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Supporting Information

Reactivity and Mechanistic Insight into Cross Coupling Reaction between Isochromans and β-Keto Esters through C-H Bond Activation under Visible Light Irradiation

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1. General Information

^1H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance DPX 400 MHz or 100 MHz instrument and referenced to the internal solvent signals. Mass spectra were obtained using a Q-Exactive instrument. Cyclic voltammetric measurement was recorded on Princeton Applied Research Model 283 Potentiostat/Galvanostat. A three-electrode-system is used for the measurement, with a 3 mm glass carbon working electrode, a platinum sheet counter electrode, and a saturated calomel electrode (SCE) reference electrode. The electrolyte solution (0.1 M of *n*-Bu_4NPF_6 in CH_3CN) was degassed by bubbling with argon for 20 min before measurement. The working electrode was polished with a 0.05 μm alumina paste for 5 min before use. ESR spectra were recorded using a Bruker E500 spectrometer at X-band, with 100Hz field modulation frequency. Commercially available reagents and solvents were used without further purification. All photoreactions were performed using common dry, inert atmosphere techniques. Irradiation with blue light was performed using High Power UV LED TY-LED 450 nm 3W®TaoYuan LED (λ = 450±10 nm, 600mA). Reactions were monitored by TLC, and column chromatography purifications were carried out using silica gel GF254.

2. Preparation of Substrates

Preparation of Isochroman Derivatives (1b~1g)

A mixture of the substituted phenylethyl alcohol (7.5 mmol), (2-methoxyethoxy)methyl (MEM) chloride (1.3 mL, 11.25 mmol) and *N,N*-diisopropylethylamine (1.5 mL, 11.25 mmol) in dry dichloromethane (15 mL) was stirred under argon atmosphere for 2.5 h at room temperature. The reaction mixture was then washed with 1 M HCl (2 × 15 mL), dried ($MgSO_4$) and the solvent was removed *in vacuo*. The crude MEM acetal was dissolved in dry dichloromethane (5 mL) and added to a cooled (0 ºC) solution of titanium tetrachloride (1.3 mL, 11.25 mmol) in dry dichloromethane (45 mL). The reaction was carried out under argon atmosphere, stirring and keeping the temperature at 0 ºC, for 2.5 h. Then the mixture was quenched by the addition of methanol (2 mL) and 1 M $NaHCO_3$ (15 mL). The organic phase was washed with brine (25 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification by column chromatography afforded the substituted isochroman.

Preparation of Substrate (1h)

A mixture of 1-(bromomethyl)-4-methylbenzene (0.56 g, 3.0 mmol) and $FeSO_4 \cdot 7H_2O$ (0.84 g, 3.0 mmol) were refluxed in methanol (5.0 mL) at 75 ºC for 12 h. After that, the reaction mixture was cooled to room temperature, $FeSO_4$ was removed by filtration. The methanol was stripped out, and the residue left out was purified by column chromatography to obtain the pure product.

Synthesis of Deuterium Substrate (1a-d_2)

To a solution of isochroman-1-one (368 μL, 3 mmol) in anhydrous THF (30 mL) under an argon atmosphere at 0 °C, was added lithium aluminum deuteride $LiAlD_4$ (252 mg, 6 mmol). The reaction mixture was carried out at room temperature for 12 h. The mixture was then quenched with H_2O, and extracted with Et_2O. The layers were separated and the organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to afford the desired 2-(2-(hydroxymethyl-d2)phenyl)ethan-1-ol.

To a solution of 2-(2-(hydroxymethyl-d2)phenyl)ethan-1-ol (133 μL, 1 mmol) in carbon tetrachloride (10 mL), was added zinc chloride (250 mg, 1.8 mmol). The solution was refluxed for 4 h. After that, the reaction mixture was cooled, washed with water and extracted with dichloromethane. The organic layer was dried ($MgSO_4$) and purified by column chromatography to obtain the pure deuterium substrate (**1a-d$_2$**).

3. General Procedure for the Photocatalytic Reaction

A 10 mL reaction tube equipped with magnetic stirring bar was charged with Acr^+-Mes ClO_4^- (0.025 mmol, 5 mol %), $Cu(OTf)_2$ (0.05 mmol, 10 mol %), Na_2HPO_4 (1.0 mmol, 2 equiv.), 2 mL anhydrous acetonitrile, isochroman derivate (1.0 mmol, 2 equiv.), β-keto ester (0.5 mmol, 1 equiv.) and $BrCCl_3$ (1.0 mmol, 2 equiv.). The reaction tube was sealed and the reaction mixture was degassed by bubbling with argon for 30 minutes. The mixture was stirred and irradiated with blue LEDs ($\lambda = 450 \pm 10$ nm) for 24 h at room temperature. After that, the solution was concentrated *in vacuo* and the mixture was purified by column chromatography on silica gel using hexane/ethyl acetate (15:1) as eluent to afford the desired cross coupling product, which was characterized by NMR and HRMS.

4. Cyclic voltammograms of Isochroman and $BrCCl_3$

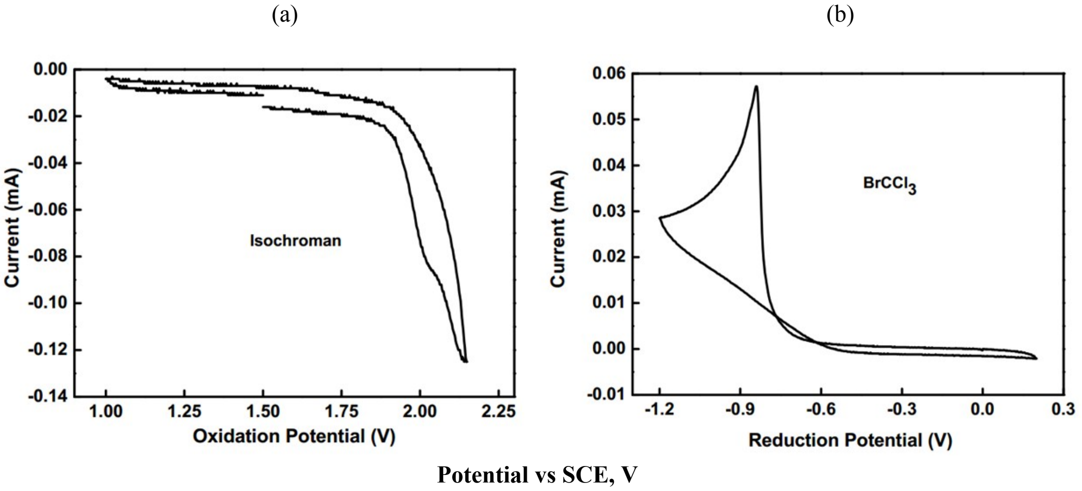
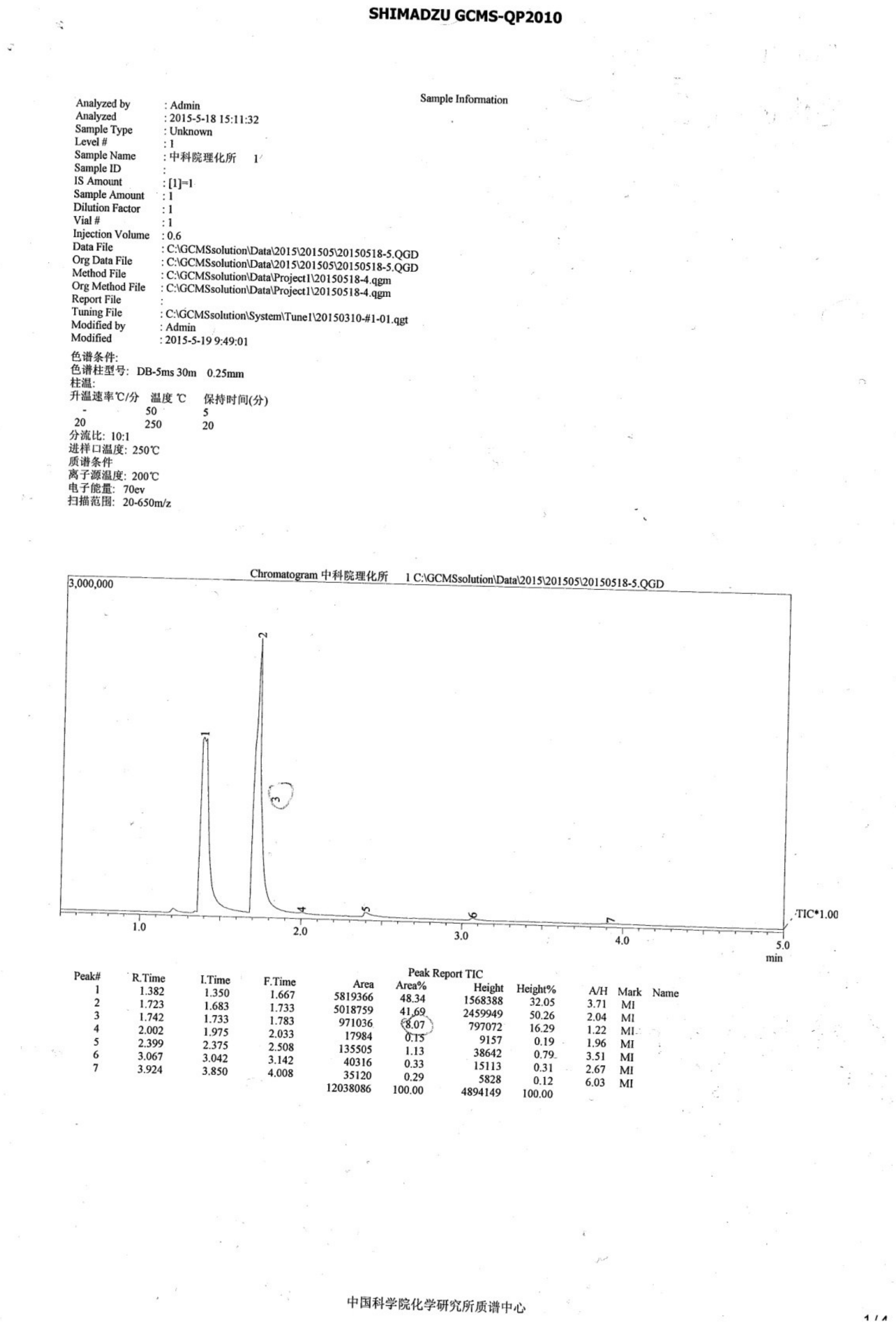


Figure S1. Cyclic voltammograms of (a) Isochroman (1 mM) and (b) $BrCCl_3$ (1 mM) in deaerated MeCN containing $TBAPF_6$ (0.1 M).

5. Copies of GC-MS spectrum



SHIMADZU GCMS-QP2010

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质谱条件
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Chromatogram 中科院理化所 1 C:\GCMSsolution\Data\2015\201505\20150518-5.QGD

Peak Report TIC

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2	1.723	1.683	1.733	5018759	41.69	2459949	50.26	2.04	MI	
3	1.742	1.733	1.783	971036	8.07	797072	16.29	1.22	MI	
4	2.002	1.975	2.033	17984	0.15	9157	0.19	1.96	MI	
5	2.399	2.375	2.508	135505	1.13	38642	0.79	3.51	MI	
6	3.067	3.042	3.142	40316	0.33	15113	0.31	2.67	MI	
7	3.924	3.850	4.008	35120	0.29	5828	0.12	6.03	MI	
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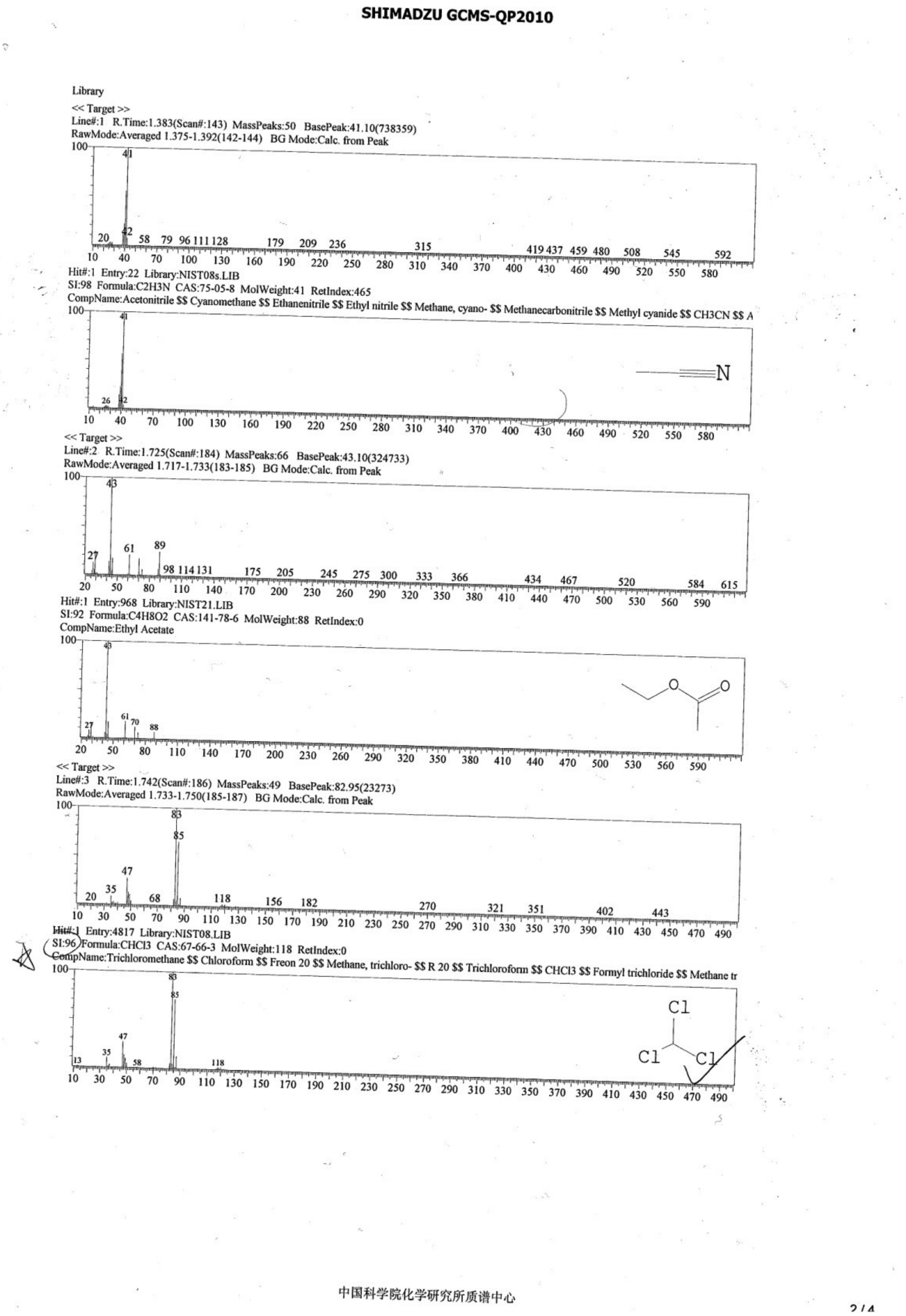
Figure S2. Copy of GC-MS spectrum (Page 1/2)



SHIMADZU GCMS-QP2010

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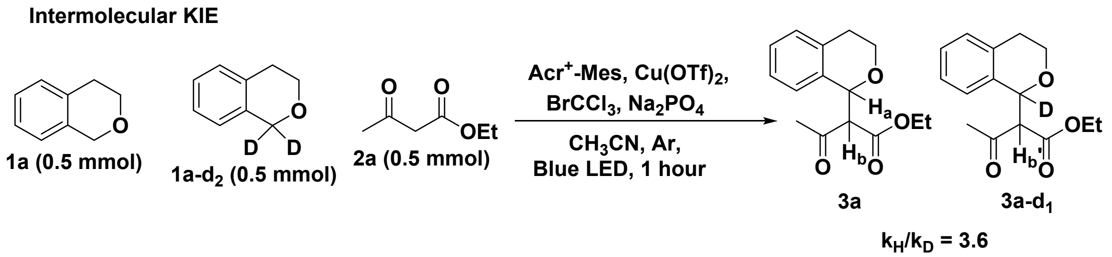
Figure S2. Copy of GC-MS spectrum (Page 2/2)

6. Procedure for intermolecular kinetic isotope effect experiment

Intermolecular Kinetic Isotope Effect (KIE) Experiment



A 10 mL reaction tube equipped with magnetic stirring bar was charged with Acr$^+$-Mes ClO_4^- (0.025 mmol), $Cu(OTf)_2$ (0.05 mmol), Na_2HPO_4 (1.0 mmol), 2 mL anhydrous acetonitrile, **1a** (0.5 mmol), **1a-d$_2$** (0.5 mmol), **2a** (0.5 mmol) and $BrCCl_3$ (1.0 mmol). The reaction tube was sealed and the reaction mixture was degassed by bubbling with argon for 30 minutes. The mixture was stirred and irradiated with blue LEDs (λ = 450±10 nm) for 1 h at room temperature. After that, the solution was concentrated *in vacuo* and purification of crude product by column chromatography on silica gel using hexane/ethyl acetate (15:1) as eluent afforded a mixture of non-deuterated (**3a**) and mono-deuterated (**3a-d$_1$**) products. The product ratio of **3a** to **3a-d$_1$** was calculated by acquiring a ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the mixture.

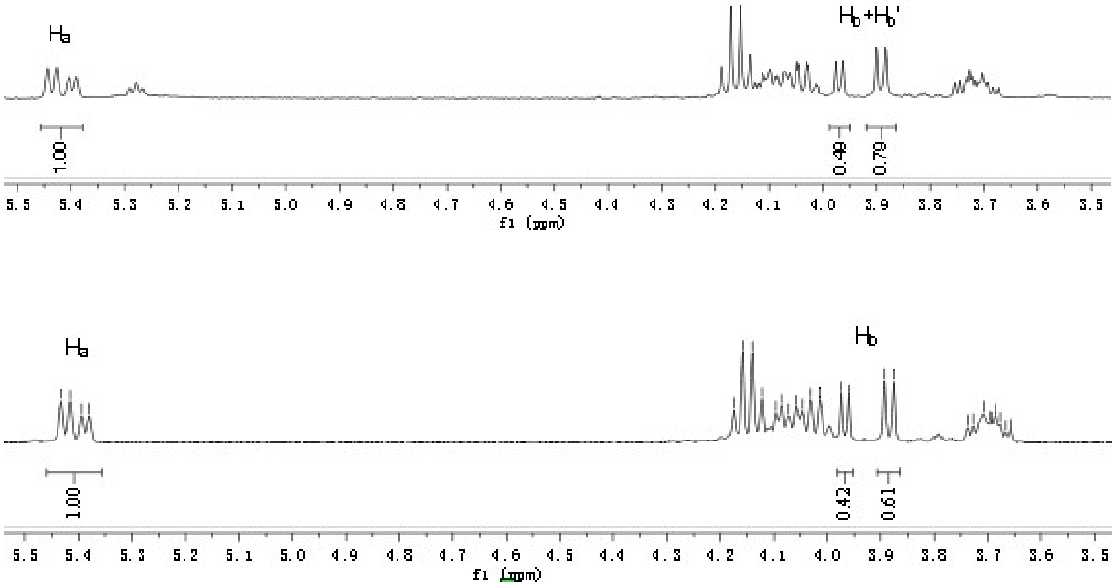


Figure S3. ^{1}H NMR spectrum of mixed 3a and 3a-d$_1$ (up); ^{1}H NMR spectrum of 3a (down)

7. Characterization data of synthesized compounds

^{1}H and ^{13}C NMR spectra data of substrates:

5-methylisochromane (1b). A colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.00 (m, 2H), 6.83 (d, J = 7.3 Hz, 1H), 4.76 (s, 2H), 4.01 (t, J = 5.8 Hz, 2H), 2.70 (t, J = 5.8 Hz, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 134.9, 131.9, 127.8, 125.8, 122.1, 68.4, 65.7, 26.2, 18.9.

7-methylisochromane (1c). A colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (q, J = 7.9 Hz, 2H), 6.79 (s, 1H), 4.73 (s, 2H), 3.95 (t, J = 5.7 Hz, 2H), 2.81 (t, J = 5.7 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6, 134.9, 130.2, 128.9, 127.3, 125.0, 68.1, 65.7, 28.1, 21.2.

7-(tert-butyl)isochromane (1d). A colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.0 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 6.99 (s, 1H), 4.77 (s, 2H), 3.97 (t, J = 5.7 Hz, 2H), 2.82 (t, J = 5.7 Hz, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 134.5, 130.4, 128.7, 123.6, 121.2, 68.4, 65.6, 34.5, 31.5, 28.1.

7-methoxyisochromane (1e). A colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, J = 8.4 Hz, 1H), 6.74 (dd, J = 8.4, 2.6 Hz, 1H), 6.51 (d, J = 2.5 Hz, 1H), 4.74 (s, 2H), 3.95 (t, J = 5.7 Hz, 2H), 3.77 (s, 3H), 2.79 (t, J = 5.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 136.0, 130.0, 125.4, 112.9, 109.2, 68.2, 65.8, 55.4, 27.7.

7-chloroisochromane (1f). A colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, J = 8.2, 2.0 Hz, 1H), 7.04 (d, J = 8.2 Hz, 1H), 6.98 (s, 1H), 4.72 (s, 2H), 3.95 (t, J = 5.7 Hz, 2H), 2.81 (t, J = 5.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 131.8, 131.7, 130.4, 126.7, 124.5, 67.7, 65.4, 27.9.

1,4-dihydro-2H-benzo[f]isochromene (1g). A white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.3 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 4.92 (s, 2H), 4.16 (t, J = 5.7 Hz, 2H), 3.18 (t, J = 5.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.4, 132.2, 128.7, 128.4, 126.5, 126.4, 125.5, 123.0, 122.6, 68.4, 65.4, 25.2.

1-(methoxymethyl)-4-methylbenzene (1h). A colorless oil: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.20 (dd, *J* = 27.6, 7.9 Hz, 4H), 4.43 (s, 2H), 3.37 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.5, 135.3, 129.2, 128.0, 74.7, 58.1, 21.3.

Isochromane-1,1-*d*$_2$ (1a-d$_2$). A colorless oil: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.19 – 7.09 (m, 3H), 7.01 – 6.95 (m, 1H), 3.97 (t, *J* = 5.7 Hz, 2H), 2.86 (t, *J* = 5.7 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 134.9, 133.4, 129.0, 126.5, 126.1, 124.5, 65.5, 28.5.

^{1}H and ^{13}C NMR spectra and HRMS data of products:

Ethyl 2-(isochroman-1-yl)-3-oxobutanoate (3a). A colorless oil: observed as two diastereomers in ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.20 – 7.08 (m, 3H), 7.01 (d, *J* = 7.4 Hz, 1H), 5.49 (d, *J* = 6.8 Hz, aH), 5.46 (d, *J* = 5.5 Hz, bH)[a+b=1], 4.25 – 4.08 (m, 3H), 4.04 (d, *J* = 5.5 Hz, cH), 3.95 (d, *J* = 6.8 Hz, dH) [c+d=1], 3.83 – 3.70 (m, 1H), 3.09 – 2.92 (m, 1H), 2.75 – 2.65 (m, 1H), 2.24 (d, *J* = 18.2 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, eH), 1.10 (t, *J* = 7.1 Hz, fH)[e+f=1]; ^{13}C NMR (100 MHz, CDCl$_3$) δ 202.1, 201.9, 168.4, 167.5, 135.2, 135.0, 134.5, 134.0, 129.3, 129.1, 127.3, 127.0, 126.5, 126.4, 124.8, 124.6, 74.5, 74.3, 65.7, 65.6, 64.0, 63.6, 61.7, 61.2, 30.1, 29.5, 28.7, 28.6, 14.1, 14.0; MS (HRESI): m/z calcd for $C_{15}H_{18}O_4$ $[M+Na]^+$ 285.1097, found 285.1087.

Ethyl 2-(isochroman-1-yl)-4-methyl-3-oxopentanoate (3b). A colorless oil: observed as two diastereomers in ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.21 – 7.08 (m, 3H), 7.04 – 6.93 (m, 1H), 5.55 – 5.49 (m, 1H), 4.27 – 4.12 (m, 4H), 3.82 – 3.77 (m, 1H), 3.05 – 2.92 (m, 1H), 2.81 – 2.61 (m, 2H), 1.23 (t, *J* = 7.1 Hz, aH), 1.18 (t, *J* = 7.1 Hz, bH)[a+b=3], 1.12 – 0.95 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 207.5, 207.3, 168.4, 167.4, 135.9, 135.5, 134.3, 134.2, 129.2, 129.1, 127.2, 126.4, 126.3, 125.3, 124.8, 75.0, 74.1, 63.8, 63.4, 63.2, 61.6, 61.4, 41.5, 41.4, 28.9, 28.8, 18.3, 18.2, 17.8, 14.1; MS (HRESI): m/z calcd for $C_{17}H_{22}O_4$ $[M+Na]^+$ 313.1410, found 313.1401.

Isopropyl 2-(isochroman-1-yl)-3-oxobutanoate (3c). A colorless oil: observed as two diastereomers in ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 – 7.11 (m, 3H), 7.02 (t, *J* = 6.7 Hz, 1H), 5.49 (d, *J* = 6.9 Hz, aH), 5.45 (d, *J* = 5.4 Hz, bH)[a+b=1], 5.10 (dt, *J* = 12.5, 6.3 Hz, cH), 4.95 (dt, *J* = 12.5, 6.3 Hz, dH)[c+d=1], 4.22 – 4.11 (m, 1H), 4.00 (d, *J* = 5.4 Hz, eH), 3.92 (d, *J* = 6.9 Hz, fH)[e+f=1], 3.81 – 3.73 (m, 1H), 3.09 – 2.93 (m, 1H), 2.78 – 2.64 (m, 1H), 2.25 (d, 3H), 1.26 – 1.08 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 202.3, 202.0, 168.0, 167.2, 135.4, 135.2, 134.5, 134.0, 129.3, 129.1, 127.3, 127.0, 126.5, 126.4, 124.9, 124.7, 74.6, 74.4, 69.4, 68.8, 66.0, 65.7, 64.0, 63.6, 30.0, 29.4, 28.8, 28.7, 21.7, 21.6, 21.5; MS (HRESI): m/z calcd for $C_{16}H_{20}O_4$ [M+Na]$^+$ 299.1254, found 299.1246.

Ethyl 2-(isochroman-1-yl)-4,4-dimethyl-3-oxopentanoate (3d). A colorless oil: observed as two diastereomers in ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.21 – 6.84 (m, 4H), 5.62 (d, *J* = 9.4 Hz, aH), 5.56 (d, *J* = 8.4 Hz, bH)[a+b=1], 4.50 (d, *J* = 9.4 Hz, cH), 4.38 (d, *J* = 8.4 Hz, dH)[c+d=1], 4.27 – 4.06 (m, 3H), 3.89 – 3.68 (m, 1H), 3.03 – 2.67 (m, 2H), 1.29 – 0.99 (m, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 207.5, 207.4, 167.7, 166.9, 135.6, 134.6, 133.8, 129.1, 129.0, 127.4, 127.1, 126.2, 126.1, 125.1, 75.5, 74.5, 63.4, 61.9, 61.6, 61.5, 60.2, 59.2, 46.0, 45.8, 29.1, 28.6, 26.3, 25.9, 14.1, 14.0; MS (HRESI): m/z calcd for $C_{18}H_{24}O_4$ [M+Na]$^+$ 327.1567, found 327.1560.

***tert*-butyl 2-(isochroman-1-yl)-3-oxobutanoate (3e).** A colorless oil: observed as two diastereomers in ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.21 – 7.10 (m, 3H), 7.08 – 7.01 (m, 1H), 5.47 (d, *J* = 6.8 Hz, aH), 5.42 (d, *J* = 5.2 Hz, bH)[a+b=1], 4.23 – 4.11 (m, 1H), 3.93 (d, *J* = 5.3 Hz, cH), 3.88 (d, *J* = 6.8 Hz, dH)[c+d=1], 3.82 – 3.73 (m, 1H), 3.08 – 2.94 (m, 1H), 2.78 – 2.63 (m, 1H), 2.25 (d, *J* = 28.0 Hz, 3H), 1.38 (d, *J* = 63.8 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 202.6, 202.3, 167.6, 166.8, 135.7, 135.4, 134.4, 134.0, 129.3, 129.1, 127.2, 126.9, 126.4, 126.3, 125.0, 124.7, 82.5, 81.7, 74.5, 66.8, 66.3, 64.0, 63.6, 30.0, 29.3, 28.8, 28.7, 28.0, 27.8; MS (HRESI): m/z calcd for $C_{17}H_{22}O_4$ [M+Na]$^+$ 313.1410, found 313.1400.

Ethyl 2-(isochroman-1-yl)-3-oxo-3-phenylpropanoate (3f). A colorless oil: observed as two diastereomers in ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 – 7.91 (m, 2H), 7.55 (q, *J* = 7.5 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.18 – 7.02 (m, 4H), 5.87 – 5.67 (m, 1H), 4.95 (d, *J* = 7.7 Hz, aH), 4.90 (d, *J* = 7.1 Hz, bH)[a+b=1], 4.23 – 4.01 (m, 3H), 3.89 – 3.68 (m, 1H), 3.02 – 2.85 (m, 1H), 2.78 (dt, *J* = 16.3, 4.8 Hz, cH), 2.69 (dt, *J* = 16.2, 4.2 Hz, dH)[c+d=1], 1.18 – 1.12 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 193.2, 168.2, 167.2, 137.4, 136.7, 136.0, 135.8, 134.5, 134.1, 133.7, 133.3, 129.1, 128.8, 128.7, 128.6, 127.2, 127.1, 126.3, 125.2, 125.1, 74.7, 74.0, 63.4, 61.7, 61.6, 61.5, 60.5, 28.9, 28.7, 14.0; MS (HRESI): m/z calcd for $C_{20}H_{20}O_4$ $[M+Na]^+$ 347.1254, found 347.1243.

Methyl 3-(4-chlorophenyl)-2-(isochroman-1-yl)-3-oxopropanoate (3g). A colorless oil: observed as two diastereomers in ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.22 – 6.94 (m, 4H), 5.73 (t, *J* = 6.9 Hz, 1H), 4.88 (d, *J* = 7.7 Hz, aH), 4.81 (d, *J* = 7.2 Hz, bH)[a+b=1], 4.23 – 3.98 (m, 1H), 3.88 – 3.66 (m, 4H), 3.00 – 2.83 (m, 1H), 2.77 (dt, *J* = 16.3, 4.7 Hz, cH), 2.67 (dt, *J* = 16.2, 3.8 Hz, dH)[c+d=1]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 192.0, 168.6, 167.6, 140.5, 139.9, 135.7, 135.6, 134.9, 134.6, 134.2, 130.2, 129.2, 129.0, 127.3, 126.5, 126.4, 125.3, 124.8, 74.8, 74.1, 63.7, 63.5, 61.5, 60.4, 52.9, 28.9, 28.8; MS (HRESI): m/z calcd for $C_{19}H_{17}ClO_4$ $[M+Na]^+$ 367.0708, found 367.0701.

Ethyl 2-(isochroman-1-yl)-3-(4-methoxyphenyl)-3-oxopropanoate (3h). A colorless oil: observed as two diastereomers in ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.9 Hz, aH), 7.93 (d, *J* = 8.9 Hz, bH)[a+b=2], 7.21 – 6.97 (m, 4H), 6.92 – 6.89 (m, 2H), 5.75 (t, *J* = 7.2 Hz, 1H), 4.87 (d, *J* = 8.2 Hz, cH), 4.82 (d, *J* = 7.4 Hz, dH)[c+d=1], 4.26 – 4.00 (m, 3H), 3.90 – 3.68 (m, 4H), 3.00 – 2.85 (m, 1H), 2.80 (dt, *J* = 16.3, 5.0 Hz, eH), 2.70 (dt, *J* = 16.2, 4.2 Hz, fH)[e+f=1], 1.21 – 1.10 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 191.5, 168.4, 167.4, 164.1, 163.8, 136.2, 135.9, 134.6, 134.0, 131.2, 129.7, 129.1, 127.2, 127.1, 126.3, 125.4, 125.2, 114.1, 113.9, 74.7, 74.1, 63.4, 61.7, 61.6, 61.3, 60.3, 55.7, 55.6, 29.0, 28.8, 14.1; MS (HRESI): m/z calcd for $C_{21}H_{22}O_5$ $[M+Na]^+$ 377.1359, found 377.1353.

3-(isochroman-1-yl)pentane-2,4-dione or 4-hydroxy-3-(isochroman-1-yl)pent-3-en-2-one (3i). A colorless oil: observed as two isomers in ^{1}H NMR (400 MHz, $CDCl_3$) δ 17.27 (s, aH), 7.18 – 7.12 (m, 3H), 6.92 (t, *J* = 7.8 Hz, 1H), 5.64 (s, cH), 5.53 (d, *J* = 6.9 Hz, dH)[c+d=1], 4.36 – 4.10 (m, (1+b)H)[a+b=1], 3.96 – 3.74 (m, 1H), 3.25 – 2.93 (m, 1H), 2.78 – 2.64 (m, 1H), 2.39 – 1.68 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 203.0, 138.0, 135.3, 133.9, 133.8, 129.5, 129.0, 127.4, 127.0, 126.8, 126.7, 124.9, 124.7, 112.4, 75.1, 74.2, 66.2, 63.7, 31.0, 29.1, 28.6; MS

(HRESI): m/z calcd for $C_{14}H_{16}O_3$ $[M+Na]^+$ 255.0992, found 255.0986.

2-(isochroman-1-yl)-2-nitro-1-phenylethan-1-one (3j). A colorless oil: observed as two isomers in ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, aH), 7.72 (d, *J* = 8.0 Hz, bH)[a+b=2], 7.64 – 7.53 (m, 1H), 7.45 (t, *J* = 7.8 Hz, cH), 7.37 (t, *J* = 7.8 Hz, dH)[c+d=2], 7.26 – 6.97 (m, 4H), 6.53 (d, *J* = 7.2 Hz, eH), 6.38 (d, *J* = 5.1 Hz, fH)[e+f=1], 5.92 (d, *J* = 5.0 Hz, gH), 5.88 (d, *J* = 7.2 Hz, hH)[g+h=1], 4.28 – 3.99 (m, 1H), 3.89 – 3.64 (m, 1H), 3.05 – 2.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 187.3, 135.3, 135.0, 134.9, 134.8, 134.7, 134.2, 132.8, 131.3, 129.4, 129.1, 128.9, 128.8, 128.0, 127.2, 126.7, 125.5, 124.7, 93.6, 92.7, 74.8, 74.2, 64.1, 63.4, 28.6; MS (HRESI): m/z calcd for $C_{17}H_{15}NO_4$ $[M+Na]^+$ 320.0893, found 320.0887.

Ethyl 2-(5-methylisochroman-1-yl)-3-oxobutanoate (3k). A colorless oil: observed as two diastereomers in ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.01 (m, 2H), 6.88 – 6.85 (m, 1H), 5.50 (d, *J* = 6.9 Hz, aH), 5.46 (d, *J* = 5.7 Hz, bH)[a+b=1], 4.26 – 4.07 (m, 3H), 4.05 (d, *J* = 5.7 Hz, cH), 3.97 (d, *J* = 6.9 Hz, dH)[c+d=1], 3.86 – 3.75 (m, 1H), 2.88 – 2.76 (m, 1H), 2.67 – 2.57 (m, 1H), 2.27 – 2.22 (m, 6H), 1.26 (t, *J* = 7.1 Hz, eH), 1.11 (d, *J* = 7.1 Hz, fH)[e+f=3]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 202.0, 168.6, 167.6, 136.8, 136.5, 135.1, 134.9, 133.0, 132.5, 128.8, 128.5, 126.1, 125.9, 122.4, 122.3, 74.8, 74.6, 65.8, 65.7, 63.8, 63.5, 61.7, 61.2, 30.2, 29.5, 26.2, 19.2, 14.2, 14.01; MS (HRESI): m/z calcd for $C_{16}H_{20}O_4$ $[M+Na]^+$ 299.1254, found 299.1247.

Ethyl 2-(7-methylisochroman-1-yl)-3-oxobutanoate (3l). A colorless oil: observed as two diastereomers in ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.95 (m, 2H), 6.82 (s, 1H), 5.46 (d, *J* = 6.8 Hz, aH), 5.42 (d, *J* = 5.4 Hz, bH)[a+b=1], 4.27 – 4.08 (m, 3H), 4.02 (d, *J* = 5.5 Hz, cH), 3.94 (d, *J* = 6.8 Hz, dH)[c+d=1], 3.79 – 3.71 (m, 1H), 3.02 – 2.90 (m, 1H), 2.71 – 2.61 (m, 1H), 2.27 – 2.23 (m, 6H), 1.27 (t, *J* = 7.1 Hz, eH), 1.11 (t, *J* = 7.1 Hz, fH)[e+f=3]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 202.0, 168.6, 167.6, 136.1, 135.9, 135.1, 134.9, 131.5, 130.9, 129.2, 129.0, 128.2, 127.9, 125.3, 125.2, 74.6, 74.3, 65.8, 65.7, 64.1, 63.8, 61.7, 61.2, 30.1, 29.5, 28.4, 28.3, 21.3, 14.2, 14.01; MS (HRESI): m/z calcd for $C_{16}H_{20}O_4$ $[M+Na]^+$ 299.1254, found 299.1248.

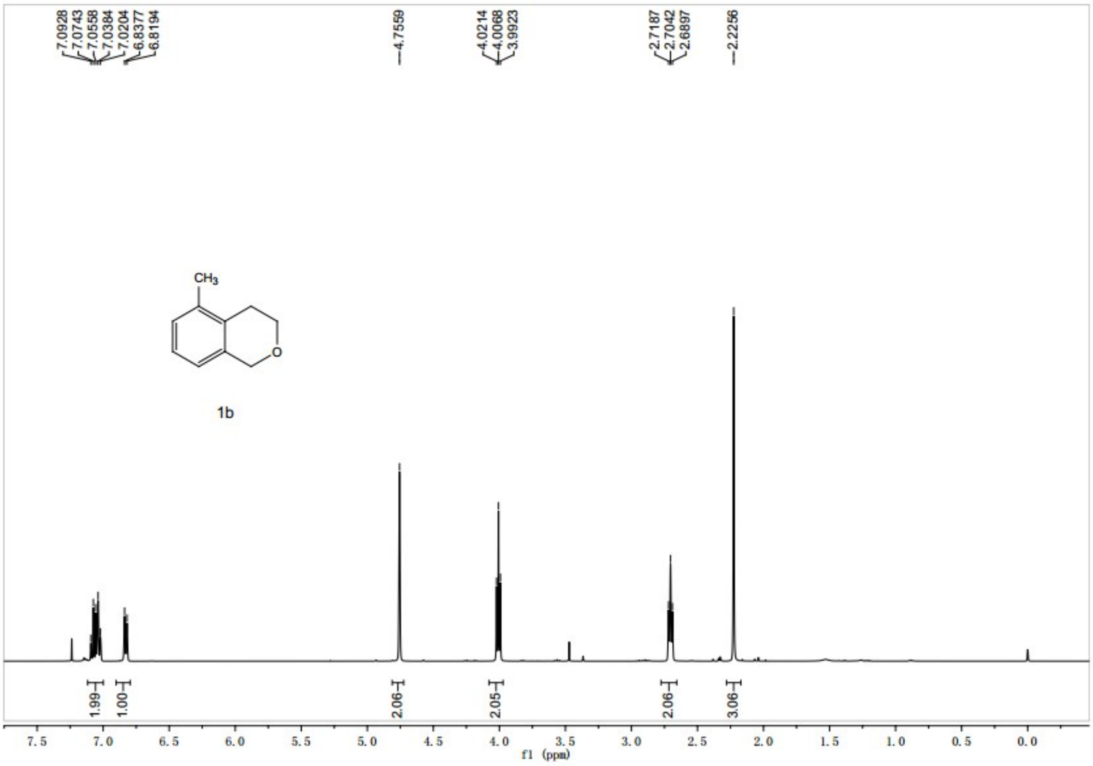
Ethyl 2-(7-(tert-butyl)isochroman-1-yl)-3-oxobutanoate (3m). A colorless oil: observed as two diastereomers in ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 1H), 7.10 – 7.01 (m, 2H), 5.51 (d, *J* = 7.4 Hz, aH), 5.47 (d, *J* = 5.8 Hz, bH)[a+b=1], 4.26 – 4.09 (m, 3H), 4.07 (d, *J* = 6.2 Hz, cH), 3.98 (d, *J* = 7.4 Hz, dH)[c+d=1], 3.81 – 3.75 (m, 1H), 3.03 – 2.87 (m, 1H), 2.79 – 2.62 (m, 1H), 2.25 (d, *J* = 4.0 Hz, 3H), 1.27 – 1.08 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 201.8, 168.5, 167.6, 149.5, 149.3, 134.6, 131.4, 130.9, 129.0, 128.8, 124.5, 124.1, 121.7, 121.6, 74.8, 66.1, 65.8, 64.0, 63.6, 61.7, 61.2, 34.6, 31.5, 31.4, 30.3, 29.4, 28.3, 28.2, 14.2, 14.0; MS (HRESI): m/z calcd for $C_{19}H_{26}O_4$ $[M+Na]^+$ 341.1723, found 341.1713.

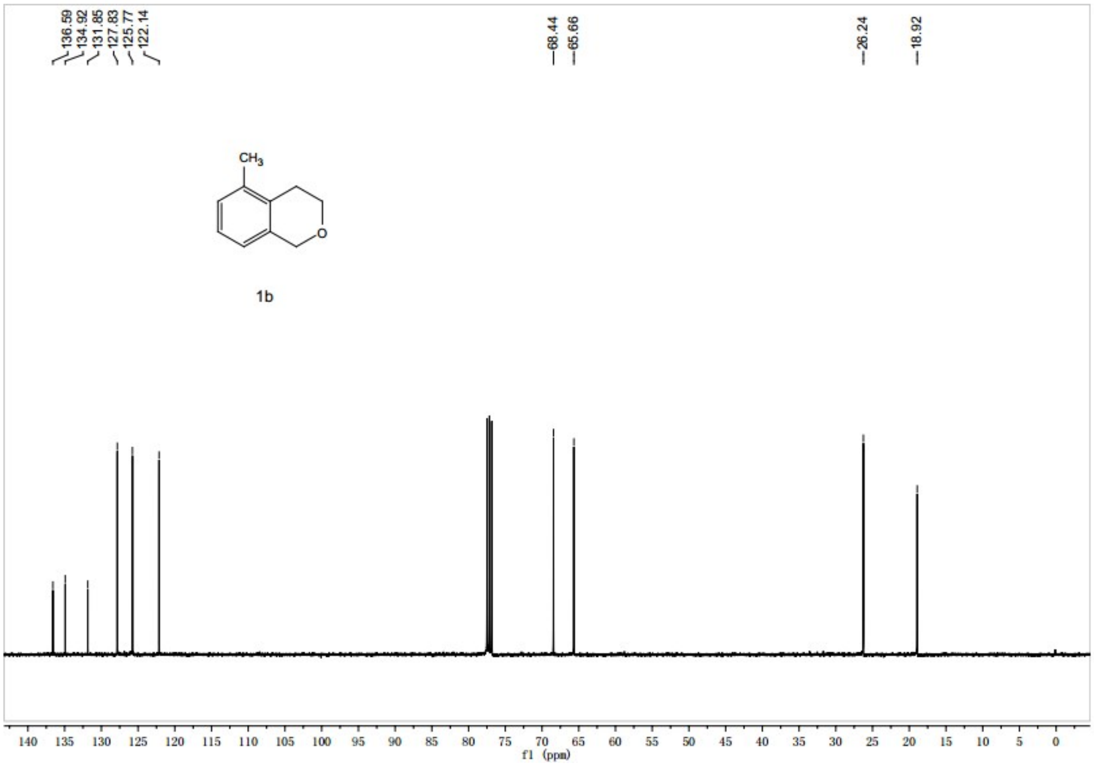
Ethyl 2-(7-(*tert*-butyl)isochroman-1-yl)-4-methyl-3-oxopentanoate (3n). A colorless oil: observed as two diastereomers in ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 1H), 7.08 – 6.96 (m, 2H), 5.53 (t, *J* = 7.0 Hz, 1H), 4.29 – 4.09 (m, 4H), 3.83 – 3.71 (m, 1H), 3.00 – 2.87 (m, 1H), 2.84 – 2.62 (m, 2H), 1.27 – 1.17 (m, 12H), 1.12 – 0.92 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 207.3, 168.4, 167.5, 149.3, 135.4, 135.0, 131.3, 131.1, 128.9, 128.8, 124.3, 122.2, 121.5, 75.3, 74.4, 64.0, 63.9, 63.5, 63.3, 61.6, 61.4, 41.5, 41.3, 34.6, 31.4, 28.5, 28.3, 18.3, 18.2, 17.8, 14.2, 14.1; MS (HRESI): m/z calcd for $C_{21}H_{30}O_4$ $[M+Na]^+$ 369.2036, found 369.2027.

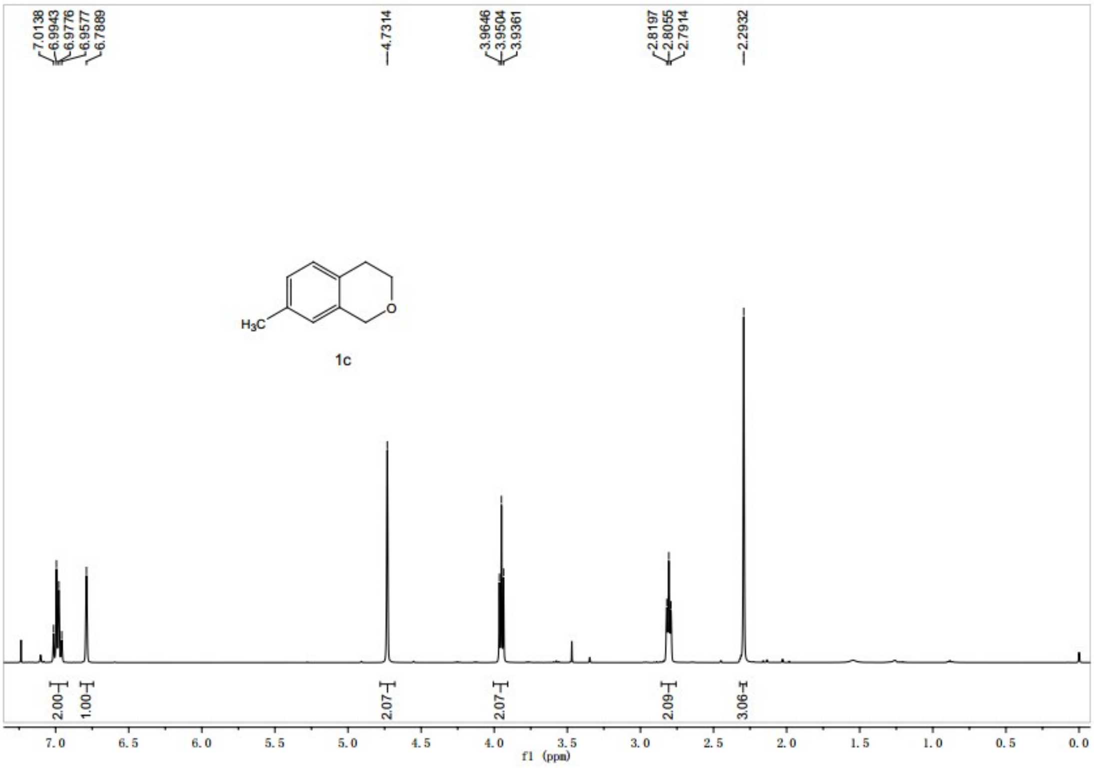
Ethyl 2-(7-(*tert*-butyl)isochroman-1-yl)-3-oxo-3-phenylpropanoate (3o). A colorless oil: observed as two diastereomers in ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 2H), 7.57 – 7.51 (m, 1H), 7.46 – 7.39 (m, 2H), 7.25 – 6.97 (m, 3H), 5.84 – 5.69 (m, 1H), 4.98 (d, *J* = 8.5 Hz, aH), 4.92 (d, *J* = 7.4 Hz, bH)[a+b=1], 4.24 – 3.99 (m, 3H), 3.91 – 3.67 (m, 1H), 2.94 – 2.62 (m, 2H), 1.28 (s, 3H), 1.24 – 1.14 (m, 4H), 1.09 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 193.4, 168.1, 167.2, 149.3, 149.2, 137.5, 137.0, 135.2, 135.1, 133.6, 133.2, 131.5, 130.9, 128.8, 128.7, 128.6, 124.3, 124.2, 122.4, 121.9, 75.2, 74.8, 63.5, 63.1, 61.7, 61.4, 60.5, 34.6, 34.4, 31.4, 31.2, 28.5, 28.3, 14.1; MS (HRESI): m/z calcd for $C_{24}H_{28}O_4$ $[M+Na]^+$ 403.1880, found 403.1868.

Ethyl 2-(1,4-dihydro-2H-benzo[f]isochromen-4-yl)-3-oxobutanoate (3p). A white solid: observed as two diastereomers ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.58 – 7.46 (m, 2H), 7.15 (d, *J* = 8.6 Hz, 1H), 5.67 (d, *J* = 6.6 Hz, aH), 5.63 (d, *J* = 5.3 Hz, bH)[a+b=1], 4.41 – 4.30 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 1H), 4.14 – 4.04 (m, 2H), 3.97 – 3.89 (m, 1H), 3.31 – 3.20 (m, 1H), 3.18 – 3.09 (m, 1H), 2.27 (d, *J* = 28.6 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, cH), 1.04 (t, *J* = 7.1 Hz, dH)[c+d=3]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 201.6, 168.6, 167.6, 132.6, 132.5, 132.4, 132.3, 132.1, 132.0, 130.3, 129.8, 128.7, 126.9, 126.8, 126.7, 126.6, 126.1, 126.0, 123.0, 122.8, 74.9, 74.7, 65.9, 65.6, 63.6, 63.3, 61.7, 61.2, 30.2, 29.4, 25.5, 25.3, 14.2, 14.0; MS (HRESI): m/z calcd for $C_{19}H_{20}O_4$ $[M+Na]^+$ 335.1254, found 335.1247.

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



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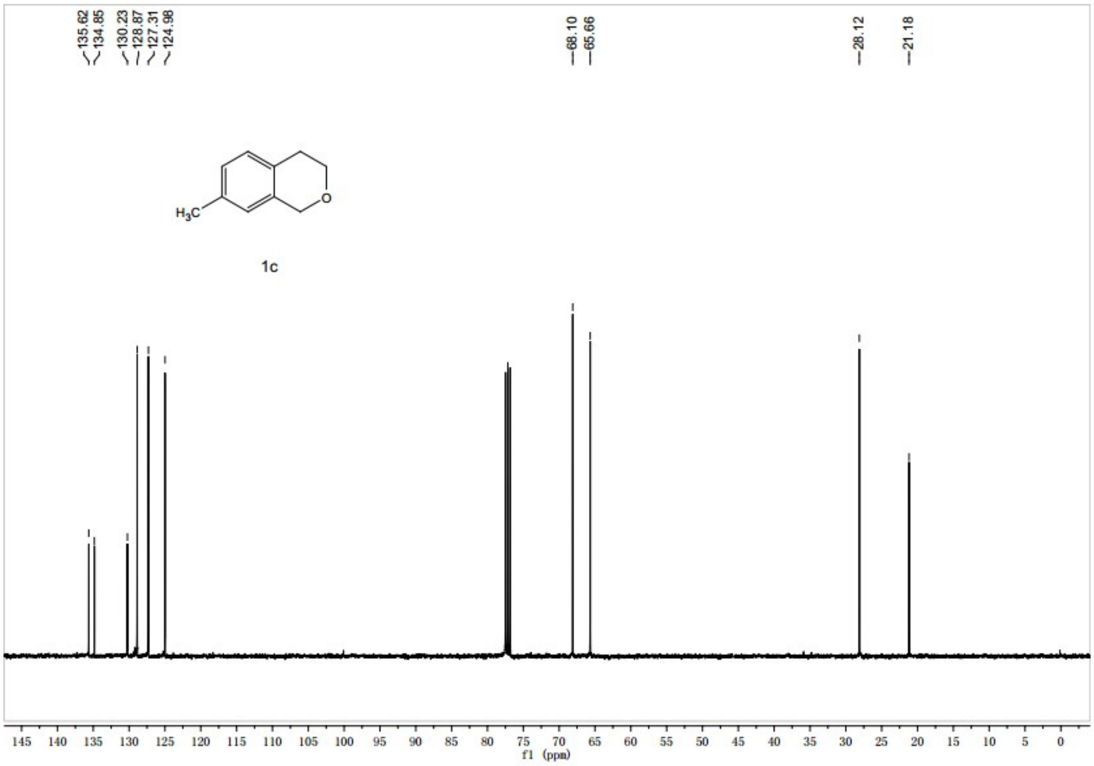
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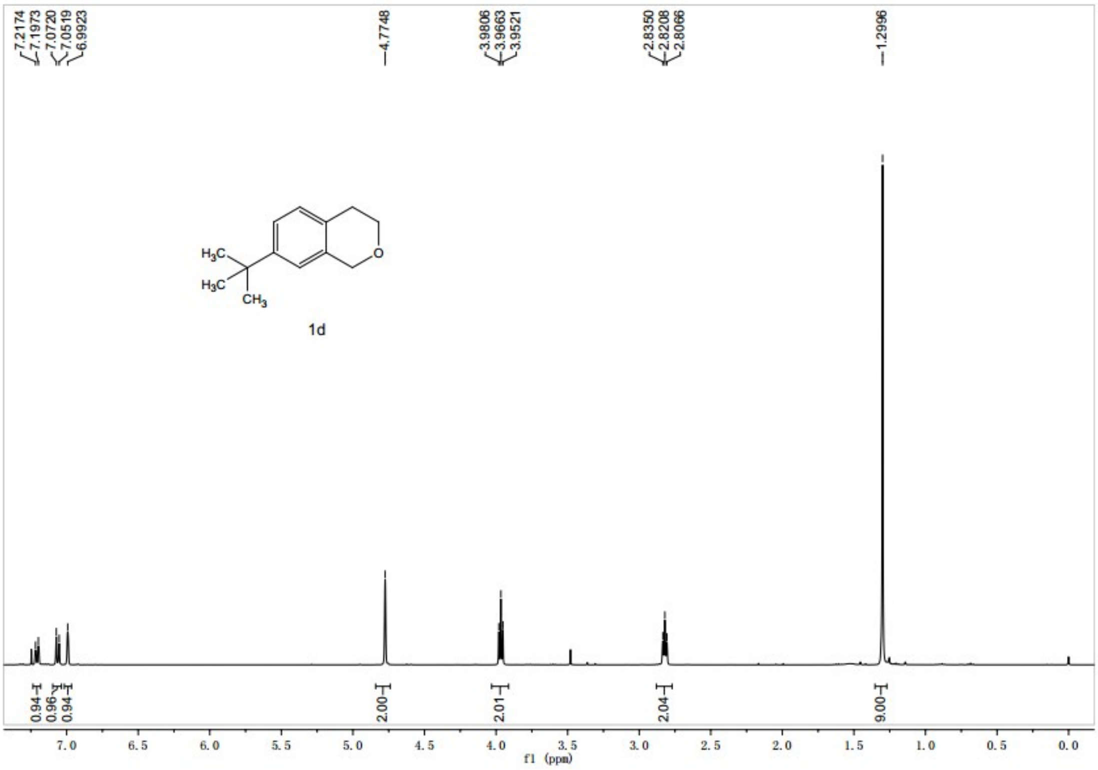
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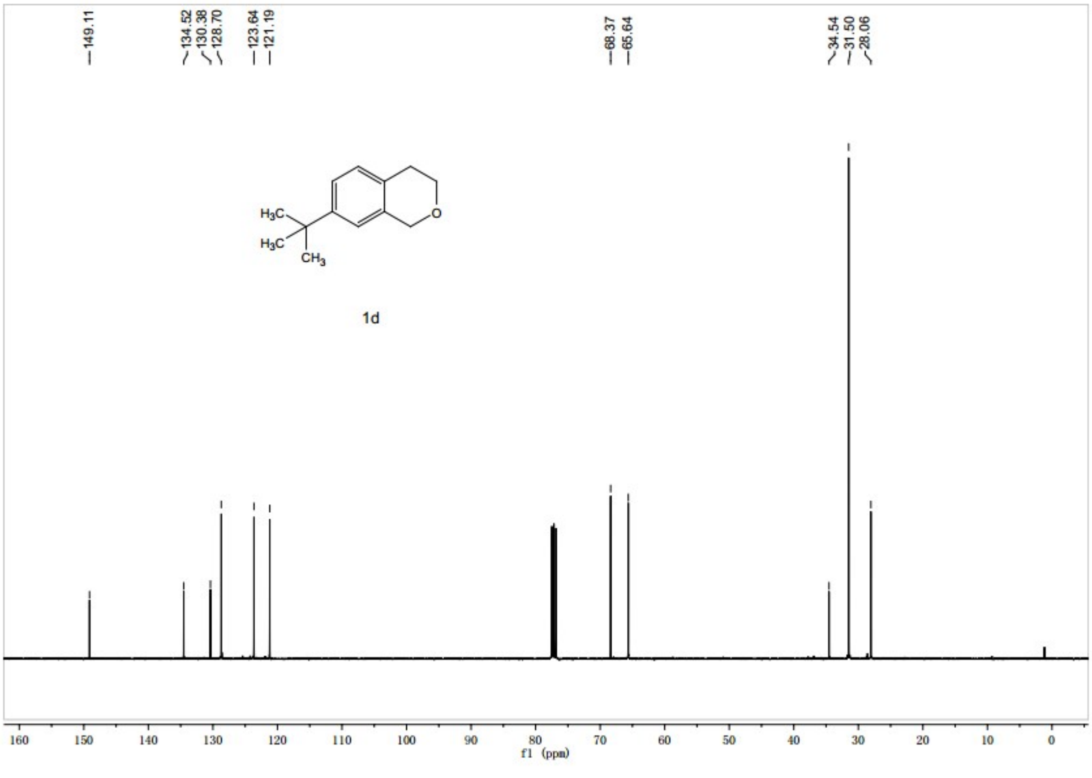
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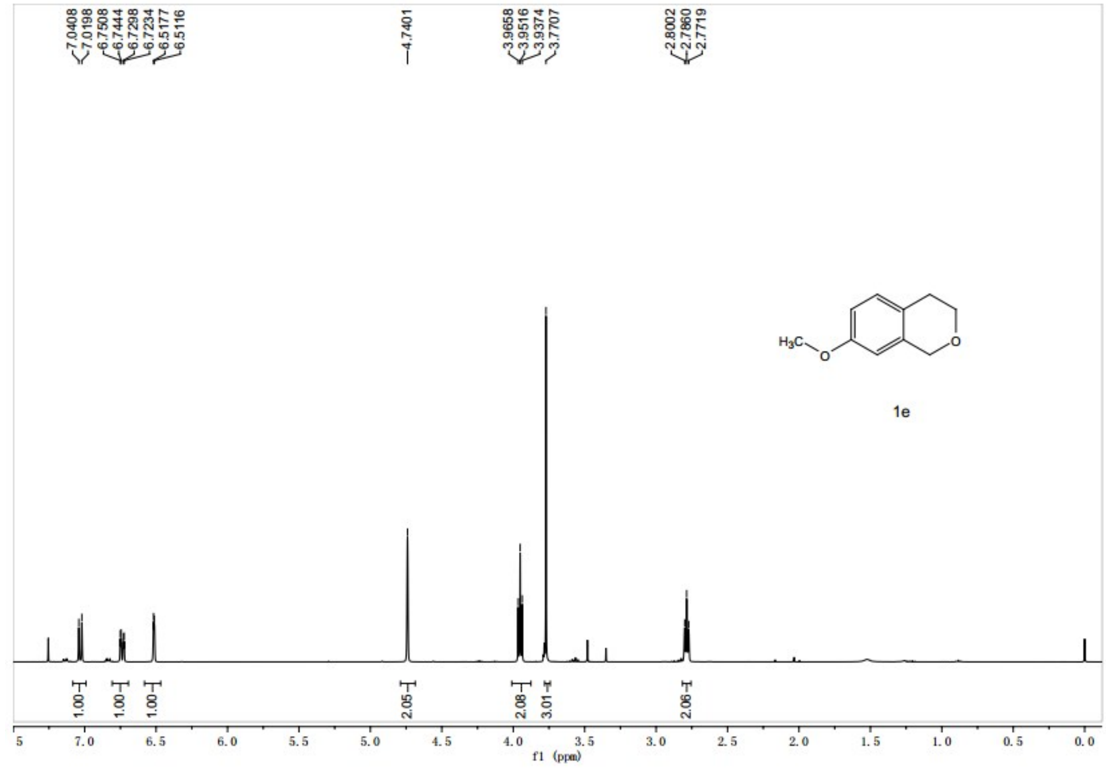
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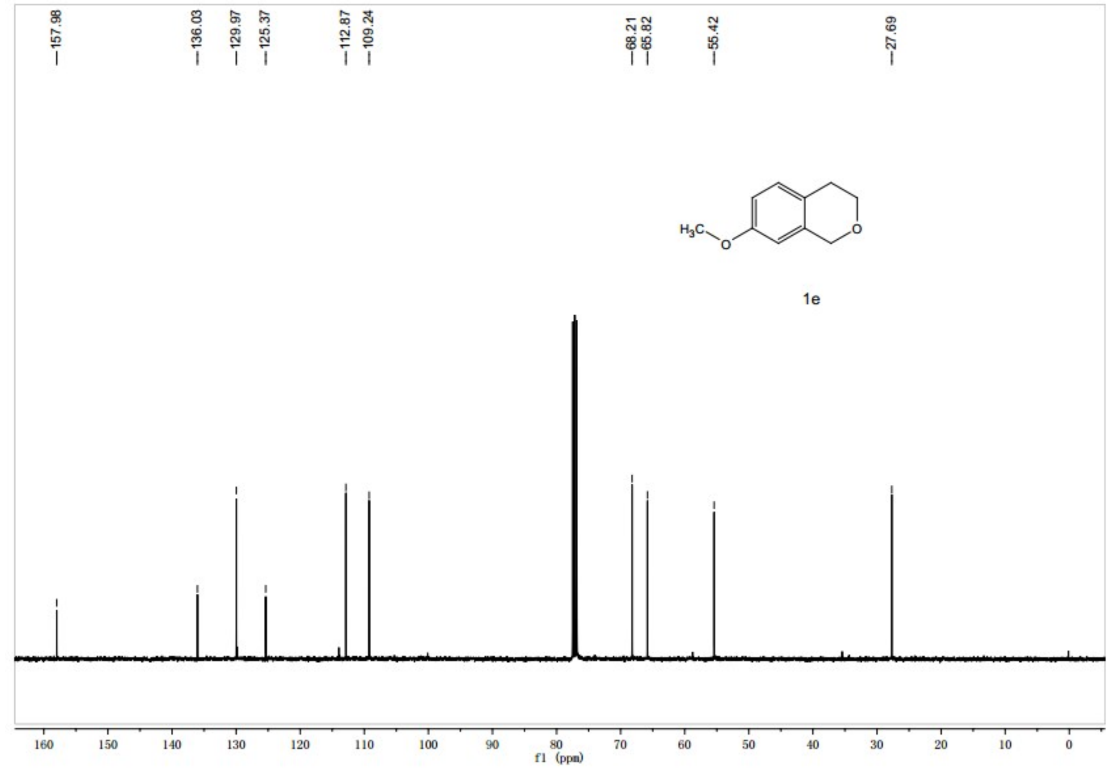
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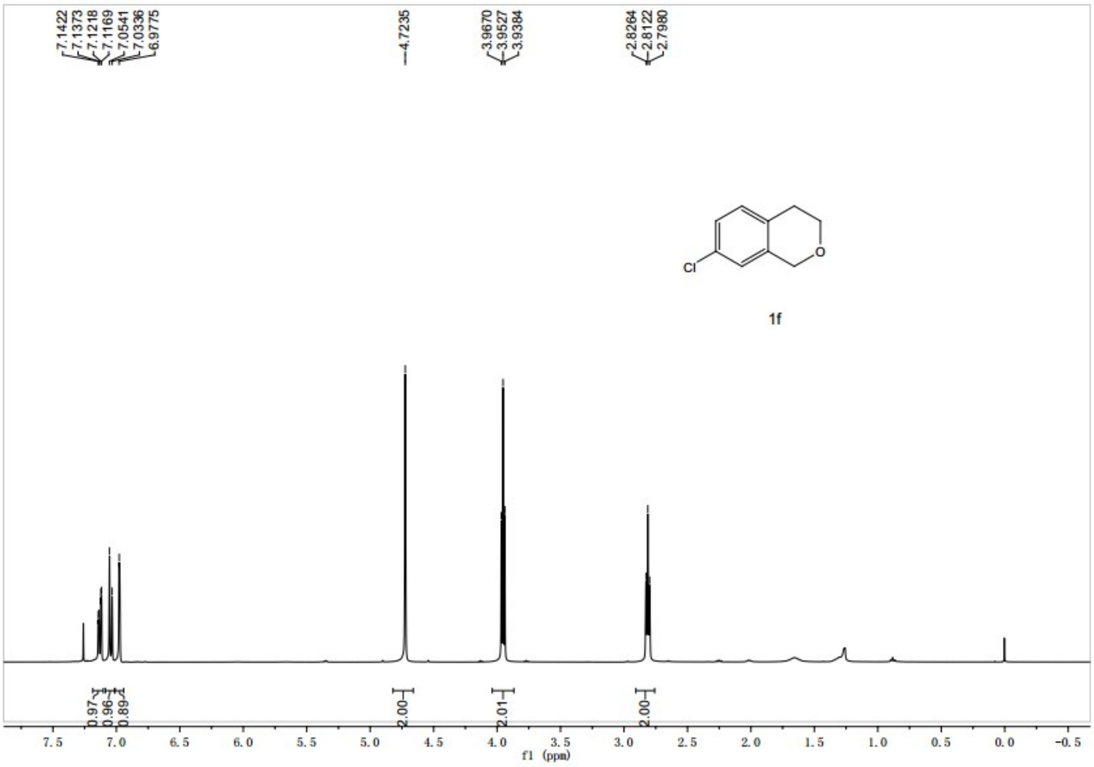
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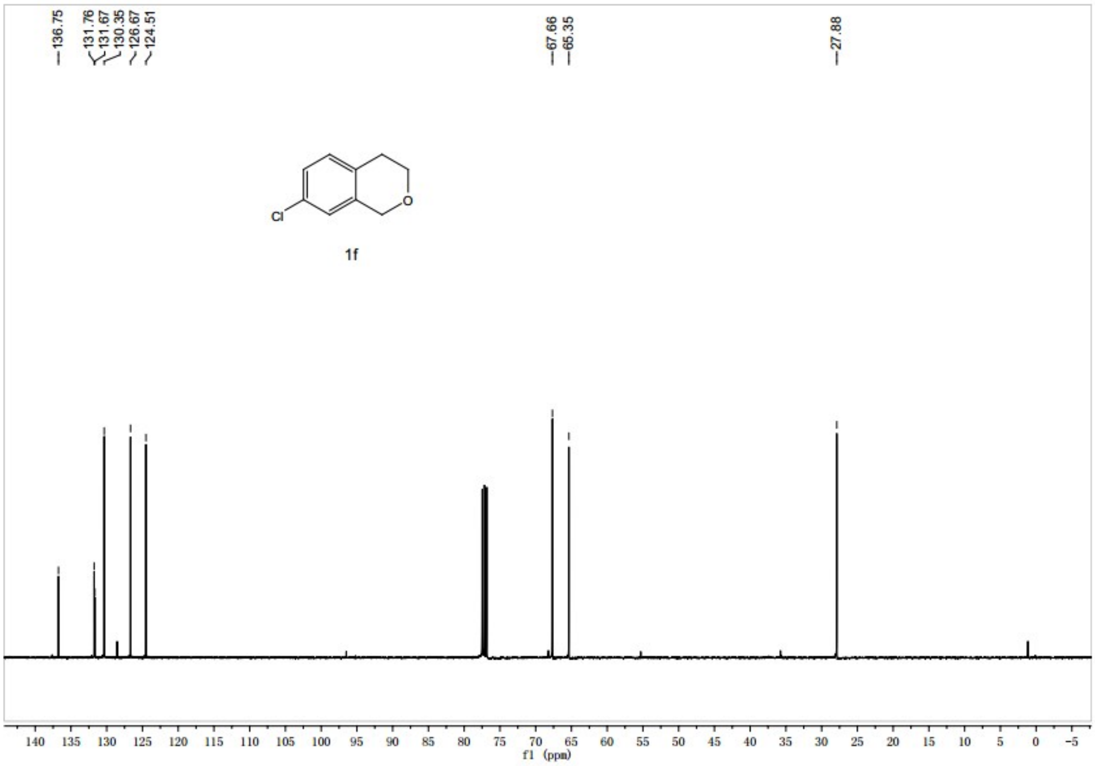
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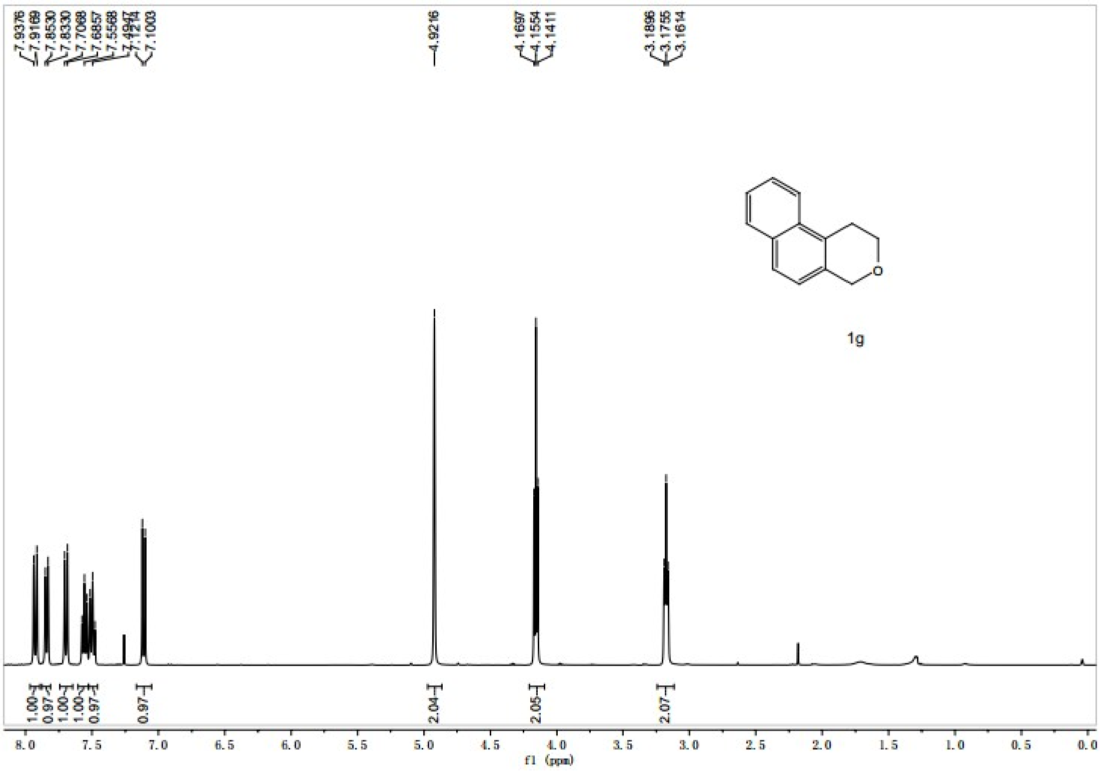
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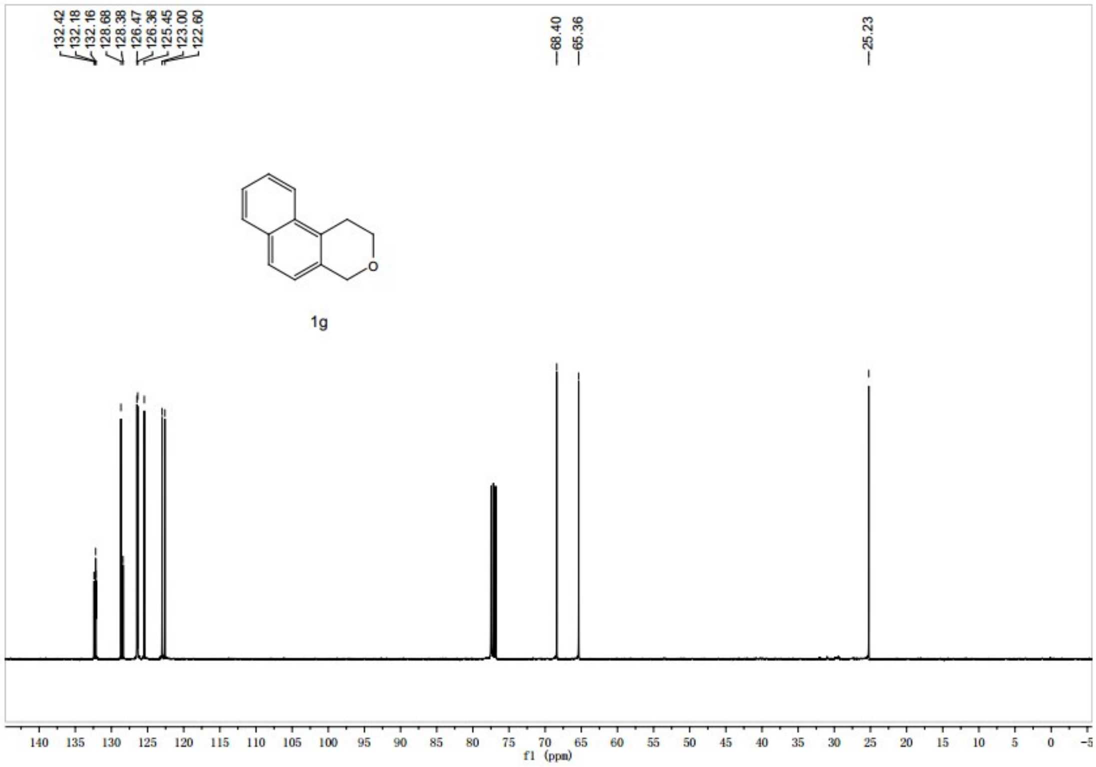
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125.45
123.00
122.60
68.40
65.36
25.23
O
1g
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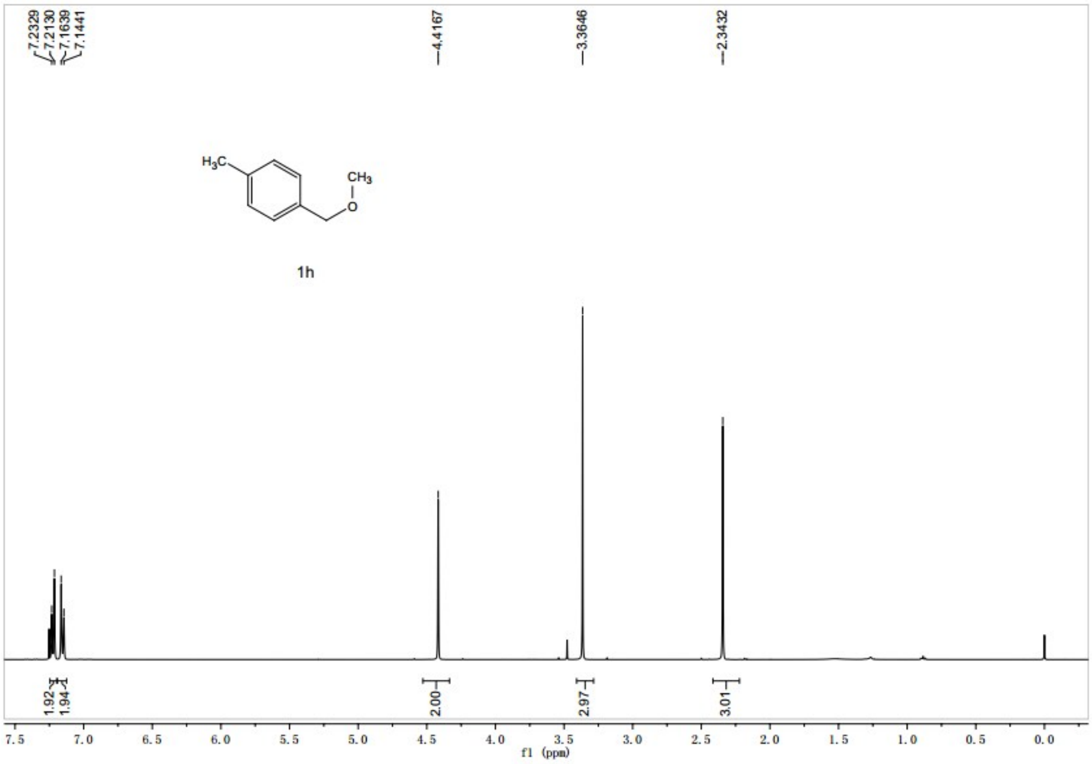
f1 (ppm)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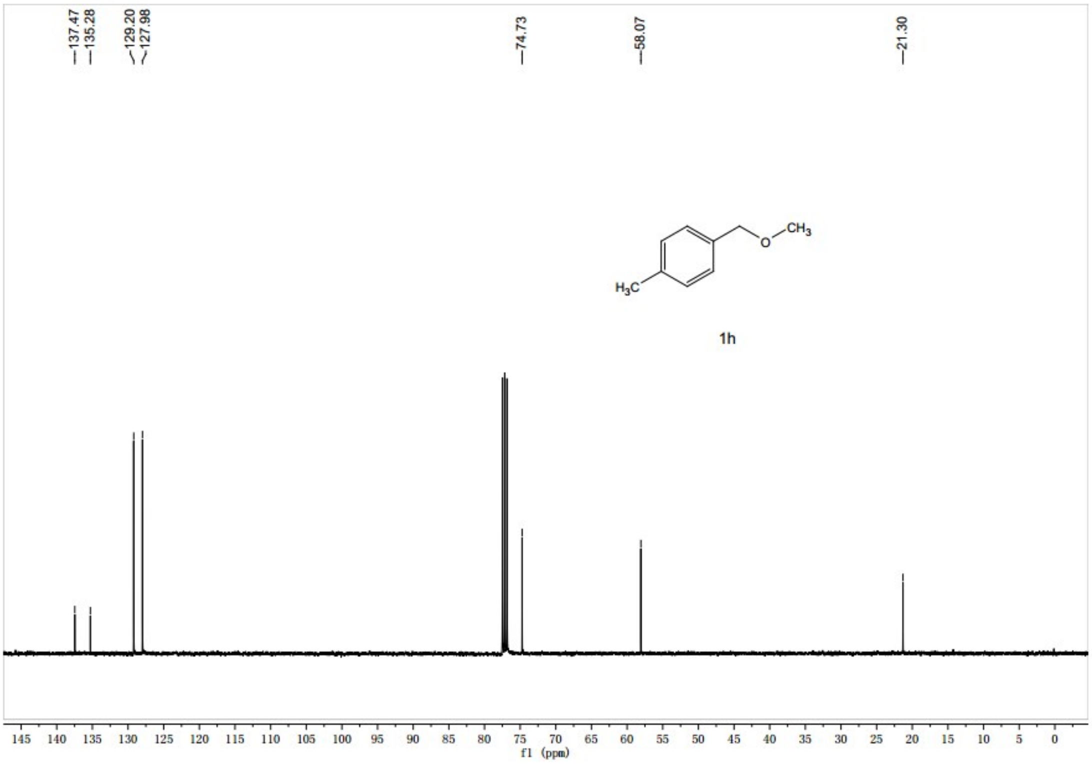
2.3432
H3C
CH3
O
1h
1.92
1.94
2.00
2.97
3.01
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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58.07
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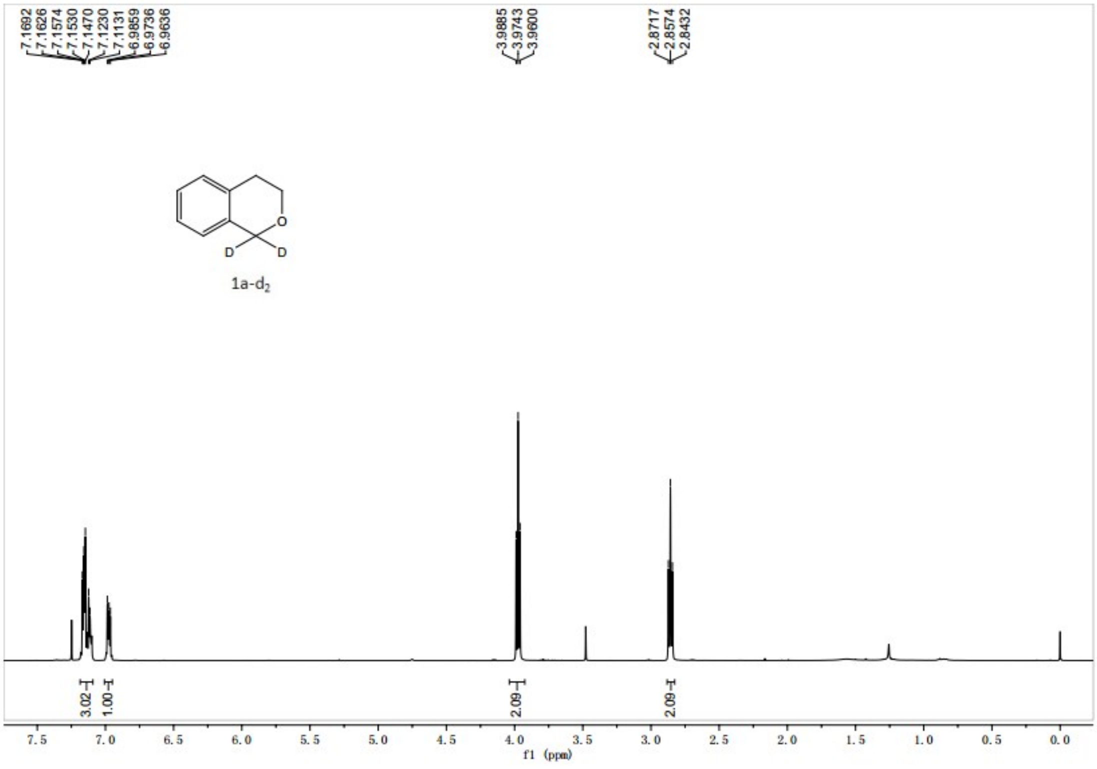
CH3
O
H3C
1h
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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7.1131
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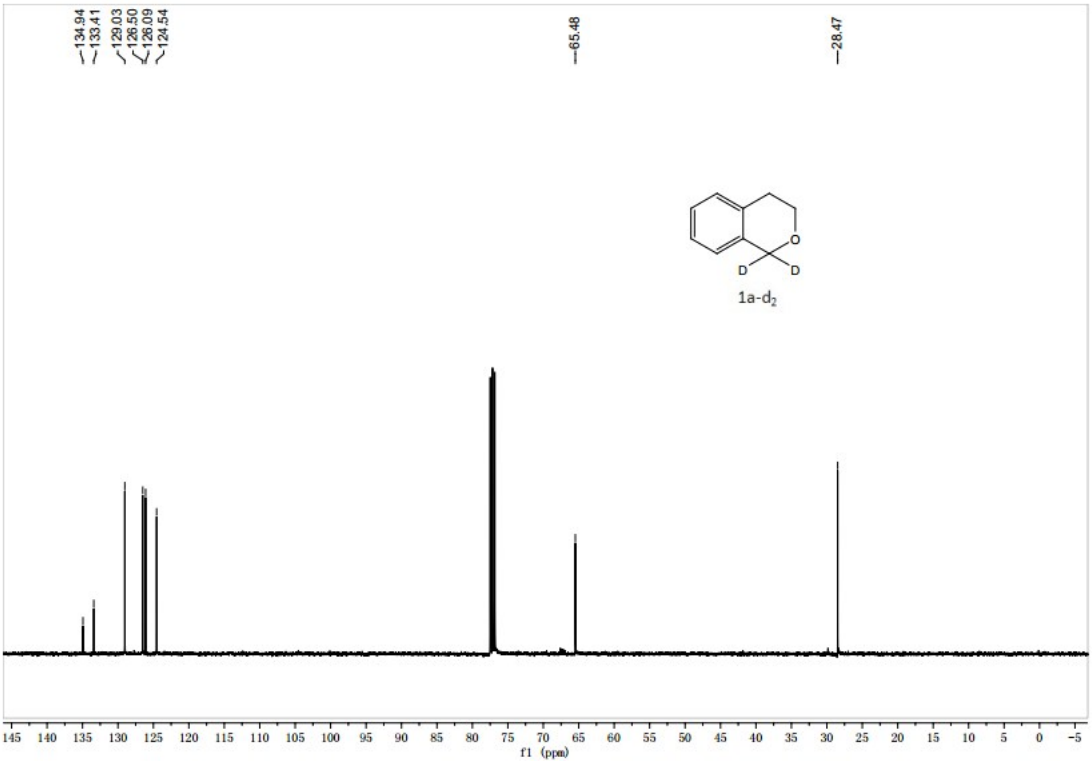
6.9736
6.9636
3.9885
3.9743
3.9600
2.8717
2.8574
2.8432
O
D
D
1a-d$_2$
3.02
1.00
2.09
2.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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133.41
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126.50
126.09
124.54
65.48
28.47
O
D
D
1a-d$_2$
145
140
135
130
125
120
115
110
105
100
95
90
85
80
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50
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40
35
30
25
20
15
10
5
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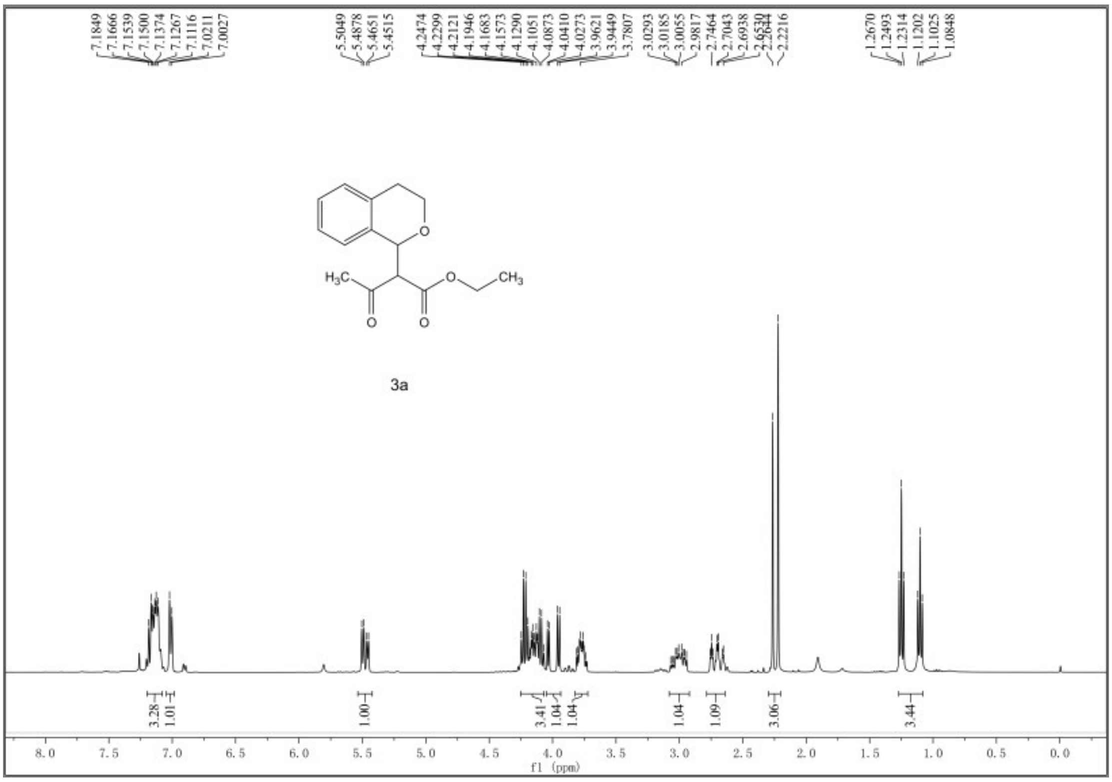
-5
f1 (ppm)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7.0027
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5.4878
5.4651
5.4515
4.2474
4.2299
4.2121
4.1946
4.1683
4.1573
4.1290
4.1051
4.0873
4.0410
4.0273
3.9621
3.9449
3.7807
3.0293
3.0185
3.0055
2.9817
2.7464
2.7043
2.6938
2.6530
2.2644
2.2216
1.2670
1.2493
1.2314
1.1202
1.1025
1.0848
H_3C
O
O
O
CH_3
O
3a
3.28
1.01
1.00
3.41
1.04
1.04
1.04
1.09
3.06
3.44
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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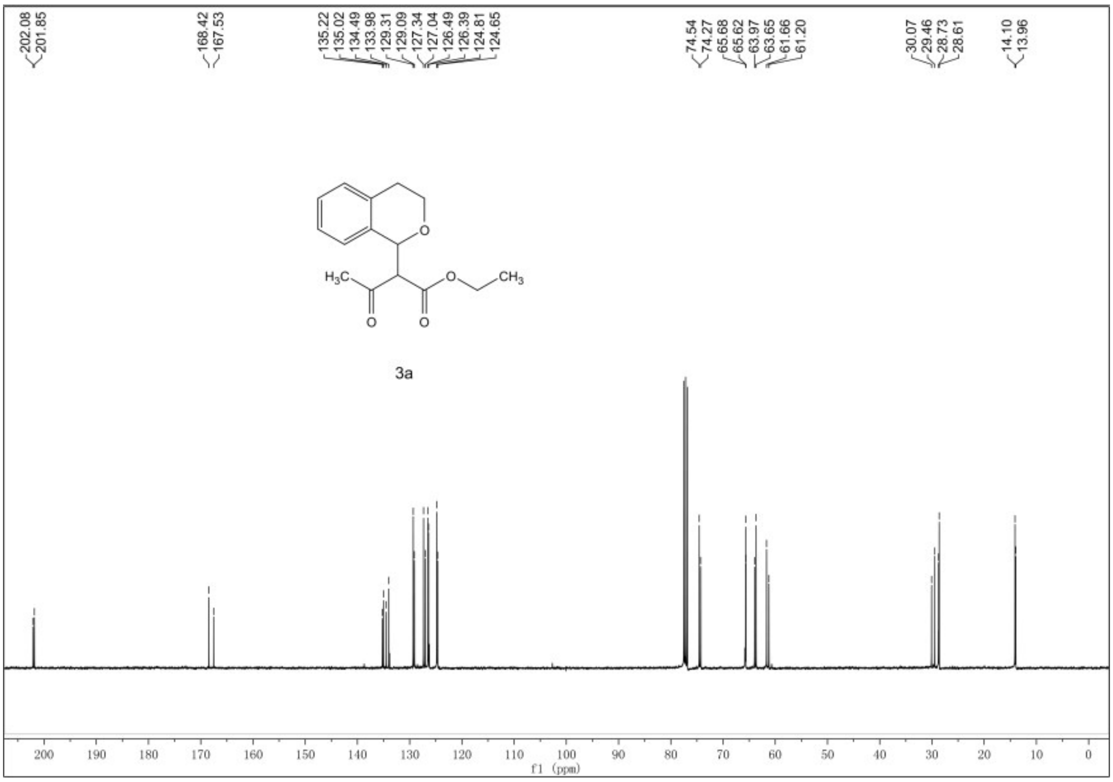
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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201.85
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135.22
135.02
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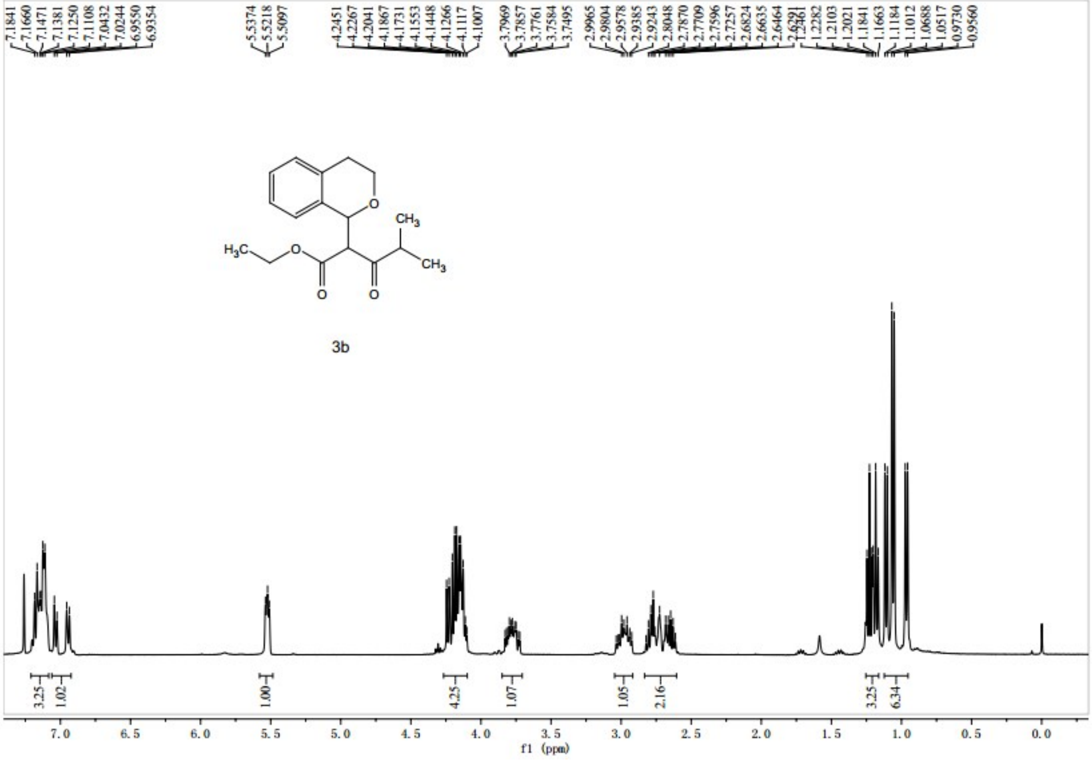
133.98
129.31
129.09
127.34
127.04
126.49
126.39
124.81
124.65
74.54
74.27
65.68
65.62
63.97
63.65
61.66
61.20
30.07
29.46
28.73
28.61
14.10
13.96
H_3C
O
O
O
CH_3
O
3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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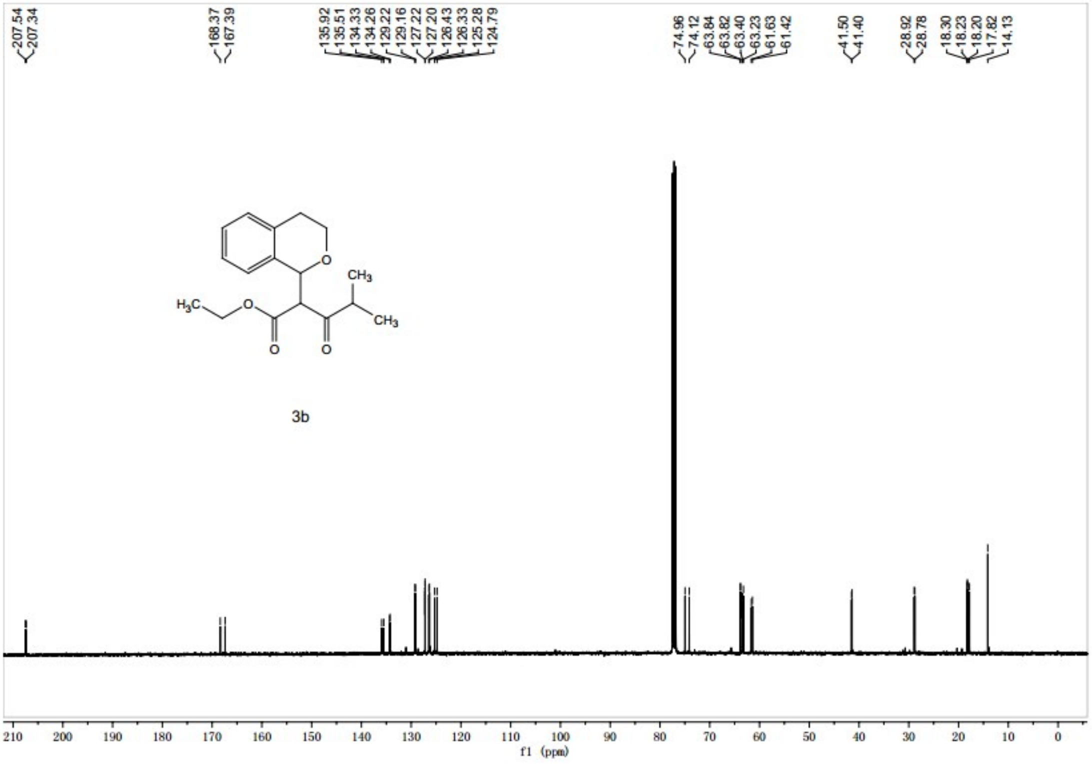
6.9354
5.5374
5.5218
5.5097
4.2451
4.2267
4.2041
4.1867
4.1731
4.1553
4.1448
4.1266
4.1117
4.1007
3.7969
3.7857
3.7761
3.7584
3.7495
2.9965
2.9804
2.9578
2.9385
2.9243
2.8048
2.7870
2.7709
2.7596
2.7257
2.6824
2.6635
2.6464
2.6291
1.2461
1.2282
1.2103
1.2021
1.1841
1.1663
1.1184
1.1012
1.0688
1.0517
0.9730
0.9560
H3C
O
O
O
O
CH3
CH3
3b
3.25
1.02
1.00
4.25
1.07
1.05
2.16
3.25
6.34
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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207.34
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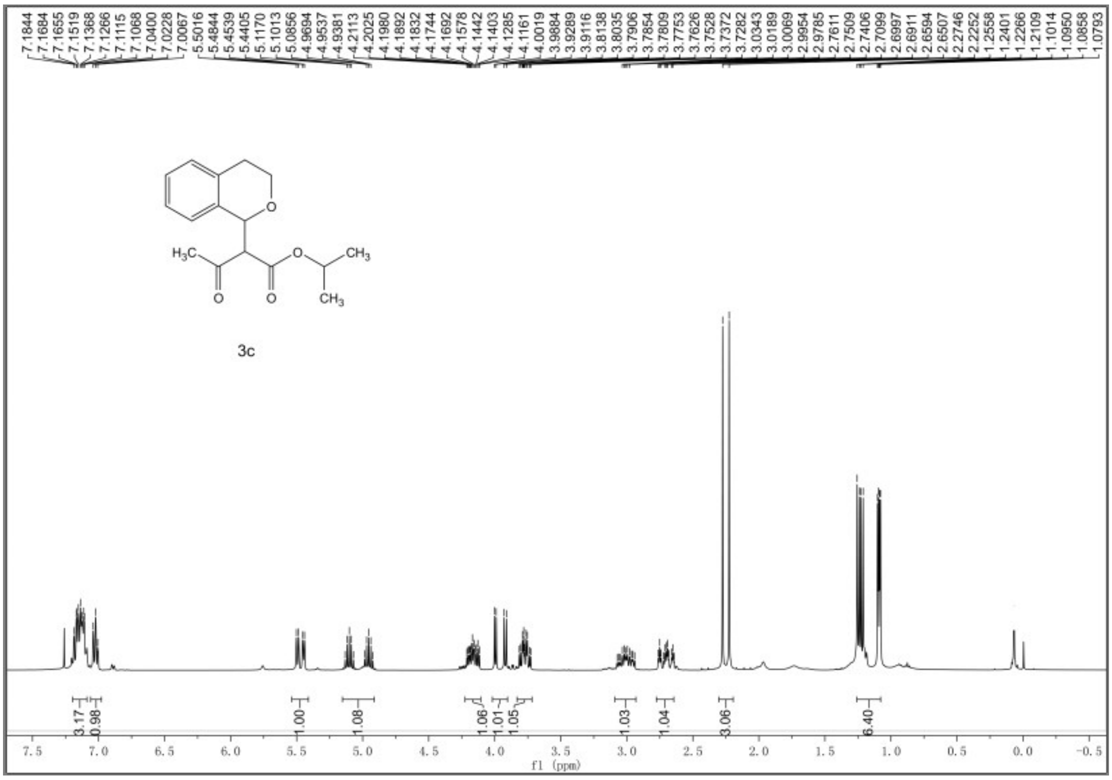
135.92
135.51
134.33
134.26
129.22
129.16
127.22
127.20
126.43
126.33
125.28
124.79
74.96
74.12
63.84
63.82
63.40
63.23
61.63
61.42
41.50
41.40
28.92
28.78
18.30
18.23
18.20
17.82
14.13
H3C
O
O
O
O
CH3
CH3
3b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.1266
7.1115
7.1068
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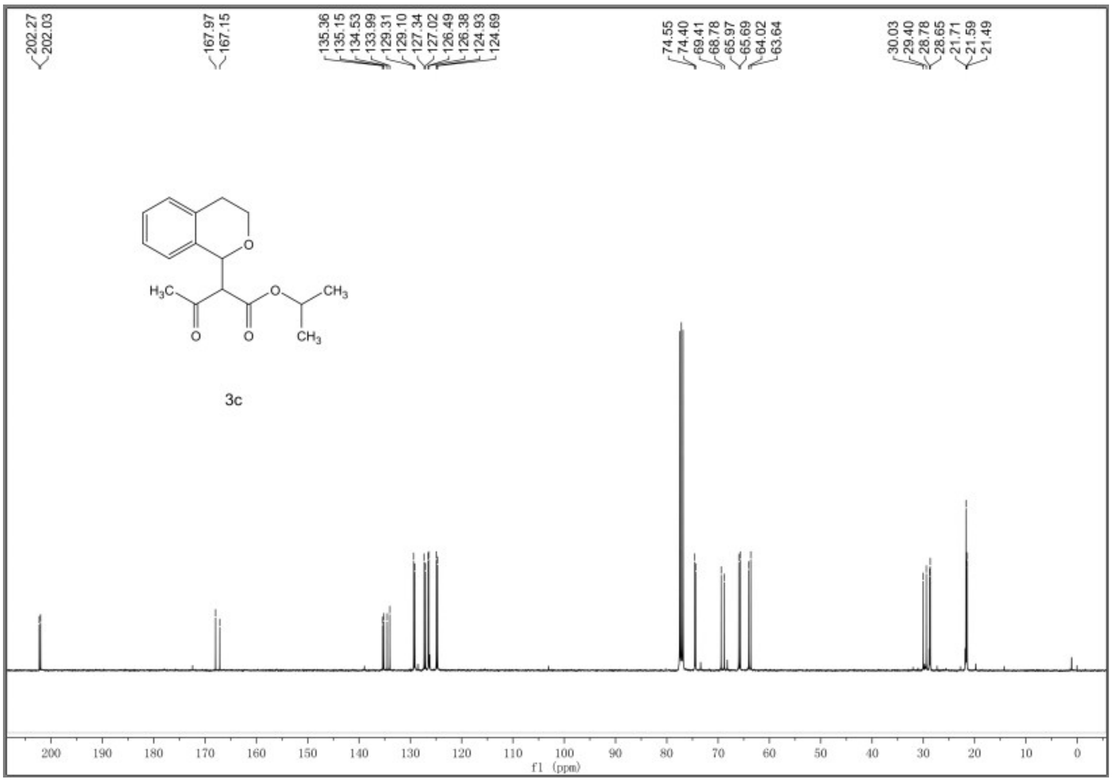
7.0228
7.0067
5.5016
5.4844
5.4539
5.4405
5.1170
5.1013
5.0856
4.9694
4.9537
4.9381
4.2113
4.2025
4.1980
4.1892
4.1832
4.1744
4.1692
4.1578
4.1442
4.1403
4.1285
4.1161
4.0019
3.9884
3.9289
3.9116
3.8138
3.8035
3.7906
3.7854
3.7809
3.7753
3.7626
3.7528
3.7372
3.7282
3.0343
3.0189
3.0069
2.9954
2.9785
2.7611
2.7509
2.7406
2.7099
2.6997
2.6911
2.6594
2.6507
2.2746
2.2252
1.2558
1.2401
1.2266
1.2109
1.1014
1.0950
1.0858
1.0793
H3C
O
O
O
CH3
CH3
3c
3.17
0.98
1.00
1.08
1.06
1.01
1.05
1.03
1.04
3.06
6.40
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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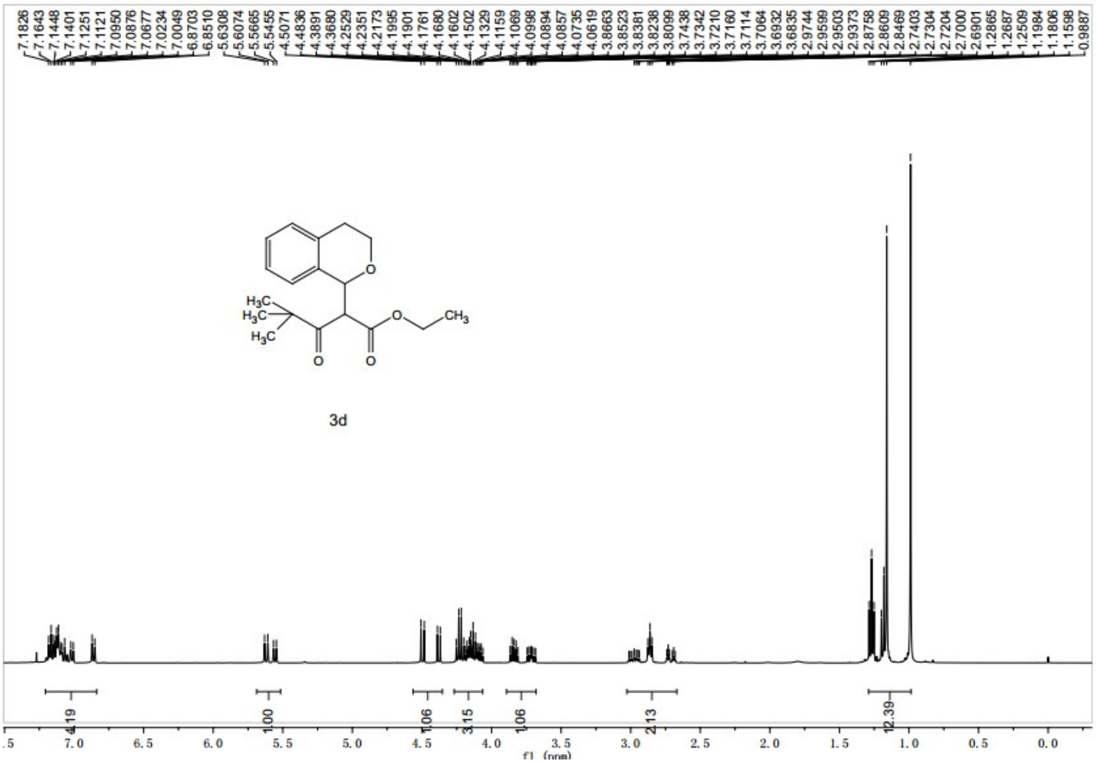
167.97
167.15
135.36
135.15
134.53
133.99
129.31
129.10
127.34
127.02
126.49
126.38
124.93
124.69
74.55
74.40
69.41
68.78
65.97
65.69
64.02
63.64
30.03
29.40
28.78
28.65
21.71
21.59
21.49
H3C
O
O
O
CH3
CH3
3c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.8510
5.6308
5.6074
5.5665
5.5455
4.5071
4.4836
4.3891
4.3680
4.2529
4.2351
4.2173
4.1995
4.1901
4.1761
4.1680
4.1602
4.1502
4.1329
4.1159
4.1069
4.0998
4.0894
4.0857
4.0735
4.0619
3.8663
3.8523
3.8381
3.8238
3.8099
3.7438
3.7342
3.7210
3.7160
3.7114
3.7064
3.6932
3.6835
2.9744
2.9599
2.9503
2.9373
2.8758
2.8609
2.8469
2.7403
2.7304
2.7204
2.7000
2.6901
1.2865
1.2687
1.2509
1.1984
1.1806
1.1598
0.9887
H_3C
H_3C
H_3C
O
O
O
O
CH_3
3d
4.19
1.00
1.06
3.15
1.06
2.13
12.39
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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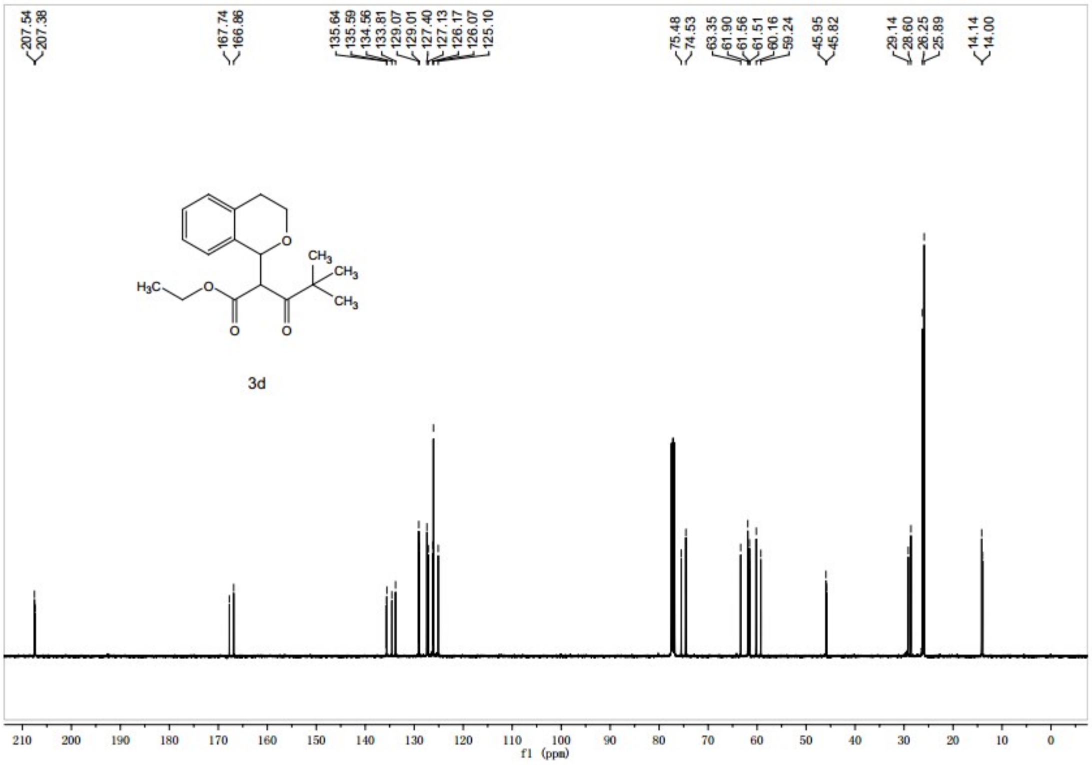
0.0
f1 (ppm)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129.01
127.40
127.13
126.17
126.07
125.10
75.48
74.53
63.35
61.90
61.56
61.51
60.16
59.24
45.95
45.82
29.14
28.60
26.25
25.89
14.14
14.00
H_3C
O
O
O
O
CH_3
CH_3
CH_3
3d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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50
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30
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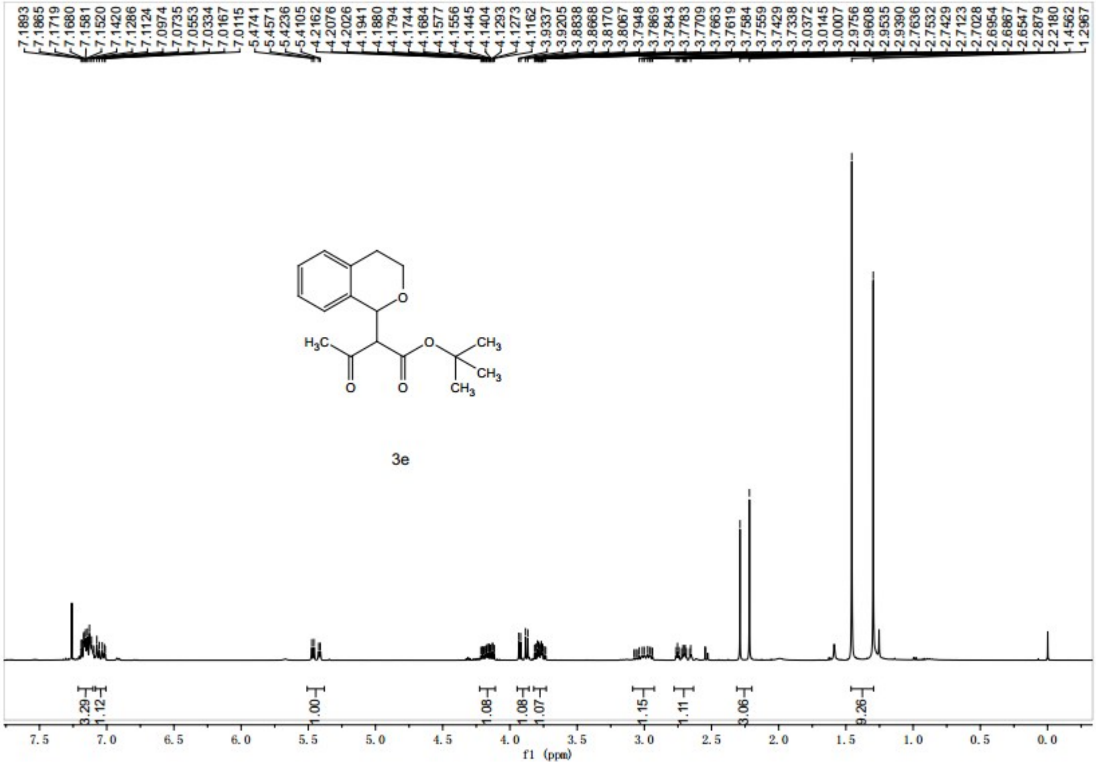
10
0
f1 (ppm)



3e

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7.1286
7.1124
7.0974
7.0735
7.0553
7.0334
7.0167
7.0115
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5.4571
5.4236
5.4105
4.2162
4.2076
4.2026
4.1941
4.1880
4.1794
4.1744
4.1684
4.1577
4.1556
4.1445
4.1404
4.1293
4.1273
4.1162
3.9337
3.9205
3.8838
3.8668
3.8170
3.8067
3.7948
3.7869
3.7843
3.7783
3.7709
3.7663
3.7619
3.7584
3.7559
3.7429
3.7338
3.0372
3.0145
3.0007
2.9756
2.9608
2.9535
2.9390
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2.7532
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2.7028
2.6954
2.6867
2.6547
2.2879
2.2180
1.4562
1.2967
H_3C
O
O
O
O
CH_3
CH_3
CH_3
3.29
1.12
1.00
1.08
1.08
1.07
1.15
1.11
3.06
9.26
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6.5
6.0
5.5
5.0
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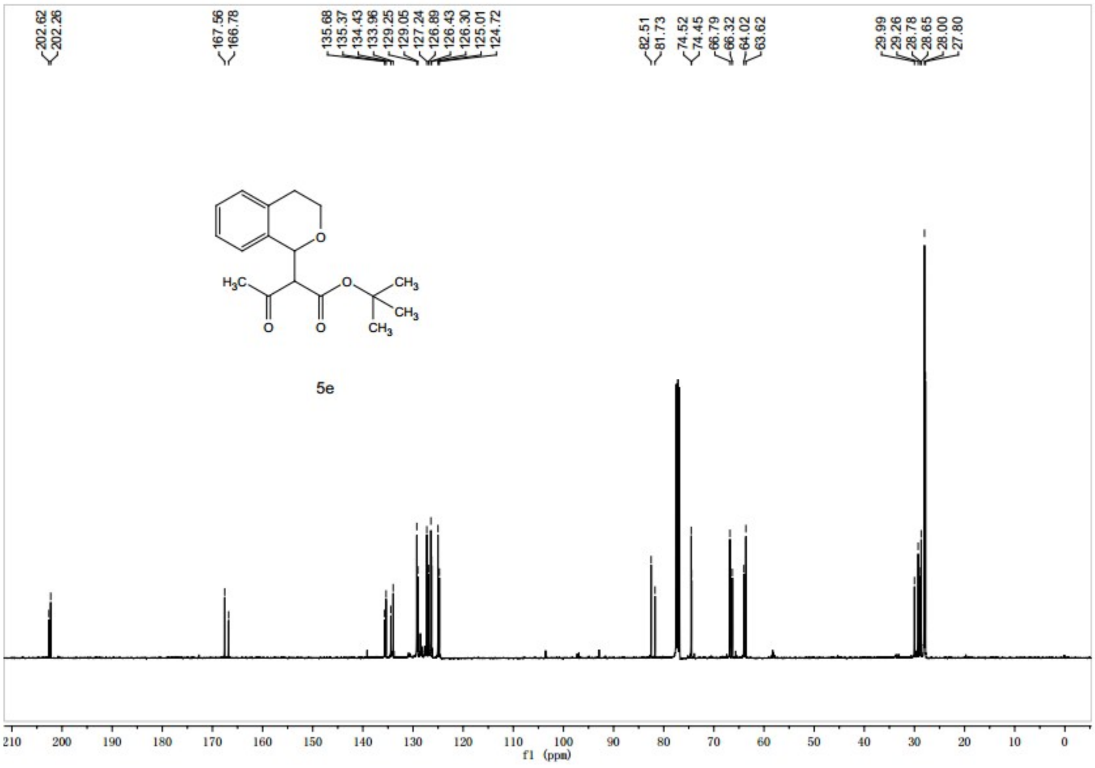
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



5e

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202.26
167.56
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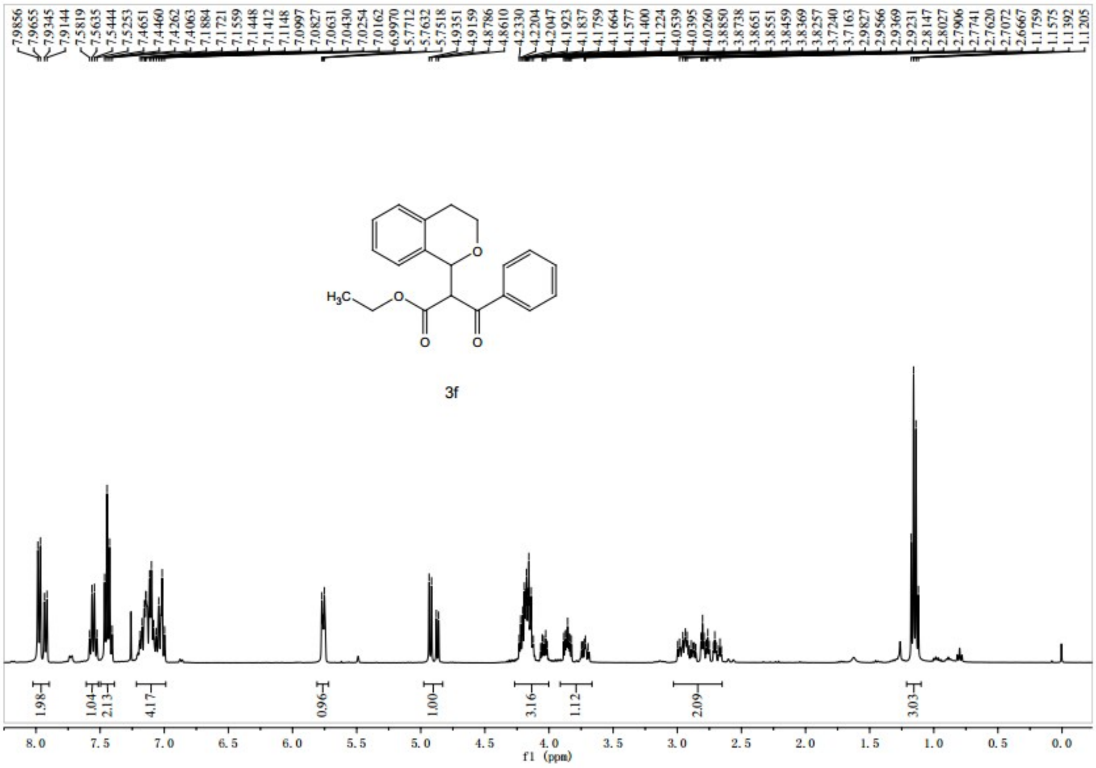
135.37
134.43
133.96
129.25
129.05
127.24
126.89
126.43
126.30
125.01
124.72
82.51
81.73
74.52
74.45
66.79
66.32
64.02
63.62
29.99
29.26
28.78
28.65
28.00
27.80
H_3C
O
O
O
O
CH_3
CH_3
CH_3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.4262
7.4063
7.1884
7.1721
7.1559
7.1448
7.1412
7.1148
7.0997
7.0827
7.0631
7.0430
7.0254
7.0162
6.9970
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5.7632
5.7518
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4.9159
4.8786
4.8610
4.2330
4.2204
4.2047
4.1923
4.1837
4.1759
4.1664
4.1577
4.1400
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3.7163
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2.9369
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2.8027
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2.7620
2.7072
2.6667
1.1759
1.1575
1.1392
1.1205
H3C
O
O
O
1.98
1.04
2.13
4.17
0.96
1.00
3.16
1.12
2.09
3.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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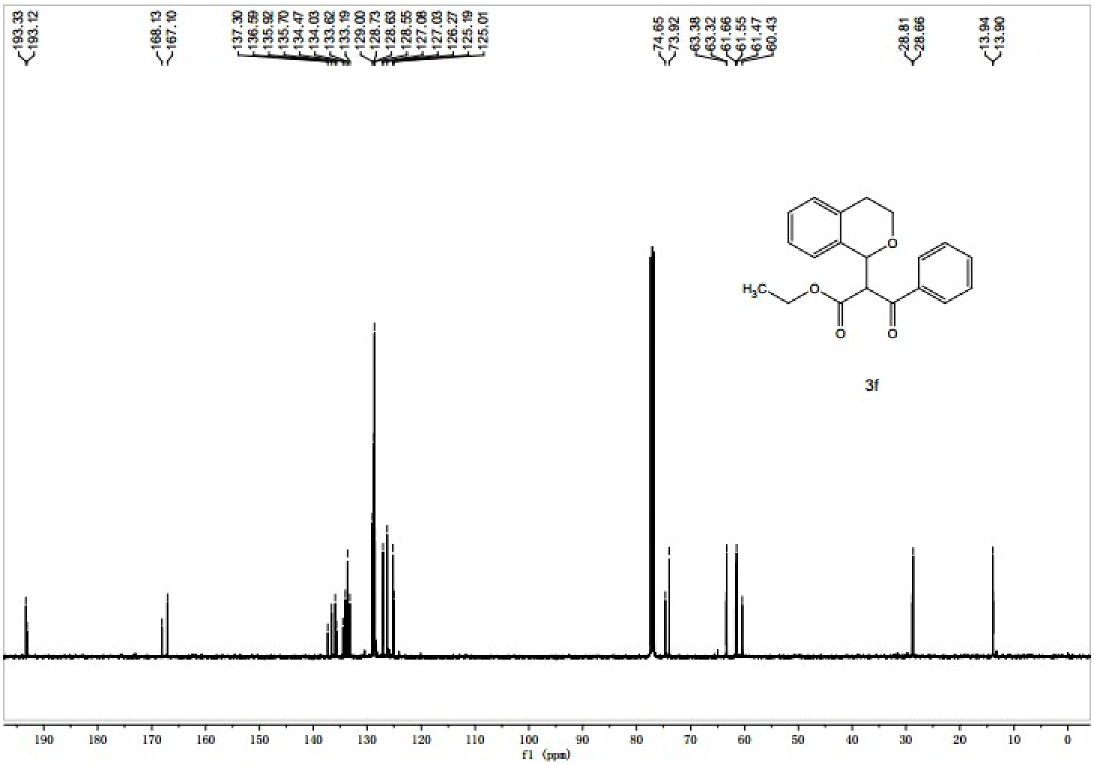
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3f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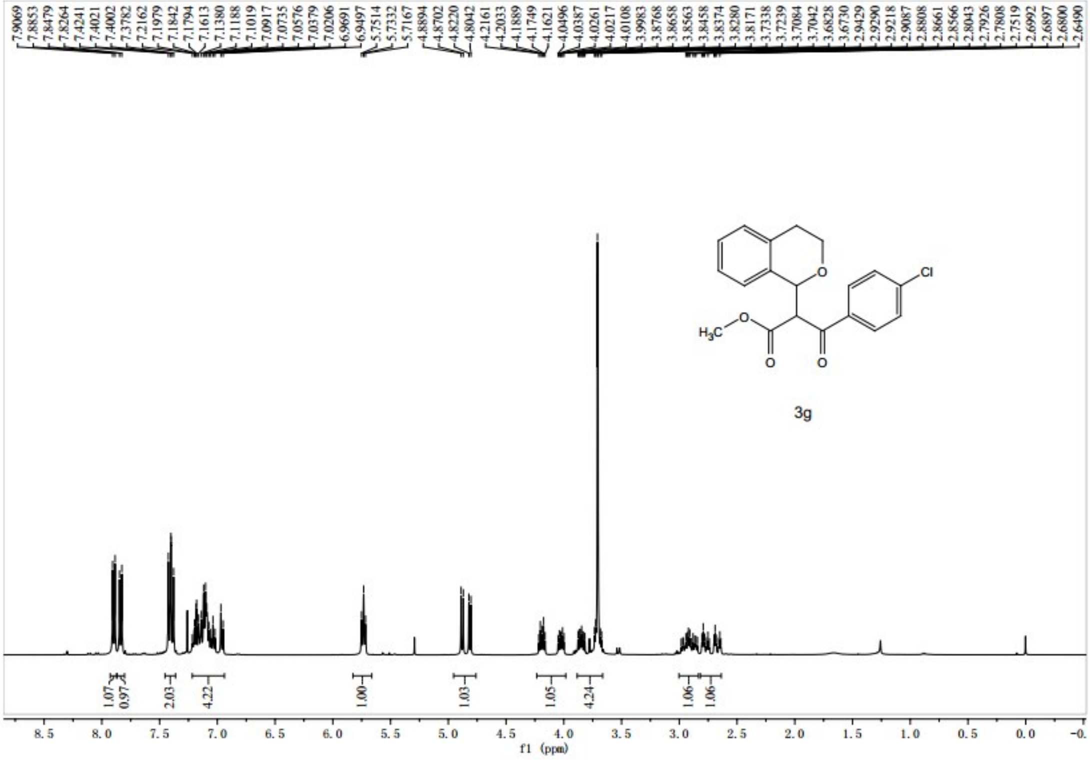
135.92
135.70
134.47
134.03
133.62
133.19
129.00
128.73
128.63
128.55
127.08
127.03
126.27
125.19
125.01
74.65
73.92
63.38
63.32
61.66
61.55
61.47
60.43
28.81
28.66
13.94
13.90
H3C
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3f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7.1842
7.1794
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7.1188
7.1019
7.0917
7.0735
7.0576
7.0379
7.0206
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4.2161
4.2033
4.1889
4.1749
4.1621
4.0496
4.0387
4.0261
4.0217
4.0108
3.9983
3.8768
3.8658
3.8563
3.8458
3.8374
3.8280
3.8171
3.7338
3.7239
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3.7042
3.6828
3.6730
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2.9290
2.9218
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2.8808
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2.8043
2.7926
2.7808
2.7519
2.6992
2.6897
2.6800
2.6490
Cl
O
H3C
O
O
O
3g
1.07
0.97
2.03
4.22
1.00
1.03
1.05
4.24
1.06
1.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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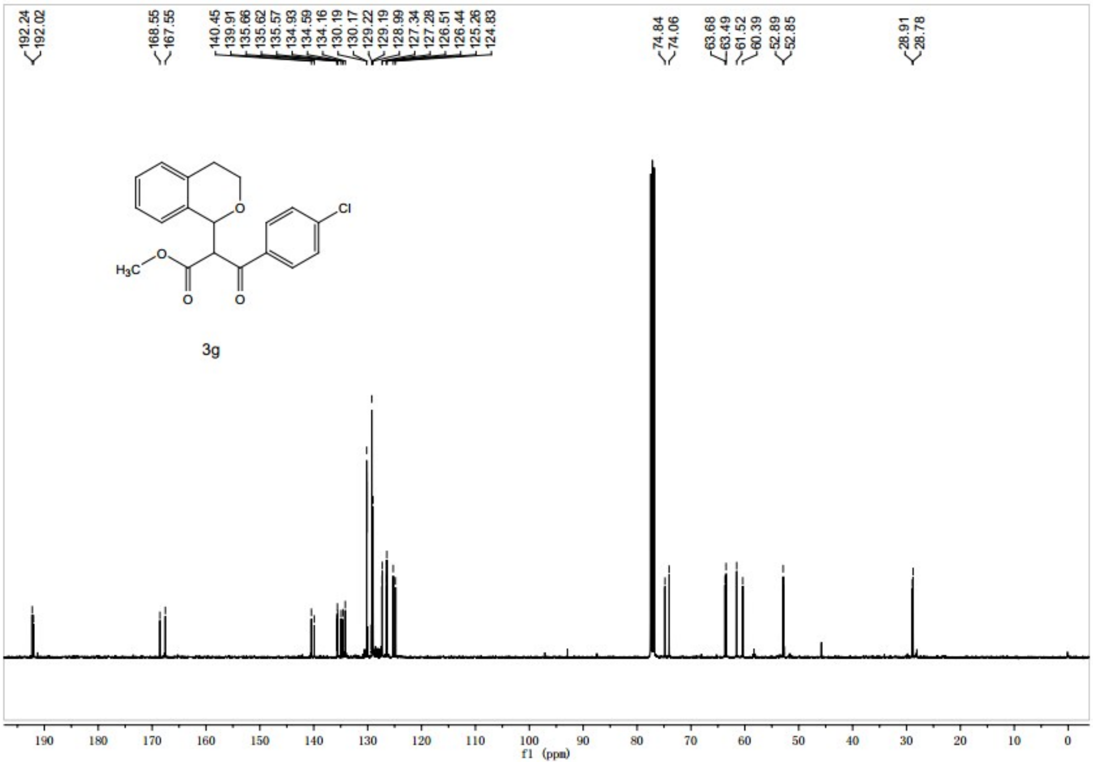
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)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130.19
130.17
129.22
129.19
128.99
127.34
127.28
126.51
126.44
125.26
124.83
74.84
74.06
63.68
63.49
61.52
60.39
52.89
52.85
28.91
28.78
Cl
O
H3C
O
O
O
3g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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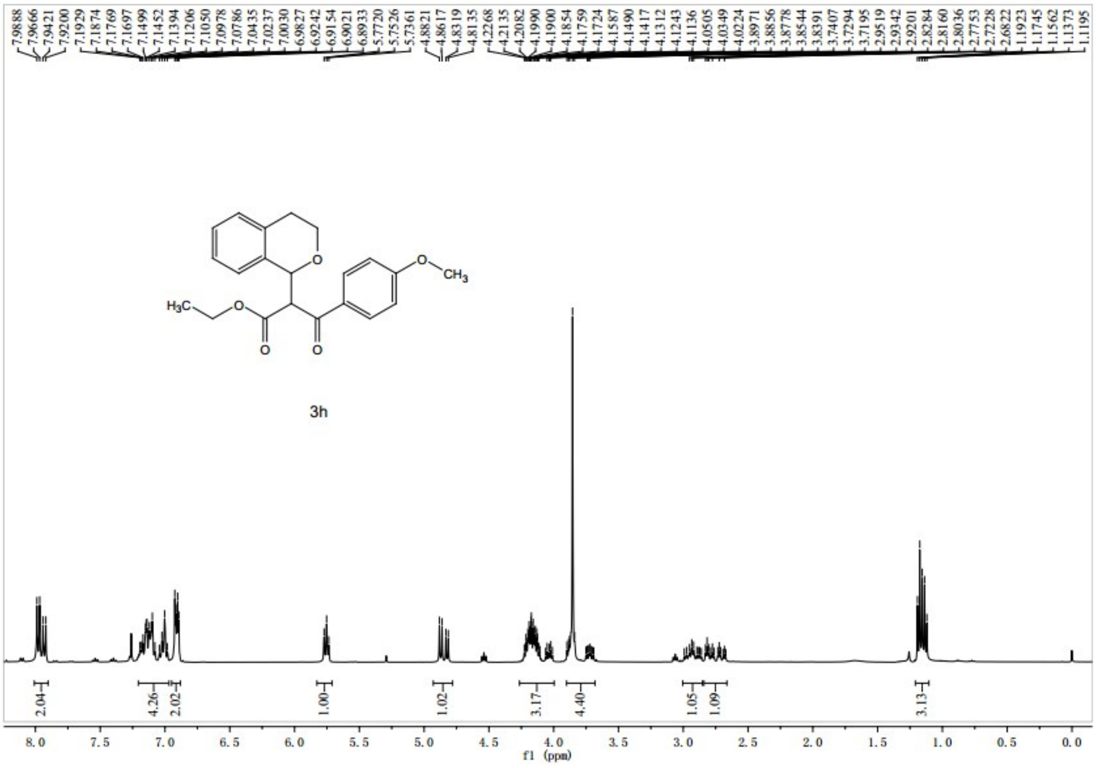
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7.1394
7.1206
7.1050
7.0978
7.0786
7.0435
7.0237
7.0030
6.9827
6.9242
6.9154
6.9021
6.8933
5.7720
5.7526
5.7361
4.8821
4.8617
4.8319
4.8135
4.2268
4.2135
4.2082
4.1990
4.1900
4.1854
4.1759
4.1724
4.1587
4.1490
4.1417
4.1312
4.1243
4.1136
4.0505
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4.0224
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3.8856
3.8778
3.8544
3.8391
3.7407
3.7294
3.7195
2.9519
2.9342
2.9201
2.8284
2.8160
2.8036
2.7753
2.7228
2.6822
1.1923
1.1745
1.1562
1.1373
1.1195
O
CH3
H3C
O
O
O
3h
2.04
4.26
2.02
1.00
1.02
3.17
4.40
1.05
1.09
3.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
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0.0
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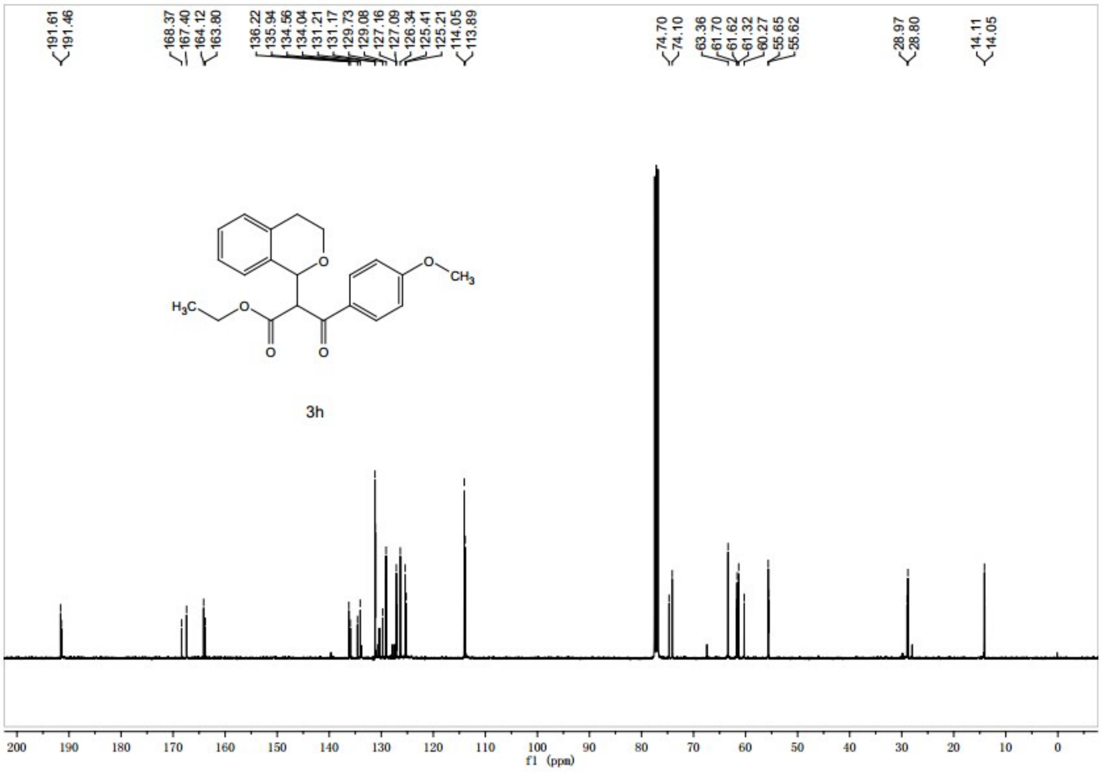
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134.04
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129.73
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127.16
127.09
126.34
125.41
125.21
114.05
113.89
74.70
74.10
63.36
61.70
61.62
61.32
60.27
55.65
55.62
28.97
28.80
14.11
14.05
O
CH3
H3C
O
O
O
3h
200
190
180
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120
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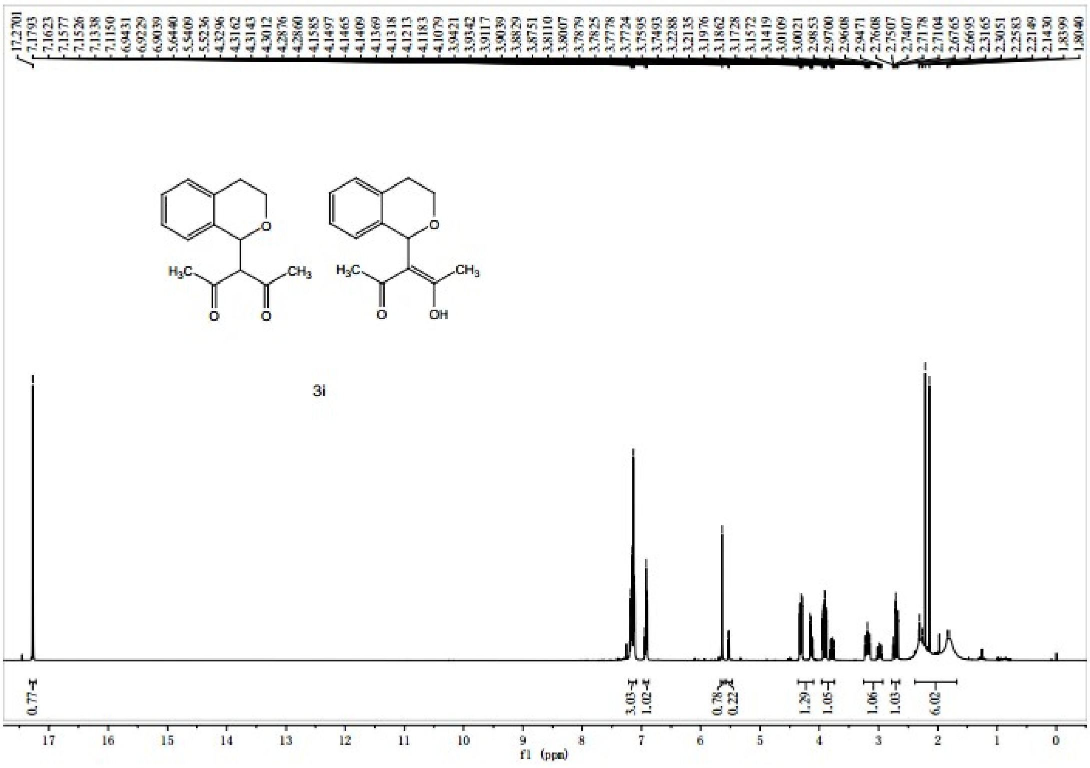
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5.6440
5.5409
5.5236
4.3296
4.3162
4.3143
4.3012
4.2876
4.2860
4.1585
4.1497
4.1465
4.1409
4.1369
4.1318
4.1213
4.1183
4.1079
3.9421
3.9342
3.9117
3.9039
3.8829
3.8751
3.8110
3.8007
3.7879
3.7825
3.7778
3.7724
3.7595
3.7493
3.2288
3.2135
3.1976
3.1862
3.1728
3.1572
3.1419
3.0109
3.0021
2.9853
2.9700
2.9608
2.9471
2.7608
2.7507
2.7407
2.7178
2.7104
2.6765
2.6695
2.3165
2.3051
2.2583
2.2149
2.1430
1.8399
1.8040
H3C
CH3
O
O
H3C
CH3
O
OH
3i
0.77
3.03
1.02
0.78
0.22
1.29
1.05
1.06
1.03
6.02
17
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14
13
12
11
10
9
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7
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5
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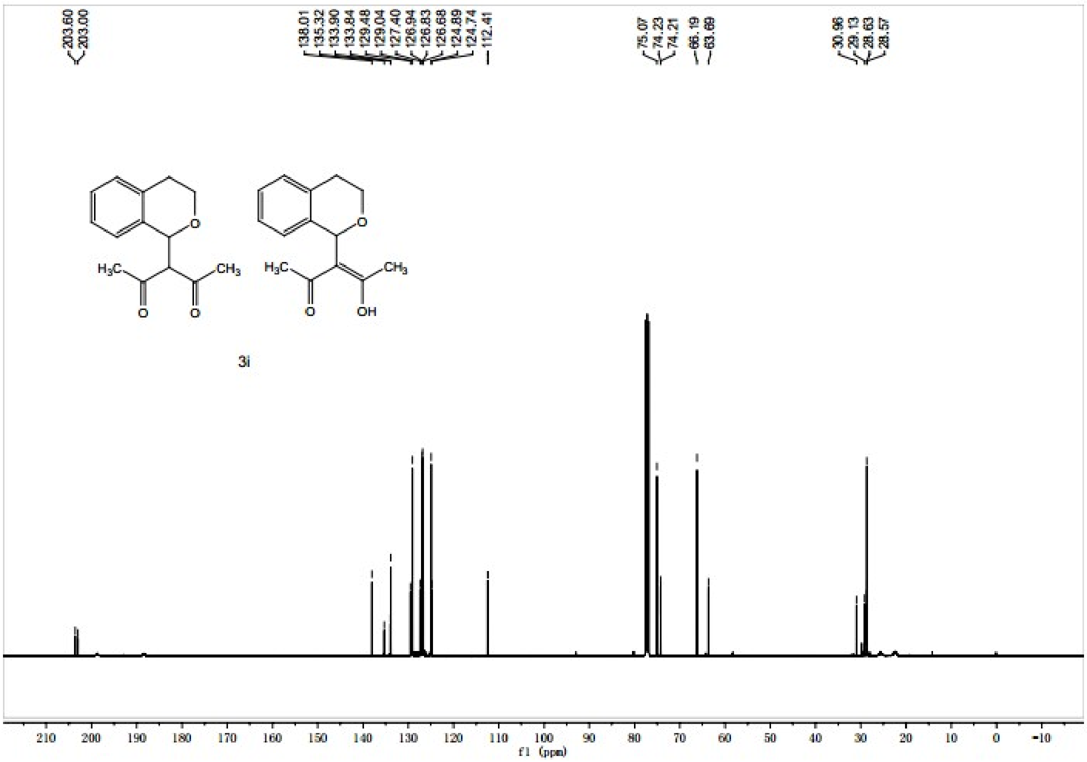
f1 (ppm)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126.83
126.68
124.89
124.74
112.41
75.07
74.23
74.21
66.19
63.69
30.96
29.13
28.63
28.57
H3C
CH3
O
O
H3C
CH3
O
OH
3i
210
200
190
180
170
160
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140
130
120
110
100
90
80
70
60
50
40
30
20
10
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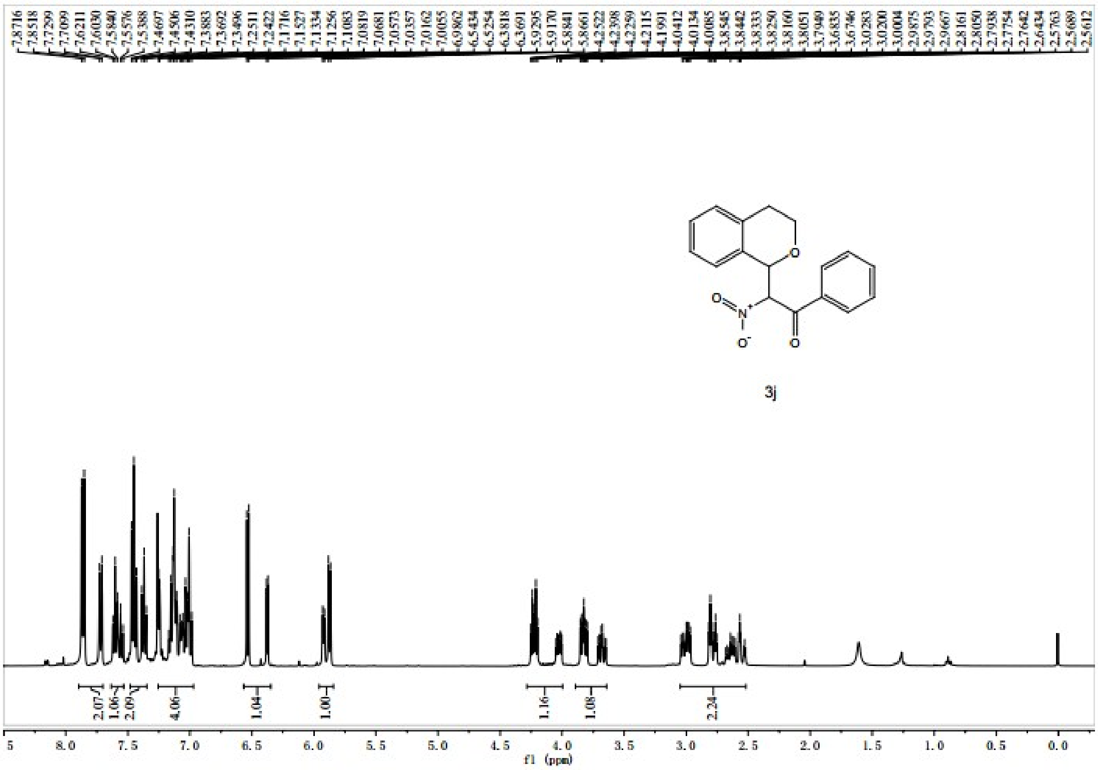
-10
f1 (ppm)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7.4697
7.4506
7.4310
7.3883
7.3692
7.3496
7.2511
7.2422
7.1716
7.1527
7.1334
7.1256
7.1083
7.0819
7.0681
7.0573
7.0357
7.0162
7.0055
6.9862
6.5434
6.5254
6.3818
6.3691
5.9295
5.9170
5.8841
5.8661
4.2522
4.2398
4.2259
4.2115
4.1991
4.0412
4.0134
4.0085
3.8545
3.8442
3.8333
3.8250
3.8160
3.8051
3.7949
3.6835
3.6746
3.0283
3.0200
3.0004
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2.9667
2.8161
2.8050
2.7938
2.7754
2.7642
2.6434
2.5763
2.5689
2.5612
O
O
N
O
O
3j
2.07
1.06
2.09
4.06
1.04
1.00
1.16
1.08
2.24
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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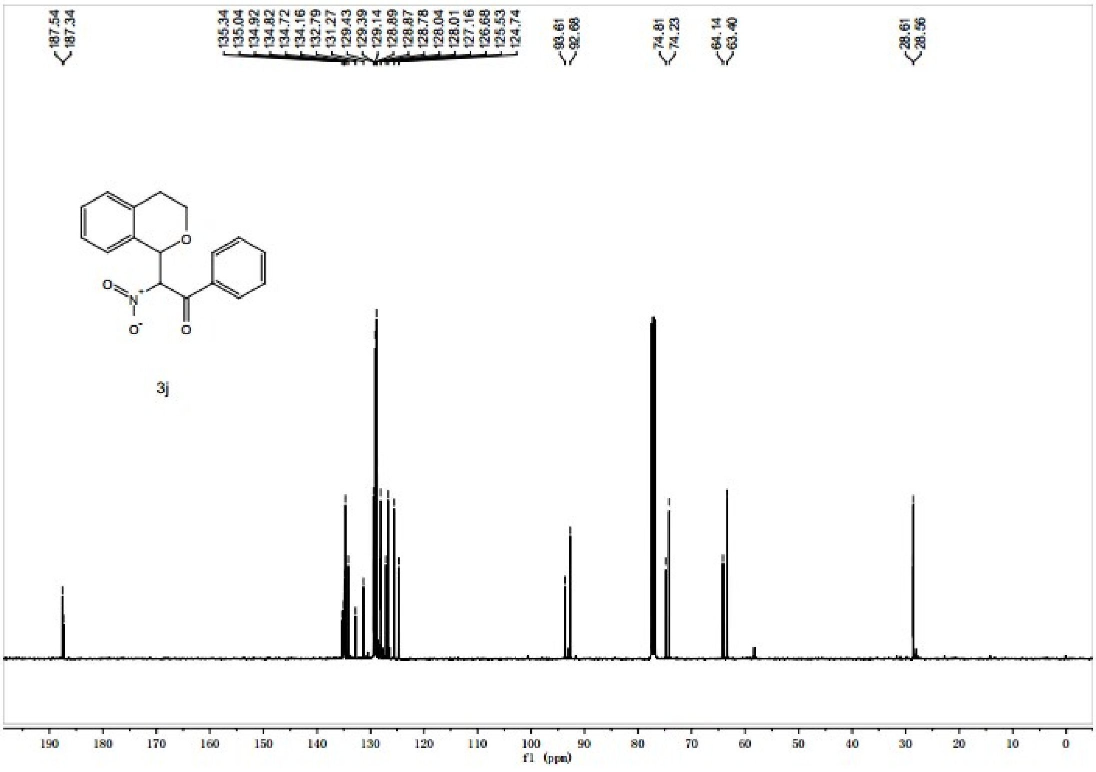
0.0
f1 (ppm)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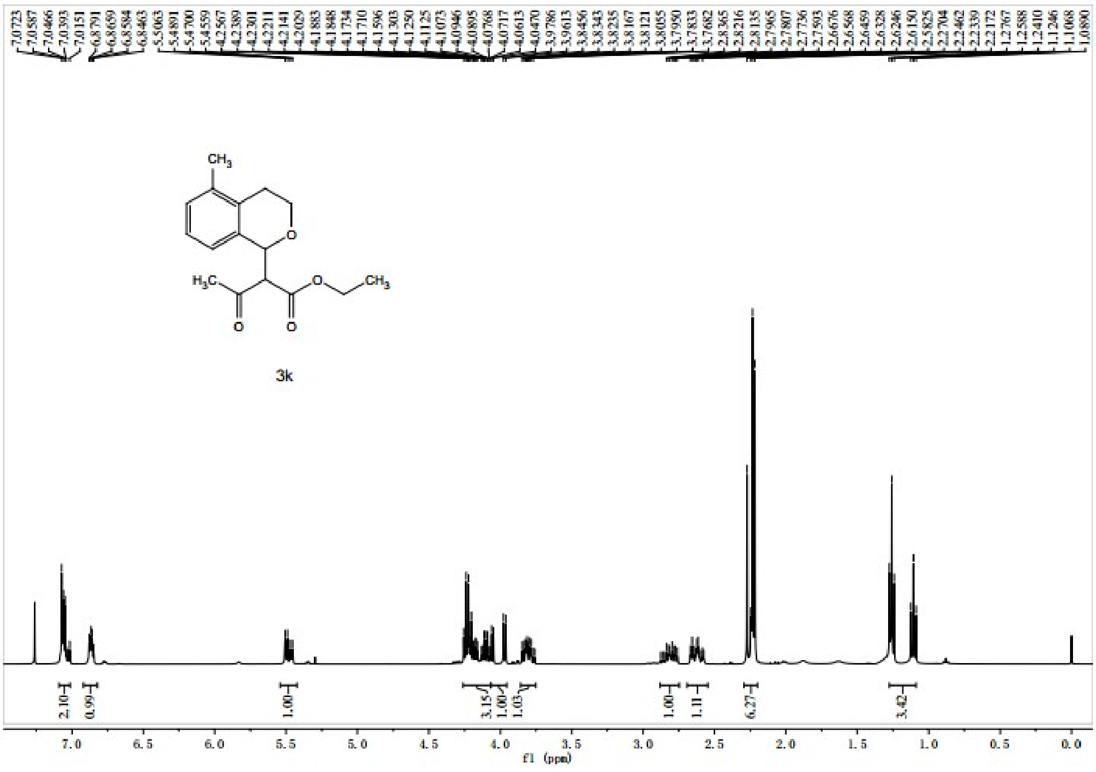
131.27
129.43
129.39
129.14
128.89
128.87
128.78
128.04
128.01
127.16
126.68
125.53
124.74
93.61
92.68
74.81
74.23
64.14
63.40
28.61
28.56
O
O
N
O
O
3j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.8463
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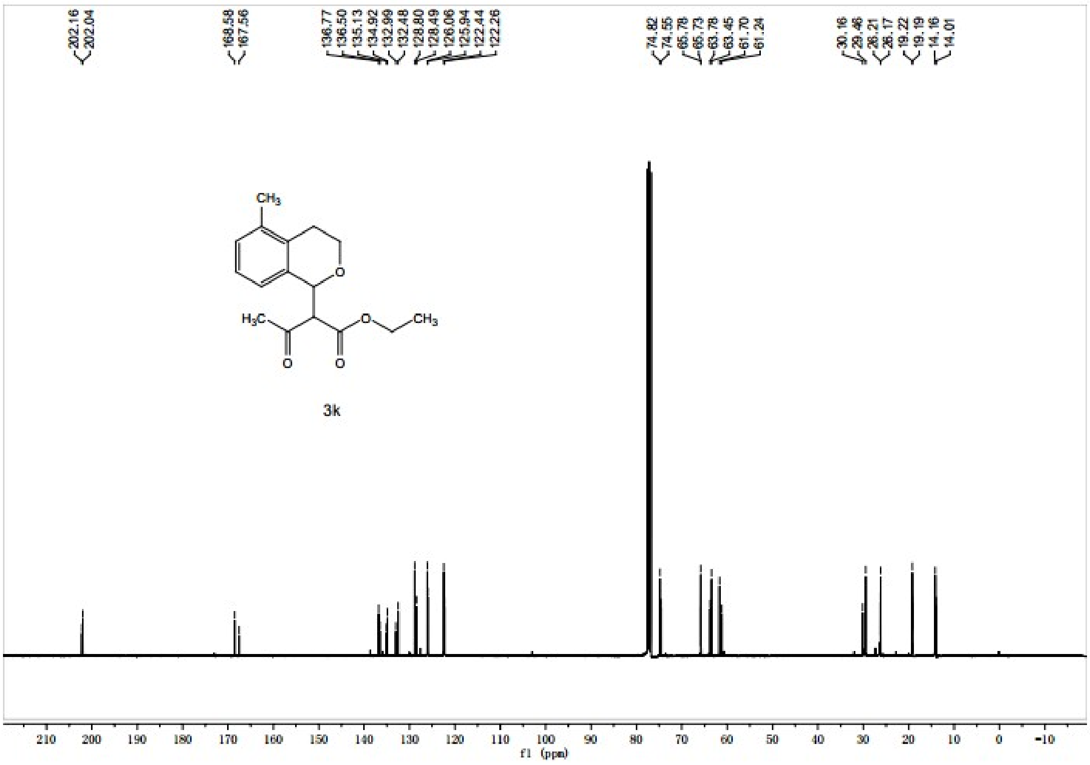
5.4891
5.4700
5.4559
4.2567
4.2389
4.2301
4.2211
4.2141
4.2029
4.1883
4.1848
4.1734
4.1710
4.1596
4.1303
4.1250
4.1125
4.1073
4.0946
4.0895
4.0768
4.0717
4.0613
4.0470
3.9786
3.9613
3.8456
3.8343
3.8235
3.8167
3.8121
3.8055
3.7950
3.7833
3.7682
2.8365
2.8216
2.8135
2.7965
2.7807
2.7736
2.7593
2.6676
2.6568
2.6459
2.6328
2.6246
2.6150
2.5825
2.2704
2.2462
2.2339
2.2172
1.2767
1.2588
1.2410
1.1246
1.1068
1.0890
CH3
O
H3C
O
O
O
CH3
3k
2.10
0.99
1.00
3.15
1.00
1.03
1.00
1.11
6.27
3.42
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.80
128.49
126.06
125.94
122.44
122.26
74.82
74.55
65.78
65.73
63.78
63.45
61.70
61.24
30.16
29.46
26.21
26.17
19.22
19.19
14.16
14.01
CH3
O
H3C
O
O
O
CH3
3k
210
200
190
180
170
160
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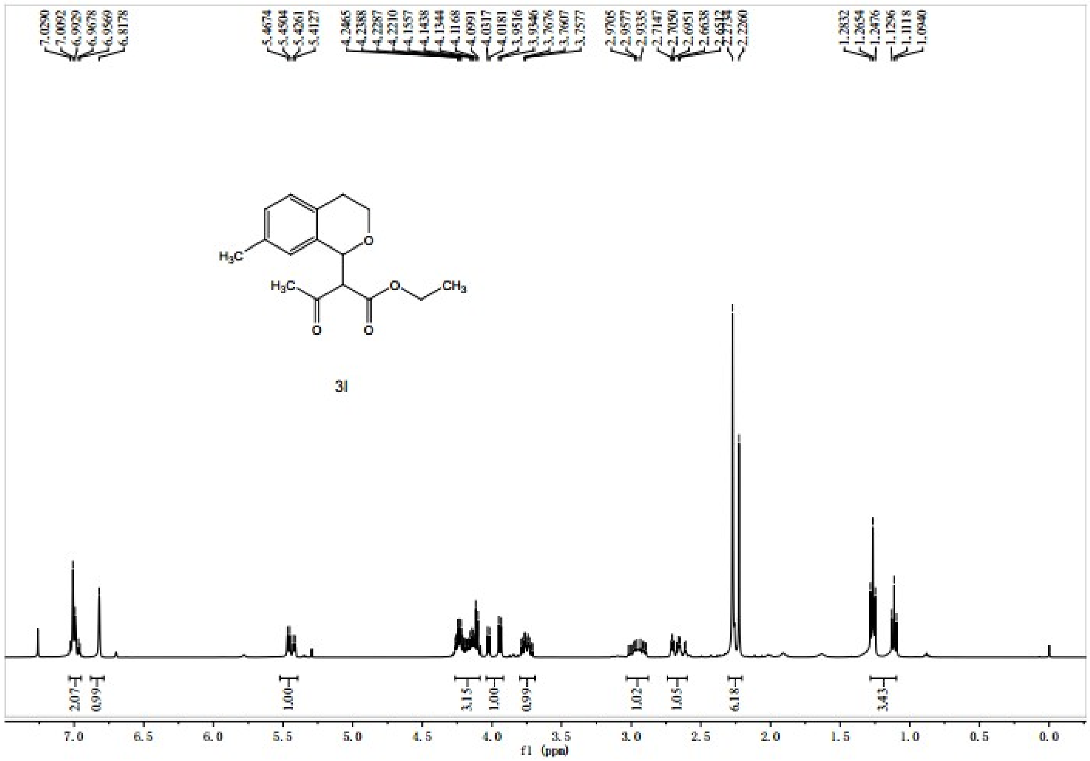
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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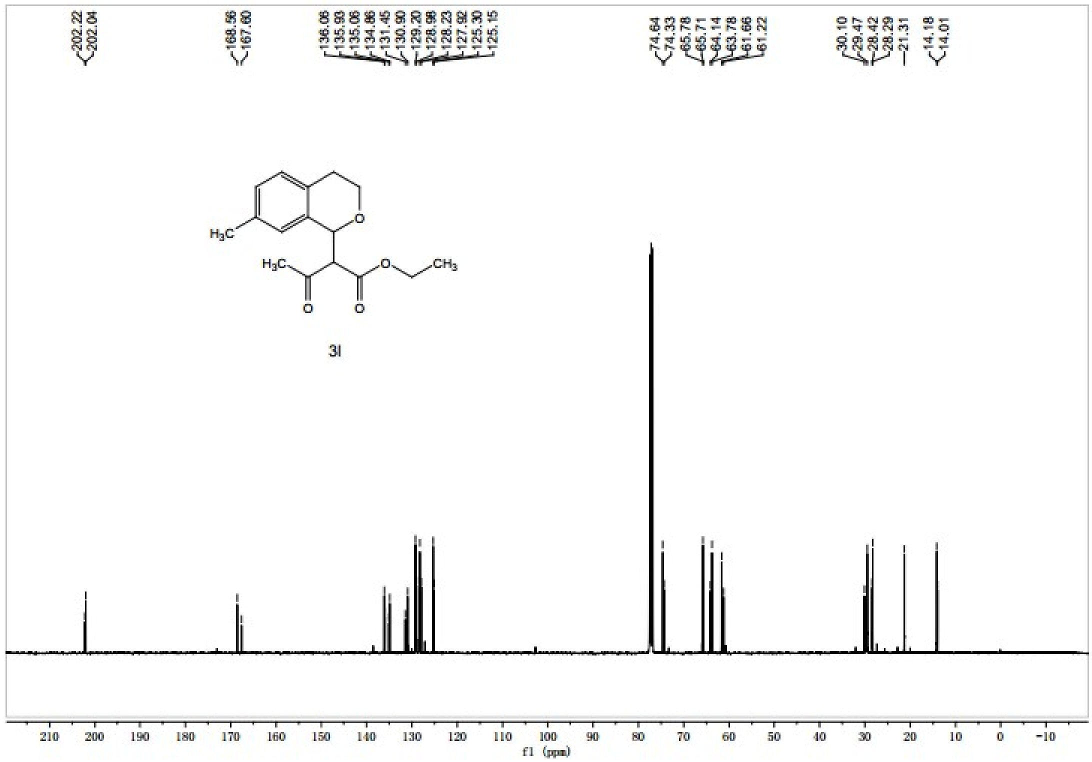
4.2210
4.1557
4.1438
4.1344
4.1168
4.0091
4.0317
4.0181
3.9516
3.9346
3.7676
3.7607
3.7577
2.9705
2.9577
2.9335
2.7147
2.7050
2.6951
2.6638
2.6512
2.2734
2.2260
1.2832
1.2654
1.2476
1.1296
1.1118
1.0940
H3C
H3C
O
CH3
O
O
O
3l
2.07
0.99
1.00
3.15
1.00
0.99
1.02
1.05
6.18
3.43
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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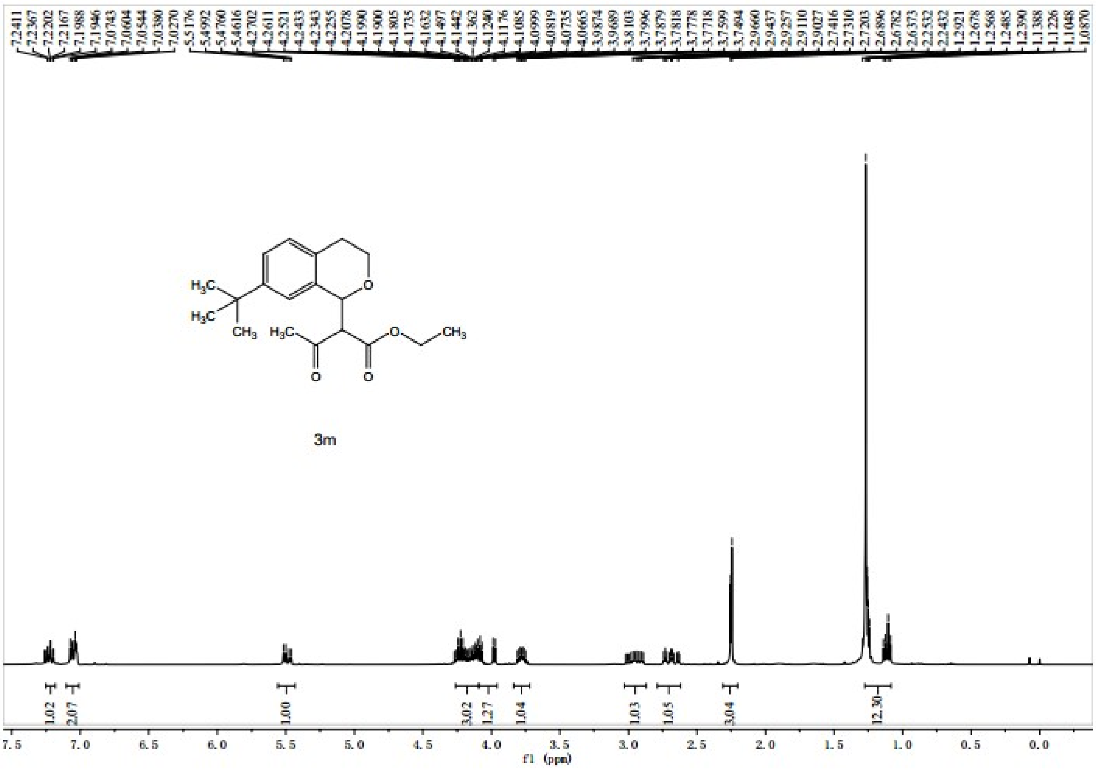
128.23
127.92
125.30
125.15
74.64
74.33
65.78
65.71
64.14
63.78
61.66
61.22
30.10
29.47
28.42
28.29
21.31
14.18
14.01
H3C
H3C
O
CH3
O
O
O
3l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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5.4992
5.4760
5.4616
4.2702
4.2611
4.2521
4.2433
4.2343
4.2255
4.2078
4.1990
4.1900
4.1805
4.1735
4.1632
4.1497
4.1442
4.1362
4.1240
4.1176
4.1085
4.0999
4.0819
4.0735
4.0665
3.9874
3.9689
3.8103
3.7996
3.7879
3.7818
3.7778
3.7599
3.7494
2.9660
2.9437
2.9257
2.9110
2.9027
2.7416
2.7310
2.7203
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2.6782
2.6373
2.2532
2.2432
1.2921
1.2678
1.2568
1.2485
1.2390
1.1388
1.1226
1.1048
1.0870
H3C
H3C
CH3
H3C
O
O
O
CH3
1.02
2.07
1.00
3.02
1.27
1.04
1.03
1.05
3.04
12.30
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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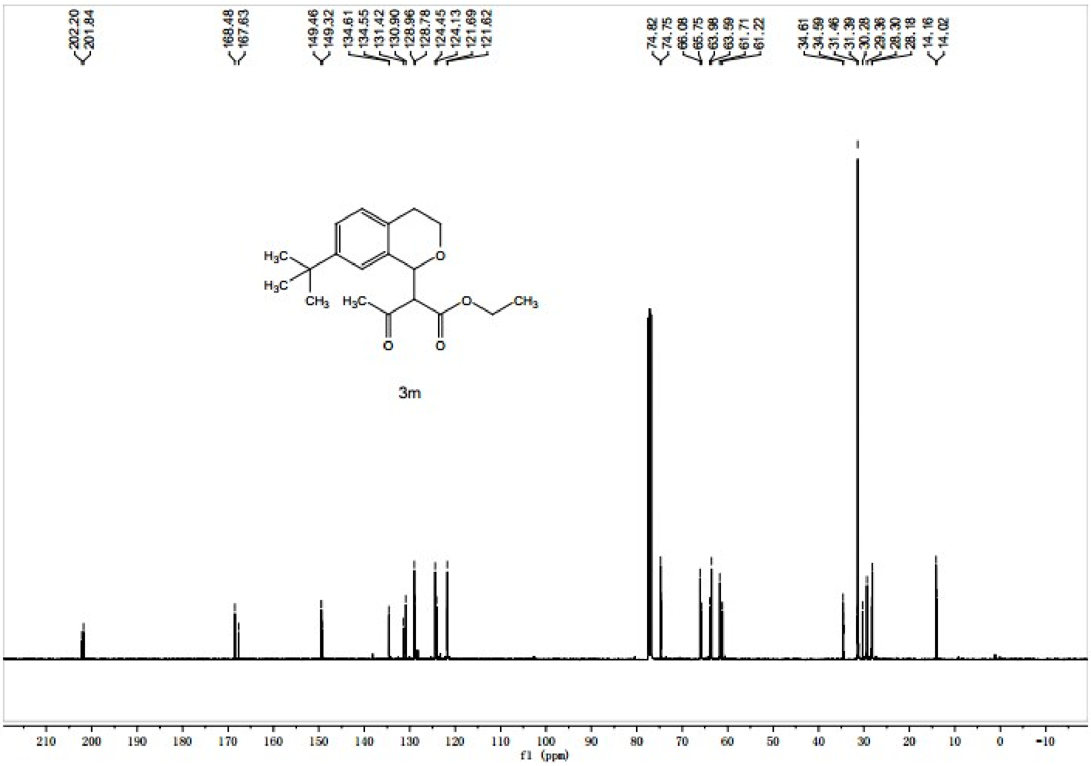
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3m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128.78
124.45
124.13
121.69
121.62
74.82
74.75
66.08
65.75
63.98
63.59
61.71
61.22
34.61
34.59
31.46
31.39
30.28
29.36
28.30
28.18
14.16
14.02
H3C
H3C
CH3
H3C
O
O
O
CH3
210
200
190
180
170
160
150
140
130
120
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100
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80
70
60
50
40
30
20
10
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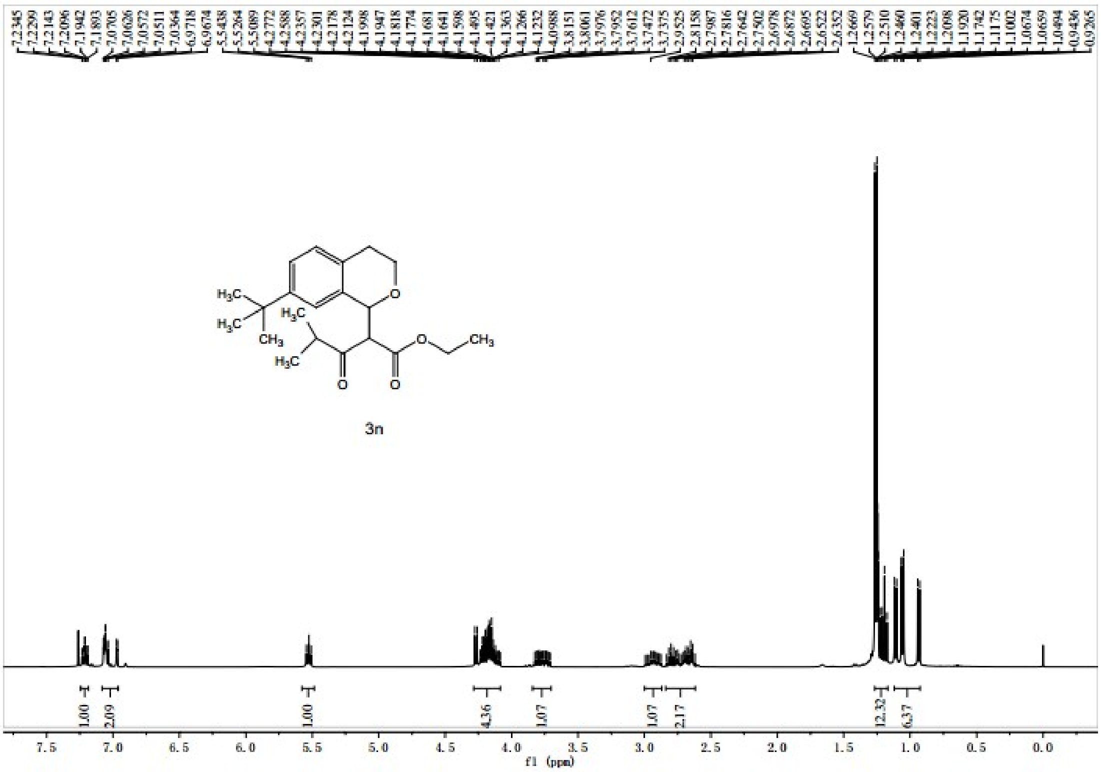
-10
f1 (ppm)

3m


3n

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7.1893
7.0705
7.0626
7.0572
7.0511
7.0364
6.9718
6.9674
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5.5264
5.5089
4.2772
4.2588
4.2357
4.2301
4.2178
4.2124
4.1998
4.1947
4.1818
4.1774
4.1681
4.1641
4.1598
4.1495
4.1421
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4.1232
4.0988
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3.8061
3.7976
3.7952
3.7612
3.7472
3.7375
2.9525
2.8158
2.7987
2.7816
2.7642
2.7502
2.6978
2.6872
2.6695
2.6522
2.6352
1.2669
1.2579
1.2510
1.2460
1.2401
1.2223
1.2008
1.1920
1.1742
1.1175
1.1002
1.0674
1.0659
1.0494
0.9436
0.9265
H3C
H3C
CH3
H3C
H3C
O
O
O
O
CH3
1.00
2.09
1.00
4.36
1.07
1.07
2.17
12.32
6.37
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
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1.0
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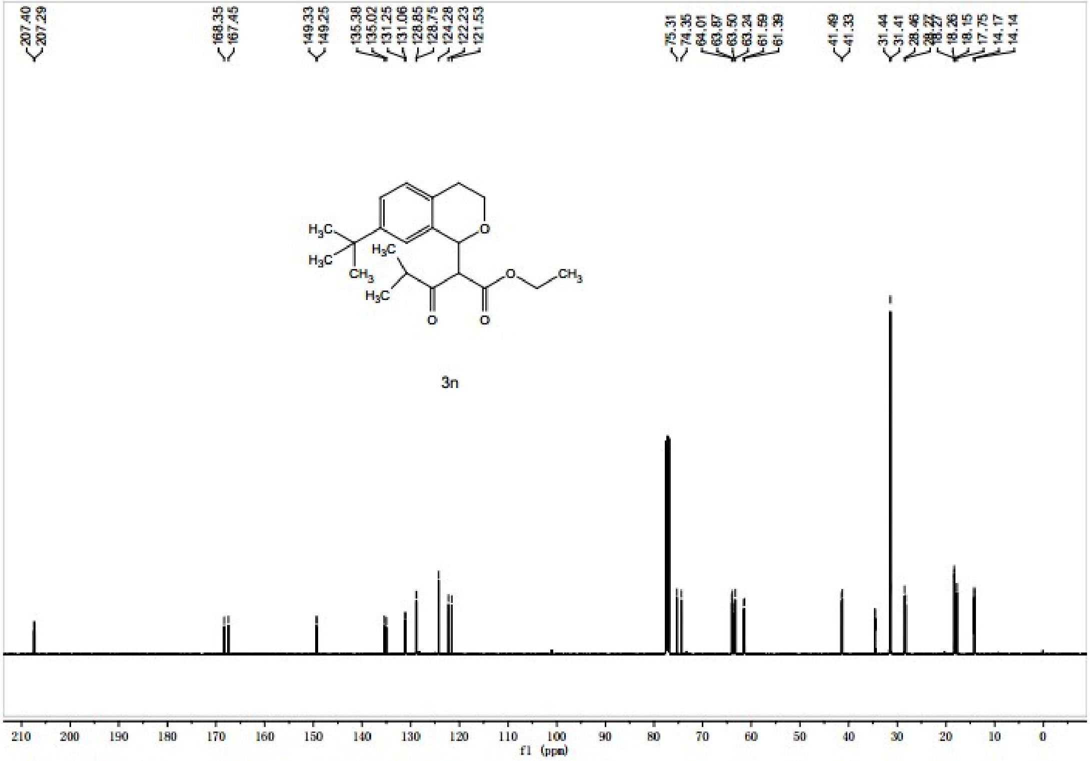
0.0
f1 (ppm)


3n

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135.38
135.02
131.25
131.06
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128.75
124.28
122.23
121.53
75.31
74.35
64.01
63.87
63.50
63.24
61.59
61.39
41.49
41.33
31.44
31.41
28.46
28.27
18.27
18.26
18.15
17.75
14.17
14.14
H3C
H3C
CH3
H3C
H3C
O
O
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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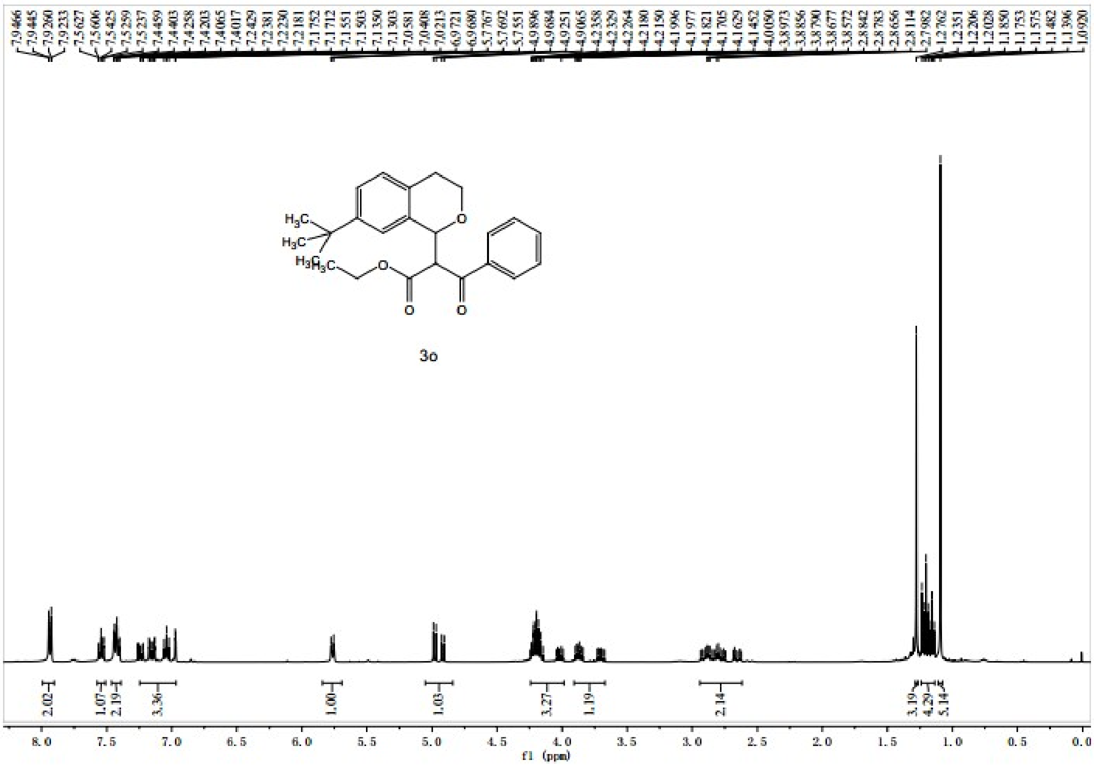
50
40
30
20
10
0
f1 (ppm)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7.4258
7.4203
7.4065
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7.2230
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7.1712
7.1551
7.1503
7.1350
7.1303
7.0581
7.0408
7.0213
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4.2190
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4.1629
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4.0090
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3.8790
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3.8572
2.8842
2.8783
2.8656
2.8114
2.7982
1.2762
1.2351
1.2206
1.2028
1.1850
1.1753
1.1575
1.1482
1.1396
1.0920
H_3C
H_3C
H_3C
H_3C
O
O
O
2.02
1.07
2.19
3.36
1.00
1.03
3.27
1.19
2.14
3.19
4.29
5.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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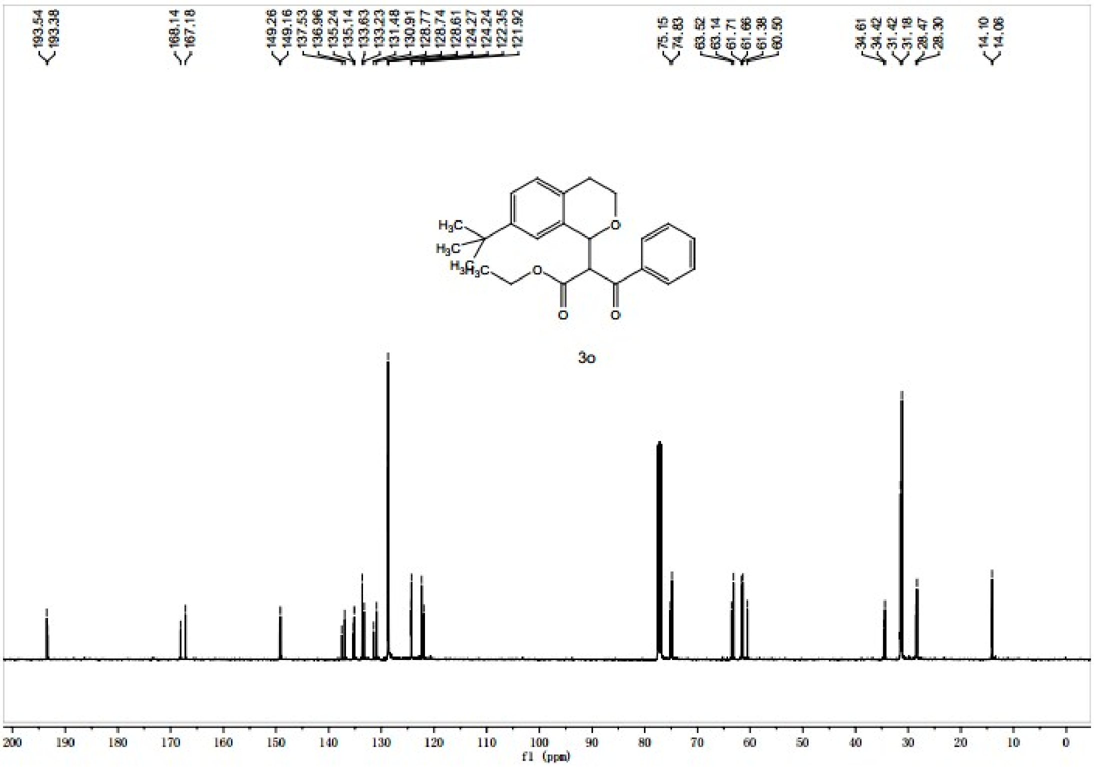
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3o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133.63
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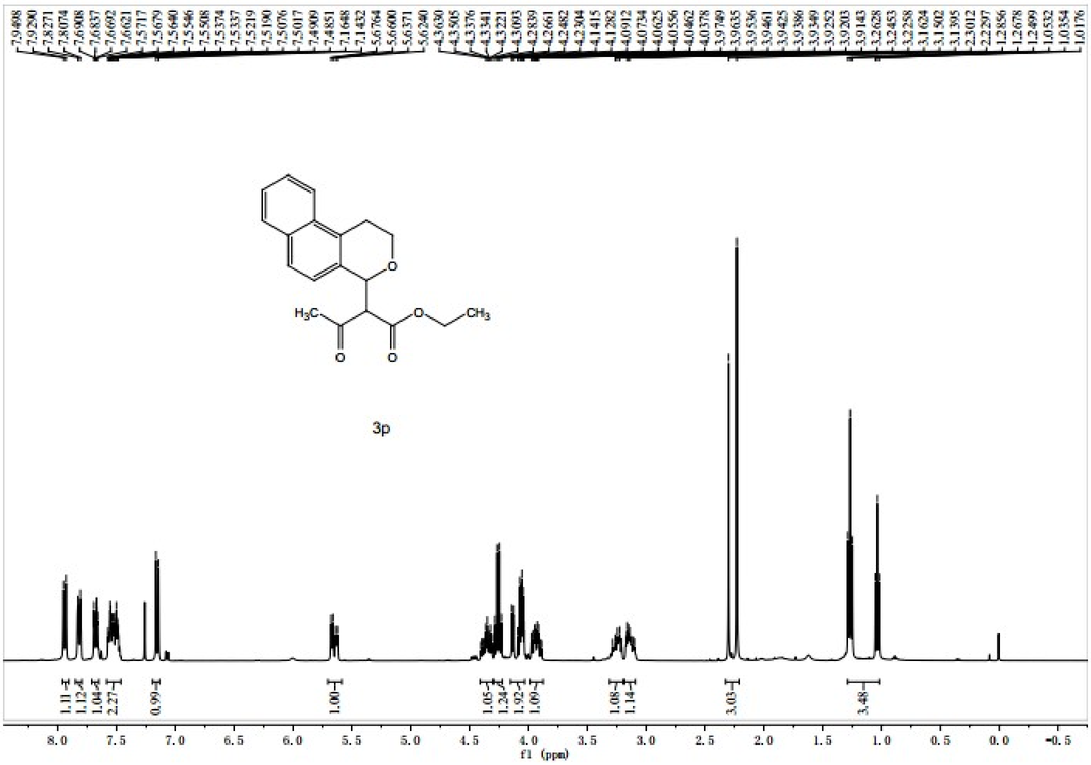
131.48
130.91
128.77
128.74
128.61
124.27
124.24
122.35
121.92
75.15
74.83
63.52
63.14
61.71
61.66
61.38
60.50
34.61
34.42
31.42
31.18
28.47
28.30
14.10
14.06
H_3C
H_3C
H_3C
H_3C
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3o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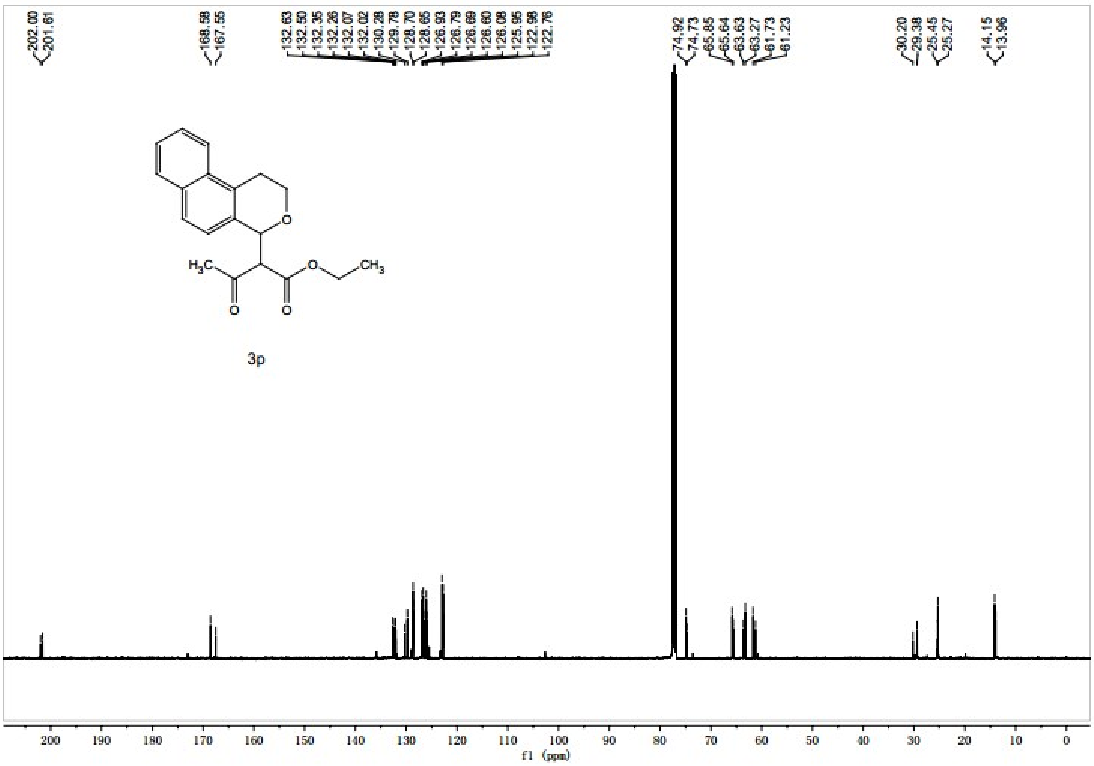
7.5546
7.5508
7.5374
7.5337
7.5219
7.5190
7.5076
7.5017
7.4909
7.4851
7.1648
7.1432
5.6764
5.6600
5.6371
5.6240
4.3630
4.3505
4.3376
4.3341
4.3221
4.3093
4.2839
4.2661
4.2482
4.2304
4.1415
4.1282
4.0912
4.0734
4.0625
4.0556
4.0462
4.0378
3.9749
3.9635
3.9536
3.9461
3.9425
3.9386
3.9349
3.9252
3.9203
3.9143
3.2628
3.2453
3.2258
3.1624
3.1502
3.1395
2.3012
2.2297
1.2856
1.2678
1.2499
1.0532
1.0354
1.0176
O
H_3C
CH_3
O
O
O
3p
1.11
1.12
1.04
2.27
0.99
1.00
1.05
1.24
1.92
1.09
1.08
1.14
3.03
3.48
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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201.61
168.58
167.55
132.63
132.50
132.35
132.26
132.07
132.02
130.28
129.78
128.70
128.65
126.93
126.79
126.69
126.60
126.08
125.95
122.98
122.76
74.92
74.73
65.85
65.64
63.63
63.27
61.73
61.23
30.20
29.38
25.45
25.27
14.15
13.96
O
H_3C
CH_3
O
O
O
3p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)