Supporting Information

Photo-induced Radical Cascade Cyclization of Acetylenic Acid Ester with Oxime Esters to Access Cyanalkylated Coumarins

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Table of Contents

1. Experimental Section

General Information. The starting materials of acetylenic acid esters (**1**) [1] and oxime esters (**2**) [2] were synthesized as previously reported. Blue LED tubes were purchased from Huada Electric Manufacturing Co., Ltd. The model information is as follows: LED T5 integrated tube, 430-455 nm, 4 W, 2835 lamp beads, size of 23 mm×34 mm×30 cm, materials of aluminum and PC. The distance is about 5 mm from the light source to the Schlenk tube container.

Melting points were obtained using a melting point instrument and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded by using a 400 MHz NMR spectrometer. Chemical shifts were reported in ppm from the $CDCl_3$ resonance as the internal reference ($CDCl_3$ δ_H = 7.26 ppm, downfield from TMS, δ_C = 77.16 ppm). Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. GC-MS was measured using electron ionization. HRMS was conducted on an EI-ion trap High Resolution mass spectrometer. Fluorescence spectra were recorded by using a Fluorescence Spectrophotometer. Thin-layer chromatography (TLC) was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm. X-ray structural analyses were recorded on an X-ray analysis instrument.

2. General procedures for Synthesis of Cyanalkylated Coumarins.

A mixture of starting materials **1** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv), K_2CO_3 (0.4 mmol, 2.0 equiv), *fac*-$Ir(PPy)_3$ (2.0 mol%), and DMSO (3 mL) was sealed in a 25.0 mL Schlenk tube under N_2 atmosphere and was placed under two 4 W blue LEDs irradiation while stirring for 20 h at room temperature. The reaction was quenched by saturated brine after completion and then extracted with ethyl acetate (3 × 15 mL). The combined ethyl acetate layer was then dried over anhydrous $MgSO_4$ and concentrated in vacuum. The residue was purified by flash column chromatography (200~300 mesh) to afford the product cyanalkylated coumarins **3**.

3. Procedure for Gram-scale Synthesis of Cyanalkylated Coumarin.

In a 100 mL sealed flask, a mixture of phenyl 3-phenylpropiolate **1a** (4.5 mmol, 1.0 equiv), 3-phenylcyclobutan-1-one *O*-(4-(trifluoromethyl) benzoyl) oxime **2a** (9.0 mmol, 2 equiv), *fac*-Ir(PPy)$_3$ (2.0 mol %), K_2CO_3 (9.0 mmol, 2 equiv), and 40 mL DMSO was placed under two 4 W blue LEDs irradiation while stirring at room temperature for 20 h under N_2 atmosphere. After completion, the reaction was quenched by brine and then extracted with ethyl acetate (3 × 60 mL). The combined organic layer was then dried over anhydrous $MgSO_4$. Then the residue was purified by flash column chromatography (10/1 petroleum ether/ethyl acetate, v/v) which eventually afforded the desired product **3a** (1.07 g, 65% yield).

4. Procedure for Synthesis of Butyl 4-(2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanoate (4)

A 100 mL sealed Schlenk flask was charged with 4-(2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile (**3a**) (0.2 mmol, 1.0 equiv) and $ZnCl_2$ (0.2 mmol, 1.0 equiv). *n*-BuOH (1 mL) was then injected into the flask by syringe while stirring at 120^{o}C for 20 h. After completion, the reaction was quenched by brine and then extracted with ethyl acetate (3 × 20 mL). The combined organic layer was then dried over anhydrous $MgSO_4$. Then the residue was purified by flash column chromatography (5/1 petroleum ether/ethyl acetate, v/v) which eventually afforded the desired product **4** (57.2 mg, 65% yield) [3].

5. Preliminary Mechanistic Studies

5.1 Radical Trapping Experiments.

A mixture of phenyl 3-phenylpropiolate **1a** (0.2 mmol, 1.0 equiv), 3-phenylcyclobutan-1-one *O*-(4-(trifluoromethyl) benzoyl) oxime **2a** (0.4 mmol, 2.0 equiv), K_2CO_3 (0.4 mmol, 2.0 equiv), *fac*-Ir(PPy)$_3$ (2.0 mol%), radical scavenger (1 equiv), and DMSO (3 mL) was sealed in a 25.0 mL Schlenk tube under N_2 atmosphere and was placed under two 4 W blue LEDs irradiation while stirring for 20 h at room temperature. After completion, the reaction was quenched by saturated

brine and then extracted with ethyl acetate (3 × 15 mL). The combined organic layer was then dried over anhydrous $MgSO_4$ and concentrated in vacuum. Further purification by flash column chromatography (200~300 mesh) to afford the the pure product **5** or **6**.

5.2 Luminescence Quenching Experiments

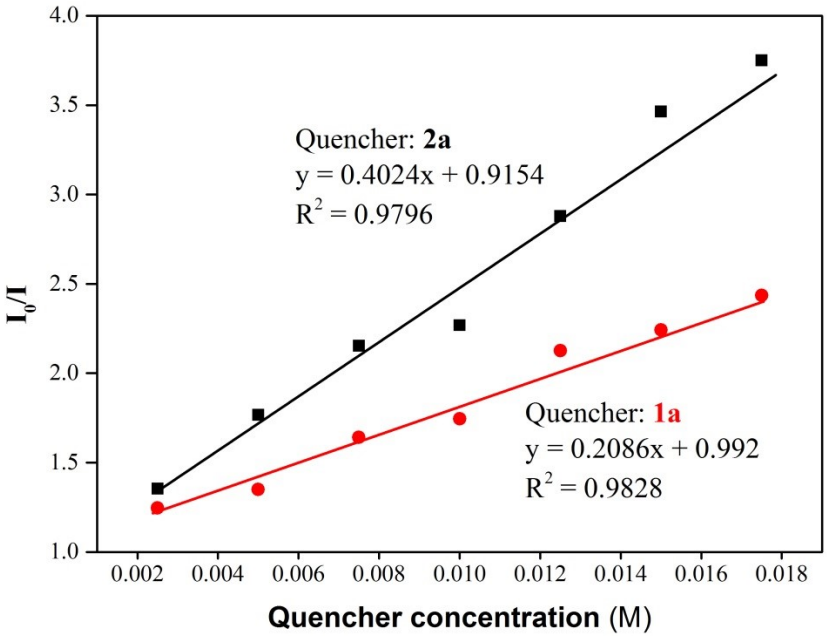
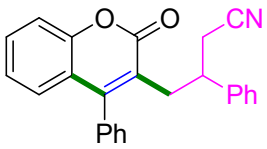


Figure S1. The excited photocatalyst *fac*-Ir(ppy)$_3$ emission quenching by **1a** and **2a**.

The *fac*-Ir(ppy)$_3$ solution was excited at 377 nm and the emission intensity was recorded at 540 nm. In a typical experiment, the emission spectrum of a 2×10^{-4} M solution of photocatalyst *fac*-Ir(ppy)$_3$ in DMSO was collected. The *fac*-Ir(ppy)$_3$ luminescence intensity were found to effectively decrease in the presence of quencher **2a** while a slightly decrease of *fac*-Ir(ppy)$_3$ luminescence was observed in the presence of substrate **1a**.

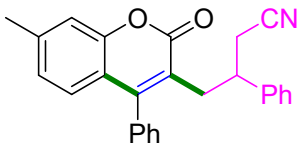
6. Analytical data of Radical Cascade Cyclization products



4-(2-Oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile (3a)

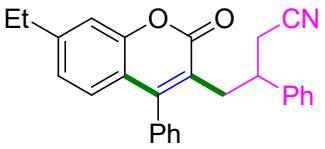
65.7 mg, 90% yield; white solid, mp: 165−166 °C; TLC (petroleum ether/ethyl acetate

= 5/1, v/v): R_f = 0.27; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.45 (m, 3H), 7.37 (qd, J = 2.7 Hz, J = 7.3 Hz, 2H), 7.2-7.20 (m, 3H), 7.17-7.15 (m, 1H), 7.12-7.08 (m, 1H), 6.94-6.91 (m, 2H), 6.87 (dd, J = 1.3 Hz, J = 8.0 Hz, 1H), 6.55 (d, J = 7.6 Hz, 1H), 3.48 (ddd, J = 6.5 Hz, J = 8.2 Hz, J = 14.7 Hz, 1H), 2.96 (dd, J = 6.3 Hz, J = 13.5 Hz, 1H), 2.75 (dd, J = 8.5 Hz, J = 13.5 Hz, 1H), 2.66-2.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 153.0, 152.7, 140.7, 133.8, 131.2, 128.8 (2C), 128.7, 128.1, 127.5 (2C), 127.3, 124.2, 123.3, 120.5, 118.4, 116.6, 40.4, 35.1, 23.9; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{19}NO_2$, 366.1494; found, 366.1497.



4-(7-Methyl-2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile (3b)

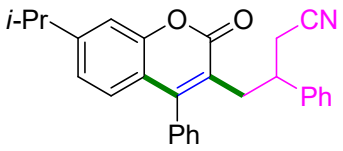
62.9 mg, 83% yield; white solid, mp: 65−67 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.45 (m, 2H), 7.39-7.35 (m, 1H), 7.22-7.18 (m, 3H), 7.16-7.13 (m, 2H), 6.94-6.89 (m, 3H), 6.74 (d, J = 8.1 Hz,1H), 6.56 (d, J = 7.6 Hz, 1H), 3.50-3.42 (m, 1H), 2.93 (dd, J = 6.4 Hz, J = 13.5 Hz, 1H), 2.72 (dd, J = 8.4 Hz, J = 13.5 Hz, 1H), 2.65-2.53 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 153.1, 152.7, 142.5, 140.8, 134.0, 128.8, 128.7 (2C), 128.1, 127.5, 127.3, 127.2, 125.4, 122.1, 118.4, 118.1, 116.8, 40.4, 35.1, 23.8, 21.6; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{26}H_{22}NO_2$, 380.1651; found, 380.1654.



4-(7-Ethyl-2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile (3c)

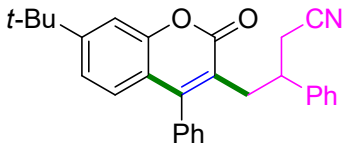
66.8 mg, 85% yield; white solid, mp: 69−70 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.29; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.45 (m, 2H), 7.39-7.35 (m, 1H), 7.20 (dd, J = 3.1 Hz, J = 6.2 Hz, 4H), 7.16-7.13 (m, 1H), 6.95-6.91 (m, 3H), 6.77 (d, J = 8.2 Hz, 1H), 6.55 (d, J = 7.6 Hz, 1H), 3.51-3.43 (m, 1H), 2.93 (dd, J = 6.4 Hz,

J = 13.5 Hz, 1H), 2.75-2.752 (m, 1H), 2.71-2.67 (m, 2H), 2.65-2.53 (m, 2H), 1.24 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 153.1, 152.8, 148.8, 140.8, 134.0, 128.8 (2C), 128.7, 128.1, 127.5, 127.3 (2C), 124.2, 122.1, 118.5, 118.2, 115.6, 40.4, 35.1, 28.8, 23.9, 15.2; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{27}H_{24}NO_2$, 394.1807; found, 394.1809.



4-(7-Isopropyl-2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile (3d)

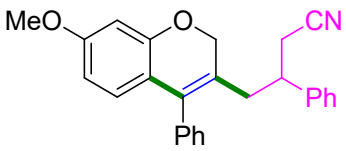
70.0 mg, 86% yield; white solid, mp: 117−118 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.29; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.45 (m, 2H), 7.39-7.35 (m, 1H), 7.22-7.20 (m, 4H), 7.16-7.13 (m, 1H), 6.97 (dd, J = 1.5 Hz, J = 8.3 Hz, 1H), 6.92 (dd, J = 3.0 Hz, J = 6.3 Hz, 2H), 6.78 (d, J = 8.2 Hz,1H), 6.55 (d, J = 7.5 Hz, 1H), 3.50-3.43 (m, 1H), 2.99-2.91 (m, 2H), 2.73 (dd, J = 8.5 Hz, J = 13.5 Hz, 1H), 2.66-2.54 (m, 2H), 1.26 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 153.4, 153.1, 152.9, 140.8, 134.0, 128.8 (2C), 128.7, 128.1, 127.5, 127.4, 127.3, 122.9, 122.1, 118.4 (2C), 114.2, 40.4, 35.0, 34.1, 23.9, 23.7; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{28}H_{26}NO_2$, 408.1964; found, 408.1962.



4-(7-(tert-Butyl)-2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile (3e)

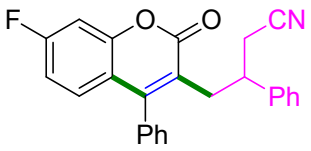
77.0 mg, 91% yield; white solid, mp: 98−99 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.46 m, 2H), 7.39-7.36 (m, 2H), 7.21-7.20 (m, 3H), 7.15-7.12 (m, 2H), 6.93-6.91 (m, 2H), 6.80 (d, J = 8.4 Hz, 1H), 6.54 (d, J = 7.5 Hz, 1H), 3.52-3.44 (m, 1H), 2.94 (dd, J = 6.2 Hz, J = 13.5 Hz, 1H), 2.74 (dd, J = 8.6 Hz, J = 13.5 Hz, 1H), 2.66-2.54 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 155.7, 153.0, 152.6, 140.8, 134.0, 128.8 (2C),

128.7, 128.1, 127.5, 127.3, 127.1, 122.2, 121.8, 118.5, 118.0, 113.4, 40.4, 35.2, 35.0, 31.0, 23.9; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{29}H_{28}NO_2$, 422.2120; found, 422.2122.



4-(7-Methoxy-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile (3f)

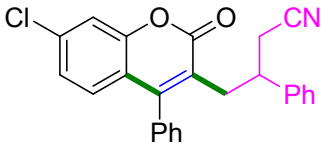
62.0 mg, 80% yield; white solid, mp: 126−127 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.45 (m, 2H), 7.39-7.35 (m, 1H), 7.23-7.19 (m, 3H), 7.16-7.13 (m, 1H), 6.93-6.91 (m, 2H), 6.85 (d, J = 2.4 Hz, 1H), 6.77 (d, J = 8.9 Hz, 1H), 6.67 (dd, J = 2.5 Hz, J = 8.9 Hz, 1H), 6.57 (d, J = 7.6 Hz, 1H), 3.85 (s, 3H), 3.48-3.41 (m, 1H), 2.91 (dd, J = 6.5 Hz, J = 13.6 Hz, 1H), 2.70 (dd, J = 8.3 Hz, J = 13.5 Hz, 1H), 2.66-2.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 154.3, 153.2, 140.9, 134.1, 128.8, 128.7 (2C), 128.6, 128.5, 128.0, 127.4, 127.3, 119.8, 118.5, 114.0, 112.4, 100.4, 55.8, 40.5, 34.9, 23.8; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{26}H_{22}NO_2$, 396.1600; found, 396.1597.



4-(7-Fluoro-2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile (3g)

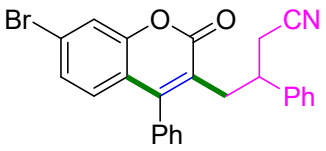
68.2 mg, 89% yield; white solid, mp: 141−142 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.29; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.47 (m, 2H), 7.40-7.36 (m, 1H), 7.24-7.20 (m, 3H), 7.17-7.13 (m, 1H), 7.08 (dd, J = 1.8 Hz, J = 8.8 Hz, 1H), 6.93-6.90 (m, 2H), 6.88-6.81 (m, 2H), 6.52 (d, J = 7.6 Hz, 1H), 3.50-3.42 (m, 1H), 2.94 (dd, J = 6.2 Hz, J = 13.5 Hz, 1H), 2.73 (dd, J = 8.6 Hz, J = 13.5 Hz, 1H), 2.66-2.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1 (d, J = 253.8 Hz), 161.6, 153.7 (d, J = 12.8 Hz), 152.6, 140.7, 133.6, 129.4 (d, J = 10.0 Hz), 129.1 (d, J = 5.8 Hz), 128.9 (d, J = 3.1 Hz), 128.7, 128.0, 127.6, 127.3, 122.2 (d, J = 2.8 Hz), 118.4, 117.3 (2C),

112.3 (d, J = 22.3 Hz), 104.1 (d, J = 25.6 Hz), 40.4, 35.1, 23.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.3 (s, 1F); HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{19}FNO_2$, 384.1400; found, 384.1399.



4-(7-Chloro-2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile (3h)

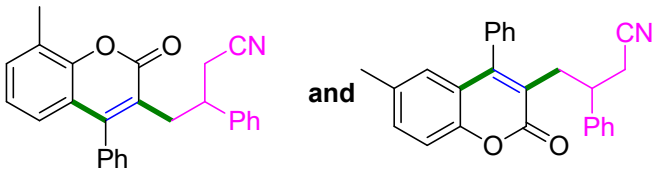
63.9 mg, 80% yield; white solid, mp: 154−155 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.26; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.47 (m, 2H), 7.40-7.34 (m, 2H), 7.22-7.20 (m, 3H), 7.15 (d, J = 6.2 Hz, 1H), 7.05 (dd, J = 2.0 Hz, J = 8.6 Hz, 1H), 6.91 (dd, J = 2.8 Hz, J = 6.5 Hz, 2H), 6.79 (d, J = 8.6 Hz, 1H), 6.51 (d, J = 7.6 Hz 1H), 3.49-3.43 (m, 1H), 2.95 (dd, J = 6.2 Hz, J = 13.5 Hz, 1H), 2.73 (dd, J = 8.7 Hz, J = 13.5 Hz, 1H), 2.65-2.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 152.8, 152.3, 140.6, 137.1, 132.4, 129.1, 129.0, 128.9 (2C), 128.6, 128.5, 128.0, 127.6, 127.2, 124.7, 123.4, 119.1, 118.3, 116.8, 40.3, 35.1, 23.9; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{19}ClNO_2$, 400.1104; found, 400.1107.



4-(7-Bromo-2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile (3i)

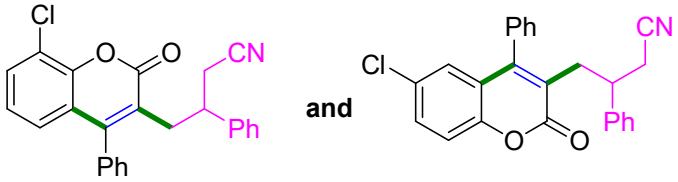
44.3 mg, 50% yield; white solid, mp: 158−159 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.29; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 1H), 7.51-7.47 (m, 2H), 7.40-7.36 (m, 1H), 7.22 (d, J = 2.0 Hz, 2H), 7.20 (d, J = 2.8 Hz, 2H), 7.15-7.13 (d, J = 6.9 Hz, 1H), 6.92-6.89 (m, 2H), 6.72 (d, J = 8.6 Hz, 1H), 6.49 (d, J = 7.5 Hz, 1H), 3.50-3.43 (m, 1H), 2.94 (dd, J = 6.2 Hz, J = 13.4 Hz, 1H), 2.72 (dd, J = 8.8 Hz, J = 13.4 Hz, 1H), 2.64-2.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 152.8, 152.4, 140.5, 133.3, 129.0 (2C), 128.9 (2C), 128.6 (2C), 128.0, 127.6, 127.2, 125.1, 123.6, 119.8, 119.4, 118.3, 40.2, 35.2, 23.9; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for

$C_{25}H_{18}BrNO_2Na$, 466.0419; found, 466.0417.



4-(8-Methyl-2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile and 4-(6-Methyl-2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile (3j and 3j')

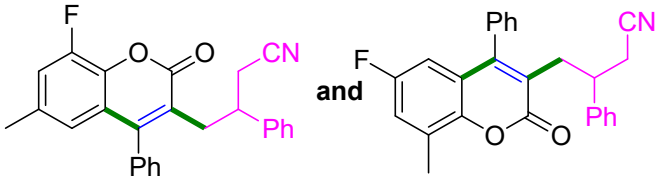
53.1 mg, 70% yield in total, the ratio of two regioisomers is 98:2; white solid, mp: 169−170 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.47 (m, 2H), 7.41-7.36 (m, 1H), 7.29-7.24 (m, 2H), 7.21-7.20 (m, 3H), 7.17-7.13 (m, 1H), 6.94-6.90 (m, 2H), 6.62 (s, 1H), 6.56 (d, J = 7.5 Hz, 1H), 3.50-3.43 (m, 1H), 2.93 (dd, J = 6.4 Hz, J = 13.5 Hz, 1H), 2.72 (dd, J = 8.4 Hz, J = 13.5 Hz, 1H), 2.66-2.54 (m, 2H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 153.0, 150.8, 140.8, 133.9 (2C), 132.3, 128.8 (2C), 128.7, 128.1, 127.5, 127.3, 127.2, 123.2, 120.1, 118.4, 116.4, 40.4, 35.2, 23.8, 20.9; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{26}H_{22}NO_2$, 380.1651; found, 380.1650.



4-(8-Chloro-2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile and 4-(6-Chloro-2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile (3k and 3k')

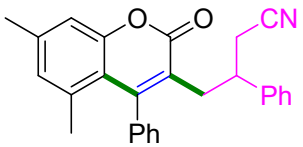
51.9 mg, 65% yield in total, the ratio of two regioisomers is 59:41; white solid, mp: 146−147 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.47 (m, 2H), 7.41-7.36 (m, 2H), 7.30-7.26 (m, 1H), 7.22-7.20 (m, 3H), 7.15 (d, J = 6.8 Hz, 1H), 6.93-6.89 (m, 2H), 6.79 (dd, J = 4.6 Hz, J = 21.4 Hz, 1H), 6.51 (d, J = 7.3 Hz, 1H), 3.52-3.43 (m, 1H), 2.99-2.93 (m, 1H), 2.77-2.70 (m, 1H), 2.65-2.54 (m, 2H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 161.2, 151.9, 151.0, 140.5, 133.1, 131.2, 129.6, 129.2, 129.0 (2C), 128.9, 128.6, 128.0, 127.6, 127.2, 126.8, 124.6,

121.6, 118.2 (2C), 40.3, 35.2, 23.9; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{19}ClNO_2$, 400.1104; found, 400.1105.



4-(8-Fluoro-6-methyl-2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile 4-(6-Fluoro-8-methyl-2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanenitrile (3l and 3l')

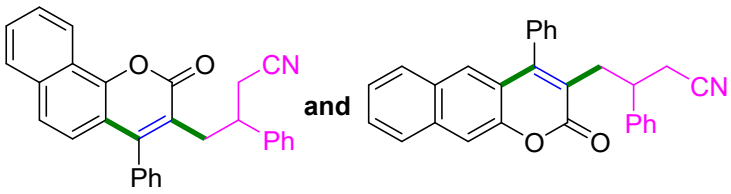
59.6 mg, 75% yield in total, the ratio of two regioisomers is 69:31; white solid, mp: 146−147 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, CDCl^3) δ 7.53-7.46 (m, 2H), 7.40-7.36 (m, 1H), 7.23-7.20 (m, 3H), 7.15-7.12 (m, 1H), 7.06 (td, J = 2.1 Hz, J = 8.7 Hz, 1H), 6.93-6.91 (m, 2H), 6.54-6.51 (m, 1H), 6.37 (dd, J = 3.0 Hz, J = 9.1 Hz, 1H), 3.51-3.44 (m, 1H), 2.95 (ddd, J = 2.7 Hz, J = 6.2 Hz, J = 13.5 Hz, 1H), 2.77-2.69 (m, 1H), 2.66-2.54 (m, 1H), 2.49 (s, 3H), 0,92 (s, 1H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 161.7, 158.2 (d, J = 249.2 Hz), 152.7, 147.3, 140.8, 133.7, 129.1 (d, J = 5.6 Hz), 129.0 (d, J = 3.7 Hz), 128.8 (d, J = 6.2 Hz), 128.5 (d, J = 8.1 Hz), 128.1 (d, J = 3.0 Hz), 127.7, 127.4, 124.2, 121.2 (d, J = 8.8 Hz), 119.9 (d, J = 24.1 Hz), 118.5 (d, J = 17.8 Hz), 110.6 (d, J = 24.9 Hz), 40.5, 35.3, 24.0, 15.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.9 (s, 1F), -134.8 (s, 1F); HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{26}H_{21}FNO_2$, 398.1556; found, 398.1559.



4-(5,7-Dimethyl-2-oxo-4-phenyl-2h-chromen-3-yl)-3-phenylbutanenitrile (3m)

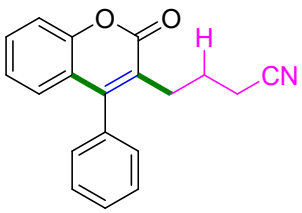
69.2 mg, 88% yield; white solid, mp: 142−143 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.45 (m, 2H), 7.40-7.36 (m, 1H), 7.22-7.18 (m, 3H), 7.14-7.11 (m, 2H), 6.92 (dd, J = 2.8 Hz, J = 6.5 Hz, 2H), 6.56 (d, J = 7.6 Hz, 1H), 6.45 (s, 1H), 3.50-3.43 (m, 1H), 2.93 (dd, J = 6.5 Hz, J = 13.5 Hz,

1H), 2.71 (dd, J = 8.3 Hz, J = 13.5 Hz, 1H), 2.65-2.53 (m, 2H), 2.45 (s, 3H), 2.17 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 162.1, 153.3, 149.2, 140.9, 134.3, 133.7, 133.2, 128.8, 128.7 (3C), 128.1, 127.4, 127.3, 125.6, 125.0, 122.8, 119.9, 118.4, 40.5, 35.2, 23.8, 20.8, 15.5; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{27}H_{24}NO_2$, 394.1807; found, 394.1811.



4-(2-Oxo-4-phenyl-2H-benzo[h]chromen-3-yl)-3-phenylbutanenitrile and 4-(2-Oxo-4-phenyl-2H-benzo[g]chromen-3-yl)-3-phenylbutanenitrile (3n and 3n')

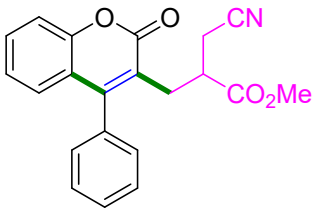
76.4 mg, 92% yield in total, the ratio of two regioisomers is 86:14; white solid, mp: 146−147 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61-8.59 (m, 1H), 7.81-7.79 (m, 1H), 7.66-7.59 (m, 2H), 7.55-7.50 (m, 2H), 7.47 (d, J = 8.0 Hz, 1H),7.43-7.39 (m, 1H), 7.21-7.18 (m, 4H), 6.95 (dd, J = 2.9 Hz, J = 6.4 Hz, 2H), 6.86 (d, J = 8.8 Hz, 1H), 6.59 (d, J = 7.6 Hz, 1H), 3.57-3.49 (m, 1H), 3.01 (dd, J = 6.3 Hz, J = 13.5 Hz, 1H), 2.79 (dd, J = 8.6 Hz, J = 13.5 Hz, 1H), 2.69-2.57 (m, 2H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 161.9, 153.9, 149.7, 140.8, 134.4, 134.2, 128.9, 128.8, 128.7 (2C), 128.1, 127.7, 127.5, 127.3, 127.2, 123.9, 123.0, 122.9, 122.8, 122.5, 118.4, 115.6, 40.4, 35.2, 23.9; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{29}H_{22}NO_2$, 416.1651; found, 416.1651.



4-(2-Oxo-4-phenyl-2h-chromen-3-yl)butanenitrile (3o)

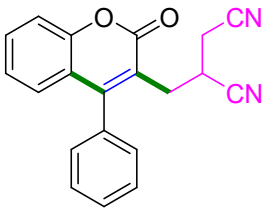
51.4 mg, 89% yield; white solid, mp: 126−127 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.55 (m, 2H), 7.53-7.47 (m,

2H), 7.37 (d, J = 8.2 Hz, 1H), 7.28-7.24(m, 2H), 7.15 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 7.7 Hz, 1H), 2.54-2.50 (m, 2H), 2.27 (t, J = 7.2 Hz, 2H), 1.91-1.83 (m, 2H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 161.7, 152.6, 152.2, 134.1, 131.2, 129.1 (2C) 128.0, 127.5, 124.9, 124.3, 120.6, 119.1, 116.6, 27.9, 24.5, 17.1; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{19}H_{16}NO_2$, 290.1181; found, 290.1185.



Methyl 3-cyano-2-((2-oxo-4-phenyl-2h-chromen-3-yl)methyl)propanoate (3p)

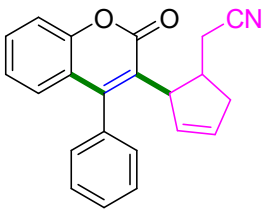
32.6 mg, 47% yield; white solid, mp: 88-89 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.29; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.56 (m, 2H), 7.55-7.49 (m, 2H), 7.40-7.38 (m, 1H), 7.28-7.25 (m, 1H), 7.23-7.20 (m, 1H), 7.19-7.15 (m, 1H), 6.99 (dd, J = 1.4 Hz, J = 8.0 Hz, 1H), 3.65 (s, 3H), 3.25-3.18 (m, 1H), 2.93 (dd, J = 7.8 Hz, J = 13.8 Hz, 1H), 2.72 (dd, J = 7.2 Hz, J = 13.8 Hz, 1H), 2.58-2.43 (m, 2H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 172.1, 161.6, 153.5, 152.8, 133.7, 131.6, 129.3, 129.2, 128.3, 128.2, 127.7, 124.4, 122.3, 120.4, 117.5, 116.7, 52.5, 40.1, 30.6, 19.4; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{18}NO_2$, 348.1236; found, 348.1238.



2-((2-Oxo-4-phenyl-2h-chromen-3-yl)methyl)succinonitrile (3q)

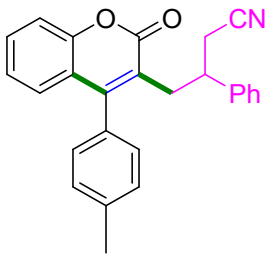
40.8mg, 65% yield; white solid, mp: 142−143 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.53 (m, 1H), 7.52-7.50 (m, 1H), 7.49-7.47 (m, 2H), 7.42-7.40 (m, 1H), 7.36-7.34 (m, 1 H), 7.16-7.11 (m, 2H), 6.95 (dd, J = 1.6 Hz, J = 8.0 Hz, 1H), 3.72-3.65 (m, 1H), 2.81-2.70 (m, 2H), 2.61-2.55 (m, 2H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 161.6, 155.4, 152.8, 133.0, 132.2, 129.5,

129.4, 129.1, 129.0, 128.2, 127.9, 124.7, 120.3, 120.0, 118.4, 116.8, 115.1, 31.2, 26.5, 21.1; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{15}NO_2$, 315.1134; found, 315.1137.



2-(2-(2-Oxo-4-phenyl-2h-chromen-3-yl)cyclopent-3-en-1-yl)acetonitrile (3r)

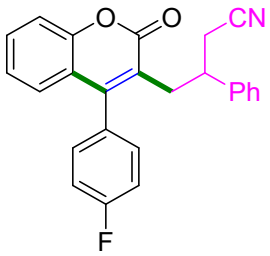
39.2 mg, 60% yield; white solid, mp: 175−176 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 1H), 7.48-7.45 (m, 2H), 7.44-7.39 (m, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 4.0 Hz, 1H), 7.14-7.12 (m, 1H), 7.10-7.05 (m, 1H), 6.88 (dd, J = 1.2 Hz, J = 4.4 Hz, 1H), 5.81-5.78 (m, 1H), 5.58-5.55 (m, 1H), 3.64-3.56 (m, 1H), 2.81-2.77 (m, 1H), 2.45-2.33 (m, 1H), 2.27 (dd, J = 6.3 Hz, J = 16.8 Hz, 1H), 2.11 (dd, J = 6.4 Hz, J = 16.8 Hz, 1H), 2.14-1.83 (m, 1H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 160.2, 153.2, 152.8, 134.6, 132.4, 131.2, 131.1, 129.3, 129.0 (2C), 128.4, 128.0, 127.8, 126.3, 124.2, 120.6, 118.1, 116.5, 45.5, 38.6, 22.4; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{22}H_{18}NO_2$, 328.1338; found, 328.1341.



4-(2-Oxo-4-(*p*-tolyl)-2h-chromen-3-yl)-3-phenylbutanenitrile (3s)

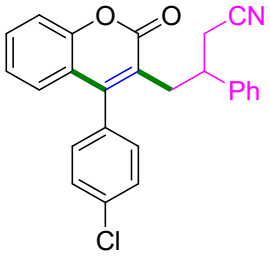
66.0 mg, 87% yield; white solid, mp: 109−110 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.42 (m, 1H), 7.32 (t, J = 8.0 Hz, 2H), 7.22-7.19 (m, 4H), 7.10-7.03 (m, 2H), 6.95 (dd, J = 2.8 Hz, J = 6.6 Hz, 2H), 6.90 (dd, J = 1.2 Hz, J = 8.0 Hz, 1H), 6.47 (dd, J = 1.7 Hz, J = 7.7 Hz, 1H), 3.53-3.46 (m, 1H), 2.95 (dd, J = 6.4 Hz, J = 13.5 Hz, 1H), 2.77 (dd, J = 8.5 Hz, J = 13.5 Hz, 1H), 2.68-2.52 (m, 2H), 2.46 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 161.9,

153.2, 152.7, 140.8, 138.8, 131.2, 130.8, 129.5, 129.4, 128.8, 128.7, 128.0, 127.6, 127.5, 127.3, 124.1, 123.3, 120.6, 118.5, 116.6, 40.4, 35.1, 23.9, 21.4; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{26}H_{22}NO_2$, 380.1651; found, 380.1652.



4-(4-(4-fluorophenyl)-2-oxo-2*H*-chromen-3-yl)-3-phenylbutanenitrile (3t)

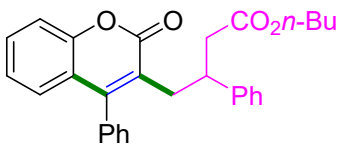
63.7 mg, 83% yield; white solid, mp: 81-82 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 1H), 7.30-7.27 (m, 1H), 7.16-7.15 (m, 2H), 7.14-7.10 (m, 2H), 7.07-7.01 (m, 2H), 6.96 (td, J = 2.6 Hz, J = 8.5 Hz, 1H), 6.87-6.85 (m, 2H), 6.74 (dd, J = 1.4 Hz, J = 8.0 Hz,1H), 6.33-6.29 (m, 1H), 3.46-3.39 (m, 1H), 2.89 (dd, J = 5.7 Hz, J = 13.4 Hz, 1H), 2.65-2.60 (m, 1H), 2.56 (dd, J = 2.6 Hz, J = 7.2 Hz, 2H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 162.9 (d, J = 249.2 Hz), 161.7, 152.7, 152.0, 140.7, 131.5, 130.8 (d, J = 8.3 Hz), 130.2 (d, J = 8.3 Hz), 129.8 (d, J = 3.6 Hz), 129.0, 127.87, 127.4, 124.4, 123.9, 120.5, 118.4, 116.8, 116.2 (d, J = 13.1 Hz), 116.0 (d, J = 13.0 Hz), 40.4, 35.4, 24.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.9 (s, 1F); HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{19}FNO_2$, 384.1400; found, 384.1403.



4-(4-(4-Chlorophenyl)-2-oxo-2h-chromen-3-yl)-3-phenylbutanenitrile (3u)

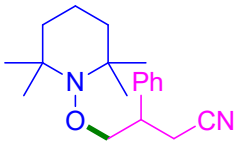
70.2 mg, 88% yield; white solid, mp: 127−128 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.44 (m, 2H), 7.35-7.29 (m,

2H), 7.22-7.21 (m, 3H), 7.12-7.08 (m, 2H), 6.96-6.91 (m, 2H), 6.81 (dd, J = 1.3 Hz, J = 8.0 Hz, 1H), 6.31 (dd, J = 2.1 Hz, J = 8.2 Hz, 1H), 3.55-3.48 (m, 1H), 2.97 (dd, J = 5.5 Hz, J = 13.4 Hz, 1H), 2.67 (dd, J = 9.2 Hz, J = 13.6 Hz, 1H), 2.64-2.59 (m, 2H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 161.5, 152.6, 151.7, 140.6, 134.9, 132.1, 131.4, 130.2, 129.6 (2C), 129.1, 129.0, 128.9, 127.6, 127.4, 127.3, 124.3, 123.7, 120.1, 118.4, 116.7, 40.3, 35.4, 24.0; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{19}ClNO_2$, 400.1104; found, 400.1106.



Butyl 4-(2-oxo-4-phenyl-2H-chromen-3-yl)-3-phenylbutanoate (4)

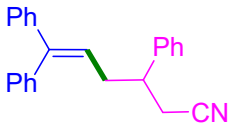
57.2 mg, 65% yield; yellow oil; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.46 (m, 2H), 7.45-7.42 (m, 1H), 7.40-7.34 (m, 2H), 7.18-7.15 (m, 2H), 7.14-7.12 (m, 2H), 7.10-7.06 (m, 1H), 6.91-6.89 (m, 2H), 6.85 (dd, J = 1.4 Hz, J = 8.0 Hz, 1H), 6.60 (d, J = 7.6 Hz, 1H), 3.85 (t, J = 6.7 Hz, 2H), 3.60 (dt, J = 7.3 Hz, J = 14.9 Hz, 1H), 2.84 (dd, J = 7.2 Hz, J = 13.3 Hz, 1H), 2.66-2.59 (m, 2H), 2.55 (dd, J = 9.1 Hz, J = 15.2 Hz, 1H), 1.44-1.37 (m, 2H), 1.23-1.16 (m, 2H), 0.82 (t, J = 7.4 Hz, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 172.1, 161.8, 152.6, 152.3, 143.1, 134.2, 130.9, 128.9, 128.6, 128.5, 128.4, 128.2, 127.5, 127.4, 126.5, 124.5, 124.0, 120.7, 116.5, 64.2, 40.5, 40.3, 36.0, 30.5, 19.0, 13.7; HRMS (ESI, m/z): $[M+H]^+$ Calcd. $C_{29}H_{29}O_4$, 441.2066; found, 441.2057.



3-phenyl-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butanenitrile (5)

15.6mg, 26% yield; brown oil; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 7.2 Hz, 2H), 7.30-7.19 (m, 4H), 3.98 (d, J = 6.3 Hz, 2H), 3.26-3.20 (m, 1H), 2.92 (dd, J = 5.7 Hz, J = 16.7 Hz, 1H), 2.74

(dd, J = 7.0 Hz, J = 16.7 Hz, 1H), 1.42 (d, J = 6.7 Hz, 4H), 1.33-1.26 (m, 1H), 1.09 (t, J = 8.7 Hz, 12H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 139.3, 128.7, 127.6, 127.6, 118.7, 78.2, 60.0, 42.0, 39.7, 39.6, 33.0, 21.1, 20.3, 20.1, 17.0; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{19}H_{29}N_2O$, 301.2280; found, 301.2271.

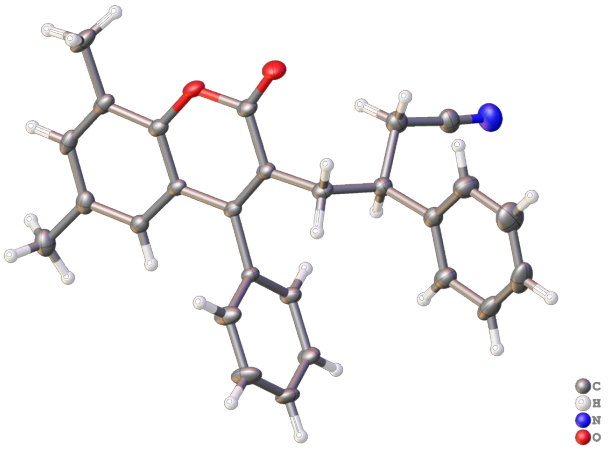


3,6,6-triphenylhex-5-enenitrile (6)

24.5mg, 38% yield; yellow oil; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 5H), 7.28-7.21 (m, 4H), 7.14 (d, J = 7.4 Hz, 2H), 7.10 (d, J = 6.1 Hz, 2H), 7.05 (d, J = 7.1 Hz, 1H), 5.90 (t, J = 7.2 Hz, 1H), 3.13-3.06 (m, 1H), 2.67-2.51 (m, 4H), 1.59 (s, 2H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 144.3, 142.1, 141.1, 139.6, 129.7, 128.9, 128.4, 128.2, 127.5, 127.3 (2C), 127.2, 125.4, 118.5, 42.8, 35.3, 24.3; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{24}H_{22}N$, 324.1752; found, 324.2509.

7. X-ray Crystallographic Data

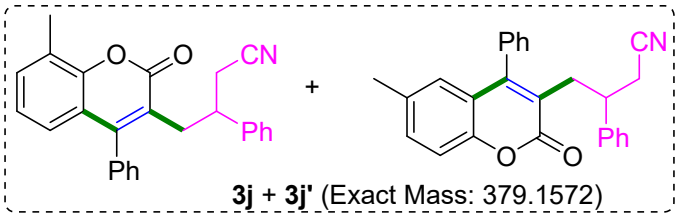
The X-ray crystallographic structures for **3m**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 2143777.



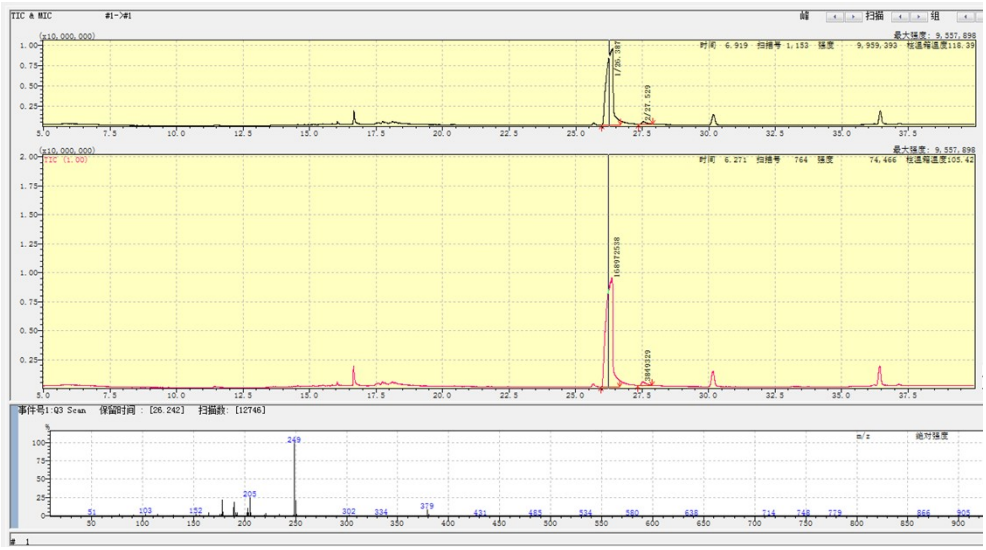
Empirical formula	$C_{27}H_{23}NO_2$

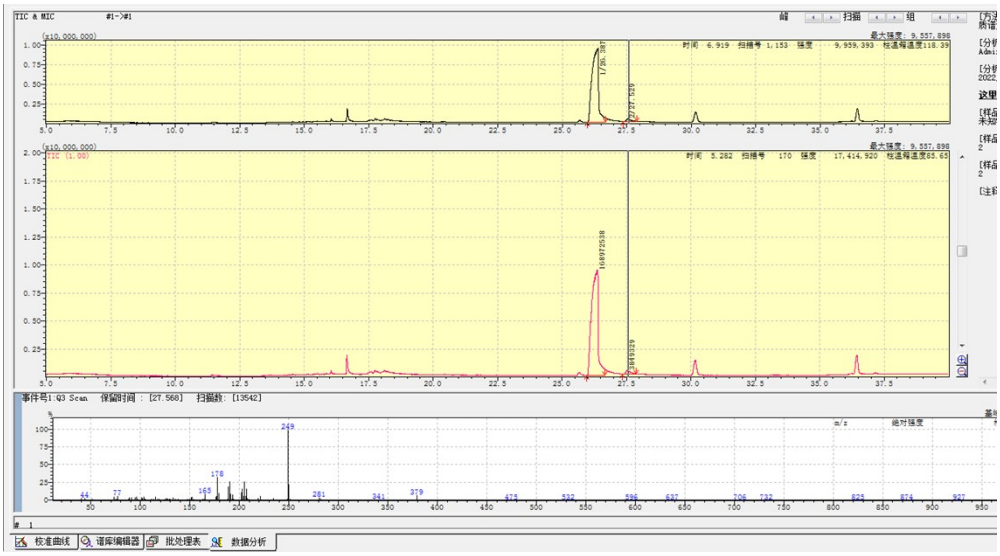
Formula weight	393.46
Temperature	180(10) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/C$
Unit cell dimensions	a = 12.8323(13) Å alpha = 90 deg. b =19.3019(19) Å beta = 101.276(10) deg. c = 8.5975(8) Å gamma = 90 deg.
Volume	2088.4 (4) $Å^3$
Z, Calculated density	4, 1.251 g/cm^3
Absorption coefficient	0.078 mm^{-1}
F(000)	832.0
Crystal size	0.15×0.12×0.11 mm
Theta range for data collection	4.22 to 49.996 deg.
Limiting indices	$-14 \leq h \leq 15$, $-17 \leq k \leq 22$, $-10 \leq l \leq 9$
Reflections collected / unique	8967 / 3673 [R(int) = 0.0363]
Completeness to theta = 25.00	99.99%
Refinement method	Goodness-of-fit on F^{2-}
Data / restraints / parameters	3673 / 0 / 273
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0576, wR2 = 0.1446
R indices (all data)	R1 = 0.0750, wR2 = 0.1581

8. GC-MS spectra of products 3j-l, n



3j + **3j'** (Exact Mass: 379.1572)





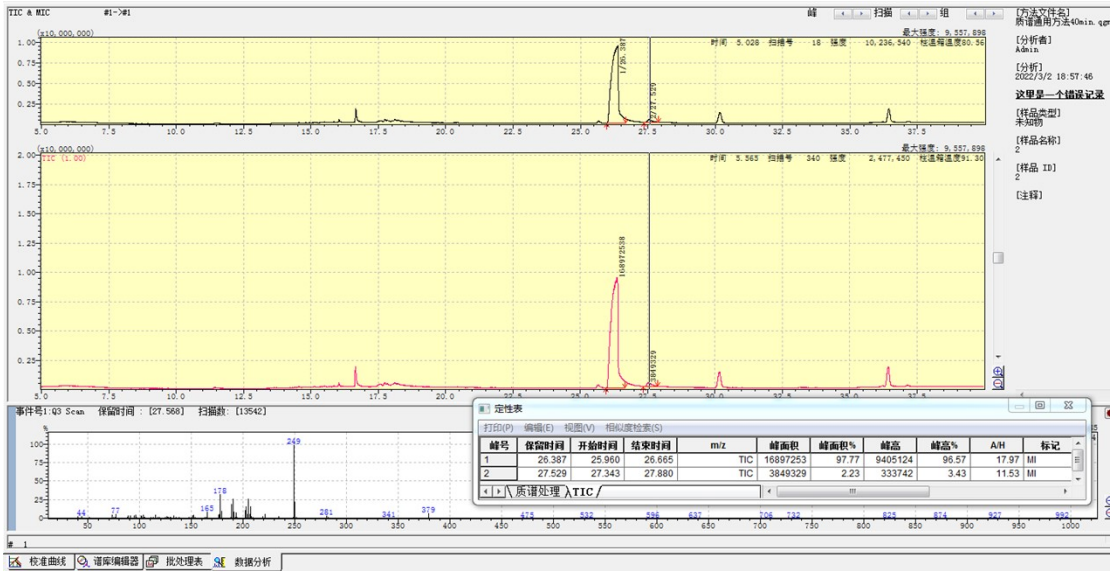
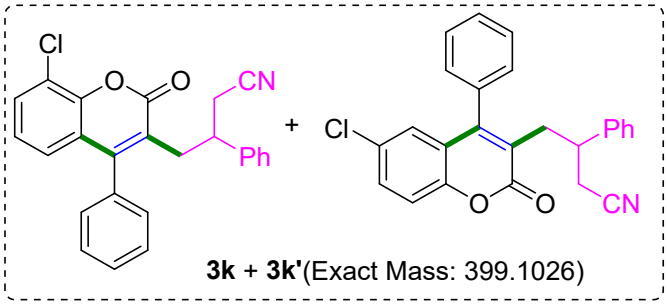
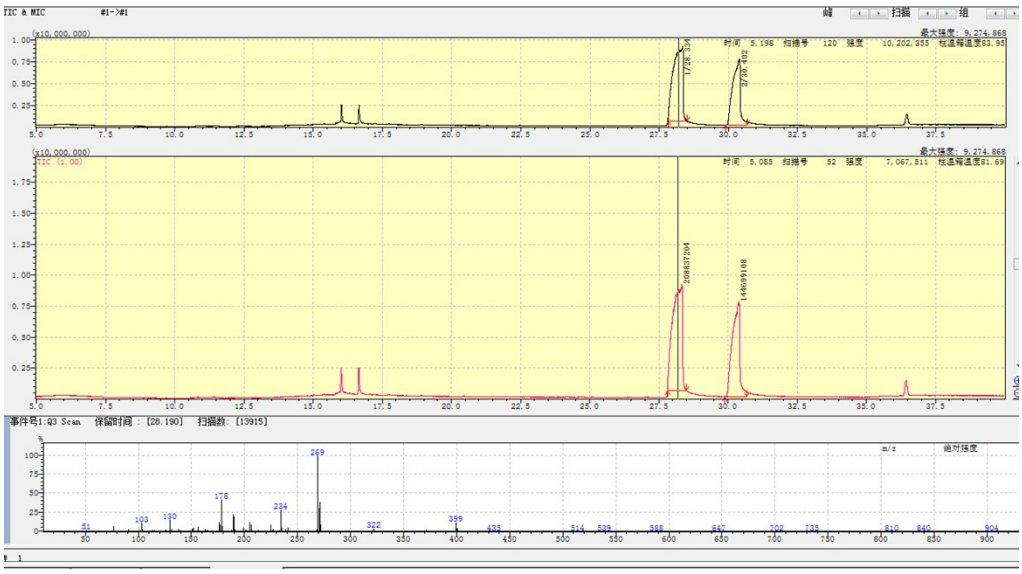


Figure S1. GC-MS spectra of product 3j and 3j': the ratio of two regioisomers is 98:2.





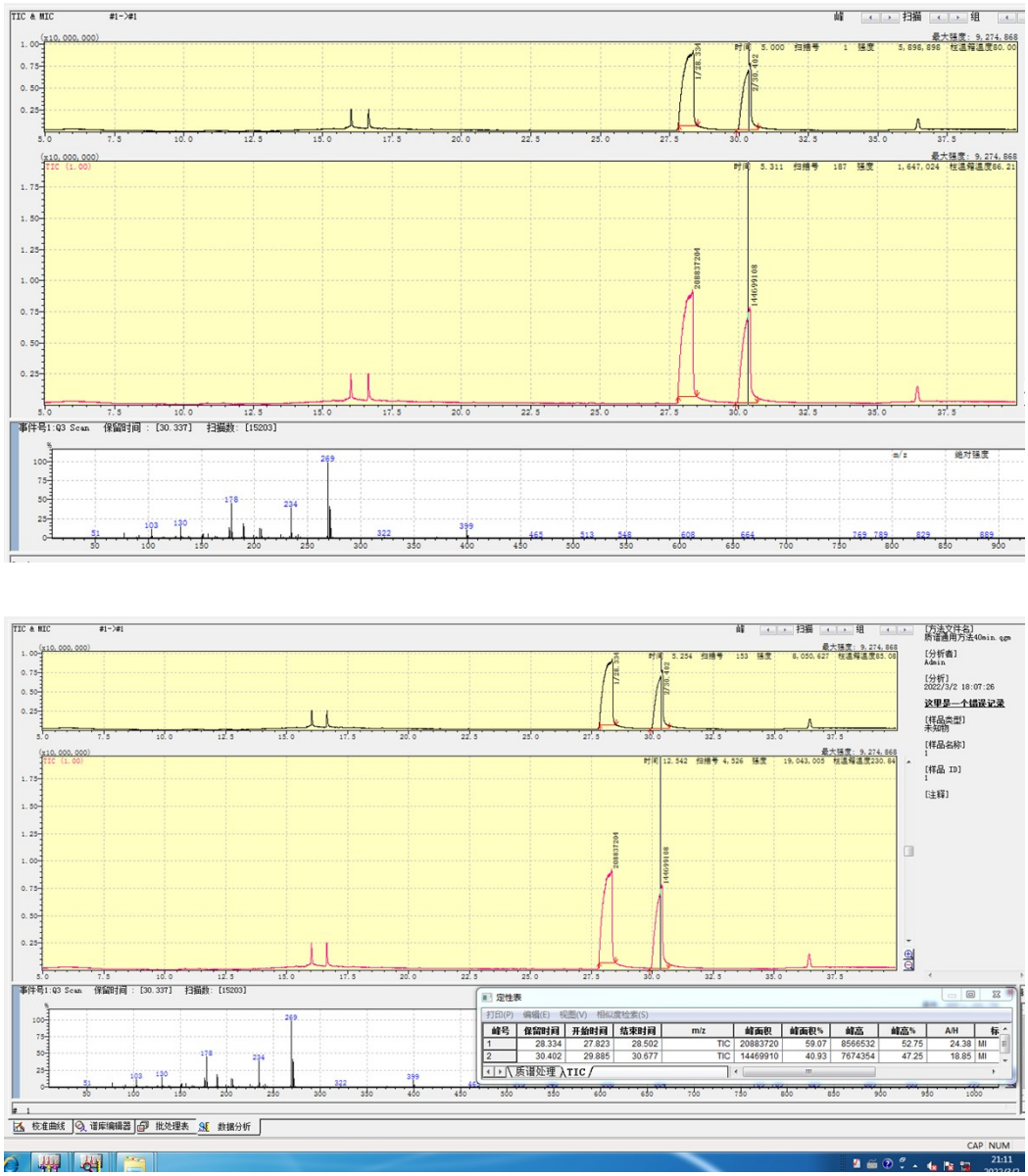
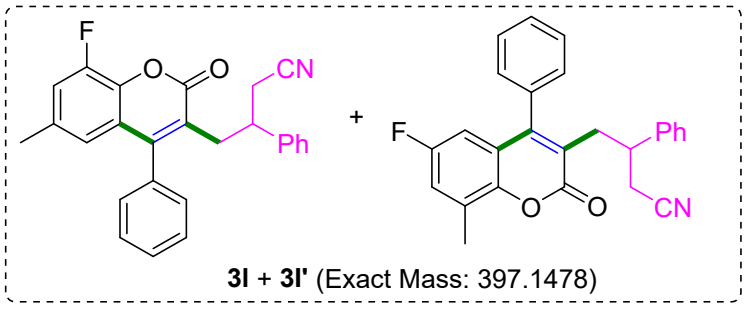


Figure S2. GC-MS spectra of product 3k+3k': the ratio of two regioisomers is 59:41.



3l + 3l' (Exact Mass: 397.1478)

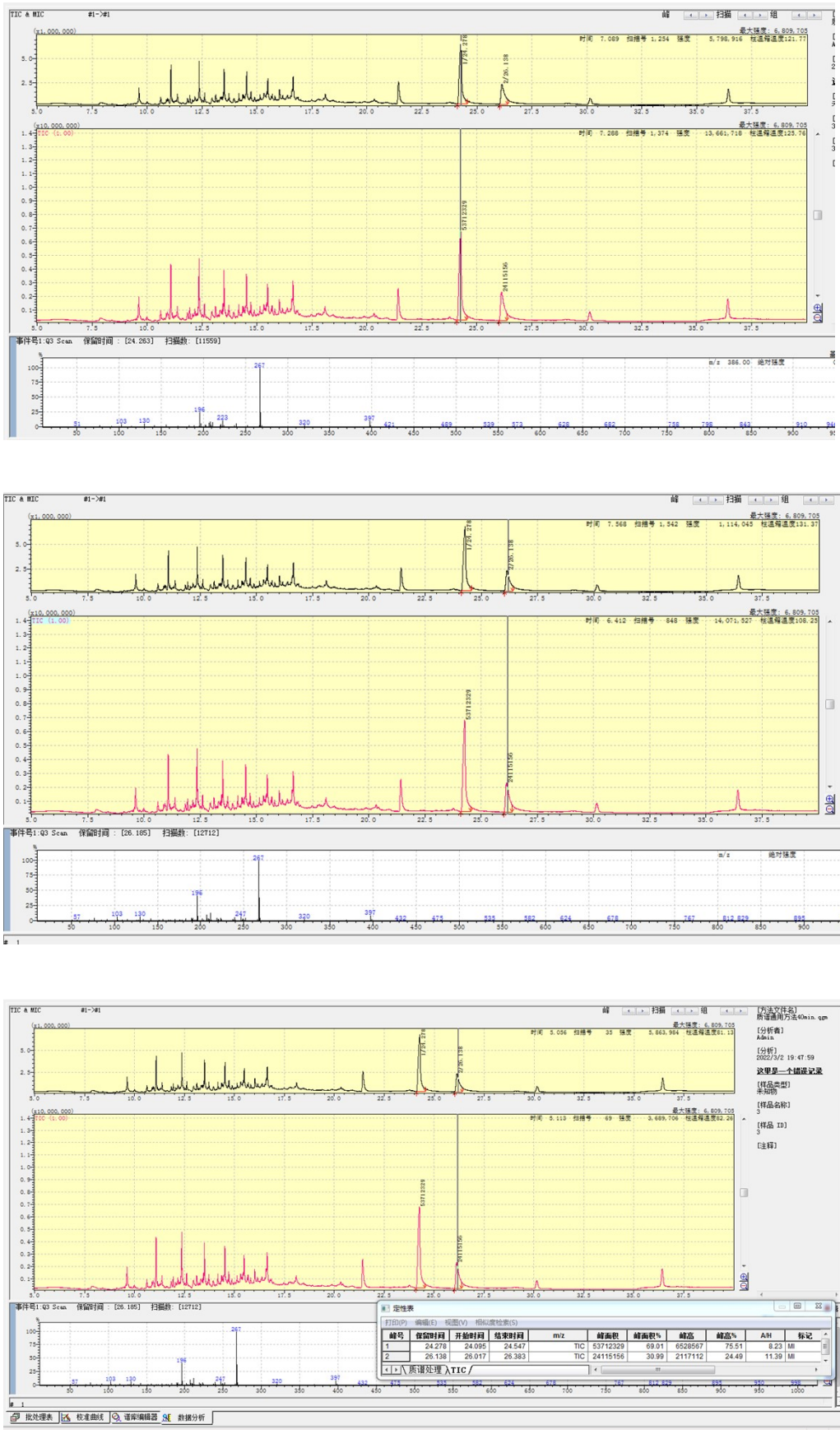
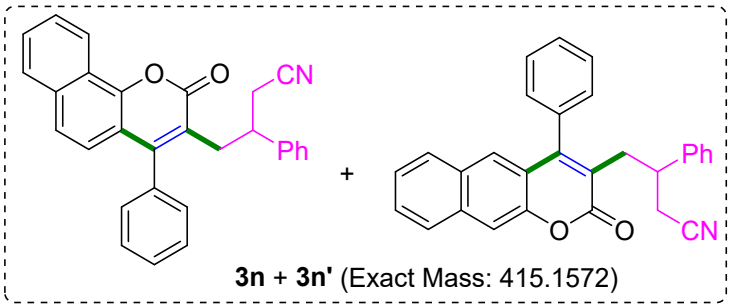


Figure S3. GC-MS spectra of product 3l+3l': the ratio of two regioisomers is 69:31.



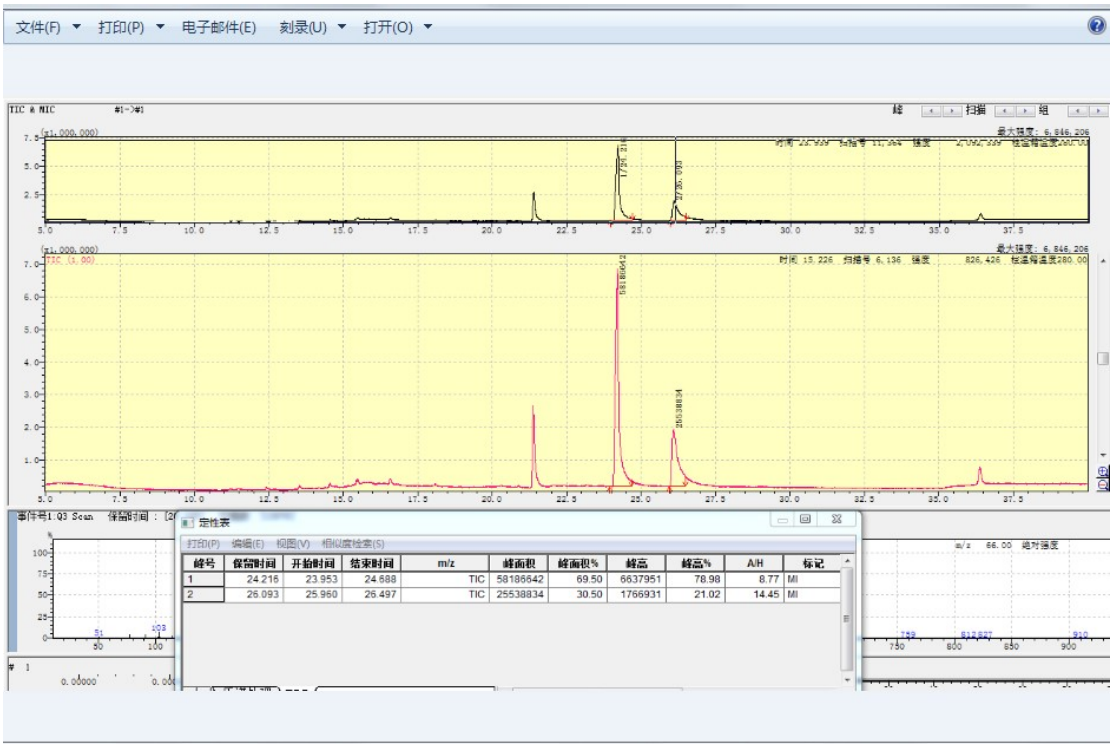


Figure S4. GC-MS spectra of product 3n+3n': the ratio of two regioisomers is 70:30.

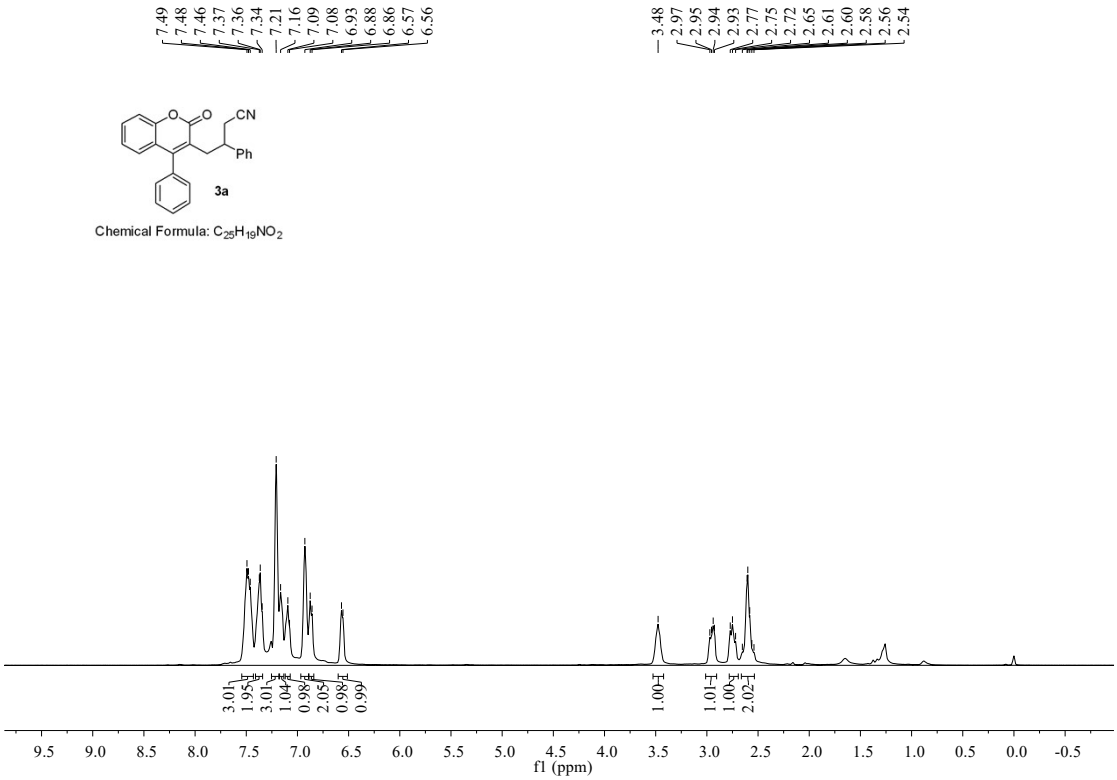
9. References

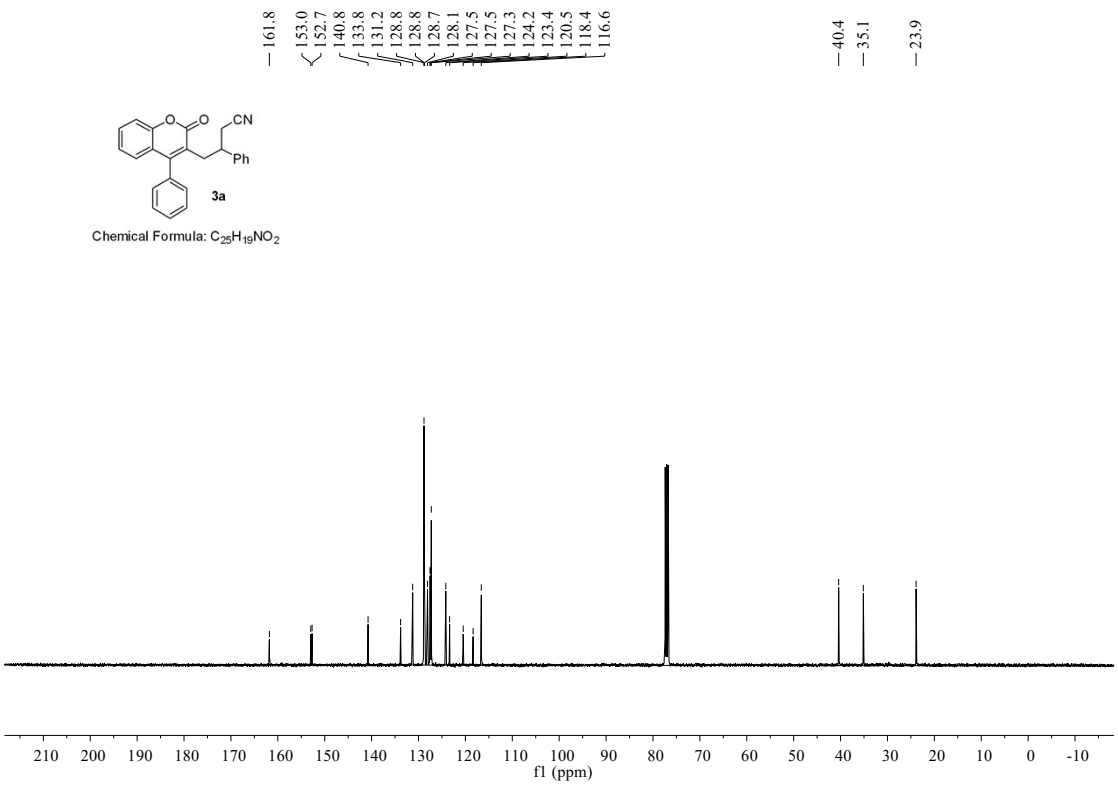
[1] (a) M. Pramanik, A. Mathuri, S. Sau, M. Das, P. Mal, *Org. Lett.* 2021, **23**, 8088−8092. (b) L. Chen, L. Wu, W. Duan, T. Wang, L. Li, K. Zhang, J. Zhu, Z. Peng, F. Xiong, *J. Org. Chem.* 2018, **83**, 8607–8614. (c) F. Gao, C. Yang, G. L. Gao, L. Zheng, W. Xia, *Org. Lett*. 2015, **17**, 3478−3481. (d) W.-C. Gao, T. Liu, B. Zhang, X. Li, W.-L. Wei, Q. Liu, J. Tian, H.-H. Chang, *J. Org. Chem.* 2016, **81**, 11297−11304.

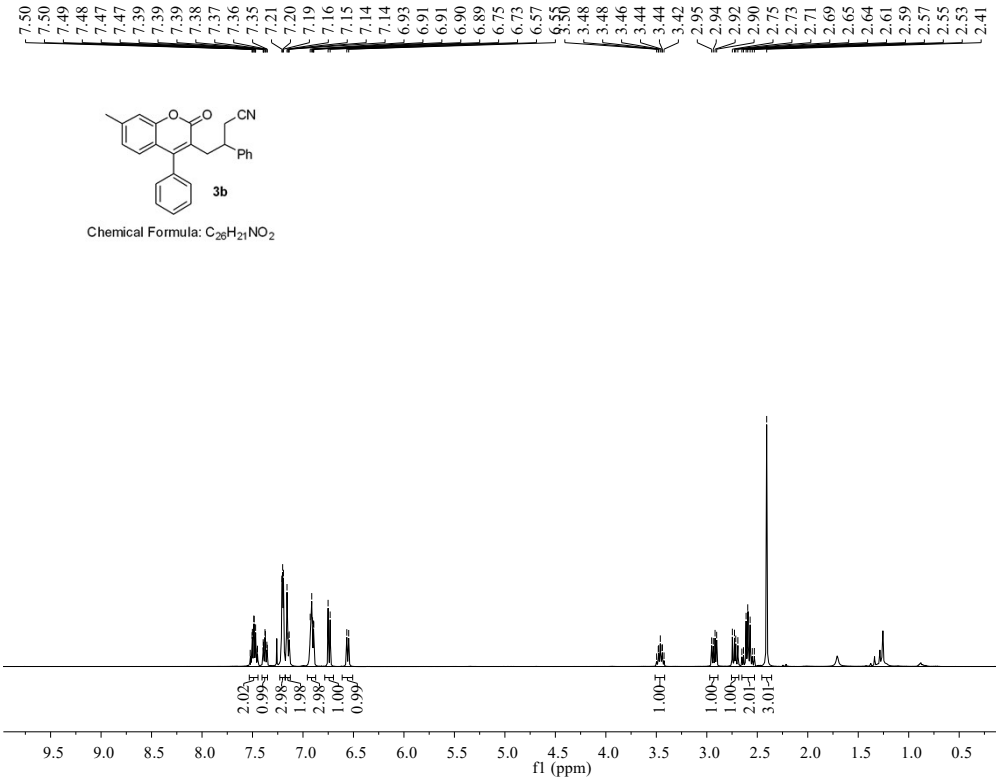
[2] Y. Yuan, W. H. Dong, X. S. Gao, X. M. Xie, Z. G. Zhang, *Chem. Commun.* 2019, **55**, 11900-11903.

[3] (a) J. Boivin, E. Fouquet, S. Z. Zard, *Tetrahedron Lett.* **1991**, *32*, 4299-4302. (b) D. Ding, C. Wang, *ACS Catal.* **2018**, *8*, 11324–11329.

10. NMR Spectra of New Compounds



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7.49
7.48
7.47
7.47
7.39
7.39
7.39
7.38
7.37
7.36
7.35
7.21
7.20
7.19
7.16
7.15
7.14
7.14
6.93
6.91
6.90
6.89
6.75
6.73
6.57
6.55
3.50
3.48
3.48
3.46
3.44
3.44
3.42
2.95
2.94
2.92
2.90
2.75
2.73
2.71
2.69
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2.64
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2.59
2.57
2.55
2.53
2.41
O
O
CN
Ph
3b
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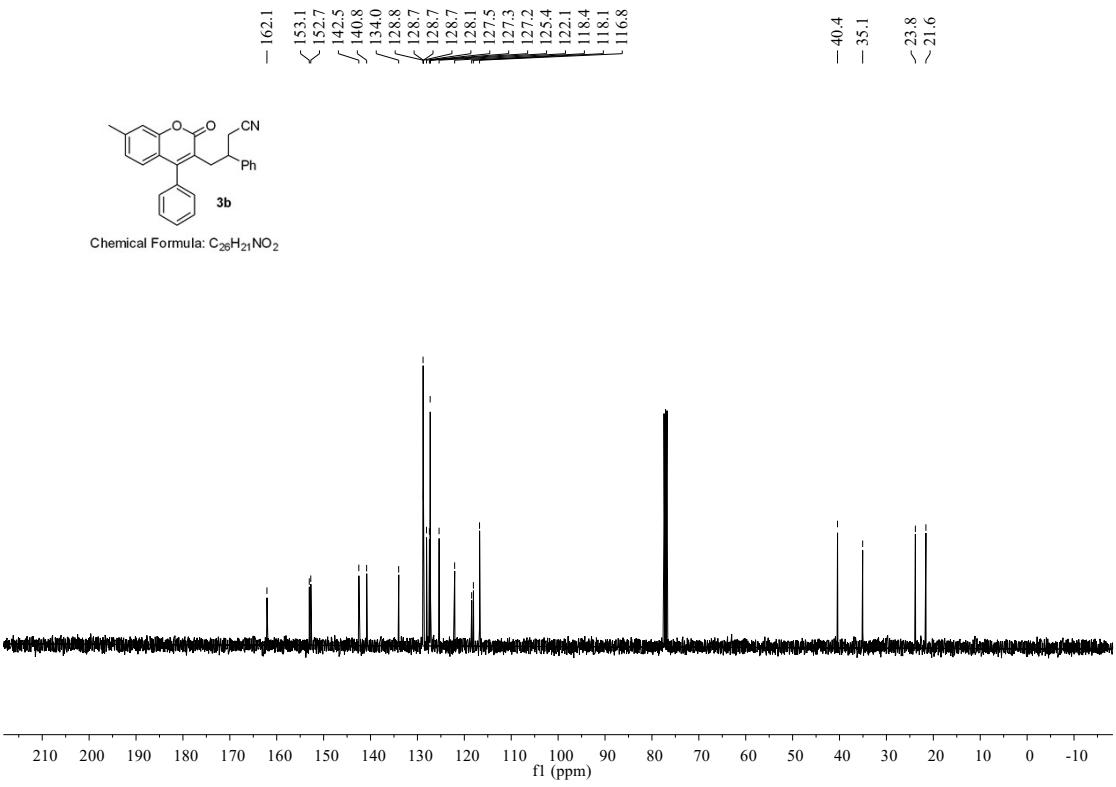
0.99
2.98
1.98
2.98
1.00
0.99
1.00
1.00
2.01
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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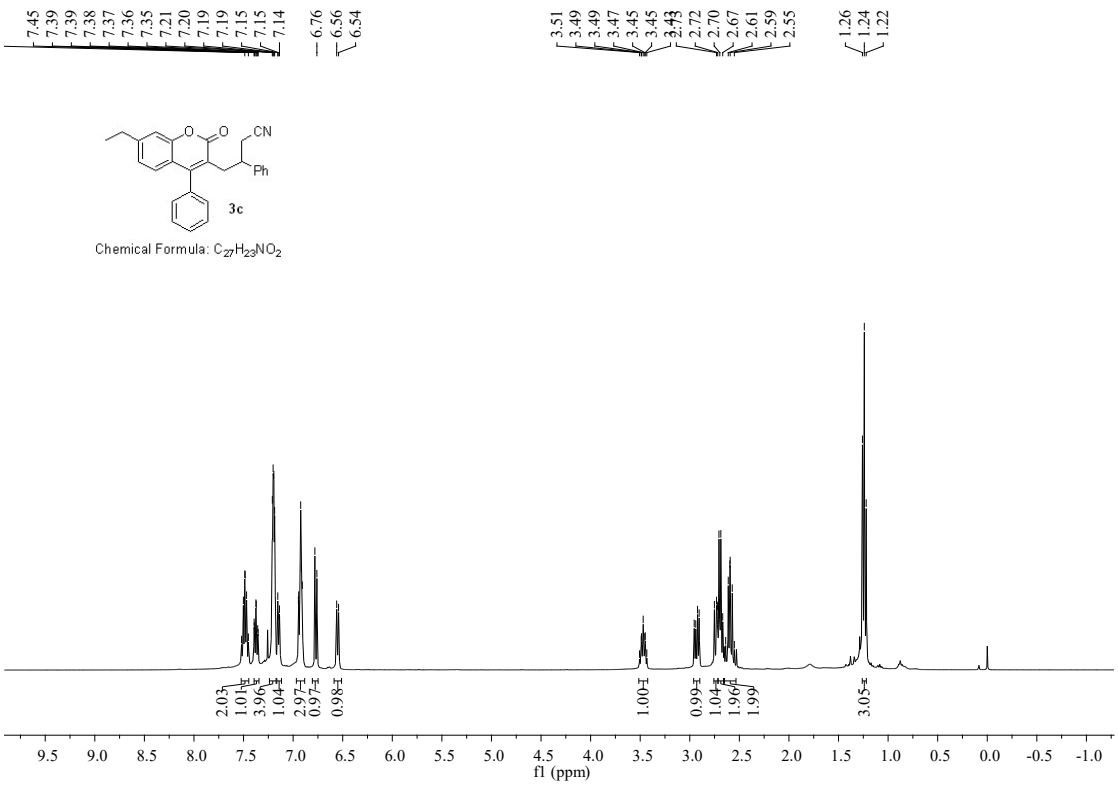
153.1
152.7
142.5
140.8
134.0
128.8
128.7
128.7
128.7
128.1
127.5
127.3
127.2
125.4
122.1
118.4
118.1
116.8
40.4
35.1
23.8
21.6
O
O
CN
Ph
3b
Chemical Formula: C26H21NO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.39
7.38
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7.21
7.20
7.19
7.19
7.15
7.15
7.14
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6.56
6.54
3.51
3.49
3.49
3.47
3.45
3.45
2.72
2.70
2.67
2.61
2.59
2.55
1.26
1.24
1.22
O
O
CN
Ph
3c
Chemical Formula: C27H23NO2
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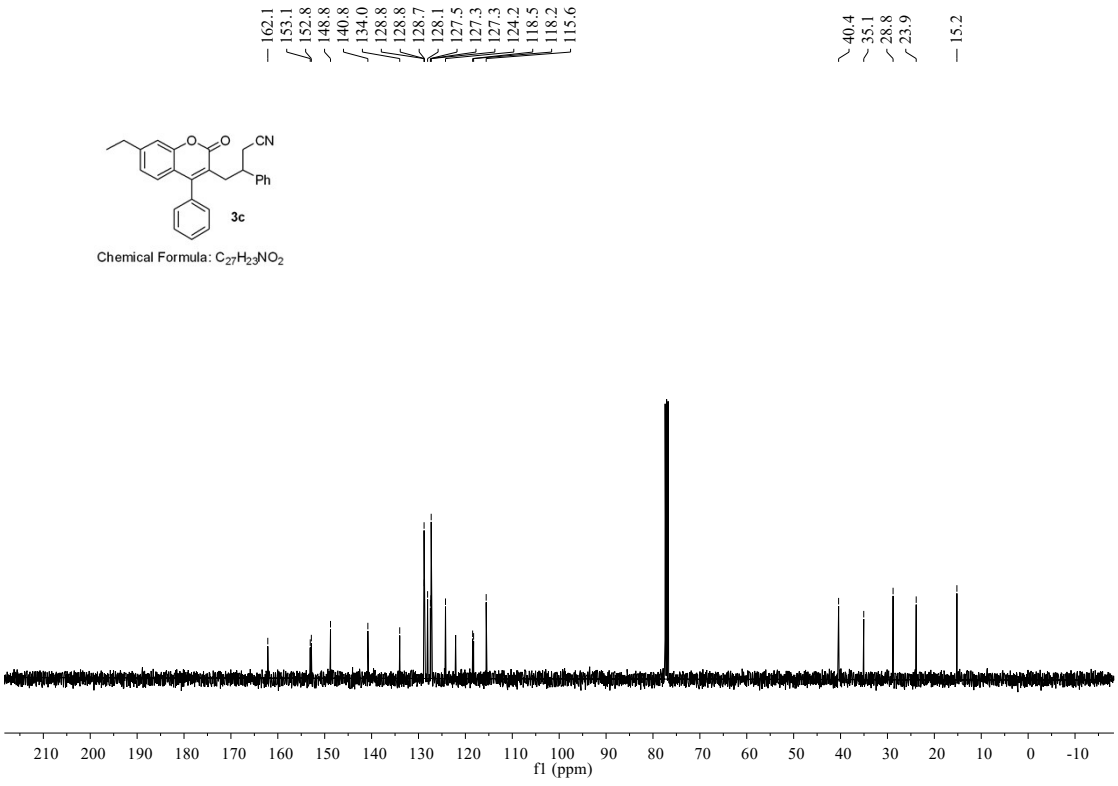
1.01
3.96
1.04
2.97
0.97
0.98
1.00
0.99
1.04
1.96
1.99
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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152.8
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140.8
134.0
128.8
128.8
128.7
128.1
127.5
127.3
127.3
124.2
118.5
118.2
115.6
40.4
35.1
28.8
23.9
15.2
O
O
CN
Ph
3c
Chemical Formula: C27H23NO2
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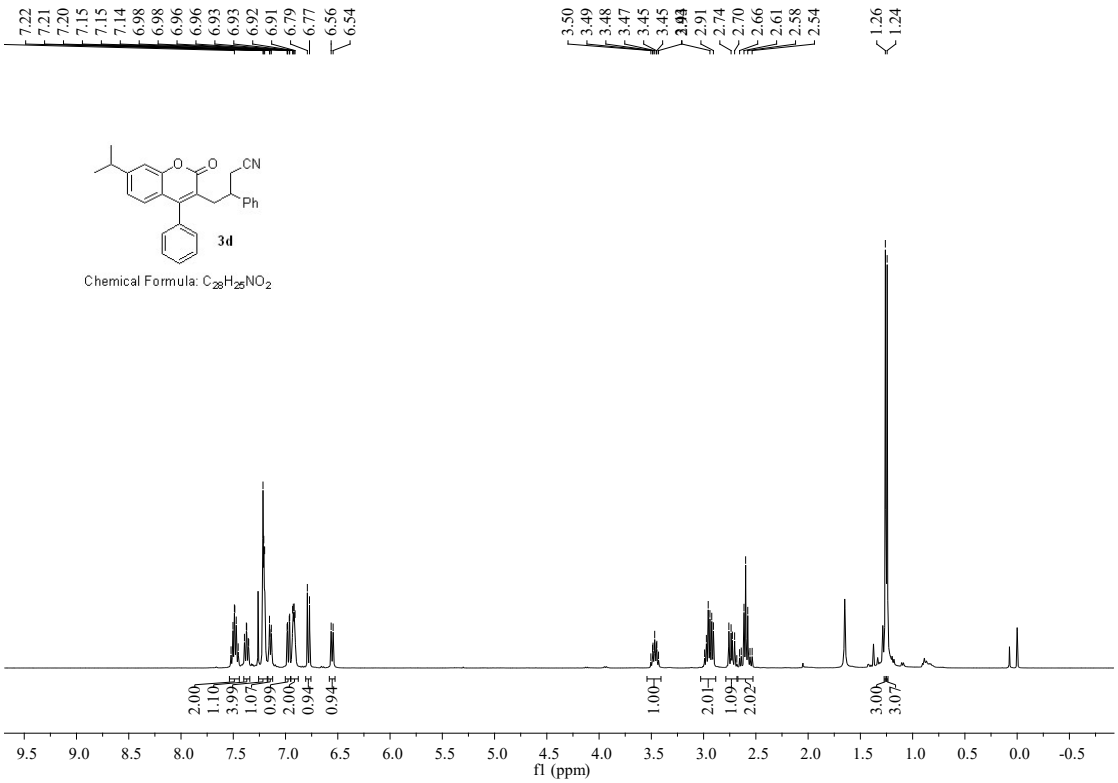
f1 (ppm)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6.98
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6.92
6.91
6.79
6.77
6.56
6.54
3.50
3.49
3.48
3.47
3.45
3.45
2.91
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2.70
2.66
2.61
2.58
2.54
1.26
1.24
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O
CN
Ph
3d
Chemical Formula: C28H25NO2
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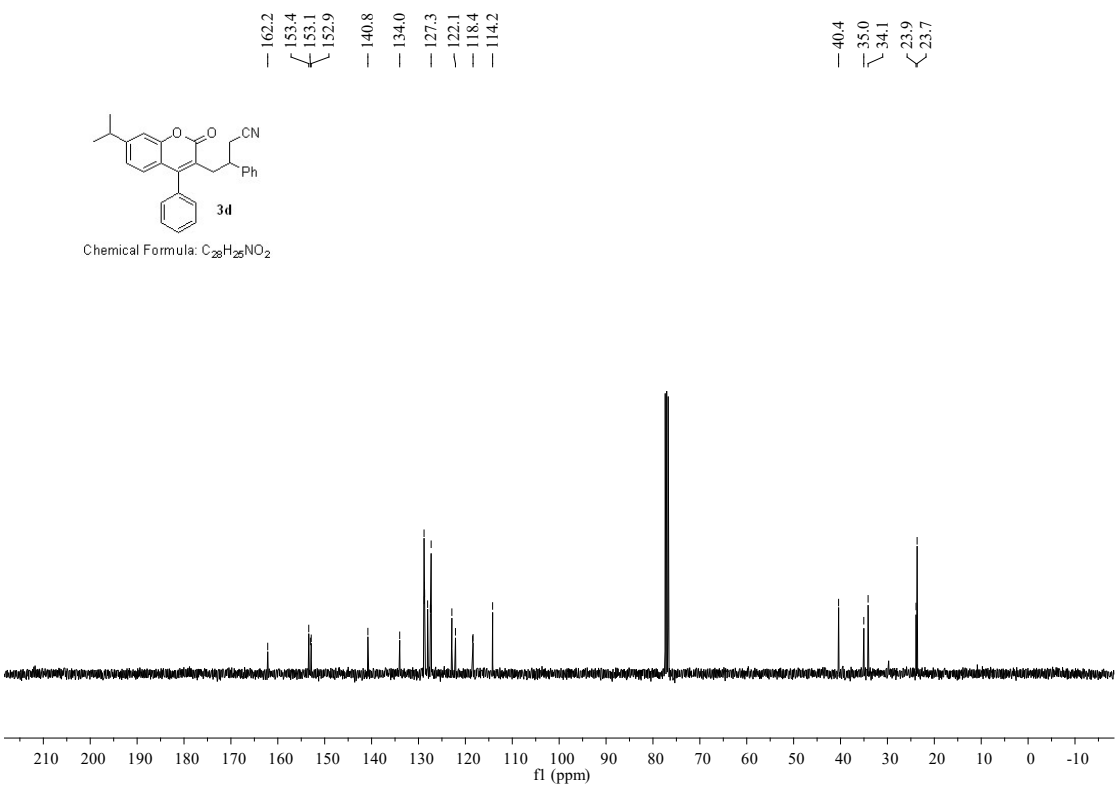
0.99
2.00
0.94
0.94
1.00
2.01
1.09
2.02
3.00
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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118.4
114.2
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35.0
34.1
23.9
23.7
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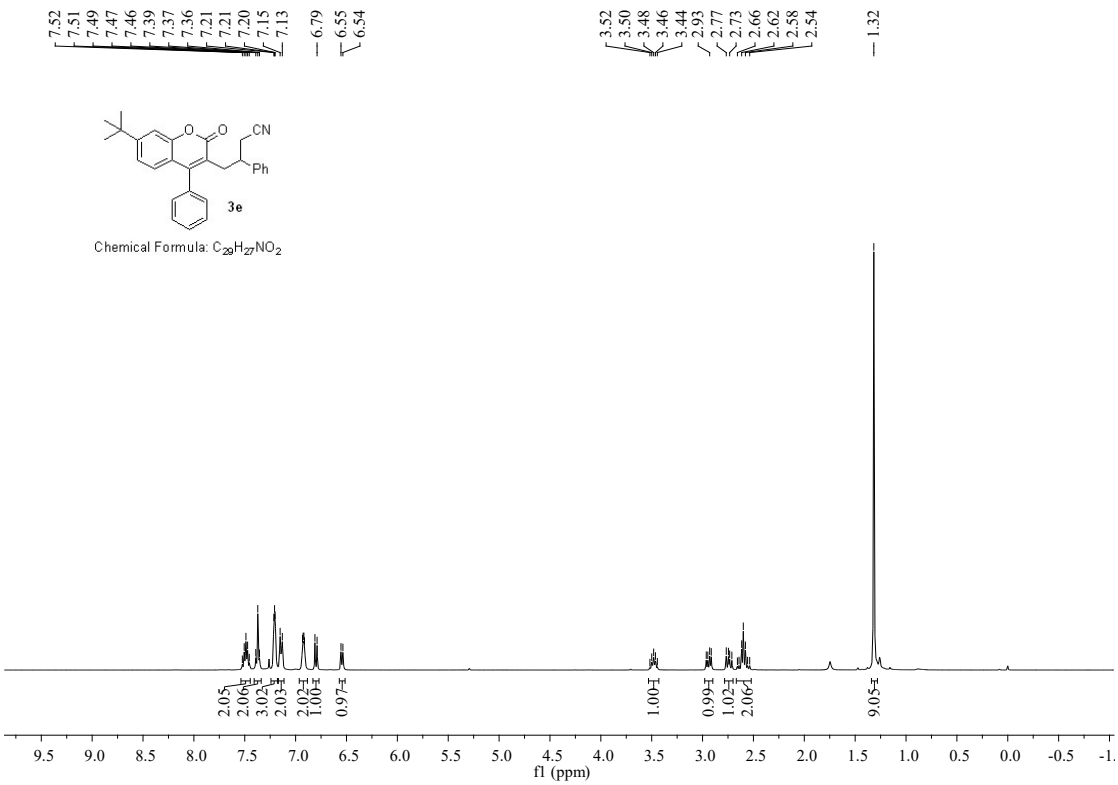
f1 (ppm)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7.36
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6.55
6.54
3.52
3.50
3.48
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3.44
2.93
2.77
2.73
2.66
2.62
2.58
2.54
1.32
O
O
CN
Ph
3e
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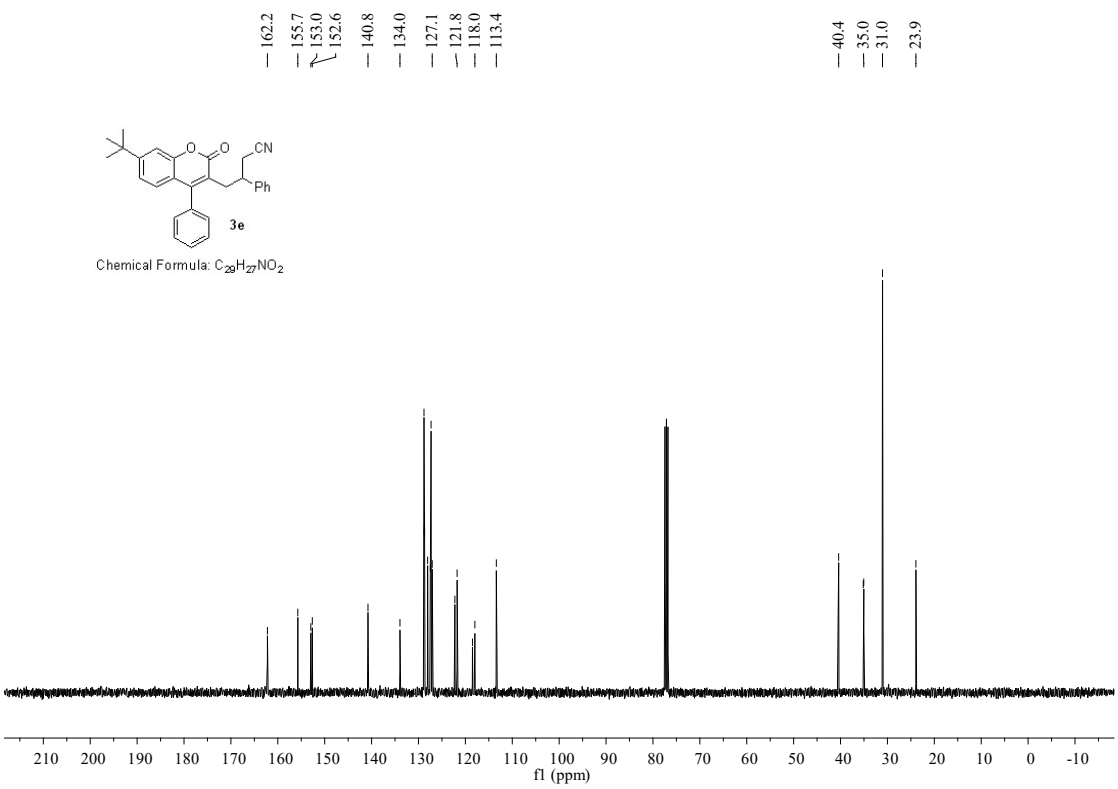
2.06
3.02
2.03
2.02
1.00
0.97
1.00
0.99
1.02
2.06
9.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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31.0
23.9
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Ph
3e
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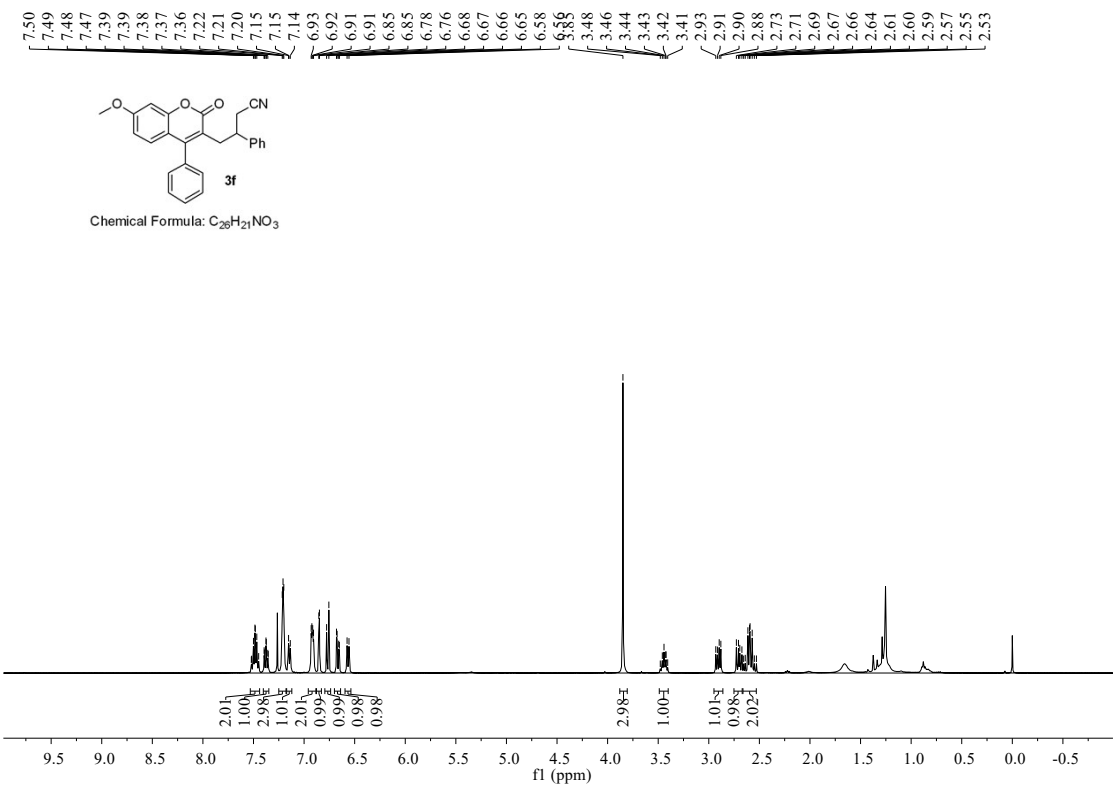
f1 (ppm)


7.50 7.49 7.48 7.47 7.39 7.39 7.38 7.37 7.36 7.22 7.21 7.20 7.15 7.15 7.14 6.93 6.92 6.91 6.91 6.85 6.85 6.78 6.76 6.68 6.67 6.66 6.65 6.58 6.56 3.85 3.48 3.46 3.44 3.43 3.42 3.41 2.93 2.91 2.90 2.88 2.73 2.71 2.69 2.67 2.66 2.64 2.61 2.60 2.59 2.57 2.55 2.53
O
O
O
CN
Ph
3f
Chemical Formula: C26H21NO3
2.01 1.00 2.98 1.01 2.01 0.99 0.99 0.98 0.98
2.98 1.00 1.01 0.98 2.02
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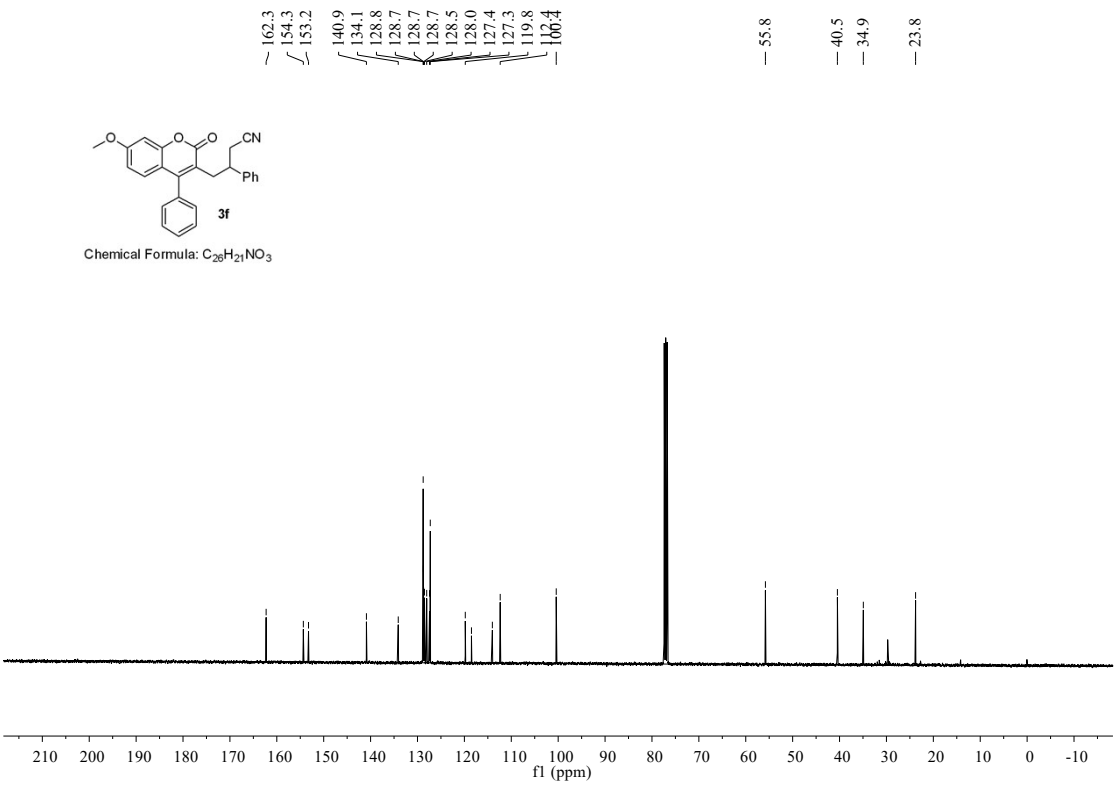
f1 (ppm)


162.3 154.3 153.2 140.9 134.1 128.8 128.7 128.7 128.7 128.5 128.0 127.4 127.3 119.8 112.4 100.4
55.8 40.5 34.9 23.8
O
O
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CN
Ph
3f
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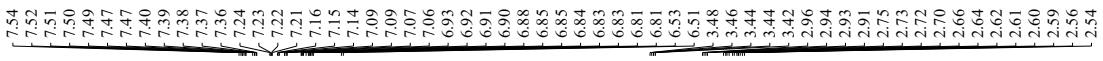
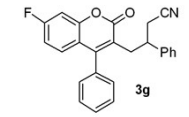
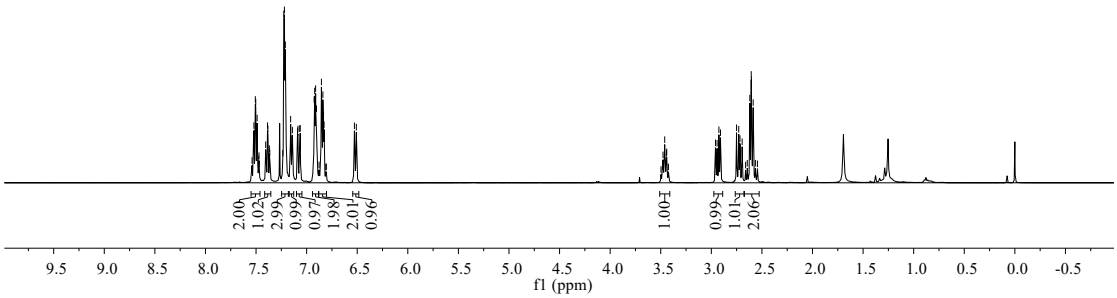
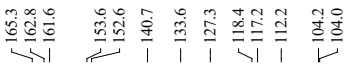
f1 (ppm)

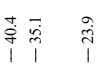


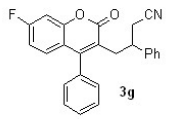


Chemical Formula: $C_{25}H_{18}FNO_2$

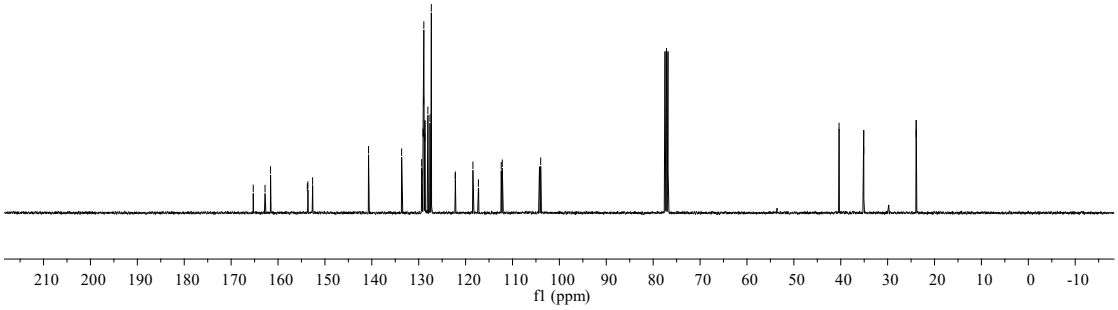


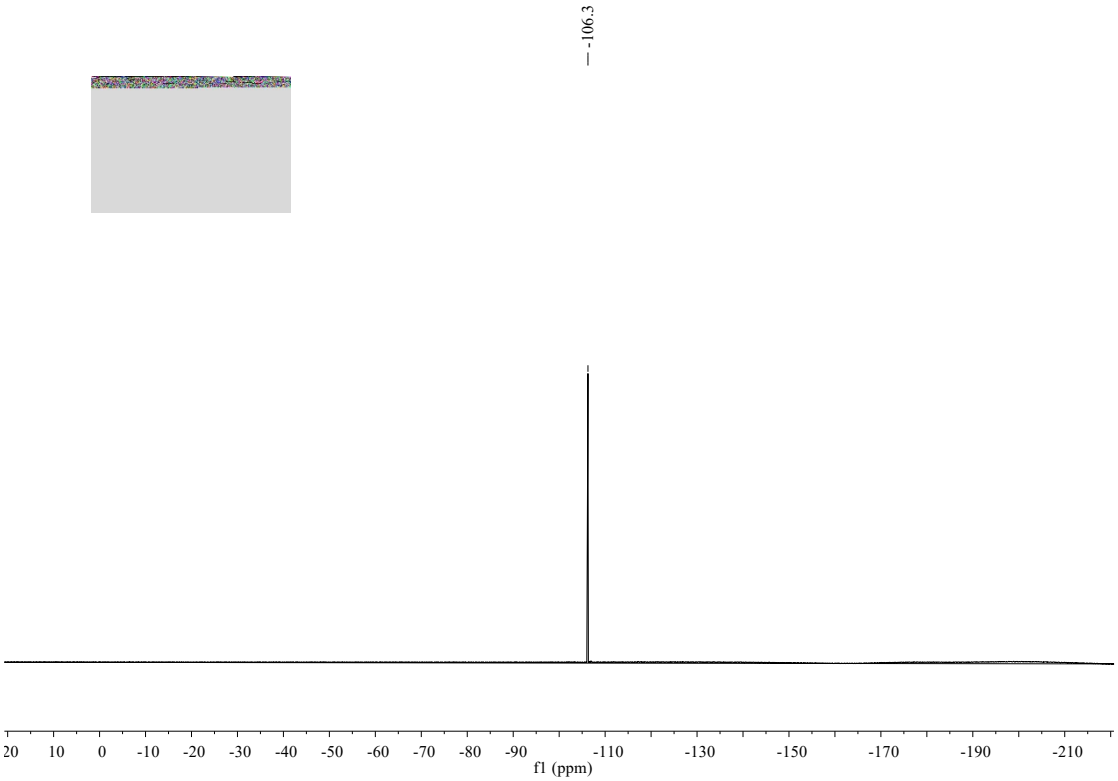


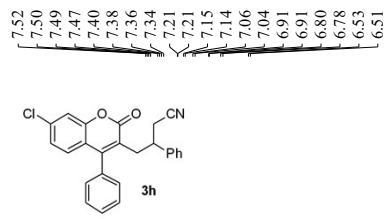




Chemical Formula: $C_{25}H_{18}FNO_2$

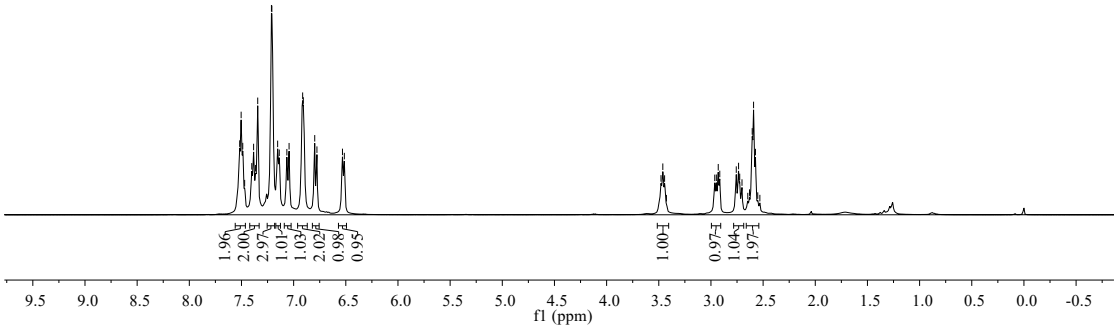


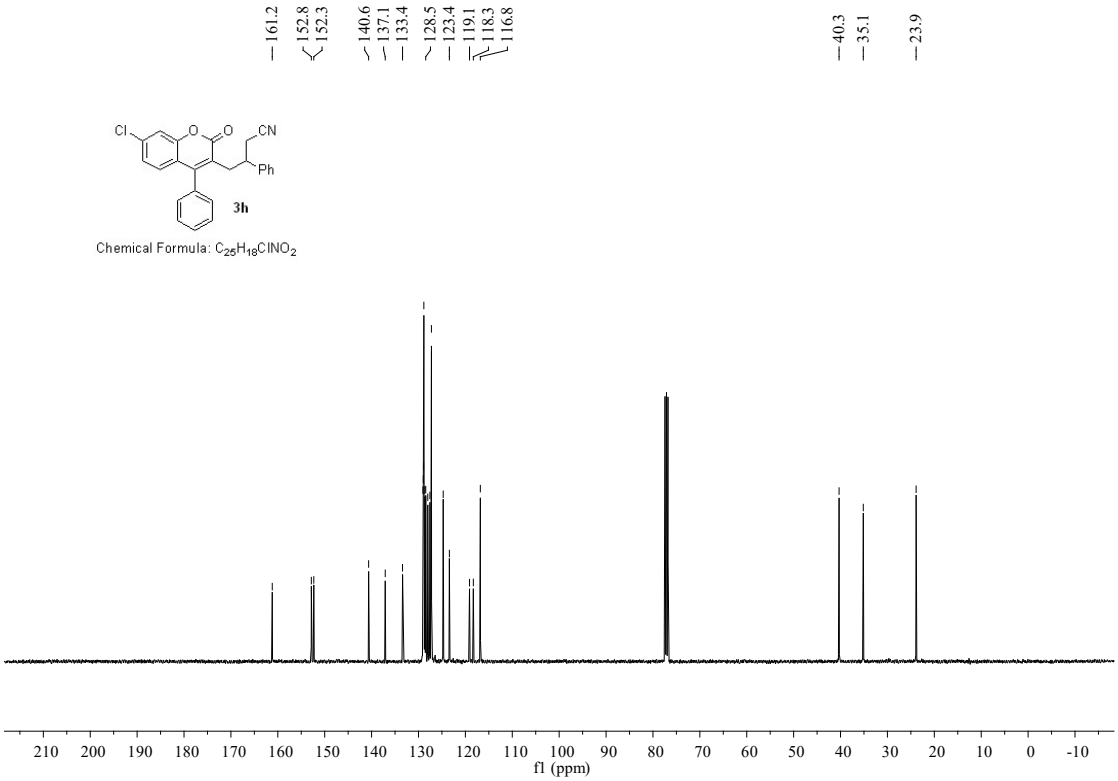


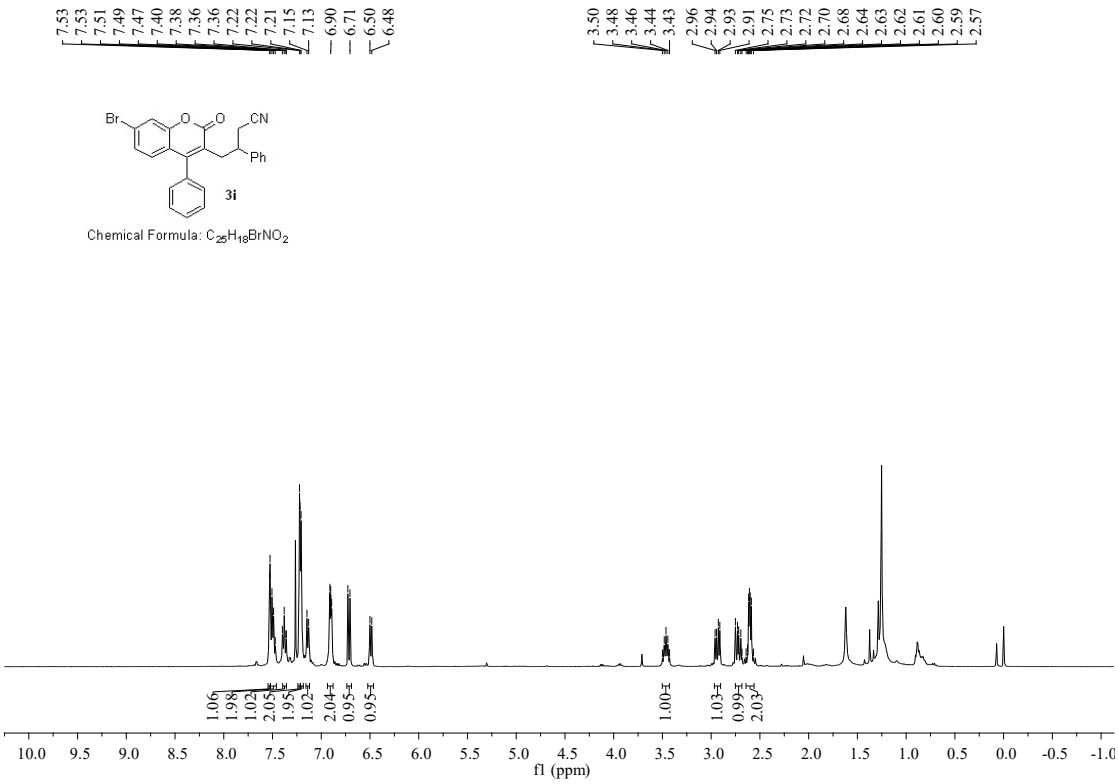


3h

Chemical Formula: $C_{25}H_{18}ClNO_2$




161.2
152.8
152.3
140.6
137.1
133.4
128.5
123.4
119.1
118.3
116.8
40.3
35.1
23.9
Cl
O
O
CN
Ph
3h
Chemical Formula: C25H18ClNO2
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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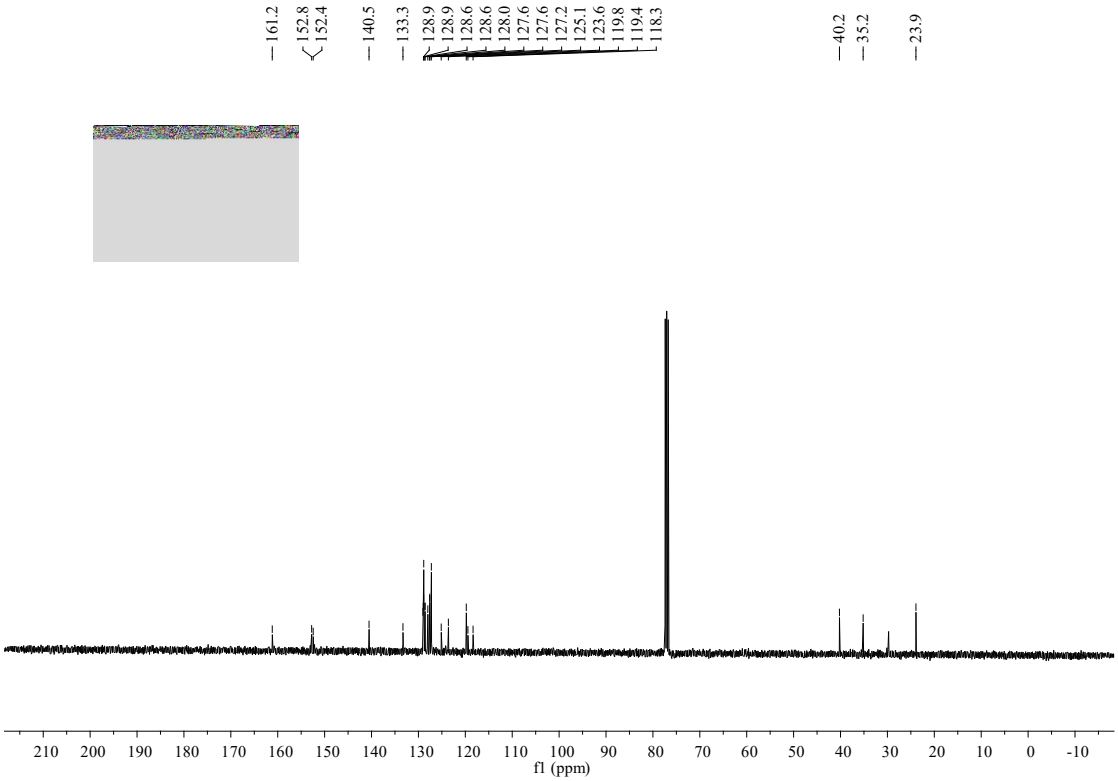
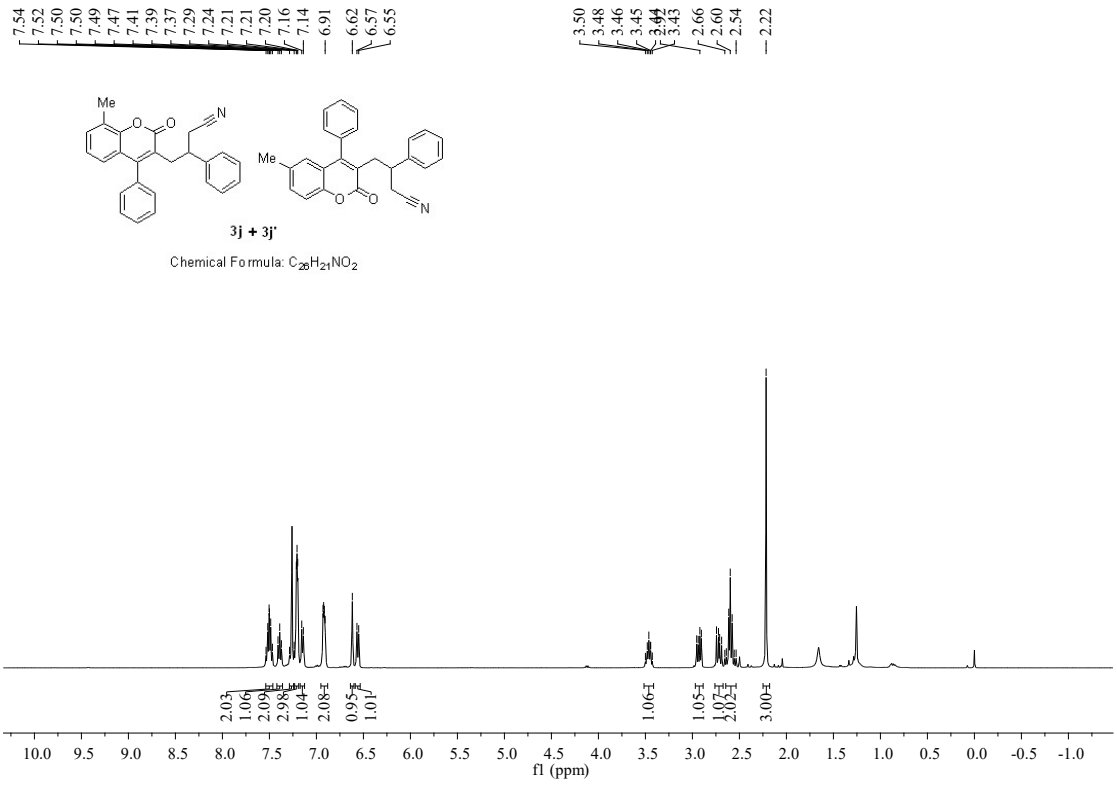
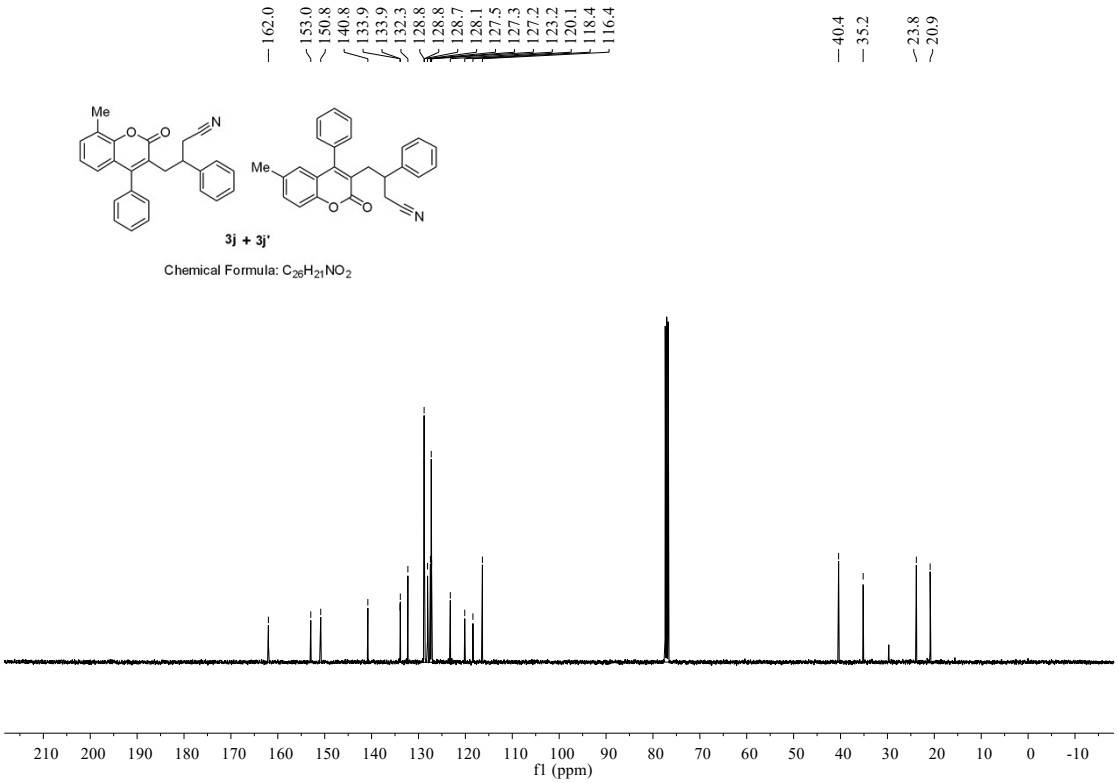
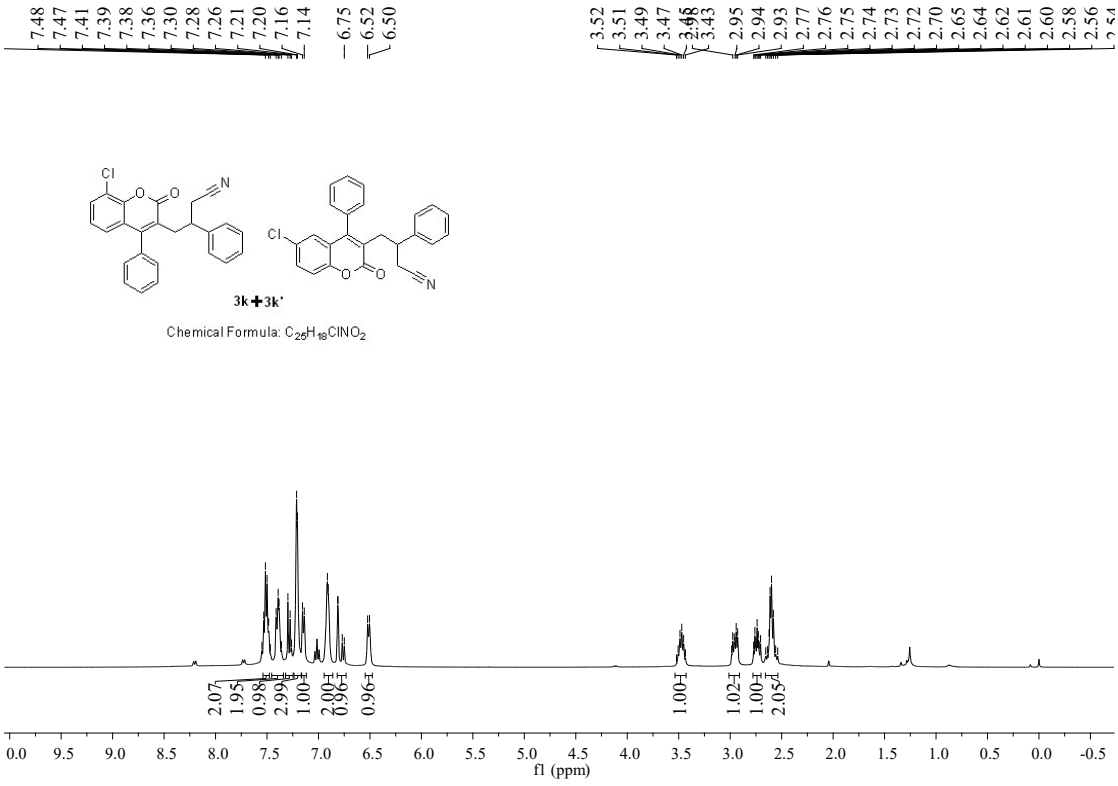
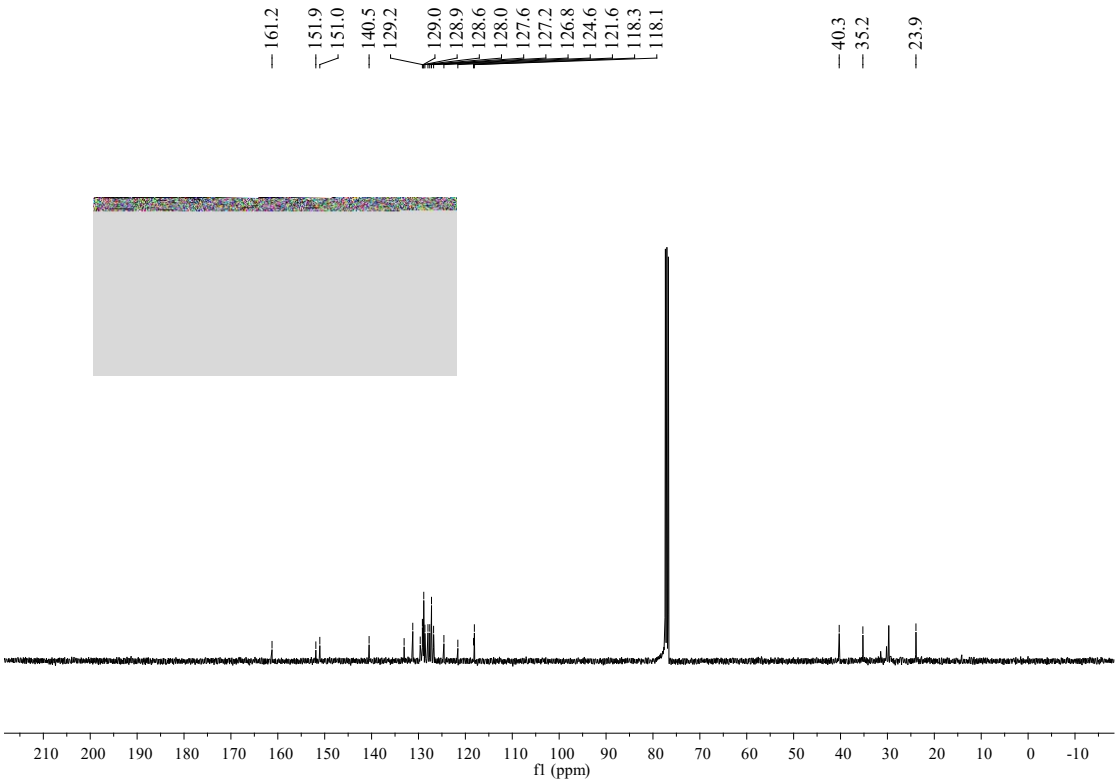
7.53
7.51
7.49
7.47
7.40
7.38
7.36
7.36
7.22
7.22
7.21
7.15
7.13
6.90
6.71
6.50
6.48
3.50
3.48
3.46
3.44
3.43
2.96
2.94
2.93
2.91
2.75
2.73
2.72
2.70
2.68
2.64
2.63
2.62
2.61
2.60
2.59
2.57
Br
O
O
CN
Ph
3i
Chemical Formula: C25H18BrNO2
1.06
1.98
1.02
2.05
1.95
1.02
2.04
0.95
0.95
1.00
1.03
0.99
2.03
10.0 9.5 9.0 8.5 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 0.5 0.0 -0.5 -1.0
f1 (ppm)

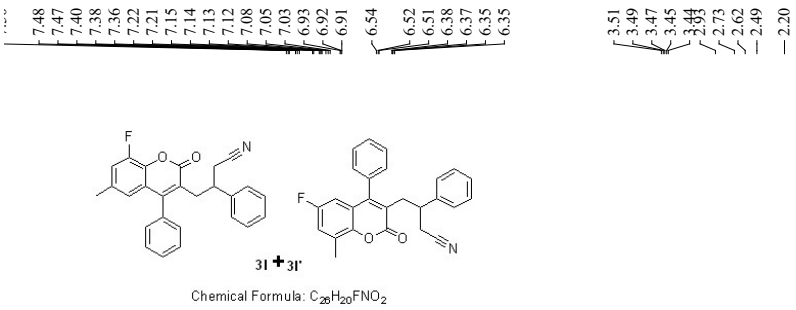

161.2
152.8
152.4
140.5
133.3
128.9
128.9
128.6
128.6
128.0
127.6
127.6
127.2
125.1
123.6
119.8
119.4
118.3
40.2
35.2
23.9
fl (ppm)


7.54
7.52
7.50
7.50
7.49
7.47
7.41
7.39
7.37
7.29
7.24
7.21
7.21
7.20
7.16
7.14
6.91
6.62
6.57
6.55
3.50
3.48
3.46
3.45
3.44
3.43
2.66
2.60
2.54
2.22
Me
N
Me
O
O
3j + 3j'
Chemical Formula: C26H21NO2
2.03
1.06
2.09
2.98
1.04
2.08
0.95
1.01
1.06
1.05
1.07
2.02
3.00
fl (ppm)


162.0
153.0
150.8
140.8
133.9
132.3
128.8
128.7
128.1
127.5
127.3
127.2
123.2
120.1
118.4
116.4
40.4
35.2
23.8
20.9
Me
O
O
N
Me
O
O
N
3j + 3j'
Chemical Formula: C26H21NO2
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)

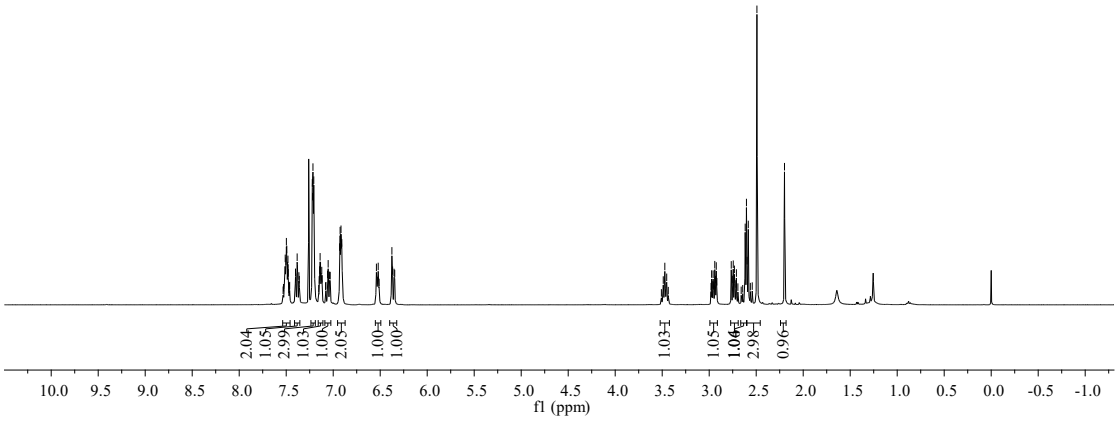

7.48
7.47
7.41
7.39
7.38
7.36
7.30
7.28
7.26
7.21
7.20
7.16
7.14
6.75
6.52
6.50
3.52
3.51
3.49
3.47
3.43
2.95
2.94
2.93
2.77
2.76
2.75
2.74
2.73
2.72
2.70
2.65
2.64
2.62
2.61
2.60
2.58
2.56
Cl
O
O
N
Cl
O
O
N
3k + 3k'
Chemical Formula: C25H18ClNO2
2.07
1.95
0.98
2.99
1.00
2.00
0.96
0.96
1.00
1.02
1.00
2.05
0.0 9.5 9.0 8.5 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 0.5 0.0 -0.5
f1 (ppm)

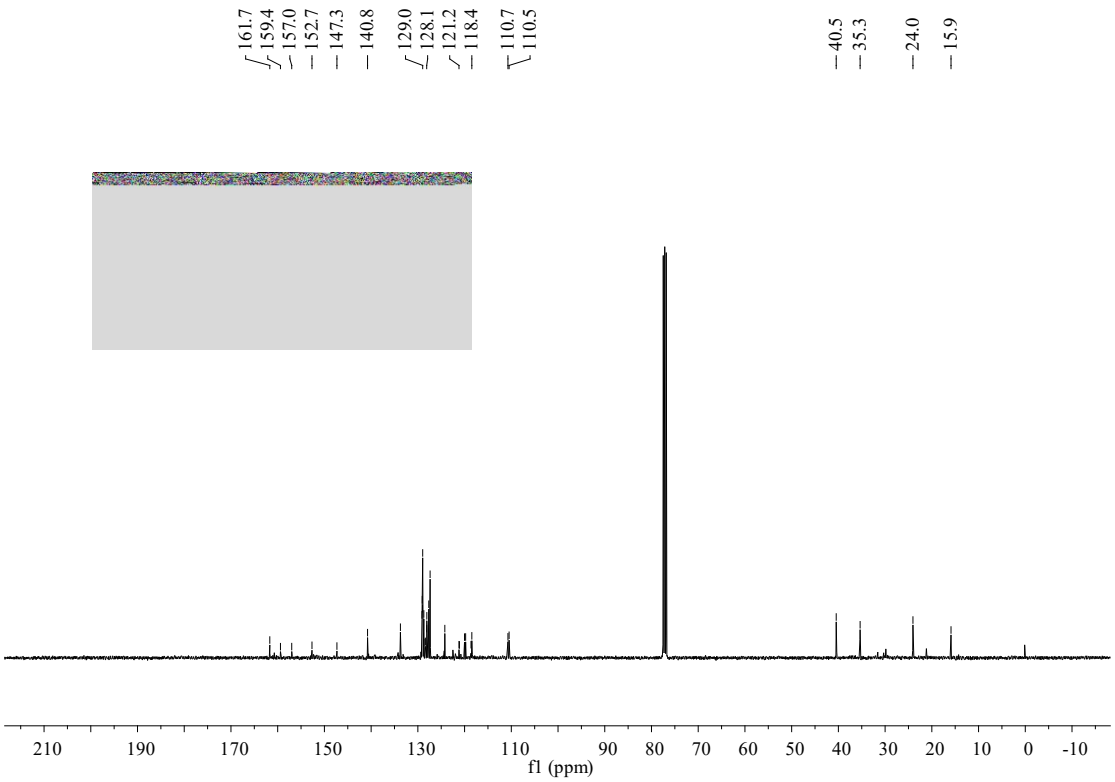


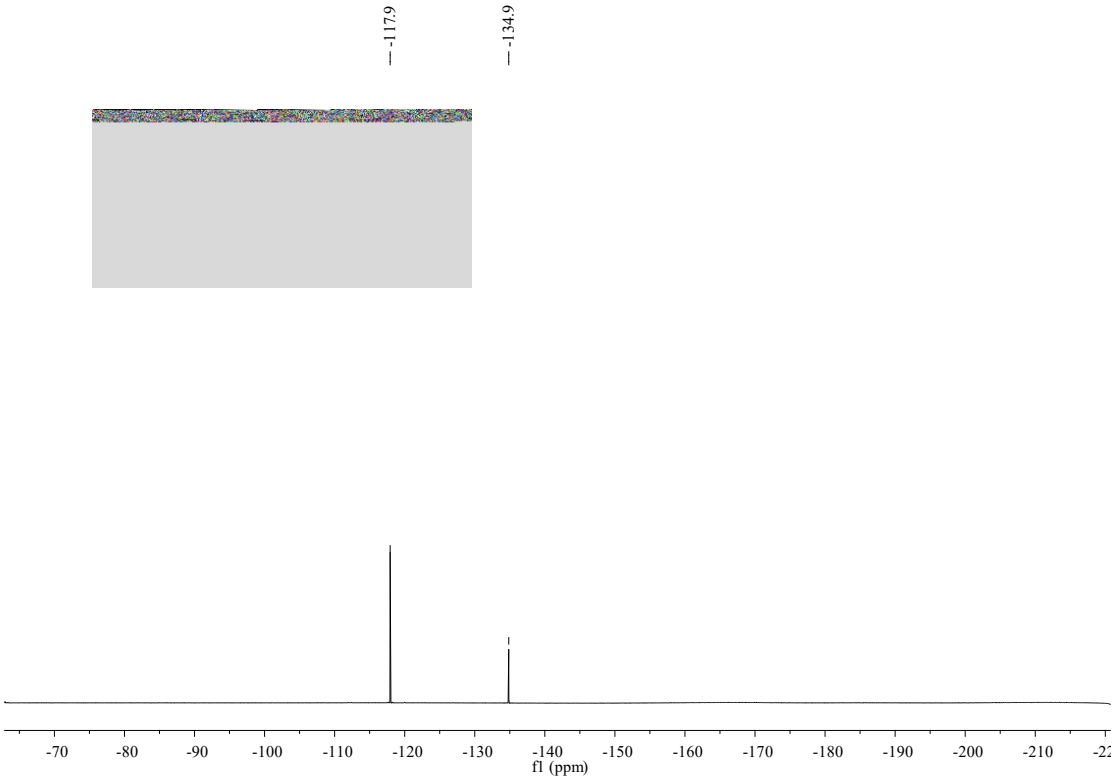


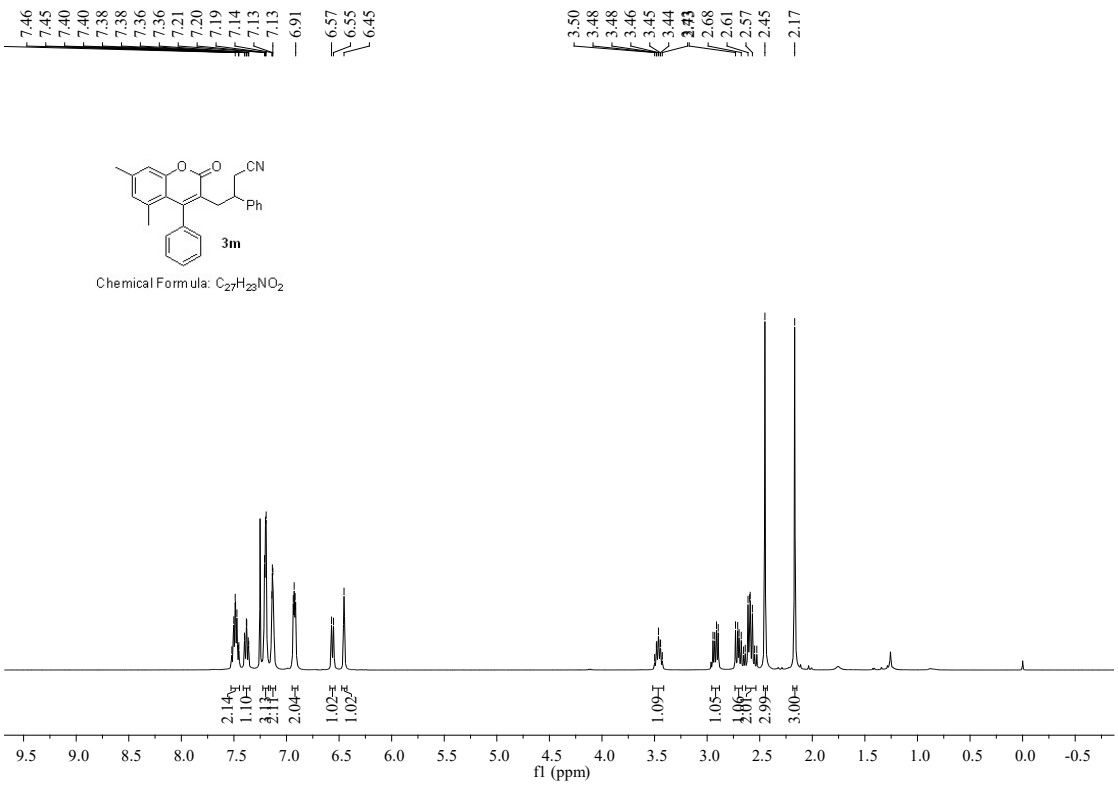
3l + 3l'

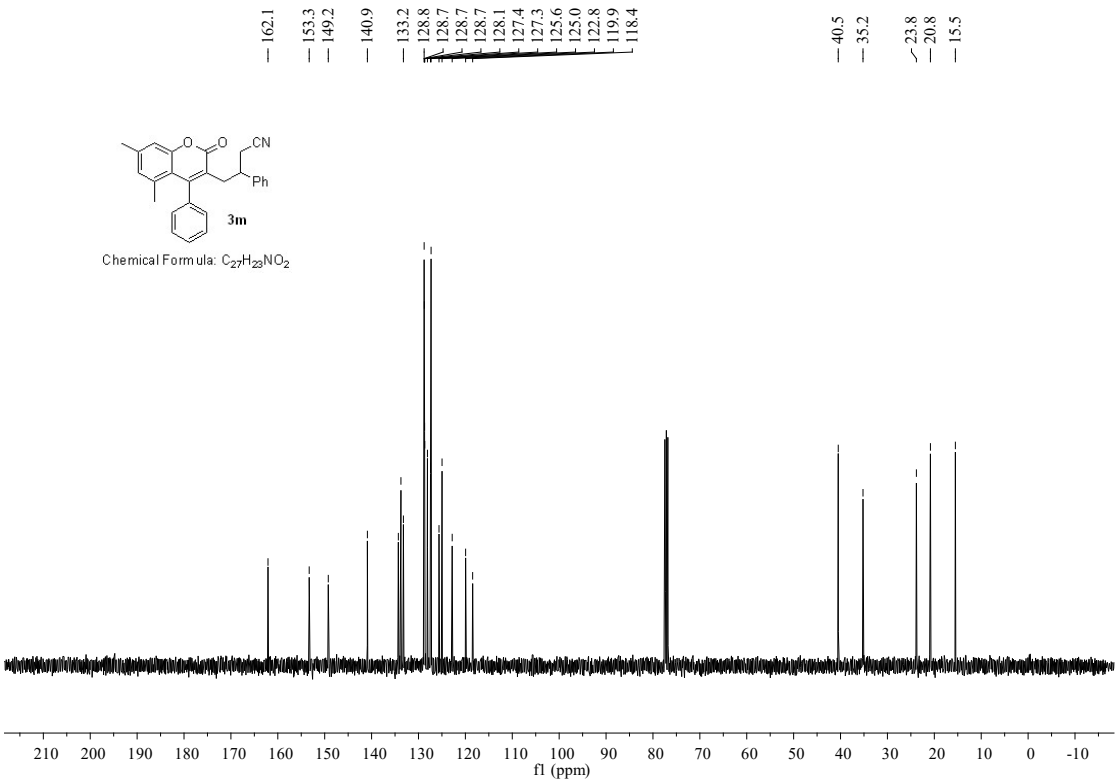
Chemical Formula: $C_{26}H_{20}FNO_2$

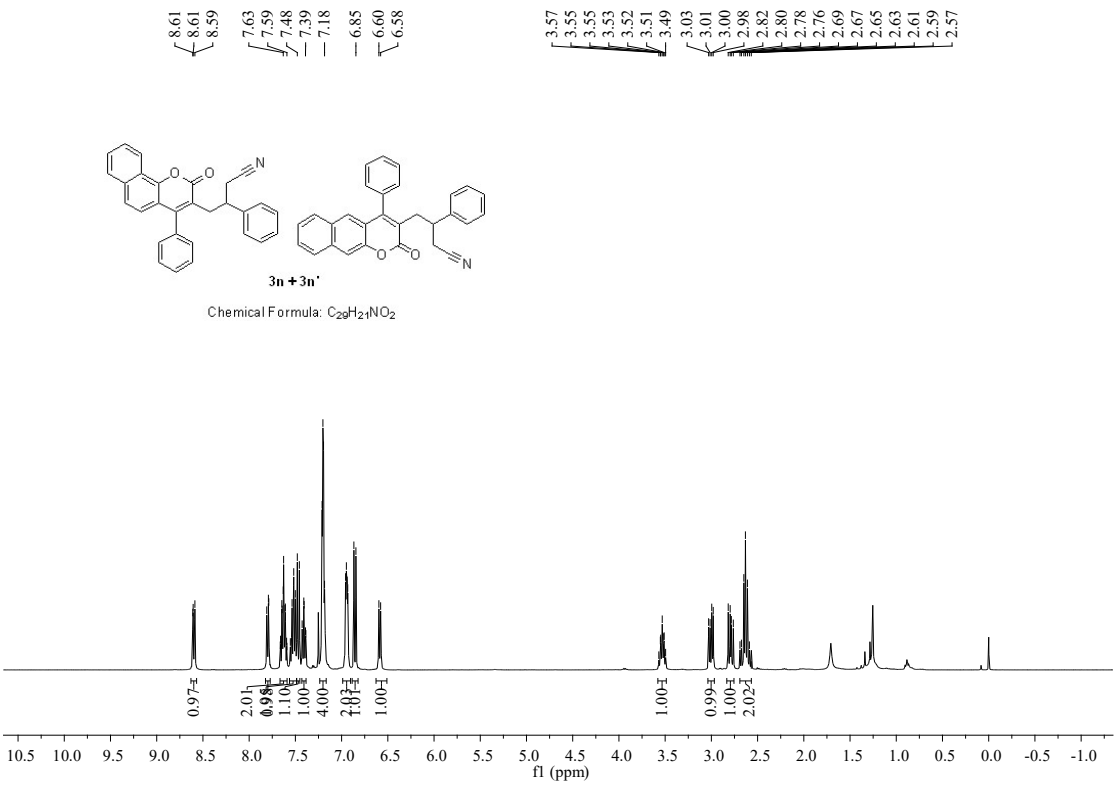


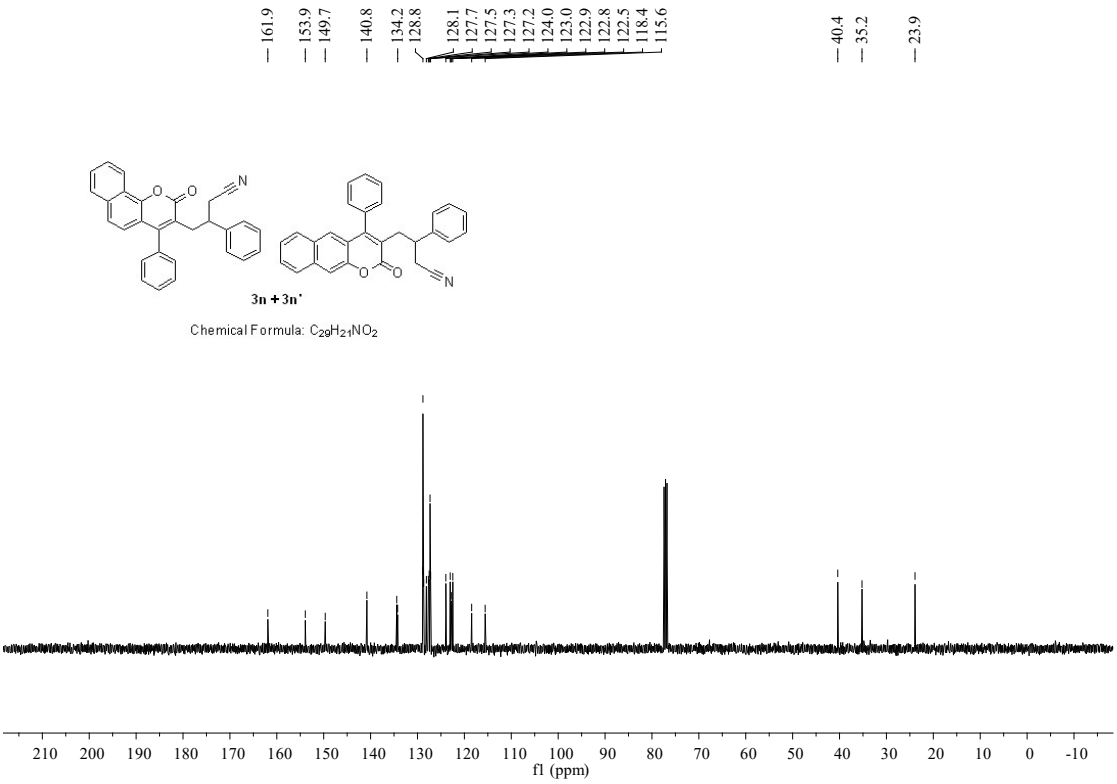

161.7
159.4
157.0
152.7
147.3
140.8
129.0
128.1
121.2
118.4
110.7
110.5
40.5
35.3
24.0
15.9
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

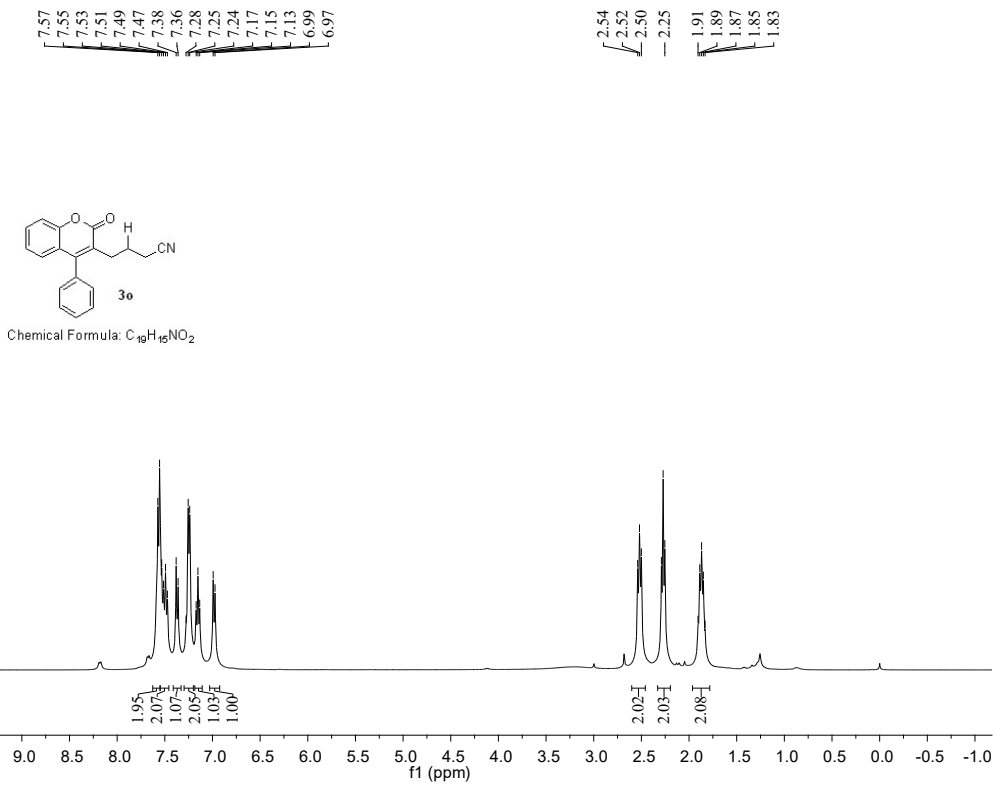

-117.9
-134.9
-70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.46
7.45
7.40
7.40
7.38
7.38
7.36
7.36
7.21
7.20
7.19
7.14
7.13
7.13
6.91
6.57
6.55
6.45
3.50
3.48
3.48
3.46
3.45
3.44
2.68
2.61
2.57
2.45
2.17
O
O
CN
Ph
3m
Chemical Formula: C27H23NO2
2.14
1.10
2.04
1.02
1.02
1.09
1.05
2.01
2.99
3.00
9.5 9.0 8.5 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 0.5 0.0 -0.5
f1 (ppm)


162.1
153.3
149.2
140.9
133.2
128.8
128.7
128.7
128.7
128.1
127.4
127.3
125.6
125.0
122.8
119.9
118.4
40.5
35.2
23.8
20.8
15.5
O
O
CN
Ph
3m
Chemical Formula: C27H23NO2
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)


8.61
8.61
8.59
7.63
7.59
7.48
7.39
7.18
6.85
6.60
6.58
3.57
3.55
3.55
3.53
3.52
3.51
3.49
3.03
3.01
3.00
2.98
2.82
2.80
2.78
2.76
2.69
2.67
2.65
2.63
2.61
2.59
2.57
3n + 3n'
Chemical Formula: C29H21NO2
0.97
2.01
0.98
1.10
1.00
4.00
2.03
1.01
1.00
1.00
0.99
1.00
2.02
10.5 10.0 9.5 9.0 8.5 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 0.5 0.0 -0.5 -1.0
f1 (ppm)


161.9
153.9
149.7
140.8
134.2
128.8
128.1
127.7
127.5
127.3
127.2
124.0
123.0
122.9
122.8
122.5
118.4
115.6
40.4
35.2
23.9
3n + 3n'
Chemical Formula: C29H21NO2
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)


7.57
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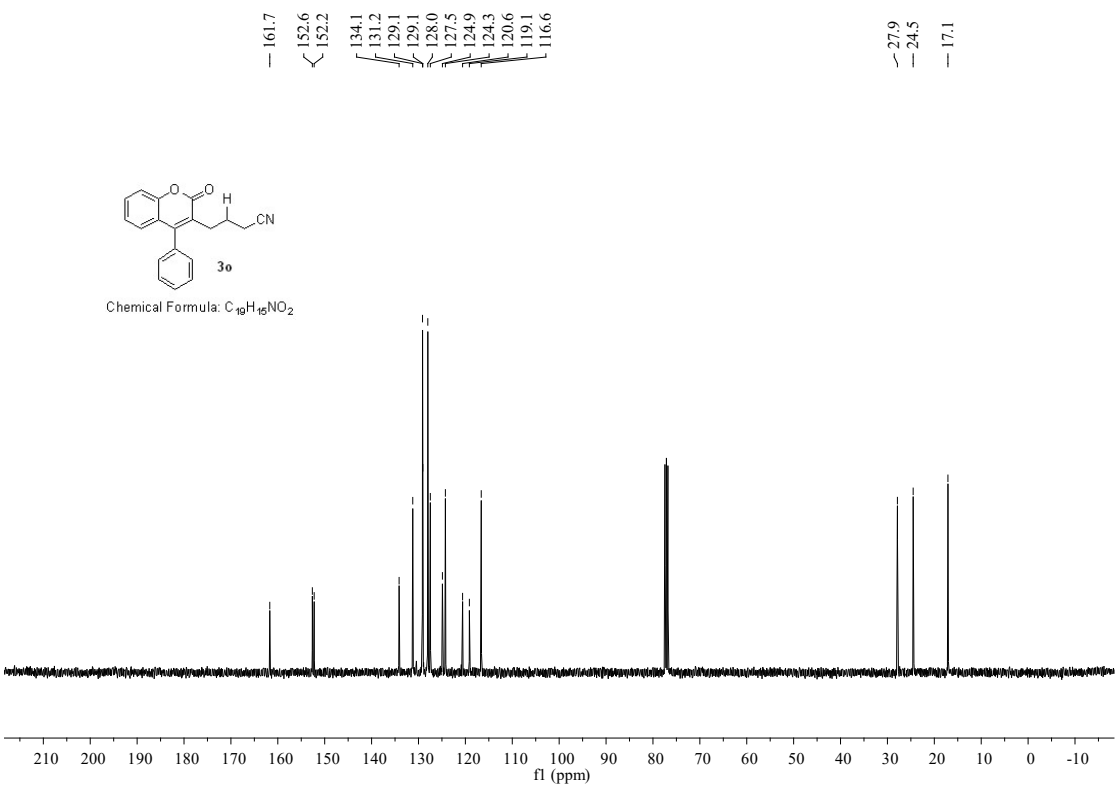
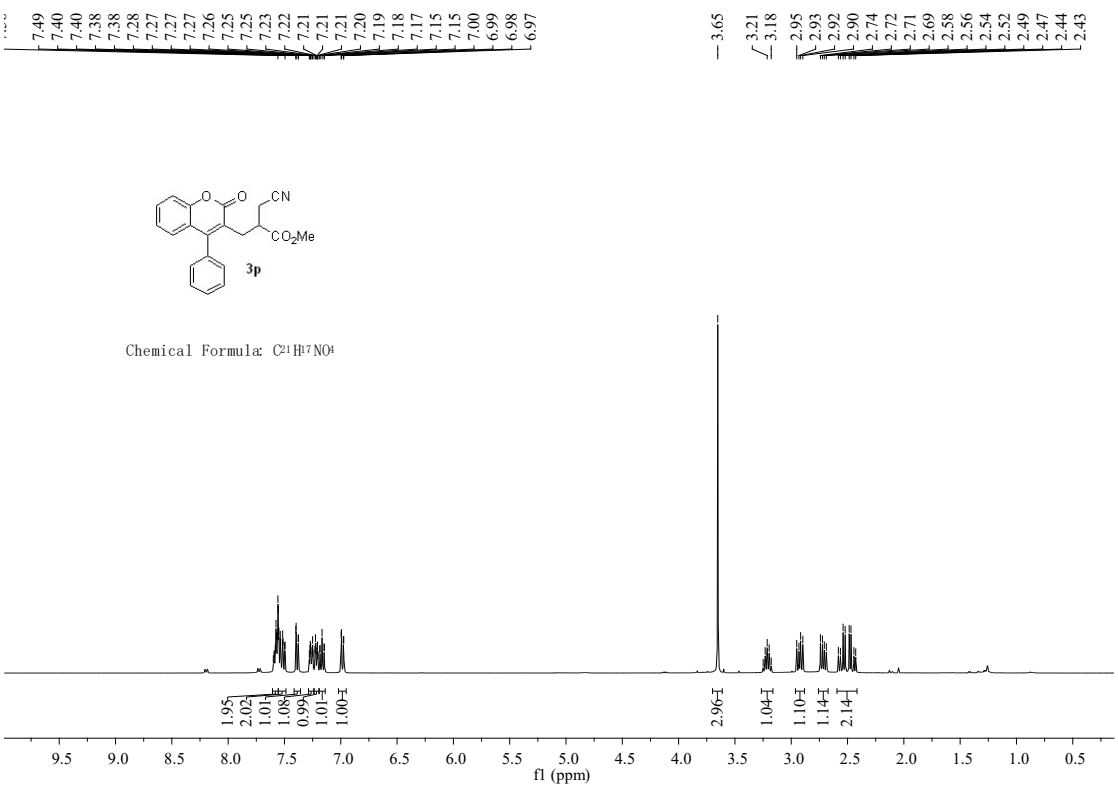
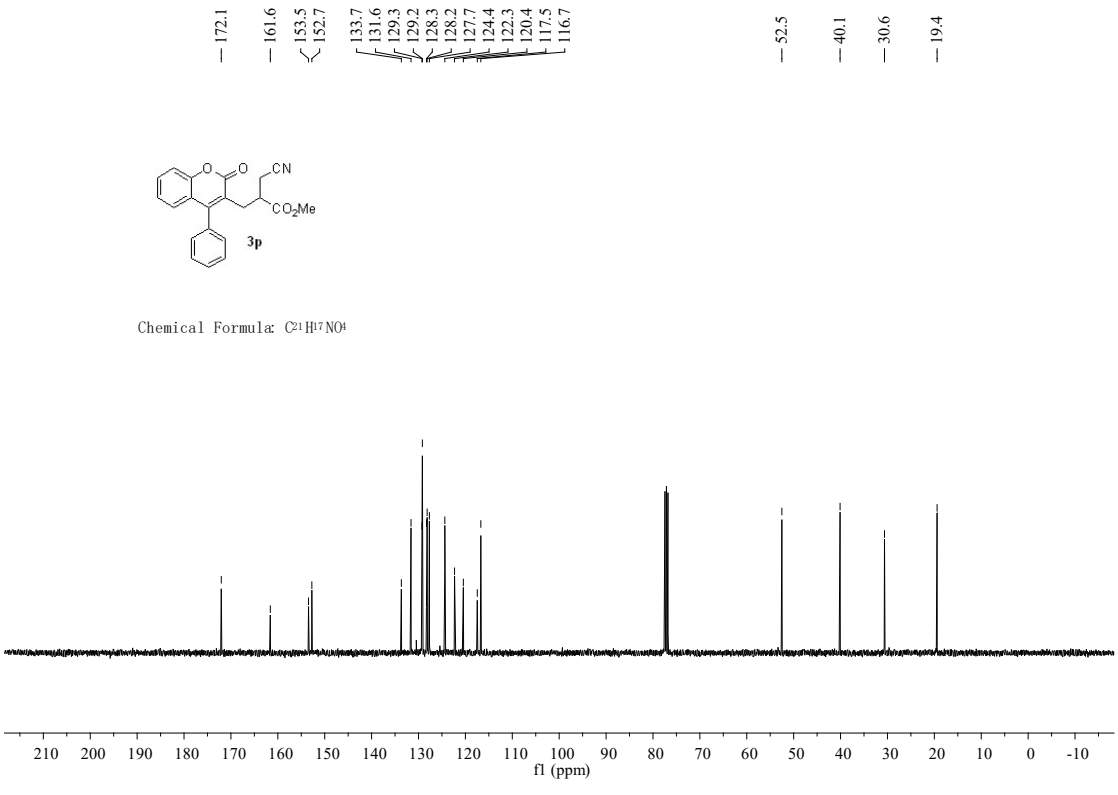
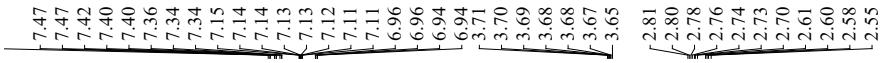
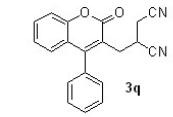
7.49
7.47
7.38
7.36
7.28
7.25
7.24
7.17
7.15
7.13
6.99
6.97
2.54
2.52
2.50
2.25
1.91
1.89
1.87
1.85
1.83
O
O
H
CN
3o
Chemical Formula: C19H15NO2
1.95
2.07
1.07
2.05
1.03
1.00
2.02
2.03
2.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


161.7
152.6
152.2
134.1
131.2
129.1
129.1
128.0
127.5
124.9
124.3
120.6
119.1
116.6
27.9
24.5
17.1
O
O
H
CN
3o
Chemical Formula: C19H15NO2
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)

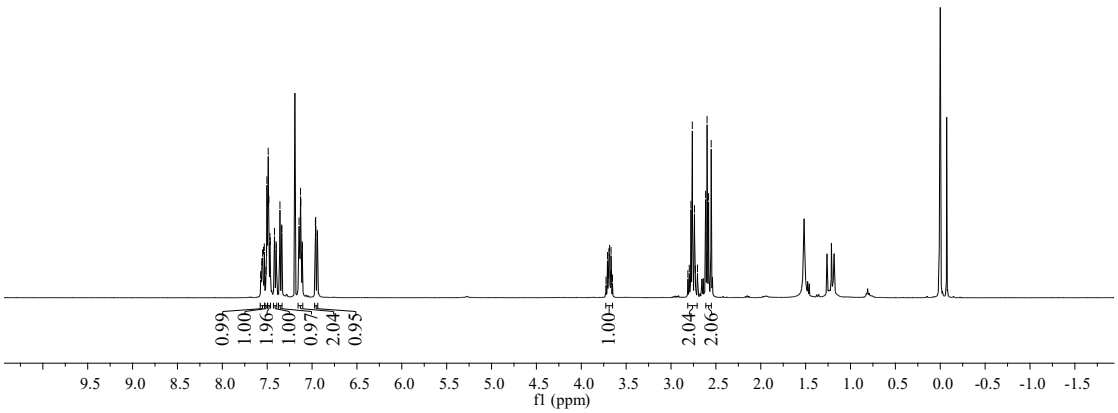

7.49 7.40 7.40 7.38 7.38 7.28 7.27 7.27 7.27 7.26 7.25 7.25 7.23 7.22 7.21 7.21 7.21 7.20 7.19 7.18 7.17 7.15 7.15 7.00 6.99 6.98 6.97
3.65 3.21 3.18 2.95 2.93 2.92 2.90 2.74 2.72 2.71 2.69 2.58 2.56 2.54 2.52 2.49 2.47 2.44 2.43
CN
O
O
CO2Me
3p
Chemical Formula: C21H17NO4
1.95 2.02 1.01 1.08 0.99 1.01 1.00 2.96 1.04 1.10 1.14 2.14
9.5 9.0 8.5 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 0.5
f1 (ppm)

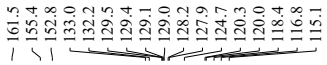

172.1 161.6 153.5 152.7 133.7 131.6 129.3 129.2 128.3 128.2 127.7 124.4 122.3 120.4 117.5 116.7
52.5 40.1 30.6 19.4
CN
O
O
CO2Me
3p
Chemical Formula: C21H17NO4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

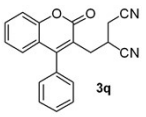




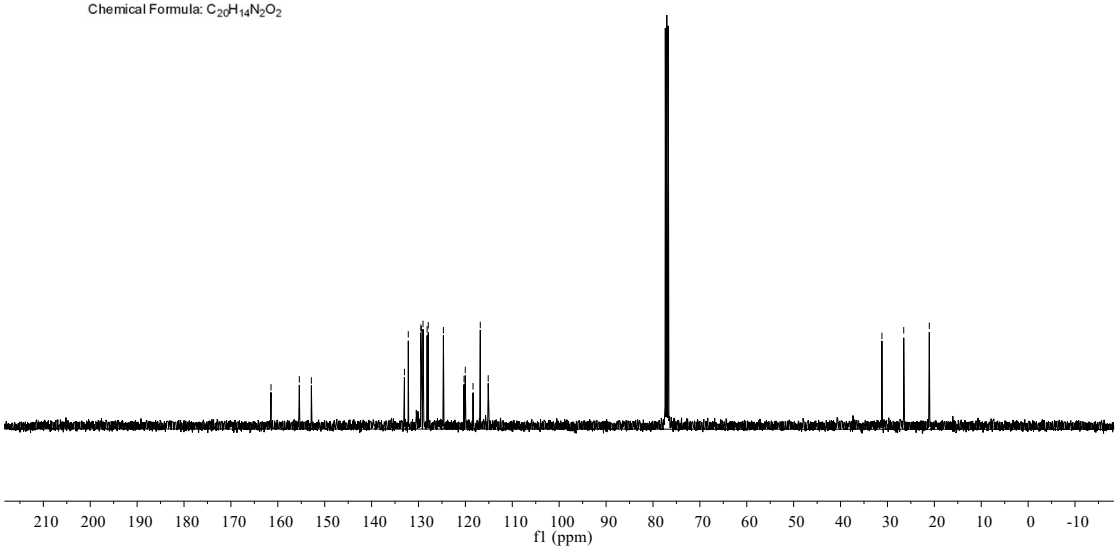
Chemical Formula: $C_{20}H_{14}N_2O_2$

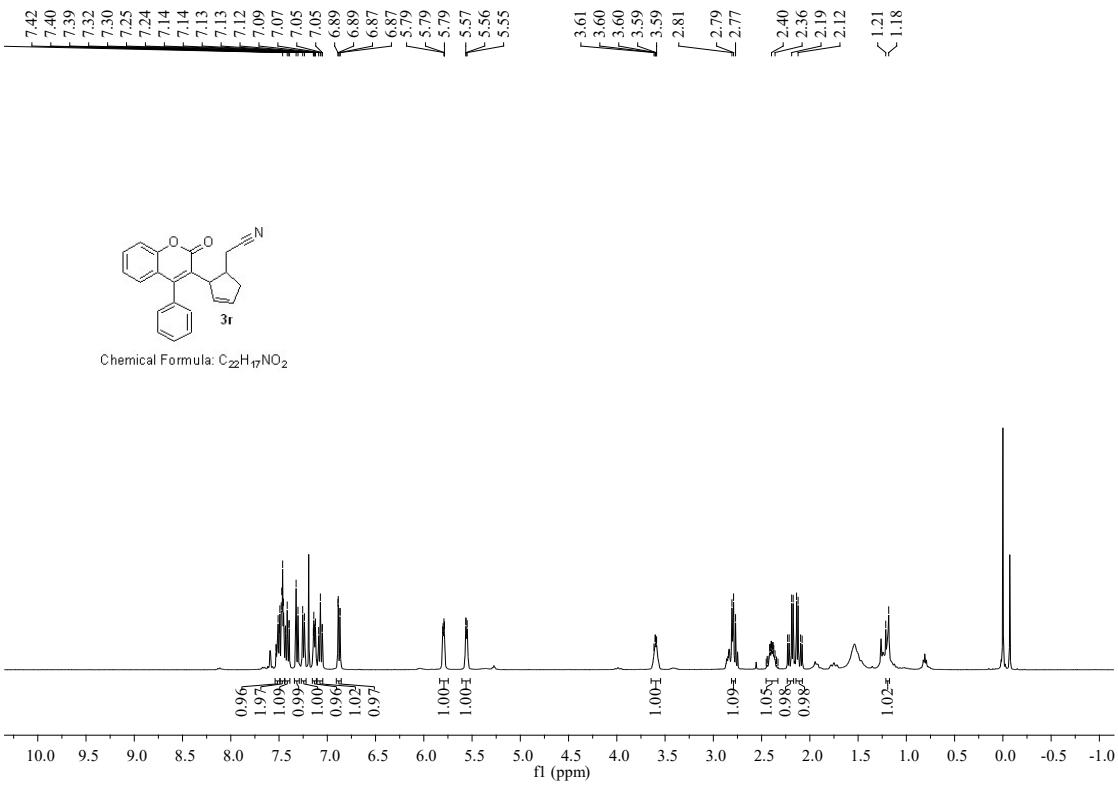






Chemical Formula: $C_{20}H_{14}N_2O_2$




7.42
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7.32
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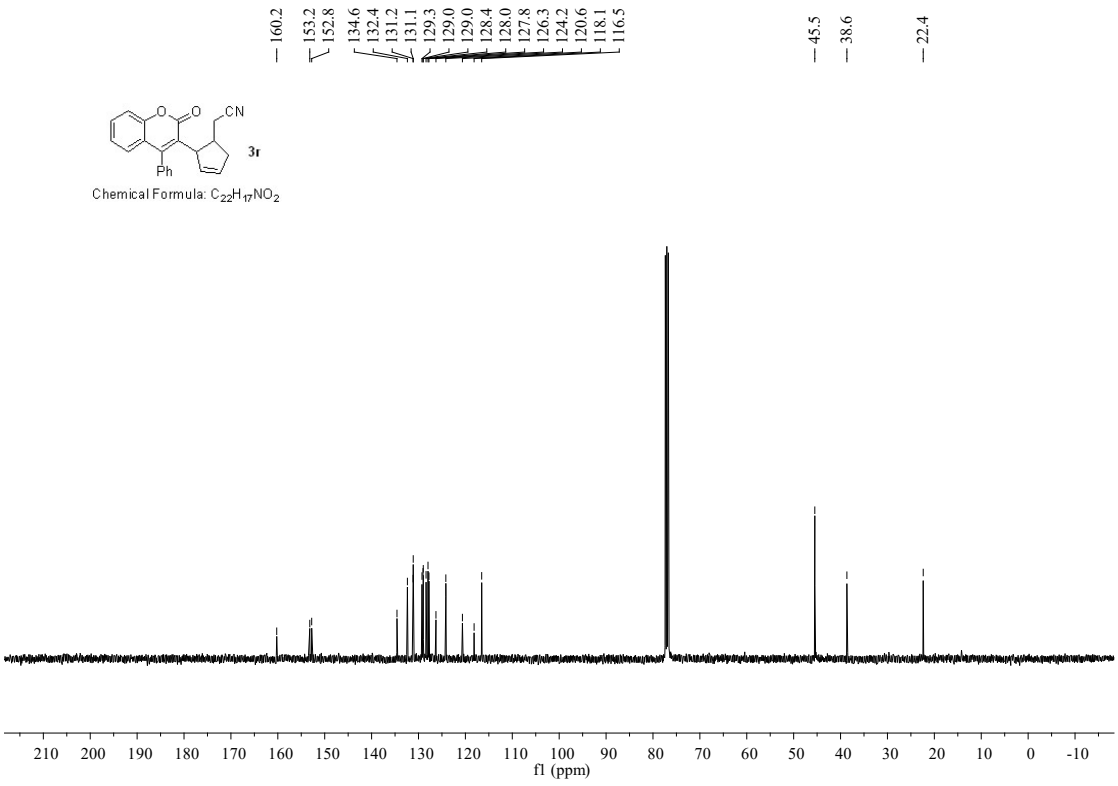
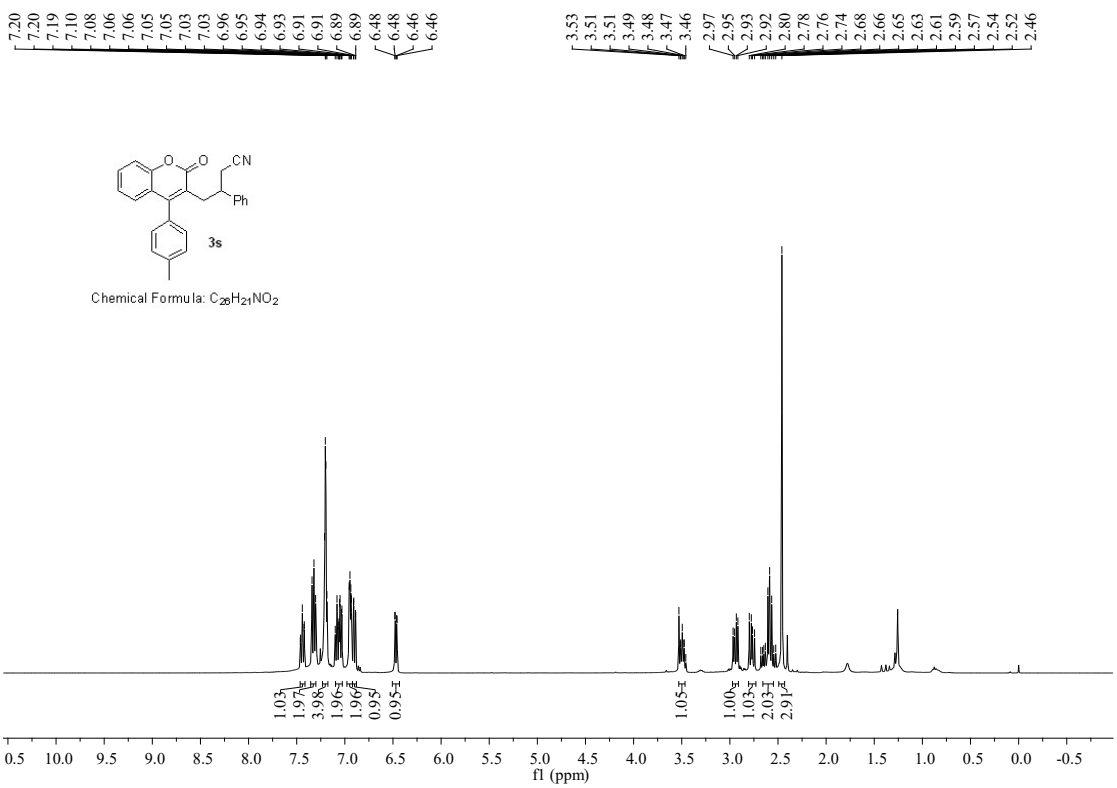
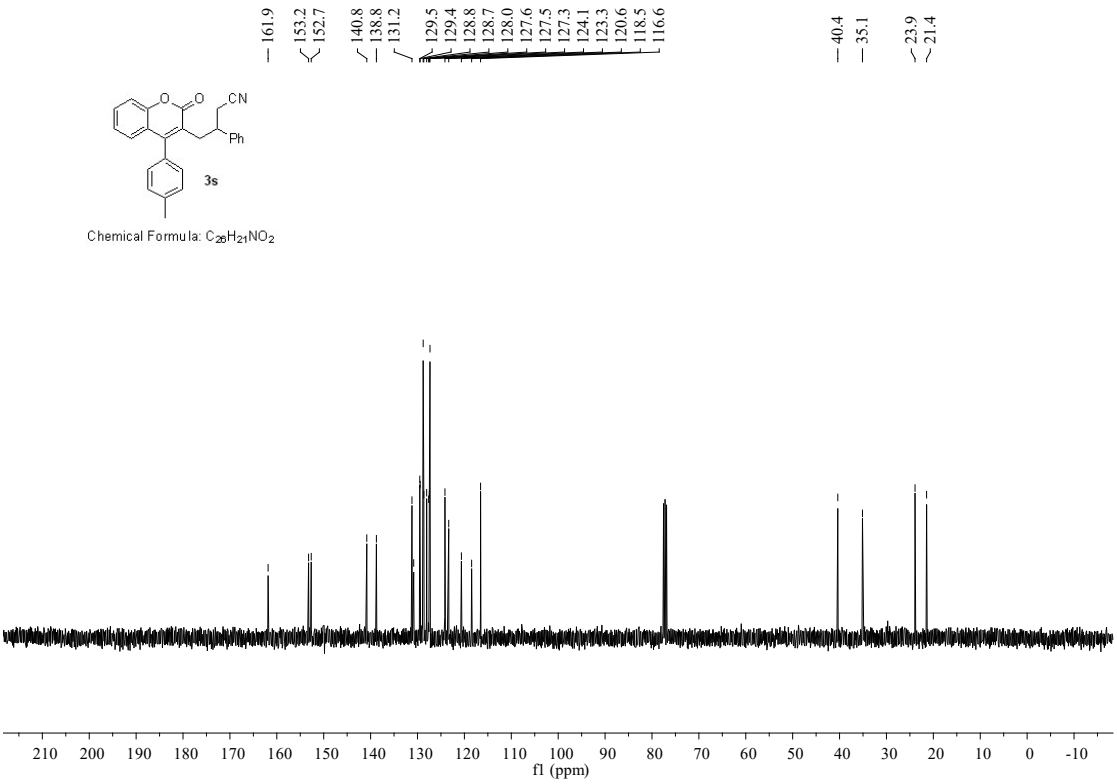
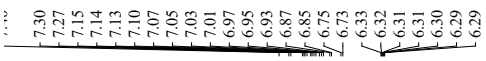
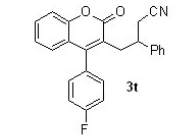
7.25
7.24
7.14
7.14
7.13
7.13
7.12
7.09
7.07
7.05
7.05
6.89
6.89
6.87
6.87
5.79
5.79
5.79
5.57
5.56
5.55
3.61
3.60
3.60
3.59
3.59
2.81
2.79
2.77
2.40
2.36
2.19
2.12
1.21
1.18
O
O
N
3r
Chemical Formula: C22H17NO2
0.96
1.97
1.09
0.99
1.00
0.96
1.02
0.97
1.00
1.00
1.00
1.09
1.05
0.98
0.98
1.02
10.0 9.5 9.0 8.5 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 0.5 0.0 -0.5 -1.0
f1 (ppm)


160.2
153.2
152.8
134.6
132.4
131.2
131.1
129.3
129.0
129.0
128.4
128.0
127.8
126.3
124.2
120.6
118.1
116.5
45.5
38.6
22.4
O
O
CN
3r
Ph
Chemical Formula: C22H17NO2
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)

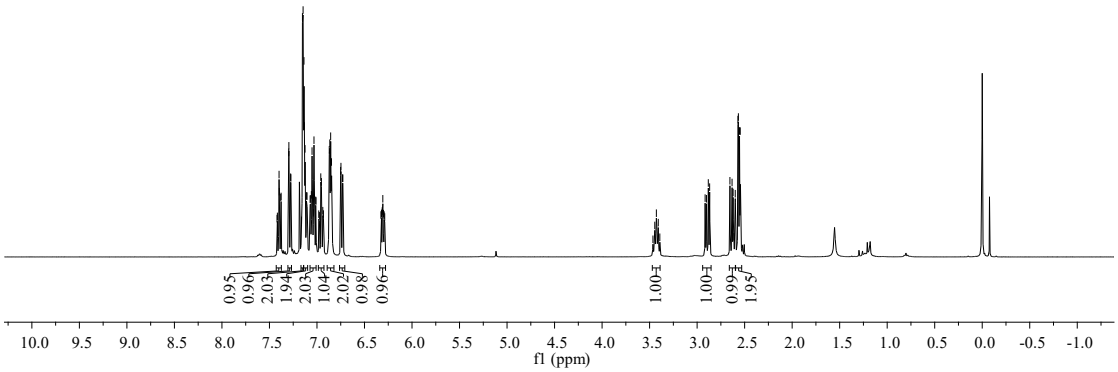

7.20 7.20 7.19 7.10 7.08 7.06 7.06 7.05 7.05 7.03 7.03 6.96 6.95 6.94 6.93 6.91 6.91 6.89 6.89 6.48 6.48 6.46 6.46
3.53 3.51 3.51 3.49 3.48 3.47 3.46 2.97 2.95 2.93 2.92 2.80 2.78 2.76 2.74 2.68 2.66 2.65 2.63 2.61 2.59 2.57 2.54 2.52 2.46
O O CN Ph
3s
Chemical Formula: C26H21NO2
1.03 1.97 3.98 1.96 1.96 0.95 0.95 1.05 1.00 1.03 2.03 2.91
0.5 10.0 9.5 9.0 8.5 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 0.5 0.0 -0.5
f1 (ppm)

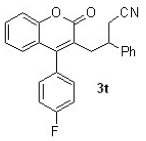

161.9 153.2 152.7 140.8 138.8 131.2 129.5 129.4 128.8 128.7 128.0 127.6 127.5 127.3 124.1 123.3 120.6 118.5 116.6
40.4 35.1 23.9 21.4
O O CN Ph
3s
Chemical Formula: C26H21NO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



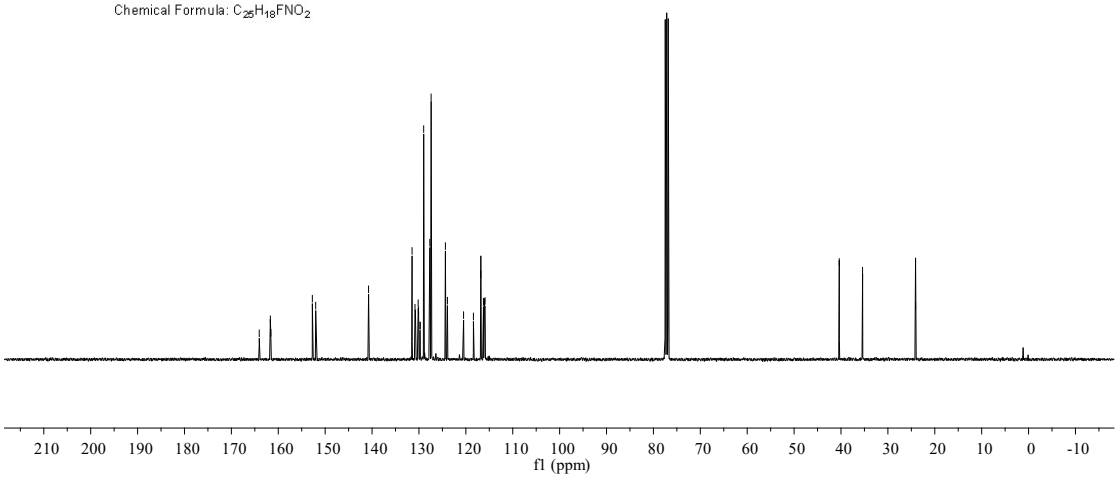


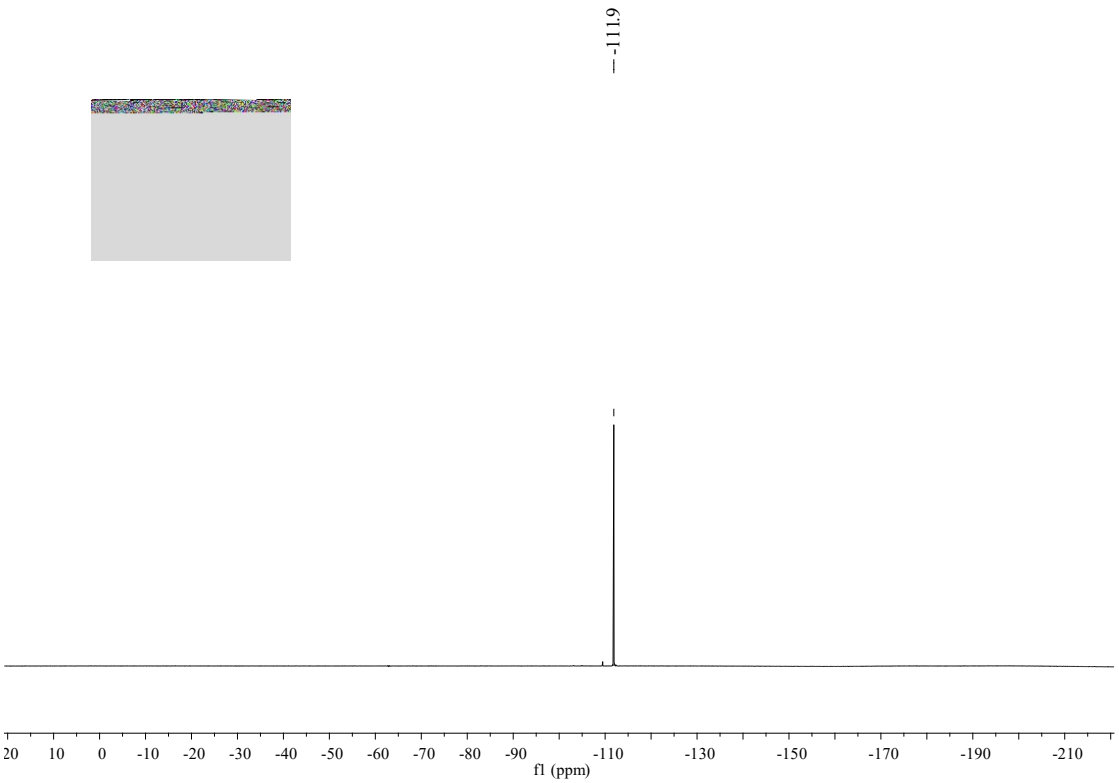
Chemical Formula: $C_{25}H_{18}FNO_2$

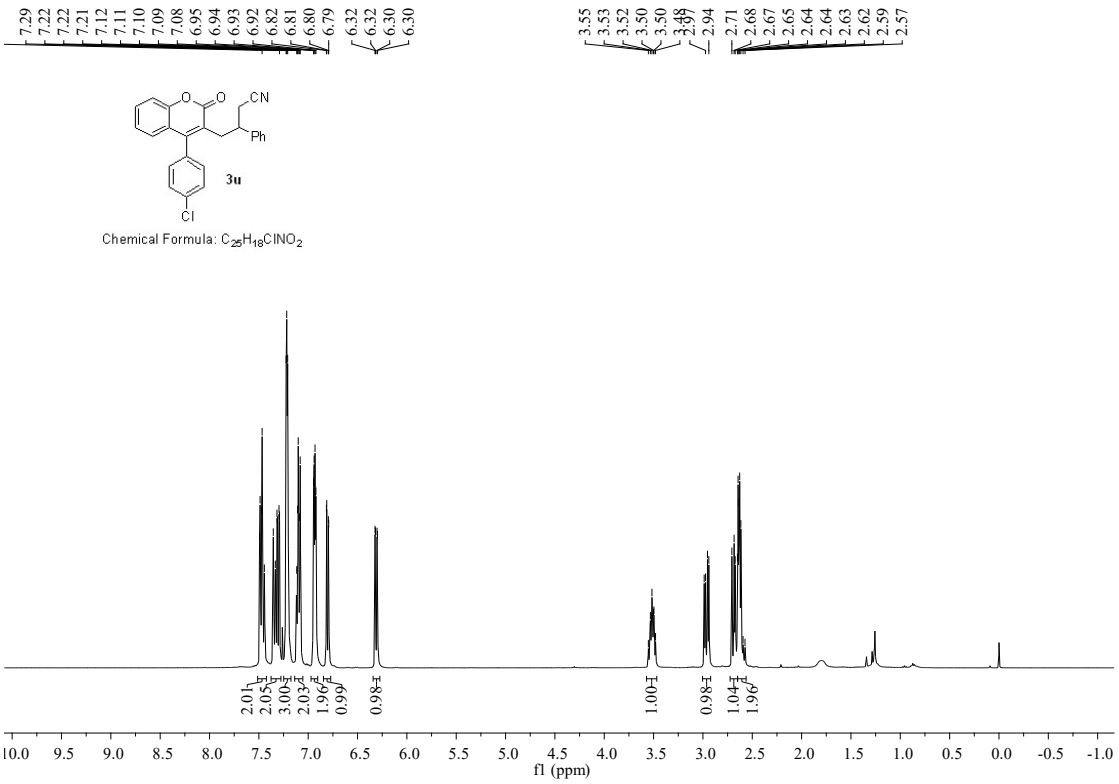


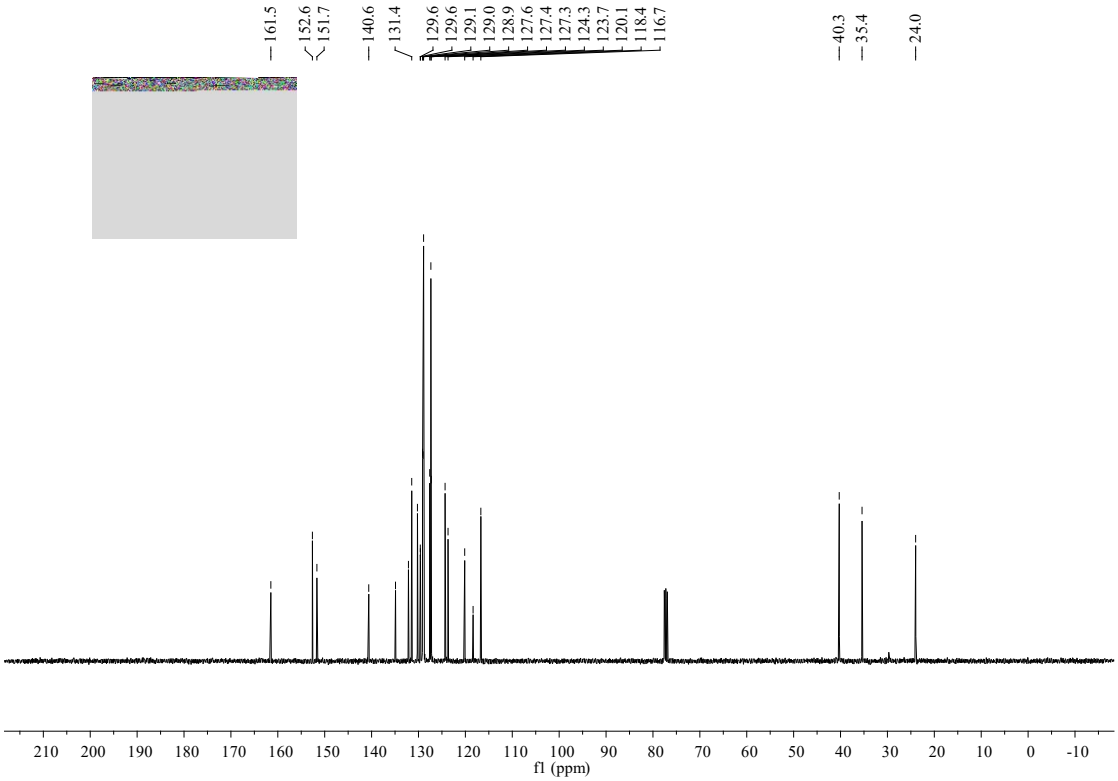


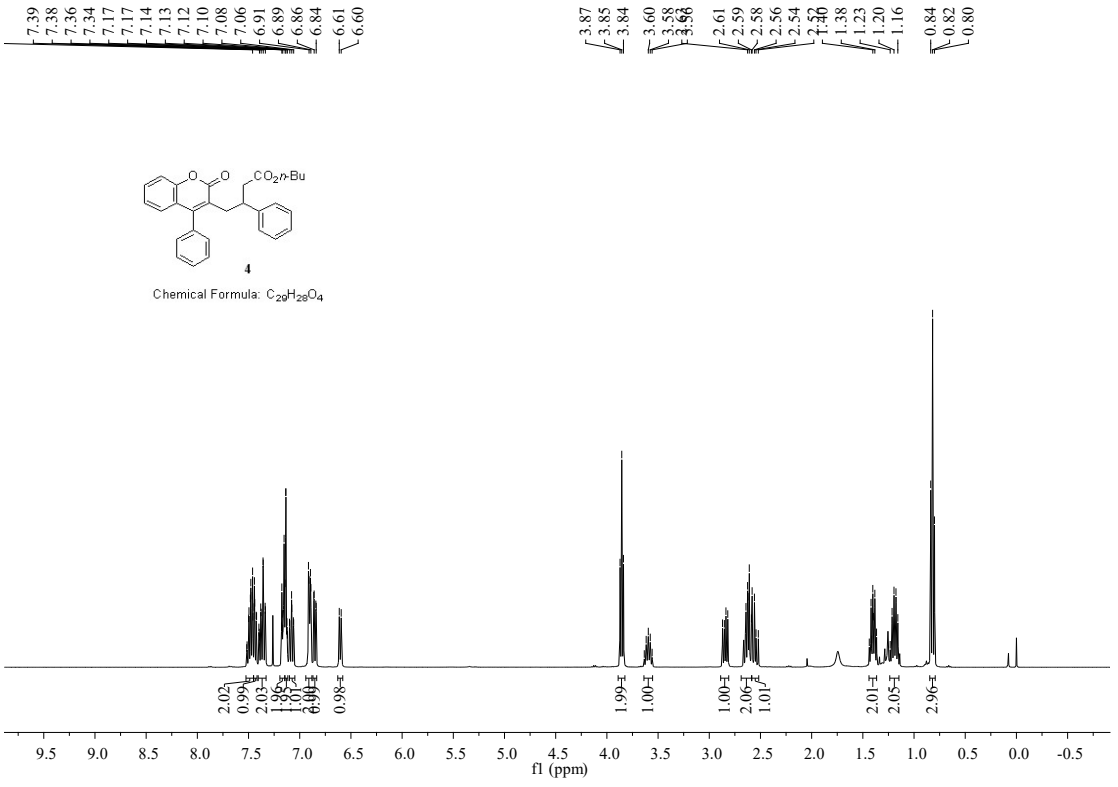
Chemical Formula: $C_{25}H_{18}FNO_2$

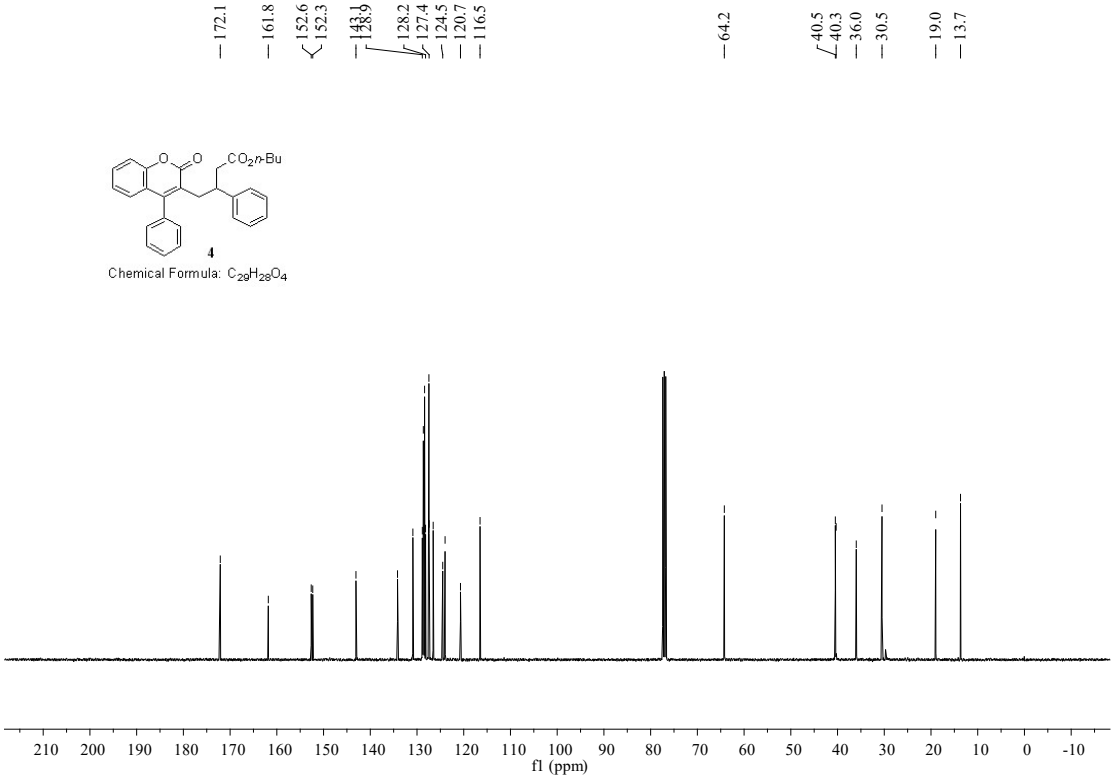


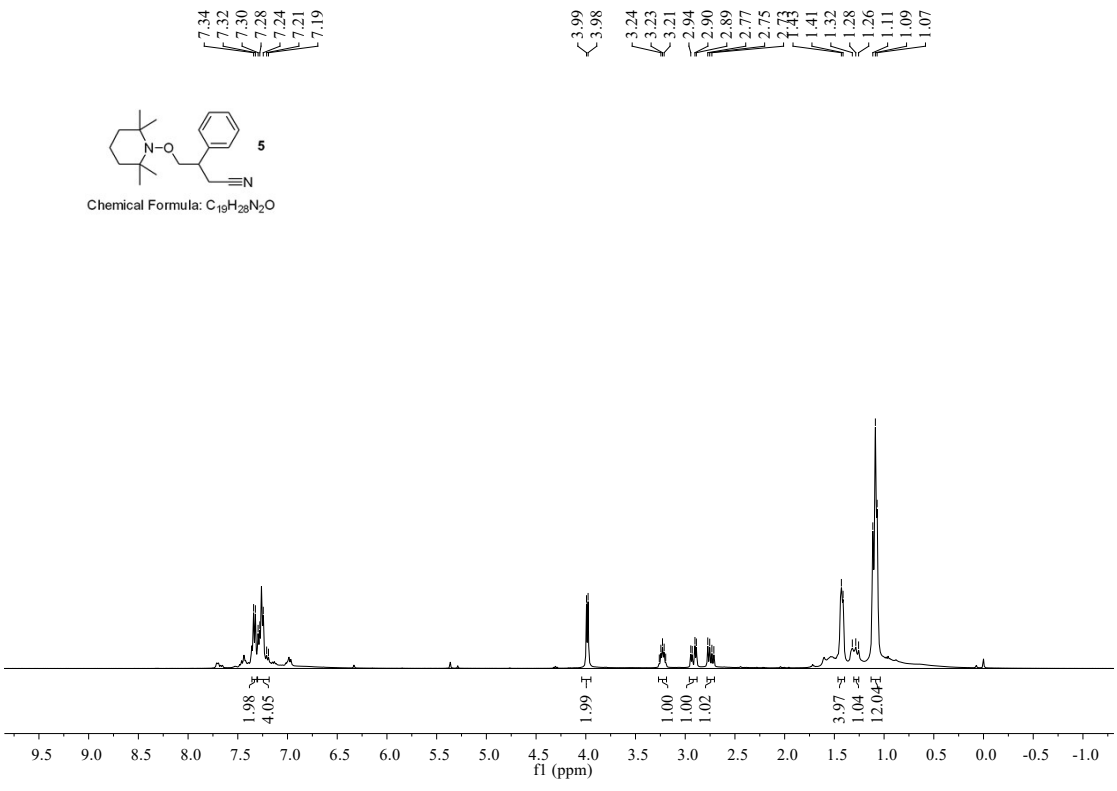

-111.9
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

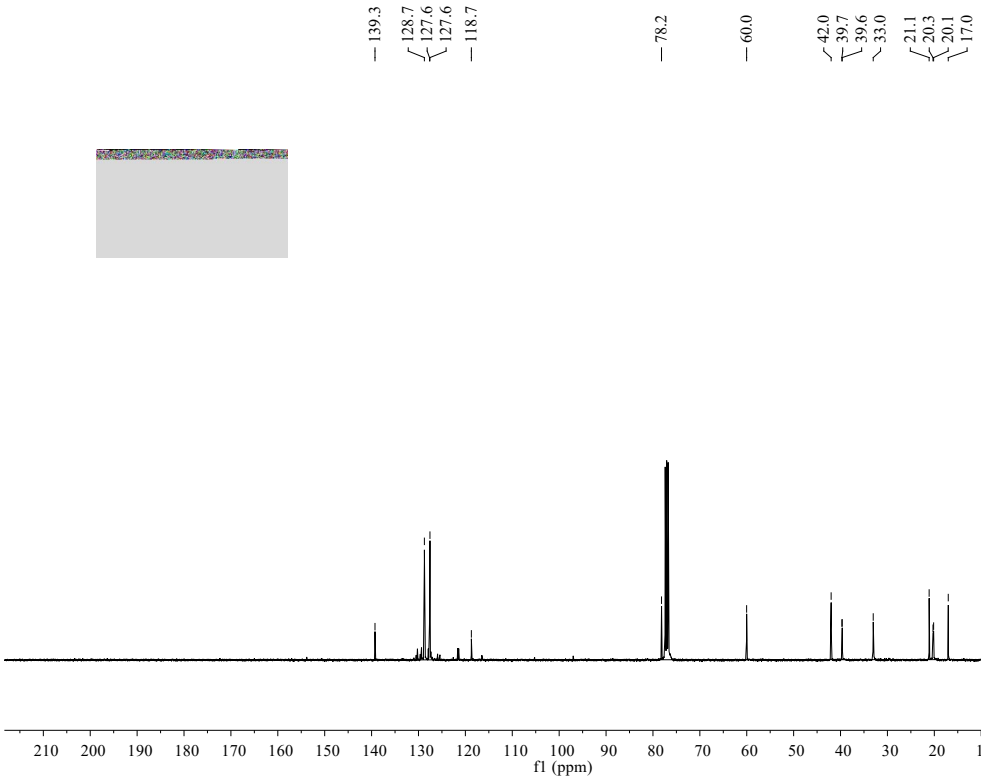

7.29 7.22 7.22 7.21 7.12 7.11 7.10 7.09 7.08 6.95 6.94 6.93 6.92 6.82 6.81 6.80 6.79 6.32 6.32 6.30 6.30
3.55 3.53 3.52 3.50 3.50 2.94 2.71 2.68 2.67 2.65 2.64 2.64 2.63 2.62 2.59 2.57
O O CN Ph Cl
3u
Chemical Formula: C25H18ClNO2
2.01 2.05 3.00 2.03 1.96 0.99 0.98 1.00 0.98 1.04 1.96
10.0 9.5 9.0 8.5 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 0.5 0.0 -0.5 -1.0
f1 (ppm)

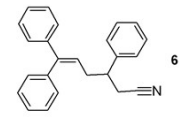

161.5
152.6
151.7
140.6
131.4
129.6
129.6
129.1
129.0
128.9
127.6
127.4
127.3
124.3
123.7
120.1
118.4
116.7
40.3
35.4
24.0
f1 (ppm)


7.39
7.38
7.36
7.34
7.17
7.17
7.14
7.13
7.12
7.10
7.08
7.06
6.91
6.89
6.86
6.84
6.61
6.60
3.87
3.85
3.84
3.60
3.58
2.61
2.59
2.58
2.56
2.54
1.38
1.23
1.20
1.16
0.84
0.82
0.80
CO2n-Bu
4
Chemical Formula: C29H28O4
2.02
0.99
2.03
1.96
1.07
1.00
0.98
1.99
1.00
1.00
2.06
1.01
2.01
2.05
2.96
f1 (ppm)

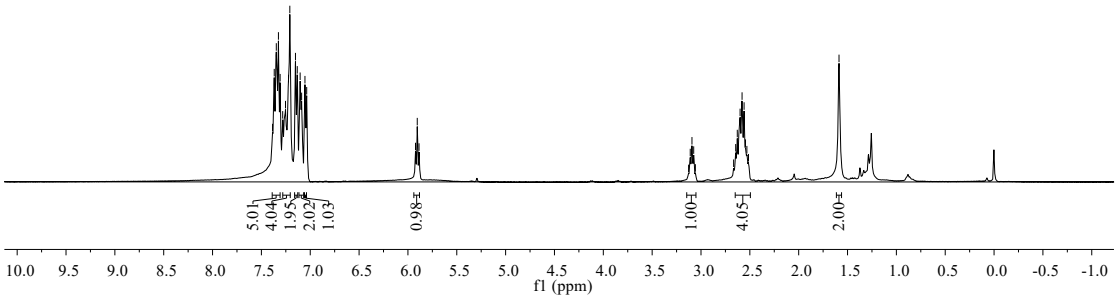

172.1
161.8
152.6
152.3
143.1
128.9
128.2
127.4
124.5
120.7
116.5
64.2
40.5
40.3
36.0
30.5
19.0
13.7
CO2n-Bu
O
O
4
Chemical Formula: C29H28O4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

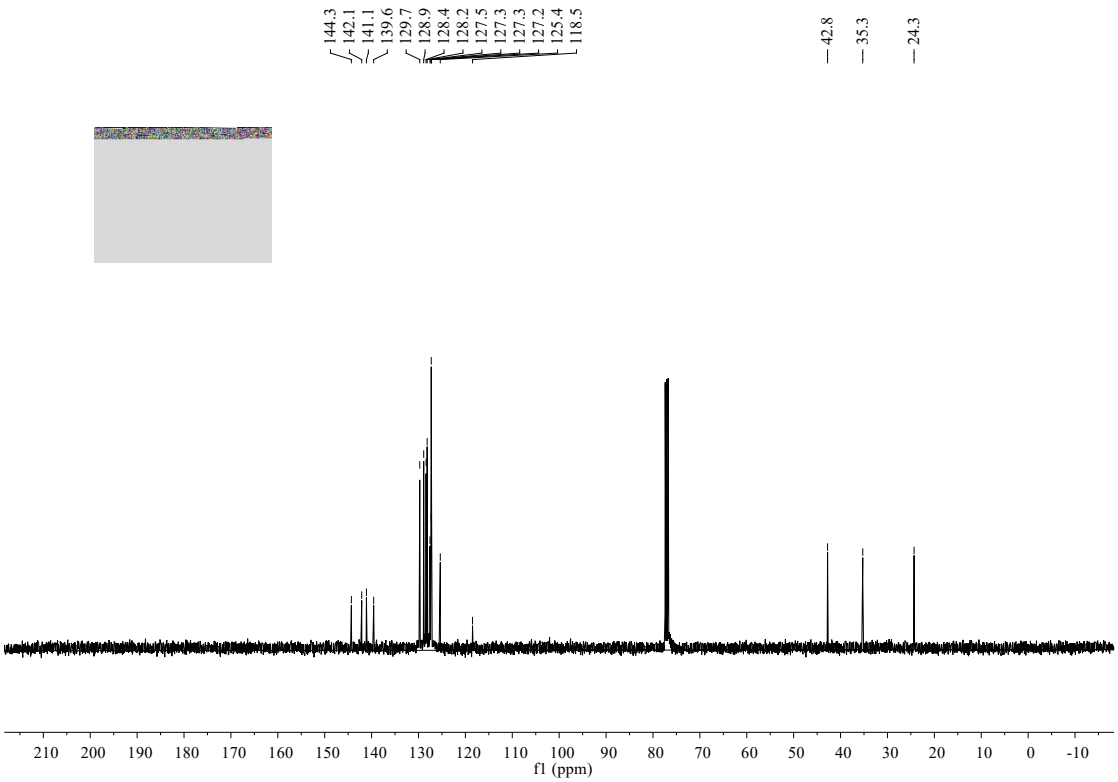

7.34
7.32
7.30
7.28
7.24
7.21
7.19
3.99
3.98
3.24
3.23
3.21
2.94
2.90
2.89
2.77
2.75
2.73
1.43
1.41
1.32
1.28
1.26
1.11
1.09
1.07
N
O
N
5
Chemical Formula: C19H28N2O
1.98
4.05
1.99
1.00
1.00
1.02
3.97
1.04
12.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)





Chemical Formula: $C_{24}H_{21}N$




144.3
142.1
141.1
139.6
129.7
128.9
128.4
128.2
127.5
127.3
127.3
127.2
125.4
118.5
42.8
35.3
24.3
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)