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Rh(III)-Catalyzed [5+1] Oxidative Cycloaddition of Arylguanidines with Alkynes: A Novel Access to C4-Disubstituted 1,4-Dihydroquinazolin-2-amines

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Supporting Information

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1. General experimental procedures

All reactions were performed under an inert atmosphere of argon and with anhydrous solvents in glassware oven or flame dried at 80 ºC unless otherwise stated. All chemicals were purchased from Acros Organics Ltd., Aldrich Chemical Co. Ltd., Alfa Aesar, Fluorochem Ltd., Strem Chemicals Inc. or TCI Europe N.V. chemical companies and used without further purification, unless otherwise stated.

Analytical thin layer chromatography was carried out on silica-coated aluminium plates (silica gel 60 F_{254} Merck) or on aluminium sheets (aluminium oxide 60 F_{254} neutral Merck) using UV light as visualizing agent (254 nm) and $KMnO_4$ (solution of 1.5 g of potassium permanganate, 10 g of potassium bicarbonate and 1.25 mL of 10% sodium hydroxide in 200 mL of water) with heat as developing agents. Flash column chromatography was performed on silica gel 60 (Merck, 230-400 mesh) or aluminium oxide Camag Brockmann I neutral (Fisher Chemical, 100-250 mesh) with the indicated eluent.

Mass spectrometry was carried out on a Bruker microTOF spectrometer.

^{1}H- and ^{13}C-NMR experiments were carried out using a Varian Inova 500MHz, a Varian Inova 400MHz or a Varian Mercury 300MHz NMR spectrometers and chemical shifts are reported relative to tetramethylsilane and trichloro-fluoro-methane as internal references. Coupling constants *J* are given in Hertz (Hz). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p=pentet, m = multiplet or as a combination of them. Multiplicities of ^{13}C NMR signals were determined by DEPT experiments.

All other reagents and solvents: dichloromethane, dichloroethane, tetrahydrofurane, toluene, ^{i}PrOH and dimethyleter (99.5-99.8%, GC) were used dry, unless otherwise indicated. Acetone was distilled from K_2CO_3 and storage over 4Å molecular sieves.

Yields refer to isolated compounds estimated to be > 95% pure as determined by ^{1}H NMR and capillary GC analysis.

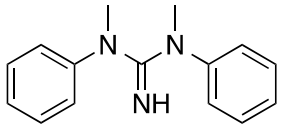
2. Preparation of starting materials

2.1. Preparation of guanidines (1)

Guanidines **1a**, **1a'**, **1b**, **1e**, **1f**, **1h**, **1i**, **1ba**, **1ha** and **1ia** were analogously prepared following the described procedure for amidine synthesis[S1] from commercially available *N*-methylanilines and the corresponding arylcyanamides.

Guanidines **1c**, **1d**, **1g**, **1ca** and **1ga** were prepared following the described procedure[S1] from the corresponding *N*-methylaniline hydrochlorides and arylcyanamides.

***N,N'*-Dimethyl-*N,N'*-diphenylguanidine (1a)**



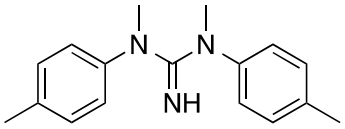
1a

According to the literature procedure,[S1] the guanidine **1a** was synthesized in 66 % yield as a yellow oil (DCM/MeOH 0.90:0.10, R_f 0.44).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.2-7.1 (m, 4H), 7.0-6.8 (m, 6H), 5.55 (bs, 1H), 3.11 (s, 6H).

^{13}C NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 162.3 (C), 145.9 (2xC), 128.6 (4xCH), 123.3 (2xCH), 122.7 (4xCH), 38.8 (2xCH_3).

***N,N'*-Dimethyl-*N,N'*-bis(4-methylphenyl)guanidine (1b)**



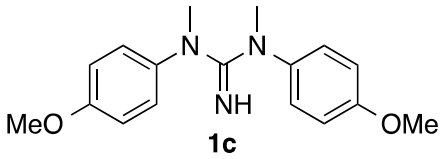
1b

According to a conveniently modified literature procedure,[S1] the guanidine **1b** was synthesized in 77 % yield as a brown oil (DCM/MeOH 0.85:0.15, R_f 0.57).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.01 (d, *J* = 8.5 Hz, 4H), 6.87 (d, *J* = 8.5 Hz, 4H), 3.09 (s, 6H), 2.27 (s, 6H).

^{13}C NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 163.1 (C), 143.9 (2xC), 133.3 (2xC), 129.6 (4xCH), 123.2 (4xCH), 39.3 (2xCH_3), 20.9 (2xCH_3).

***N,N'*-Bis(4-methoxyphenyl)-*N,N'*-dimethylguanidine (1c)**



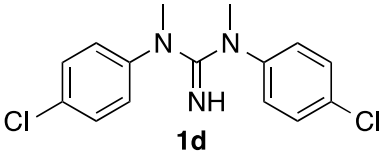
1c

According to literature procedure,[S2] the guanidine **1c** was synthesized in 30 % yield as a yellow oil (DCM/MeOH 0.95:0.05, R_f 0.53).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 6.74 (d, *J* = 8.9 Hz, 4H), 6.65 (d, *J* = 8.9 Hz, 4H), 6.13 (bs, 1H), 3.68 (s, 6H), 3.08 (s, 6H).

^{13}C NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 162.8 (C), 156.6 (2xC), 139.1 (2xC), 125.7 (4xCH), 114.1 (4xCH), 55.4 (2xCH_3), 40.3 (2xCH_3).

***N,N'*-Bis(4-chlorophenyl)-*N,N'*-dimethylguanidine (1d)**



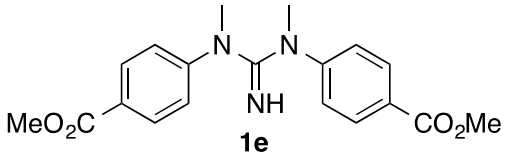
1d

According to the literature procedure,[S1] the guanidine **1d** was synthesized in 89 % yield as a yellow oil (DCM/MeOH 0.90:0.10, R_f 0.64).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.1-7.0 (m, 4H), 6.8-6.7 (m, 4H), 5.60 (bs, 1H), 3.12 (s, 6H).

^{13}C NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 161.7 (C), 144.5 (2xC), 129.1 (2xC), 129.0 (4xCH), 124.3 (4xCH), 39.2 (2xCH_3).

Dimethyl 4,4'-[(iminomethylene)bis(methylimino)]dibenzoate (1e)



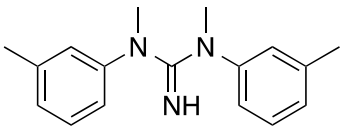
1e

According to the literature procedure,[S2] the guanidine **1e** was synthesized in 40 % yield as a yellow oil (DCM/MeOH 0.90:0.10, R_f 0.33).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.9-7.8 (m, 4H), 7.0-6.9 (m, 4H), 3.85 (s, 6H), 3.21 (s, 6H).

^{13}C NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 166.7 (2xCO), 160.7 (C), 149.4 (2xC), 130.7 (4xCH), 124.4 (2xC), 120.4 (4xCH), 52.1 (2xCH_3), 38.3 (2xCH_3).

***N,N'*-Dimethyl-*N,N'*-bis(3-methylphenyl)guanidine (1f)**



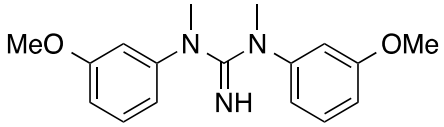
1f

According to the literature procedure,[S1] the guanidine **1f** was synthesized in 95 % yield as a yellow oil (DCM/MeOH 0.90:0.10, R_f 0.25).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.1-7.0 (m, 2H), 6.9-6.7 (m, 6H), 5.22 (bs, 1H), 3.13 (s, 6H), 2.25 (s, 6H).

^{13}C NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 162.7 (C), 146.1 (2xC), 138.7 (2xC), 128.7 (2xCH), 124.5 (2xCH), 123.9 (2xCH), 120.2 (2xCH), 39.2 (2xCH_3), 21.5 (2xCH_3).

***N,N'*-Bis(3-methoxyphenyl)-*N,N'*-dimethylguanidine (1g)**



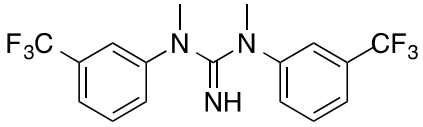
1g

According to the literature procedure,[S2] the guanidine **1g** was synthesized in 59 % yield as a yellow oil (DCM/MeOH 0.85:0.15, R_f 0.44).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.09 (t, *J* = 8.1 Hz, 2H), 6.58 (ddd, *J* = 8.1, 2.2, 0.9 Hz, 2H), 6.53 (ddd, *J* = 8.1, 2.2, 0.9 Hz, 2H), 6.49 (t, *J* = 2.2 Hz, 2H), 3.69 (s, 6H), 3.13 (s, 6H).

^{13}C NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 162.1 (C), 160.3 (2xC), 147.3 (2xC), 129.6 (2xCH), 115.1 (2xCH), 109.1 (2XCH), 108.6 (2xCH), 55.4 (2xCH_3), 39.0 (2xCH_3).

***N,N'*-Dimethyl-*N,N'*-bis[3-(trifluoromethyl)phenyl]guanidine (1h)**



1h

According to the literature procedure,[S1] the guanidine **1h** was synthesized in 83 % yield as a brown oil (DCM/MeOH 0.85:0.15, R_f 0.46).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.3-7.1 (m, 4H), 7.0-6.9 (m, 4H), 3.32 (s, 6H).

^{19}F NMR (300 MHz, $CDCl_3$), δ (ppm): -63.2.

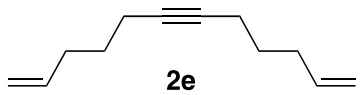
^{13}C NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 160.9 (C), 145.7 (2xC), 131.3 (q, *J* = 32.2 Hz, 2xC-CF_3), 123.3 (2xCH), 126.5 (2xCH), 124.1 (q, *J* = 272.5 Hz, 2xCF_3), 120.7 (q, *J* = 4.2 Hz, 2xCH), 120.2 (q, *J* = 4.2 Hz, 2xCH), 39.5 (2xCH_3).

2.2. Preparation of alkynes (2)

Alkynes **2a-d** and **2h-q** were purchased from commercial sources.

Alkynes **2e**,[S3] **2f**,[S4a] **2g**[S4] and **2r**[S5] were prepared following literature procedures.

Dodeca-1,11-dien-6-yne (2e)



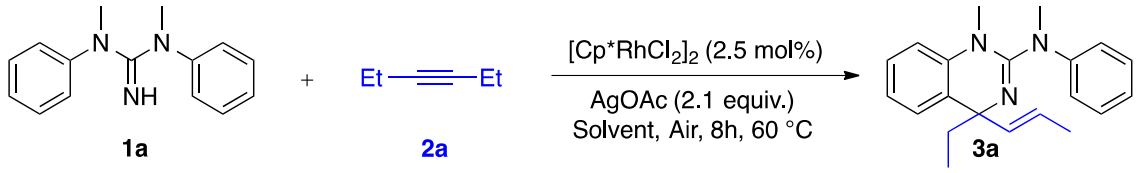
According to the literature procedure[S3], alkyne **2e** was synthesized from hept-1-en-6-yne in 50 % yield as a transparent oil (100% pentane, R_f 0.95).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 5.79 (ddt, J = 17.0, 10.2, 6.7 Hz, 2H), 5.1-4.9 (m, 4H), 2.2-2.1 (m, 8H), 1.6-1.5 (m, 4H).

^{13}C NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 138.2 (2xCH), 115.0 (2xCH_2), 80.2 (2xC), 32.9 (2xCH_2), 28.5 (2xCH_2), 18.3 (2xCH_2).

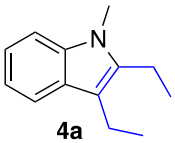
3. Optimization data

a) Solvent effect

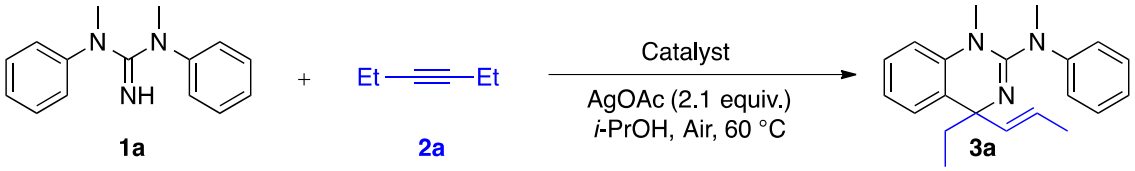


Entry	Solvent	Yield 3a (%)[a]
1	DCE	31
2	*i*-PrOH	91
3[b]	CH_3CN	60
4	1,4-Dioxane	SM
5	Toluene	SM
6	*t*-BuOH	44
7	*t*-AmOH	73
8[c]	*t*-AmOH	40
9[d]	MeOH	traces
10	AcOH	SM

[a]Isolated yields. [b]Indole **4a** was isolated as minor product (25%). [c]Reaction was carried out under argon atmosphere. [d]Traces of **4a** (<3%) was observed by ^{1}H NMR.



b) Type of catalyst

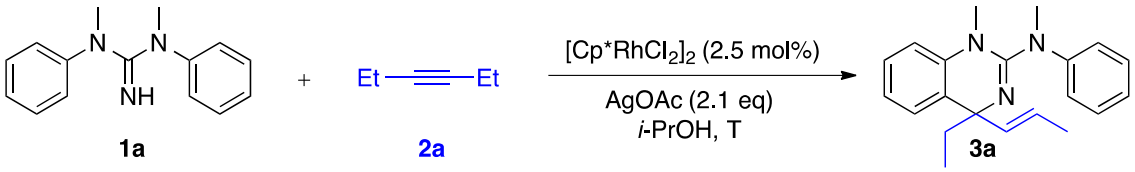


1a 2a 3a

Entry	Catalyst	Yield 3a (%)[a]
1	$[Cp^*RhCl_2]_2$	91
2[b]	$Pd(OAc)_2$	SM
3	$[Cp^*IrCl_2]_2$	traces
4	$Cp^*Rh(OAc)_2$	94
5	-	SM
6	$[Cp^*Rh(CH_3CN)_3]$ $(SbF_6)_2$	SM
7	$[Rh(COD)Cl_2]$	SM
8	$[Cp^*CoI_2CO]$	SM

[a]Isolated yields. [b]Traces of benzimidazole (<5%) were observed by ^{1}H NMR.

c) Temperature

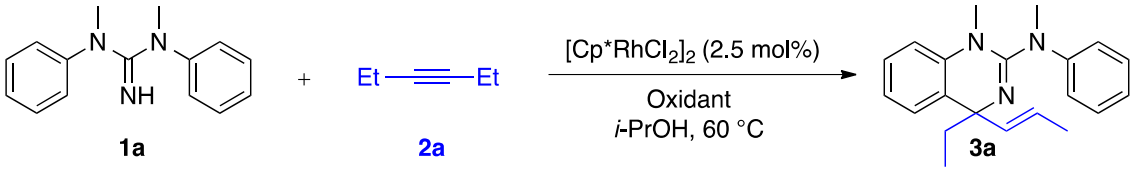


1a 2a 3a

Entry	T (ºC)	Time (h)	Yield 3a (%)[a]
1	r.t.	17	27
2[b]	120	3	Decomposition
3[b]	80→95	3	Decomposition
4	40	16	65
5	75	8	84
6	60	8	91

[a]Isolated yields. [b]*t*-AmOH as solvent.

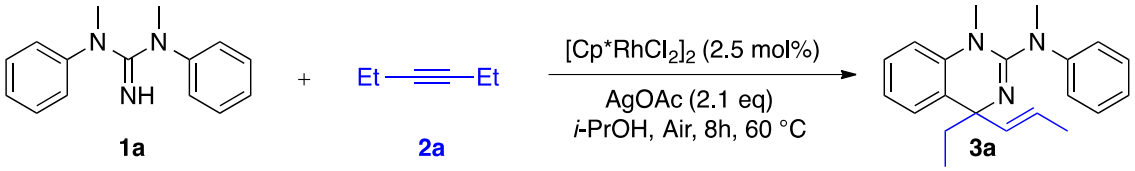
d) Additives and oxidants



Entry	Additive[a]	Oxidant[b]	Yield 3a (%)[c]
1	$AgSbF_6$	$Cu(OAc)_2.H_2O$	traces
2[d]	Na_2CO_3	$AgOAc/O_2$	39
3[e]	AcOH	$Cu(OAc)_2$	SM
4	-	$Ag(O_2CCF_3)$	Traces
5	Na_2CO_3	-	SM
6	$AgCO_3$	-	SM
7	-	Ag(OPiv)	51
8[f]	-	AgOAc	80
9	-	AgOAc	91
10[g]	Na_2CO_3	AgOAc	50
11[g]	KO^{t}Bu	AgOAc	45
12[g]	AcOH	AgOAc	31
13[d]	DABCO	AgOAc	78

[a]Additive (13 mol%). [b]Oxidant (2.1 equiv). [c]Isolated yields. [d]AgOAc (25 mol%). [e]AcOH (10 mol%) in dioxane. [f]AgOAc (1.3 equiv). [g]Additive (10 mol%). [d]Oxidant (100 mol%).

e) Alkyne loading

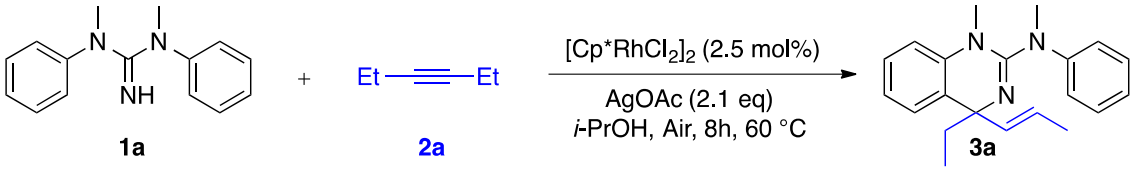


1a 2a 3a

Entry	Alkyne (equiv)	Yield 3a (%)[a]
1	0.8	65
2	1	91
3	2	90
4[b]	-	SM

[a]Isolated yields. [b]Traces of benzimidazole (<5%) were observed by ^{1}H NMR.

f) Concentration effect

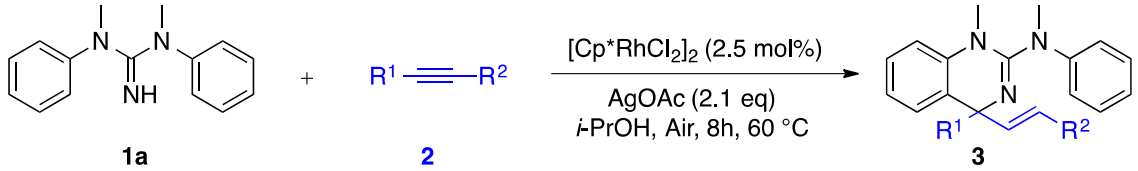


1a 2a 3a

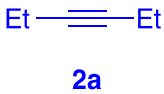
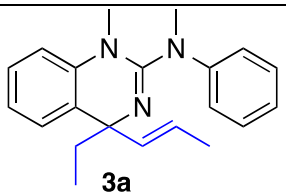
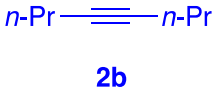
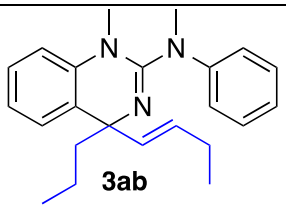
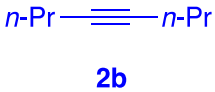
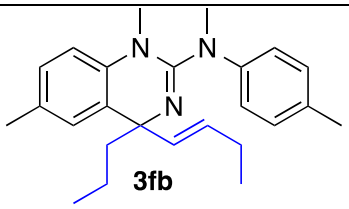
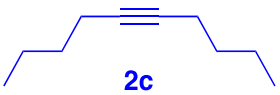
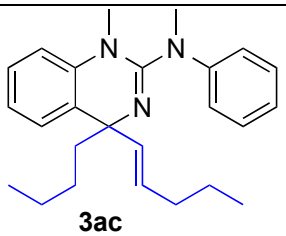
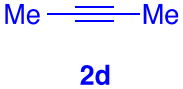
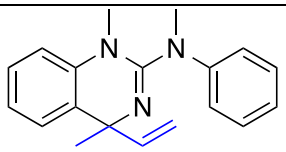
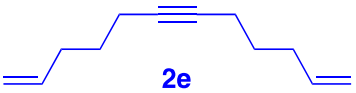
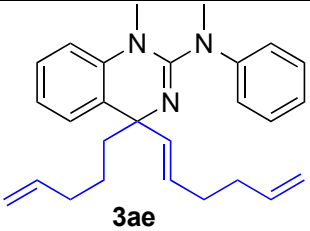
Entry	Concentration (M)	Yield 3a (%)[a]
1	0.037	86
2	0.2	91

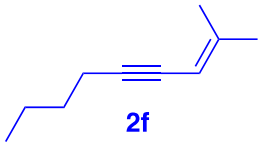
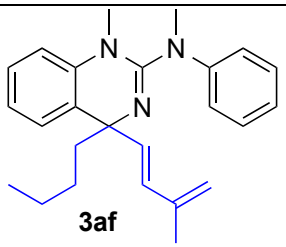
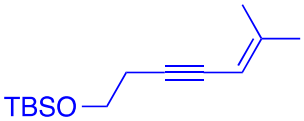
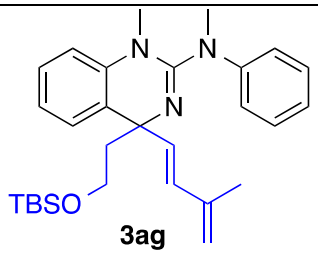
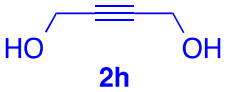
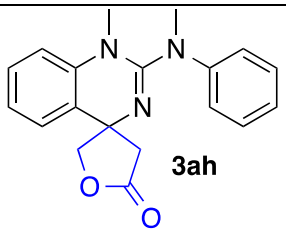
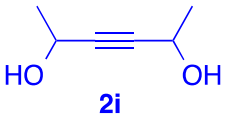
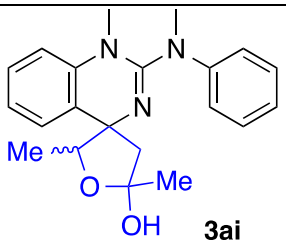
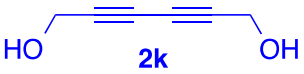
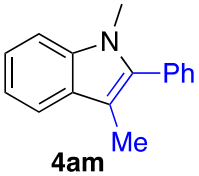
[a]Isolated yields.

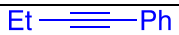
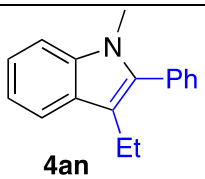
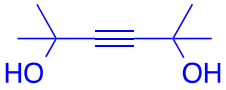
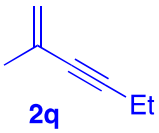
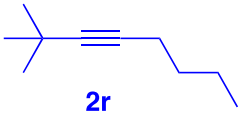
g) Alkyne partner



1a + 2 → 3

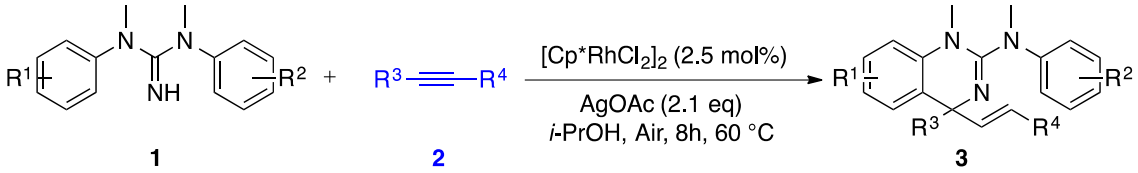
Entry	Alkyne Partner	Product	Yield 3 (%)[a]
1	 **2a**	 **3a**	91
2	 **2b**	 **3ab**	70
3	 **2b**	 **3fb**	64
4	 **2c**	 **3ac**	72
5	 **2d**	 **3ad**	41
6	 **2e**	 **3ae**	48

7	 **2f**	 **3af**	76
8	 **2g**	 **3ag**	62
9	 **2h**	 **3ah**	68
10	 **2i**	 **3ai**	65
11	 **2j**	-	-
12	 **2k**	-	-
13	 **2l**	-	-
14	 **2m**	 **4am**	traces[b]
15			traces[b]

	 **2n**	 **4an**	
16	 **2o**	-	-
17	 **2p**	-	-
18	 **2q**	-	-
19	 **2r**	-	-

[a]Isolated yields. [b]Traces (GCMS, ^{1}H NMR), spectroscopic data matched to those in the literature.[S6]

4. General Procedure for the Synthesis of 1,4-Dihydroquinazolin-2-amines (3)

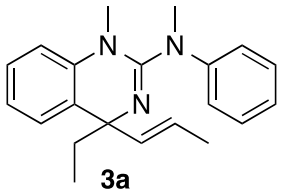


1 2 3

A 25 mL round-bottomed flask was charged with $[Cp^*RhCl_2]_2$ (0.01 mmol, 2.5 mol%), AgOAc (0.84 mmol, 2.1 equiv), *i*-PrOH (2 mL), guanidine **1** (0.40 mmol, 1.0 equiv), and alkyne **2** (0.40 mmol, 1.0 equiv) under air atmosphere. The mixture was heated at 60 ºC for 8 h until disappearance of the starting material (TLC and/or GCMS). The reaction mixture was concentrated and the residue purified by flash column chromatography through alumina Brockmann I neutral using a mixture of Hex/EtOAc with a few drops of *i*-PrOH as eluent to afford the corresponding1,4-dihydroquinazoline **3**.

5. Data for C4-Disubstituted-1,4-dihydroquinazolin-2-amines (3)

4-Ethyl-*N*,1-dimethyl-*N*-phenyl-4-[(1*E*)-prop-1-en-1-yl]-1,4-dihydroquinazolin-2-amine (3a)



3a

Yellow oil, 91 % yield, (Hex/EtOAc/*i*-PrOH 0.90:0.099:0.001, R_f 0.82).

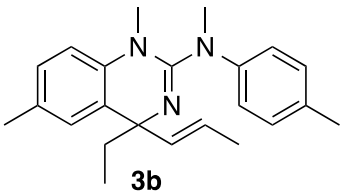
^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.2-7.1 (m, 4H), 7.0-6.9 (m, 1H), 6.9-6.8 (m, 1H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 7.9 Hz, 1H), 5.53 (dq, *J* = 15.2, 0.9 Hz, 1H), 5.23 (dq, *J* = 15.2, 6.4 Hz, 1H), 3.28 (s, 3H), 2.79 (s, 3H), 2.0-1.9 (m, 1H), 1.8-1.7 (m, 1H), 1.59 (dd, *J* = 6.4, 0.9 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR, DEPT (126 MHz, $CDCl_3$), δ (ppm): 151.6 (C), 147.9 (C), 140.7 (C), 137.9 (CH), 129.6 (C), 129.4 (2xCH), 127.0 (CH), 125.7 (CH), 122.8 (CH), 122.6 (CH), 122.2 (CH), 120.2 (2xCH), 112.8 (CH), 61.0 (C), 40.6 (CH_3), 33.5 (CH_3), 33.2 (CH_2), 18.1 (CH_3), 8.9 (CH_3).

MS, m/z (% relative intensity): 320 $[M+H]^+$, 100), 276 (69).

HRMS (CI) calculated for $C_{21}H_{26}N_3$ $[M+H]^+$: 320.2121; found: 320.2130.

4-Ethyl-*N*,1,6-trimethyl-*N*-(4-methylphenyl)-4-[(1*E*)-prop-1-en-1-yl]-1,4-dihydroquinazolin-2-amine (3b)



3b

Brown oil, 94 % yield, (Hex/EtOAc/*i*-PrOH 0.90:0.099:0.001, R_f 0.64).

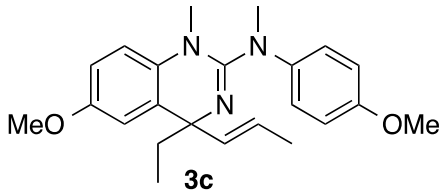
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.04 (d, *J* = 8.2 Hz, 2H), 7.0-6.9 (m, 2H), 6.76 (d, *J* = 8.2 Hz, 2H), 6.55 (d, *J* = 8.6 Hz, 1H), 5.61 (d, *J* = 15.4 Hz, 1H), 5.4-5.3 (m, 1H), 3.31 (s, 3H), 2.84 (s, 3H), 2.34 (s, 3H), 2.28 (s, 3H), 1.98 (dq, *J* = 14.3, 7.3 Hz, 1H), 1.87 (dq, *J* = 14.3, 7.3 Hz, 1H), 1.68 (dd, *J* = 6.5, 1.6 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 151.7 (C), 145.7 (C), 138.5 (C), 138.0 (CH), 131.8 (C), 131.7 (C), 129.9 (2xCH), 129.8 (C), 127.4 (CH), 126.1 (CH), 122.5 (CH), 120.8 (2xCH), 112.6 (CH), 60.8 (C), 41.0 (CH_3), 33.6 (CH_3), 33.2 (CH_2), 21.1 (CH_3), 20.8 (CH_3), 18.1 (CH_3), 8.9 (CH_3).

MS, m/z (% relative intensity): 348 ($[M+H]^+$, 100), 304 (34).

HRMS (ESI) calculated for $C_{23}H_{30}N_3$ $[M+H]^+$: 348.2434; found: 348.2436.

4-Ethyl-6-methoxy-*N*-(4-methoxyphenyl)-*N*,1-dimethyl-4-[(1*E*)-prop-1-en-1-yl]-1,4-dihydroquinazolin-2-amine (3c)



3c

Following the general procedure, the reaction was carried out at 40 °C. Brown oil, 45 % yield, (Hex/EtOAc/*i*-PrOH 0.85:0.24:0.01, R_f 0.53).

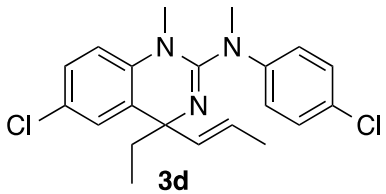
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 6.9-6.8 (m, 5H), 6.72 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.54 (d, *J* = 8.7 Hz, 1H), 5.59 (d, *J* = 15.4 Hz, 1H), 5.35 (dq, *J* = 15.4, 6.5 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.27 (s, 3H), 2.80 (s, 3H), 1.95 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.9-1.8 (m, 1H), 1.67 (dd, *J* = 6.5, 1.5 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 155.6 (C), 155.4 (C), 152.1 (C), 141.7 (C), 137.7 (CH), 135.0 (C), 131.9 (C), 123.2 (2xCH), 122.7 (CH), 114.7 (2xCH), 113.4 (CH), 111.9 (CH), 111.3 (CH), 60.9 (C), 55.8 (CH_3), 55.6 (CH_3), 41.7 (CH_3), 33.8 (CH_3), 33.2 (CH_2), 18.1 (CH_3), 8.9 (CH_3).

MS, m/z (% relative intensity): 380 ($[M+H]^+$, 100), 336 (29).

HRMS (ESI) calculated for $C_{23}H_{30}N_3O_2$ $[M+H]^+$: 380.2333; found: 380.2337.

6-Chloro-*N*-(4-chlorophenyl)-4-ethyl-*N*,1-dimethyl-4-[(1*E*)-prop-1-en-1-yl]-1,4-dihydroquinazolin-2-amine (3d)



3d

Pale yellow oil, 50 % yield, (Hex/*i*-PrOH 0.999:0.001, R_f 0.56).

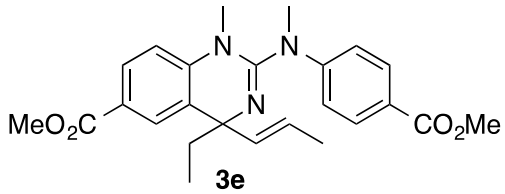
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.20 (d, *J* = 8.9 Hz, 2H), 7.17-6.13 (m, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.59 (d, *J* = 7.9 Hz, 1H), 5.57 (d, *J* = 15.3 Hz, 1H), 5.33 (dq, *J* = 15.3, 6.5 Hz, 1H), 3.31 (s, 3H), 2.85 (s, 3H), 2.0-1.8 (m, 2H), 1.68 (d, *J* = 6.5 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 151.1 (C), 146.4 (C), 139.2 (C), 137.1 (CH), 131.4 (C), 129.5 (2xCH), 127.9 (C), 127.5 (C), 127.0 (CH), 125.7 (CH), 123.5 (CH), 121.4 (2xCH), 114.0 (CH), 61.0 (C), 40.7 (CH_3), 33.6 (CH_3), 33.2 (CH_2), 18.0 (CH_3), 8.8 (CH_3).

MS, m/z (% relative intensity): 388 ($[M+H]^+$, 100), 344 (26).

HRMS (CI) calculated for $C_{21}H_{24}Cl_2N_3$ $[M+H]^+$: 388.1342; found: 388.1351.

Methyl 4-ethyl-2-[[4-(methoxycarbonyl)phenyl](methyl)amino]-1-methyl-4-[(1*E*)-prop-1-en-1-yl]-1,4-dihydroquinazoline-6-carboxylate (3e) and methyl[4-cyano(methyl)amino)]benzoate (8e)



3e

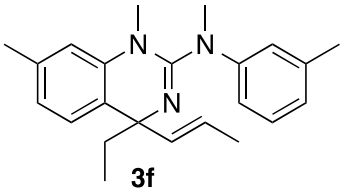
Compounds **3e** and **8e** were obtained as an inseparable mixture (5.5:1) in 32 % yield as yellow oil, (Hex/EtOAc/*i*-PrOH 0.85:0.24:0.01, R_f 0.78).

Spectroscopic data of the major product **3e***:*

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.92 (dt, *J* = 8.9, 1.5 Hz, 3H), 7.84 (d, *J* = 1.9, 1H), 6.76 (dd, *J* = 8.6, 3.0 Hz, 3H), 5.62 (d, *J* = 15.3 Hz, 1H), 5.3-5.2 (m, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.39 (s, 3H), 2.97 (s, 3H), 2.1-2.0 (m, 1H), 1.92 (dq, *J* = 14.5, 7.4 Hz, 1H), 1.67 (d, *J* = 6.3 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 167.1 (CO), 167.0 (CO), 151.0 (C), 150.2 (C), 144.0 (C), 137.4 (CH), 131.4 (3xCH), 129.4 (CH), 128.1 (C), 127.9 (CH), 124.8 (C), 122.5 (C), 116.6 (2xCH), 112.5 (CH), 61.5 (C), 52.1 (CH_3), 52.0 (CH_3), 39.2 (CH_3), 33.7 (CH_2), 33.4 (CH_3), 18.0 (CH_3), 9.0 (CH_3).

4-Ethyl-*N*,1,7-trimethyl-*N*-(3-methylphenyl)-4-[(1*E*)-prop-1-en-1-yl]-1,4-dihydroquinazolin-2-amine (3f)



3f

Yellow oil, 79 % yield, (Hex/EtOAc/*i*-PrOH 0.90:0.099:0.001, R_f 0.81).

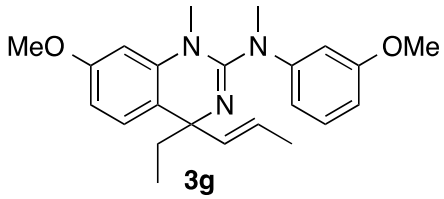
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.11 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.72 (s, 1H), 6.61 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.48 (s, 1H), 5.61 (d, *J* = 15.4 Hz, 1H), 5.31 (dq, *J* = 15.4, 6.5 Hz, 1H), 3.33 (m, 3H), 2.88 (s, 3H), 2.33 (s, 3H), 2.29 (s, 3H), 1.98 (dq, *J* = 13.8, 7.2 Hz, 1H), 1.87 (dq, *J* = 13.8, 7.2 Hz, 1H), 1.67 (dd, *J* = 6.5 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 151.5 (C), 147.9 (C), 140.7 (C), 139.1 (C), 138.2 (CH), 136.7 (C), 129.1 (CH), 126.7 (C), 125.5 (CH), 123.2 (CH), 122.9 (CH), 122.5 (CH), 120.8 (CH), 117.1 (CH), 113.5 (CH), 60.8 (C), 40.5 (CH_3), 33.5 (CH_3), 33.4 (CH_2), 21.7 (CH_3), 21.6 (CH_3), 18.1 (CH_3), 8.9 (CH_3).

MS, m/z (% relative intensity): 348 ($[M+H]^+$, 100), 304 (30).

HRMS (ESI) calculated for $C_{23}H_{30}N_3$ $[M+H]^+$: 348.2434; found: 348.2448.

4-Ethyl-7-methoxy-*N*-(3-methoxyphenyl)-*N*,1-dimethyl-4-[(1*E*)-prop-1-en-1-yl]-1,4-dihydroquinazolin-2-amine (3g)



3g

Pale yellow oil, 42 % yield, (Hex/EtOAc/*i*-PrOH 0.85:0.24:0.01, R_f 0.75).

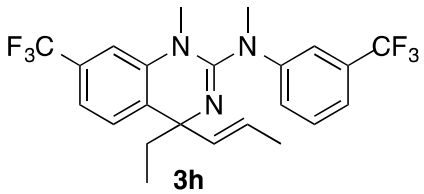
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.2-7.1 (m, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.61 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.51 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.44-6.40 (m, 2H), 6.25 (s, 1H), 5.60 (d, *J* = 15.0 Hz, 1H), 5.3-5.2 (m, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 3.33 (s, 3H), 2.90 (s, 3H), 2.01-1.92 (m, 1H), 1.91-1.83 (m, 1H), 1.66 (dd, *J* = 6.5, 1.5 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 160.6 (C), 158.9 (C), 151.3 (C), 149.0 (C), 141.7 (C), 138.2 (CH), 130.0 (CH), 126.5 (CH), 122.5 (CH), 121.7 (C), 112.1 (CH), 107.1 (CH), 106.7 (CH), 105.5 (CH), 99.8 (CH), 60.7 (C), 55.4 (CH_3), 55.2 (CH_3), 40.2 (CH_3), 33.41 (CH_3), 33.39 (CH_2), 18.0 (CH_3), 8.9 (CH_3).

MS, m/z (% relative intensity): 380 ($[M+H]^+$, 100), 336 (31), 218 (16).

HRMS (ESI) calculated for $C_{23}H_{30}N_3O_2$ $[M+H]^+$: 380.2333; found: 380.2341.

4-Ethyl-*N*,1-dimethyl-4-[(1*E*)-prop-1-en-1-yl]-7-(trifluoromethyl)-*N*-[3-(trifluoromethyl)phenyl]-1,4-dihydroquinazolin-2-amine (3h)



3h

Pale yellow oil, 72 % yield, (Hex/EtOAc/*i*-PrOH 0.95:0.04:0.01, R_f 0.87).

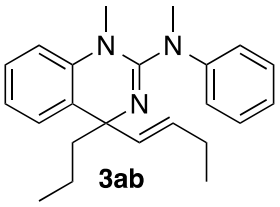
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.27 (t, *J* = 7.9 Hz, 2H), 7.22-7.18 (m, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.06 (s, 1H), 6.9-6.8 (m, 2H), 5.52 (dq, *J* = 15.4, 2.0 Hz, 1H), 5.21 (dq, *J* = 15.4, 6.5 Hz, 1H), 3.28 (s, 3H), 2.88 (s, 3H), 1.93 (dq, *J* = 14.4, 7.3 Hz, 1H), 1.82 (dq, *J* = 14.4, 7.3 Hz, 1H), 1.60 (dd, *J* = 6.5, 2.0 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 150.8 (C), 147.9 (C), 140.8 (C), 137.1 (CH), 132.8 (C), 132.0 (q, *J* = 32.2 Hz, C-CF_3), 130.0 (CH), 129.7 (q, *J* = 32.2 Hz, C-CF_3), 126.4 (CH), 124.3 (q, *J* = 272.1 Hz, CF_3), 124.1 (q, *J* = 272.4 Hz, CF_3), 124.0 (CH), 121.9 (CH), 119.8 (q, *J* = 3.9 Hz, CH), 118.5 (q, *J* = 3.8 Hz, CH), 115.9 (q, *J* = 3.8 Hz, CH), 109.6 (q, *J* = 3.9 Hz, CH), 61.4 (C), 39.9 (CH_3), 33.5 (CH_3), 33.4 (CH_2), 18.0 (CH_3), 8.8 (CH_3).

MS, m/z (% relative intensity): 456 ($[M+H]^+$, 100).

HRMS (ESI) calculated for $C_{23}H_{24}F_6N_3$ $[M+H]^+$: 456.1869; found: 456.1869.

4-[(1*E*)-but-1-en-yl]-*N*,1-dimethyl-*N*-phenyl-4-propyl-1,4-dihydroquinazolin-2-amine (3ab)



3ab

Yellow oil, 70 % yield, (Hex/EtOAc/*i*-PrOH 0.90:0.099:0.001, R_f 0.81).

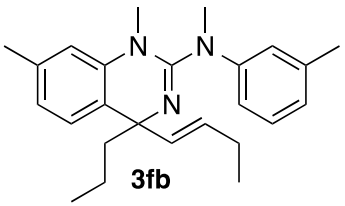
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.2-7.1 (m, 2H), 7.1-7.0 (m, 2H), 6.98 (td, *J* = 7.4, 1.2 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.8-6.7 (m, 2H), 6.59 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.49 (dt, *J* = 15.3, 1.5 Hz, 1H), 5.25 (dt, *J* = 15.3, 6.3 Hz, 1H), 3.27 (s, 3H), 2.79 (s, 3H), 2.0-1.9 (m, 2H), 1.9-1.8 (m, 1H), 1.8-1.7 (s, 1H), 1.4-1.3 (m, 2H), 0.9-0.8 (m, 6H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 151.4 (C), 147.9 (C), 140.6 (C), 135.8 (CH), 130.1 (C), 129.6 (CH), 129.4 (2xCH), 127.0 (CH), 125.5 (CH), 122.6 (CH), 122.1 (CH), 120.1 (2xCH), 112.8 (CH), 60.7 (C), 43.2 (CH_2), 40.5 (CH_3), 33.5 (CH_3), 25.5 (CH_2), 17.7 (CH_2), 14.8 (CH_3), 14.0 (CH_3).

MS, m/z (% relative intensity): 348 (M, 93), 304 (100).

HRMS (CI) calculated for $C_{23}H_{30}N_3$: 348.2440; found: 348.2447.

4-[(1*E*)-But-1-en-1-yl]-*N*,1,7-trimethyl-*N*-(3-methylphenyl)-4-propyl-1,4-dihydroquinazolin-2-amine (3fb)



3fb

Yellow oil, 64 % yield, (Hex/EtOAc/*i*-PrOH 0.90:0.099:0.001, R_f 0.68).

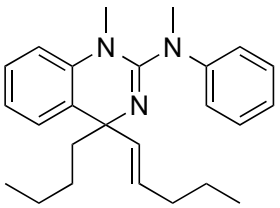
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.1-7.0 (m, 2H), 6.88 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.72 (s, 1H). 6.62 (d, *J* = 8.7 Hz, 1H), 6.49 (s, 1H), 5.58 (d, *J* = 15.3 Hz, 1H), 5.34 (dt, *J* = 15.3, 6.3 Hz, 1H), 3.33 (s, 3H), 2.88 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H), 2.1-2.0 (m, 2H), 2.0-1.9 (m, 1H), 1.9-1.8 (m, 1H), 1.5-1.4 (m, 2H), 1.0-0.9 (m, 6H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 151.4 (C), 147.9 (C), 140.6 (C), 139.1 (C), 136.6 (C), 136.1 (CH), 129.3 (CH), 129.1 (CH), 127.2 (C), 125.4 (CH), 123.2 (CH), 122.8 (CH), 120.6 (CH), 117.0 (CH), 113.5 (CH), 60.5 (C), 43.5 (CH_2), 40.4 (CH_3), 33.5 (CH_3), 25.5 (CH_2), 21.7 (CH_3), 21.5 (CH_3), 17.7 (CH_2), 14.8 (CH_3), 14.0 (CH_3).

MS, m/z (% relative intensity): 376 ($[M+H]^+$, 100), 318 (23), 158 (25).

HRMS (ESI) calculated for $C_{25}H_{34}N_3$ $[M+H]^+$: 376.2747; found: 376.2754.

4-Butyl-*N*,1-dimethyl-4-[(1*E*)-pent-1-en-1-yl]-*N*-phenyl-1,4-dihydroquinazolin-2-amine (3ac)



3ac

Pale yellow oil, 72 % yield, (Hex/EtOAc/*i*-PrOH 0.90:0.099:0.001, R_f 0.67).

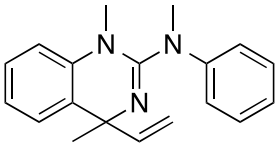
^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.2-7.1 (m, 4H), 7.0-6.9 (m, 1H), 6.9-6.8 (m, 1H), 6.76 (d, *J* = 7.5 Hz, 2H), 6.59 (d, *J* = 7.5 Hz, 1H), 5.48 (d, *J* = 15.4 Hz, 1H), 5.16 (dt, *J* = 15.4, 6.8 Hz, 1H), 3.27 (s, 3H), 2.79 (m, 3H), 1.9-1.8 (m, 3H), 1.8-1.7 (m, 1H), 1.4-1.2 (m, 6H), 0.9-0.7 (m, 6H).

^{13}C NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 151.4 (C), 147.9 (C), 140.7 (C), 136.9 (CH), 130.2 (C), 129.4 (2xCH), 127.8 (CH), 126.9 (CH), 125.5 (CH), 122.6 (CH), 122.0 (CH), 120.0 (2xCH), 112.7 (CH), 60.8 (C), 40.5 (CH_3), 40.4 (CH_2), 34.6 (CH_2), 33.4 (CH_3), 26.7 (CH_2), 23.5 (CH_2), 22.8 (CH_2), 14.4 (CH_3), 13.7 (CH_3).

MS, m/z (% relative intensity): 376 ($[M+H]^+$, 100), 318 (63).

HRMS (CI) calculated for $C_{25}H_{34}N_3$ $[M+H]^+$: 376.2753; found: 376.2755.

***N*,1,4-Trimethyl-*N*-phenyl-4-vinyl-1,4-dihydroquinazolin-2-amine (3ad)**



3ad

Following the general procedure, the reaction was carried out in a sealed tube at 40 °C. Yellow oil, 41 % yield, (Hex/EtOAc/*i*-PrOH 0.90:0.099:0.001, R_f 0.45).

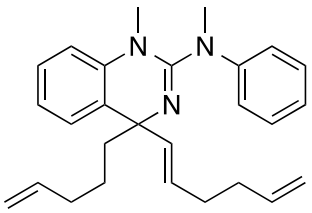
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.2-7.1 (m, 4H), 7.03 (td, *J* = 7.4, 1.2 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 7.8 Hz, 1H), 5.91 (dd, *J* = 17.2, 10.2 Hz, 1H), 4.91 (d, *J* = 10.2 Hz, 1H), 4.70 (d, *J* = 17.2, 1H), 3.31 (s, 3H), 2.80 (s, 3H), 1.62 (s, 3H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 152.5 (C), 147.5 (C), 144.8 (CH), 140.3 (C), 130.7 (C), 129.4 (2xCH), 127.4 (CH), 124.9 (CH), 123.1 (CH), 122.4 (CH), 120.5 (2xCH), 112.9 (CH), 111.1 (CH_2), 58.6 (C), 40.7 (CH_3), 33.6 (CH_3), 27.4 (CH_3).

MS, m/z (% relative intensity): 292 ($[M+H]^+$, 100), 262 (32), 185 (11).

HRMS (ESI) calculated for $C_{19}H_{22}N_3$ $[M+H]^+$: 292.1808; found: 292.1810.

4-[(1*E*)-hexa-1,5-dien-1-yl]-*N*,1-dimethyl-4-pent-4-en-1-yl-*N*-phenyl-1,4-dihydroquinazolin-2-amine (3ae)



3ae

Yellow oil, 48 % yield, (Hex/EtOAc/*i*-PrOH 0.95:0.049:0.001, R_f 0.71).

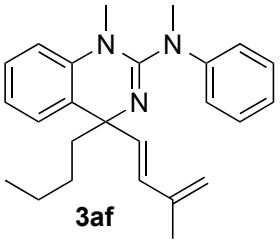
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.3-7.1 (m, 4H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 2H), 6.64 (d, *J* = 7.7 Hz, 1H), 5.9-5.7 (m, 2H), 5.55 (d, *J* = 15.3 Hz, 1H), 5.25 (dt, *J* = 15.3, 6.1 Hz, 1H), 5.0-4.9 (m, 2H), 4.9-4.8 (m, 2H), 3.32 (s, 3H), 2.84 (s, 3H), 2.1-2.0 (m. 6H), 1.96 (ddd, *J* = 13.2, 11.1, 5.4 Hz, 1H), 1.85 (ddd, *J* = 13.2, 11.1, 5.4 Hz, 1H), 1.6-1.5 (m, 2H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 151.5 (C), 147.9 (C), 140.7 (C), 139.5 (CH), 138.6 (CH), 137.1 (CH), 129.9 (C), 129.4 (2xCH), 127.2 (CH), 127.0 (CH), 125.4 (CH), 122.6 (CH), 122.2 (CH), 120.2 (2xCH), 114.6 (CH_2), 114.3 (CH_2), 112.8 (CH), 60.7 (C), 40.6 (CH_3), 40.0 (CH_2), 34.5 (CH_2), 33.9 (CH_2), 33.5 (CH_3), 31.9 (CH_2), 23.8 (CH_2).

MS, m/z (% relative intensity): 400 ($[M+H]^+$, 100), 316 (10).

HRMS (ESI) calculated for $C_{27}H_{34}N_3$ $[M+H]^+$: 400.2747; found: 400.2752.

4-Butyl-*N*,1-dimethyl-4-[(1*E*)-3-methylbuta-1,3-dien-1-yl]-*N*-phenyl-1,4-dihydroquinazolin-2-amine (3af)



3af

Yellow oil, 76 % yield, (Hex/EtOAc/*i*-PrOH 0.90:0.099:0.001, R_f 0.67).

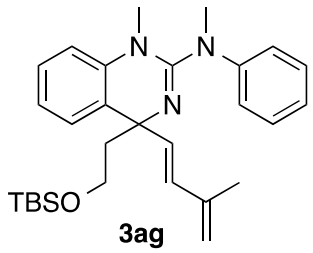
^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.3-7.2 (m, 4H), 7.1-7.0 (m, 1H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.86 (t, *J* = 7.8 Hz, 2H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.01 (d, *J* = 15.7 Hz, 1H), 5.82 (d, *J* = 15.7 Hz, 1H), 4.87 (d, *J* = 6.9 Hz, 2H), 3.36 (s, 3H), 2.87 (s, 3H), 2.1-1.9 (m, 1H), 1.9-1.8 (m, 1H), 1.84 (s, 3H), 1.4-1.3 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 151.5 (C), 147.9 (C), 142.3 (C), 140.6 (C), 137.2 (CH), 130.3 (CH), 129.8 (C), 129.4 (2xCH), 127.1 (CH), 125.6 (CH), 122.7 (CH), 122.2 (CH), 120.2 (2xCH), 115.5 (CH_2), 112.9 (CH), 60.8 (C), 40.9 (CH_2), 40.6 (CH_3), 33.5 (CH_3), 26.7 (CH_2), 23.4 (CH_2), 19.1 (CH_3), 14.4 (CH_3).

MS, m/z (% relative intensity): 374 ($[M+H]^+$, 100), 316 (48).

HRMS (CI) calculated for $C_{25}H_{32}N_3$ $[M+H]^+$: 374.2596; found: 374.2597.

4-(2-{[tert-butyl(dimethyl)silyl]oxy}ethyl)-*N*,1-dimethyl-4-[(1*E*)-3-methylbuta-1,3-dien-1-yl]-*N*-phenyl-1,4-dihydroquinazolin-2-amine (3ag)



3ag

Pale yellow oil, 62 % yield, (Hex/EtOAc/*i*-PrOH 0.90:0.099:0.001, R_f 0.72).

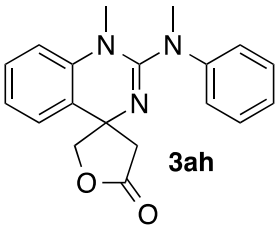
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.3-7.2 (m, 4H), 7.09 (td, *J* = 7.3, 1.2 Hz, 1H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 7.3 Hz, 2H), 6.67 (d, *J* = 6.7 Hz, 1H), 6.05 (d, *J* = 15.7 Hz, 1H), 5.84 (d, *J* = 15.7 Hz, 1H), 4.90 (d, *J* = 8.5 Hz, 2H), 3.9-3.8 (m, 2H), 3.35 (s, 3H), 2.87 (s, 3H), 2.34 (ddd, *J* = 13.0, 9.2, 6.3 Hz, 1H), 2.19 (ddd, *J* = 13.0, 9.2, 6.3 Hz, 1H), 1.86 (s, 3H), 0.90 (s, 9H), 0.06 (s, 6H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 151.6 (C), 148.1 (C), 142.1 (C), 140.4 (C), 136.2 (CH), 130.5 (CH), 129.5 (2xCH), 129.4 (C), 127.3 (CH), 125.4 (CH), 122.8 (CH), 122.7 (CH), 121.1 (2xCH), 115.7 (CH_2), 112.9 (CH), 60.5 (CH_2), 59.6 (C), 43.4 (CH_2), 41.1 (CH_3), 33.6 (CH_3), 29.2 (3xCH_3), 19.0 (CH_3), 18.5 (C), -5.0 (2xCH_3).

MS, m/z (% relative intensity): 476 ($[M+H]^+$, 100).

HRMS (ESI) calculated for $C_{29}H_{42}N_3OSi$ $[M+H]^+$: 476.3092; found: 476.3093.

1'-Methyl-2'-[methyl(phenyl)amino]-1'*H*-spiro[furan-3,4'-quinazolin]-5(4*H*)-one (3ah)



3ah

Following the general procedure, but the reaction residue was purified by flash column chromatography through activated alumina (Brockmann V grade). Brown oil, 68 % yield, (DCM, R_f 0.65).

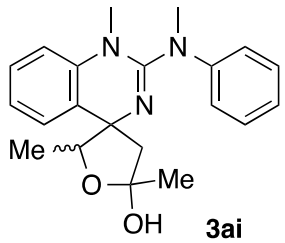
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.33-7.27 (m, 2H), 7.26-7.22 (m, 2H), 7.14 (dt, *J* = 7.5, 1.1 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.83 (dd, *J* = 7.2, 1.3 Hz, 2H), 6.75 (dd, *J* = 8.1, 1.1 Hz, 1H), 4.55 (d, *J* = 8.9 Hz, 1H), 4.46 (d, *J* = 8.9 Hz, 1H), 3.31 (s, 3H), 2.87 (s, 3H), 2.86 (s, 2H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 175.9 (CO), 153.8 (C), 147.1 (C), 140.1 (C), 129.6 (2xCH), 128.6 (CH), 126.9 (C), 123.8 (CH), 123.7 (CH), 123.1 (CH), 121.7 (2xCH), 113.5 (CH), 79.1 (CH_2), 61.2 (C), 43.5 (CH_2), 41.4 (CH_3), 34.0 (CH_3).

MS, m/z (% relative intensity): 322 ($[M+H]^+$, 62), 280 (100).

HRMS (ESI) calculated for $C_{19}H_{20}N_3O_2$ $[M+H]^+$: 322.1550; found: 322.1561.

1',2,5-trimethyl-2'-[methyl(phenyl)amino]-4,5-dihydro-1'*H*-spiro[furan-3,4'-quinazolin]-5-ol (3ai)



3ai

Following the general procedure, but the reaction residue was purified by flash column chromatography through activated alumina (Brockmann V grade). Pale yellow oil as an inseparable diastereoisomer mixture 8.5:1 in 65% yield, (100% DCM, R_f 0.60).

*Spectroscopic data of major product (**3ai**):*

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.3-7.2 (m, 3H), 7.15 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.08 (td, *J* = 7.6, 1.1 Hz, 1H), 7.03 (ddt, *J* = 8.7, 7.3, 1.1 Hz, 1H), 6.83 (d, *J* = 7.3 Hz, 2H), 6.67 (d, *J* = 7.6 Hz, 1H), 4.25 (q, *J* = 6.5 Hz, 1H), 3.25 (s, 3H), 2.81 (s, 3H), 2.67 (d, *J* = 12.1 Hz, 1H), 2.25 (d, *J* = 12.1 Hz, 1H), 1.62 (s, 3H), 0.58 (d, *J* = 6.5 Hz, 3H).

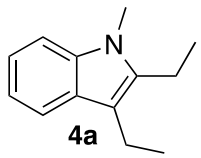
^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 152.6 (C), 147.1 (C), 140.4 (C), 129.6 (2xCH), 128.1 (CH), 125.7 (C), 124.4 (CH), 124.0 (CH), 123.2 (CH), 122.3 (2xCH), 113.1 (CH), 104.6 (C), 85.3 (CH), 68.0 (C), 44.4 (CH_2), 41.6 (CH_3), 33.8 (CH_3), 26.9 (CH_3), 20.3 (CH_3).

MS, m/z (% relative intensity): 352 ($[M+H]^+$, 30), 334 (66), 294 (100).

HRMS (ESI) calculated for $C_{21}H_{26}N_3O_2$ $[M+H]^+$: 352.2020; found: 352.2024.

6. Data for Indoles 4a and 4e

2,3-Diethyl-1-methyl-1*H*-indole (4a)

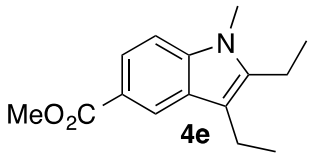


Follow the general procedure using CH_3CN as solvent. Pale yellow oil, 25 % yield, (Hex/EtOAc 0.90:0.10, R_f 0.88).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.55 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.16 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.07 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 3.68 (s, 3H), 2.8-2.7 (m, 4H), 1.3-1.2 (s, 6H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 138.1 (C), 136.8 (C), 127.6 (C), 120.6 (CH), 118.7 (CH), 118.3 (CH), 112.8 (C), 108.7 (CH), 29.5 (CH_3), 17.8 (2xCH_2), 16.4 (CH_3), 15.1 (CH_3).

Methyl 2,3-diethyl-1-methyl-1*H*-indole-5-carboxylate (4e)[S7]



Pale yellow oil, 19 % yield, (Hex/EtOAc/*i*-PrOH 0.85:0.024:0.001, R_f 0.95).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.30 (s, 1H), 7.86 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 1H), 3.93 (s, 3H), 3.70 (s, 3H), 2.77 (p, *J* = 7.7 Hz, 4H), 1.3-1.2 (s, 6H).

^{13}C NMR, DEPT (100 MHz, $CDCl_3$), δ (ppm): 168.7 (CO), 139.5 (C), 139.4 (C), 127.3 (C), 122.3 (CH), 121.3 (CH), 120.6 (C), 114.5 (C), 108.3 (CH), 51.9 (CH_3), 29.6 (CH_3), 17.9 (CH_2), 17.6 (CH_2), 16.5 (CH_3), 14.9 (CH_3).

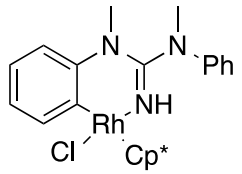
MS, m/z (% relative intensity): 246 ($[M+H]^+$, 13), 202 (100), 172 (88).

HRMS (ESI) calculated for $C_{15}H_{19}NNaO_3$ $[M+Na]^+$: 268.1308; found: 268.1308.

7. Mechanistic experiments

7.1. Experimental Procedure and Spectroscopic Data of Complexes 5 and 6

Preparation of rhodacycle 5a



5a

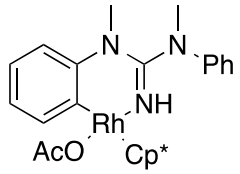
A 25 mL Schlenk tube was charged with $[Cp^*RhCl_2]_2$ (50.0 mg, 0.081 mmol), NaOAc (40.0 mg, 0.486 mmol) and *N*,*N*′-dimethyl-*N*,*N*′-diphenylguanidine (**1a**) (43.0 mg, 0.18 mmol) in methanol (5 ml). The reaction mixture was stirred at room temperature for 2 h and then solvents were removed under vacuum. The residue was purified by flash column chromatography through alumina Brockmann I neutral (DCM) affording complex **5a** as a yellow microcrystalline solid (67.0 mg, 81%). The crystals used in the X-ray study were grown by slow diffusion of layers of diethylether and petroleum ether into a dichloromethane solution of the complex at 273 K.

^{1}H NMR (300 MHz, CD_2Cl_2), δ (ppm): 7.57 (m, 1H), 7.34 (m, 2H), 7.15 (m, 1H), 6.98 (m, 2H), 6.91 (m, 2H), 6.53 (m, 1H), 5.41 (bs, 1H, NH), 3.42, 2.84 (2s, 2x3H, NMe), 1.54 (s, 15H, Cp*).

^{13}C NMR (75 MHz, CD_2Cl_2), δ (ppm): 159.8 (s, C=NH), 155.6 (d, J_{Rh-C} = 31.4 Hz, C-Rh), 145.6, 145.4 (2s, 2xC^1-N), 140.5 (d, J_{Rh-C} = 2.7 Hz, CH), 130.0 (s, 2xCH), 125.0 (s, CH), 124.7 (s, CH), 123.2 (s, 2xCH), 123.1 (s, CH), 115.9 (s, CH), 95.0 (d, J_{Rh-C} = 6.5 Hz, Cp*), 40.3, 38.4 (2s, 2xNMe), 9.2 (s, Cp*).

Anal calculated for $C_{25}H_{31}ClN_3Rh$: C, 58.66, H, 6.10, N, 8.21; found: C, 58.27, H, 6.69, N, 8.00.

Preparation of rhodacycle 5b



5b

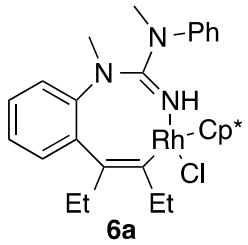
Method A: A mixture of [Cp*Rh(OAc)$_2$] (50.0 mg, 0.140 mmol) and *N*,*N*′-dimethyl-*N*,*N*′-diphenylguanidine (**1a**) (43.0 mg, 0.18 mmol) was stirred at room temperature in dichloromethane (5 mL) for 2 h. The mixture was then filtered through Celite and evaporated to dryness. The reaction crude was washed with petroleum ether (3 x 2 mL) to remove excess of **1a**. Cyclometalated complex **5b** was isolated as a yellow microcrystalline solid (67.0 mg, 90%). Further purification of this compound could be achieved through chromatography on silica with a significant decrease in yield.

Method B: Silver acetate (16.7 mg, 0.100 mmol) was added to a solution of complex **5a** (51.1 mg, 0.100 mmol) in 5 mL of dichloromethane and the mixture was stirred for 30 min. The solution was then filtered *via* cannula. Removal of solvent from the filtrate gave complex **5b** as a pale yellow microcrystalline solid (51 mg, 95%).

^{1}H NMR (300 MHz, CD_2Cl_2), δ (ppm): 7.72 (dd, *J* = 6.6, 2.4 Hz, 1H), 7.43 (bs, 1H, NH), 7.33 (t, *J* = 7.7 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.01-6.88 (m, 4H), 6.54 (dd, *J* = 7.0, 2.2 Hz, 1H), 3.46, 2.79 (2s, 2x3H, NMe), 1.88 (s, 3H, OAc), 1.53 (s, 15H, Cp*).

^{13}C NMR (75 MHz, CD_2Cl_2), δ (ppm): 178.5 (s, OAc), 158.5 (s, C=NH), 157.5 (d, J_{Rh-C} = 32.1 Hz, C-Rh), 146.2, 145.8 (2s, 2xC^1-N), 138.4 (d, J_{Rh-C} = 2.8 Hz, CH), 139.9 (s, 2xCH), 124.7 (s, CH), 124.6 (s, CH), 123.2 (s, CH), 123.0 (s, 2xCH), 116.0 (s, CH), 93.8 (d, J_{Rh-C} = 6.3 Hz, Cp*), 40.4, 37.9 (2s, 2xNMe), 25.7 (s, 3H, OAc), 9.1 (s, Cp*).

Preparation of rhodacycle 6a



6a

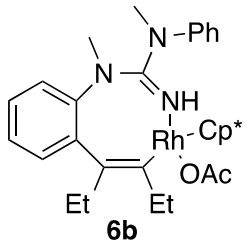
3-Hexyne (14 μL, 0.120 mmol) was added to a solution of complex **5a** (51.1 mg, 0.100 mmol) in methanol (2 mL), upon which the mixture changed instantaneously from orange to dark red. The solvent was then removed under vacuum and the residue was solved in dichloromethane and filtered through Celite. After solvents removal under vacuum, complex **6a** was obtained as a brown microcrystalline solid (55.0 mg, 93%). The crystals used in the X-ray study were grown by slow diffusion of layers of diethylether and petroleum ether into a dichloromethane solution of the complex at 273 K.

^{1}H NMR (300 MHz, CD_3OD), δ (ppm): 7.75 (ddd, J = 8.1, 7.0, 1.4 Hz, 1H), 7.63 (ddd, J = 8.6, 7.0, 1.7 Hz, 1H), 7.51-7.39 (m, 2H), 7.31 (ddd, J = 9.5, 8.0, 1.4 Hz, 2H), 7.22-7.01 (m, 3H), 3.37, 2.53 (2s, 2x3H, NMe), 2.93 (dq, J = 14.8, 7.4 Hz, 1H, CH_2), 2.58 (dq, J = 15.1, 7.5 Hz, 1H, CH_2), 2.44 (dq, J = 15.3, 7.5 Hz, 1H, CH_2), 2.22 (dq, J = 14.8, 7.5 Hz, 1H, CH_2), 1.32 (s, 15H, Cp*), 1.16, 0.92 (2t, J = 7.6, 7.6 Hz, 2x3H, CH_3).

^{13}C NMR (75 MHz, CD_2Cl_2), δ (ppm): 168.4 (bs, C-Rh), 166.8 (s, C=NH), 146.4 (s, C^1-N), 140.9 (bs, C^1-N), 131.9 (bs, C), 131.7 (bs, C), 129.9 (s, CH), 129.8 (s, 2xCH), 128.4 (s, CH), 127.4 (s, CH), 126.5 (s, CH), 124.0 (s, CH), 122.1 (s, 2xCH), 95.3 (d, J_{Rh-C} = 6.6 Hz, Cp*), 40.6, 40.4 (2s, 2xNMe), 33.7 (bs, CH_2), 28.2 (s, CH_2), 15.6, 15.4 (2s, 2xCH_3), 8.8 (s, Cp*).

Anal calculated for $C_{31}H_{41}ClN_3Rh$: C, 62.68, H, 6.96, N, 7.07; found: C, 62.41, H, 7.09, N, 6.79.

Preparation of rhodacycle 6b



6b

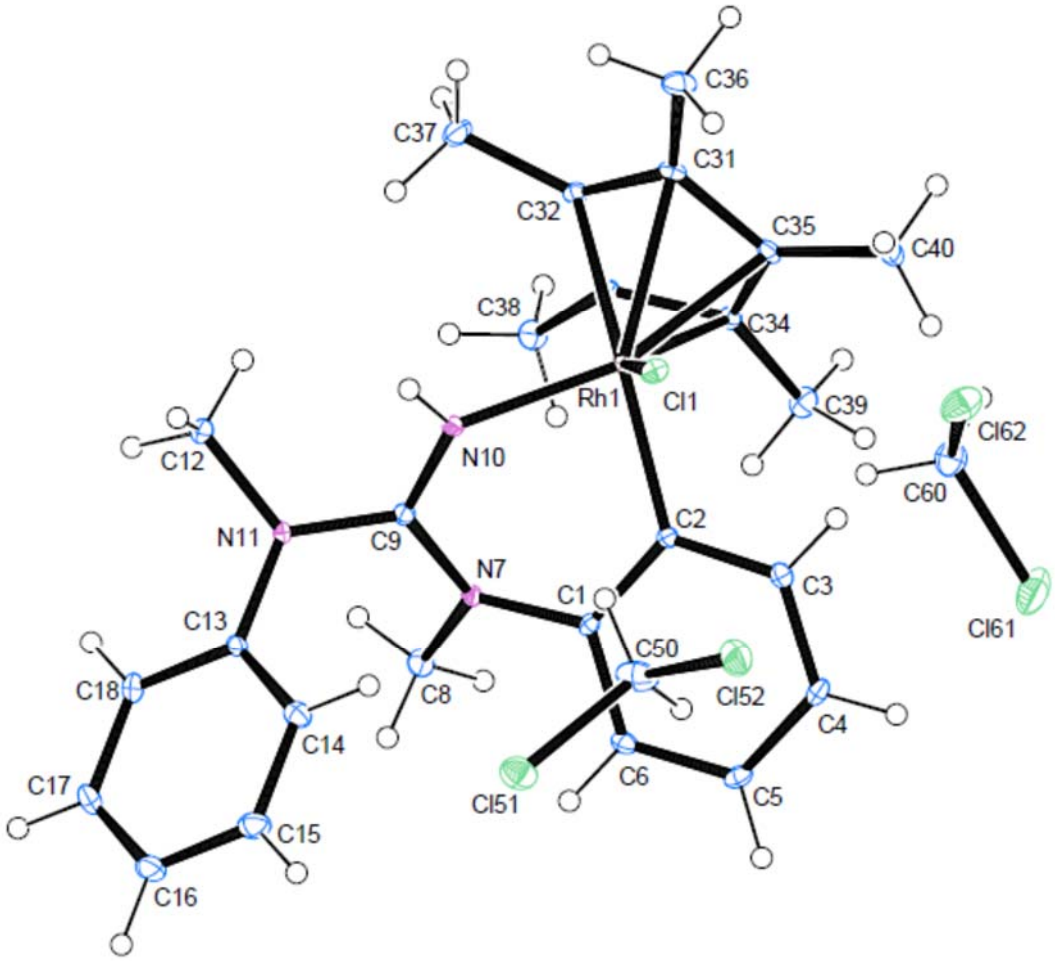
Method A: 3-Hexyne (14 μL, 0.120 mmol) was added to a solution of complex **5b** (53.5 mg, 0.100 mmol) in methanol (2 mL), upon which the color mixture changed instantaneously from orange to brown. Removal of the solvent gave a brown residue containing **6b** as the major component.

Method B: Silver acetate (16.7 mg, 0.100 mmol) was added to a solution of complex **6a** (59.3 mg, 0.100 mmol) in dichloromethane (5 mL) and the mixture was stirred for 15 min. The solution was then filtered with a cannula. Removal of solvent from the filtrate gave complex **6b** as a brown solid (56.3 mg, 91%).

^{1}H NMR (300 MHz, CD_3OD), δ (ppm): 7.75 (ddd, J = 8.2, 7.0, 1.3 Hz, 1H), 7.63 (ddd, J = 8.6, 7.0, 1.7 Hz, 1H), 7.51 – 7.40 (m, 2H), 7.31 (ddd, J = 9.8, 8.1, 1.5 Hz, 2H), 7.17 – 7.05 (m, 3H), 3.37, 2.52 (2s, 2x3H, NMe), 2.93 (dq, J = 14.8, 7.4 Hz, 1H, CH_2), 2.58 (dq, J = 15.1, 7.6 Hz, 1H, CH_2), 2.43 (dq, J = 15.2, 7.8 Hz, 1H, CH_2), 2.22 (dq, J = 14.9, 7.6 Hz, 1H, CH_2), 1.90 (s, 3H, OAc), 1.32 (s, 15H, Cp*), 1.14, 0.92 (2t, J = 7.6, 7.6 Hz, 2x3H, CH_3).

7.2. X-Ray Crystallographic Data

The X-Ray intensity data were collected on a Bruker X8 Apex-II CCD diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 100 K. The software APEX-II was used for collecting frames with omega/phi scans measurement method. The SORTAV software was used for the data reduction, and a multi-scan absorption correction was applied with SADABS2014. SHELXT-2014 program was used to solve the structure and refinement was performed by full-matrix least squares on F^2 with SHELXL2014. During the solution process, complex **5a** was found to crystallize with two molecules of dichloromethane. On the other hand, in complex **6a**, one of the NMe groups and a terminal methyl group of the 3-hexyne chain were found to be disordered in two positions. In addition, the hydrogen atom of nitrogen linked to Rh does not appear clearly in the electron density map. It has been placed in this position and refined given geometric constraints.



X-Ray structure (ellipsoids at 30% probability) of complex **5a**.

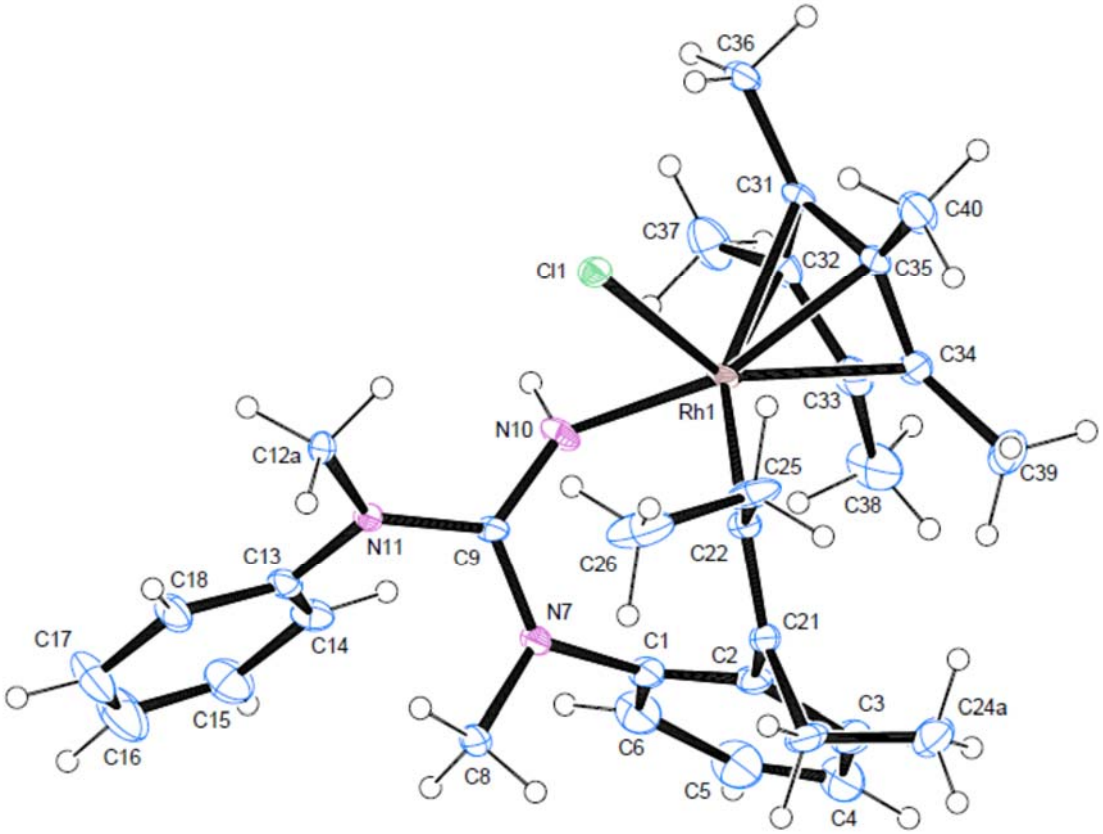
Table 1. Crystal data and structure refinement for complex **5a**.

Identification code	shelx	
Empirical formula	$C_{25}H_{31}ClN_3Rh$, $2(CH_2Cl_2)$	
Formula weight	681.74	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 11.1440(2) Å	α= 80.6465(11)°
	b = 11.7173(2) Å	β= 68.8848(10)°
	c = 13.5405(2) Å	γ = 63.5599(10)°
Volume	1476.85(5) $Å^3$	
Z	2	
Density (calculated)	1.533 Mg/m^3	
Absorption coefficient	1.052 mm^{-1}	
F(000)	696	
Crystal size	0.390 x 0.230 x 0.200 mm^3	
Theta range for data collection	1.612 to 31.611°	
Index ranges	-16<=h<=16, -17<=k<=17, -19<=l<=19	
Reflections collected	58363	
Independent reflections	9859 [R(int) = 0.0583]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9859 / 0 / 336	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0344, wR2 = 0.0646	
R indices (all data)	R1 = 0.0466, wR2 = 0.0686	
Largest diff. peak and hole	0.856 and -0.790 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex **5a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	2888(1)	4124(1)	1427(1)	8(1)
Cl(1)	5453(1)	3150(1)	778(1)	13(1)
C(1)	2353(2)	4750(2)	3664(1)	10(1)
C(2)	2942(2)	3777(2)	2924(1)	10(1)
C(3)	3536(2)	2526(2)	3284(1)	12(1)
C(4)	3547(2)	2240(2)	4319(2)	14(1)
C(5)	2976(2)	3220(2)	5029(1)	14(1)
C(6)	2389(2)	4470(2)	4701(1)	13(1)
N(7)	1682(2)	6061(1)	3398(1)	10(1)
C(8)	471(2)	6915(2)	4221(2)	15(1)
C(9)	2225(2)	6530(2)	2432(1)	11(1)
N(10)	2912(2)	5823(2)	1599(1)	11(1)
N(11)	1944(2)	7811(1)	2428(1)	13(1)
C(12)	1809(2)	8574(2)	1475(2)	16(1)
C(13)	2315(2)	8232(2)	3158(1)	13(1)
C(14)	3435(2)	7389(2)	3510(2)	16(1)
C(15)	3787(2)	7791(2)	4232(2)	21(1)
C(16)	3052(3)	9024(2)	4600(2)	26(1)
C(17)	1947(3)	9866(2)	4245(2)	28(1)
C(18)	1567(2)	9474(2)	3530(2)	22(1)
C(31)	2655(2)	3575(2)	7(1)	13(1)
C(32)	1615(2)	4809(2)	308(1)	12(1)
C(33)	782(2)	4767(2)	1415(1)	11(1)
C(34)	1265(2)	3455(2)	1749(1)	12(1)
C(35)	2474(2)	2724(2)	912(1)	12(1)
C(36)	3792(2)	3162(2)	-1038(2)	20(1)
C(37)	1386(2)	5992(2)	-352(2)	18(1)
C(38)	-486(2)	5863(2)	2026(2)	17(1)
C(39)	604(2)	2962(2)	2786(2)	17(1)
C(40)	3324(2)	1310(2)	894(2)	19(1)
C(50)	6329(2)	3279(2)	2996(2)	26(1)
Cl(51)	6609(1)	4430(1)	3475(1)	26(1)

Cl(52)	7908(1)	1892(1)	2560(1)	32(1)
C(60)	6856(2)	-70(2)	1664(2)	24(1)
Cl(61)	6860(1)	-798(1)	2912(1)	43(1)
Cl(62)	8573(1)	-653(1)	727(1)	30(1)



X-Ray structure (ellipsoids at 30% probability) of complex **6a**.

Table 3. Crystal data and structure refinement for complex **6a**.

Identification code	shelx	
Empirical formula	$C_{31}H_{41}ClN_3Rh$	
Formula weight	594.03	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 15.6033(8) Å	α= 90°
	b = 11.0447(5) Å	β= 99.361(3)°
	c = 16.5835(9) Å	γ = 90°
Volume	2819.8(2) $Å^3$	
Z	4	
Density (calculated)	1.399 Mg/m^3	

Absorption coefficient	0.725 mm^{-1}
F(000)	1240
Crystal size	0.500 x 0.040 x 0.030 mm^3
Theta range for data collection	1.323 to 26.413°
Index ranges	-19<=h<=19, -13<=k<=13, -20<=l<=20
Reflections collected	39042
Independent reflections	5770 [R(int) = 0.1368]
Completeness to theta = 25.242°	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5770 / 366 / 356
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0726, wR2 = 0.1123
R indices (all data)	R1 = 0.1292, wR2 = 0.1294
Largest diff. peak and hole	0.821 and -1.175 e.$Å^{-3}$

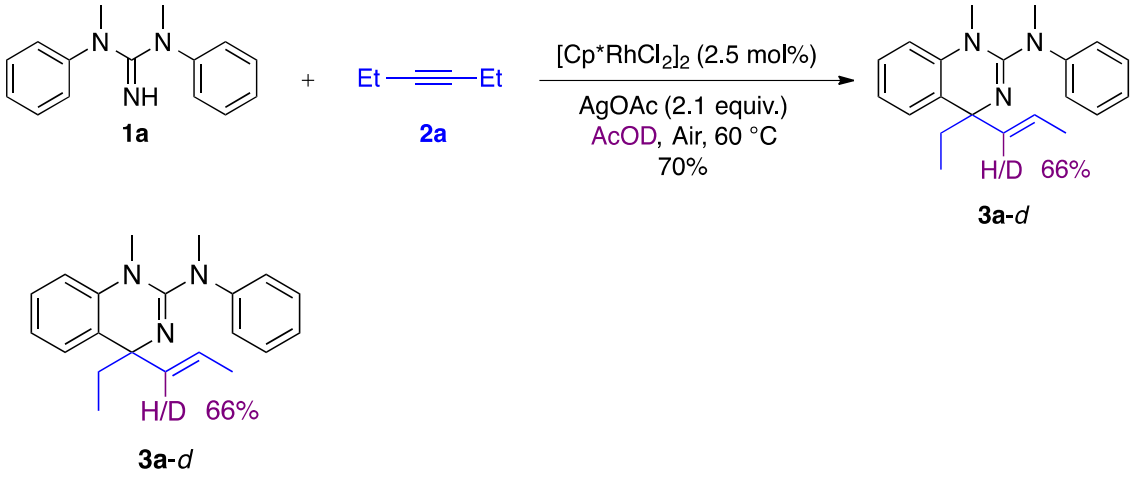
Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex **6a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

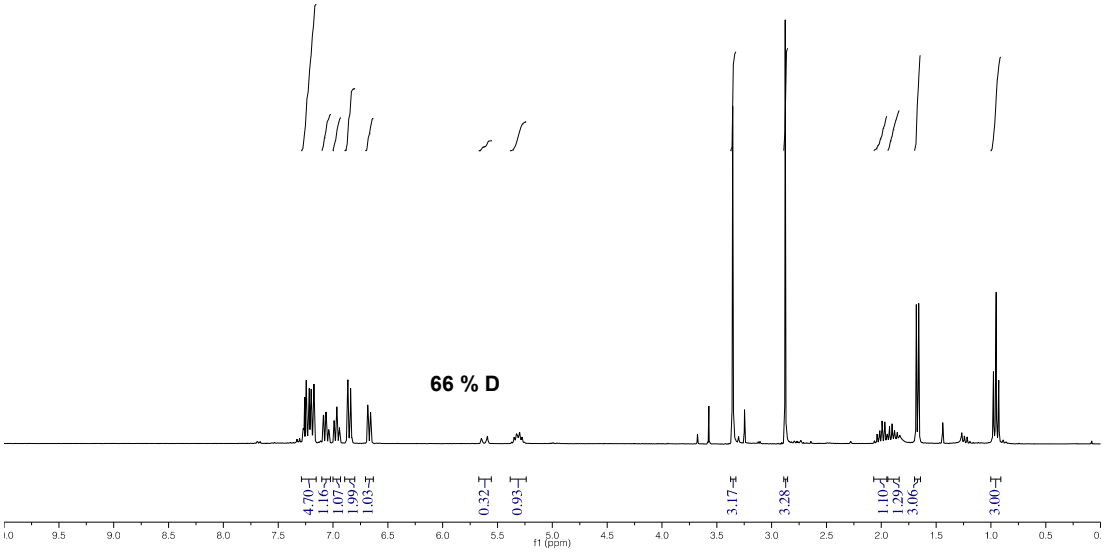
	x	y	z	U(eq)
Rh(1)	2073(1)	2418(1)	3904(1)	21(1)
Cl(1)	3080(1)	1227(1)	4888(1)	24(1)
C(1)	2801(4)	4983(6)	2797(4)	34(2)
C(2)	2225(4)	5391(6)	3297(5)	35(2)
C(3)	1537(5)	6128(6)	2920(5)	47(2)
C(4)	1418(5)	6391(7)	2098(6)	56(2)
C(5)	1970(5)	5919(8)	1617(5)	57(2)
C(6)	2674(5)	5226(7)	1964(5)	45(2)
N(7)	3620(3)	4452(4)	3149(3)	24(1)
C(8)	4309(4)	5322(5)	3424(4)	25(2)
C(9)	3745(4)	3253(5)	3212(4)	20(1)
N(10)	3108(3)	2489(5)	3248(3)	26(1)
N(11)	4597(3)	2842(4)	3262(3)	21(1)
C(12A)	5022(11)	2159(18)	3995(12)	24(5)
C(12B)	4760(13)	1657(18)	3611(16)	36(6)
C(13)	5122(4)	3215(5)	2678(4)	23(1)

C(14)	4739(5)	3465(6)	1876(4)	29(2)
C(15)	5265(5)	3826(7)	1315(5)	46(2)
C(16)	6134(6)	3917(9)	1536(6)	64(3)
C(17)	6512(5)	3613(8)	2315(5)	54(2)
C(18)	6017(4)	3261(6)	2896(4)	32(2)
C(21)	2351(4)	5149(6)	4192(4)	30(1)
C(22)	2383(4)	4021(5)	4519(4)	24(1)
C(23)	2401(5)	6299(6)	4715(5)	42(2)
C(24A)	1575(9)	6625(12)	4897(8)	38(4)
C(24B)	3151(9)	7140(11)	4799(9)	30(4)
C(25)	2552(5)	3880(6)	5437(4)	37(2)
C(26)	3506(5)	4006(7)	5777(5)	66(3)
C(31)	1164(4)	797(6)	3725(4)	28(1)
C(32)	1164(4)	1346(7)	2966(4)	36(2)
C(33)	898(4)	2601(7)	3025(4)	39(2)
C(34)	700(4)	2790(6)	3836(5)	35(2)
C(35)	923(4)	1702(6)	4286(4)	28(1)
C(36)	1409(4)	-479(6)	3964(4)	33(2)
C(37)	1394(5)	814(7)	2208(4)	48(2)
C(38)	686(5)	3426(8)	2310(5)	57(2)
C(39)	303(5)	3893(7)	4134(5)	51(2)
C(40)	806(5)	1462(6)	5142(4)	42(2)

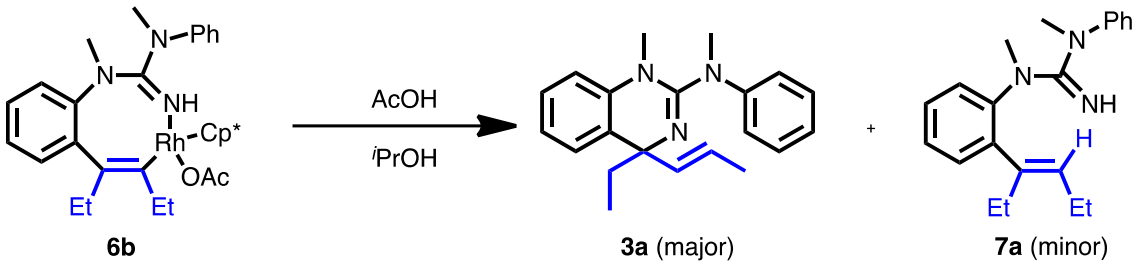
7.3. Deuterium Experiments

Guanidine **1a** and 3-hexyne (**2a**) were subjected to the standard cyclization reaction conditions employing AcOD as solvent. After complete consumption of guanidine, solvents were evaporated to dryness followed by flash column chromatography isolating the 1,4-dihydroquinazolin-2-amine **3a**-*d* in 70% yield (66% D)**.**

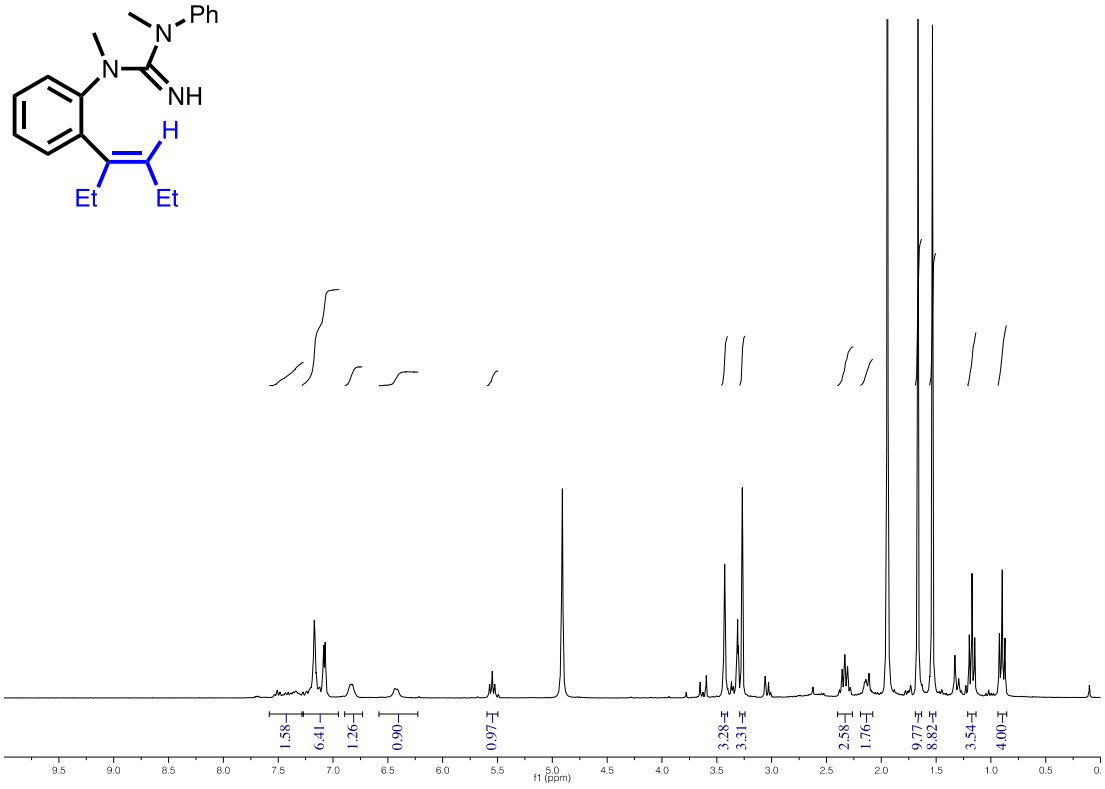




To a solution of rhodacycle **6b** in ^{i}PrOH was added acetic acid at room temperature. After 1 hour, the reaction was monitored by ^{1}H NMR affording quinazoline **3a** (major compound) and styrene derivative **7a** (minor compound).



6b **3a** (major) **7a** (minor)



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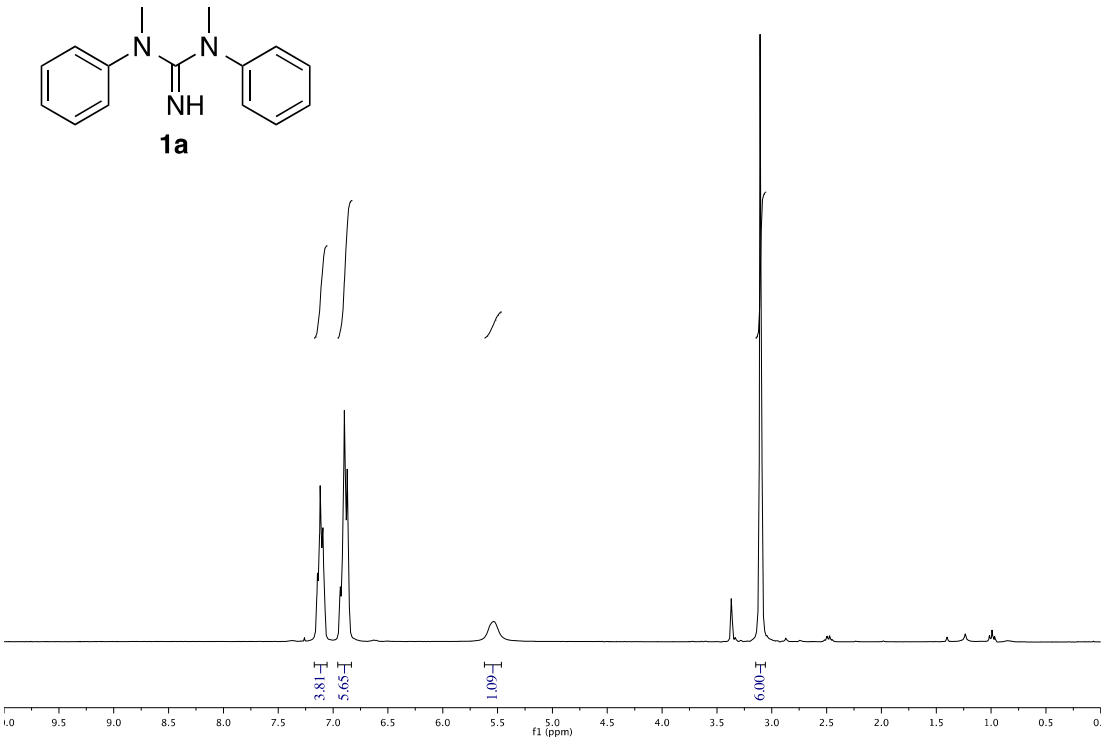
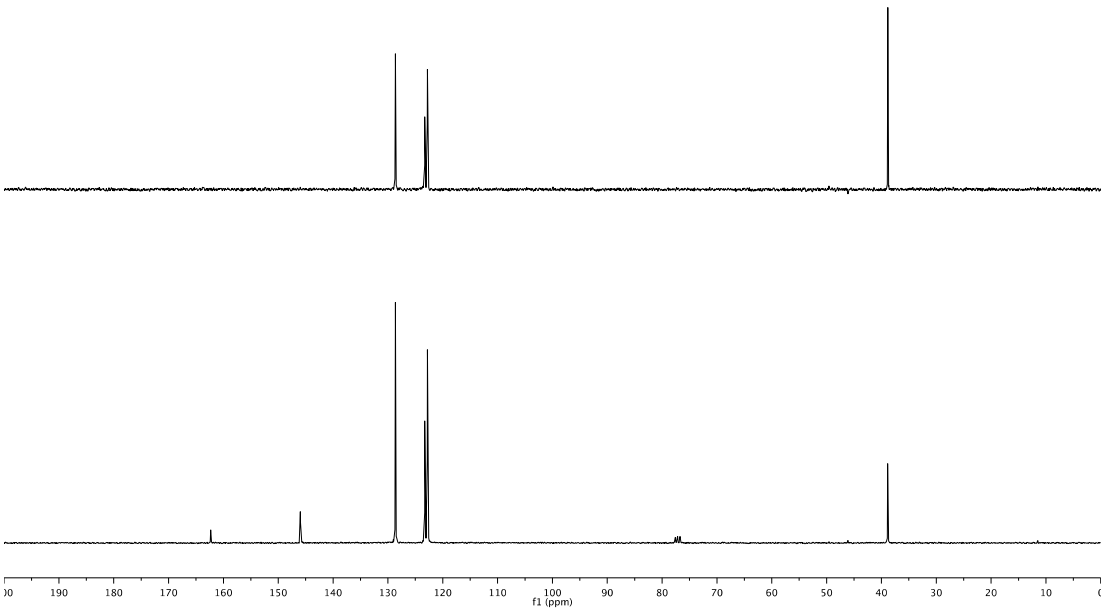
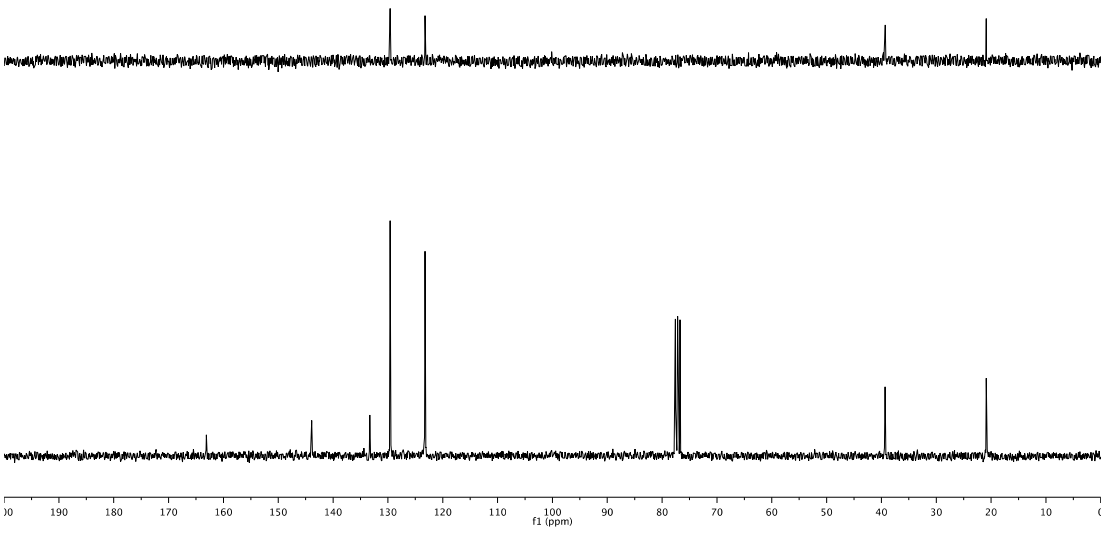
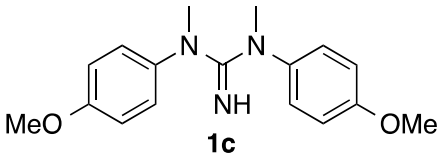
8. Spectra



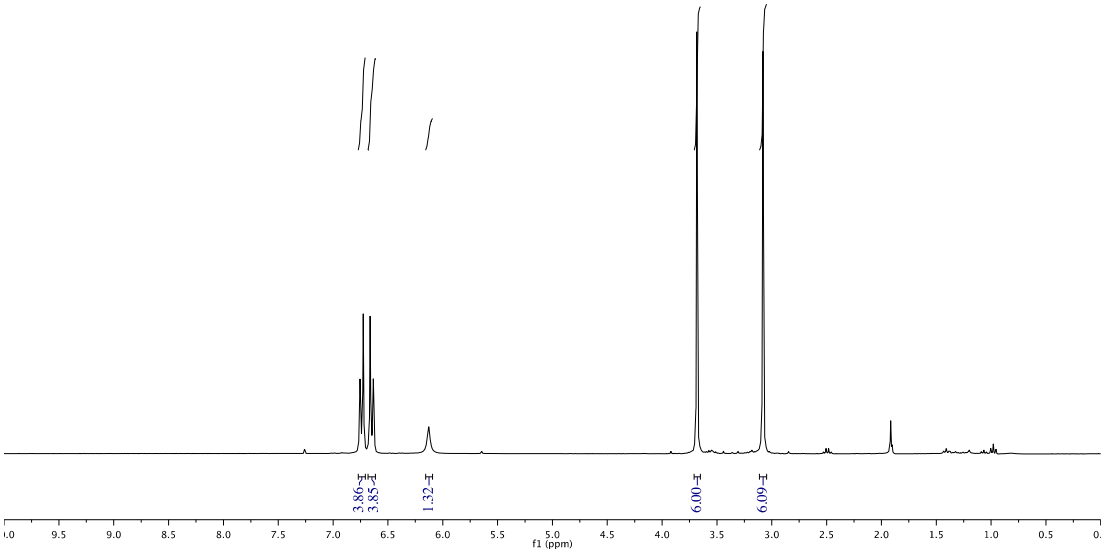


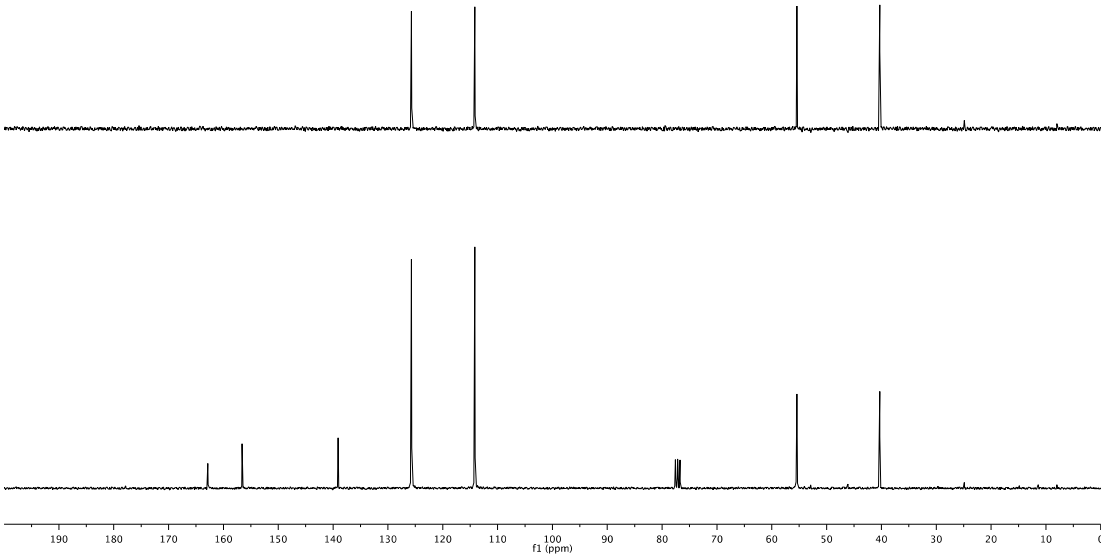

N
N
NH
1b
3.89
3.92
6.11
6.00
f1 (ppm)

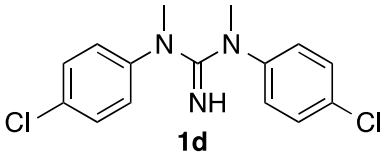

f1 (ppm)



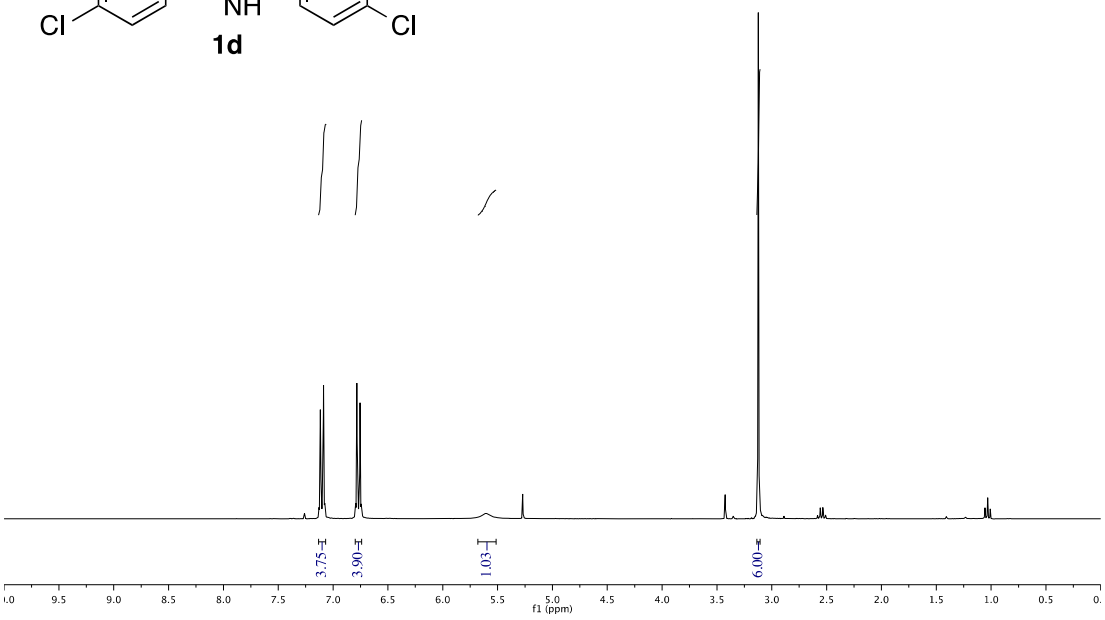
1c

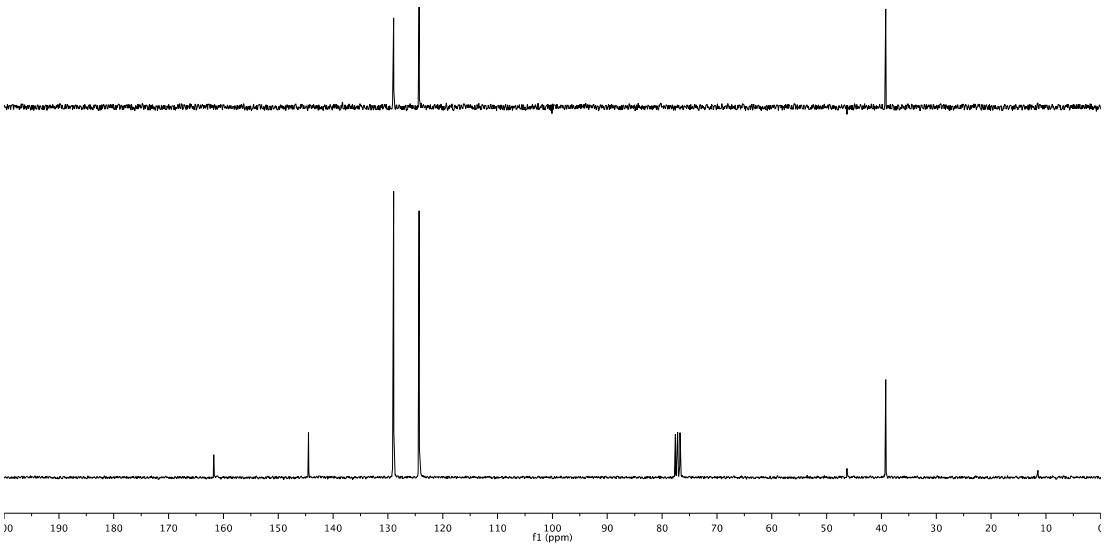


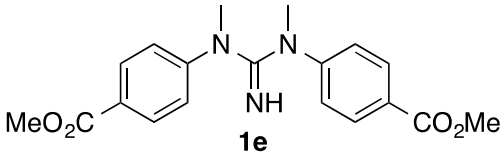




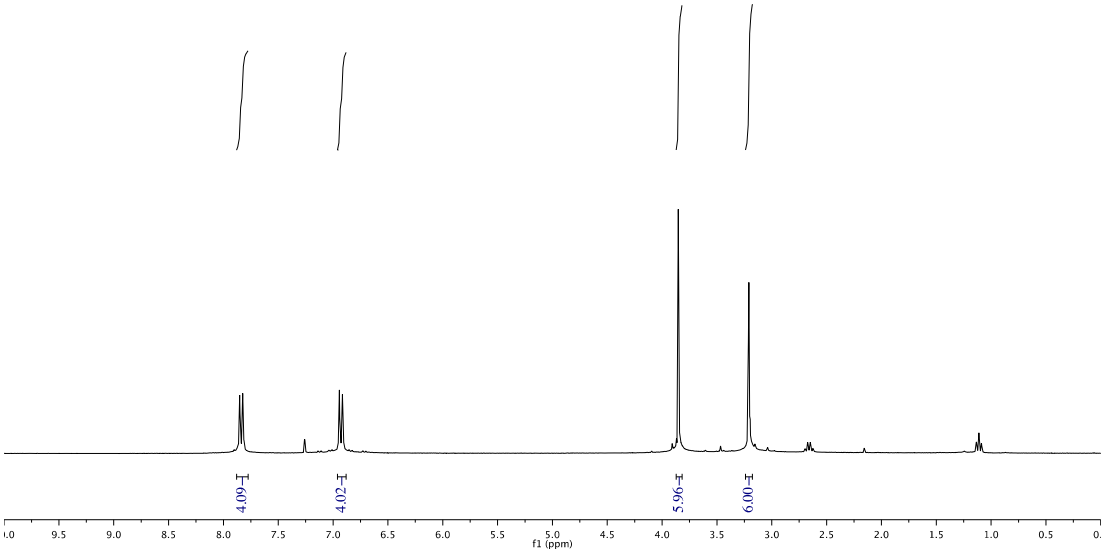
1d

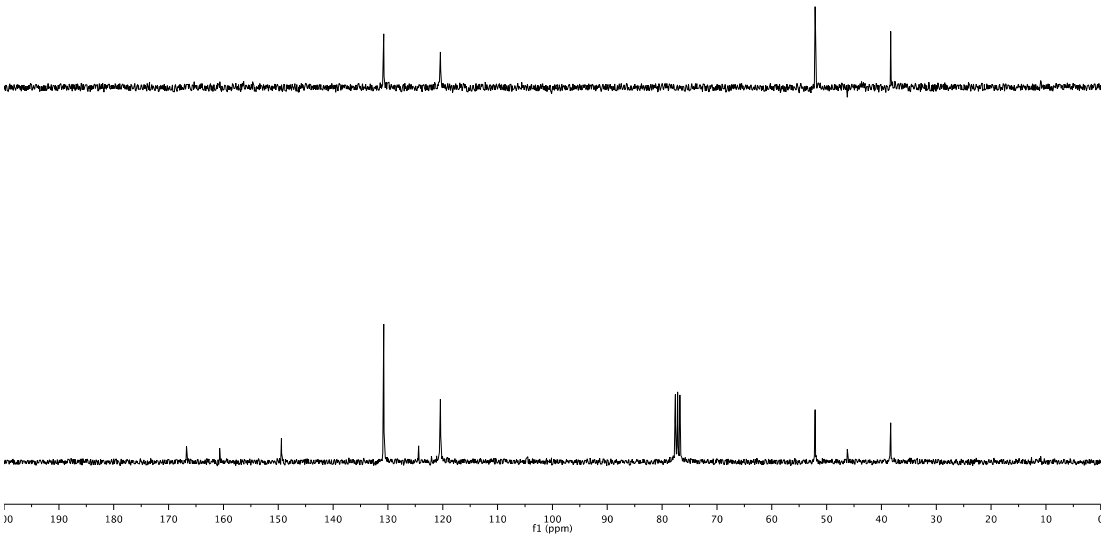


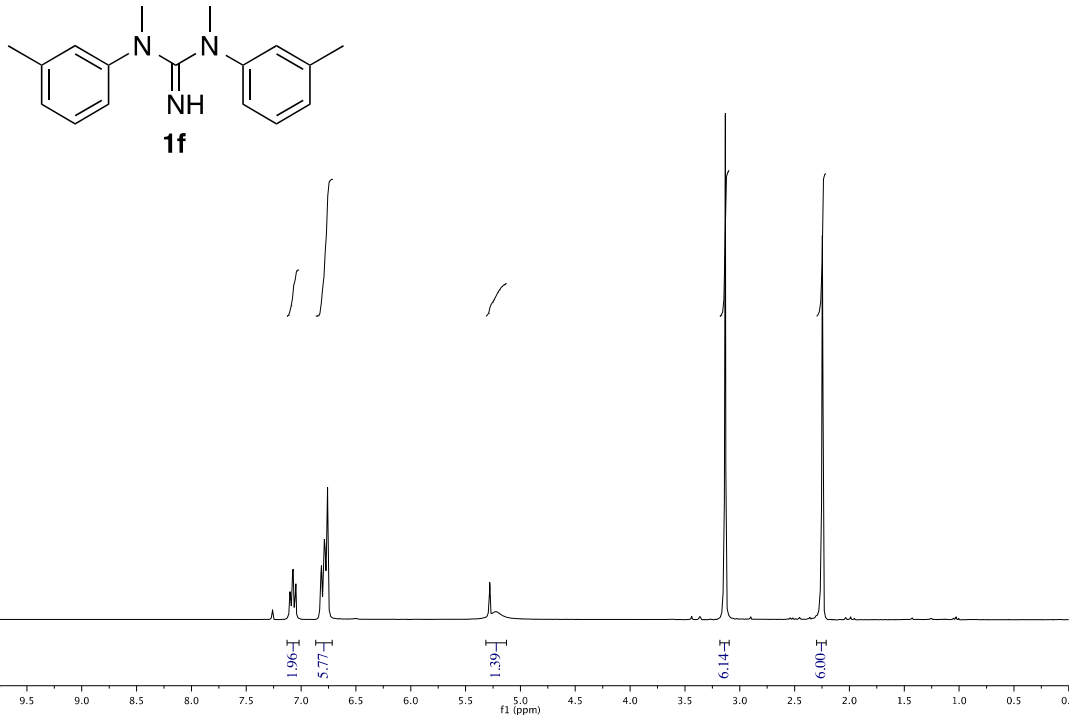


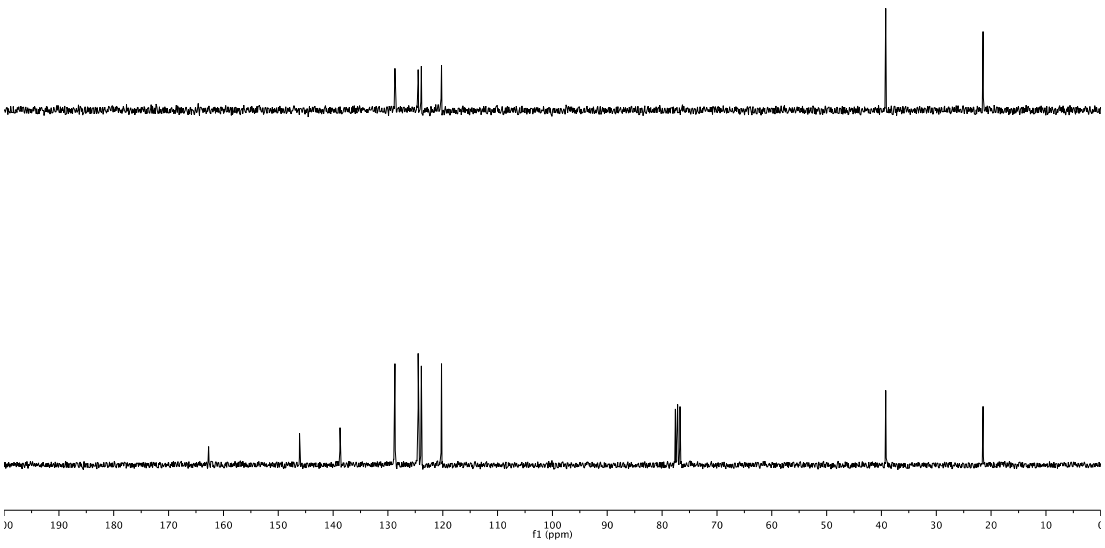


1e






N
N
NH
1f
1.96
5.77
1.39
6.14
6.00
f1 (ppm)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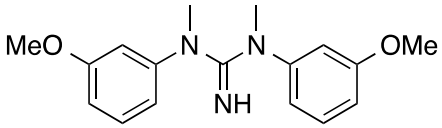
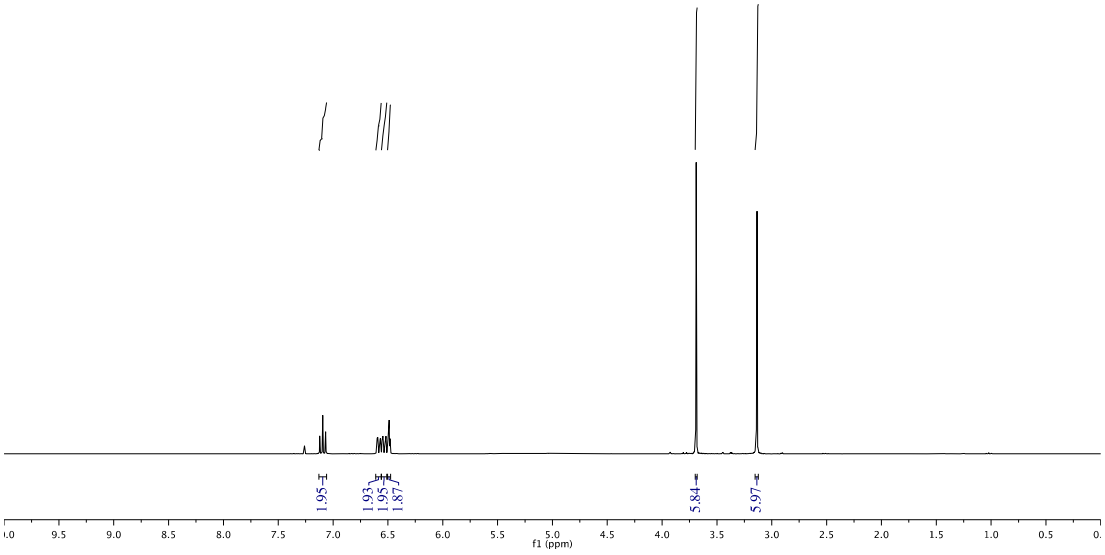
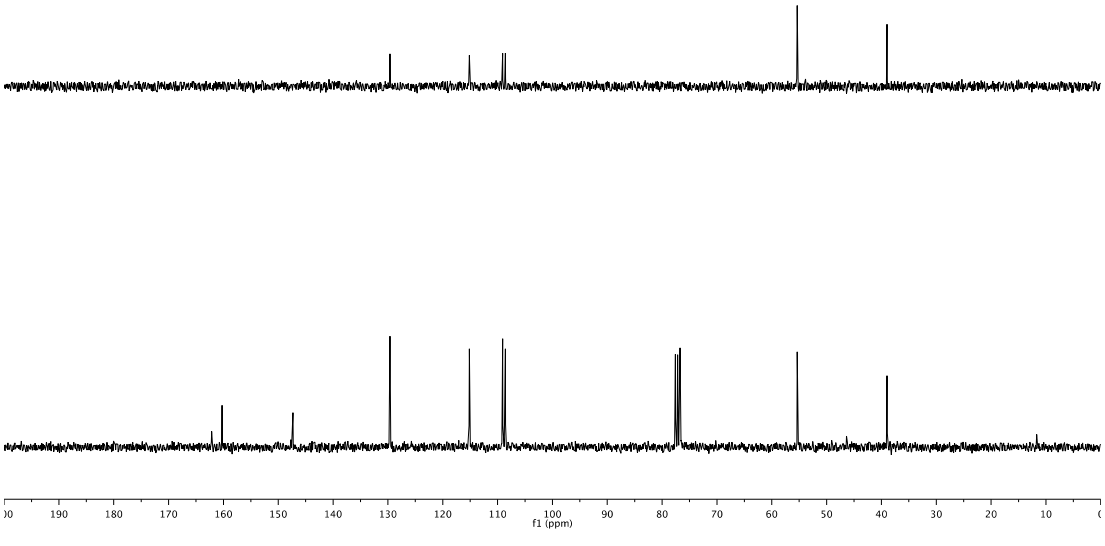
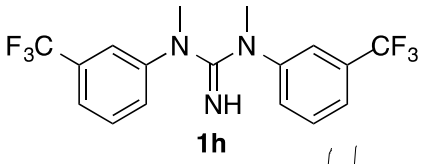


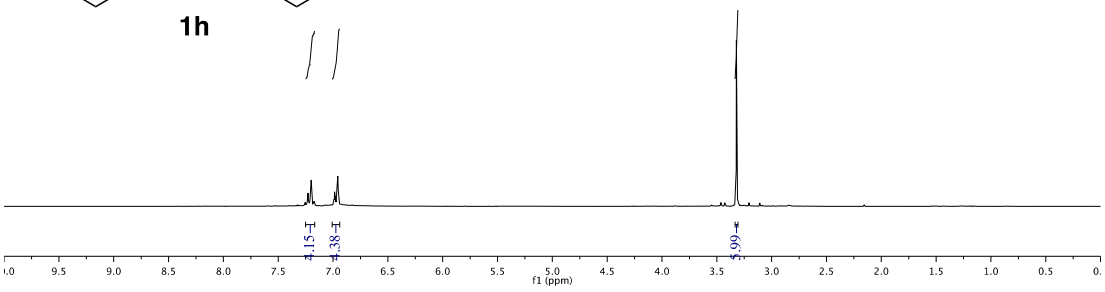
1g

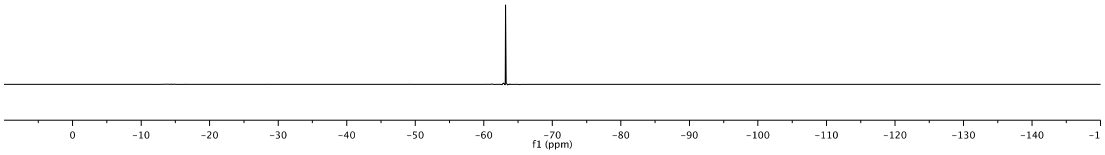


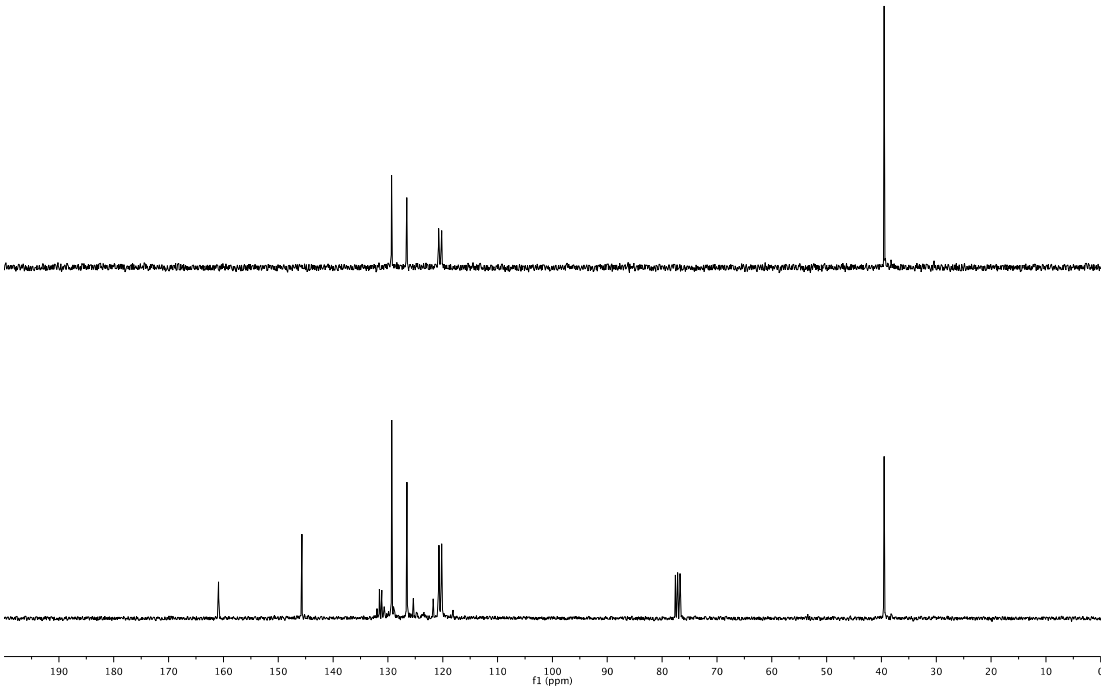


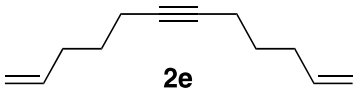


1h

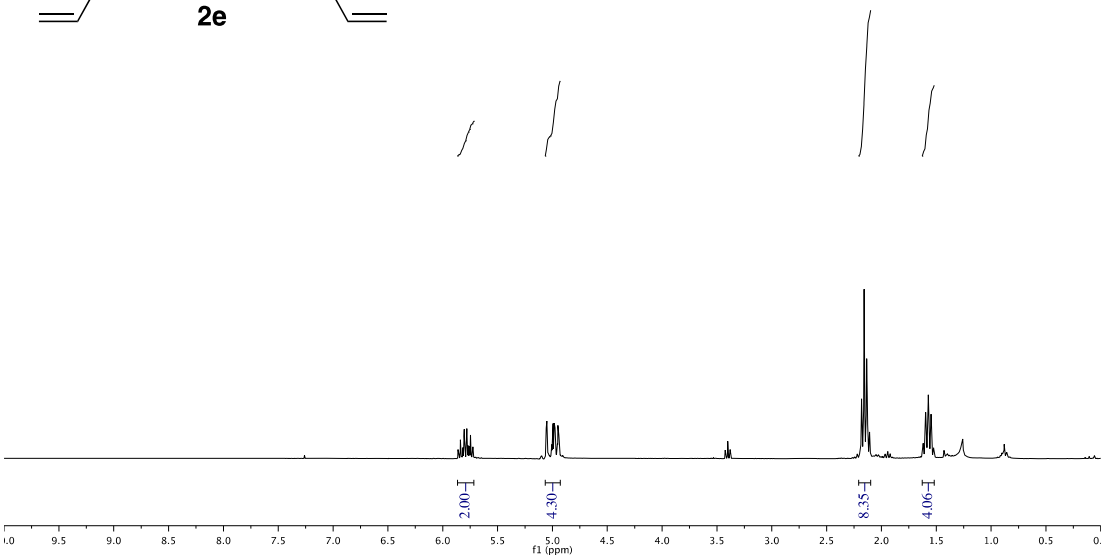


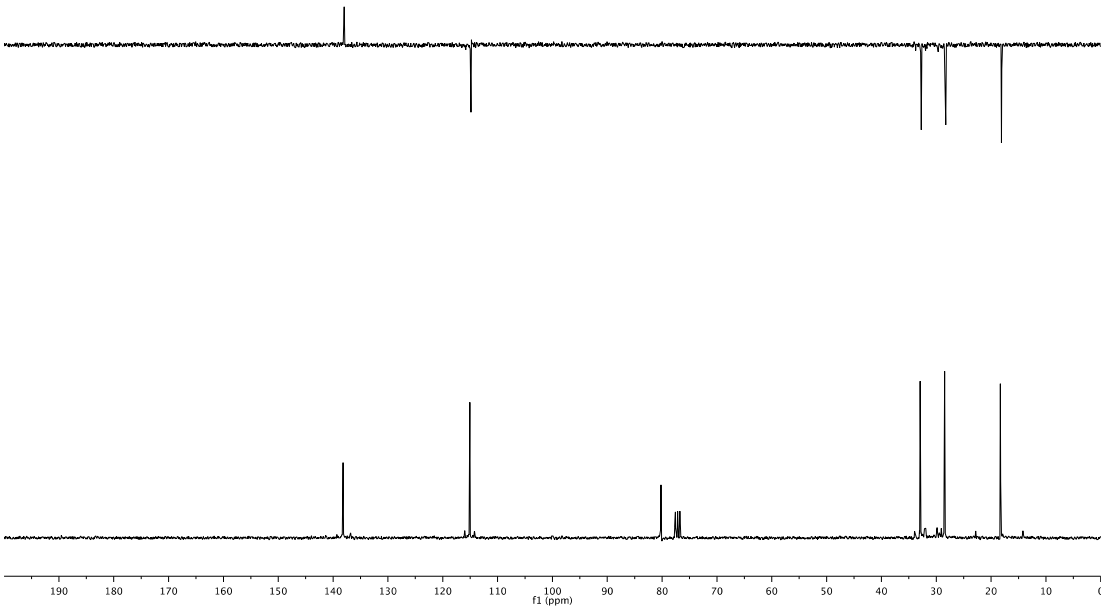


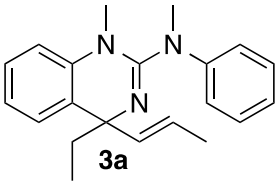




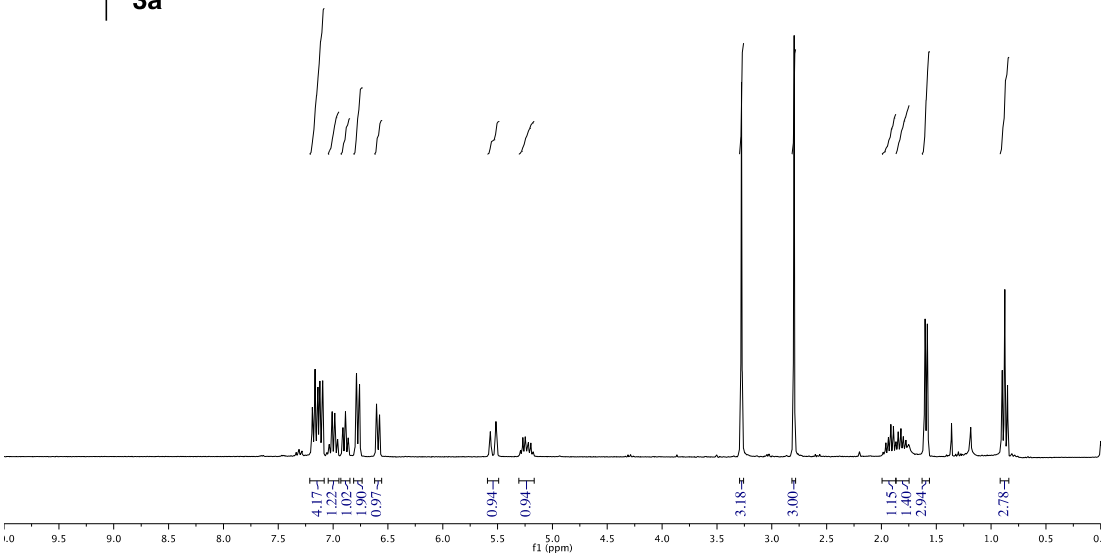
2e

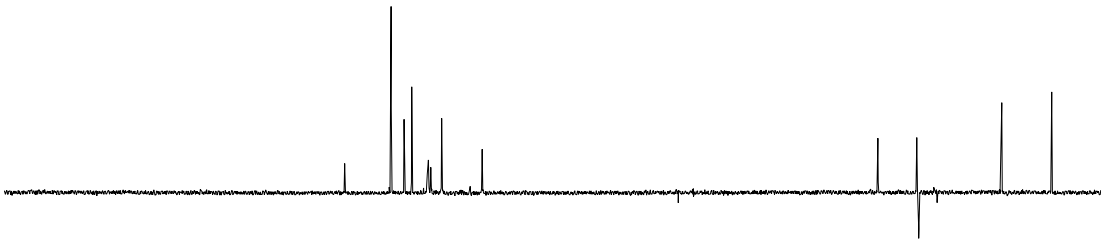


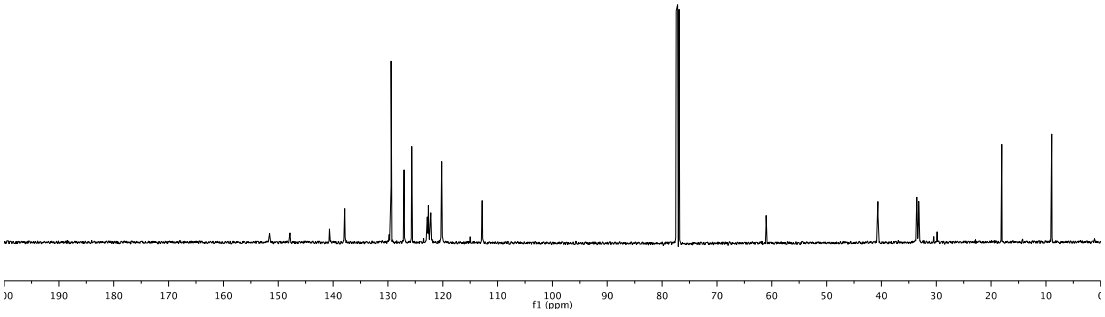


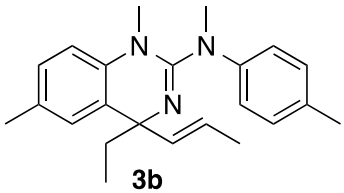

N
N
N

3a

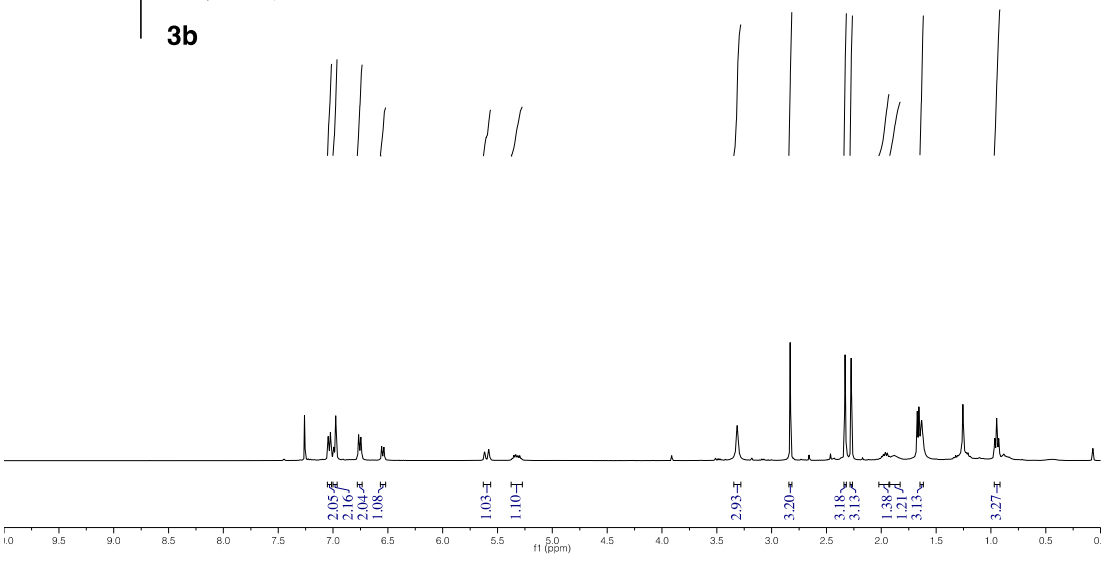

4.17
1.22
1.02
1.90
0.97
0.94
0.94
3.18
3.00
1.15
1.40
2.94
2.78
f1 (ppm)

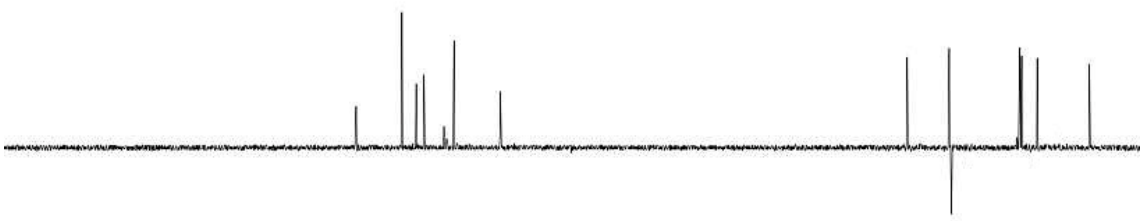


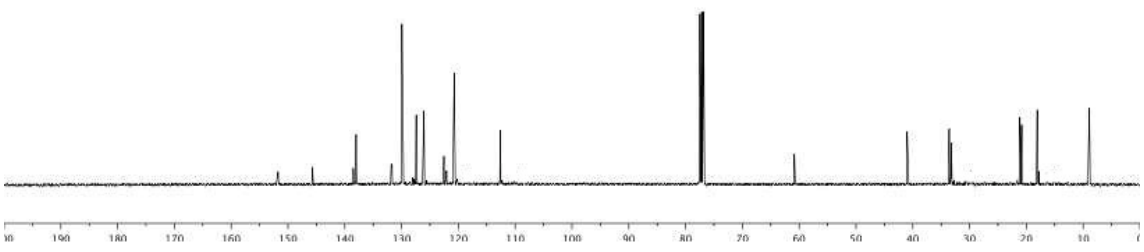

f1 (ppm)

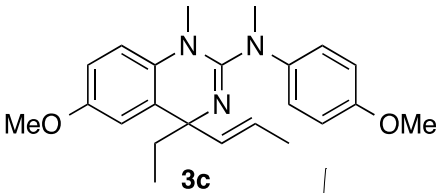


3b

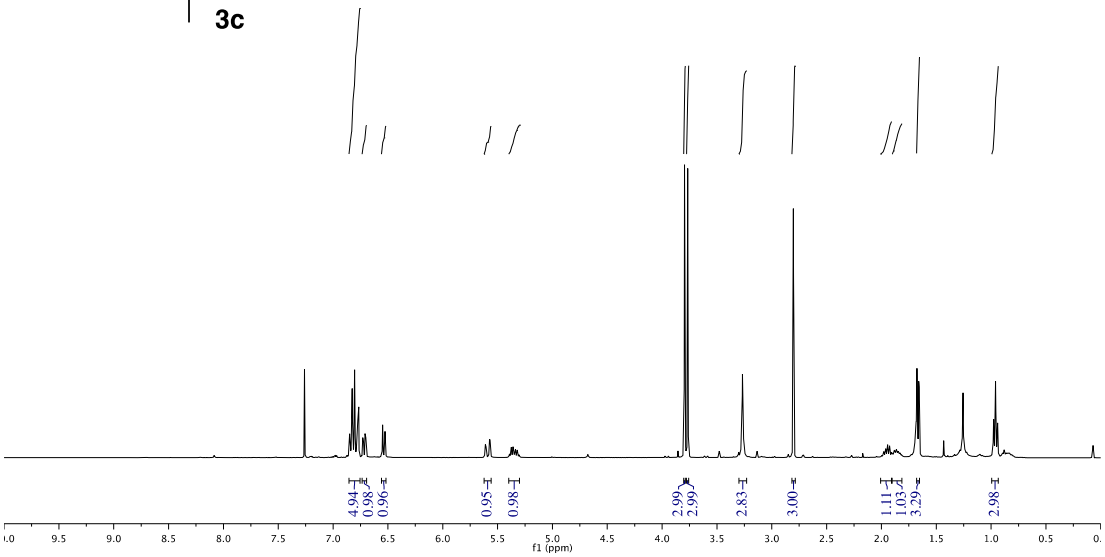


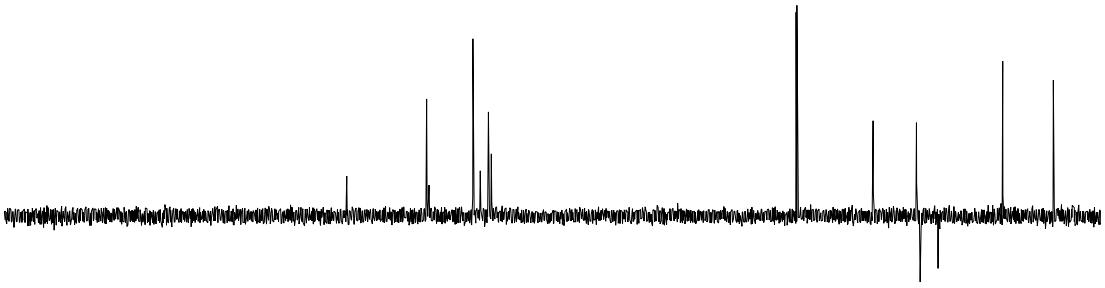


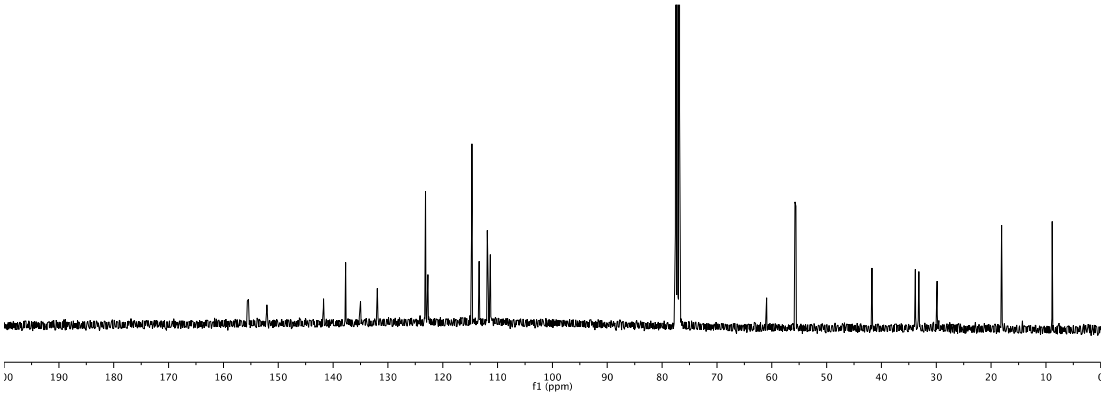


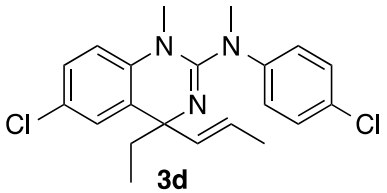

MeO
OMe
N
N
N

3c

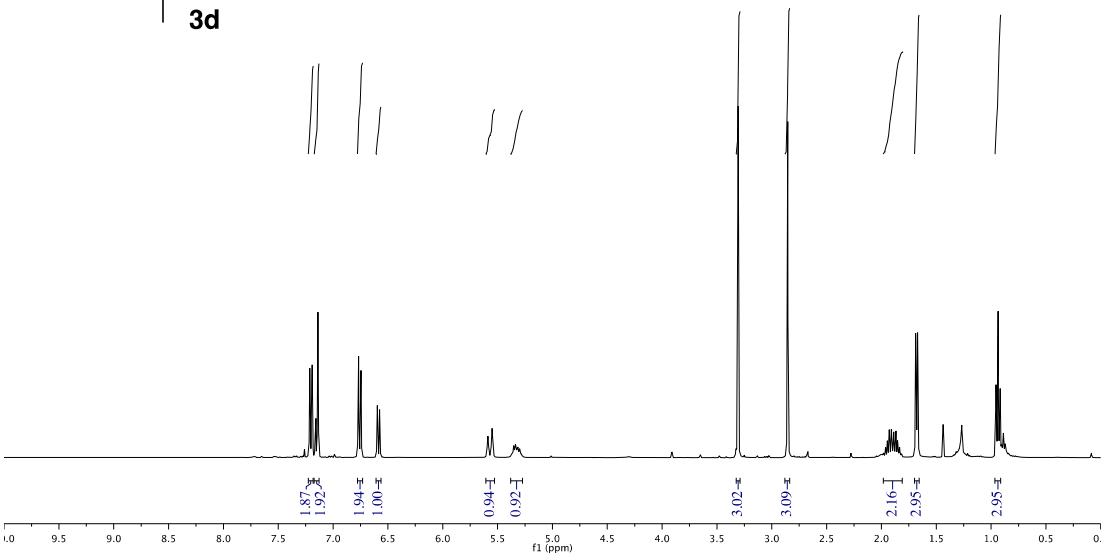

4.94
0.98
0.96
0.95
0.98
2.99
2.99
2.83
3.00
1.11
1.03
3.29
2.98
f1 (ppm)




f1 (ppm)


N
N
N
Cl
Cl

3d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1.94
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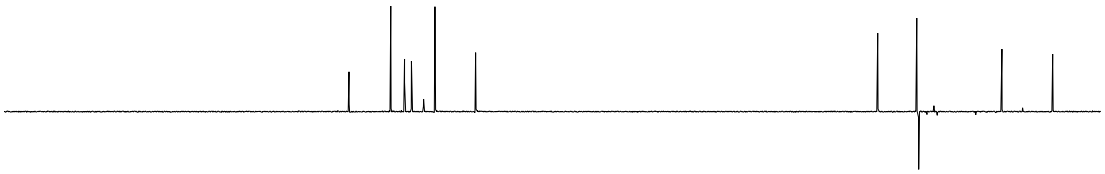
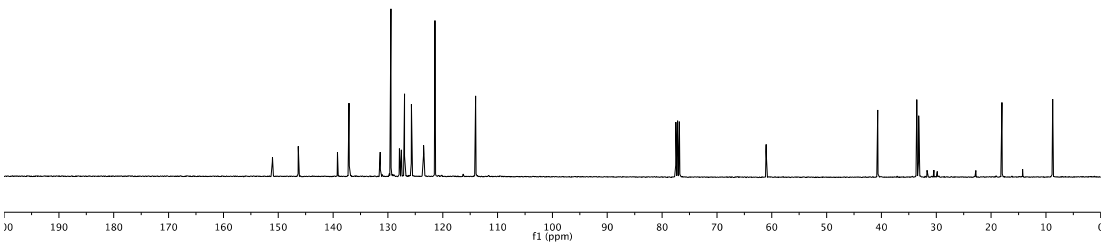
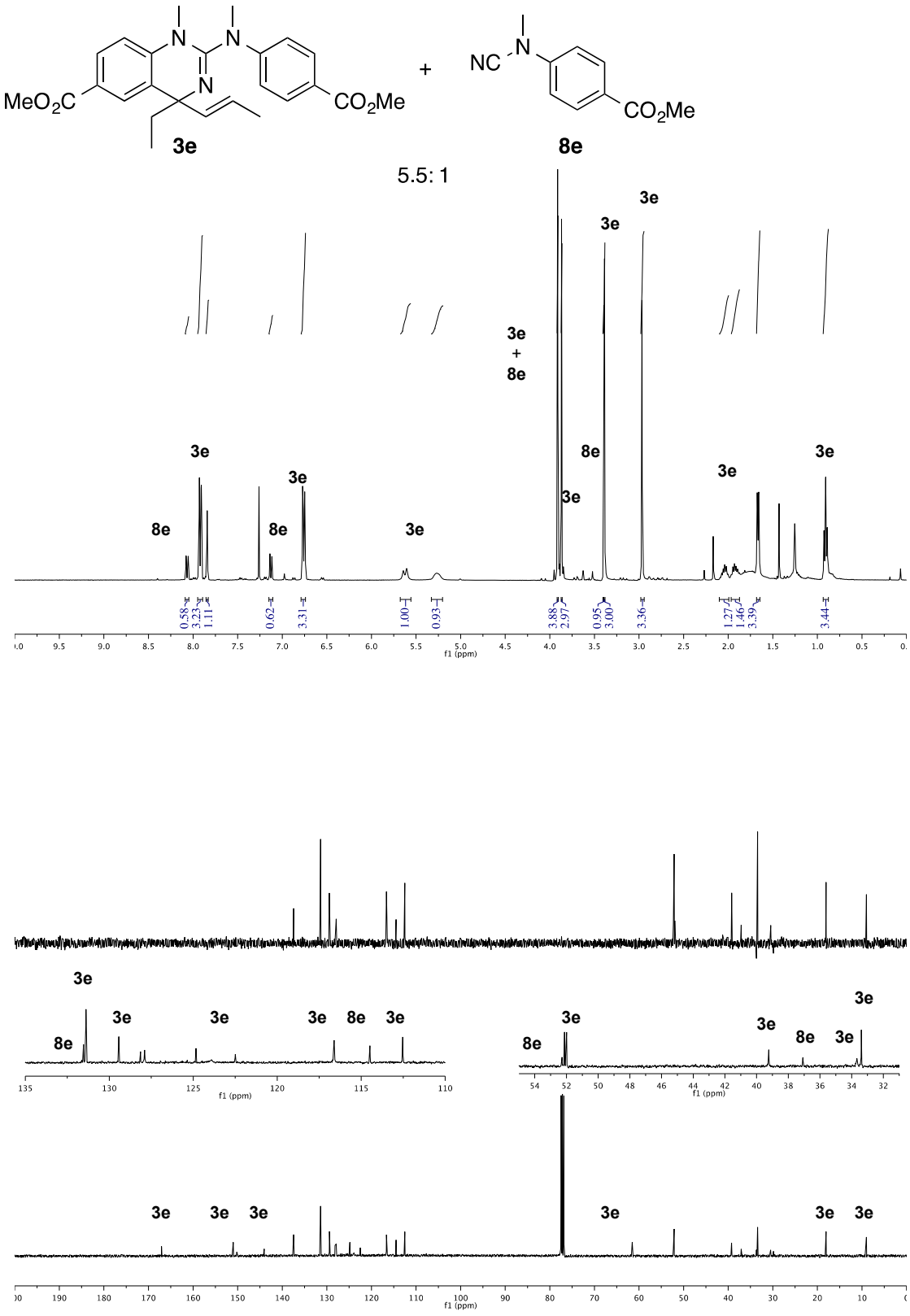
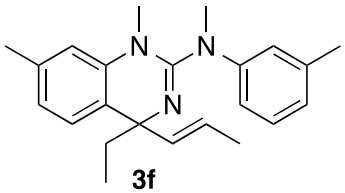
0.94
0.92
3.02
3.09
2.16
2.95
2.95
f1 (ppm)

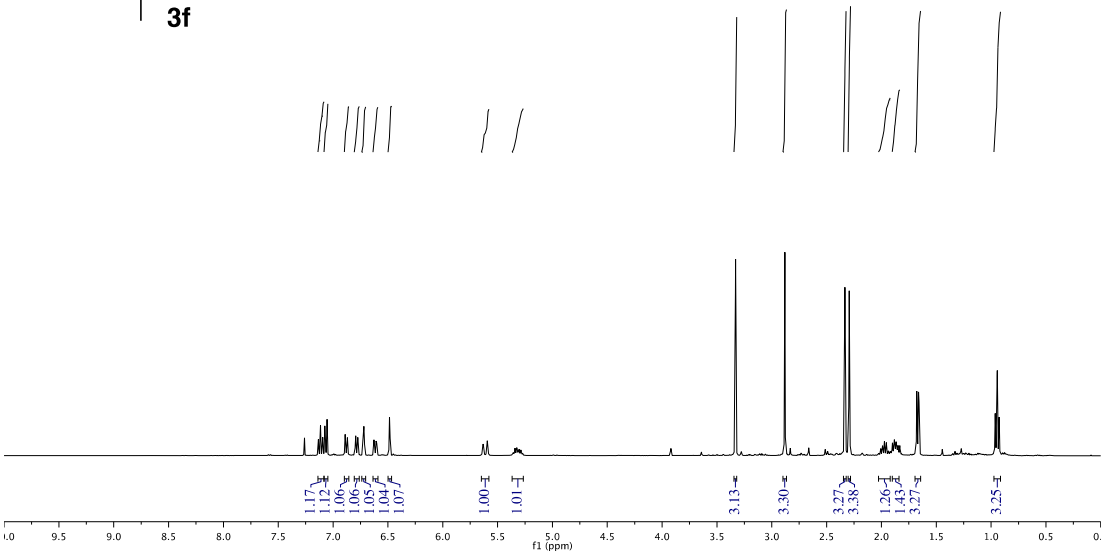


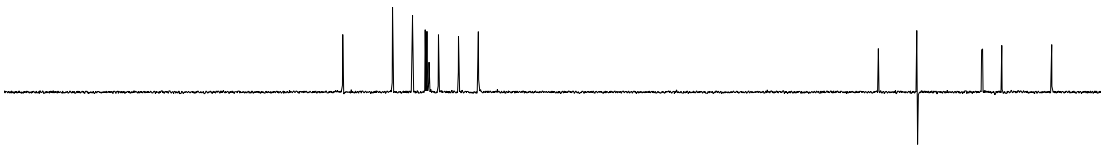

f1 (ppm)

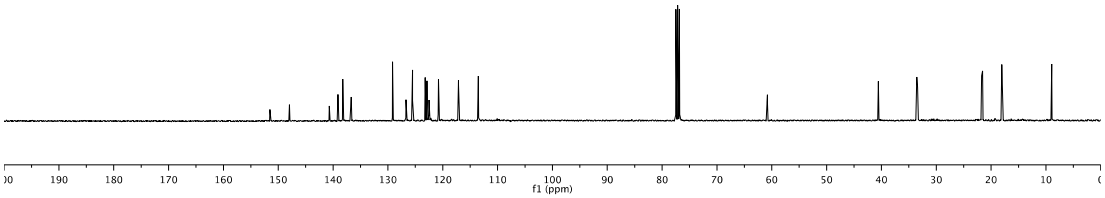

MeO2C
CO2Me
3e
+
NC
N
CO2Me
8e
5.5: 1
3e
8e
f1 (ppm)

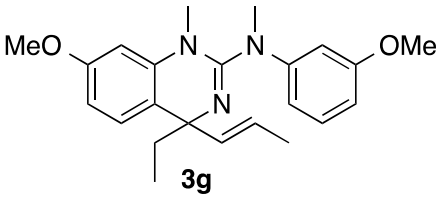


3f

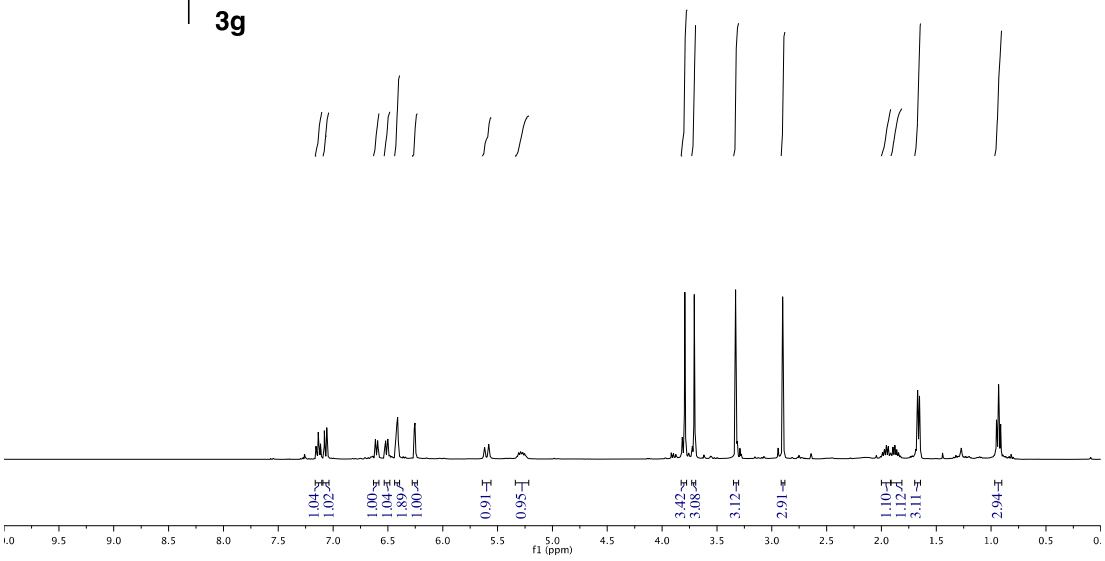

1.17
1.12
1.06
1.06
1.05
1.04
1.07
1.00
1.01
3.13
3.30
3.27
3.38
1.26
1.43
3.27
3.25
f1 (ppm)

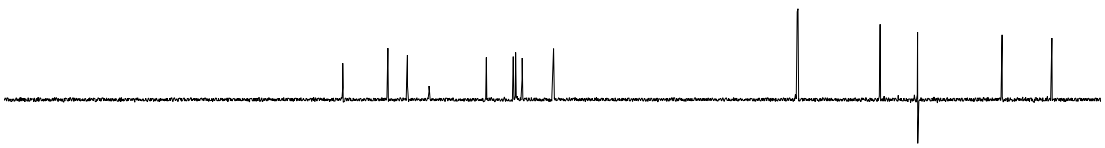


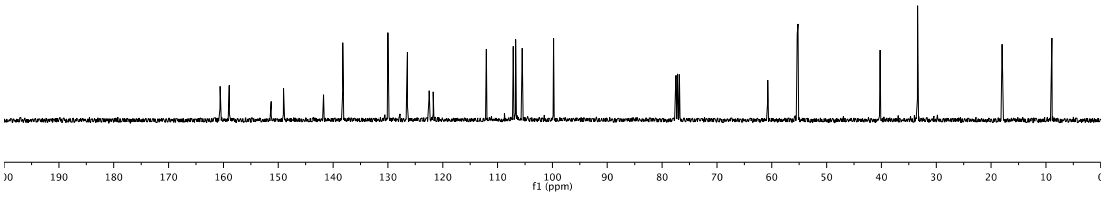

f1 (ppm)

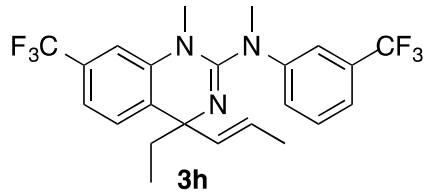

MeO
N
N
OMe
N

3g

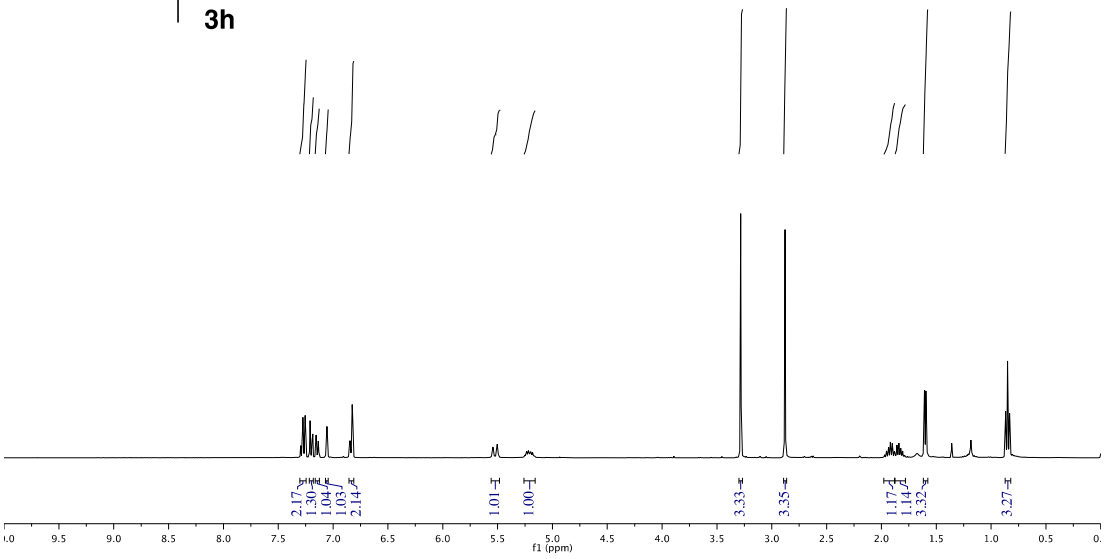

1.04
1.02
1.00
1.04
1.89
1.00
0.91
0.95
3.42
3.08
3.12
2.91
1.10
1.12
3.11
2.94
f1 (ppm)

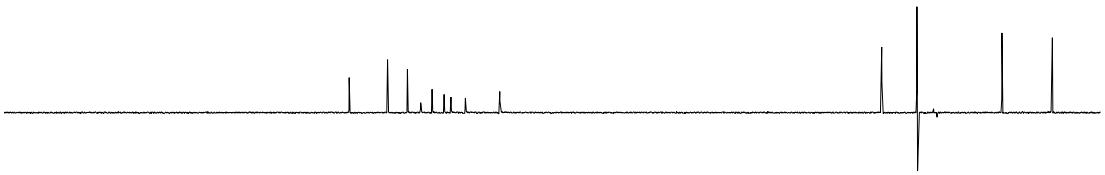


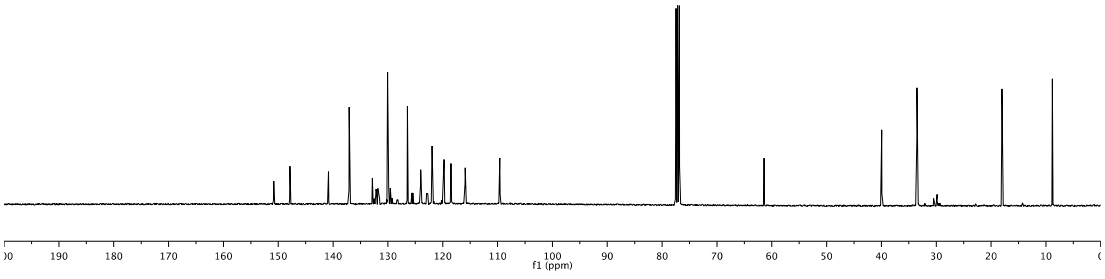

f1 (ppm)

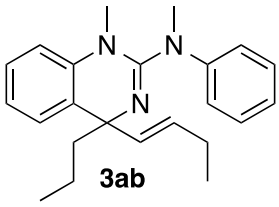

F3C
N
N
CF3
N

3h

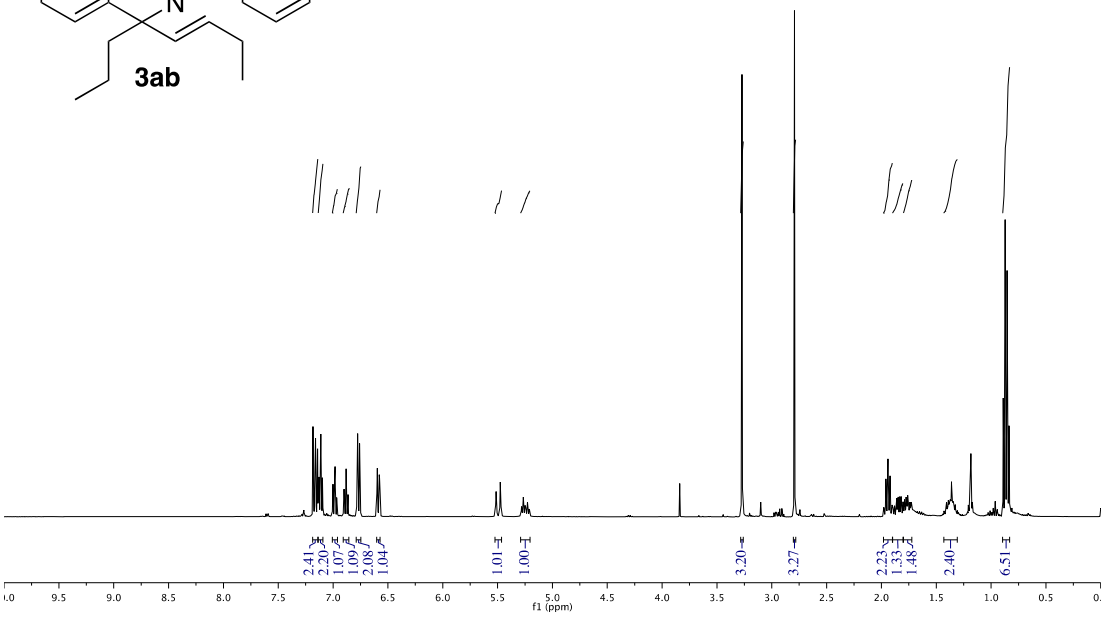

2.17
1.30
1.04
1.03
2.14
1.01
1.00
3.33
3.35
1.17
1.14
3.32
3.27
f1 (ppm)

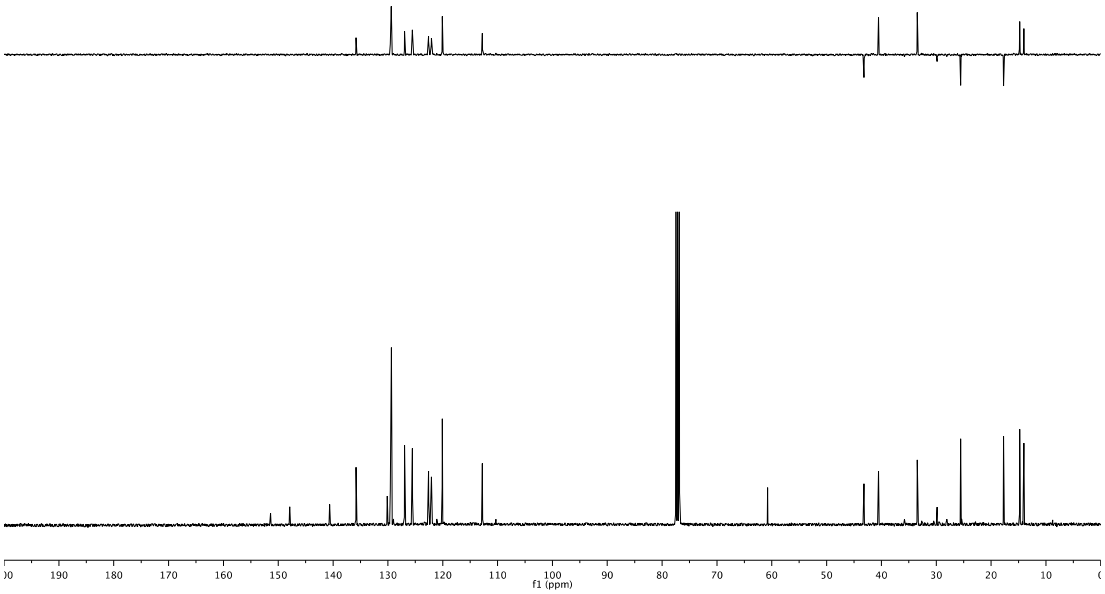


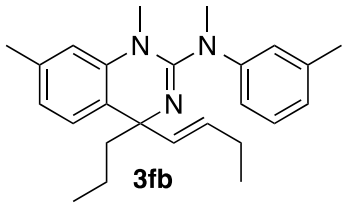

f1 (ppm)


N
N
N

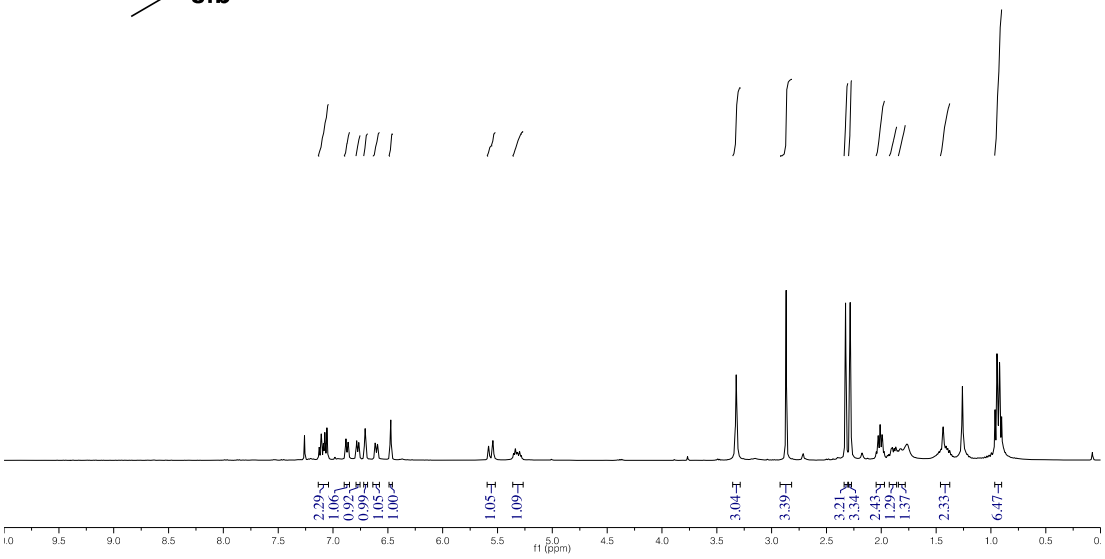
3ab

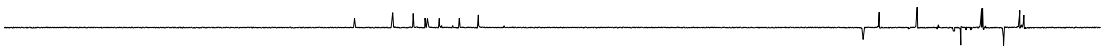

2.41
2.20
1.07
1.09
2.08
1.04
1.01
1.00
3.20
3.27
2.23
1.33
1.48
2.40
6.51
f1 (ppm)

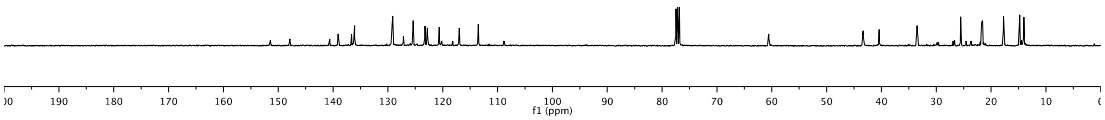

f1 (ppm)

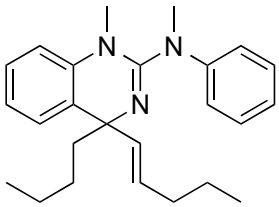

N
N
N

3fb

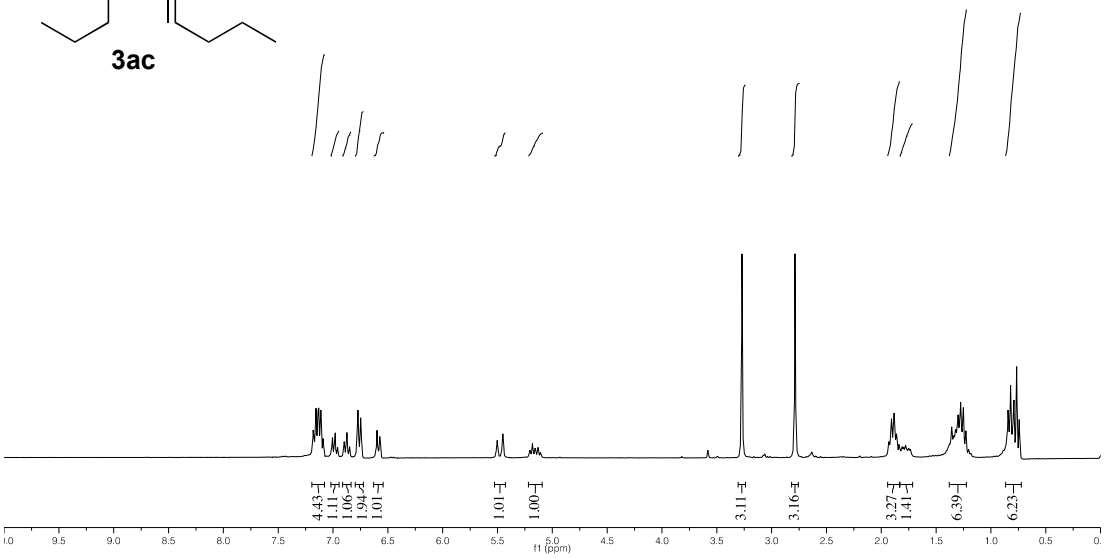

2.29
1.06
0.92
0.99
1.05
1.00
1.05
1.09
3.04
3.39
3.21
3.34
2.43
1.29
1.37
2.33
6.47
f1 (ppm)

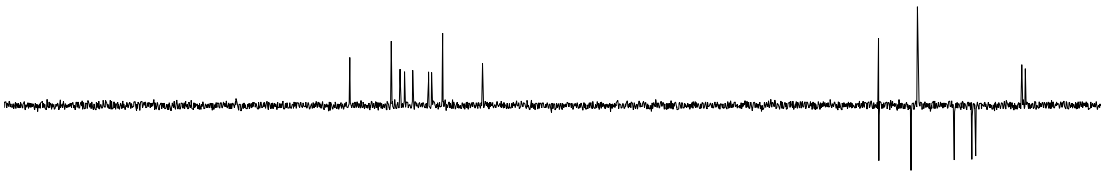


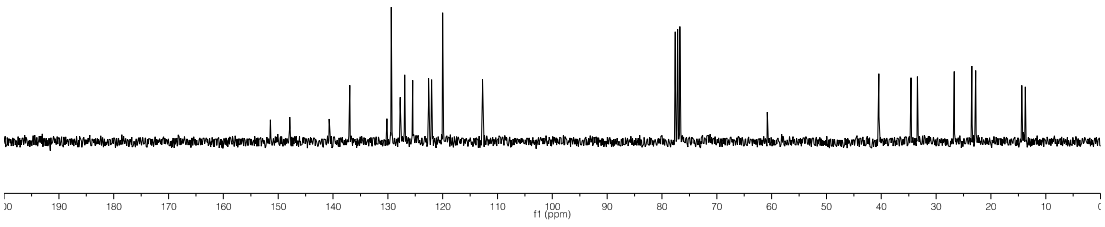

f1 (ppm)

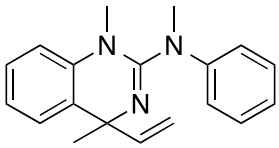


3ac

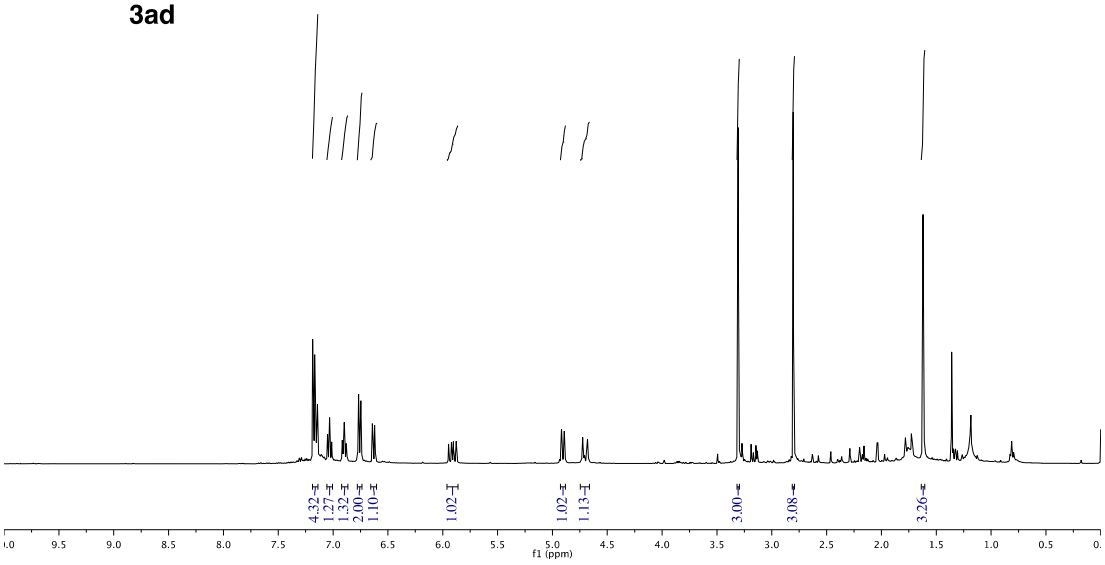


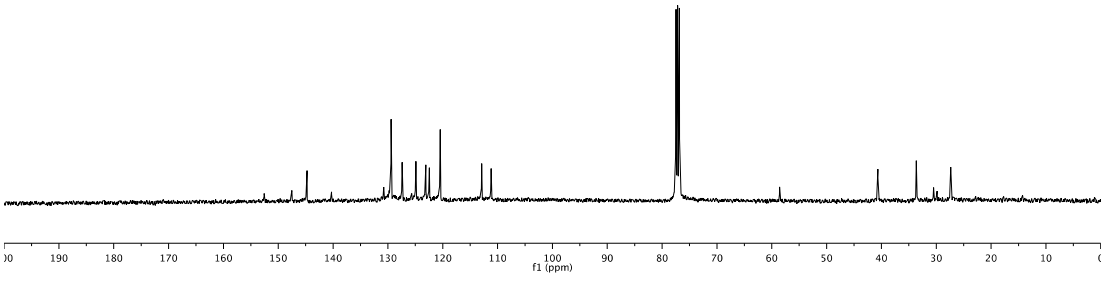


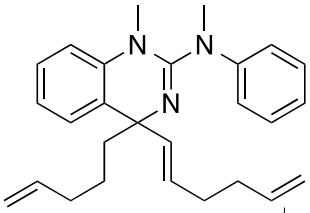




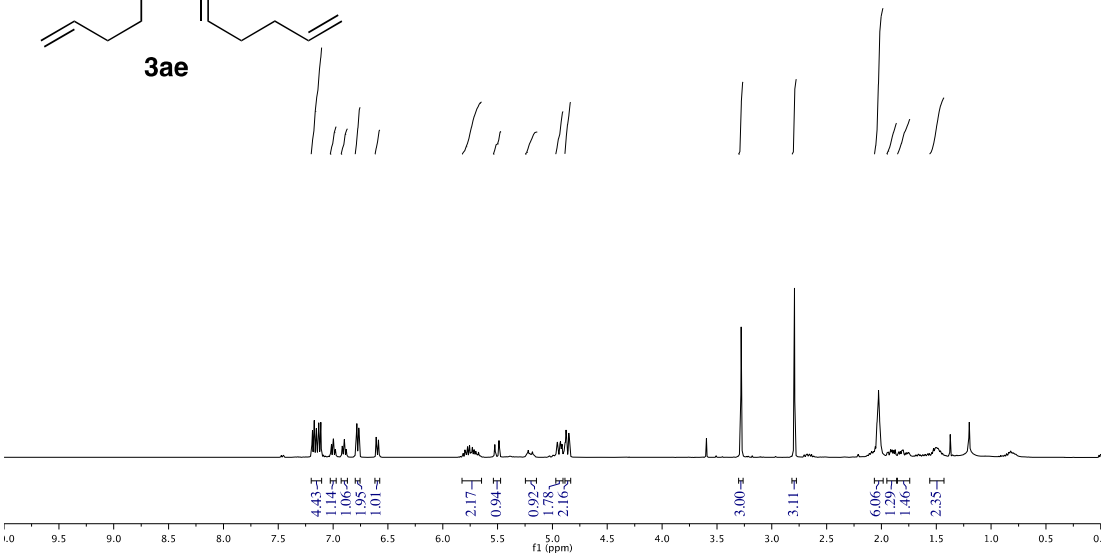
3ad

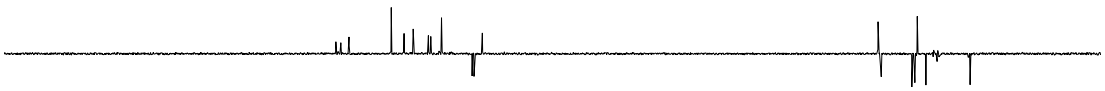


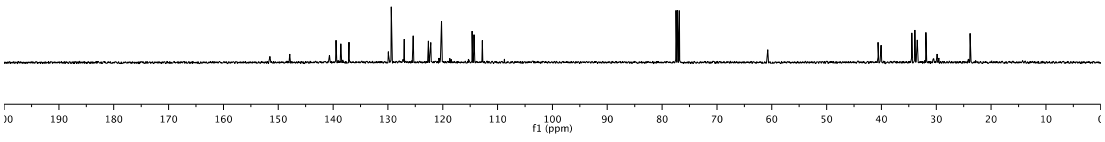


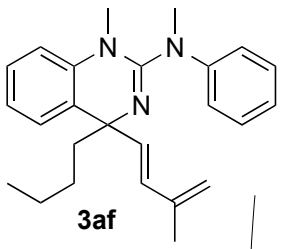

N
N
N

3ae

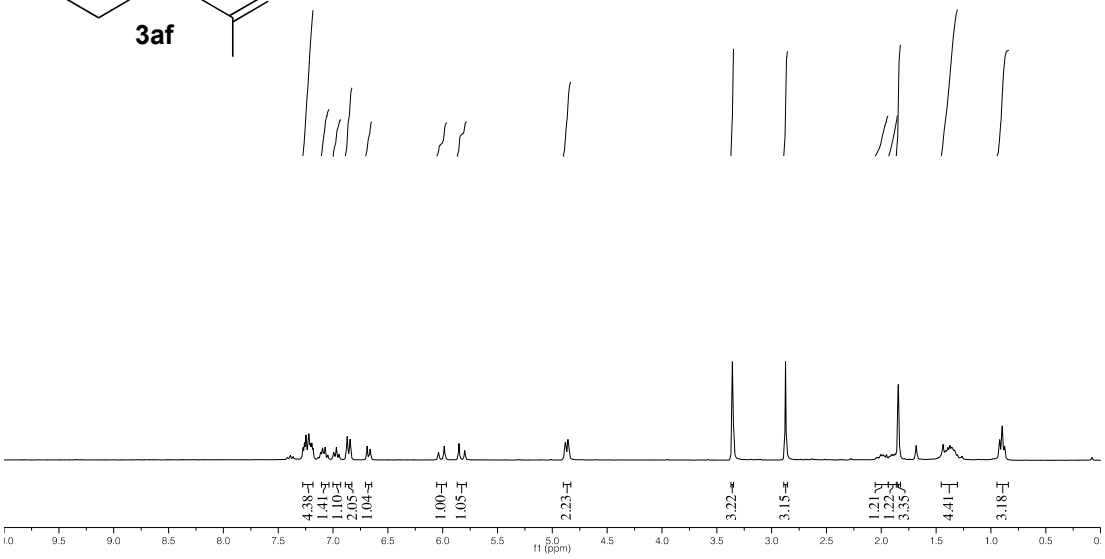

4.43
1.14
1.06
1.95
1.01
2.17
0.94
0.92
1.78
2.16
3.00
3.11
6.06
1.29
1.46
2.35
f1 (ppm)

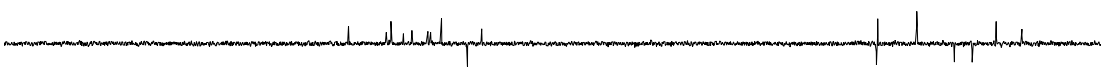


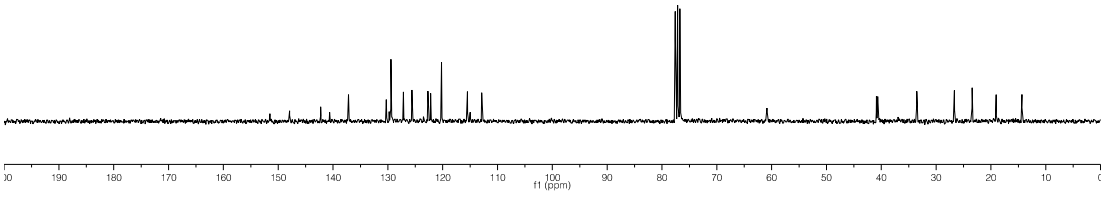

f1 (ppm)

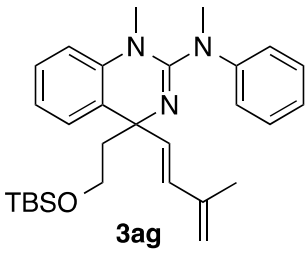


3af

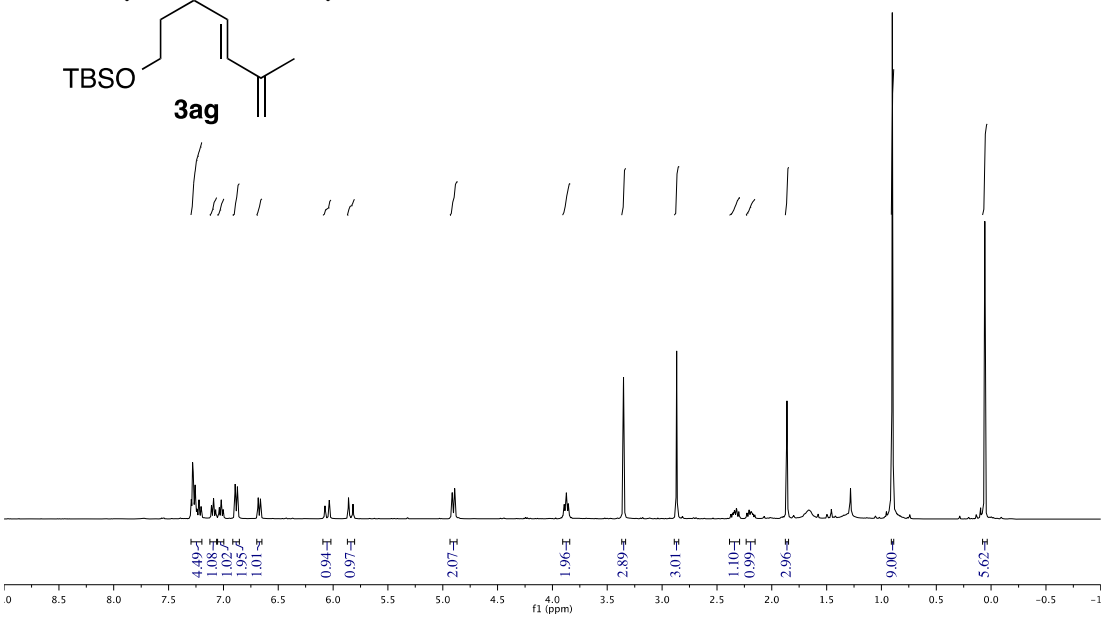

4.38
1.41
1.10
2.05
1.04
1.00
1.05
2.23
3.22
3.15
1.21
1.22
3.35
4.41
3.18
f1 (ppm)

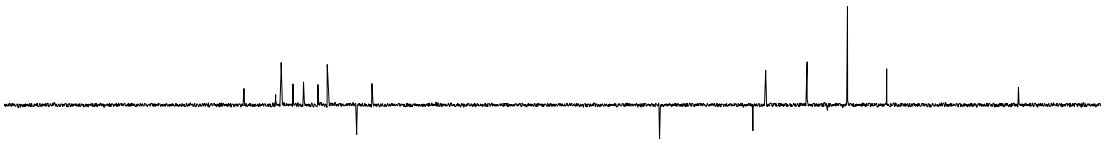


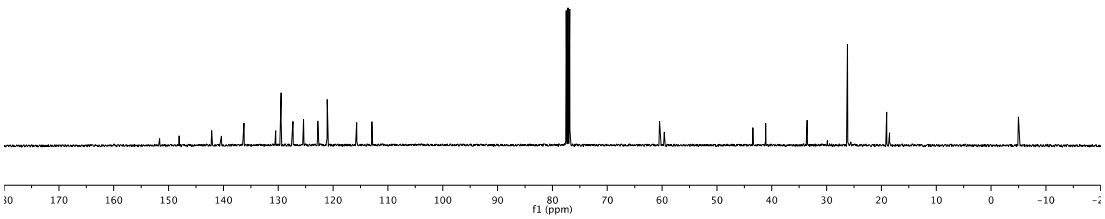

f1 (ppm)

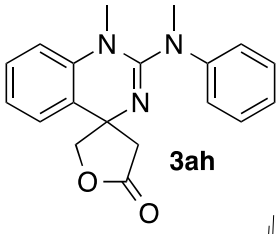

N
N
N
TBSO

3ag

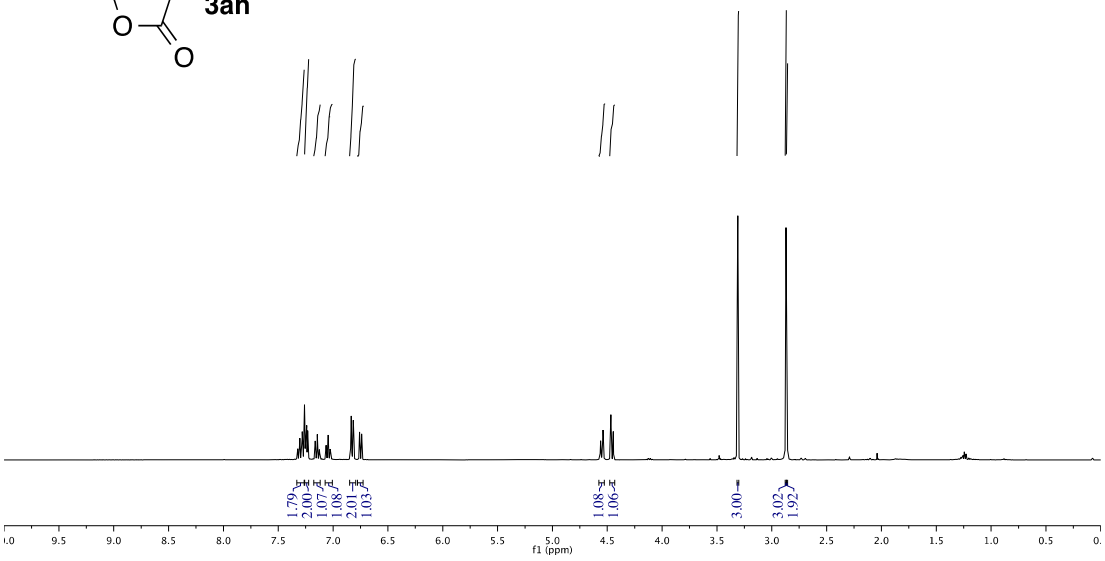

4.49
1.08
1.02
1.95
1.01
0.94
0.97
2.07
1.96
2.89
3.01
1.10
0.99
2.96
9.00
5.62
f1 (ppm)

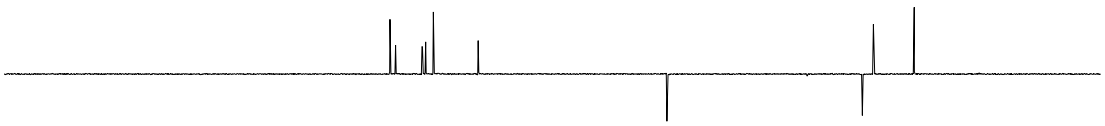


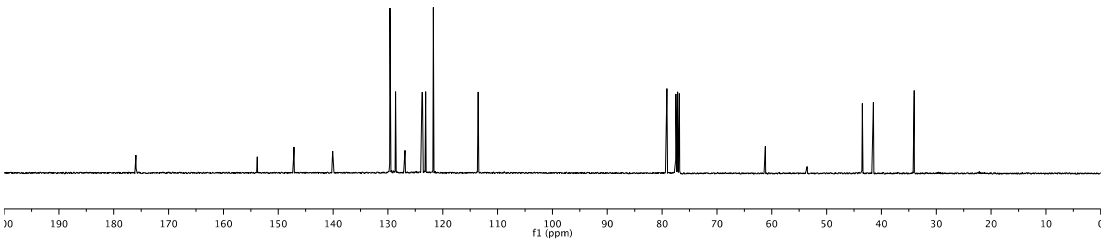

f1 (ppm)

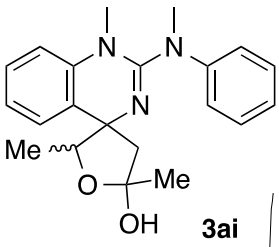


3ah

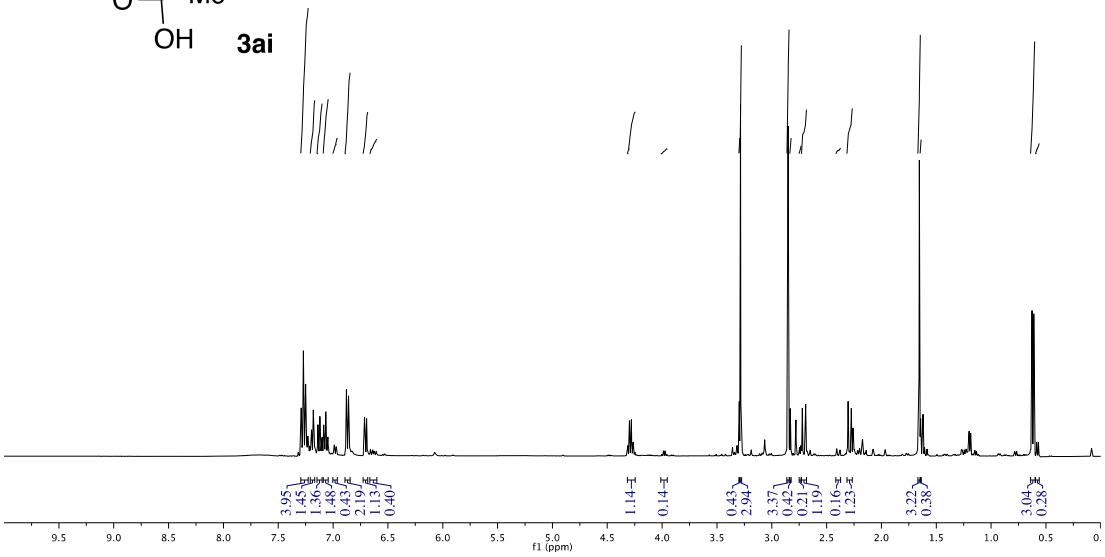


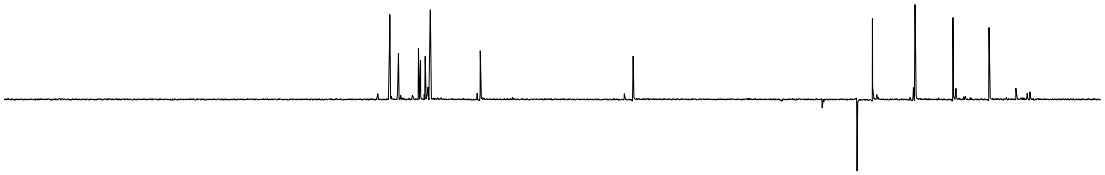


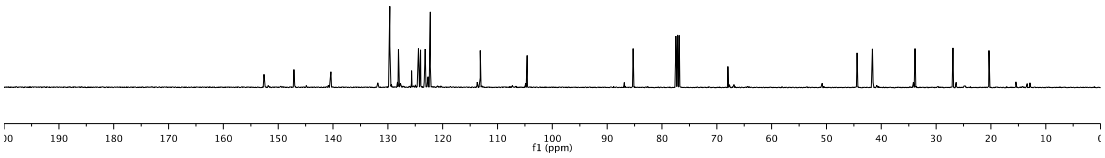


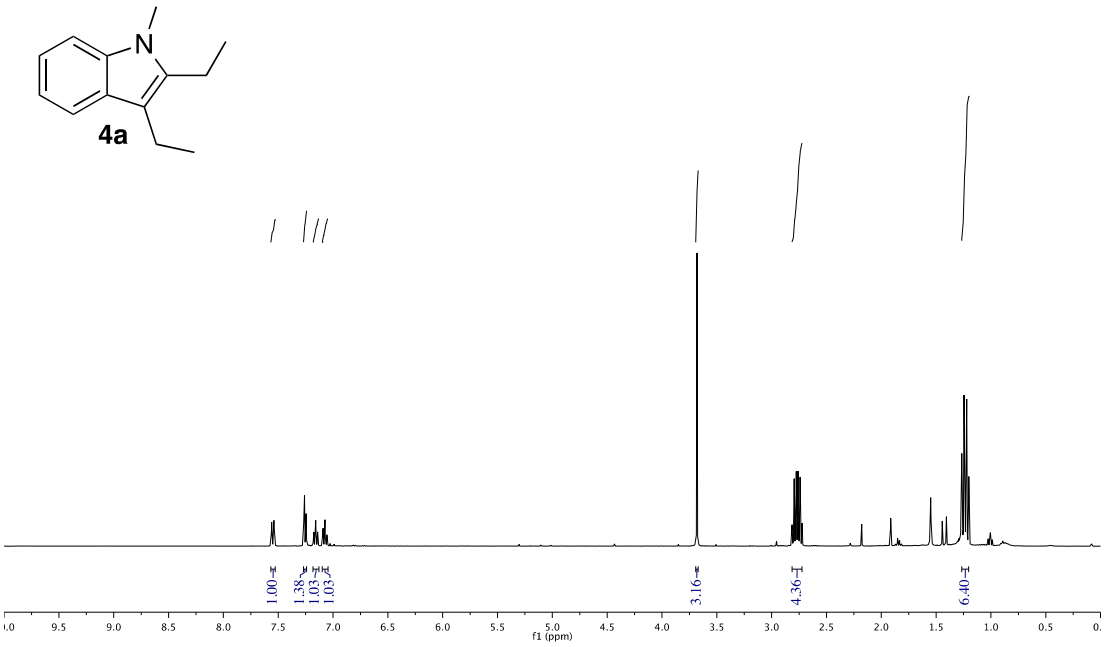

N
N
N
Me
O
Me
OH

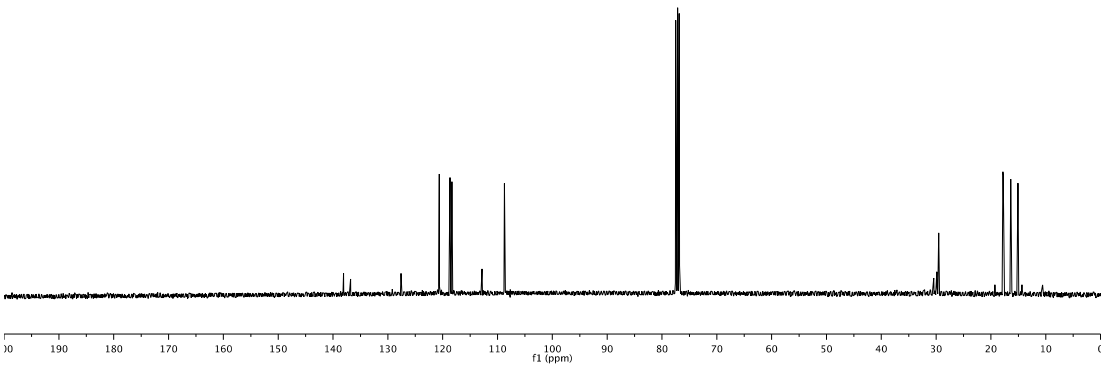
3ai

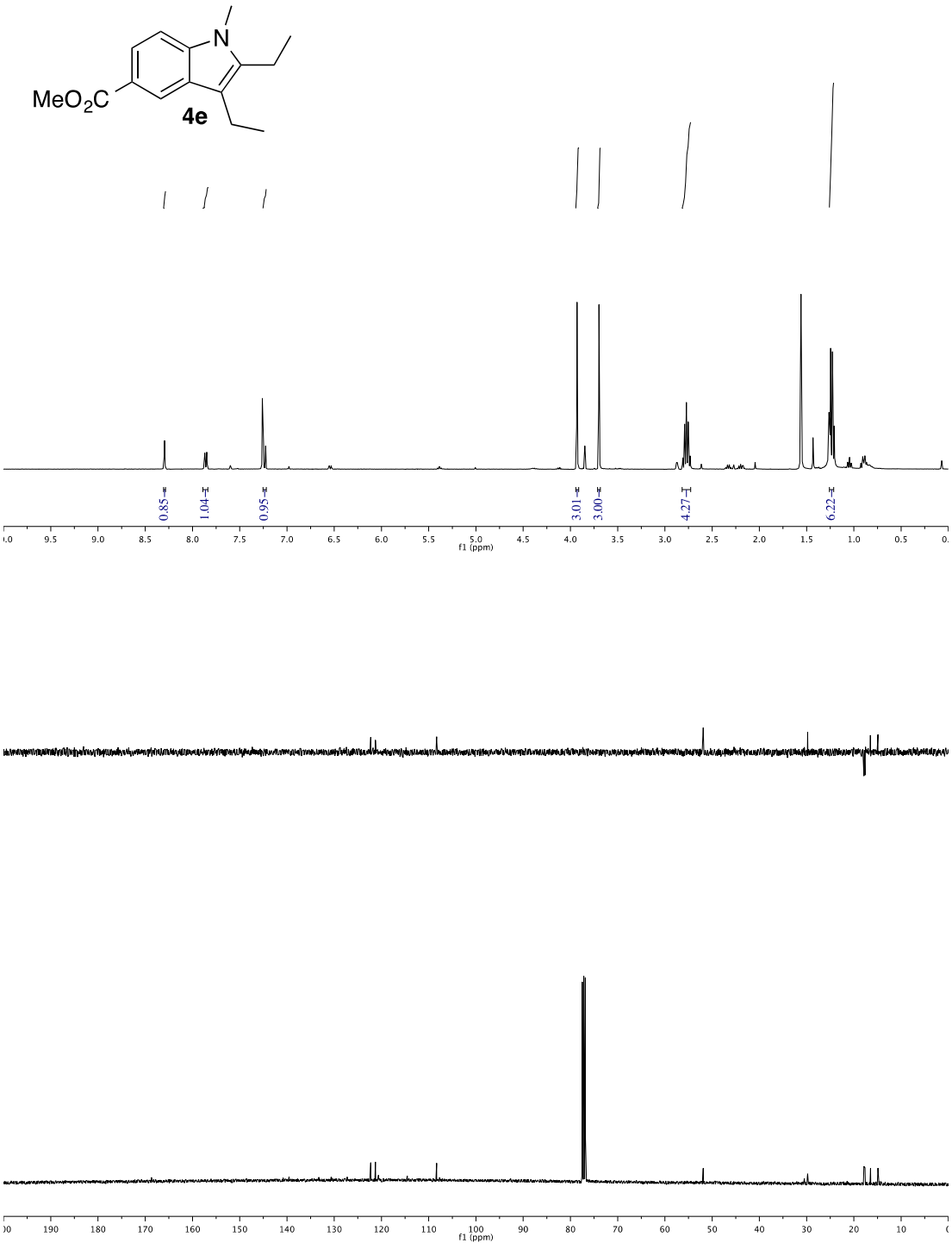

3.95
1.45
1.36
1.48
0.43
2.19
1.13
0.40
1.14
0.14
0.43
2.94
3.37
0.42
0.21
1.19
0.16
1.23
3.22
0.38
3.04
0.28
f1 (ppm)

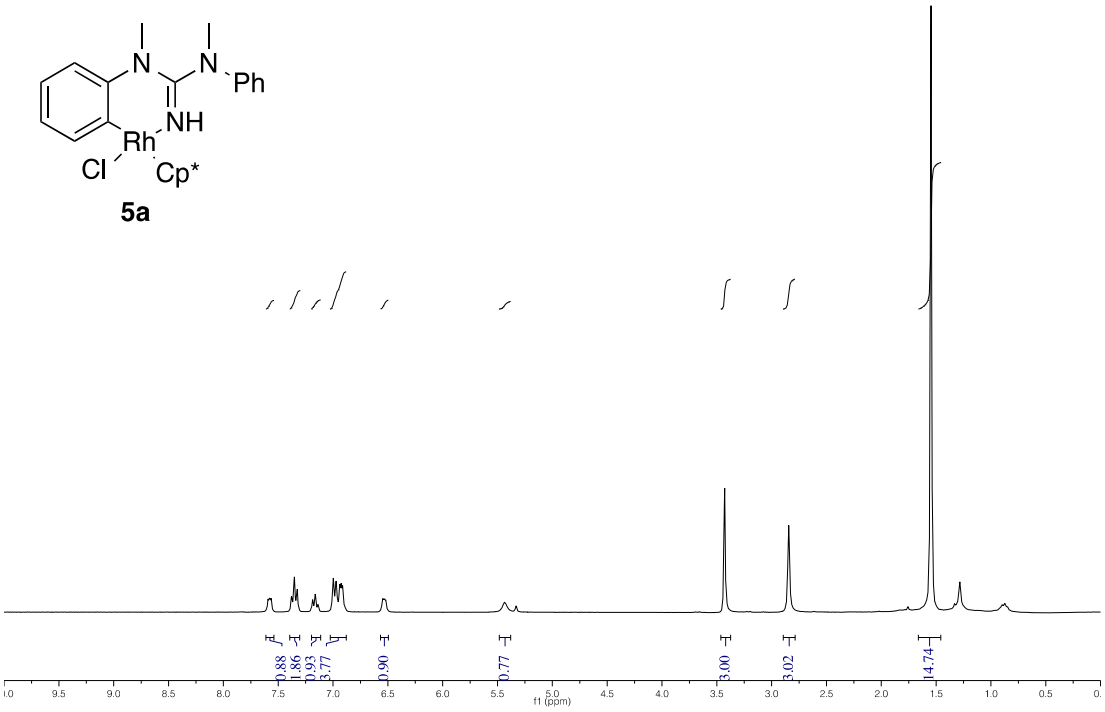



f1 (ppm)

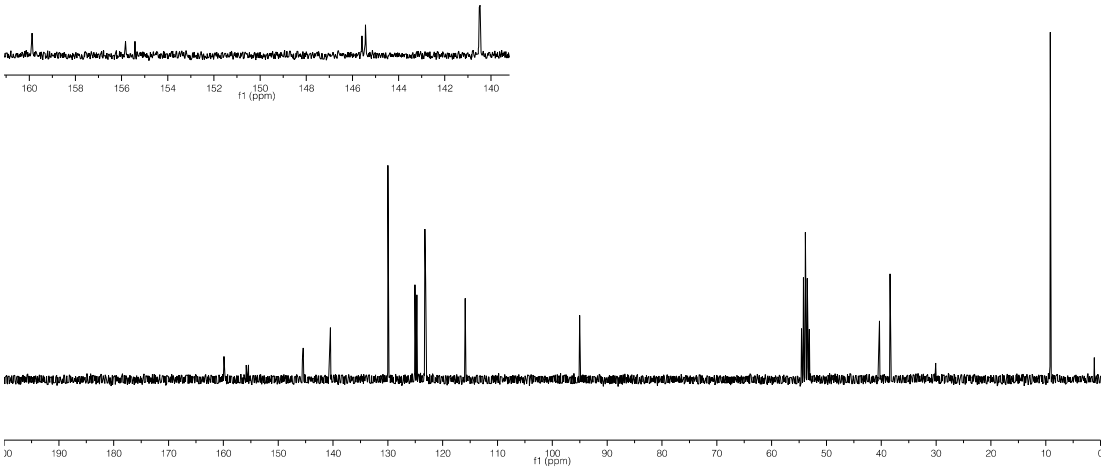

4a
1.00
1.38
1.03
1.03
3.16
4.36
6.40
f1 (ppm)

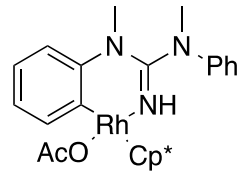

f1 (ppm)


MeO2C
4e
0.85
1.04
0.95
3.01
3.00
4.27
6.22
f1 (ppm)
f1 (ppm)

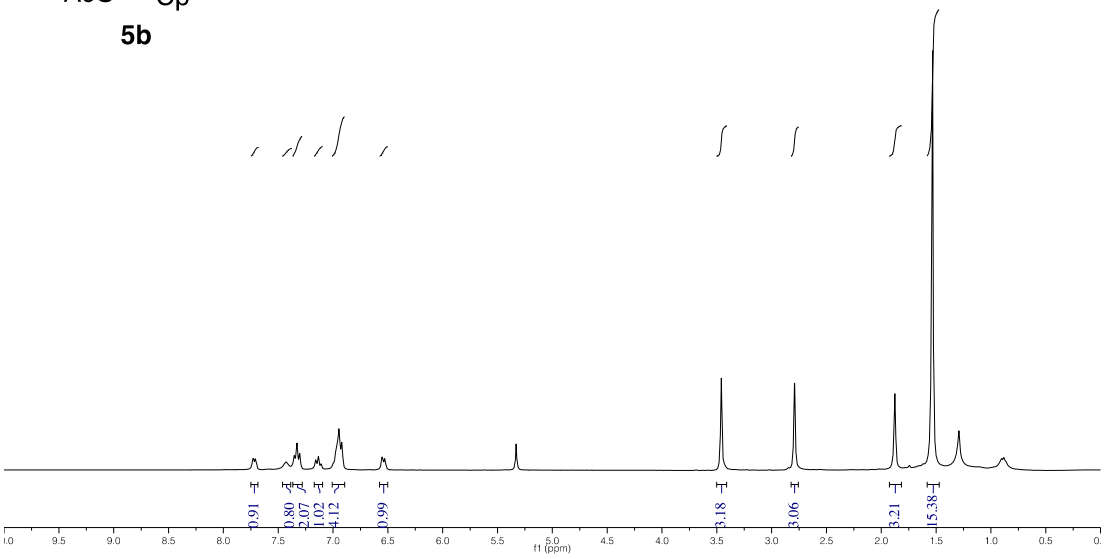

N
N
Ph
NH
Rh
Cl
Cp*
0.88
1.86
0.93
3.77
0.90
0.77
3.00
3.02
14.74
f1 (ppm)

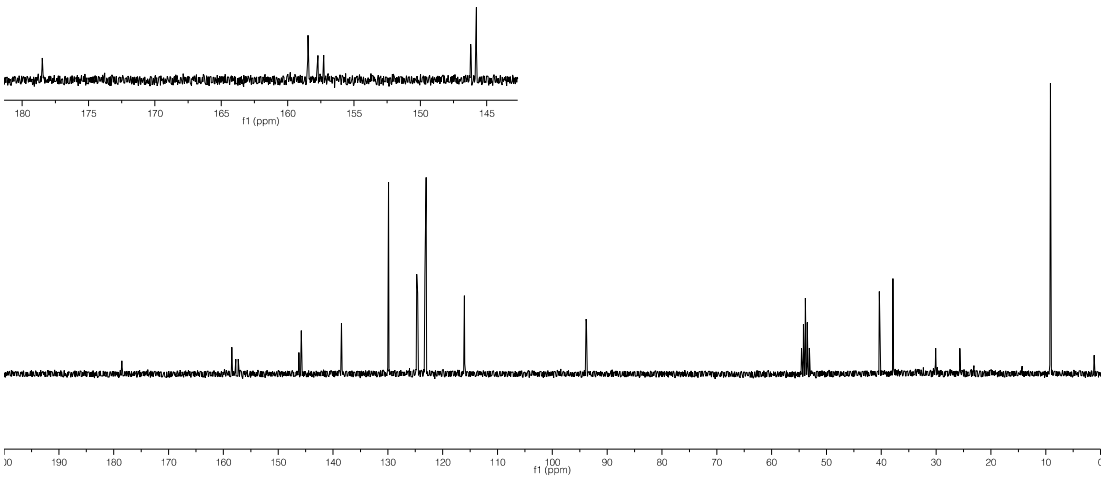
5a

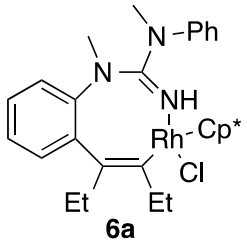

f1 (ppm)
f1 (ppm)


N
N
Ph
NH
Rh
AcO
Cp*

5b

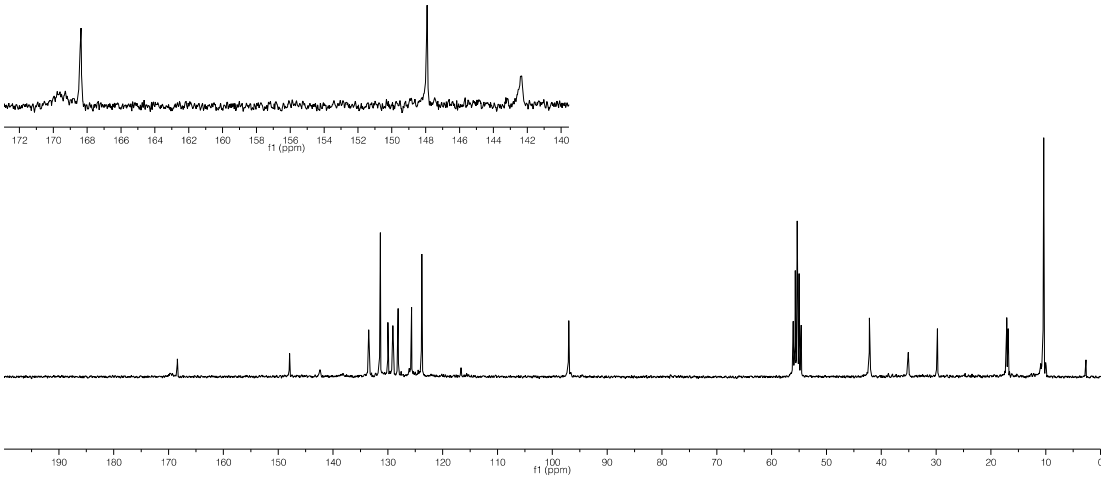

0.91
0.80
2.07
1.02
4.12
0.99
3.18
3.06
3.21
15.38
f1 (ppm)

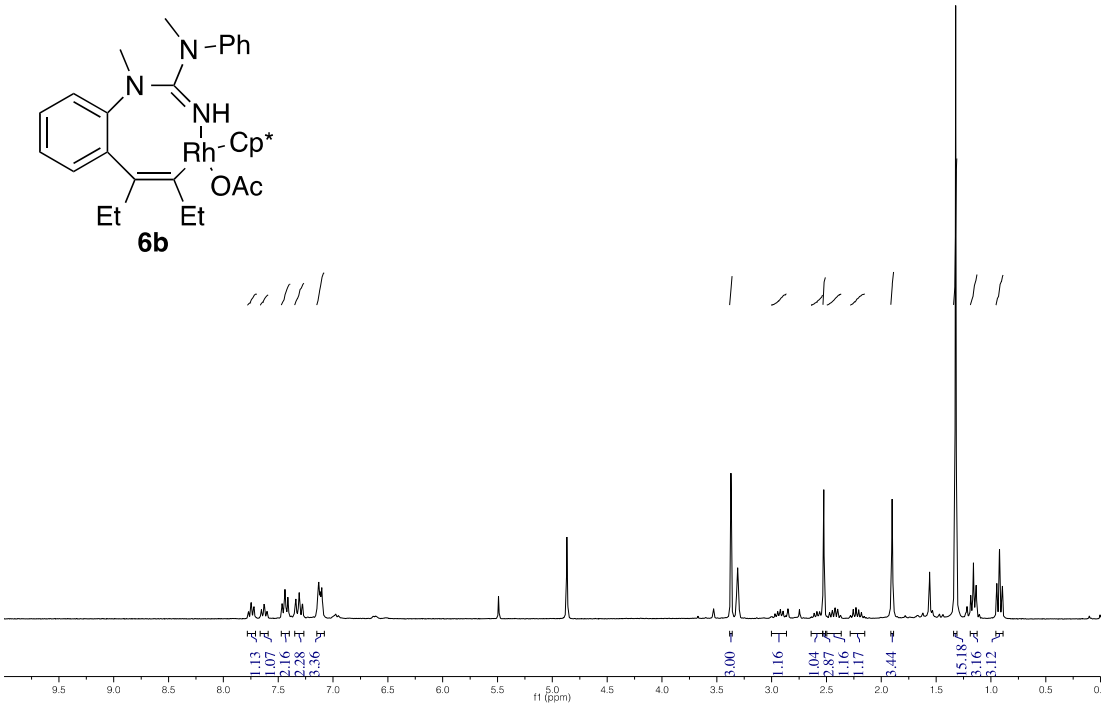

f1 (ppm)
f1 (ppm)


N
Ph
N
NH
Rh
Cp*
Cl
Et
Et

6a

1.08
1.11
2.26
2.29
3.39
3.00
1.42
1.20
3.20
1.34
1.47
15.32
3.49
3.36
f1 (ppm)


f1 (ppm)
f1 (ppm)


N
Ph
N
NH
Rh
Cp*
OAc
Et
Et
6b
1.13
1.07
2.16
2.28
3.36
3.00
1.16
1.04
2.87
1.16
1.17
3.44
15.18
3.16
3.12
f1 (ppm)