Supporting Information

Possible competitive modes of decarboxylation in the annulation reactions of ortho-substituted anilines and arylglyoxylates

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1. GENERAL CONSIDERATION

Unless noted otherwise, all reagents and solvents were purchased from commercial sources and used as received. All palladium-catalyzed reactions were performed in a screw-cap sealed tube. The ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ as solvent using a 400 MHz spectrometer with Me_4Si as an internal standard. Coupling constants (*J* values) are reported in Hz. Column chromatography was performed using silica gel (60-120, 100-200, or 230-400 mesh). High Resolution Mass Spectra (HRMS) were obtained using Electron spay ionization (ESI) technique and as TOF mass analyzer. New compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR, and HRMS data. The glassware's to be used in reaction were thoroughly washed and dried in an oven and the experiments were carried out with required precautions. All the reagents are obtained from the commercial sources and were used as received. Reactions were monitored by TLC, which was performed with 0.2 mm Merck pre-coated silica gel 60 F254 Aluminium sheets. TLC plates were visualized with UV light, ^{1}H and ^{13}C spectra were recorded on Bruker Avance 400 MHz and 100 MHz NMR spectrometer in $CDCl_3$ with residual undeuterated solvent ($CDCl_3$: 7.26/7.00) using Me_3SiCl as an internal standard. Chemical shifts (δ) are given in ppm and *J* values are given in Hz, pattern was designated as s, singlet; bs, broad singlet; d, doublet; dd, doublet of doublet; dt, triplet of doublet; t, triplet; m, multiplet.

1. EXPERIMENTATION SECTION

1.1 Preparation of substituted α-oxocarboxylic acids

All submitted α- oxoacid were synthesized from oxidation of corresponding methyl ketones with SeO_2 as reported in the literature.[1]

2.2 General procedure for the synthesis of potassium salts of the α-oxocarboxylic acids

Following a literature procedure, a solution of potassium tert-butoxide (1 mmol) in ethanol (1 mL) was added drop by drop to a solution of α-oxocarboxylic acids (1 mmol) in ethanol (1 mL) over 30 minutes. After complete addition, the reaction mixture was stirred for another 2 h at room temperature. A gradual formation of a precipitate was observed. The resulting solid was collected by filtration, washed with ethanol (2 x 10.0 mL), diethyl ether (10.0 mL) respectively, transferred to a round-bottomed flask and dried it under vacuum to give corresponding potassium salts of α-oxocarboxylic acids.

2.3 General procedure for the preparation of 2-Aryl Quinazoline

2.3.1 Synthesis of 2-Aryl Quinazoline from salt of *α*-oxocarboxylic acid and Amine (3a)

2-aminobenzylamine (0.3 mmol), salt of α-oxocarboxylic acid (1.2 equiv) and potassium persulphate (3 equiv) were dissolved in 2 mL of CH_3CN in an oven dried seal tube and stirred the reaction at 80 ^oC for 12 h. After completion of reaction, water (20 mL) was added and layers were separated. The organic layer was extracted with ethyl acetate (3 x 20 mL) and dried over sodium sulphate. Removal of the solvent under vacuum afforded the crude product, which was purified by column chromatography using hexane/ethyl acetate mixture and was analyzed by ^1H NMR, ^{13}C NMR gave the corresponding pale yellow cyclic product (**92%).**

2.4 General procedure for the preparation of N-(2-aminobenzyl)benzamide

2-aminobenzylamine (0.3 mmol), triethylamine (2 equiv) and Benzoyl chloride (2 equiv) were dissolved in 2Ml of DCM in an oven dried round bottomed flask maintained at 0 ^oC. The reaction was allowed to run for 12 h at room temperature. After completion of reaction, water (20 mL) was added and layers were separated. The organic layer was extracted with ethyl acetate (3 x 20 mL) and dried over sodium sulphate. Removal of the solvent under vacuum afforded the crude product, which was purified by column chromatography using hexane/ethyl acetate mixture and was analyzed by ^1H NMR, ^{13}C NMR gave the corresponding off white solid product (**92%).**

2.5. General Procedure for the Synthesis of 2H-1,2,4-benzothiadiazine-1,1-dioxide In an oven-dried sealed tube, 2-aminobenzenesulphonamide (51.6 mg, 0.30 mmol), phenylglyoxylate (67.7 mg, 0.36 mmol) and potassium persulphate (243.27 mg, 0.90 mmol) were dissolved in CH_3CN (2 mL) and the mixture was heated at 80 ℃ for 16 h. After completion of the reaction, water (20 mL) was added and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 x 20 mL) and the combined organic layer was dried over Na_2SO_4. Removal of the solvent with rotary evaporator afforded the crude product, which upon purification by chromatography using hexane/ethyl acetate (3:7) afforded a dark yellow solid.

3 CHARACTERIZATION DATA

2-Phenylquinazoline (**3a**):[2] (89% yield); white solid; mp 97-98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.62-8.60 (dd, *J* = 7.9, 1.6 Hz, 2H), 8.10-8.08 (d, *J* = 8.5 Hz, 1H), 7.94 – 7.91 (m, 2H), 7.61-7.60 (t, *J* = 7.5 Hz, 1H), 7.60 – 7.56 (m, 3H). ^{13}C NMR (500 MHz, $CDCl_3$-d) δ 160.61, 134.24, 130.71, 128.70, 127.31, 77.36, 77.10, 76.85.

2-(o-Tolyl)quinazoline (**3b**):[3] (83% yield); a pale yellow solid; mp 43-45 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.50 (s, 1H), 8.10-8.08 (d, *J* = 8.5 Hz, 1H), 7.99-7.86 (m, 3H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.37-7.32 (dt, *J* = 13.1,6.4 Hz, 3H), 2.60 (s, 3H).

2-(3-Methoxyphenyl)quinazoline (**3c**):[4](72% yield); a pale yellow solid; mp 119-122°C ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.49 (s, 1H), 8.26-8.24 (d, J = 7.72 Hz, 1H), 8.22 (d, J = 2.3 Hz,1H), 8.13-8.11 (d, *J* = 8.44, 1H), 7.96-7.91 (m, 2H), 7.66-7.62 (t, *J* = 7.5 Hz, 1H), 7.49-7.46 (t, J = 7.9 Hz, 1H), 7.11-7.08 (dd, J = 8.12, 2.4 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.28,159.86, 159.46, 150.17, 138.93, 133.52, 129.06, 128.11, 126.63,123.09, 120.60, 116.68, 112.48,54.89, 31.36,29.13, 22.12.

2-(p-Tolyl)quinazoline (**3d**):[5] (88% yield); a yellow solid; mp 97-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48 (s, 1H), 8.54-8.52 (d, J = 8.12 Hz, 2H), 8.10-8.09 (d, J = 8.44 Hz, 1H), 7.97-7.87 (m, 2H), 7.64-7.62 (t, *J* = 7.44 Hz, 2H), 7.38-7.36 (d, *J* = 8.0, 1H), 2.47 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 161.15,160.46, 150.80, 140.89, 134.07, 129.44, 128.54, 127.10,123.52,21.55.

2-(4-Chlorophenyl)quinazoline (**3e**):[5] (52.5 mg, 80% yield); a yellow solid; mp 136-138 °C; ^{1}H NMR (400 MHz, CDCl3): δ 9.48 (s, 1H), 8.61-8.59 (d, *J* = 8.52 Hz, 2H), 8.11-8.09 (d, J = 8.44 Hz, 1H), 7.96-7.93 (m, 2H), 7.68-7.64 (t, *J* = 7.5 Hz, 1H), 7.54-7.52 (d, *J* = 8.5 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.57, 136.85, 134.30, 129.90, 128.85, 128.60, 127.50, 127.18, 123.63, 77.34, 77.03, 76.71.

2-(4-Fluorophenyl)quinazoline (**3f**):[5] (82% yield); a pale yellow solid; mp 131-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.44 (s, 1H), 8.63-8.61 (m, 2H), 8.07-8.06 (d, *J* = 8.44 Hz, 1H), 7.94-7.88 (m, 2H), 7.61-7.60 (t, *J* = 7.4 Hz, 1H), 7.20-7.18 (t, J = 8.76 Hz, 2H).

2-(2-Bromophenyl)quinazoline (**3g**):[6] (72% yield); a yellow solid; mp 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.56 (s, 1H), 8.18-8.15 (d, *J* = 8.5 Hz, 1H), 8.06-7.97 (m, 2H), 7.83-7.77(m,3H), 7.51-7.47 (dd, J = 7.5, 6.9 Hz,1H), 7.37-7.35 (dt, *J* = 15, 1.64 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.82 , 160.28, 150.27, 140.16, 134.47, 133.72, 131.67, 130.44 , 128.64, 128.12, 127.51, 127.19, 123.31, 121.91, 77.36, 77.04, 76.72, 29.72, 14.15.

2-(Naphthalen-2-yl)quinazoline (**3h**):[7] (82% yield); a pale yellow solid; mp 120-121°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (s, 1H), 9.18 (s, 1H), 8.77-8.75 (dd, *J* = 8.64 Hz, 1.4 Hz, 1H), 8.18-8.16 (d, *J* = 8.40 Hz, 1H), 8.10-8.06 (m, 1H), 8.04-8.02 (d, *J* = 6.6 Hz, 1H), 7.98-7.92 (dd, *J* = 15.3, 7.7 Hz, 3H), 7.69-7.65 (t, *J* = 7.5 Hz, 1H), 7.60-7.55 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 160.56, 134.24, 133.42, 129.29, 128.97, 128.50, 127.74, 127.59 – 127.03, 126.26, 125.41, 77.34 , 77.03, 76.71.

2-(Thiophen-2-yl)quinazoline (**3i**):[7] (91% yield); a yellow solid; mp 108–110 °C; ^{1}H NMR (400 MHz, CDCl3): δ 9.38 (s, 1H), 8.18-8.17 (d, *J* = 3.6 Hz, 1H), 8.05-8.02 (d, 8.80 Hz, 1H), 7.92–7.89 (m, 2H), 7.62-7.58 (t, *J* = 7.59 Hz, 1H), 7.55-7.54 (d, *J* = 5 Hz, 1H), 7.23-7.21 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.55, 157.86, 150.63,143.84,134.38,129.96, 129.23, 128.40, 128.20, 127.29, 127.02, 123.38, 77.35, 77.04, 76.72.

2-(Furan-2-yl)quinazoline (**3j**):[8] (85% yield); a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.38 (s, 1H), 8.11-8.09 (d, *J* = 8.9 Hz, 1H), 7.93-7.88 (m, 2H), 7.69 (d, *J* = 0.8 Hz, 1H), 7.63-7.58 (m, 1H), 7.46 (d, *J* = 3.5 Hz, 1H), 6.62 (dd, J = 3.4 Hz, 1.8 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$-d) δ 134.67, 128.49, 127.41, 114.23, 112.45, 77.33, 77.10, 76.85.

3-Phenyl-2H-benzo[e][1,2,4]thiadiazine 1,1-dioxide (**5a**):[6] (55% yield); a dark yellow solid; mp. 308-310 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.2 (s, 1H), 8.06-8.04 (d, J = 7.32, 2H), 7.88-7.86 (d, J = 7.88, 1H), 7.77-7.69 (m, 2H), 7.65-7.62 (m, 3H), 7.53-7.49 (t, J = 7.28 Hz, 1H).

3-(3-Methoxyphenyl)-2H-benzo[e][1,2,4]thiadiazine 1,1-dioxide (**5b**):[6] (48% yield); a dark yellow solid; ; mp. 323-325 °C ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.13 (s, 1H), 7.84-7.82 (d, *J* = 7.92, 1H), 7.77-7.73 (m, 1H), 7.62-7.57 (m, 2H), 7.55-7.48 (m, 3H), 7.26-7.23 (m, 1H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 133.6, 123.87, 121.00, 119.07, 113.87, 41.21, 40.08, 39.52.

3-(4-Bromophenyl)-2H-benzo[e][1,2,4]thiadiazine1,1-dioxide (**5c**):[6] (42% yield); a dark yellow solid; mp 236-238 °C ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.21 (s, 1H), 7.97-7.96 (d, J = 8.56, 2H), 7.84-7.81 (m, 3H), 7.73-7.69 (t, J = 7.7 Hz, 1H), 7.60-7.58 (m, 1H), 7.49-7.48 (t, J = 7.48 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 123.74, 122.65, 109.4, 107.68, 72.78, 72.28, 72.09, 71.70.

Tert-butyl 2-benzamidobenzylcarbamate (**24**) White solid; ^{1}H NMR (400 MHz, DMSO): *δ* 10.17 (s, 1H), 8.02-8.00 (d, *J* = 7.44 Hz, 2H), 7.62-7.59 (m, 1H), 7.55-7.45 (m, 4H), 7.31=7.28 (t, *J* = 7.24, 7.12 Hz, 2H), 7.25-7.23 (d, *J*= 7.76,1H), 6.0 (d, 2H), 1.37 (s, 9H); 13C NMR (100 MHz, DMSO): *δ* 165.9, 156.7, 135.9, 134.8, 132.1, 128.8, 1128.5**,** 128.1, 127.5, 126.3, 126.1,78.6, 28.6

N-phenylbenzamide (6)[9]: White solid; 1H NMR (400 MHz, $CDCl_3$): *δ* 7.8 (dd *J* = 7.9, 0.9 Hz, 2H), 7.83 (brs, 1H), 7.64 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.56 (tt, *J* = 7.3, 1.3 Hz, 1H), 7.50-7.46 (m, 2H), 7.40-7.35 (m, 2H), 7.15 (tt, *J* = 7.4, 1.0 Hz, 1H).

2-Phenylquinazolin-4(3H)-one(7)[9]: White solid (63 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H), 8.36 (d, *J* = 7.8 Hz, 1H), 8.29 (dd, *J* = 6.3, 2.8 Hz, 2H), 7.93 – 7.74 (m, 2H), 7.64 – 7.59 (m, 3H), 7.54 (d, *J* = 6.7 Hz, 1H).

2-Phenyl-1H-benzo[d]imidazole (8)[9]: White solid (23 mg, 40%);^{1}H NMR (400 MHz, DMSO) δ 12.59 (s, 1H), 8.31 (d, *J* = 6.7 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.53 (dd, *J* = 21.7, 6.7 Hz, 4H), 7.34 (t, *J* = 8.1 Hz, 2H).

2-Phenylbenzo[d]thiazole (9)[9]: White solid (47 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (ddd, *J* = 9.7, 5.0, 3.3 Hz, 3H), 7.94 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.56 – 7.49 (m, 4H), 7.45 – 7.39 (m, 1H).

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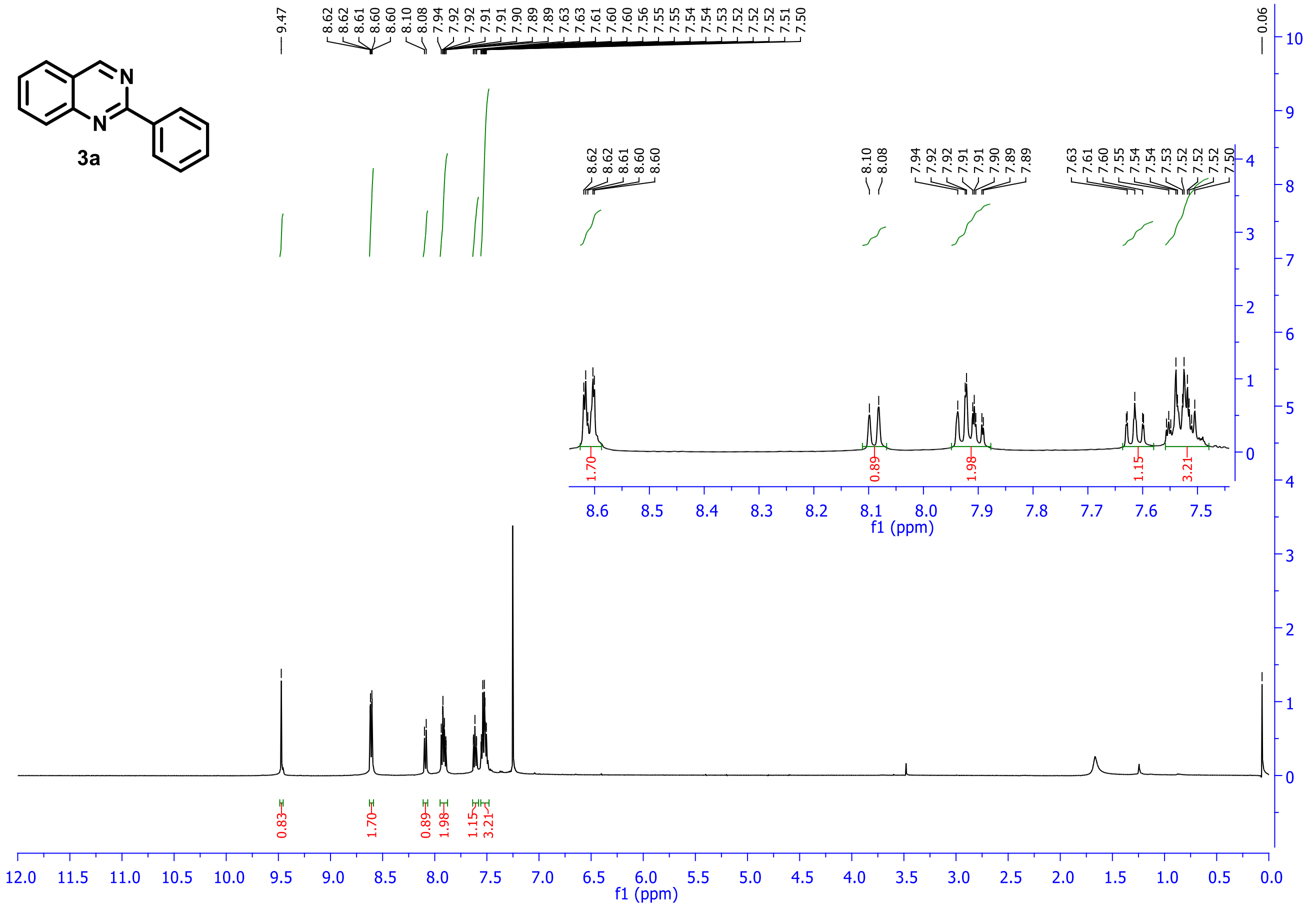
5.1 Copies of ^{1}H and ^{13}C NMR spectra



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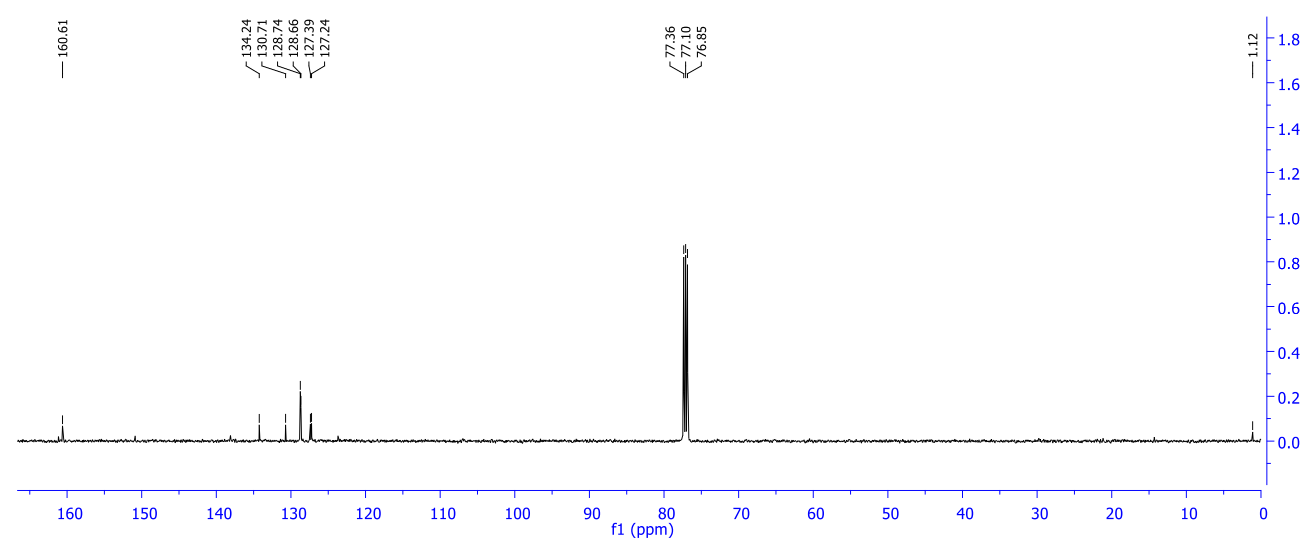

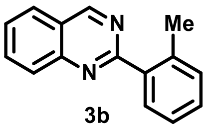
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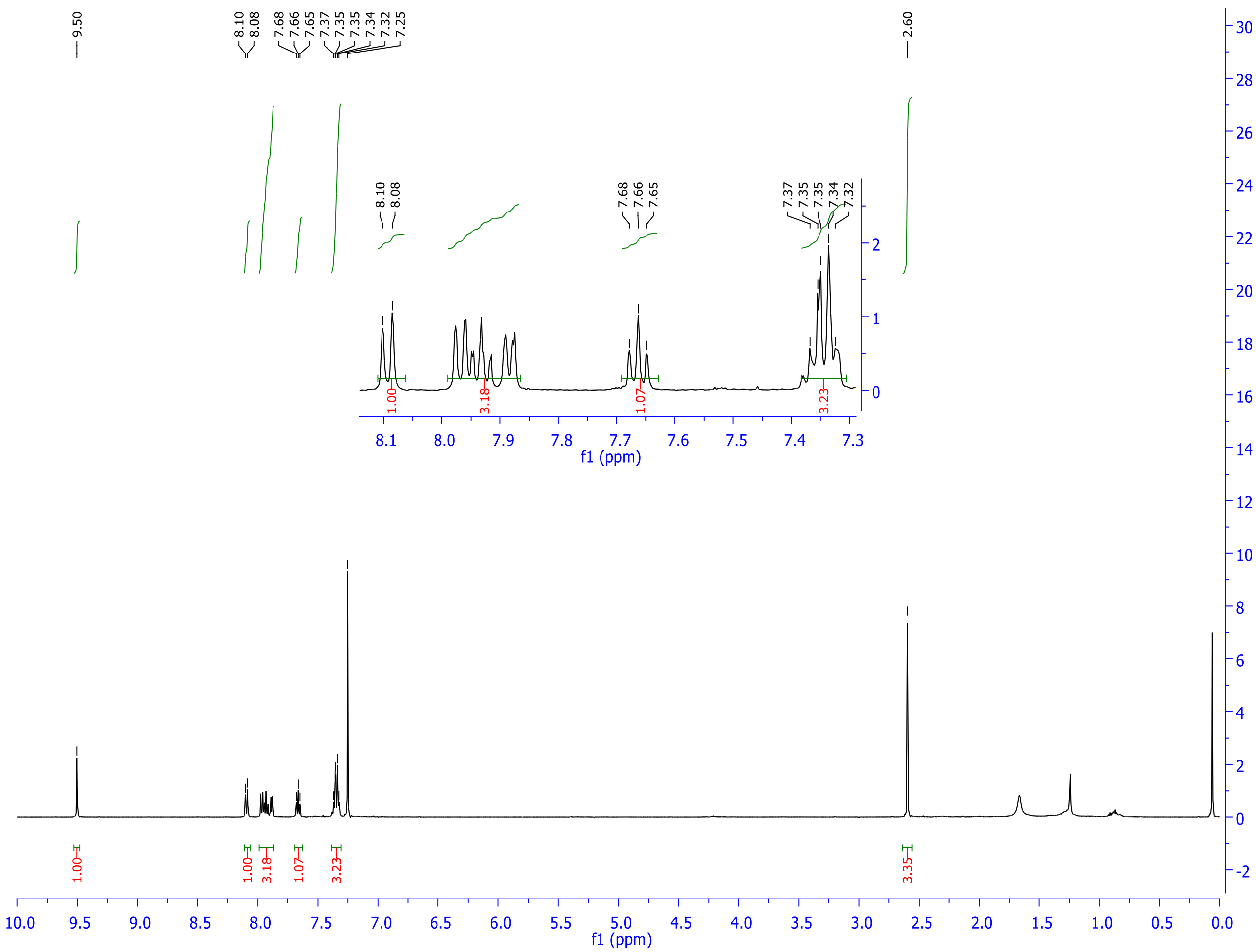
3b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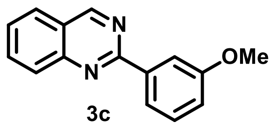

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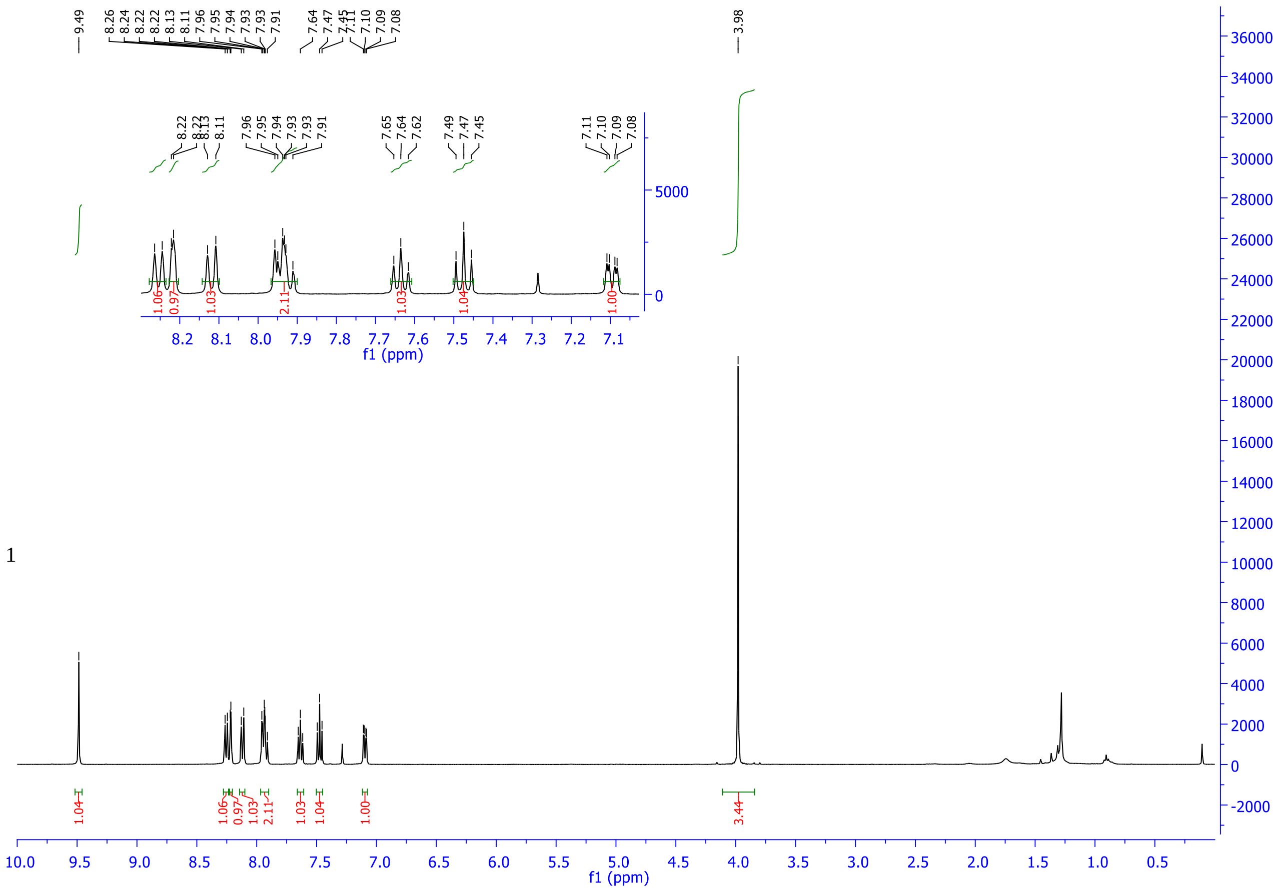

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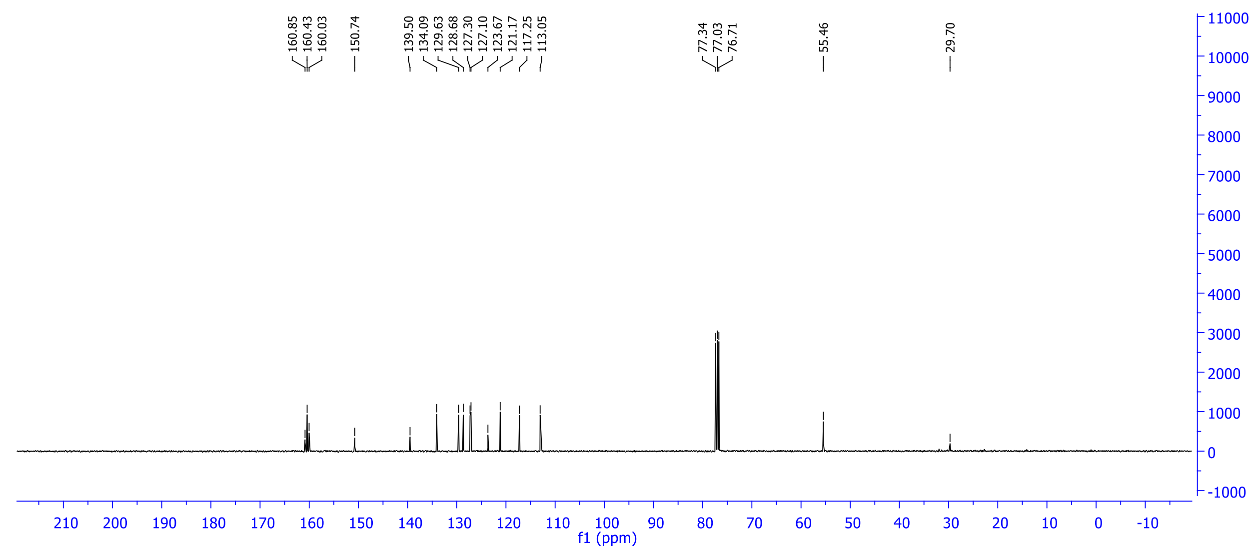

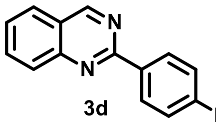

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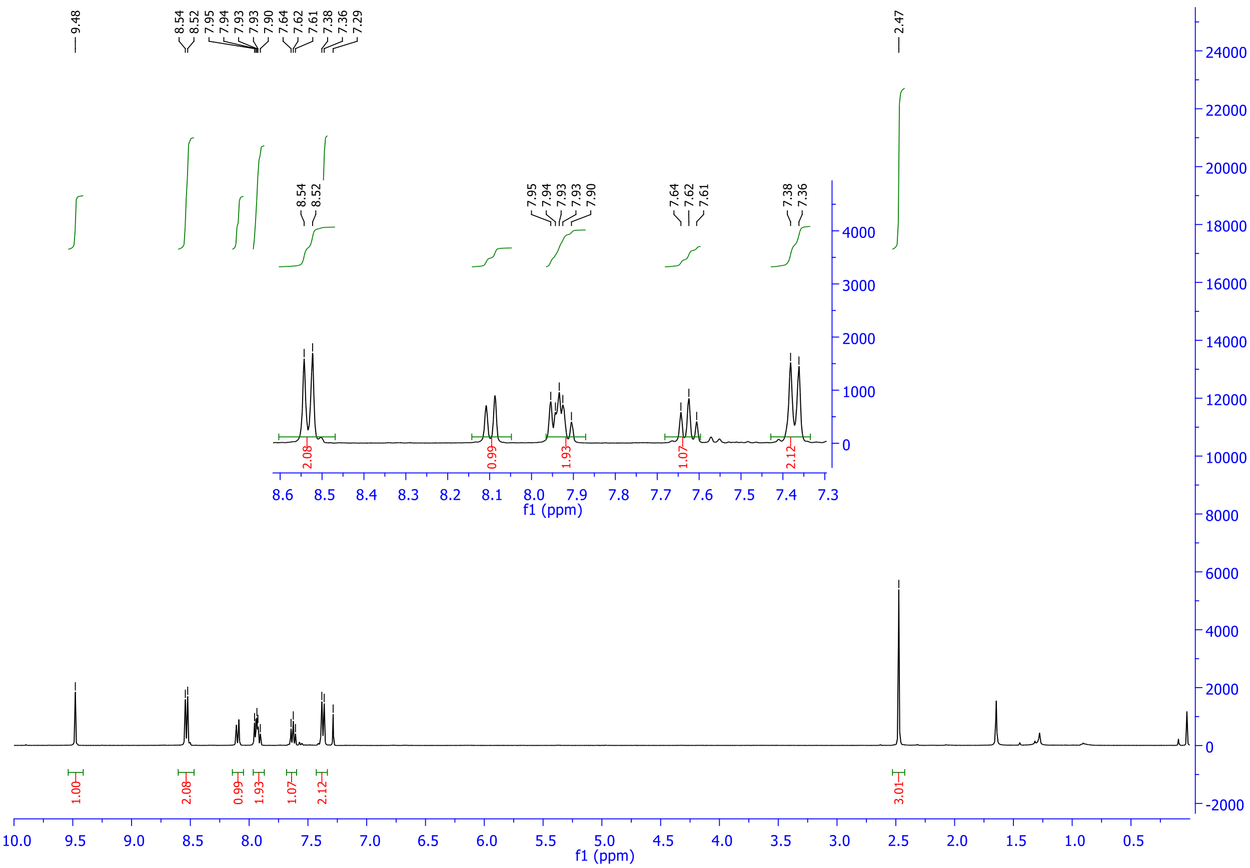

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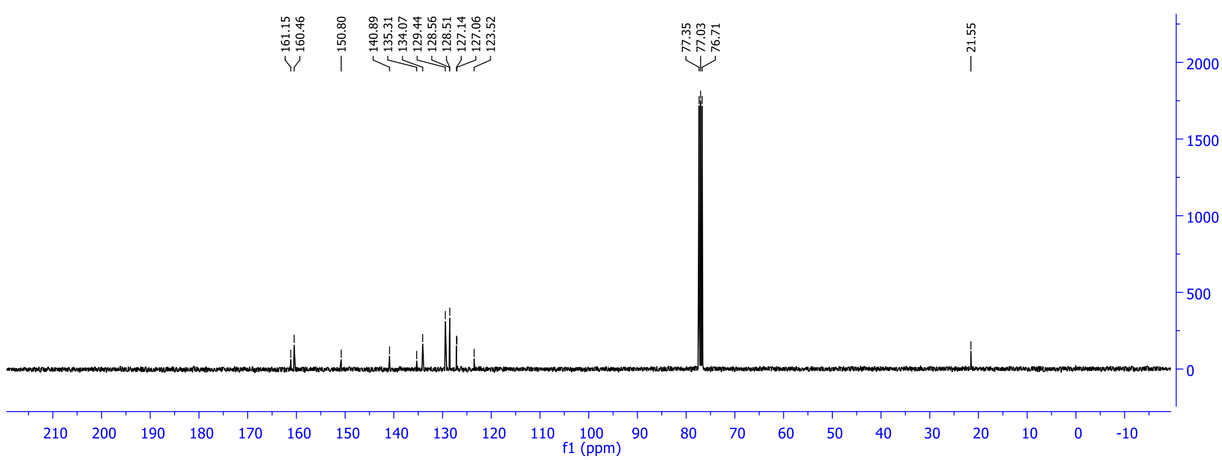

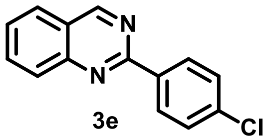

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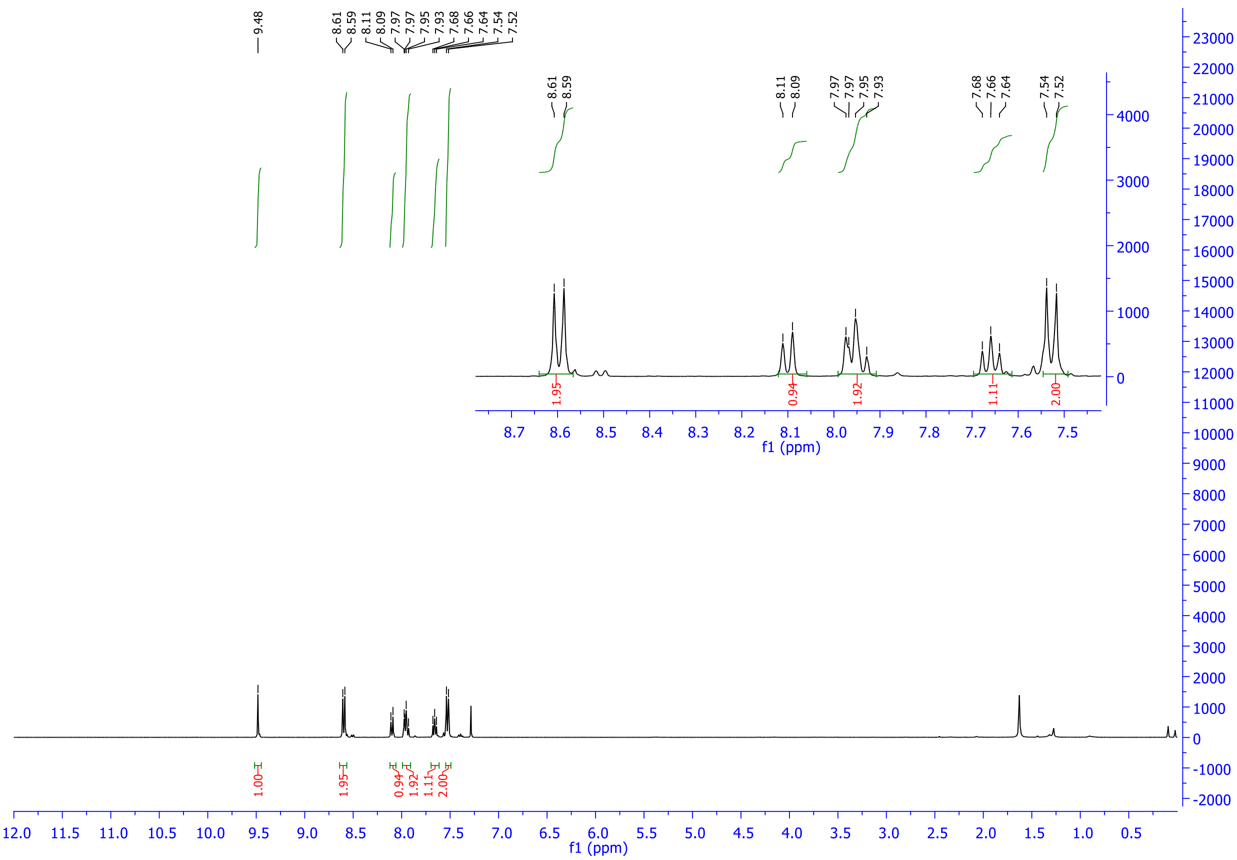

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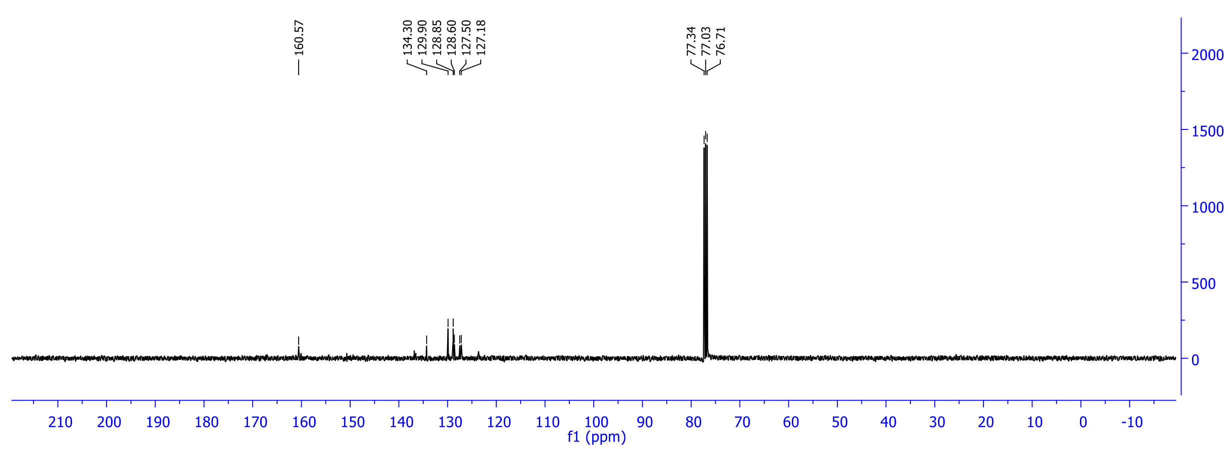

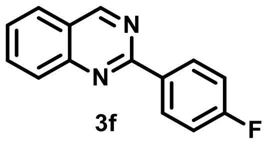

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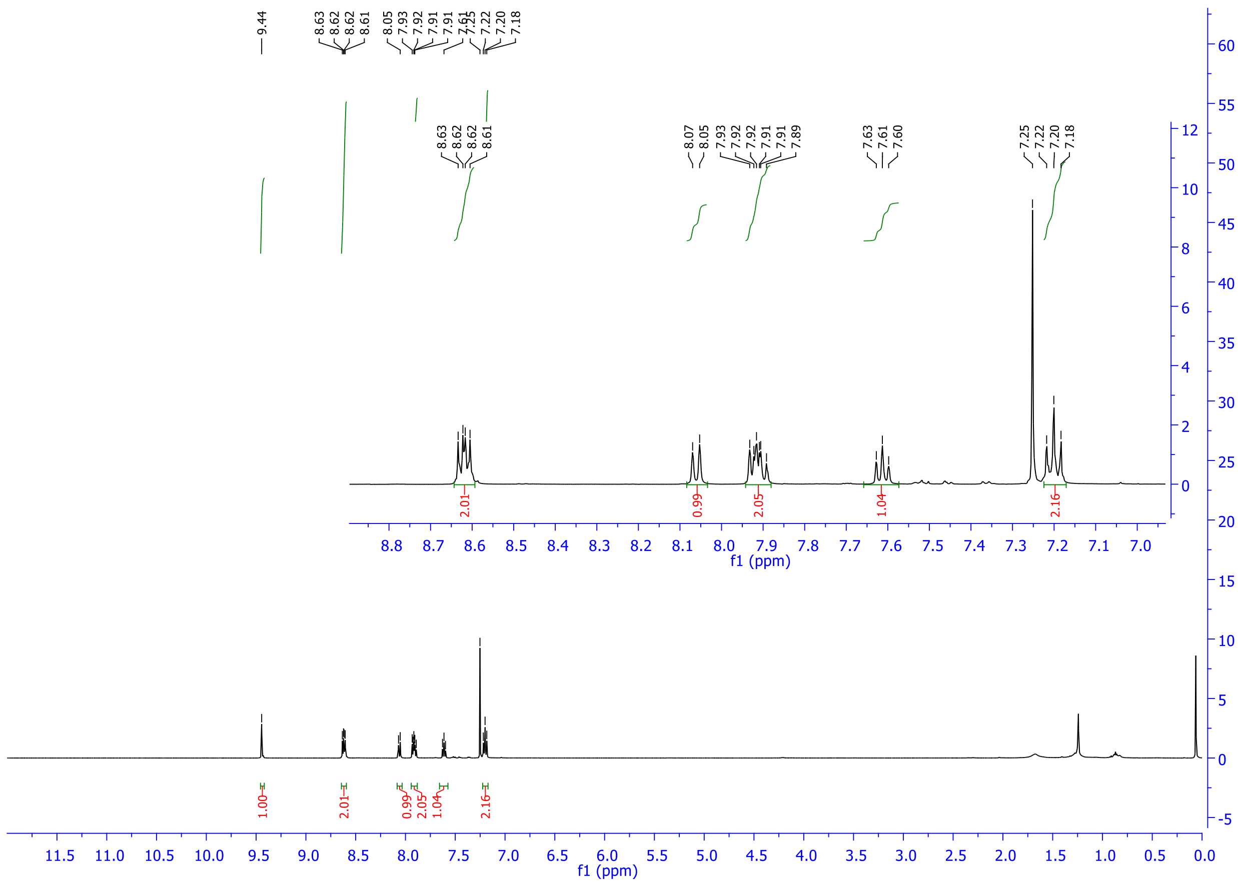

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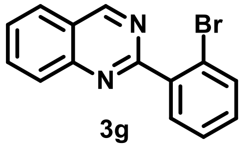

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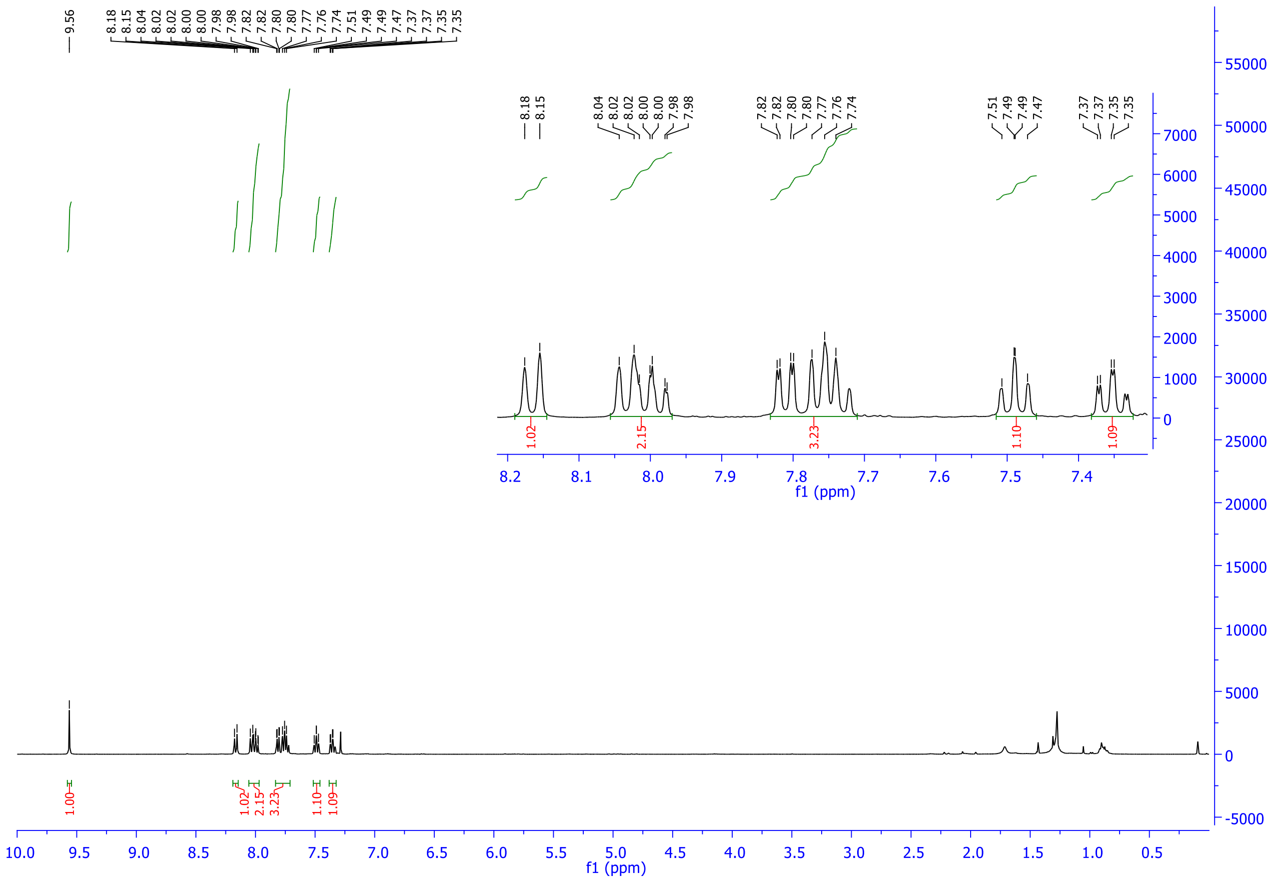

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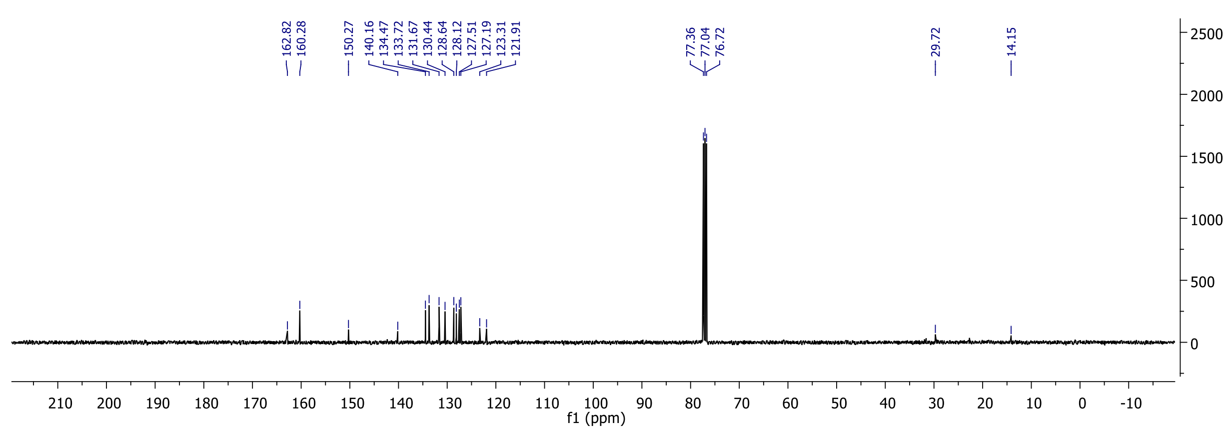

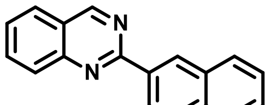

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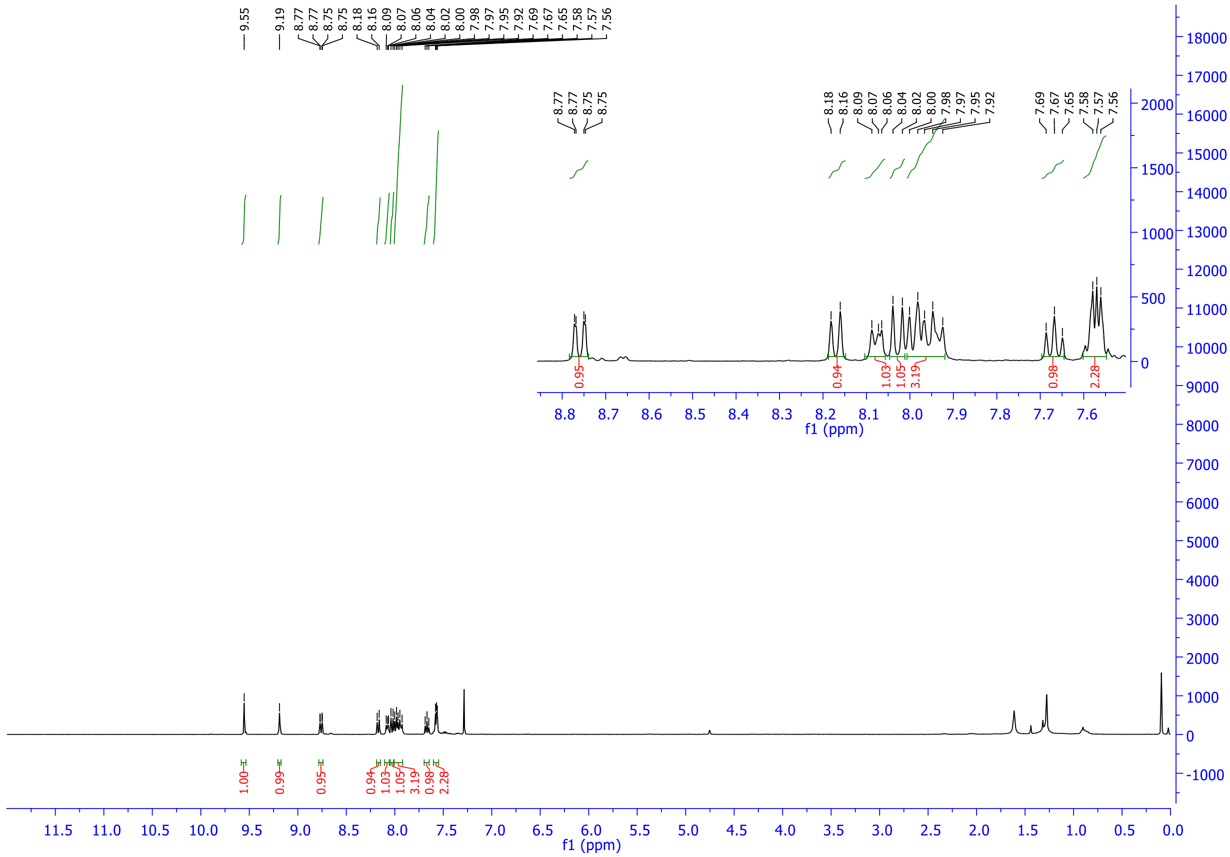

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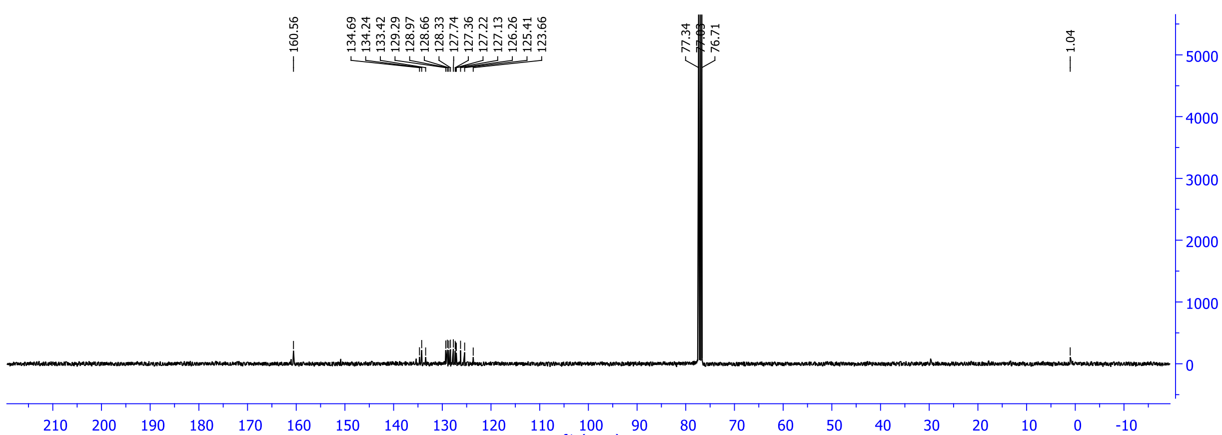

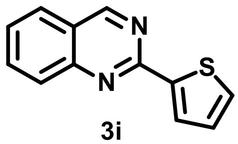

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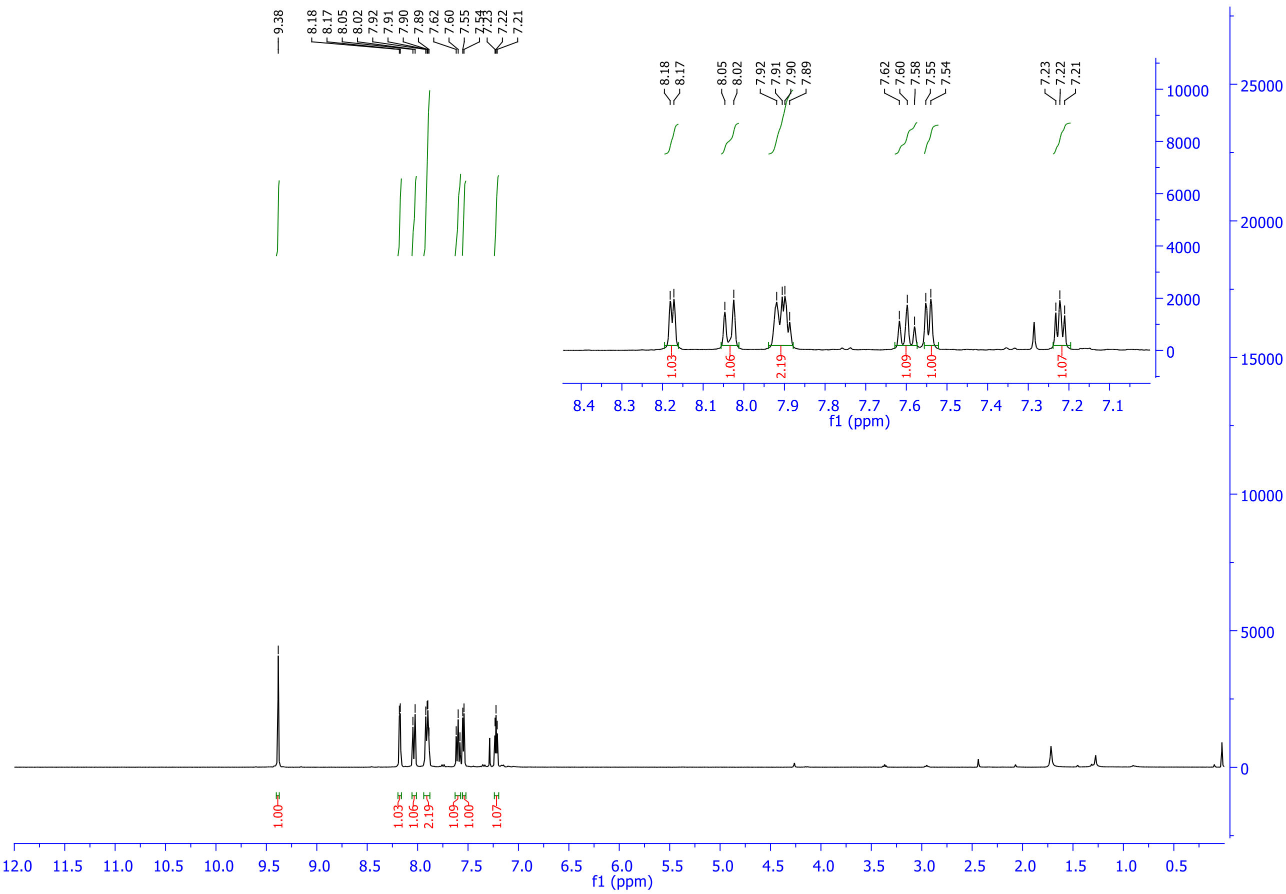

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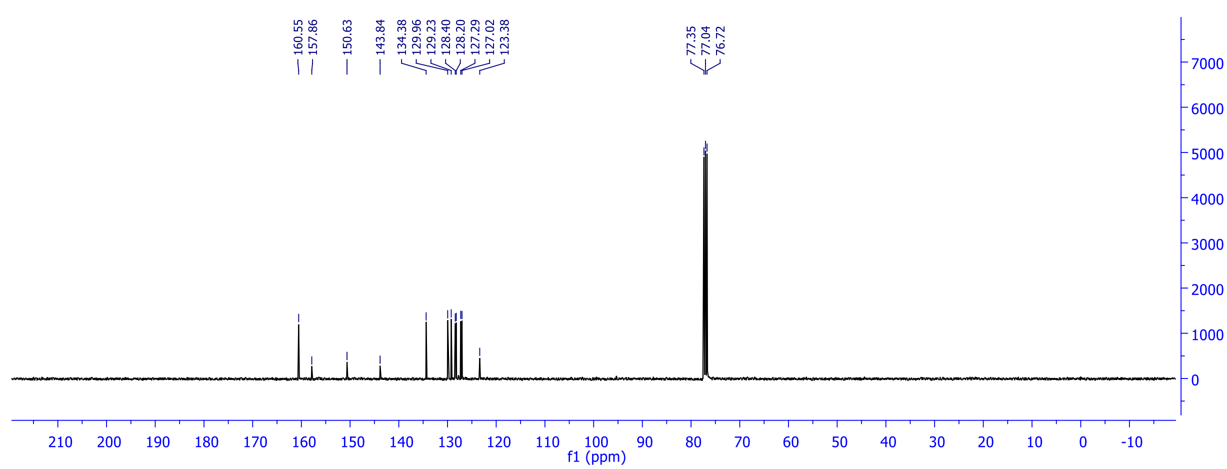

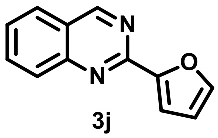

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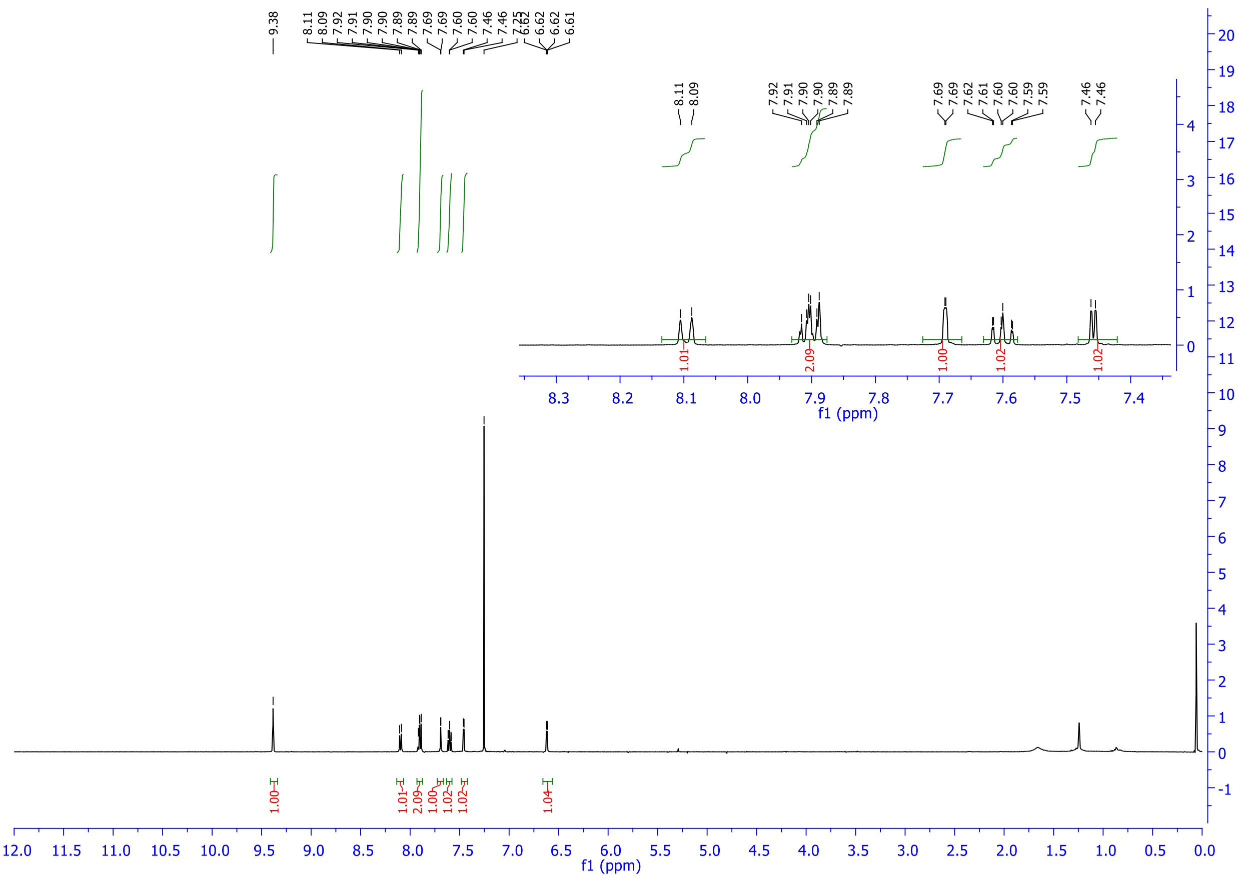
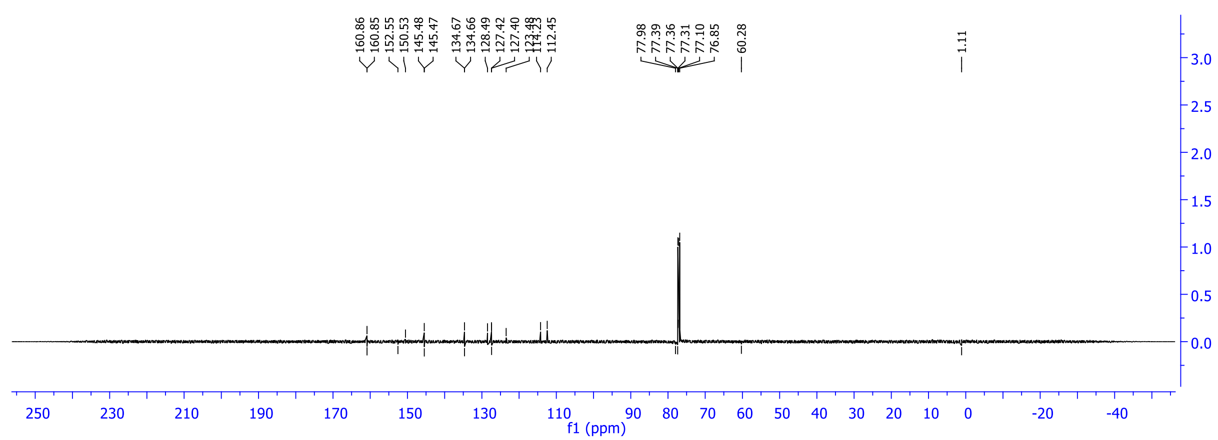
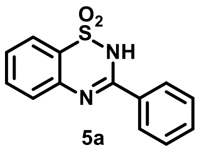
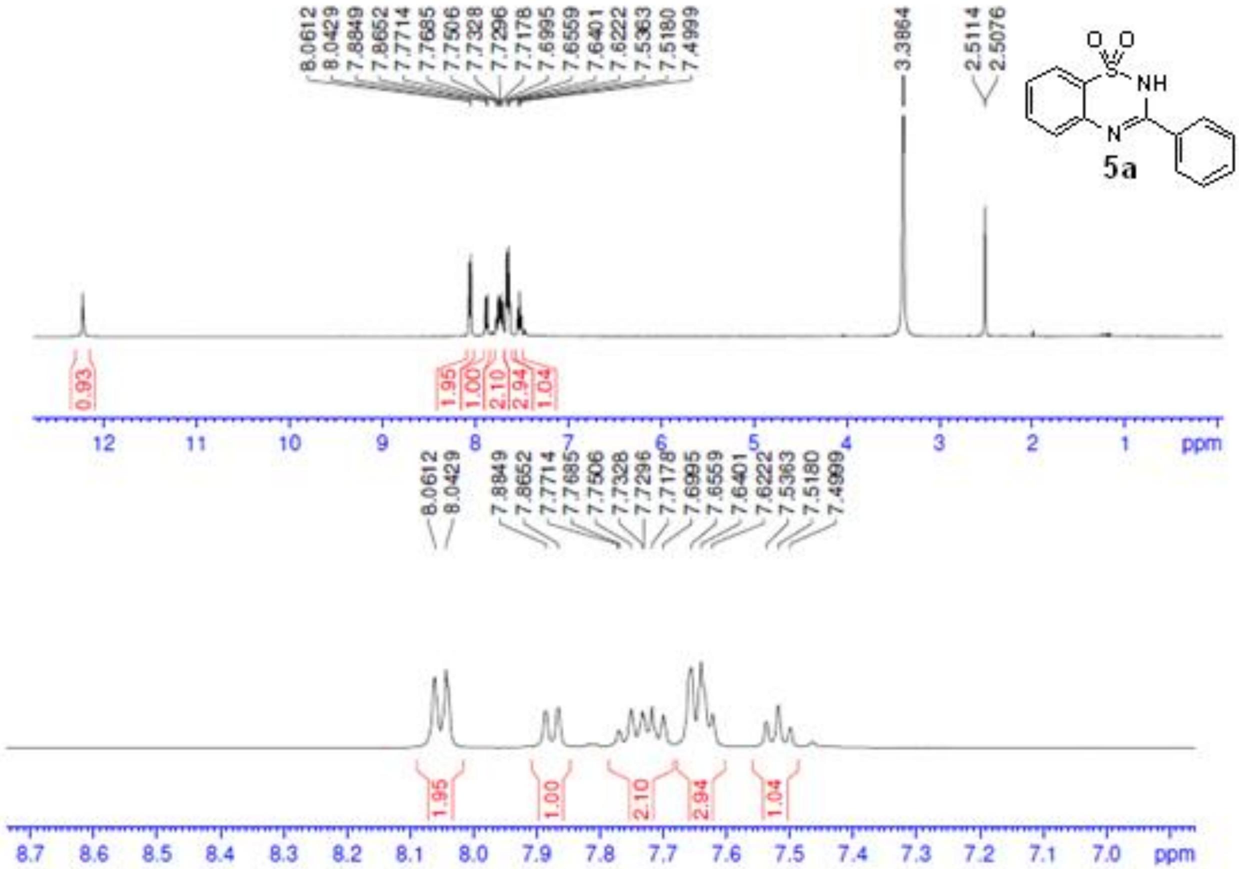


^{13}C Spectra




O2
S
NH
N

5a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7.7506
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7.7178
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7.6559
7.6401
7.6222
7.5363
7.5180
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5a
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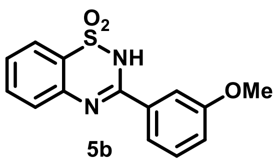
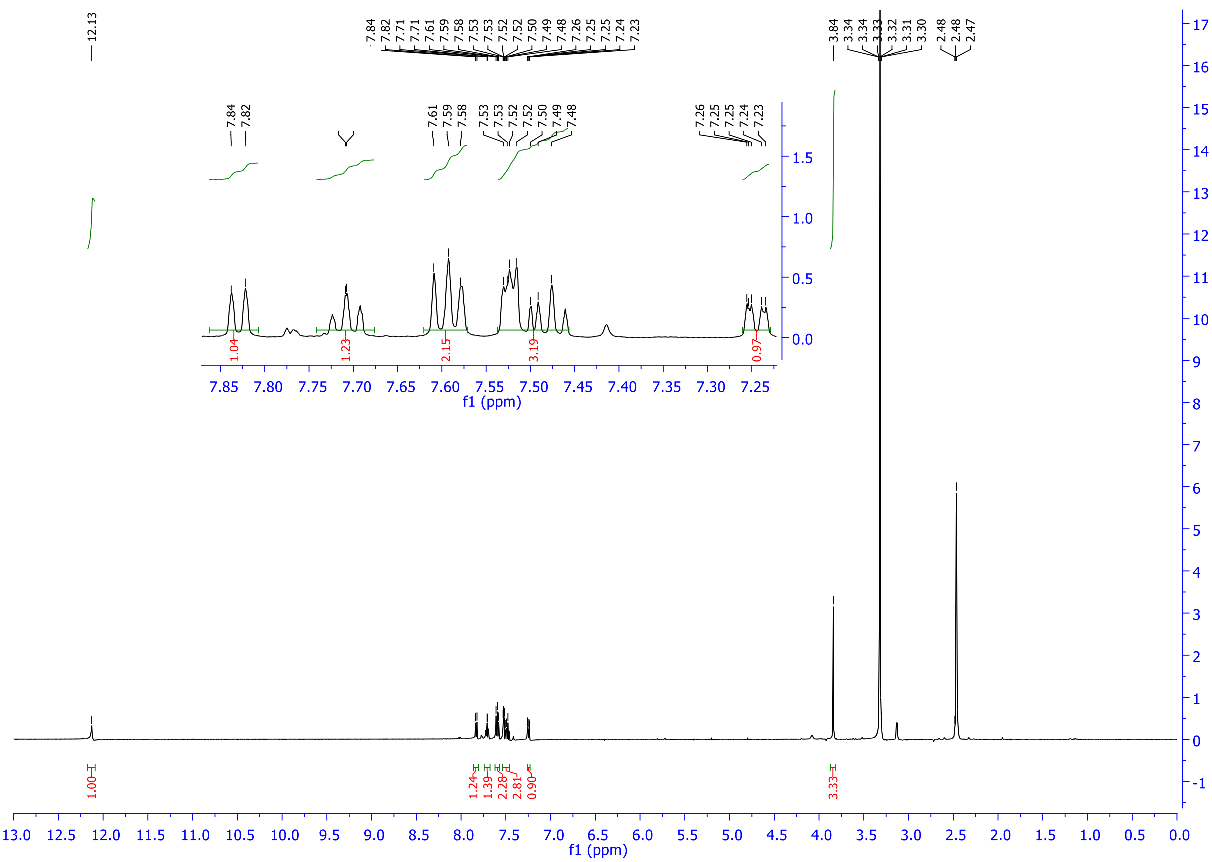
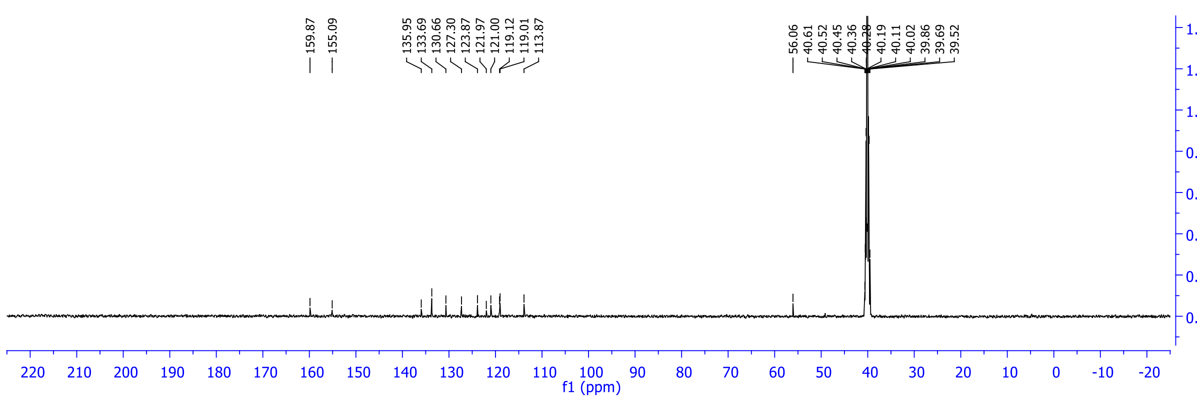
1.00
2.10
2.94
1.04
ppm

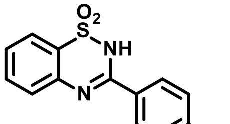


5b



^{13}C Spectra





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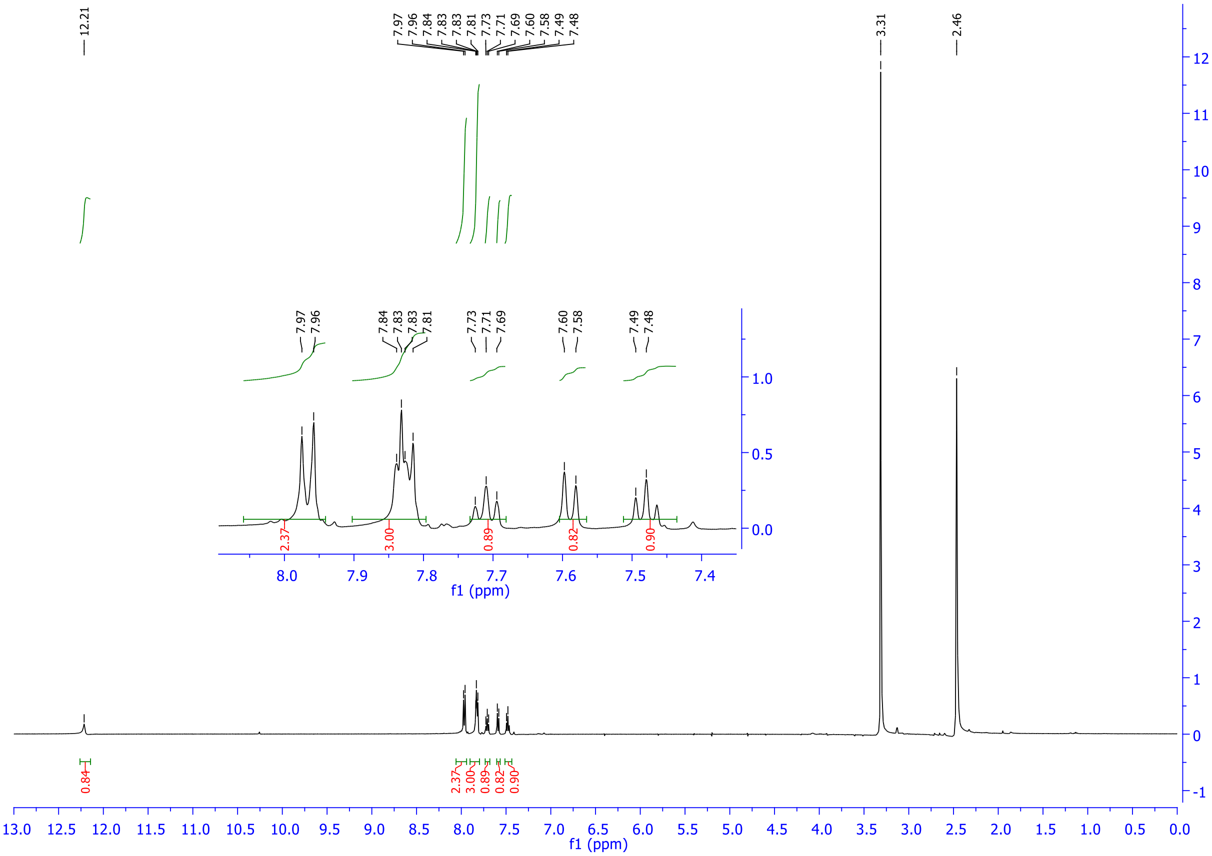

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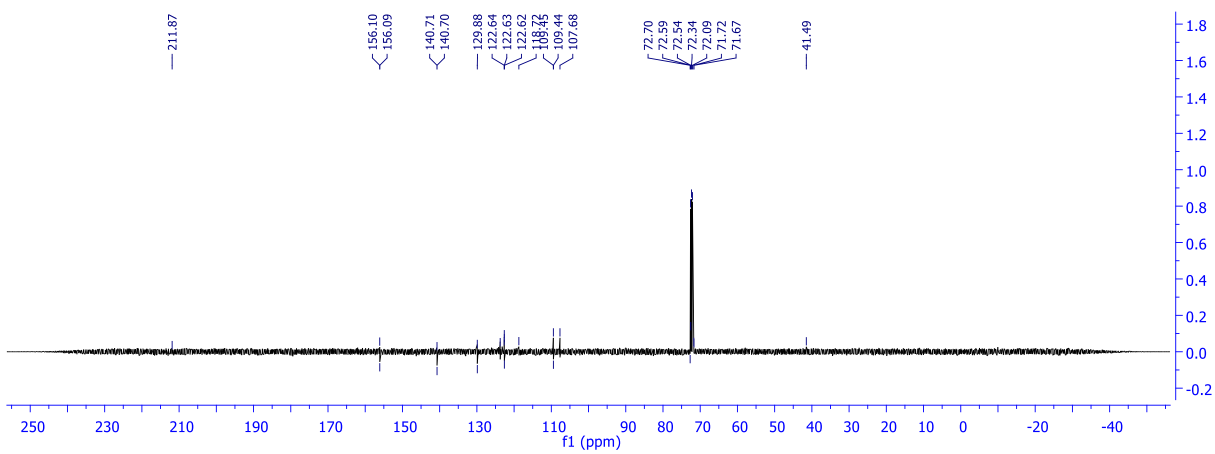

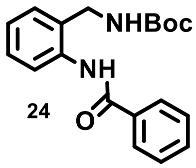

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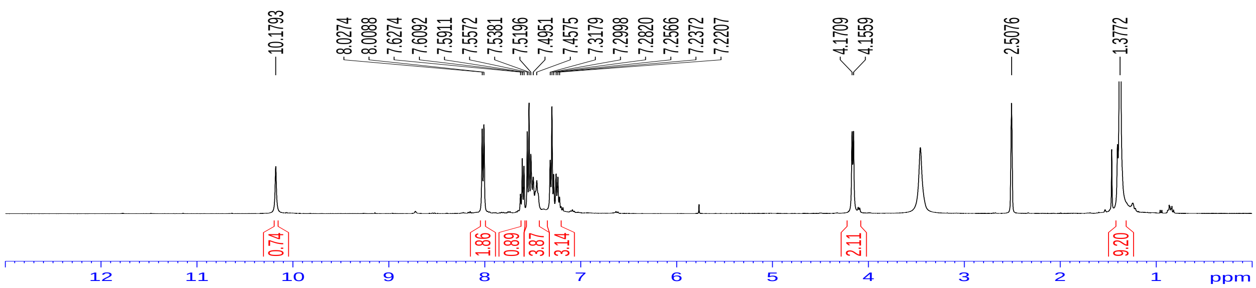
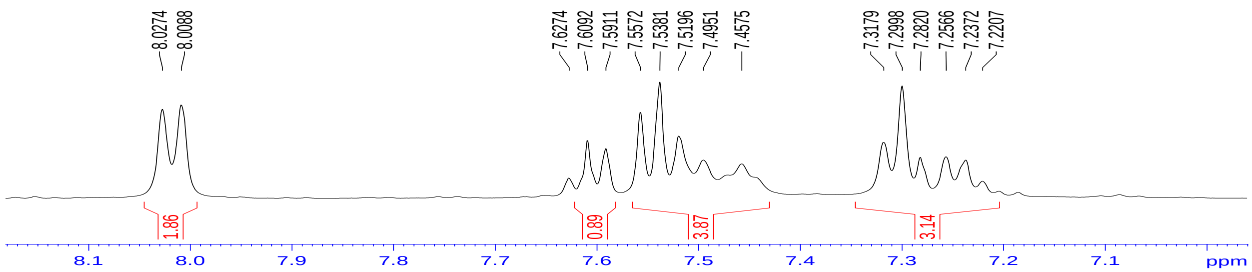
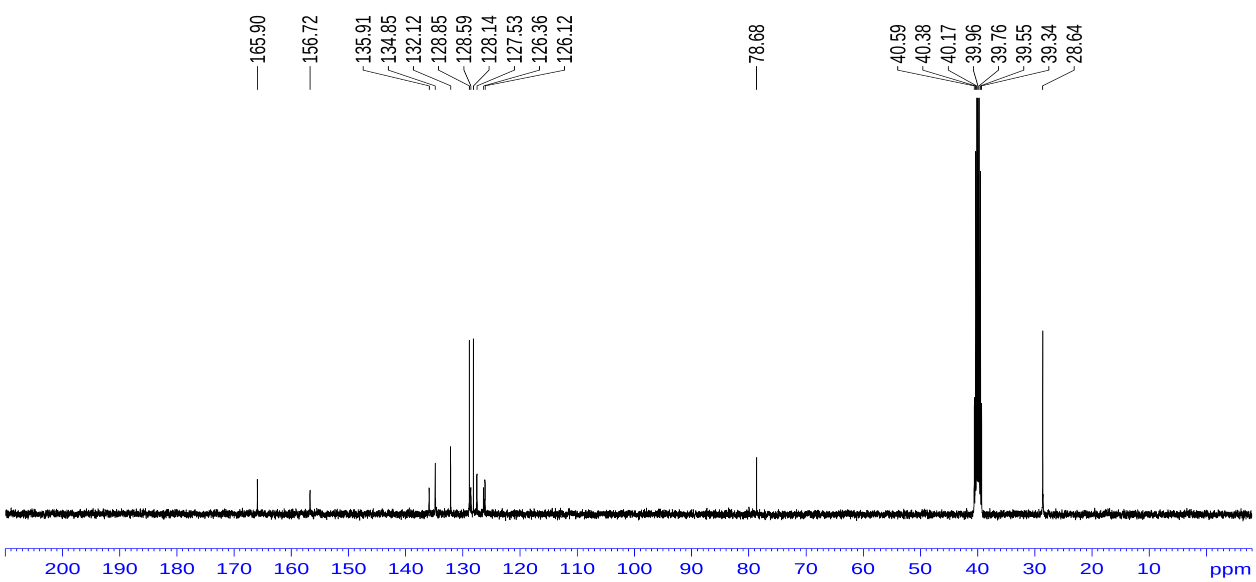
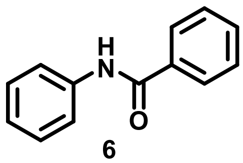


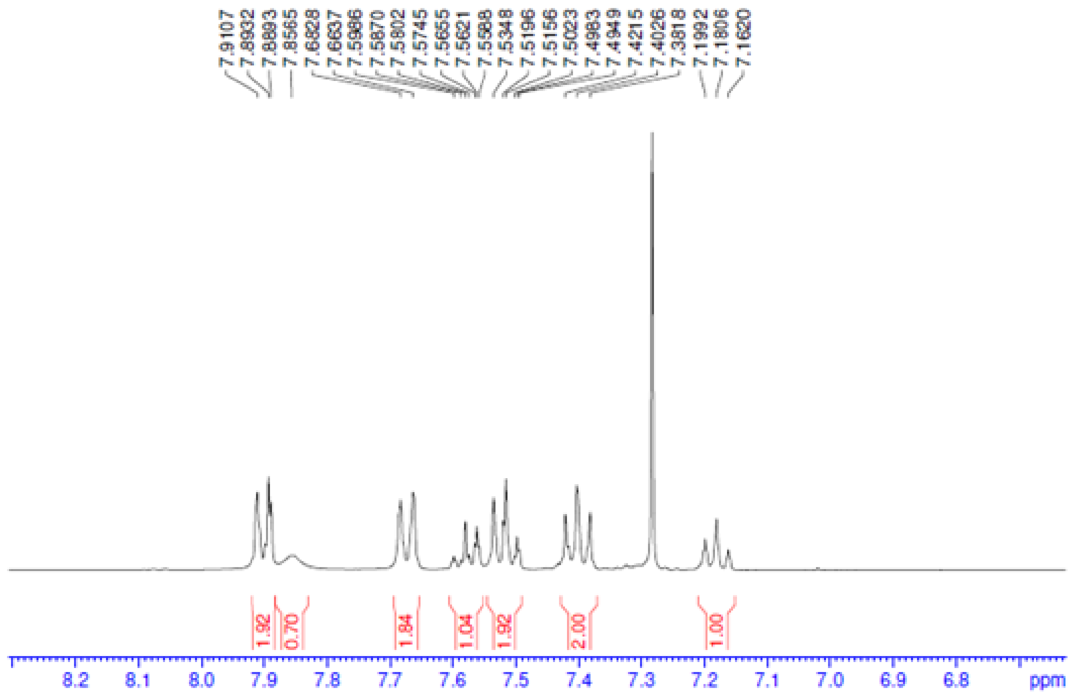


^{13}C Spectra





6



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7.5745
7.5655
7.5621
7.5588
7.5348
7.5196
7.5156
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7.4949
7.4215
7.4026
7.3818
7.1992
7.1806
7.1620
1.92
0.70
1.84
1.04
1.92
2.00
1.00
8.2
8.1
8.0
7.9
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7.6
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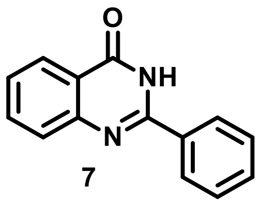
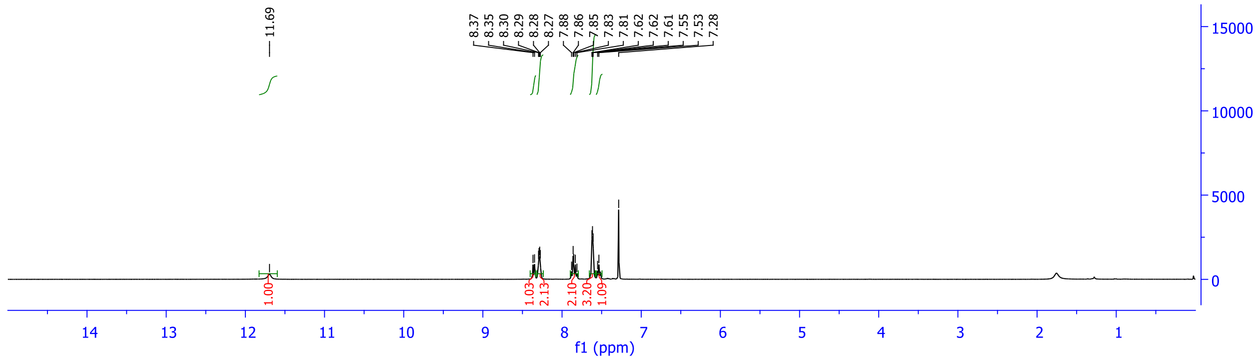
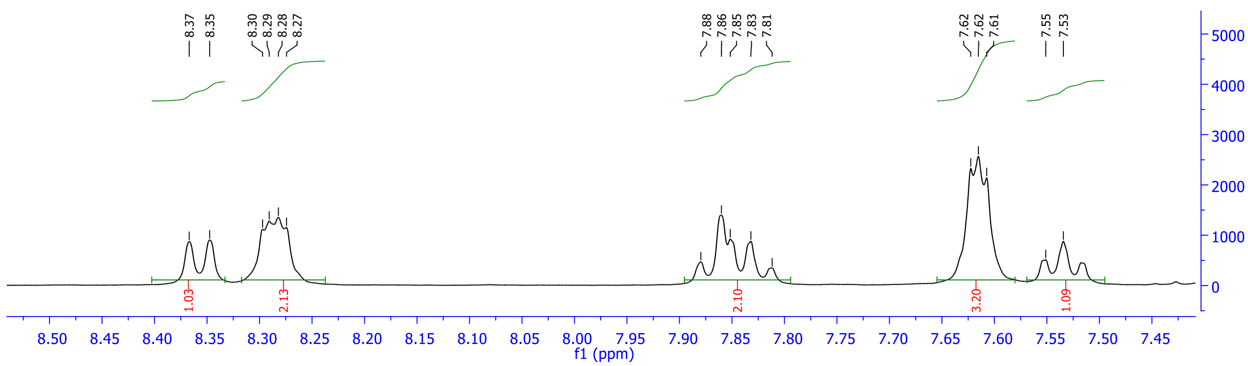
7.4
7.3
7.2
7.1
7.0
6.9
6.8
ppm

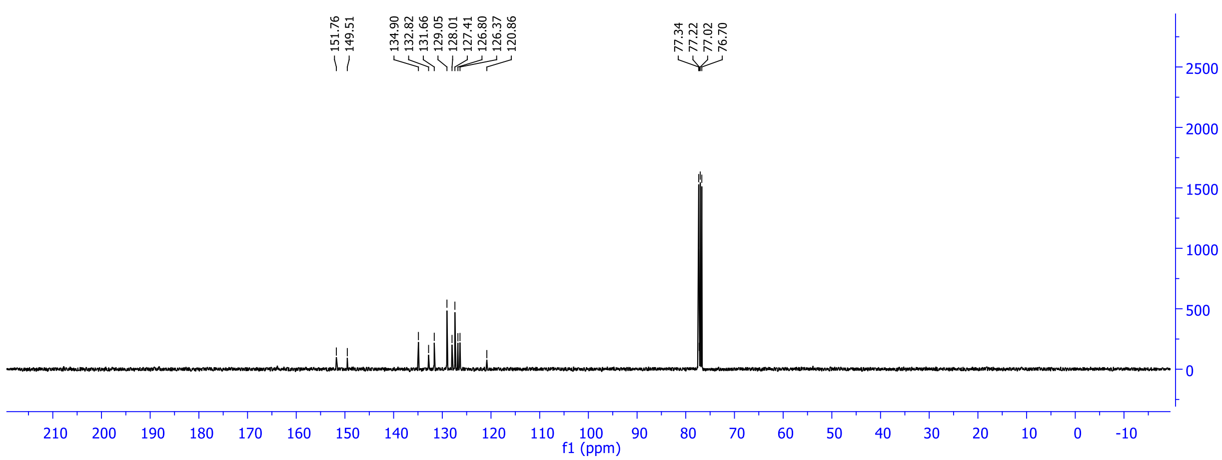


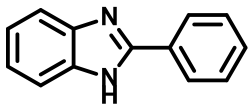
7





^{13}C Spectra





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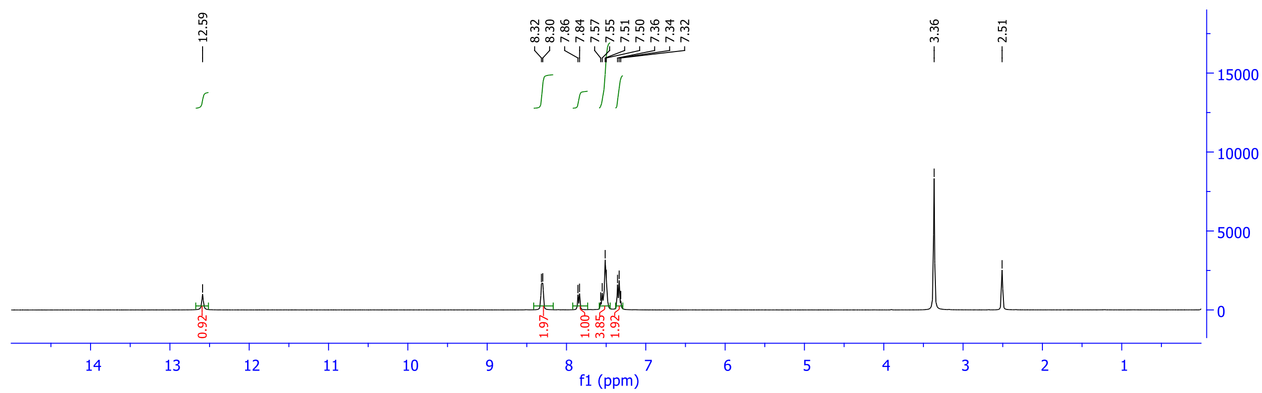

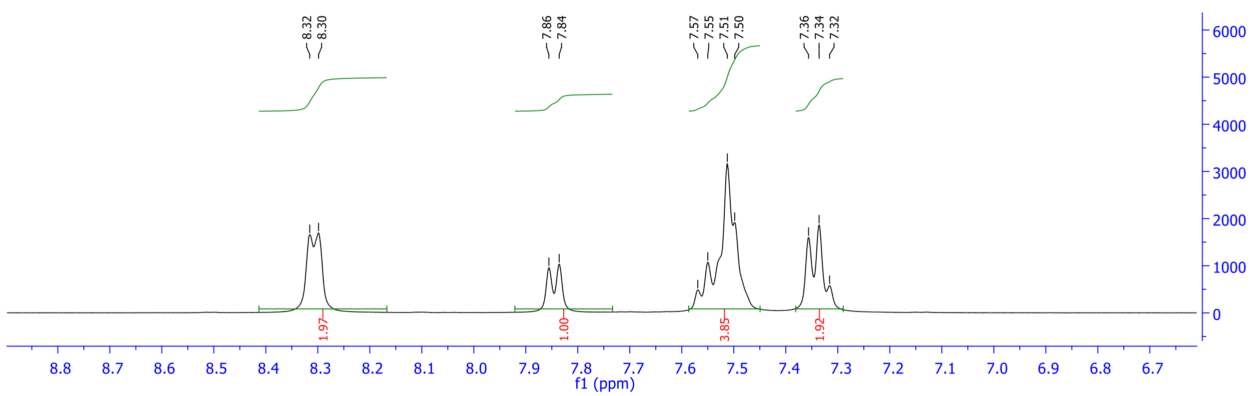

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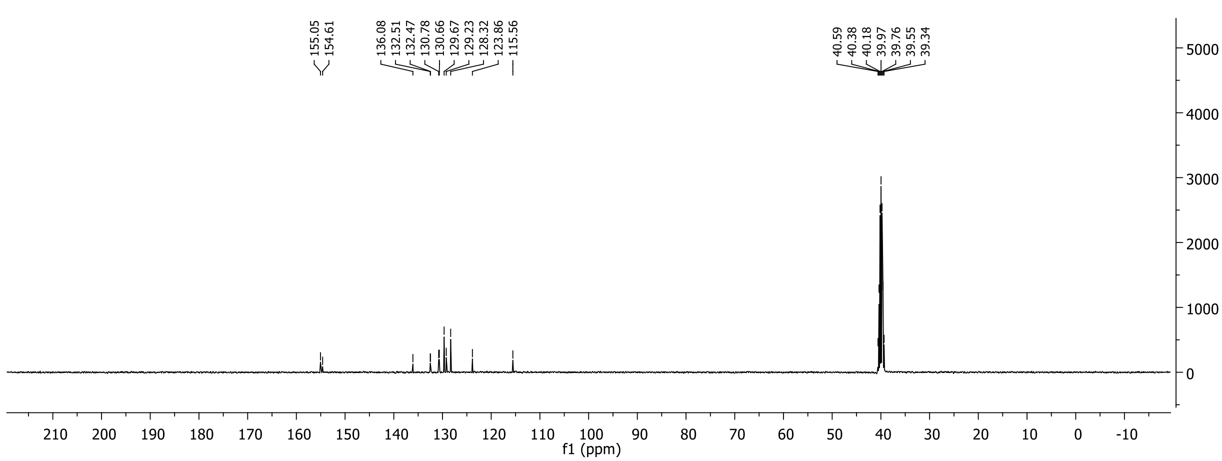

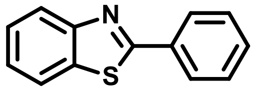

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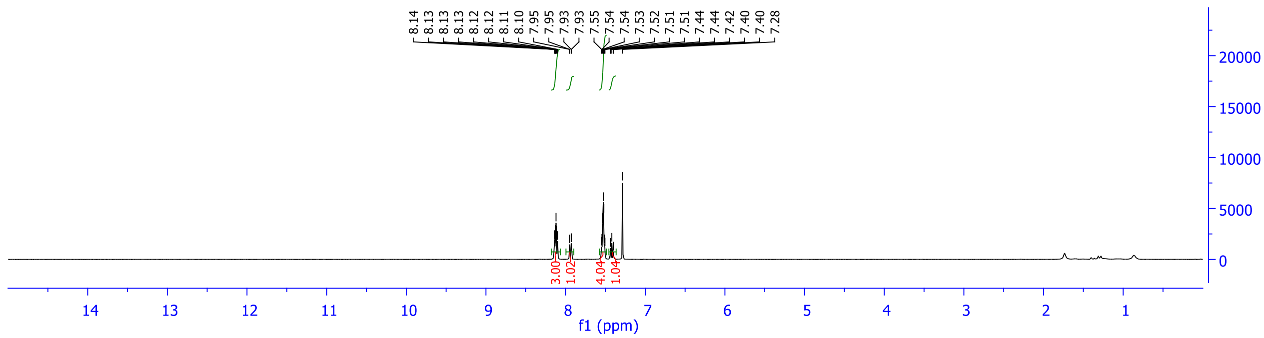
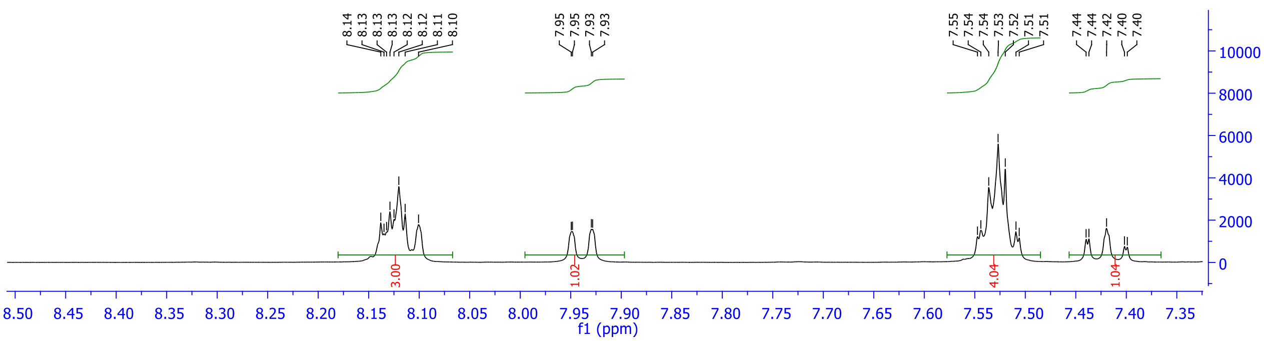
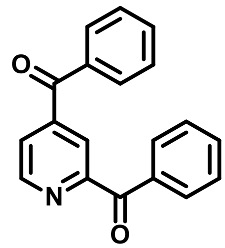
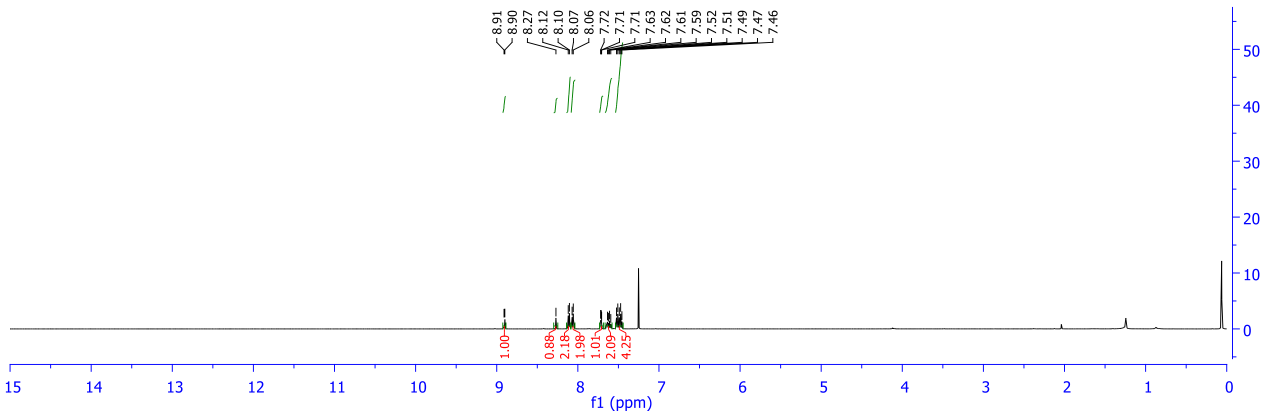


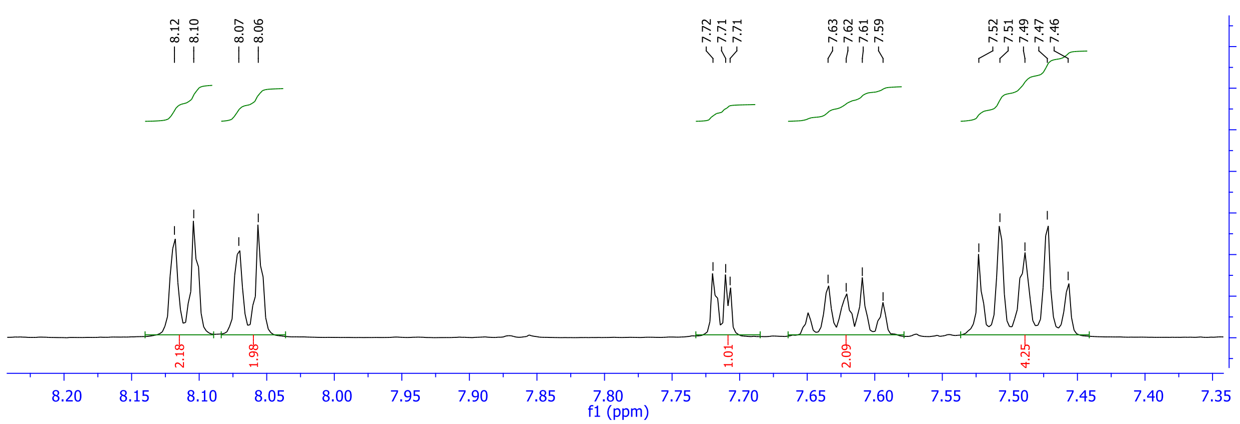
8.14 8.13 8.13 8.13 8.12 8.12 8.11 8.10 7.95 7.95 7.93 7.93 7.55 7.54 7.54 7.53 7.52 7.51 7.51 7.44 7.44 7.42 7.40 7.40 7.28
3.00
1.02
4.04
1.04
20000
15000
10000
5000
0
14 13 12 11 10 9 8 7 6 5 4 3 2 1
f1 (ppm)



8.14 8.13 8.13 8.13 8.12 8.12 8.11 8.10
7.95 7.95 7.93 7.93
7.55 7.54 7.54 7.53 7.52 7.51 7.51
7.44 7.44 7.42 7.40 7.40
3.00
1.02
4.04
1.04
10000
8000
6000
4000
2000
0
8.50 8.45 8.40 8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)



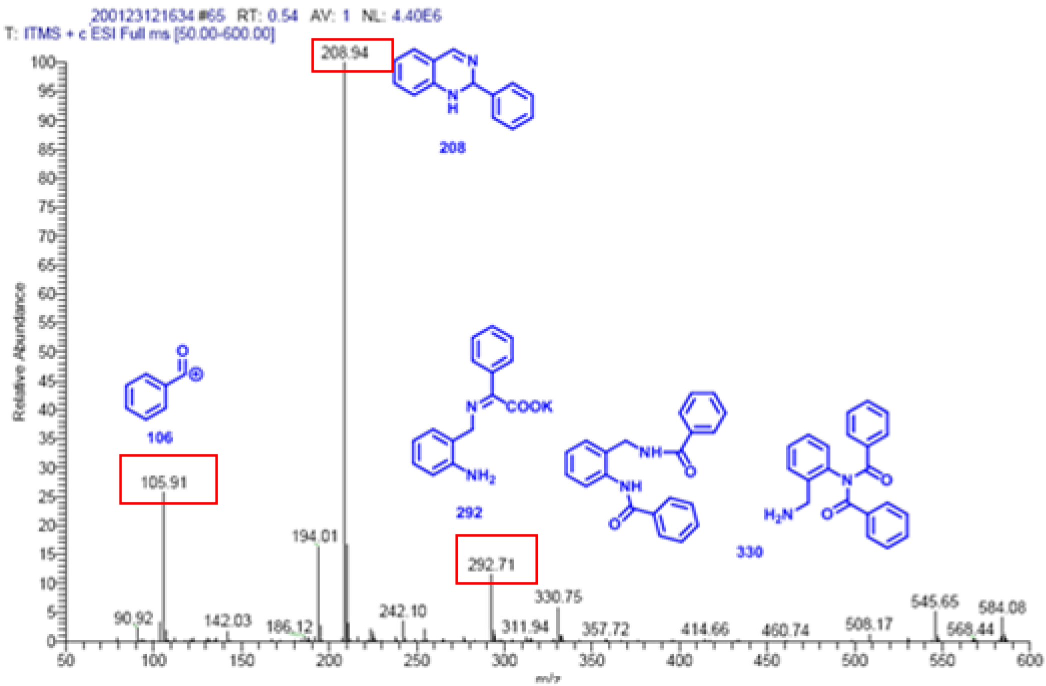


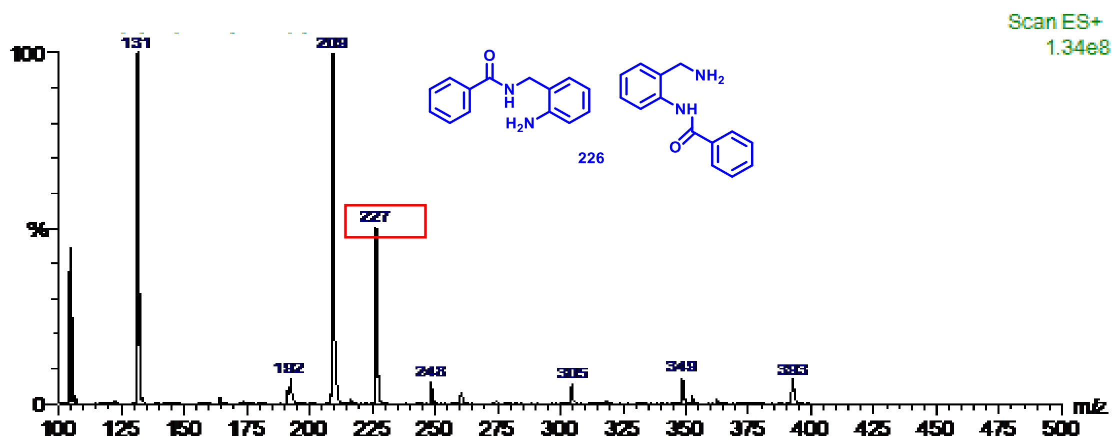


Diacylated pyridine (minisci acylated product) Spectra with reference to scheme 6)

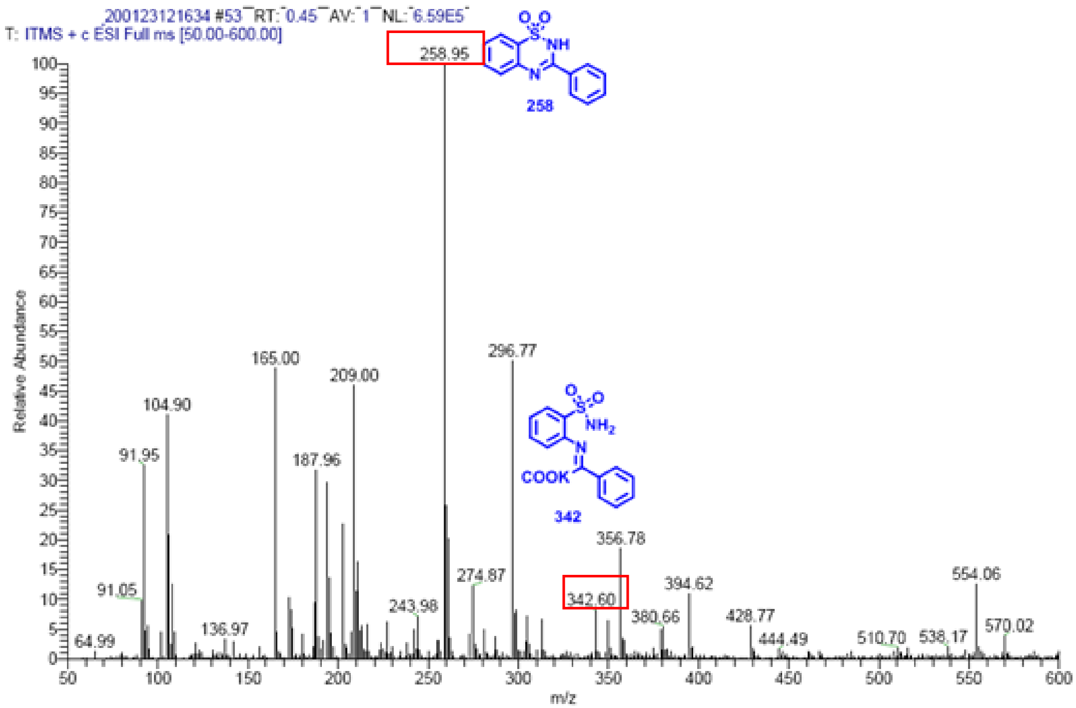
5.1 Mass Spectra

(Mass spectra with reference to scheme 4)

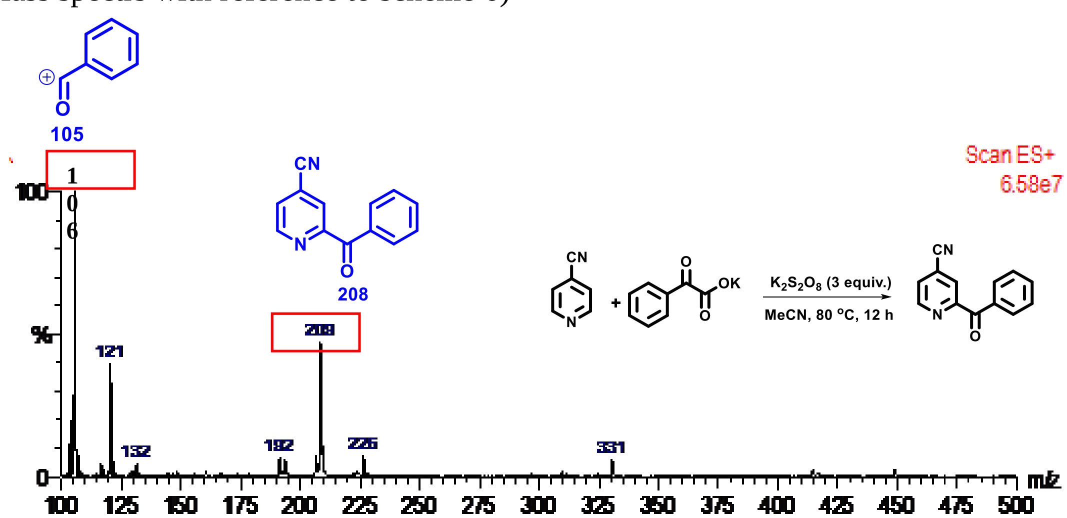


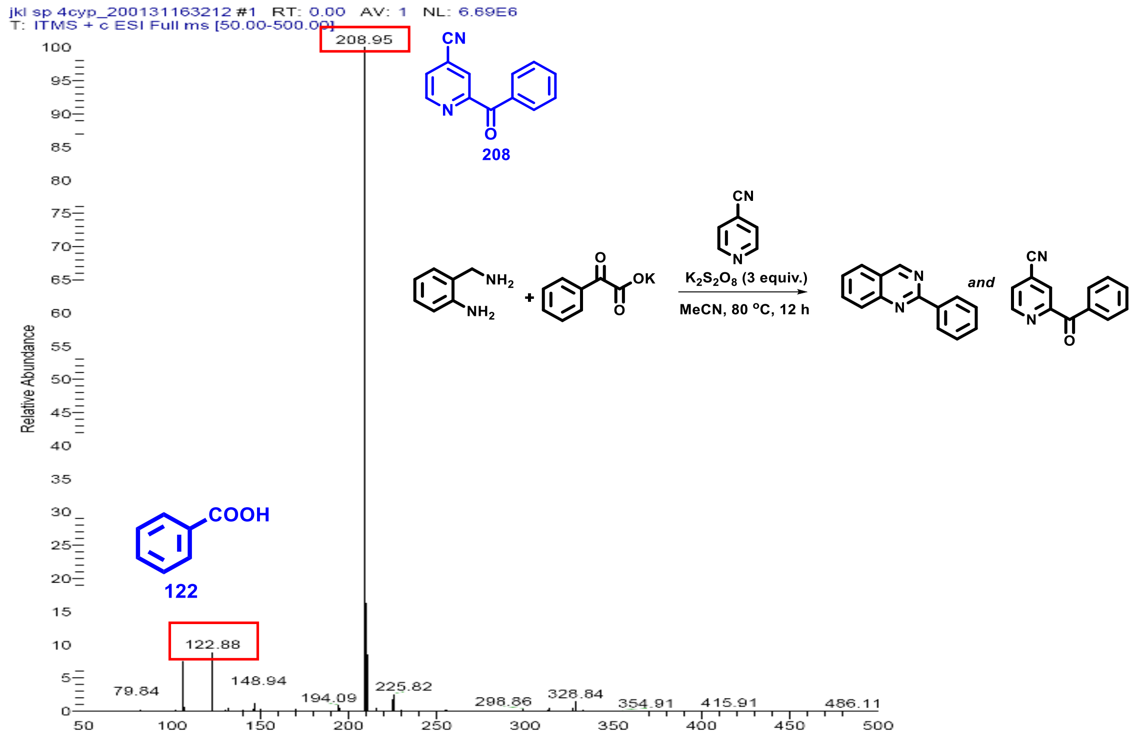


(Mass with reference to scheme 5)

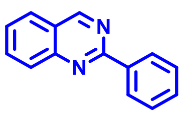


(Mass spectrs with reference to scheme 6)



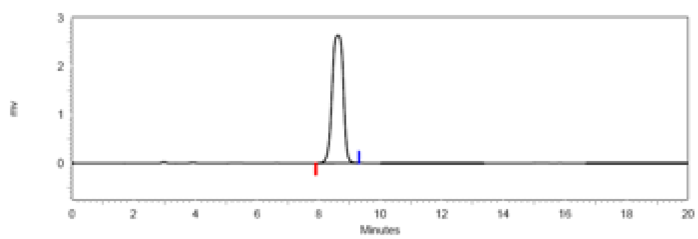


5.2 HPLC SPECTRA (With reference to scheme



C.I.L
NIPER

Sample Name Sample-JKL-SP-Q
Method Name D:\Class-vp\Methods\IPSITA.met
File Name D:\Class-vp\Data\Instrument1\JK Laha1\2020-02-03 Sample-JKL- SP-Q
Injection Volume 20
RunTime 2/3/2020 4:09:57 PM
Print Time 2/3/2020 4:58:02 PM



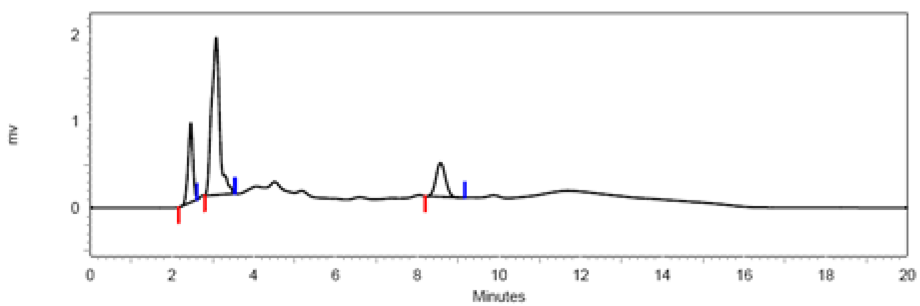
Detector A (254nm)

Retention Time	Area	Area Percent
8.633	66245057	100.00
Totals		
	66245057	100.00

Reaction with 4-cyanopyridine

C.I.L
NIPER

Sample Name Sample-JKL-SP-4CVP
Method Name D:\Class-vp\Methods\IPSITA.met
File Name D:\Class-vp\Data\Instrument1\JK Laha1\2020-02-03 Sample-JKL-SP- 4CVP
Injection Volume 20
RunTime 2/3/2020 3:48:03 PM
Print Time 2/3/2020 4:55:18 PM



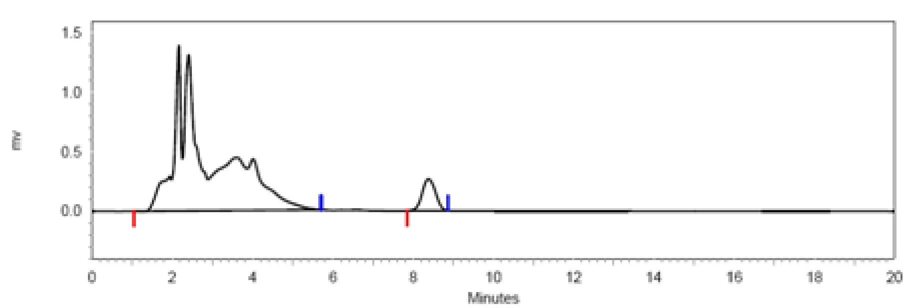
Detector A (254nm)

Retention Time	Area	Area Percent
2.458	7364292	18.98
3.083	25141540	64.79
8.575	6301114	16.24
Totals	38806946	100.00

Reaction with methylacrylate

C.I.L
NIPER

Sample Name Sample-JKL-SP-METHA
Method Name D:\Class-vp\Methods\IPSITA.met
File Name D:\Class-vp\Data\Instrument1\JK Laha1\2020.02.25 Sample-JKL-SP-METHA
Injection Volume 20
RunTime 2/5/2020 4:34:15 PM
Print Time 2/5/2020 5:11:47 PM



Detector A (254nm)

Retention Time	Area	Area Percent
2.167	79968472	92.88
8.383	6128735	7.12
Totals	86097207	100.00