Supporting Information

Catalyst free C–N bond formation by the reaction of amines with diimides activation: Bulky guanidines

Ashim Baishya,[a] Thota Peddarao,[a] Milan Kr. Barman,[a] and Sharanappa Nembenna*[a]

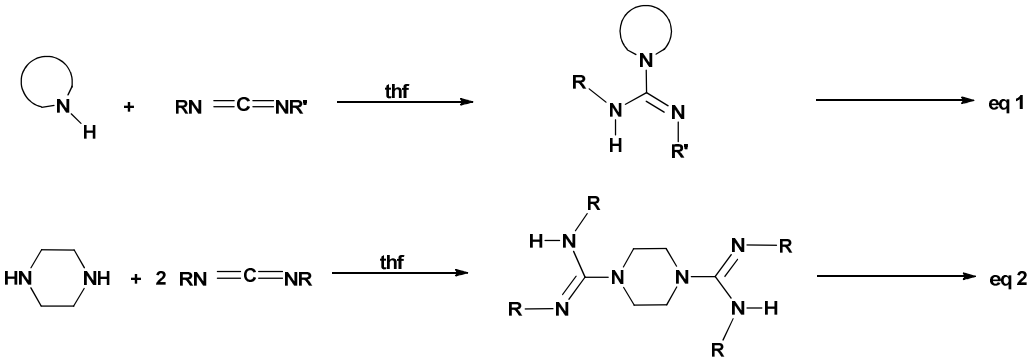
[a]*School of Chemical Sciences, National Institute of Science Education and Research (NISER) Bhubaneswar, India 751005*

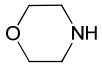
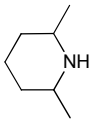
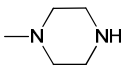
Corresponding Author: Sharanappa Nembenna

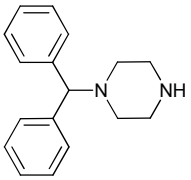
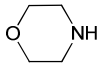
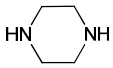
Fax: +91-674-2302436; Tel.: +91-674-2304126
Email: *snembenna@niser.ac.in*

Contents

Table S1. Addition of amines to bulky aromatic carbodiimides:



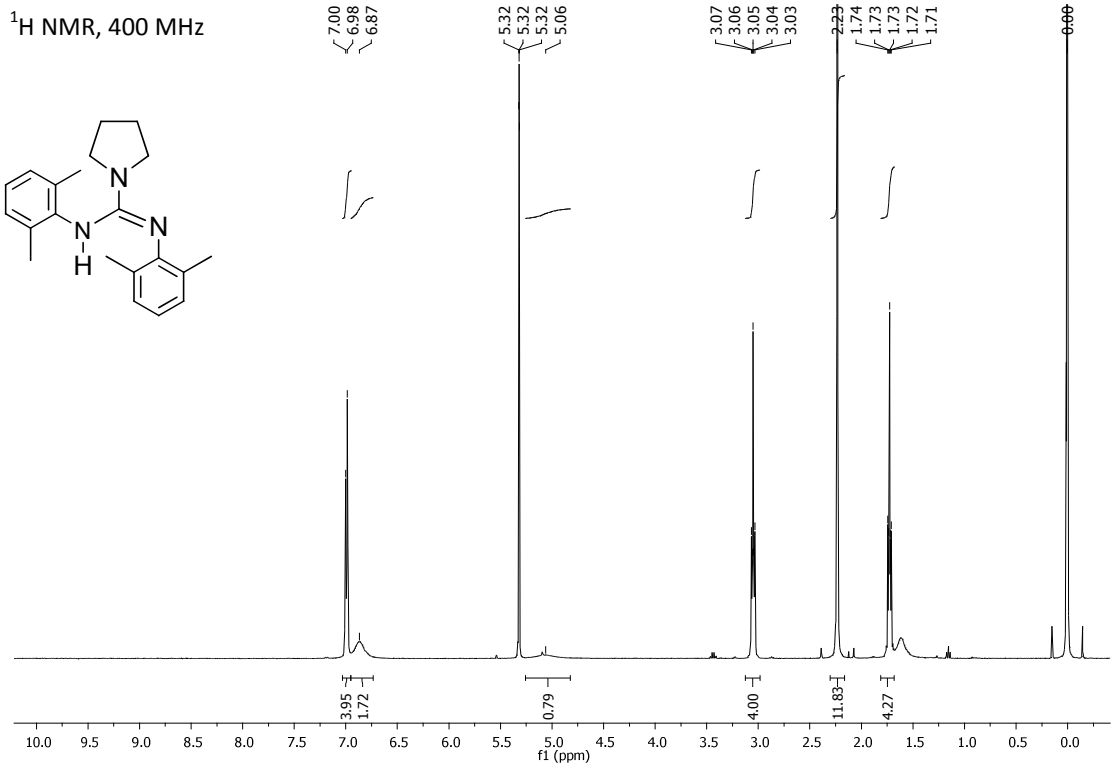
Entry	amines	R, R'	Temp. (^{o}C)/ Time (h)	Product	Yield[a] %
1		2,6-$Me_2C_6H_3$	r.t. / 1	**1a**	99
		2,4,6-$Me_3C_6H_2$	r.t. / 1.33	**2a**	86
		2,6-$Et_2C_6H_3$	r.t. / 1.5	**3a**	86
		2,6-$^{i}Pr_2C_6H_3$	r.t./ 2	**4a**	99
		4-$^{i}PrC_6H_4$	r.t. / 1.16	**5a**	84
		4-$^{t}ButC_6H_4$	r.t./ 1	**6a**	96
2		2,6-$Me_2C_6H_3$	r.t./ 2	**7a**	97
		2,4,6-$Me_3C_6H_2$	r.t./ 2	**8a**	99
		2,6-$Et_2C_6H_3$	r.t./ 2	**9a**	99
		2,6-$^{i}Pr_2C_6H_3$	r.t./ 2	**10a**	99
		4-$^{i}PrC_6H_4$	r.t./ 1	**11a**	77
		4-$^{t}ButC_6H_4$	r.t./ 1	**12a**	89
3		2,6-$Me_2C_6H_3$	r.t./ 1.83	**13a**	99
		2,4,6-$Me_3C_6H_2$	r.t. / 2	**14a**	98
		2,6-$Et_2C_6H_3$	r.t./ 2	**15a**	89
		2,6-$^{i}Pr_2C_6H_3$	r.t. / 2	**16a**	99
		4-$^{i}PrC_6H_4$	r.t./ 2	**17a**	99
		4-$^{t}ButC_6H_4$	r.t. / 2	**18a**	99
4		2,6-$Me_2C_6H_3$	80 / 24	**19a**	42
		2,4,6-$Me_3C_6H_2$	80 / 24	**20a**	37
5		2,4,6-$Me_3C_6H_2$	r.t. / 1	**21a**	92
		2,6-$^{i}Pr_2C_6H_3$	60/ 2	**22a**	89

6		2,6-$Me_2C_6H_3$	r.t. / 12	**23a**	86
		2,6-(^{i}Pr_2)C_6H_3	r.t. / 24	**24a**	76
7		2,6-^{i}$Pr_2C_6H_3$(R) 2,4,6-$Me_3C_6H_2$(R')	r.t. / 2	**25a**	99
8		2,6-^{i}$Pr_2C_6H_3$(R) 2,4,6-$Me_3C_6H_3$(R')	r.t. / 2	**26a**	93
9		2,6-$Me_2C_6H_3$	r.t. / 4	**27a**	90
		2,6-^{i}$Pr_2C_6H_3$	80 / 12	**28a**	60

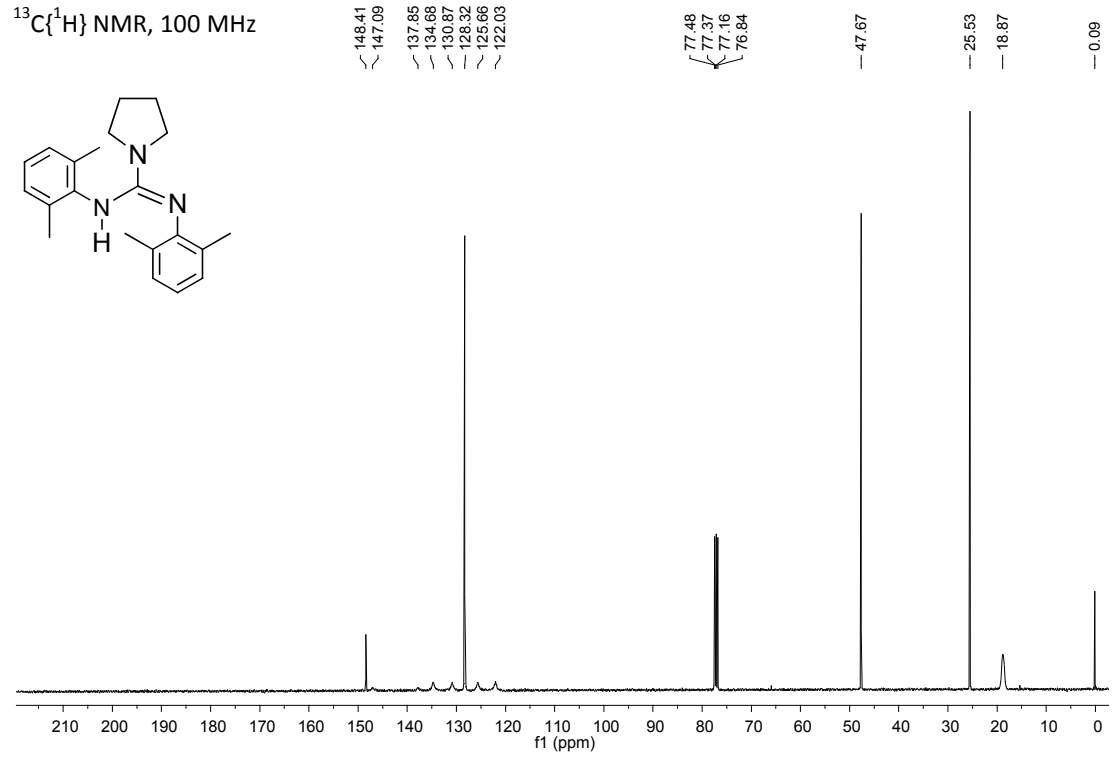
[a]Isolated yield

Copy of ^{1}H and ^{13}C NMR Spectra of the products:

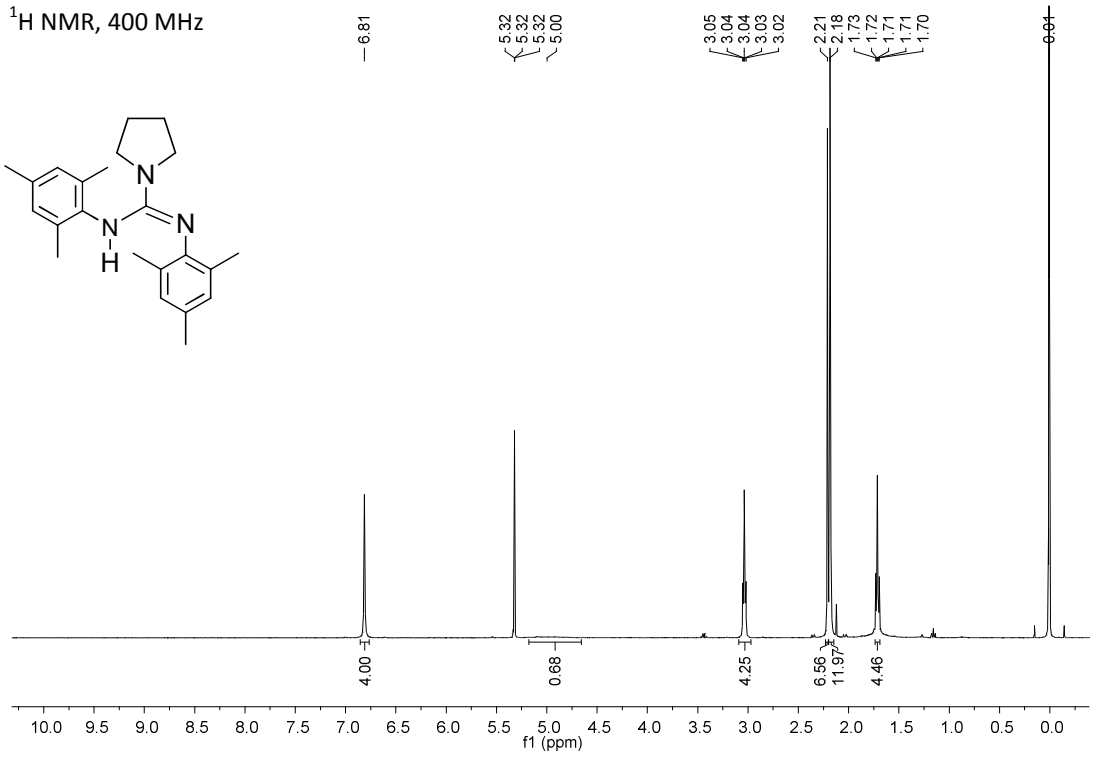
^{1}H NMR, 400 MHz



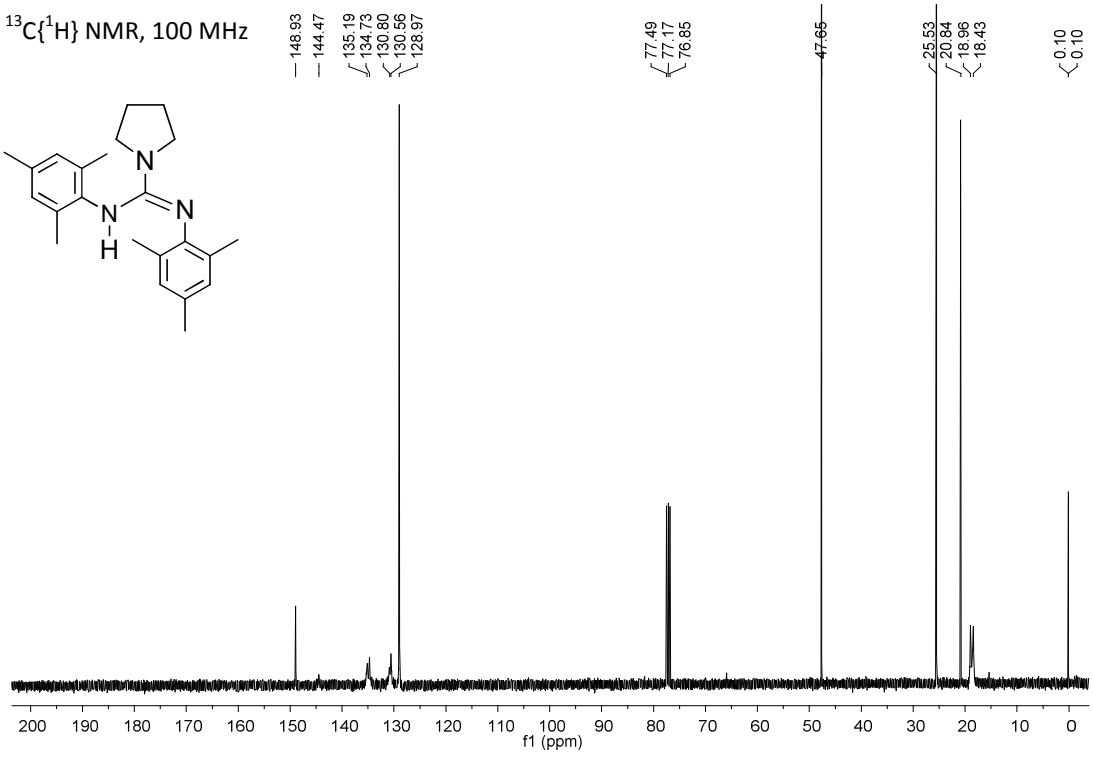
$^{13}C\{^{1}H\}$ NMR, 100 MHz



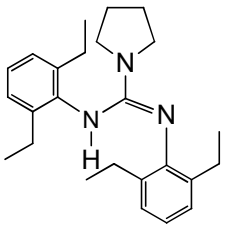
^{1}H NMR, 400 MHz



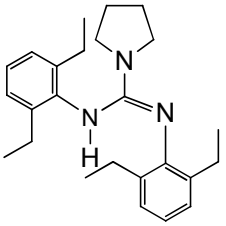
^{13}C{^{1}H} NMR, 100 MHz



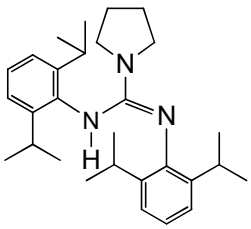
^{1}H NMR, 400 MHz



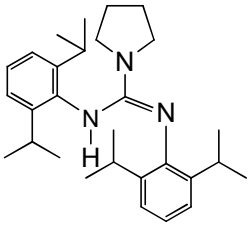
^{13}C{^{1}H} NMR, 100 MHz



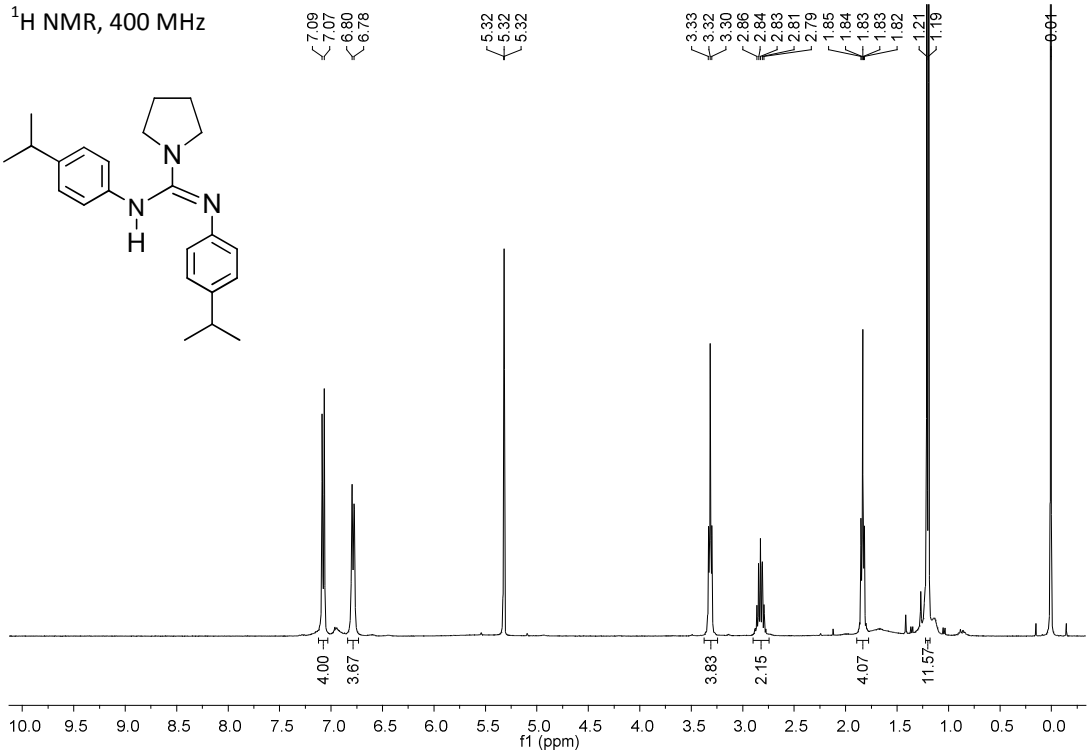
^{1}H NMR, 400 MHz



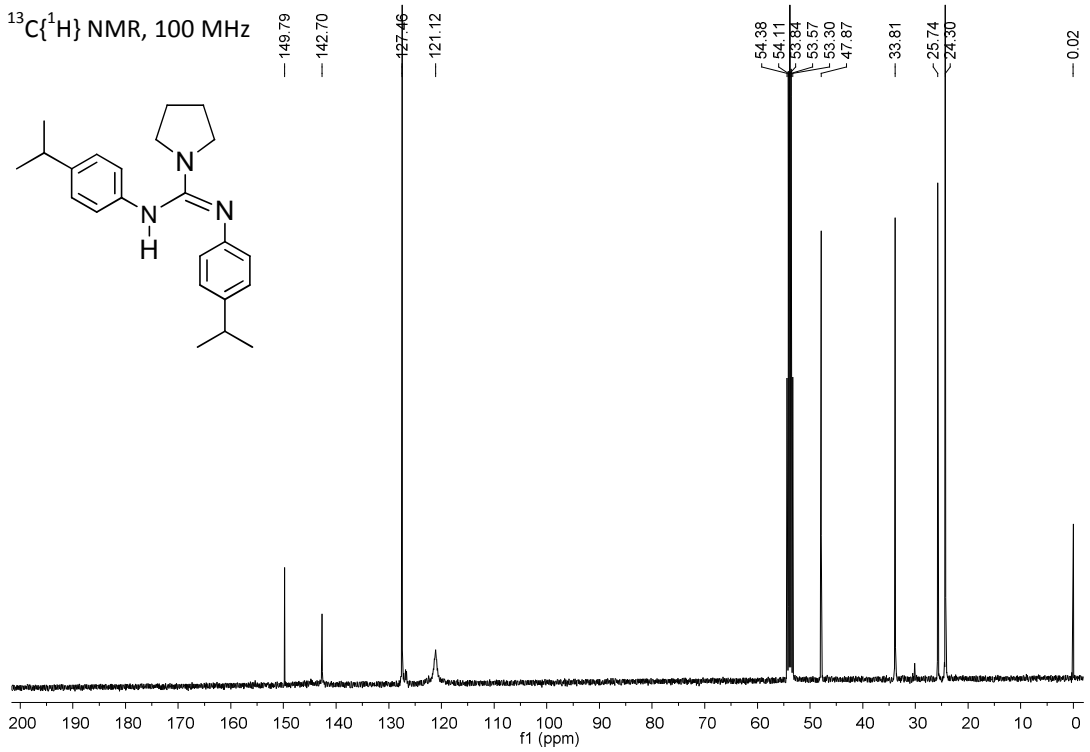
^{13}C{^{1}H} NMR, 100 MHz



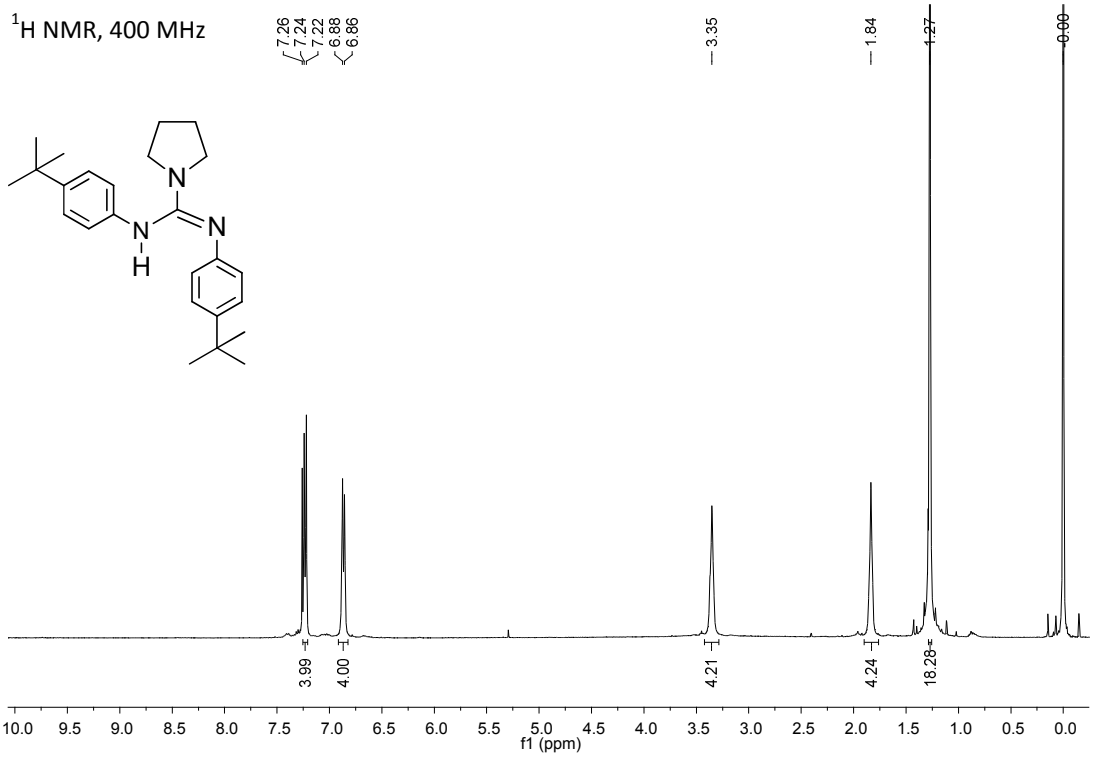
^{1}H NMR, 400 MHz



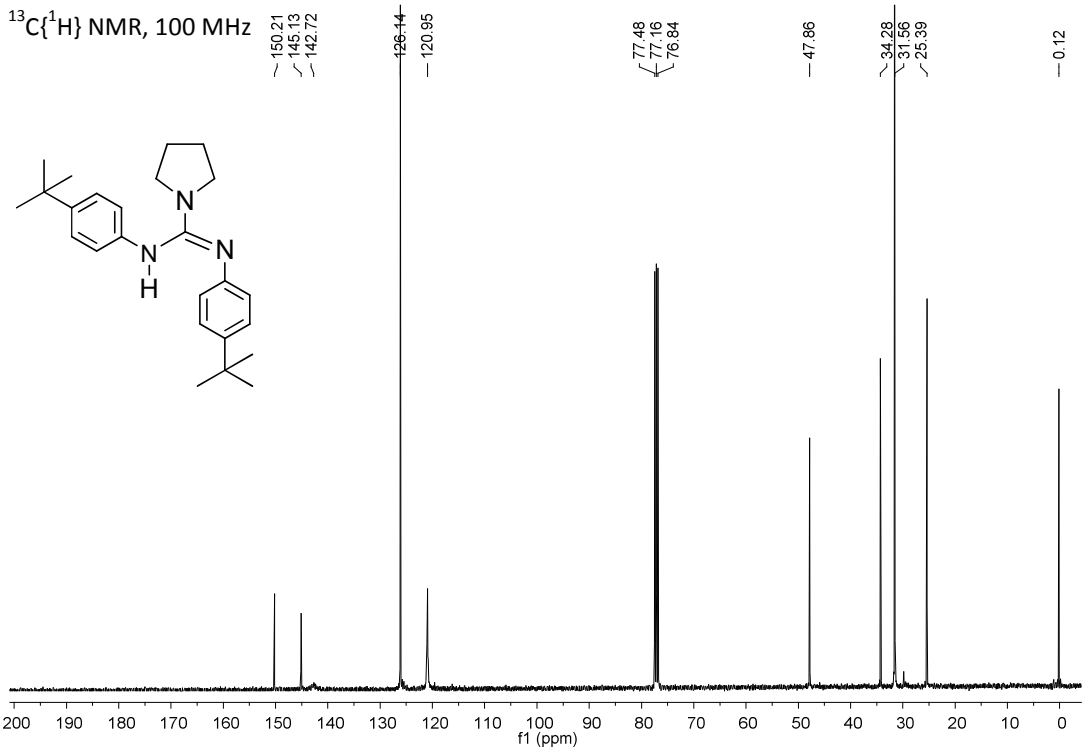
^{13}C{^{1}H} NMR, 100 MHz



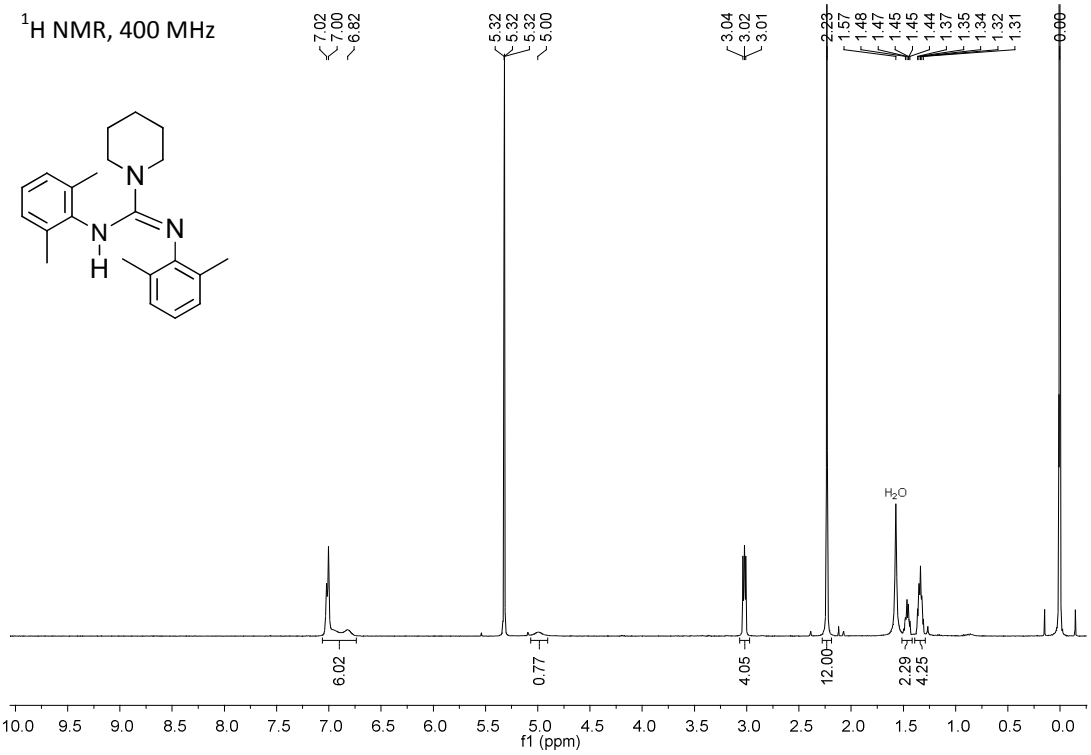
^{1}H NMR, 400 MHz



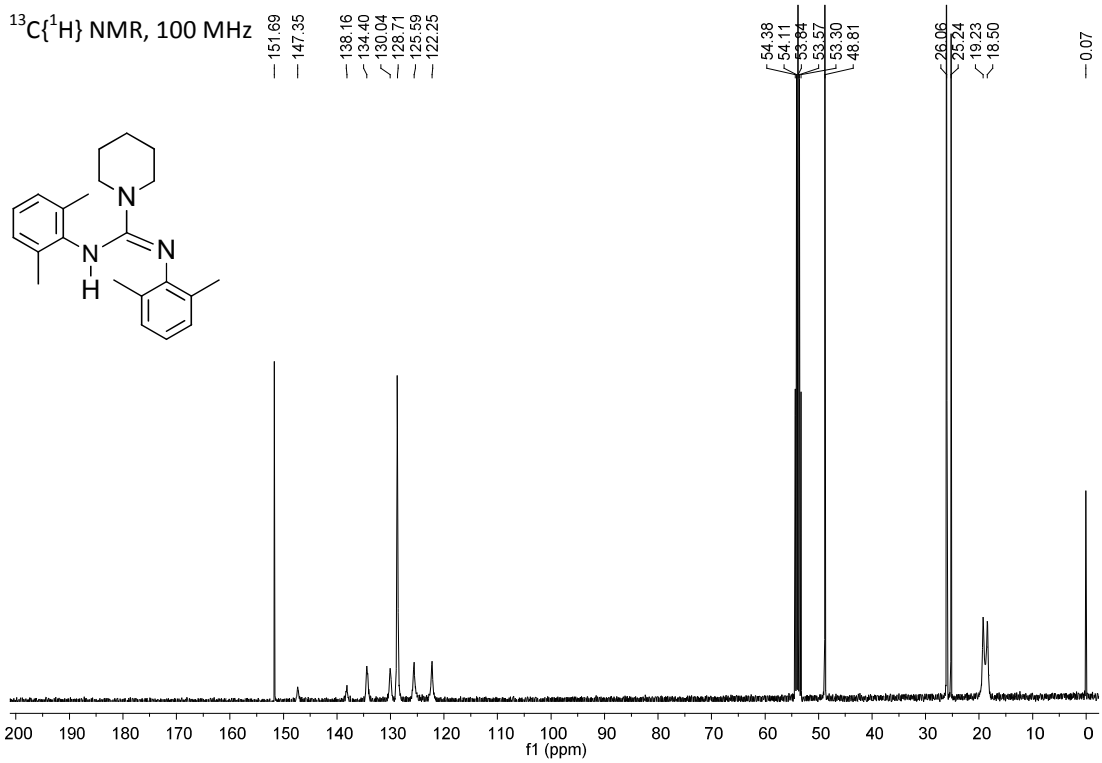
^{13}C{^{1}H} NMR, 100 MHz



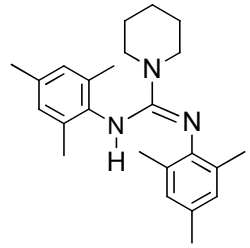
^{1}H NMR, 400 MHz



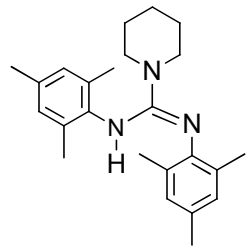
^{13}C{^{1}H} NMR, 100 MHz



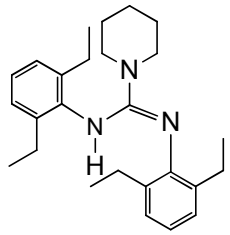
^{1}H NMR, 400 MHz



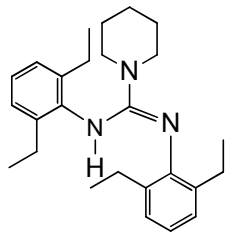
^{13}C{^{1}H} NMR, 100 MHz



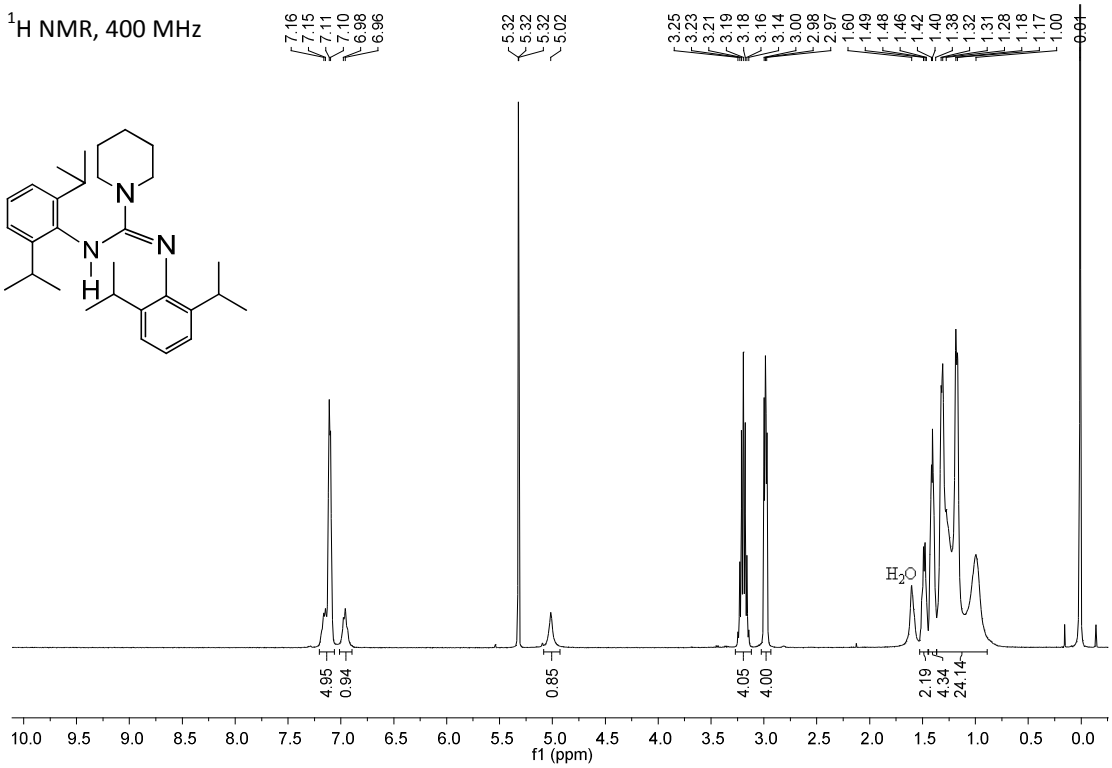
^{1}H NMR, 400 MHz



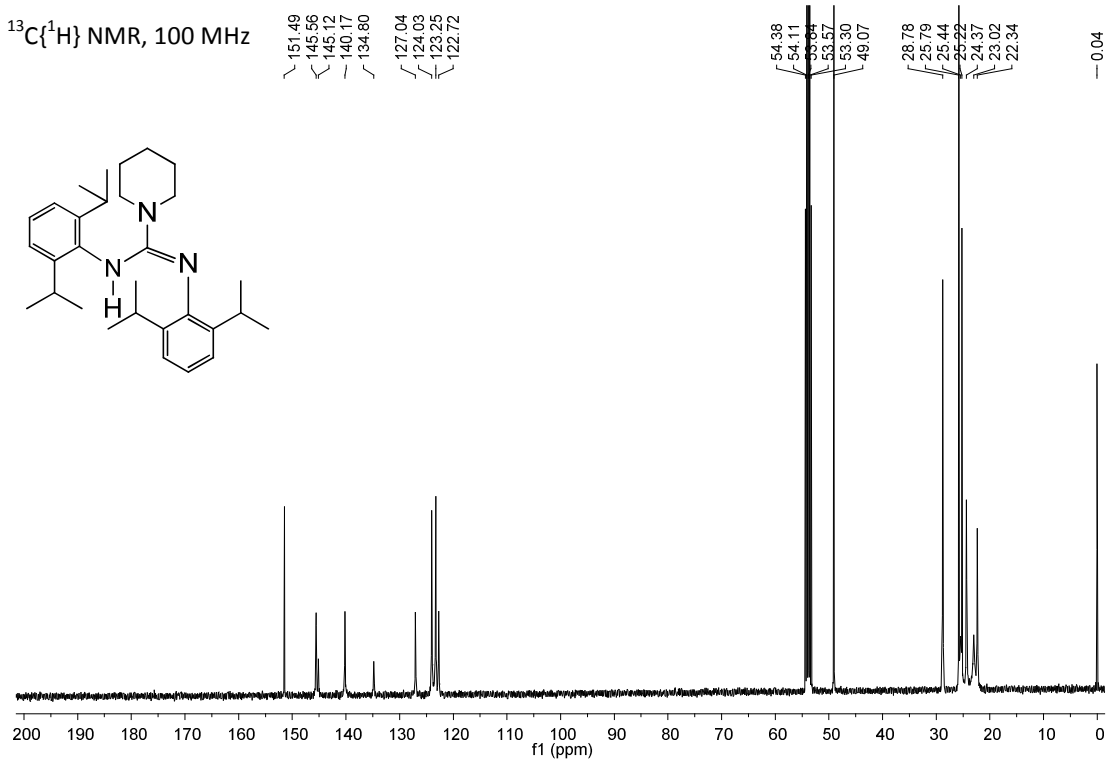
^{13}C{^{1}H} NMR, 100 MHz



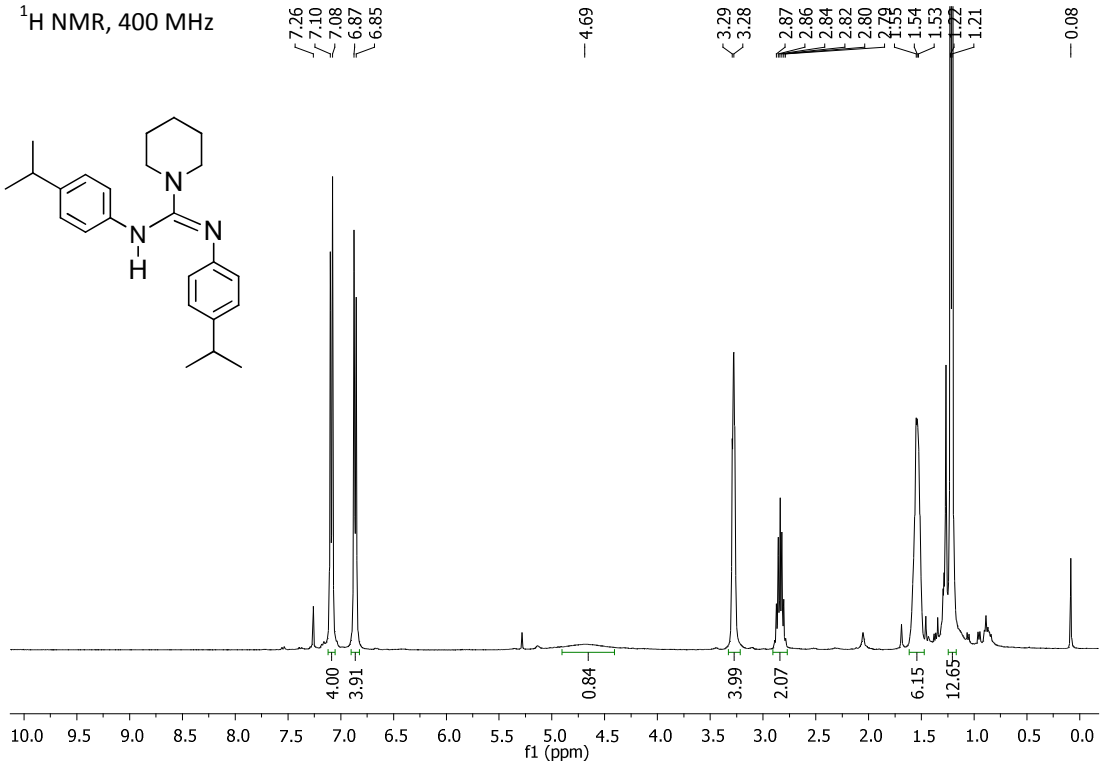
^{1}H NMR, 400 MHz



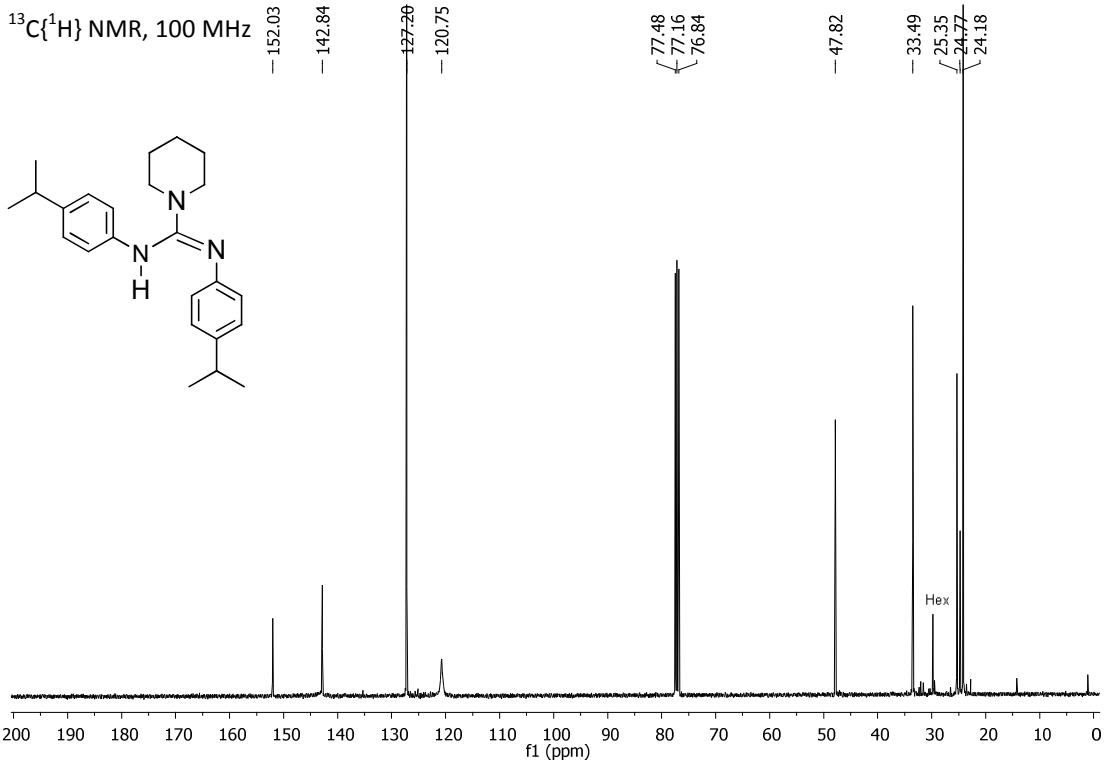
^{13}C{^{1}H} NMR, 100 MHz

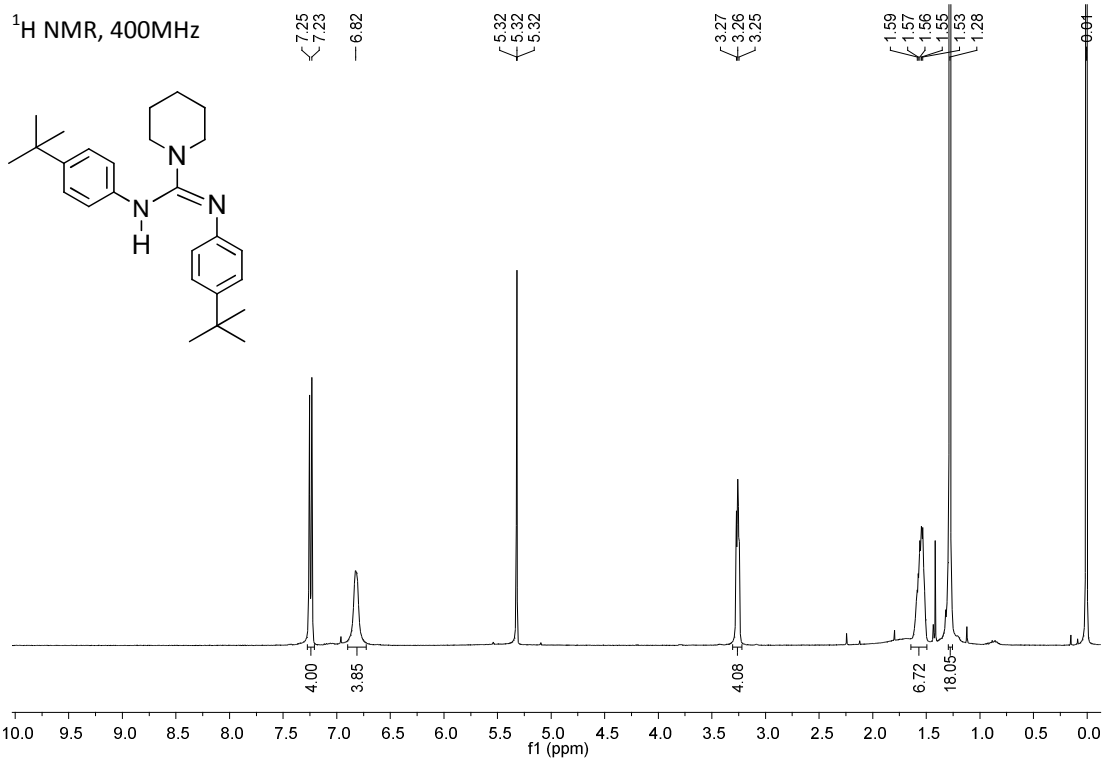


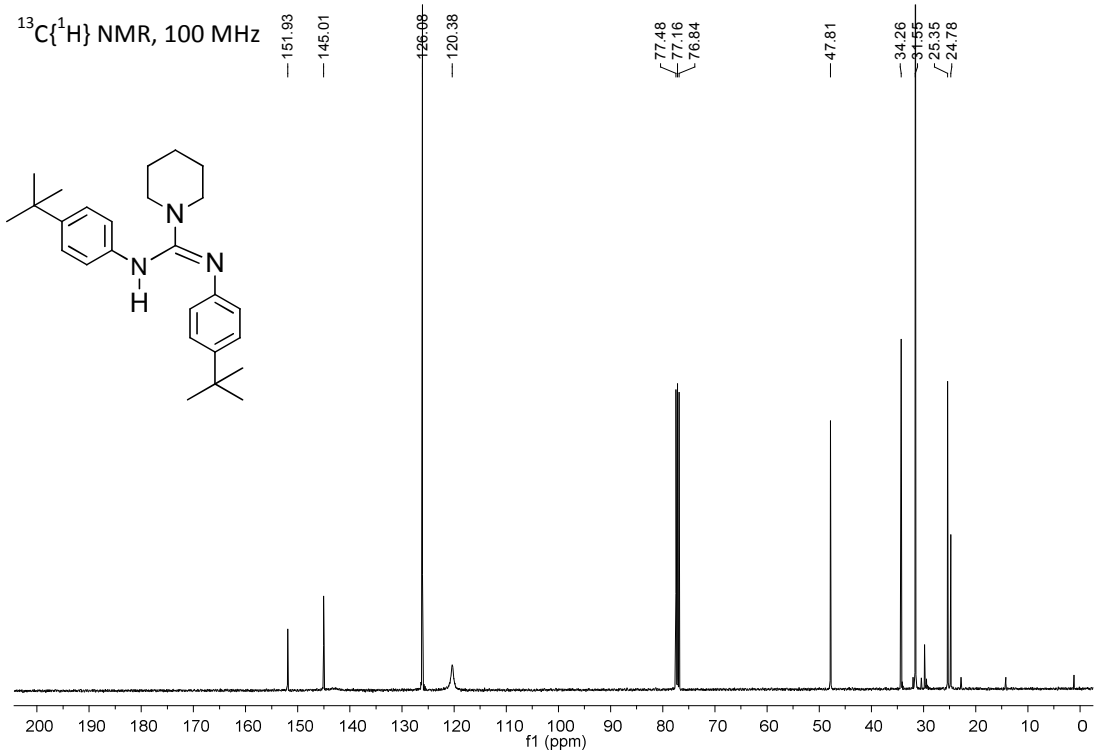
^{1}H NMR, 400 MHz



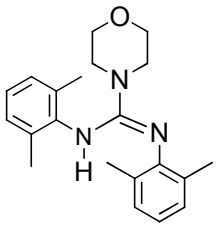
^{13}C{^{1}H} NMR, 100 MHz



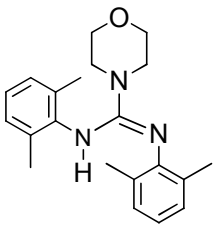

^{1}H NMR, 400MHz
7.25
7.23
6.82
5.32
5.32
5.32
3.27
3.26
3.25
1.59
1.57
1.56
1.55
1.53
1.28
0.01
4.00
3.85
4.08
6.72
18.05
f1 (ppm)


^{13}C{^{1}H} NMR, 100 MHz
151.93
145.01
126.08
120.38
77.48
77.16
76.84
47.81
34.26
31.55
25.35
24.78
f1 (ppm)

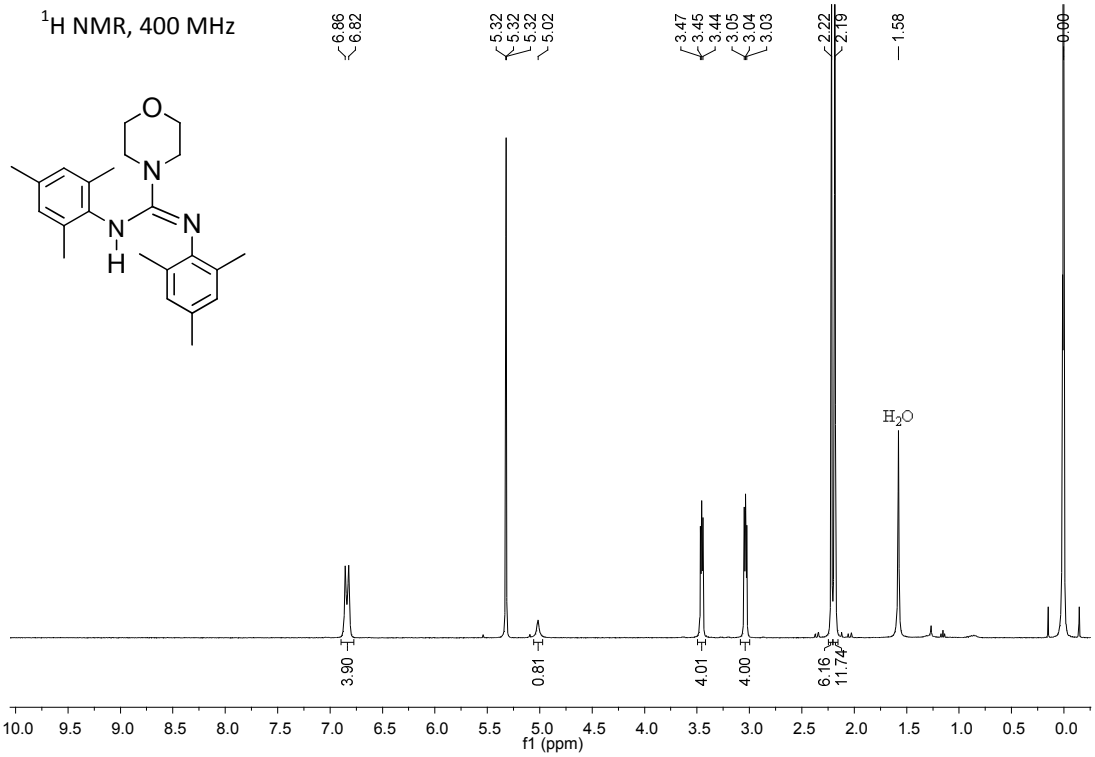
^{1}H NMR, 400 MHz



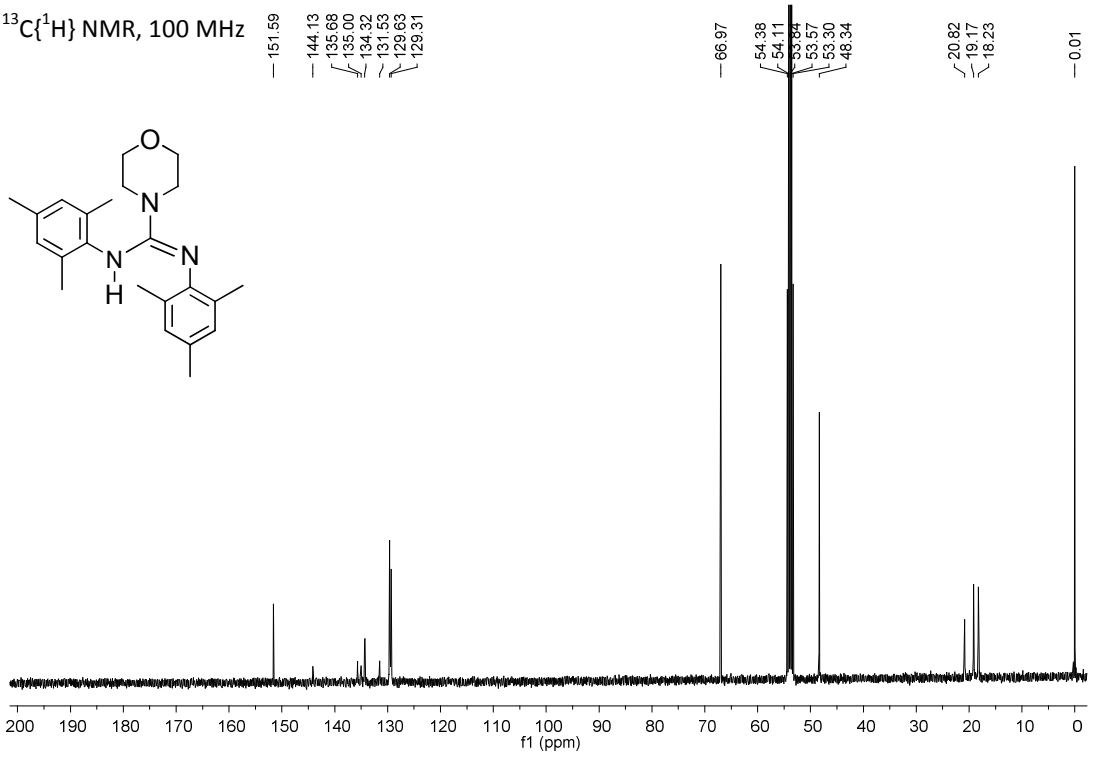
^{13}C{^{1}H} NMR, 100 MHz



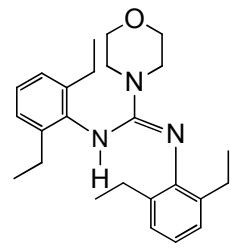
^{1}H NMR, 400 MHz



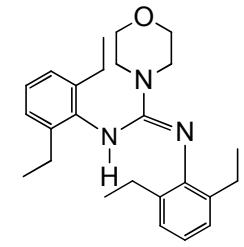
^{13}C{^{1}H} NMR, 100 MHz



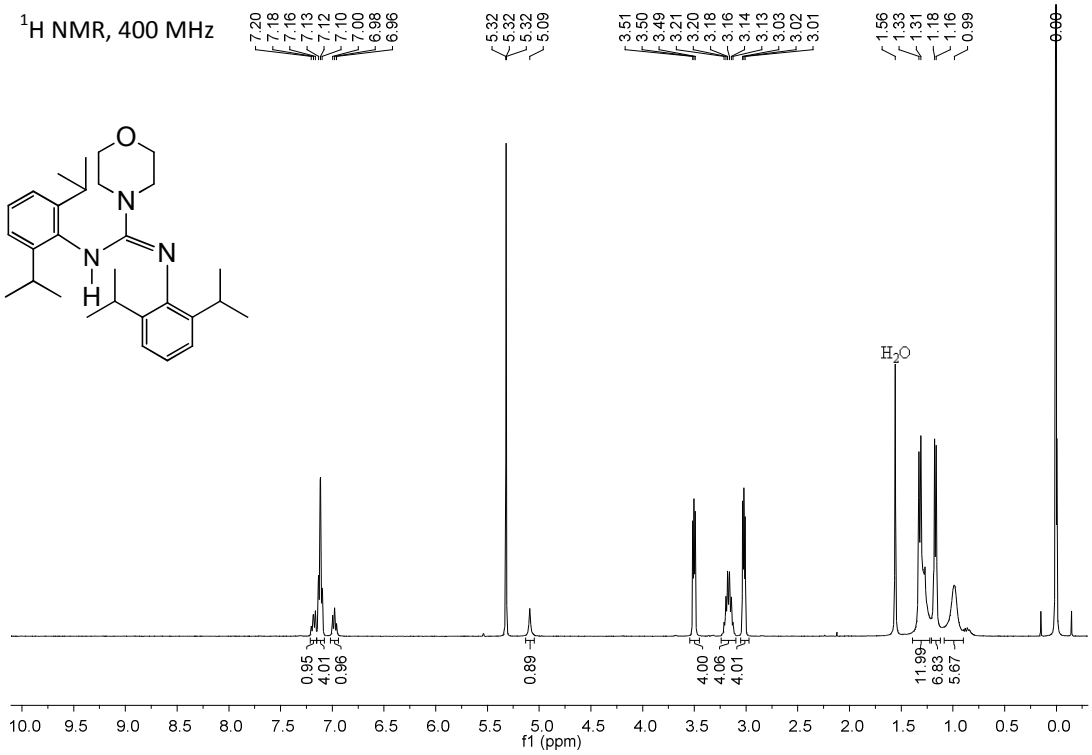
^{1}H NMR, 400 MHz



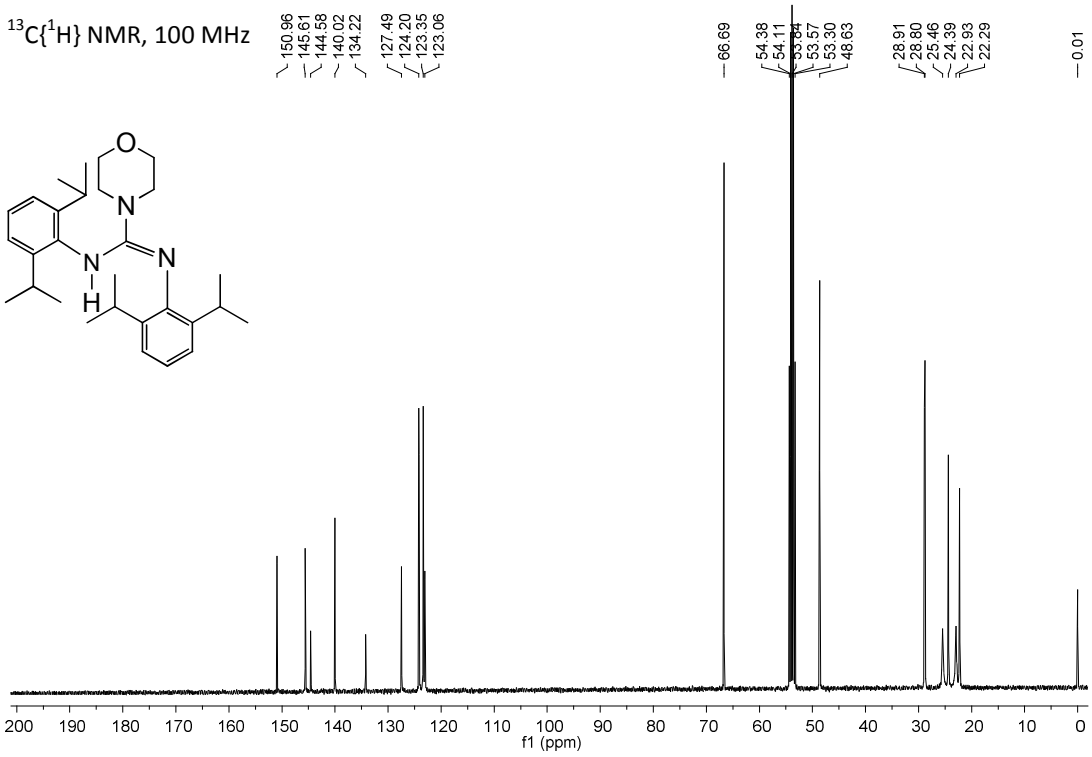
^{13}C{^{1}H} NMR, 100 MHz



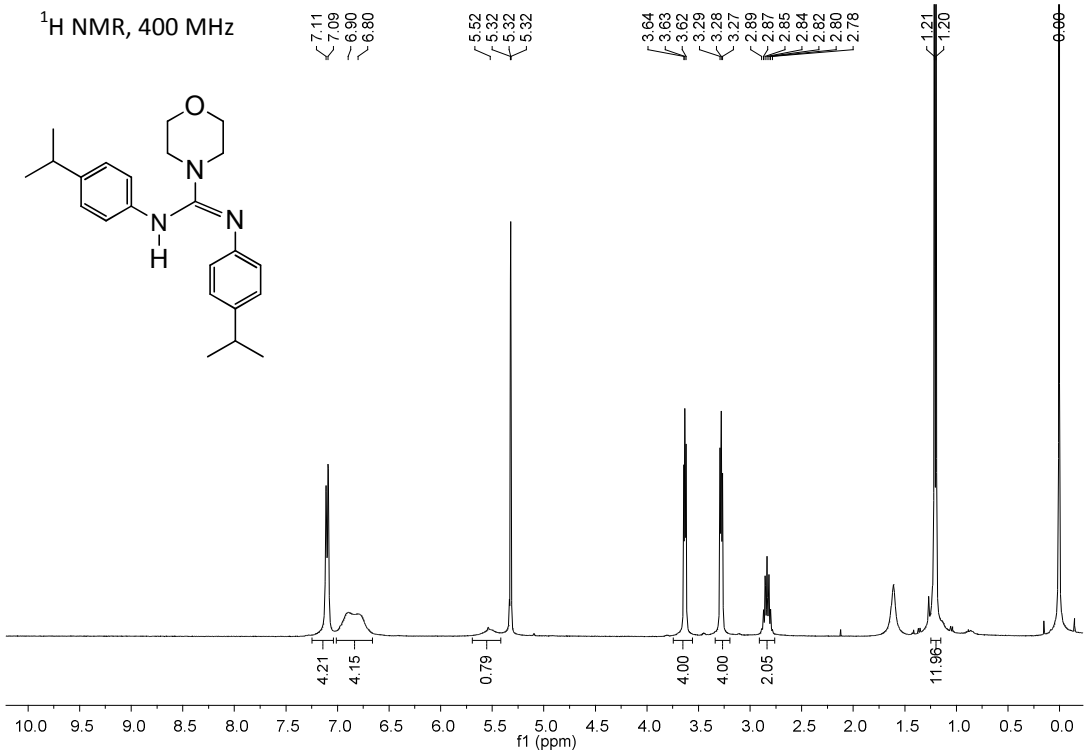
^{1}H NMR, 400 MHz



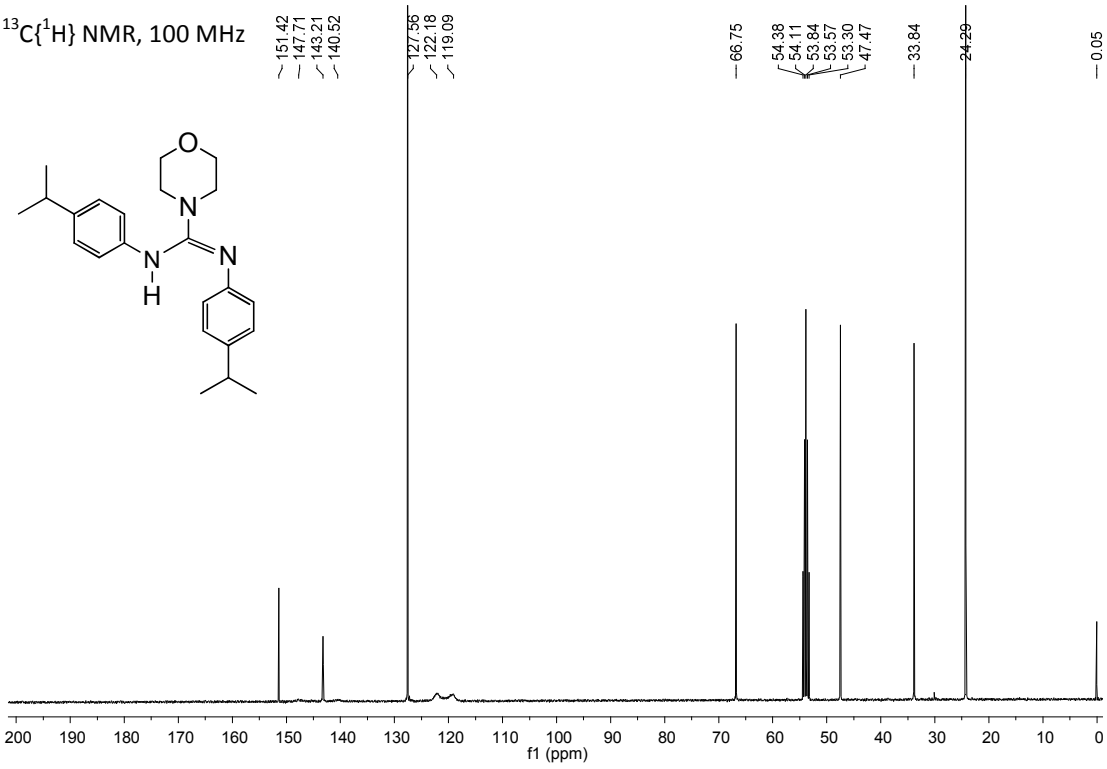
^{13}C{^{1}H} NMR, 100 MHz



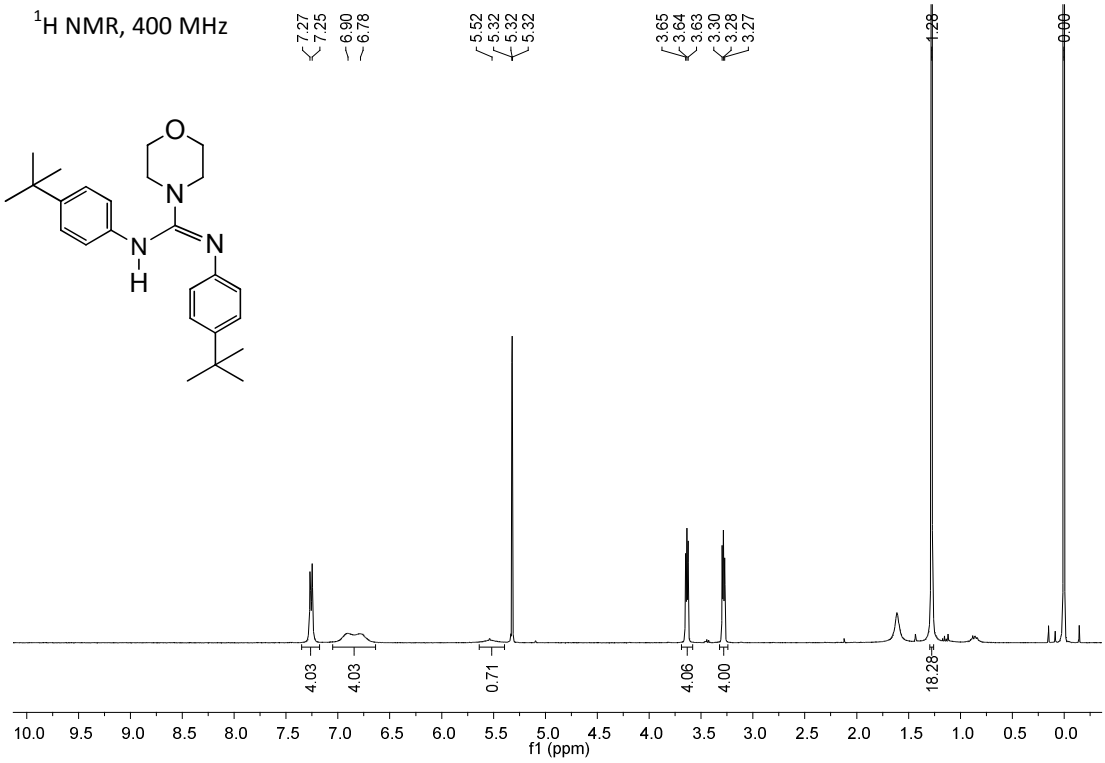
^{1}H NMR, 400 MHz



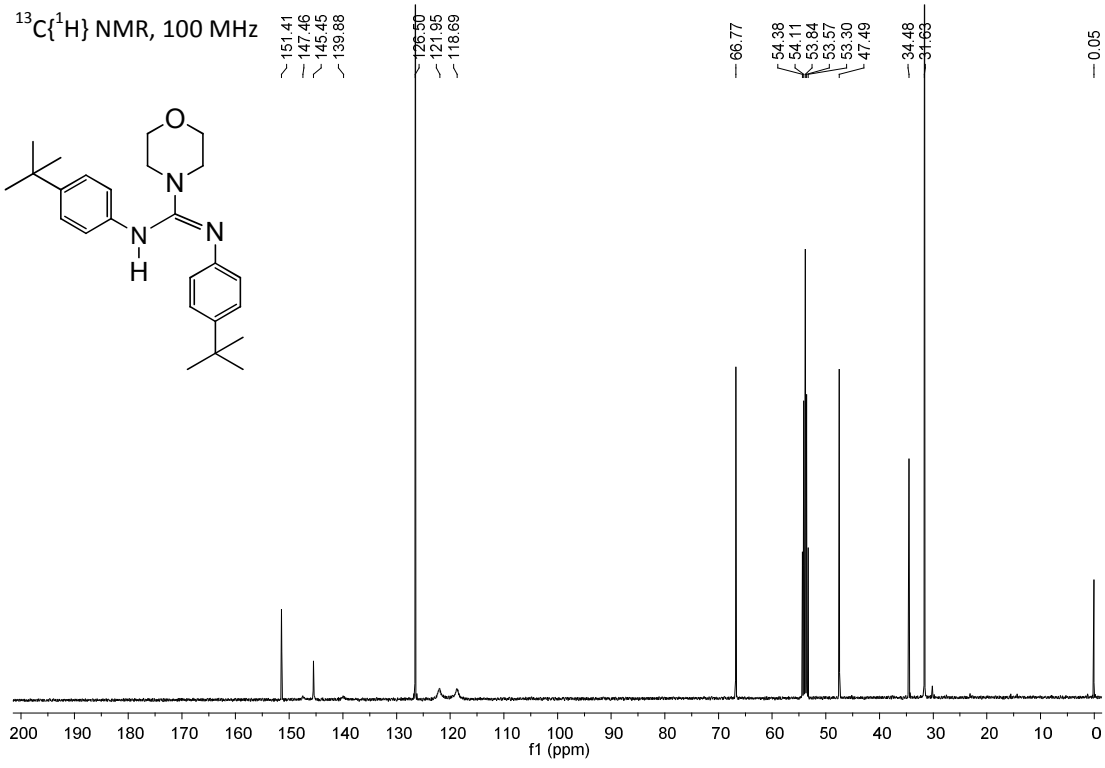
^{13}C{^{1}H} NMR, 100 MHz



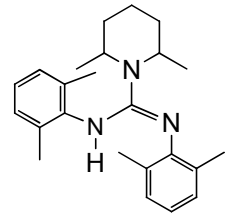
^{1}H NMR, 400 MHz



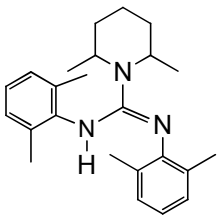
^{13}C{^{1}H} NMR, 100 MHz



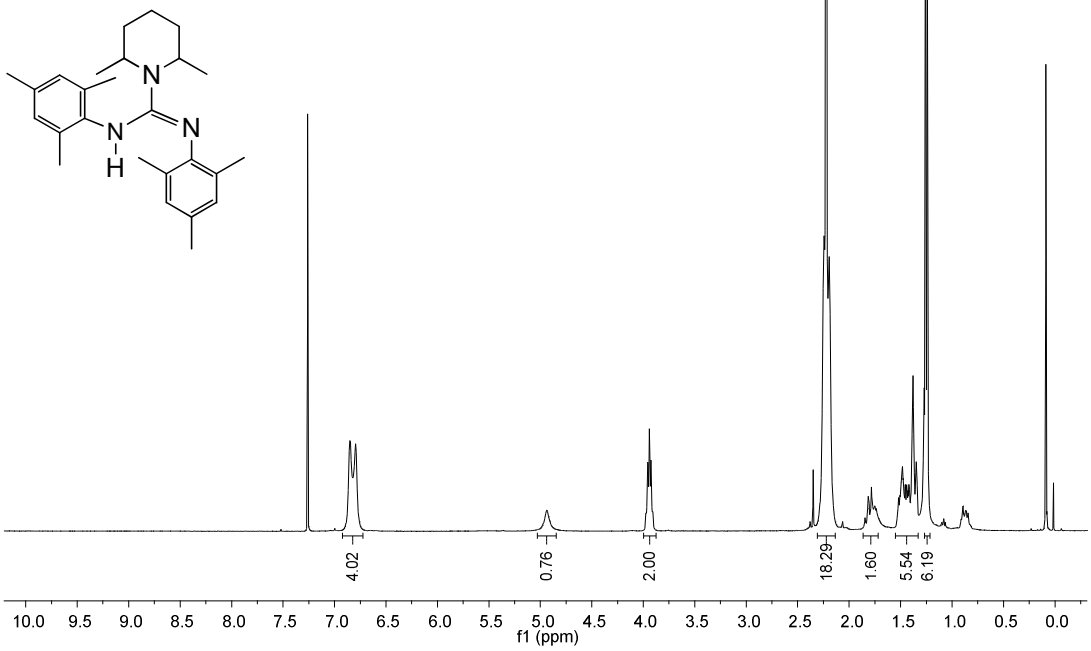
^{1}H NMR, 400 MHz



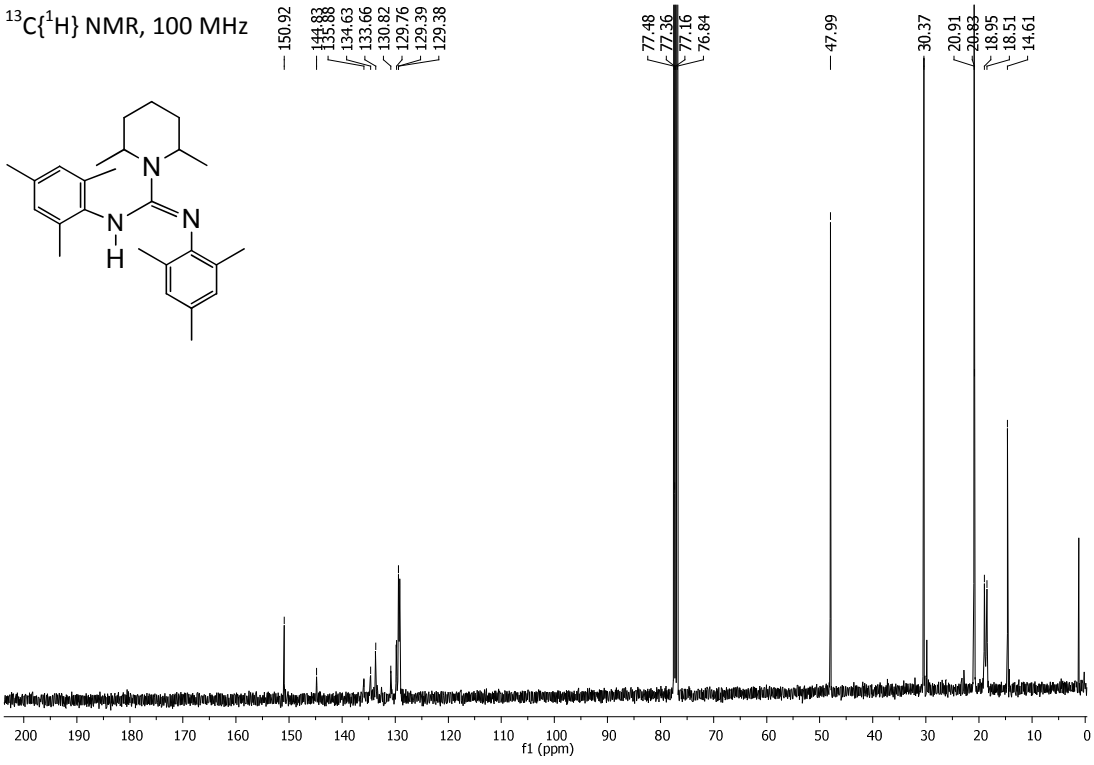
^{13}C{^{1}H} NMR, 100 MHz



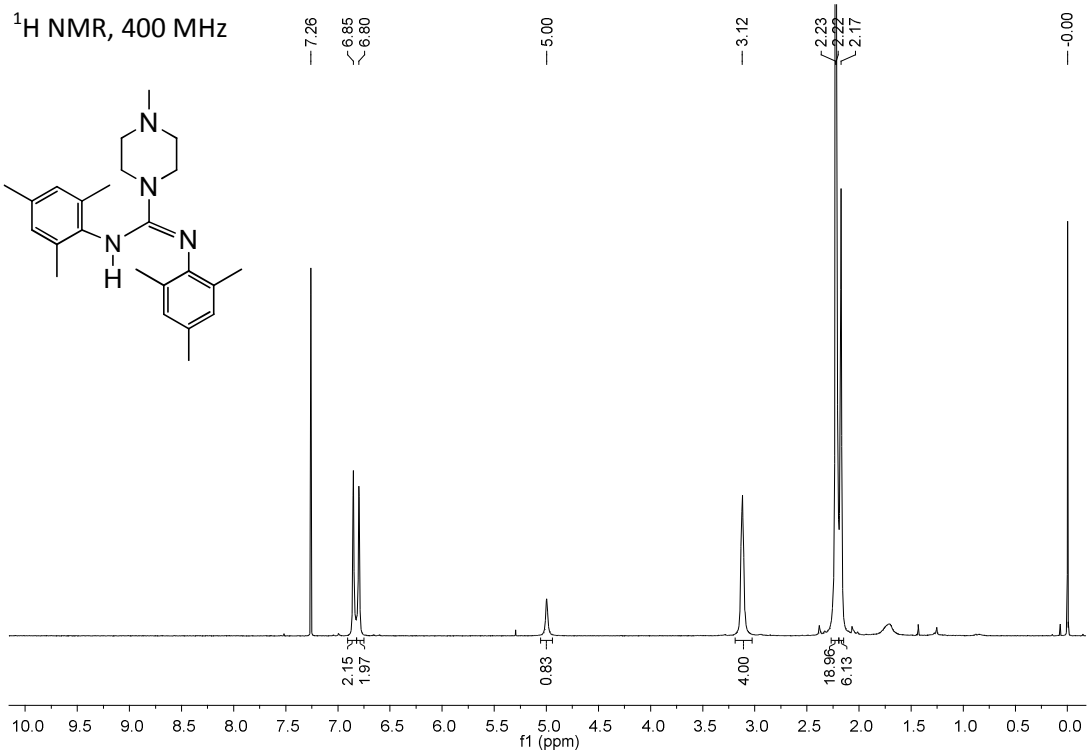
^{1}H NMR, 400 MHz



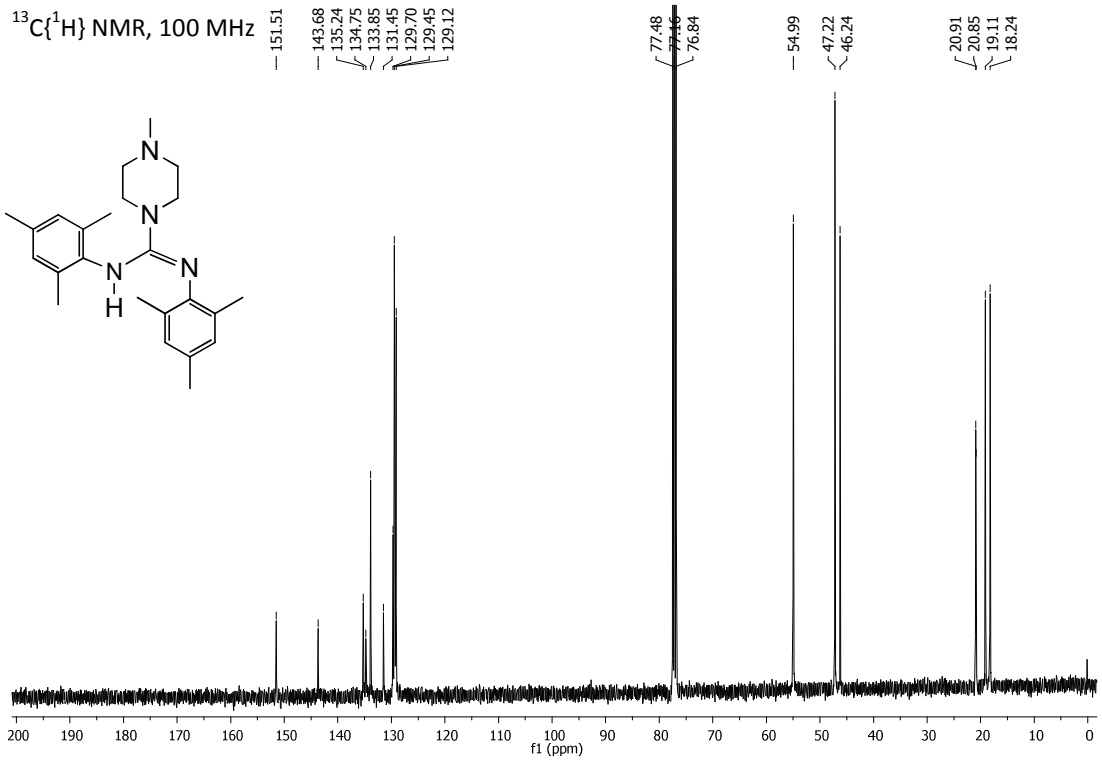
^{13}C{^{1}H} NMR, 100 MHz



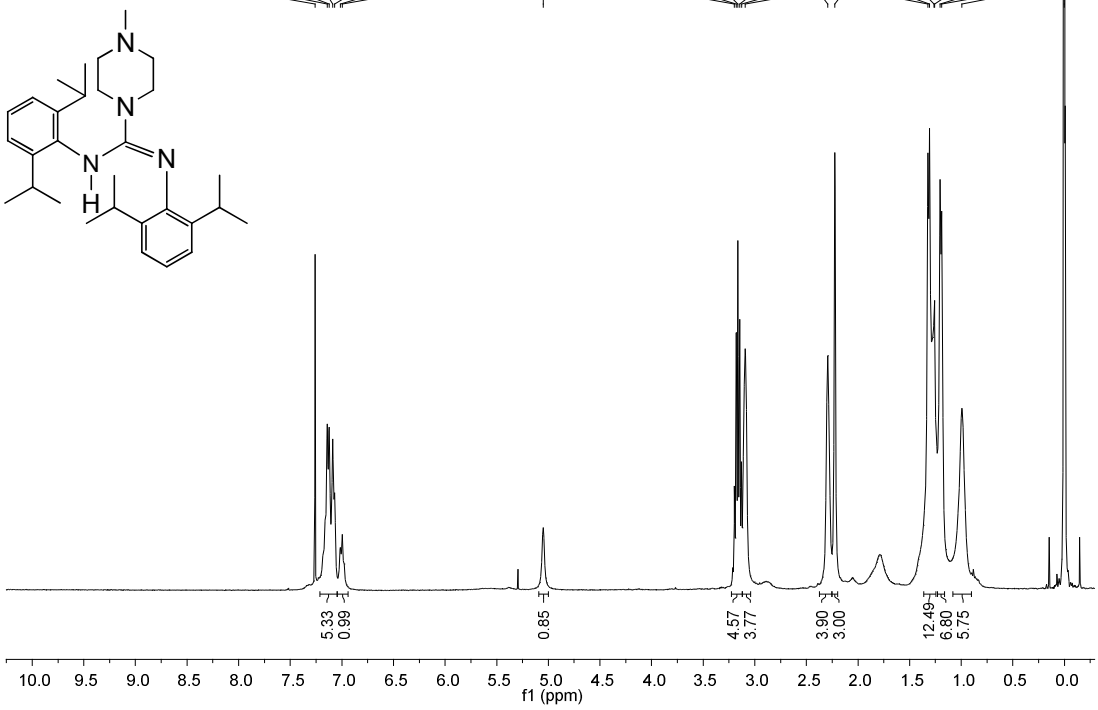
^{1}H NMR, 400 MHz



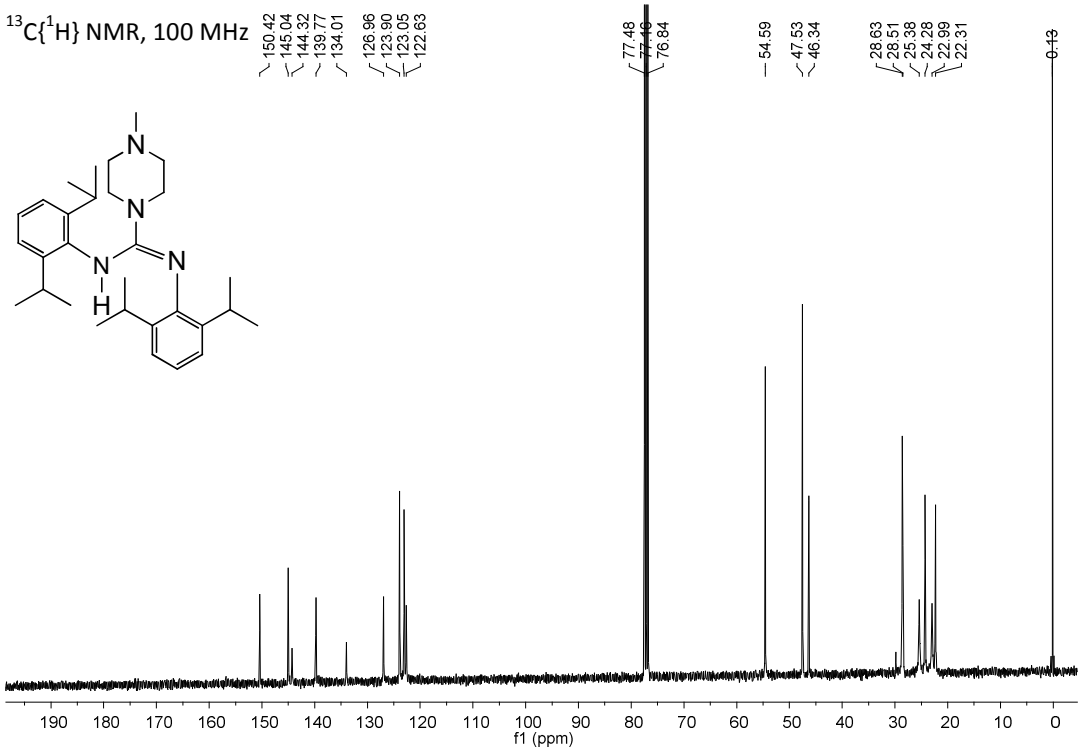
^{13}C{^{1}H} NMR, 100 MHz



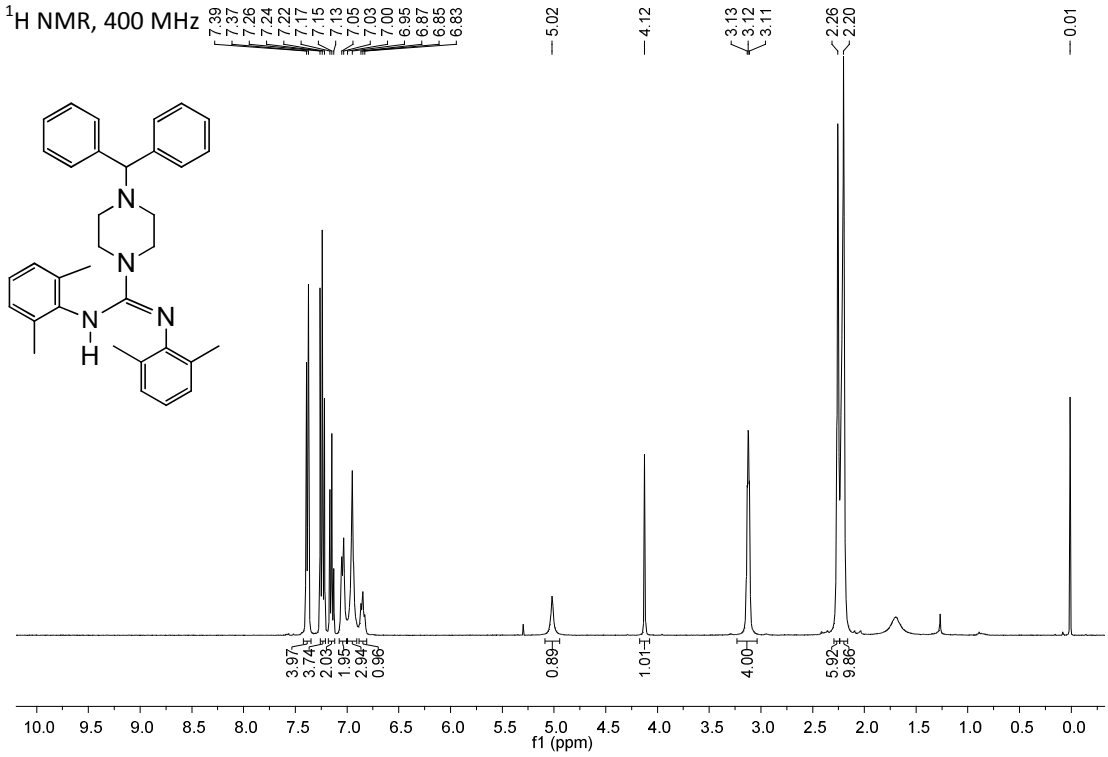
^{1}H NMR, 400 MHz



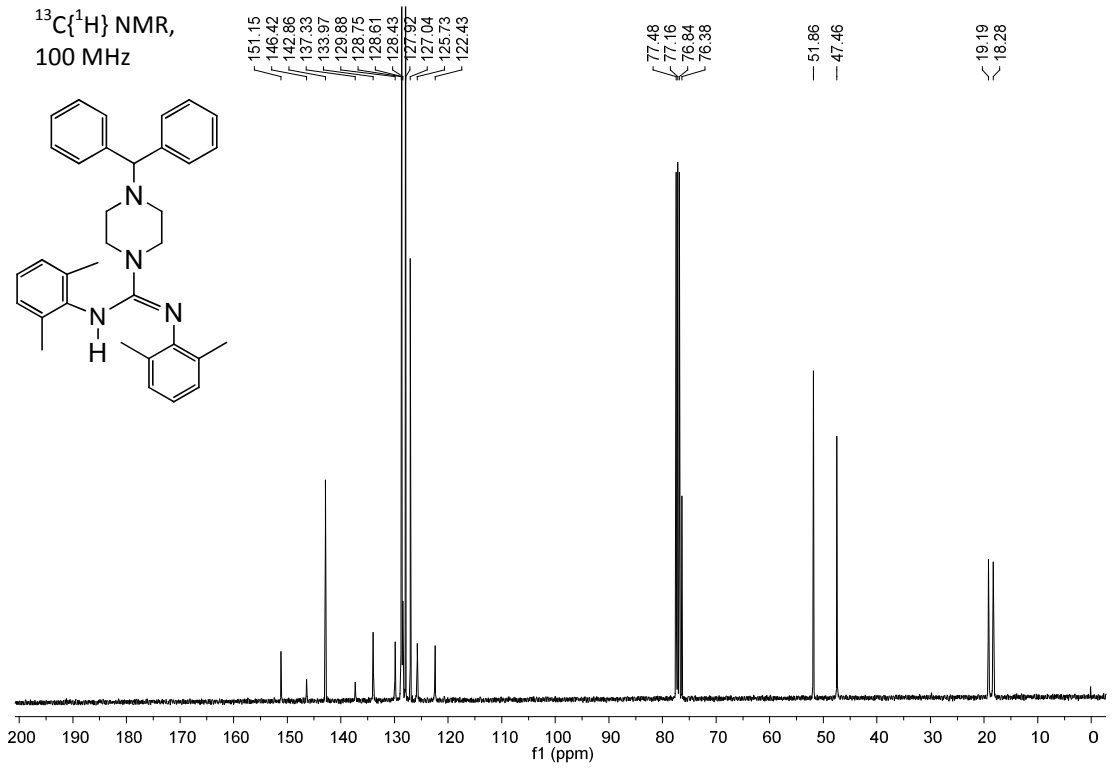
^{13}C{^{1}H} NMR, 100 MHz

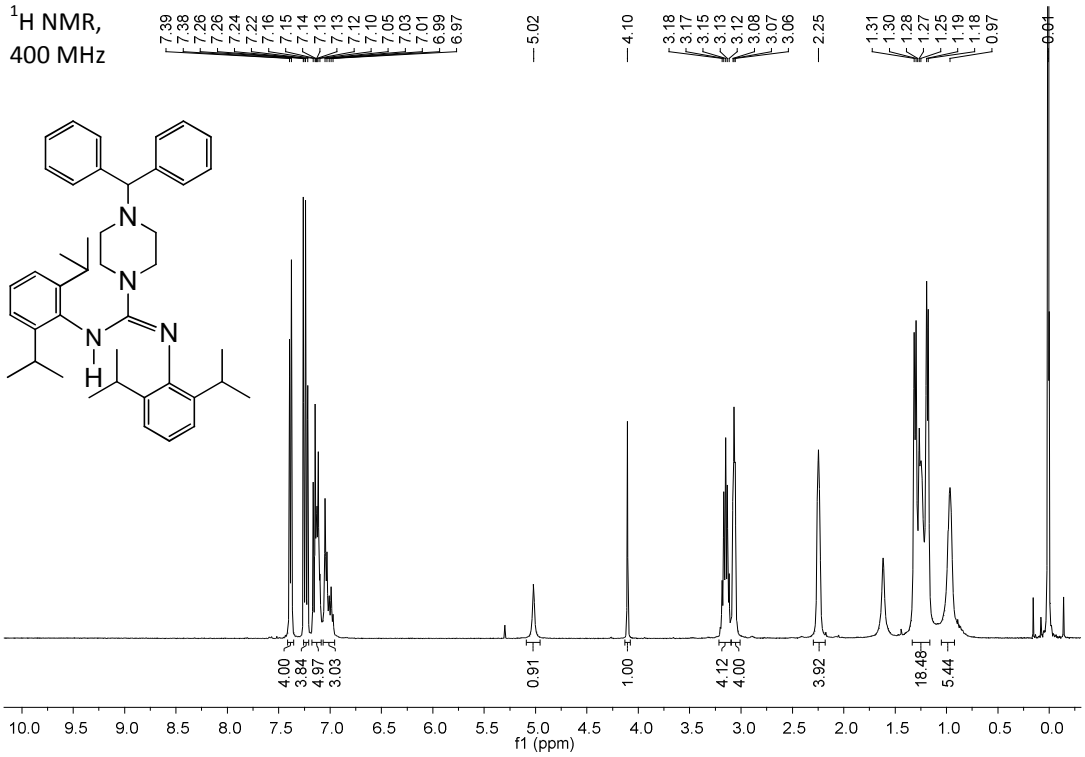


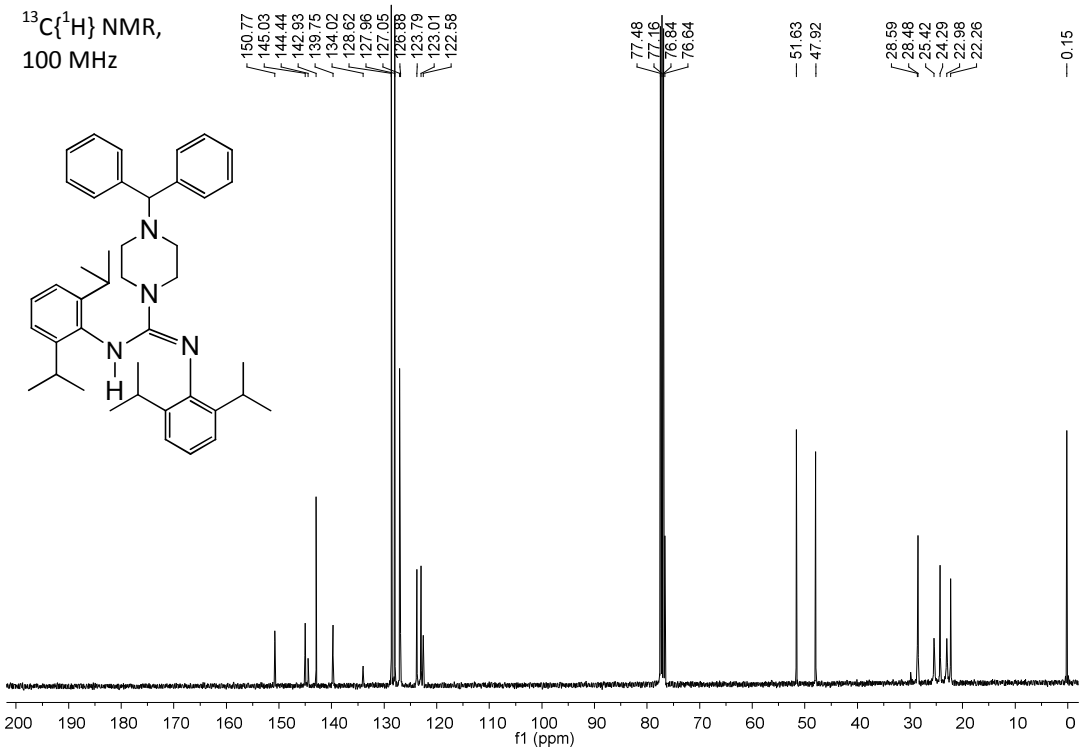
^{1}H NMR, 400 MHz



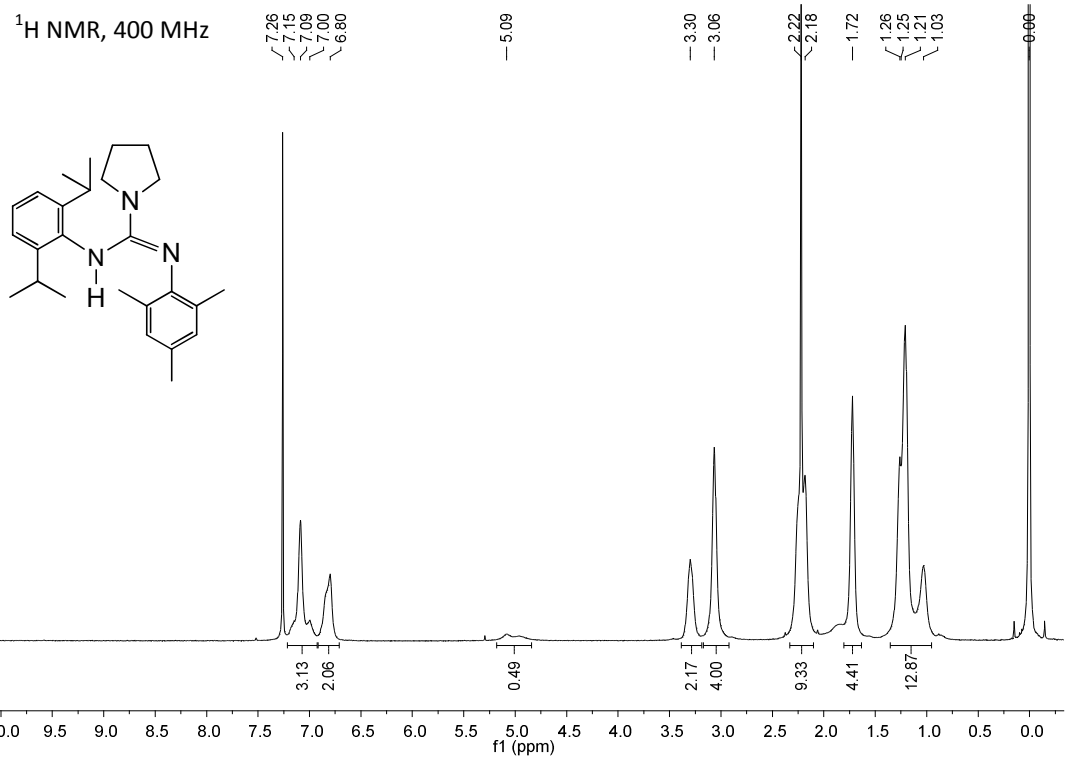
^{13}C{^{1}H} NMR, 100 MHz



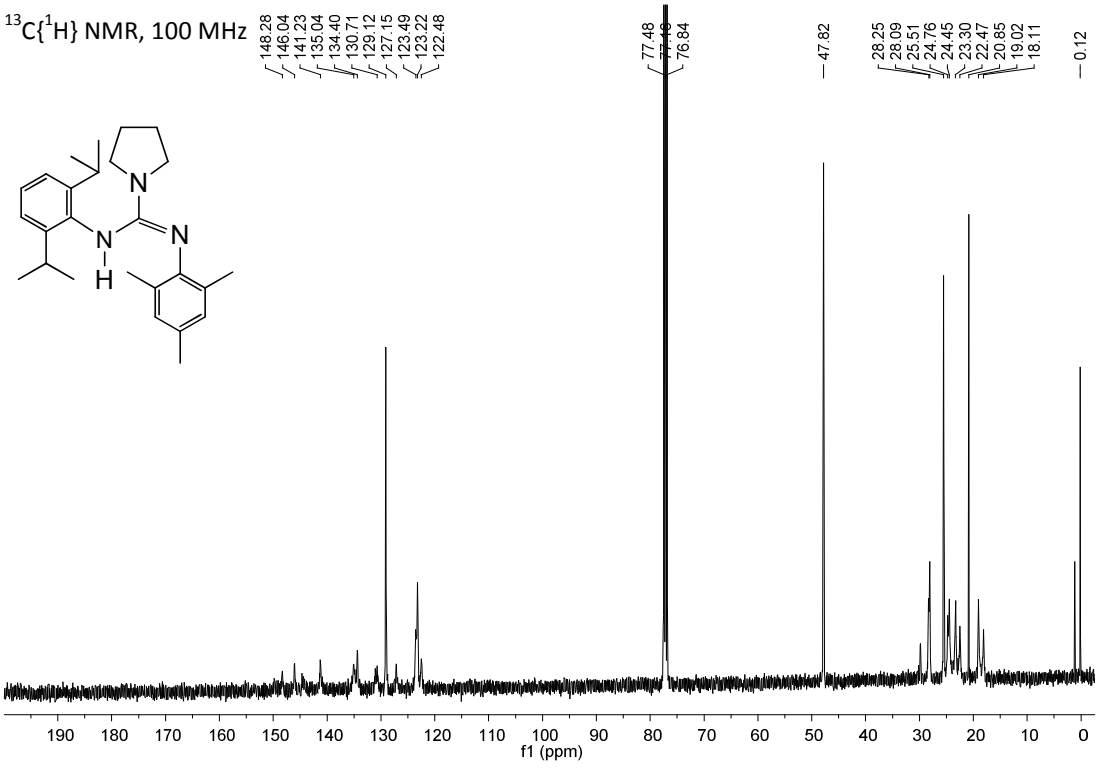

1H NMR,
400 MHz
7.39
7.38
7.26
7.26
7.24
7.22
7.16
7.15
7.14
7.13
7.13
7.12
7.10
7.05
7.03
7.01
6.99
6.97
5.02
4.10
3.18
3.17
3.15
3.13
3.12
3.08
3.07
3.06
2.25
1.31
1.30
1.28
1.27
1.25
1.19
1.18
0.97
0.01
4.00
3.84
4.97
3.03
0.91
1.00
4.12
4.00
3.92
18.48
5.44
f1 (ppm)


13C{1H} NMR,
100 MHz
150.77
145.03
144.44
142.93
139.75
134.02
128.62
127.96
127.05
126.88
123.79
123.01
122.58
77.48
77.16
76.84
76.64
51.63
47.92
28.59
28.48
25.42
24.29
22.98
22.26
0.15
f1 (ppm)

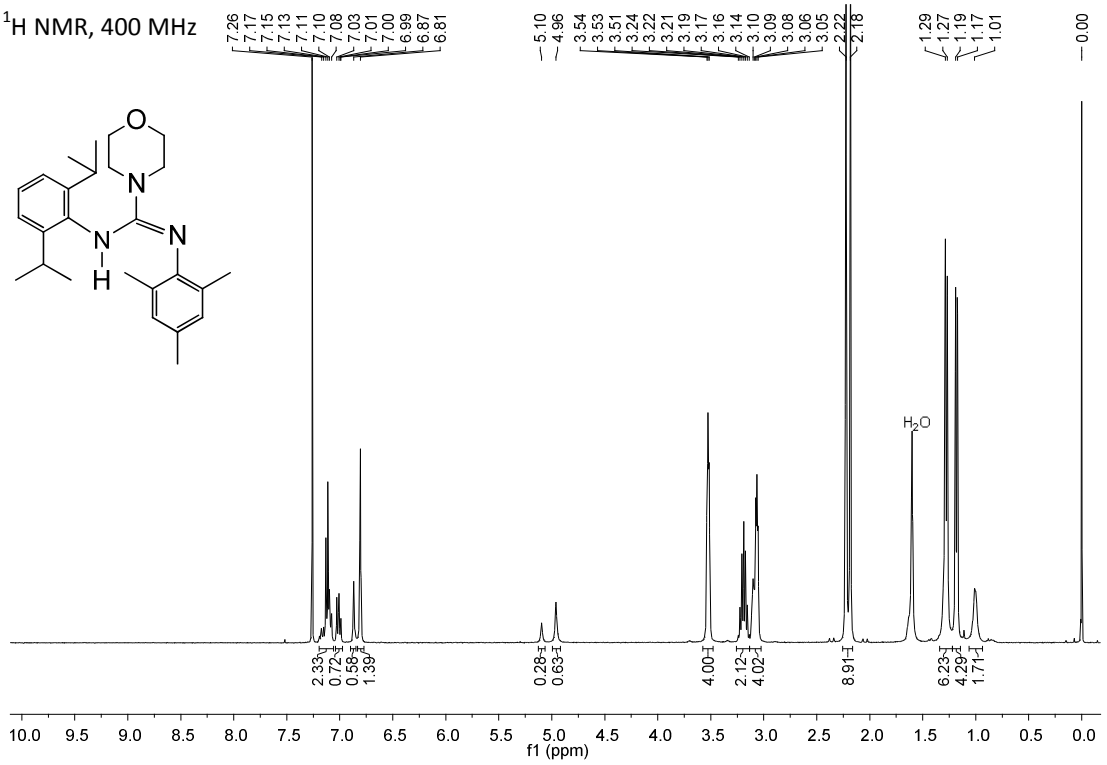
^{1}H NMR, 400 MHz



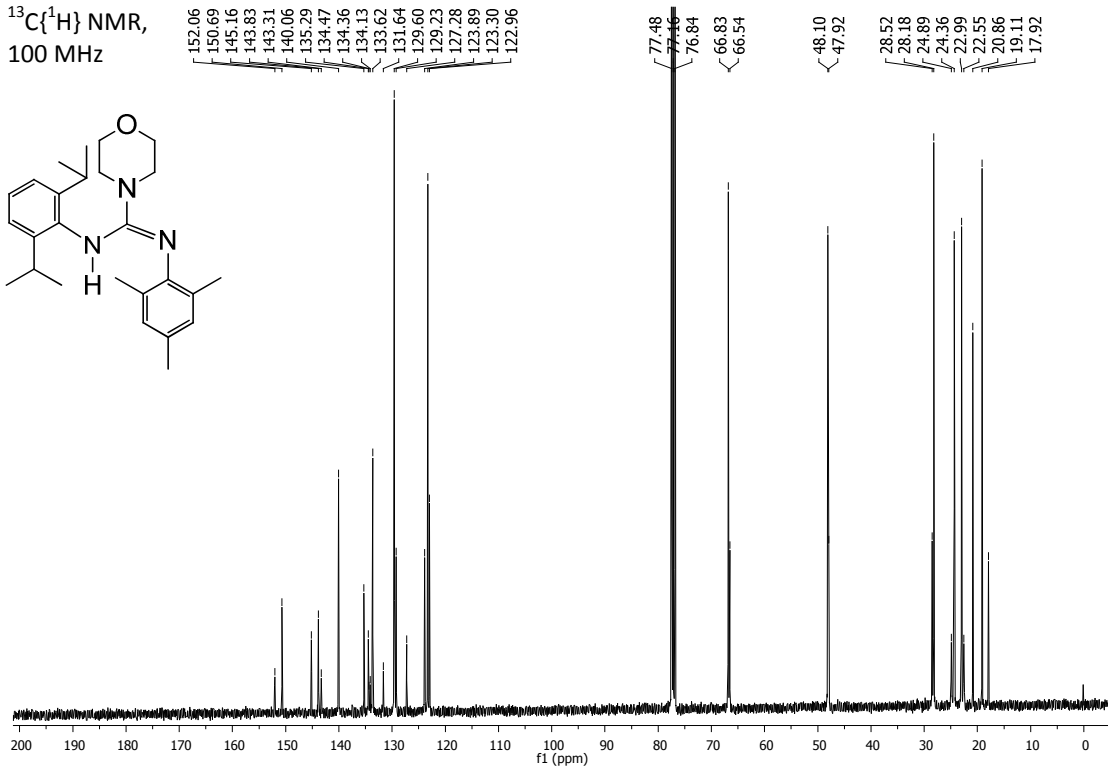
^{13}C{^{1}H} NMR, 100 MHz

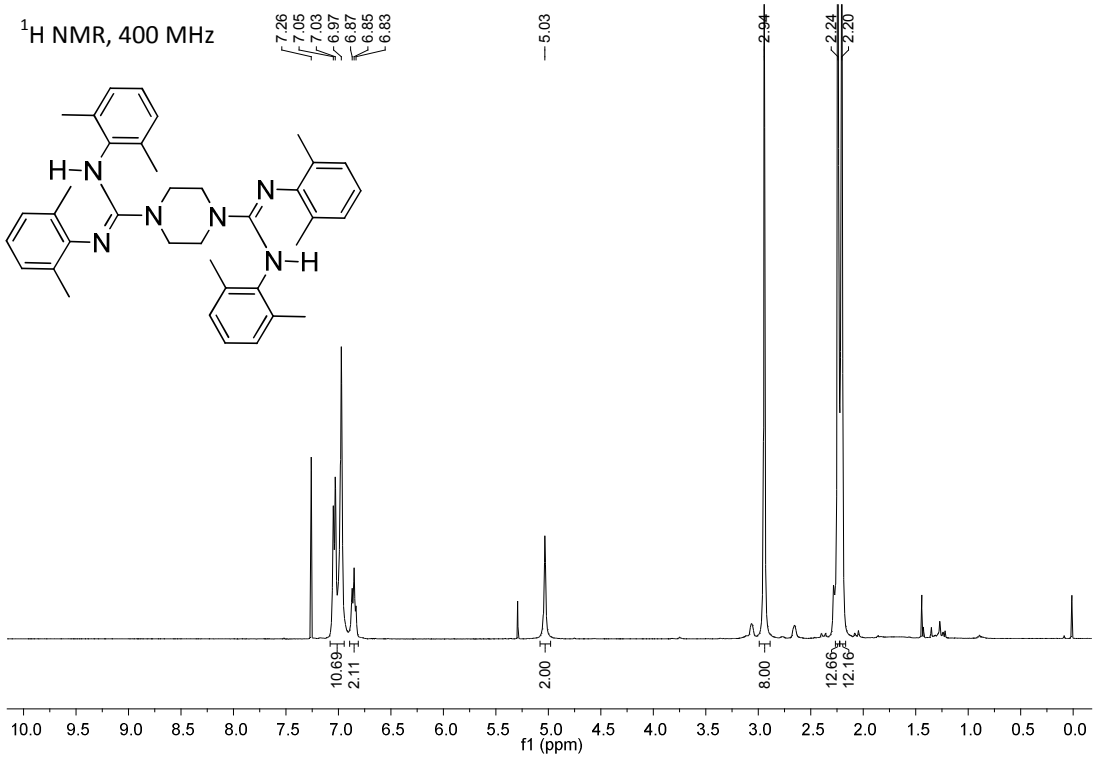


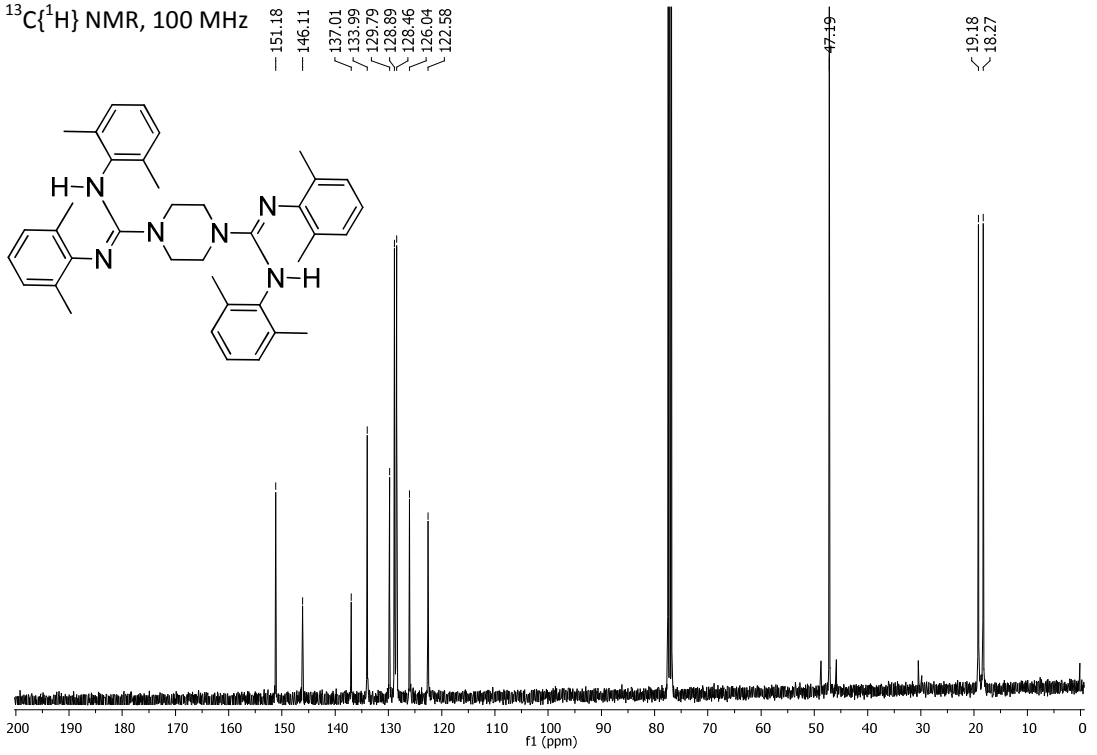
^{1}H NMR, 400 MHz



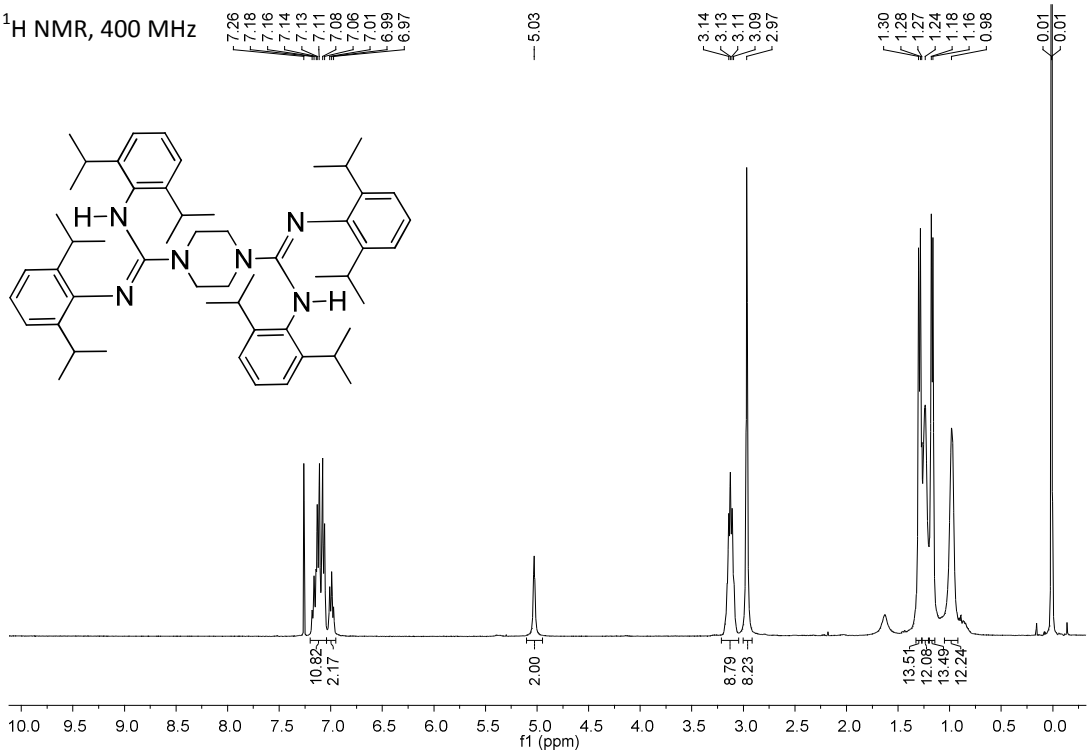
^{13}C{^{1}H} NMR, 100 MHz




^{1}H NMR, 400 MHz
7.26
7.05
7.03
6.97
6.87
6.85
6.83
5.03
2.94
2.24
2.20
H–N
N
N
N
N
N–H
10.69
2.11
2.00
8.00
12.66
12.16
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)


^{13}C{^{1}H} NMR, 100 MHz
151.18
146.11
137.01
133.99
129.79
128.89
128.46
126.04
122.58
47.19
19.18
18.27
H–N
N
N
N
N
N–H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR, 400 MHz



^{13}C{^{1}H} NMR, 100 MHz

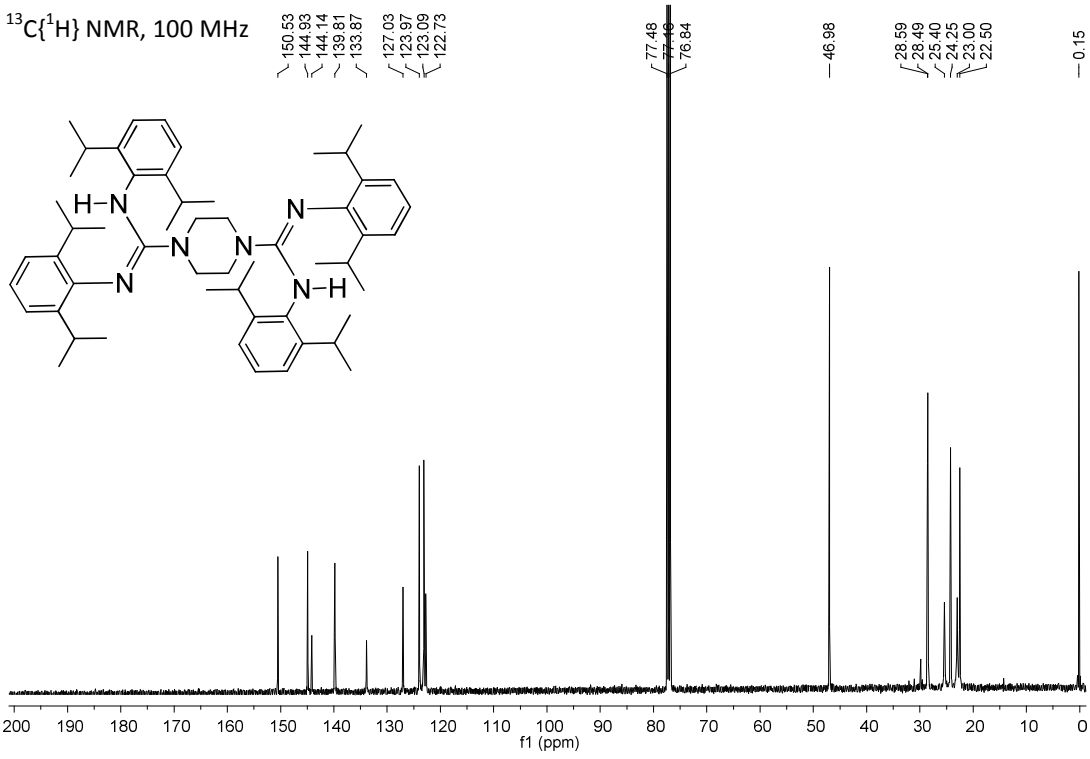


Table S2. Crystal data and structural refinement of compounds 1a, 21a, & 27a,

	1a	**22a**	**27a**
Empirical formula	$C_{21}H_{27}N_3$	$C_{30}H_{46}N_4$	$C_{38}H_{46}N_6$
CCDC	1400660	1400662	1400661
Formula weight	321.46	462.71	586.81
Temperature, K	296(2)	296(2)	296(2)
Wavelength , Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P2(1)/c	C2/c
Unit cell dimensions, Å &°	a = 8.443(2) α= 69.409(10) b = 10.304(2) β= 81.907(10) c = 12.134(2) γ = 77.454(10)	a = 9.405(2) α= 90.000 b =17.120(3) β= 102.705 c = 18.715(3) γ = 90.000	a = 18.0078(7) α= 90 b = 13.9272(7) β= 113.869(4) c = 15.5355(7) γ = 90
Volume, $Å^3$	962.2(8)	2939.6(19)	3563.0(3)
Z	2	4	4
Density (calculated), Mg/m^3	1.110	1.046	1.094
Absorption coefficient, mm^{-1}	0.066	0.062	0.065
F(000)	348	1016	1264
Crystal size, mm^3	0.18 x 0.12 x 0.098	0.12 x 0.097 x 0.089	0.22 x 0.16 x 0.10
Theta range for data collection, °	2.96 to 25.50	2.22 to 25.50	2.68 to 27.76
Index ranges	-10<=h<=10, -12<=k<=12, -14<=l<=14	-11<=h<=11, -20<=k<=20, -22<=l<=22	-23<=h<=23, -18<=k<=18, -18<=l<=20
Reflections collected	13541	42851	25181
Independent reflections	3582 [R(int) = 0.0280]	5475 [R(int) = 0.0382]	4188 [R(int) = 0.0542]
Completeness to theta = 25.50°	99.8 %	99.9 %	99.7 %
Absorption correction	Empirical	Empirical	Empirical
Max. and min. transmission	0.7461 and 0.7010	0.7461 and 0.6946	0.7456 and 0.7002
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3582 / 0 / 225	5475 / 0 / 320	4188 / 6 / 203
Goodness-of-fit on F^2	1.041	1.052	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0587, wR2 = 0.1640	R1 = 0.0549, wR2 = 0.1445	R1 = 0.0513, wR2 = 0.1291
R indices (all data)	R1 = 0.0810, wR2 = 0.1838	R1 = 0.0724, wR2 = 0.1691	R1 = 0.0885, wR2 = 0.1504
Largest diff. peak and hole, $e.Å^{-3}$	0.369 and -0.206	0.283 and -0.369	0.156 and -0.179

Table S3. Selected bond lengths (Å) and bond angles (^{o}) of compound 1a, 22a & 27a,

1a		**22a**		**27a**	
N–H	0.800	N–H	0.831	N–H	0.860
N(1)–C(1)	1.288(2)	N(1)–C(1)	1.2810(19)	C(2)–N(4)	1.3966(18)
N(2)–C(1)	1.365(2)	N(2)–C(1)	1.3805(19)	C(2)–N(6)	1.2734(18)
N(3)–C(1)	1.364(2)	N(3)–C(1)	1.3941(19)	C(2)–N(5)	1.3705(18)
N(1)–C(2)	1.397(3)	N(1)–C(2)	1.416(2)	C(22)–N(5)	1.4336(19)
N(2)–C(10)	1.431(2)	N(2)–C(14)	1.4370(19)	C(27)–N(6)	1.417(2)
N(1)–C(1)–N(2)	123.60(17)	N(1)–C(1)–N(2)	125.02(13)	N(6)–C(2)–N(5)	124.92(13)
N(1)–C(1)–N(3)	118.75(17)	N(1)–C(1)–N(3)	119.43(13)	N(6)–C(2)–N(4)	119.84(13)
N(3)–C(1)–N(2)	117.65(16)	N(3)–C(1)–N(2)	115.54(13)	N(5)–C(2)–N(4)	115.23(12)
C(1)–N(2)–C(10)	128.37(17)	C(1)–N(2)–C(14)	126.52(13)	C(2)–N(5)–C(22)	126.62(12)
C(1)–N(1)–C(2)	122.71(17)	C(1)–N(1)–C(2)	121.83(12)	C(2)–N(6)–C(27)	121.23(13)