Supporting Information

Regioselective Alkenylation of Masked Carboxylic Acid Derivatives of Coumarins with Acrylates via Oxidative C(sp^2) –C(sp^2) Cross-Coupling

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Table of Contents

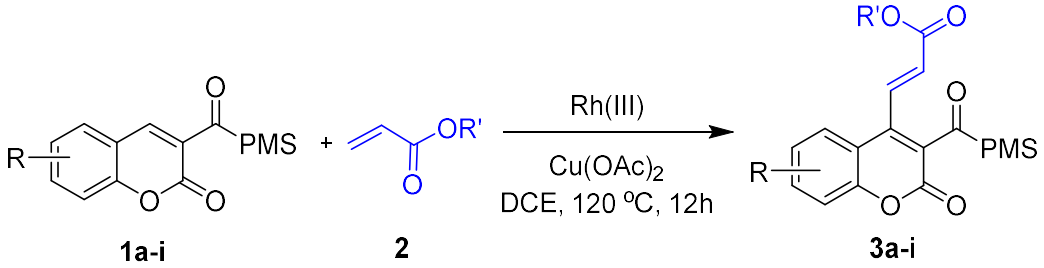
1. General experimental procedures:

All solvents were dried by a standard literature procedure. Crude products were purified by column chromatography on silica gel of 60–120 or 100-200 mesh. Thin layer chromatography (**TLC**) plates were visualized by exposure to ultraviolet light at 254 nm, and by exposure to iodine vapors and/or by exposure to methanolic acidic solution of *p*-anisaldehyde followed by heating (<1 min) on a hot plate (~250°C). Organic solvents were concentrated on rotary evaporator at 35–40 °C. Melting points (**mp**) were measured on Buchi B-540. **^{1}H** and **^{13}C NMR** (proton-decoupled) spectra were recorded in $CDCl_3$ solvent on 300, 400 or 500 MHz NMR spectrometer. Chemical shifts (δ) were reported in parts per million (ppm) with respect to TMS as an internal standard. Coupling constants (*J*) are quoted in hertz (Hz). Mass spectra and **HRMS** were recorded on mass spectrometer by Electro spray ionization (ESI) or Atmospheric pressure chemical ionization (APCI) technique.

Materials and Methods:

All reactions were performed under air atmosphere. Analytical thin layer chromatography was performed using TLC pre-coated silica gel 60 F254 (20 x 20 cm). TLC plates were visualized by exposing UV light or by iodine vapors or immersion in an acidic staining solution of p-anisaldehyde followed by heating on a hot plate. Organic solvents were concentrated by rotary evaporation. Column chromatography was performed on flash silica gel of 230-400 mesh size. Melting points were recorded on BUCHI Melting Point B-545 instrument and were uncorrected. 1H NMR spectra were recorded with 400 and 500 MHz NMR instruments. Chemical data for protons are reported in parts per million (ppm, scale) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent (CDCl3: δ 7.26 or other solvents as mentioned). Mass spectra were recorded with LCMS-QTOF instrument. The coupling constant (J) are mentioned in Hz.

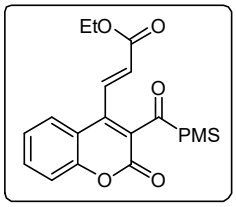
General Experimental Procedure for the Synthesis of Compounds:



To an oven dried seal tube *N*-(methyl (oxo) (phenyl)-sulfaneylidene)-2-oxo-2H-chromene-3-carboxamide (**1a** 1.0 equiv, 100mg), and Oxidant$Cu(OAc)_2$ (1.5 equiv) in 3ml of dichloroethane (DCE) as a solvent followed by the addition of ethylacrylate (**2**) then $AgSbF_6$ as an additive (20 mol %) and ([CP*$RhCl_2$]) as catalyst (4 mol %) at 25^{o}C. The resulting mixture was stirred at 120^{o}C for 12 h and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using EtOAc/hexane as an eluent to afford the pure product **3a**.

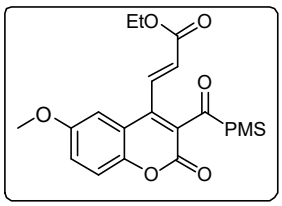
3. Characterization data:

Ethyl (E)-3-(3-((methyl (oxo) (phenyl)-l6-sulfaneylidene)carbamoyl)-2-oxo-2H-chromen-4-yl) acryl ate (3aa):



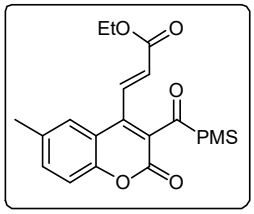
White solid (74%); Melting point:106 - 110 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 7.6 Hz, 2H), 7.83 (d, *J* = 16.2 Hz, 1H), 7.70 (t, *J* = 7.3 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 3H), 7.59 – 7.55 (m, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 16.2 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.46 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR(101MHz, $CDCl_3$)** δ 171.58, 165.20, 158.52, 152.99, 144.06, 137.85, 135.75, 134.22, 132.44, 129.81, 129.24, 127.53, 126.12, 124.70, 117.87, 117.25, 61.26, 44.28, 14.23, 13.64; **HRMS**(ESI) calcd for $C_{22}H_{20}O_6NS$: 426.0989 $[M+H]^+$, found: 426.1005.

Ethyl (E)-3-(6-methoxy-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3ba):



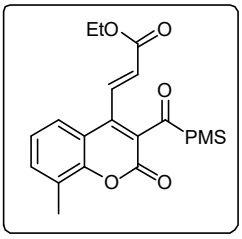
Yellow solid (59%); Melting point**:** 180-184 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 – 8.13 (m, 2H), 7.79 (d, *J* = 16.2 Hz, 1H), 7.71 – 7.68 (m, 1H), 7.64 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 9.1 Hz, 1H), 7.15 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.03 (d, *J* = 2.8 Hz, 1H), 6.60 – 6.55 (m, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.46 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.74, 165.23, 158.69, 158.53, 156.22, 147.35, 143.76, 138.06, 137.81, 135.77, 134.23, 129.81, 129.20, 127.54, 125.93, 119.63, 118.30, 118.19, 108.87, 61.27, 55.98, 44.46, 44.27, 14.23. **HRMS**(ESI) calcd for $C_{23}H_{21}NO_7S$:456.1098 $[M+H]^+$, found:456.1111.

Ethyl (E)-3-(6-methyl-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3ca):



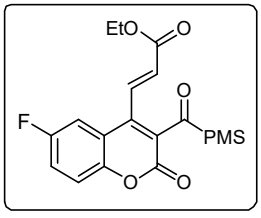
White solid (60%); Melting point**:** 186-188 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 – 8.13 (m, 2H), 7.82 (d, *J* = 16.2 Hz, 1H), 7.70 (dd, *J* = 8.4, 6.3 Hz, 1H), 7.63 (dd, *J* = 10.3, 4.7 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.27 (d, *J* = 1.8 Hz, 1H), 6.57 (d, *J* = 16.2 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.46 (s, 3H), 2.41 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.81, 171.61, 165.54, 165.35, 158.77, 151.09, 144.07, 137.84, 135.97, 134.50, 134.21, 133.50, 129.81, 129.05, 127.55, 125.81, 116.95, 61.27, 44.27, 20.99, 14.24; **HRMS**(ESI) calcd for $C_{23}H_{21}NO_6S$: 440.1146 $[M+H]^+$, found: 440.1162.

Ethyl (E)-3-(8-methyl-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3da):



White solid (65%); Melting point:188-190 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.16 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.83 (d, *J* = 16.2 Hz, 1H), 7.71 – 7.69 (m, 1H), 7.63 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.0 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 6.57 – 6.52 (m, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.46 (s, 3H), 2.48 (s, 3H), 1.33 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 171.79, 165.27, 158.69, 151.30, 144.54, 137.84, 136.19, 134.21, 133.81, 129.80, 129.02, 127.57, 126.67, 125.21, 124.16, 123.83, 117.57, 61.24, 44.31, 15.68, 14.24; **HRMS** (ESI) calcd for $C_{23}H_{21}NO_6S$: 440.1146 $[M+H]^+$, found: 440.1162.

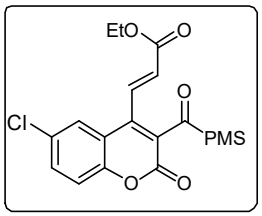
Ethyl (E)-3-(6-fluoro-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3ea):



White solid (59%); Melting point: 120-126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 2H), 7.76 – 7.61 (m, 4H), 7.40 – 7.29 (m, 3H), 6.57 (d, *J* = 16.2 Hz, 1H), 4.29 (q, *J* = 14.0, 7.0 Hz, 2H), 3.46 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 3H);**^{13}C NMR** (101 MHz, $CDCl_3$) δ171.23, 165.12, 137.70, 135.03, 134.31, 129.86, 129.69, 127.64, 127.49, 126.46, 119.99, 119.75, 118.85,

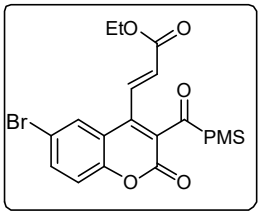
118.77, 111.91, 111.66, 65.30, 64.98, 44.47, 44.29, 30.60, 19.15, 13.76; **HRMS**(ESI) calcd for $C_{22}H_{18}FNO_6S$ [M+H]444.0898 and found: 444.0911.

Ethyl (E)-3-(6-chloro-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3fa):



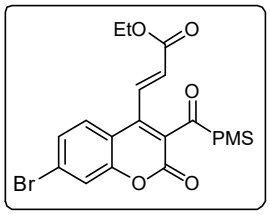
White solid (60%); Melting point:132-134 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 – 8.11 (m, 2H), 7.72 (dd, *J* = 4.9, 2.8 Hz, 1H), 7.64 (ddd, *J* = 7.1, 4.0, 1.6 Hz, 3H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.34 – 7.31 (m, 1H), 6.57 (d, *J* = 16.2 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.46 (s, 3H), 1.35 (dd, *J* = 7.4, 3.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ171.12, 165.04, 157.98, 151.33, 142.92, 137.67, 134.94, 134.32, 132.40, 130.23, 129.86, 129.76, 127.63, 127.48, 125.49, 119.06, 118.65, 61.41, 44.29, 14.23; **HRMS**(ESI) calcd for $C_{22}H_{18}ClNO_6S$ [M+H]460.0599 and found: 460.0616.

Ethyl (E)-3-(6-bromo-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3ga):



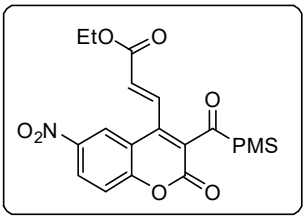
White solid (50%); Melting point: 186-188 °C**;** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 – 8.11 (m, 2H), 7.74 – 7.71 (m, 2H), 7.67 – 7.61 (m, 4H), 7.27 (d, *J* = 2.3 Hz, 1H), 6.57 (d, *J* = 16.1, 7.8 Hz, 1H), 4.30 (q, 2H), 3.46 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.08, 165.05, 157.90, 151.79, 142.85, 137.66, 135.25, 134.94, 134.32, 129.86, 129.76, 128.47, 127.48, 126.43, 119.53, 118.94, 117.54, 61.42, 44.31, 29.73, 14.23; **HRMS**(ESI) calcd for $C_{22}H_{18}BrNO_6S$ [M+H]504.0097 and found: 504.0111.

Ethyl (E)-3-(6-bromo-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3ha):



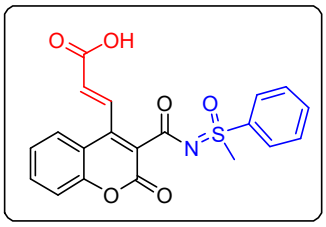
White solid (52%); Melting point: 186-188 °C**; ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 – 8.12 (m, 2H), 7.77 (d, *J* = 16.2 Hz, 1H), 7.70 (dd, *J* = 5.7, 1.7 Hz, 1H), 7.64 (dd, *J* = 7.0, 5.6 Hz, 2H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.43 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.56 (d, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.46 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H);**^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.27, 165.09, 157.89, 153.12, 143.62, 137.64, 135.23, 134.34, 129.89, 129.62, 128.16, 127.53, 127.15, 126.53, 125.62, 120.48, 116.89, 61.41, 44.41,14.25; **HRMS**(ESI) calcd for $C_{22}H_{18}BrNO_6S$[M+H]504.0095 and found: 504.0111.

Ethyl (E)-3-(3-((methyl(oxo)(phenyl)-sulfaneylidene)carbamoyl)-6-nitro-2-oxo-2H-chromen-4-yl)acrylate (3ia):



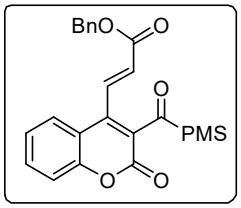
Brownish Solid (58%); Melting point:126 - 129 °C **; ^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (d, *J* = 2.6 Hz, 1H), 8.06 – 8.03 (m, 2H), 7.73 (d, *J* = 16.2 Hz, 1H), 7.62 – 7.54 (m, 4H), 7.44 (d, *J* = 9.1 Hz, 1H), 6.55 (d, *J* = 16.2 Hz, 1H), 4.24 (t, *J* = 7.1 Hz, 2H), 3.40 (s, 3H), 1.29 (t, *J* = 5.1 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)**δ 156.36 (s), 144.26 (s), 142.84 (s), 137.51 (s), 134.44 (s), 134.10 (s), 130.57 (s), 129.92 (s), 127.55 (s), 127.41 (s), 127.09 (s), 122.14 (s), 118.46 (s), 61.58 (s), 44.32 (s), 29.72 (s), 14.22 (s); **MS**(ESI) calcd for $C_{22}H_{18}N_2O_8S$ [M+H] 471.

(E)-3-(3-((methyl(oxo)(phenyl)-sulfaneylidene)carbamoyl)-2-oxo-2H-chromen-4-yl)acrylic acid (3la):



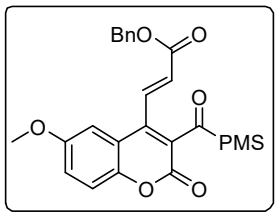
Pale yellow Solid (78%); Melting point:111 - 115 °C **; ^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.20 (d, *J* = 7.4 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.64 (ddd, *J* = 26.8, 17.0, 8.0 Hz, 7H), 7.35 (dd, *J* = 14.9, 7.4 Hz, 2H), 3.46 (s, 3H); **^{13}C NMR (101 MHz, CDCl3) δ** 175.32 (s), 172.81 (s), 165.90 (s), 158.73 (s), 153.67 – 153.35 (m), 149.88 (s), 137.67 (s), 134.30 (s), 133.85 (s), 132.26 (s), 129.90 (s), 129.61 (s), 127.96 (s), 127.66 (s), 124.82 (s), 118.33 (s), 117.44 (s), 44.49 (s); **MS**(ESI) calcd for $C_{20}H_{15}NO_6S$ [M-H] 396.

Benzyl (E)-3-(3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3ab):



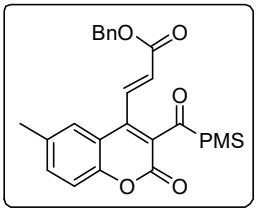
White solid (64%); Melting point:160 - 163 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 2H), 7.88 (d, *J* = 16.2 Hz, 1H), 7.69 – 7.55 (m, 6H), 7.40 (s, 1H), 7.39 – 7.34 (m, 4H), 7.32 – 7.29 (m, 1H), 6.62 (d, *J* = 16.2 Hz, 1H), 5.27 (s, 2H), 3.42 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.55, 171.40, 165.01, 158.47, 152.97, 143.94, 137.75, 136.45, 135.52, 134.25, 132.51, 129.83, 128.80, 128.66, 128.41, 127.48, 126.12, 125.66, 124.75, 117.74, 117.27, 67.01, 44.22; **HRMS**(ESI) calcd for $C_{27}H_{21}NO_6S$:488.1090[M+H] and found: 488.1123.

Benzyl (E)-3-(6-methoxy-3-((methyl (oxo)(phenyl)-l6-sulfaneylidene)carbamoyl)-2-oxo-2H-chromen-4-yl)acrylate (3bb):



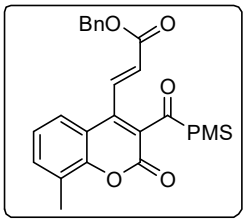
Yellow solid (68%); Melting point: 163-166 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 16.2 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 9.5 Hz, 3H), 7.35 – 7.28 (m, 3H), 7.14 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.00 (d, *J* = 2.7 Hz, 1H), 6.63 (d, *J* = 16.2 Hz, 1H), 5.27 (s, 2H), 3.83 (s, 3H), 3.42 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$)δ 171.68, 165.03, 158.64, 156.23, 147.35, 143.63, 137.79, 136.47, 135.53, 134.24, 129.83, 128.78, 128.65, 128.41, 128.36, 127.51, 126.00, 119.71, 118.23, 108.80, 67.00, 56.00, 44.28; **HRMS**(ESI) calcd for $C_{28}H_{23}NO_7S$: 518.1248 [M+H] , and found:518.1268.

Benzyl (E)-3-(6-methyl-3-((methyl (oxo)(phenyl)-l6-sulfaneylidene)carbamoyl)-2-oxo-2H-chromen-4-yl)acrylate (3cb):



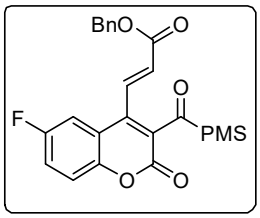
White solid (61%); Melting point:160-163 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.5 Hz, 2H), 7.86 (d, *J* = 16.2 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.60 (t, *J* = 6.8 Hz, 2H), 7.38 (tdd, *J* = 8.8, 8.0, 2.5 Hz, 8H), 6.62 (d, *J* = 16.2 Hz, 1H), 5.28 (s, 2H), 3.42 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.74, 165.13, 158.69, 151.09, 143.91, 137.82, 136.65, 135.56, 134.52, 134.21, 133.53, 129.80, 128.65, 128.61, 128.40, 128.28, 127.68, 127.50, 125.79, 125.55, 117.47, 117.12, 116.96, 66.99, 66.74, 44.41, 44.18, 20.99; **HRMS** (ESI) calcd for $C_{28}H_{23}NO_6S$ 502.1280 [M+H] and found:502.1246.

Benzyl (E)-3-(8-methyl-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3db):



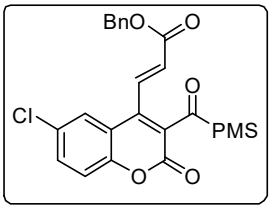
White solid (65%); Melting point:186 - 188 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 7.2 Hz, 2H), 7.88 (d, *J* = 16.1 Hz, 1H), 7.64 (dd, *J* = 22.6, 6.8 Hz, 3H), 7.44 – 7.33 (m, 7H), 7.19 (d, *J* = 7.1 Hz, 1H), 6.60 (d, *J* = 16.2 Hz, 1H), 5.27 (s, 2H), 3.42 (s, 3H), 2.47 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) δ** 171.72, 165.05, 158.60, 151.31, 144.37, 137.82, 136.88, 135.55, 134.23, 133.85, 129.82, 128.66, 128.59, 128.41, 127.55, 126.69, 125.29, 124.19, 123.83, 117.47, 66.98, 44.33, 15.70; **HRMS (ESI)** calcd for $C_{28}H_{23}NO_6S$: 502.1318[M+H]$^+$, and found: 502.1303.

Benzyl (E)-3-(6-fluoro-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3eb):



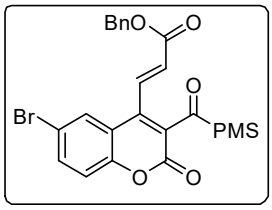
White solid (54%); Melting point: 144-146 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 16.2 Hz, 1H), 7.61 (d, *J* = 6.7 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.36 – 7.22 (m, 8H), 6.55 (d, *J* = 16.2 Hz, 1H), 5.20 (s, 2H), 3.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.16, 164.82, 160.09, 158.14, 149.09, 142.94, 137.66, 135.71, 135.43, 134.31, 129.85, 129.25, 128.67, 128.45, 127.45, 120.04, 119.80, 118.87, 118.79, 111.90, 111.65, 67.11, 44.23; **HRMS** (ESI)calcd for $C_{27}H_{20}FNO_6S$: 505.5160[M+H]$^+$, and found: 506.0995.

Benzyl (E)-3-(6-chloro-3-((methyl (oxo)(phenyl)-l6-sulfaneylidene)carbamoyl)-2-oxo-2H-chromen-4-yl)acrylate(3fb):



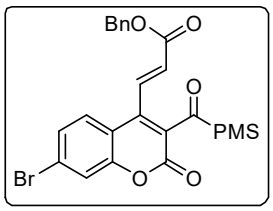
White solid (44%); Melting point: 147-149 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.79 (d, *J* = 16.2 Hz, 1H), 7.63 – 7.57 (m, 3H), 7.51 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.43 – 7.30 (m, 7H), 6.62 (d, *J* = 16.2 Hz, 1H), 5.28 (s, 2H), 3.42 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 171.05 , 164.84 , 157.90 , 151.32 , 142.74 , 137.63 , 135.52 , 134.31 , 132.43 , 130.23 , 129.84 , 129.30 , 128.67 , 128.44 , 127.42 , 125.45 , 118.95 , 118.67 , 67.13 , 44.19 , 29.72 ; **HRMS (ESI)** calcd for $C_{27}H_{20}ClNO_6S$: 522.0700 $[M+H]^+$and found: 522.0670.

Benzyl (E)-3-(6-bromo-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3gb):



White solid (45%); Melting point: 130-133 °C**; ^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.81 – 7.77 (m, 1H), 7.73 – 7.68 (m, 2H), 7.65 – 7.58 (m, 4H), 7.40 (dt, *J* = 13.4, 6.3 Hz, 4H), 7.26 (s, 1H), 6.62 (d, *J* = 16.2 Hz, 1H), 5.28 (s, 2H), 3.42 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.01, 164.85, 157.84, 151.79, 142.68, 137.65, 135.60, 135.28, 134.31, 129.84, 129.33, 128.67, 128.44, 127.43, 118.95, 117.56, 67.13, 44.22; **HRMS**(ESI) calcd for $C_{27}H_{20}BrNO_6S$: 566.0247 $[M+H]^+$, found: 566.0267.

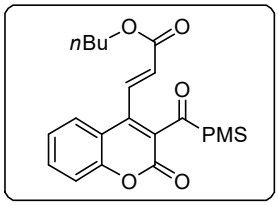
Benzyl (E)-3-(6-bromo-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3hb):



White solid (48%); Melting point: 140-143 °C**; ^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 16.2 Hz, 1H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 2H), 7.54 (d, *J* =

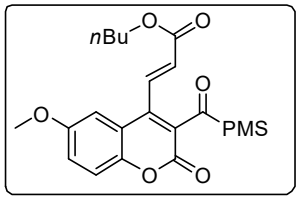
1.5 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.44 – 7.36 (m, 6H), 6.60 (d, *J* = 16.2 Hz, 1H), 5.27 (s, 2H), 3.42 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.27, 165.19, 157.89, 153.11, 143.59, 137.64, 135.21, 134.33, 129.88, 129.61, 128.68, 128.45, 128.17, 127.50, 127.46, 127.13, 120.48, 116.88, 65.31, 44.29. **HRMS**(ESI) calcd for $C_{27}H_{20}BrNO_6S$: 566.0247 $[M+H]^+$ and found: 566.0267.

Butyl (E)-3-(3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3ac):



White solid (70%); Melting point: 120-122 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 7.4 Hz, 2H), 7.83 (dd, *J* = 16.2, 1.2 Hz, 1H), 7.71 – 7.68 (m, 1H), 7.63 (t, *J* = 6.3 Hz, 3H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.38 – 7.30 (m, 2H), 6.58 (dd, *J* = 16.2, 1.2 Hz, 1H), 4.22 (dd, *J* = 9.5, 3.9 Hz, 2H), 3.46 (s, 3H), 1.71 – 1.67 (m, 2H), 1.45 – 1.39 (m, 2H), 0.95 (t, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.57, 165.28, 158.48, 152.93, 143.96, 137.78, 135.74, 134.23, 132.47, 129.81, 129.21, 127.48, 126.08, 125.59, 124.73, 117.80, 117.22, 65.15, 64.85, 44.43, 44.24, 30.60, 29.69, 19.14, 18.96, 13.76; **HRMS**(ESI) calcd for $C_{24}H_{23}NO_6S$:454.1280 $[M+H]^+$and found: 454.1380.

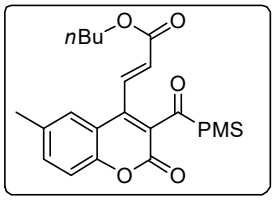
Butyl (E)-3-(6-methoxy-3-((methyl (oxo)(phenyl)-l6-sulfaneylidene)carbamoyl)-2-oxo-2H-chromen-4-yl)acrylate (3bc):



Yellow solid (68%); Melting point: 128-132 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.72 (d, *J* = 16.2 Hz, 1H), 7.62 (d, *J* = 7.1 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 2H), 7.23 (dd, *J* = 8.6, 3.0 Hz, 1H), 7.07 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.95 (t, *J* = 5.1 Hz, 1H), 6.51 (d, *J* = 16.2 Hz, 1H), 4.16 (t, *J* = 6.7 Hz, 2H), 3.77 (s, 3H), 3.39 (s, 3H), 1.64 – 1.59 (m, 2H), 1.36 (dd, *J* = 13.2, 5.7 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)**δ 171.75, 165.34, 156.22, 147.36, 143.77, 137.81, 135.76, 134.23, 129.82, 129.21, 127.68, 127.54, 119.68, 118.30, 118.21,

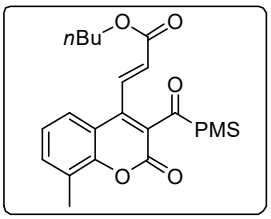
108.81, 65.20, 55.97, 44.30, 30.60, 19.16, 13.76; **HRMS**(ESI) calcd for $C_{25}H_{25}NO_7S$: 484.1408 $[M+H]^+$, and found:484.1424.

Butyl (E)-3-(6-methyl-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3cc):



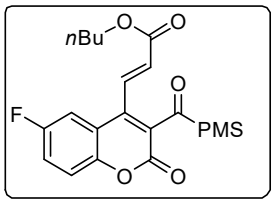
White solid (65%); Melting point**:** 120-125 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 7.5 Hz, 2H), 7.82 (d, *J* = 16.2 Hz, 1H), 7.69 (d, *J* = 7.3 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.27 (s, 1H), 6.57 (d, *J* = 16.2 Hz, 1H), 4.23 (t, *J* = 6.8 Hz, 2H), 3.46 (s, 3H), 2.41 (s, 3H), 1.72 – 1.67 (m, 2H), 1.43 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.80, 165.44, 158.76, 151.08, 144.02, 137.86, 135.95, 134.50, 134.20, 133.49, 129.81, 129.06, 127.54, 125.80, 117.56, 116.95, 65.19, 64.86, 44.26, 30.62, 20.99, 19.16, 13.77; **HRMS**(ESI) calcd for $C_{25}H_{25}NO_6S$: 468.1457 $[M+H]^+$, and found: 468.1475.

Butyl (E)-3-(8-methyl-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3dc):



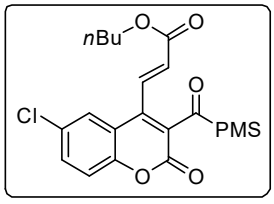
White solid (65%); Melting point**:** 120-125 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 – 8.14 (m, 2H), 7.83 (d, *J* = 16.2 Hz, 1H), 7.69 (dt, *J* = 2.4, 1.8 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.55 (dd, *J* = 16.2, 4.9 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 3.46 (s, 3H), 2.47 (d, *J* = 2.9 Hz, 3H), 1.69 (dd, *J* = 9.7, 5.2 Hz, 2H), 1.45 – 1.39 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) δ** 171.77, 165.36, 158.67, 151.30, 144.48, 137.86, 136.16, 134.20, 133.80, 129.79, 129.02, 127.56, 126.66, 125.22, 124.16, 123.82, 117.57, 65.14, 44.29, 30.62, 19.16, 15.68, 13.77; **HRMS (ESI)** calcd for $C_{25}H_{25}NO_6S$: 468.1456 $[M+H]^+$, and found: 468.1475.

Butyl (E)-3-(6-fluoro-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3ec):



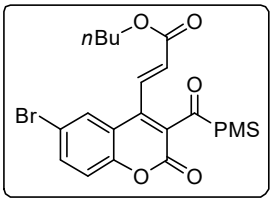
White solid (56%); Melting point: 140-145 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 7.6 Hz, 2H), 7.72 (dd, *J* = 20.0, 11.8 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.29 (m, 3H), 6.58 (d, *J* = 16.2 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 3.46 (s, 3H), 1.72 – 1.68 (m, 2H), 1.43 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) δ** 171.24, 165.13, 160.09, 158.22, 149.09, 143.07, 137.67, 135.04, 134.31, 129.86, 129.69, 127.48, 126.44, 112.25, 111.91, 111.66, 111.22, 65.31, 44.29, 30.60, 19.15, 13.77; **HRMS**(ESI) calcd for $C_{24}H_{22}FNO_6S$: 472.1209 $[M+H]^+$, and found: 472.1224.

Butyl (E)-3-(6-chloro-3-((methyl (oxo)(phenyl)-l6-sulfaneylidene)carbamoyl)-2-oxo-2H-chromen-4-yl)acrylate (3fc):



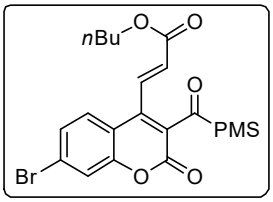
White solid (44%); Melting point: 130-135 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.13 – 8.12 (m, 2H), 7.75 (d, *J* = 16.1 Hz, 1H), 7.67 – 7.62 (m, 3H), 7.59 (d, *J* = 2.4 Hz, 1H), 7.52 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 3.46 (s, 3H), 1.70 (dd, *J* = 9.9, 5.1 Hz, 2H), 1.43 (dd, *J* = 14.1, 6.5 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 71.12, 165.14, 157.99, 151.33, 142.91, 137.69, 134.93, 134.32, 132.40, 130.23, 129.86, 129.77, 127.48, 125.49, 118.66, 65.33, 65.01, 44.31, 30.60, 29.73, 19.16, 13.77; **HRMS**(ESI) calcd for $C_{24}H_{22}ClNO_6S$: 488.9510;$[M+H]^+$, and found: 488.0856.

Butyl (E)-3-(6-bromo-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3gc):



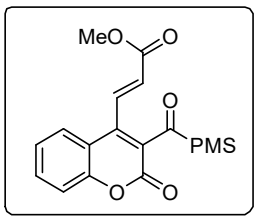
White solid (25%); Melting point: 130-136 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 7.6 Hz, 2H), 7.72 (dd, *J* = 20.3, 10.3 Hz, 3H), 7.68 – 7.63 (m, 3H), 7.27 (d, *J* = 3.0 Hz, 1H), 6.58 (d, *J* = 16.2 Hz, 1H), 4.24 (t, *J* = 6.5 Hz, 2H), 3.46 (s, 3H), 1.73 – 1.67 (m, 2H), 1.43 (dd, *J* = 14.6, 7.3 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.08, 165.14, 157.90, 151.78, 142.80, 137.67, 135.24, 134.91, 134.31, 129.85, 129.77, 128.46, 127.46, 126.43, 119.53, 118.93, 117.54, 65.32, 44.28, 30.59, 19.15, 13.77; **HRMS**(ESI) calcd for $C_{24}H_{22}BrNO_6S$: 533.0289 $[M+H]^+$, and found: 533.0264.

Butyl (E)-3-(7-bromo-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3hc):



White solid (28%); Melting point: 130-133 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 16.2 Hz, 1H), 7.70 (d, *J* = 7.3 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 2H), 7.56 – 7.54 (m, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.43 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.55 (dd, *J* = 16.2, 5.7 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 3.46 (s, 3H), 1.72 – 1.66 (m, 2H), 1.42 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.23, 165.17, 157.87, 153.12, 143.55, 137.68, 135.19, 134.31, 129.86, 129.61, 128.15, 127.49, 127.12, 120.47, 116.89, 65.28, 44.33, 30.97, 30.60, 19.15, 13.76; **HRMS**(ESI) calcd for $C_{24}H_{22}BrNO_6S$: 533.0289 $[M+H]^+$, and found: 533.0292.

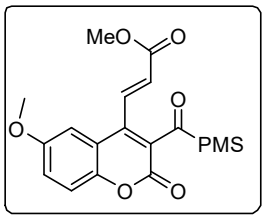
Methyl (E)-3-(3-((methyl (oxo)(phenyl)-l6-sulfaneylidene)carbamoyl)-2-oxo-2H-chromen-4-yl)acrylate (3ad):



White solid (79%); Melting point**:** 160-162 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 – 8.12 (m, 2H), 7.84 (d, *J* = 16.2 Hz, 1H), 7.70 (d, *J* = 7.3 Hz, 1H), 7.64 (ddd, *J* = 7.1, 4.2, 2.7 Hz, 3H), 7.57

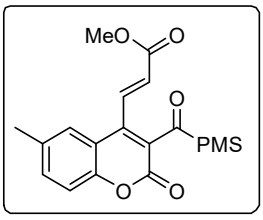
(dd, *J* = 11.4, 4.3 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.29 (m, 1H), 6.59 (d, *J* = 16.2 Hz, 1H), 3.83 (s, 3H), 3.46 (s, 3H); **^{13}C NMR (126 MHz,$CDCl_3$)** δ 171.61, 165.63, 158.51, 152.96, 143.99, 137.74, 136.05, 134.26, 132.51, 129.84, 128.77, 127.54, 126.08, 124.75, 117.81, 117.26, 52.28, 44.33; **HRMS**(ESI) calcd for $C_{21}H_{17}NO_6S$: 412.0836$[M+H]^+$, and found:412.0849.

Methyl (E)-3-(6-methoxy-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3bd):



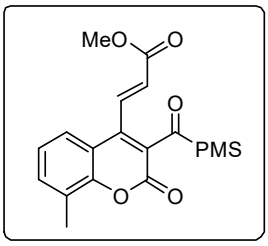
White solid (72%); Melting point**:**166-168 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 – 8.13 (m, 2H), 7.80 (d, *J* = 16.2 Hz, 1H), 7.70 (d, *J* = 7.3 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 6.9 Hz, 1H), 7.15 (dd, *J* = 9.1, 2.9 Hz, 1H), 7.01 (d, *J* = 2.9 Hz, 1H), 6.59 (d, *J* = 16.2 Hz, 1H), 3.84 (d, *J* = 3.6 Hz, 6H), 3.46 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.77, 165.67, 156.25, 147.36, 137.75, 136.07, 134.25, 129.83, 128.74, 127.55, 119.77, 118.22, 108.73, 55.98, 52.27, 44.30; **HRMS**(ESI) calcd for $C_{22}H_{19}NO_7S$: 442.0940 $[M+H]^+$, and found:442.0955.

Methyl (E)-3-(6-methyl-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3cd):



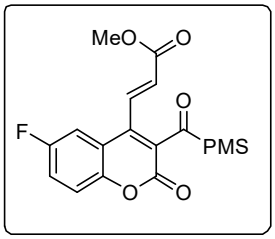
White solid (65%); Melting point:166-168 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 – 8.13 (m, 2H), 7.82 (d, *J* = 16.2 Hz, 1H), 7.69 (dd, *J* = 5.7, 1.6 Hz, 1H), 7.63 (dd, *J* = 10.3, 4.7 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.27 (s, 1H), 6.58 (d, *J* = 16.2 Hz, 1H), 3.84 (s, 3H), 3.46 (s, 3H), 2.41 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.81, 165.76, 158.74, 151.08, 143.99, 137.78, 136.25, 134.54, 134.23, 133.54, 129.81, 128.58, 127.55, 125.77, 52.26, 44.28,20.98; **HRMS**(ESI) calcd for $C_{22}H_{19}NO_6S$:426.0987 $[M+H]^+$, and found:426.1005.

Methyl (E)-3-(8-methyl-3-((methyl (oxo)(phenyl)-l6-sulfaneylidene)carbamoyl)-2-oxo-2H-chromen-4-yl)acrylate (3dd):



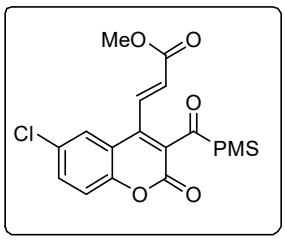
White solid (65%); Melting point: 166-168 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 7.2 Hz, 2H), 7.84 (d, *J* = 16.1 Hz, 1H), 7.70 (d, *J* = 6.7 Hz, 1H), 7.64 (d, *J* = 7.0 Hz, 2H), 7.45 (dd, *J* = 17.6, 7.5 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 16.1 Hz, 1H), 3.83 (s, 3H), 3.46 (s, 3H), 2.48 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 171.80, 165.69, 158.67, 151.30, 144.45, 137.80, 136.47, 134.23, 133.84, 129.81, 128.56, 127.59, 126.69, 125.24, 124.19, 123.79, 117.55, 52.23, 44.33, 15.68; **HRMS**(ESI) calcd for $C_{22}H_{19}NO_6S$: 426.0991 $[M+H]^+$, and found: 426.1005.

Methyl (E)-3-(6-fluoro-3-((methyl (oxo) (phenyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3ed):



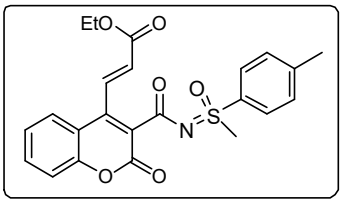
White solid (56%); Melting point: 144-147 °C**; ^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.75 (d, *J* = 16.2 Hz, 1H), 7.72 – 7.69 (m, 1H), 7.65 (dd, *J* = 6.4, 1.5 Hz, 2H), 7.39 – 7.29 (m, 3H), 6.59 (d, *J* = 16.2 Hz, 1H), 3.84 (s, 3H), 3.46 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.25, 165.47, 158.21, 149.08, 143.04, 137.61, 135.34, 134.33, 129.87,129.21, 128.63, 127.50, 120.06, 119.82, 118.87, 118.78, 111.87, 111.62, 52.36, 44.31; **HRMS**(ESI) calcd for $C_{21}H_{16}FNO_6S$: 430.0742 $[M+H]^+$, and found: 430.0721.

Methyl (E)-3-(6-chloro-3-((methyl (oxo)(phenyl)-l6-sulfaneylidene)carbamoyl)-2-oxo-2H-chromen-4-yl)acrylate (3fd):



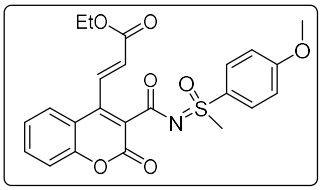
White solid (44%); Melting point: 140-143 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 – 8.12 (m, 2H), 7.74 – 7.69 (m, 2H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 2.3 Hz, 1H), 7.52 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 6.59 (d, *J* = 16.2 Hz, 1H), 3.84 (s, 3H), 3.46 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.12, 165.46, 157.97, 151.32, 142.85, 137.62, 135.23, 134.33, 132.43, 130.26, 129.86, 129.29, 127.49, 125.45, 119.02, 118.66, 52.36, 44.31; **HRMS**(ESI) calcd for $C_{21}H_{16}NO_6S$: 446.0447 $[M+H]^+$, and found: 446.0459.

Ethyl (E)-3-(3-((methyl (oxo) (p-tolyl)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acryl ate (3ja):



White solid (63%); Melting point:153-156 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 16.2 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.40 (dd, *J* = 19.7, 8.1 Hz, 4H), 6.57 (d, *J* = 16.2 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.44 (s, 3H), 2.47 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.58, 165.25, 152.96, 145.45, 143.97, 135.80, 134.64, 132.42, 130.45, 129.21, 127.52, 126.11, 124.70, 117.87, 117.25, 61.27, 44.41, 21.70, 14.24; **HRMS**(ESI) calcd for $C_{23}H_{21}NO_6S$: 440.1090 $[M+H]^+$, and found: 440.9903.

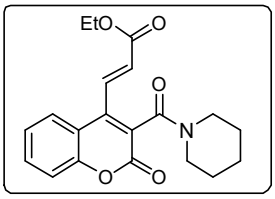
Ethyl (E)-3-(3-(((4-methoxyphenyl) (methyl) (oxo)-l6-sulfaneylidene) carbamoyl)-2-oxo-2H-chromen-4-yl) acrylate (3ka):



White solid (50%); Melting point: 170-177°C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 16.2 Hz, 1H), 7.60 (ddd, *J* = 29.9, 11.2, 4.1 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 8.9 Hz, 2H), 6.56 (d, *J* = 16.2 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 3.44 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.50, 165.24, 164.23, 158.57, 152.92, 143.89, 135.82, 132.43, 129.73, 129.16, 128.56, 126.09,

124.72, 117.21, 115.07, 61.27, 55.84, 44.66, 14.22; **HRMS**(ESI) calcd for$C_{23}H_{21}NO_7S$: 456.4810 $[M+H]^+$, and found: 456.1072.

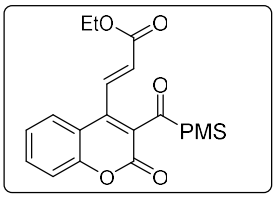
Ethyl (E)-3-(2-oxo-3-(piperidine-1-carbonyl)-2H-chromen-4-yl) acrylate (7aa):



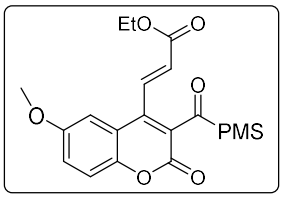
White solid (65%); Melting point:110-135 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 16.2 Hz, 1H), 7.67 – 7.57 (m, 2H), 7.41 – 7.32 (m, 2H), 6.54 (d, *J* = 16.2 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.82 – 3.74 (m, 1H), 3.69 – 3.61 (m, 1H), 3.33 (d, *J* = 4.1 Hz, 2H), 1.67 (s, 6H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.08, 162.16, 157.95, 153.01, 144.10, 135.25, 132.69, 129.58, 125.84, 124.91, 117.42, 61.42, 47.84, 42.68, 26.28, 25.30, 24.47, 14.23; **HRMS**(ESI) calcd for $C_{20}H_{21}NO_5$: 356.3900 $[M+H]^+$, and found: 356.1420.

Spectral data of products:

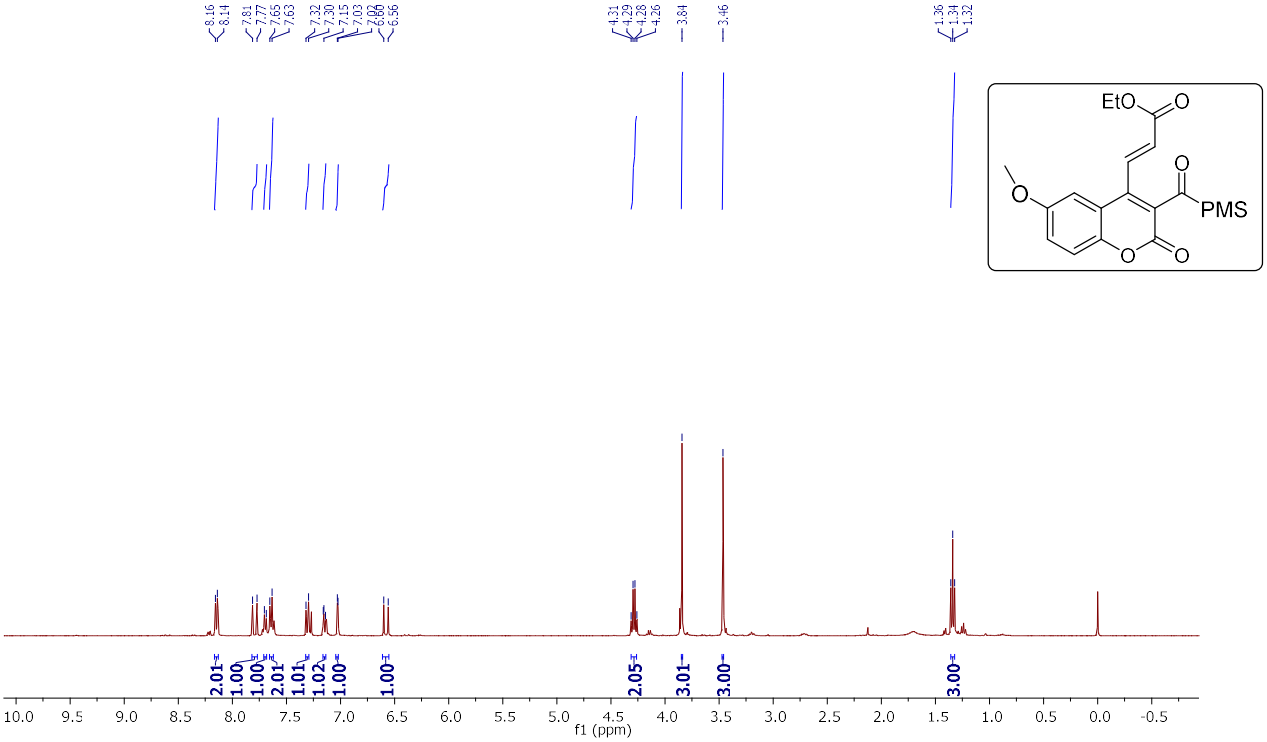
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (3aa):



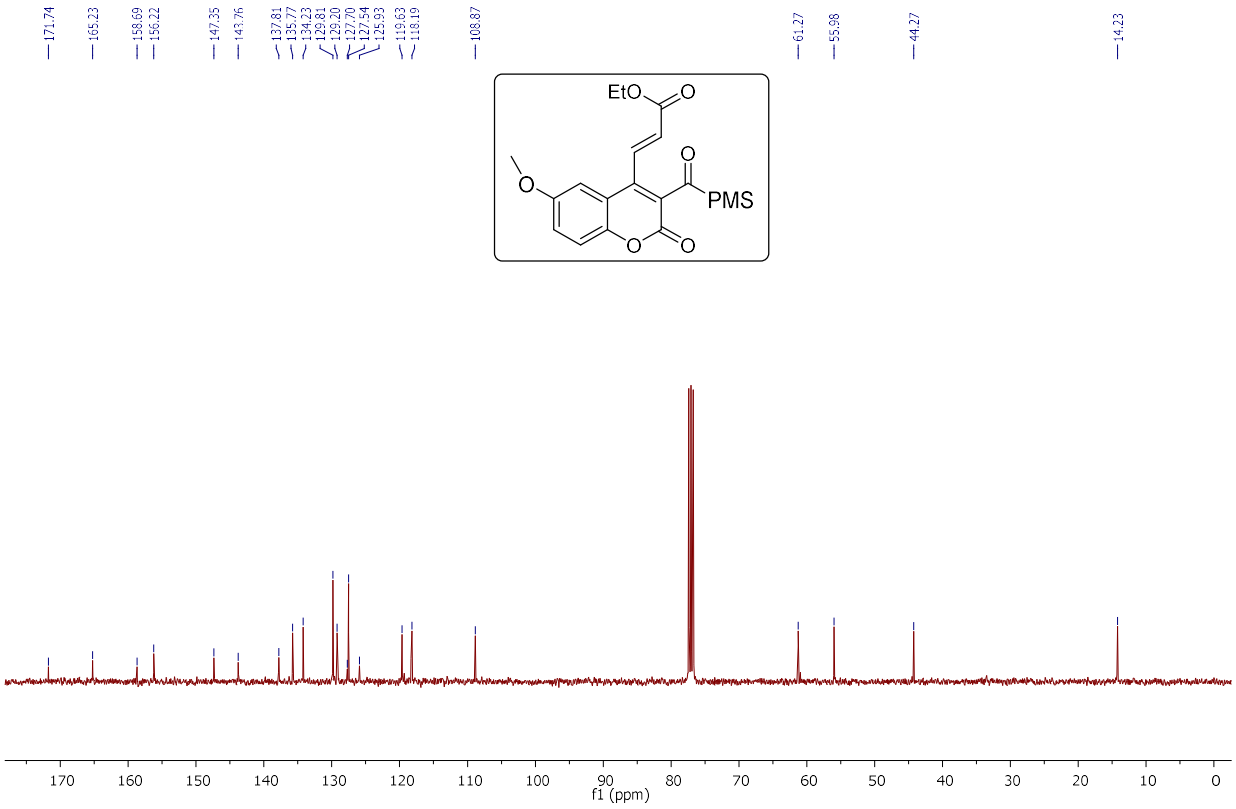
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound (3aa):



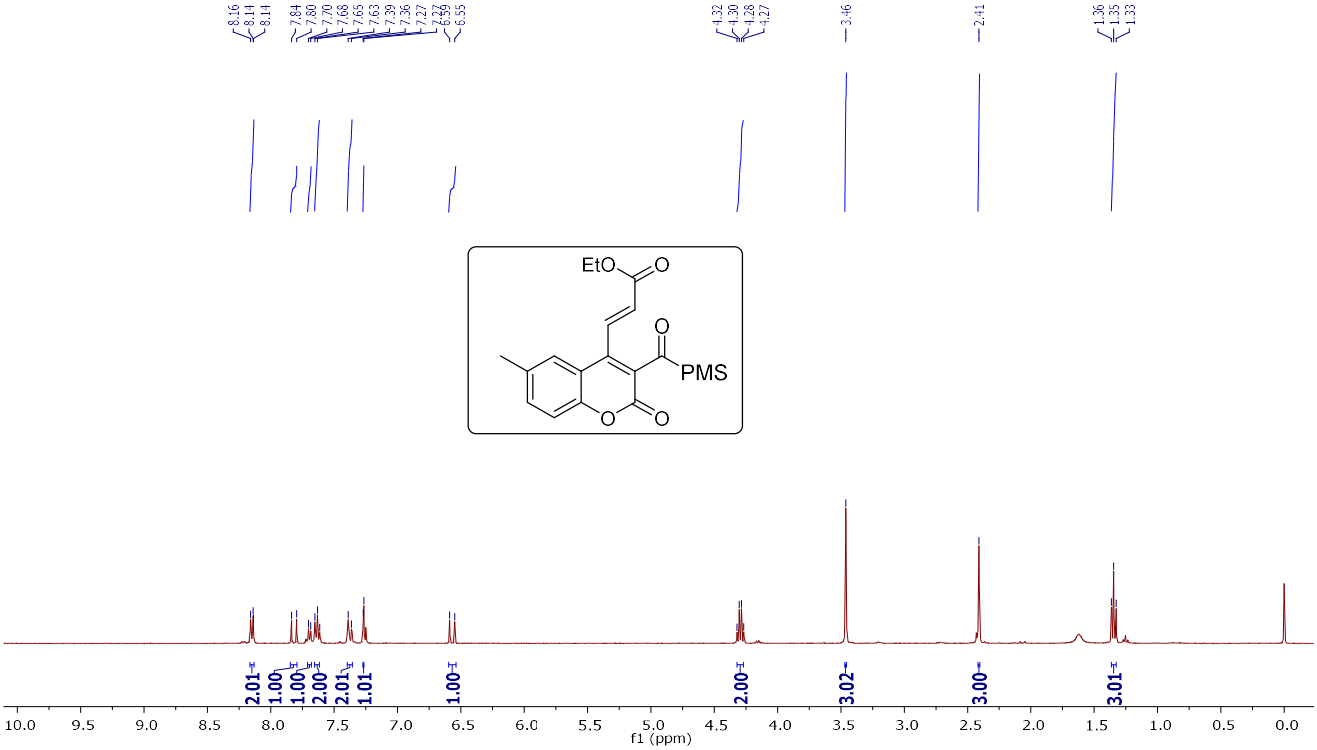
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (3ba):



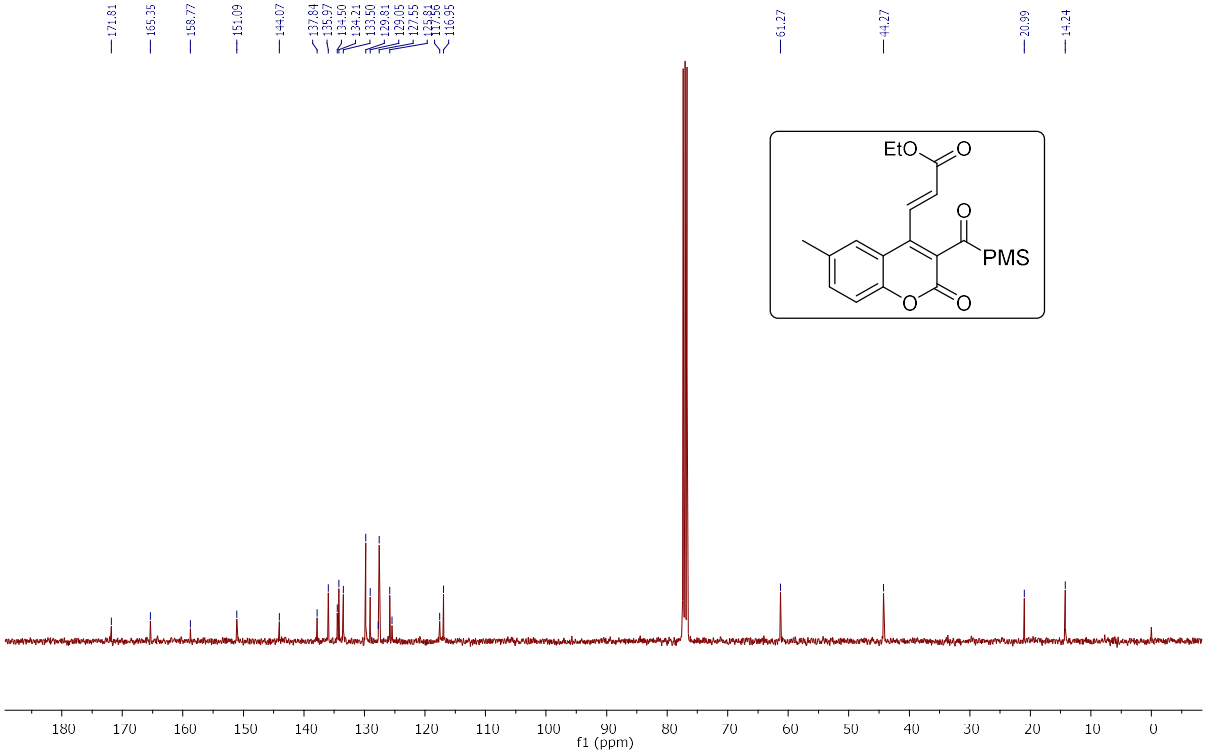
^{13}CNMR (101 MHz, $CDCl_3$) spectrum of compound (3ba):



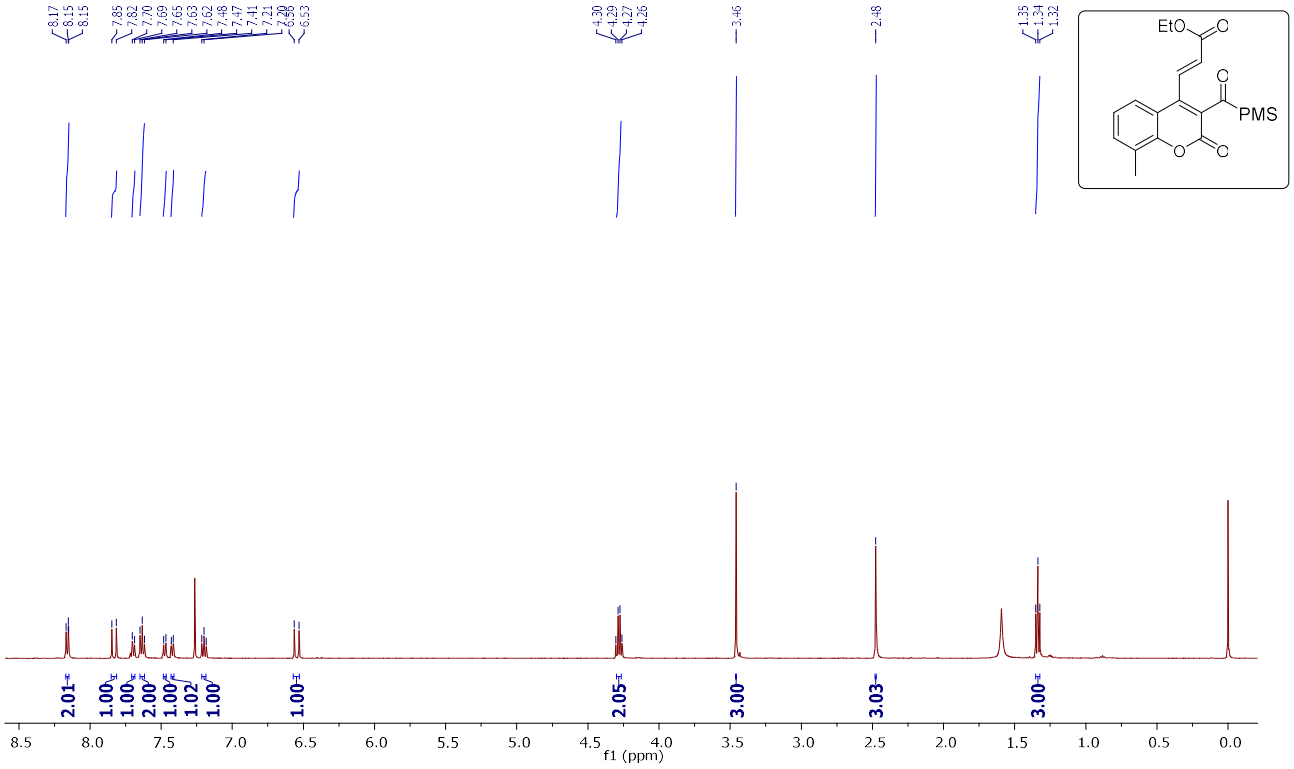
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound (3ca):



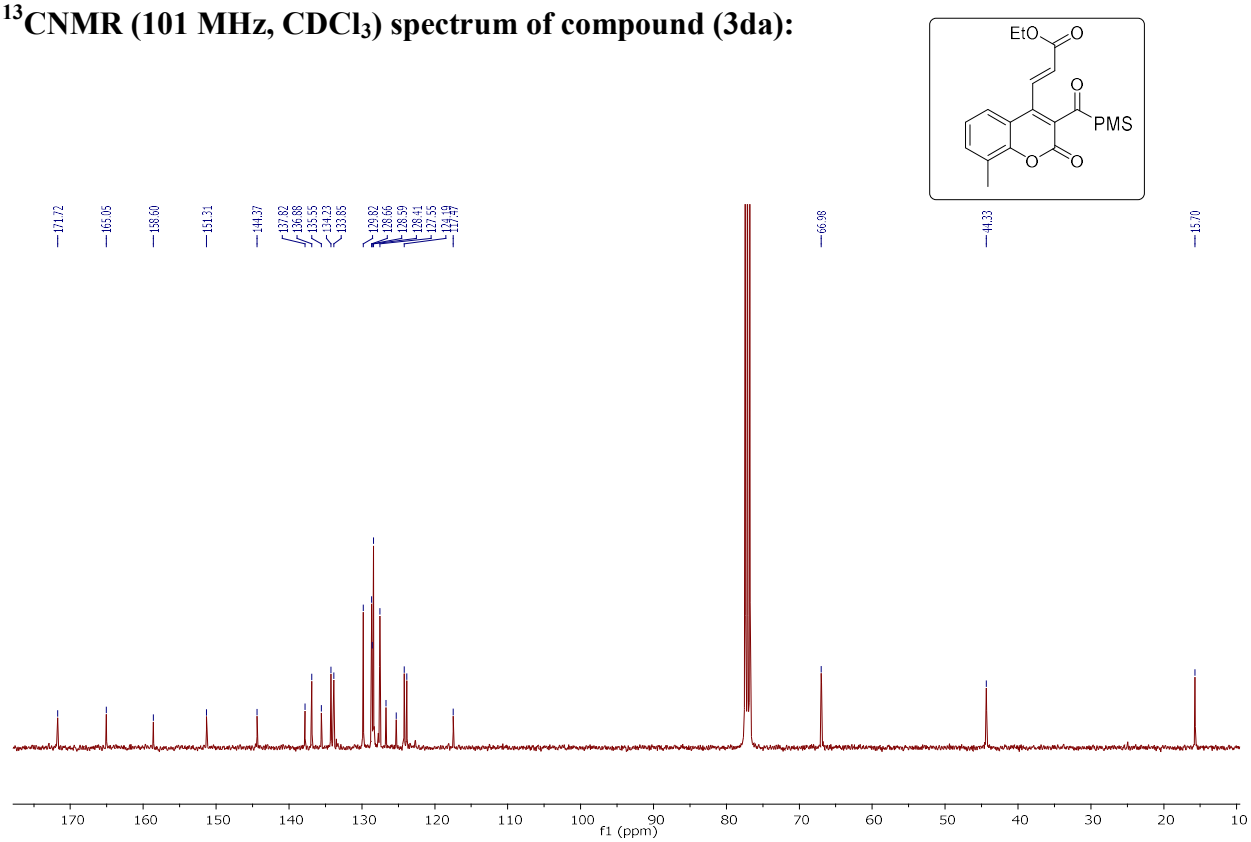
^{13}CNMR (101 MHz, $CDCl_3$) spectrum of compound (3ca):



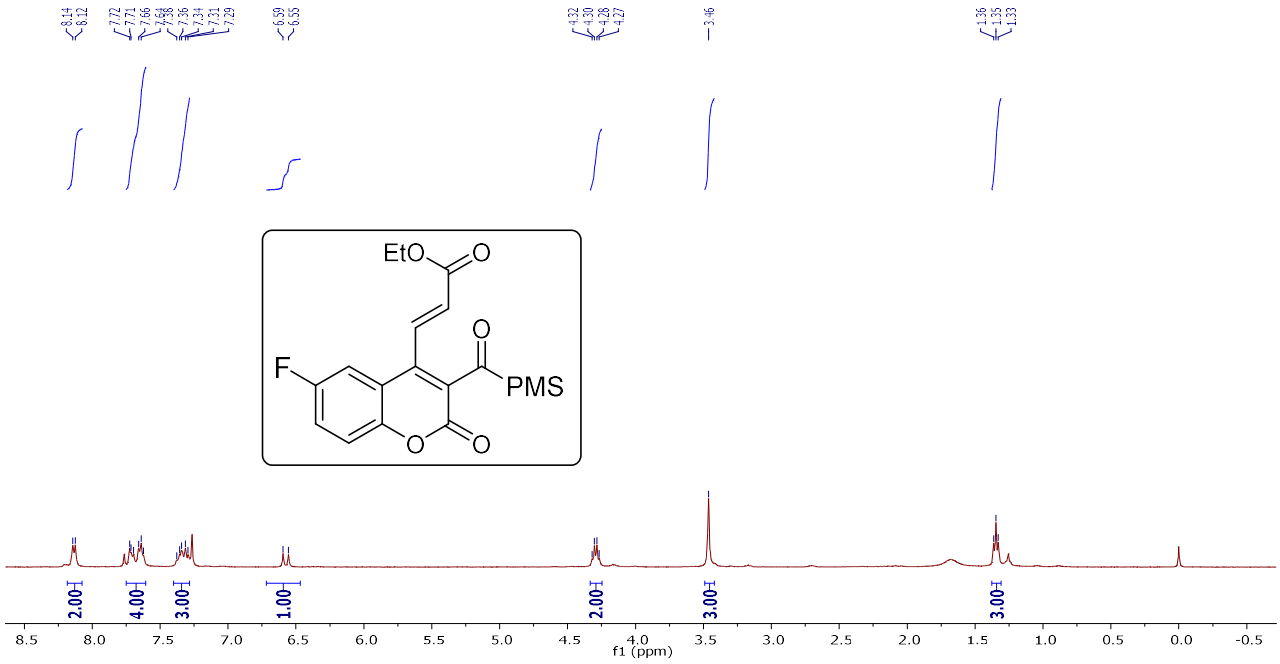
[1]HNMR (400MHz, $CDCl_3$) spectrum of compound (3da):



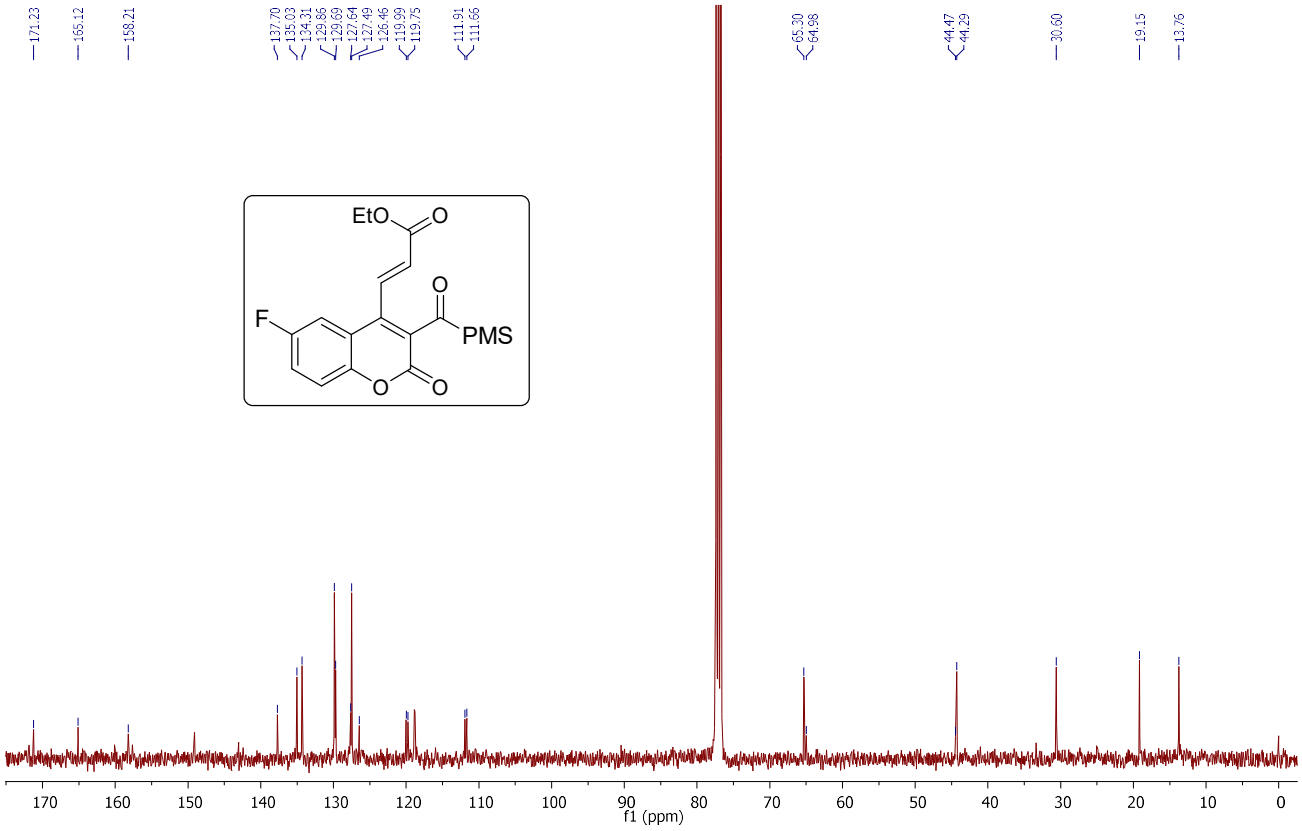
[13]CNMR (101 MHz, $CDCl_3$) spectrum of compound (3da):



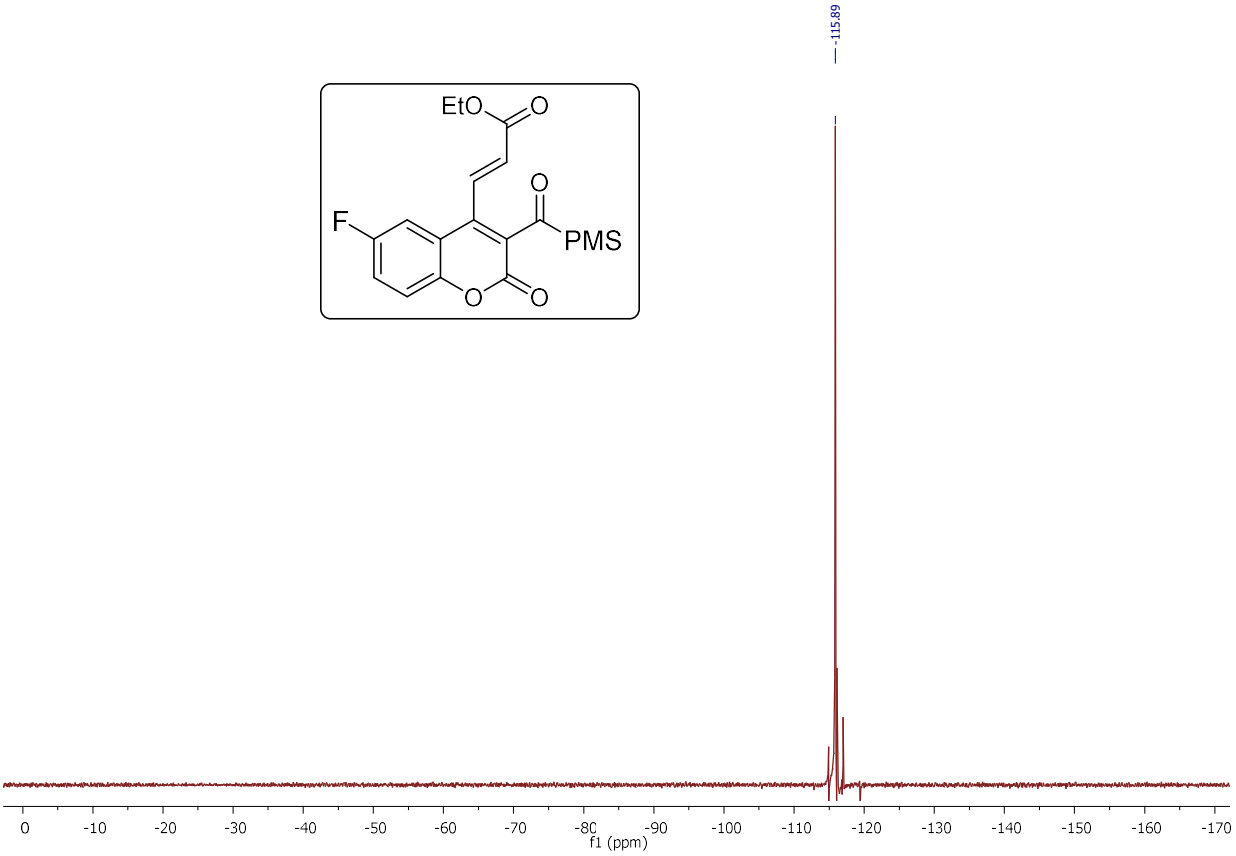
[1]HNMR (400MHz, $CDCl_3$) spectrum of compound (3ea):



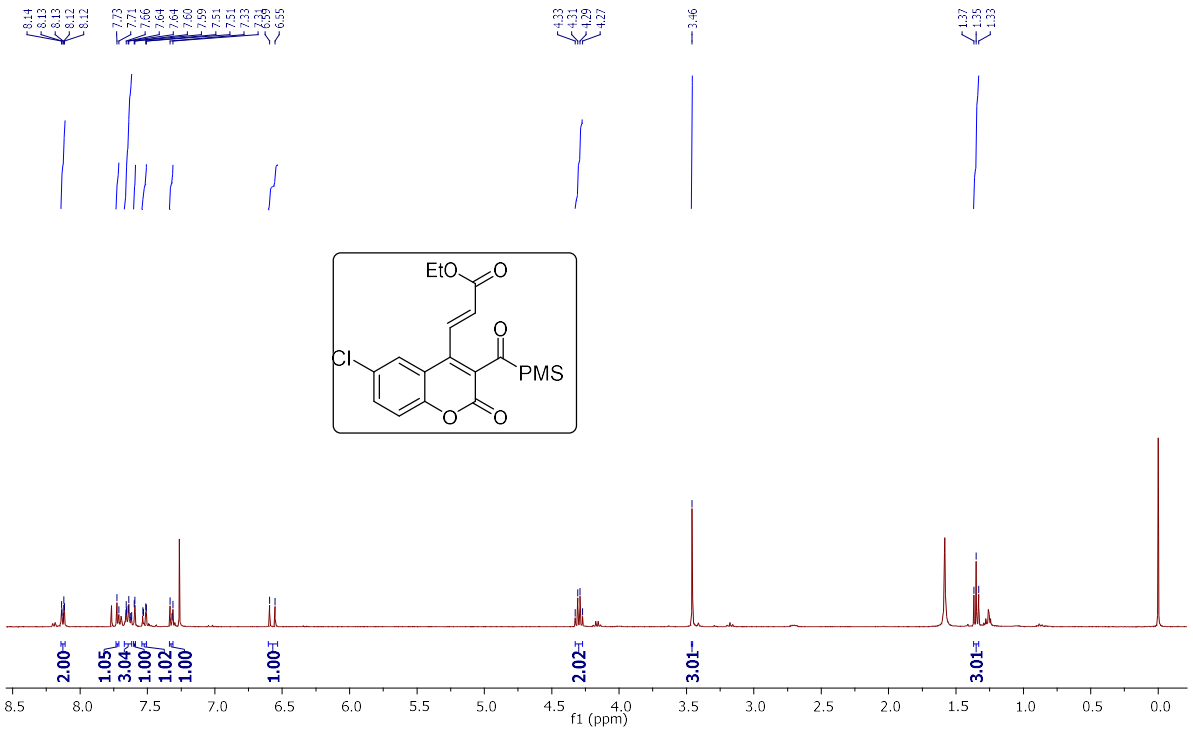
[13]CNMR (101 MHz, $CDCl_3$) spectrum of compound (3ea):



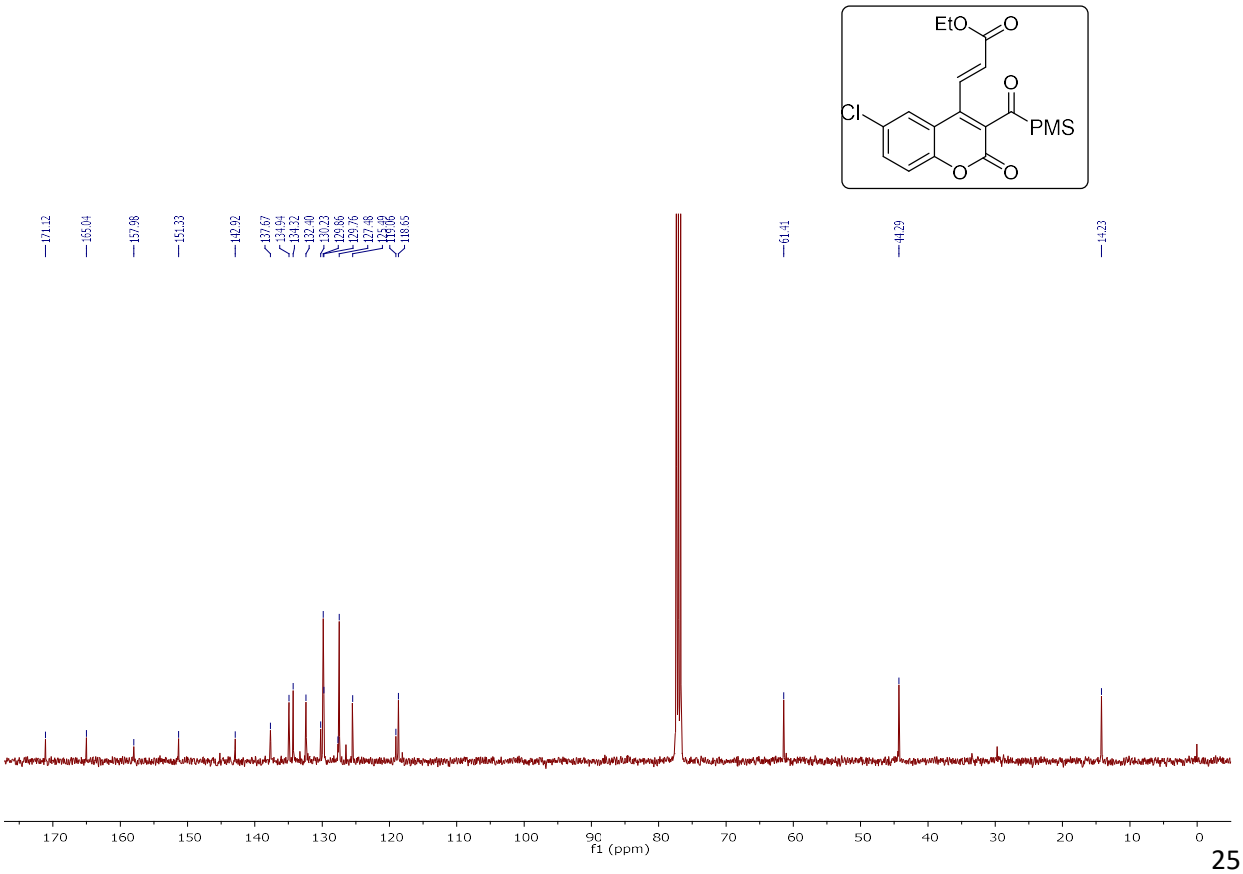
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound (3ea):



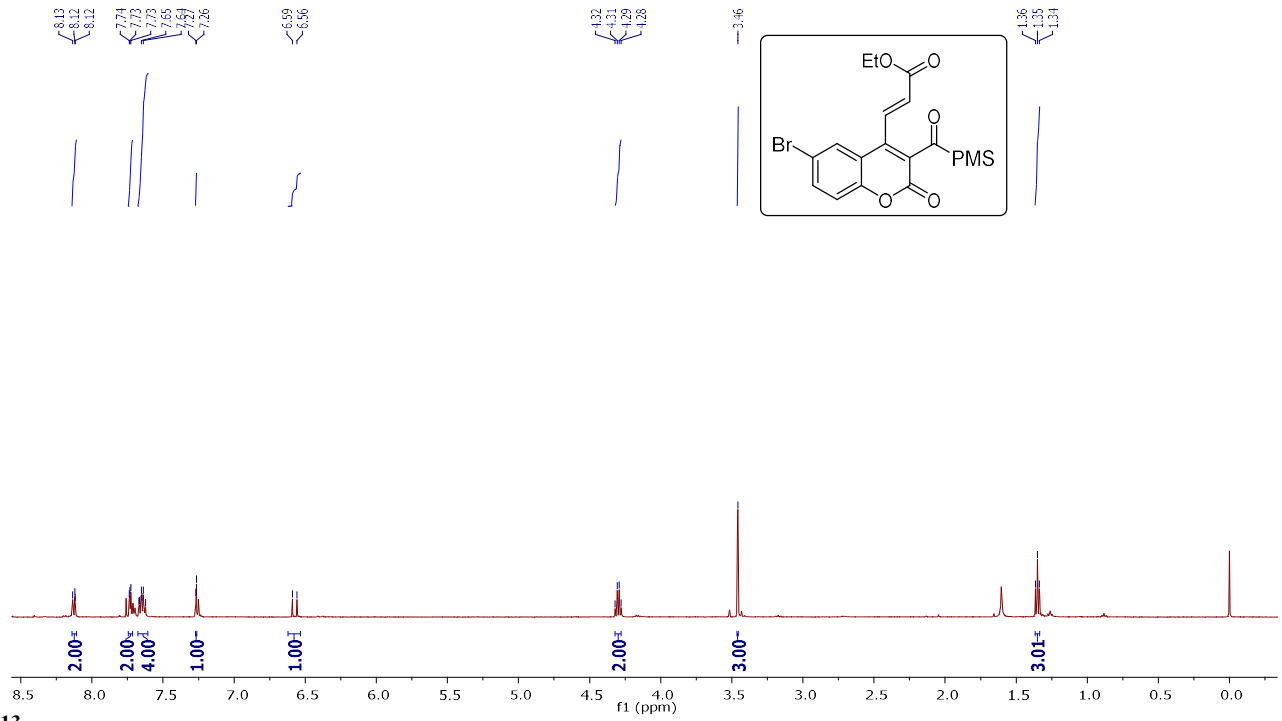
^{1}HNMR (400MHz, $CDCl_3$) spectrum of compound (3fa):



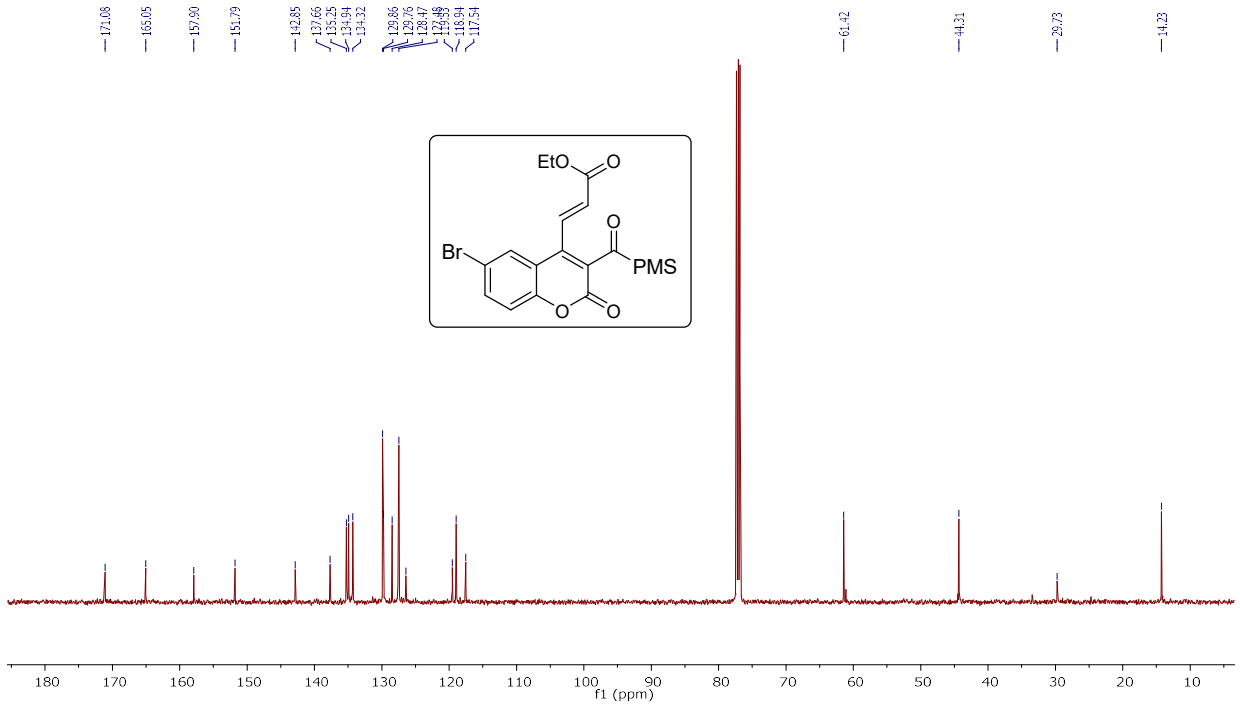
^{13}CNMR (101 MHz, $CDCl_3$) spectrum of compound (3fa):



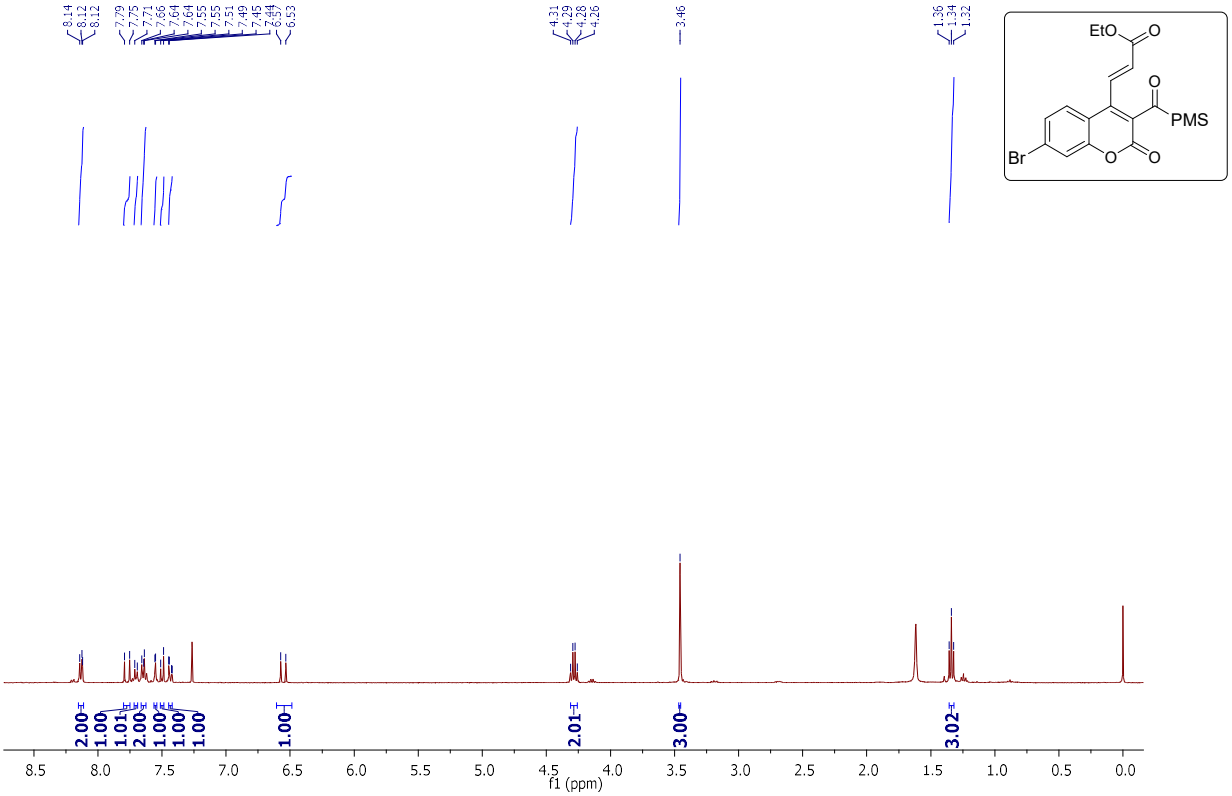
^{1}HNMR (400MHz, $CDCl_3$) spectrum of compound (3ga):



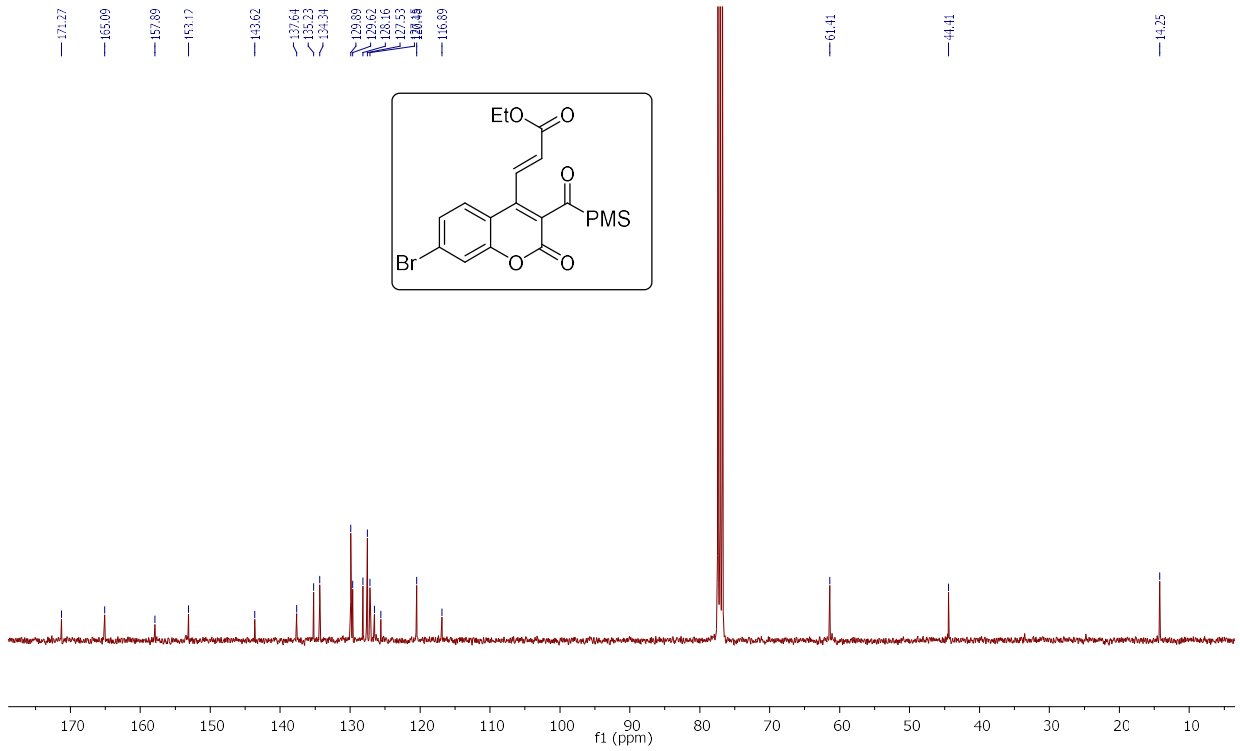
^{13}CNMR (101 MHz, $CDCl_3$) spectrum of compound (3ga):



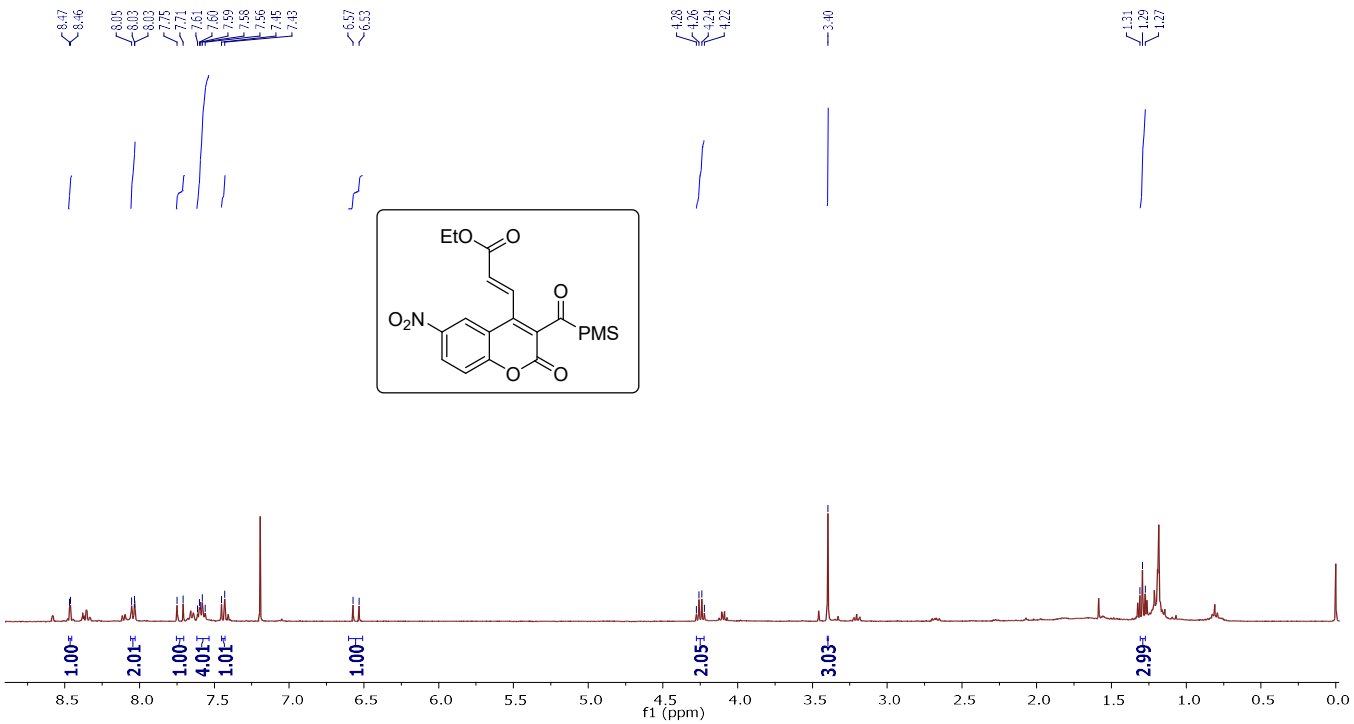
^{1}HNMR (400MHz, $CDCl_3$) spectrum of compound (3ha):



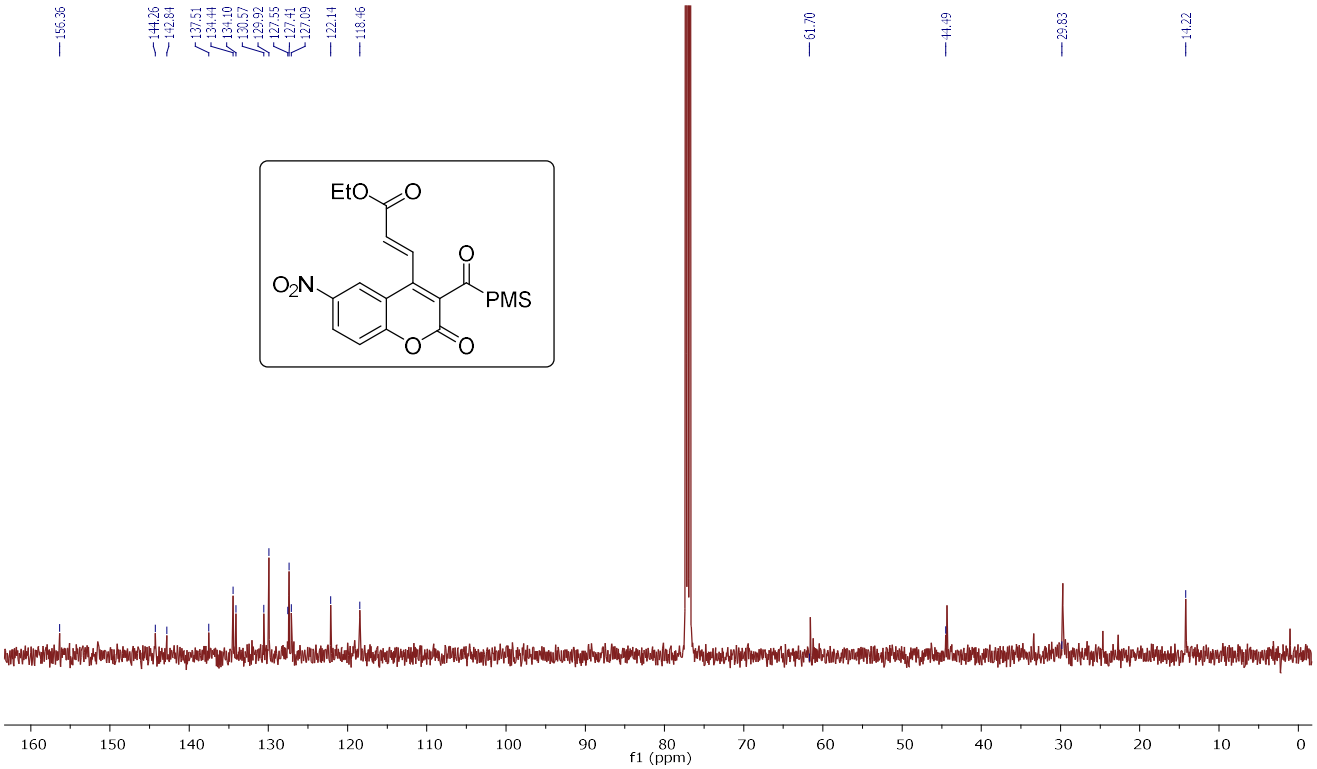
^{13}CNMR (101 MHz, $CDCl_3$) spectrum of compound (3ha):



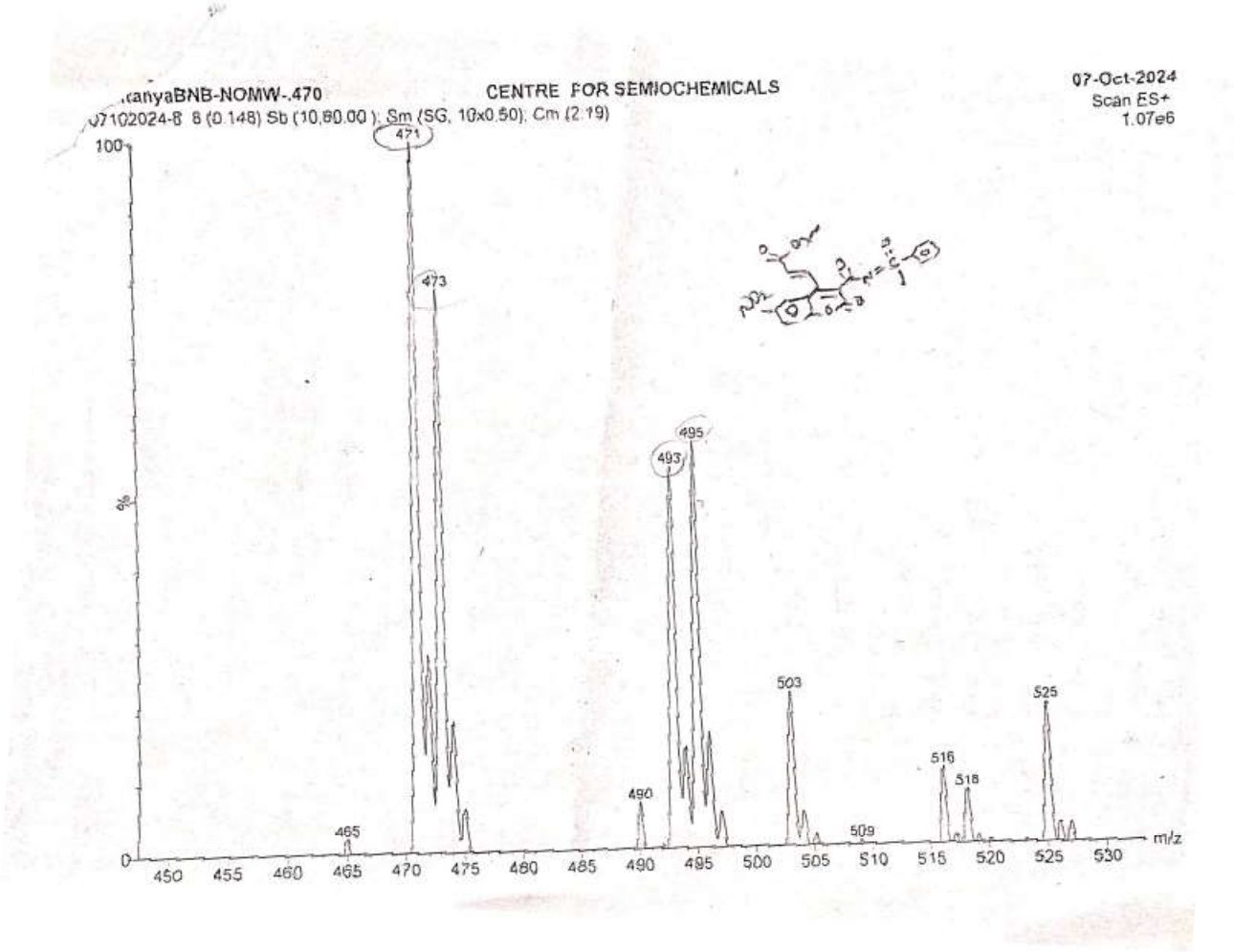
[1]HNMR (400MHz, $CDCl_3$)spectrum of compound (3ia):



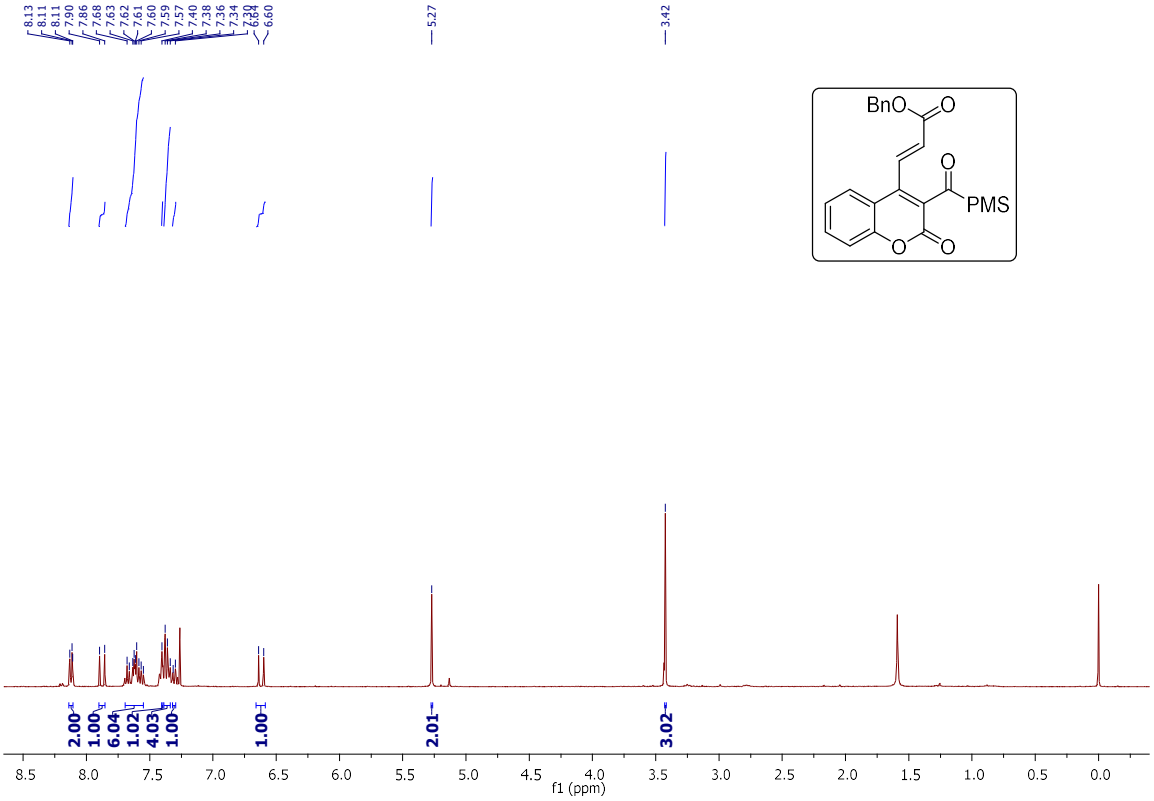
[13]C NMR (126 MHz, $CDCl_3$)spectrum of compound (3ia):



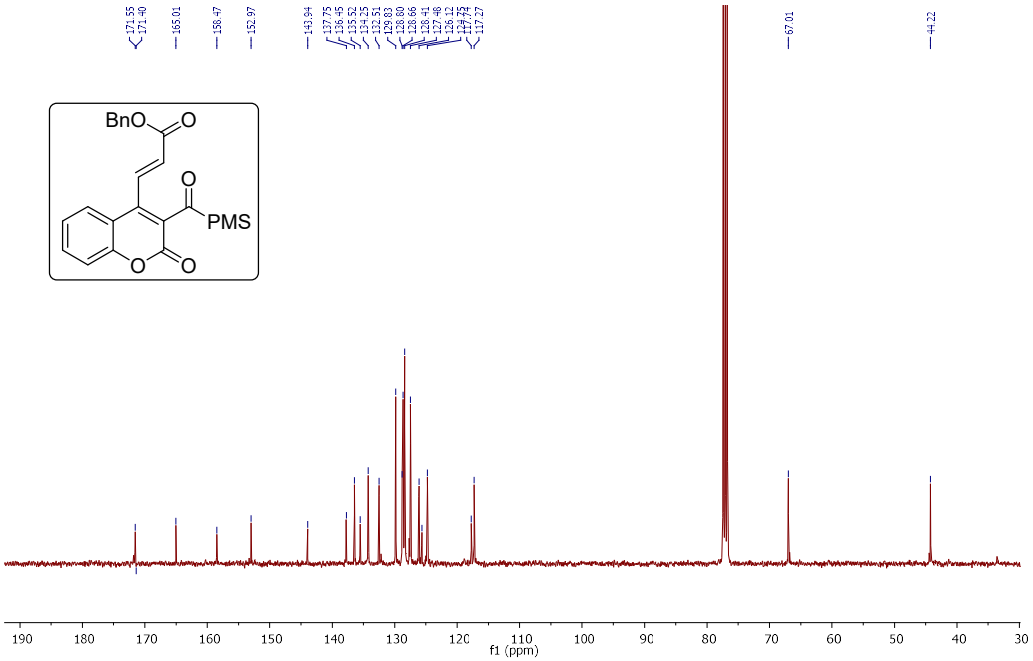
LCMSspectrum of compound (3ia):



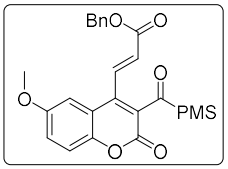
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (3ab):



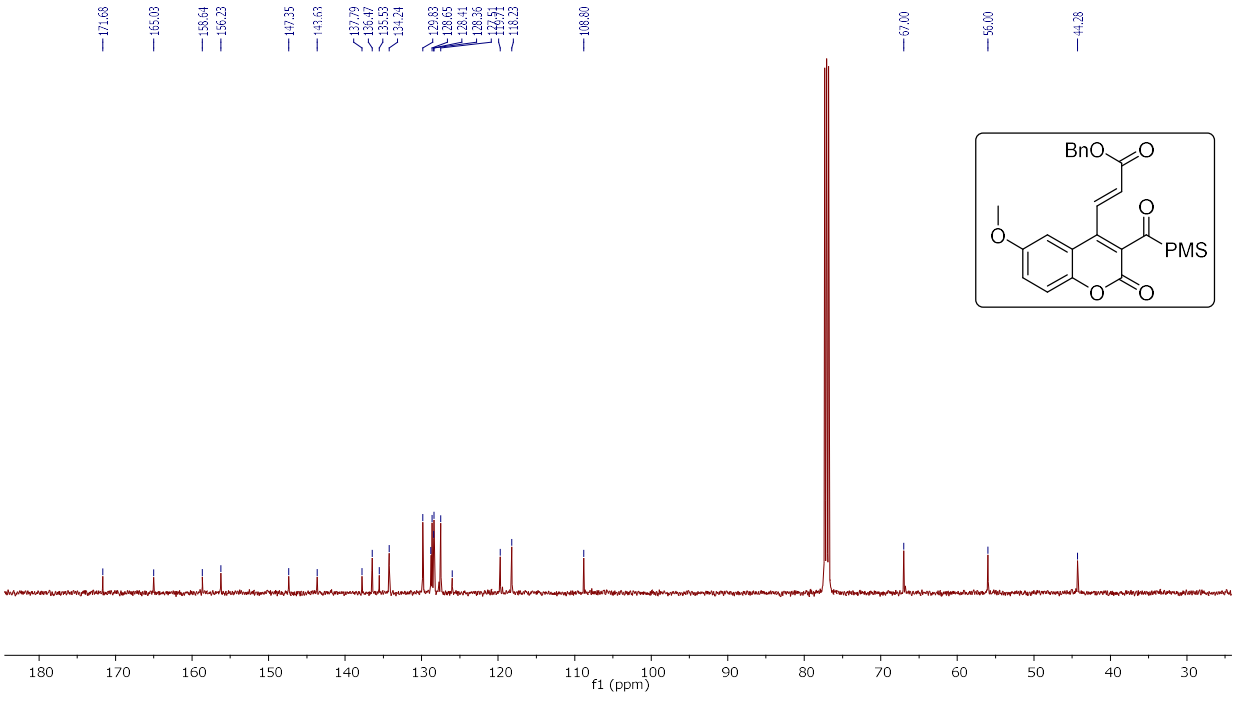
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound (3ab):



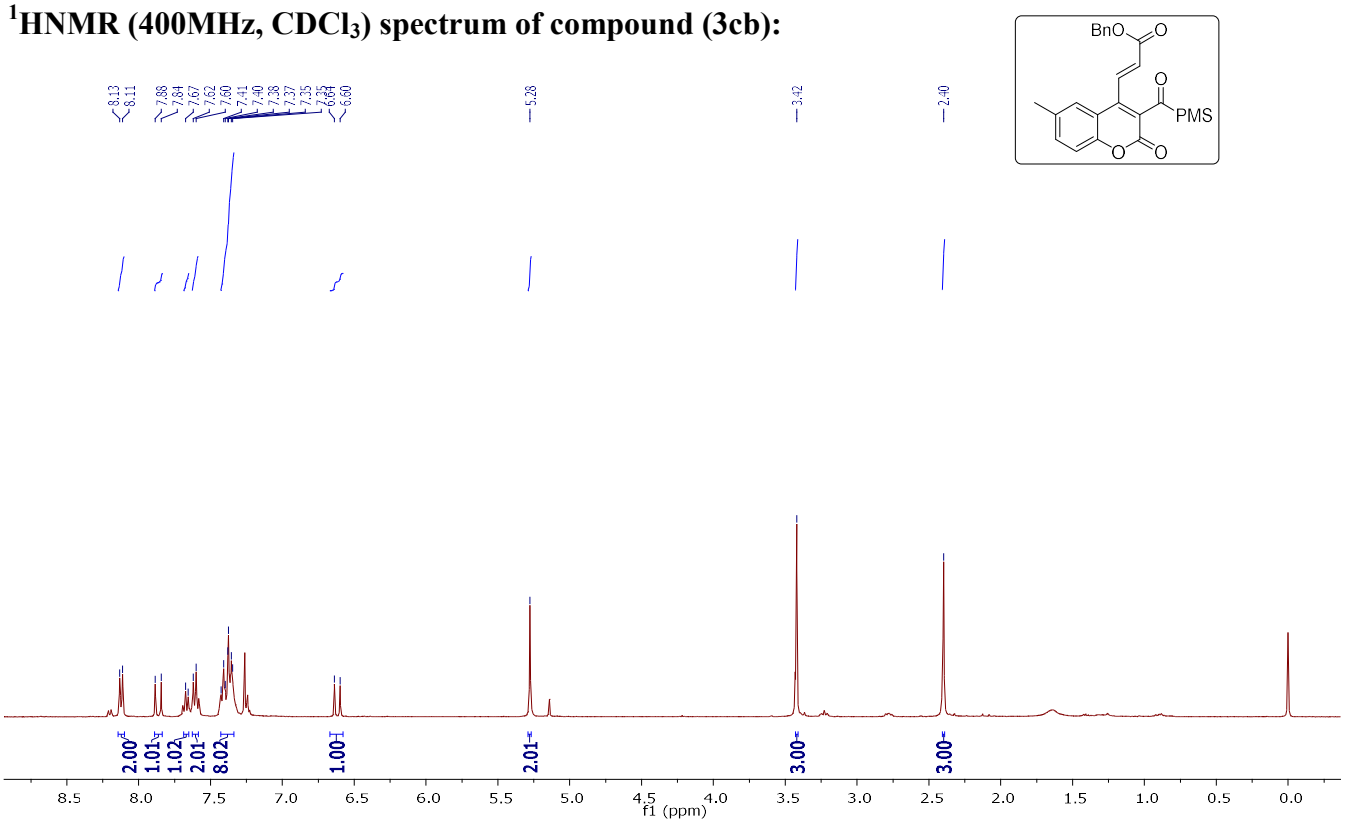
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound (3bb):



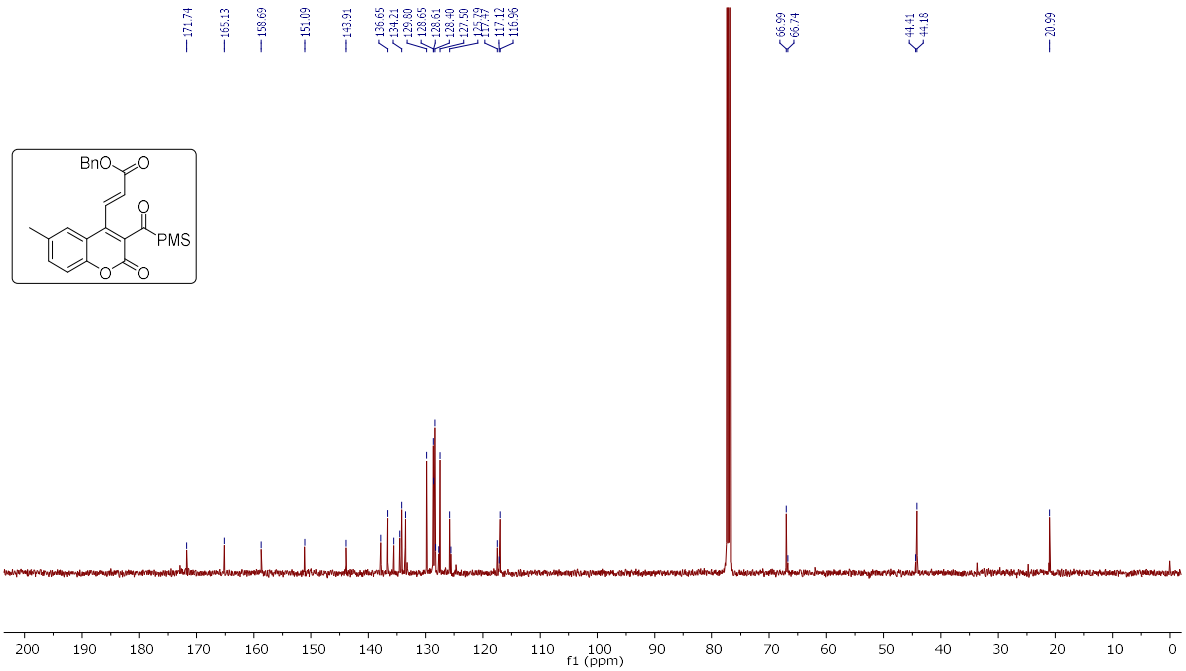
^{13}CNMR (126MHz, $CDCl_3$) spectrum of compound (3bb):



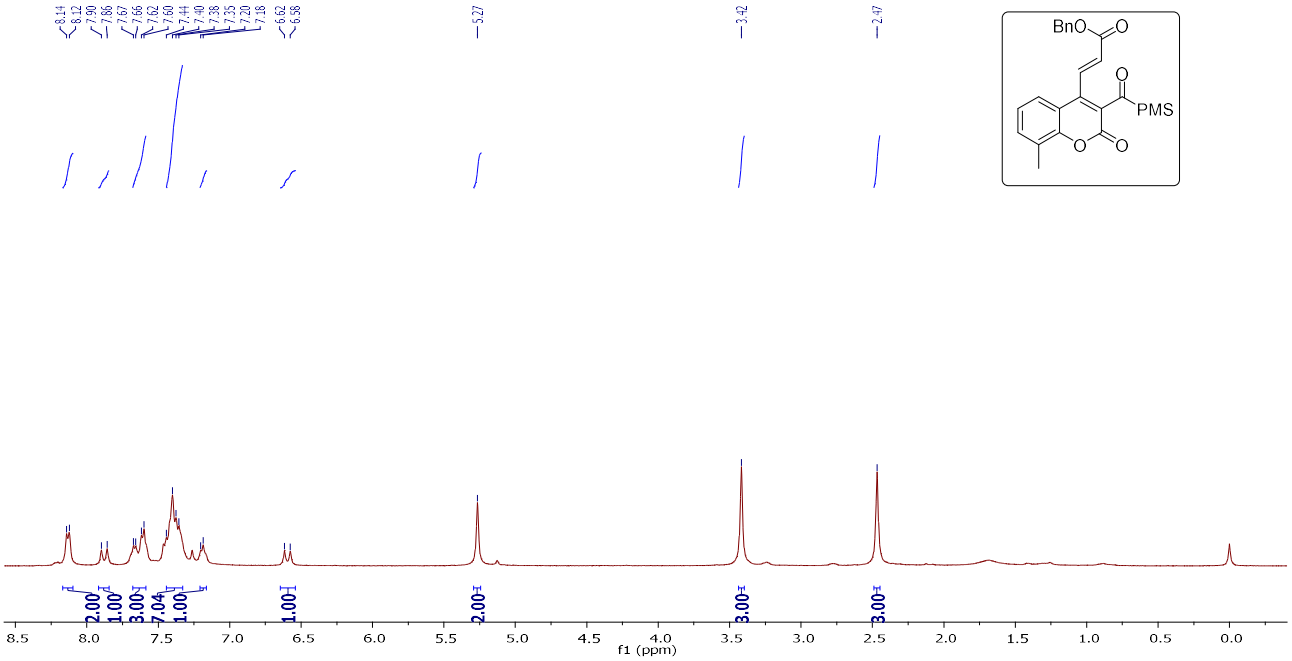
[1]HNMR (400MHz, $CDCl_3$) spectrum of compound (3cb):



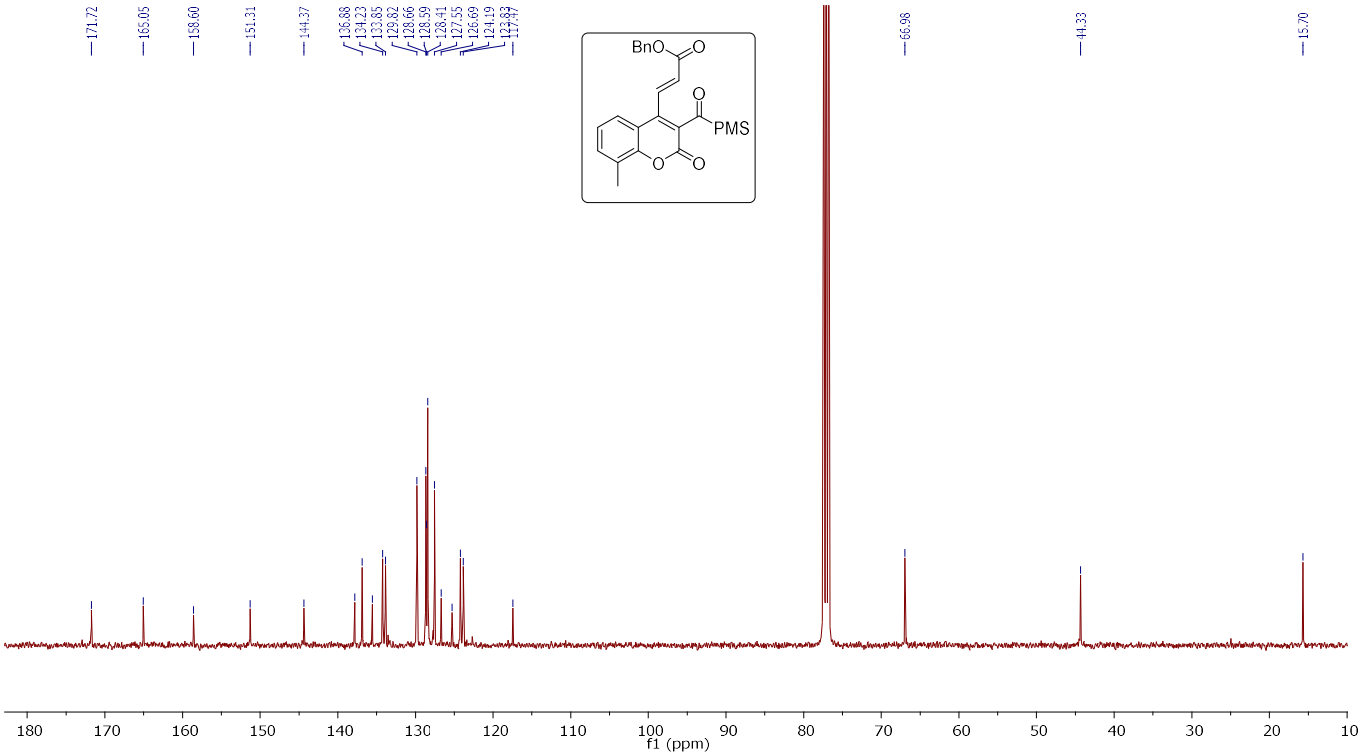
[13]CNMR (101MHz, $CDCl_3$) spectrum of compound (3cb):



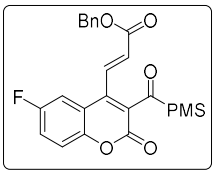
[1]HNMR (400MHz, $CDCl_3$) spectrum of compound (3db):



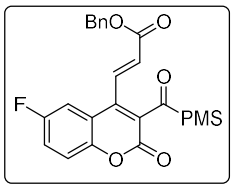
[13]CNMR (101 MHz, $CDCl_3$) spectrum of compound (3db):



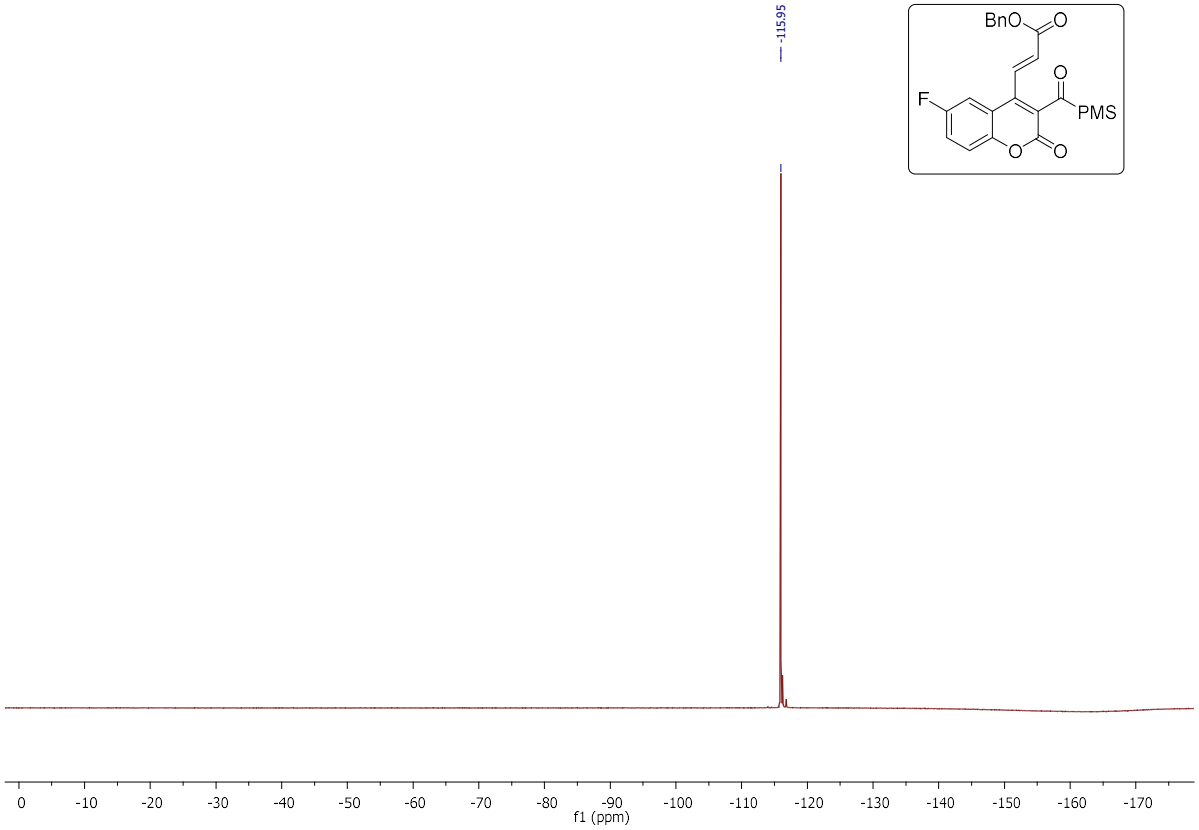
[1]HNMR (400MHz, $CDCl_3$) spectrum of compound (3eb):



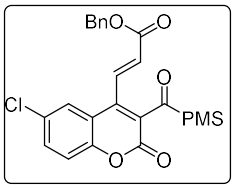
[13]CNMR (101 MHz, $CDCl_3$) spectrum of compound (3eb):

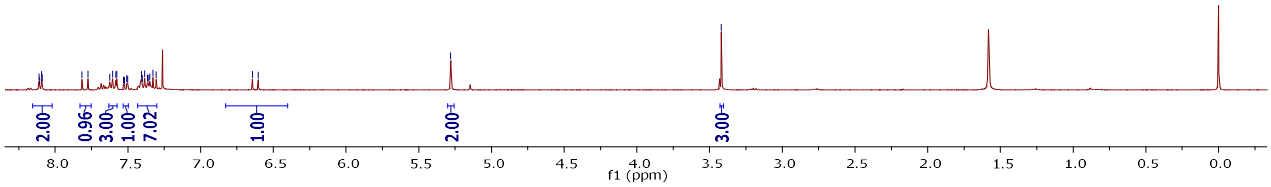


^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound (3eb):

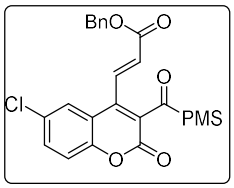


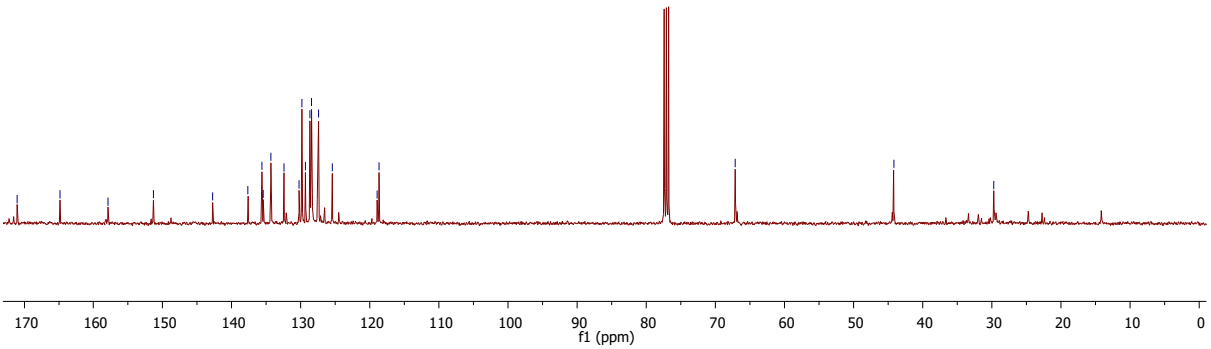
[1]HNMR (400MHz, $CDCl_3$) spectrum of compound (3fb):



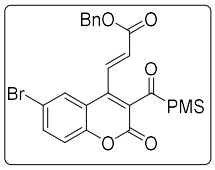


[13]CNMR (101 MHz, $CDCl_3$) spectrum of compound (3fb):

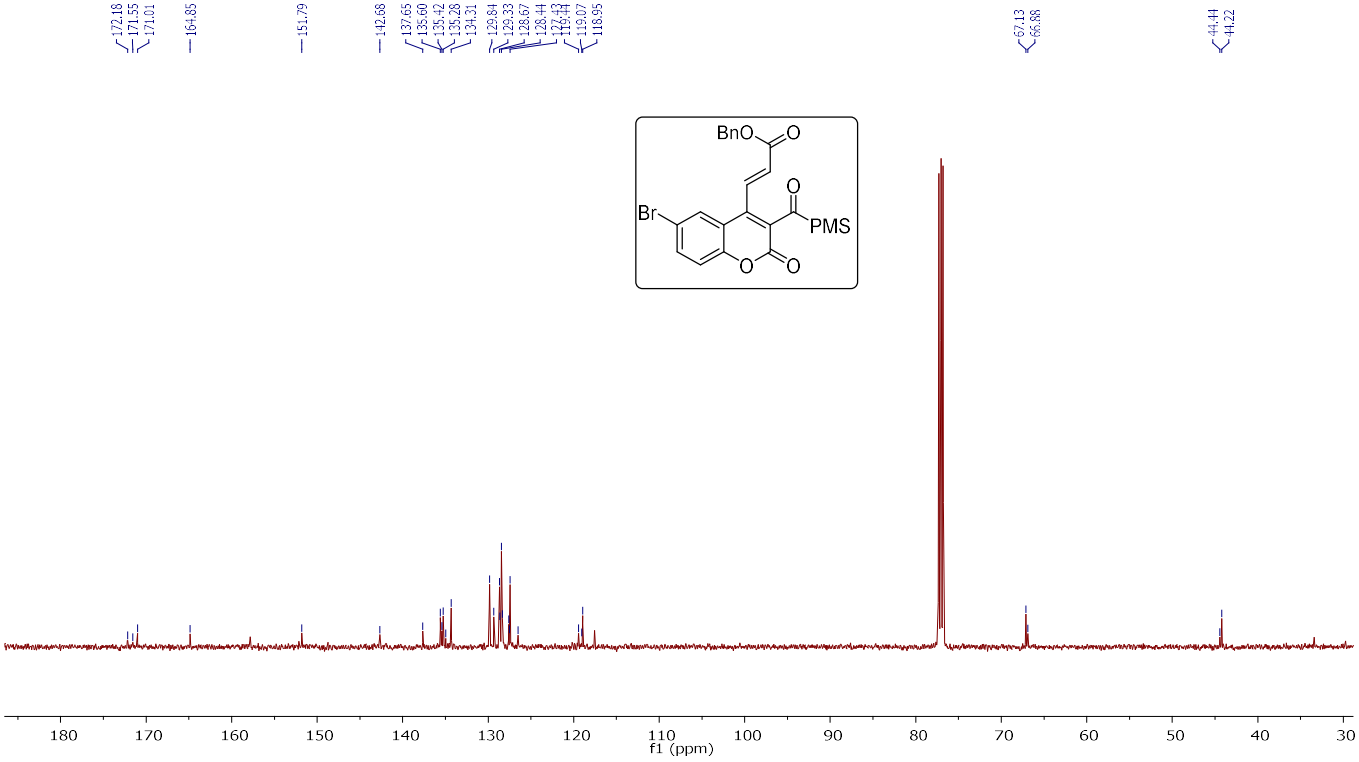




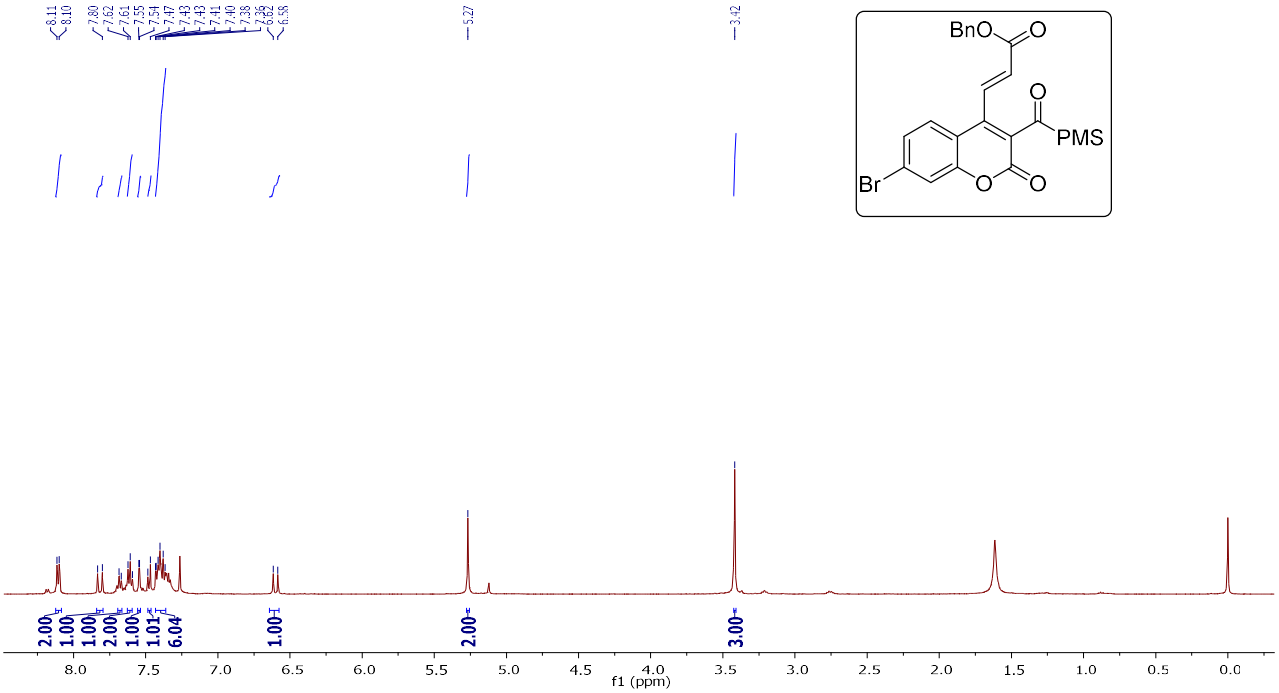
^{1}HNMR (400MHz, $CDCl_3$) spectrum of compound (3gb)



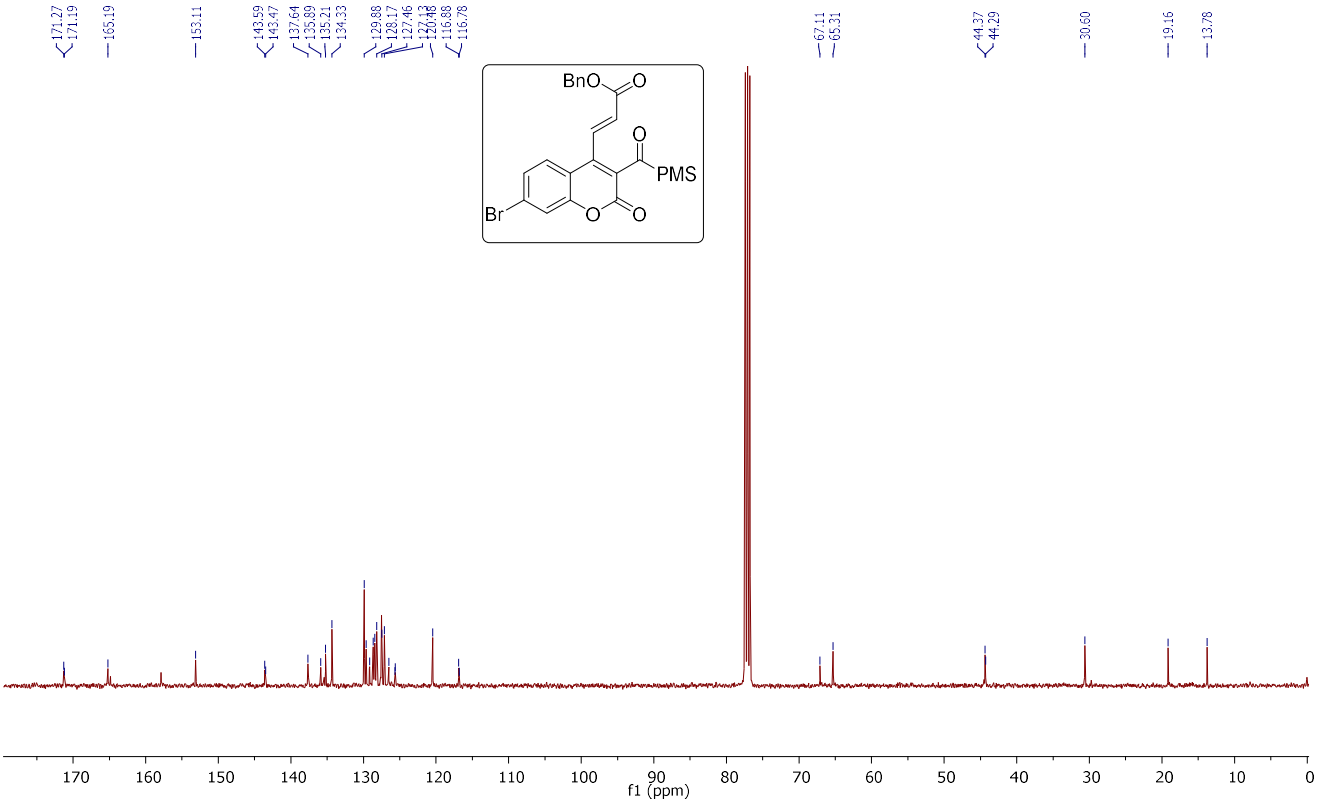
^{13}CNMR (101 MHz, $CDCl_3$) spectrum of compound (3gb):



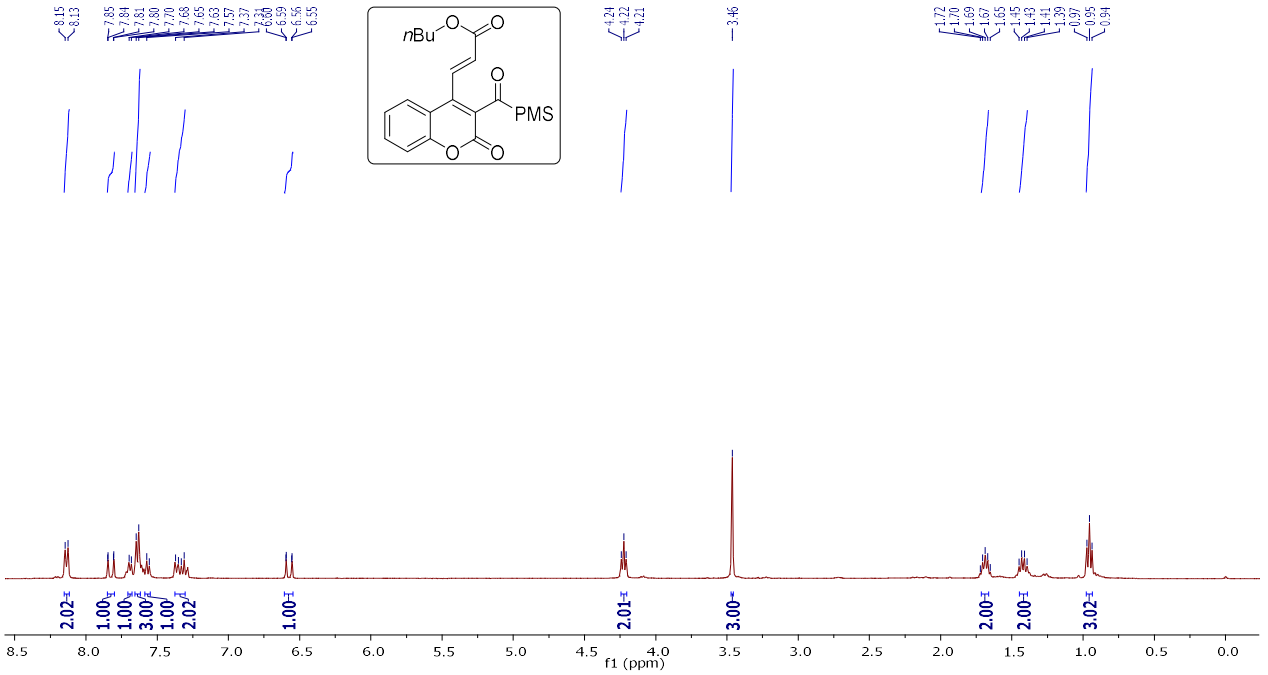
[1]HNMR (400MHz, $CDCl_3$) spectrum of compound (3hb):



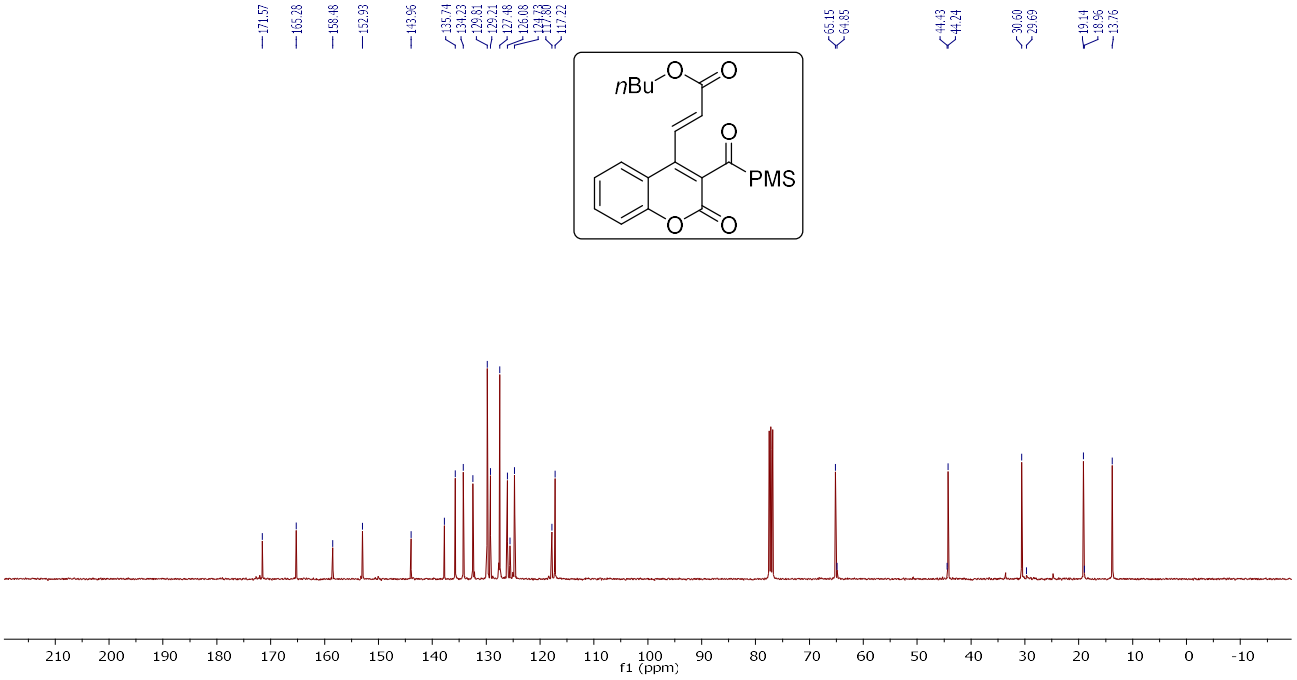
[13]CNMR (101 MHz, $CDCl_3$) spectrum of compound (3hb):



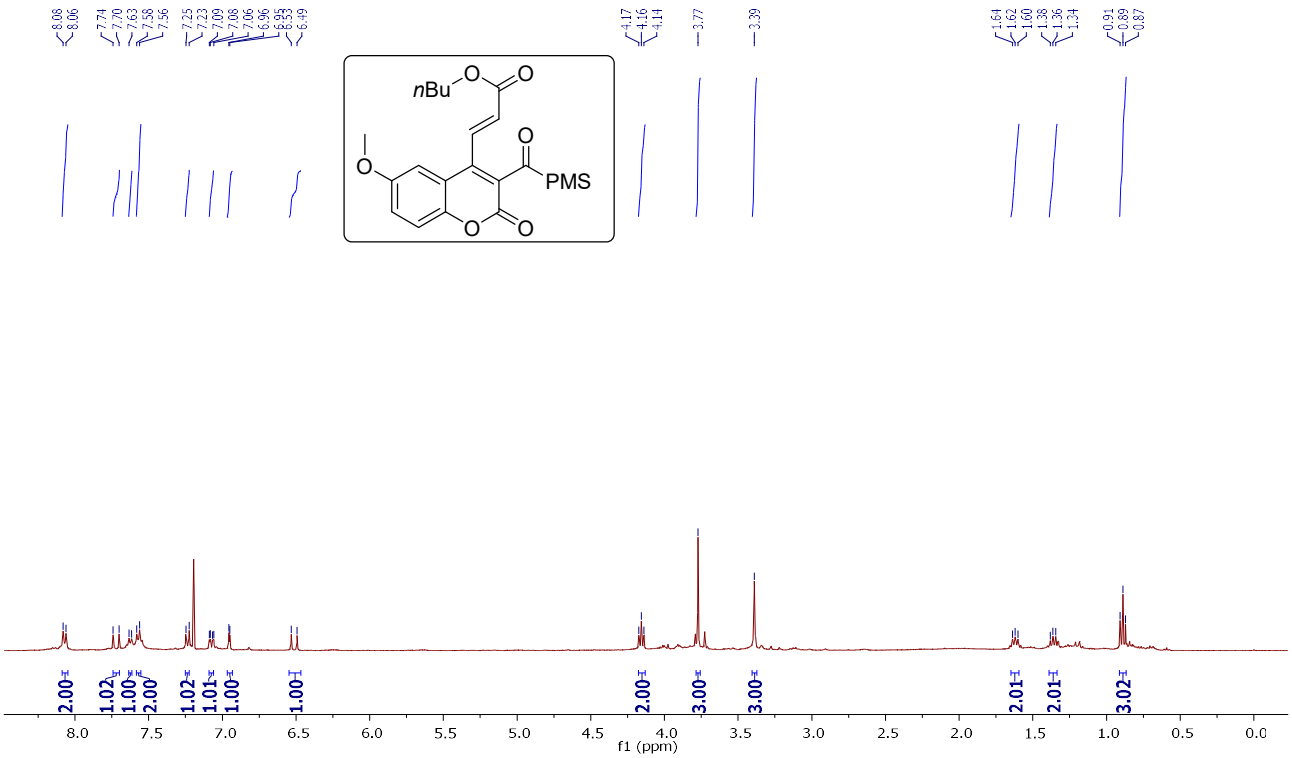
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (3ac):



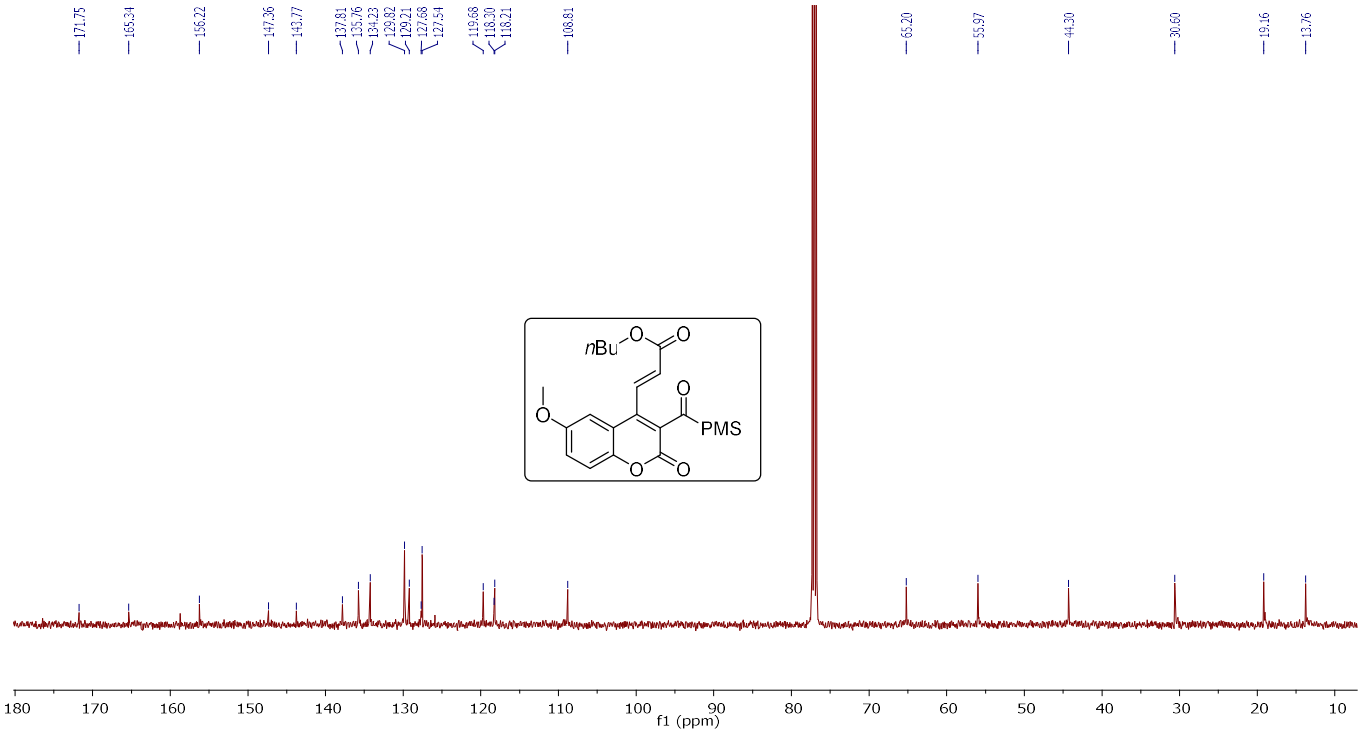
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound (3ac):



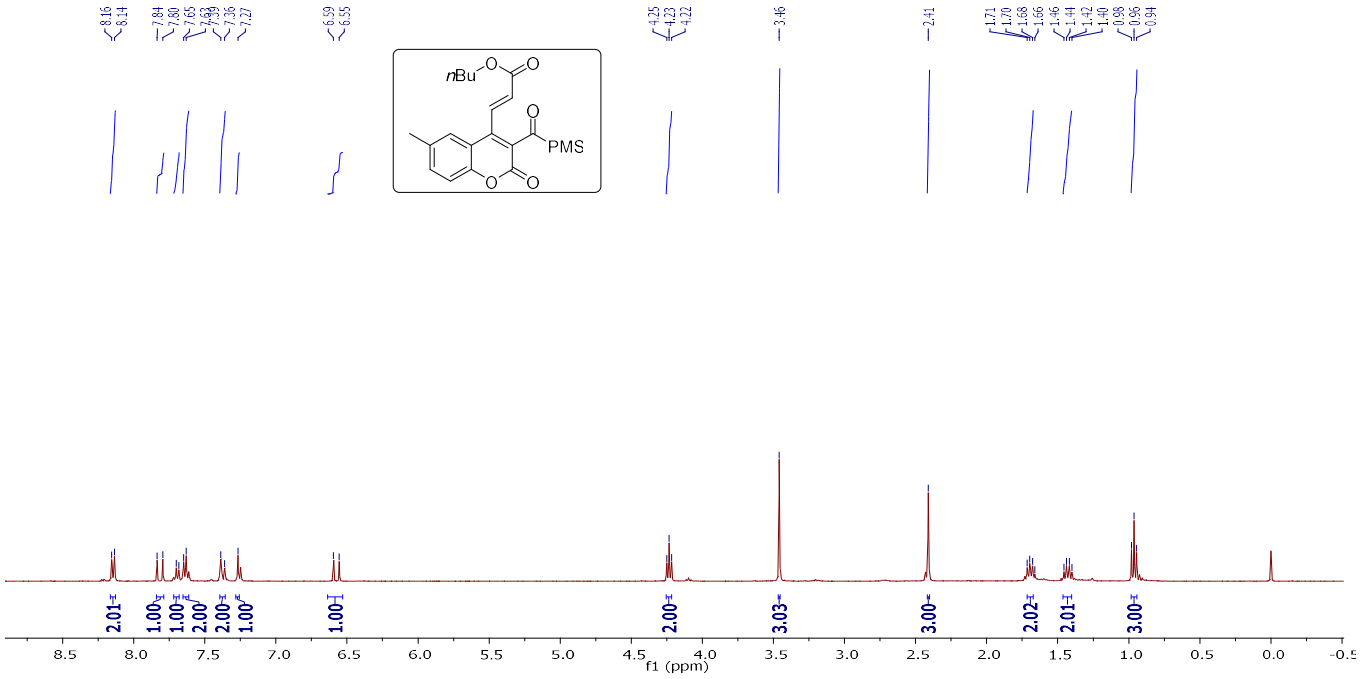
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound (3bc):



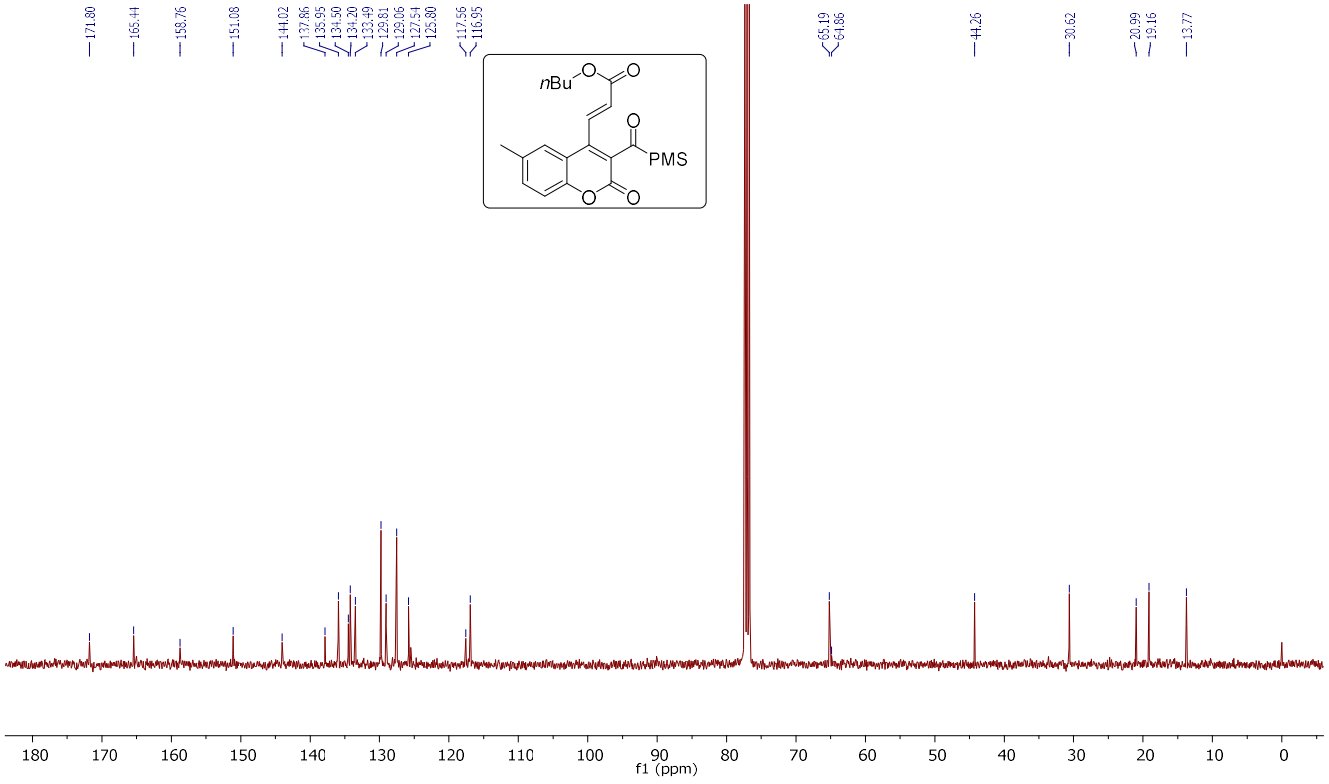
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound (3bc):



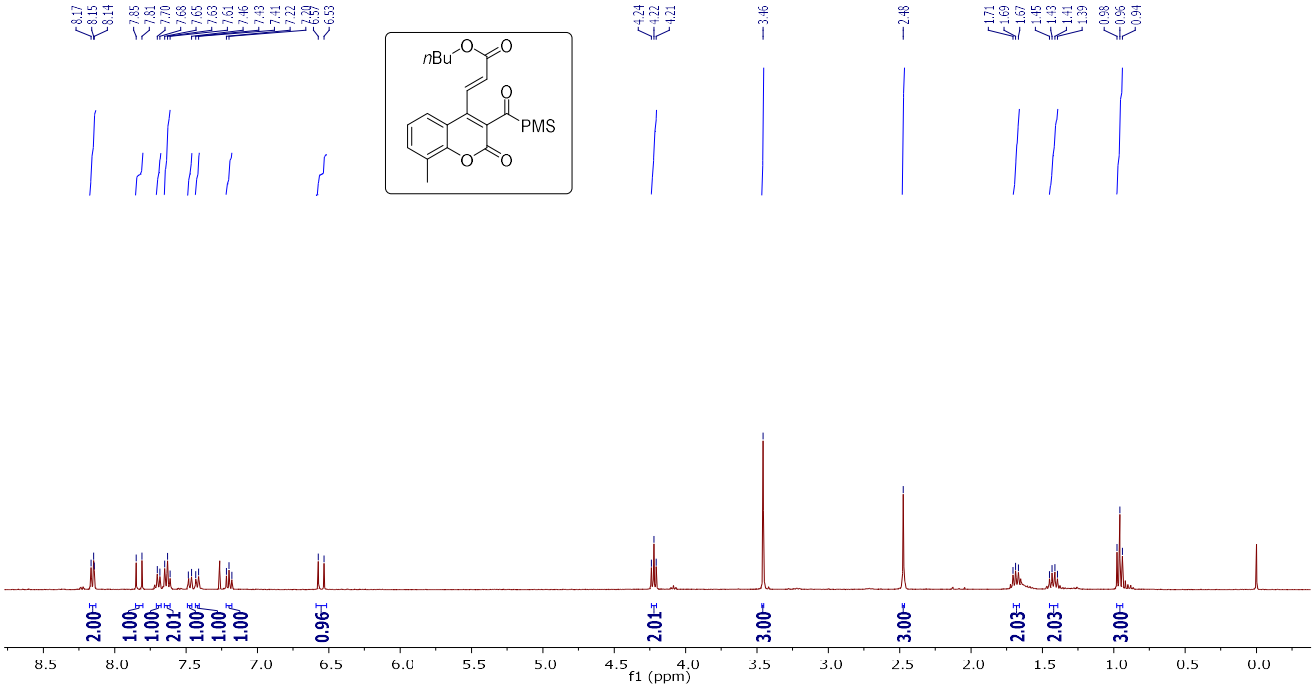
[1]HNMR (400MHz, $CDCl_3$) spectrum of compound (3cc):



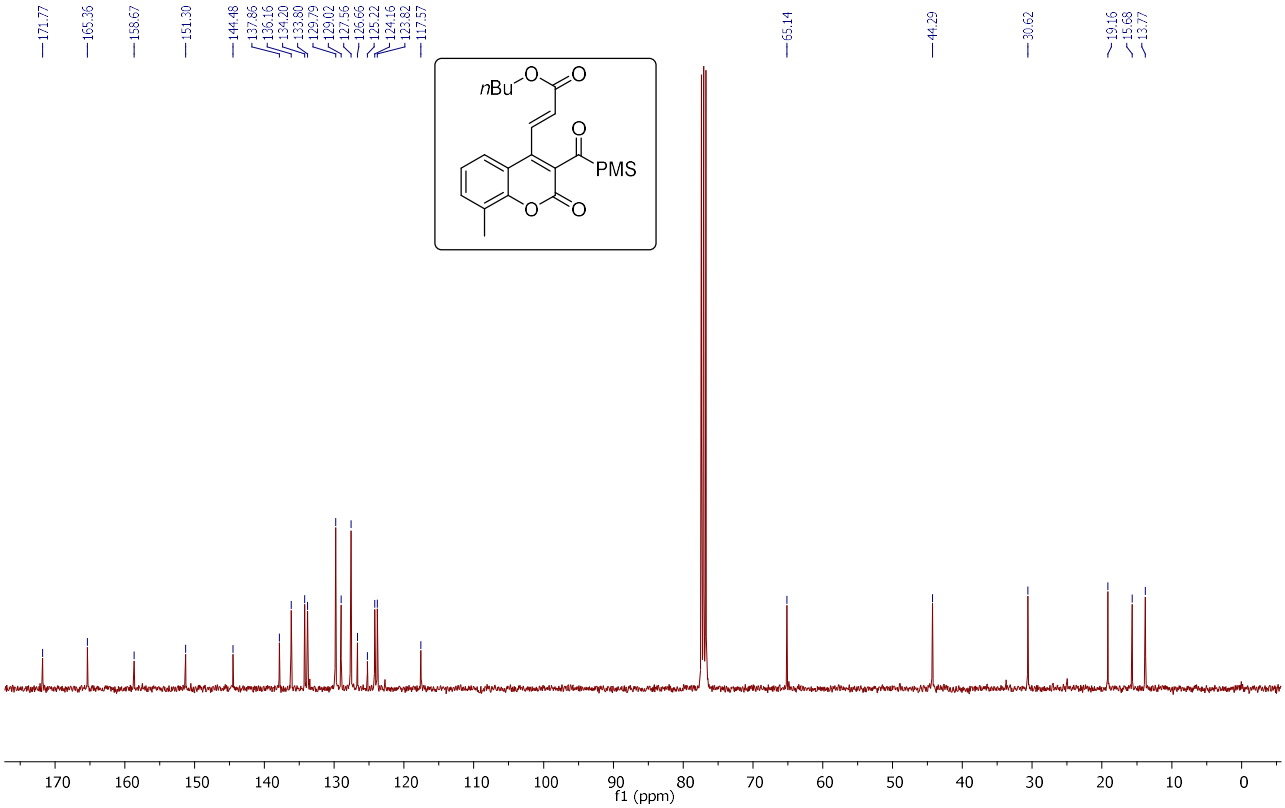
[13]CNMR (101MHz, $CDCl_3$) spectrum of compound (3cc):



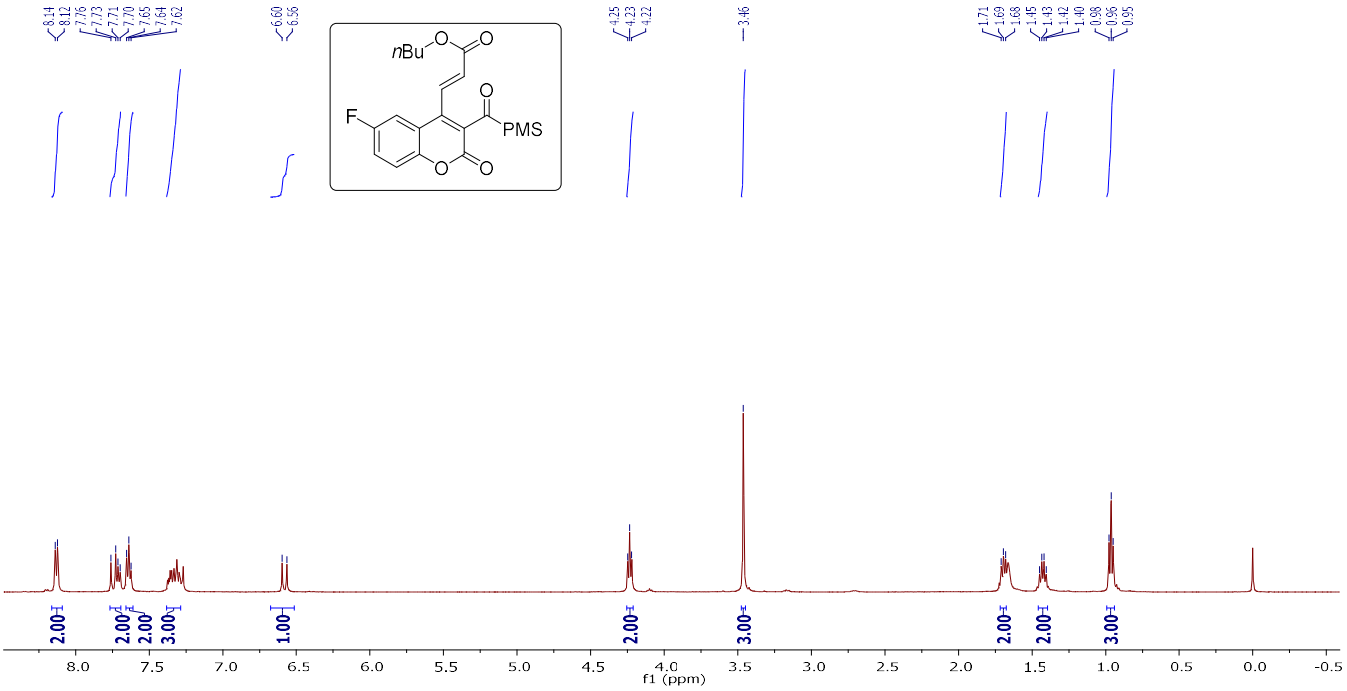
[1]HNMR (400MHz, $CDCl_3$) spectrum of compound (3dc):



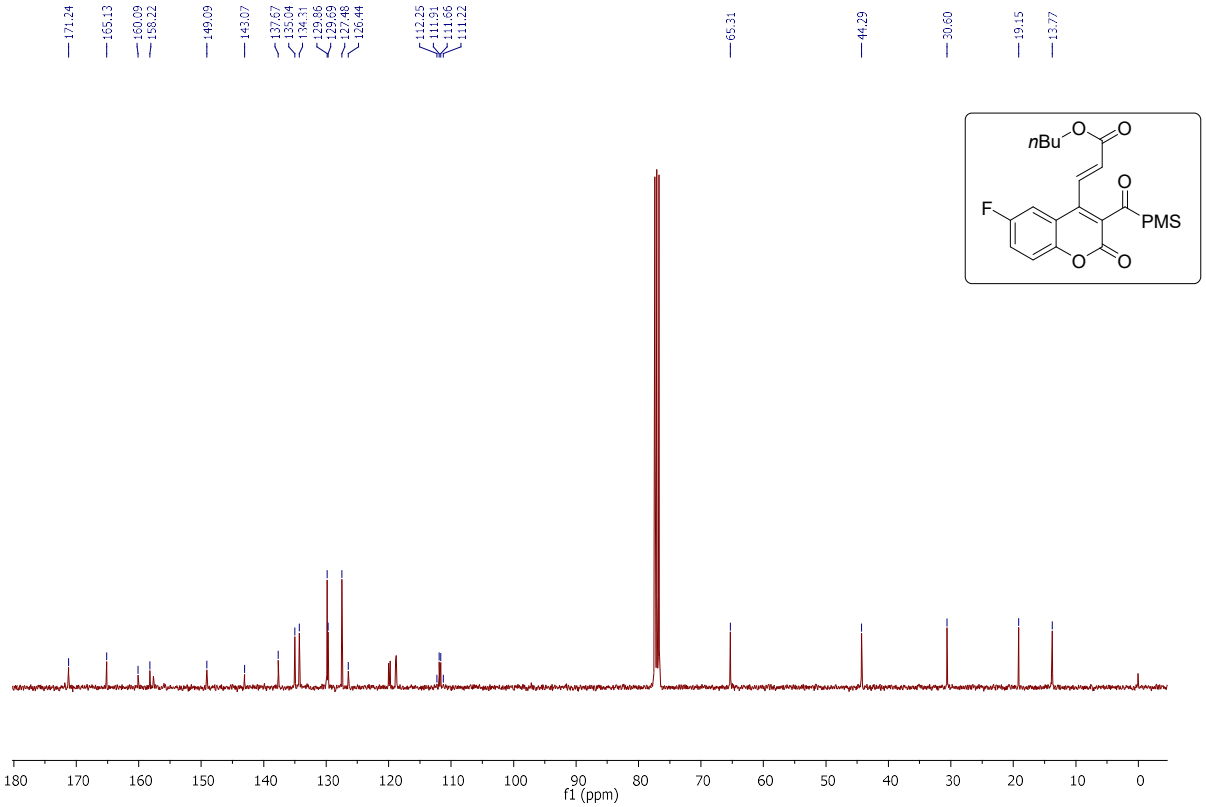
[13]CNMR (101 MHz, $CDCl_3$) spectrum of compound (3dc):



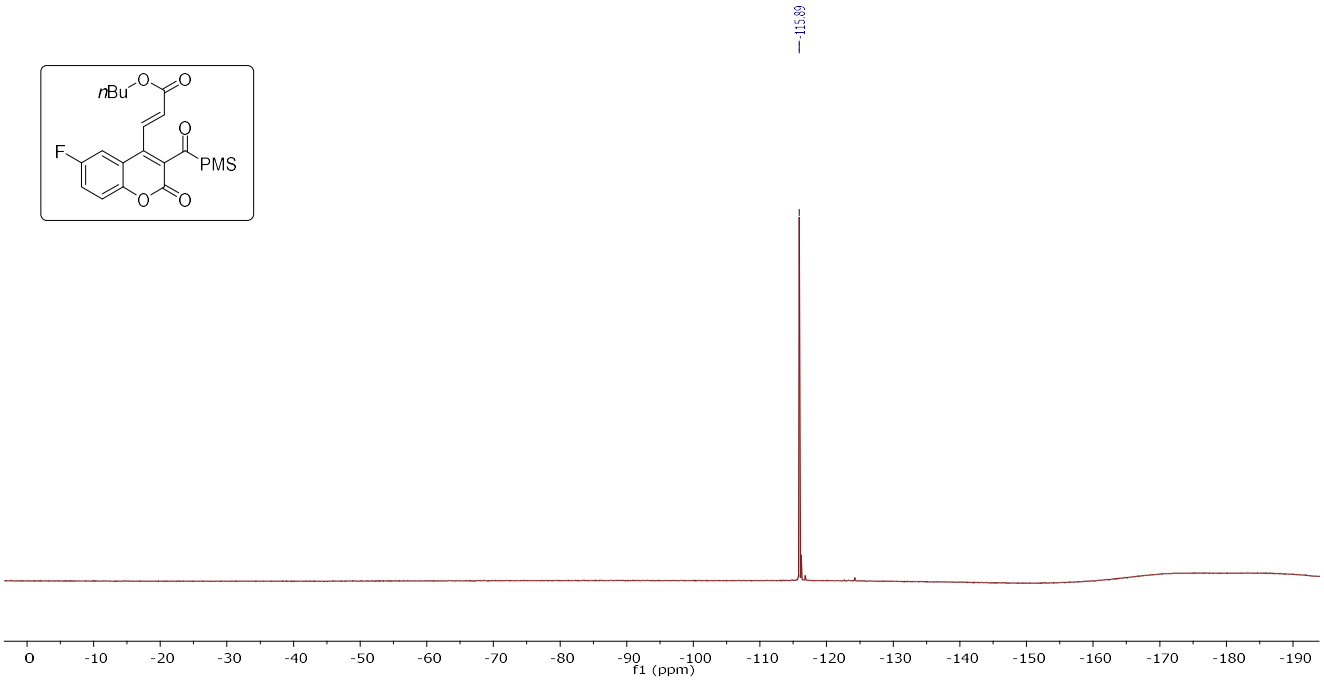
[1]HNMR (400MHz, $CDCl_3$) spectrum of compound (3ec):



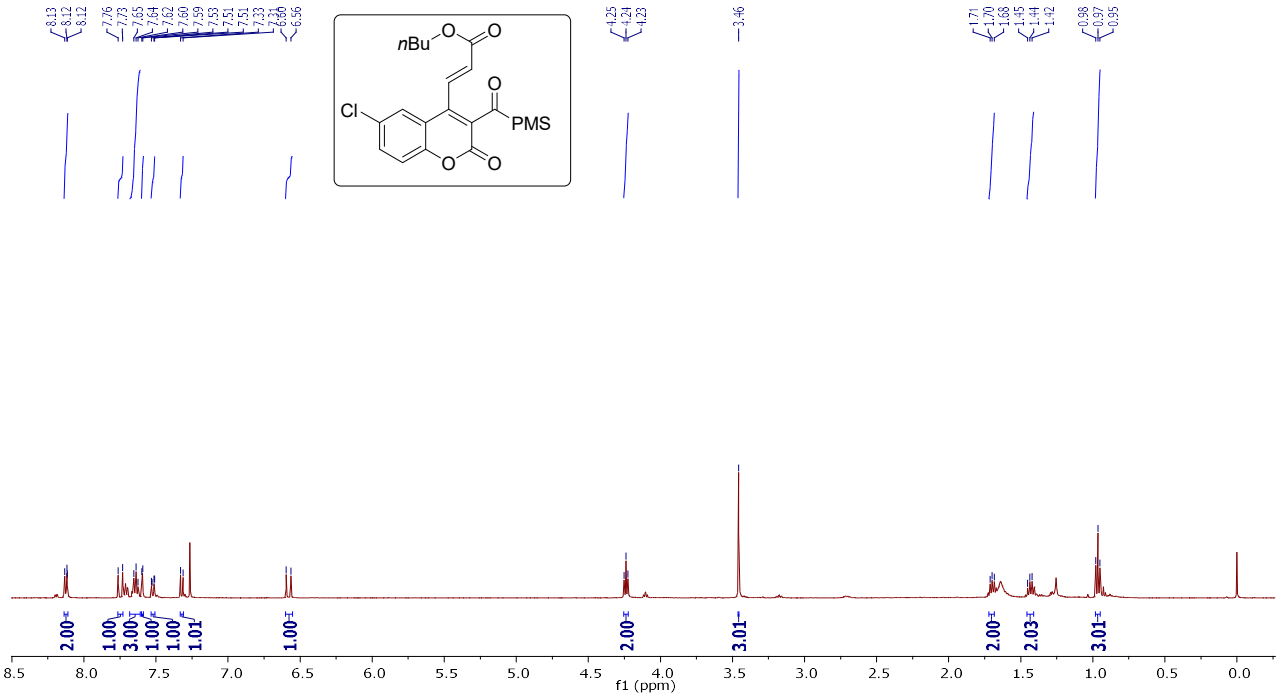
[13]CNMR (101 MHz, $CDCl_3$) spectrum of compound (3ec):



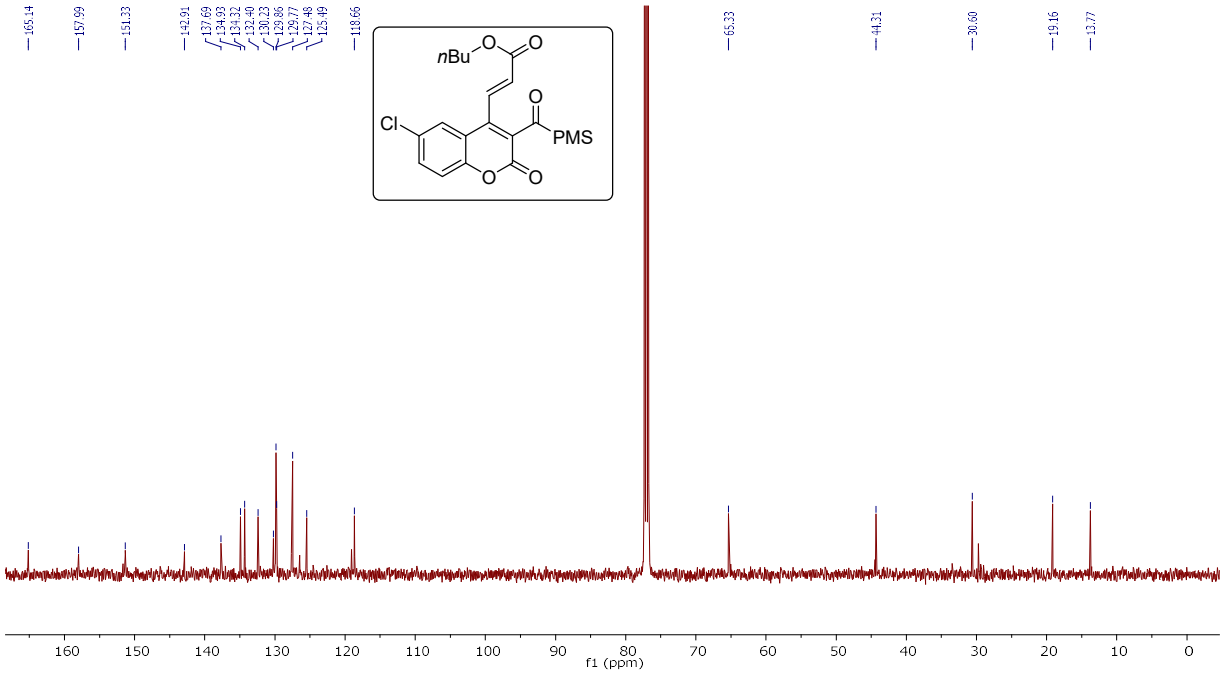
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound (3ec):



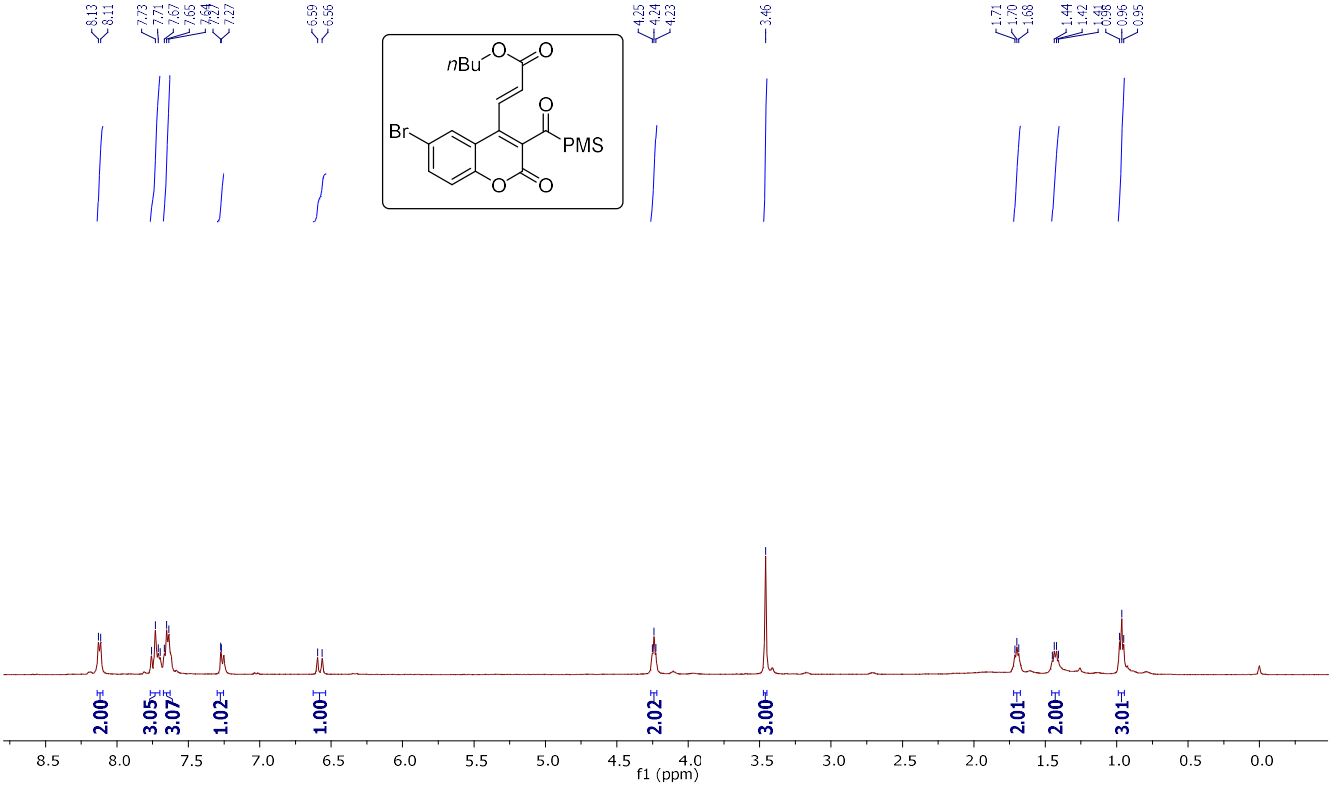
[1]HNMR (400MHz, $CDCl_3$) spectrum of compound (3fc):



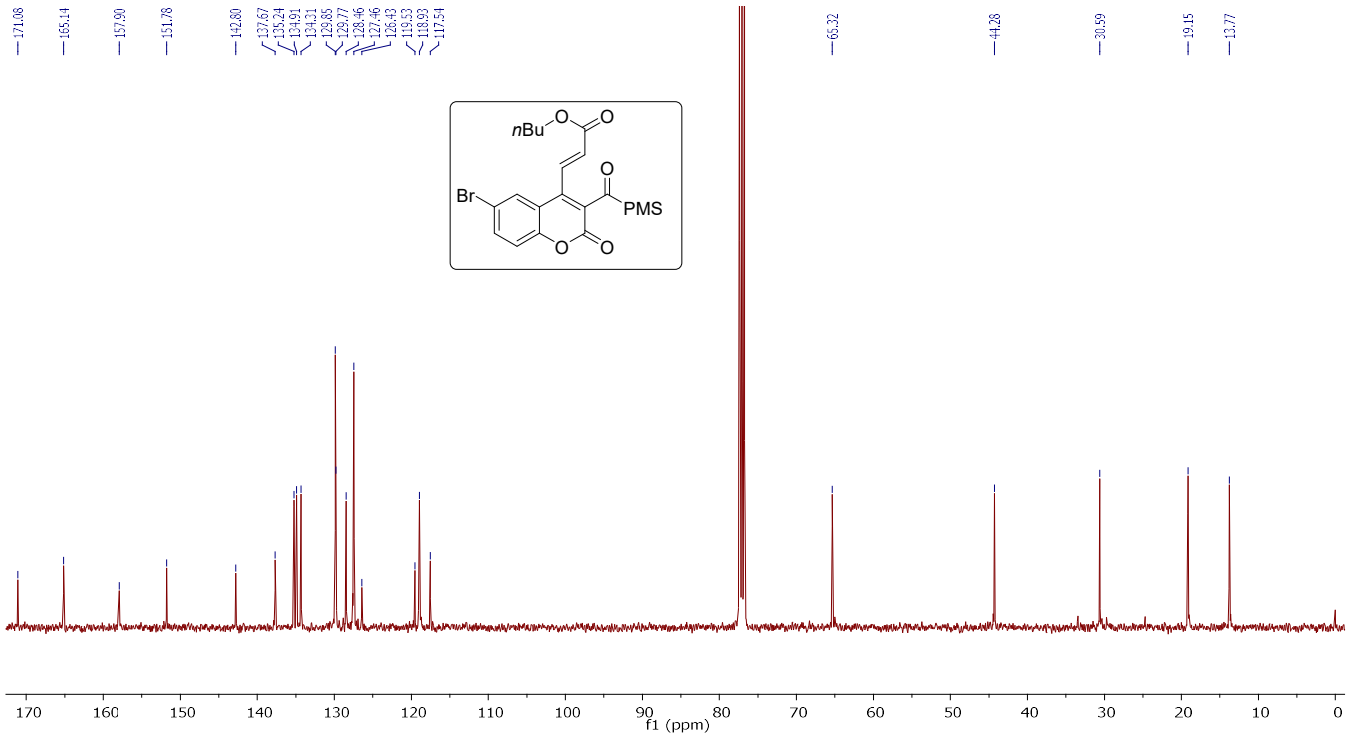
[13]CNMR (101 MHz, $CDCl_3$) spectrum of compound (3fc):



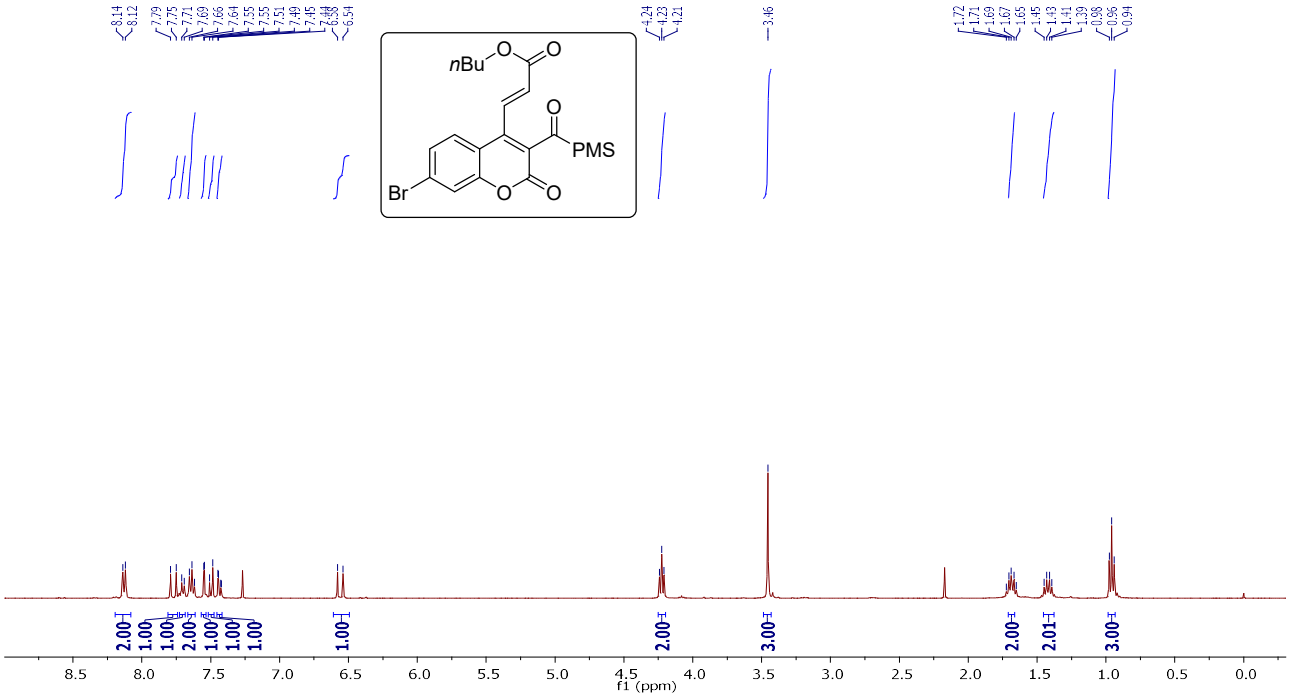
[1]HNMR (400MHz, $CDCl_3$) spectrum of compound (3gc):



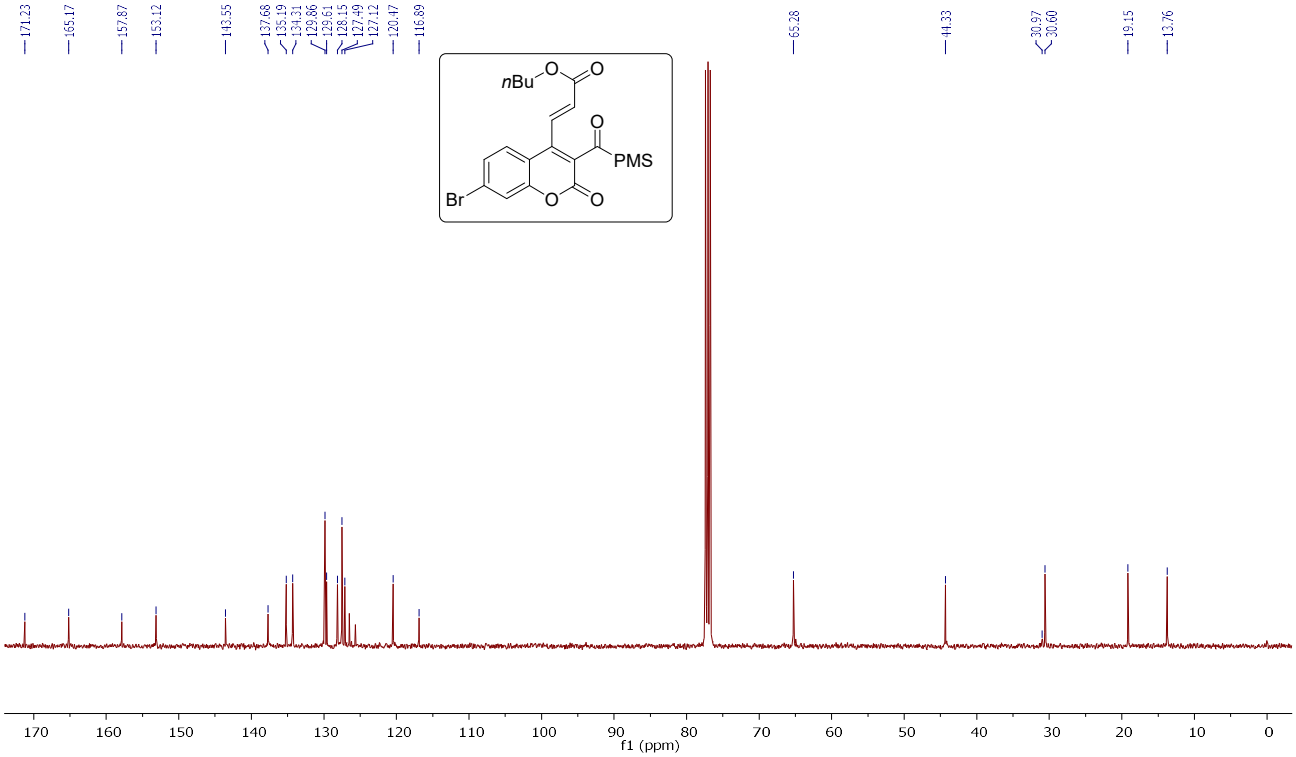
[13]CNMR (101 MHz, $CDCl_3$) spectrum of compound (3gc):



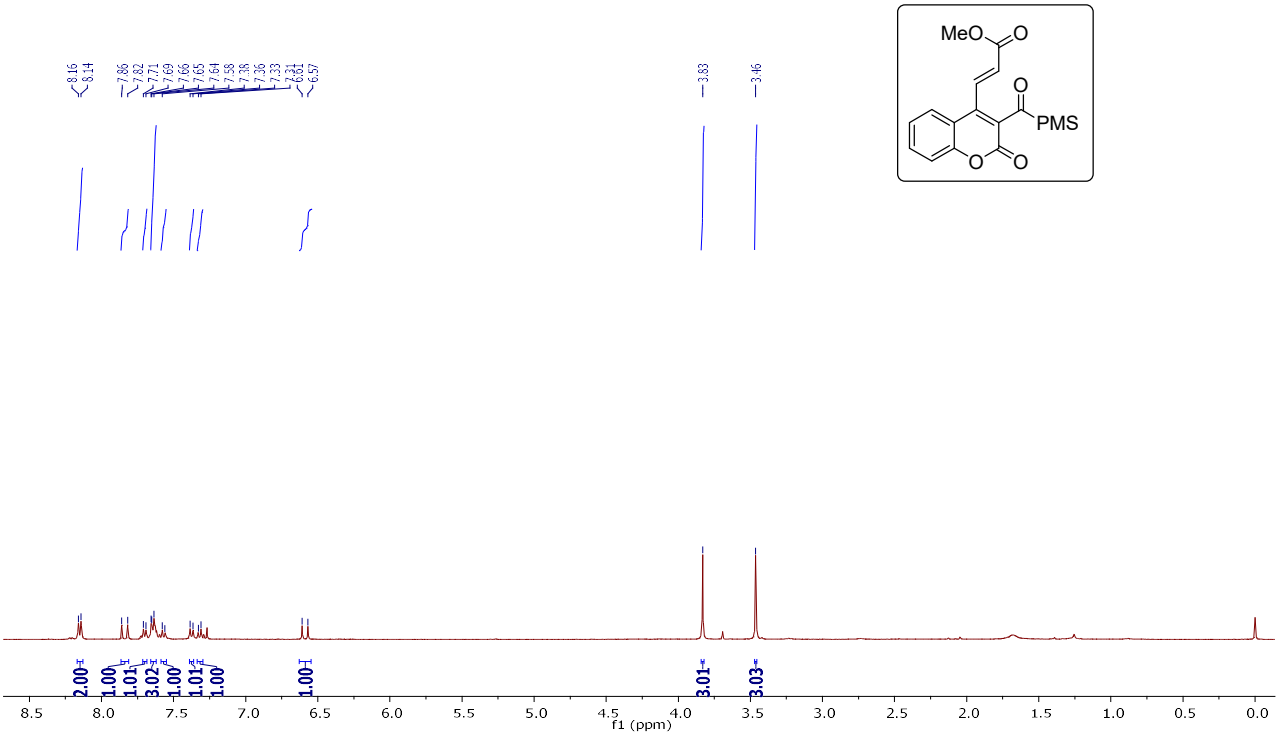
^{1}HNMR (400MHz, $CDCl_3$) spectrum of compound (3hc):



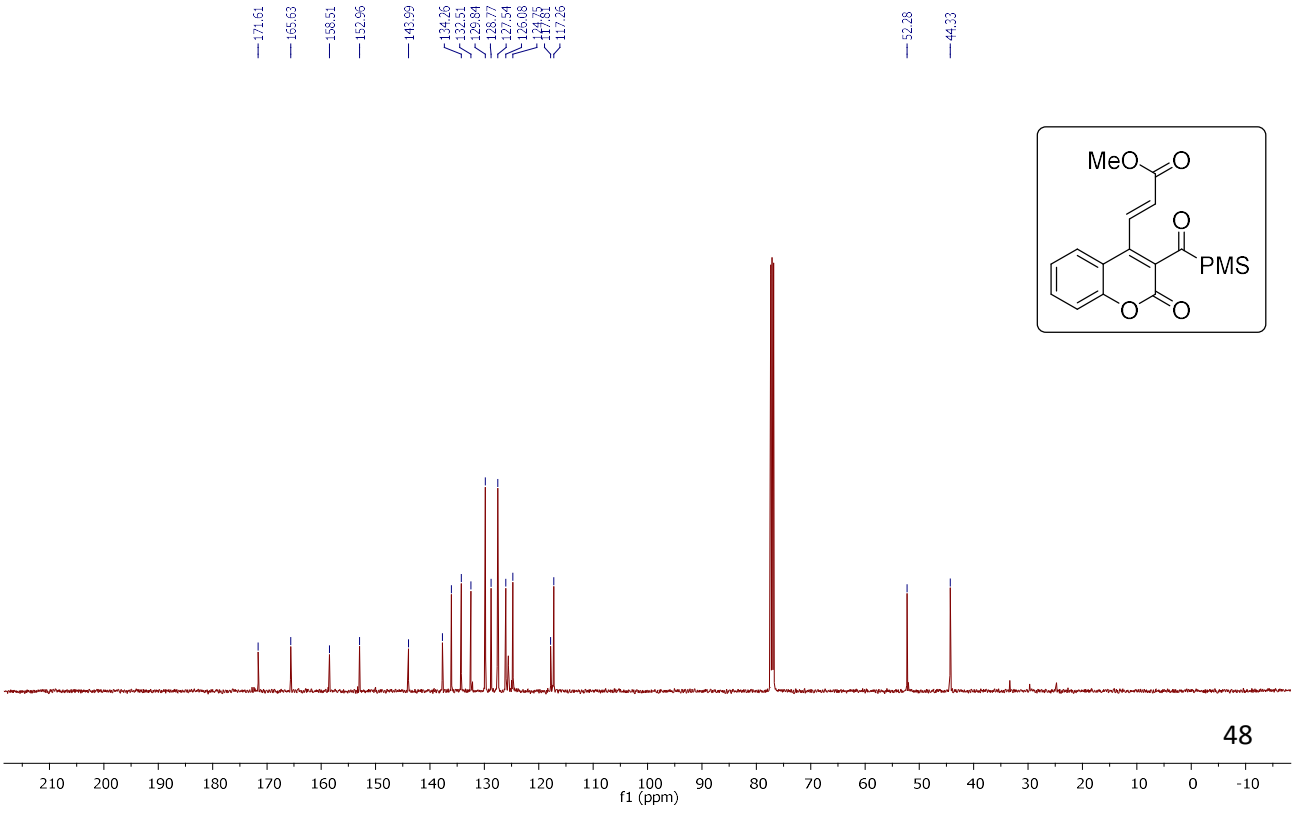
^{13}CNMR (101 MHz, $CDCl_3$) spectrum of compound (3hc):



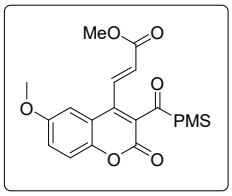
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (3ad):



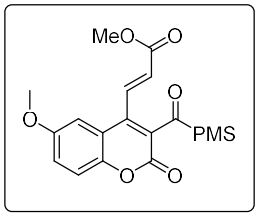
^{13}CNMR (101 MHz, $CDCl_3$) spectrum of compound (3ad):



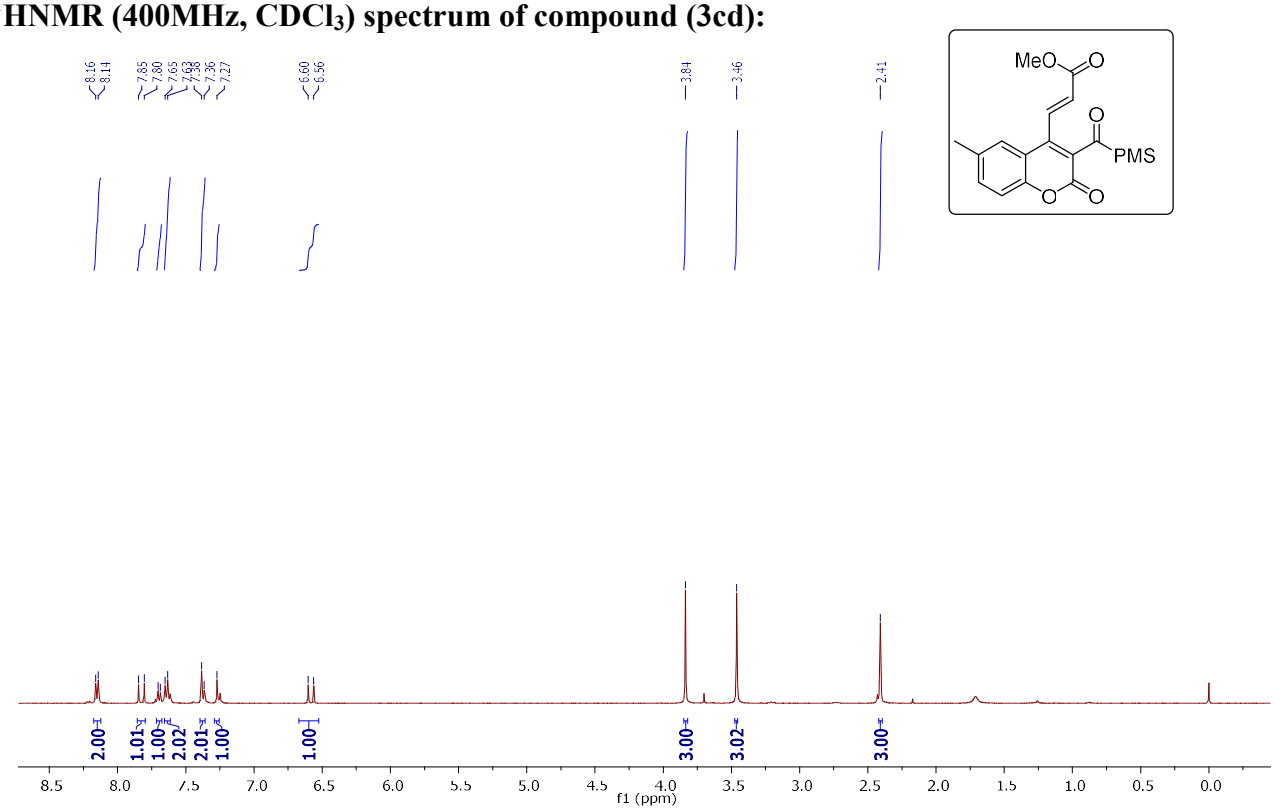
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound (3bd):



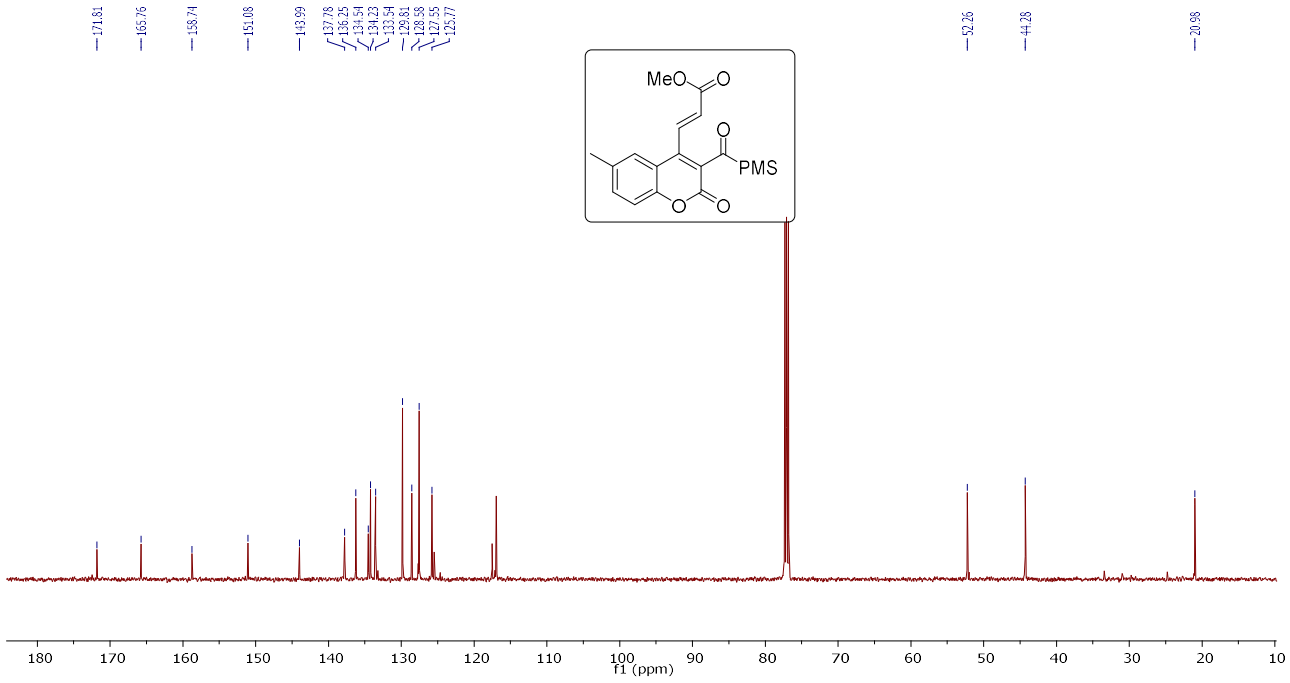
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound (3bd):



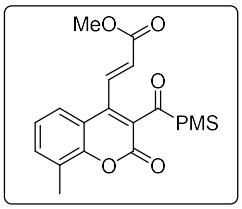
[1]HNMR (400MHz, $CDCl_3$) spectrum of compound (3cd):



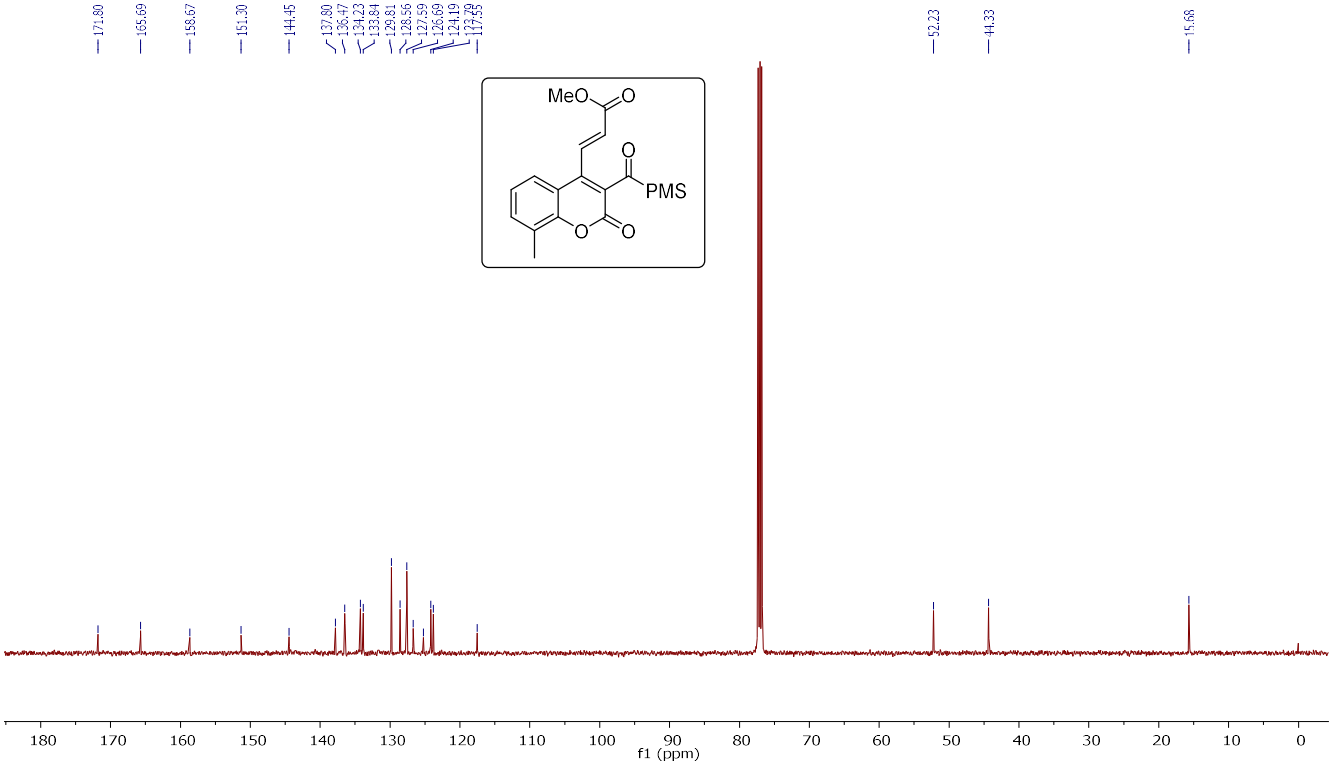
[13]CNMR (101MHz, $CDCl_3$) spectrum of compound (3cd):



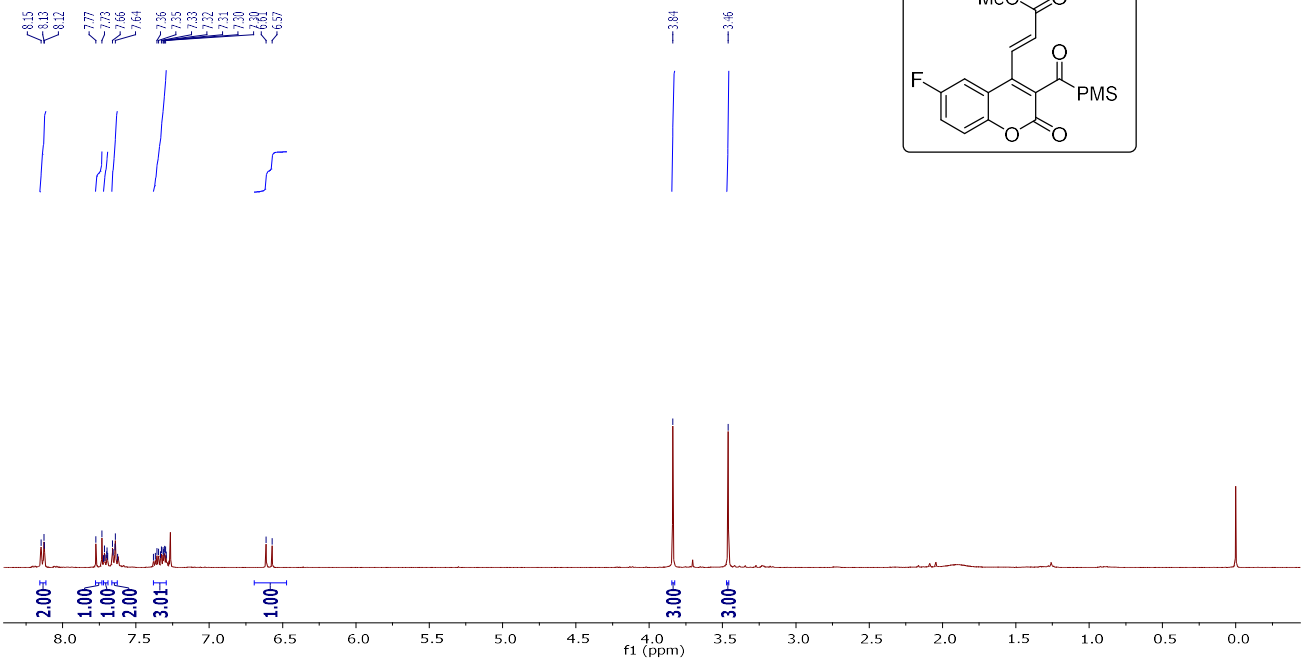
[1]HNMR (400MHz, $CDCl_3$) spectrum of compound (3dd):



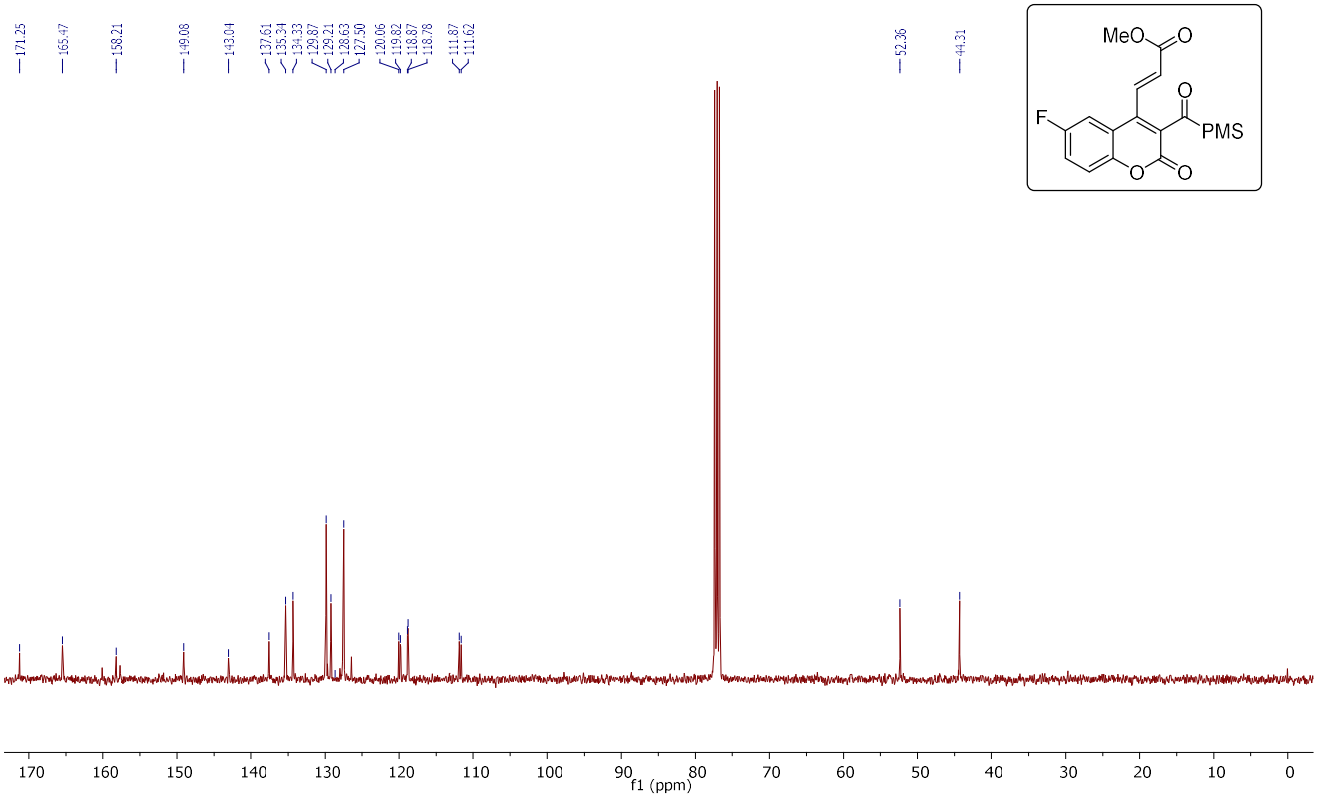
[13]CNMR (101 MHz, $CDCl_3$) spectrum of compound (3dd):



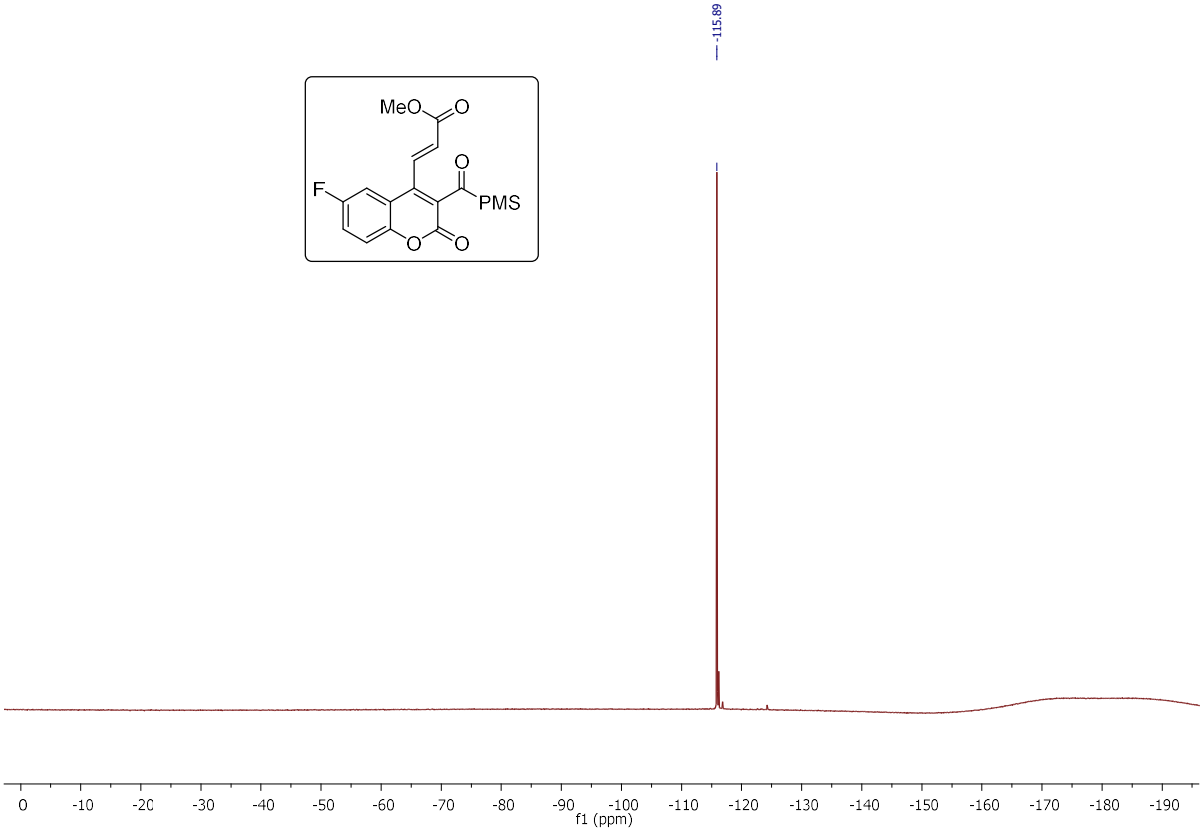
^{1}HNMR (400MHz, $CDCl_3$) spectrum of compound (3ed):



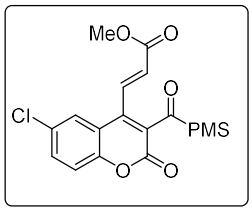
^{13}CNMR (101 MHz, $CDCl_3$) spectrum of compound (3ed):



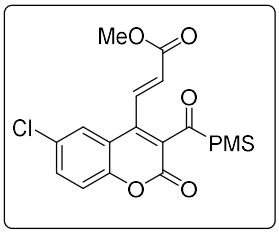
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound (3ed):



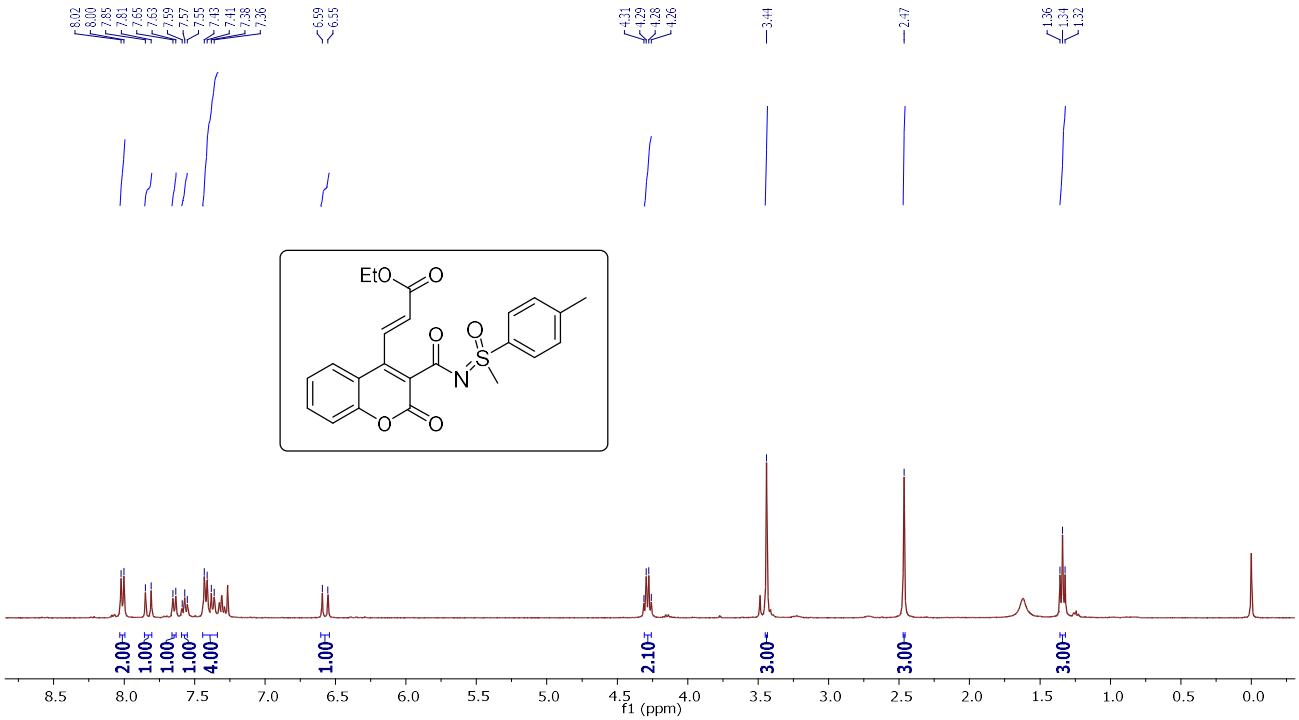
^{1}HNMR (400MHz, $CDCl_3$) spectrum of compound (3fd):



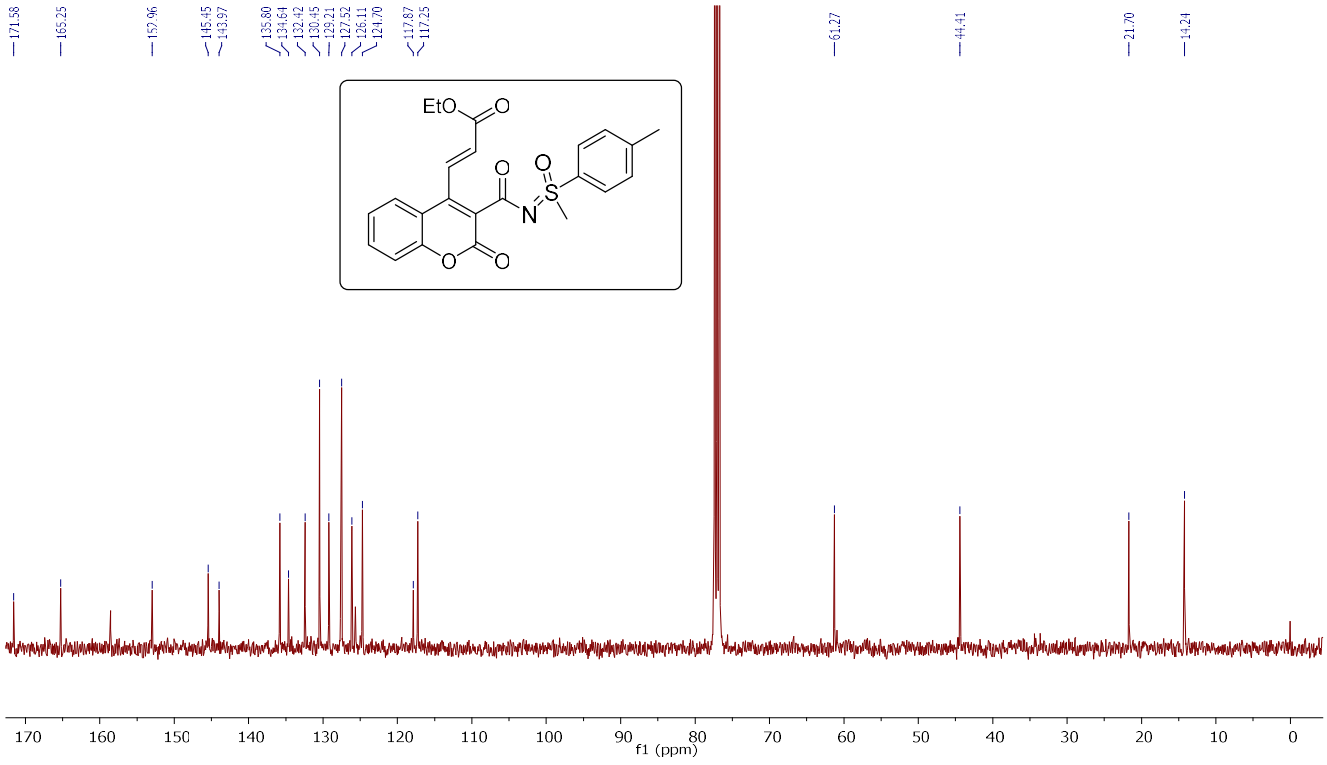
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound (3fd):



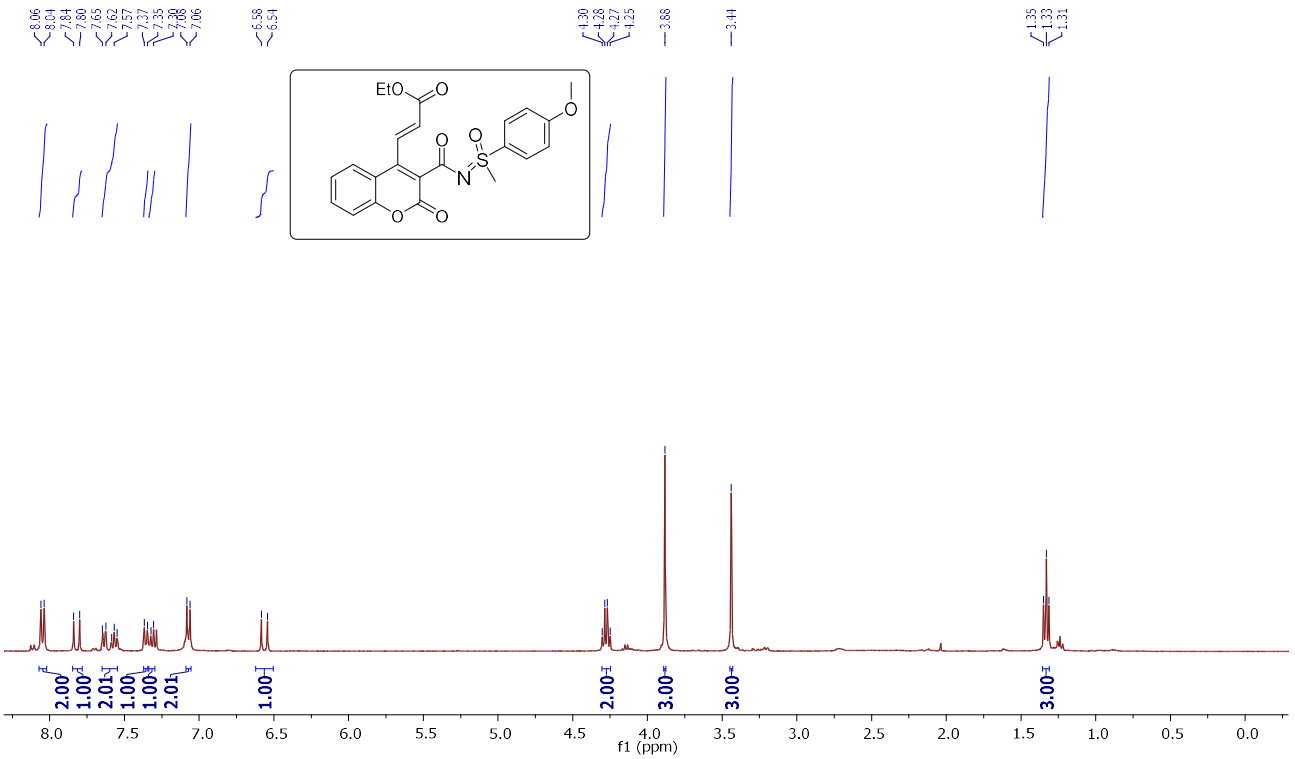
^{1}HNMR (400MHz, $CDCl_3$) spectrum of compound (3ja):



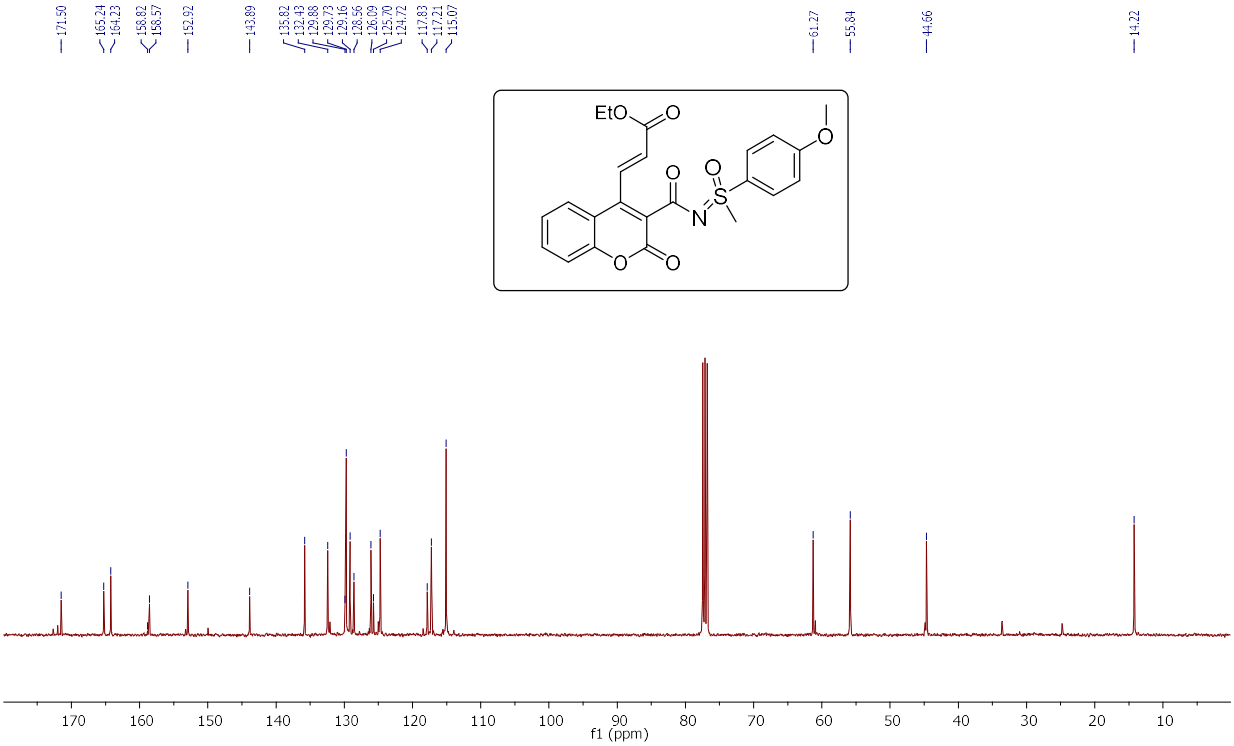
^{13}CNMR (101 MHz, $CDCl_3$) spectrum of compound (3ja):



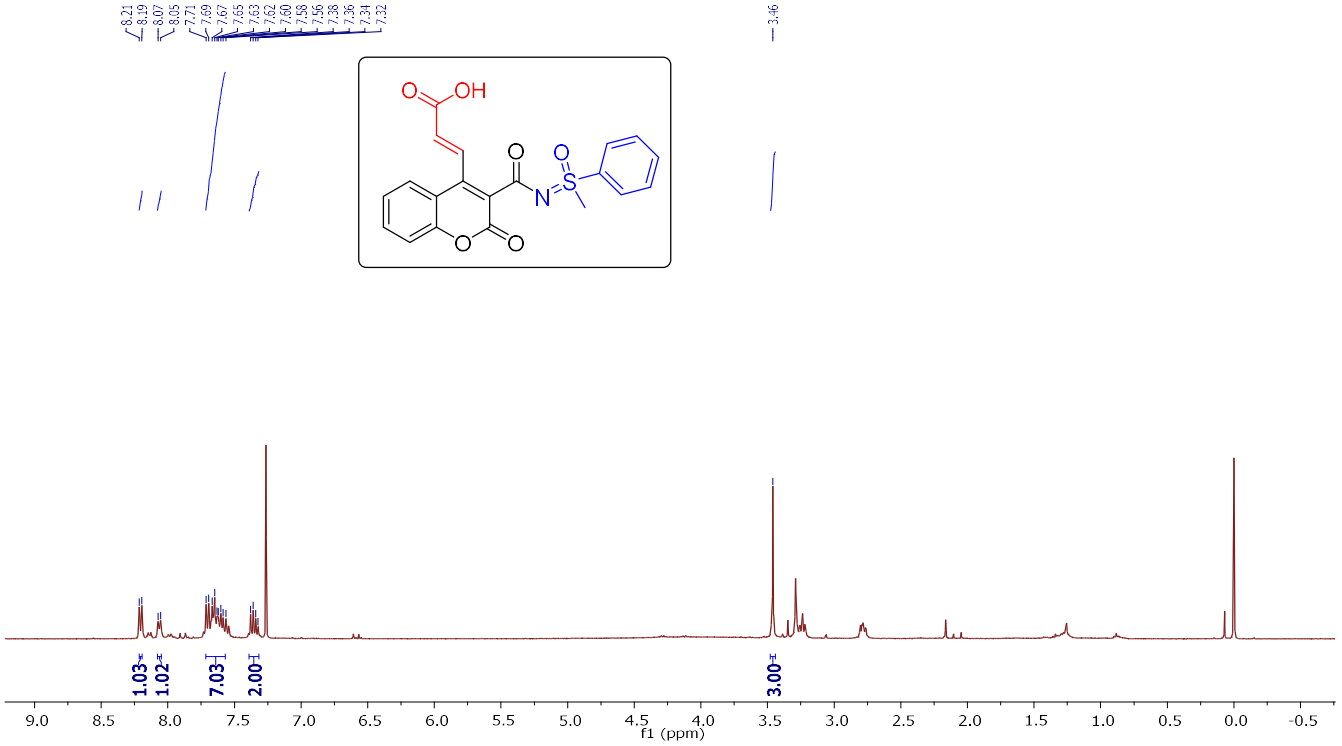
[1]HNMR (400MHz, $CDCl_3$) Spectrum of compound (3ka):



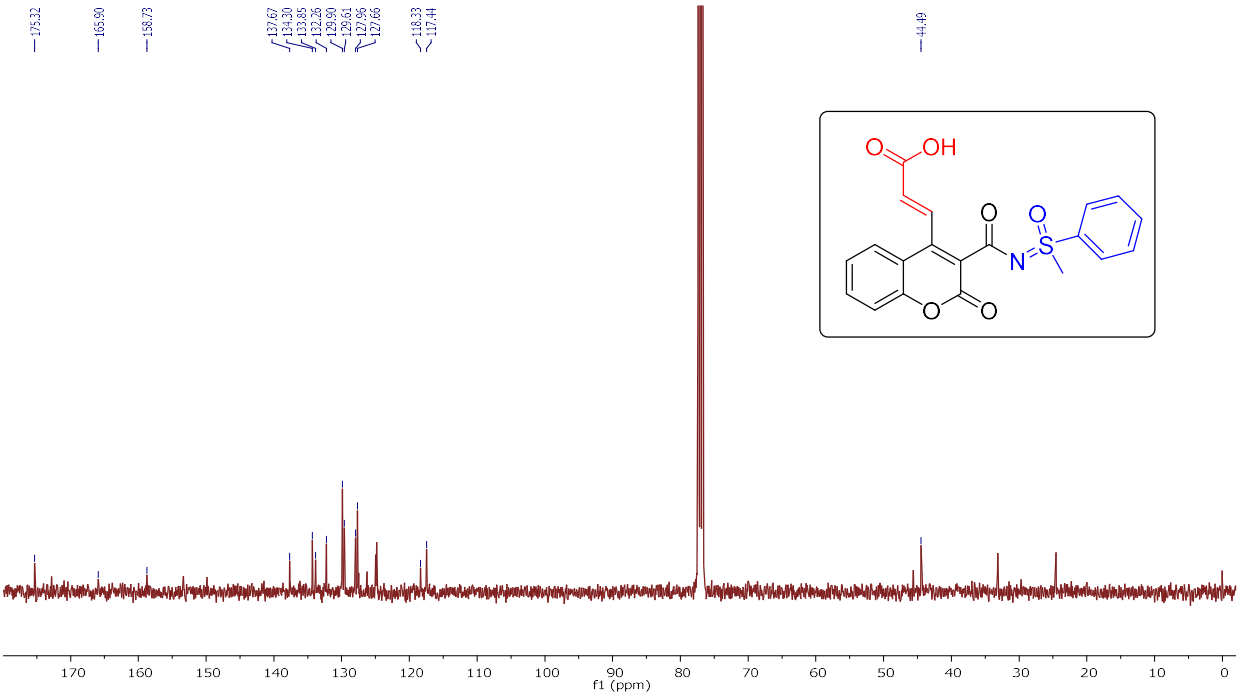
[13]CNMR (101 MHz, $CDCl_3$) spectrum of compound (3ka):



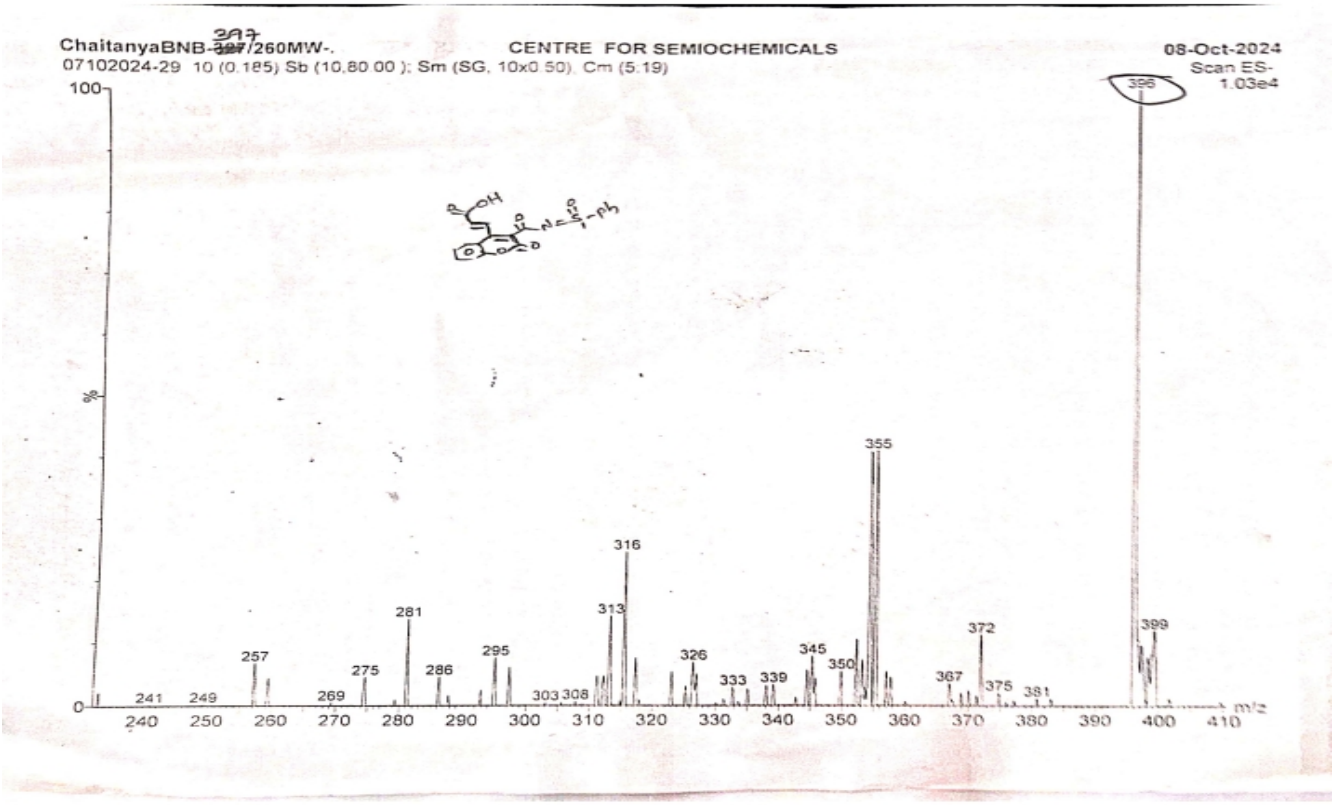
^{1}HNMR (400MHz, $CDCl_3$) spectrum of compound (3la):



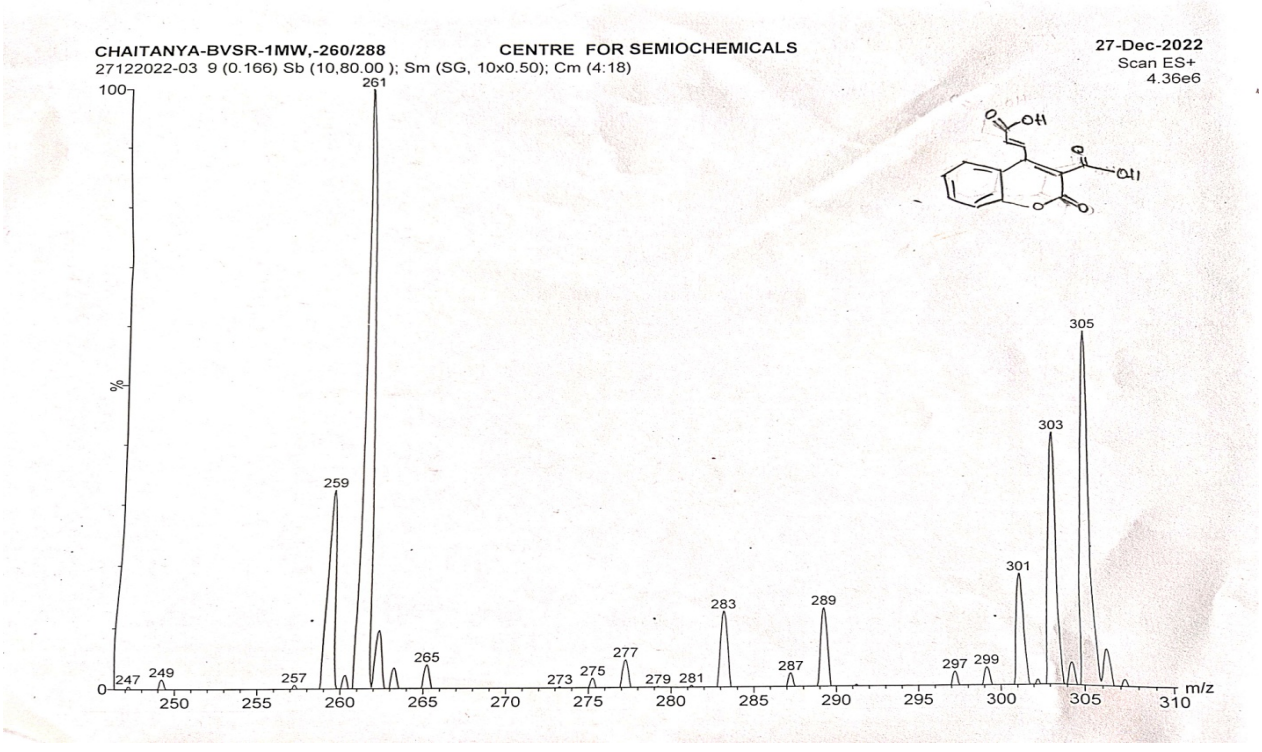
^{13}C NMR (101 MHz, CDCl3) Spectrum of compound (3la):



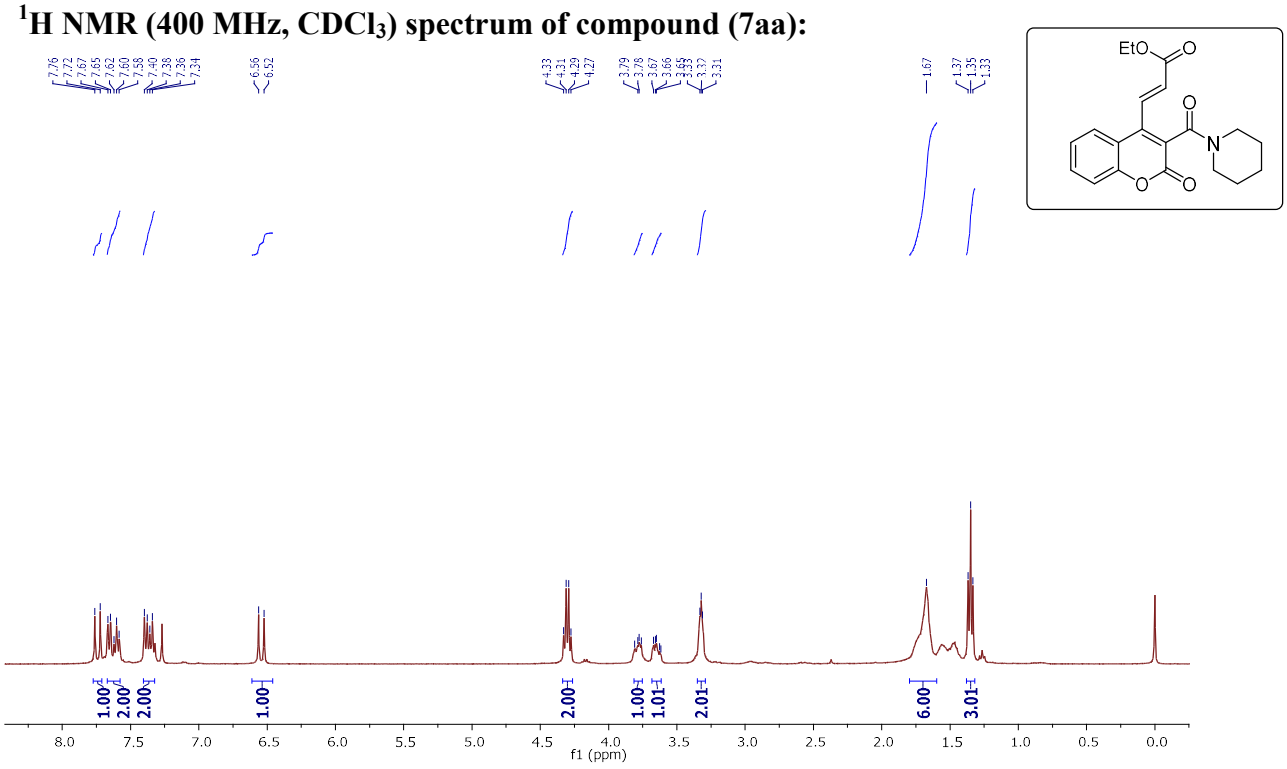
LCMS Spectrum of compound (3la):



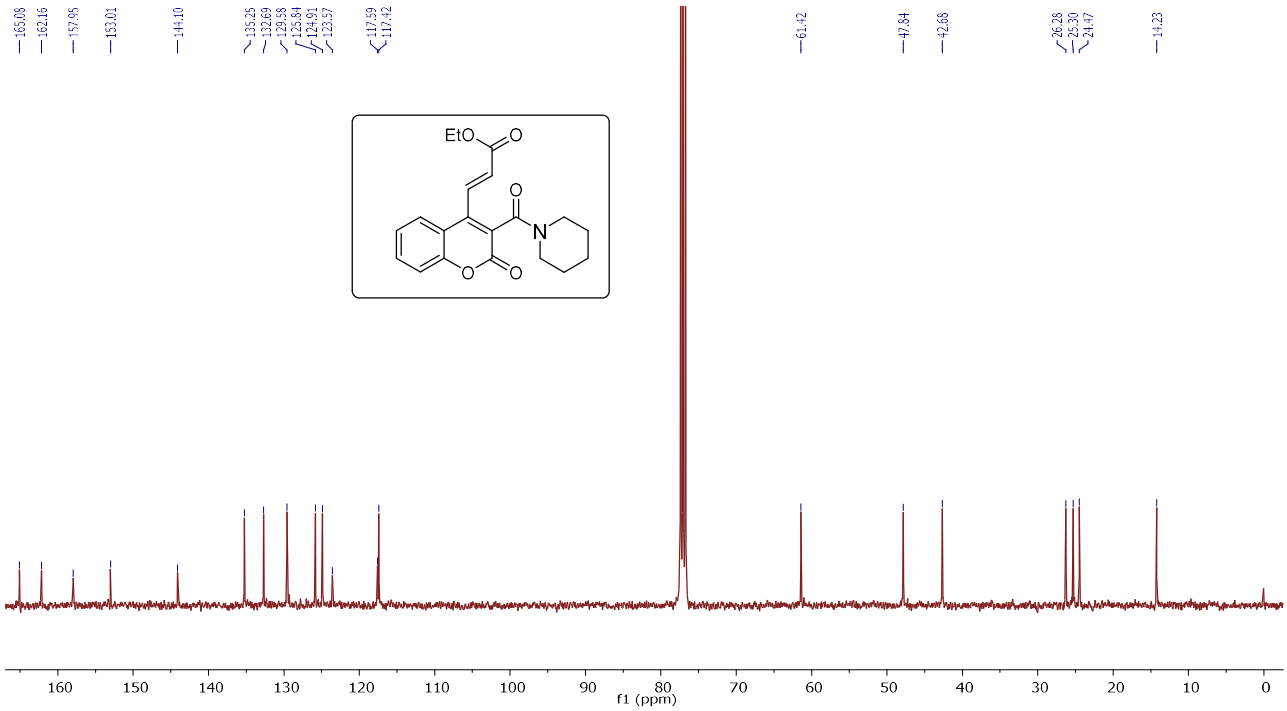
LCMS Spectrum of compound (3ma):



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound (7aa):



^{13}C NMR (101 MHz, $CDCl_3$)spectrum of compound (7aa):



X-ray Crystallographic Data of compounds 3ad:

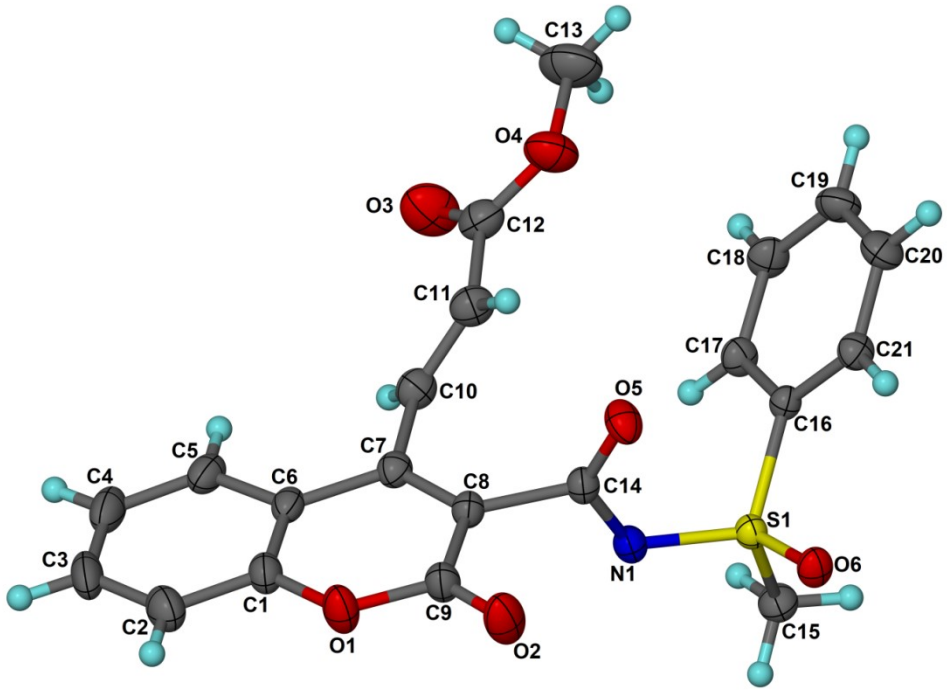


Figure caption: ORTEP diagram of KB844 compound with the atom-numbering. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal data for KB844: $C_{21}H_{17}NO_6S$, M = 411.42, Monoclinic, Space group $P2_1/c$(No.14), a =18.2329(19)Å, b =7.2566(8)Å, c = 15.731(2)Å, α = 90°, β = 113.051(5)°, γ = 90°, V = 1915.1(4)Å^3, Z = 4, D_c = 1.427 g/cm^3, F_{000} = 856, Bruker D8 QUEST PHOTON III C7 HPAD detector, Mo-Kα radiation, λ = 0.71073 Å, T = 294(2)K, $2\theta_{max}$ = 55º, μ = 0.209 mm^{-1}, 17317 reflections collected, 4392 unique (R_{int} = 0.0512), 264 parameters, *R1* = 0.0596, *wR2* =0.1358, *R* indices based on 2995 reflections with I > 2σ(I) (refinement on F^2), Final *GooF* = 1.068, largest difference hole and peak = -0.448 and 0.486 e.Å^{-3}. **CCDC deposition number2368323**contains

the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

Data collection and Structure solution details for KB844:

X-ray data for the compound were collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 Å) and a PHOTON-III C7 HPAD detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[1] The structure was solved using intrinsic phasing method[2] and further refined with the SHELXL program[2-4] and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms]. The oxygen atoms of perchlorate anion were disordered over two sites. **CCDC deposition number2368323**containsthe supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. G. M. Sheldrick, ActaCrystallogr., 2015, C71: 3-8.
3. C. B. Hübschle, G. M. Sheldrick and B. Dittrich, ShelXle: a Qt graphical user interface for SHELXL, *J. Appl. Cryst.*, 2011, 44, 1281-1284.
4. Muller, P, Herbst-Imer, R, Spek, A. L, Schneider, T. R, and Sawaya, M. R. Crystal Structure Refinement: A Crystallographer's Guide to SHELXL. Muller, P. Ed. 2006 Oxford University Press: Oxford, New York, pp. 57–91.