

Supporting information

Enantioselective synthesis of chiral 3-alkyl-3-nitro-4-chromanones via chiral thiourea-catalysed intramolecular Michael-type cyclizations

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Table of Contents

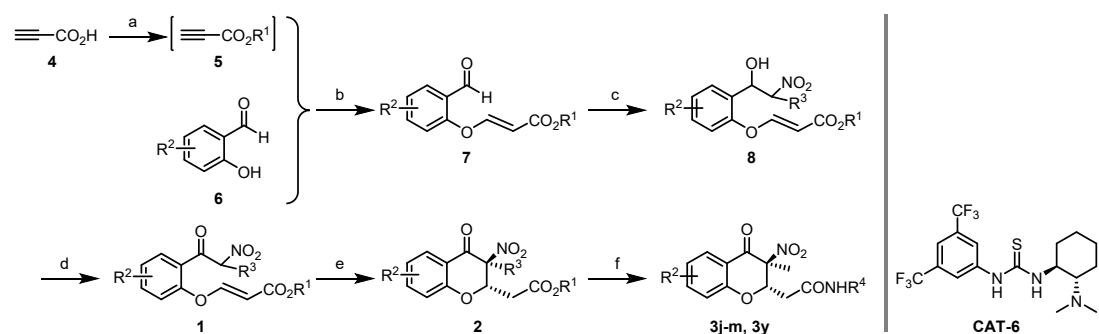
1. General experimental details	S2
2. Experimental procedures and spectral data	S2
3. References	S34
4. Biology materials and methods	S34
5. X-Ray crystallography of 3y (CCDC 2094077).....	S35
6. Chiral HPLC charts	S39
7. NMR charts	S70

1. General experimental details

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. The progress of reactions was monitored by silica gel thin layer chromatography (TLC) plates, visualized under UV. Flash column chromatography was performed using Qingdao Haiyang 200-300 mesh silica gel. Proton, carbon, and fluorine magnetic resonance spectra (^1H NMR, ^{13}C NMR and ^{19}F NMR) were recorded on a Bruker Ascend spectrometer (^1H NMR at 400 MHz; ^{13}C NMR at 100 MHz; ^{19}F NMR at 375 MHz). Chemical shifts (δ) are reported in ppm from the solvent resonance as the internal standard (^1H NMR: CDCl_3 at 7.26 ppm; ^{13}C NMR: CDCl_3 at 77.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. Optically rotations were measured on a Rudolph AUTOPOL VI digital

polarimeter with a sodium lamp and reported as follows: $[\alpha]$ ($c = \text{g}/100 \text{ mL}$, solvent). High resolution mass spectra were performed using a Bruker micrOTOF II high resolution mass spectrometer. Melting points were uncorrected and recorded on a WRR melting point apparatus. Diffraction data were collected on Bruker CCD-APEX X-ray diffractometer. Chiral HPLC was performed with a Chiralpak IF column (1 mL/min, 254 nm) eluting with *n*-hexane/*i*PrOH (90:10) at ambient temperature and monitored by DAD (Diode Array Detector).

2. Experimental procedures and spectral data



(a) R^1OH , TsOH , PhMe , reflux, Dean-Stark trap; (b) NMM, 0 °C-rt, 33-52% for 2 steps; (c) $\text{R}^3\text{CH}_2\text{NO}_2$, KOt-Bu (0.1 equiv.), rt, 83-95%; (d) DMP (1.2 equiv.), dry CH_2Cl_2 , rt, 81-95%; (e) **CAT-6** (10 mol%), toluene, -30 °C, 90-99%; (f) 1) HCl/HOAc , 100 °C; 2) R^4NH_2 , Et_3N , HOBT, EDCI, CH_2Cl_2 , 0 °C, 52-76%.

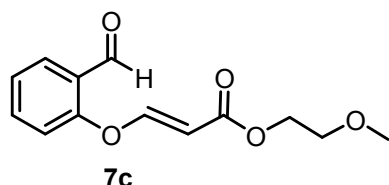
Preparation of **7a-b**, **7h**, **8a-b**, **8h**, **1a-b** and **1h** was carried out following the literature procedure.¹

General Procedure for the synthesis of 7

Propiolic acid (700 mg, 10.0 mmol, 1 equiv.) and corresponding alcohol R^2OH (10.0 mmol, 1 equiv.) were added to the toluene (20 mL) with 5 mol% *p*-toluenesulfonic acid used as catalyst. A Dean-Stark trap and a condenser were attached, and the reaction was protected under nitrogen. The mixture was heated to reflux for 2 h. Then the mixture was allowed to reach 0 °C. To the mixture was added corresponding salicylaldehyde **6** (10.0 mmol, 1 equiv.) and 4-methylmorpholine (1.2 mmol, 0.2 equiv.). The resulting mixture was allowed to stir at

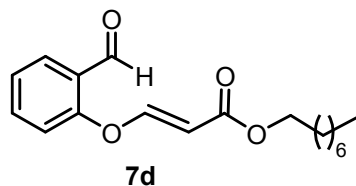
room temperature for 12 h. Then 1 N HCl (10 mL) was added and the biphasic mixture was allowed to warm to room temperature. The phases were separated and the aqueous phase was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine (20 mL), then dried over Na₂SO₄, filtered and concentrated in vacuo to give a crude residue. The residue was purified by silica gel chromatography (petroleum ether:EtOAc, 20:1-5:1) to afford desired products **7** (33-52%).

2-methoxyethyl (*E*)-3-(2-formylphenoxy)acrylate (**7c**)



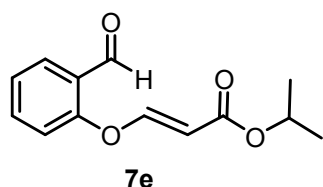
7c (1.12 g, 45%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 10.34 (s, 1H), 7.91 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.86 (d, *J* = 12.4 Hz, 1H), 7.66-7.62 (m, 1H), 7.34-7.30 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 5.65 (d, *J* = 12.0 Hz, 1H), 4.30 (t, *J* = 4.4 Hz, 2H), 3.62 (t, *J* = 4.8 Hz, 2H), 3.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 188.20, 166.67, 158.71, 157.55, 136.14, 129.12, 126.74, 125.64, 118.66, 103.81, 70.62, 63.53, 59.12. HRMS (ESI): Calcd for C₁₃H₁₄NaO₅ [M+Na]⁺: 273.0733. Found: 273.0739.

octyl (*E*)-3-(2-formylphenoxy)acrylate (**7d**)



7d (1.40 g, 47%), yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 10.37 (s, 1H), 7.93 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.83 (d, *J* = 12.4 Hz, 1H), 7.66-7.62 (m, 1H), 7.33-7.29 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 5.63 (d, *J* = 12.0 Hz, 1H), 4.14 (t, *J* = 6.8 Hz, 2H), 1.63 (t, *J* = 5.2 Hz, 2H), 1.35-1.27 (m, 10H), 0.87 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 188.25, 166.78, 158.06, 157.71, 136.14, 129.10, 126.69, 125.50, 118.40, 104.36, 64.77, 31.90, 29.34, 29.29, 28.80, 26.07, 22.75, 14.20. HRMS (ESI): Calcd for C₁₈H₂₅O₄ [M+H]⁺: 305.1747. Found: 305.1752.

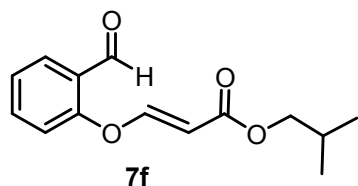
isopropyl (*E*)-3-(2-formylphenoxy)acrylate (**7e**)



7e (0.97 g, 42%), yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 10.36 (s, 1H), 7.92 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.82 (d, *J* = 12.4 Hz, 1H), 7.66-7.62 (m, 1H), 7.33-7.29 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 5.60 (d, *J* = 12.0 Hz, 1H), 5.08 (hept, *J* = 6.4 Hz, 1H), 1.27 (d, *J* = 6.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 188.30, 166.23, 157.99, 157.73, 136.16, 129.05, 126.68, 125.49,

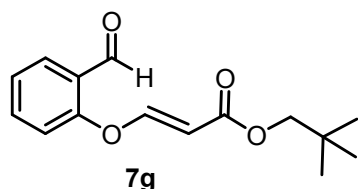
118.51, 104.76, 67.90, 22.03 (2C). HRMS (ESI): Calcd for C₁₃H₁₄NaO₄ [M+Na]⁺: 257.0784. Found: 257.0777.

isobutyl (*E*)-3-(2-formylphenoxy)acrylate (**7f**)



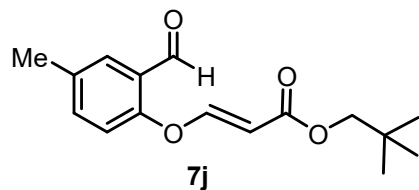
7f (1.01 g, 41%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 10.36 (s, 1H), 7.93 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.84 (d, *J* = 12.0 Hz, 1H), 7.67-7.63 (m, 1H), 7.34-7.30 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 5.65 (d, *J* = 12.0 Hz, 1H), 3.94 (d, *J* = 6.8 Hz, 2H), 1.97 (hept, *J* = 6.8 Hz, 1H), 0.95 (d, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 188.29, 166.79, 158.06, 157.72, 136.18, 129.13, 126.67, 125.52, 118.38, 104.34, 70.68, 27.92, 19.26 (2C). HRMS (ESI): Calcd for C₁₄H₁₆NaO₄ [M+Na]⁺: 271.0941. Found: 271.0942.

neopentyl (*E*)-3-(2-formylphenoxy)acrylate (**7g**)



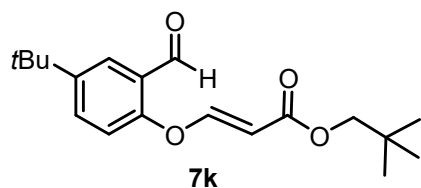
7g (1.33 g, 51%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 10.37 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 12.0 Hz, 1H), 7.67-7.63 (m, 1H), 7.34-7.30 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 5.67 (d, *J* = 12.0 Hz, 1H), 3.85 (s, 2H), 0.95 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 188.31, 166.85, 157.97, 157.71, 136.21, 129.10, 126.59, 125.49, 118.28, 104.35, 73.83, 31.55, 26.61 (3C). HRMS (ESI): Calcd for C₁₅H₁₈NaO₄ [M+Na]⁺: 285.1097. Found: 285.1086.

neopentyl (*E*)-3-(2-formyl-4-methylphenoxy)acrylate (**7j**)



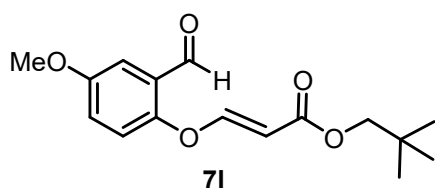
7j (1.40 g, 52%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 10.31 (s, 1H), 7.81 (d, *J* = 12.0 Hz, 1H), 7.71 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 5.60 (d, *J* = 12.0 Hz, 1H), 3.84 (s, 2H), 2.38 (s, 3H), 0.94 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 188.49, 166.95, 158.64, 155.68, 136.84, 135.51, 129.07, 126.28, 118.49, 103.70, 73.76, 31.53, 26.60, 20.75 (3C). HRMS (ESI): Calcd for C₁₆H₂₀NaO₄ [M+Na]⁺: 299.1254. Found: 299.1264.

neopentyl (*E*)-3-(4-(*tert*-butyl)-2-formylphenoxy)acrylate (**7k**)



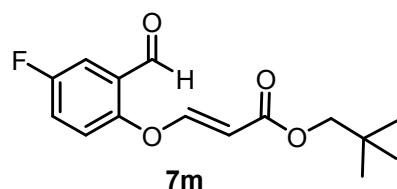
7k (1.51 g, 48%), white solid, m.p. 70-71 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.35 (s, 1H), 7.93 (d, *J* = 2.0 Hz, 1H), 7.83 (d, *J* = 12.0 Hz, 1H), 7.67 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 5.63 (d, *J* = 12.0 Hz, 1H), 3.85 (s, 2H), 1.34 (s, 9H), 0.96 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 188.66, 166.96, 158.51, 155.64, 148.81, 133.47, 125.96, 125.57, 118.15, 103.82, 73.78, 34.82, 31.56, 31.33 (3C), 26.62 (3C). HRMS (ESI): Calcd for C₁₉H₂₆NaO₄ [M+Na]⁺: 341.1723. Found: 341.1735.

neopentyl (*E*)-3-(2-formyl-4-methoxyphenoxy)acrylate (**7l**)



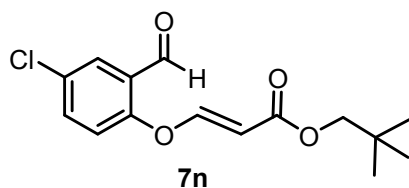
7l (1.24 g, 43%), white solid, m.p. 68-70 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.28 (s, 1H), 7.80 (d, *J* = 12.0 Hz, 1H), 7.37 (d, *J* = 2.0 Hz, 1H), 7.18 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 5.52 (d, *J* = 12.0 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 2H), 0.94 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 188.09, 166.95, 159.52, 157.15, 151.69, 127.32, 123.51, 120.66, 110.75, 103.22, 73.75, 56.01, 31.53, 26.60 (3C). HRMS (ESI): Calcd for C₁₆H₂₀NaO₅ [M+Na]⁺: 315.1203. Found: 315.1213.

neopentyl (*E*)-3-(4-fluoro-2-formylphenoxy)acrylate (**7m**)



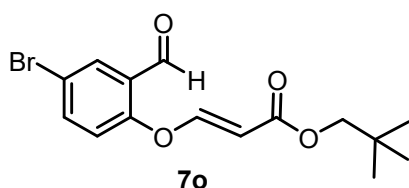
7m (1.08 g, 39%), yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 10.28 (s, 1H), 7.80 (d, *J* = 12.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.37-7.33 (m, 1H), 7.15 (dd, *J* = 8.8, 3.2 Hz, 1H), 5.61 (d, *J* = 12.0 Hz, 1H), 3.84 (s, 2H), 0.94 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 187.06, 166.65, 159.77 (d, *J* = 246.1 Hz, 1C), 158.39, 153.67 (d, *J* = 2.6 Hz, 1C), 127.97 (d, *J* = 6.3 Hz, 1C), 123.05 (d, *J* = 24.1 Hz, 1C), 120.66 (d, *J* = 7.7 Hz, 1C), 114.92 (d, *J* = 23.8 Hz, 1C), 104.31, 73.89, 31.54, 26.59 (3C). HRMS (ESI): Calcd for C₁₅H₁₇FN₄ [M+Na]⁺: 303.1003. Found: 303.0986.

neopentyl (*E*)-3-(4-chloro-2-formylphenoxy)acrylate (**7n**)



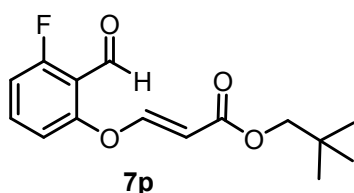
7n (1.22 g, 42%), white solid, m.p. 83-84 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.32 (s, 1H), 7.89 (d, *J* = 2.8 Hz, 1H), 7.80 (d, *J* = 12.0 Hz, 1H), 7.61 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 1H), 5.69 (d, *J* = 12.0 Hz, 1H), 3.87 (s, 2H), 0.96 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 186.93, 166.56, 157.50, 156.02, 135.84, 131.41, 128.73, 127.50, 119.85, 104.94, 73.94, 31.55, 26.60 (3C). HRMS (ESI): Calcd for C₁₅H₁₇ClNaO₄ [M+Na]⁺: 319.0708. Found: 319.0725 ([M+Na]⁺), 321.0672 ([M+2+Na]⁺).

neopentyl (*E*)-3-(4-bromo-2-formylphenoxy)acrylate (**7o**)



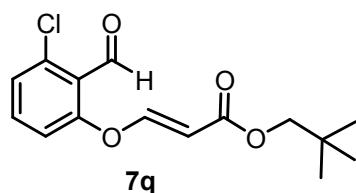
7o (1.50 g, 44%), white solid, m.p. 62-63 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.30 (s, 1H), 8.03 (s, 1H), 7.79 (d, *J* = 12.4 Hz, 1H), 7.74 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 1H), 5.69 (d, *J* = 12.0 Hz, 1H), 3.87 (s, 2H), 0.96 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 186.85, 166.56, 157.33, 156.54, 138.76, 131.81, 127.77, 120.08, 118.72, 105.05, 73.95, 31.55, 26.60 (3C). HRMS (ESI): Calcd for C₁₅H₁₇BrNaO₄ [M+Na]⁺: 363.0202. Found: 363.0218 ([M+Na]⁺), 365.0198 ([M+2+Na]⁺).

neopentyl (*E*)-3-(3-fluoro-2-formylphenoxy)acrylate (**7p**)



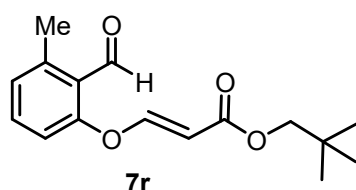
7p (0.93 g, 33%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 10.37 (s, 1H), 7.76 (d, *J* = 12.4 Hz, 1H), 7.62-7.58 (m, 1H), 7.05-7.00 (m, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 5.69 (d, *J* = 12.0 Hz, 1H), 3.85 (s, 2H), 0.95 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 185.67, 185.63, 166.72, 163.44 (d, *J* = 262.5 Hz, 1C), 157.20 (d, *J* = 4.9 Hz, 1C), 157.17, 136.34 (d, *J* = 1.4 Hz, 1C), 116.10 (d, *J* = 9.6 Hz, 1C), 114.20 (d, *J* = 3.7 Hz, 1C), 113.46 (d, *J* = 21.3 Hz, 1C), 73.89, 31.54, 26.60 (3C). HRMS (ESI): Calcd for C₁₅H₁₇FNaO₄ [M+Na]⁺: 303.1003. Found: 303.1018.

neopentyl (*E*)-3-(3-chloro-2-formylphenoxy)acrylate (**7q**)



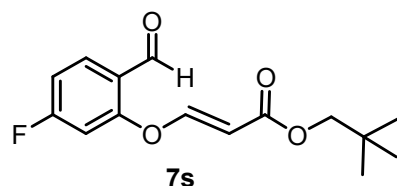
7q (1.07 g, 37%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.45 (s, 1H), 7.72 (d, $J = 12.4$ Hz, 1H), 7.54-7.50 (m, 1H), 7.33 (d, $J = 8.4$ Hz, 1H), 7.07 (d, $J = 8.4$ Hz, 1H), 5.59 (d, $J = 12.4$ Hz, 1H), 3.85 (s, 2H), 0.95 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 187.75, 166.76, 158.06, 156.94, 137.35, 134.91, 127.91, 124.51, 118.04, 104.17, 73.83, 31.55, 26.61 (3C). HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{17}\text{ClNaO}_4$ $[\text{M}+\text{Na}]^+$: 319.0708. Found: 319.0694 ($[\text{M}+\text{Na}]^+$), 321.0674 ($[\text{M}+2+\text{Na}]^+$).

neopentyl (*E*)-3-(2-formyl-3-methylphenoxy)acrylate (**7r**)



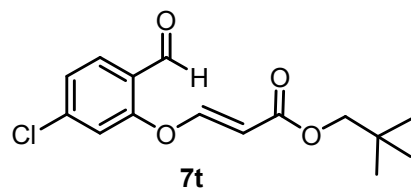
7r (1.33 g, 49%), yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.50 (s, 1H), 7.79 (d, $J = 12.4$ Hz, 1H), 7.49-7.45 (m, 1H), 7.09 (d, $J = 8.0$ Hz, 1H), 6.98 (d, $J = 8.4$ Hz, 1H), 5.61 (d, $J = 12.4$ Hz, 1H), 3.85 (s, 2H), 2.61 (s, 3H), 0.95 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 190.62, 166.91, 159.09, 158.44, 142.76, 134.72, 128.80, 125.05, 116.13, 103.93, 73.76, 31.53, 26.60, 21.40 (3C). HRMS (ESI): Calcd for $\text{C}_{16}\text{H}_{20}\text{NaO}_4$ $[\text{M}+\text{Na}]^+$: 299.1254. Found: 299.1260.

neopentyl (*E*)-3-(5-fluoro-2-formylphenoxy)acrylate (**7s**)



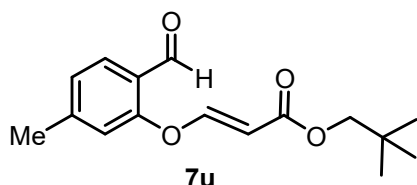
7s (1.06 g, 39%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.29 (s, 1H), 7.98-7.94 (m, 1H), 7.78 (dd, $J = 12.4, 1.2$ Hz, 1H), 7.03-6.99 (m, 1H), 6.88 (d, $J = 9.2$ Hz, 1H), 5.75 (dd, $J = 12.4, 1.2$ Hz, 1H), 3.86 (d, $J = 0.8$ Hz, 2H), 0.95 (d, $J = 1.2$ Hz, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 186.79, 167.15 (d, $J = 257.7$ Hz, 1C), 166.46, 159.10 (d, $J = 10.7$ Hz, 1C), 156.67, 131.42 (d, $J = 10.9$ Hz, 1C), 123.20 (d, $J = 3.1$ Hz, 1C), 112.94 (d, $J = 21.8$ Hz, 1C), 105.74 (d, $J = 25.3$ Hz, 1C), 105.59, 73.98, 31.55, 26.60 (3C). HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{17}\text{FNaO}_4$ $[\text{M}+\text{Na}]^+$: 303.1003. Found: 303.1012.

neopentyl (*E*)-3-(5-chloro-2-formylphenoxy)acrylate (**7t**)



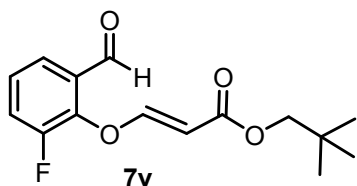
7t (1.24 g, 43%), white solid, m.p. 52-53 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.31 (s, 1H), 7.87 (d, $J = 8.4$ Hz, 1H), 7.78 (d, $J = 12.4$ Hz, 1H), 7.29 (d, $J = 8.4$ Hz, 1H), 7.17 (d, $J = 1.2$ Hz, 1H), 5.75 (d, $J = 12.4$ Hz, 1H), 3.87 (s, 2H), 0.95 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 187.11, 166.51, 157.94, 156.90, 142.15, 130.17, 125.95, 124.97, 118.57, 105.50, 74.00, 31.57, 26.61 (3C). HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{17}\text{ClNaO}_4$ $[\text{M}+\text{Na}]^+$: 319.0708. Found: 319.0724 ($[\text{M}+\text{Na}]^+$), 321.0670 ($[\text{M}+2+\text{Na}]^+$).

neopentyl (*E*)-3-(2-formyl-5-methylphenoxy)acrylate (**7u**)



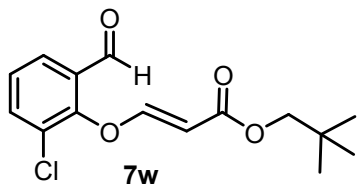
7u (1.38 g, 51%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.31 (s, 1H), 7.83 (d, $J = 12.4$ Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.12 (d, $J = 8.0$ Hz, 1H), 6.94 (s, 1H), 5.66 (d, $J = 12.4$ Hz, 1H), 3.87 (s, 2H), 2.44 (s, 3H), 0.95 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 188.02, 167.01, 158.17, 157.77, 148.02, 129.02, 126.46, 124.31, 118.79, 104.12, 73.82, 31.57, 26.63, 22.16 (3C). HRMS (ESI): Calcd for $\text{C}_{16}\text{H}_{20}\text{NaO}_4$ $[\text{M}+\text{Na}]^+$: 299.1254. Found: 299.1277.

neopentyl (*E*)-3-(6-fluoro-2-formylphenoxy)acrylate (**7v**)



7v (1.21 g, 44%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.24 (s, 1H), 7.82 (d, $J = 12.4$ Hz, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.49-7.45 (m, 1H), 7.38-7.33 (m, 1H), 5.38 (d, $J = 12.4$ Hz, 1H), 3.83 (s, 2H), 0.95 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 187.17 (d, $J = 3.3$ Hz, 1C), 166.52, 160.17 (d, $J = 2.4$ Hz, 1C), 154.07 (d, $J = 251.9$ Hz, 1C), 144.22 (d, $J = 12.5$ Hz, 1C), 129.81, 127.05 (d, $J = 7.0$ Hz, 1C), 124.33 (d, $J = 3.6$ Hz, 1C), 123.22 (d, $J = 18.3$ Hz, 1C), 102.50, 73.90, 31.53, 26.60 (3C). HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{17}\text{FNaO}_4$ $[\text{M}+\text{Na}]^+$: 303.1003. Found: 303.1019.

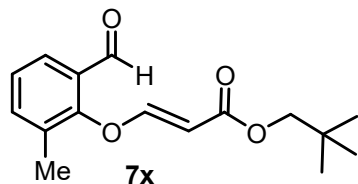
neopentyl (*E*)-3-(6-chloro-2-formylphenoxy)acrylate (**7w**)



7w (1.37 g, 47%), yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.18 (s, 1H), 7.85 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.80 (d, $J = 12.4$ Hz, 1H), 7.73 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.39-7.35 (m, 1H), 5.20 (d, $J = 12.4$ Hz, 1H), 3.83 (s, 2H), 0.93 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 187.43, 166.61, 160.13, 152.43, 136.78, 129.86, 127.98, 127.71, 127.52, 102.17, 73.92, 31.51, 26.60 (3C). HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{17}\text{ClNaO}_4$ $[\text{M}+\text{Na}]^+$: 319.0708. Found: 319.0724

$[\text{M}+\text{Na}]^+$, 321.0684 ($[\text{M}+2+\text{Na}]^+$).

neopentyl (*E*)-3-(2-formyl-6-methylphenoxy)acrylate (**7x**)

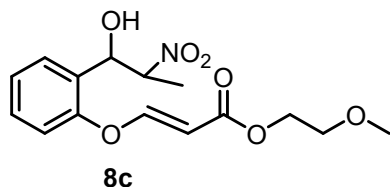


7x (1.44 g, 52%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.18 (s, 1H), 7.84 (d, $J = 12.4$ Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.34-7.30 (m, 1H), 5.06 (d, $J = 12.4$ Hz, 1H), 3.80 (s, 2H), 2.28 (s, 3H), 0.93 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 188.65, 166.92, 160.92, 154.63, 137.98, 131.52, 128.18, 127.24, 126.72, 101.11, 73.77, 31.51, 26.62 (3C), 15.69. HRMS (ESI): Calcd for $\text{C}_{16}\text{H}_{20}\text{NaO}_4$ $[\text{M}+\text{Na}]^+$: 299.1254. Found: 299.1258.

General Procedure for the synthesis of **8**

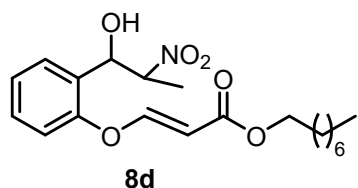
To a solution of compound **7** (3 mmol, 1 equiv.) in 5 mL of $\text{R}^3\text{CH}_2\text{NO}_2$ was added 56 mg (0.3 mmol, 0.1 equiv.) of $\text{KO}t\text{-Bu}$. The resulting mixture was stirred at room temperature for 2 h. 1 N HCl (10 mL) was added and the biphasic mixture was extracted with EtOAc (3×20 mL). The combined organic extracts were washed with brine (20 mL), then dried over Na_2SO_4 , filtered and concentrated in vacuo to give a crude residue. The residue was purified by silica gel chromatography (petroleum ether:EtOAc:HOAc, 100:20:0.5) to afford desired products **8** (83-95%).

2-methoxyethyl (*E*)-3-(2-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8c**)



8c (895.8 mg, 92%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (d, $J = 12.4$ Hz, 1H), 7.51-7.49 (m, 1H), 7.41-7.37 (m, 1H), 7.27 (d, $J = 8.0$ Hz, 1H), 7.07 (d, $J = 8.0$ Hz, 1H), 5.62 (d, $J = 12.4$ Hz, 1H), 5.35 (d, $J = 8.8$ Hz, 1H), 4.85-4.78 (m, 1H), 4.27 (t, $J = 4.8$ Hz, 2H), 3.61 (t, $J = 4.8$ Hz, 2H), 3.38 (s, 3H), 3.18 (br s, 1H), 1.35 (d, $J = 6.8$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.97, 158.89, 152.92, 130.57, 129.26, 128.60, 126.05, 118.18, 103.11, 88.14, 70.61, 70.28, 63.47, 59.08, 16.34. HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{19}\text{NNaO}_7$ $[\text{M}+\text{Na}]^+$: 348.1054. Found: 348.1077.

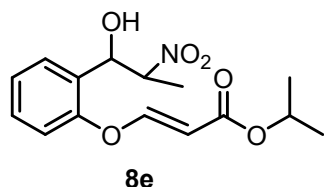
octyl (*E*)-3-(2-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8d**)



8d (1.04 g, 93%), yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.74 (d, $J = 12.4$ Hz, 1H),

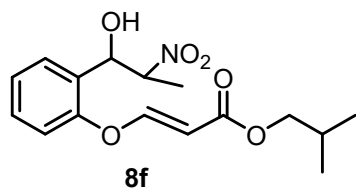
7.51-7.49 (m, 1H), 7.41-7.37 (m, 1H), 7.27 (d, $J = 8.0$ Hz, 1H), 7.07 (d, $J = 8.0$ Hz, 1H), 5.62 (d, $J = 12.4$ Hz, 1H), 5.35 (d, $J = 8.8$ Hz, 1H), 4.85-4.78 (m, 1H), 4.12 (t, $J = 4.8$ Hz, 2H), 3.08 (br s, 1H), 1.66-1.61 (m, 2H), 1.37 (d, $J = 6.8$ Hz, 3H), 1.32-1.25 (m, 10H), 0.88 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.15, 158.24, 153.07, 130.59, 129.08, 128.60, 125.91, 117.91, 103.71, 88.12, 70.40, 64.81, 31.91, 29.35, 29.30, 28.79, 26.07, 22.76, 16.36, 14.20. HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{29}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 402.1892. Found: 402.1899.

isopropyl (*E*)-3-(2-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8e**)



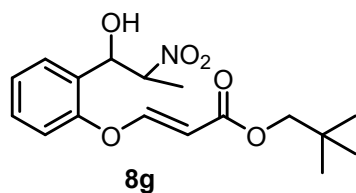
8e (816.4 mg, 88%), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 12.4$ Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.41-7.37 (m, 1H), 7.28-7.26 (m, 1H), 7.07 (d, $J = 8.0$ Hz, 1H), 5.59 (d, $J = 12.4$ Hz, 1H), 5.36 (d, $J = 8.8$ Hz, 1H), 5.07 (hept, $J = 2.4$ Hz, 1H), 4.87-4.79 (m, 1H), 3.04 (br s, 1H), 1.37 (d, $J = 6.8$ Hz, 3H), 1.26 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.56, 158.07, 153.07, 130.58, 129.07, 128.59, 125.88, 117.96, 104.15, 88.13, 70.44, 67.96, 22.03 (2C), 16.37. HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{19}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 332.1105. Found: 332.1127.

isobutyl (*E*)-3-(2-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8f**)



8f (883.2 mg, 91%), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 12.4$ Hz, 1H), 7.51-7.49 (m, 1H), 7.42-7.38 (m, 1H), 7.27 (d, $J = 8.0$ Hz, 1H), 7.07 (d, $J = 8.0$ Hz, 1H), 5.63 (d, $J = 12.4$ Hz, 1H), 5.37 (d, $J = 8.8$ Hz, 1H), 4.87-4.79 (m, 1H), 3.91 (d, $J = 6.8$ Hz, 2H), 3.04 (br s, 1H), 1.96 (hept, $J = 6.4$ Hz, 1H), 1.37 (d, $J = 6.8$ Hz, 3H), 0.94 (d, $J = 6.0$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.15, 158.22, 153.06, 130.61, 129.02, 128.60, 125.92, 117.85, 103.68, 88.12, 70.70, 70.39, 27.89, 19.24 (2C), 16.36. HRMS (ESI): Calcd for $\text{C}_{16}\text{H}_{21}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 346.1261. Found: 346.1268.

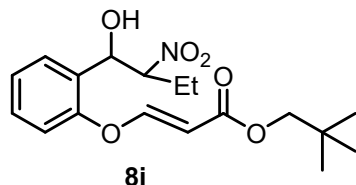
neopentyl (*E*)-3-(2-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8g**)



8g (930.3 mg, 92%), yellow solid, m.p. 75-76 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 12.4$ Hz, 1H), 7.51-7.49 (m, 1H), 7.42-7.38 (m, 1H), 7.27 (d, $J = 8.0$ Hz, 1H), 7.07 (d, $J = 8.0$ Hz, 1H), 5.66 (d, $J = 12.4$ Hz, 1H), 5.38 (d, $J = 8.8$ Hz, 1H), 4.87-4.79 (m, 1H), 3.84 (s,

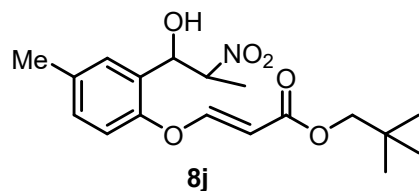
2H), 2.99 (br s, 1H), 1.37 (d, $J = 6.8$ Hz, 3H), 0.96 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.17, 158.12, 153.10, 130.62, 129.00, 128.61, 125.89, 117.76, 103.75, 88.11, 73.87, 70.42, 31.54, 26.61 (3C), 16.36. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{23}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 360.1418. Found: 360.1427.

neopentyl (*E*)-3-(2-(1-hydroxy-2-nitrobutyl)phenoxy)acrylate (**8i**)



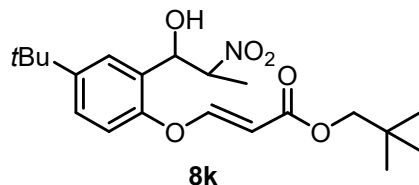
8i (966.3 mg, 92%), colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 12.0$ Hz, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.41-7.38 (m, 1H), 7.28-7.24 (m, 1H), 7.07 (d, $J = 8.0$ Hz, 1H), 5.66 (d, $J = 12.0$ Hz, 1H), 5.37 (d, $J = 8.4$ Hz, 1H), 4.71-4.66 (m, 1H), 3.84 (s, 2H), 2.95 (br s, 1H), 1.99-1.91 (m, 1H), 1.52-1.45 (m, 1H), 0.96 (s, 9H), 0.90 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.18, 158.11, 153.03, 130.60, 129.24, 128.54, 125.92, 117.75, 103.73, 94.81, 73.88, 69.67, 31.54, 26.61 (3C), 23.82, 10.32. HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{25}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 374.1574. Found: 374.1589.

neopentyl (*E*)-3-(2-(1-hydroxy-2-nitropropyl)-4-methylphenoxy)acrylate (**8j**)



8j (977.5 mg, 93%), yellow solid, m.p. 70-71 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 12.0$ Hz, 1H), 7.40 (s, 1H), 7.16 (d, $J = 8.0$ Hz, 1H), 6.93 (d, $J = 8.0$ Hz, 1H), 5.63-5.61 (m, 1H), 5.60 (d, $J = 12.0$ Hz, 1H), 4.80-4.74 (m, 1H), 3.84 (s, 2H), 2.91 (d, $J = 4.0$ Hz, 1H), 2.36 (s, 3H), 1.46 (d, $J = 6.8$ Hz, 3H), 0.95 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.23, 158.38, 149.93, 135.45, 130.51, 128.44, 128.37, 117.35, 103.14, 85.21, 73.79, 69.06, 31.54, 26.62 (3C), 21.09, 11.99. HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{25}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 374.1574. Found: 374.1565.

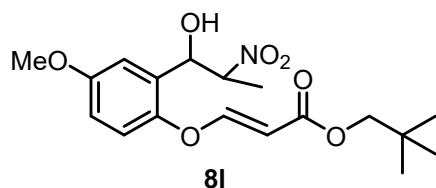
neopentyl (*E*)-3-(4-(tert-butyl)-2-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8k**)



8k (1.02 g, 87%), colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 12.0$ Hz, 1H), 7.61 (d, $J = 1.6$ Hz, 1H), 7.37 (dd, $J = 8.0, 1.6$ Hz, 1H), 6.97 (d, $J = 8.0$ Hz, 1H), 5.66-5.64 (m, 1H), 5.63 (d, $J = 12.0$ Hz, 1H), 4.80-4.74 (m, 1H), 3.84 (s, 2H), 2.92 (d, $J = 3.2$ Hz, 1H), 1.45 (d, $J = 6.8$ Hz, 3H), 1.33 (s, 9H), 0.95 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.21, 158.26, 149.84, 148.71, 127.92, 126.81, 125.01, 116.86, 103.24, 85.25, 73.78, 69.24, 34.80, 31.54,

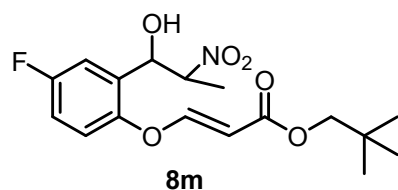
31.49 (3C), 26.63 (3C), 11.94. HRMS (ESI): Calcd for C₂₁H₃₁NNaO₆ [M+Na]⁺: 416.2044. Found: 416.2059.

neopentyl (*E*)-3-(2-(1-hydroxy-2-nitropropyl)-4-methoxyphenoxy)acrylate (**8l**)



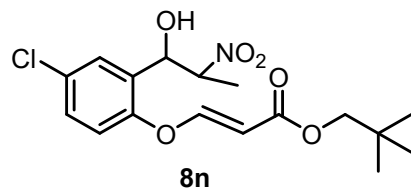
8l (915.4 mg, 84%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 12.0 Hz, 1H), 7.01 (d, *J* = 2.8 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.8 Hz, 1H), 5.54 (d, *J* = 12.0 Hz, 1H), 5.33-5.30 (m, 1H), 4.84-4.77 (m, 1H), 3.84 (s, 2H), 3.82 (s, 3H), 2.80 (d, *J* = 4.2 Hz, 1H), 1.39 (d, *J* = 6.8 Hz, 3H), 0.95 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 167.20, 159.33, 157.47, 146.59, 130.23, 119.72, 115.79, 113.20, 102.76, 88.12, 73.79, 70.40, 55.92, 31.56, 26.64 (3C), 16.40. HRMS (ESI): Calcd for C₁₈H₂₅NNaO₇ [M+Na]⁺: 390.1523. Found: 390.1538.

neopentyl (*E*)-3-(4-fluoro-2-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8m**)



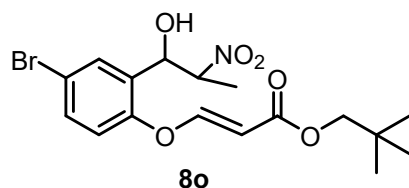
8m (903.9 mg, 85%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 12.0 Hz, 1H), 7.25-7.24 (m, 1H), 7.11-7.03 (m, 2H), 5.60 (d, *J* = 12.0 Hz, 1H), 5.34 (d, *J* = 8.0 Hz, 1H), 4.81-4.74 (m, 1H), 3.83 (s, 2H), 3.16 (br s, 1H), 1.41 (d, *J* = 6.8 Hz, 3H), 0.95 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 167.14, 160.06 (d, *J* = 244.7 Hz, 1C), 158.53, 148.79 (d, *J* = 2.7 Hz, 1C), 131.39 (d, *J* = 7.1 Hz, 1C), 119.74 (d, *J* = 8.2 Hz, 1C), 117.24 (d, *J* = 23.5 Hz, 1C), 115.34 (d, *J* = 24.3 Hz, 1C), 103.58, 87.86, 73.96, 69.73, 31.53, 26.60 (3C), 16.24. HRMS (ESI): Calcd for C₁₇H₂₂FNNaO₆ [M+Na]⁺: 378.1323. Found: 378.1332.

neopentyl (*E*)-3-(4-chloro-2-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8n**)



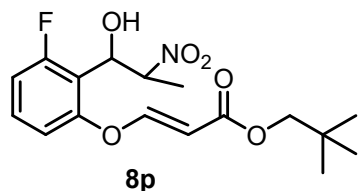
8n (950.3 mg, 86%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 12.0 Hz, 1H), 7.63 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 5.69-5.67 (m, 1H), 5.66 (d, *J* = 12.0 Hz, 1H), 4.78-4.73 (m, 1H), 3.84 (s, 2H), 3.14 (br s, 1H), 1.44 (d, *J* = 6.8 Hz, 3H), 0.95 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 166.97, 157.38, 150.38, 131.16, 130.75, 129.96, 128.30, 118.49, 104.20, 84.72, 73.98, 68.46, 31.53, 26.60 (3C), 11.64. HRMS (ESI): Calcd for C₁₇H₂₂ClNNaO₆ [M+Na]⁺: 394.1028. Found: 394.1029 ([M+Na]⁺), 396.1005 ([M+2+Na]⁺).

neopentyl (*E*)-3-(4-bromo-2-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8o**)



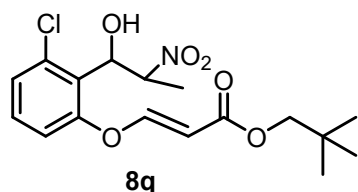
8o (1.08 g, 88%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 (d, $J = 1.6$ Hz, 1H), 7.70 (d, $J = 12.0$ Hz, 1H), 7.50 (dd, $J = 8.4, 1.6$ Hz, 1H), 6.94 (d, $J = 8.4$ Hz, 1H), 5.69-5.67 (m, 1H), 5.66 (d, $J = 12.0$ Hz, 1H), 4.78-4.73 (m, 1H), 3.84 (s, 2H), 3.10 (br s, 1H), 1.45 (d, $J = 6.8$ Hz, 3H), 0.95 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.94, 157.20, 150.95, 132.96, 131.21, 130.99, 118.77, 118.64, 104.33, 84.73, 73.99, 68.41, 31.53, 26.60 (3C), 11.66. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{22}\text{BrNNaO}_6$ $[\text{M}+\text{Na}]^+$: 438.0528. Found: 438.0559 ($[\text{M}+\text{Na}]^+$), 440.0537 ($[\text{M}+2+\text{Na}]^+$).

neopentyl (*E*)-3-(3-fluoro-2-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8p**)



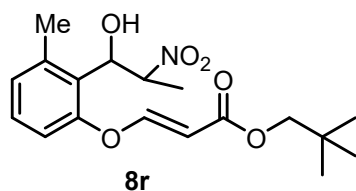
8p (883.7 mg, 83%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.73 (d, $J = 12.0$ Hz, 1H), 7.43-7.37 (m, 1H), 7.02-6.98 (m, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 5.78 (d, $J = 12.0$ Hz, 1H), 5.55-5.51 (m, 1H), 5.15-5.08 (m, 1H), 3.86 (s, 2H), 2.90 (d, $J = 8.0$ Hz, 1H), 1.36 (d, $J = 6.8$ Hz, 3H), 0.97 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.73, 158.63, 157.08, 154.84 (d, $J = 7.3$ Hz, 1C), 131.47 (d, $J = 6.7$ Hz, 1C), 116.48 (d, $J = 5.9$ Hz, 1C), 113.69 (d, $J = 3.4$ Hz, 1C), 113.06 (d, $J = 22.7$ Hz, 1C), 105.05, 86.73, 74.00, 68.36 (d, $J = 2.8$ Hz, 1C), 31.56, 26.62 (3C), 16.46. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{22}\text{FNNaO}_6$ $[\text{M}+\text{Na}]^+$: 378.1323. Found: 378.1326.

neopentyl (*E*)-3-(3-chloro-2-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8q**)



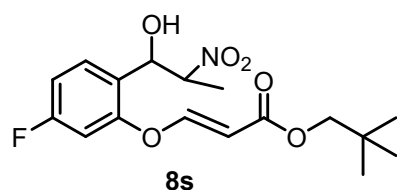
8q (922.1 mg, 83%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (d, $J = 12.0$ Hz, 1H), 7.37-7.30 (m, 1H), 7.29-7.28 (m, 1H), 7.04 (d, $J = 8.4$ Hz, 1H), 5.78 (d, $J = 12.0$ Hz, 1H), 5.75 (d, $J = 8.4$ Hz, 1H), 5.25-5.18 (m, 1H), 3.86 (s, 2H), 3.15 (br s, 1H), 1.37 (d, $J = 6.8$ Hz, 3H), 0.96 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.72, 157.04, 155.43, 135.24, 131.06, 127.19, 126.39, 117.03, 105.17, 86.64, 74.03, 71.56, 31.54, 26.61 (3C), 16.31. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{22}\text{ClNNaO}_6$ $[\text{M}+\text{Na}]^+$: 394.1028. Found: 394.1029 ($[\text{M}+\text{Na}]^+$), 396.0994 ($[\text{M}+2+\text{Na}]^+$).

neopentyl (*E*)-3-(2-(1-hydroxy-2-nitropropyl)-3-methylphenoxy)acrylate (**8r**)



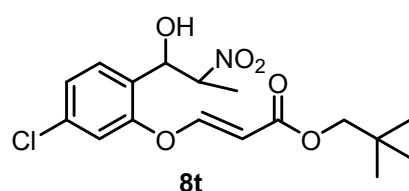
8r (985.2 mg, 94%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (d, $J = 12.0$ Hz, 1H), 7.31-7.27 (m, 1H), 7.07 (d, $J = 8.0$ Hz, 1H), 6.94 (d, $J = 8.0$ Hz, 1H), 5.75 (d, $J = 12.0$ Hz, 1H), 5.70-5.46 (m, 1H), 5.19-5.11 (m, 1H), 3.86 (s, 2H), 2.86 (d, $J = 8.0$ Hz, 1H), 2.51 (s, 3H), 1.31 (d, $J = 6.8$ Hz, 3H), 0.97 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.95, 157.61, 154.66, 139.30, 130.25, 128.33, 126.32, 115.94, 104.34, 87.30, 73.91, 71.26, 31.55, 26.64 (3C), 20.55, 16.46. HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{25}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 374.1574. Found: 374.1588.

neopentyl (*E*)-3-(5-fluoro-2-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8s**)



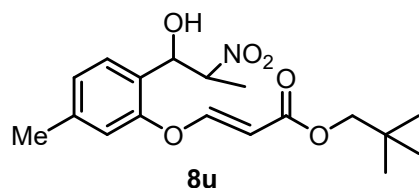
8s (911.3 mg, 86%), yellow solid, m.p. 83-85 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.71 (d, $J = 12.0$ Hz, 1H), 7.62-7.58 (m, 1H), 7.00-6.95 (m, 1H), 6.80 (dd, $J = 8.0, 2.4$ Hz, 1H), 5.72 (d, $J = 12.0$ Hz, 1H), 5.64 (s, 1H), 4.75 (dq, $J = 6.8, 2.8$ Hz, 1H), 3.85 (s, 2H), 2.99 (br s, 1H), 1.45 (d, $J = 6.8$ Hz, 3H), 0.96 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.79, 163.39 (d, $J = 248.8$ Hz, 1C), 156.72, 152.65 (d, $J = 9.8$ Hz, 1C), 129.50 (d, $J = 9.6$ Hz, 1C), 124.50 (d, $J = 3.6$ Hz, 1C), 112.34 (d, $J = 21.0$ Hz, 1C), 105.05 (d, $J = 25.3$ Hz, 1C), 104.82, 85.06, 74.00, 68.60, 31.55, 26.61 (3C), 11.86. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{22}\text{FNNaO}_6$ $[\text{M}+\text{Na}]^+$: 378.1323. Found: 378.1331.

neopentyl (*E*)-3-(3-chloro-6-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8t**)



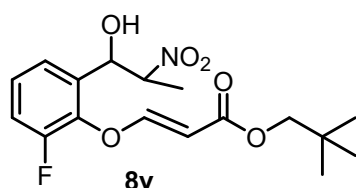
8t (973.4 mg, 88%), yellow solid, m.p. 141-143 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 (d, $J = 12.0$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.25-7.23 (m, 1H), 7.07 (d, $J = 2.8$ Hz, 1H), 5.71 (d, $J = 12.0$ Hz, 1H), 5.65 (d, $J = 1.6$ Hz, 1H), 4.75 (dq, $J = 6.8, 2.8$ Hz, 1H), 3.86 (s, 2H), 2.99 (br s, 1H), 1.44 (d, $J = 6.8$ Hz, 3H), 0.97 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.83, 156.83, 152.30, 135.50, 129.23, 127.30, 125.71, 117.54, 104.81, 84.87, 74.03, 68.56, 31.55, 26.61 (3C), 11.79. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{22}\text{ClNNaO}_6$ $[\text{M}+\text{Na}]^+$: 394.1028. Found: 394.1046 ($[\text{M}+\text{Na}]^+$), 396.1024 ($[\text{M}+2+\text{Na}]^+$).

neopentyl (*E*)-3-(2-(1-hydroxy-2-nitropropyl)-5-methylphenoxy)acrylate (**8u**)



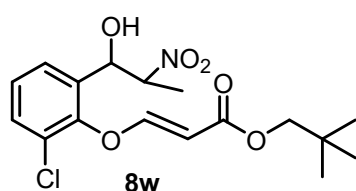
8u (996.2 mg, 95%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 (d, $J = 12.0$ Hz, 1H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.06 (d, $J = 8.0$ Hz, 1H), 6.86 (s, 1H), 5.65 (d, $J = 12.0$ Hz, 1H), 5.62-5.61 (m, 1H), 4.77 (dq, $J = 6.8, 3.2$ Hz, 1H), 3.85 (s, 2H), 2.79 (br s, 1H), 2.37 (s, 3H), 1.46 (d, $J = 6.8$ Hz, 3H), 0.97 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.20, 157.98, 152.04, 140.69, 127.88, 126.29, 125.57, 117.94, 103.55, 85.31, 73.82, 69.09, 31.56, 26.64 (3C), 21.36, 12.06. HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{25}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 374.1574. Found: 374.1584.

neopentyl (*E*)-3-(2-fluoro-6-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8v**)



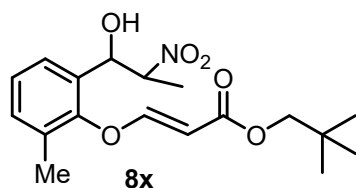
8v (921.1 mg, 87%), yellow solid, m.p. 90-92 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.71 (dd, $J = 12.0, 1.6$ Hz, 1H), 7.42 (d, $J = 8.0$ Hz, 1H), 7.30-7.27 (m, 1H), 7.27-7.16 (m, 1H), 5.60 (d, $J = 1.2$ Hz, 1H), 5.37 (d, $J = 12.0$ Hz, 1H), 4.74 (dq, $J = 6.8, 2.8$ Hz, 1H), 3.81 (s, 2H), 3.15 (br s, 1H), 1.44 (d, $J = 6.8$ Hz, 3H), 0.94 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.88, 159.59 (d, $J = 2.6$ Hz, 1C), 153.71 (d, $J = 249.9$ Hz, 1C), 138.67 (d, $J = 12.5$ Hz, 1C), 133.02, 127.08 (d, $J = 7.4$ Hz, 1C), 123.17 (d, $J = 3.5$ Hz, 1C), 117.37 (d, $J = 18.1$ Hz, 1C), 101.77, 85.02, 73.92, 68.72 (d, $J = 2.9$ Hz, 1C), 31.51, 26.60 (3C), 11.74. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{22}\text{FNNaO}_6$ $[\text{M}+\text{Na}]^+$: 378.1323. Found: 378.1338.

neopentyl (*E*)-3-(2-chloro-6-(1-hydroxy-2-nitropropyl)phenoxy)acrylate (**8w**)



8w (988.4 mg, 89%), white solid, m.p. 163-165 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.67 (dd, $J = 12.0, 1.6$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.31-7.27 (m, 1H), 5.57 (s, 1H), 5.23 (dd, $J = 12.0, 1.6$ Hz, 1H), 4.79-4.74 (m, 1H), 3.81 (s, 2H), 3.10 (br s, 1H), 1.42 (d, $J = 6.8$ Hz, 3H), 0.94 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.87, 159.12, 146.80, 133.18, 131.09, 127.51, 127.01, 126.62, 101.48, 84.89, 73.91, 68.93, 31.52, 26.62 (3C), 11.57. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{22}\text{ClNNaO}_6$ $[\text{M}+\text{Na}]^+$: 394.1028. Found: 394.1031 ($[\text{M}+\text{Na}]^+$), 396.1014 ($[\text{M}+2+\text{Na}]^+$).

neopentyl (*E*)-3-(2-(1-hydroxy-2-nitropropyl)-6-methylphenoxy)acrylate (**8x**)

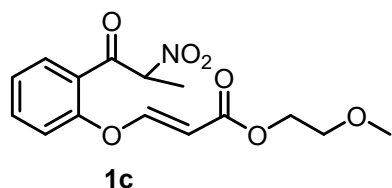


8x (983.3 mg, 93%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 12.0 Hz, 1H), 7.50-7.48 (m, 1H), 7.27-7.26 (m, 1H), 7.25-7.24 (m, 1H), 5.53 (s, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 4.78 (dq, *J* = 6.8, 2.4 Hz, 1H), 3.81 (s, 2H), 2.82 (br s, 1H), 2.22 (s, 3H), 1.44 (d, *J* = 6.8 Hz, 3H), 0.94 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 167.15, 159.78, 148.96, 132.08, 130.68, 130.52, 126.75, 125.68, 100.32, 85.24, 73.78, 69.03, 31.52, 26.63 (3C), 16.19, 11.67. HRMS (ESI): Calcd for C₁₈H₂₅NNaO₆ [M+Na]⁺: 374.1574. Found: 374.1582.

General Procedure for the synthesis of **1**

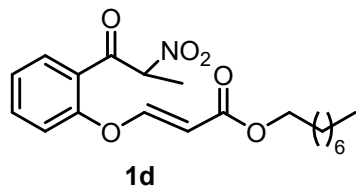
To a solution of compound **8** (2 mmol, 1 equiv.) in 20 mL of CH₂Cl₂ at 0 °C was added 1 g (2.4 mmol, 1.2 equiv.) of Dess-Martin periodinane. The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was purified by silica gel chromatography (CH₂Cl₂:HOAc, 100:0.5) to afford desired products **1** (81-95%).

2-methoxyethyl (*E*)-3-(2-(2-nitropropanoyl)phenoxy)acrylate (**1c**)



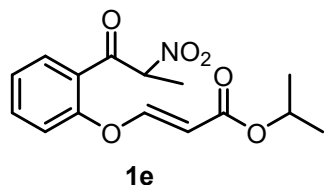
1c (553.1 mg, 86%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.77 (d, *J* = 12.0 Hz, 1H), 7.66-7.61 (m, 1H), 7.34-7.30 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 5.97 (q, *J* = 6.8 Hz, 1H), 5.81 (d, *J* = 12.0 Hz, 1H), 4.32 (t, *J* = 4.4 Hz, 2H), 3.63 (t, *J* = 4.4 Hz, 2H), 3.40 (s, 3H), 1.80 (d, *J* = 8.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 189.52, 166.29, 156.66, 154.52, 135.72, 131.99, 125.91, 125.70, 117.82, 105.39, 88.26, 70.56, 63.70, 59.12, 15.69. HRMS (ESI): Calcd for C₁₅H₁₇NNaO₇ [M+Na]⁺: 346.0897. Found: 346.0903.

octyl (*E*)-3-(2-(2-nitropropanoyl)phenoxy)acrylate (**1d**)



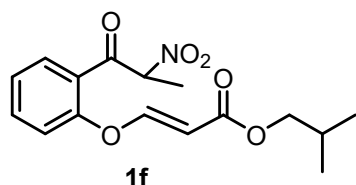
1d (628.6 mg, 84%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.89 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.76 (d, *J* = 12.0 Hz, 1H), 7.66-7.62 (m, 1H), 7.34-7.30 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 5.98 (q, *J* = 6.8 Hz, 1H), 5.78 (d, *J* = 12.0 Hz, 1H), 4.15 (t, *J* = 6.8 Hz, 2H), 1.80 (d, *J* = 6.8 Hz, 3H), 1.68-1.63 (m, 2H), 1.34-1.27 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 189.53, 166.38, 156.08, 154.65, 135.73, 132.02, 125.83, 125.59, 117.63, 105.92, 88.31, 64.96, 31.91, 29.34, 29.30, 28.77, 26.06, 22.76, 15.70, 14.21. HRMS (ESI): Calcd for C₂₀H₂₇NNaO₆ [M+Na]⁺: 400.1736. Found: 400.1741.

isopropyl (*E*)-3-(2-(2-nitropropanoyl)phenoxy)acrylate (**1e**)



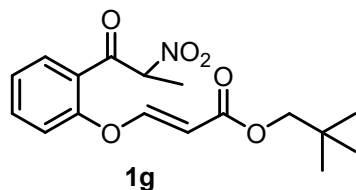
1e (525.2 mg, 86%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.89 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.72 (d, $J = 12.0$ Hz, 1H), 7.66-7.62 (m, 1H), 7.34-7.30 (m, 1H), 7.15 (d, $J = 8.0$ Hz, 1H), 5.98 (q, $J = 6.8$ Hz, 1H), 5.75 (d, $J = 12.0$ Hz, 1H), 5.10 (hept, $J = 6.4$ Hz, 1H), 1.80 (d, $J = 6.8$ Hz, 3H), 1.28 (d, $J = 6.4$ Hz, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 189.58, 165.84, 155.91, 154.68, 135.76, 132.04, 125.79, 125.57, 117.64, 106.39, 88.34, 68.21, 22.03 (2C), 15.71. HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{17}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 330.0948. Found: 330.0953.

isobutyl (*E*)-3-(2-(2-nitropropanoyl)phenoxy)acrylate (**1f**)



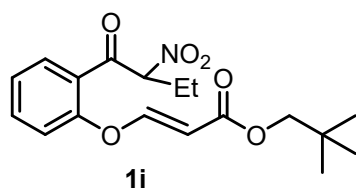
1f (597.7 mg, 93%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.89 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.74 (d, $J = 12.0$ Hz, 1H), 7.67-7.62 (m, 1H), 7.34-7.30 (m, 1H), 7.14 (d, $J = 8.0$ Hz, 1H), 5.99 (q, $J = 6.8$ Hz, 1H), 5.78 (d, $J = 12.0$ Hz, 1H), 3.95 (d, $J = 6.8$ Hz, 2H), 1.97 (hept, $J = 6.8$ Hz, 1H), 1.80 (d, $J = 6.8$ Hz, 3H), 0.95 (d, $J = 6.4$ Hz, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 189.53, 166.38, 156.07, 154.64, 135.76, 132.03, 125.78, 125.60, 117.59, 105.87, 88.33, 70.84, 27.89, 19.24 (2C), 15.71. HRMS (ESI): Calcd for $\text{C}_{16}\text{H}_{19}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 344.1105. Found: 344.1106.

neopentyl (*E*)-3-(2-(2-nitropropanoyl)phenoxy)acrylate (**1g**)



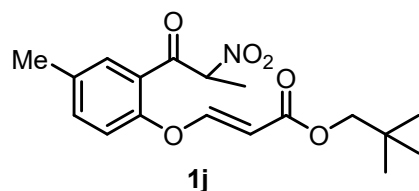
1g (627.9 mg, 94%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 12.0$ Hz, 1H), 7.67-7.62 (m, 1H), 7.34-7.30 (m, 1H), 7.14 (d, $J = 8.0$ Hz, 1H), 5.99 (q, $J = 6.8$ Hz, 1H), 5.81 (d, $J = 12.0$ Hz, 1H), 3.87 (s, 2H), 1.81 (d, $J = 6.8$ Hz, 3H), 0.97 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 189.53, 166.44, 156.02, 154.65, 135.79, 132.04, 125.72, 125.59, 117.52, 105.89, 88.35, 74.01, 31.54, 26.60 (3C), 15.71. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{21}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 358.1261. Found: 358.1278.

neopentyl (*E*)-3-(2-(2-nitrobutanoyl)phenoxy)acrylate (**1i**)



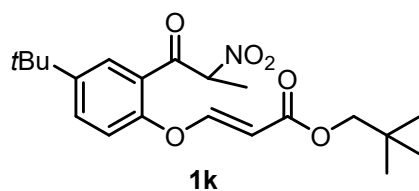
1i (664.2 mg, 95%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.75 (d, $J = 12.0$ Hz, 1H), 7.66-7.62 (m, 1H), 7.34-7.30 (m, 1H), 7.14 (d, $J = 8.0$ Hz, 1H), 5.88-5.85 (m, 1H), 5.81 (d, $J = 12.0$ Hz, 1H), 3.88 (s, 2H), 2.33-2.27 (m, 1H), 2.20-2.15 (m, 1H), 1.08 (t, $J = 7.2$ Hz, 3H), 0.97 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 189.08, 166.44, 156.15, 154.55, 135.67, 131.94, 126.09, 125.62, 117.64, 105.86, 94.99, 74.01, 31.56, 26.61 (3C), 23.98, 11.00. HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{23}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 372.1418. Found: 372.1427.

neopentyl (*E*)-3-(4-methyl-2-(2-nitropropanoyl)phenoxy)acrylate (**1j**)



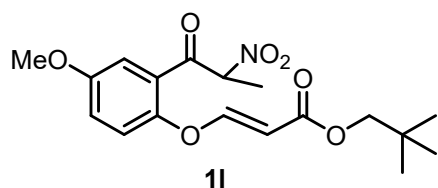
1j (629.2 mg, 90%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 (d, $J = 12.0$ Hz, 1H), 7.68 (s, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.03 (d, $J = 8.0$ Hz, 1H), 5.99 (q, $J = 6.8$ Hz, 1H), 5.76 (d, $J = 12.0$ Hz, 1H), 3.86 (s, 2H), 2.38 (s, 3H), 1.79 (d, $J = 6.8$ Hz, 3H), 0.96 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 189.76, 166.58, 156.59, 152.62, 136.40, 135.67, 132.07, 125.40, 117.66, 105.30, 88.35, 73.96, 31.55, 26.61 (3C), 20.69, 15.73. HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{23}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 372.1418. Found: 372.1429.

neopentyl (*E*)-3-(4-(tert-butyl)-2-(2-nitropropanoyl)phenoxy)acrylate (**1k**)



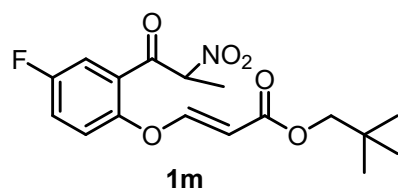
1k (689.0 mg, 88%), colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.90 (s, 1H), 7.73 (d, $J = 12.0$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.06 (d, $J = 8.0$ Hz, 1H), 5.99 (q, $J = 6.8$ Hz, 1H), 5.78 (d, $J = 12.0$ Hz, 1H), 3.87 (s, 2H), 1.81 (d, $J = 6.8$ Hz, 3H), 1.33 (s, 9H), 0.97 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 189.75, 166.56, 156.47, 152.62, 148.94, 133.14, 128.72, 124.96, 117.37, 105.42, 88.42, 73.98, 34.83, 31.56, 31.30 (3C), 26.63 (3C), 15.78. HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{29}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 414.1887. Found: 414.1892.

neopentyl (*E*)-3-(4-methoxy-2-(2-nitropropanoyl)phenoxy)acrylate (**1l**)



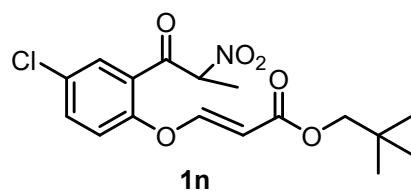
1l (663.9 mg, 91%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 12.0 Hz, 1H), 7.36 (d, *J* = 2.4 Hz, 1H), 7.18-7.16 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 5.98 (q, *J* = 6.8 Hz, 1H), 5.71 (d, *J* = 12.0 Hz, 1H), 3.85 (s, 2H), 3.84 (s, 3H), 1.80 (d, *J* = 6.8 Hz, 3H), 0.96 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 189.29, 166.59, 157.25, 156.99, 148.54, 126.35, 122.53, 119.66, 114.67, 104.87, 88.20, 73.95, 56.07, 31.54, 26.61 (3C), 15.75. HRMS (ESI): Calcd for C₁₈H₂₃NNaO₇ [M+Na]⁺: 388.1367. Found: 388.1352.

neopentyl (*E*)-3-(4-fluoro-2-(2-nitropropanoyl)phenoxy)acrylate (**1m**)



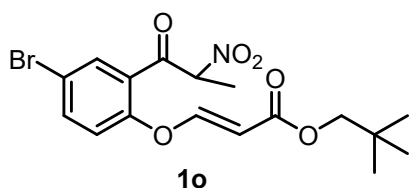
1m (593.5 mg, 84%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 12.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.37-7.33 (m, 1H), 7.13 (dd, *J* = 8.0, 3.6 Hz, 1H), 5.95 (q, *J* = 6.8 Hz, 1H), 5.79 (d, *J* = 12.0 Hz, 1H), 3.86 (s, 2H), 1.81 (d, *J* = 6.8 Hz, 3H), 0.96 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 188.11, 166.30, 159.47 (d, *J* = 246.1 Hz, 1C), 156.19, 150.75 (d, *J* = 2.6 Hz, 1C), 127.08 (d, *J* = 6.6 Hz, 1C), 122.65 (d, *J* = 23.8 Hz, 1C), 119.63 (d, *J* = 7.9 Hz, 1C), 118.20 (d, *J* = 24.9 Hz, 1C), 105.99, 87.93, 74.07, 31.54, 26.59 (3C), 15.69. HRMS (ESI): Calcd for C₁₇H₂₀FNNaO₆ [M+Na]⁺: 376.1167. Found: 376.1163.

neopentyl (*E*)-3-(4-chloro-2-(2-nitropropanoyl)phenoxy)acrylate (**1n**)



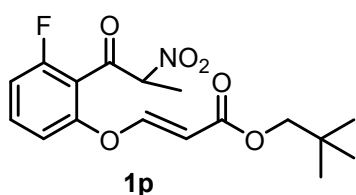
1n (626.7 mg, 85%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 2.4 Hz, 1H), 7.68 (d, *J* = 12.0 Hz, 1H), 7.59 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 5.93 (q, *J* = 6.8 Hz, 1H), 5.82 (d, *J* = 12.0 Hz, 1H), 3.87 (s, 2H), 1.81 (d, *J* = 6.8 Hz, 3H), 0.96 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 188.18, 166.23, 155.53, 153.06, 135.43, 131.63, 131.34, 126.87, 118.95, 106.53, 88.02, 74.14, 31.55, 26.60 (3C), 15.70. HRMS (ESI): Calcd for C₁₇H₂₀ClNNaO₆ [M+Na]⁺: 392.0871. Found: 392.0887 ([M+Na]⁺), 394.0931 ([M+2+Na]⁺).

neopentyl (*E*)-3-(4-bromo-2-(2-nitropropanoyl)phenoxy)acrylate (**1o**)



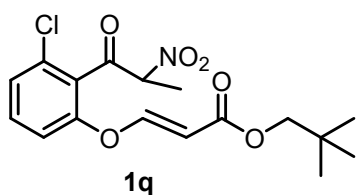
1o (700.2 mg, 85%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 2.4 Hz, 1H), 7.73 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.68 (d, *J* = 12.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 5.93 (q, *J* = 6.8 Hz, 1H), 5.83 (d, *J* = 12.0 Hz, 1H), 3.87 (s, 2H), 1.81 (d, *J* = 6.8 Hz, 3H), 0.96 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 188.11, 166.20, 155.38, 153.59, 138.37, 134.60, 127.15, 119.18, 118.58, 106.64, 88.02, 74.15, 31.56, 26.61 (3C), 15.71. HRMS (ESI): Calcd for C₁₇H₂₀BrNNaO₆ [M+Na]⁺: 436.0366. Found: 436.0362 ([M+Na]⁺), 438.0370 ([M+2+Na]⁺).

neopentyl (*E*)-3-(3-fluoro-2-(2-nitropropanoyl)phenoxy)acrylate (**1p**)



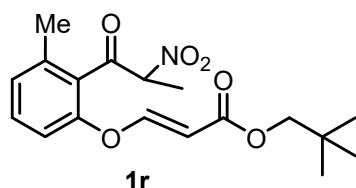
1p (577.2 mg, 82%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 12.0 Hz, 1H), 7.56-7.50 (m, 1H), 7.05-7.01 (m, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 5.76 (q, *J* = 6.8 Hz, 1H), 5.75 (d, *J* = 12.0 Hz, 1H), 3.85 (s, 2H), 1.80 (d, *J* = 6.8 Hz, 3H), 0.96 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 188.14, 166.49, 160.27 (d, *J* = 253.3 Hz, 1C), 156.37, 154.12 (d, *J* = 6.1 Hz, 1C), 134.20 (d, *J* = 10.3 Hz, 1C), 116.73 (d, *J* = 18.3 Hz, 1C), 113.26 (d, *J* = 3.5 Hz, 1C), 112.92 (d, *J* = 21.6 Hz, 1C), 105.66, 89.31, 73.98, 31.54, 26.60 (3C), 15.03. HRMS (ESI): Calcd for C₁₇H₂₀FNNaO₆ [M+Na]⁺: 376.1167. Found: 376.1147.

neopentyl (*E*)-3-(3-chloro-2-(2-nitropropanoyl)phenoxy)acrylate (**1q**)



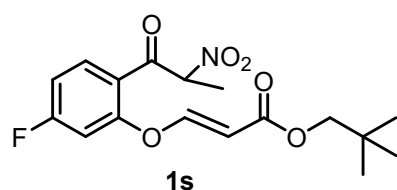
1q (598.9 mg, 81%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 12.0 Hz, 1H), 7.48-7.44 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 5.76 (q, *J* = 6.8 Hz, 1H), 5.75 (d, *J* = 12.0 Hz, 1H), 3.85 (s, 2H), 1.81 (d, *J* = 6.8 Hz, 3H), 0.96 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 190.94, 166.51, 156.10, 153.47, 132.91, 132.27, 127.45, 126.53, 115.33, 105.76, 89.51, 74.02, 31.54, 26.60 (3C), 14.85. HRMS (ESI): Calcd for C₁₇H₂₀ClNNaO₆ [M+Na]⁺: 392.0871. Found: 392.0876 ([M+Na]⁺), 394.0929 ([M+2+Na]⁺).

neopentyl (*E*)-3-(3-methyl-2-(2-nitropropanoyl)phenoxy)acrylate (**1r**)



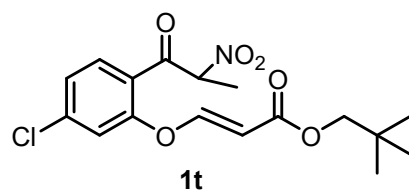
1r (641.3 mg, 92%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 12.0 Hz, 1H), 7.42-7.38 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.76 (q, *J* = 6.8 Hz, 1H), 5.73 (d, *J* = 12.0 Hz, 1H), 3.86 (s, 2H), 2.33 (s, 3H), 1.78 (d, *J* = 6.8 Hz, 3H), 0.96 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 194.02, 166.67, 156.74, 153.20, 139.58, 132.48, 127.79, 127.48, 114.23, 105.00, 89.49, 73.93, 31.56, 26.62 (3C), 19.51, 15.06. HRMS (ESI): Calcd for C₁₈H₂₃NNaO₆ [M+Na]⁺: 372.1418. Found: 372.1430.

neopentyl (*E*)-3-(5-fluoro-2-(2-nitropropanoyl)phenoxy)acrylate (**1s**)



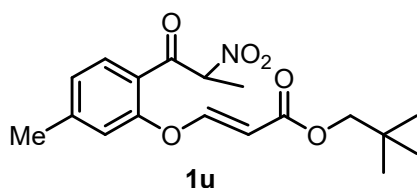
1s (599.1 mg, 85%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.01-7.98 (m, 1H), 7.69 (d, *J* = 12.0 Hz, 1H), 7.05-7.01 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 5.95 (q, *J* = 6.8 Hz, 1H), 5.88 (d, *J* = 12.0 Hz, 1H), 3.88 (s, 2H), 1.81 (d, *J* = 6.8 Hz, 3H), 0.97 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 187.81, 166.87 (d, *J* = 258.3 Hz, 1C), 166.07, 156.23 (d, *J* = 10.6 Hz, 1C), 154.79, 134.59 (d, *J* = 10.8 Hz, 1C), 121.96 (d, *J* = 3.5 Hz, 1C), 113.05 (d, *J* = 21.5 Hz, 1C), 107.23, 105.16 (d, *J* = 25.6 Hz, 1C), 88.11, 74.20, 31.56, 26.61 (3C), 15.76. HRMS (ESI): Calcd for C₁₇H₂₀FNNaO₆ [M+Na]⁺: 376.1167. Found: 376.1175.

neopentyl (*E*)-3-(5-chloro-2-(2-nitropropanoyl)phenoxy)acrylate (**1t**)



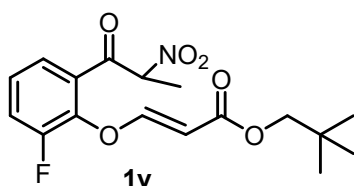
1t (643.2 mg, 87%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 12.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.15 (s, 1H), 5.95 (q, *J* = 6.8 Hz, 1H), 5.87 (d, *J* = 12.0 Hz, 1H), 3.89 (s, 2H), 1.81 (d, *J* = 6.8 Hz, 3H), 0.98 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 188.17, 166.15, 155.04, 155.00, 141.95, 133.22, 125.99, 124.00, 117.84, 107.10, 88.12, 74.21, 31.56, 26.61 (3C), 15.72. HRMS (ESI): Calcd for C₁₇H₂₀ClNNaO₆ [M+Na]⁺: 392.0871. Found: 392.0894 ([M+Na]⁺), 394.0927 ([M+2+Na]⁺).

neopentyl (*E*)-3-(5-methyl-2-(2-nitropropanoyl)phenoxy)acrylate (**1u**)



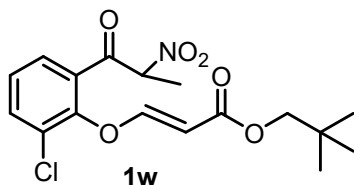
1u (649.3 mg, 93%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 12.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.93 (s, 1H), 5.98 (q, *J* = 6.8 Hz, 1H), 5.81 (d, *J* = 12.0 Hz, 1H), 3.87 (s, 2H), 2.44 (s, 3H), 1.79 (d, *J* = 6.8 Hz, 3H), 0.97 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 188.90, 166.61, 156.18, 154.85, 147.79, 132.07, 126.53, 122.90, 118.10, 105.70, 88.32, 74.02, 31.56, 26.61 (3C), 21.91, 15.77. HRMS (ESI): Calcd for C₁₈H₂₃NNaO₆ [M+Na]⁺: 372.1418. Found: 372.1428.

neopentyl (*E*)-3-(6-fluoro-2-(2-nitropropanoyl)phenoxy)acrylate (**1v**)



1v (606.1 mg, 86%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 12.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.48-7.44 (m, 1H), 7.38-7.32 (m, 1H), 5.89 (q, *J* = 6.8 Hz, 1H), 5.53 (d, *J* = 12.0 Hz, 1H), 3.84 (s, 2H), 1.80 (d, *J* = 6.8 Hz, 3H), 0.95 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 188.71, 166.21, 158.88 (d, *J* = 3.6 Hz, 1C), 154.05 (d, *J* = 251.8 Hz, 1C), 141.67 (d, *J* = 12.8 Hz, 1C), 129.55, 127.15 (d, *J* = 7.4 Hz, 1C), 126.45 (d, *J* = 3.5 Hz, 1C), 122.71 (d, *J* = 18.6 Hz, 1C), 103.52, 87.78, 73.98, 31.53, 26.60 (3C), 15.66. HRMS (ESI): Calcd for C₁₇H₂₀FNNaO₆ [M+Na]⁺: 376.1167. Found: 376.1149.

neopentyl (*E*)-3-(6-chloro-2-(2-nitropropanoyl)phenoxy)acrylate (**1w**)



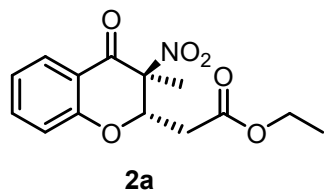
1w (633.2 mg, 86%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.70 (d, *J* = 1.6 Hz, 1H), 7.63 (d, *J* = 12.0 Hz, 1H), 7.39-7.35 (m, 1H), 5.89 (q, *J* = 6.8 Hz, 1H), 5.35 (d, *J* = 12.0 Hz, 1H), 3.83 (s, 2H), 1.79 (d, *J* = 6.8 Hz, 3H), 0.94 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 189.39, 166.32, 159.01, 149.28, 136.17, 130.39, 129.54, 128.28, 127.65, 103.01, 87.60, 73.97, 31.53, 26.61 (3C), 15.73. HRMS (ESI): Calcd for C₁₇H₂₀ClNNaO₆ [M+Na]⁺: 392.0871. Found: 392.0883 ([M+Na]⁺), 394.0907 ([M+2+Na]⁺).

General Procedure for the synthesis of **2**

Catalyst **CAT-6** (0.05 mmol, 0.1 equiv.) was added to a solution of compound **1** (0.5 mmol, 1 equiv.) in dry toluene (5 mL) at -30 °C. After 12 h of stirring, the reaction mixture was quenched with 1 N HCl solution, extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine (20 mL), dried over Na₂SO₄, filtered and concentrated in

vacuo to give a residue. The residue was purified by silica gel chromatography (petroleum ether:EtOAc, 20:1-10:3) to afford desired products **2** (90-99%).

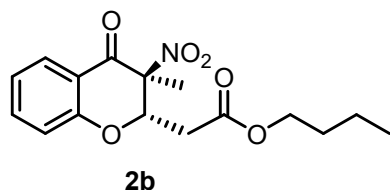
ethyl 2-((2*S*,3*S*)-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2a**)



2a (143.1 mg, 98%), > 20:1 d.r., 97% ee, white solid, m.p. 63-65 °C. Optical rotation [α]_D

= -33.4 (*c* 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.93 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.60-7.55 (m, 1H), 7.16-7.12 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 5.60 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.85 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.45 (dd, *J* = 16.0, 2.4 Hz, 1H), 1.74 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 185.06, 168.52, 159.80, 137.65, 128.60, 123.28, 118.36, 118.27, 92.28, 78.13, 61.66, 34.65, 14.47, 14.25. HRMS (ESI): Calcd for C₁₄H₁₅NNaO₆ [M+Na]⁺: 316.0792. Found: 316.0800.

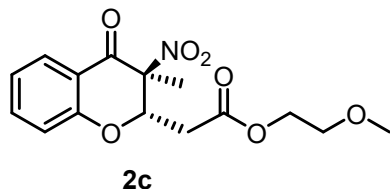
butyl 2-((2*S*,3*S*)-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2b**)



2b

2b (158.8 mg, 99%), > 20:1 d.r., 96% ee, colorless oil. Optical rotation [α] = -37.1 (*c* 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.61-7.57 (m, 1H), 7.17-7.13 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 5.61 (d, *J* = 10.0 Hz, 1H), 4.21-4.15 (m, 2H), 2.86 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.45 (d, *J* = 16.0 Hz, 1H), 1.76 (s, 3H), 1.68-1.61 (m, 2H), 1.42-1.36 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 185.07, 168.60, 159.79, 137.64, 128.61, 123.29, 118.36, 118.25, 92.29, 78.16, 65.51, 34.67, 30.64, 19.17, 14.47, 13.77. HRMS (ESI): Calcd for C₁₆H₁₉NNaO₆ [M+Na]⁺: 344.1105. Found: 344.1128.

2-methoxyethyl 2-((2*S*,3*S*)-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2c**)

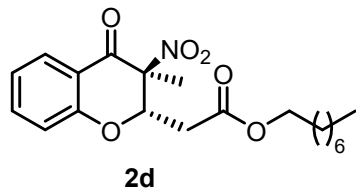


2c

2c (158.0 mg, 98%), > 20:1 d.r., 95% ee, colorless oil. Optical rotation [α] = -65.5 (*c* 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.94 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.61-7.56 (m, 1H), 7.16-7.13 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 5.61 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.33-4.31 (m, 2H), 3.61 (t, *J* = 4.4 Hz, 2H), 3.38 (s, 3H), 2.93 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.48 (dd, *J* = 16.0,

2.0 Hz, 1H), 1.74 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.04, 168.60, 159.76, 137.65, 128.58, 123.29, 118.29 (2C), 92.23, 77.94, 70.27, 64.56, 59.14, 34.45, 14.47. HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{17}\text{NNaO}_7$ $[\text{M}+\text{Na}]^+$: 346.0897. Found: 346.0914.

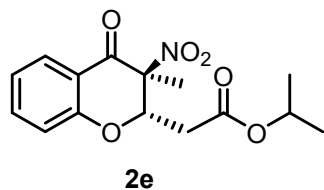
octyl 2-((2*S*,3*S*)-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2d**)



10

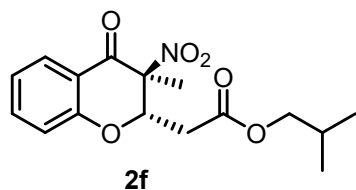
2d (182.1 mg, 97%), > 20:1 d.r., 88% ee, colorless oil. Optical rotation $[\alpha]_D^{25} = -46.0$ (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.0$ Hz, 1H), 7.61-7.57 (m, 1H), 7.17-7.13 (m, 1H), 7.03 (d, $J = 8.0$ Hz, 1H), 5.60 (dd, $J = 10.0, 2.0$ Hz, 1H), 4.20-4.13 (m, 2H), 2.86 (dd, $J = 16.0, 10.0$ Hz, 1H), 2.45 (dd, $J = 16.0, 2.0$ Hz, 1H), 1.75 (s, 3H), 1.68-1.61 (m, 2H), 1.33-1.26 (m, 10H), 0.88 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.09, 168.60, 159.80, 137.64, 128.64, 123.30, 118.37, 118.27, 92.29, 78.16, 65.86, 34.68, 31.89, 29.30 (2C), 28.64, 25.98, 22.77, 14.48, 14.22. HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{27}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 400.1736. Found: 400.1752.

isopropyl 2-((2*S*,3*S*)-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2e**)



2e (151.8 mg, 99%), > 20:1 d.r., 95% ee, white solid, m.p. 56-57 °C. Optical rotation $[\alpha]_D^{25} = -65.6$ (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.95 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.60-7.56 (m, 1H), 7.16-7.13 (m, 1H), 7.02 (d, $J = 8.0$ Hz, 1H), 5.59 (dd, $J = 10.0, 2.0$ Hz, 1H), 5.10 (hept, $J = 6.8$ Hz, 1H), 2.82 (dd, $J = 16.0, 10.0$ Hz, 1H), 2.43 (dd, $J = 16.0, 2.0$ Hz, 1H), 1.75 (s, 3H), 1.28 (d, $J = 6.8$ Hz, 3H), 1.25 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.10, 168.01, 159.82, 137.65, 128.61, 123.27, 118.39, 118.22, 92.28, 78.26, 69.34, 34.92, 21.89, 21.83, 14.49. HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{17}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 330.0948. Found: 330.0964.

isobutyl 2-((2*S*,3*S*)-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2f**)

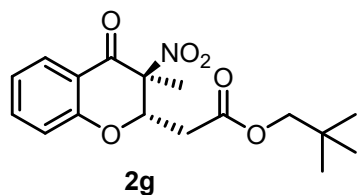


10

2f (158.7 mg, 99%), > 20:1 d.r., 97% ee, colorless oil. Optical rotation $[\alpha]_D^{25} = -62.2$ (c

1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.61-7.56 (m, 1H), 7.17-7.13 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 5.61 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.00-3.96 (m, 1H), 3.95 (dd, *J* = 6.4, 4.4 Hz, 1H), 2.87 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.47 (dd, *J* = 16.0, 2.0 Hz, 1H), 1.96 (hept, *J* = 6.8 Hz, 1H), 1.76 (s, 3H), 0.94 (d, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 185.10, 168.58, 159.79, 137.66, 128.64, 123.31, 118.35, 118.25, 92.30, 78.16, 71.68, 34.67, 27.81, 19.14 (2C), 14.46. HRMS (ESI): Calcd for C₁₆H₁₉NNaO₆ [M+Na]⁺: 344.1105. Found: 344.1123.

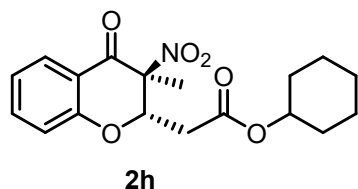
neopentyl 2-((2*S*,3*S*)-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2g**)



10

2g (165.2 mg, 99%), > 20:1 d.r., 98% ee, colorless oil. Optical rotation [α] = -42.7 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.61-7.57 (m, 1H), 7.17-7.13 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 5.61 (d, *J* = 10.0 Hz, 1H), 3.90 (d, *J* = 10.4 Hz, 1H), 3.85 (d, *J* = 10.4 Hz, 1H), 2.90 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.47 (d, *J* = 16.0 Hz, 1H), 1.76 (s, 3H), 0.94 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 185.13, 168.61, 159.76, 137.68, 128.65, 123.32, 118.31, 118.24, 92.30, 78.15, 74.86, 34.69, 31.54, 26.51 (3C), 14.44. HRMS (ESI): Calcd for C₁₇H₂₁NNaO₆ [M+Na]⁺: 358.1261. Found: 358.1283.

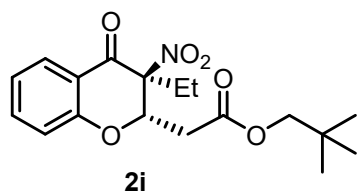
cyclohexyl 2-((2*S*,3*S*)-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2h**)



10

2h (168.0 mg, 97%), 17:1 d.r., 93% ee, colorless oil. Optical rotation [α] = -23.4 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.60-7.56 (m, 1H), 7.17-7.13 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 5.59 (d, *J* = 10.0 Hz, 1H), 4.89-4.84 (m, 1H), 2.84 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.44 (d, *J* = 16.0 Hz, 1H), 1.87-1.83 (m, 2H), 1.75 (s, 3H), 1.73-1.70 (m, 2H), 1.57-1.28 (m, 6H). HRMS (ESI): Calcd for C₁₈H₂₁NNaO₆ [M+Na]⁺: 370.1261. Found: 370.1282.

neopentyl 2-((2*S*,3*S*)-3-ethyl-3-nitro-4-oxochroman-2-yl)acetate (**2i**)

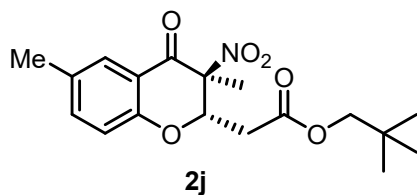


10

2i (172.2 mg, 99%), > 20:1 d.r., 95% ee, colorless oil. Optical rotation [α] = -53.7 (*c*

1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.95 (d, J = 8.0 Hz, 1H), 7.58-7.54 (m, 1H), 7.16-7.12 (m, 1H), 6.99 (d, J = 8.0 Hz, 1H), 5.61 (dd, J = 10.0, 2.4 Hz, 1H), 3.89 (d, J = 10.4 Hz, 1H), 3.84 (d, J = 10.4 Hz, 1H), 2.89 (dd, J = 16.0, 10.0 Hz, 1H), 2.47 (d, J = 16.0, 2.4 Hz, 1H), 2.31-2.15 (m, 2H), 1.02 (t, J = 8.0 Hz, 3H), 0.93 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃) δ 184.06, 168.66, 159.25, 137.49, 128.29, 123.16, 119.09, 118.23, 95.23, 78.75, 74.84, 34.36, 31.53, 26.50 (3C), 21.44, 8.35. HRMS (ESI): Calcd for C₁₈H₂₃NNaO₆ [M+Na]⁺: 372.1418. Found: 372.1417.

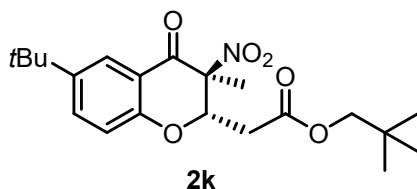
neopentyl 2-((2*S*,3*S*)-3,6-dimethyl-3-nitro-4-oxochroman-2-yl)acetate (**2j**)



10

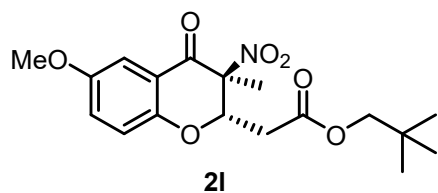
2j (172.2 mg, 99%), > 20:1 d.r., > 99% ee, colorless oil. Optical rotation [α] = -54.6 (*c* 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.73 (s, 1H), 7.39 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 5.57 (d, J = 10.0 Hz, 1H), 3.90 (d, J = 10.4 Hz, 1H), 3.85 (d, J = 10.4 Hz, 1H), 2.88 (dd, J = 16.0, 10.0 Hz, 1H), 2.45 (d, J = 16.0 Hz, 1H), 2.33 (s, 3H), 1.75 (s, 3H), 0.94 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃) δ 185.30, 168.64, 157.89, 138.81, 133.03, 128.07, 118.01, 117.94, 92.41, 78.14, 74.81, 34.73, 31.54, 26.52 (3C), 20.59, 14.45. HRMS (ESI): Calcd for C₁₈H₂₃NNaO₆ [M+Na]⁺: 372.1418. Found: 372.1418.

neopentyl 2-((2*S*,3*S*)-6-(*tert*-butyl)-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2k**)



2k (187.1 mg, 97%), > 20:1 d.r., 95% ee, white solid, m.p. 118-119 °C. Optical rotation [α] = -56.6 (*c* 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.91 (d, J = 2.0 Hz, 1H), 7.63 (dd, J = 8.0, 2.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 5.58 (dd, J = 10.0, 1.6 Hz, 1H), 3.91 (d, J = 10.4 Hz, 1H), 3.85 (d, J = 10.4 Hz, 1H), 2.89 (dd, J = 16.0, 10.0 Hz, 1H), 2.46 (dd, J = 16.0, 1.6 Hz, 1H), 1.76 (s, 3H), 1.31 (s, 9H), 0.94 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃) δ 185.47, 168.66, 157.85, 146.43, 135.56, 124.51, 117.86, 117.56, 92.51, 78.12, 74.81, 34.76, 34.64, 31.54, 31.27 (3C), 26.53 (3C), 14.45. HRMS (ESI): Calcd for C₂₁H₂₉NNaO₆ [M+Na]⁺: 414.1887. Found: 414.1901.

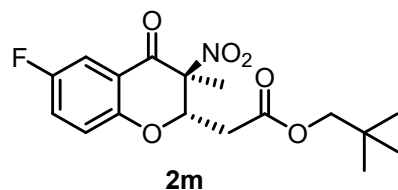
neopentyl 2-((2*S*,3*S*)-6-methoxy-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2l**)



2l (168.9 mg, 93%), > 20:1 d.r., 90% ee, white solid, m.p. 77-78 °C. Optical rotation [α]_D

= -50.1 (*c* 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.32 (d, *J* = 2.8 Hz, 1H), 7.17 (dd, *J* = 8.0, 2.8 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 5.56 (dd, *J* = 10.0, 1.2 Hz, 1H), 3.91 (d, *J* = 10.4 Hz, 1H), 3.84 (d, *J* = 10.4 Hz, 1H), 3.81 (s, 3H), 2.88 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.44 (dd, *J* = 16.0, 1.2 Hz, 1H), 1.75 (s, 3H), 0.94 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃) δ 185.26, 168.63, 155.36, 154.54, 127.11, 119.57, 118.26, 108.34, 92.47, 78.39, 74.81, 56.02, 34.69, 31.54, 26.51 (3C), 14.46. HRMS (ESI): Calcd for C₁₈H₂₃NNaO₇ [M+Na]⁺: 388.1367. Found: 388.1379.

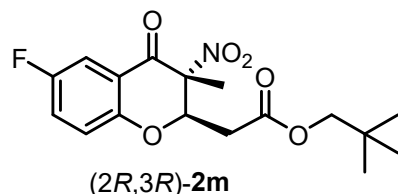
neopentyl 2-((2*S*,3*S*)-6-fluoro-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2m**)



20

2m (159.7 mg, 91%), 9:1 d.r., 91% ee, white solid, m.p. 51-53 °C. Optical rotation [α] = -52.7 (*c* 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.60 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.34-7.29 (m, 1H), 7.01 (dd, *J* = 8.0, 4.0 Hz, 1H), 5.59 (dd, *J* = 10.0, 1.2 Hz, 1H), 3.90 (d, *J* = 10.4 Hz, 1H), 3.87 (d, *J* = 10.4 Hz, 1H), 2.88 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.47 (d, *J* = 16.0 Hz, 1H), 1.76 (s, 3H), 0.94 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃) δ 184.45, 168.46, 158.17 (d, *J* = 243.6 Hz, 1C), 156.01 (d, *J* = 1.6 Hz, 1C), 125.42 (d, *J* = 24.6 Hz, 1C), 120.14 (d, *J* = 7.5 Hz, 1C), 119.01 (d, *J* = 7.0 Hz, 1C), 113.55 (d, *J* = 23.8 Hz, 1C), 92.06, 78.56, 74.92, 34.54, 31.54, 26.51 (3C), 14.49. **¹⁹F NMR** (375 MHz, CDCl₃) δ -118.30. HRMS (ESI): Calcd for C₁₇H₂₀FNNaO₆ [M+Na]⁺: 376.1167. Found: 376.1172.

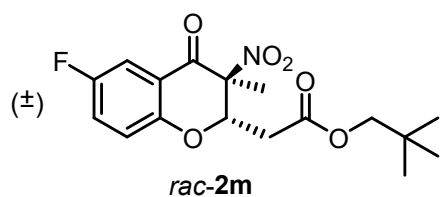
neopentyl 2-((2*R*,3*R*)-6-fluoro-3-methyl-3-nitro-4-oxochroman-2-yl)acetate ((2*R*,3*R*)-**2m**)



(**2R,3R**)-**2m** was prepared according to general procedure using (1*R*,2*R*)-**CAT-6** as catalyst. **20**

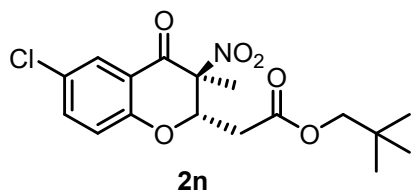
161.8 mg, 92%, 9:1 d.r., 91% ee, white solid, m.p. 63-64 °C. Optical rotation [α] = +54.6 (*c* 1.0, CHCl₃). HRMS (ESI): Calcd for C₁₇H₂₀FNNaO₆ [M+Na]⁺: 376.1167. Found: 376.1160.

neopentyl 2-(6-fluoro-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (*rac*-**2m**)



Preparation of **rac-2m** was carried out following the literature procedure.¹ 172.5 mg, 98%, 10:1 d.r., white solid, m.p. 59-62 °C.

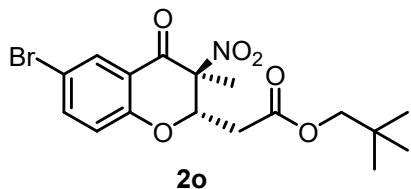
neopentyl 2-((2*S*,3*S*)-6-chloro-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2n**)



10

2n (169.4 mg, 92%), 9:1 d.r., 91% ee, colorless oil. Optical rotation $[\alpha]_D^{25} = -51.8$ (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 2.0 Hz, 1H), 7.52 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 5.60 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.91 (d, *J* = 10.4 Hz, 1H), 3.85 (d, *J* = 10.4 Hz, 1H), 2.88 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.48 (dd, *J* = 16.0, 1.6 Hz, 1H), 1.75 (s, 3H), 0.94 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 184.07, 168.38, 158.12, 137.57, 129.04, 127.78, 119.99, 119.28, 91.91, 78.48, 74.95, 34.51, 31.54, 26.51 (3C), 14.53. HRMS (ESI): Calcd for C₁₇H₂₀ClNNaO₆ [M+Na]⁺: 392.0871. Found: 392.0898 ([M+Na]⁺), 394.0869 ([M+2+Na]⁺).

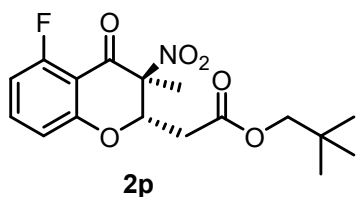
neopentyl 2-((2*S*,3*S*)-6-bromo-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2o**)



10

2o (189.9 mg, 92%), 10:1 d.r., 90% ee, colorless oil. Optical rotation $[\alpha]_D^{25} = -43.6$ (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 2.0 Hz, 1H), 7.66 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 5.60 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.90 (d, *J* = 10.4 Hz, 1H), 3.85 (d, *J* = 10.4 Hz, 1H), 2.88 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.48 (dd, *J* = 16.0, 2.0 Hz, 1H), 1.75 (s, 3H), 0.94 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 183.92, 168.37, 158.58, 140.35, 130.89, 120.28, 119.73, 116.11, 91.85, 78.44, 74.96, 34.51, 31.54, 26.52 (3C), 14.54. HRMS (ESI): Calcd for C₁₇H₂₀BrNNaO₆ [M+Na]⁺: 436.0366. Found: 436.0391 ([M+Na]⁺), 438.0390 ([M+2+Na]⁺).

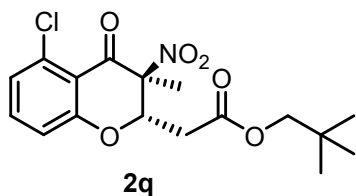
neopentyl 2-((2*S*,3*S*)-5-fluoro-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2p**)



10

2p (158.8 mg, 90%), 6:1 d.r., 87% ee, colorless oil. Optical rotation $[\alpha]_D^{25} = -42.0$ (c 1.0, CHCl_3). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.56-7.50 (m, 1H), 6.86-6.82 (m, 2H), 5.62 (dd, $J = 10.0, 2.0$ Hz, 1H), 3.90 (d, $J = 10.4$ Hz, 1H), 3.85 (d, $J = 10.4$ Hz, 1H), 2.87 (dd, $J = 16.0, 10.0$ Hz, 1H), 2.49 (dd, $J = 16.0, 2.0$ Hz, 1H), 1.77 (s, 3H), 0.94 (s, 9H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 182.16, 168.41, 162.47 (d, $J = 267.9$ Hz, 1C), 160.13 (d, $J = 2.5$ Hz, 1C), 137.83 (d, $J = 11.6$ Hz, 1C), 114.01 (d, $J = 4.0$ Hz, 1C), 110.78 (d, $J = 20.3$ Hz, 1C), 108.82 (d, $J = 9.5$ Hz, 1C), 92.25, 78.08, 74.93, 34.50, 31.52, 26.50 (3C), 14.65. **$^{19}\text{F NMR}$** (375 MHz, CDCl_3) δ -107.74. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{20}\text{FNNaO}_6$ $[\text{M}+\text{Na}]^+$: 376.1167. Found: 376.1187.

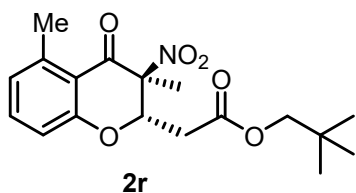
neopentyl 2-((2S,3S)-5-chloro-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2q**)



10

2q (167.6 mg, 91%), 8:1 d.r., 92% ee, colorless oil. Optical rotation $[\alpha]_D^{25} = -34.1$ (c 1.0, CHCl_3). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.46-7.42 (m, 1H), 7.18 (d, $J = 8.0$ Hz, 1H), 6.95 (d, $J = 8.0$ Hz, 1H), 5.63 (dd, $J = 10.0, 2.0$ Hz, 1H), 3.90 (d, $J = 10.4$ Hz, 1H), 3.85 (d, $J = 10.4$ Hz, 1H), 2.85 (dd, $J = 16.0, 10.0$ Hz, 1H), 2.48 (dd, $J = 16.0, 2.0$ Hz, 1H), 1.77 (s, 3H), 0.94 (s, 9H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 182.74, 168.42, 160.97, 136.37, 136.21, 126.53, 117.25, 115.92, 92.30, 77.67, 74.93, 34.53, 31.52, 26.51 (3C), 14.82. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{20}\text{ClNaO}_6$ $[\text{M}+\text{Na}]^+$: 392.0871. Found: 392.0882 ($[\text{M}+\text{Na}]^+$), 394.0845 ($[\text{M}+2+\text{Na}]^+$).

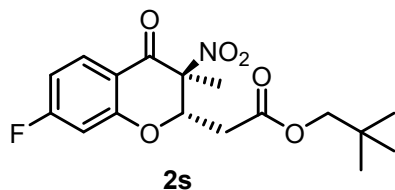
neopentyl 2-((2S,3S)-3,5-dimethyl-3-nitro-4-oxochroman-2-yl)acetate (**2r**)



10

2r (159.1 mg, 91%), > 20:1 d.r., 97% ee, colorless oil. Optical rotation $[\alpha]_D^{25} = -50.4$ (c 1.0, CHCl_3). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.43-7.39 (m, 1H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.87 (d, $J = 8.0$ Hz, 1H), 5.59 (dd, $J = 10.0, 1.6$ Hz, 1H), 3.91 (d, $J = 10.4$ Hz, 1H), 3.85 (d, $J = 10.4$ Hz, 1H), 2.87 (dd, $J = 16.0, 10.0$ Hz, 1H), 2.84 (s, 3H), 2.47 (dd, $J = 16.0, 1.6$ Hz, 1H), 1.75 (s, 3H), 0.94 (s, 9H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 186.09, 168.70, 160.81, 144.11, 136.35, 126.35, 116.80, 116.14, 92.99, 77.25, 74.80, 34.77, 31.54, 26.53 (3C), 22.84, 14.62. HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{23}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 372.1418. Found: 372.1424.

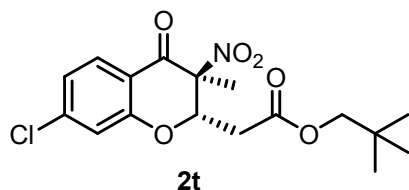
neopentyl 2-((2*S*,3*S*)-7-fluoro-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2s**)



20

2s (162.5 mg, 92%), 10:1 d.r., 94% ee, colorless oil. Optical rotation $[\alpha]_D^{25} = -60.5$ (c 1.0, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.99 (dd, $J = 8.0, 6.4$ Hz, 1H), 6.91-6.86 (m, 1H), 6.72 (dd, $J = 10.0, 2.0$ Hz, 1H), 5.63 (dd, $J = 10.0, 1.6$ Hz, 1H), 3.90 (d, $J = 10.4$ Hz, 1H), 3.86 (d, $J = 10.4$ Hz, 1H), 2.88 (dd, $J = 16.0, 10.0$ Hz, 1H), 2.48 (dd, $J = 16.0, 1.6$ Hz, 1H), 1.76 (s, 3H), 0.95 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 183.74, 168.39 (d, $J = 258.5$ Hz, 1C), 168.40, 161.43 (d, $J = 13.8$ Hz, 1C), 131.33 (d, $J = 11.5$ Hz, 1C), 115.24 (d, $J = 2.4$ Hz, 1C), 112.08 (d, $J = 22.9$ Hz, 1C), 105.33 (d, $J = 24.9$ Hz, 1C), 91.91, 78.69, 74.94, 34.55, 31.52, 26.50 (3C), 14.55. $^{19}\text{F NMR}$ (375 MHz, CDCl_3) δ -96.57. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{20}\text{FNNaO}_6$ $[\text{M}+\text{Na}]^+$: 376.1167. Found: 376.1182.

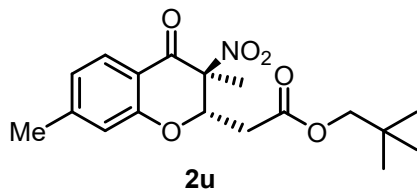
neopentyl 2-((2*S*,3*S*)-7-chloro-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2t**)



20

2t (170.2 mg, 92%), 10:1 d.r., 95% ee, white solid, m.p. 73-75 °C. Optical rotation $[\alpha]_D^{25} = -64.0$ (c 1.0, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.0$ Hz, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.06 (s, 1H), 5.62 (d, $J = 10.0$ Hz, 1H), 3.90 (d, $J = 10.4$ Hz, 1H), 3.87 (d, $J = 10.4$ Hz, 1H), 2.88 (dd, $J = 16.0, 10.0$ Hz, 1H), 2.47 (d, $J = 16.0$ Hz, 1H), 1.75 (s, 3H), 0.95 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 184.09, 168.39, 159.95, 143.92, 129.78, 124.28, 118.52, 116.94, 91.93, 78.58, 74.97, 34.50, 31.52, 26.51 (3C), 14.56. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{20}\text{ClNNaO}_6$ $[\text{M}+\text{Na}]^+$: 392.0871. Found: 392.0874 ($[\text{M}+\text{Na}]^+$), 394.0847 ($[\text{M}+2+\text{Na}]^+$).

neopentyl 2-((2*S*,3*S*)-3,7-dimethyl-3-nitro-4-oxochroman-2-yl)acetate (**2u**)

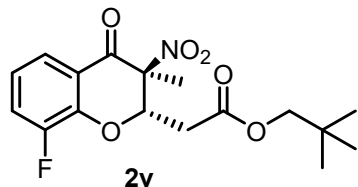


20

2u (169.4 mg, 98%), > 20:1 d.r., 94% ee, colorless oil. Optical rotation $[\alpha]_D^{25} = -63.1$ (c 1.0, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83 (d, $J = 8.0$ Hz, 1H), 6.96 (d, $J = 8.0$ Hz, 1H), 6.82 (s, 1H), 5.58 (dd, $J = 10.0, 1.6$ Hz, 1H), 3.90 (d, $J = 10.4$ Hz, 1H), 3.86 (d, $J = 10.4$ Hz, 1H), 2.88 (dd, $J = 16.0, 10.0$ Hz, 1H), 2.46 (dd, $J = 16.0, 1.6$ Hz, 1H), 2.38 (s, 3H), 1.74 (s,

3H), 0.95 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 184.78, 168.68, 159.81, 149.75, 128.47, 124.72, 118.22, 115.98, 92.31, 78.11, 74.82, 34.69, 31.52, 26.52 (3C), 22.24, 14.49. HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{23}\text{NNaO}_6$ $[\text{M}+\text{Na}]^+$: 372.1418. Found: 372.1431.

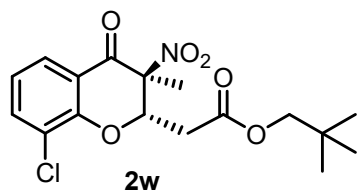
neopentyl 2-((2*S*,3*S*)-8-fluoro-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2v**)



2v

2v (164.5 mg, 93%), 15:1 d.r., 92% ee, white solid, m.p. 97-99 °C. Optical rotation $[\alpha] = -47.6$ (*c* 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 8.0$ Hz, 1H), 7.41-7.37 (m, 1H), 7.13-7.08 (m, 1H), 5.68 (dd, $J = 10.0, 1.6$ Hz, 1H), 3.90 (d, $J = 10.4$ Hz, 1H), 3.87 (d, $J = 10.4$ Hz, 1H), 2.94 (dd, $J = 16.0, 10.0$ Hz, 1H), 2.51 (dd, $J = 16.0, 1.6$ Hz, 1H), 1.79 (s, 3H), 0.95 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 184.22 (d, $J = 3.3$ Hz, 1C), 168.27, 151.35 (d, $J = 250.2$ Hz, 1C), 148.09 (d, $J = 12.2$ Hz, 1C), 123.67 (d, $J = 7.1$ Hz, 1C), 123.57 (d, $J = 6.1$ Hz, 1C), 123.05 (d, $J = 6.3$ Hz, 1C), 120.43, 92.10, 79.00, 75.04, 34.57, 31.48, 26.46 (3C), 14.56. ^{19}F NMR (375 MHz, CDCl_3) δ -132.96. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{20}\text{FNNaO}_6$ $[\text{M}+\text{Na}]^+$: 376.1167. Found: 376.1183.

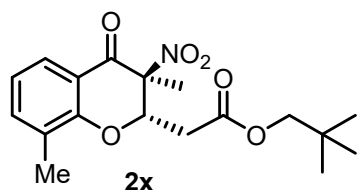
neopentyl 2-((2*S*,3*S*)-8-chloro-3-methyl-3-nitro-4-oxochroman-2-yl)acetate (**2w**)



2w

2w (173.9 mg, 94%), 17:1 d.r., 93% ee, white solid, m.p. 90-92 °C. Optical rotation $[\alpha] = -66.1$ (*c* 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.66 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.13-7.09 (m, 1H), 5.68 (dd, $J = 10.0, 1.6$ Hz, 1H), 3.92 (d, $J = 10.4$ Hz, 1H), 3.87 (d, $J = 10.4$ Hz, 1H), 2.96 (dd, $J = 16.0, 10.0$ Hz, 1H), 2.52 (dd, $J = 16.0, 1.6$ Hz, 1H), 1.78 (s, 3H), 0.95 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 184.44, 168.29, 155.32, 137.69, 127.09, 123.46, 123.44, 119.76, 91.86, 79.02, 75.08, 34.56, 31.46, 26.52 (3C), 14.56. HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{20}\text{ClNNaO}_6$ $[\text{M}+\text{Na}]^+$: 392.0871. Found: 392.0885 ($[\text{M}+\text{Na}]^+$), 394.0846 ($[\text{M}+2+\text{Na}]^+$).

neopentyl 2-((2*S*,3*S*)-3,8-dimethyl-3-nitro-4-oxochroman-2-yl)acetate (**2x**)



2x (171.4 mg, 98%), > 20:1 d.r., 95% ee, white solid, m.p. 86-88 °C. Optical rotation $[\alpha]$

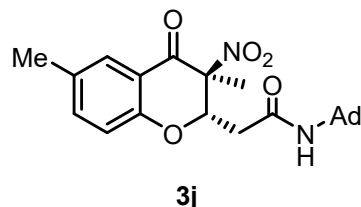
10

= -54.1 (*c* 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.06-7.03 (m, 1H), 5.59 (d, *J* = 10.0, 1.6 Hz, 1H), 3.90 (d, *J* = 10.4 Hz, 1H), 3.84 (d, *J* = 10.4 Hz, 1H), 2.91 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.49 (dd, *J* = 16.0, 1.6 Hz, 1H), 2.21 (s, 3H), 1.76 (s, 3H), 0.95 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃) δ 185.47, 168.72, 158.01, 138.54, 127.75, 126.21, 122.82, 118.09, 92.26, 78.18, 74.89, 34.63, 31.46, 26.51 (3C), 15.38, 14.43. HRMS (ESI): Calcd for C₁₈H₂₃NNaO₆ [M+Na]⁺: 372.1418. Found: 372.1414.

General Procedure for the synthesis of 3

To a solution of **2** (0.5 mmol, 1 equiv.) in 20 mL of 1,4-dioxane was added 20 mL of 6 N HCl. The resulting mixture was heated to 100 °C and stirred for 2 h. After cooling to rt, the mixture was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine (20 mL), then dried over Na₂SO₄, filtered and concentrated in vacuo to give a crude carboxylic acid product. To the solution of crude carboxylic acid in 20 mL of dry CH₂Cl₂ was added R⁴NH₂ (0.55 mmol, 1.1 equiv.), Et₃N (1.1 mmol, 2 equiv.), HOBT (1.1 mmol, 2 equiv.) and EDCI (1.1 mmol, 2 equiv.) at 0 °C. The resulting mixture was stirred at 0 °C for 12 h. 1 N HCl (10 mL) was added and the biphasic mixture was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic extracts were washed with brine (20 mL), then dried over Na₂SO₄, filtered, concentrated in vacuo to give a residue. The residue was purified by silica gel chromatography (petroleum ether:EtOAc, 5:1) and recrystallized with petroleum ether/EtOAc to afford desired products **3** (52-76%).

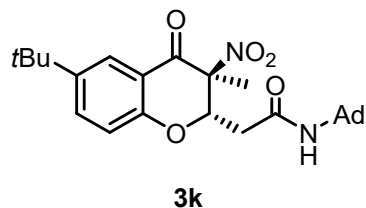
N-(adamantan-1-yl)-2-((2*S*,3*S*)-3,6-dimethyl-3-nitro-4-oxochroman-2-yl)acetamide (**3j**)



10

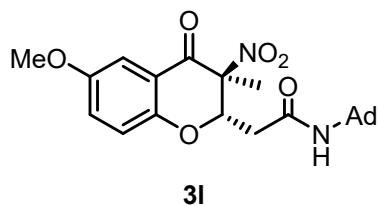
3j (115.3 mg, 56%), > 20:1 d.r., > 99% ee, colorless oil. Optical rotation [α] = -40.6 (*c* 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.73 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 5.54 (dd, *J* = 10.0, 2.4 Hz, 1H), 5.31 (br s, 1H), 2.53 (dd, *J* = 14.8, 10.0 Hz, 1H), 2.33 (s, 3H), 2.25 (dd, *J* = 14.8, 2.4 Hz, 1H), 2.10-2.06 (m, 3H), 2.04-2.00 (m, 6H), 1.72 (s, 3H), 1.70-1.66 (m, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 185.20, 166.14, 157.69, 138.69, 132.95, 128.03, 118.23, 118.03, 92.41, 78.99, 52.68, 41.69 (3C), 37.14, 36.39 (3C), 29.51 (3C), 20.60, 14.87. HRMS (ESI): Calcd for C₂₃H₂₈N₂NaO₅ [M+Na]⁺: 435.1890. Found: 435.1907.

N-(adamantan-1-yl)-2-((2*S*,3*S*)-6-(tert-butyl)-3-methyl-3-nitro-4-oxochroman-2-yl)acetamide (**3k**)



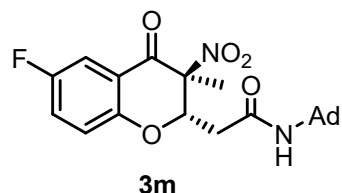
3k (118.2 mg, 52%), > 20:1 d.r., 95% ee, yellow solid, m.p. 189-191 °C. Optical rotation $[\alpha]_D^{20} = -39.1$ (*c* 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.91 (d, *J* = 2.0 Hz, 1H), 7.63 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 5.53 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.34 (br s, 1H), 2.55 (dd, *J* = 14.8, 10.0 Hz, 1H), 2.25 (dd, *J* = 14.8, 2.0 Hz, 1H), 2.10-2.05 (m, 3H), 2.04-2.00 (m, 6H), 1.73 (s, 3H), 1.70-1.66 (m, 6H), 1.31 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃) δ 185.38, 166.20, 157.67, 146.39, 135.45, 124.48, 117.85 (2C), 92.52, 79.03, 52.66, 41.68 (3C), 37.23, 36.39 (3C), 34.63, 31.28 (3C), 29.51 (3C), 14.83. HRMS (ESI): Calcd for C₂₆H₃₄N₂NaO₅ [M+Na]⁺: 477.2360. Found: 477.2379.

N-(adamantan-1-yl)-2-((2*S*,3*S*)-6-methoxy-3-methyl-3-nitro-4-oxochroman-2-yl)acetamide (**3l**)



3l (142.5 mg, 67%), > 20:1 d.r., 90% ee, white solid, m.p. 215-218 °C. Optical rotation $[\alpha]_D^{20} = -39.3$ (*c* 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.32 (d, *J* = 1.6 Hz, 1H), 7.17 (dd, *J* = 8.8, 1.6 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 5.52 (dd, *J* = 10.0, 2.4 Hz, 1H), 5.32 (br s, 1H), 3.81 (s, 3H), 2.53 (dd, *J* = 14.8, 10.0 Hz, 1H), 2.24 (dd, *J* = 14.8, 2.4 Hz, 1H), 2.10-2.06 (m, 3H), 2.04-1.98 (m, 6H), 1.73 (s, 3H), 1.70-1.67 (m, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 185.19, 166.15, 155.31, 154.35, 126.98, 119.58, 118.52, 108.35, 92.46, 79.19, 56.02, 52.69, 41.69 (3C), 37.10, 36.37 (3C), 29.50 (3C), 14.84. HRMS (ESI): Calcd for C₂₃H₂₈N₂NaO₆ [M+Na]⁺: 451.1840. Found: 451.1862.

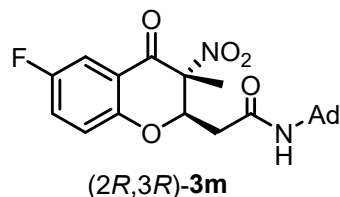
N-(adamantan-1-yl)-2-((2*S*,3*S*)-6-fluoro-3-methyl-3-nitro-4-oxochroman-2-yl)acetamide (**3m**)



3m (158.6 mg, 76%), 9:1 d.r., 91% ee, white solid, m.p. 122-125 °C. Optical rotation $[\alpha]_D^{20} = -39.9$ (*c* 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.60 (dd, *J* = 8.0, 2.8 Hz, 1H), 7.33-7.28 (m, 1H), 7.01 (dd, *J* = 8.0, 4.4 Hz, 1H), 5.59 (dd, *J* = 10.0, 2.4 Hz, 1H), 5.22 (br s,

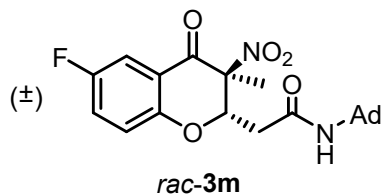
1H), 2.53 (dd, $J = 14.8, 10.0$ Hz, 1H), 2.27 (dd, $J = 14.8, 2.4$ Hz, 1H), 2.10-2.06 (m, 3H), 2.04-2.00 (m, 6H), 1.74 (s, 3H), 1.70-1.67 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 184.41, 165.84, 158.09 (d, $J = 243.5$ Hz, 1C), 155.92 (d, $J = 1.7$ Hz, 1C), 125.26 (d, $J = 24.5$ Hz, 1C), 120.17 (d, $J = 7.6$ Hz, 1C), 119.25 (d, $J = 7.0$ Hz, 1C), 113.46 (d, $J = 23.8$ Hz, 1C), 92.07, 79.33, 52.78, 41.69 (3C), 36.89, 36.36 (3C), 29.50 (3C), 14.88. HRMS (ESI): Calcd for $\text{C}_{22}\text{H}_{25}\text{FN}_2\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 439.1640. Found: 439.1649.

N-(adamantan-1-yl)-2-((2*R*,3*R*)-6-fluoro-3-methyl-3-nitro-4-oxochroman-2-yl)acetamide ((2*R*,3*R*)-**3m**)



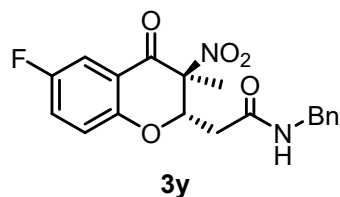
(2*R*,3*R*)-**3m** (150.6 mg, 72%), 9:1 d.r., 91% ee, white solid, m.p. 63-64 °C. Optical rotation $[\alpha]_{\text{D}}^{20} = +54.6$ (c 1.0, CHCl_3). HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{20}\text{FNNaO}_6$ $[\text{M}+\text{Na}]^+$: 376.1167. Found: 376.1160.

N-(adamantan-1-yl)-2-(6-fluoro-3-methyl-3-nitro-4-oxochroman-2-yl)acetamide (*rac*-**3m**)



Preparation of *rac*-**3m** was carried out following the literature procedure.² 160.8 mg, 77%, 10:1 d.r., white solid, m.p. 59-62 °C.

N-benzyl-2-((2*S*,3*S*)-6-fluoro-3-methyl-3-nitro-4-oxochroman-2-yl)acetamide (**3y**)



3y (131.8 mg, 71%), 9:1 d.r., 91% ee, white solid, m.p. 101-103 °C. Optical rotation $[\alpha]_{\text{D}}^{20} = -25.8$ (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.50 (m, 1H), 7.28-7.26 (m, 1H), 7.22-7.18 (m, 5H), 6.86-6.84 (m, 1H), 5.80 (s, 1H), 5.58 (d, $J = 10.0$ Hz, 1H), 4.48 (dd, $J = 15.0, 4.0$ Hz, 1H), 4.34 (dd, $J = 15.0, 4.0$ Hz, 1H), 2.55 (dd, $J = 15.0, 10.0$ Hz, 1H), 2.31 (d, $J = 15.0$ Hz, 1H), 1.66 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 184.37 (d, $J = 2.0$ Hz, 1C), 167.04, 158.09 (d, $J = 243.5$ Hz, 1C), 155.83 (d, $J = 1.6$ Hz, 1C), 137.79, 128.89 (2C), 127.87 (3C), 125.33 (d, $J = 24.5$ Hz, 1C), 120.13 (d, $J = 7.6$ Hz, 1C), 119.10 (d, $J = 7.0$ Hz, 1C), 113.42 (d, $J = 23.9$ Hz, 1C), 92.08, 79.07, 44.03, 35.98, 14.66. ^{19}F NMR (375 MHz, CDCl_3) δ -118.29. HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{17}\text{FN}_2\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 395.1019. Found: 395.1010.

3. References

- 1 H. Chen, J. Xie, D. Xing, J. Wang, J. Tang, Z. Yi, F. Xia, W.-W. Qiu and F. Yang, *Org. Biomol. Chem.*, 2019, **17**, 1062-1066.
- 2 H. Chen, Y. Xing, J. Xie, J. Xie, D. Xing, J. Tang, F. Yang, Z. Yi and W.-W. Qiu, *RSC Adv.*, 2019, **9**, 33794–33799.

4. Biology materials and methods

4.1 Cell lines and culture conditions

Human prostate cancer cell lines DU145 and PC3 were obtained from the American Type Culture Collection (ATCC). DU145 and PC3 cell lines were cultured in RPMI 1640 medium (Gibco). Both media were supplemented with 10% FBS (Wisent, St. Bruno, QC, Canada). All cells were incubated at 37 °C and 5% CO₂ incubator.

4.2 Cell viability assay

The cell viability of cell lines in the presence of this series of compounds was determined by Sulforhodamine B (SRB) assay (Sigma Aldrich). Cells were seeded in 96-well plates (3000 cells/well) and incubated with indicated concentrations of compounds. After incubation for indicated time, the cells were then fixed with trichloroacetic acid, stained with SRB (Sigma Aldrich, Argentina, Cat# S1402), and analyzed for percent of survival on 96-well plate reader. The IC₅₀ (half maximal inhibitory concentration) value was calculated using GraphPad software.

5. X-Ray crystallography of **3y** (CCDC 2094077)

A single crystal of **3y** was obtained from EtOAc solvent at room temperature. Diffraction data were collected on Bruker CCD-APEX X-ray diffractometer. Refinement was carried out on F².

Table S1 Crystal data and structure refinement for **3y**

Identification code	cu_d8v19901_0m
Empirical formula	C ₁₉ H ₁₇ F N ₂ O ₅
Formula weight	372.34
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Tetragonal
Space group	P 41
Unit cell dimensions	a = 9.5302(3) Å α = 90°. b = 9.5302(3) Å β = 90°. c = 19.3236(5) Å γ = 90°.
Volume	1755.06(12) Å ³
Z	4
Density (calculated)	1.409 Mg/m ³
Absorption coefficient	0.931 mm ⁻¹
F(000)	776
Crystal size	0.200 x 0.170 x 0.140 mm ³
Theta range for data collection	4.640 to 67.489°.
Index ranges	-10 ≤ h ≤ 9, -11 ≤ k ≤ 11, -23 ≤ l ≤ 22
Reflections collected	16115
Independent reflections	3121 [R(int) = 0.0372]
Completeness to theta = 67.679°	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.5199
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3121 / 1 / 246
Goodness-of-fit on F ²	1.048
Final R indices [I > 2σ(I)]	R1 = 0.0290, wR2 = 0.0713
R indices (all data)	R1 = 0.0307, wR2 = 0.0726
Absolute structure parameter	0.03(7)
Extinction coefficient	0.021(2)

Largest diff. peak and hole

0.090 and -0.098 e.Å⁻³**Table S2** bond lengths [Å] and angles [°] for **3y**

F(1)-C(4)	1.356(3)	F(1)-C(4)-C(3)	118.3(2)
O(1)-C(7)	1.207(3)	C(5)-C(4)-C(3)	122.3(2)
O(2)-C(1)	1.370(3)	C(4)-C(5)-C(6)	118.7(2)
O(2)-C(9)	1.434(3)	C(4)-C(5)-H(5)	120.6
O(3)-C(11)	1.236(3)	C(6)-C(5)-H(5)	120.6
O(4)-N(2)	1.208(3)	C(1)-C(6)-C(5)	119.1(2)
O(5)-N(2)	1.200(3)	C(1)-C(6)-C(7)	120.5(2)
N(1)-C(11)	1.333(3)	C(5)-C(6)-C(7)	120.2(2)
N(1)-C(13)	1.449(3)	O(1)-C(7)-C(6)	124.2(2)
N(1)-H(1)	0.8600	O(1)-C(7)-C(8)	121.3(2)
N(2)-C(8)	1.519(3)	C(6)-C(7)-C(8)	114.24(18)
C(1)-C(2)	1.382(3)	N(2)-C(8)-C(12)	110.5(2)
C(1)-C(6)	1.392(3)	N(2)-C(8)-C(7)	106.47(19)
C(2)-C(3)	1.365(3)	C(12)-C(8)-C(7)	108.9(2)
C(2)-H(2)	0.9300	N(2)-C(8)-C(9)	106.6(2)
C(3)-C(4)	1.378(3)	C(12)-C(8)-C(9)	114.1(2)
C(3)-H(3)	0.9300	C(7)-C(8)-C(9)	110.00(18)
C(4)-C(5)	1.359(4)	O(2)-C(9)-C(10)	105.80(18)
C(5)-C(6)	1.400(3)	O(2)-C(9)-C(8)	108.61(18)
C(5)-H(5)	0.9300	C(10)-C(9)-C(8)	114.74(19)
C(6)-C(7)	1.470(3)	O(2)-C(9)-H(9)	109.2
C(7)-C(8)	1.536(4)	C(10)-C(9)-H(9)	109.2
C(8)-C(12)	1.520(3)	C(8)-C(9)-H(9)	109.2
C(8)-C(9)	1.541(3)	C(11)-C(10)-C(9)	110.14(18)
C(9)-C(10)	1.512(3)	C(11)-C(10)-H(10A)	109.6
C(9)-H(9)	0.9800	C(9)-C(10)-H(10A)	109.6
C(10)-C(11)	1.510(4)	C(11)-C(10)-H(10B)	109.6
C(10)-H(10A)	0.9700	C(9)-C(10)-H(10B)	109.6
C(10)-H(10B)	0.9700	H(10A)-C(10)-H(10B)	108.1
C(12)-H(12A)	0.9600	O(3)-C(11)-N(1)	123.2(2)
C(12)-H(12B)	0.9600	O(3)-C(11)-C(10)	120.9(2)
C(12)-H(12C)	0.9600	N(1)-C(11)-C(10)	115.8(2)
C(13)-C(14)	1.506(4)	C(8)-C(12)-H(12A)	109.5
C(13)-H(13A)	0.9700	C(8)-C(12)-H(12B)	109.5
C(13)-H(13B)	0.9700	H(12A)-C(12)-H(12B)	109.5
C(14)-C(15)	1.380(4)	C(8)-C(12)-H(12C)	109.5
C(14)-C(19)	1.388(4)	H(12A)-C(12)-H(12C)	109.5
C(15)-C(16)	1.383(4)	H(12B)-C(12)-H(12C)	109.5
C(15)-H(15)	0.9300	N(1)-C(13)-C(14)	115.4(2)

C(16)-C(17)	1.367(5)	N(1)-C(13)-H(13A)	108.4
C(16)-H(16)	0.9300	C(14)-C(13)-H(13A)	108.4
C(17)-C(18)	1.374(5)	N(1)-C(13)-H(13B)	108.4
C(17)-H(17)	0.9300	C(14)-C(13)-H(13B)	108.4
C(18)-C(19)	1.374(5)	H(13A)-C(13)-H(13B)	107.5
C(18)-H(18)	0.9300	C(15)-C(14)-C(19)	117.8(3)
C(19)-H(19)	0.9300	C(15)-C(14)-C(13)	123.4(2)
C(1)-O(2)-C(9)	115.87(16)	C(19)-C(14)-C(13)	118.8(2)
C(11)-N(1)-C(13)	123.1(2)	C(14)-C(15)-C(16)	121.1(3)
C(11)-N(1)-H(1)	118.5	C(14)-C(15)-H(15)	119.5
C(13)-N(1)-H(1)	118.5	C(16)-C(15)-H(15)	119.5
O(5)-N(2)-O(4)	123.4(3)	C(17)-C(16)-C(15)	120.5(3)
O(5)-N(2)-C(8)	119.3(3)	C(17)-C(16)-H(16)	119.8
O(4)-N(2)-C(8)	117.4(2)	C(15)-C(16)-H(16)	119.8
O(2)-C(1)-C(2)	116.90(18)	C(16)-C(17)-C(18)	119.1(3)
O(2)-C(1)-C(6)	122.48(19)	C(16)-C(17)-H(17)	120.5
C(2)-C(1)-C(6)	120.5(2)	C(18)-C(17)-H(17)	120.5
C(3)-C(2)-C(1)	119.8(2)	C(19)-C(18)-C(17)	120.7(3)
C(3)-C(2)-H(2)	120.1	C(19)-C(18)-H(18)	119.6
C(1)-C(2)-H(2)	120.1	C(17)-C(18)-H(18)	119.6
C(2)-C(3)-C(4)	119.5(2)	C(18)-C(19)-C(14)	120.9(3)
C(2)-C(3)-H(3)	120.2	C(18)-C(19)-H(19)	119.6
C(4)-C(3)-H(3)	120.2	C(14)-C(19)-H(19)	119.6
F(1)-C(4)-C(5)	119.4(2)		

Symmetry transformations used to generate equivalent atoms.

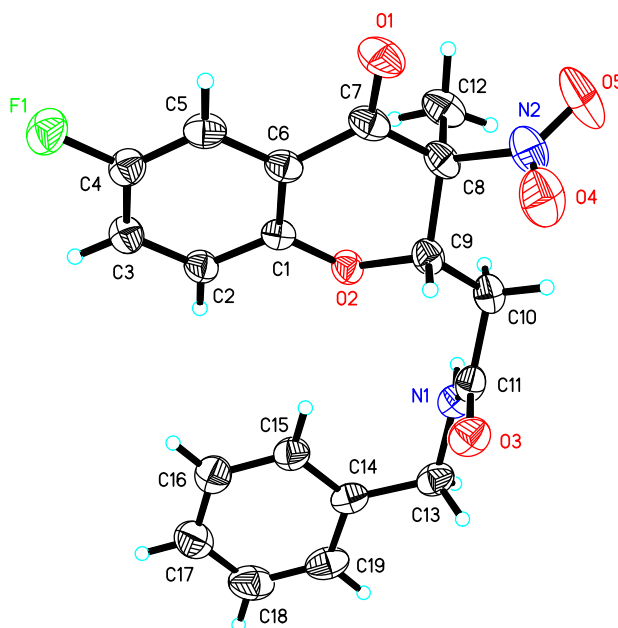


Figure S1 Molecular structure of **3y**.

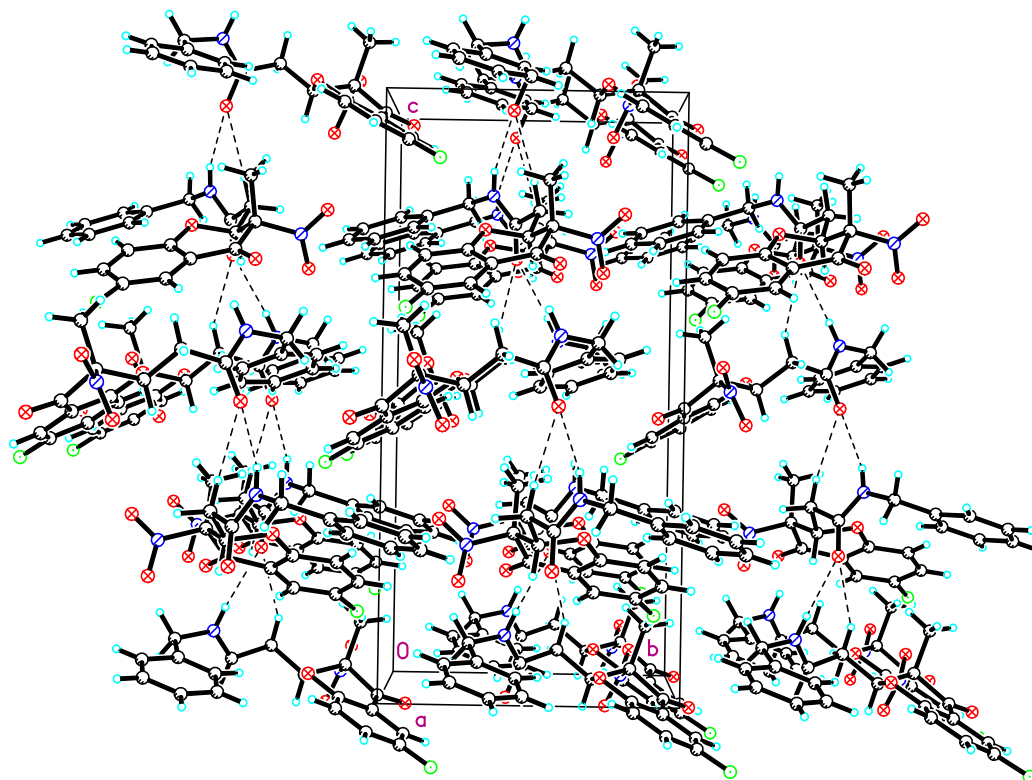
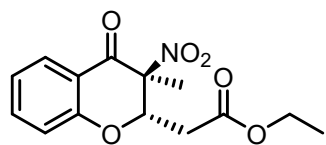


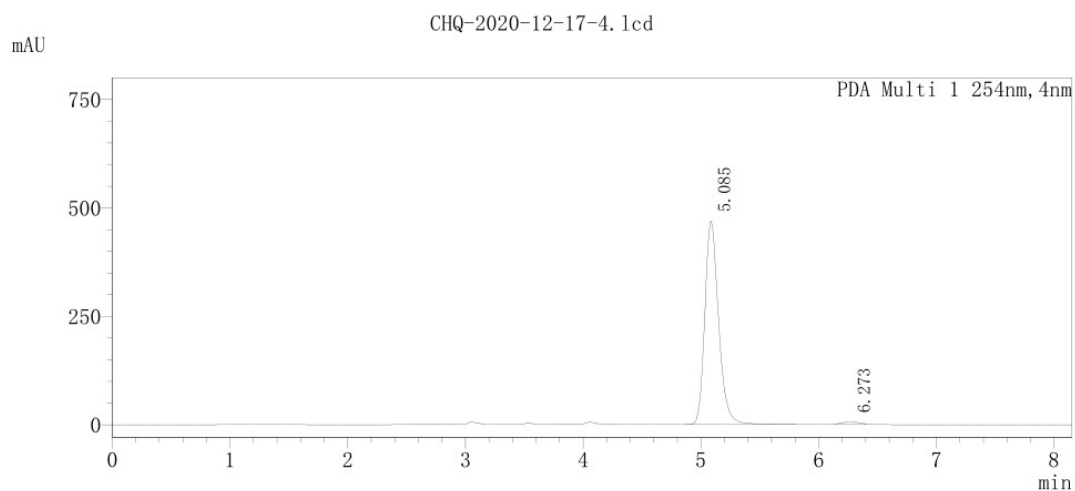
Figure S2 Unit cell molecular packing arrangement of **3y**.

6. Chiral HPLC charts



2a

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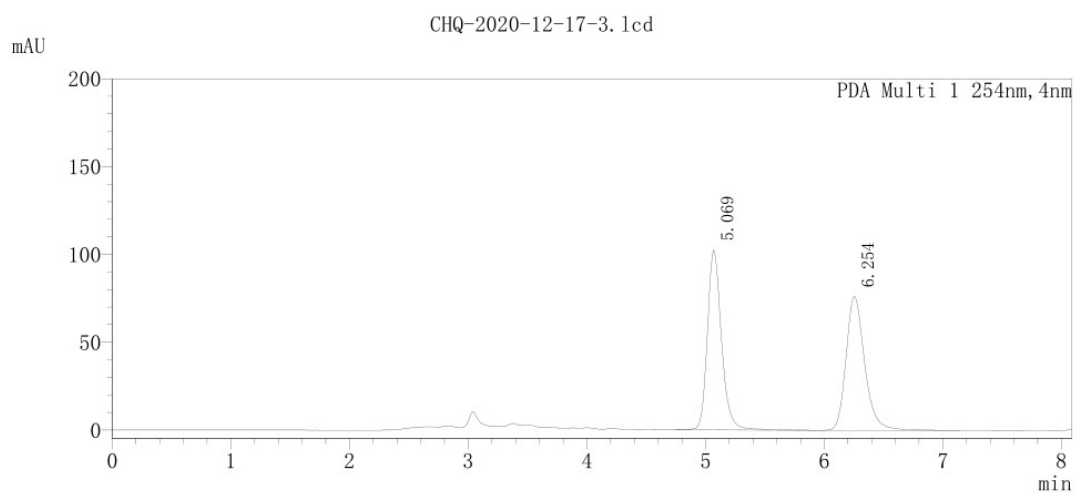
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CHQ-2020-12-17-4. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	5.085	3827164	470050	98.806	98.923
2	6.273	46258	5119	1.194	1.077
总计		3873423	475169	100.000	100.000

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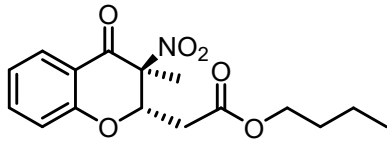


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CHQ-2020-12-17-3. lcd

PDA Ch1 254nm

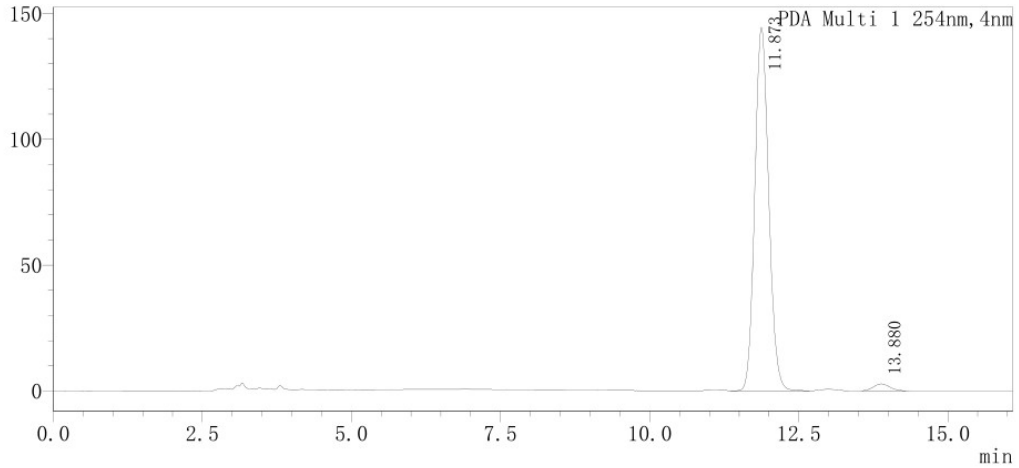
峰号	保留时间	面积	高度	面积%	高度%
1	5.069	853485	102590	50.651	57.368
2	6.254	831534	76239	49.349	42.632
总计		1685018	178829	100.000	100.000



2b

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<峰表>

CHQ-2021-1-20-2.lcd

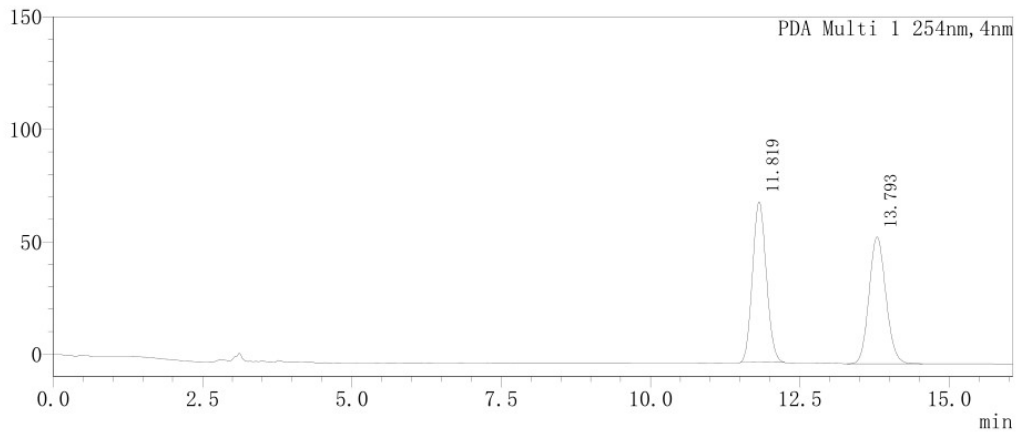
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	11.873	2346545	144271	97.877	98.150
2	13.880	50893	2719	2.123	1.850
总计		2397438	146989	100.000	100.000

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CHQ-2021-1-20-1-1.lcd

mAU

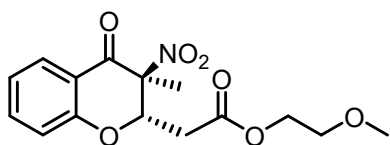


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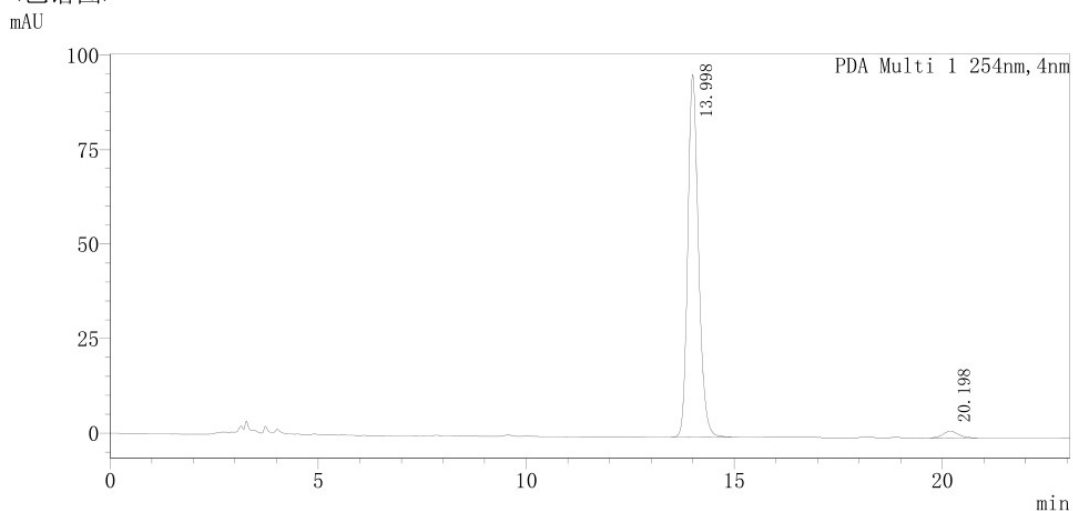
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	11.819	1151212	71456	50.940	55.876
2	13.793	1108717	56427	49.060	44.124
总计		2259929	127883	100.000	100.000



2c

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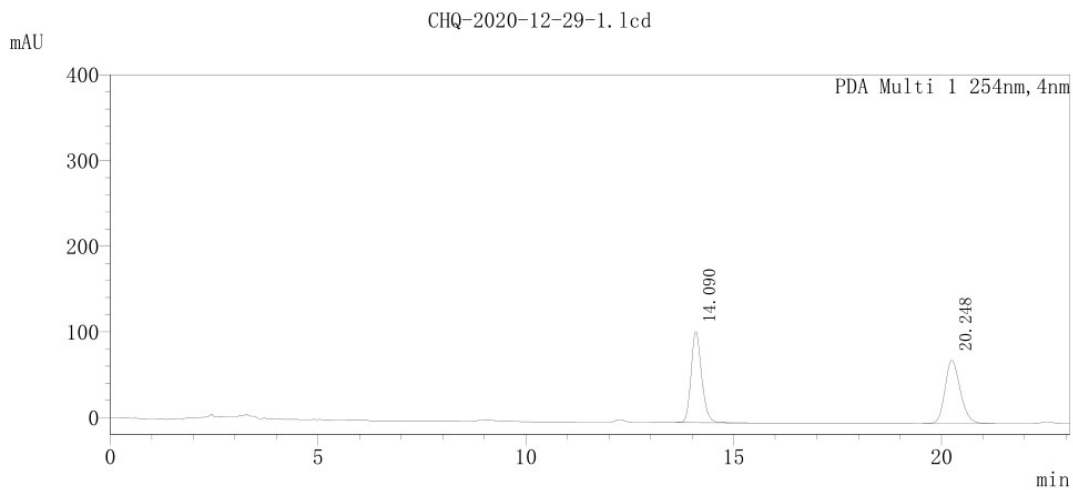
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CHQ-2020-12-29-2. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	13.998	1711144	95939	97.474	98.210
2	20.198	44343	1749	2.526	1.790
总计		1755487	97688	100.000	100.000

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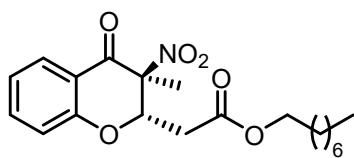


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CHQ-2020-12-29-1. lcd

PDA Ch1 254nm

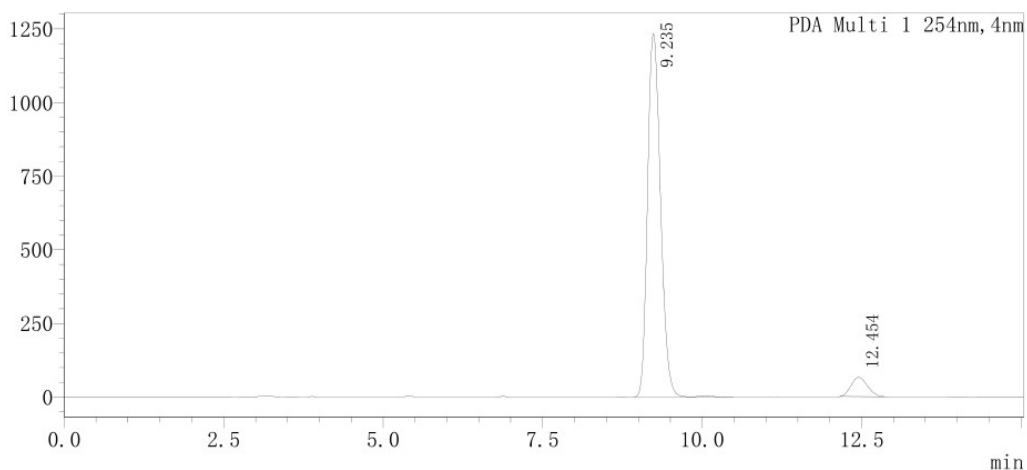
峰号	保留时间	面积	高度	面积%	高度%
1	14.090	1885190	106320	49.952	58.949
2	20.248	1888826	74039	50.048	41.051
总计		3774016	180359	100.000	100.000



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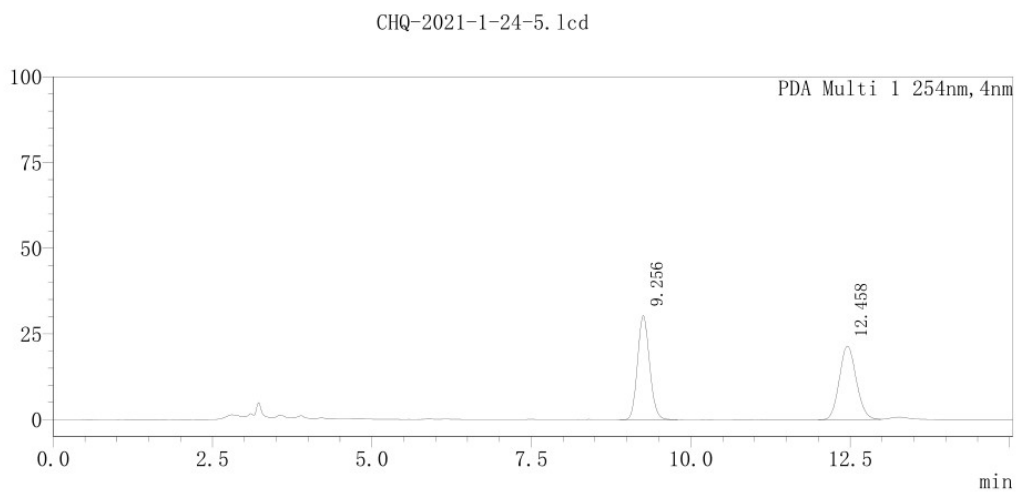
CHQ-2021-1-24-6.1cd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	9.235	17534331	1234034	93.778	94.994
2	12.454	1163275	65036	6.222	5.006
总计		18697606	1299070	100.000	100.000

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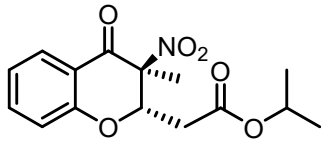


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CHQ-2021-1-24-5.1cd

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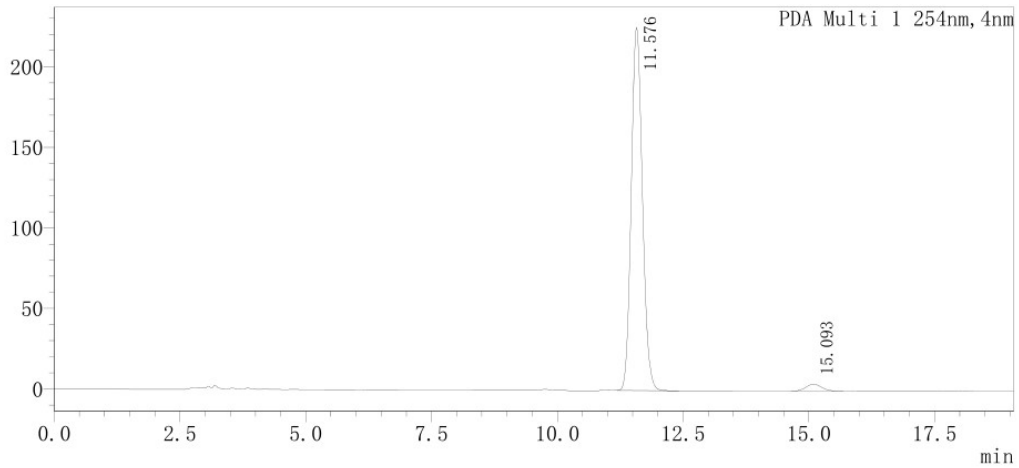
峰号	保留时间	面积	高度	面积%	高度%
1	9.256	400090	30416	50.261	58.636
2	12.458	395936	21456	49.739	41.364
总计		796026	51872	100.000	100.000



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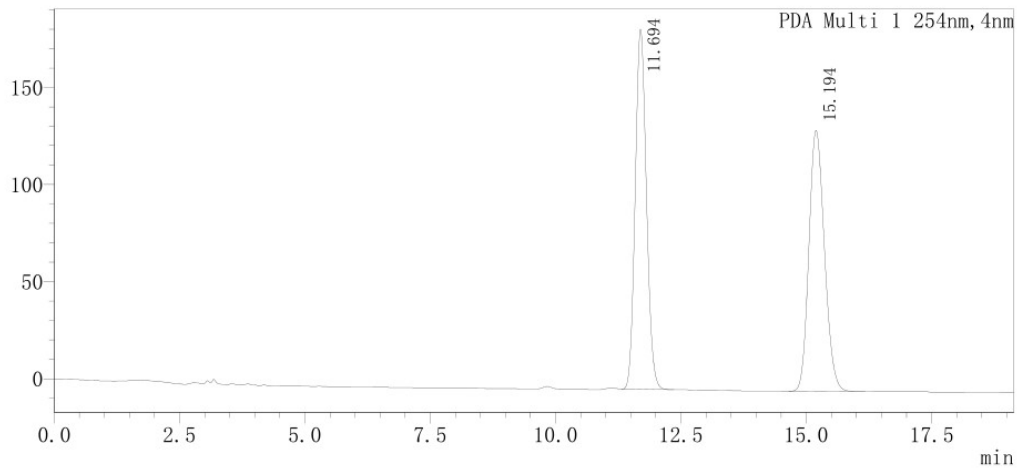
CHQ-2021-1-3-2.1cd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	11.576	3500285	225319	97.452	98.125
2	15.093	91529	4305	2.548	1.875
总计		3591815	229623	100.000	100.000

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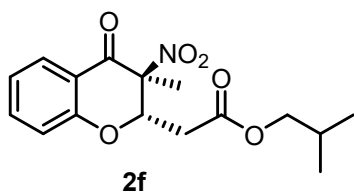


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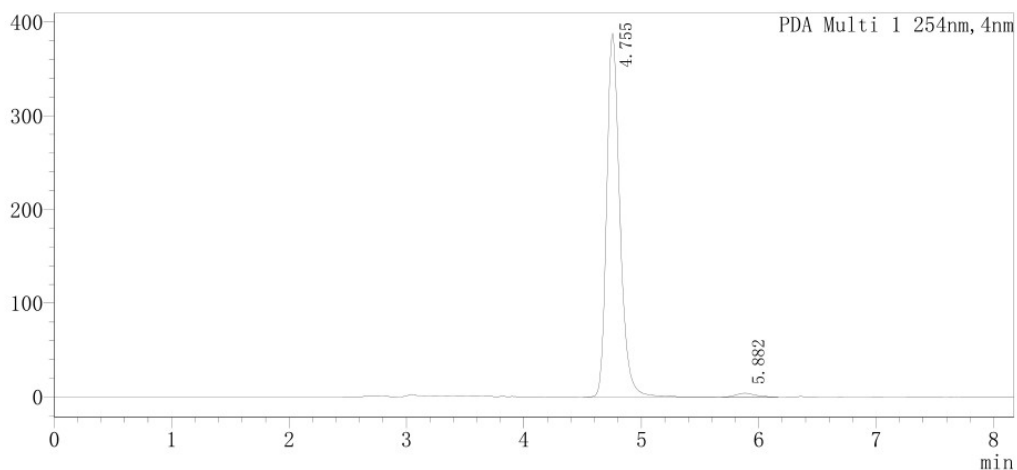
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	11.694	2903013	185437	49.876	57.972
2	15.194	2917436	134436	50.124	42.028
总计		5820450	319872	100.000	100.000



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CHQ-2020-11-21-4. lcd

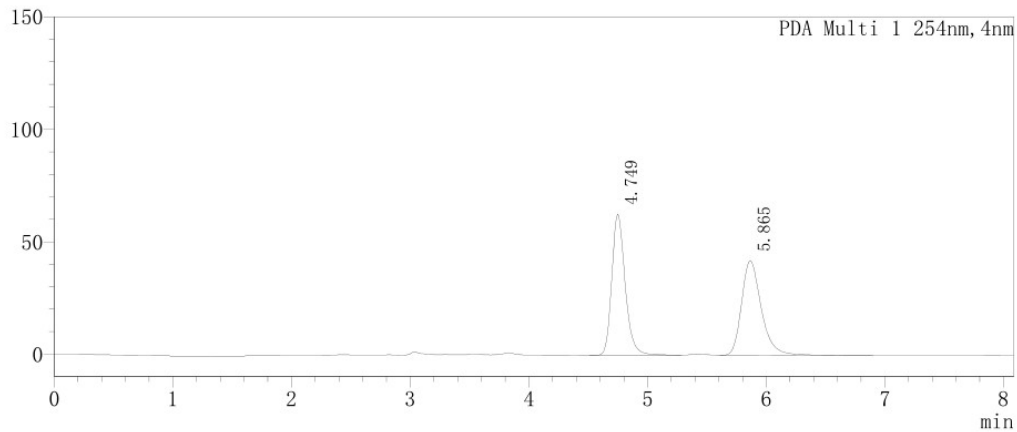
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	4.755	3037562	387549	98.613	99.001
2	5.882	42709	3910	1.387	0.999
总计		3080271	391458	100.000	100.000

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CHQ-2020-11-21-2. lcd

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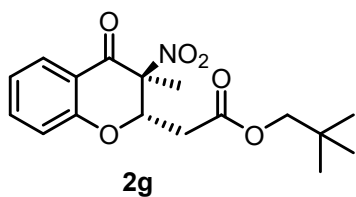


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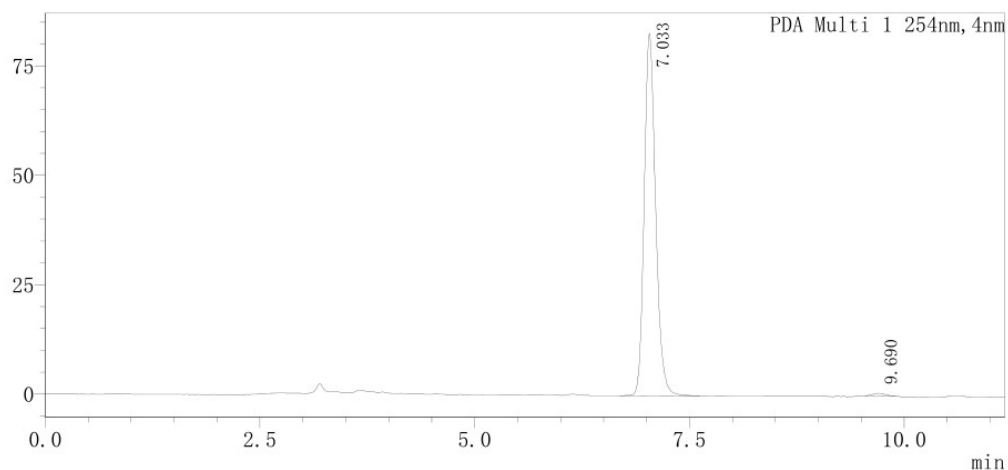
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	4.749	493081	62821	50.236
2	5.865	488446	42141	49.764
总计		981526	104962	100.000



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CHQ-2020-12-5-5.lcd

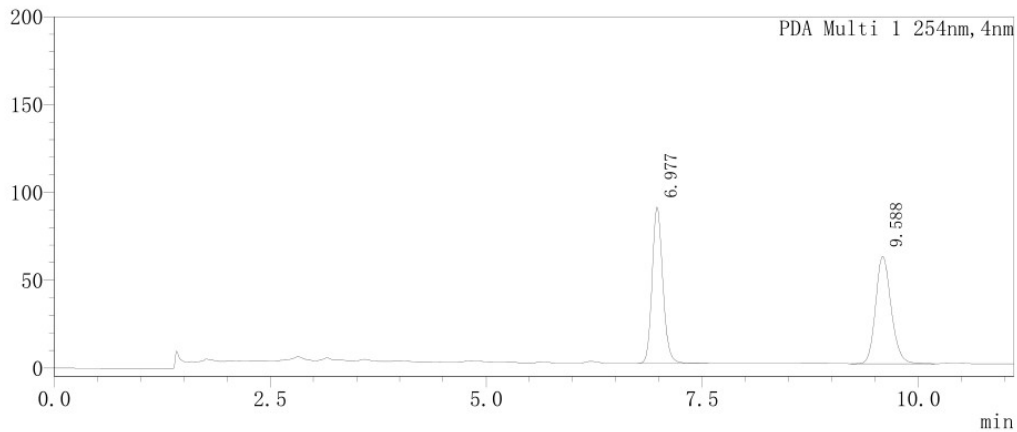
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	7.033	765928	82781	99.059	99.218
2	9.690	7272	653	0.941	0.782
总计		773200	83434	100.000	100.000

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CHQ-2020-12-9-3.lcd

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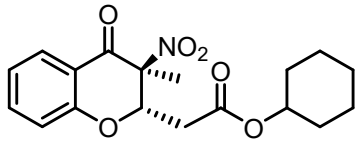


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PDA Ch1 254nm

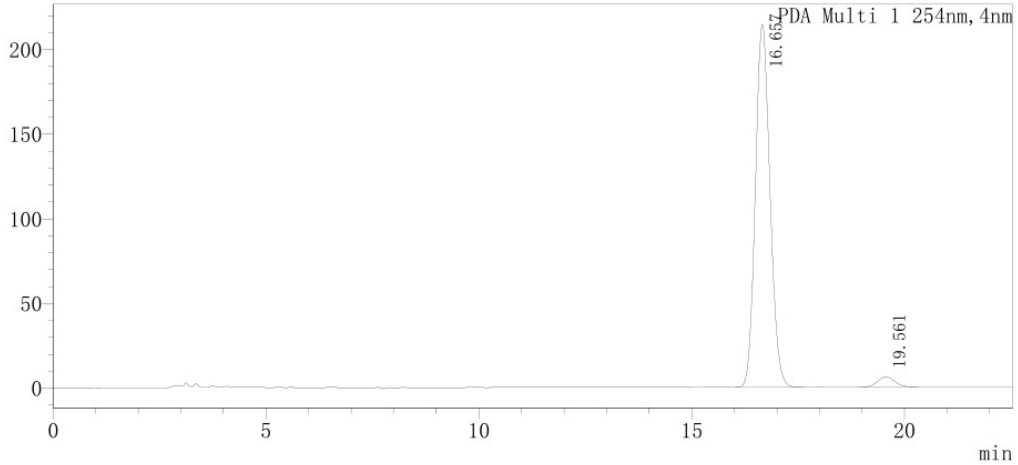
峰号	保留时间	面积	高度	面积%	高度%
1	6.977	766631	89010	49.987	59.245
2	9.588	767035	61230	50.013	40.755
总计		1533665	150240	100.000	100.000



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CHQ-2021-1-20-4. lcd

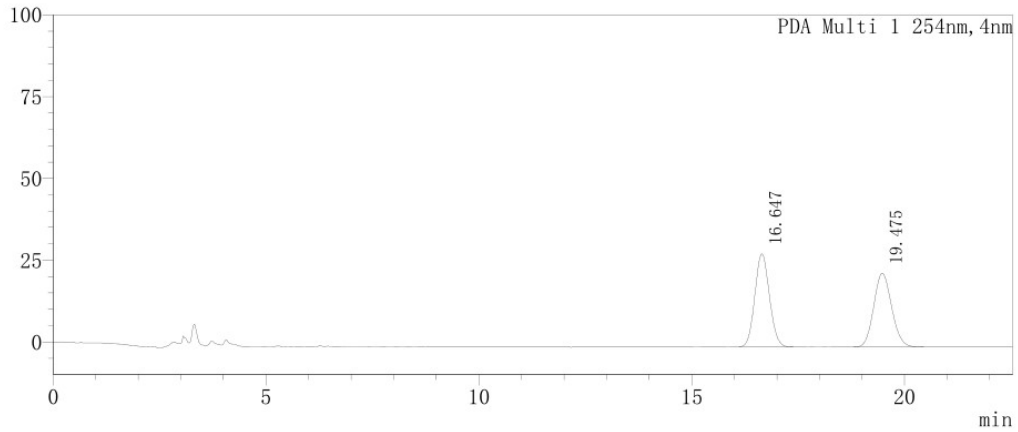
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	16.657	5118821	214327	96.689	97.254
2	19.561	175288	6052	3.311	2.746
总计		5294109	220379	100.000	100.000

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CHQ-2021-1-20-3-1. lcd

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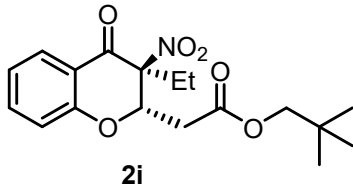


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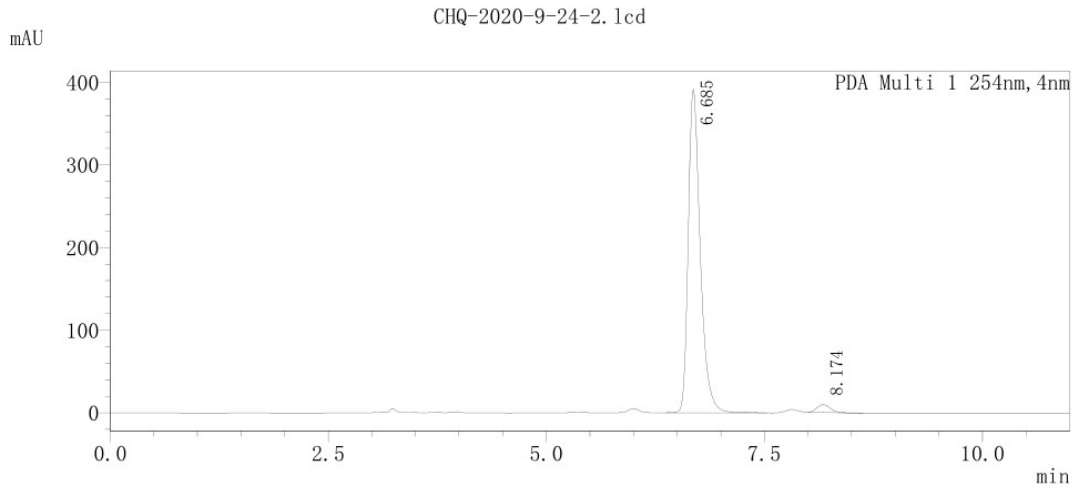
CHQ-2021-1-20-3-1. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	16.647	677751	28429	50.560	55.708
2	19.475	662742	22603	49.440	44.292
总计		1340493	51032	100.000	100.000



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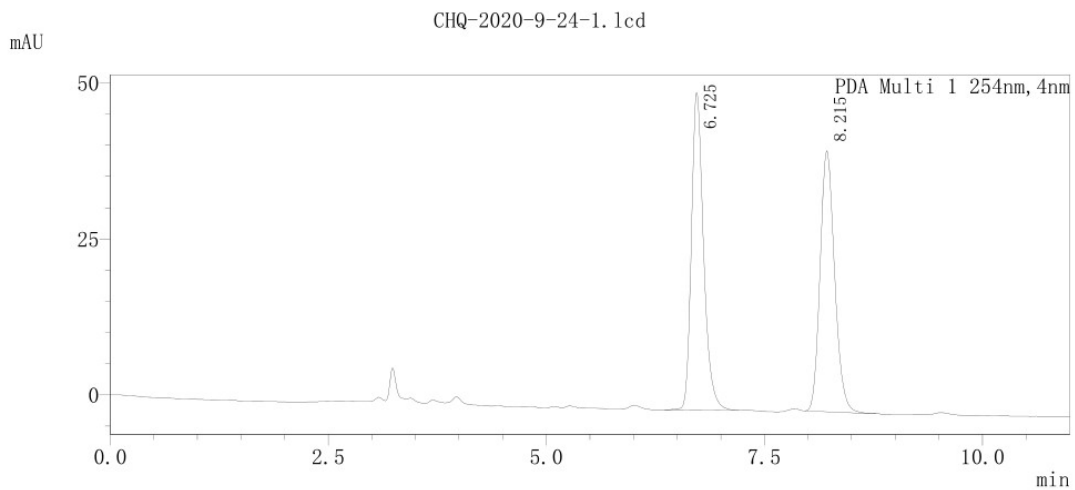
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CHQ-2020-9-24-2.lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.685	3752265	391660	97.342	97.650
2	8.174	102466	9424	2.658	2.350
总计		3854730	401084	100.000	100.000

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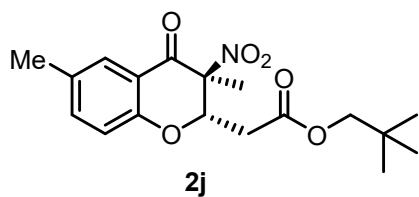


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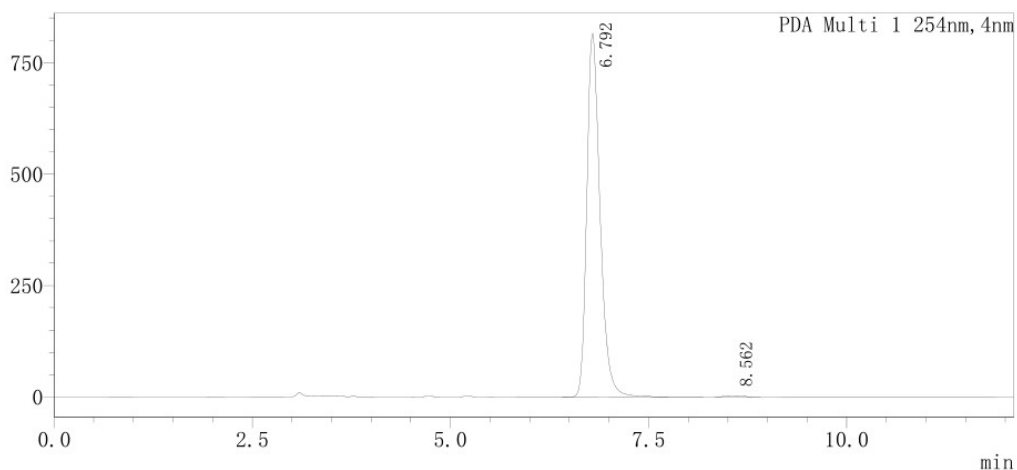
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.725	494950	50870	50.525	54.850
2	8.215	484656	41874	49.475	45.150
总计		979606	92744	100.000	100.000



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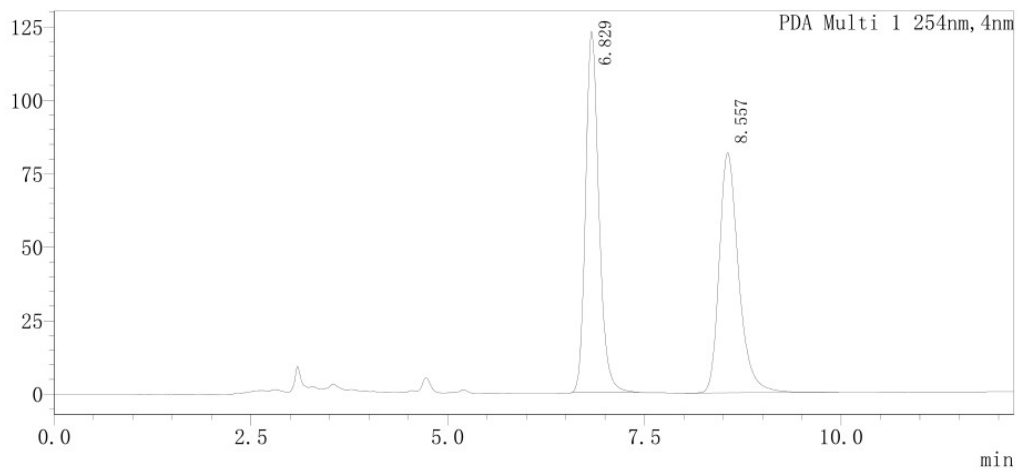
CHQ-2020-11-26-3. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.792	9536222	815636	99.543	99.657
2	8.562	43816	2810	0.457	0.343
总计		9580038	818447	100.000	100.000

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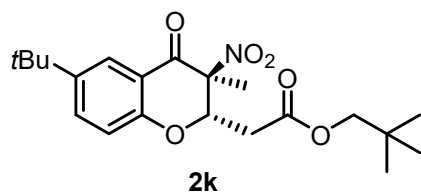


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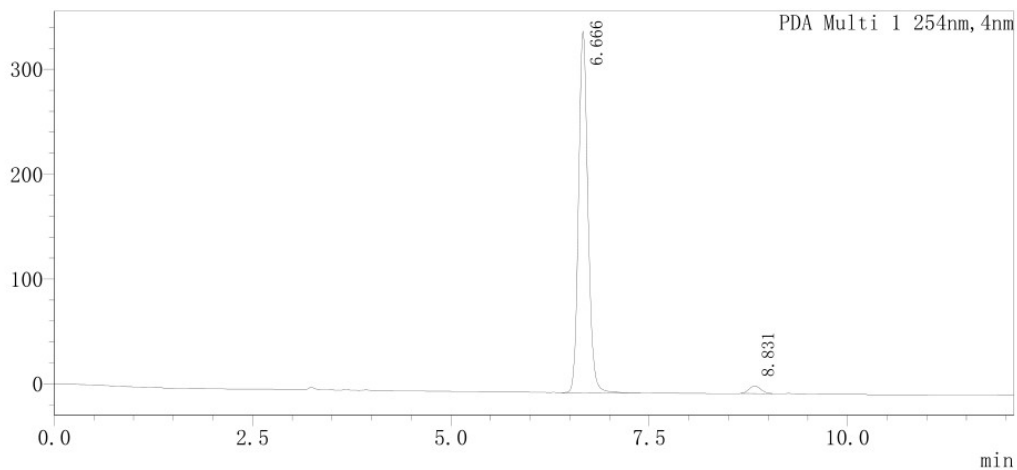
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.829	1449115	122878	50.771	60.038
2	8.557	1405114	81789	49.229	39.962
总计		2854229	204667	100.000	100.000



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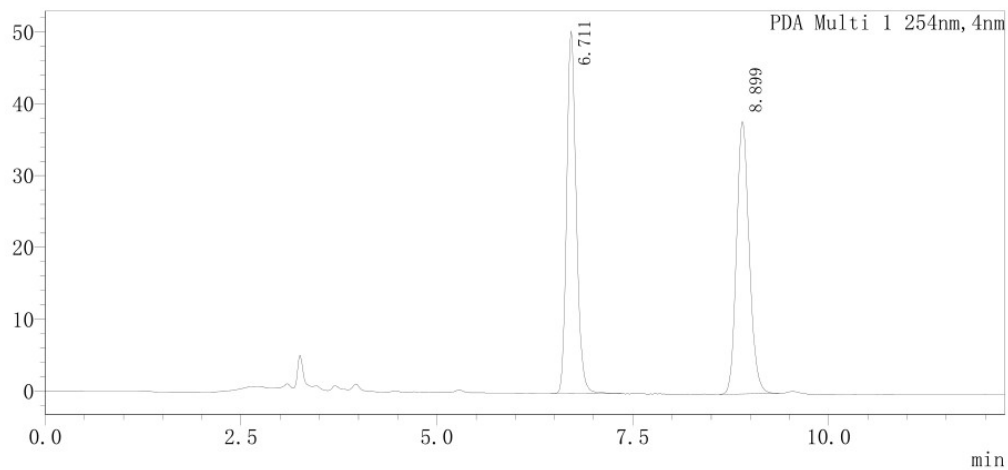
CHQ-2020-10-8-1.lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.666	2836521	344439	97.449	97.956
2	8.831	74268	7188	2.551	2.044
总计		2910789	351627	100.000	100.000

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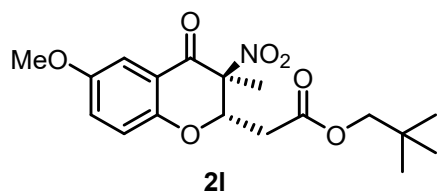


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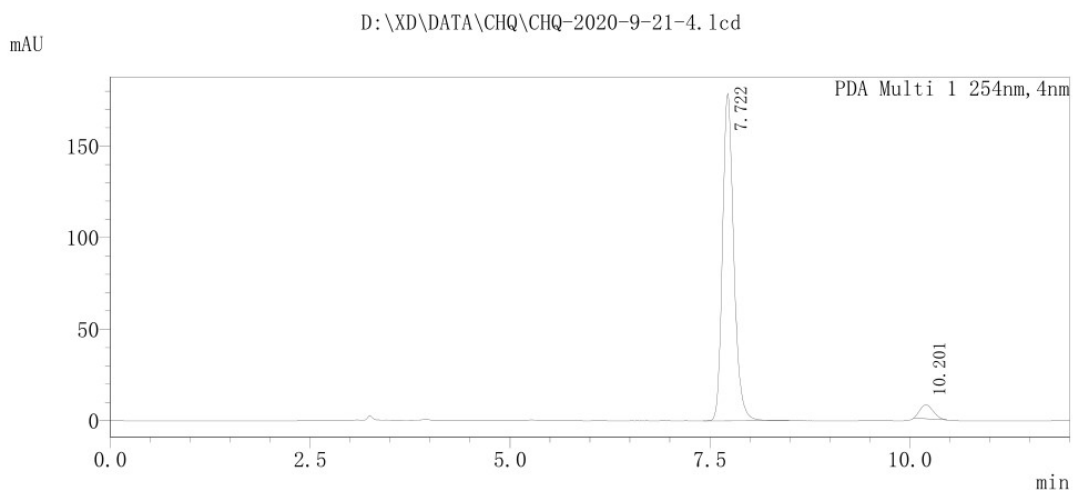
CHQ-2020-9-21-6.lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.711	430030	50451	50.173	57.089
2	8.899	427067	37922	49.827	42.911
总计		857097	88372	100.000	100.000



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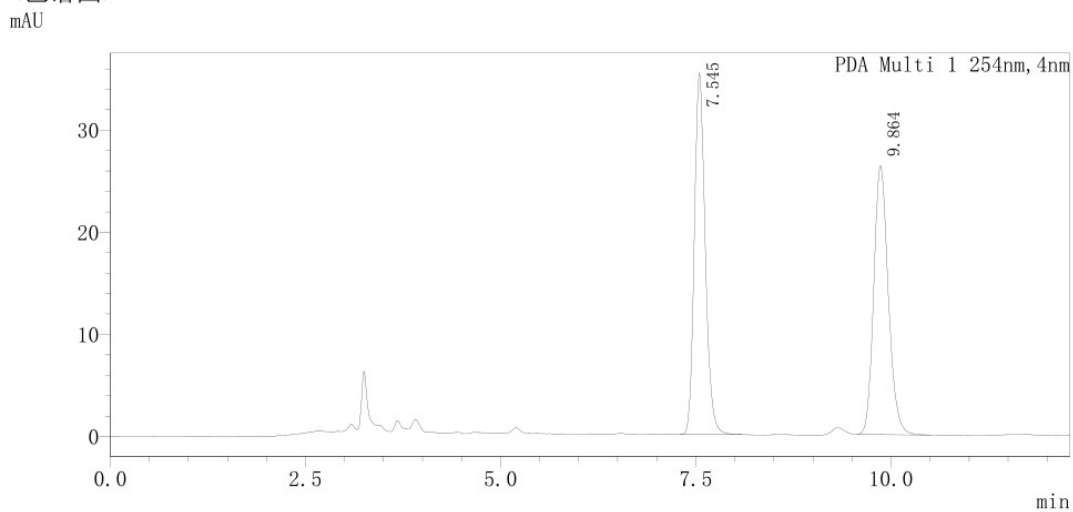
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CHQ-2020-9-21-4. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	7.722	1752456	178835	95.149	95.895
2	10.201	89346	7655	4.851	4.105
总计		1841802	186490	100.000	100.000

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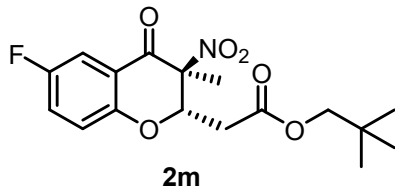


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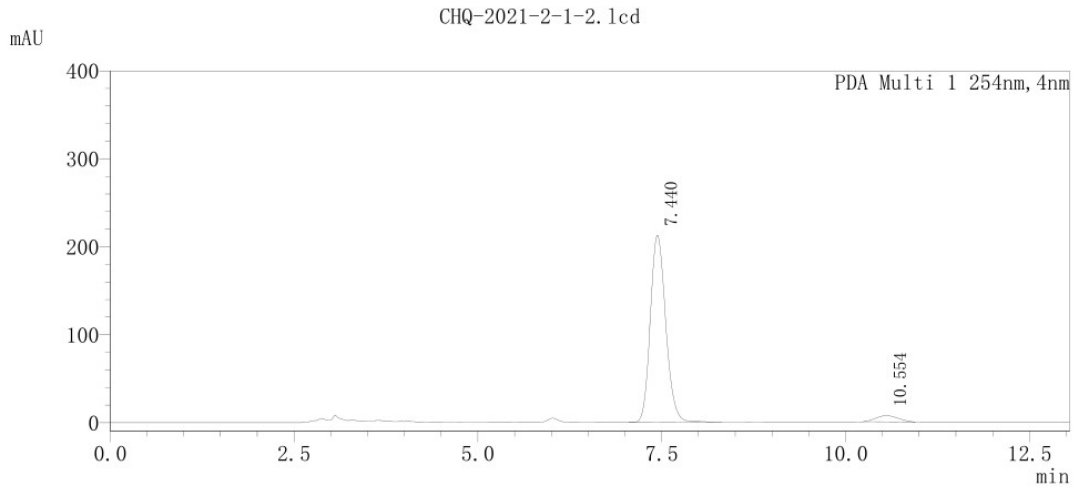
CHQ-2020-9-21-8. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	7.545	344153	35375	50.150	57.288
2	9.864	342091	26374	49.850	42.712
总计		686244	61750	100.000	100.000



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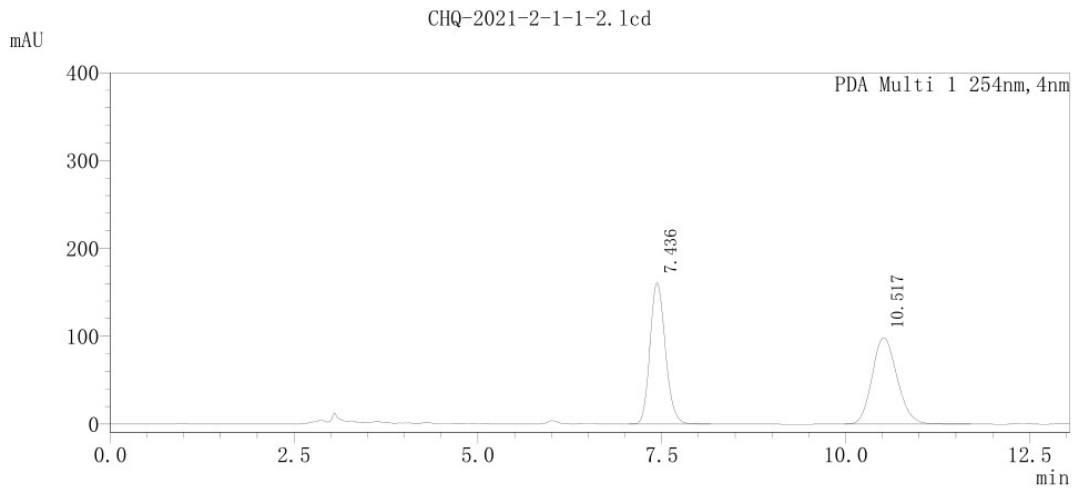
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CHQ-2021-2-1-2. 1cd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	7.440	3114362	212848	95.442	96.797
2	10.554	148727	7043	4.558	3.203
总计		3263089	219891	100.000	100.000

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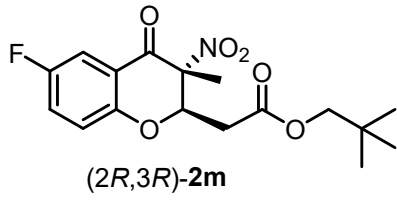


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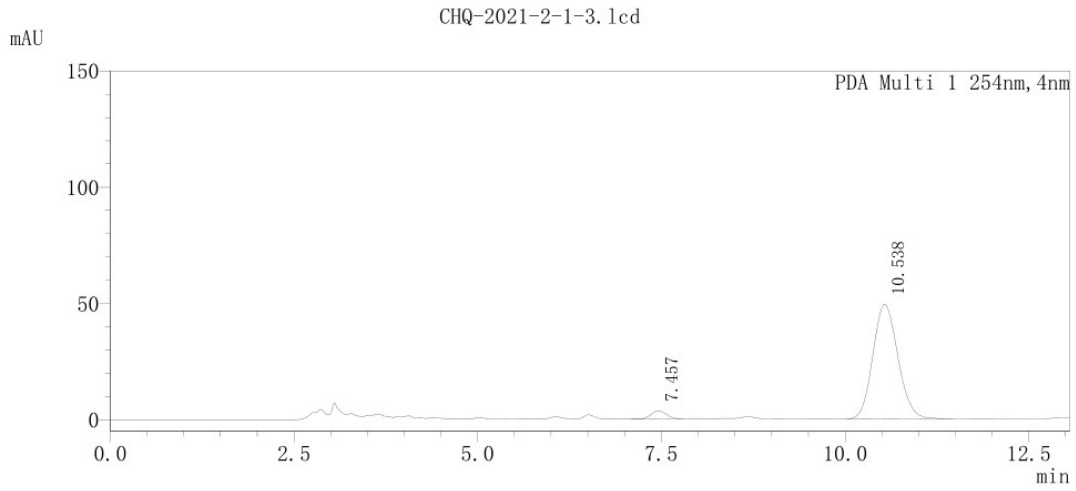
CHQ-2021-2-1-1-2. 1cd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	7.436	2346743	161022	50.199	62.021
2	10.517	2328107	98601	49.801	37.979
总计		4674849	259623	100.000	100.000



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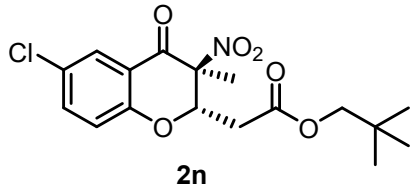
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CHQ-2021-2-1-3. 1cd

PDA Ch1 254nm

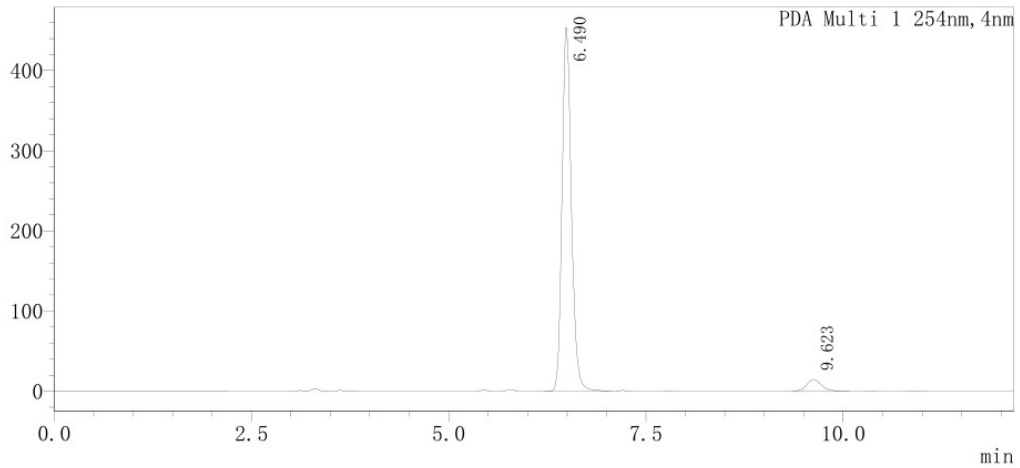
峰号	保留时间	面积	高度	面积%	高度%
1	7.457	53693	3599	4.388	6.797
2	10.538	1169836	49343	95.612	93.203
总计		1223529	52942	100.000	100.000





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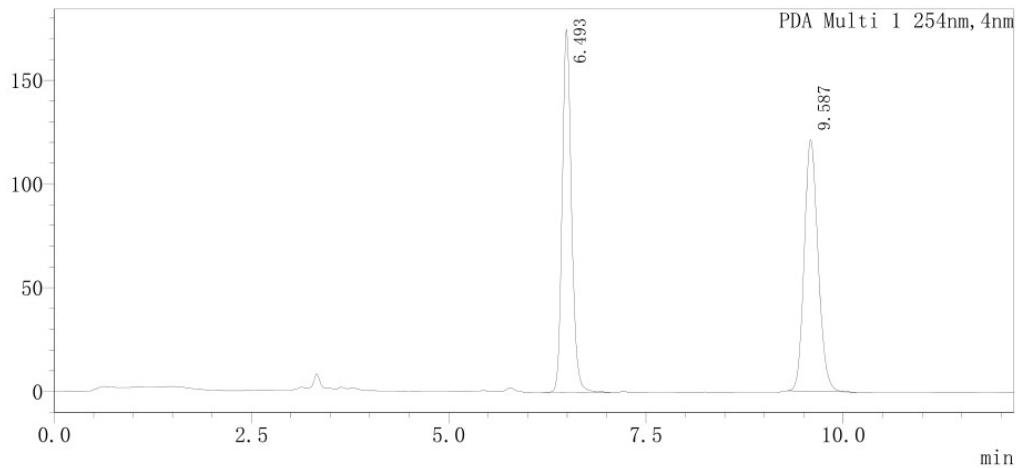
CHQ-2020-10-14-3. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.490	3761093	453673	95.375	96.935
2	9.623	182396	14344	4.625	3.065
总计		3943489	468017	100.000	100.000

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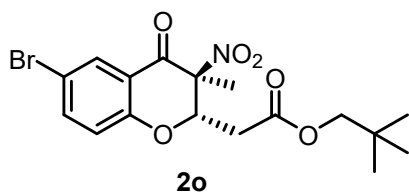


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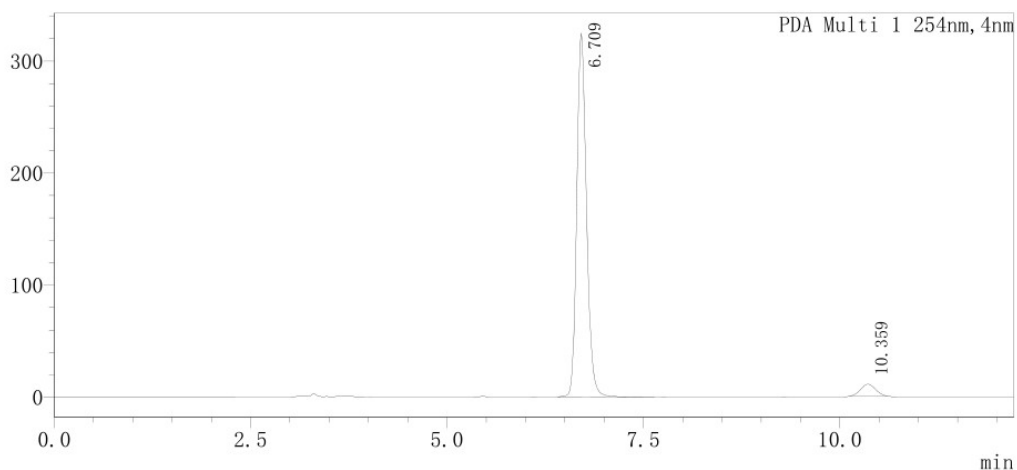
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.493	1435278	174936	49.275	59.053
2	9.587	1477523	121297	50.725	40.947
总计		2912801	296234	100.000	100.000



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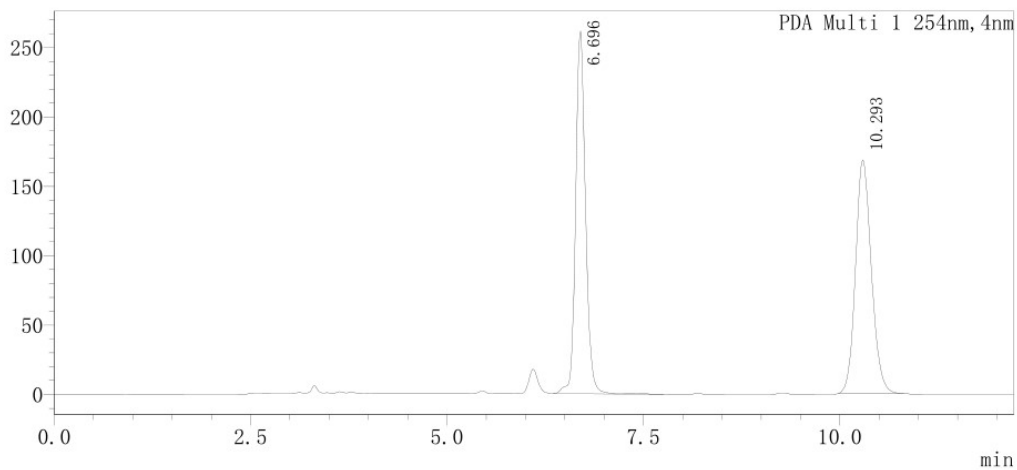
CHQ-2020-10-14-4. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.709	2795850	324413	95.160	96.799
2	10.359	142205	10727	4.840	3.201
总计		2938056	335140	100.000	100.000

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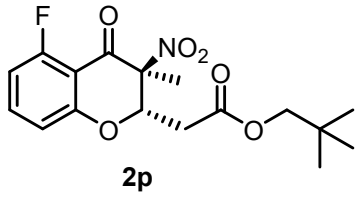


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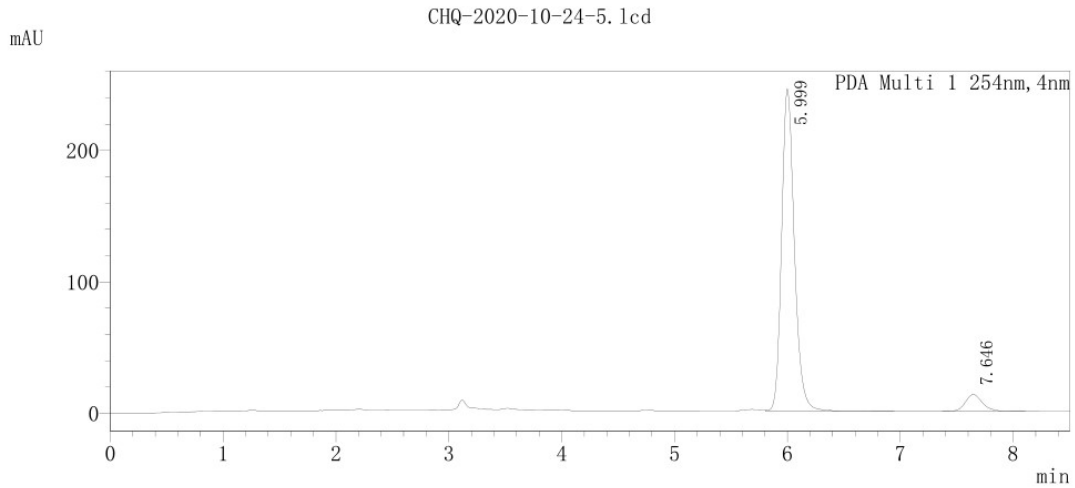
CHQ-2020-10-14-2. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.696	2286378	261079	49.150	60.799
2	10.293	2365450	168332	50.850	39.201
总计		4651829	429411	100.000	100.000



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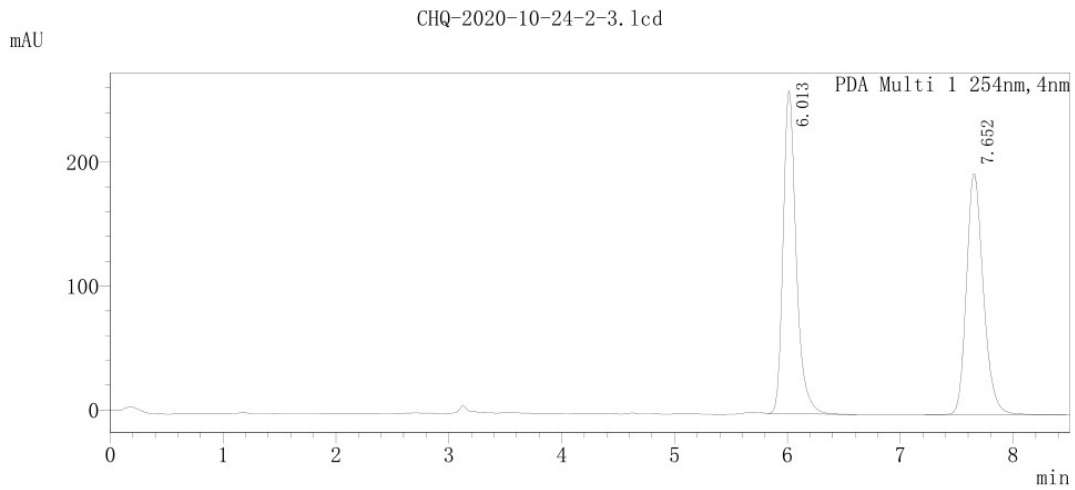
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CHQ-2020-10-24-5. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	5.999	1923111	245098	93.557	95.061
2	7.646	132446	12733	6.443	4.939
总计		2055557	257832	100.000	100.000

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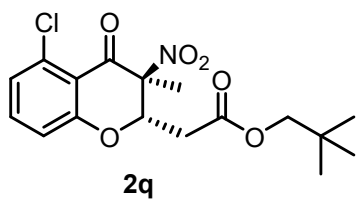


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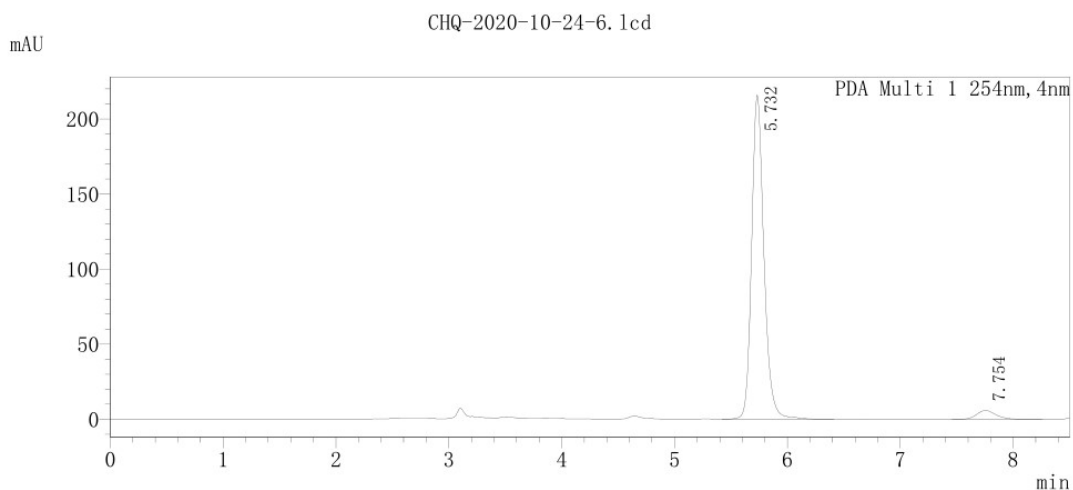
CHQ-2020-10-24-2-3. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.013	2083284	260402	50.598	57.239
2	7.652	2034026	194534	49.402	42.761
总计		4117310	454936	100.000	100.000



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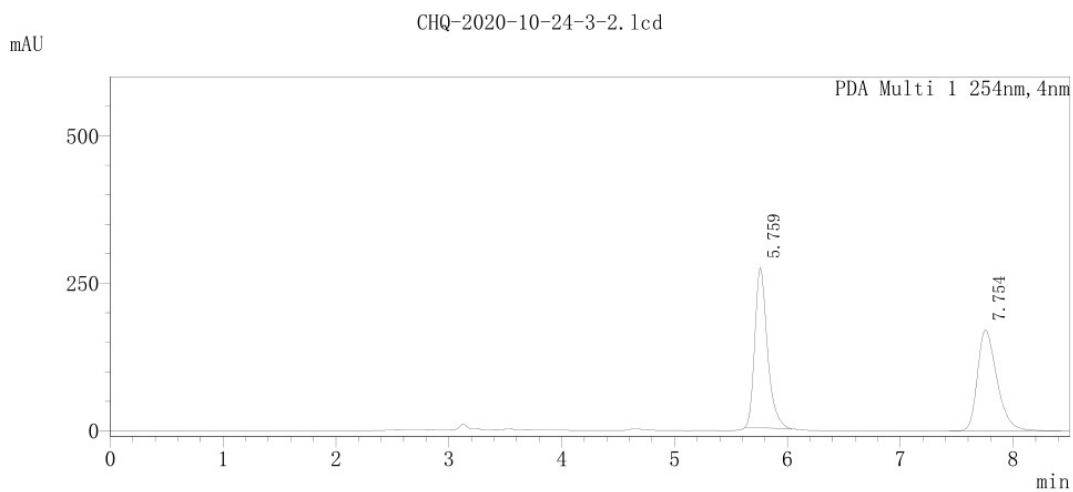
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CHQ-2020-10-24-6. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	5.732	1636036	215840	95.875	97.339
2	7.754	70386	5901	4.125	2.661
总计		1706422	221742	100.000	100.000

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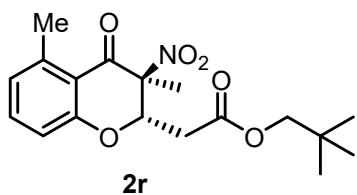


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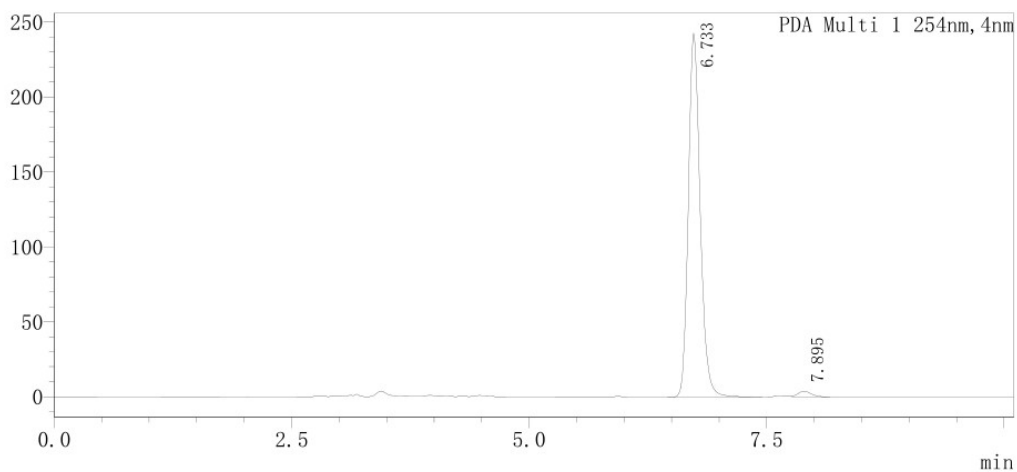
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	5.759	2107461	272053	50.713	61.370
2	7.754	2048209	171246	49.287	38.630
总计		4155670	443299	100.000	100.000



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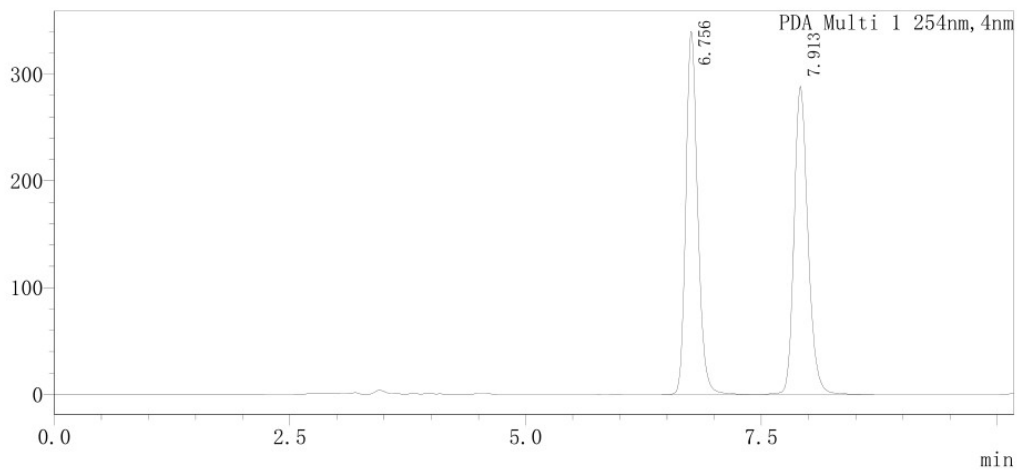
CHQ-2020-10-24-4-2.1cd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.733	2104036	242556	98.280	98.481
2	7.895	36821	3742	1.720	1.519
总计		2140857	246298	100.000	100.000

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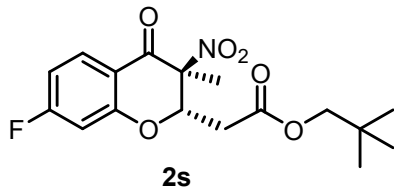


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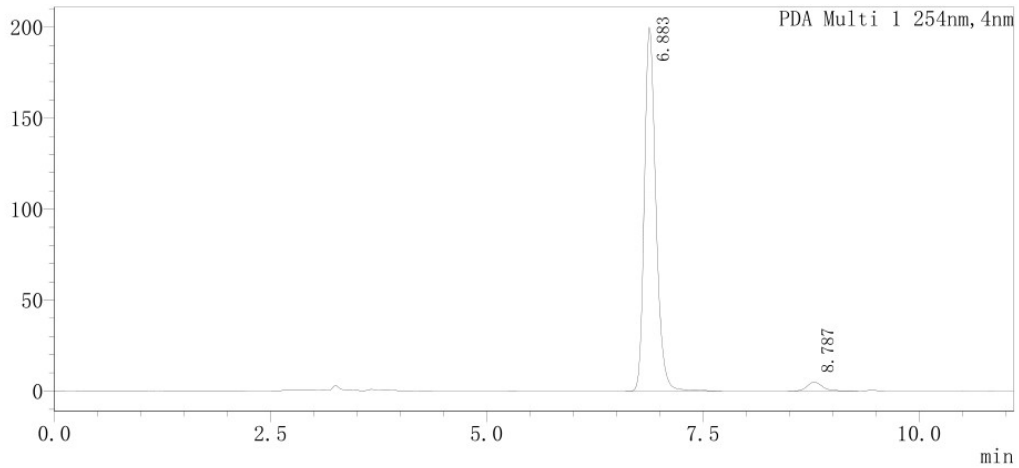
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.756	2961049	339890	50.105	54.087
2	7.913	2948600	288519	49.895	45.913
总计		5909649	628409	100.000	100.000



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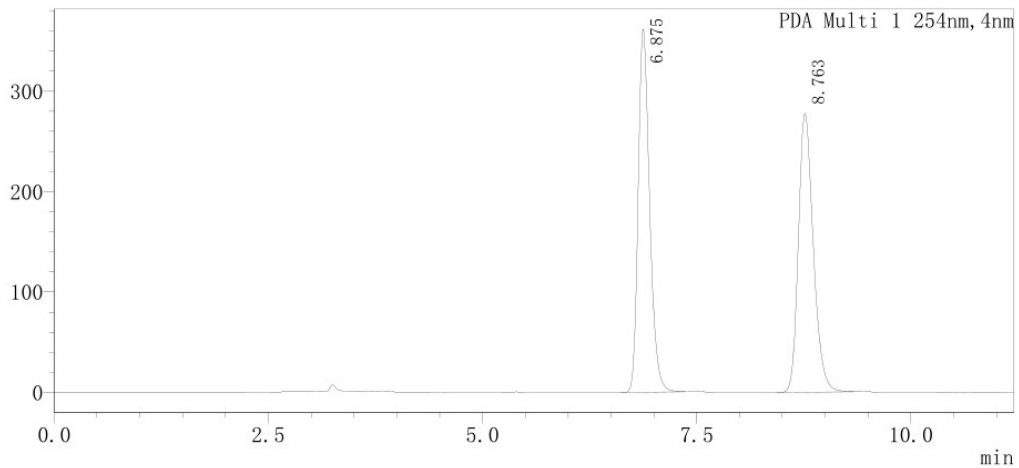
CHQ-2020-10-29-6. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.883	1849214	199809	96.907	97.620
2	8.787	59013	4872	3.093	2.380
总计		1908228	204681	100.000	100.000

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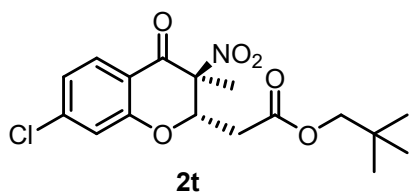


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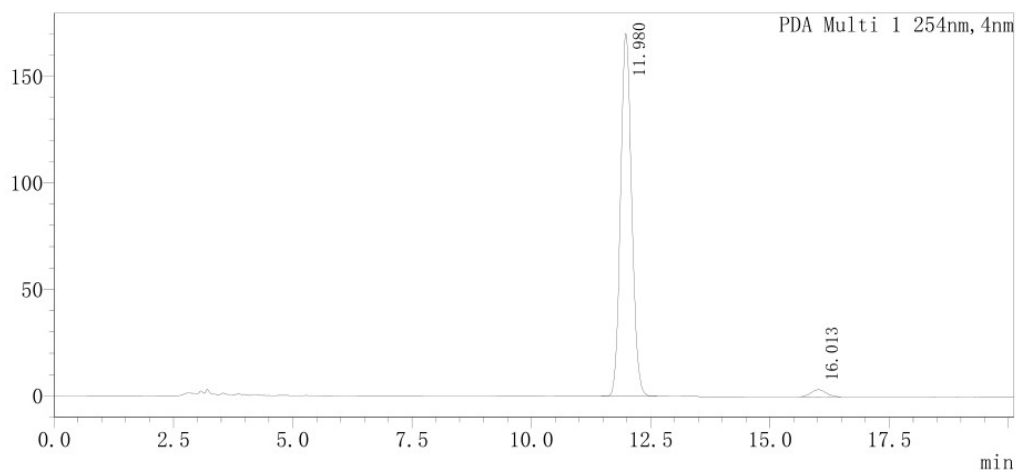
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.875	3369873	361187	50.004	56.536
2	8.763	3369368	277674	49.996	43.464
总计		6739241	638861	100.000	100.000



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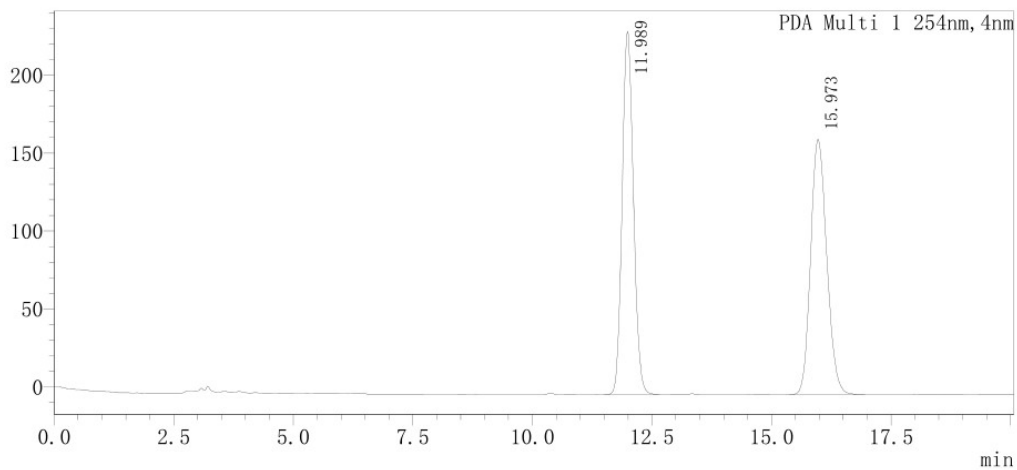
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PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	11.980	2778756	170458	97.481	98.114
2	16.013	71800	3277	2.519	1.886
总计		2850556	173735	100.000	100.000

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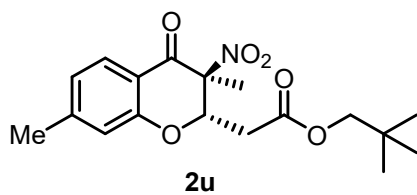


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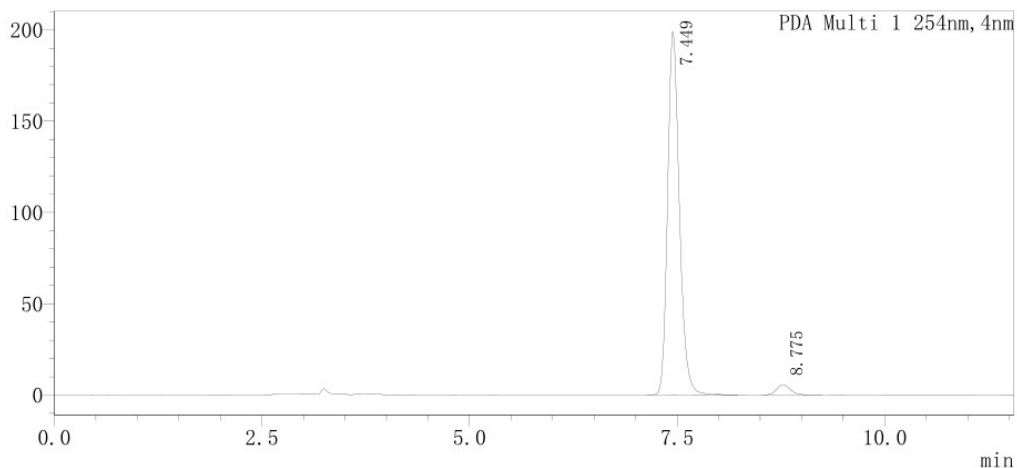
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	11.989	3812253	232834	49.893	58.719
2	15.973	3828619	163688	50.107	41.281
总计		7640872	396522	100.000	100.000



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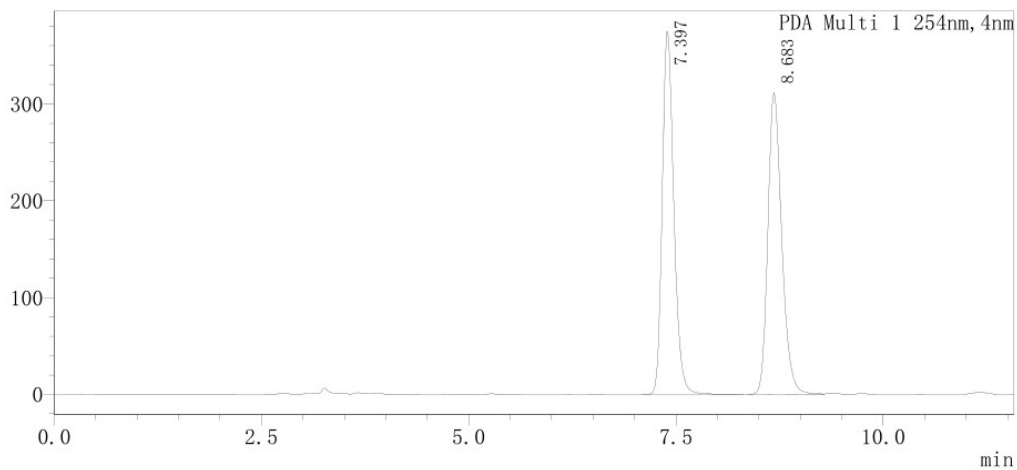
CHQ-2020-10-29-5. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	7.449	1961591	199090	96.778	97.264
2	8.775	65302	5600	3.222	2.736
总计		2026893	204690	100.000	100.000

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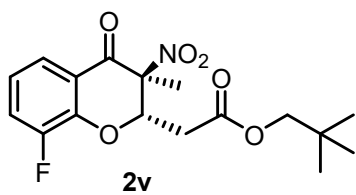


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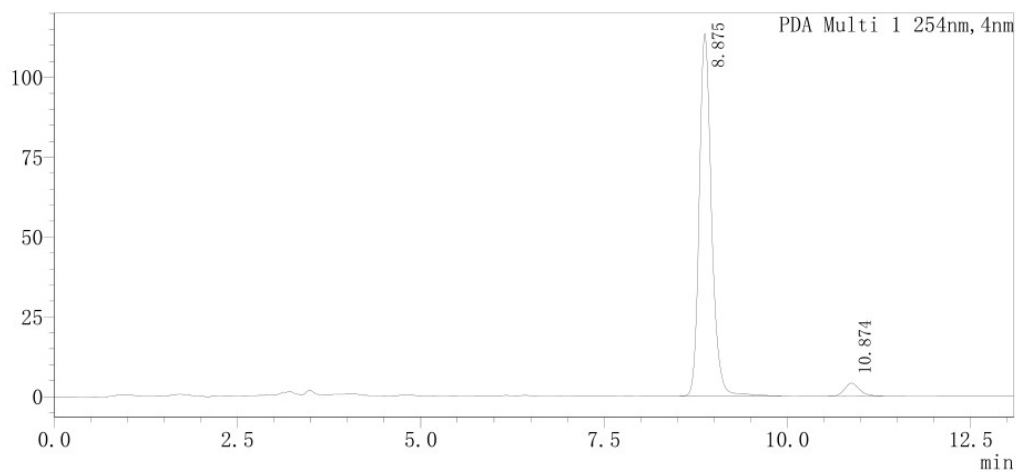
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	7.397	3633533	374770	50.064	54.644
2	8.683	3624254	311074	49.936	45.356
总计		7257787	685844	100.000	100.000



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CHQ-2020-12-29-4. lcd

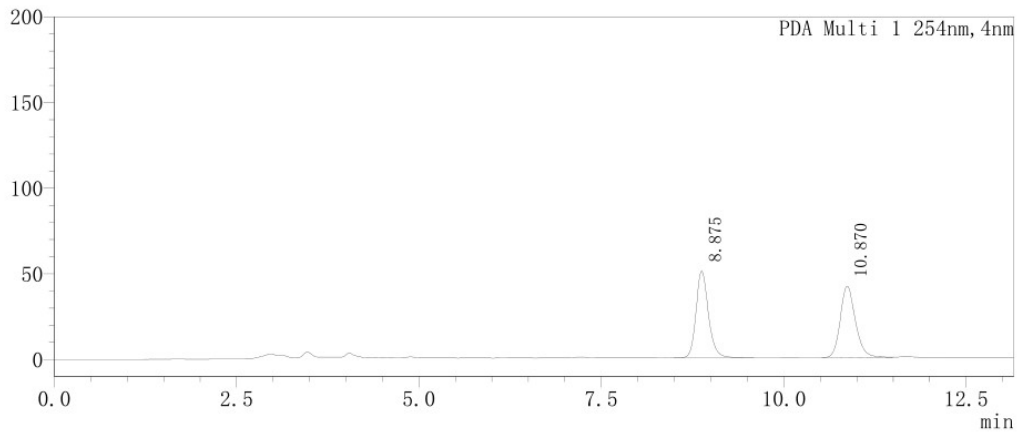
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	8.875	1321134	113523	95.894	96.575
2	10.874	56561	4026	4.106	3.425
总计		1377695	117549	100.000	100.000

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CHQ-2020-12-29-3-2. lcd

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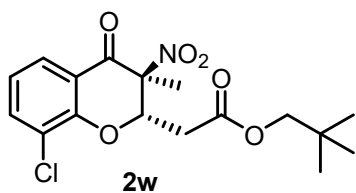


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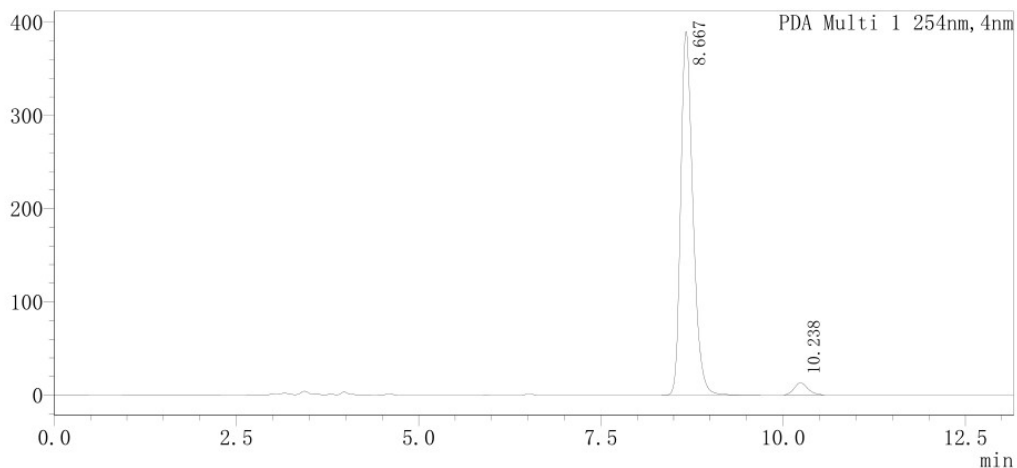
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	8.875	599523	50619	49.988	54.818
2	10.870	599800	41720	50.012	45.182
总计		1199323	92339	100.000	100.000



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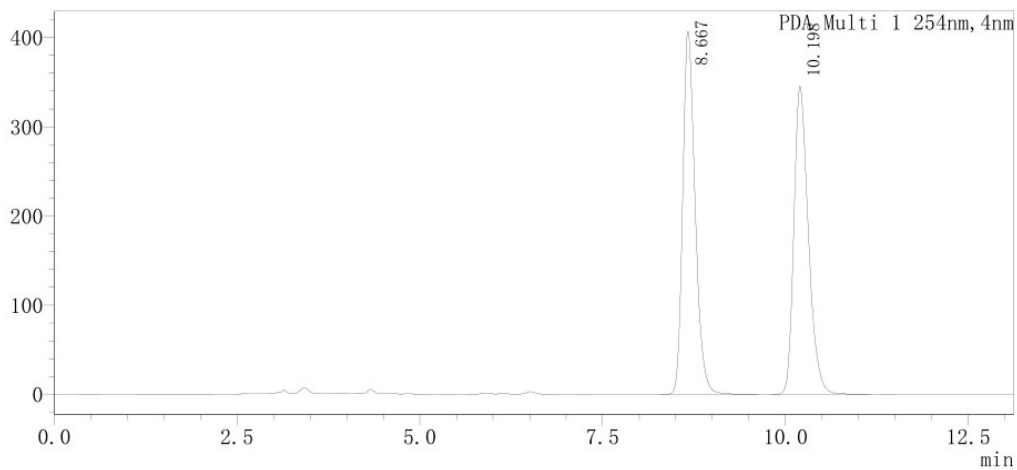
CHQ-2020-11-8-4.1cd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	8.667	4551190	390119	96.547	96.848
2	10.238	162778	12698	3.453	3.152
总计		4713968	402818	100.000	100.000

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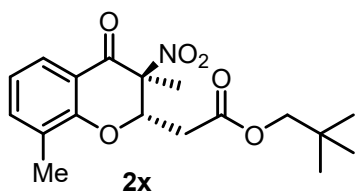


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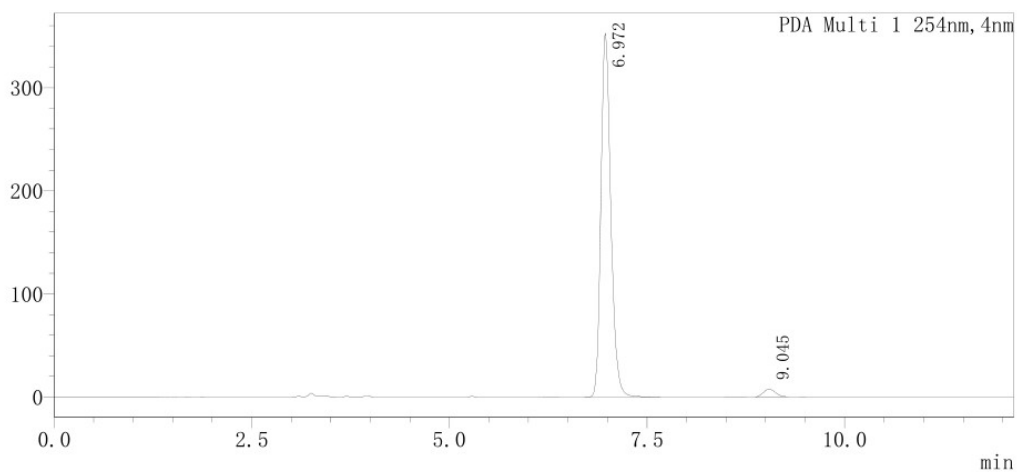
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	8.667	4822094	406722	50.298	54.056
2	10.198	4765019	345688	49.702	45.944
总计		9587113	752410	100.000	100.000



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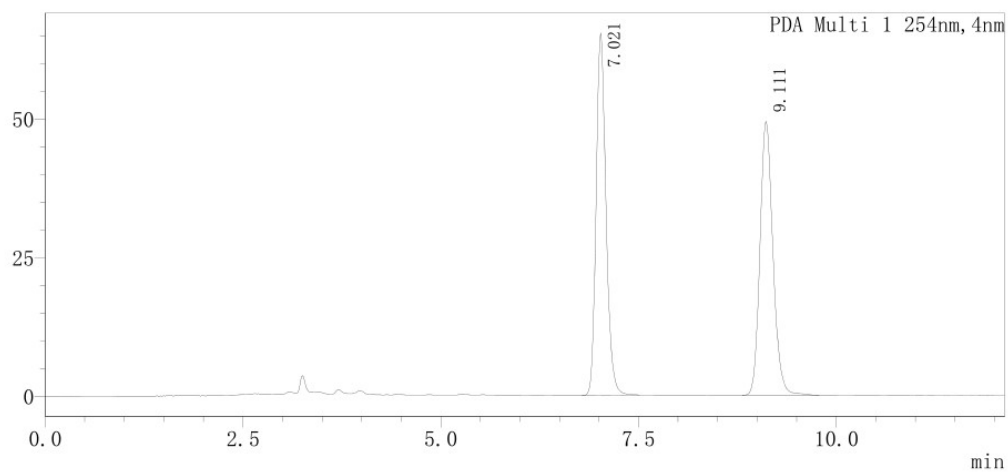
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PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.972	3073453	352413	97.554	97.938
2	9.045	77057	7419	2.446	2.062
总计		3150510	359832	100.000	100.000

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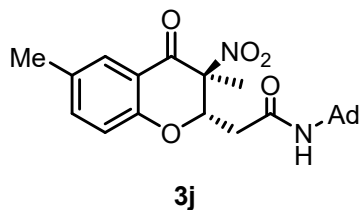


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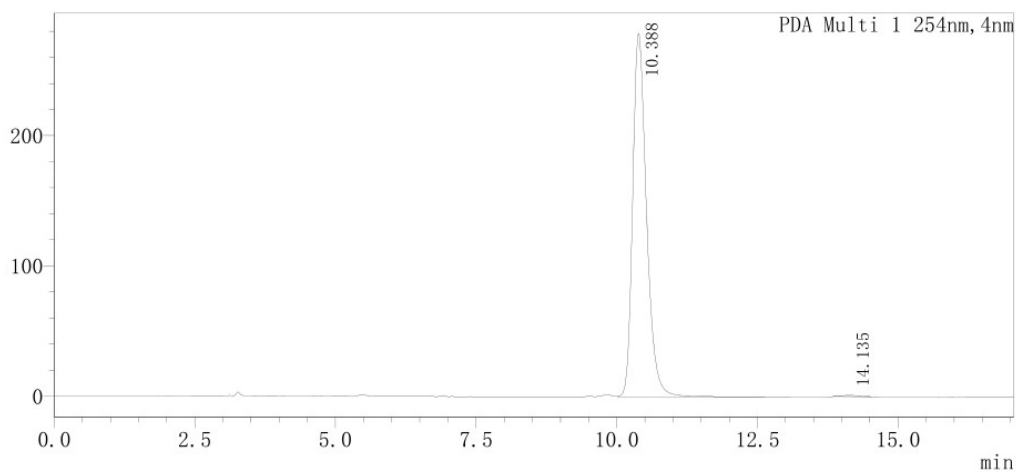
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	7.021	566984	65249	50.099	56.917
2	9.111	564749	49391	49.901	43.083
总计		1131733	114640	100.000	100.000



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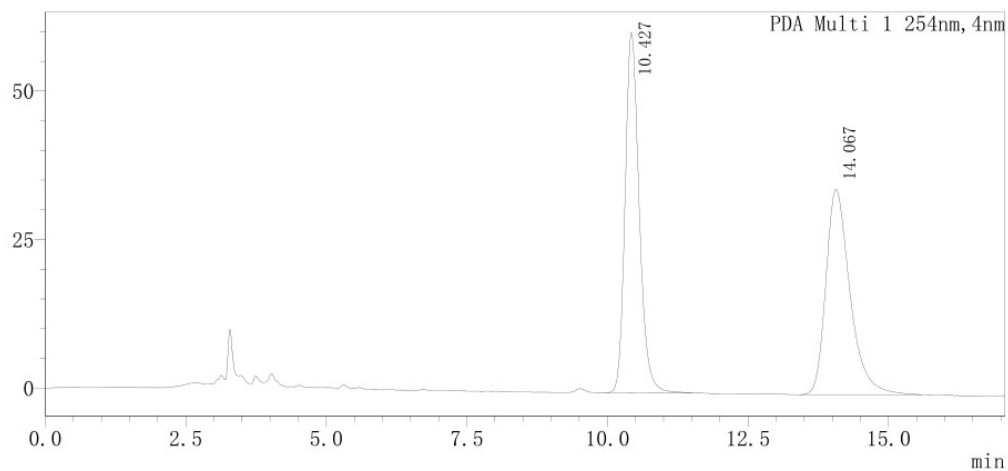
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PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	10.388	4778740	278875	99.562	99.663
2	14.135	21003	944	0.438	0.337
总计		4799743	279820	100.000	100.000

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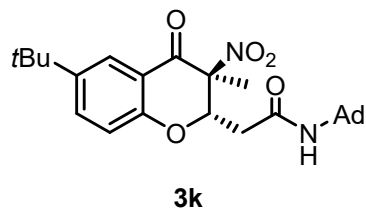


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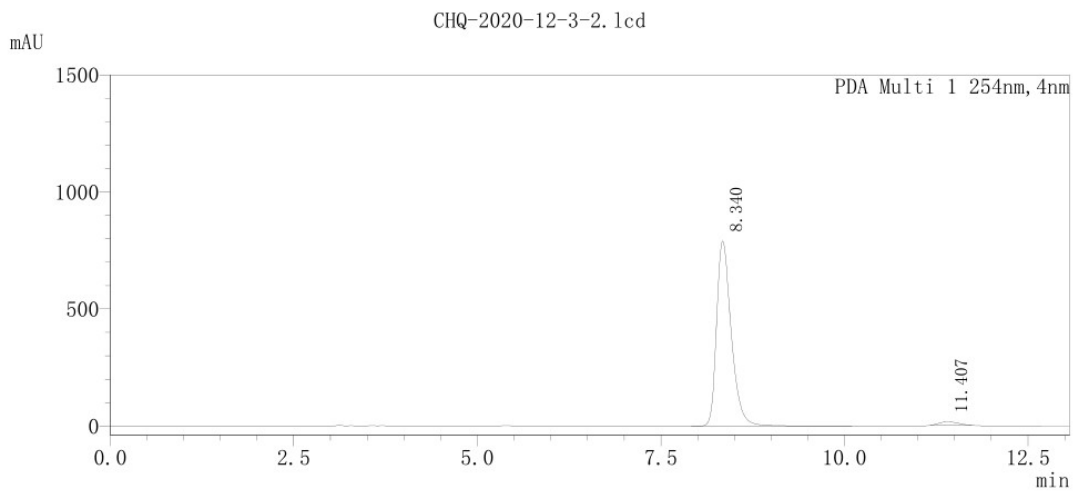
CHQ-2020-11-29-1-2.1cd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	10.427	1061684	60668	50.608	63.684
2	14.067	1036171	34596	49.392	36.316
总计		2097854	95264	100.000	100.000



<色谱图>

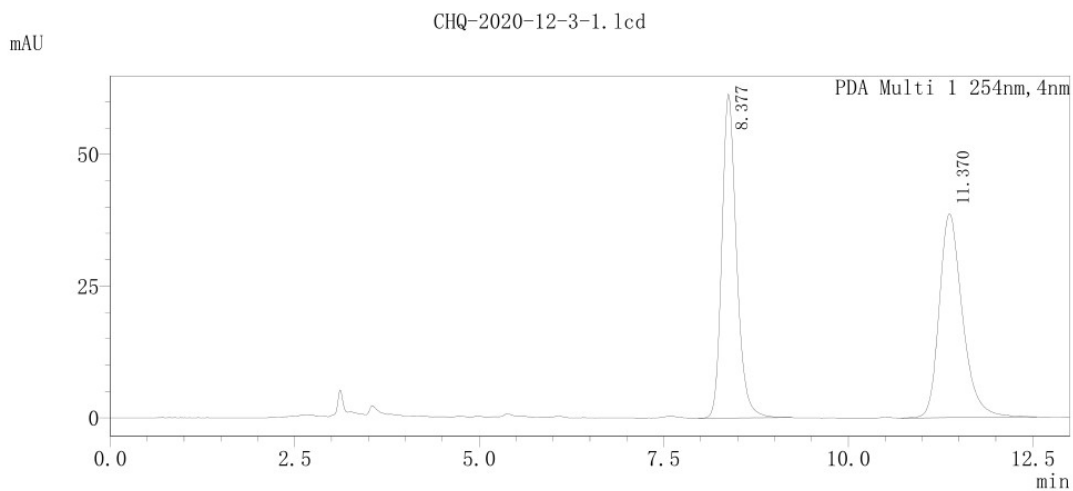


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CHQ-2020-12-3-2.1cd

PDA Ch1 254nm				
峰号	保留时间	面积	高度	面积%
1	8.340	10976222	791514	97.545
2	11.407	276207	15635	2.455
总计		11252429	807149	100.000

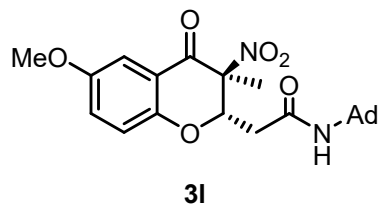
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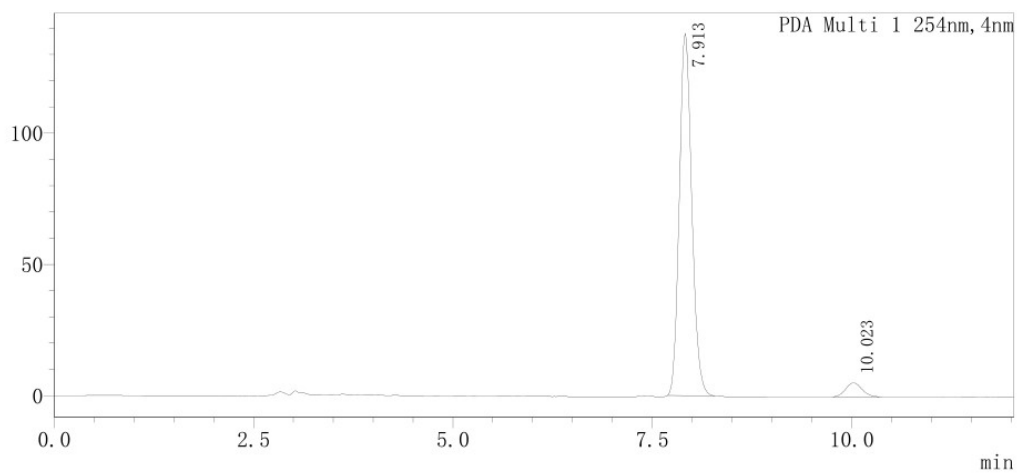
CHQ-2020-12-3-1.1cd

PDA Ch1 254nm					
峰号	保留时间	面积	高度	面积%	高度%
1	8.377	851674	61483	50.108	61.374
2	11.370	848011	38694	49.892	38.626
总计		1699685	100177	100.000	100.000



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mAU



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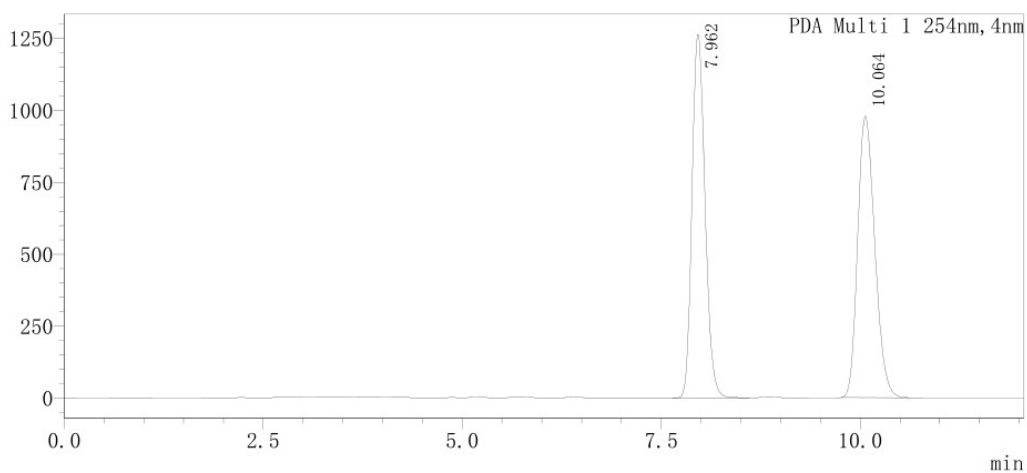
CHQ-2021-1-29-2.1cd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	7.913	1503485	137998	95.265	96.292
2	10.023	74734	5315	4.735	3.708
总计		1578219	143312	100.000	100.000

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mAU

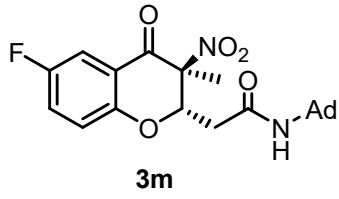


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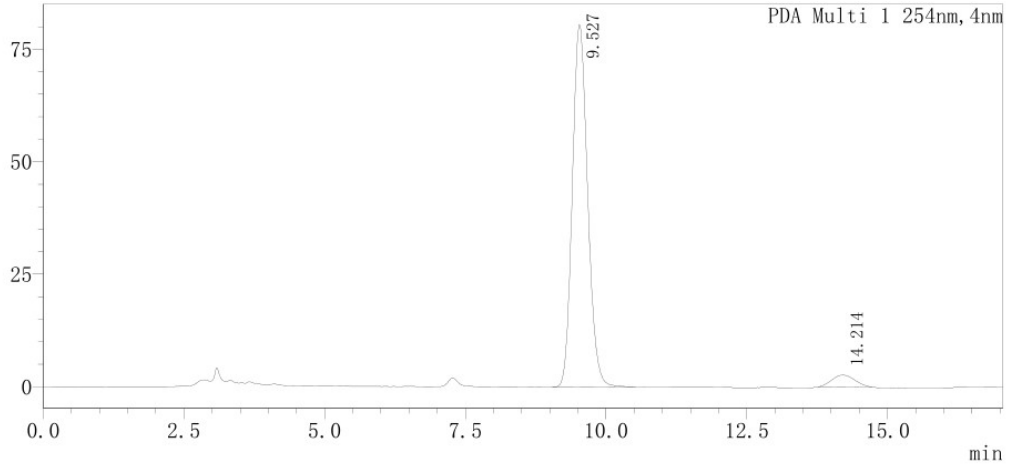
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	7.962	14383519	1262418	49.498	56.354
2	10.064	14675373	977758	50.502	43.646
总计		29058892	2240176	100.000	100.000



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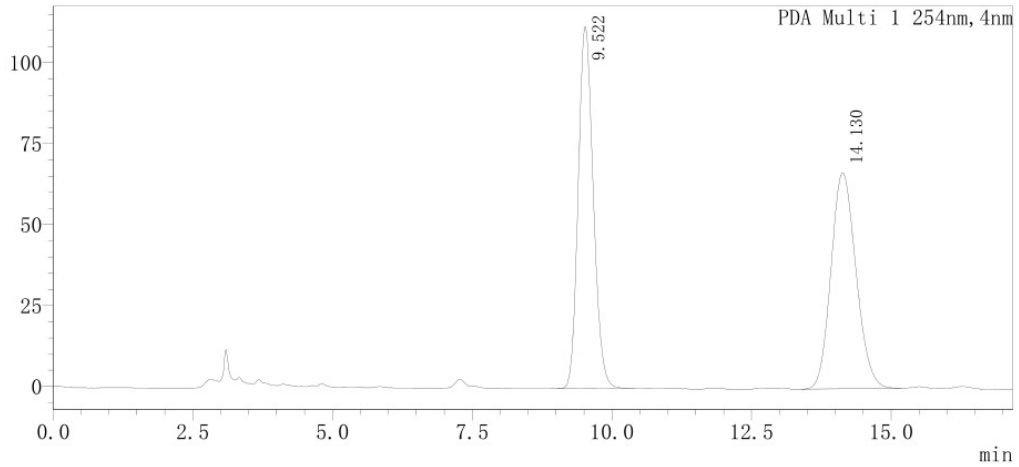
CHQ-2021-2-2-2. lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	9.527	1527627	80578	95.268	96.806
2	14.214	75877	2659	4.732	3.194
总计		1603504	83237	100.000	100.000

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mAU

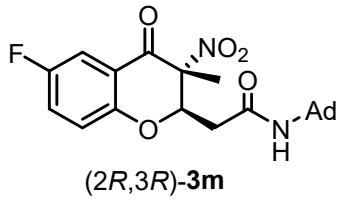


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CHQ-2021-2-2-1-1. lcd

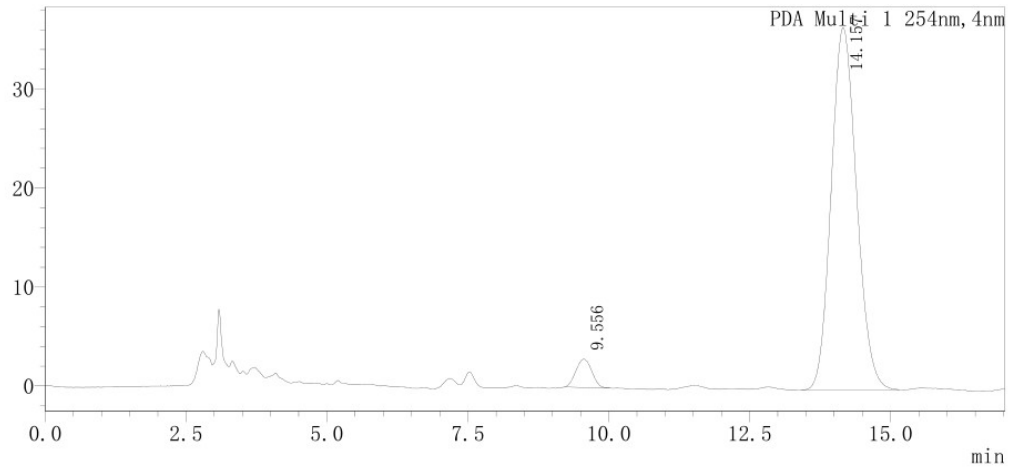
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	9.522	2110757	111986	50.339	62.636
2	14.130	2082358	66803	49.661	37.364
总计		4193115	178789	100.000	100.000



<色谱图>

mAU

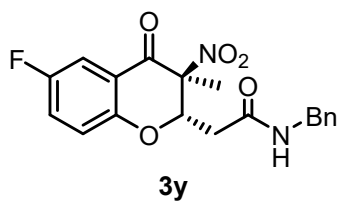


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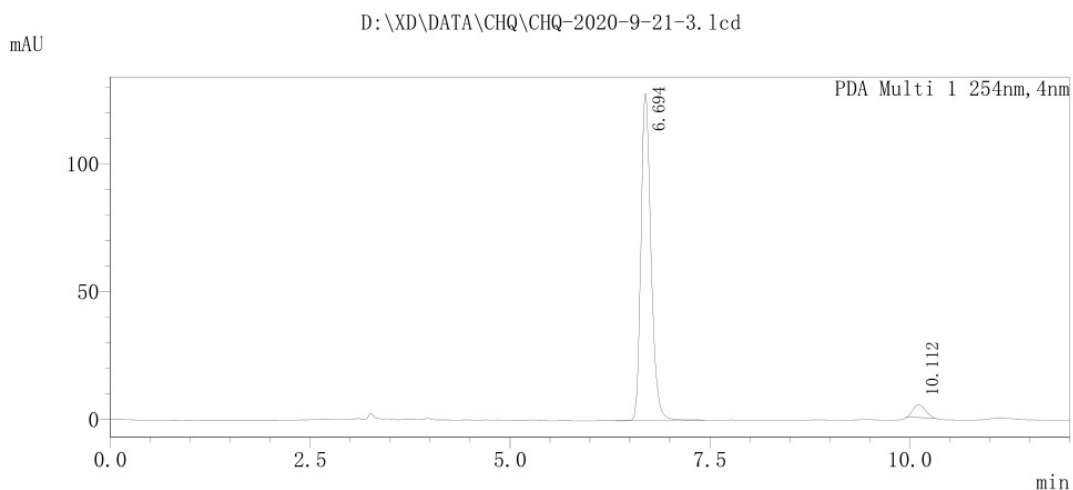
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PDA Ch1 254nm

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1	9.556	56257	2864	4.663	7.251
2	14.157	1150233	36629	95.337	92.749
总计		1206490	39493	100.000	100.000



<色谱图>



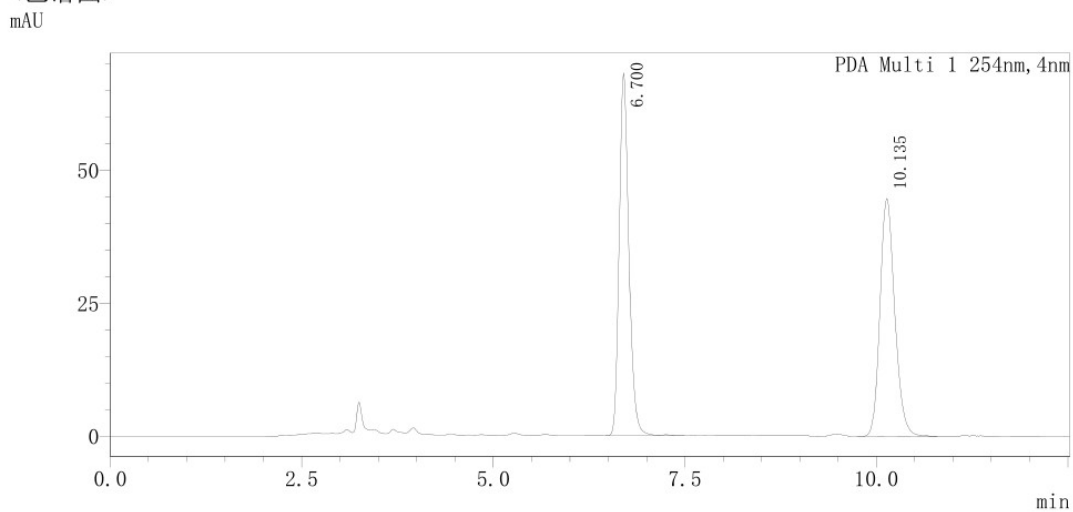
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CHQ-2020-9-21-3.lcd

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.694	1116047	127915	95.323	96.210
2	10.112	54758	5039	4.677	3.790
总计		1170805	132955	100.000	100.000

<色谱图>



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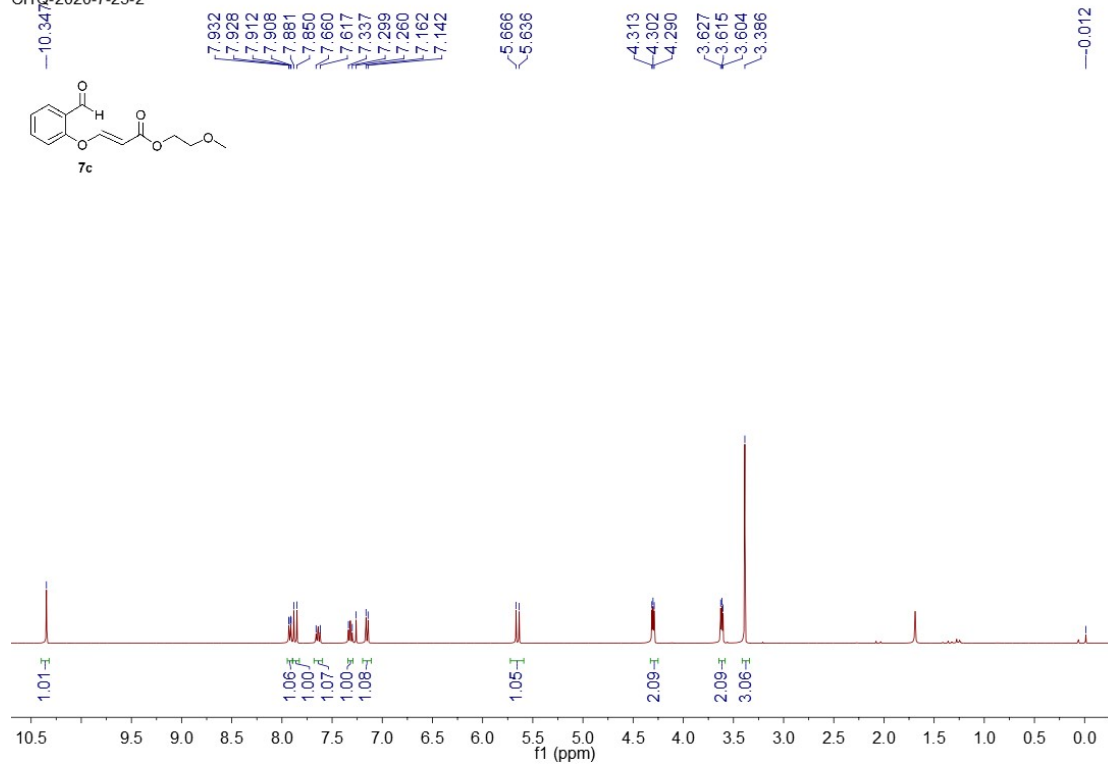
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PDA Ch1 254nm

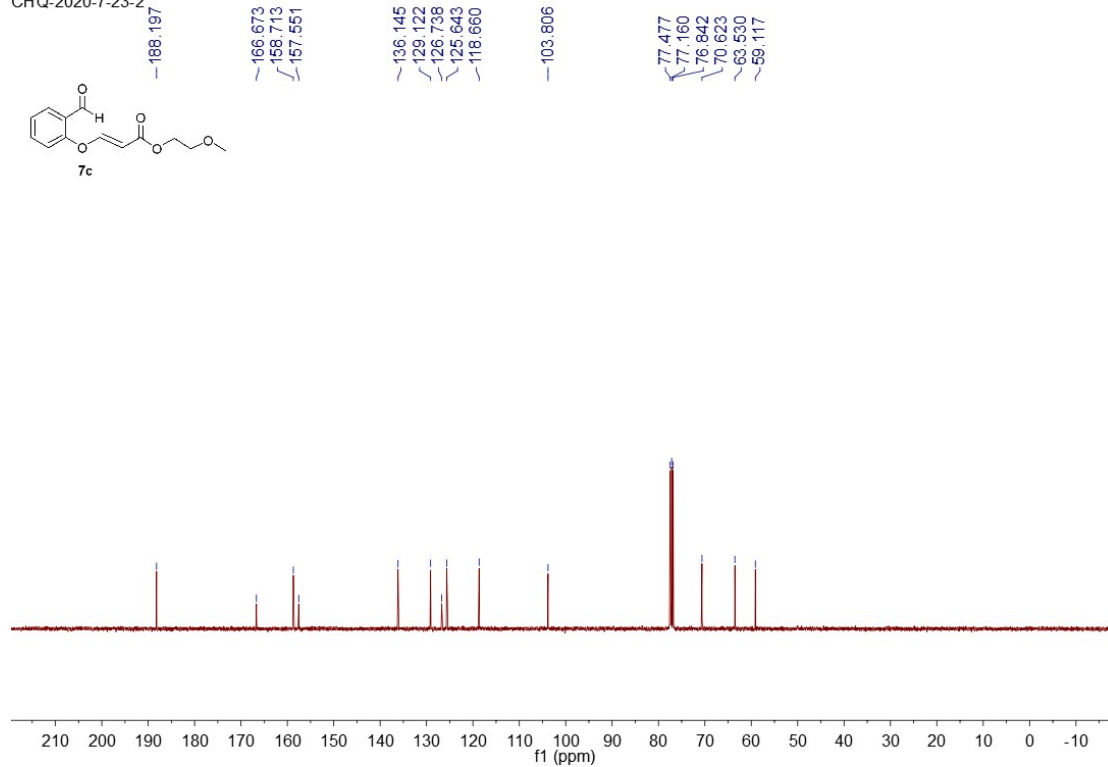
峰号	保留时间	面积	高度	面积%	高度%
1	6.700	601023	68135	50.051	60.368
2	10.135	599790	44731	49.949	39.632
总计		1200814	112867	100.000	100.000

7. NMR charts

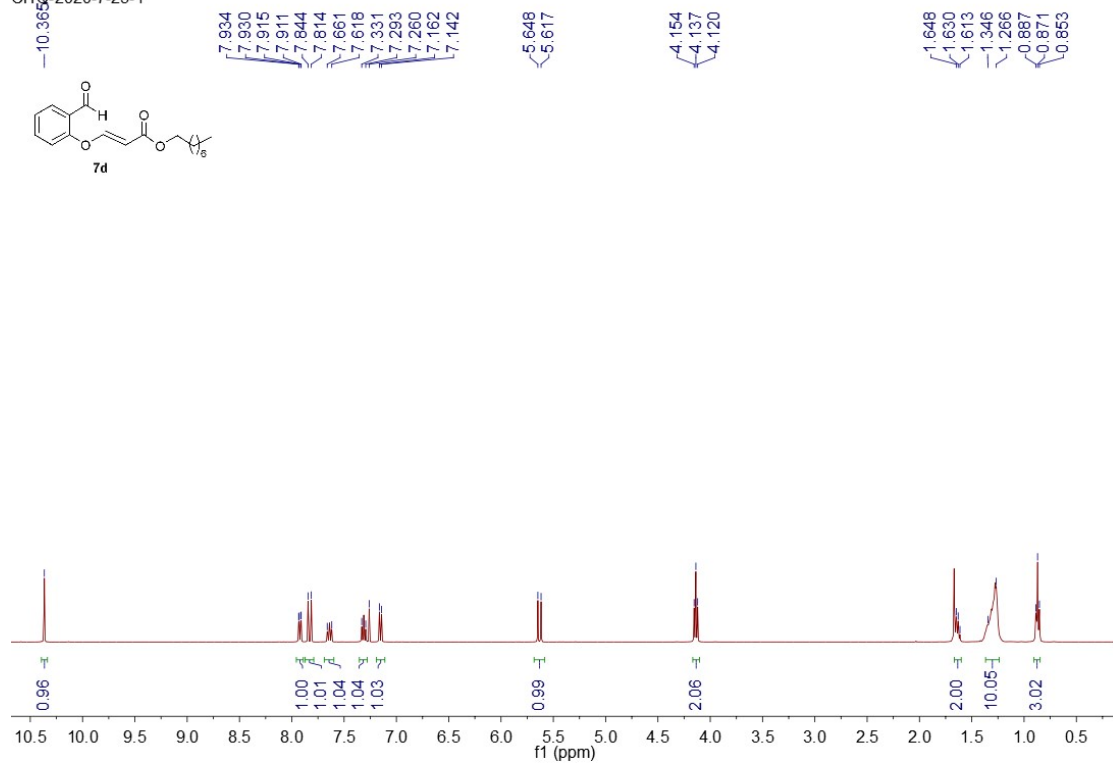
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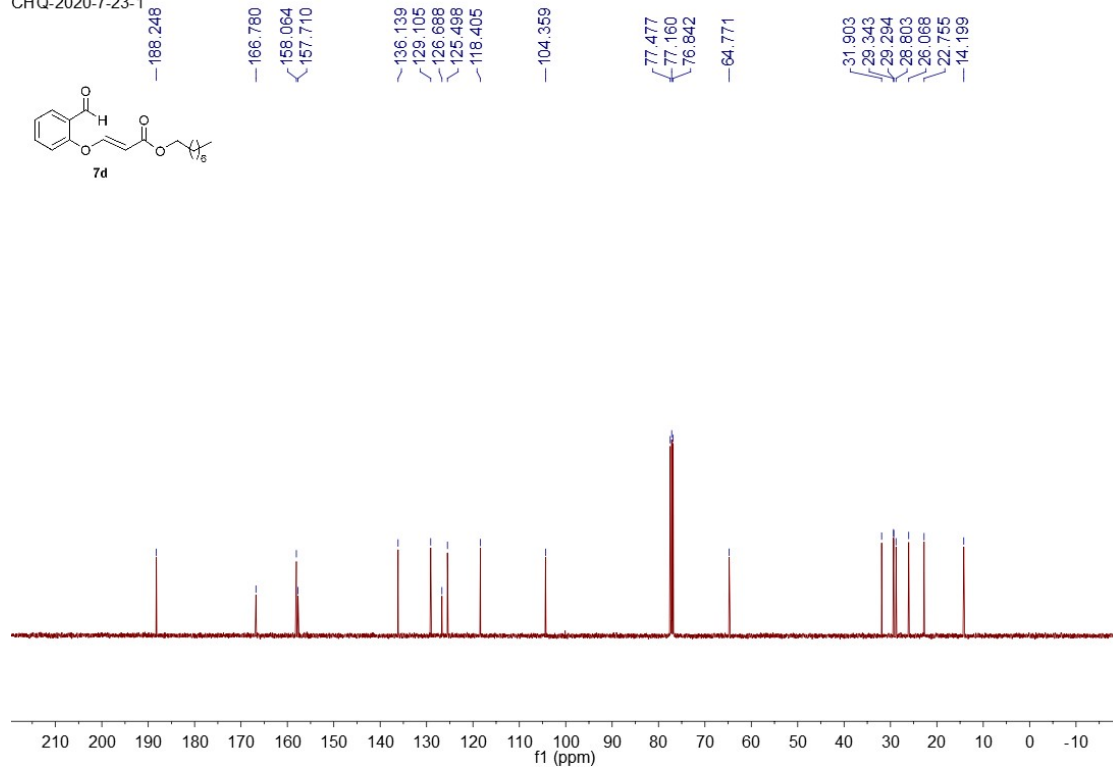
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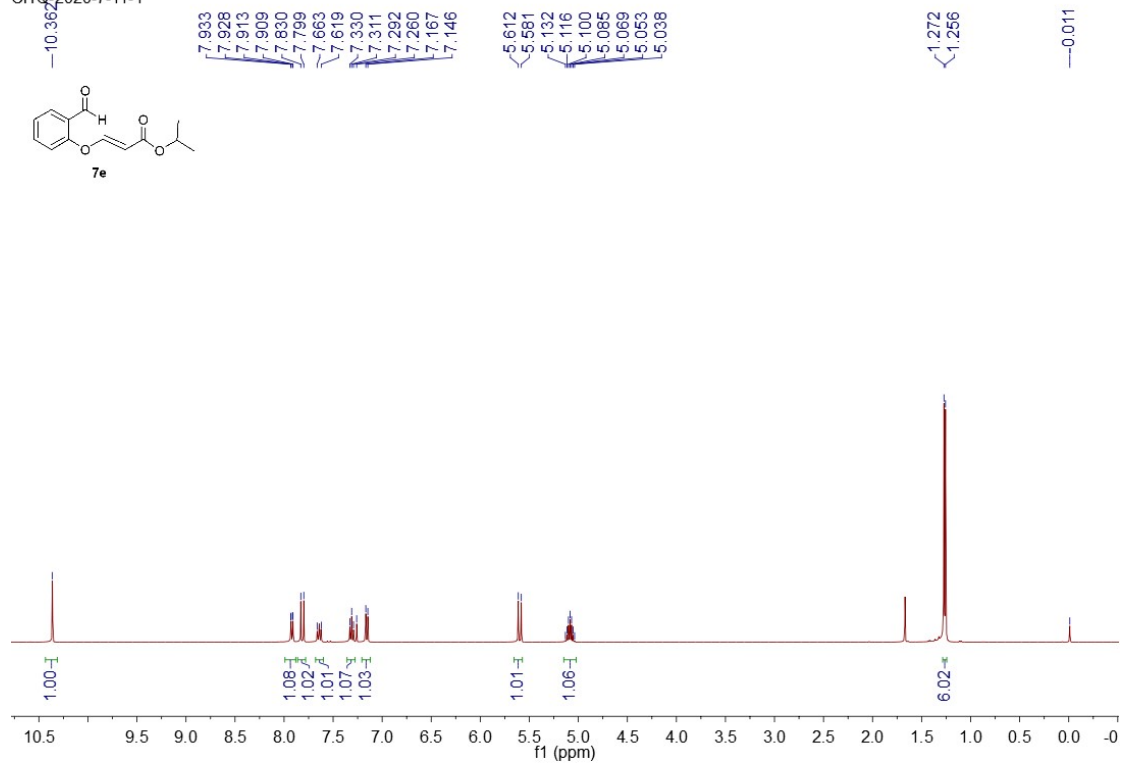
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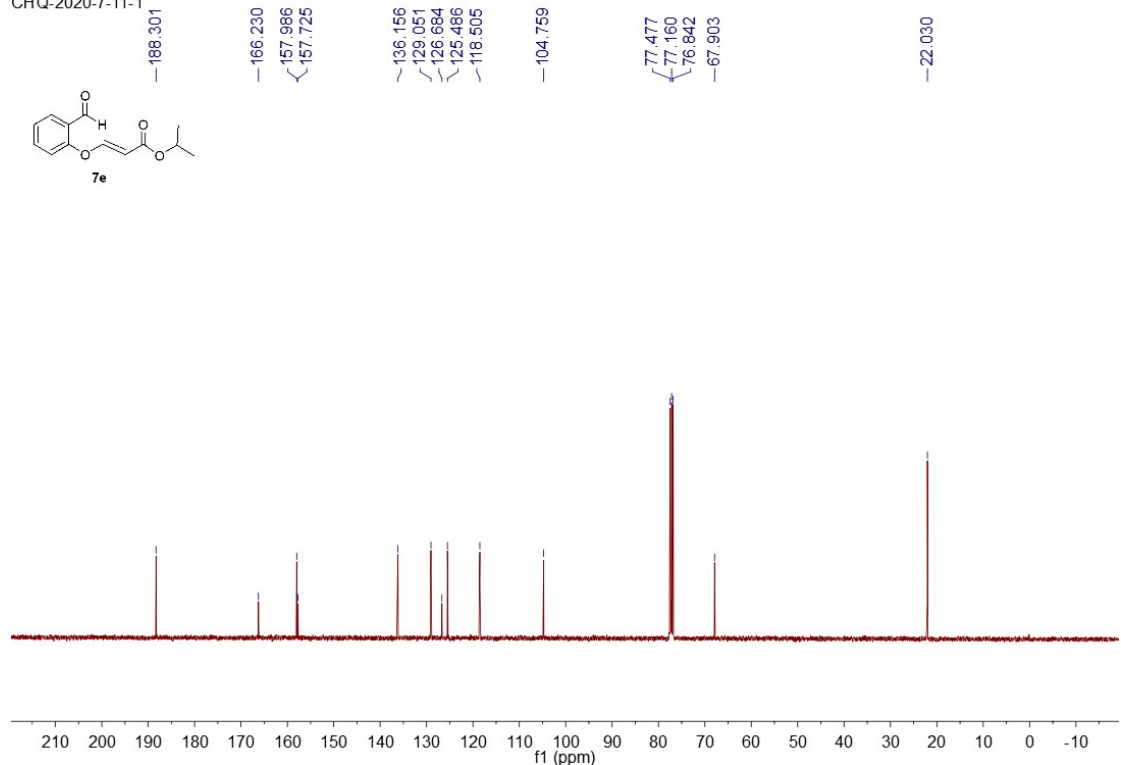
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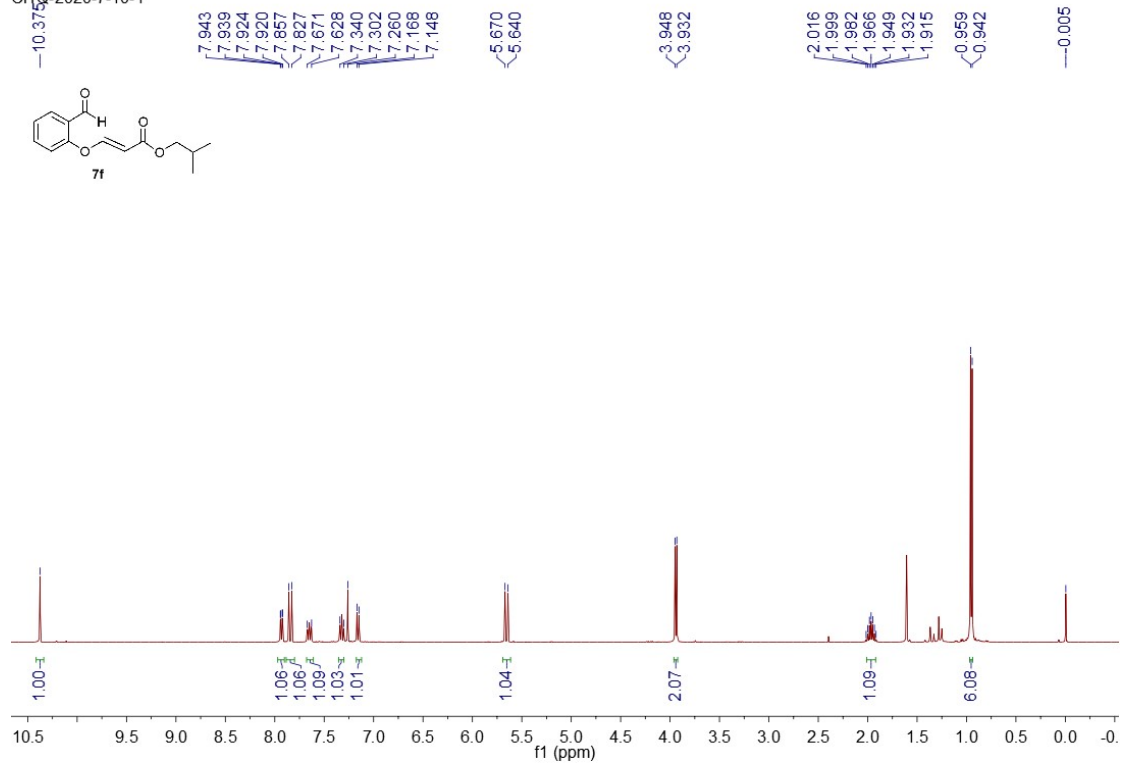
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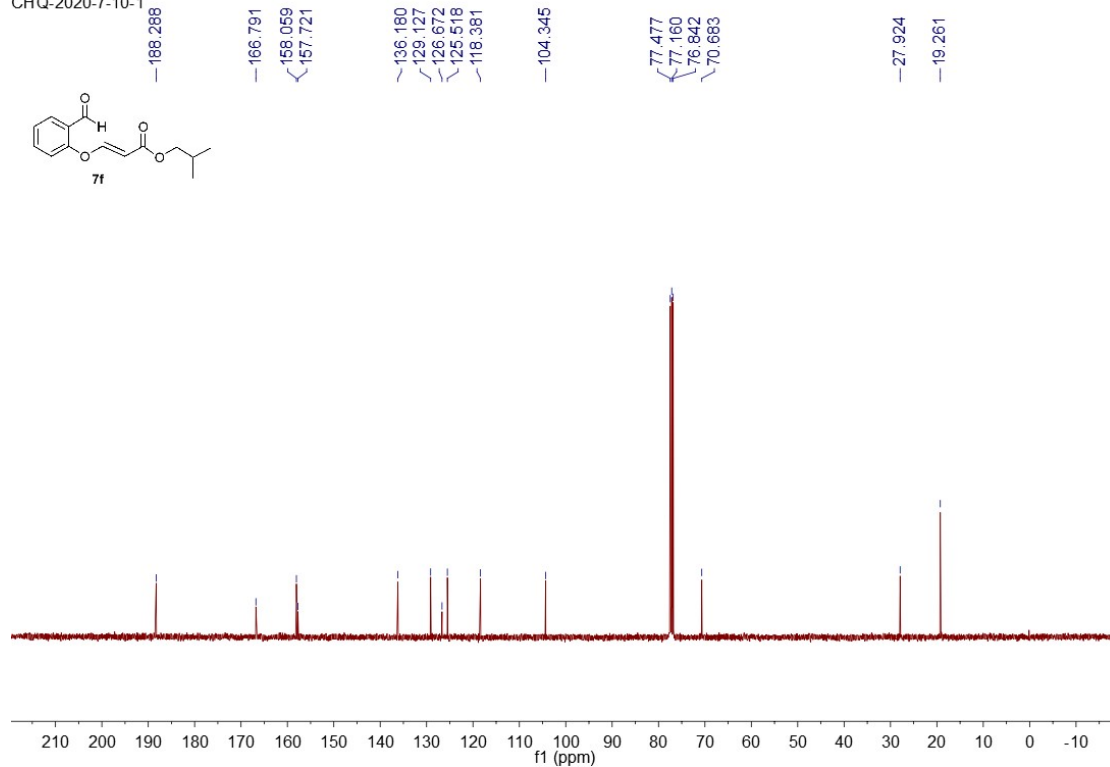
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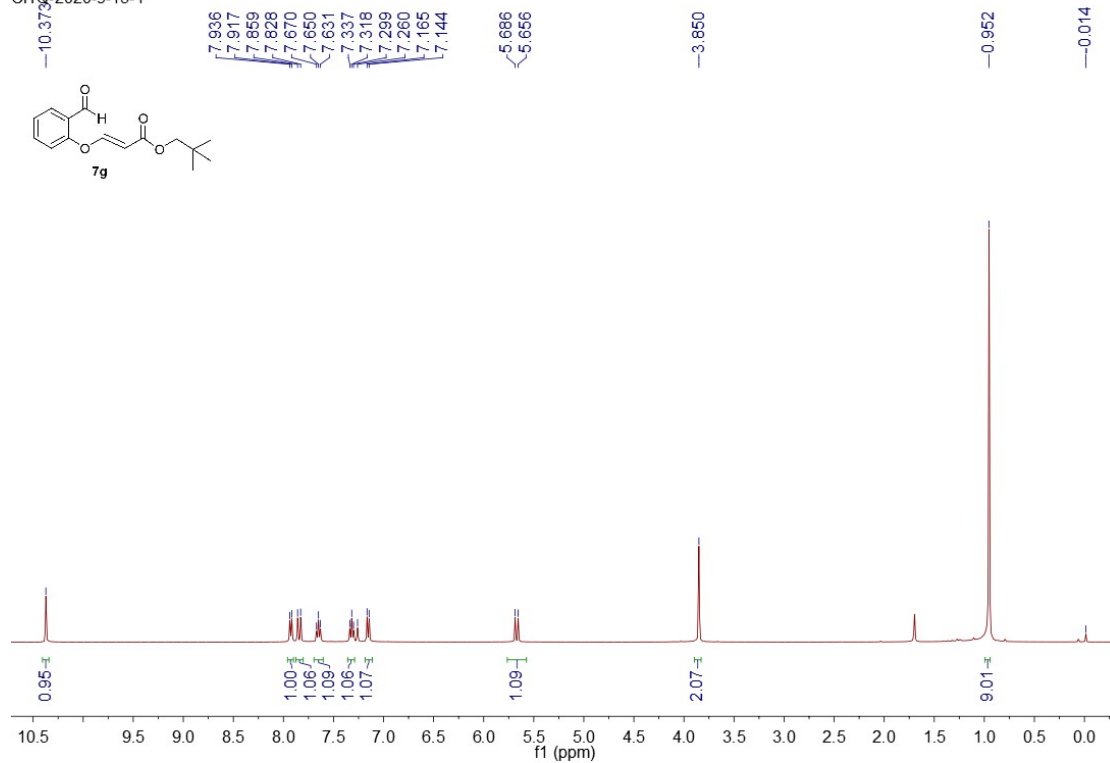
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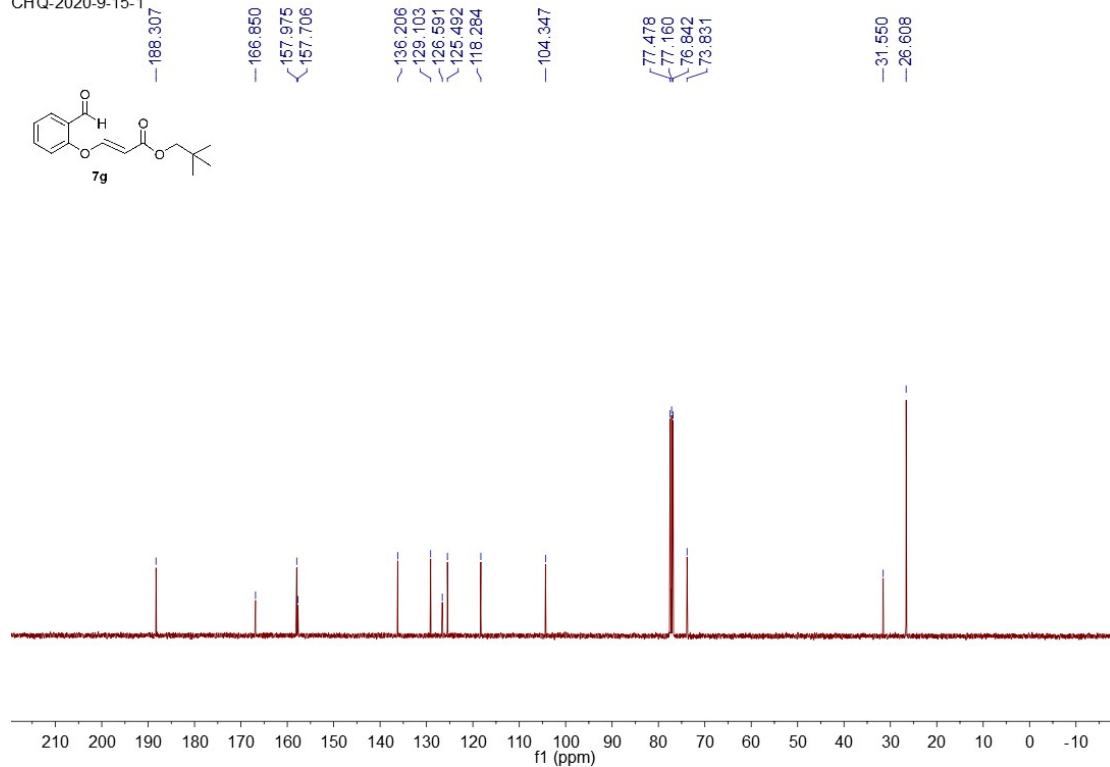
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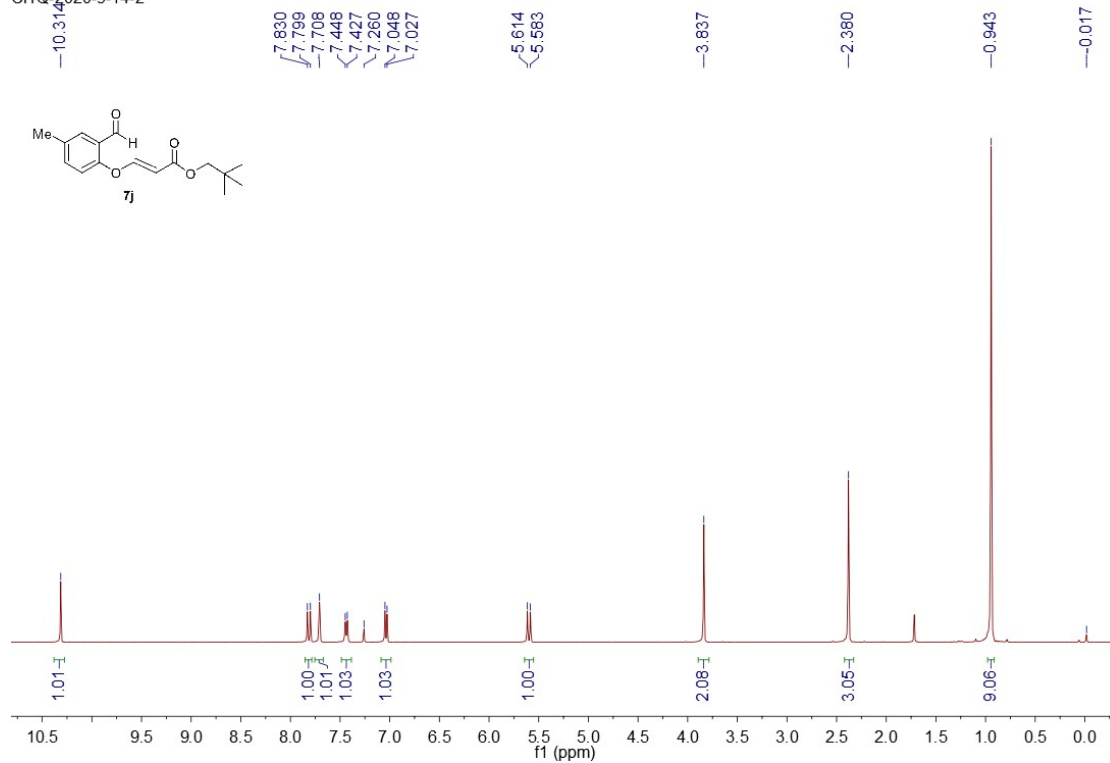
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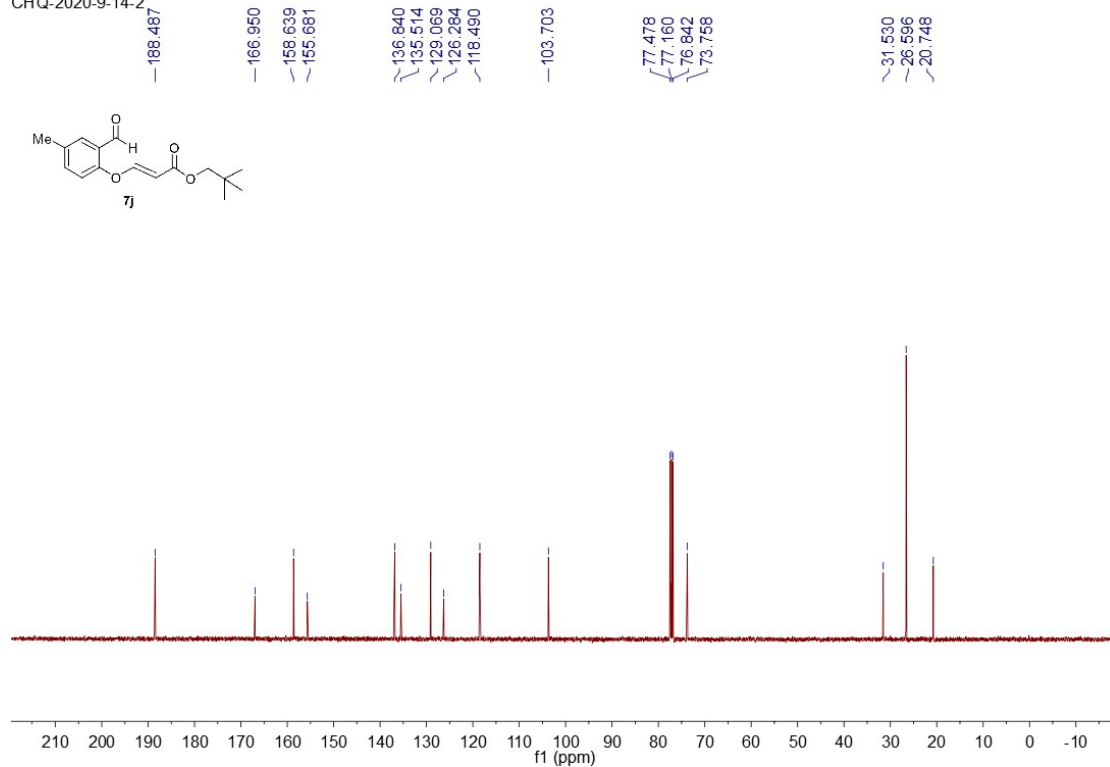
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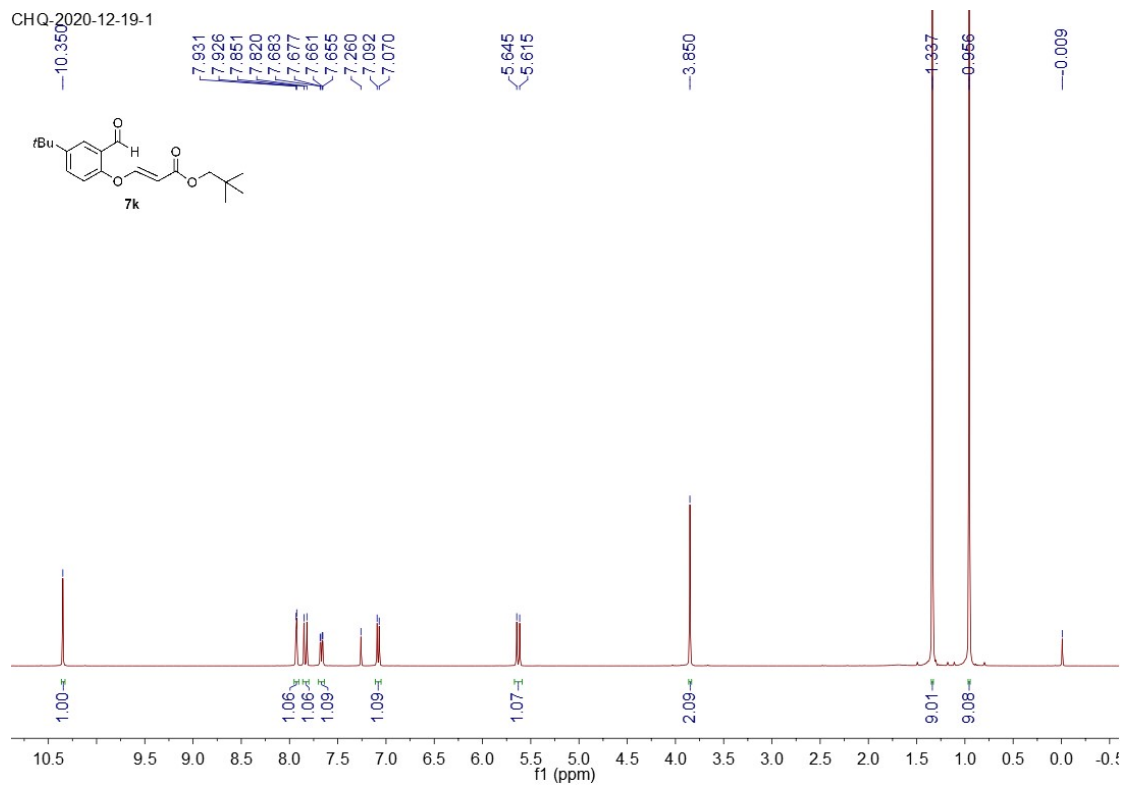
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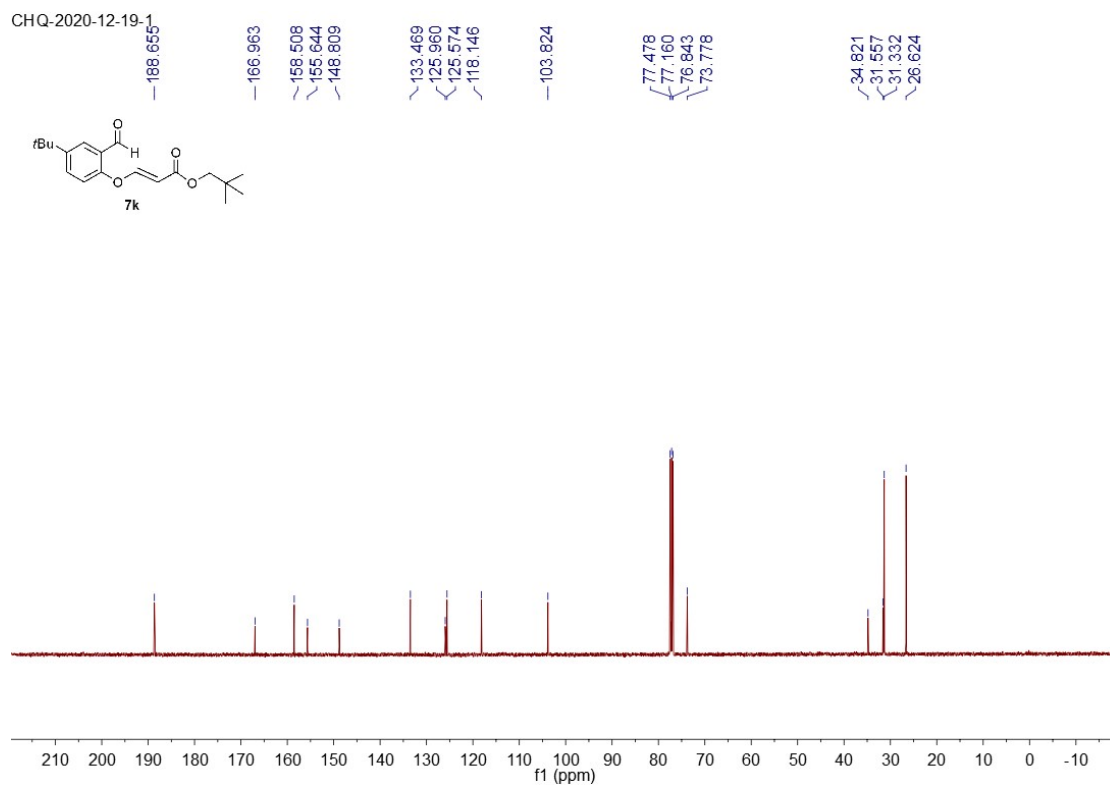
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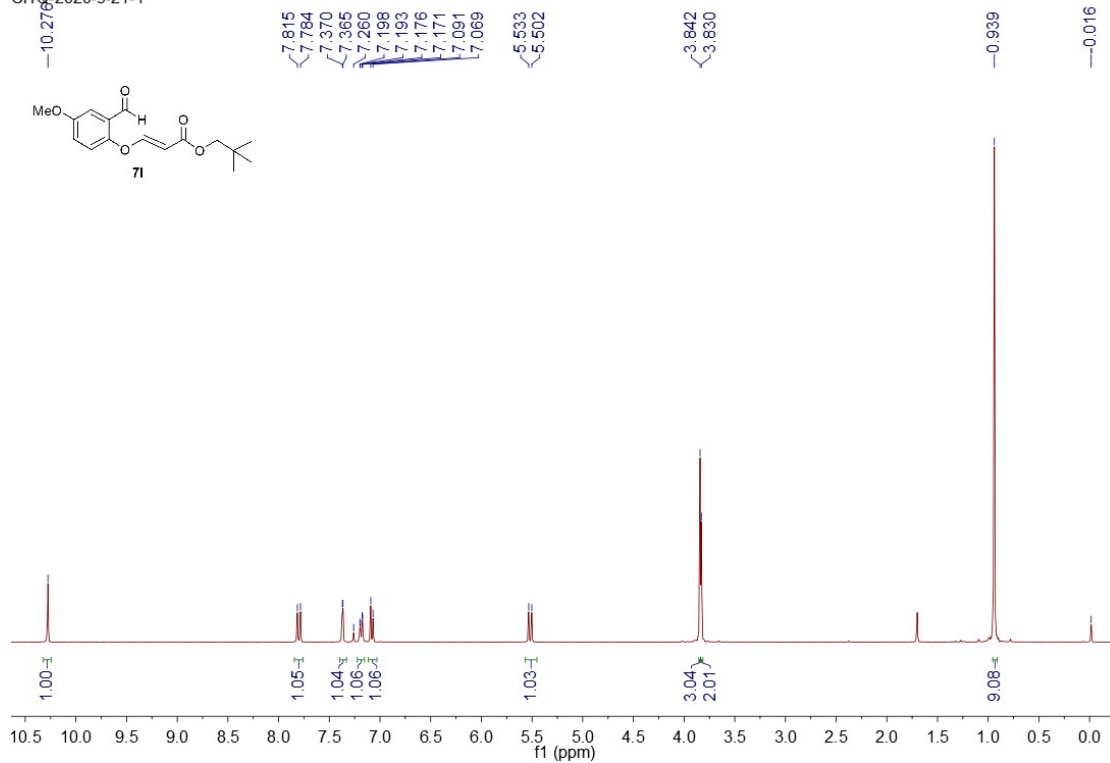
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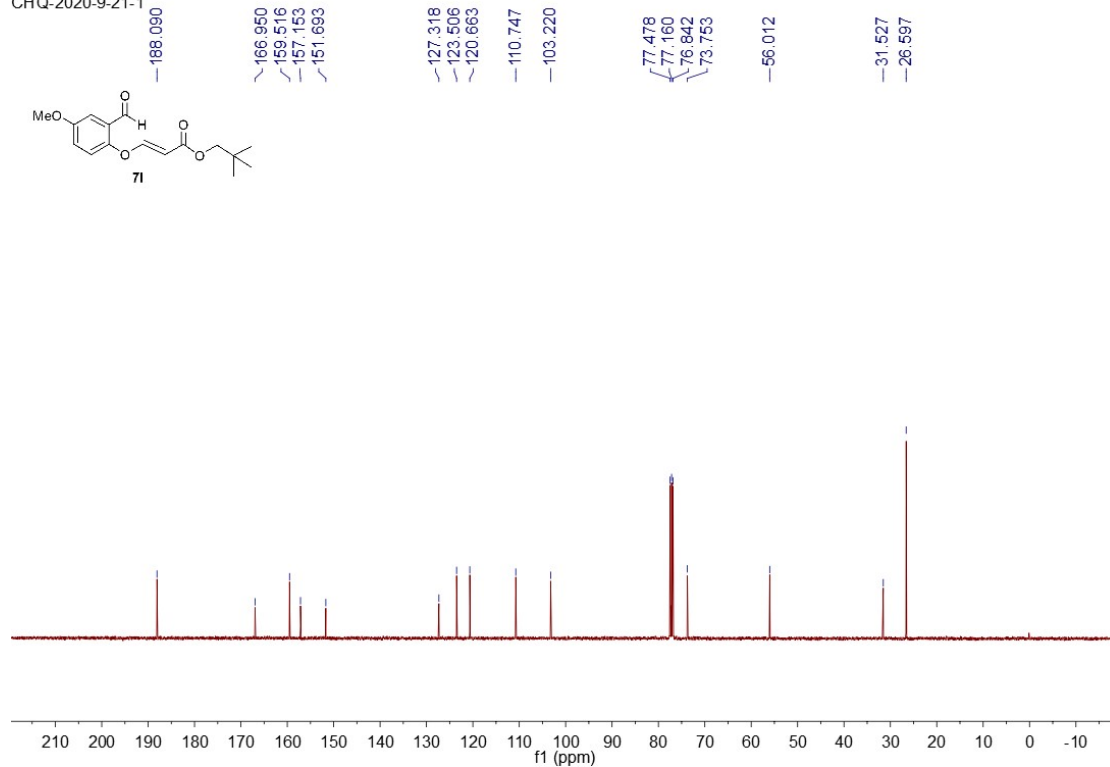
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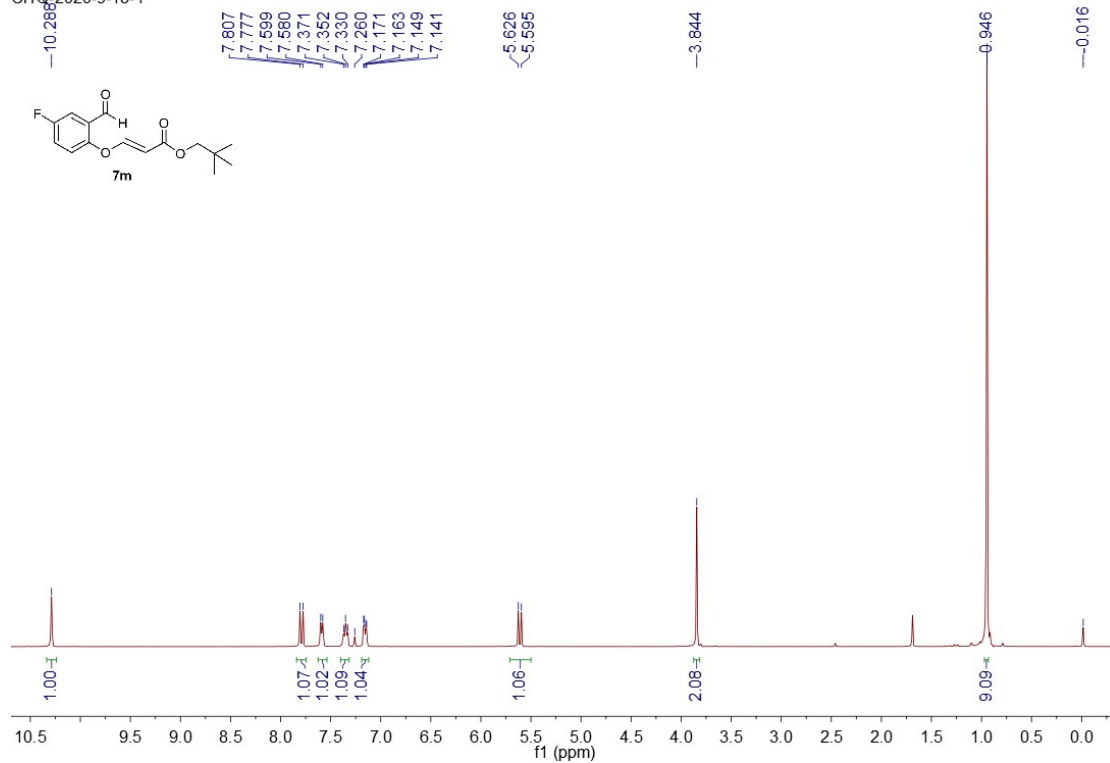
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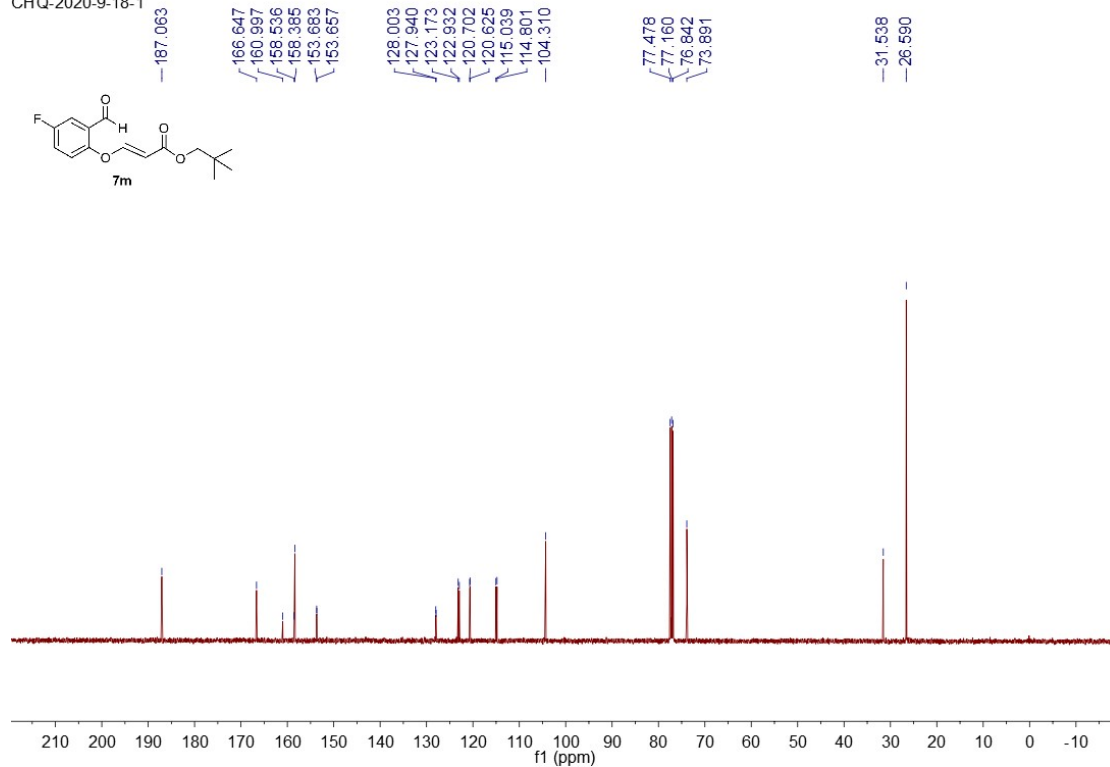
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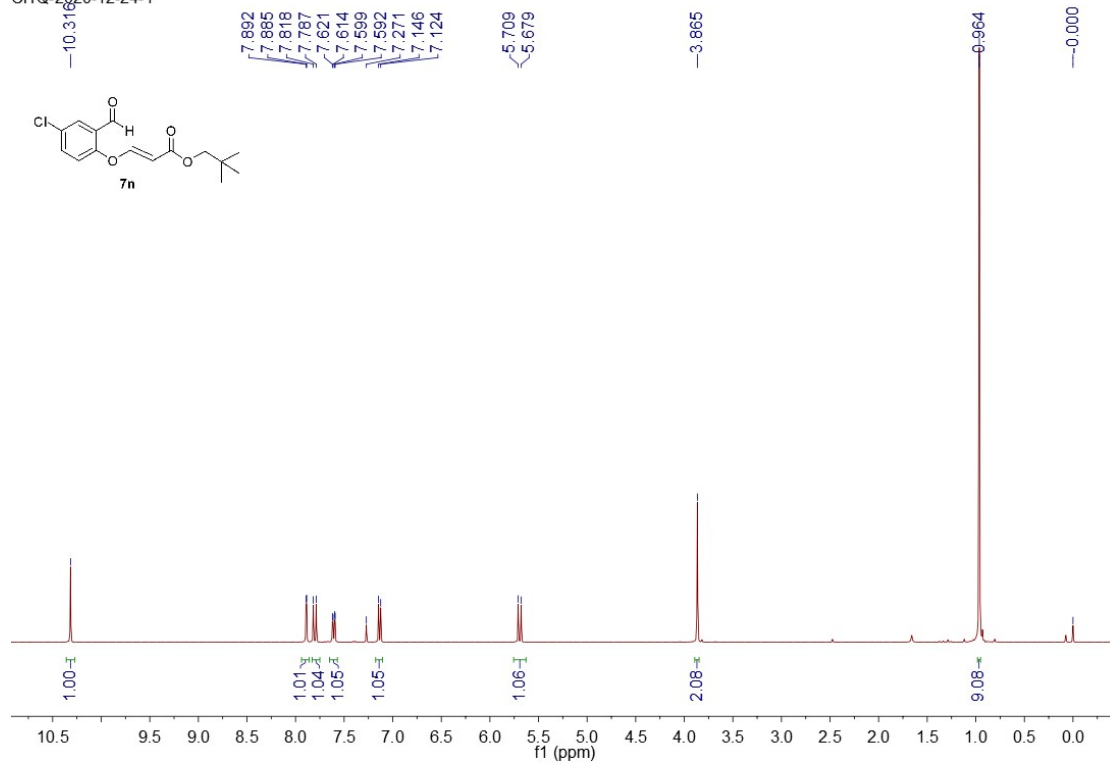
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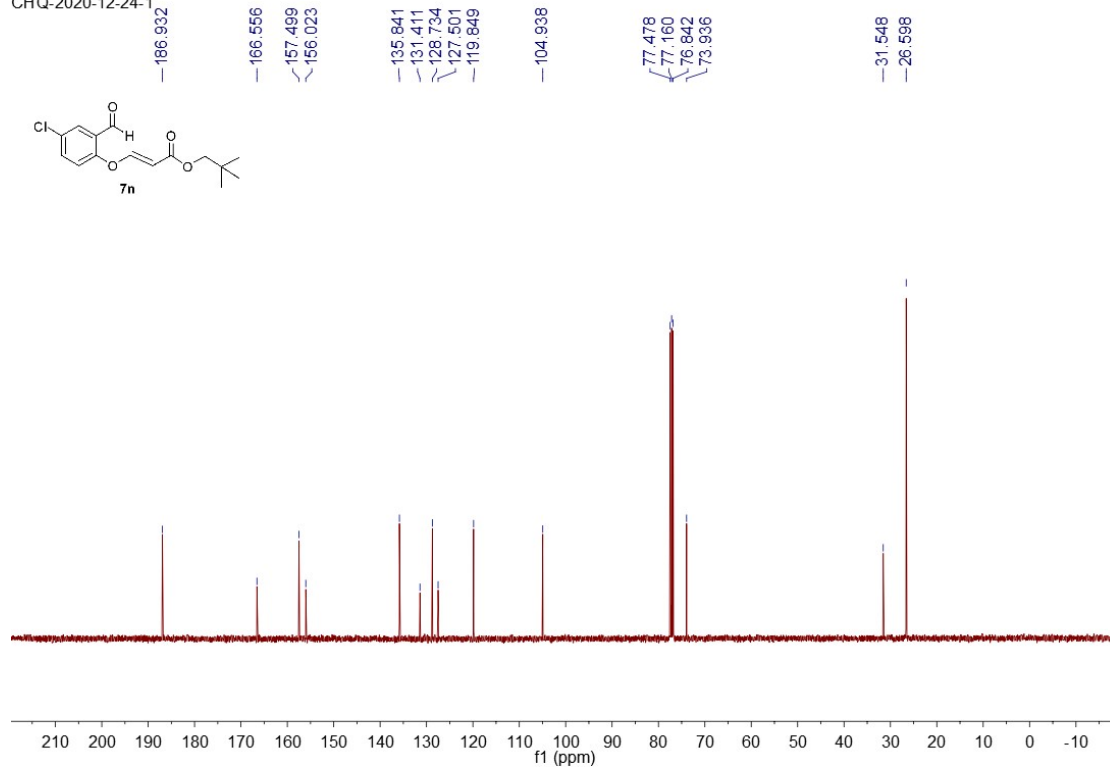
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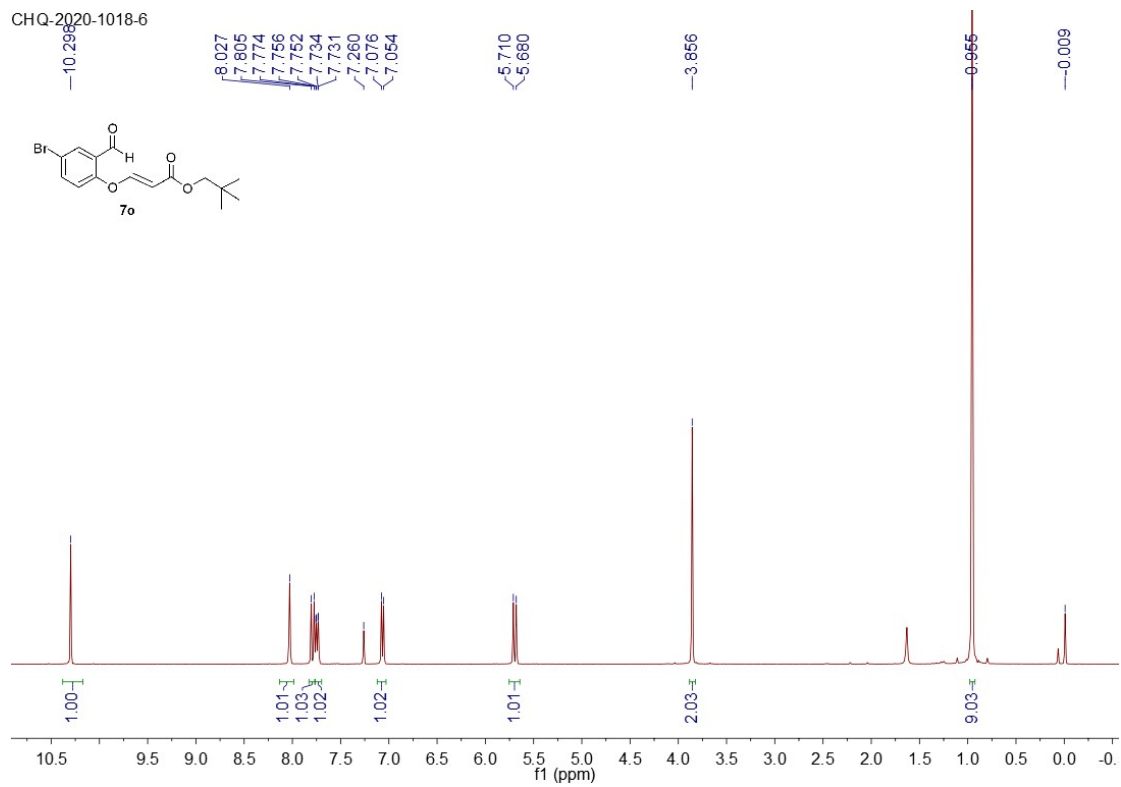
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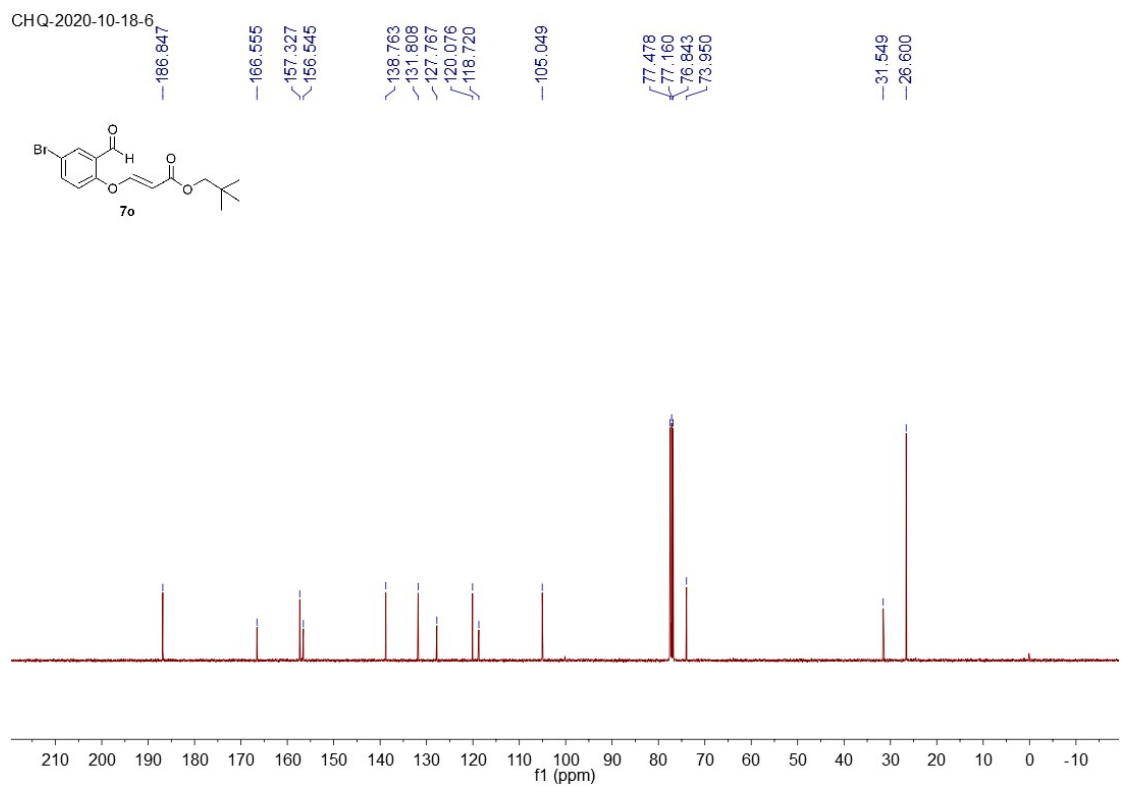
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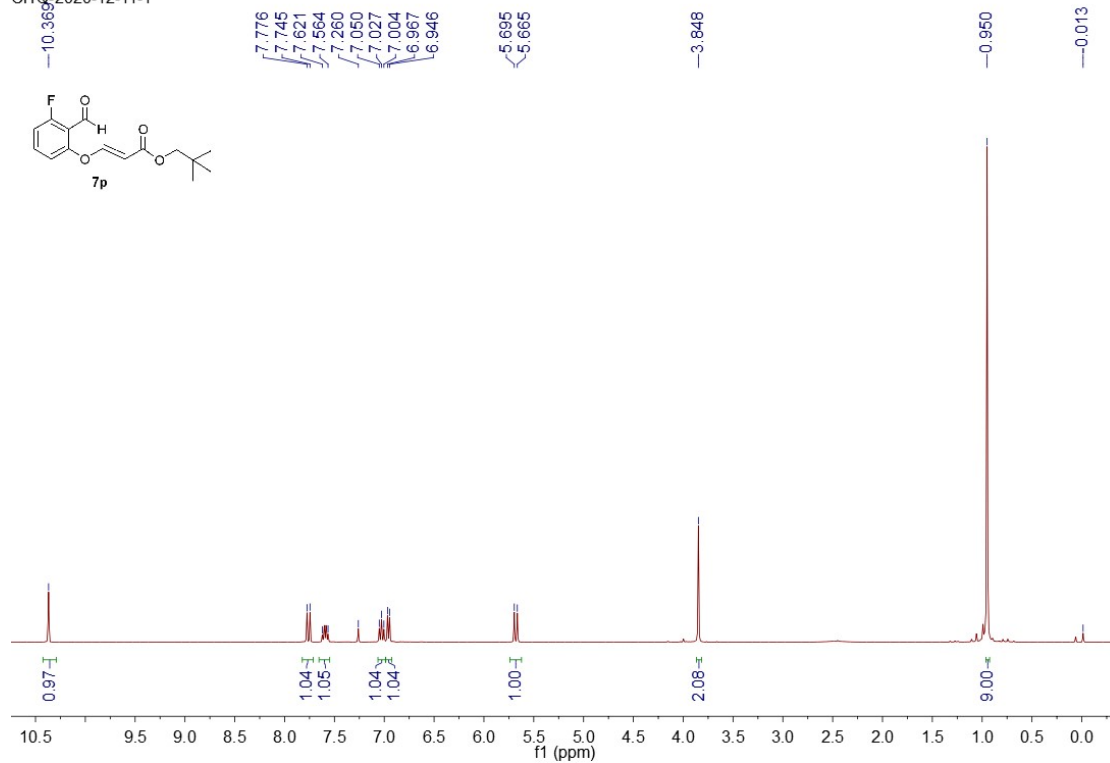
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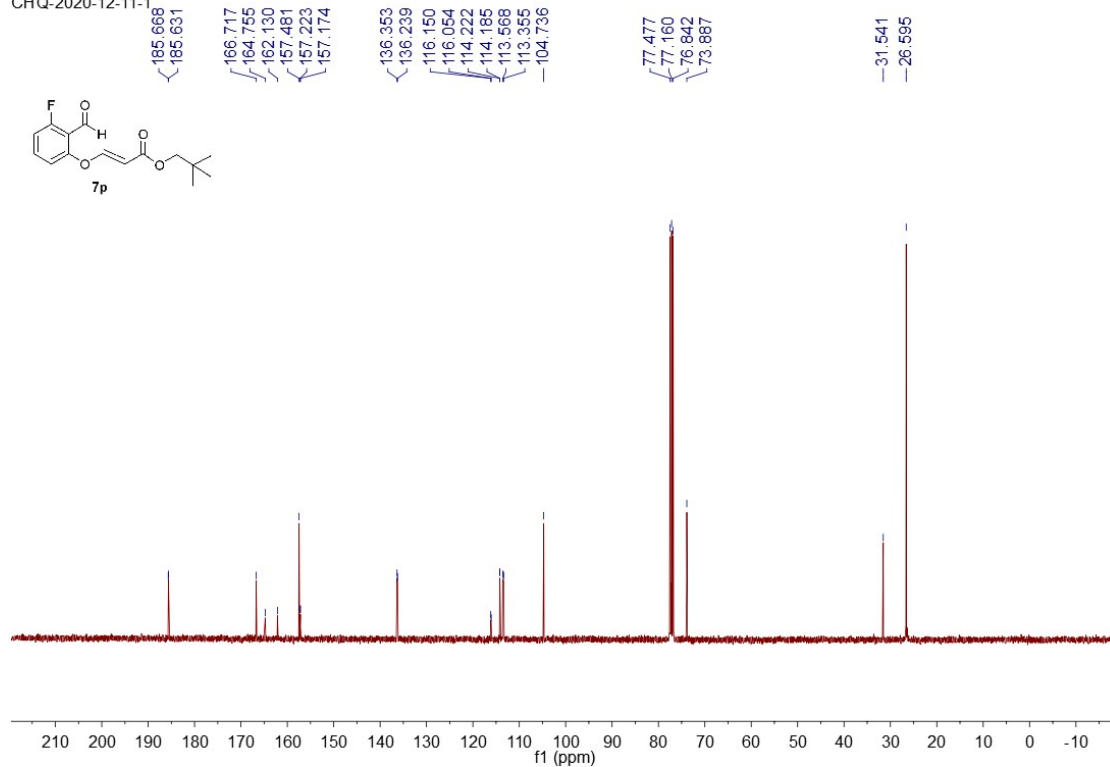
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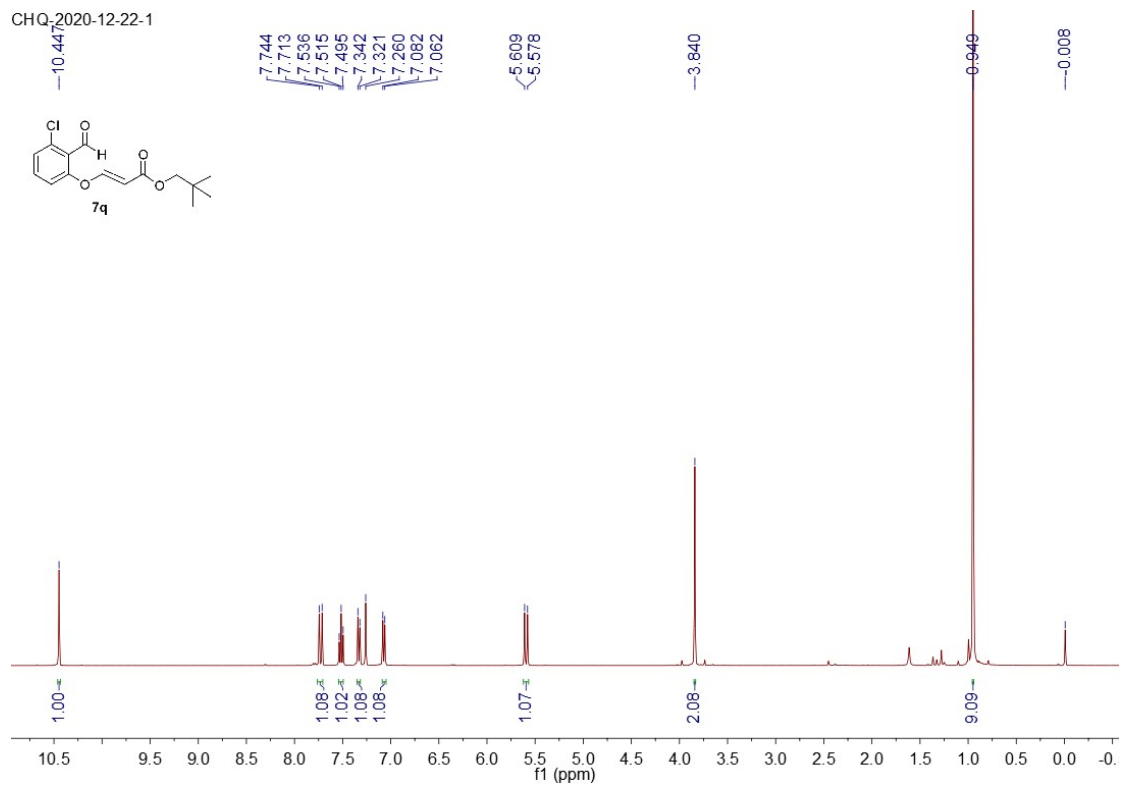
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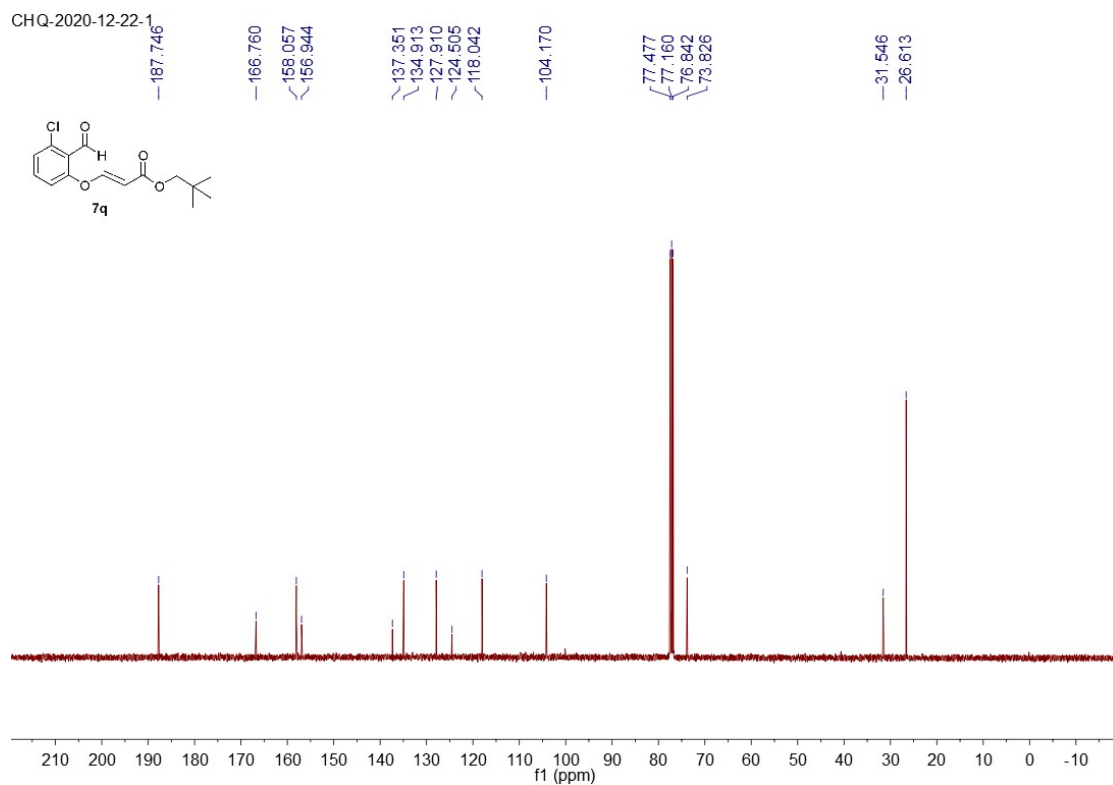
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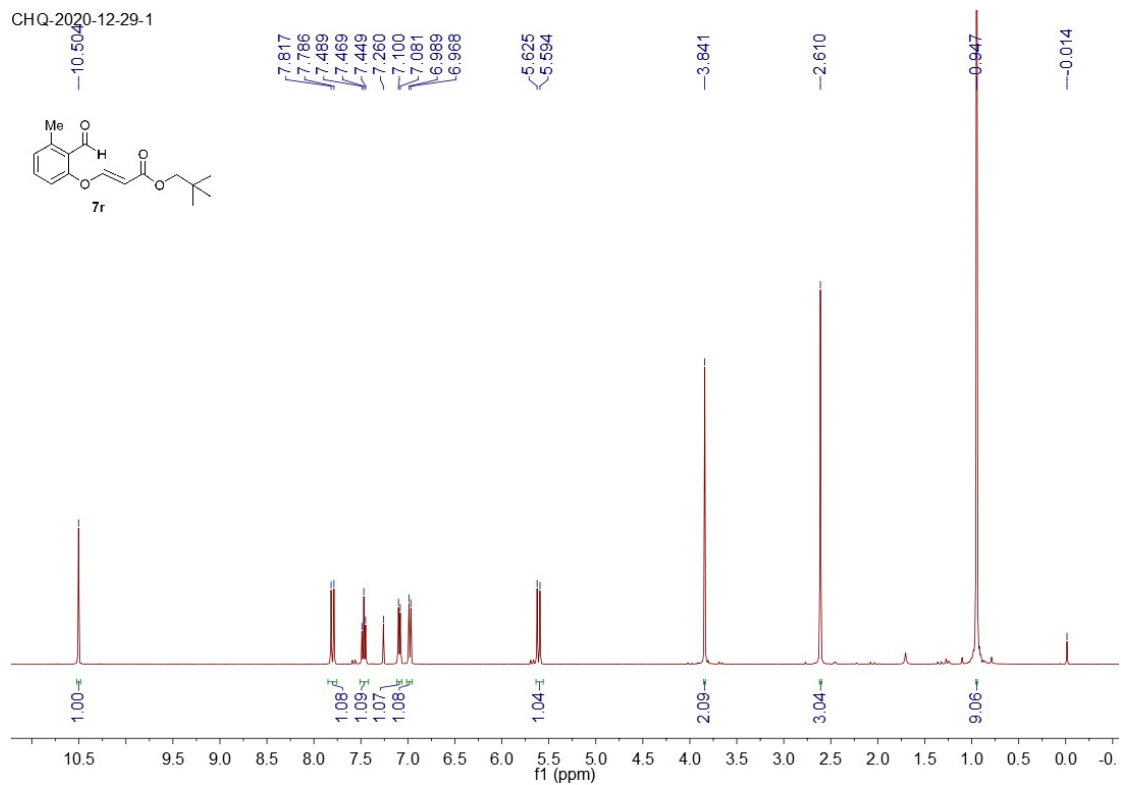
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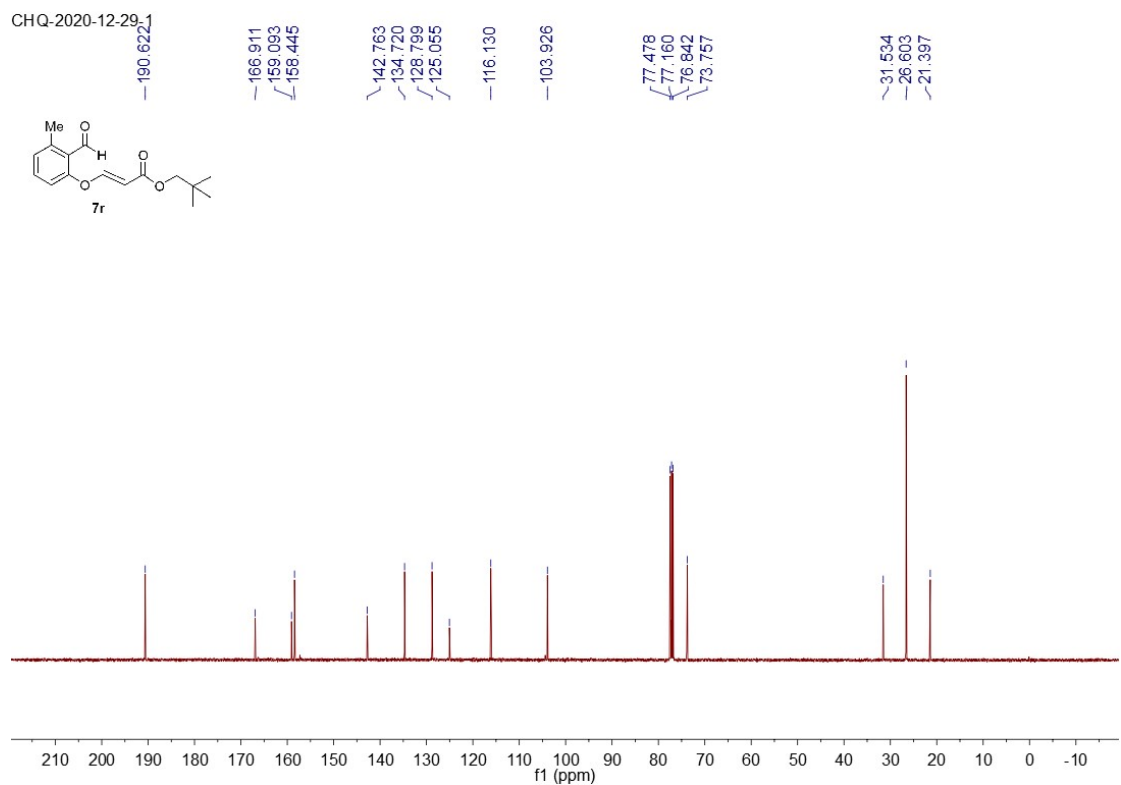
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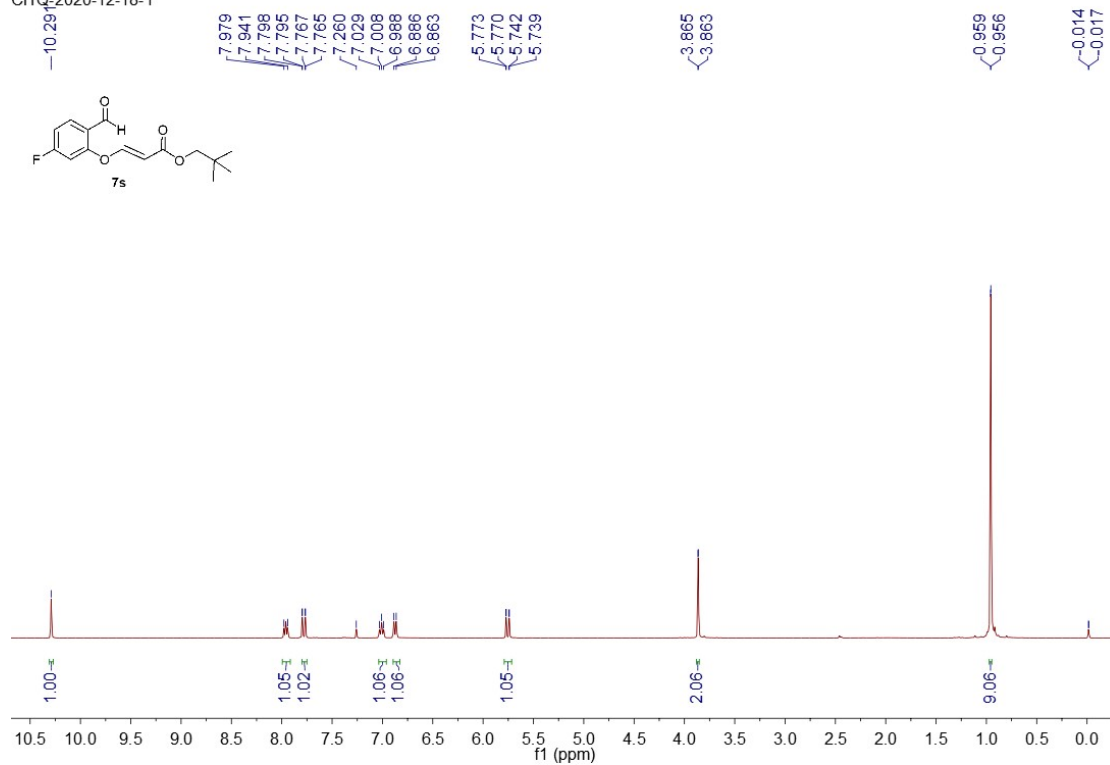
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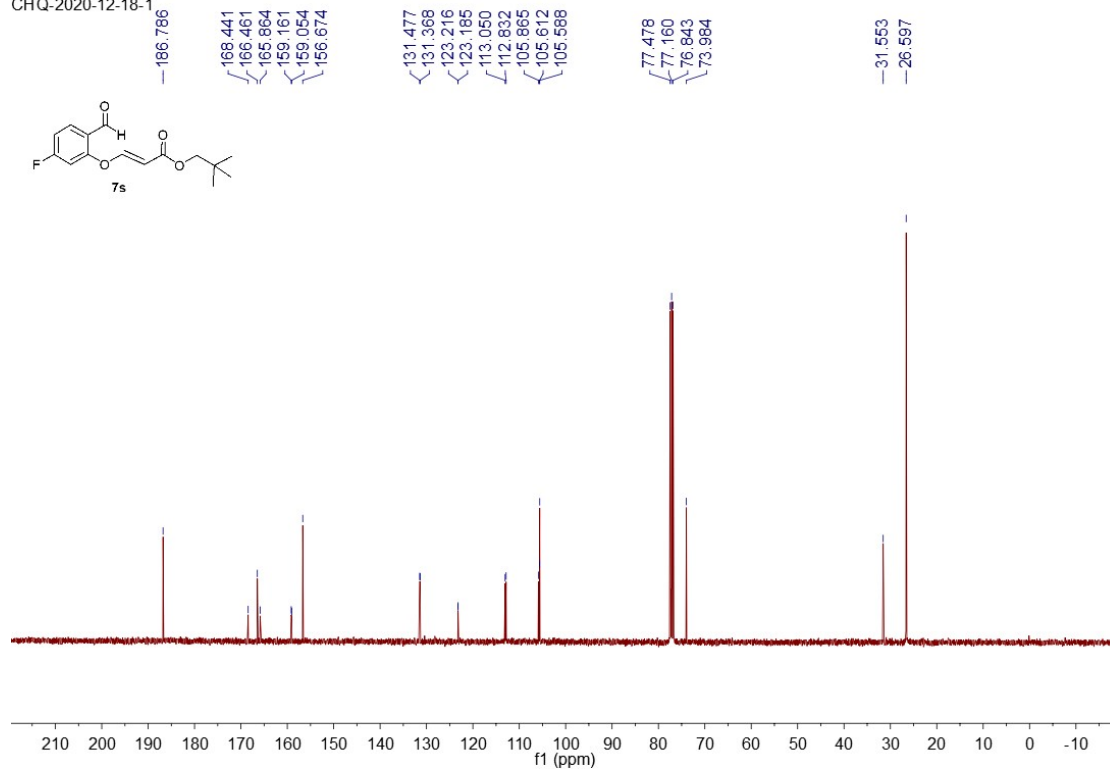
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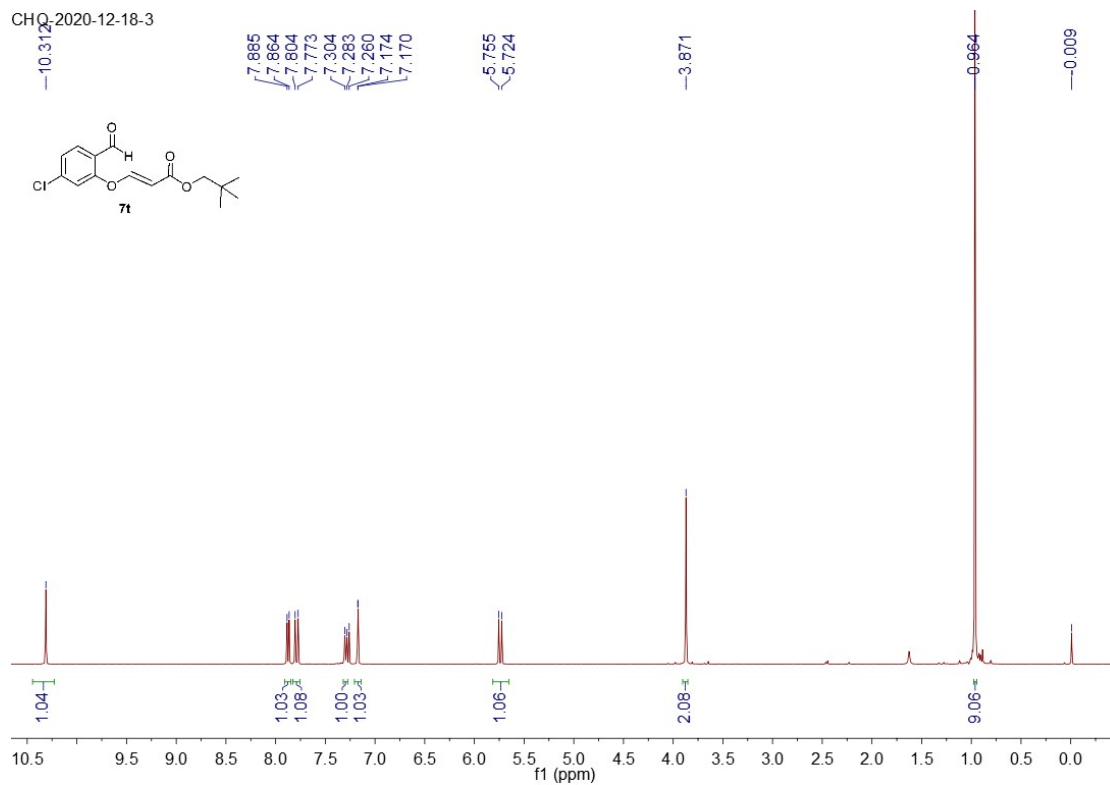
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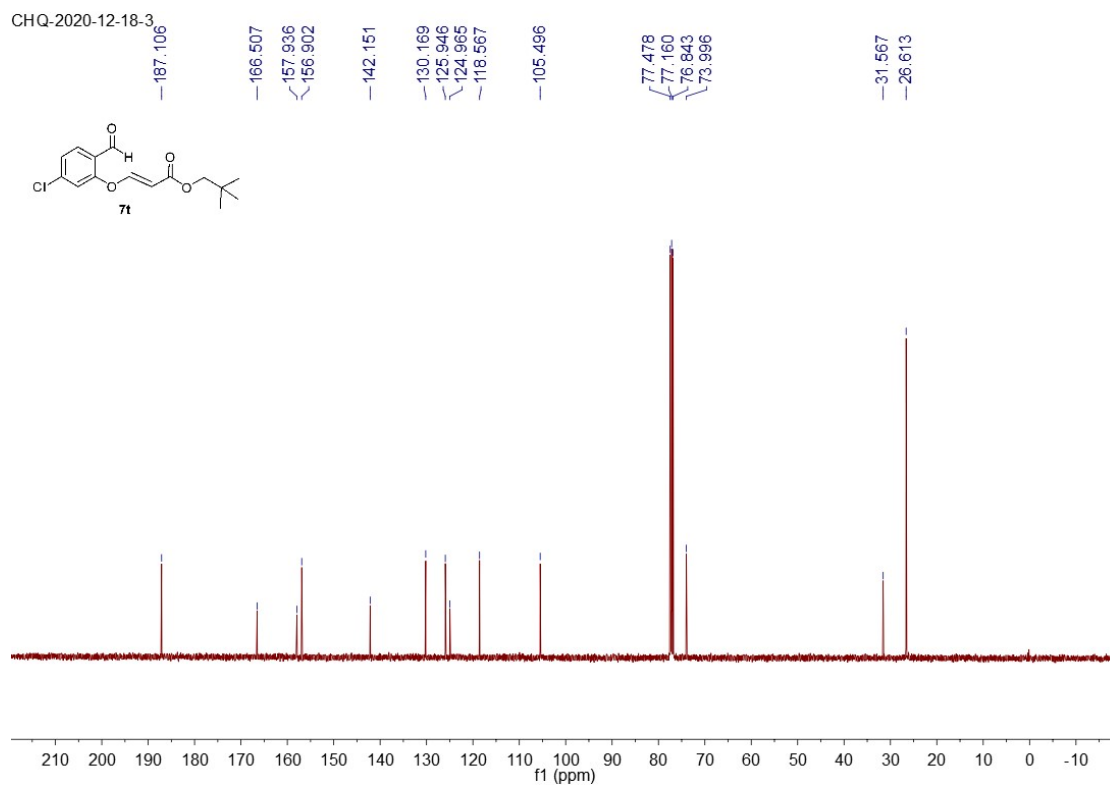
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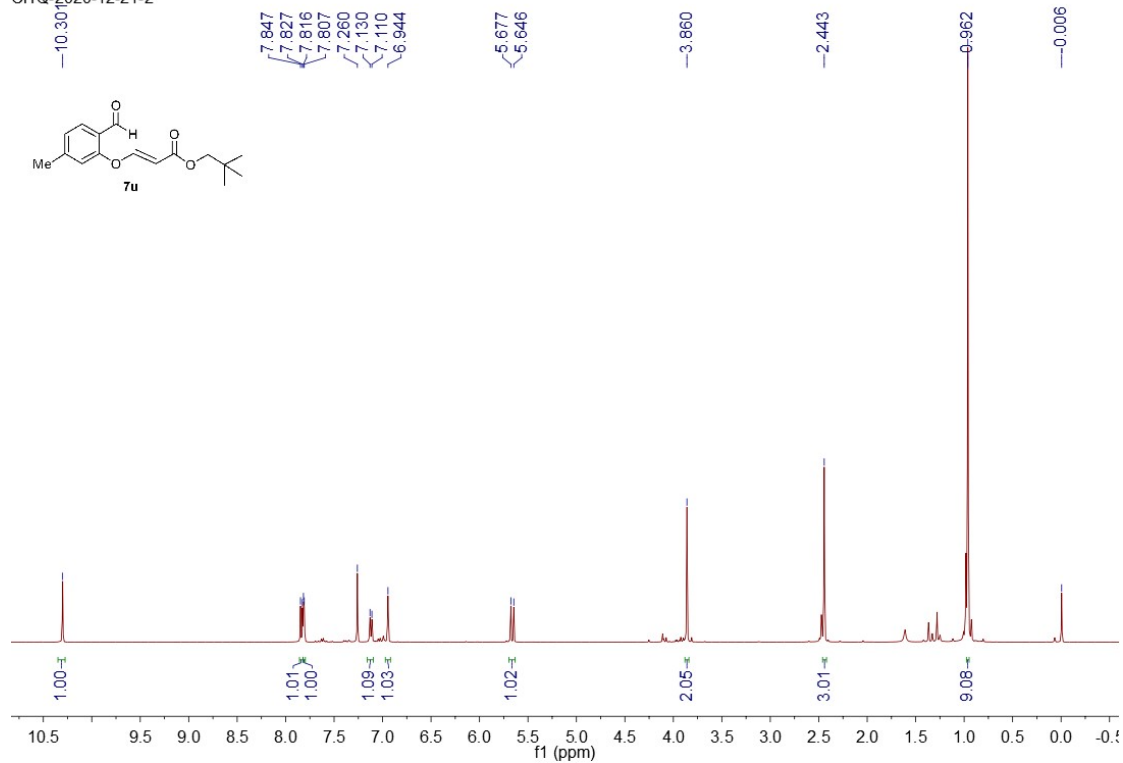
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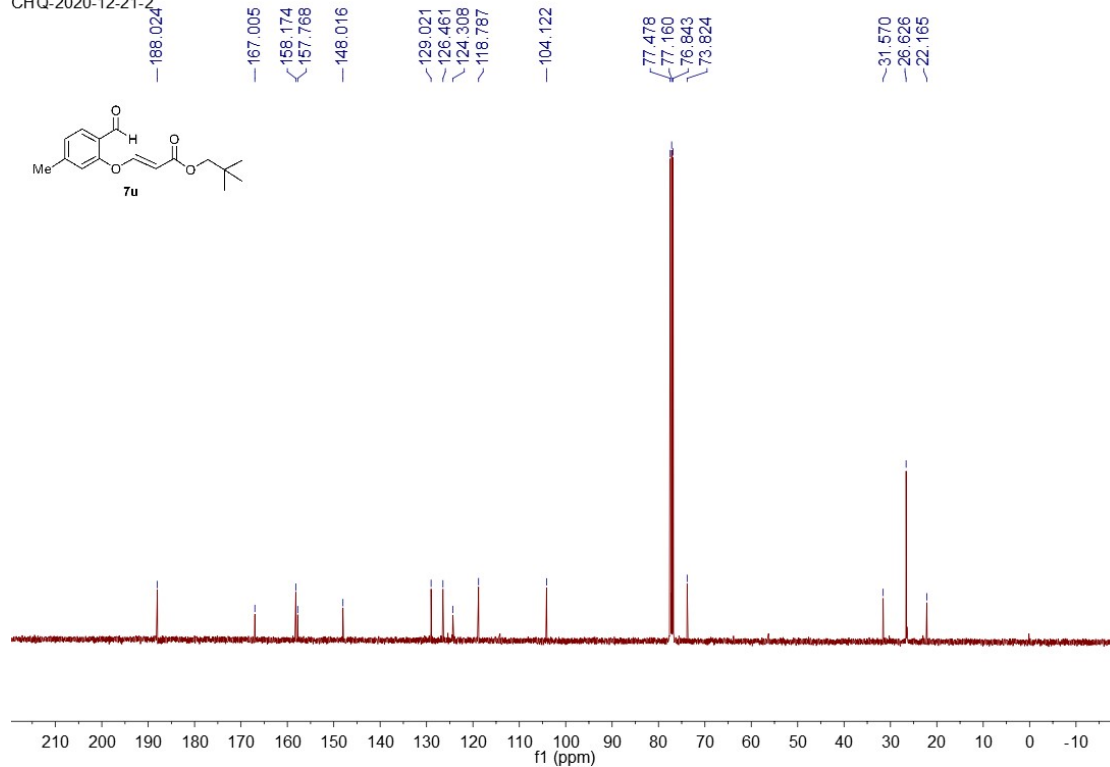
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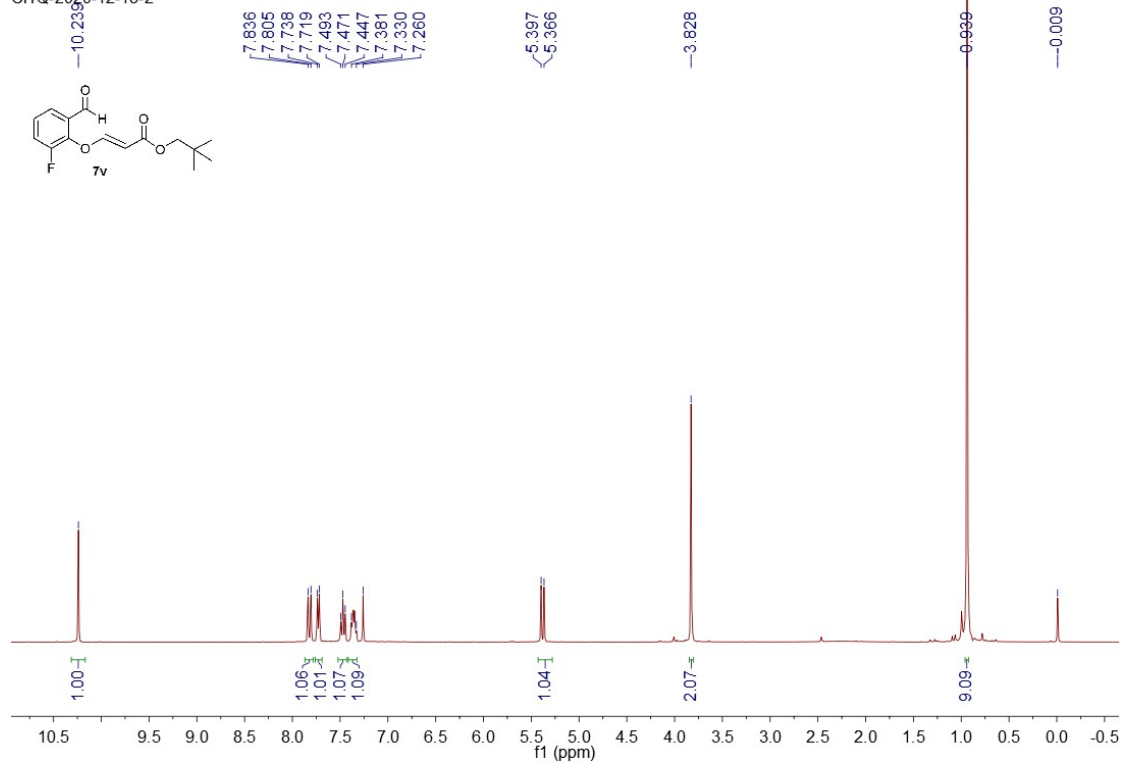
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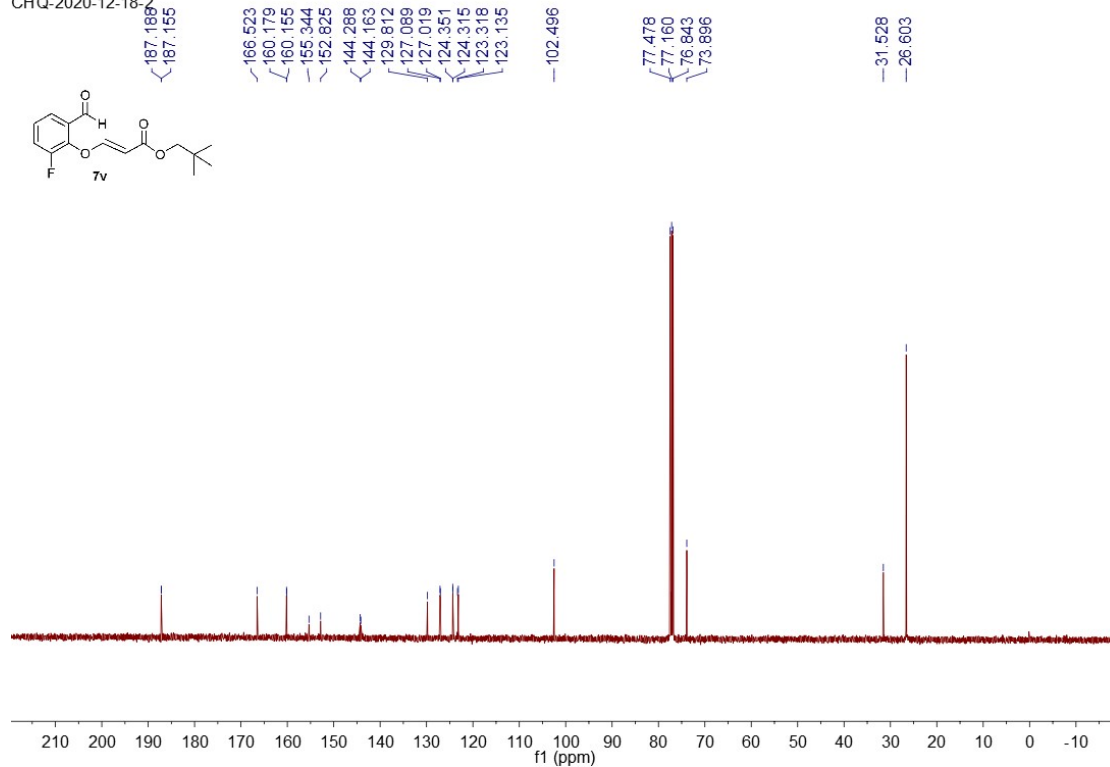
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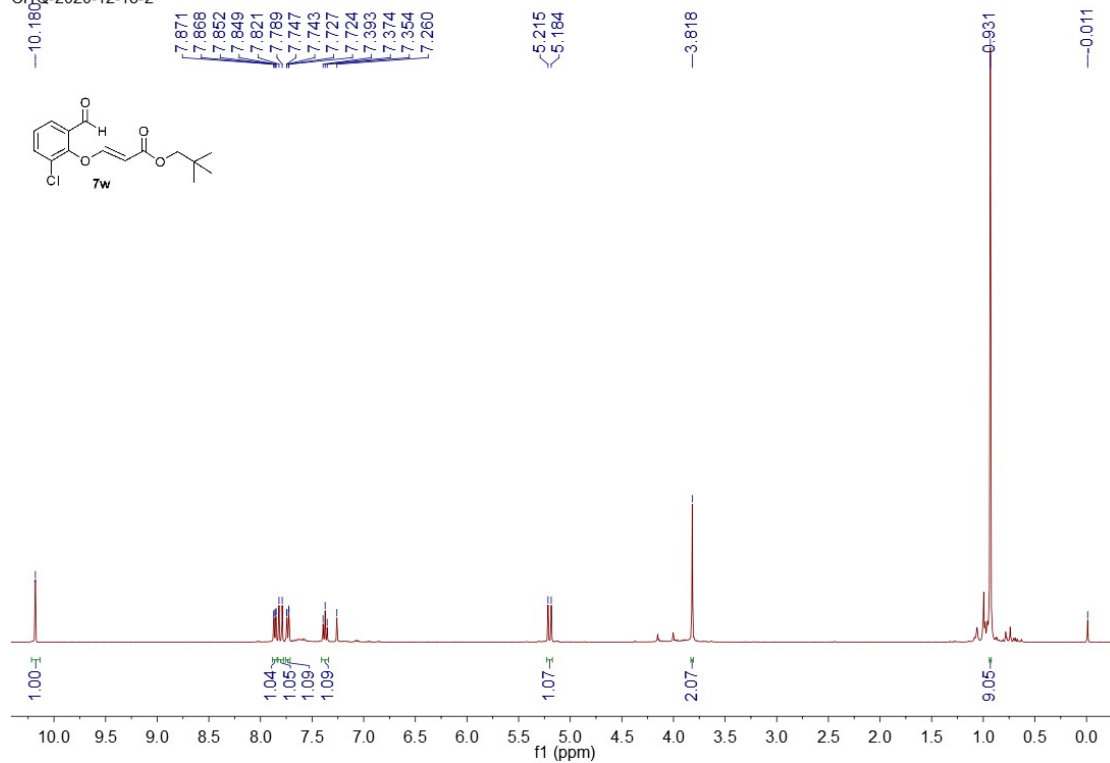
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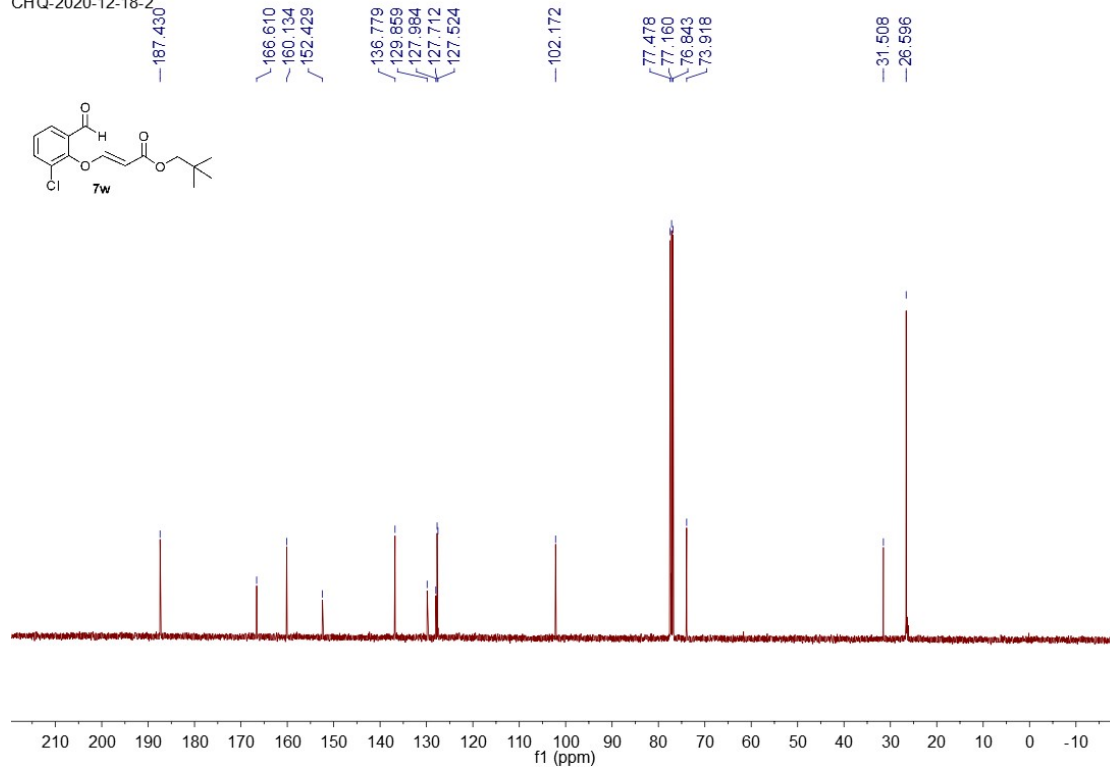
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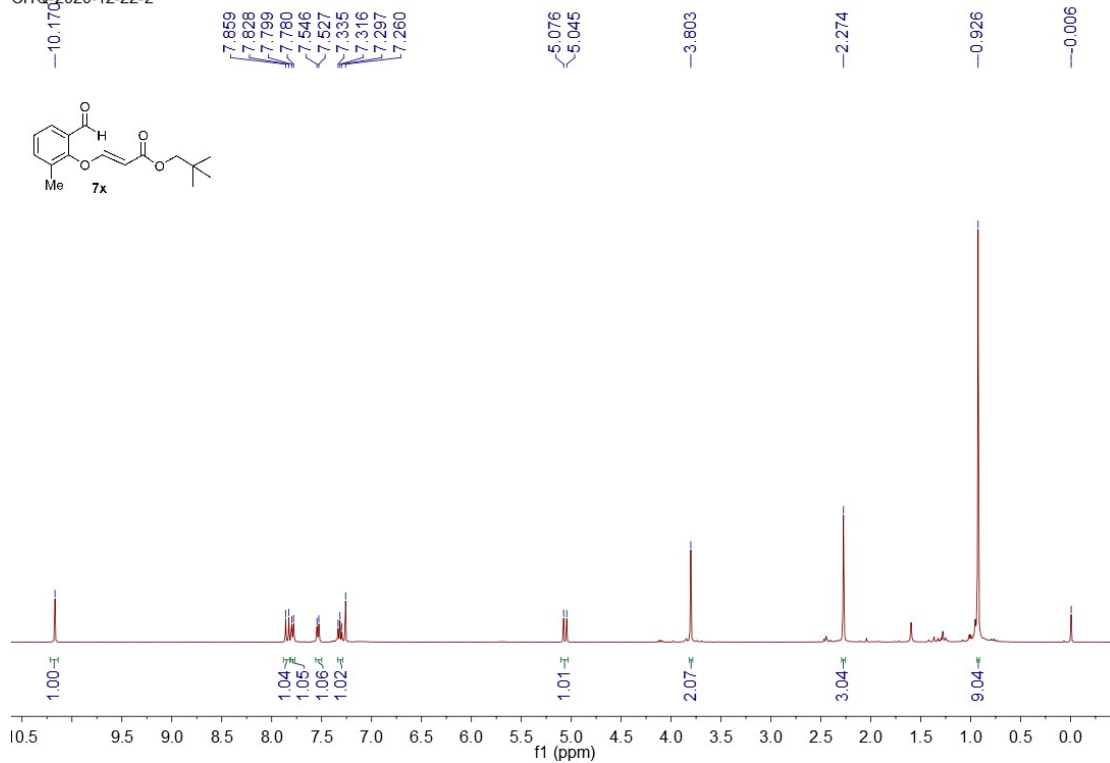
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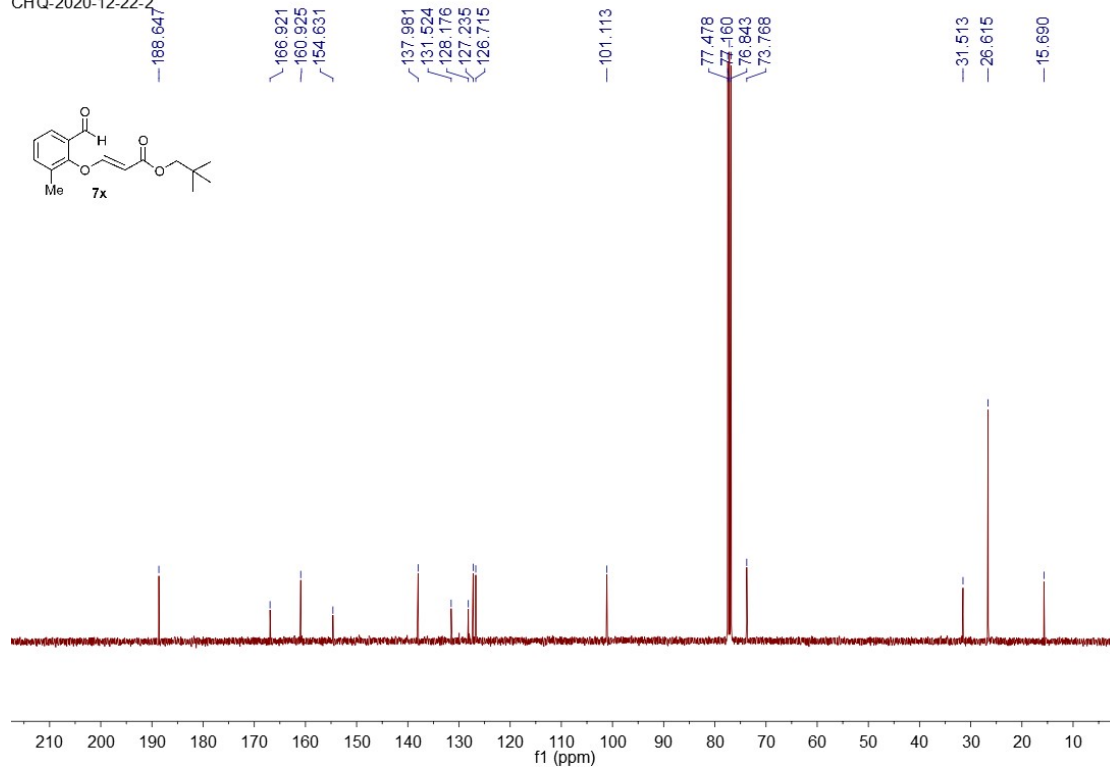
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CHQ-2020-12-22-2



CHQ-2020-12-22-2



CHQ-2020-7-28-1

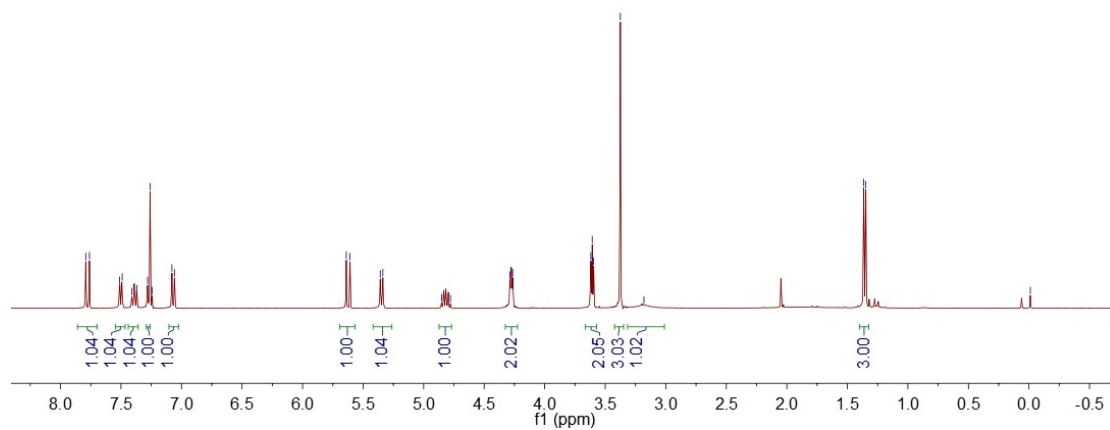
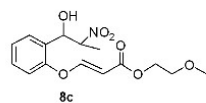
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7.079
7.059

5.639
5.608
5.359
5.337
4.852
4.776
4.288
4.265

3.619
3.607
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1.365
1.348

-0.011



CHQ-2020-7-28-1

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152.920

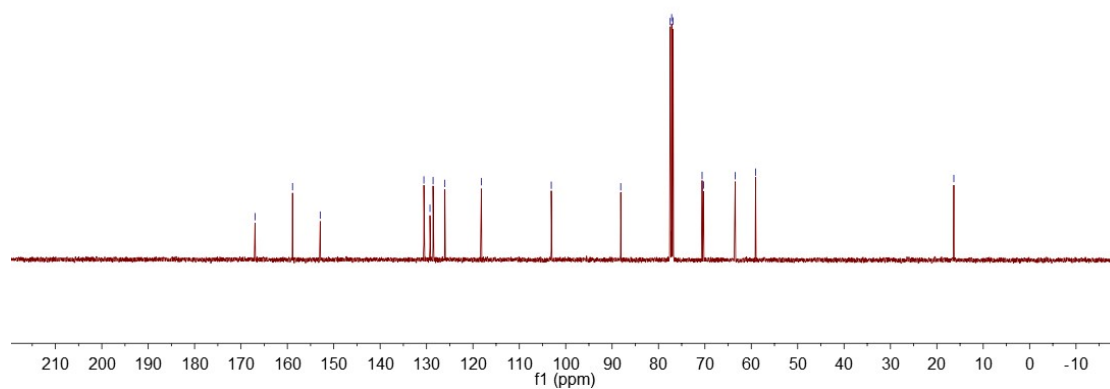
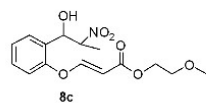
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118.176

103.110

88.139

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59.079

16.336



CHQ-2020-7-24-1

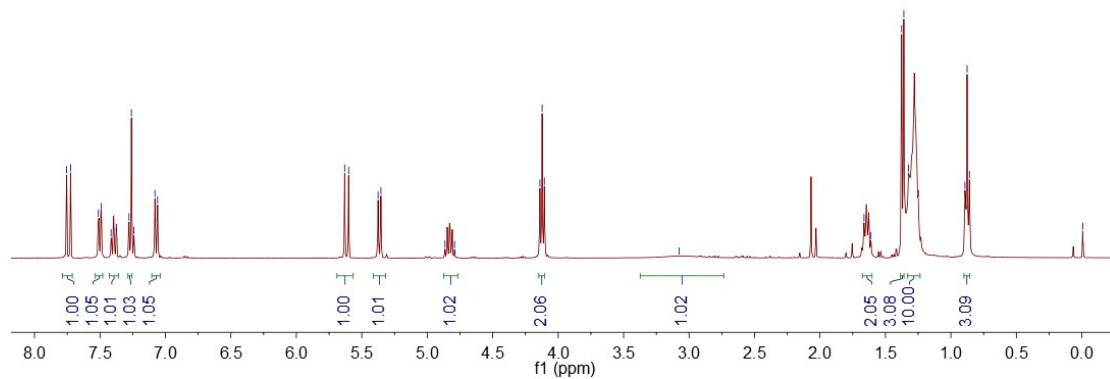
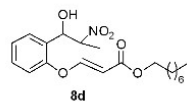
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7.260
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7.080
7.060

5.631
5.600
5.376
5.354
4.864
4.791
4.139
4.122
4.105

-3.076

1.664
1.611
1.377
1.359
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0.876
0.859

-0.007



CHQ-2020-7-24-1

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-153.068

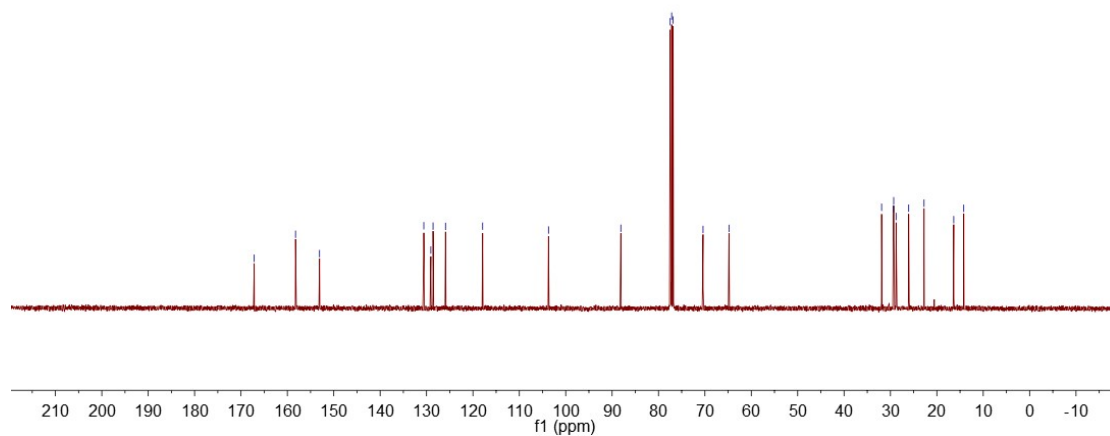
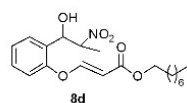
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128.598
125.912
117.907

-103.708

-88.121

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77.160
76.842
70.399
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29.348
29.298
28.789
26.068
22.758
16.356
14.202



CHQ-2020-7-13-1

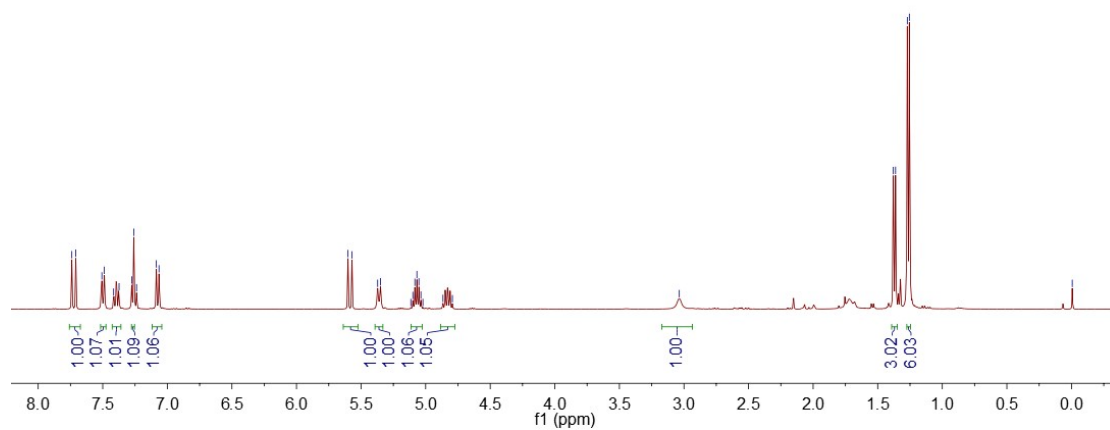
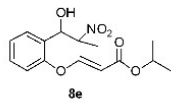
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7.064

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5.099
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5.068
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5.037
5.021
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4.793

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1.362
1.271
1.255

—0.006



CHQ-2020-7-13-1

—166.557

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128.587

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77.160

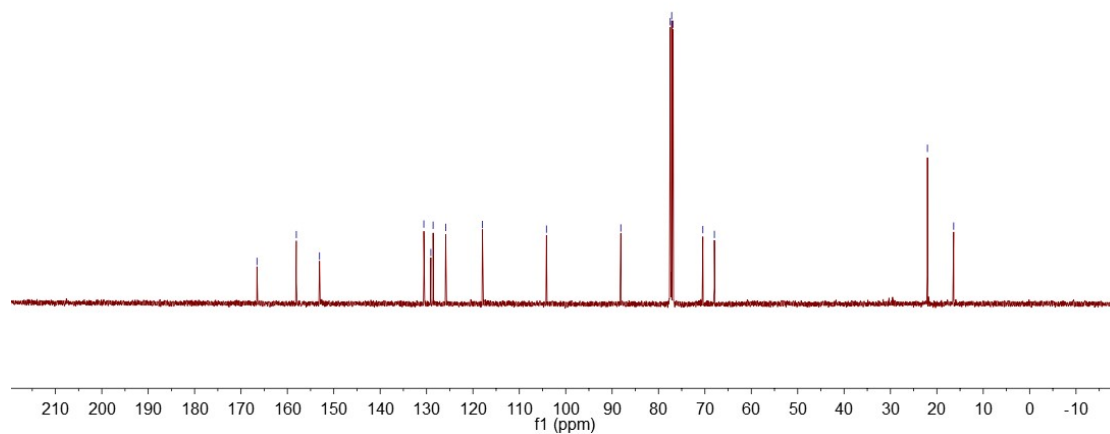
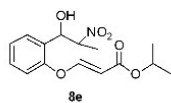
76.842

70.439

67.955

—22.028

—16.373



CHQ-2020-7-16-1

7.759
7.729
7.513
7.490
7.420
7.377
7.280
7.260
7.242
7.081
7.060

5.649
5.619
5.379
5.358
4.867
4.794

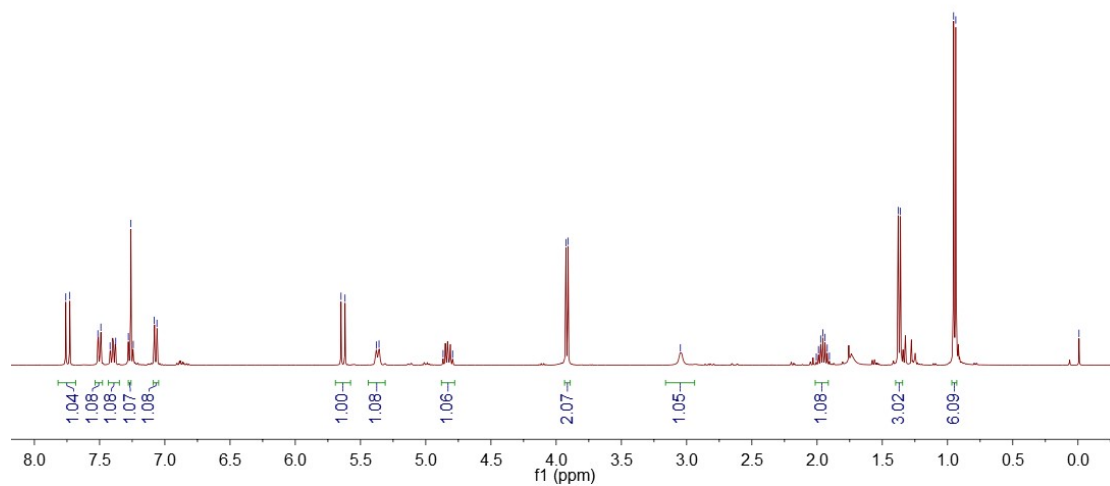
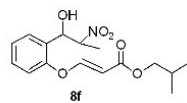
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3.909

3.048

2.006
1.989
1.972
1.956
1.939
1.922
1.905
1.378
1.361

0.953
0.937

-0.008



CHQ-2020-7-16-1

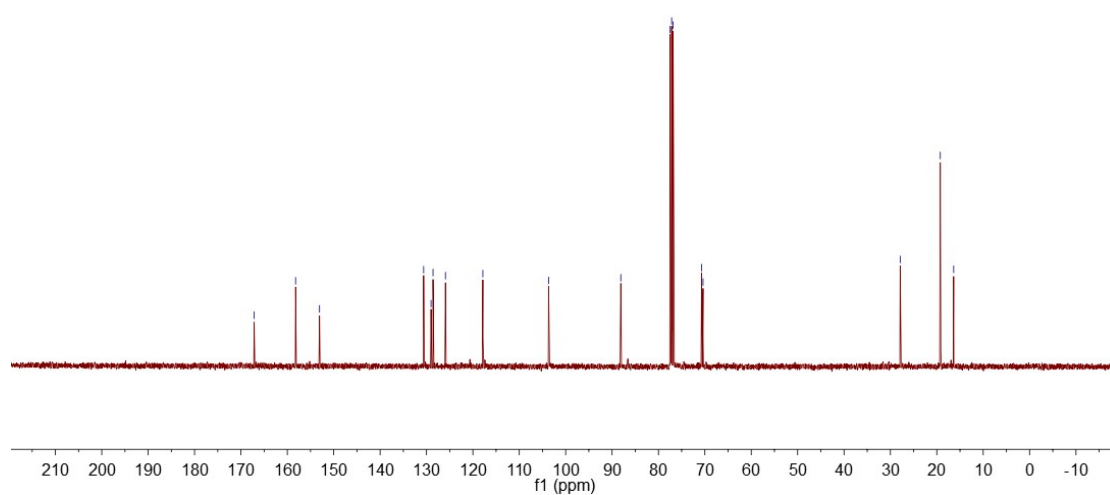
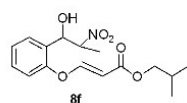
167.151
158.215
153.061

130.613
129.019
128.595
125.916
117.850

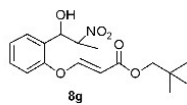
103.676

88.118
77.478
77.160
76.842
70.704
70.388

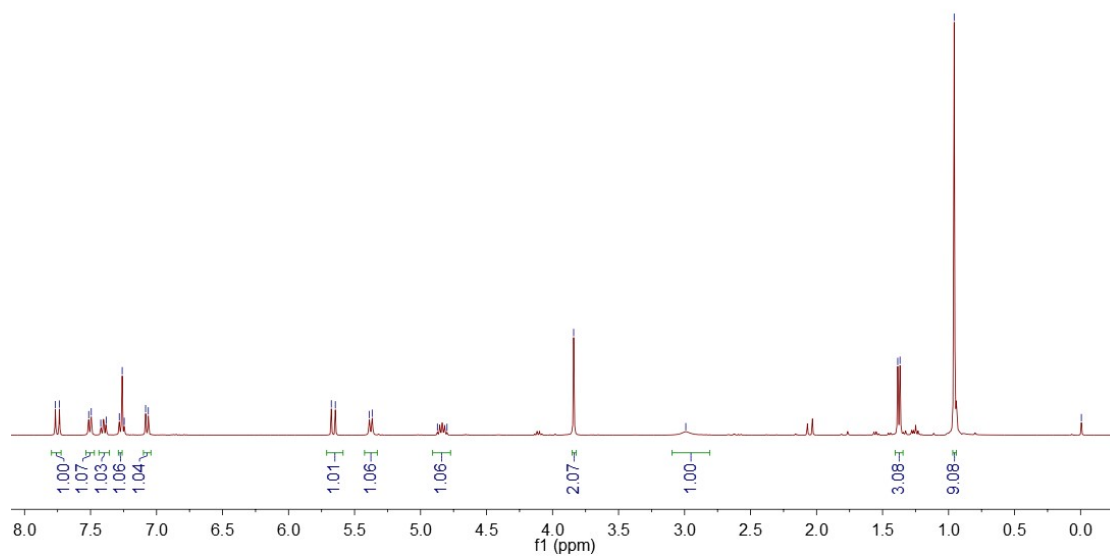
27.889
19.243
16.351



CHQ-2020-12-31-1
 7.766
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 7.514
 7.495
 7.423
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 7.282
 7.260
 7.245
 7.083
 7.062

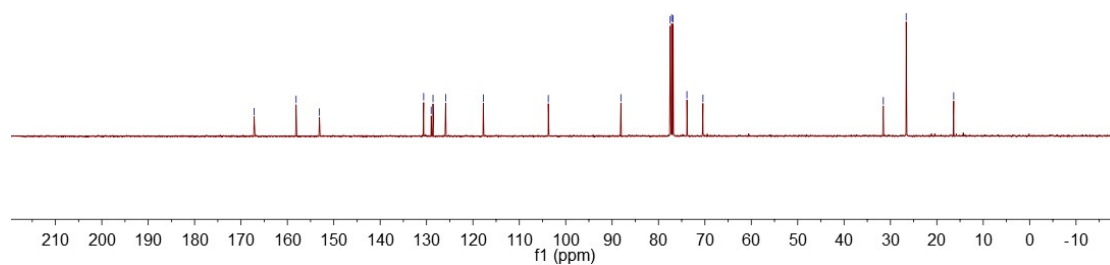
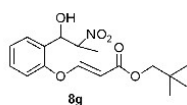


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 5.646
 5.388
 5.366
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 4.799
 3.840
 2.991
 1.385
 1.368
 0.958
 -0.006



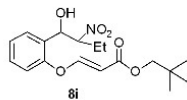
CHQ-2020-12-31-1

167.173
 158.116
 153.097
 130.624
 129.001
 128.609
 125.893
 117.764
 103.754
 88.109
 77.478
 77.160
 76.842
 73.875
 70.417
 31.537
 26.612
 16.365



CHQ-2020-9-23-1

7.771
7.741
7.503
7.484
7.419
7.401
7.382
7.281
7.260
7.244
7.080
7.059



5.675
5.644
5.383
5.362

4.712
4.702
4.684
4.664
4.655

3.844

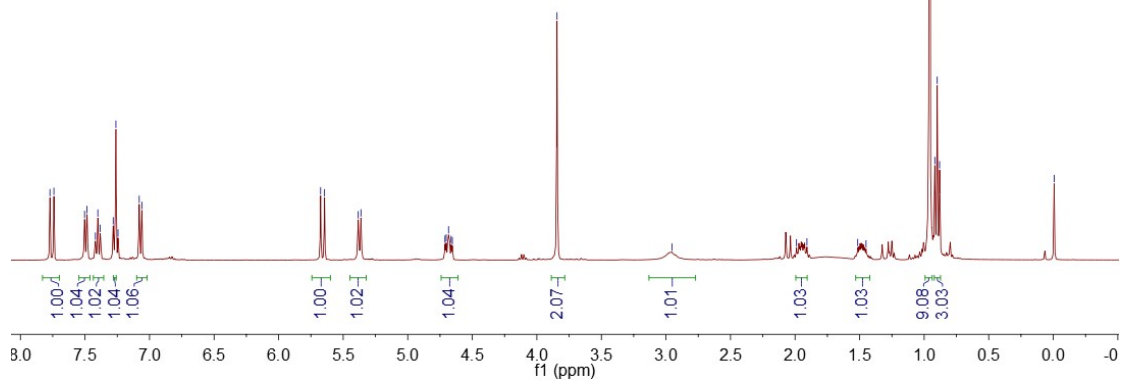
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1.989
1.908

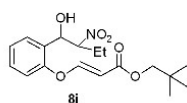
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1.450

0.959
0.917
0.899
0.881

-0.007



CHQ-2020-9-23-1



167.181

158.114

153.028

130.605

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125.918

117.753

103.734

94.812

77.477

77.160

76.842

73.880

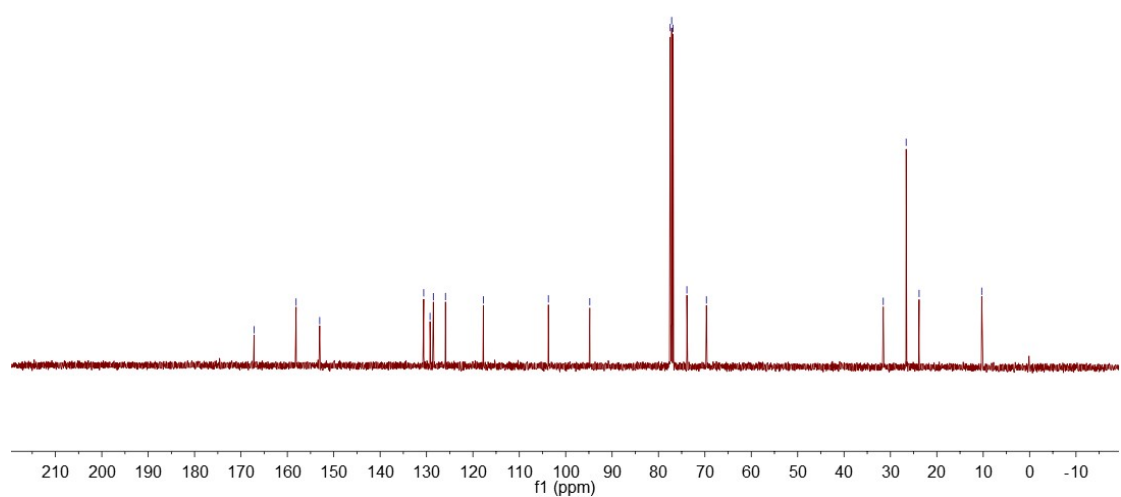
69.671

31.543

26.612

23.817

10.323



CHQ-2020-9-21-5

7.760
7.730
7.396
7.260
7.174
7.153
6.942
6.922

5.619
5.589

4.785
4.745

3.835

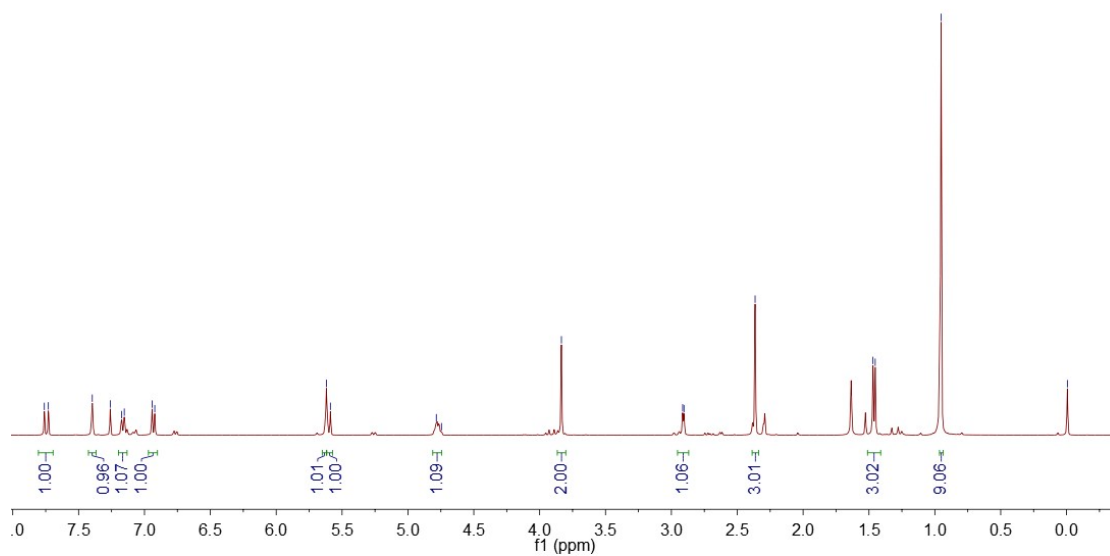
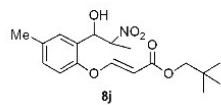
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2.904

2.364

1.470
1.453

0.953

0.006



CHQ-2020-9-21-5

167.229

158.376

149.932

135.451

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128.367

117.354

103.141

85.205

77.477

77.160

76.842

73.789

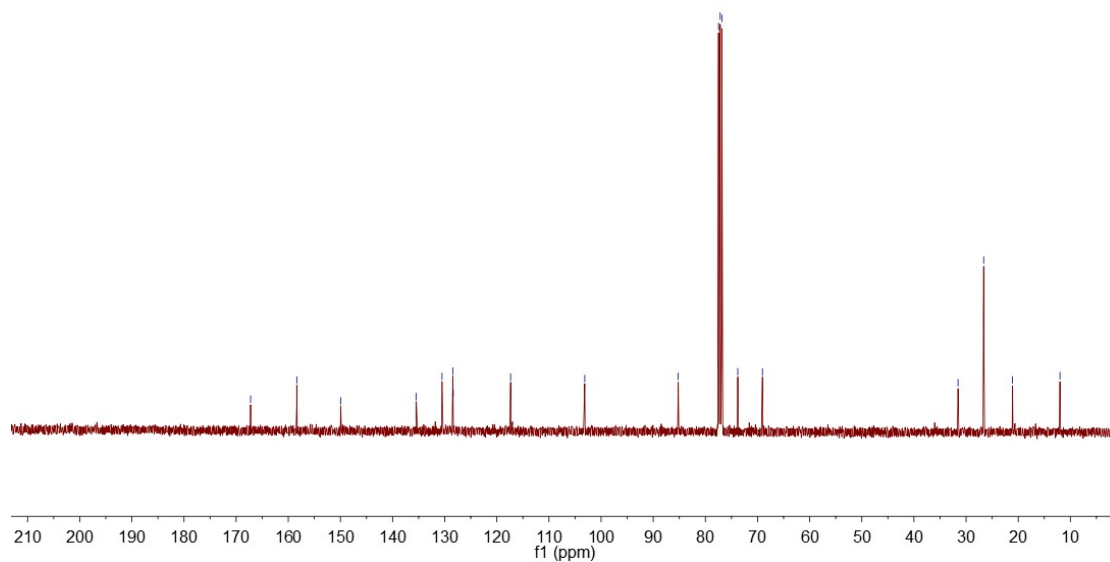
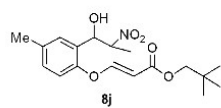
69.057

31.541

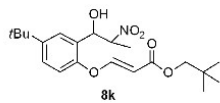
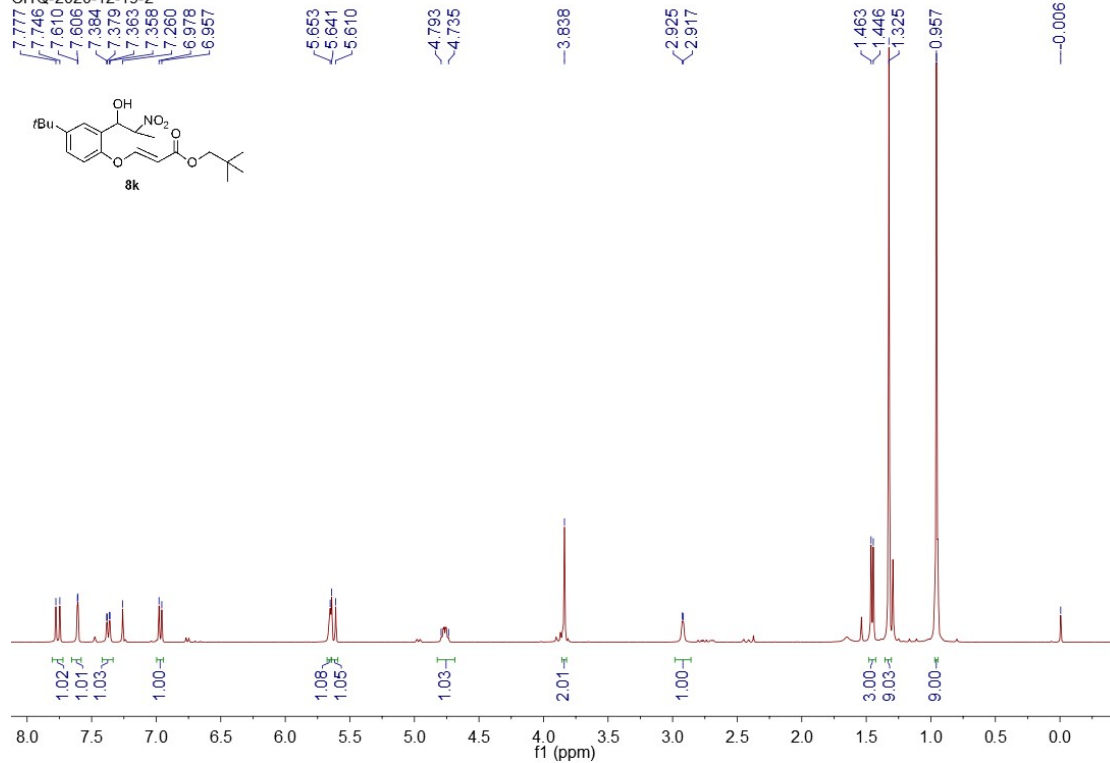
26.624

21.093

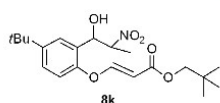
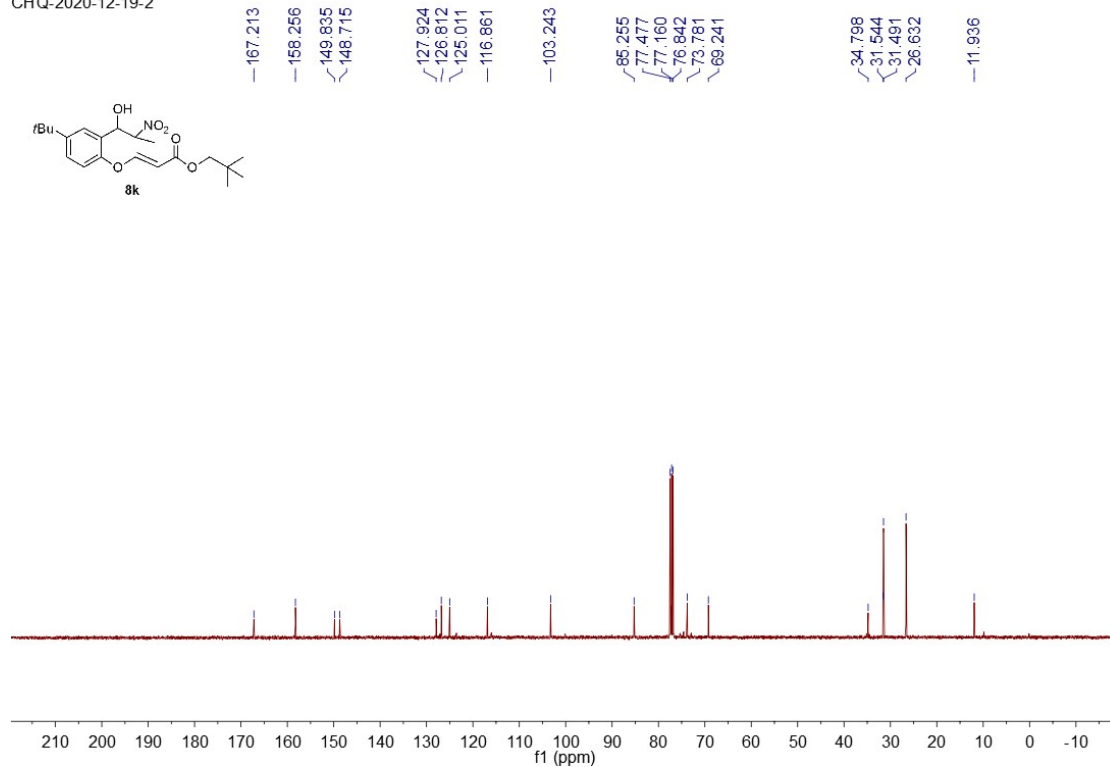
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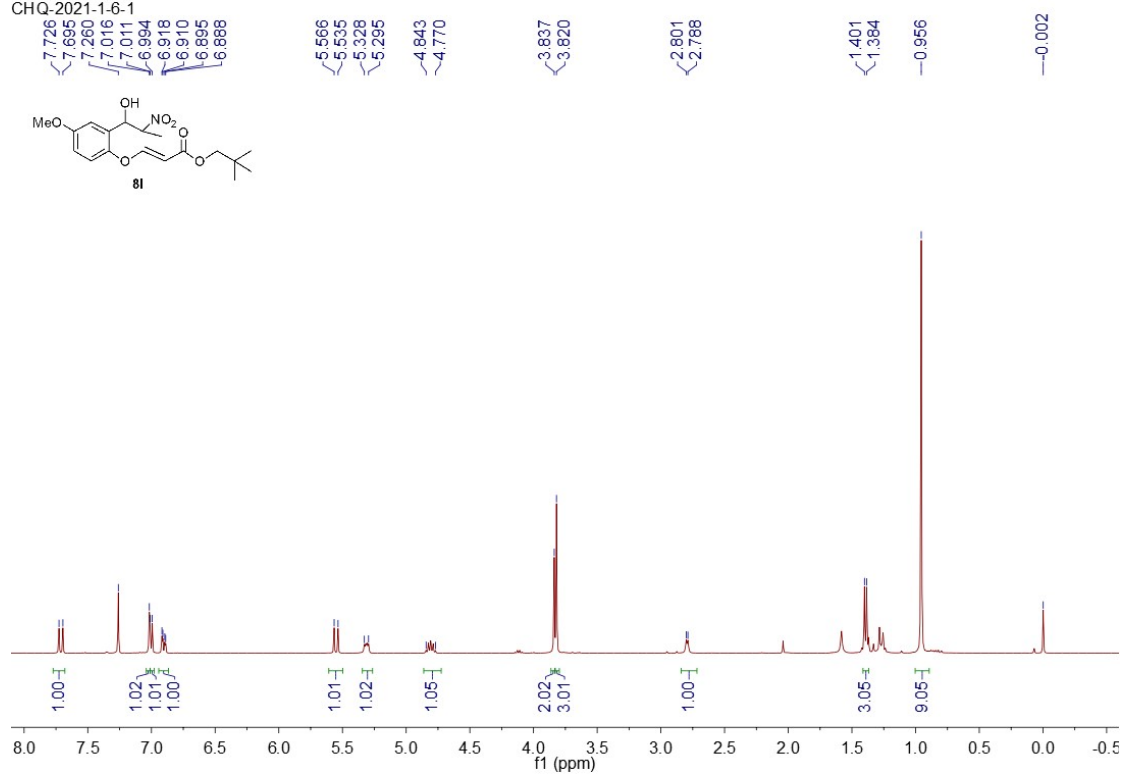
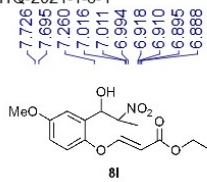
CHQ-2020-12-19-2



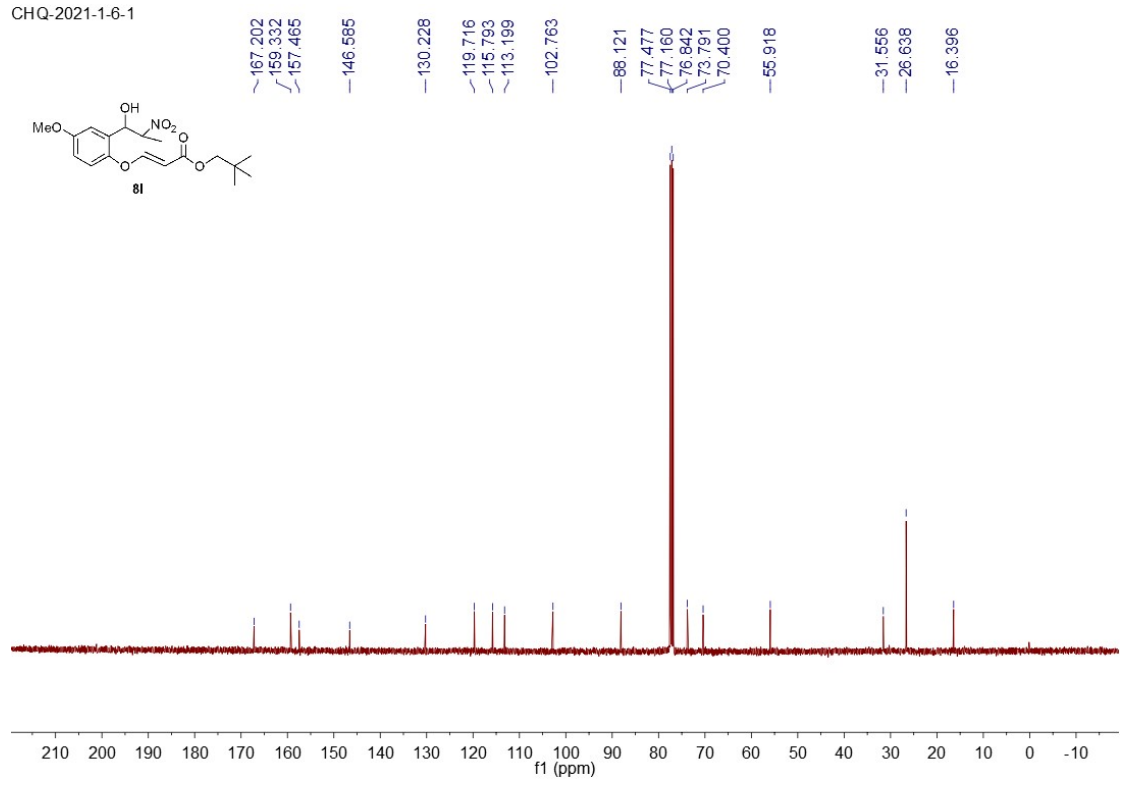
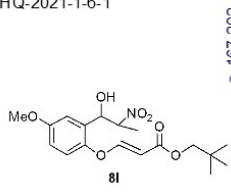
CHQ-2020-12-19-2



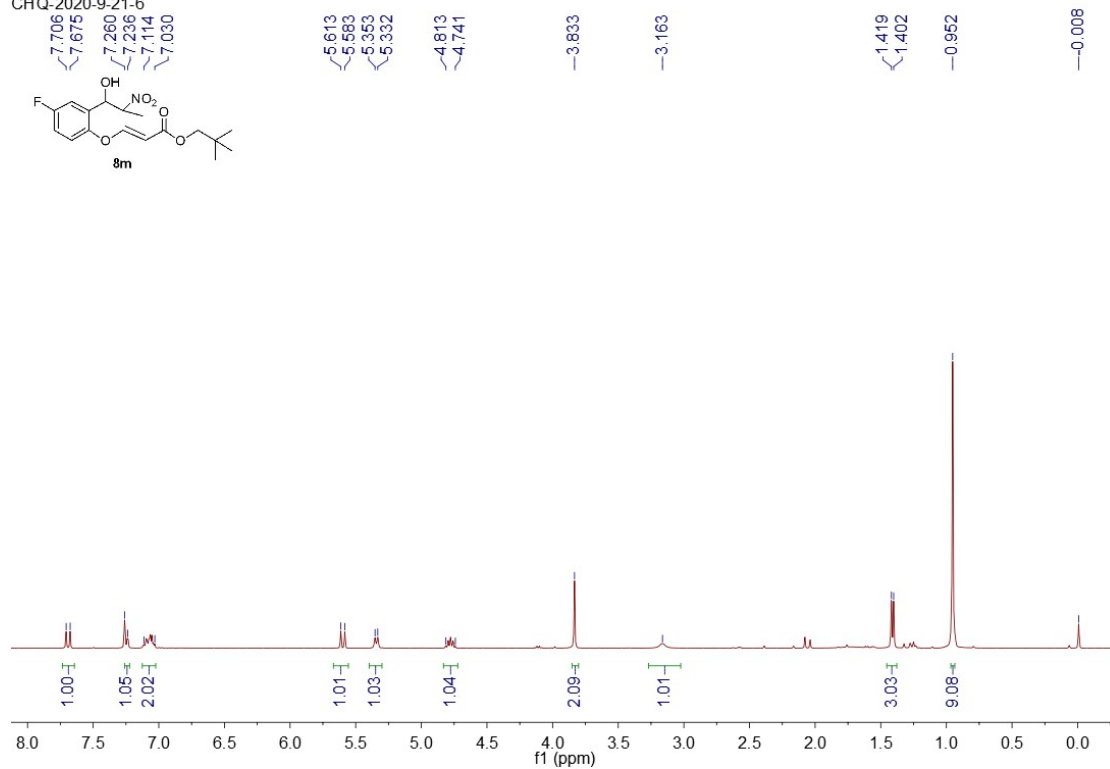
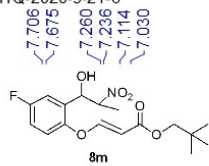
CHQ-2021-1-6-1



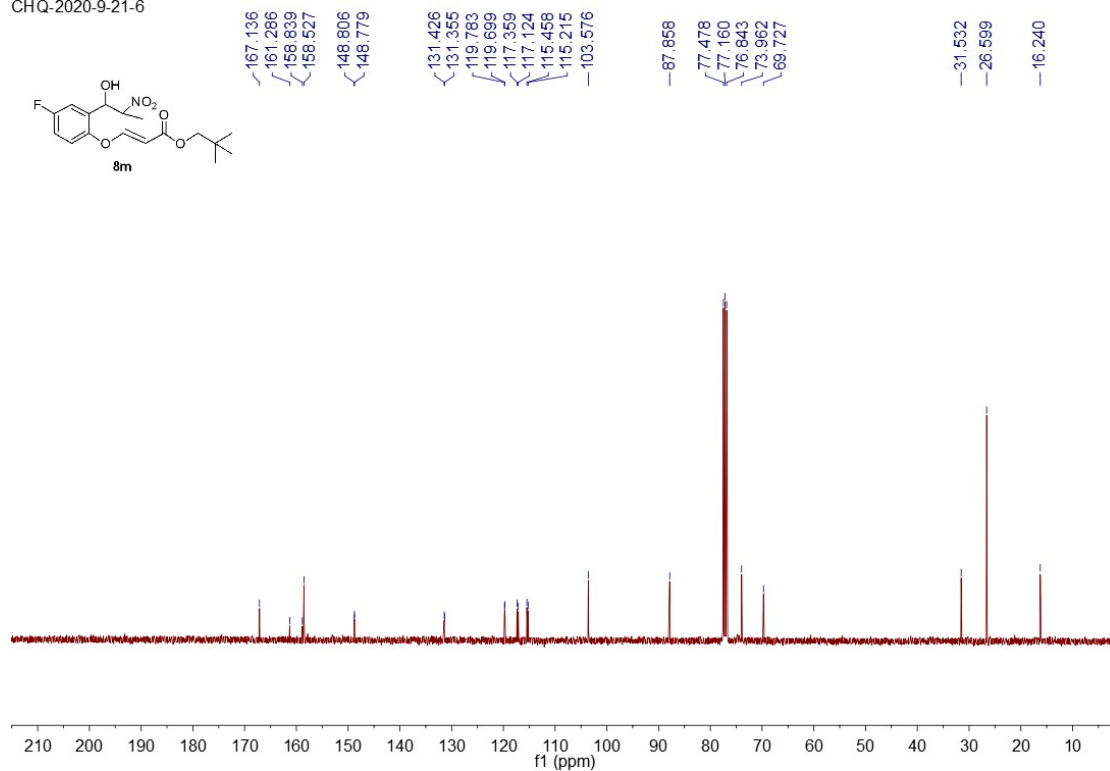
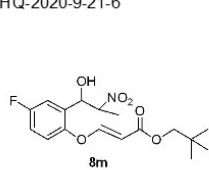
CHQ-2021-1-6-1



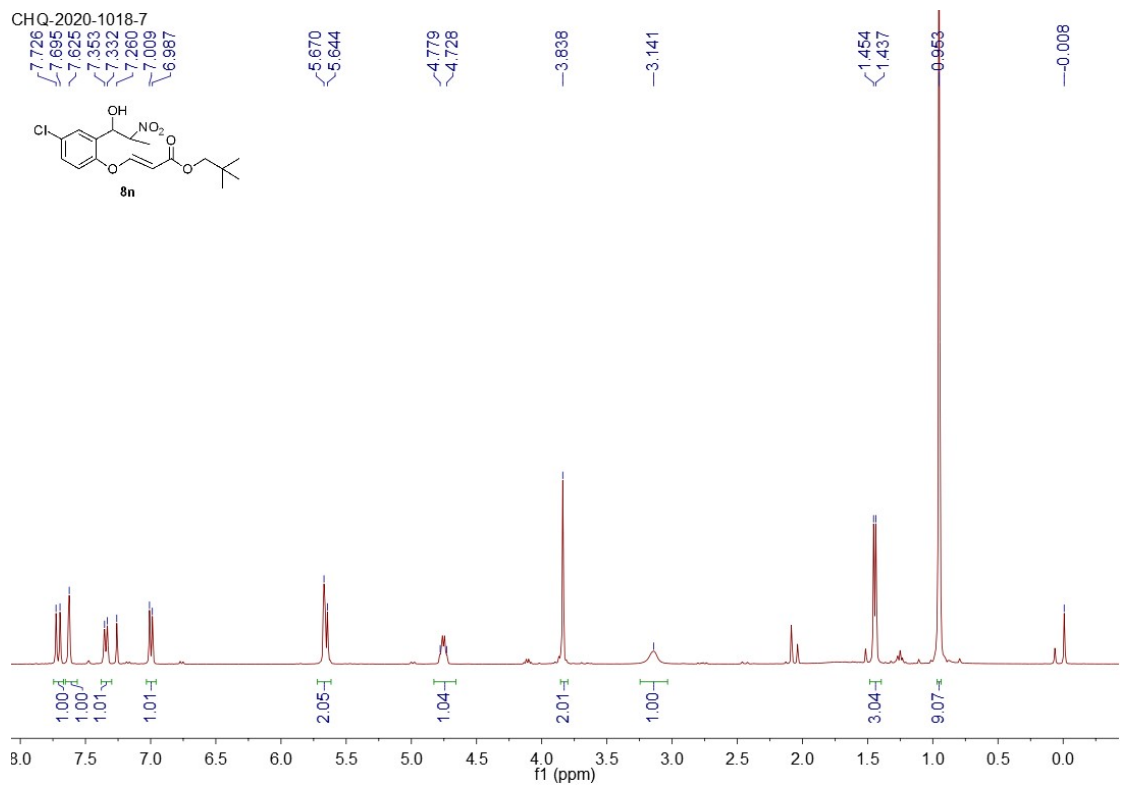
CHQ-2020-9-21-6



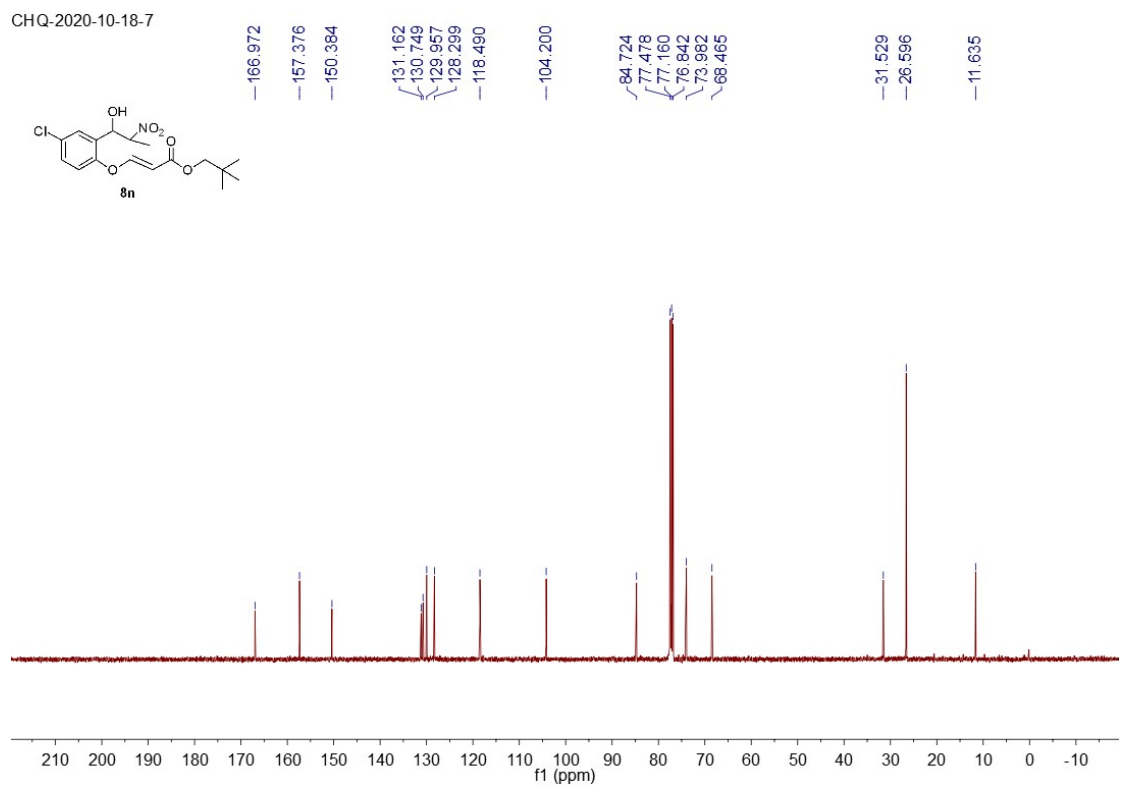
CHQ-2020-9-21-6



CHQ-2020-1018-7



CHQ-2020-10-18-7



CHQ-2020-1018-8

7.773
7.769
7.724
7.693
7.489
7.484
7.363
6.931

5.685
5.670
5.655

4.782
4.726

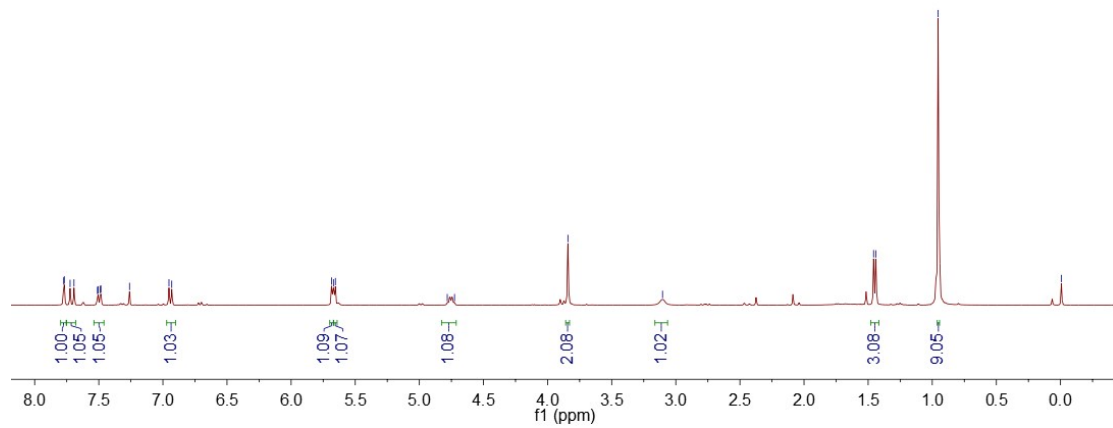
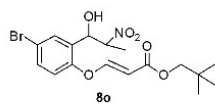
3.841

3.104

1.458
1.440

0.954

0.007



CHQ-2020-10-18-8

166.935

157.195

150.949

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131.212

130.989

118.772

118.635

104.333

84.730

77.477

77.160

76.842

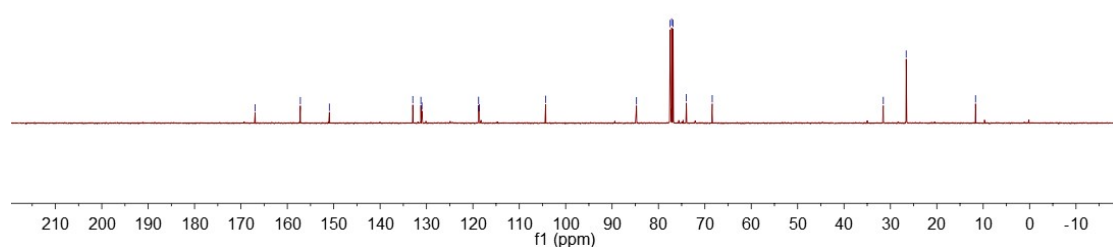
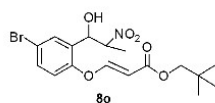
73.987

68.408

31.532

26.600

11.657



CHQ-2020-12-25-1

7.746
7.716
7.430
7.373
7.260
7.023
7.001
6.978
6.916

5.788
5.757
5.551
5.511
5.155
5.080

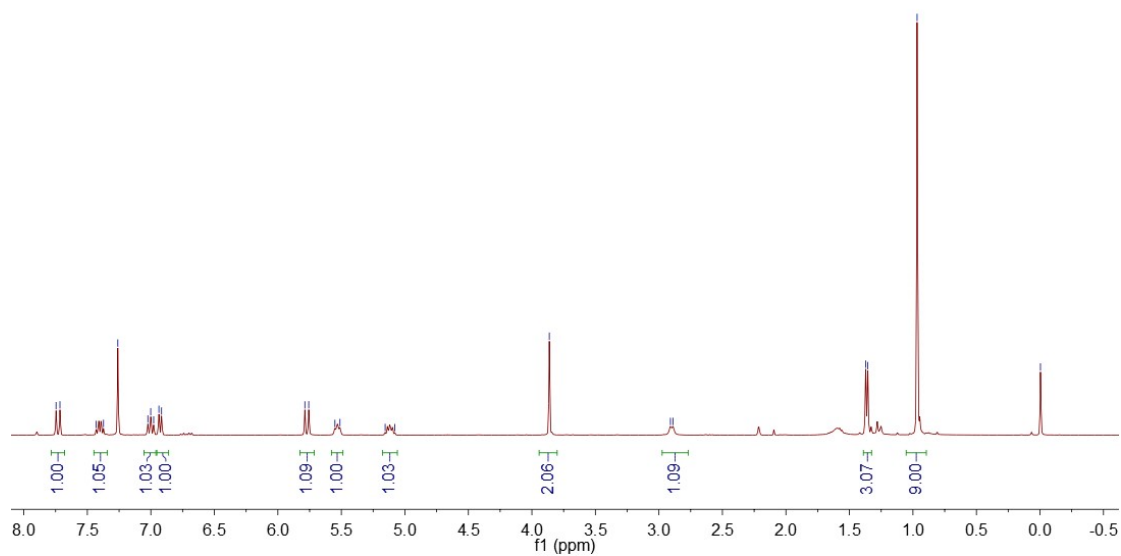
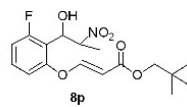
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2.909
2.889

1.372
1.355

-0.967

-0.004



CHQ-2020-12-25-1

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157.078
154.877
154.804

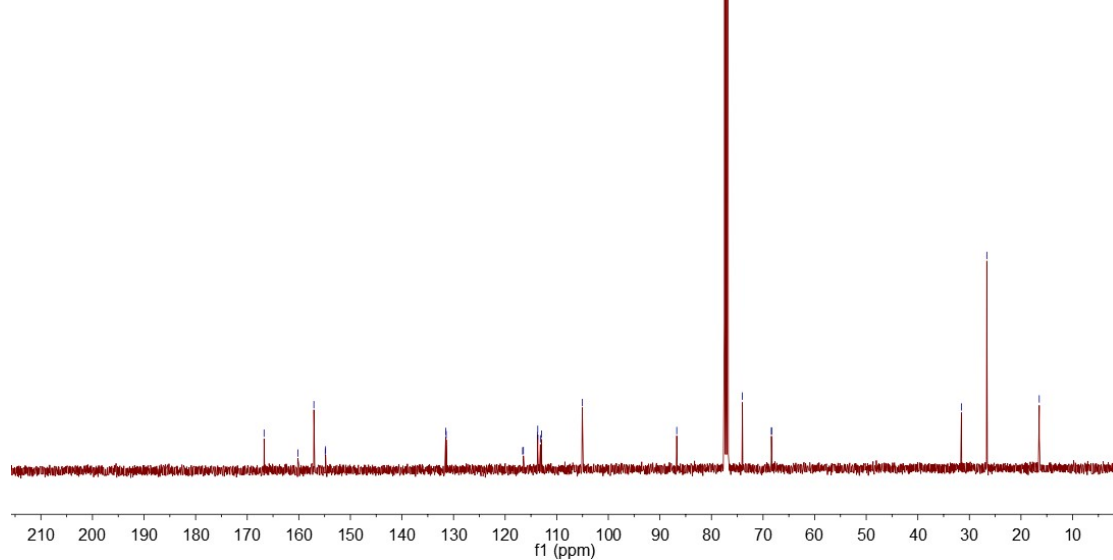
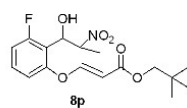
131.531
131.424

116.456
113.712
113.678
113.179
108.552

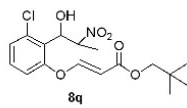
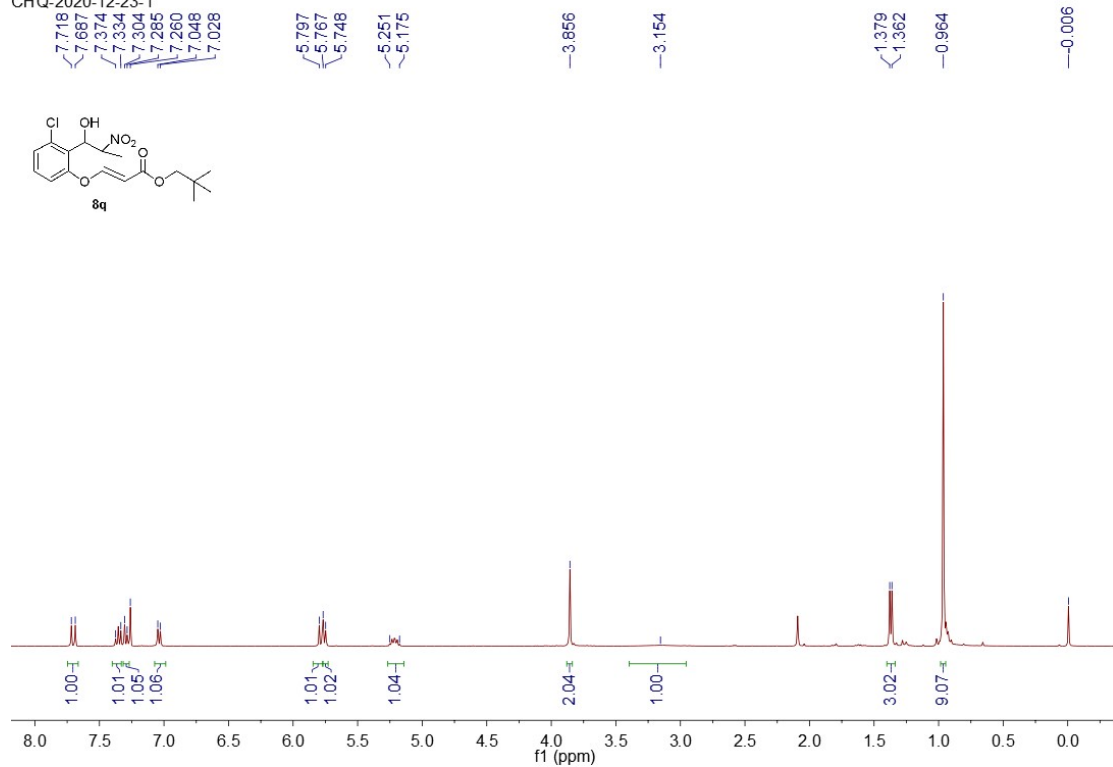
86.734
77.478
77.160
76.842
74.000
68.375
68.347

31.560
26.623

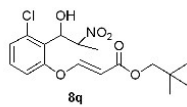
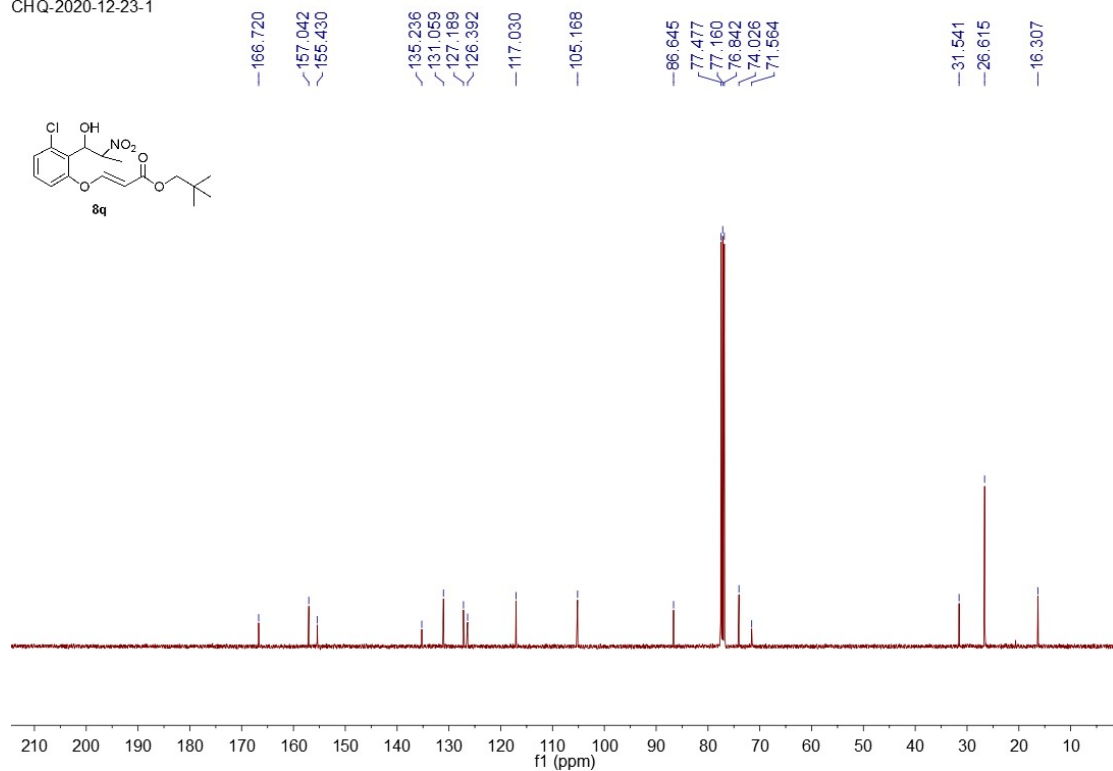
16.460



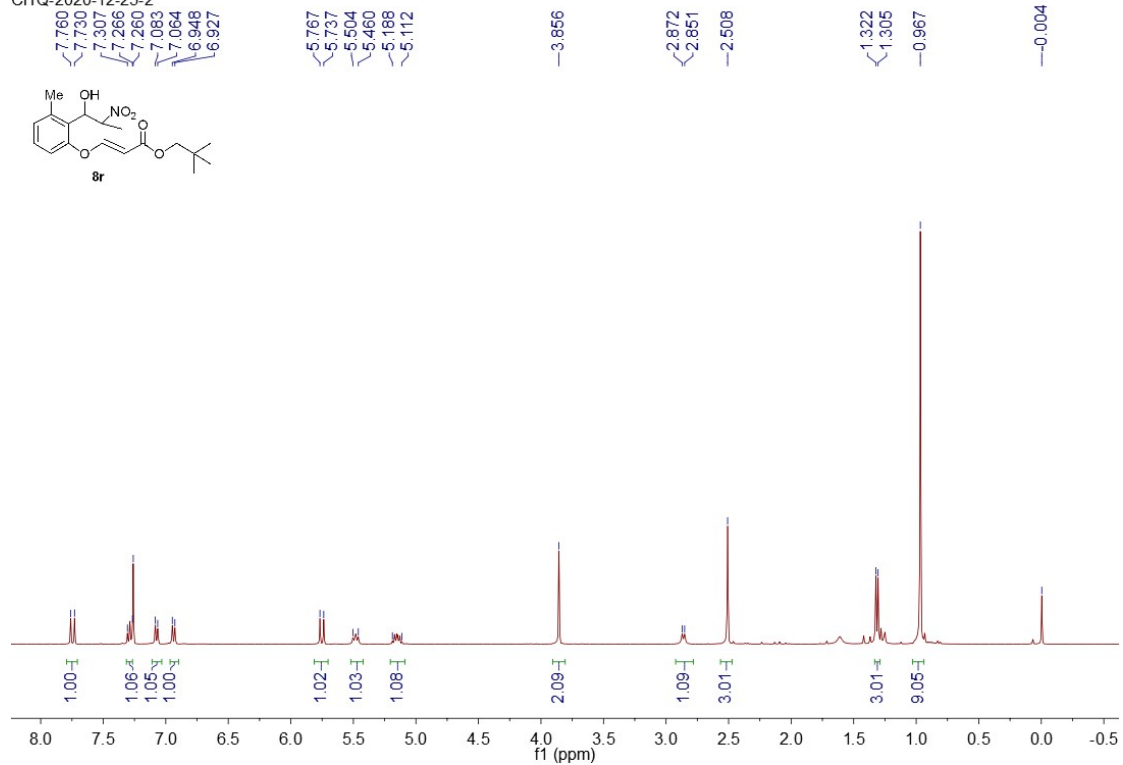
CHQ-2020-12-23-1



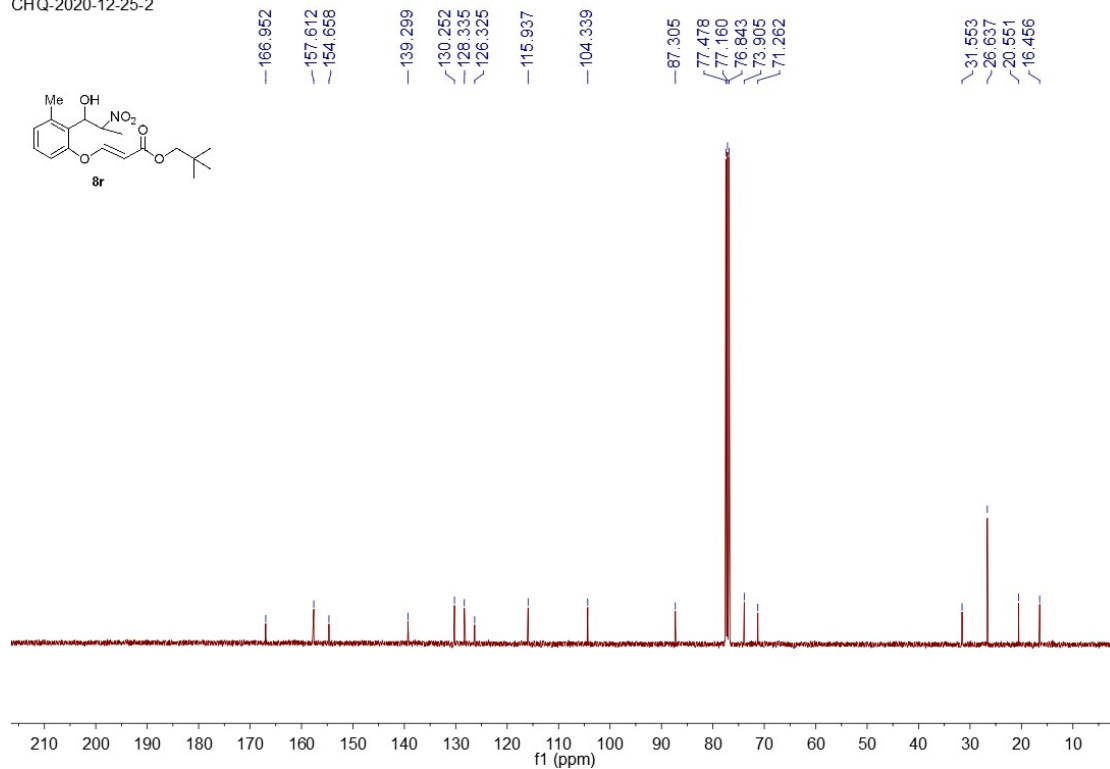
CHQ-2020-12-23-1



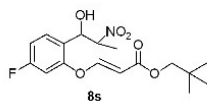
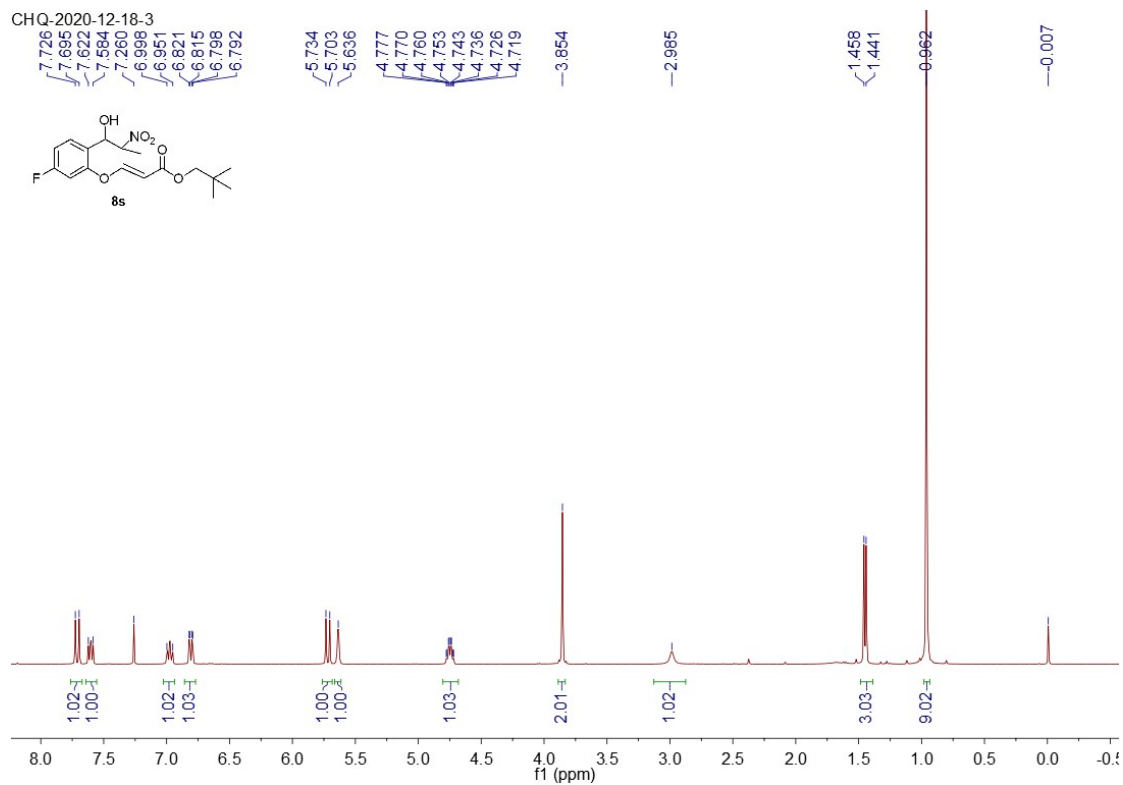
CHQ-2020-12-25-2



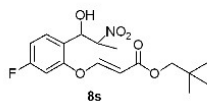
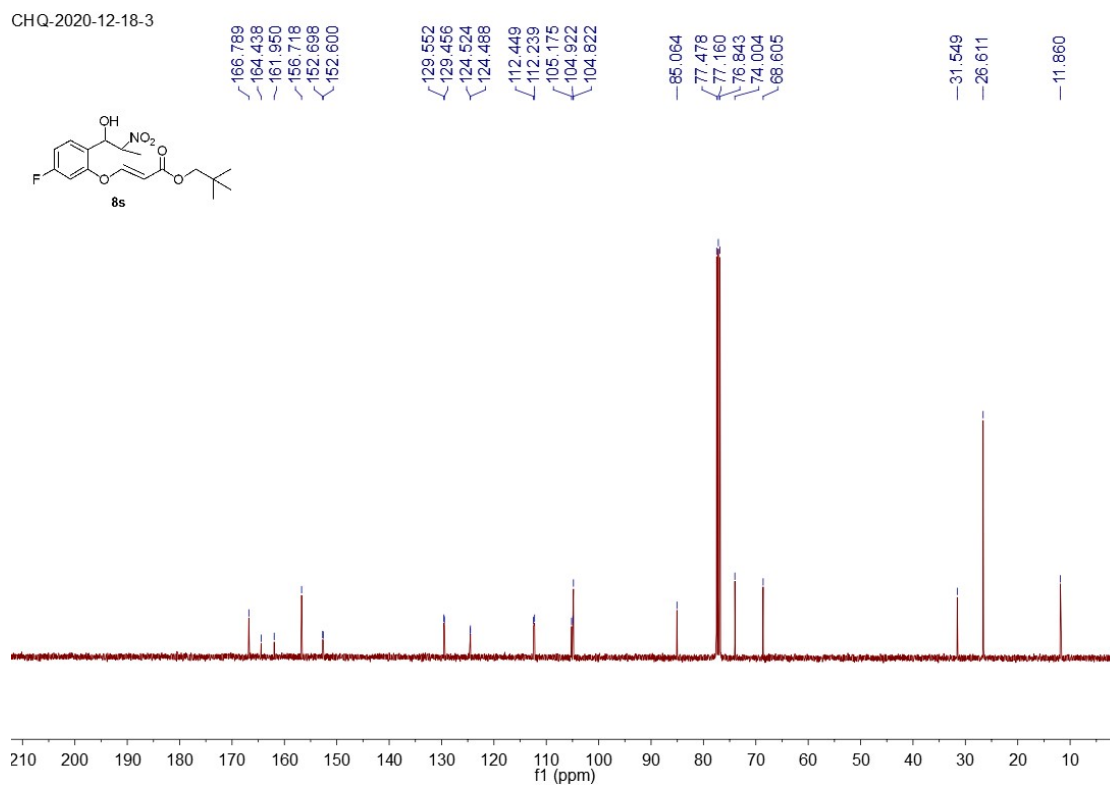
CHQ-2020-12-25-2



CHQ-2020-12-18-3



CHQ-2020-12-18-3



CHQ-2020-12-18-4

7.728
7.699
7.581
7.560
7.260
7.236
7.071
7.067

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4.757
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4.740
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4.723
4.717

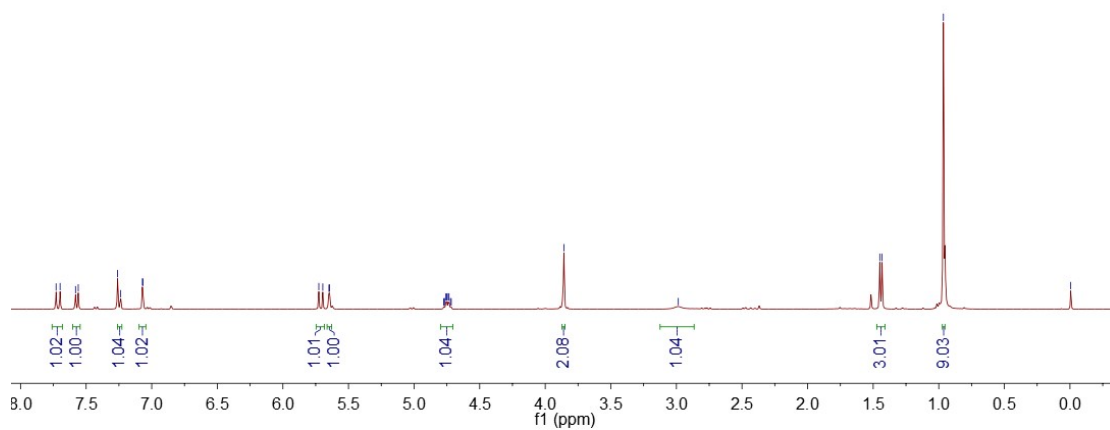
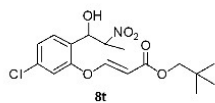
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-2.986

1.450
1.432

-0.965

-0.006



CHQ-2020-12-18-4

-166.835

-156.829

-152.302

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129.226

127.301

125.708

-117.544

-104.806

84.875

77.478

77.160

76.843

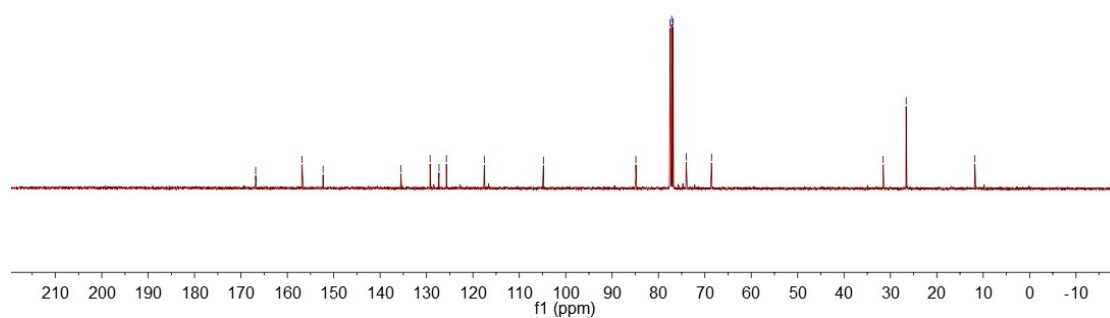
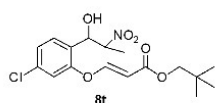
74.026

68.558

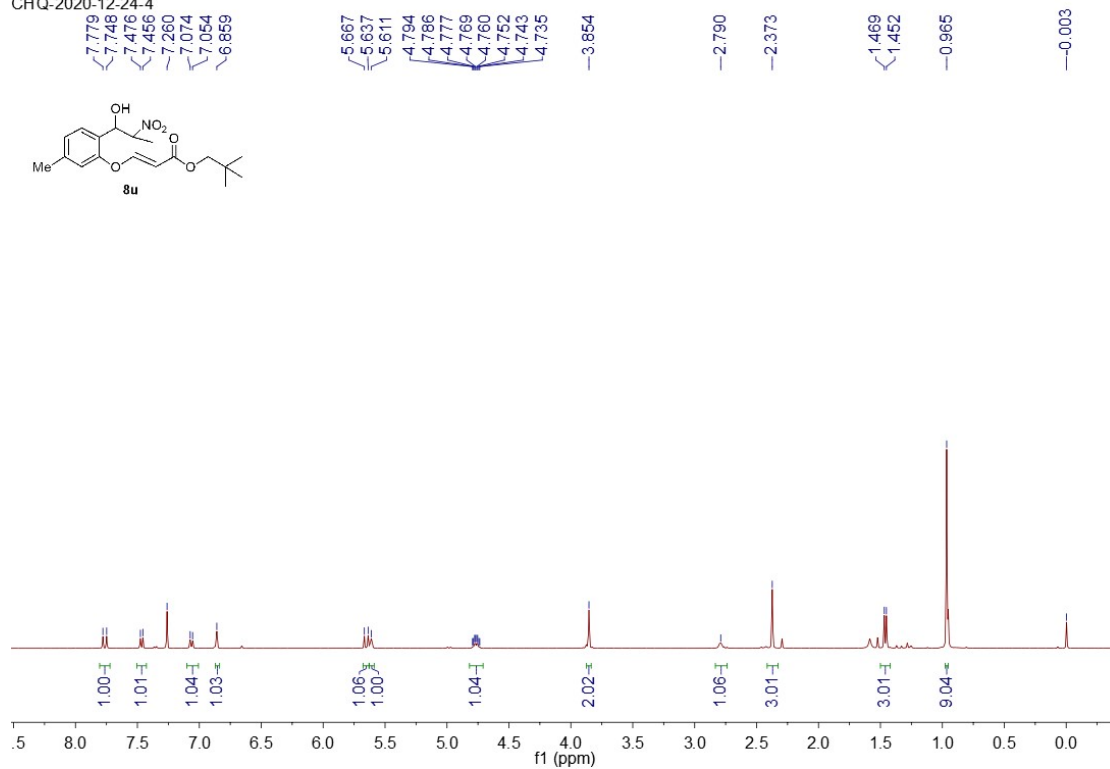
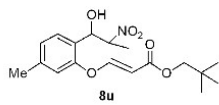
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-26.614

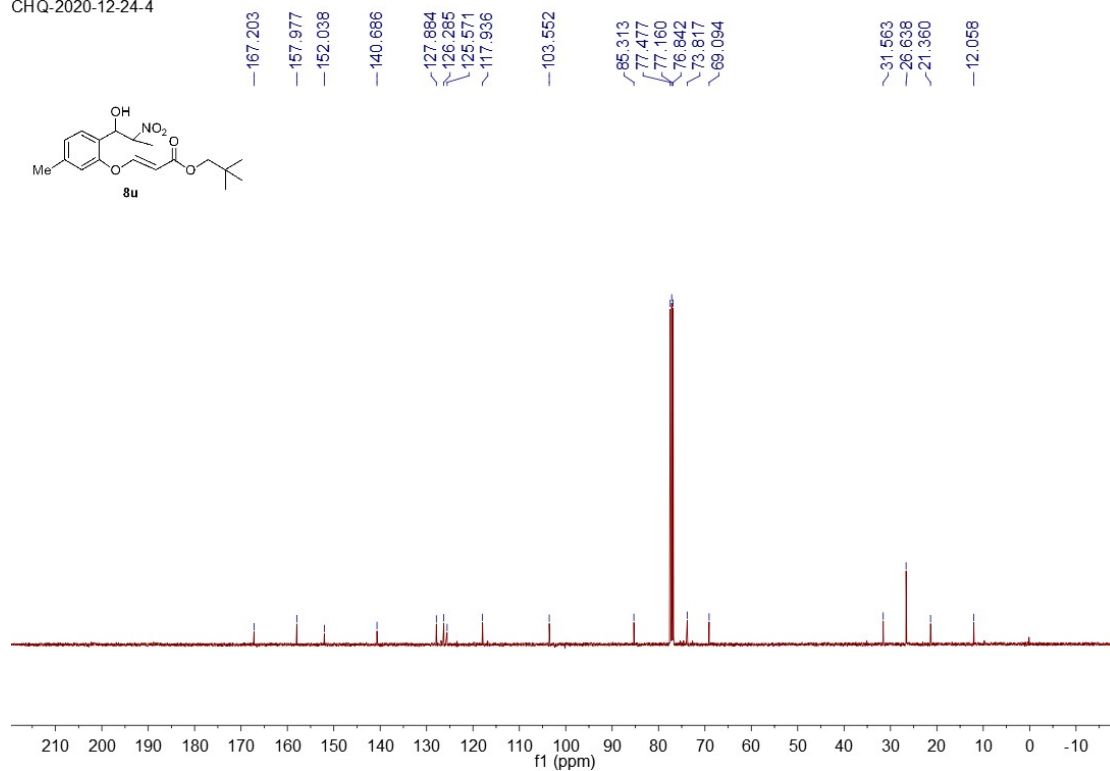
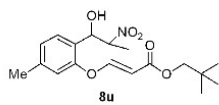
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CHQ-2020-12-24-4

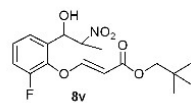


CHQ-2020-12-24-4



CHQ-2020-12-18-4

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7.728
7.701
7.697
7.432
7.412
7.306
7.273
7.260
7.208
7.164



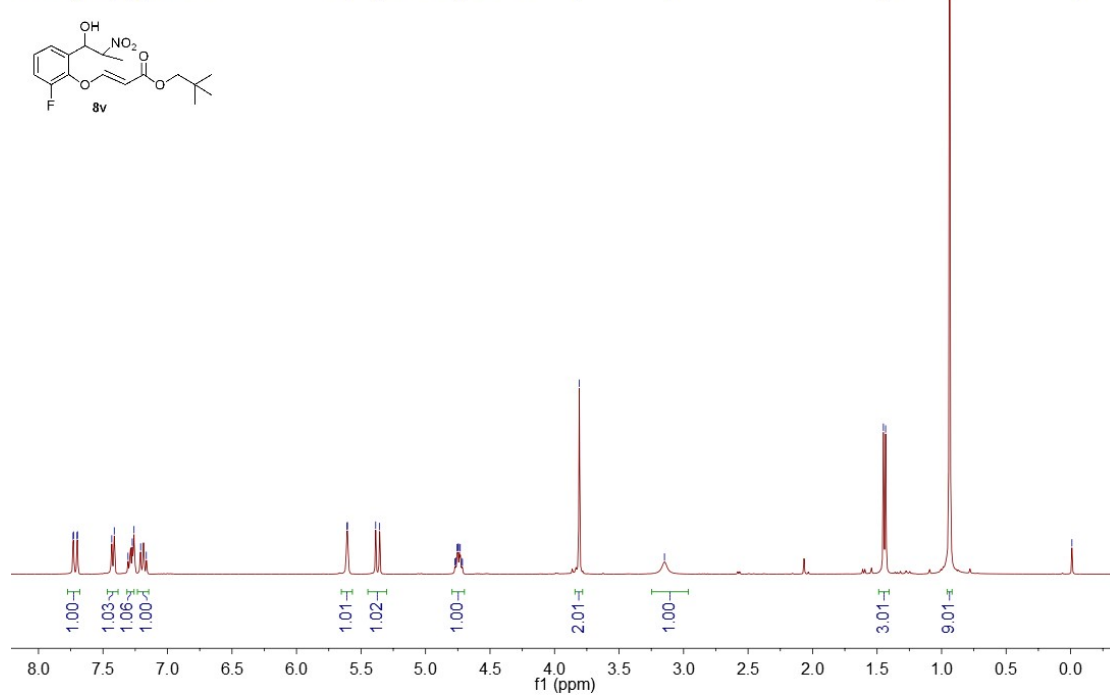
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5.605
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5.356
4.772
4.765
4.755
4.748
4.738
4.731
4.721
4.714

3.808
3.148

1.451
1.434

0.998

0.010

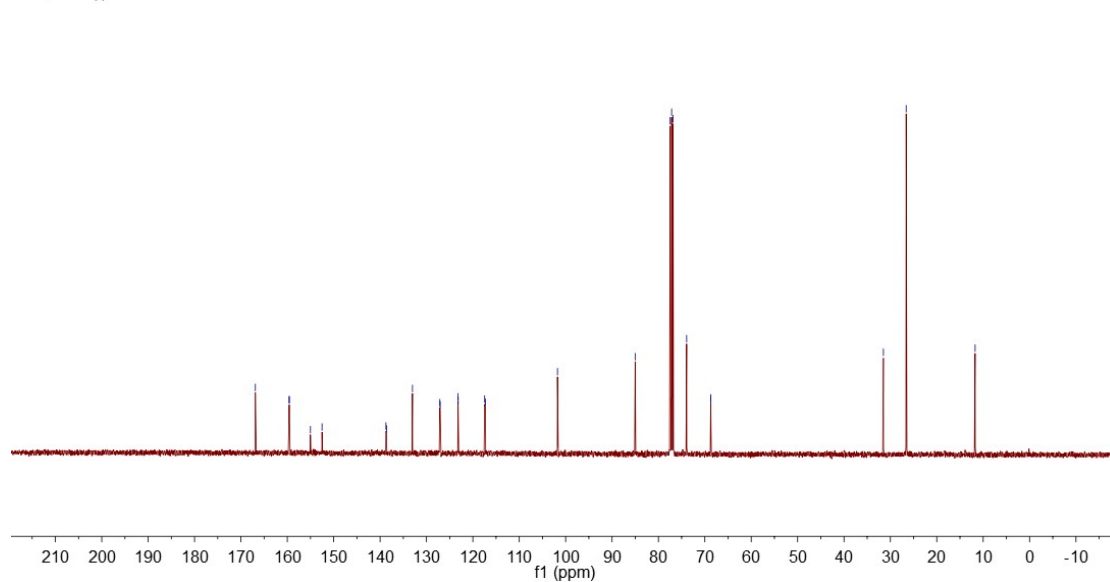
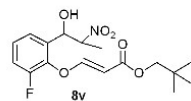


CHQ-2020-12-18-4

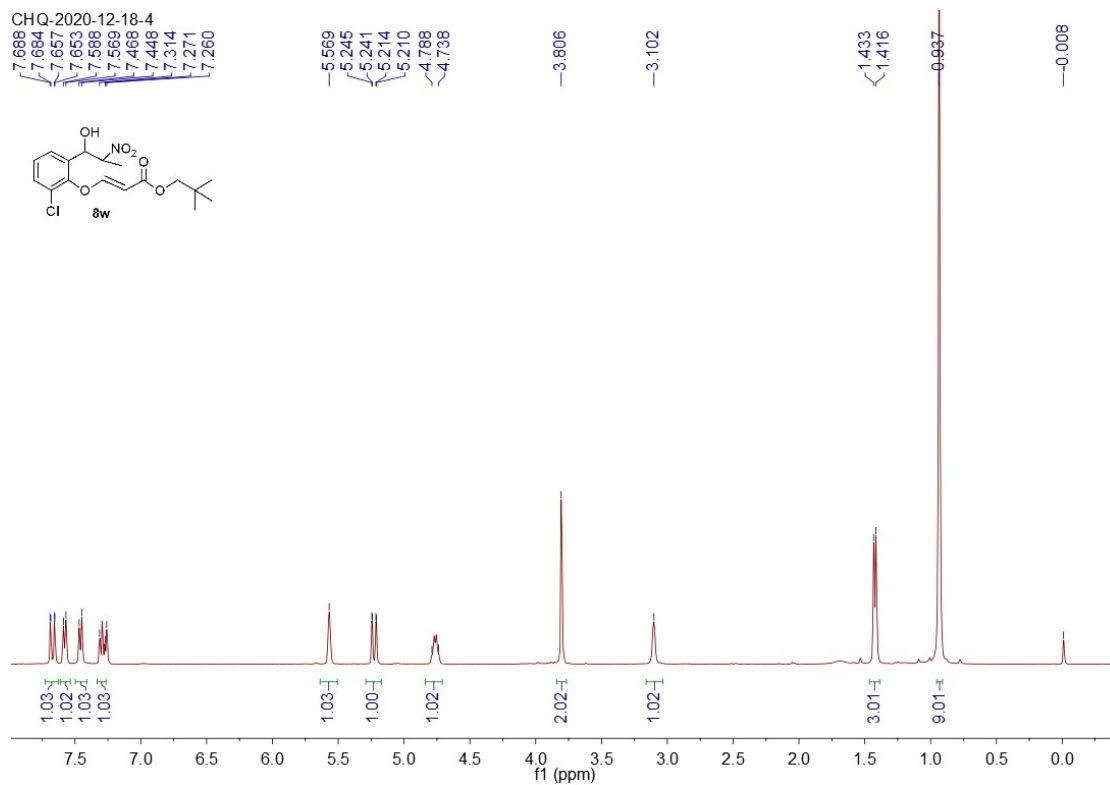
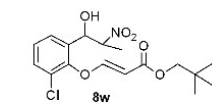
166.883
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159.574
155.014
152.515
138.740
138.615
133.018
127.123
127.049
123.194
123.159
117.464
117.283
101.765

85.016
77.478
77.160
76.843
73.920
68.739
68.710

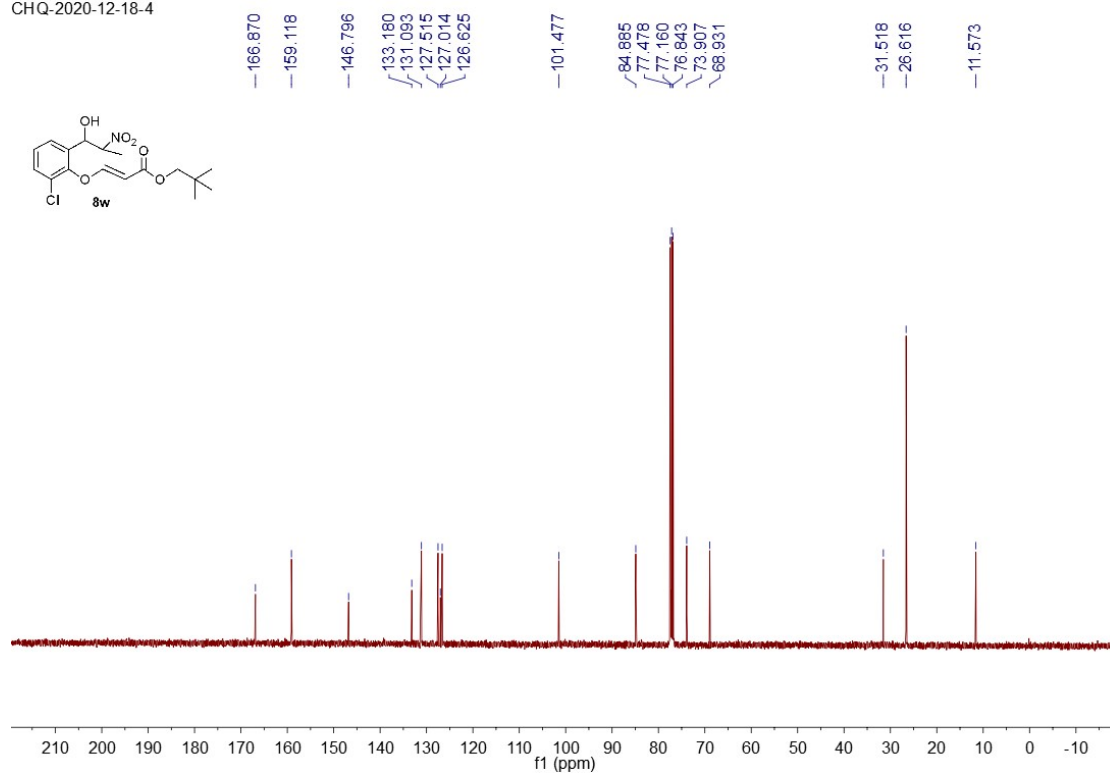
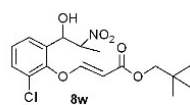
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26.599
11.735



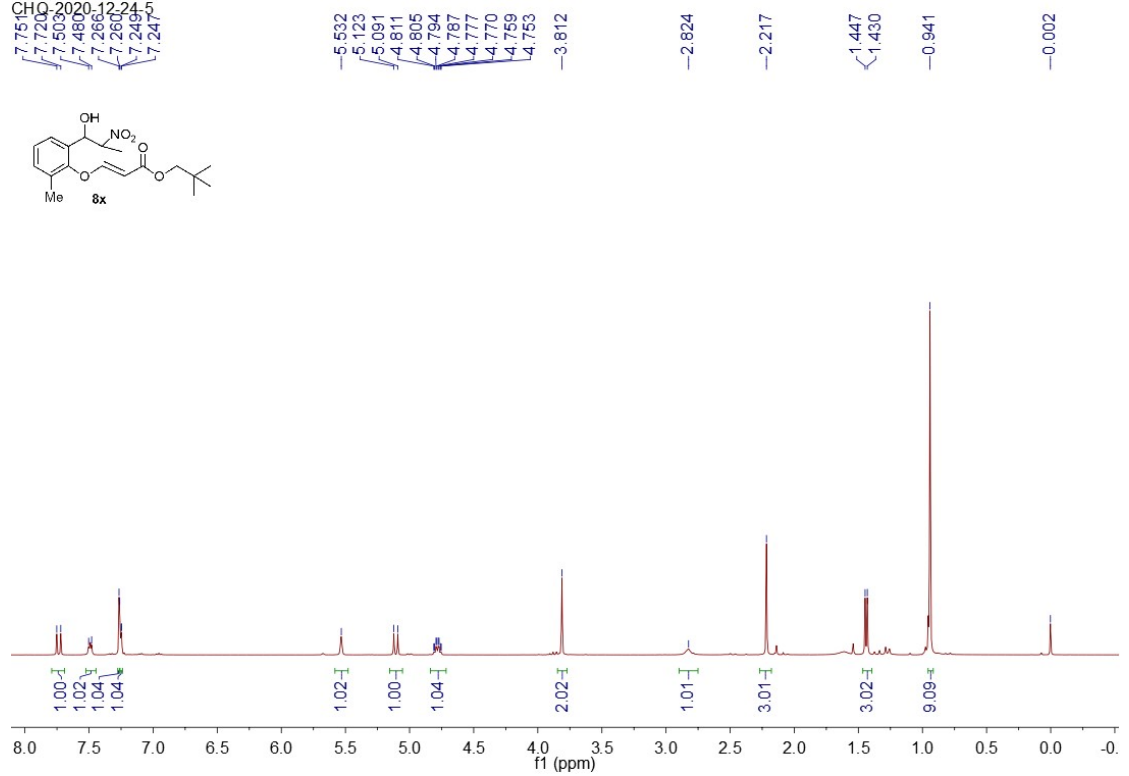
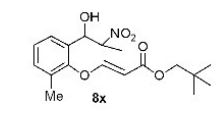
CHQ-2020-12-18-4



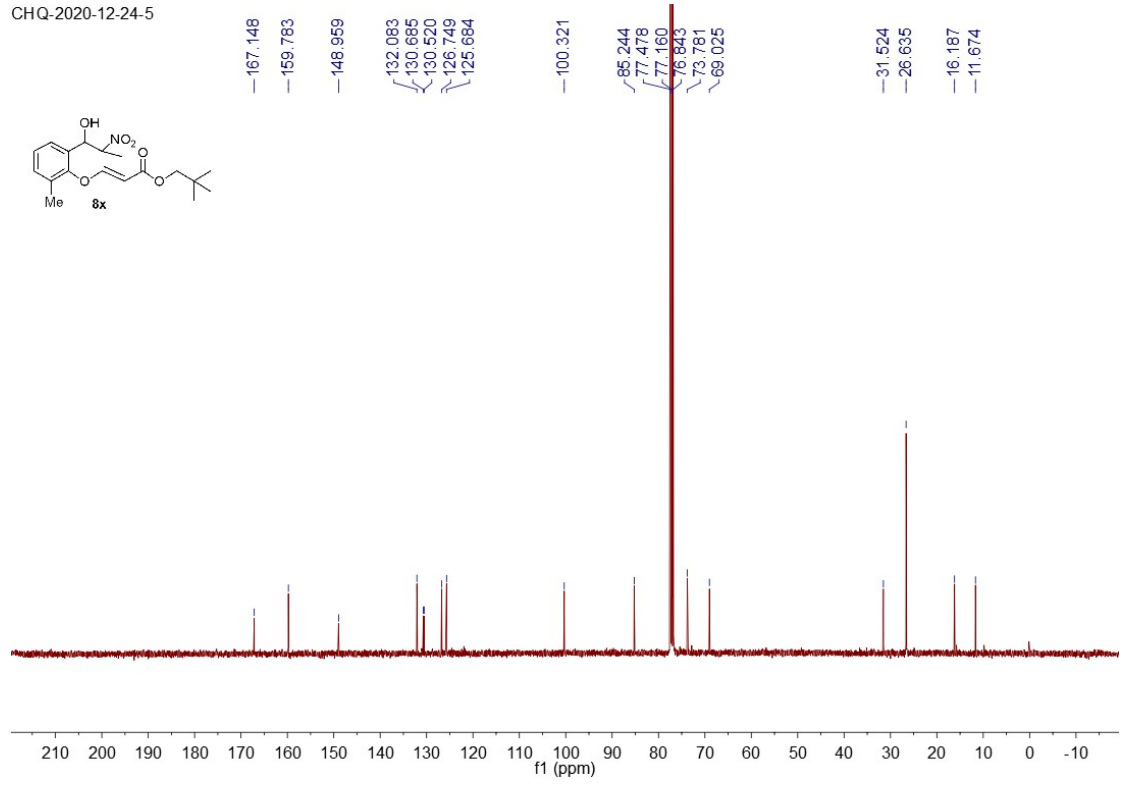
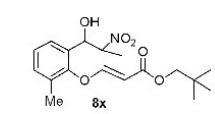
CHQ-2020-12-18-4



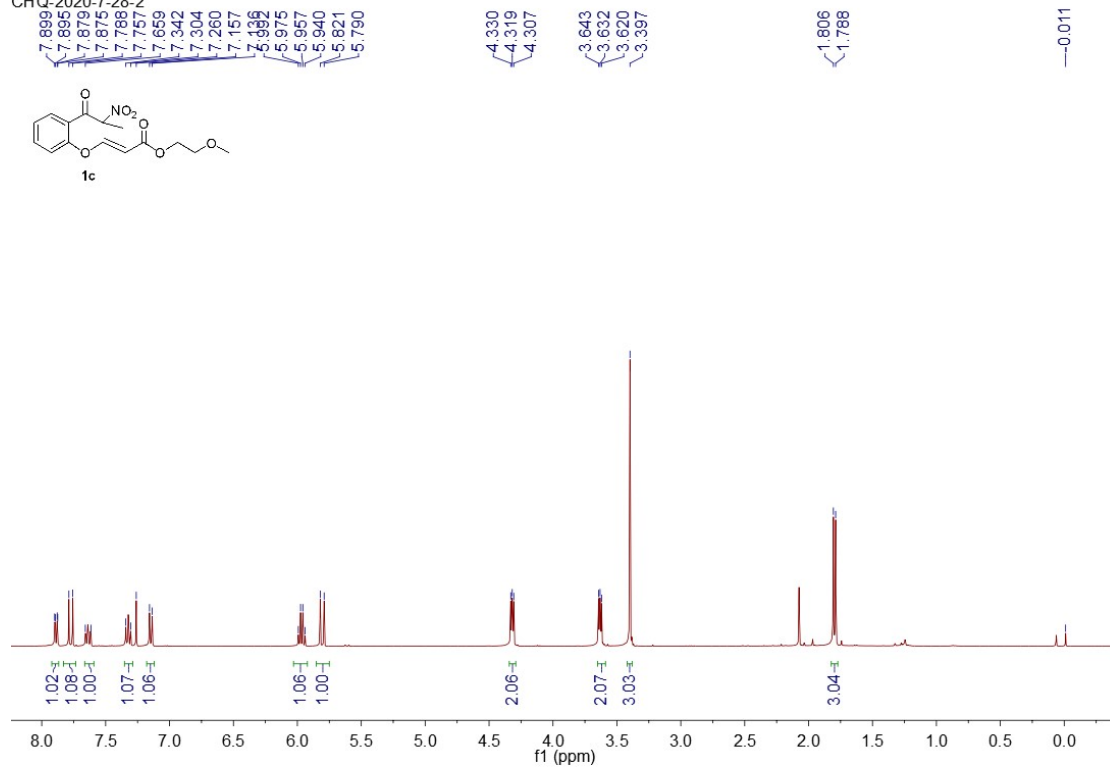
CHQ-2020-12-24-5



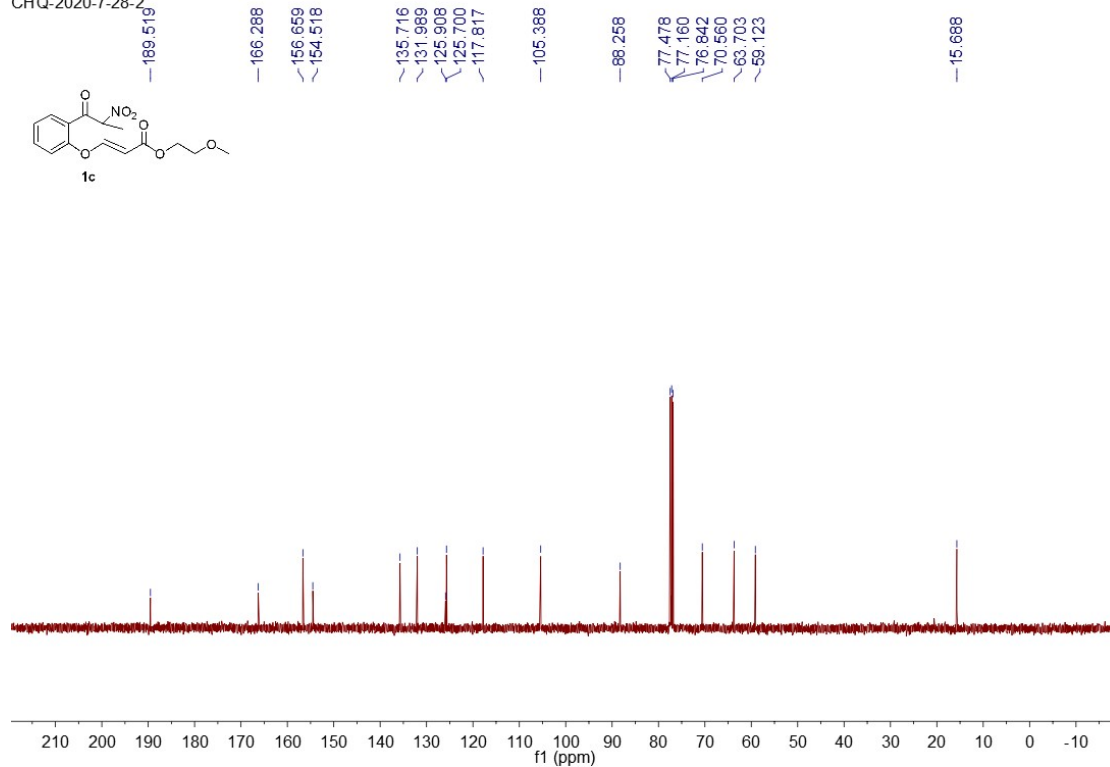
CHQ-2020-12-24-5



CHQ-2020-7-28-2



CHQ-2020-7-28-2



CHQ-2020-7-25-1

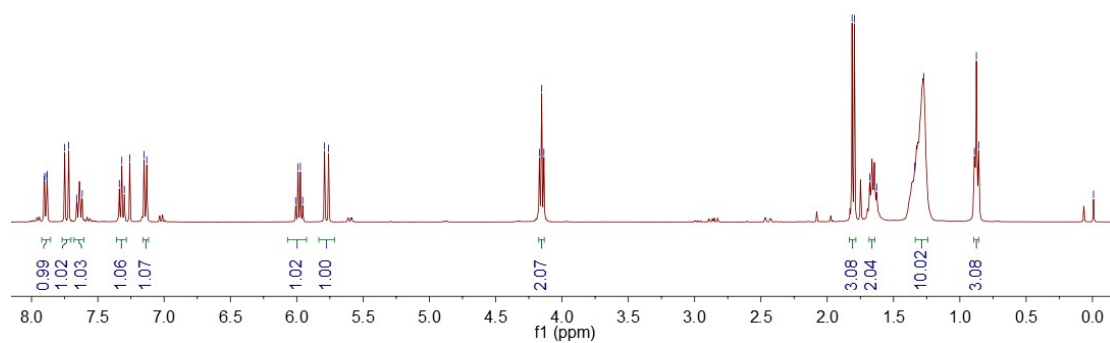
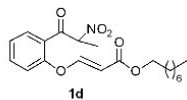
7.905
7.901
7.885
7.882
7.780
7.720
7.338
7.319
7.300
7.260
7.152
6.008
5.990
5.973
5.955
5.791
5.760

4.170
4.153
4.137

1.813
1.795
1.680
1.627
1.341
1.272

0.890
0.875
0.858

-0.008



CHQ-2020-7-25-1

189.534
166.383
156.077
154.649

135.726
132.021
125.831
125.593
117.627

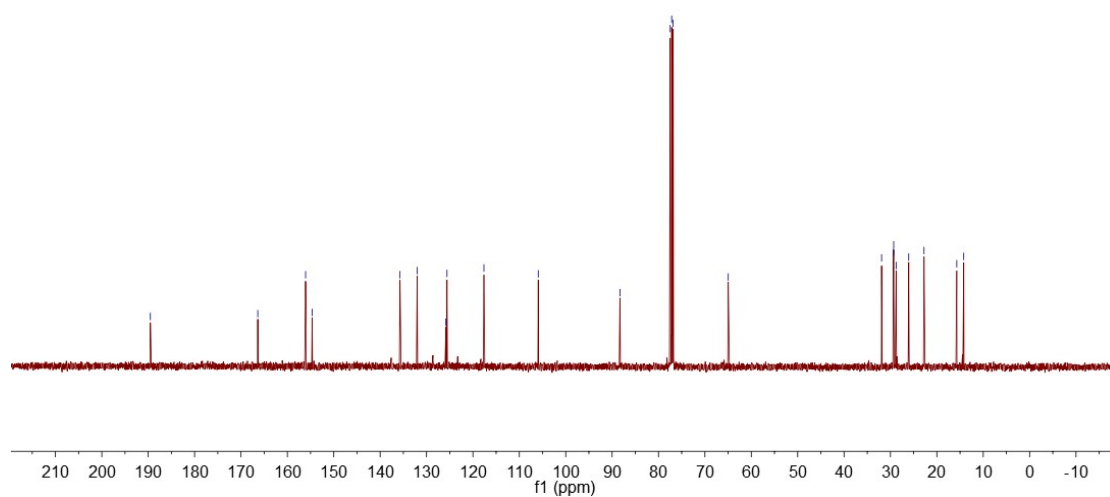
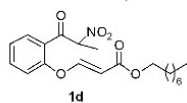
105.918

88.308

77.478
77.160
76.842

64.964

31.907
29.345
29.298
28.774
26.061
22.761
15.702
14.208



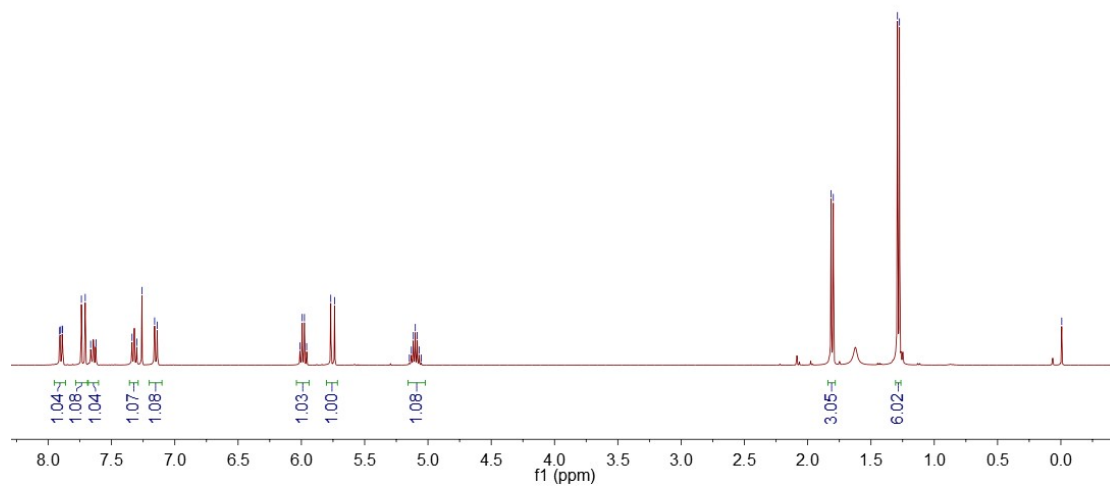
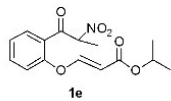
CHQ-2020-7-17-3

7.910
7.906
7.890
7.886
7.738
7.708
7.665
7.621
7.338
7.300
7.260
7.159
7.139
6.011
5.994
5.976
5.958
5.768
5.738
5.147
5.131
5.116
5.100
5.084
5.069
5.053

1.815
1.798

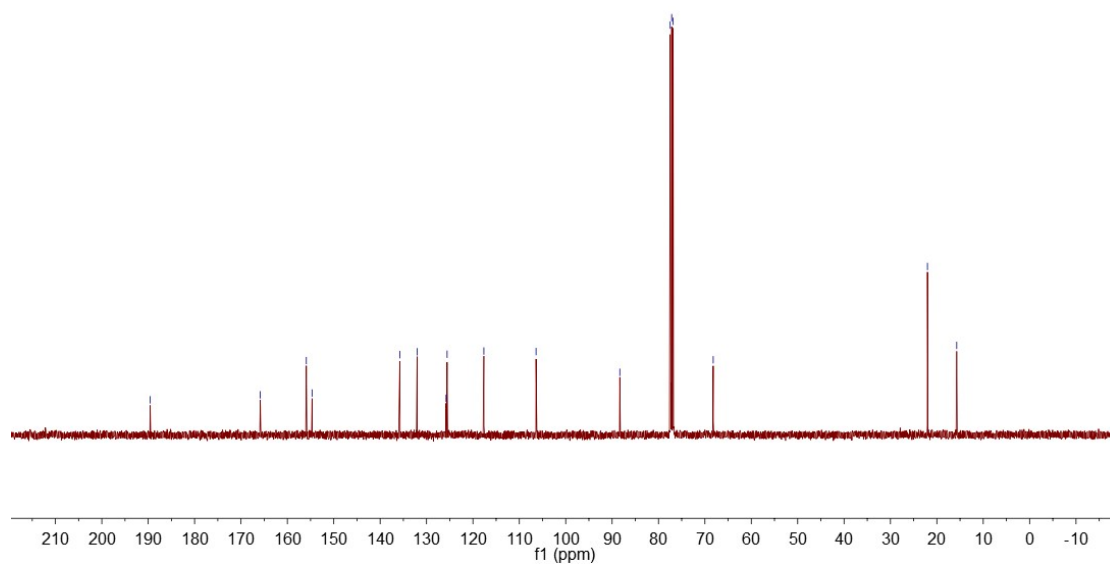
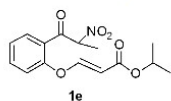
1.291
1.275

-0.007

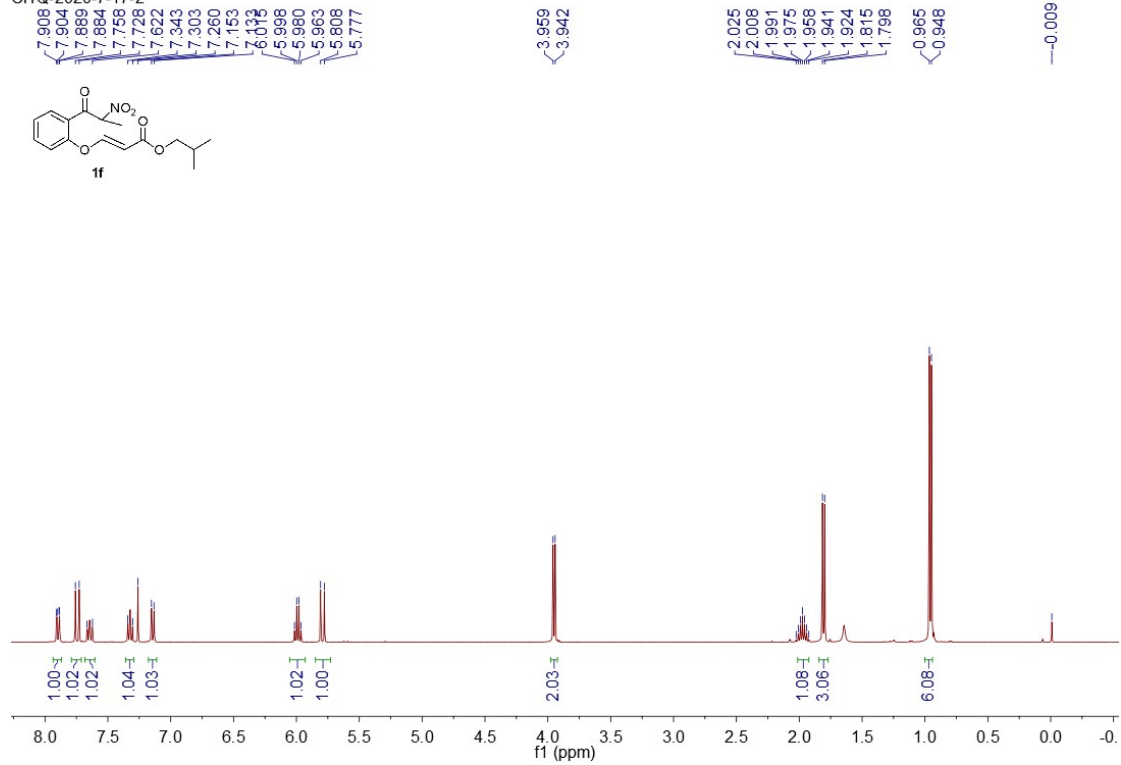


CHQ-2020-7-17-3

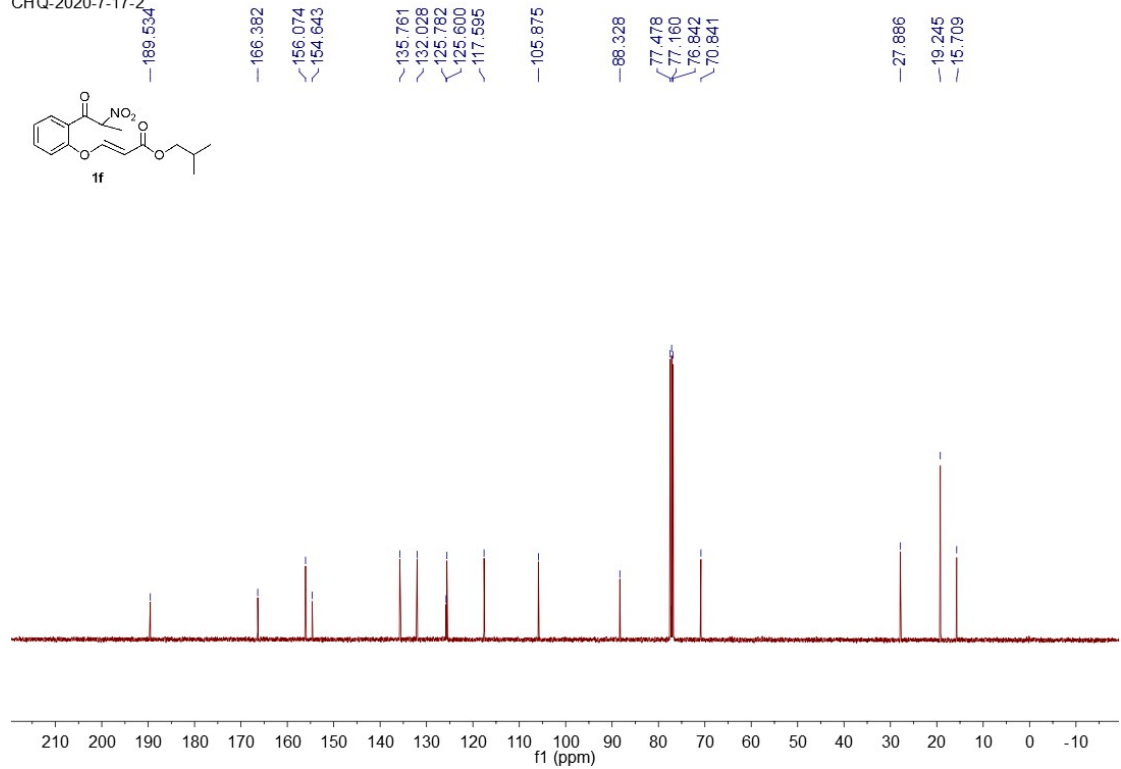
189.578
165.841
155.912
154.680
135.757
132.036
125.792
117.644
106.391
88.339
77.478
77.160
76.842
68.206
22.026
15.714



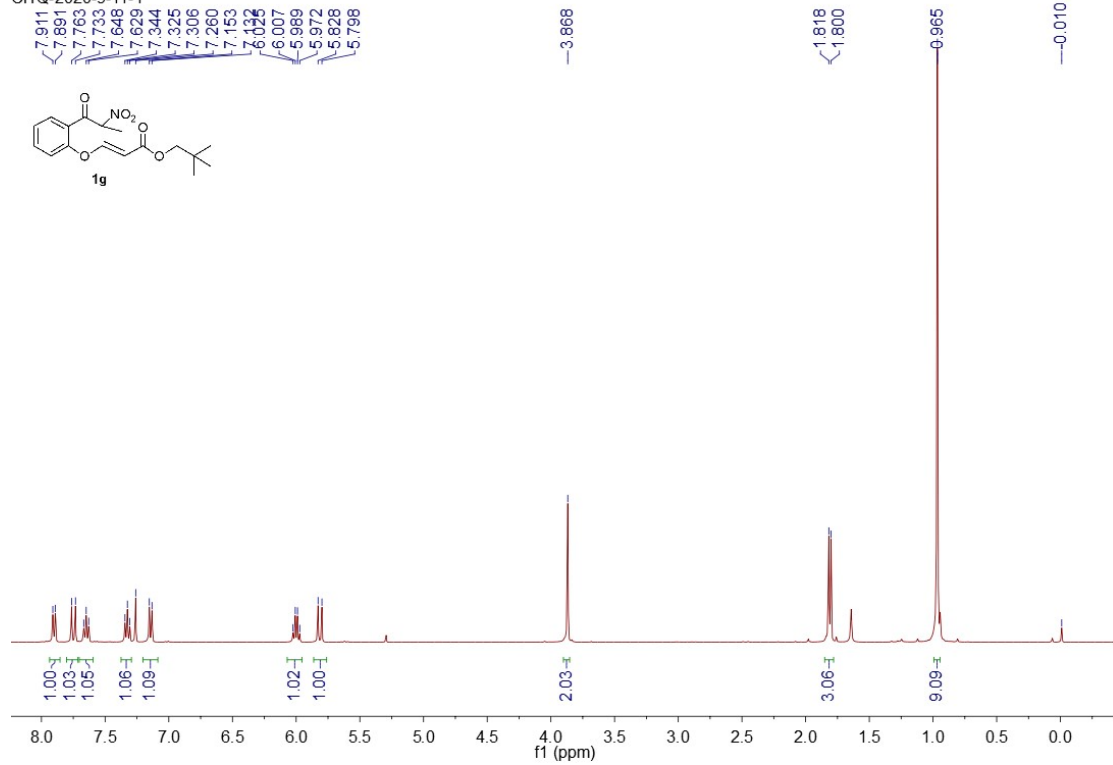
CHQ-2020-7-17-2



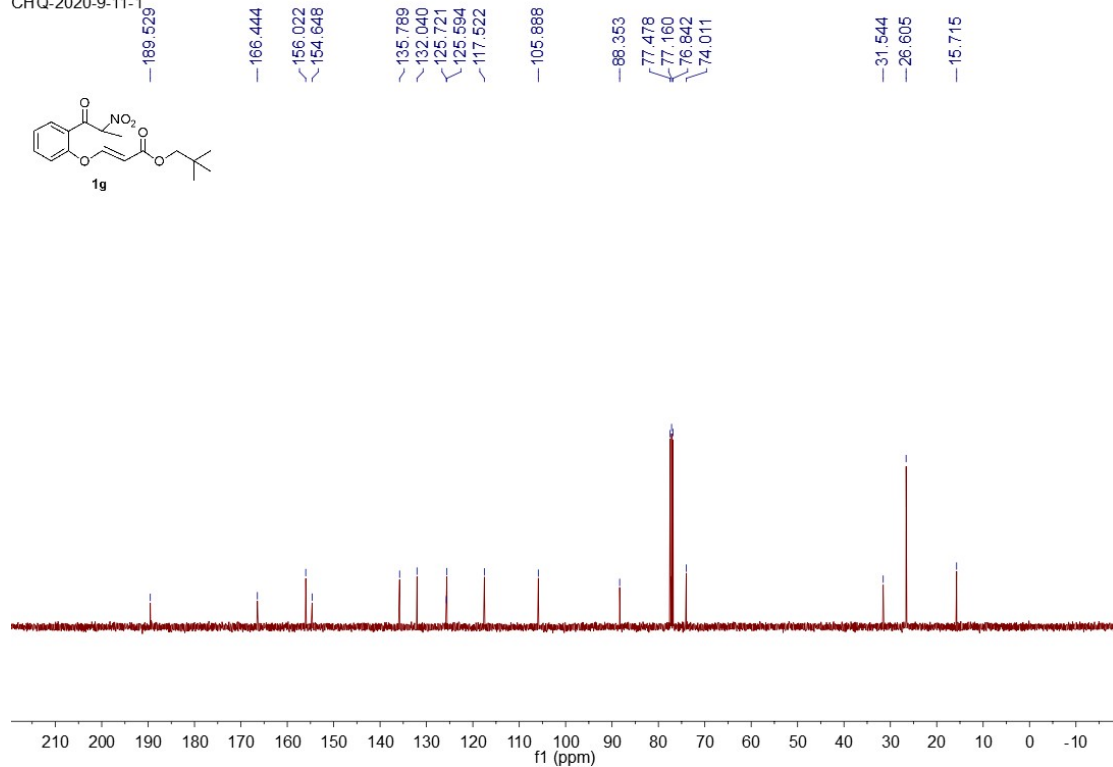
CHQ-2020-7-17-2



CHQ-2020-9-11-1

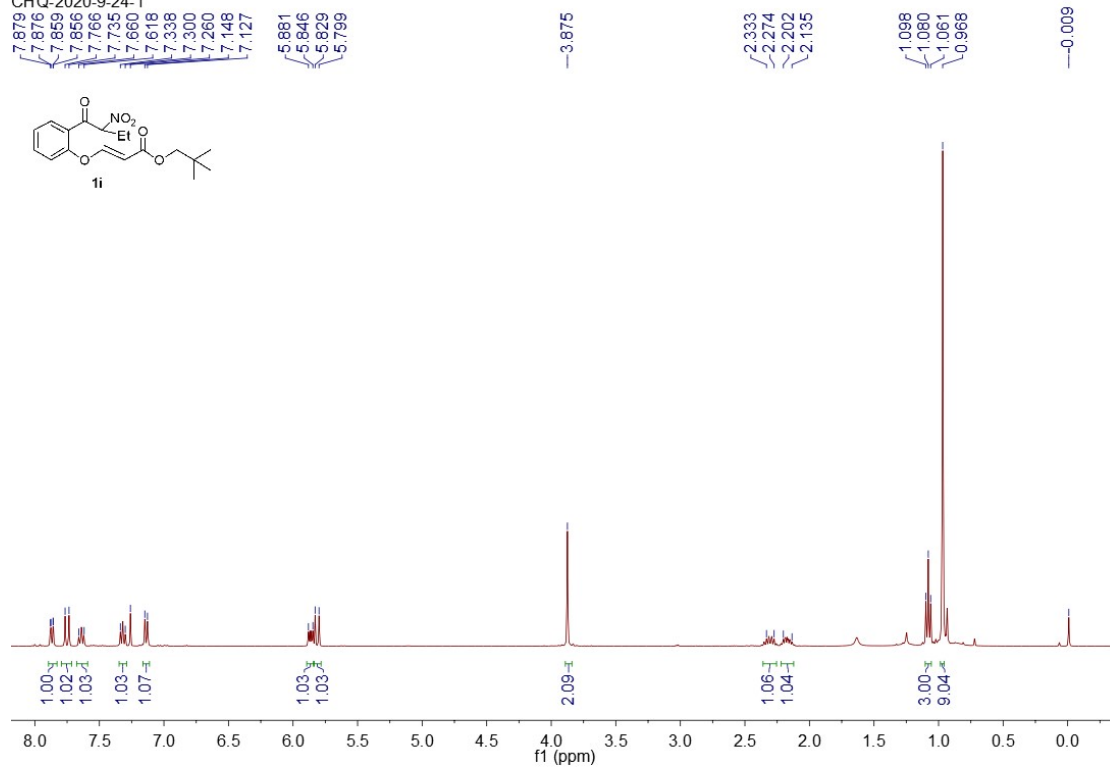
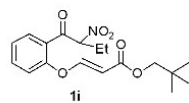


CHQ-2020-9-11-1



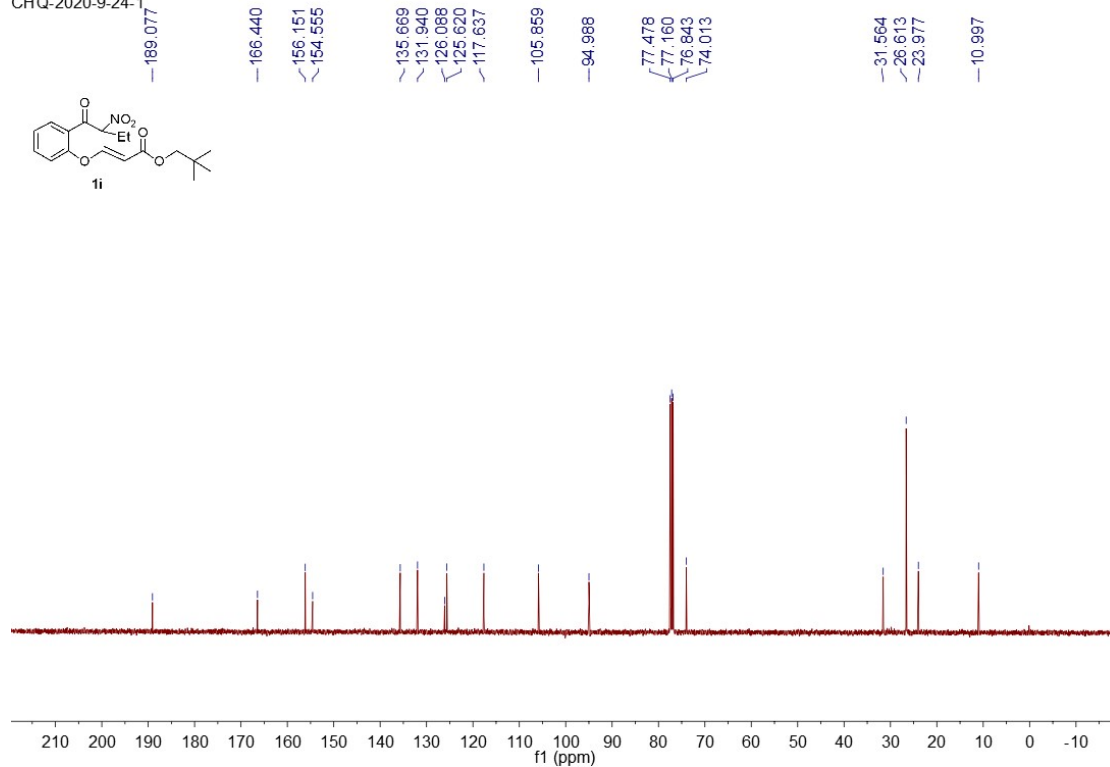
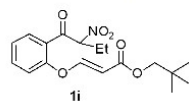
CHQ-2020-9-24-1

7.879
7.876
7.859
7.856
7.766
7.735
7.660
7.618
7.338
7.300
7.260
7.148
7.127
5.881
5.846
5.829
5.799

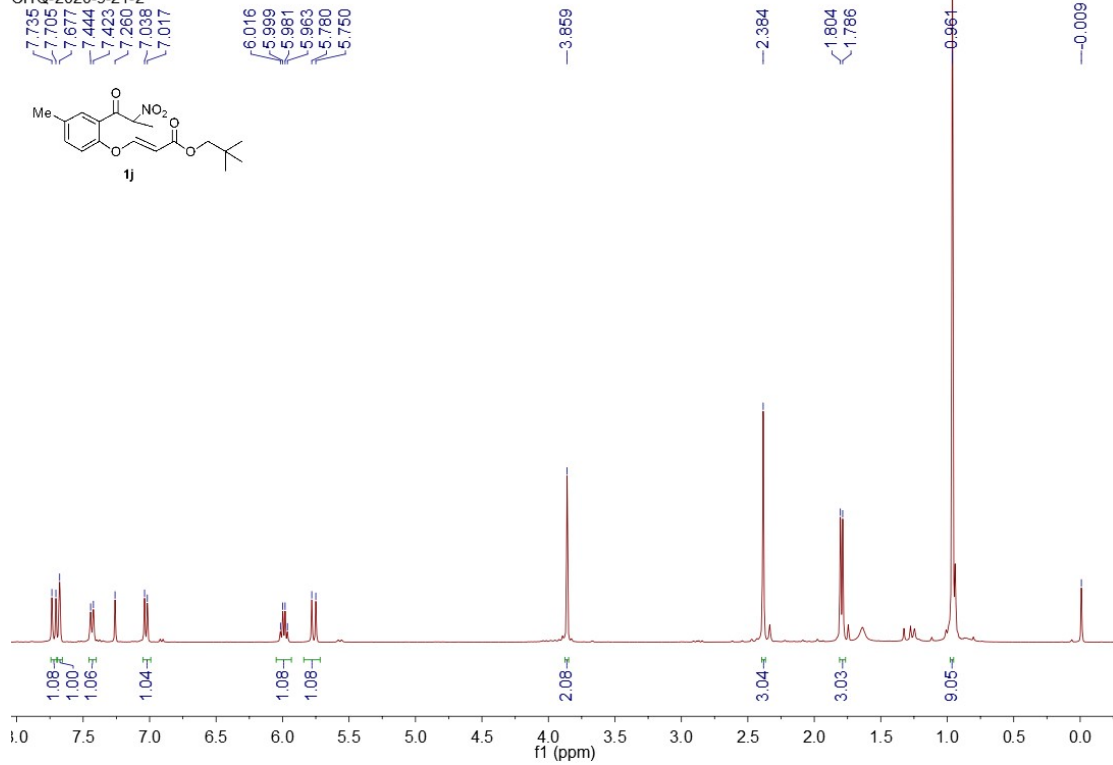


CHQ-2020-9-24-1

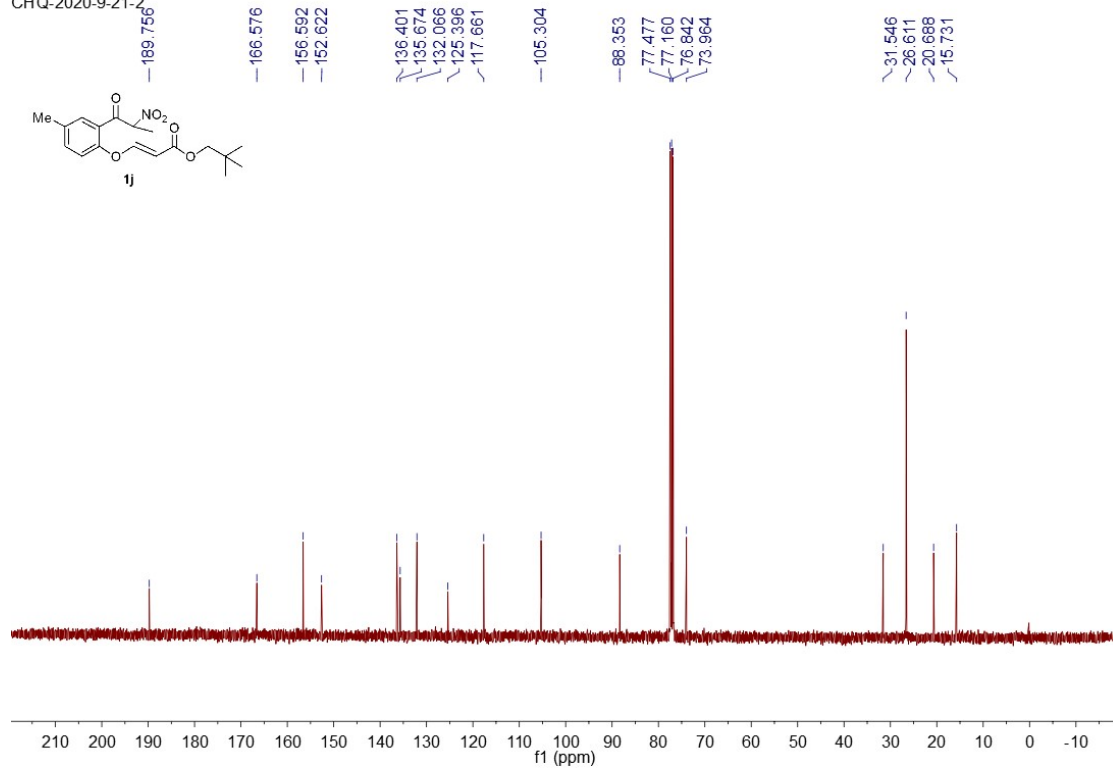
189.077
166.440
156.151
154.555
135.669
131.940
126.088
125.620
117.637
105.859
94.988
77.478
77.160
76.843
74.013
31.564
26.613
23.977
10.997



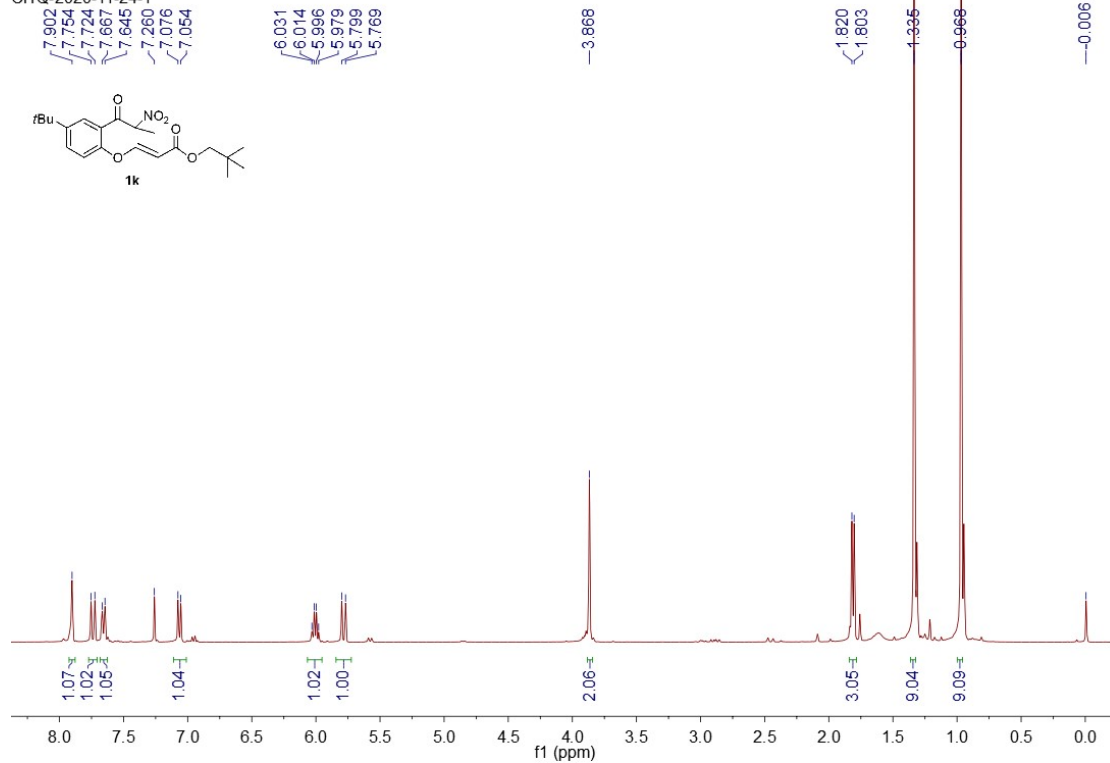
CHQ-2020-9-21-2



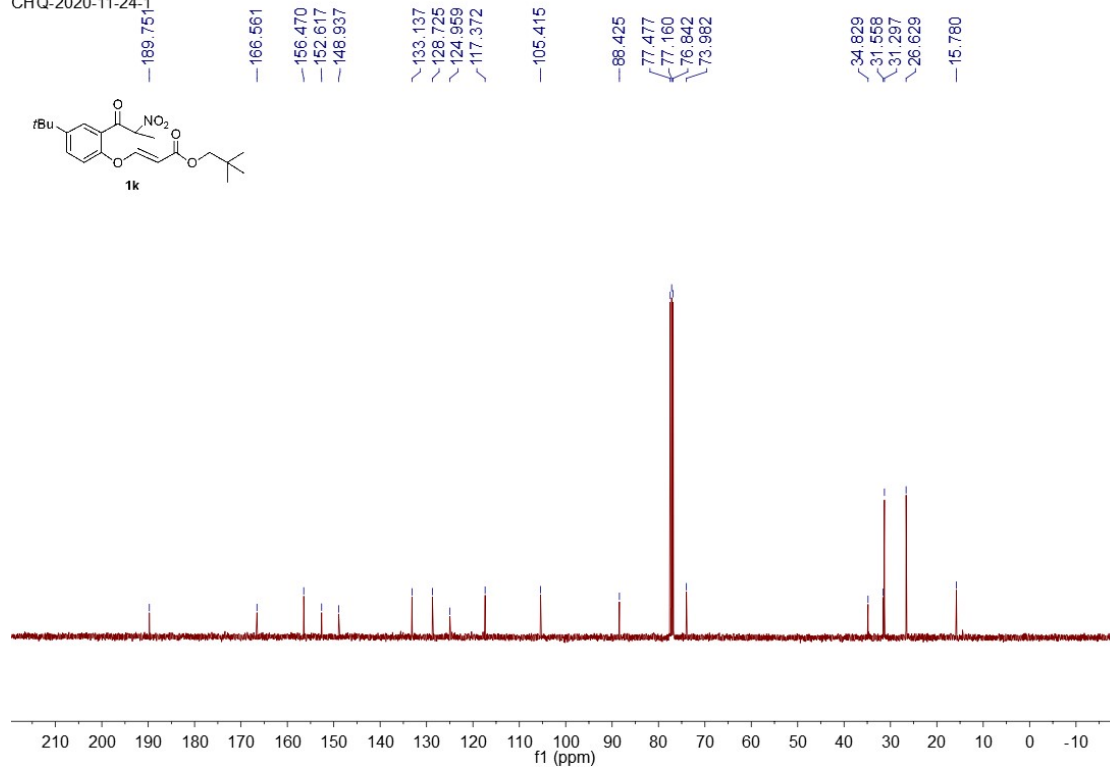
CHQ-2020-9-21-2



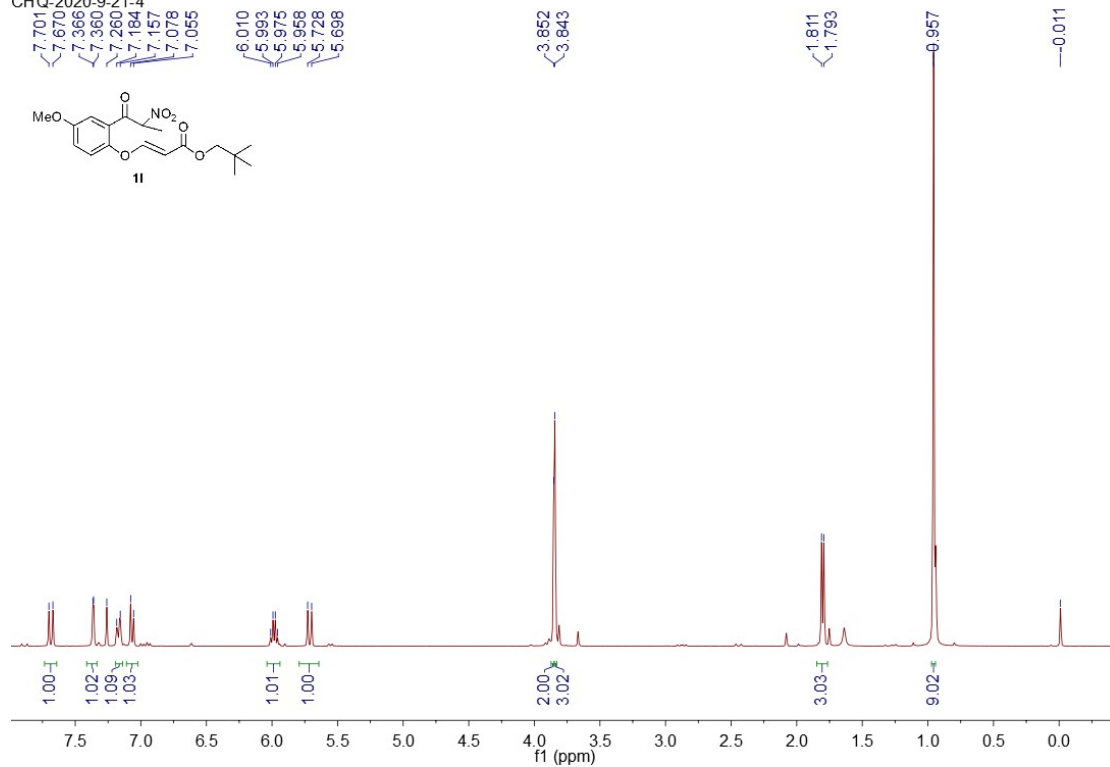
CHQ-2020-11-24-1



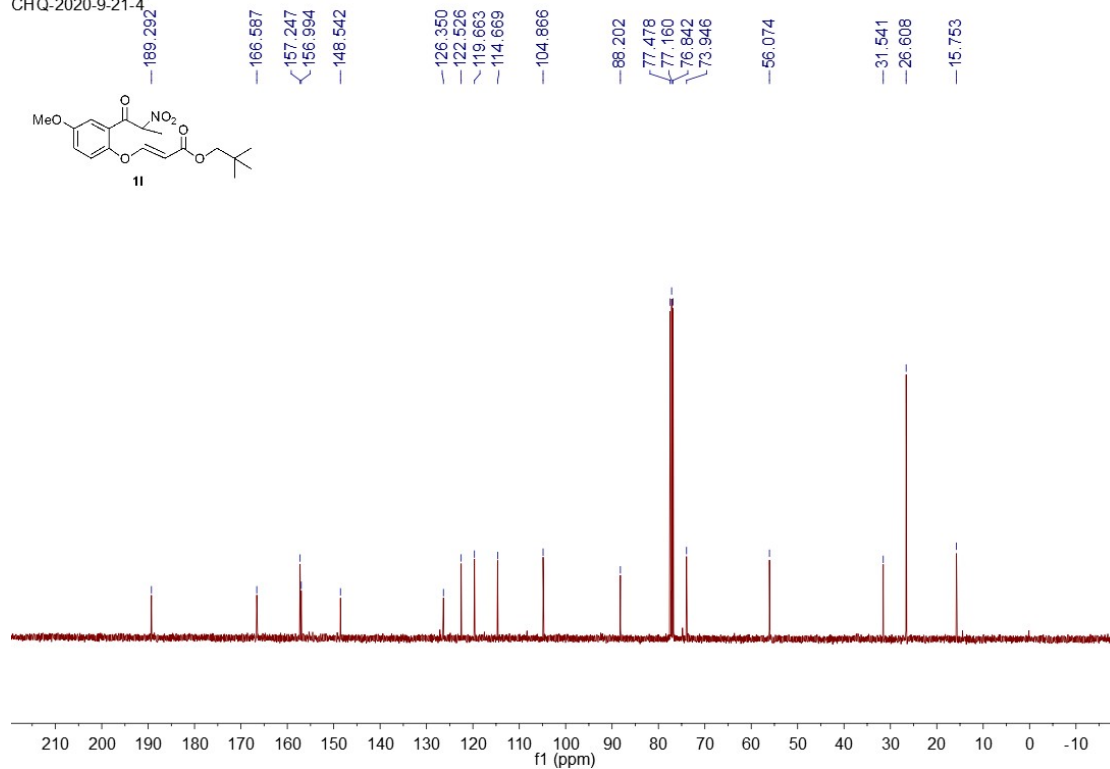
CHQ-2020-11-24-1



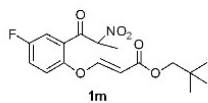
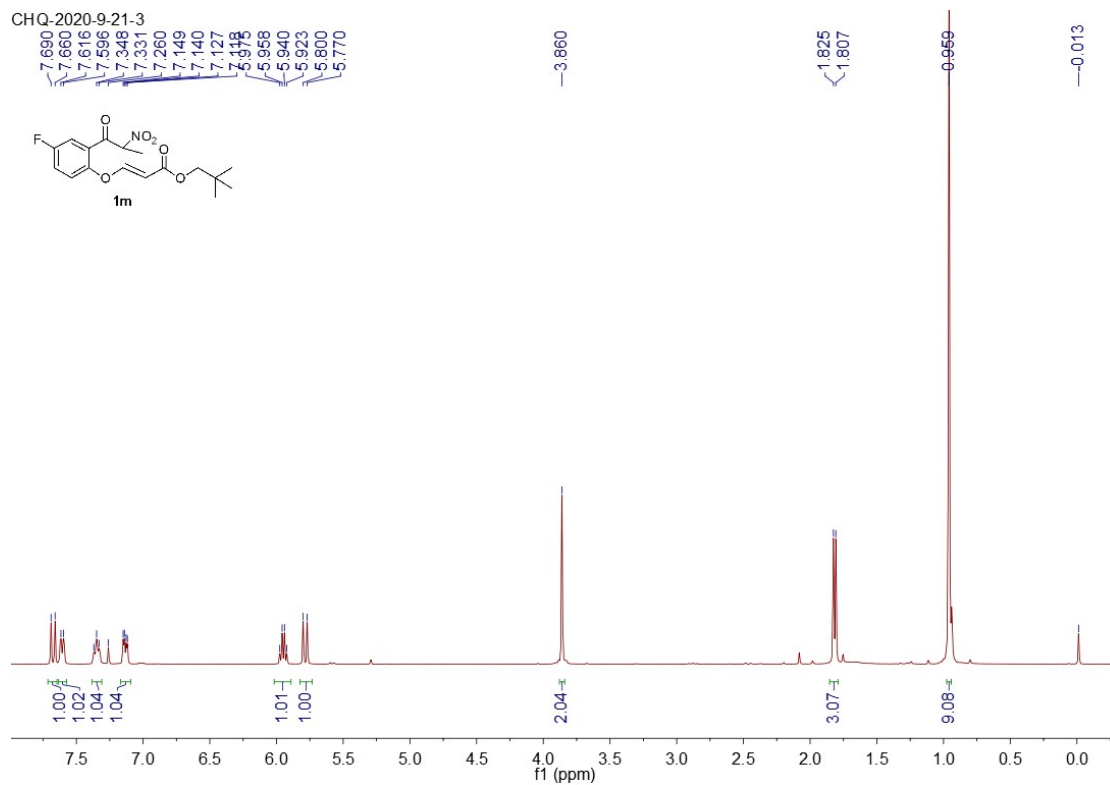
CHQ-2020-9-21-4



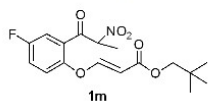
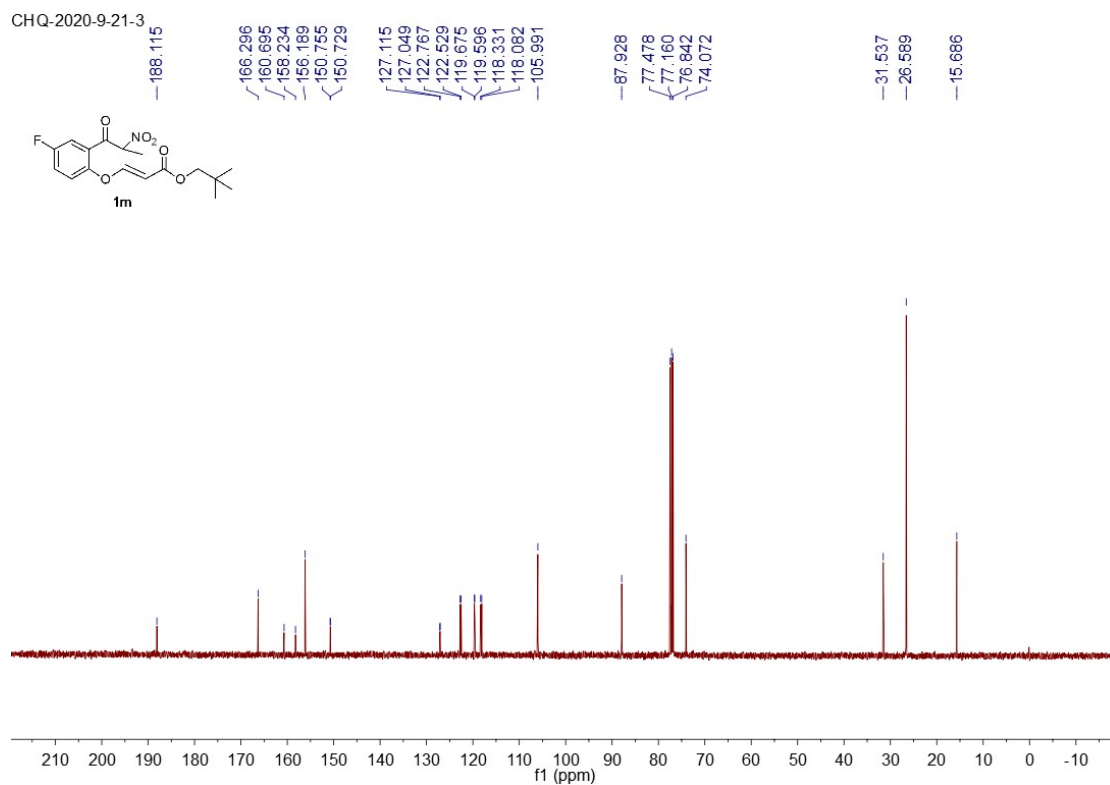
CHQ-2020-9-21-4



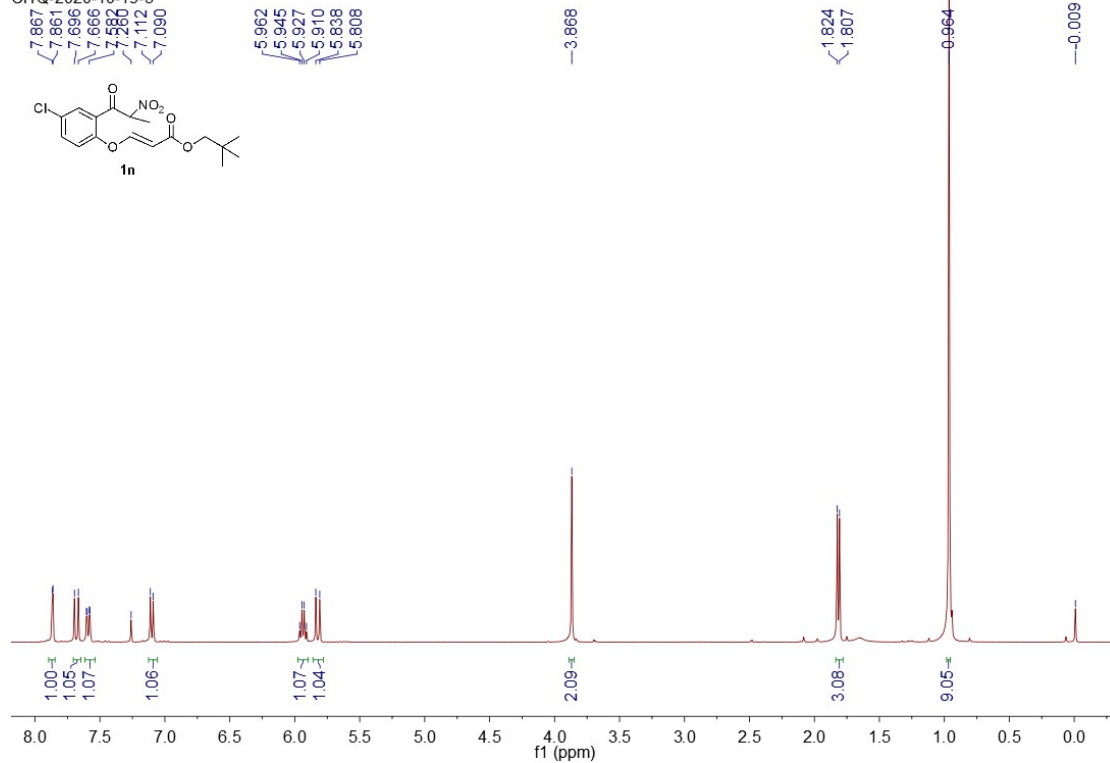
CHQ-2020-9-21-3



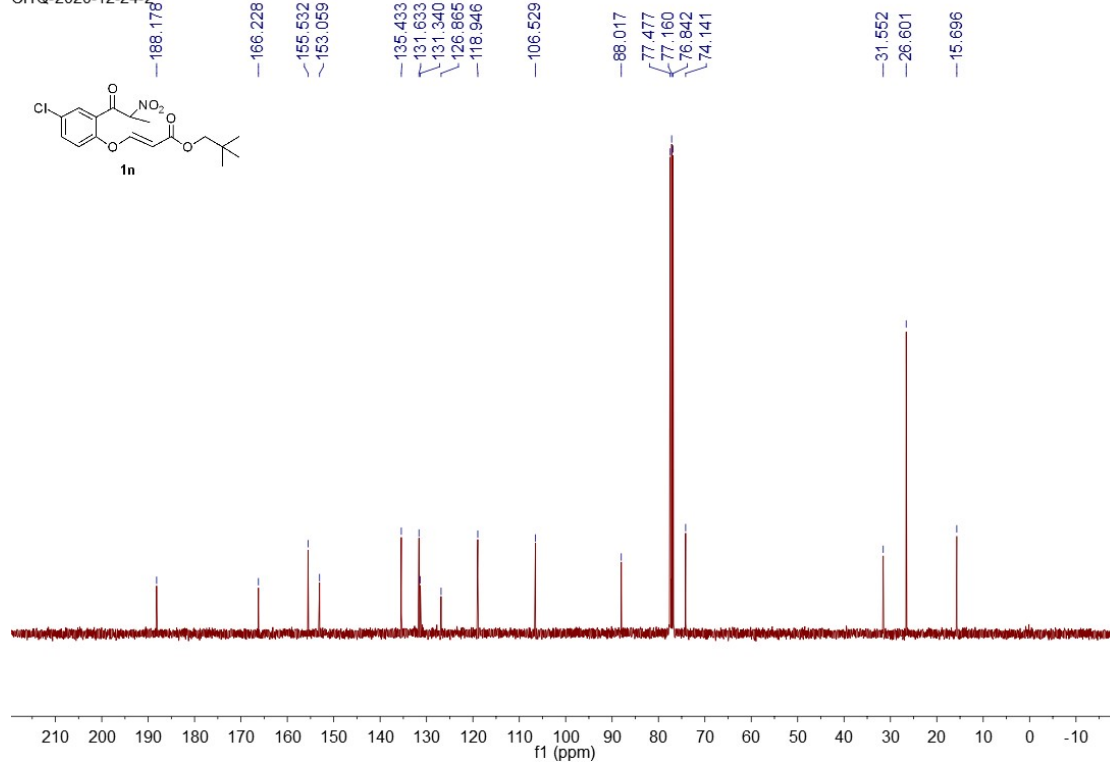
CHQ-2020-9-21-3



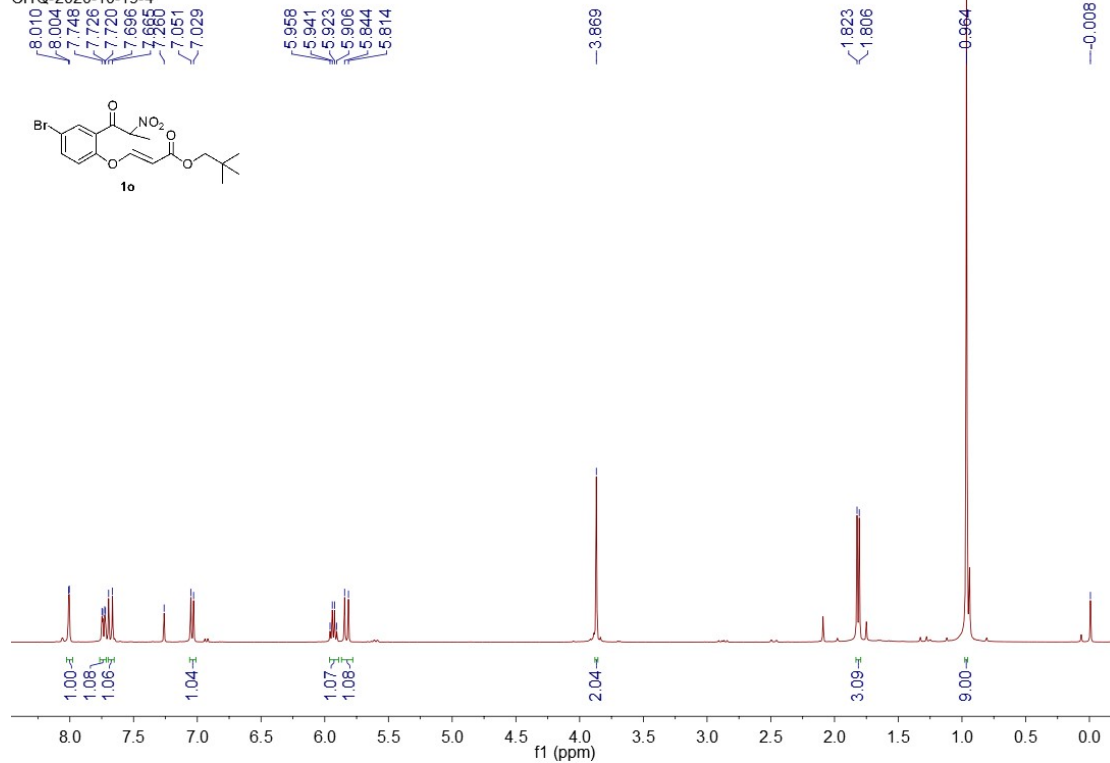
CHQ-2020-10-19-3



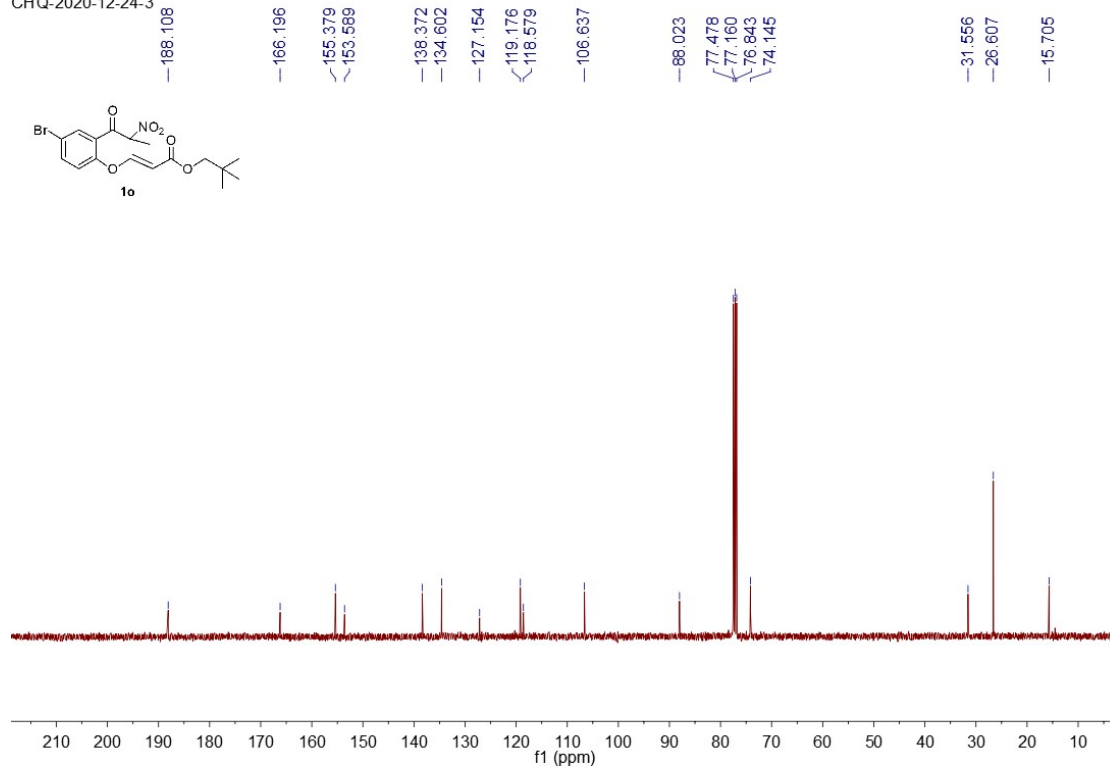
CHQ-2020-12-24-2



CHQ-2020-10-19-4



CHQ-2020-12-24-3



CHQ-2020-11-30-1

7.718
7.687
7.559
7.501
7.260
7.051
7.008
6.979
6.958

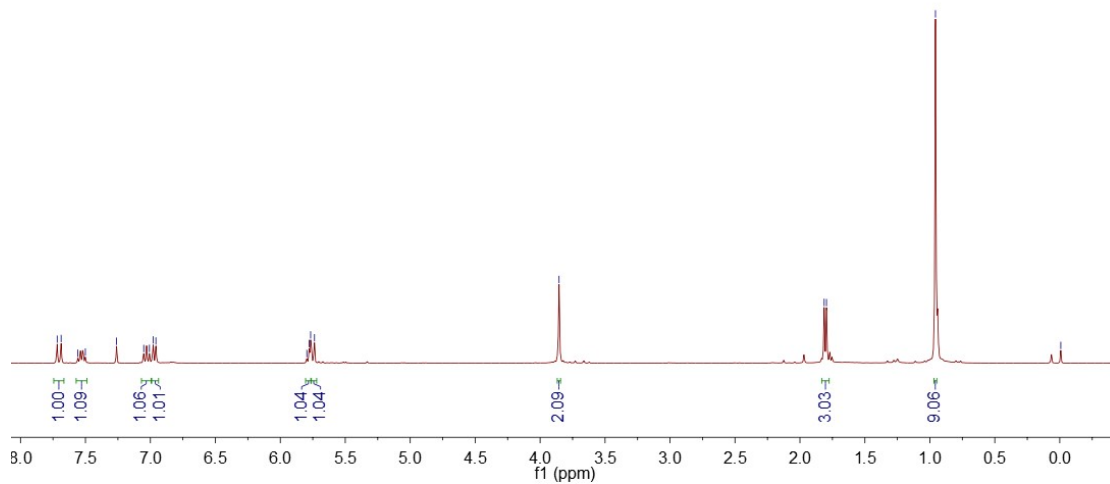
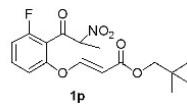
5.796
5.778
5.767
5.737

-3.854

1.814
1.796

-0.957

-0.008



CHQ-2020-11-30-1

188.140

166.494
161.541
159.008
156.365
154.148
154.087

134.253
134.150

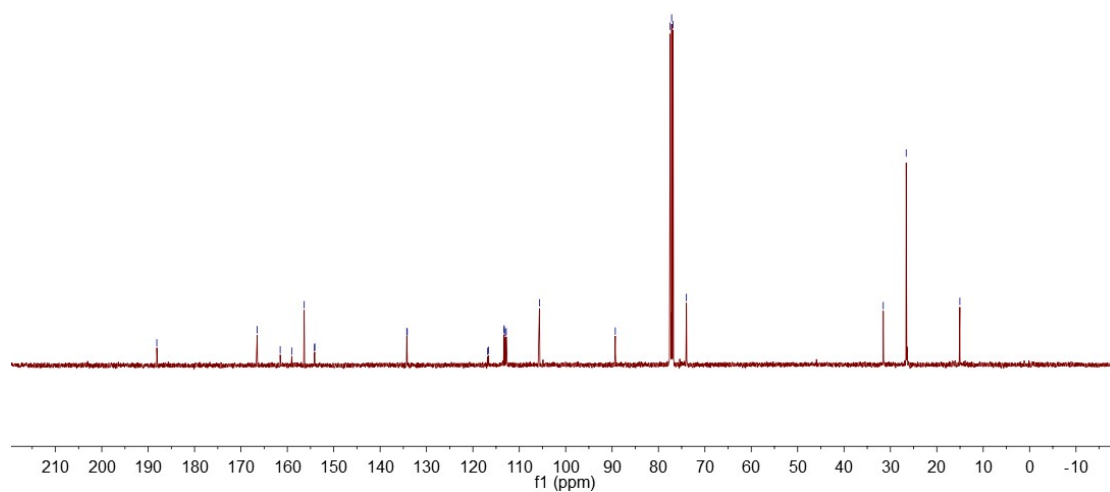
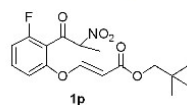
116.822
116.639
113.275
113.240
113.029
112.813
105.659

-89.310

77.478
77.160
76.842
73.977

-31.541
-26.599

-15.032



CHQ-2020-12-1-1

7.708
7.679
7.478
7.437
7.300
7.278
7.260
7.083
7.062

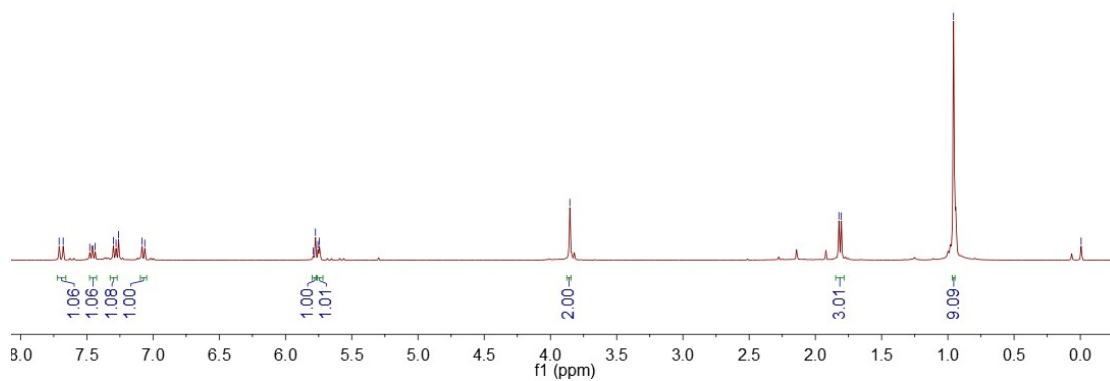
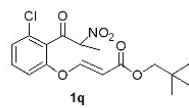
5.791
5.774
5.755
5.744

3.854

1.822
1.805

0.957

0.006



CHQ-2020-12-1-1

190.944

166.512

156.096
153.468

132.905
132.272
127.446
126.530

115.333

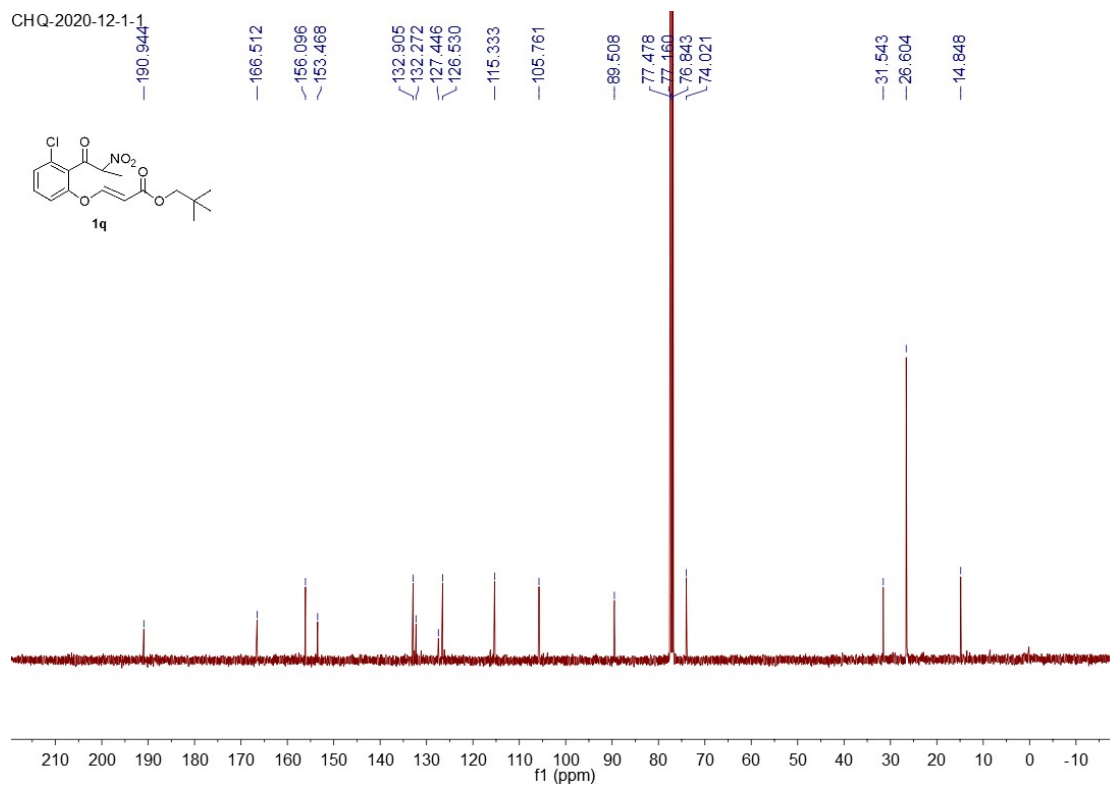
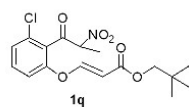
105.761

89.508

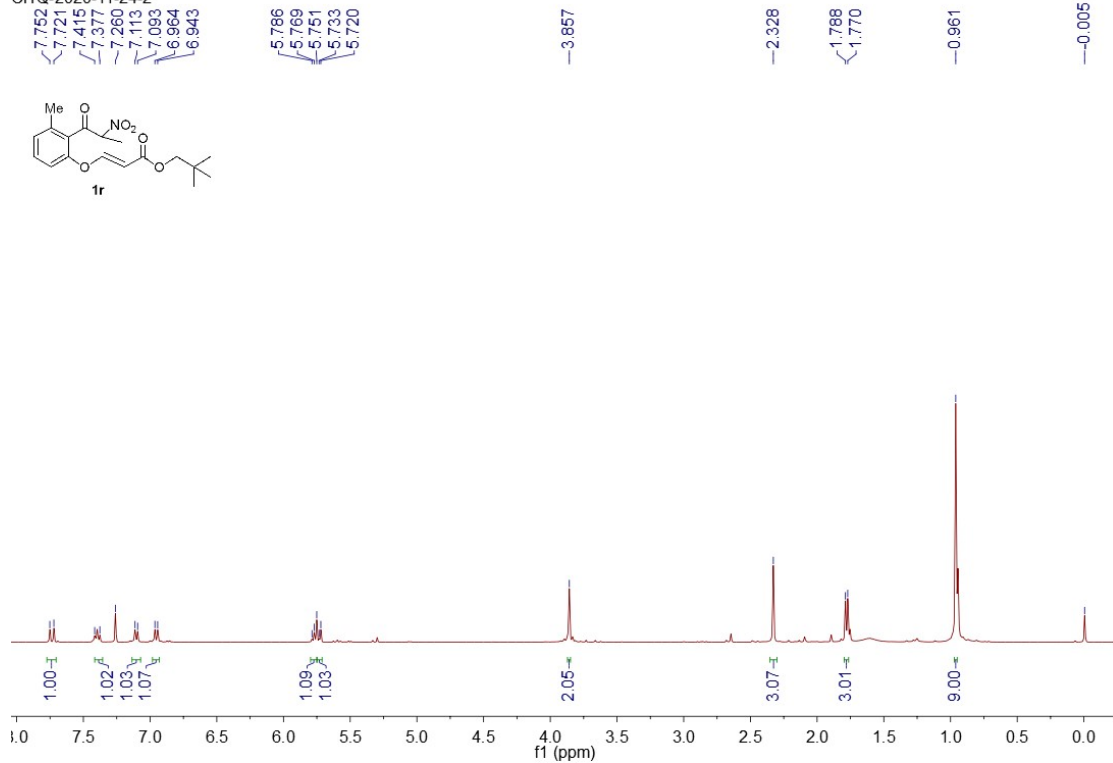
77.478
77.160
76.843
74.021

31.543
26.604

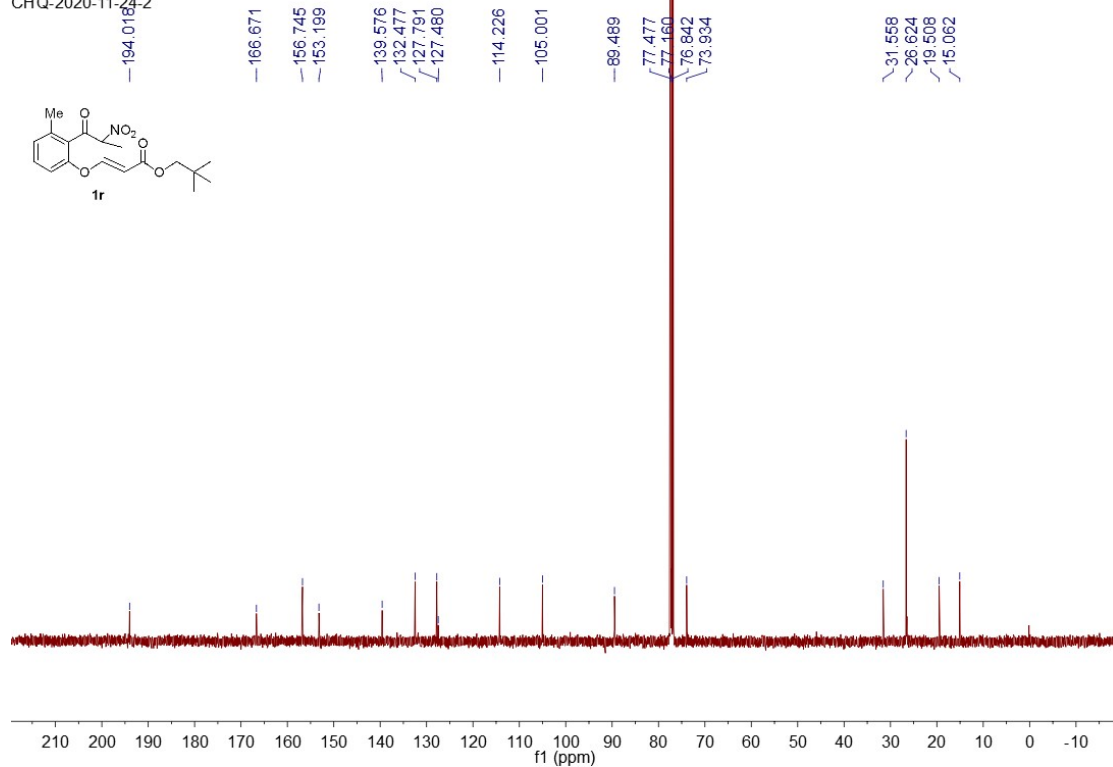
14.848



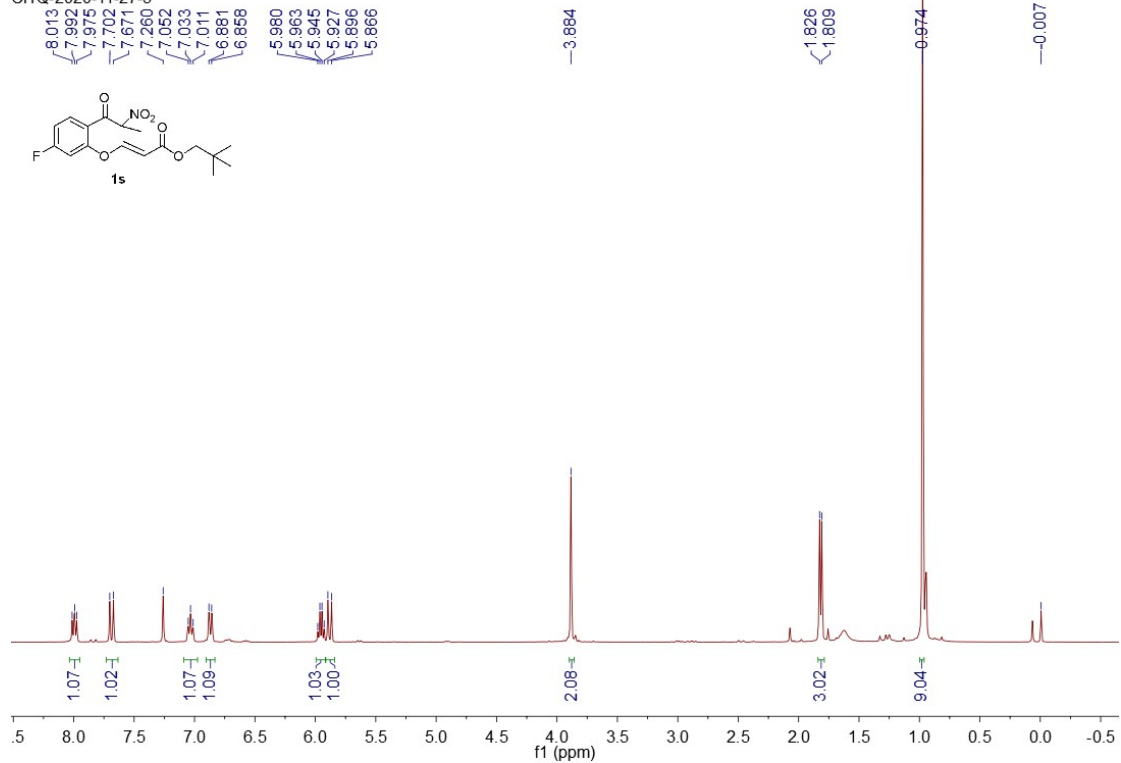
CHQ-2020-11-24-2



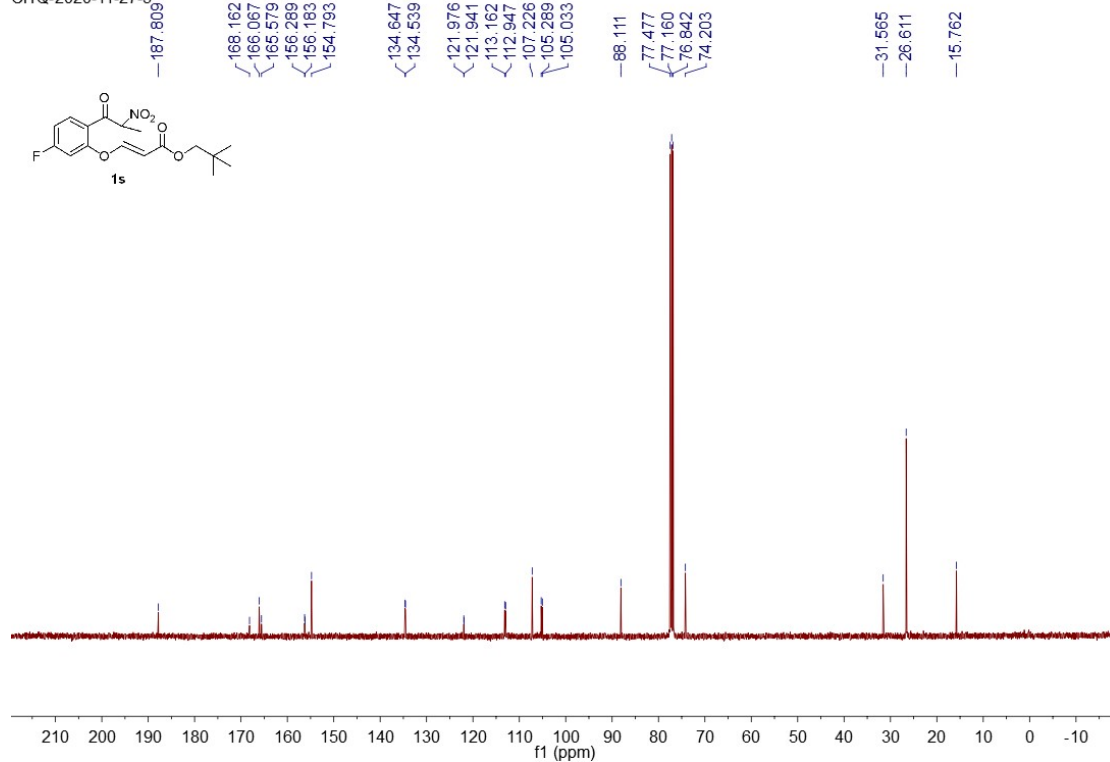
CHQ-2020-11-24-2



CHQ-2020-11-27-3



CHQ-2020-11-27-3



CHQ-2020-12-1-2

7.895
7.873
7.707
7.677
7.314
7.292
7.260
7.149

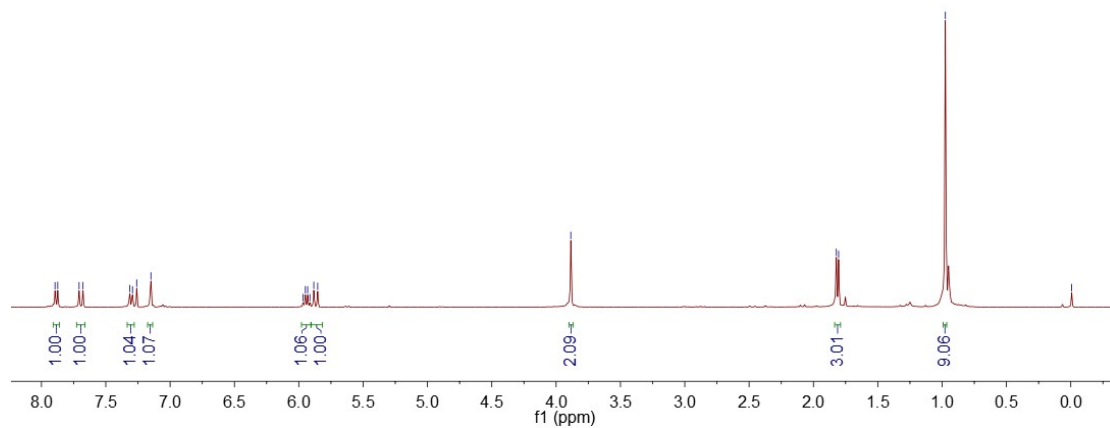
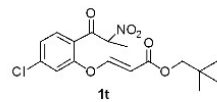
5.966
5.949
5.931
5.914
5.883
5.853

-3.886

1.822
1.804

-0.975

-0.007



CHQ-2020-12-1-2

-188.170

-166.151

155.041
155.003

-141.947

133.224

125.993

123.999

117.837

-107.095

-88.121

77.478

77.160

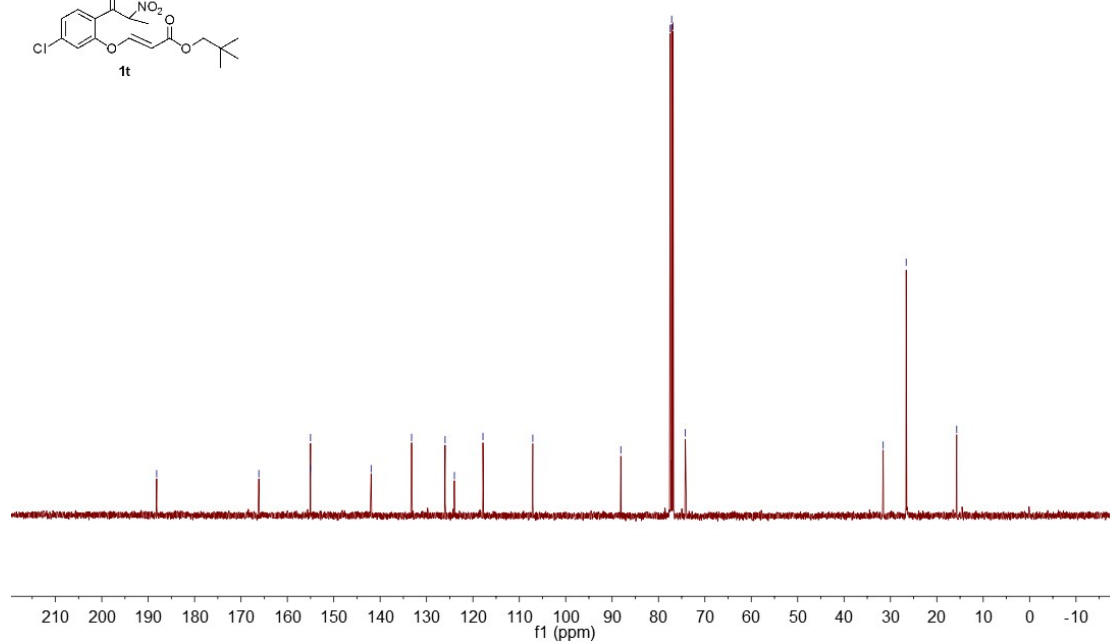
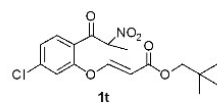
76.843

74.205

-31.564

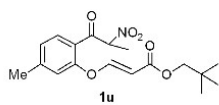
-26.611

-15.716



CHQ-2020-11-24-3

7.834
7.814
7.753
7.723
7.260
7.131
7.111
6.925
6.013
5.996
5.978
5.961
5.822
5.792



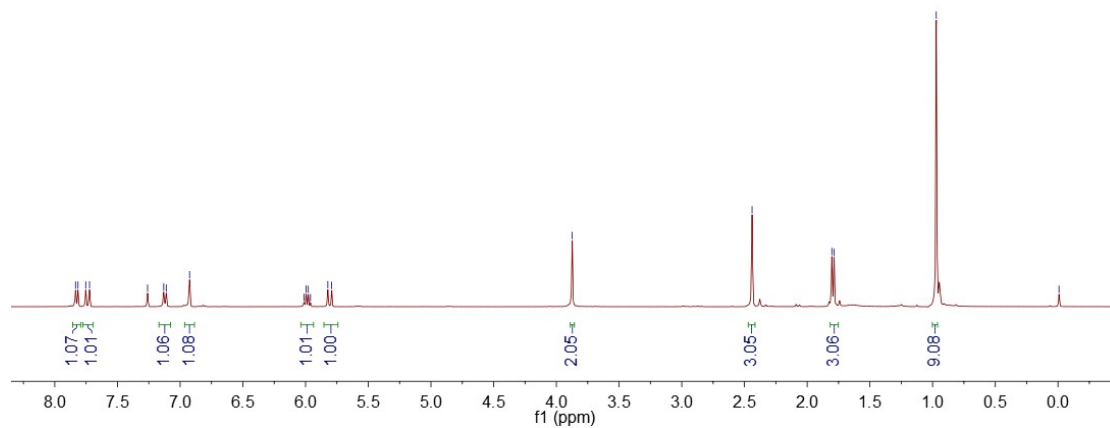
-3.874

-2.439

1.803
1.786

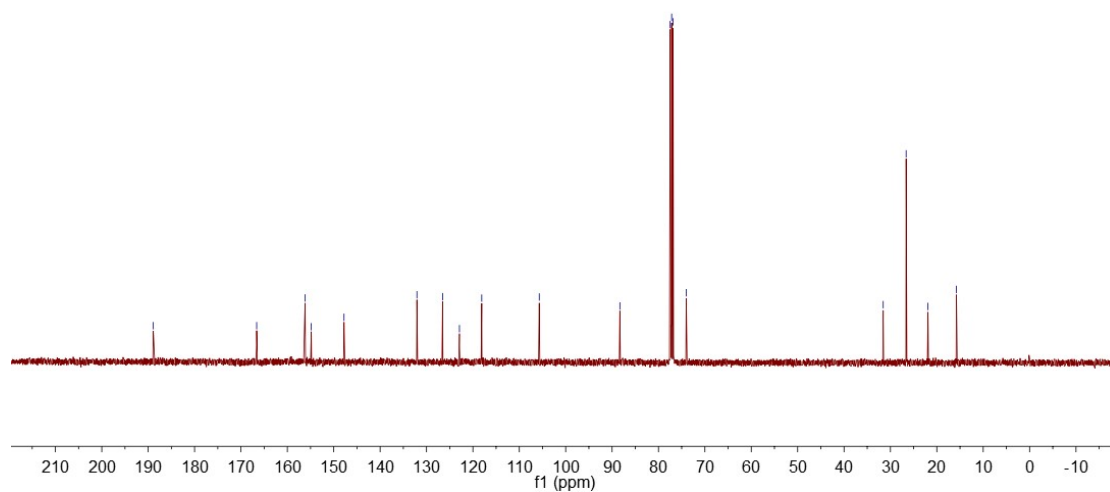
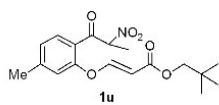
-0.971

-0.008



CHQ-2020-11-24-3

188.895
166.614
156.177
154.850
147.788
132.071
126.530
122.903
118.099
105.701
88.320
77.478
77.160
76.843
74.018
31.557
26.614
21.909
15.768



CHQ-2020-12-28-3

7.692
7.661
7.646
7.627
7.484
7.438
7.376
7.324
7.260

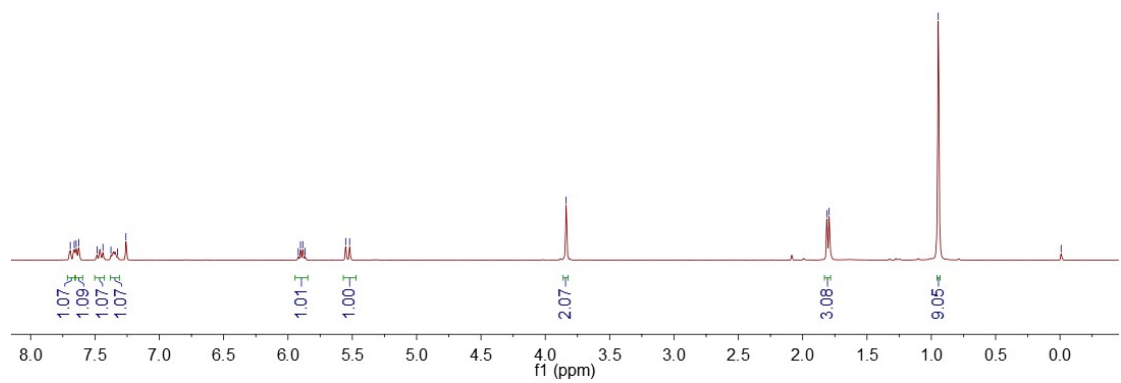
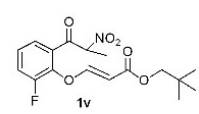
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5.903
5.885
5.867
5.552
5.521

-3.838

1.812
1.795

-0.946

-0.009



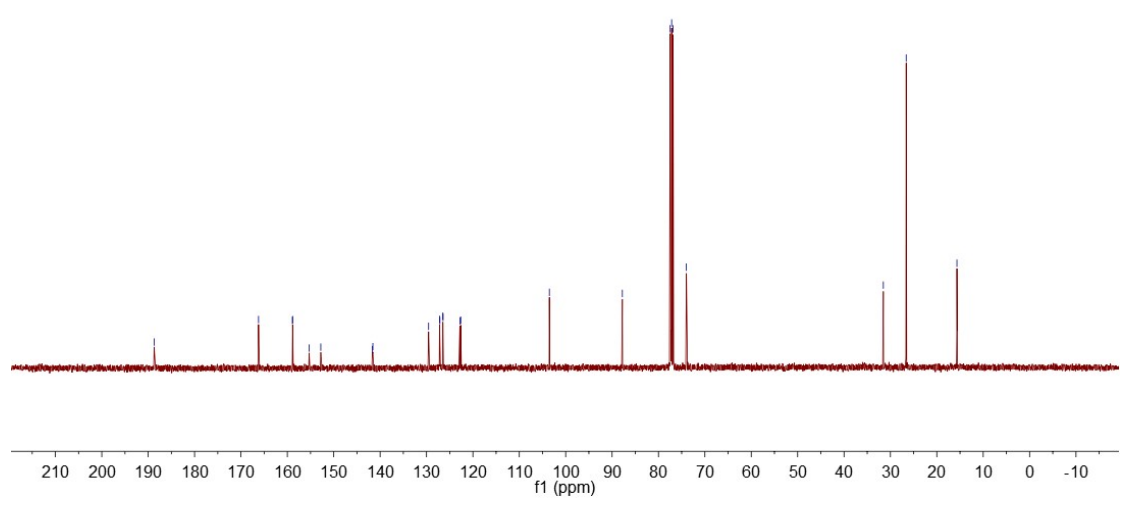
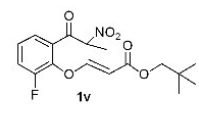
CHQ-2020-12-28-3

188.713

166.209
158.902
158.866
155.308
152.790
141.694
141.566
129.549
127.192
127.118
126.473
126.438
122.807
122.621
103.518

87.785
77.477
77.160
76.842
73.983

31.529
26.599
15.661



CHQ-2020-12-1-3

7.724
7.720
7.704
7.700
7.641
7.610
7.390
7.350
7.260

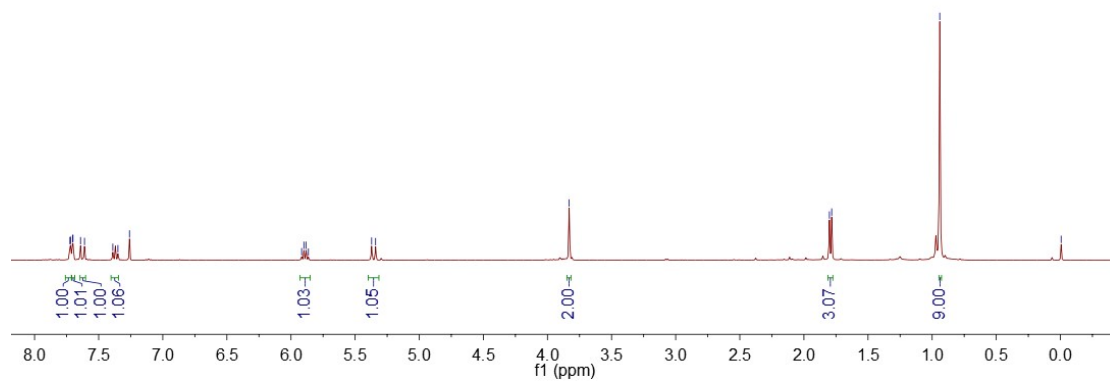
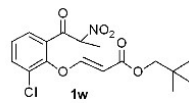
5.917
5.900
5.882
5.864
5.371
5.340

3.831

1.801
1.783

0.941

0.006



CHQ-2020-12-1-3

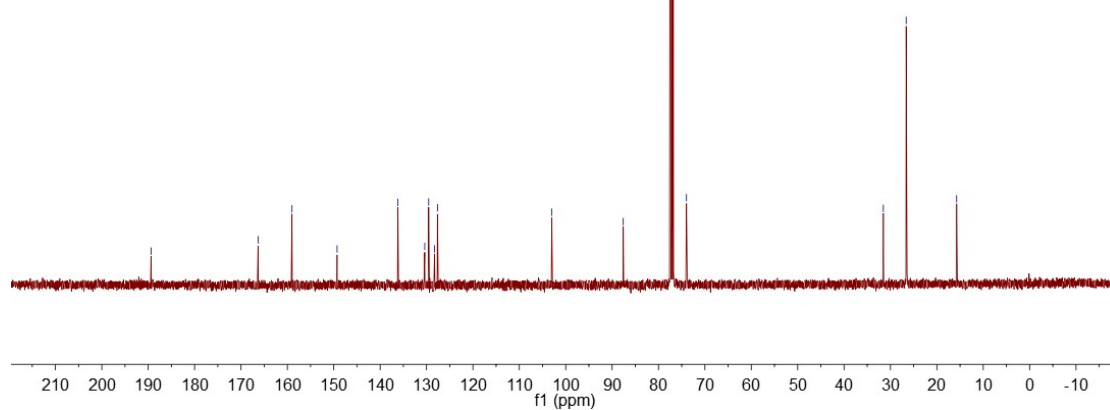
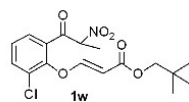
189.387
166.319
159.006
149.282

136.175
130.387
129.542
128.279
127.653

103.009

87.600
77.477
77.160
76.842
73.970

31.534
26.609
15.730



CHQ-12-10-2

7.946
7.926
7.554
7.260
7.156
7.118
7.032
7.011

5.611
5.605
5.586
5.580

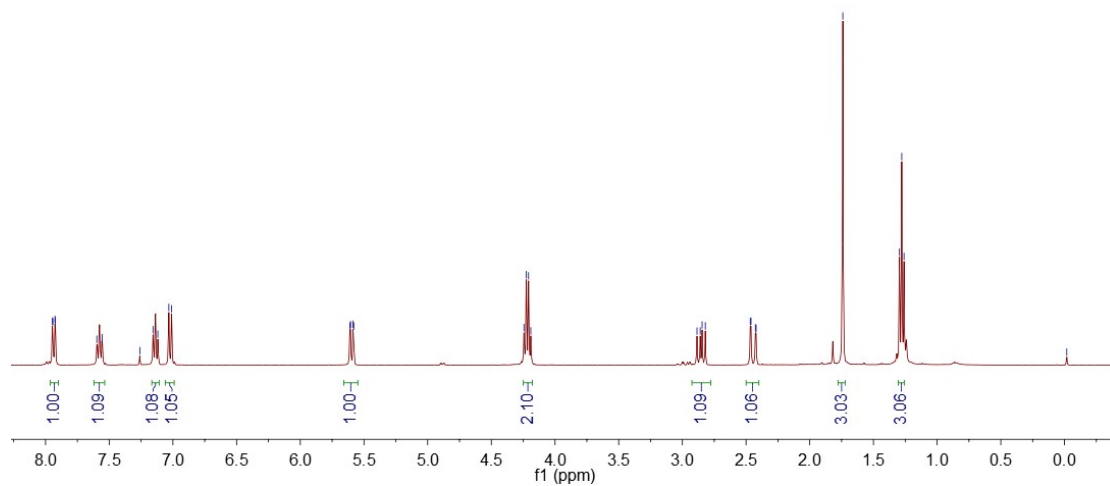
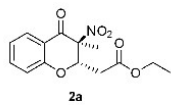
4.244
4.226
4.208
4.190

2.885
2.860
2.845
2.820
2.467
2.461
2.427
2.421

1.740

1.295
1.277
1.260

-0.018



CHQ-2021-7-20-1

165.059

168.519

159.798

137.648

128.597

123.282

118.360

118.266

92.280

78.130

77.478

77.160

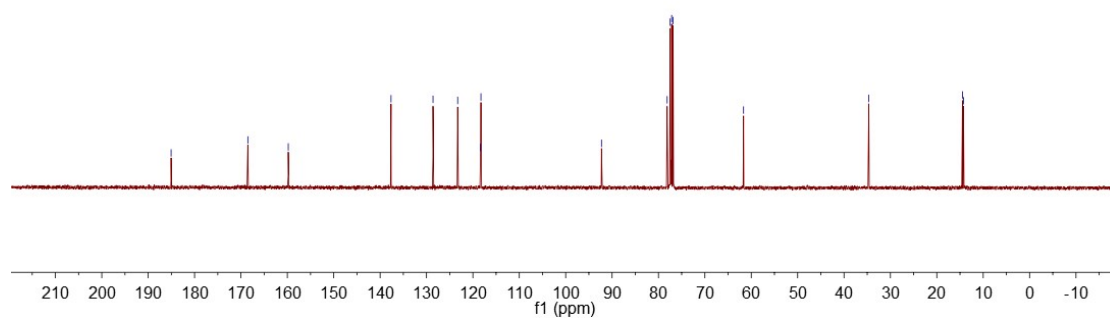
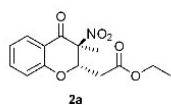
76.842

61.656

34.652

14.471

14.253



CHQ-2021-1-18-3

7.970
7.951
7.610
7.571
7.260
7.173
7.136
7.038
7.017

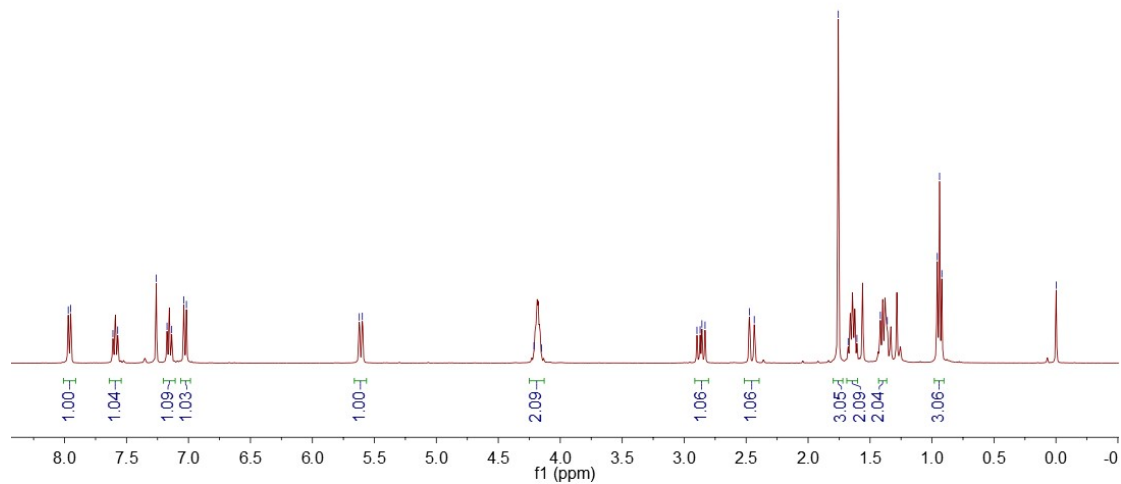
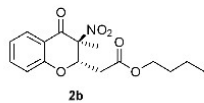
5.622
5.597

4.212
4.152

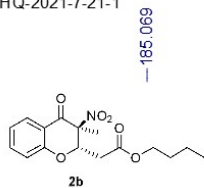
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2.871
2.857
2.832
2.474
2.434

1.756
1.677
1.606
1.417
1.361
0.958
0.939
0.921

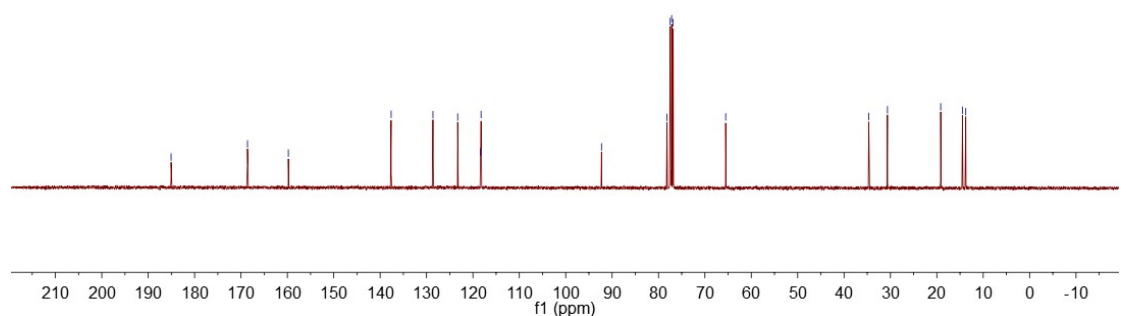
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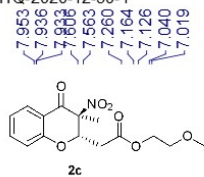
CHQ-2021-7-21-1



165.069
168.597
159.791
137.636
128.615
123.289
118.364
118.249
92.287
78.162
77.477
77.160
76.842
65.515
34.666
30.642
19.165
14.466
13.767



CHQ-2020-12-30-1



5.628
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5.603
5.598

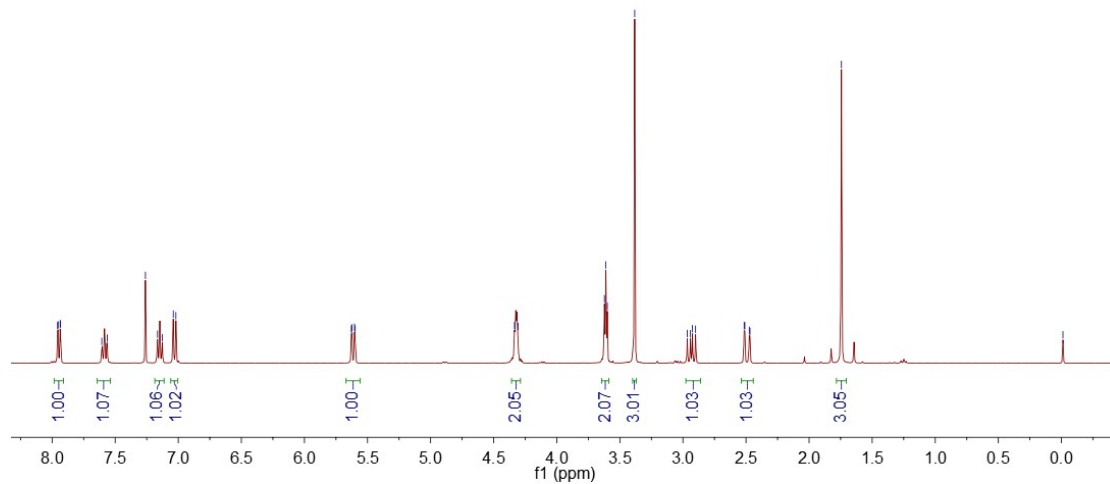
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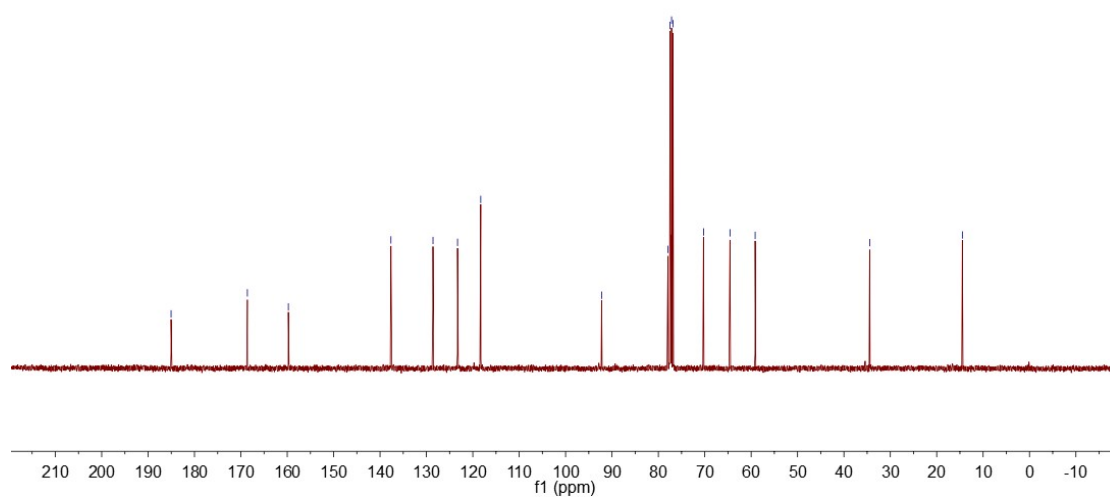
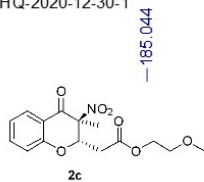
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2.910
2.509
2.474
2.469

-1.744

-0.012



CHQ-2020-12-30-1



CHQ-2020-8-3-1

7.967
7.948
7.606
7.567
7.260
7.172
7.134
7.038
7.017

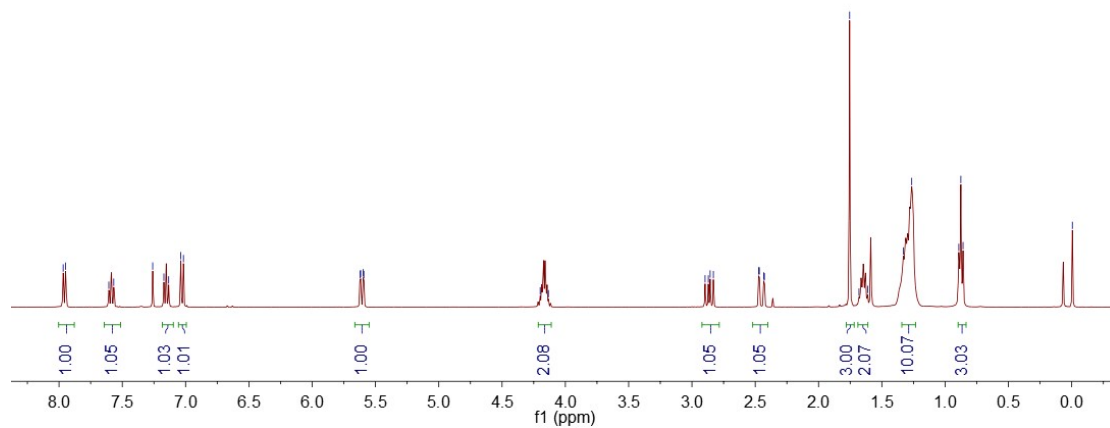
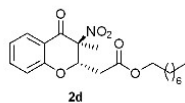
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5.597
5.592

4.199
4.134

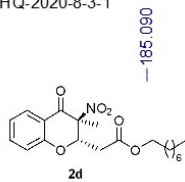
2.896
2.871
2.856
2.831
2.473
2.468
2.433
2.428

1.754
1.681
1.612
1.329
1.264
0.892
0.876
0.858

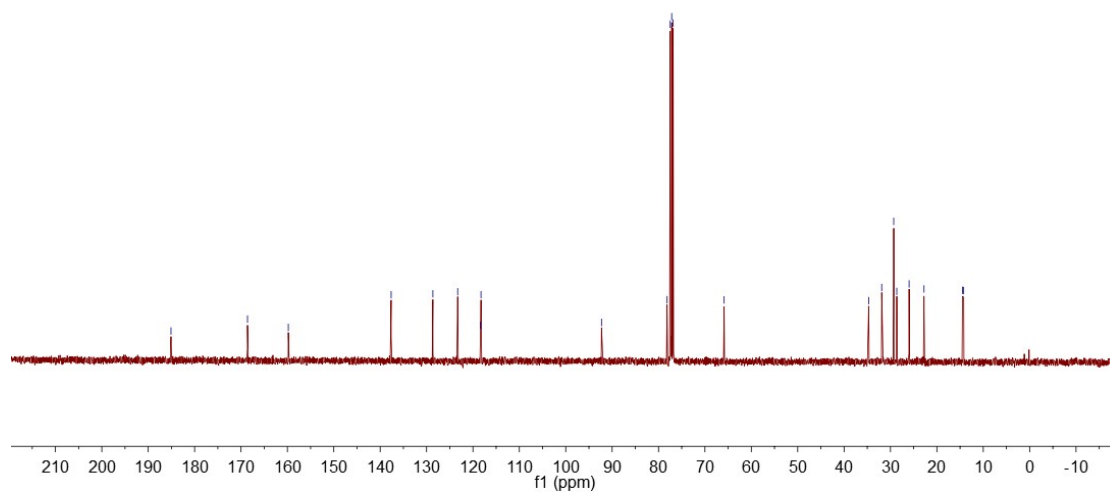
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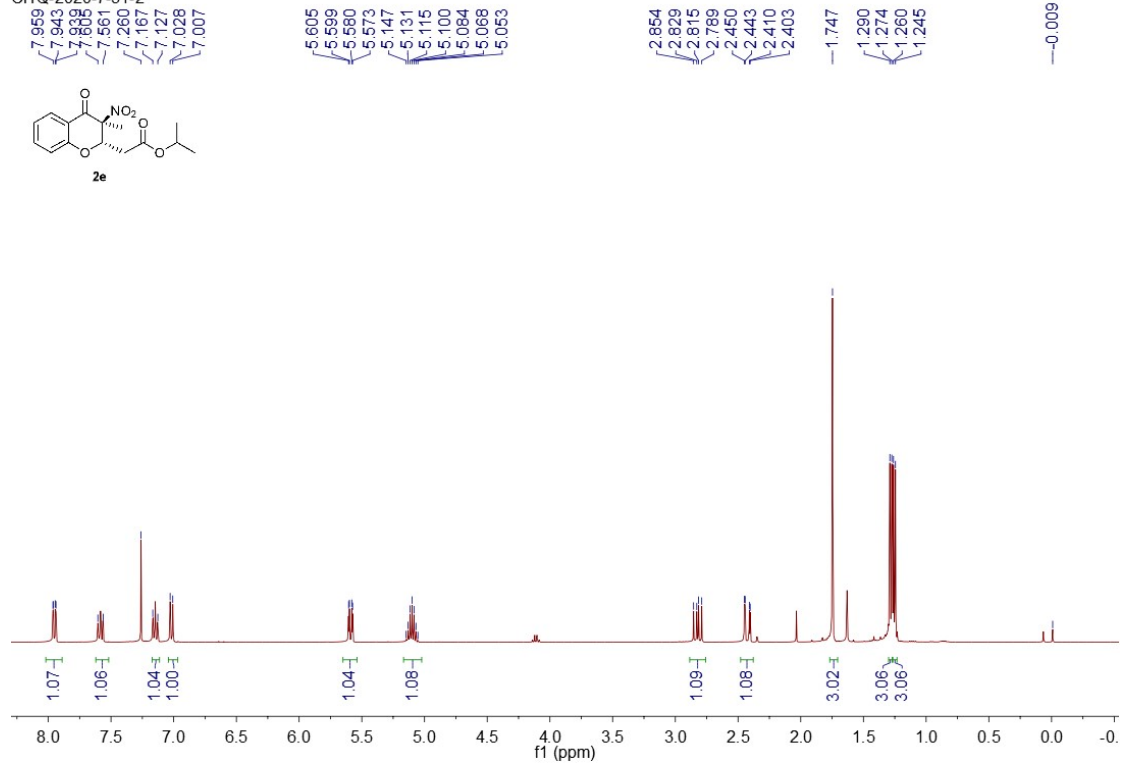
CHQ-2020-8-3-1



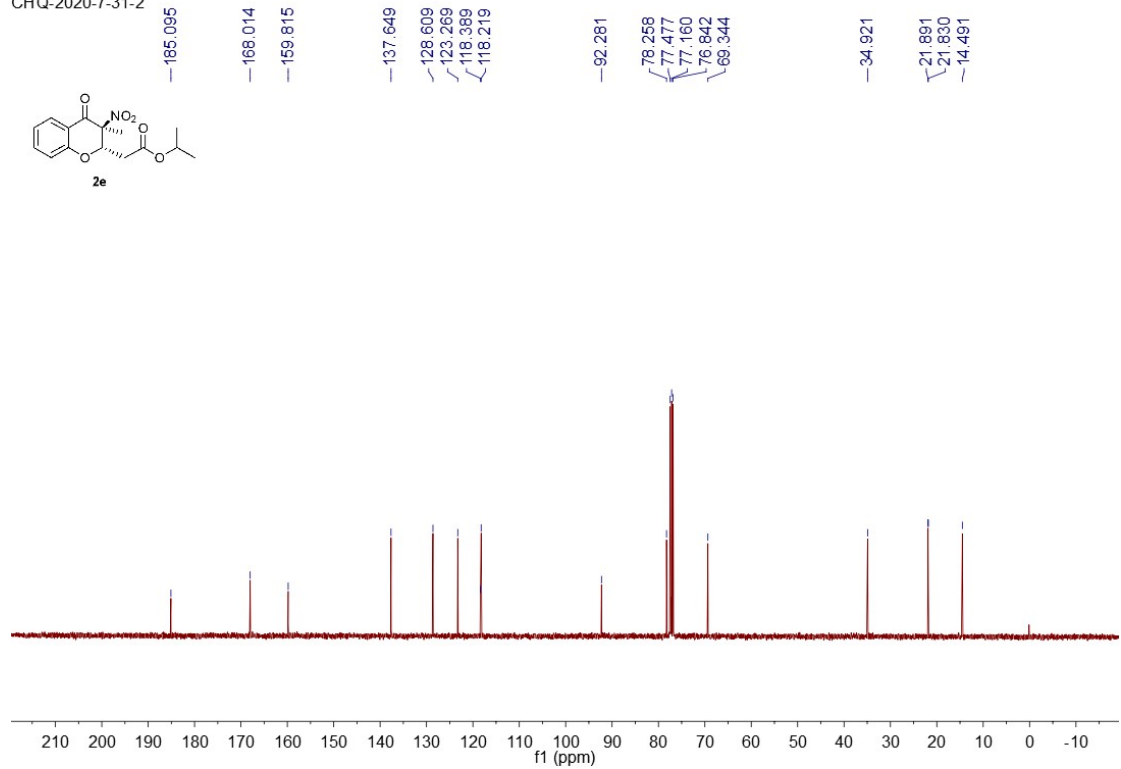
165.090
168.601
159.802
137.636
128.638
123.298
118.368
118.267
92.288
78.158
77.477
77.160
76.842
65.656
34.679
31.891
29.300
28.643
25.985
22.768
14.477
14.219



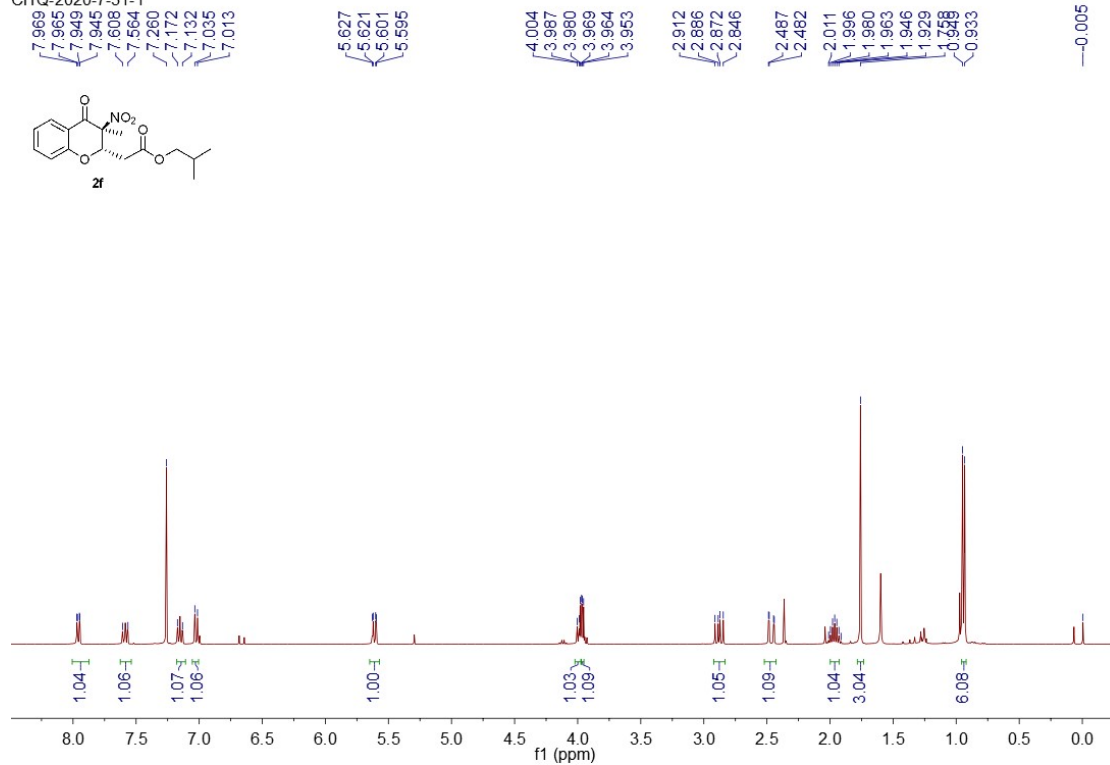
CHQ-2020-7-31-2



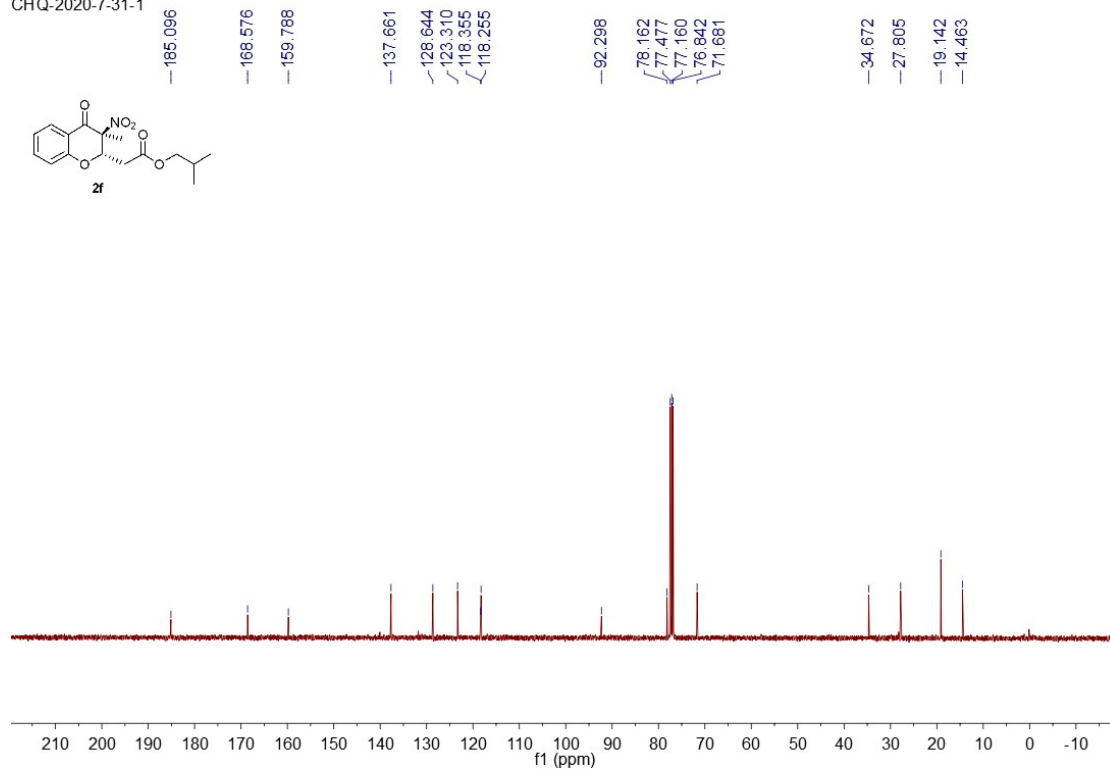
CHQ-2020-7-31-2



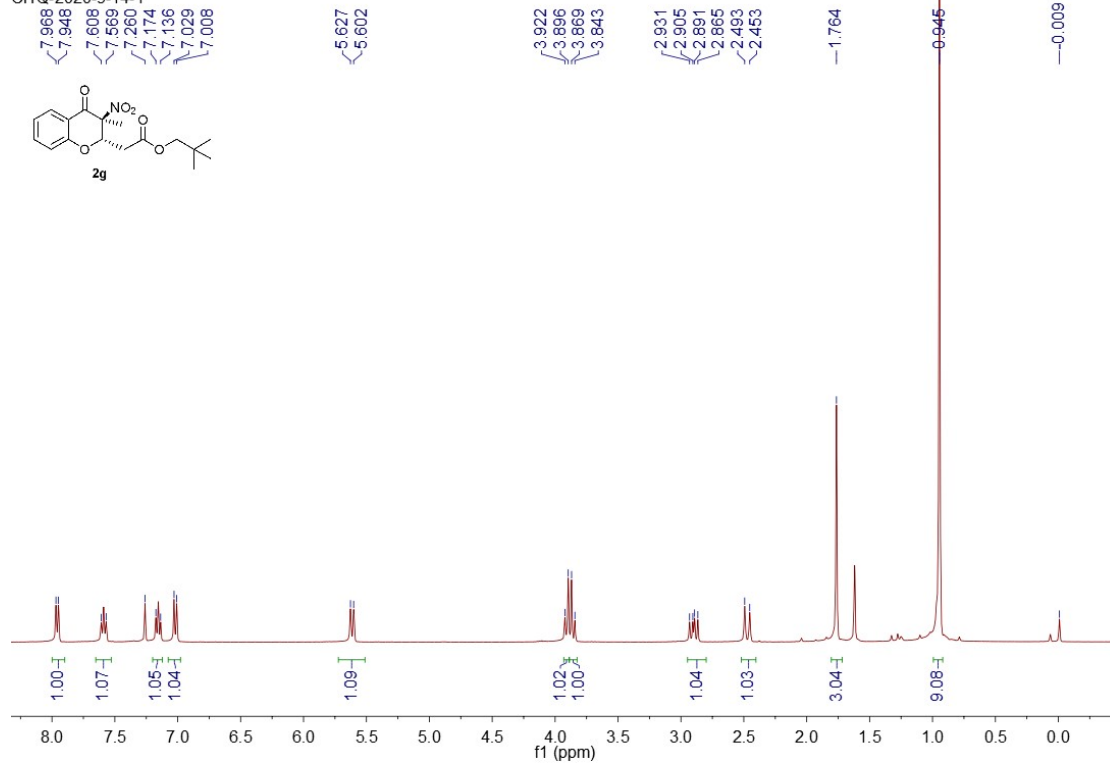
CHQ-2020-7-31-1



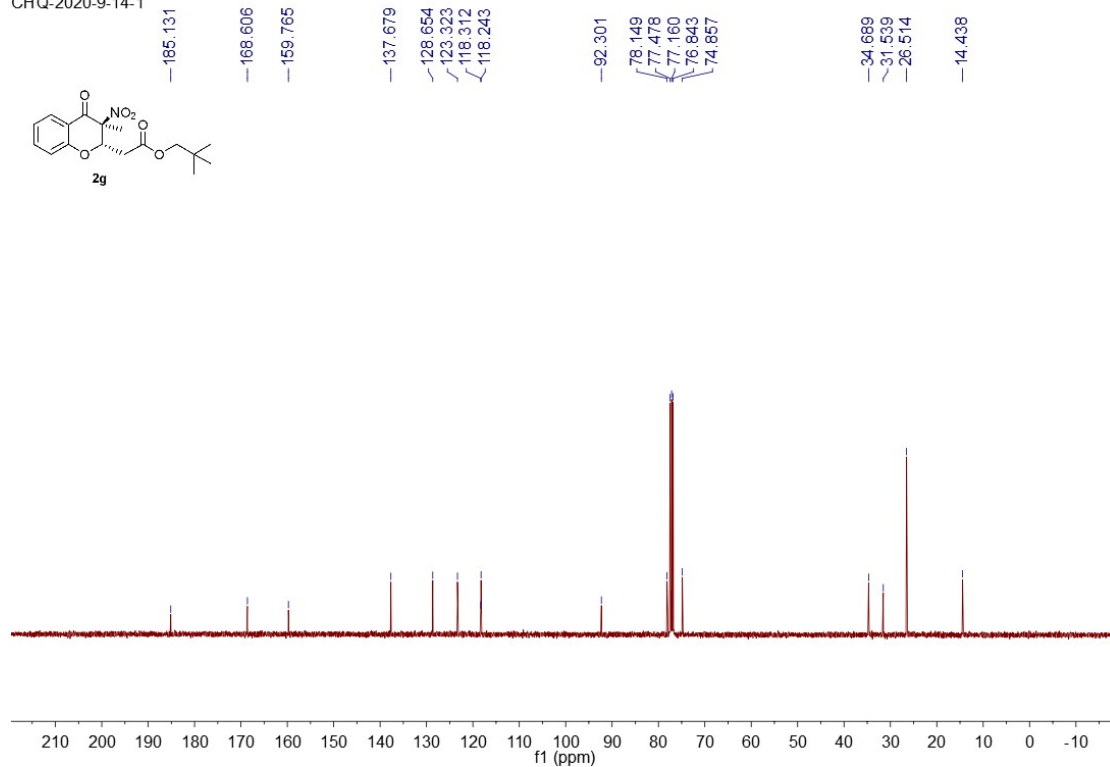
CHQ-2020-7-31-1



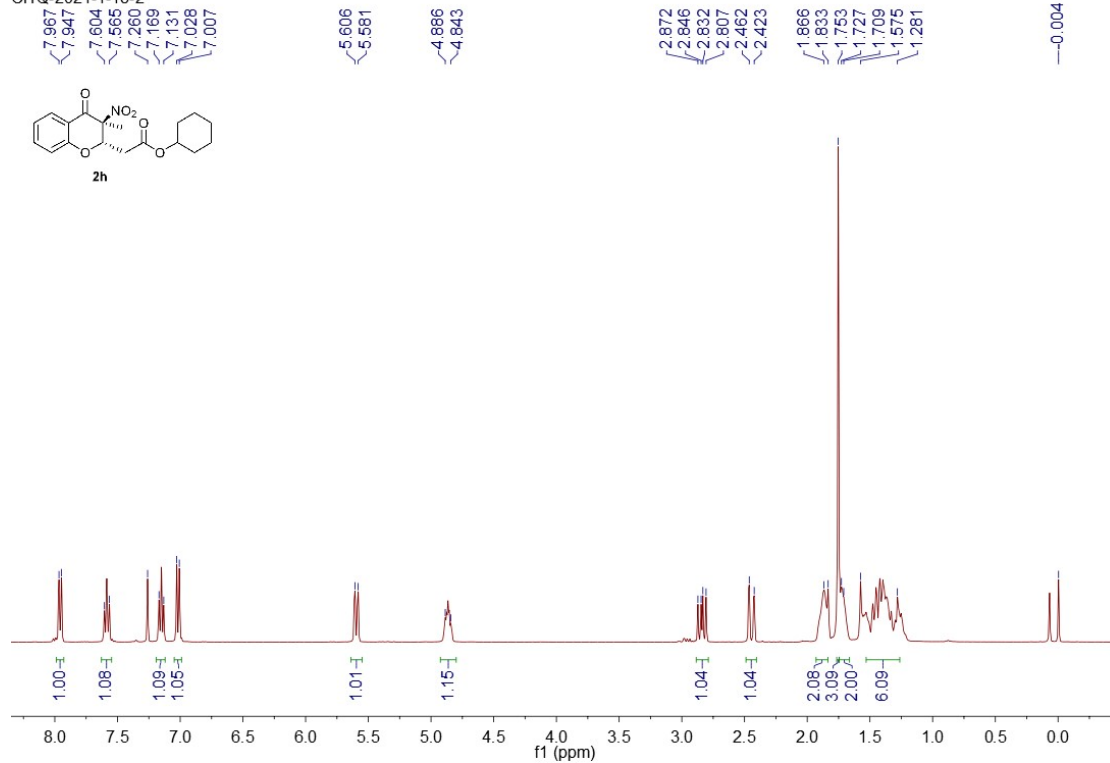
CHQ-2020-9-14-1



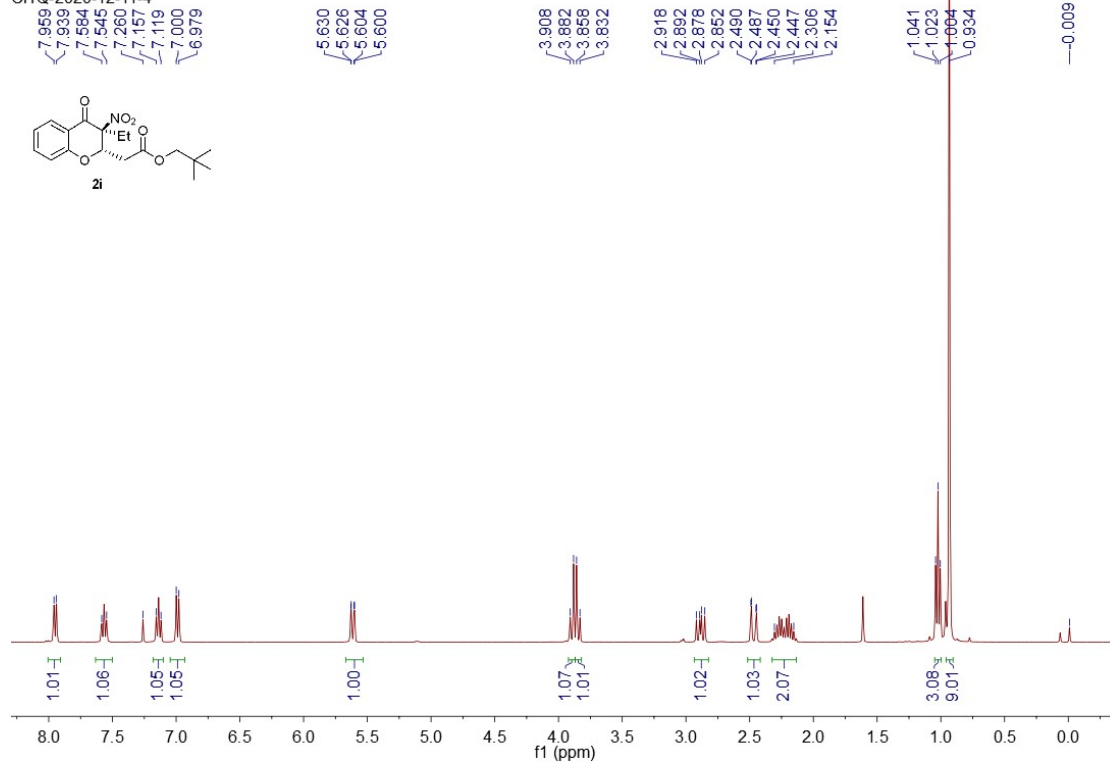
CHQ-2020-9-14-1



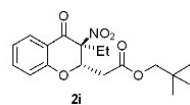
CHQ-2021-1-18-2



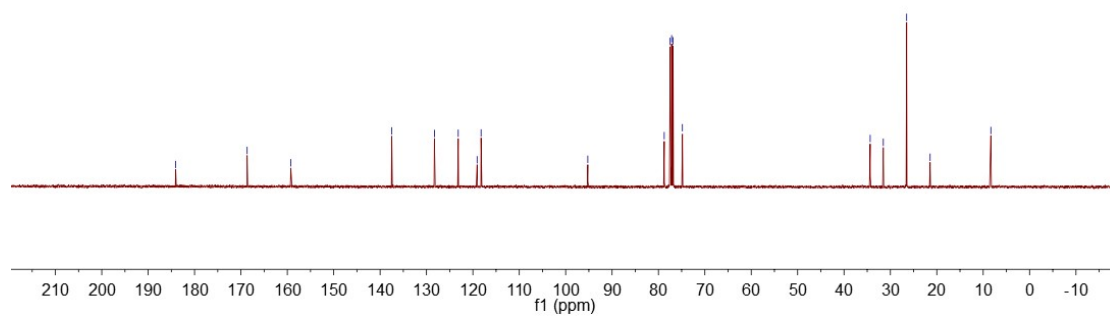
CHQ-2020-12-11-4



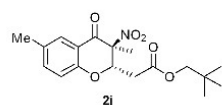
CHQ-2020-12-11-4



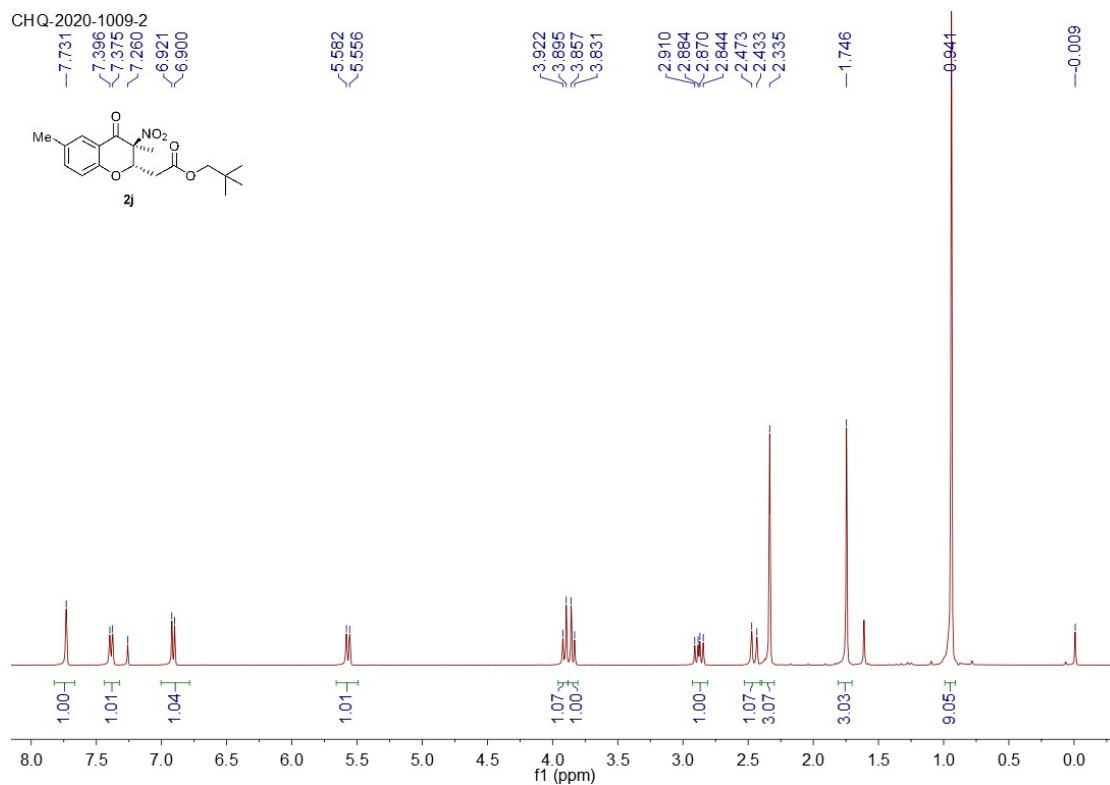
- 184.064
- 168.661
- 159.247
- 137.488
- 128.294
- 123.160
- 119.088
- 118.235
- 95.229
- 78.754
- 77.478
- 77.160
- 76.842
- 74.839
- 34.359
- 31.530
- 26.500
- 21.438
- 8.348



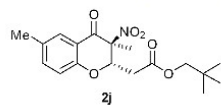
CHQ-2020-1009-2



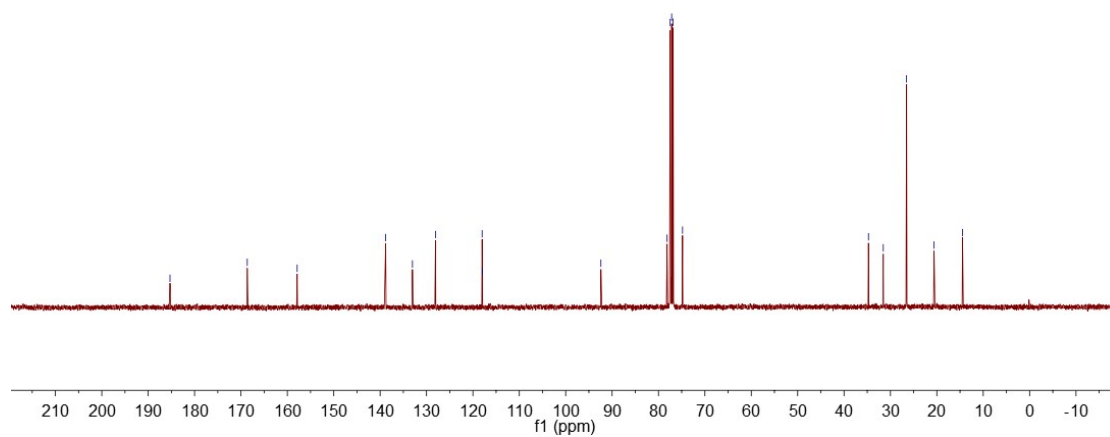
- 7.731
- 7.396
- 7.375
- 7.260
- 6.921
- 6.900
- 5.582
- 5.556
- 3.922
- 3.895
- 3.857
- 3.831
- 2.910
- 2.884
- 2.870
- 2.844
- 2.473
- 2.433
- 2.335
- 1.746
- 0.941
- 0.009



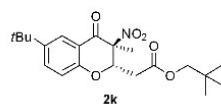
CHQ-2020-12-24-1



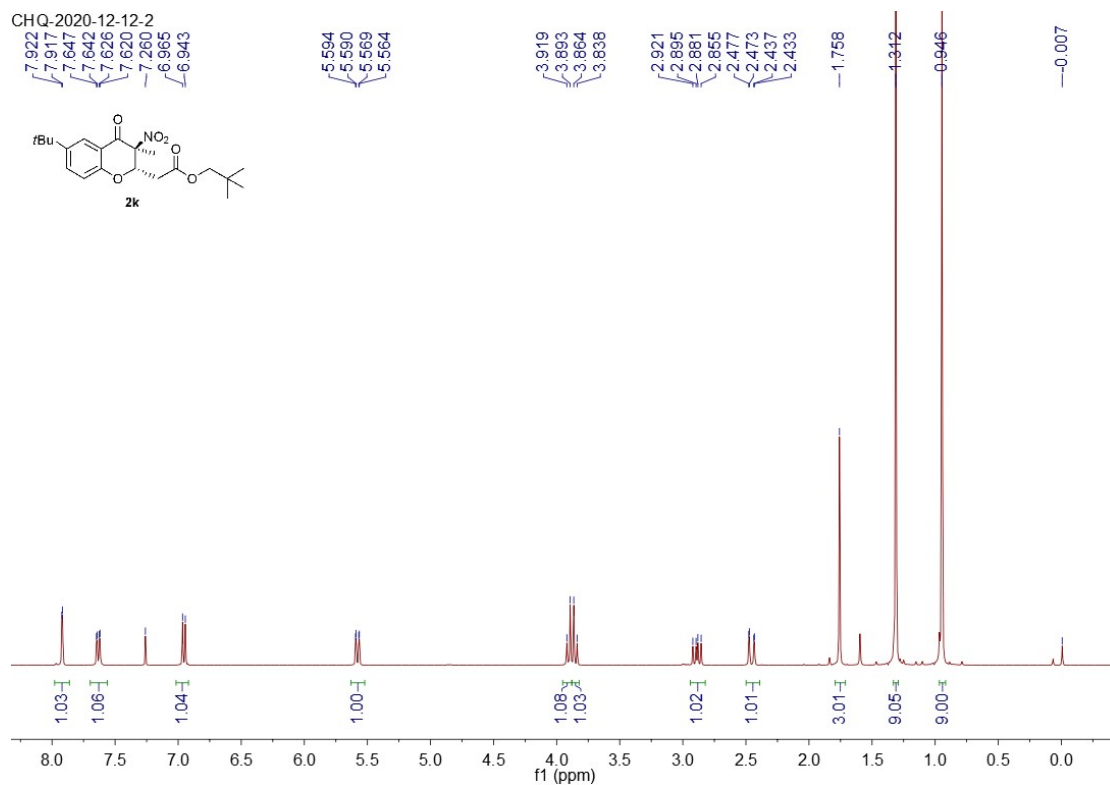
185.296
168.643
157.889
138.805
133.034
128.069
118.014
117.938
92.414
78.145
77.477
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76.842
74.814
34.733
31.543
26.521
20.591
14.454



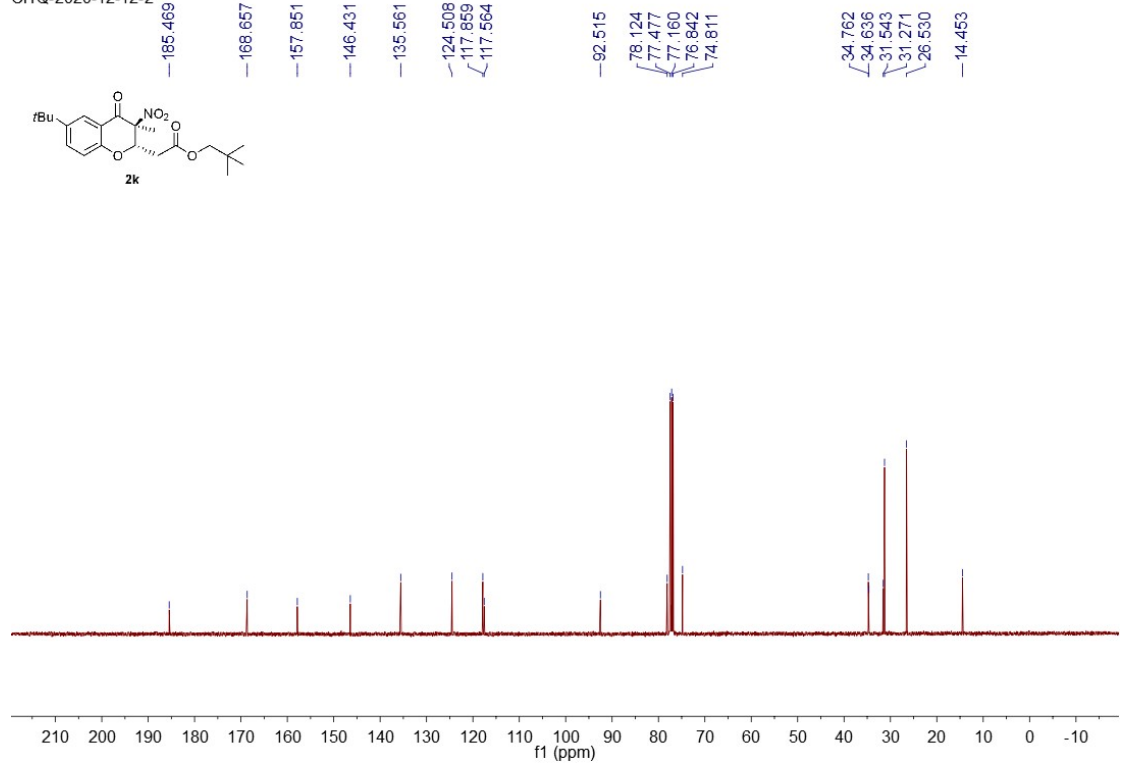
CHQ-2020-12-12-2



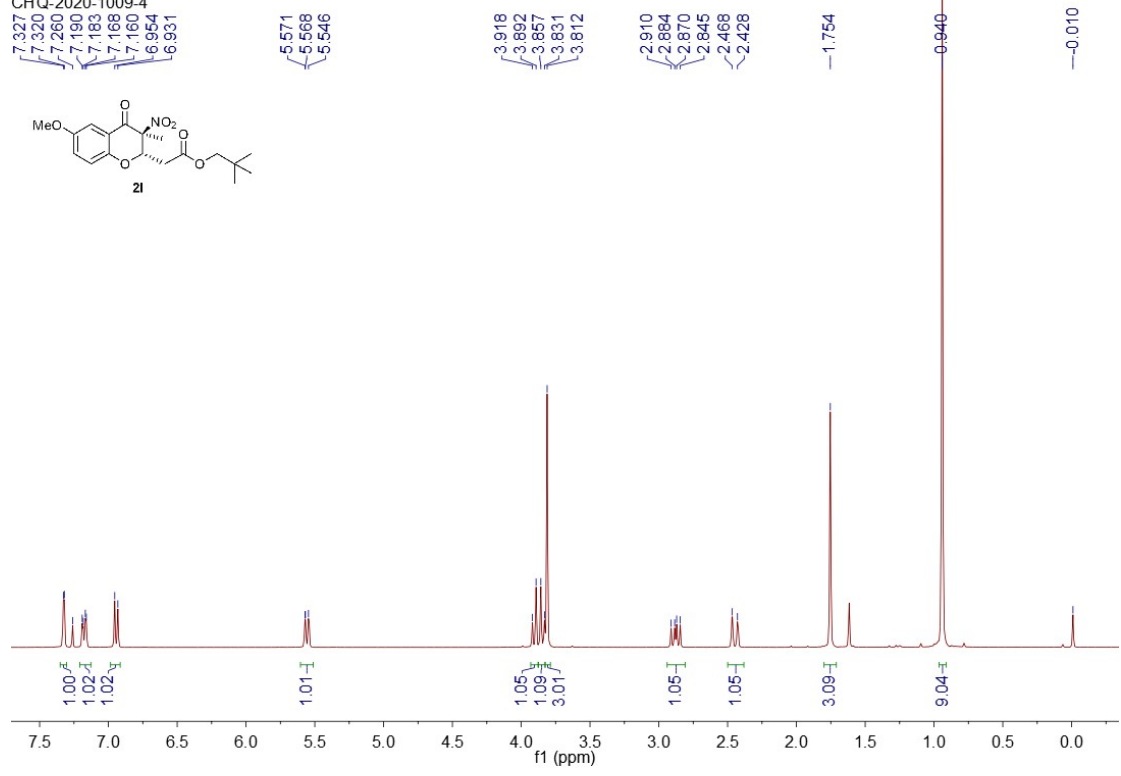
7.922
7.917
7.647
7.642
7.626
7.620
6.965
6.943
5.594
5.590
5.569
5.564
3.919
3.893
3.864
3.838
2.921
2.885
2.881
2.855
2.477
2.473
2.437
2.433
1.758
1.342
0.946
-0.007



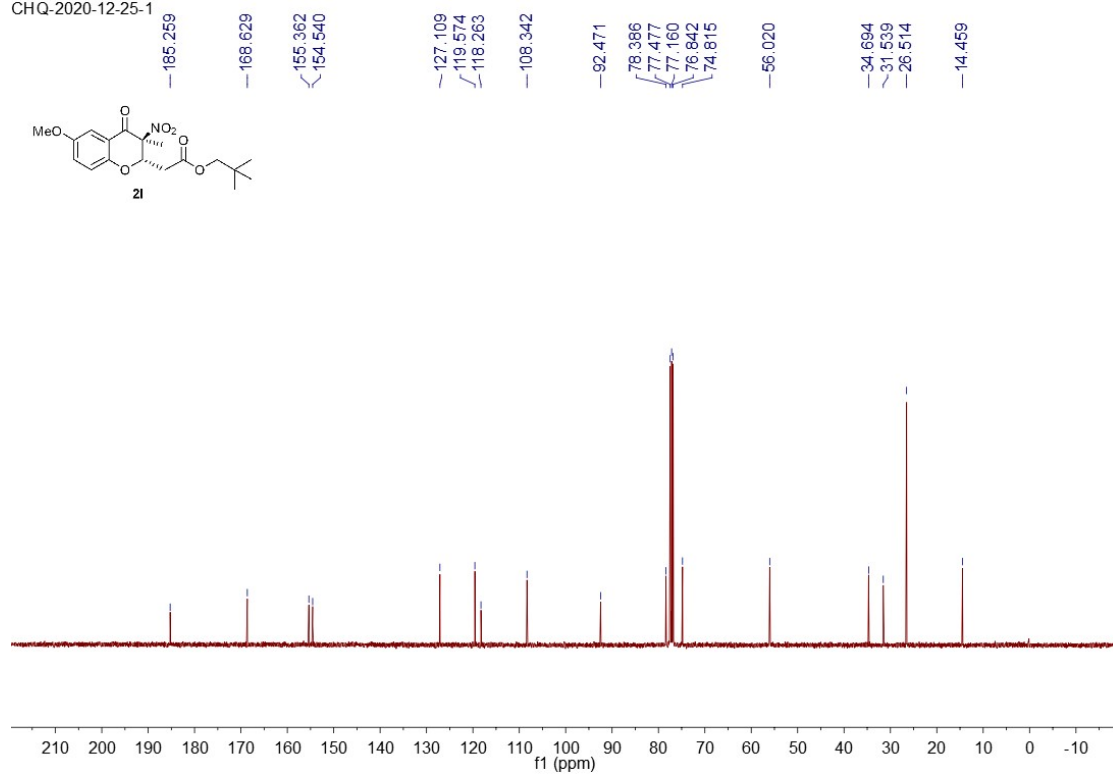
CHQ-2020-12-12-2



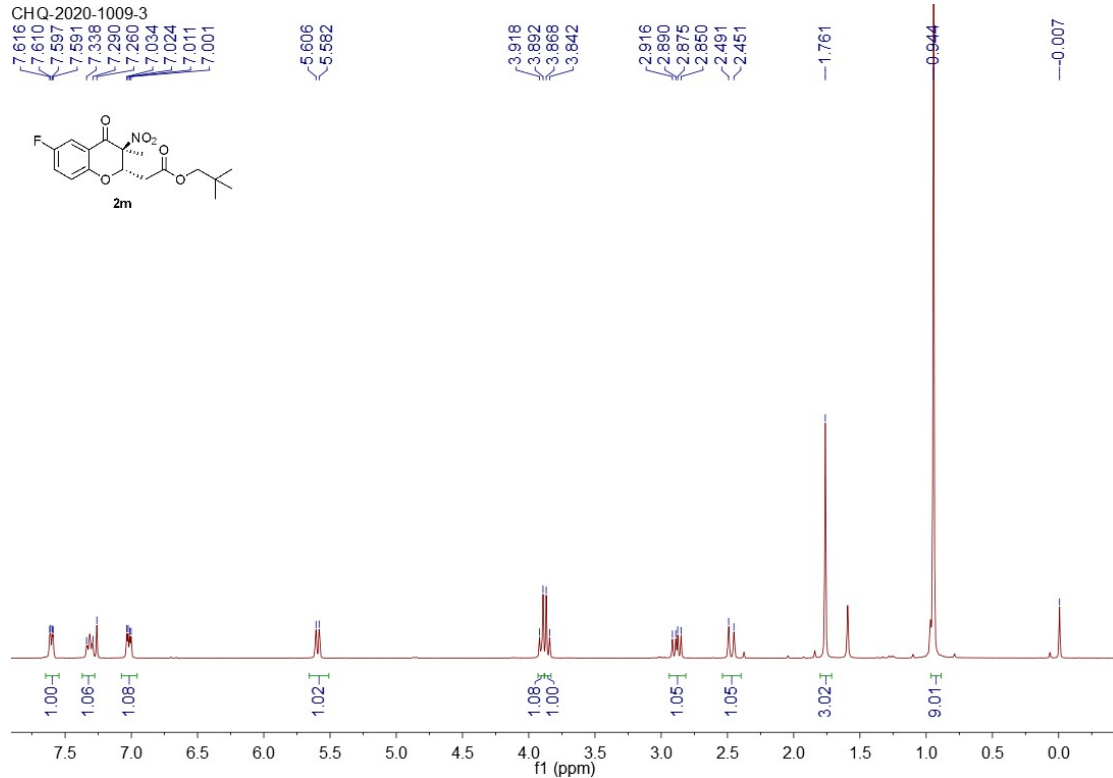
CHQ-2020-1009-4



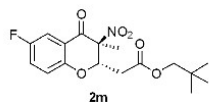
CHQ-2020-12-25-1



CHQ-2020-1009-3



CHQ-2020-12-24-2



184.451

168.457

159.386

156.950

156.025

156.009

125.548

125.302

120.179

120.104

119.052

118.982

113.670

113.432

92.068

78.569

77.478

77.160

76.842

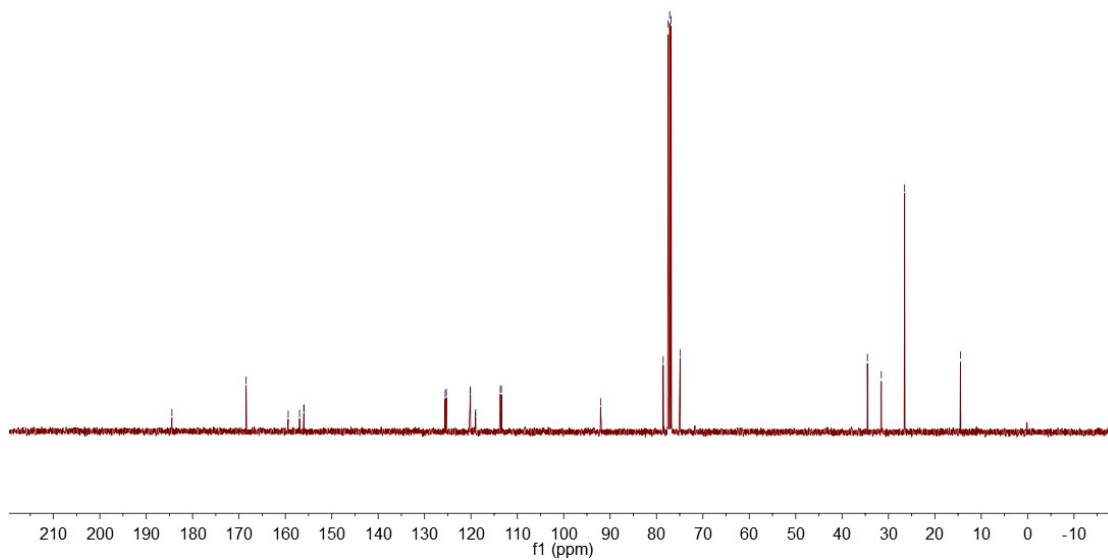
74.924

34.536

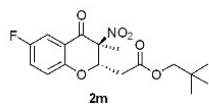
31.539

26.514

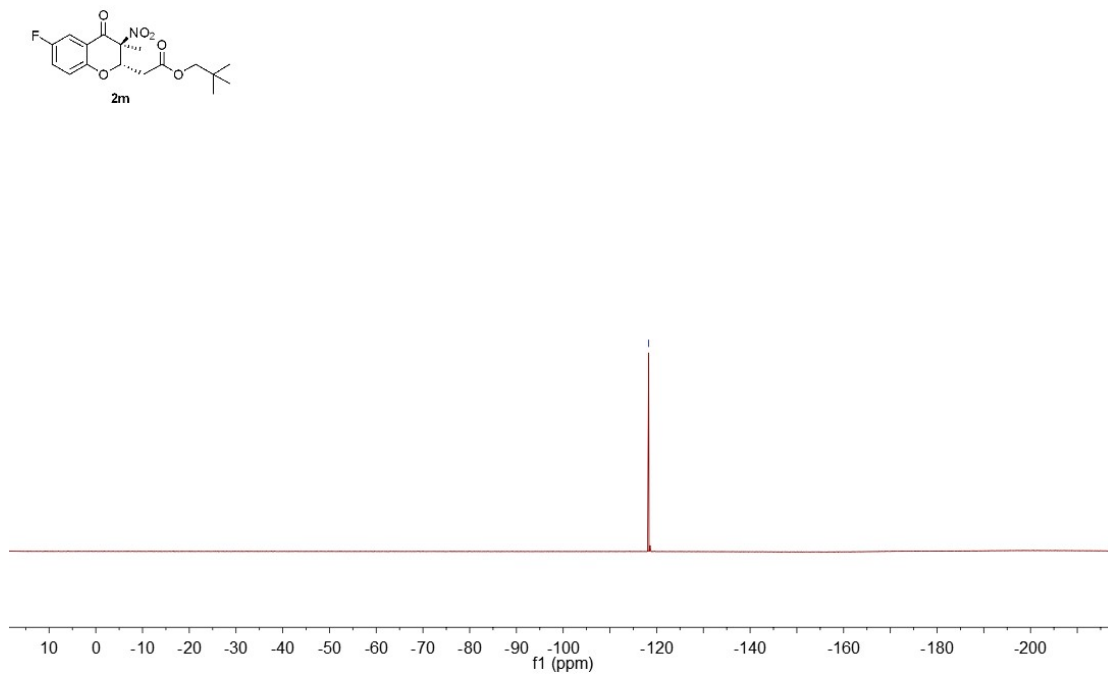
14.488



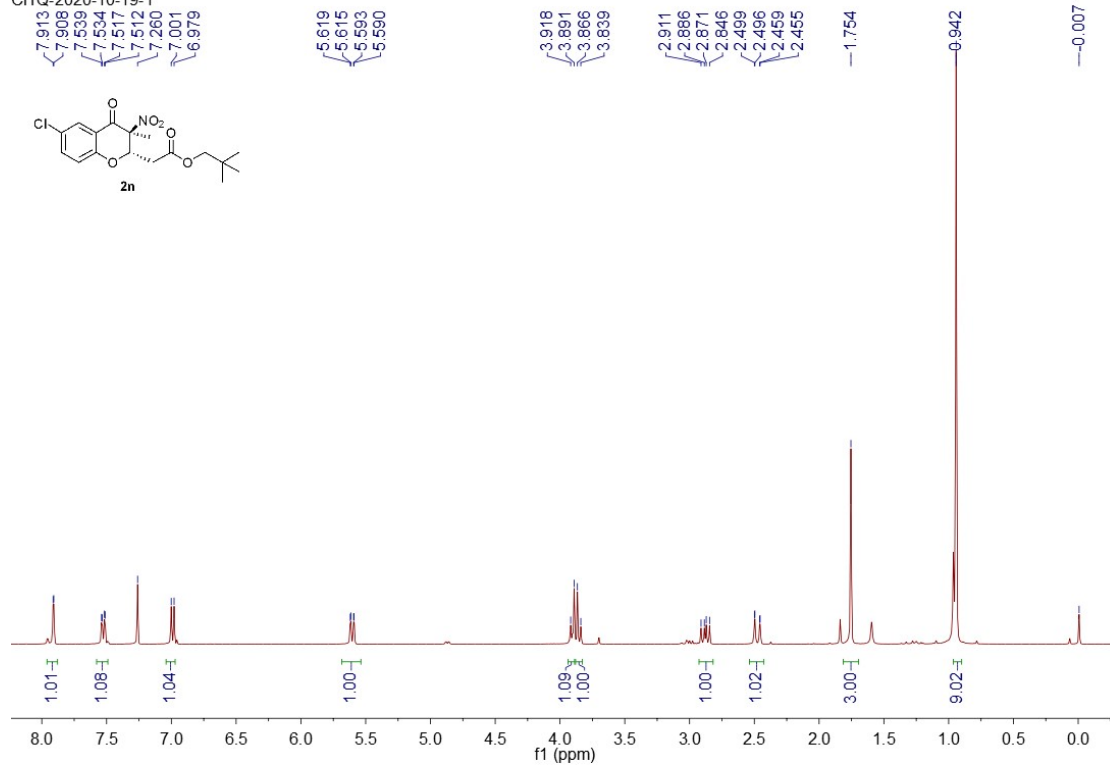
CHQ-2020-12-24-2



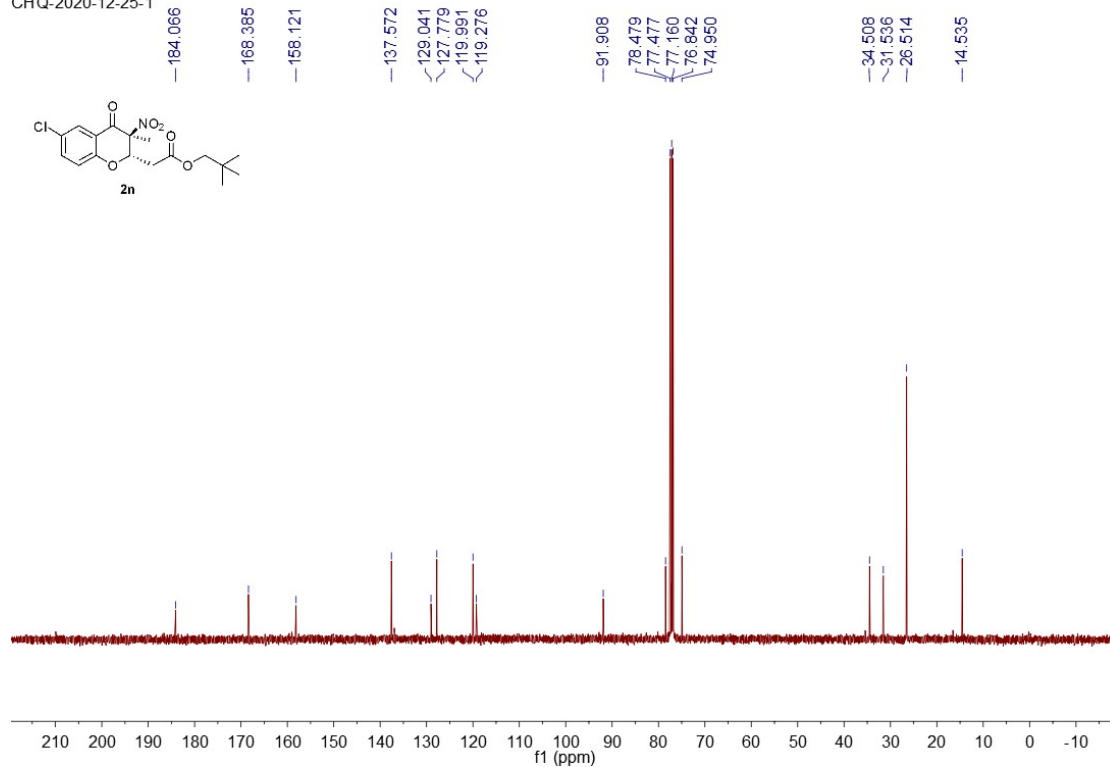
118.302



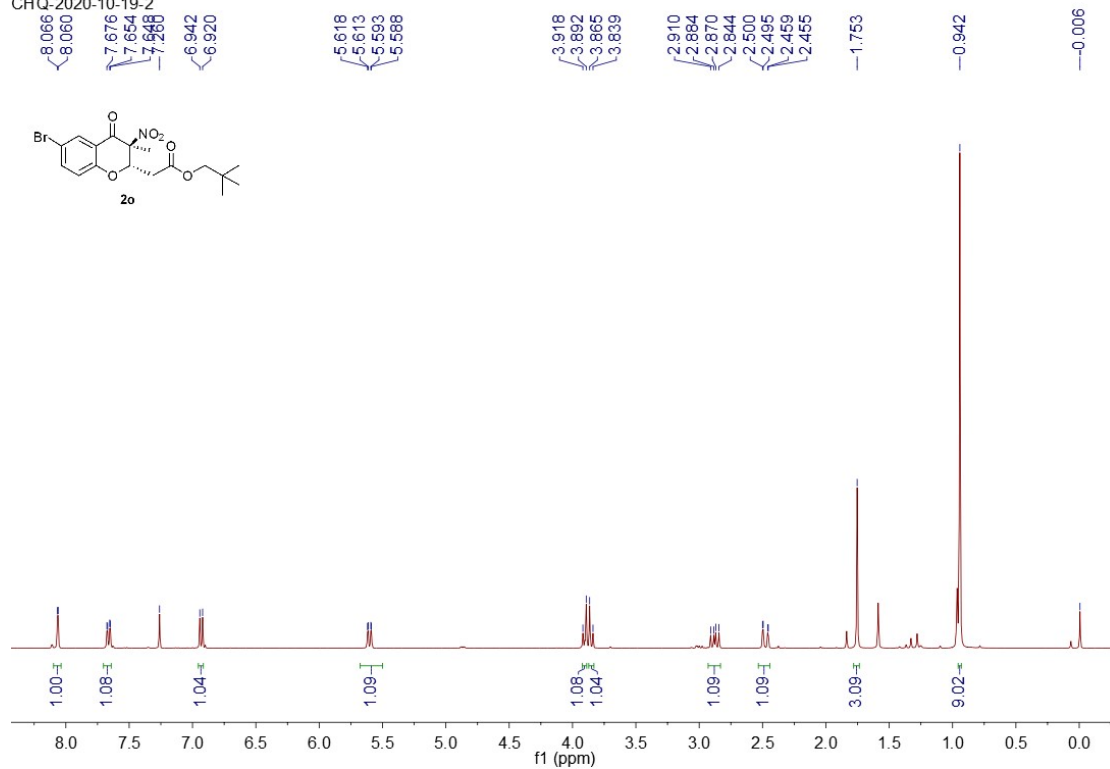
CHQ-2020-10-19-1



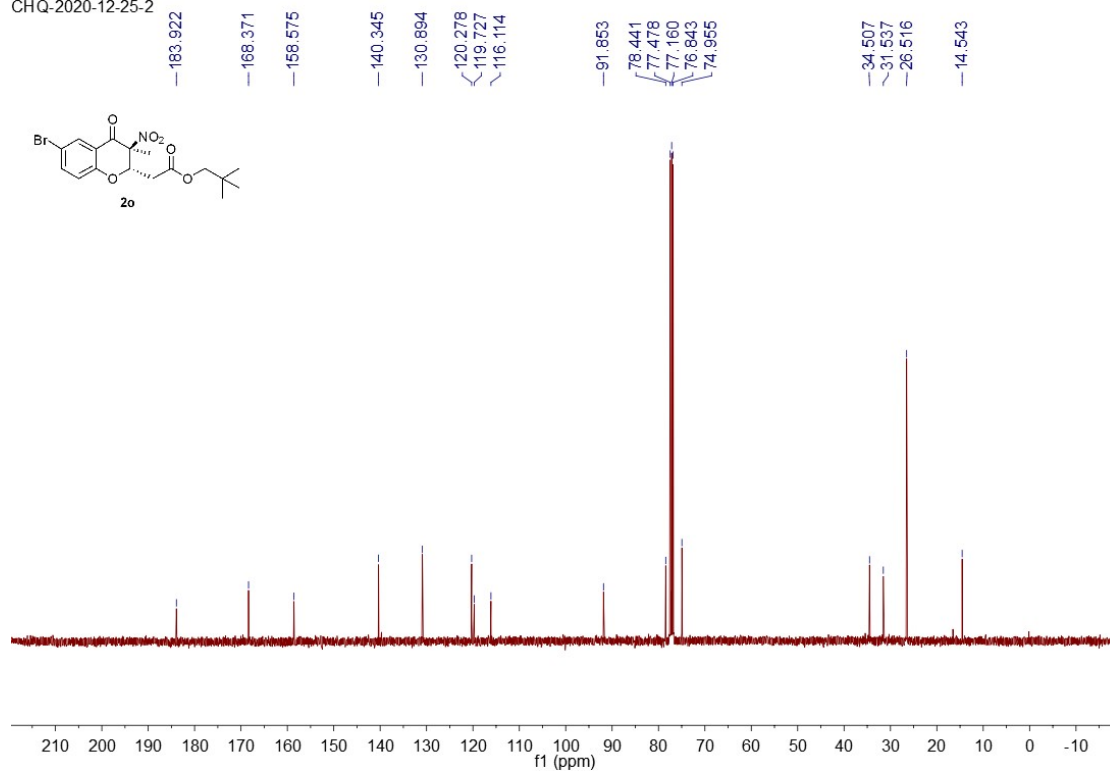
CHQ-2020-12-25-1



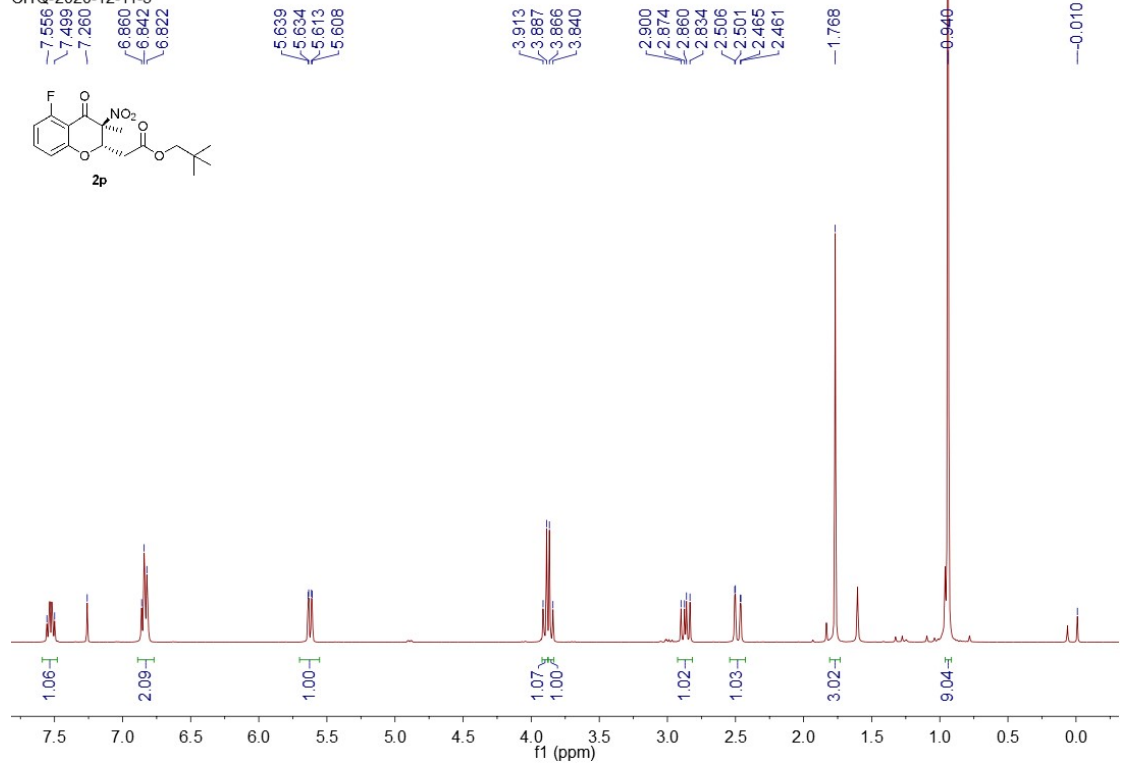
CHQ-2020-10-19-2



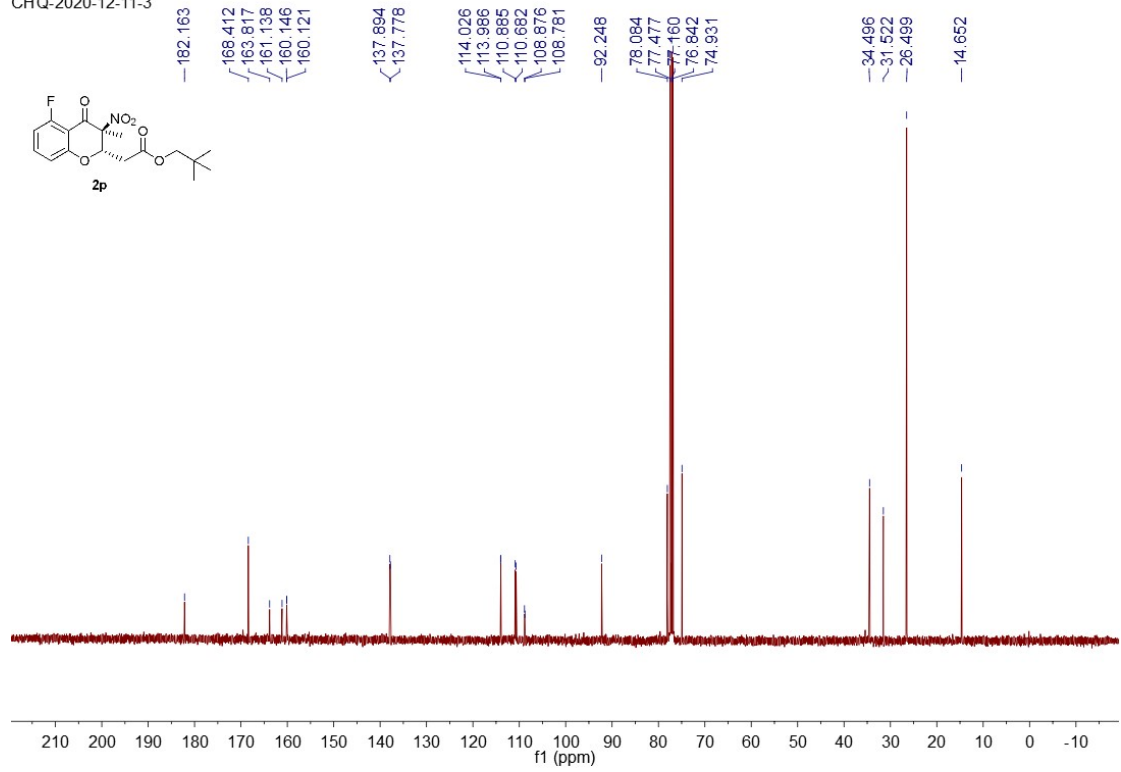
CHQ-2020-12-25-2



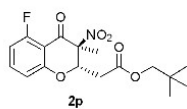
CHQ-2020-12-11-3



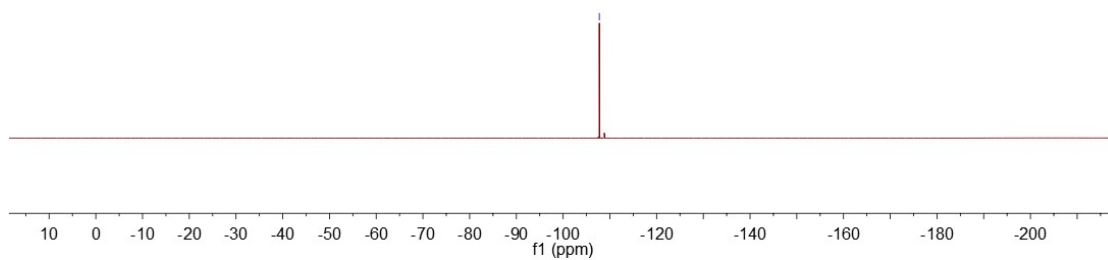
CHQ-2020-12-11-3



CHQ-2020-12-26-3



--107.742



CHQ-2020-12-17-1

7.456
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7.260
7.187
7.168
6.957
6.936

5.641
5.616

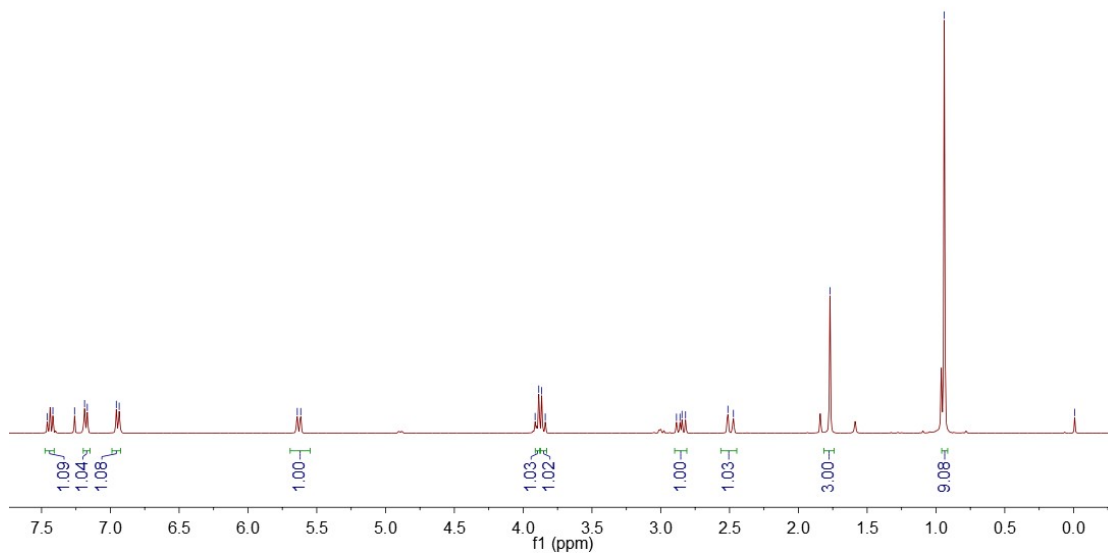
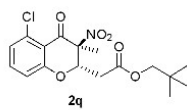
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3.887
3.866
3.839

2.866
2.860
2.845
2.820
2.512
2.472

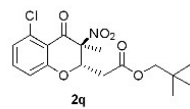
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-0.940

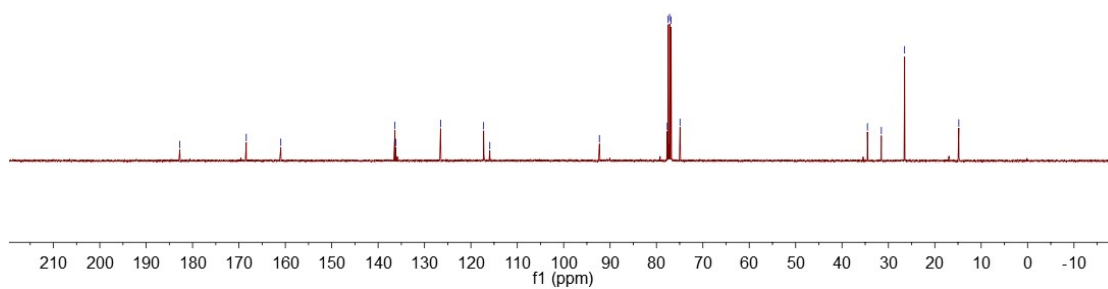
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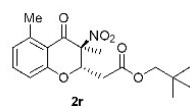
CHQ-2020-12-17-1



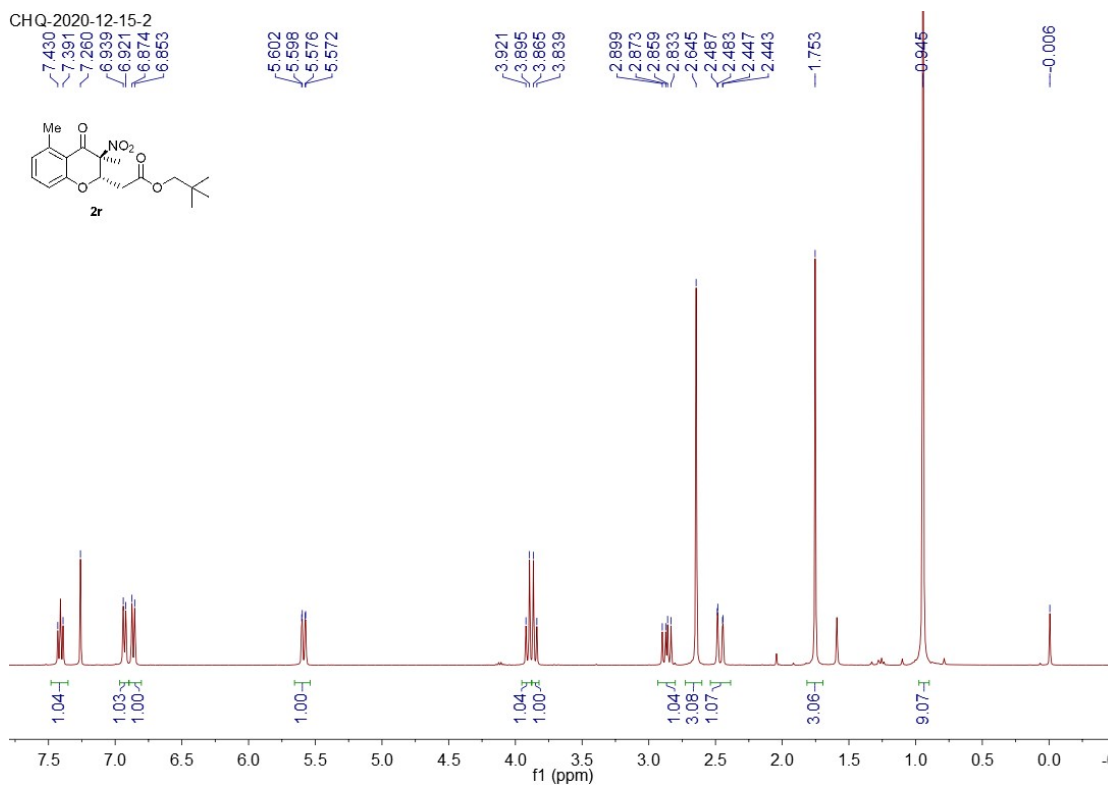
182.742
168.424
160.973
136.374
136.207
126.534
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77.478
77.160
76.843
74.927
34.527
31.522
26.507
14.821



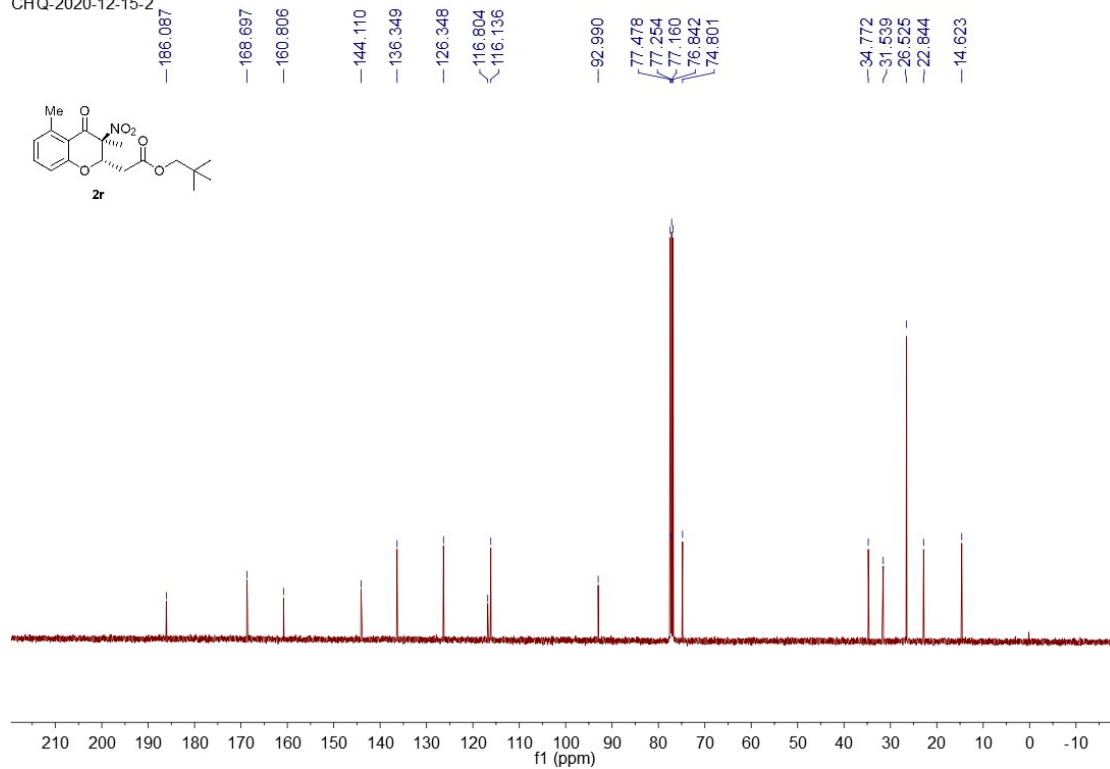
CHQ-2020-12-15-2



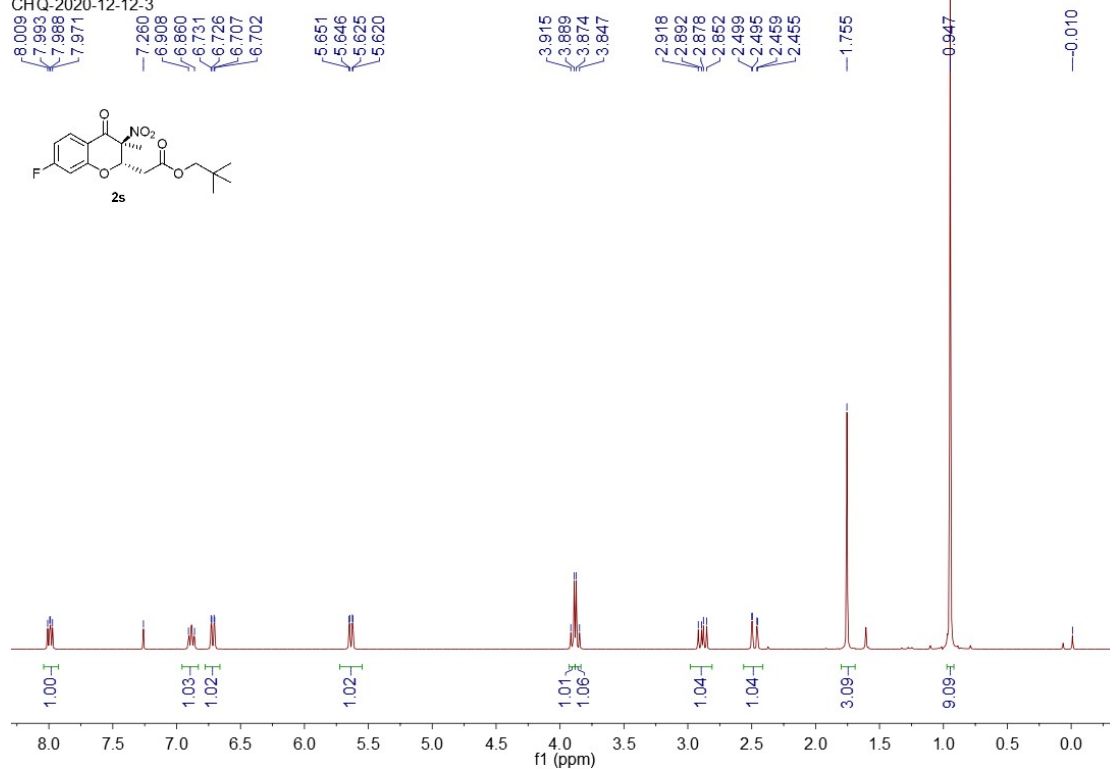
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6.921
6.874
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5.602
5.598
5.576
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3.895
3.865
3.839
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0.945
0.006



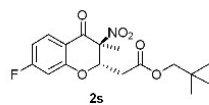
CHQ-2020-12-15-2



CHQ-2020-12-12-3



CHQ-2020-12-12-3



183.739
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168.395
167.095
161.500
161.362

131.393
131.278

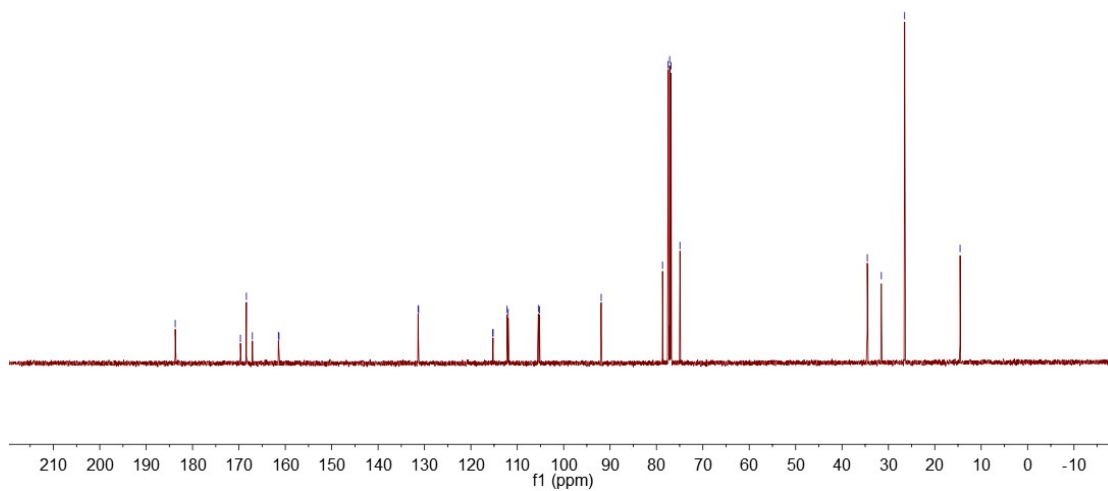
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91.915

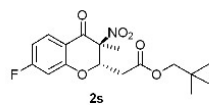
78.693
77.478
77.160
76.842
74.940

34.551
31.523
26.498

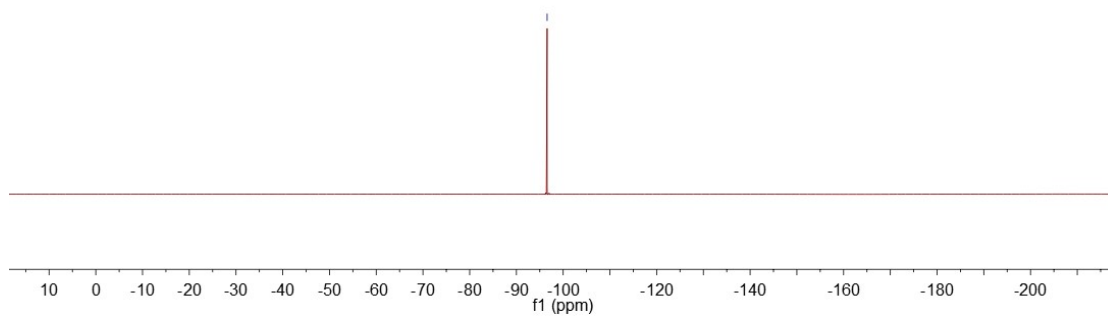
14.552



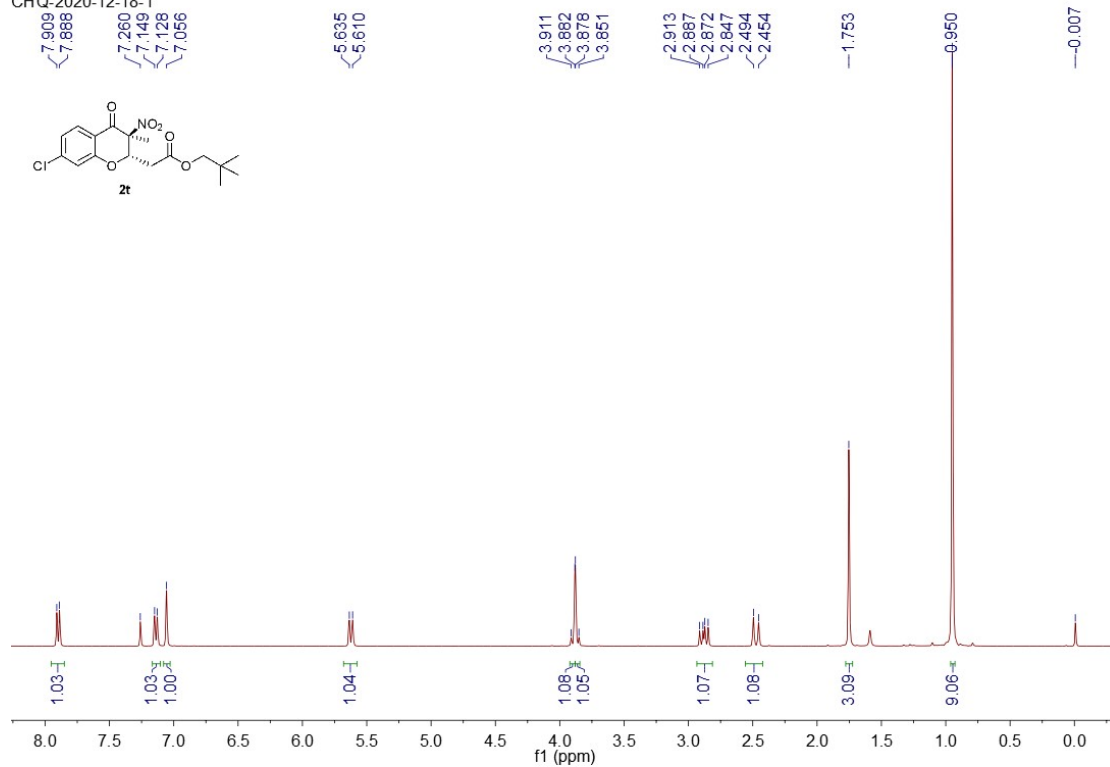
CHQ-2020-12-12-3



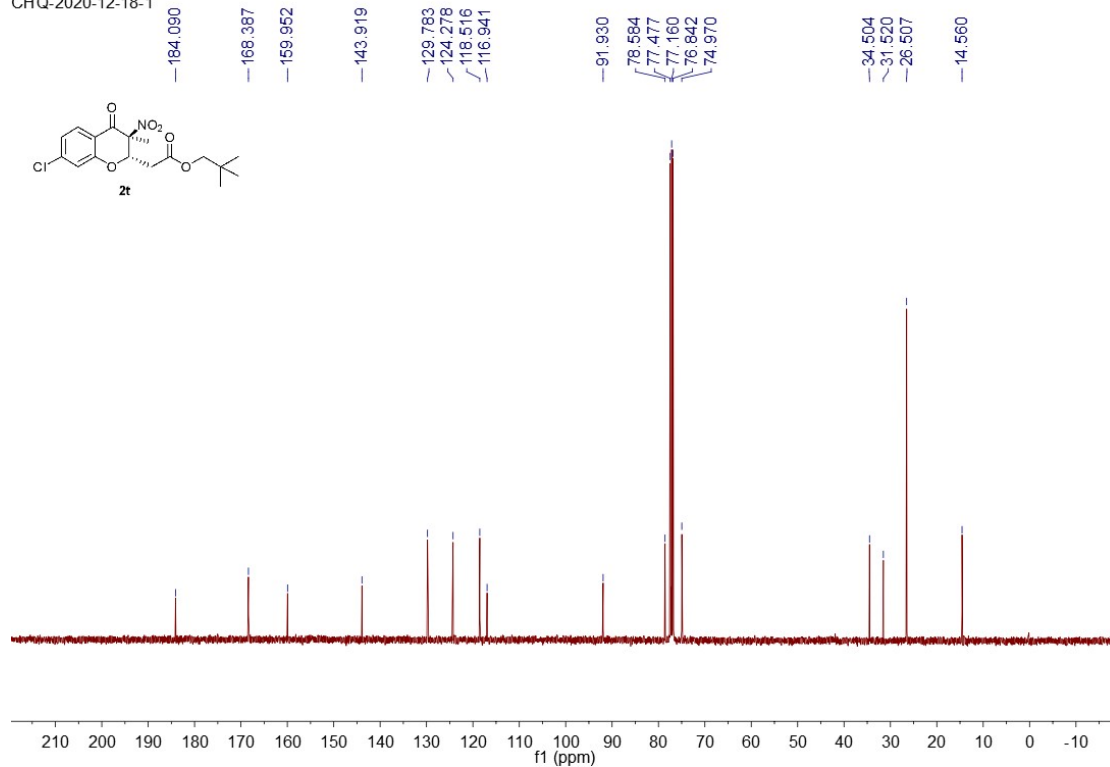
96.569



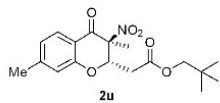
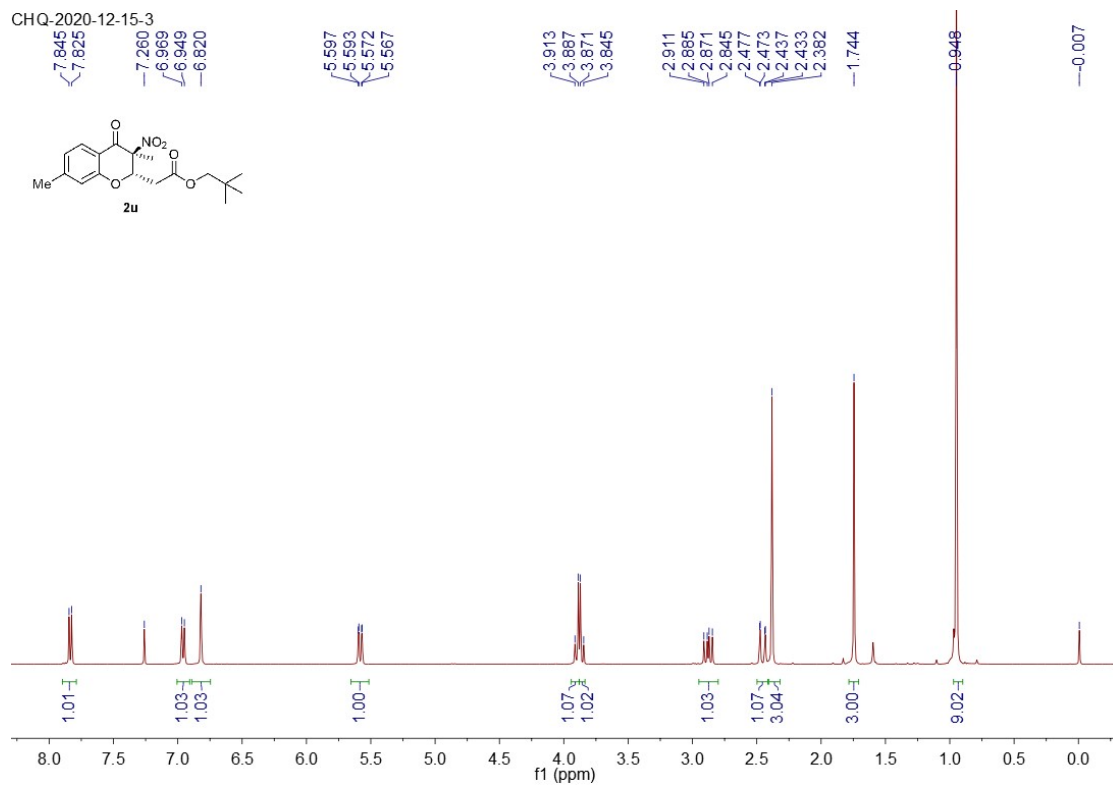
CHQ-2020-12-18-1



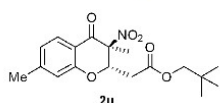
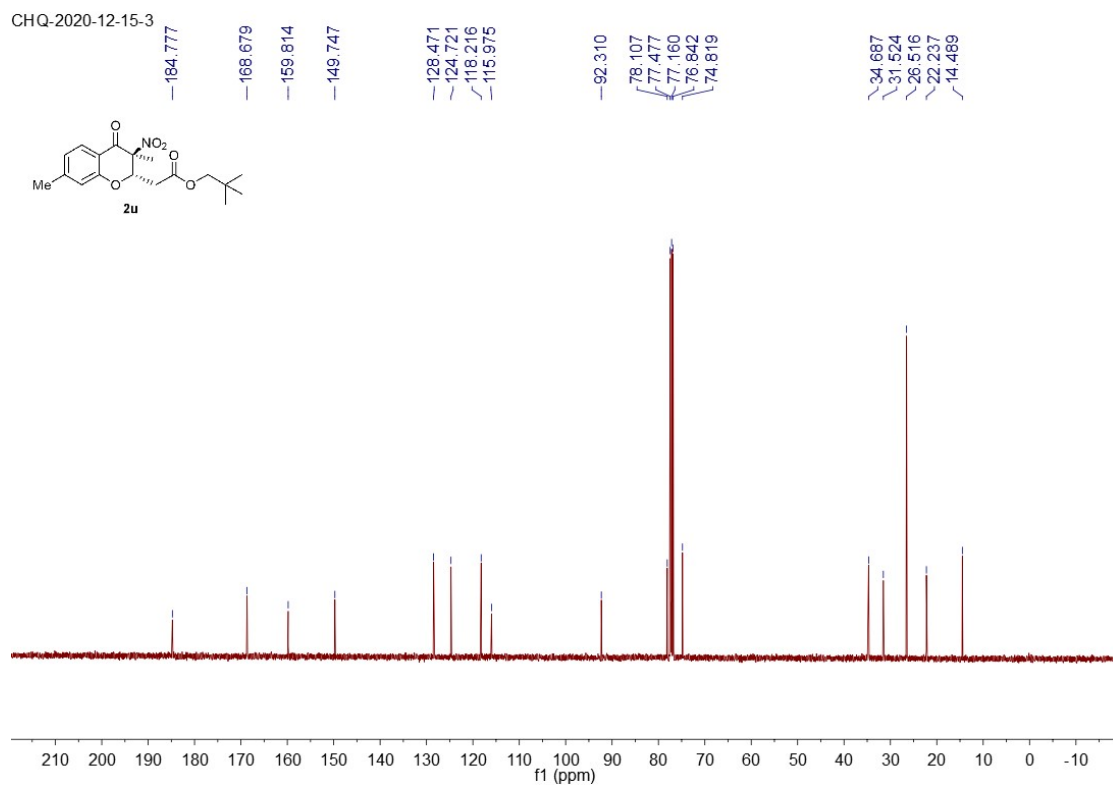
CHQ-2020-12-18-1



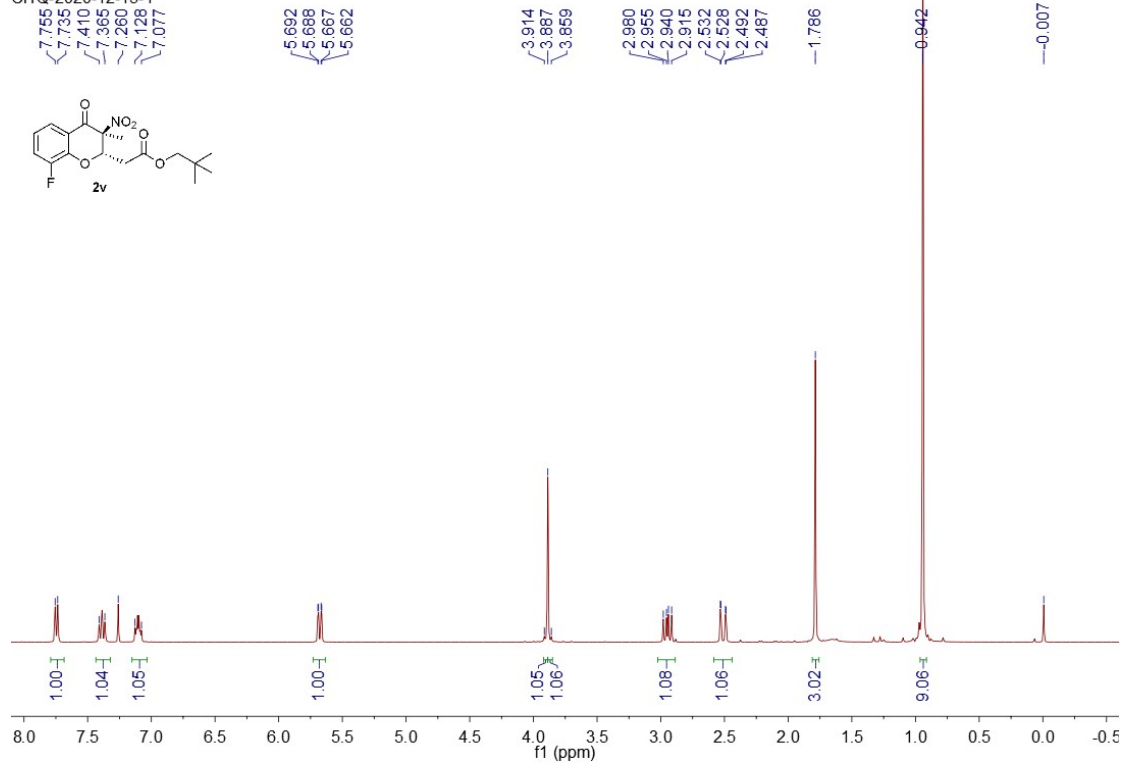
CHQ-2020-12-15-3



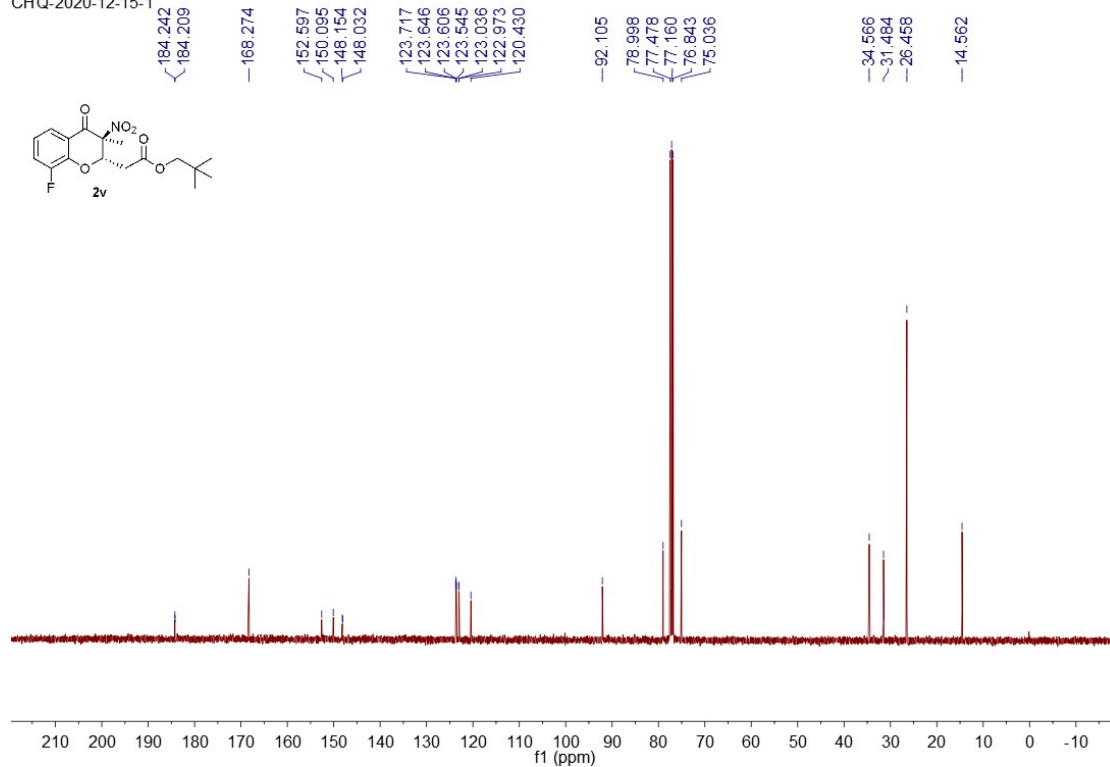
CHQ-2020-12-15-3



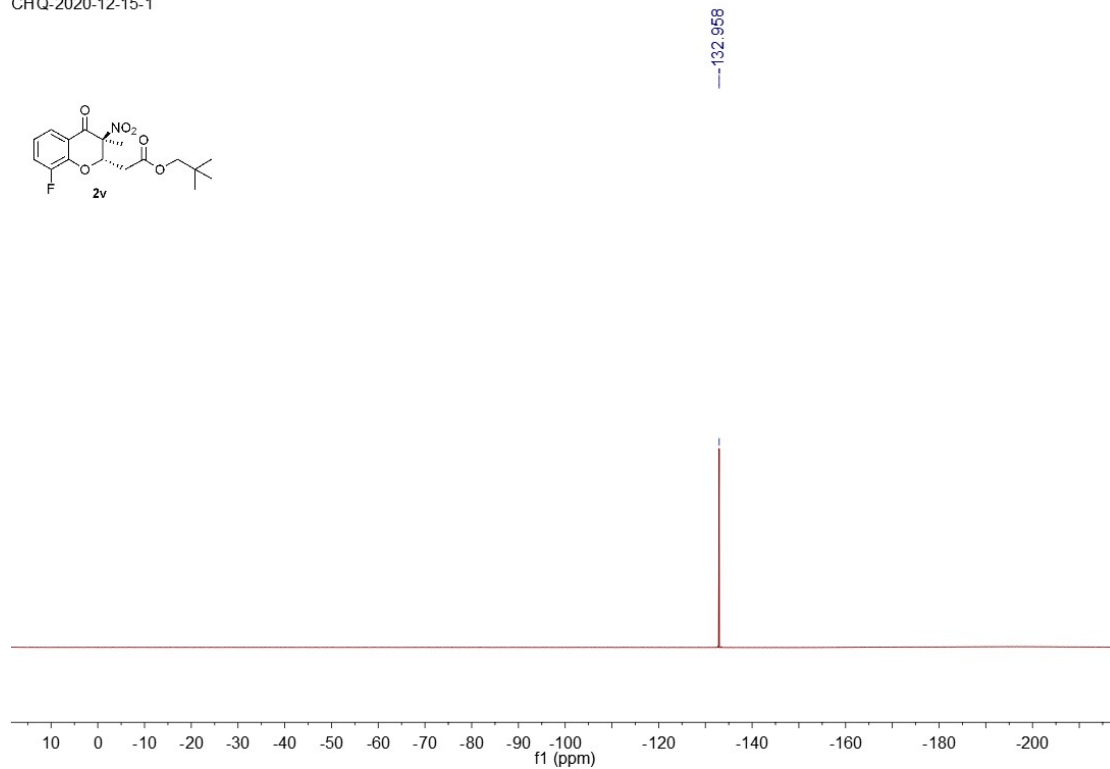
CHQ-2020-12-15-1



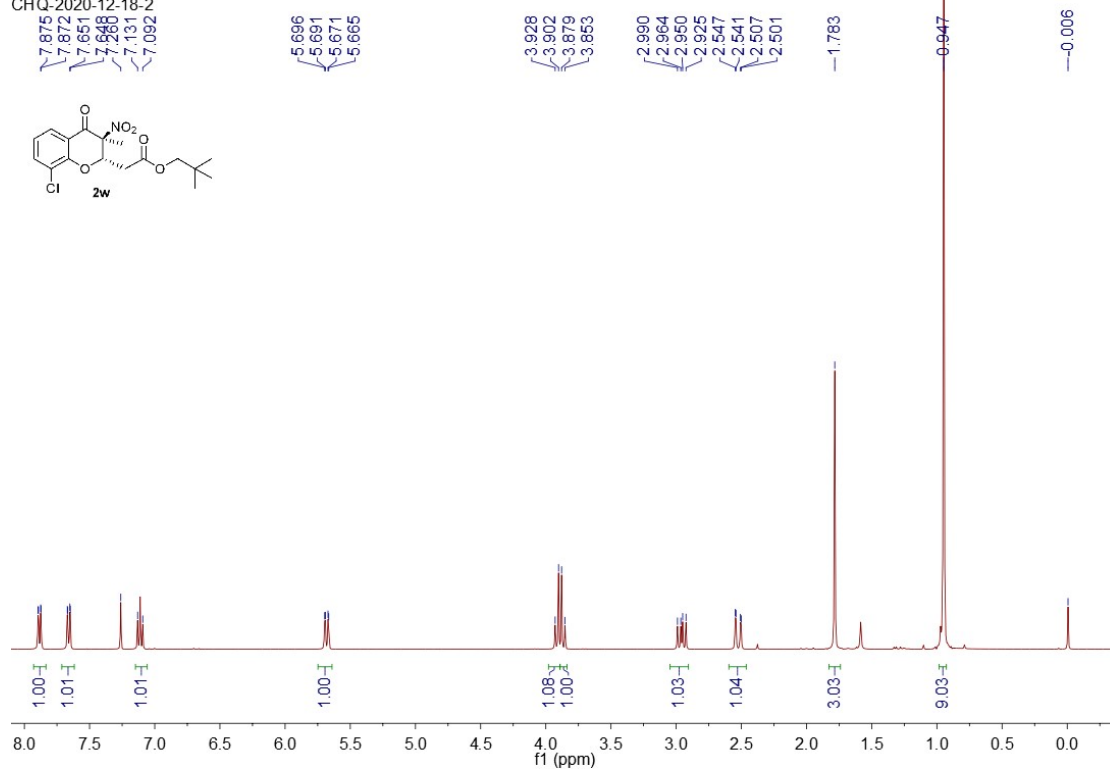
CHQ-2020-12-15-1



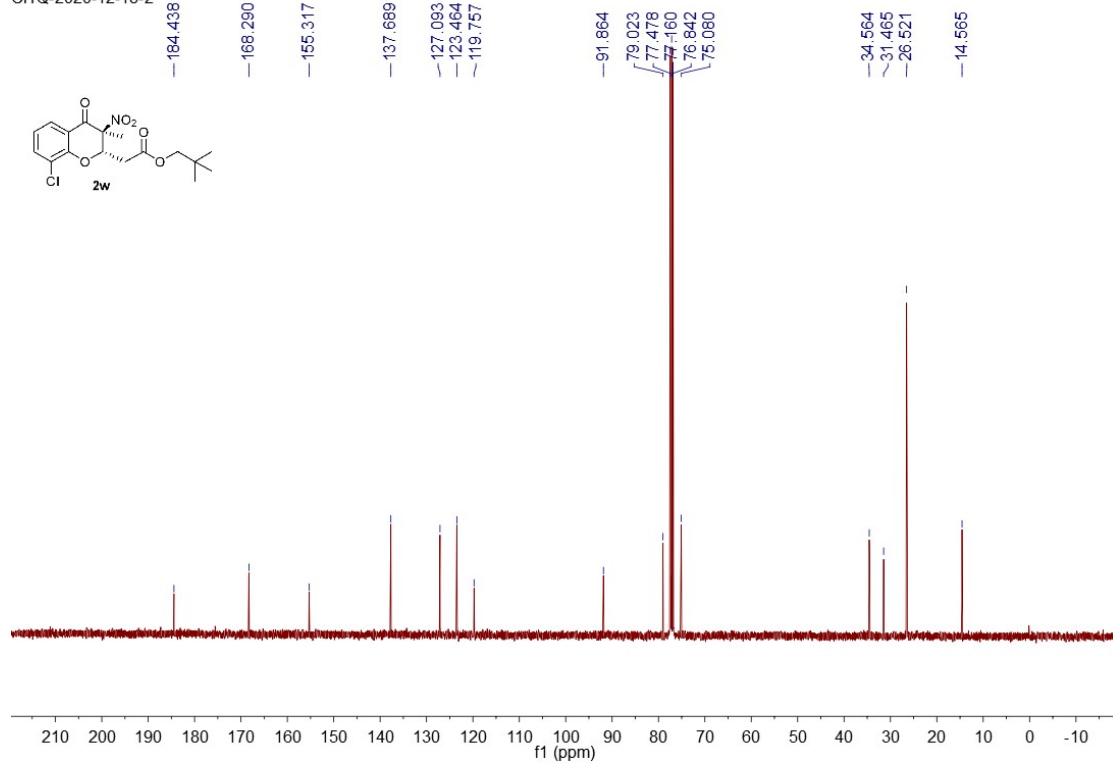
CHQ-2020-12-15-1



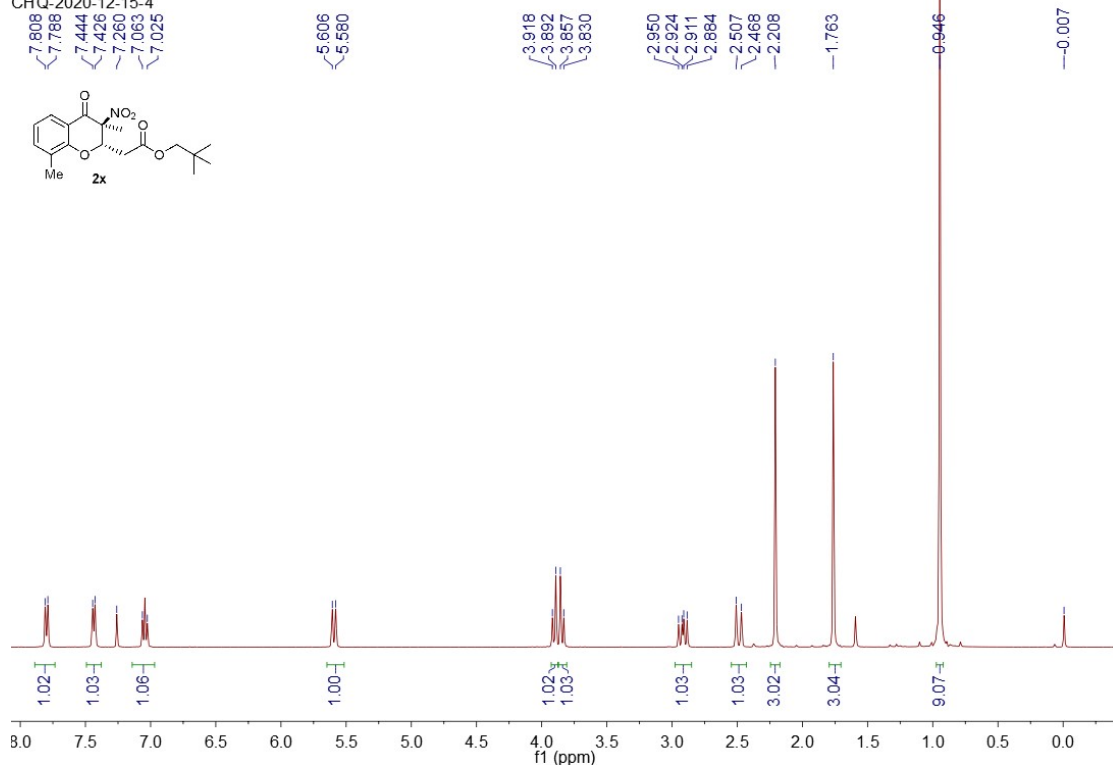
CHQ-2020-12-18-2



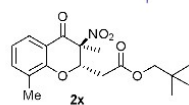
CHQ-2020-12-18-2



CHQ-2020-12-15-4



CHQ-2020-12-15-4



185.470

168.716

158.012

138.544

127.750

126.207

122.815

118.087

92.264

78.176

77.477

77.160

76.842

74.890

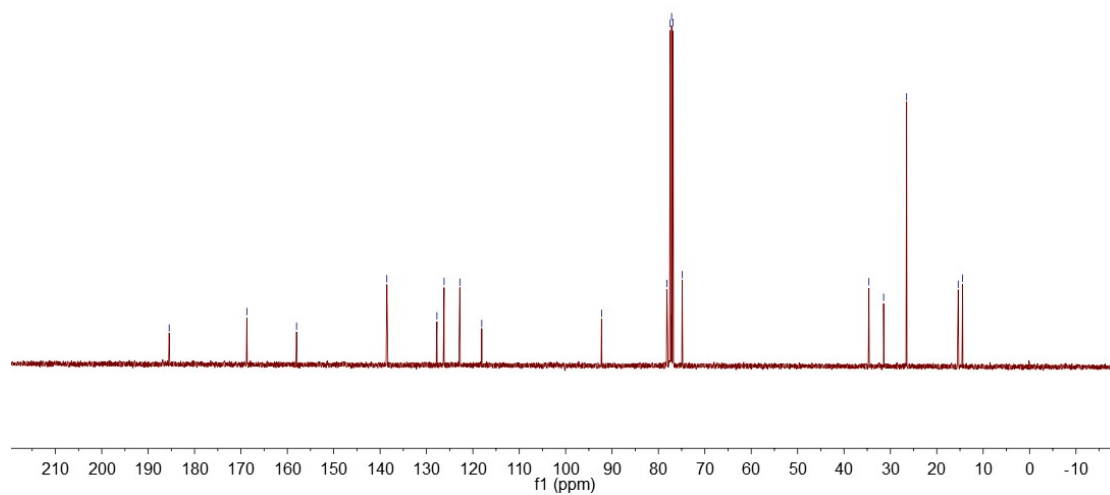
34.629

31.462

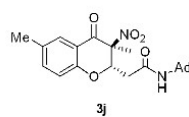
26.505

15.379

14.433



CHQ-2020-11-30-3



7.727

7.394

7.373

7.260

6.925

6.904

5.548

5.527

5.307

2.563

2.538

2.526

2.501

2.334

2.267

2.232

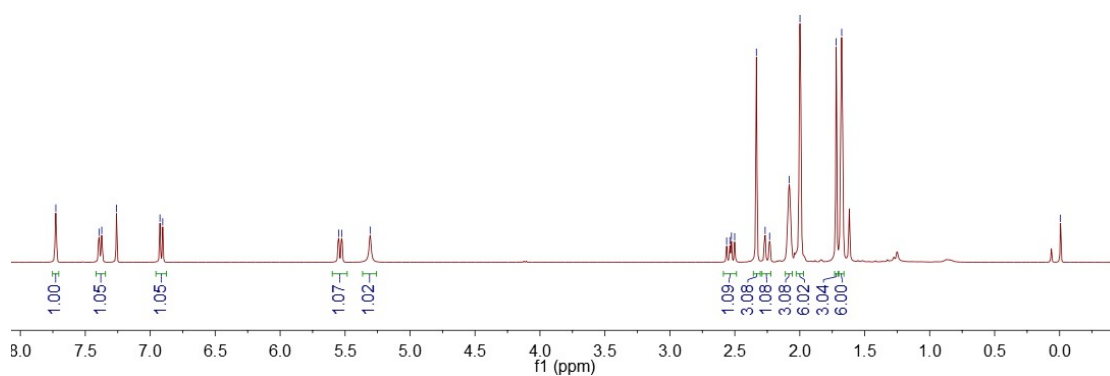
2.061

1.998

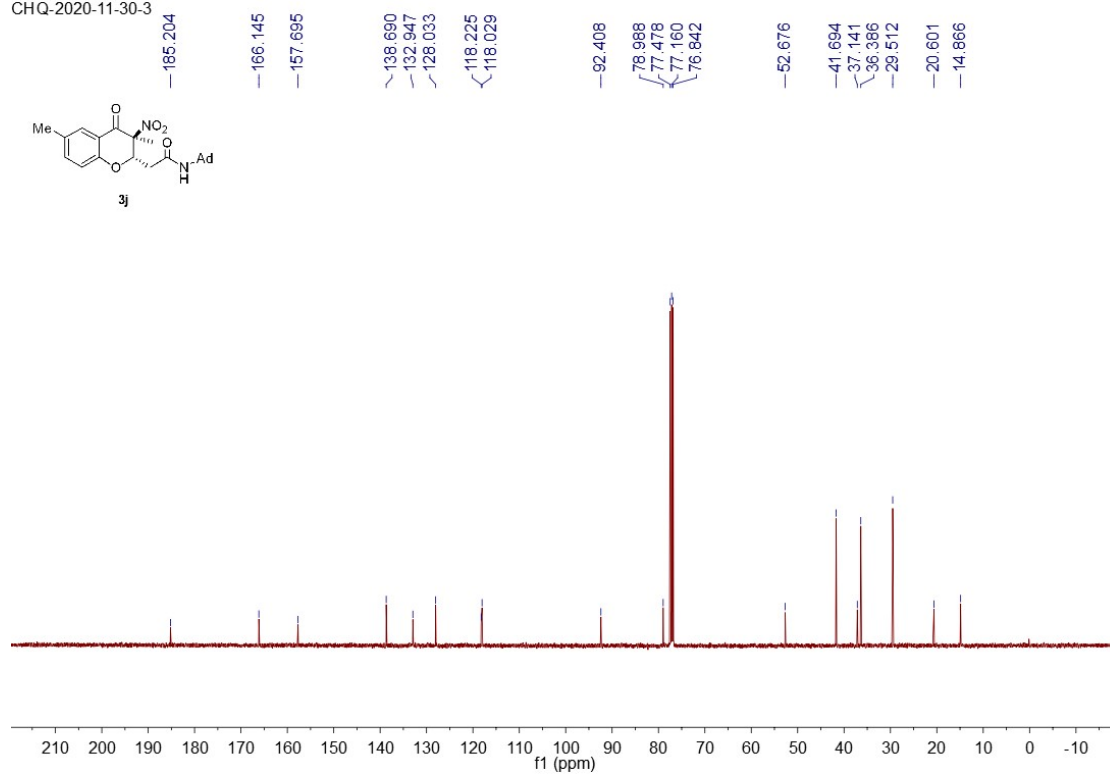
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1.677

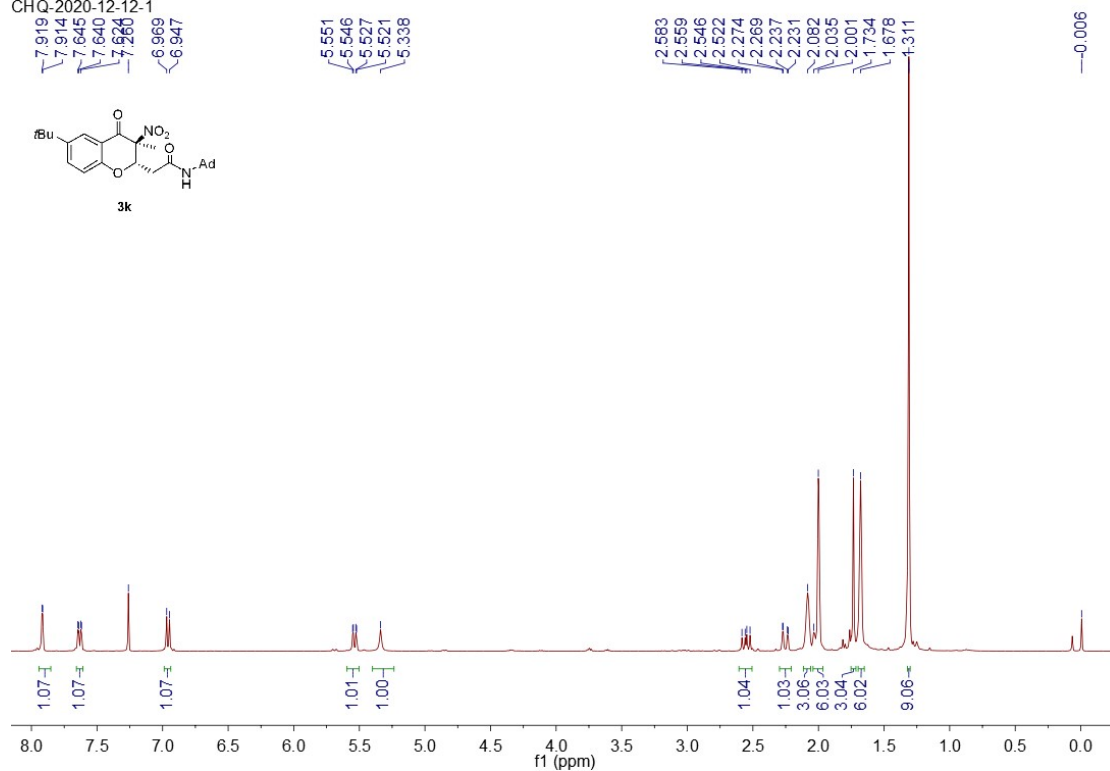
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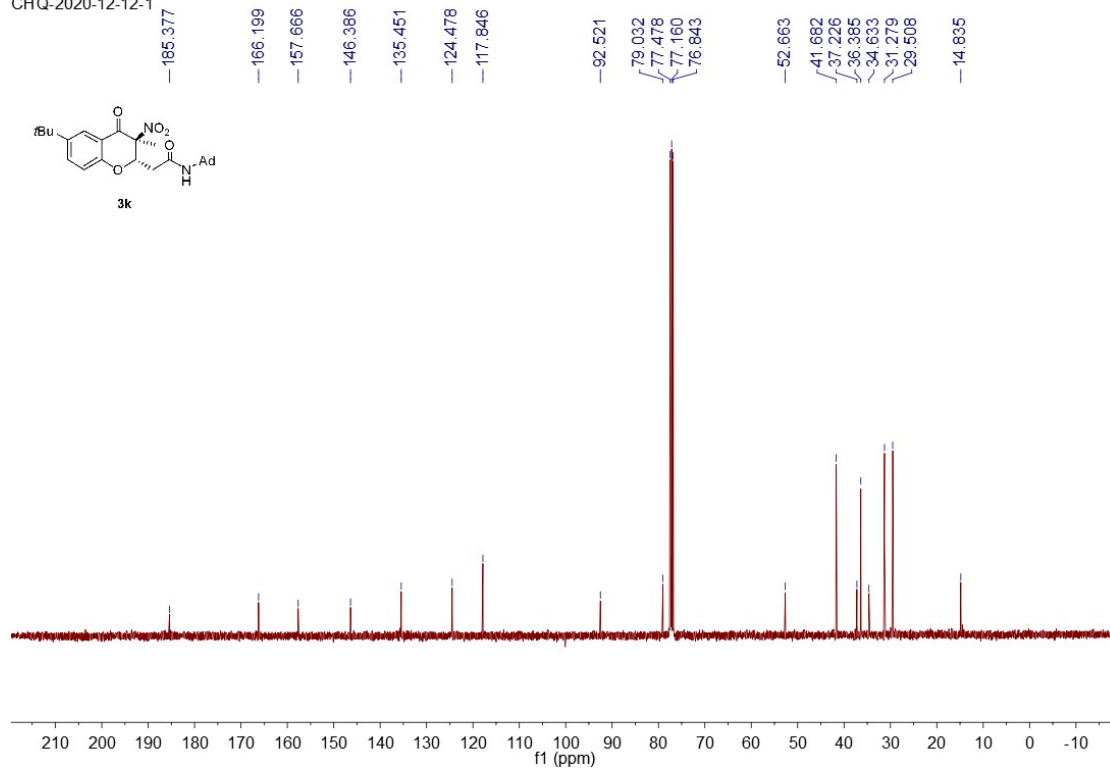
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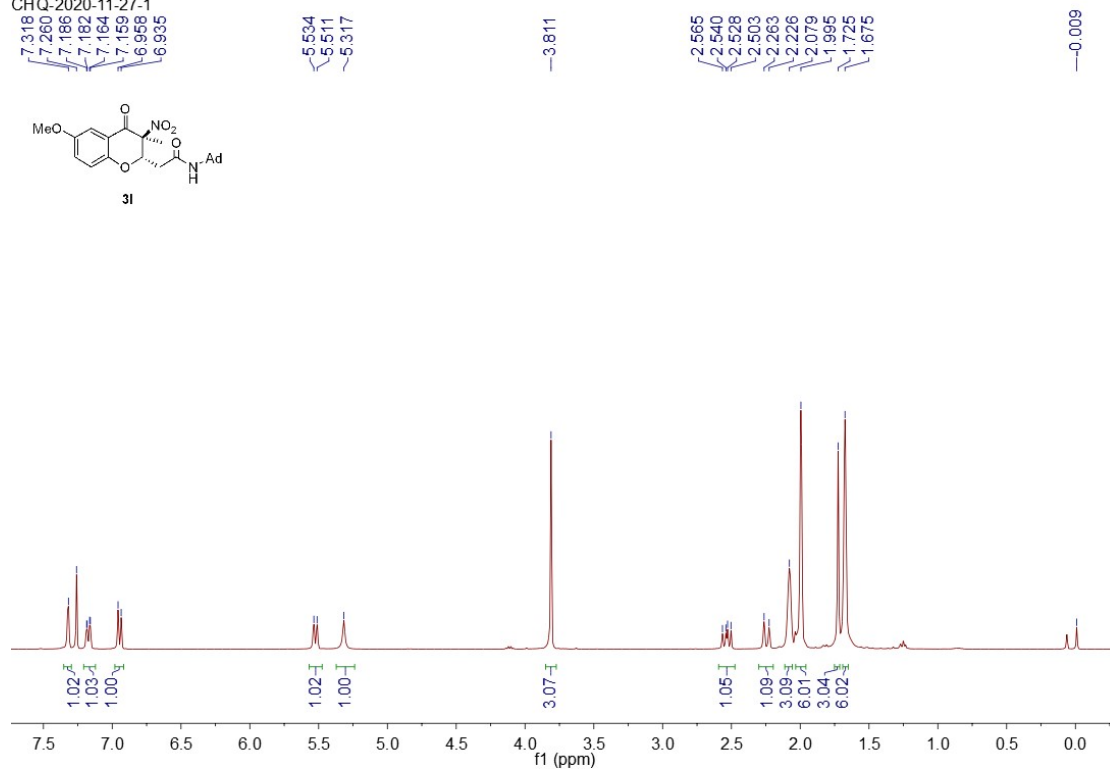
CHQ-2020-12-12-1



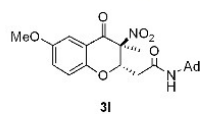
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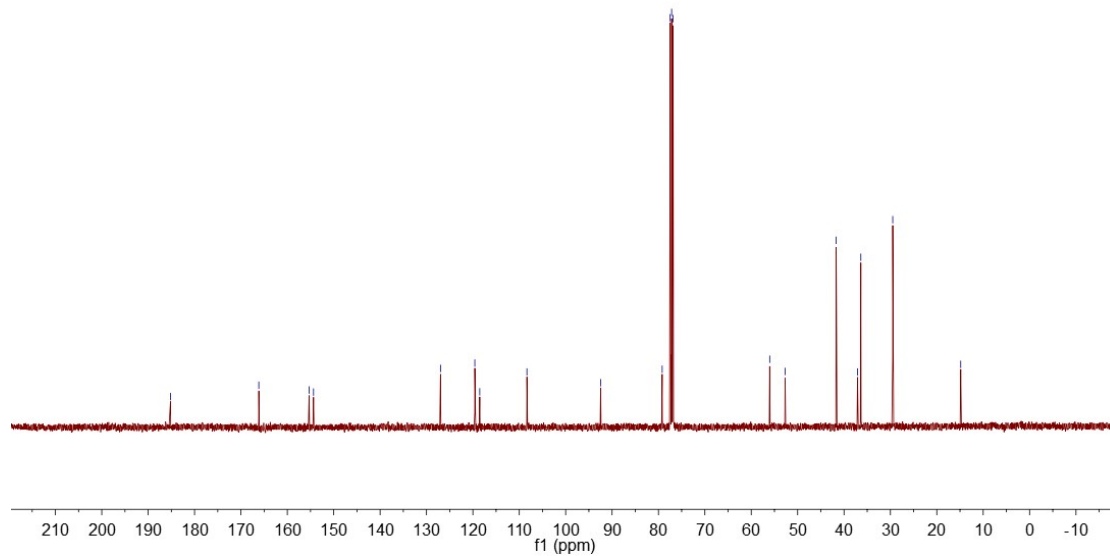
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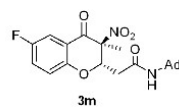
CHQ-2020-11-27-1



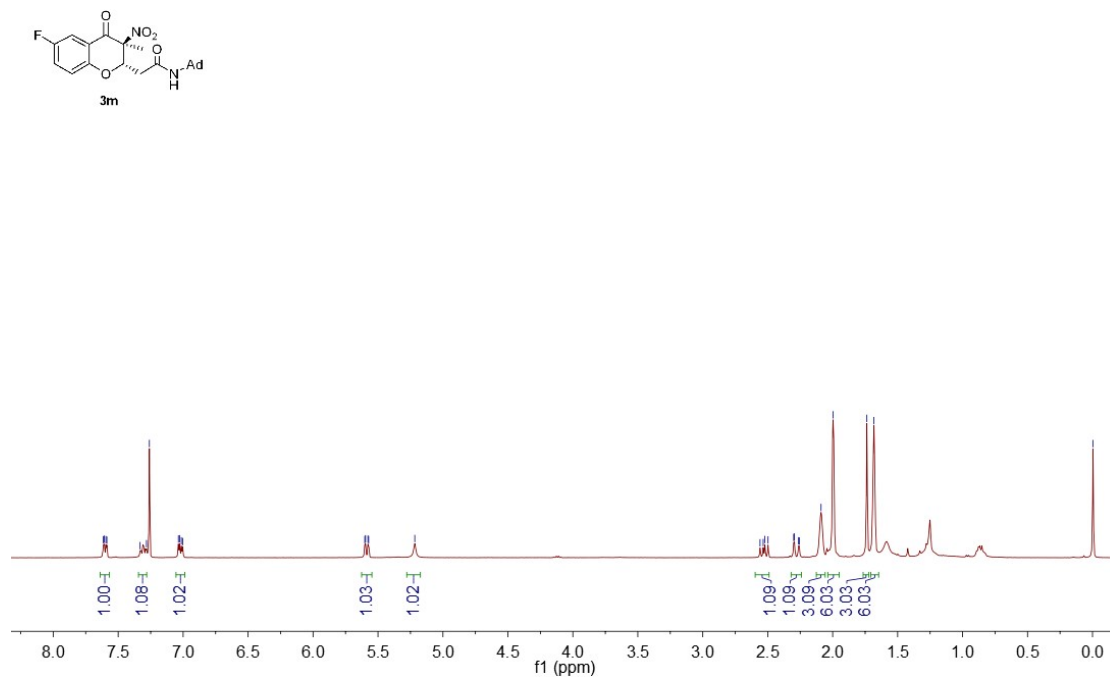
185.192
166.149
155.313
154.354
126.983
119.582
118.525
108.353
92.465
79.194
77.478
77.160
76.842
56.021
52.686
41.686
37.101
36.374
29.501
14.842



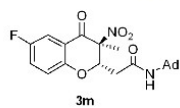
CHQ-2020-12-26-2



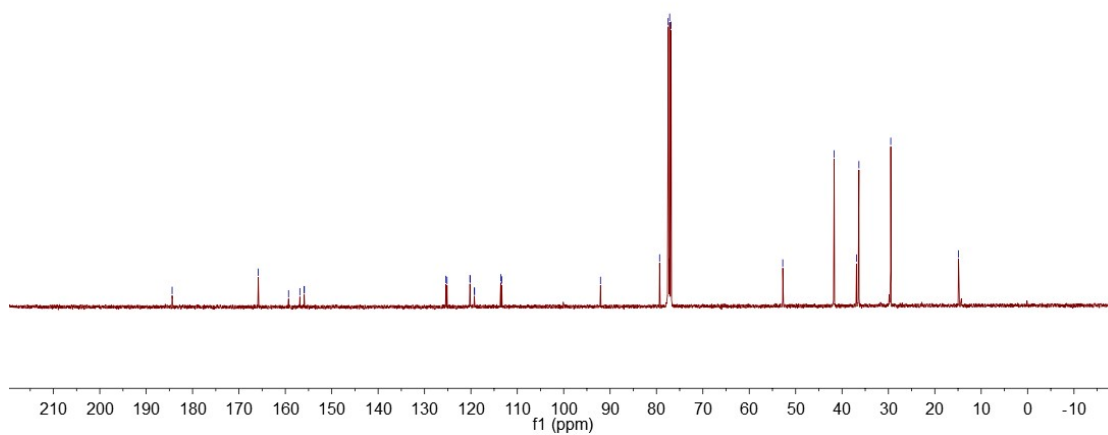
7.614
7.607
7.595
7.587
7.331
7.282
7.260
7.037
7.026
7.014
7.004
5.602
5.596
5.578
5.572
5.217
2.559
2.535
2.522
2.497
2.300
2.294
2.263
2.257
2.089
1.997
1.737
1.682
0.004



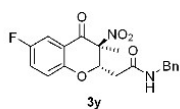
CHQ-2020-12-26-2



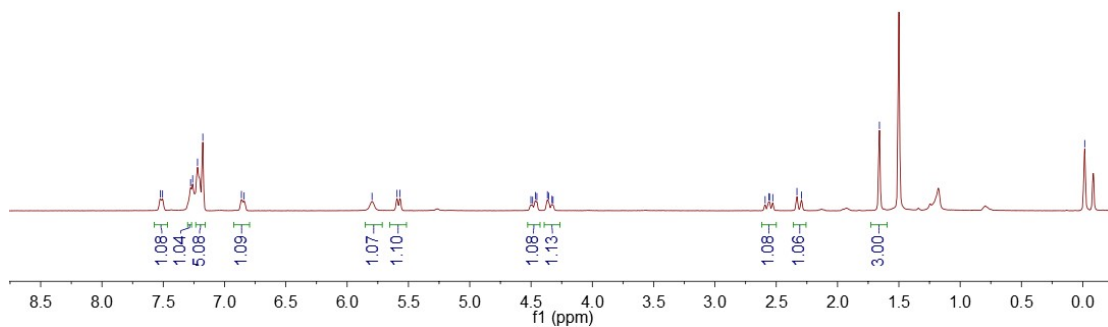
184.409
165.836
159.312
156.877
155.927
155.910
125.389
125.144
120.214
120.138
119.286
119.216
113.576
113.338
92.066
79.329
77.478
77.160
76.843
52.779
41.692
36.889
36.359
29.496
14.878



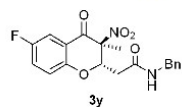
CHQ-10-5-372



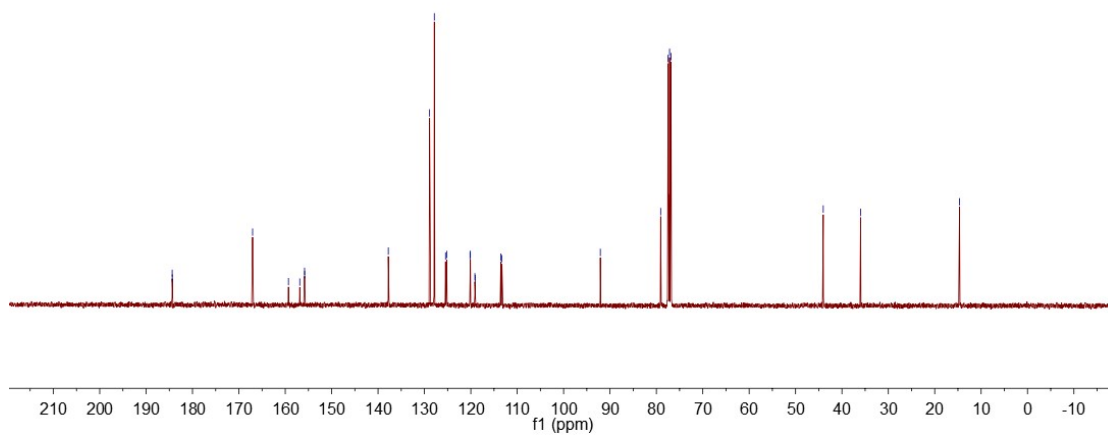
7.524
7.506
7.277
7.260
7.220
7.177
6.862
6.840
5.797
5.593
5.569
4.501
4.487
4.463
4.452
4.367
4.356
4.329
4.320
2.591
2.559
2.554
2.528
2.331
2.294
1.658
0.016



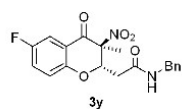
CHQ-2020-4-29-2



184.377
184.357
167.042
159.312
156.877
155.840
155.824
137.786
128.892
127.867
125.452
125.207
120.172
120.096
119.129
119.059
113.536
113.297
92.080
79.074
77.477
77.160
76.842
44.031
35.976
14.662



CHQ-10-5-372



118.285

