

Supporting Information
for
Transition-metal-free synthesis of 3-sulphenylated
chromones via KIO₃-catalyzed radical C(sp²)-H
sulphenylation

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General experimental information, experimental details on the
synthesis of products 3; full characterization data as well as
¹H/¹³C NMR spectra of all products

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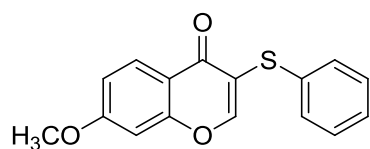
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General information

All experiments were carried out under air atmosphere. All enaminones **1** were synthesized following a literature process,¹ and other chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further treatment. ¹H and ¹³C NMR spectra were recorded in a 400 MHz apparatus and the frequencies for ¹H NMR and ¹³C NMR were 400 MHz and 100 MHz, respectively. The chemical shifts were reported in ppm with TMS as internal standard. Melting points were measured with a X-4A instrument and are uncorrected. The HRMS spectra were obtained in ESI mode with a TOF analyzer.

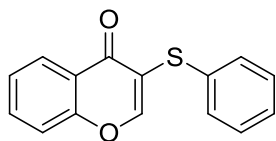
General procedure for the synthesis of 3-sulphenyl chromones 3. Into a 25 mL round-bottom flask were added enaminone **1** (0.3 mmol), sulfonyl hydrazide **2** (0.36 mmol), KIO₃ (0.15 mmol) and DMF (2 mL). Then the mixture was heated up to 130 °C, and stirred at the same temperature for 24 h (TLC). After cooling down to room temperature, 5 mL of water were added, and the resulting mixture was extracted with ethyl acetate (3 × 8 mL). The organic phases were combined and washed with small amount of water for three times. After drying with anhydrous Na₂SO₄, the solid was filtered and the solvent in the acquired solution was removed under reduced pressure. The resulting residue was subjected to flash silica gel column chromatography to provide pure products with the elution of mixed petroleum ether/ethyl acetate (v/v = 10:1).

Characterization data for products 3

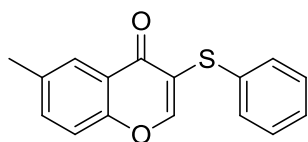


7-Methoxy-3-(phenylthio)-4H-chromen-4-one (3a).² Yield: 71 mg (84%); *R*_f = 0.3; white solid; m.p. 96-98 °C [lit. 98-100 °C]; ¹H NMR (400 MHz, CDCl₃): δ 8.15 (d, 1 H, *J* = 9.2 Hz), 8.09 (s, 1 H), 7.39-7.37 (m, 2 H), 7.30-7.26 (m, 2 H), 7.23-7.19 (m, 1 H), 7.99 (dd, 1 H, *J* = 8.8 Hz, 2.4 Hz), 6.84 (d, 1 H, *J* = 2.4 Hz), 3.91 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 174.4, 164.3, 158.2, 157.0, 134.3, 129.7, 129.2, 127.9,

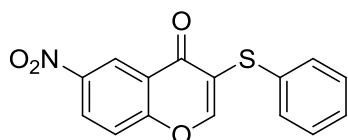
127.0, 119.8, 117.6, 115.0, 100.3, 55.9; ESI-HRMS: Calcd for $C_{16}H_{13}O_3S$ $[M+H]^+$ 285.0580, found 285.0580.



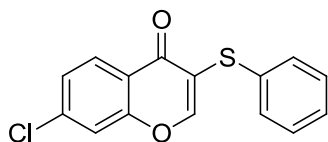
3-(Phenylthio)-4H-chromen-4-one (3b).³ Yield: 61 mg (80%); R_f = 0.4; white solid; m.p. 98-100 °C [lit. 98-101 °C]; 1H NMR (400 MHz, $CDCl_3$): δ 8.25 (dd, 1 H, J = 7.6 Hz, 1.2 Hz), 8.15 (s, 1 H), 7.71-7.67 (m, 1 H), 7.48-7.39 (m, 4 H), 7.30-7.28 (m, 2 H), 7.24-7.22 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 157.4, 156.4, 134.0, 129.9, 129.2, 127.1, 126.5, 125.8, 123.7, 120.0, 118.2.



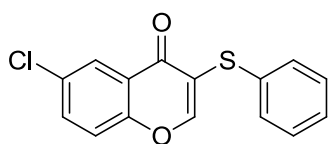
6-Methyl-3-(phenylthio)-4H-chromen-4-one (3c).³ Yield: 68 mg (85%); R_f = 0.6; white solid; m.p. 105-107 °C [lit. 107-109 °C]; 1H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1 H), 8.00 (s, 1 H), 7.47 (d, 1 H, J = 8.4 Hz), 7.37-7.33 (m, 3 H), 7.25 (t, 2 H, J = 7.2 Hz), 7.18 (t, 1 H, J = 7.2 Hz), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 157.5, 154.6, 135.8, 135.3, 134.3, 129.6, 129.2, 127.0, 125.7, 123.4, 119.4, 117.9, 21.0.



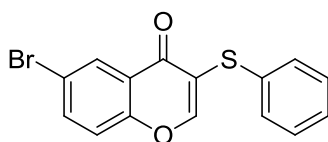
6-Nitro-3-(phenylthio)-4H-chromen-4-one (3d). Yield: 70 mg (78%); R_f = 0.3; yellow solid; m.p. 147-149 °C; 1H NMR (400 MHz, $CDCl_3$): δ 9.08 (d, 1 H, J = 2.8 Hz), 8.50 (dd, 1 H, J = 9.2 Hz, 2.8 Hz), 8.03 (s, 1 H), 7.63 (d, 1 H, J = 9.2 Hz), 7.45 (d, 2 H, J = 6.8 Hz), 7.36-7.27 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 159.0, 155.8, 145.1, 132.1, 131.4, 129.5, 128.2, 128.1, 123.4, 123.1, 122.6, 120.1; ESI-HRMS: Calcd for $C_{15}H_{10}NO_4S$ $[M+H]^+$ 300.0325, found 300.0327.



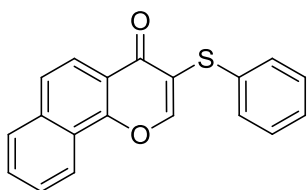
7-Chloro-3-(phenylthio)-4H-chromen-4-one (3e). Yield: 68 mg (79%); $R_f = 0.6$; white solid; m.p. 126-128 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.16 (d, 1 H, $J = 8.8$ Hz), 8.05 (s, 1 H), 7.47 (d, 1 H, $J = 1.2$ Hz), 7.41-7.37 (m, 3 H), 7.31-7.28 (m, 2 H), 7.26-7.22 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 174.3, 156.7, 156.4, 140.1, 133.4, 130.4, 129.3, 127.8, 127.5, 126.6, 122.1, 121.0, 118.2; ESI-HRMS: Calcd for $\text{C}_{15}\text{H}_{10}\text{ClO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 289.0085, found 289.0084.



6-Chloro-3-(phenylthio)-4H-chromen-4-one (3f).⁴ Yield: 69 mg (80%); $R_f = 0.6$; white solid; m.p. 133-135 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.18 (d, 1 H, $J = 2.4$ Hz), 8.09 (s, 1H), 7.62 (dd, 1 H, $J = 8.8$ Hz, 2.4 Hz), 7.44-7.39 (m, 3 H), 7.31-7.22 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 174.0, 157.0, 154.7, 134.2, 133.4, 131.7, 130.3, 129.3, 127.5, 125.7, 124.5, 120.6, 119.9; ESI-HRMS: Calcd for $\text{C}_{15}\text{H}_{10}\text{ClO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 289.0085, found 289.0083.

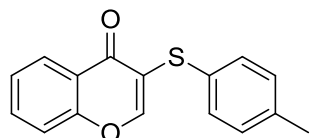


6-Bromo-3-(phenylthio)-4H-chromen-4-one (3g).³ Yield: 79 mg (79%); $R_f = 0.5$; yellow solid; m.p. 118-120 °C [lit. 118-121 °C]; ^1H NMR (400 MHz, CDCl_3): δ 8.31 (d, 1 H, $J = 2.0$ Hz), 8.08 (s, 1 H), 7.73 (dd, 1 H, $J = 8.8$ Hz, 2.4 Hz), 7.39-7.34 (m, 3 H), 7.29-7.20 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.8, 157.0, 155.1, 137.0, 133.4, 130.3, 129.3, 128.9, 127.5, 124.8, 120.6, 120.2, 119.1.

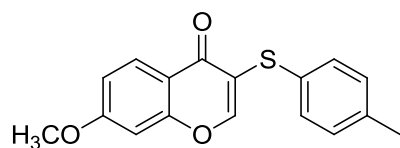


3-(Phenylthio)-4H-benzo[h]chromen-4-one (3h).² Yield: 73 mg (80%); $R_f = 0.2$;

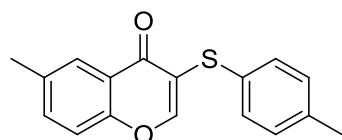
white solid; m.p. 136-138 °C [lit. 117-119 °C]; ^1H NMR (400 MHz, CDCl_3): δ 8.40 (d, 1 H, $J = 8.0$ Hz), 8.18 (s, 1 H), 8.13 (d, 1 H, $J = 8.8$ Hz), 7.89 (d, 1 H, $J = 8.0$ Hz), 7.75-7.63 (m, 3 H), 7.47-7.45 (m, 2 H), 7.32-7.28 (m, 2 H), 7.26-7.24 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 174.8, 155.5, 153.8, 135.9, 133.5, 130.6, 129.6, 129.3, 128.2, 127.5, 127.4, 125.9, 123.8, 122.2, 122.1, 121.1, 119.8; ESI-HRMS: Calcd for $\text{C}_{19}\text{H}_{13}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 305.0631, found 305.0631.



3-(p-Tolylthio)-4H-chromen-4-one (3i).³ Yield: 63 mg (79%); white solid; $R_f = 0.6$; m.p. 106-108 °C [lit. 108-110 °C]; ^1H NMR (400 MHz, CDCl_3): δ 8.24 (d, 1 H, $J = 7.6$ Hz), 8.04 (s, 1 H), 7.68 (t, 1 H, $J = 7.2$ Hz), 7.46-7.40 (m, 2 H), 7.35 (d, 2 H, $J = 7.6$ Hz), 7.11 (d, 2 H, $J = 7.6$ Hz), 2.31 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 175.1, 156.3, 156.2, 137.6, 133.9, 131.0, 130.1, 129.8, 129.4, 125.6, 123.6, 121.1, 118.1, 21.1.

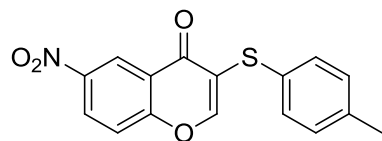


7-Methoxy-3-(p-tolylthio)-4H-chromen-4-one (3j).³ Yield: 76 mg (85 %); $R_f = 0.3$; white solid; m.p. 124-126 °C [lit. 127-130 °C]; ^1H NMR (400 MHz, CDCl_3): δ 8.14 (d, 1 H, $J = 8.8$ Hz), 7.98 (s, 1H), 7.34 (d, 2 H, $J = 8.0$ Hz), 7.11 (d, 2 H, $J = 8.0$ Hz), 6.98 (dd, 1 H, $J = 8.8$ Hz, 2.0 Hz), 6.82 (d, 1 H, $J = 2.0$ Hz), 3.90 (s, 3 H), 2.31 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 174.4, 164.2, 158.1, 155.9, 137.5, 130.9, 130.1, 130.0, 127.7, 120.9, 117.5, 114.9, 100.3, 55.9, 21.1.

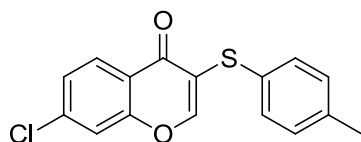


6-Methyl-3-(p-tolylthio)-4H-chromen-4-one (3k).³ Yield: 71mg (84%); $R_f = 0.6$; white solid; m.p. 118-120 °C [lit. 117-120 °C]; ^1H NMR (400 MHz, CDCl_3): δ 8.00 (d, 2 H, $J = 8.8$ Hz), 7.45 (d, 2 H, $J = 8.4$ Hz), 7.32-7.27 (m, 3 H), 7.08 (d, 2 H, $J = 7.6$

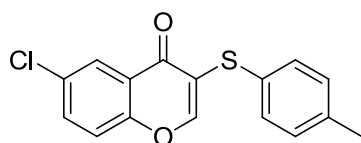
Hz), 2.41 (s, 3 H), 2.28 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 175.1, 156.4, 154.6, 137.4, 135.7, 135.2, 130.8, 130.1, 130.0, 125.6, 123.2, 120.6, 117.9, 21.1, 21.0.



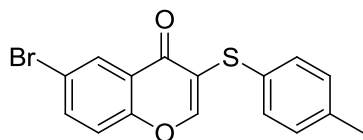
6-Nitro-3-(p-tolylthio)-4H-chromen-4-one (3l).³ Yield: 74 mg (79%); R_f = 0.3; yellow solid; m.p. 155-158 °C [lit. 153-155 °C]; ^1H NMR (400 MHz, CDCl_3): δ 9.08 (d, 1 H, J = 2.8 Hz), 8.49 (dd, 1 H, J = 9.2 Hz, 2.8 Hz), 7.89 (s, 1 H), 7.61 (d, 1 H, J = 9.2 Hz), 7.40 (d, 2 H, J = 8.0 Hz), 7.16 (d, 2 H, J = 8.0 Hz), 2.34 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.6, 159.0, 154.6, 145.0, 138.8, 132.4, 130.4, 128.1, 127.8, 123.8, 123.2, 123.1, 120.0, 21.2.



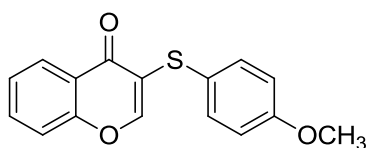
7-Chloro-3-(p-tolylthio)-4H-chromen-4-one (3m). Yield: 74 mg (81%); R_f = 0.7; white solid; m.p. 128-130 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.14 (d, 1 H, J = 8.4 Hz), 7.92 (s, 1 H), 7.43 (s, 1 H), 7.35 (d, 3 H, J = 8.0 Hz), 7.11 (d, 2 H, J = 7.6 Hz), 2.31 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 174.2, 156.3, 155.5, 140.0, 138.0, 131.5, 130.2, 129.1, 127.7, 126.5, 122.1, 122.0, 118.2, 21.1; ESI-HRMS: Calcd for $\text{C}_{16}\text{H}_{12}\text{ClO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 303.0241, found 303.0243.



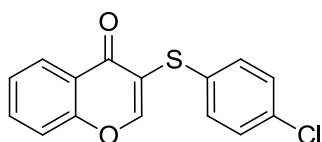
6-Chloro-3-(p-tolylthio)-4H-chromen-4-one (3n).³ Yield: 75 mg (82%); R_f = 0.5; white solid; m.p. 175-178 °C [lit. 173-177 °C]; ^1H NMR (400 MHz, CDCl_3): δ 8.18 (d, 1 H, J = 2.4 Hz), 7.98 (s, 1 H), 7.60 (dd, 1 H, J = 8.8 Hz, 2.4 Hz), 7.41 (d, 1 H, J = 9.2 Hz), 7.35 (d, 2 H, J = 8.0 Hz), 7.12 (d, 2 H, J = 8.0 Hz), 2.32 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 174.0, 155.8, 154.6, 138.0, 134.1, 131.6, 131.5, 130.2, 129.2, 125.7, 124.4, 121.8, 119.9, 21.1.



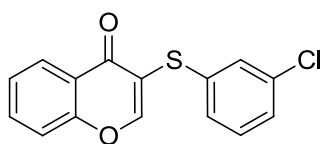
6-Bromo-3-(*p*-tolylthio)-4*H*-chromen-4-one (3o).³ Yield: 79 mg (76%); R_f = 0.5; Yellow solid; m.p. 198-200 °C [lit. 199-202 °C]; ^1H NMR (400 MHz, CDCl_3): δ 8.35 (d, 1 H, J = 2.4 Hz), 7.98 (s, 1 H), 7.75 (dd, 1 H, J = 9.2 Hz, 2.8 Hz), 7.36-7.34 (m, 3 H), 7.12 (d, 2 H, J = 8.0 Hz), 2.32 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.8, 155.8, 155.1, 138.0, 136.9, 131.5, 130.2, 129.2, 128.9, 124.7, 121.9, 120.1, 119.0, 21.1.



3-((4-Methoxyphenyl)thio)-4*H*-chromen-4-one (3p).³ Yield: 68 mg (80%); R_f = 0.2; white solid; m.p. 110-113 °C [lit. 117-119 °C]; ^1H NMR (400 MHz, CDCl_3): δ 8.23 (d, 1 H, J = 9.6 Hz), 7.90 (s, 1 H), 7.68-7.64 (m, 1 H), 7.48 (d, 2 H, J = 8.8 Hz), 7.44-7.39 (m, 2 H), 6.86 (d, 2 H, J = 8.8 Hz), 3.79 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 175.1, 159.9, 156.3, 154.9, 134.3, 133.8, 126.3, 125.5, 123.4, 123.2, 122.6, 118.1, 115.0, 55.4.

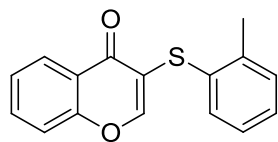


3-((4-Chlorophenyl)thio)-4*H*-chromen-4-one (3q).³ Yield: 65 mg (76%); R_f = 0.3; white solid; m.p. 165-169 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.25-8.23 (m, 2 H), 7.73-7.69 (m, 1 H), 7.49-7.43 (m, 2 H), 7.32 (d, 2 H, J = 8.4 Hz), 7.26-7.23 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3): δ 174.9, 157.8, 156.4, 134.1, 133.2, 132.8, 131.0, 129.3, 126.5, 125.9, 123.8, 119.3, 118.2.



3-((3-Chlorophenyl)thio)-4*H*-chromen-4-one (3r). Yield: 64 mg (74%); R_f = 0.4; white solid; m.p. 128-130 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.27 (s, 1 H), 7.24 (d, 1

H, $J = 8.0$ Hz), 7.71 (t, 1 H, $J = 7.2$ Hz), 7.50-7.43 (m, 2 H), 7.30 (s, 1 H), 7.26-7.23 (m, 1 H), 7.21-7.14 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3): δ 174.8, 158.5, 156.4, 136.7, 134.9, 134.2, 130.1, 128.6, 127.1, 127.0, 126.5, 126.0, 123.8, 118.5, 118.2; ESI-HRMS: Calcd for $\text{C}_{15}\text{H}_{10}\text{ClO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 289.0085, found 289.0085.



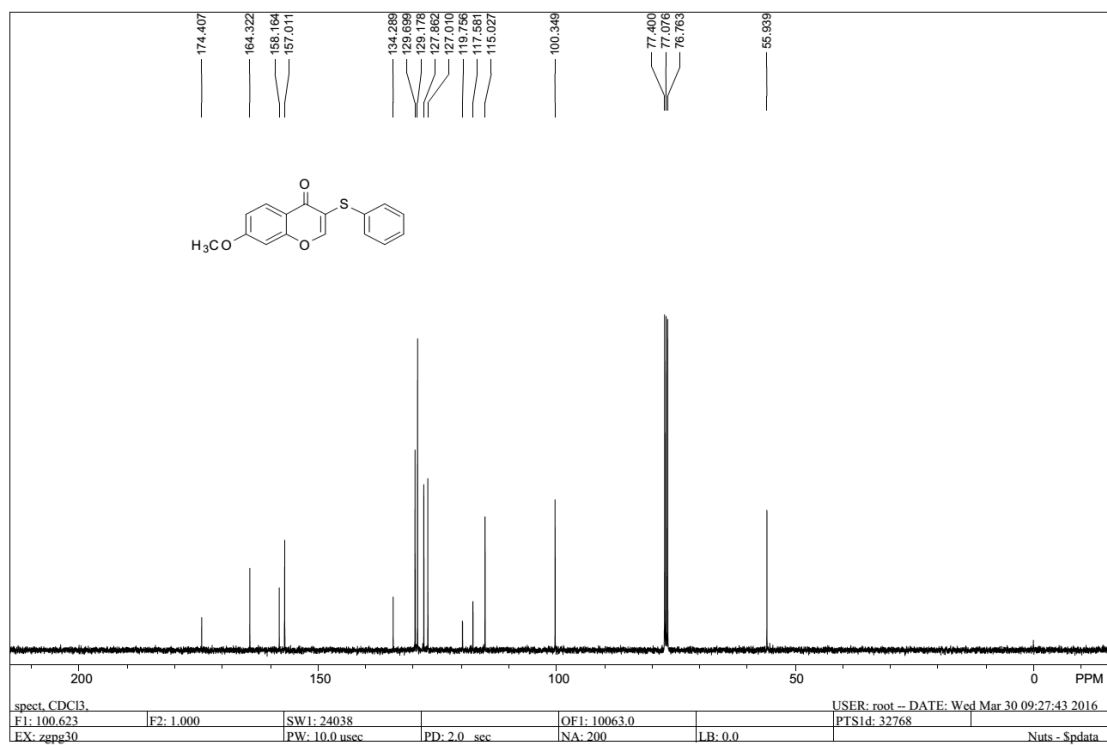
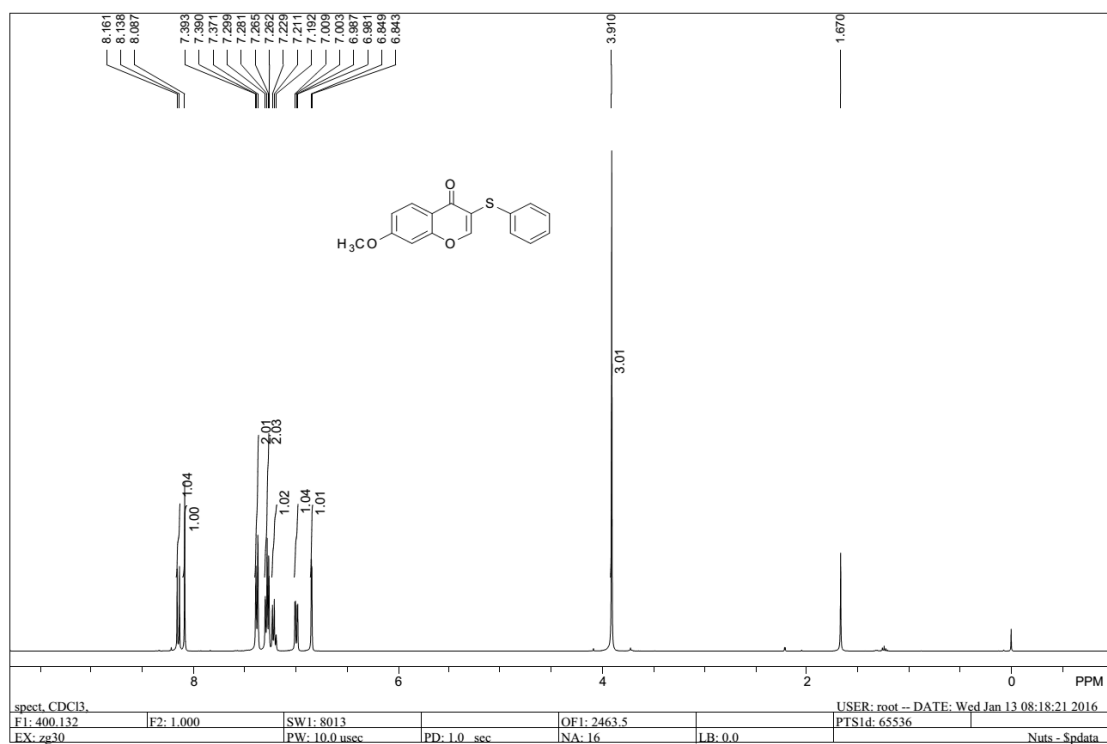
3-(o-Tolylthio)-4H-chromen-4-one (3s).³ Yield: 61 mg (76%); $R_f = 0.4$; white solid; m.p. 156-159 °C [lit. 154-155 °C]; ^1H NMR (400 MHz, CDCl_3): δ 8.25 (dd, 1 H, $J = 8.0$ Hz, 1.2 Hz), 7.86 (s, 1 H), 7.68 (t, 1 H, $J = 6.8$ Hz), 7.46-7.41 (m, 2 H), 7.27-7.22 (m, 2 H), 7.19-7.15 (m, 1 H), 7.13-7.09 (m, 1 H), 2.49 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 175.0, 156.4, 155.5, 138.9, 133.9, 132.2, 131.0, 130.7, 127.6, 126.8, 126.4, 125.6, 123.4, 120.5, 118.1, 20.4.

References

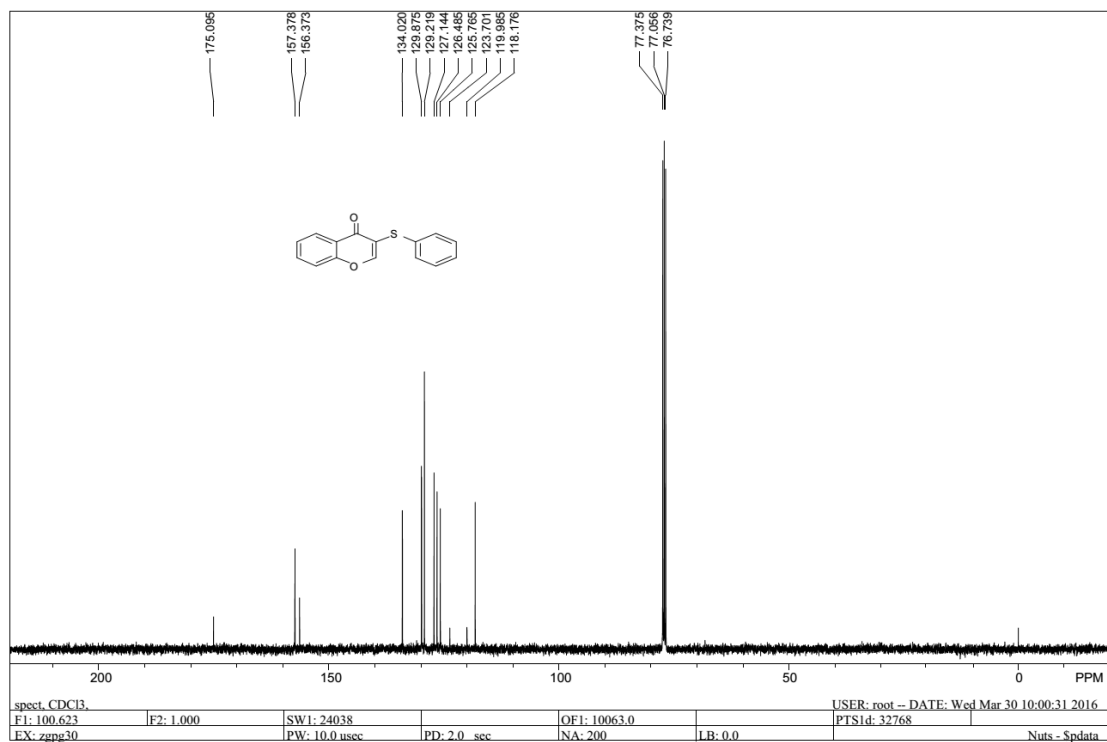
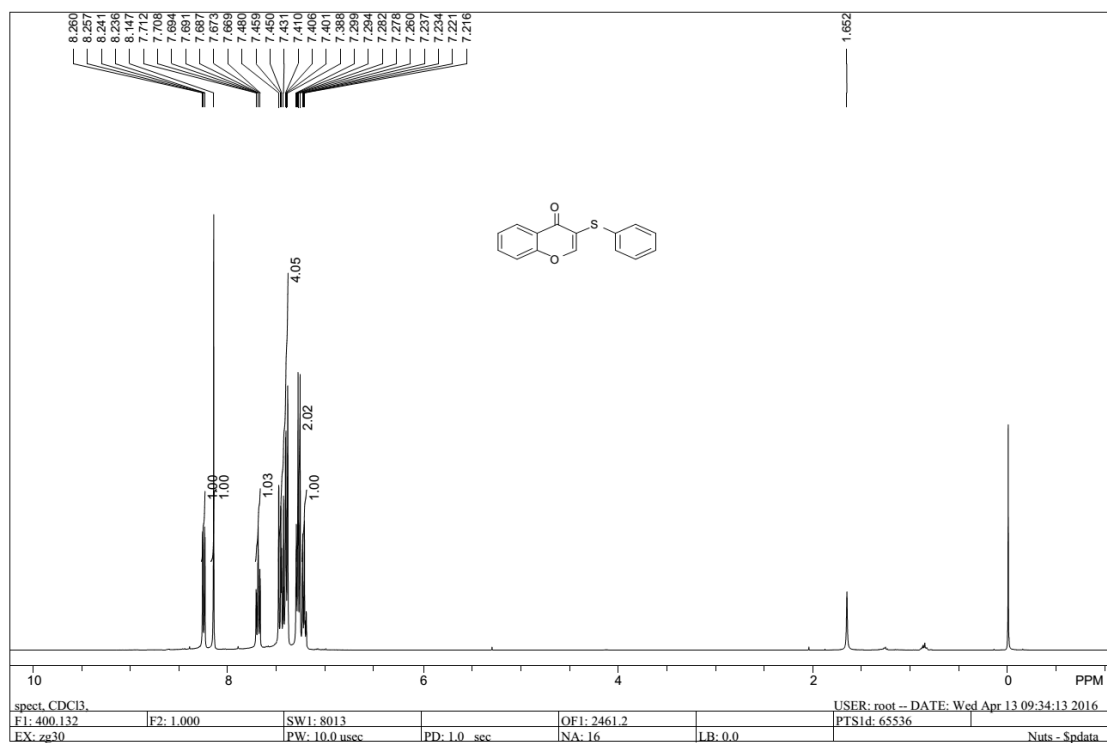
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- 2) Rafique, J.; Saba, S.; Schneider, A. R.; Franco, M. S.; Silva, S. M.; Braga, A. L. *ACS Omega* **2017**, 2, 2280.
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¹H and ¹³C NMR spectra of all products

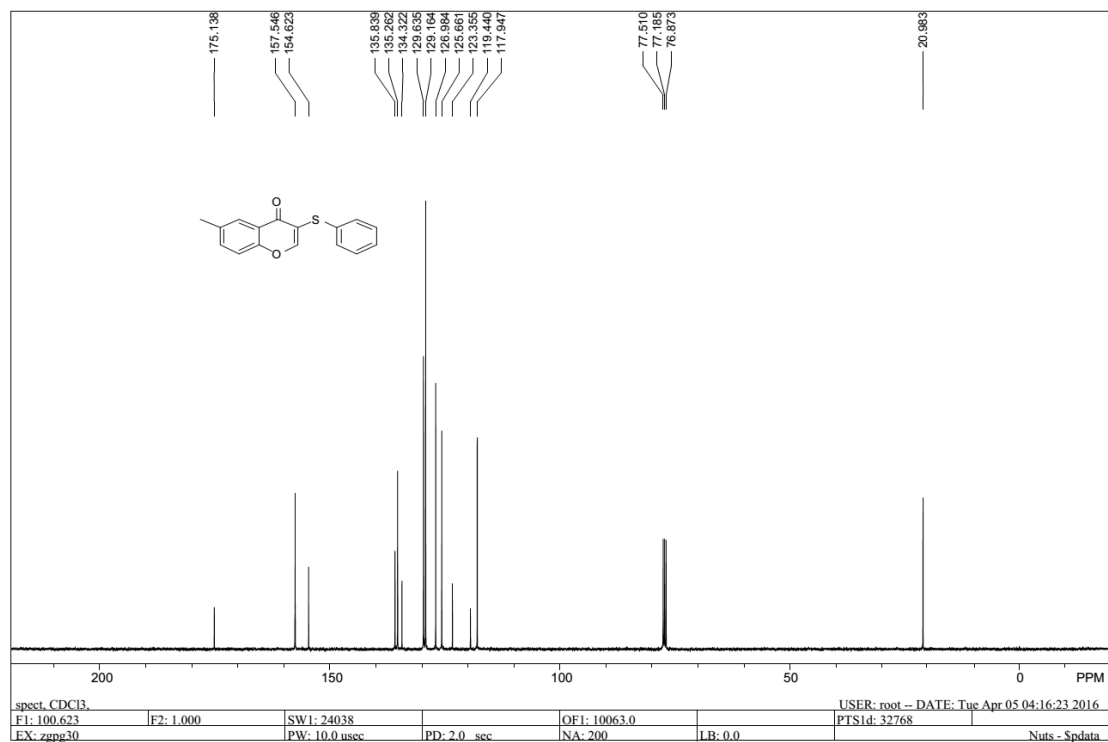
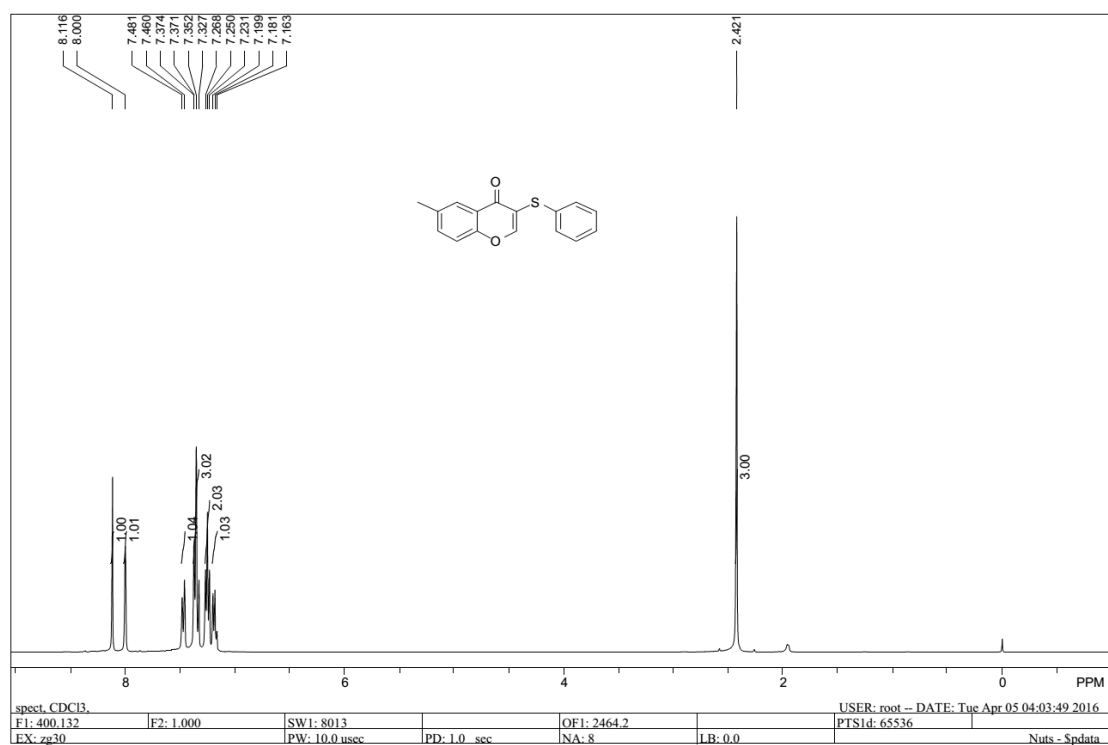
¹H and ¹³C NMR spectra of 3a



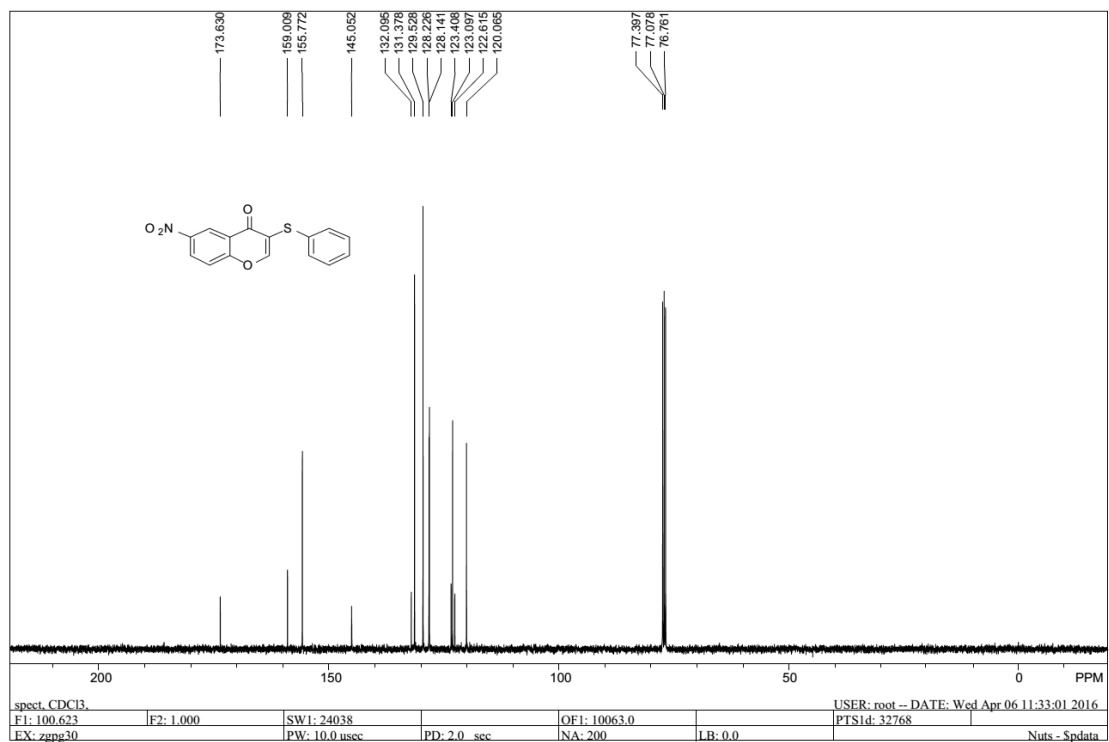
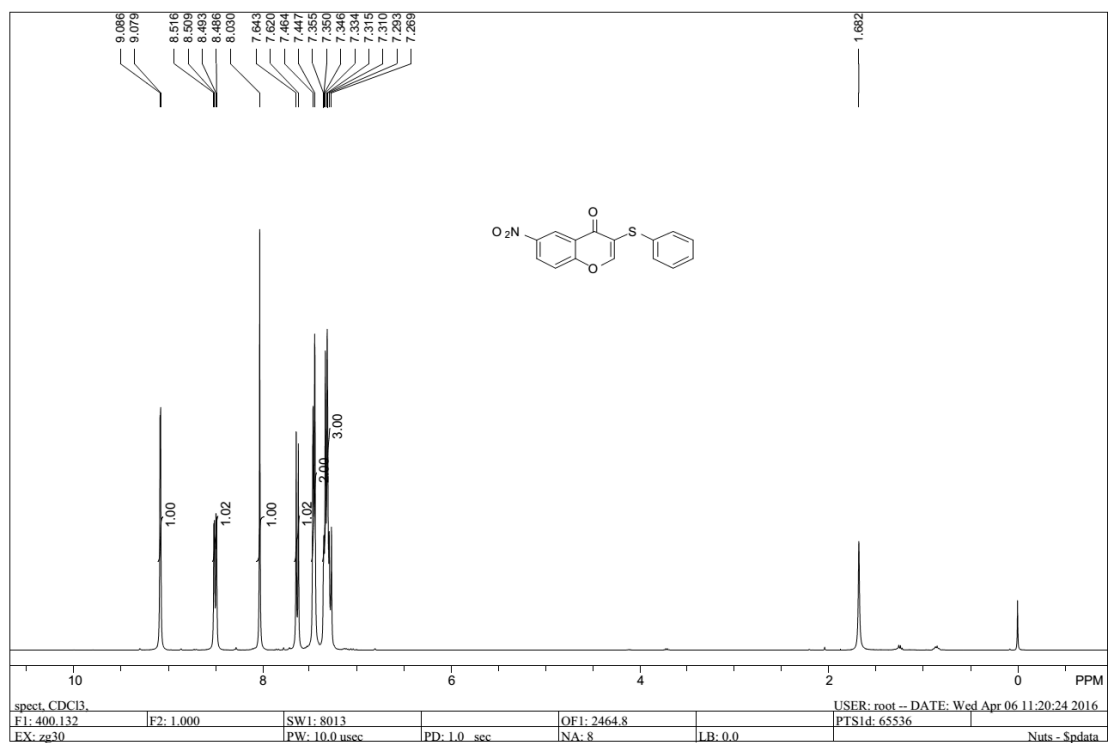
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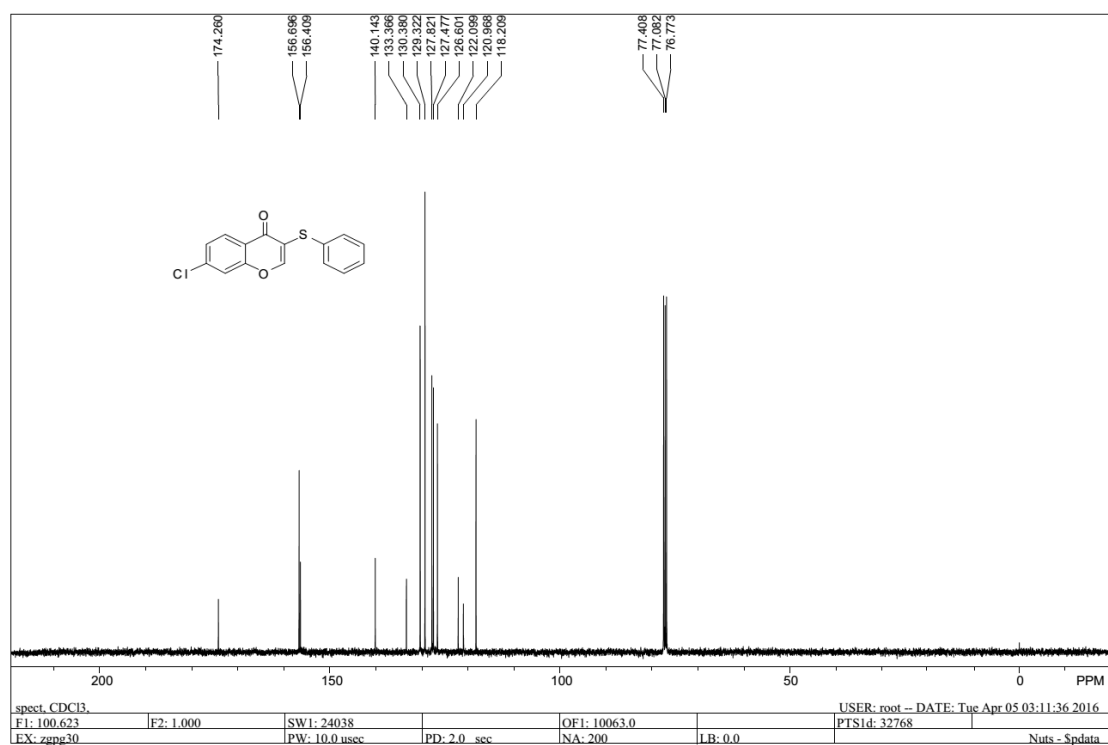
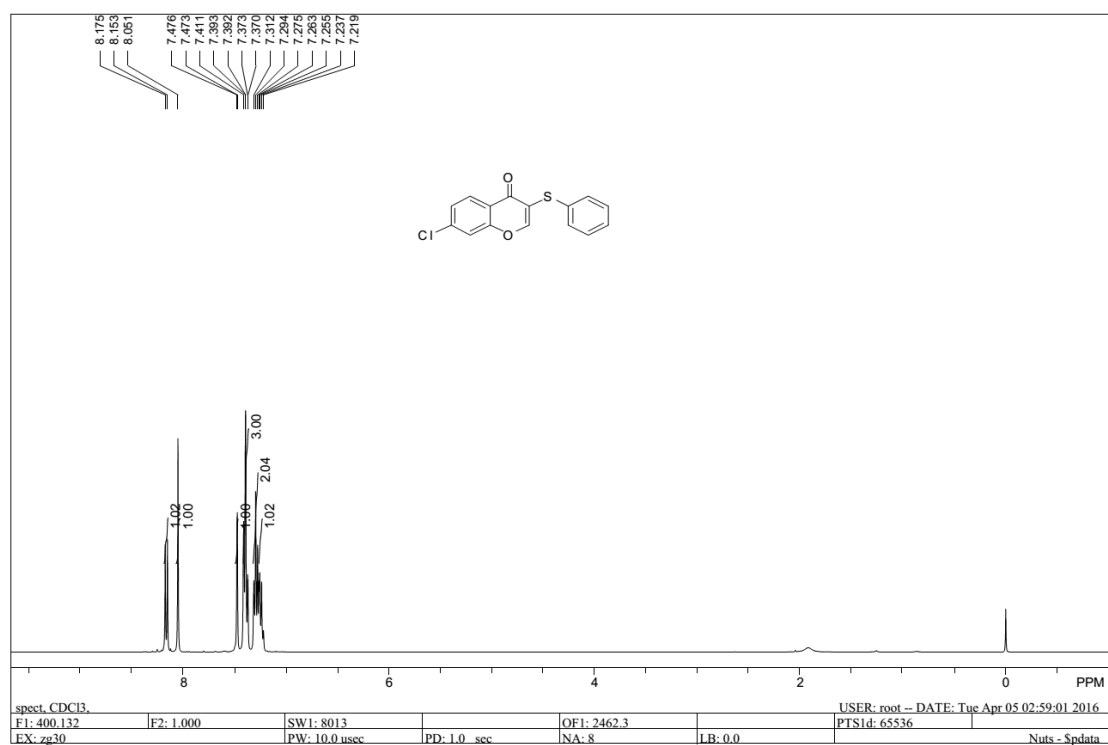
^1H and ^{13}C NMR spectra of **3c**



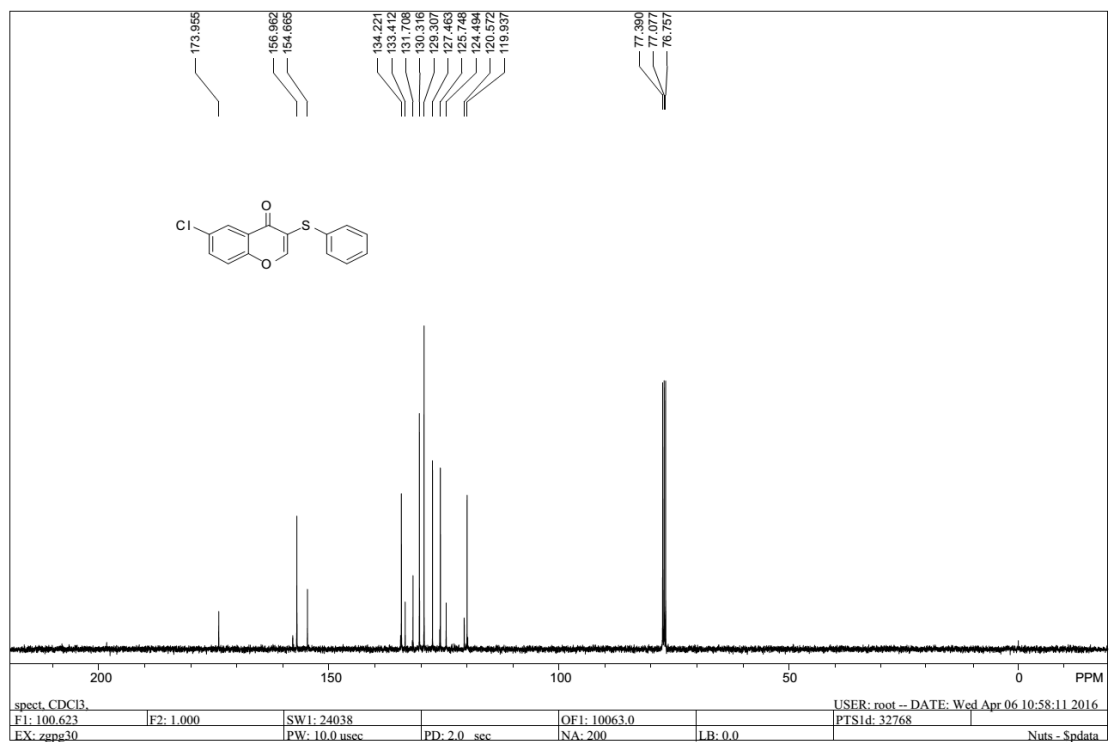
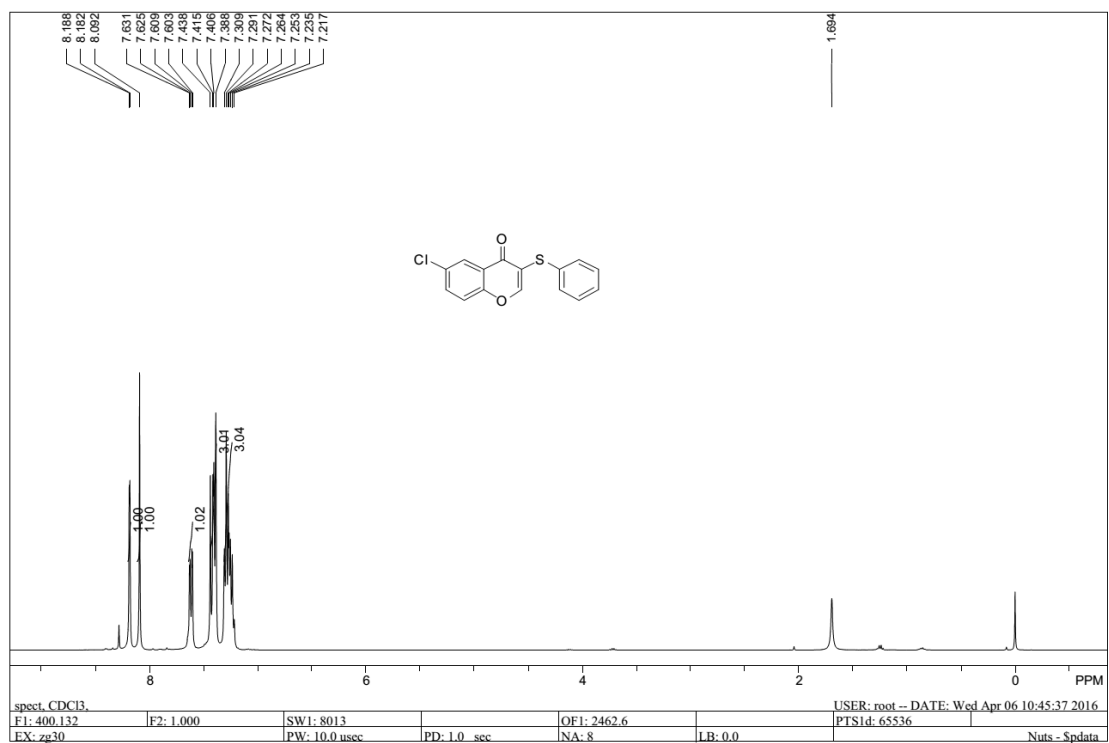
^1H and ^{13}C NMR spectra of **3d**



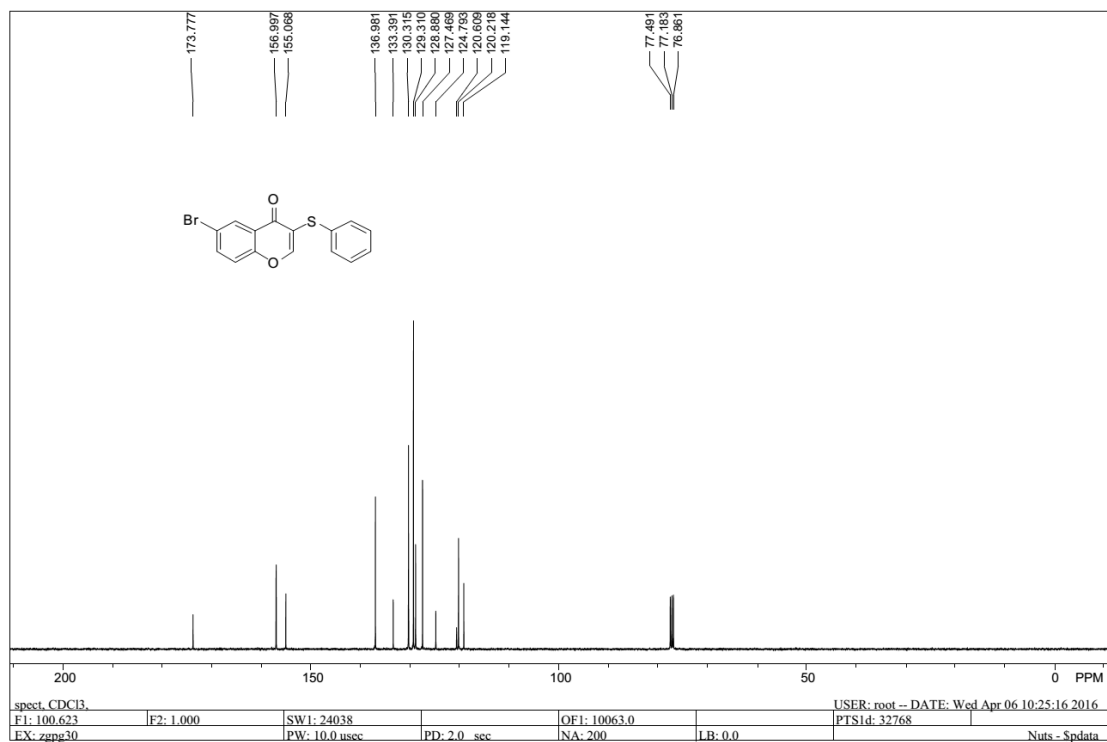
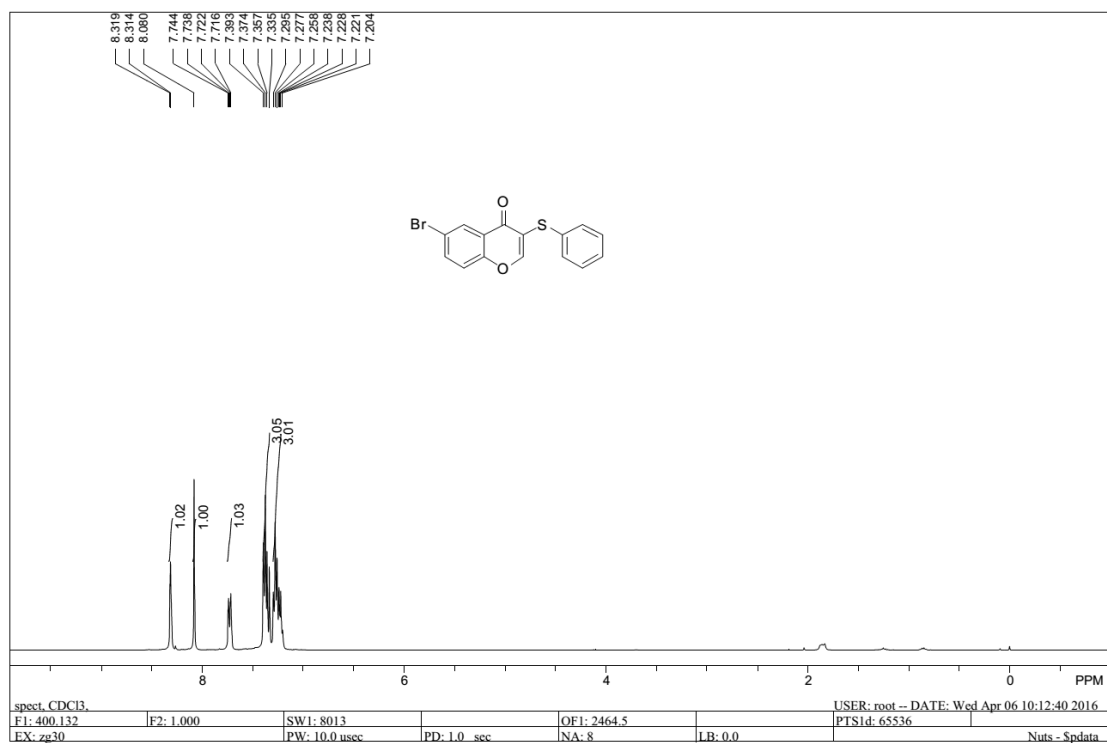
^1H and ^{13}C NMR spectra of **3e**



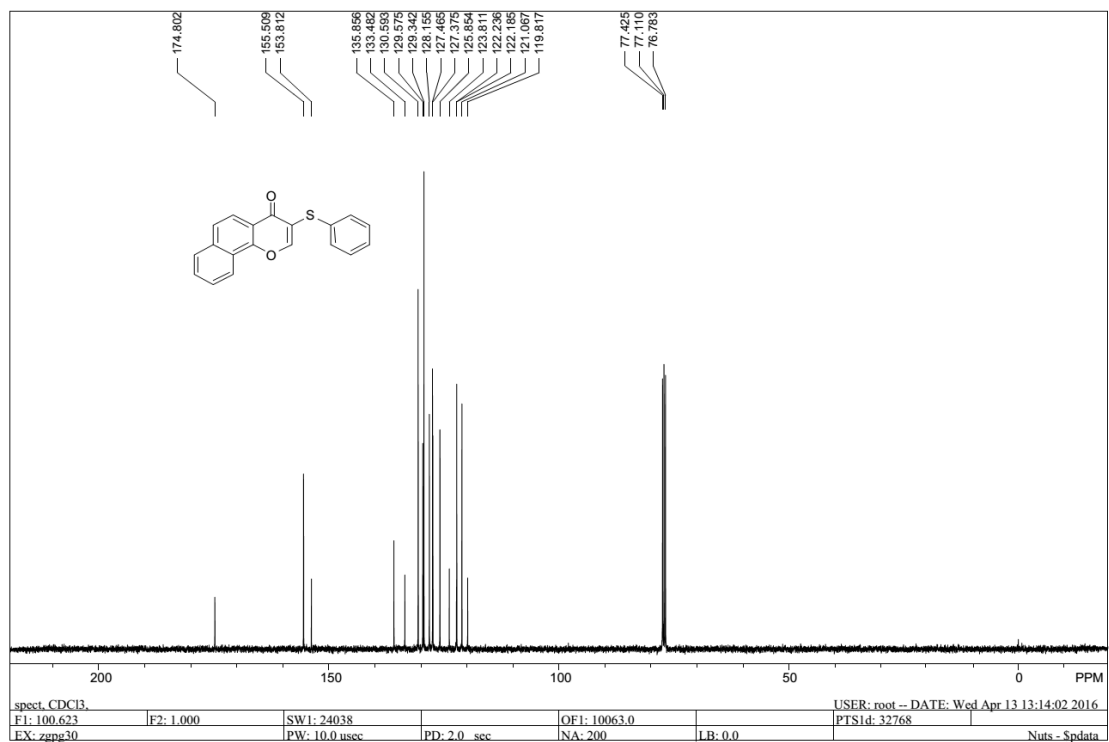
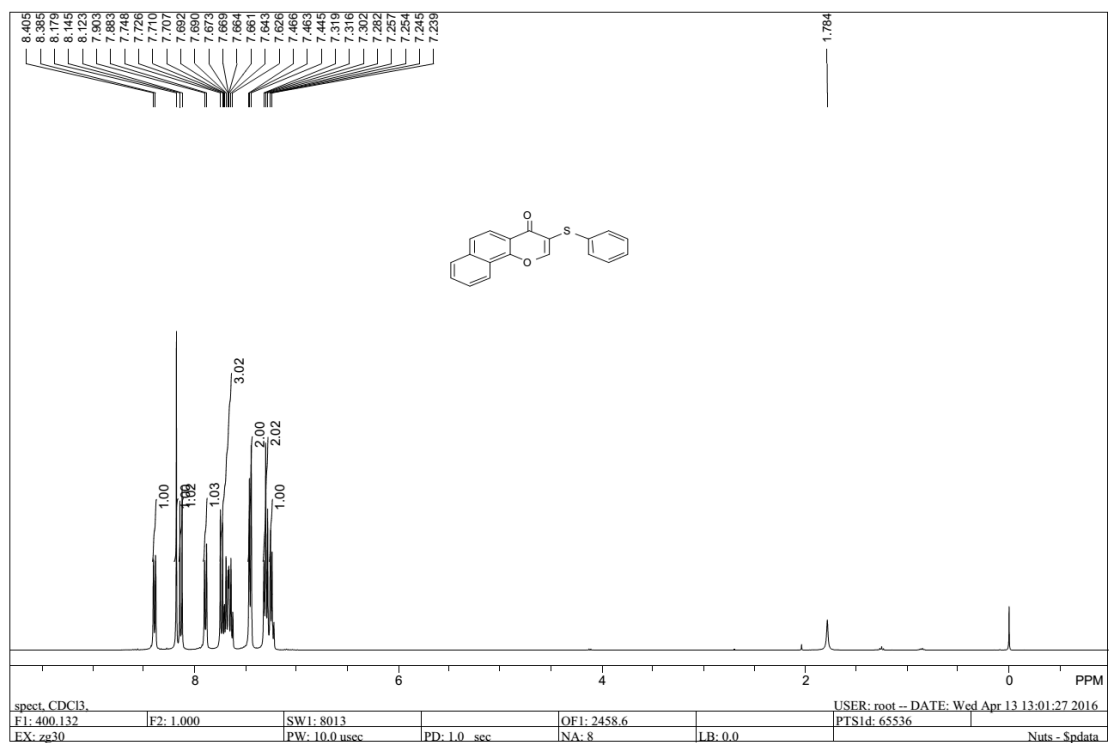
^1H and ^{13}C NMR spectra of **3f**



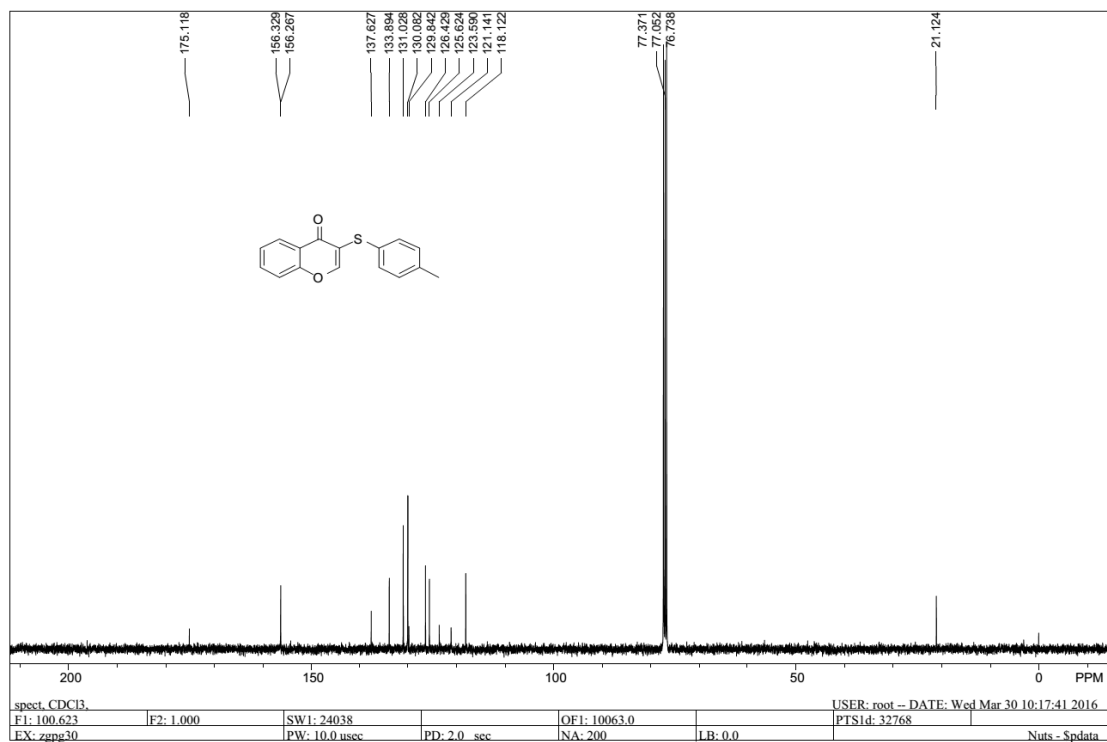
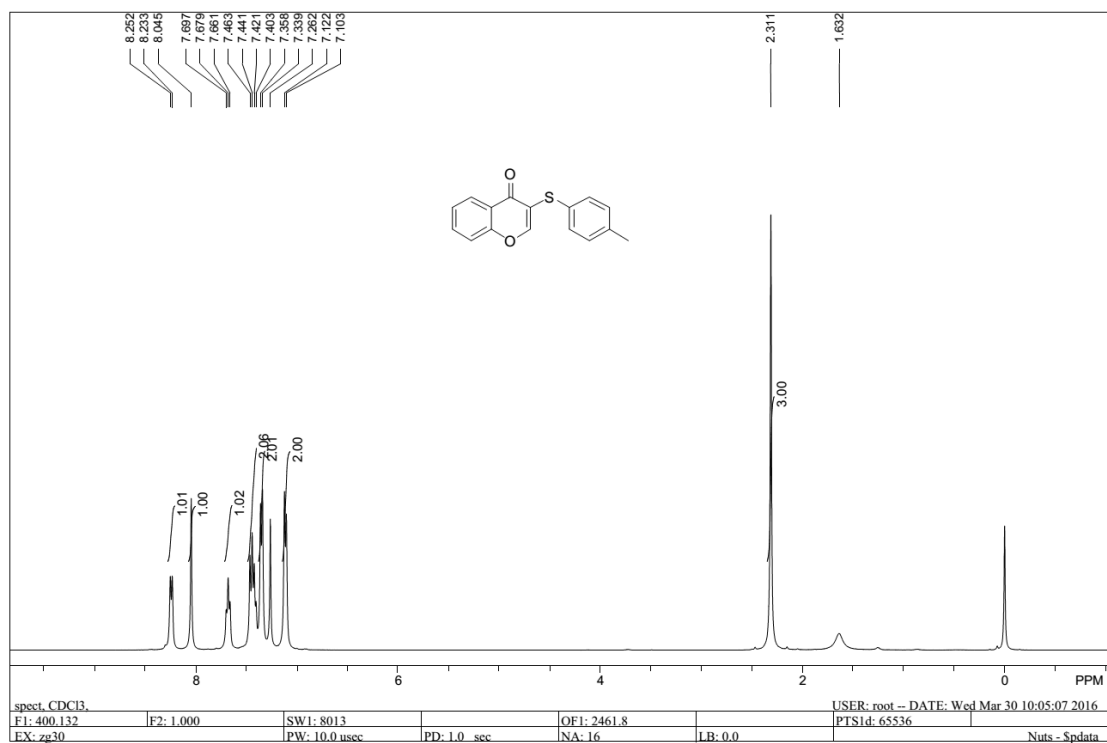
^1H and ^{13}C NMR spectra of **3g**



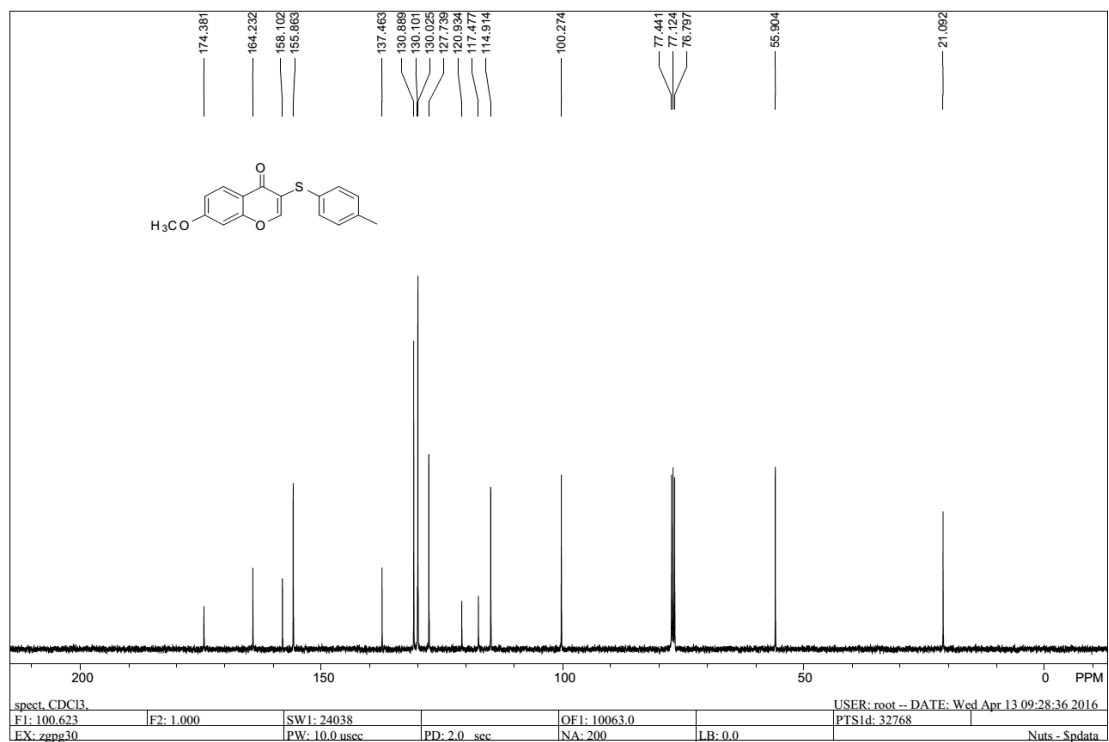
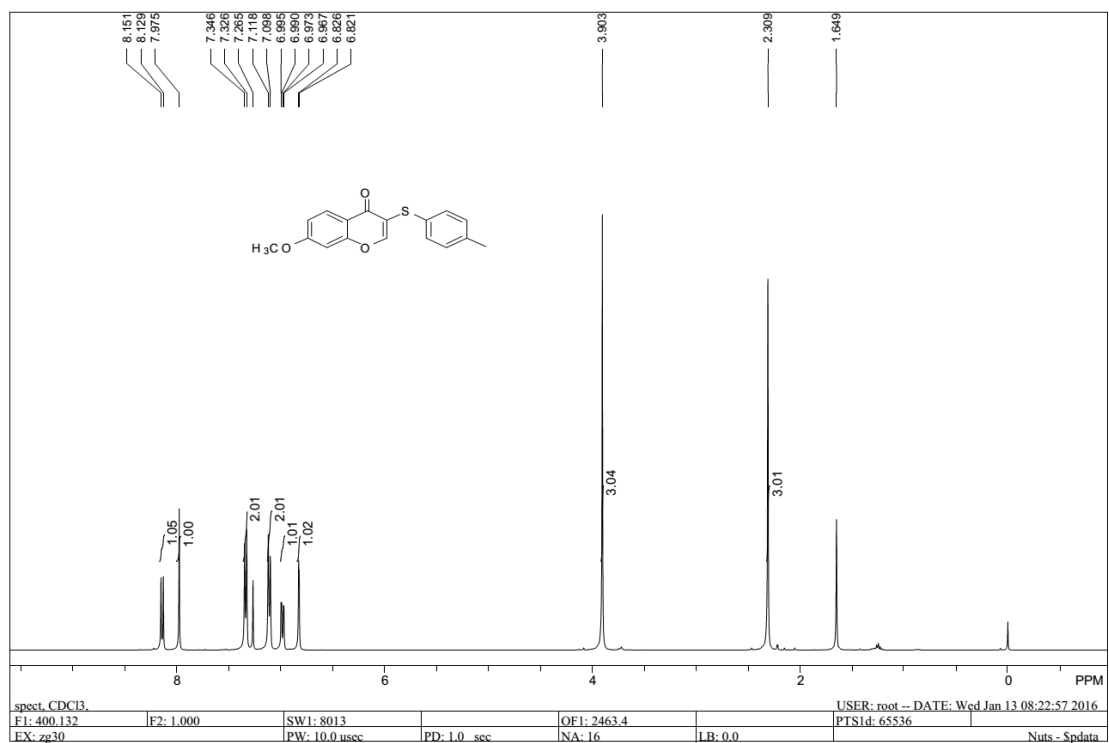
^1H and ^{13}C NMR spectra of **3h**



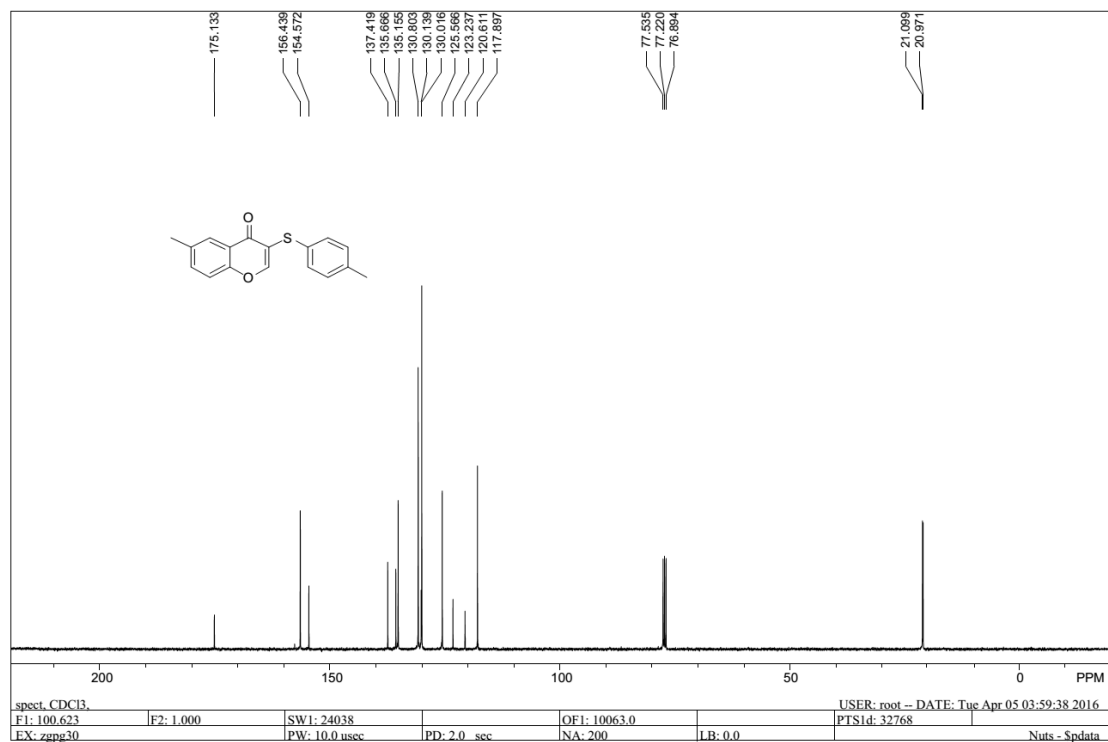
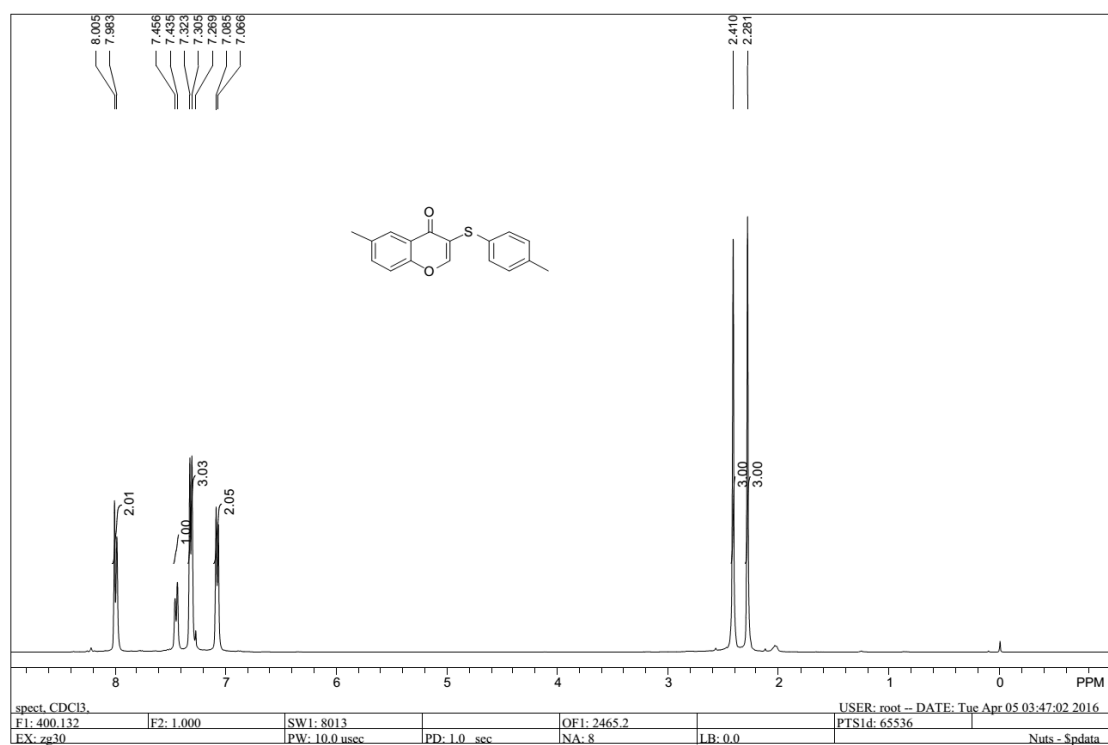
^1H and ^{13}C NMR spectra of **3i**



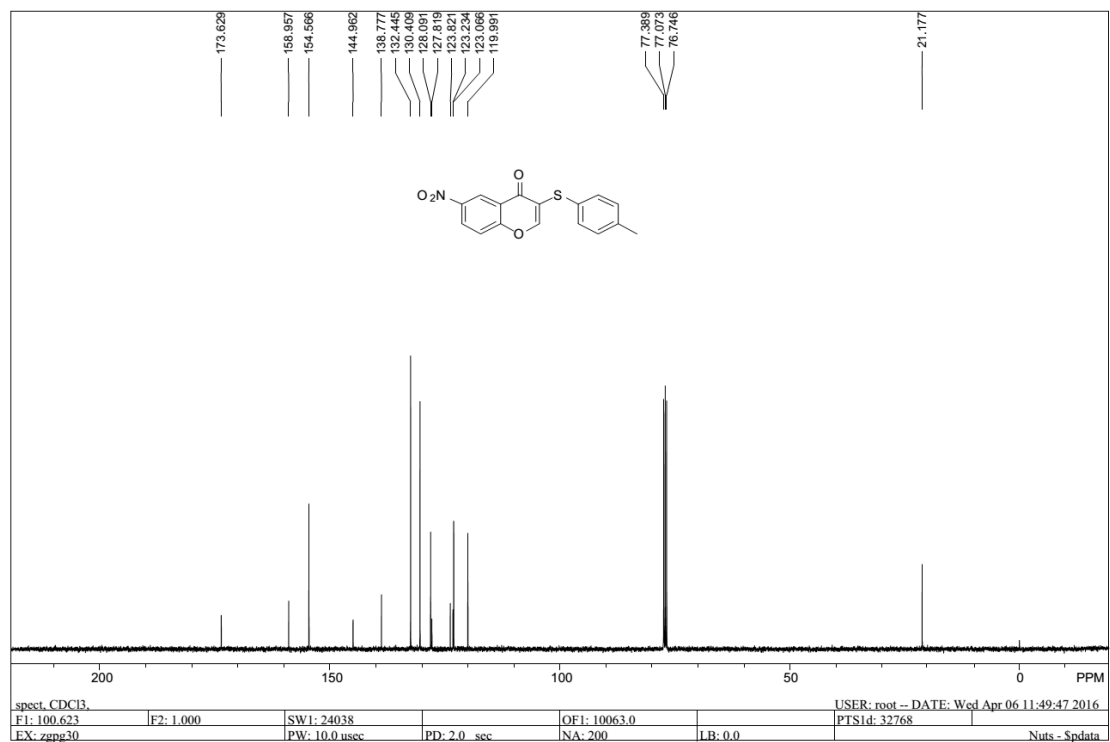
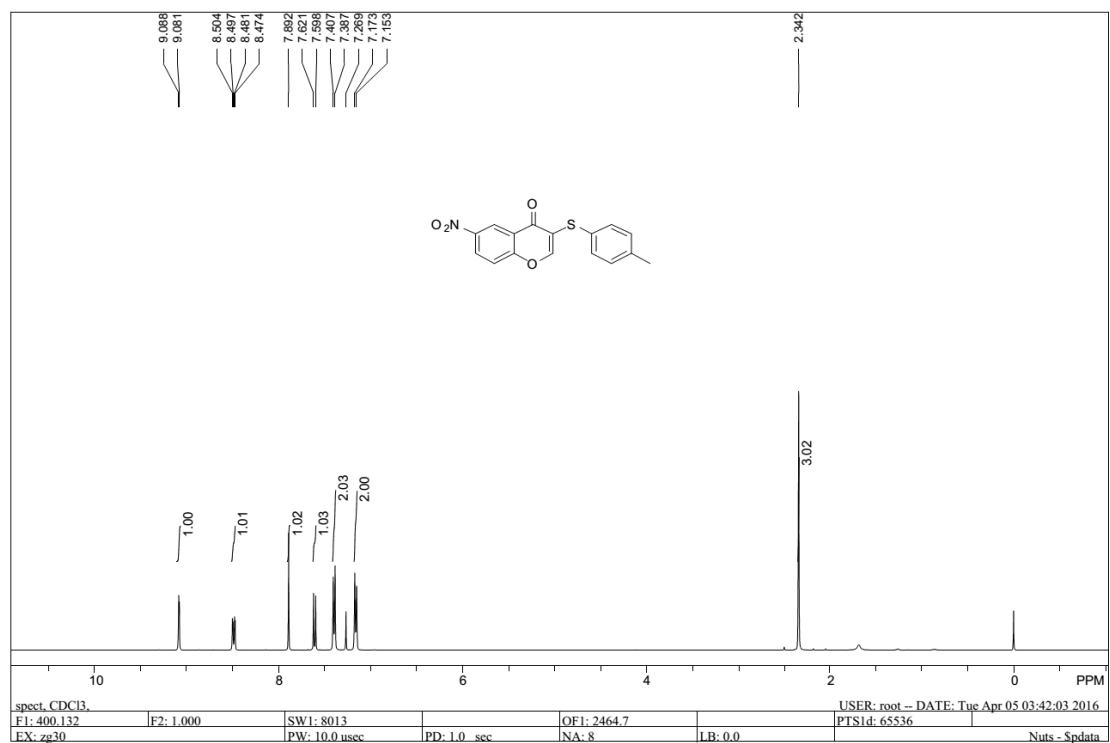
^1H and ^{13}C NMR spectra of **3j**



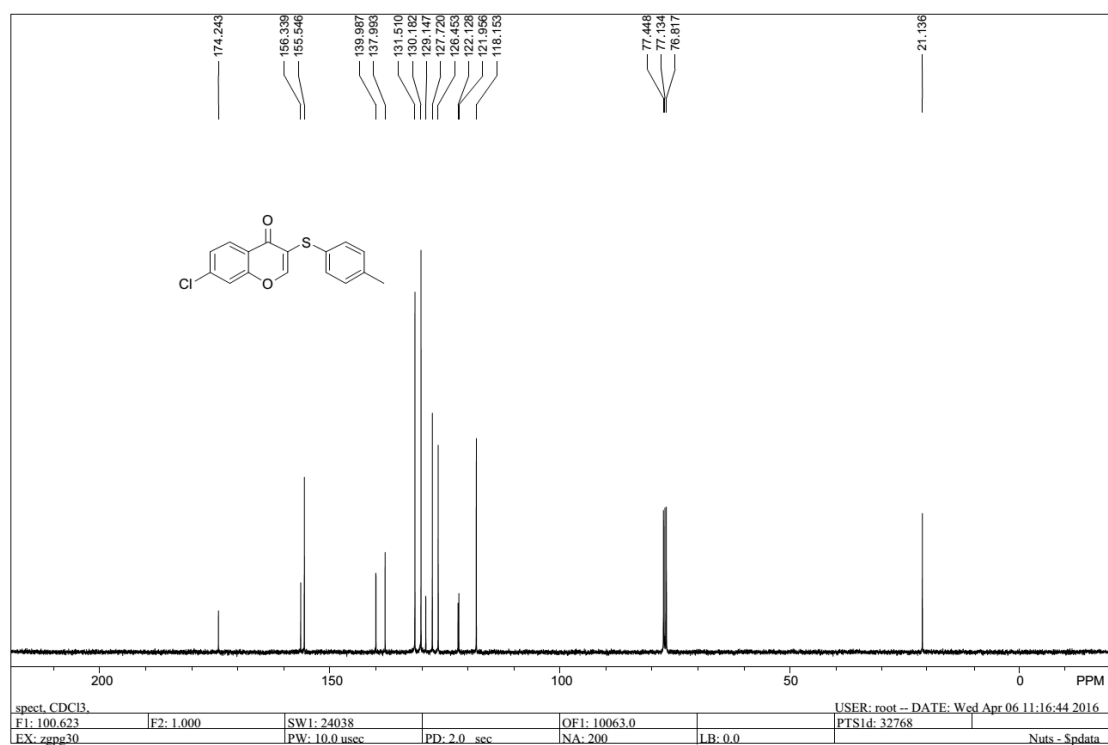
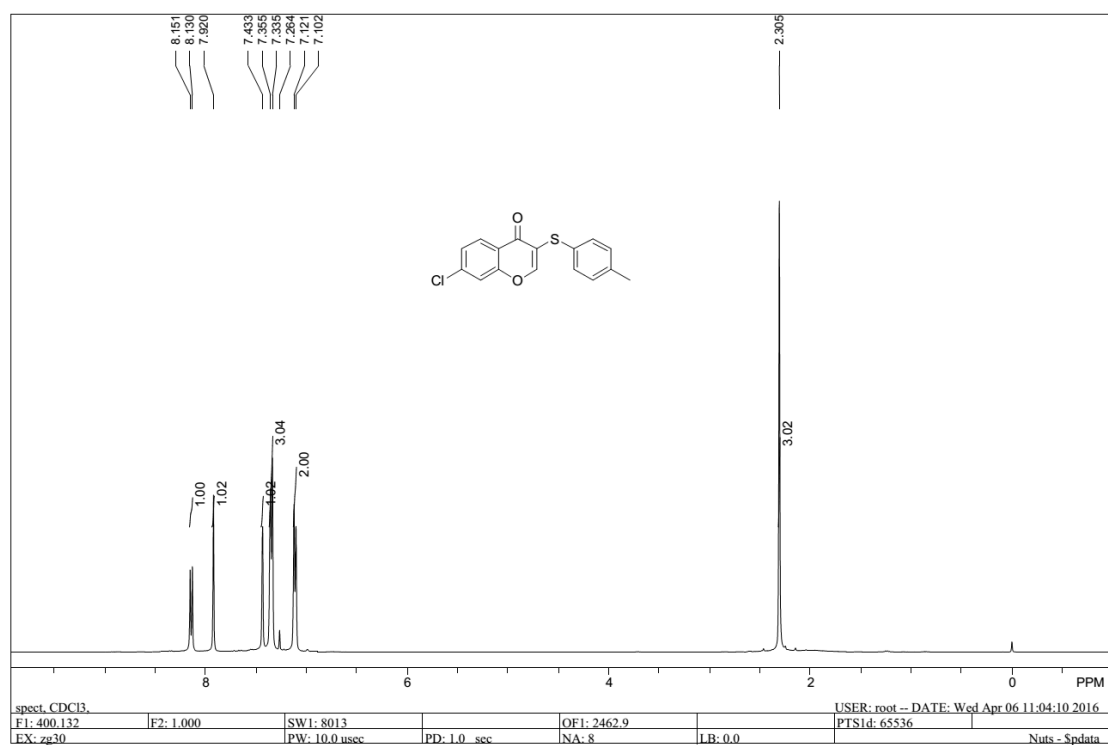
^1H and ^{13}C NMR spectra of **3k**



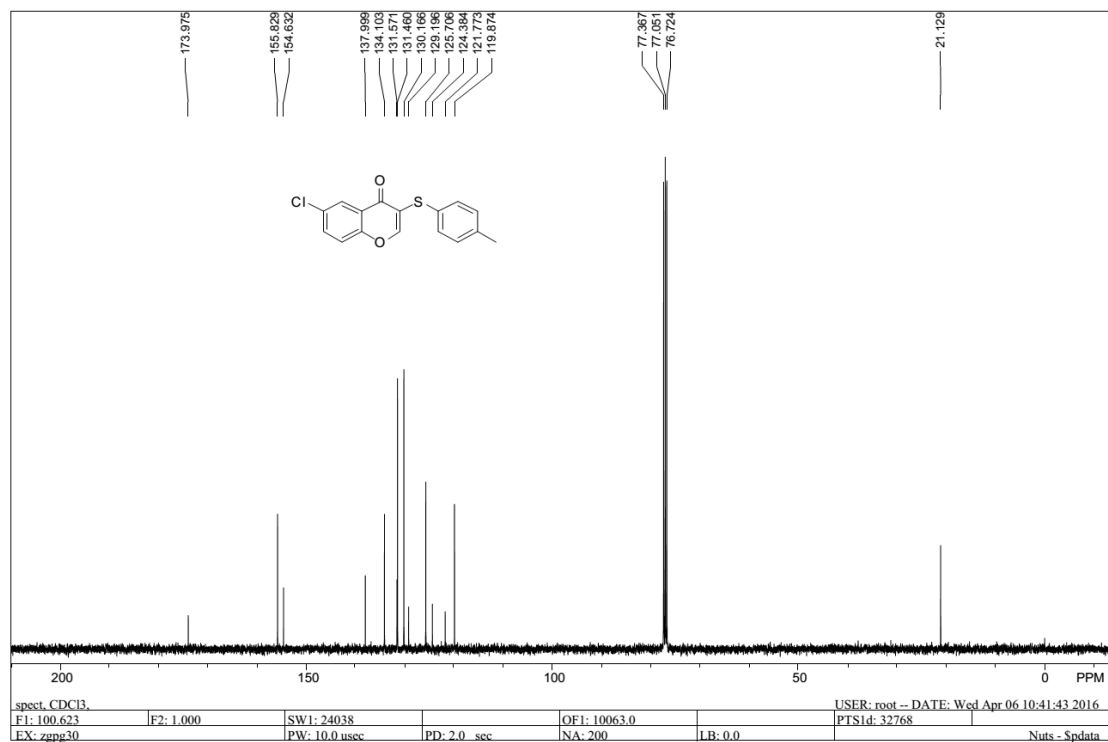
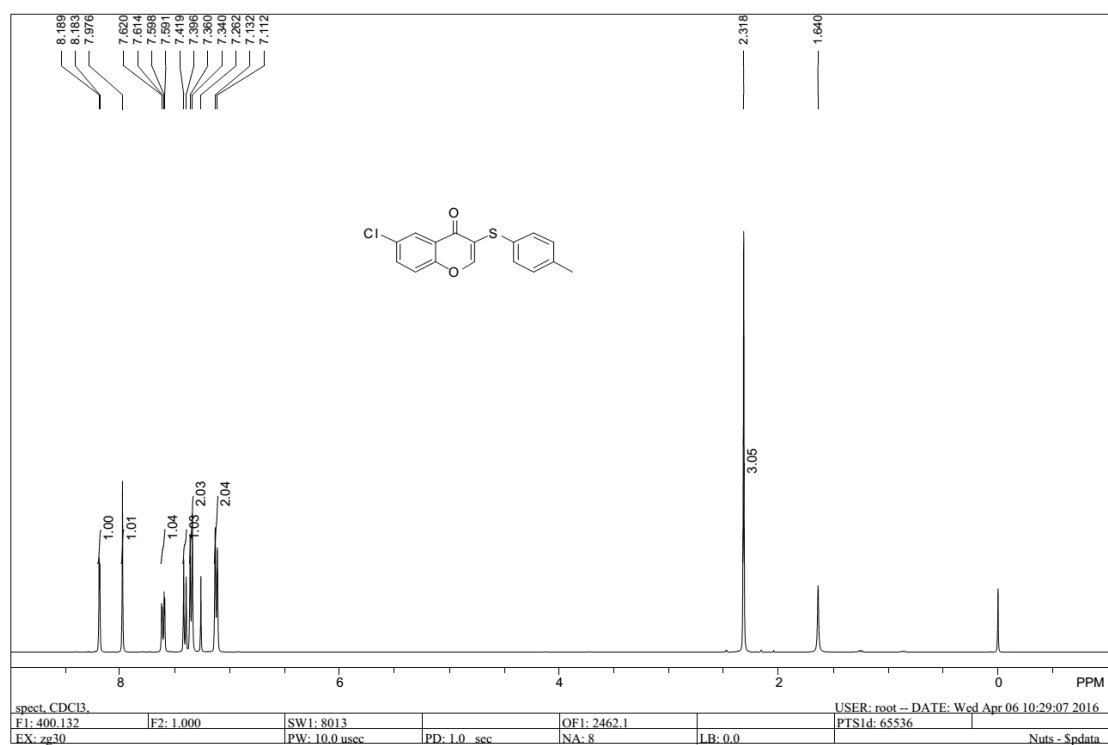
^1H and ^{13}C NMR spectra of **3l**



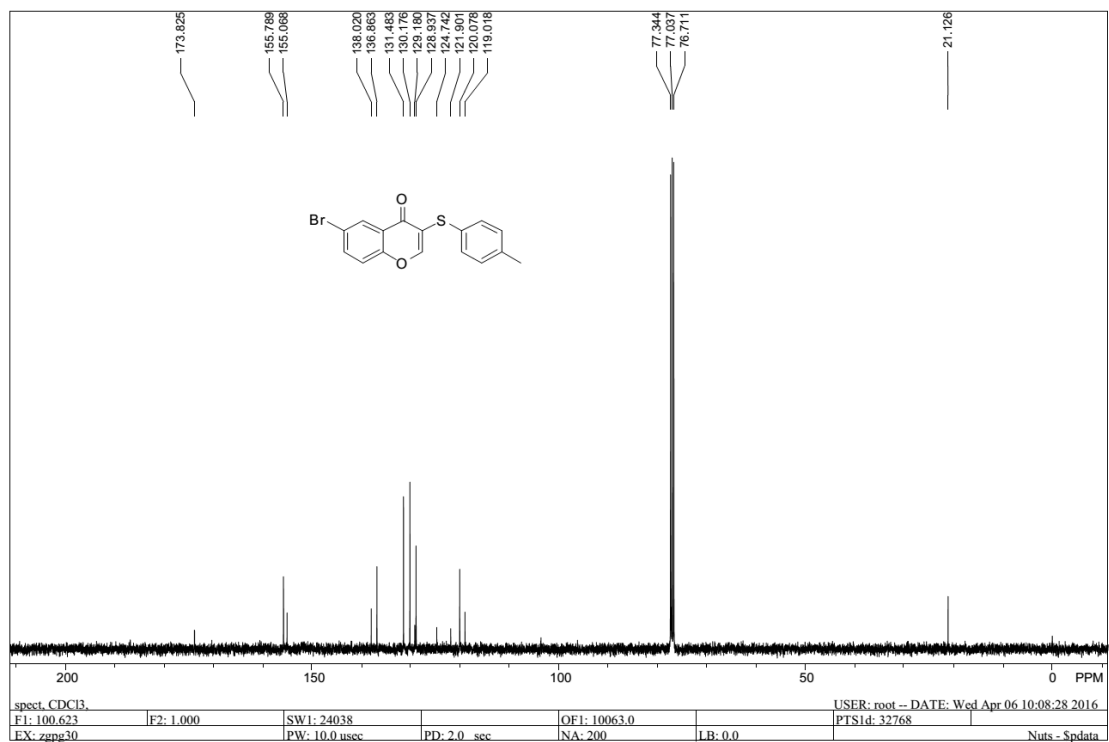
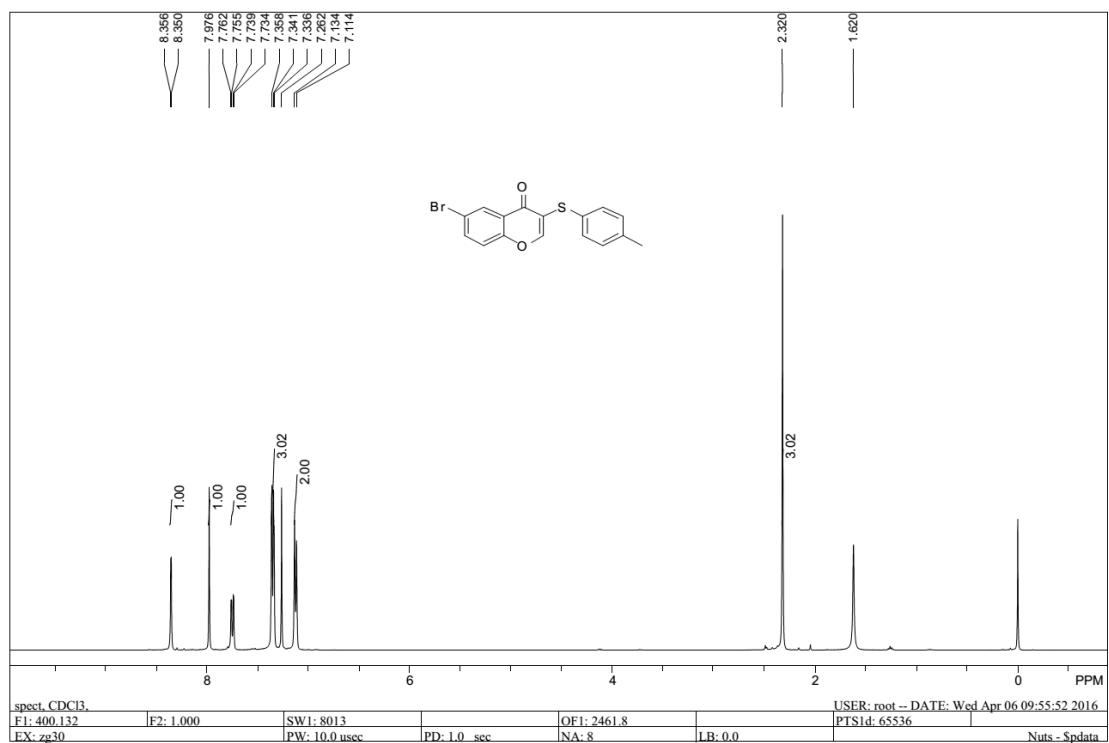
^1H and ^{13}C NMR spectra of **3m**



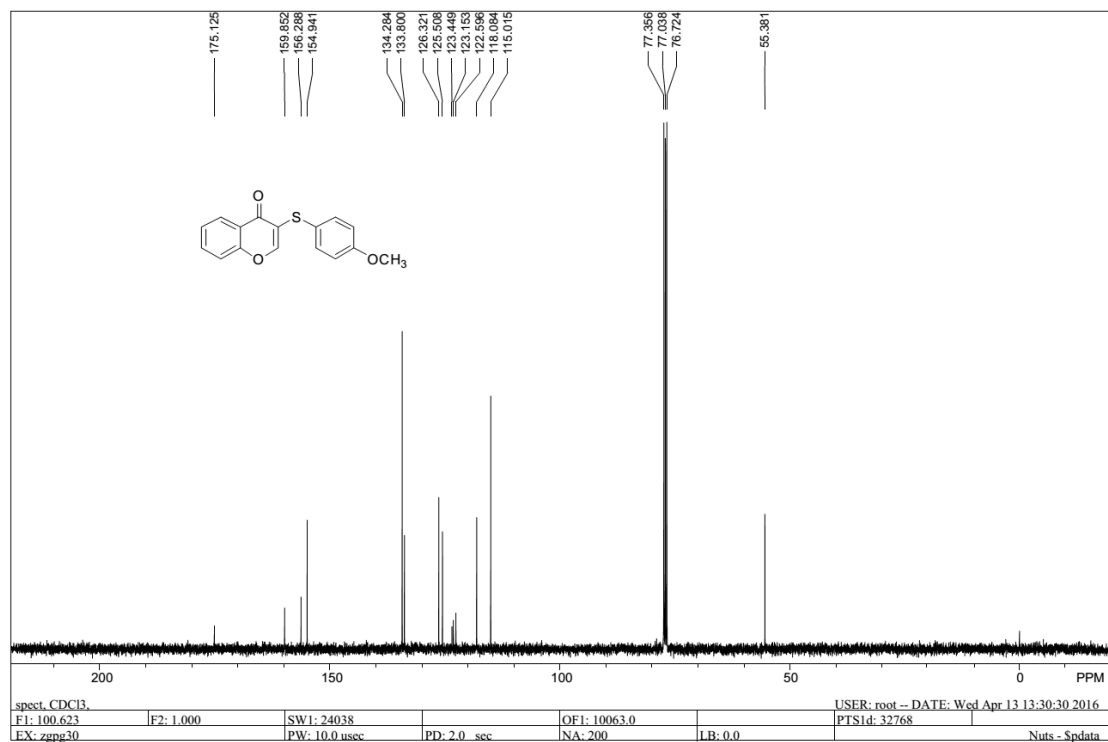
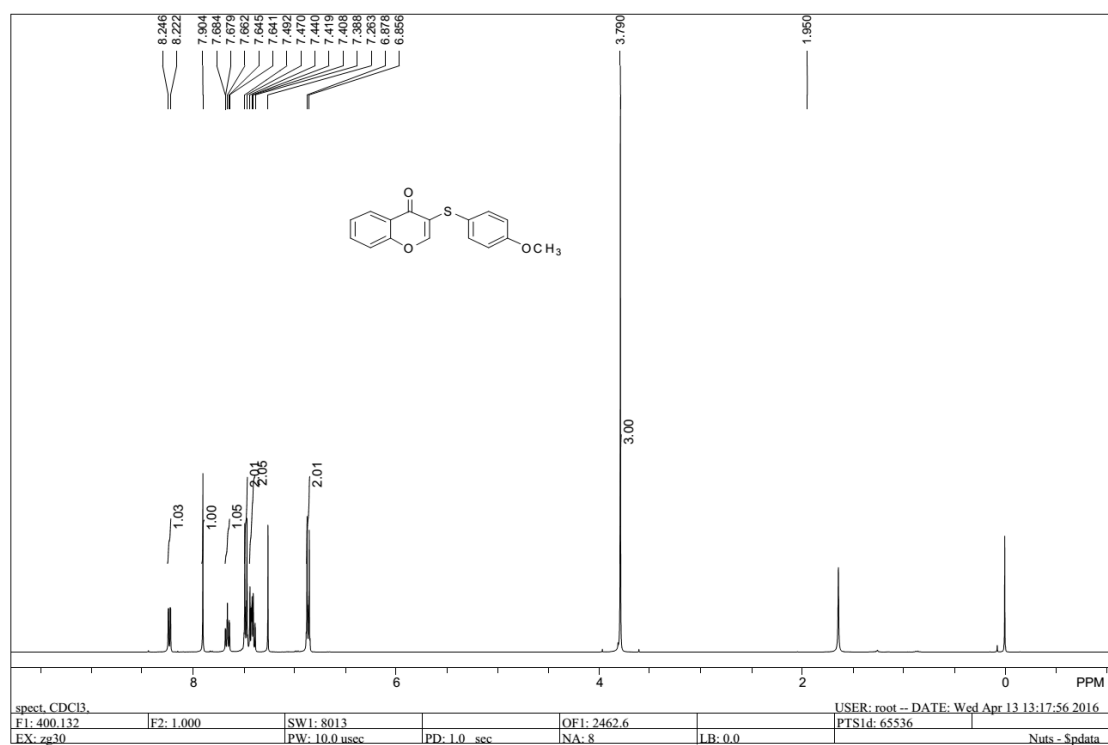
^1H and ^{13}C NMR spectra of **3n**



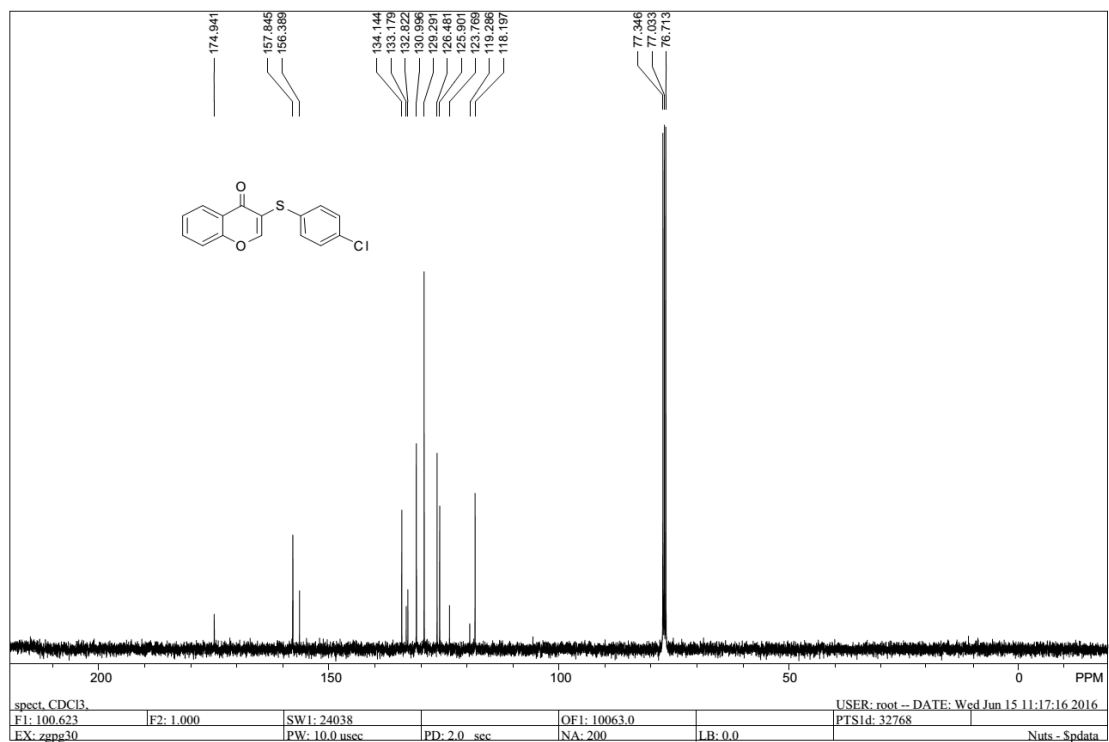
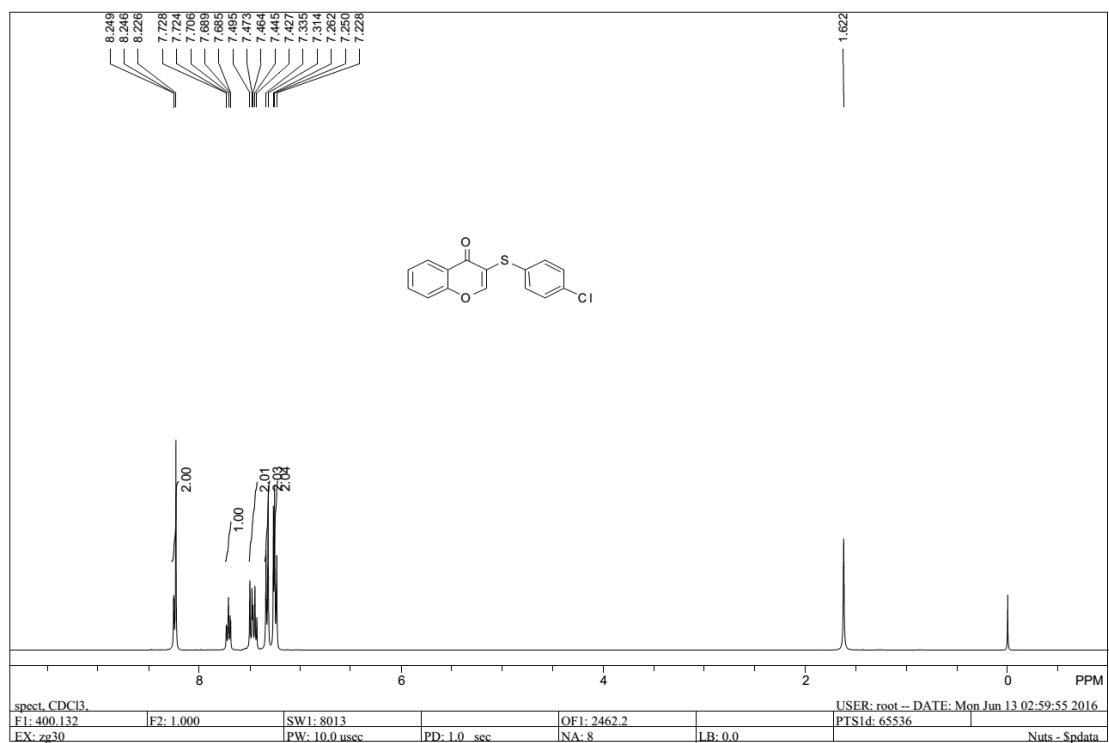
^1H and ^{13}C NMR spectra of **3o**



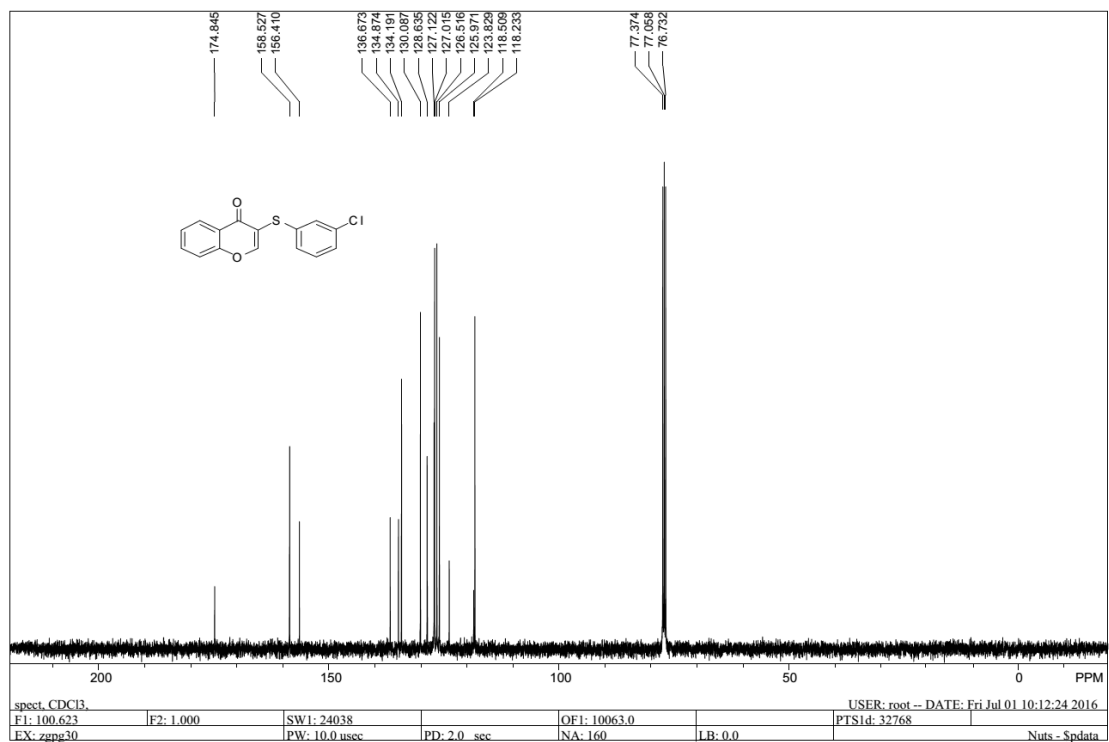
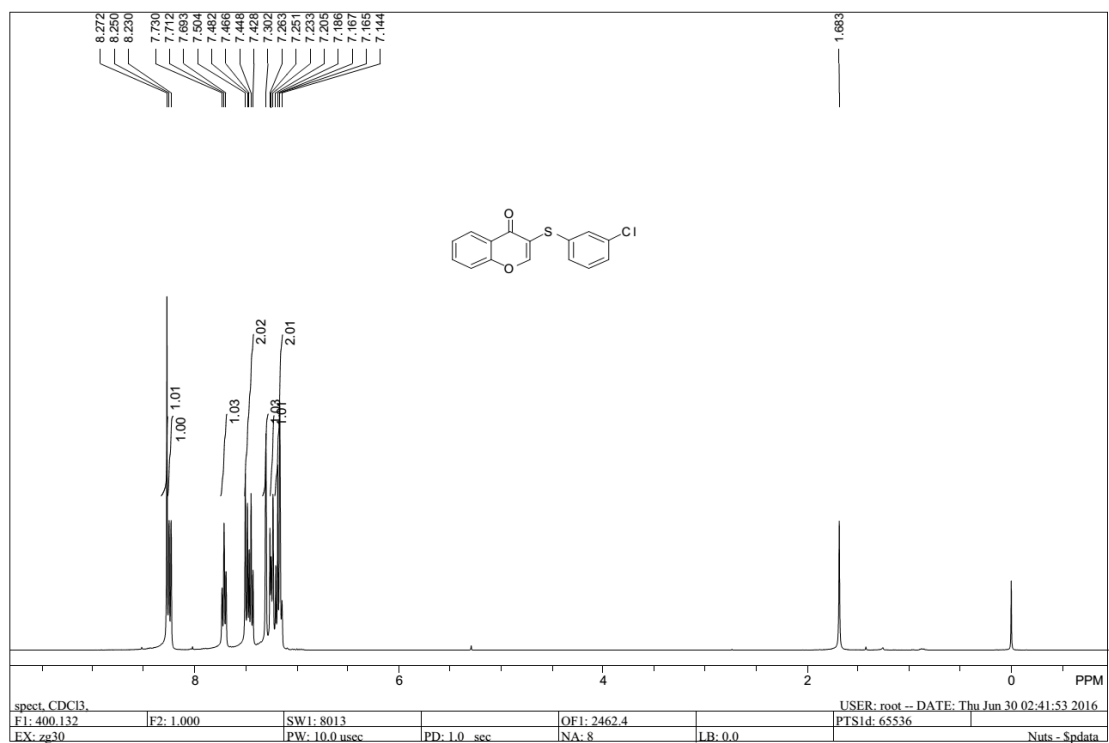
^1H and ^{13}C NMR spectra of **3p**



^1H and ^{13}C NMR spectra of **3q**



^1H and ^{13}C NMR spectra of **3r**



^1H and ^{13}C NMR spectra of **3s**

