

PIDA-Mediated α -C-H Functionalization of Enaminones: Synthesis of Thiocyano Enaminones and Chromones in Water

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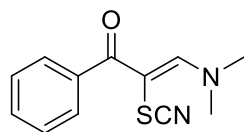
Experimental:

^1H (400 MHz), ^{13}C (101 MHz) spectra were recorded on a Bruker 400MHz spectrometer in CDCl_3 using TMS as internal standard. HRMS was recorded on a Bruker micrOTOF-Q II. Reagents and solvents used were mostly AR grade from Adamas-beta® and Energy Chemical. Silica gel coated plates were used for TLC. Melting points were tested in X-4 instrument without correcting the temperature.

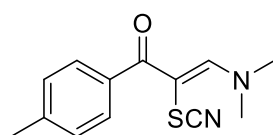
Typical Procedure.

The mixture of enaminone **1** (0.2 mmol), KSCN (0.4 mmol), PIDA (0.22 mmol), H_2O (1 mL) was stirred at r.t. for 1 h until the reaction was complete (TLC). After, the reaction mixture was diluted with EtOAc (20 mL). The obtained top organic layer was dried with anhydrous Na_2SO_4 . The mixture was concentrated in vacuo and the residue was purified by column chromatography on silica gel (PE : EA = 4:1~1:1) to afford pure product.

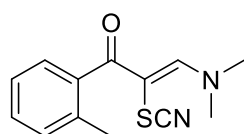
Characteristic Data.



(Z)-3-(dimethylamino)-1-phenyl-2-thiocyanatoprop-2-en-1-one (2a).¹ Yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 7.66 (s, 1H), 7.59 – 7.36 (m, 5H), 3.39 (brs, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.9, 158.5, 139.8, 130.5, 128.3, 128.1, 113.4, 87.4.

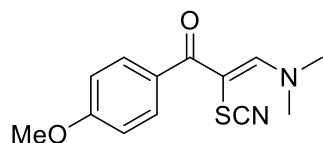


(Z)-3-(dimethylamino)-2-thiocyanato-1-(p-tolyl)prop-2-en-1-one (2b).¹ Yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 7.66 (s, 1H), 7.45 (, $J = 7.8$ Hz, 2H), 7.22 (, $J = 7.6$ Hz, 2H), 3.38 (brs, 6H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.9, 158.8, 140.5, 136.9, 129.0, 128.4, 113.4, 87.4, 21.6.

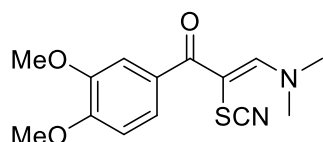


(Z)-3-(dimethylamino)-2-thiocyanato-1-(o-tolyl)prop-2-en-1-one (2c). Yellow solid, mp 135-138 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.50 (s, 1H), 7.33 – 7.25 (m, 1H), 7.25 – 7.17 (m, 2H), 7.13

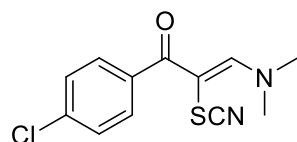
(d, $J = 7.4$ Hz, 1H), 3.53 (s, 3H), 3.14 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.0, 158.3, 139.9, 134.9, 130.7, 129.1, 126.4, 125.5, 113.1, 88.5, 19.2. HRMS (ESI-TOF) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{OS}$ $[\text{M}+\text{H}]^+$ 246.0824, found 246.0817.



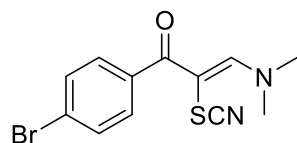
(Z)-3-(dimethylamino)-1-(4-methoxyphenyl)-2-thiocyanatoprop-2-en-1-one (2d). Yellow solid, mp 85-87 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.67 (s, 1H), 7.53 (d, $J = 8.7$ Hz, 2H), 6.92 (d, $J = 8.7$ Hz, 2H), 3.86 (s, 3H), 3.39 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.1, 161.6, 158.2, 131.9, 130.8, 130.5, 113.5, 87.1, 55.4. HRMS (ESI-TOF) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 262.0770, found 262.0765.



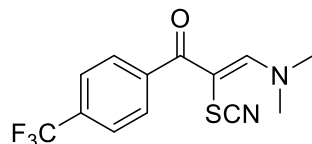
(Z)-1-(3,4-dimethoxyphenyl)-3-(dimethylamino)-2-thiocyanatoprop-2-en-1-one (2e). Yellow solid, mp 76-78 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.78 (s, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.37 (s, 1H), 6.93 (d, $J = 8.3$ Hz, 1H), 3.96 (s, 3H), 3.94 (s, 3H), 3.23 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 185.6, 152.3, 150.0, 149.0, 131.2, 128.9, 122.8, 111.3, 110.2, 77.5, 77.4, 77.2, 76.8, 56.2, 56.1. HRMS (ESI-TOF) m/z calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 292.0876, found 292.0882.



(Z)-1-(4-chlorophenyl)-3-(dimethylamino)-2-thiocyanatoprop-2-en-1-one (2f).¹ Yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 7.64 (s, 1H), 7.47 – 7.39 (m, 4H), 3.40 (brs, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.3, 158.2, 138.1, 136.2, 129.5, 128.4, 113.1, 86.8.

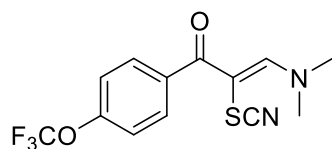


(Z)-1-(4-bromophenyl)-3-(dimethylamino)-2-thiocyanatoprop-2-en-1-one (2g). Yellow solid, mp 131-132 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.59 (s, 1H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.3$ Hz, 2H), 3.34 (brs, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.9, 158.3, 138.6, 131.5, 129.7, 124.9, 113.2, 86.9. HRMS (ESI-TOF) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{BrN}_2\text{OS}$ $[\text{M}+\text{H}]^+$ 309.9770, found 309.9765.



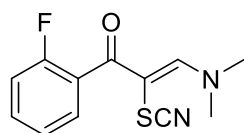
(Z)-3-(dimethylamino)-2-thiocyanato-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (2h).

Yellow solid, mp 65-66 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.82 – 7.64 (m, 4H), 7.57 (t, *J* = 7.7 Hz, 1H), 3.41 (d, *J* = 59.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 191.6, 158.4, 140.6, 131.2, 130.9, 130.6, 128.9, 127.1, 127.0, 127.0, 127.0, 125.1, 124.9, 124.9, 124.9, 124.8, 122.4, 113.1, 86.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.7. HRMS (ESI-TOF) *m/z* calcd for C₁₃H₁₁F₃N₂OS [M+H]⁺ 300.0539, found 300.0533.

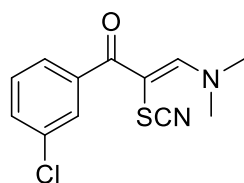


(Z)-3-(dimethylamino)-2-thiocyanato-1-(4-(trifluoromethoxy)phenyl)prop-2-en-1-one (2i).

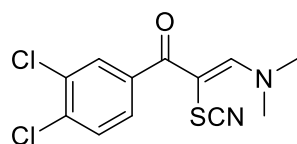
Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 3.33 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 191.5, 158.4, 150.5, 138.3, 129.9, 120.5, 113.2, 86.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -57.7. HRMS (ESI-TOF) *m/z* calcd for C₁₃H₁₁F₃N₂O₂S [M+H]⁺ 316.0488, found 316.0484.



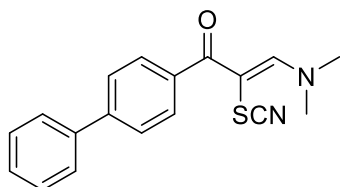
(Z)-3-(dimethylamino)-1-(2-fluorophenyl)-2-thiocyanatoprop-2-en-1-one (2j). Yellow solid, mp 145-146 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (s, 1H), 7.54 – 7.37 (m, 2H), 7.04 (t, *J* = 8.5 Hz, 2H), 3.34 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 191.8, 165.2, 162.7, 158.3, 135.8, 130.5, 130.4, 115.5, 115.3, 113.4, 86.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -109.1. HRMS (ESI-TOF) *m/z* calcd for C₁₂H₁₁FN₂OS [M+H]⁺ 250.0571, found 250.0574.



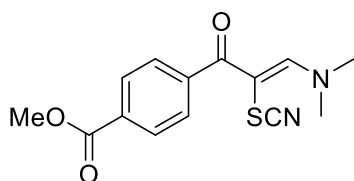
(Z)-1-(3-chlorophenyl)-3-(dimethylamino)-2-thiocyanatoprop-2-en-1-one (2k). Yellow solid, mp 113-114 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.56 (s, 1H), 7.43 – 7.32 (m, 2H), 7.29 (d, *J* = 4.9 Hz, 2H), 3.29 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 191.3, 158.5, 141.6, 134.4, 130.4, 129.7, 128.0, 126.1, 113.2, 87.0. HRMS (ESI-TOF) *m/z* calcd for C₁₂H₁₁ClN₂OS [M+H]⁺ 266.0275, found 266.0271.



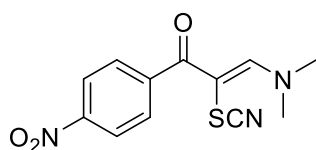
(Z)-1-(3,4-dichlorophenyl)-3-(dimethylamino)-2-thiocyanatoprop-2-en-1-one (2l). Yellow solid, mp 127-128 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 1H), 7.56 – 7.48 (m, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.27 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.28 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 190.5, 158.3, 139.6, 134.7, 132.8, 130.4, 130.0, 127.2, 113.1, 86.5. HRMS (ESI-TOF) *m/z* calcd for C₁₂H₁₀Cl₂N₂OS [M+H]⁺ 299.9885, found 299.9880.



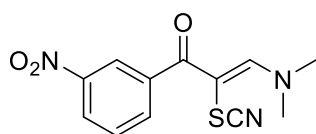
(Z)-1-([1,1'-biphenyl]-4-yl)-3-(dimethylamino)-2-thiocyanatoprop-2-en-1-one (2m). Yellow solid, mp 142-144 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (s, 1H), 7.69 – 7.54 (m, 6H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 3.38 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 192.6, 158.6, 143.3, 140.1, 138.5, 129.0, 128.8, 128.0, 127.2, 127.0, 113.5, 87.3. HRMS (ESI-TOF) *m/z* calcd for C₁₈H₁₆N₂OS [M+H]⁺ 308.0978, found 308.0985.



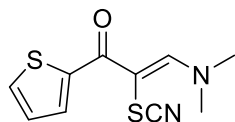
methyl (Z)-4-(3-(dimethylamino)-2-thiocyanatoacryloyl)benzoate (2n). Yellow solid, mp 125-126 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 8.1 Hz, 2H), 7.68 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 3.95 (s, 3H), 3.41 (brs, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 192.3, 166.5, 158.3, 144.2, 131.5, 129.6, 127.8, 113.1, 87.1, 52.4. HRMS (ESI-TOF) *m/z* calcd for C₁₄H₁₄N₂O₃S [M+H]⁺ 290.0720, found 290.0713.



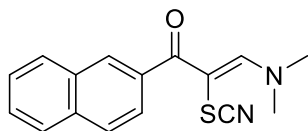
(Z)-3-(dimethylamino)-1-(4-nitrophenyl)-2-thiocyanatoprop-2-en-1-one (2o). Yellow solid, mp 127-128 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 8.7 Hz, 2H), 7.77 (s, 1H), 7.66 (d, *J* = 8.6 Hz, 2H), 3.62 (s, 3H), 3.30 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 191.3, 158.3, 148.5, 146.2, 128.6, 123.7, 113.0, 86.2. HRMS (ESI-TOF) *m/z* calcd for C₁₂H₁₁N₃O₃S [M+H]⁺ 277.0516, found 277.0510.



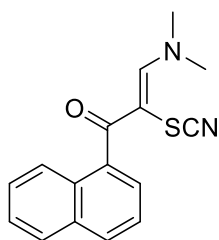
(Z)-3-(dimethylamino)-1-(3-nitrophenyl)-2-thiocyanatoprop-2-en-1-one (2p). Yellow solid, mp 134-135 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.80 (s, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 3.47 (d, *J* = 97.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 190.7, 158.2, 147.8, 141.5, 133.7, 129.6, 125.0, 122.9, 112.9, 85.9. HRMS (ESI-TOF) *m/z* calcd for C₁₂H₁₁N₃O₃S [M+H]⁺ 277.0516, found 277.0510.



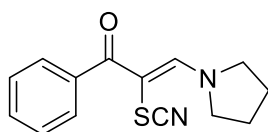
(Z)-3-(dimethylamino)-2-thiocyanato-1-(thiophen-2-yl)prop-2-en-1-one (2q). Yellow solid, mp 130-132 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.89 (s, 1H), 7.61 – 7.42 (m, 2H), 7.02 (s, 1H), 3.35 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 181.9, 157.1, 141.9, 130.7, 130.5, 126.2, 112.3, 84.4. HRMS (ESI-TOF) *m/z* calcd for C₁₀H₁₀N₂OS₂ [M+H]⁺ 238.0229, found 238.0221.



(Z)-3-(dimethylamino)-1-(naphthalen-2-yl)-2-thiocyanatoprop-2-en-1-one (2r). Yellow solid, mp 117-119 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.71 (m, 3H), 7.51 (s, 1H), 7.45 – 7.37 (m, 3H), 7.31 (d, *J* = 6.9 Hz, 1H), 3.45 (s, 3H), 2.98 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 193.4, 158.5, 138.0, 133.5, 130.4, 129.5, 128.3, 127.0, 126.5, 125.2, 124.8, 124.5, 113.3, 85.7. HRMS (ESI-TOF) *m/z* calcd for C₁₆H₁₄N₂OS [M+H]⁺ 282.0821, found 282.0815.

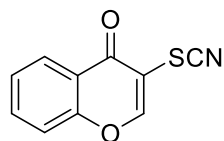


(Z)-3-(dimethylamino)-1-(naphthalen-1-yl)-2-thiocyanatoprop-2-en-1-one (2s). Yellow solid, mp 123-124 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (s, 1H), 7.79 (dt, *J* = 8.6, 4.3 Hz, 3H), 7.58 (s, 1H), 7.55 – 7.40 (m, 3H), 3.24 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 191.7, 157.6, 136.1, 133.0, 131.3, 127.7, 127.2, 127.1, 126.7, 126.4, 125.7, 124.1, 112.4, 86.4. HRMS (ESI-TOF) *m/z* calcd for C₁₆H₁₄N₂OS [M+H]⁺ 282.0821, found 282.0815.

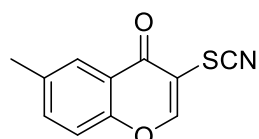


(Z)-1-phenyl-3-(pyrrolidin-1-yl)-2-thiocyanatoprop-2-en-1-one (2v).¹ Yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (s, 1H), 7.84 – 7.40 (m, 5H), 4.09 (brs, 1H), 3.57 (brs, 1H), 2.07 (brs,

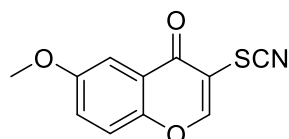
1H), 1.89 (brs, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 192.3, 155.1, 139.8, 130.2, 128.0, 127.9, 113.5, 87.6.



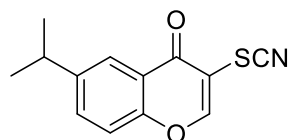
3-thiocyanato-4H-chromen-4-one (3a).² White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.28 (s, 1H), 8.18 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.72 (m, 1H), 7.50 – 7.43 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 173.1, 156.3, 155.6, 135.1, 126.7, 126.1, 122.6, 118.5, 112.4, 109.1.



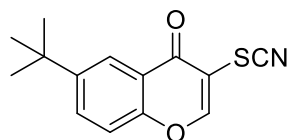
6-methyl-3-thiocyanato-4H-chromen-4-one (3b).² White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.31 (s, 1H), 7.98 (s, 1H), 7.59 (d, *J* = 8.6, 1H), 7.45 (d, *J* = 8.4, 1H), 2.47 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.3, 155.7, 154.8, 137.1, 136.3, 125.8, 122.6, 118.3, 112.3, 109.3, 20.9.



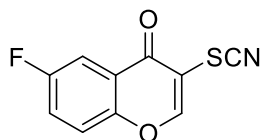
6-methoxy-3-thiocyanato-4H-chromen-4-one (3c).² White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.35 (s, 1H), 7.60 (s, 1H), 7.51 (d, *J* = 8.7, 1H), 7.39 (d, *J* = 8.9, 1H), 3.95 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.1, 157.9, 155.5, 151.5, 125.1, 123.5, 119.9, 111.6, 109.1, 105.1, 56.0.



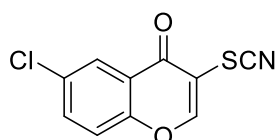
6-isopropyl-3-thiocyanato-4H-chromen-4-one (3d). Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.35 (s, 1H), 8.06 (d, *J* = 2.3 Hz, 1H), 7.66 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 3.06 (p, *J* = 6.9 Hz, 1H), 1.31 (s, 3H), 1.30 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.2, 155.8, 154.8, 147.8, 134.0, 122.7, 122.5, 118.3, 111.9, 109.1, 33.8, 23.8. HRMS (ESI-TOF) *m/z* calcd for C₁₃H₁₁NO₂S [M+H]⁺ 245.0505, found 245.0512.



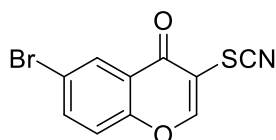
6-(tert-butyl)-3-thiocyanato-4H-chromen-4-one (3e). White solid, mp 123-125 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 1H), 8.14 (d, *J* = 2.4 Hz, 1H), 7.76 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.41 (d, *J* = 8.9 Hz, 1H), 1.31 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 173.4, 155.4, 154.6, 150.2, 133.1, 122.1, 121.8, 118.0, 112.2, 109.2, 35.1, 31.3. HRMS (ESI-TOF) *m/z* calcd for C₁₄H₁₃NO₂S [M+H]⁺ 259.0662, found 259.0668.



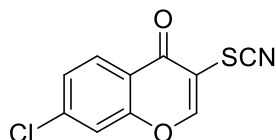
6-fluoro-3-thiocyanato-4H-chromen-4-one (3f).² White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.36 (s, 1H), 7.88 (m, 1H), 7.59 (m, 1H), 7.51 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 172.37, 172.35, 161.41, 158.93, 155.67, 155.65, 152.61, 152.60, 124.38, 123.92, 123.84, 123.52, 123.48, 123.27, 120.81, 120.73, 112.12, 111.20, 110.96, 108.68. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.1.



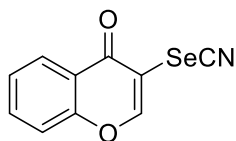
6-chloro-3-thiocyanato-4H-chromen-4-one (3g).² White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (s, 1H), 8.19 (d, *J* = 4.8 Hz, 1H), 7.75 – 7.72 (m, 1H), 7.53 (d, *J* = 7.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 172.1, 155.6, 154.8, 135.4, 132.8, 125.6, 123.6, 120.2, 113.0, 108.8.



6-bromo-3-thiocyanato-4H-chromen-4-one (3h).² White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.42 – 8.29 (m, 2H), 7.86 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.45 (d, *J* = 8.9 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 171.8, 155.3, 155.1, 138.1, 128.7, 123.8, 120.3, 120.2, 113.0, 108.6.



7-chloro-3-thiocyanato-4H-chromen-4-one (3i).² White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.32 (s, 1H), 8.19 (d, *J* = 8.6 Hz, 1H), 7.57 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 172.3, 156.4, 155.2, 141.4, 127.6, 127.5, 121.1, 118.5, 113.3, 108.6.



3-selenocyanato-4H-chromen-4-one (3j).² White solid, mp 160-162 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (s, 1H), 8.19 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.79 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 174.2, 156.6, 153.2, 135.0, 126.5, 125.8, 121.9, 118.5, 112.6, 100.0. HRMS (ESI-TOF) *m/z* calcd for C₁₀H₅NO₂Se [M+H]⁺ 250.9480, found 250.9491.

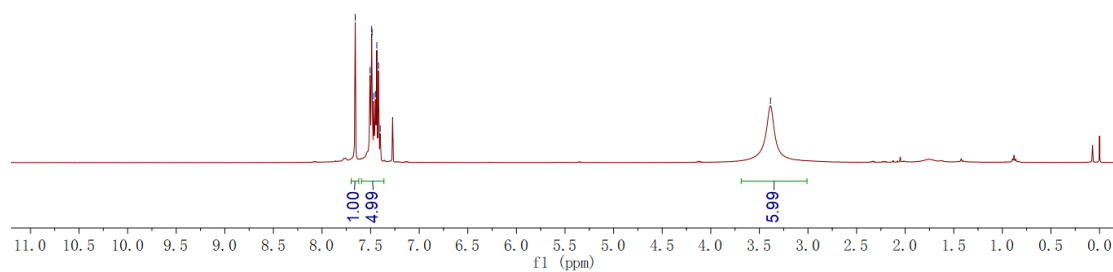
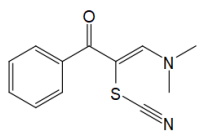
Reference

1. Y. Gao, Y. Liu, J.-P. Wan, J. Org. Chem., 2019, 84, 2243
2. X.-Z. Zhang, D.-L. Ge, S.-Y. Chen, X.-Q. Yu, RSC Adv., 2016, 6, 66320

Yz-2018121704.1.fid

7.658
7.506
7.489
7.486
7.467
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7.418
7.401

3.386



Yz-2018121704.2.fid

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158.490

139.804

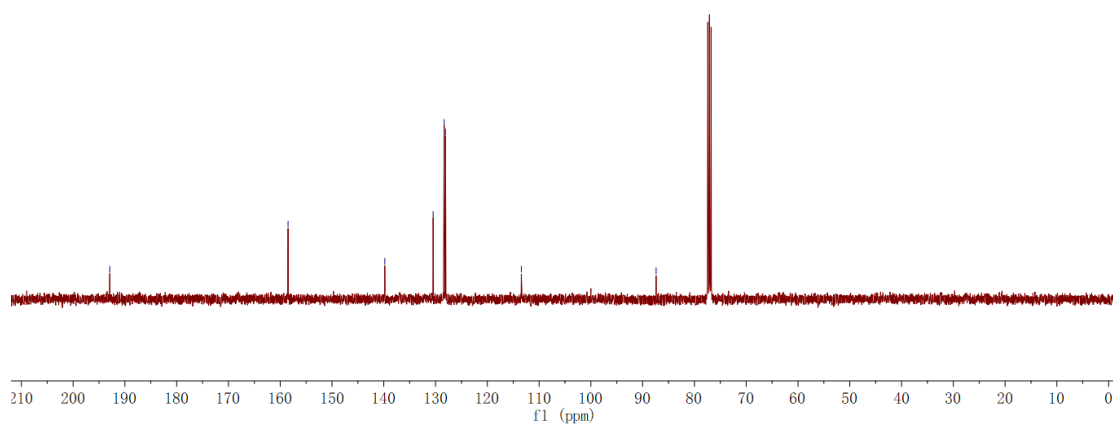
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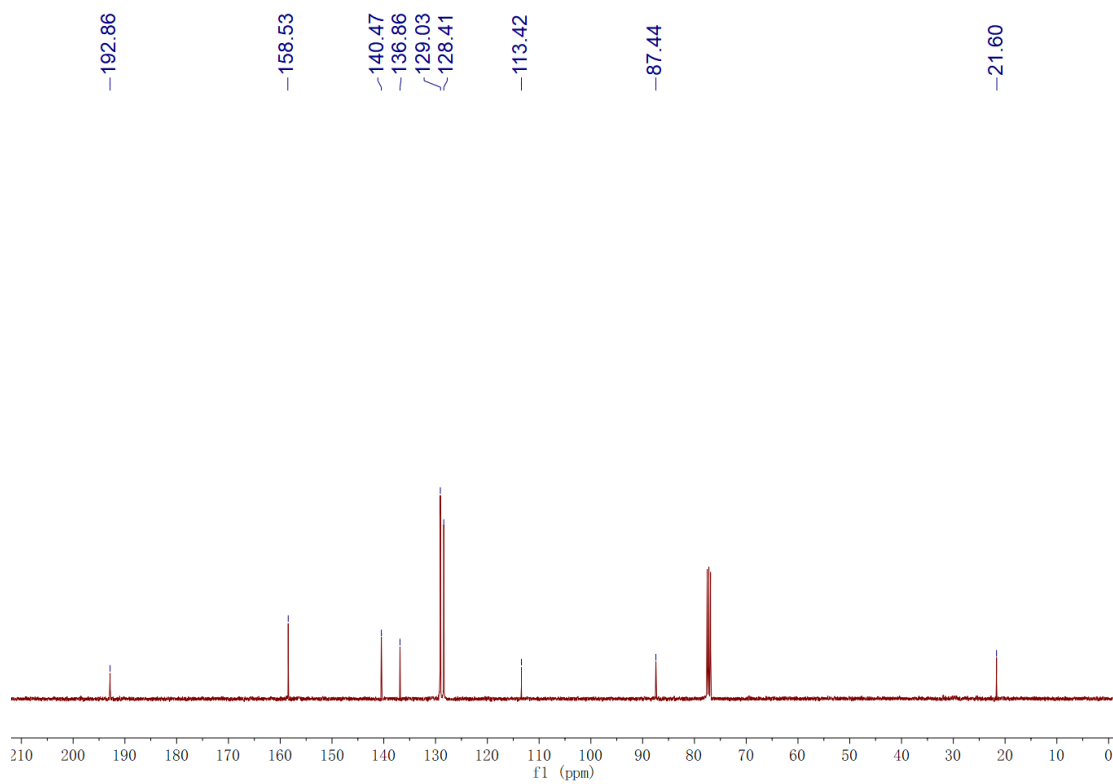
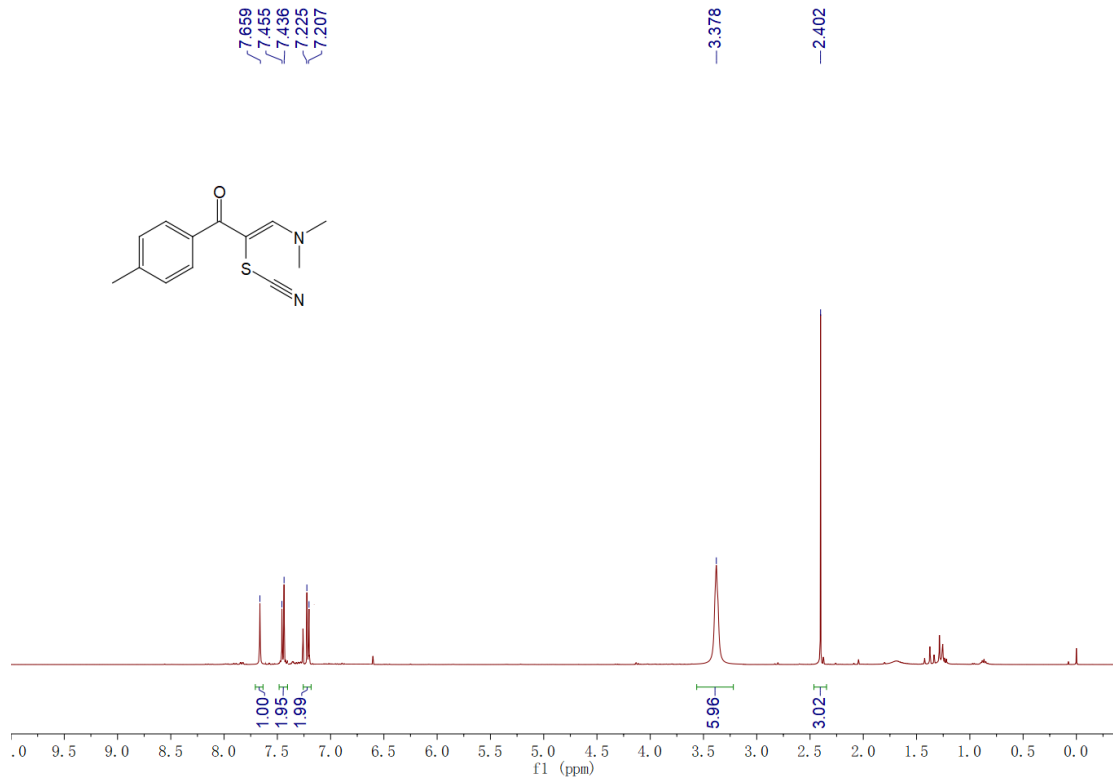
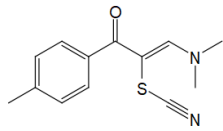
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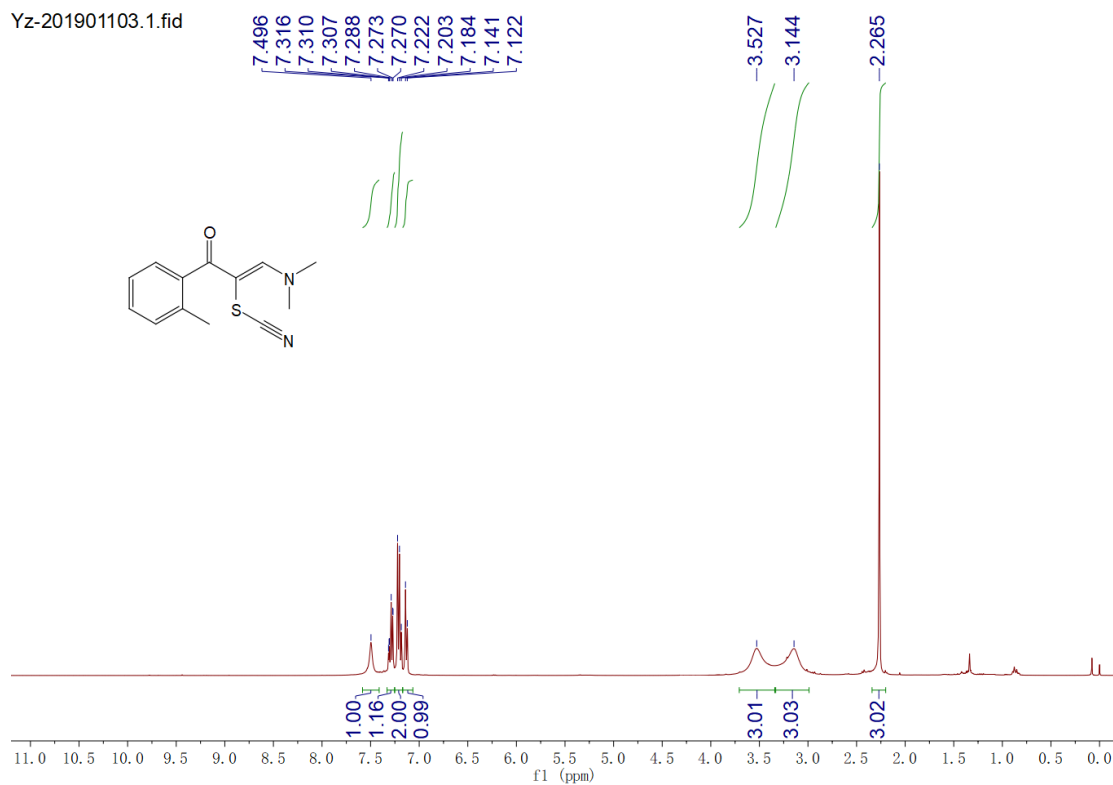
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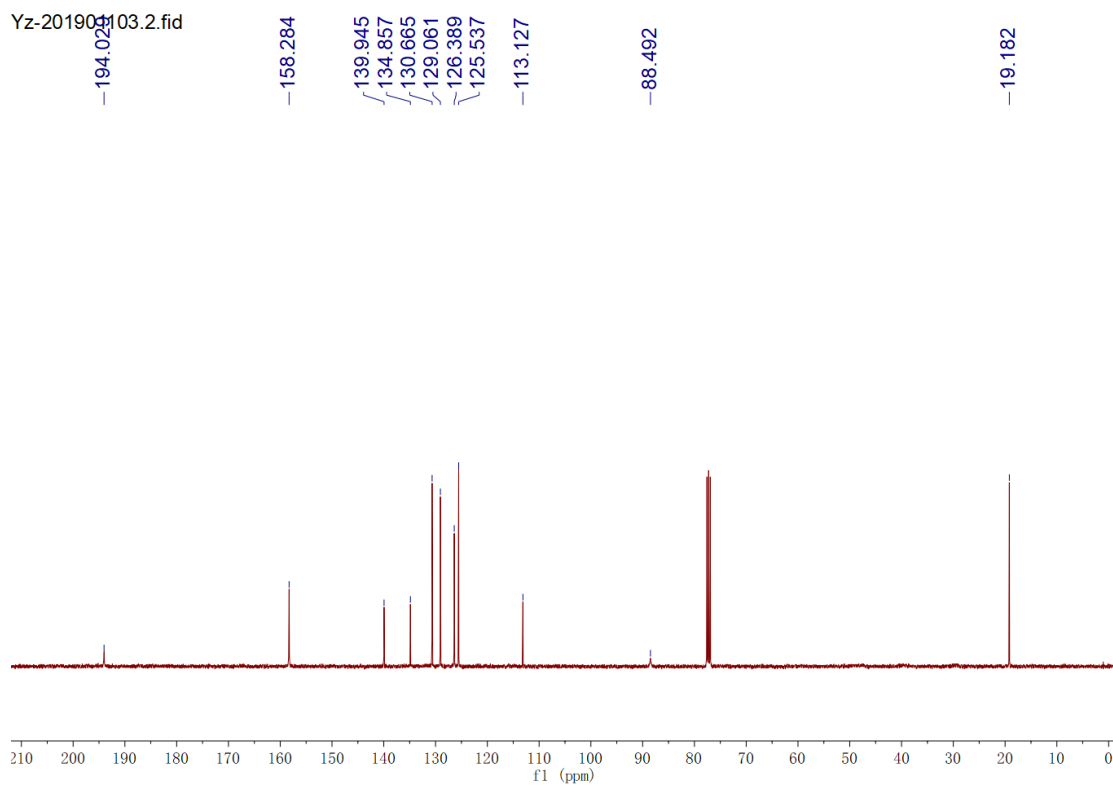


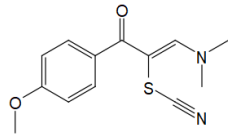


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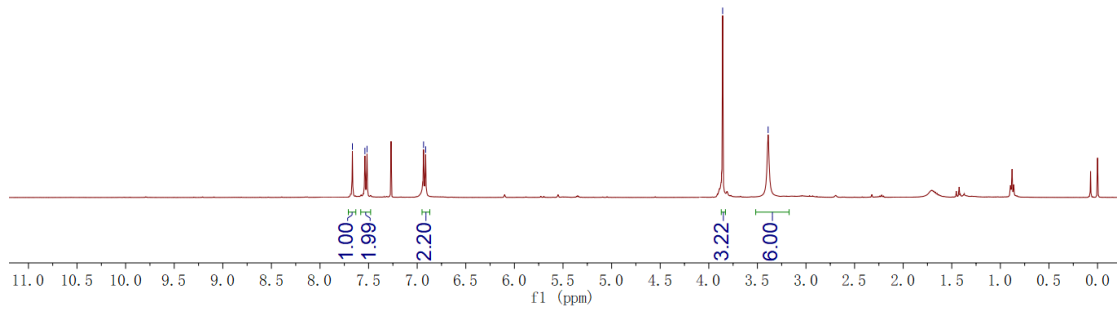


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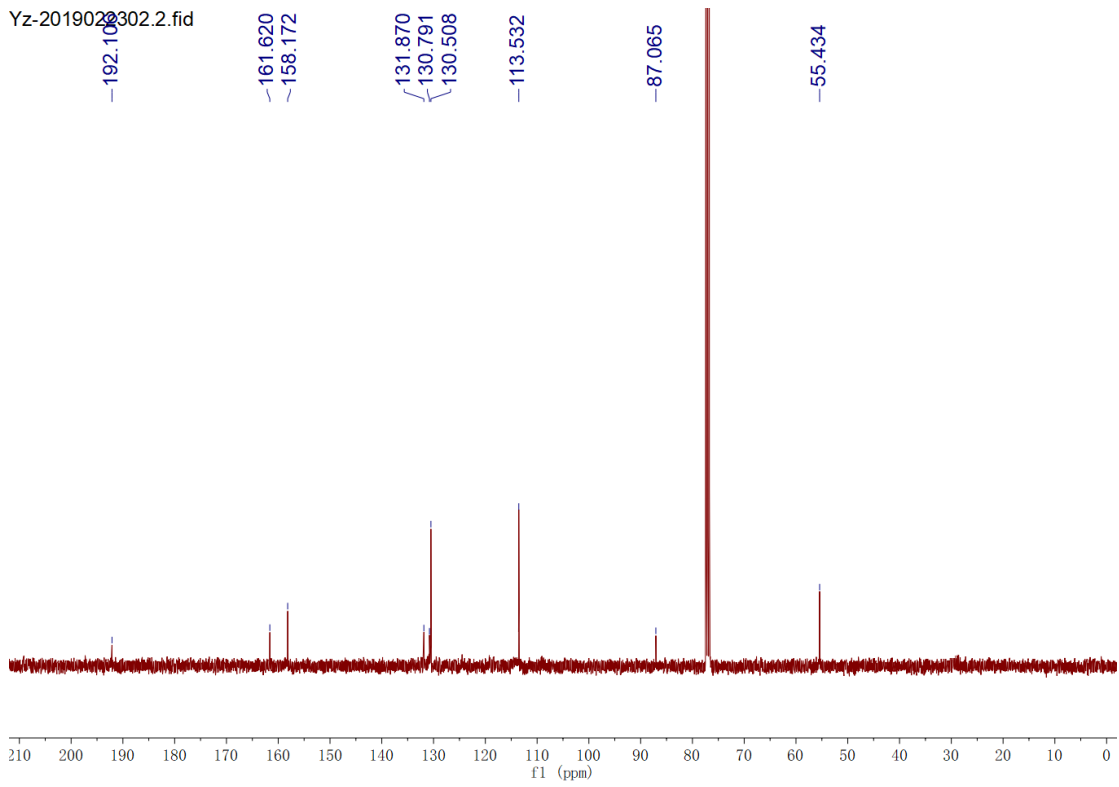


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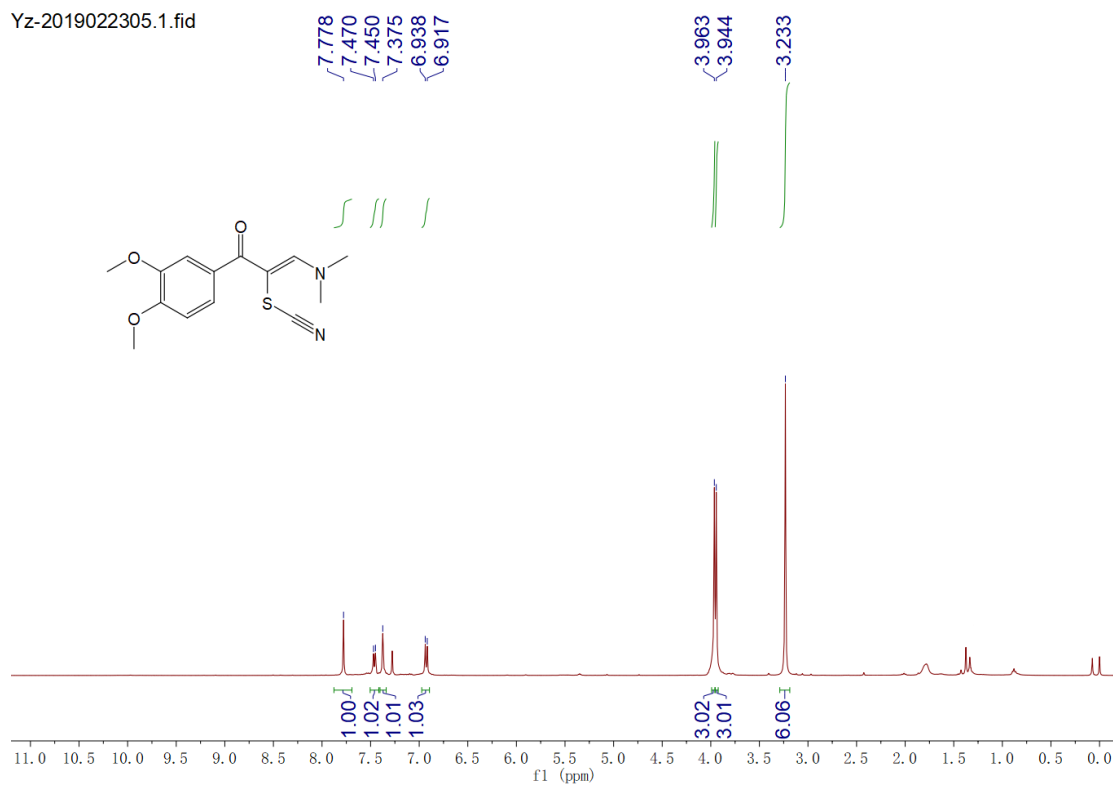


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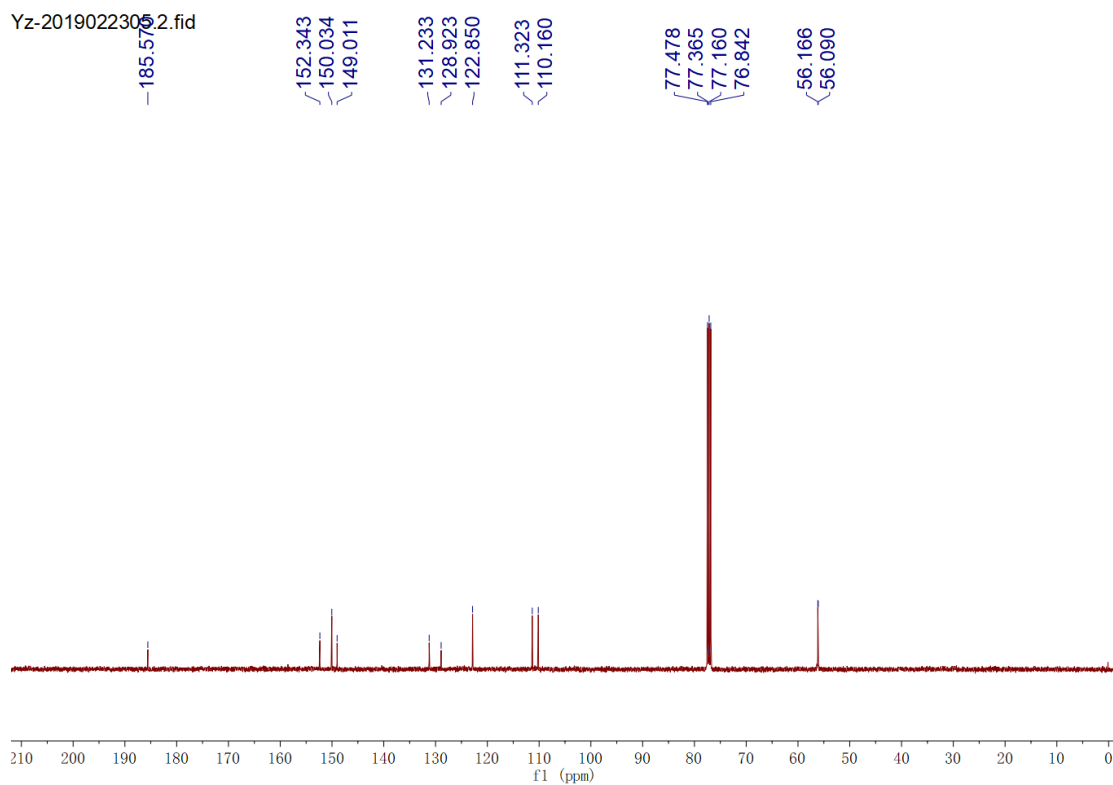
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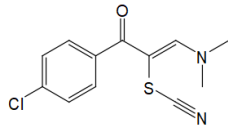


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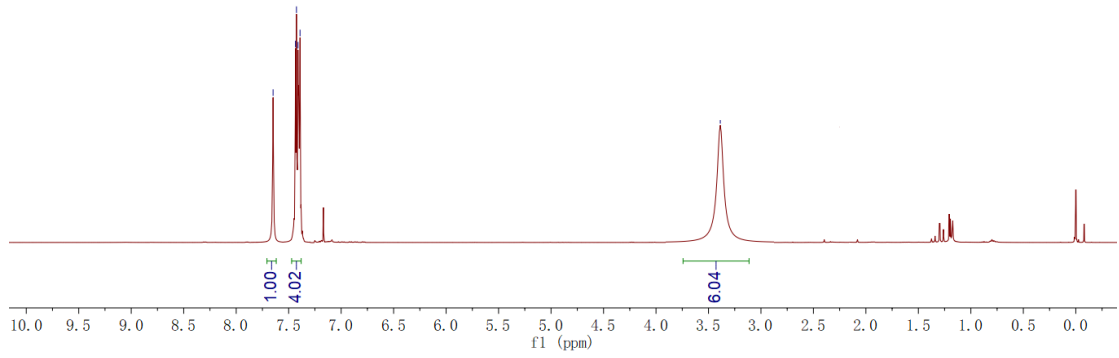
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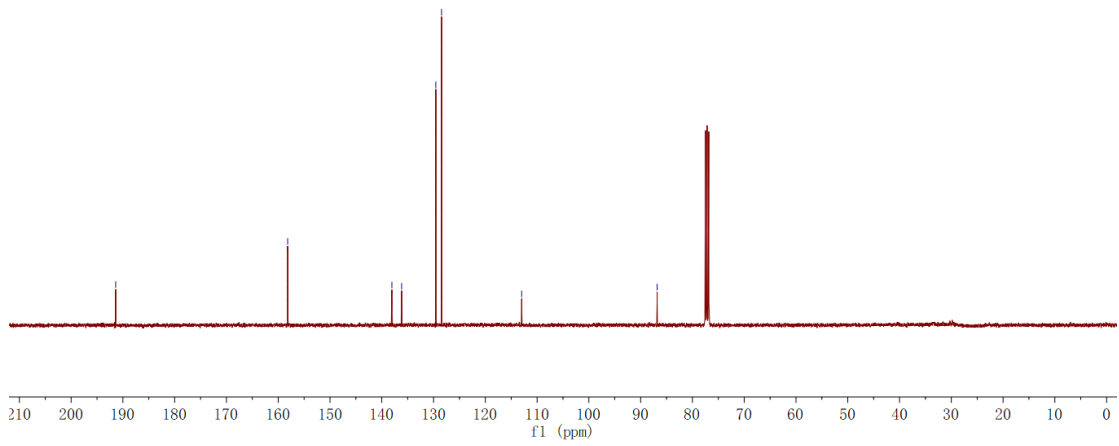
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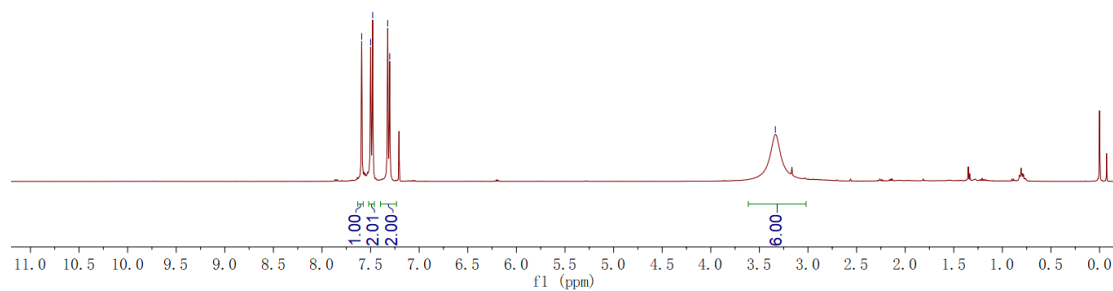
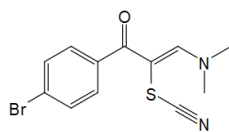
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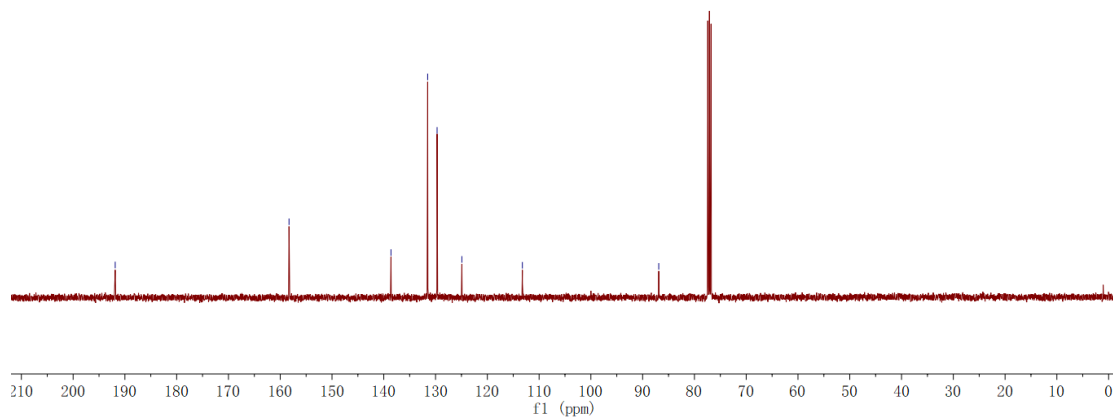
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3.336

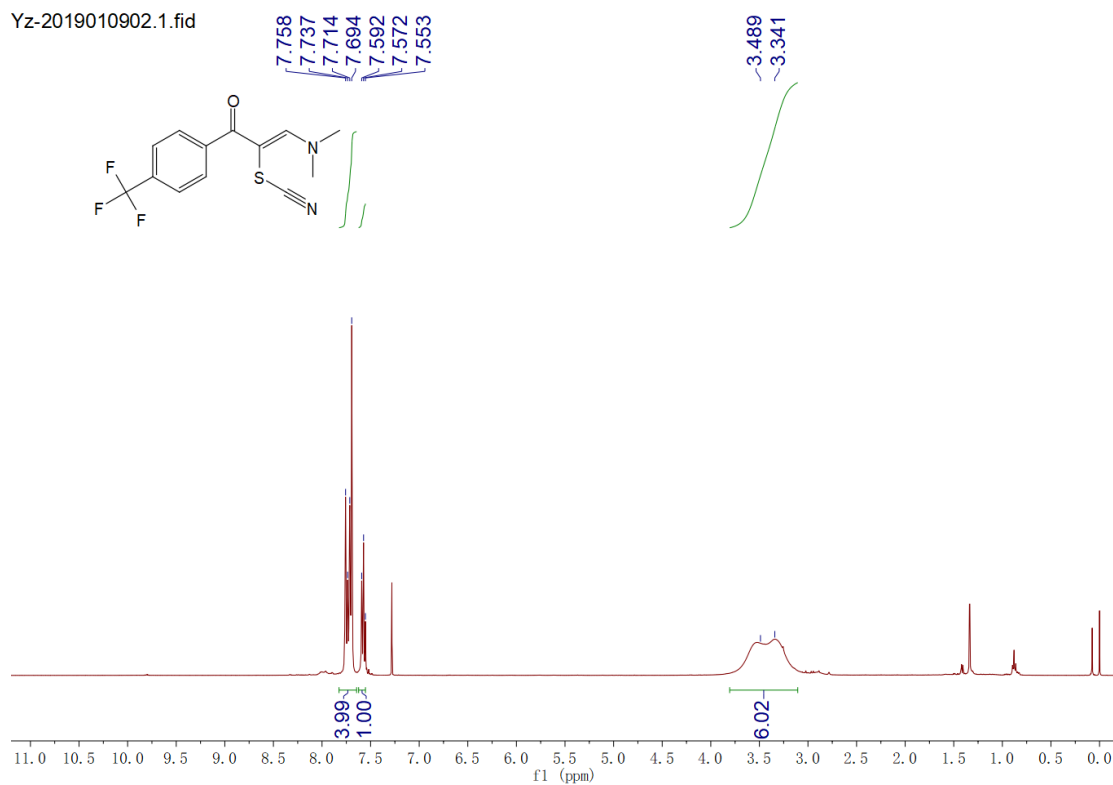


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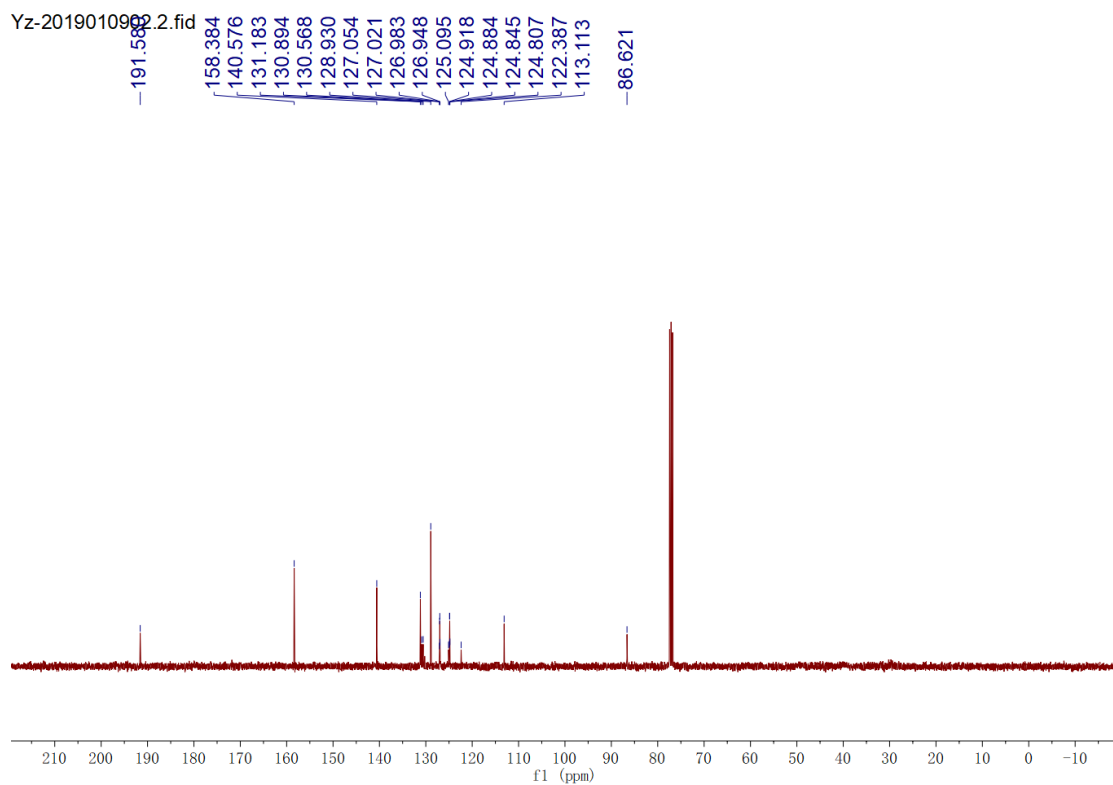
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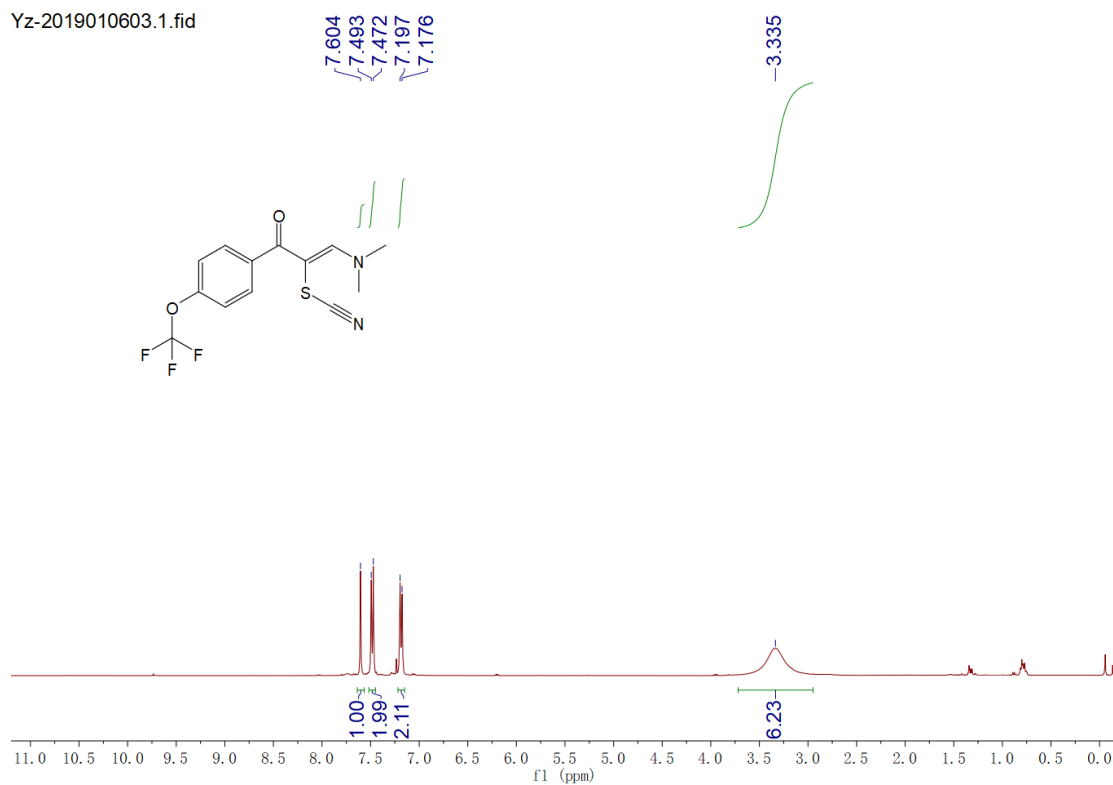
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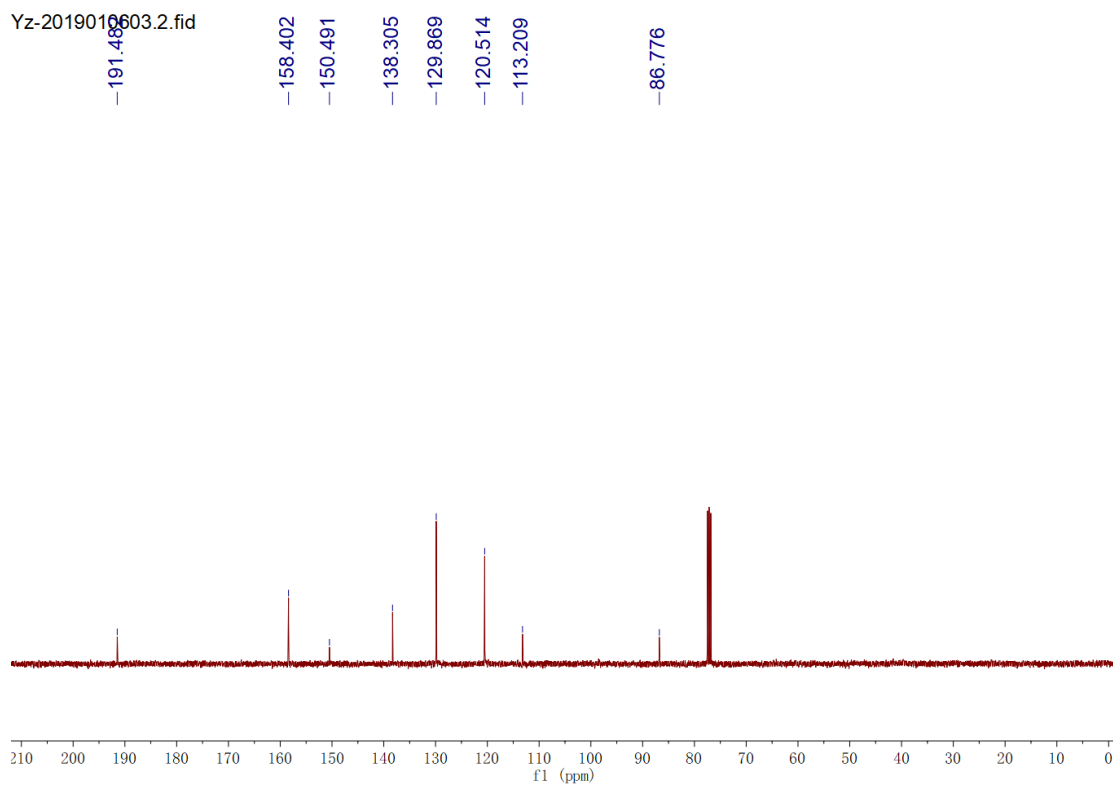
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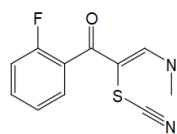
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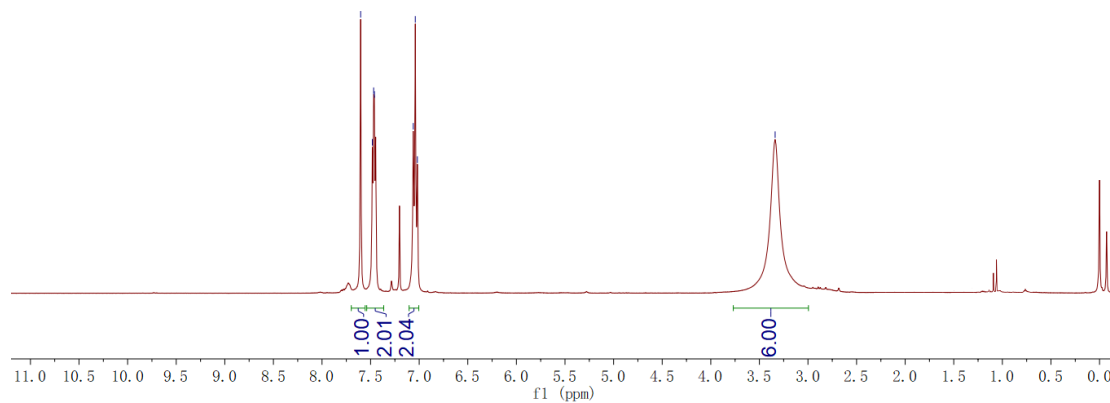


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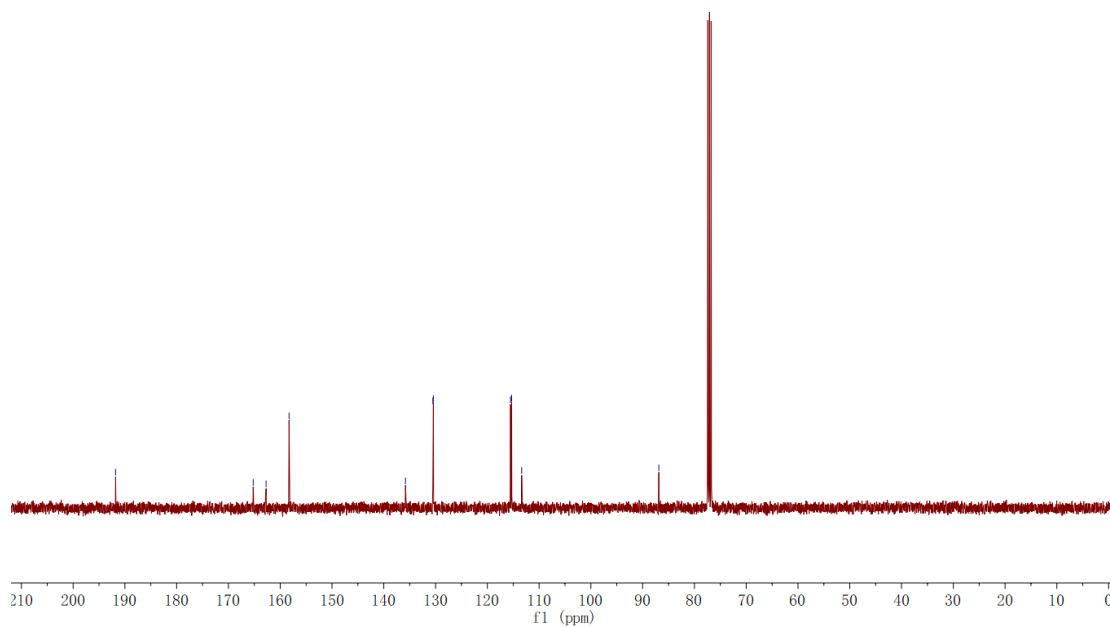
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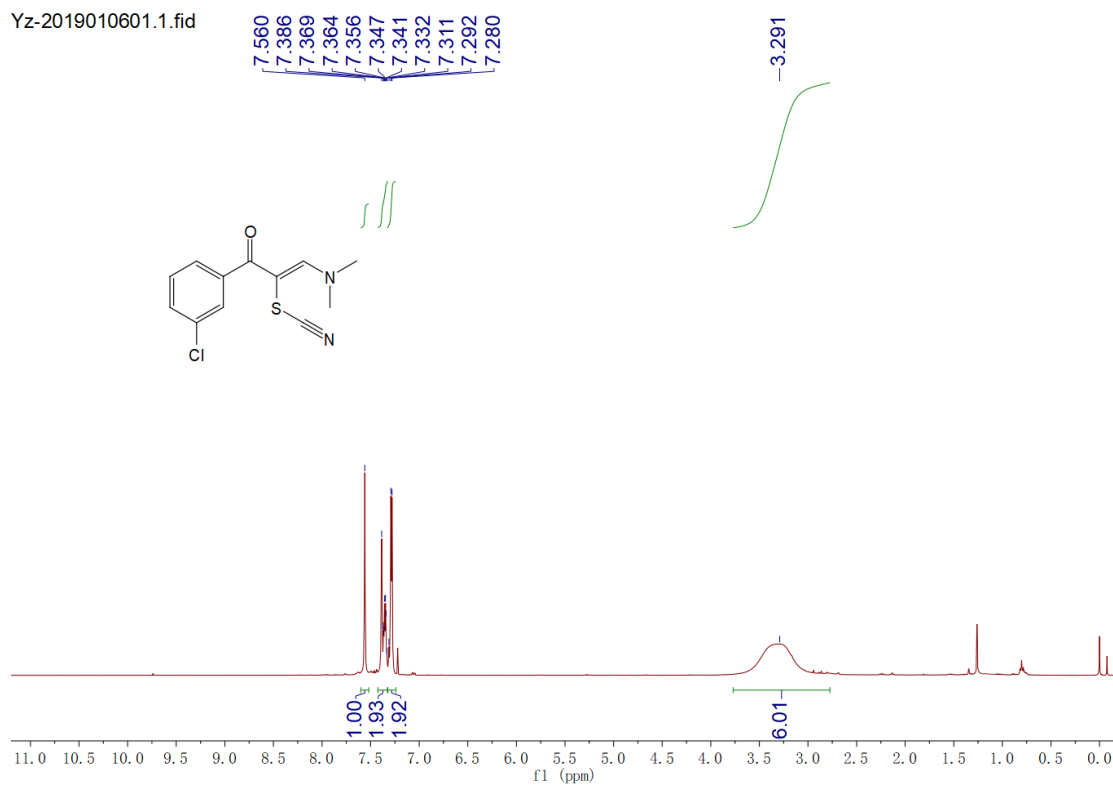
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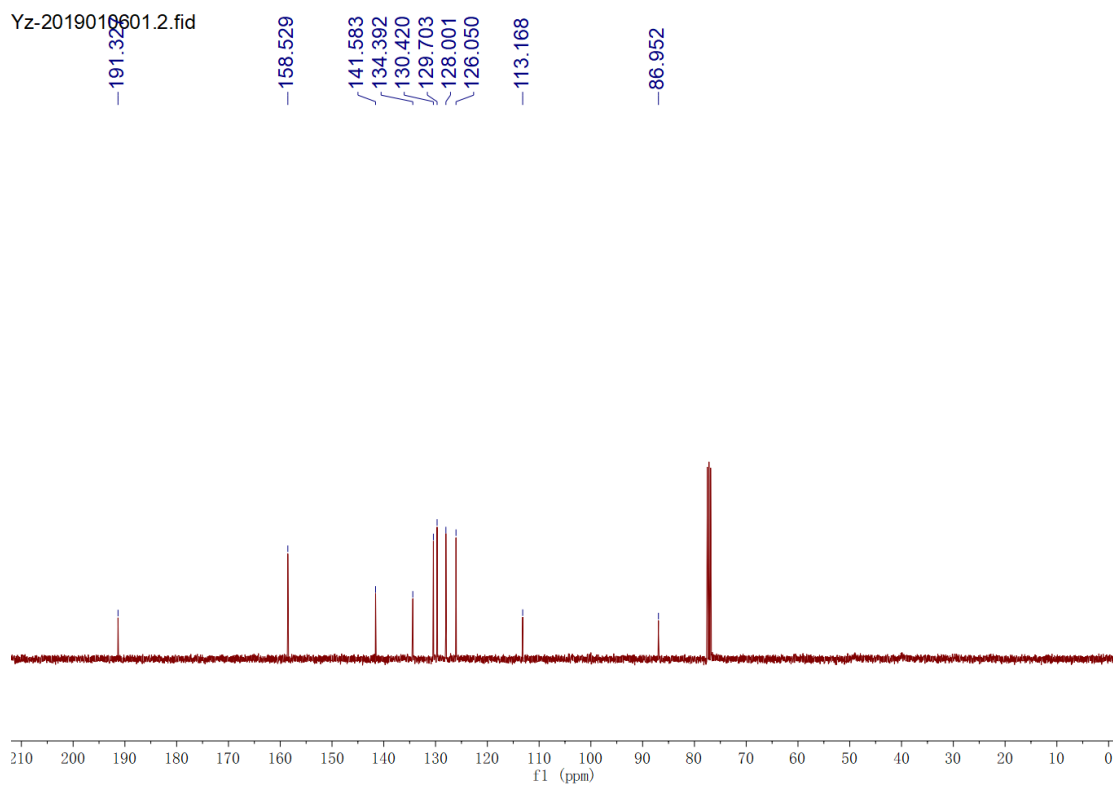
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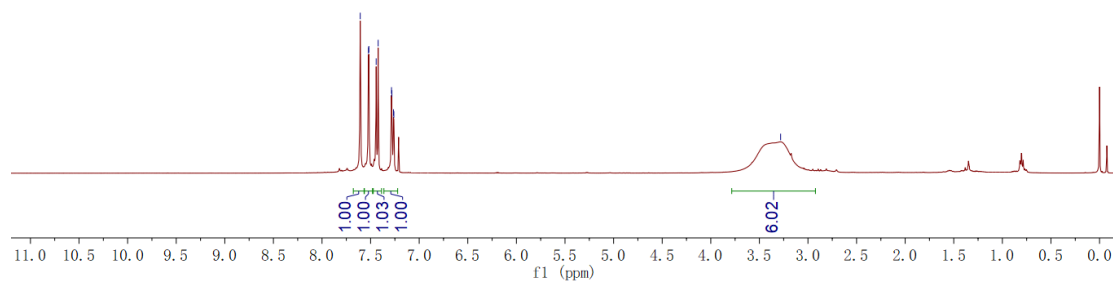
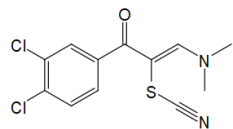
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Yz-2019011202.1.fid

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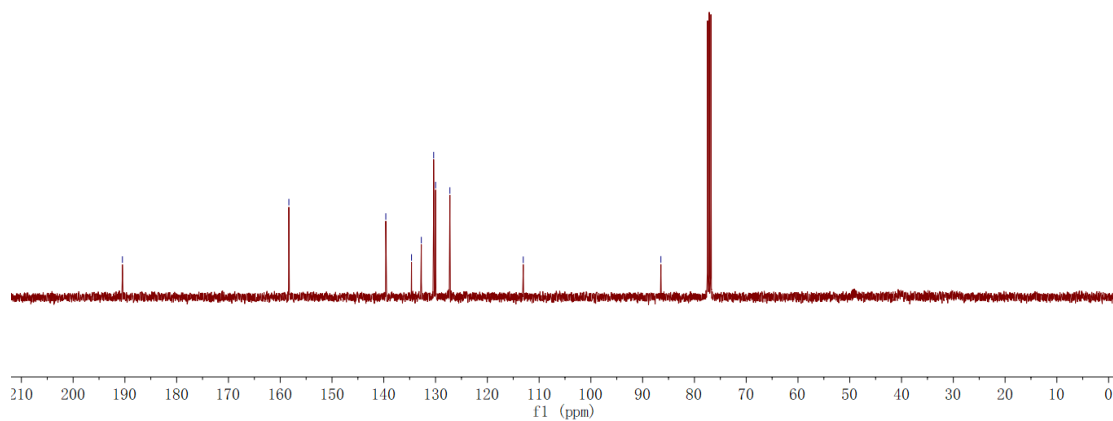
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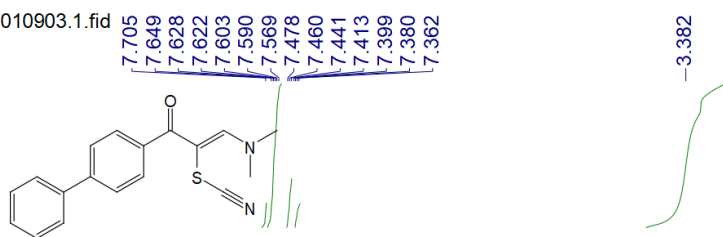
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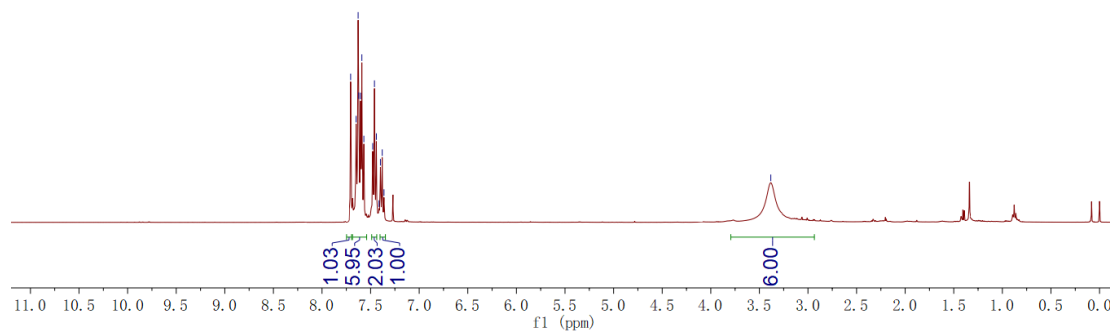


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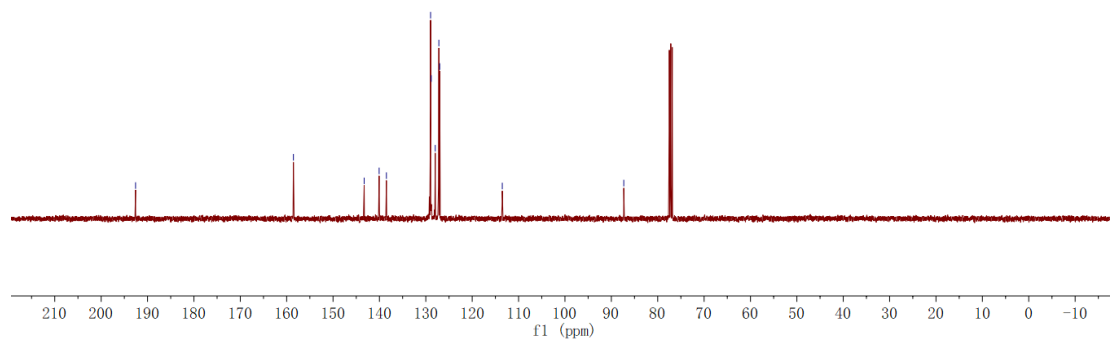
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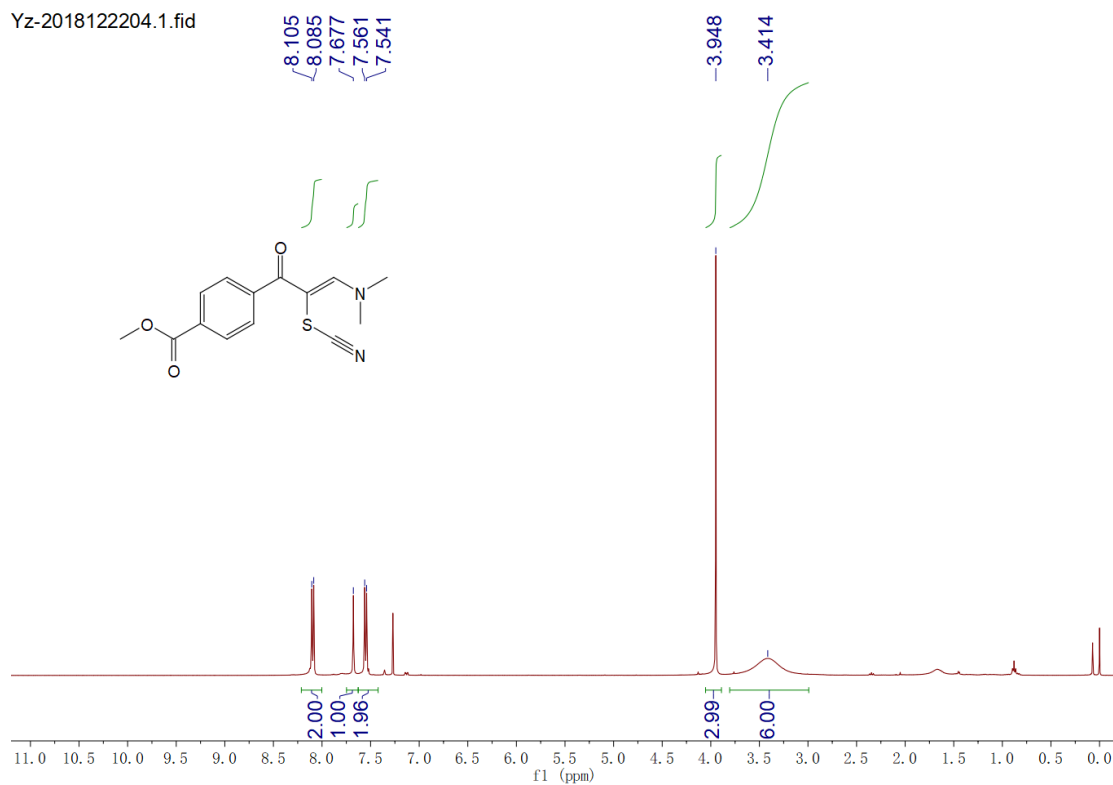


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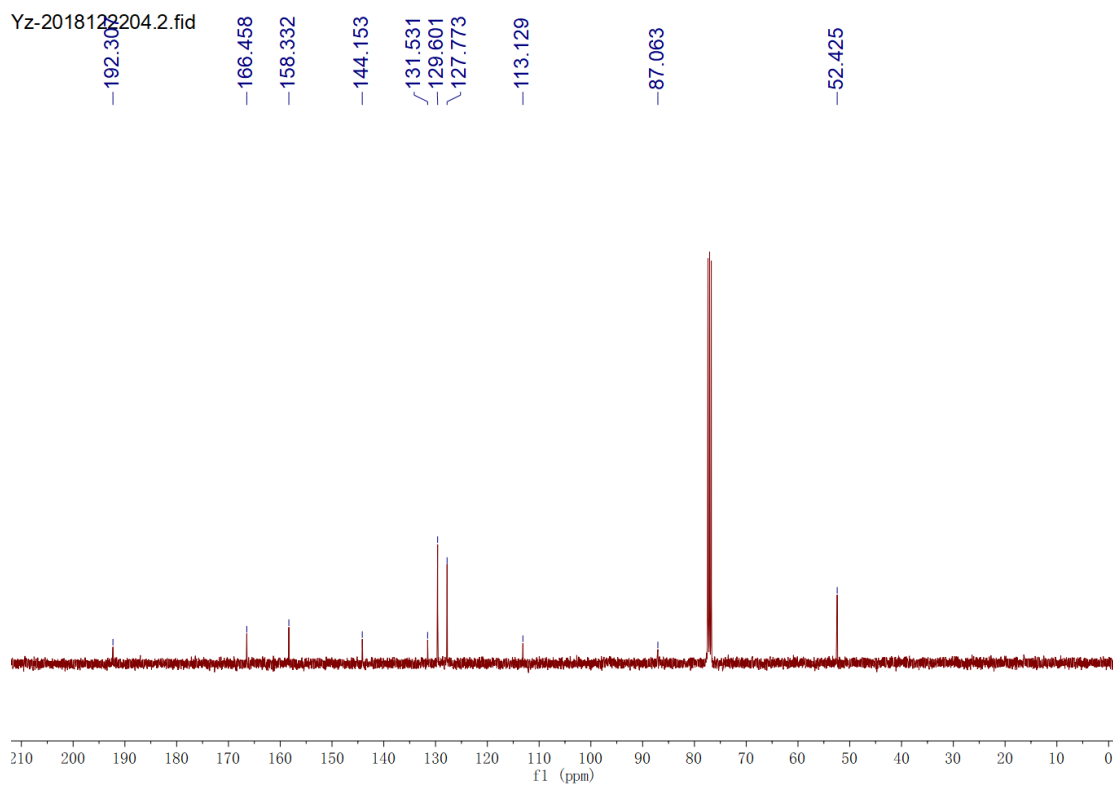
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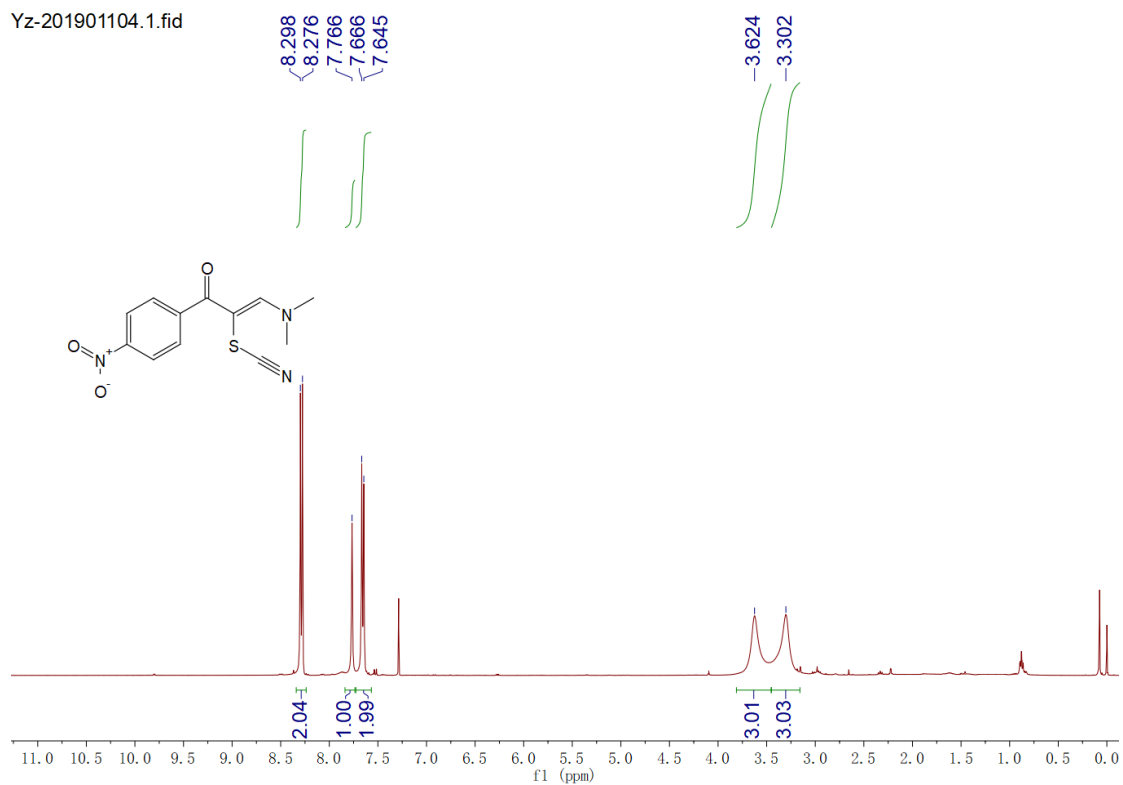
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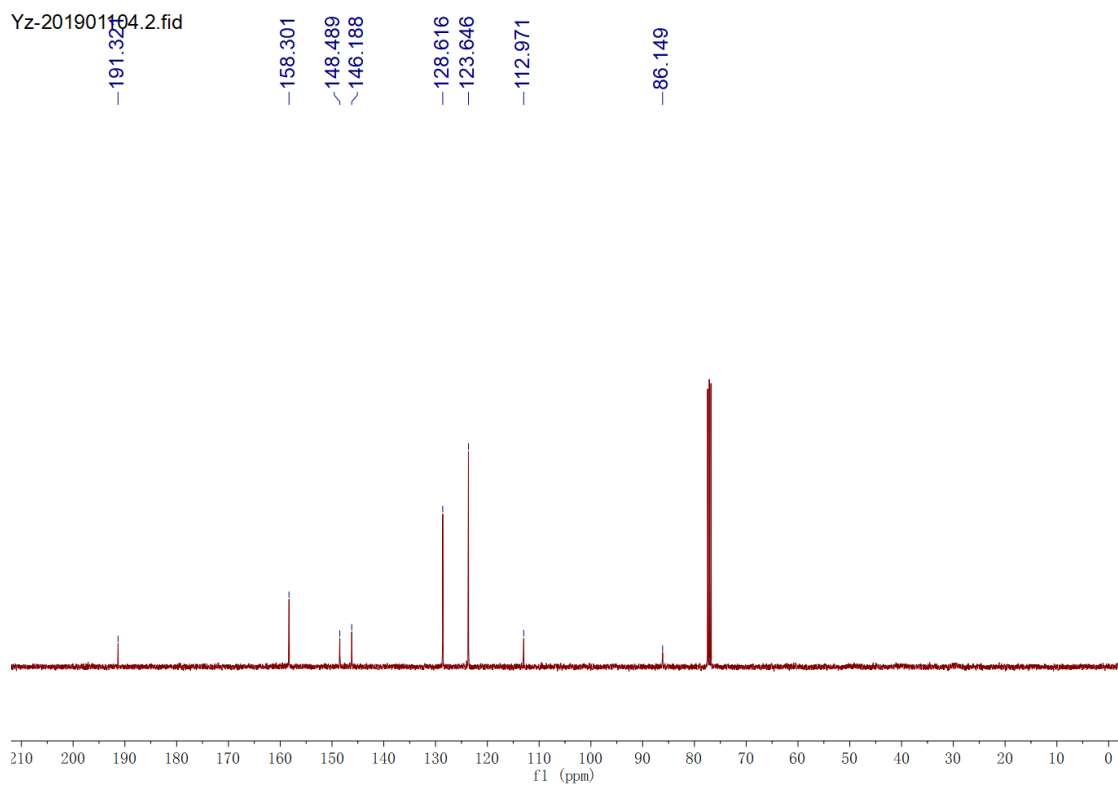
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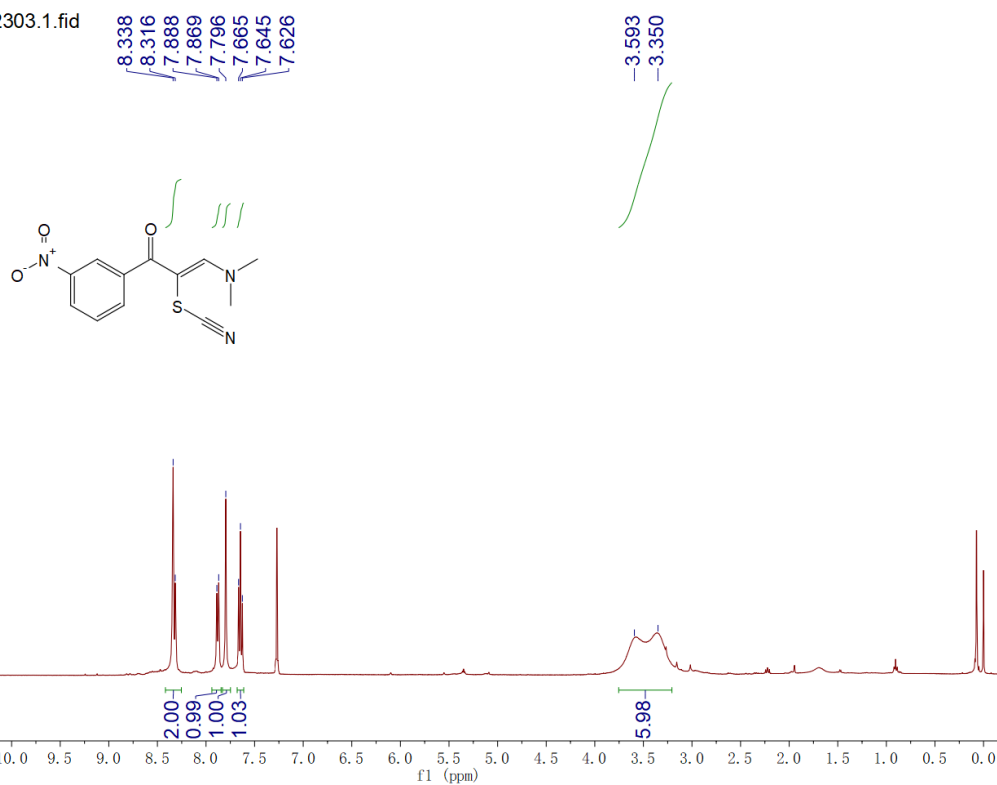
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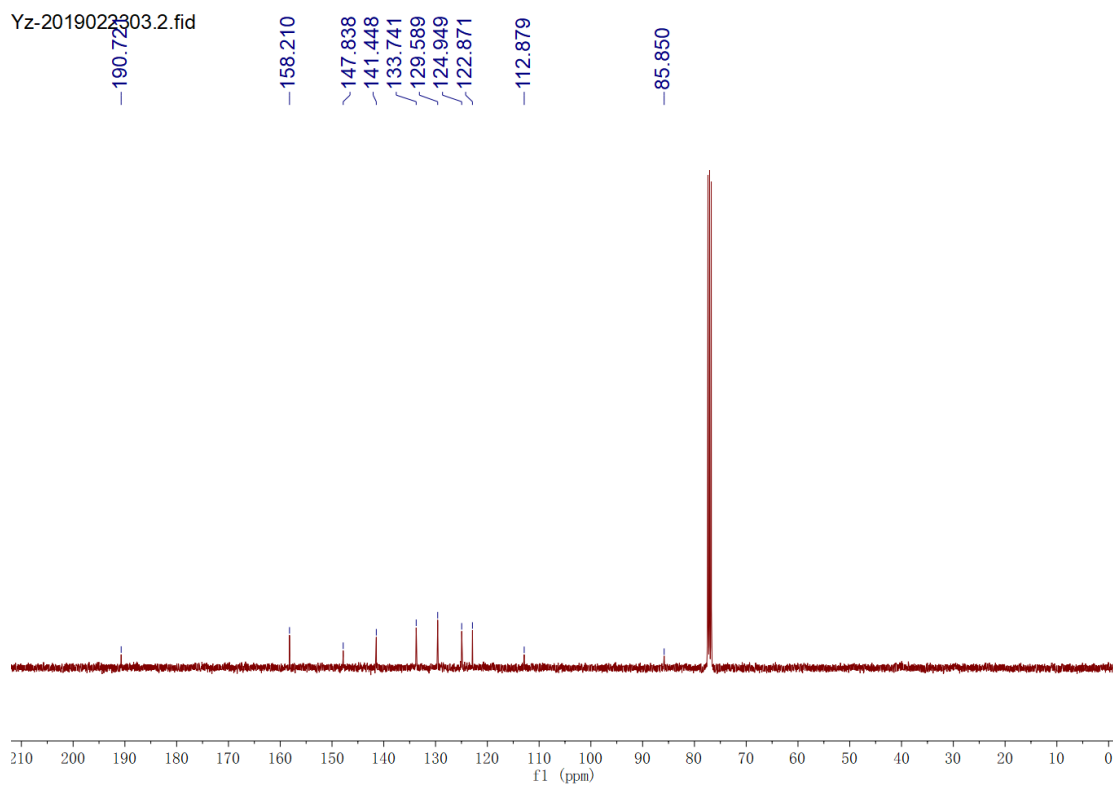
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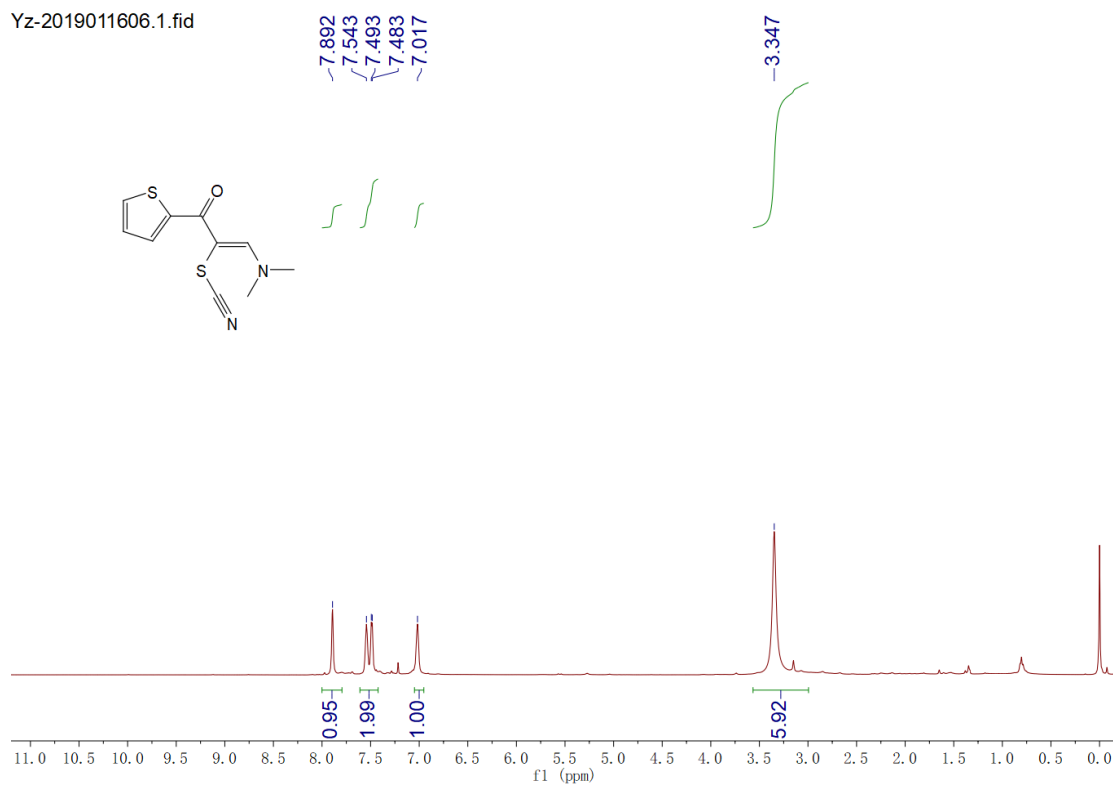
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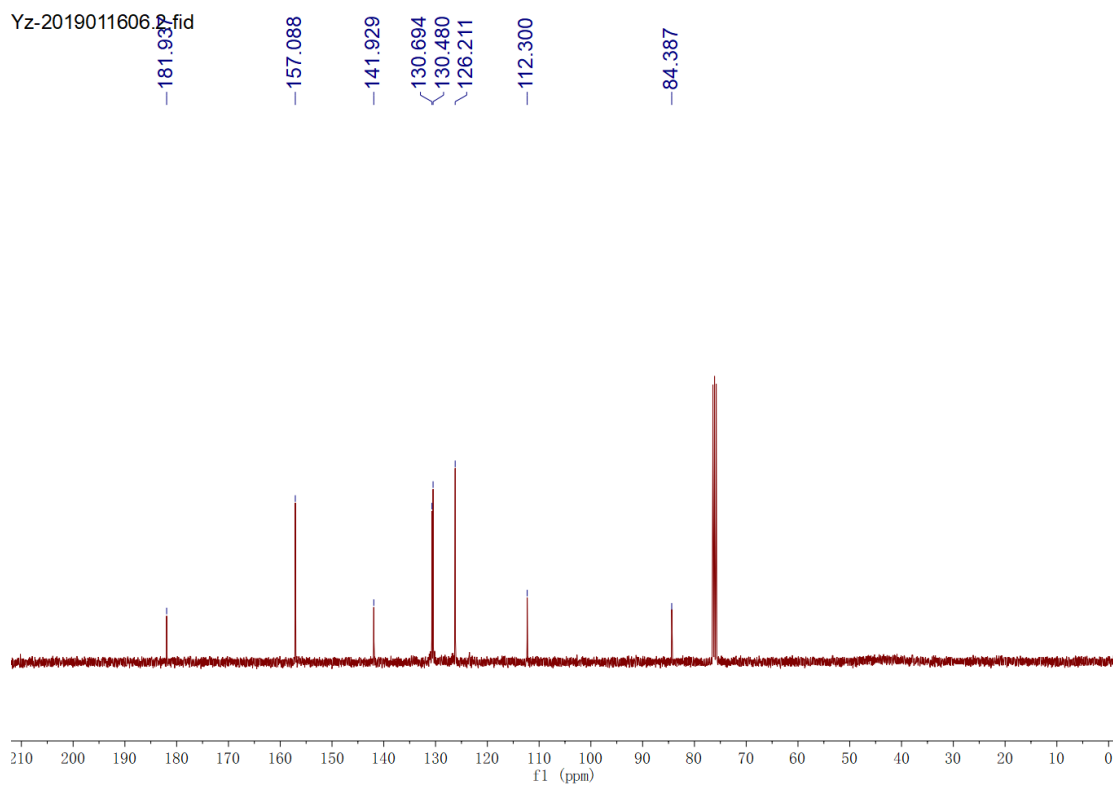
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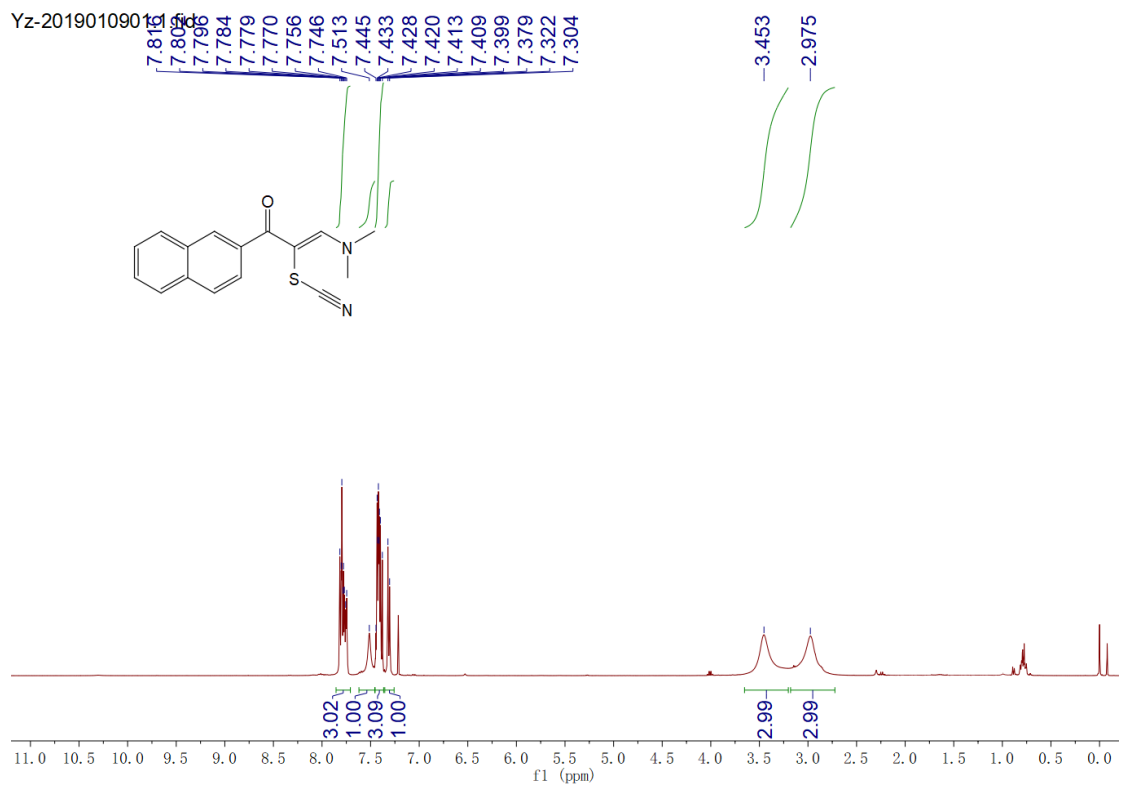
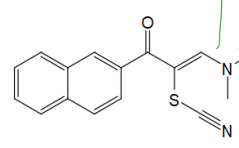
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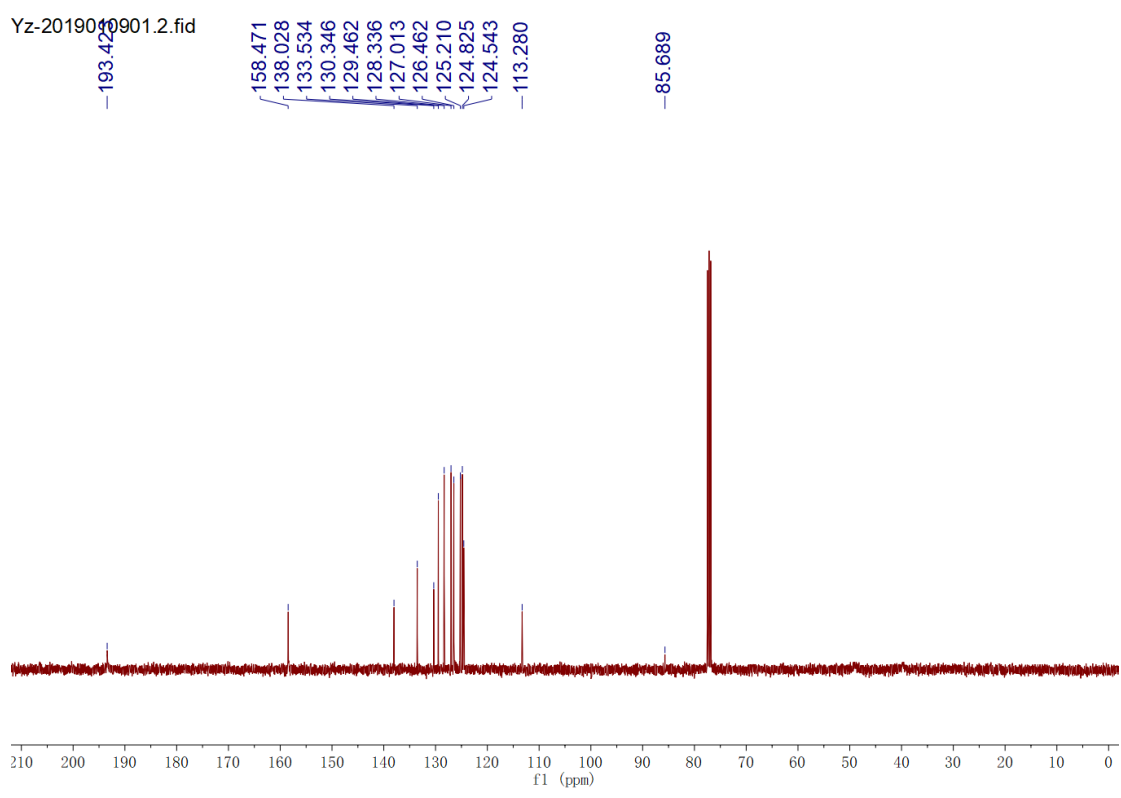
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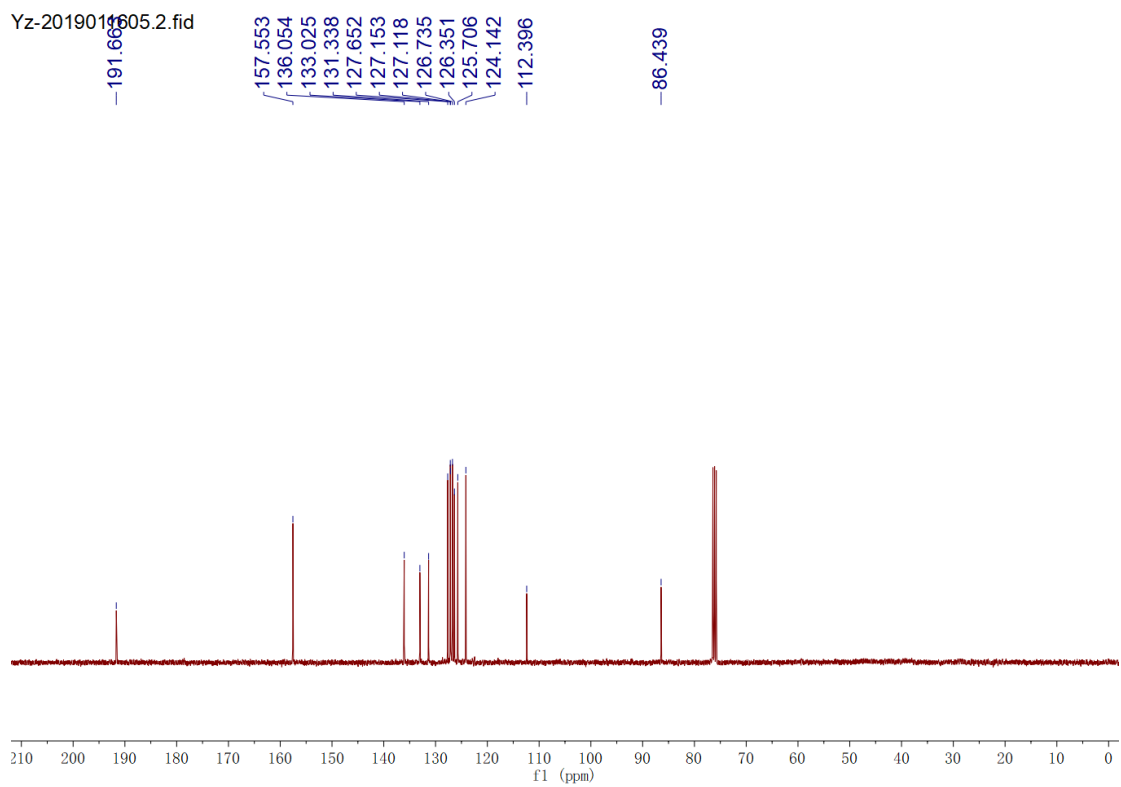
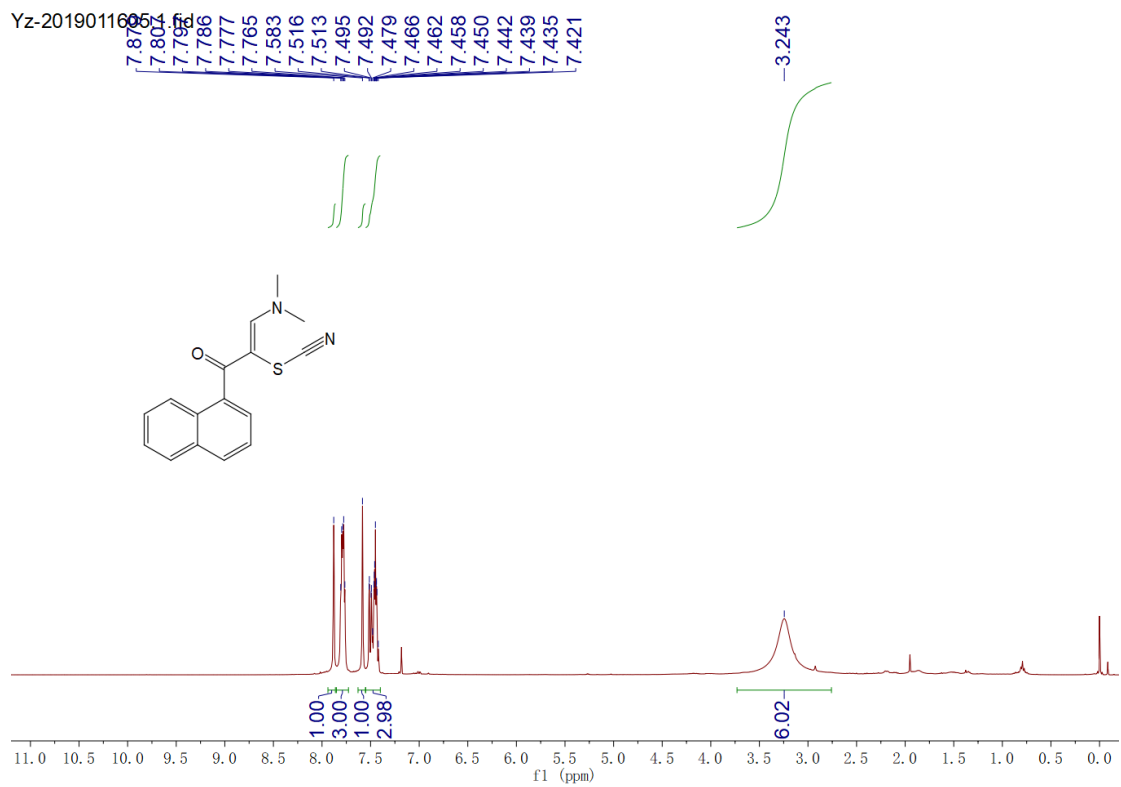


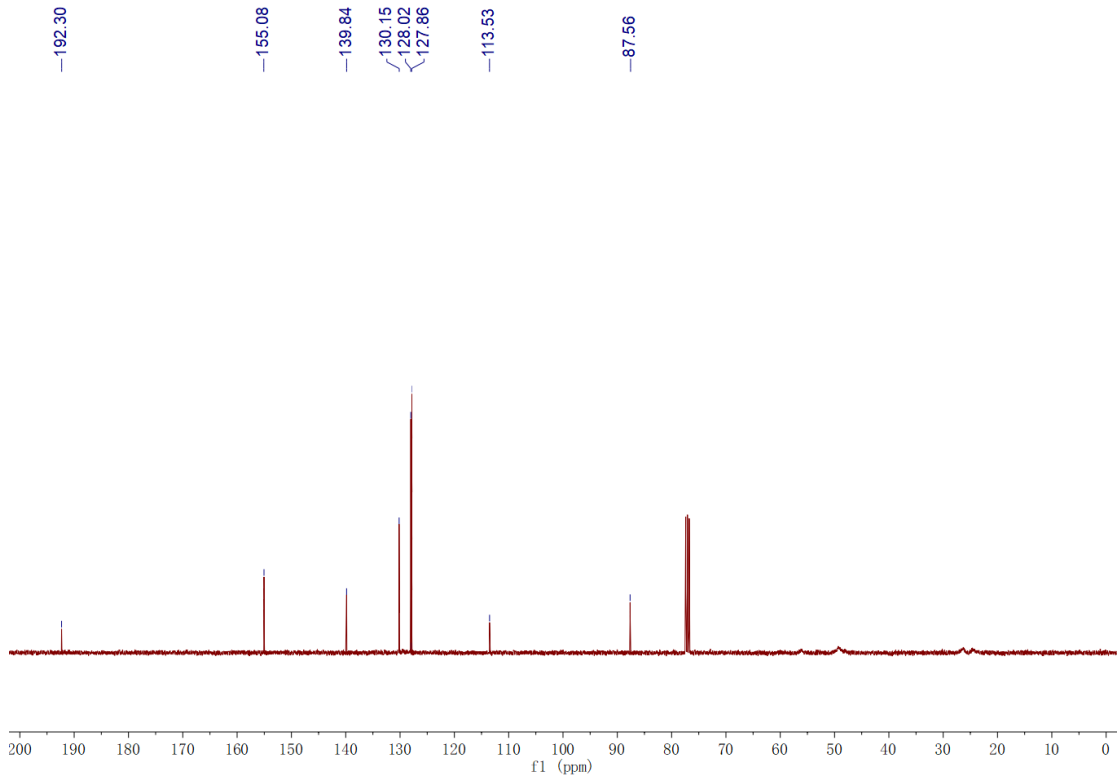
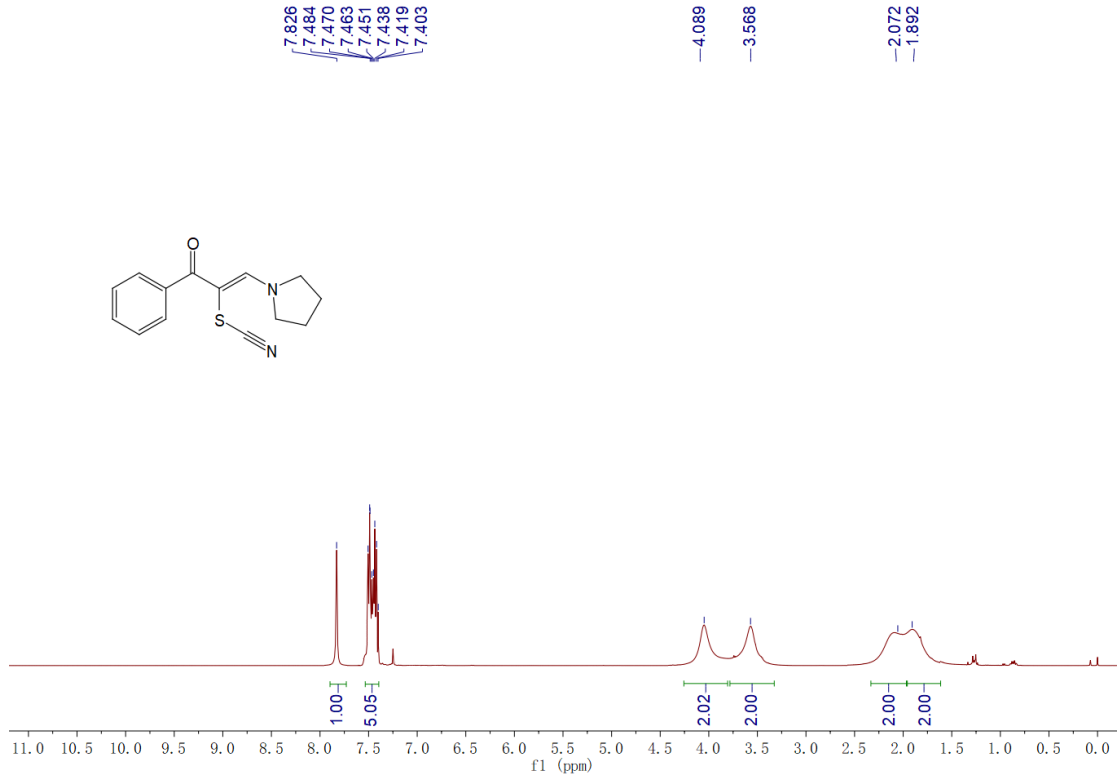
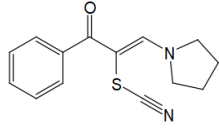
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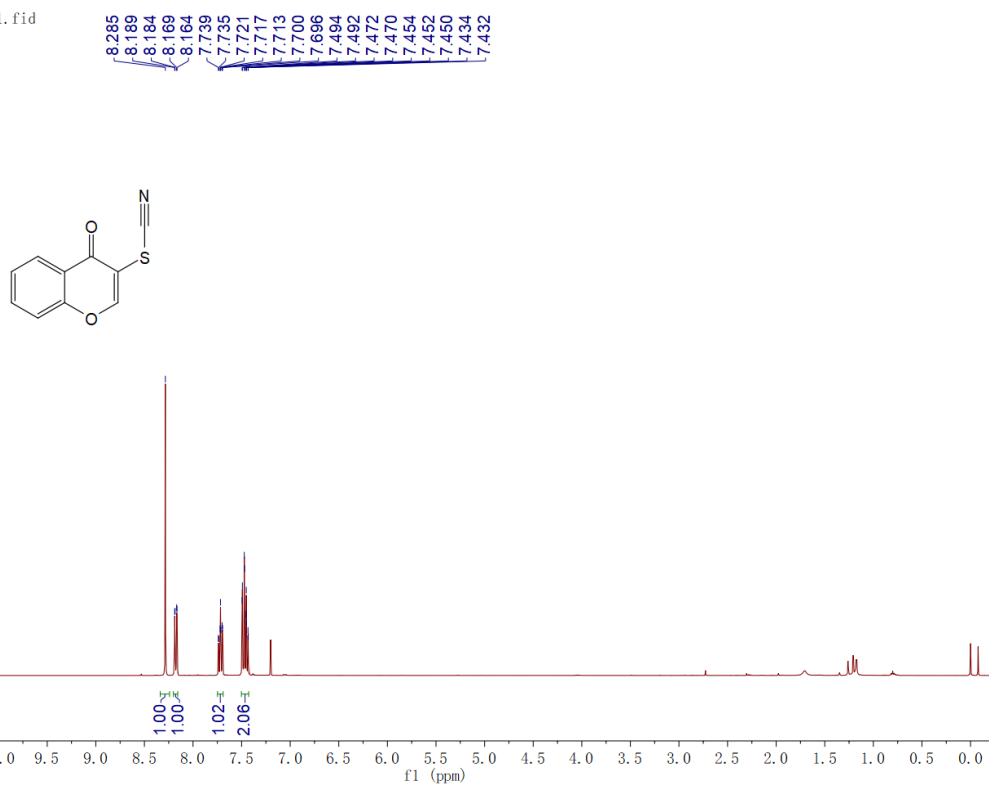
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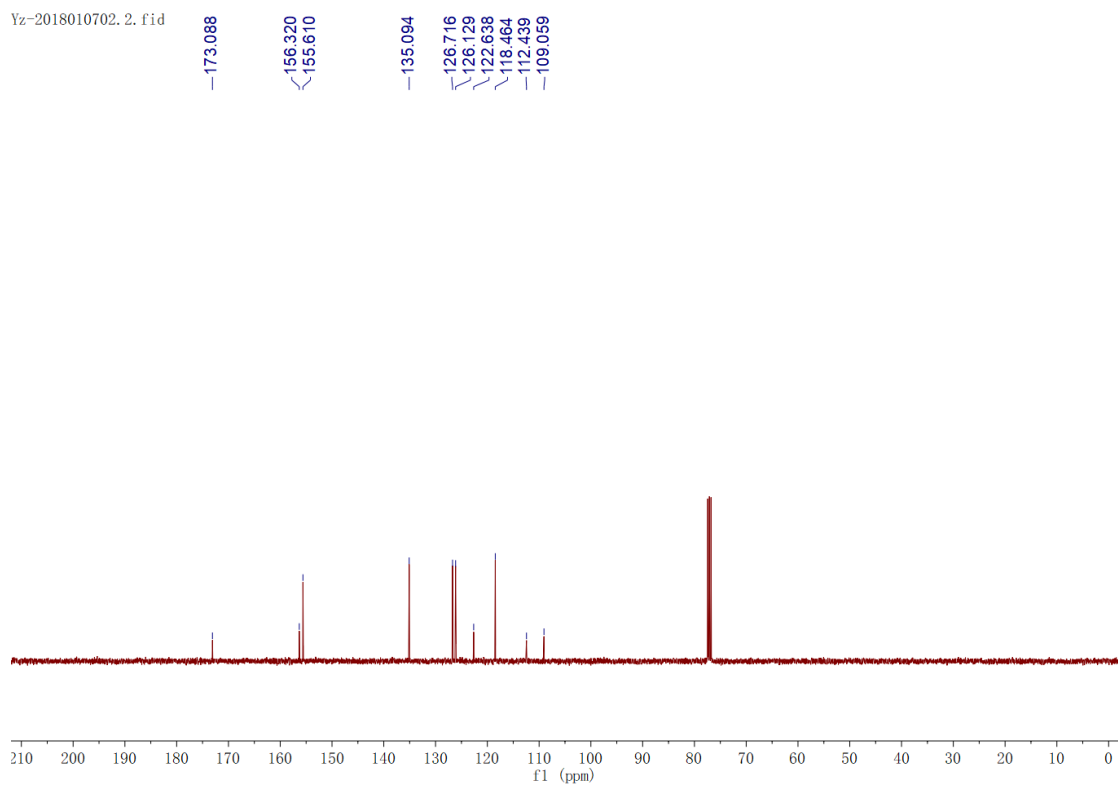


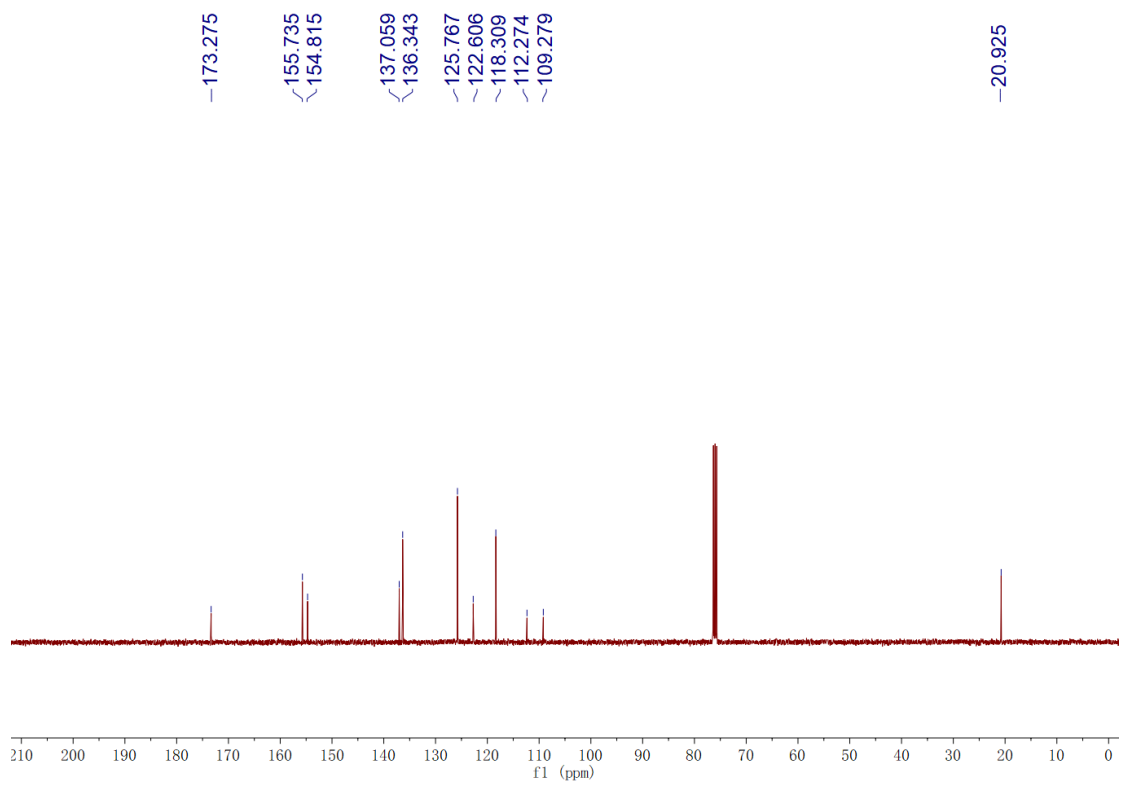
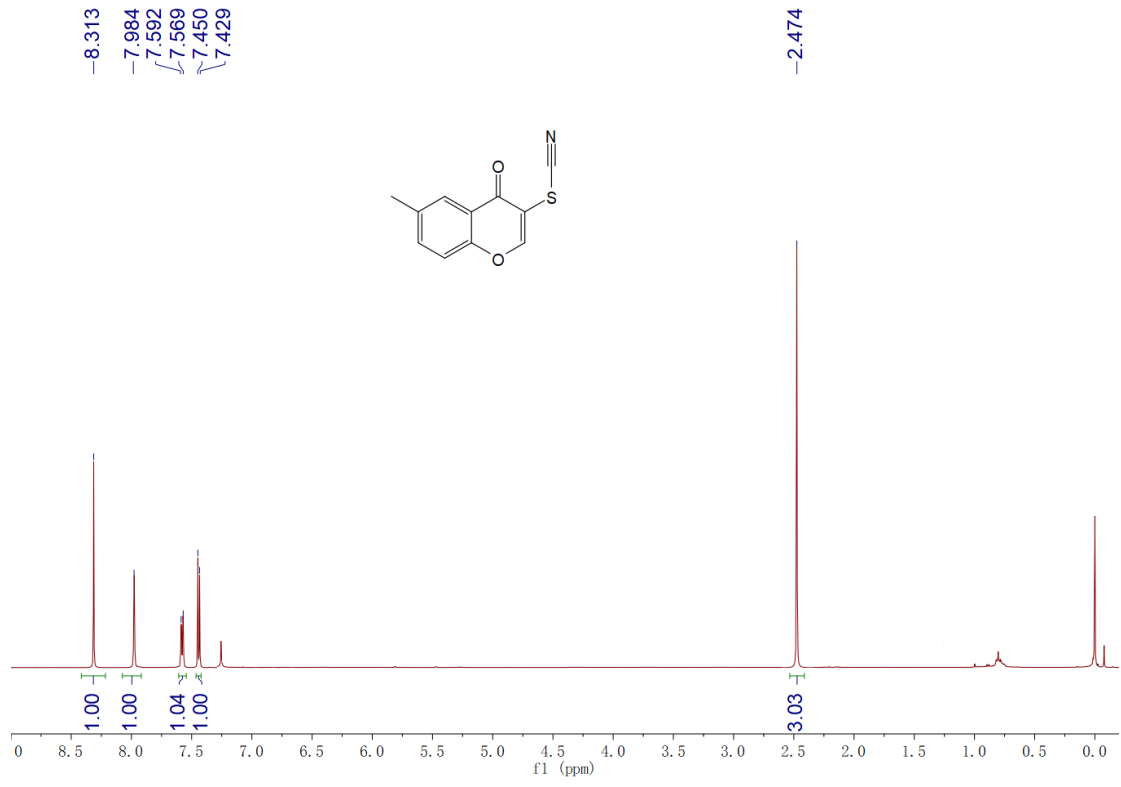


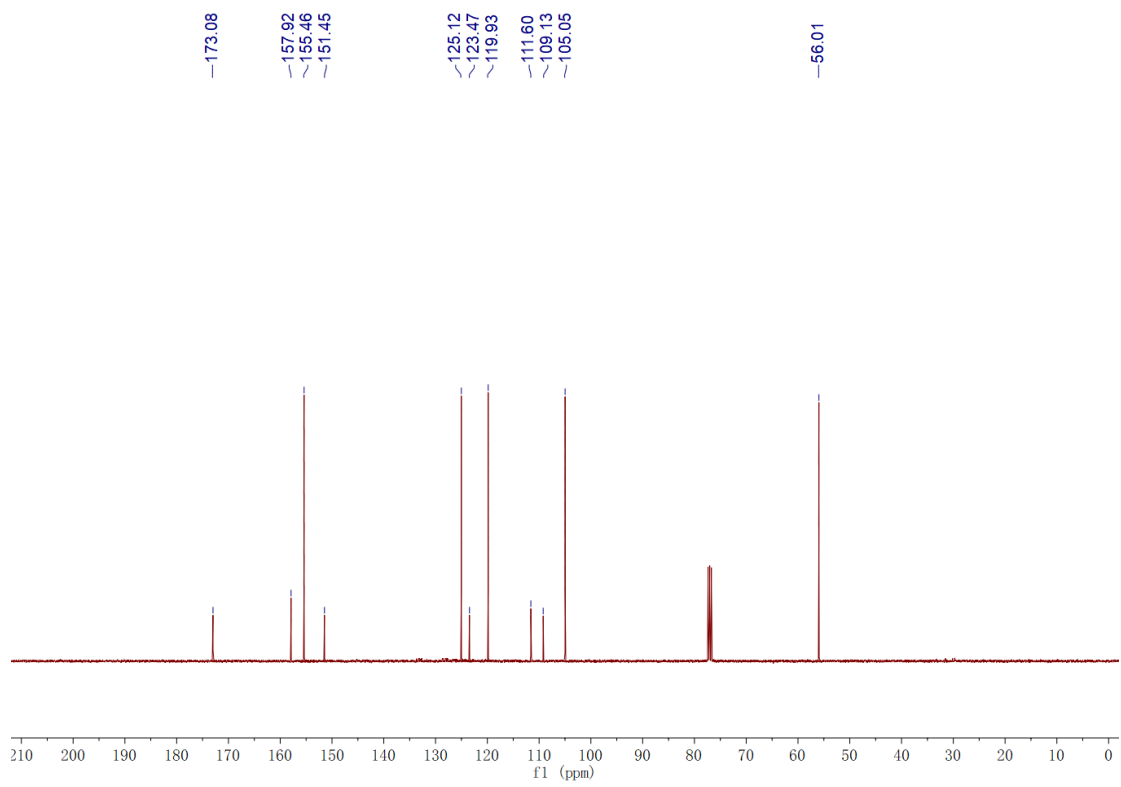
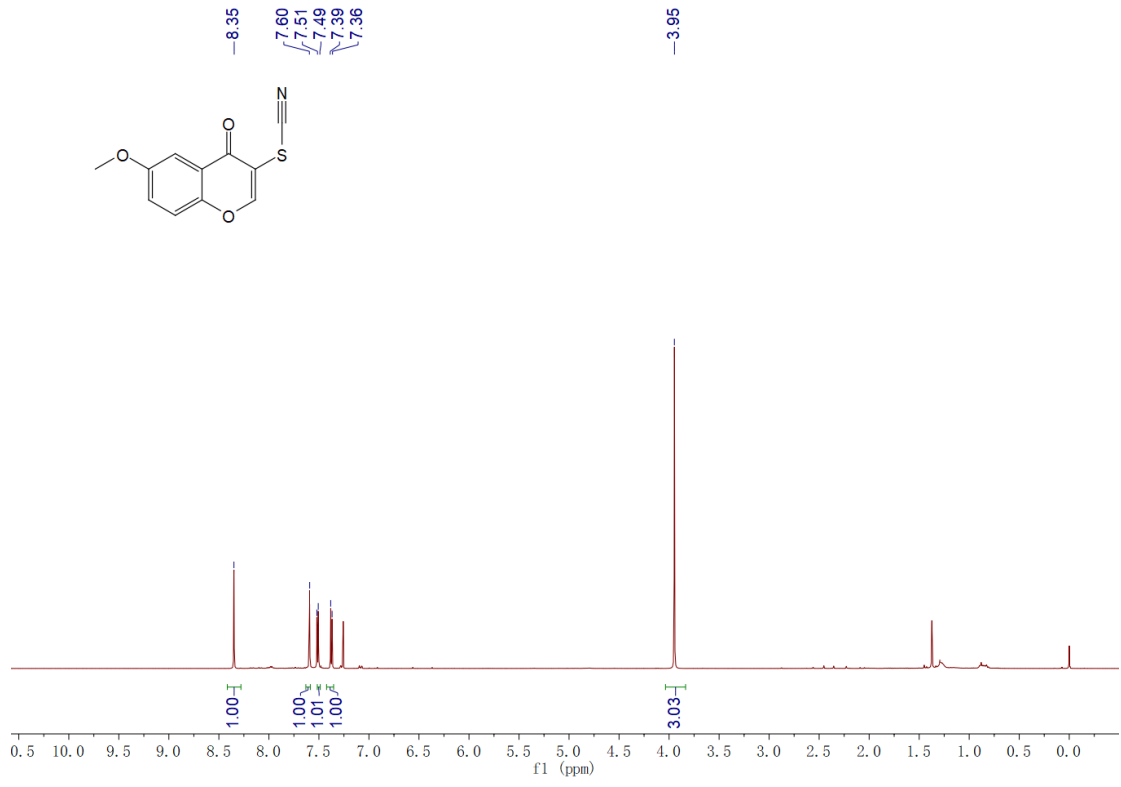
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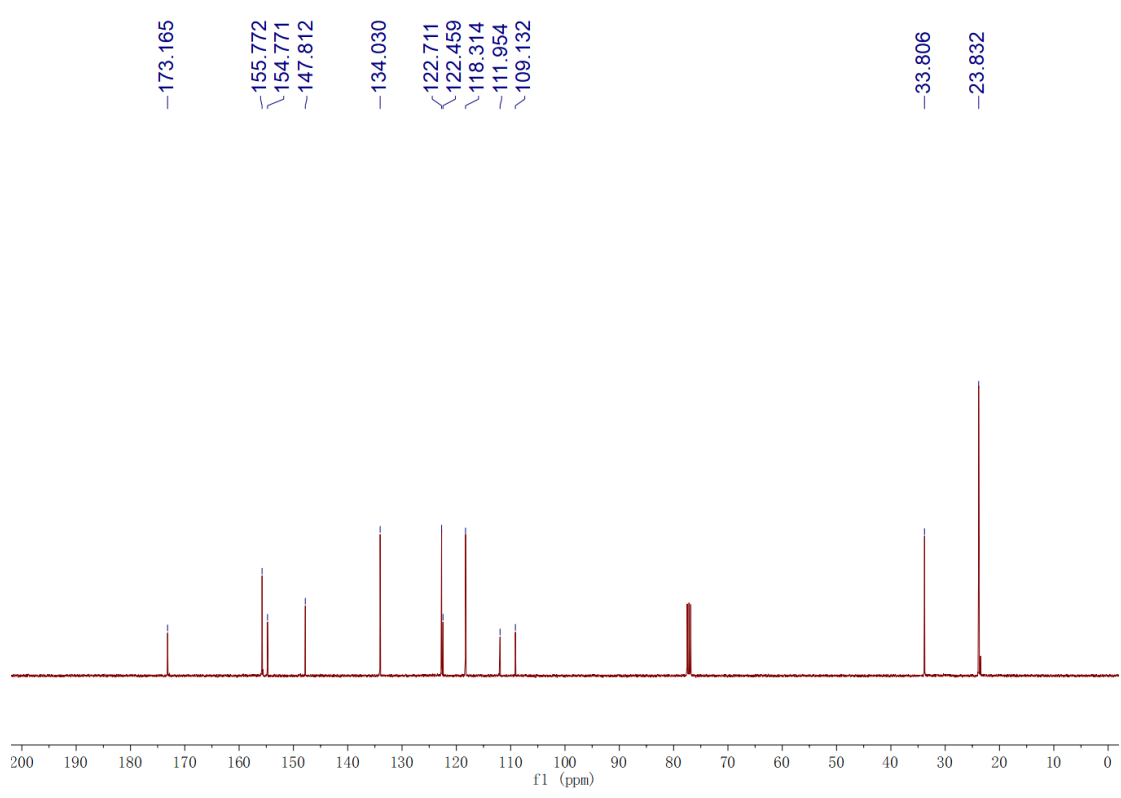
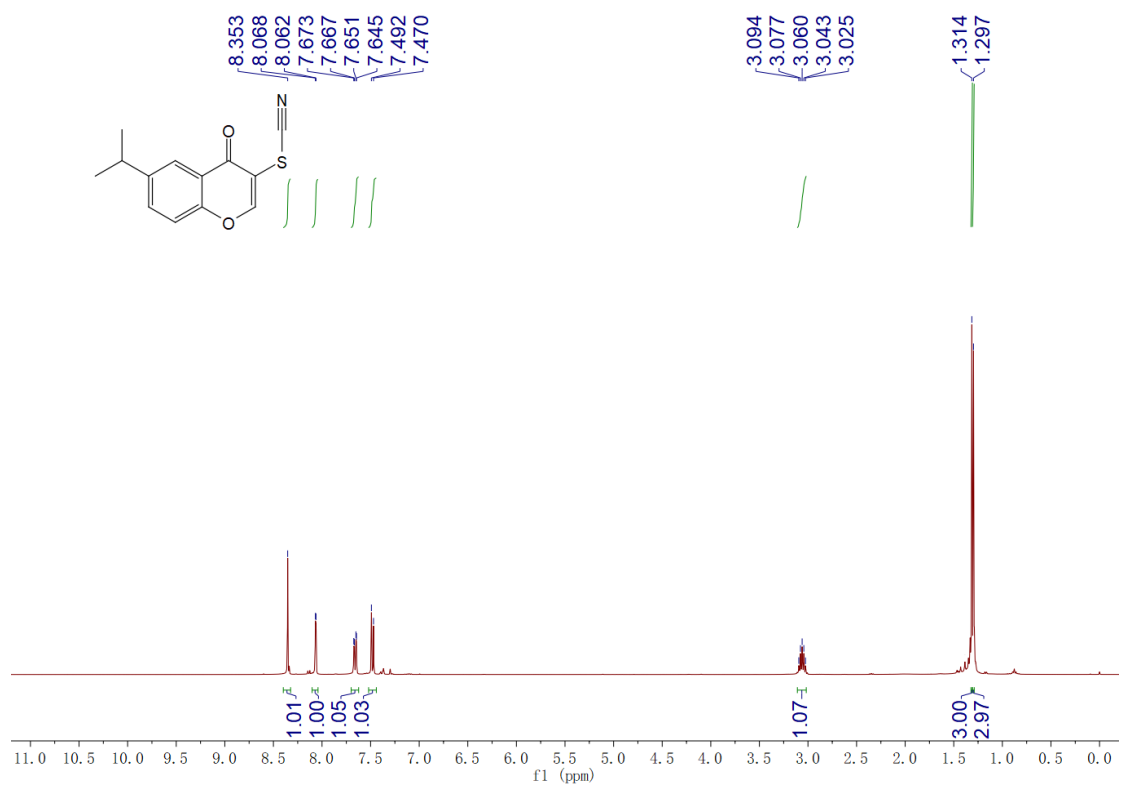


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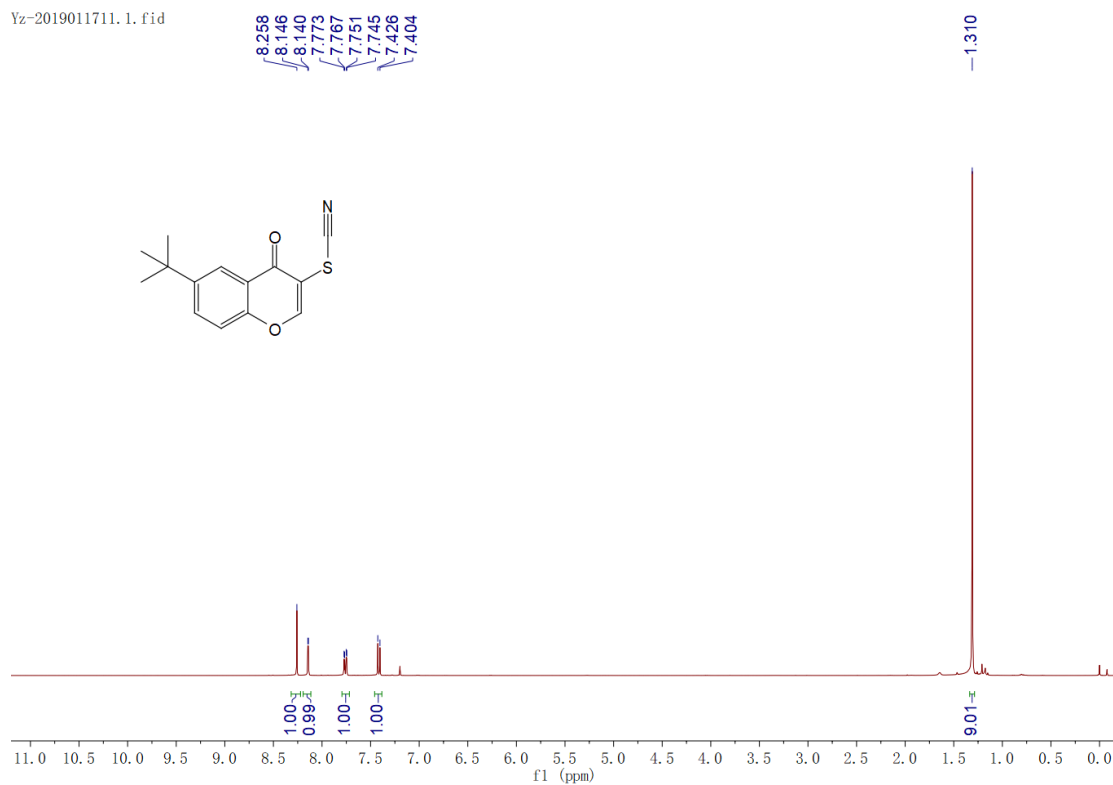




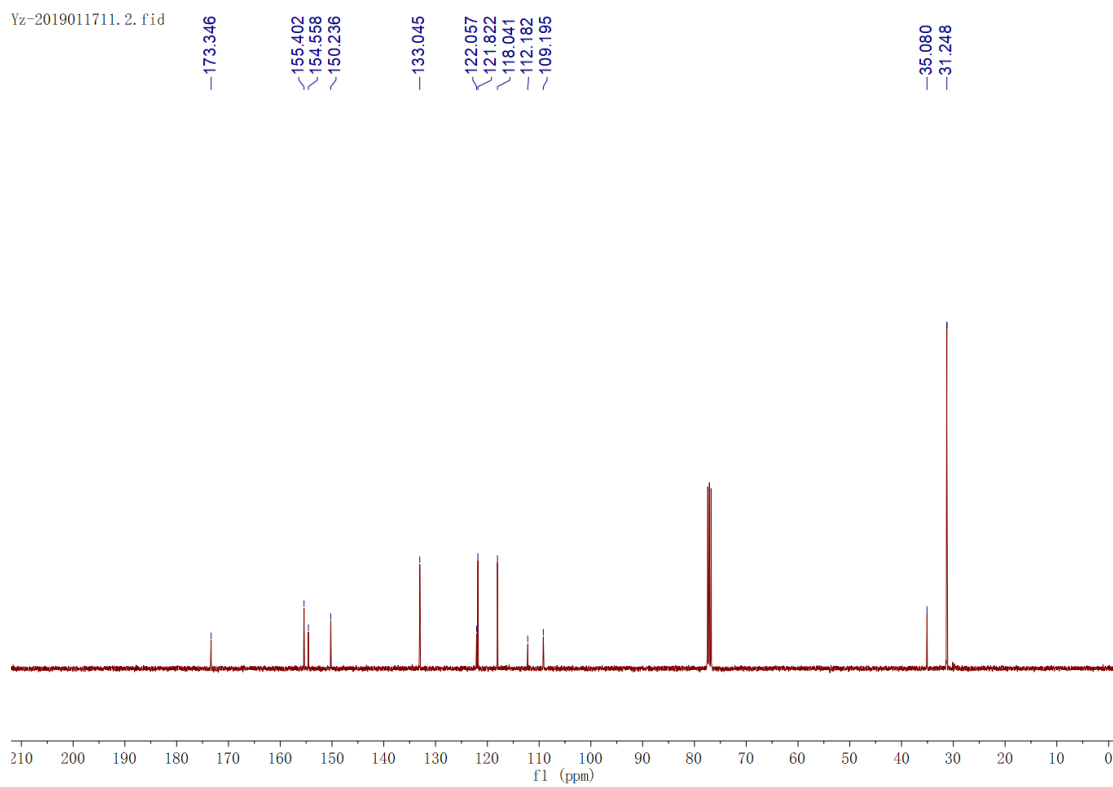


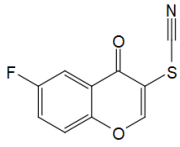


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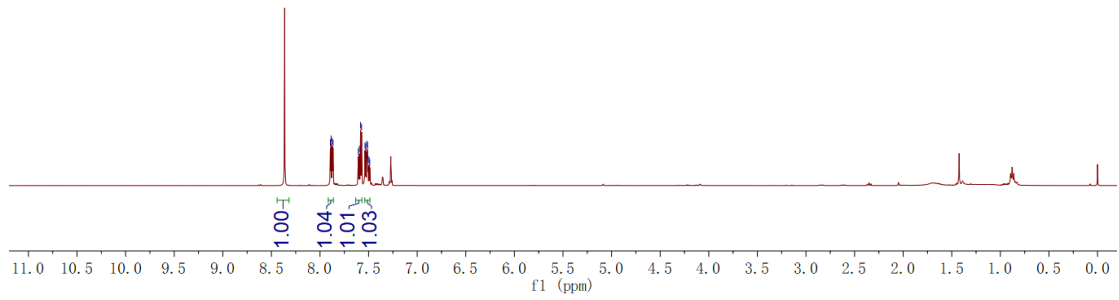


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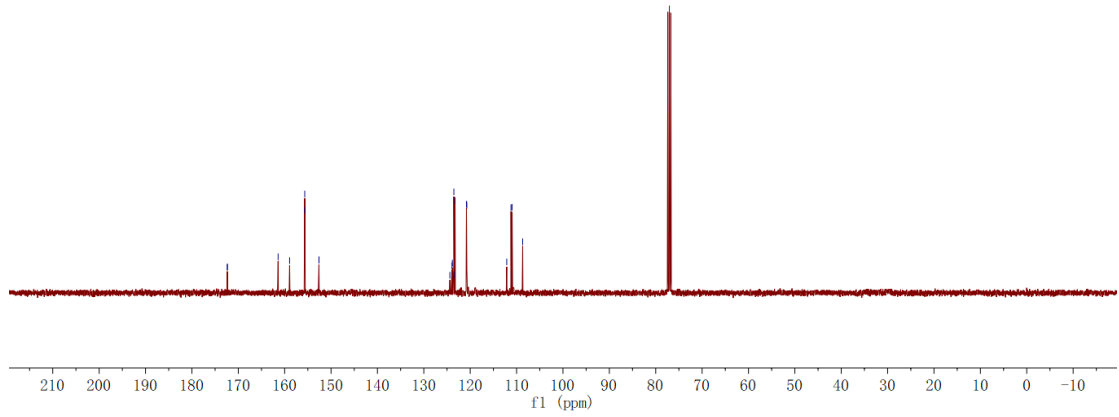


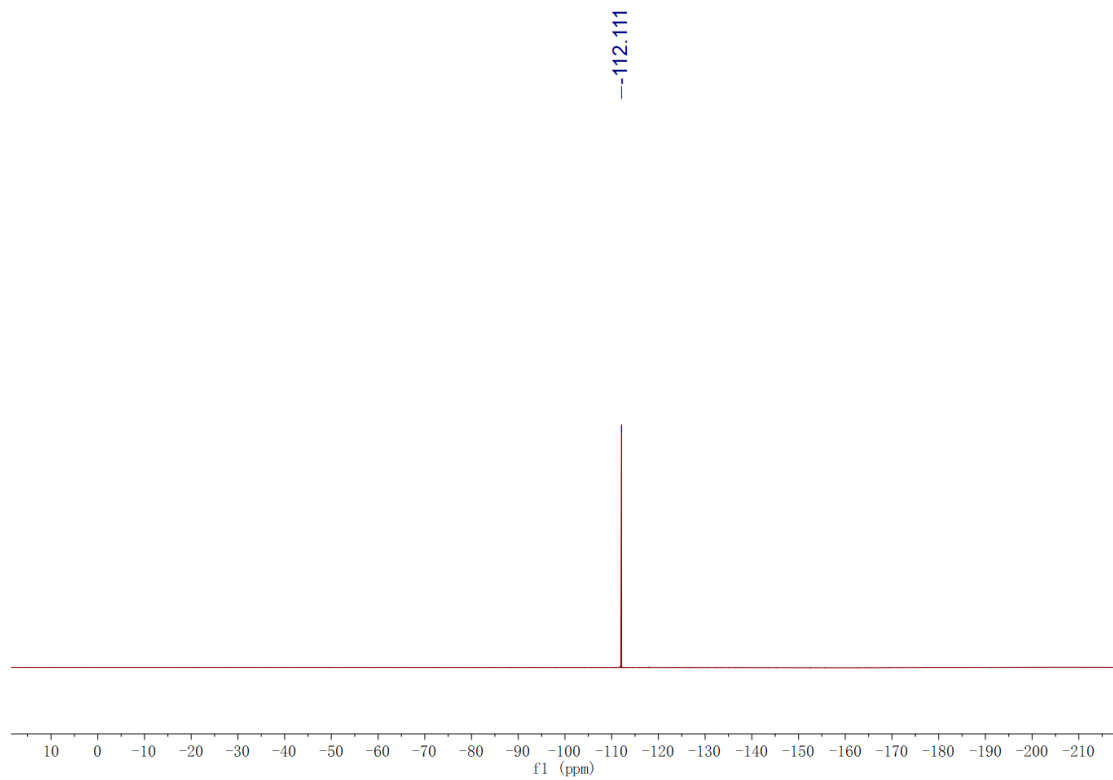


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7.488

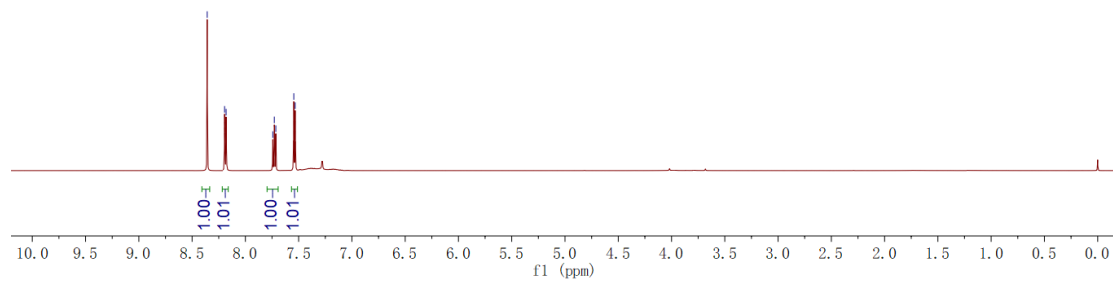
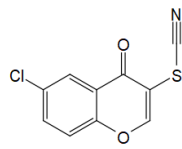


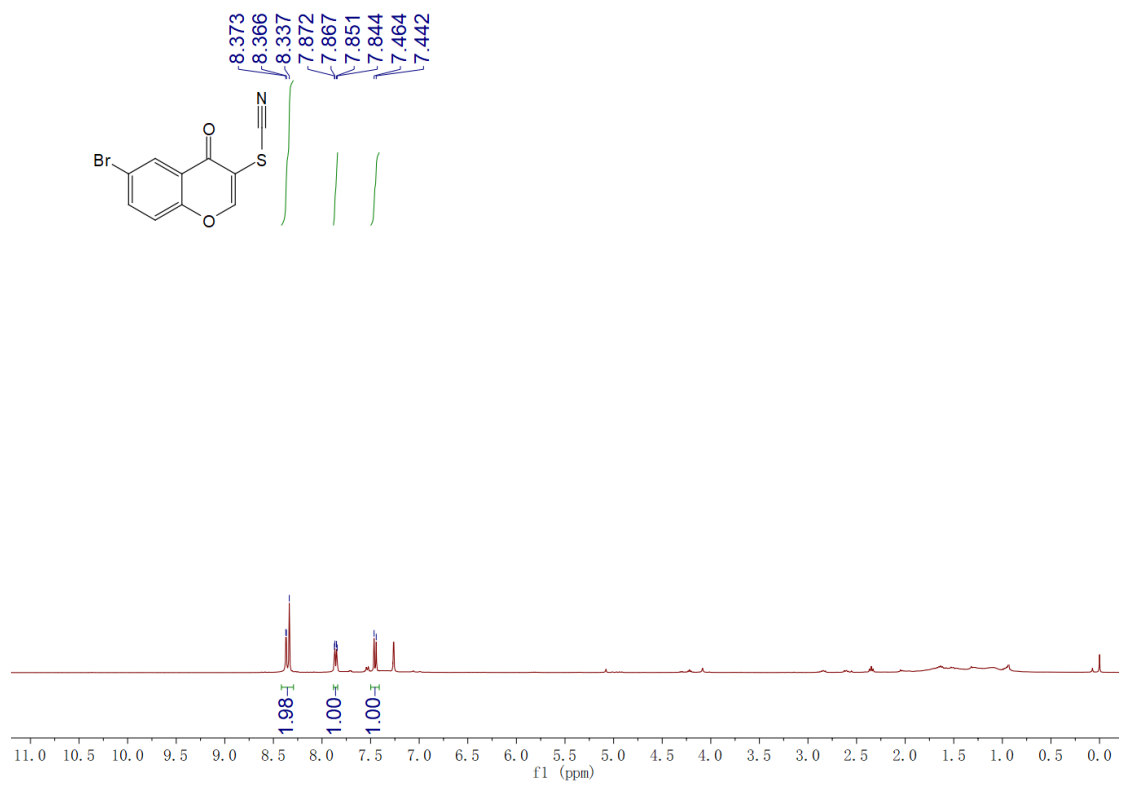
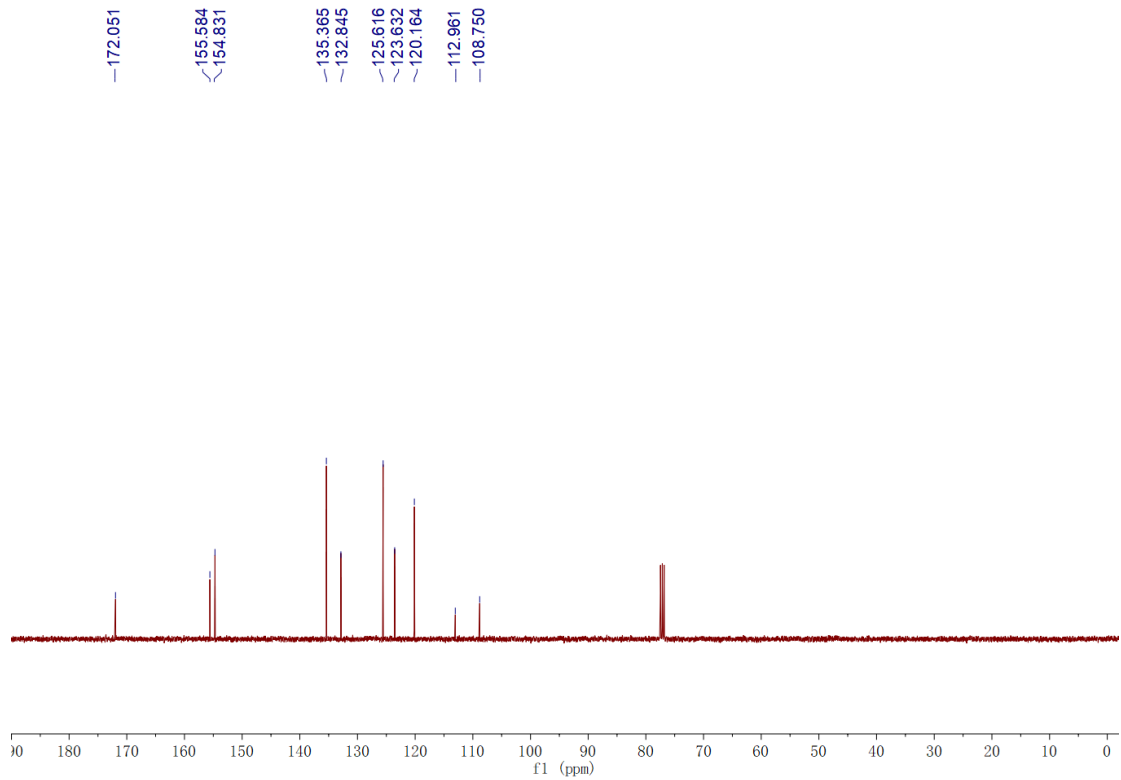
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158.930
155.674
155.652
152.613
152.595
124.383
123.920
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123.520
123.485
123.267
120.811
120.728
112.121
111.204
110.965
108.683



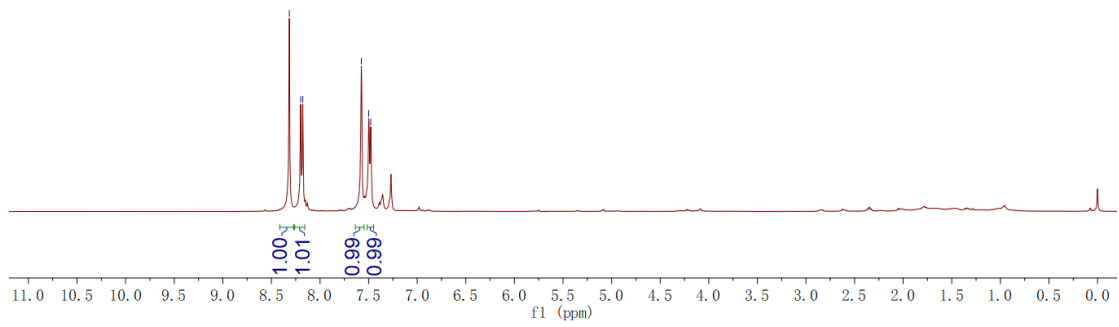
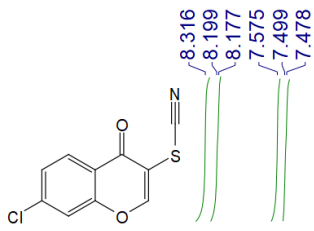
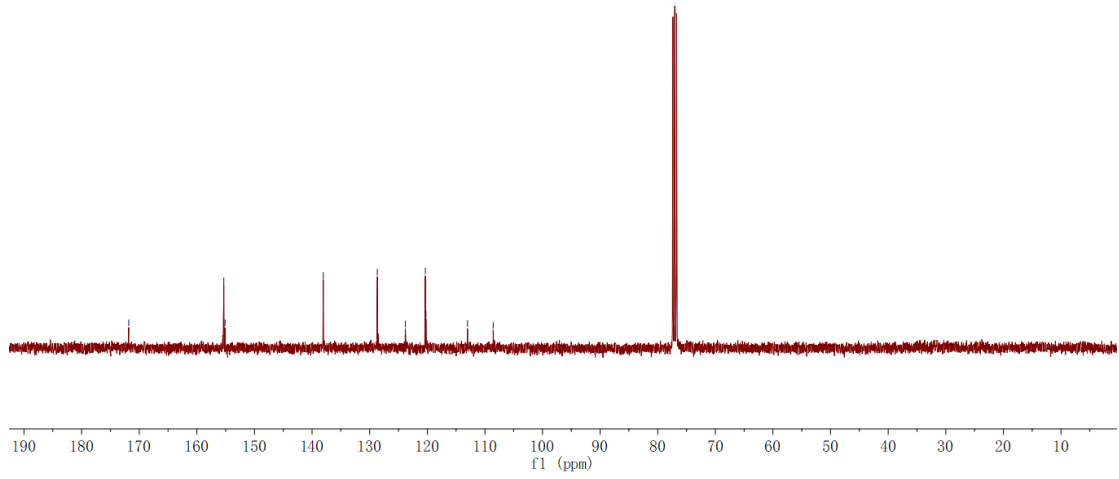


8.356
8.188
8.186
7.746
7.735
7.724
7.540
7.522

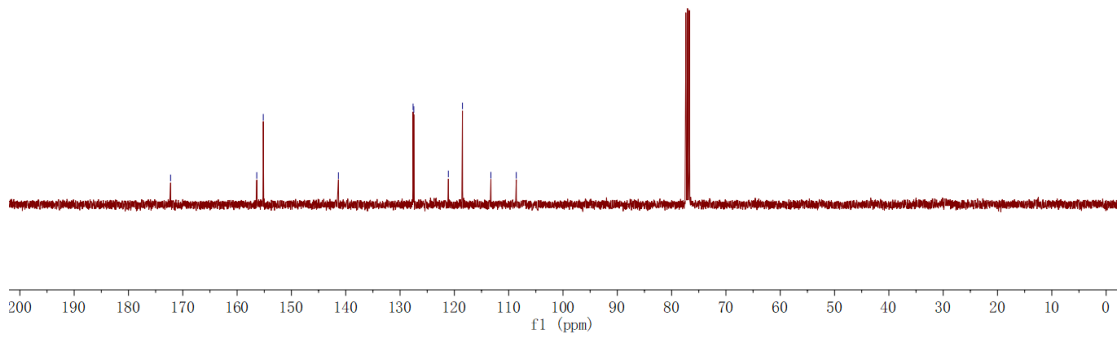




-171.82
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-155.10
-138.06
-128.67
-123.82
-120.34
-120.23
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-108.56

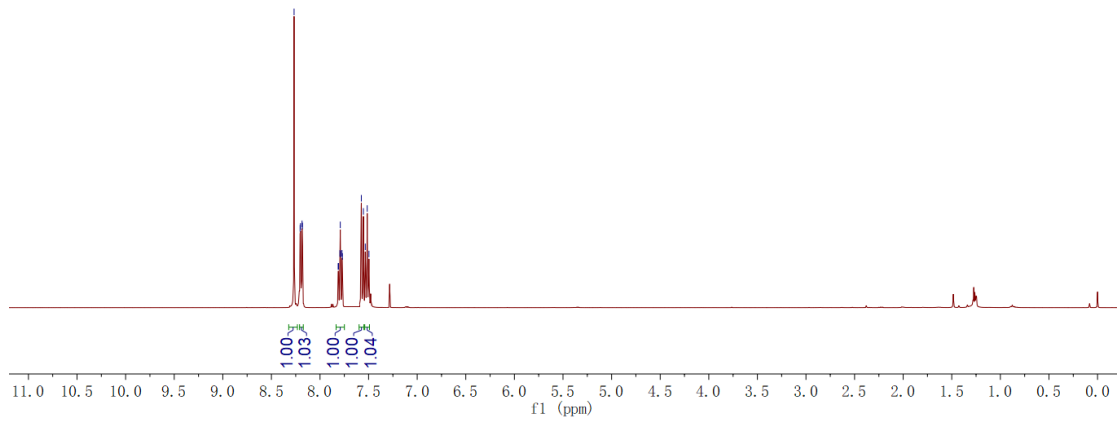
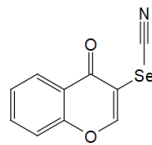


-172.250
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 ~155.182
 -141.347
 ~127.603
 ~127.464
 ~121.107
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 ~108.602



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8.267
 8.205
 8.201
 8.185
 8.181
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 7.795
 7.792
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 7.496



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-174.187
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-99.983

