

Electronic Supplementary Information

Visible-light-promoted sulfenylation of 6-aminouracils under catalyst-free condition

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GLOSSARY

Sl. No.	Abbrreviation	Full forms
1.	BHT	Butylated hydroxytoluene
2.	Br	Bromo
3.	°C	Degree centigrade
4.	CDCl ₃	Deuterated chloroform
5.	CFL	Compact Fluorescent Light
6.	Cl	Chloro
7.	cm ⁻¹	Centimeter inverse
8.	δ	Chemical shifts
9.	DMF	Dimethylformamide
10.	DMS	dimethylsulfide
11.	DMSO	Dimethyl sulfoxide
12.	DMSO- <i>d</i> ₆	Dimethyl sulfoxide-deuterated
13.	DNA	Deoxyribonucleic acid
14.	ESI-HRMS	High resolution electrospray ionization mass spectrometry
15.	eq.	Equivalent
16.	F	Floro
17.	FT-IR	Fourier Transform Infrared Spectroscopy
18.	g	Gram
19.	h	Hour
20.	HIV	Human immunodeficiency virus
21.	Hz	Hertz
22.	I ₂	Iodine
23.	I.R.	Infrared
24.	<i>J</i>	Coupling constants
25.	KBr	Potassium bromide
26.	KMnO ₄	Potassium permanganate
27.	LC/MS	Liquid Chromatography/mass spectrometry
28.	LED	light-emitting diode
29.	Me	Methyl
30.	MHz	Megahertz
31.	mg	Milligram
32.	mmol	Millimole

33.	mL	Milliliter
34.	M.P.	Melting point
35.	MW	Microwave
36.	NCS	N-chlorosuccinimide
37.	nm	Nanometer
38.	NMR	Nuclear Magnetic Resonance
39.	O ₂	Oxygen
40.	Ph	Phenyl
41.	ppm	Parts per million
42.	Pr	Propyl
43.	Q-TOF	Quadrupole Time-of-Flight
44.	RNA	Ribonucleic acid
45.	r.t.	Room temperature
46.	TEMPO	(2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl
47.	TLC	Thin layer chromatography
48.	TMS	Tetramethylsilane
49.	UV	Ultraviolet
50.	W	Watt

On-Off mechanistic experiments

In a round bottom flask equipped with a stir bar were added the compound **1** (1 mmol), **2** (1 mmol) and DMSO (2 mL) as solvent. The reaction was carried out under CFL (20 W) irradiation in open air for 2 h. Then, the reaction mixture was placed under dark conditions for another 0.5 h. The procedure was repeated for 10 h in total. Between the intervals, the reaction was monitored to calculate the reaction yield.

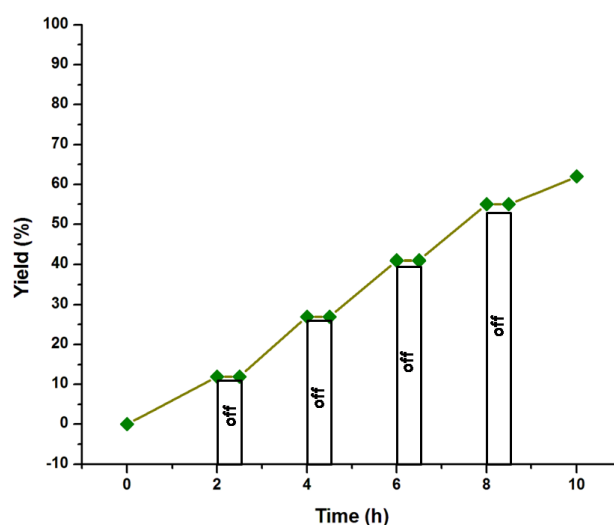


Figure. The “On/Off” experiment showing the effect of visible light on the reaction

Control reaction with TEMPO

To a small round bottom flask equipped with a stir bar were added the compound **1** (1 mmol), **2** (1 mmol), TEMPO (1.5 eq.) and DMSO (2 mL) as solvent. The reaction was carried out under CFL (20 W) irradiation in open air for 8 h. The reaction mixture was analyzed by High resolution mass spectrometry (HRMS) in which the presence of 2,2,6,6-tetramethyl-1-((phenylthio)oxy)piperidine was observed ($[M+H]^+ = 266.1572$), suggesting the formation of thiyl radical in the reaction. The spectrum recorded is presented below.

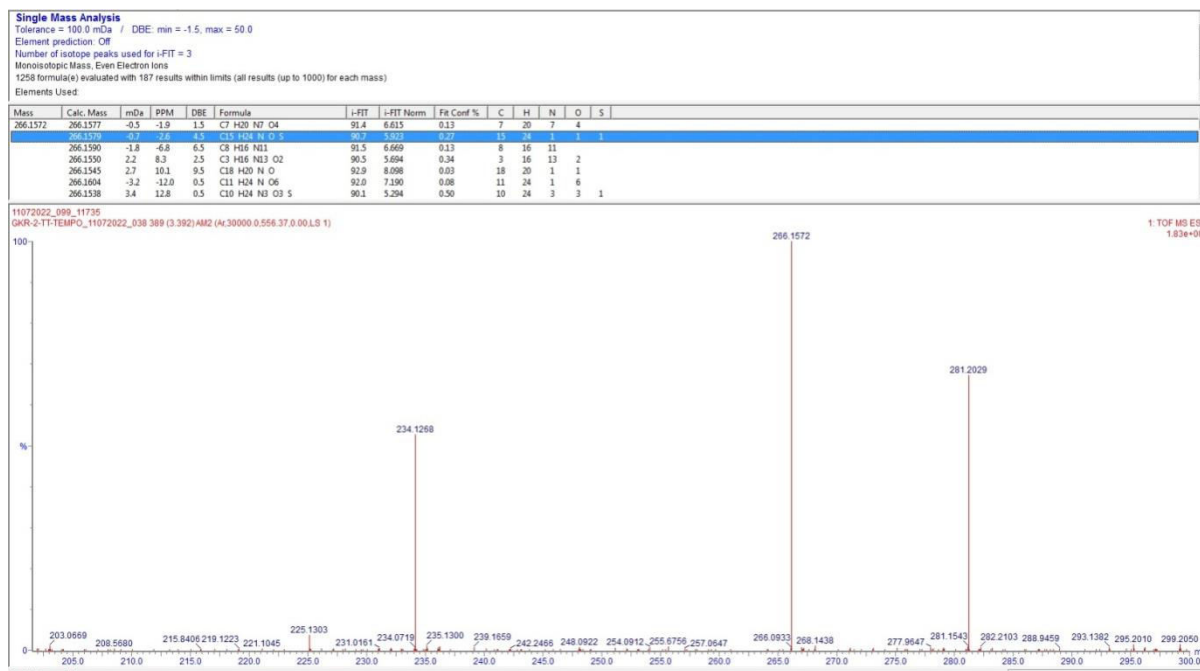


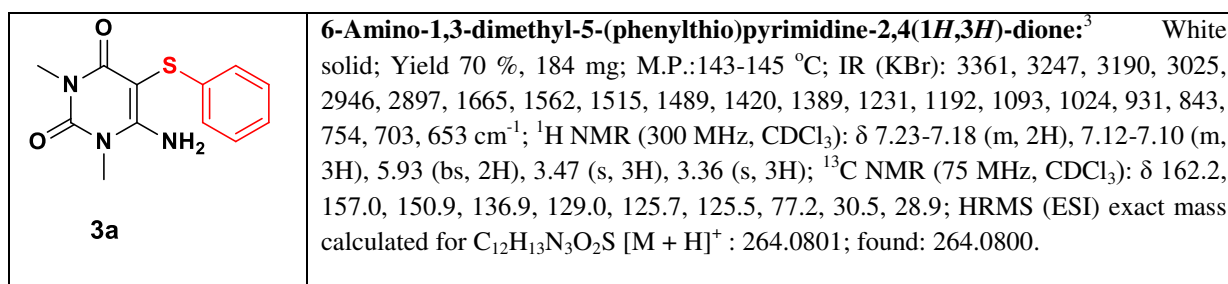
Figure. The adduct formed between thyl radical and TEMPO identified by HRMS

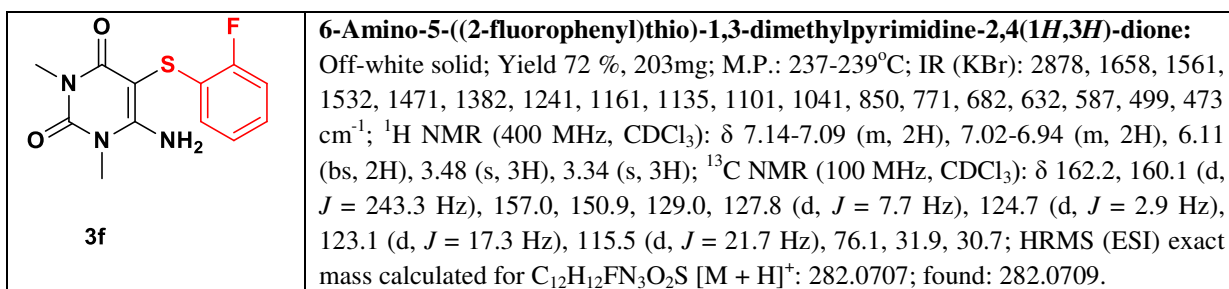
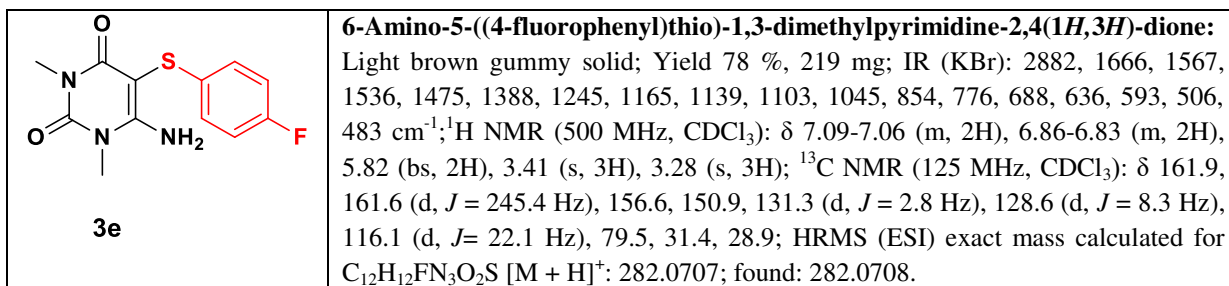
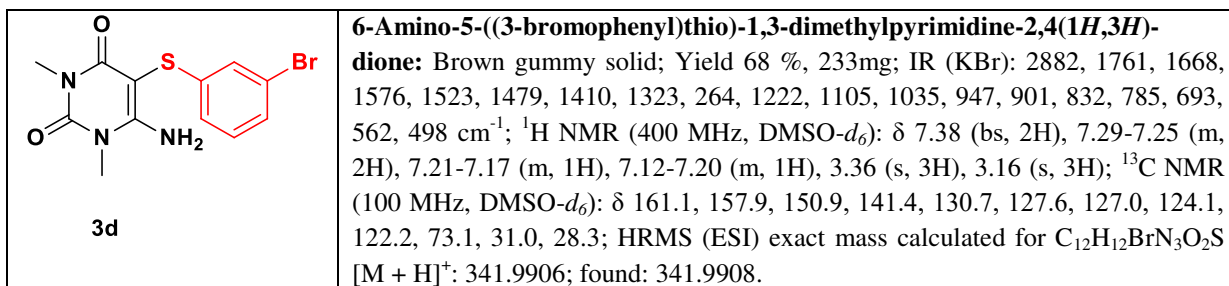
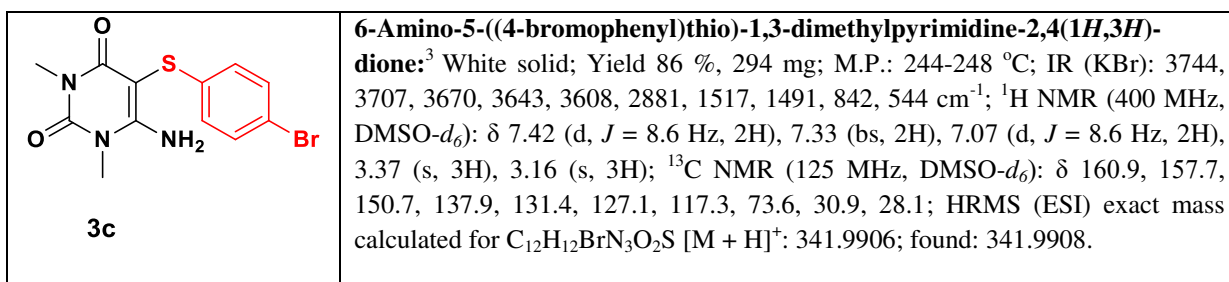
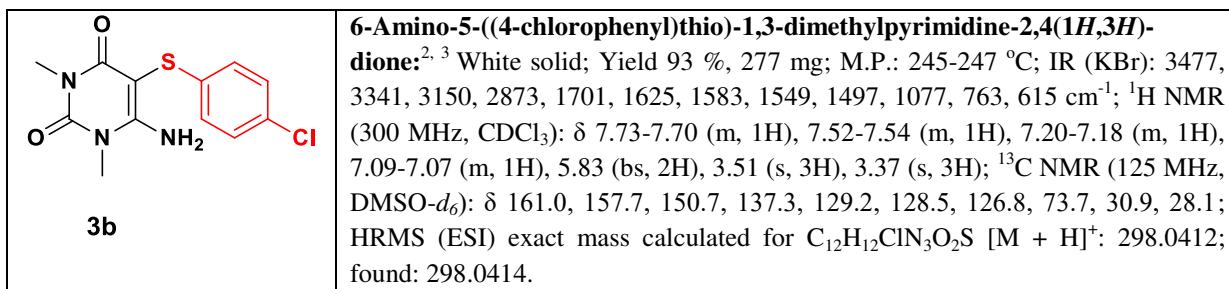
An image of the photoreactor for the reaction

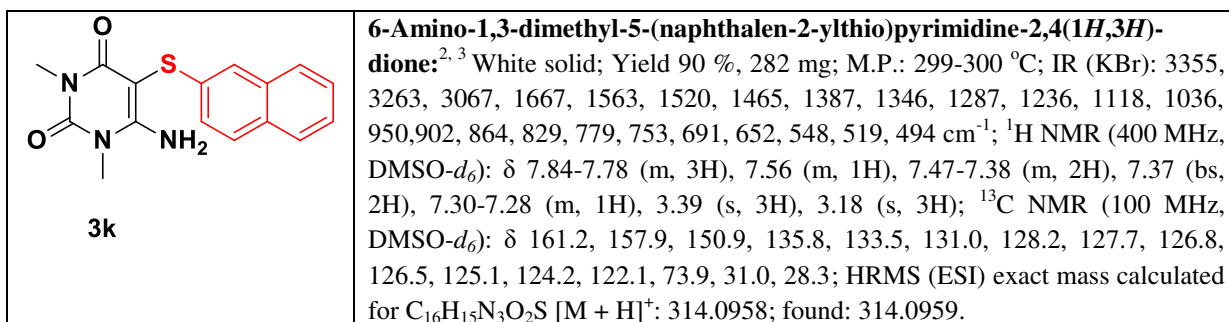
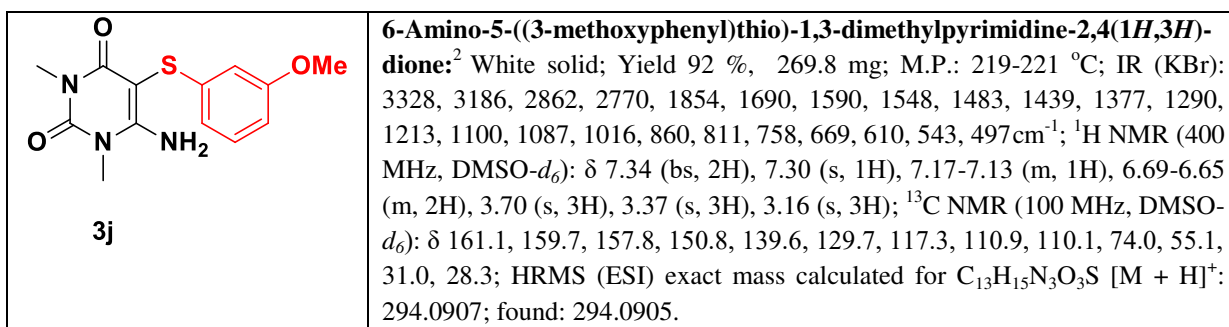
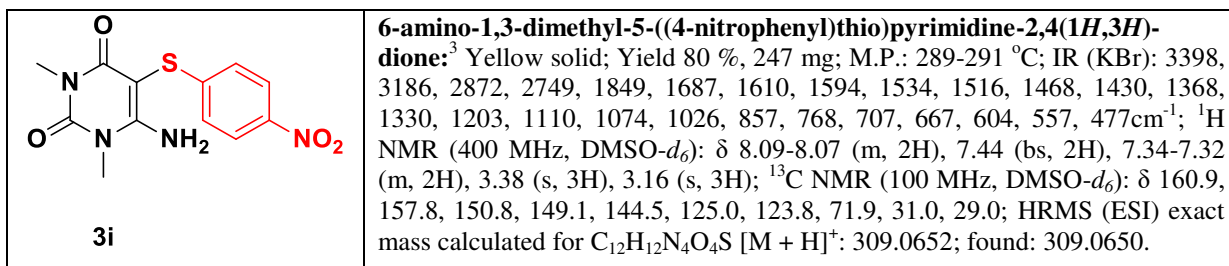
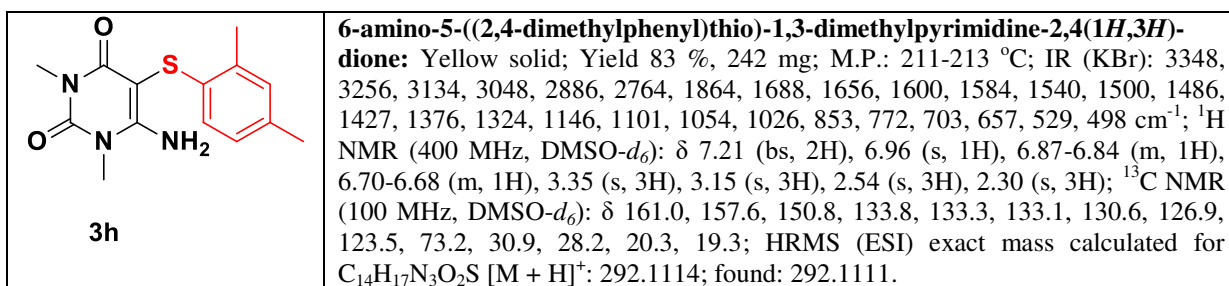
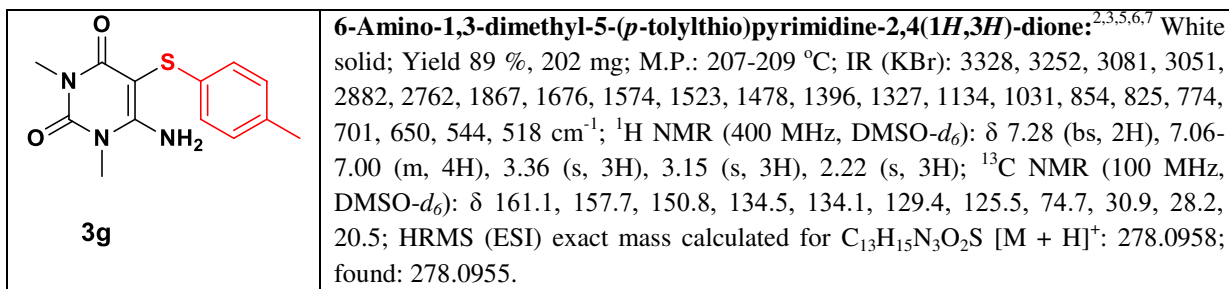


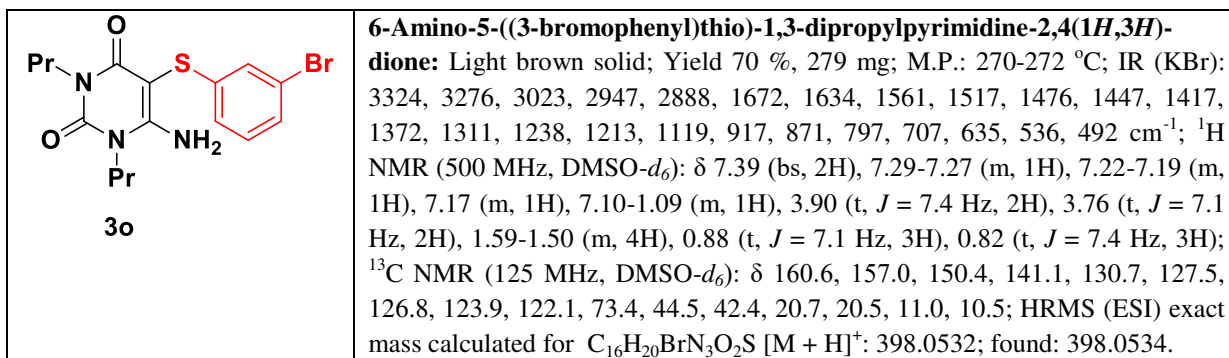
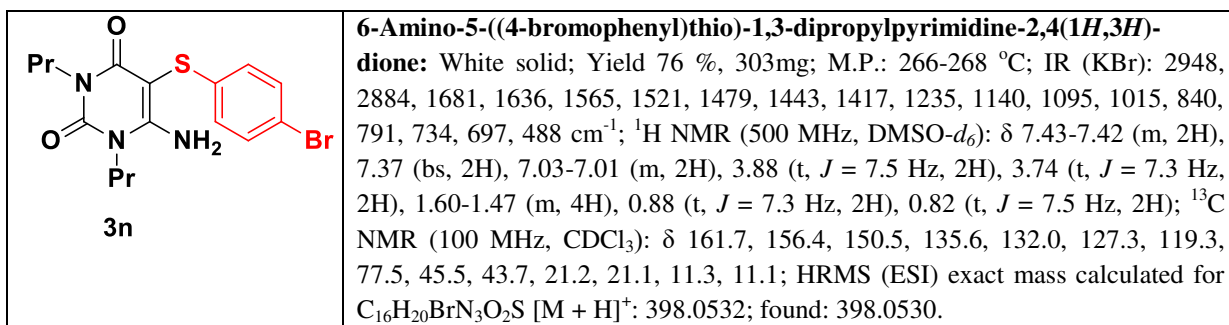
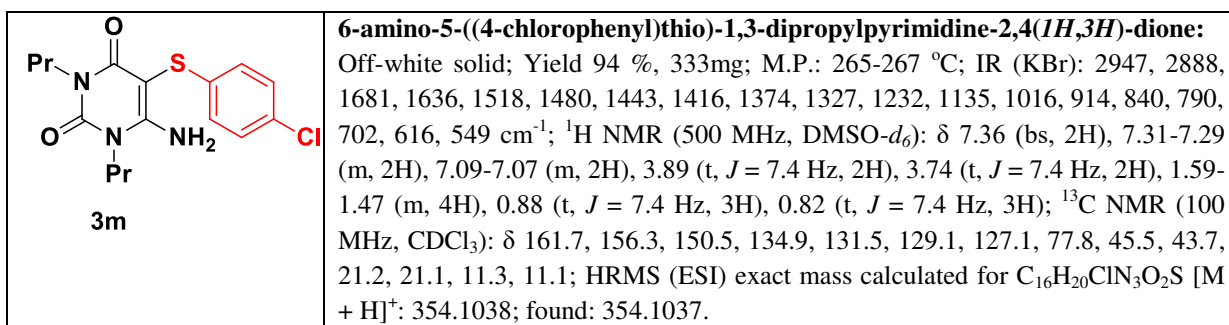
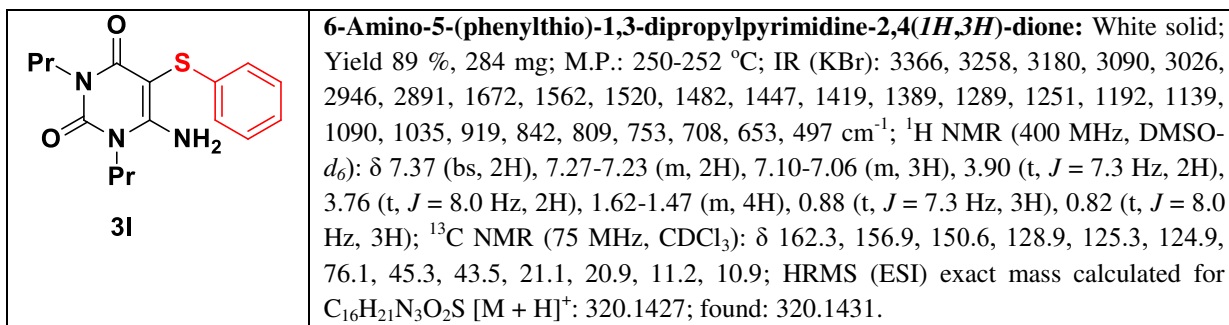
Figure. 20 W CFL bulb utilized for the photochemical reaction

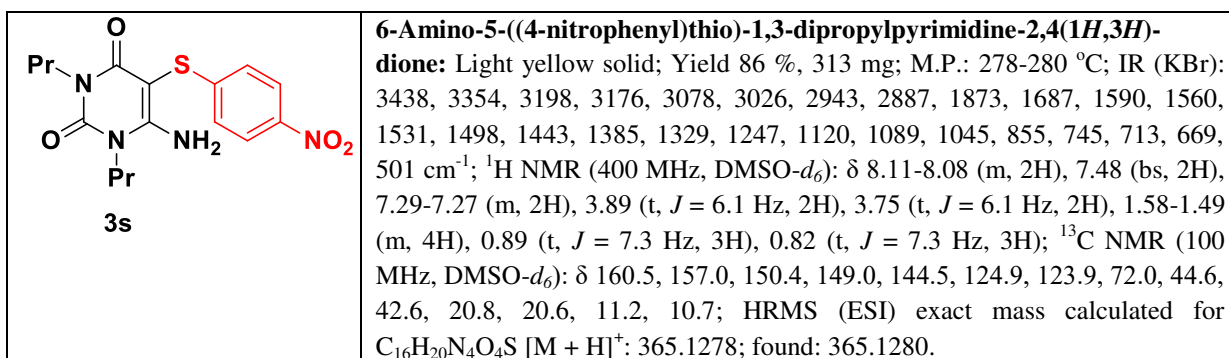
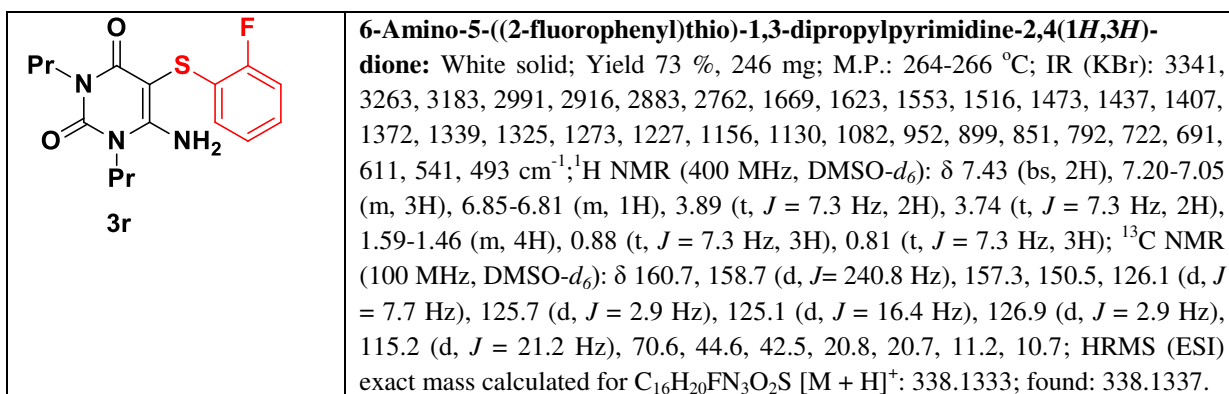
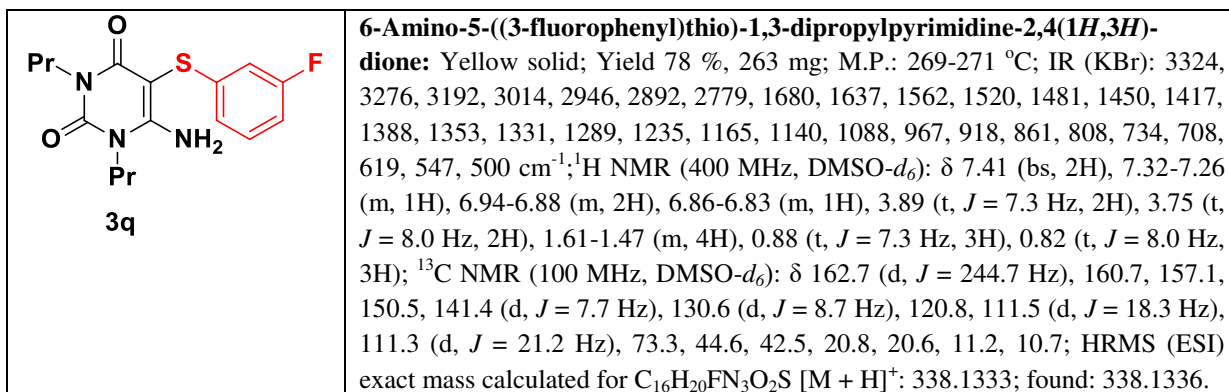
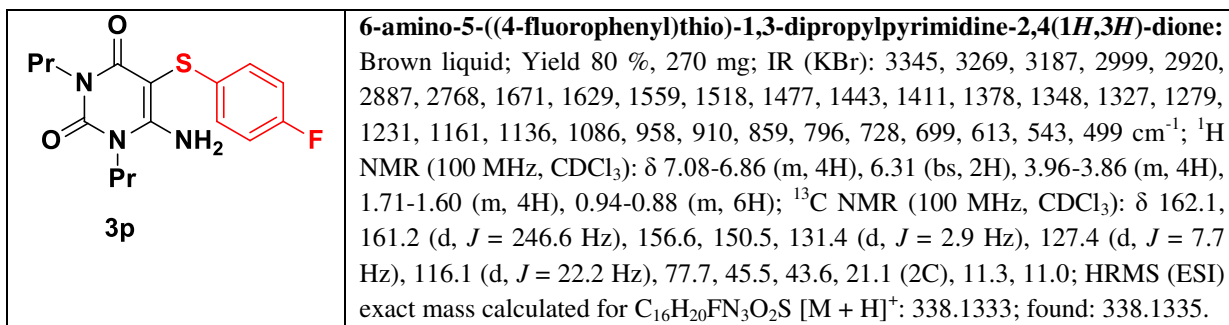
Characterization of the products

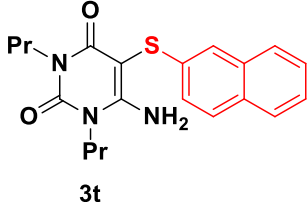


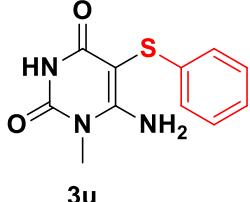


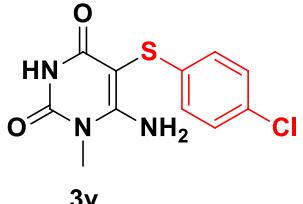


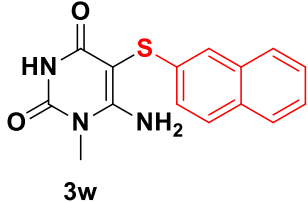


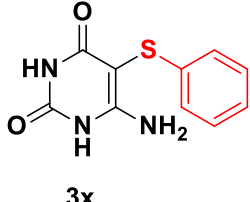


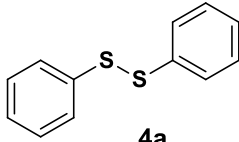
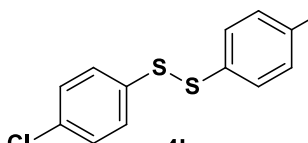
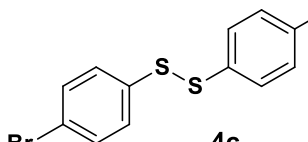
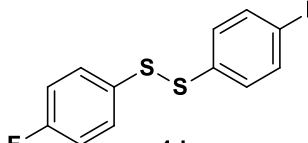
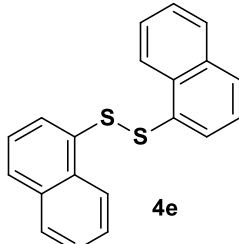
 <p style="text-align: center;">3t</p>	<p>6-Amino-5-(naphthalen-2-ylthio)-1,3-dipropylpyrimidine-2,4(1H,3H)-dione: Brown gummy liquid; Yield 92 %, 340 mg; IR (KBr): 3369, 3024, 2887, 2455, 1930, 1867, 1565, 1522, 1478, 1421, 1390, 1314, 1244, 1163, 1101, 1042, 985, 921, 868, 837, 792, 712, 692, 657, 582, 494 cm^{-1}; ^1H NMR (500 MHz, CDCl_3): δ 7.57-7.55 (m, 1H), 7.47-7.43 (m, 2H), 7.30-7.24 (m, 3H), 6.99-6.98 (m, 1H), 6.28 (bs, 2H), 3.78 (m, 4H), 1.56-1.52 (m, 4H), 0.81-0.71 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ 162.2, 156.8, 150.6, 133.9, 133.7, 131.6, 128.6, 127.7, 126.8, 126.5, 125.3, 124.0, 123.1, 77.1, 45.4, 43.6, 21.1 (2C), 11.2, 10.8; HRMS (ESI) exact mass calculated for $\text{C}_{20}\text{H}_{23}\text{N}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$: 370.1584; found: 370.1582.</p>
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 <p style="text-align: center;">3u</p>	<p>6-Amino-1-methyl-5-(phenylthio)pyrimidine-2,4(1H,3H)-dione:⁷ Off-white solid; Yield 63 %, 157 mg; M.P.: 278-280 °C; IR (KBr): 3391, 3301, 3121, 2965, 2883, 1717, 1612, 1553, 1491, 1417, 1011, 845, 751, 631 cm^{-1}; ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 10.8 (bs, 1H), 7.27-7.23 (m, 4H), 7.10-7.09 (m, 3H), 3.30 (s, 3H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$): δ 161.5, 159.0, 150.3, 138.1, 128.7, 124.9, 124.6, 74.0, 29.8; HRMS (ESI) exact mass calculated for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$: 250.0645; found: 250.0642.</p>
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 <p style="text-align: center;">3v</p>	<p>6-Amino-5-((4-chlorophenyl)thio)-1-methylpyrimidine-2,4(1H,3H)-dione:² White solid; Yield 67 %, 190 mg; M.P.: 293-295°C; IR (KBr): 2882, 1682, 1568, 1531, 1483, 1404, 1213, 1105, 1032, 846, 777, 516 cm^{-1}; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 11.1 (bs, 1H), 7.81 (bs, 2H), 7.65-7.63 (m, 2H), 7.62-7.59 (m, 2H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 162.4, 156.6, 151.2, 147.7, 136.2, 129.1, 128.7, 126.6, 126.2, 75.1, 31.4; HRMS (ESI) exact mass calculated for $\text{C}_{11}\text{H}_{10}\text{ClN}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$: 284.0255; found: 284.0258.</p>
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 <p style="text-align: center;">3w</p>	<p>6-Amino-1-methyl-5-(naphthalen-2-ylthio)pyrimidine-2,4(1H,3H)-dione:² Off-white solid; Yield 66 %, 198 mg; M.P.: 297-299 °C; IR (KBr): 2881, 1682, 1566, 1525, 1478, 1417, 1323, 1252, 1116, 1133, 1088, 1045, 873, 843, 785, 717, 691, 667, 557, 527, 491 cm^{-1}; ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 11.05 (bs, 1H), 8.28 (m, 1H), 8.10-8.08 (m, 1H), 8.06-8.05 (m, 1H), 8.00-7.98 (m, 1H), 7.82 (bs, 2H), 7.63-7.61 (m, 3H), 3.15 (s, 3H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$): δ 159.7, 156.1, 150.0, 142.2, 133.6, 132.2, 129.3, 128.4, 127.8, 127.6, 127.2, 123.9, 120.9, 85.6, 28.2; HRMS (ESI) exact mass calculated for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$: 300.0801; found: 300.0803.</p>
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 <p style="text-align: center;">3x</p>	<p>6-Amino-5-(phenylthio)pyrimidine-2,4(1H,3H)-dione:⁷ White solid; Yield 59 %, 139 mg; M.P.: >300°C; IR (KBr): 3390, 3408, 3283, 2958, 2879, 2787, 1713, 1627, 1608, 1558, 1482, 1400, 1006, 843, 749, 627 cm^{-1}; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 10.6 (bs, 1H), 10.4 (bs, 1H), 7.27-7.23 (m, 2H), 7.11-7.06 (m, 3H), 6.64 (bs, 2H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 163.2, 158.0, 149.9, 138.3, 128.9, 124.9, 124.7, 73.2; HRMS (ESI) exact mass calculated for $\text{C}_{10}\text{H}_9\text{N}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$: 236.0488; found: 236.0485.</p>
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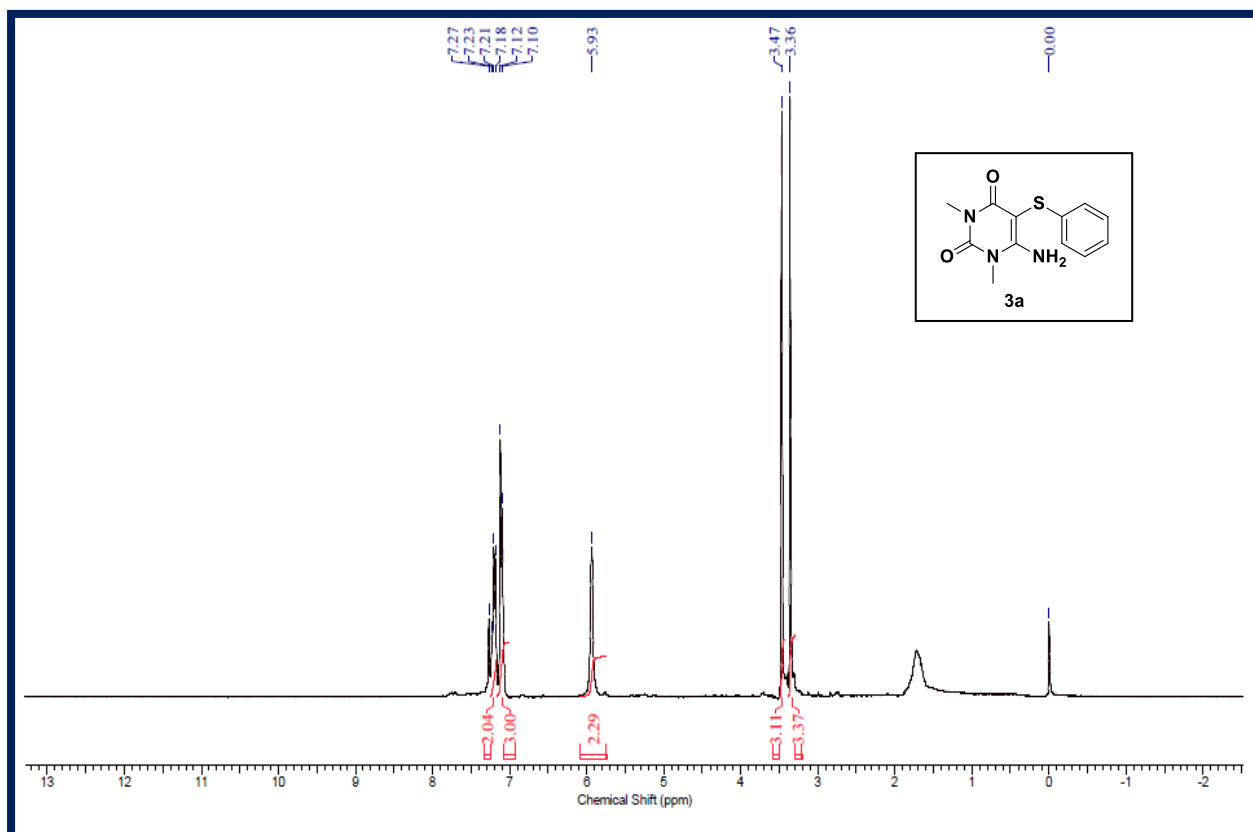
 <p style="text-align: center;">4a</p>	<p>1,2-Diphenyldisulfane:^{1,4} White solid; Yield 78%, 170 mg; M.P.:58-59 °C; IR (KBr): 3876, 3800, 3653, 3051, 2872, 2322, 1600, 1569, 1465, 1424, 1268, 1157, 1124, 754, 690, 510, 450 cm⁻¹; ¹H NMR (500 MHz, DMSO-<i>d</i>₆): δ 7.51-7.50 (m, 4H), 7.38-7.35 (m, 4H), 7.29-7.26 (m, 2H); ¹³C NMR (125 MHz, DMSO-<i>d</i>₆): δ 135.9, 129.6, 127.7, 127.2; HRMS (ESI) exact mass calculated for C₁₂H₁₀S₂[M + H]⁺ : 219.0297; found: 219.0295.</p>
 <p style="text-align: center;">4b</p>	<p>1,2-Bis(4-chlorophenyl)disulfane:^{1,4} White solid; Yield 76%, 218 mg; M.P.:68-70 °C; IR (KBr): 2880, 1577, 1487, 1400, 1302, 1130, 1017, 961, 848, 751, 701, 560, 524 cm⁻¹; ¹H NMR (500 MHz, DMSO-<i>d</i>₆): δ 7.52-7.50 (m, 4H), 7.44-7.41 (m, 4H); ¹³C NMR (125 MHz, DMSO-<i>d</i>₆): δ 134.6, 132.7, 129.6, 129.3; HRMS (ESI) exact mass calculated for C₁₂H₈Cl₂S₂[M + H]⁺ : 286.9517; found: 286.9514.</p>
 <p style="text-align: center;">4c</p>	<p>1,2-Bis(4-bromophenyl)disulfane:⁴ White solid; Yield 80%, 301mg; M.P.:90-93 °C; IR (KBr): 2876, 1574, 1479, 1394, 1301, 1131, 1095, 1013, 841, 730, 698, 509, 482 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.42-7.39 (m, 4H), 7.33-7.30 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 135.6, 132.1, 129.3, 121.5; HRMS (ESI) exact mass calculated for C₁₂H₈Br₂S₂ [M + H]⁺ : 374.8507; found: 374.8504.</p>
 <p style="text-align: center;">4d</p>	<p>1,2-Bis(4-fluorophenyl)disulfane: Off-white solid; Yield 78 %, 198 mg; M.P.:74-76°C; IR (KBr): 3880, 3816, 3683, 2882, 2328, 1606, 1535, 1414, 1278, 1171, 1127, 854, 667, 642, 444 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.45-7.41 (m, 4H), 7.02-6.97 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 162.6 (d, <i>J</i> = 248.5 Hz), 132.1 (d, <i>J</i> = 2.9 Hz), 131.2 (d, <i>J</i> = 8.7 Hz), 116.4 (d, <i>J</i> = 22.2 Hz); HRMS (ESI) exact mass calculated for C₁₂H₈F₂S₂[M + H]⁺ : 255.0108; found: 255.0105.</p>
 <p style="text-align: center;">4e</p>	<p>1,2-Di(naphthalen-1-yl)disulfane:^{1,4} White solid; Yield 82 %, 261 mg; M.P.:138-140°C; IR (KBr): 2878, 1586, 1500, 1467, 1409, 1383, 1271, 1121, 1088, 1015, 853, 839, 775, 707, 671, 537, 517, 471 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.98 (m, 2H), 7.80-7.72 (m, 6H), 7.63-7.60 (m, 2H), 7.46-7.45 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 134.1, 133.4, 132.4, 128.9, 127.7, 127.4, 126.7, 126.4, 126.2, 125.5; HRMS (ESI) exact mass calculated for C₂₀H₁₄S₂[M + H]⁺ : 319.0610; found: 319.0607.</p>

References:

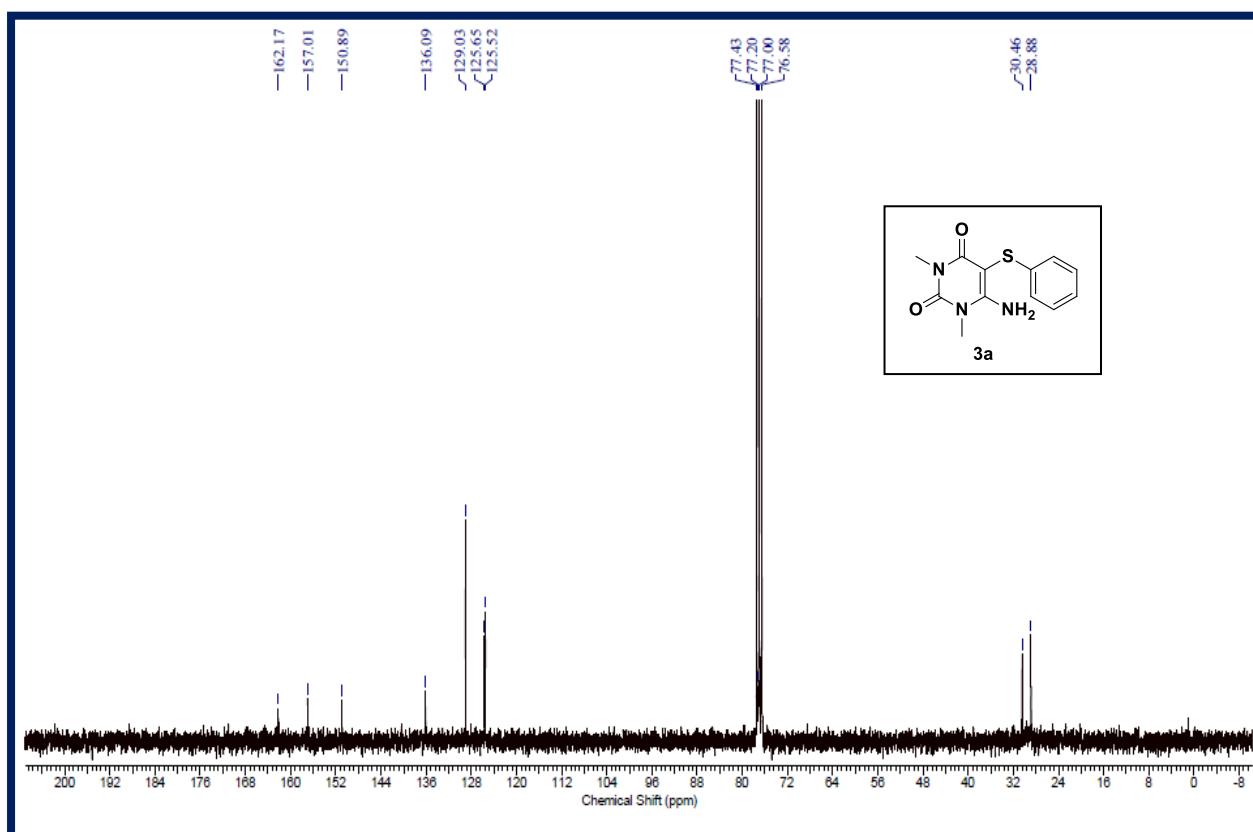
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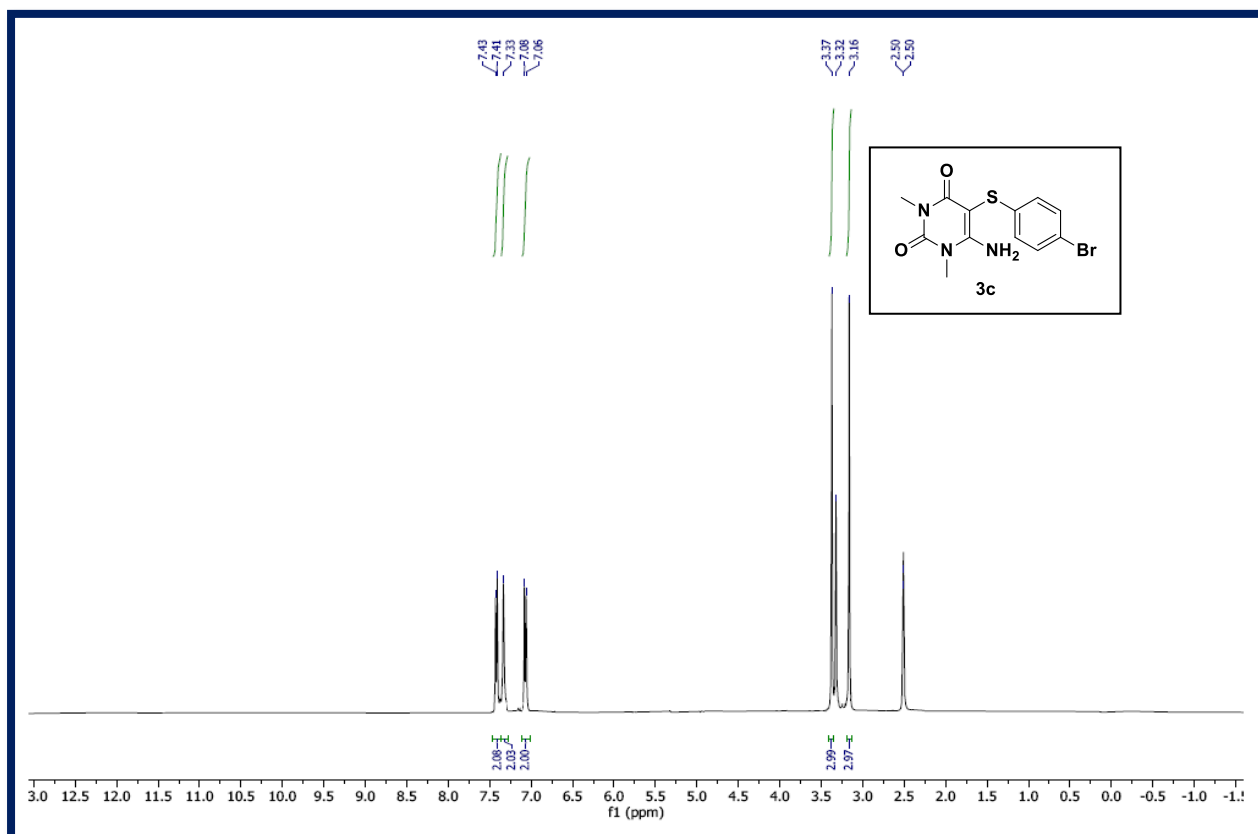
¹H NMR 3a



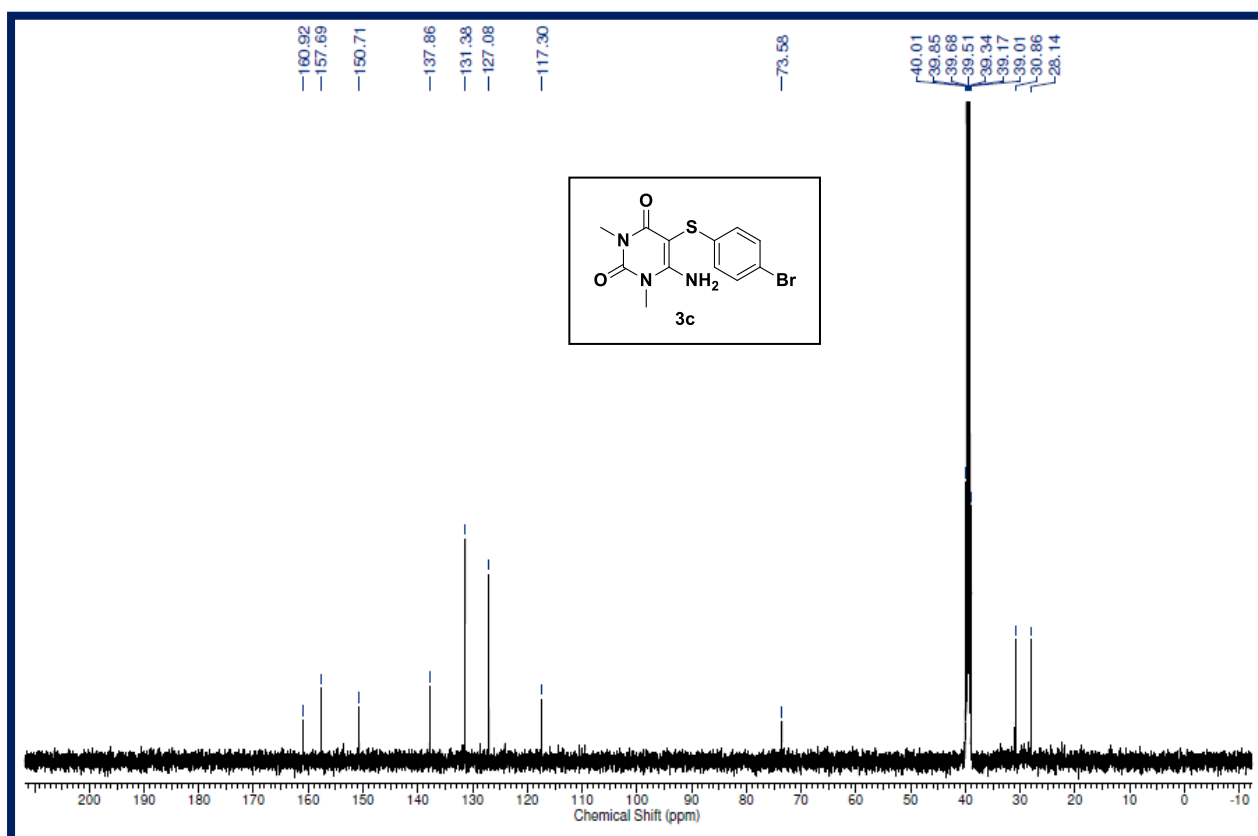
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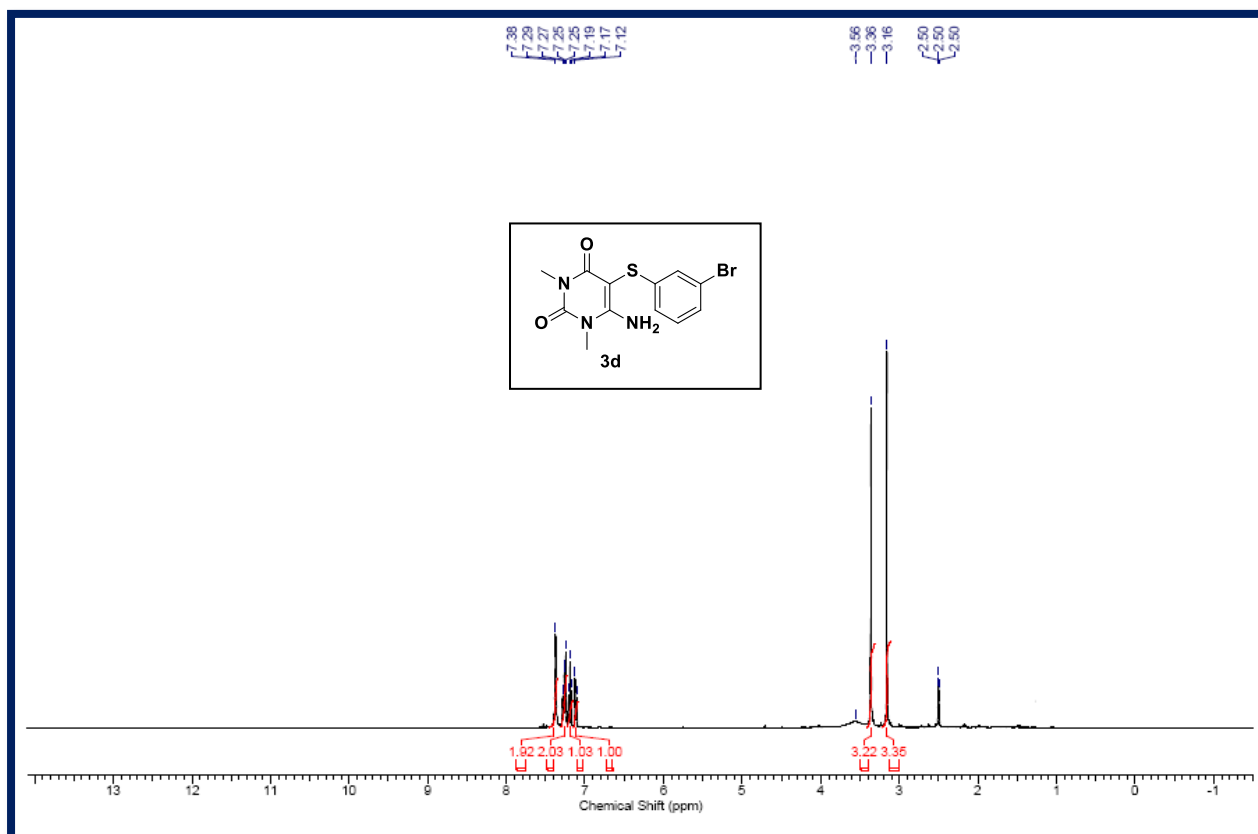
¹H NMR 3c



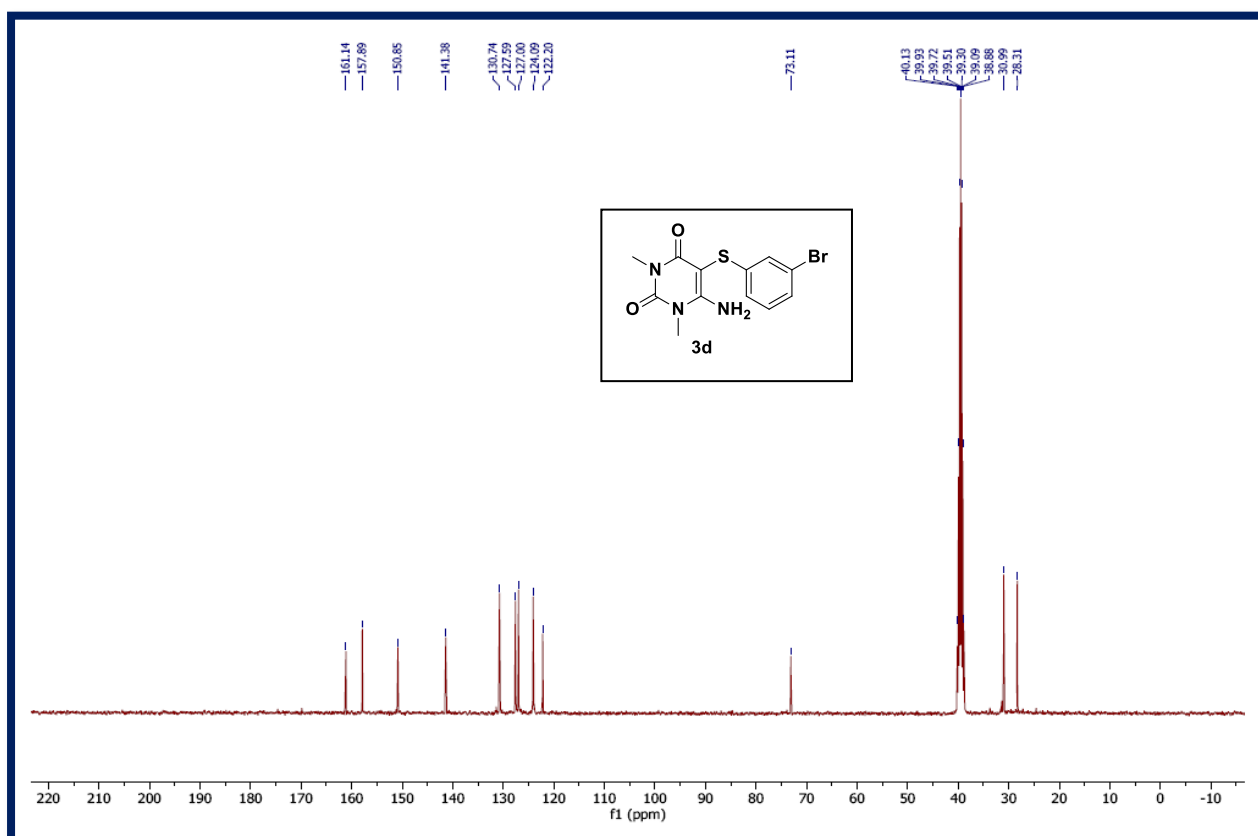
¹³C NMR 3c



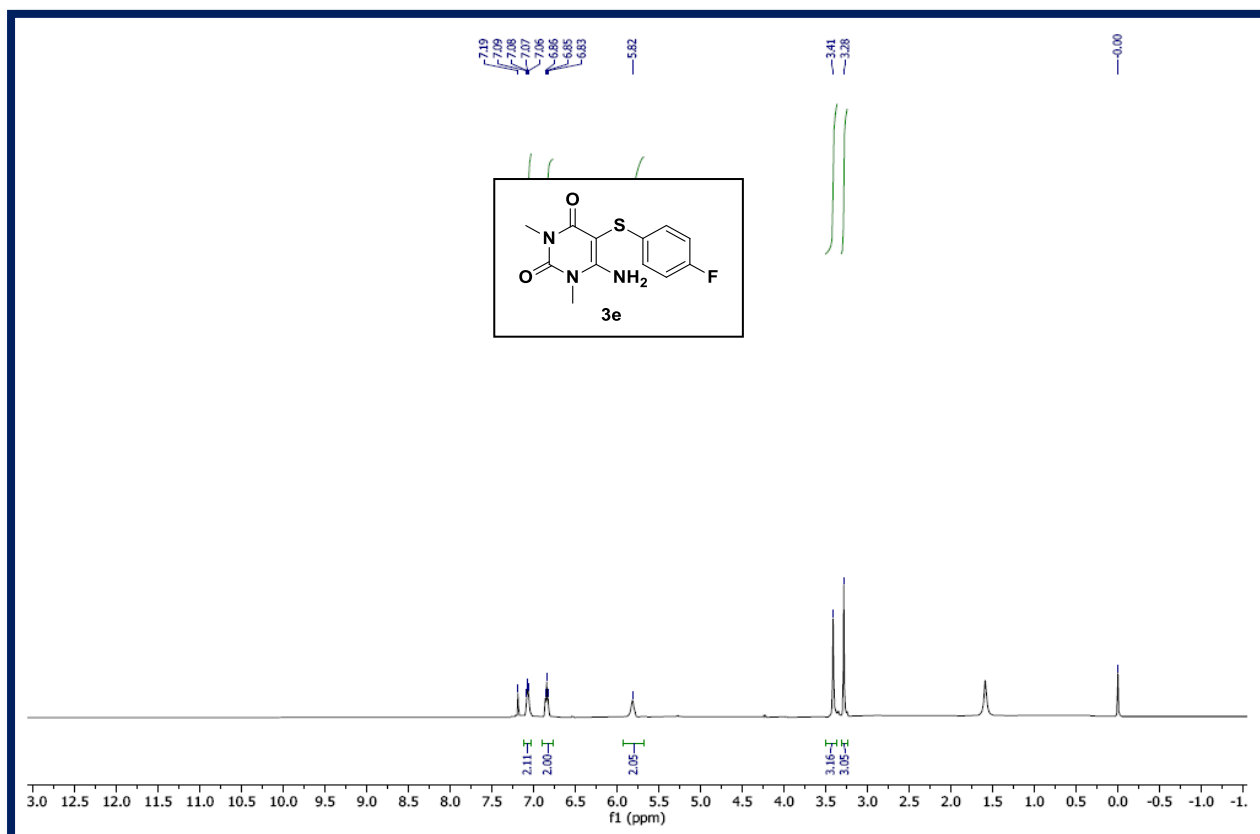
¹H NMR 3d



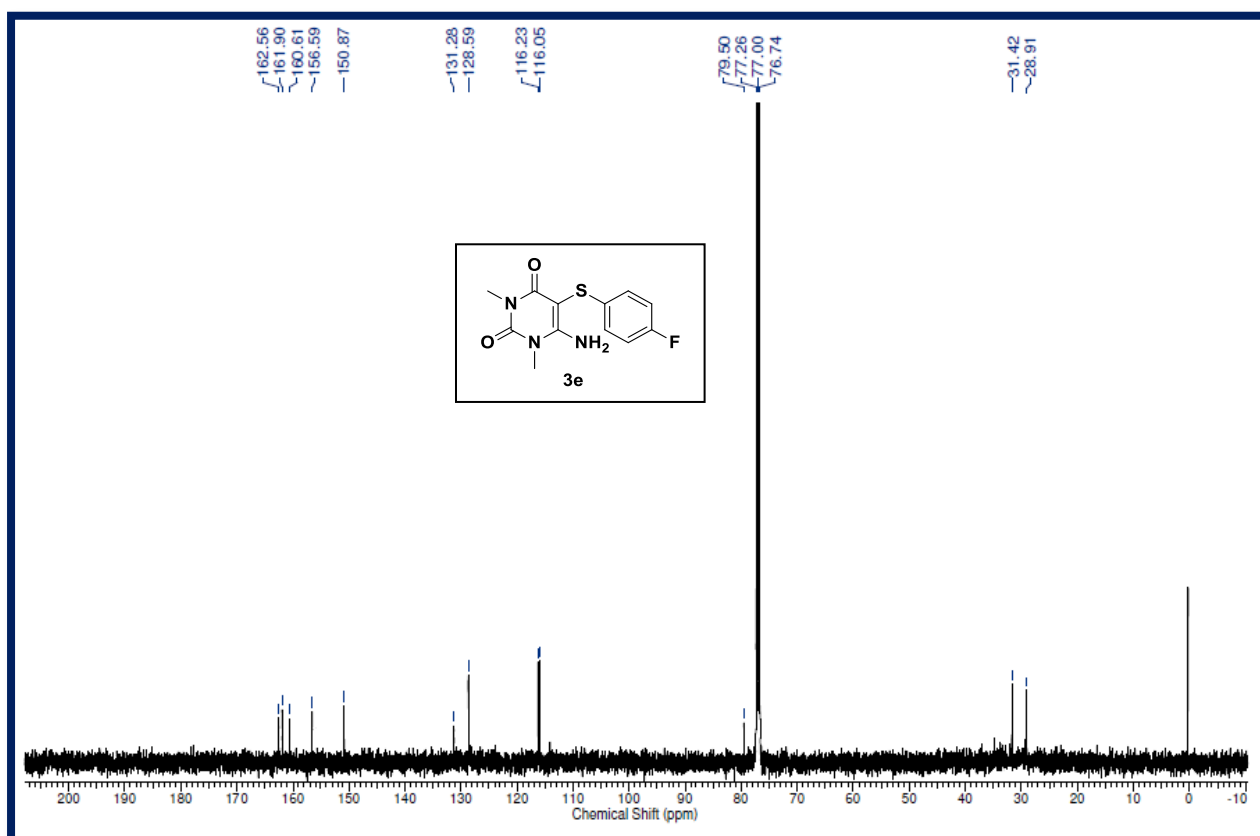
¹³C NMR 3d



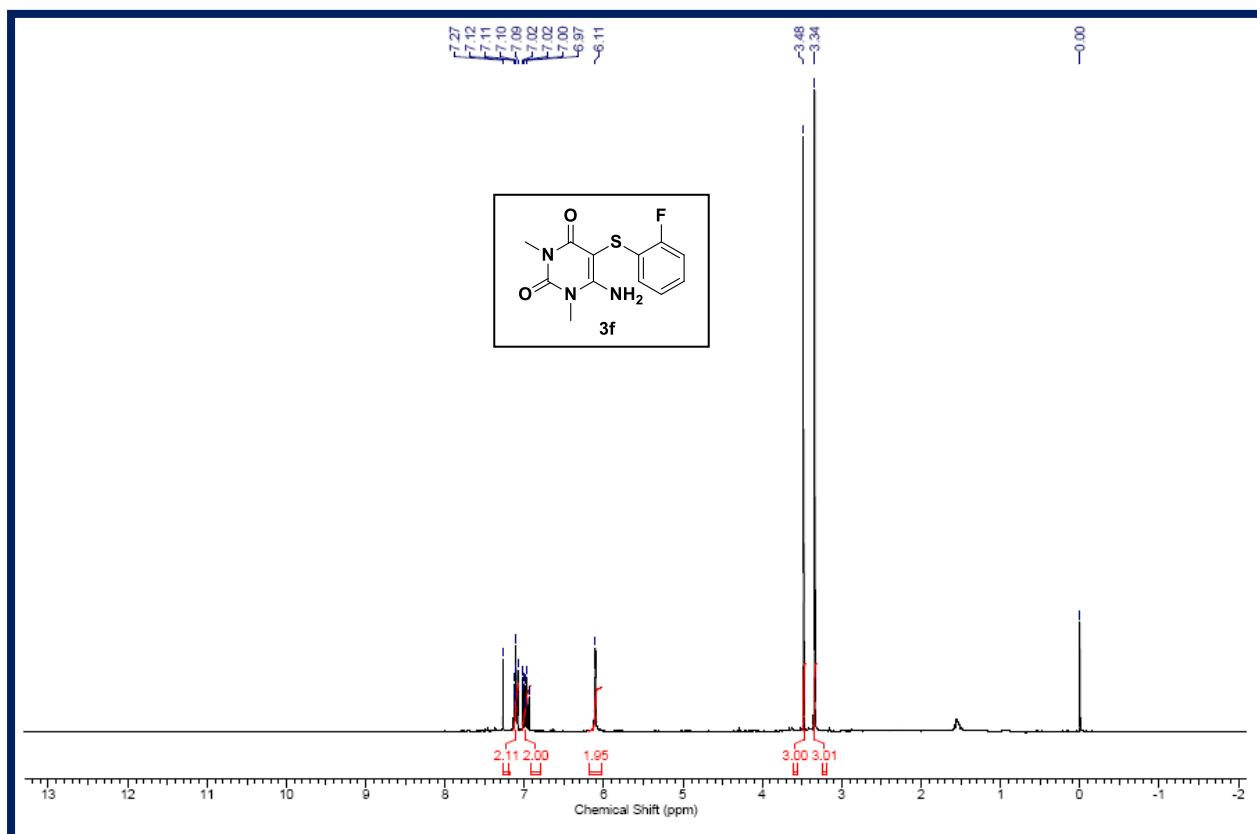
¹H NMR 3e



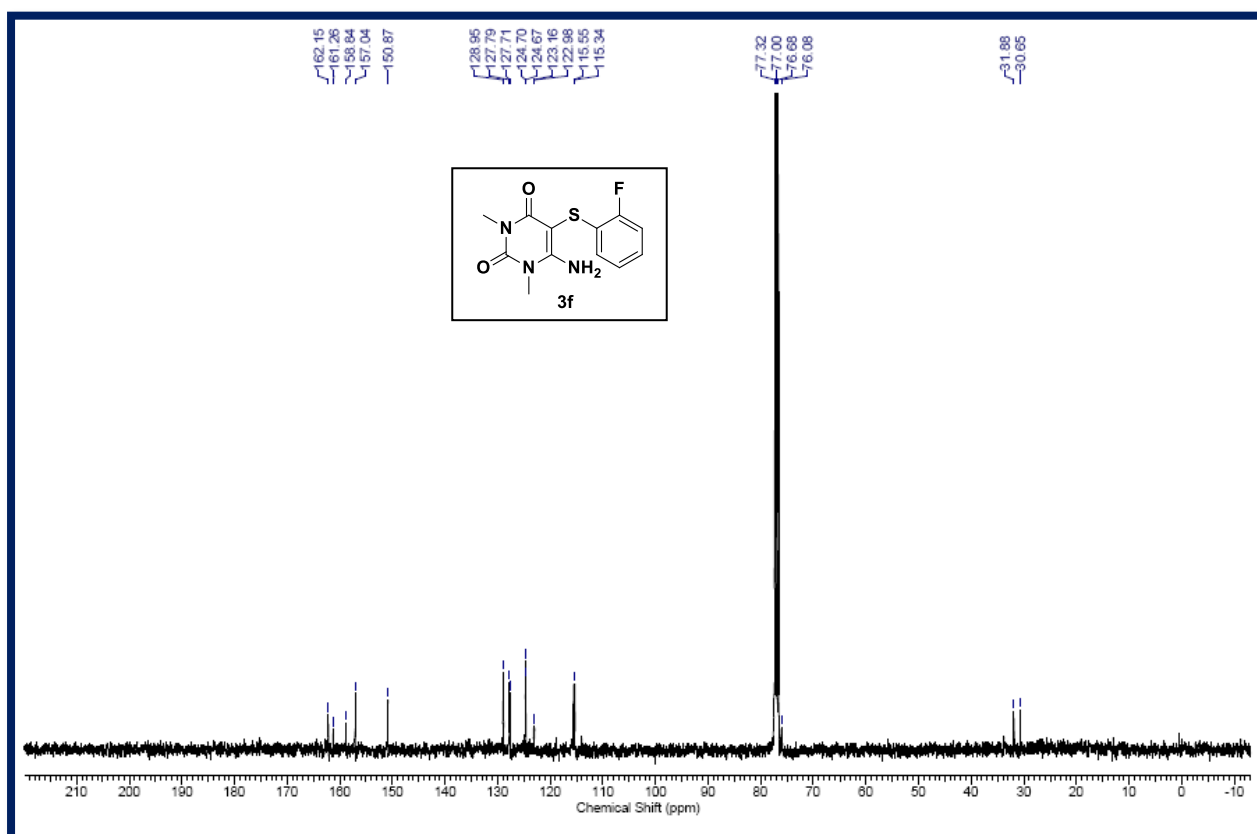
¹³C NMR 3e



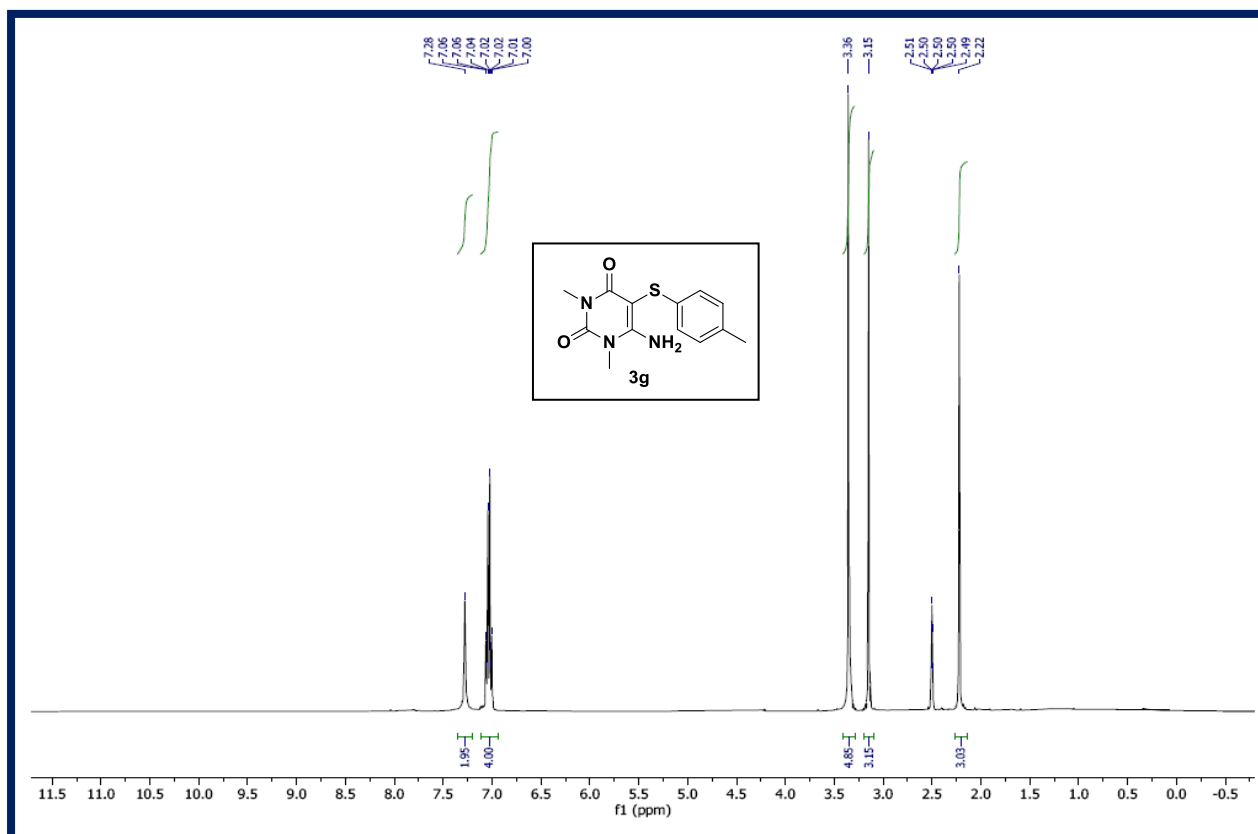
¹H NMR 3f



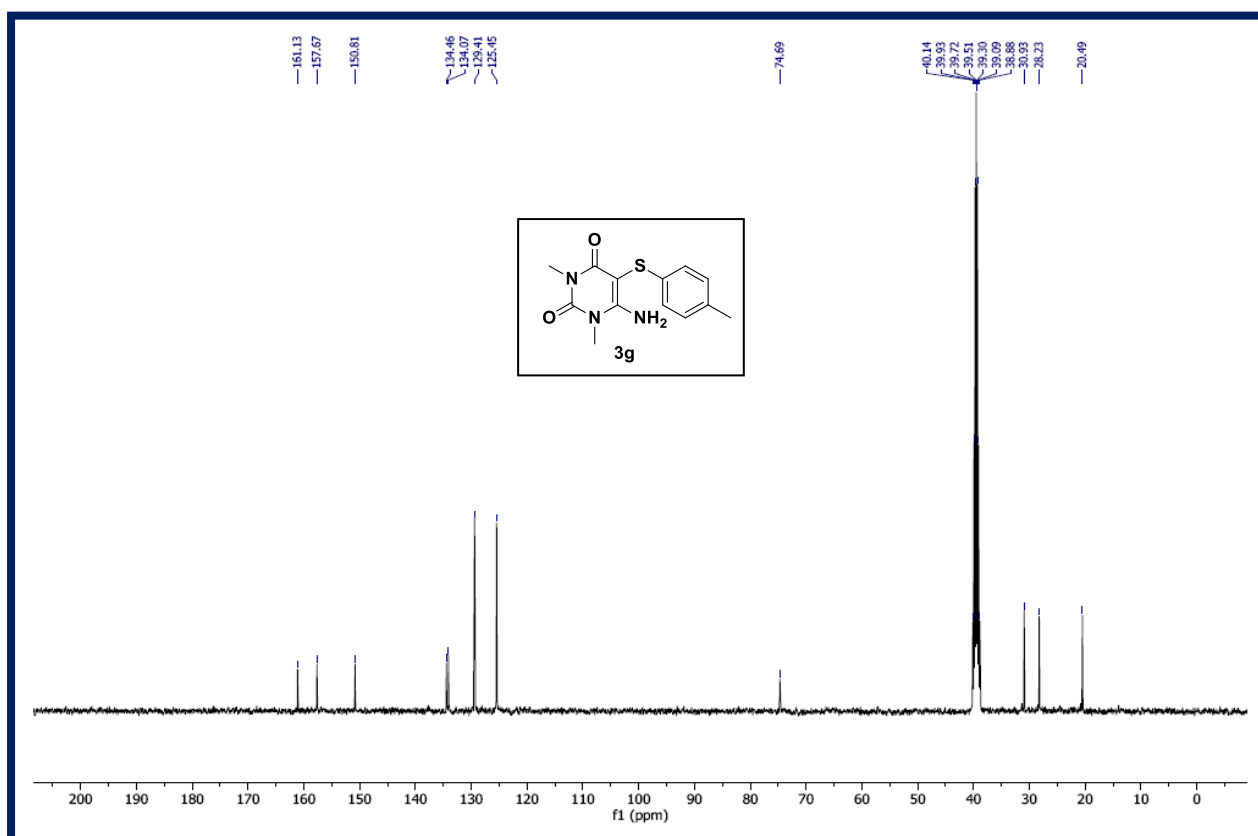
¹³C NMR 3f



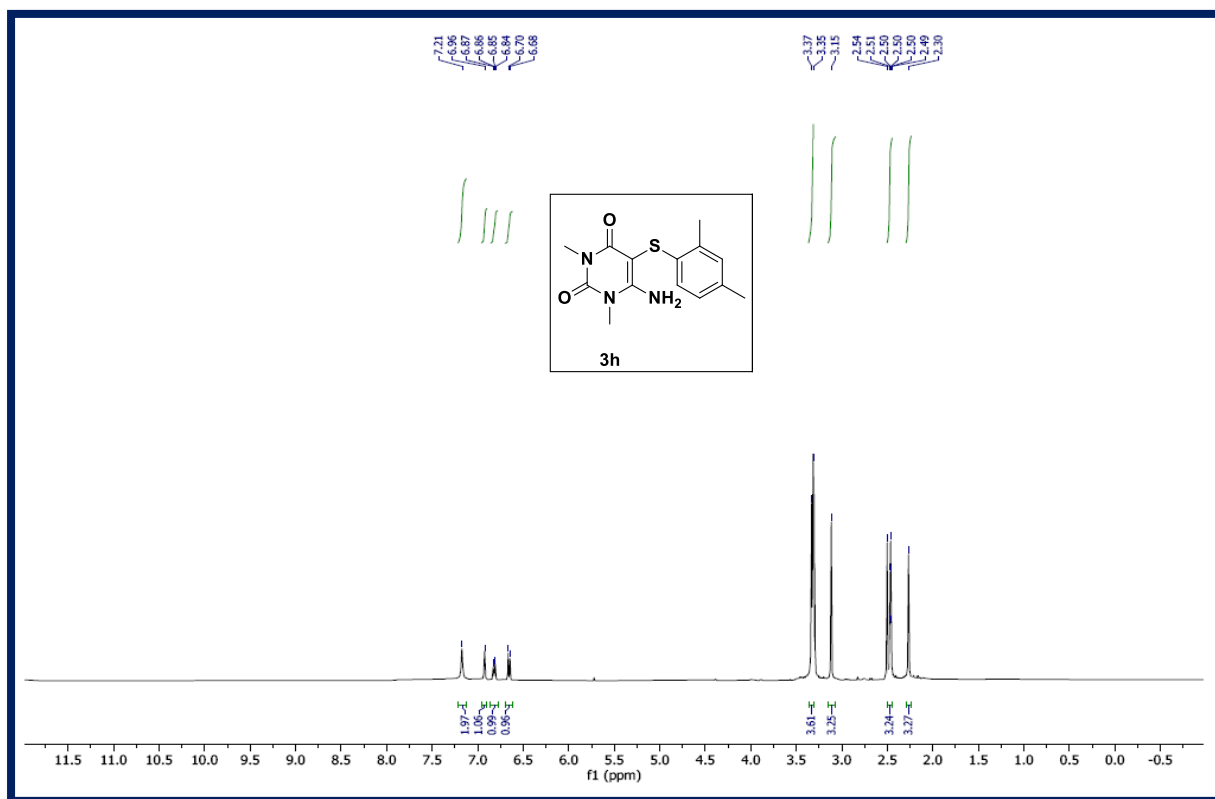
¹H NMR 3g



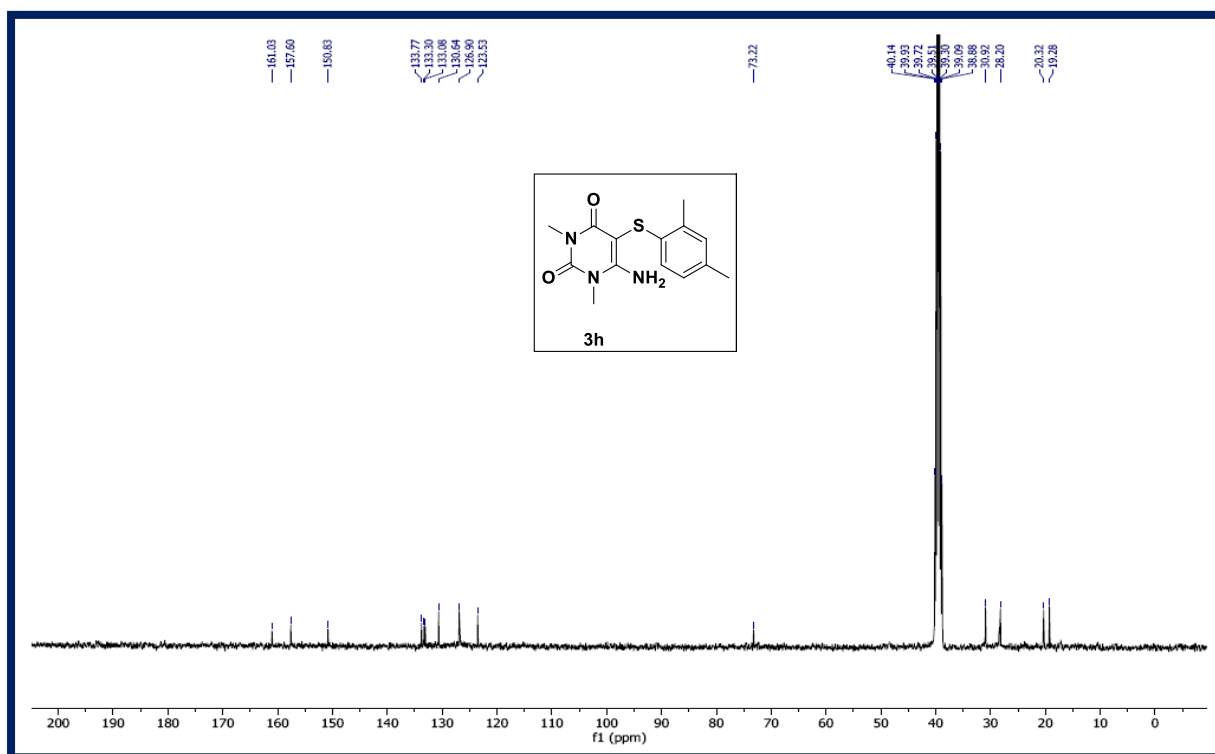
¹³C NMR 3g



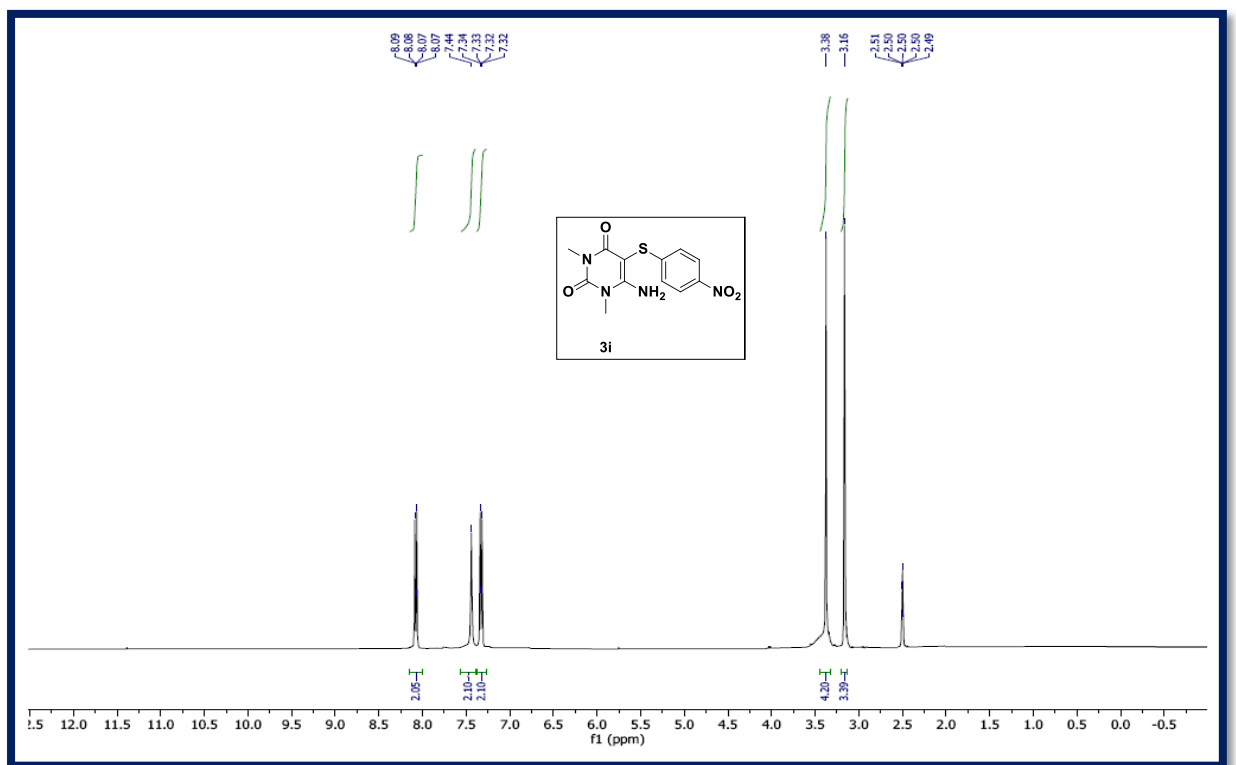
¹H NMR 3h



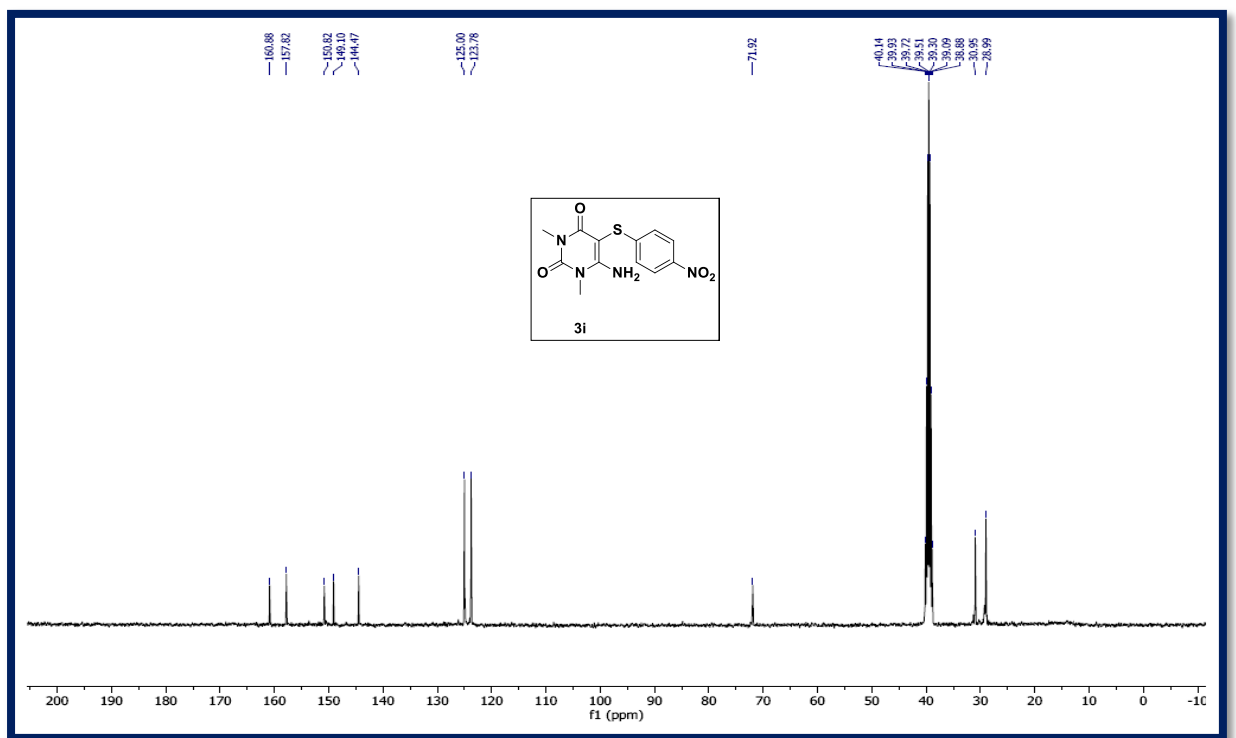
¹³C NMR 3h



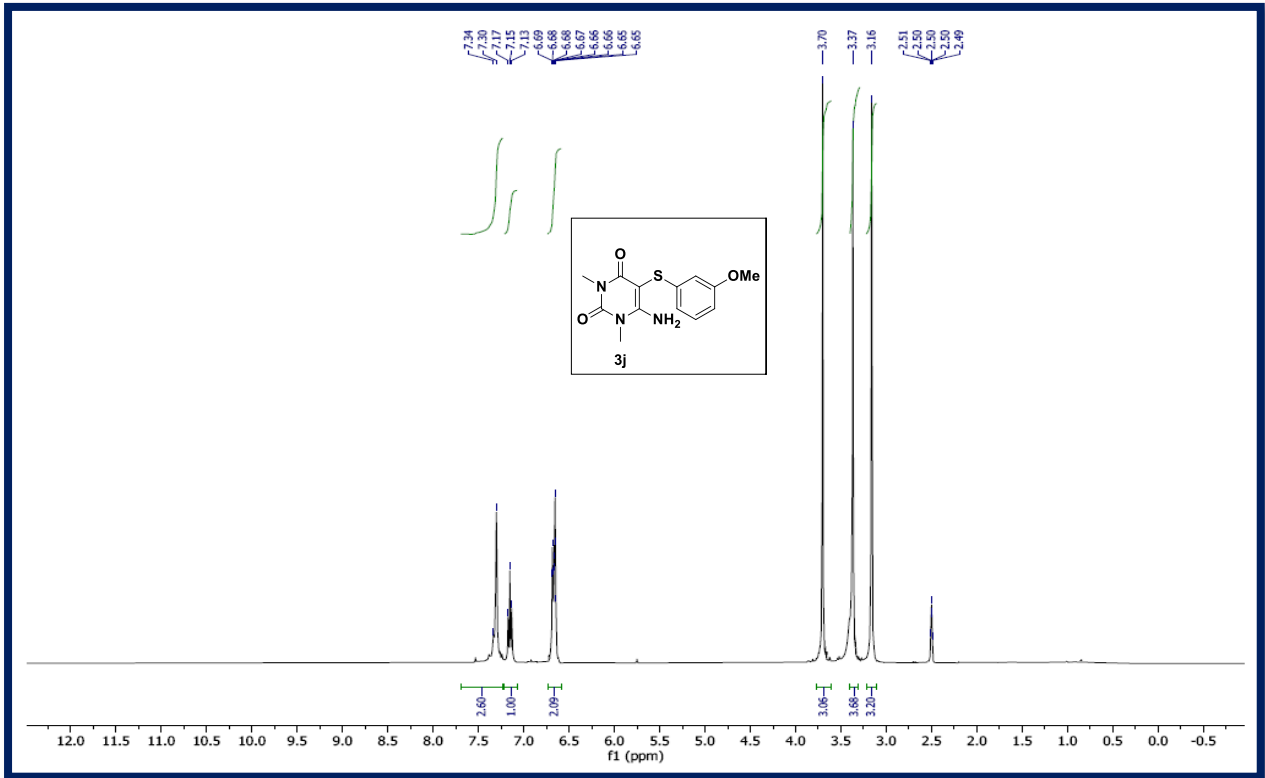
¹H NMR 3i



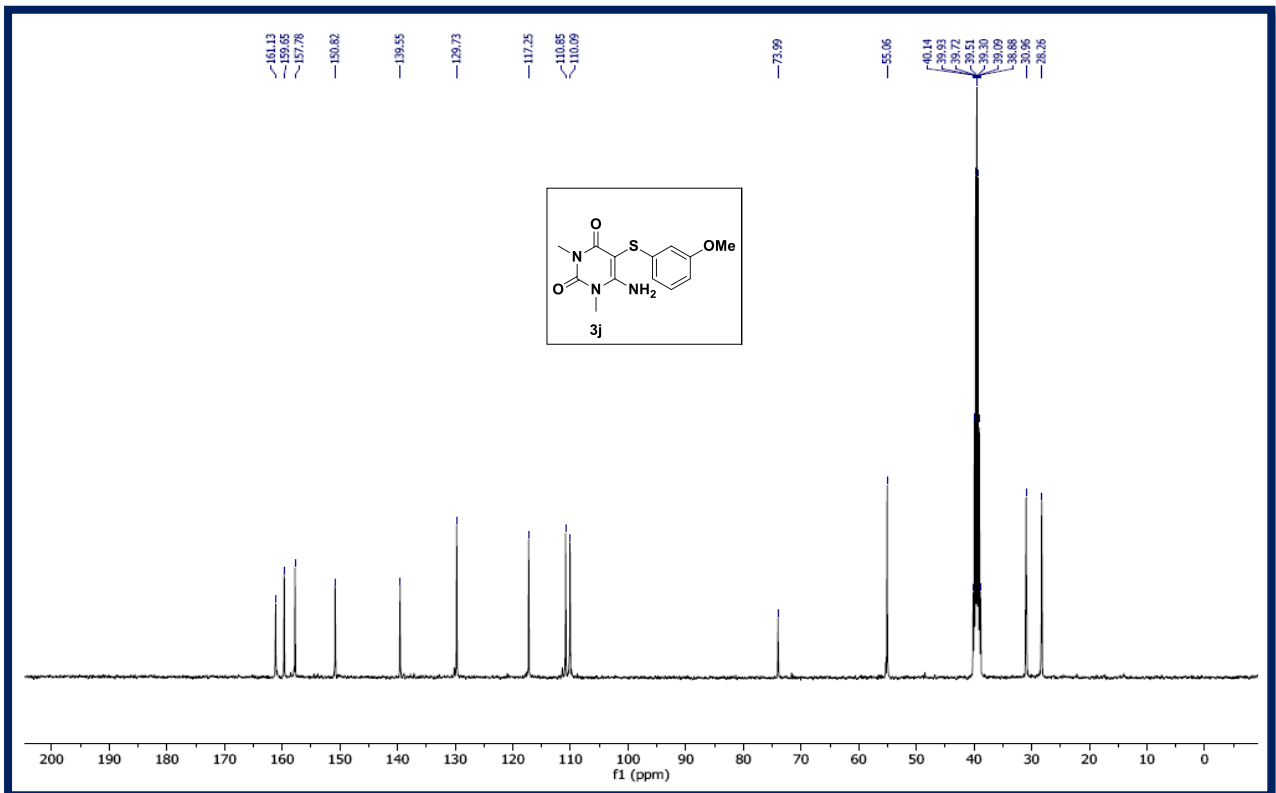
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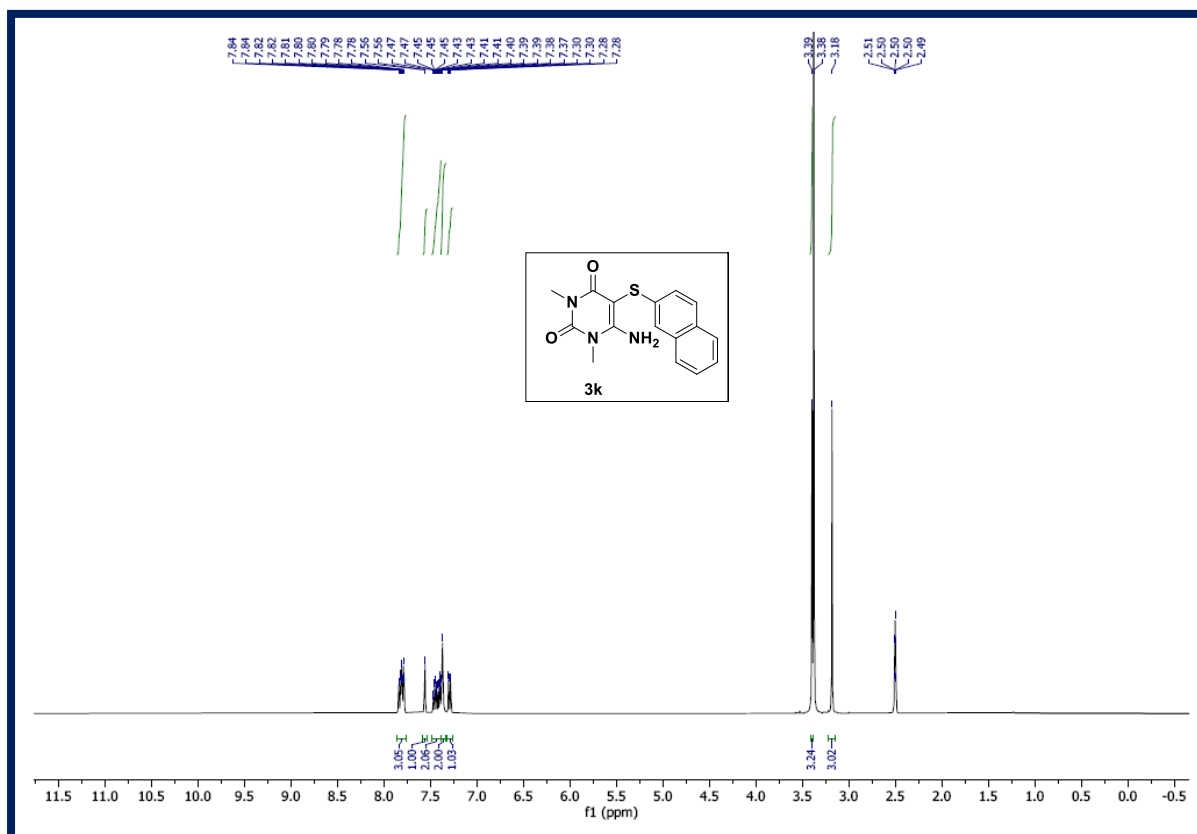
¹H NMR 3j



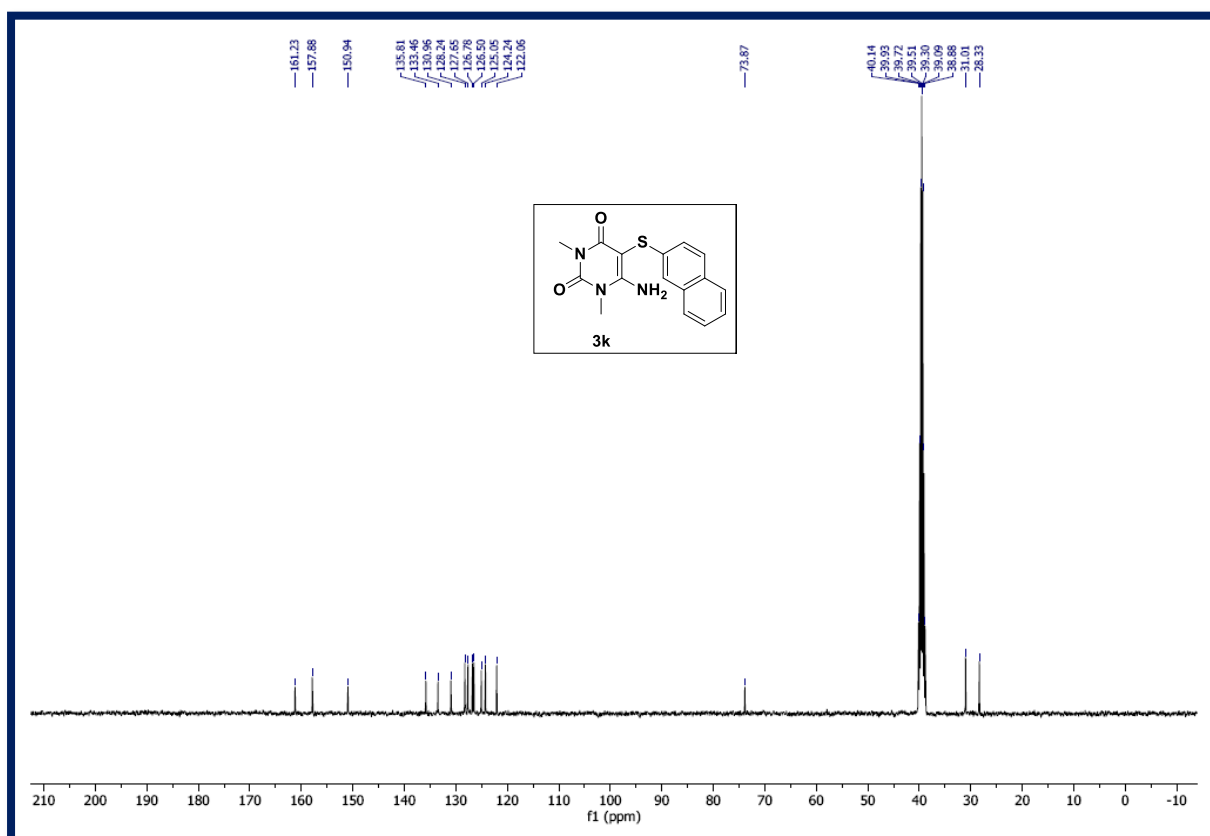
¹³C NMR 3j



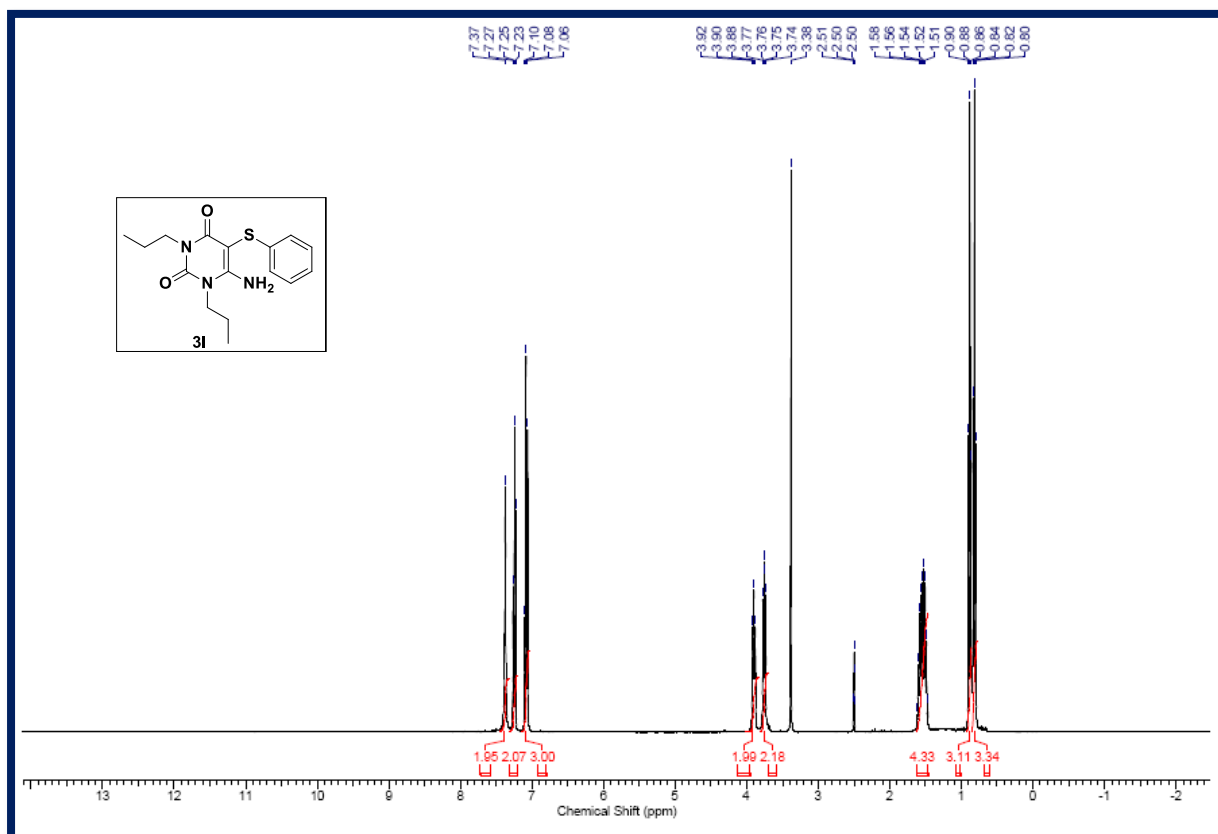
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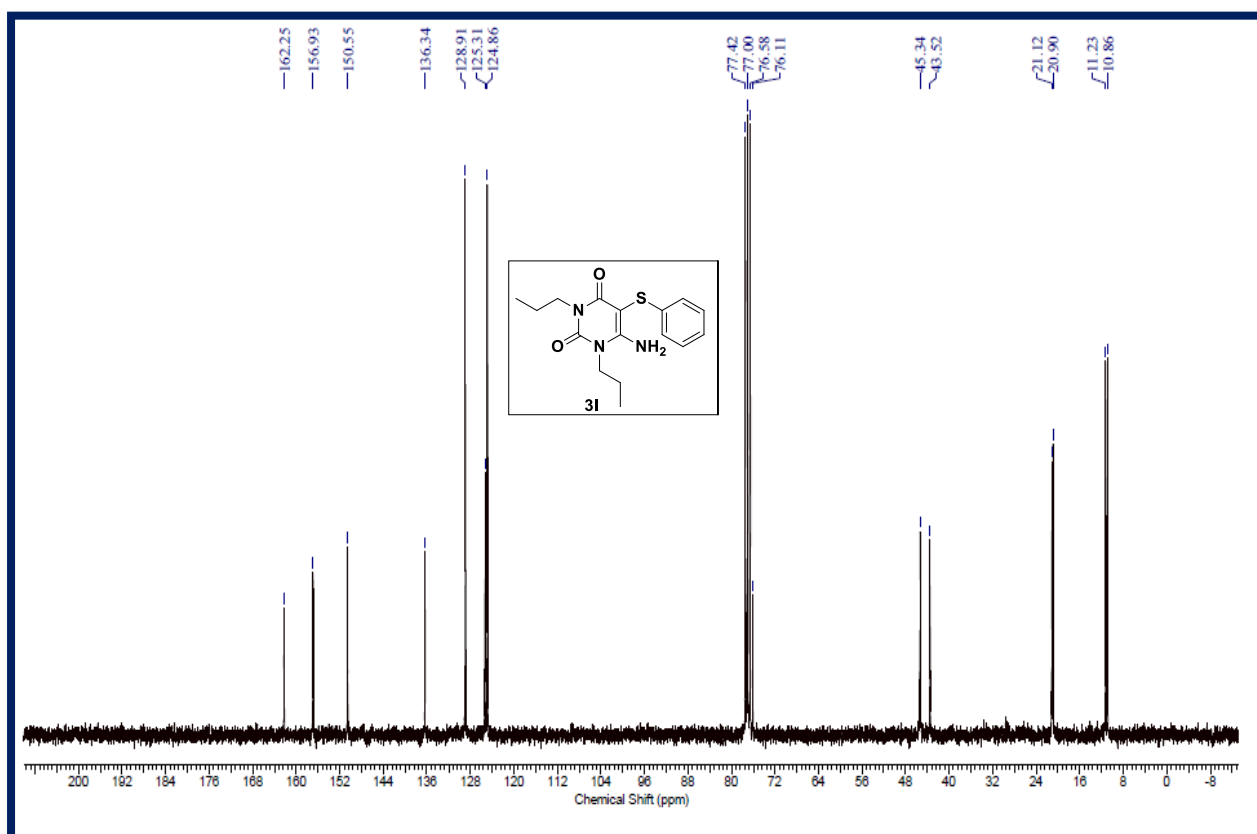
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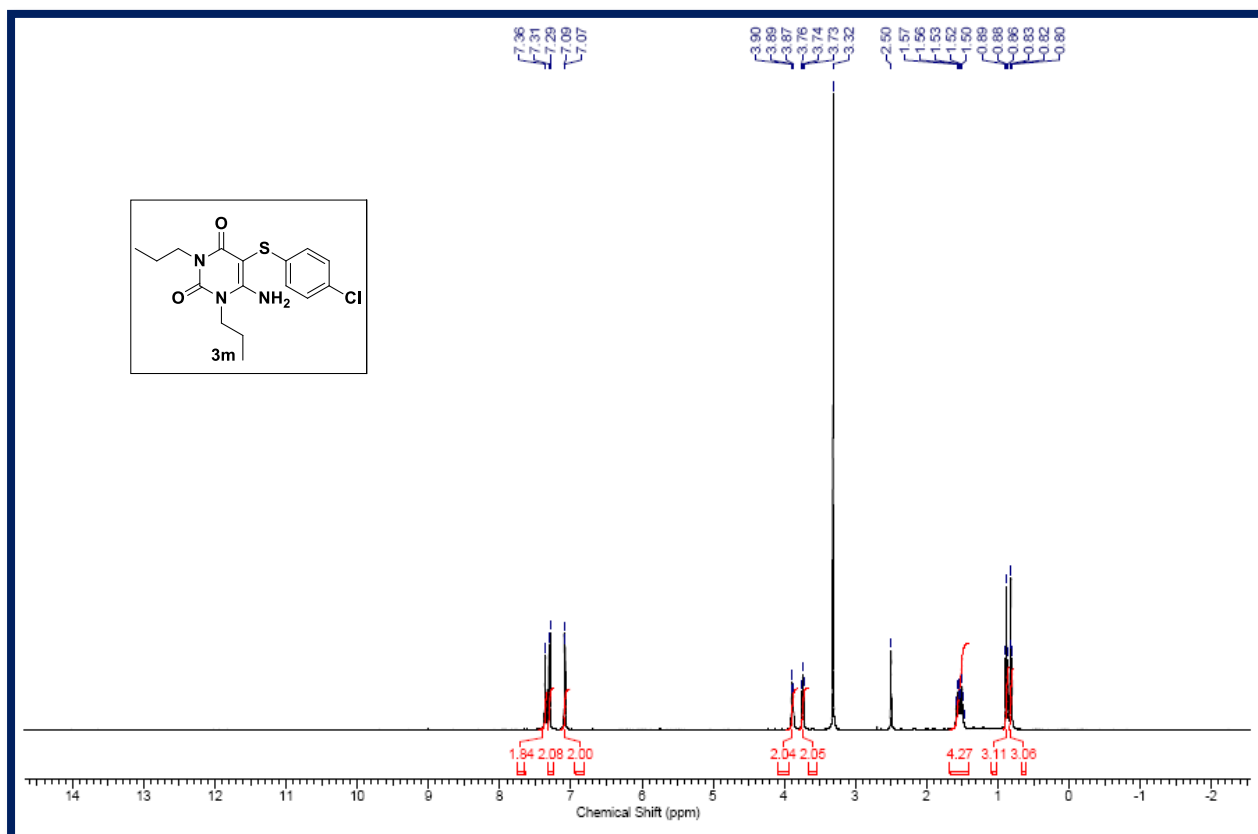
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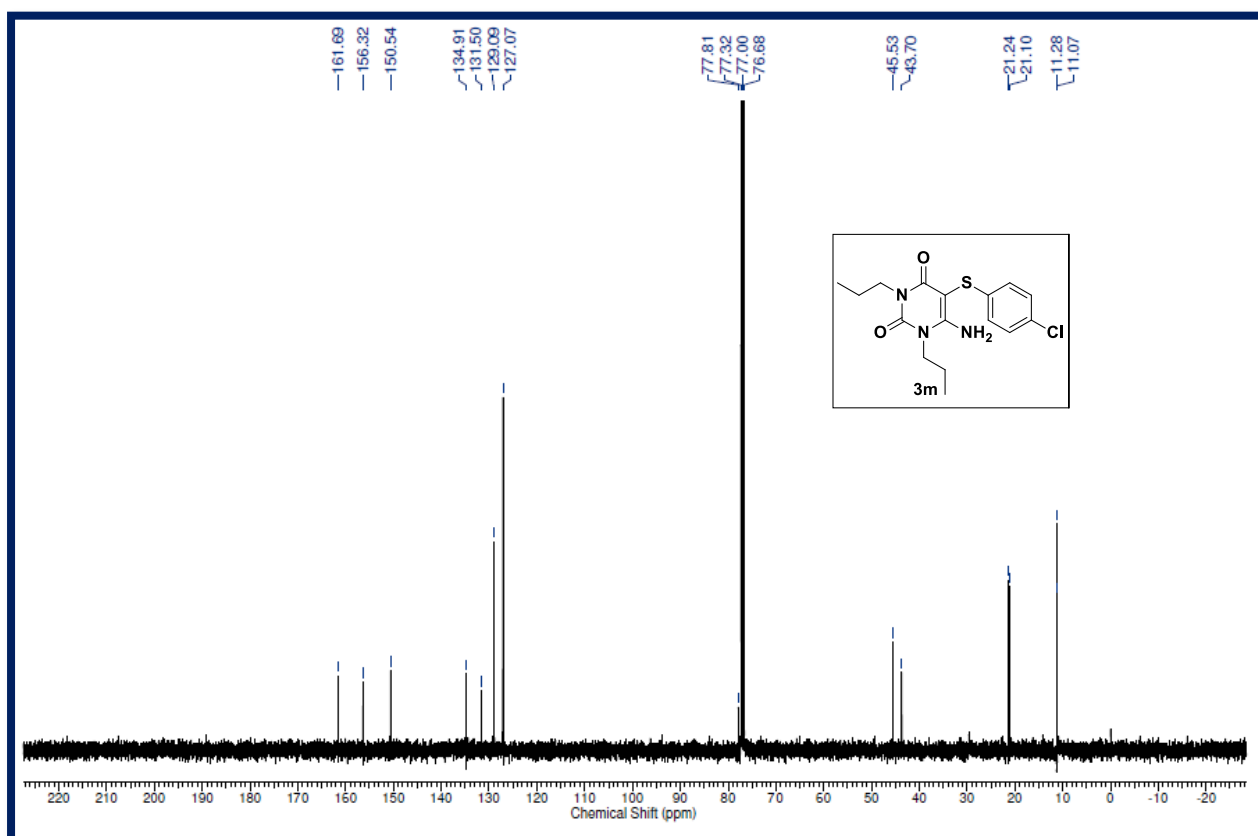
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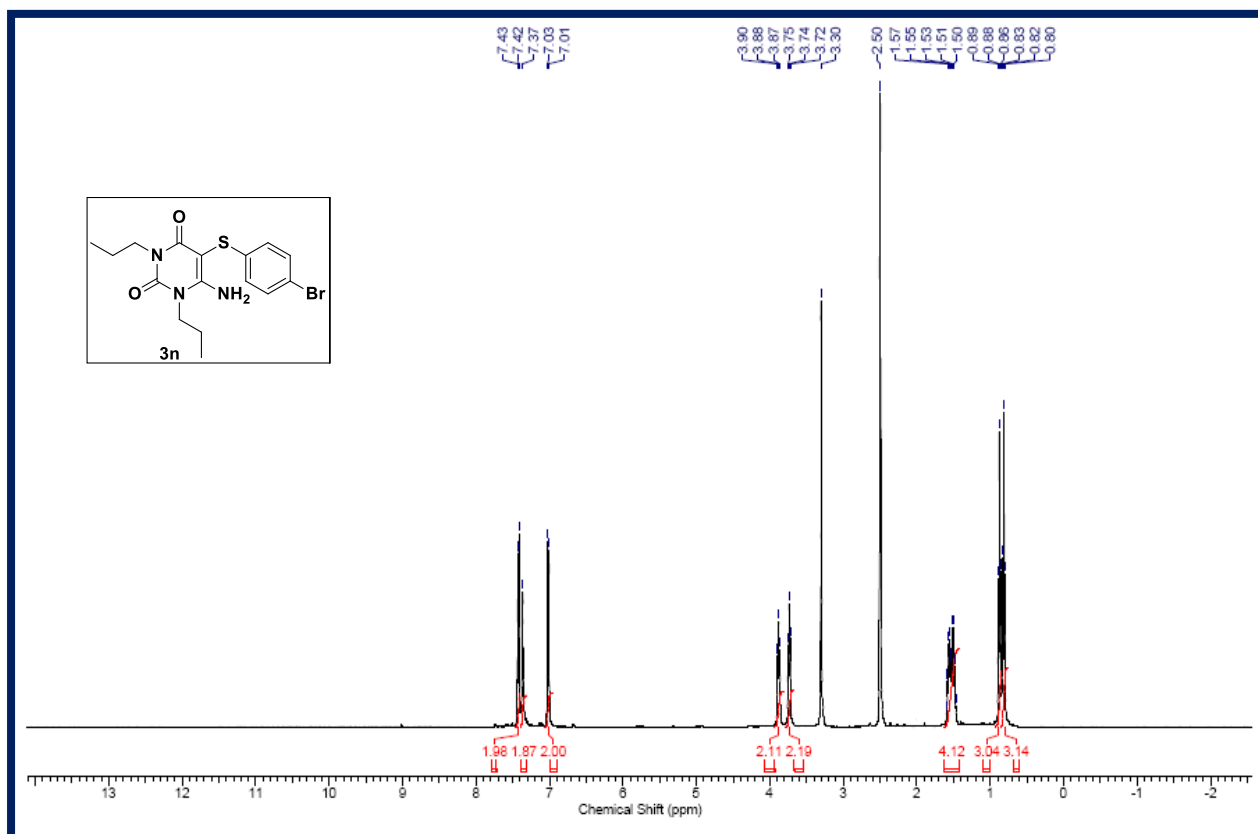
¹H NMR 3m



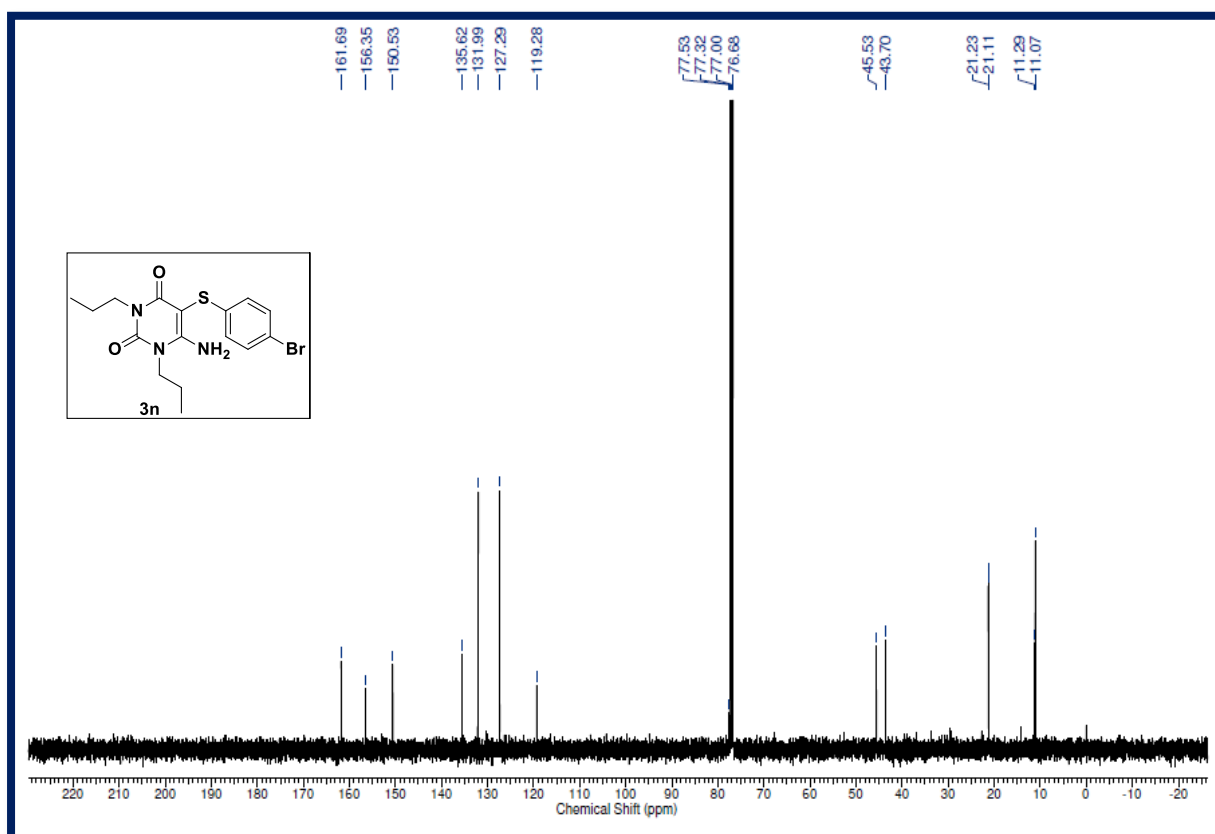
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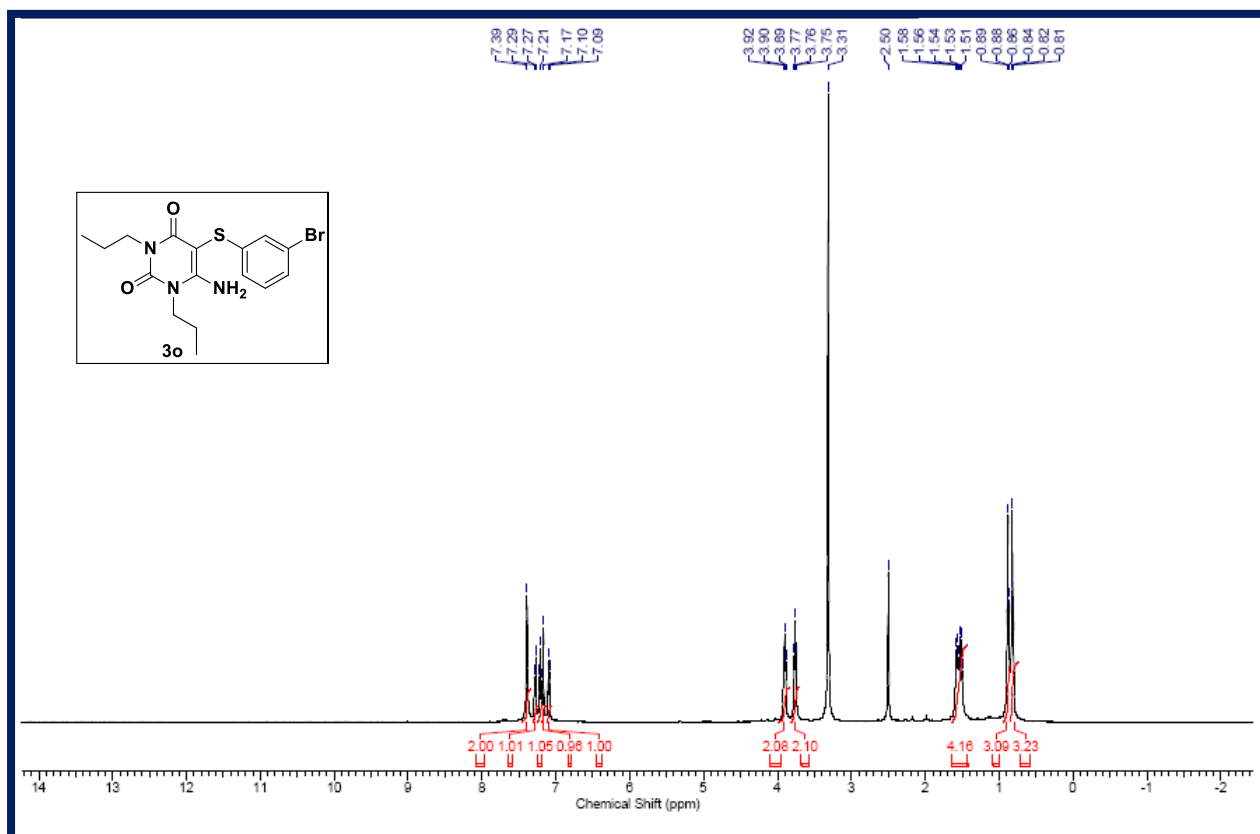
¹H NMR 3n



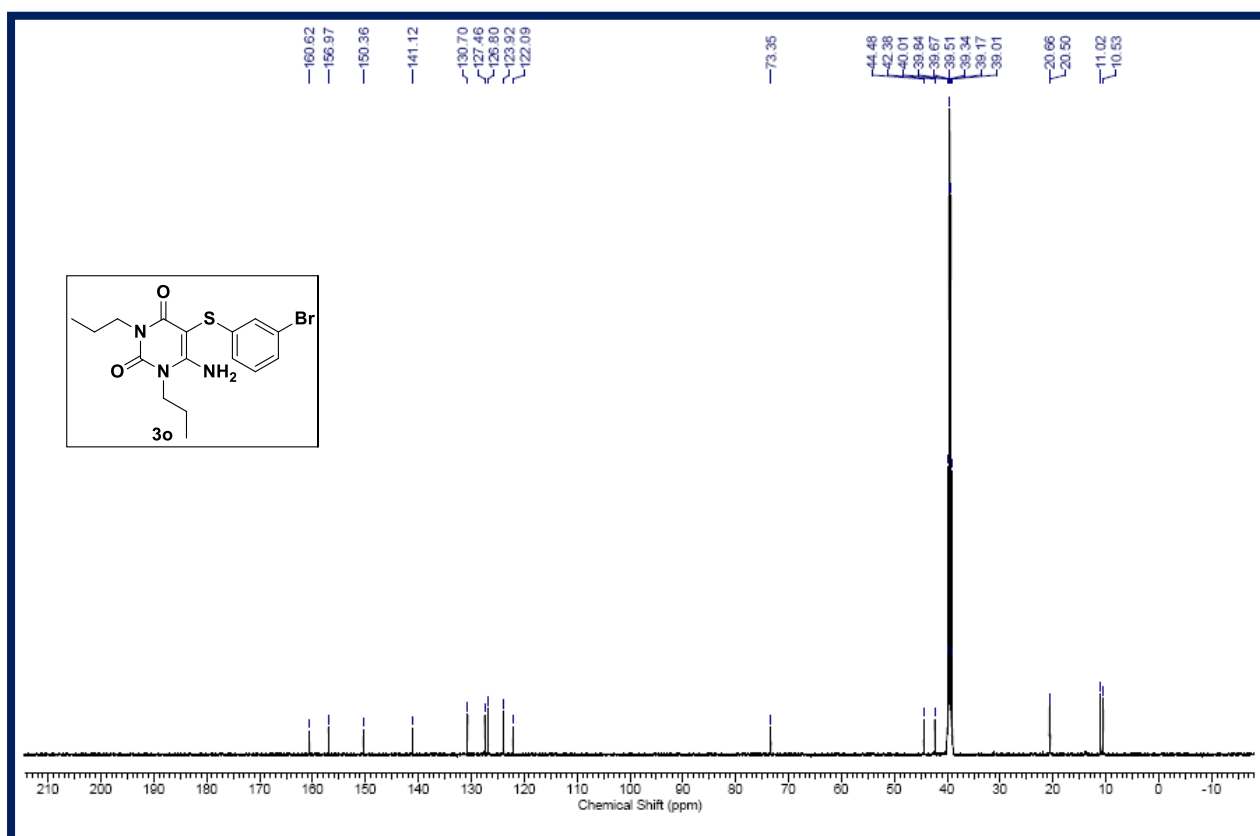
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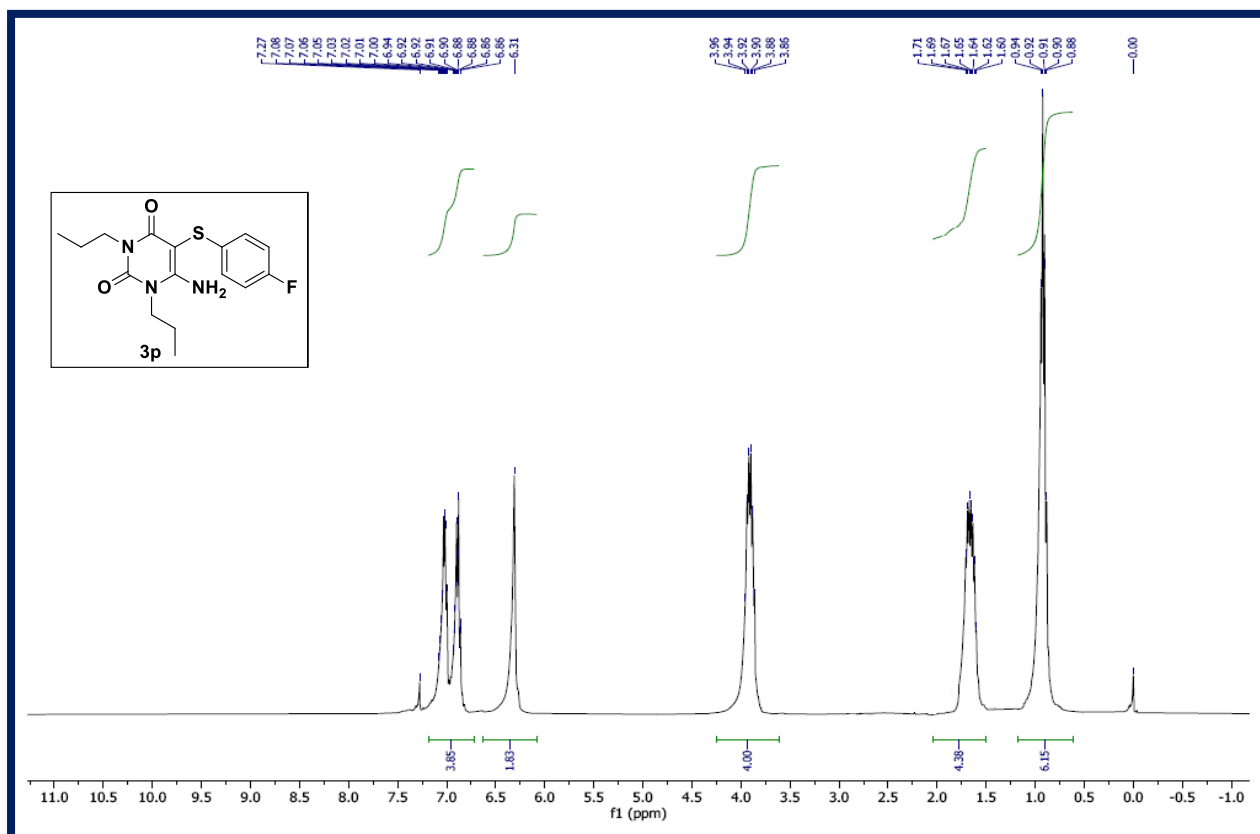
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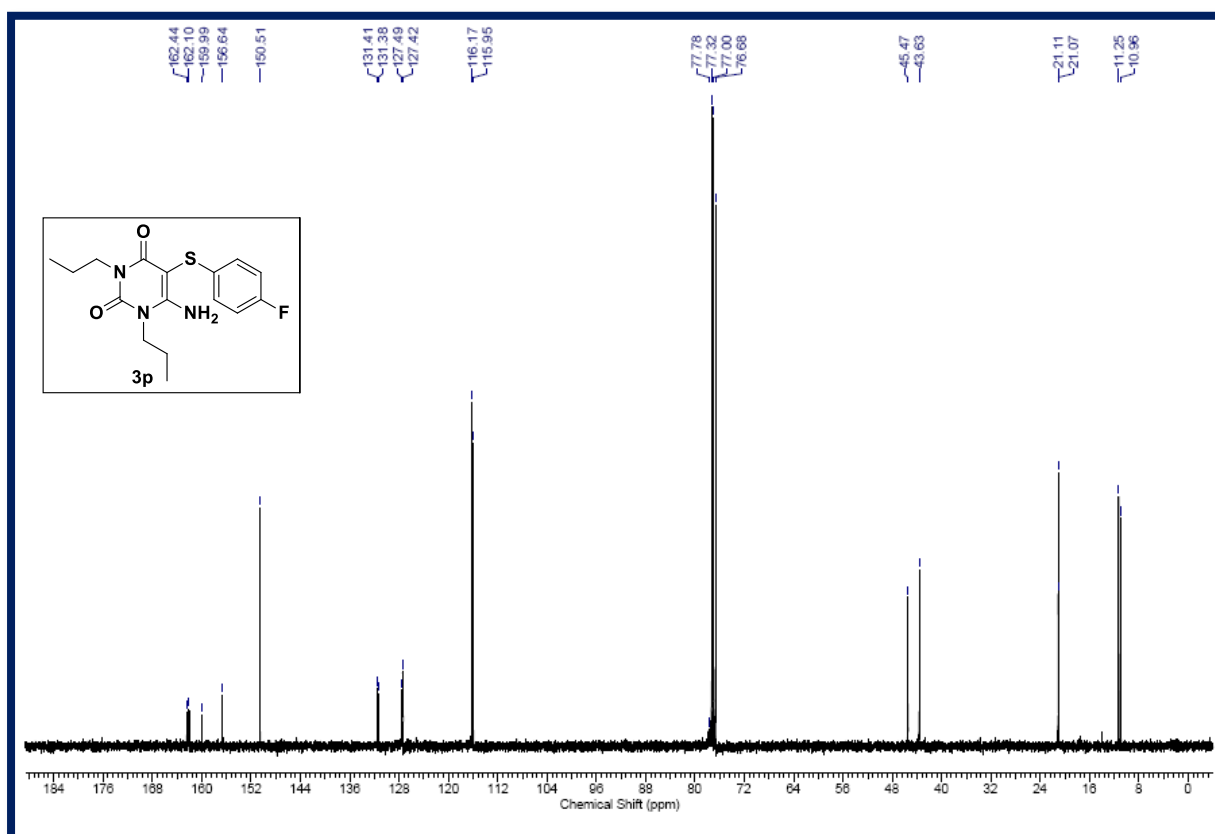
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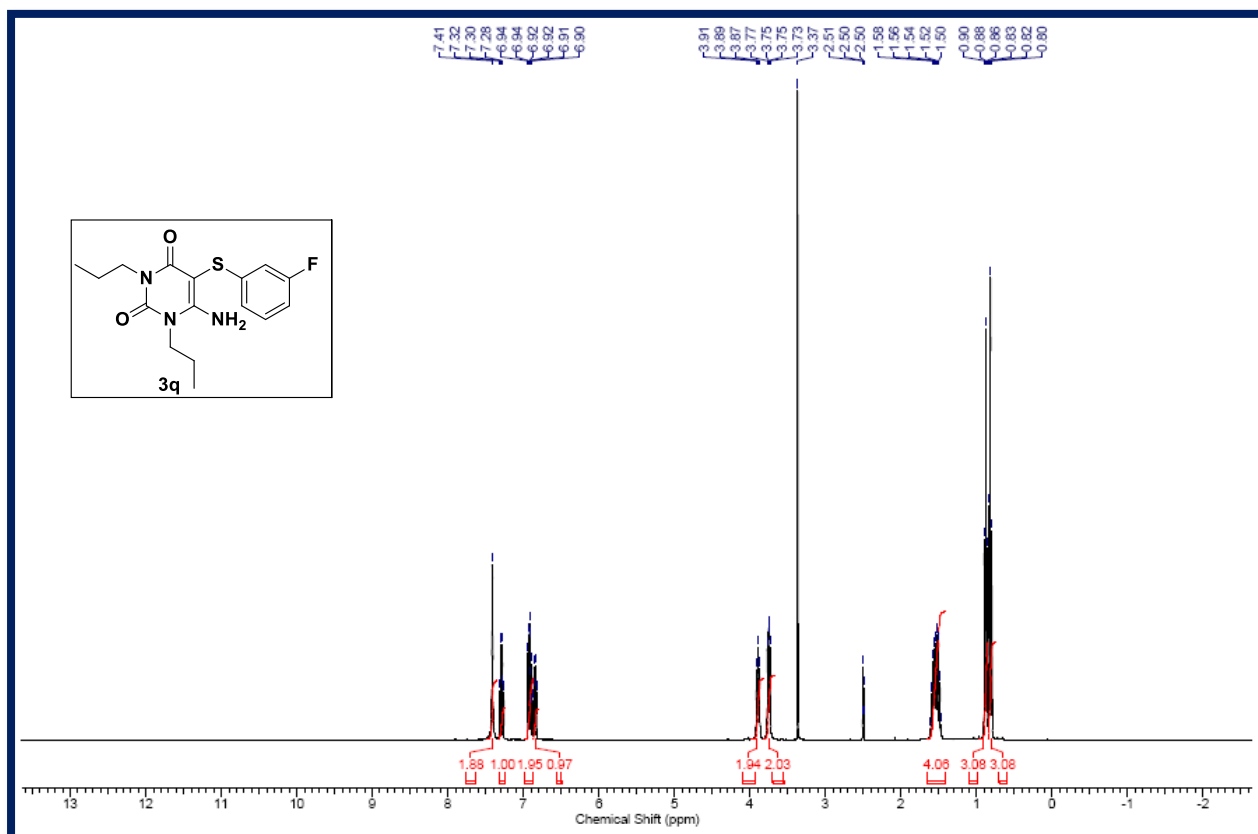
¹H NMR 3p



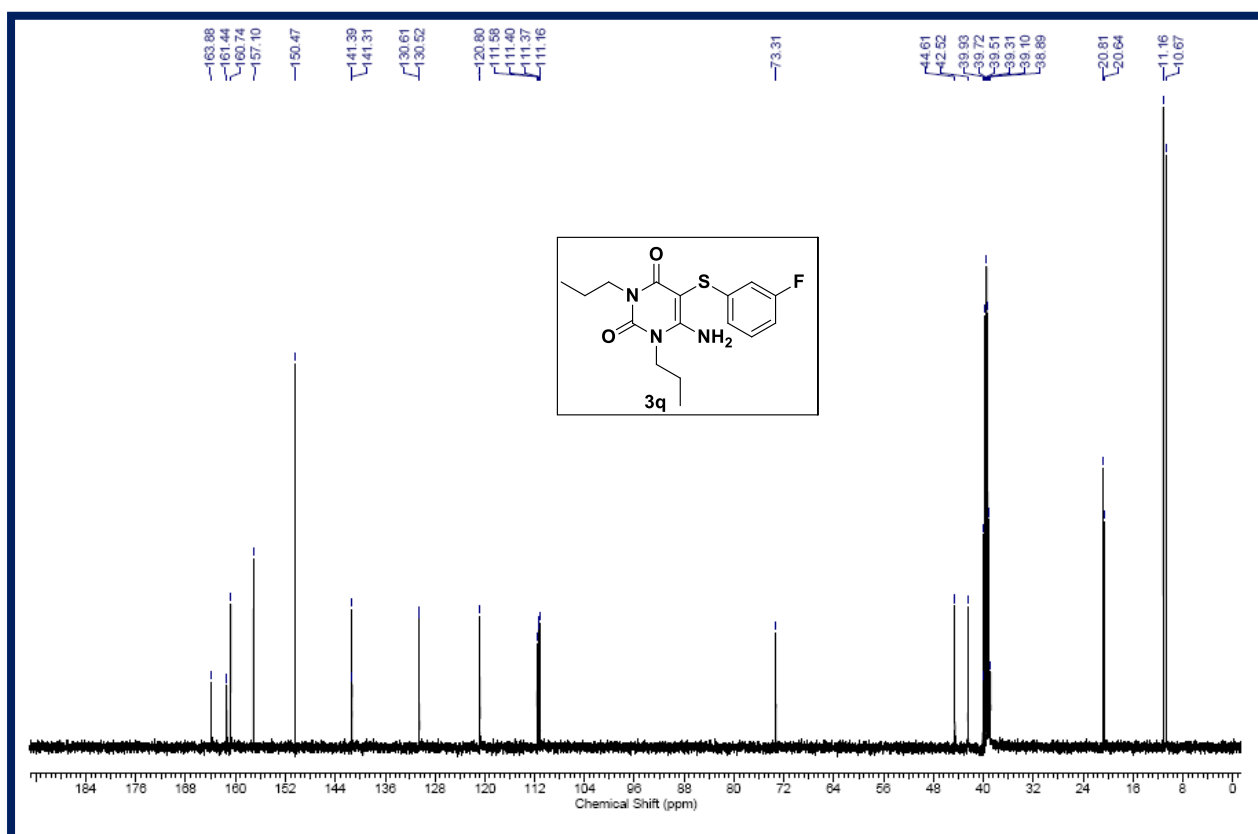
¹³C NMR 3p



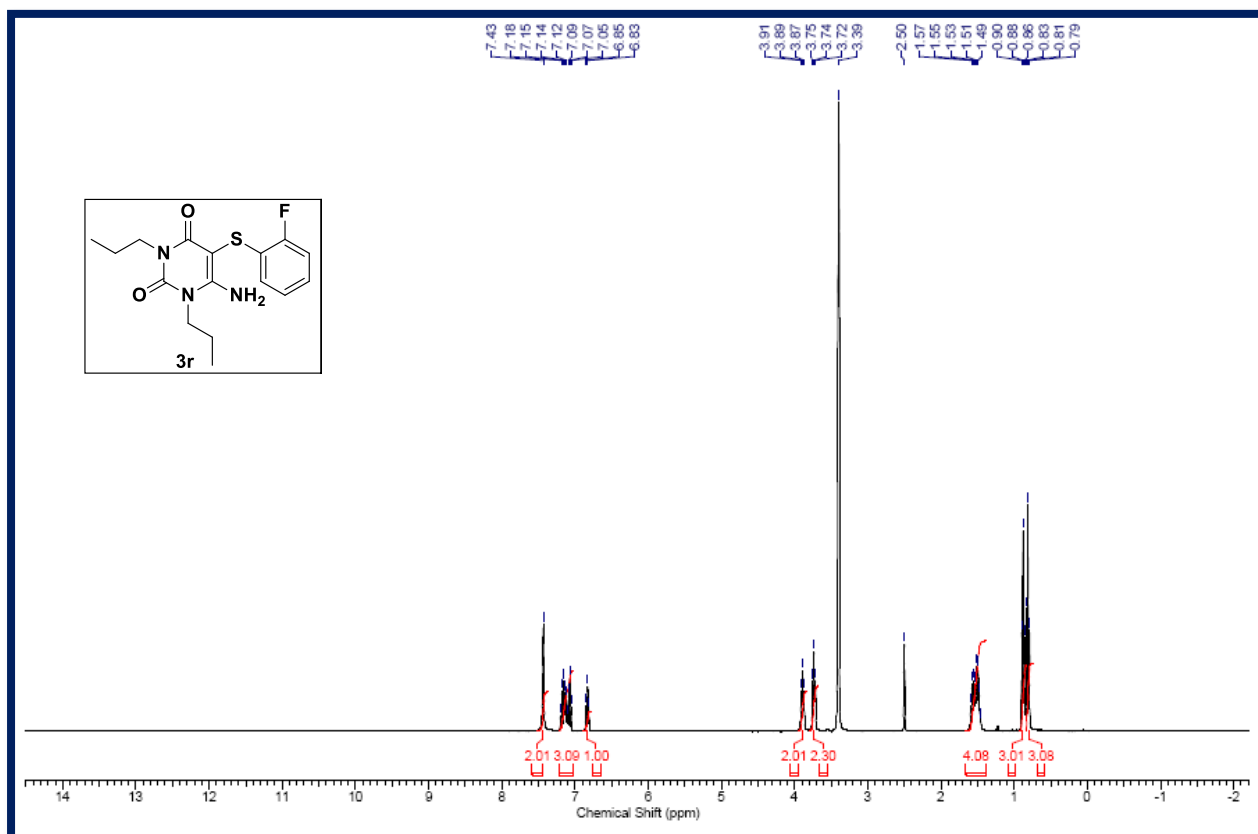
¹H NMR 3q



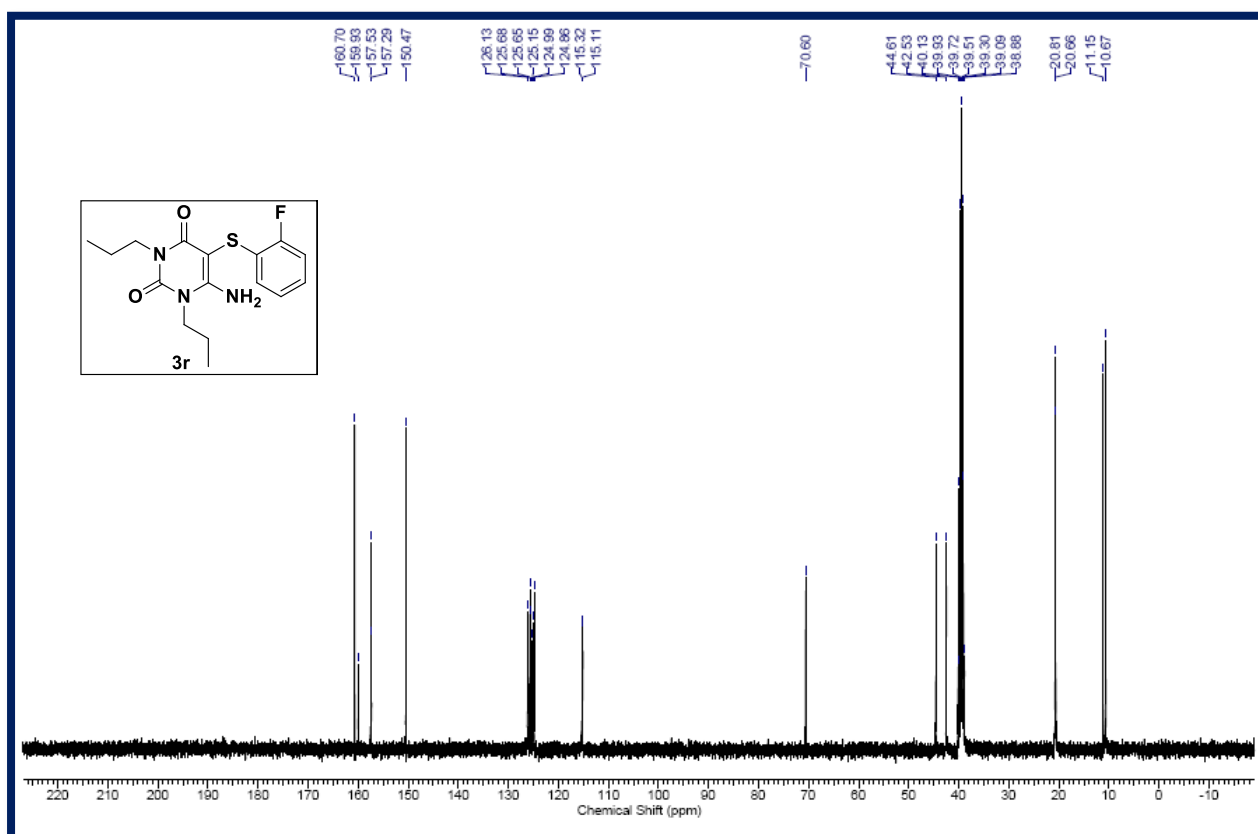
¹³C NMR 3q



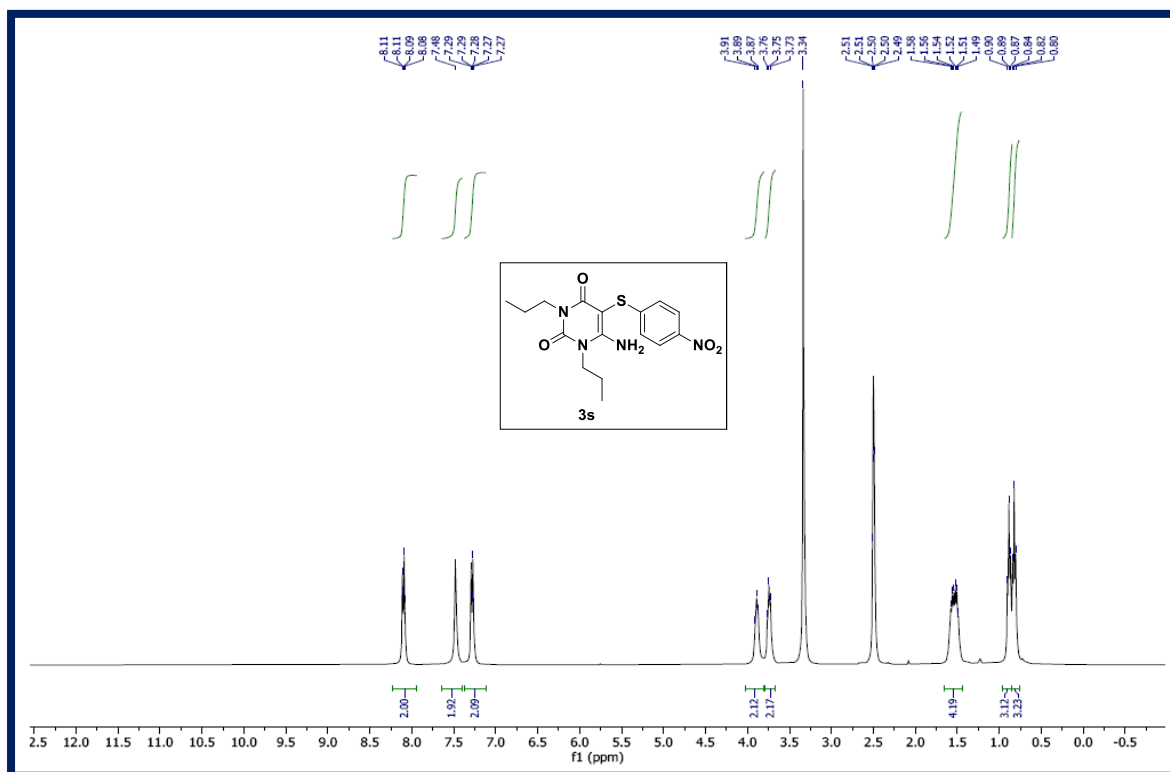
¹H NMR 3r



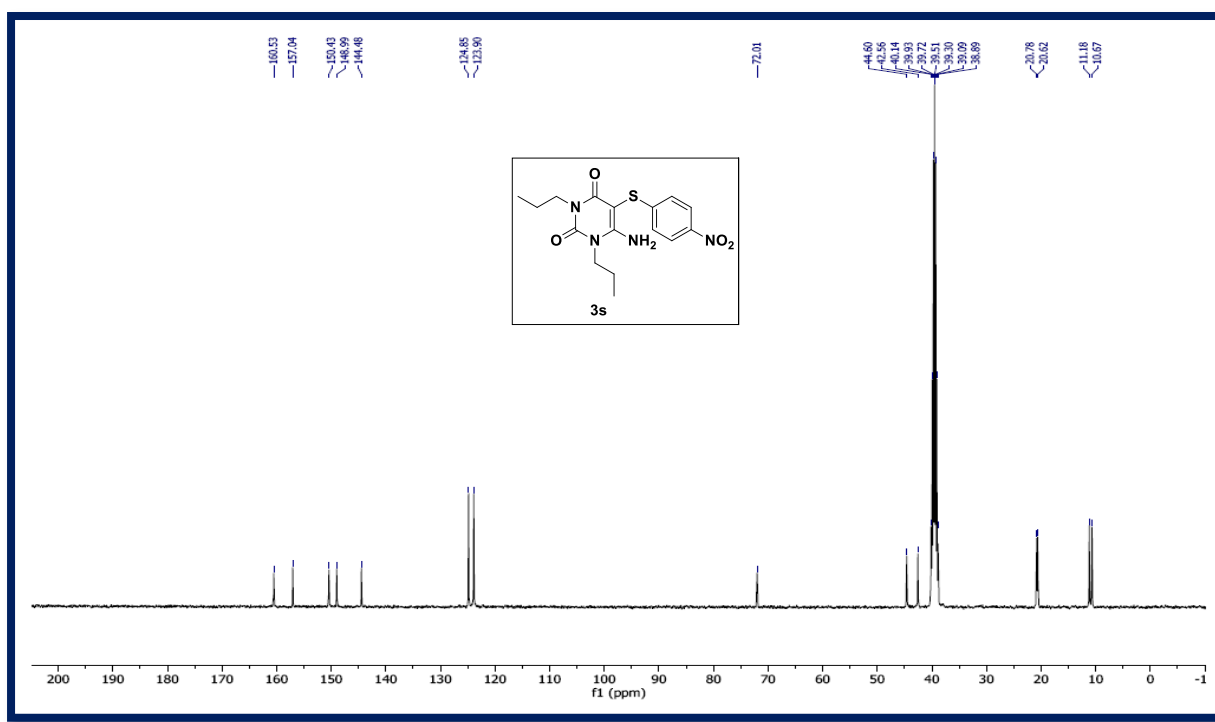
¹³C NMR 3r



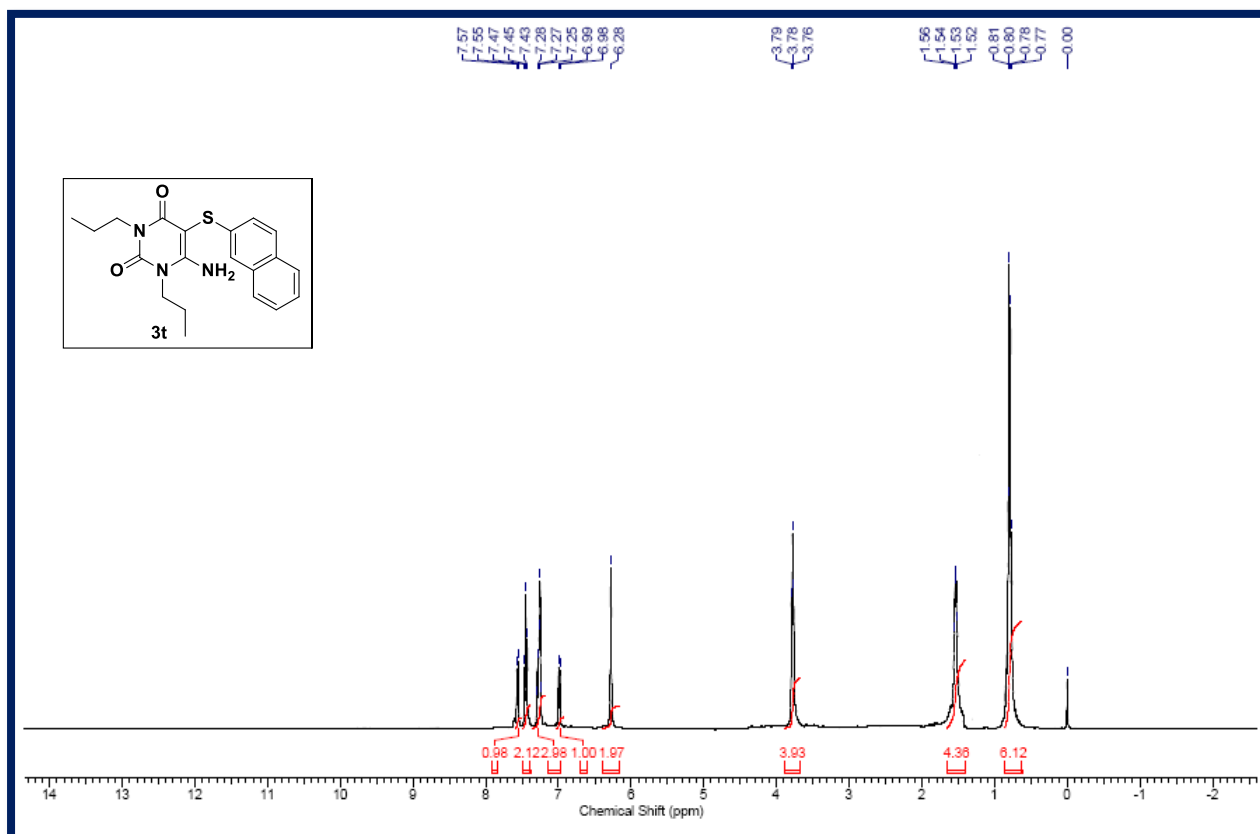
¹H NMR 3s



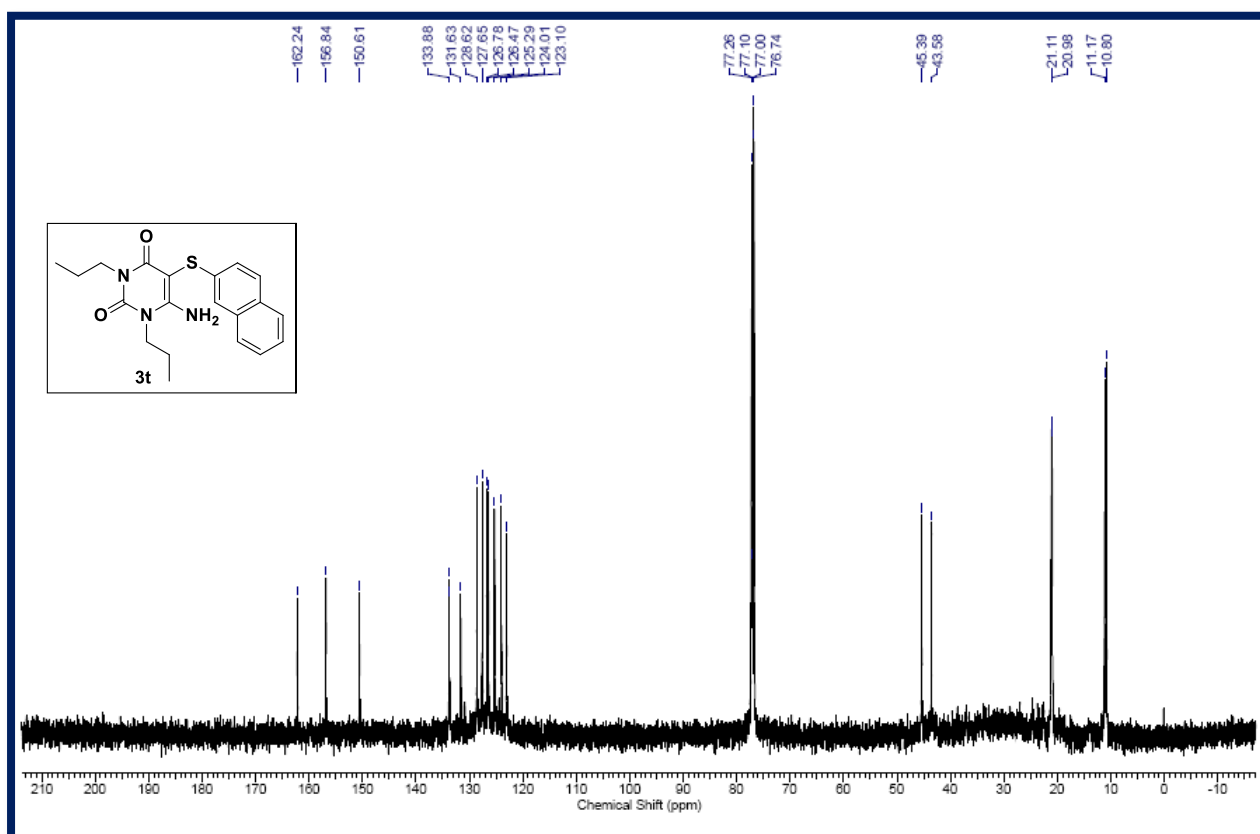
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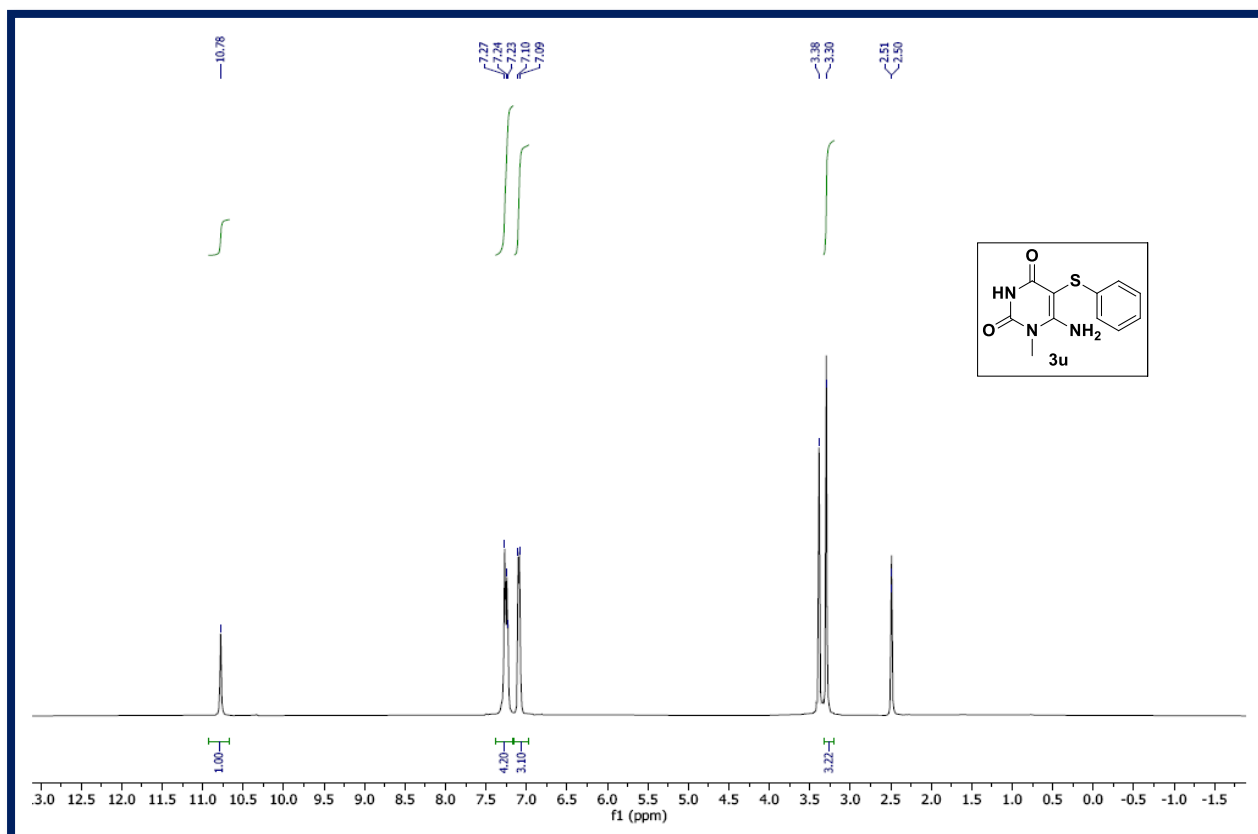
¹H NMR 3t



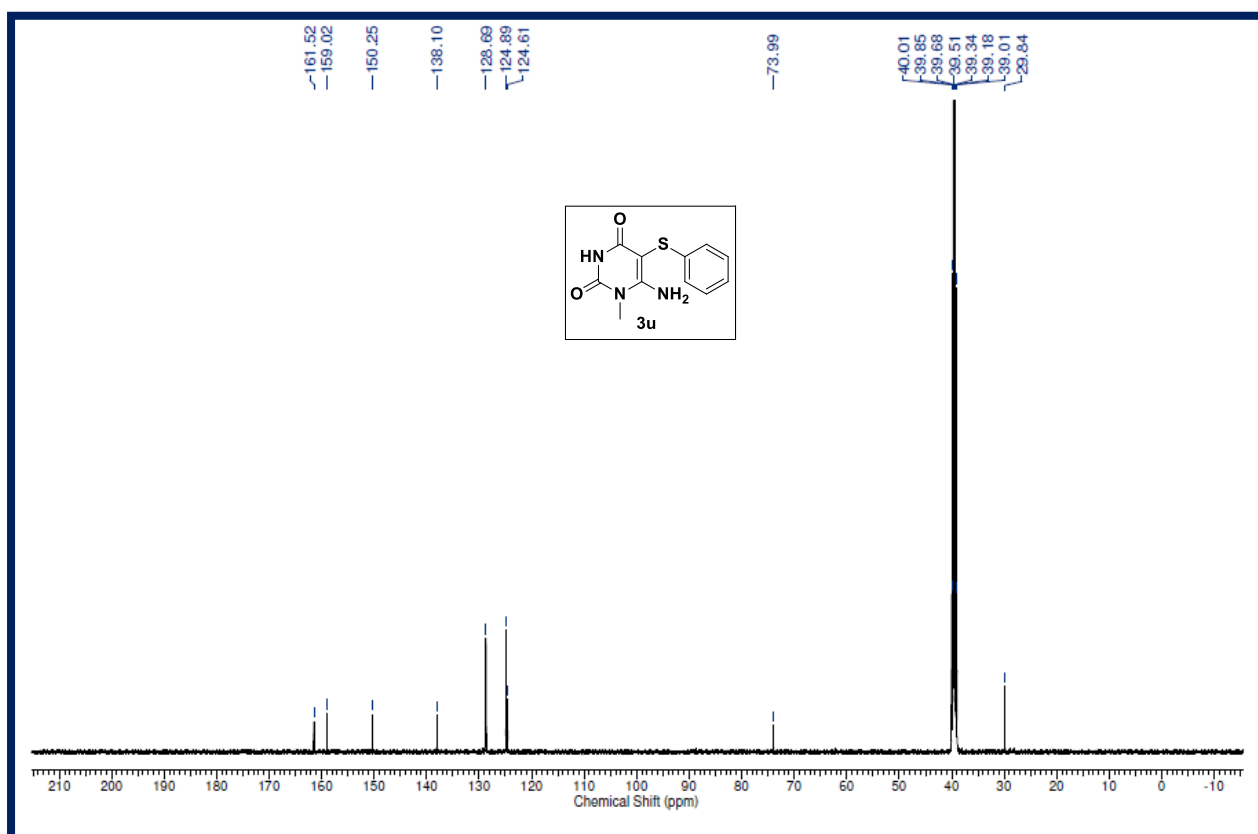
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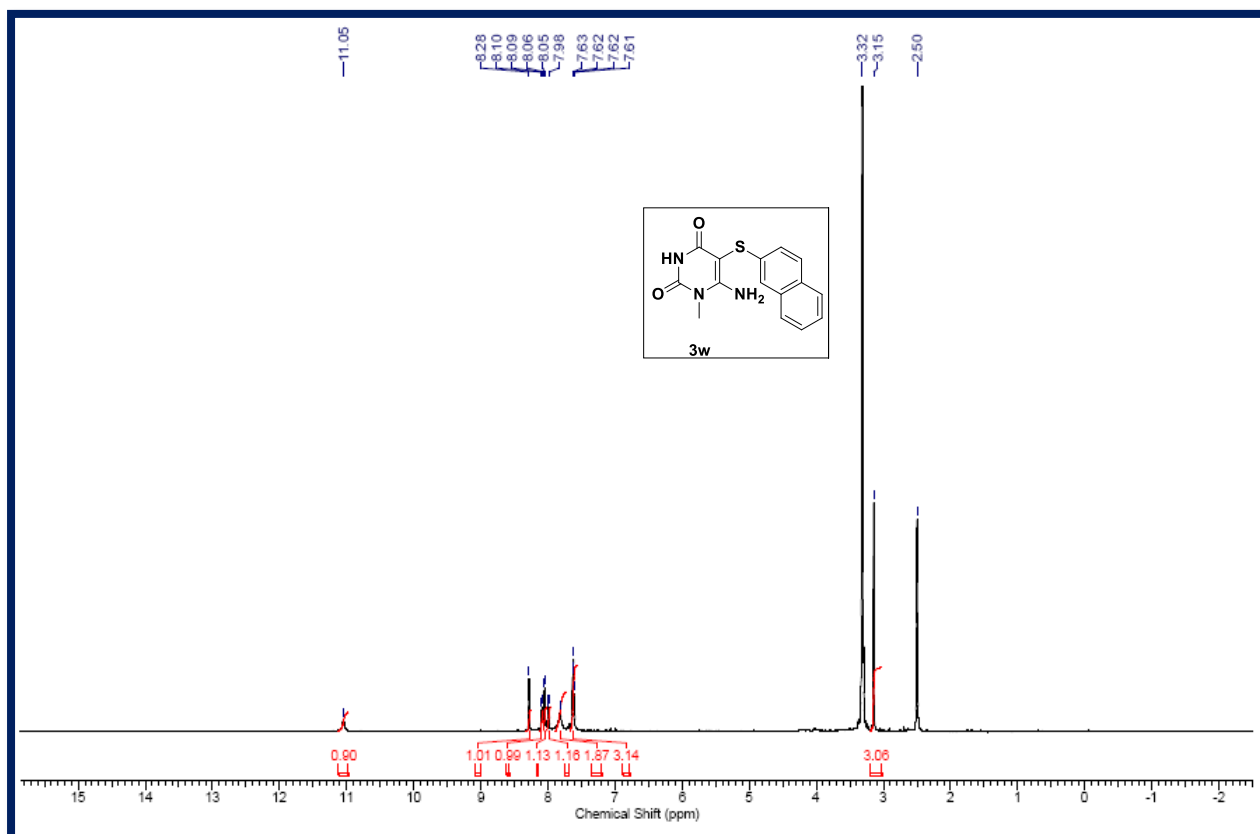
¹H NMR 3u



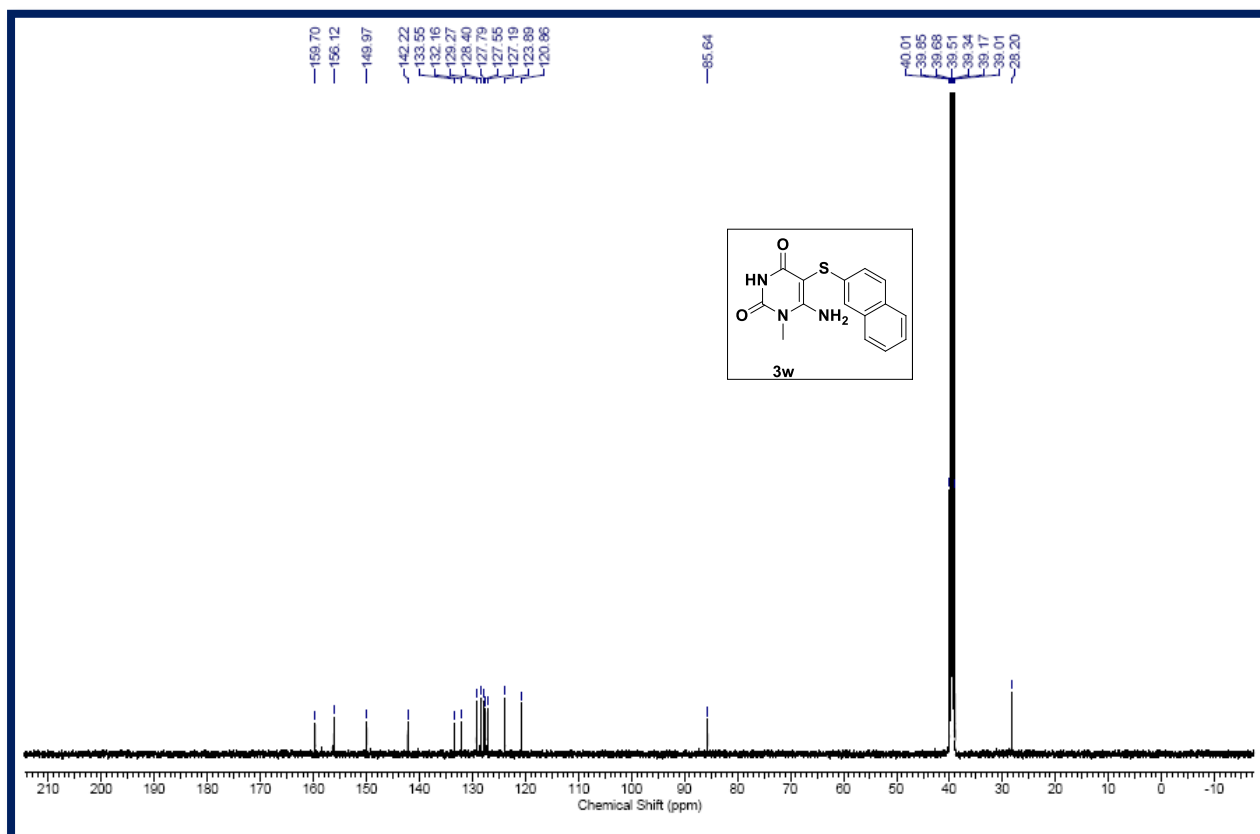
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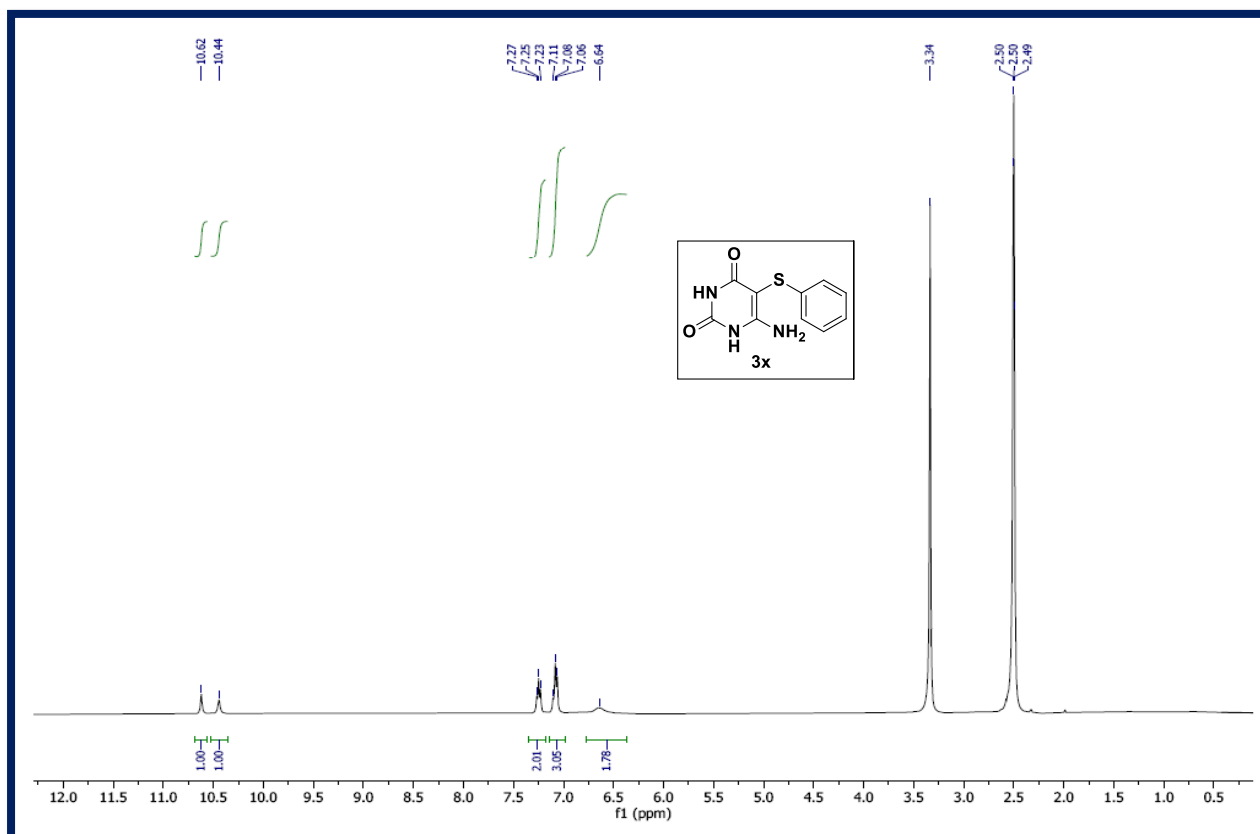
¹H NMR 3w



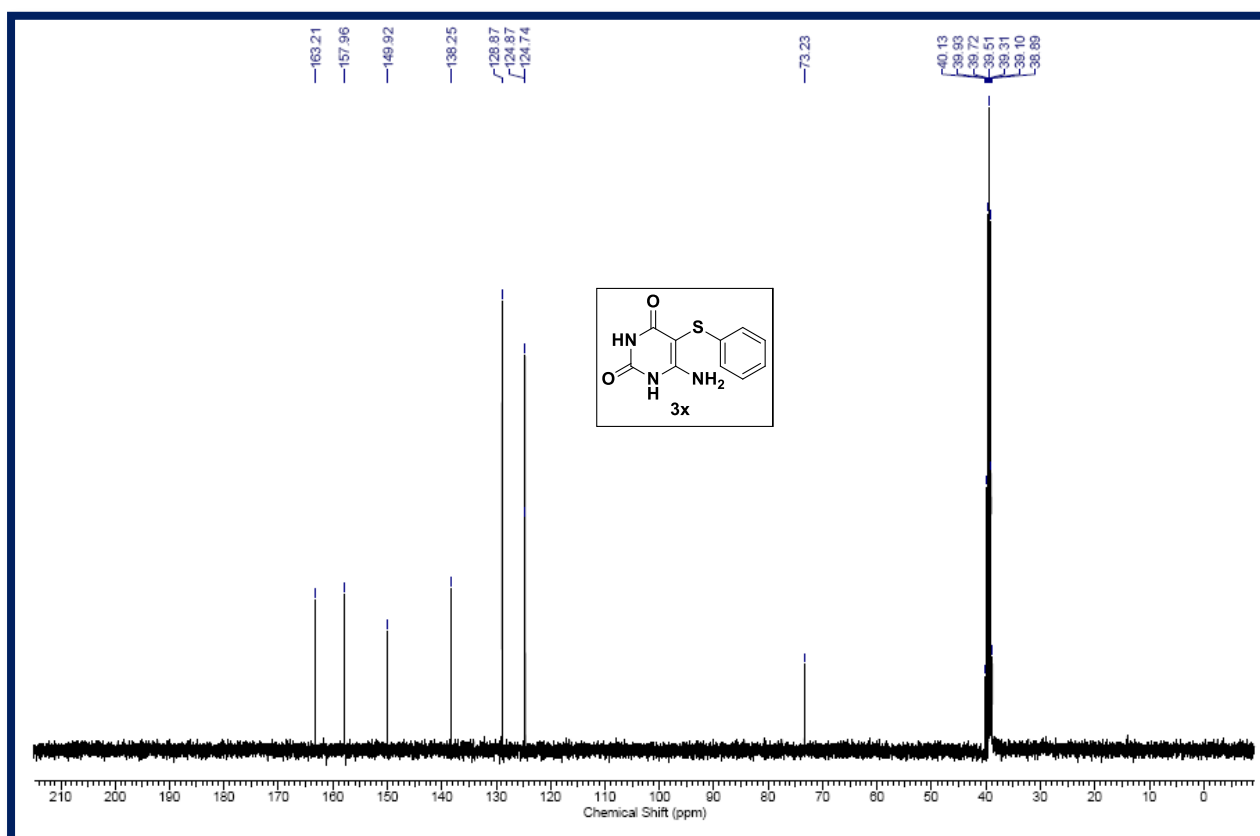
¹³C NMR 3w



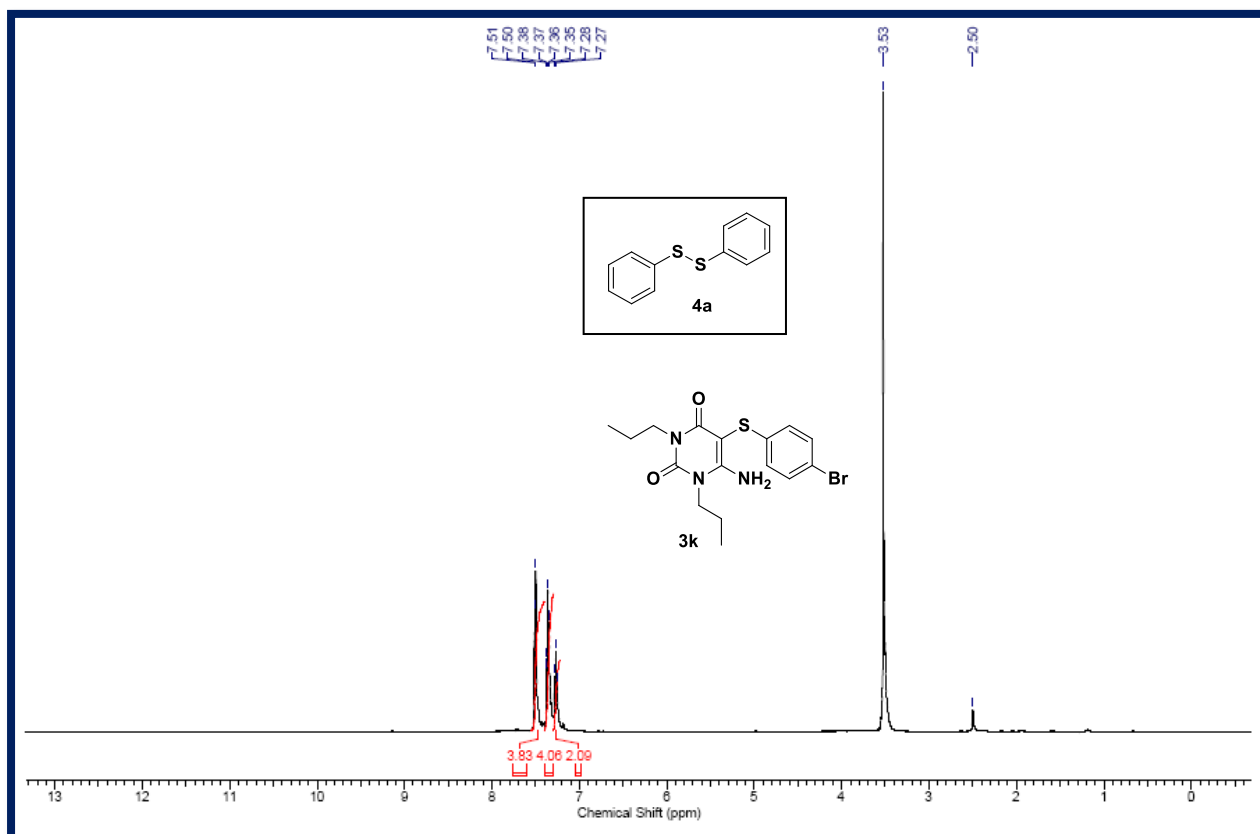
¹H NMR 3x



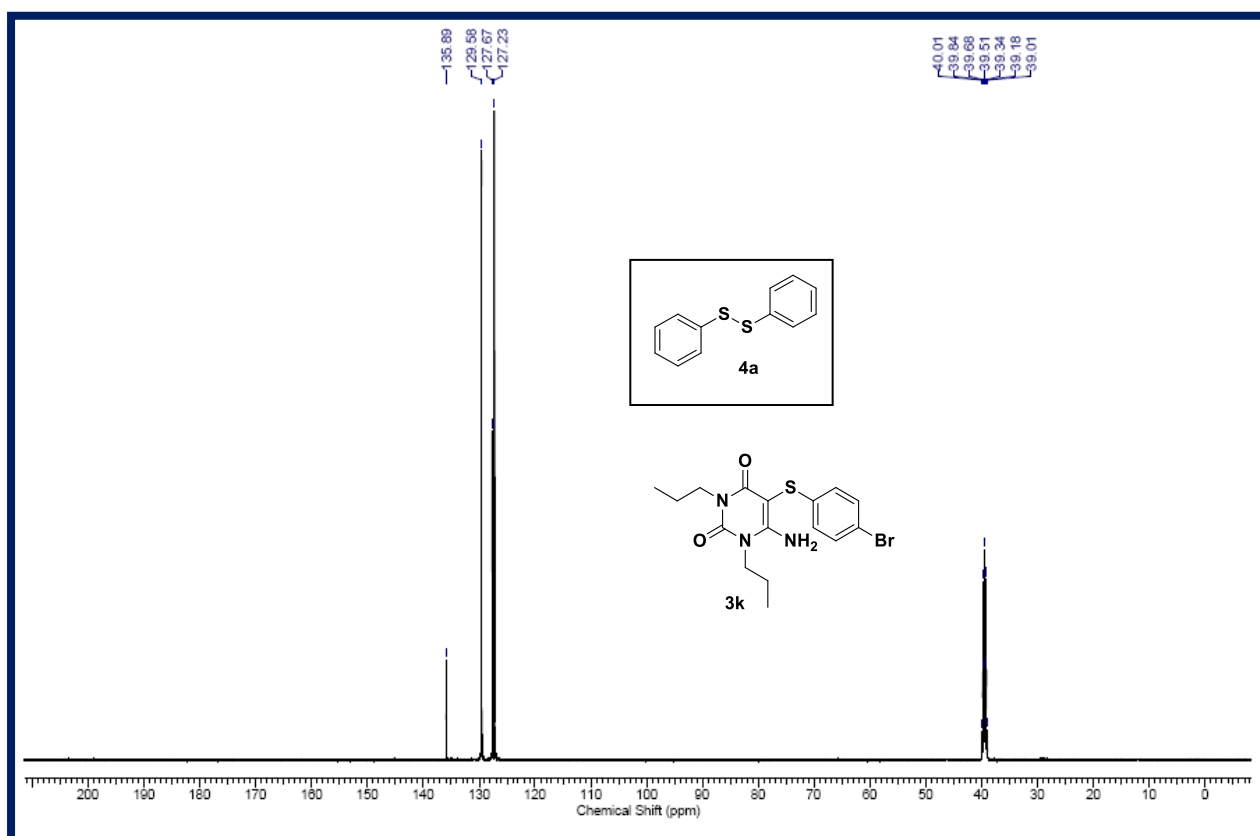
¹³C NMR 3x



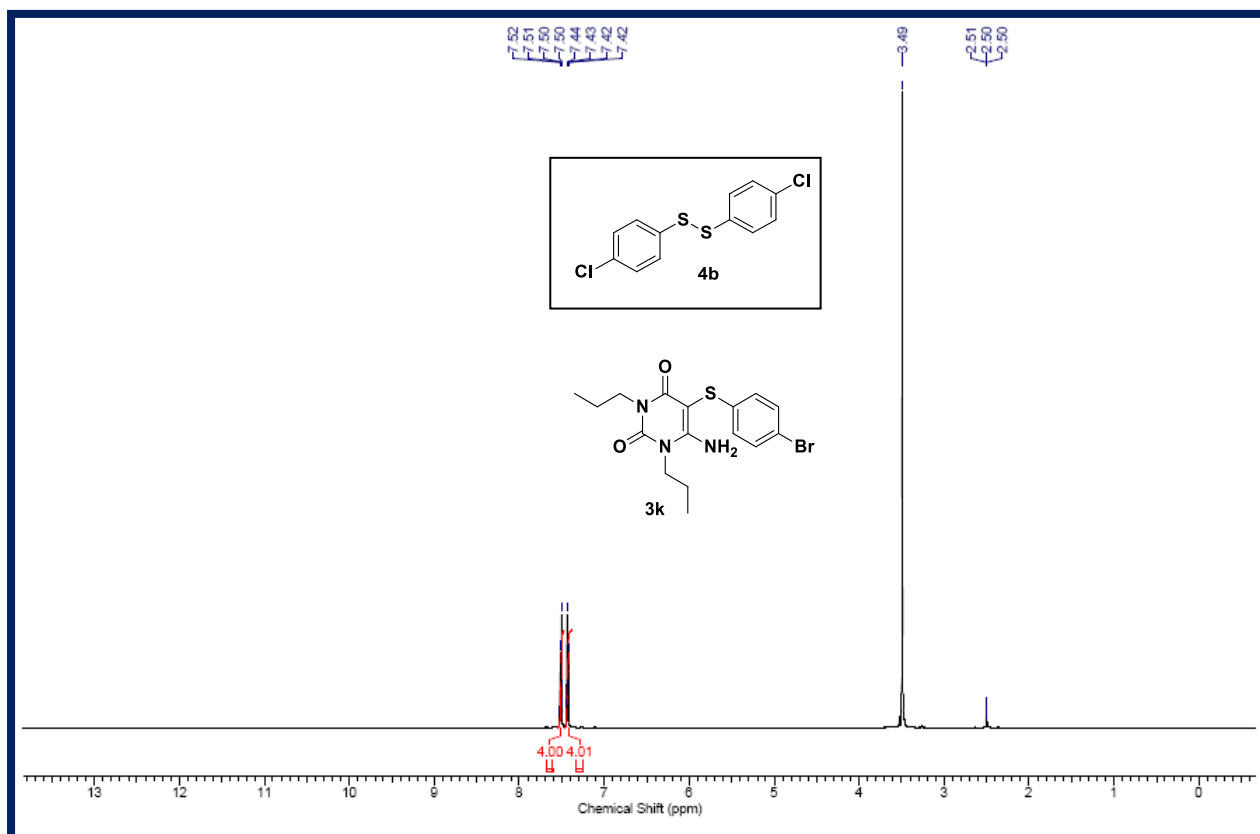
¹H NMR 4a



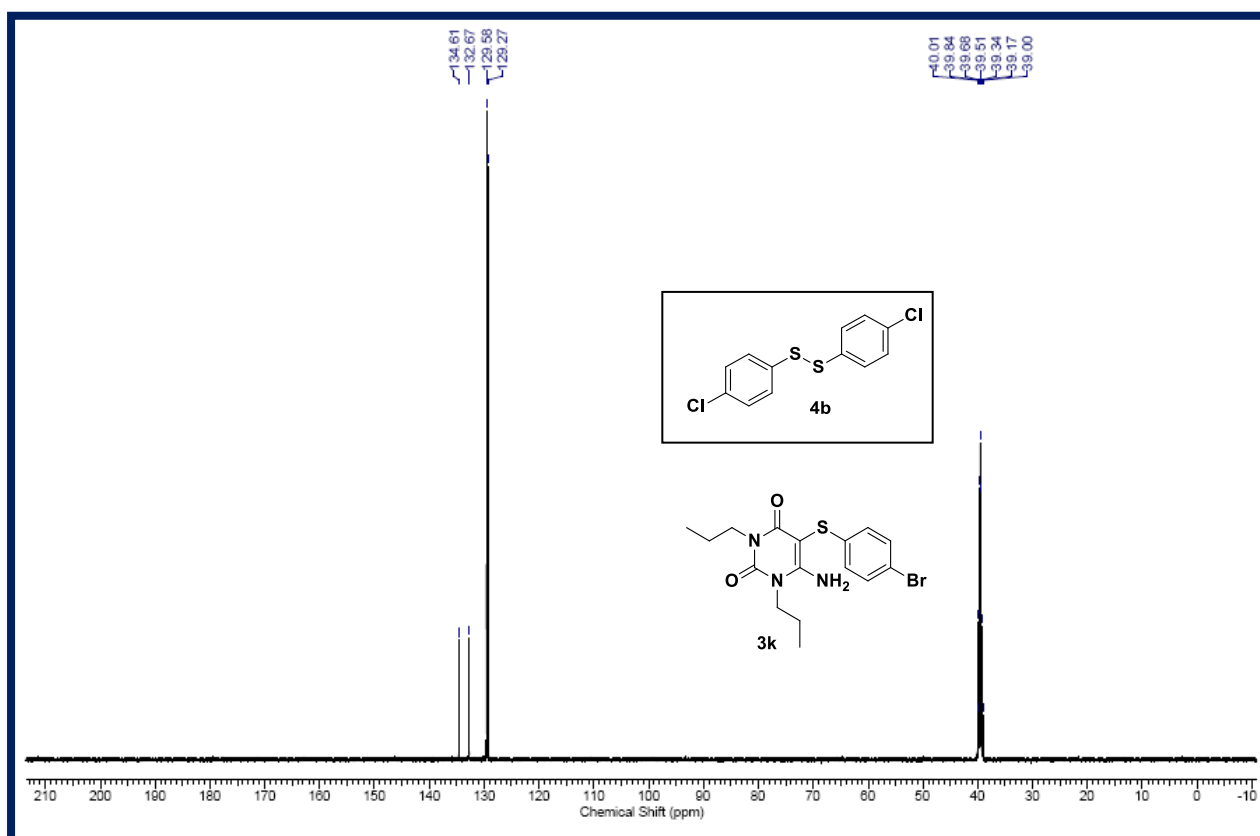
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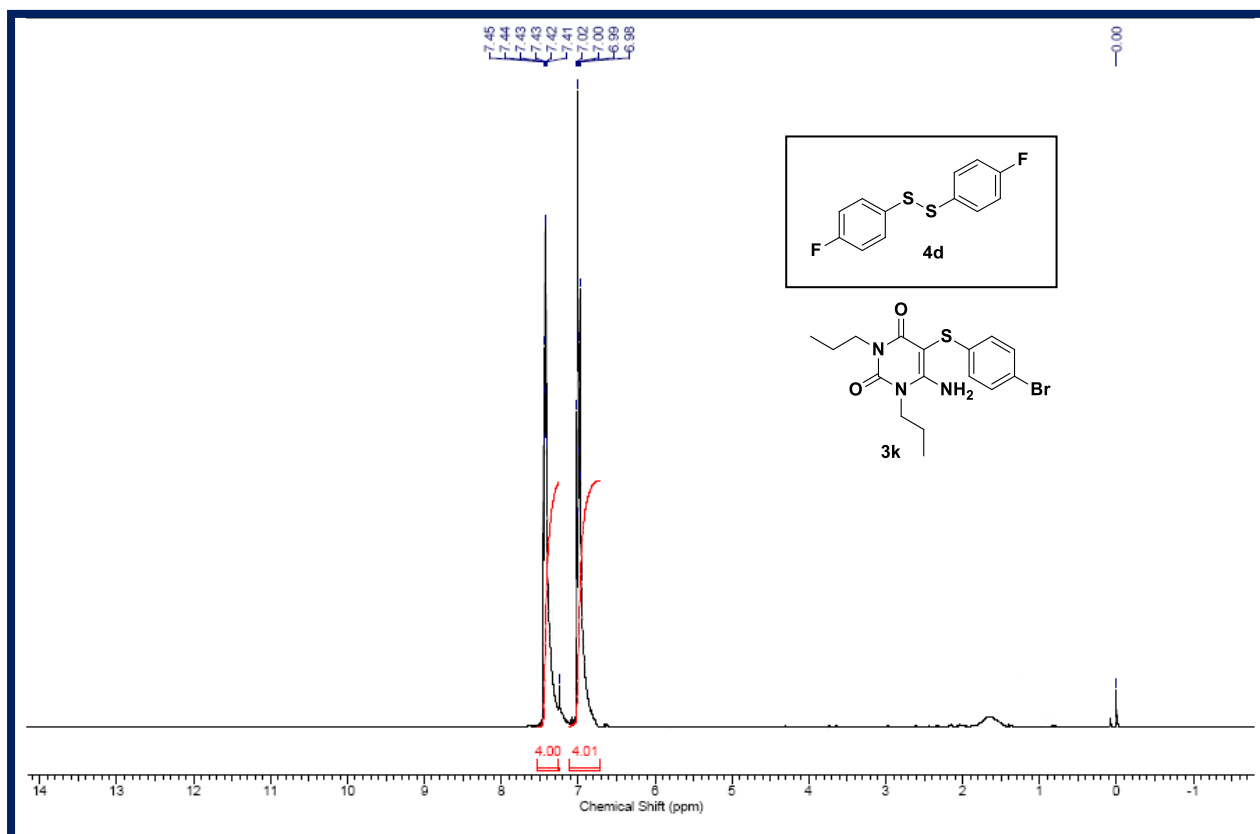
¹H NMR 4b



¹³C NMR 4b



¹H NMR 4d



¹³C NMR 4d

