

Supporting Information

Access to S,C-Sulfonium Ylides from Iodonium Ylides via Iron Catalysis

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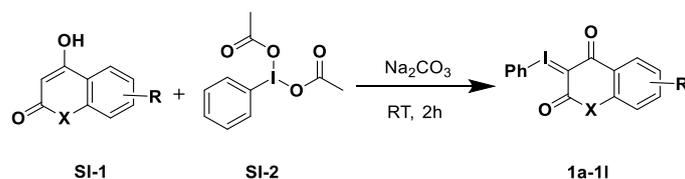
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General Information

Unless otherwise specified, the chemical reagents were purchased from commercial sources and used directly without purification. Analytical thin-layer chromatography (TLC): HSGF 254 (0.15-0.2 mm thickness). Detection was conducted under UV light at 254 nm. Preparative thin layer chromatography was HSGF 254 (0.4-0.5 mm thickness). Yields refer to isolated compounds. ^1H , ^{13}C , and ^{19}F NMR spectra were collected on Bruker 500 MHz and 600 MHz instrument in chloroform-*d* or DMSO-*d*₆. Chemical shifts (δ) are expressed as parts per million (ppm). Proton coupling patterns were recorded as singlet (s), doublet (d), triplet (t), quartet (q), and multiple (m). HRMS (high-resolution mass spectrometry) were obtained by using a quadrupole mass analyzer with electrospray ionization (ESI) source.

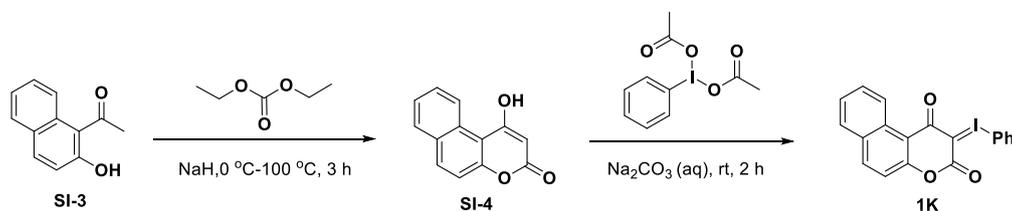
Preparation of Starting Materials

General procedure for the preparation of 1a-1l^[1-3]:



A solution of $\text{PhI}(\text{OAc})_2$ (10.0 mmol, 1.0 equiv.), Na_2CO_3 (10.0 mmol, 1.0 equiv.) in 50 mL H_2O , stir at room temperature for 0.5 h, followed by addition of a solution of 4-hydroxy-6-methyl-2H-pyran-2-ones (10.0 mmol, 1.0 equiv.) and Na_2CO_3 (10.0 mmol, 1.0 equiv.) in 50 mL H_2O . The resulting white precipitate was filtered and concentrated in vacuum to afford the product.

General procedure for the preparation of 1m^[4]:

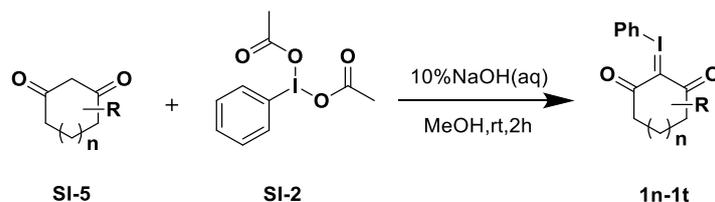


Step 1: A solution of 1-(2-hydroxy-3,4-dimethylphenyl)ethanone in diethylcarbonate (1 g/5 mL) was added dropwise to a suspension of NaH (60% dispersion in mineral oil) in diethylcarbonate (1

g/5 mL) at 0 °C. The resulting mixture was heated at 100 °C for 3 h when it was cooled first to rt and then to 0 °C. Water was then carefully added dropwise to quench residual NaH. The remaining diethylcarbonate was extracted into diethyl ether. The aqueous phase was carefully acidified to pH 3 with 2 N HCl (significant foaming occurred). The resulting precipitated solid was collected by filtration, washed sequentially with water followed by petroleum ether.

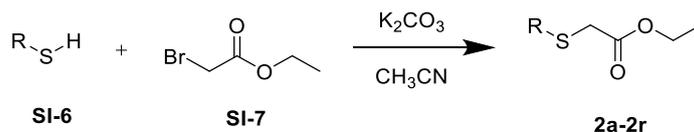
Step 2: $\text{PhI}(\text{OAc})_2$ (2.3 mmol) was added to 47.0 mL of a saturated sodium carbonate aqueous solution and stirred at room temperature for 30 minutes. Subsequently, 47.0 mL of a saturated sodium carbonate aqueous solution containing 4-hydroxycoumarin compounds (2.4 mmol) was added. The reaction mixture was stirred for an additional 2 hours at room temperature and then cooled in an ice bath. The reaction mixture was filtered, and the resulting solid was washed with water. The product obtained was a white precipitate.

General procedure for the preparation of 1n-1t^{[5]-[6]}:



To a solution of cyclic 1,3-dione (10.0 mmol, 1.0 equiv.) in 30 mL MeOH, added at room temperature, 20mL of a 10% aqueous solution of NaOH, followed by addition of a solution of $\text{PhI}(\text{OAc})_2$ (1.1 equiv.) in 40 mL MeOH. The reaction mixture was stirred for 2 h at room temperature and then quenched with ice water. The resulting white precipitate was filtered, and filtrate was extracted with DCM, then washed with water, dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuum. The resultant white solid was mixed with the first crop and the mixture recrystallized from DCM/hexanes.

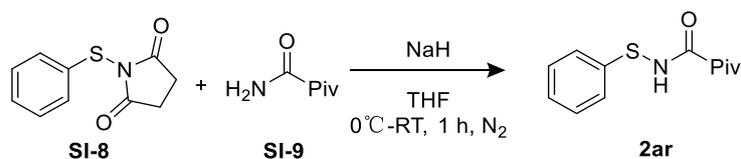
General procedure for the preparation of 2a-2r^{[7][8]}:



To a solution of substituted thiophenols (2.0 mmol, 1 equiv.) in CH_3CN (10 mL), K_2CO_3 (3.0 mmol, 1.5 equiv.) was added. Following, ethyl bromoacetate (3.0 mmol, 1.5 equiv.) was added drop-wise

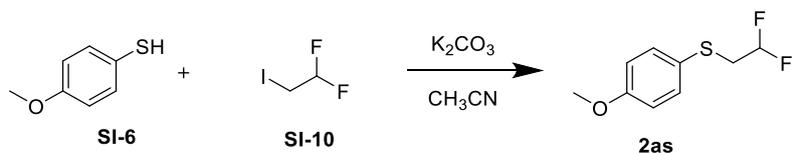
over 5 min. The reaction mixture was stirred at room temperature for 4 h to 6 h. After completion (checked by TLC), the reaction mixture was quenched by adding water (50 mL) and extracted with ethyl acetate (3 × 50 mL). Then, the collected organic layer was washed with water and brine and dried over anhydrous Na₂SO₄. The organic layer was filtered and evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (PE/EA = 6/1) to afford the pure aryl thioacetates.

General procedure for the preparation of **2ar**^[9]



SI-9 (3.3 mmol, 1.1 equiv.) was added to a flame dried round bottom flask under nitrogen. THF (0.15 M) was added, and the solution was cooled to 0 °C, then NaH (7.5 mmol, 2.5 equiv.) was added, and the solution was stirred for 30 minutes at 0 °C. Then the solution of **SI-8** (3.0 mmol, 1.0 equiv.) in THF (0.2 M) was added dropwise in the solution over one hour. Upon completion of the addition, the reaction mixture was stirred at room temperature for 1 h, then the reaction mixture was diluted with saturated aqueous ammonium chloride and extracted 3x with ethyl acetate. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated. The crude residue was purified by the corresponding chromatographic method to afford desired **2ar**.

General procedure for the preparation of **2as**

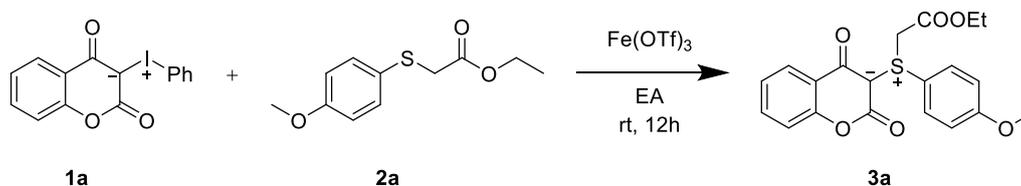


To a solution of 4-Methoxyphenylthiophenol (2.0 mmol, 1 equiv.) in CH₃CN (10 mL), K₂CO₃ (3.0 mmol, 1.5 equiv.) was added. Following, **SI-10** (3.0 mmol, 1.5 equiv.) was added drop-wise over 5 min. The reaction mixture was stirred at room temperature for 4 h to 6 h. After completion (checked by TLC), the reaction mixture was quenched by adding water (50 mL) and extracted with ethyl acetate (3 × 50 mL). Then, the collected organic layer was washed with water and brine and dried over anhydrous Na₂SO₄. The organic layer was filtered and evaporated under reduced pressure. The

purification was performed by flash column chromatography on silica gel (PE/EA = 6/1) to afford desired **2a**. ¹H NMR (500 MHz, CDCl₃) δ 7.46 – 7.40 (m, 2H), 6.89 – 6.83 (m, 2H), 5.82 (m, 1H), 3.80 (s, 3H), 3.11 (m, 2H).

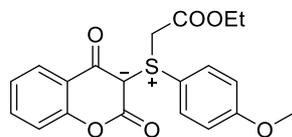
General Procedure for the preparation of **3**

Representative Procedure for the preparation of **3a**

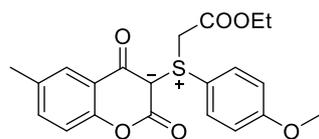


In a 10 mL reaction tube, to the mixture of **1a** (36.4 mg, 0.10 mmol, 1.0 equiv.), **2a** (34.0 mg, 0.15 mmol, 1.5 equiv.) and Fe(OTf)₃ (2.5 mg, 0.005 mmol, 0.5 equiv.) was added EA (2.0 mL). Then the resulting mixture was stirred at RT for 12.0 h. When the reaction was finished, the products are purified by preparative thin layer chromatography (DCM/MeOH = 20/1). The product **3a** was obtained as a white solid (35 mg, 91% yield). Other products **3** were prepared by a similar procedure.

Characterization Data of Products **3**

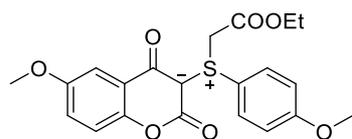


Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(4-methoxyphenyl)-λ⁴-sulfaneyl)acetate (3a**):** column solvent: DCM/MeOH = 20:1, white solid (35 mg, yield 91%); ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, *J* = 8.7 Hz, 2H), 8.00 (d, *J* = 6.3 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 5.34 (d, *J* = 16.0 Hz, 1H), 4.80 (d, *J* = 16.0 Hz, 1H), 4.18 (q, *J* = 6.9 Hz, 2H), 3.82 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 176.56, 164.27, 163.55, 162.80, 154.35, 133.37, 132.48, 125.70, 123.72, 121.49, 119.45, 116.96, 115.79, 79.17, 77.16, 63.11, 55.79, 44.96, 14.00. **HRMS (ESI) *m/z*:** calculated for C₂₀H₁₉O₆S [*M* + H]⁺: 387.0897, found: 387.0905.



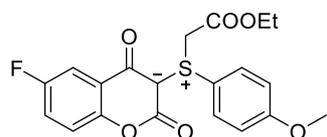
Ethyl (Z)-2-((4-methoxyphenyl)(6-methyl-2,4-dioxochroman-3-ylidene)-λ⁴-sulfaneyl)acetate (3b**):** column solvent: DCM/MeOH = 20:1, yellow oil (60 mg, yield

75%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.03 – 7.97 (m, 2H), 7.75 – 7.71 (m, 1H), 7.27 – 7.22 (m, 1H), 7.07 – 7.01 (m, 1H), 6.96 – 6.91 (m, 1H), 5.30 (d, $J = 16.0$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.14 (q, $J = 8.3, 7.8$ Hz, 2H), 3.78 (s, 3H), 2.32 (s, 3H), 1.20 – 1.11 (m, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 176.57, 164.24, 163.37, 162.83, 152.30, 134.15, 133.23, 132.32, 125.23, 120.97, 119.42, 116.59, 115.65, 78.96, 62.95, 55.68, 44.80, 20.68, 13.89. **HRMS (ESI) m/z** : calculated for $\text{C}_{21}\text{H}_{21}\text{O}_6\text{S}$ [$M + \text{H}$] $^+$: 401.1053, found: 401.1060.



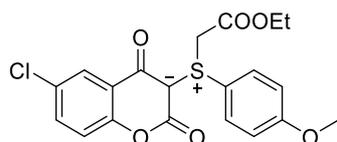
Ethyl (Z)-2-((6-methoxy-2,4-dioxochroman-3-ylidene)(4-

methoxyphenyl)- λ^4 -sulfaneyl)acetate (3c): column solvent: DCM/MeOH = 20:1, colorless oil (45 mg, yield 54%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.04 – 7.98 (m, 2H), 7.40 (d, $J = 3.1$ Hz, 1H), 7.13 – 7.06 (m, 1H), 7.03 (dd, $J = 9.0, 3.1$ Hz, 1H), 6.98 – 6.92 (m, 2H), 5.32 (d, $J = 16.1$ Hz, 1H), 4.83 (d, $J = 16.0$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 1.18 (t, $J = 7.2$ Hz, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 176.35, 164.26, 163.47, 162.83, 155.81, 148.66, 132.36, 121.89, 121.76, 119.38, 118.14, 115.73, 106.48, 79.21, 77.16, 63.05, 55.83, 55.74, 44.82, 13.95. **HRMS (ESI) m/z** : calculated for $\text{C}_{21}\text{H}_{21}\text{O}_7\text{S}$ [$M + \text{H}$] $^+$: 417.1003, found: 417.1009.



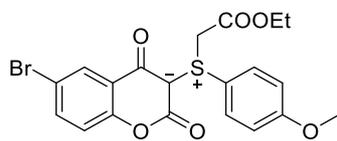
Ethyl (Z)-2-((6-fluoro-2,4-dioxochroman-3-ylidene)(4-

methoxyphenyl)- λ^4 -sulfaneyl)acetate (3d): column solvent: DCM/MeOH = 20:1, white solid (58 mg, yield 72%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.02 – 7.96 (m, 2H), 7.62 – 7.55 (m, 1H), 7.19 – 7.08 (m, 2H), 6.98 – 6.92 (m, 2H), 5.29 (d, $J = 16.2$ Hz, 1H), 4.85 (d, $J = 16.1$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 3.78 (s, 3H), 1.16 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 175.34, 164.16, 163.54, 162.38, 159.69, 157.75, 150.25, 132.39, 122.61, 122.56, 120.62, 120.43, 119.03, 118.54, 118.47, 115.75, 111.12, 110.92, 79.42, 77.16, 63.06, 55.72, 44.72, 13.90. $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -118.51. **HRMS (ESI) m/z** : calculated for $\text{C}_{20}\text{H}_{18}\text{FO}_6\text{S}$ [$M + \text{H}$] $^+$: 405.0803, found: 405.0810.



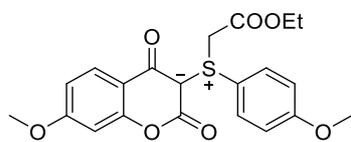
Ethyl (Z)-2-((6-chloro-2,4-dioxochroman-3-ylidene)(4-

methoxyphenyl)-λ⁴-sulfaneyl)acetate (3e): column solvent: DCM/MeOH = 20:1, yellow oil (71 mg, yield 85%); ¹H NMR (500 MHz, CDCl₃) δ 8.06 – 7.99 (m, 2H), 7.96 – 7.90 (m, 1H), 7.44 – 7.38 (m, 1H), 7.16 – 7.09 (m, 1H), 7.00 – 6.94 (m, 2H), 5.31 (d, *J* = 16.0 Hz, 1H), 4.83 (d, *J* = 16.1 Hz, 1H), 4.22 – 4.14 (m, 2H), 3.82 (s, 3H), 1.22 – 1.17 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 175.20, 164.15, 163.66, 162.29, 152.67, 133.20, 132.51, 129.34, 129.32, 125.29, 122.65, 119.06, 118.53, 115.86, 79.54, 77.16, 63.18, 55.81, 44.83, 14.00. **HRMS (ESI) *m/z*:** calculated for C₂₀H₁₈ClO₆S [*M* + H]⁺: 421.0507, found: 421.0514.



Ethyl (Z)-2-((6-bromo-2,4-dioxochroman-3-ylidene)(4-

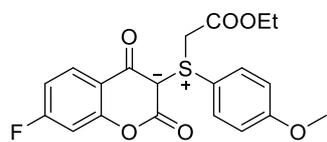
methoxyphenyl)-λ⁴-sulfaneyl)acetate (3f): column solvent: DCM/MeOH = 20:1, yellow oil (79 mg, yield 85%); ¹H NMR (500 MHz, CDCl₃) δ 8.03 – 7.95 (m, 3H), 7.49 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 5.28 (d, *J* = 16.0 Hz, 1H), 4.88 (d, *J* = 16.0 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 174.86, 164.12, 163.47, 162.05, 152.96, 135.82, 132.33, 128.18, 122.88, 118.88, 118.69, 116.48, 115.70, 79.42, 77.16, 63.01, 55.69, 44.64, 13.88. **HRMS (ESI) *m/z*:** calculated for C₂₀H₁₈BrO₆S [*M* + H]⁺: 466.9982, found: 466.9988.



Ethyl (Z)-2-((7-methoxy-2,4-dioxochroman-3-ylidene)(4-

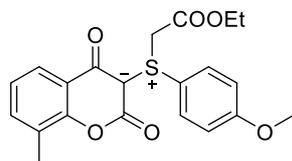
methoxyphenyl)-λ⁴-sulfaneyl)acetate (3g): column solvent: DCM/MeOH = 20:1, colorless oil (66 mg, yield 80%); ¹H NMR (500 MHz, CDCl₃) δ 8.02 – 7.95 (m, 2H), 7.87 – 7.80 (m, 1H), 6.96 – 6.90 (m, 2H), 6.73 – 6.67 (m, 1H), 6.62 – 6.57 (m, 1H), 5.32 – 5.26 (m, 1H), 4.86 – 4.78 (m, 1H), 4.17 – 4.10 (m, 2H), 3.77 (s, 3H), 3.77 (s, 3H), 1.19 – 1.12 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 176.17, 164.29, 163.80, 163.31, 162.89, 155.83, 132.26, 126.82, 119.60, 115.61, 114.83, 111.42,

100.44, 77.71, 77.16, 62.91, 55.66, 55.64, 44.90, 13.88. **HRMS (ESI) *m/z***: calculated for C₂₁H₂₁O₇S [M + H]⁺: 417.1003, found: 417.1010.



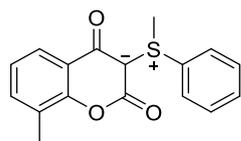
Ethyl (Z)-2-((7-fluoro-2,4-dioxochroman-3-ylidene)(4-

methoxyphenyl)-λ⁴-sulfaneyl)acetate (3h): column solvent: DCM/MeOH = 20:1, white solid (70 mg, yield 86%); **¹H NMR (500 MHz, CDCl₃)** δ 8.04 (d, *J* = 8.8 Hz, 2H), 8.03 – 7.98 (m, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.98 – 6.89 (m, 2H), 5.32 (d, *J* = 16.0 Hz, 1H), 4.78 (d, *J* = 16.0 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.84 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 175.55, 165.55 (d, *J* = 252.8 Hz), 163.54, 162.42, 155.40 (d, *J* = 13.2 Hz), 132.40, 127.76 (d, *J* = 10.6 Hz), 119.19, 118.12 (d, *J* = 2.8 Hz), 115.77, 111.61 (d, *J* = 22.5 Hz), 104.01 (d, *J* = 25.6 Hz), 78.68, 63.08, 55.74, 44.82, 13.93. **¹⁹F NMR (471 MHz, CDCl₃)** δ -104.64. **HRMS (ESI) *m/z***: calculated for C₂₀H₁₈FO₆S [M + H]⁺: 405.0803, found: 405.0811.



Ethyl (Z)-2-((4-methoxyphenyl)(8-methyl-2,4-dioxochroman-3-

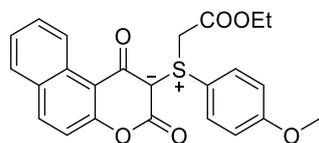
ylidene)-λ⁴-sulfaneyl)acetate (3i): column solvent: DCM/MeOH = 20:1, white solid (62 mg, yield 78%); **¹H NMR (500 MHz, CDCl₃)** δ 8.03 – 7.97 (m, 2H), 7.83 – 7.75 (m, 1H), 7.32 – 7.25 (m, 1H), 7.10 – 7.01 (m, 1H), 6.97 – 6.90 (m, 2H), 5.35 – 5.27 (m, 1H), 4.90 – 4.82 (m, 1H), 4.19 – 4.10 (m, 2H), 3.80 – 3.75 (m, 3H), 2.36 – 2.31 (m, 3H), 1.20 – 1.12 (m, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 176.77, 164.28, 163.36, 162.66, 152.56, 134.42, 132.29, 126.10, 123.18, 123.12, 121.18, 119.40, 115.64, 78.91, 77.16, 62.96, 55.68, 44.77, 44.76, 15.79, 13.90. **HRMS (ESI) *m/z***: calculated for C₂₁H₂₁O₆S [M + H]⁺: 401.1053, found: 401.1062.



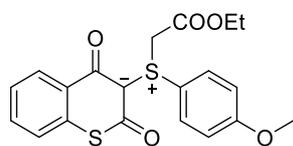
(Z)-8-methyl-3-(methyl(phenyl)-λ⁴-sulfaneylidene)chromane-2,4-dione

(3j): column solvent: DCM/MeOH = 20:1, white solid (52 mg, yield 87%); **¹H NMR (500 MHz, CDCl₃)** δ 7.92 – 7.84 (m, 2H), 7.88 – 7.83 (m, 1H), 7.59 – 7.48 (m, 3H), 7.35 (d, *J* = 7.2 Hz, 1H),

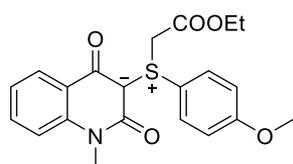
7.11 (t, $J = 7.6$ Hz, 1H), 3.53 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.06, 162.67, 152.81, 134.58, 132.50, 130.32, 129.79, 128.71, 126.33, 123.35, 123.28, 121.37, 77.88, 77.16, 25.40, 15.96. HRMS (ESI) m/z : calculated for $\text{C}_{17}\text{H}_{15}\text{O}_3\text{S}$ [$M + \text{H}$] $^+$: 299.0736, found: 299.0731.



Ethyl (Z)-2-((1,3-dioxo-1H-benzo[f]chromen-2(3H)-ylidene)(4-methoxyphenyl)- λ^4 -sulfaneyl)acetate (3k): column solvent: DCM/MeOH = 20:1, colorless oil (64 mg, yield 74%); ^1H NMR (500 MHz, CDCl_3) δ 9.93 (d, $J = 8.7$ Hz, 1H), 8.09 (d, $J = 9.1$ Hz, 2H), 7.95 (d, $J = 8.9$ Hz, 1H), 7.85 – 7.79 (m, 1H), 7.68 – 7.61 (m, 1H), 7.50 (t, 1H), 7.36 (d, $J = 8.9$ Hz, 1H), 7.00 (d, $J = 8.9$ Hz, 2H), 5.39 (d, $J = 16.0$ Hz, 1H), 4.81 (d, $J = 16.0$ Hz, 1H), 4.26 – 4.14 (m, 2H), 3.84 (s, 3H), 1.23 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 179.05, 164.40, 163.42, 162.20, 155.48, 134.61, 132.31, 131.02, 130.41, 128.55, 128.17, 126.31, 125.46, 119.57, 117.49, 115.72, 113.36, 80.83, 77.16, 63.01, 55.70, 44.96, 13.95. HRMS (ESI) m/z : calculated for $\text{C}_{24}\text{H}_{21}\text{O}_6\text{S}$ [$M + \text{H}$] $^+$: 437.1053, found: 437.1061.

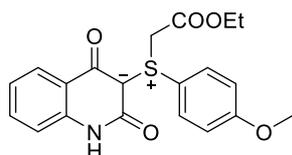


Ethyl (Z)-2-((2,4-dioxothiochroman-3-ylidene)(4-methoxyphenyl)- λ^4 -sulfaneyl)acetate (3l): column solvent: DCM/MeOH = 20:1, yellow oil (73 mg, yield 91%); ^1H NMR (500 MHz, CDCl_3) δ 8.28 – 8.22 (m, 1H), 7.99 – 7.91 (m, 2H), 7.42 – 7.34 (m, 1H), 7.30 – 7.19 (m, 2H), 6.97 – 6.90 (m, 2H), 5.31 – 5.23 (m, 1H), 4.81 – 4.73 (m, 1H), 4.20 – 4.11 (m, 2H), 3.79 – 3.76 (m, 3H), 1.20 – 1.14 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 179.00, 178.52, 164.58, 163.16, 135.91, 132.23, 131.45, 129.60, 128.61, 125.86, 125.11, 119.40, 115.61, 92.00, 77.16, 62.91, 55.67, 44.87, 13.92. HRMS (ESI) m/z : calculated for $\text{C}_{20}\text{H}_{19}\text{O}_5\text{S}_2$ [$M + \text{H}$] $^+$: 403.0668, found: 403.0676.

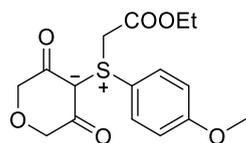


Ethyl (Z)-2-((4-methoxyphenyl)(1-methyl-2,4-dioxo-1,4-dihydroquinolin-3(2H)-ylidene)- λ^4 -sulfaneyl)acetate (3m): column solvent: DCM/MeOH = 20:1,

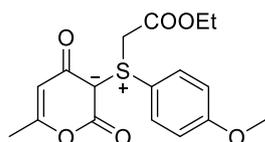
yellow solid (33 mg, yield 41%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.22 – 8.13 (m, 1H), 8.05 (d, $J = 9.0$ Hz, 2H), 7.49 (t, $J = 7.0$ Hz, 1H), 7.16 – 7.10 (m, 2H), 6.93 (d, $J = 9.0$ Hz, 2H), 5.48 (d, $J = 16.1$ Hz, 1H), 4.83 (d, $J = 16.1$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 3.78 (s, 3H), 3.51 (s, 3H), 1.17 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 175.85, 164.91, 163.12, 163.10, 141.47, 132.41, 132.34, 126.30, 122.93, 121.39, 120.70, 115.53, 114.04, 84.03, 77.16, 62.76, 55.66, 44.93, 29.01, 13.96. **HRMS (ESI) m/z** : calculated for $\text{C}_{21}\text{H}_{22}\text{NO}_5\text{S}$ [$M + \text{H}$] $^+$: 400.1213, found: 400.1219.



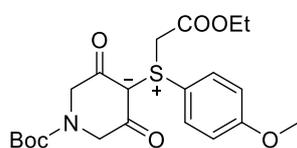
Ethyl (Z)-2-((2,4-dioxo-1,4-dihydroquinolin-3(2H)-ylidene)(4-methoxyphenyl)- λ^4 -sulfaneyl)acetate (3n): column solvent: DCM/MeOH = 20:1, yellow solid (24 mg, yield 31%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 10.56 – 10.38 (m, 1H), 8.07 (d, $J = 9.2$ Hz, 3H), 7.44 – 7.37 (m, 1H), 7.13 – 7.05 (m, 2H), 6.96 – 6.90 (m, 2H), 5.49 (d, $J = 16.1$ Hz, 1H), 4.86 (d, $J = 16.7$ Hz, 1H), 4.26 – 4.03 (m, 2H), 3.80 – 3.76 (m, 3H), 1.22 – 1.14 (m, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 177.31, 164.91, 164.67, 163.17, 139.96, 132.34, 132.28, 125.87, 121.82, 121.65, 120.51, 115.85, 115.57, 83.05, 77.16, 62.89, 55.71, 45.06, 14.00. **HRMS (ESI) m/z** : calculated for $\text{C}_{20}\text{H}_{20}\text{NO}_5\text{S}$ [$M + \text{H}$] $^+$: 386.1057, found: 386.1062.



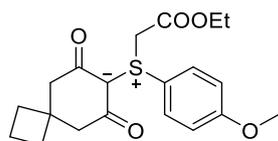
Ethyl 2-((3,5-dioxotetrahydro-4H-pyran-4-ylidene)(4-methoxyphenyl)- λ^4 -sulfaneyl)acetate (3o): column solvent: DCM/MeOH = 20:1, colorless oil (29 mg, yield 43%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.94 (d, $J = 8.9$ Hz, 2H), 6.95 (d, $J = 8.9$ Hz, 2H), 5.23 (d, $J = 16.0$ Hz, 1H), 4.56 (d, $J = 16.0$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 4.14 – 4.13 (m, 4H), 3.82 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 189.31, 164.36, 163.35, 132.65, 119.84, 115.70, 87.14, 77.16, 72.53, 63.00, 55.76, 44.87, 14.00. **HRMS (ESI) m/z** : calculated for $\text{C}_{16}\text{H}_{19}\text{O}_6\text{S}$ [$M + \text{H}$] $^+$: 339.0897, found: 339.0903.



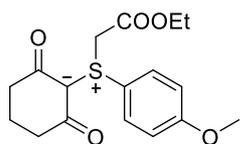
Ethyl (Z)-2-((4-methoxyphenyl)(6-methyl-2,4-dioxo-2H-pyran-3(4H)-ylidene)- λ^4 -sulfaneyl)acetate (3p): column solvent: DCM/MeOH = 20:1, colorless oil (20 mg, yield 29%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.02 – 7.96 (m, 2H), 6.99 – 6.92 (m, 2H), 5.67 – 5.64 (m, 1H), 5.24 (d, $J = 16.0$ Hz, 1H), 4.69 (d, $J = 16.0$ Hz, 1H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.82 (s, 3H), 2.07 (s, 3H), 1.20 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 179.47, 164.24, 163.87, 163.51, 162.73, 132.46, 119.60, 115.72, 108.26, 78.52, 77.16, 63.04, 55.77, 44.83, 19.84, 13.99. **HRMS (ESI) m/z :** calculated for $\text{C}_{17}\text{H}_{19}\text{O}_6\text{S}$ [$M + \text{H}$] $^+$: 351.0897, found: 351.0901.



Tert-butyl 4-((2-ethoxy-2-oxoethyl)(4-methoxyphenyl)- λ^4 -sulfaneylidene)-3,5-dioxopiperidine-1-carboxylate (3q): column solvent: DCM/MeOH = 20:1, yellow oil (15 mg, yield 17%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.95 (d, $J = 8.6$ Hz, 2H), 6.96 (d, $J = 8.4$ Hz, 2H), 5.24 (d, $J = 15.7$ Hz, 1H), 4.53 (d, $J = 15.8$ Hz, 1H), 4.17 (q, $J = 7.3$ Hz, 2H), 4.14 – 4.10 (m, 4H), 3.83 (s, 3H), 1.45 (s, 9H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 188.00, 164.47, 163.40, 154.11, 132.74, 119.83, 115.74, 80.90, 77.16, 63.03, 55.82, 44.83, 29.81, 28.45, 14.05. **HRMS (ESI) m/z :** calculated for $\text{C}_{21}\text{H}_{28}\text{NO}_7\text{S}$ [$M + \text{H}$] $^+$: 438.1580, found: 438.1576.

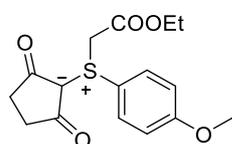


Ethyl 2-((6,8-dioxospiro[3.5]nonan-7-ylidene)(4-methoxyphenyl)- λ^4 -sulfaneyl)acetate (3r): column solvent: DCM/MeOH = 20:1, yellow oil (8 mg, yield 11%); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.87 (d, $J = 8.5$ Hz, 2H), 6.93 (d, $J = 8.3$ Hz, 2H), 5.09 (d, $J = 15.8$ Hz, 1H), 4.59 (d, $J = 15.8$ Hz, 1H), 4.21 – 4.11 (m, 2H), 3.82 (s, 3H), 2.58 – 2.55 (m, 4H), 1.92 – 1.85 (m, 2H), 1.85 – 1.81 (m, 4H), 1.22 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 192.03, 164.82, 162.99, 132.19, 120.82, 115.53, 77.16, 62.83, 55.74, 50.34, 45.16, 37.78, 31.93, 15.21, 14.10. **HRMS (ESI) m/z :** calculated for $\text{C}_{20}\text{H}_{25}\text{O}_5\text{S}$ [$M + \text{H}$] $^+$: 377.1417, found: 377.1413.



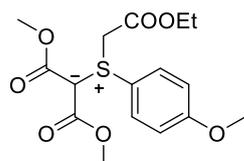
Ethyl 2-((2,6-dioxocyclohexylidene)(4-methoxyphenyl)- λ^4 -

sulfaneyl)acetate (3s): column solvent: DCM/MeOH = 20:1, yellow oil (11 mg, yield 16%); ^1H NMR (500 MHz, CDCl_3) δ 7.95 – 7.88 (m, 2H), 6.97 – 6.91 (m, 2H), 5.19 (d, J = 15.9 Hz, 1H), 4.53 (d, J = 16.0 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 2.44 (t, J = 6.4 Hz, 4H), 1.95 – 1.87 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 193.06, 164.88, 163.01, 132.40, 120.83, 115.50, 90.50, 77.16, 62.79, 55.74, 44.94, 38.03, 20.46, 14.07. HRMS (ESI) m/z : calculated for $\text{C}_{17}\text{H}_{21}\text{O}_5\text{S}$ [$M + \text{H}$] $^+$: 337.1104, found: 337.1107.



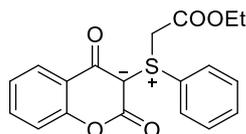
Ethyl 2-((2,5-dioxocyclopentylidene)(4-methoxyphenyl)- λ^4 -

sulfaneyl)acetate (3t): column solvent: DCM/MeOH = 20:1, yellow oil (25 mg, yield 39%); ^1H NMR (500 MHz, CDCl_3) δ 7.99 (d, J = 9.0 Hz, 2H), 6.95 (d, J = 9.0 Hz, 2H), 5.22 (d, J = 15.9 Hz, 1H), 4.51 (d, J = 15.9 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 2.54 – 2.30 (m, 4H), 1.18 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.79, 164.12, 163.58, 132.79, 120.59, 115.83, 85.51, 77.16, 63.02, 55.79, 44.41, 33.89, 13.99. HRMS (ESI) m/z : calculated for $\text{C}_{16}\text{H}_{19}\text{O}_5\text{S}$ [$M + \text{H}$] $^+$: 323.0948, found: 323.0942.



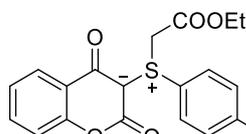
Dimethyl 2-((2-ethoxy-2-oxoethyl)(4-methoxyphenyl)- λ^4 -

sulfaneylidene)malonate (3u): column solvent: DCM/MeOH = 20:1, colorless oil (22 mg, yield 31%); ^1H NMR (500 MHz, CDCl_3) δ 7.73 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 4.88 (d, J = 15.6 Hz, 1H), 4.50 (d, J = 15.6 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 3.71 (s, 6H), 1.25 – 1.21 (m, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 167.05, 165.01, 162.47, 130.47, 122.29, 115.30, 77.16, 62.85, 55.72, 51.28, 47.03, 29.82, 14.07. HRMS (ESI) m/z : calculated for $\text{C}_{16}\text{H}_{21}\text{O}_7\text{S}$ [$M + \text{H}$] $^+$: 357.1003, found: 357.0996.



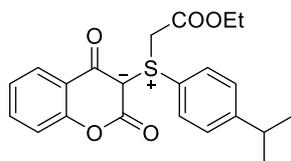
Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(phenyl)- λ^4 -sulfaneyl)acetate

(3v): column solvent: DCM/MeOH = 20:1, white solid (48 mg, yield 68%); **^1H NMR (500 MHz, CDCl_3)** δ 8.03 – 7.98 (m, 2H), 8.00 – 7.94 (m, 1H), 7.59 – 7.52 (m, 1H), 7.53 – 7.44 (m, 3H), 7.19 (t, $J = 7.9$ Hz, 2H), 5.33 (d, $J = 16.1$ Hz, 1H), 4.90 (d, $J = 16.1$ Hz, 1H), 4.18 (q, $J = 7.1$ Hz, 2H), 1.18 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR (126 MHz, CDCl_3)** δ 176.60, 164.21, 162.68, 154.33, 133.41, 133.07, 130.36, 129.77, 129.05, 125.63, 123.72, 121.35, 116.94, 77.53, 77.16, 63.18, 44.63, 13.93. **HRMS (ESI) m/z :** calculated for $\text{C}_{19}\text{H}_{17}\text{O}_5\text{S}$ [$M + \text{H}$] $^+$: 357.0791, found: 357.0787.



Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(p-tolyl)- λ^4 -sulfaneyl)acetate

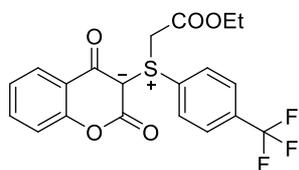
(3w): column solvent: DCM/MeOH = 20:1, white solid (59 mg, yield 80%); **^1H NMR (500 MHz, CDCl_3)** δ 8.03 (d, $J = 7.7$ Hz, 1H), 7.97 (d, $J = 8.5$ Hz, 2H), 7.57 – 7.50 (m, 1H), 7.34 (d, $J = 8.7$ Hz, 2H), 7.26 – 7.21 (m, 2H), 5.38 (d, $J = 16.1$ Hz, 1H), 4.95 (d, $J = 16.1$ Hz, 1H), 4.24 (q, $J = 7.2$ Hz, 2H), 2.42 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR (126 MHz, CDCl_3)** δ 176.48, 164.22, 162.65, 154.27, 144.13, 133.29, 130.97, 129.82, 125.58, 123.62, 121.36, 116.87, 78.09, 77.16, 63.06, 44.54, 21.50, 13.90. **HRMS (ESI) m/z :** calculated for $\text{C}_{20}\text{H}_{19}\text{O}_5\text{S}$ [$M + \text{H}$] $^+$: 371.0948, found: 371.0956.



Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(4-isopropylphenyl)- λ^4 -sulfaneyl)acetate (3x):

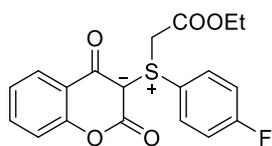
column solvent: DCM/MeOH = 20:1, white solid (64 mg, yield 80%); **^1H NMR (500 MHz, CDCl_3)** δ 8.05 – 7.99 (m, 1H), 7.97 (d, $J = 8.5$ Hz, 2H), 7.55 – 7.48 (m, 1H), 7.36 (d, $J = 8.5$ Hz, 2H), 7.23 (t, $J = 7.5$ Hz, 2H), 5.32 (d, $J = 16.2$ Hz, 1H), 4.86 (d, $J = 16.1$ Hz, 1H), 4.26 – 4.17 (m, 2H), 2.98 – 2.91 (m, 1H), 1.25 – 1.20 (m, 9H). **^{13}C NMR (126 MHz, CDCl_3)** δ 176.53, 164.25, 162.70, 154.80, 154.30, 133.32, 130.02, 128.53, 127.59, 125.71, 125.62, 124.43,

123.66, 121.39, 116.90, 78.13, 77.16, 63.09, 44.54, 34.17, 23.60, 23.58, 13.92. **HRMS (ESI) m/z :** calculated for $C_{22}H_{23}O_5S$ [$M + H$] $^+$: 399.1261, found: 399.1257.



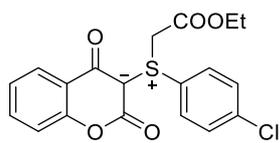
Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(4-

(trifluoromethyl)phenyl)- λ^4 -sulfaneyl)acetate (3y): column solvent: DCM/MeOH = 20:1, white solid (23 mg, yield 27%); 1H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, $J = 8.4$ Hz, 2H), 8.00 – 7.95 (m, 1H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.56 – 7.48 (m, 1H), 7.26 – 7.19 (m, 2H), 5.50 (d, $J = 16.3$ Hz, 1H), 4.83 (d, $J = 16.4$ Hz, 1H), 4.26 – 4.20 (m, 2H), 1.23 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.79, 164.22, 162.65, 154.42, 133.80, 130.24, 127.35 (d, $J = 3.8$ Hz), 125.71, 123.99, 121.21, 117.13, 76.51, 63.59, 44.98, 14.01. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.33. **HRMS (ESI) m/z :** calculated for $C_{20}H_{16}F_3O_5S$ [$M + H$] $^+$: 425.0665, found: 425.0674.



Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(4-fluorophenyl)- λ^4 -

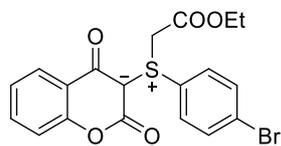
sulfaneyl)acetate (3z): column solvent: DCM/MeOH = 20:1, white solid (43 mg, yield 57%); 1H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.08 (m, 2H), 7.99 – 7.93 (m, 1H), 7.52 – 7.45 (m, 1H), 7.23 – 7.15 (m, 4H), 5.42 (d, $J = 16.3$ Hz, 1H), 4.87 – 4.80 (m, 1H), 4.22 – 4.14 (m, 2H), 1.19 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.61, 165.44 (d, $J = 256.5$ Hz), 164.20, 162.66, 154.31, 133.53, 132.89 (d, $J = 9.0$ Hz), 125.62, 124.66 (d, $J = 3.7$ Hz), 123.81, 121.29, 117.78 (d, $J = 23.2$ Hz), 116.98, 77.89, 63.27, 45.03, 13.95. ^{19}F NMR (471 MHz, $CDCl_3$) δ -103.65. **HRMS (ESI) m/z :** calculated for $C_{19}H_{16}FO_5S$ [$M + H$] $^+$: 375.0697, found: 375.0692.



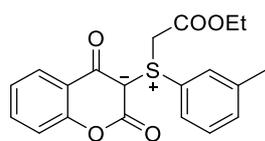
Ethyl (Z)-2-((4-chlorophenyl)(2,4-dioxochroman-3-ylidene)- λ^4 -

sulfaneyl)acetate (3aa): column solvent: DCM/MeOH = 20:1, white solid (46 mg, yield 59%); 1H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.96 (m, 3H), 7.57 – 7.45 (m, 3H), 7.26 – 7.18 (m, 2H), 5.43 (d, $J = 16.2$ Hz, 1H), 4.79 (d, $J = 16.3$ Hz, 1H), 4.25 – 4.17 (m, 2H), 1.22 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR

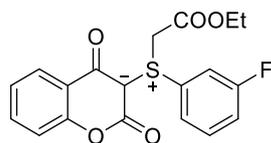
(126 MHz, CDCl₃) δ 176.73, 164.20, 162.70, 154.39, 140.04, 133.66, 131.43, 130.70, 127.51, 125.72, 123.91, 121.32, 117.08, 77.16, 63.43, 44.98, 14.02. **HRMS (ESI) *m/z***: calculated for C₁₉H₁₆ClO₅S [*M* + H]⁺: 391.0401, found: 391.0399.



Ethyl (Z)-2-((4-bromophenyl)(2,4-dioxochroman-3-ylidene)- λ^4 -sulfaneyl)acetate (3ab): column solvent: DCM/MeOH = 20:1, white solid (46 mg, yield 59%); **¹H NMR (500 MHz, CDCl₃)** δ 7.98 – 7.93 (m, 1H), 7.94 – 7.89 (m, 2H), 7.66 – 7.60 (m, 2H), 7.52 – 7.45 (m, 1H), 7.23 – 7.16 (m, 2H), 5.42 (d, *J* = 16.3 Hz, 1H), 4.83 (d, *J* = 16.2 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.22 – 1.18 (m, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 176.64, 164.20, 162.63, 154.31, 133.59, 131.38, 128.31, 128.07, 125.64, 123.85, 121.24, 117.01, 77.27, 77.16, 63.36, 44.83, 13.98. **HRMS (ESI) *m/z***: calculated for C₁₉H₁₆BrO₅S [*M* + H]⁺: 434.9896, found: 434.9891.

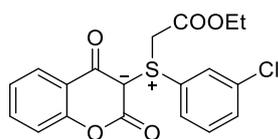


Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(*m*-tolyl)- λ^4 -sulfaneyl)acetate (3ac): column solvent: DCM/MeOH = 20:1, white solid (51 mg, yield 69%); **¹H NMR (500 MHz, CDCl₃)** δ 8.05 – 7.99 (m, 1H), 7.87 – 7.82 (m, 1H), 7.82 – 7.78 (m, 1H), 7.55 – 7.48 (m, 1H), 7.44 – 7.35 (m, 2H), 7.27 – 7.20 (m, 2H), 5.32 (d, *J* = 16.1 Hz, 1H), 4.87 (d, *J* = 16.2 Hz, 1H), 4.26 – 4.13 (m, 2H), 2.40 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 176.58, 164.25, 162.71, 154.34, 140.81, 133.96, 133.38, 130.20, 130.03, 128.77, 126.73, 125.67, 123.71, 121.39, 116.95, 77.81, 77.16, 63.16, 44.46, 21.49, 13.95. **HRMS (ESI) *m/z***: calculated for C₂₀H₁₉O₅S [*M* + H]⁺: 371.0948, found: 371.0946.

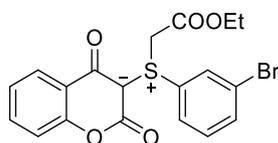


Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(3-fluorophenyl)- λ^4 -sulfaneyl)acetate (3ad): column solvent: DCM/MeOH = 20:1, yellow oil (49 mg, yield 65%); **¹H NMR (500 MHz, CDCl₃)** δ 8.04 – 7.99 (m, 1H), 7.86 – 7.78 (m, 2H), 7.57 – 7.48 (m, 2H), 7.33 – 7.28 (m, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 5.42 (d, *J* = 16.4 Hz, 1H), 4.82 (d, *J* = 16.2 Hz, 1H), 4.28 –

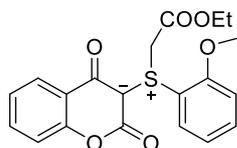
4.17 (m, 2H), 1.25 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 176.67, 164.19, 162.80 (d, $J = 253.7$ Hz), 162.63, 154.33, 133.62, 131.91 (d, $J = 7.7$ Hz), 130.73 (d, $J = 7.6$ Hz), 125.67, 125.61 (d, $J = 4.1$ Hz), 123.86, 121.21, 120.52 (d, $J = 21.0$ Hz), 117.21, 117.01, 63.40, 45.04, 13.96. ^{19}F NMR (471 MHz, CDCl_3) δ -106.87. HRMS (ESI) m/z : calculated for $\text{C}_{19}\text{H}_{16}\text{FO}_5\text{S}$ [$M + \text{H}$] $^+$: 375.0697, found: 375.0694.



Ethyl (Z)-2-((3-chlorophenyl)(2,4-dioxochroman-3-ylidene)- λ^4 -sulfaneyl)acetate (3ae): column solvent: DCM/MeOH = 20:1, yellow solid (29 mg, yield 37%); ^1H NMR (500 MHz, CDCl_3) δ 8.04 – 7.99 (m, 1H), 8.00 – 7.95 (m, 1H), 7.95 – 7.89 (m, 1H), 7.56 – 7.41 (m, 3H), 7.25 – 7.17 (m, 2H), 5.40 (d, $J = 16.3$ Hz, 1H), 4.87 (d, $J = 16.3$ Hz, 1H), 4.21 (q, $J = 7.1$ Hz, 2H), 1.22 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 176.69, 164.16, 162.63, 154.36, 136.27, 133.64, 133.38, 131.44, 130.73, 129.61, 127.88, 125.71, 123.88, 121.24, 117.04, 77.16, 63.43, 44.93, 13.98. HRMS (ESI) m/z : calculated for $\text{C}_{19}\text{H}_{16}\text{ClO}_5\text{S}$ [$M + \text{H}$] $^+$: 391.0401, found: 391.0406.

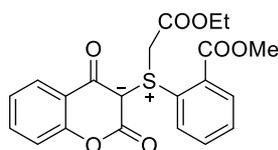


Ethyl (Z)-2-((3-bromophenyl)(2,4-dioxochroman-3-ylidene)- λ^4 -sulfaneyl)acetate (3af): column solvent: DCM/MeOH = 20:1, yellow solid (28 mg, yield 32%); ^1H NMR (500 MHz, CDCl_3) δ 8.16 (t, $J = 1.9$ Hz, 1H), 8.03 – 7.97 (m, 2H), 7.74 – 7.68 (m, 1H), 7.56 – 7.49 (m, 1H), 7.40 (t, $J = 8.0$ Hz, 1H), 7.27 – 7.20 (m, 2H), 5.41 (d, $J = 16.3$ Hz, 1H), 4.82 (d, $J = 16.3$ Hz, 1H), 4.26 – 4.21 (m, 2H), 1.25 – 1.22 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 176.76, 164.13, 162.69, 154.43, 136.40, 133.71, 132.46, 131.73, 130.97, 128.39, 125.80, 124.01, 123.94, 121.32, 117.12, 77.16, 63.51, 44.99, 29.81, 14.04. HRMS (ESI) m/z : calculated for $\text{C}_{19}\text{H}_{16}\text{BrO}_5\text{S}$ [$M + \text{H}$] $^+$: 434.9896, found: 434.9893.

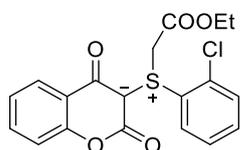


Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(2-methoxyphenyl)- λ^4 -

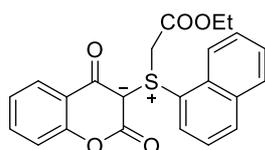
sulfaneyl)acetate (3ag): column solvent: DCM/MeOH = 20:1, colorless oil (65 mg, yield 84%); ^1H NMR (500 MHz, CDCl_3) δ 8.09 – 7.99 (m, 1H), 7.62 – 7.50 (m, 3H), 7.30 – 7.25 (m, 1H), 7.27 – 7.22 (m, 1H), 7.11 – 7.02 (m, 2H), 5.56 (d, $J = 15.5$ Hz, 1H), 4.47 (d, $J = 15.4$ Hz, 1H), 4.30 – 4.16 (m, 2H), 4.01 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 176.95, 164.23, 162.83, 156.79, 154.53, 134.33, 133.43, 129.81, 125.72, 123.70, 122.28, 121.40, 117.02, 113.76, 112.19, 77.16, 72.07, 62.91, 56.74, 42.71, 13.95. HRMS (ESI) m/z : calculated for $\text{C}_{20}\text{H}_{19}\text{O}_6\text{S}$ [$M + \text{H}$] $^+$: 387.0897, found: 387.0894.



Methyl (Z)-2-((2,4-dioxochroman-3-ylidene)(2-ethoxy-2-oxoethyl)- λ^4 -sulfaneyl)benzoate (3ah): column solvent: DCM/MeOH = 20:1, colorless oil (31 mg, yield 37%); ^1H NMR (500 MHz, CDCl_3) δ 8.47 – 7.83 (m, 3H), 7.80 – 7.34 (m, 5H), 4.38 – 4.17 (m, 4H), 4.01 (s, 3H), 1.26 – 1.17 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 134.57, 133.59, 132.58, 132.34, 130.91, 129.07, 125.80, 123.79, 117.02, 77.16, 62.91, 53.61, 13.99. HRMS (ESI) m/z : calculated for $\text{C}_{21}\text{H}_{19}\text{O}_7\text{S}$ [$M + \text{H}$] $^+$: 415.0846, found: 415.0844.

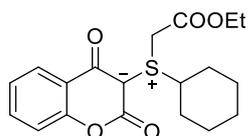


Ethyl (Z)-2-((2-chlorophenyl)(2,4-dioxochroman-3-ylidene)- λ^4 -sulfaneyl)acetate (3ai): column solvent: DCM/MeOH = 20:1, yellow oil (17 mg, yield 22%); ^1H NMR (500 MHz, CDCl_3) δ 8.04 – 7.99 (m, 2H), 7.58 – 7.49 (m, 3H), 7.48 – 7.41 (m, 1H), 7.27 – 7.20 (m, 2H), 5.45 (d, $J = 15.7$ Hz, 1H), 4.83 (d, $J = 15.7$ Hz, 1H), 4.29 – 4.15 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 176.94, 163.63, 162.60, 154.55, 134.42, 134.07, 133.68, 131.34, 131.24, 128.63, 126.16, 125.78, 123.89, 121.35, 117.12, 77.16, 73.70, 63.37, 42.71, 13.99. HRMS (ESI) m/z : calculated for $\text{C}_{19}\text{H}_{16}\text{ClO}_5\text{S}$ [$M + \text{H}$] $^+$: 391.0401, found: 391.0396.



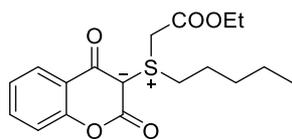
Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(naphthalen-1-yl)- λ^4 -sulfaneyl)acetate (3aj): column solvent: DCM/MeOH = 20:1, white solid (42 mg, yield 52%); ^1H

NMR (500 MHz, CDCl₃) δ 8.71 (d, J = 8.5 Hz, 1H), 8.58 – 8.53 (m, 1H), 8.07 (d, J = 8.2 Hz, 1H), 8.04 – 7.98 (m, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.66 – 7.56 (m, 2H), 7.52 – 7.45 (m, 1H), 7.26 – 7.17 (m, 2H), 5.44 (d, J = 16.0 Hz, 1H), 5.10 (d, J = 15.9 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 1.12 (t, J = 7.1 Hz, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 176.72, 163.81, 162.60, 154.39, 134.15, 133.70, 133.37, 131.16, 129.56, 129.17, 129.03, 127.58, 125.66, 124.07, 123.71, 123.40, 121.45, 116.97, 77.16, 63.25, 42.40, 13.88. **HRMS (ESI) m/z :** calculated for C₂₃H₁₉O₅S [$M + H$]⁺: 407.0948, found: 407.0944.



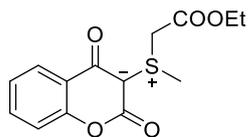
Ethyl (Z)-2-(cyclohexyl(2,4-dioxochroman-3-ylidene)- λ^4 -

sulfaneyl)acetate (3ak): column solvent: DCM/MeOH = 20:1, colorless oil (50 mg, yield 69%); **¹H NMR (500 MHz, CDCl₃)** δ 7.97 – 7.91 (m, 1H), 7.50 – 7.43 (m, 1H), 7.22 – 7.15 (m, 2H), 4.70 (d, J = 15.5 Hz, 1H), 4.36 – 4.29 (m, 2H), 4.24 – 4.11 (m, 2H), 2.09 – 2.02 (m, 1H), 1.98 – 1.86 (m, 2H), 1.81 – 1.75 (m, 1H), 1.67 – 1.57 (m, 2H), 1.54 – 1.45 (m, 1H), 1.43 – 1.35 (m, 1H), 1.34 – 1.25 (m, 2H), 1.25 – 1.15 (m, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 176.96, 164.47, 162.90, 154.40, 133.25, 125.47, 123.61, 121.18, 116.92, 77.16, 73.83, 63.05, 53.73, 40.80, 28.85, 28.10, 24.90, 24.76, 13.90. **HRMS (ESI) m/z :** calculated for C₁₉H₂₃O₅S [$M + H$]⁺: 323.1261, found: 323.1257.



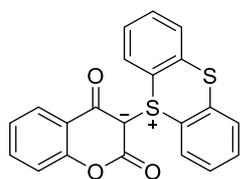
Ethyl (E)-2-((2,4-dioxochroman-3-ylidene)(pentyl)- λ^4 -

sulfaneyl)acetate (3al): column solvent: DCM/MeOH = 20:1, yellow oil (57 mg, yield 81%); **¹H NMR (500 MHz, CDCl₃)** δ 7.94 (d, J = 7.7 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.23 – 7.16 (m, 2H), 5.02 – 4.95 (m, 1H), 4.26 – 4.18 (m, 3H), 4.20 – 4.11 (m, 1H), 3.31 – 3.22 (m, 1H), 1.73 – 1.63 (m, 2H), 1.47 – 1.34 (m, 2H), 1.34 – 1.21 (m, 5H), 0.91 – 0.79 (m, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 177.14, 164.89, 162.75, 154.39, 133.34, 125.47, 123.69, 121.21, 116.97, 77.16, 72.69, 63.16, 43.15, 40.65, 30.14, 24.24, 21.96, 14.00, 13.67. **HRMS (ESI) m/z :** calculated for C₁₈H₂₃O₅S [$M + H$]⁺: 351.1261, found: 351.1257.



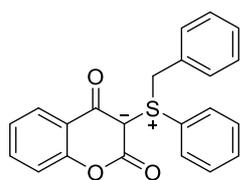
Ethyl (E)-2-((2,4-dioxochroman-3-ylidene)(methyl)- λ^4 -sulfaneyl)acetate

(3am): column solvent: DCM/MeOH = 20:1, yellow oil (48mg, yield 81%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.92 – 7.87 (m, 1H), 7.48 – 7.41 (m, 1H), 7.19 – 7.10 (m, 2H), 5.07 (d, $J = 16.2$ Hz, 1H), 4.27 – 4.11 (m, 3H), 3.21 (s, 3H), 1.23 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 176.68, 164.85, 162.35, 154.19, 133.33, 125.37, 123.70, 121.14, 116.88, 77.16, 75.13, 63.18, 43.94, 24.84, 13.96. **HRMS (ESI) m/z** : calculated for $\text{C}_{14}\text{H}_{15}\text{O}_5\text{S}$ [$M + \text{H}$] $^+$: 295.0635, found: 295.0631.



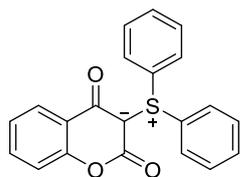
3-(5 λ^4 -thianthren-5-ylidene)chromane-2,4-dione (3an): column solvent:

DCM/MeOH = 20:1, white solid (27 mg, yield 36%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.10 – 8.04 (m, 1H), 7.74 – 7.65 (m, 2H), 7.66 – 7.59 (m, 1H), 7.59 – 7.47 (m, 4H), 7.47 – 7.40 (m, 2H), 7.37 (d, $J = 8.2$ Hz, 1H), 7.34 – 7.27 (m, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 176.35, 162.38, 154.80, 134.06, 131.37, 131.23, 129.92, 128.97, 126.40, 126.37, 126.25, 124.04, 121.28, 117.35, 77.16, 68.55. **HRMS (ESI) m/z** : calculated for $\text{C}_{21}\text{H}_{13}\text{O}_3\text{S}_2$ [$M + \text{H}$] $^+$: 377.0301; found: 377.0300.

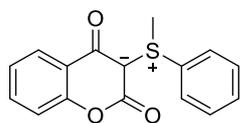


(Z)-3-(benzyl(phenyl)- λ^4 -sulfaneylidene)chromane-2,4-dione (3ao):

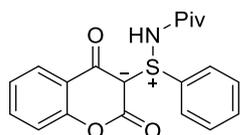
column solvent: DCM/MeOH = 20:1, white solid (37 mg, yield 51%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.02 (d, $J = 7.7$ Hz, 1H), 7.91 – 7.85 (m, 2H), 7.57 – 7.42 (m, 4H), 7.34 – 7.26 (m, 5H), 7.25 – 7.19 (m, 2H), 5.51 (d, $J = 12.2$ Hz, 1H), 5.32 – 5.26 (m, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 177.16, 163.17, 154.44, 133.32, 132.86, 130.69, 130.25, 130.22, 129.75, 129.36, 129.10, 128.93, 125.71, 123.69, 121.55, 116.98, 77.16, 76.80, 47.45. **HRMS (ESI) m/z** : calculated for $\text{C}_{22}\text{H}_{17}\text{O}_3\text{S}$ [$M + \text{H}$] $^+$: 361.0893, found: 361.0891.



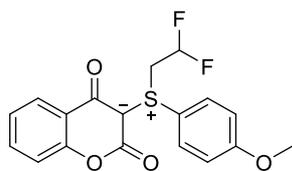
3-(diphenyl- λ^4 -sulfaneylidene)chromane-2,4-dione (3ap): column solvent: DCM/MeOH = 20:1, white solid (18 mg, yield 26%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.04 – 7.98 (m, 1H), 7.79 – 7.74 (m, 4H), 7.61 – 7.54 (m, 2H), 7.55 – 7.48 (m, 5H), 7.28 – 7.18 (m, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 176.26, 162.62, 154.55, 133.48, 132.45, 131.20, 130.19, 130.16, 129.47, 127.83, 125.99, 124.93, 123.72, 121.64, 117.06, 78.40, 77.16. **HRMS (ESI) m/z :** calculated for $\text{C}_{21}\text{H}_{15}\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$: 347.0736; found: 347.0735.



(Z)-3-(methyl(phenyl)- λ^4 -sulfaneylidene)chromane-2,4-dione (3aq): column solvent: DCM/MeOH = 20:1, white solid (56 mg, yield 98%); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.99 – 7.94 (m, 1H), 7.88 – 7.82 (m, 2H), 7.54 – 7.46 (m, 1H), 7.49 – 7.45 (m, 3H), 7.18 (m, 2H), 3.51 (s, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.50, 162.48, 154.29, 133.26, 132.38, 130.20, 129.59, 128.54, 125.55, 123.62, 121.41, 116.87, 77.97, 77.16, 25.26. **HRMS (ESI) m/z :** calculated for $\text{C}_{16}\text{H}_{13}\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$: 285.0580; found: 285.0576.

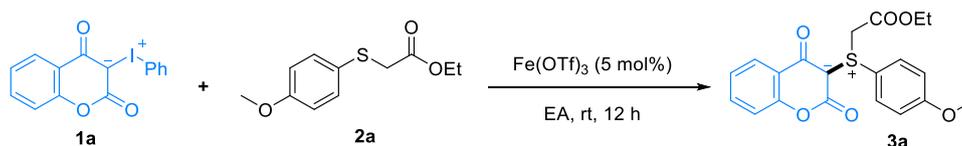


(E)-N-((2,4-dioxochroman-3-ylidene)(phenyl)- λ^4 -sulfanyl)pivalamide (3ar): column solvent: PE/EA = 2/1, yellow solid (44 mg, yield 60%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 12.91 (s, 1H), 8.09 – 7.99 (m, 1H), 7.91 – 7.86 (m, 2H), 7.62 – 7.56 (m, 2H), 7.55 – 7.50 (m, 2H), 7.30 – 7.26 (m, 2H), 1.29 (s, 9H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 178.48, 177.77, 162.43, 154.60, 134.66, 133.91, 133.61, 130.48, 127.76, 125.45, 124.17, 121.19, 117.31, 81.09, 77.16, 40.36, 27.19. **HRMS (ESI) m/z :** [$\text{M} + \text{H}$] $^+$ calculated for $\text{C}_{20}\text{H}_{20}\text{NO}_4\text{S}$: 370.1108; Found: 370.1112.



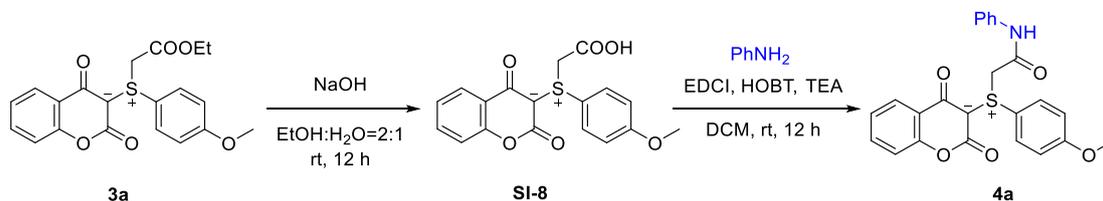
(Z)-3-((2,2-difluoroethyl)(4-methoxyphenyl)-14-sulfaneylidene)chromane-2,4-dione (3as): column solvent: DCM/MeOH = 20:1, yellow solid (54 mg, yield 74%); ¹H NMR (500 MHz, CDCl₃) δ 8.06 – 7.98 (m, 3H), 7.55 – 7.48 (m, 1H), 7.27 – 7.19 (m, 2H), 7.03 – 6.98 (m, 2H), 6.08 (tt, *J* = 54.5, 4.0 Hz, 1H), 4.85 – 4.73 (m, 1H), 4.44 (qd, *J* = 13.8, 4.8 Hz, 1H), 3.84 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 176.58, 163.83, 162.69, 154.33, 133.56, 132.37, 125.66, 123.84, 121.35, 119.25, 117.01, 116.11, 113.83, 111.89, 109.94, 78.25, 55.84, 45.24 (t, *J* = 24.9 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -115.56. HRMS (ESI) *m/z*: [M+H]⁺ calculated for C₁₈H₁₅F₂O₄S: 365.0654; Found: 365.0656.

Gram-Scale Experiments



In a 100 mL reaction tube, the mixture of **1a** (728.3 mg, 2.0 mmol, 1.0 equiv.), **2a** (680.0 mg, 3.0 mmol, 2.0 equiv.) and Fe(OTf)₃ (39.8 mg, 0.1 mmol, 5 mol%) was added EA (8.0 mL). Then, the resulting mixture was stirred at room temperature for 12.0 hours. When the reaction was finished, the products are purified by preparative thin layer chromatography (DCM/MeOH = 20/1). The product **3a** was obtained as a white solid (635 mg, 82% yield).

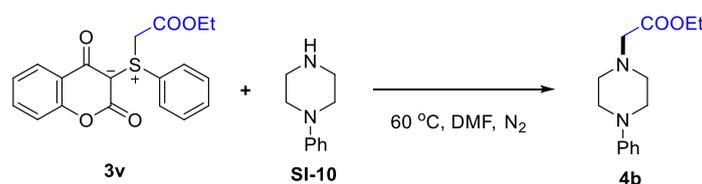
Transformation experiments



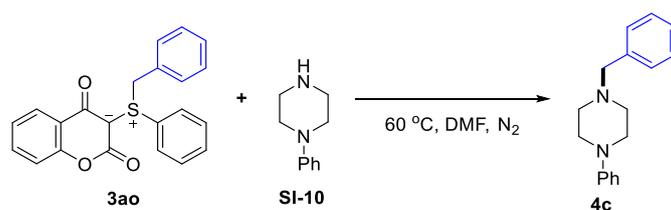
Step 1: In a 10 mL reaction tube, compound **3a** (38.6 mg, 0.1 mmol, 1.0 equiv.) and NaOH (24.0 mg, 0.6 mol, 6.0 equiv.) were dissolved in EtOH/H₂O (2:1, 3 mL). Then the resulting mixture was stirred at room temperature for 12.0 h. When the reaction was finished, the reaction was cooled

down to room temperature and acidified with 2N HCl. The aqueous phase was extracted with ethyl acetate (30.0 mL x 3). The combined organic phase was dried over anhydrous Na₂SO₄, filtered, and evaporated under reduced pressure. the product **SI-8** was obtained as a white solid.

Step 2: In a 10 mL reaction tube, compound **SI-8** (35.8 mg, 0.1 mmol, 1.0 equiv.), EDCI (23.0 mg, 0.12 mol, 1.2 equiv.), HOBT (16.2 mg, 0.12 mol, 1.2 equiv.) and TEA (30.3 mg, 0.3 mol, 3.0 equiv.) were dissolved in DCM (2.0 mL). The mixture is pre-stirred at room temperature for 1.0 h, and then aniline(**SI-9**) was added to the reaction system. The resulting mixture stirred at room temperature for 12 hours. When the reaction was finished, the products are purified by preparative thin layer chromatography (DCM/MeOH = 20/1). The product **4a** was obtained as a white solid (15 mg, 35% yield).

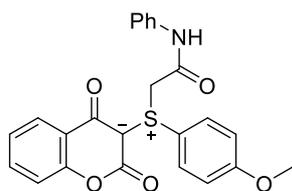


In a 10 mL reaction tube, compound **3v** (98.0 mg, 0.27 mmol, 2.0 equiv.), and **SI-10** (22.0 mg, 0.14 mmol, 1.0 equiv.) were dissolved in DMF (2.0 mL). Then the resulting mixture was stirred at 60 °C for 12.0 h. When the reaction was finished, the reaction solution was purified by preparative thin layer chromatography (PE/EA = 1/1). The product **4b** was obtained as a white solid (20 mg, 57% yield).

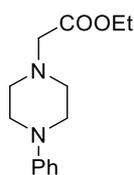


In a 10 mL reaction tube, compound **3ao** (90.0 mg, 0.25 mmol, 2.0 equiv.), and **SI-10** (20.1 mg, 0.13 mmol, 1.0 equiv.) were dissolved in DMF (2.0 mL). Then the resulting mixture was stirred at 60 °C for 12.0 h. When the reaction was finished, the reaction solution was purified by preparative thin layer chromatography (PE/EA = 1/1). The product **4c** was obtained as a white solid (17 mg, 55% yield).

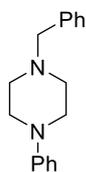
Characterization Data of Products 4



(Z)-2-((2,4-dioxochroman-3-ylidene)(4-methoxyphenyl)- λ^4 -sulfaneyl)-N-phenylacetamide (4a): column solvent: DCM/MeOH = 20:1, white solid (15 mg, yield 35%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.83 (s, 1H), 7.99 – 7.90 (m, 3H), 7.50 – 7.43 (m, 3H), 7.30 – 7.20 (m, 2H), 7.22 – 7.15 (m, 1H), 7.15 – 7.05 (m, 3H), 6.90 – 6.83 (m, 2H), 5.38 (d, $J = 14.0$ Hz, 1H), 5.02 (d, $J = 14.1$ Hz, 1H), 3.73 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 163.46, 160.82, 154.26, 137.46, 133.64, 131.99, 129.10, 125.65, 125.07, 124.06, 120.17, 118.87, 116.99, 115.86, 77.16, 55.76, 48.72. **HRMS (ESI) m/z :** calculated for $\text{C}_{24}\text{H}_{20}\text{NO}_5\text{S}$ [$M + \text{H}$] $^+$: 434.1057, found: 434.1053.



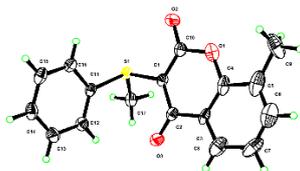
Ethyl 2-(4-phenylpiperazin-1-yl)acetate (4b): column solvent: PE/EA = 1:1, white solid (20 mg, yield 57%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.30 – 7.22 (m, 2H), 6.96 – 6.90 (m, 2H), 6.89 – 6.82 (m, 1H), 4.21 (q, $J = 7.1$ Hz, 2H), 3.28 – 3.27 (m, 2H), 3.27 – 3.24 (m, 4H), 2.77 – 2.73 (m, 4H), 1.29 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 170.30, 151.34, 129.23, 119.94, 116.29, 77.16, 60.82, 59.59, 53.15, 49.12, 14.36. **HRMS (ESI) m/z :** calculated for $\text{C}_{14}\text{H}_{21}\text{N}_2\text{O}_2$ [$M + \text{H}$] $^+$: 249.1598, found: 249.1597.



1-benzyl-4-phenylpiperazine (4c): column solvent: PE/EA = 1:1, white solid (17 mg, yield 55%); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.40 – 7.32 (m, 4H), 7.32 – 7.23 (m, 3H), 6.94 (d, $J = 8.2$ Hz, 2H), 6.86 (t, $J = 7.3$ Hz, 1H), 3.61 – 3.58 (m, 2H), 3.25 – 3.19 (m, 4H), 2.67 – 2.61 (m, 4H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 151.51, 138.01, 129.38, 129.22, 128.43, 127.31, 119.76, 116.19, 77.16, 63.19, 53.23, 49.24. **HRMS (ESI) m/z :** calculated for $\text{C}_{17}\text{H}_{21}\text{N}_2$ [$M + \text{H}$] $^+$: 253.1699, found: 253.1698.

X-ray data of compound 3j (CCDC: 2450446)

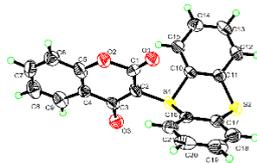
Deposition Data: CCDC 2450446, with an ellipsoid contour probability level of 50%.

**Table S1. Crystal data and structure refinement for compound 3j.**

Identification code	3j
Empirical formula	C ₁₇ H ₁₄ O ₃ S
Formula weight	298.34
Temperature/K	170
Crystal System	triclinic
Space group	P-1
a/Å	8.8557(4)
b/Å	13.0872(5)
c/Å	13.2877(6)
α /°	80.525(2)
β /°	71.175(2)
γ /°	76.443(2)
Volume /Å ³	1410.37(11)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.405
μ/mm^{-1}	0.236
F(000)	624.0
Crystal size/mm ³	0.12×0.06×0.05
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.348 to 52.782
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 16, -15 ≤ l ≤ 16
Reflections collected	16587
Independent reflections	5759 [R _{int} = 0.0786, R _{sigma} = 0.0565]
Data/restraints/parameters	5759/268/426
Goodness-of-fit on F ²	1.043
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0687, wR ₂ = 0.1675
Final R indexes [all data]	R ₁ = 0.1057, wR ₂ = 0.1955
Largest diff. peak/hole / e Å ⁻³	1.41/-0.39

X-ray data of compound 3an (CCDC: 2473480)

Deposition Data: CCDC 2473480, with an ellipsoid contour probability level of 50%.

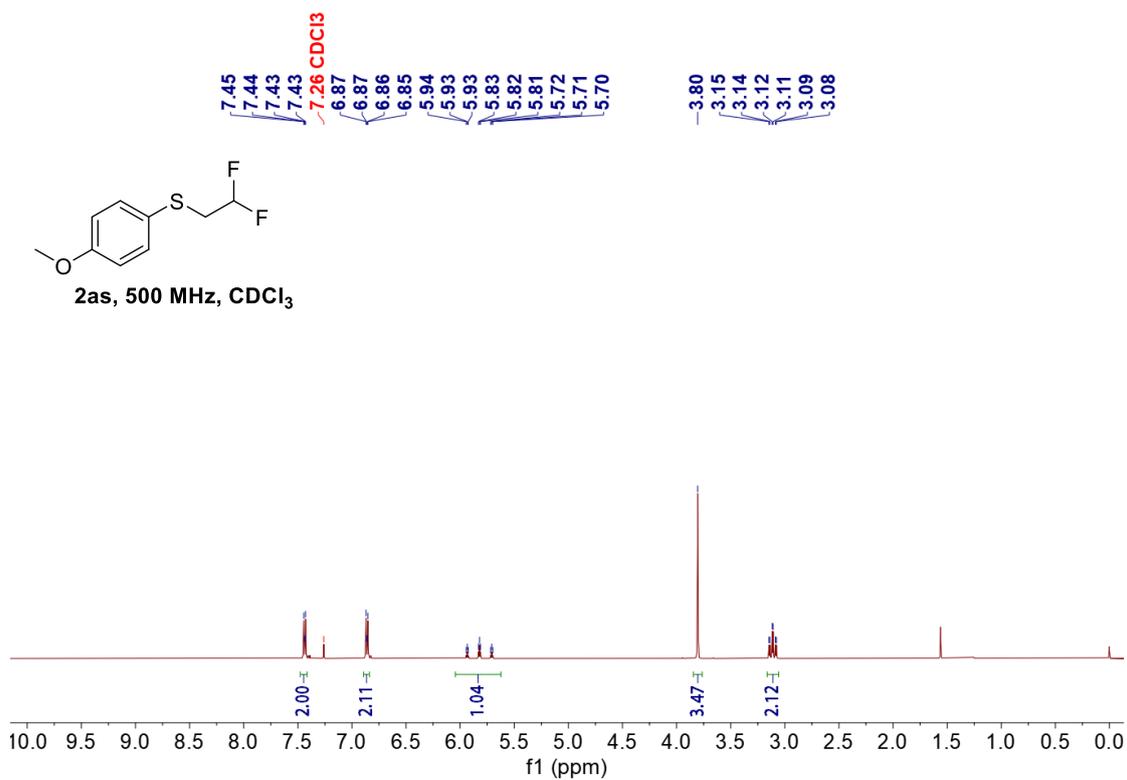
**Table S. Crystal data and structure refinement for compound 3an.**

Identification code	3an
Empirical formula	C ₂₁ H ₁₂ O ₃ S ₂
Formula weight	376.43
Temperature/K	150
Crystal System	triclinic
Space group	P-1
a/Å	9.6461(3)
b/Å	11.6280(4)
c/Å	16.8233(6)
α /°	103.7620(10)
β /°	94.4470(10)
γ /°	111.6600(10)
Volume /Å ³	1674.58(10)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.493
μ/mm^{-1}	3.045
F(000)	776.0
Crystal size/mm ³	0.16×0.13×0.12
Radiation	CuK α (λ = 1.54178)
2 Θ range for data collection/°	8.542 to 133.154
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	24676
Independent reflections	5722 [R _{int} = 0.0350, R _{sigma} = 0.0281]
Data/restraints/parameters	5722/887/687
Goodness-of-fit on F ²	1.112
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0672, wR ₂ = 0.1677
Final R indexes [all data]	R ₁ = 0.0685, wR ₂ = 0.1684
Largest diff. peak/hole / e Å ⁻³	0.91/-0.57

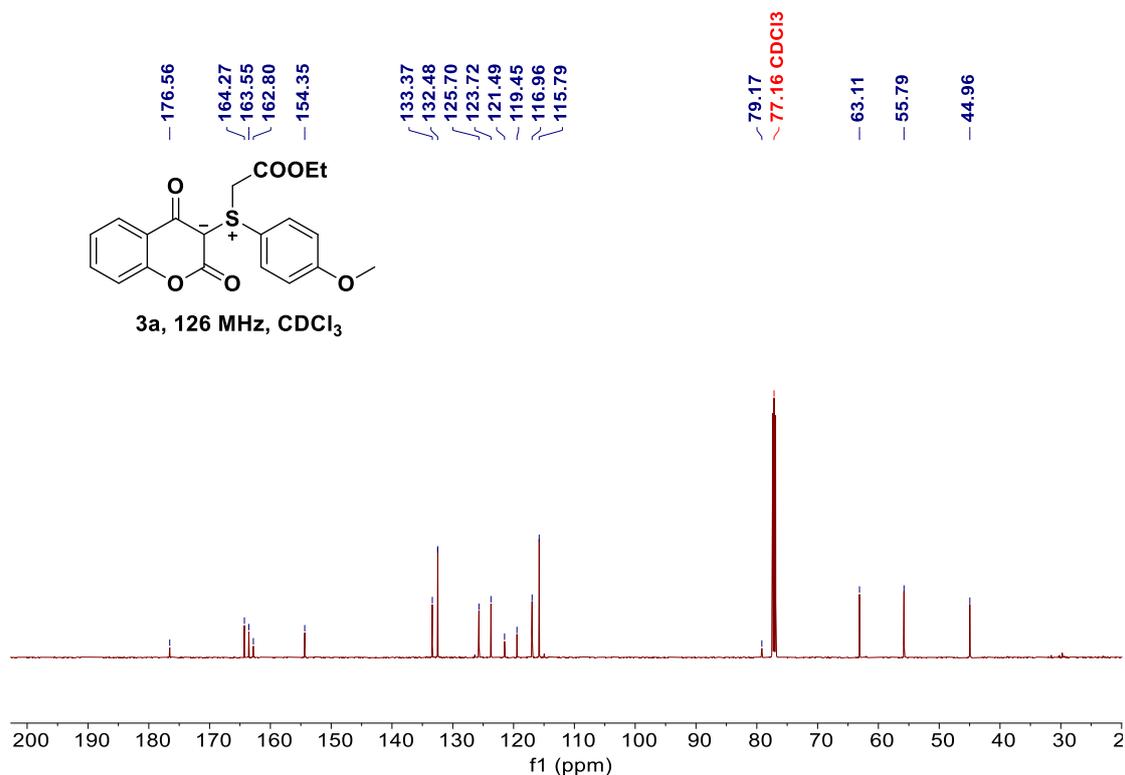
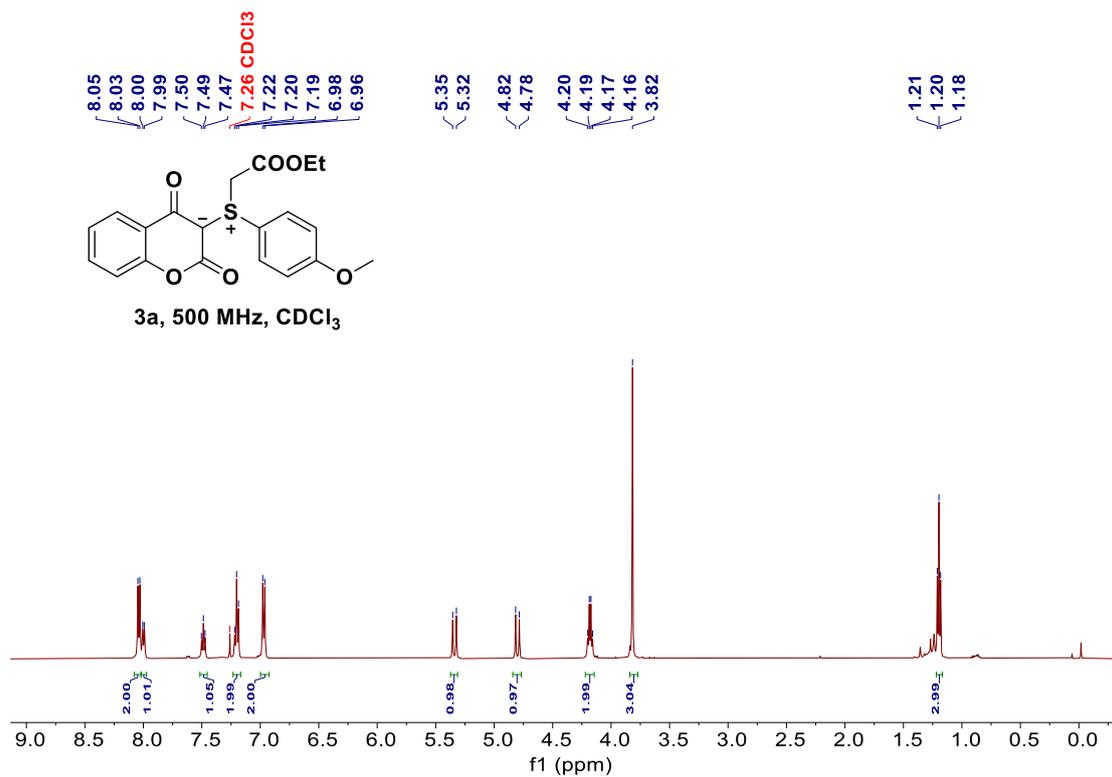
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Copies of ^1H , ^{13}C NMR and ^{19}F NMR spectra
(2,2-difluoroethyl)(4-methoxyphenyl)sulfane (2as)

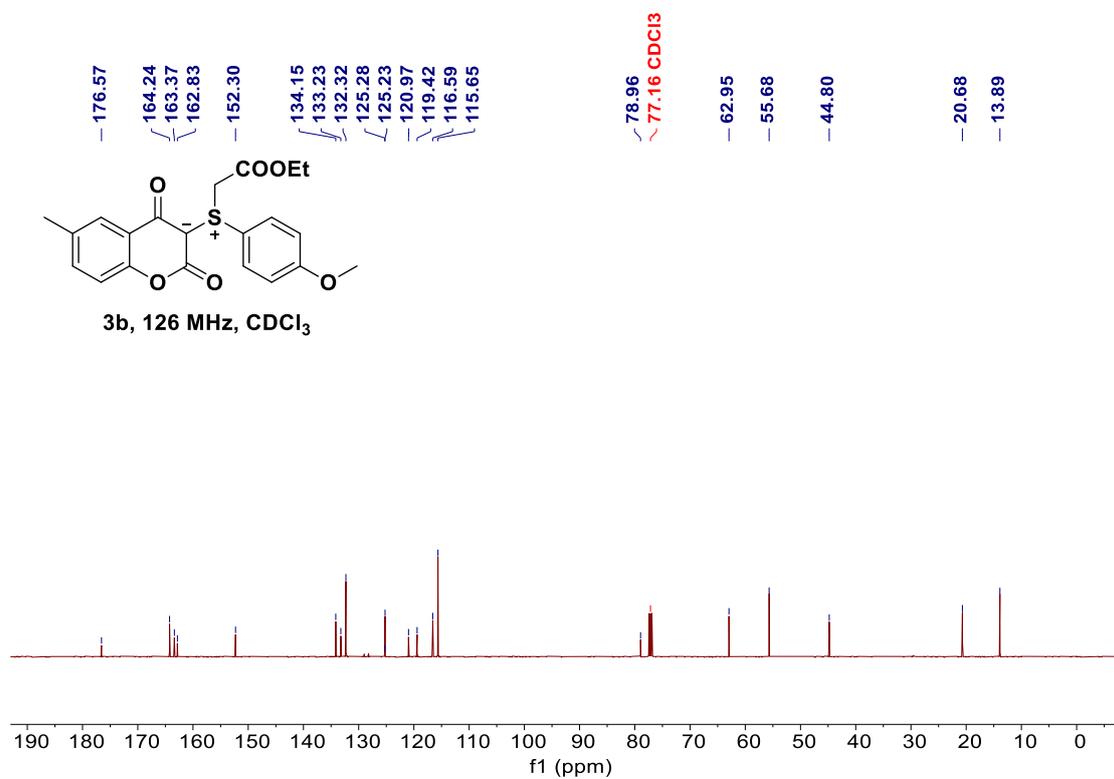
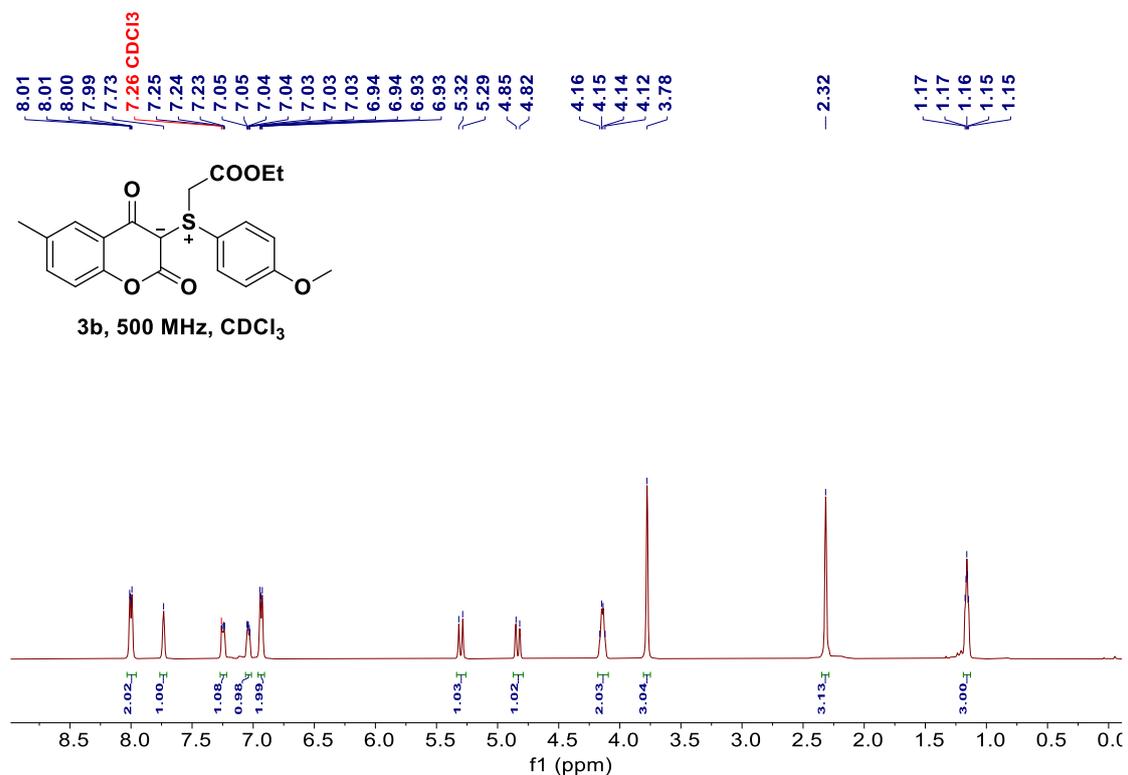


Ethyl(Z)-2-((2,4-dioxochroman-3-ylidene)(4-methoxyphenyl)-λ⁴-sulfaneyl)acetate (3a)



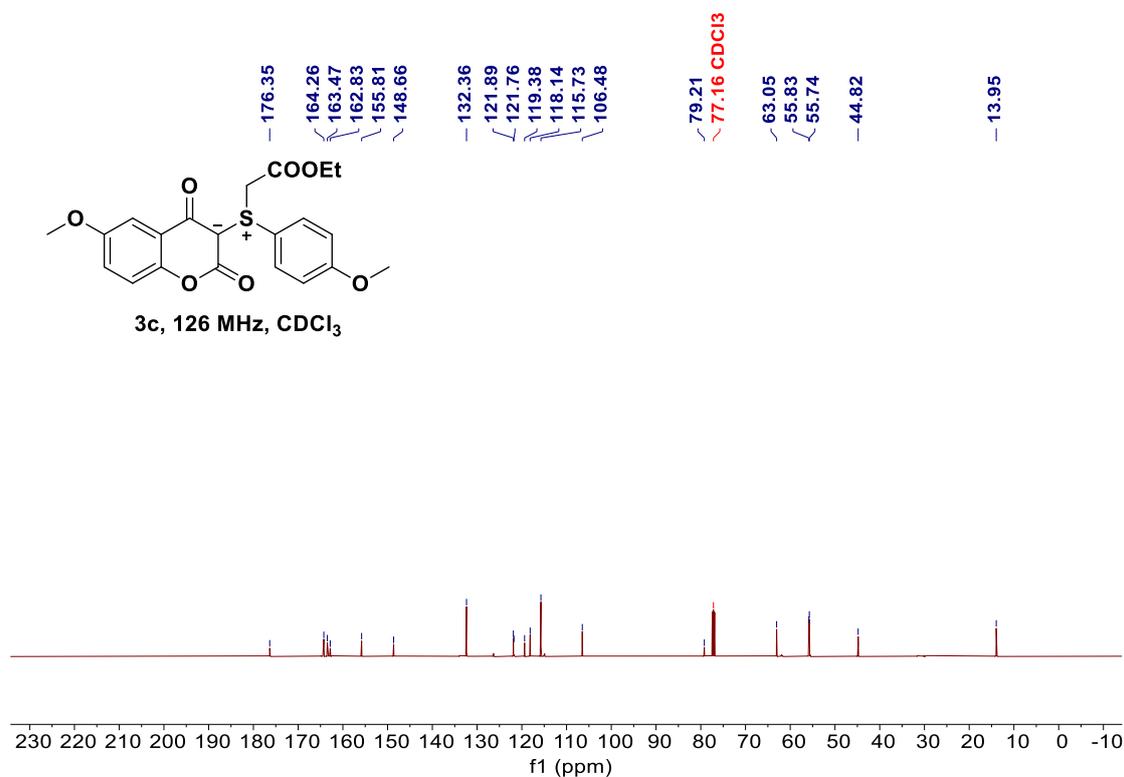
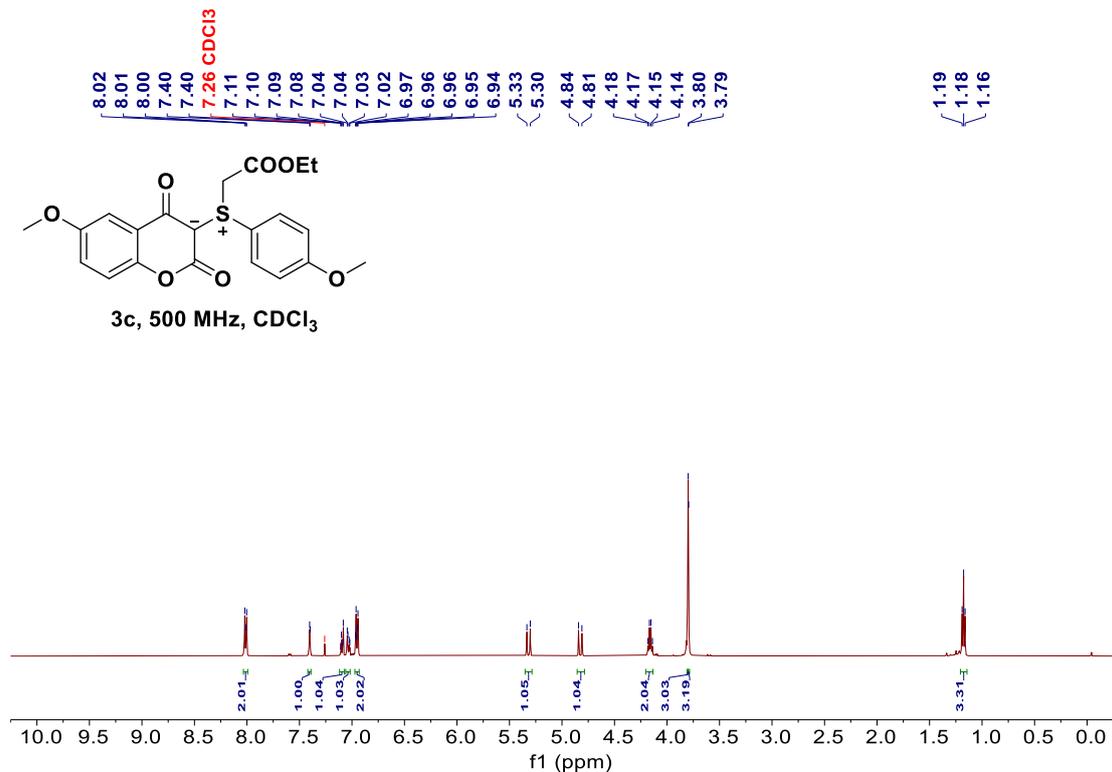
Ethyl (Z)-2-((4-methoxyphenyl)(6-methyl-2,4-dioxochroman-3-ylidene)- λ^4 -sulfanyl)acetate

(3b)



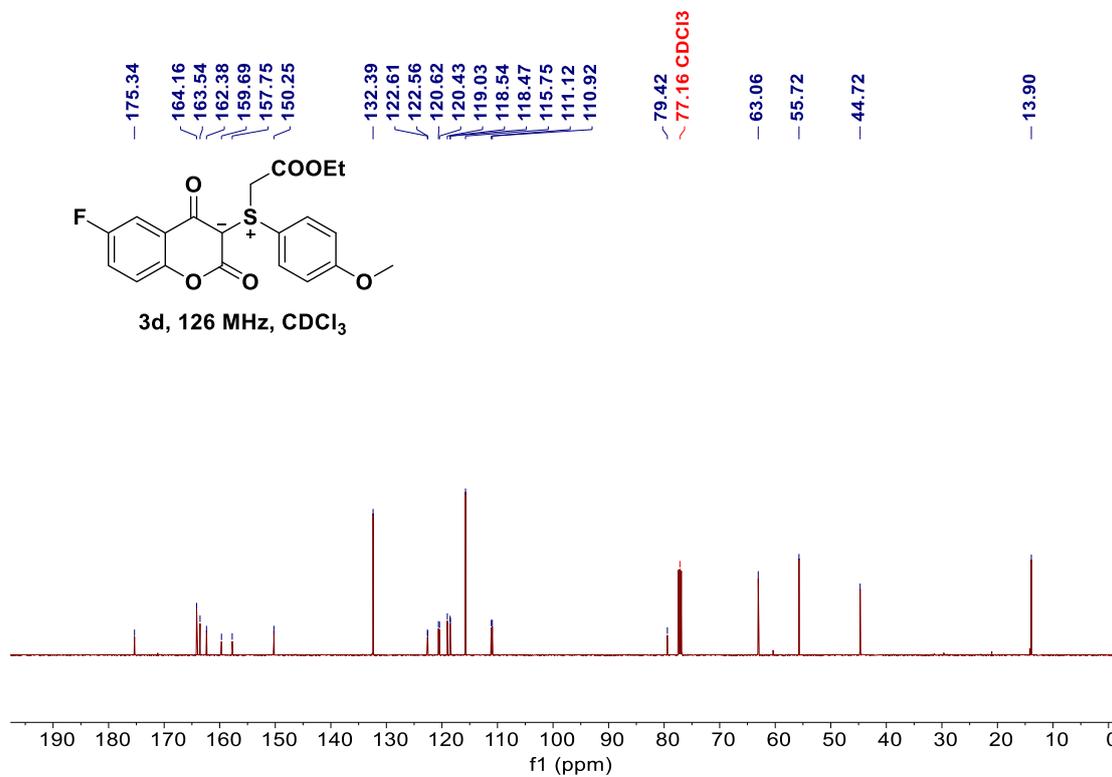
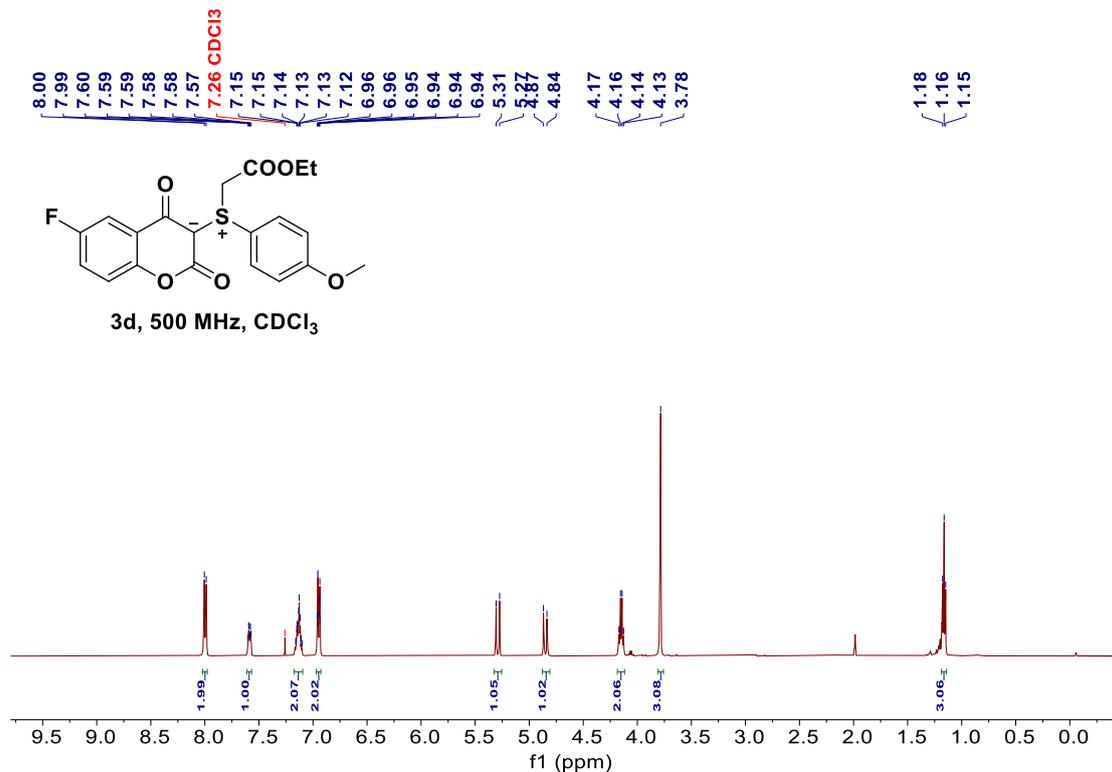
Ethyl (Z)-2-((6-methoxy-2,4-dioxochroman-3-ylidene)(4-methoxyphenyl)- λ^4 -sulfaneyl)acetate

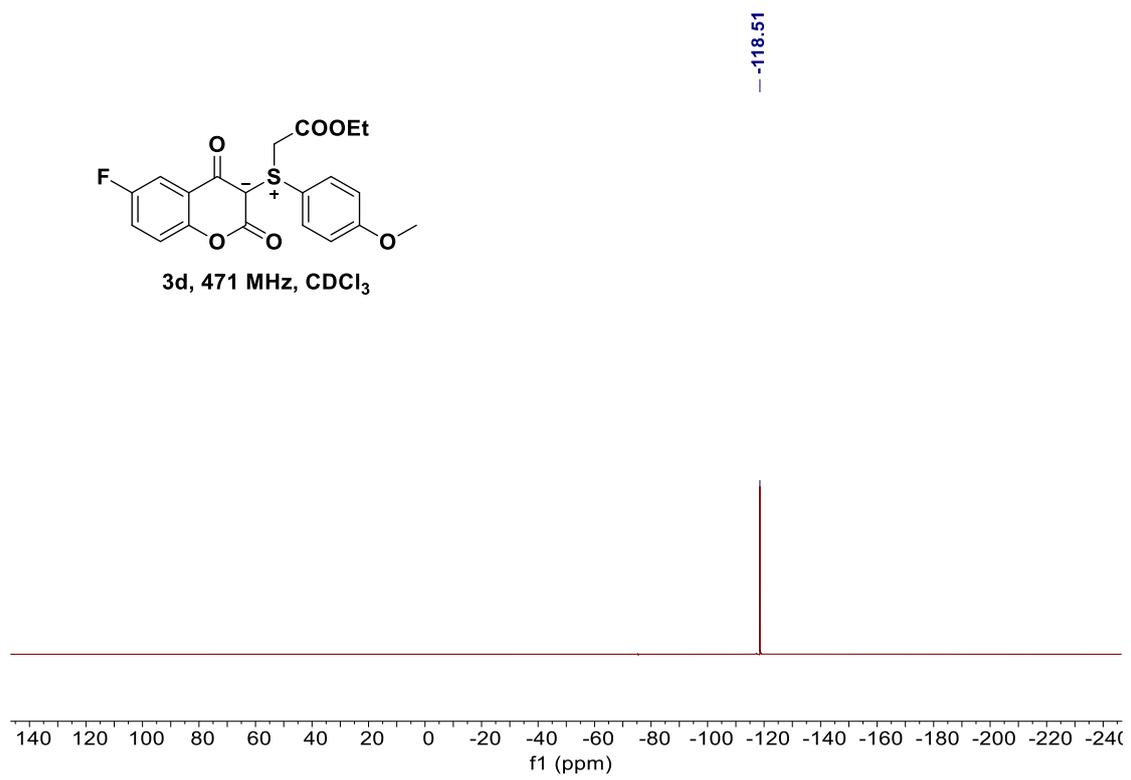
(3c)



Ethyl (Z)-2-((6-fluoro-2,4-dioxochroman-3-ylidene)(4-methoxyphenyl)- λ^4 -sulfaneyl)acetate

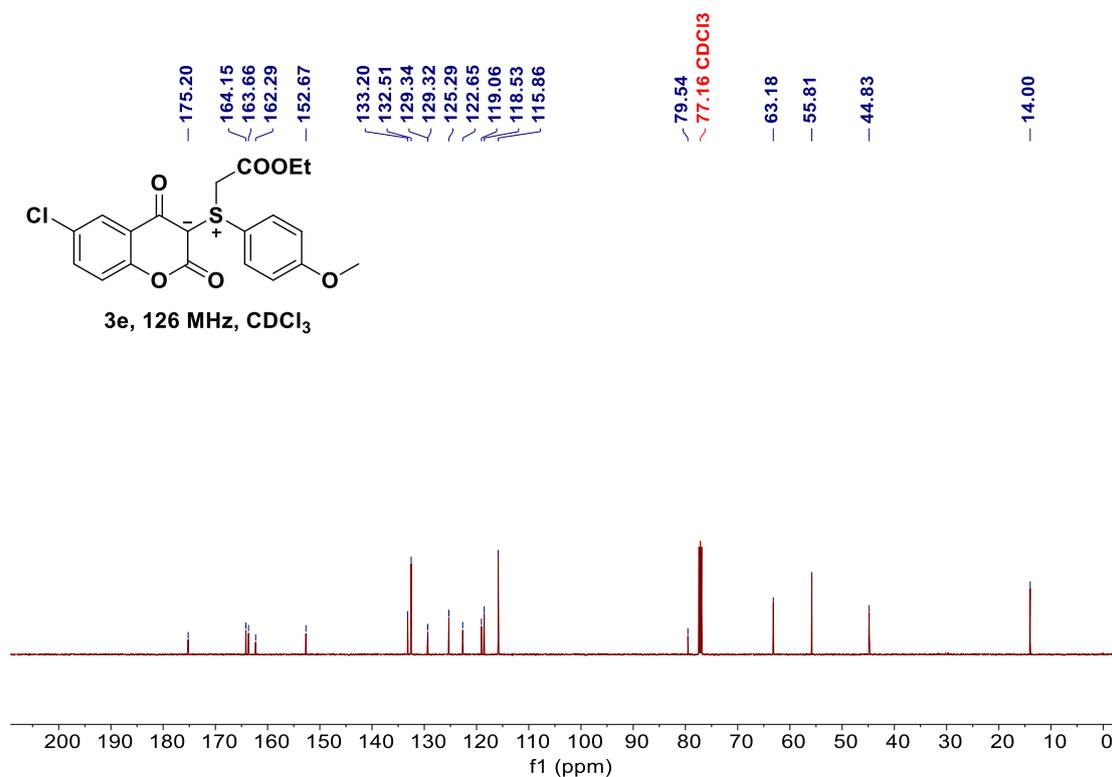
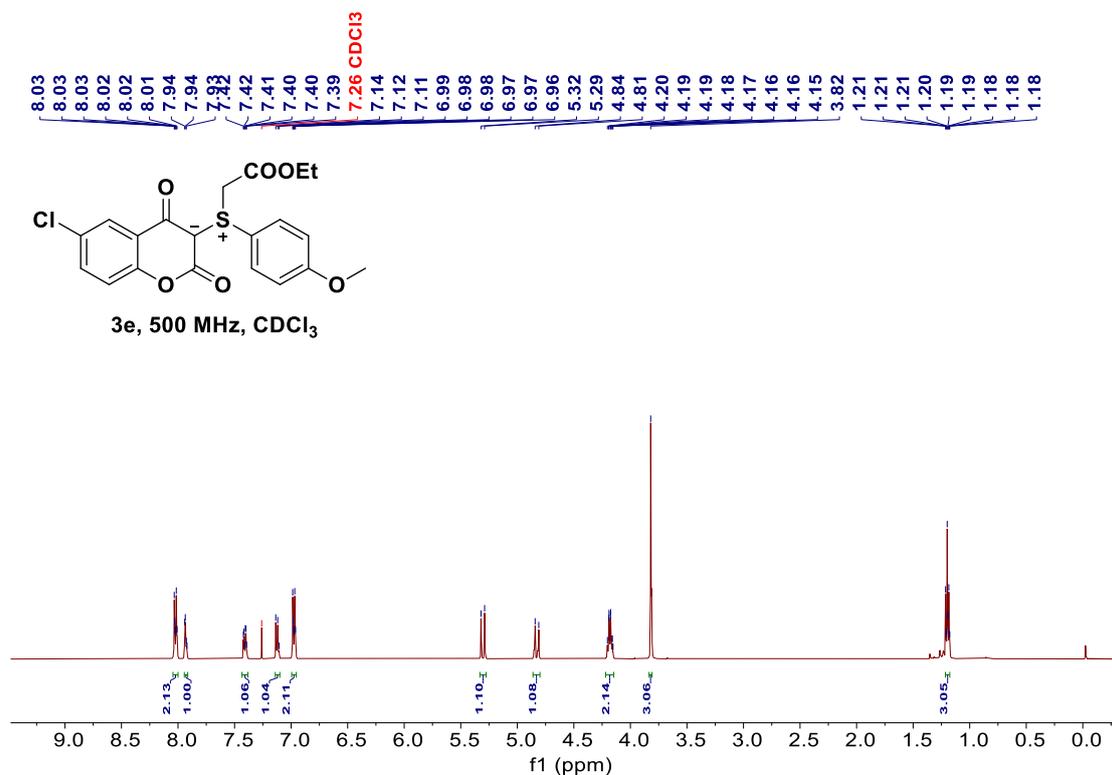
(3d)





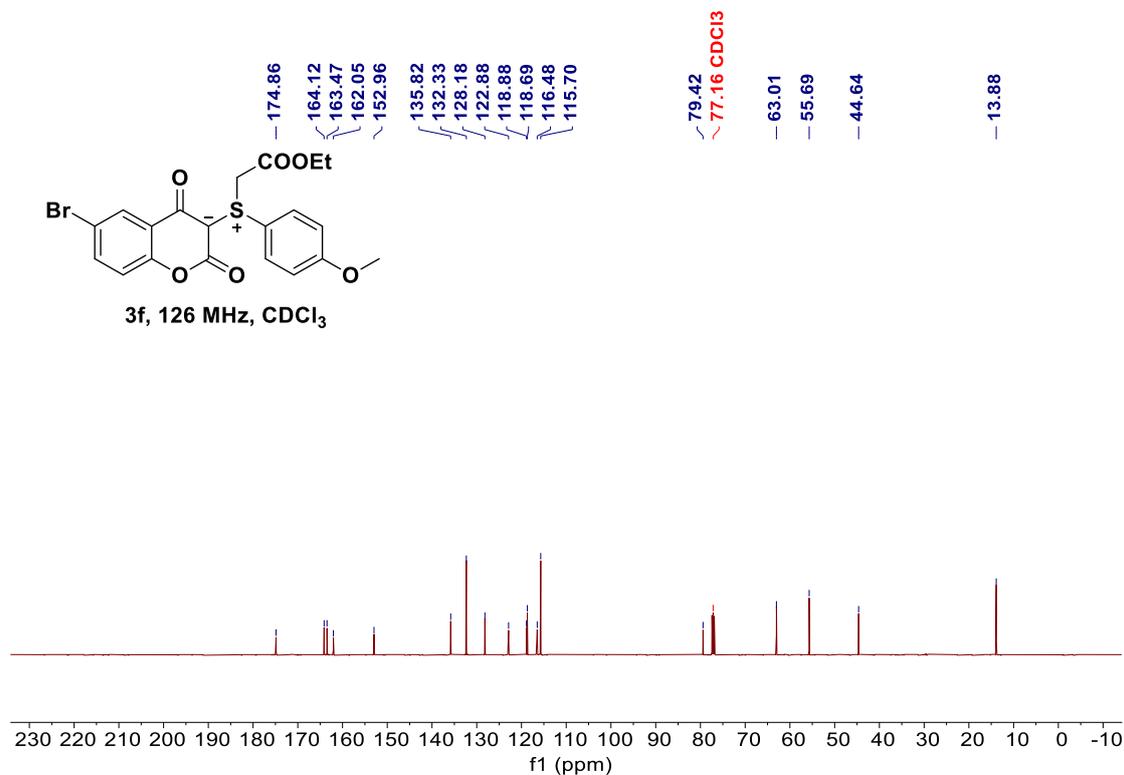
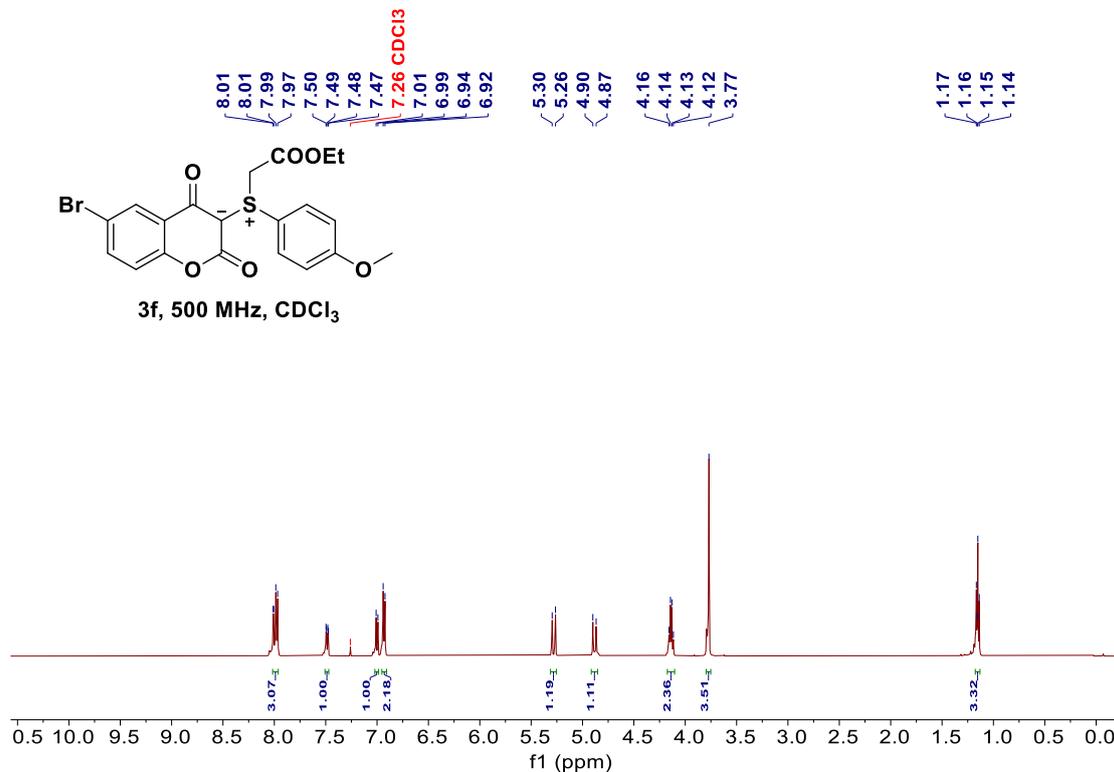
Ethyl (Z)-2-(((6-chloro-2,4-dioxochroman-3-ylidene)(4-methoxyphenyl)-λ⁴-sulfaneyl)acetate

(3e)



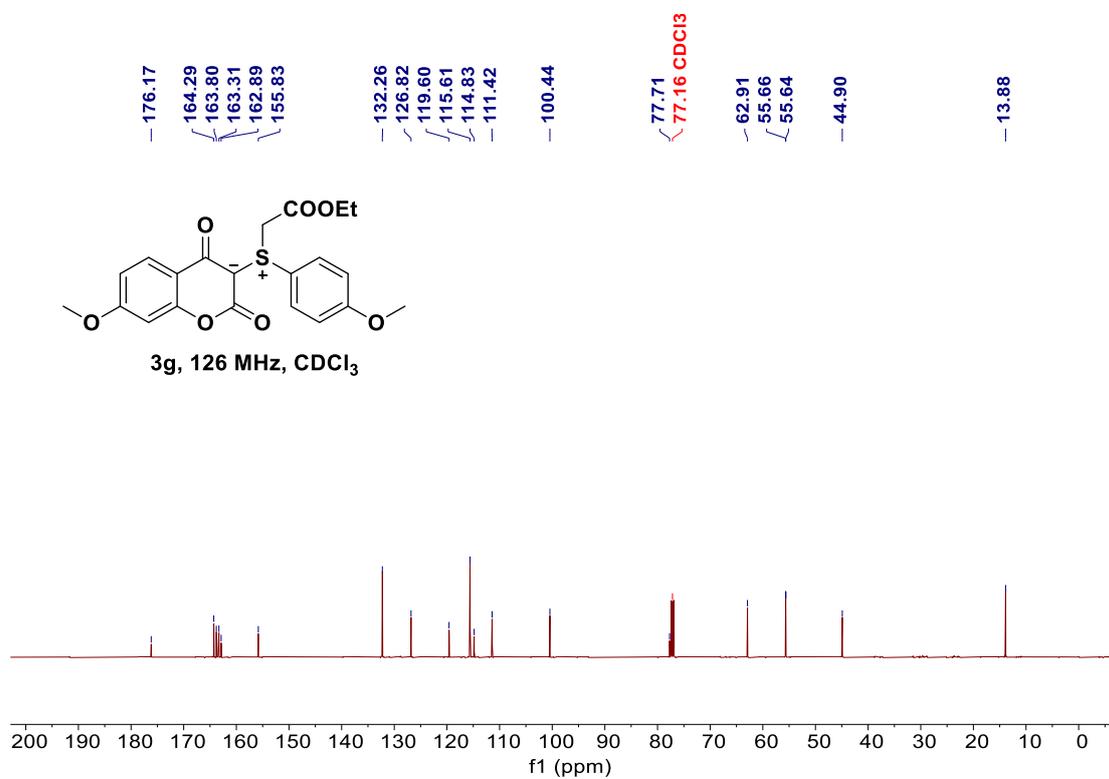
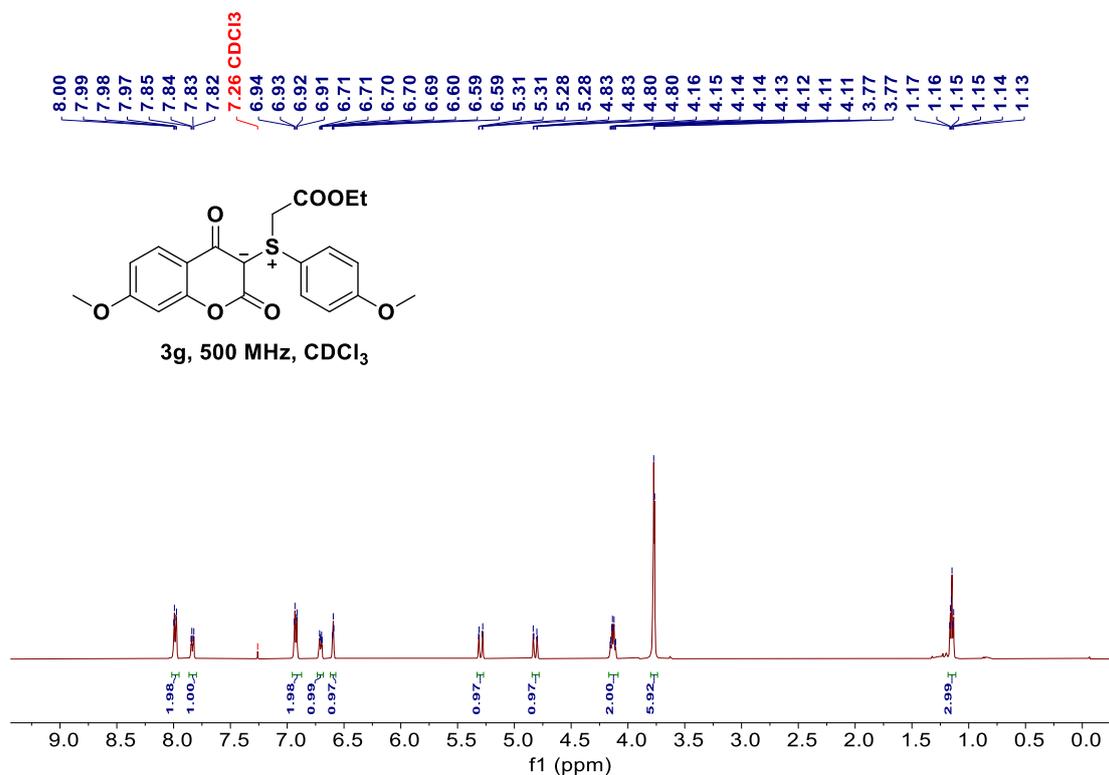
Ethyl (Z)-2-((6-bromo-2,4-dioxochroman-3-ylidene)(4-methoxyphenyl)- λ^4 -sulfanyl)acetate

(3f)



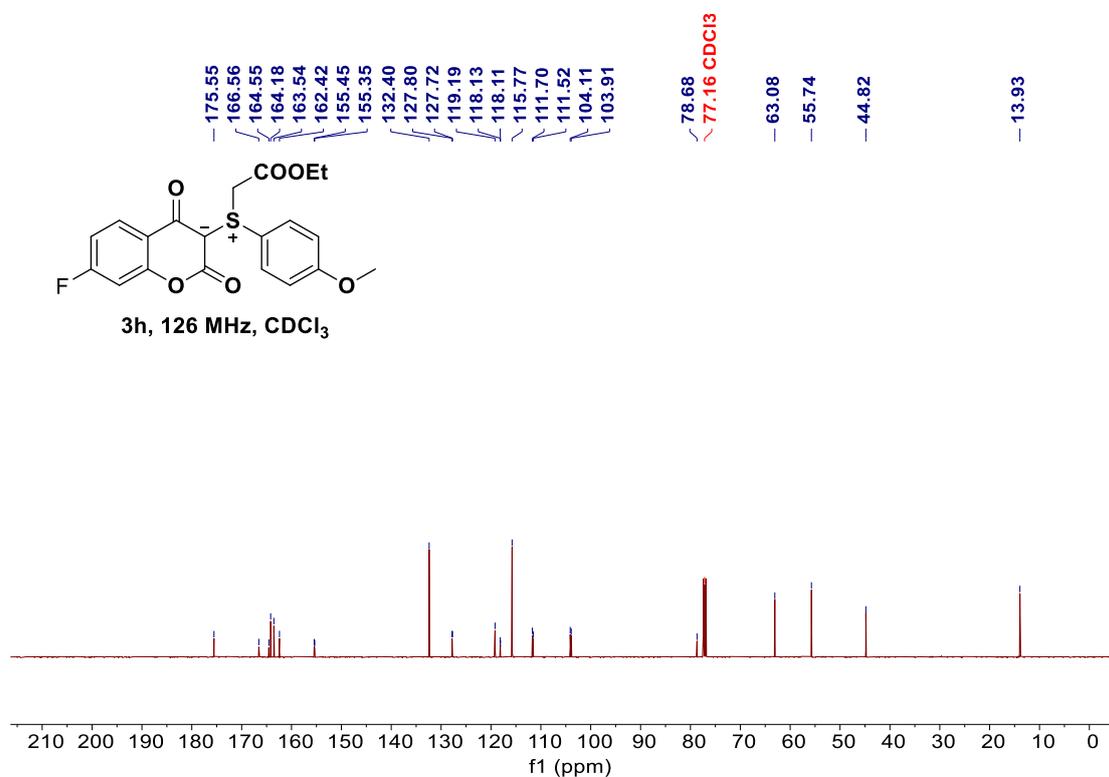
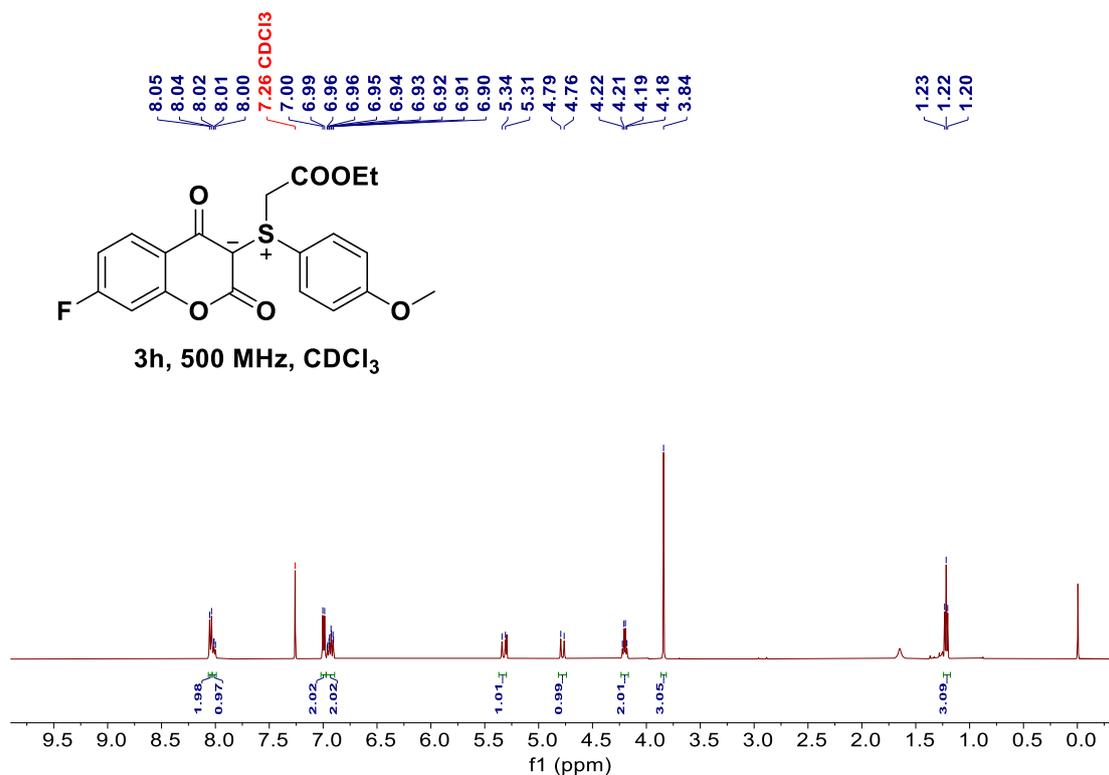
Ethyl (Z)-2-((7-methoxy-2,4-dioxochroman-3-ylidene)(4-methoxyphenyl)- λ^4 -sulfanyl)acetate

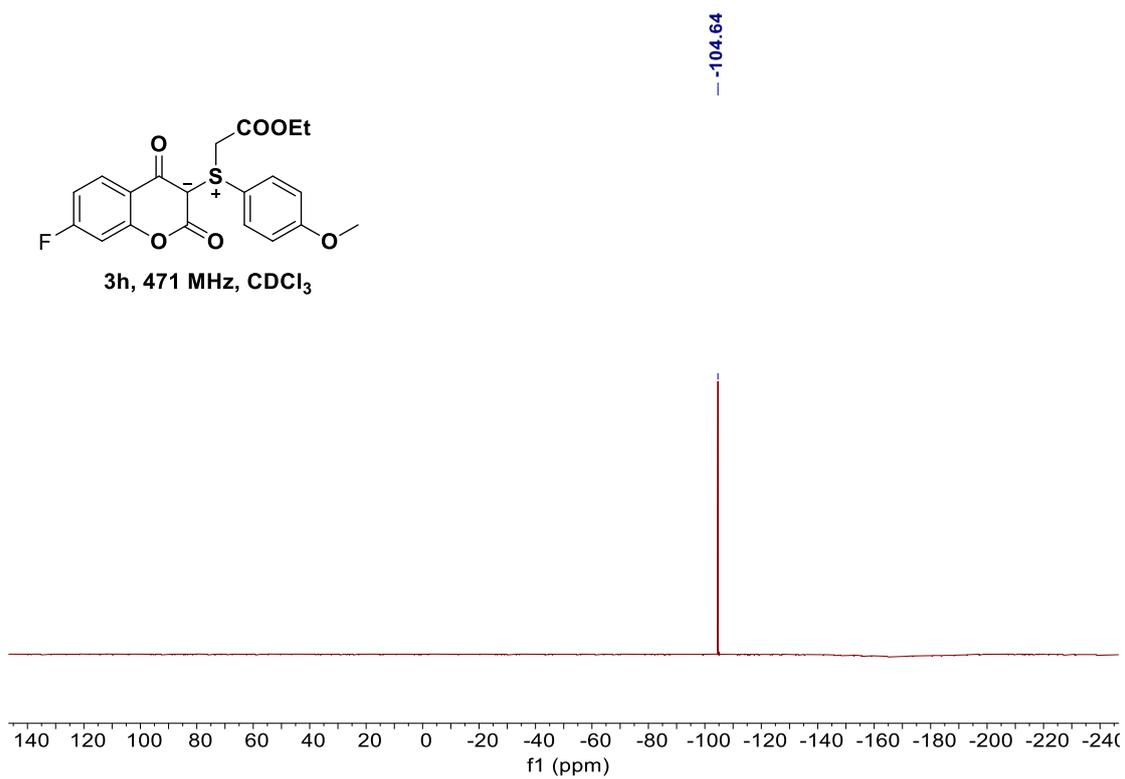
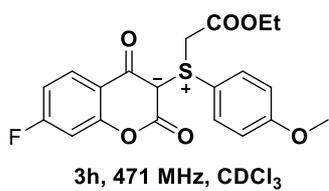
(3g)



Ethyl (Z)-2-((7-fluoro-2,4-dioxochroman-3-ylidene)(4-methoxyphenyl)-λ⁴-sulfaneyl)acetate

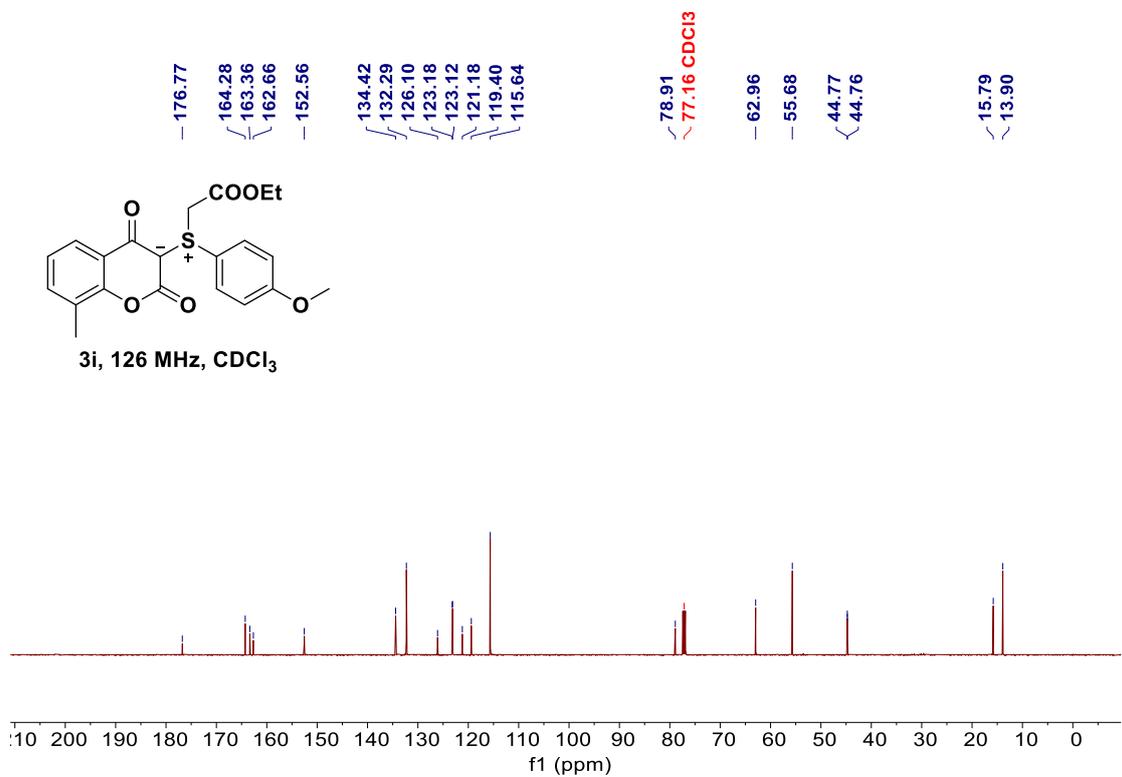
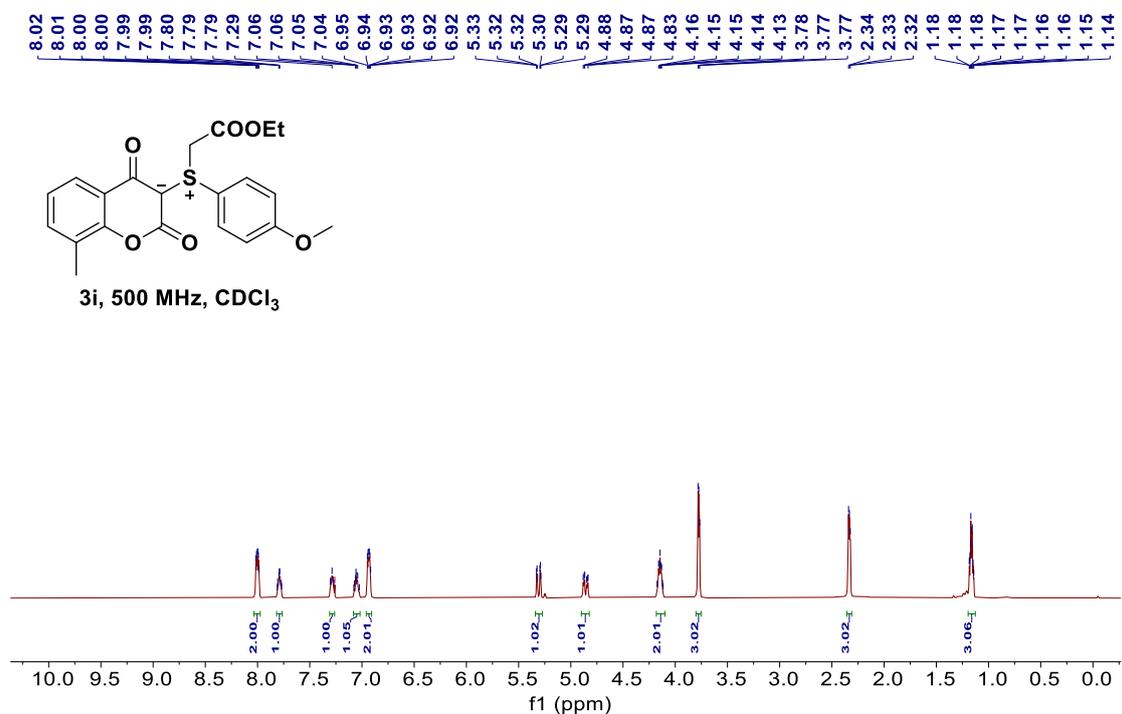
(3h)



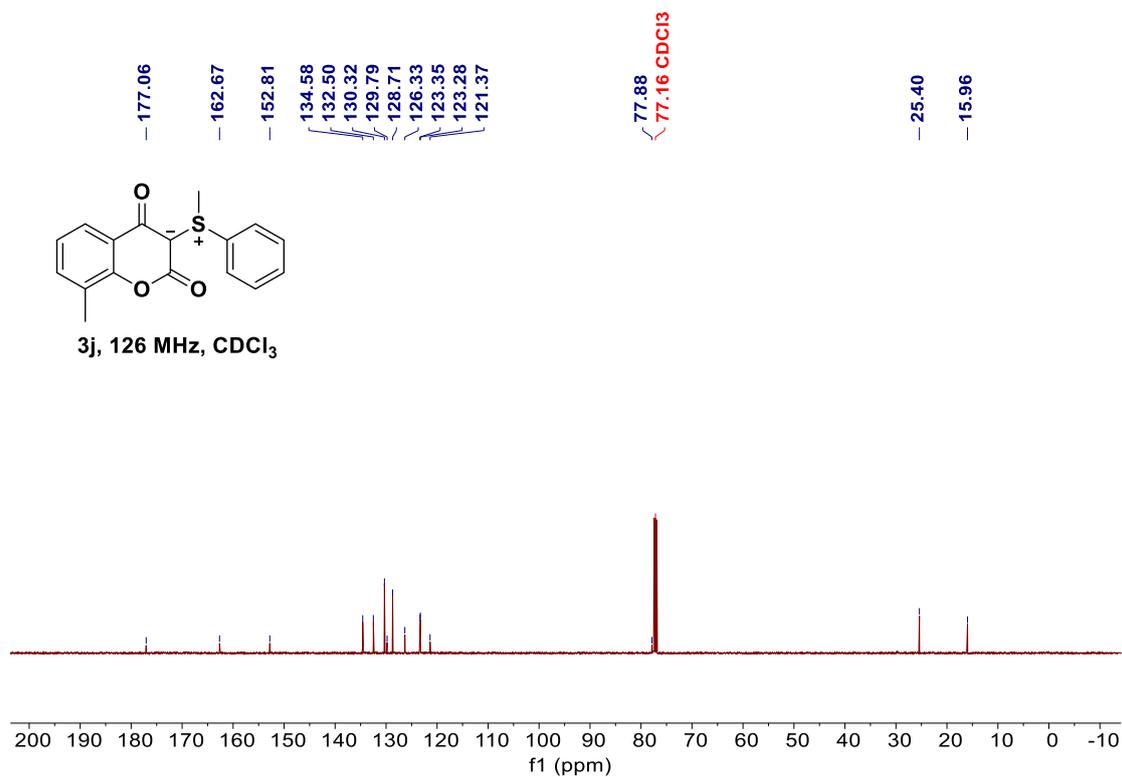
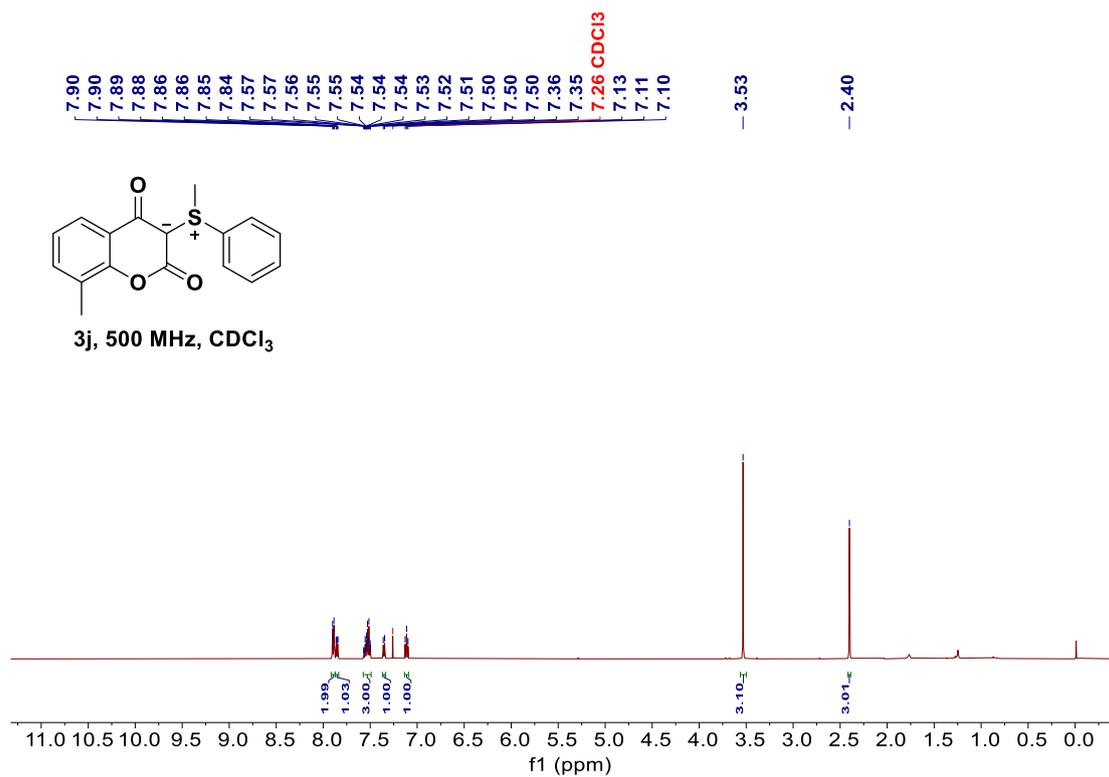


Ethyl (Z)-2-((4-methoxyphenyl)(8-methyl-2,4-dioxochroman-3-ylidene)- λ^4 -sulfaneyl)acetate

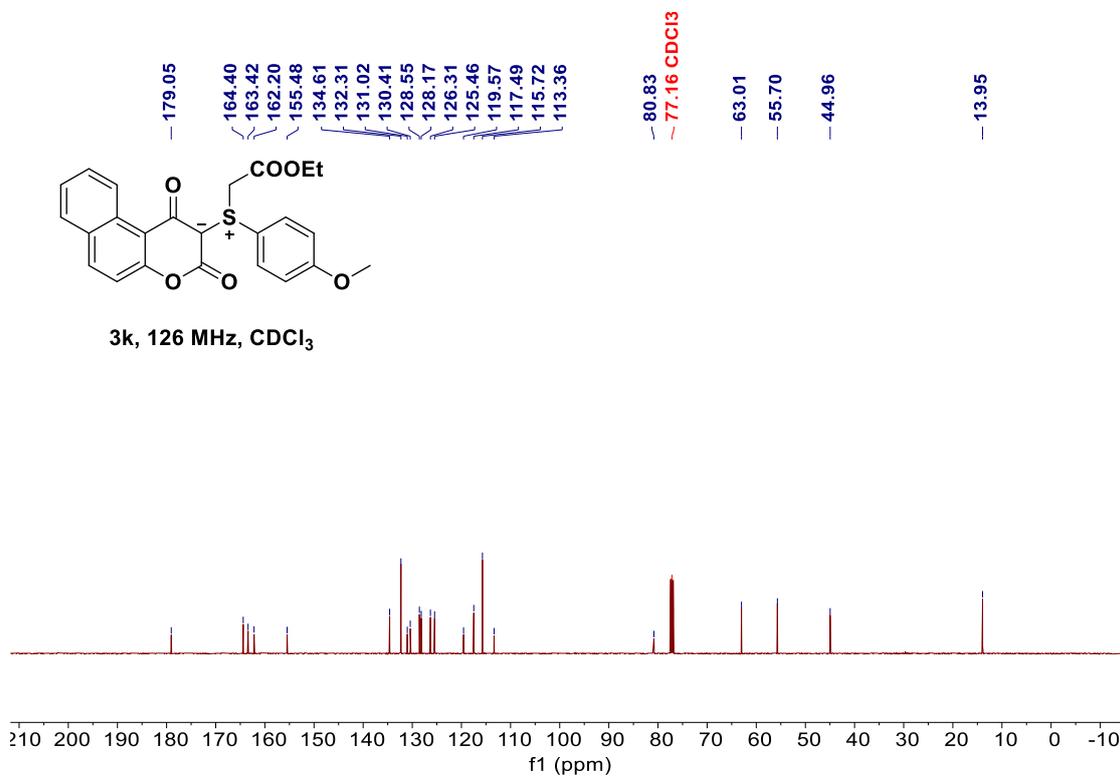
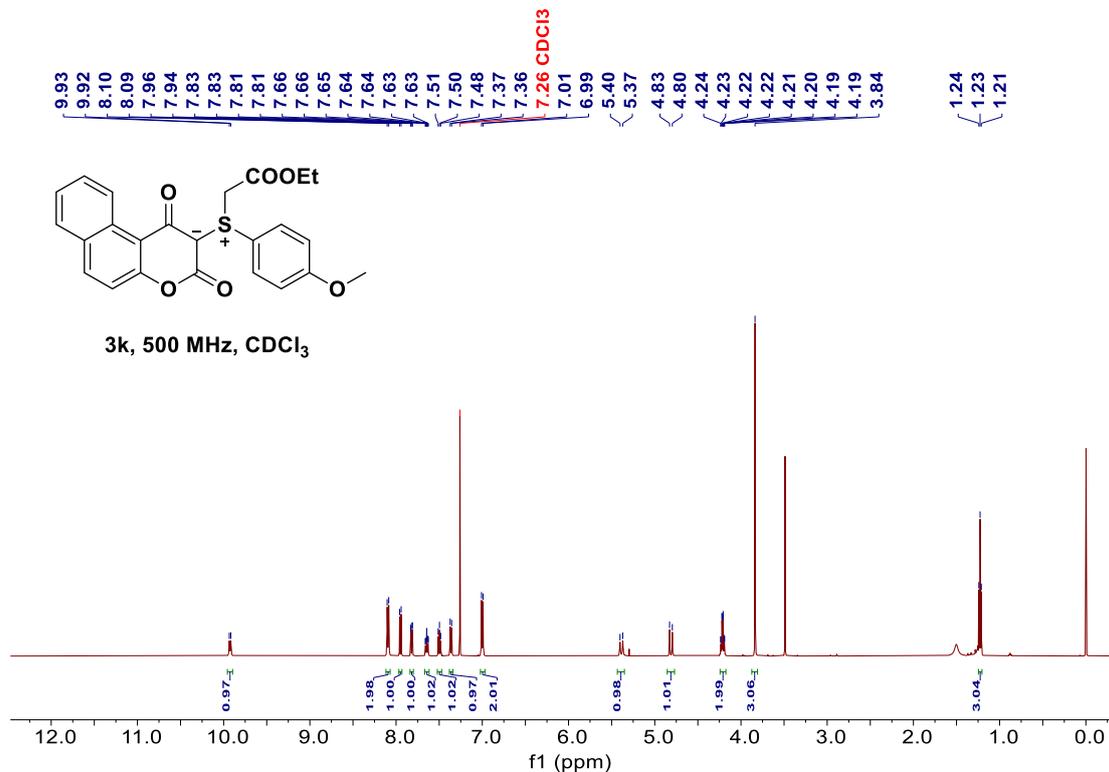
(3i)



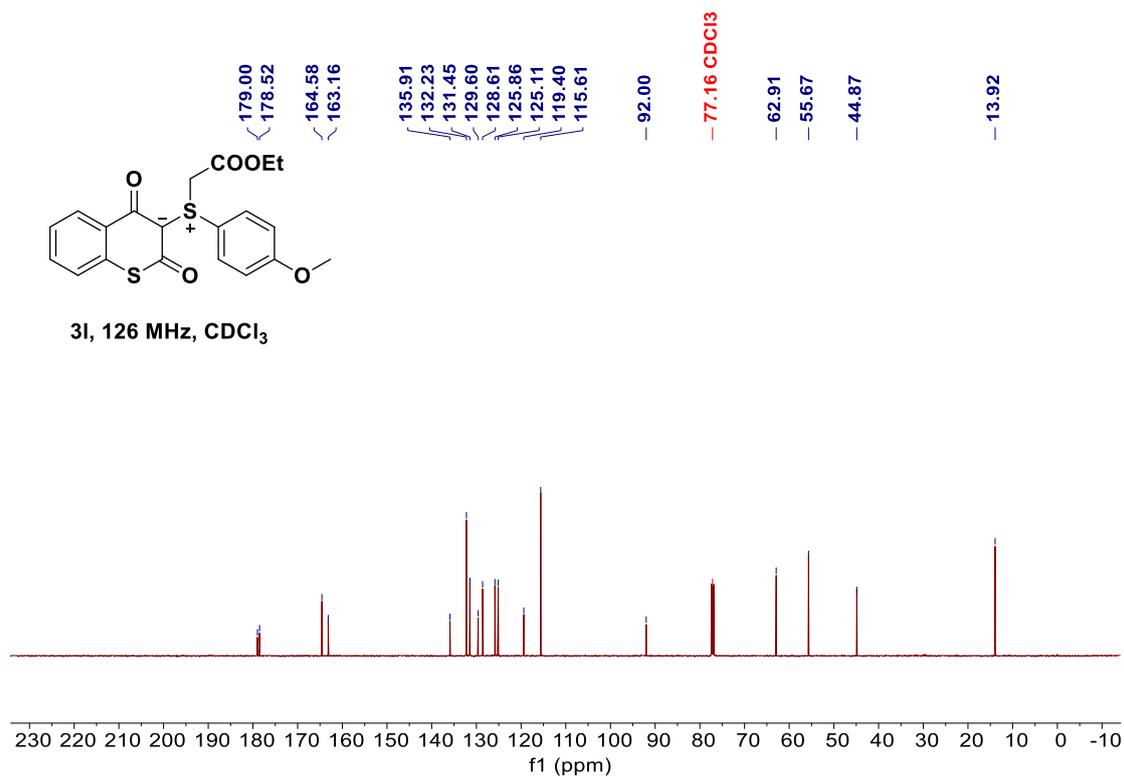
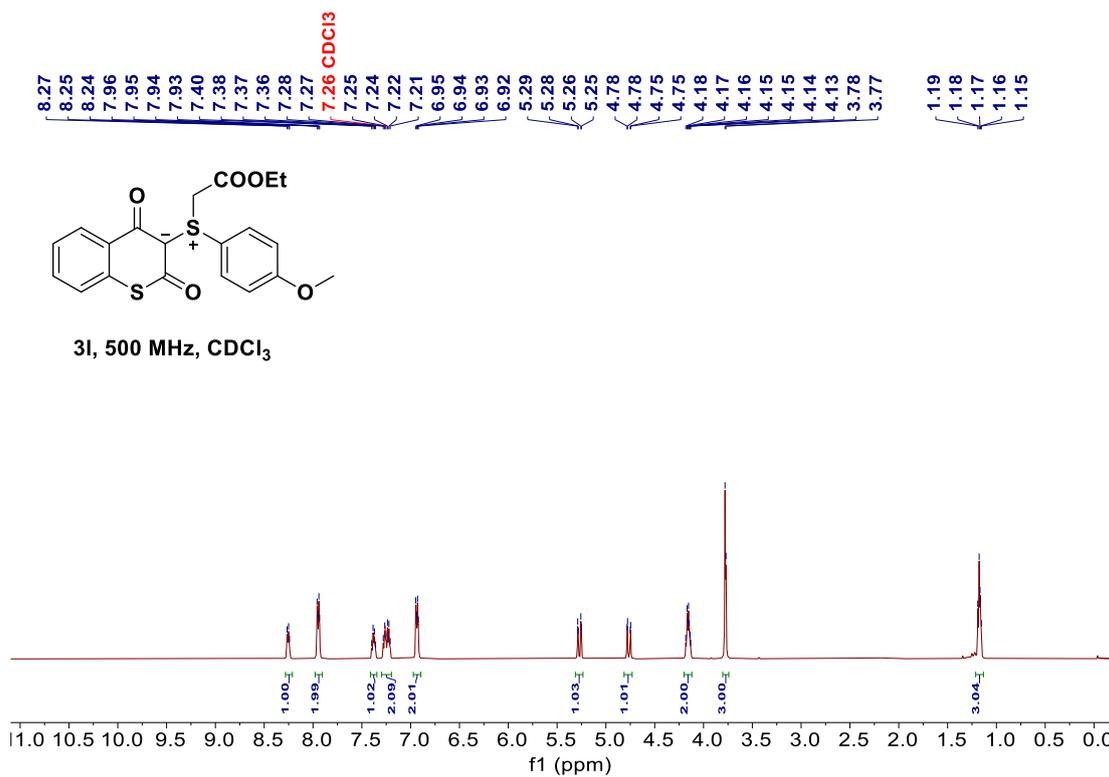
(Z)-8-methyl-3-(methyl(phenyl)- λ^4 -sulfanylidene)chromane-2,4-dione (3j)



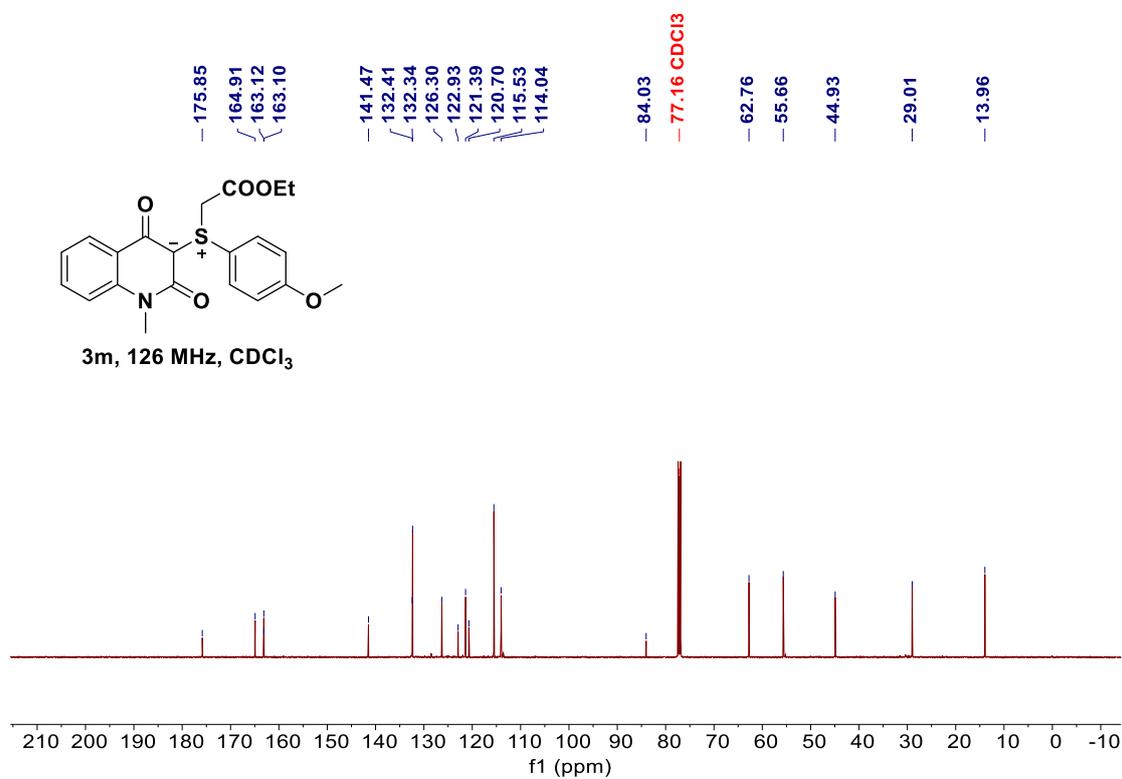
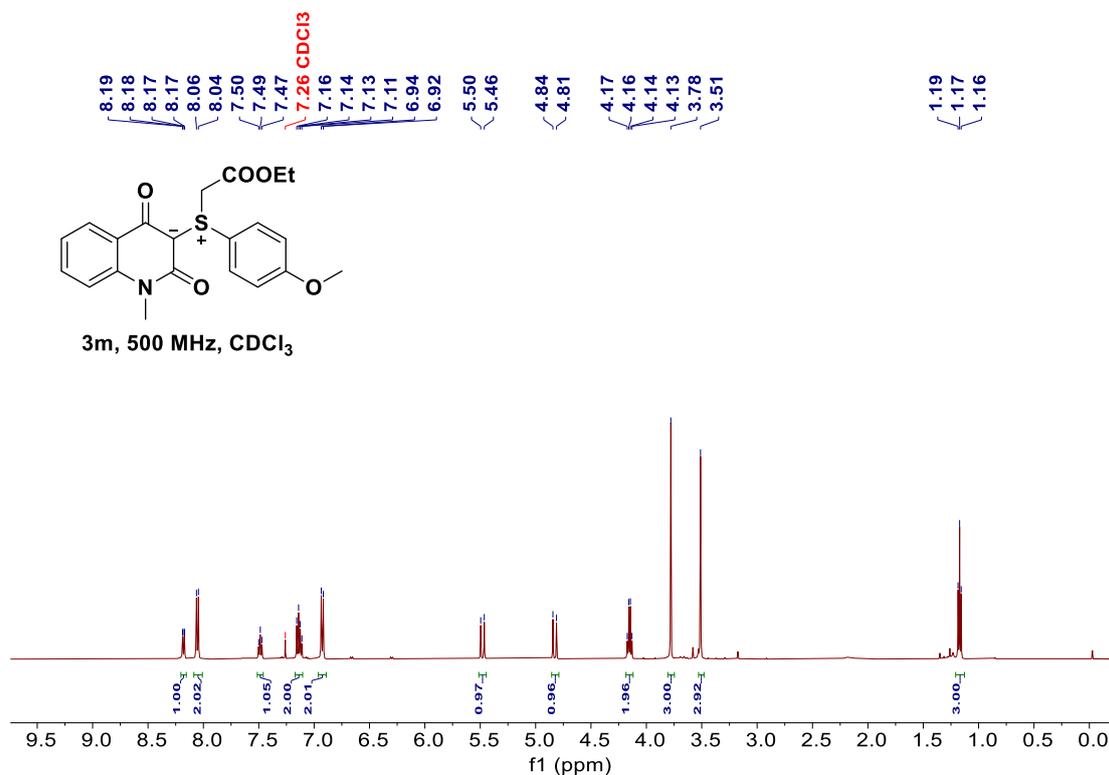
Ethyl (Z)-2-((1,3-dioxo-1H-benzo[f]chromen-2(3H)-ylidene)(4-methoxyphenyl)-λ⁴-sulfaneyl)acetate (3k)



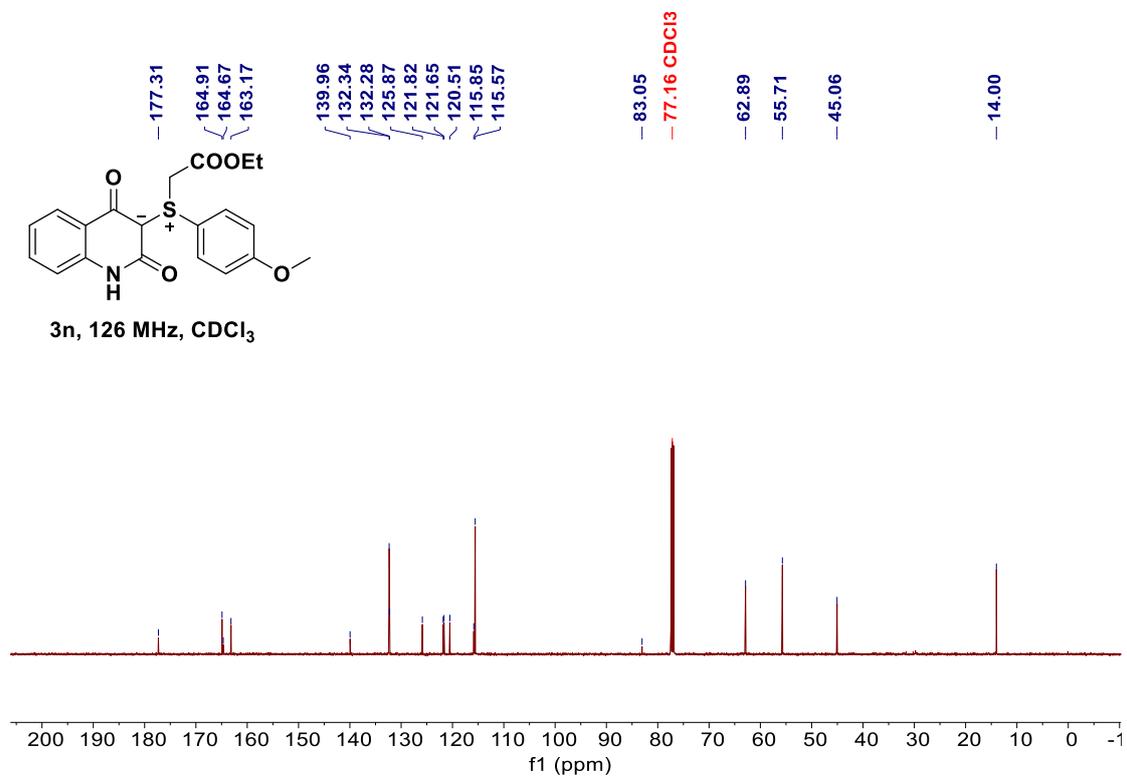
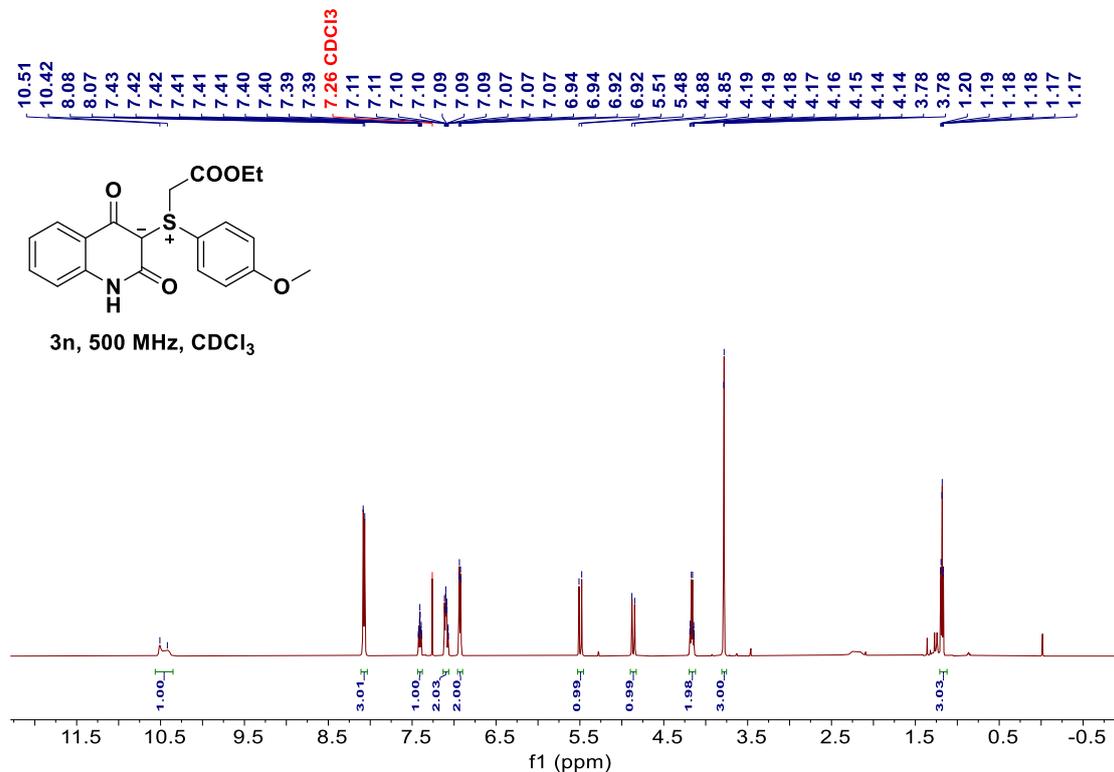
Ethyl (Z)-2-((2,4-dioxothiochroman-3-ylidene)(4-methoxyphenyl)-λ⁴-sulfanyl)acetate (3l)



Ethyl (Z)-2-((4-methoxyphenyl)(1-methyl-2,4-dioxo-1,4-dihydroquinolin-3(2H)-ylidene)- λ^4 -sulfaneyl)acetate (3m)

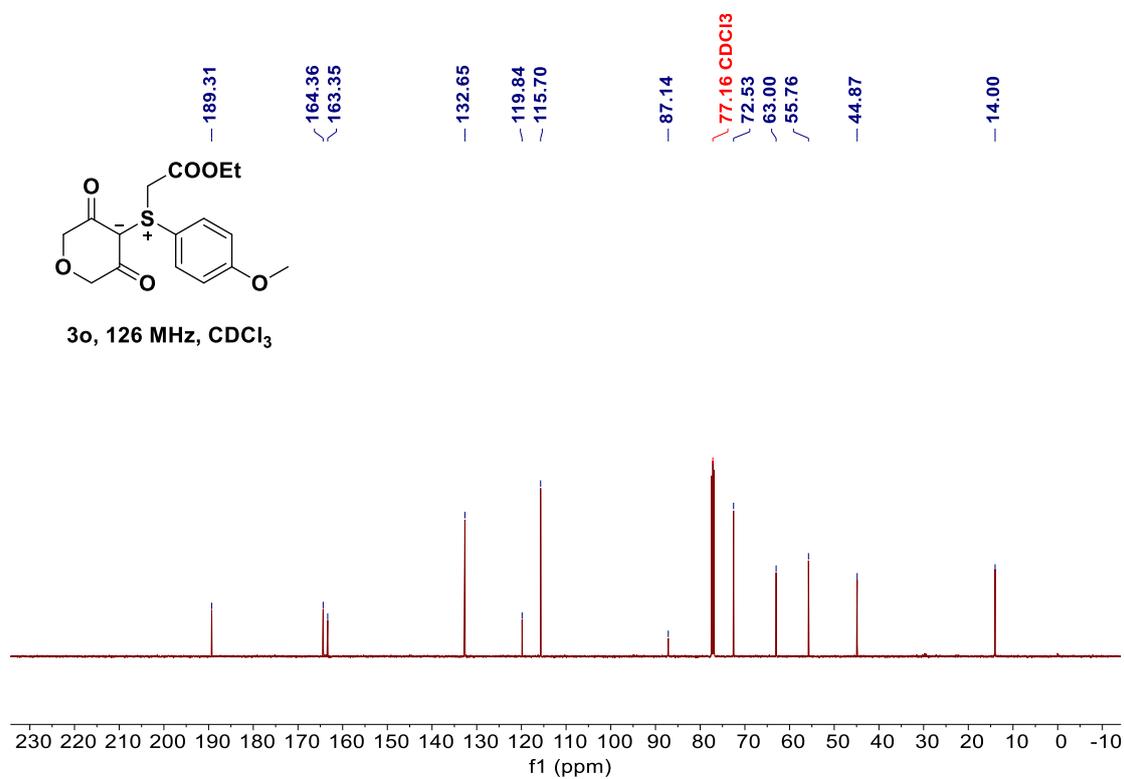
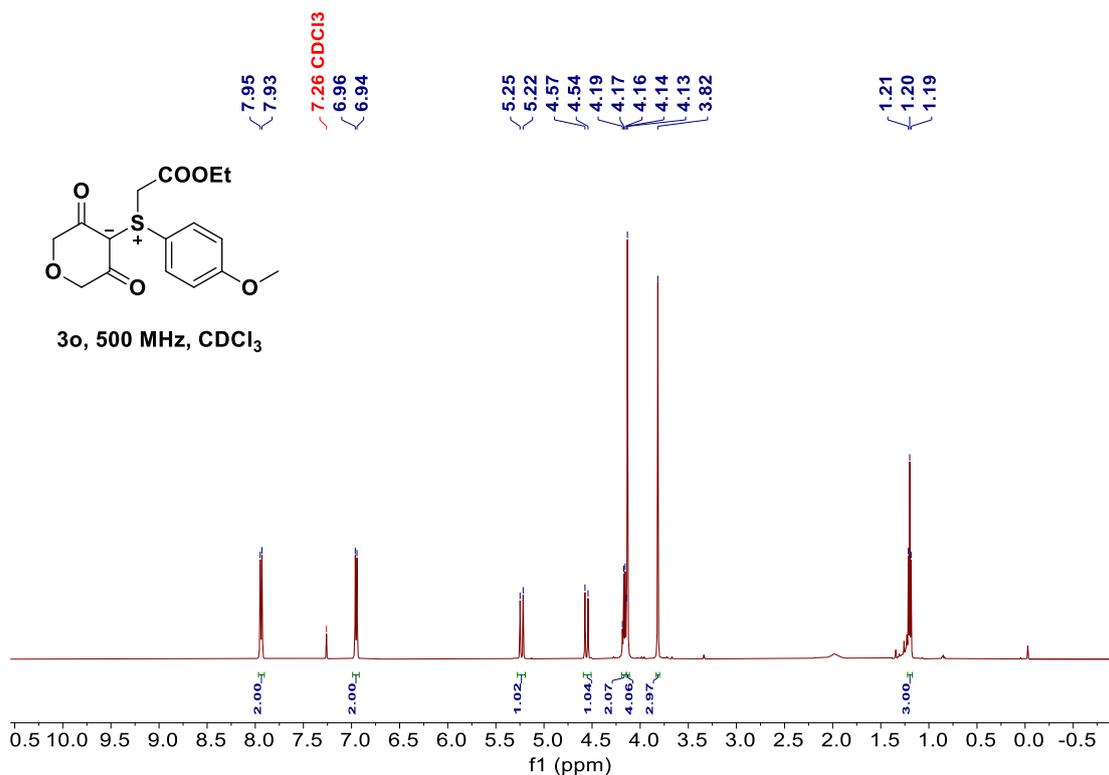


Ethyl (Z)-2-((2,4-dioxo-1,4-dihydroquinolin-3(2H)-ylidene)(4-methoxyphenyl)-λ⁴-sulfaneyl)acetate (3n)



Ethyl 2-((3,5-dioxotetrahydro-4H-pyran-4-ylidene)(4-methoxyphenyl)- λ^4 -sulfaneyl)acetate

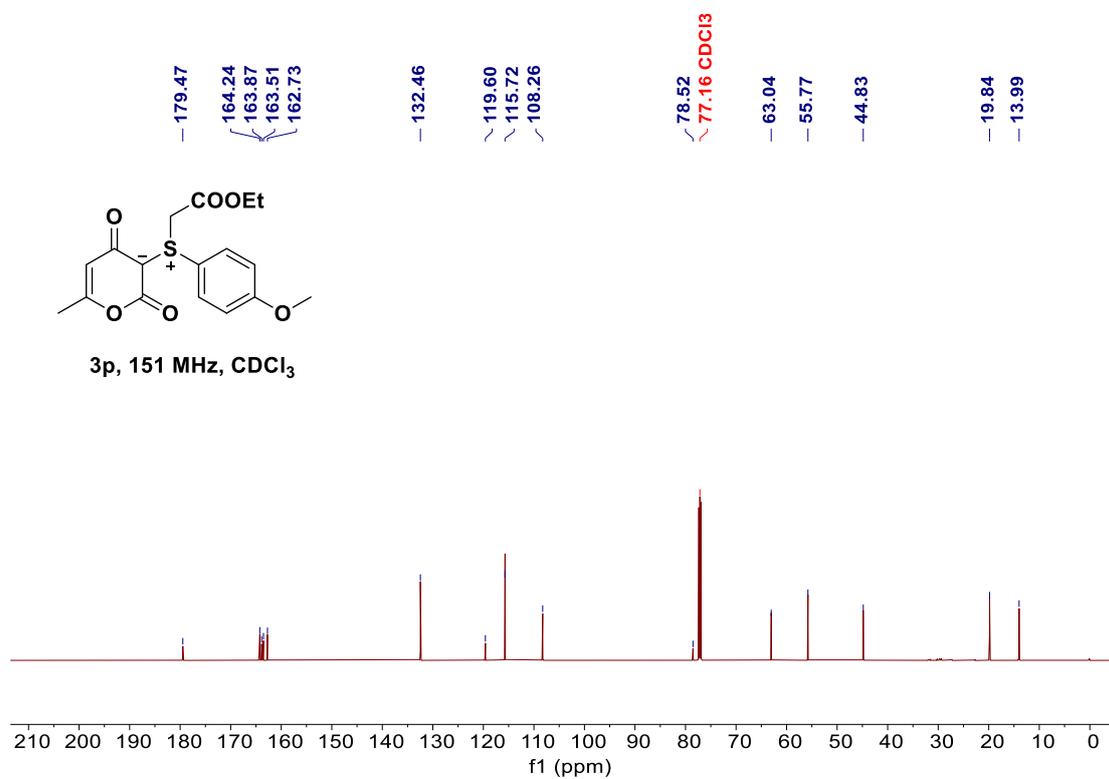
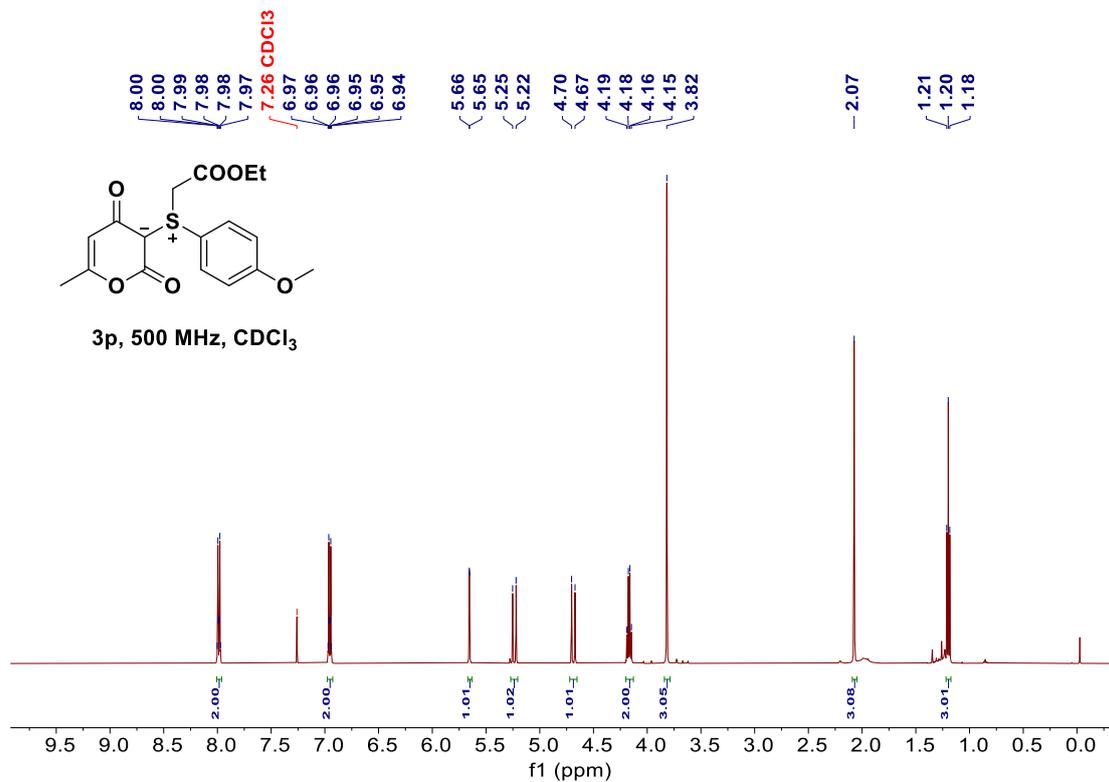
(3o)



Ethyl

(Z)-2-((4-methoxyphenyl)(6-methyl-2,4-dioxo-2H-pyran-3(4H)-ylidene)- λ^4 -

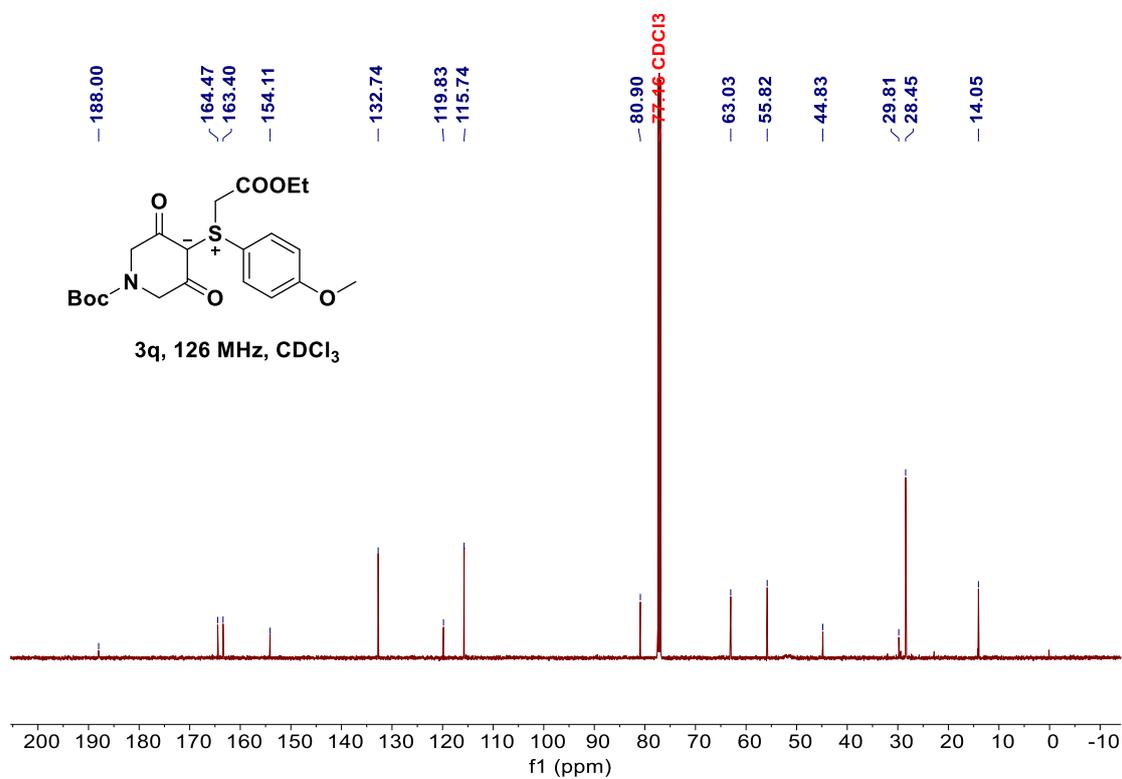
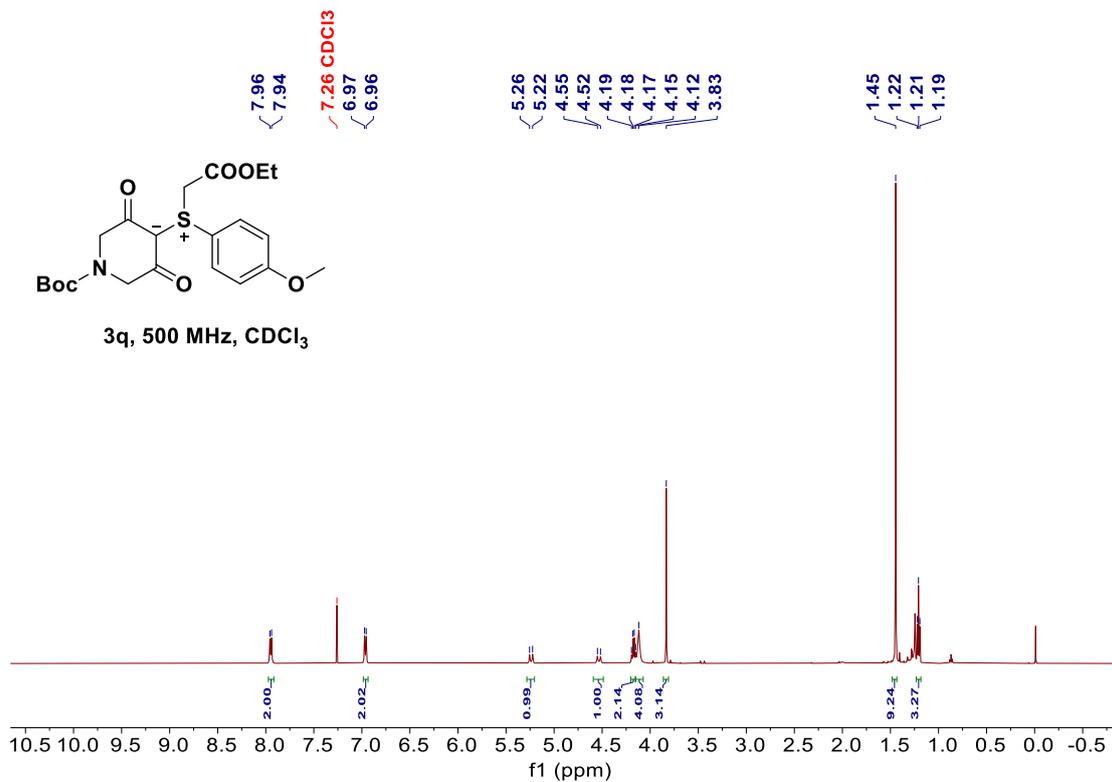
sulfaneyl)acetate (3p)



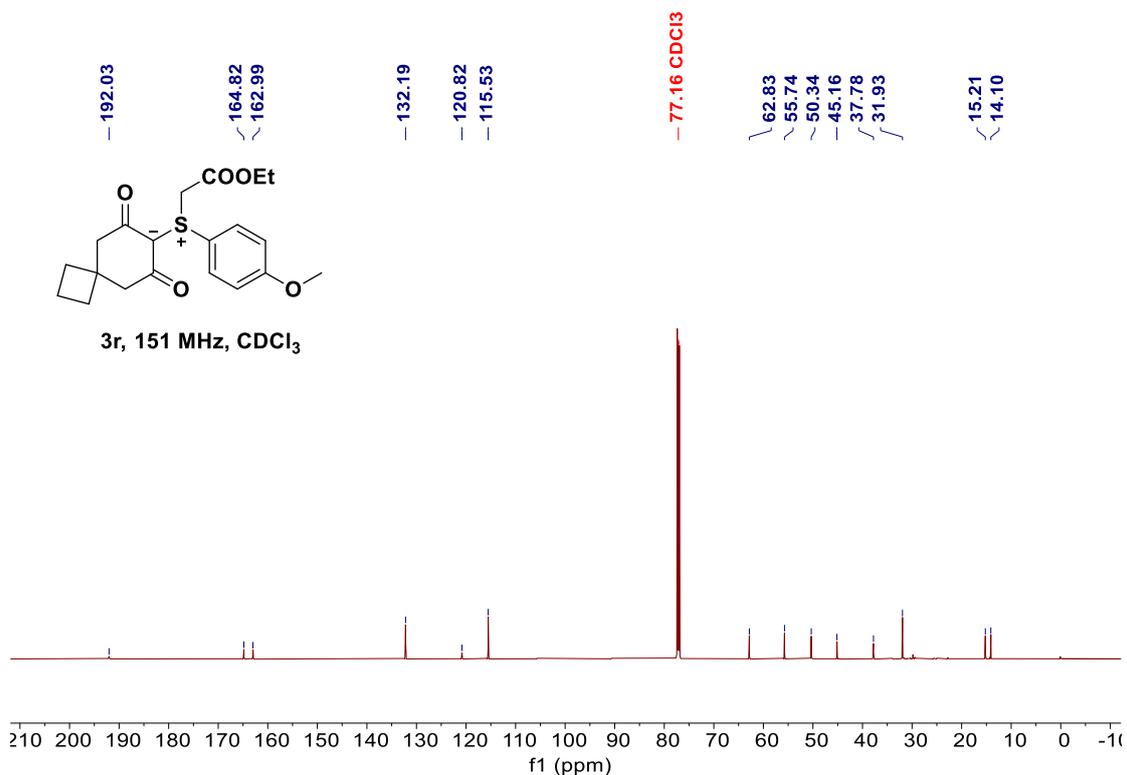
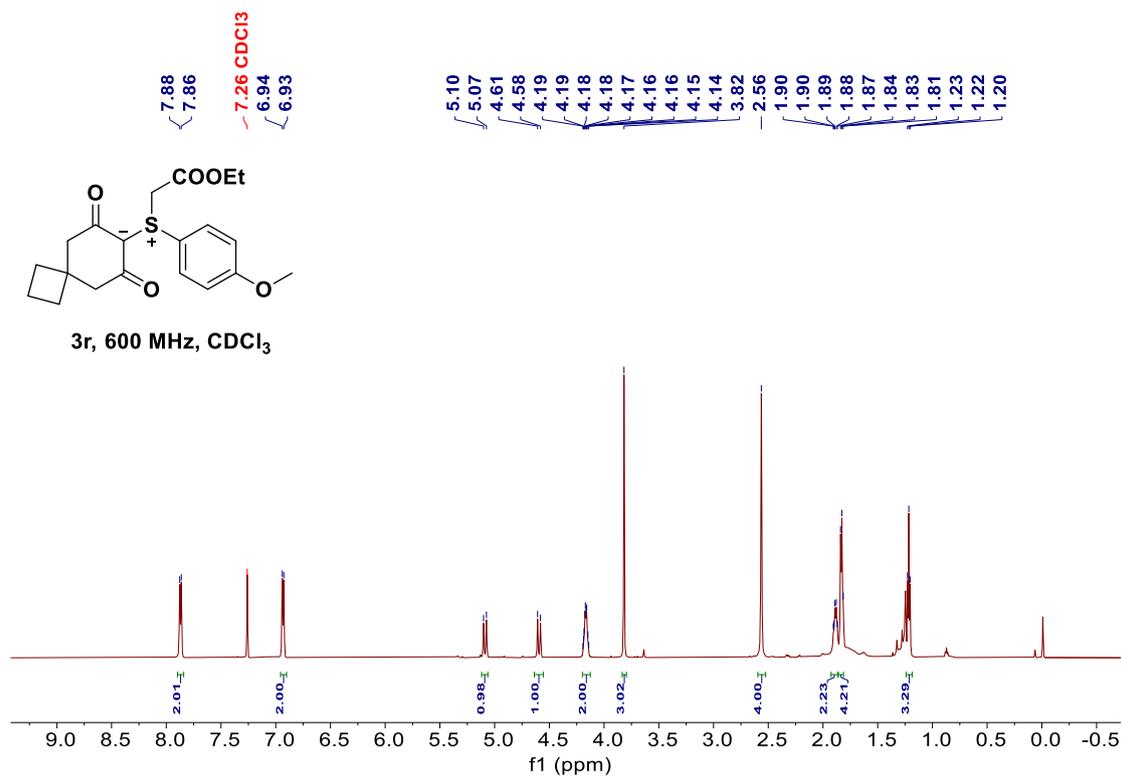
Tert-butyl

4-((2-ethoxy-2-oxoethyl)(4-methoxyphenyl)- λ^4 -sulfaneylidene)-3,5-

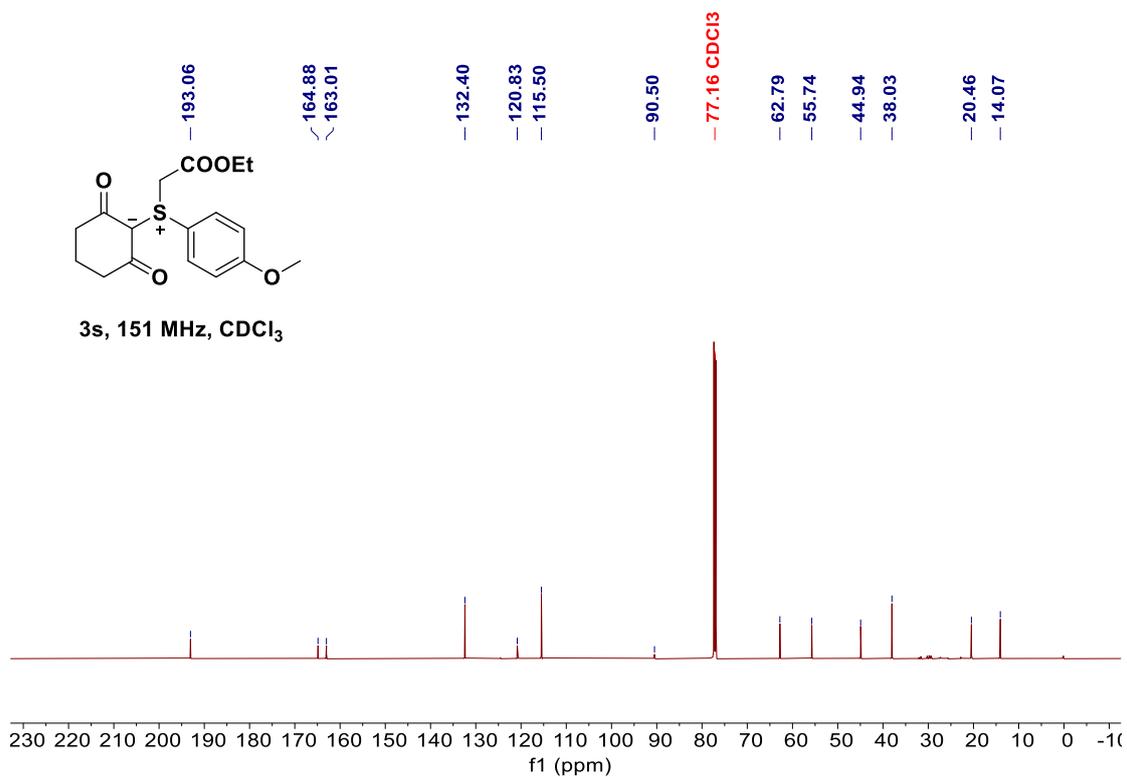
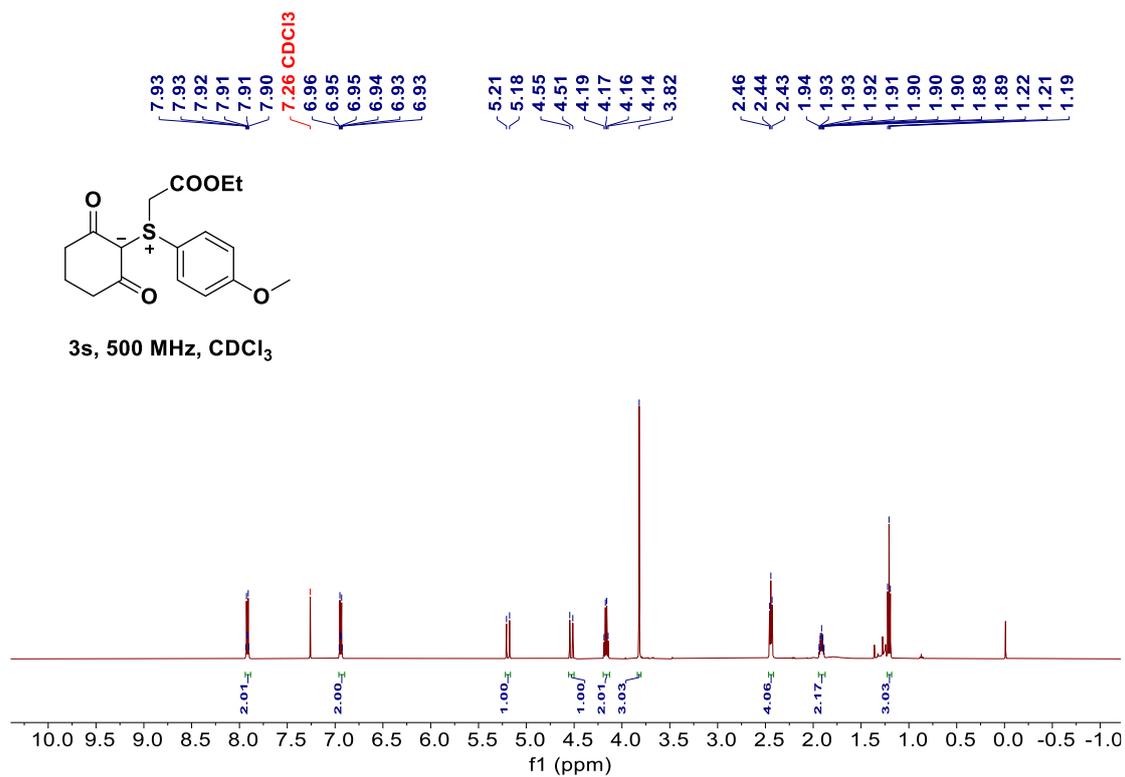
dioxopiperidine-1-carboxylate (3q)



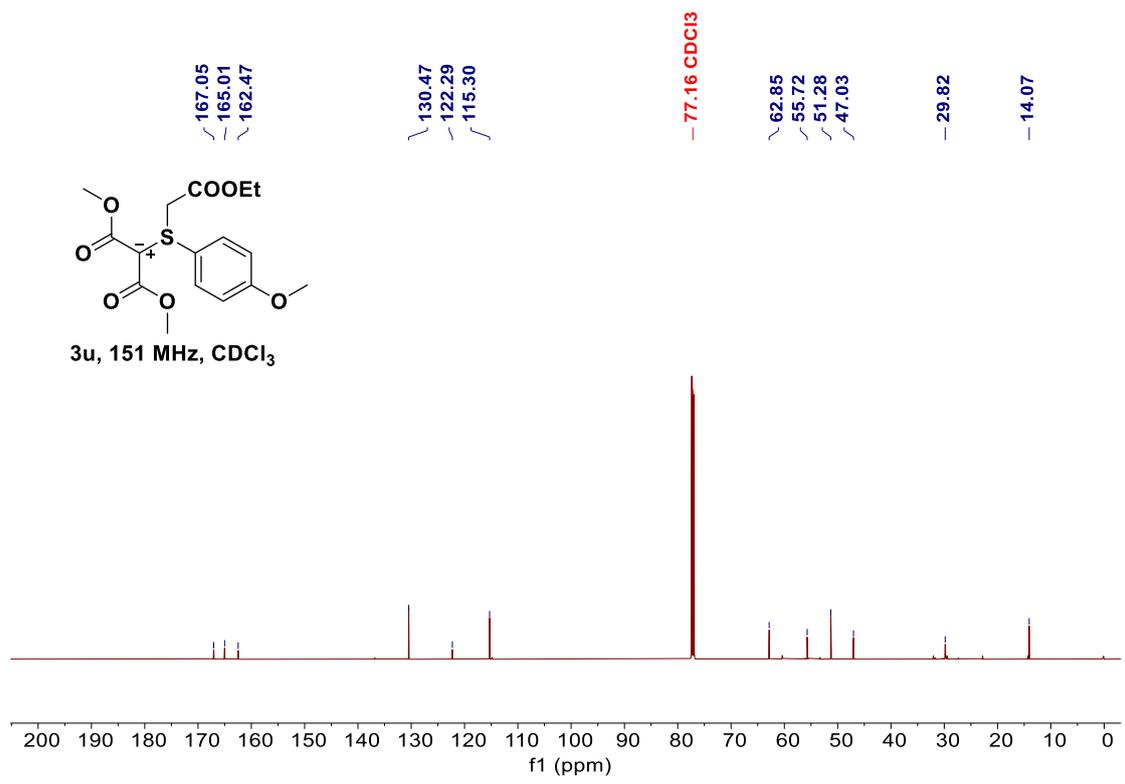
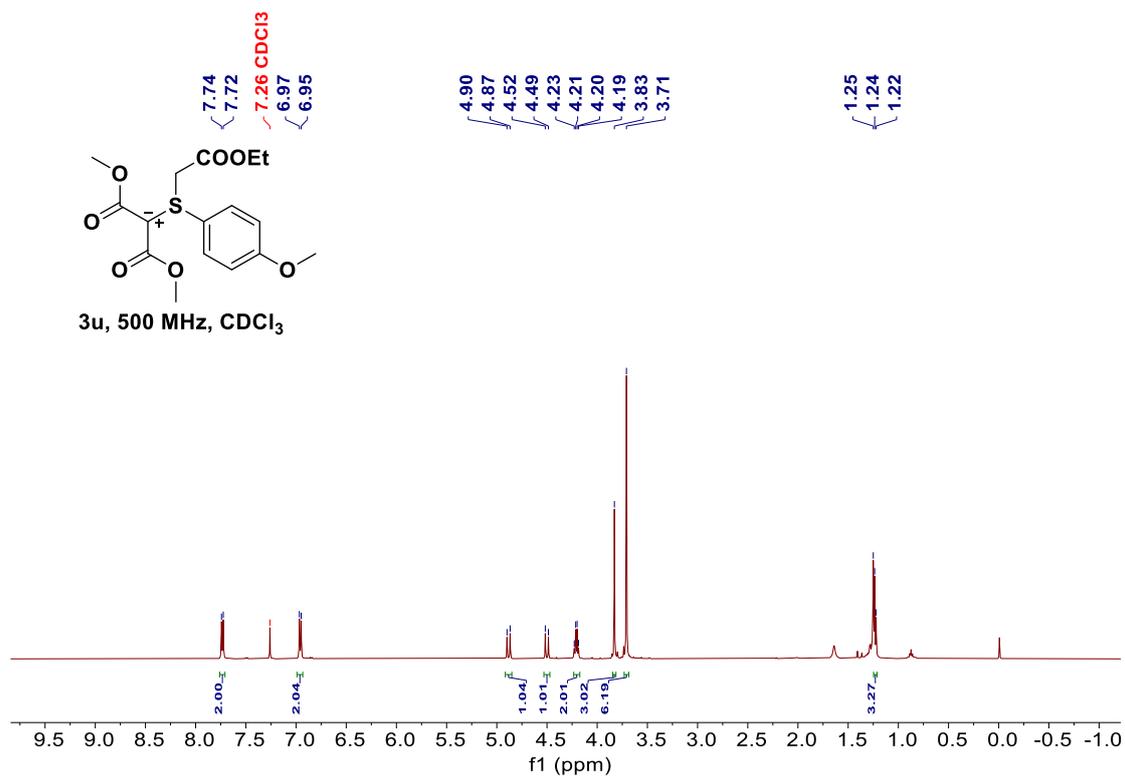
Ethyl 2-((6,8-dioxospiro[3.5]nonan-7-ylidene)(4-methoxyphenyl)- λ^4 -sulfaneyl)acetate (3r)



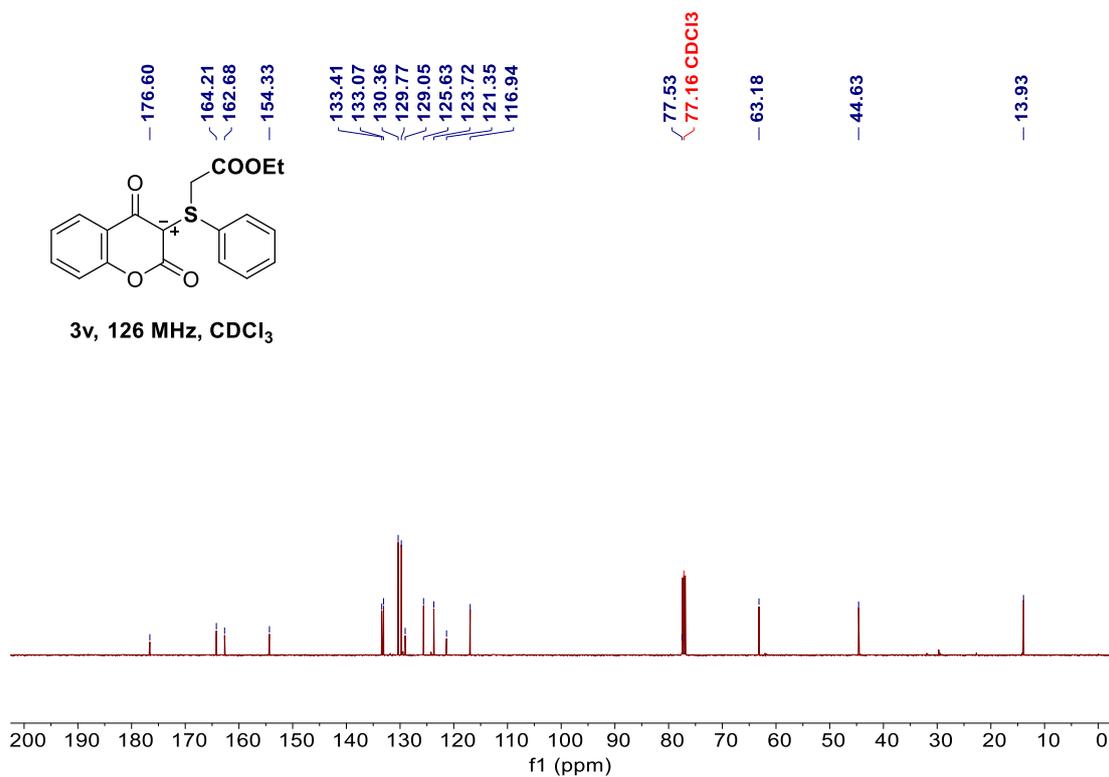
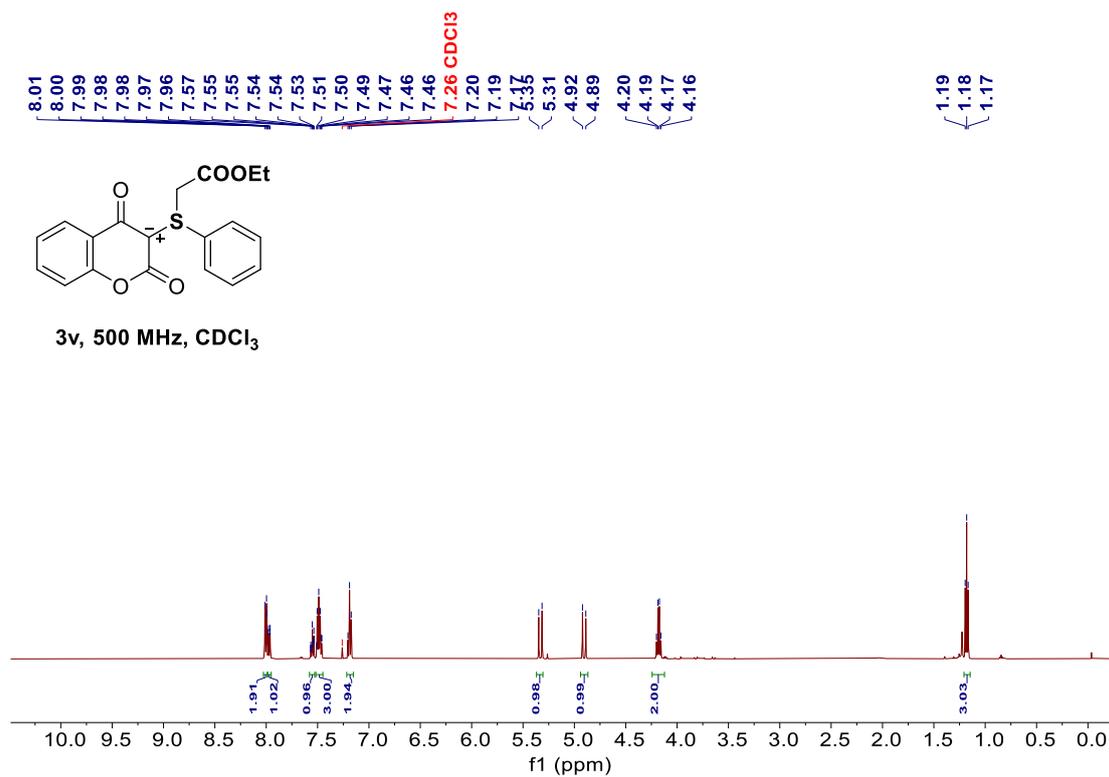
Ethyl 2-((2,6-dioxocyclohexylidene)(4-methoxyphenyl)- λ^4 -sulfanyl)acetate (3s)



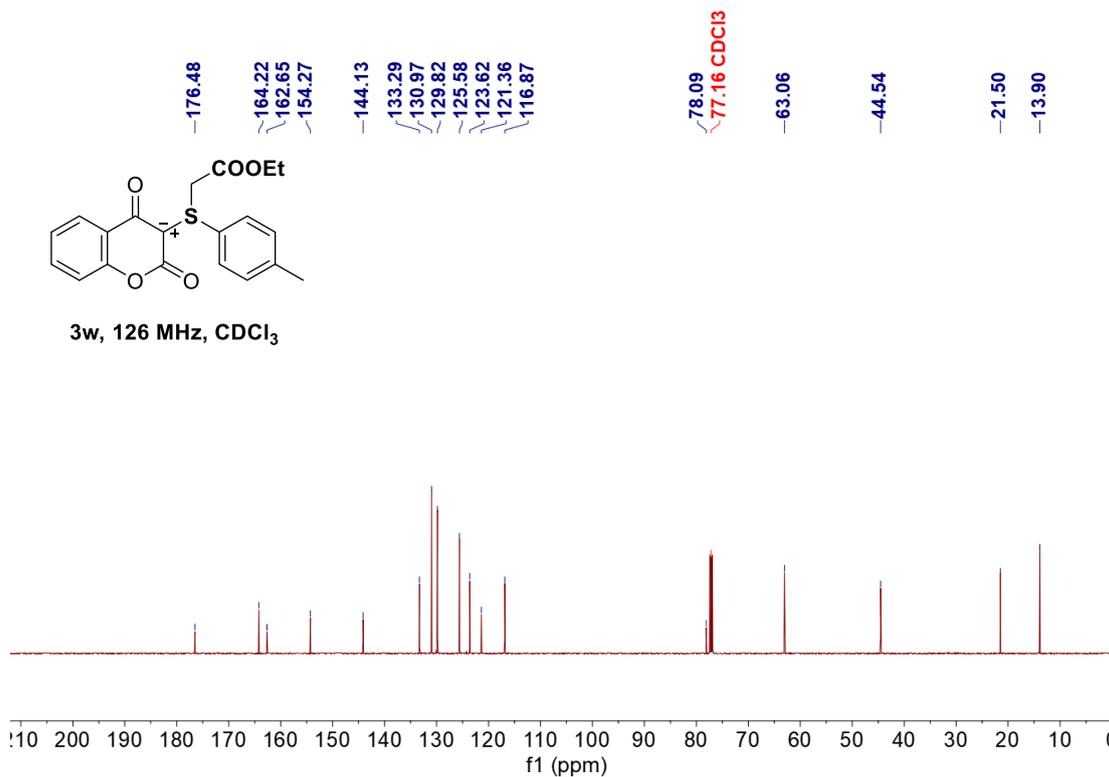
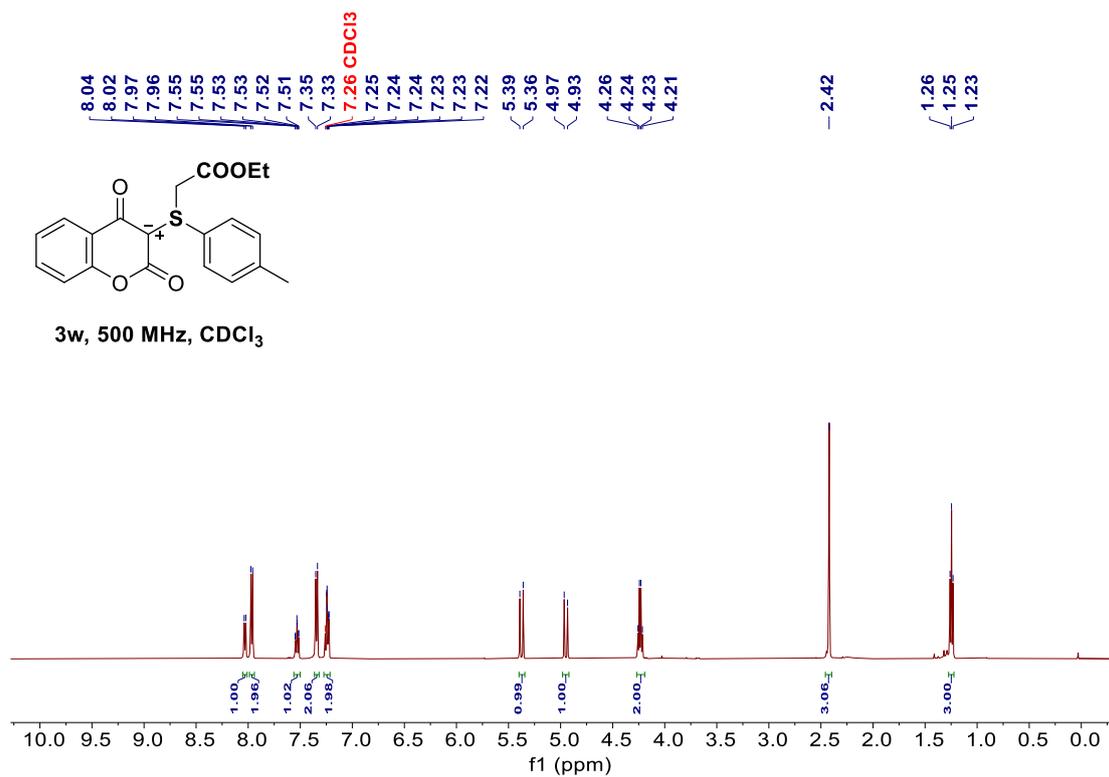
Dimethyl 2-((2-ethoxy-2-oxoethyl)(4-methoxyphenyl)- λ^4 -sulfanylidene)malonate (3u)



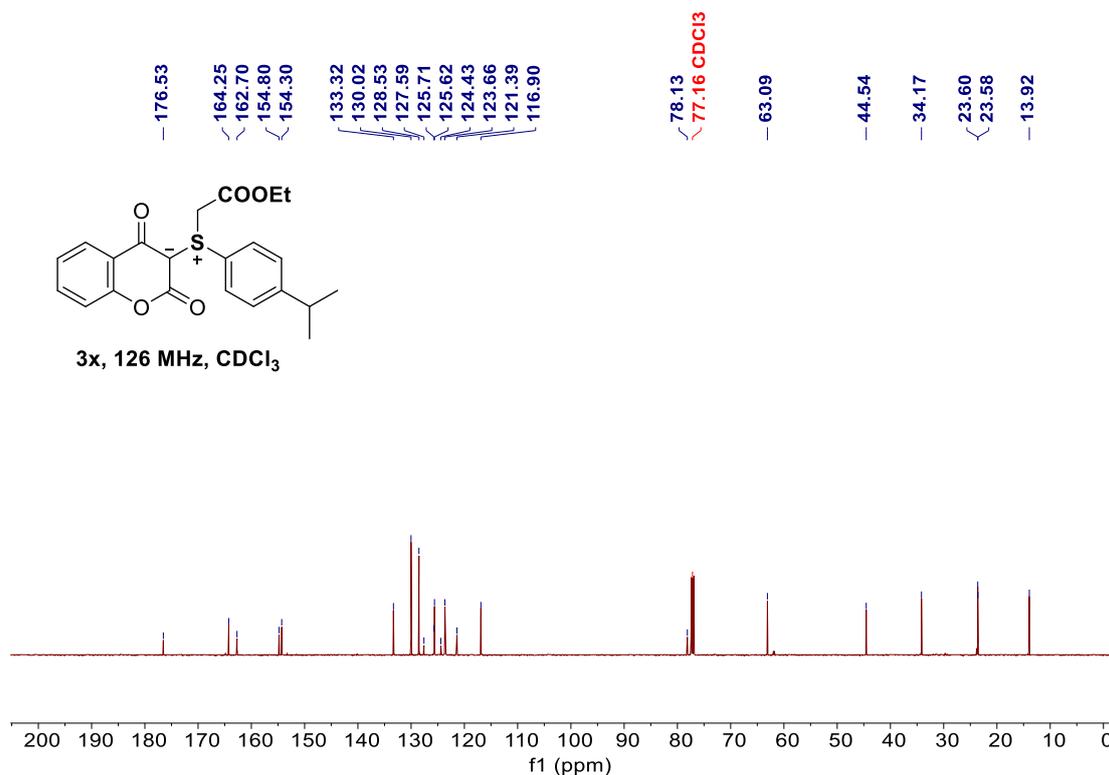
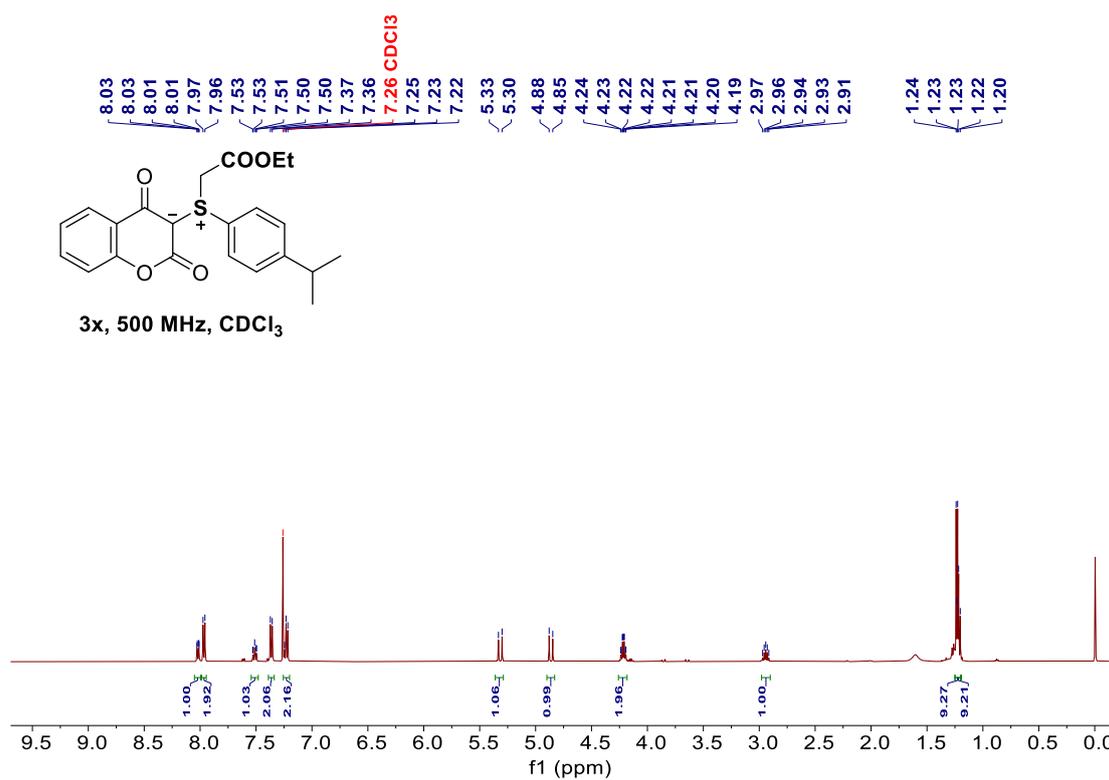
Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(phenyl)- λ^4 -sulfaneyl)acetate (3v)



Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(p-tolyl)- λ^4 -sulfanyl)acetate (3w)

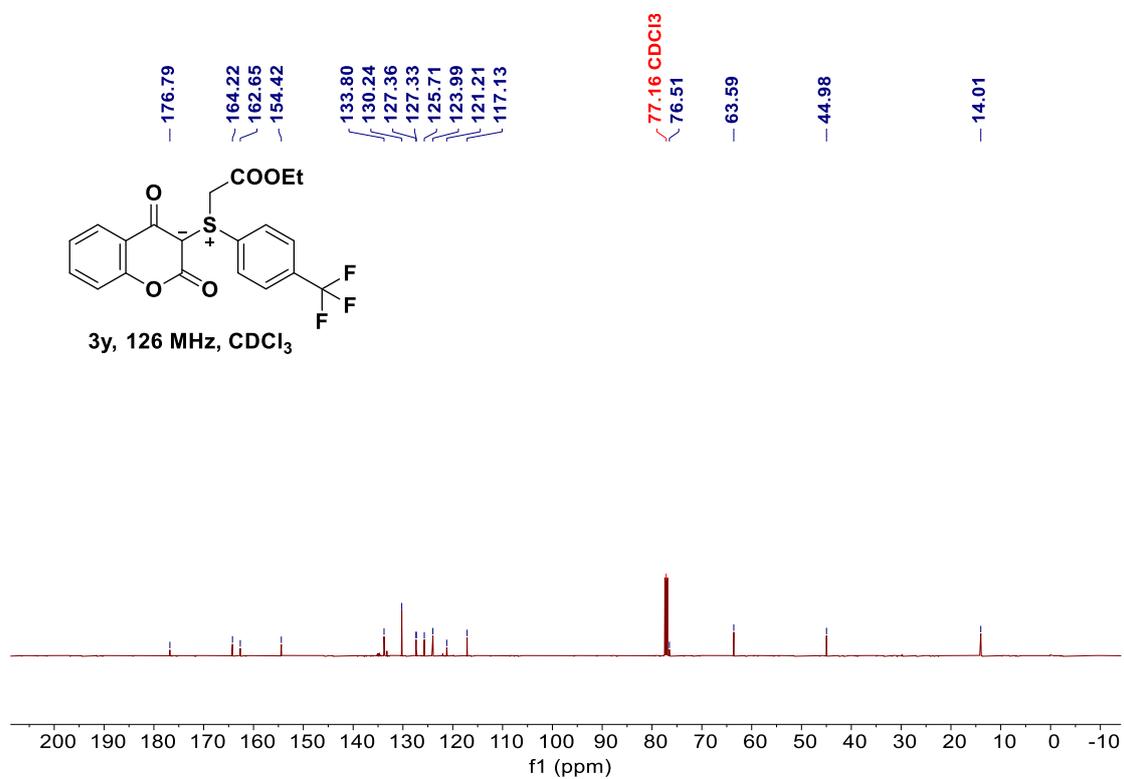
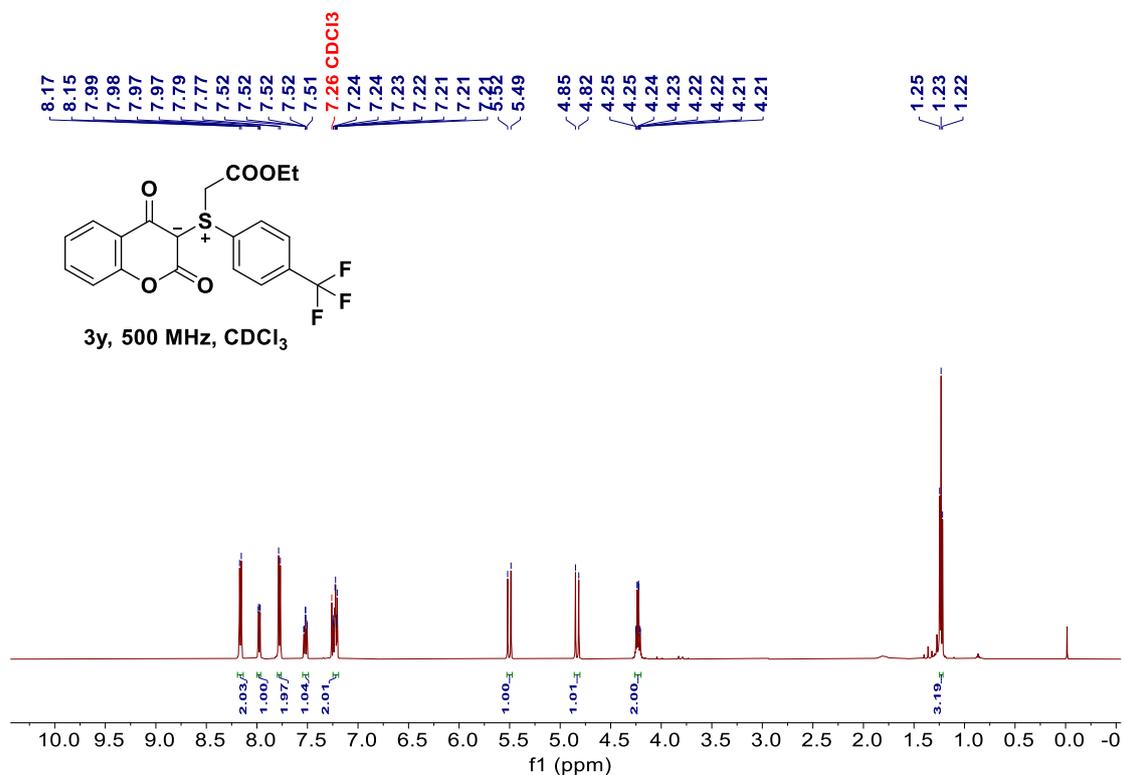


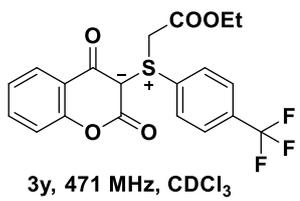
Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(4-isopropylphenyl)- λ^4 -sulfaneyl)acetate (3x)



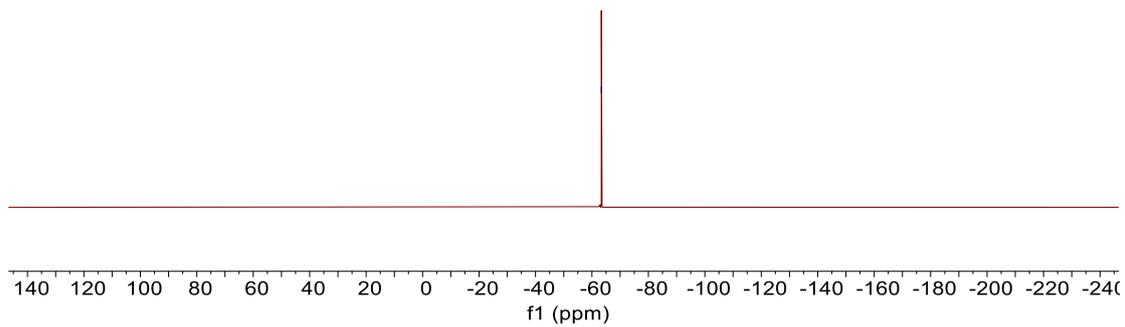
Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(4-(trifluoromethyl)phenyl)-λ⁴-sulfaneyl)acetate

(3y)

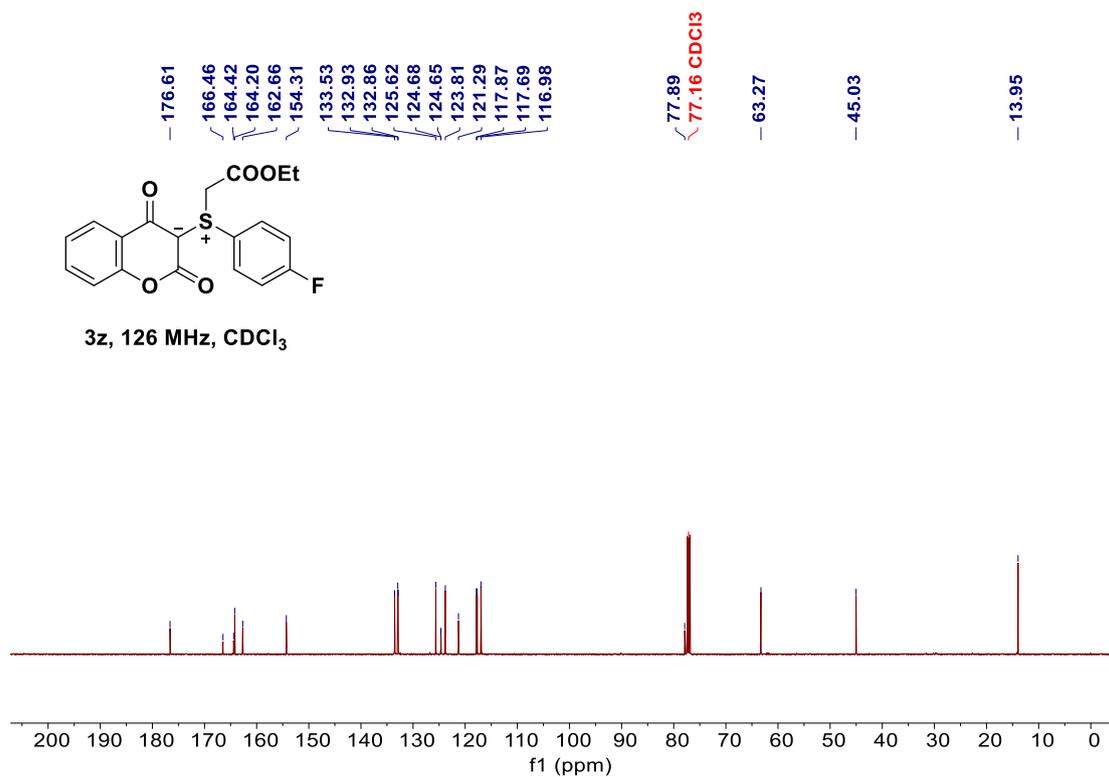
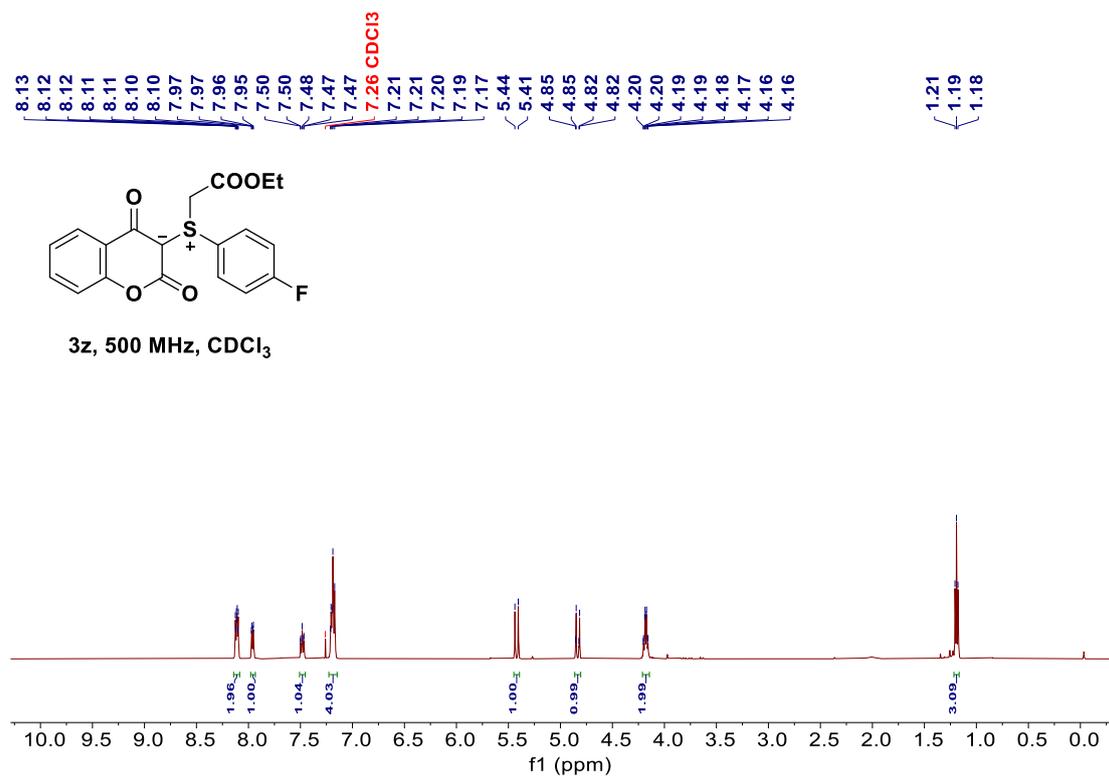


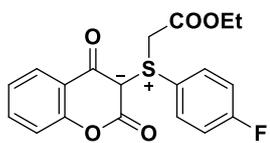


-63.33

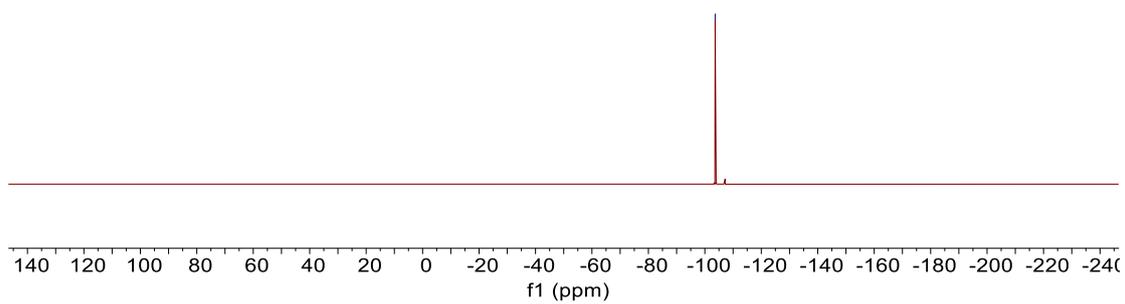


Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(4-fluorophenyl)- λ^4 -sulfanyl)acetate (3z)



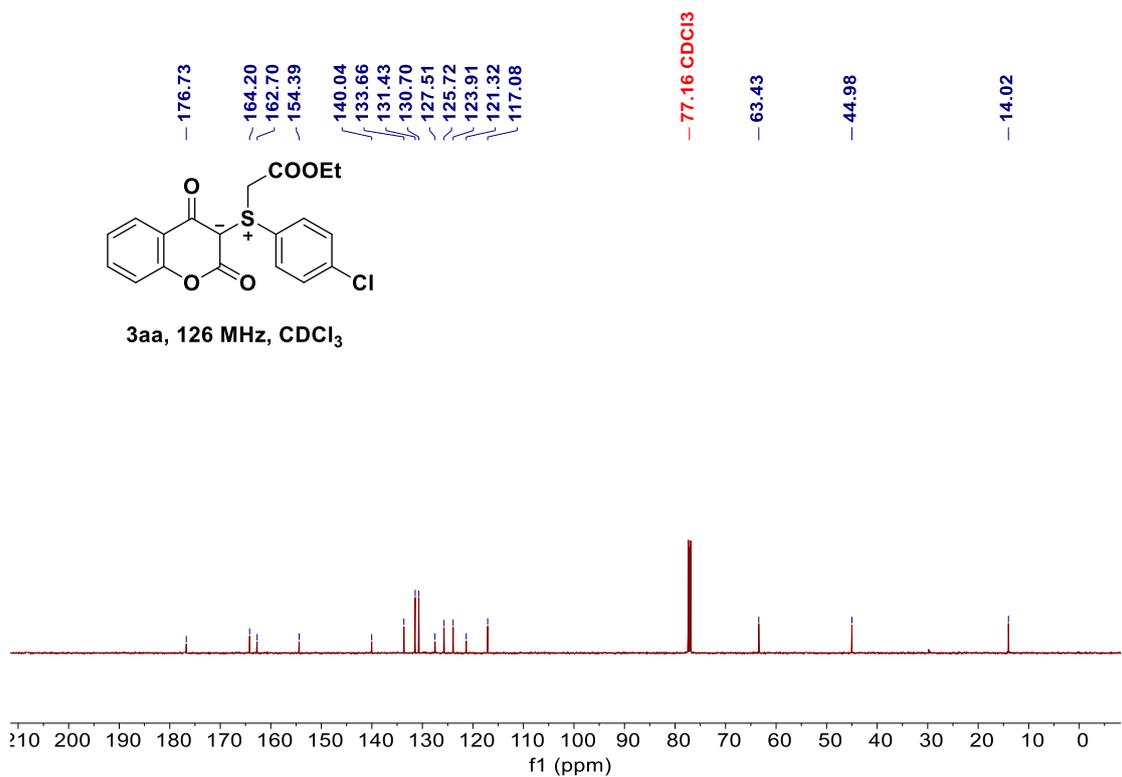
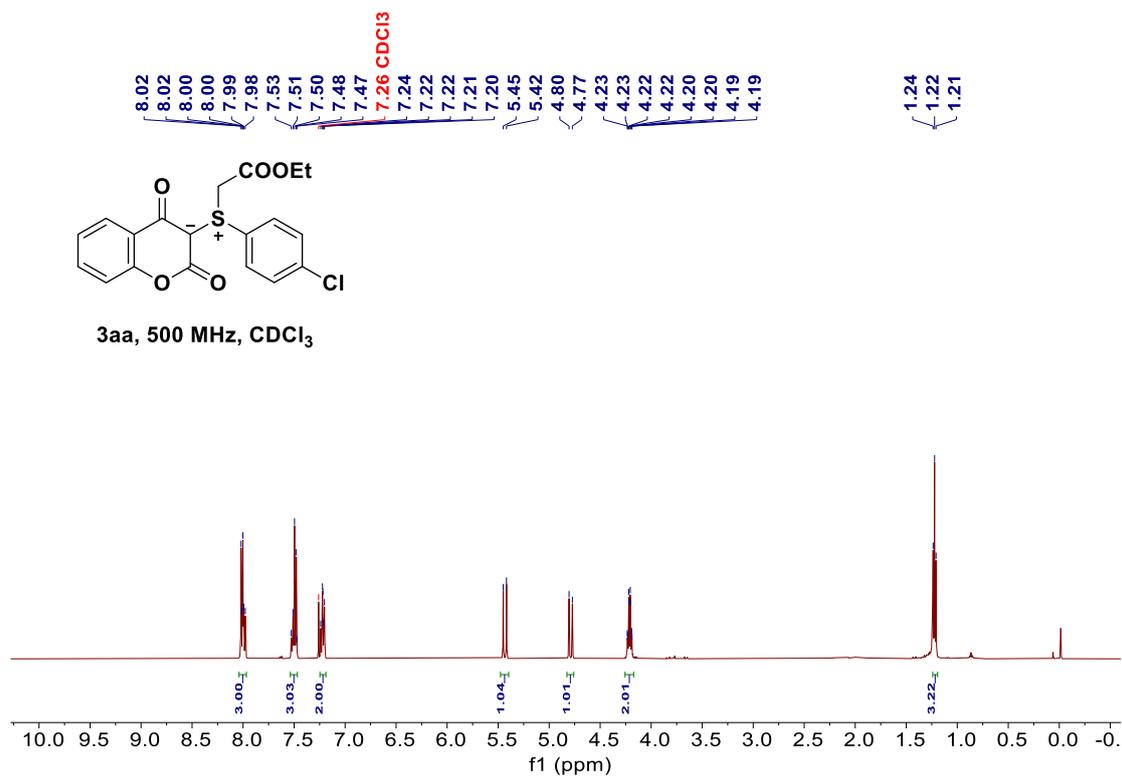


3z, 471 MHz, CDCl₃

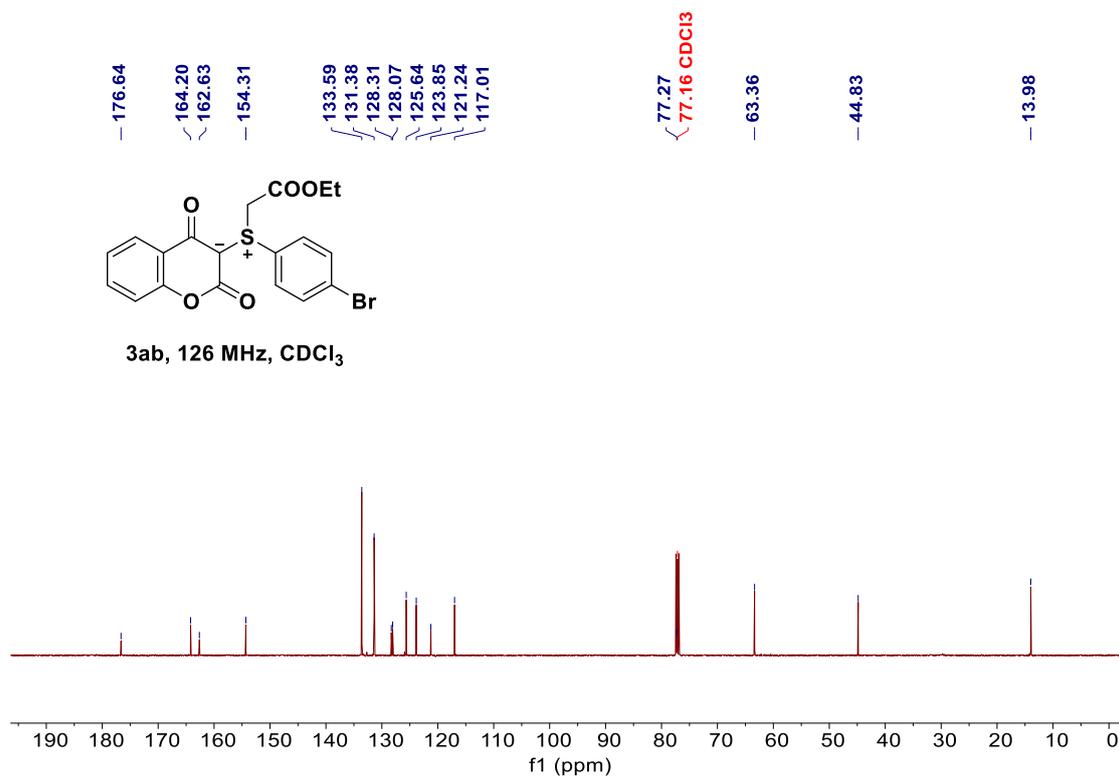
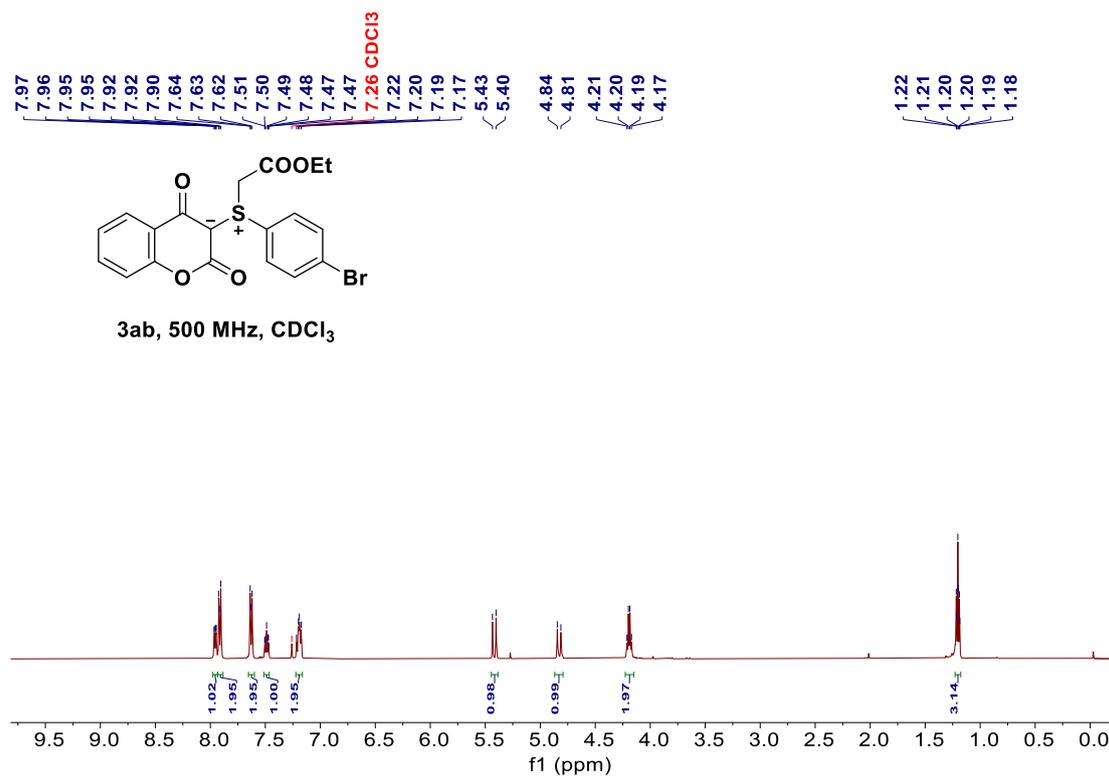


-103.65

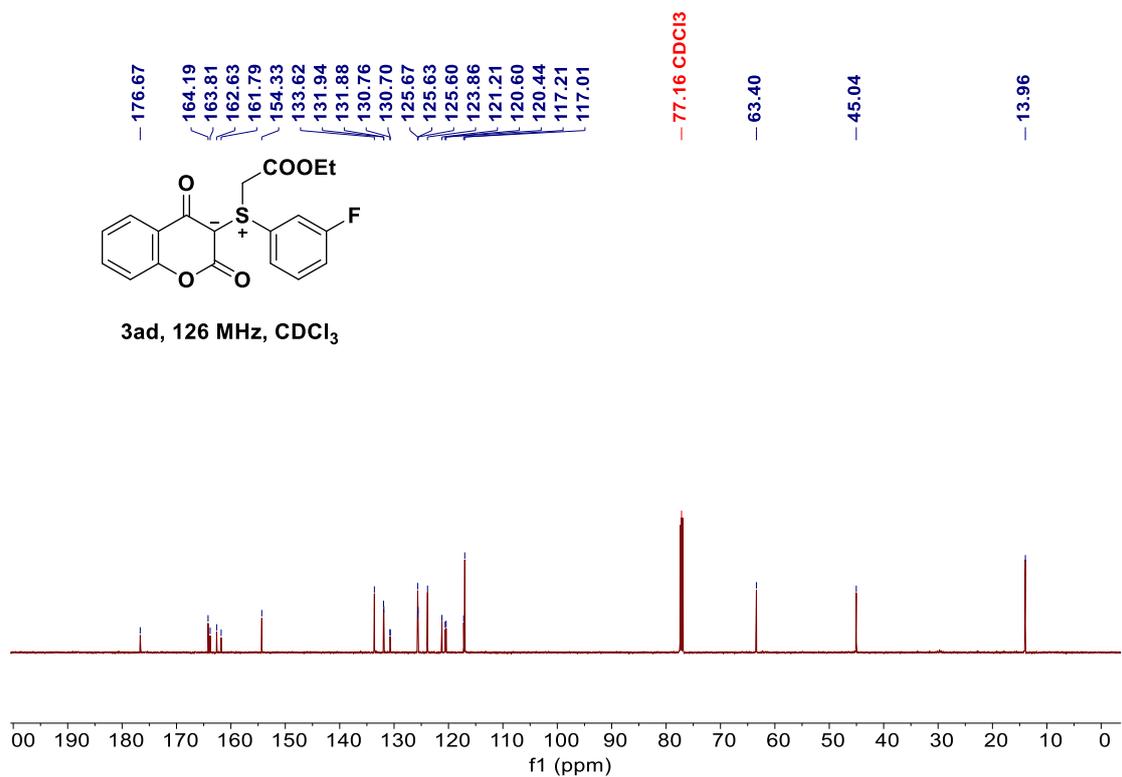
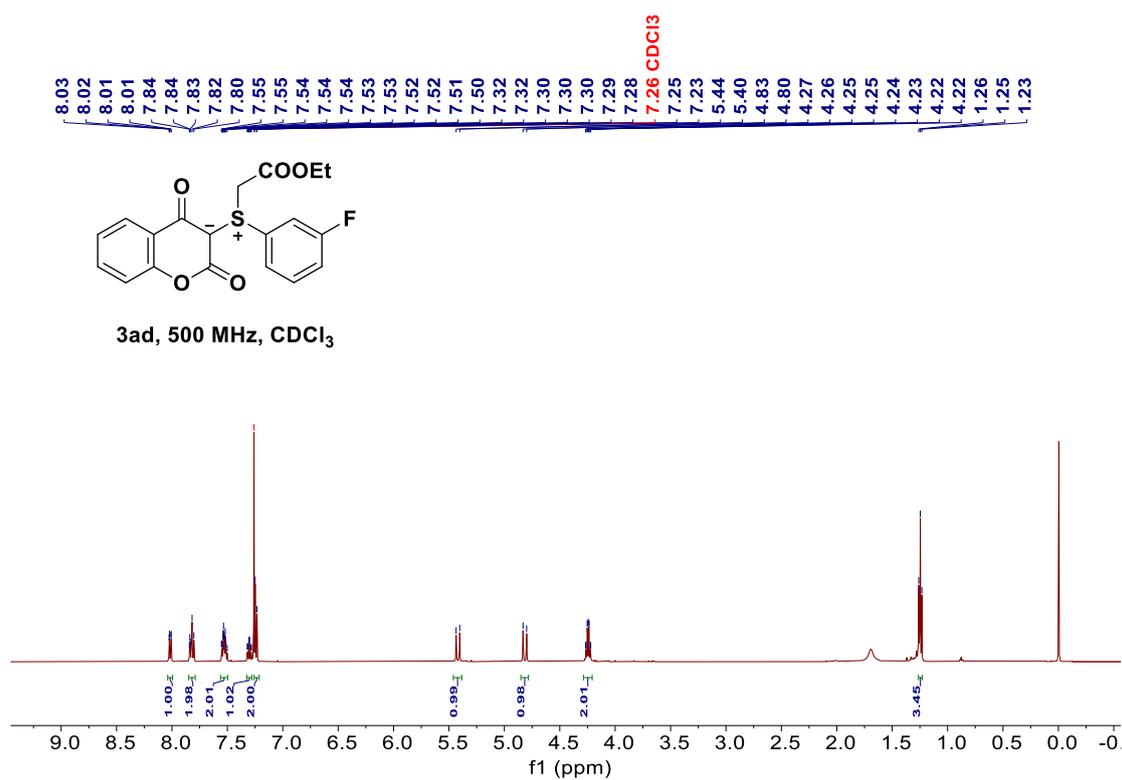
Ethyl (Z)-2-((4-chlorophenyl)(2,4-dioxochroman-3-ylidene)- λ^4 -sulfaneyl)acetate (3aa)

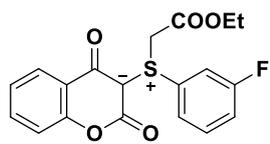


Ethyl (Z)-2-((4-bromophenyl)(2,4-dioxochroman-3-ylidene)- λ^4 -sulfaneyl)acetate (3ab)

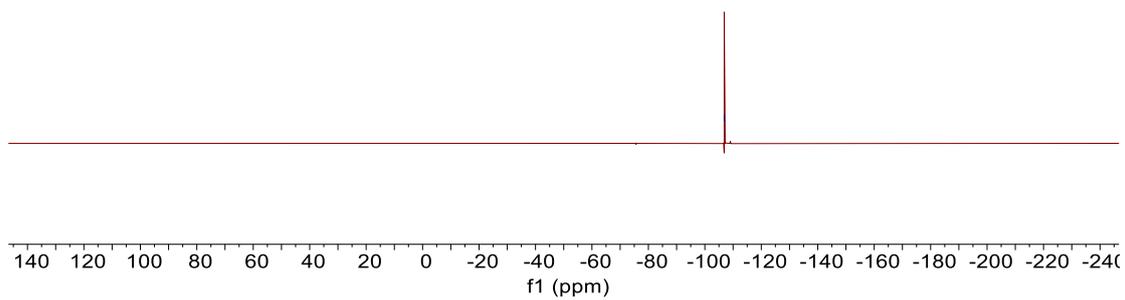


Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(3-fluorophenyl)- λ^4 -sulfanyl)acetate (3ad)

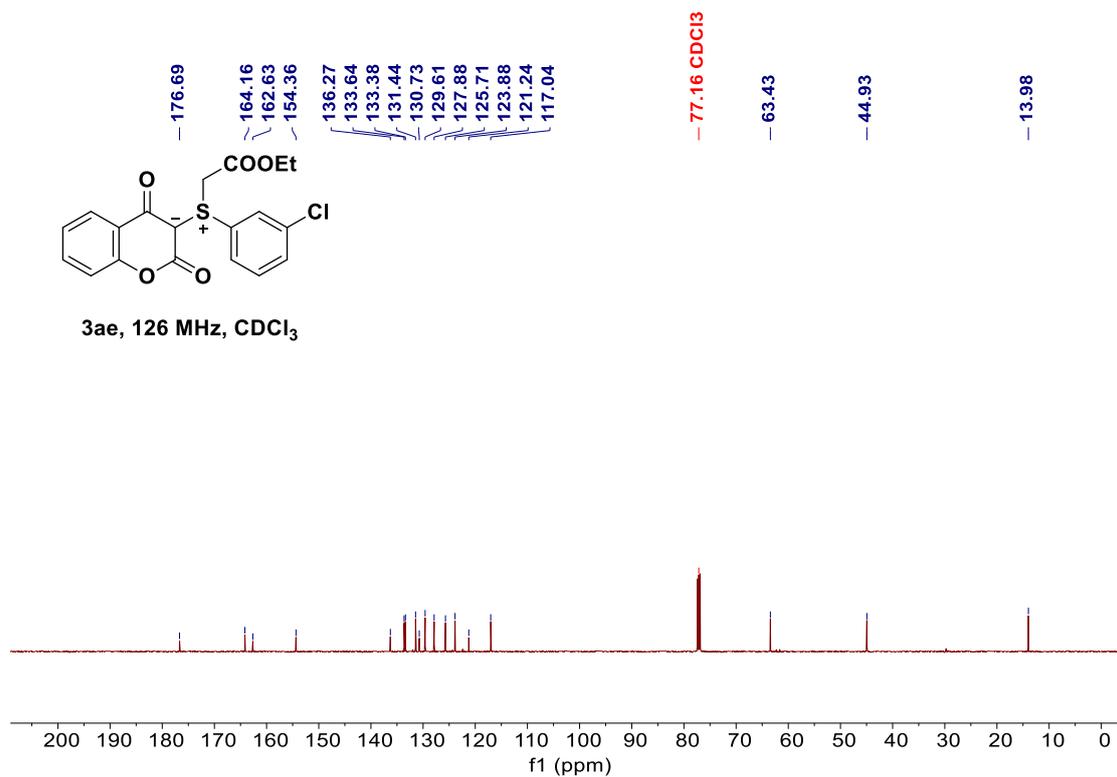
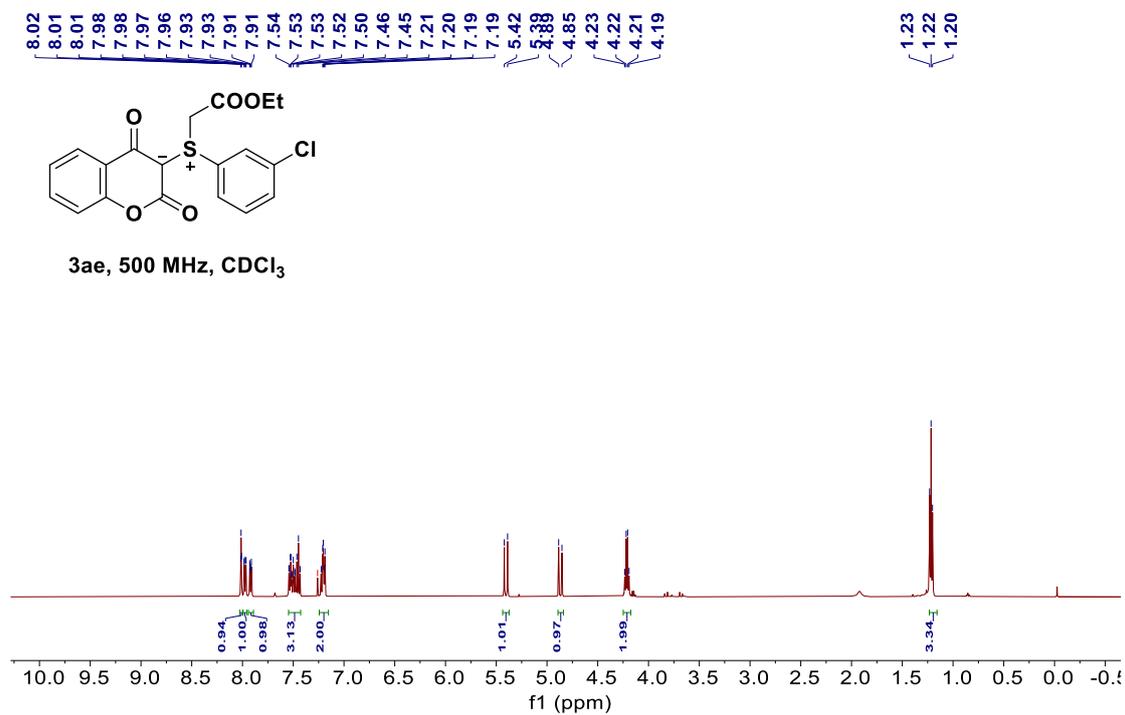




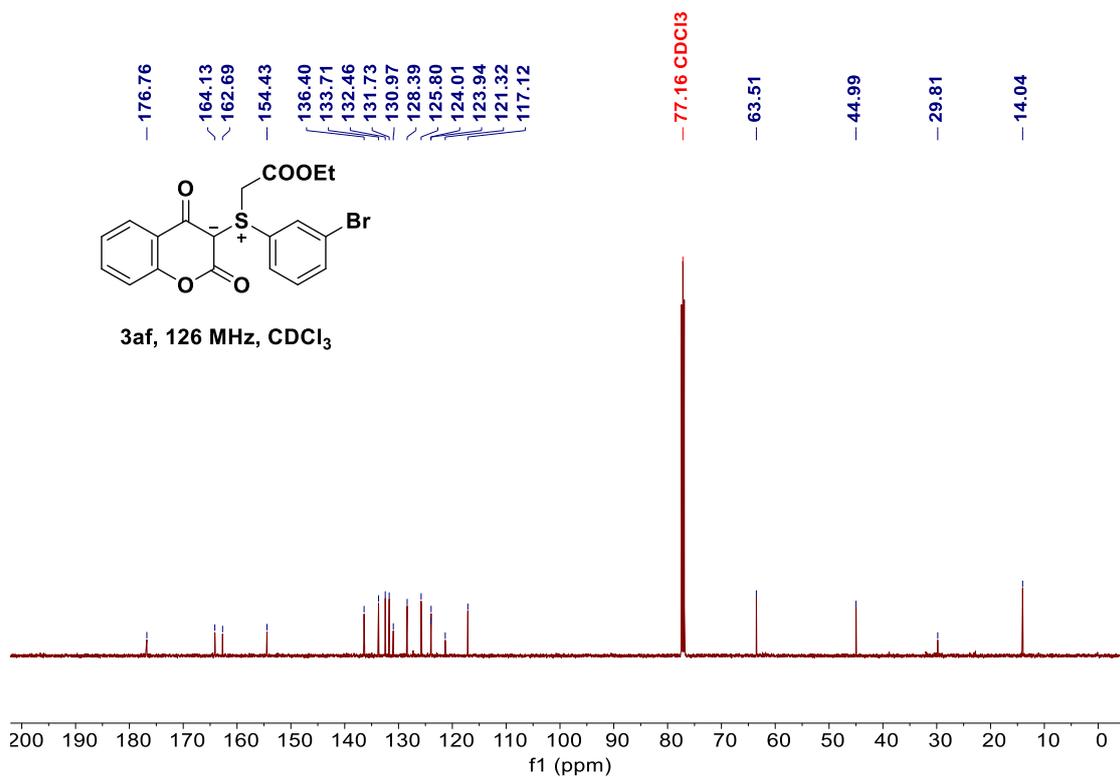
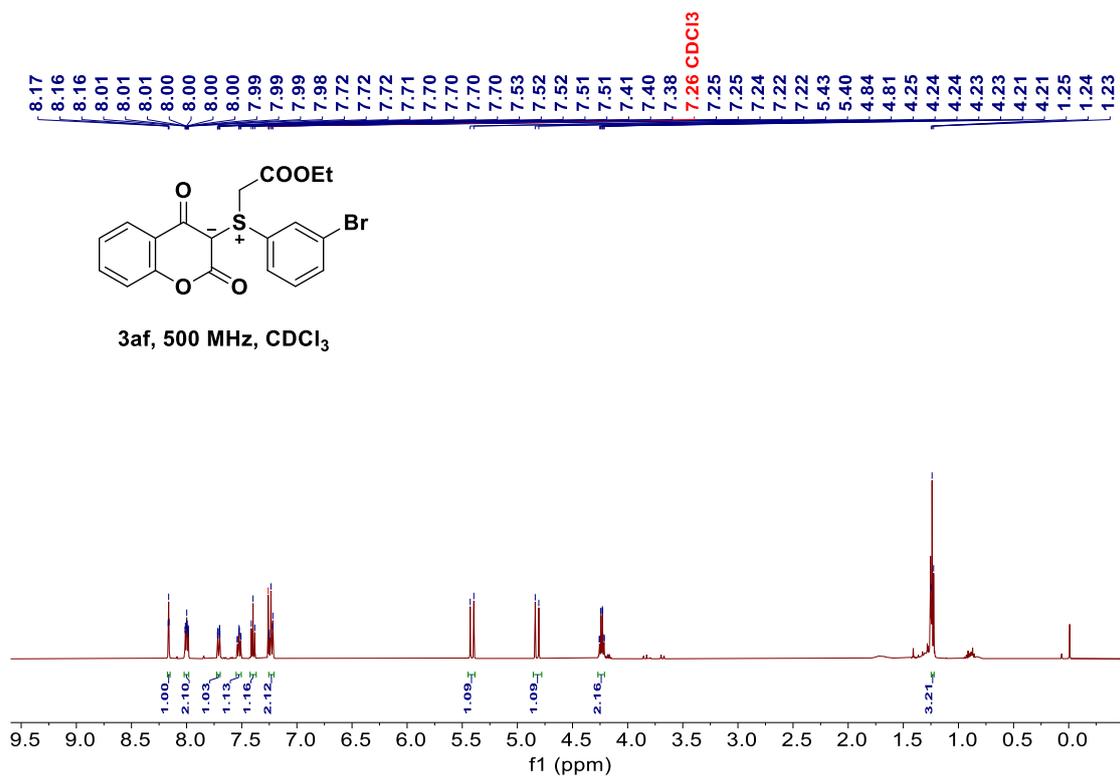
3ad, 471 MHz, CDCl₃



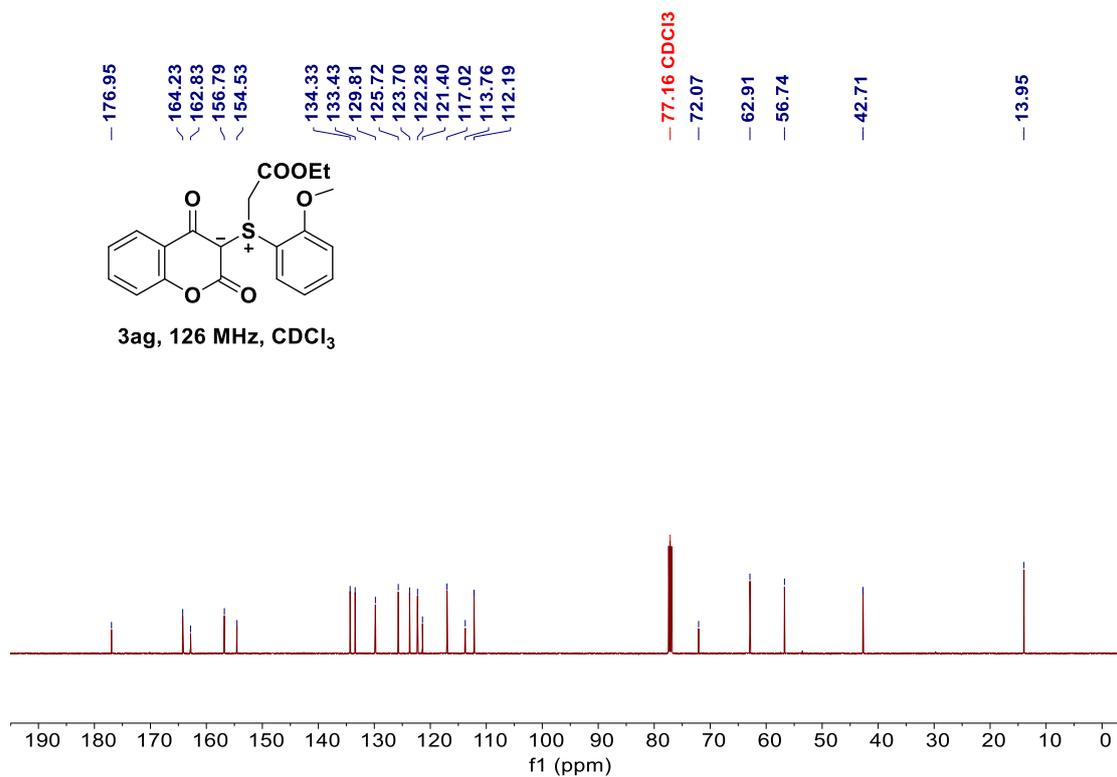
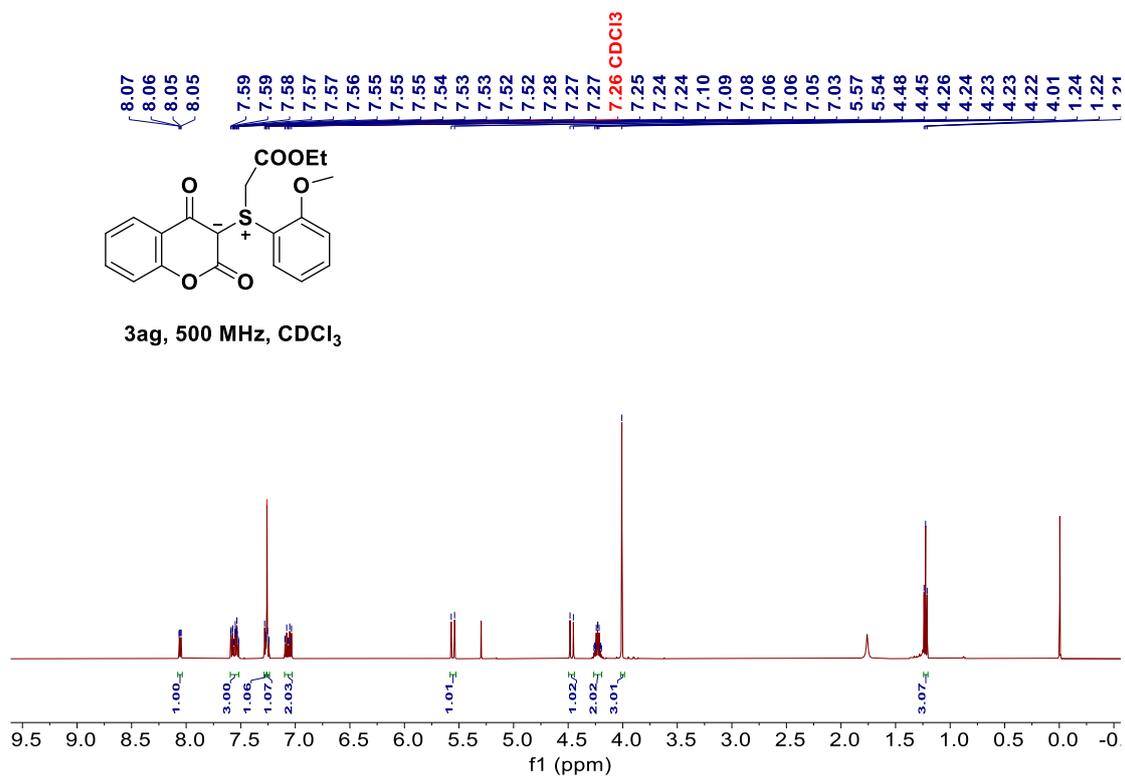
Ethyl (Z)-2-((3-chlorophenyl)(2,4-dioxochroman-3-ylidene)- λ^4 -sulfaneyl)acetate (3ae)



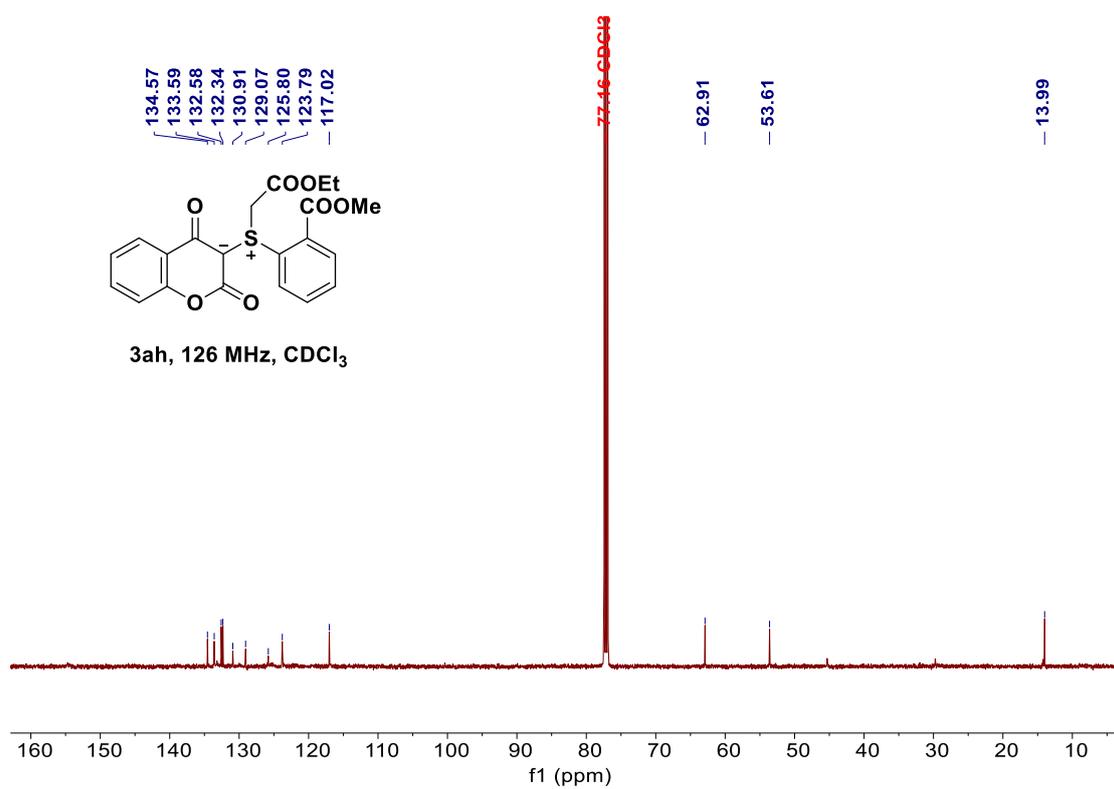
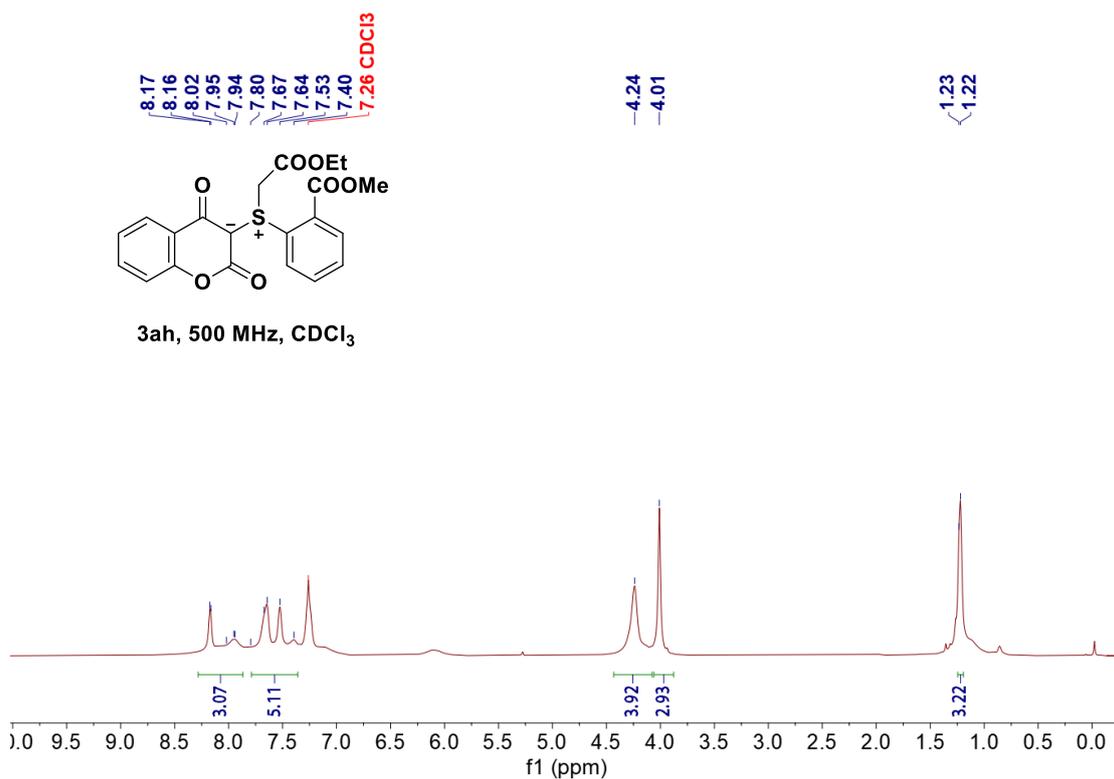
Ethyl (Z)-2-((3-bromophenyl)(2,4-dioxochroman-3-ylidene)- λ^4 -sulfaneyl)acetate (3af)



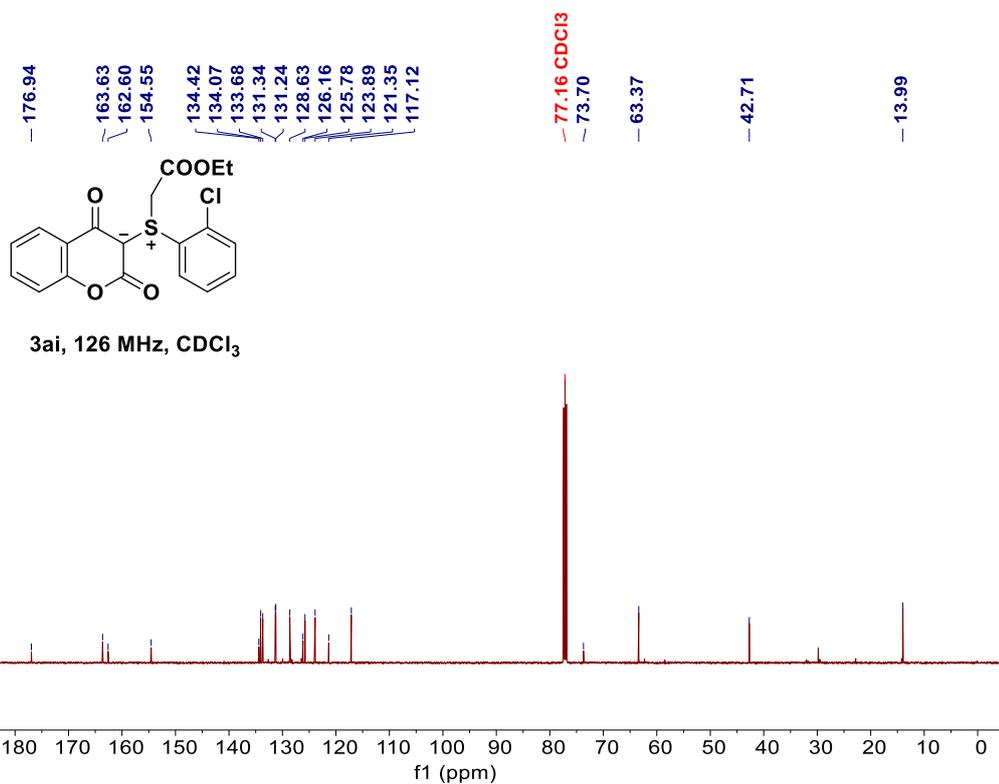
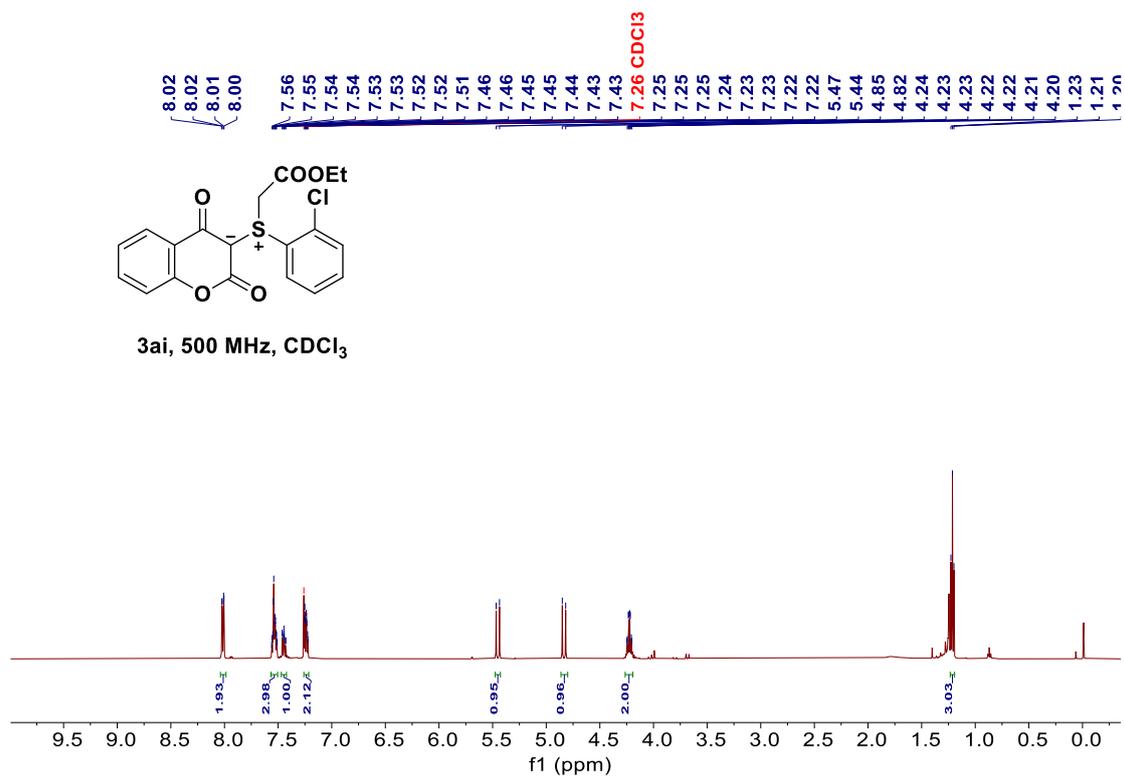
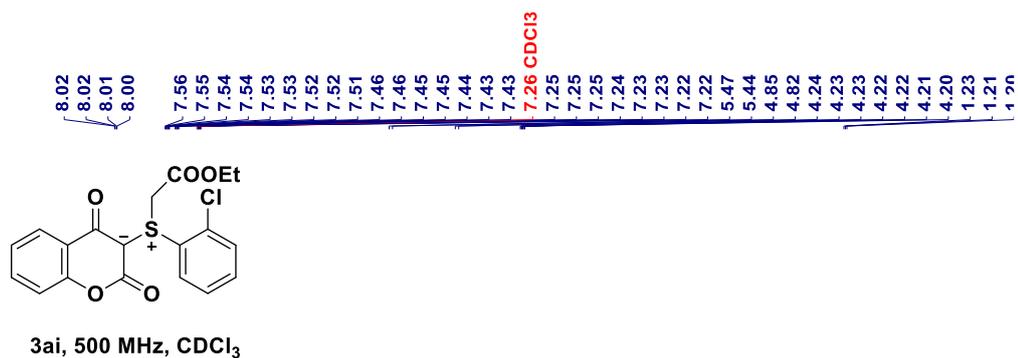
Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(2-methoxyphenyl)- λ^4 -sulfaneyl)acetate (3ag)



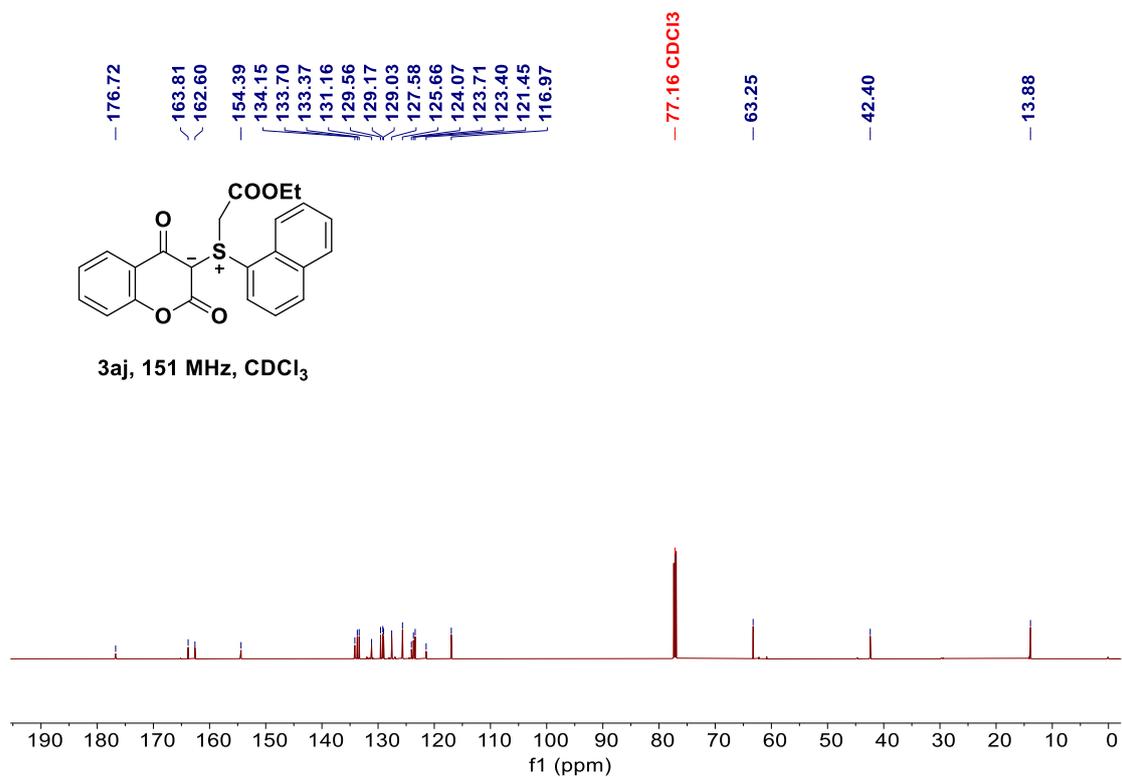
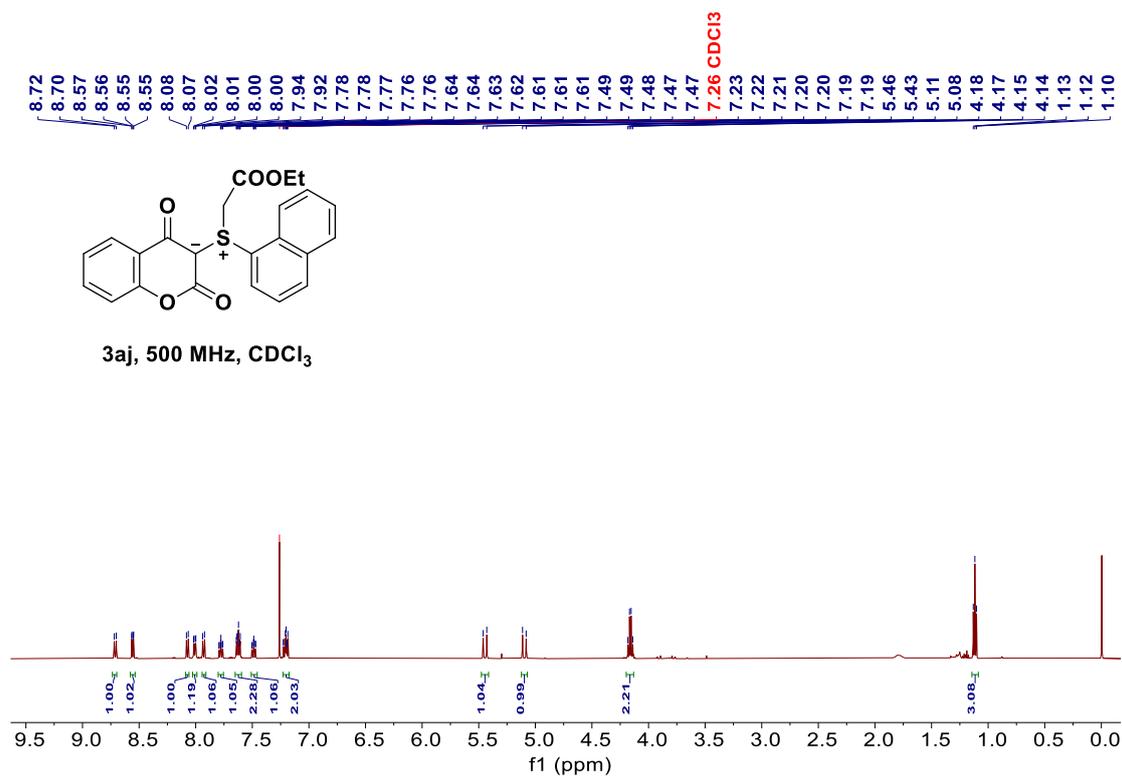
Methyl (Z)-2-((2,4-dioxochroman-3-ylidene)(2-ethoxy-2-oxoethyl)- λ^4 -sulfaneyl)benzoate (3ah)



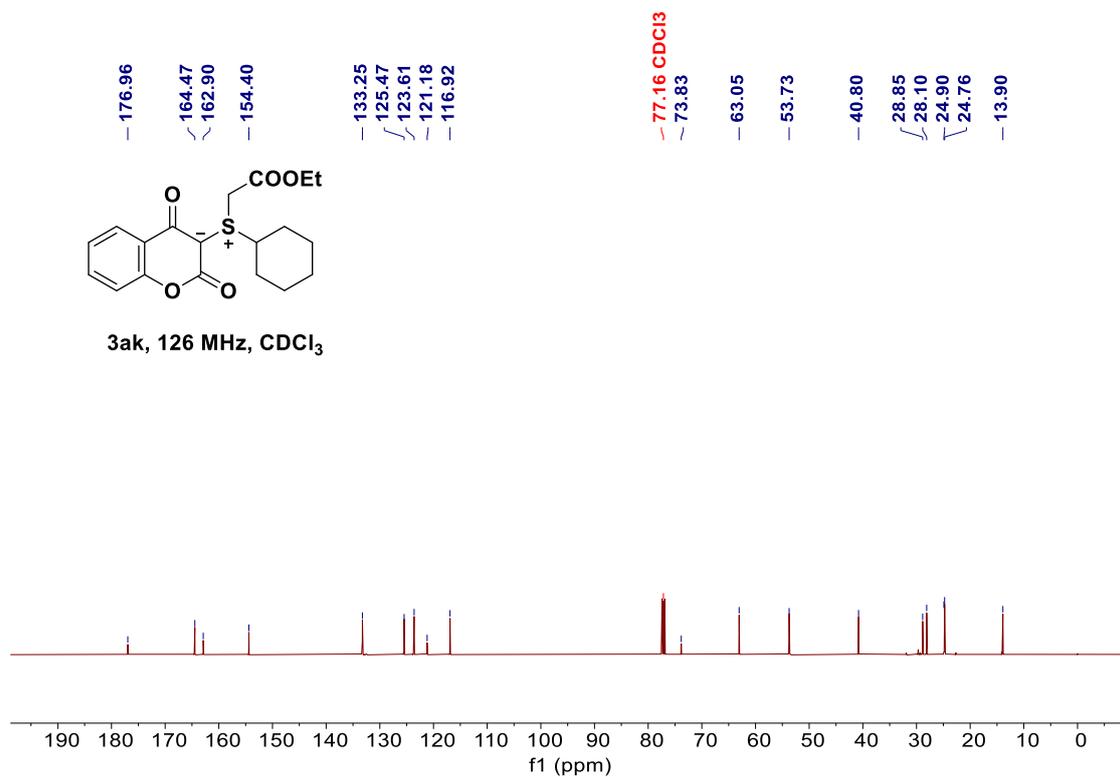
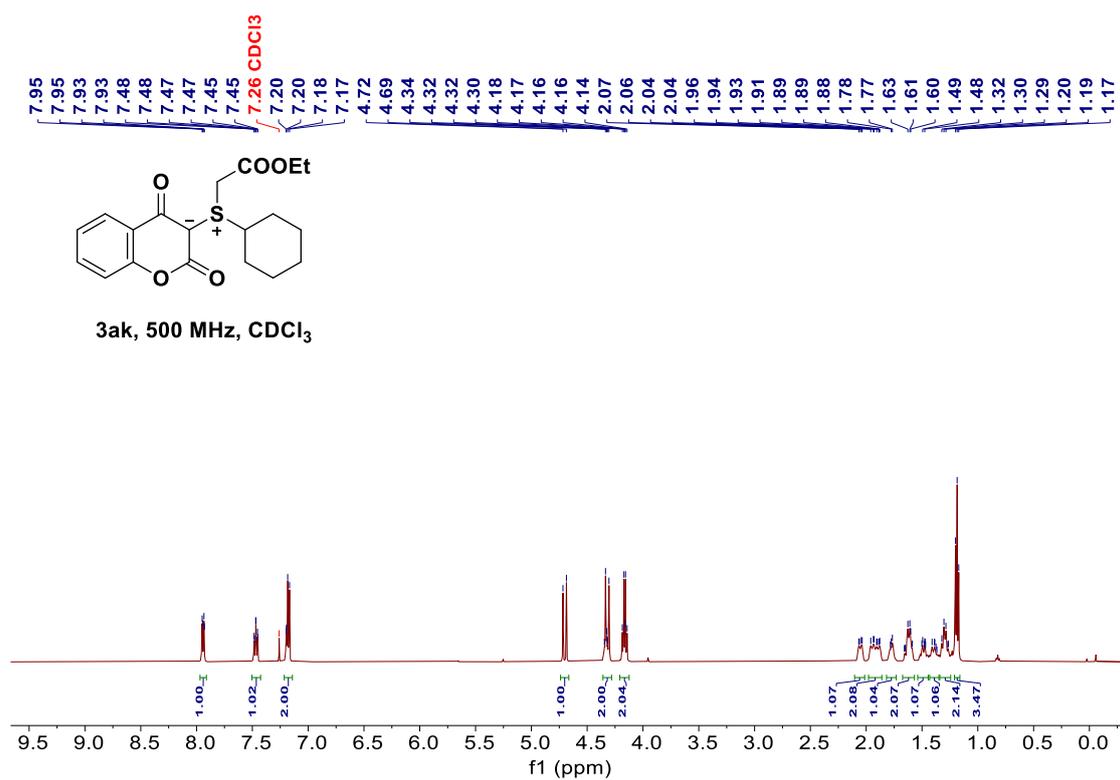
Ethyl (Z)-2-((2-chlorophenyl)(2,4-dioxochroman-3-ylidene)- λ^4 -sulfaneyl)acetate (3ai)



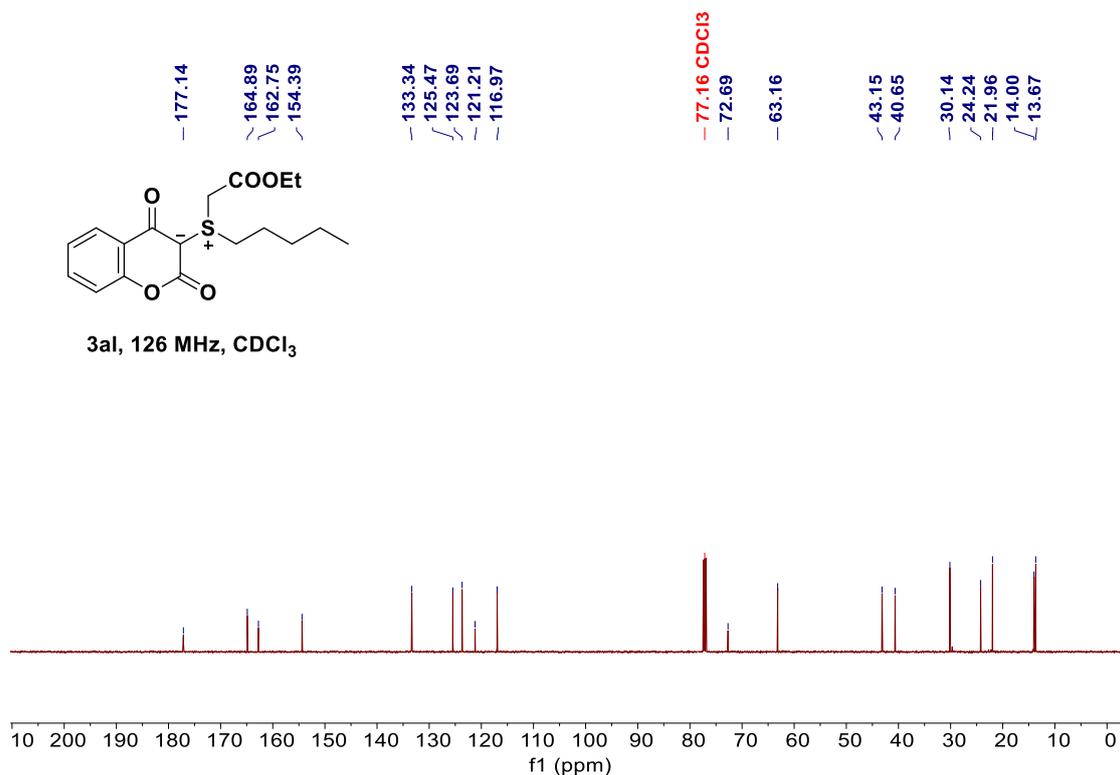
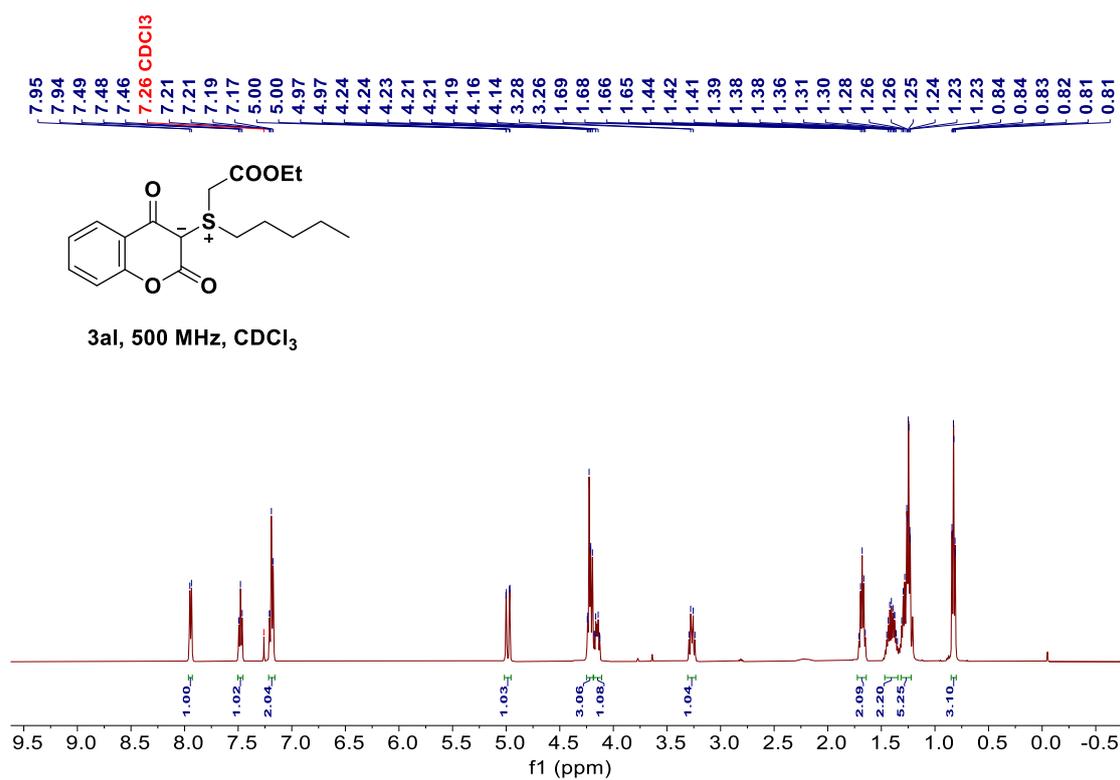
Ethyl (Z)-2-((2,4-dioxochroman-3-ylidene)(naphthalen-1-yl)- λ^4 -sulfanyl)acetate (3aj)



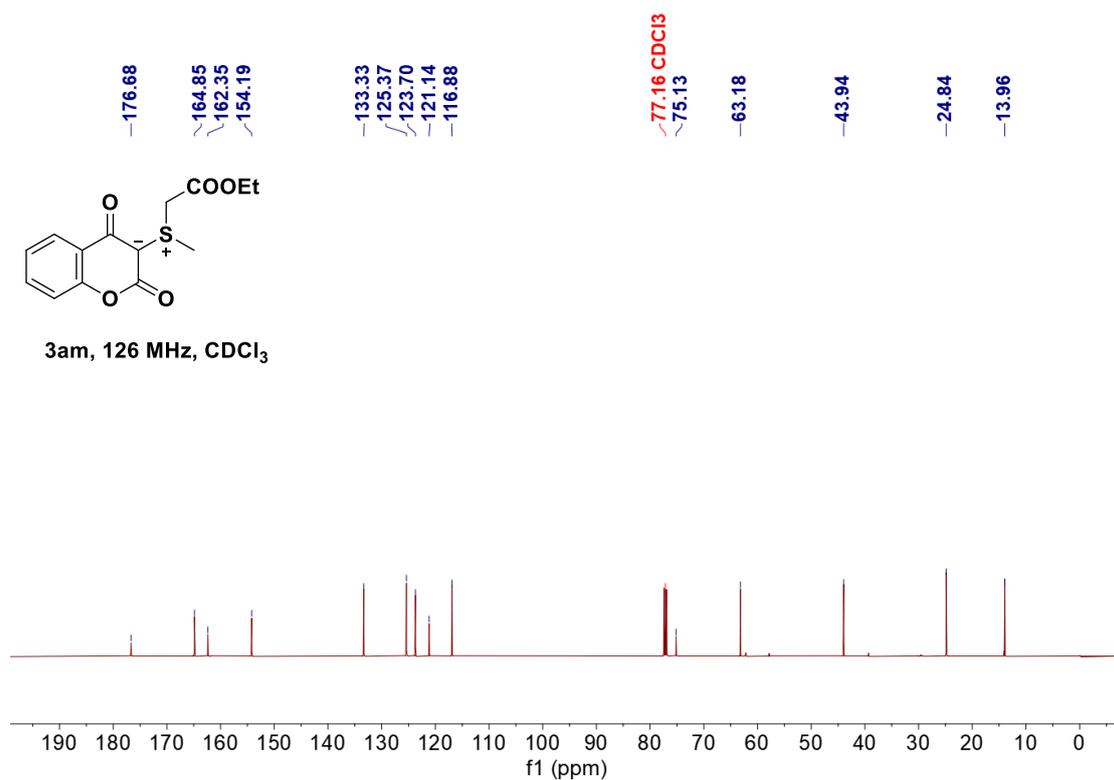
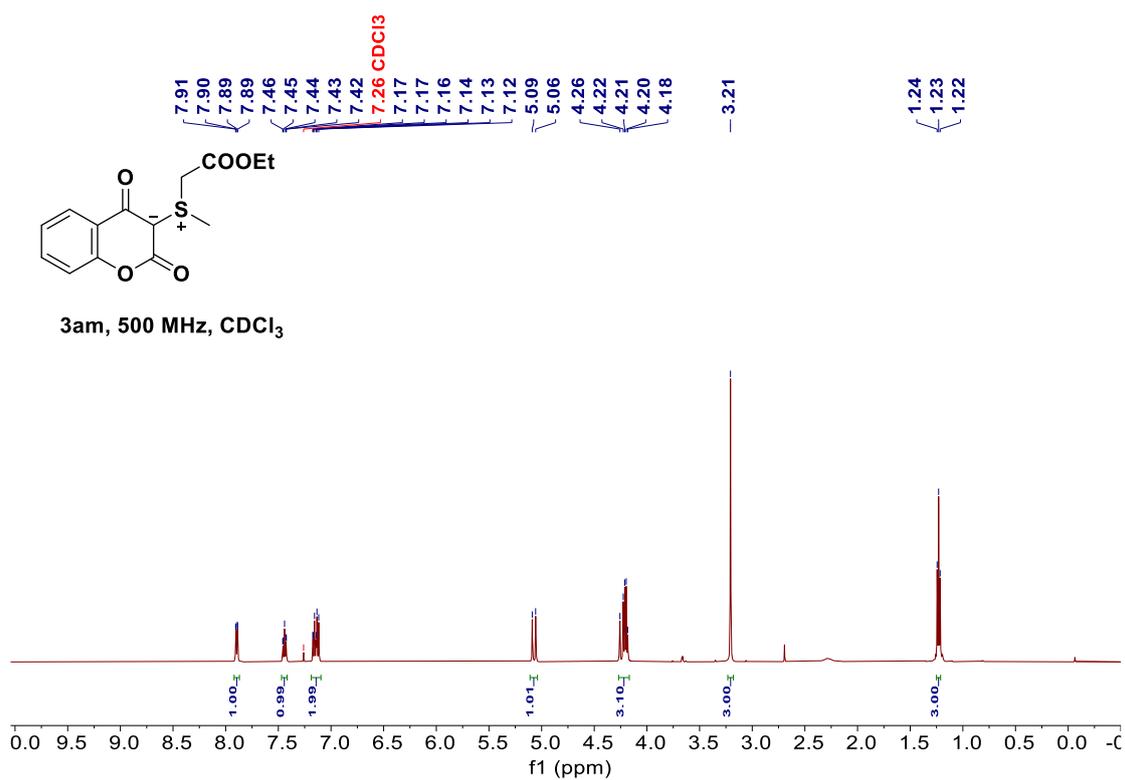
Ethyl (Z)-2-(cyclohexyl(2,4-dioxochroman-3-ylidene)- λ^4 -sulfaneyl)acetate (3ak)



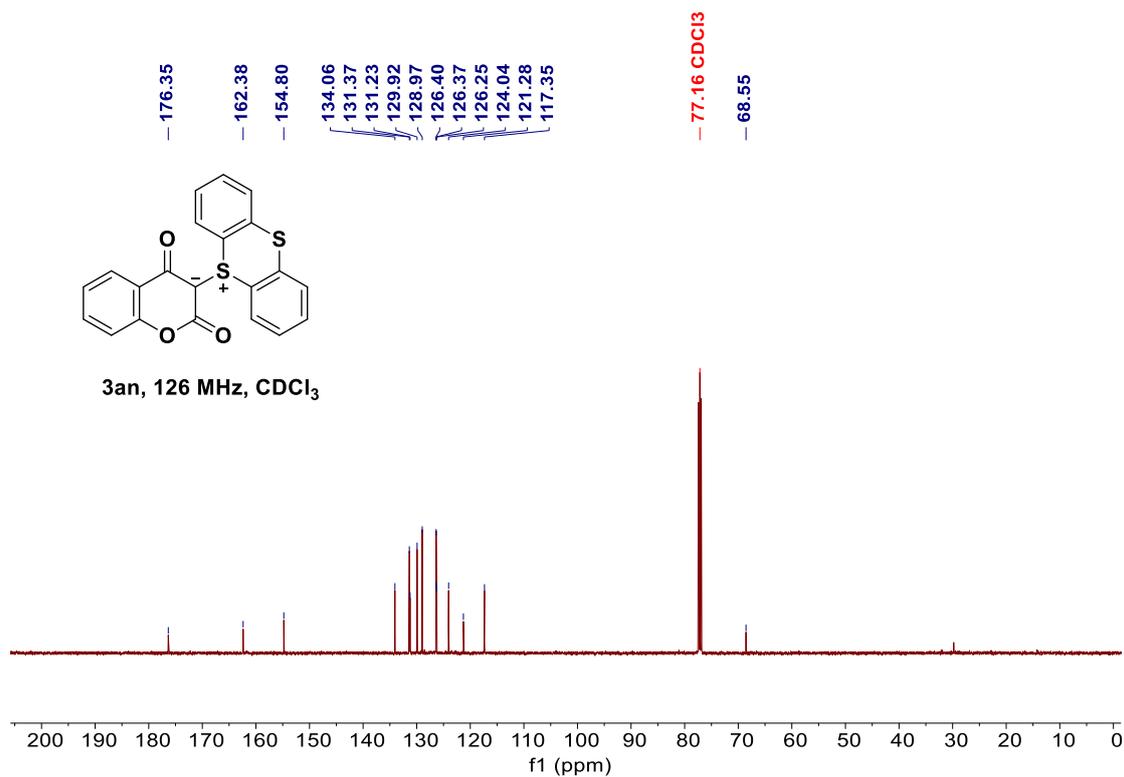
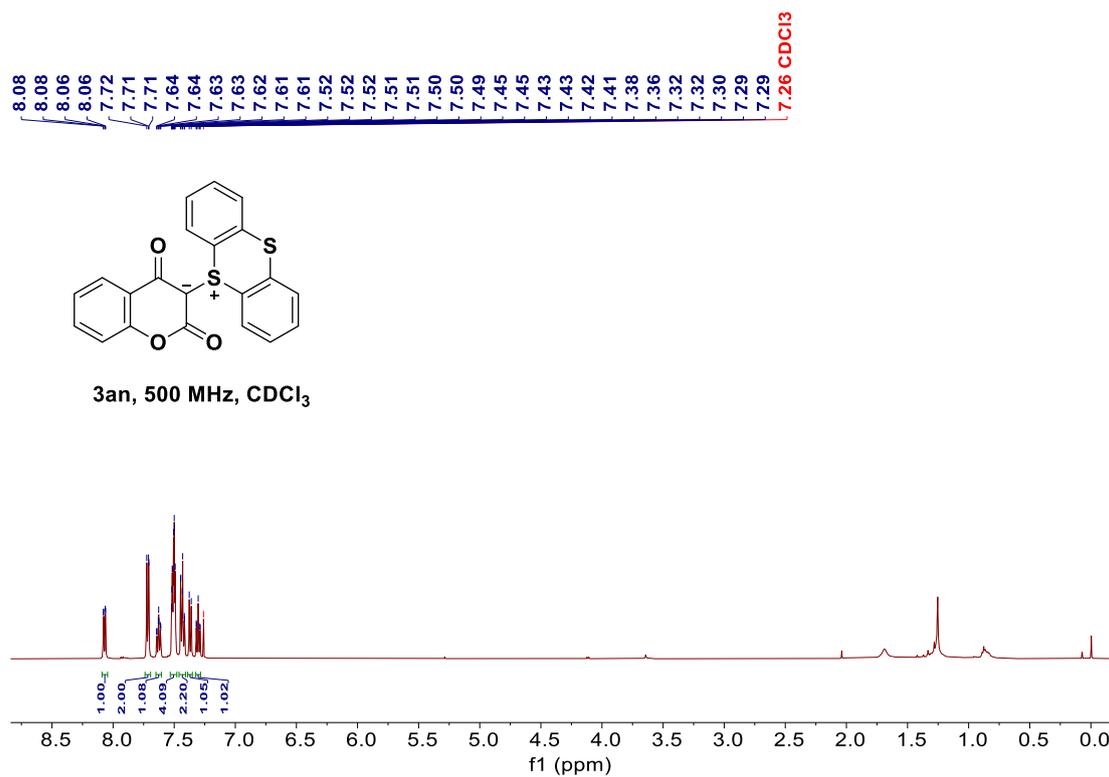
Ethyl (*E*)-2-((2,4-dioxochroman-3-ylidene)(pentyl)- λ^4 -sulfaneyl)acetate (3a)



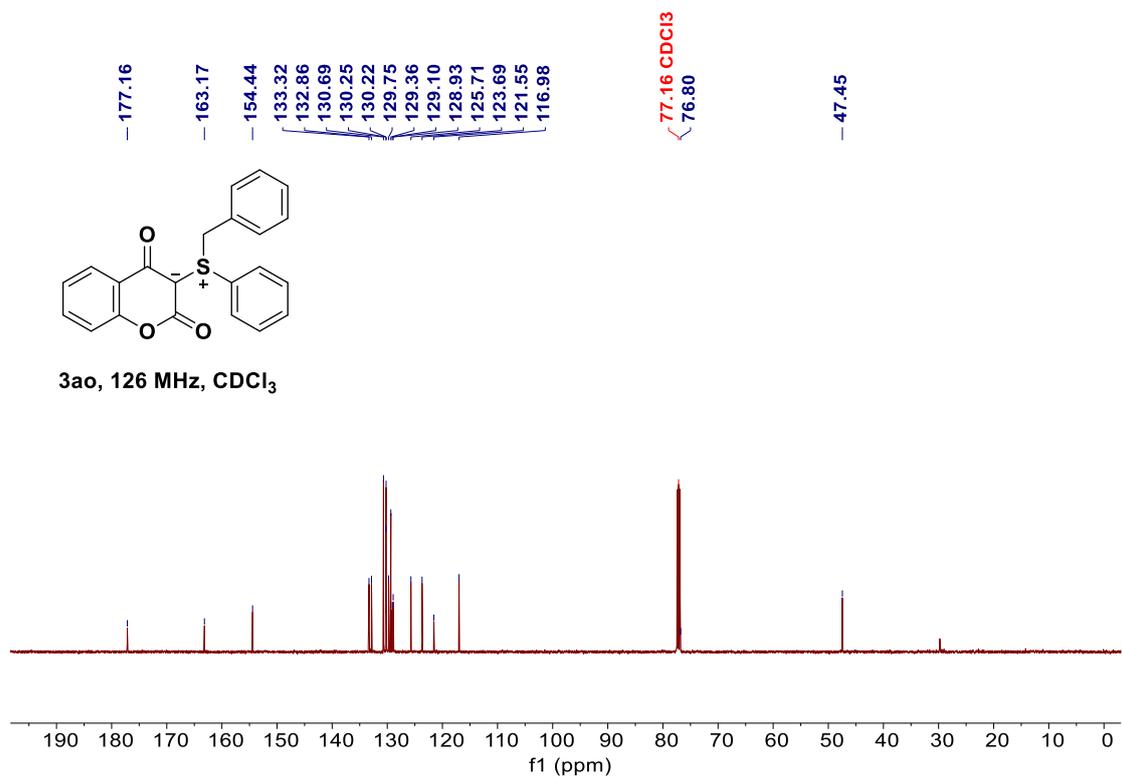
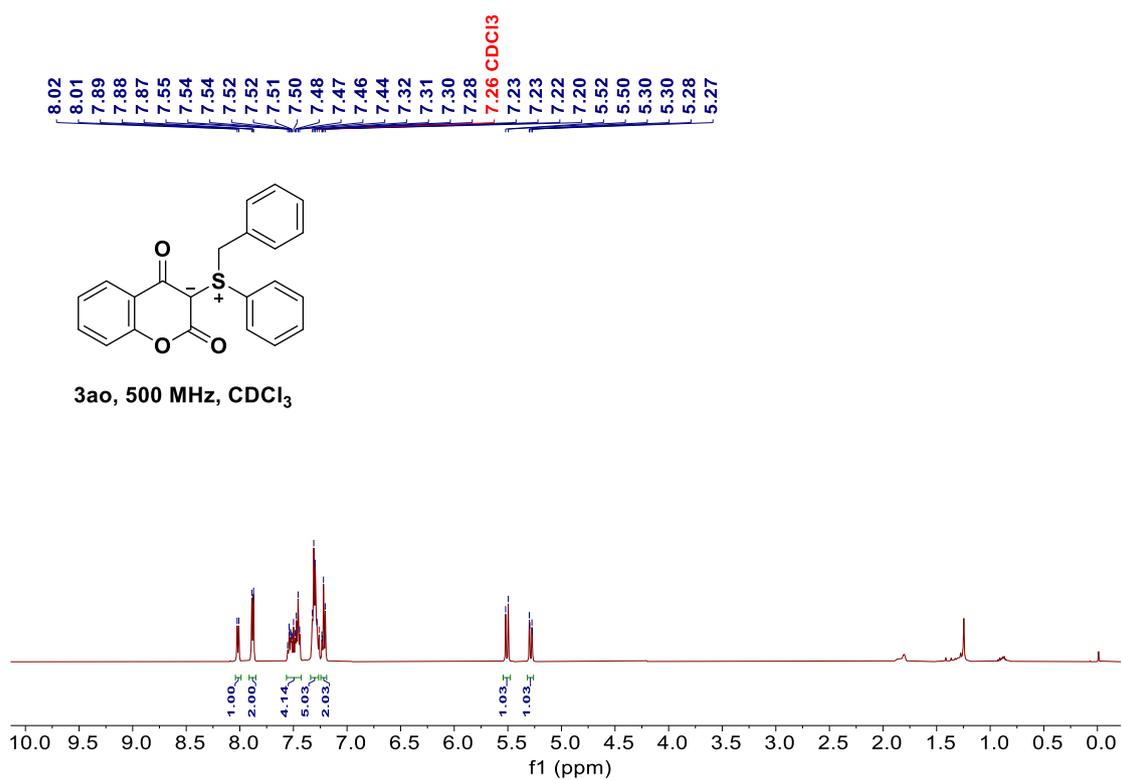
Ethyl (*E*)-2-((2,4-dioxochroman-3-ylidene)(methyl)- λ^4 -sulfaneyl)acetate (**3am**)



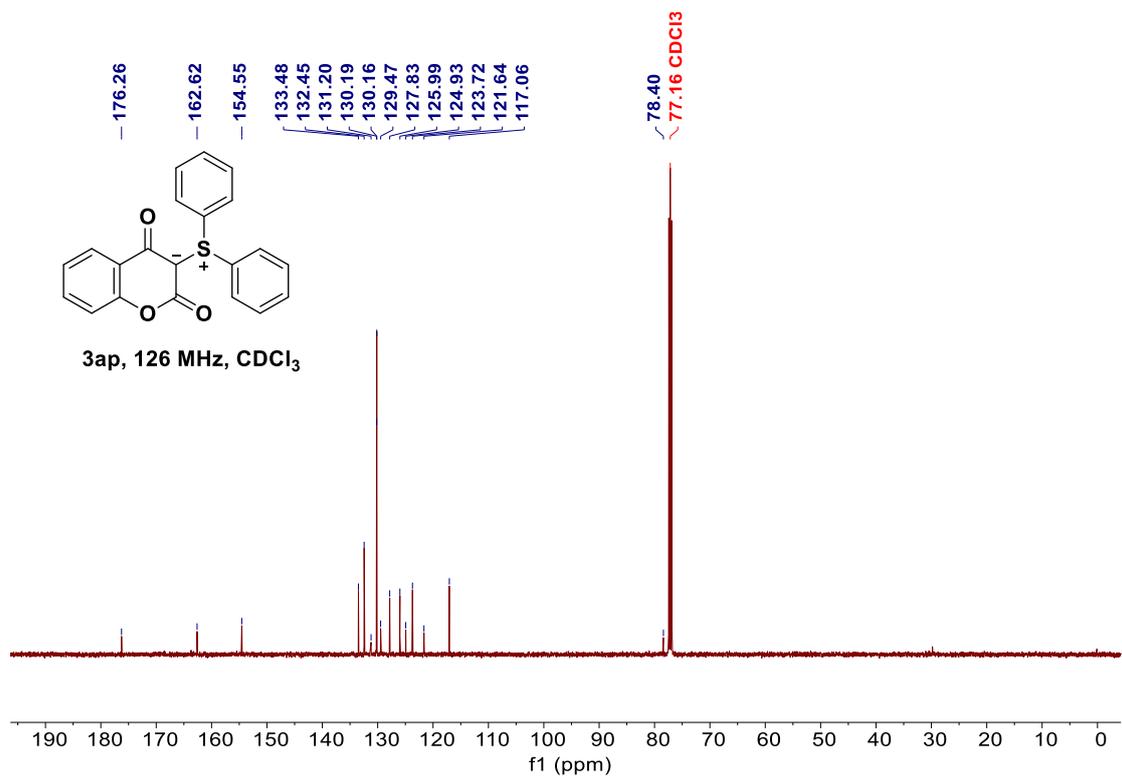
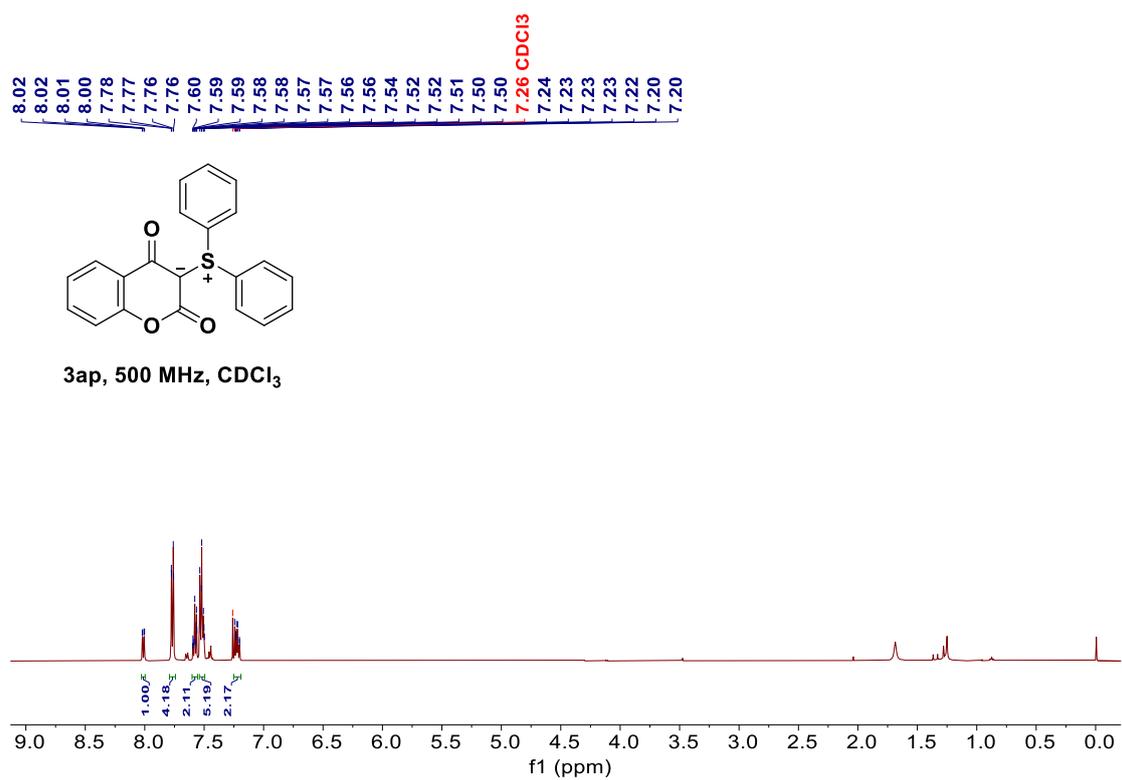
3-(5λ⁴-thianthren-5-ylidene)chromane-2,4-dione (3an)



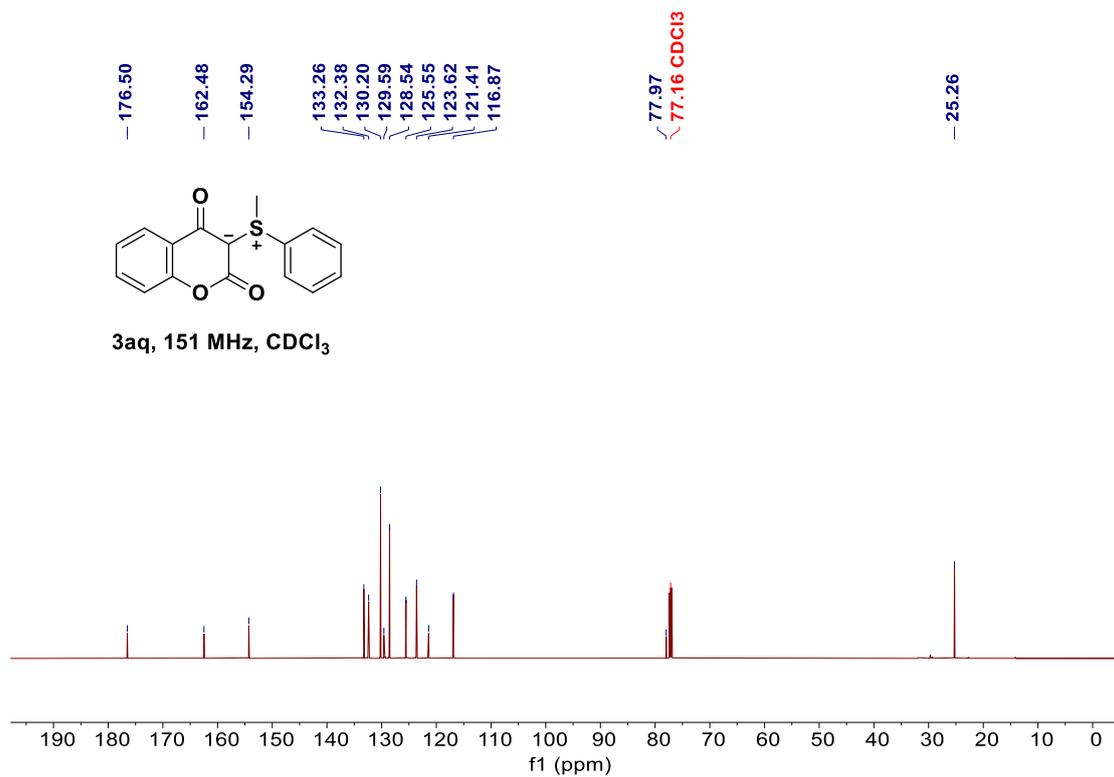
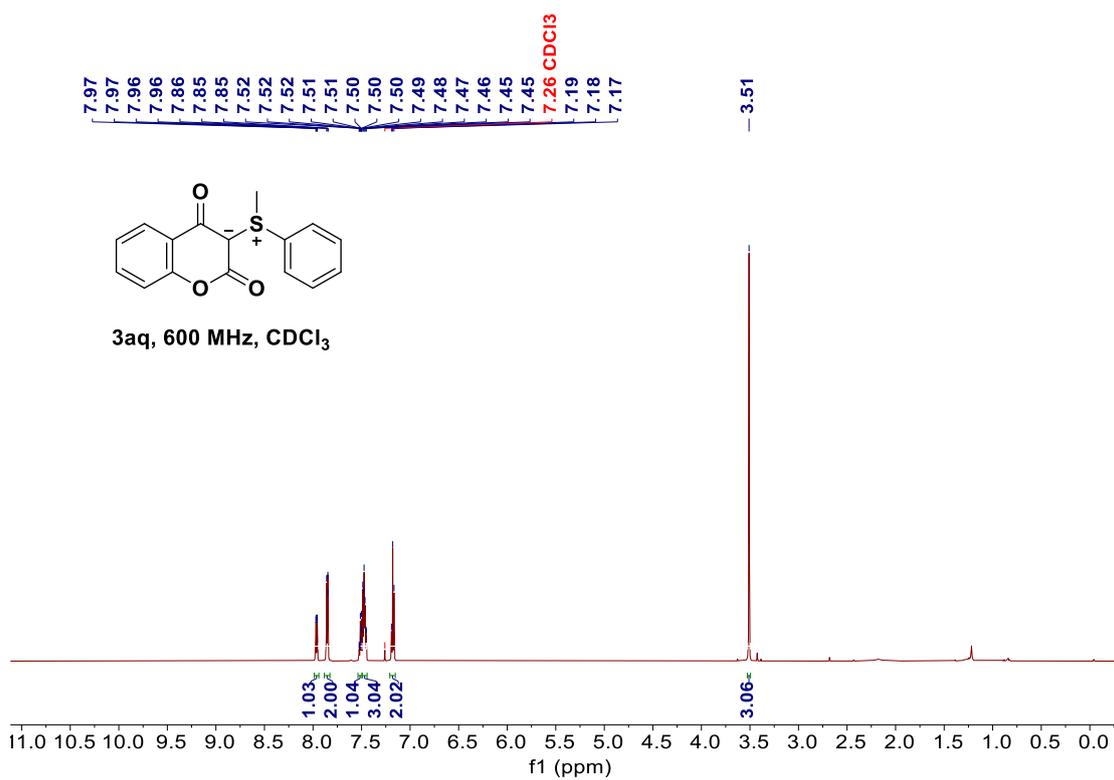
(Z)-3-(benzyl(phenyl)- λ^4 -sulfanylidene)chromane-2,4-dione (3ao)



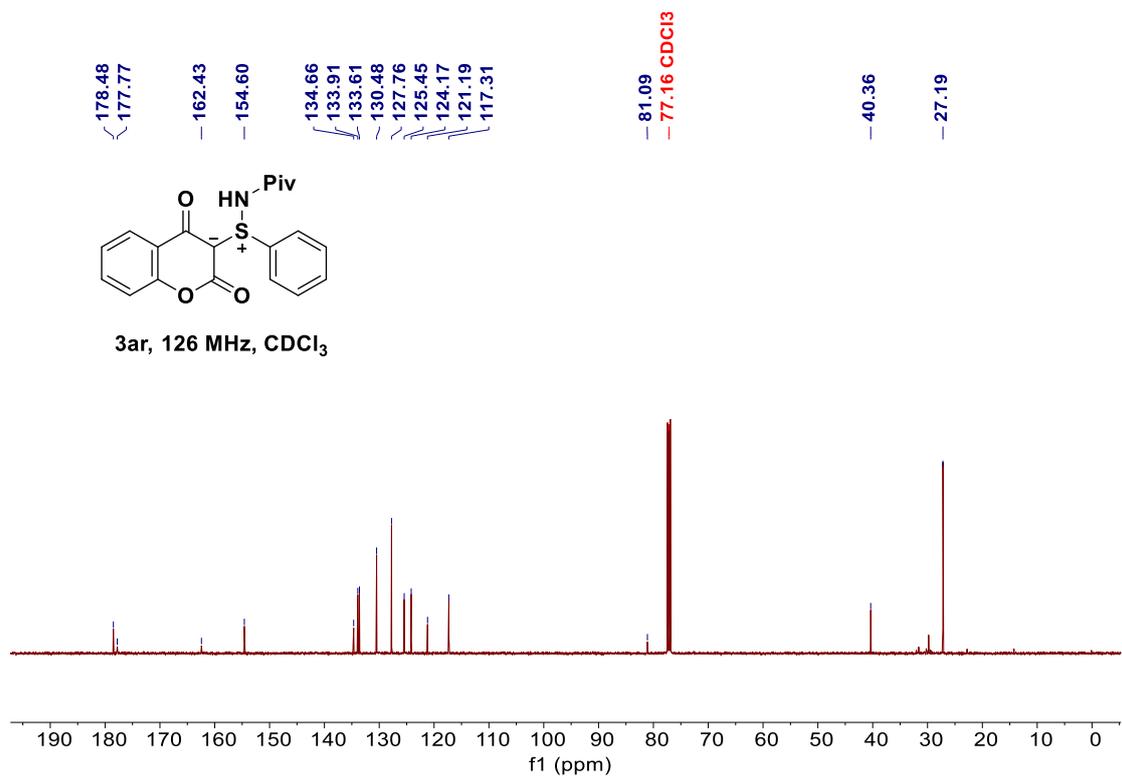
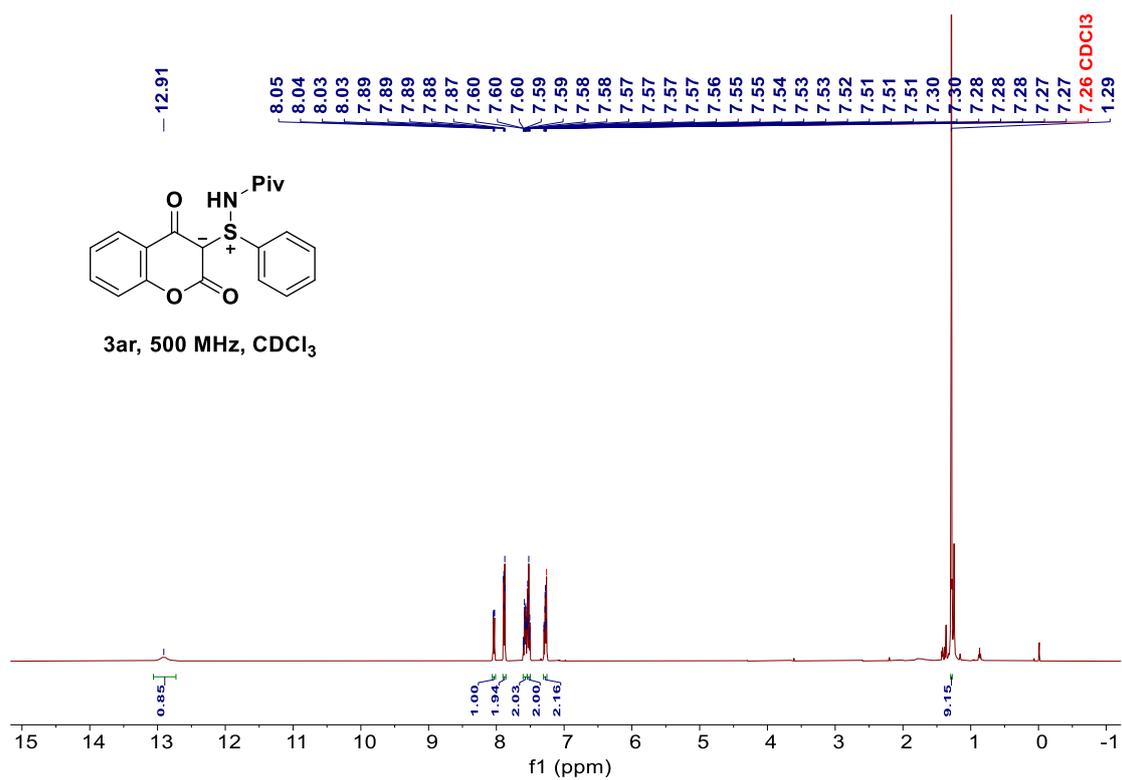
3-(diphenyl- λ^4 -sulfaneylidene)chromane-2,4-dione (3ap)



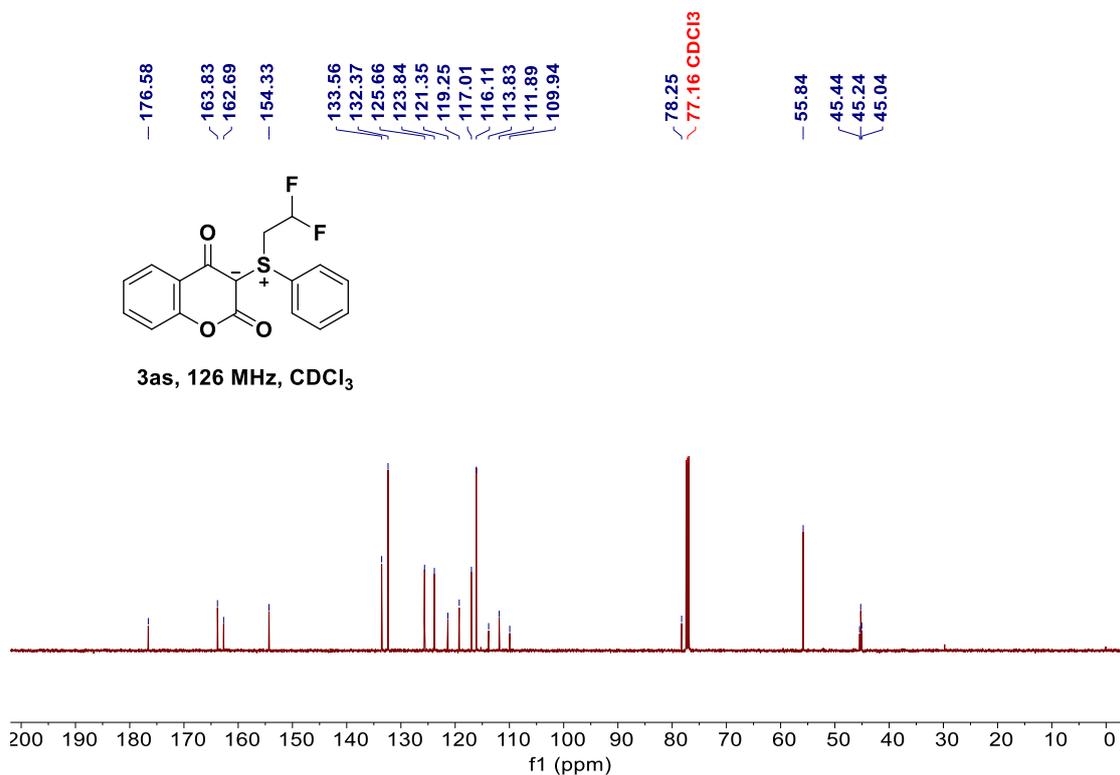
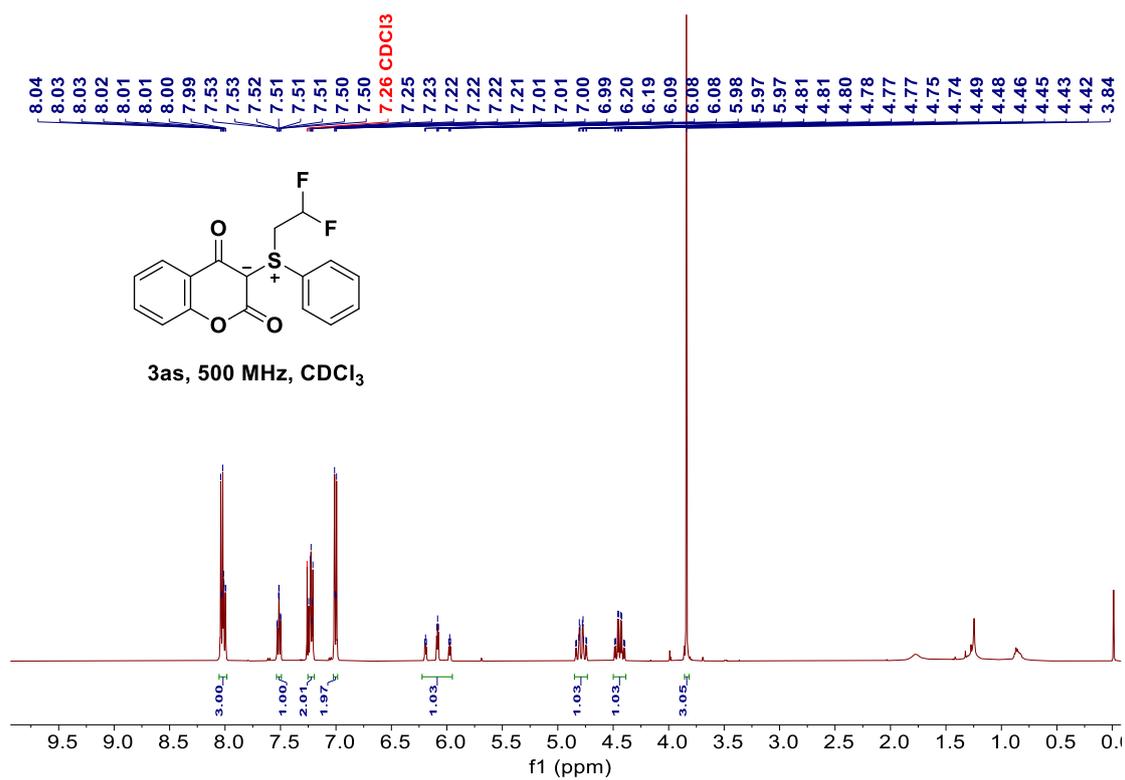
(Z)-3-(methyl(phenyl)- λ^4 -sulfanylidene)chromane-2,4-dione (3aq)

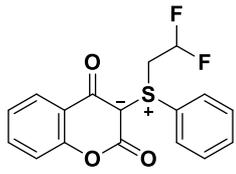


(E)-N-((2,4-dioxochroman-3-ylidene)(phenyl)-λ⁴-sulfanyl)pivalamide (3ar)

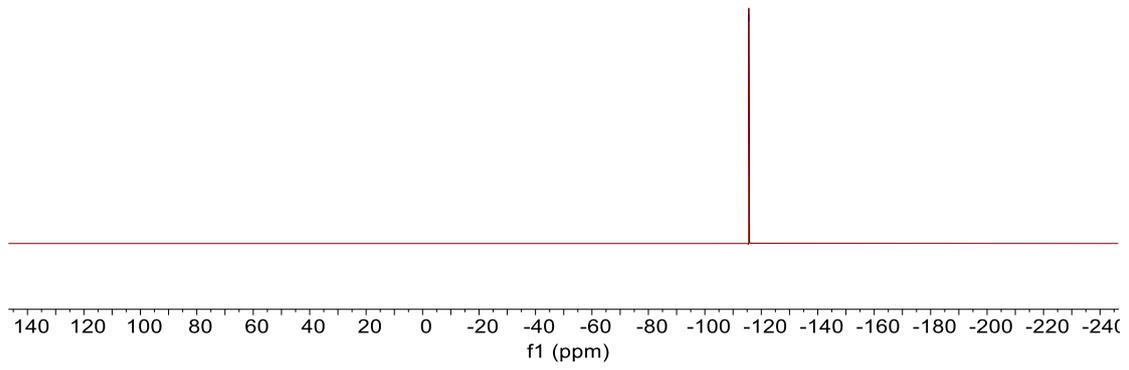


(Z)-3-((2,2-difluoroethyl)(4-methoxyphenyl)-14-sulfanylidene)chromane-2,4-dione (3as)

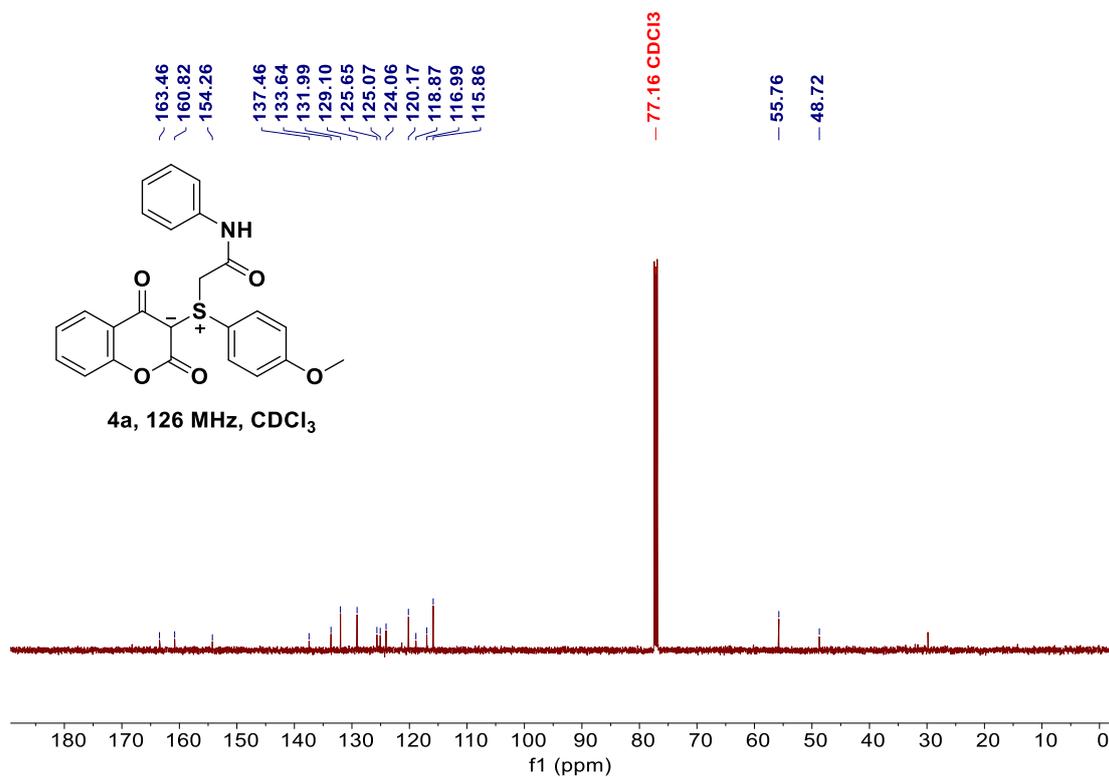
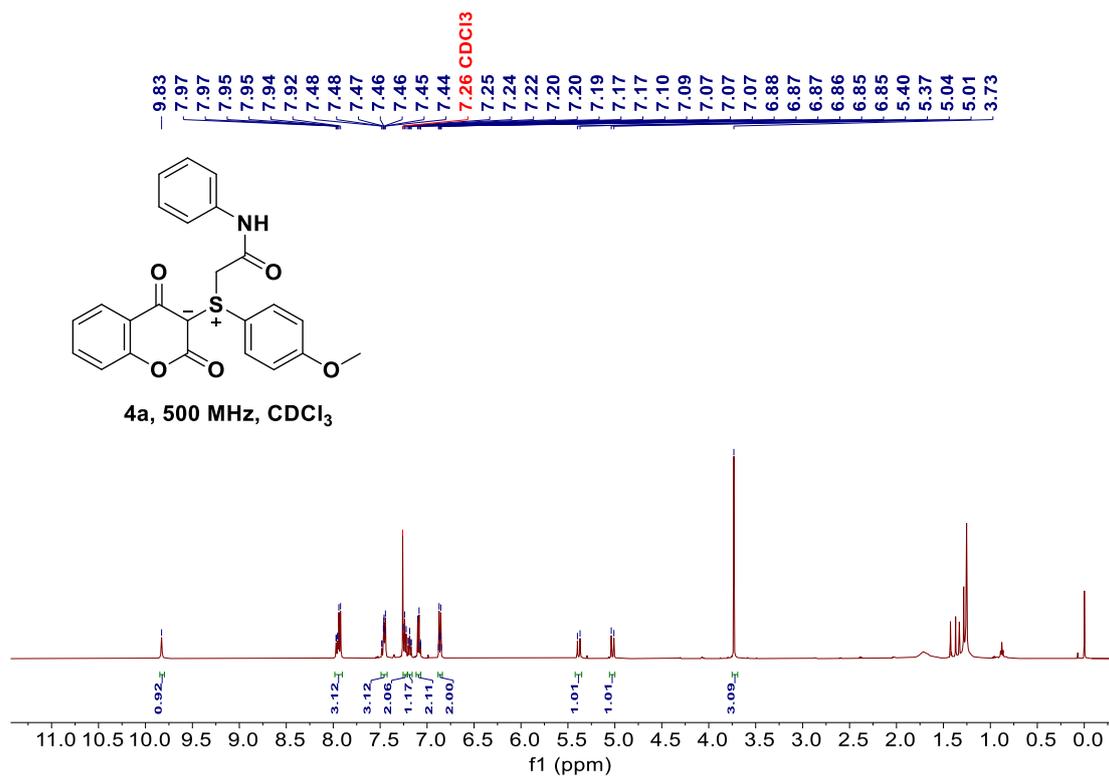




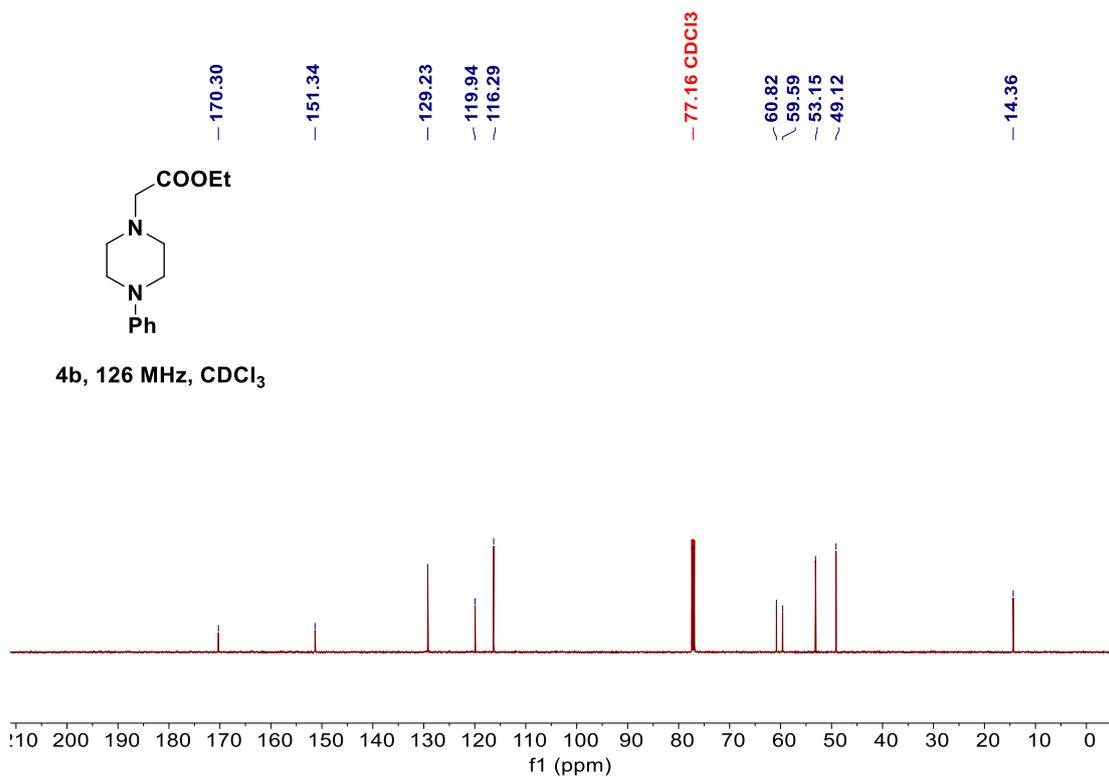
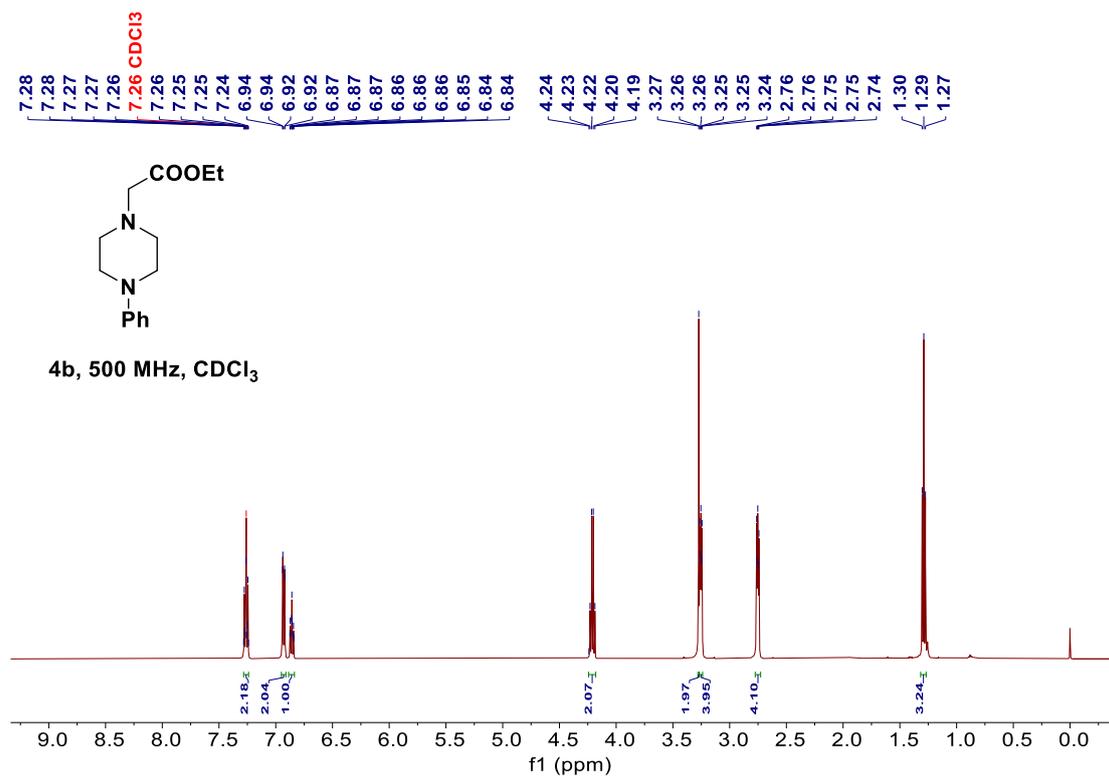
3as, 471 MHz, CDCl₃



(Z)-2-((2,4-dioxochroman-3-ylidene)(4-methoxyphenyl)- λ^4 -sulfaneyl)-N-phenylacetamide (4a)



Ethyl 2-(4-phenylpiperazin-1-yl)acetate (4b)



1-benzyl-4-phenylpiperazine (4c)

