Metal-Free Arylation of Diazines Through Photochemical Process

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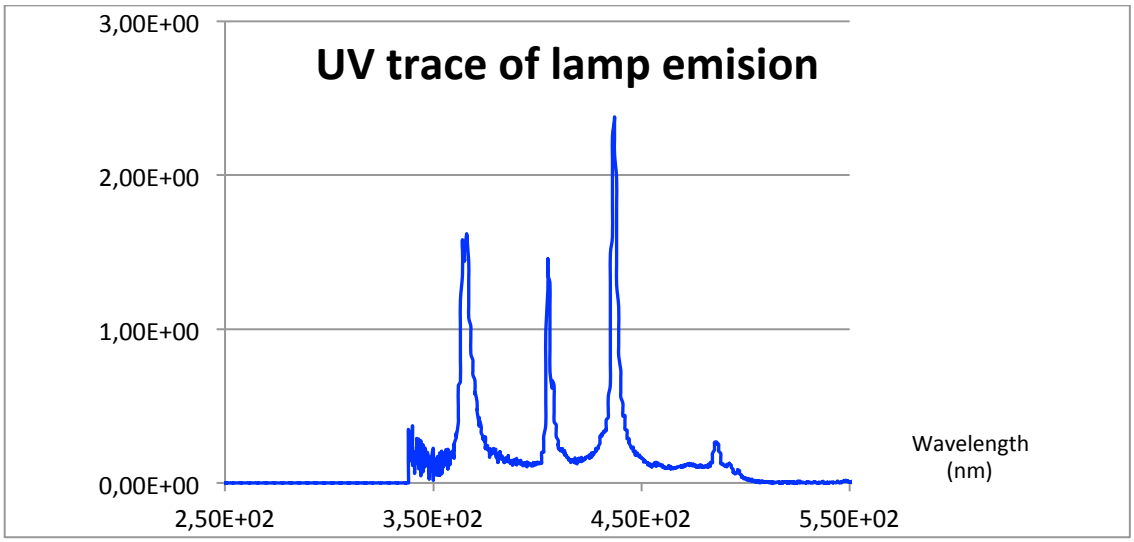
General Remarks.

Reactions were carried out under nitrogen, with magnetic stirring and common technical solvents (not distilled). The UV source is an Omnicure® S1000 system equipped with an anticaloric filter (f = 338nm). Thin layer chromatography (TLC) was performed on Merck 60 F254 silica gel. Merck Geduran SI 60 A silica gel (35−70 mm) was used for column chromatography. FTIR spectra were recorded by ATR technique, using Brüker Vertex 70.

^{1}H, ^{13}C, ^{19}F and ^{11}B NMR spectra were recorded at 300 and 400 MHz respectively, using a Brüker AVANCE spectrometer fitted with a *QNP* probehead. Chemical shifts are given in ppm using the $CDCl_3$ signal as reference (^{1}H = 7.27 ppm, ^{13}C = 77.00 ppm). NMR spectra were recorded in $CDCl_3$ at 300 K. The terms m, s, d, t, q, quint. and sept. stand for multiplet, singlet, doublet, triplet, quadruplet, quintuplet, and septet, respectively, and the term bs means a broad signal. The chemicals were used as received without further purification. Regioisomers ratio were determined from crude ^{1}H NMR spectra and do not necessary correspond to the reported purified fractions in the SI.

1. Irradiation

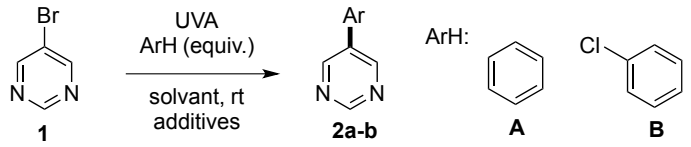
Experimental measurement of the emission spectrum of UV lamp Omnicure (medium pressure mercury vapors lamp 100W) used for photoarylation of diazines.



2. Photoarylation

Base Optimization

Other base modifications without significant improvement compare to potassium carbonate:



Entry	ArH (equiv.)	solvant	Additives	Yield (%)[c-d]
1	B (20)	CH_2Cl_2/ACN [a]	CsOH (3)	41[e]
2	B (20)	CH_2Cl_2/ACN [a]	KOH (3)	42[e]
3	A (20)	CH_2Cl_2/ACN [a]	DBU (3)	14[f]
4	A (20)	CH_2Cl_2/ACN [a]	Et_3N (3)	4[f]

[a] CH_2Cl_2/MeCN 95/5 (v/v). [b] Reaction conducted in the dark. [c] Irradiation was done with a medium-pressure mercury-vapors lamp (100 W) with an anticaloric filter (338-500 nm). [d] See Scheme 2 for regioselectivity with B. [e] Isolated Yield. [f] 1H NMR yield.

Procedure A: *for volatile aryl acceptor*

A solution of 5-bromopyrimidine (1 eq., 80 mg, 0.503 mmol), K_2CO_3 (1.1 eq., 76.5 mg, 0.554 mmol) and aryl acceptor (10 eq., 5.03 mmol) in of ACN (5 ml) is stirred under nitrogen atmosphere in a glass tube. The solution is irradiated by the side of the tube with a UV lamp (distance 8-10cm power 100%) during 24h.

The reaction is monitored by TLC until completion. Then, the crude mixture is directly filtrated over a plug of silica gel and washed with ethyl acetate. The remaining amount of 5-bromopyrimidine and acceptor are evaporated under high vacuum In order to directly recover a clean product

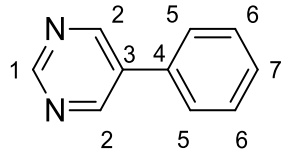
Procedure B: *general method*

A solution of 5-bromopyrimidine (1 eq., 80 mg, 0.503 mmol), K_2CO_3 (1.1 eq., 76.5 mg, 0.554 mmol) and aryl acceptor (10 eq., 5.03 mmol) in of ACN (5 ml) is stirred under nitrogen atmosphere in a glass tube. The solution is irradiated by the side of the tube with a UV lamp (distance 8-10cm power 100%) during 24h.

The reaction is monitored by TLC until completion. Then, the crude mixture is directly filtrated over a plug of silica gel and washed with ethyl acetate. The remaining amount of 5-bromopyrimidine is evaporated under high vacuum. Then the crude mixture is purified by column chromatography (eluent : Cyclohexane/Ethyl Acetate).

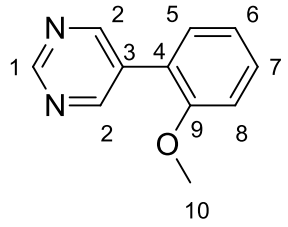
Experimental information

2a, 5-phenylpyrimidine



The procedure A affords 53 mg of **2a** as slightly yellow oil (67 %).^{1}H NMR ($CDCl_3$, 300MHz): δ = 7.46–7.60 (m, 5H, H_5, H_6 and H_7), 8.95 (s, 2H, H_2) and 9.20 (s, 1H, H_1); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 127.0 (C_5), 129.0 (C_7), 129.4 (C_6), 134.2 (C_3 or C_4), 134.3 (C_3 or C_4), 154.9 (C_2), 157.4 (C_1). HR-MS (ESI-Q-Tof) calcd for $C_{10}H_8N_2$ $[M+H]^+$: 157.0760, found: 157.0761. FTIR (ATR): ν = 3003, 2959, 2924, 1580, 1557, 1415, 1362, 1223 cm^{-1}. Spectral data are in agreement with the literature. [1]

2c, 5-(2-methoxyphenyl)pyrimidine and regioisomers



The procedure A affords 60 mg of **2c** as slightly yellow oil (63 %, *ortho:meta:para* 68:18:14). **2c**(ortho): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.84 (s, 3H, H10), 7.03 (dd, J = 8.3, 1.0 Hz, 1H, H_8), 7.09 (1H, td, J = 7.5, 1.0 Hz, H_6), 7.32 (dd, J = 7.5, 1.7 Hz, 1H, H5) , 7.39 – 7.45 (ddd, J = 8.3, 7.5, 1.7 Hz, 1H, H7), 8.91 (s, 2H, H2) and 9.14 (s, 1H, H1) ^{13}C NMR ($CDCl_3$, 75MHz): δ = 55.4 (C10), 111.2, 121.1, 123.2 (C4), 130.1, 130.4, 132.1 (C3), 154.3 (C1), 156.7 (C2), 157.4 (C9). Spectral data are in agreement with the literature. [2] **2c**(meta) characteristic signals: ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.88 (s, 3H), 8.94 (s, 2H), 9.20 (s, 1H). ^{13}C NMR ($CDCl_3$, 75MHz): δ = 55.4, 112.7, 114, 119.2, 134, 135.5, 156.4, 160.2. **2c**(para) characteristic signals: ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.86 (s, 3H), 7.04 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 8.91 (s, 2H) and 9.14 (s, 1H). ^{13}C NMR ($CDCl_3$, 75MHz): δ = 55.2, 114.8, 126.3, 128, 133.8, 154.8, 156.4, 160.3. HR-MS (ESI-Q-Tof) calcd for $C_{10}H_8N_2$ $[M+H]^+$: 187.0866, found: 187.0864. FTIR (ATR): ν = 3038, 2938, 2836, 1600, 1579, 1552, 1494, 1462, 1244 cm^{-1}Spectral data are in agreement with the literature. [3]

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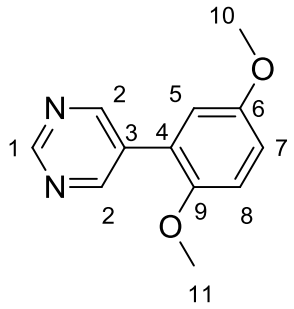
[1] E. Bratt, O. Verho, *J. Org. Chem.* **2014**, *79*, 3946

[2] WO2001068585A1, **2002,** Fujisawa Pharmaceutical Co.

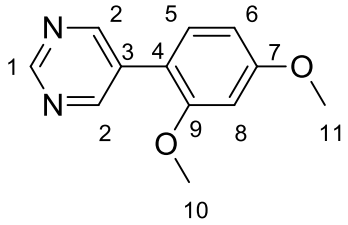
[3]Kitamura, Y., Sako, S., Tsutsui, A., Monguchi, Y., Maegawa, T., Kitade, Y. and Sajiki, H. *Adv. Synth. Catal.,* **2010**, *352*, 718.

2d, 5-(2,5-dimethoxyphenyl)pyrimidine



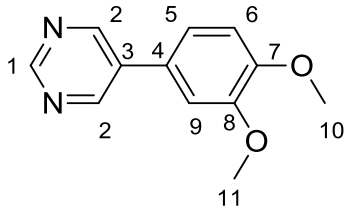
The procedure B (purification by column chromatography eluent 8/2 and then 100% ethyl acetate) leads to 69 mg of **2d** as a white solid (63%). ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.78 (s, 3H, H11), 3.81 (s, 3H, H10), 6.88 (dd, J = 2.2 , 1.3 Hz, 1H, H7); , 6.94 (d , J = 1.4 Hz, 1H, H5); 6.94 (d, J = 2.4 Hz, 1H, H8), 8.90 (s, 2H, H2) and 9.14 (s, 1H, H1). ^{13}C NMR ($CDCl_3$, 75MHz): δ = 55.8 (C11), 56.0 (C10), 112.5 (C8), 114.7 (C5), 116.1 (C7), 124.0 (C4), 132.0 (C3), 150.7 (C9), 153.9 (C6), 156.8 (C2), 156.9 (C1). HR-MS (ESI-Q-Tof) calcd for $C_{12}H_{12}N_2O_2$ $[M+H]^+$: 217.0972, found: 217.0976. FTIR (ATR): ν = 3042, 2964, 2921, 2839, 1584, 1504, 1451, 1438, 1414, 1402, 1237, 1217, 1181, 1050, 1017 cm^{-1}

2e, 5-(2,4-dimethoxyphenyl)pyrimidine and regioisomer



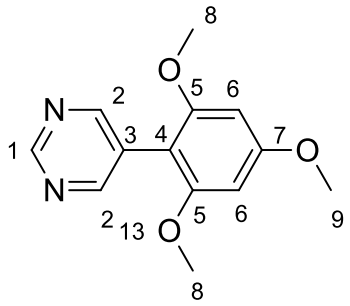
The procedure B affords 84.6 mg of **2e** as slightly yellow solid (79%, (*ortho,para*):(*ortho,ortho*) 59:41). **2e**(*ortho,para*): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.82 (s, 3H, H10), 3.86 (s, 3H, H11), 6.59 (d, J = 2.3 Hz, 1H, H5) , 6.62 (dd, J = 2.3, 8.3 Hz, 1H, H6), 7.25 (d, J = 8.3 Hz, 1H, H8), 8.87 (s, 2H, H2) and 9.10 (s, 1H, H1). ^{13}C NMR ($CDCl_3$, 100MHz): δ = 55.5 (C10 and C11), 99.1 (C8), 105.3 (C6), 116.0 (C4), 130.8 (C5), 132.0 (C3), 156.4 (C1), 156.6 (C2), 157.7 (C9), 161.7 (C7). **2e**(*ortho,ortho*): δ = 3.78 (s, 6H), 6.68 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 8.4 Hz, 1H), 8.75 (s, 2H) and 9.11 (s, 1H); ^{13}C NMR ($CDCl_3$, 100MHz): δ = 55.8 (2CH3), 104 (2CH), 128.3 (1C), 130.4 (1CH), 156.4 (1CH), 157.5 (2C), 158.5 (2CH). HR-MS (ESI-Q-Tof) calcd for $C_{12}H_{12}N_2O_2$ $[M+H]^+$: 217.0972, found: 217.0979. FTIR (ATR): ν = 3014, 2960, 2935, 2836, 1612, 1579, 1551, 1456, 1407, 1207, 1156, 1104 cm^{-1}

2f, 5-(3,4-dimethoxyphenyl)pyrimidine and regioisomers:



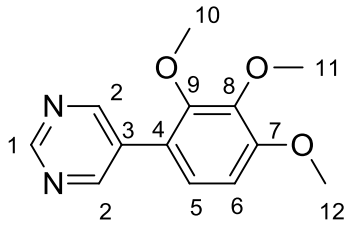
The procedure B affords 61.2 mg of **2f** as slightly yellow solid (56%, (*ortho,meta*):(*meta,para*) 30:70). **2f**(*meta,para*) ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.94 (s, 3H, H10 or H11), 3.96 (s, 3H, H11 or H10), 7.01 (d , J = 8.3 Hz, 1H, H6), 7.06 (d, J = 2.1 Hz, 1H, H9), 7.14 (dd, J = 8.2, 2.1 Hz, 1H, H5), 8.92 (s, 2H) and 9.16 (s, 1H, H1)); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 56.0 (C10 or C11), 56.0 (C11 or C10), 109.8 (C9 or C6), 111.8 (C6 or C9), 119.6 (C5), 126.9 (C3), 134.1 (C4), 149.7 (C8 or C7), 149.9 (C7 or C8), 154.5 (C2), 157.0 (C1). **2f**(*ortho,meta*) ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.69 (s, 3H), 3.94 (s, 3H), 6.96 (dd, J = 7.7, 1.5 Hz, 1H) , 7.03 (dd, J = 8.2, 1.5 Hz, 1H), 7.20 (dd, J = 8.1, 7.9, 1H), 8.95 (s, 2H) and 9.19 (s, 1H**);** ^{13}C NMR ($CDCl_3$, 75MHz): δ = 56.0 (1CH3), 60.8 (1CH3), 113.3 (1CH), 121.6 (1CH), 124.8 (1CH), 128.6, 130.3, 130.6, 153.3,156.7(2CH), 157.1(1CH). HR-MS (ESI-Q-Tof) calcd for $C_{12}H_{12}N_2O_2$ $[M+H]^+$: 217.0972, found: 217.0980. FTIR (ATR): ν = 3035, 2998, 2967, 2942, 2920, 2838, 1588, 1556, 1520, 1417, 1397, 1257, 1229, 1179, 1151, 1022 cm^{-1}

2g, 5-(2,4,6-trimethoxyphenyl)pyrimidine;



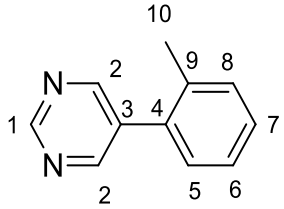
The procedure B (purification by column chromatography eluent 8/2 and then 100% ethyl acetate) leads to 102.5 mg of **2g** as a white solid (83%). ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.75 (s, 6H, H8), 3.87 (s, 3H, H9), 6.23 (s, 2H, H6), 8.72 (s, 2H, H2) and 9.07 (s, 1H, H1); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 55.4 (C9), 55.7 (C8), 90.7 (C6), 104.7 (C4), 128.3 (C3), 156.1 (C1), 158.4 (C5), 158.6 (C2), 161.9 (C7); HR-MS (ESI-Q-Tof) calcd for $C_{13}H_{14}N_2O_3$ $[M+H]^+$: 247.1077, found: 247.1082. FTIR (ATR): ν = 2993, 2948, 2839, 1586, 1555, 1351, 1229, 1115 cm^{-1}

2h, 5-(2,3,4-trimethoxyphenyl)pyrimidine and regioisomers



The procedure B affords 58.6 mg of **2h** as slightly yellow solid (67%, (*ortho,meta,para*):(*meta,para,ortho*) 80:20). **2h**(*ortho,meta,para*)**:** ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.79 (s, 3H, H11), 3.93 (s, 3H, H10), 3.95 (s, 3H, H12), 6.81 (d, J = 8.6 Hz, 1H, H6) , 7.06 (d, J = 8.6 Hz, 1H, H5), 8.91 (s, 2H, H2) and 9.17 (s, 1H, H1); ^{13}C NMR ($CDCl_3$, 100MHz) δ = 56.3 (CH3), 61.1 (CH3), 61.3 (CH3), 106.1 (CH), 121.2 (C), 124.4 (CH), 132.1 (C), 142.8 (C) 151.6 (C), 154.9 (C), 156.6(CH). HR-MS (ESI-Q-Tof) calcd for $C_{13}H_{14}N_2O_3$ $[M+H]^+$: 247.1077, found: 247.1076. FTIR (ATR): ν = 2970, 2937, 2842, 1597, 1580, 1469, 1404, 1297, 1215, 1100, 1178 cm^{-1}

2i, 5-(2-methylphenyl)pyrimidine and regioisomers;

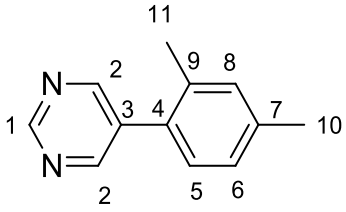


The procedure B, followed by a chromatography column (eluent : 8/2 cyclohexane /AcOEt) leads to 41 mg of **2i** as a slightly yellow oil (48%, *ortho:meta:para* 57:25:18). **2i**(*ortho*): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.31 (s, 3H, H10), 7.24 – 7.40 (m, 4H, H5 H6 H7 and H8), 8.75 (s, 2H, H2), 9.21 (s, 1H, H1); ^{13}C NMR ($CDCl_3$ 75MHz): δ = 20.6 (C10), 126.8 (C5 or C8), 129.3 (C8 or C5), 130.1 (C6 or C7), 131.2 (C7 or C6), 134.5 (C3), 135.6 (C9 or C4), 136.0 (C4 or C9), 156.9 (C2), 157.5 (C1). Spectral data are in agreement with the literature.[4] **2i**(*meta*): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.46 (s, 3H), 7.31-7.43 (m, 4H),8.94 (s, 2H), 9.20 (s, 2H); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 21.5, 124.1, 127.7, 129.3, 134.4, 139.1, 154.7. **2i**(*para*): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.43 (s, 3H), 7.34 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 8.93 (s, 2H) 9.18 (s, 2H). ^{13}C NMR ($CDCl_3$, 75MHz): δ = 21.2, 126.8, 129.8, 130.1, 134.2, 139.2, 154.9, 157.7 Spectral data are in agreement with the literature.[5] HR-MS (ESI-Q-Tof) calcd for $C_{11}H_{10}N_2$ $[M+H]^+$: 171.0917, found: 217.0915. FTIR (ATR): ν = 3030, 2922, 2864, 1550, 1408, 1186 cm^{-1}

2j, 5-(2,4-dimethylphenyl)pyrimidine and regioisomers

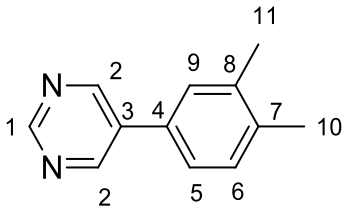
[4] M. Feuerstein et al. J. Org. Chem. **2003**, 687, 327

[5] T. Iwasawa, D. Ajami, J. R. J, Org. Lett., **2006**, 8, 2925



The procedure B, (eluent : 7/3 cyclohexane /AcOEt) leads to 52 mg of **2j** as a slightly yellow oil (57%, (*ortho,ortho*):(*ortho,para*):(*meta,meta*) 40:53:7). **2j**(*ortho,ortho*): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.28 (s, 3H, H11), 2.39 (s, 3H, H10), 7.12-718 (m, 3H, H5, H6 and H8), 8.73 (s, 2H, H2), 9.20 (s, 1H, H1). ^{13}C NMR ($CDCl_3$, 75MHz): δ = 20.2 (C11 or C10), 21.1 (C10 or C11), 127.1 (C5), 129.7 (C6), 131.3 (C3), 131.6 (C8), 135.3 (C9 or C4), 135.4 (C4 or C9), 138.9 (C7), 156.7 (C2), 157 (C1). **2j**(*ortho,para*): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.06 (s, 6H), 8.61 (s, 2H), 9.24 (s, 1H); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 21, 127.8, 128.7, 133.9, 134.6, 136.4, 157.1, 157.4. Spectral data are in agreement with the literature.[6] **2j**(*meta,meta*): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.41 (s, 6H), 8.93 (s, 2H), 9.19 (s, 1H); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 21.3, 124.8, 130.6, 139.1, 154.8, 157.3. HR-MS (ESI-Q-Tof) calcd for $C_{12}H_{12}N_2$ $[M+H]^+$: 185.1073, found: 185.1076. FTIR (ATR): ν = 3031, 2921, 2859, 1580, 1552, 1408, 1186 cm^{-1}

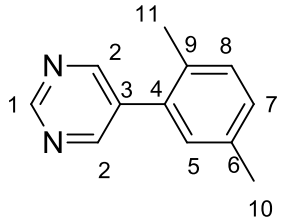
2k, 5-(3,4-dimethylphenyl)pyrimidine and regioisomer;



The procedure B, (eluent: 8/2 cyclohexane /AcOEt) leads to 58 mg of **2k** as a slightly yellow oil (62%, (*meta,para*):(*ortho,meta*) 52:48); **2k**(*ortho,meta*): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.18 (s, 3H), 2.37 (s, 3H), 7.07 (dd, J = 7.5, 1.5 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 8.72 (s, 2H), 9.21 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 16.9 (C11 or C10), 20.6 (C10 or C11), 125.9 (C9), 127.7 (C5), 130.5 (C6), 134.3 (C3 or C4), 134.5 (C4 or C3), 135.9 (C7 or C8), 137.9 (C8 or C7). 156.7 (C2), 157.1 (C1). **2k**(*meta,para*): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.34 (s, 3H, H10 or H11), 2.36 (s, 3H, H11 or H10), 7.29 - 7.35 (m, 2H, H5 or H6), 7.36 (bs, 1H, H9), 8.93 (s, 2H, H2), 9.18 (s, 1H, H1); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.5, 19.9, 124.3, 128.1, 130.6, 131.7, 134.3, 137.8, 137.8, 154.7, 157.1. HR-MS (ESI-Q-Tof) calcd for $C_{12}H_{12}N_2$ $[M+H]^+$: 185.1073, found: 185.1073. FTIR (ATR): ν = 3030, 2970, 2942, 2920, 2862, 1574, 1549, 1411, 1385 cm^{-1}

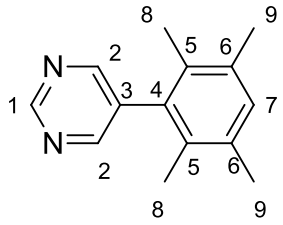
2l, 5-(2,5-dimethylphenyl)pyrimidine

[6] L. Jin-Heng, Z. Qi-Ming, X. Ye-Xiang *Tetrahedron*, **2006**, 62, 10888



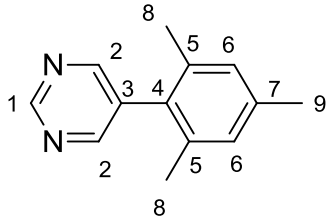
The procedure B, (eluent : 8/2 cyclohexane/AcOEt) leads to 47 mg of **2l** as a slightly yellow oil (50%); ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.25 (s, 3H, H11), 2.37 (s, 3H, H10), 7.03 (m, 1H, H5), 7.16 (dd, J = 7.9, 1.1 Hz, 1H, H7), 7.22 (d, J = 7.8 Hz, 1H, H8), 8.73 (s, 2H, H2), 9.20 (s, 1H, H1); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 19.8 (C11), 20.9 (C10), 129.8 (C5), 130.5 (C8), 130.9 (C7), 132.6 (C3), 134.2 (C9 or C6), 135.5 (C6 or C9), 136.1 (C4), 156.7 (C2), 157.2 (C1). HR-MS (ESI-Q-Tof) calcd for $C_{12}H_{12}N_2$ $[M+H]^+$: 185.1073, found: 185.1079. FTIR (ATR): 3021, 2922, 2863, 1549, 1502, 1411, 1185 cm^{-1}

2m, 5-(2,3,5,6-tetramethylphenyl)pyrimidine



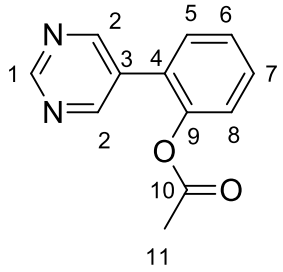
The procedure B, (eluent : 8/2 cyclohexane /AcOEt) leads to 67 mg of **2m** as a white solid (63%); ^{1}H NMR ($CDCl_3$, 300MHz): δ = 1.91 (s, 6H, H9), 2.29 (s, 6H, H6), 7.08 (s, 1H, H7), 8.56 (s, 2H, H2), 9.24 (s, 1H, H1); ^{13}C NMR ($CDCl_3$,75MHz): δ = 17.4 (C8), 20.1 (C9), 132 (C7), 132.3 (C3), 134.2 (C4), 134.2 (C5), 135.9 (C6), 157.1 (C1), 157.3 (C2). HR-MS (ESI-Q-Tof) calcd for $C_{14}H_{17}N_2$ $[M+H]^+$: 213.1386, found: 213.1383. FTIR (ATR): ν = 3015, 2970, 1738, 1366, 1229, 1217 cm^{-1}

2n, 5-(2,4,6-trimethylphenyl)pyrimidine



The procedure B, (eluent : 8/2 cyclohexane /AcOEt) leads to 74 mg of **2n** as a white solid (74%); ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.03 (s, 6H, H8), 2.35 (s, 3H, H9), 7.00 (s, 2H, H6), 8.59 (s, 2H, H2), 9.23 (s, 1H, H1); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 20.8 (C8), 21.0 (C9), 128.6 (C6), 131.1 (C3), 134.7 (C4), 136.3 (C5), 138.5 (C7), 157.2 (C1), 157.3 (C2). HR-MS (ESI-Q-Tof) calcd for $C_{13}H_{15}N_2$ $[M+H]^+$: 199.1230, found: 199.1231. FTIR (ATR): ν = 3030, 2955, 2915, 2862, 1606, 1572, 1549, 1452, 1434, 1405 cm^{-1}

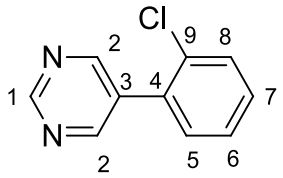
2o, 2-(pyrimidin-5-yl)phenyl acetate



The procedure B, (eluent : 8/2 to 6/4 cyclohexane /AcOEt) leads to 55 mg of **2o** as a white solid (51%, *ortho*:*meta*:*para* 36:37:27); **2o**(ortho): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.17 (s, 3H, H11), 7.25 (d, J =.7.9 Hz 1H, H8), 7.40 – 7.44 (m, 2H, H5 and H7), 7.51 (ddd, J = 7.9, 3.6 Hz 1H, H6), 8.84 (s, 2H, H2), 9.22 (s, 1H, H1); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 20.8 (C11), 123.4 (C8), 126.9 (C6), 127.7 (C3), 130.4 (C5), 130.4 (C7), 131.4 (C4), 147.9 (C9), 156.4 (C2), 157.6 (C1), 169.0 (C10). **2o**(meta): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.36 (s, 3H), 7.22 (ddd, , J = 7.9, 2.3, 1.1 Hz, 1H), 7.33 (dd, , J =.1.9 Hz, 1H), 7.46 (ddd, J =.1.1, 7.9 Hz, 1H), 7.55(t, J = 7.9 Hz, 1H) 8.94 (s, 2H), 9.21 (s, 1H); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 21.1 (1CH3), 120.2 (1CH), 122.7 (1CH), 124.4 (1CH), 130.5 (1CH), 133.4 (1C), 135.7 (1C), 151.4 (1C), 154.9 (2CH), 157.7(1CH), 169.2(1C). **2o**(para): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.36 (s, 3H),7.28 (d, J =.8.7 Hz, 2H), 7.61 (d, J =.8.7 Hz, 2H), 8.95 (s, 2H), 9.23 (s, 1H); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 21.1 (CH3), 122.2 (2CH), 128.1 (2CH), 131.9 (1C), 133.6 (1C), 151.4 (1C), 154.8 (2CH), 157.5(1CH), 169.2 (1C).

HR-MS (ESI-Q-Tof) calcd for $C_{12}H_{10}N_2O_2$ $[M+H]^+$: 215.0815, found: 215.0819. FTIR (ATR): ν = 3041, 2927, 1762, 1583, 1553, 1412, 1370, 1181 cm^{-1}

2p, 5-(2-chlorophenyl)pyrimidine and regioisomers; ;

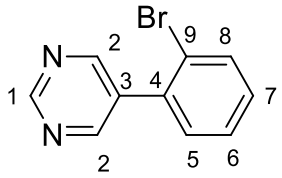


The procedure B leads to 52 mg of **2p** as a yellow oil (54%, *ortho*:*meta*:*para* 60:21:19); **2p**(ortho): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 7.33–7.57 (m, 4H, from H5 to H8), 8.85 (s, 2H, H2), 9.23 (s, 1H ,H1); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 127.5 (C5), 130.3 (C6 or C7 or C8), 130.4 (C6 or C7 or C8), 131.0 (C6 or C7 or C8), 132.8(C3 or C4 or C9), 133.1 (C3 or C4 or C9), 136.1 (C4 or C3 or C9), 156.8 (C2), 157.7 (C1). **2p**(meta) characteristic signals: ^{1}H NMR ($CDCl_3$, 300MHz): δ = 8.93(s, 2H), 9.24 (s, 1H); ^{13}C NMR ($CDCl_3$, 300MHz): δ =125.1 (1CH), 127.1 (1CH), 129.1 (1CH), 130.7 (1CH), 133.1 (1C), 154.7 (2CH), 157.7 (1CH). **2p**(para) characteristic signals: ^{1}H NMR ($CDCl_3$, 300MHz): δ = 8.94 (s, 2H), 9.22 (s, 1H);

^{13}C NMR ($CDCl_3$, 75MHz): δ =128.2 (1CH), 129.7 (1CH), 132.7 (1C), 133.4 (1C), 135.4 (1C), 154.9 (2CH), 157.9(1CH). Spectral data are in agreement with the literature.[7]

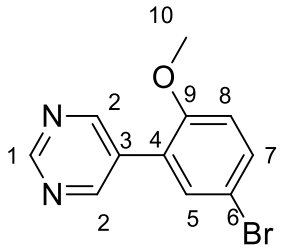
HR-MS (ESI-Q-Tof) calcd for $C_{10}H_8ClN_2$ $[M+H]^+$: 191.0371, found: 191.0369. FTIR (ATR): 3035, 2924, 2854, 1574, 1551, 1409 cm^{-1}

2q, 5-(2-bromophenyl)pyrimidine and regioisomers



The procedure B leads to 44 mg of **2q** as a white solid (40%, *ortho*:*meta*+*para* 50:50); **2q**(ortho): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 7.32 (d, J = 7.4 Hz, 2H, H5 and H8),7.41-7.44 (m, 1H), 7.70-7.73 (m, 1H) 8.82 (s, 2H, H2), 9.23 (s, 1H ,H1); ^{13}C NMR ($CDCl_3$, 100MHz): δ = 122.6 (C9), 128.4 (C5), 130.4 (C8 and C7), 132.6 (C6), 134.6 (C3), 136.3 (C4), 156.7 (C2), 157.6 (C1). **2q**(meta): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 7.38 (d, J = 7.8 Hz, 1H) 7.50 (dt, J = 1.3, 7.8 Hz, 2H), 7.57-7.61 (m, 1H), 8.92 2H), 9.21 (1H); ^{13}C NMR ($CDCl_3$, 100MHz): δ = 123.6 (1C), 126.9(1CH), 129.4 (1CH), 130.9 (1CH) 132 (1CH), 133 (1C), 134.3 (1C), 154.6 (2CH), 157.4 (1CH). Spectral data are in agreement with the literature.[8] **2q**(para): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 7.45 (d, J = 8.5 Hz), 7.65 (d, J = 8.5 Hz), 8.92(2H), 9.22 (1H)**;** ^{13}C NMR ($CDCl_3$, 100MHz): δ = 123.5 (1C), 128 (2CH), 132.3 (1C), 133.5 (2CH), 135.4 (1C), 154.8 (2CH), 157.7 (1CH)**.** Spectral data are in agreement with the literature.[9] HR-MS (ESI-Q-Tof) calcd for $C_{10}H_8B_rN_2$ $[M+H]^+$: 234.9865, found: 234.9864. FTIR (ATR): ν = 3040, 2924, 2853, 1577, 1568, 1552, 1409 cm^{-1}

2r, 5-(5-bromo-2-methoxyphenyl)pyrimidine and regioisomer ;



The procedure A leads to 55 mg of **2r** as a slightly yellow solid (41% *o*-OMe:*o*-Br 73:27); **2r**(o-OMe): ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.83 (s, 3H, H10), 6.91 (d, J = 8.8 Hz, 1H, H8), 7.44 (d, J = 2.4 Hz, 1H, H5), 7.51 (dd, J = 8.8, 2.4 Hz, 1H, H7), 8.88 (s, 2H, H2), 9.17 (s, 1H, H1); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 55.8

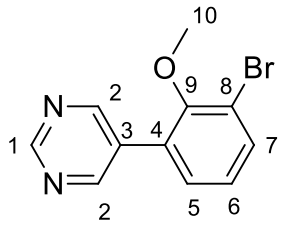
[7] C. Liu, W. Yang Chem. Commun, **2009**, 6267

[8] WO 2005/019238, **2005**, Meji Seika Kaisha, Ltd Tokyo

[9] G.-G. Hou, H.-J. Zhao, J.-F. Sun, D. Lin, X.-P. Dai, J.-T. Han, H. Zhao, Cryt. Eng. Comm. **2013**, 15, 577

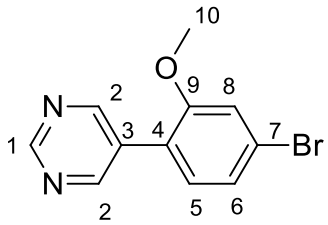
(C10), 113.0 (C8), 113.3 (C6) pas sur, 125.3 (C4), 130.9 (C3), 155.7 (C9), 156.7 (C2), 157.3 (C1). **2r**(o-Br): ^{1}H NMR ($CDCl_3$, 300MHz): characteristic signals δ = 3.84 (s, 3H), 7.60 (dd, J = 9.2, 1.5 Hz, 1H) 8.83 (s, 2H), 9.24 (s, 1H). ^{13}C NMR ($CDCl_3$, 75MHz): characteristic signals δ = 55.6, 116.0, 116.7, 134.2, 157.7, 159.2. HR-MS (ESI-Q-Tof) calcd for $C_{11}H_{10}BrN_2O$ $[M+H]^+$: 264.9971 and 266.9951, found: 264.9972 and 266.9955. FTIR (ATR): ν = 3032, 2937, 2840, 1571, 1552, 1492, 1412, 1385, 1273, 1240 , 1228, 1180, 1011 cm^{-1}

2s, 5-(3-bromo-2-methoxyphenyl)pyrimidine and regioisomers ;



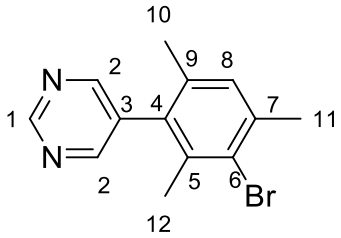
The procedure A leads to 60 mg of **2s** as a slightly yellow solid (45%, mixture). Major: ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.95 (s, 3H), 7.13 (t, J = 7.9 Hz, 3H), (dd, J = 7.9, 2.3 Hz, 1H), 7.78 (d, J = 2.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 300MHz): δ = 56.4 (C10), 112.5 (C5), 127.1 (C6), 131.7 (C7), 154.4 (C2), 154.8 (C1) 154.9 or 156.6 (C9). HR-MS (ESI-Q-Tof) calcd for $C_{11}H_{10}BrN_2O$ $[M+H]^+$: 264.9971 and 266.9951, found: 264.9972 and 266.9954. FTIR (ATR): ν = 3038, 2938, 2838, 1601, 1567, 1554, 1411, 1314, 1287, 1265 cm^{-1}

2t, 5-(4-bromo-2-methoxyphenyl)pyrimidine and regioisomers;



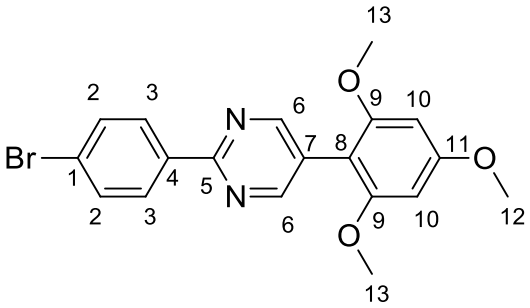
The procedure A leads to 58 mg of **2t** as a slightly yellow solid (43%, *ortho,ortho:ortho,para:meta,meta* 39:51:10); **2t**(*ortho,para*) ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.78 (s, 3H, H10), 6.99 – 7.03 (m, 1H, H8), 7.19 – 7.25 (m 1H, H7), 7.30 – 7.34 (m, 1H, H8), 8.71 (s, 2H, H2), 9.23 (s, 1H, H1); ^{13}C NMR ($CDCl_3$, 300MHz): δ = 55.9 (C10), 110 (C8), 125.1 (C6), 130.5 (C3 or C4), 131.0 (C5), 131.3 (C4 or C3), 154.9 (C9), 156.9 (C1), 160.5 (C2). HR-MS (ESI-Q-Tof) calcd for $C_{11}H_{10}BrN_2O$ $[M+H]^+$: 264.9971 and 266.9951, found: 264.9977 and 266.9959. FTIR (ATR): ν = 3038, 2940, 2837, 1592, 1577, 1568, 1551, 1406, 1284, 1259, 1228, 1028 cm^{-1}

2u, 5-(3-bromo-2,4,6-trimethylphenyl)pyrimidine ;



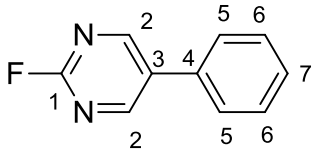
The procedure B leads to 82 mg of **2u** as a white solid (59%); ^{1}H NMR ($CDCl_3$, 300MHz): δ = 1.97 (s, 3H, H10), 2.16 (s, 3H, H12), 2.46 (s, 3H, H11), 7.08 (s, 1H, H8), 8.56 (s, 2H, H2), 9.25 (s, 1H, H1); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 20.8 (C10), 22.2 (C11), 24.1 (C12), 125.8 (C6), 130.0 (C8), 132.9 (C3), 134.8 (C4), 135.1 (C9 or C5), 136.4 (C5 or C9), 139.0 (C7), 157.2 (C2), 157.5 (C1). HR-MS (ESI-Q-Tof) calcd for $C_{13}H_{14}BrN_2$ $[M+H]^+$: 277.0335 and 279.0315, found: 277.0331 and 279.0317. FTIR (ATR): ν = 3025, 2965, 2923, 28551683, 1546, 1417, 1403, 1381, 1016 cm^{-1}

4, 2-(4-bromophenyl)-5-(2,4,6-trimethoxyphenyl)pyrimidine :



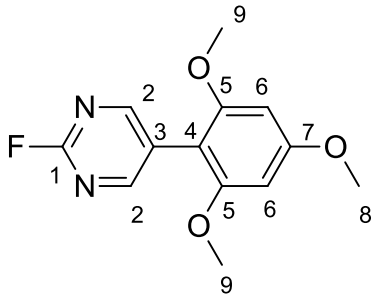
The procedure B, (eluent : cyclohexane/ethyl acetate 9/1) leads to 91 mg of **4** as a orange oil (44%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.79 (s, 6H, H12), 3.89 (s, 3H, H11), 6.26 (s, 2H, H10), 7.63 (d, J= 8.6 Hz, 2H, H3), 8.36 (d, J= 8.6 Hz, 2H, H2), 8.81 (s, 2H, H6). ^{13}C NMR ($CDCl_3$, 400 MHz) δ = 55.5 (C12), 55.8 (C13), 90.9 (C10), 104.9 (C8), 125.0 (C7), 126.1 (C1), 129.6 (C3 or C2), 131.7 (C2 or C3), 136.9 (C4), 158.5 (C9), 158.9 (C6), 161.0 (*C*11), 161.9 (C5); HR-MS (ESI-Q-Tof) calcd for $C_{19}H_{17}BrN_2O_3$ $[M+H]^+$: 401.0501 and 403.0480 ; found: 401.0496 and 403.0478. FTIR (ATR): ν = 3027, 2932, 2838, 1611, 1583, 1532, 1427, 1225, 1125 cm^{-1}

5a, 2-fluoro-5-phenylpyrimidine



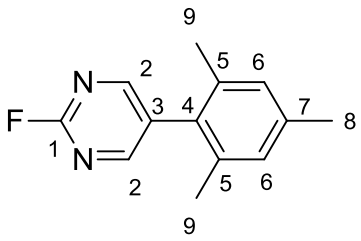
The procedure A leads to 44 mg of **5a** as a yellow/brown solid (74%); ^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.42 – 7.51 (m, 5H, H5-H6-H7), 8.73 (d, J = 1.4Hz, 2H, H2); ^{13}C NMR ($CDCl_3$, 100MHz): δ = 126.9 (C5 or C6), 129.1 (C7), 129.5 (C6 or C5), 133 (C3), 133.0 (s, C4), 158.8(d, J = 12 Hz C2), 162.4 (d, J = 220.4Hz, C1); ^{19}F NMR ($CDCl_3$, 162MHz): δ = -47.7. HRMS (ESI-Q-Tof) calcd for $C_{10}H_8FN_2$ $[M+H]^+$: 175.0666, found: 175.0672. FTIR (ATR): ν = 3015, 2971, 1739, 1366, 1229, 1217 cm^{-1}

5b, 2-fluoro-5-(2,4,6-trimethoxybenzene)pyrimidine



The procedure B, (eluent : 8/2 cyclohexane /AcOEt) leads to 106 mg of **5b** as a white solid (89%); mp: 172°C; ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.75 (s, 6H, H9), 3.87 (s, 3H, H8), 6.22 (s, 2H, H6), 8.60 (d, 1.8 Hz 2H, H2); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 55.4 (C8), 55.7 (C9), 90.7 (C6), 103.3 (C4), 126.5 (d, J = 5.3 Hz 1C, C3), 158.2 (C5), 161.2 (d, J = 217.8 Hz, C1), 162 (C7), 162.3 (d, J = 11.6 Hz, C2); ^{19}F NMR ($CDCl_3$, 162MHz): δ = -49.0 (F10). HR-MS (ESI-Q-Tof) calcd for $C_{11}H_{10}BrN_2O$ $[M+H]^+$: 265.0983, found: 265.0983. FTIR (ATR): ν = 3015, 2970, 2947, 1738, 1365, 1217 cm^{-1}

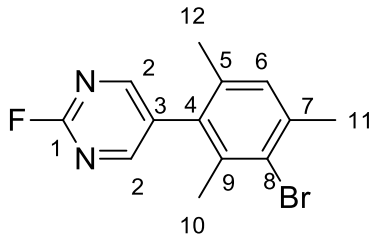
5c, 2-fluoro-5-(2,4,6-trimethylphenyl)pyrimidine



The procedure B, (eluent : 9/1 cyclohexane /AcOEt) leads to 78 mg of **5c** as a white solid (80%); ^{1}H NMR ($CDCl_3$, 400MHz): δ = 2.04 (s, 6H, H9), 2.35 (s, 3H, H9), 7.01 (s, 2H, H6), 8.47 (d, J = 1.8 Hz, 2H, H2); ^{13}C NMR ($CDCl_3$, 100MHz): δ = 20.8 (C9), 21.0 (C8), 128.7 (C6), 129.7 (d, J = 2.1 Hz C4), 132.7 (d, J = 5.0Hz, C3), 136.4 (C5), 138.8 (C7), 162 (d, J= 219.7 Hz, C1), 161.2 (d, J= 12 Hz C2); ^{19}F NMR ($CDCl_3$,

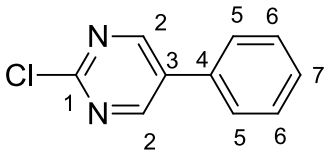
162MHz): δ = -47.4. HR-MS (ESI-Q-Tof): calcd for $C_{13}H_{14}FN_2$ $[M+H]^+$: 277.1135, found: 217.1100. FTIR (ATR): ν = 3039, 2964, 2921, 2862, 1562, 1421, 1298, 1276 cm^{-1}

5d, 2-fluoro-5-(3-bromo-2,4,6-trimethylphenyl)pyrimidine ;



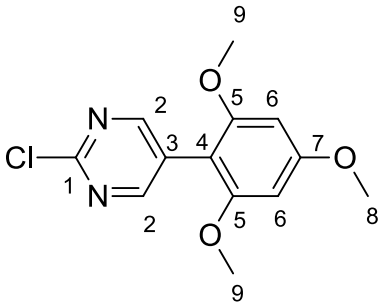
The procedure B, (eluent : 95/05 cyclohexane /AcOEt) leads to 45.5mg of **5d** as a white solid (45%). ^1H NMR ($CDCl_3$, 400MHz): δ = 1.98 (s, 3H, H12), 2.17 (s, 3H, H10 or H11), 2.46 (s, 3H, H11 or H10), 7.09 (s, 1H, H6), 8.45 (d, J = 1.7Hz, 2H, H2). ^{13}C NMR ($CDCl_3$, 75MHz): δ = 20.8 (C10), 22.2 (C11), 24.1 (C12), 125.9 (d, J = 6.2 Hz 1C, C3), 130.5 (C6), 131.2 (C4), 132.4 (C5), 135.3 (C7), 136.2 (C9), 139.3 (C8), 161.1 (d, J = 12.1 Hz, C2), 163.3 (d, J = 223.1 Hz, C1). ^{19}F NMR ($CDCl_3$, 162MHz): δ = -47.7. HR-MS (ESI-Q-Tof) calcd for $C_{13}H_{13}BrFN_2$ $[M+H]^+$: 295.0241 and 297.0221, found: 295.0237 and 297.0234. FTIR (ATR): ν = 2949, 2923, 2856, 1566, 1433, 1416, 1381, 1302, 1068 cm^{-1}

6a, 2-chloro-5-phenylpyrimidine ;



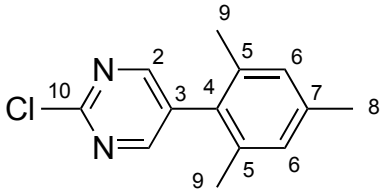
The procedure A leads to 77 mg of **6a** as a yellow/brown solid (79%). ^1H NMR ($CDCl_3$, 400MHz): δ = 7.49 – 7.57 (m, 5H, H5-H6-H7), 8.83 (s, 2H, H2). ^{13}C NMR ($CDCl_3$, 100MHz): δ = 126.9 (C5 or C6), 129.3 (C7), 129.5 (C6 or C5), 132.9 (C3 or C4), 133.0 (C4 or C3), 157.4 (C2), 160.1 (C1). HR-MS (ESI-Q-Tof) calcd for $C_{10}H_8ClN_2$ $[M+H]^+$: 191.0371, found: 191.0369. FTIR (ATR): ν = 3035, 2929, 1580, 1536, 1402, 1376, 1168, 1151 cm^{-1}

6b, 2-chloro-5-(2,4,6-trimethoxybenzene)pyrimidine



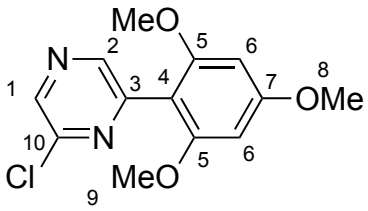
The procedure B, (eluent : 8/2 cyclohexane /AcOEt) leads to 77 mg of **6b** as a white solid (77%). ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.75 (s, 6H, H9), 3.86 (s, 3H, H8), 6.21 (s, 2H, H6), 8.60 (s, 2H, H2);.^{13}C NMR ($CDCl_3$, 75MHz): δ = 55.4 (C8), 55.7 (C9), 90.7 (C6), 103.2 (C4), 126.9 (C3), 158.2 (C5), 158.2 (C7), 161.1 (C2), 162.1 (C1). HR-MS (ESI-Q-Tof) calcd for $C_{13}H_{14}ClN_2O_3$ $[M+H]^+$: 281.0688, found: 281.0692. FTIR (ATR): ν = 2994, 2971, 2950, 2838, 1738, 1616, 1599, 1579, 1536, 1472, 1447, 1395, 1370, 1335, 1226, 1204, 1167, 1128 cm^{-1}

6c, 2-chloro-5-mesitylpyrazine ;



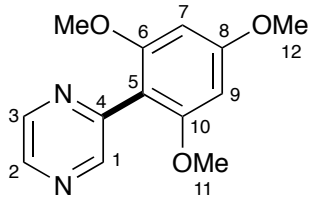
The procedure B, (eluent : cyclohexane /AcOEt) leads to 49 mg of **6c** as a slightly yellow solid (66%); ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.03 (s, 6H, H9), 2.34 (s, 3H, H8), 6.99 (s, 2H, H6), 8.47 (d, J = 1.4 Hz, 1H, H1), 8.72 (d, J = 1.4 Hz, H2); ^{13}C NMR ($CDCl_3$, 100MHz): δ = 20.2 (C9), 21.1 (C8), 128.7 (C6), 132.6 (C4), 136.2 (C5), 138.8 (C7), 144.2 (C1 or C2), 144.8 (C2 or C1), 147.4 (C10), 153.7 (C3). HR-MS (ESI-Q-Tof) calcd for $C_{13}H_{14}ClN_2$ $[M+H]^+$: 233.0840, found: 233.0842 FTIR (ATR): ν = 2952, 2920, 2858, 1737, 1612, 1453, 1308, 1127, 1011 cm^{-1}

7a, 2-chloro-6-(2,4,6-trimethoxyphenyl)pyrazine :



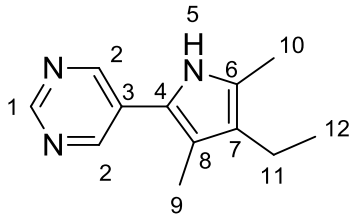
The procedure B, (eluent : cyclohexane /AcOEt) leads to 69 mg of **7a** as a white solid (79%). ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.74 (s, 6H, H9), 3.86 (s, 3H, H8), 6.21 (s, 2H, H6), 8.35 (d, J = 1.0 Hz, 1H, H1), 8.65 (d, J = 1.2Hz, 1H, H2); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 55.4 (C8), 55.8 (C9), 90.7 (C6), 107 (C4), 143.5 (C2), 146.5 (C3), 146.8 (C1*),* 148.5 (C10), 159 (C5), 162.4 (C7). HR-MS (ESI-Q-Tof) calcd for $C_{13}H_{14}ClN_2O_3$ $[M+H]^+$: 281.0688, found: 281.0693. FTIR (ATR): ν = 3068, 3010, 2966, 2940, 2839, 1607, 1585, 1451, 1415, 1226, 1204, 1158, 1121 cm^{-1}

7b, 2-(2,4,6-trimethoxyphenyl)pyrazine :



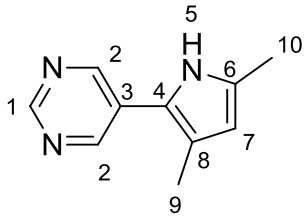
The procedure B, (eluent : cyclohexane /AcOEt) leads to 26 mg of **7b** as a white solid (34% with a purity of 90%). ^{1}H NMR ($CDCl_3$, 300MHz): δ = 3.74 (s, 6H, H11), 3.87 (s, 3H, H12), 6.22 (s, 2H, H7,H9), 8.43 (d, J = 2.6 Hz, 1H, H1), 8.58 (d, J = 1.6 Hz, 1H, H2), 8.66 (dd, J = 2.6, 1.6 Hz, 1H, H3); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 55.5 (C12), 55.9 (C11), 90.8 (C7 C9), 108.1(C4), 141.8 (C2), 143.9 (C3), 148.0 (C1*)*, 150.6 (C5), 159.1 (C6 C10), 162.2 (C8). Spectral data are in agreement with the literature.[10]

8a, 5-(4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)pyrimidine;



The procedure A (purification by column chromatography eluent 6/4 to 100% ethyl acetate) leads to 60 mg of **8a** as a red purple solid/oil (60%). ^{1}H NMR ($CDCl_3$, 300MHz): δ = 1.11 (t, J = 7.6 Hz, 3H, H12), 2.20 (s, 3H, H9), 2.27 (s, 3H, H10), 2.45 (q, J = 7.5 Hz, 2H, H11), 8.43 (s, 1H, H5), 8.78 (s, 2H, H2), 8.97 (s, 1H, H1); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 10.3 (C9 or C10), 11.2 (C10 or C9), 15.5 (C12), 17.4 (C11), 118.3 (C8 or C6 or C7), 118.9 (C6 or C8 or C7), 123.5 (C7 or C6 or C8), 126.6 (C3 or C4), 128.3 (C4 or C3), 153 (C2), 154.6 (C1). HR-MS (ESI-Q-Tof) calcd for $C_{12}H_{16}N_3$ $[M+H]^+$: 202.1339, found: 202.1342. FTIR (ATR): ν = 3331, 3254, 3197, 3067, 2951, 2922, 2862, 1737, 1698, 1570, 1556, 1507, 1449 cm^{-1}

8b, 5-(3,5-dimethyl-1H-pyrrol-2-yl)pyrimidine;

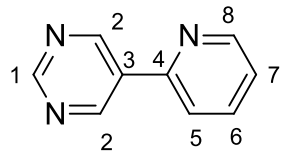


The procedure A (purification by column chromatography eluent 6/4 to 100% ethyl acetate) leads to 54 mg of **8b** as a red purple solid/oil (62%). ^{1}H NMR ($CDCl_3$, 300MHz): δ = 2.26 (s, 3H, H9 or H10), 2.32

[10] A. Kodimuthali, B. C. Chary, P. L. Prasunamba, M. Pal *Tetrahedron Lett.* **2009**, *50*, 1618.

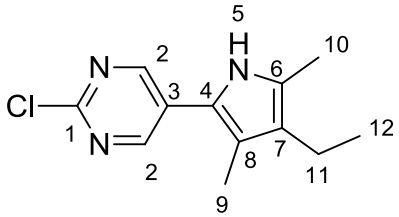
(s, 3H, H10 or H9), 5.90 (d, J = 2.6Hz, 1H, H7), 8.26 (s, 1H, H5), 8.78 (s, 2H, H2), 9.00 (s, 1H, H1); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 12.5 (C9 or C10), 13.0 (C10 or C9), 111.2 (C7), 119.7 (C8 or C6), 119.9 (C6 or C8), 128.1 (C3or C4), 130.4 (C4 or C3), 152.9 (C2), 154.9 (C1). HR-MS (ESI-Q-Tof) calcd for $C_{10}H_{12}N_3$ $[M+H]^+$: 174.1026, found: 174.1028. FTIR (ATR): ν = 3311, 3229, 3192, 3098, 2962, 1686, 1574, 1505, 1478 cm^{-1}

8c, 5-(pyridin-2-yl)pyrimidine and regioisomers;



The procedure A leads to 25 mg of **8c** as a yellow oil (32%, *ortho:meta:para* 60:9:31); **8c**(ortho): ^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.37 (ddd, J = 7.6, 4.8, 1.0 Hz, 1H, H7), 7.78 (dt, J = 7.8, 0.9 Hz, 1H, H5), 7.85 (td, J = 7.7, 1.8 Hz, H6) 8.77 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H, H8), 8.99 (s, 1H, H1), 9.35 (s, 2H, H2); ^{13}C NMR ($CDCl_3$, 100MHz): δ = 120.5 (C7), 123.6 (C5),132.4 (C3), 137.2 (C6), 150.4 (C6), 150.9 (C4), 155.1 (C2), 158.6 (C1). Spectral data are in agreement with the literature.[11] **8c**(meta): ^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.48 (ddd, J = 7.8, 4.8, 0.8 Hz, 1H) (td, J = 8.1, 2.3 Hz, 1H), 8.74 (dd, J = 4.8, 1.6 Hz, 1H), 8.87(dd, J = 2.5, 0.8 Hz, 1H), 8.98 (s, 2H), 9.29 (s, 1H); ^{13}C NMR ($CDCl_3$, 100MHz): δ = 124.0, 130.2, 131.5, 134.3, 147.9, 150.3, 154.9, 158.2. **8c**(para): ^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.53 (d, J = 6.3 Hz, 2H), 8.79 (d, J = 6.3 Hz, 2H), 9.02 (s, 1H), 9.31(s, 1H); ^{13}C NMR ($CDCl_3$, 100MHz): δ = 121.3, 136.3, 140.8, 152.0, 155.0, 158.9. HR-MS (ESI-Q-Tof) calcd for $C_9H_8N_3$ $[M+H]^+$: 158.0713, found: 158.0712. FTIR (ATR): ν = 3007, 2970, 2928, 2826, 1572, 1409, 1365, 1228, 1218 cm^{-1}

9a, 2-chloro-5-(4-ethyl-3,5-dimethyl-1*H*-pyrrol-2-yl)pyrimidine

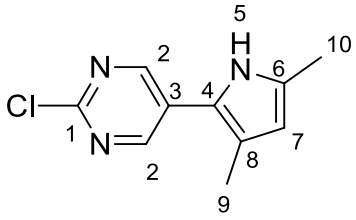


The procedure B (purification by column chromatography 8/2 cyclohexane /AcOEt) leads to 69 mg of **9a** as a red purple oil (58%). ^{1}H NMR ($CDCl_3$ 400 MHz) : δ = 1.11 (t, J = 7.6 Hz, 3H, H12), 2.18 (s, 3H, H9 or H10), 2.27 (s, 3H, H10 or H9), 2.44 (q, J = 7.6 Hz, 2H, H11) 7.92 (bs, 1H, H5), 8.64 (s, 2H, H2); ^{13}C NMR ($CDCl_3$, 100MHz): δ = 10.3 (C12), 11.2 (C10 or C9), 15.4 (C9 or C10), 17.5 (C11), 117.8 (C4), 118.9 (C6), 123.9 (C7 or C8), 126.8 (C8 or C7), 127.1 (C3), 155.4(C2), 156.9 (C1). HR-MS (ESI-Q-Tof) calcd for

[11] S. Ganesamoorthy, H.Shanmugasundaram, R. Karvembu, *J. Mol. Cat.*, **2013**, *371*, 118

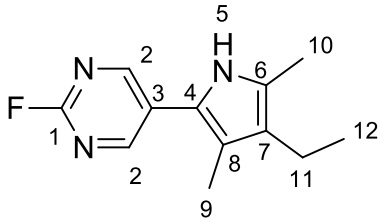
$C_{12}H_{15}ClN_3$ $[M+H]^+$: 236.0949, found: 236.0946. FTIR (ATR): ν = 3302, 3016, 2971, 2954, 1739, 1366, 1229, 1217 cm^{-1}

9b, 2-chloro-5-(3,5-dimethyl-1H-pyrrol-2-yl)pyrimidine;



The procedure B (purification by column chromatography 8/2 cyclohexane /AcOEt) leads to 71 mg of **9b** as a red purple solid (68%). ^1H NMR ($CDCl_3$, 300MHz): δ = 2.23 (s, 3H, H9 or H10), 2.32 (s, 3H, H10 or H9), 5.91 (d, J = 2.6Hz, 1H, H7), 8.11 (s, 1H, H5), 8.64 (s, 2H, H2); ^{13}C NMR ($CDCl_3$, 100MHz): δ = 12.5 (C9 or C10), 13.0 (C10 or C9), 111.5 (C7), 118.5 (C8 or C6), 120.5 (C6 or C8), 126.7 (C3 or C4), 130.9 (C4 or C3), 155.2 (C2), 156.8 (C1). HR-MS (ESI-Q-Tof) calcd for $C_{10}H_{11}ClN_3$ $[M+H]^+$: 208.0636, found: 208.0629. FTIR (ATR): ν = 3311, 2961, 2910, 2871, 1531, 1500, 1473, 1448, 1400, 1387, 1164 cm^{-1}

10, 2-fluoro-5-(4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)pyrimidine ;



The procedure B, (eluent : 9/1 to 8/2 Cyclohexane/AcOEt) leads to 70 mg of **10** as a yellow which quickly turns black (64%); ^1H NMR ($CDCl_3$, 300MHz): δ = 1.12 (t, J = 7.5Hz, 3H, H12), 2.17 (s, 3H, H9 or H10), 2.27 (s, 3H, H10 or H9), 2.45 (q, J = 7.6 Hz, 2H, H11), 7.93 (bs, 1H, H5), 8.63 (d, J = 1.4Hz, 2H, H2); ^{13}C NMR ($CDCl_3$, 100MHz): δ = 10.1 (C12), 11.2 (C10 or C9), 15.5 (C9 or C10), 17.5 (C11), 117.9 (d, J = 2.1 Hz, C4), 118.0 (C6), 123.4 (C8 or C7), 126.4 (C7 or C8), 126.7 (d, J = 5.7 Hz, C3), 157.1 (d, J = 11.3 Hz, C2), 160.6 (d, J = 219 Hz, C1); ^{19}F NMR ($CDCl_3$, 162MHz): δ = -49.6. HR-MS (ESI-Q-Tof) calcd for $C_{12}H_{15}FN_3$ $[M+H]^+$: 220.1245, found: 220.1248. FTIR (ATR): ν = 3320, 3211, 2956, 2925, 2865, 1567, 1507, 1469, 1450, 1436, 1427, 1303 cm^{-1}

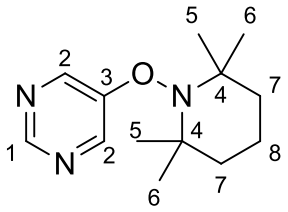
General procedure with trapping using TEMPO:

A solution of 5-bromopyrimidine (1 eq., 80 mg, 0.503 mmol), TEMPO (1eq) is stirred in (5ml of) ACN under nitrogen atmosphere in a glass tube. The solution is irradiated with a UV lamp (distance 8-10cm power 100%) during 24h.

After reaction the crude mixture is directly concentrated and then purified by column chromatography (eluent: Cyclohexane/Ethyl Acetate).

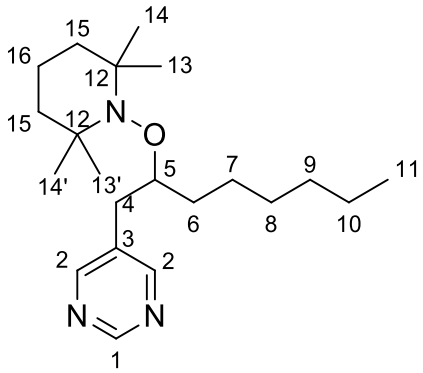
The second reaction used the same protocol with additional 10 equivalents of 1-octene.

11, 5-[(2,2,6,6-tetramethylpiperidin-1-yl)oxy]pyrimidine ;



The procedure B, (eluent : 8/2 cyclohexane /AcOEt) leads to 40 mg of **11** as a oil (34%). ^{1}H NMR ($CDCl_3$, 400MHz) = δ = 1.00 (s, 6H, H5 or H6), 1.23(s, 6H, H6 or H5) 1.42 – 1.65 (m, 6H, H7 and H8), 8.64 (s, 2H, H2), 8.75 (s, 1H, H1); ^{13}C NMR ($CDCl_3$, 100MHz): δ = 16.7 (C8), 20.3 (C7), 32.3 (C5 or C6), 39.6 (C6 or C5), 60.9 (C4), 143.2 (C2), 151.1 (C1), 157.1 (C3). HR-MS (ESI-Q-Tof) calcd for $C_{13}H_{22}N_3O$ $[M+H]^+$: 236.1757, found: 236.1762. FTIR (ATR): ν = 3016, 2978, 2950, 2934, 1737, 1557, 1399, 1255, 1230, 1183 cm^{-1}

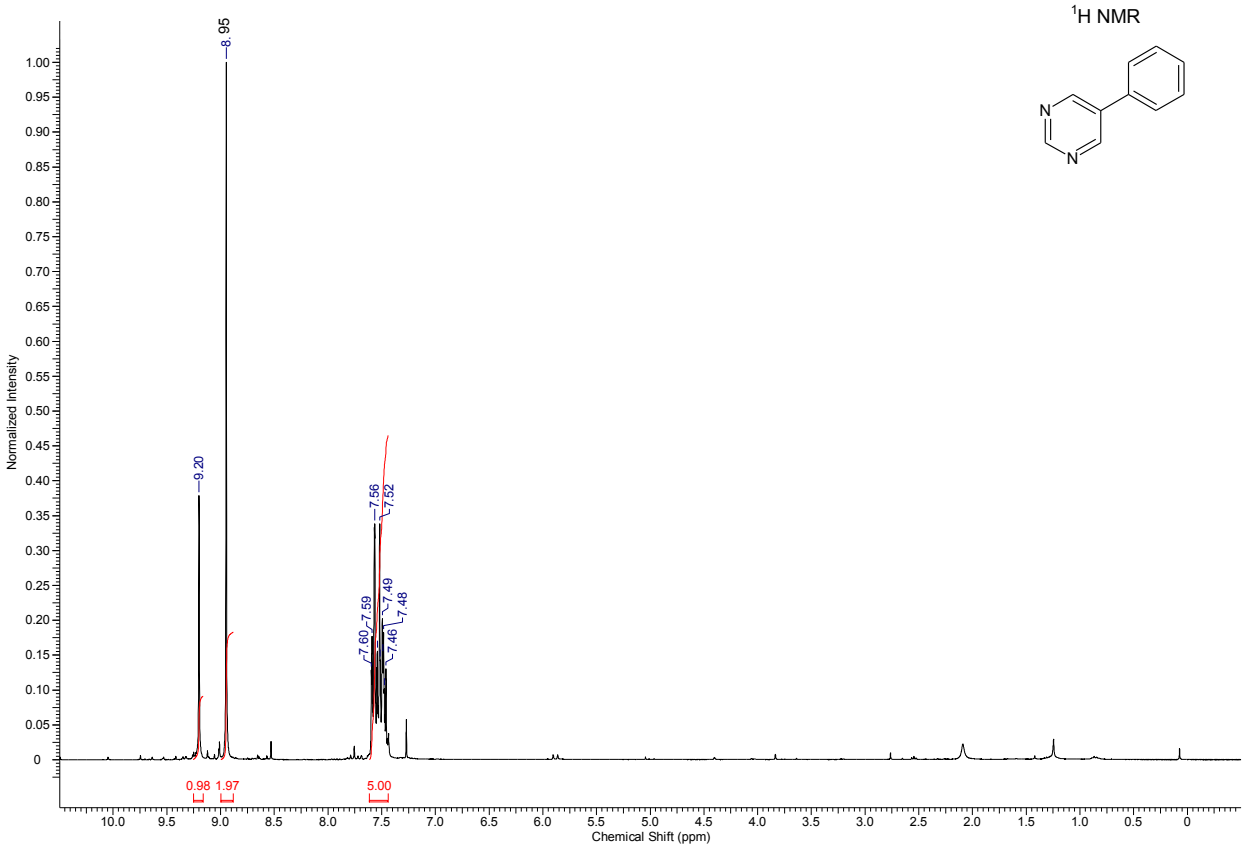
12, 5-(2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)octyl)pyrimidine)



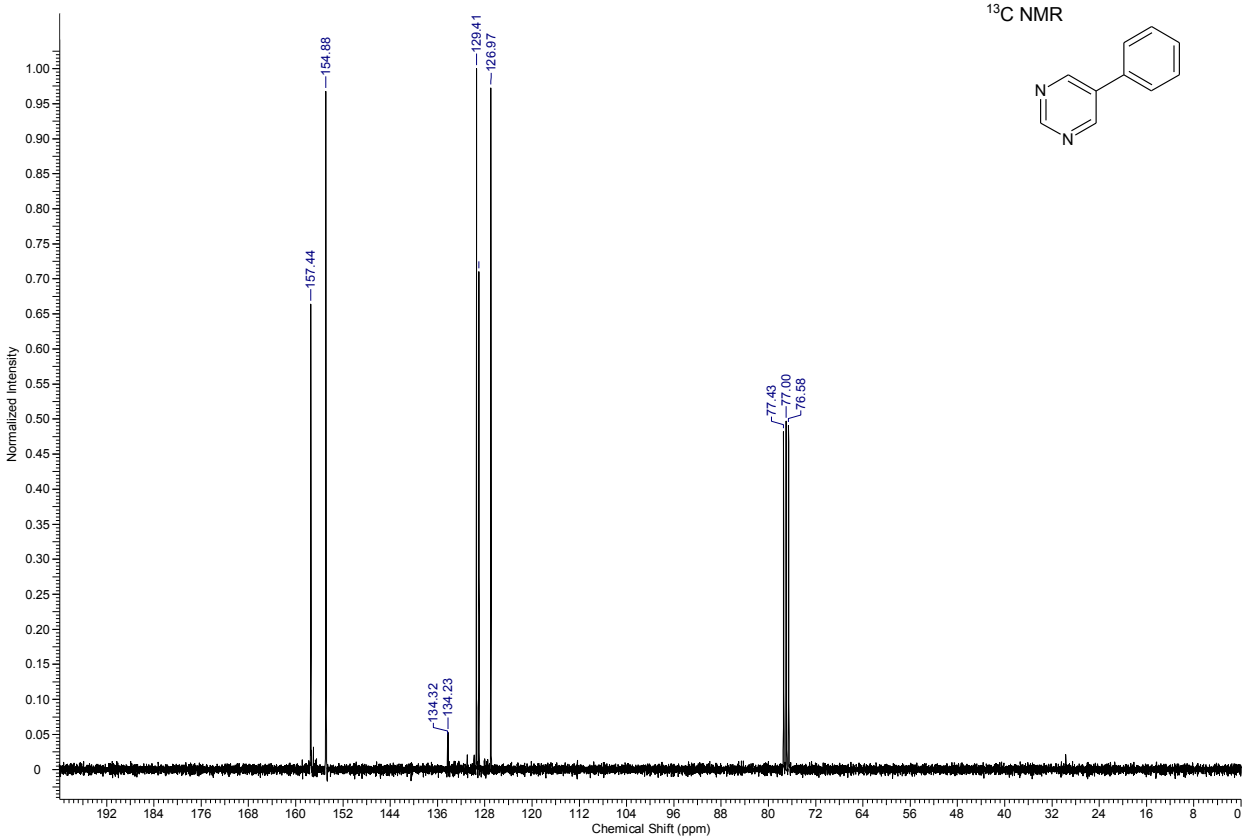
Purification (eluent : 95/05 cyclohexane /AcOEt) leads to 98 mg of **12** as a yellow soild (50%); ^{1}H NMR ($CDCl_3$, 400MHz): δ = 0.86 (m, 3H, H11), 0.98 (s, 3H, H13 or 13' or H14 or H14'), 1.03 (s, 3H, H13 or H13' or H14 or H14'), 1.09 (s, 6H H14/14' or H13/13'), 1.25 (m, 8H, H7, to H10), 1.61-1.41 (m, 7H, H6,H15 and H16), 1.78 (m, 1H, H6), 2.62 (dd, J = 13.7, 6.9 Hz, 1H, H4), 3.10 (dd, J = 13.6, 5.5 Hz, 1H, H4), 3.93 (q, J = 6.1 Hz, 1H, H5), 8.59 (d, J = 1.4 Hz, 2H, H2), 9.05 (s, 1H, H1). ^{13}C NMR ($CDCl_3$, 100MHz): δ = 14 (C11), 17.2 (C16), 20.4 (C13/C13' or C14/14'), 20.6 (C13/13' or C14/14'), 22.5 (C7),

29.4 (C8 or C9), 31.7 (C9 or C8), 32.4 (C6 or C4), 34.3 (C4 or C6), 34.2 (C13/C13' or C14/14'), 34.3 (C13/C13' or C14/14'), 40.2 (C15), 59.8 (C12), 82 (C5), 133.1 (C3), 156.5(C1), 157.5 (C2). HR-MS (ESI-Q-Tof) calcd for $C_{21}H_{39}N_3O$ $[M+H]^+$: 348.3009, found: 348.3008 FTIR (ATR): ν = 2928, 2871, 2857, 1558, 1466, 1408, 1377, 1360, 1257 cm^{-1}

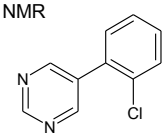
^{1}H NMR



^{13}C NMR

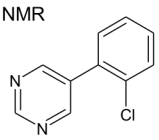


^{1}H NMR

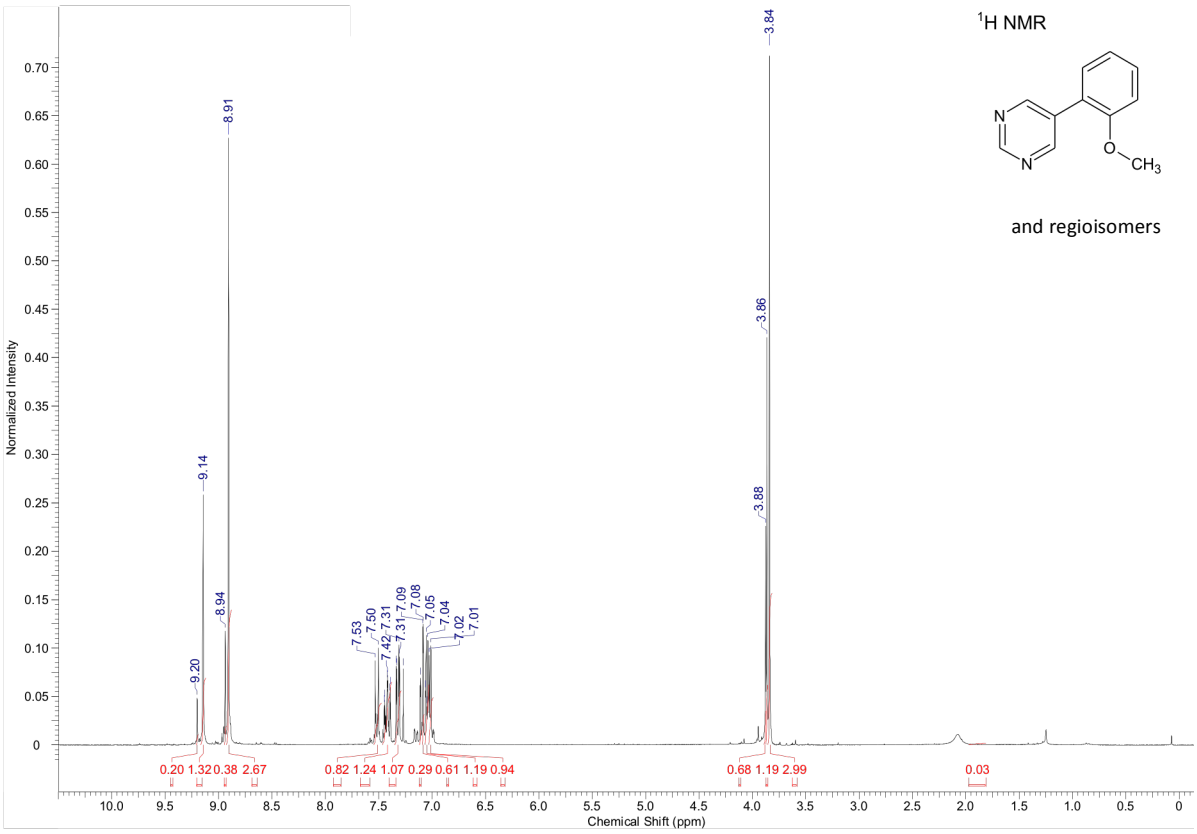


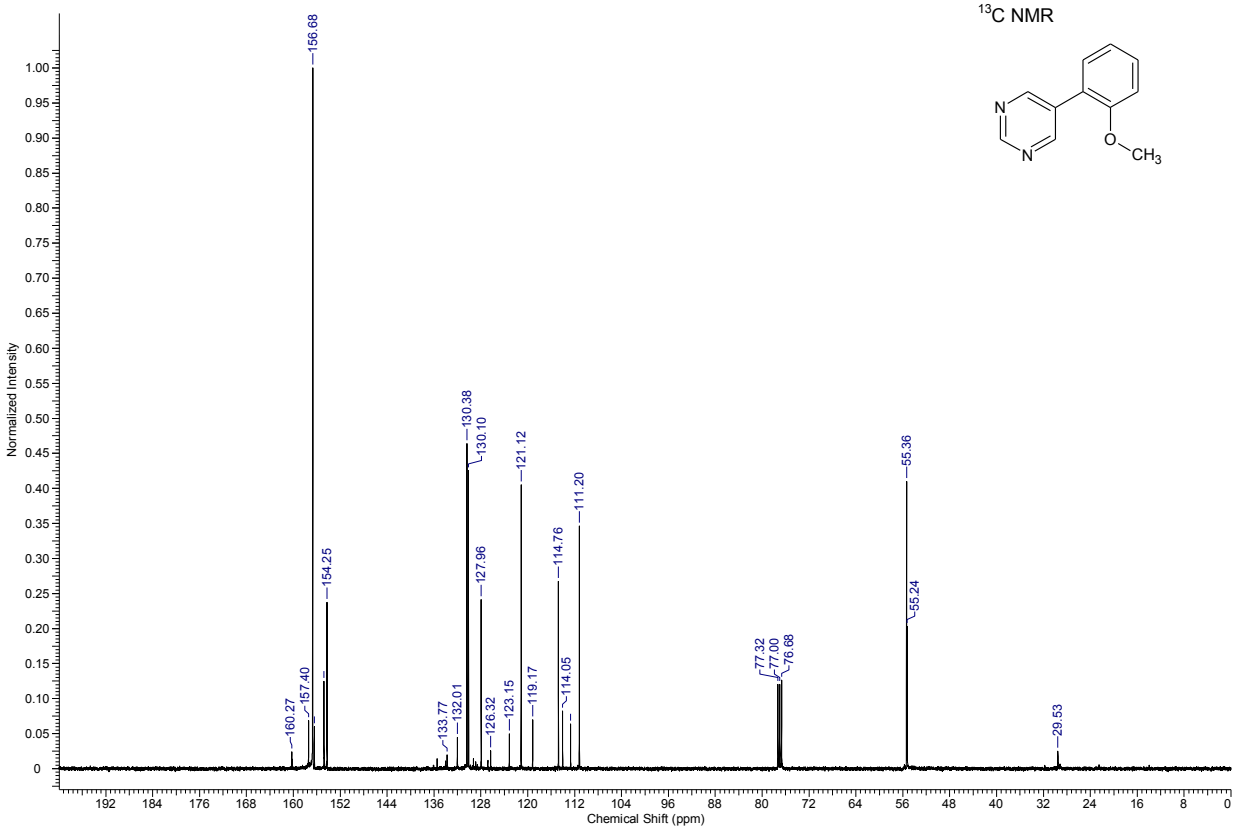
and regioisomers

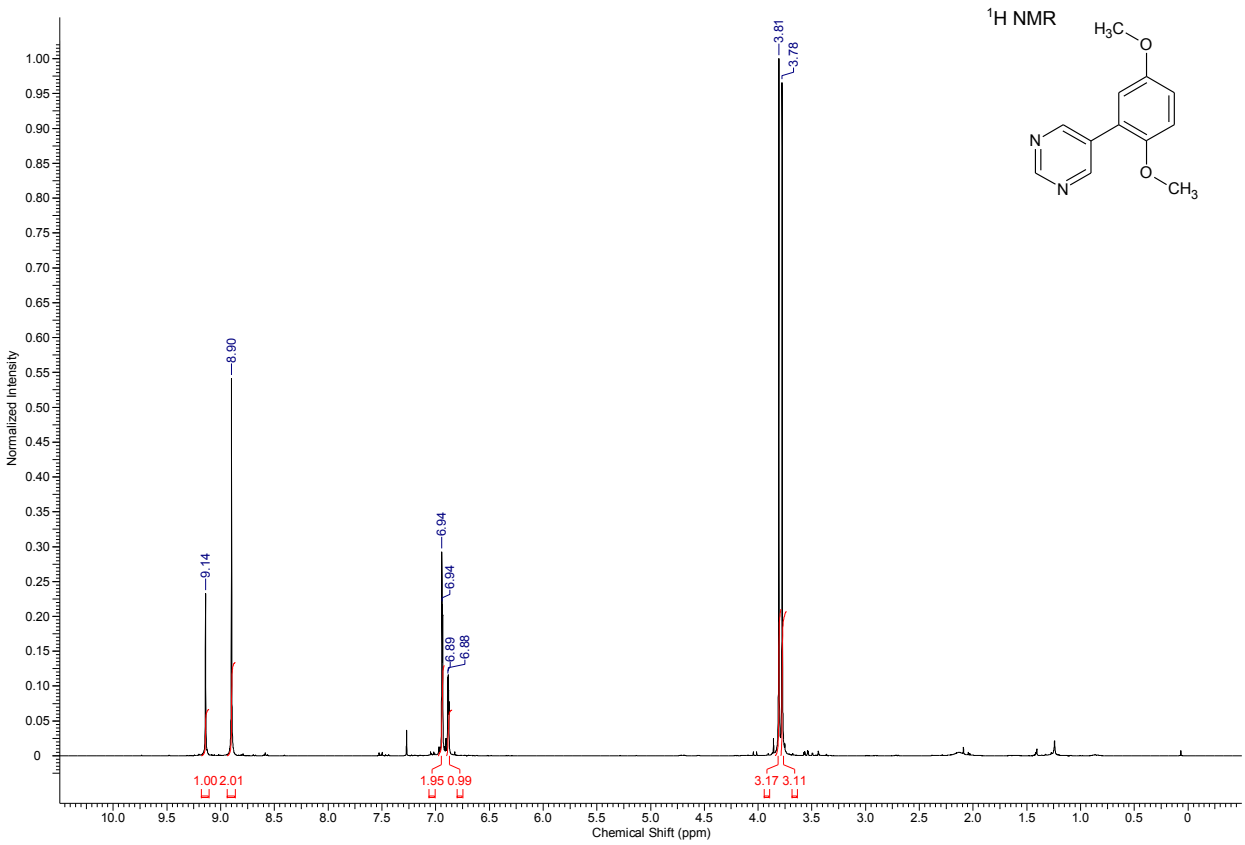
^{13}C NMR

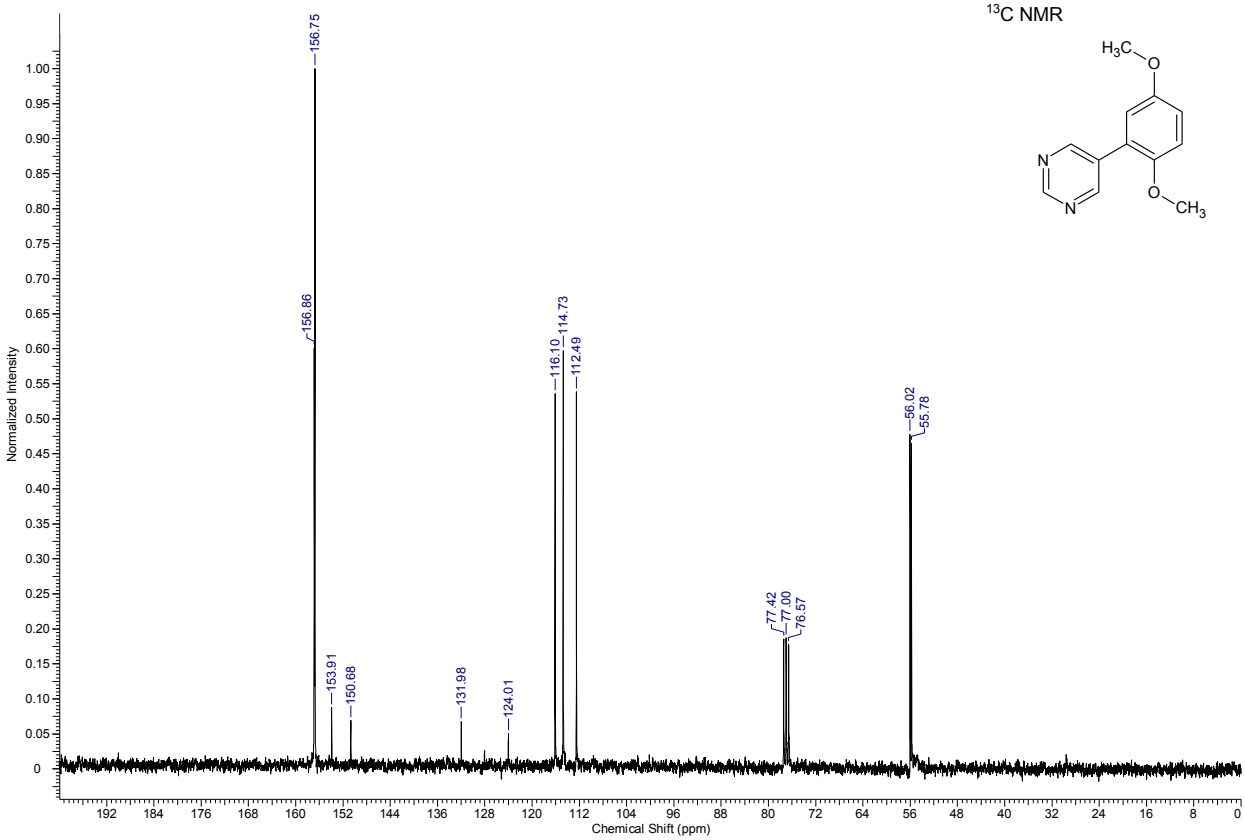


and regioisomers

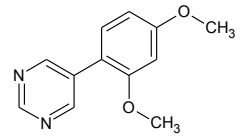

^{1}H NMR
and regioisomers
Normalized Intensity
Chemical Shift (ppm)
3.84
8.91
3.86
9.14
3.88
8.94
9.20
7.53
7.50
7.42
7.31
7.31
7.09
7.08
7.05
7.04
7.02
7.01
0.20 1.32 0.38 2.67
0.82 1.24 1.07 0.29 0.61 1.19 0.94
0.68 1.19 2.99
0.03


^{13}C NMR
Normalized Intensity
Chemical Shift (ppm)
156.68
154.25
130.38
130.10
121.12
127.96
111.20
114.76
55.36
55.24
160.27
157.40
133.77
132.01
126.32
123.15
119.17
114.05
77.32
77.00
76.68
29.53


^{1}H NMR
Normalized Intensity
Chemical Shift (ppm)
9.14
8.90
6.94
6.94
6.89
6.88
3.81
3.78
1.00 2.01
1.95 0.99
3.17 3.11

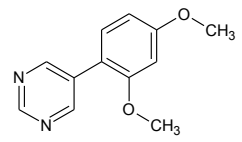

^{13}C NMR
Normalized Intensity
Chemical Shift (ppm)
156.75
156.86
153.91
150.68
131.98
124.01
116.10
114.73
112.49
77.42
77.00
76.57
56.02
55.78

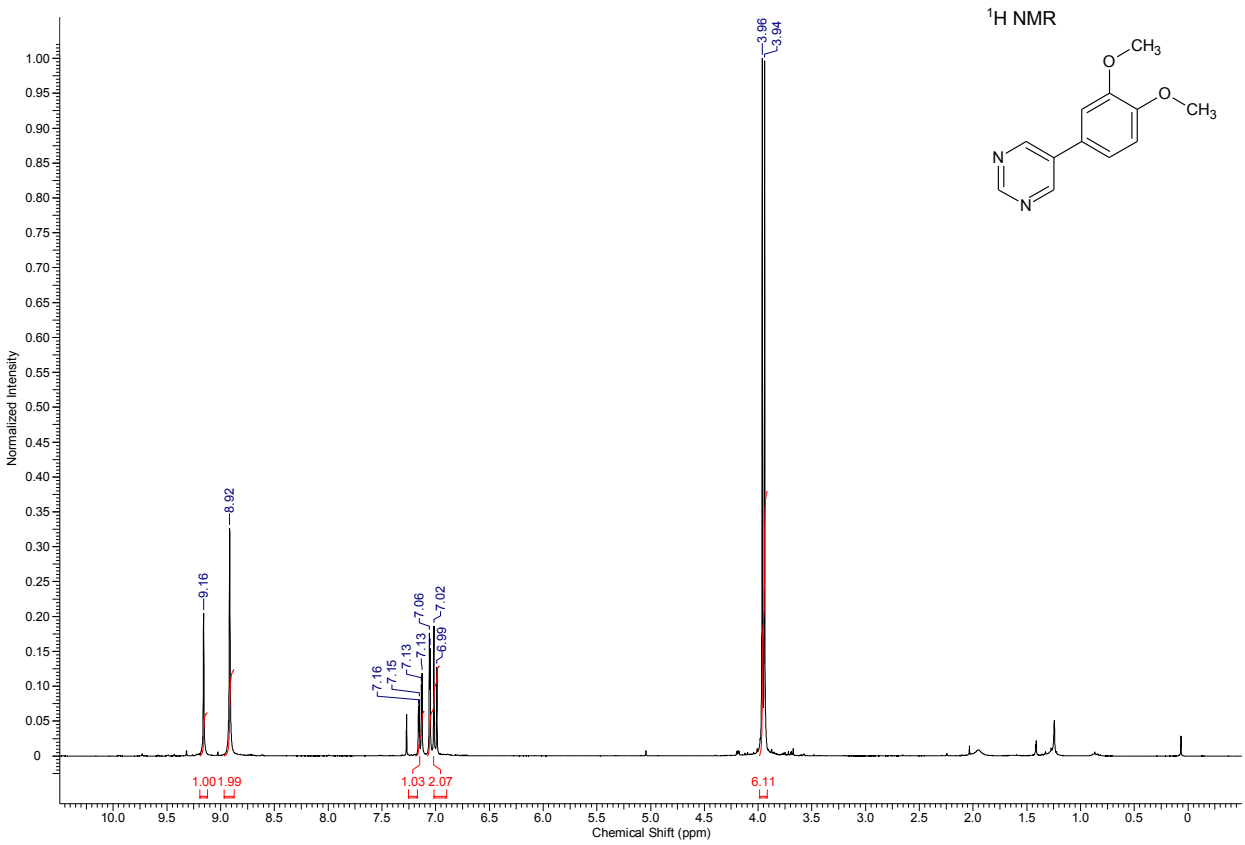
^{1}H NMR

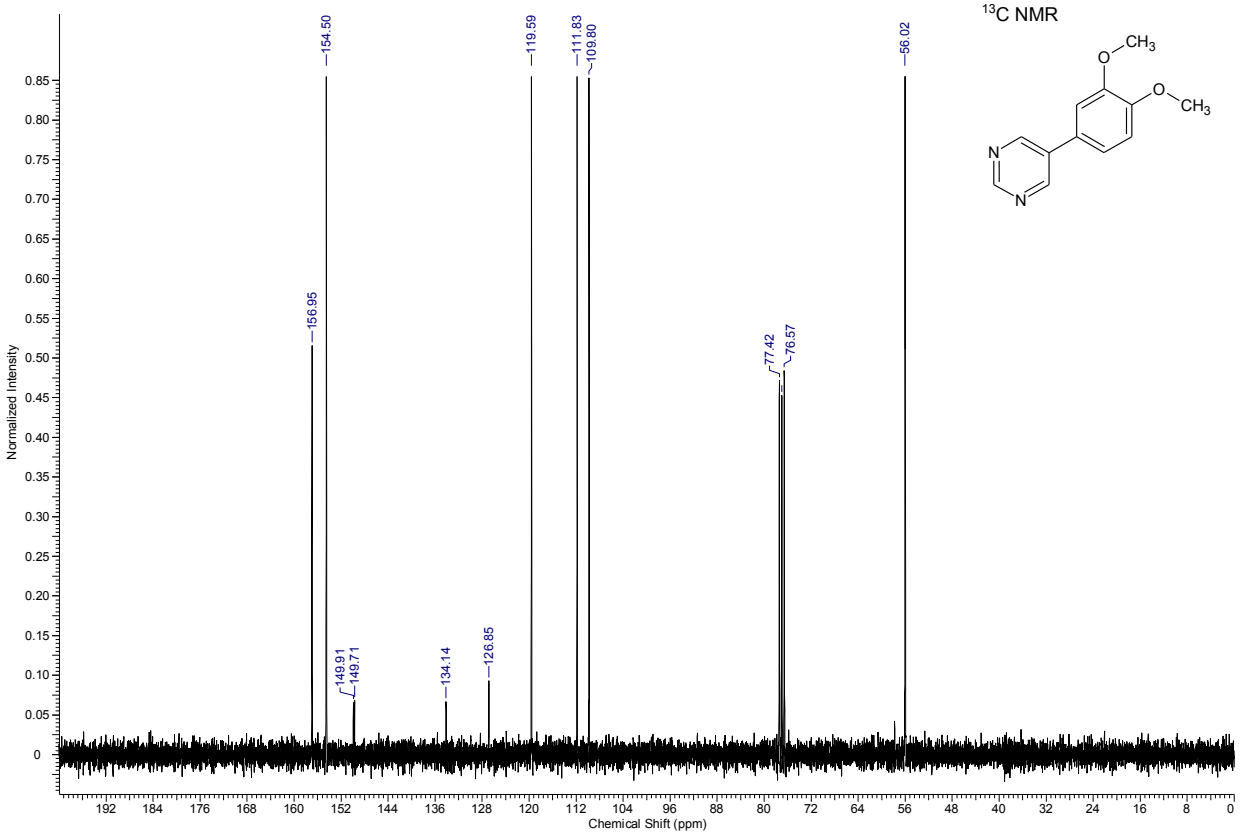


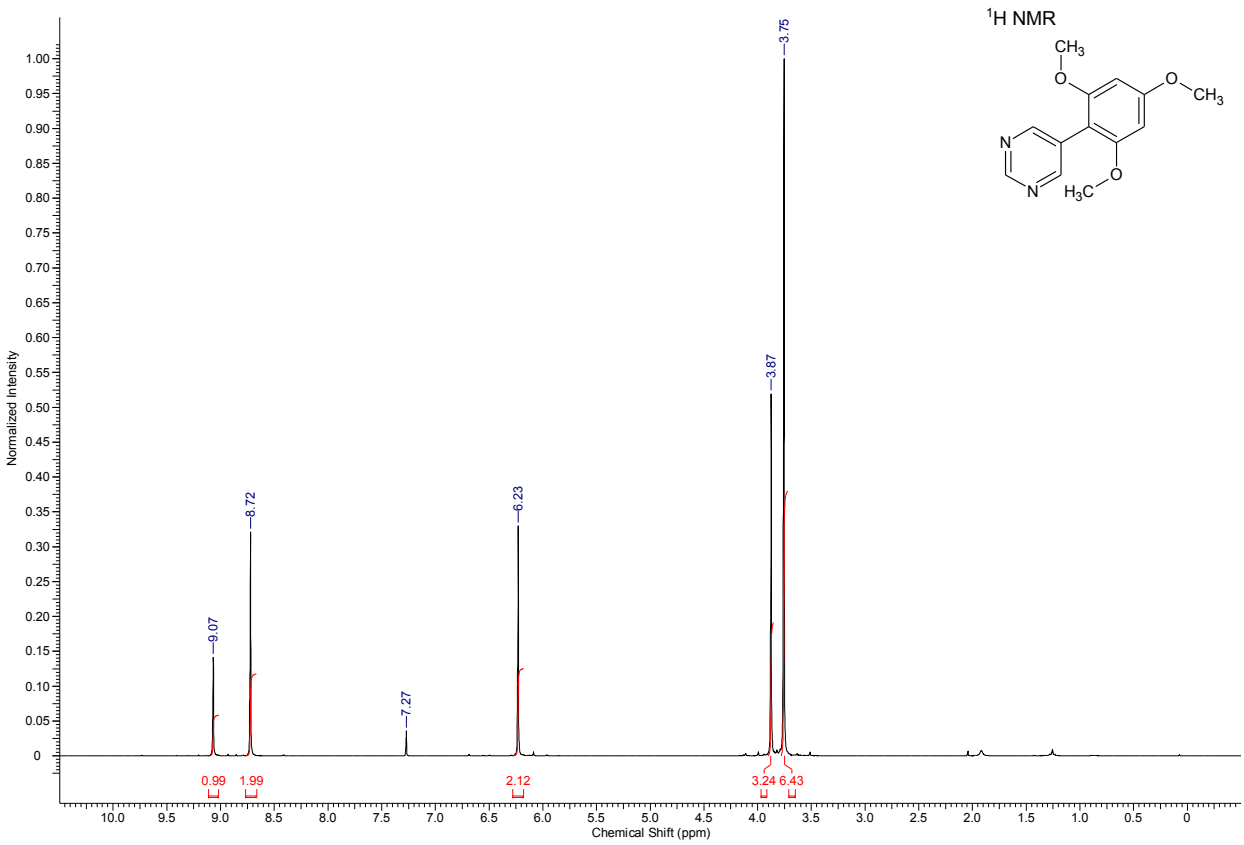
Contaminated by regioisomers

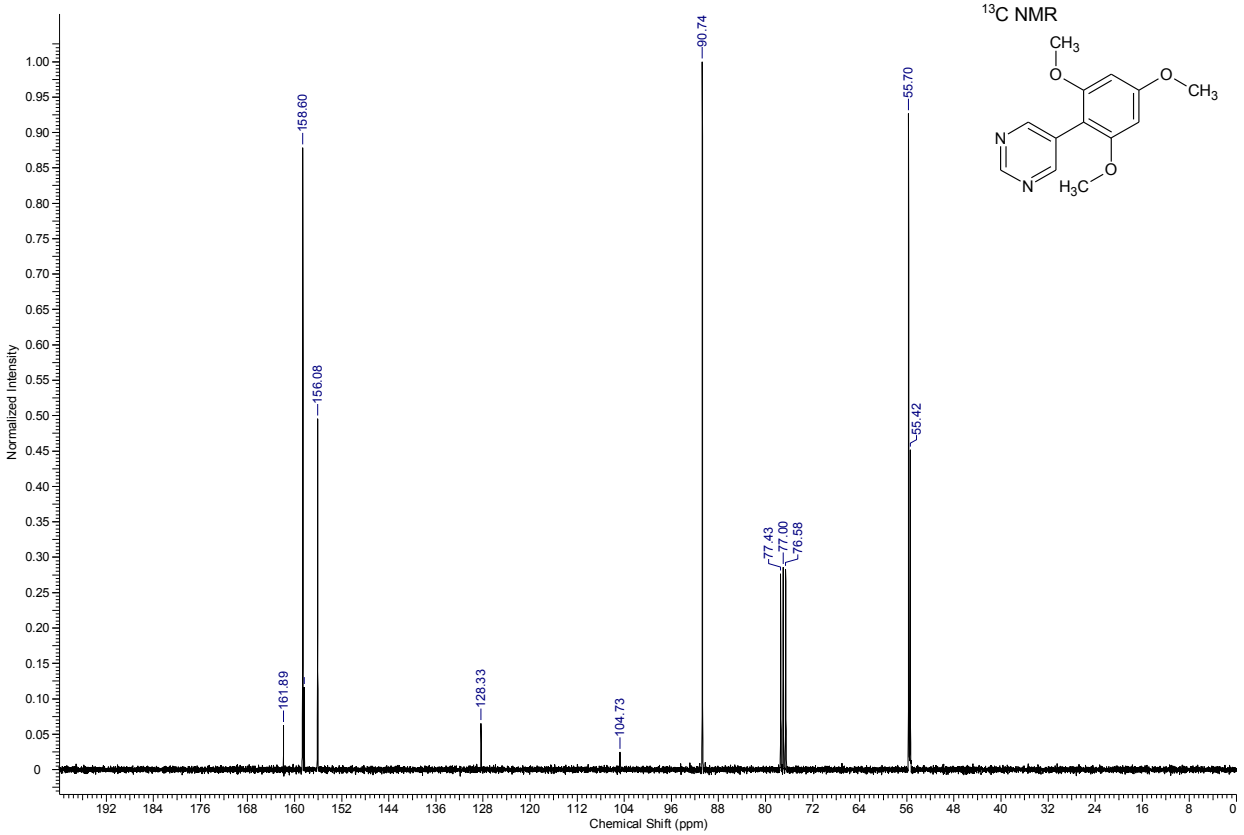
^{13}C NMR

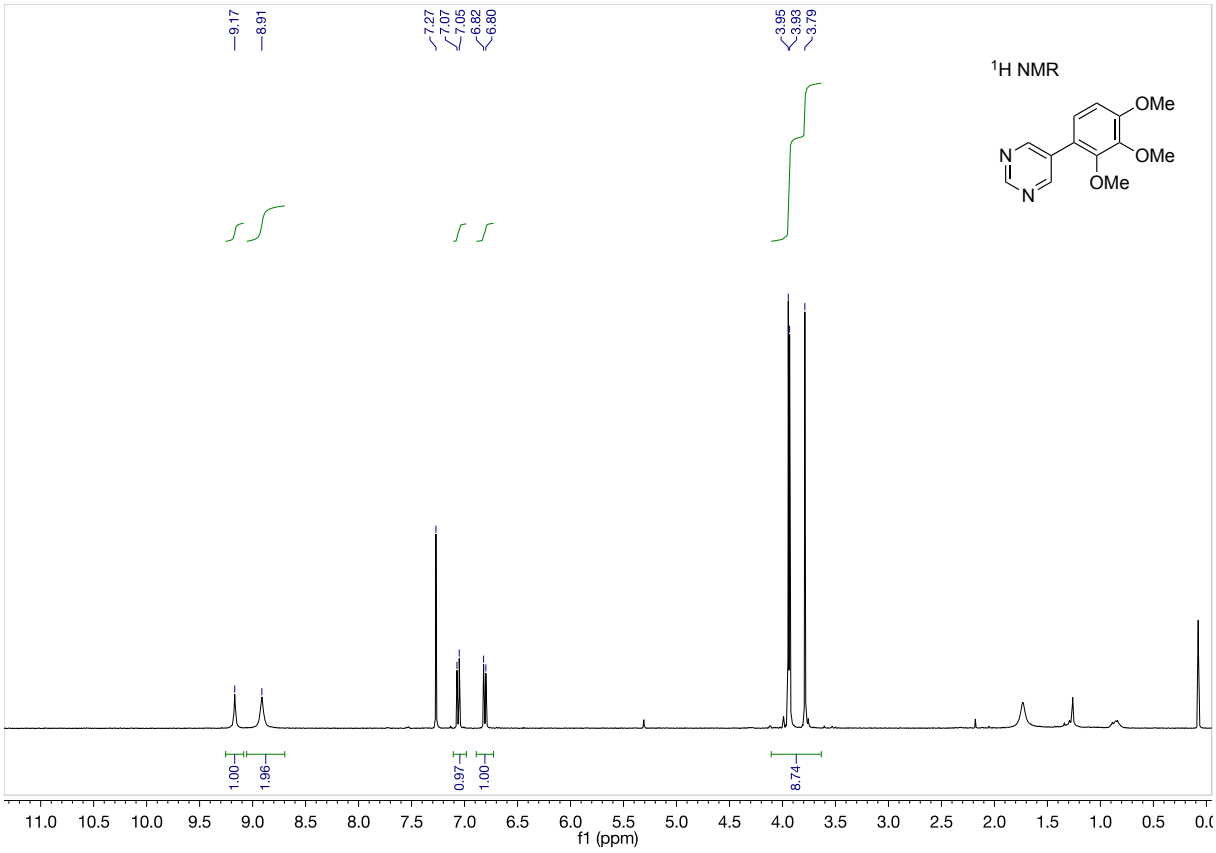


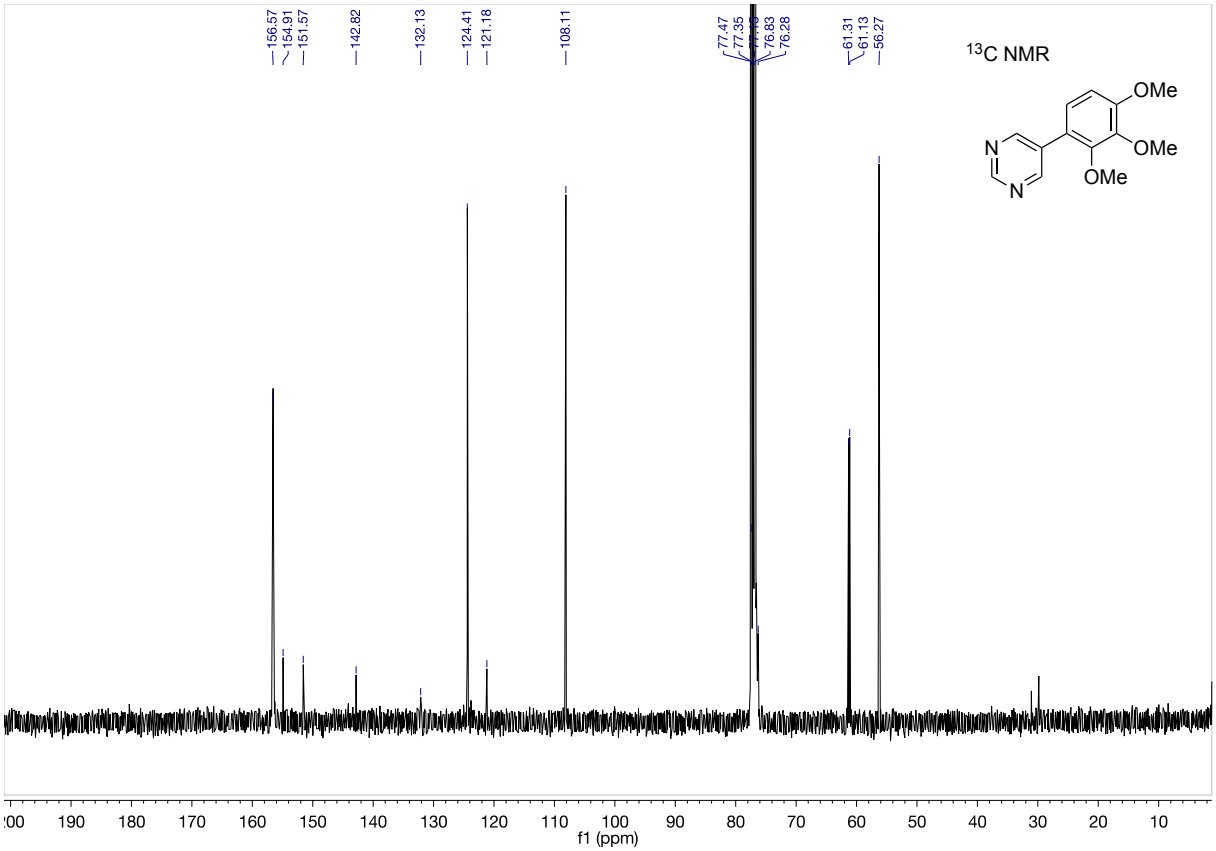

^{1}H NMR
Normalized Intensity
Chemical Shift (ppm)
9.16
8.92
7.16
7.15
7.13
7.06
7.02
6.99
3.96
3.94
1.00 1.99 1.03 2.07 6.11

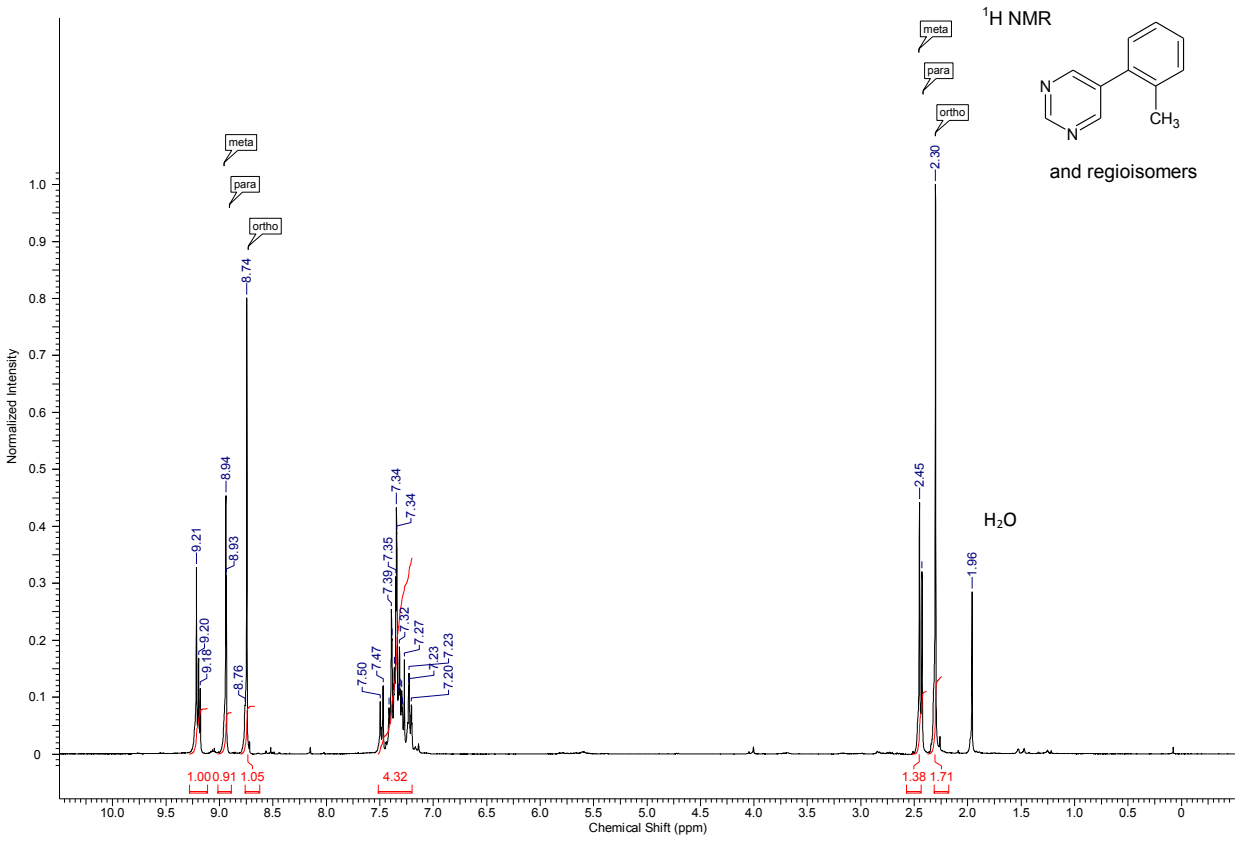

^{13}C NMR
Normalized Intensity
Chemical Shift (ppm)
154.50
156.95
149.91
149.71
134.14
126.85
119.59
111.83
109.80
77.42
76.57
56.02

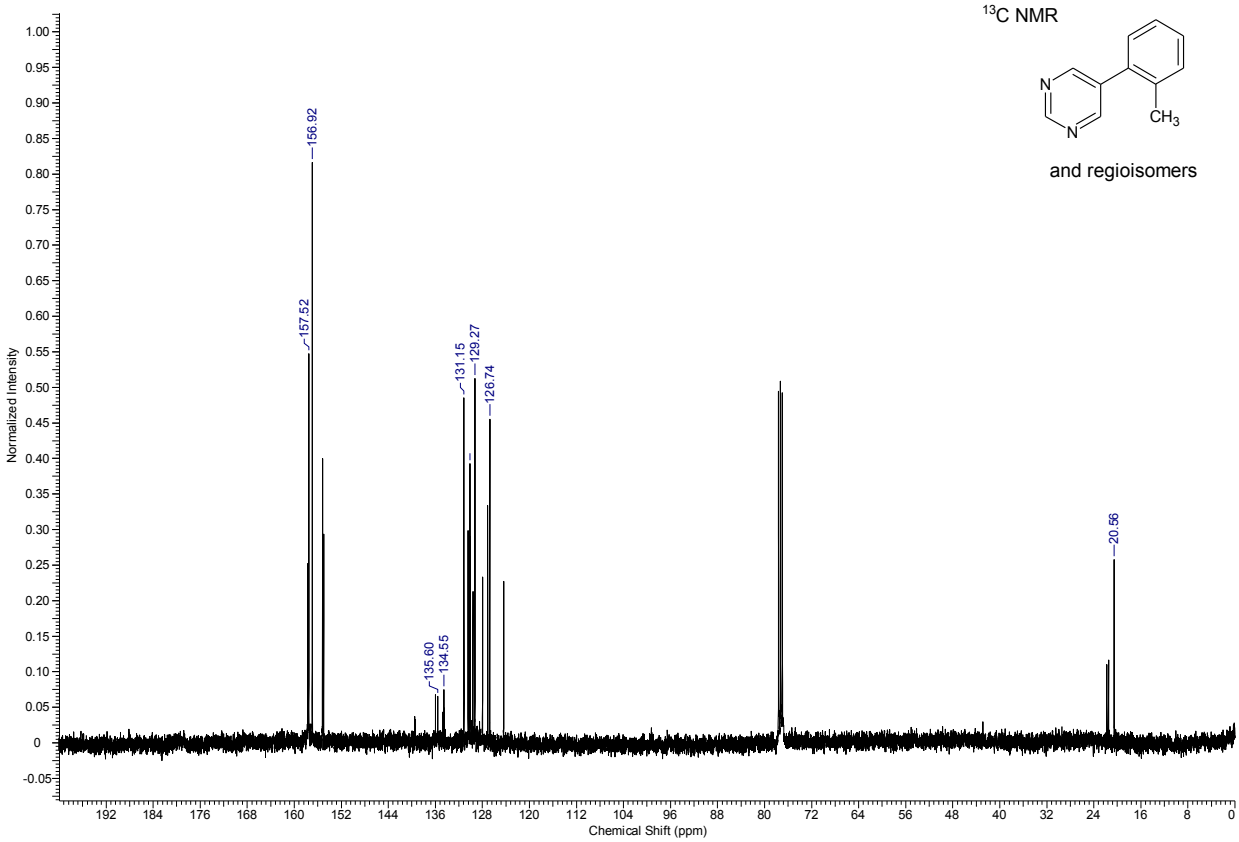

^{1}H NMR
Normalized Intensity
Chemical Shift (ppm)
9.07
8.72
7.27
6.23
3.87
3.75
0.99
1.99
2.12
3.24
6.43

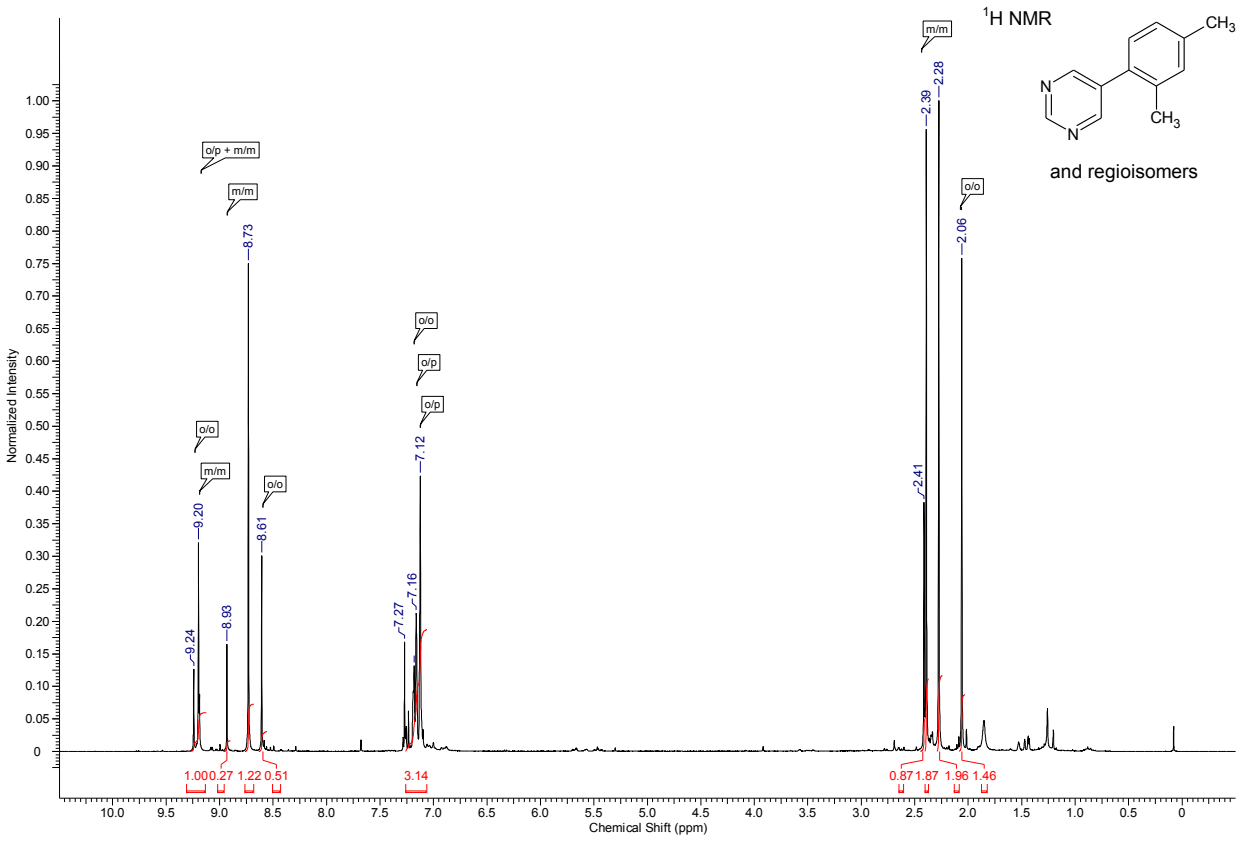

^{13}C NMR
Normalized Intensity
Chemical Shift (ppm)
161.89
158.60
156.08
128.33
104.73
90.74
77.43
77.00
76.58
55.70
55.42

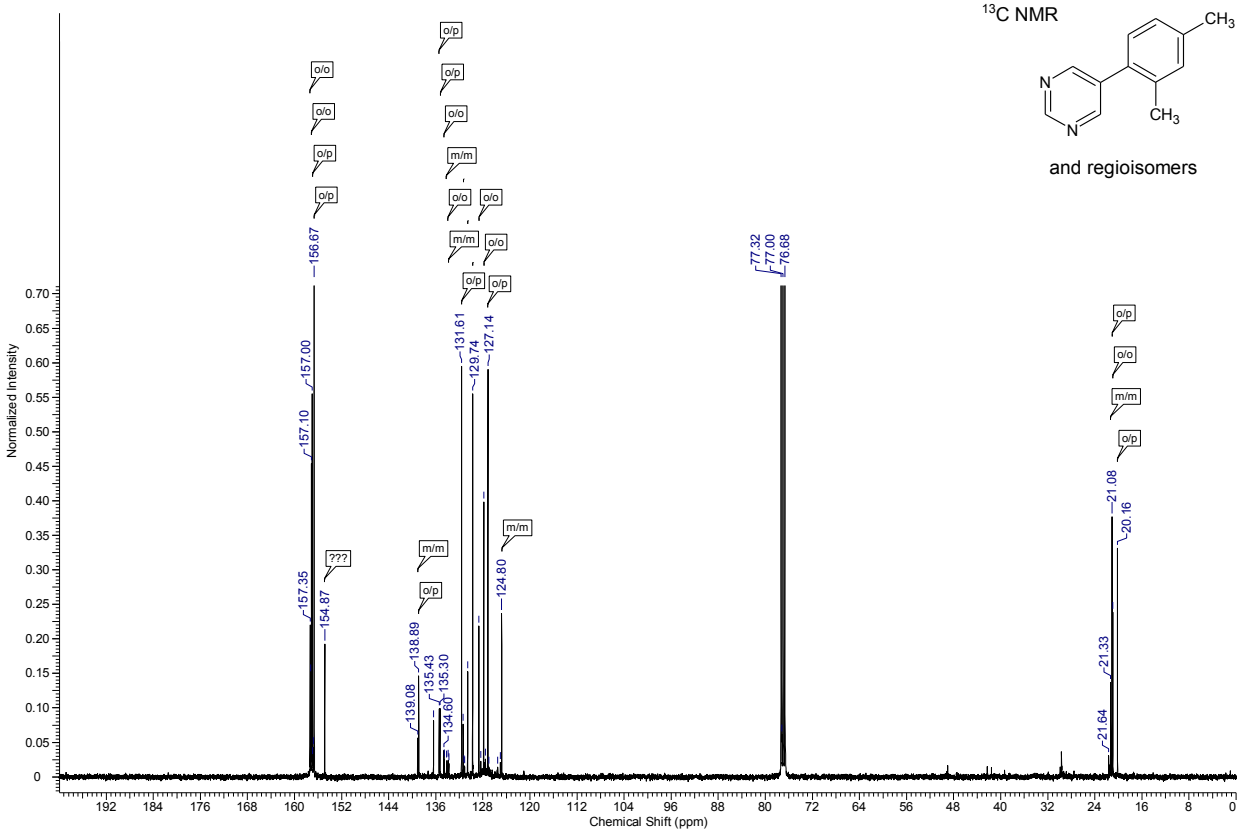

9.17
8.91
7.27
7.07
7.05
6.82
6.80
3.95
3.93
3.79
1H NMR
OMe
OMe
OMe
N
N
1.00
1.96
0.97
1.00
8.74
f1 (ppm)

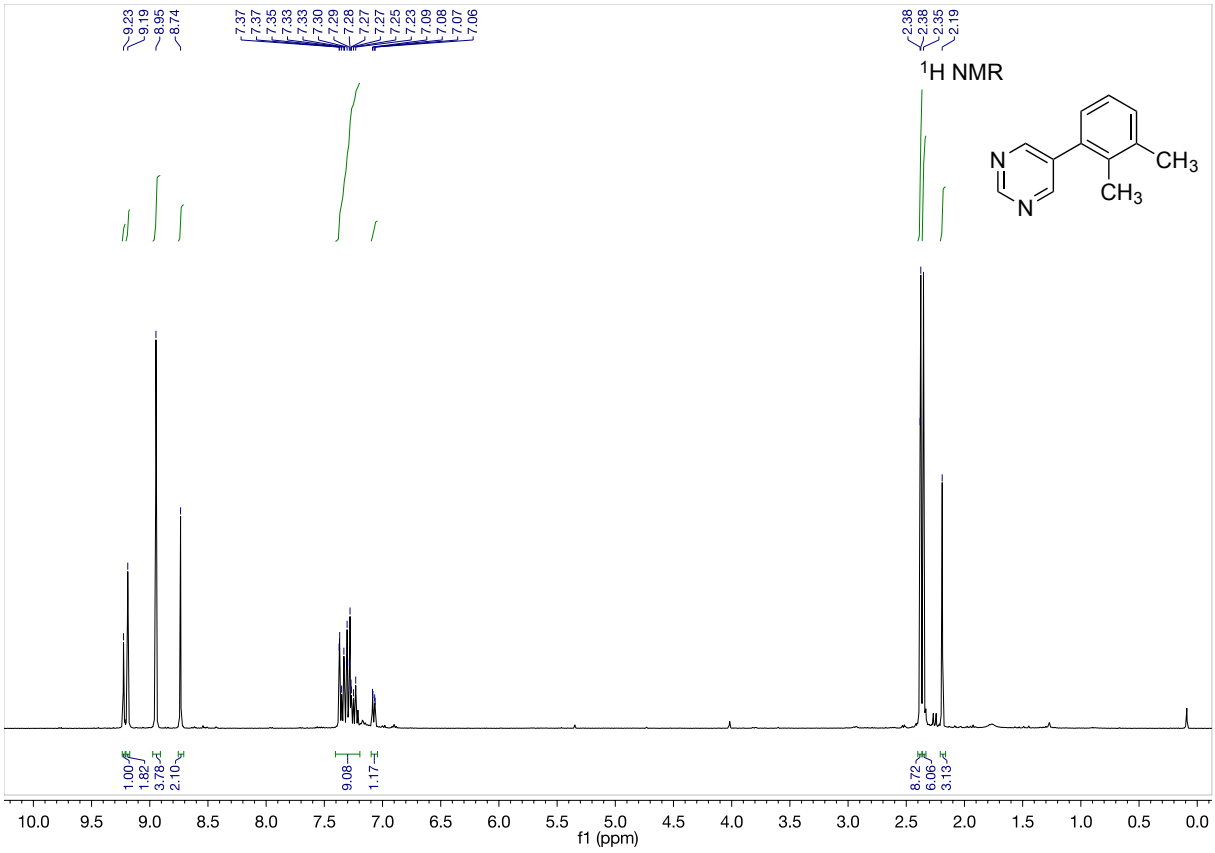

156.57
154.91
151.57
142.82
132.13
124.41
121.18
108.11
77.47
77.35
76.83
76.28
61.31
61.13
56.27
13C NMR
OMe
OMe
OMe
N
N
f1 (ppm)

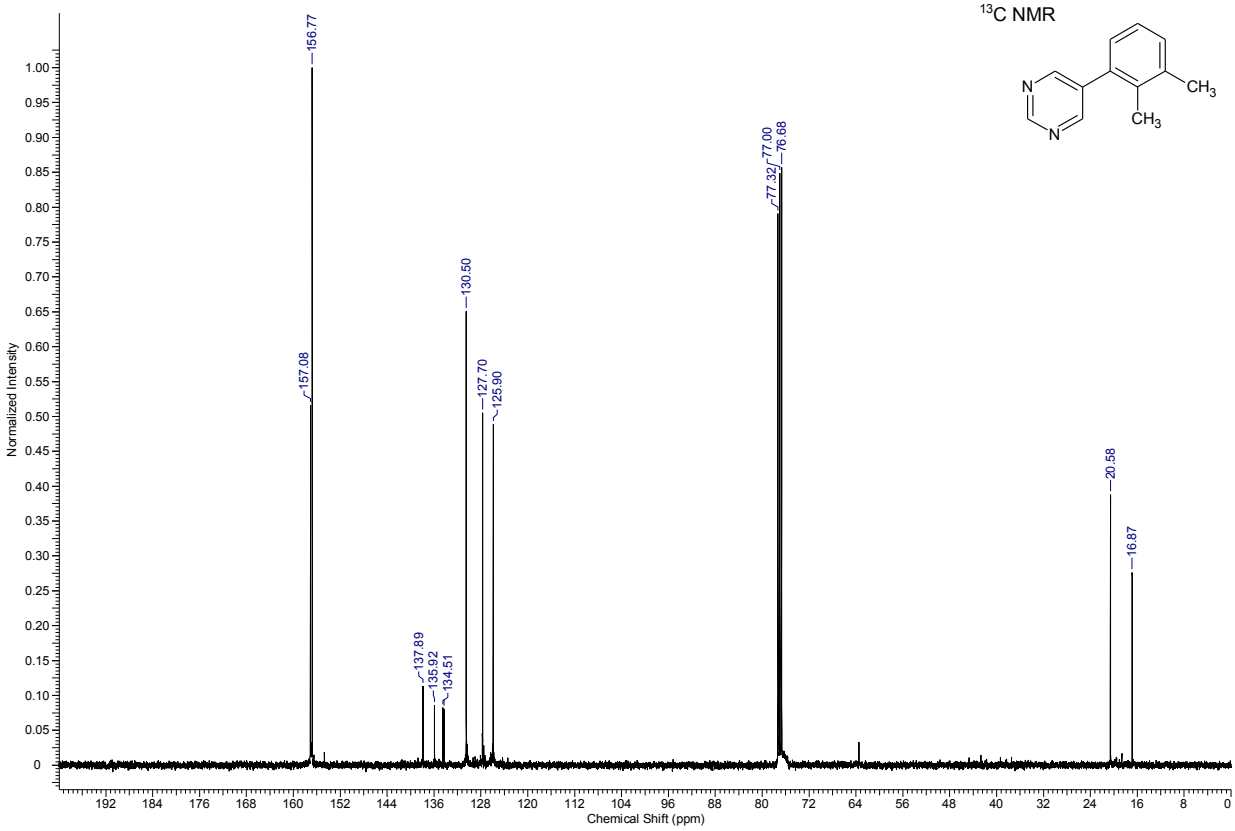

^{1}H NMR
meta
para
ortho
and regioisomers
meta
para
ortho
8.74
2.30
8.94
9.21
8.93
9.20
9.18
8.76
7.34
7.34
7.35
7.39
7.32
7.27
7.50
7.47
7.23
7.20
7.23
2.45
H_2O
1.96
1.00 0.91 1.05
4.32
1.38 1.71
Normalized Intensity
Chemical Shift (ppm)

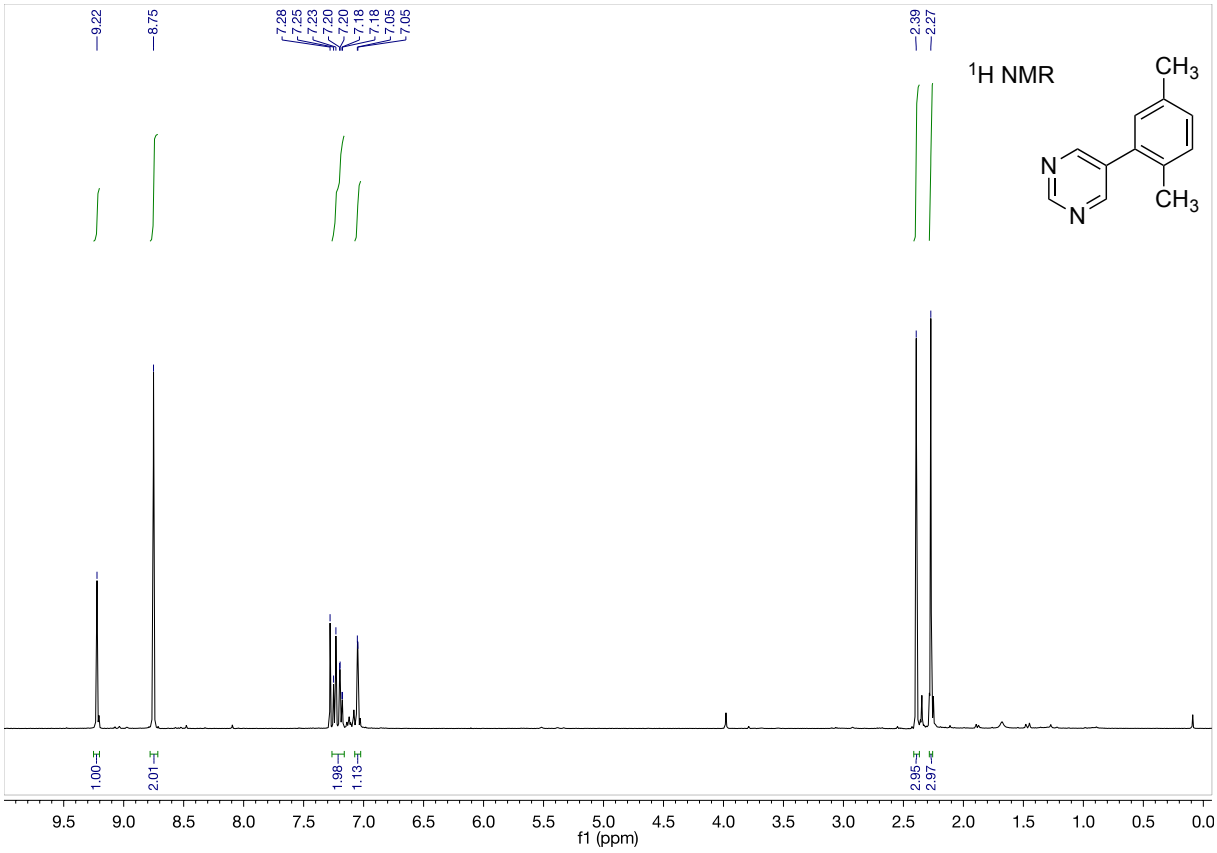

^{13}C NMR
and regioisomers
156.92
157.52
131.15
129.27
126.74
135.60
134.55
20.56
Normalized Intensity
Chemical Shift (ppm)

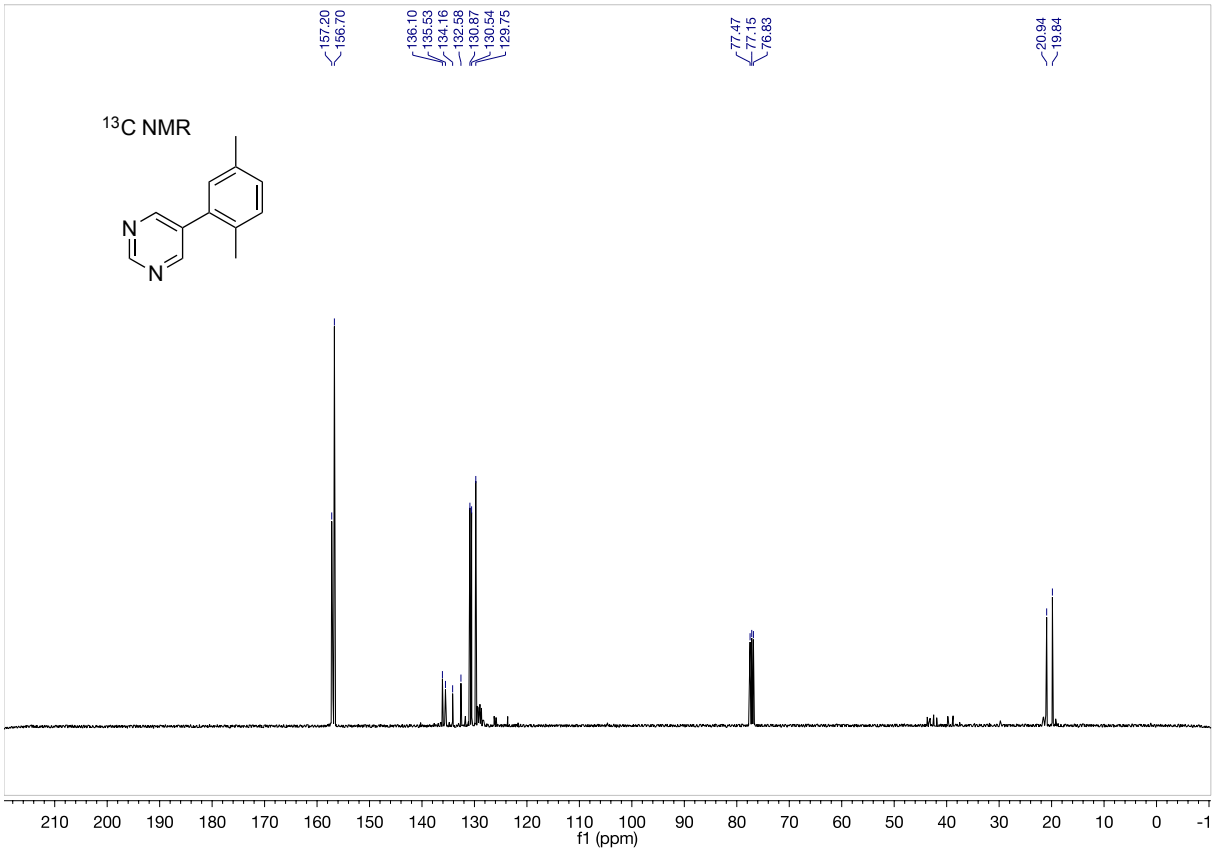

^{1}H NMR
and regioisomers
Normalized Intensity
Chemical Shift (ppm)
9.24
9.20
8.93
8.73
8.61
7.27
7.16
7.12
2.41
2.39
2.28
2.06
1.00 0.27 1.22 0.51
3.14
0.87 1.87 1.96 1.46

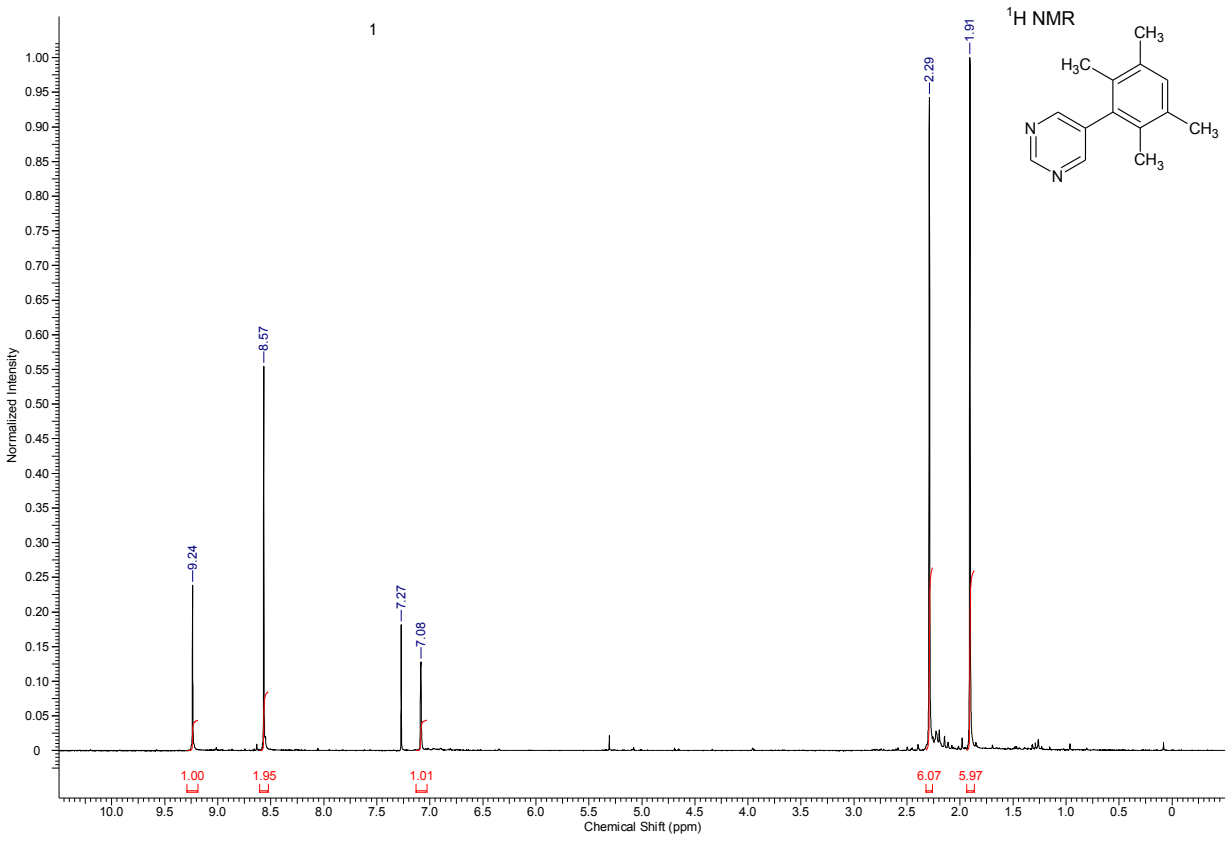

^{13}C NMR
and regioisomers
Normalized Intensity
Chemical Shift (ppm)
156.67
157.00
157.10
157.35
154.87
139.08
138.89
135.43
135.30
134.60
131.61
129.74
127.14
124.80
77.32
77.00
76.68
21.08
20.16
21.33
21.64

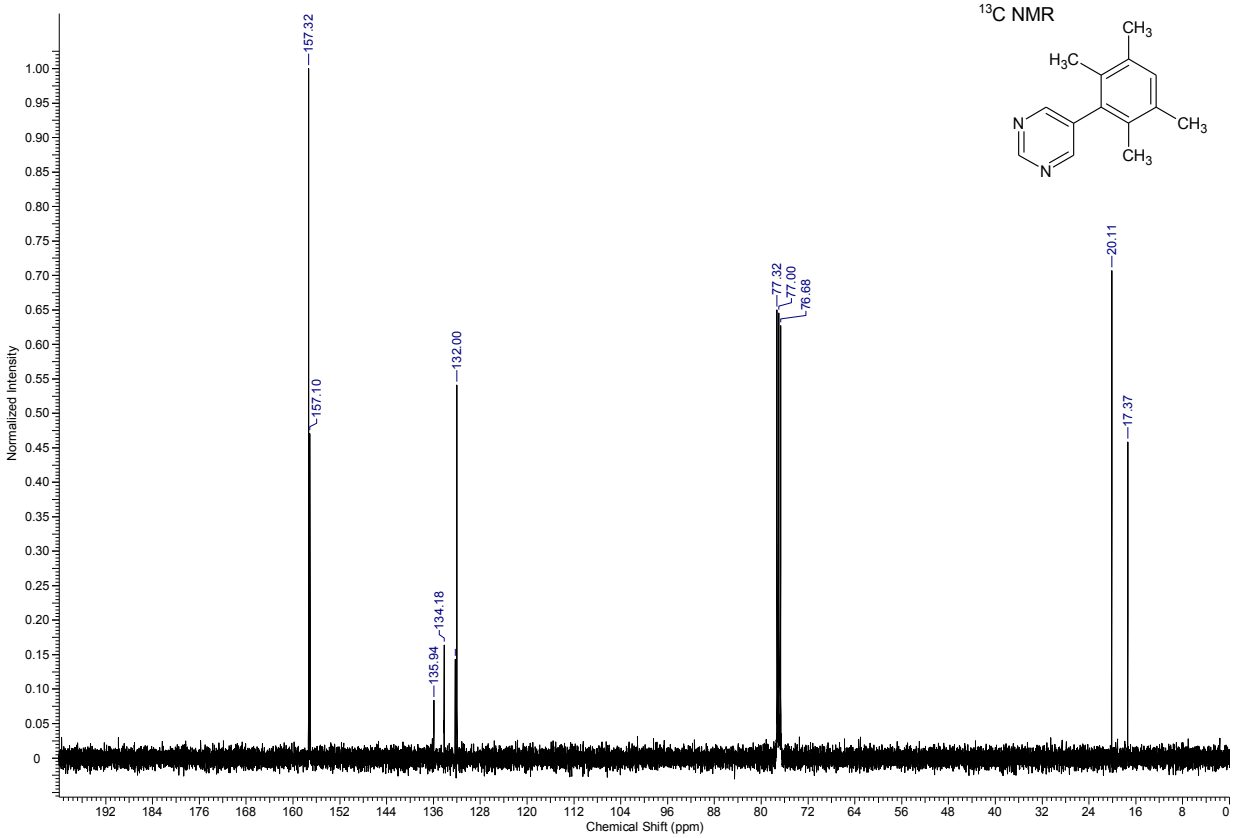

9.23
9.19
8.95
8.74
7.37
7.37
7.35
7.33
7.33
7.30
7.29
7.28
7.27
7.27
7.25
7.23
7.09
7.08
7.07
7.06
2.38
2.38
2.35
2.19
1H NMR
N
N
CH3
CH3
1.00
1.82
3.78
2.10
9.08
1.17
8.72
6.06
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

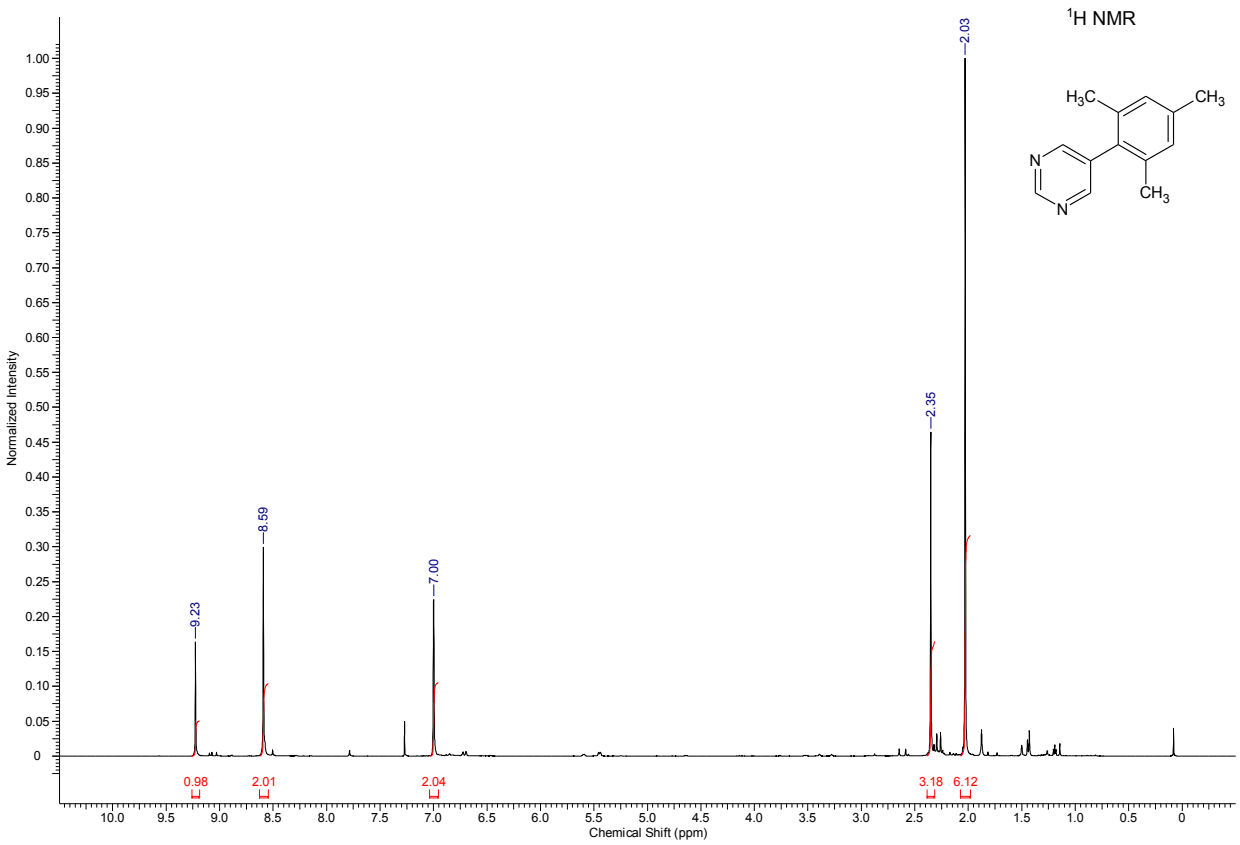

13C NMR
N
N
CH3
CH3
156.77
157.08
130.50
127.70
125.90
137.89
135.92
134.51
77.32
77.00
76.68
20.58
16.87
Normalized Intensity
Chemical Shift (ppm)

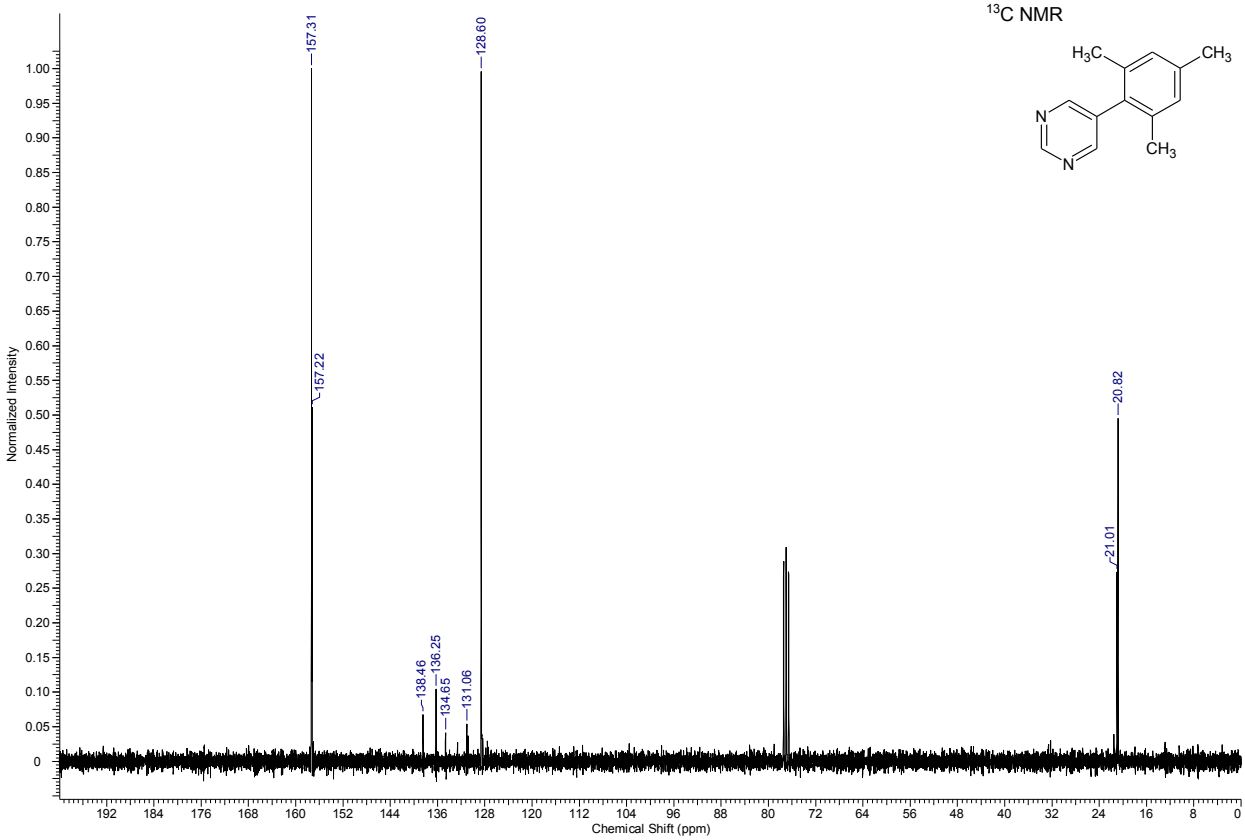

9.22
8.75
7.28
7.25
7.23
7.20
7.20
7.18
7.18
7.05
7.05
2.39
2.27
1H NMR
CH3
CH3
N
N
1.00
2.01
1.98
1.13
2.95
2.97
f1 (ppm)

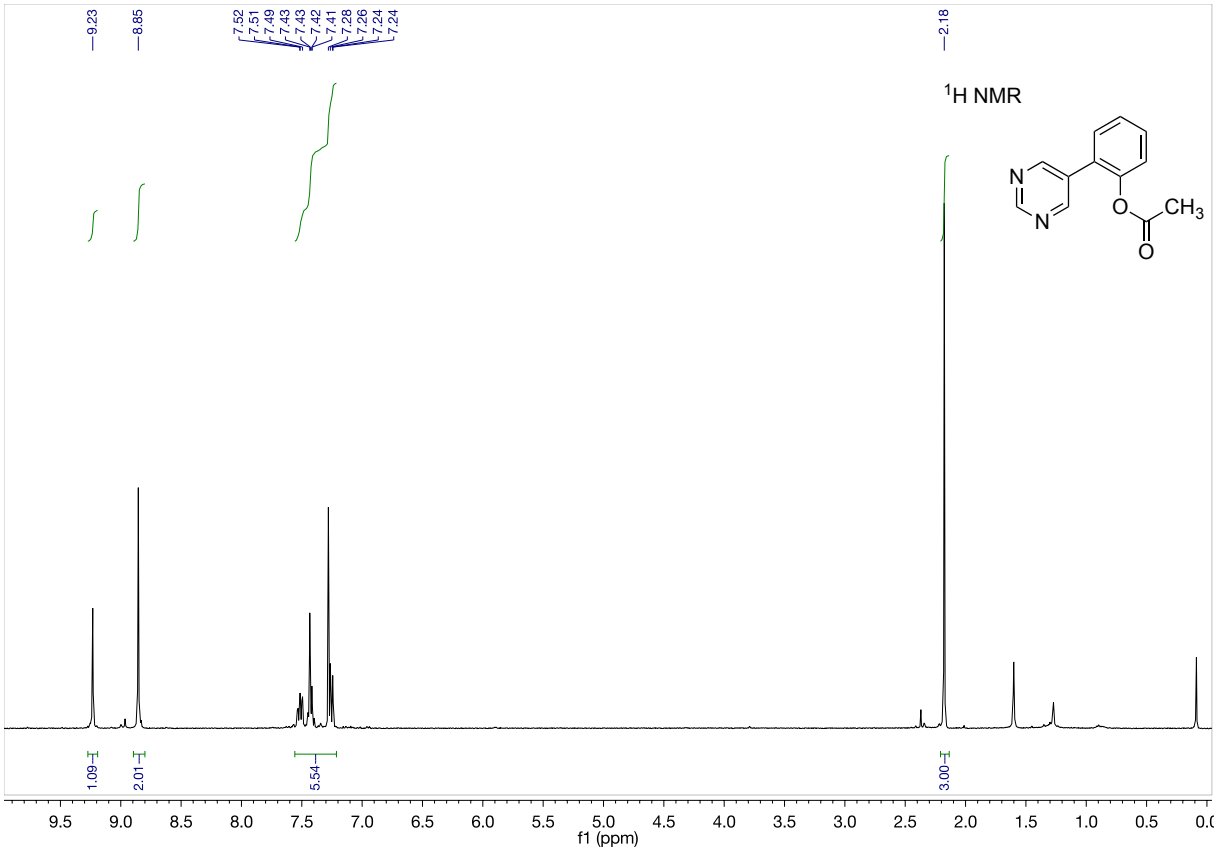

157.20
156.70
136.10
135.53
134.16
132.58
130.87
130.54
129.75
77.47
77.15
76.83
20.94
19.84
13C NMR
N
N
f1 (ppm)

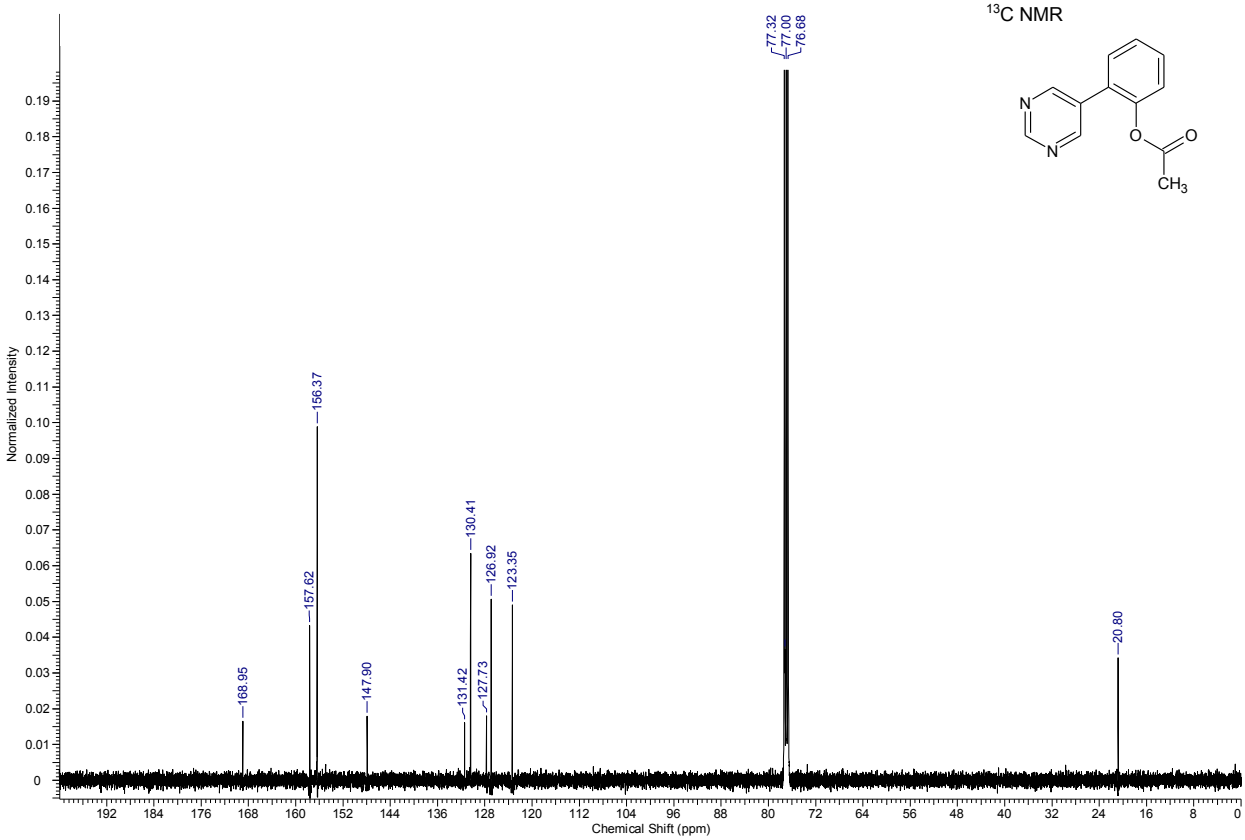

1
^{1}H NMR
CH3
H3C
CH3
CH3
N
N
9.24
8.57
7.27
7.08
2.29
1.91
1.00
1.95
1.01
6.07
5.97
Normalized Intensity
Chemical Shift (ppm)

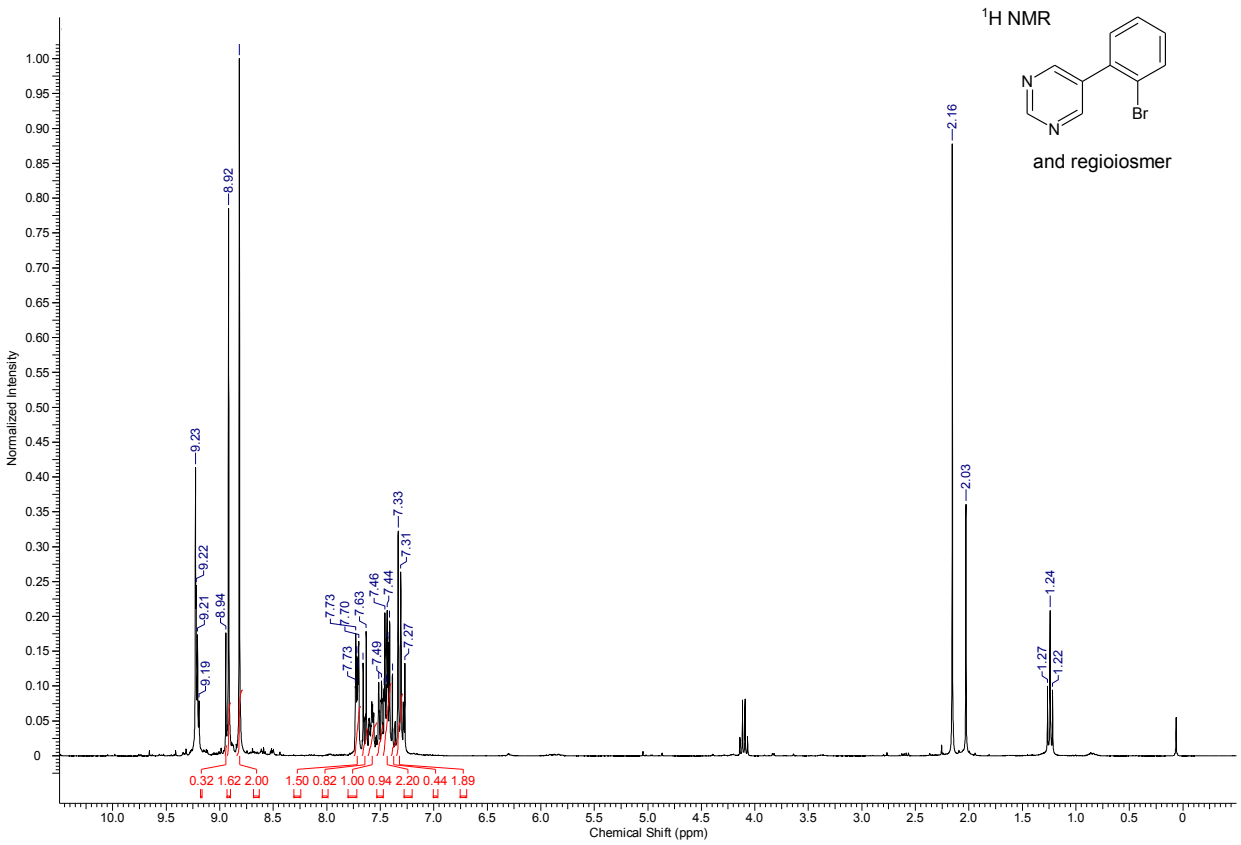

^{13}C NMR
CH3
H3C
CH3
CH3
N
N
157.32
157.10
135.94
134.18
132.00
77.32
77.00
76.68
20.11
17.37
Normalized Intensity
Chemical Shift (ppm)

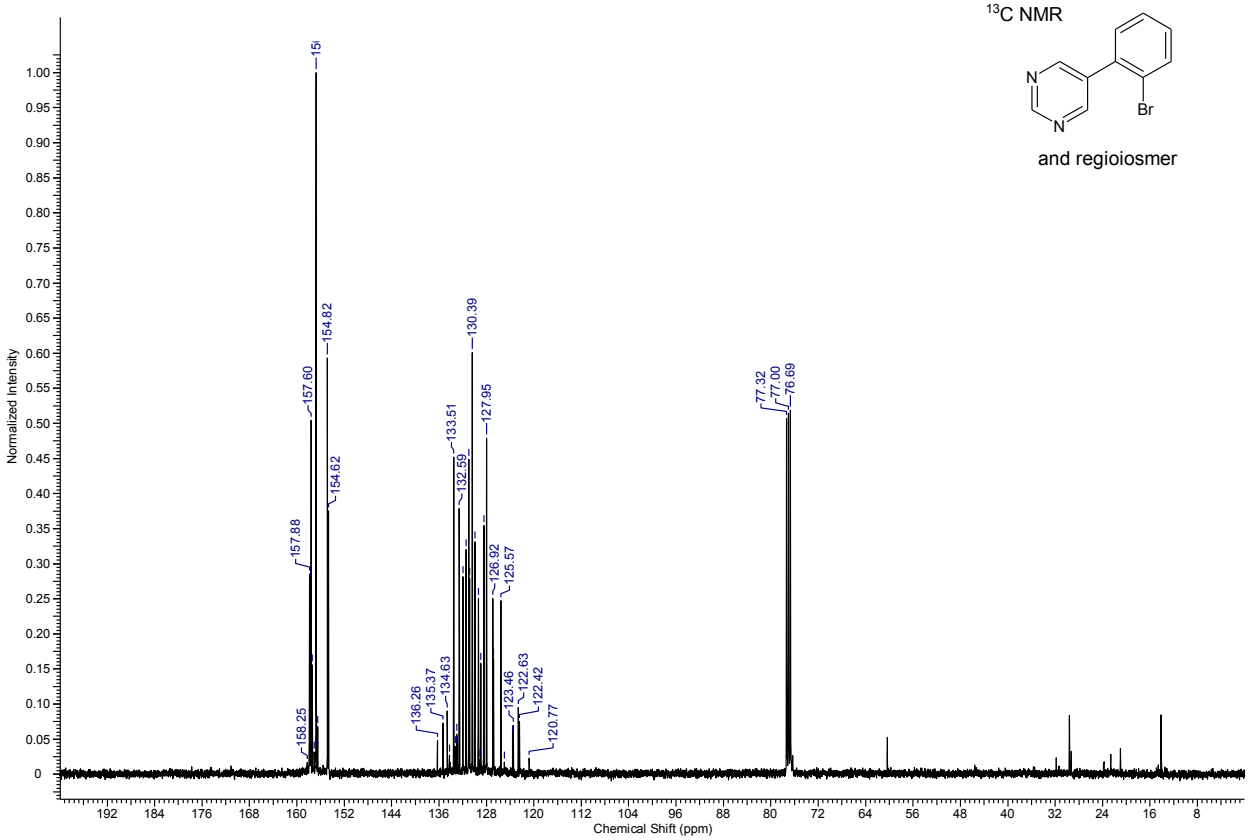

^{1}H NMR
2.03
2.35
8.59
7.00
9.23
0.98
2.01
2.04
3.18
6.12
Normalized Intensity
Chemical Shift (ppm)

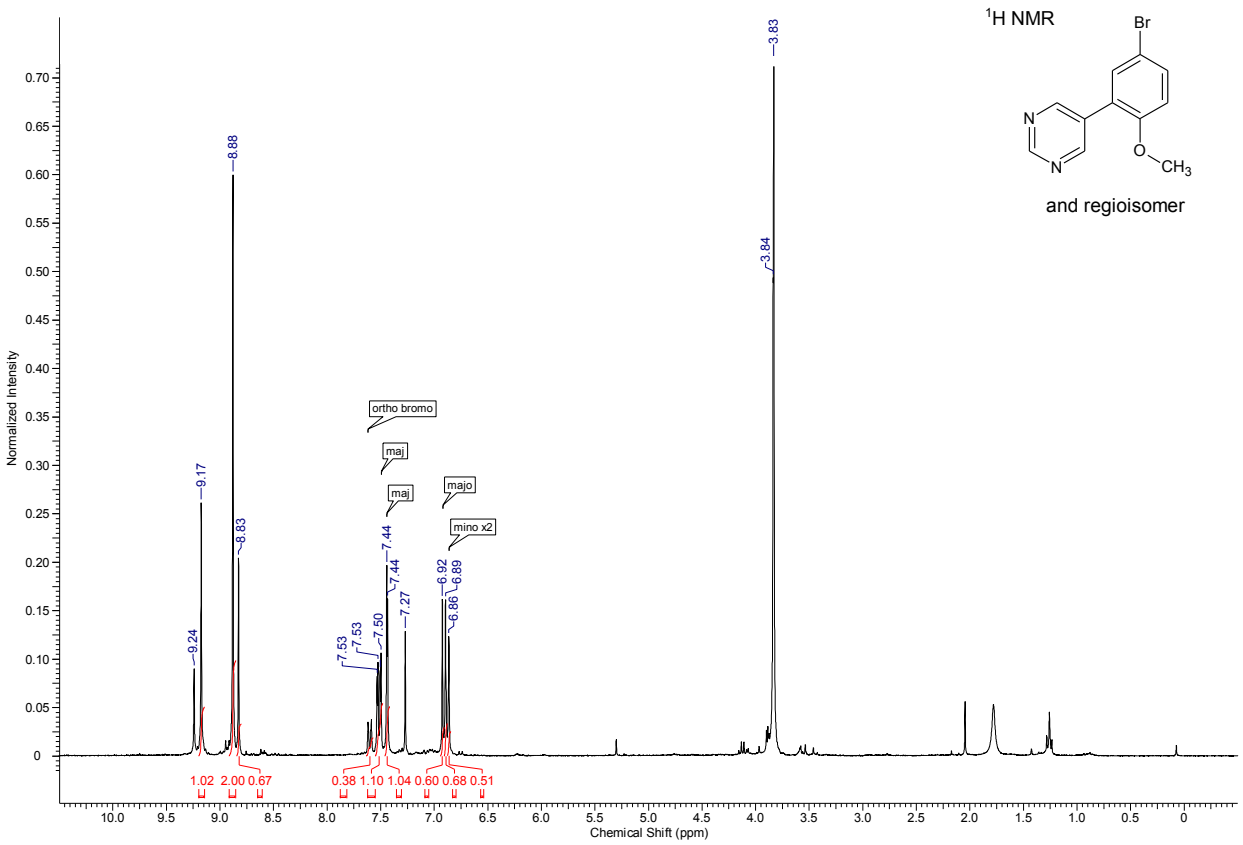

^{13}C NMR
157.31
128.60
157.22
20.82
21.01
138.46
136.25
134.65
131.06
Normalized Intensity
Chemical Shift (ppm)

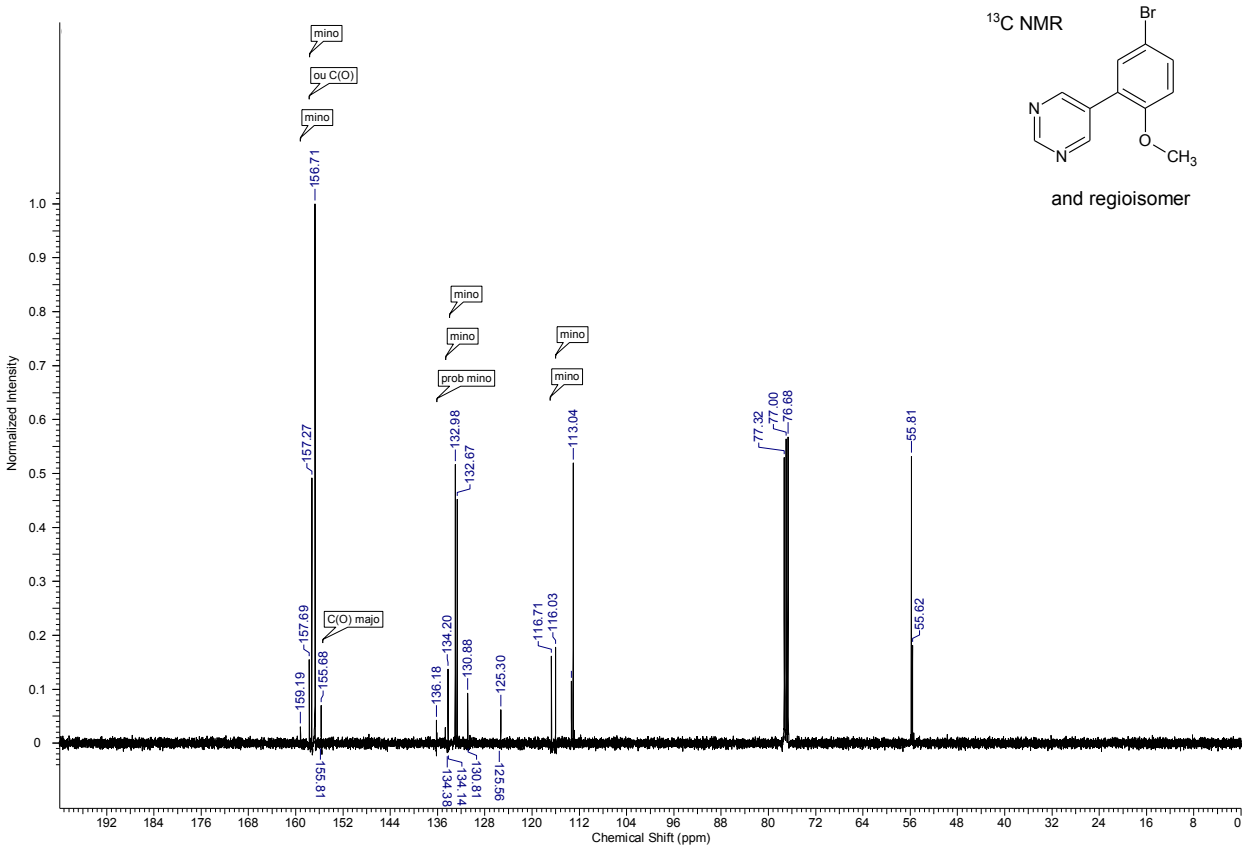

9.23
8.85
7.52
7.51
7.49
7.43
7.43
7.42
7.41
7.28
7.26
7.24
7.24
2.18
1H NMR
N
N
O
CH3
O
1.09
2.01
5.54
3.00
f1 (ppm)

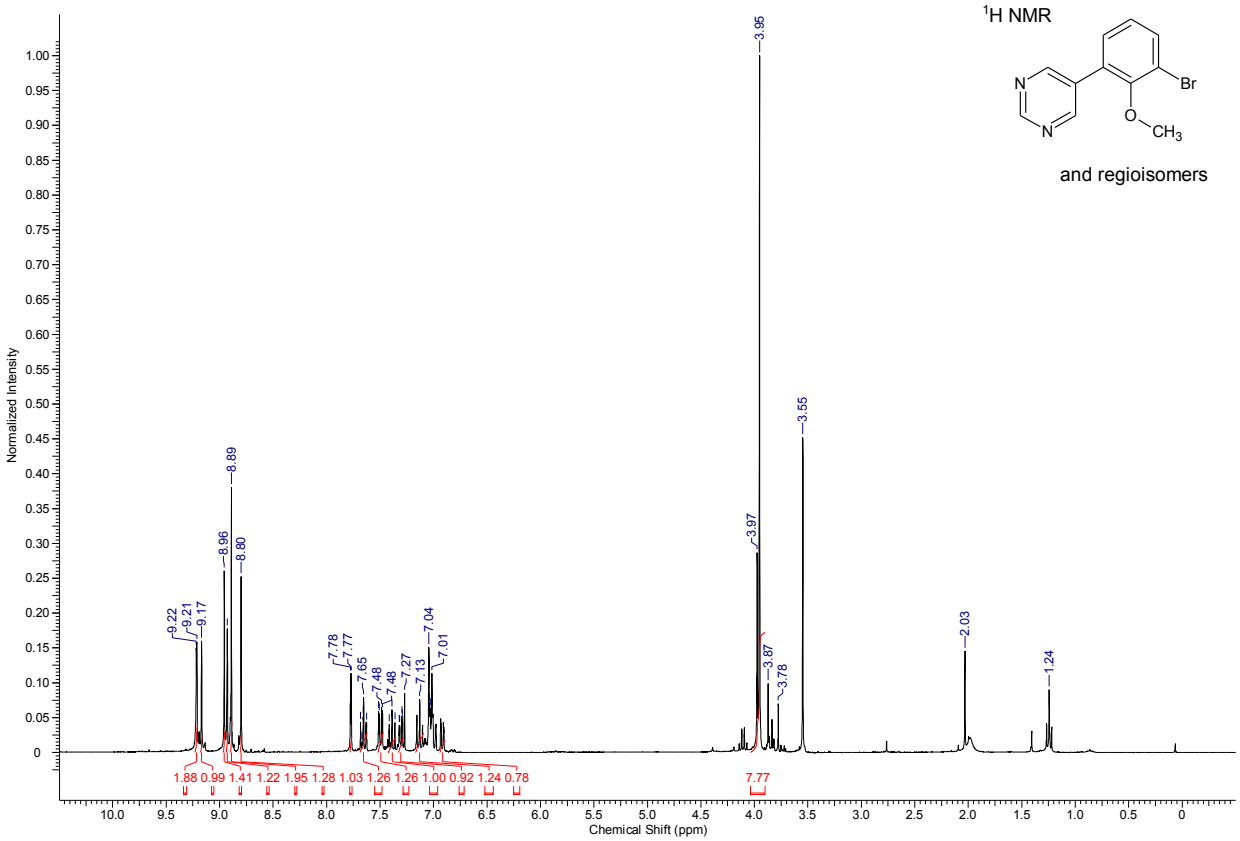

13C NMR
77.32
77.00
76.68
N
N
O
O
CH3
Normalized Intensity
156.37
157.62
130.41
126.92
123.35
168.95
147.90
131.42
127.73
20.80
Chemical Shift (ppm)

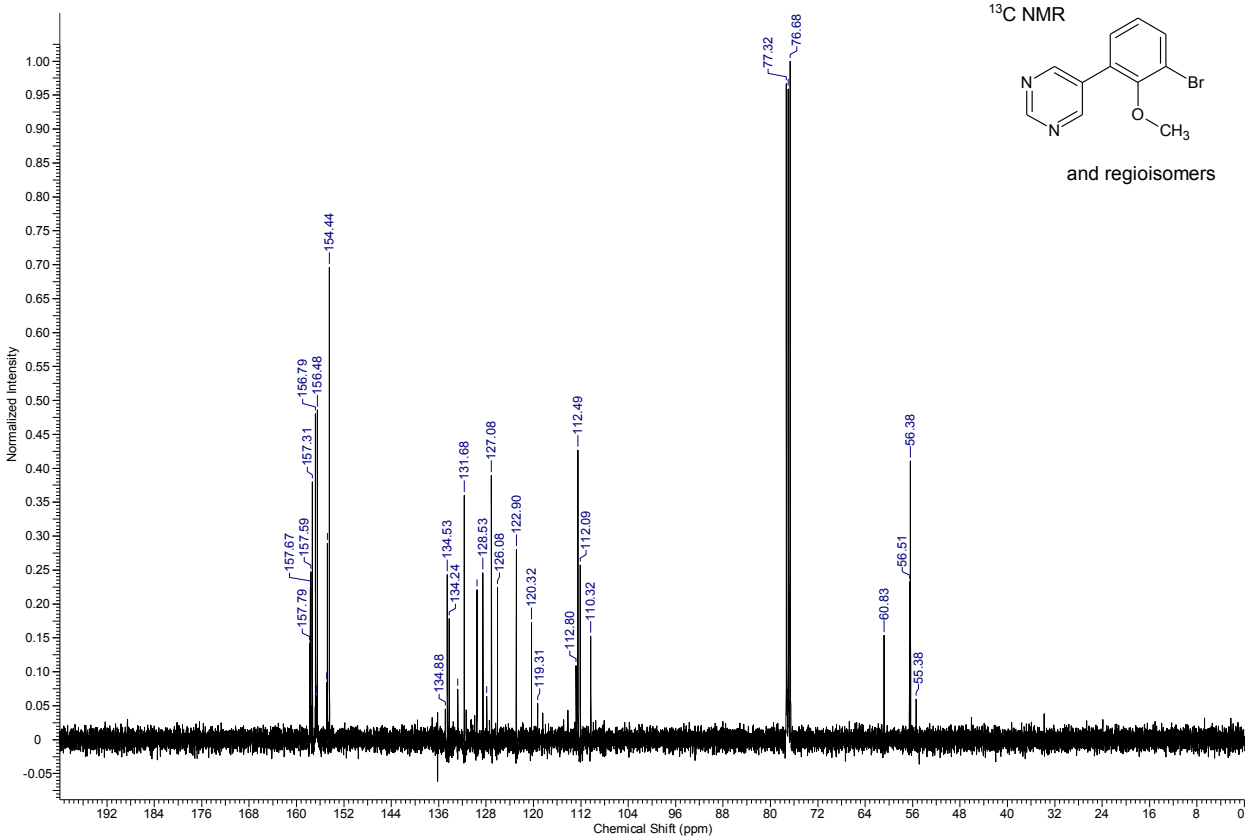

^{1}H NMR
N
N
Br
and regioiosmer
Normalized Intensity
Chemical Shift (ppm)
9.23
9.22
9.21
9.19
8.94
8.92
7.73
7.70
7.63
7.46
7.44
7.33
7.31
7.27
7.73
7.49
2.16
2.03
1.24
1.27
1.22
0.32 1.62 2.00
1.50 0.82 1.00 0.94 2.20 0.44 1.89

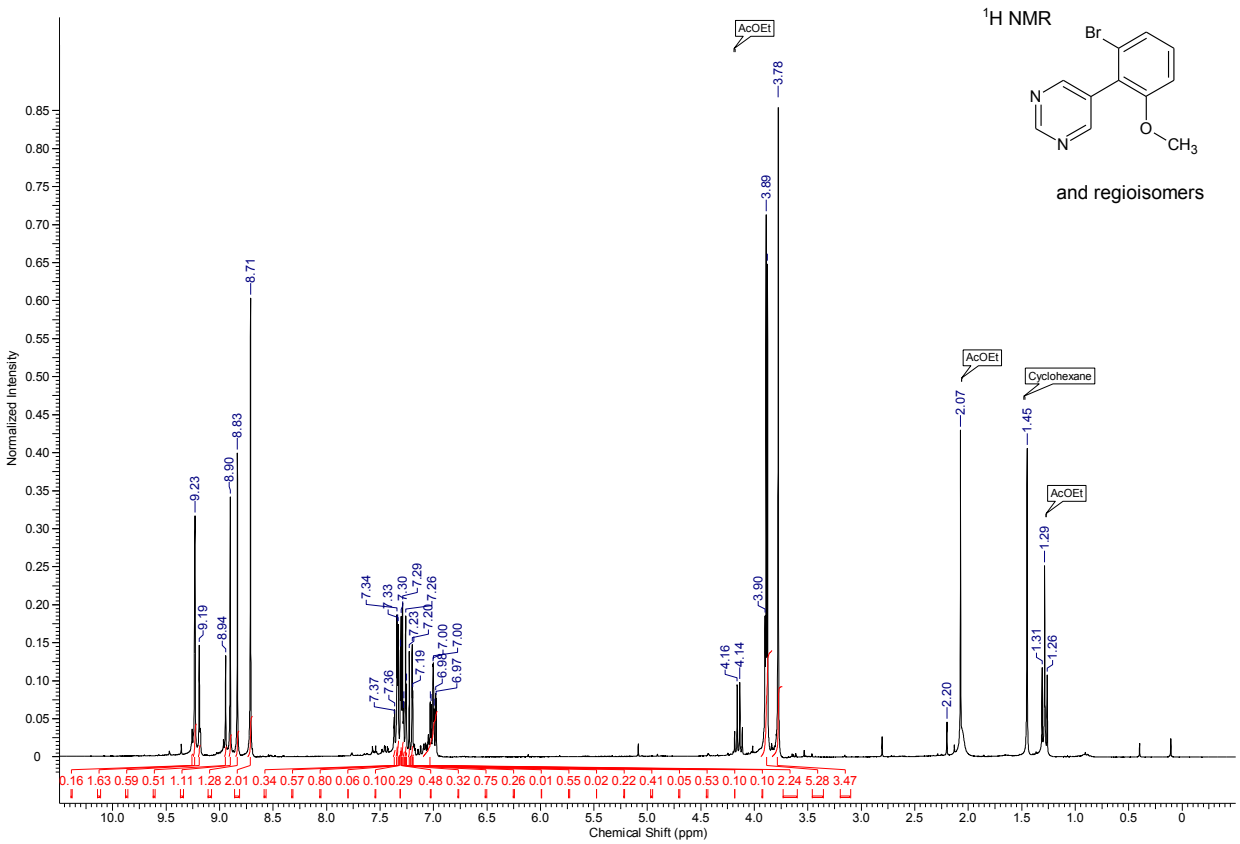

^{13}C NMR
N
N
Br
and regioiosmer
Normalized Intensity
Chemical Shift (ppm)
154.82
157.60
154.62
157.88
158.25
130.39
133.51
132.59
127.95
126.92
125.57
136.26
135.37
134.63
123.46
122.63
122.42
120.77
77.32
77.00
76.69

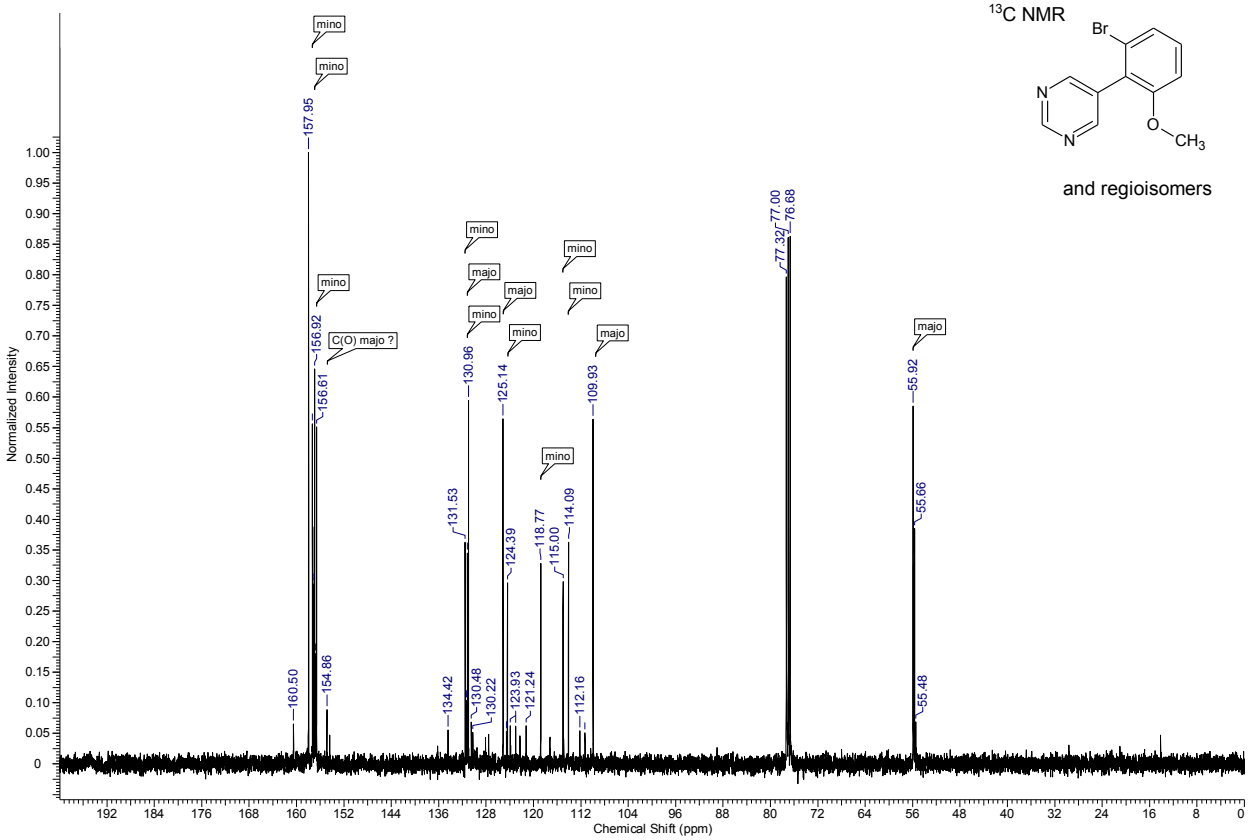

^{1}H NMR
Br
N
N
O
CH$_3$
and regioisomer
3.83
8.88
3.84
9.17
8.83
ortho bromo
maj
maj
majo
mino x2
7.44
7.44
7.27
6.92
6.89
6.86
9.24
7.53
7.53
7.50
1.02 2.00 0.67
0.38 1.10 1.04 0.60 0.68 0.51
Normalized Intensity
Chemical Shift (ppm)

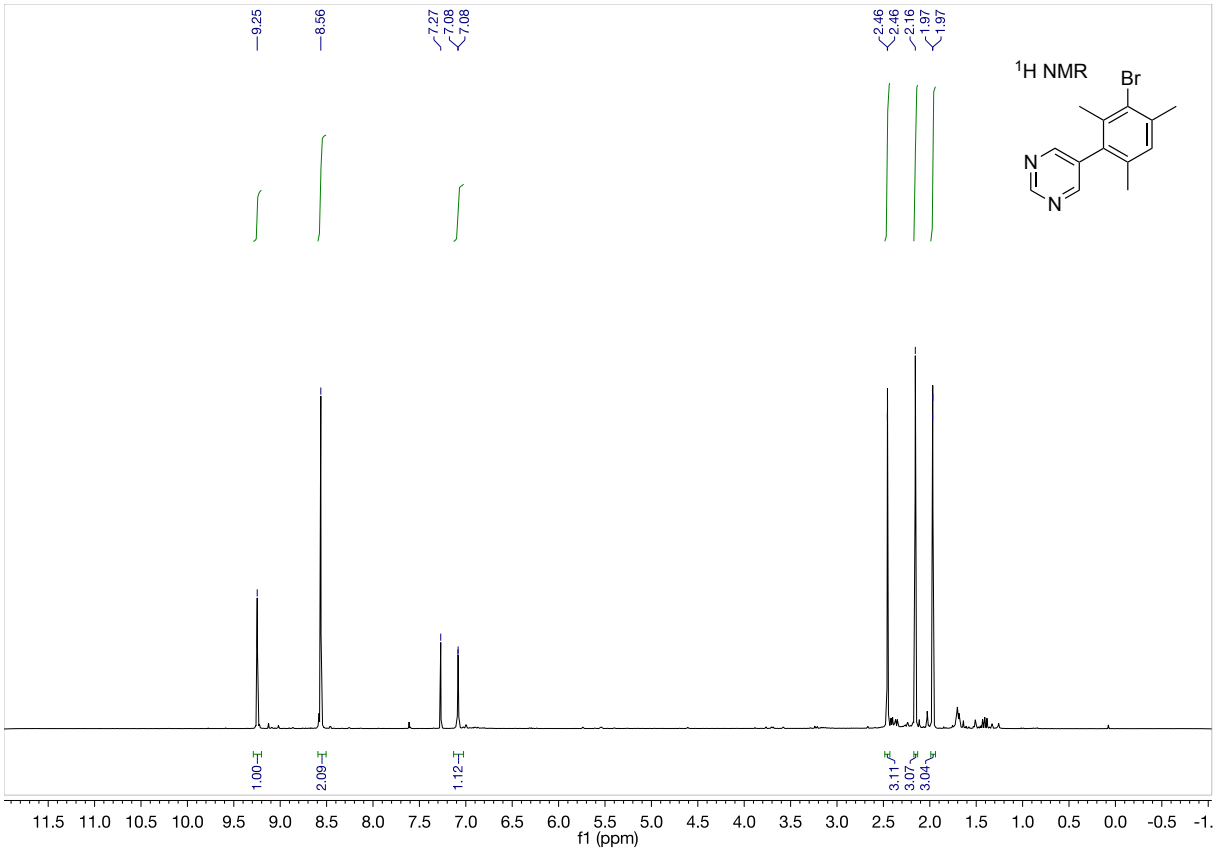

^{13}C NMR
Br
N
N
O
CH$_3$
and regioisomer
mino
ou C(O)
mino
156.71
157.27
157.69
159.19
155.68
C(O) majo
mino
mino
prob mino
132.98
132.67
134.20
136.18
130.88
125.30
mino
mino
113.04
116.71
116.03
77.32
77.00
76.68
55.81
55.62
Normalized Intensity
Chemical Shift (ppm)

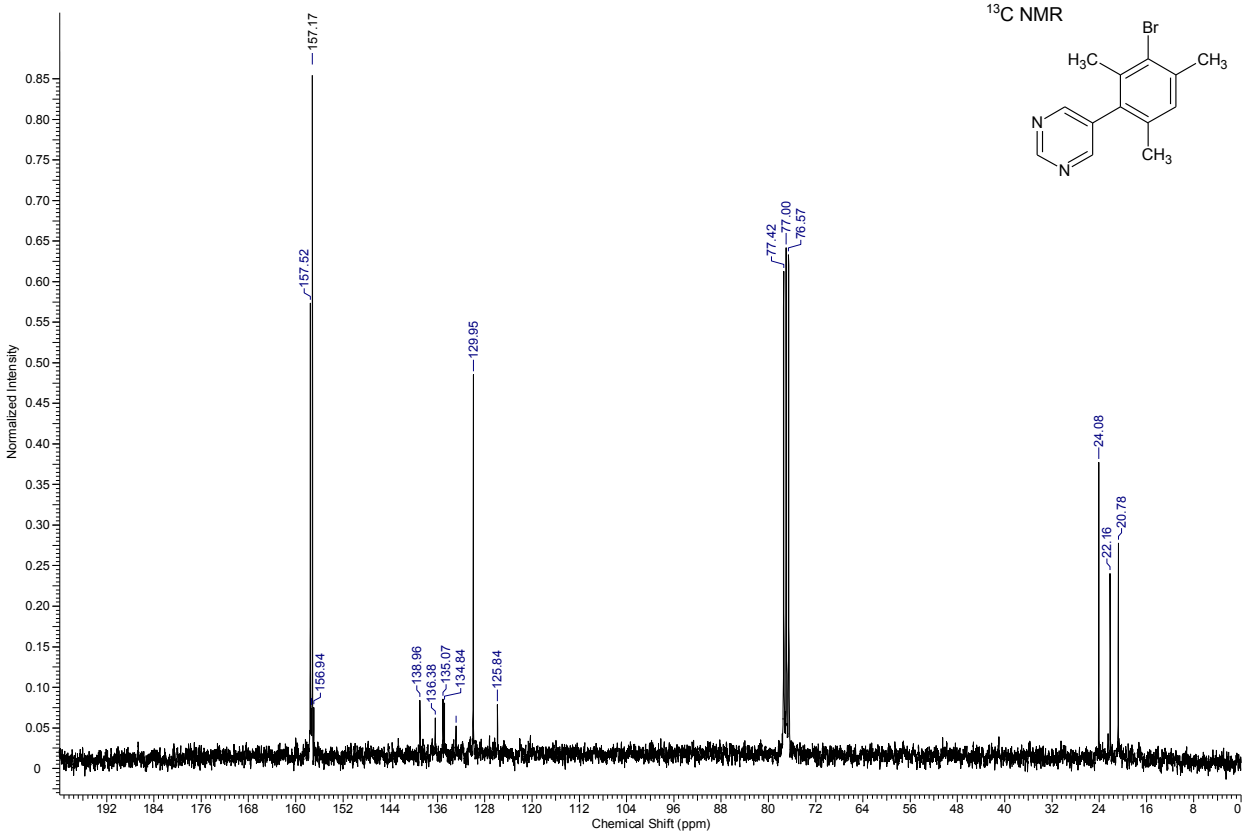

^{1}H NMR
and regioisomers
Normalized Intensity
Chemical Shift (ppm)
9.22
9.21
9.17
8.96
8.89
8.80
7.78
7.77
7.65
7.48
7.48
7.27
7.13
7.04
7.01
3.95
3.97
3.87
3.78
3.55
2.03
1.24
1.88 0.99 1.41 1.22 1.95 1.28 1.03 1.26 1.26 1.00 0.92 1.24 0.78
7.77

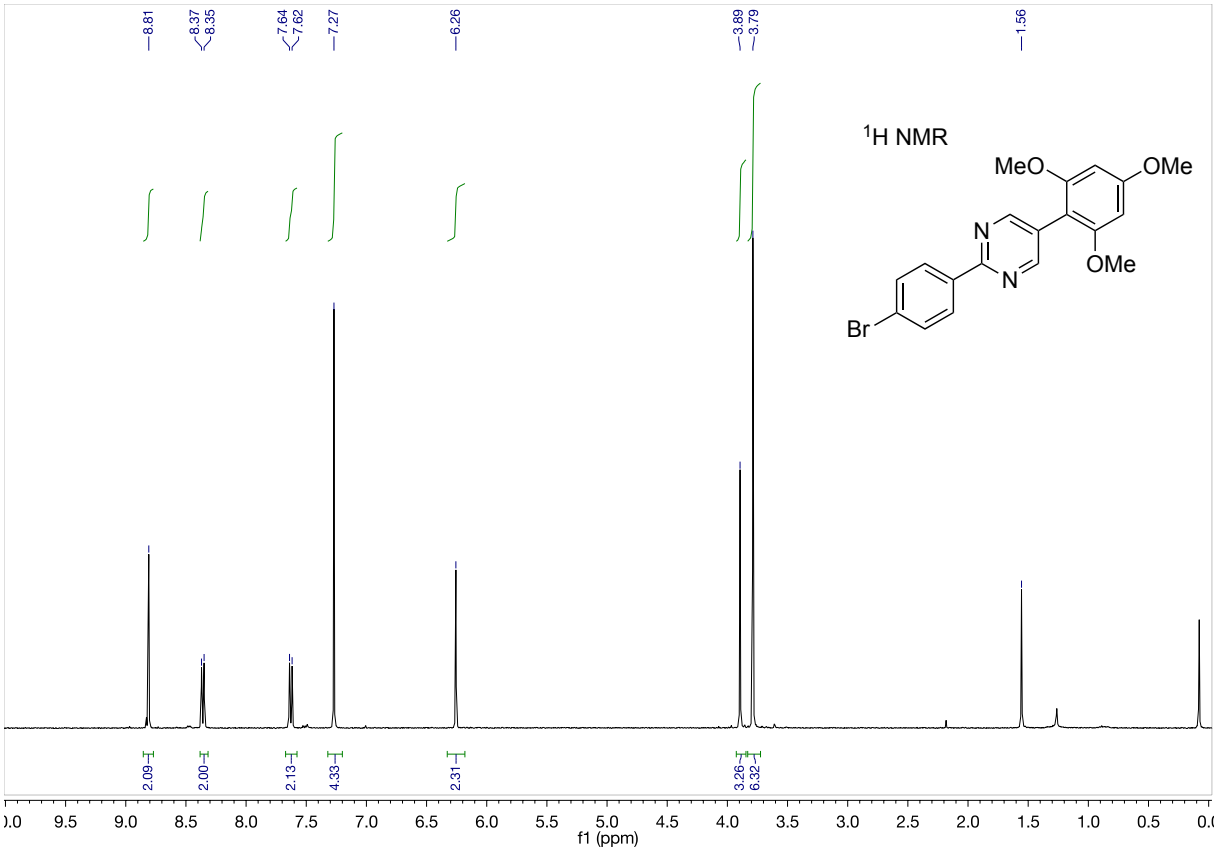

^{13}C NMR
and regioisomers
Normalized Intensity
Chemical Shift (ppm)
154.44
157.67
157.59
157.79
157.31
156.79
156.48
134.88
134.53
134.24
131.68
128.53
127.08
126.08
122.90
120.32
119.31
112.80
112.49
112.09
110.32
77.32
76.68
60.83
56.51
56.38
55.38

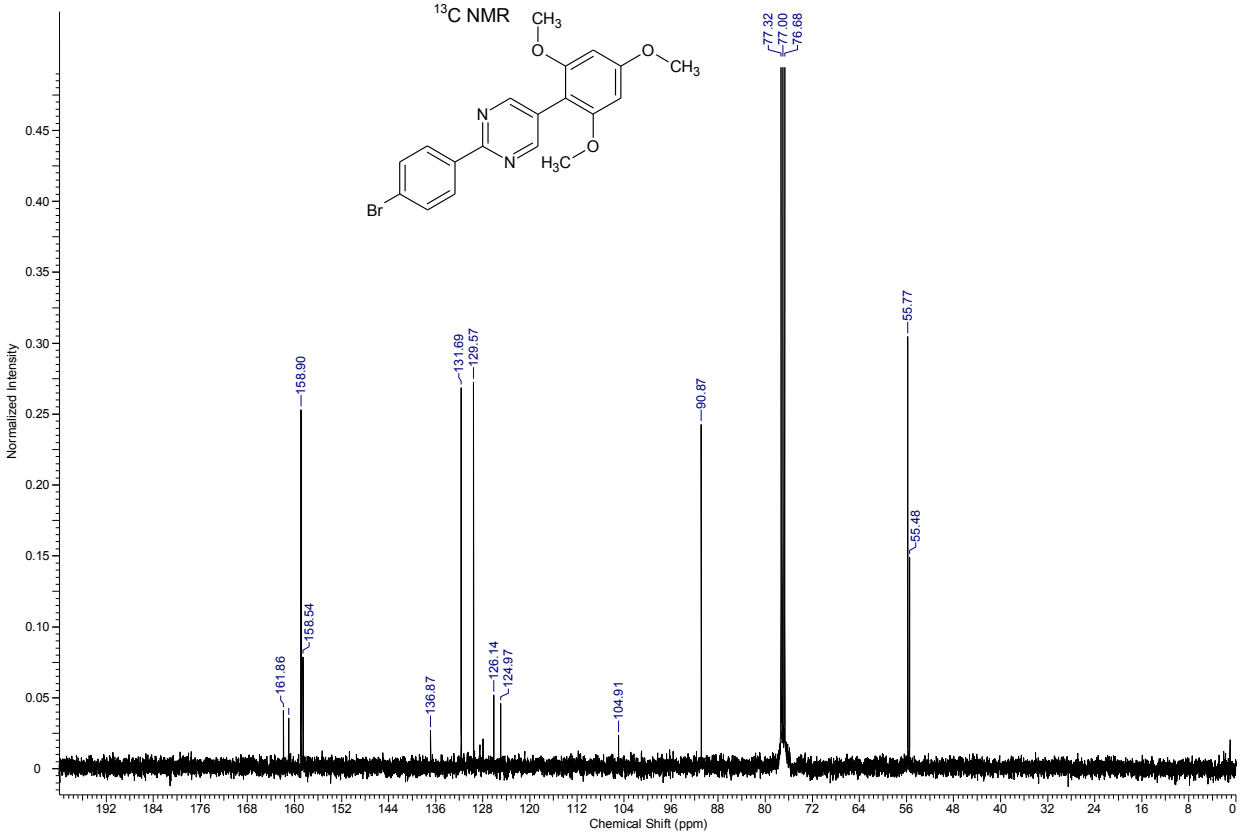

^{1}H NMR
Br
N
N
O
CH3
and regioisomers
AcOEt
Cyclohexane
Normalized Intensity
Chemical Shift (ppm)

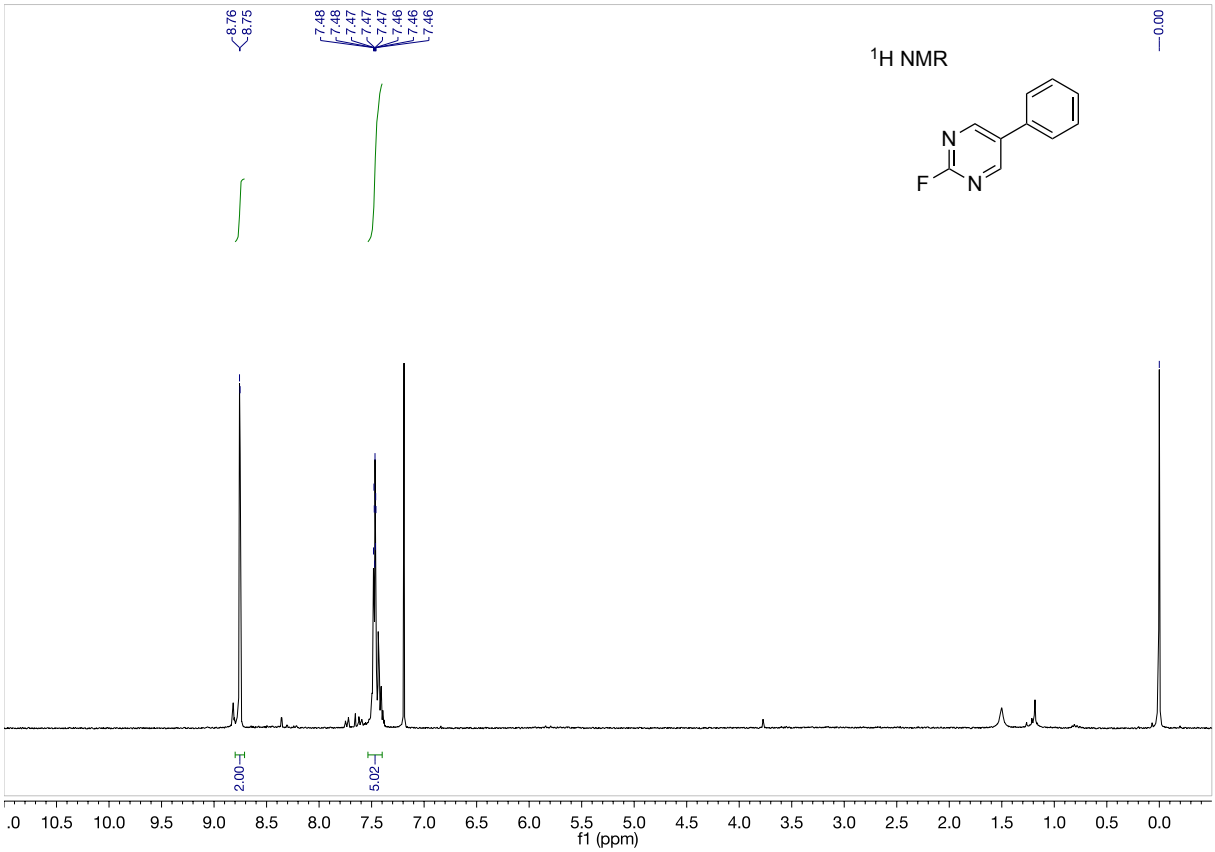

^{13}C NMR
Br
N
N
O
CH3
and regioisomers
mino
majo
C(O) majo ?
Normalized Intensity
Chemical Shift (ppm)

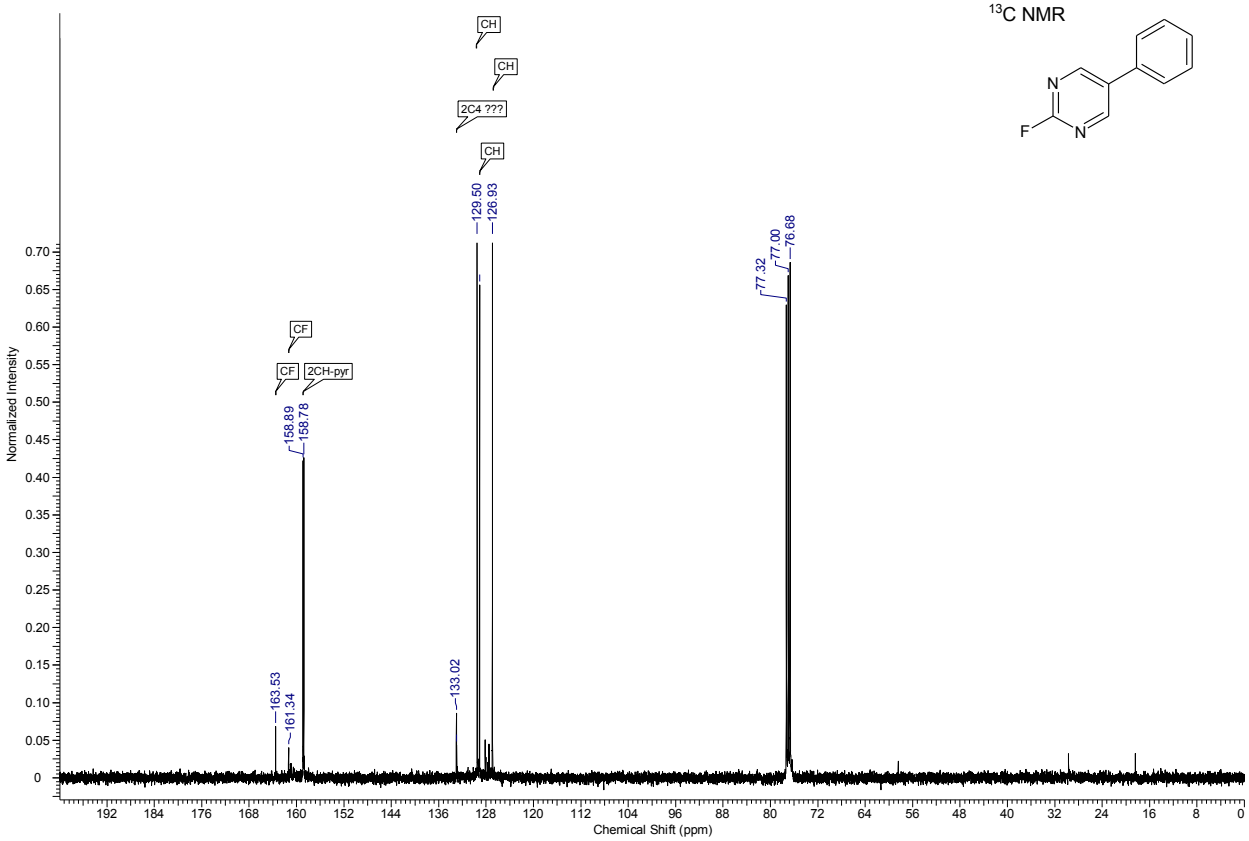

9.25
8.56
7.27
7.08
7.08
2.46
2.46
2.16
1.97
1.97
1H NMR
Br
N
N
1.00
2.09
1.12
3.11
3.07
3.04
f1 (ppm)

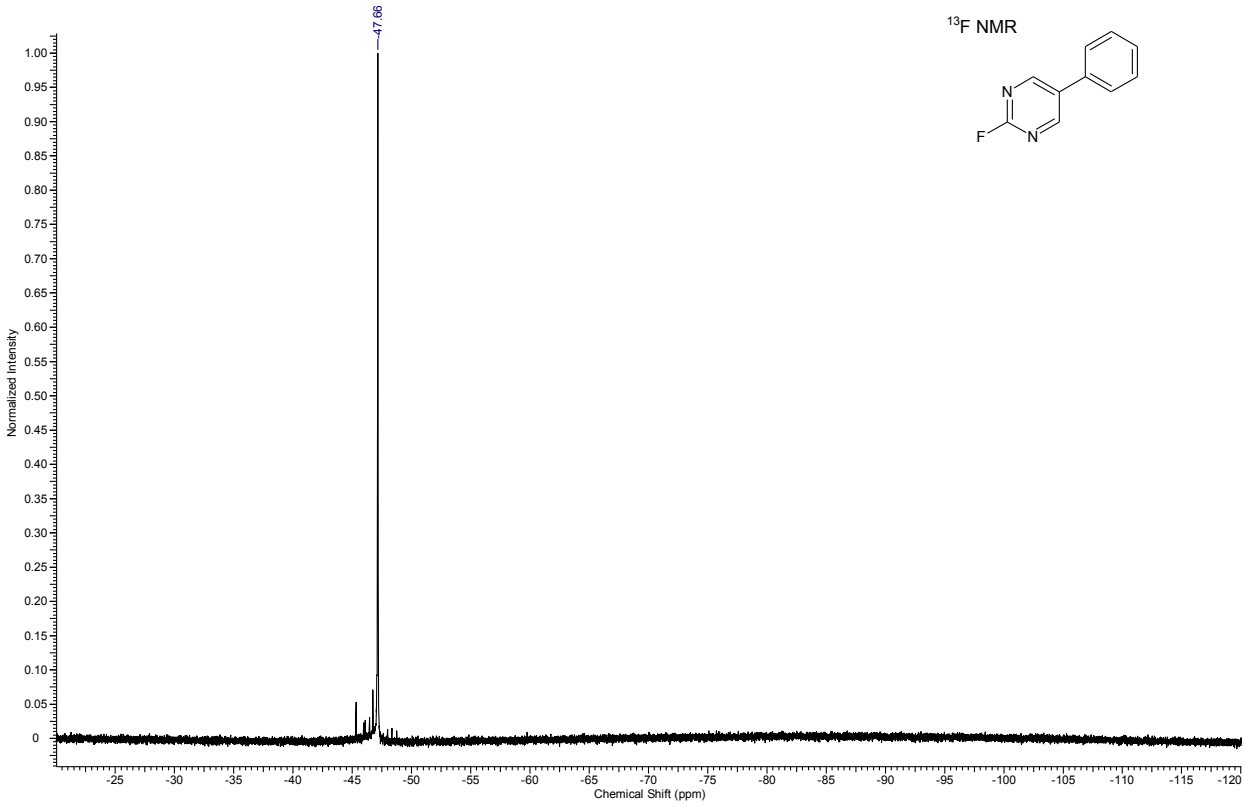

13C NMR
Br
H3C
CH3
CH3
N
N
157.17
157.52
156.94
138.96
136.38
135.07
134.84
129.95
125.84
77.42
77.00
76.57
24.08
22.16
20.78
Normalized Intensity
Chemical Shift (ppm)

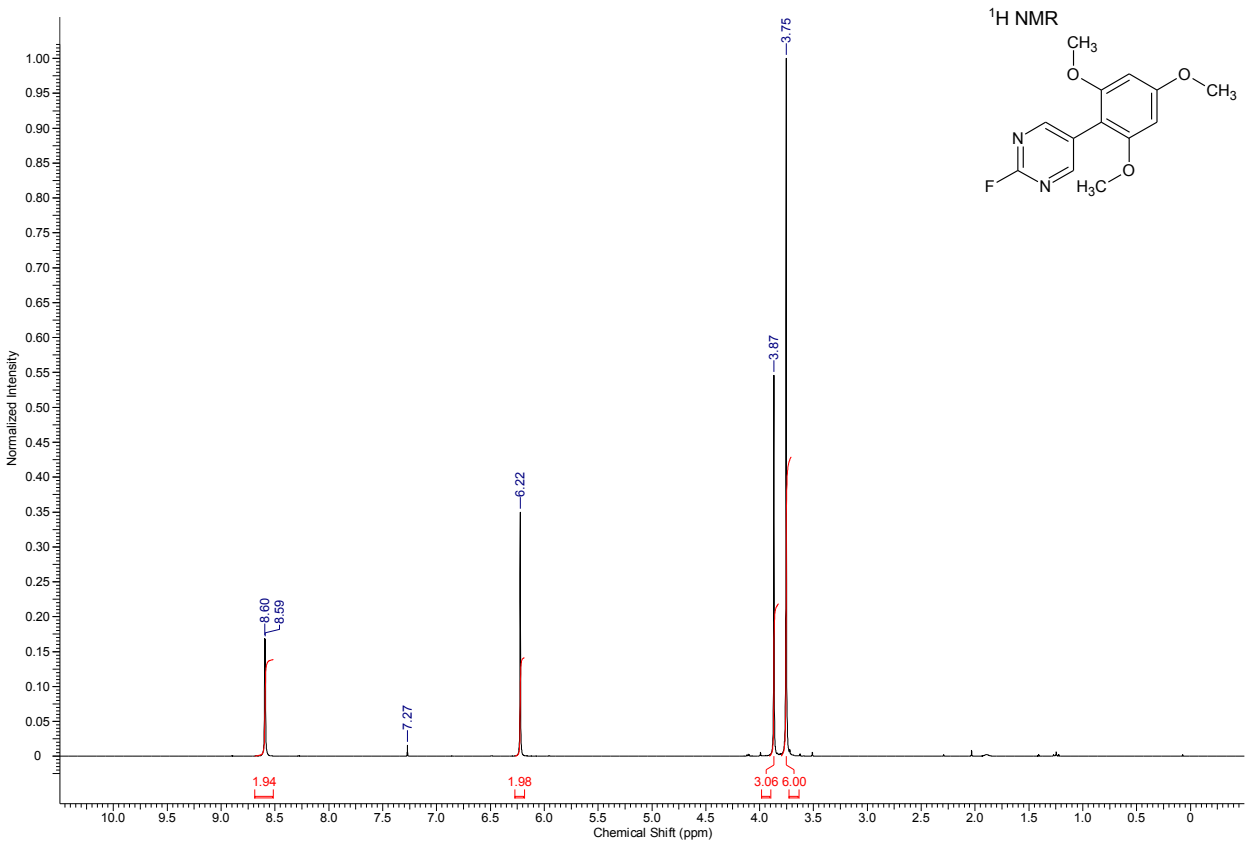

8.81
8.37
8.35
7.64
7.62
7.27
6.26
3.89
3.79
1.56
2.09
2.00
2.13
4.33
2.31
3.26
6.32
f1 (ppm)
1H NMR
MeO
OMe
OMe
N
N
Br

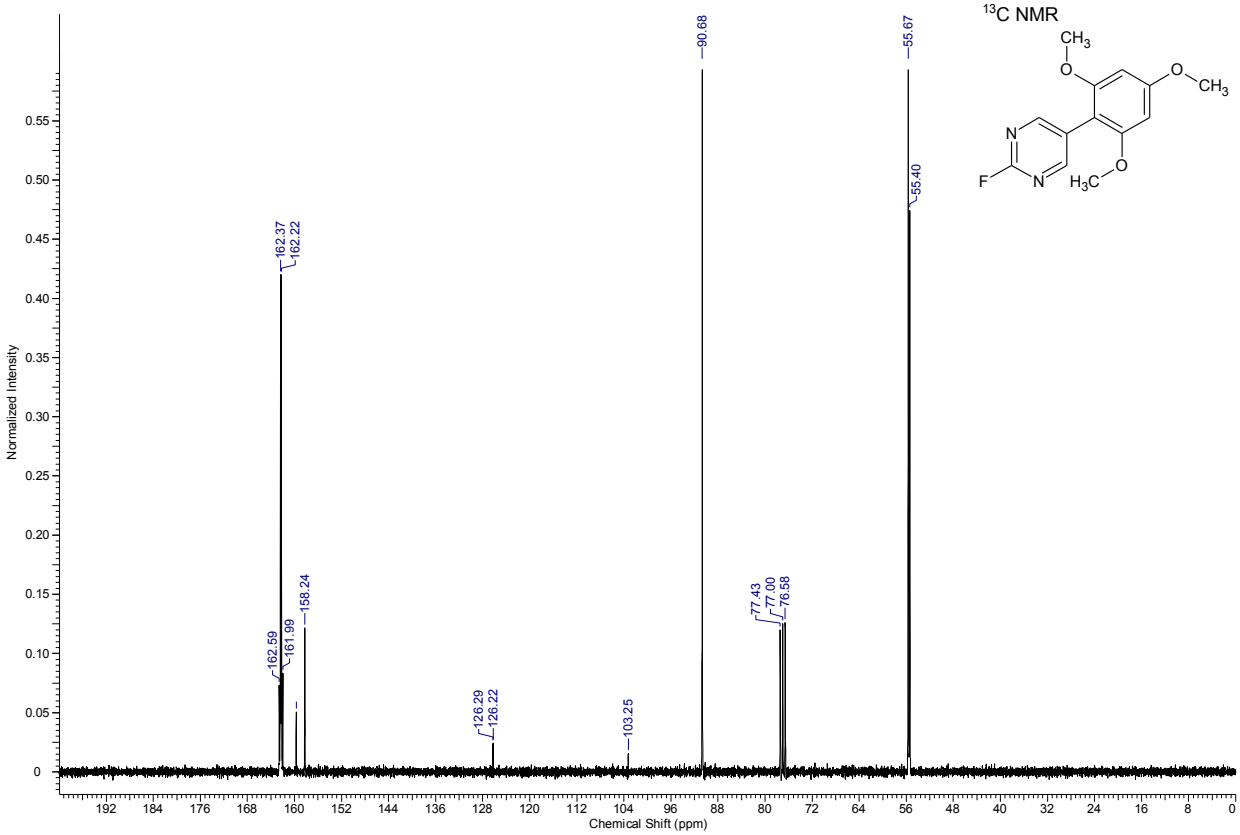

13C NMR
CH3
O
O
CH3
N
N
H3C
O
Br
77.32
77.00
76.68
55.77
55.48
131.69
129.57
158.90
90.87
158.54
161.86
136.87
126.14
124.97
104.91
Normalized Intensity
Chemical Shift (ppm)

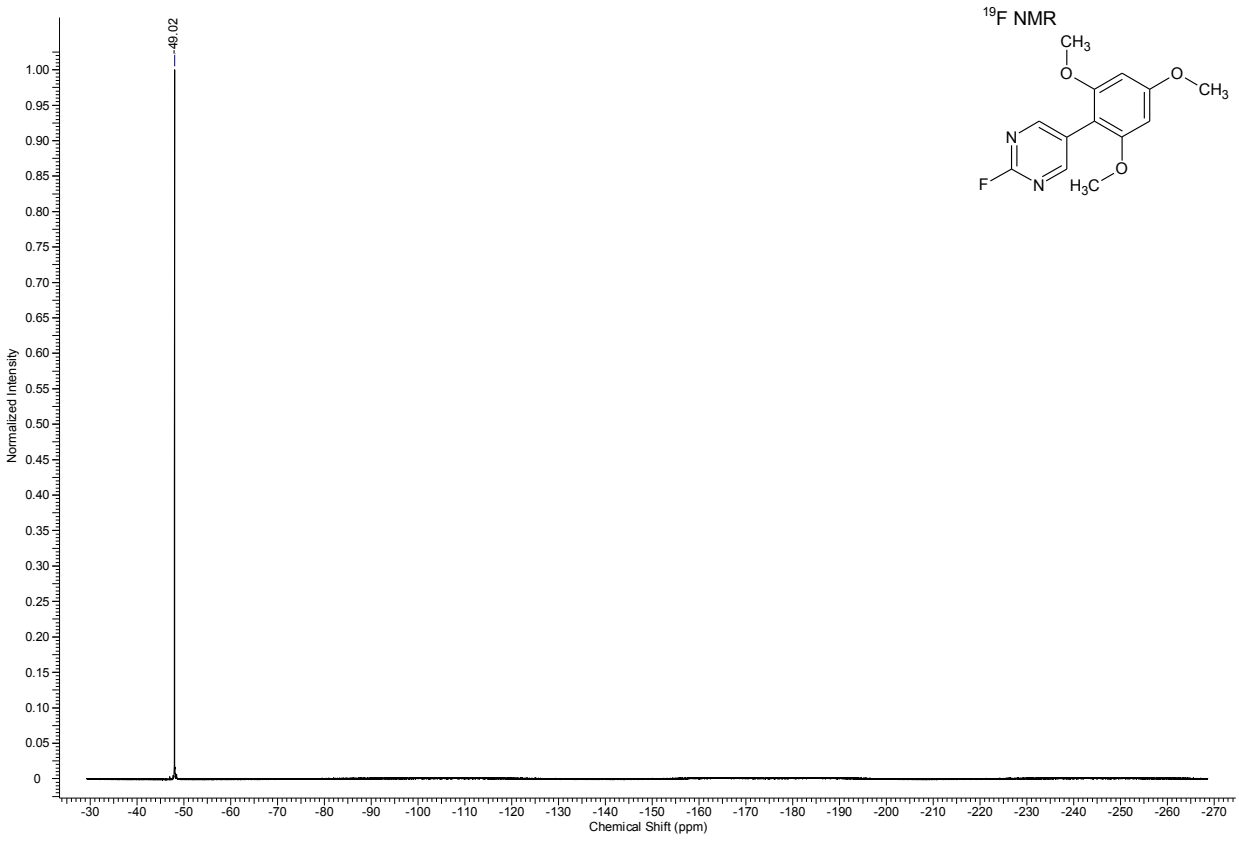

8.76
8.75
7.48
7.48
7.47
7.47
7.47
7.46
7.46
7.46
0.00
^{1}H NMR
N
F
N
2.00
5.02
f1 (ppm)

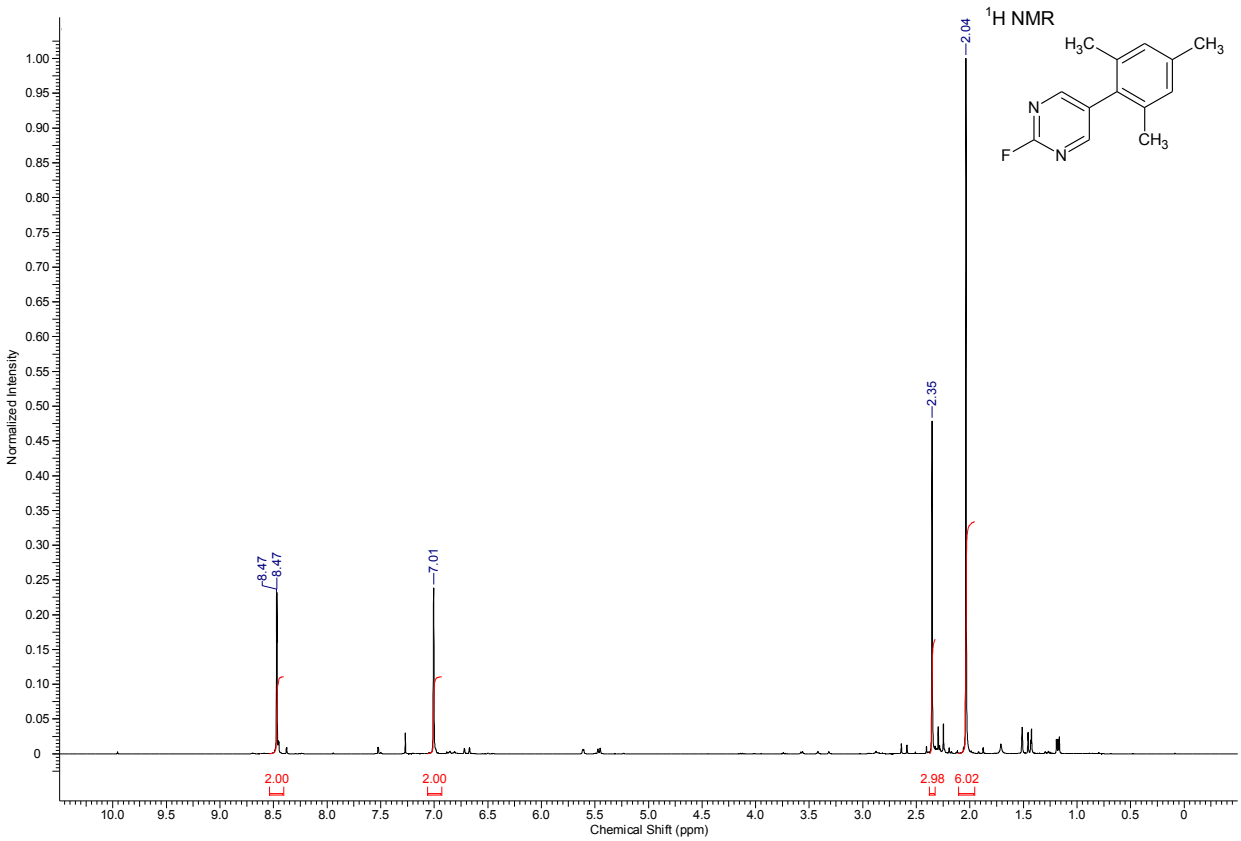

^{13}C NMR
CH
CH
2C4 ???
CH
129.50
126.93
77.32
77.00
76.68
CF
CF
2CH-pyr
158.89
158.78
163.53
161.34
133.02
Normalized Intensity
Chemical Shift (ppm)

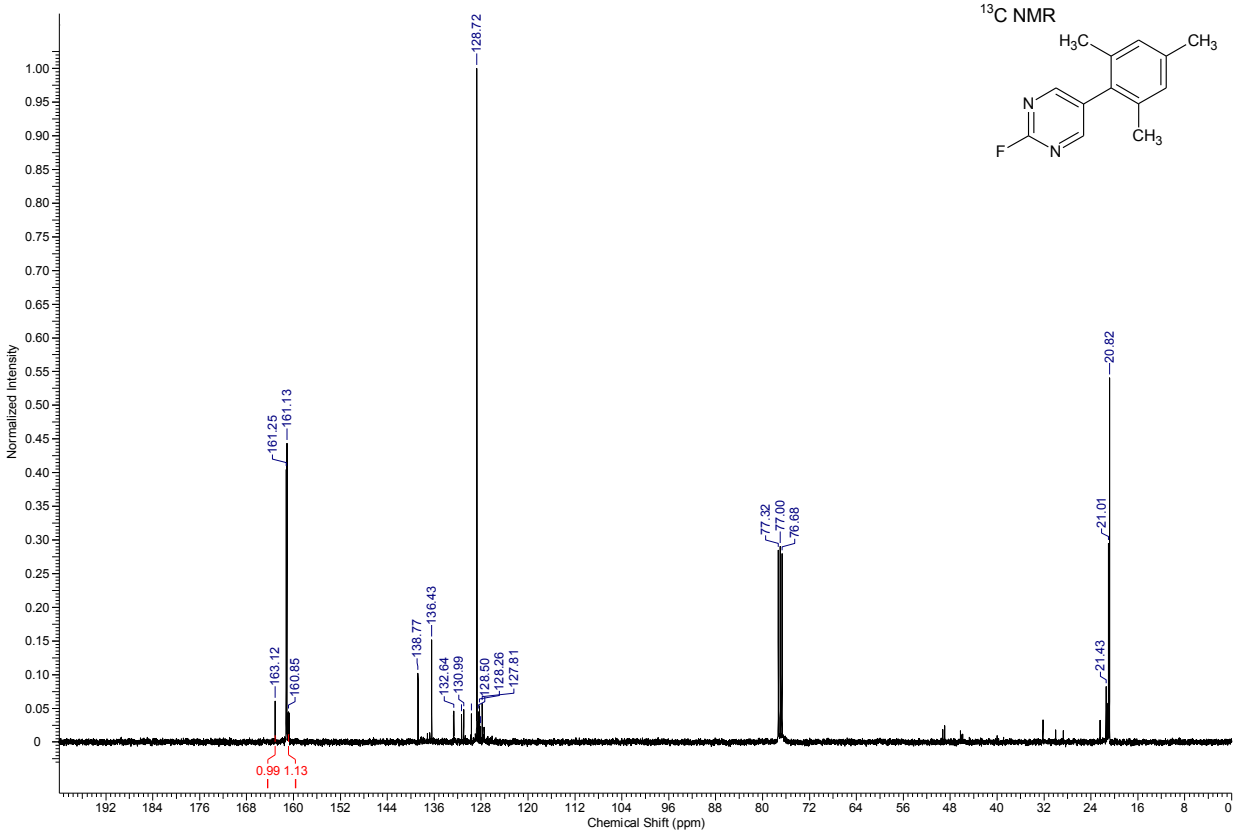

^{13}F NMR
-47.66
Normalized Intensity
Chemical Shift (ppm)
N
F
N

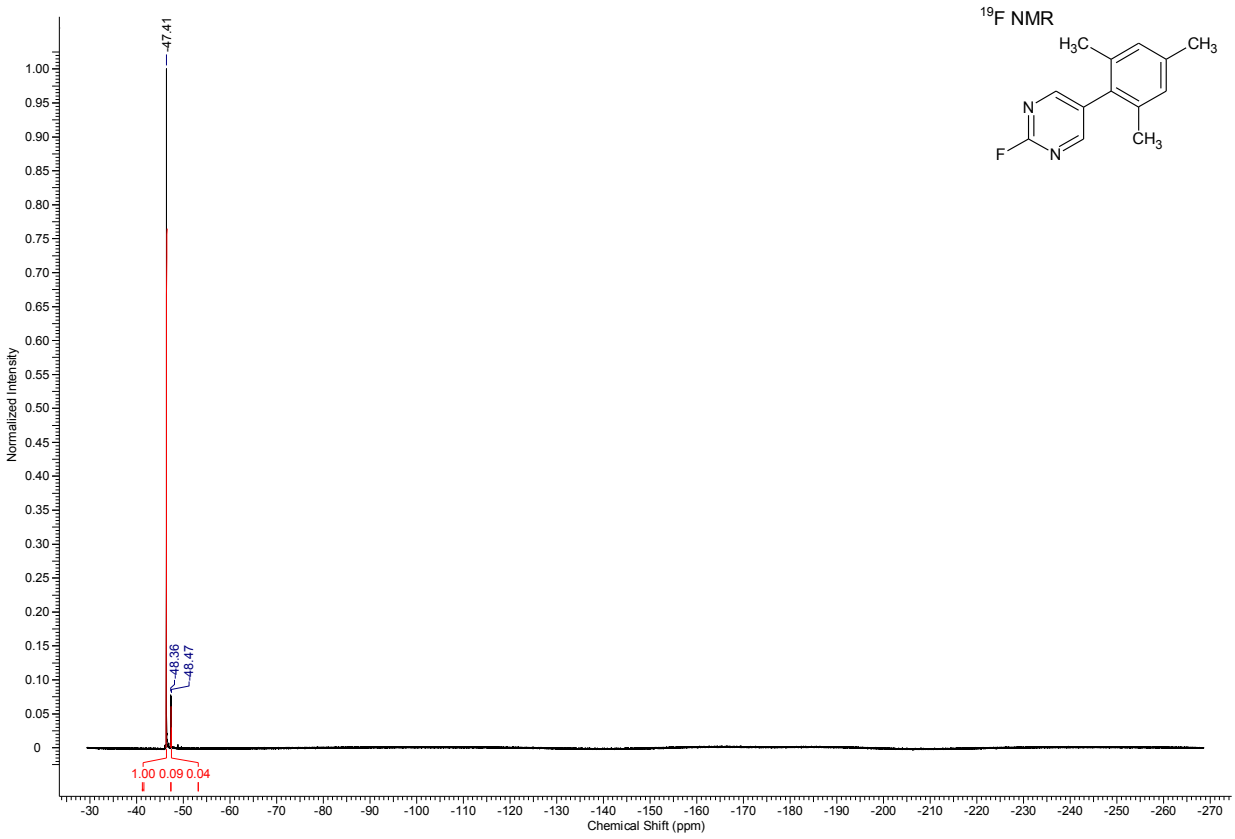

^{1}H NMR
Normalized Intensity
Chemical Shift (ppm)
8.60
8.59
7.27
6.22
3.87
3.75
1.94
1.98
3.06
6.00

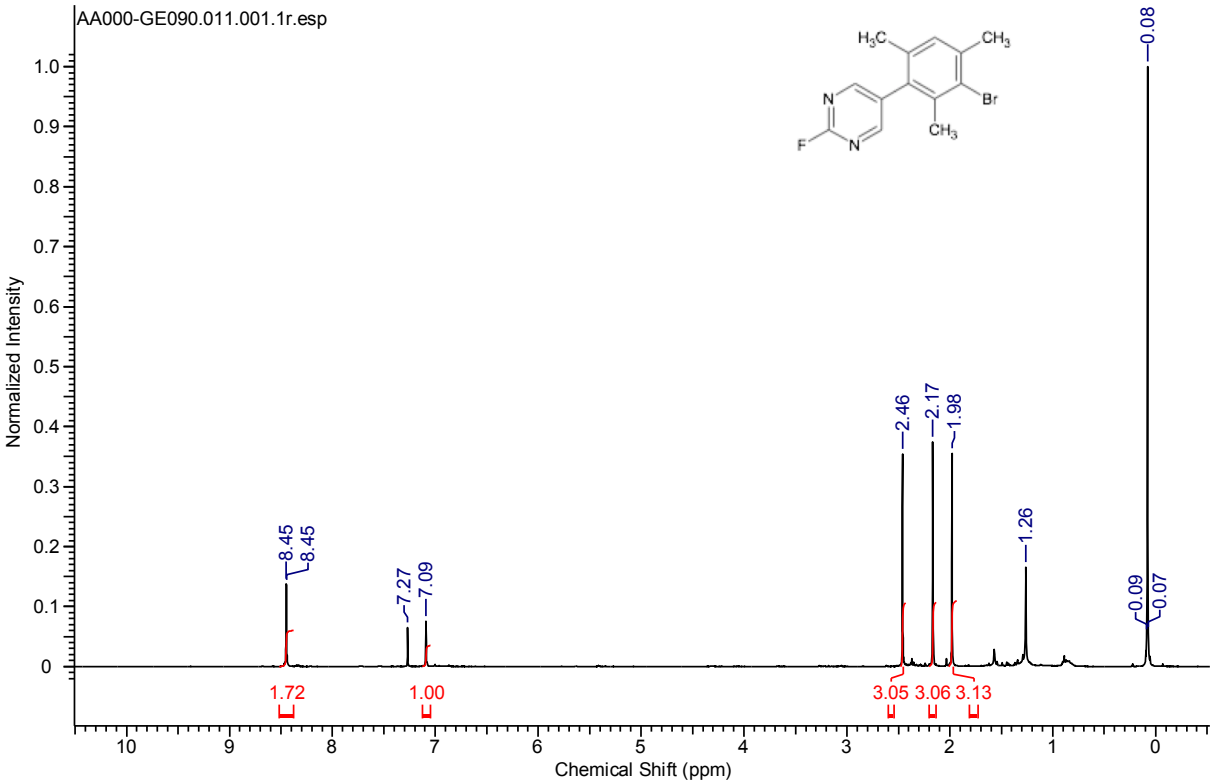

^{13}C NMR
Normalized Intensity
Chemical Shift (ppm)
162.37
162.22
162.59
161.99
158.24
126.29
126.22
103.25
90.68
77.43
77.00
76.58
55.67
55.40

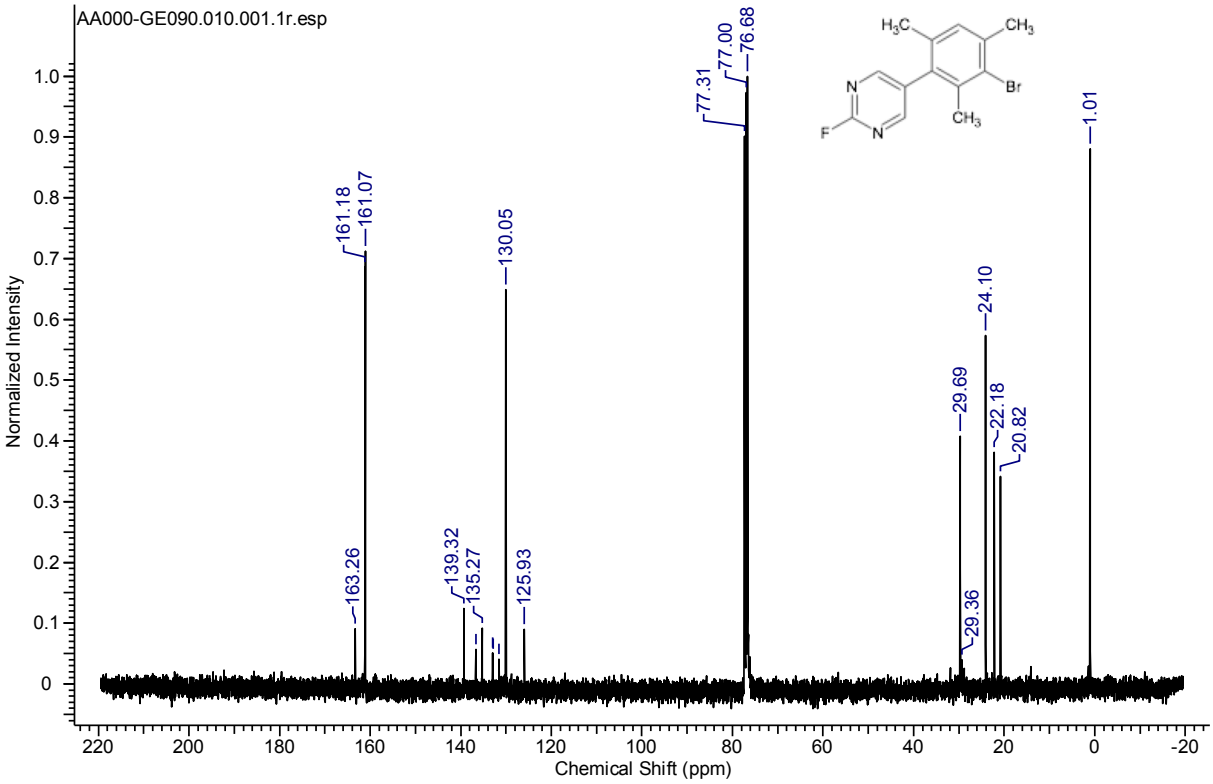

19F NMR
-49.02
Normalized Intensity
Chemical Shift (ppm)
CH3
O
O
CH3
N
F
N
H3C
O

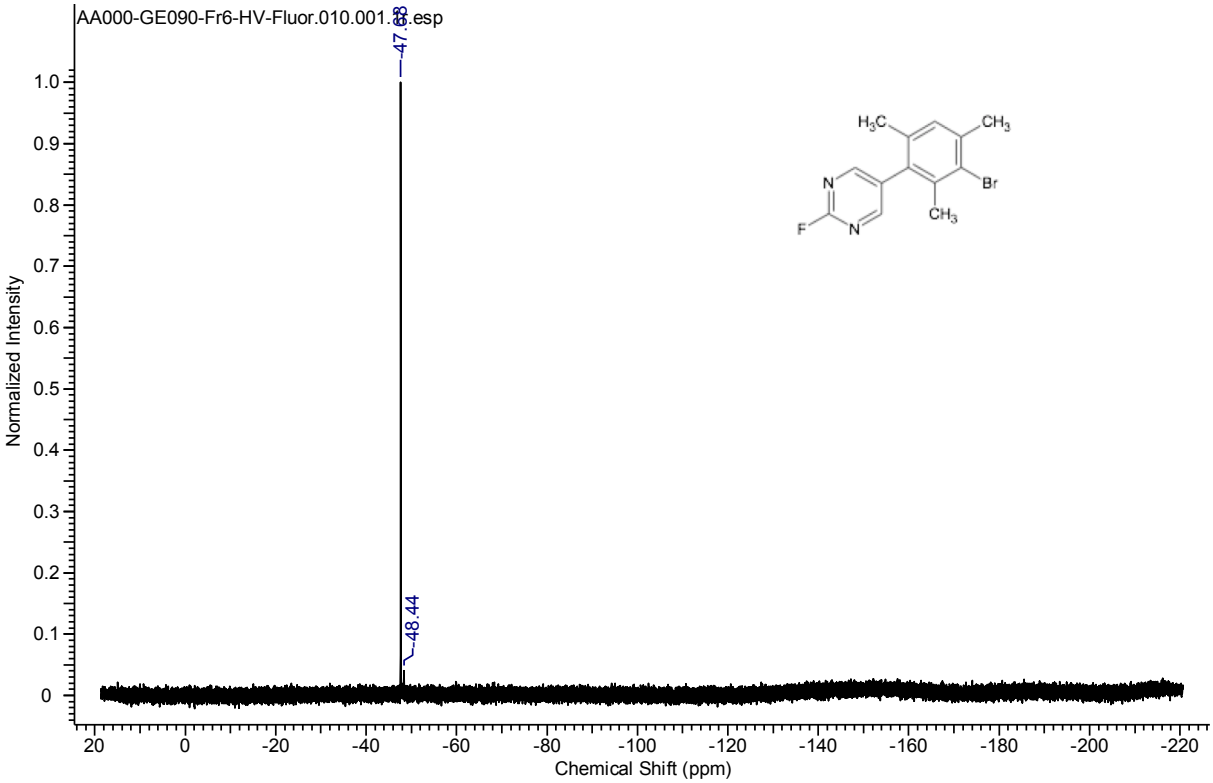

^{1}H NMR
Normalized Intensity
Chemical Shift (ppm)
8.47
8.47
7.01
2.35
2.04
2.00
2.00
2.98
6.02

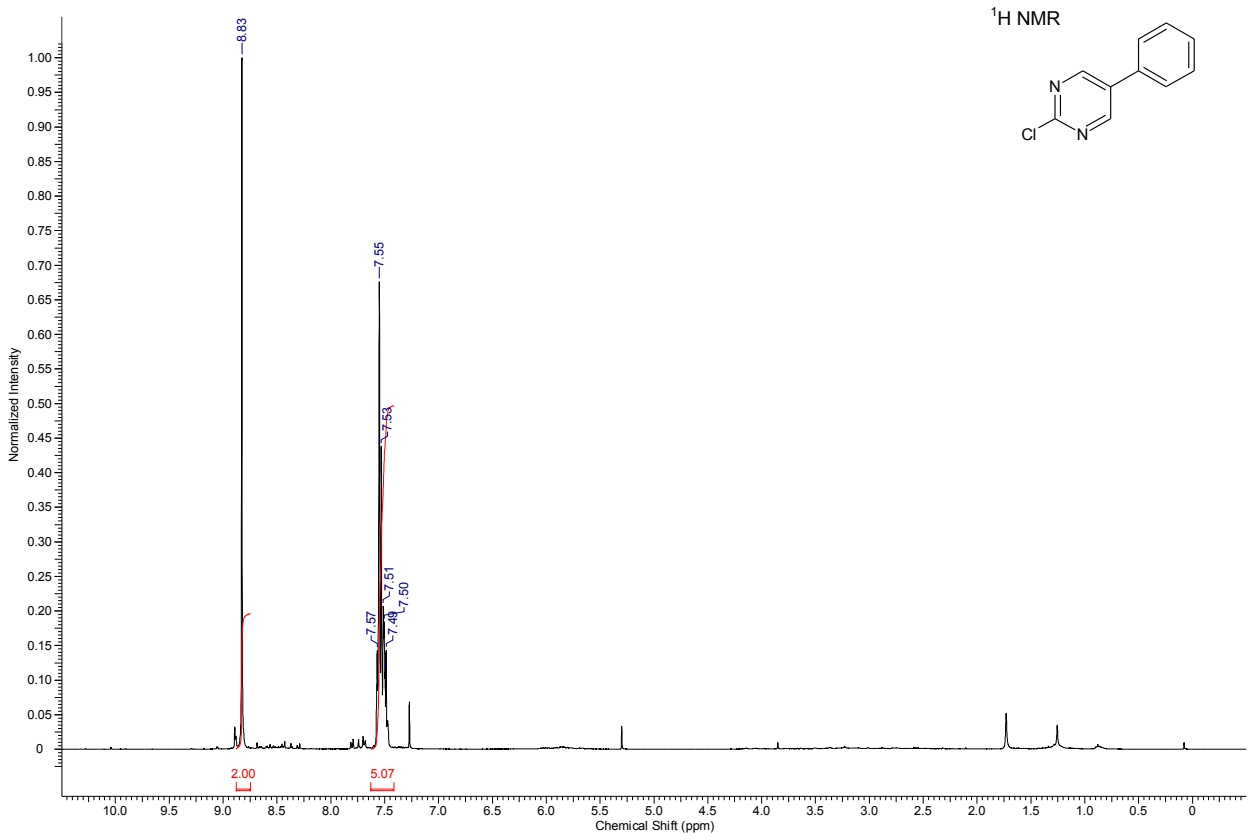

^{13}C NMR
Normalized Intensity
Chemical Shift (ppm)
128.72
161.25
161.13
163.12
160.85
138.77
136.43
132.64
130.99
128.50
128.26
127.81
77.32
77.00
76.68
20.82
21.01
21.43
0.99
1.13

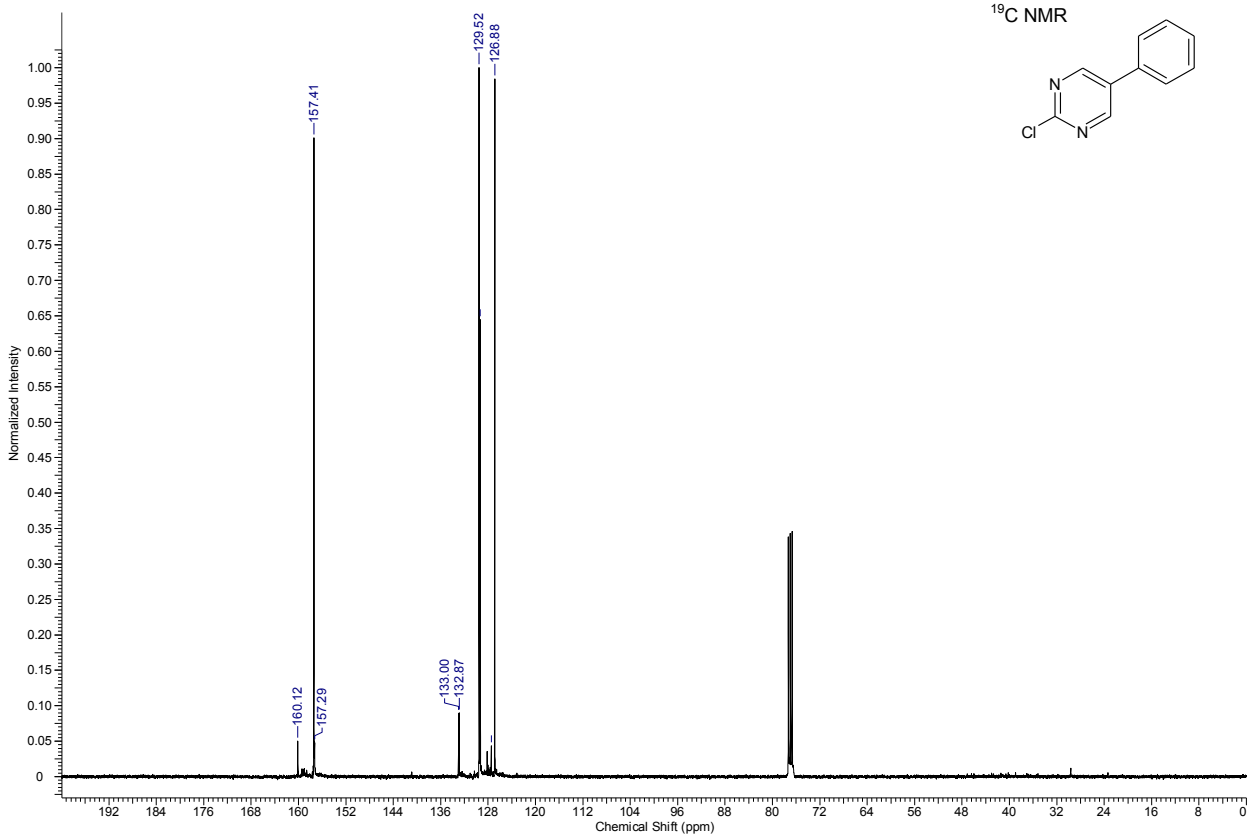

19F NMR
H3C
CH3
CH3
N
F
N
-47.41
-48.36
-48.47
1.00 0.09 0.04
Normalized Intensity
Chemical Shift (ppm)

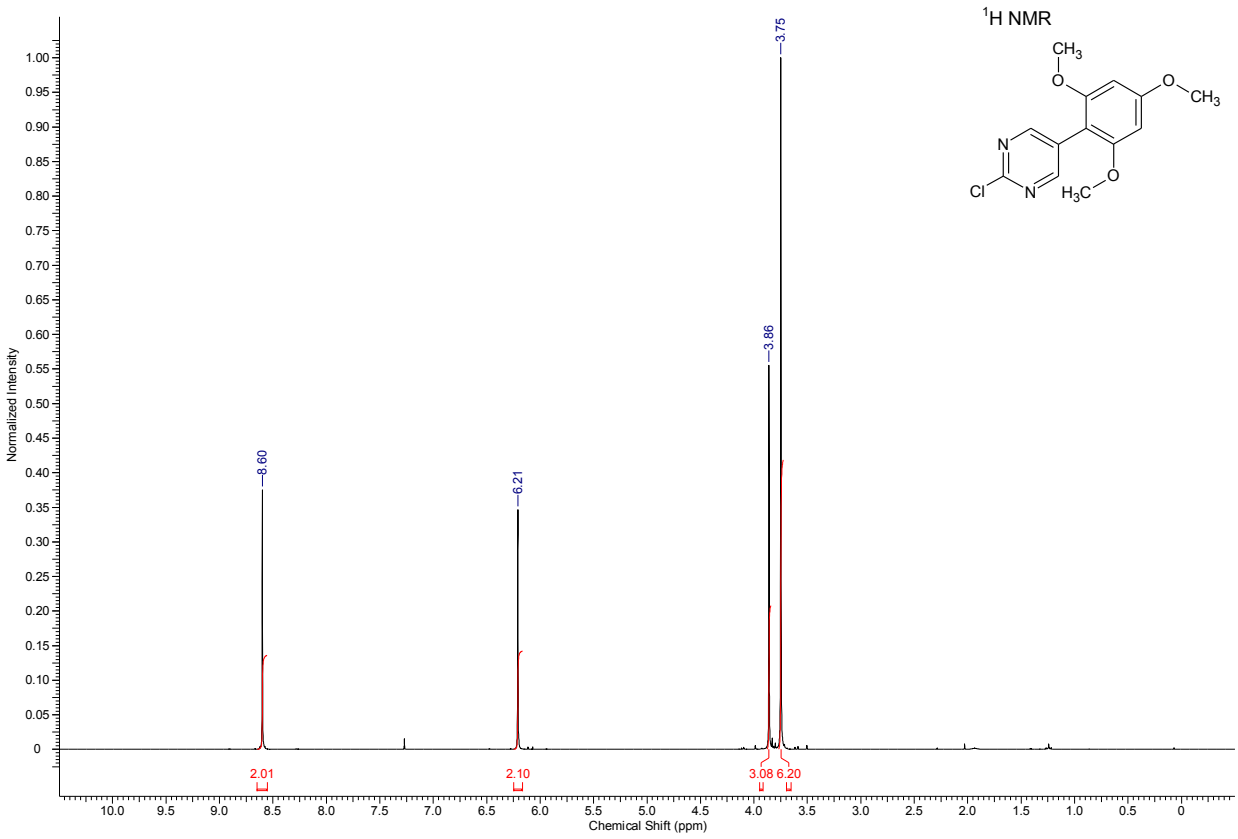

AA000-GE090.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
8.45
8.45
7.27
7.09
2.46
2.17
1.98
1.26
0.09
0.07
0.08
1.72
1.00
3.05
3.06
3.13

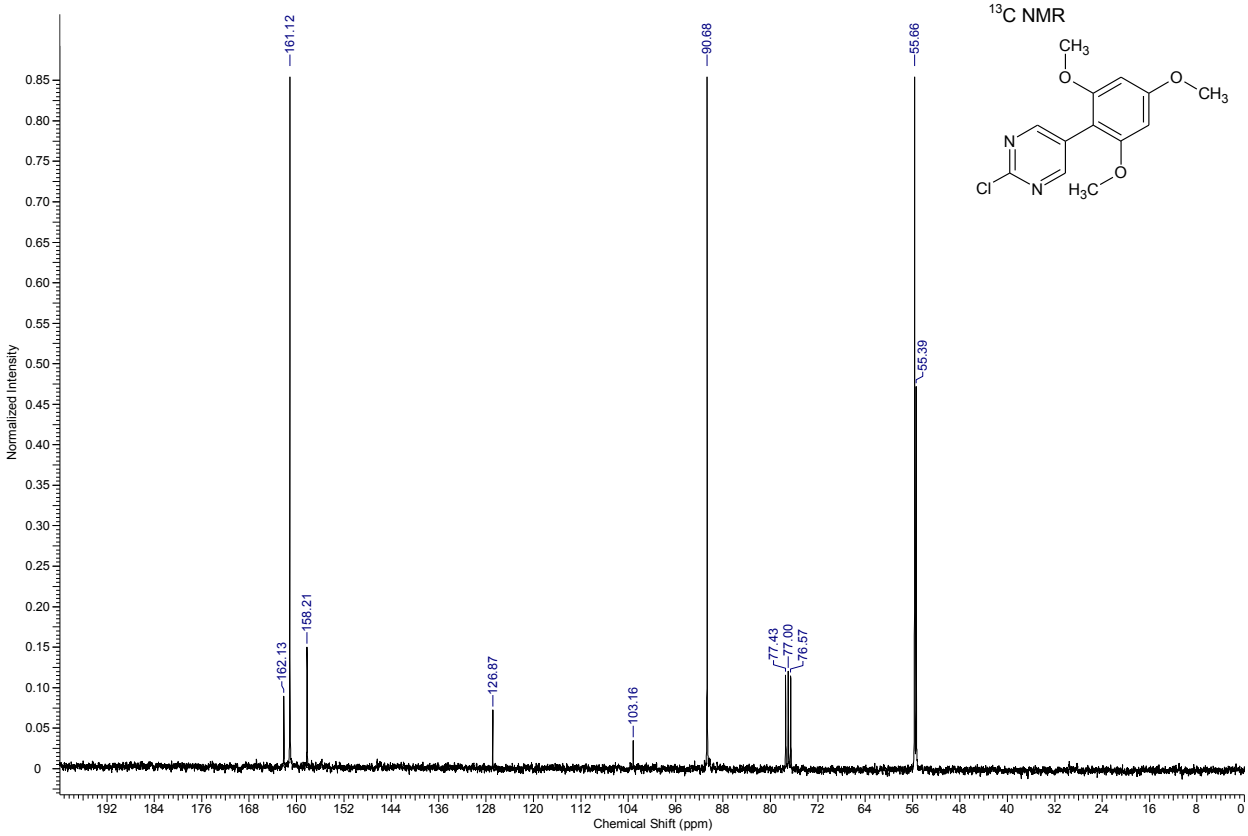

AA000-GE090.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
161.18
161.07
130.05
77.31
77.00
76.68
1.01
24.10
29.69
22.18
20.82
163.26
139.32
135.27
125.93
29.36

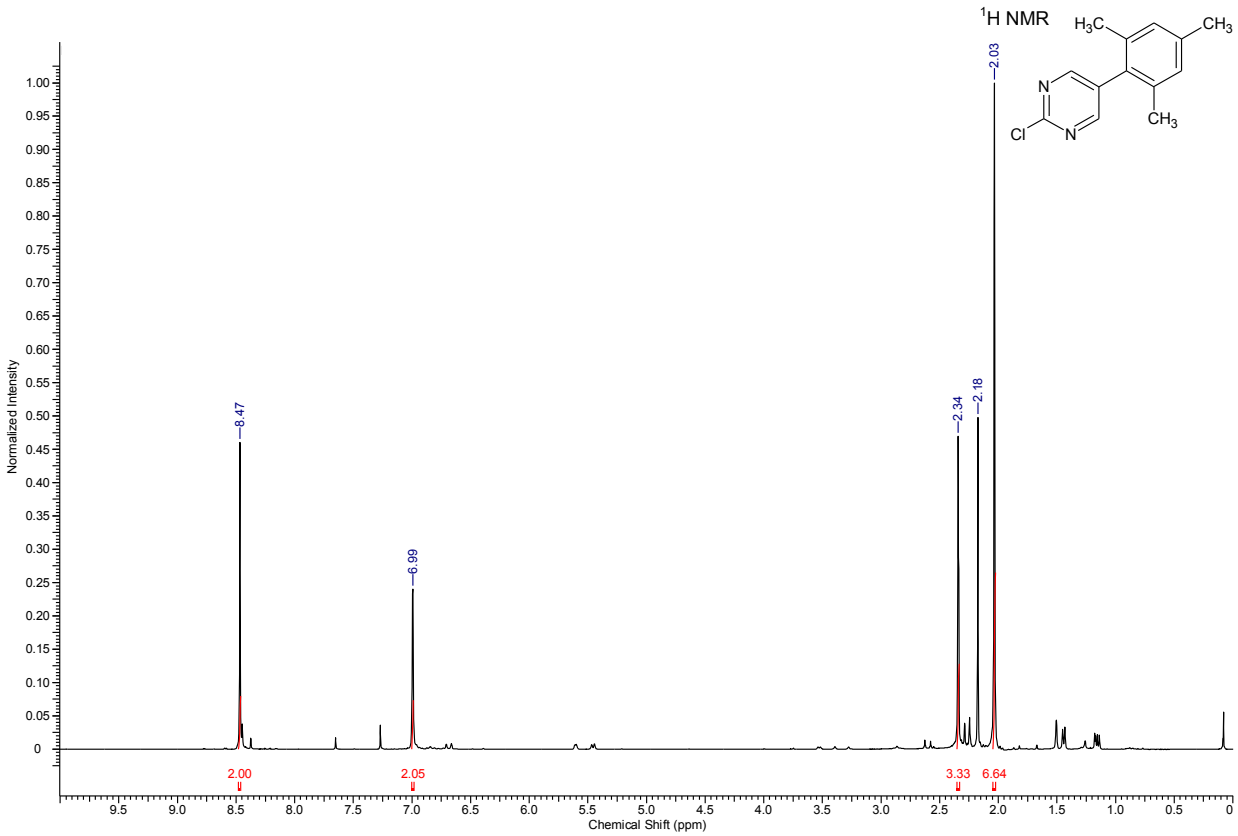

AA000-GE090-Fr6-HV-Fluor.010.001.esp
-47.88
-48.44
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)
H3C
CH3
Br
CH3
N
F
N

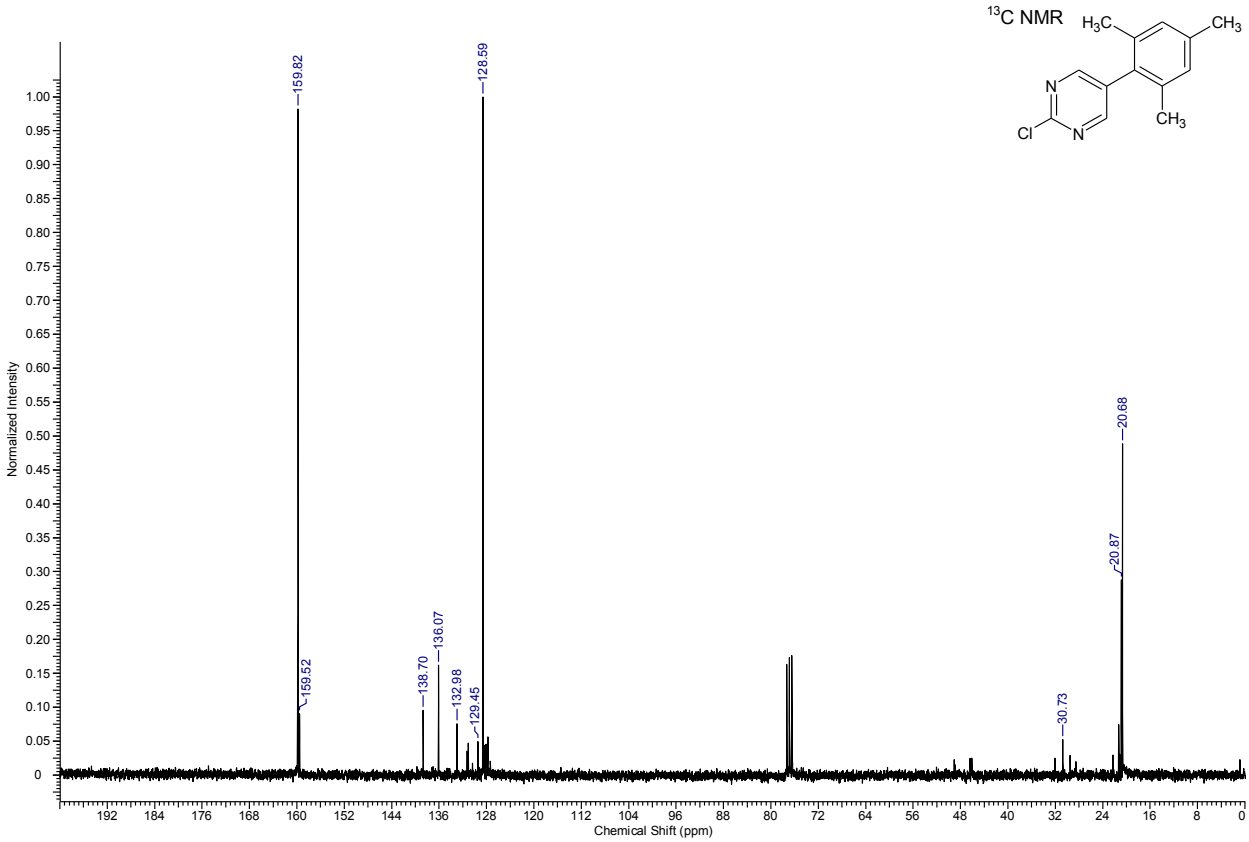

^{1}H NMR
N
Cl
N
8.83
7.55
7.53
7.51
7.50
7.49
7.57
2.00
5.07
Normalized Intensity
Chemical Shift (ppm)

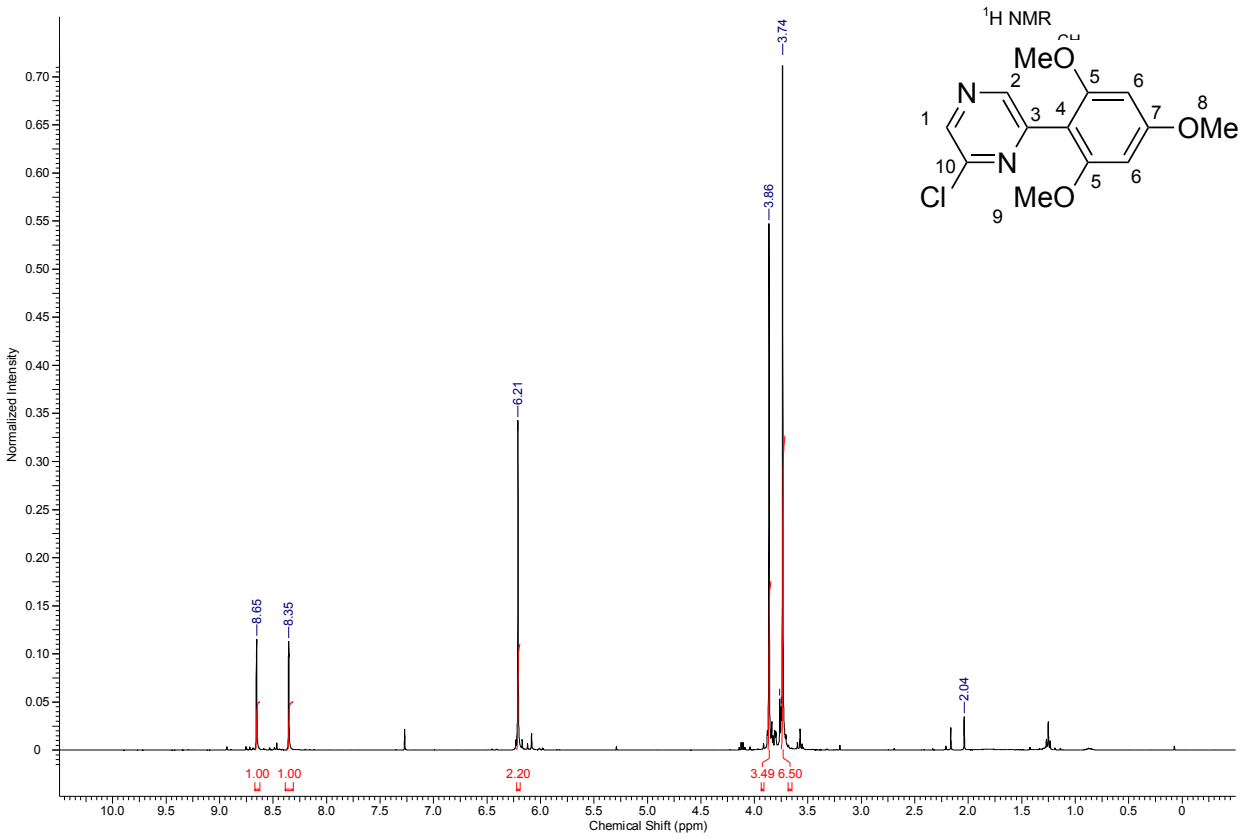

^{19}C NMR
N
Cl
N
157.41
129.52
126.88
160.12
157.29
133.00
132.87
Normalized Intensity
Chemical Shift (ppm)

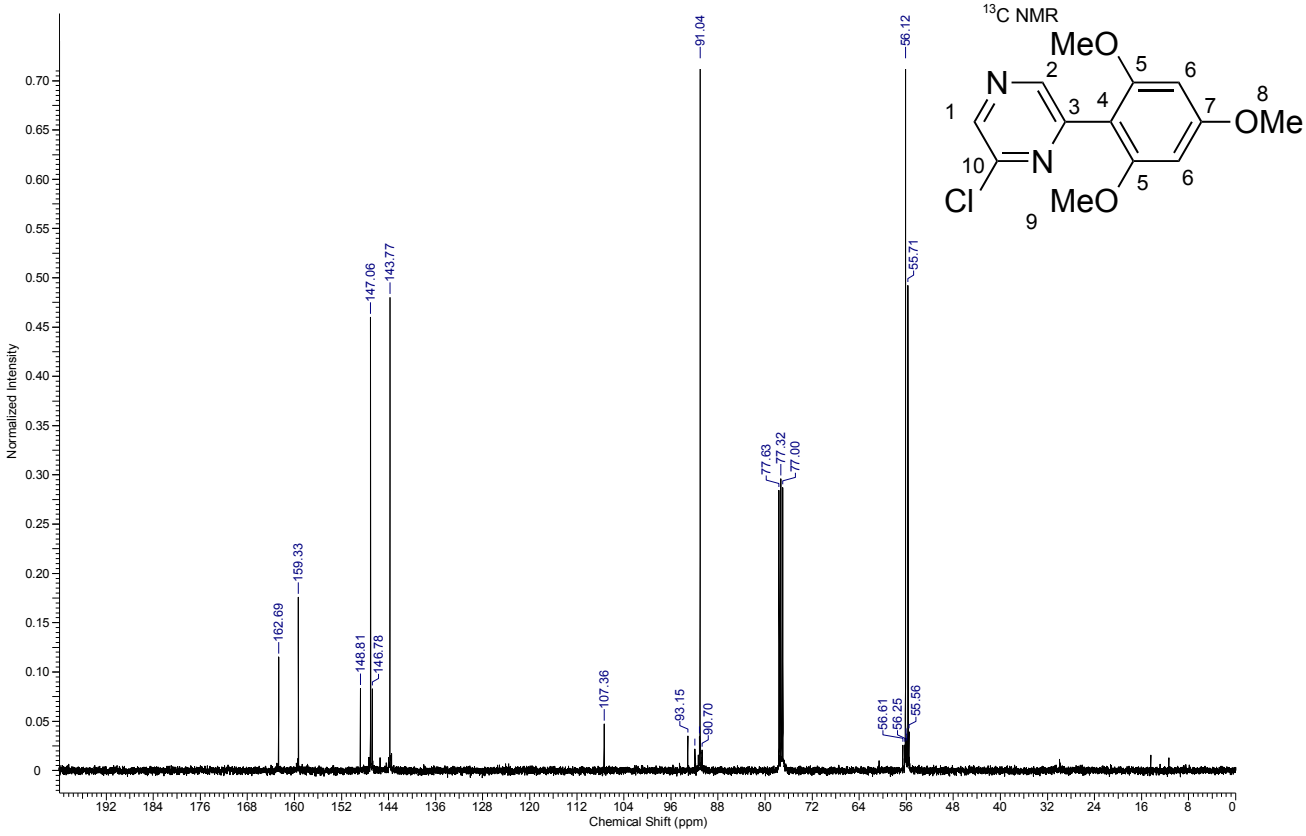

^{1}H NMR
Normalized Intensity
Chemical Shift (ppm)
8.60
6.21
3.86
3.75
2.01
2.10
3.08
6.20

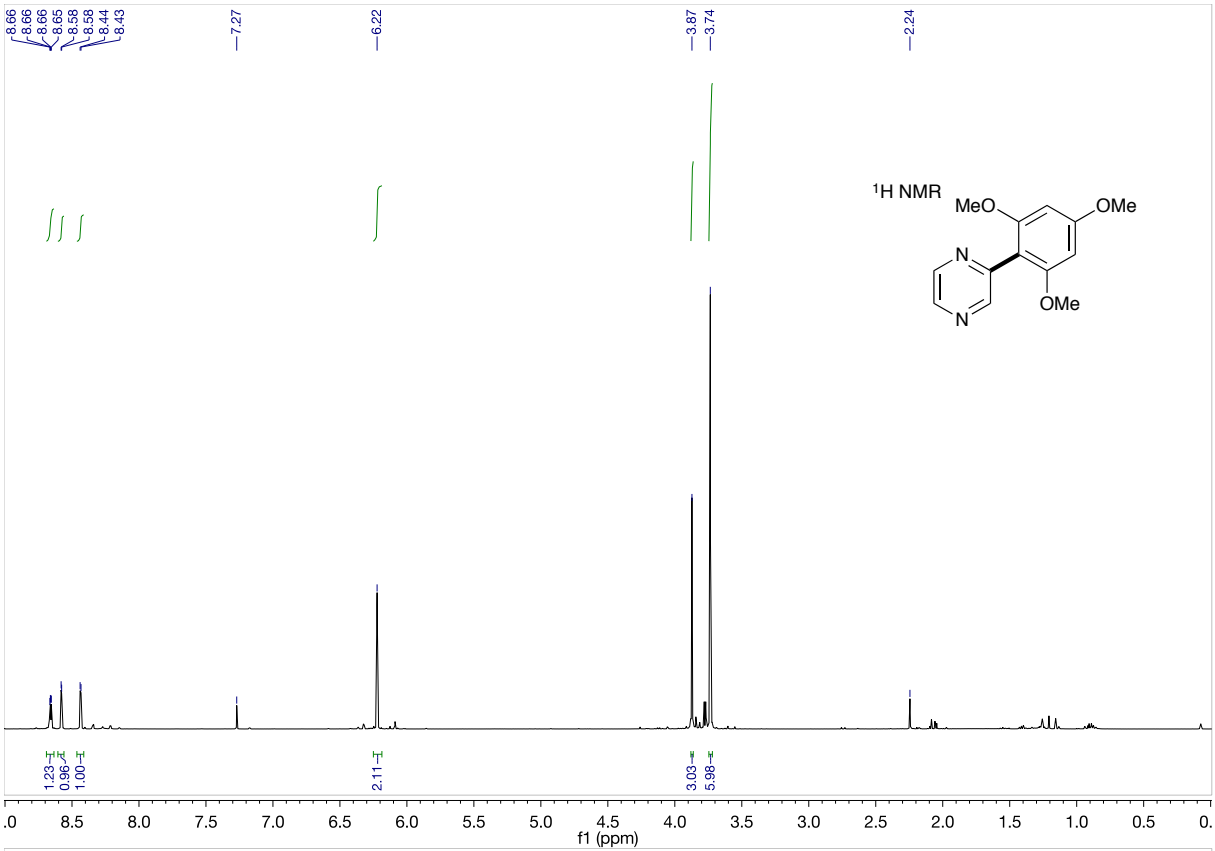

^{13}C NMR
Normalized Intensity
Chemical Shift (ppm)
161.12
90.68
55.66
55.39
158.21
162.13
126.87
103.16
77.43
77.00
76.57

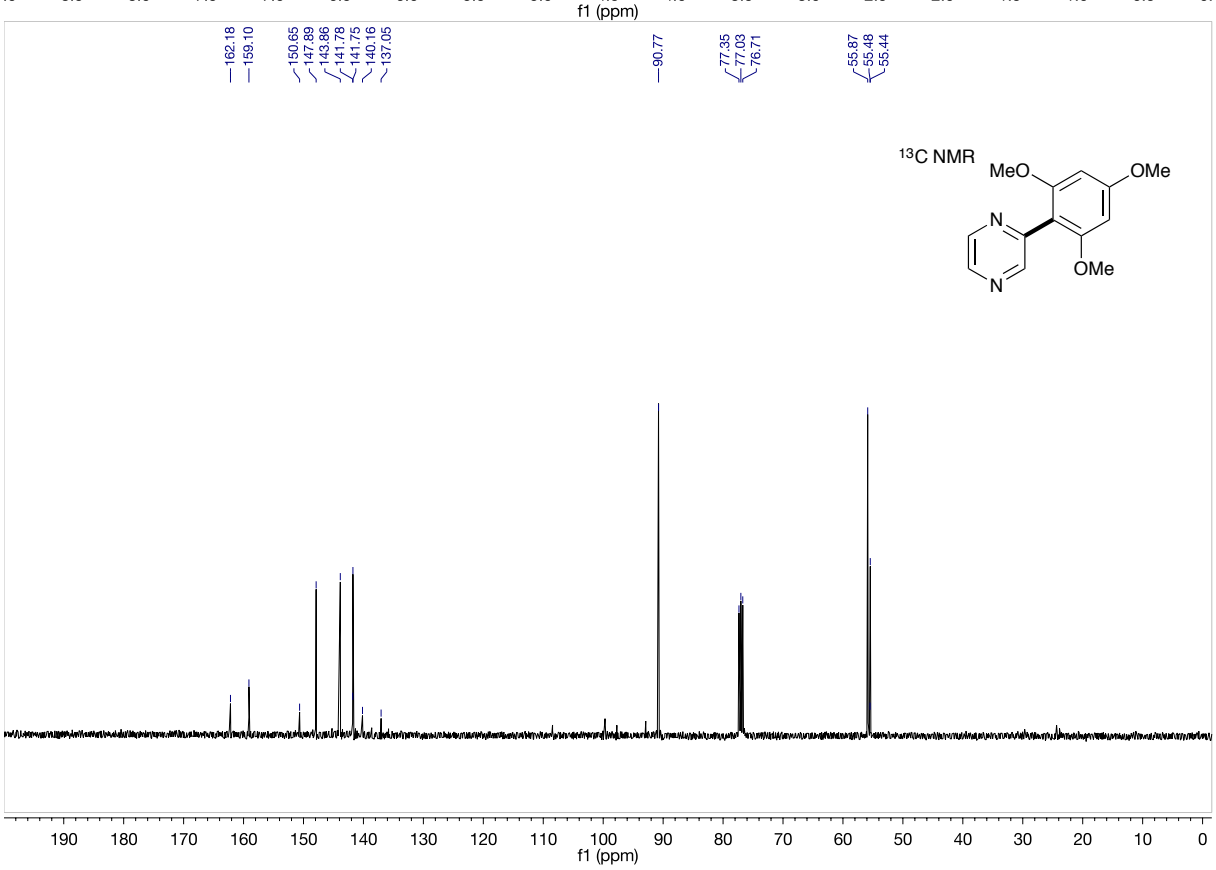

^{1}H NMR
H3C
CH3
CH3
N
Cl
N
2.03
8.47
6.99
2.34
2.18
2.00
2.05
3.33
6.64
Normalized Intensity
Chemical Shift (ppm)

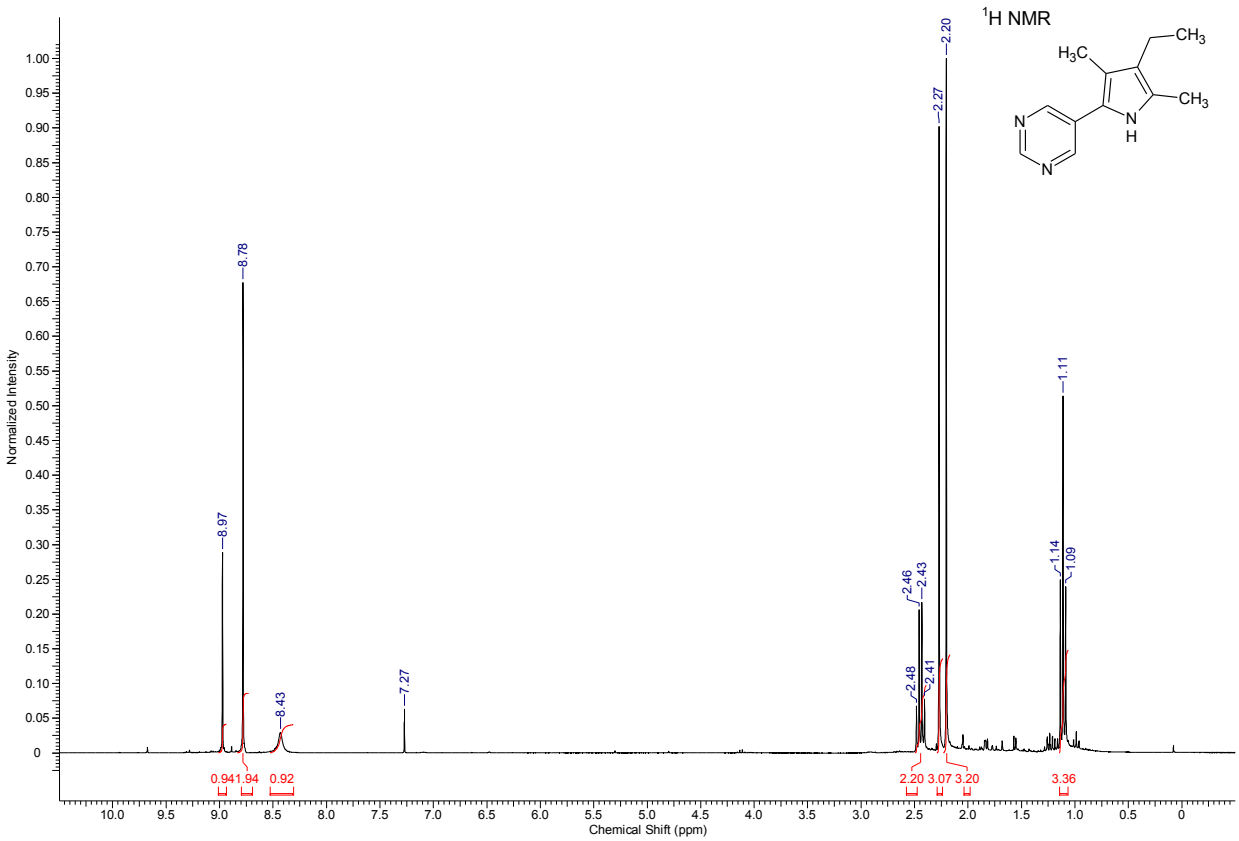

^{13}C NMR
H3C
CH3
CH3
N
Cl
N
159.82
128.59
159.52
138.70
136.07
132.98
129.45
20.68
20.87
30.73
Normalized Intensity
Chemical Shift (ppm)

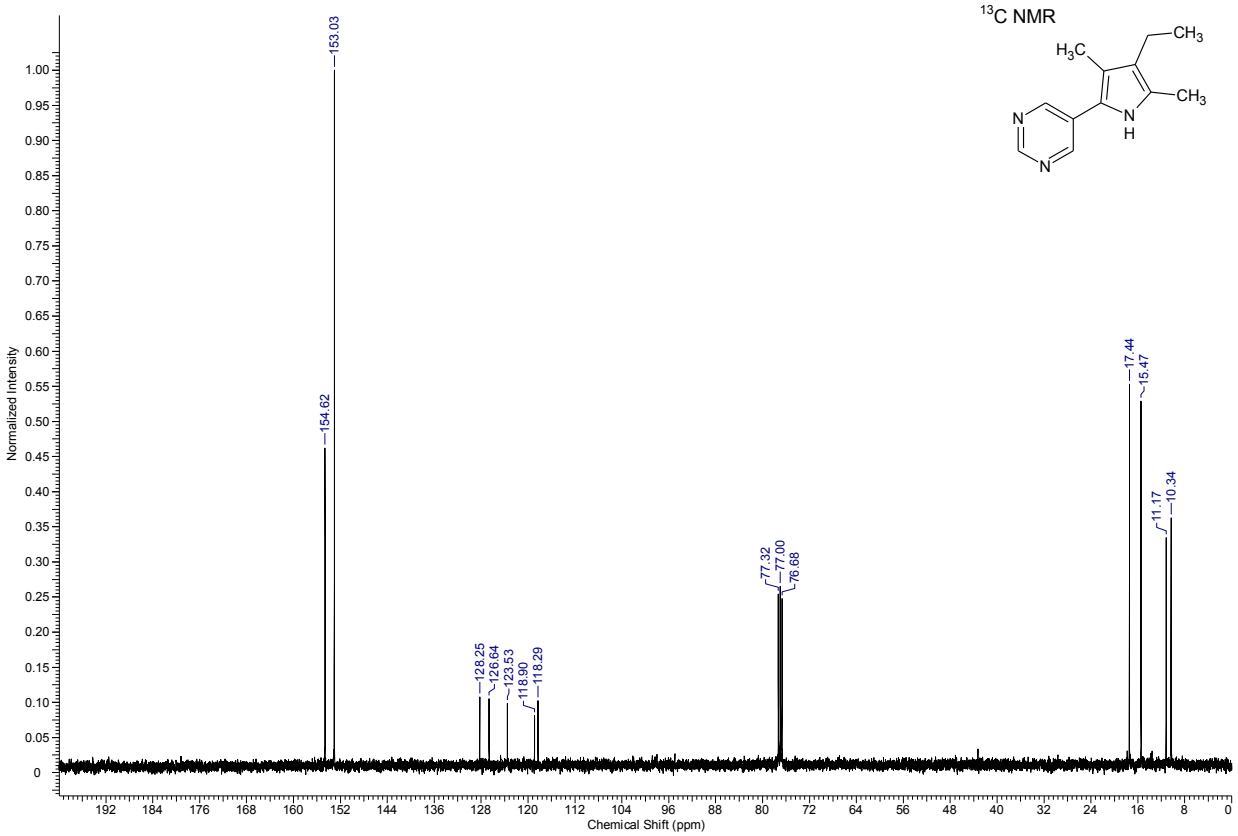

^{1}H NMR
MeO
N
OMe
N
Cl
MeO
Normalized Intensity
Chemical Shift (ppm)
8.65
8.35
6.21
3.74
3.86
2.04
1.00
1.00
2.20
3.49
6.50

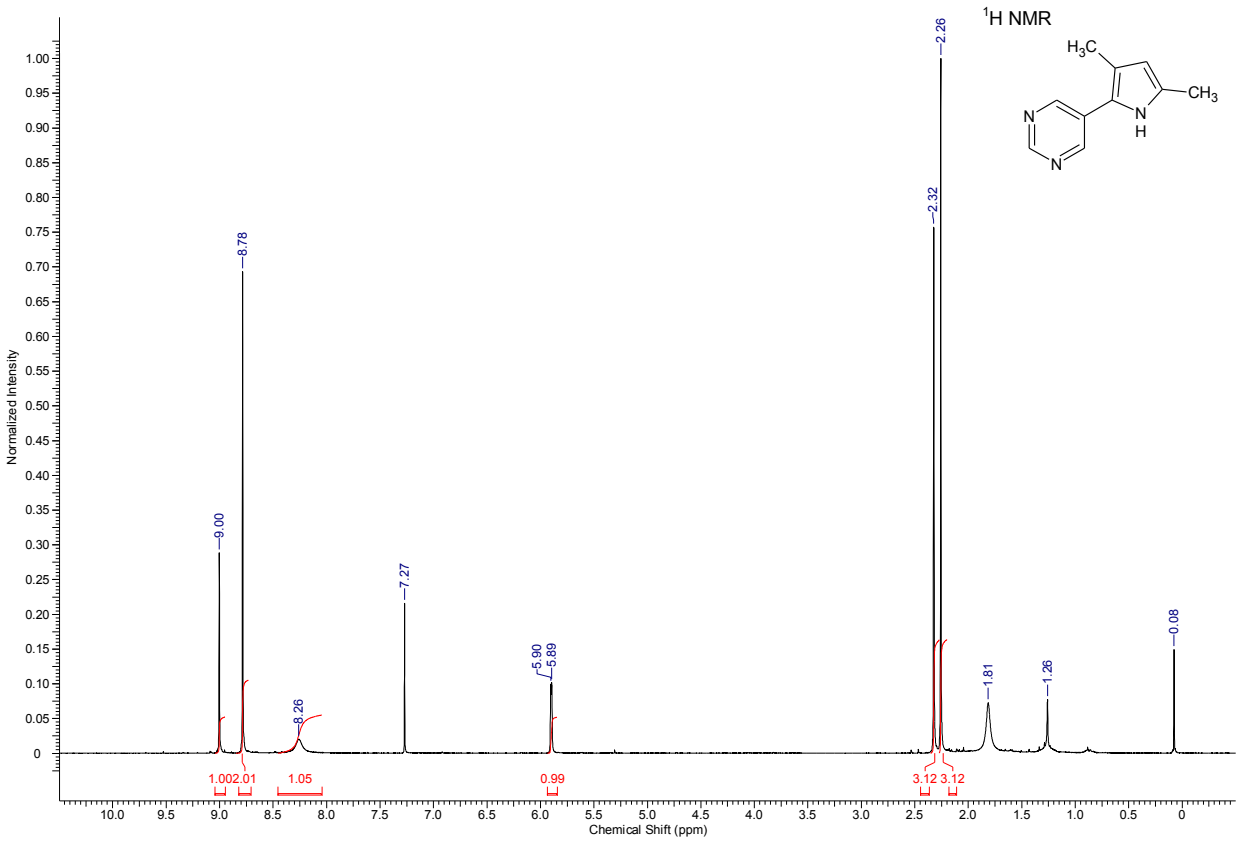

^{13}C NMR
MeO
N
OMe
N
Cl
MeO
Normalized Intensity
Chemical Shift (ppm)
91.04
56.12
147.06
143.77
55.71
77.63
77.32
77.00
159.33
162.69
148.81
146.78
107.36
93.15
90.70
56.61
56.25
55.56

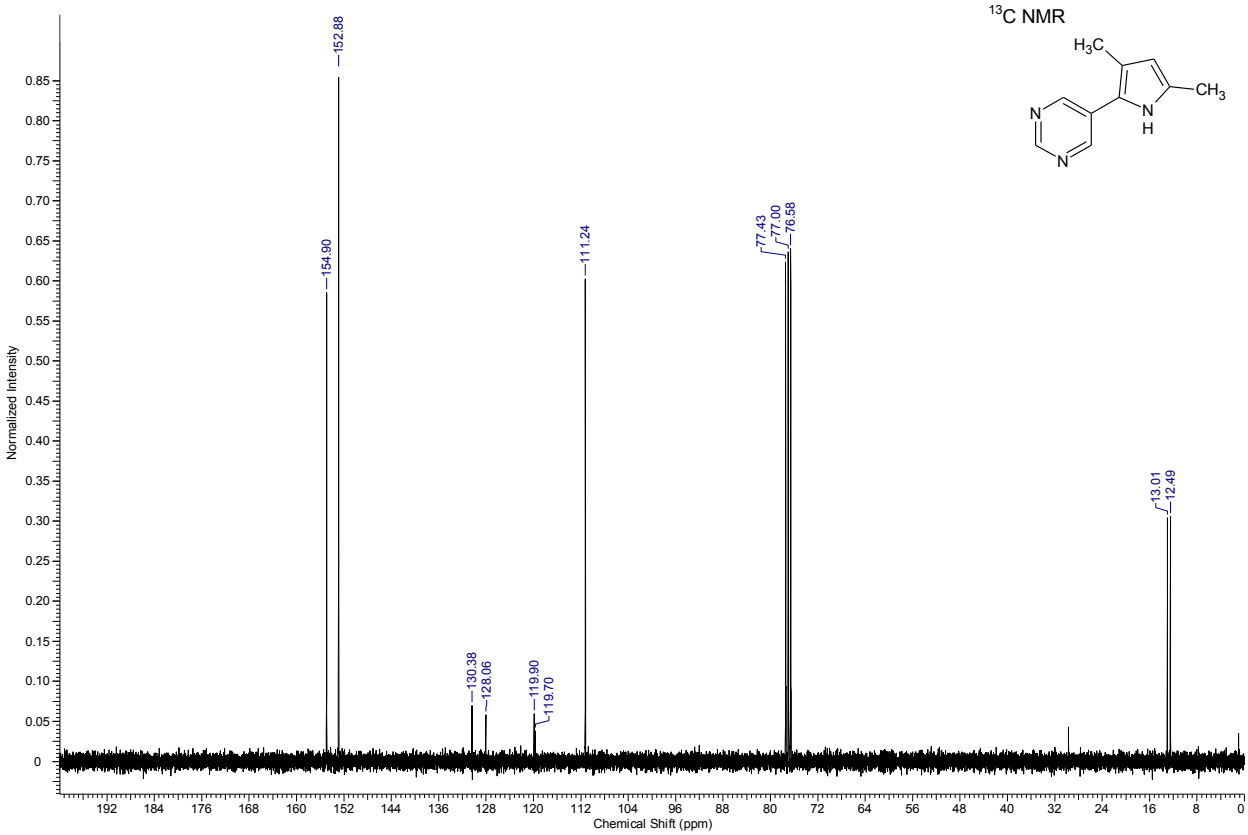

8.66
8.66
8.66
8.65
8.58
8.58
8.44
8.43
7.27
6.22
3.87
3.74
2.24
1H NMR
MeO
OMe
N
N
OMe
1.23
0.96
1.00
2.11
3.03
5.98
f1 (ppm)

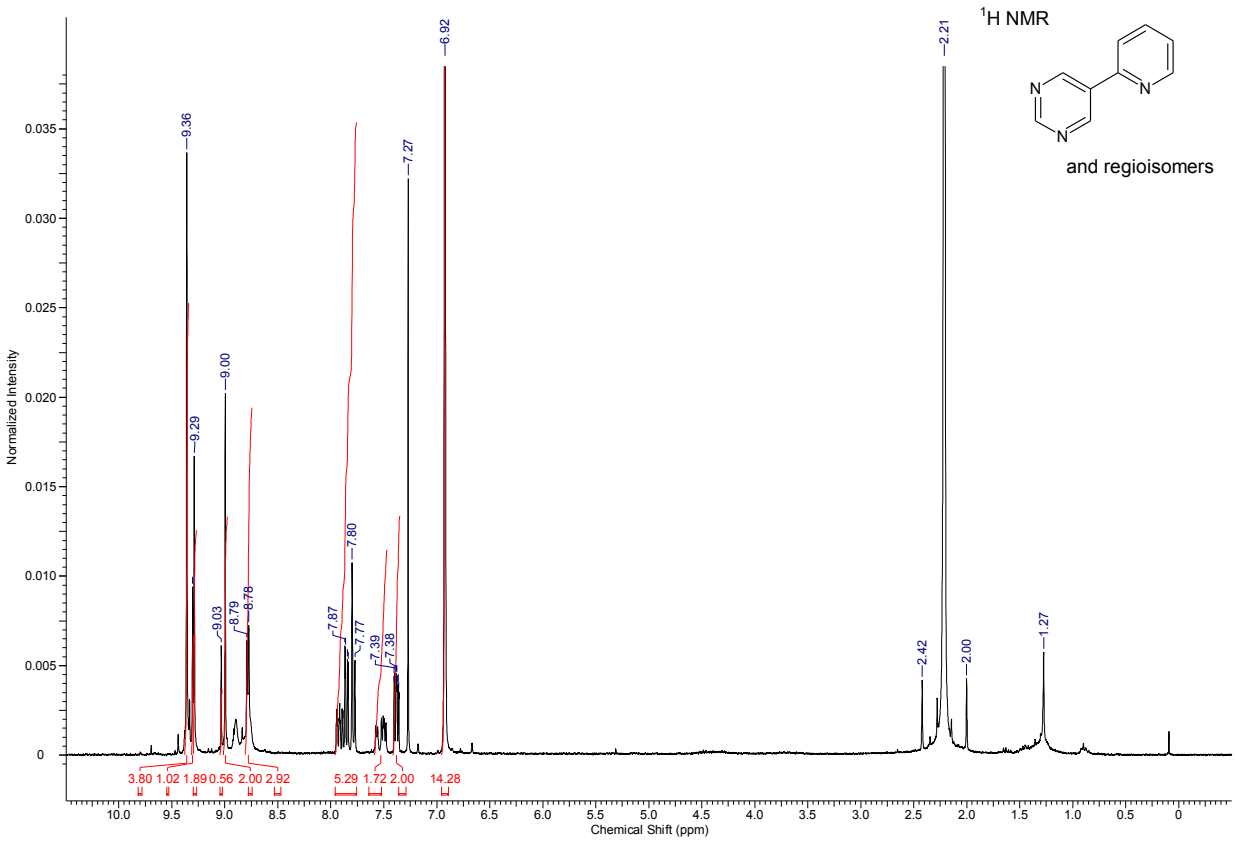

162.18
159.10
150.65
147.89
143.86
141.78
141.75
140.16
137.05
90.77
77.35
77.03
76.71
55.87
55.48
55.44
13C NMR
MeO
OMe
N
N
OMe
f1 (ppm)

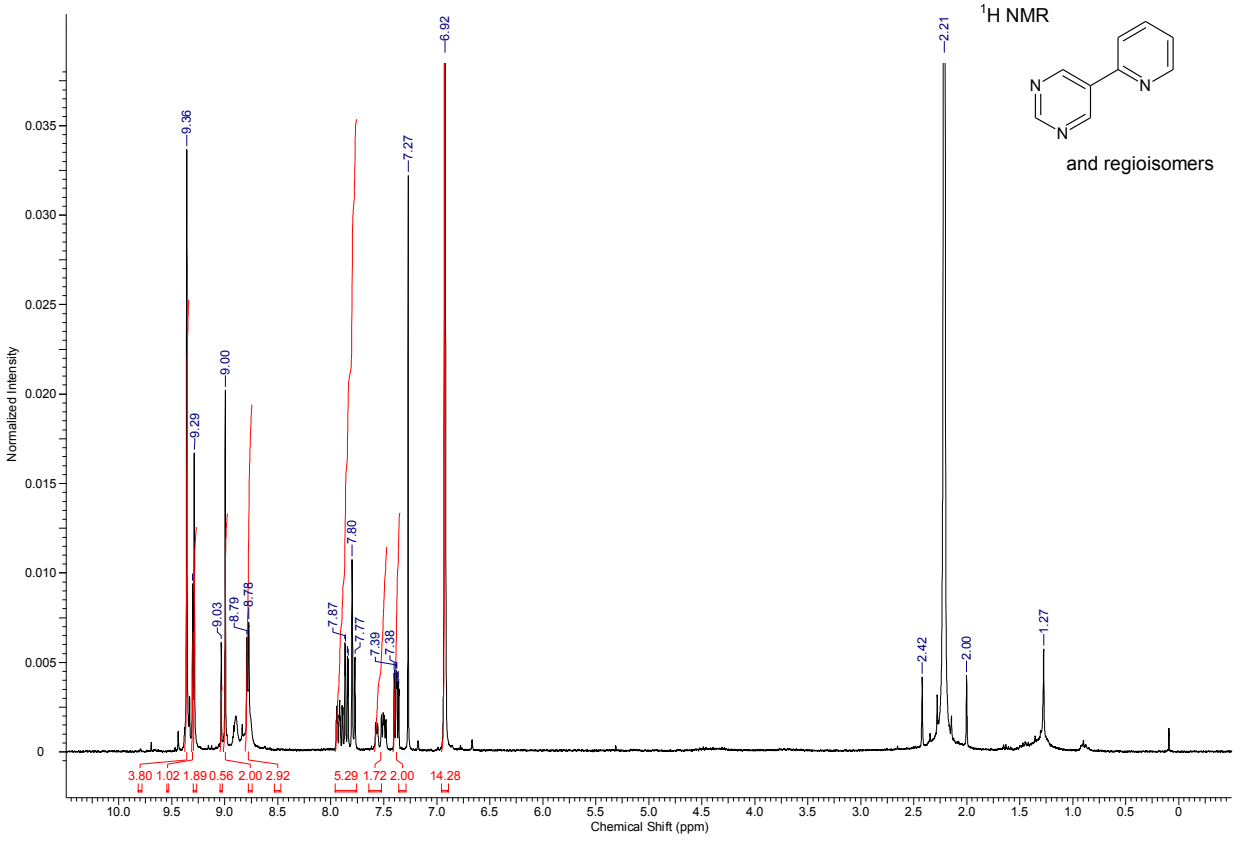

^{1}H NMR
Normalized Intensity
Chemical Shift (ppm)
8.97
8.78
8.43
7.27
2.48
2.46
2.43
2.41
2.27
2.20
1.14
1.11
1.09
0.94
1.94
0.92
2.20
3.07
3.20
3.36

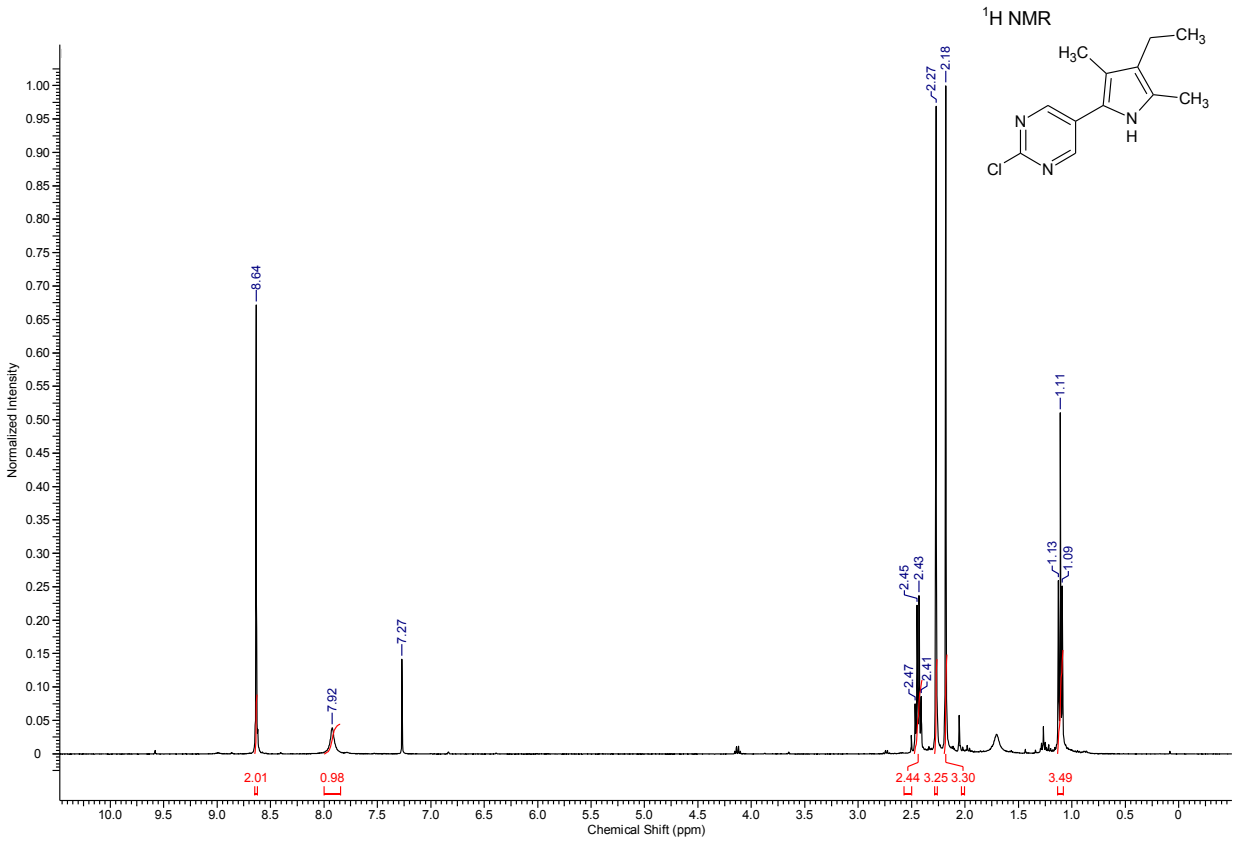

^{13}C NMR
Normalized Intensity
Chemical Shift (ppm)
153.03
154.62
128.25
126.64
123.53
118.90
118.29
77.32
77.00
76.68
17.44
15.47
11.17
10.34

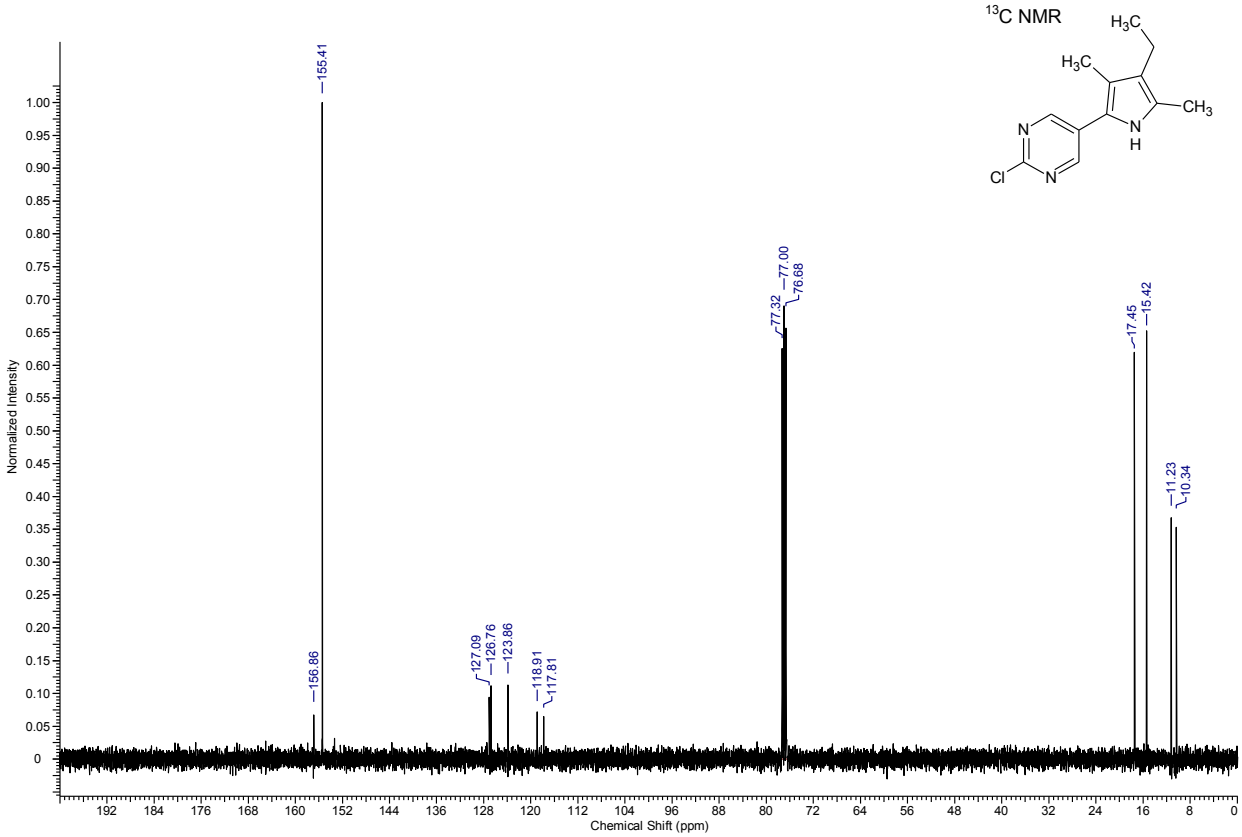

^{1}H NMR
Normalized Intensity
Chemical Shift (ppm)
9.00
8.78
8.26
7.27
5.90
5.89
2.32
2.26
1.81
1.26
0.08
1.00
2.01
1.05
0.99
3.12
3.12

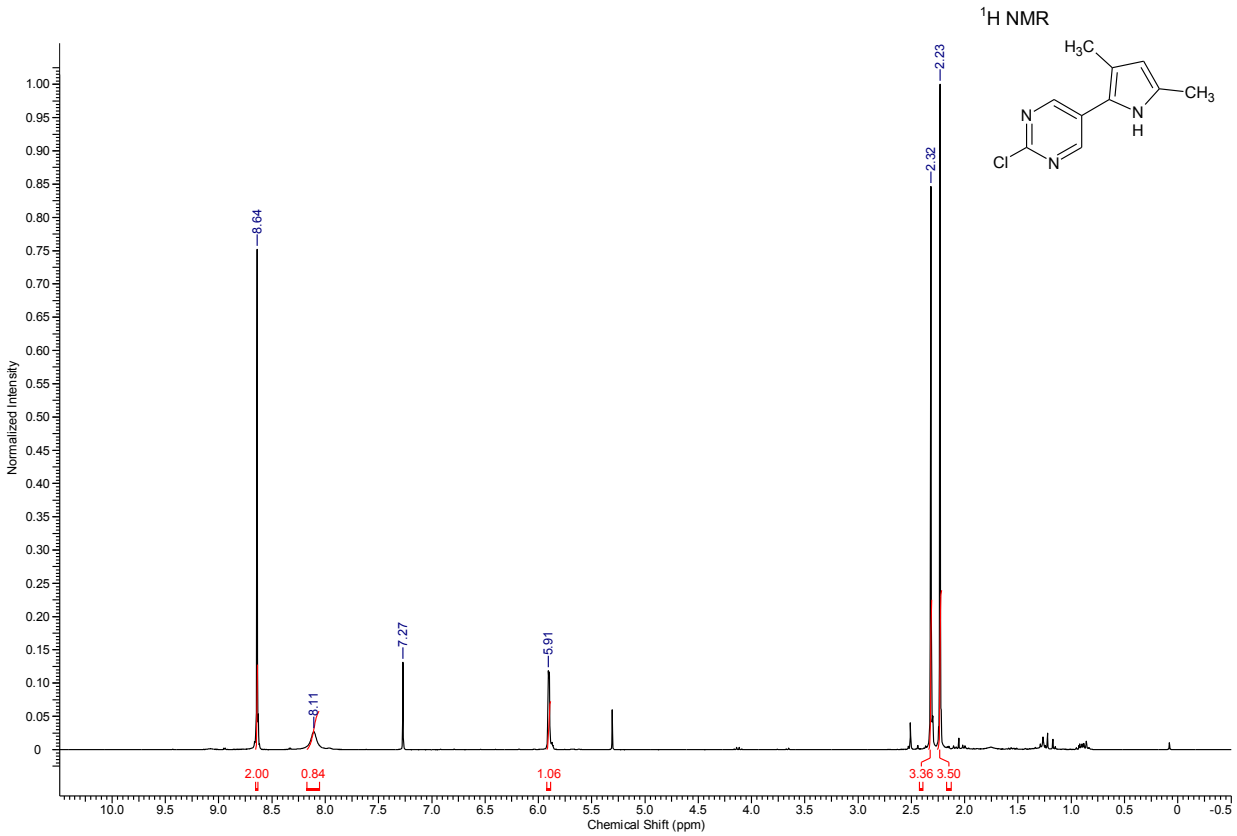

^{13}C NMR
Normalized Intensity
Chemical Shift (ppm)
152.88
154.90
130.38
128.06
119.90
119.70
111.24
77.43
77.00
76.58
13.01
12.49

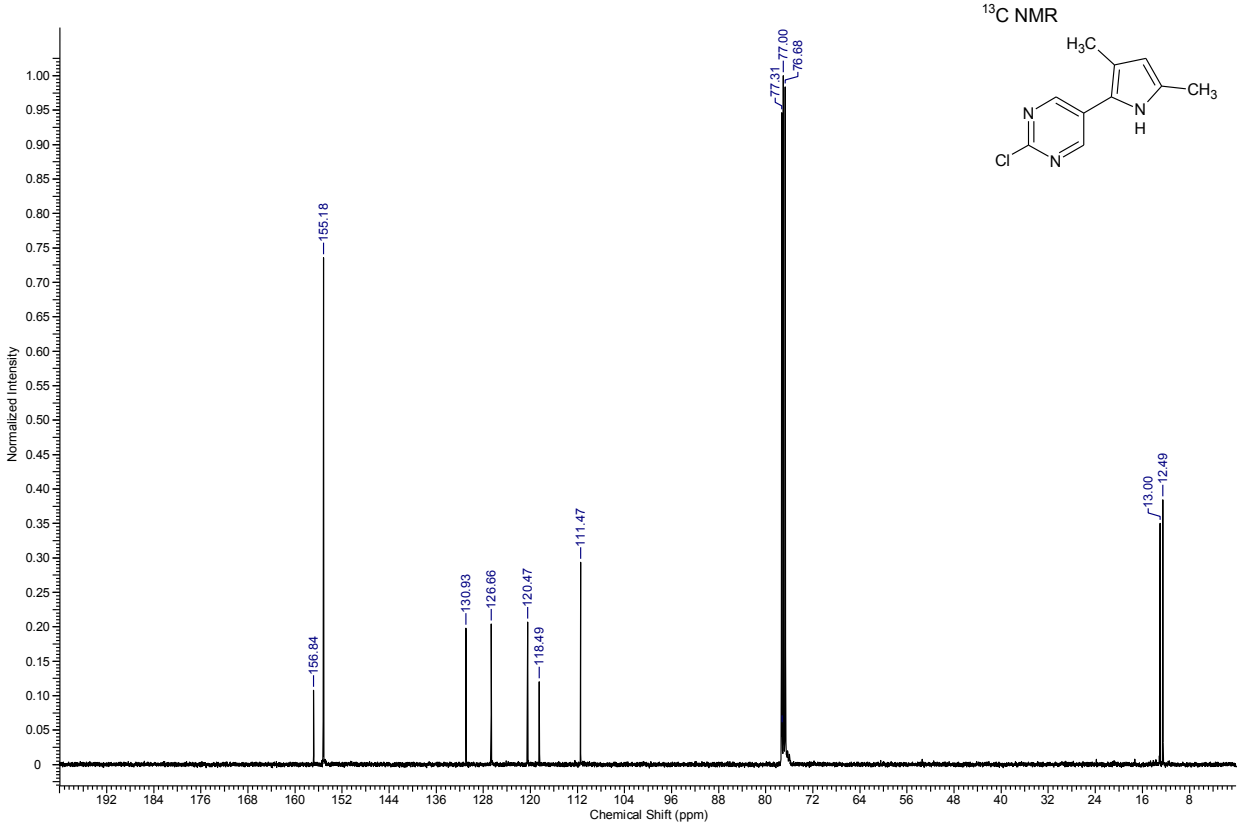

^{1}H NMR
and regioisomers
Normalized Intensity
Chemical Shift (ppm)
9.36
9.29
9.00
9.03
8.79
8.78
7.87
7.80
7.77
7.39
7.38
7.27
6.92
2.42
2.21
2.00
1.27
3.80 1.02 1.89 0.56 2.00 2.92
5.29 1.72 2.00 14.28

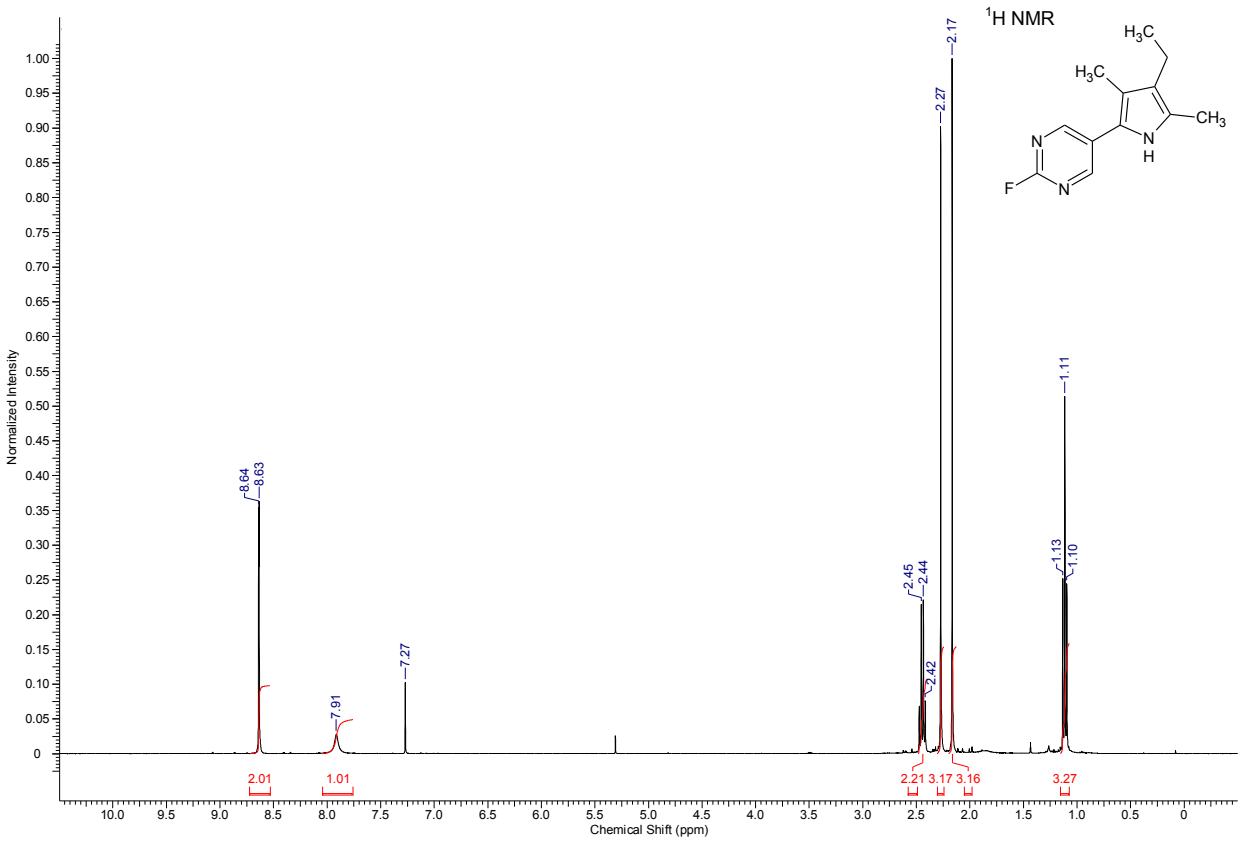

^{1}H NMR
and regioisomers
Normalized Intensity
Chemical Shift (ppm)
9.36
9.29
9.00
9.03
8.79
8.78
7.87
7.80
7.77
7.39
7.38
7.27
6.92
2.42
2.21
2.00
1.27
3.80 1.02 1.89 0.56 2.00 2.92
5.29 1.72 2.00 14.28

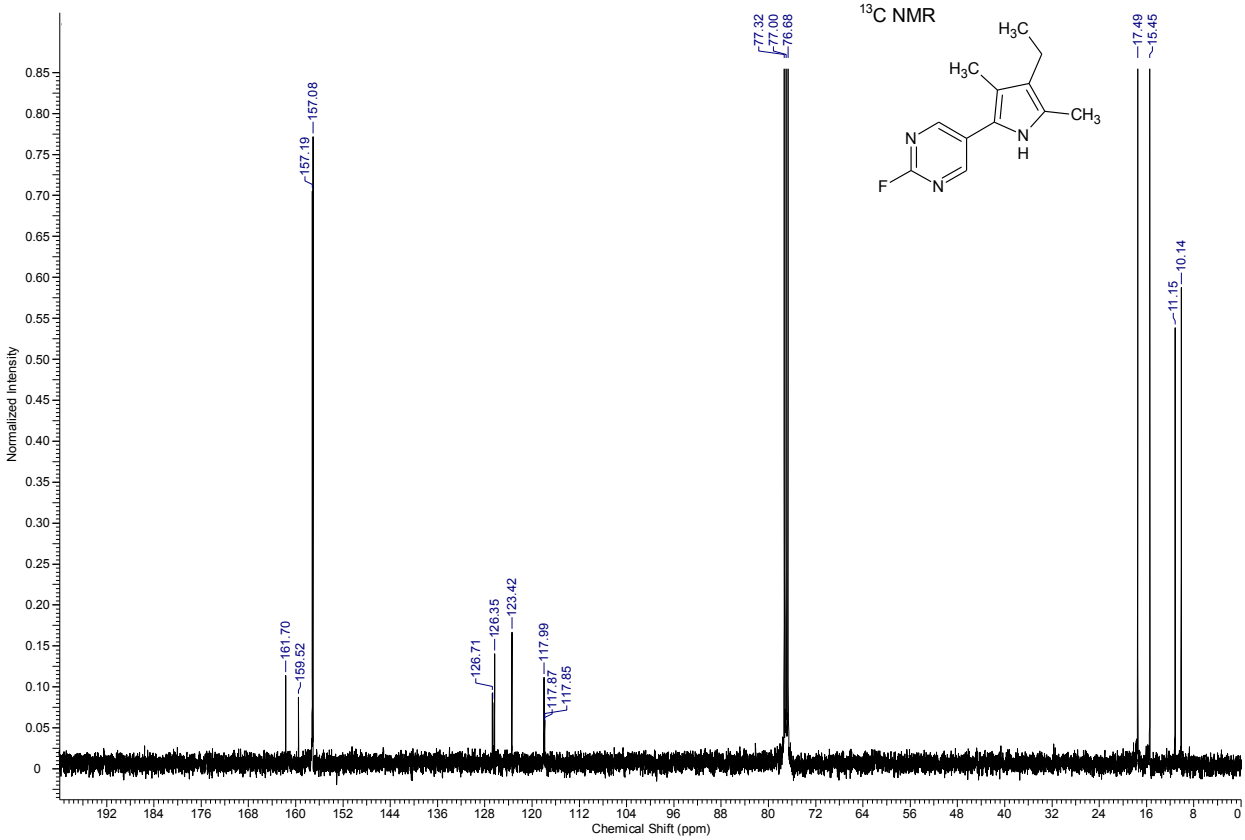

^{1}H NMR
Normalized Intensity
Chemical Shift (ppm)
8.64
7.92
7.27
2.27
2.18
2.45
2.43
2.47
2.41
1.13
1.09
1.11
2.01
0.98
2.44
3.25
3.30
3.49

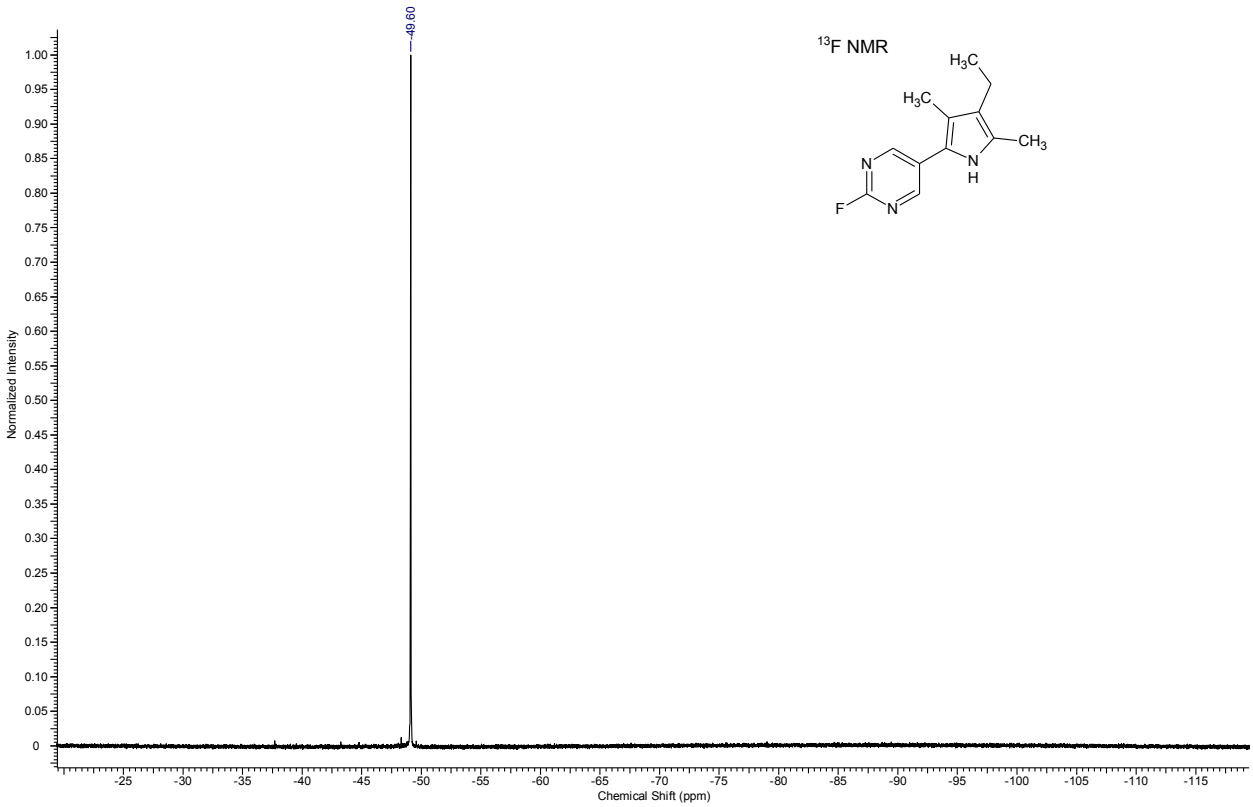

^{13}C NMR
Normalized Intensity
Chemical Shift (ppm)
155.41
156.86
127.09
126.76
123.86
118.91
117.81
77.32
77.00
76.68
17.45
15.42
11.23
10.34

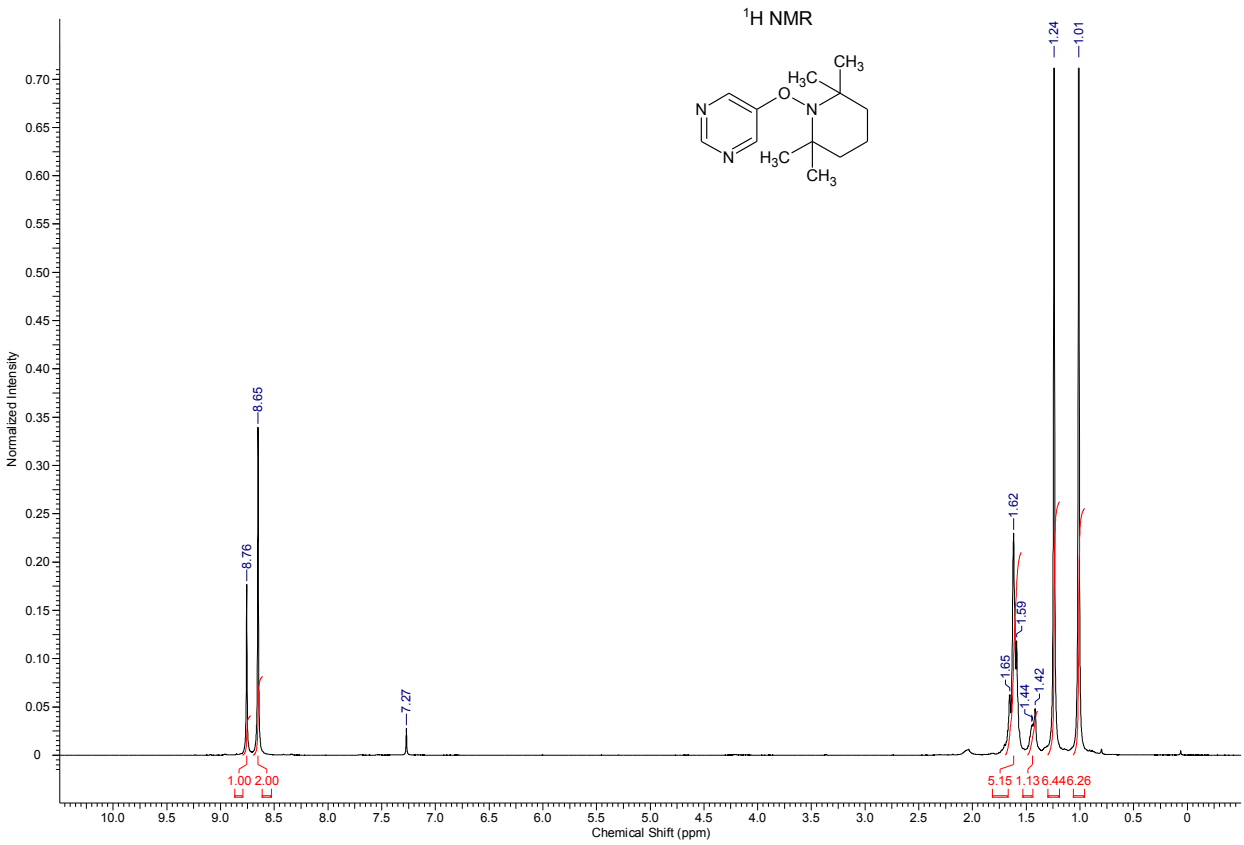

^{1}H NMR
H3C
CH3
N
N
H
Cl
N
8.64
8.11
7.27
5.91
2.32
2.23
2.00
0.84
1.06
3.36
3.50
Normalized Intensity
Chemical Shift (ppm)

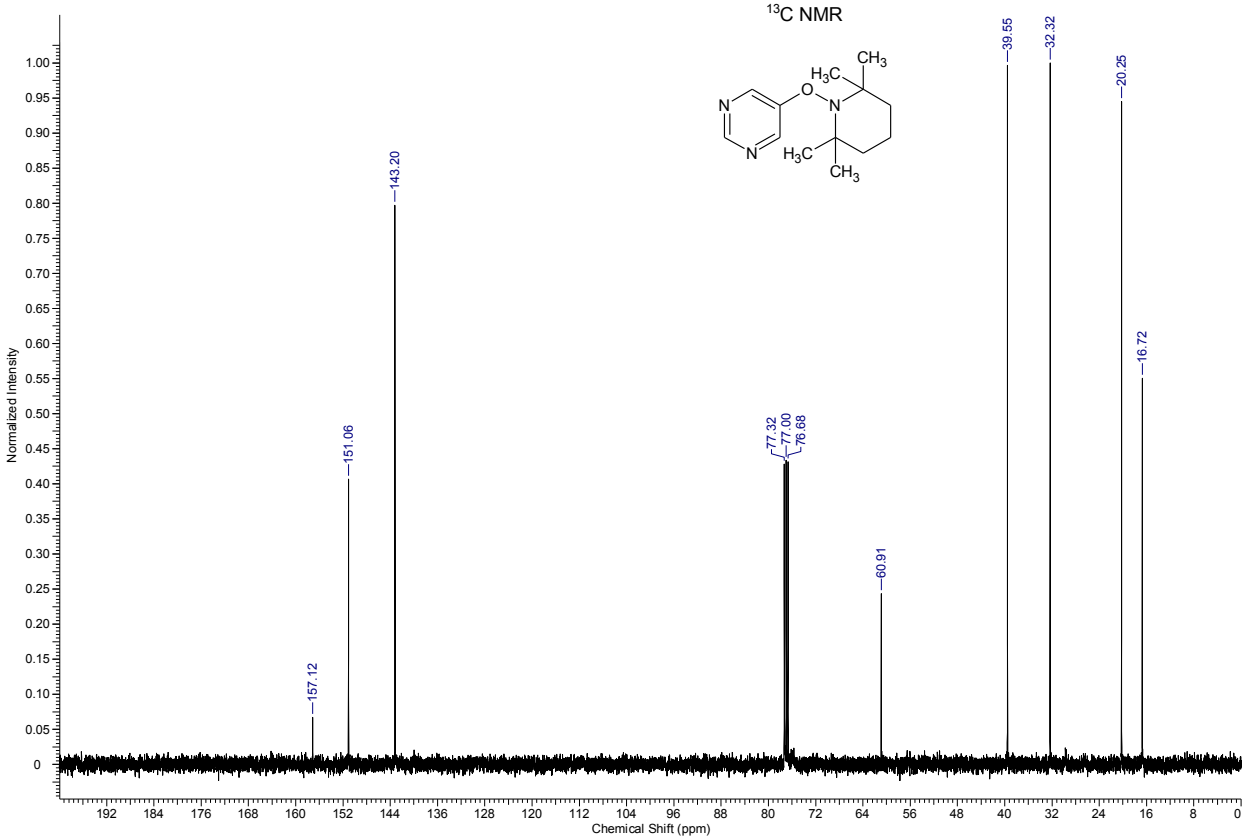

^{13}C NMR
H3C
CH3
N
N
H
Cl
N
155.18
156.84
130.93
126.66
120.47
118.49
111.47
77.31
77.00
76.68
13.00
12.49
Normalized Intensity
Chemical Shift (ppm)

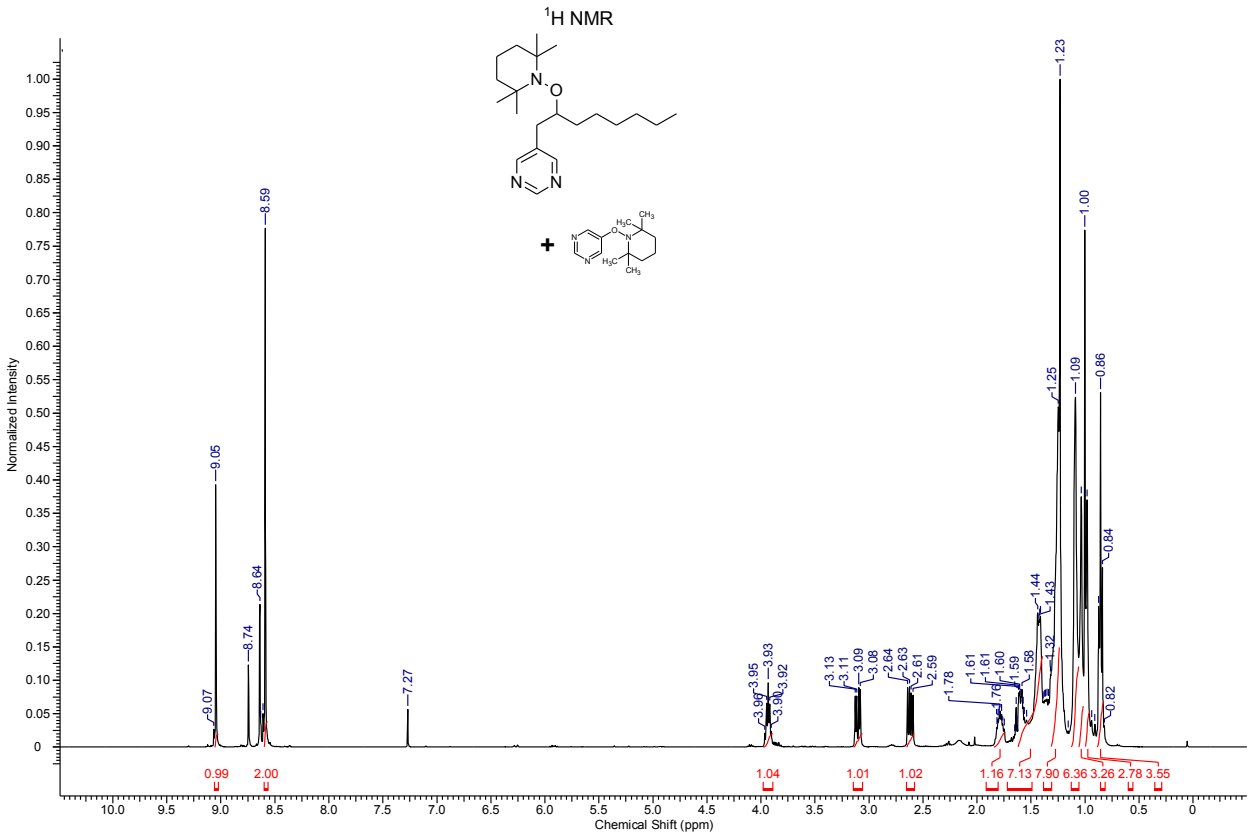

^{1}H NMR
Normalized Intensity
Chemical Shift (ppm)
8.64
8.63
7.91
7.27
2.45
2.44
2.42
2.27
2.17
1.13
1.10
1.11
2.01
1.01
2.21
3.17
3.16
3.27

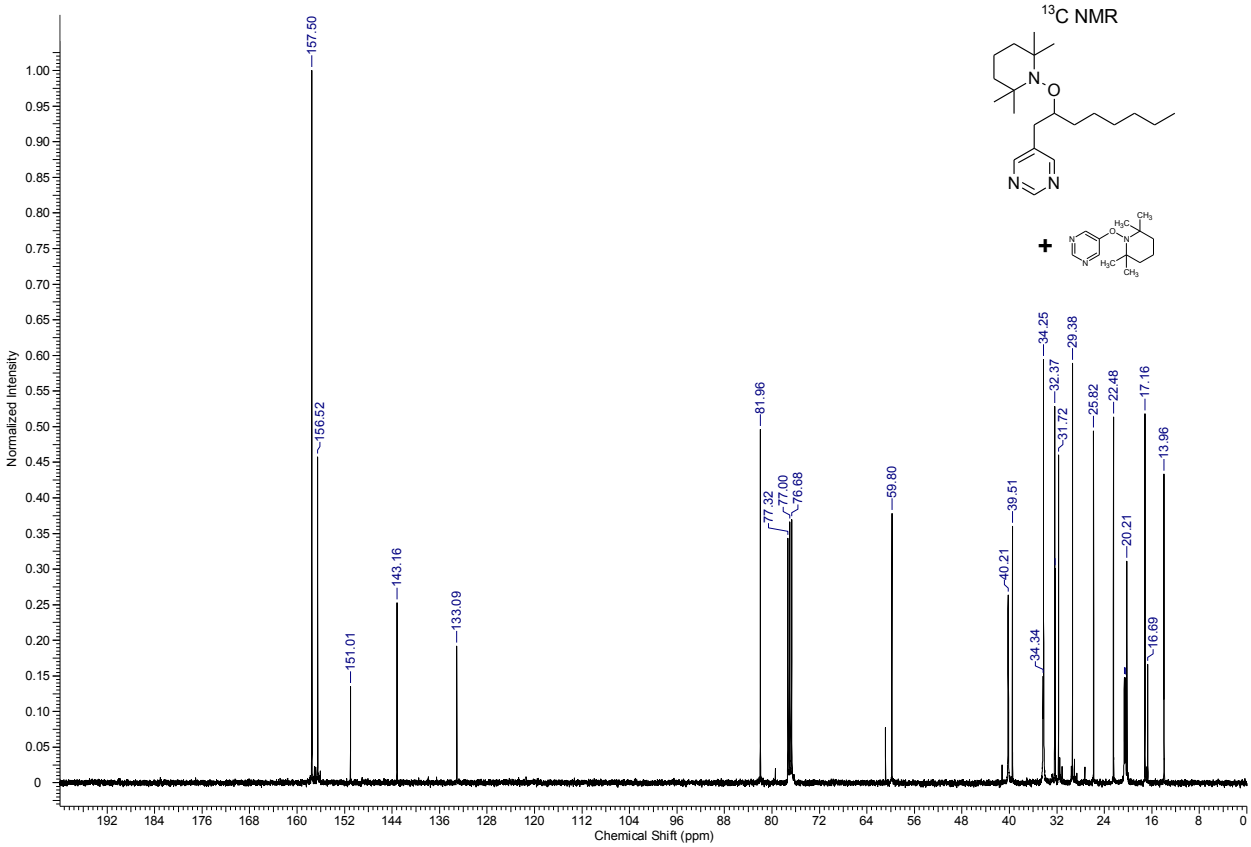

^{13}C NMR
Normalized Intensity
Chemical Shift (ppm)
77.32
77.00
76.68
157.08
157.19
161.70
159.52
126.71
126.35
123.42
117.99
117.87
117.85
17.49
15.45
11.15
10.14


-49.60
^{13}F NMR
H_3C
H_3C
CH_3
N
H
F
N
Normalized Intensity
Chemical Shift (ppm)


^{1}H NMR
Normalized Intensity
Chemical Shift (ppm)
8.76
8.65
7.27
1.62
1.59
1.65
1.44
1.42
1.24
1.01
1.00 2.00
5.15 1.13 6.44 6.26


^{13}C NMR
Normalized Intensity
Chemical Shift (ppm)
143.20
151.06
157.12
77.32
77.00
76.68
60.91
39.55
32.32
20.25
16.72


^{1}H NMR
Normalized Intensity
Chemical Shift (ppm)
9.07
9.05
8.74
8.64
8.59
7.27
3.96
3.95
3.93
3.92
3.13
3.11
3.09
3.08
2.64
2.63
2.61
2.59
1.78
1.61
1.61
1.60
1.59
1.58
1.44
1.43
1.32
1.25
1.23
1.09
1.00
0.86
0.84
0.82
0.99
2.00
1.04
1.01
1.02
1.16
7.13
7.90
6.36
3.26
2.78
3.55


^{13}C NMR
Normalized Intensity
Chemical Shift (ppm)
157.50
156.52
151.01
143.16
133.09
81.96
77.32
77.00
76.68
59.80
40.21
39.51
34.34
34.25
32.37
31.72
29.38
25.82
22.48
20.21
17.16
16.69
13.96