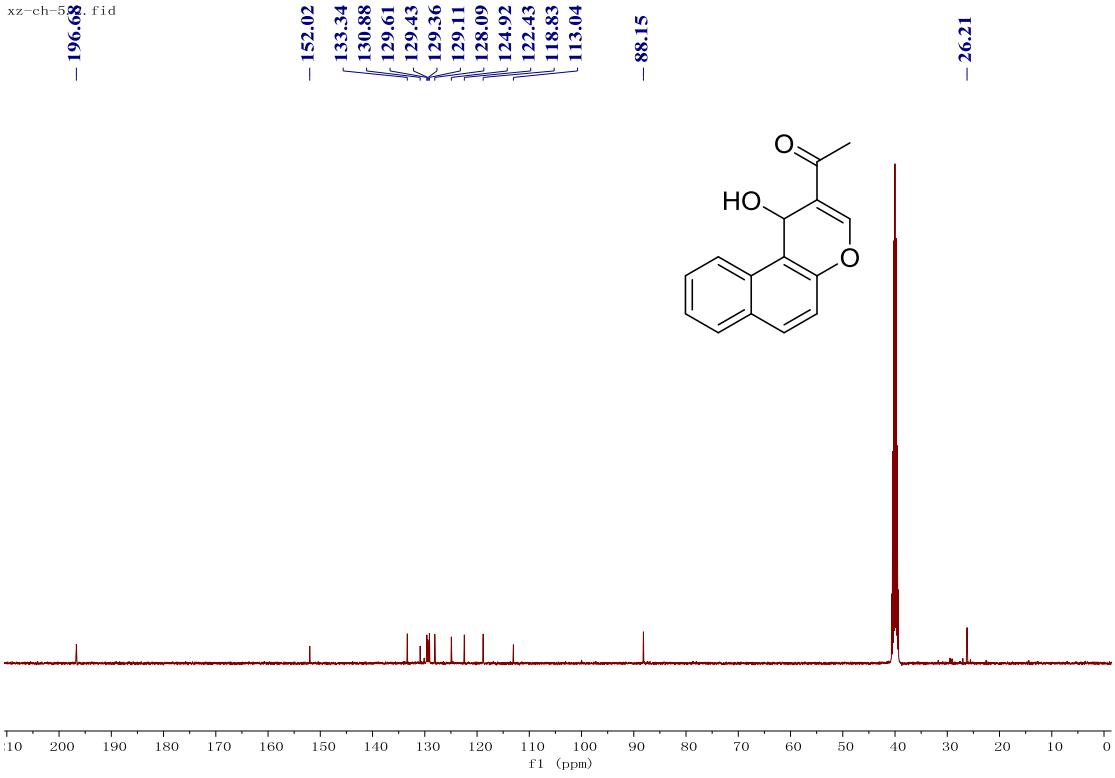
Product 3v: ^{13}C NMR



Product 3w: ^{1}H NMR



Product 3w: ^{13}C NMR



8. Crystal structure of product 3s (CCDC: 1948700) for absolute determination

Datablock: ja

Bond precision: C-C = 0.0026 A Wavelength=0.71073

Cell: a=11.3742(4) b=18.0280(7) c=7.5166(3)
alpha=90 beta=106.736(2) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1476.02(10)	1476.02(10)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	C15 H12 Cl2 O4	?
Sum formula	C15 H12 Cl2 O4	C2.50 H2 Cl0.33 O0.67
Mr	327.15	54.52
Dx,g cm-3	1.472	1.472
Z	4	24
Mu (mm-1)	0.451	0.451
F000	672.0	672.0
F000'	673.50	
h,k,lmax	14,23,9	14,23,9
Nref	3462	3386
Tmin,Tmax	0.897,0.914	
Tmin'	0.873	

Correction method= Not given

Data completeness= 0.978 Theta(max)= 27.730

R(reflections)= 0.0451(2894) wR2(reflections)= 0.1359(3386)

S = 1.052 Npar= 198
