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Graphical Abstract

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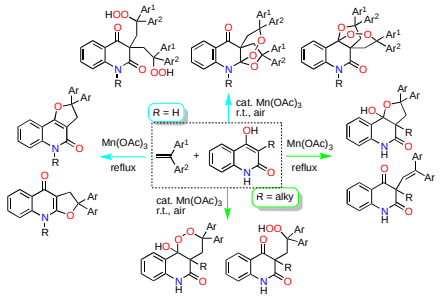

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Mn(III)-based reaction of alkenes with quinolinones. Formation of peroxyquinolinones and quinoline-related derivatives

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ABSTRACT

The reactions of 1,1-disubstituted alkenes with 4-hydroxyquinolin-2(1*H*)-ones under both Mn(III)-catalyzed aerobic oxidation conditions at room temperature and Mn(III)-mediated oxidation conditions at reflux temperature are described. The Mn(III)-catalyzed aerobic oxidation afforded bis(hydroperoxyethyl)quinolinones and azatrioxa[4.4.3]propellanes, while the oxidation with $Mn(OAc)_3 \cdot 2H_2O$ produced furo[3,2-*c*]quinolin-4-one analogues. The existence of a substituent at the 3-position of the 4-hydroxyquinolin-2(1*H*)-ones prevented a double reaction with the alkenes, and (endoperoxy)quinolinones and/or (hydroperoxyethyl)quinolinones were obtained under the Mn(III)-catalyzed aerobic conditions, while furo[3,2-*c*]quinolinone hemiacetals and vinylquinolinones were selectively produced under the Mn(III)-mediated oxidation conditions depending on the reaction temperature and times. Cyclic assembly of quinolinone-related 1,3-dicarbonyl compounds such as dihydropyridinones, pyranones, and dimedone derivatives was also examined under elevated temperature conditions.

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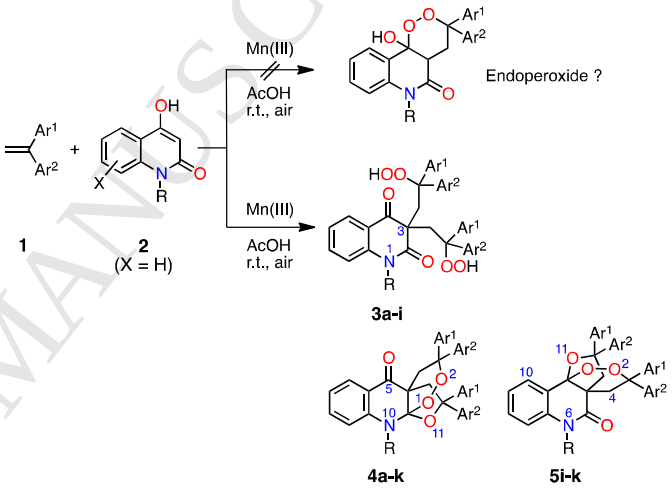
1. Introduction

Quinoline alkaloids are some of the most important natural products and the synthesis of heterocycles containing the quinoline core is interesting from the standpoint of searching for new biologically active compounds.[1,2] Mn(III)-assisted oxidation is one of the useful tools for formation of the carbon-carbon bond to a heterocyclic ring such as addition and substitution.[3,4] For example, the aerobic oxidation[5] of pyrazolidine-3,5-diones,[6] tetronic acids[7] and tetramic acids[8] using $Mn(OAc)_3$•$2H_2O$ as a catalyst in the presence of alkenes gave hydroperoxides and endoperoxides such as bis(hydroperoxyethyl)pyrazolidinediones, 1-hydroxy-2,3,8-trioxabicyclo[4.3.0]nonan-7-ones, and 8-aza-1-hydroxy-2,3-dioxabicyclo[4.3.0]nonan-7-ones, while the direct hydroperoxidation to a heterocyclic ring occurred by a similar reaction using substituted cyclic diamides in the absence of alkenes.[9] On the other hand, the oxidation of alkenes with the Mn(III)-enolate complex as an oxidant caused oxidative cyclization, producing dihydrofurans[10] and lactones.[11] In order to construct a complex quinoline core, 4-hydroxyquinolin-2(1*H*)-ones are a suitable reagent for the Mn(III)-based peroxidation and dihydrofuranation.[12] We initially demonstrated the Mn(III)-catalyzed aerobic oxidation of 1,1-diarylethenes in the presence of the 4-hydroxyquinolinones at room temperature to produce (hydroperoxyethyl)quinolinediones and [4.4.3]propellane-type endoperoxides.[13] A similar reaction using a stoichiometric amount of Mn(III) at elevated temperature formed furo[3,2-*c*]quinolin-4(2*H*)-ones and 3-vinylquinoline-2,4-diones.[14] In this paper, we describe the results of the oxidation of a mixture of 1,1-disubstituted alkenes and 4-hydroxyquinolinones, and the synthetic application of the dihydrofuranation using the quinolinones and related 1,3-dicarbonyl compounds together with the full experimental results of these reactions.

2. Results and discussion

2.1. Aerobic oxidation of a mixture of alkenes 1 and 4-hydroxyquinolin-2(1*H*)-ones 2 (X = H)[13]

Based on our study of the Mn(III)-catalyzed peroxidation,[5a] it was predicted that the reaction of 1,1-diphenylethene **1** (Ar^1 = Ar^2 = Ph) with 1-methyl-4-hydroxyquinolin-2(1*H*)-one **2** (X = H, R = Me) must form an endoperoxide such as 4,4a,6,10b-tetrahydro-10b-hydroxy-6-methyl-3,3-diphenyl-1,2-dioxino[4,3-*c*]quinolin-5(3*H*)-one (Scheme 1). The reaction did not occur in the absence of $Mn(OAc)_3$ (Table 1, entry 1), and the use of 1 mmol of $Mn(OAc)_3$ gave an intractable mixture (entry 2). Surprisingly, a bis(hydroperoxide) **3a** was isolated from the reaction mixture when a catalytic amount of $Mn(OAc)_3$ was used in air (Scheme 1 and Table 1, entry 3). In order to prevent the double substitution, the reaction was carried out using two equivalents of quinolinone **2** toward the alkene **1** (entries 4-6). However, the reaction resulted in the bis(hydroperoxide) **3a** as an isolable product, and the monohydroperoxide and the desired endoperoxide as well as **1** unchanged were not obtained. In addition, use of excess amount of **1** toward quinolinone **2** caused the reaction complicated. Another combination of alkenes **1** (Ar^1 = Ar^2 = 4-ClC_6H_4, 4-Me-C_6H_4) and quinolinones **2** (X = H, R = Et, Bn, H, Me) also underwent the aerobic oxidation to afford similar bis(hydroperoxide)s **3b-h** (entries 7-13). When a combination of the alkene **1** (Ar^1 = Ar^2 = Ph) and the quinolinone **2** (X = H, R = Et) was used, the best yield of bis(hydroperoxide)



Scheme 1. Mn(III)-based aerobic oxidation of a mixture of 1,1-disubstituted ethenes **1** and quinolinones **2** (X = H).

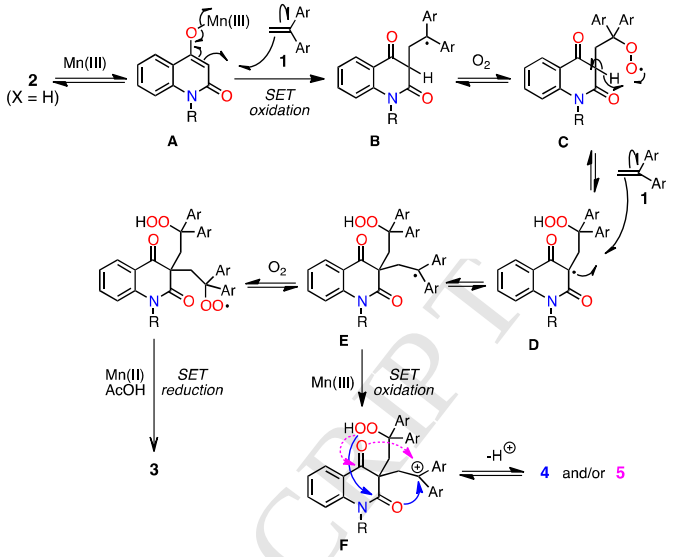
Table 1
Mn(III)-based aerobic oxidation of a mixture of 1,1-disubstituted ethenes **1** and quinolinones **2** (X = H)[a]

Entry	Alkene **1**		Quinolinone **2**	Molar ratio	Time	Product (yield/%)[b]		
	Ar^1	Ar^2	R	**1**:**2**:$Mn(OAc)_3$•$2H_2O$	h			
1	Ph	Ph	Me	1:1:0	4	no reaction		
2	Ph	Ph	Me	1:2:1	4	intractable mixture		
3	Ph	Ph	Me	2:1:0.5	12	**3a** (32)		
4	Ph	Ph	Me	1:2:0.1	4	**3a** (29)		
5	Ph	Ph	Me	1:2:0.5	12	**3a** (43)		
6	Ph	Ph	Me	1:2:0.5	4	**3a** (71)	**4a** (13)	
7	4-Cl-C_6H_4	4-Cl-C_6H_4	Me	1:2:0.5	12	**3b** (76)	**4b** (10)	
8	4-Me-C_6H_4	4-Me-C_6H_4	Me	1:2:0.5	4	**3c** (59)	**4c** (10)	
9	Ph	Ph	Et	1:2:0.5	15	**3d** (91)	**4d** (5)	
10	Ph	Ph	Bn	1:2:0.5	12	**3e** (52)	**4e** (trace)	
11	4-Cl-C_6H_4	4-Cl-C_6H_4	Bn	1:2:0.5	24	**3f** (48)	**4f** (trace)	
12	4-Me-C_6H_4	4-Me-C_6H_4	Bn	1:2:0.5	4	**3g** (44)	**4g** (trace)	
13	Ph	Ph	H	1:2:0.5	4	**3h** (trace)	**4h** (34)	
14	Ph	2-thienyl	Me	2:1:0.5	18	**3i** (trace)	**4i** (7)	**5i** (28)
15	Ph	2-thienyl	Me	2:1:3	12		**4i** (39)	**5i** (27)
16	Ph	2-thienyl	Me	2:1:3	12		**4i** (22)	**5i** (39)
17	4-F-C_6H_4	2-thienyl	Me	2:1:3	12		**4j** (22)	**5j** (32)
18	4-Me-C_6H_4	2-thienyl	Me	2:1:3	18		**4k** (22)	**5k** (47)

[a] The reaction of alkene **1** (1 mmol) with quinoline **2** (2 mmol) was carried out in glacial acetic acid (25 mL) at room temperature in air.
[b] The yield was based on the amount of the alkene **1** used.

3d was achieved (entry 9). In order to search for other products, we scrutinized the reaction and found another product, [4.4.3]propellanes **4b-h** (entries 6-13). The structure of bis(hydroperoxide)s **3** and [4.4.3]propellanes **4** was determined by spectroscopic methods as well as X-ray crystallography for a single crystal of bis(hydroperoxide) **3b** and [4.4.3]propellane **4a** (see Supplementary material).[13] Although it is known that the aerobic oxidation of cyclic diamides in the presence of alkenes does not give the corresponding endoperoxides, but bis(hydroperoxide)s,[9] it is remarkable that the dual hydroperoxidation was favored even using cyclic keto-amides such as **2** (enol form of quinoline-2,4-diones). In addition, it is surprising that the propellane **4**, which was cyclized at the amide carbonyl group, was also isolated as a by-product.[12d] The reaction using **2** (R = X = H) with no *N*-protection actually gave the bis(hydroperoxide) **3h** with a trace amount (entry 13). However, most of the bis(hydroperoxide) **3h** seemed to be further oxidized under the conditions and we could not separate the fragments. When the reaction using 2-(1-phenylvinyl)thiophene **1** (Ar^1 = Ph, Ar^2 = 2-thienyl)[10f,i,o] was carried out under similar conditions, the reaction was rather sluggish and gave the corresponding propellane **4i** together with another propellane **5i** as an inseparable stereoisomeric mixture (entry 14). The propellane **5i** was distinguishable from the other propellane **4i** based on the absence of the ketocarbonyl carbon in the ^{13}C NMR spectrum. The yield was improved by increasing the amount of thiophene **1** and oxidant (entries 15 and 16). The reaction of other 2-(1-arylvinyl)thiophenes **1** (Ar^1 = 4-F-C_6H_4 and 4-Me-C_6H_4, Ar^2 = 2-thienyl) also led to a similar result (entries 17 and 18).

In order to investigate the interconversion between the bis(hydroperoxide) **3** and the propellane **4** during the reaction, the bis(hydroperoxide) **3a** (R = Me, Ar^1 = Ar^2 = Ph) and the propellane **4a** (R = Me, Ar^1 = Ar^2 = Ph), respectively, were then treated both in the absence and presence of $Mn(OAc)_3$ (see Experimental section). As a result, it was confirmed that the bis(hydroperoxide) **3a** and the propellane **4a** were not converted into each other during the reaction. Therefore, we proposed the aerobic oxidation pathway as shown in Scheme 2.[6,7] The Mn(III)-enolate complex **A** produced in situ by the reaction of $Mn(OAc)_3$ with quinolinone **2** (X = H) undergoes single-electron transfer (SET) oxidation with the alkene **1** to form the corresponding tertiary radical **B** which captures the dissolved molecular oxygen followed by hydrogen abstraction, affording the monohydroperoxyethyl radical **D**.[6,7] The radical intermediate **D** undergoes a similar aerobic oxidation via an alkyl radical intermediate **E** to furnish the bis(hydroperoxide)s **3**. The radical intermediate **E** would also be oxidized by the oxidant to produce the corresponding cation **F** which undergoes double cyclization to afford the propellanes **4** and/or **5**. The use of an excess amount of the catalyst accelerated the oxidation of the tertiary radical **E** which resulted in the exclusive production of the propellanes **4i-k**



Scheme 2. Mn(III)-based aerobic oxidation pathway for the formation of **3**, **4** and/or **5**.

2.2. Aerobic oxidation of a mixture of alkenes 1 and 3-substituted quinolinones 6[13]

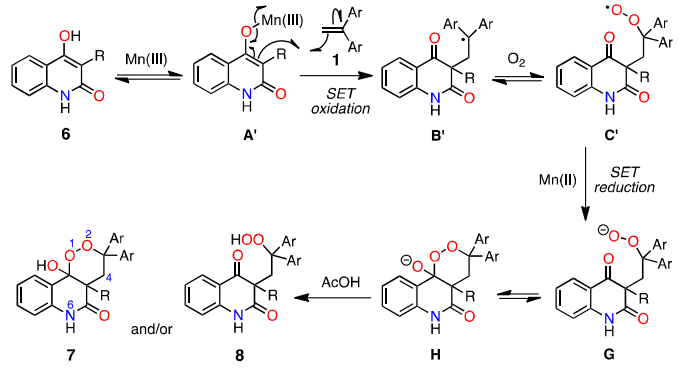
In order to investigate the possibility of the synthesis of endoperoxides, we designed the reaction using 3-substituted quinolinones **6** (Scheme 3). When a substituent is present at the 3-position of the 2-hydroxyquinolinones **2**, the SET reduction of the peroxy radical intermediate **C'** would preferentially proceed because the intramolecular hydrogen abstraction, such as the peroxy radical **C** in Scheme 2, could not occur and the formation of endoperoxides **7** or monohydroperoxides **8** would be expected (Scheme 3). The reaction of 3-methylquinolinone **6** (R = Me) was then carried out under similar aerobic oxidation conditions. The alkene **1** was completely consumed and the desired endoperoxide **7a** was obtained (Table 2, entry 1). However, **7a** seemed to interconvert into the corresponding hydroperoxide **8a** (R = Me, Ar = Ph) even in the NMR time scale because the methyl and methylene carbons were unclear in the ^{13}C NMR spectrum (see supplementary material). In fact, for the quinolinones **6** bearing a bulky substituent, such as the propyl, butyl, and phenyl group, hydroperoxides **8b-d** were predominantly produced along with the endoperoxides **7b-d** (entries 2-4).[15] Since it was difficult to separate endoperoxides **7** and hydroperoxides **8** by chromatographic separation, the product yield was calculated based on the crude ^{1}H NMR

Table 2
Mn(III)-based aerobic oxidation of a mixture of 1,1-disubstituted ethenes **1** and 3-substituted quinolinones **6**[a]

Entry	Alkene **1**	Qunolinone **6**	Molar ratio	Time	Product (yield/%)[b]	
	Ar	R	**1**:**6**:$Mn(OAc)_3$•$2H_2O$	h		
1	Ph	Me	1:2:0.5	15	**7a** (89)	
2	Ph	Pr	1:2:0.5	18	**7b** (22)	**8b** (60)[c]
3	Ph	Bu	1:2:0.5	15	**7c** (24)	**8c** (52)[c]
4	Ph	Ph	1:2:0.5	15	**7d** (32)	**8d** (43)[c]
5	4-Cl-C_6H_4	Me	1:2:0.5	18	**7e** (88)	
6	4-Me-C_6H_4	Me	1:2:0.5	15	**7f** (38)	**8f** (58)[c]

[a] The reaction was carried out at room temperature in air.
[b] The yield was based on the amount of the alkene **1** used.
[c] The yield was calculated by crude NMR analysis.

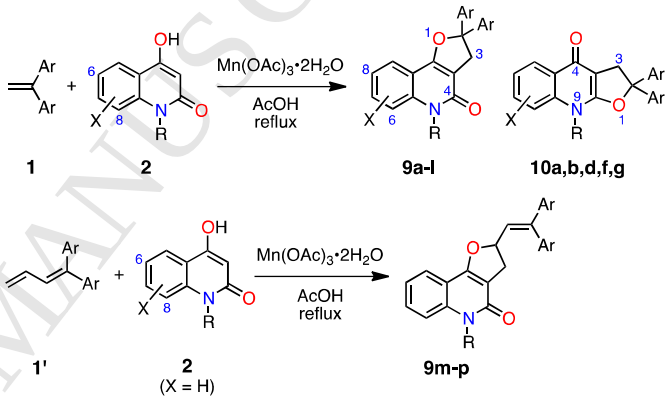
spectrum as shown in Table 2. The cyclization might be difficult because the steric repulsion would exist between the diphenyl group and the bulky R group or quinolinone skeleton in the transition state of the conversion of **G** into **H** as well as the intermediate **H** itself. In addition, the use of alkene **1** (Ar = 4-MeC_6H_4) also led to the formation of the hydroperoxide **8f** as the major product (entry 6). Although the tendency was also observed for the reaction of tetronic acid with **1** (Ar = 4-MeC_6H_4), the reason was not clear.[7] In either event, the peroxy anion **G** did not cyclize at the amide carbonyl group probably due to the weak electrophilicity of the amide carbonyl carbon.



Scheme 3. Mn(III)-based aerobic oxidation of a mixture of substituted ethenes **1** and quinolinones **6**.

2.3. Mn(III)-mediated oxidation of alkenes in the presence of 4-hydroxyquinolin-2(1*H*)-ones and other related compounds[14]

4-Hydroxyquinolin-2(1*H*)-ones **2** as a reagent are very good candidates not only as a radical source in the Mn(III)-mediated oxidation,[3] but also as a starting material for the synthesis of quinolinone alkaloids such as atanine, araliopsine, and isoplatydesmine.[10c] The 1,3-dicarbonyl compounds, such as 2,4-pentanedione, malonic acid, malonate esters, acetic anhydride, malonamides, and 3-oxobutanoates, undergo oxidative cyclization with alkene using $Mn(OAc)_3•2H_2O$ at elevated temperature to produce dihydrofurans,[10] spirolactones,[11a,b] γ-lactones,[11c,e-g] lactams,[4c,11h-j] and dihydroquinolinones.[4d] We then applied the reaction to a combination of alkenes **1** and 4-hydroxyquinolinones **2**, and obtained the desired thermodynamically stable angular products, 3,5-dihydrofuro[3,2-*c*]quinolin-4-ones **9**, along with a small amount of linear byproducts, i.e., 3,9-dihydrofuro[2,3-*b*]quinolin-4-ones **10** (upper part in Scheme 4 and Table 3).[10c,14] Since the use of stoichiometric amount of $Mn(OAc)_3•2H_2O$ (2 equiv.) led to the moderate yield of the product **9a** (R = Me, X = H, Ar = Ph) (Table 3, entry 1), an excess amount of the oxidant was necessary to improve the product yield (entry 2). Although other combinations of **1** and **2** also gave a similar result (entries 3-13), the product yield from the quinolinones **2** bearing a substituent at the 6-position was not improved (entries 9 and 11). The reaction of conjugated butadienes **1'** with quinolinones **2** is quite interesting (lower part in Scheme 4). The 1,4-addition did not occur but 1,2-addition, giving vinyl-substituted dihydrofuroquinolinones **9m-p** (entries 14-17) similar to copper-mediated reaction of 2,2-dibromodimedone with conjugated dienes.[16]



Scheme 4. Mn(III)-mediated oxidation of substituted ethenes **1** and **1'** in the presence of quinolinones **2**.

The mechanism for the formation of **9** and **10** has been reported by Parsons et al.[10c] 1,1-Diarylethene **2** should be

Table 3

Mn(III)-mediated oxidation of substituted ethenes **1** and **1'** in the presence of quinolinones **2**[a]

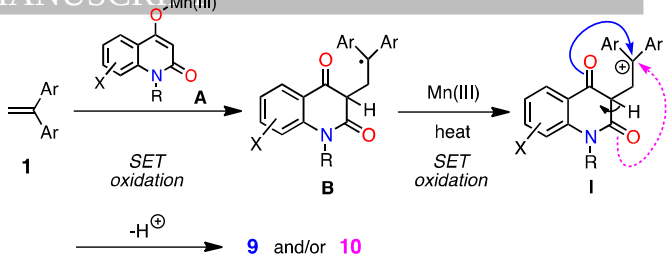
Entry	Alkene **1**	Quinolinone **2**		**1**:**2**:$Mn(OAc)_3•2H_2O$	Time	Product (yield/%)[b]	
	Ar	R	X		min		
1	**1**: Ph	Me	H	1:1.5:2	2	**9a** (60)	**10a** (4)
2	**1**: Ph	Me	H	1:2:3	3	**9a** (87)	**10a** (7)
3	**1**: Ph	Et	H	1:2:3	1.5	**9b** (73)	**10b** (trace)
4	**1**: Ph	Pr	H	1:2:3	1.5	**9c** (76)	
5	**1**: Ph	Bn	H	1:2:3	3	**9d** (85)	**10d** (trace)
6	**1**: Ph	H	H	1:2:3	2	**9e** (73)	
7	**1**: 4-Cl-C_6H_4	Me	H	1:2:3	3	**9f** (87)	**10f** (12)
8	**1**: 4-Me-C_6H_4	Me	H	1:2:3	5	**9g** (93)	**10g** (trace)
9	**1**: Ph	H	6-Me	1:2:3	30	**9h** (44)	
10	**1**: Ph	H	8-Me	1:2:3	3	**9i** (67)	
11	**1**: Ph	H	6-Cl	1:2:3	4	**9j** (58)	
12	**1**: Ph	H	8-Cl	1:2:3	3	**9k** (98)	
13	**1**: Ph	H	6-F	1:2:3	30	**9l** (74)	
14	**1'**: Ph	Me	H	1:1:3	2	**9m** (71)	
15	**1'**: 4-F-C_6H_4	Me	H	1:1:3	3	**9n** (58)	
16	**1'**: 4-Cl-C_6H_4	Me	H	1:1:3	4	**9o** (69)	
17	**1'**: 4-Me-C_6H_4	Me	H	1:1:3	2	**9p** (71)	

[a] The reaction was carried out in glacial acetic acid at reflux temperature in air.

[b] The yield was based on the amount of the alkene **1** or **1'** used.

oxidized by the Mn(III)-enolate complex **A** to give the expected tertiary carbon radical **B** which underwent the SET oxidation under the conditions to produce the tertiary cation **I** (Scheme 5). Although Parsons reported the product yield of **9a** and **10a** as 39% and 41%, respectively,[10c] the reaction conditions (*heat at 60 °C* in an ultrasonic bath in the presence of $KMnO_4$ as the co-oxidant) are different from those of ours (*heat under reflux*) (compared to Table 3, entry 2), therefore, it is obvious that the cyclization is prone to occur at the enolic ketocarbonyl group in the cation **I** and a thermodynamically more stable angular product **9** would be exclusively produced in our case.

Gratifyingly, the 4-hydroxyquinolinone analogue,[14] such as 4-hydroxy-5,6,7,8-tetrahydroquinolin-2(1*H*)-one (**11**), 1-benzyl-4-hydroxy-5,6-dihydropyridin-2(1*H*)-one (**13**),[4a] 4-hydroxy-2*H*-chromen-2-one (**15**),[10h] and 4-hydroxy-6-methyl-2*H*-pyran-2-one (**17**) also underwent the oxidative cyclization with alkenes **1** to afford the corresponding 2,3-dihydrofuro[3,2-*c*]pyridin-4-ones **12**, **14** and furo[3,2-*c*]pyran-4-ones **16a-c**, **18** in moderate to high yields (Table 4, entries 1-6). The cyclization only took place at the enolic ketocarbonyl group, and no products cyclized at the amide and ester carbonyl groups were isolated. Dimedones **19**

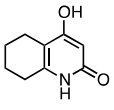
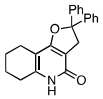
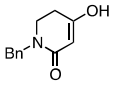
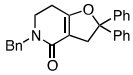
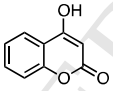
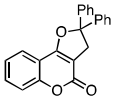
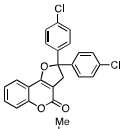
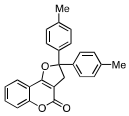
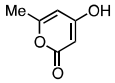
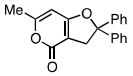
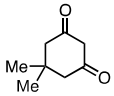
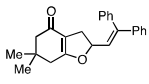
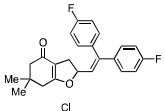
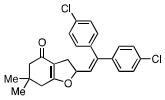
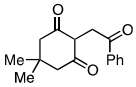
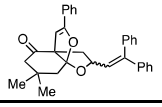


Scheme 5. Reaction pathway for the formation of **9** and/or **10**.

and **21** were also subjected to the reaction with butadienes **2'** and the corresponding benzofuran-4(5*H*)-ones **20a-c**[17] and propellane **22**[12] were obtained (Table 4, entries 7-10). In this case, the reaction with butadienes **1'** led to 1,2-addition similar to the reaction of **1'** with quinolinone **2** in Scheme 4.

2.4. Mn(III)-mediated oxidation of a mixture of alkenes 2 and 3-substituted quinolinones 6[14]

Table 4
Mn(III)-mediated oxidation of substituted ethenes **1** and **1'** in the presence of quinolinone-related compounds[a]

Entry	Alkene **1** or **1'**/Ar	Reagent	Time/min	Product (yield/%)[b]
1	**1**: Ph	 **11**	1	 **12** (53)
2	**1**: Ph	 **13**	1	 **14** (52)
3	**1**: Ph	 **15**	5	 **16a** (89)
4	**1**: 4-Cl-C_6H_4	**15**	2	 **16b** (87)
5	**1**: 4-Me-C_6H_4	**15**	4	 **16c** (82)
6	**1**: Ph	 **17**	1	 **18** (56)
7	**1'**: Ph	 **19**	1	 **20a** (78)
8	**1'**: 4-F-C_6H_4	**19**	1	 **20b** (55)
9	**1'**: 4-Cl-C_6H_4	**19**	1	 **20c** (63)
10[c]	**1'**: Ph	 **21**	1	 **22** (58)[d]

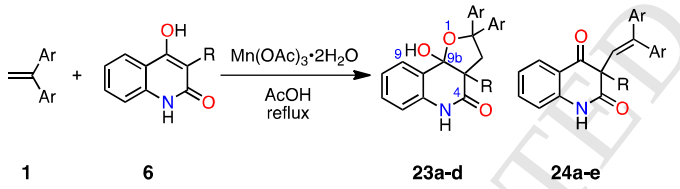
[a] The reaction was heated under reflux in air at the molar ratio of alkene **1** or **1'**:reagent:$Mn(OAc)_3 \cdot 2H_2O$ = 1:2:3.
[b] The yield was based on the amount of the alkene **1** or **1'** used.
[c] The molar ratio of the alkene **1'**:reagent **21**:$Mn(OAc)_3 \cdot 2H_2O$ = 1:1:2.
[d] A 7:1 diastereomixture based on the ^1H NMR spectrum.

Table 5
Mn(III)-mediated oxidation of 1,1-disubstituted ethenes **1** in the presence of 3-substituted quinolinones **6**[a]

Entry	Alkene **1**	Quinolinone **6**	Molar ratio	Temperature	Time	Product (yield/%)[b]	
	Ph	Ar	**1**:**6**:$Mn(OAc)_3$•$2H_2O$	°C	min		
1	Ph	Me	1:2:3	reflux	1.5	**23a** (56)	**24a** (25)[c]
2	Ph	Me	1:2:3	reflux	2.5	**23a** (48)	**24a** (37)[c]
3	Ph	Me	1:2:3	reflux	30		**24a** (79)
4	Ph	Me	1:2:3	80	24 h		**24a** (97)
5	Ph	Me	1:2:2:2[d]	23	3.5 h	**23a** (72)	**24a** (trace)[c]
6	Ph	Pr	1:2:3	reflux	2	**23b** (51)	**24b** (32)[c]
7	Ph	Bu	1:2:3	reflux	6	**23c** (36)	**24c** (27)[c]
8	4-Cl-C_6H_4	Bu	1:2:3	reflux	30	**23c** (trace)	**24c** (78)[c]
9	4-Me-C_6H_4	Me	1:2:3	reflux	2	**23d** (35)	**24d** (37)[c]
10	Ph	Me	1:2:3	reflux	0.5		**24e** (55)

[a] The reaction was carried out under heated conditions in air except for entry 5.
[b] The yield was based on the amount of the alkene **1** used.
[c] The yield was calculated by crude NMR analysis.
[d] $Cu(OAc)_2$ was added as a co-oxidant and the reaction was conducted under an argon atmosphere.

We were next interested in the Mn(III)-mediated oxidation of quinolinones having a substituent at the 3-position since the deprotonation could not occur at the intermediate cation **I** stage in Scheme 5. The oxidation of a mixture of alkene **1** (Ar = Ph) and 3-substituted quinolinone **6** (R = Me) with $Mn(OAc)_3$•$2H_2O$ was then carried out at the reflux temperature. After 1.5 minutes, the dark-brown color of the reaction mixture turned transparent and we recognized the complete consumption of the oxidant, and the absence of the oxidant was finally confirmed by a KI-starch test paper. After the usual work-up, furo[3,2-*c*]quinolinone hemiacetal **23a** was obtained along with the vinyl-substituted quinolinone **24a** (Scheme 6 and Table 5, entry 1). Since the hemiacetal **23a** might be unstable under the high temperature conditions, an additional heating for 1 minute was conducted after the oxidation. As a result, we found that the yield of **23a**

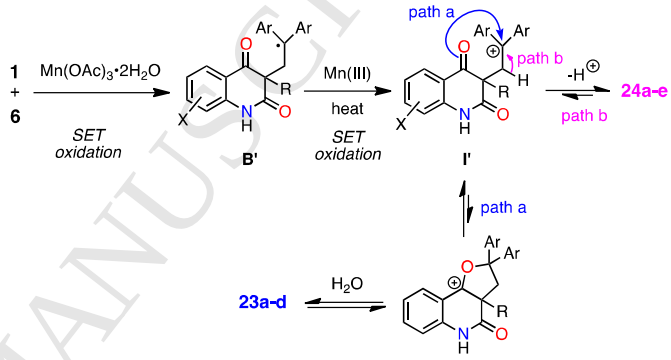


Scheme 6. Mn(III)-mediated oxidation of a mixture of 1,1-disubstituted ethenes **1** and 3-substituted quinolinones **6**.

decreased and that of **24a** increased (entry 2). Further additional heating led to only the production of **24a** (entry 3), and the oxidation at 80 °C for 24 hours quantitatively gave **24a** (entry 4). These results suggested that the pathway of the hemiacetal **23a** and the vinyl-substituted quinolinone **24a** were in equilibrium under the stated oxidation conditions and the additional heating after the oxidation resulted in the thermodynamically stable **24a** (Scheme 7). Interestingly, the use of $Cu(OAc)_2$ as a co-oxidant[3c] at 23 °C led to the exclusive production of the hemiacetal **23a** (entry 5).

3. Conclusions

We obtained various type of quinolinone derivatives from the simple Mn(III)-based reaction depending on the reaction conditions. The Mn(III)-catalyzed aerobic oxidation of alkenes **1** in the presence of 4-hydroxyquinolin-2(1*H*)-ones **2** formed the bis(hydroperoxyethyl)quinolinones **3**, and the use of an excess



Scheme 7. Oxidation pathway for the formation of **23** and **24**.

amount of the Mn(III) catalyst in the case of 2-(1-arylvinyl)thiophene led to the azatrioxa[4.4.3]propellanes **4** and **5**. A similar reaction using 3-substituted quinolinones **6** afforded the endoperoxides **7** and/or hydroperoxides **8** depending on the bulkiness of the substituent at the 3-position of **6**. The oxidation of alkenes **1** with Mn(III)-quinolinone enolate complexes **A** at elevated temperature furnished the 3,5-dihydrofuro[3,2-*c*]quinolin-4-ones **9a-l** in high yields, and the reaction with conjugated butadienes **1'** proceeded in a 1,2-fashion to afford vinyl-substituted dihydrofuroquinolinones **9m-p**. The quinolinone analogues **11**, **13**, **15**, **17**, and **21** also produced the corresponding 2,3-dihydrofuro[3,2-*c*]pyridin-4-ones **12**, **14**, furo[3,2-*c*]pyran-4-ones **16**, **18**, benzofuran-4(5*H*)-ones **20**, and propellane **22** in moderate to high yields. The hemiacetals **23** and vinylquinolinones **24** could be synthesized depending on the reaction conditions. The new quinolinone derivatives and the related compounds obtained in the reactions will be screened for their biological activities such as antimalarial, insecticidal, bactericidal, cytotoxic, and antifeeding activities.

4. Experimental section

4.1. Measurements

Melting points were taken using a micromelting point apparatus and are uncorrected. The NMR spectra were recorded at 300 or 500 MHz for ^1H and 75 or 125 MHz for ^{13}C, with tetramethylsilane as the internal standard. The chemical shifts are reported in δ values (ppm) and the coupling constants in Hz. The IR spectra were measured in $CHCl_3$ or KBr and expressed in cm^{-1}. The EI MS spectra were obtained by a gas chromatograph-mass spectrometer at an ionizing voltage of 70 eV. The high-

resolution mass spectra and the elemental analyses were performed at the Instrumental Analysis Center, Kumamoto University, Kumamoto, Japan.

4.2. Materials

Manganese(II) acetate tetrahydrate, $Mn(OAc)_2$•$4H_2O$, was purchased from Wako Pure Chemical Ind., Ltd. Manganese(III) acetate dihydrate, $Mn(OAc)_3$•$2H_2O$, was prepared according to the modified method described in the literature.[18,19] 4-Hydroxy-2-quinolinones **2**, **6**, 4-hydroxy-5,6,7,8-tetrahydroquinolin-2(1*H*)-one (**11**)[20] and 1-benzyl-4-hydroxy-5,6-dihydropyridin-2(1*H*)-one (**13**)[4a] were also prepared according to the methods reported in the literature. The 1,1-disubstituted alkenes **1** were prepared by the Grignard reaction of the corresponding acetophenones with arylmagnesium bromides followed by dehydration. 4-Hydroxy-2*H*-chromen-2-one (**15**), 4-hydroxy-6-methyl-2*H*-pyran-2-one (**17**), and dimedone (**19**) were purchased from Tokyo Kasei Co., Ltd., and Wako Pure Chemical Ind., Ltd., respectively, and used as received. The 2-(2-oxoethenyl)cyclohexane-1,3-dione **21** was prepared by the reaction of dimedone (**19**) with α-bromoacetophenone.

4.3. Mn(III)-catalyzed aerobic oxidation of a mixture of alkenes 2 and 4-hydroxyquinolin-2(1*H*)-ones

To a mixture of 1,1-diphenylethene **1** (Ar^1 = Ar^2 = Ph) (179.0 mg; 1 mmol) and quinolinone **2** (R = Me) (362.7 mg; 2.1 mmol) in glacial acetic acid (25 mL), $Mn(OAc)_3$•$2H_2O$ (131.9 mg; 0.53 mmol) was added. The mixture was stirred at 23 °C in air for 4 h, and then the reaction was quenched by adding water (40 mL) to the reaction mixture. The aqueous solution was extracted five times with CH_2Cl_2 (10 mL x 5) and the combined extracts were washed twice with water, a saturated aqueous solution of sodium hydrogencarbonate, dried over anhydrous sodium sulfate, and concentrated to dryness. The residue was separated by silica gel flash column chromatography eluting with CH_2Cl_2-hexane (7:3 v/v), giving bis(hydroperoxide) **3a** (210.1 mg; 71% yield based on the alkene **1** used) (Table 1, entry 6). Molar ratio and reaction times of other aerobic oxidation are shown in Table 1 and 2. The products **3-5**, **7**, and **8** were further purified by recrystallization from an appropriate solvent for the analytical sample, and their physical data are given below.

*4.3.1. 3,3-Bis(2-hydroperoxy-2,2-diphenylethyl)-1-methylquinoline-2,4(1H,3H)-dione (**3a**: R = Me, Ar^1 = Ar^2 = Ph).* Colorless microcrystals (from MeOH), m.p. 134-135 °C. IR (KBr): ν 3400-3050 (OOH), 1668, 1624 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.14 (2H, s, OO*H*), 7.52-7.46 (1H, m, arom *H*), 7.24-7.10 (11H, m, arom *H*), 6.97-6.80 (12H, m, arom *H*), 3.66 (4H, s, CH_2 x 2), 3.00 (3H, s, NMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.3, 174.5 (*C*=O), 142.8 (2C, arom *C*), 142.5 (arom *C*), 141.8 (2C, arom *C*), 136.1 (C-7), 127.7 (8C, arom *C*H), 127.5 (C-5), 127.3 (8C, arom *C*H), 126.5 (2C, arom *C*H), 126.3 (2C, arom *C*H), 122.8 (C-6), 121.2 (arom *C*), 114.2 (C-8), 86.6 (2C, *C*OOH x 2), 53.8 (C-3), 49.1 (2C, *C*H_2 x 2), 29.9 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{38}H_{32}NO_4$ 566.2331 (M-OOH); found 566.2332.

*4.3.2. 3,3-Bis[2,2-bis(4-chlorophenyl)-2-hydroperoxyethyl]-1-methylquinoline-2,4(1H,3H)-dione (**3b**: R = Me, Ar^1 = Ar^2 = 4-Cl-C_6H_4).* Colorless microcrystals (from CH_2Cl_2/hexane), m.p. 215-216 °C. IR (KBr): ν 3440-3100 (OOH), 1670,1629 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.20 (2H, s, OO*H*), 7.63-7.58 (1H, m, arom *H*), 7.29-7.01 (10H, m, arom *H*), 6.91-6.76 (9H, m, arom *H*), 3.60 (2H, d, *J* = 14.1 Hz, *H*CH), 3.54 (2H, d, *J* = 14.1 Hz, HC*H*), 3.16 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.5, 174.6 (*C*=O), 142.0 (2C, arom *C*), 141.0 (3C, arom *C*), 139.3 (2C, arom *C*), 136.8 (C-7), 133.6 (4C, arom *C*), 128.1 (8C, arom *C*H), 127.9 (C-5), 127.8 (4C, arom *C*H), 127.6 (4C, arom *C*H), 123.0 (C-6), 120.9 (arom *C*), 114.2 (C-8), 85.9 (2C, *C*OOH x 2), 53.7 (C-3), 48.6 (*C*H_2 x 2), 29.9 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{38}H_{30}Cl_4NO_6$ 736.0827 (M+H); found 736.0839. CCDC reference number, CCDC 217001.

*4.3.3. 3,3-Bis[2-hydroperoxy-2,2-bis(4-methylphenyl)ethyl]-1-methylquinoline-2,4(1H,3H)-dione (**3c**: R = Me, Ar^1 = Ar^2 = 4-Me-C_6H_4).* Pale yellow microcrystals (from MeOH), m.p. 134-136 °C. IR (KBr): ν 3300-3000 (OOH), 1668, 1600 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.15 (2H, s, OO*H*), 7.51-7.46 (1H, m, arom *H*), 7.13-6.96 (10H, m, arom *H*), 6.88-6.77 (5H, m, arom *H*)、6.61-6.58 (4H, m, arom *H*), 3.61 (4H, s, CH_2 x 2), 3.08 (3H, s, NCH_3), 2.28 (6H, s, Me x 2), 2.04 (6H, s, Me x 2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.7, 174.8 (*C*=O), 142.4 (2C, arom *C*), 140.3 (1C, arom *C*), 138.6 (2C, arom *C*), 136.7 (2C, arom *C*), 136.5 (2C, arom *C*), 135.8 (C-7), 128.4 (8C, arom *C*), 127.8 (6C, arom *C*), 127.0 (C-5), 126.4 (C-4), 126.1, 121.7 (2C, arom *C*), 121.0 (arom *C*), 114.0 (C-8), 86.4 (2C, *C*OOH x 2), 53.7 (C-3), 49.2 (*C*H_2 x 2), 29.7 (Me), 20.9 (Me x 2), 20.6 (Me x 2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{42}H_{40}NO_4$ 622.2957 (M-OOH); found 622.2924.

*4.3.4. 1-Ethyl-3,3-bis(2-hydroperoxy-2,2-diphenylethyl)quinoline-2,4(1H,3H)-dione (**3d**: R = Et, Ar^1 = Ar^2 = Ph).* Yellow microcrystals (from MeOH), m.p. 138-140 °C. IR (KBr): ν 3300-3057(OOH), 1666, 1608 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.39 (2H, s, OO*H*), 7.47-7.41 (1H, m, arom *H*), 7.34-7.09 (13H, m, arom *H*), 6.94-6.71 (10H, m, arom *H*), 3.79 (2H, q, *J* = 6.7 Hz, CH_2), 3.66 (4H, s, CH_2 x 2), 0.88 (3H, t, *J* = 6.7 Hz, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.6, 175.4 (*C*=O), 143.7 (2C, arom *C*), 141.1 (2C, arom *C*), 140.9 (arom *C*), 135.7 (C-7), 128.2 (2C, arom *C*), 128.1 (2C, arom *C*), 127.9 (4C, arom *C*), 127.7 (C-5), 127.6, 127.3, 127.1 (3C, arom *C*), 127.0 (4C, arom *C*), 126.5 (arom *C*), 126.3 (4C, arom*C*), 122.6 (C-6), 121.4 (arom *C*), 113.9 (C-8), 86.7 (2C, *C*OOH x 2), 53.7 (C-3), 49.4 (2C, *C*H_2 x 2), 38.3 (*C*H_2), 11.4 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{39}H_{34}NO_4$ 580.2488 (M-OOH); found 580.2499.

*4.3.5. 1-Benzyl-3,3-bis(2-hydroperoxy-2,2-diphenylethyl)quinoline-2,4(1H,3H)-dione (**3e**: R = Bn, Ar^1 = Ar^2 = Ph).* Yellow microcrystals (from MeOH), m.p. 105-110 °C. IR (KBr): ν 3400-3026 (OOH), 1650, 1638 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.40 (2H, s, OO*H*), 7.98-6.57 (29H, m, arom *H*), 5.04 (2H, s, CH_2), 3.74 (4H, s, CH_2 x 2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.5, 177.3 (*C*=O), 143.9 (3C, arom *C*), 141.4, 140.7(2C, arom *C*), 135.9 (arom *C*), 135.3 (C-7), 129.1 (C-5), 128.1 (6C, arom *C*H), 128.1 (arom *C*H), 127.7 (2C, arom *C*H), 127.3 (arom *C*H), 127.1 (2C, arom *C*H), 127.0 (6C, arom *C*H), 126.8 (2C, arom *C*H), 126.5 (2C, arom *C*H), 126.2 (3C, arom *C*H), 122.7 (C-6), 121.2 (arom *C*), 115.2 (C-8), 86.7 (2C, *C*OOH x 2), 54.0 (*C*H_2), 49.6 (C-3), 49.1 (*C*H_2 x 2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{44}H_{38}NO_6$ 676.2699 (M+H); found 676.2701.

*4.3.6. 1-Benzyl-3,3-bis[2,2-bis(4-chlorophenyl)-2-hydroperoxyethyl]quinoline-2,4(1H,3H)-dione (**3f**: R = Bn, Ar^1 = Ar^2 = 4-Cl-C_6H_4).* Yellow microcrystals (from MeOH), m.p. 115-118 °C. IR (KBr): ν 3400-3060 (OOH), 1662, 1597 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.43 (2H, s, OO*H*), 7.88-6.59 (25H, m, arom *H*), 5.11 (2H, s, CH_2), 3.68 (2H, d, *J* = 13.6 Hz, *H*CH), 3.59 (2H, d, *J* = 13.6 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.3, 177.1 (*C*=O), 141.8 (4C, arom *C*), 141.2, 138.3 (2C, arom *C*), 136.1 (C-7), 135.5 (arom *C*), 133.7 (2C, arom *C*), 133.5 (2C, arom *C*), 131.3 (2C, arom *C*H), 129.2 (C-5), 128.7

(2C, arom *C*H), 128.4 (4C, arom *C*H), 128.2 (arom CH), 128.0 (2C, arom *C*H), 127.7 (4C, arom *C*H), 127.2 (4C, arom *C*H), 127.0 (2C, arom *C*H), 122.9 (C-6), 115.2 (C-8), 86.1 (2C, *C*OOH x 2), 53.9 (*C*H_2), 49.2 (C-3), 49.0 (*C*H_2 x 2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{44}H_{34}Cl_4NO_6$ 812.1140 (M+H); found 812.1149.

*4.3.7. 1-Benzyl-3,3-bis[2-hydroperoxy-2,2-bis(4-methylphenyl)ethyl]quinoline-2,4(1H,3H)-dione (**3g**: R = Bn, Ar^1 = Ar^2 = 4-Me-C_6H_4).* Pale yellow microcrystals (from MeOH), m.p. 58-60 °C. IR (KBr): ν 3400-3000 (OOH), 1665, 1654 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.39 (2H, s, OO*H*), 7.71-6.39 (25H, m, arom *H*), 5.10 (2H, s, CH_2Ph), 3.70 (4H, s, CH_2 x 2), 2.28 (6H, s, Me x 2), 1.95 (6H, s, Me x 2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.3, 177.6 (*C*=O), 141.6 (arom *C*), 141.2 (2C, arom *C*), 137.6 (2C, arom *C*), 136.8 (2C, arom *C*), 136.4 (2C, arom *C*), 136.0 (arom *C*), 135.1 (C-7), 130.2 (arom *C*H), 129.1 (2C, arom *C*H), 128.8 (2C, arom *C*H), 128.7 (4C, arom *C*H), 127.7 (C-6), 127.5 (4C, arom *C*H), 126.9 (2C, arom *C*H), 126.1 (arom *C*), 126.6 (2C, arom *C*H), 126.2 (4C, arom *C*), 121.4 (C-5), 115.2 (C-8), 86.6 (2C, *C*OOH x 2), 54.0 (C-3), 49.6 (2C, *C*H_2 x 2), 49.3 (*C*H_2), 20.9 (2C, Me x 2), 20.5 (2C, Me x 2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{48}H_{44}NO_4$ 698.3270 (M-OOH); found 698.3268.

*4.3.8. 3,4-Dihydro-10-methyl-3,3,12,12-tetraphenyl-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one (**4a**: R = Me, Ar^1 = Ar^2 = Ph).* Colorless microcrystals (from CH_2Cl_2/hexane), m.p. 134-135 °C. IR (KBr): ν 1658 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82-7.79 (2H, m, arom *H*), 7.58-6.92 (21H, m, arom *H*), 6.77-6.72 (1H, m, arom *H*), 3.33 (3H, s, Me), 3.25 (1H, d, *J* = 12.9 Hz, *H*CH), 3.10 (1H, d, *J* = 14.4 Hz, *H*CH), 2.80 (1H, d, *J* = 12.9 Hz, HC*H*), 2.54 (1H, d, *J* = 14.4 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.7 (*C*=O), 148.2, 145.2, 143.9, 142.5, 142.4 (arom *C*), 136.3, 132.4, 130.1, 128.4 (2C), 128.3 (2C), 128.2 (2C), 127.8 (2C), 127.6 (2C), 127.3, 127.1, 126.9, 126.6 (2C), 126.4 (2C), 126.0 (2C), 118.4, 113.4 (arom *C*H), 117.1, 114.6 (C-5a and C-10a), 87.1 (C-3), 84.3 (C-12), 53.4 (C-4a), 43.2 (*C*H_2), 38.3 (*C*H_2), 30.3 (Me) ppm. Anal. Calcd for $C_{38}H_{31}NO_4 \cdot 1/4H_2O$: C, 80.05; H,5.57; N, 2.46. Found: C, 80.13; H, 5.63; N, 2.52. CCDC reference number, CCDC 218561.

*4.3.9. 3,3,12,12-Tetrakis(4-chlorophenyl)-3,4-dihydro-10-methyl-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one (**4b**: R = Me, Ar^1 = Ar^2 = 4-Cl-C_6H_4).* Yellow microcrystals (from MeOH), m.p. 115-116 °C. IR (KBr): ν 1651 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58-6.75 (20H, m, arom *H*), 3.33 (3H, s, Me), 3.27 (1H, d, *J* = 12.2 Hz, *H*CH), 3.10 (1H, d, *J* = 14.0 Hz, *H*CH), 2.80 (1H, d, *J* = 12.2 Hz, HC*H*), 2.54 (1H, d, *J* = 14.0 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.6 (*C*=O), 148.2 (2C), 145.2 (2C), 143.9 (2C), 142.4 (2C, arom *C*), 136.3, 128.4 (2C), 128.3 (2C), 127.9, 127.7 (2C), 127.5 (2C), 126.9, 126.6 (2C), 126.4 (2C), 126.0 (4C), 118.4, 113.4 (arom *C*H), 117.1, 114.6 (C-5a and C-10a), 87.1 (C-3), 84.3 (C-12), 53.5 (C-4a), 43.2, 38.4 (*C*H_2), 30.3 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{38}H_{28}Cl_4NO_4$ 702.0772 (M+H); found 702.0768.

*4.3.10. 3,4-Dihydro-3,3,12,12-tetrakis(4-methylphenyl)-10-methyl-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one (**4c**: R = Me, Ar^1 = Ar^2 = 4-Me-C_6H_4).* Pale yellow microcrystals (from MeOH), m.p. 174-175 °C. IR (KBr): ν 1672 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75-6.64 (20H, m, arom *H*), 3.29(3H, s, Me), 3.17 (1H, d, *J* = 13.0 Hz, *H*CH), 3.04 (1H, d, *J* = 11.0 Hz, *H*CH), 2.83 (1H, d, *J* = 13.0 Hz, HC*H*), 2.48 (1H, d, *J* = 11.0 Hz, HC*H*), 2.37 (3H, s, Me), 2.26 (3H, s, Me), 2.20 (3H, s, Me), 2.17 (3H, s, Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.9 (*C*=O), 148.3, 136.8 (2C), 136.6 (2C), 136.2 (2C), 136.1 (2C, arom *C*), 136.6, 130.2, 129.3 (2C), 128.9 (2C), 128.7 (2C), 128.4 (2C), 128.4 (2C), 128.2 (2C), 126.6 (2C), 125.4 (2C), 118.2, 113.3 (arom *C*H), 117.0, 114.5 (C-5a and C-10a), 92.0 (C-3), 87.0 (C-12), 51.0 (C-4a), 39.1, 38.4 (*C*H_2), 30.3 (Me), 21.0 (Me), 20.9 (Me x 3) ppm. FAB HRMS (acetone/NBA): calcd for $C_{42}H_{40}NO_4$ 622.2957 (M+H); found 622.2958.

*4.3.11. 10-Ethyl-3,4-dihydro-3,3,12,12-tetraphenyl-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one (**4d**: R = Et, Ar^1 = Ar^2 = Ph).* Yellow microcrystals (from MeOH), m.p. 159-161 °C. IR (KBr): ν 1674 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82-7.79 (1H, m, arom *H*), 7.61-7.57 (4H, m, arom *H*), 7.51-7.45 (4H, m, arom *H*), 7.37-7.28 (4H, m, arom *H*), 7.19-7.00 (8H, m, arom *H*), 6.89-6.85 (2H, m, arom *H*), 6.75-6.70 (1H, m, arom *H*), 4.09-3.83 (2H, m, CH_2), 3.24 (1H, d, *J* = 12.5 Hz, *H*CH), 3.10 (1H, d, *J* = 14.5 Hz, *H*CH), 2.78 (1H, d, *J* = 12.5 Hz, HC*H*), 2.46 (1H, d, *J* = 14.5 Hz, HC*H*), 1.49 (3H, t, *J* = 7.0 Hz, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.6 (*C*=O), 147.3, 145.5, 144.2, 142.8, 142.2 (arom *C*), 136.2, 132.4, 130.1, 128.7, 128.4 (2C), 128.3 (2C), 127.9, 127.7 (2C), 127.6 (2C), 126.9, 126.6 (2C), 126.2 (2C), 125.9 (2C), 125.8 (2C), 118.0, 113.5 (arom *C*H), 117.0, 114.9 (C-5a and C-10a), 87.0 (C-3), 84.2 (C-12), 53.6 (C-4a), 42.6, 38.6, 38.2 (*C*H_2), 13.3 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{39}H_{34}NO_4$ 580.2488 (M+H); found 580.2487.

*4.3.12. 3,4-Dihydro-3,3,12,12-tetraphenyl-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one (**4h**: R = H, Ar^1 = Ar^2 = Ph).* Yellow microcrystals (from MeOH), m.p. 190-192 °C. IR (KBr): ν 3200-2940 (NH), 1660 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82-7.79 (2H, m, arom *H*), 7.57-7.44 (5H, m, arom *H*), 7.35-6.91 (15H, m, arom *H*), 6.75-6.70 (2H, m, arom *H*), 5.76 (1H, s, N*H*), 3.25 (1H, d, *J* = 13.2 Hz, *H*CH), 3.15 (1H, d, *J* = 14.4 Hz, *H*CH), 2.84 (1H, d, *J* = 13.2 Hz, HC*H*), 2.57 (1H, d, *J* = 14.4 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.9 (*C*=O), 146.3, 145.1, 142.4, 142.1, 137.6 (arom *C*), 135.9, 132.4, 130.1 (2C), 128.4, 128.3 (2C), 128.2 (2C), 128.0, 127.8 (2C), 127.6, 126.9, 126.6 (2C), 126.3 (2C), 126.0 (2C), 125.9 (2C), 119.5, 115.9 (arom *C*H), 116.3, 112.7 (C-5a and C-10a), 87.5 (C-3), 84.4 (C-12), 53.2 (C-4a) , 43.0, 37.9 (*C*H_2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{37}H_{30}NO_4$ 552.2175 (M+H); found 552.2092.

*4.3.13. 3,4-Dihydro-10-methyl-3,12-diphenyl-3,12-bis(2-thienyl)-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one (**4i**: R = Me, Ar^1 = Ph, Ar^2 = 2-thienyl).* The diastereomixture could not be purified and the physical data of one of the diasteromers are shown as follows. Colourless needles (from EtOAc/hexane), m.p. 185-187 °C (decompd). IR ($CHCl_3$): ν 1672 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78-6.76 (20H, m, arom *H*), 3.40 (1H, d, *J* = 13.0 Hz, *H*CH), 3.33 (3H, s, Me), 3.05 (1H, d, *J* = 15.0 Hz, *H*CH), 2.90 (1H, d, *J* = 13.0 Hz, HC*H*), 2.52 (1H, d, *J* = 15.0 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.9 (*C*=O), 150.2, 147.3, 145.4, 143.4, 141.8 (arom *C*), 136.4, 128.2 (2C), 128.0 (2C), 127.7, 127.4 (2C), 126.7, 126.6, 126.3, 126.2 (2C), 126.1, 125.9, 125.8 (2C), 125.7, 118.6, 113.4 (arom *C*H), 117.0, 114.7 (C-5a and C-10a), 84.7 (C-3), 83.0 (C-12), 53.3 (C-4a) , 45.3, 39.6 (*C*H_2), 30.3 (Me) ppm. FAB HRMS (acetone/NBA/NaI): calcd for $C_{34}H_{27}NO_4S_2Na$ 600.1279 (M+Na); found 600.1284.

*4.3.14. 3,12-Bis(4-fluorophenyl)-3,4-dihydro-10-methyl-3,12-bis(2-thienyl)-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one(**4j**: R = Me, Ar^1 = 4-F-C_6H_4, Ar^2 = 2-thienyl).* The diastereomixture could not be purified and the physical data of one of the diasteromers are shown as follows. Amorphous. IR

(CHCl$_3$): ν 1670 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.72-6.74 (18H, m, arom *H*), 3.33 (3H, s, Me), 3.08 (1H, d, *J* = 15.0 Hz, *H*CH), 2.98 (1H, d, *J* = 12.6 Hz, *H*CH), 2.80 (1H, d, *J* = 12.6 Hz, HC*H*), 2.58 (1H, d, *J* = 15.0 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 192.9 (*C*=O), 160.8, 160.3, 149.6, 148.1, 146.8, 141.4, 138.9 (arom *C*), 136.7, 136.5, 128.7, 128.6, 128.4 (2C), 127.7 (2C), 127.1, 126.7, 126.4 (2C), 126.3 (4C), 118.8, 113.6 (arom *C*H), 116.9, 114.7 (C-5a and C-10a), 84.4 (C-3), 82.9 (C-12), 53.6 (C-4a) , 44.5, 39.4 (*C*H$_2$), 30.3 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{34}H_{26}F_2NO_4S_2$ 614.1271 (M+H); found 614.1269.

*4.3.15. 3,4-Dihydro-3,12-bis(4-methylphenyl)-10-methyl-3,12-bis(2-thienyl)-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one (**4k**: R = Me, Ar^1 = 4-Me-C$_6$H$_4$, Ar^2 = 2-thienyl).* The diastereomixture could not be purified and the physical data of one of the diasteromers are shown as follows. Amorphous. IR (CHCl$_3$): ν 1670 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.76-6.71 (18H, m, arom *H*), 3.30 (3H, s, Me), 3.26 (1H, d, *J* = 12.9 Hz, *H*CH), 3.06 (1H, d, *J* = 15.0 Hz, *H*CH), 2.90 (1H, d, *J* = 12.9 Hz, HC*H*), 2.56 (1H, d, *J* = 15.0 Hz, HC*H*), 2.29 (3H, s, Me), 2.19 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 193.1 (*C*=O), 147.5, 138.1, 137.4, 136.9, 136.5, 136.4, 136.4 (arom *C*), 136.3, 129.2, 128.9, 128.4, 128.2, 128.1, 126.7 (2C), 126.0 (2C), 125.9 (2C), 125.7 (2C), 125.5 (2C), 118.4, 113.5 (arom CH), 117.0, 114.7 (C-5a and C-10a), 84.6 (C-3), 82.9 (C-12), 53.7 (C-4a), 45.0, 39.6 (*C*H$_2$), 30.3 (N-*C*H$_3$), 21.0, 20.9 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{36}H_{32}NO_4S_2$ 606.1773 (M+H); found 606.1782.

*4.3.16. 3,4-Dihydro-6-methyl-3,12-diphenyl-3,12-bis(2-thienyl)-10b,4a-(epoxyethano)-1,2-dioxino[4,3-c]quinolin-5(6H)-one (**5i**: R = Me, Ar^1 = Ph, Ar^2 = 2-thienyl).* The diastereomixture could not be purified and the physical data of one of the diasteromers are shown as follows. Colourless needles (from EtOAc/hexane), m.p. 244-246 °C (decompd). IR (CHCl$_3$): ν 1662 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ □□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□, 7.49-6.70 (19H, m, arom *H*), 3.07 (3H, s, Me), 3.23 (1H, d, *J* = 14.7 Hz, *H*CH), 3.18 (1H, d, *J* = 15.0 Hz, *H*CH), 2.90 (1H, d, *J* = 15.0 Hz, HC*H*), 2.33 (1H, d, *J* = 14.7 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 169.2 (*C*=O), 149.7, 148.7, 147.2, 146.9, 144.8, 143.3, 130.7, 130.6, 128.6, 128.3, 128.2, 128.0, 127.9, 127.7, 127.5, 127.3, 126.7, 126.5, 126.4, 126.3, 126.2, 126.0, 125.9, 125.8, 125.5, 125.4, 125.3, 125.1, 124.9, 123.6, 123.5, 120.7, 120.5, 114.4, 106.8 (C-10b), 86.9 (C-3), 83.5 (C-12), 51.5 (C-4a), 46.2 (C-4), 40.2 (C-13), 29.8 (N-*C*H$_3$) ppm. FAB HRMS (acetone/NBA/NaI): calcd for $C_{34}H_{27}NO_4S_2Na$ 600.1279 (M+Na); found 600.1357.

*4.3.17. 3,12-Bis(4-fluorophenyl)-3,4-dihydro-6-methyl-3,12-bis(2-thienyl)-10b,4a-(epoxyethano)-1,2-dioxino[4,3-c]quinolin-5(6H)-one (**5j**: R = Me, Ar^1 = 4-F-C$_6$H$_4$, Ar^2 = 2-thienyl).* The diastereomixture could not be purified and the physical data of one of the diasteromers are shown as follows. Colourless needles (from EtOAc/hexane), m.p. 172-173 °C. IR (CHCl$_3$): ν 1668 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.00-6.44 (18H, m, arom *H*), 3.45 (2H, s, C*H*$_2$), 3.18 (1H, d, *J* = 14.4 Hz, *H*CH), 2.95 (3H, s, Me), 2.30 (1H, d, *J* = 14.4 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 169.0 (*C*=O), 163.7, 160.3, 149.4, 146.8, 139.2 (arom *C*), 130.8, 130.7, 128.7, 128.6, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 126.8, 126.5, 126.4, 126.3, 126.2, 126.0, 123.8 (arom *C*H), 120.5 (arom *C*), 115.6, 115.3, 115.2, 114.9, 114.5, 114.4, 114.1 (arom *C*H), 106.5 (C-10b), 86.5 (C-3), 83.2 (C-12), 51.7 (C-4a), 46.2 (C-4), 40.2 (C-13), 29.8 (N-*C*H$_3$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{34}H_{26}F_2NO_4S_2$ 614.1271 (M+H); found 614.1288.

*4.3.18. 3,4-Dihydro-3,12-bis(4-methylphenyl)-6-methyl-3,12-bis(2-thienyl)-10b,4a-(epoxyethano)-1,2-dioxino[4,3-c]quinolin-5(6H)-one (**5k**: R = Me, Ar^1 = 4-Me-C$_6$H$_4$, Ar^2 = 2-thienyl).* The diastereomixture could not be purified and the physical data of one of the diasteromers are shown as follows. Amorphous. IR (CHCl$_3$): ν1652 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.01-7.98 (1H, m, arom *H*), 7.67-6.94 (15H, m, arom *H*), 6.76-6.72 (1H, m, arom *H*), 6.53-6.47 (1H, m, arom *H*), 3.45 (2H, s, C*H*$_2$), 3.20 (1H, d, *J* = 15.0 Hz, *H*CH), 2.91 (3H, s, Me), 2.32 (1H, d, *J* = 15.0 Hz, HC*H*), 2.27 (3H, s, Me), 2.20 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 169.3 (*C*=O), 149.9, 140.5, 137.7, 137.0 (arom *C*), 130.6, 129.2, 128.9, 128.1, 127.9, 126.6, 126.4, 126.3, 126.2, 126.1, 125.9, 125.8, 125.7, 125.2, 123.6, 120.8, 114.4 (arom *C*H), 106.5 (C-10b), 86.9 (C-3), 83.4 (C-12), 51.5 (C-4a), 46.1 (C-4), 40.2 (C-13), 29.8 (N-*C*H$_3$), 21.1 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{36}H_{31}NO_4S_2$ 606.1773 (M+H); found 606.1765.

*4.3.19. 4,4a,6,10b-Tetrahydro-10b-hydroxy-3,3-diphenyl-4a-methyl-1,2-dioxino[4,3-c]quinolin-5(3H)-one (**7a**: R = Me, Ar = Ph).* Colorless microcrystals (from CH$_2$Cl$_2$/hexane), m.p. 195 °C (decomp). IR (KBr): ν 3382-2929 (OH and NH), 1678 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 10.1 (1H, s, N*H*), 7.73-7.70 (1H, m, arom *H*), 7.57 (1H, br. S, arom *H*), 7.46-7.43 (3H, m, arom *H*), 7.34-7.01 (8H, m, arom *H*), 6.77-6.75 (1H, m, arom *H*), 3.47 (1H, br s, O*H*), 3.34 (1H, br, *H*CH), 2.75 (1H, d, *J* = 13.5 Hz, HC*H*), 1.10 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 171.2 (*C*=O), 144.8, 142.0 (2C, arom *C*), 136.7 (2C, arom *C*), 130.4 (arom *C*), 128.0 (4C, arom *C*H), 127.2 (2C, arom *C*H), 127.1 (arom *C*), 127.0 (2C, arom *C*H), 126.3 (arom *C*H), 125.4 (2C, arom *C*H), 122.0 (arom *C*H), 99.0 (C-10b), 84.4 (C-3), 44.0 (C-4a), 30.3 (*C*H$_2$), 22.3 (Me) ppm. Anal. Calcd for $C_{24}H_{21}NO_4$: C, 74.40; H, 5.46; N, 3.62. Found: C, 74.20; H, 5.41; N, 3.59.

*4.3.20. 4,4a,6,10b-Tetrahydro-10b-hydroxy-3,3-diphenyl-4a-propyl-1,2-dioxino[4,3-c]quinolin-5(3H)-one (**7b**: R = Pr, Ar = Ph).* Colorless microcrystals (from MeOH), m.p. 145-147 °C. IR (KBr): ν 3392-2873 (OH and NH), 1662 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 10.02 (1H, s, NH), 7.70-7.66 (1H, m, arom *H*), 7.49-7.40 (2H, m, arom *H*), 7.32-6.98 (10H, m arom *H*), 6.70-6.68 (1H, m, arom *H*), 3.79 (1H, d, *J* = 13.1 Hz, *H*CH), 2.59 (1H, d, *J* = 13.1 Hz, HC*H*), 2.50 (1H, s, O*H*), 1.52 (2H, t, *J* = 5.8 Hz, C*H*$_2$), 1.09-0.91 (2H, m, C*H*$_2$), 0.68 (3H, t, *J* = 7.0 Hz, Me) ppm. ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 169.8 (*C*=O), 145.4, 142.0, 136.9 (arom *C*), 130.6, 128.1, 127.3, 127.0, 126.7, 125.4, 122.0 (arom *C*H), 121.1 (arom *C*), 114.3 (arom *C*H), 98.7 (C-10b), 84.4 (C-3), 47.4 (C-4a), 39.4, 34.6, 16.5 (*C*H$_2$), 14.4 (Me) ppm. FAB HRMS (acetone/NBA): calcd for$C_{26}H_{26}NO_4$ 416.1862 (M+H); found 416.1862.

*4.3.21. 4a-Butyl-4,4a,6,10b-Tetrahydro-10b-hydroxy-3,3-diphenyl-1,2-dioxino[4,3-c]quinolin-5(3H)-one (**7c**: R = Bu, Ar = Ph).* The product **7c** could not be separated from **8c** by silica gel chromatography. Yellow microcrystals (from CH$_2$Cl$_2$/hexane), m.p.148-152 °C. IR (KBr): ν 3600-2900 (OH and NH), 1658 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 10.05 (1H, s, N*H*), 7.81-6.61 (14H, m, arom *H*), 5.43 (1H, s, O*H*), 3.81 (1H, d, *J* = 14.1 Hz, *H*CH), 2.73 (1H, d, *J* = 14.1 Hz, HC*H*), 2.13 (2H, m, C*H*$_2$), 1.34-1.16 (4H, m, C*H*$_2$ x 2), 0.74 (3H, t, *J* = 6.9 Hz, Me) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 171.6 (*C*=O), 143.5, 141.9, 140.3 (arom *C*), 135.9, 128.5, 127.8, 127.6, 127.4, 126.6, 123.3, 115.0 (arom *C*H), 99.5 (C-10b), 86.0 (C-3), 48.3 (C-4a), 36.7, 35.2, 25.3, 23.1 (*C*H$_2$), 13.8 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{27}H_{28}NO_4$ 430.2018 (M+H); found 430.2021.

*4.3.22. 4,4a,6,10b-Tetrahydro-10b-hydroxy-4a,3,3-triphenyl-1,2-dioxino[4,3-c]quinolin-5(3H)-one (**7d**: R = Ar = Ph).* The

product **7d** could not be separated from **8d** by silica gel chromatography. Colorless microcrystals (from MeOH), m.p. 151 °C. IR (KBr): ν 3400-2940 (OH and NH), 1697, 1659 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 10.32 (1H, s, N*H*), 7.52-7.01 (17H, m, arom *H*), 6.83-6.80 (1H, m, arom *H*), 6.44-6.41 (1H, m, arom *H*), 5.27 (O*H*), 4.16 (1H, d, *J* = 14.1 Hz, *H*CH), 3.25 (1H, d, *J* = 14.1 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4 (*C*=O), 143.4, 142.2, 140.3, 139.8 (arom *C*), 131.2, 129.1, 128.5, 128.3, 128.2, 128.0, 127.8, 127.6, 127.4, 127.0, 126.9, 126.7, 126.6, 126.4, 126.1, 123.7, 123.5, 116.5 (arom *C*H), 118.7 (arom *C*), 99.0 (C-10b), 86.0 (C-3), 52.4 (C-4a), 36.4 (CH_2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{29}H_{24}NO_4$ 450.1705 (M+H); found 450.1650.

*4.3.23. 3,3-Bis(4-chlorophenyl)-4,4a,6,10b-tetrahydro-10b-hydroxy-4a-methyl-1,2-dioxino[4,3-c]quinolin-5(3H)-one (**7e**: R = Me, Ar = 4-Cl-C_6H_4).* Pale yellow microcrystals (from MeOH), m.p. 155-157 °C. IR (KBr): ν 3400-3060 (OH), 3300-2900 (NH), 1678 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 10.0 (1H, s, N*H*), 7.85-7.76 (1H, m, arom *H*), 7.49-6.89 (10H, m, arom *H*), 6.79-6.77 (1H, m, arom *H*), 5.45 (1H, s, O*H*), 3.54 (1H, d, *J* = 13.1 Hz, *H*CH), 2.78 (1H, d, *J* = 13.1 Hz, HC*H*), 1.15 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2 (*C*=O), 141.6 (arom *C*), 139.0 (2C, arom *C*), 135.6 (arom *C*), 130.5 (2C, arom *C*), 129.3 (2C, arom *C*H), 128.0 (C-5), 126.9 (2C, arom *C*H), 126.2 (2C, arom *C*H), 126.1 (acom *C*H), 125.8 (2C, arom *C*H), 122.3 (arom *C*H), 114.8 (arom *C*H), 98.0 (C-10b), 83.1 (C-3), 52.6 (C-4a), 43.0 (CH_2), 21.4 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{24}H_{20}Cl_2NO_4$ 456.0769 (M+H); found 456.0779.

*4.3.24. 4,4a,6,10b-Tetrahydro-10b-hydroxy-3,3-bis(4-methylphenyl)-4a-methyl-1,2-dioxino[4,3-c]quinolin-5(3H)-one (**7f**: R = Me, Ar = 4-Me-C_6H_4).* The product **7f** could not be separated from **8f** by silica gel chromatography. Orange microcrystals (from MeOH), m.p. 192-193 °C; IR (KBr): ν 3400-2877 (OH and NH), 1683 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 10.2 (1H, s, N*H*), 7.54-6.64 (12H, m, arom *H*), 5.22 (1H, s, O*H*), 3.84 (1H, d, *J* = 14.4 Hz, *H*CH), 2.75 (1H, d, *J* = 14.4 Hz, HC*H*), 2.15, 2.11 (6H, s, Me x 2), 1.53 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.2 (*C*=O), 141.2, 140.9, 138.2, 137.8, 136.1, 136.0 (arom *C*), 129.9, 129.0 128.9, 128.1, 128.0, 127.4, 127.3, 126.9, 126.2, 126.6, 124.8, 122.9 (arom *C*H), 99.5 (C-10b), 86.0 (C-3), 52.4 (C-4a), 45.4 (CH_2), 20.8 (Me), 20.7 (Me), 8.4 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{24}NO_2$ 382.1807 (M-OOH); found 382.1847.

*4.3.25. 3-(2-Hydroperoxy-2,2-diphenylethyl)-3-propylquinoline-2,4(1H,3H)-dione (**8b**: R = Pr, Ar = Ph).* The product **8b** could not be separated from **7b** by silica gel chromatography. Colorless microcrystals (from MeOH), m.p. 145-147 °C. IR (KBr): ν 3392-2873 (OOH and NH), 1680, 1662 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CHCl_3$): δ 9.68 (1H, s, N*H*), 9.33 (1H, s, OO*H*), 7.81-6.62 (14H, m, arom *H*), 3.58 (1H, d, *J* = 14.7 Hz, *H*CH), 3.51 (1H, d, *J* = 14.7 Hz, HC*H*), 2.12-2.08 (2H, t, *J* = 5.2 Hz, CH_2), 1.23-0.96 (2H, m, CH_2), 0.792 (3H, t, *J* = 7.0 Hz, Me) ppm. ^{13}C NMR (75 MHz, $CHCl_3$): δ 197.2, 176.9 (*C*=O), 143.5, 140.4, 136.2 (arom *C*), 127.5, 127.4, 127.0, 126.5, 126.3, 125.5, 120.1, 119.8 (arom *C*H), 86.0 (*C*OOH), 57.2 (C-3), 39.3, 36.0, 16.7 (CH_2), 14.5 (Me) ppm. FAB HRMS (acetone/NBA): calcd for$C_{26}H_{26}NO_4$ 416.1862 (M+H); found 416.1862.

*4.3.26. 3-Butyl-3-(2-hydroperoxy-2,2-diphenylethyl)quinoline-2,4(1H,3H)-dione (**8c**: R = Bu, Ar =Ph).* The product **8c** could not be separated from **7c** by silica gel chromatography. Yellow microcrystals (from CH_2Cl_2/hexane), m.p. 148-152 °C. IR (KBr): ν 3500-2770 (OOH and NH), 1680, 1658 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.65 (1H, s, N*H*), 9.17 (1H, s, OO*H*), 7.81-6.61 (14H, m, arom *H*), 3.59 (1H, d, *J* = 14.7 Hz, *H*CH), 3.53 (1H, d, *J* = 14.7 Hz, HC*H*), 1.78-1.16 (6H, m, CH_2 x 3), 0.74, (3H, t, *J* = 7.0 Hz, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.4, 176.9 (*C*=O), 143.5, 141.9, 140.9, 140.3 (arom *C*), 135.9, 128.5, 127.8, 127.6, 127.4, 127.3, 127.2, 126.6, 126.3, 125.7, 123.3, 116.3 (arom *C*H), 86.9 (*C*OOH), 57.0 (C-3), 45.5, 44.8, 25.3, 22.8 (CH_2 x 4), 13.5 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{27}H_{28}NO_4$ 430.2018 (M+H); found 430.2021.

*4.3.27. 3-(2-Hydroperoxy-2,2-diphenylethyl)-3-phenylquinoline-2,4(1H,3H)-dione (**8d**: R = Ar =Ph).* The product **8d** could not be separated from **7d** by silica gel chromatography. Colorless microcrystals (from CH_2Cl_2/hexane), m.p. 151 °C. IR (KBr): ν 3400-2940 (OOH and NH), 1697, 1659 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.87 (1H, s, N*H*), 9.02 (1H, s, OO*H*), 7.77-7.74 (1H, m, arom *H*), 7.65-7.63 (1H, m, arom *H*), 7.52-7.01 (17H, m, arom *H*), 4.10 (1H, d, *J* = 14.1 Hz, *H*CH), 3.91 (1H, d, *J* = 14.1 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.3, 175.3 (*C*=O), 143.8, 141.0, 138.1, 135.7 (arom *C*), 129.1, 128.5, 128.3, 128.2, 128.0, 127.8, 127.6, 127.4, 127.0, 126.9, 126.7, 126.6, 126.4, 126.1, 123.7, 123.5, 115.5 (arom *C*H), 120.5 (arom *C*), 87.2 (*C*OOH), 60.8 (C-3), 42.6 (CH_2). FAB HRMS (acetone/NBA): calcd for $C_{29}H_{24}NO_4$ 450.1705 (M+H); found 450.1650.

*4.3.28. 3-[2-Hydroperoxy-2,2-bis(4-methylphenylethyl)]-3-methylquinoline-2,4(1H,3H)-dione (**8f**: R = Me, Ar = 4-Me-C_6H_4).* The product **8f** could not be separated from **7f** by silica gel chromatography. IR (KBr): ν 3400-2877 (OOH and NH), 1683 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.80 (1H, s, N*H*), 9.43 (1H, s, OO*H*), 7.83-6.67 (12H, m, arom *H*), 3.75 (1H, d, *J* = 14.4 Hz, *H*CH), 3.70 (1H, d, *J* = 14.47 Hz, HC*H*), 2.04 (3H, s, Me), 1.93 (3H, s, Me), 1.28 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.8, 175.5 (*C*=O), 141.1, 141.0, 140.5, 137.0, 136.6, 136.5 (arom *C*), 135.9, 130.2, 129.1, 128.9, 128.7, 128.5, 128.3, 127.4, 123.5, 122.5 (arom *C*H), 84.0 (*C*OOH), 53.4 (C-3), 44.6 (CH_2), 22.1 (Me), 21.0 (Me), 16.2 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{24}NO_2$ 382.1807 (M-OOH); found 382.1847.

4.4. Approach to the interconversion between 3a and 4a

The bis(hydroperoxide) **3a** (R = Me, Ar^1 = Ar^2 = Ph) and the propellane **4a** (R = Me, Ar^1 = Ar^2 = Ph) (0.1 mmol), respectively, were stirred in glacial acetic acid (10 mL) at room temperature in the absence and the presence of $Mn(OAc)_3$ (0.1 mmol) for 4 hours. After the usual work-up, the bis(hydroperoxide) **3a** and the propellane **4a** were recovered in 99% and 91%, respectively, in the absence of the oxidant, while **3a** in 48% and **4a** in 83% recoveries in the presence of $Mn(OAc)_3$. No isolable products were obtained from both reactions.

4.5. Mn(III)-mediated oxidation of alkenes in the presence of 4-hydroxyquinolin-2(1*H*)-ones and the related substrates at reflux temperature

A mixture of 1,1-diphenylethene **1** (Ar = Ph) (181.3 mg; 1 mmol), 4-hydroxy-2-quinolinone **2** (R = Me, X = H) (351.4 mg; 2 mmol), and $Mn(OAc)_3$•$2H_2O$ (814.4 mg; 3 mmol) in glacial acetic acid (25 mL) was heated under reflux until the brown color of Mn(III) disappeared (normally for 3 minutes). The solvent was removed in vacuo and water (25 mL) was added to the reaction mixture. The aqueous solution was then extracted three times with dichloromethane (20 mL). The combined extracts were washed with a saturated aqueous solution of sodium hydrogencarbonate, dried over anhydrous sodium sulfate, and then concentrated to dryness. The residue was separated on silica gel TLC developed with 5% methanol/dichloromethane, giving

the products **9a** (310.6 mg; 87%) and **10a** (23.6 mg; 7%) (Table 3, entry 2). Molar ratio and reaction times of other oxidation are shown in Tables 3, 4, and 5. The products were further purified by recrystallization from an appropriate solvent for the analytical sample, and their physical data are given below.

*4.5.1. 3,5-Dihydro-5-methyl-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9a**: R = Me, X = H, Ar = Ph).*[10c] Yield 87% (Table 3, entry 2).

*4.5.2. 3,9-Dihydro-9-methyl-2,2-diphenylfuro[2,3-b]quinolin-4(2H)-one (**10a**: R = Me, Ar = Ph).*[10c] Yield 7% (Table 3, entry 2).

*4.5.3. 5-Ethyl-3,5-dihydro-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9b**: R = Et, X = H, Ar = Ph).* Yield 73% (Table 3, entry 3). Colorless microcrystals (from MeOH), m.p. 181-182 °C. IR (KBr): ν 1666 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ8.01-7.99 (1H, m, arom *H*), 7.59-7.25 (13H, m, arom *H*), 4.35 (2H, q, *J* = 7.0 Hz, C*H*$_2$), 3.97 (2H, s, C*H*$_2$), 1.33 (3H, t, *J* = 7.0 Hz, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ161.0, 160.6 (*C*=O and *C*=C), 144.5, 139.8 (arom *C*), 130.9, 128.3, 127.7, 125.8, 123.3, 121.4, 114.5 (arom *C*H), 112.8, 107.7 (arom *C*), 95.7 (C-2), 42.8, 36.9 (*C*H$_2$ x 2), 13.1 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{25}H_{22}NO_2$ 368.1651 (M+H); found 368.1688.

*4.5.4. 3,5-Dihydro-2,2-diphenyl5-propylfuro[3,2-c]quinolin-4(2H)-one (**9c**: R = Pr, X = H, Ar = Ph).* Yield 76% (Table 3, entry 4). Colorless needles (from MeOH), m.p. 161 °C. IR (KBr): ν 1662 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ8.07-7.98 (1H, m, arom *H*), 7.57-7.11 (13H, m, arom *H*), 4.23 (2H, m, C*H*$_2$), 3.97 (2H, s, C*H*$_2$), 1.76-1.55 (2H, m, $CH_2CH_2CH_3$), 1.03 (3H, t, *J* = 7.3 Hz, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ161.0, 160.9 (*C*=O and *C*=C), 144.6, 140.0 (arom *C*), 130.8, 128.4, 128.3, 127.7, 127.5, 125.8, 123.2, 114.6 (arom *C*H), 121.4, 112.7, 107.6 (arom *C*), 95.6 (C-2), 43.5, 42.8, 21.1 (*C*H$_2$), 11.4 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{24}NO_2$ 382.1807 (M+H); found 382.1834.

*4.5.5. 5-Benzyl-3,5-Dihydro-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9d**: R = Bn, X = H, Ar = Ph).* Yield 85% (Table 3, entry 5). Pale orange microcrystals (from MeOH), m.p. 221 °C. IR (KBr): ν 1656 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.99-7.97 (1H, m, arom *H*), 7.53-7.17 (18H, m, arom *H*), 5.52 (2H, br. s, C*H*$_2$), 4.04 (2H, s, C*H*$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ161.5, 161.3 (*C*=O and *C*=C), 144.5, 140.2, 136.8 (arom *C*), 131.1, 128.7, 128.5, 127.9, 127.1, 126.5, 125.8, 123.2, 121.9, 115.6 (arom *C*H), 112.7 107.4 (arom *C*), 95.9 (C-2), 45.6, 42.7 (*C*H$_2$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{30}H_{24}NO_2$ 430.1807 (M+H); found 430.1815.

*4.5.6. 3,5-Dihydro-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9e**: R = X = H, Ar = Ph).* Yield 73% (Table 3, entry 6). Colorless microcrystals (from MeOH), m.p. 242 °C (decompd). IR (KBr): ν 3200-2740 (N*H*), 1654 (C=O) cm^{-1}.^{1}H NMR (300 MHz, DMSO-d_6): δ11.5 (1H, s, NH), 8.30-7.79 (2H, m, arom *H*), 7.64-7.22 (12H, m, arom *H*), 3.80 (2H, C*H*$_2$) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ161.1, 160.5 (*C*=O and *C*=C), 144.5, 139.7 (arom *C*), 131.0, 128.8, 1.28.5, 127.7, 127.2, 126.2, 125.3, 121.9, 121.7, 115.6 (arom *C*H), 110.6, 107.8 (arom *C*), 95.2 (C-2), 41.6 (*C*H$_2$) ppm. Anal. Calcd for $C_{23}H_{17}NO_2 \cdot 2H_2O$: C, 79.29; H, 5.21; N, 4.02. Found: C, 79.45; H, 4.87; N, 4.04.

*4.5.7. 2,2-Bis(4-chlorophenyl)-3,5-dihydro-5-methylfuro[3,2-c]quinolin-4(2H)-one (**9f**: R = Me, X = H, Ar = 4-Cl-C_6H_4).* Yield 87% (Table 3, entry 7). Colorless microcrystals (from EtOH), m.p. 194-195 °C. IR (KBr): ν 1645 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.94-7.92 (1H, m, arom *H*), 7.59-7.57 (1H, m, arom *H*), 7.41-7.25 (10H, m, arom H), 3.90 (2H, s, C*H*$_2$), 3.69 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ160.8, 160.7 (*C*=O and *C*=C), 142.5, 140.8, 134.0 (arom *C*), 131.2, 128.7, 127.3, 122.9, 121.8, 114.7 (arom *C*H), 112.3, 107.4 (arom *C*), 94.7 (C-2), 42.6 (*C*H$_2$), 29.1 (Me) ppm. Anal. Calcd for $C_{24}H_{17}Cl_2NO_2$: C, 68.26; H, 4.06; N, 3.32. Found: C, 68.29; H, 4.17; N, 3.59.

*4.5.8. 2,2-Bis(4-chlorophenyl)-3,9-dihydro-9-methylfuro[2,3-b]quinolin-4(2H)-one (**10f**: R = Me, X = H, Ar = 4-Cl-C_6H_4).* Yield 12% (Table 3, entry 7). Colorless microcrystals (from MeOH), m.p. 124-125 °C. IR (KBr): ν 1589 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ8.43 (1H, d, *J* = 7.8 Hz, arom H), 7.63-7.28 (11H, m, arom H), 3.95 (2H, s, C*H*$_2$), 3.82 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ191.7 (*C*=O), 159.5 (*C*=C), 141.5, 138.6, 134.3 (arom *C*), 131.3, 128.7, 127.2, 126.4, 123.4, 114.3 (arom *C*H), 98.3 (C-9a), 95.0 (C-2), 40.9 (*C*H$_2$), 31.5 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{24}H_{18}Cl_2NO_2$ 422.0715 (M+H); found 422.0720.

*4.5.9. 3,5-Dihydro-2,2-bis(4-methylphenyl)-5-methylfuro[3,2-c]quinolin-4(2H)-one (**9g**: R = Me, X = H, Ar = 4-Me-C_6H_4).* Yield 93% (Table 3, entry 8). Colorless microcrystals (from MeOH), m.p. 148-150 °C. IR (KBr): ν 1640 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.907.88 (1H, m, arom *H*), 7.43-7.08 (11H, m, arom H), 3.93 (2H, s, C*H*$_2$), 3.58 (3H, s, Me), 2.25 (6H, s, Me x 2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ160.7, 160.6 (*C*=O and *C*=C), 141.4, 140.2, 137.1 (arom *C*), 130.6, 128.7, 125.4, 122.6, 121.2, 114.1 (arom *C*H), 112.1, 107.3 (arom *C*), 95.5 (C-2), 42.3 (*C*H$_2$), 28.6 (Me), 20.6 (2C, Me x 2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{24}NO_2$ 382.1807 (M+H); found 382.1852.

*4.5.10. 3,5-Dihydro-8-methyl-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9h**: R = H, X = 8-Me, Ar = Ph).* Yield 44% (Table 3, entry 9). Colorless microcrystals (from MeOH), m.p. 269-270 °C. IR (KBr): ν 3000-2729 (NH), 1654 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ11.5 (1H, s, N*H*), 7.89-7.35 (13H, m, arom *H*), 3.88 (2H, s, C*H*$_2$), 2.59 (3H, Me) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ161.0, 160.3 (*C*=O and *C*=C), 144.6, 137.8, 130.9 (arom *C*), 132.3, 128.5, 127.7, 125.3, 121.2, 115.5 (arom *C*H), 110.5, 107.7 (arom *C*), 95.0 (C-2), 41.6 (*C*H$_2$), 20.4 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{24}H_{20}NO_2$ 354.1494 (M+H); found 354.1505.

*4.5.11. 3,5-Dihydro-6-methyl-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9i**: R = H, X = 6-Me, Ar = Ph).* Yield 67% (Table 3, entry 10). Only slightly soluble in organic solvents. Colorless microcrystals (from MeOH), m.p. 263-267 °C. IR (KBr): ν 3300-3000 (NH), 1670 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ10.7 (1H, s, N*H*), 7.90-7.18 (13H, m, arom *H*), 3.83 (2H, s, C*H*$_2$), 2.39 (3H, Me) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ169.5, 165.4 (*C*=O and *C*=C), 144.4, 140.2, 139.1, 138.0, 137.0, 133.7, 132.2, 128.8, 128.4, 127.7, 127.6, 127.1, 126.1, 125.2, 124.4, 124.0, 121.9, 121.5, 119.8, 97.9, 95.1, 41.5, 17.6 ppm. FAB HRMS (acetone/NBA): calcd for $C_{24}H_{20}NO_2$ 354.1494 (M+H); found 354.1495.

*4.5.12. 8-Chloro-3,5-dihydro-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9j**: R = H, X = 8-Cl, Ar = Ph).* Yield 58% (Table 3, entry 11). Colorless microcrystals (from MeOH), m.p. 281-283 °C. IR (KBr): ν 3150-2721 (NH), 1680 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ11.6 (1H, s, NH), 7.96 (1H, m, arom *H*), 7.61-7.58 (5H, m, arom *H*), 7.35-7.28 (7H, m, arom *H*), 3.81 (2H, C*H*$_2$) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ160.2, 160.1 (*C*=O and *C*=C), 144.4, 138.4, 125.8 (arom C), 131.0, 128.5, 127.7, 125.3, 121.0, 117.5 (arom *C*H), 111.7, 109.0 (arom

C), 95.6 (C-2), 41.5 (*C*H_2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{23}H_{17}ClNO_2$ 374.0948 (M+H); found 374.0952.

*4.5.13. 6-Chloro-3,5-dihydro-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9k**: R = H, X = 6-Cl, Ar = Ph).* Yield 99% (Table 3, entry 12). Only slightly soluble in organic solvents. Colorless microcrystals (from MeOH), m.p. 254-255 °C. IR (KBr): ν 3200-3000 (NH), 1660 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.8 (1H, s, NH), 7.95-7.28 (13H, m, arom H), 3.85 (2H, s, CH_2) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.0, 160.2 (*C*=O and *C*=C), 144.3, 136.0, 131.3 (arom *C*), 128.6, 127.2, 126.2, 125.4, 122.6, 121.3, 118.9 (arom *C*H), 112.4, 108.9 (arom *C*), 95.8 (C-2), 41.5 (*C*H_2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{23}H_{17}ClNO_2$ 374.0948 (M+H); found 374.0945.

*4.5.14. 8-Fluoro-3,5-dihydro-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9l**: R = H, X = 8-F, Ar = Ph).* Yield 74% (Table 3, entry 13). Colorless microcrystals (from MeOH), m.p. 248 °C (decompd). IR (KBr): ν 3180-2900 (NH), 1670 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.6 (1H, s, N*H*), 7.84-7.25 (13H, m, arom *H*), 3.81 (2H, CH_2) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 160.5, 160.2 (*C*=O and *C*=C), 155.3 (C-8), 144.4, 136.5 (arom *C*), 128.5, 127.7, 125.3, 119.3, 117.6, 107.2 (arom *C*H), 109.0 (arom *C*), 95.4 (C-2), 41.6 (*C*H_2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{23}H_{17}FNO_2$ 358.1243 (M+H); found 358.1244.

*4.5.15. 3,5-Dihydro-5-methyl-2-(2,2-diphenylethenyl)furo[3,2-c]quinolin-4(2H)-one (**9m**: R = Me, X = H, Ar = Ph).* Yield 71% (Table 3, entry 14). R_f = 0.16 (Et_2O-hexane 8:2 v/v). Colorless microcrystals (from Et_2O), mp 161 °C. IR (KBr): ν 1659 (C=O), 1638 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78-7.76 (1H, m, arom *H*), 7.57-7.17 (13H, m, arom *H*), 6.29 (1H, d, *J* = 9.5 Hz, =C*H*-), 5.50 (1H, dt, *J* = 7.7, 9.5 Hz, >C*H*-), 3.67 (3H, s, Me), 3.39 (1H, dd, *J* = 15.4, 9.5 Hz, -CH_2-), 3.13 (1H, dd, *J* = 15.4, 7.7 Hz, -CH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.2 (*C*=O), 161.2 (-*C*O=), 146.0 (Ph$_2$>*C*=), 141.1, 140.5, 138.6 (arom *C*), 130.9, 129.9, 128.4, 128.3, 128.1, 128.0, 127.8, 126.5, 123.2, 121.5 (arom *C*H), 114.4 (=*C*H-), 112.6 (arom *C*), 108.0 (>*C*=), 83.5 (>*C*H-), 35.2 (-CH_2-), 29.0 (Me). Anal. calcd for $C_{26}H_{21}NO_2$: C, 82.30; H, 5.58; N, 3.69. Found: C, 82.08; H, 5.53; N, 3.60.

*4.5.16. 2-[2,2-Bis(4-fluorophenyl)ethenyl]-3,5-dihydro-5-methylfuro[3,2-c]quinolin-4(2H)-one (**9n**: R = Me, X = H, Ar = 4-F-C_6H_4).* Yield 58% (Table 3, entry 15). R_f = 0.12 (Et_2O-hexane 8:2 v/v). Colorless microcrystals (from Et_2O), mp 179-181 °C. IR (KBr): ν 1659 (C=O), 1636 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79-7.77 (1H, m, arom *H*), 7.60-7.58 (1H, m, arom *H*), 7.55-6.97 (10H, m, arom *H*), 6.23 (1H, d, *J* = 9.5 Hz, =C*H*-), 5.47 (1H, dt, *J* = 7.7, 9.5 Hz, >C*H*-), 3.70 (3H, s, Me), 3.41 (1H, dd, *J* = 15.4, 9.5 Hz, -CH_2-), 3.13 (1H, dd, *J* = 15.4, 7.7 Hz, -CH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.4, 161.2 (*C*=O and *C*=C), 162.1 (*C*-F), 144.2 (Ph$_2$>*C*=), 140.6, 137.2, 137.1, 134.4, 134.3 (arom *C*), 131.7, 131.6, 131.0, 129.6, 129.5, 126.7, 123.2, 121.6, 115.7, 115.4, 115.1 (arom *C*H), 114.5 (=*C*H-), 112.5 (arom *C*), 107.9 (>*C*=), 83.3 (>*C*H-), 35.2 (-CH_2-), 29.1 (Me) ppm. Anal. calcd for $C_{26}H_{19}F_2NO_2$: C, 75.17; H, 4.61; N, 3.37. Found: C, 75.16; H, 4.73; N, 3.36.

*4.5.17. 2-[2,2-Bis(4-chlorophenyl)ethenyl]-3,5-dihydro-5-methylfuro[3,2-c]quinolin-4(2H)-one (**9o**: R = Me, X = H, Ar = 4-Cl-C_6H_4).* Yield 69% (Table 3, entry 16). R_f = 0.13 (Et_2O-hexane 8:2 v/v). Colorless microcrystals (from Et_2O), mp 123-124 °C. IR (KBr): ν 1659 (C=O), 1636 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76-7.74 (1H, m, arom *H*), 7.59-7.53 (1H, m, arom *H*), 7.43-7.18 (10H, m, arom *H*), 6.27 (1H, d, *J* = 9.5 Hz, =C*H*-), 5.45 (1H, dt, *J* = 7.7, 9.5 Hz, >C*H*-), 3.68 (3H, s, Me), 3.39 (1H, dd, *J* = 15.4, 9.5 Hz, -CH_2-), 3.12 (1H, dd, *J* = 15.4, 7.7 Hz, -CH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.0, 161.1 (*C*=O and -*C*O=), 143.8 (Ph$_2$>*C*=), 140.5, 139.2, 136.5, 134.3 (arom *C*), 131.2, 131.0, 129.0, 128.8, 128.5, 127.4, 123.1, 121.6 (arom *C*H), 114.5 (=*C*H-), 112.4 (arom *C*), 107.8 (>*C*=), 83.0 (>*C*H-), 35.1 (-CH_2-), 29.1 (Me) ppm. Anal. calcd for $C_{26}H_{19}Cl_2NO_2$: C, 69.65; H, 4.27; N, 3.12. Found: C, 69.37; H, 4.18; N, 3.04.

*4.5.18. 3,5-Dihydro-2-[2,2-bis(4-methylphenyl)ethenyl]-5-methylfuro[3,2-c]quinolin-4(2H)-one (**9p**: R = Me, X = H, Ar = 4-Me-C_6H_4).* Yield 71% (Table 3, entry 17). R_f = 0.30 (Et_2O-hexane 8:2 v/v). Colorless microcrystals (from Et_2O), mp 160 °C. IR (KBr): ν 1657 (C=O), 1636 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79-7.76 (1H, m, arom *H*), 7.57-7.52 (1H, m, arom *H*), 7.35-7.08 (10H, m, arom *H*), 6.23 (1H, d, *J* = 9.5 Hz, =C*H*-), 5.52 (1H, dt, *J* = 7.7, 9.5 Hz, >C*H*-), 3.68 (3H, s, N-Me), 3.39 (1H, dd, *J* = 15.4, 9.5 Hz, -CH_2-), 3.12 (1H, dd, *J* = 15.4, 7.7 Hz, -CH_2-), 2.40 (3H, s, Me), 2.33 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.2, 161.2 (*C*=O and -*C*O=), 145.9 (Ph$_2$>*C*=), 140.5, 138.5, 138.0, 137.7, 135.8 (arom *C*), 130.8, 129.9, 129.0, 128.9, 127.8, 125.4, 123.2, 121.5 (arom *C*H), 114.4 (=*C*H-), 112.6 (arom *C*), 108.0 (>*C*=), 83.8 (>*C*H-), 35.2 (-CH_2-), 29.0 (N-Me), 21.3 (Me), 21.1 (Me) ppm. Anal. calcd for $C_{28}H_{25}NO_2$: C, 82.53; H, 6.18; N, 3.44. Found: C, 82.24; H, 6.19; N, 3.33.

*4.5.19. 3,5,6,7,8,9-Hexahydro-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**12**).* Yield 53% (Table 4, entry 1). Only slightly soluble in organic solvents. Colorless cubics (from MeOH), m.p. 281-283 °C. IR (KBr): ν 3200-2900 (NH), 1651 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.05 (1H, s, N*H*), 7.50-7.48 (4H, m, arom *H*), 7.38-7.35 (4H, m, arom *H*), 7.29-7.26 (2H, m, arom *H*), 3.63 (2H, s, CH_2), 2.45 (2H, s, CH_2), 1.69 (6H, s, CH_2) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.4, 160.1 (*C*=O and -*C*O=), 144.9, 144.6 (arom *C*), 128.4, 127.5, 125.3 (arom *C*H), 104.4, 101.3 (arom *C*), 94.1 (C-2), 41.1 (*C*H_2), 26.0 (*C*H_2), 21.34 (*C*H_2), 21.30 (*C*H_2), 20.4 (*C*H_2) ppm. Anal. Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.47; H, 6.16; N, 3.98.

*4.5.20. 5-Benzyl-3,5,6,7-tetrahydro-2,2-diphenylfuro[3,2-c]pyridin-4(2H)-one (**14**).*[4a] Yield 52% (Table 4, entry 2). Yellow oil; IR ($CHCl_3$): ν 1680 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.20 (15H, m, arom *H*), 4.58 (2H, s, Ph-CH_2), 3.67 (2H, t, *J* = 2.2 Hz, H-3), 3.35 (2H, t, *J* = 7.2 Hz, H-6), 2.55 (2H, tt, *J* = 7.2, 2.2 Hz, H-7) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.6, 164.7 (*C*=O and C-7a), 144.8, 137.9 (arom *C*), 128.6, 128.4, 128.0, 127.7, 127.3, 125.7 (arom *C*H), 104.8 (C-3a), 95.4 (C-2), 48.9 (Ph-*C*H_2), 44.3 (C-6), 42.0 (C-3), 23.3 (C-7). FAB HRMS (acetone/NBA): calcd for $C_{26}H_{23}NO_2$ 382.1807 (M+H); found 382.1812.

*4.5.21. 2,3-Dihydro-2,2-diphenyl-4H-furo[3,2-c][1]benzopyran-4-one (**16a**).* Yield 89% (Table 4, entry 3). Colorless microcrystals (from EtOH), m.p. 185-186 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87-7.84 (1H, m, arom *H*), 7.61-7.56 (1H, m, arom *H*), 7.47-7.25 (12H, m, arom *H*), 3.91 (2H, s, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.0 (*C*=O), 155.1 (*C*=C), 143.5 (arom *C*), 132.4, 128.6, 128.2, 125.7, 124.0, 122.7, 117.0 (arom *C*H), 112.4 (C-9a), 101.7 (C-3a), 97.4 (C-2), 41.5 (*C*H_2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{23}H_{17}O_3$ 341.1178 (M+H); found 341.1207.

*4.5.22. 2,2-Bis(4-chlorophenyl)-2,3-dihydro-4H-furo[3,2-c][1]benzopyran-4-one (**16b**).* Yield 87% (Table 4, entry 4). Colorless microcrystals (from EtOH), m.p. 196-197 °C. IR (KBr): ν 1717 (C=O), 1651 (C=C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83-7.81 (1H, m arom *H*), 7.61-7.58 (1H, m arom *H*), 7.41-7.32 (10H, m, arom *H*), 3.84 (2H, s, CH_2) ppm. ^{13}C NMR

(125 MHz, $CDCl_3$): δ164.7 (O-*C*=C), 159.9 (*C*=O), 155.1 (arom *C*-O), 141.6, 134.4 (arom *C*), 132.7, 128.9, 127.1, 124.1, 122.6, 117.1 (arom *C*H), 112.2 (C-9a), 101.5 (C-3a), 96.3 (C-2), 41.3 (CH_2) ppm. Anal. Calcd for $C_{23}H_{14}Cl_2O_3$•1/9H_2O: C, 67.17; H, 3.49. Found: C, 67.03; H, 3.37.

*4.5.23. 2,3-Dihydro-2,2-bis(4-methylphenyl)-4H-furo[3,2-c][1]benzopyran-4-one (**16c**).* Yield 82% (Table 4, entry 5). Colorless needles (from EtOH), m.p. 121 °C. IR (KBr): ν1719 (C=O), 1649 (C=C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ7.83-7.82 (1H, m, arom *H*), 7.57-7.54 (1H, m arom *H*), 7.39-7.37 (1H, m, arom *H*), 7.33-7.31 (5H, m, arom *H*), 7.17-7.15 (4H, m, arom *H*), 3.86 (2H, s, CH_2), 2.33 (6H, s, Me x 2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ165.0 (O-*C*=C), 160.3 (*C*=O), 155.0 (arom C-O), 140.8, 138.0 (arom *C*), 132.3, 129.1, 125.7, 123.9, 122.7, 116.9 (arom *C*H), 112.5 (C-9a), 101.7 (C-3a), 97.6 (C-2), 41.45 (*C*H_2), 21.0 (Me x 2) ppm. Anal. Calcd for $C_{25}H_{20}O_3$•1/8H_2O: C, 81.01; H, 5.51. Found: C, 80.94; H, 5.34.

*4.5.24. 2,3-Dihydro-6-methyl-2,2-diphenyl-4H-furo[3,2-c]pyran-4-one (**18**).* Yield 56% (Table 4, entry 6). Colorless microcrystals (from MeOH), m.p. 151-152 °C. IR (KBr): ν1716 (C=O), 1273 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ7.38-7.29 (10H, m, arom H), 6.08 (1H, s, =C*H*), 3.74 (2H, s, CH_2), 2.26 (3H, s, Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ169.7 (C-7a), 165.5 (*C*=O), 161.7 (C-6), 143.6 (arom *C*), 128.4, 1278.0, 125.6 (arom *C*H), 98.9 (C-3a), 96.8 (C-2), 95.6 (C-7), 40.2 (*C*H_2), 20.4 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{20}H_{17}O_3$ 305.1178 (M+H); found 305.1211.

*4.5.25. 6,6-Dimethyl-2-(2,2-diphenylethenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**20a**).* Yield 78% (Table 4, entry 7). R_f = 0.22 (Et_2O-hexane 5:5 v/v). Colorless needles (from EtOH), mp 139-141 °C. IR (KBr): ν 1647, 1626 (C=C-C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.21 (10H, m, arom *H*), 6.15 (1H, d, *J* = 9.5 Hz, =C*H*-), 5.28 (1H, dt, *J* = 7.7, 9.5 Hz, >C*H*-), 3.01 (1H, dd, *J* = 14.3, 9.5 Hz, -CH_2-, H-3), 2.74 (1H, dd, *J* = 14.3, 7.7 Hz, -CH_2-, H-3), 2.29 (2H, s, -CH_2-, H-5), 2.22 (2H, s, -CH_2-, H-7), 1.11 (3H, s, Me), 1.08 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ194.6 (*C*=O), 176.1 (-*C*O=), 146.1 (arom *C*), 141.0 (Ph_2>*C*=), 138.5 (arom *C*), 129.8, 128.3, 128.2, 128.1, 127.9, 127.8 (arom *C*H), 126.2 (=*C*H-), 111.5 (>*C*=), 83.6 (>*C*H-), 50.9 (-*C*H_2-, C-5), 37.9 (-*C*H_2-, C-7), 34.0 (>*C*<), 32.9 (-*C*H_2-, C-3), 28.7 (2Me) ppm. Anal. calcd for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02. Found: C, 83.43; H, 7.01.

*4.5.26. 2-[2,2-Bis(4-fluorophenyl)ethenyl]-6,6-dimethyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**20b**).* Yield 55% (Table 4, entry 8). R_f = 0.18 (Et_2O-hexane 5:5 v/v). Colorless amorphous. IR (KBr): ν 1634 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-6.96 (8H, m, arom *H*), 6.10 (1H, d, *J* = 9.5 Hz, =C*H*-), 5.240 (1H, dt, *J* = 7.7, 9.5 Hz, >C*H*-), 3.02 (1H, dd, *J* = 14.3, 9.9 Hz, -CH_2-, H-3), 2.73 (1H, dd, *J* = 14.3, 7.7 Hz, -CH_2-, H-3), 2.31 (2H, s, -CH_2-, H-5), 2.24 (2H, s, -CH_2-, H-7), 1.12 (3H, s, Me), 1.01 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ194.6 (*C*=O), 176.0 (-*C*O=), 164.4, 164.2, 161.1, 160.9 (arom *C*), 144.2 (Ph_2>*C*=), 137.1, 134.3, 134.2 (arom *C*), 131.6, 131.5, 129.6, 129.4 (arom *C*H), 126.5 (=*C*H-), 115.6, 115.4, 115.1 (arom *C*H), 111.5 (>*C*=), 83.3 (>*C*H-), 50.9 (-*C*H_2-, C-5), 37.9 (-*C*H_2-, C-7), 34.1 (>*C*<), 33.0 (-*C*H_2-, C-3), 28.7 (2Me) ppm. FAB HRMS (acetone-NBA) calcd for $C_{24}H_{23}F_2O_2$ 380.1666 (M+1). Found 381.1669.

*4.5.27. 2-[2,2-Bis(4-chlorophenyl)ethenyl]-6,6-dimethyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**20c**).* Yield 63% (Table 4, entry 9). R_f = 0.22 (Et_2O-hexane 5:5 v/v). Colorless plates (from EtOH); mp 144-146 °C. IR (KBr): ν 1630 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.14 (8H, m, arom *H*), 6.14 (1H, d, *J* = 9.5 Hz, =C*H*-), 5.23 (1H, dt, *J* = 7.7, 9.5 Hz, >C*H*-), 3.01 (1H, dd, *J* = 14.7, 9.9 Hz, -CH_2-, H-3), 2.73 (1H, dd, *J* = 14.7, 7.7 Hz, -CH_2-, H-3), 2.30 (2H, s, -CH_2-, H-5), 2.23 (2H, s, -CH_2-, H-7), 1.12 (3H, s, Me), 1.09 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.6 (*C*=O), 175.9 (-*C*O=), 143.9, 139.1 (arom *C*), 136.4 (Ph_2>*C*=), 134.3 (arom *C*), 131.2, 129.0, 128.8, 128.5 (arom *C*H), 127.2 (=*C*H-), 111.5 (>*C*=), 83.0 (>*C*H-), 50.9 (-*C*H_2-, C-5), 37.9 (-CH_2-, C-7), 34.1 (>*C*<), 32.9 (-*C*H_2-, C-3), 28.7 (2Me) ppm. Anal. calcd for $C_{24}H_{22}Cl_2O_2$: C, 69.74; H, 5.36. Found: C, 69.44; H, 5.26.

*4.5.28. 7a,3a-(Epoxyethano)-6,7-dihydro-6,6-dimethyl-9-(2,2-diphenylethenyl)-2-phenylbenzofuran-4(5H)-one (**22**).* A 7:1 diastereomixture was obtained and the diasteromers could not be isolated each other. Yield 58% (Table 4, entry 10). R_f = 0.43 (Et_2O-hexane 3:7 v/v). Colorless amorphous. IR ($CHCl_3$): ν1705 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.66-7.07 (15H, m, arom *H*), 5.98 (1H, d, *J* = 8.8 Hz, =C*H*-), 5.24 (1H, s, =C*H*-), 4.70-4.62 (1H, m, >C*H*-), 2.43-2.09 (6H, m, -C$\underline{H_2}$- x 3), 1.05 (3H, s, Me), 0.97 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.9 (*C*=O), 156.5 (Ph-$\underline{C}$O=), 146.2 (acom *C*), 141.8 (Ph_2>$\underline{C}$=), 138.7 (arom *C*), 129.7, 129.1, 128.3, 128.1, 127.8, 126.7 (arom *C*H), 125.5 (Ph_2>C=$\underline{C}$H-), 118.5 (C-7a), 98.0 (C-3), 76.3 (C-9), 67.3 (C-3a), 51.7, 46.8, 43.9 (-$\underline{C}H_2$- x 3), 32.0 (C-6), 29.2, 28.7 (Me) ppm. FAB HRMS (acetone-NBA) calcd for $C_{32}H_{30}O_3$ 462.2195 (M). Found 462.2196.

*4.5.29. 3,3a,5,9b-Tetrahydro-9b-hydroxy-3a-methyl-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**23a**: R = Me, Ar = Ph).* Colorless microcrystals (from MeOH), m.p. 217-225 °C (decompd). IR (KBr): ν 3500-3400 (NH), 3400-3060 (OH), 1649 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.2, (1H, s, NH), 7.92-7.90 (1H, m, arom *H*), 7.54-7.51 (2H, m, arom *H*), 7.32-6.91 (10H, m, arom *H*), 6.64 (1H, m, arom *H*), 3.73 (1H, d, *J* = 11.9 Hz, *H*a-3), 3.42 (1H, s, OH), 2.96 (1H, d, *J* = 11.9 Hz, *H*b-3), 2.07 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ172.1 (*C*=O), 149.6, 147.0 (arom *C*), 135.7, 129.5, 127.8, 127.6, 126.8, 126.7, 126.1, 125.9, 125.5, 125.0, 123.5, 121.9, 102.7, 85.9 (C-2), 53.6 (C-3a), 46.7 (*C*H_2), 18.4 (Me) ppm. Anal. Calcd for $C_{24}H_{21}NO_3$: C, 77.61; H, 5.70; N, 3.77. Found: C, 77.46; H, 5.52; N, 3.80.

*4.5.30. 3,3a,5,9b-Tetrahydro-9b-Hydroxy-2,2-diphenyl-3a-propylfuro[3,2-c]quinolin-4(2H)-one (**23b**: R = Pr, Ar = Ph).* The compound **23b** could not be separated from **24b**. Colorless microcrystals (from MeOH), m.p. 220-222 °C. IR (KBr): ν 3454-2875 (OH and NH), 1689 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.76 (1H, s, N*H*), 7.71-6.66 (14H, m, arom *H*), 3.45 (2H, s, CH_2), 2.08-1.01 (4H, m, CH_2 x 2), 2.01 (1H, s, OH), 0.86 (3H, t, *J* = 7.0 Hz, Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{25}NO_3$ 399.1834 (M); found 399.1836.

*4.5.31. 3a-Butyl-3,3a,5,9b-tetrahydro-9b-hydroxy-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**23c**: R = Bu, Ar = Ph).* The compound **23c** could not be separated from **24c**. Pale yellow microcrystals (from MeOH), m.p. 166 °C. IR (KBr): ν 3400-2900 (OH, NH), 1657 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ9.92 (1H, s, N*H*), 7.61-6.84 (14H, m, arom H), 2.88 (1H, d, *J* = 13.8 Hz, *H*CH), 2.39 (1H, d, *J* = 13.8 Hz, HC*H*), 2.37 (1H, s, O*H*), 1.28-1.07 (6H, m, CH_2 x 3), 0.78 (3H, t, *J* = 7.0 Hz, Me) ppm.

*4.5.32. 2,2-Bis(4-chlorophenyl)-3,3a,5,9b-tetrahydro-9b-hydroxy-3a-methylfuro[3,2-c]quinolin-4(2H)-one (**23d**: R = Me, Ar = 4-Cl-C_6H_4).* The compound **23d** could not be separated from **24d**. Colorless microcrystals (from MeOH); mp 221-223 °C. IR (KBr): ν 3400-2877 (OH and NH), 1697 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ10.7 (1H, s, N*H*), 7.83-6.72 (12H,

m, arm *H*), 3.40 (1H, s, O*H*), 3.53 (1H, d, *J* = 13.0 Hz, *H*CH), 3.17 (1H, d, *J* = 13.0 Hz, HC*H*), 1.36 (3H, s, Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{24}H_{19}Cl_2NO_3$ 439.0742 (M); found 439.0648.

*4.5.33. 3-Methyl-3-(2,2-diphenylethenyl)quinoline-2,4(1H,3H)-dione (**24a**: R = Me, Ar = Ph).* Colorless microcrystals (from MeOH), m.p. 160-161 °C. IR (KBr): ν 3550-3400 (NH), 1701, 1655 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.97 (1H, s, N*H*), 7.73-7.71 (1H, m, arom *H*), 7.39-7.21 (6H, m, arom *H*), 7.02-6.80 (7H, m, arom *H*), 6.42 (1H, s, *H*C=), 1.79 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.9, 175.9 (C=O), 144.5,140.8, 140.7, 138.7 (arom C), 135.6, 131.1, 129.9, 128.1, 127.7,127.6, 127.5, 127.4, 127.2, 123.0 (arom CH), 118.2 (CH=*C*), 116.2 (*C*H=C), 56.3 (C-3), 27.6 (Me) ppm. Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.57; H, 5.31; N, 3.91. FAB HRMS (acetone/NBA): calcd for $C_{29}H_{22}NO_2$ 416.1651 (M+H); found 416.1638.

*4.5.34. 3-(2,2-Diphenylethenyl)-3-propylquinoline-2,4(1H,3H)-dione (**24b**: R = Pr, Ar = Ph).* The compound **24b** could not be separated from **23b**. Colorless microcrystals (from MeOH), m.p. 220-222 °C. IR (KBr): ν 3200-2875 (NH), 1689, 1647 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.90 (1H, s, N*H*), 7.71-6.86 (14H, m, arom *H*), 6.39 (1H, s, *H*C=), 2.37-2.34 (2H, m, CH_2), 1.50-1.00 (2H, m, CH_2), 0.79 (3H, t, *J* = 5.5 Hz, Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{24}NO_2$ 382.1807 (M+H); found 382.1885.

*4.5.35. 3-Butyl-3-(2,2-diphenylethenyl)quinoline-2,4(1H,3H)-dione (**24c**: R = Bu, Ar = Ph).* The compound **24c** could not be separated from **23c**. Pale yellow microcrystals (from MeOH), m.p. 166 °C. IR (KBr): ν 3250-2869 (NH), 1697, 1656 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ9.92 (1H, s, N*H*), 7.71-7.68 (1H, m, arom *H*), 7.34-7.32 (1H, m, arom *H*), 7.26-7.21 (5H, m, arom *H*), 7.01-6.98 (1H, m, arom *H*), 6.92-6.84 (5H, m, arom *H*), 6.73-6.70 (1H, m, arom *H*), 6.40 (1H, s, vinyl *H*), 2.39 (2H, t, *J* = 5.8 Hz), 1.28-1.19 (4H, m, CH_2 x 2), 0.757 (3H, t, *J* = 6.4 Hz, Me) ppm. HRMS (acetone/NBA): calcd for $C_{267}H_{26}NO_2$ 396.1964 (M+H); found 396.1884.

*4.5.36. 3-[2,2-bis(4-Chlorophenyl)ethenyl]-3-methylquinoline-2,4(1H,3H)-dione (**24d**: R = Me, Ar = 4-Cl-C_6H_4).* The compound **24d** could not be separated from **23d**. Colorless microcrystals (from MeOH), m.p. 221-223 °C. IR (KBr): ν 3200-2877 (NH), 1697, 1658 (C=O) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ10.2 (1H, s, N*H*), 7.83-6.72 (12H, m, arom *H*), 6.46 (1H, s, =C*H*), 1.60 (3H, s, Me) ppm. HRMS (acetone/NBA): calcd for $C_{24}H_{18}Cl_2NO_2$ 422.0715 (M+H); found 422.0715.

*4.5.37. 3-[2,2-Bis(4-methylphenyl)ethenyl]-3-methylquinoline-2,4(1H,3H)-dione (**24e**: R = Me, Ar = 4-Me-C_6H_4).* Colorless microcrystals (from MeOH), m.p. 160-161 °C.IR (KBr): ν 3260-2868 (NH), 1678, 1654 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.96 (1H, s, N*H*), 7.66-7.64 (1H, m, arom *H*), 7.39-7.34 (1H, m, arom *H*), 7.19-7.16 (2H, m, arom *H*), 7.05-6.95 (3H, m, arom *H*), 6.80-6.73 (3H, m, arom *H*), 6.66-6.63 (2H, m, arom *H*), 6.39 (1H, s, *H*C=), 2.30 (3H, s, Me), 1.98 (3H, s, Me), 1.78 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ197.0, 176.3 (C=O), 144.3 (*C*=CH), 140.8, 138.0, 137.5, 137.0, 136.0 (arom *C*), 135.2, 130.8, 129.9, 128.7, 128.3, 127.4, 127.0, 122.8 (arom *C*H), 118.3 (arom *C*), 116.0 (*C*H=C), 56.3 (C-3), 27.4, 21.1, 20.9 (Me) ppm. Anal. Calcd for $C_{26}H_{23}NO_2$: C, 81.86; H, 6.08; N, 3.67. Found: C, 81.78; H, 6.01; N, 3.70.

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References and notes

1. For review, see: a) Sainsbury, M. In *Rodd's Chemistry of Carbon Compounds*, 2nd ed.; Coffey, S., Ed.; Elsevier: Amsterdam, 1978; Vol. 4, pp 171–255; b) Grundon, M. F. *Nat. Prod. Rep*. **1984**, *1*, 195–200; c) Grundon, M. F. *Nat. Prod. Rep*. **1985**, *2*, 393–400; d) Grundon, M. F. *Nat. Prod. Rep*. **1987**, *4*, 225–236; e) Grundon, M. F. *Nat. Prod. Rep*. **1988**, *5*, 293–307; f) Grundon, M. F. *The Alkaloids*: *Quinoline Alkaloids Related to Anthranilic Acid*, Academic Press: London, 1988; Vol. 32, pp 341–439; g) Grundon, M. F. *Nat. Prod. Rep*. **1990**, *7*, 131-138; h) Michael, J. P. *Nat. Prod. Rep*. **1999**, *16*, 697–709; h) Larsen, R. D. *Sci. Synth.* **2005**, *15*, 551–660; i) Hradil, P.; Hlavác, J.; Soural, M.; Hajdúch, M.; Kolái, M.; Veceiova, R. *Mini-Rev. Med. Chem*. **2009**, *9*, 696–702; j) Mphahlele, M. J. *J. Heterocycl. Chem*. **2010**, *47*, 1–14.
2. a) Ahsan, M.; Gray, A. I.; Waterman, P. G. *J. Nat, Prod*. **1994**, *57*, 670–672; b) He, J.; Lion, U.; Sattler, I.; Gollmick, F. A.; Grabley, S.; Cai, J.; Meiners, M.; Schünke, H.; Schaumann, K.; Dechert, U.; Krohn, M. *J. Nat, Prod*. **2005**, *58*, 1387–1399; c) Detsi, A.; Bouloumbasi, D.; Prousis, K. C.; Koufaki, M.; Athanasellis, G.; Melagraki, G.; Afantitis, A.; Igglessi-Markopoulou, O.; Kontogiorgis, C.; Hadjipavlou-Litina, D. J. *J. Med. Chem*. **2007**, *50*, 2450–2458; d) Butenschön, I.; Möller, K.; Hänsel, W. *J. Med. Chem*. **2001**, *44*, 1249–1256; e) Marques, E. F.; Bueno, M. A.; Duarte, P. D.; Silva, L. R. S. P.; Martinelli, A. M.; dos Santos, C. Y.; Severino, R. P.; Bruomme, D.; Vieira, P. C.; Corrêa, A. G. *Eur. J. Med. Chem*. **2012**, *54*, 10–21; f) Asahara, M.; Takayama, T.; Tohda, Y.; Nishiwaki, N.; Ariga, M. *Chem. Pharm. Bull*. **2004**, *52*, 1334–1338; g) Liu, X.; Xin, X.; Xiang, D.; Zhang, R.; Kumar, S.; Zhou, K.; Dong, D. *Org. Biomol. Chem.* **2012**, *10*, 5643–5646.
3. For review, see: a) de Klein, W. J. In *Organic Syntheses by Oxidation with Metal Compounbds*, Mijis, W. J.; de Jonge, C. R. H. I., Eds.; Plenum Press: New York, 1986; pp 261–314; b) Iqbal, J.; Bhatia, B.; Nayyar, N. K. *Chem. Rev*. **1994**, *94*, 519–564; c) Snider, B. B. *Chem. Rev*. **1996**, *96*, 339–363; d) Melikyan, G. G. *Org. React*. **1997**, *49*, 427–675; e) Melikyan, G. G. *Aldrichimica Acta* **1998**, *31*, 50–98; f) Demir, A. S.; Emrullahoglu, M. *Current Organic Synthesis* **2007**, *4*, 321–351; g) Pan, X.-Q.; Zou, J.-P.; Zhang, W. *Mol. Divers.* **2009**, *13*, 421–438. h) Burton, J. W. In *Encyclopedia of Radicals in Chemistry, Biology and Materials*, Chatgilialoglu, C.; Studer A., Eds.; Wiley: New York, 2012, pp 901–941.
4. a) Asahi, K.; Nishino, H. *Tetrahedron* **2005**, *61*, 11107–11124; b) Cong, Z.-Q.; Nishino, H. *Synthesis* **2008**, 2686–2694; c) Asahi, K.; Nishino, H. *Synthesis* **2009**, 409–423; d) Tsubusaki, T.; Nishino, H. *Tetrahedron* **2009**, *65*, 9448–9459.
5. For review, see: a) Nishino, H. In *Bioactive Heterocycles I*, Eguchi, S., Ed.; Springer: Berlin, 2006, pp 39–76; b) Zmitek, K.; Zupan, M.; Iskra, J. *Org. Biomol. Chem.* **2007**, *5*, 3895–3908; c) Lesce, M. R.; DellaGreca, M. *Sci. Synth*. **2009**, *38*, 231–274.
6. a) Rahman, M. T.; Nishino, H.; Qian, C.-Y. *Tetrahedron Lett*. **2003**, *44*, 5225–5228; b) Rahman, M. T.; Nishino, H. *Tetrahedron* **2003**, *59*, 8383–8392.
7. Haque, M. D.; Nishino, H. *Heterocycles* **2011**, *83*, 1783–1805.
8. Haque, M. D.; Nishino, H. *J. Heterocycl. Chem.* **2013**, *50*, in press.
9. a) Qian, C.-Y.; Nishino, H.; Kurosawa, K.; Korp, J. D. *J. Org. Chem*. **1993**, *58*, 4448–4451; b) Rahman, M. T.; Nishino, H. *Org. Lett*. **2003**, *5*, 2887–2890; c) Rahman, M. T.; Haque, M. A.; Igarashi, H.; Nishino, H. ・・・・・・・・・ **2011**, *16*, 9562–9581.

10. a) Heiba, E. I.; Dessau, R. M. *J. Org. Chem.* **1974**, *39*, 3456–3457; b) Nishino, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1922–1927; c) Bar, G.; Parsons, A. W.; Thomas, C. B. *Tetrhedron* **2001**, *57*, 4719–4728; d) Huang, J.-W.; Shi, M. *J. Org. Chem.* **2005**, *70*, 3859–3863; e) Yilmaz, M.; Pekel, A. T. *J. Fluorine Chem.* **2005**, *126*, 401–406; f) Yilmaz, M.; Uzunalioglu, N.; Pekel, A. T. *Tetrahedron* **2005**, *61*, 8860–8867; g) Burgaz, E. V.; Yilmaz, M.; Pekel, A. T.; Öktemer, A. *Tetrahedron* **2007**, *63*, 7229–7239; h) Yilmaz, M.; Yakut, M.; Pekel, A. T. *Synth. Commun.* **2008**, *38*, 914–927; i) Yilmaz, M.; Uzunalioglu, N.; Yakut, M.; Pekel, A. T. *Turk. J. Chem.* **2008**, *32*, 411–422; j) Ito, Y.; Yoshinaga, T.; Nishino, H. *Tetrahedron* **2010**, *66*, 2683–2694; k) Loğoğlu, E.; Yilmaz, M.; Katircioğlu, H.; Yakut, M.; Mercan, S. *Med. Chem. Res.* **2010**, *19*, 490–497; l) Yilmaz, M.; Pekel, A. T. *J. Fluorine Chem.* **2011**, *132*, 628–635; m) Ito, Y.; Tomiyasu, Y.; Kawanabe, T.; Uemura, K.; Ushimizu, Y.; Nishino, H. *Org. Biomol. Chem.* **2011**, *9*, 1491–1507; n) Ito, Y.; Jogo, S.; Fukuda, N.; Okumura, R.; Nishino, H. *Synthesis* **2011**, 1365–1374; o) Yilmaz, M. *Tetrahedron* **2011**, *67*, 8255–8263; p) Deliomeroglu, M. K.; Dengiz, C.; Caliskan, R.; Balci, M. *Tetrahedron* **2012**, *68*, 5838–5844. Also refer the oxidative cyclization using CAN; q) Yokoe, H.; Mitsuhashi, C.; Matsuoka, Y.; Yoshimura, T.; Yoshida, M.; Shishido, K. *J. Am. Chem. Soc.* **2011**, *133*, 8854-8857; r) Yoshida, M.; Takai, H.; Yodokawa, S.; Shishido, K. *Tetrahedron* **2013**, *69*, 5273-5280.
11. a) Ito, N.; Nishino, H.; Kurosawa, K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3527–3528; b) Corey, E. J.; Kang, M.-C. *J. Org. Chem.* **1984**, *106*, 5384–5385. c) Fristad, W. E.; Peterson, J. R. *J. Org. Chem.* **1985**, *50*, 10–18; d) Fristad, W. E.; Hershberger, S. S. *J. Org. Chem.***1985**, *50*, 1026–1031; e) Sung, K.; Wang, Y. Y. *J. Org. Chem.* **2003**, *68*, 2771–2778; f) Cong, Z.-Q.; Miki, T.; Urakawa, O.; Nishino, H. *J. Org. Chem.* **2009**, *74*, 3978–3981; g) Maemura, Y.; Tanoue, Y.; Nishino, H. *Heterocycles* **2012**, *85*, 2492–2503; h) Nishino, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 217–222; i) Nishino, H.; Hashimoto, H.; Korp, J. D.; Kurosawa, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1999–2009; j) Nishino, H.; Ishida, K.; Hashimoto, H.; Kurosawa, K. *Synthesis* **1996**, 888–896.
12. a) Asahi, K.; Nishino, H. *Tetrahedron Lett.* **2006**, *47*, 7259–7262; b) Asahi, K.; Nishino, H. *Heterocycl. Commun.* **2008**, *14*, 21–26. c) Asahi, K.; Nishino, H. *Tetrahedron* **2008**, *64*, 1620–1634. d) Asahi, K.; Nishino, H. *Eur. J. Org. Chem.* **2008**, 2404–2416.
13. Kumabe, R.; Nishino, H. *Tetrahedron Lett.* **2004**, *45*, 703–706.
14. Kumabe, R.; Nishino, H. *Heterocycl. Commun.* **2004**, *10*, 135–138.
15. The energy calculations of **7b** (R = Pr, Ar = Ph) and **8b** (R = Pr, Ar = Ph) were performed at the ground state based on Hartree-Fock 3-21G, and it was found that the energy of **7b** and **8b** was very similar.
16. Yoshida, S.; Yano, S.; Ozawa, T.; Kawabata, N. *J. Org. Chem.* **1985**, *50*, 3467-3473. A similar 1,2-addition, see a) Yoshida, S.; Yamamoto, M.; Kawabata, N. *Tetrahedron Lett.* **1985**, *26*, 6217-6220. b) Alexiou, I.; Gogonas, E. P.; Hadjiarapoglou, L. P. *Synlett.* **1999**, 1925-1926. c) Karade, N. N.; Shirodkar, S. G.; Patil, M. N.; Potrekar, R. A.; Karade, H. N. *Tetrahedron Lett.* **2003**, *44*, 6729-6731.
17. a) Nair, V.; Mathew, J. *J. Chem. Soc., Perkin Trans. 1*, **1995**, 187-188. b) Nair, V.; Mathew, J.; Radhakrishman, K. V. *J. Chem. Soc., Perkin Trans. 1*, **1996**, 1487-1492. c) Kajikawa, S.; Nishino, H.; Kurosawa, K. *Heteocycles* **2001**, *54*, 171-183. d) Li, C.; Zhang, D.; Zhang, X.; Wu, S.; Gao, X. *Org. Biomol. Chem.* **2004**, *2*, 3464-3469. e) Wang, G.-W.; Li, F.-B. *Org. Biomol. Chem.* **2005**, *3*, 794-797. f) Ali, M. F.; Çalışkan, R.; Şahin, E.; Balci, M. *Tetrahedron* **2009**, *65*, 1430-1437. g) Biçer, E.; Yılmaz, M.; Karataş, M.; Pekel, A. T. *Hel. Chim. Acta*, **2012**, *95*, 795-804. h) Bolte, M. L.; Crow, W. D.; Yoshida, S. *Aust. J. Chem.* **1982**, *35*, 1411-1419.
18. Andrulis, Jr., P. J.; Dewar, M. J. S.; Dietz, R.; Hunt, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5473–5478.
19. Heiba, E. I.; Dessau, R. M. Koehl, Jr., W. J. *J. Am. Chem. Soc.* **1969**, *91*, 138–145.
20. Buckle, D. R.; Cantello, B. C. C.; Smith, H.; Spicer, B. A. *J. Med. Chem.* **1975**, *18*, 726–732.

Supplementary Material

X ray data of **3b** (R = Me, $Ar^1 = Ar^2$ = 4-Cl-C_6H_4) and **4a** (R = Me, $Ar^1 = Ar^2$ = Ph), ^{1}H NMR, ^{13}C NMR, and also DEPT-135 spectra of the products. Supplementary data associated with this article can be found in the online version.

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Mn(III)-based reaction of alkenes with quinolinones. Formation of peroxyquinolinones and quinoline-related derivatives

Hiroshi Nishino [a,*], Ryoukou Kumabe [a], Ryoichi Hamada [a], Mehtap Yakut [b]

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[b] *Department of Chemistry, Faculty of Science, Ankara University, 06100 Tandoğan, Ankara, Turkey*

Supplementary Material

X ray data of **3b** (R = Me, Ar^1 = Ar^2 = 4-Cl-C_6H_4) and **4a** (R = Me, Ar^1 = Ar^2 = Ph), ^{1}H NMR, ^{13}C NMR, and also DEPT-135 spectra of the products. Supplementary data associated with this article can be found in the online version.

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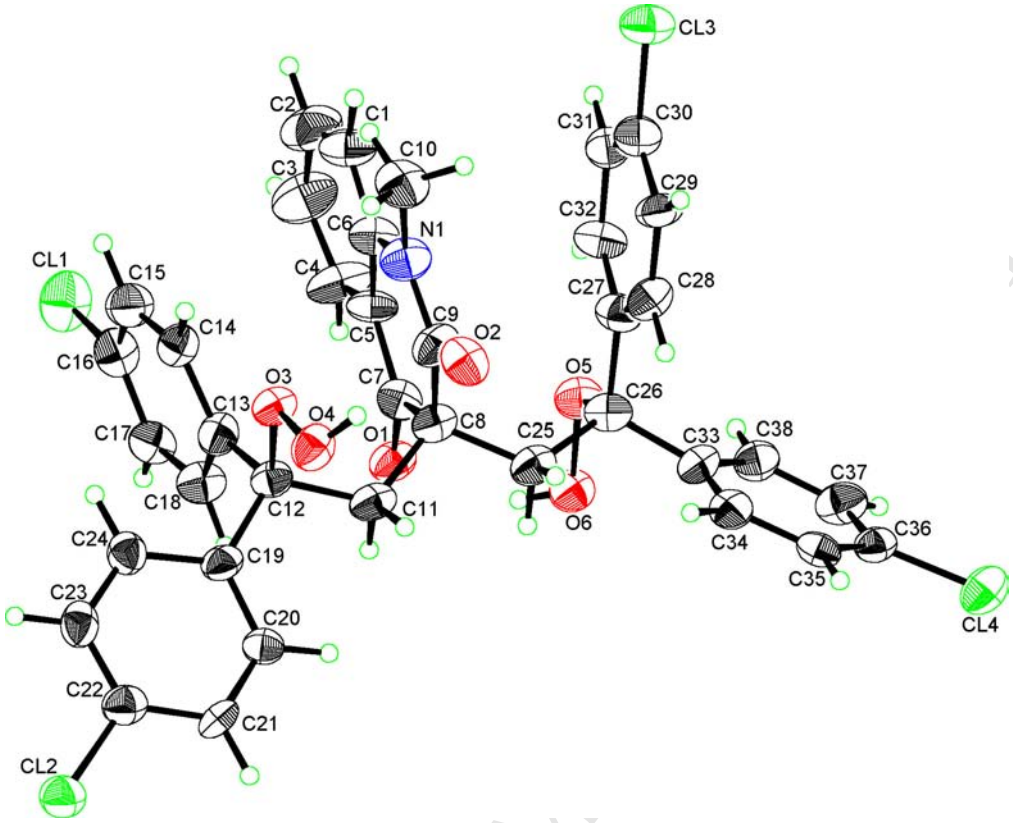
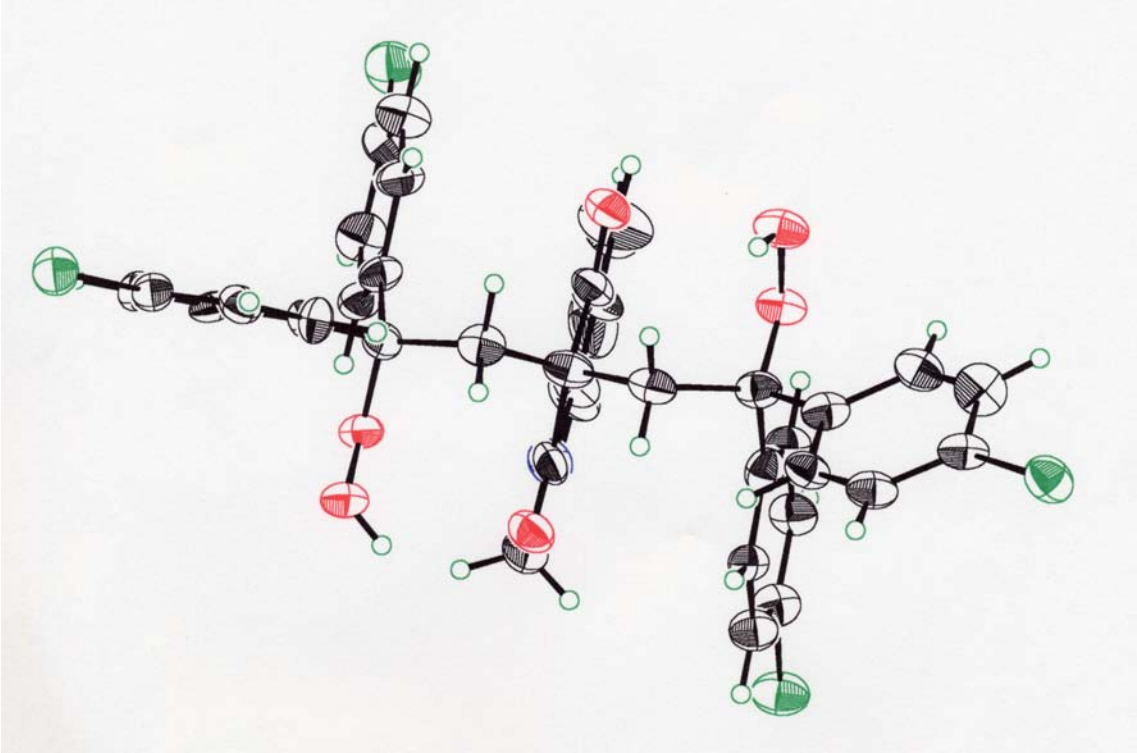
X ray data of 3,3-Bis[2,2-bis(4-chlorophenyl)-2-hydroperoxyethyl]-1-methylquinoline-2,4(1*H*,3*H*)-dione (**3b**: R = Me, Ar^1 = Ar^2 = 4-Cl-C_6H_4): CCDC reference number, CCDC 217001.





A. Crystal Data of **3b** (R = Me, $Ar^1 = Ar^2$ = 4-Cl-C_6H_4)

Empirical Formula	$C_{38}H_{29}Cl_4NO_6$
Formula Weight	737.46
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.03 X 0.40 X 0.50 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	20550 (6.4 - 135.5^o)
Indexing Images	2 oscillations at 2.0 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 15.095(6) Å b = 22.04(1) Å c = 11.093(4) Å α = 90.04(2)^o β = 111.48(2)^o γ = 101.71(1)^o V = 3351(2) Å^3
Space Group	P-1 (#2)
Z value	4
D_{calc}	1.461 g/cm^3
F_{000}	1520.00
μ(CuKα)	36.28 cm^{-1}

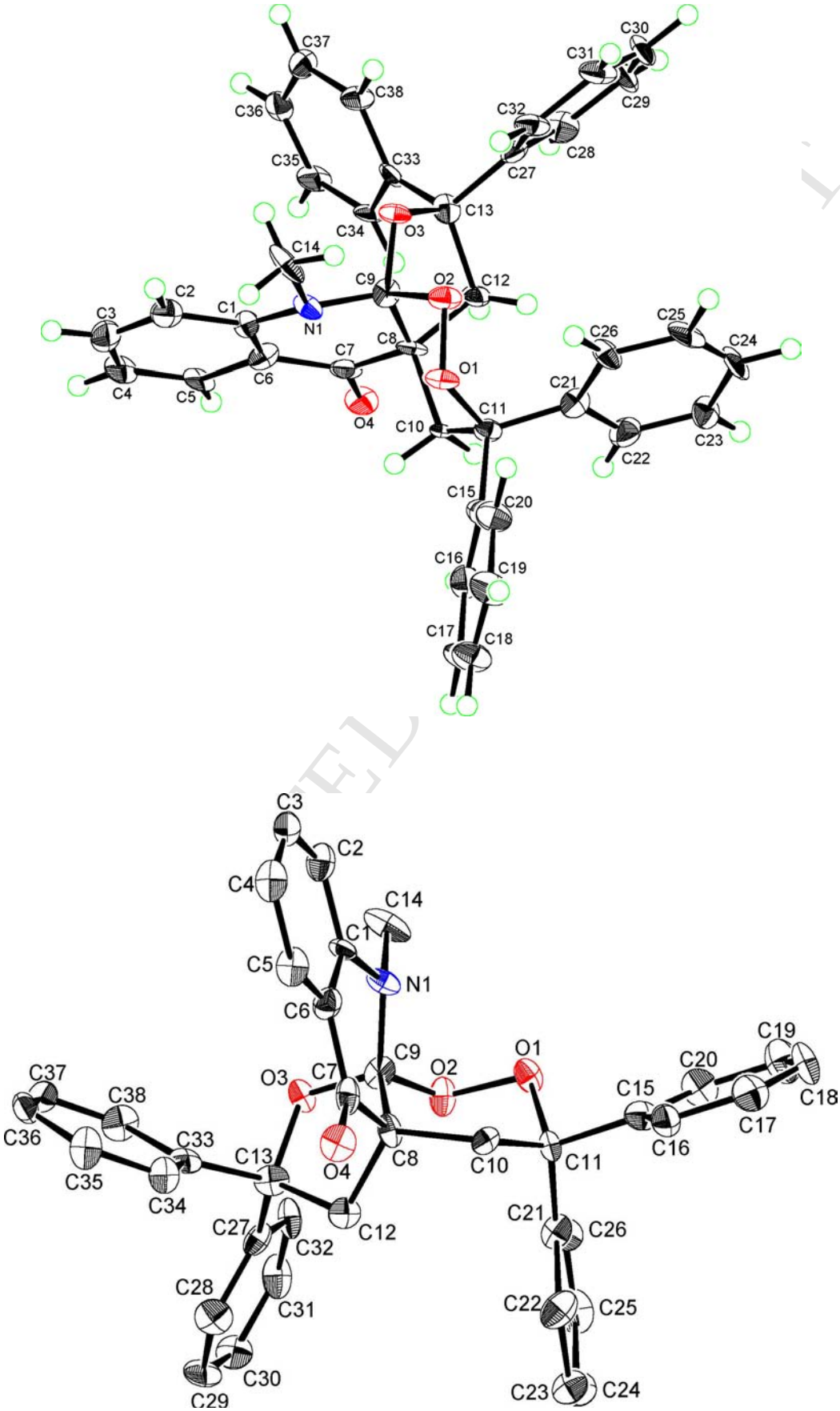
B. Intensity Measurements of **3b** (R = Me, $Ar^1 = Ar^2$ = 4-Cl-C_6H_4)

Diffractometer	Rigaku RAXIS-RAPID Imaging Plate
Radiation	CuKα (λ = 1.54178 Å) graphite monochromated
Temperature	-150.0 ^{o}C
Voltage, Current	40 kV, 100 mA
Collimator Size	0.5 mm
Detector Aperture	450.0 mm x 256.0 mm
Data Images	45 exposures at 0.3 minutes per degree
Oscillation Range (ϕ=0.0^o,χ=50.0^o)	ω 50.0 - 230.0^o with 20.0^o step
Oscillation Range (ϕ=90.0^o,χ=50.0^o)	ω 50.0 - 230.0^o with 20.0^o step
Oscillation Range (ϕ=180.0^o,χ=50.0^o)	ω 50.0 - 230.0^o with 20.0^o step
Oscillation Range (ϕ=270.0^o,χ=50.0^o)	ω 50.0 - 230.0^o with 20.0^o step
Oscillation Range (ϕ=0.0^o,χ=0.0^o)	ω 50.0 - 230.0^o with 20.0^o step
Camera Radius	127.40 mm
Pixel Size	0.100 mm
$2θ_{max}$	136.5^o
No. of Reflections Measured	Total: 14897 Unique: 10315 (R_{int} = 0.063)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.3949 - 0.8969)

C. Structure Solution and Refinement of **3b** (R = Me, $Ar^1 = Ar^2$ = 4-Cl-C_6H_4)

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares (SHELXL-97)
Function Minimized	Σ w (Fo^2 - Fc^2)^2
Least Squares Weights	w = 1/[$σ^2$(Fo^2) + (0.1491P)^2 + 0.0000P] where P = (Fo^2 + 2Fc^2)/3
No. of Reflections (All, 2σ < 136.49^o)	3333
No. Variables	890
Reflection/Parameter Ratio	3.74
Residuals: R; Rw	0.103 ; 0.340
Goodness of Fit Indicator	0.92
Max Shift/Error in Final Cycle	-3.01
Maximum peak in Final Diff. Map	0.58 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.36 e$^-$/Å^3

X ray data of 3,4-dihydro-10-methyl-3,3,12,12-tetraphenyl-10a,4a-(epoxyethano)-1,2-dioxino[3,4-*b*]quinolin-5(10*H*)-one (**4a**: R = Me, Ar^1 = Ar^2 = Ph): CCDC reference number, CCDC 218561.



A. Crystal Data of **4a** (R = Me, Ar^1 = Ar^2 = Ph)

Empirical Formula	$C_{39.50}O_4NH_{31}$
Formula Weight	583.68
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.20 X 0.10 X 0.10 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	12168 (4.6 - 54.9^o)
Indexing Images	3 oscillations at 5.0 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 9.207(1) Å b = 14.317(2) Å c = 23.581(3) Å α = 77.550(5)^o β = 82.279(4)^o γ = 77.79(1)^o V = 2953.8(6) Å^3
Space Group	P-1 (#2)
Z value	4
D_{calc}	1.312 g/cm^3
F_{000}	1228.00
μ(MoKα)	0.84 cm^{-1}

B. Intensity Measurements of **4a** (R = Me, Ar^1 = Ar^2 = Ph)

Diffractometer	Rigaku RAXIS-RAPID Imaging Plate
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Temperature	-160.0 ^{o}C
Voltage, Current	50 kV, 32 mA
Collimator Size	0.5 mm
Detector Aperture	270.0 mm x 256.0 mm
Data Images	74 exposures at 10.8 minutes per degree
Oscillation Range (ϕ=0.0^o,χ=45.0^o)	ω 130.0 - 190.0^o with 3.0^o step
Oscillation Range (ϕ=180.0^o,χ=45.0^o)	ω 0.0 - 162.0^o with 3.0^o step
Camera Radius	127.40 mm
Pixel Size	0.100 mm
$2θ_{max}$	55.0^o
No. of Reflections Measured	Total: 20843 Unique: 12021 (R_{int} = 0.080)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.6012 - 0.9916)

C. Structure Solution and Refinement of **4a** (R = Me, Ar^1 = Ar^2 = Ph)

Structure Solution	Direct Methods (SIR88)
Refinement	Full-matrix least-squares
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	$1/σ^2(Fo) = 4Fo^2/σ^2(Fo^2)$
p-factor	0.1290
Anomalous Dispersion	All non-hydrogen atoms
No. of Observations (I>3.00σ(I), 2θ < 54.97^o)	3336
No. Variables	802
Reflection/Parameter Ratio	4.16
Residuals: R; Rw	0.068 ; 0.105
Residuals: R1	0.068
No. of Reflections to calc R1	3336
Goodness of Fit Indicator	1.34
Max Shift/Error in Final Cycle	0.757
Maximum peak in Final Diff. Map	0.40 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.32 e$^-$/Å^3

NMe Ph rt Bis

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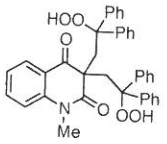
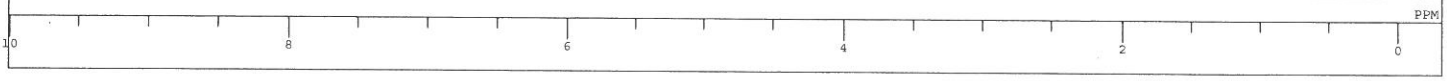


3a



NMe Ph rt Bis

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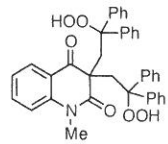

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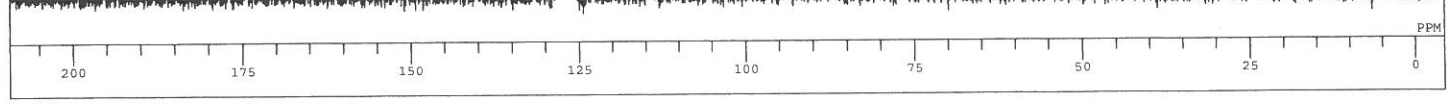

NMe Ph rt Bis

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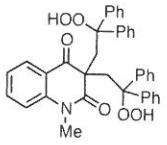

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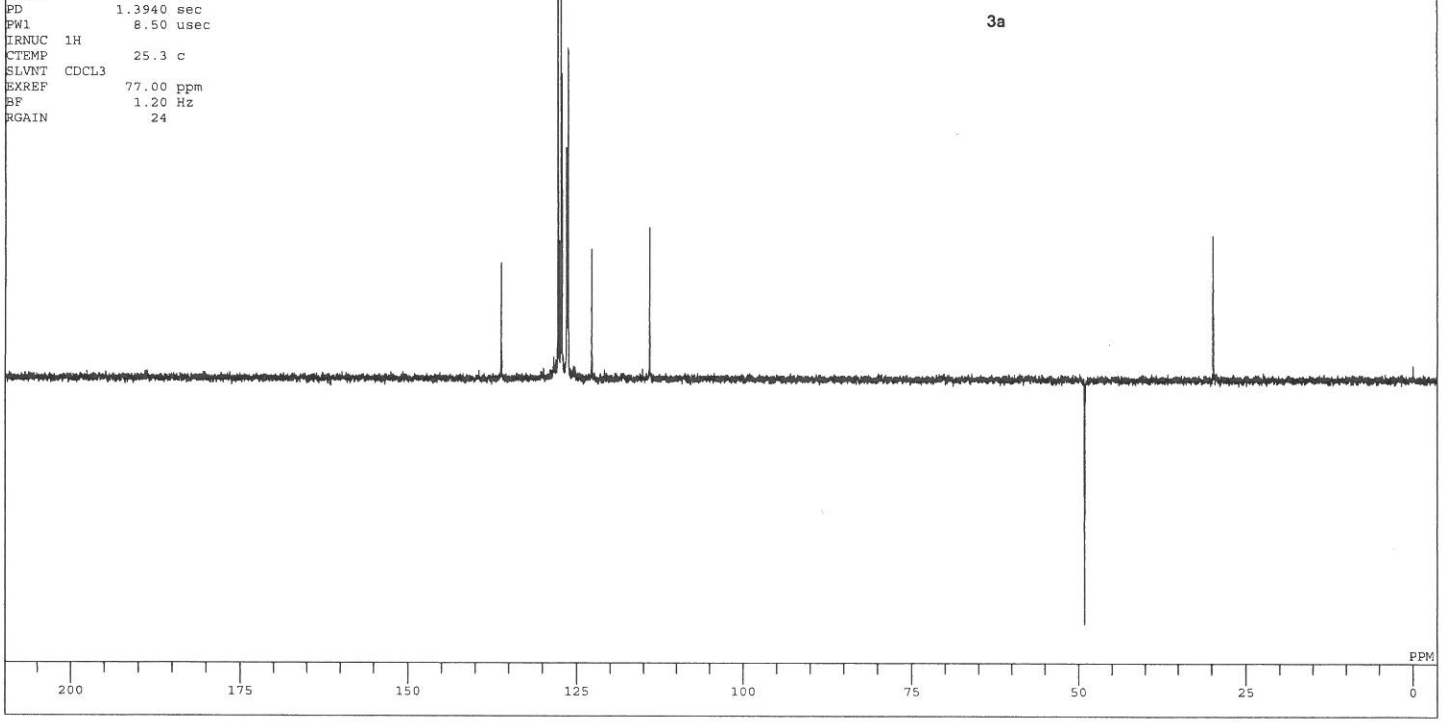

NME ClPh bis

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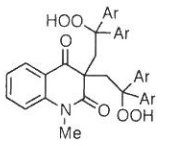

3b: Ar = 4-Cl-C_6H_4

NME ClPh bis

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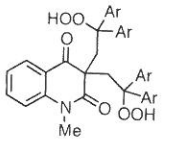

3b: Ar = 4-Cl-C_6H_4

NME ClPh bis

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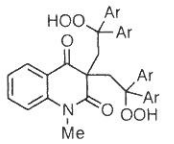

3b: Ar = 4-Cl-C_6H_4

NMe MePh rt F2(Bis)

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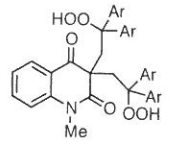
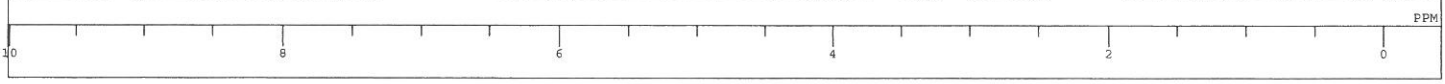
DFILE  kumabe-bis-4-MeC6H4-2013.als
COMNT  NMe MePh rt F2(Bis)
DATIM  Fri Sep 14 04:20:26 2001
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           23.7 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             12
```



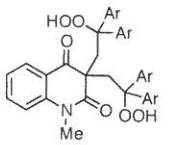
3c: Ar = 4-Me-C_6H_4



NMe MePh rt F2(Bis)

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino Lab\kumabe-NMR data\ŽÀŒ±\NMe-MePh_rt\kumabe-bis-4-MeC6H4-bcm-2013.als

```
DFILE  kumabe-bis-4-MeC6H4-bcm-2013.als
COMNT  NMe MePh rt F2(Bis)
DATIM  Fri Sep 14 04:24:13 2001
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            50
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           24.4 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              1.20 Hz
RGAIN             23
```

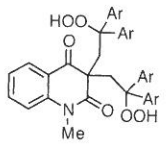


3c: Ar = 4-Me-C_6H_4

NMe MePh rt bis

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NMe-MePh_rt\kumabe-bis-4-MeC6H4-dept-2013.als

```
DFILE  kumabe-bis-4-MeC6H4-dept-2013.als
COMNT  NMe MePh rt bis
DATIM  Tue Jun 03 12:56:07 2003
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET       124.00 KHz
OBFIN      1840.00 Hz
POINT        32768
FREQU     20408.10 Hz
SCANS          100
ACQTM       1.6056 sec
PD          1.3940 sec
PW1           8.50 usec
IRNUC  1H
CTEMP         23.3 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            1.20 Hz
RGAIN           24
```



3c: Ar = 4-Me-C_6H_4

NEt Ph bisperoxide

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\NEt-Bis\bis_NON-2013.als

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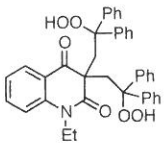
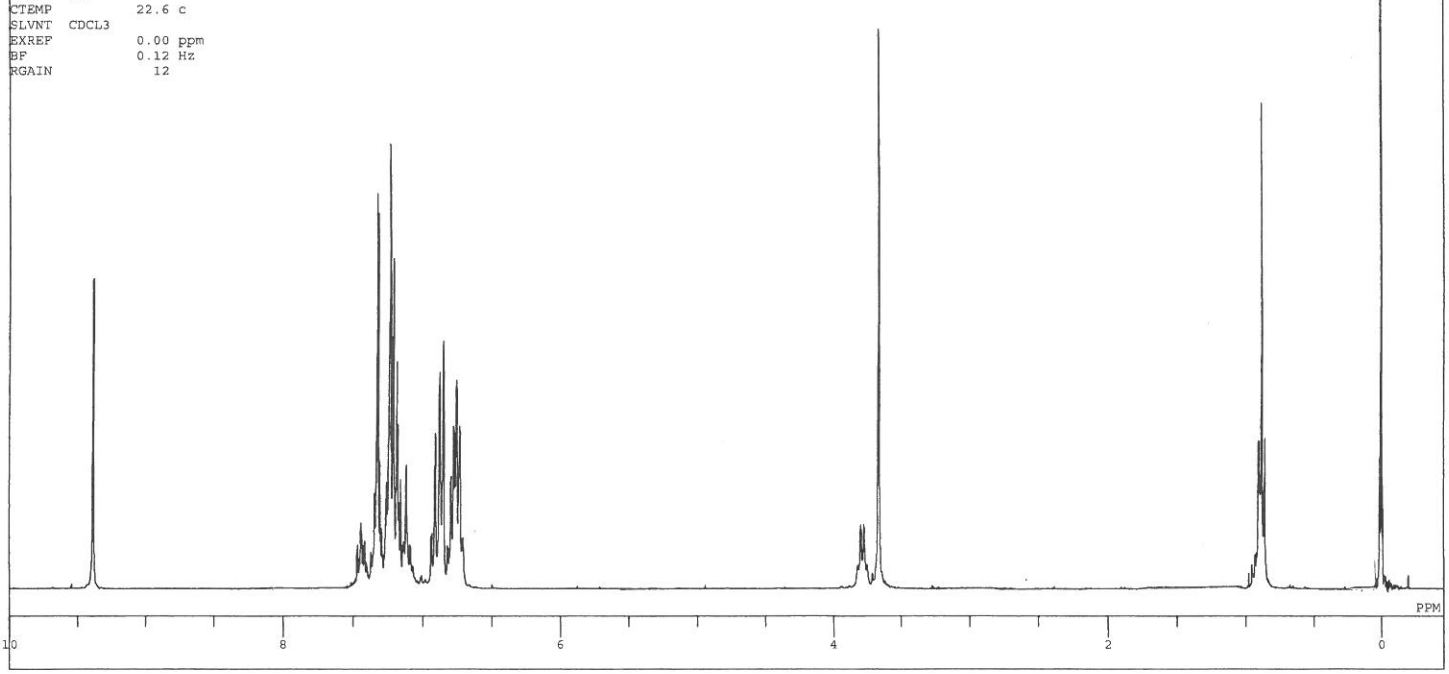
DFILE  bis_NON-2013.als
COMNT  NEt Ph bisperoxide
DATIM  Sat Oct 05 01:12:07 2002
OBNUC  1H
EXMOD  NON
OBFRQ       300.40 MHz
OBSET       130.00 KHz
OBFIN      1150.00 Hz
POINT        32768
FREQU      6013.20 Hz
SCANS           16
ACQTM       5.4493 sec
PD          1.5510 sec
PW1           5.20 usec
IRNUC  1H
CTEMP         22.6 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           12
```



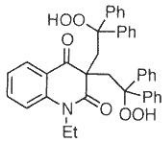
3d



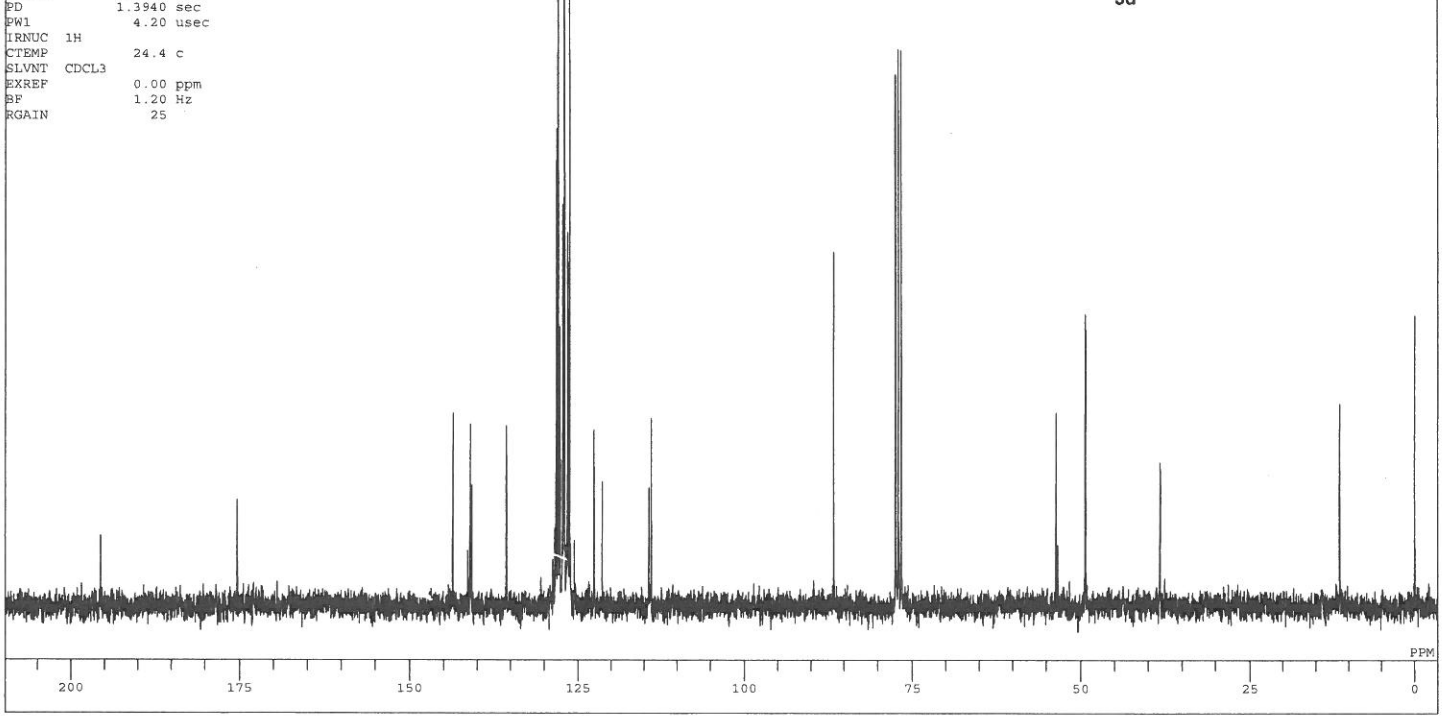
NEt Ph bisperoxide

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\NEt-Bis\bis_BCM-2013.als

```
DFILE  bis_BCM-2013.als
COMNT  NEt Ph bisperoxide
DATIM  Sat Oct 05 00:40:56 2002
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           24.4 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             25
```



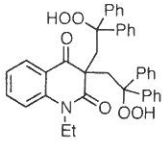
3d



NEt Ph bisperoxide

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\NEt-Bis\bis_DEPT-2013.als

```
DFILE  bis_DEPT-2013.als
COMNT  NEt Ph bisperoxide
DATIM  Sat Oct 05 00:47:16 2002
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           23.8 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             25
```

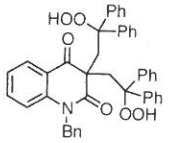


3d

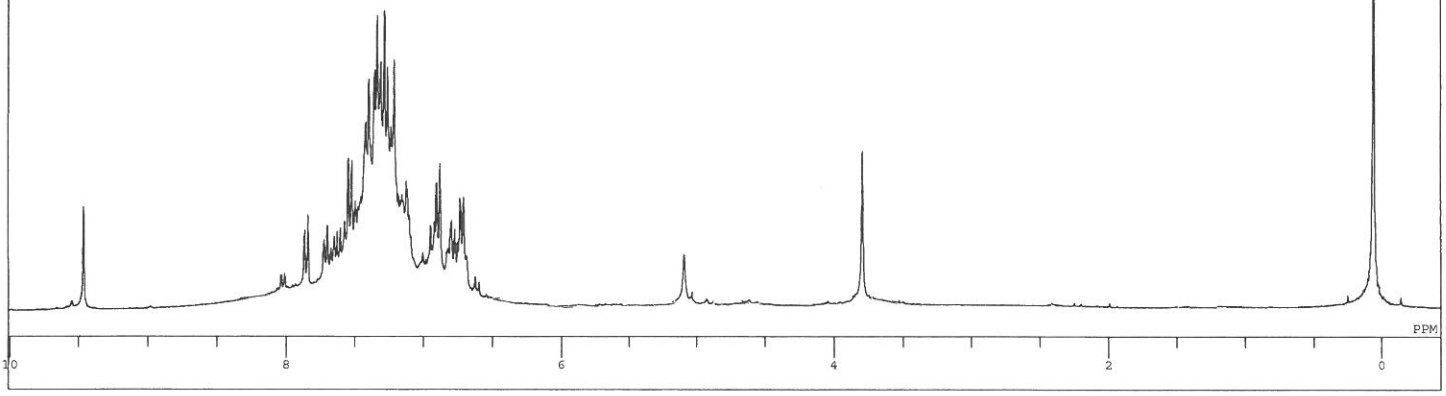
Nbn Ph bis

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NBn-Ph_r.t\F2NON-2013.als

```
DFILE  F2NON-2013.als
COMNT  Nbn Ph bis
DATIM  Tue Mar 09 17:25:08 2004
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            32
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.80 usec
IRNUC  1H
CTEMP           22.8 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             13
```



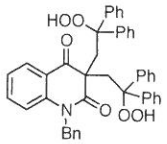
3e



NBn Ph r.t. 12H bis

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NBn-Ph_r.t\F2BCM_E1-2013.als

```
DFILE  F2BCM_E1-2013.als
COMNT  NBn Ph r.t. 12H bis
DATIM  Wed Jul 25 01:15:53 2001
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            200
ACQTM         1.6056 sec
PD            1.3944 sec
PW1             4.25 usec
IRNUC  1H
CTEMP           25.3 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              1.20 Hz
RGAIN             23
```

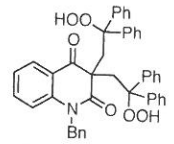


3e

NBn Ph r.t. 12H BIS

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NBn-Ph_r.t\F2DEPT_E1-2013.als

```
DFILE  F2DEPT_E1-2013.als
COMNT  NBn Ph r.t. 12H BIS
DATIM  Wed Jul 25 01:21:29 2001
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP          24.6 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            24
```



3e

NBn ClPh bis

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NBn-ClPh_rt\F2_NON(BIS)-2013.als

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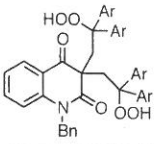
DFILE  F2_NON(BIS)-2013.als
COMNT  NBn ClPh bis
DATIM  Sun Mar 07 20:07:07 2004
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.80 usec
IRNUC  1H
CTEMP          19.0 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            16
```

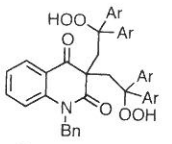


3f: Ar = 4-Cl-C_6H_4

NBn ClPh rt 12h F1

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NBn-ClPh_rt\F2_BCM(BIS)-2013.als

```
DFILE  F2_BCM(BIS)-2013.als
COMNT  NBn ClPh rt 12h F1
DATIM  Fri Aug 31 22:25:27 2001
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS          100
ACQTM        1.6056 sec
PD           1.3940 sec
PW1            4.20 usec
IRNUC  1H
CTEMP          24.9 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            24
```

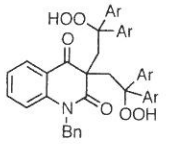


3f: Ar = 4-Cl-C_6H_4

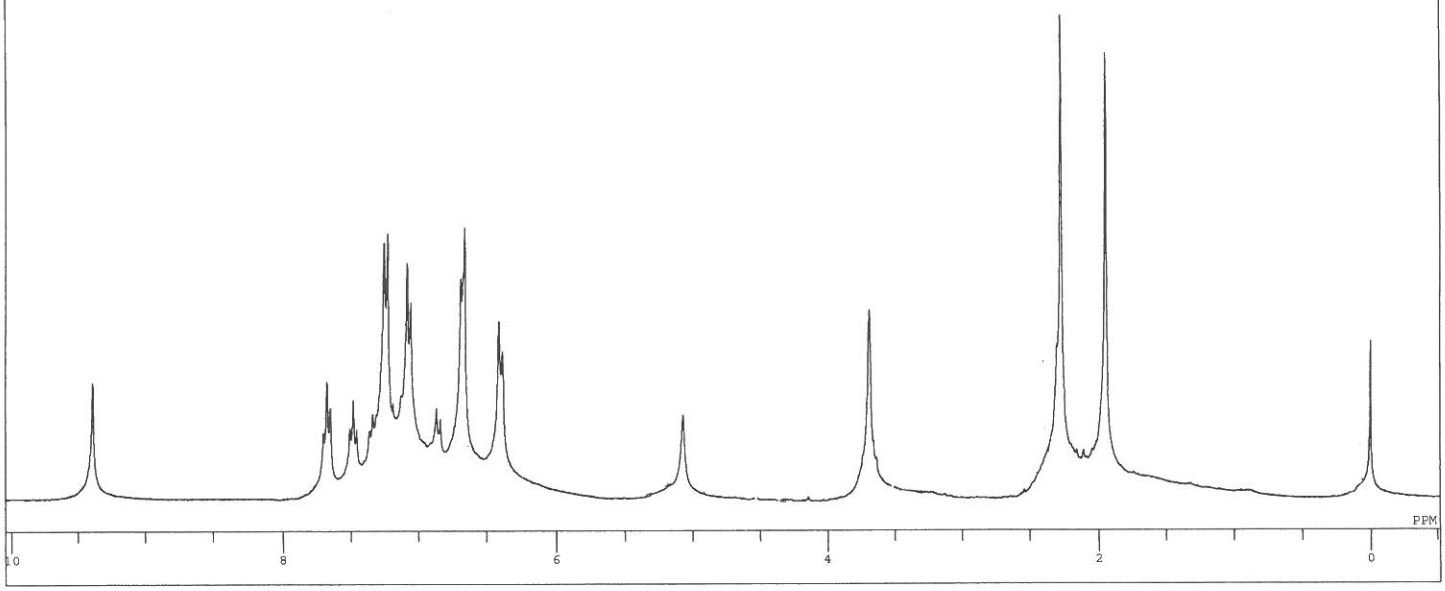
NBn MePh rt 4h F3 (bis)

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NBn-MePh_rt\4H_F3_NON-2013.als

```
DFILE  4H_F3_NON-2013.als
COMNT  NBn MePh rt 4h F3 (bis)
DATIM  Wed Sep 12 01:27:30 2001
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            4
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP          23.7 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            12
```



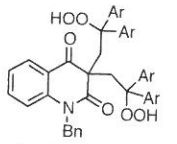
3g: Ar = 4-Me-C_6H_4



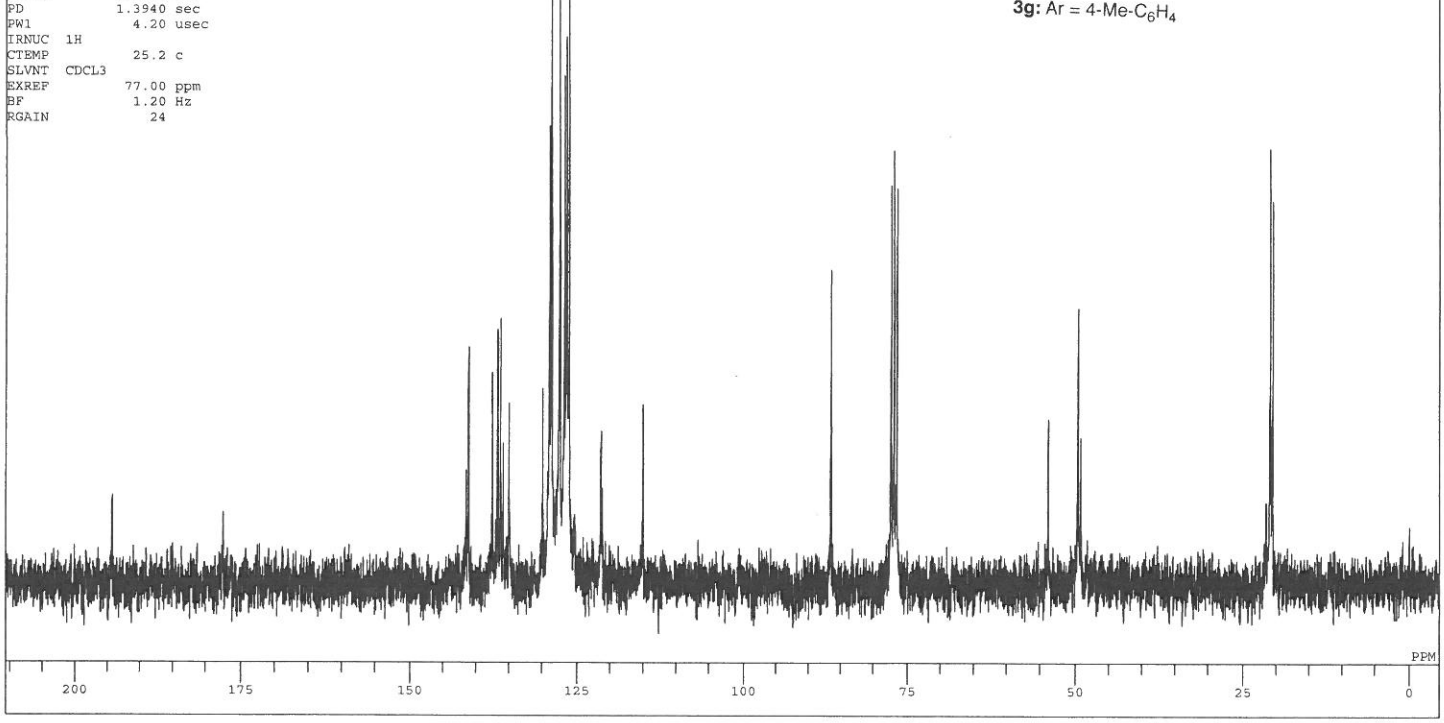
NBn MePh rt 4h F3 (bis)

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NBn-MePh_rt\4H_F3_BCM-2013.als

```
DFILE  4H_F3_BCM-2013.als
COMNT  NBn MePh rt 4h F3 (bis)
DATIM  Wed Sep 12 01:33:59 2001
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           25.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            24
```



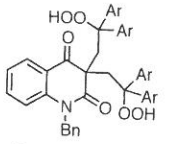
3g: Ar = 4-Me-C_6H_4



NBn MePh rt 4h F3 (bis)

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NBn-MePh_rt\4H_F3_DEPT-2013.als

```
DFILE  4H_F3_DEPT-2013.als
COMNT  NBn MePh rt 4h F3 (bis)
DATIM  Wed Sep 12 01:37:38 2001
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            50
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           24.5 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            23
```

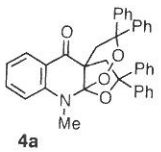


3g: Ar = 4-Me-C_6H_4

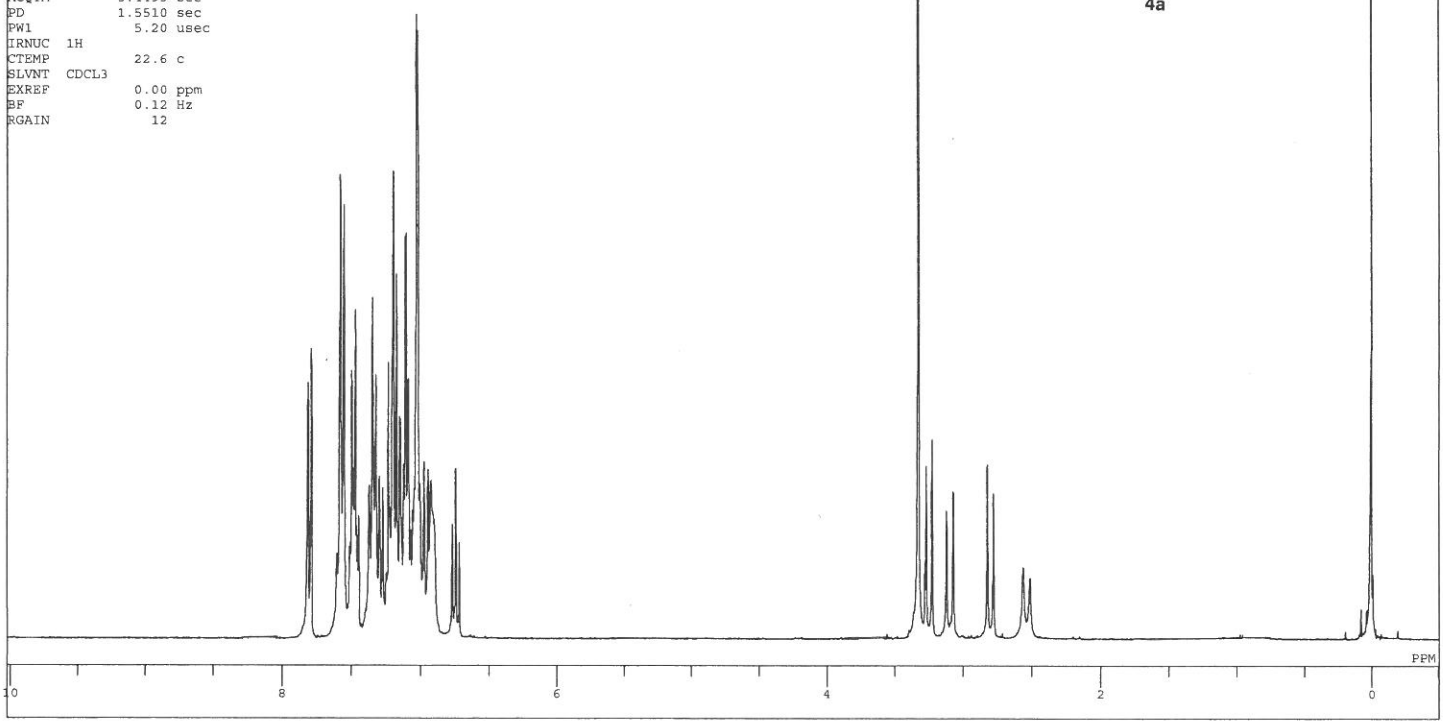
NME Ph F1 ƒvƒ‹ƒyƒ‰ƒ"‹H

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NMe-Ph_rt\ƒvƒ‹ƒyƒ‰ƒ"\NON-2013.als

```
DFILE  NON-2013.als
COMNT  NME Ph F1 ƒvƒ‹ƒyƒ‰ƒ"‹H
DATIM  Mon Sep 01 11:45:10 2003
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           22.6 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             12
```



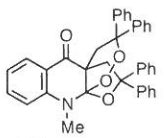
4a



NME Ph F1 ƒvƒ‹ƒyƒ‰ƒ"‹H

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NMe-Ph_rt\ƒvƒ‹ƒyƒ‰ƒ"\BCM-2013.als

```
DFILE  BCM-2013.als
COMNT  NME Ph F1 ƒvƒ‹ƒyƒ‰ƒ"‹H
DATIM  Mon Sep 01 11:35:48 2003
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           23.7 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             25
```

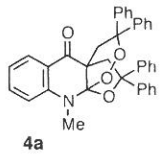


4a

NME Ph F1 ƒvƒ‰ƒyƒ‰ƒ"‰H

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NMe-Ph_rt\ƒvƒ‰ƒyƒ‰ƒ"\DEPT-2013.als

```
DFILE  DEPT-2013.als
COMNT  NME Ph F1 ƒvƒ‰ƒyƒ‰ƒ"‰H
DATIM  Mon Sep 01 11:42:04 2003
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           23.1 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            24
```

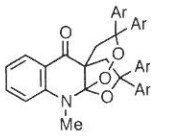


4a

NMe ClPh ƒvƒ‰ƒyƒ‰ƒ"

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NMe-ClPh_rt\ƒvƒ‰ƒyƒ‰ƒ"_NON-2013.als

```
DFILE  ƒvƒ‰ƒyƒ‰ƒ"_NON-2013.als
COMNT  NMe ClPh ƒvƒ‰ƒyƒ‰ƒ"
DATIM  Tue Sep 02 11:45:05 2003
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           22.4 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            13
```

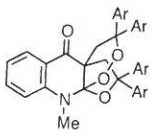


4b: Ar = 4-Cl-C_6H_4

NME ClPh ƒvƒlƒyƒ‰ƒ"

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\NEt-Bis\NMe-4-Cl-propellane_BCM-2013.als

```
DFILE  NMe-4-Cl-propellane_BCM-2013.als
COMNT  NME ClPh ƒvƒlƒyƒ‰ƒ"
DATIM  Mon Sep 15 17:11:44 2003
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS          1000
ACQTM        1.6056 sec
PD           1.3940 sec
PW1            4.20 usec
IRNUC  1H
CTEMP          23.0 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            25
```

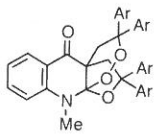


4b: Ar = 4-Cl-C_6H_4

NMe ClPh ƒvƒlƒyƒ‰ƒ"

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NMe-ClPh_rt\ƒvƒlƒyƒ‰ƒ"_DEPT-2013.als

```
DFILE  ƒvƒlƒyƒ‰ƒ"_DEPT-2013.als
COMNT  NMe ClPh ƒvƒlƒyƒ‰ƒ"
DATIM  Tue Sep 02 11:41:29 2003
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           200
ACQTM        1.6056 sec
PD           1.3940 sec
PW1            8.50 usec
IRNUC  1H
CTEMP          22.9 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            24
```

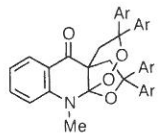


4b: Ar = 4-Cl-C_6H_4

single_pulse

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NMe-MePh_rt\kumabe-propelane-4-MeC6H4-2013.als

```
DFILE  kumabe-propelane-4-MeC6H4-2013.als
COMNT  single_pulse
DATIM  2012-09-07 19:01:46
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         16384
FREQU       9384.38 Hz
SCANS            16
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            5.63 usec
IRNUC  1H
CTEMP          21.1 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            44
```

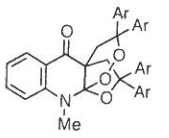


4c: Ar = 4-Me-C_6H_4

single pulse decoupled gated NOE

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NMe-MePh_rt\kumabe-propellane-4-MeC6H4-13C-2013.als

```
DFILE  kumabe-propellane-4-MeC6H4-13C-2013.als
COMNT  single pulse decoupled gated NOE
DATIM  2012-09-07 19:16:46
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32768
FREQU      39308.18 Hz
SCANS           300
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.33 usec
IRNUC  1H
CTEMP          21.5 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            52
```

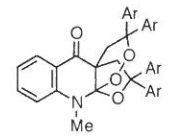


4c: Ar = 4-Me-C_6H_4

DEPT with decoupling

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒt\NMe-MePh_rt\kumabe-prollene-4-MeC6H4-DEPT-2013.als

```
DFILE  kumabe-prollene-4-MeC6H4-DEPT-2013.als
COMNT  DEPT with decoupling
DATIM  2012-09-07 19:32:02
OBNUC  13C
EXMOD  dept.ex2
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32768
FREQU      39308.18 Hz
SCANS           300
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           10.00 usec
IRNUC  1H
CTEMP          21.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            56
```

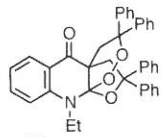


4c: Ar = 4-Me-C_6H_4

NEt Ph rt ƒvƒŒƒyƒ‰ƒ"

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\NEt-Bis\"ñ‰ñ-Ú\NET_ƒvƒŒƒyƒ‰_NON-2013.als

```
DFILE  NET_ƒvƒŒƒyƒ‰_NON-2013.als
COMNT  NEt Ph rt ƒvƒŒƒyƒ‰ƒ"
DATIM  Wed Sep 10 13:50:40 2003
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP          22.1 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            13
```

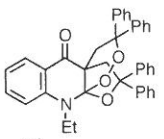


4d

NEt Ph rt ƒvfÛƒyf‰f"

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino Lab\kumabe-NMR data\NEt-Bis\"ñ‰ñ-Ú\NET ƒvfÛƒyf‰ BCM-2013.als

```
DFILE  NET_ƒvfÛƒyf‰_BCM-2013.als
COMNT  NEt Ph rt ƒvfÛƒyf‰f"
DATIM  Wed Sep 10 13:58:04 2003
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           23.1 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             25
```

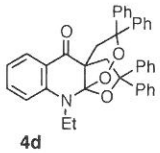


4d

NEt Ph rt ƒvfÛƒyf‰f"

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino Lab\kumabe-NMR data\NEt-Bis\"ñ‰ñ-Ú\NET ƒvfÛƒyf‰ DEPT-2013.als

```
DFILE  NET_ƒvfÛƒyf‰_DEPT-2013.als
COMNT  NEt Ph rt ƒvfÛƒyf‰f"
DATIM  Wed Sep 10 14:04:09 2003
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           22.6 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              1.20 Hz
RGAIN             25
```

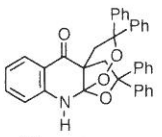


4d

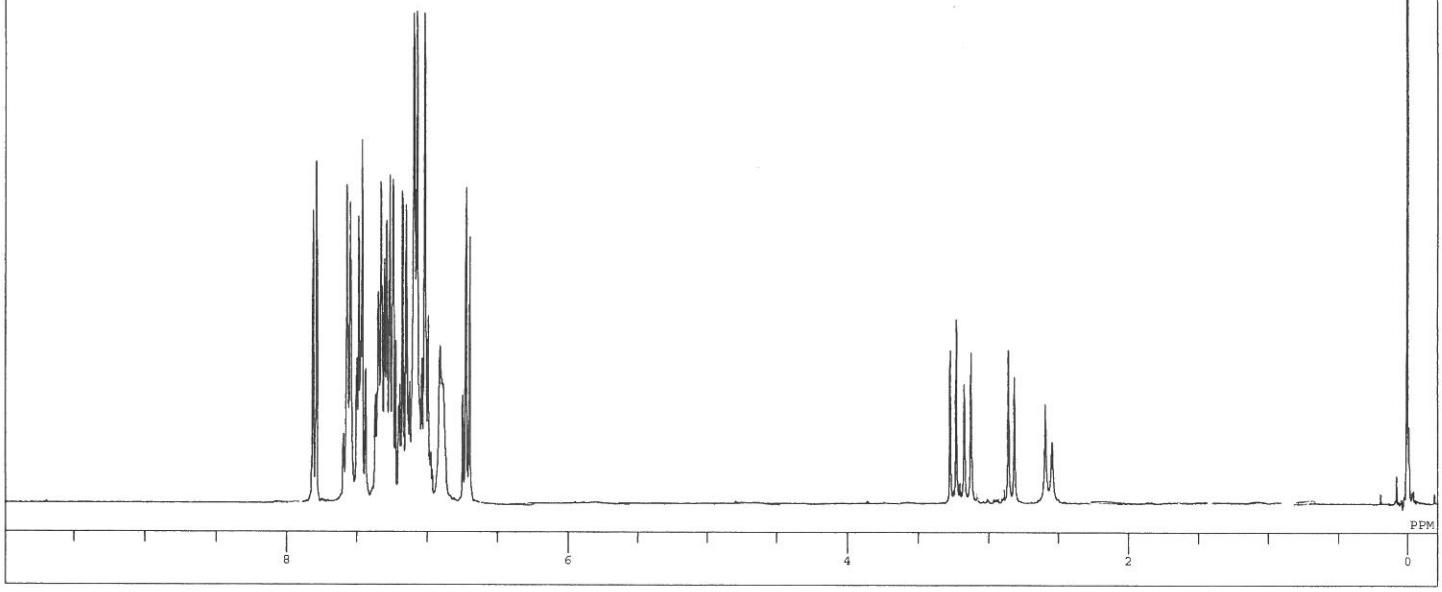
NH Ph rt yellow‰ifvf‰fyf%f"‰j

C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NH-Ph_rt\3days\YELLOW_NON-2013.als

```
DFILE  YELLOW_NON-2013.als
COMNT  NH Ph rt yellow‰ifvf‰fyf%f"‰j
DATIM  Mon Apr 21 12:41:52 2003
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           22.0 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             11
```



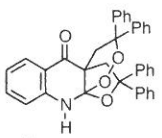
4h



NH Ph rt yellow(fvf‰fyf%f"‰j

C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NH-Ph_rt\3days\YELLOW_BCM-2013.als

```
DFILE  YELLOW_BCM-2013.als
COMNT  NH Ph rt yellow(fvf‰fyf%f"‰j
DATIM  Mon Apr 21 12:29:13 2003
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           23.8 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             25
```

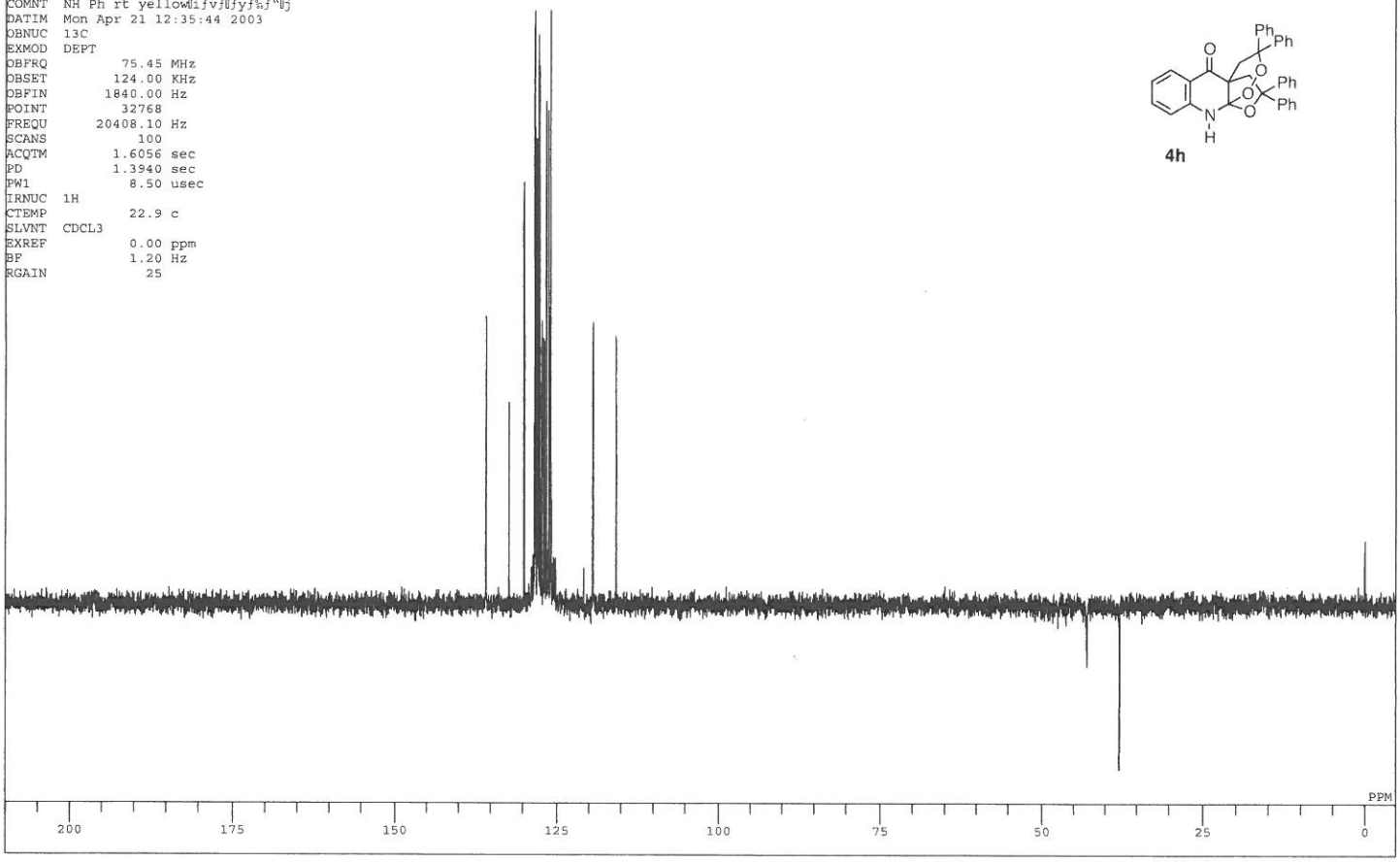


4h

NH Ph rt yellow‰ífvfÎƒyƒ‰ƒ"Îj

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÅŒ‡\NH-Ph_rt\3days\YELLOW_DEPT-2013.als

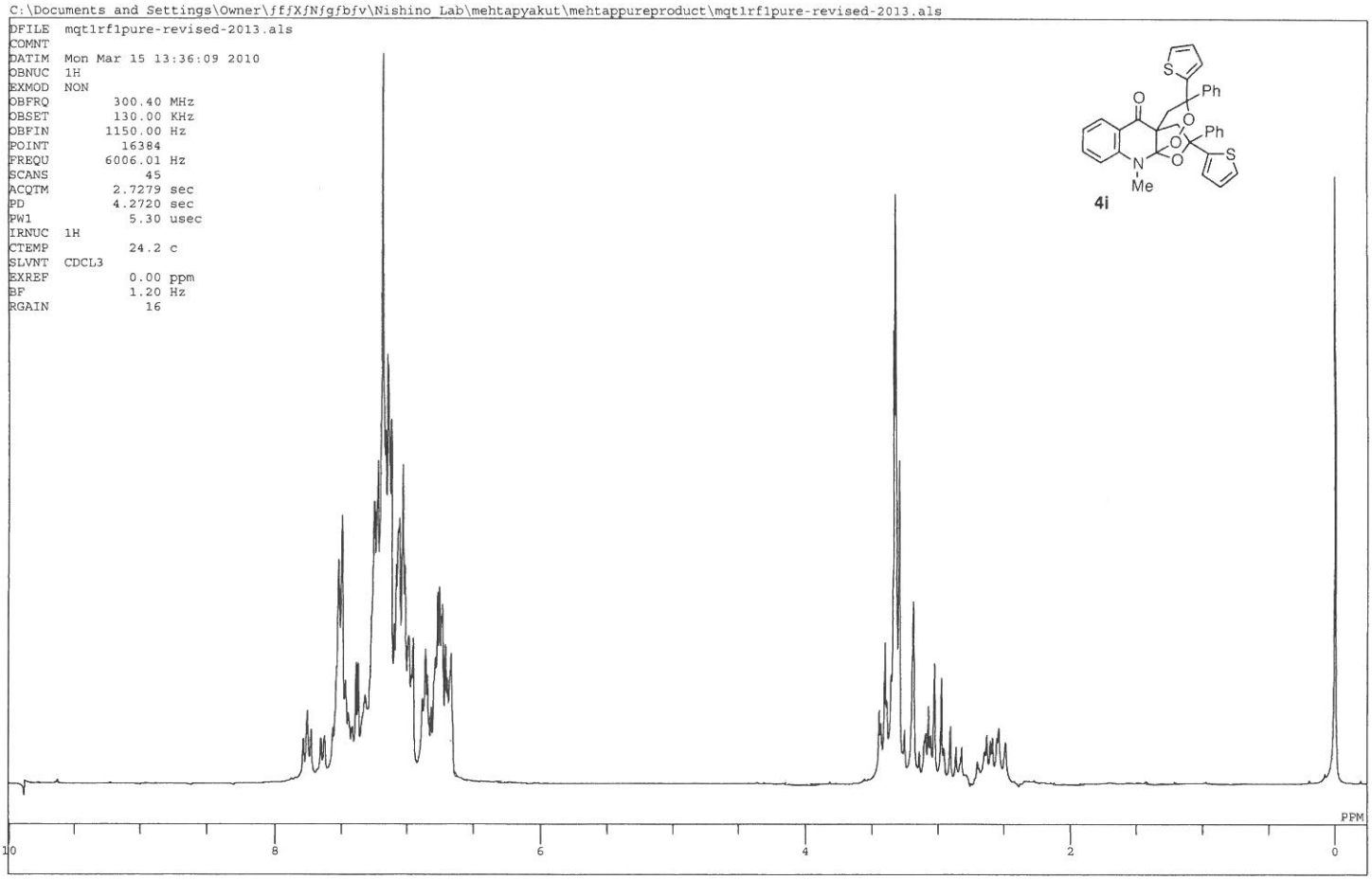
```
DFILE  YELLOW_DEPT-2013.als
COMNT  NH Ph rt yellow‰ífvfÎƒyƒ‰ƒ"Îj
DATIM  Mon Apr 21 12:35:44 2003
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           22.9 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             25
```



4h

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\mehtapyakut\mehtappureproduct\mqt1rf1pure-revised-2013.als

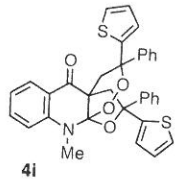
```
DFILE  mqt1rf1pure-revised-2013.als
COMNT
DATIM  Mon Mar 15 13:36:09 2010
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         16384
FREQU       6006.01 Hz
SCANS            45
ACQTM         2.7279 sec
PD            4.2720 sec
PW1             5.30 usec
IRNUC  1H
CTEMP           24.2 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             16
```



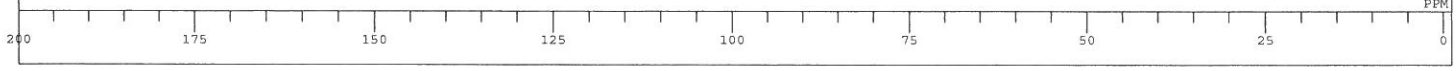
4i

C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\mehtapyakut\mehtappureproduct\mqt1_1bcm-revised-2013.als

```
DFILE  mqt1_1bcm-revised-2013.als
COMNT
DATIM  Mon Mar 15 13:59:27 2010
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS           433
ACQTM         1.6097 sec
PD            1.3900 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           24.9 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             24
```

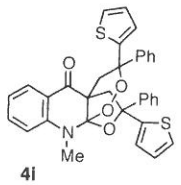


4i

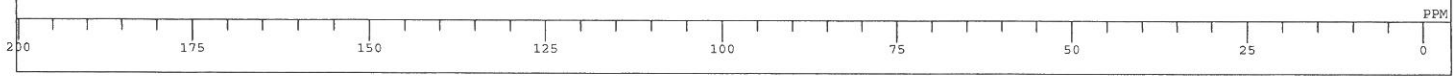


C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\mehtapyakut\mehtappureproduct\mqt1_1dept-revised-2013.als

```
DFILE  mqt1_1dept-revised-2013.als
COMNT
DATIM  Mon Mar 15 14:19:40 2010
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS           374
ACQTM         1.6097 sec
PD            1.3900 sec
PW1             8.30 usec
IRNUC  1H
CTEMP           24.4 c
SLVNT  CDCL3
EXREF          30.40 ppm
BF              1.20 Hz
RGAIN             26
```

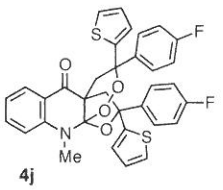


4i

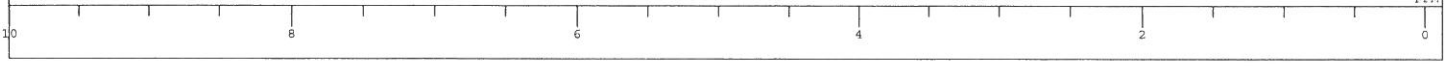


C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\mehtapyakut\mehtappureproduct\mqt2_1-revised-2013.als

```
DFILE  mqt2_1-revised-2013.als
COMNT
DATIM  Wed Mar 10 10:40:28 2010
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         16384
FREQU       6006.01 Hz
SCANS            57
ACQTM         2.7279 sec
PD            4.2720 sec
PW1             5.30 usec
IRNUC  1H
CTEMP           19.4 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             16
```

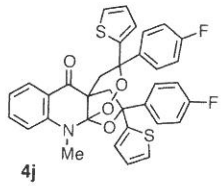


4j



C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\mehtapyakut\mehtappureproduct\mqt2_1.bcmALS-revised-2013.als

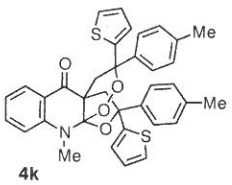
```
DFILE  mqt2_1.bcmALS-revised-2013.als
COMNT
DATIM  Wed Mar 10 10:56:27 2010
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS           298
ACQTM         1.6097 sec
PD            1.3900 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           20.5 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             26
```



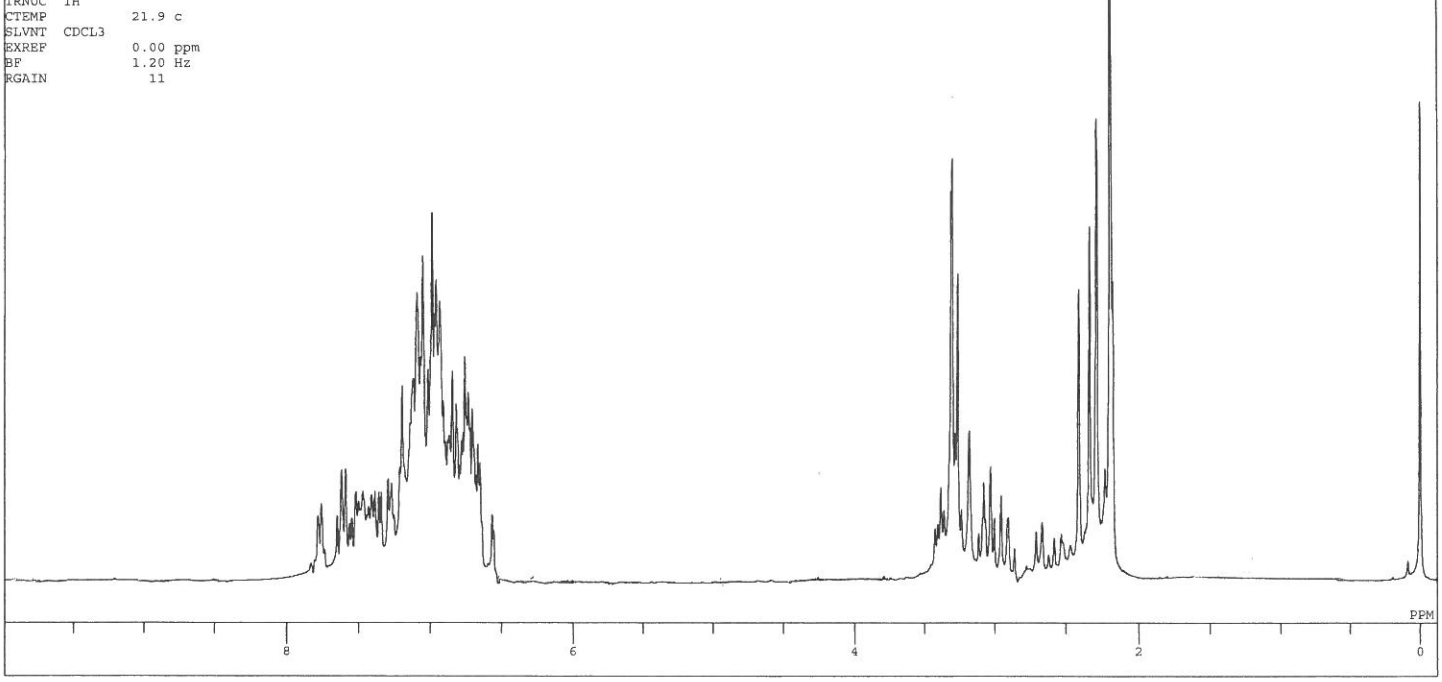
4j

C:\Documents and Settings\Owner\fffXfNfgfbfv\Nishino_Lab\mehtapyakut\mehtappureproduct\mqt3_1non-revised-2013.als

```
DFILE  mqt3_1non-revised-2013.als
COMNT
DATIM  Sat Apr 03 14:41:21 2010
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         16384
FREQU       6006.01 Hz
SCANS            25
ACQTM         2.7279 sec
PD            4.2720 sec
PW1             5.30 usec
IRNUC  1H
CTEMP           21.9 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             11
```

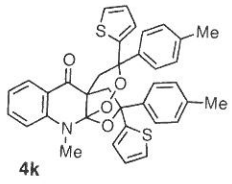


4k

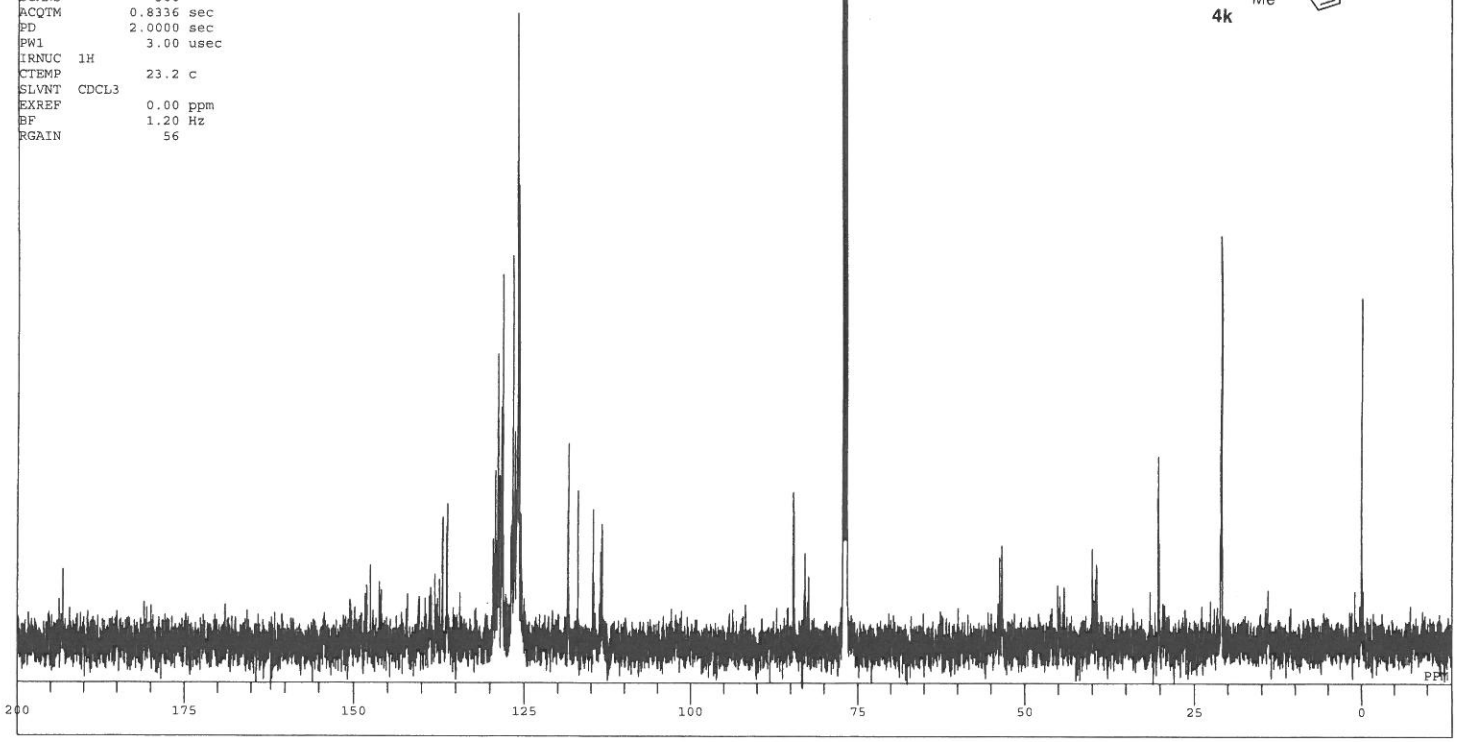


C:\Documents and Settings\Owner\fffXfNfgfbfv\Nishino_Lab\mehtapyakut\mehtappureproduct\mqt3_1bcm-revised-2013.als

```
DFILE  mqt3_1bcm-revised-2013.als
COMNT
DATIM  2010-04-14 15:53:02
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS            300
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.00 usec
IRNUC  1H
CTEMP           23.2 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             56
```

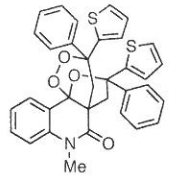


4k

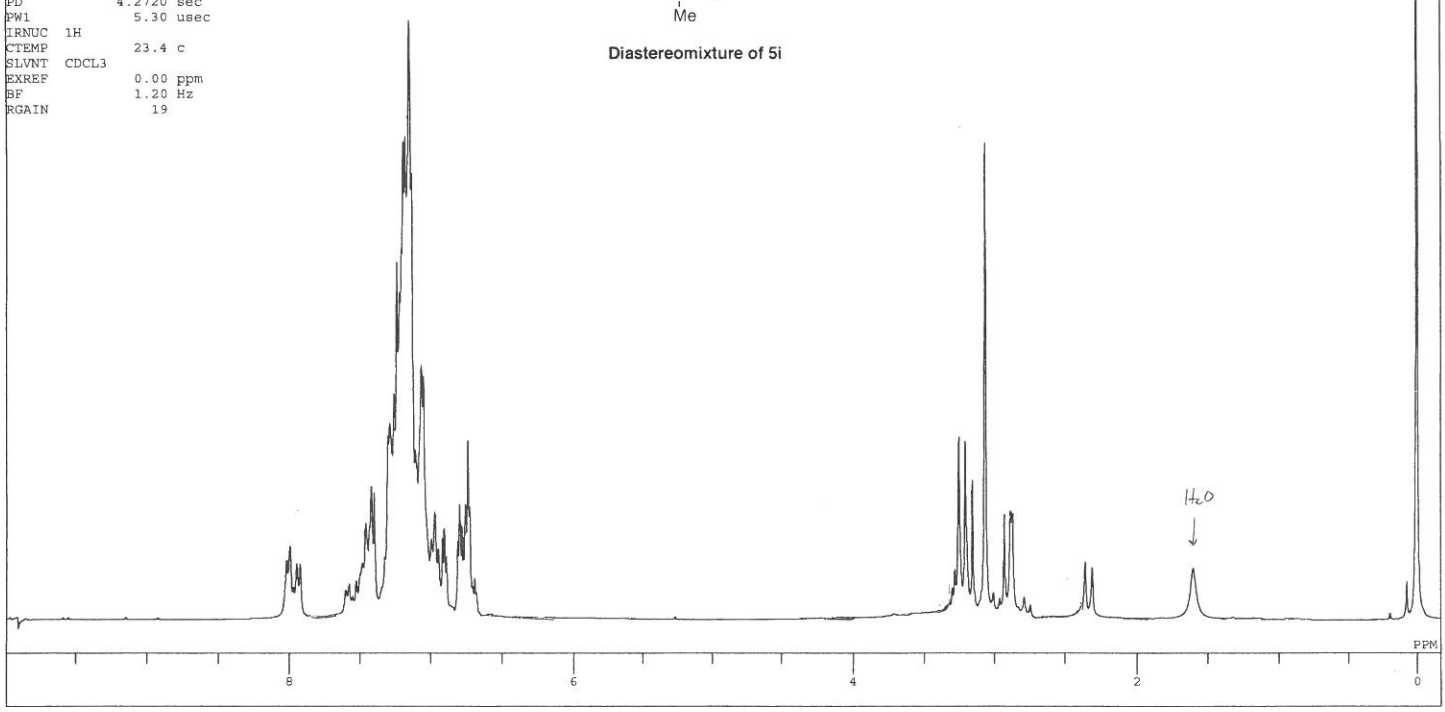


C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino Lab\mehtapyakut\mehtappureproduct\mqt1-2non.ALS

```
DFILE  mqt1-2non.ALS
COMNT
DATIM  Sat Mar 06 10:48:07 2010
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         16384
FREQU       6006.01 Hz
SCANS           101
ACQTM        2.7279 sec
PD           4.2720 sec
PW1            5.30 usec
IRNUC  1H
CTEMP          23.4 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            19
```



Diastereomixture of 5i



C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino Lab\mehtapyakut\mehtappureproduct\mqt1-2bcmALS.ALS

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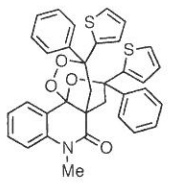
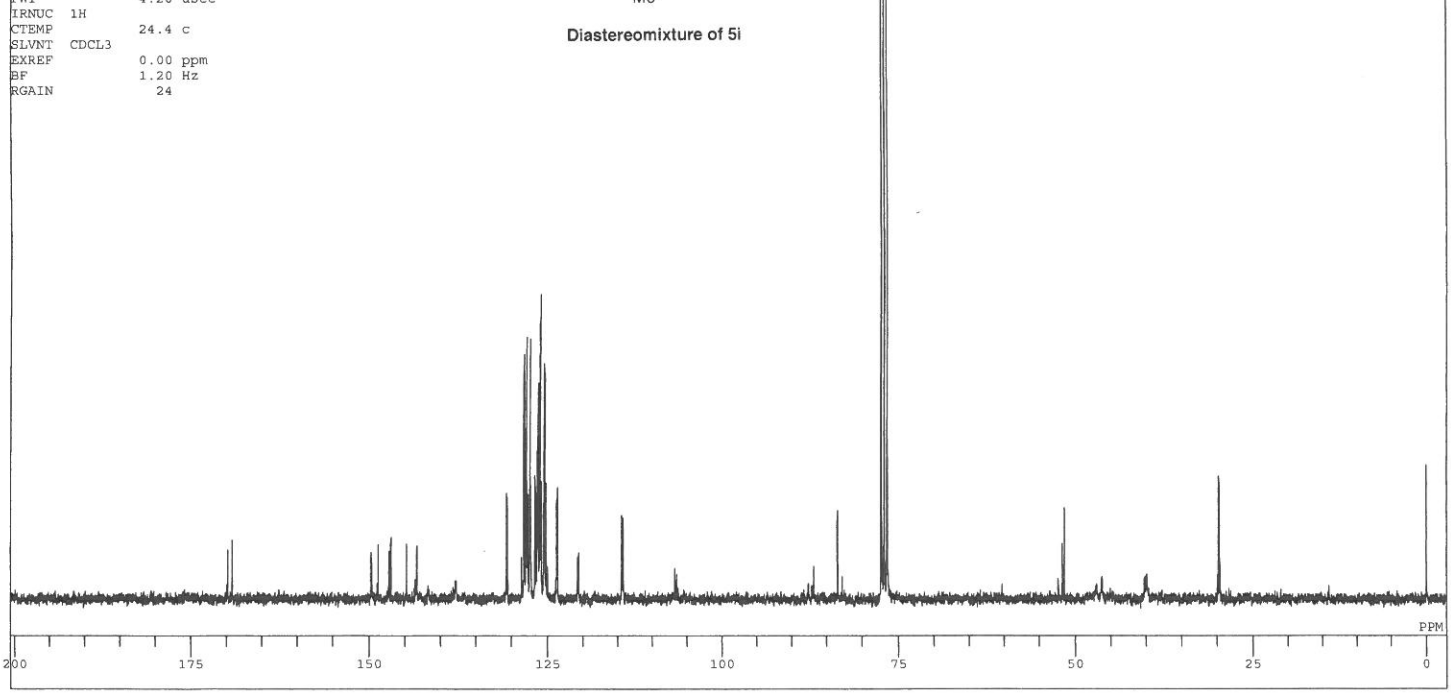
DFILE  mqt1-2bcmALS.ALS
COMNT
DATIM  Sat Mar 06 11:56:33 2010
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS          1342
ACQTM        1.6097 sec
PD           1.3900 sec
PW1            4.20 usec
IRNUC  1H
CTEMP          24.4 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            24
```

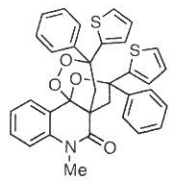


Diastereomixture of 5i



C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\mehtapyakut\mehtappureproduct\mqt1_1dept-revised.als

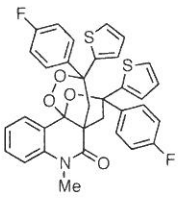
```
DFILE  mqt1_1dept-revised.als
COMNT
DATIM  Mon Mar 15 14:19:40 2010
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS           374
ACQTM        1.6097 sec
PD           1.3900 sec
PW1             8.30 usec
IRNUC  1H
CTEMP          24.4 c
SLVNT  CDCL3
EXREF         30.40 ppm
BF             1.20 Hz
RGAIN            26
```



Diastereomixture of 5i

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\mehtapyakut\mehtappureproduct\mqt2_2non.ALS

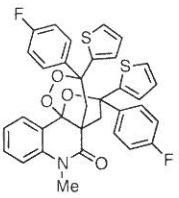
```
DFILE  mqt2_2non.ALS
COMNT
DATIM  Tue Mar 23 11:41:14 2010
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         16384
FREQU       6006.01 Hz
SCANS            41
ACQTM         2.7279 sec
PD            4.2720 sec
PW1              5.30 usec
IRNUC  1H
CTEMP          22.5 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            17
```



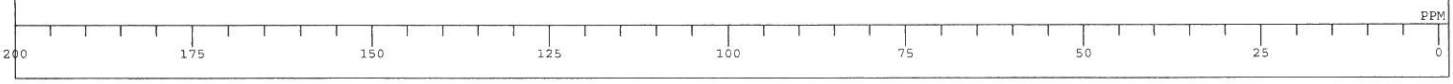
Diastereomixture of 5j

C:\Documents and Settings\Owner\ƒƒfXfNfgfbfv\Nishino_Lab\mehtapyakut\mehtappureproduct\mqt2_2bcm.ALS

```
DFILE  mqt2_2bcm.ALS
COMNT
DATIM  Tue Mar 23 11:58:17 2010
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS           313
ACQTM        1.6097 sec
PD           1.3900 sec
PW1            4.20 usec
IRNUC  1H
CTEMP          23.1 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            24
```

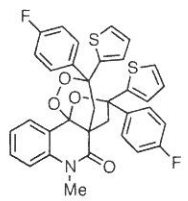


Diastereomixture of 5j

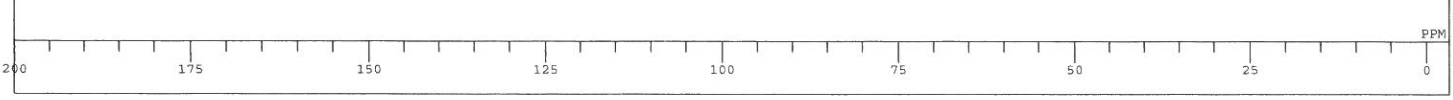


C:\Documents and Settings\Owner\ƒƒfXfNfgfbfv\Nishino_Lab\mehtapyakut\mehtappureproduct\mqt2_2dept.ALS

```
DFILE  mqt2_2dept.ALS
COMNT
DATIM  Tue Mar 23 12:14:49 2010
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS           301
ACQTM        1.6097 sec
PD           1.3900 sec
PW1            8.30 usec
IRNUC  1H
CTEMP          22.6 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            26
```

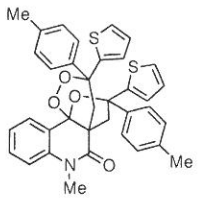


Diastereomixture of 5j



C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\mehtapyakut\mehtappureproduct\mqt3_2non.ALS

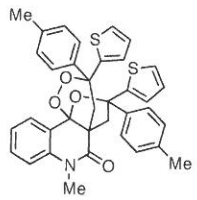
```
DFILE  mqt3_2non.ALS
COMNT
DATIM  Sat Apr 03 12:13:06 2010
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         16384
FREQU       6006.01 Hz
SCANS            37
ACQTM         2.7279 sec
PD            4.2720 sec
PW1             5.30 usec
IRNUC  1H
CTEMP           22.9 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             16
```



Diastereomixture of 5k

C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\mehtapyakut\mehtappureproduct\5-Me-bcm.als

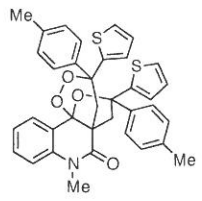
```
DFILE  5-Me-bcm.als
COMNT
DATIM  Sat Apr 03 12:40:50 2010
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS            518
ACQTM         1.6097 sec
PD            1.3900 sec
PW1              4.20 usec
IRNUC  1H
CTEMP           23.3 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             24
```



Diastereomixture of 5k

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\mehtapyakut\mehtappureproduct\5-Me-dept.als

```
DFILE  5-Me-dept.als
COMNT
DATIM  Sat Apr 03 13:15:58 2010
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS           673
ACQTM        1.6097 sec
PD           1.3900 sec
PW1             8.30 usec
IRNUC  1H
CTEMP          22.8 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            26
```

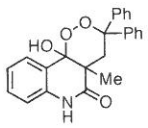


Diastereomixture of 5k

3-Me Ph rt dioxane

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Me-NH\3-MePh-rt_NON-2013.als

```
DFILE  3-MePh-rt_NON-2013.als
COMNT  3-Me Ph rt dioxane
DATIM  Tue Mar 19 16:21:17 2002
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1              5.20 usec
IRNUC  1H
CTEMP          25.0 c
SLVNT  DMSO
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            15
```

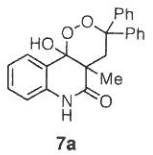


7a

3-Me Ph rt dioxane

C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\kumabe-NMR_data\3-Me-NH\3-MePh-rt_BCM-2013.als

```
DFILE  3-MePh-rt_BCM-2013.als
COMNT  3-Me Ph rt dioxane
DATIM  Tue Mar 19 16:35:29 2002
OBNUC  13C
EXMOD  BCM
OBFRQ          75.45 MHz
OBSET         124.00 KHz
OBFIN        1840.00 Hz
POINT          32768
FREQU       20408.10 Hz
SCANS            200
ACQTM          1.6056 sec
PD             1.3940 sec
PW1              4.20 usec
IRNUC  1H
CTEMP           25.9 c
SLVNT  DMSO
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             24
```

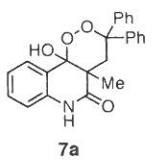


7a

3-Me Ph rt dioxane

C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\kumabe-NMR_data\3-Me-NH\3-MePh-rt_DEPT-2013.als

```
DFILE  3-MePh-rt_DEPT-2013.als
COMNT  3-Me Ph rt dioxane
DATIM  Tue Mar 19 16:46:39 2002
OBNUC  13C
EXMOD  DEPT
OBFRQ          75.45 MHz
OBSET         124.00 KHz
OBFIN        1840.00 Hz
POINT          32768
FREQU       20408.10 Hz
SCANS            200
ACQTM          1.6056 sec
PD             1.3940 sec
PW1              8.50 usec
IRNUC  1H
CTEMP           25.3 c
SLVNT  DMSO
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             25
```

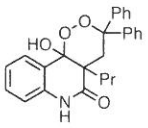


7a

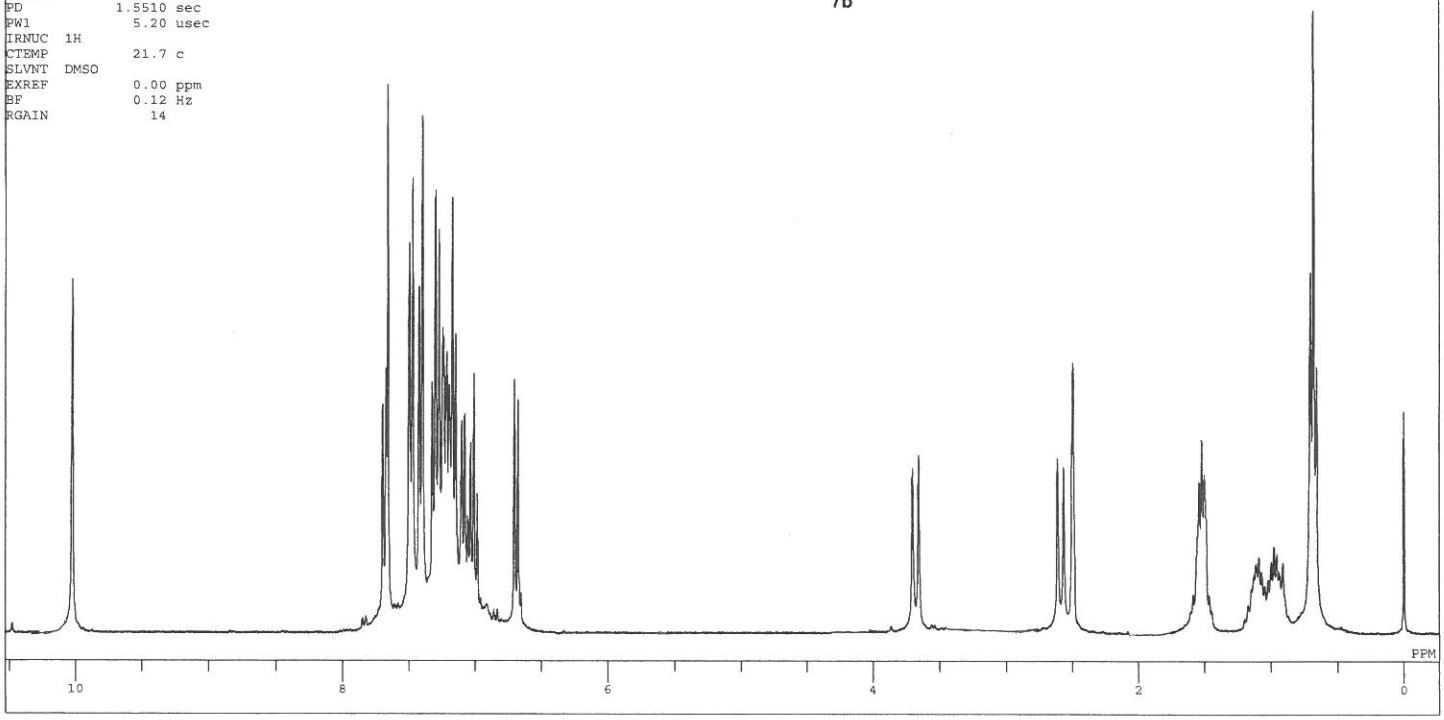
3-Pr rt dioxane

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Pr-NH\3-Pr-DIOXANE_NON-2013.als

```
DFILE  3-Pr-DIOXANE_NON-2013.als
COMNT  3-Pr rt dioxane
DATIM  Mon Apr 07 10:31:06 2003
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           21.7 c
SLVNT  DMSO
EXREF            0.00 ppm
BF               0.12 Hz
RGAIN              14
```



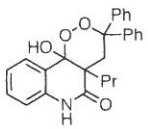
7b



3-Pr rt main

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Pr-NH\3-Pr-DIOXANE_BCM-2013.als

```
DFILE  3-Pr-DIOXANE_BCM-2013.als
COMNT  3-Pr rt main
DATIM  Mon Apr 07 10:21:28 2003
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           22.8 c
SLVNT  DMSO
EXREF           39.50 ppm
BF               1.20 Hz
RGAIN              22
```

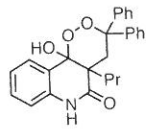


7b

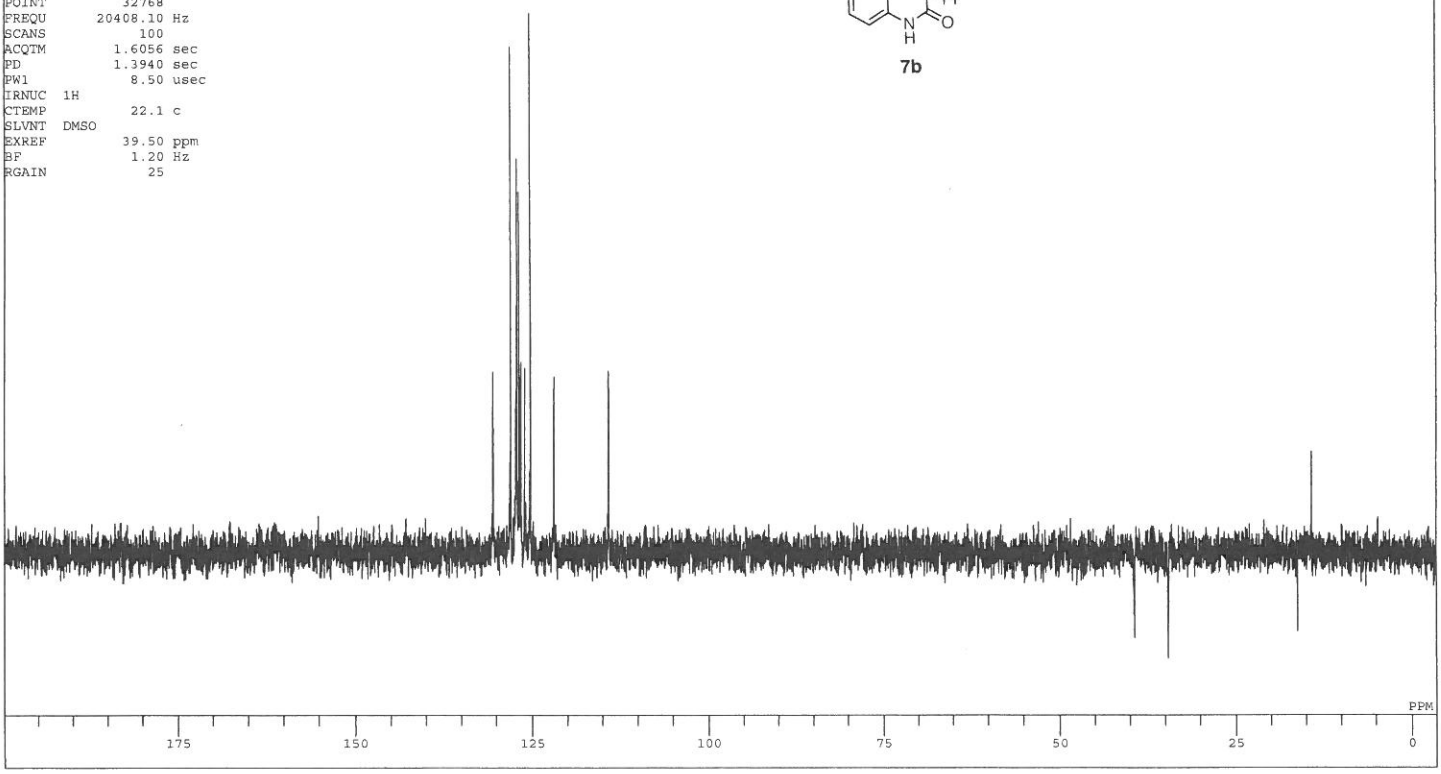
3-Pr rt dioxane

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Pr-NH\3-Pr-DIOXANE_DEPT-2013.als

```
DFILE  3-Pr-DIOXANE_DEPT-2013.als
COMNT  3-Pr rt dioxane
DATIM  Mon Apr 07 10:27:55 2003
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           22.1 c
SLVNT  DMSO
EXREF         39.50 ppm
BF             1.20 Hz
RGAIN            25
```



7b

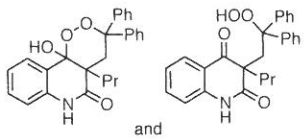


3-PrNH r.t. peroxide & dioxane

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Pr-NH\3-Pr-RT_MIX_NON-2013.als

```
DFILE  3-Pr-RT_MIX_NON-2013.als
COMNT  3-PrNH r.t. peroxide & dioxane
DATIM  Sun Mar 09 14:57:38 2003
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           22.4 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN              9
```

A mixture of

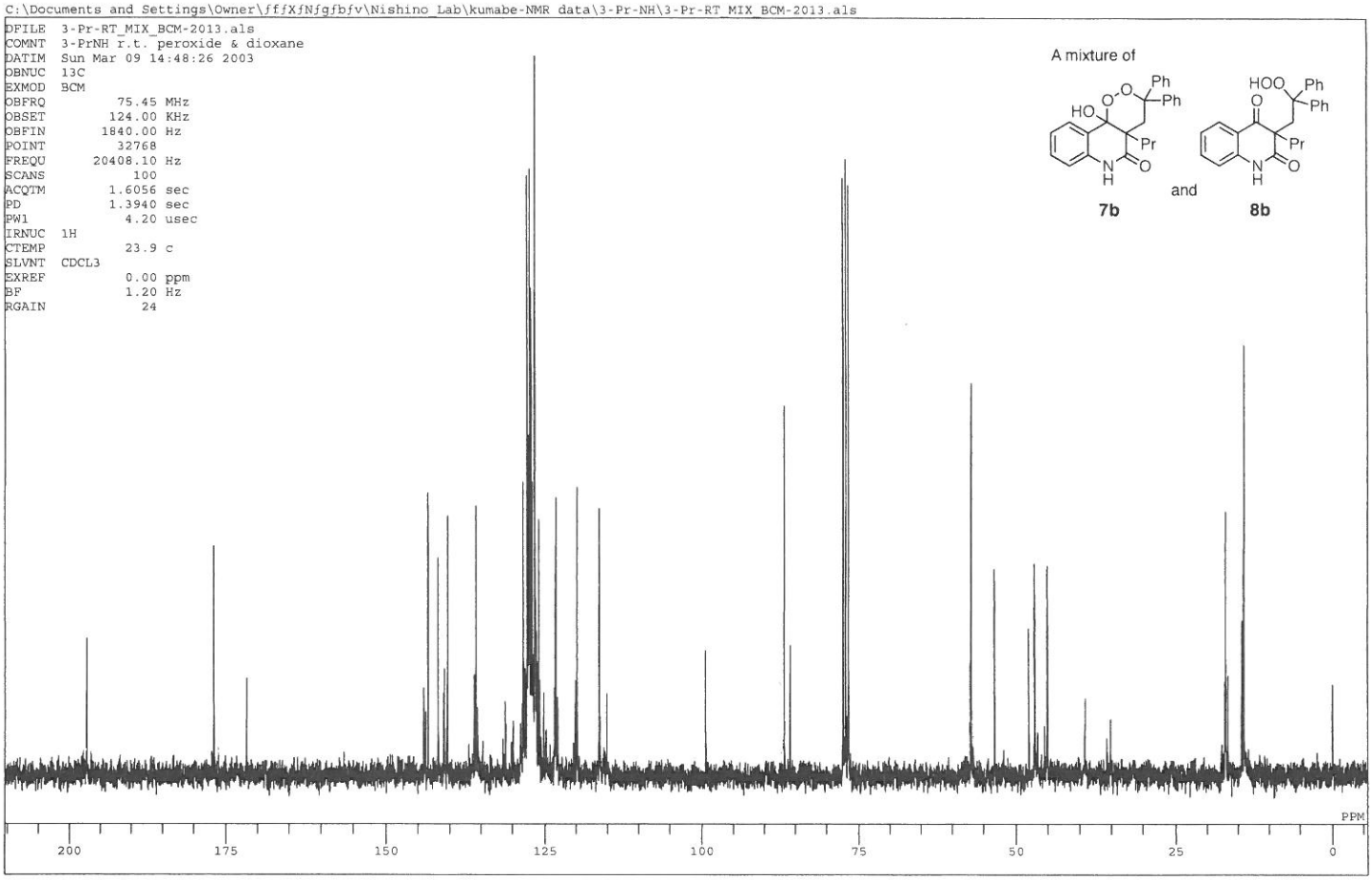


7b and **8b**

3-PrNH r.t. peroxide & dioxane

C:\Documents and Settings\Owner\ƒƒfXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Pr-NH\3-Pr-RT_MIX_BCM-2013.als

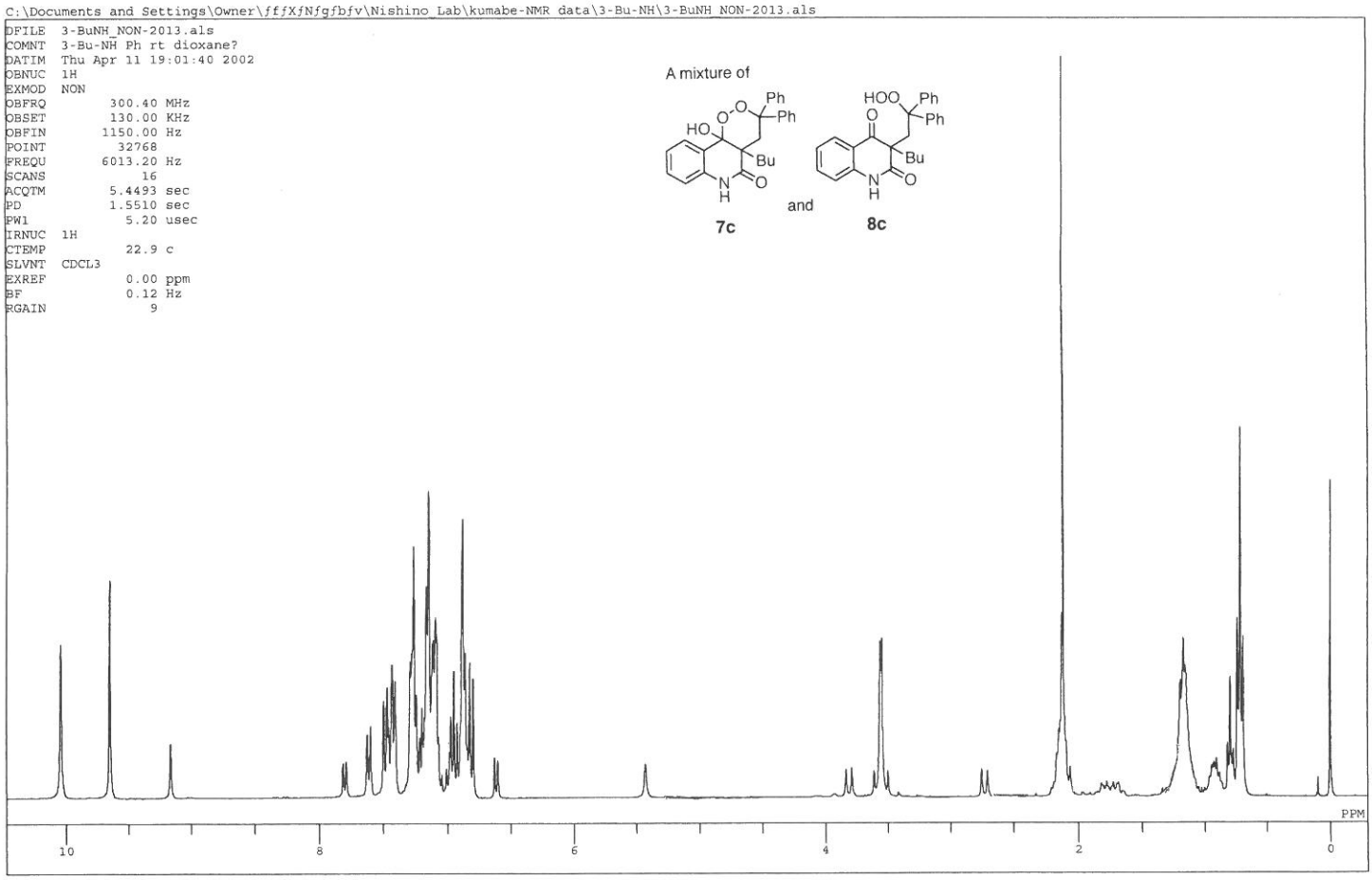
```
DFILE   3-Pr-RT_MIX_BCM-2013.als
COMNT   3-PrNH r.t. peroxide & dioxane
DATIM   Sun Mar 09 14:48:26 2003
OBNUC   13C
EXMOD   BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC   1H
CTEMP          23.9 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            24
```



3-Bu-NH Ph rt dioxane?

C:\Documents and Settings\Owner\ƒƒfXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Bu-NH\3-BuNH_NON-2013.als

```
DFILE   3-BuNH_NON-2013.als
COMNT   3-Bu-NH Ph rt dioxane?
DATIM   Thu Apr 11 19:01:40 2002
OBNUC   1H
EXMOD   NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC   1H
CTEMP          22.9 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN             9
```



3-Bu-NH Ph rt dioxane?

C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\kumabe-NMR_data\3-Bu-NH\3-BuNH_BCM-2013.als

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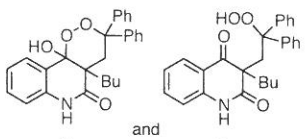
DFILE  3-BuNH_BCM-2013.als
COMNT  3-Bu-NH Ph rt dioxane?
DATIM  Thu Apr 11 18:52:19 2002
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           23.9 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             25
```

A mixture of



7c and 8c

3-Bu-NH Ph rt dioxane?

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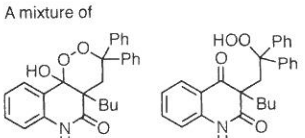
DFILE  MAIN_DEPT.ALS
COMNT  3-Bu-NH Ph rt dioxane?
DATIM  Thu Apr 11 18:58:35 2002
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           23.1 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             23
```

A mixture of



7c and 8c

3-Ph NH Ph rt F1

C:\Documents and Settings\Owner\ƒƒfXfNfgfbfv\Nishino Lab\kumabe-NMR data\3-PhNH\3-Ph-NH-mix-RT_F1_NON-2013.als

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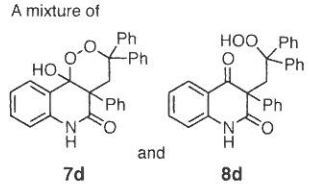
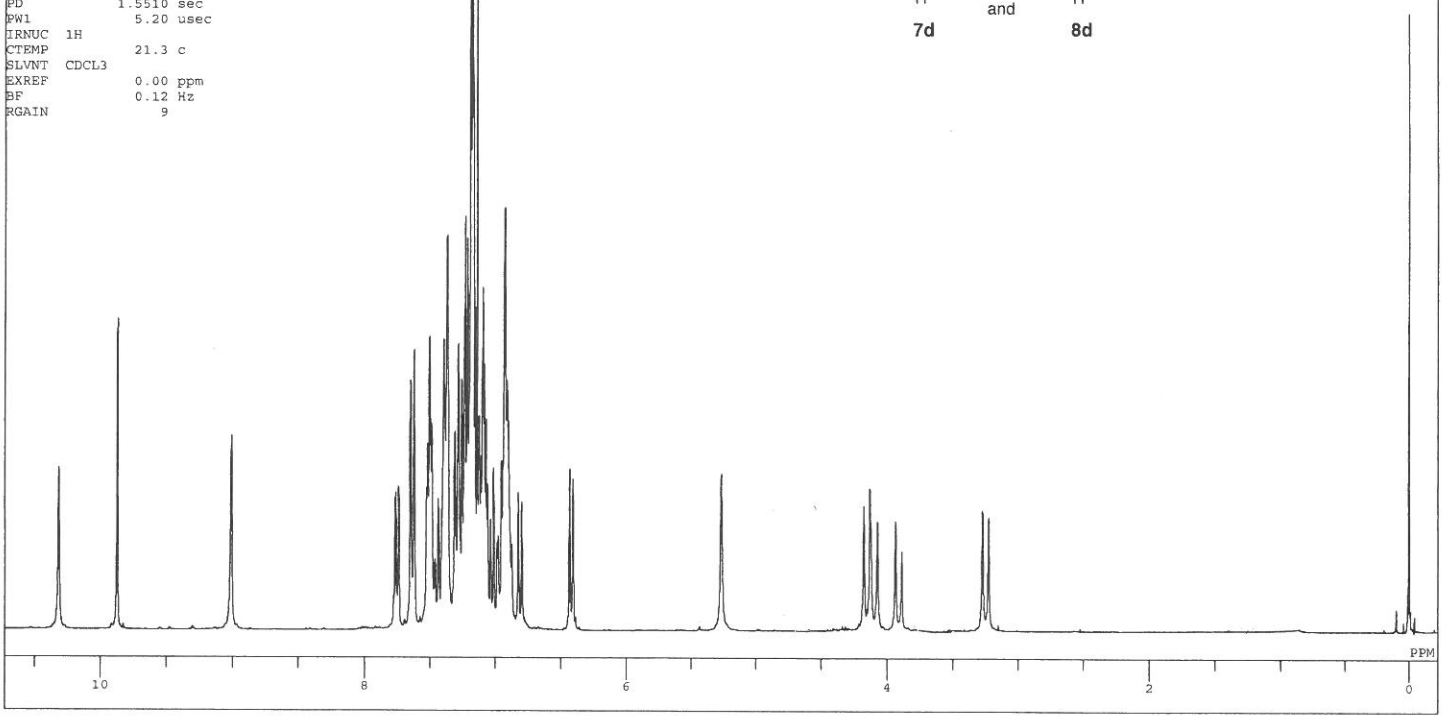
DFILE  3-Ph-NH-mix-RT_F1_NON-2013.als
COMNT  3-Ph NH Ph rt F1
DATIM  Mon May 27 09:14:12 2002
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           21.3 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN              9
```



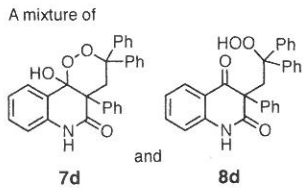
7d and **8d**



3-Ph NH Ph rt F1

C:\Documents and Settings\Owner\ƒƒfXfNfgfbfv\Nishino Lab\kumabe-NMR data\3-PhNH\3-Ph-NH-mix-RT_F1_BCM-2013.als

```
DFILE  3-Ph-NH-mix-RT_F1_BCM-2013.als
COMNT  3-Ph NH Ph rt F1
DATIM  Mon May 27 09:04:47 2002
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           22.4 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              1.20 Hz
RGAIN             23
```

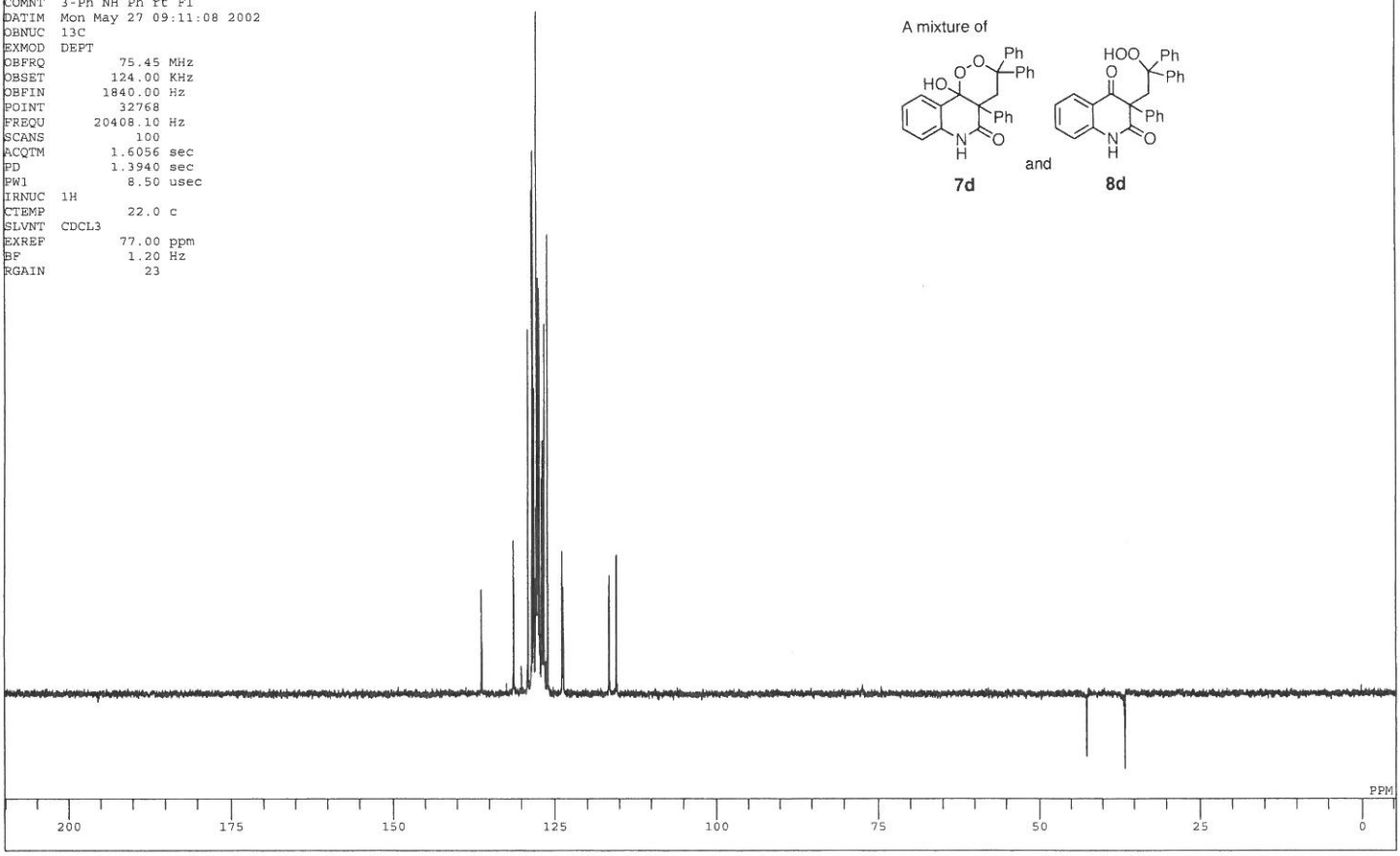


7d and **8d**

3-Ph NH Ph rt F1

C:\Documents and Settings\Owner\ƒƒXfNfgfbƒv\Nishino_Lab\kumabe-NMR data\3-PhNH\3-Ph-NH-mix-RT_F1_DEPT-2013.als

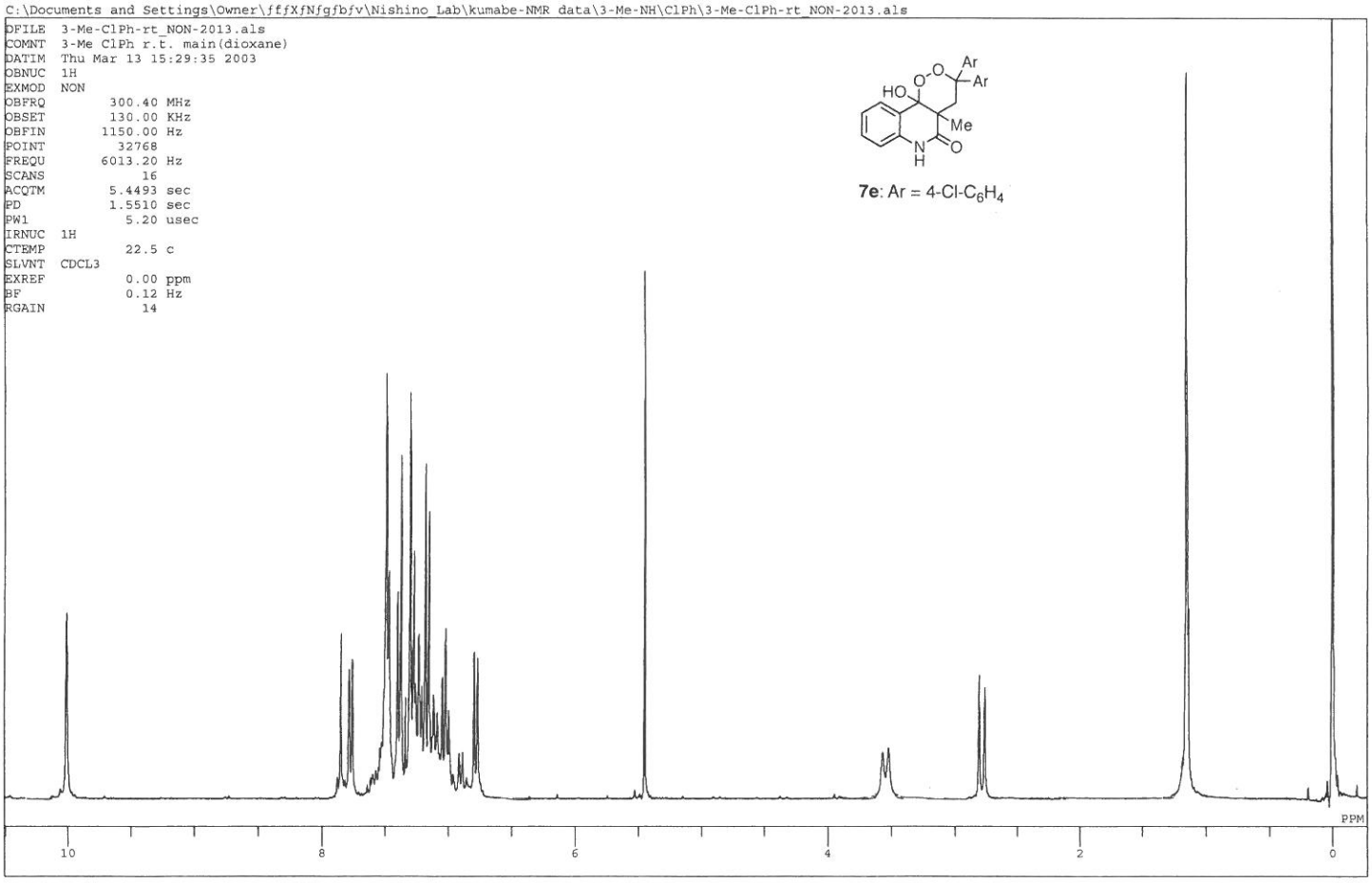
```
DFILE  3-Ph-NH-mix-RT_F1_DEPT-2013.als
COMNT  3-Ph NH Ph rt F1
DATIM  Mon May 27 09:11:08 2002
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET       124.00 KHz
OBFIN      1840.00 Hz
POINT        32768
FREQU     20408.10 Hz
SCANS          100
ACQTM       1.6056 sec
PD          1.3940 sec
PW1           8.50 usec
IRNUC  1H
CTEMP         22.0 c
SLVNT  CDCL3
EXREF       77.00 ppm
BF           1.20 Hz
RGAIN          23
```



3-Me ClPh r.t. main(dioxane)

C:\Documents and Settings\Owner\ƒƒXfNfgfbƒv\Nishino_Lab\kumabe-NMR data\3-Me-NH\ClPh\3-Me-ClPh-rt_NON-2013.als

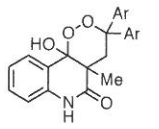
```
DFILE  3-Me-ClPh-rt_NON-2013.als
COMNT  3-Me ClPh r.t. main(dioxane)
DATIM  Thu Mar 13 15:29:35 2003
OBNUC  1H
EXMOD  NON
OBFRQ       300.40 MHz
OBSET       130.00 KHz
OBFIN      1150.00 Hz
POINT        32768
FREQU      6013.20 Hz
SCANS           16
ACQTM       5.4493 sec
PD          1.5510 sec
PW1           5.20 usec
IRNUC  1H
CTEMP         22.5 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           14
```



3-Me ClPh r.t. main(dioxane)

C:\Documents and Settings\Owner\ƒƒfXfNfgfbfv\Nishino_Lab\kumabe-NMR data\3-Me-NH\ClPh\3-Me-ClPh-rt_BCM-2013.als

```
DFILE  3-Me-ClPh-rt_BCM-2013.als
COMNT  3-Me ClPh r.t. main(dioxane)
DATIM  Thu Mar 13 15:19:13 2003
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN      1840.00 Hz
POINT        32768
FREQU     20408.10 Hz
SCANS          100
ACQTM       1.6056 sec
PD          1.3940 sec
PW1           4.20 usec
IRNUC  1H
CTEMP         23.4 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            1.20 Hz
RGAIN           25
```



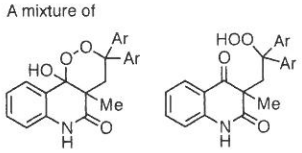
7e: Ar = 4-Cl-C_6H_4

3-Me MePh r.t.

C:\Documents and Settings\Owner\ƒƒfXfNfgfbfv\Nishino_Lab\kumabe-NMR data\3-Me-NH\MePh\3-Me-MePh-rt_NON-2013.als

```
DFILE  3-Me-MePh-rt_NON-2013.als
COMNT  3-Me MePh r.t.
DATIM  Thu Mar 13 16:58:49 2003
OBNUC  1H
EXMOD  NON
OBFRQ       300.40 MHz
OBSET       130.00 KHz
OBFIN      1150.00 Hz
POINT        32768
FREQU      6013.20 Hz
SCANS           16
ACQTM       5.4493 sec
PD          1.5510 sec
PW1           5.20 usec
IRNUC  1H
CTEMP         22.8 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           10
```

A mixture of

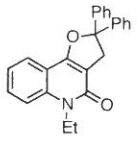


7f and **8f**: Ar = 4-Me-C_6H_4

N-Et Ph reflux F1

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒqƒhƒlƒtƒ‰ƒ"\N-Et_reflux\N-Et-Ph-reflux-NON-2013.als

```
DFILE  N-Et-Ph-reflux-NON-2013.als
COMNT  N-Et Ph reflux F1
DATIM  Thu Oct 10 22:55:57 2002
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           23.2 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             15
```

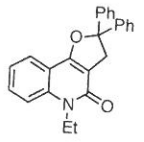


9b

N-Et Ph reflux F1

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒqƒhƒlƒtƒ‰ƒ"\N-Et_reflux\N-Et-Ph-reflux-BCM-2013.als

```
DFILE  N-Et-Ph-reflux-BCM-2013.als
COMNT  N-Et Ph reflux F1
DATIM  Thu Oct 10 23:24:36 2002
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            500
ACQTM         1.6056 sec
PD            1.3944 sec
PW1             4.25 usec
IRNUC  1H
CTEMP           23.6 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             25
```

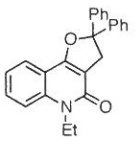


9b

N-Et Ph reflux F1

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒqƒhƒlƒtƒ‰ƒ"\N-Et_reflux\N-Et-Ph-reflux-DEPT-2013.als

```
DFILE  N-Et-Ph-reflux-DEPT-2013.als
COMNT  N-Et Ph reflux F1
DATIM  Thu Oct 10 23:40:13 2002
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           300
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           23.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            25
```

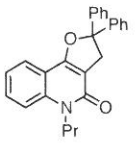


9b

NPr Ph reflux

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒqƒhƒlƒtƒ‰ƒ"\NPr\NPr-Ph_REF_NON-2013.als

```
DFILE  NPr-Ph_REF_NON-2013.als
COMNT  NPr Ph reflux
DATIM  Thu Feb 26 20:07:41 2004
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.80 usec
IRNUC  1H
CTEMP           23.8 c
SLVNT  CDCL3
EXREF            0.00 ppm
BF               0.12 Hz
RGAIN              12
```

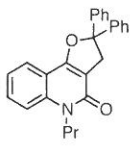


9c

NPr reflux

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒgƒhƒfƒtƒ‰ƒ"\NPr\NPr-Ph_REF_BCM-2013.als

```
DFILE  NPr-Ph_REF_BCM-2013.als
COMNT  NPr reflux
DATIM  Thu Feb 26 20:15:55 2004
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            40
ACQTM         1.6056 sec
PD            1.3940 sec
PW1            5.00 usec
IRNUC  1H
CTEMP          23.7 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            25
```

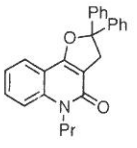


9c

NPr reflux

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒgƒhƒfƒtƒ‰ƒ"\NPr\NPr-Ph_REF_DEPT-2013.als

```
DFILE  NPr-Ph_REF_DEPT-2013.als
COMNT  NPr reflux
DATIM  Thu Feb 26 20:19:10 2004
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            40
ACQTM         1.6056 sec
PD            1.3940 sec
PW1           10.00 usec
IRNUC  1H
CTEMP          23.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            25
```

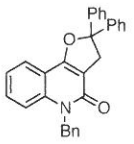


9c

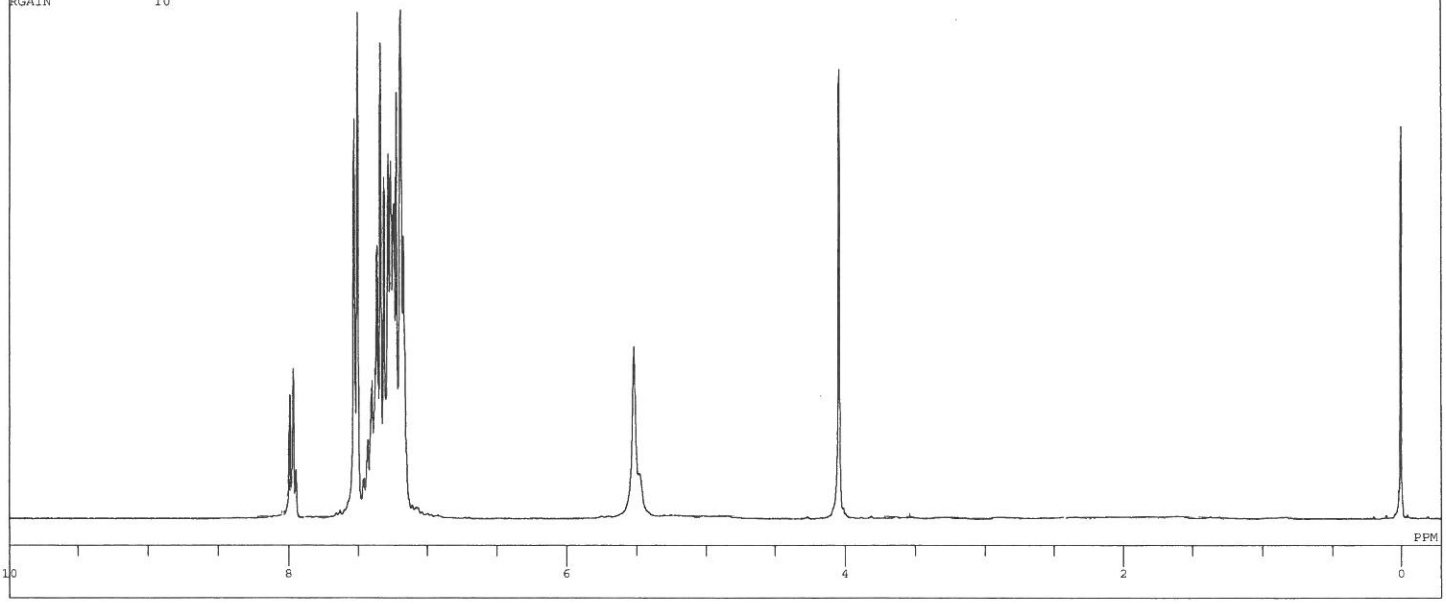
NBn Ph reflux F1

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NBn-Ph_reflux\NBn-Ph-reflux-non-2013.als

```
DFILE  NBn-Ph-reflux-non-2013.als
COMNT  NBn Ph reflux F1
DATIM  Sun Jul 08 12:12:02 2001
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           24.8 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             10
```



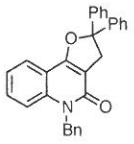
9d



NBn Ph reflux F1

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NBn-Ph_reflux\NBn-Ph-reflux-BCM-2013.als

```
DFILE  NBn-Ph-reflux-BCM-2013.als
COMNT  NBn Ph reflux F1
DATIM  Sun Jul 08 12:08:51 2001
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET       124.00 KHz
OBFIN      1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            76
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           25.6 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             25
```

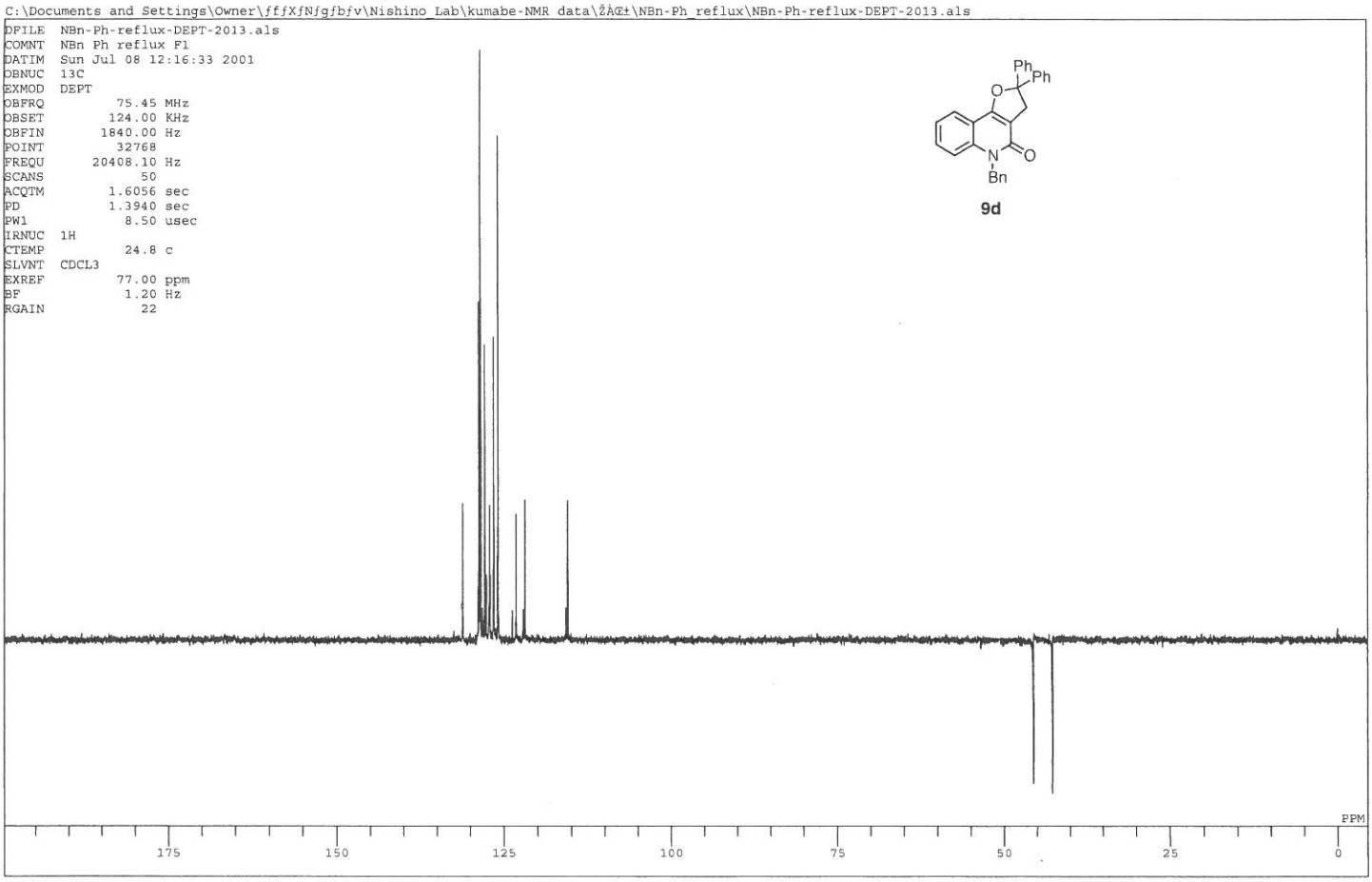


9d

NBn Ph reflux F1

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\ŽÀŒ±\NBn-Ph_reflux\NBn-Ph-reflux-DEPT-2013.als

```
DPILE  NBn-Ph-reflux-DEPT-2013.als
COMNT  NBn Ph reflux F1
DATIM  Sun Jul 08 12:16:33 2001
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            50
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           24.8 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            22
```

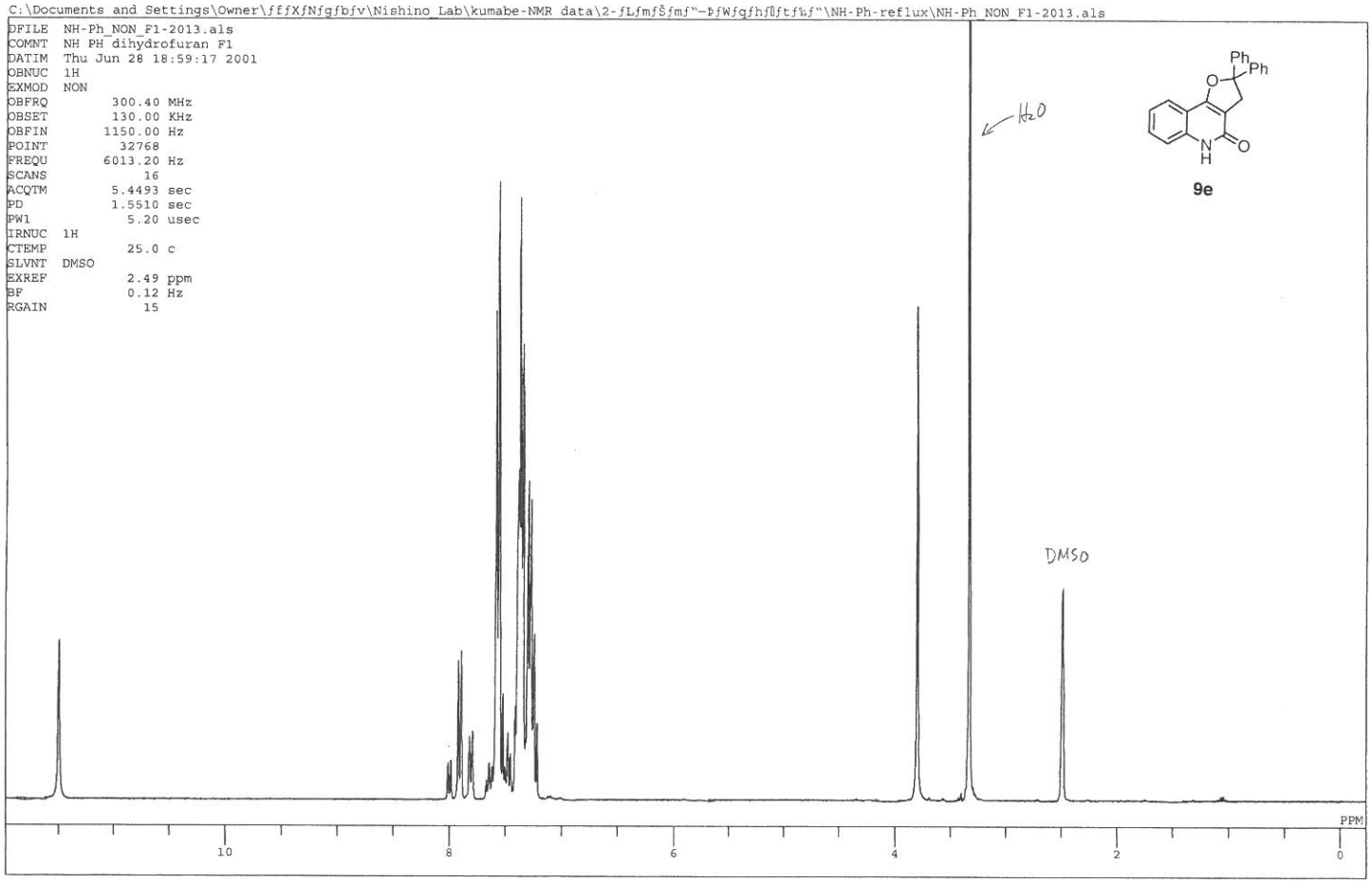


9d

NH PH dihydrofuran F1

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–þƒWƒqƒhƒ‰ƒtƒ‰ƒ"\NH-Ph-reflux\NH-Ph_NON_F1-2013.als

```
DPILE  NH-Ph_NON_F1-2013.als
COMNT  NH PH dihydrofuran F1
DATIM  Thu Jun 28 18:59:17 2001
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           25.0 c
SLVNT  DMSO
EXREF           2.49 ppm
BF              0.12 Hz
RGAIN            15
```

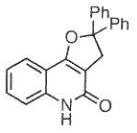


9e

NH PH dihydrofuran F1

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒqƒhƒlƒtƒ‰ƒ"\NH-Ph-reflux\NH-Ph_BCM_F1-2013.als

```
DFILE  NH-Ph_BCM_F1-2013.als
COMNT  NH PH dihydrofuran F1
DATIM  Thu Jun 28 18:55:59 2001
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           26.0 c
SLVNT  DMSO
EXREF         39.50 ppm
BF             1.20 Hz
RGAIN            23
```

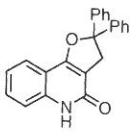


9e

NH PH dihydrofuran F1

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒqƒhƒlƒtƒ‰ƒ"\NH-Ph-reflux\NH-Ph_DEPT_F1-2013.als

```
DFILE  NH-Ph_DEPT_F1-2013.als
COMNT  NH PH dihydrofuran F1
DATIM  Thu Jun 28 19:06:31 2001
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           24.9 c
SLVNT  DMSO
EXREF         39.50 ppm
BF             1.20 Hz
RGAIN            24
```

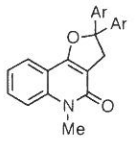


9e

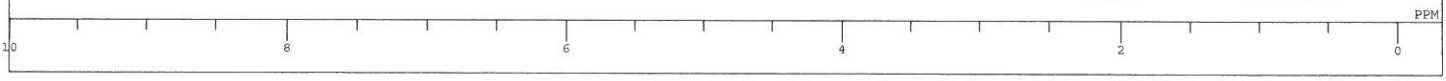
NMe ClPh reflux_F1

C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\kumabe-NMR data\2-fLfmfŠfmf"-þfWfqfhflftf‰f"\NMe-ClPh\NMe-ClPH_NON_F1-2013.als

```
DFILE  NMe-ClPH_NON_F1-2013.als
COMNT  NMe ClPh reflux_F1
DATIM  Thu Jun 21 16:01:43 2001
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           24.4 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             12
```



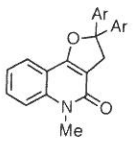
9f: Ar = 4-Cl-C_6H_4



NMe ClPh reflux_F1

C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\kumabe-NMR data\2-fLfmfŠfmf"-þfWfqfhflftf‰f"\NMe-ClPh\NMe-ClPH_BCM_F1-2013.als

```
DFILE  NMe-ClPH_BCM_F1-2013.als
COMNT  NMe ClPh reflux_F1
DATIM  Thu Jun 21 15:57:55 2001
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           25.4 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             24
```

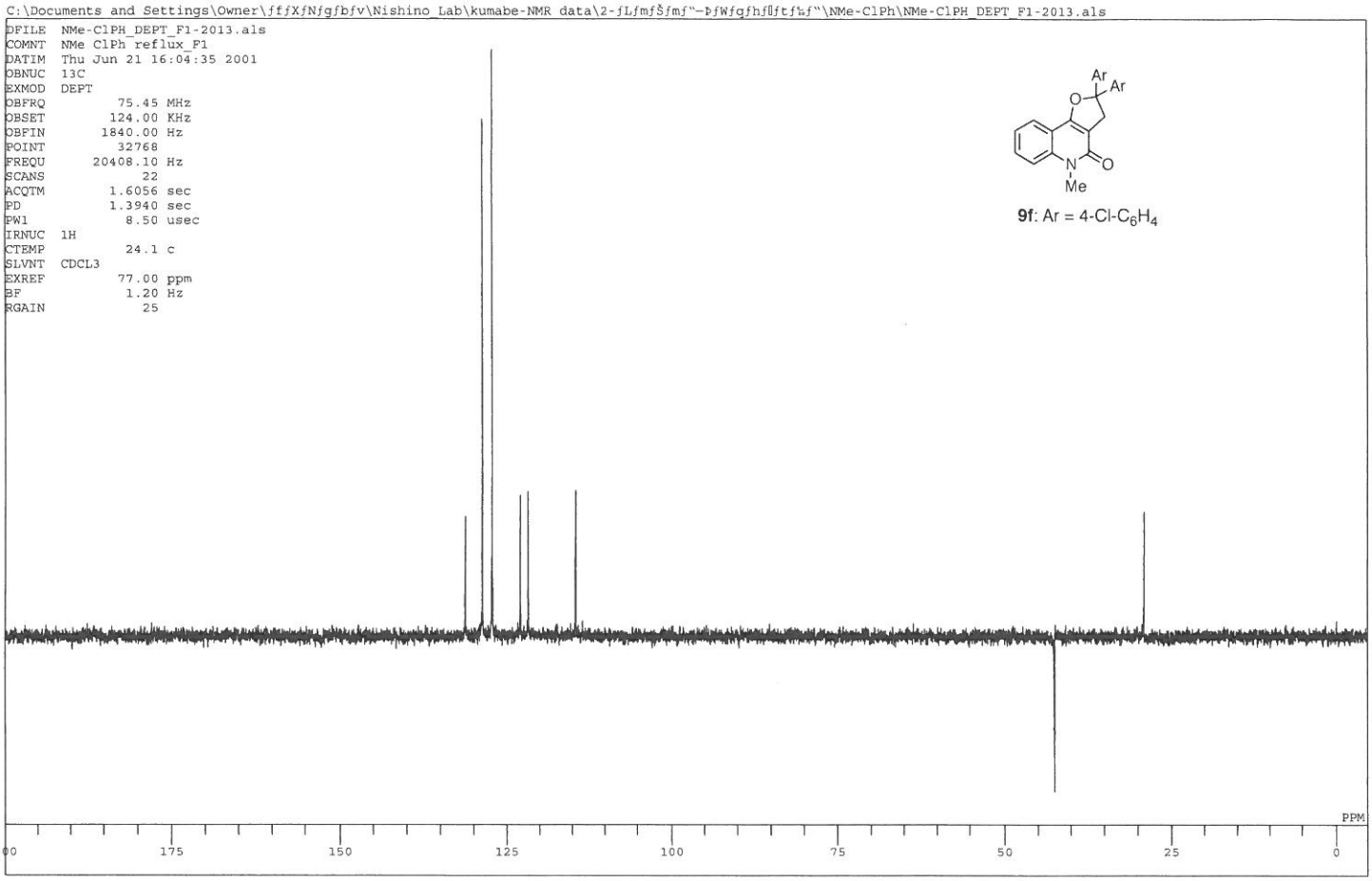


9f: Ar = 4-Cl-C_6H_4

NMe ClPh reflux_F1

C:\Documents and Settings\Owner\ffƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒqƒhƒlƒtƒ‰ƒ"\NMe-ClPh\NMe-ClPH_DEPT_F1-2013.als

```
DFILE  NMe-ClPH_DEPT_F1-2013.als
COMNT  NMe ClPh reflux_F1
DATIM  Thu Jun 21 16:04:35 2001
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            22
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           24.1 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            25
```

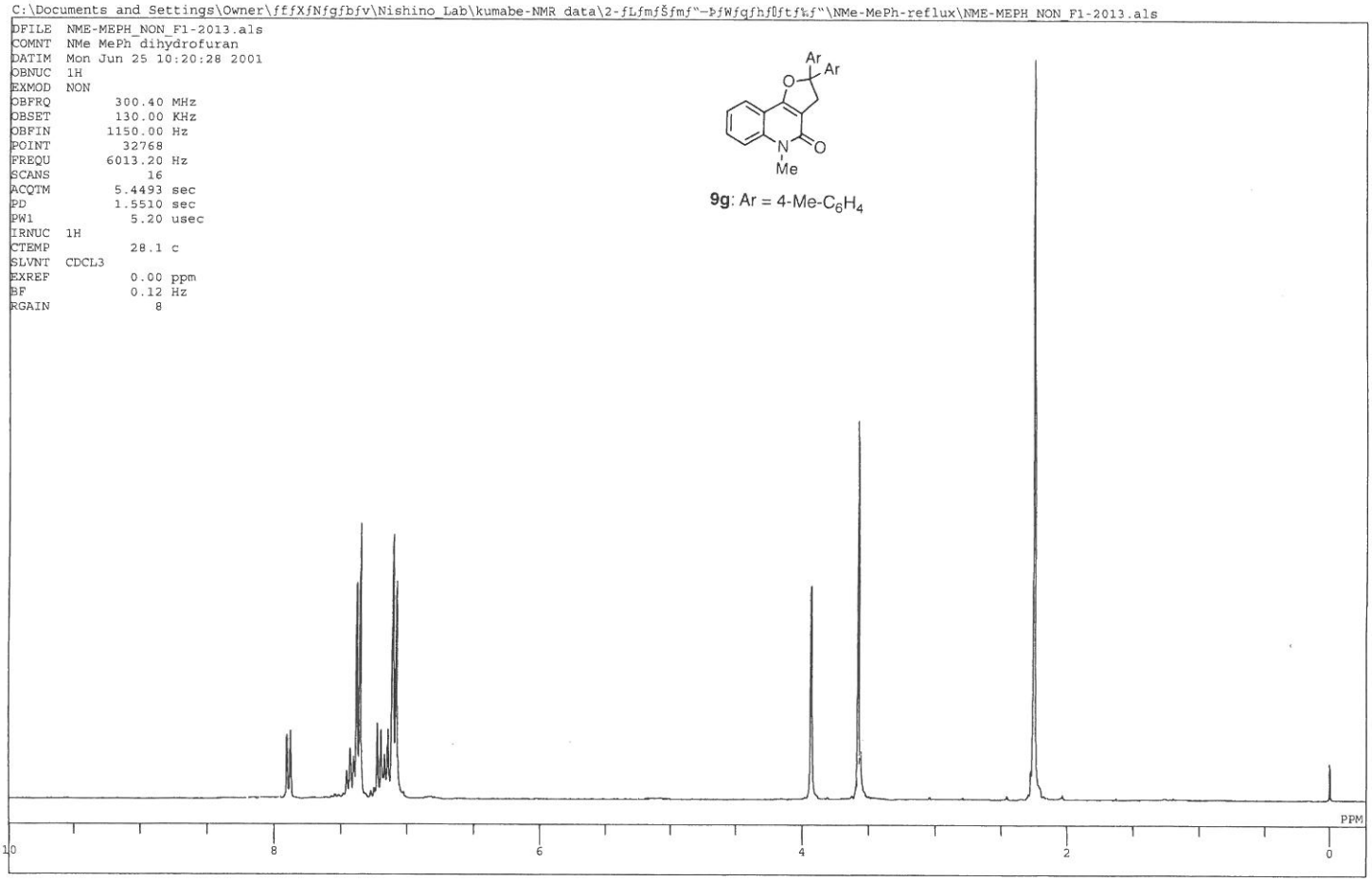


9f: Ar = 4-Cl-C_6H_4

NMe MePh dihydrofuran

C:\Documents and Settings\Owner\ffƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒqƒhƒlƒtƒ‰ƒ"\NMe-MePh-reflux\NME-MEPH_NON_F1-2013.als

```
DFILE  NME-MEPH_NON_F1-2013.als
COMNT  NMe MePh dihydrofuran
DATIM  Mon Jun 25 10:20:28 2001
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           28.1 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN              8
```

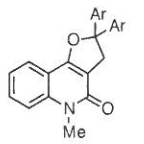


9g: Ar = 4-Me-C_6H_4

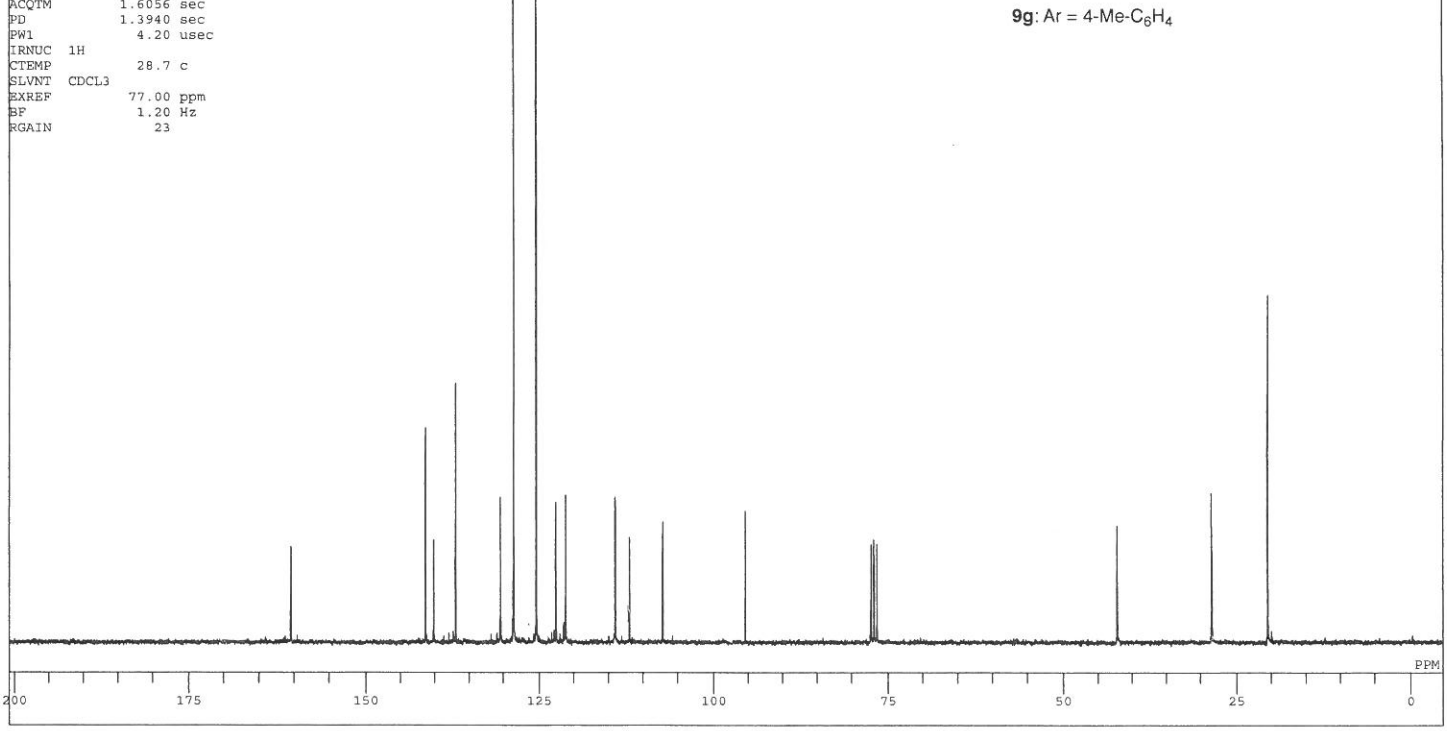
NMe MePh dihydrofuran

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒqƒhƒlƒtƒ‰ƒ"\NMe-MePh-reflux\NME-MEPH_bcm_F1-2013.als

```
DFILE  NME-MEPH_bcm_F1-2013.als
COMNT  NMe MePh dihydrofuran
DATIM  Mon Jun 25 10:13:01 2001
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            50
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           28.7 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            23
```



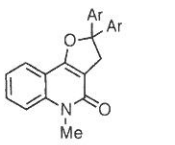
9g: Ar = 4-Me-C_6H_4



NME MePh dihydrofuran

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒqƒhƒlƒtƒ‰ƒ"\NMe-MePh-reflux\NME-MEPH_dept_F1-2013.als

```
DFILE  NME-MEPH_dept_F1-2013.als
COMNT  NME MePh dihydrofuran
DATIM  Mon Jun 25 10:17:03 2001
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            50
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           28.8 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            23
```

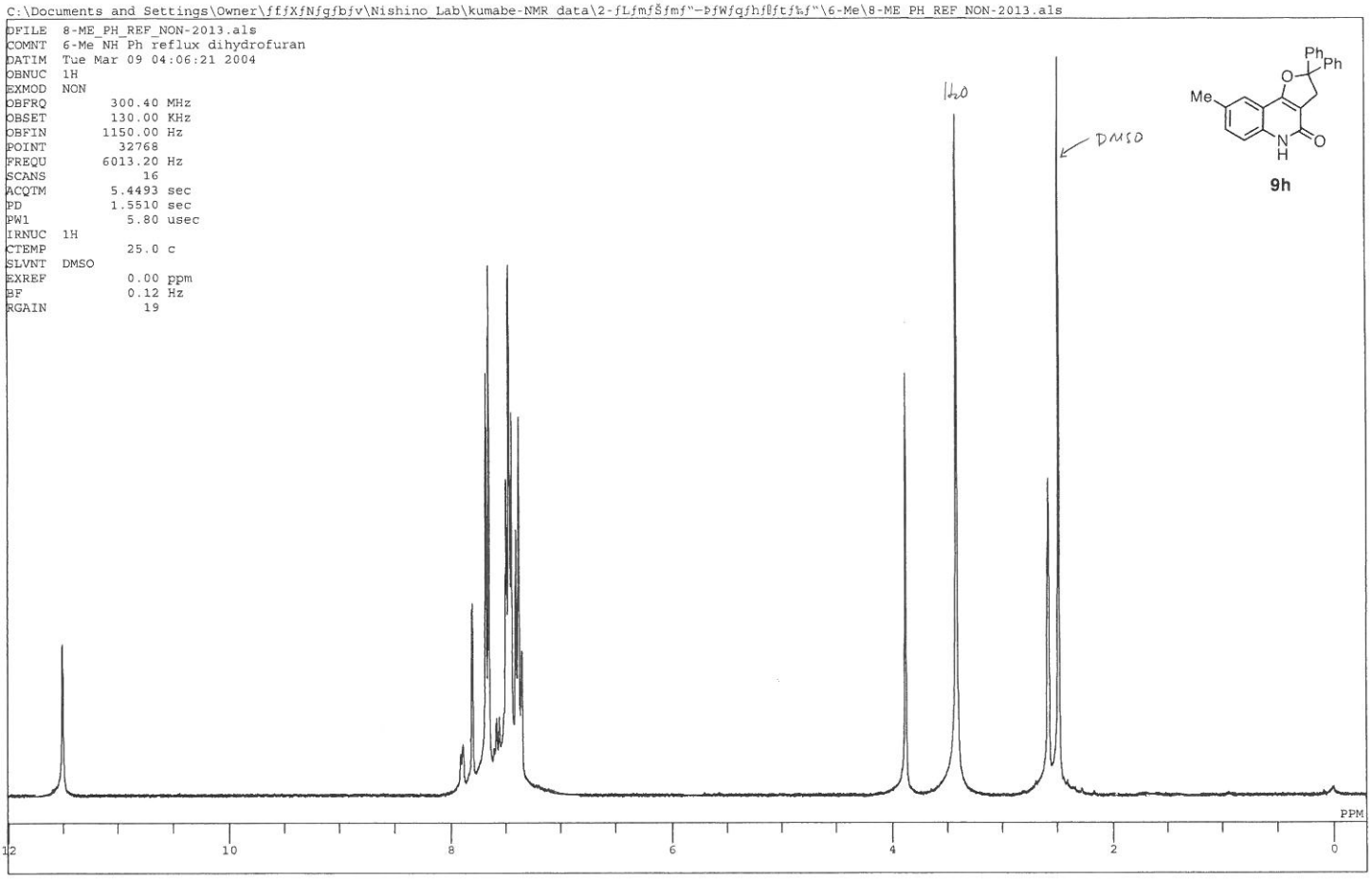


9g: Ar = 4-Me-C_6H_4

6-Me NH Ph reflux dihydrofuran

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒqƒhƒ‰ƒtƒ‰ƒ"\6-Me\8-ME_PH_REF_NON-2013.als

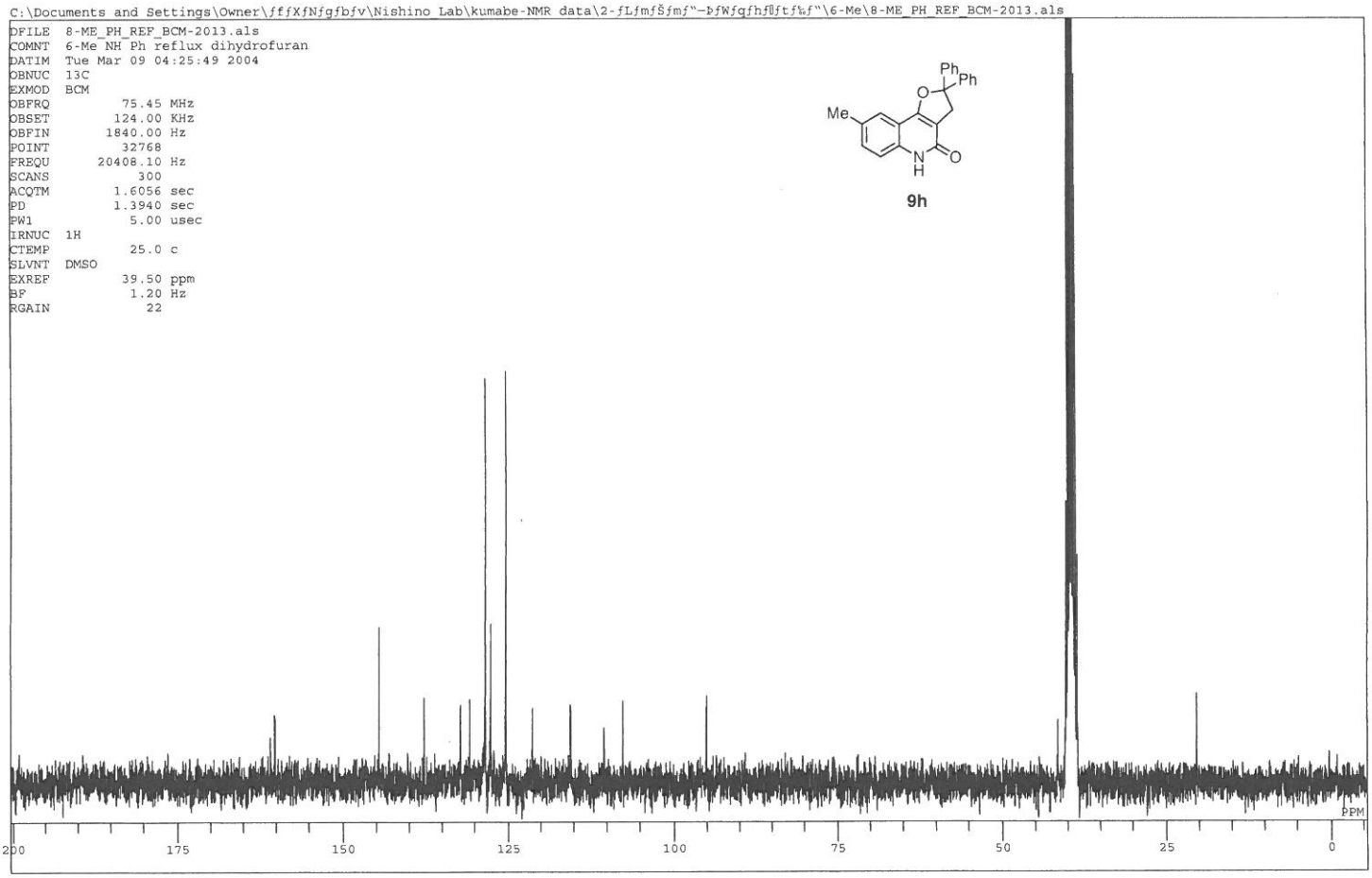
```
DFILE  8-ME_PH_REF_NON-2013.als
COMNT  6-Me NH Ph reflux dihydrofuran
DATIM  Tue Mar 09 04:06:21 2004
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.80 usec
IRNUC  1H
CTEMP           25.0 c
SLVNT  DMSO
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             19
```



6-Me NH Ph reflux dihydrofuran

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒqƒhƒ‰ƒtƒ‰ƒ"\6-Me\8-ME_PH_REF_BCM-2013.als

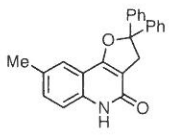
```
DFILE  8-ME_PH_REF_BCM-2013.als
COMNT  6-Me NH Ph reflux dihydrofuran
DATIM  Tue Mar 09 04:25:49 2004
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            300
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             5.00 usec
IRNUC  1H
CTEMP           25.0 c
SLVNT  DMSO
EXREF          39.50 ppm
BF              1.20 Hz
RGAIN             22
```



6-Me NH Ph reflux dihydrofuran

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"-ƒÞƒWƒqƒhƒlƒtƒ‰ƒ"\6-Me\8-ME_PH_REF_DEPT-2013.als

```
DFILE  8-ME_PH_REF_DEPT-2013.als
COMNT  6-Me NH Ph reflux dihydrofuran
DATIM  Tue Mar 09 04:42:50 2004
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           300
ACQTM         1.6056 sec
PD            1.3940 sec
PW1            10.00 usec
IRNUC  1H
CTEMP          25.3 c
SLVNT  DMSO
EXREF         39.50 ppm
BF             1.20 Hz
RGAIN            25
```

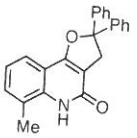


9h

single_pulse

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"-ƒÞƒWƒqƒhƒlƒtƒ‰ƒ"\6-Me-NH-reflux\6-Me-NH-Ph-non-2013.als

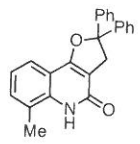
```
DFILE  6-Me-NH-Ph-non-2013.als
COMNT  single_pulse
DATIM  2012-09-10 10:21:54
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         16384
FREQU       9384.38 Hz
SCANS            16
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             5.63 usec
IRNUC  1H
CTEMP          21.2 c
SLVNT  DMSO
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            38
```



9i

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"-ÞƒWƒqƒhƒlƒtƒ‰ƒ"\8-Me-quinoline\6-Me-NH-Ph-bcm-2013.als

```
DFILE  6-Me-NH-Ph-bcm-2013.als
COMNT
DATIM  2012-09-11 04:44:00
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS         10000
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.33 usec
IRNUC  1H
CTEMP          22.0 c
SLVNT  DMSO
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            54
```

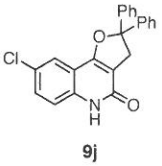


9i

6-Cl Ph reflux dihydrofuran

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"-ÞƒWƒqƒhƒlƒtƒ‰ƒ"\6-Cl\6-CL_PH_REF_NON-2013.als

```
DFILE  6-CL_PH_REF_NON-2013.als
COMNT  6-Cl Ph reflux dihydrofuran
DATIM  Mon Mar 08 14:02:14 2004
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.80 usec
IRNUC  1H
CTEMP           25.0 c
SLVNT  DMSO
EXREF           2.49 ppm
BF              0.12 Hz
RGAIN             19
```

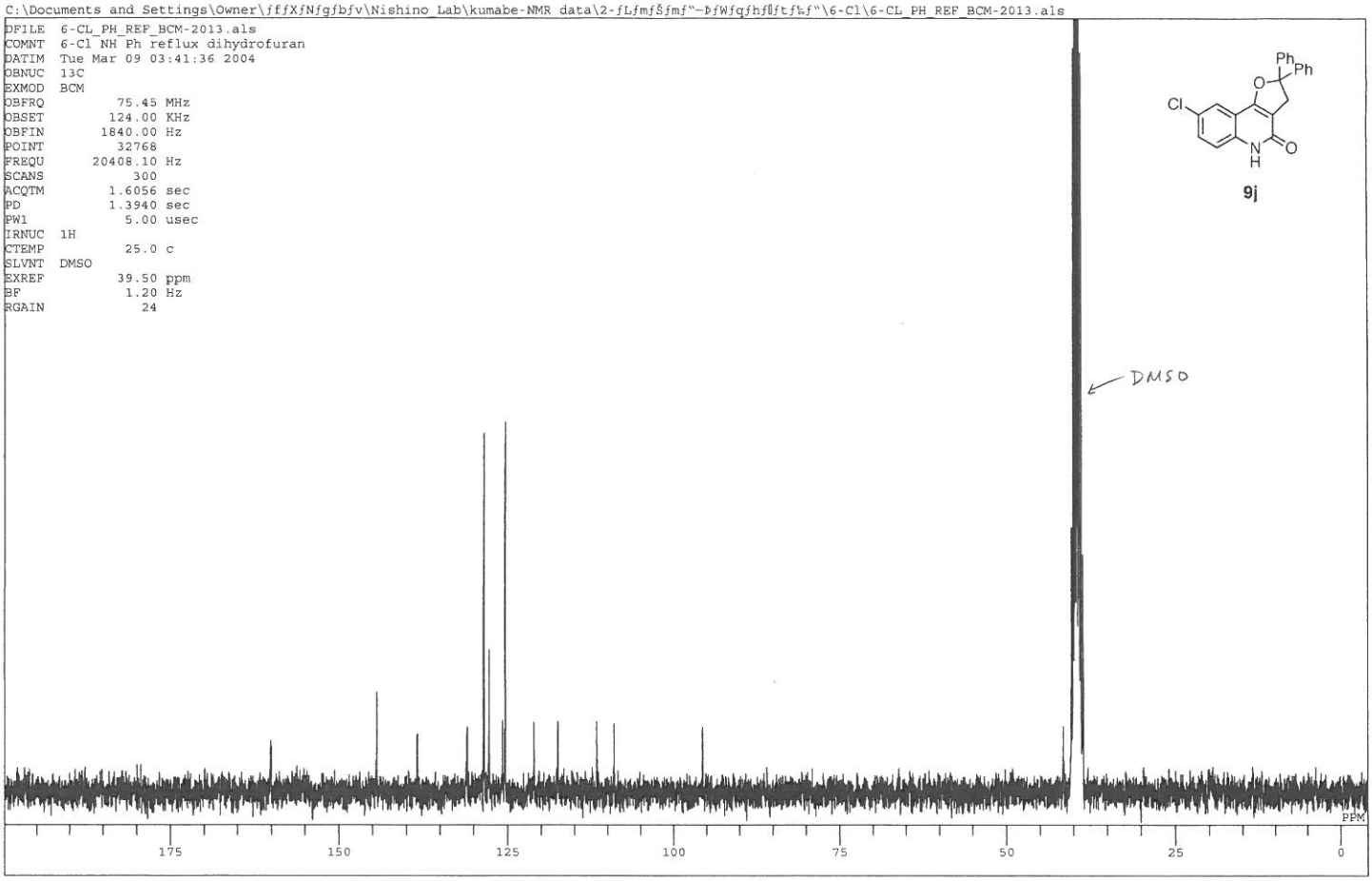


9j

6-Cl NH Ph reflux dihydrofuran

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"-ƒÞƒWƒqƒhƒlƒtƒ‰ƒ"\6-Cl\6-CL_PH_REF_BCM-2013.als

```
DFILE  6-CL_PH_REF_BCM-2013.als
COMNT  6-Cl NH Ph reflux dihydrofuran
DATIM  Tue Mar 09 03:41:36 2004
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN      1840.00 Hz
POINT        32768
FREQU     20408.10 Hz
SCANS          300
ACQTM       1.6056 sec
PD          1.3940 sec
PW1           5.00 usec
IRNUC  1H
CTEMP         25.0 c
SLVNT  DMSO
EXREF        39.50 ppm
BF            1.20 Hz
RGAIN           24
```

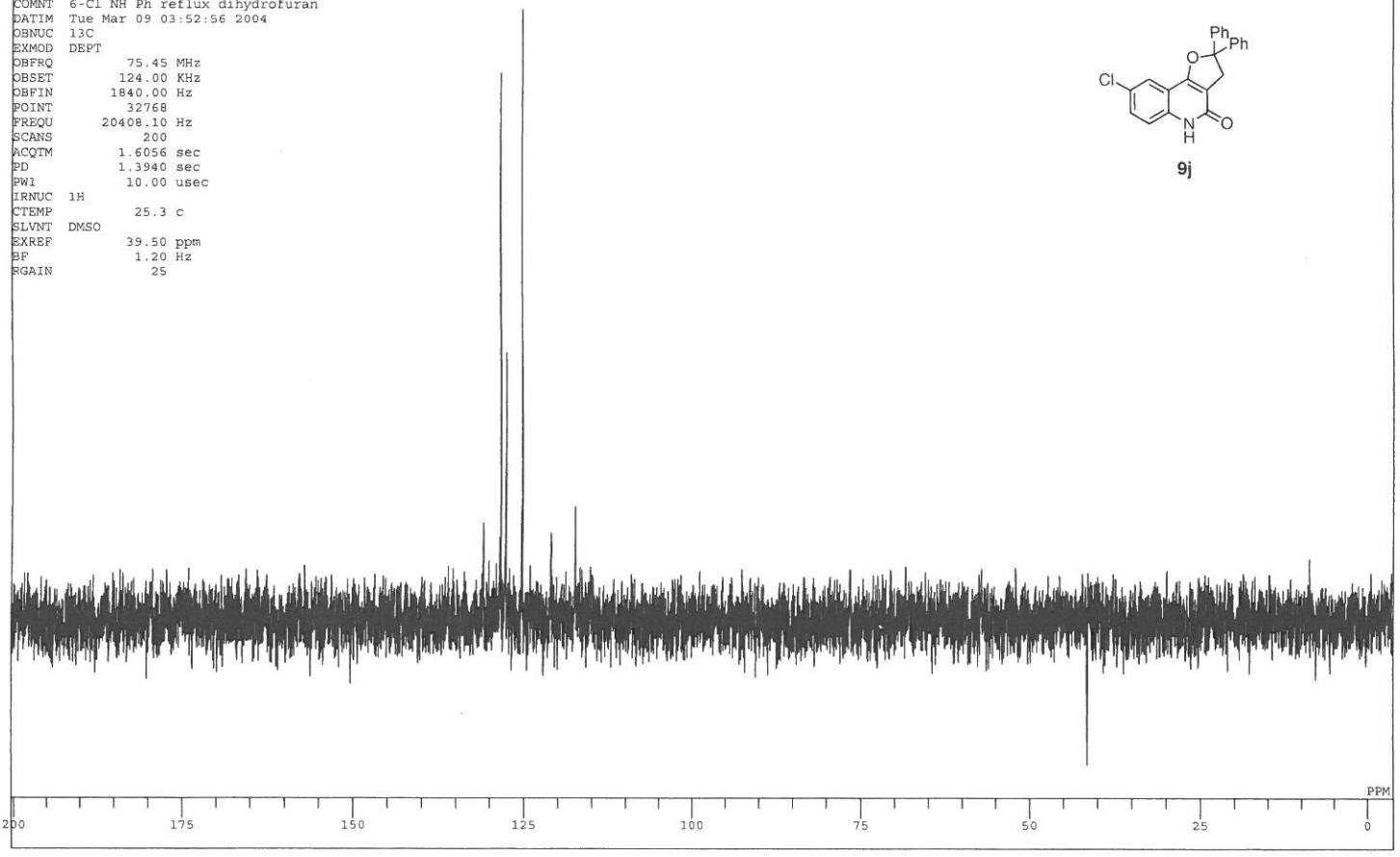


9j

6-Cl NH Ph reflux dihydrofuran

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"-ƒÞƒWƒqƒhƒlƒtƒ‰ƒ"\6-Cl\6-CL_PH_REF_DEPT-2013.als

```
DFILE  6-CL_PH_REF_DEPT-2013.als
COMNT  6-Cl NH Ph reflux dihydrofuran
DATIM  Tue Mar 09 03:52:56 2004
OBNUC  13C
EXMOD  DEPT
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN      1840.00 Hz
POINT        32768
FREQU     20408.10 Hz
SCANS          200
ACQTM       1.6056 sec
PD          1.3940 sec
PW1           10.00 usec
IRNUC  1H
CTEMP         25.3 c
SLVNT  DMSO
EXREF        39.50 ppm
BF            1.20 Hz
RGAIN           25
```

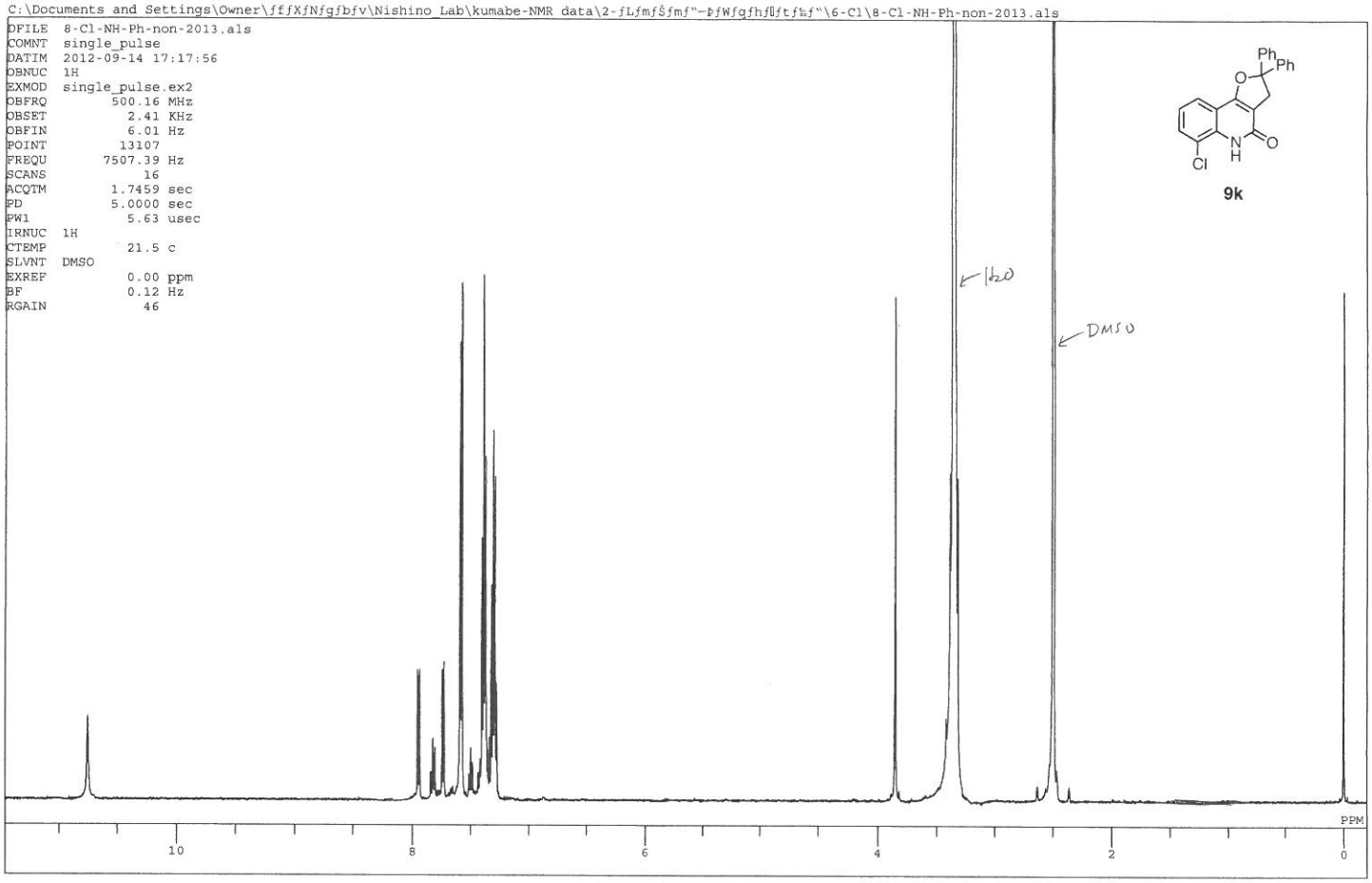


9j

single_pulse

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒgƒhƒßƒtƒ‰ƒ"\6-Cl\8-Cl-NH-Ph-non-2013.als

```
DFILE  8-Cl-NH-Ph-non-2013.als
COMNT  single_pulse
DATIM  2012-09-14 17:17:56
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS            16
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             5.63 usec
IRNUC  1H
CTEMP           21.5 c
SLVNT  DMSO
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             46
```

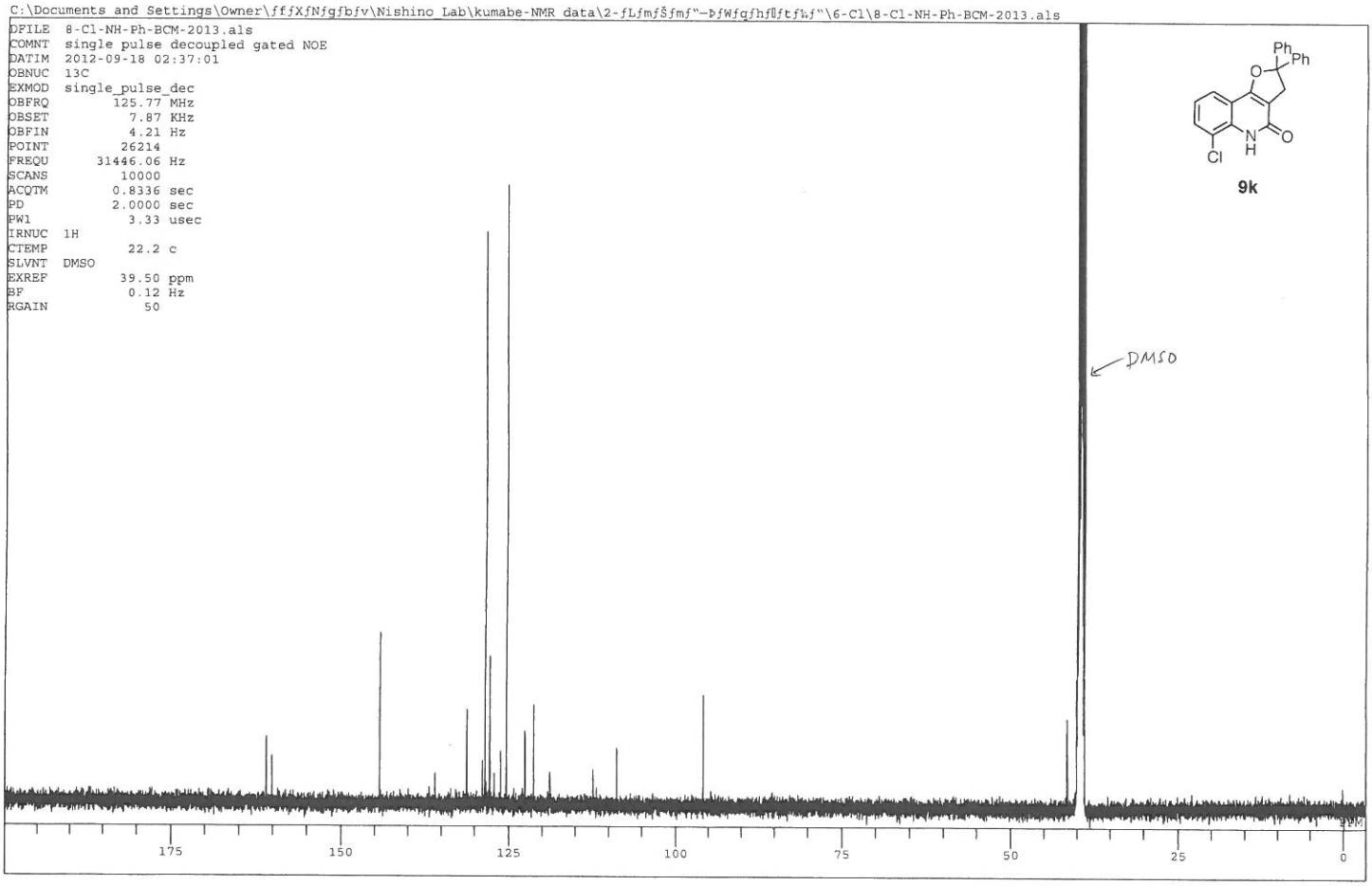


9k

single pulse decoupled gated NOE

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"–ÞƒWƒgƒhƒßƒtƒ‰ƒ"\6-Cl\8-Cl-NH-Ph-BCM-2013.als

```
DFILE  8-Cl-NH-Ph-BCM-2013.als
COMNT  single pulse decoupled gated NOE
DATIM  2012-09-18 02:37:01
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS         10000
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.33 usec
IRNUC  1H
CTEMP           22.2 c
SLVNT  DMSO
EXREF          39.50 ppm
BF              0.12 Hz
RGAIN             50
```

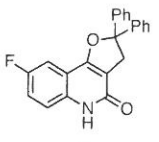


9k

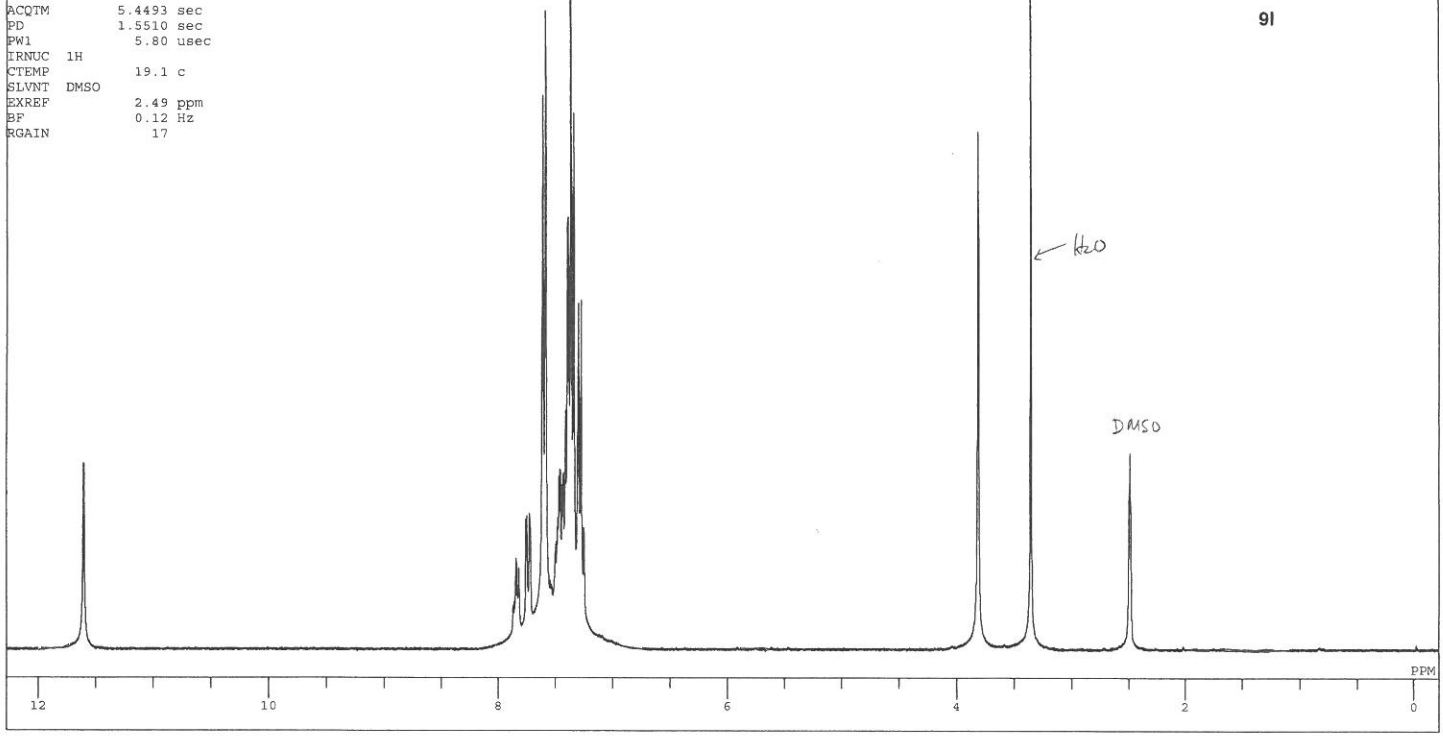
6-F NH Ph reflux dihydrofuran

C:\Documents and Settings\Owner\ffƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"−ÞƒWƒqƒhƒ‖ƒtƒ‰ƒ"\6-F-NH-Ph\6-F-NH-PH_NON-2013.als

```
DFILE  6-F-NH-PH_NON-2013.als
COMNT  6-F NH Ph reflux dihydrofuran
DATIM  Tue Mar 09 04:56:32 2004
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.80 usec
IRNUC  1H
CTEMP           19.1 c
SLVNT  DMSO
EXREF           2.49 ppm
BF              0.12 Hz
RGAIN             17
```



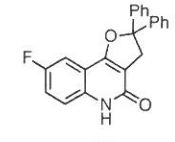
9l



6-F NH Ph reflux dihydrofuran

C:\Documents and Settings\Owner\ffƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"−ÞƒWƒqƒhƒ‖ƒtƒ‰ƒ"\6-F-NH-Ph\6-F-NH_PH_BCM-2013.als

```
DFILE  6-F-NH_PH_BCM-2013.als
COMNT  6-F NH Ph reflux dihydrofuran
DATIM  Tue Mar 09 05:21:15 2004
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           400
ACQTM         1.6056 sec
PD            1.3944 sec
PW1             5.00 usec
IRNUC  1H
CTEMP           20.2 c
SLVNT  DMSO
EXREF           39.50 ppm
BF              1.20 Hz
RGAIN             22
```

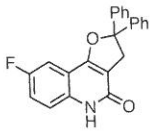


9l

6-F NH Ph reflux dihydrofuran

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\2-ƒLƒmƒŠƒmƒ"-ÞƒWƒqƒhƒlƒtƒ‰ƒ"\6-F-NH-Ph\6-F-NH_PH_DEPT-2013.als

```
DFILE  6-F-NH_PH_DEPT-2013.als
COMNT  6-F NH Ph reflux dihydrofuran
DATIM  Tue Mar 09 05:41:54 2004
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           400
ACQTM         1.6056 sec
PD            1.3940 sec
PW1           10.00 usec
IRNUC  1H
CTEMP          19.6 c
SLVNT  DMSO
EXREF         39.50 ppm
BF             1.20 Hz
RGAIN            24
```

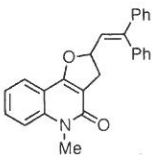


9l

7a

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\Hamada\products\Nishino-9m-non-2013.als

```
DFILE  Nishino-9m-non-2013.als
COMNT  7a
DATIM  Thu Nov 29 03:32:22 2007
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         16384
FREQU       6006.01 Hz
SCANS            16
ACQTM         2.7279 sec
PD            4.2720 sec
PW1              5.20 usec
IRNUC  1H
CTEMP          23.7 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            12
```

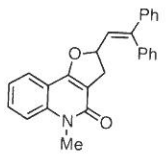


9m

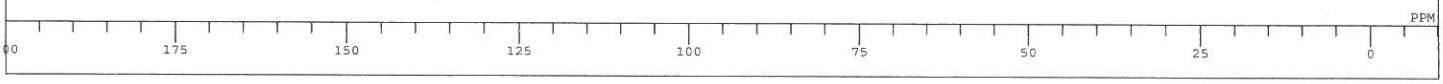
p169-f2

C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\Hamada\products\Nishino-9m-bcm-2013.als

```
DFILE  Nishino-9m-bcm-2013.als
COMNT  p169-f2
DATIM  Thu Jul 19 09:44:08 2007
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS          1045
ACQTM        1.6097 sec
PD           1.3900 sec
PW1            4.20 usec
IRNUC  1H
CTEMP          23.4 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            25
```



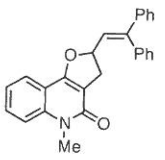
9m



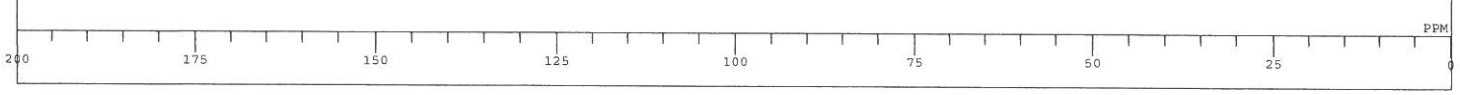
7a

C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\Hamada\products\Nishino-9m-dept-2013.als

```
DFILE  Nishino-9m-dept-2013.als
COMNT  7a
DATIM  Thu Nov 29 03:47:05 2007
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS            53
ACQTM        1.6097 sec
PD           1.3900 sec
PW1            8.50 usec
IRNUC  1H
CTEMP          24.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            25
```



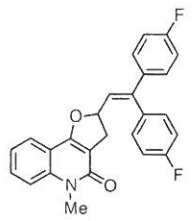
9m



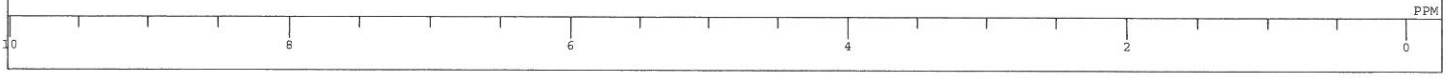
7d

C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\Hamada\products\Nishino-9n-non-2013.als

```
DFILE  Nishino-9n-non-2013.als
COMNT  7d
DATIM  Wed Nov 28 09:16:09 2007
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         16384
FREQU       6006.01 Hz
SCANS            16
ACQTM         2.7279 sec
PD            4.2720 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           23.2 c
SLVNT  CDCL3
EXREF            0.00 ppm
BF               0.12 Hz
RGAIN              16
```



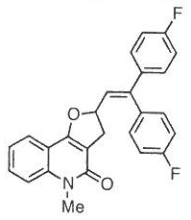
9n: Ar = 4-F-C_6H_4



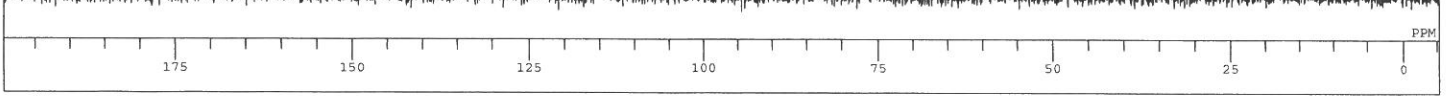
7d

C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\Hamada\products\Nishino-9n-bcm-2013.als

```
DFILE  Nishino-9n-bcm-2013.als
COMNT  7d
DATIM  Wed Nov 28 10:22:27 2007
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS          1302
ACQTM         1.6097 sec
PD            1.3900 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           24.2 c
SLVNT  CDCL3
EXREF            0.00 ppm
BF               0.12 Hz
RGAIN              25
```



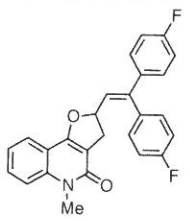
9n: Ar = 4-F-C_6H_4



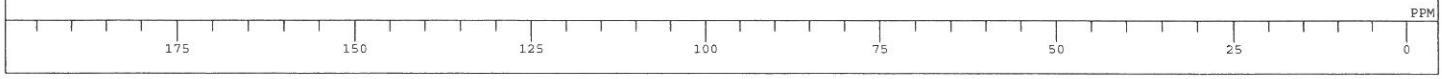
7d

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\Hamada\products\Nishino-9n-dept-2013.als

```
DFILE  Nishino-9n-dept-2013.als
COMNT  7d
DATIM  Wed Nov 28 10:36:52 2007
OBNUC  13C
EXMOD  DEPT
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN      1840.00 Hz
POINT        32768
FREQU     20356.23 Hz
SCANS          266
ACQTM       1.6097 sec
PD          1.3900 sec
PW1           8.50 usec
IRNUC  1H
CTEMP         23.9 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           25
```



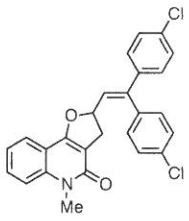
9n: Ar = 4-F-C_6H_4



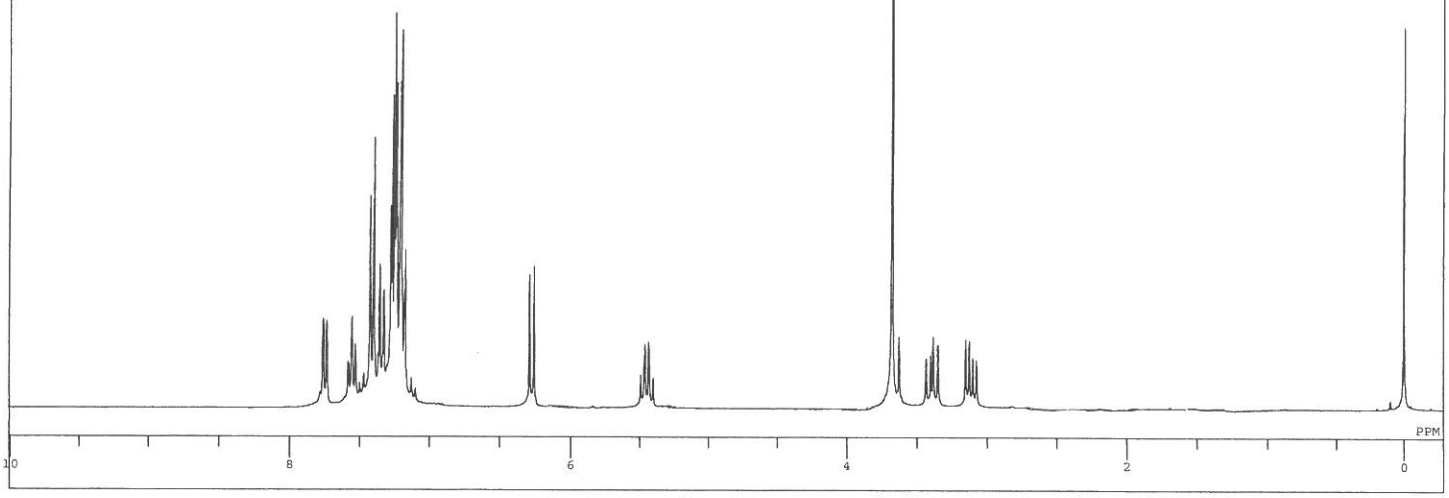
7c

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\Hamada\products\Nishino-9o-non-2013.als

```
DFILE  Nishino-9o-non-2013.als
COMNT  7c
DATIM  Thu Nov 29 00:38:49 2007
OBNUC  1H
EXMOD  NON
OBFRQ       300.40 MHz
OBSET       130.00 KHz
OBFIN      1150.00 Hz
POINT        16384
FREQU      6006.01 Hz
SCANS            16
ACQTM       2.7279 sec
PD          4.2720 sec
PW1           5.20 usec
IRNUC  1H
CTEMP         23.7 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           12
```



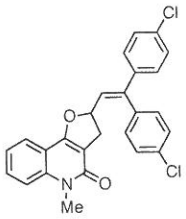
9o



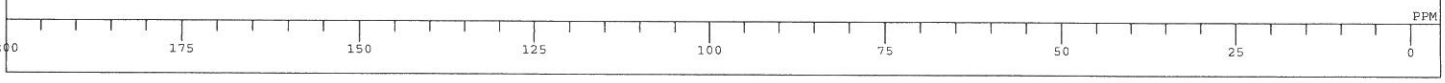
7c

C:\Documents and Settings\Owner\ƒƒXfNfgfbfv\Nishino_Lab\Hamada\products\Nishino-9o-bcm-2013.als

```
DFILE  Nishino-9o-bcm-2013.als
COMNT  7c
DATIM  Thu Nov 29 00:53:19 2007
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS           262
ACQTM         1.6097 sec
PD            1.3900 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           24.5 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             25
```



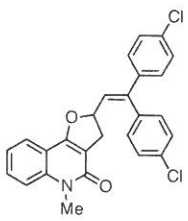
9o



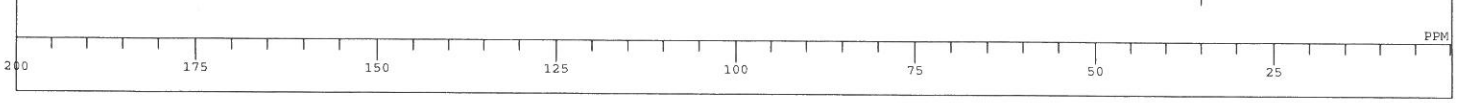
7b

C:\Documents and Settings\Owner\ƒƒXfNfgfbfv\Nishino_Lab\Hamada\products\Nishino-9o-dept-2013.als

```
DFILE  Nishino-9o-dept-2013.als
COMNT  7b
DATIM  Thu Nov 29 09:20:44 2007
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS            93
ACQTM         1.6097 sec
PD            1.3900 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           23.9 c
SLVNT  CDCL3
EXREF           77.00 ppm
BF              0.12 Hz
RGAIN             25
```



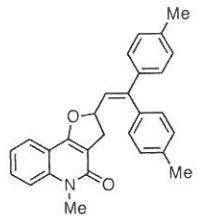
9o



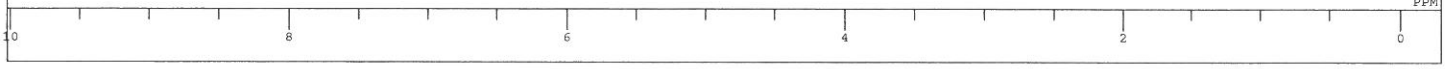
7b

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino Lab\Hamada\products\Nishino-9p-non-2013.als

```
DFILE  Nishino-9p-non-2013.als
COMNT  7b
DATIM  Thu Nov 29 08:58:18 2007
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         16384
FREQU       6006.01 Hz
SCANS            16
ACQTM         2.7279 sec
PD            4.2720 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           23.8 c
SLVNT  CDCL3
EXREF            0.00 ppm
BF               0.12 Hz
RGAIN              12
```



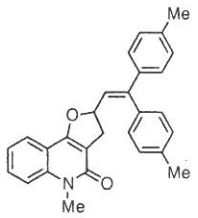
9p



7b

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino Lab\Hamada\products\Nishino-9p-bcm-2013.als

```
DFILE  Nishino-9p-bcm-2013.als
COMNT  7b
DATIM  Thu Nov 29 09:14:56 2007
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS           310
ACQTM         1.6097 sec
PD            1.3900 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           24.3 c
SLVNT  CDCL3
EXREF            0.00 ppm
BF               0.12 Hz
RGAIN              25
```

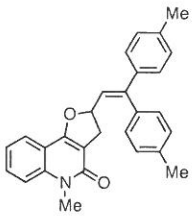


9p

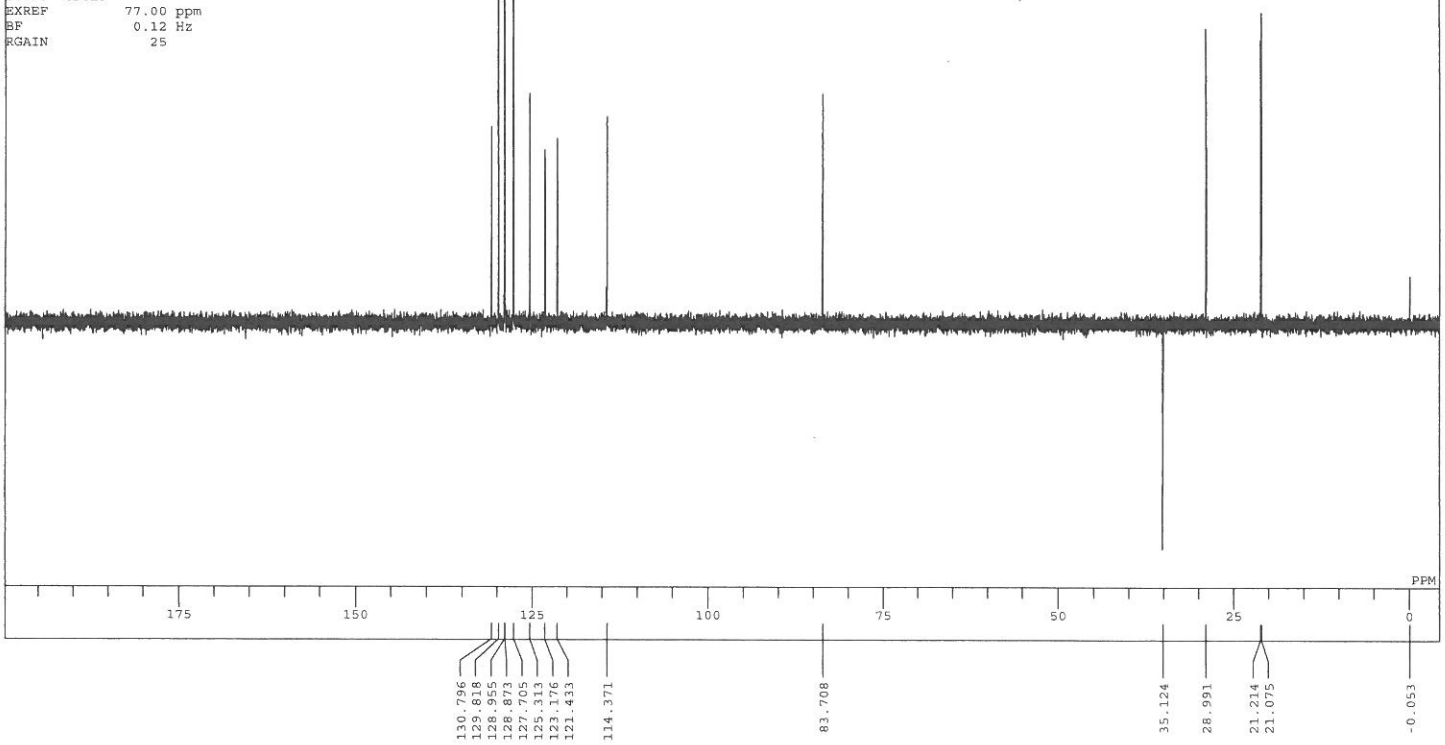
7b

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\Hamada\products\Nishino-9p-dept-2013.als

```
DFILE  Nishino-9p-dept-2013.als
COMNT  7b
DATIM  Thu Nov 29 09:20:44 2007
OBNUC  13C
EXMOD  DEPT
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN      1840.00 Hz
POINT        32768
FREQU     20356.23 Hz
SCANS           93
ACQTM       1.6097 sec
PD          1.3900 sec
PW1            8.50 usec
IRNUC  1H
CTEMP         23.9 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.12 Hz
RGAIN           25
```



9p

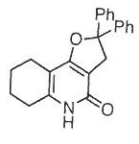


130.796
129.818
128.955
128.873
127.705
125.313
123.176
121.433
114.371
83.708
35.124
28.991
21.214
21.075
-0.053

single_pulse

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\Tetrahydroquinoline\Tetrahydroquinoline-non-2013.als

```
DFILE  Tetrahydroquinoline-non-2013.als
COMNT  single_pulse
DATIM  2012-09-18 10:23:30
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ       500.16 MHz
OBSET         2.41 KHz
OBFIN         6.01 Hz
POINT        13107
FREQU      7507.39 Hz
SCANS           16
ACQTM       1.7459 sec
PD          5.0000 sec
PW1            5.63 usec
IRNUC  1H
CTEMP         21.1 c
SLVNT  DMSO
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           38
```

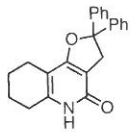


12

single pulse decoupled gated NOE

C:\Documents and Settings\Owner\ƒƒfXfNfgfbfv\Nishino_Lab\kumabe-NMR data\Tetrahydroquinoline\Tetrahydroquinoline-bcm-2013.als

```
DFILE  Tetrahydroquinoline-bcm-2013.als
COMNT  single pulse decoupled gated NOE
DATIM  2012-09-18 10:42:47
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           300
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.33 usec
IRNUC  1H
CTEMP           21.5 c
SLVNT  DMSO
EXREF         39.50 ppm
BF             0.12 Hz
RGAIN            56
```

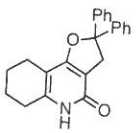


12

DEPT with decoupling

C:\Documents and Settings\Owner\ƒƒfXfNfgfbfv\Nishino_Lab\kumabe-NMR data\Tetrahydroquinoline\Tetrahydroquinoline-dept-2013.als

```
DFILE  Tetrahydroquinoline-dept-2013.als
COMNT  DEPT with decoupling
DATIM  2012-09-18 10:51:27
OBNUC  13C
EXMOD  dept.ex2
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS            114
ACQTM        0.8336 sec
PD           2.0000 sec
PW1           10.00 usec
IRNUC  1H
CTEMP           21.3 c
SLVNT  DMSO
EXREF         39.50 ppm
BF             0.12 Hz
RGAIN            56
```

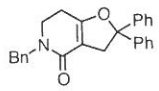


12

2-P131-F3

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\,»,Ì‘ã‡Œ¬•¨\dihydropyridinone\14-NON-2013.als

```
DFILE  14-NON-2013.als
COMNT  2-P131-F3
DATIM  Sun Aug 15 23:25:37 2004
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS             1
ACQTM        5.4493 sec
PD           1.5510 sec
PW1            5.80 usec
IRNUC  1H
CTEMP           20.9 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN              0
```

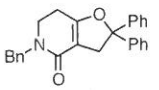


14

2-P131-F3

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\,»,Ì‘ã‡Œ¬•¨\dihydropyridinone\14-BCM-2013.als

```
DFILE  14-BCM-2013.als
COMNT  2-P131-F3
DATIM  Sun Aug 15 23:30:40 2004
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            53
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             5.00 usec
IRNUC  1H
CTEMP           21.6 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             24
```

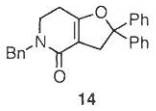


14

2-P131-F3

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\,»,Ì‘¼‡Ð¬•¨\dihydropyridinone\14-DEPT-2013.als

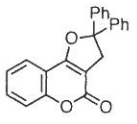
```
DFILE  14-DEPT-2013.als
COMNT  2-P131-F3
DATIM  Sun Aug 15 23:34:44 2004
OBNUC  13C
EXMOD  DEPT
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN      1840.00 Hz
POINT        32768
FREQU     20408.10 Hz
SCANS           61
ACQTM       1.6056 sec
PD          1.3940 sec
PW1          10.00 usec
IRNUC  1H
CTEMP         21.2 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           25
```



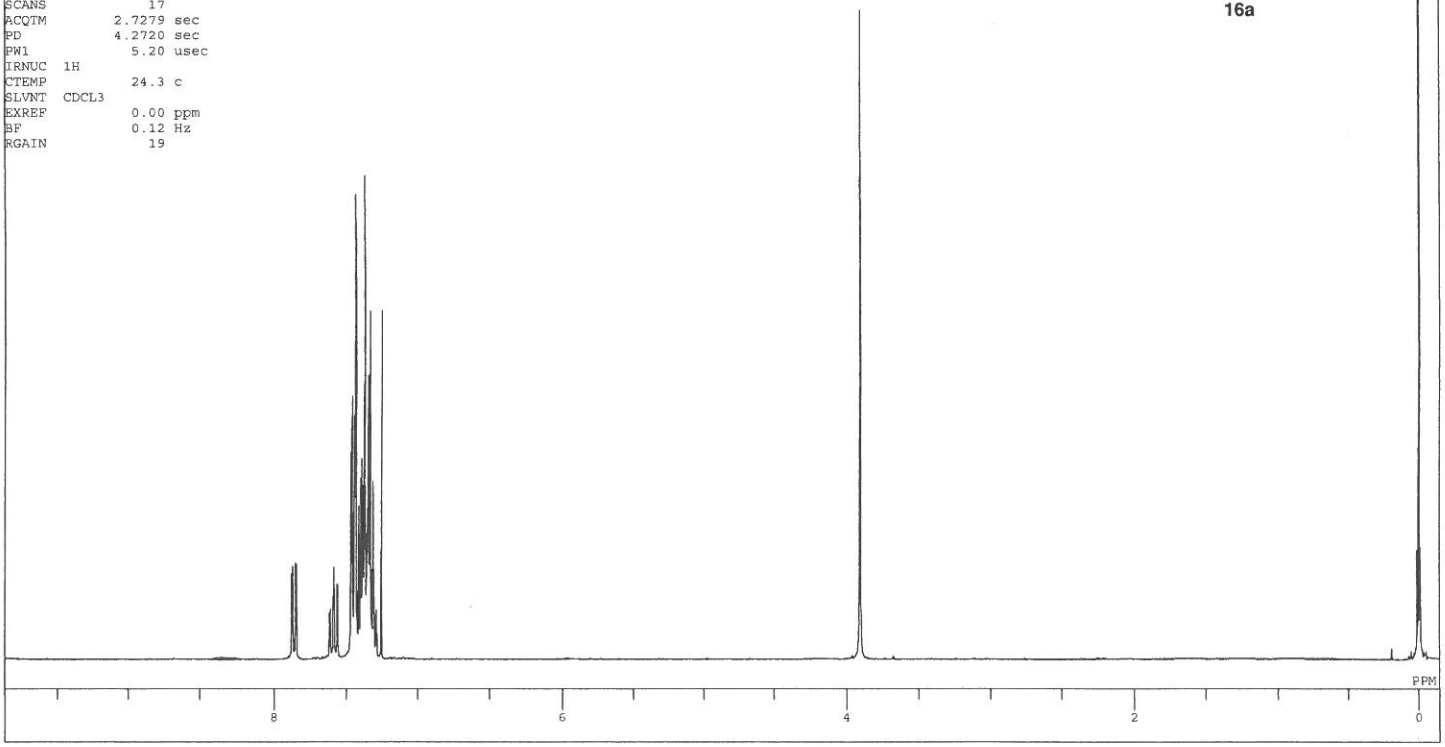
14

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\Coumarin\coumrin-Ph-non-2013.als

```
DFILE  coumrin-Ph-non-2013.als
COMNT
DATIM  Thu Dec 03 19:14:34 2009
OBNUC  1H
EXMOD  NON
OBFRQ       300.40 MHz
OBSET       130.00 KHz
OBFIN      1150.00 Hz
POINT        16384
FREQU      6006.01 Hz
SCANS           17
ACQTM       2.7279 sec
PD          4.2720 sec
PW1           5.20 usec
IRNUC  1H
CTEMP         24.3 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           19
```

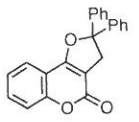


16a

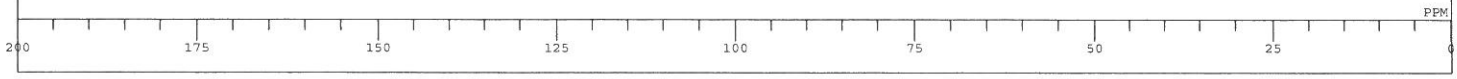


C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\kumabe-NMR data\Coumarin\coumrin-Ph-bcm-2013.als

```
DFILE  coumrin-Ph-bcm-2013.als
COMNT
DATIM  Sat Feb 06 17:55:00 2010
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN      1840.00 Hz
POINT        32768
FREQU     20356.23 Hz
SCANS          114
ACQTM       1.6097 sec
PD          1.3900 sec
PW1           4.20 usec
IRNUC  1H
CTEMP         21.0 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.12 Hz
RGAIN           25
```

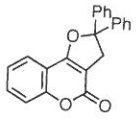


16a

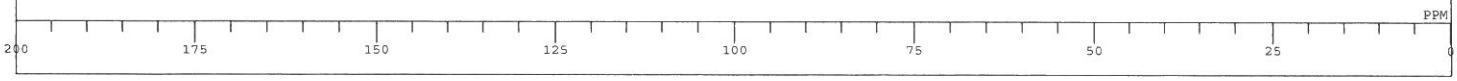


C:\Documents and Settings\Owner\ffXfNfgfbfv\Nishino_Lab\kumabe-NMR data\Coumarin\coumrin-Ph-dept-2013.als

```
DFILE  coumrin-Ph-dept-2013.als
COMNT
DATIM  Sat Feb 06 18:01:29 2010
OBNUC  13C
EXMOD  DEPT
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN      1840.00 Hz
POINT        32768
FREQU     20356.23 Hz
SCANS          102
ACQTM       1.6097 sec
PD          1.3900 sec
PW1           8.50 usec
IRNUC  1H
CTEMP         20.6 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.12 Hz
RGAIN           26
```



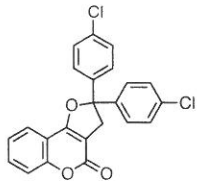
16a



single_pulse

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\Coumarin\coumrin-ClC6H4-non-2013.als

```
DFILE  coumrin-ClC6H4-non-2013.als
COMNT  single_pulse
DATIM  2012-11-02 08:44:32
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS            16
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             5.63 usec
IRNUC  1H
CTEMP           21.9 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             36
```

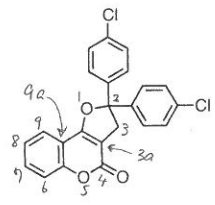


16b

single pulse decoupled gated NOE

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\Coumarin\coumrin-ClC6H4-bcm-2013.als

```
DFILE  coumrin-ClC6H4-bcm-2013.als
COMNT  single pulse decoupled gated NOE
DATIM  2012-11-02 08:58:14
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS            202
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.33 usec
IRNUC  1H
CTEMP           22.2 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             54
```

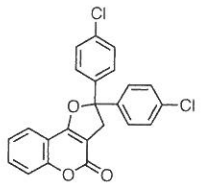


16b

DEPT with decoupling

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\Coumarin\coumrin-ClC6H4-dept-2013.als

```
DFILE  coumrin-ClC6H4-dept-2013.als
COMNT  DEPT with decoupling
DATIM  2012-11-02 09:10:52
OBNUC  13C
EXMOD  dept.ex2
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           202
ACQTM        0.8336 sec
PD           2.0000 sec
PW1           10.00 usec
IRNUC  1H
CTEMP          22.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            54
```

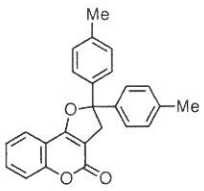


16b

kuma-Me-coumnarin

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\Coumarin\coumrin-MeC6H4-non-2013.als

```
DFILE  coumrin-MeC6H4-non-2013.als
COMNT  kuma-Me-coumnarin
DATIM  2012-11-01 11:02:01
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS            16
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            5.63 usec
IRNUC  1H
CTEMP          22.6 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            36
```

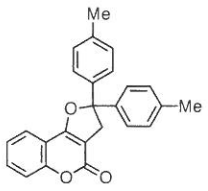


16c

single pulse decoupled gated NOE

C:\Documents and Settings\Owner\ƒƒfXfNfgfbfv\Nishino_Lab\kumabe-NMR data\Coumarin\coumrin-MeC6H4-bcm-2013.als

```
DFILE   coumrin-MeC6H4-bcm-2013.als
COMNT   single pulse decoupled gated NOE
DATIM   2012-11-01 11:15:06
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.06 Hz
SCANS            202
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.33 usec
IRNUC   1H
CTEMP           22.9 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             58
```

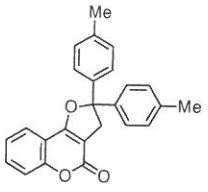


16c

DEPT with decoupling

C:\Documents and Settings\Owner\ƒƒfXfNfgfbfv\Nishino_Lab\kumabe-NMR data\Coumarin\coumrin-MeC6H4-dept-2013.als

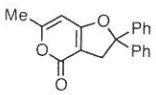
```
DFILE   coumrin-MeC6H4-dept-2013.als
COMNT   DEPT with decoupling
DATIM   2012-11-01 11:28:04
OBNUC   13C
EXMOD   dept.ex2
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.06 Hz
SCANS            209
ACQTM         0.8336 sec
PD            2.0000 sec
PW1            10.00 usec
IRNUC   1H
CTEMP           22.5 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             54
```



16c

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino Lab\kumabe-NMR data\,»,Ì‘ã‰ß¬•¨\ƒsƒ[ƒ"\Pyranone-non-2013.als

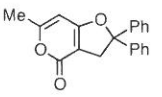
```
DFILE  Pyranone-non-2013.als
COMNT
DATIM  Wed Mar 06 21:20:53 2002
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           24.9 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN              9
```



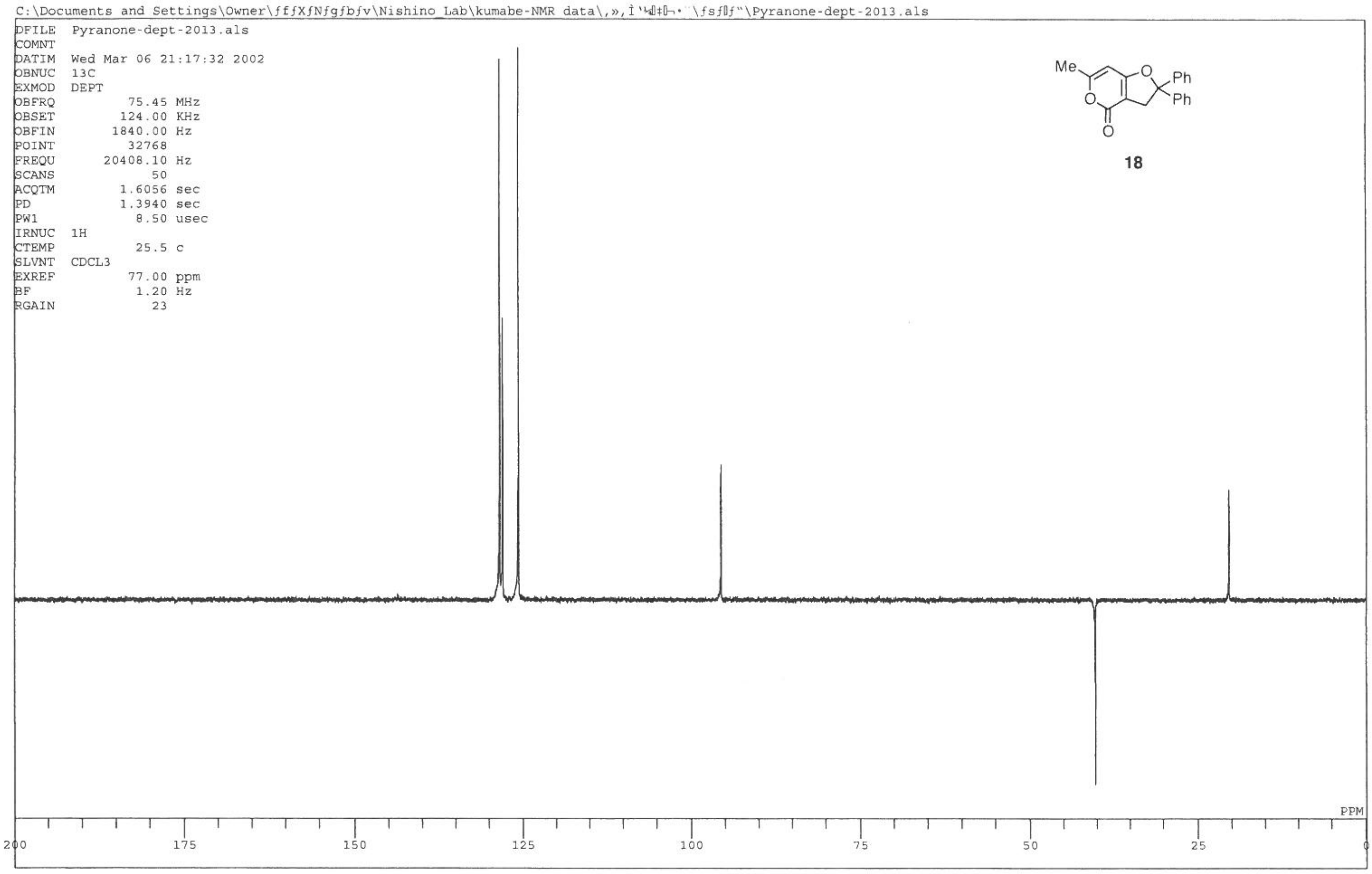
18

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino Lab\kumabe-NMR data\,»,Ì‘ã‰ß¬•¨\pyranone\Pyranone-bcm-2013.als

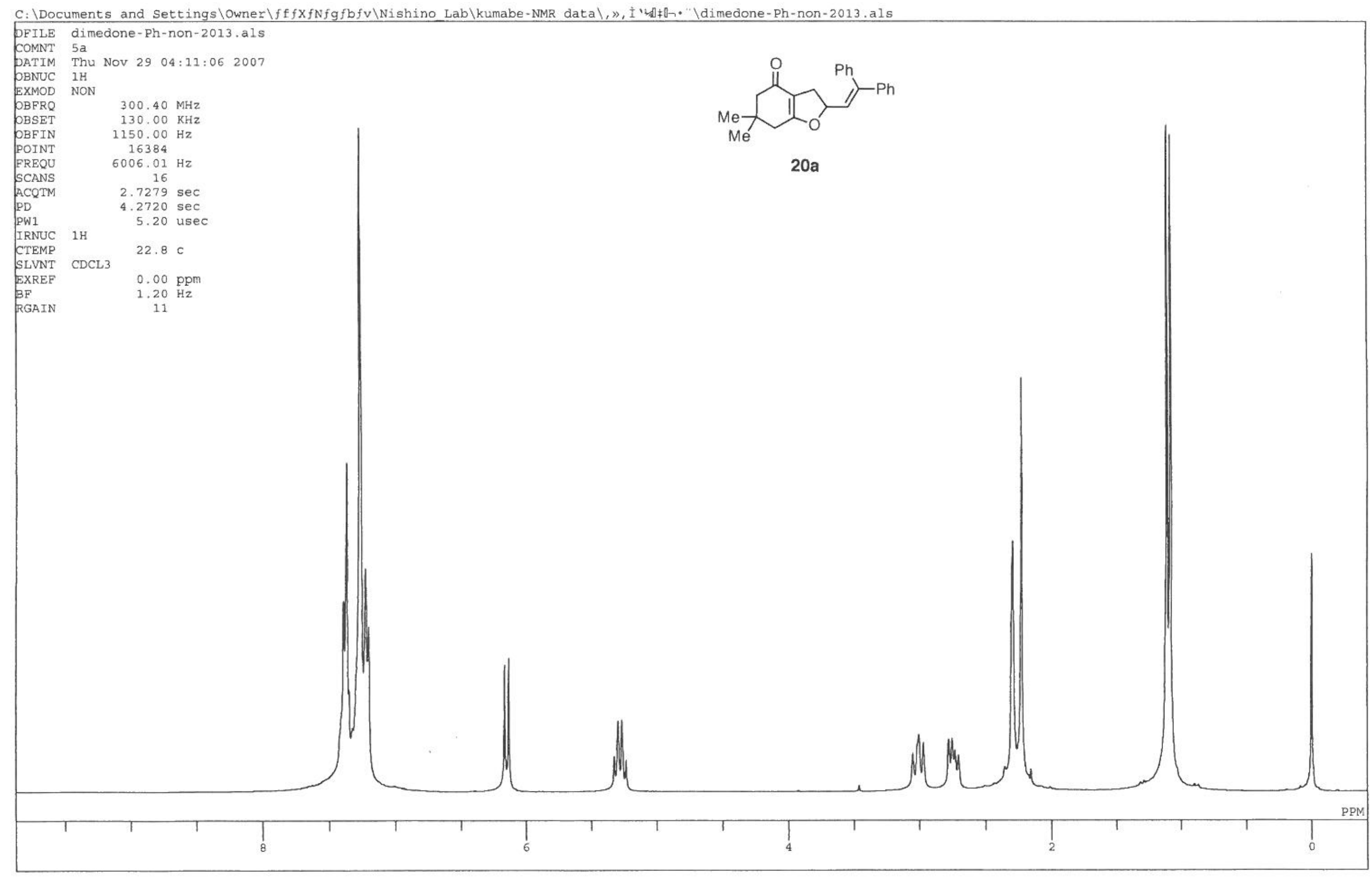
```
DFILE  Pyranone-bcm-2013.als
COMNT
DATIM  Wed Mar 06 21:13:44 2002
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           26.0 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              1.20 Hz
RGAIN             22
```



18


C:\Documents and Settings\Owner\…\Nishino_Lab\kumabe-NMR data\…\Pyranone-dept-2013.als
DFILE Pyranone-dept-2013.als
COMNT
DATIM Wed Mar 06 21:17:32 2002
OBNUC 13C
EXMOD DEPT
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20408.10 Hz
SCANS 50
ACQTM 1.6056 sec
PD 1.3940 sec
PW1 8.50 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 23
Me
O
Ph
Ph
O
O
18
PPM
200
175
150
125
100
75
50
25
0

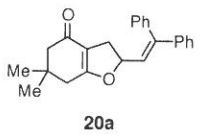
5a


C:\Documents and Settings\Owner\…\Nishino_Lab\kumabe-NMR data\…\dimedone-Ph-non-2013.als
DFILE dimedone-Ph-non-2013.als
COMNT 5a
DATIM Thu Nov 29 04:11:06 2007
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 16384
FREQU 6006.01 Hz
SCANS 16
ACQTM 2.7279 sec
PD 4.2720 sec
PW1 5.20 usec
IRNUC 1H
CTEMP 22.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 11
O
Ph
Ph
Me
Me
O
20a
PPM
8
6
4
2
0

5a

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\,»,Ì‘¼‡Ð¬•¨\dimedone\dimedone-Ph-bcm-2013.als

```
DFILE  dimedone-Ph-bcm-2013.als
COMNT  5a
DATIM  Thu Nov 29 04:21:55 2007
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS           197
ACQTM         1.6097 sec
PD            1.3900 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           24.2 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             25
```



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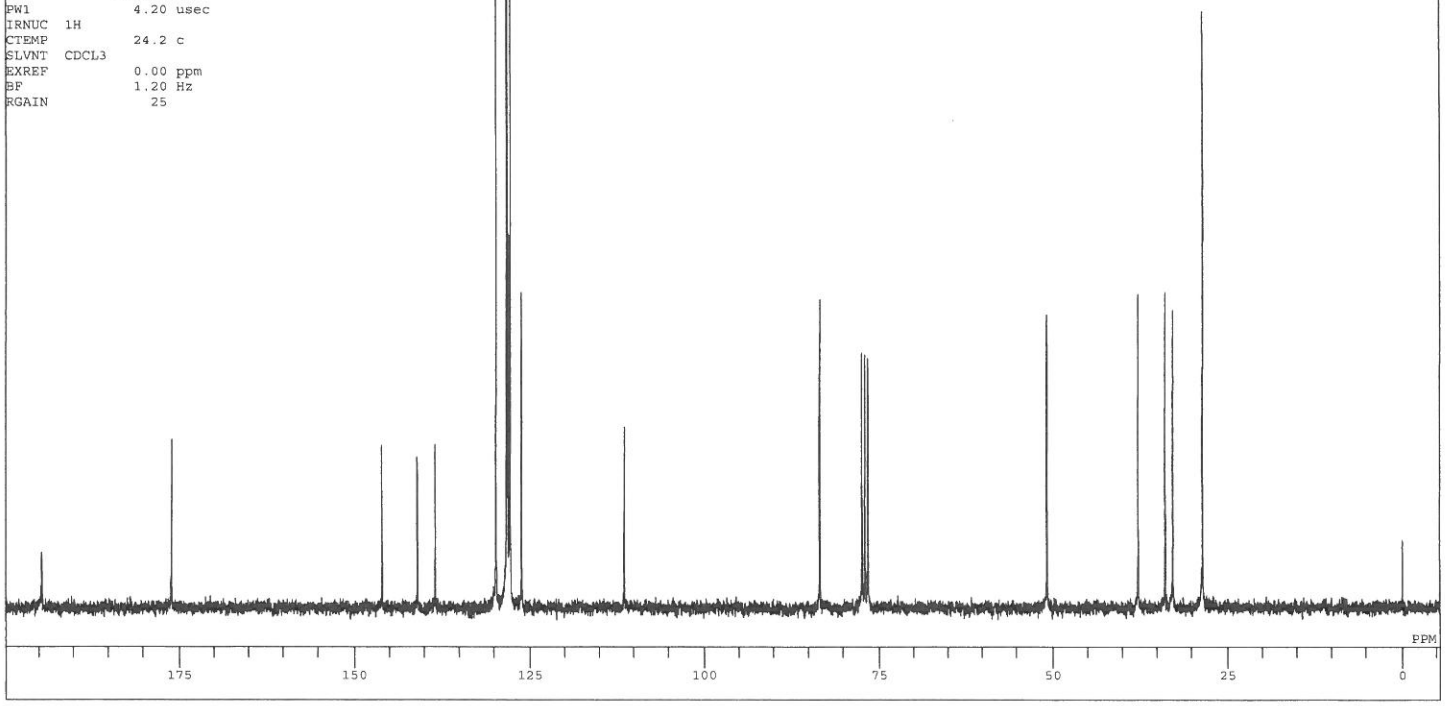
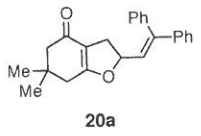


5a

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\,»,Ì‘¼‡Ð¬•¨\dimedone\dimedone-Ph-dept-2013.als

```
DFILE  dimedone-Ph-dept-2013.als
COMNT  5a
DATIM  Thu Nov 29 04:24:54 2007
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS            37
ACQTM         1.6097 sec
PD            1.3900 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           23.9 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              1.20 Hz
RGAIN             25
```

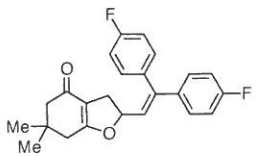


20a

5d

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\,»,Ì‘¼Ð¬•¨\dimedone\dimedone-F-C6H4-non-2013.als

```
DFILE  dimedone-F-C6H4-non-2013.als
COMNT  5d
DATIM  Fri Nov 30 08:45:33 2007
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         16384
FREQU       6006.01 Hz
SCANS            16
ACQTM         2.7279 sec
PD            4.2720 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           22.7 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             11
```

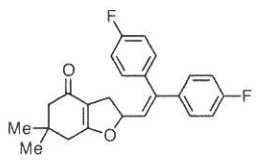


20b

5d

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\,»,Ì‘¼Ð¬•¨\dimedone\dimedone-F-C6H4-bcm-2013.als

```
DFILE  dimedone-F-C6H4-bcm-2013.als
COMNT  5d
DATIM  Fri Nov 30 08:57:12 2007
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS           214
ACQTM         1.6097 sec
PD            1.3900 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           23.3 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             23
```



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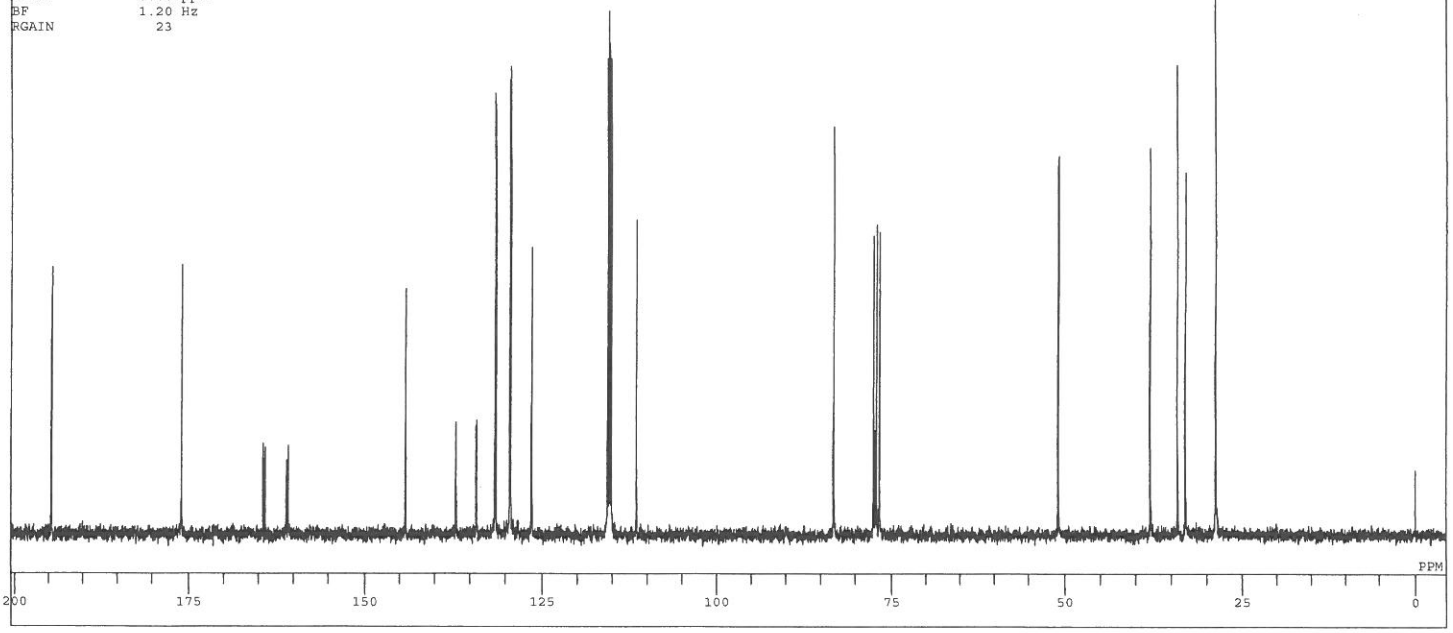
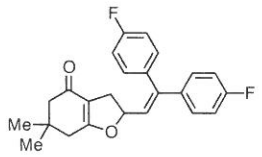


5d

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\,»,Ì‘¼¬•¨\dimedone\dimedone-F-C6H4-dept-2013.als

```
DFILE  dimedone-F-C6H4-dept-2013.als
COMNT  5d
DATIM  Fri Nov 30 09:00:49 2007
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS            49
ACQTM         1.6097 sec
PD            1.3900 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           23.1 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             25
```



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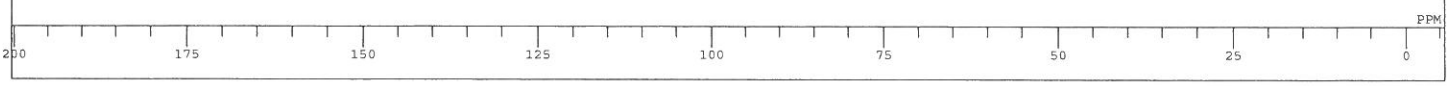
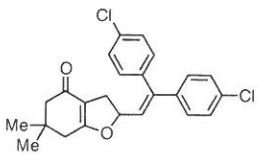


5c

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\,»,Ì‘¼¬•¨\dimedone\dimedone-Cl-C6H4-non-2013.als

```
DFILE  dimedone-Cl-C6H4-non-2013.als
COMNT  5c
DATIM  Fri Nov 30 10:51:35 2007
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         16384
FREQU       6006.01 Hz
SCANS            16
ACQTM         2.7279 sec
PD            4.2720 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           23.2 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             11
```

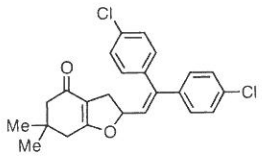


20c

5c

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\,»,Ì¼ª¶¬•¨\dimedone\dimedone-Cl-C6H4-bcm-2013.als

```
DFILE  dimedone-Cl-C6H4-bcm-2013.als
COMNT  5c
DATIM  Fri Nov 30 10:58:31 2007
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS           114
ACQTM        1.6097 sec
PD           1.3900 sec
PW1            4.20 usec
IRNUC  1H
CTEMP          23.9 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            25
```

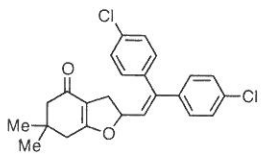


20c

5c

C:\Documents and Settings\Owner\ƒƒƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\,»,Ì¼ª¶¬•¨\dimedone\dimedone-Cl-C6H4-dept-2013.als

```
DFILE  dimedone-Cl-C6H4-dept-2013.als
COMNT  5c
DATIM  Fri Nov 30 11:01:20 2007
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS            29
ACQTM        1.6097 sec
PD           1.3900 sec
PW1            8.50 usec
IRNUC  1H
CTEMP          23.6 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            25
```

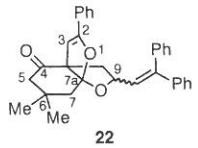


20c

9a

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\,»,Ì¼Ú‡Ì¬•¨\dimedone\dimedone-propellane-non-2013.als

```
DFILE  dimedone-propellane-non-2013.als
COMNT  9a
DATIM  Thu Nov 29 08:22:20 2007
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         16384
FREQU       6006.01 Hz
SCANS            16
ACQTM         2.7279 sec
PD            4.2720 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           22.9 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             13
```

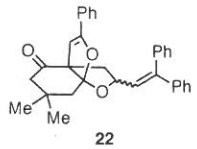


22

9a

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\,»,Ì¼Ú‡Ì¬•¨\dimedone\dimedone-propellane-bcm-2013.als

```
DFILE  dimedone-propellane-bcm-2013.als
COMNT  9a
DATIM  Thu Nov 29 08:34:23 2007
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS            222
ACQTM         1.6097 sec
PD            1.3900 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           24.4 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             25
```

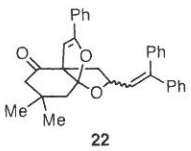


22

9a

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\,»,Ì'¼Œ‡¬•¨\dimedone\dimedone-propellane-deptm-2013.als

```
DFILE  dimedone-propellane-deptm-2013.als
COMNT  9a
DATIM  Thu Nov 29 08:38:32 2007
OBNUC  13C
EXMOD  DEPT
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN      1840.00 Hz
POINT        32768
FREQU      20356.23 Hz
SCANS           61
ACQTM       1.6097 sec
PD          1.3900 sec
PW1           8.50 usec
IRNUC  1H
CTEMP         24.1 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.12 Hz
RGAIN           25
```

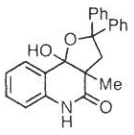


22

3-Me Ph reflux F2(THFŠÂ)

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Me-NH\REFLUX_F2_NON-19a.als

```
DFILE  REFLUX_F2_NON-19a.als
COMNT  3-Me Ph reflux F2(THFŠÂ)
DATIM  Tue Apr 23 18:35:24 2002
OBNUC  1H
EXMOD  NON
OBFRQ       300.40 MHz
OBSET       130.00 KHz
OBFIN      1150.00 Hz
POINT        32768
FREQU      6013.20 Hz
SCANS           16
ACQTM       5.4493 sec
PD          1.5510 sec
PW1           5.20 usec
IRNUC  1H
CTEMP         22.1 c
SLVNT  DMSO
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           11
```

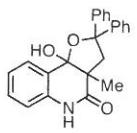


23a

3-Me Ph reflux F2(THFŠÃ)

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Me-NH\REFLUX_F2_BCM.ALS

```
DFILE   REFLUX_F2_BCM.ALS
COMNT   3-Me Ph reflux F2(THFŠÃ)
DATIM   Tue Apr 23 18:27:54 2002
OBNUC   13C
EXMOD   BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM        1.6056 sec
PD           1.3940 sec
PW1            4.20 usec
IRNUC   1H
CTEMP         23.0 c
SLVNT   DMSO
EXREF        39.50 ppm
BF            1.20 Hz
RGAIN           22
```



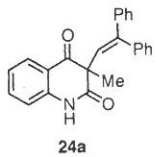
23a

172.116, 149.633, 147.012, 135.672, 129.490, 128.337, 127.826, 127.562, 126.828, 126.663, 126.070, 125.946, 125.485, 125.040, 123.523, 121.925, 114.911, 102.755, 85.958, 53.552, 46.670, 40.341, 40.052, 39.780, 39.500, 39.220, 38.948, 38.668, 18.426

3-Me Ph 80Ž main(diketone)

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Me-NH\80Ž\NON.als

```
DFILE   NON.als
COMNT   3-Me Ph 80Ž main(diketone)
DATIM   Sat May 11 12:02:33 2002
OBNUC   1H
EXMOD   NON
OBFRQ       300.40 MHz
OBSET       130.00 KHz
OBFIN      1150.00 Hz
POINT        32768
FREQU      6013.20 Hz
SCANS            4
ACQTM        5.4493 sec
PD           1.5510 sec
PW1            5.20 usec
IRNUC   1H
CTEMP         22.4 c
SLVNT   CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN            9
```

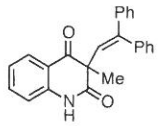


24a

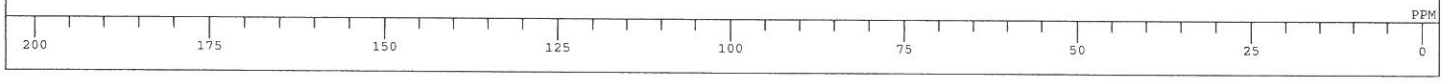
3-Me Ph 80Ž main (diketone)

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Me-NH\80Ž\BCM.als

```
DFILE  BCM.als
COMNT  3-Me Ph 80Ž main (diketone)
DATIM  Sat May 11 11:57:10 2002
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            60
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           23.4 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             23
```



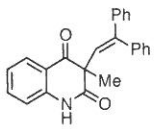
24a



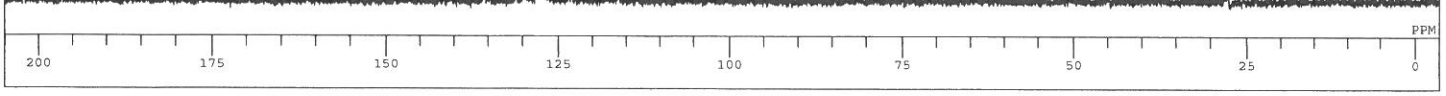
3-Me Ph 80Ž main(diketone)

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Me-NH\80Ž\DEPT.als

```
DFILE  DEPT.als
COMNT  3-Me Ph 80Ž main(diketone)
DATIM  Sat May 11 12:01:05 2002
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS            50
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           22.7 c
SLVNT  CDCL3
EXREF           77.00 ppm
BF              1.20 Hz
RGAIN             22
```



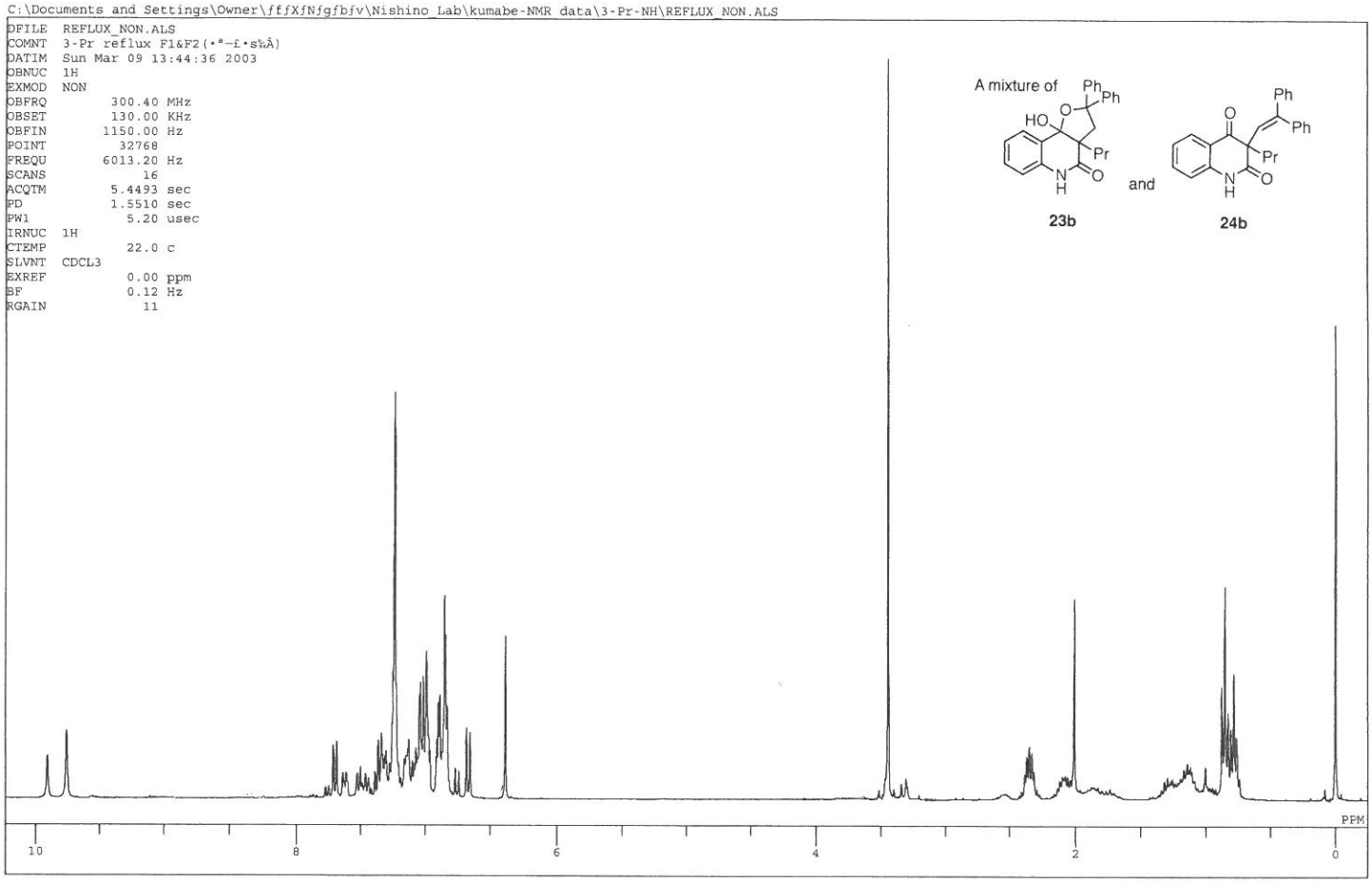
24a



3-Pr reflux F1&F2(･ᵒ—£･s%Å)

C:\Documents and Settings\Owner\ƒƒfXfNfgfbfv\Nishino_Lab\kumabe-NMR data\3-Pr-NH\REFLUX_NON.ALS

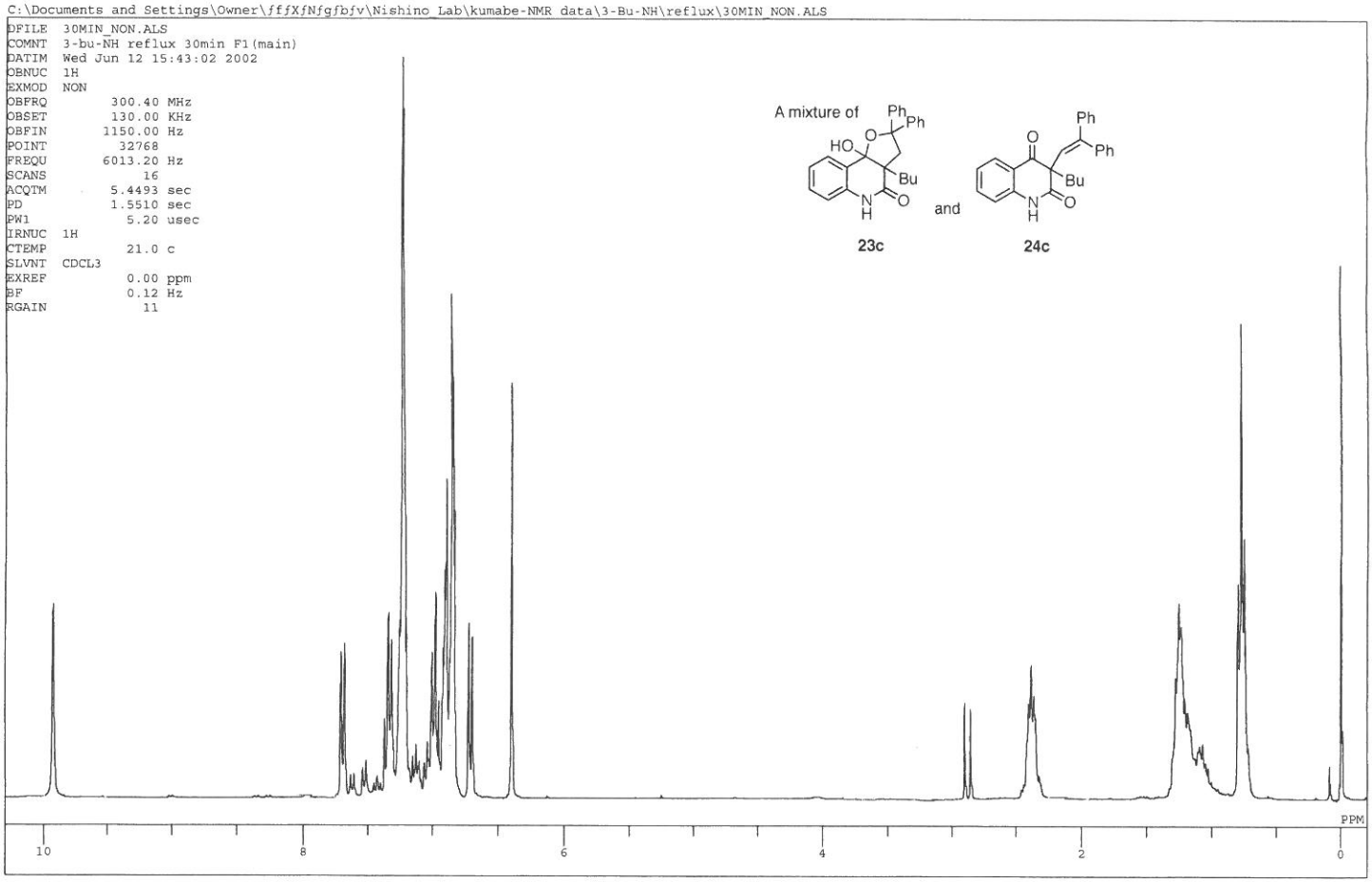
```
DFILE  REFLUX_NON.ALS
COMNT  3-Pr reflux F1&F2(･ᵒ—£･s%Å)
DATIM  Sun Mar 09 13:44:36 2003
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           22.0 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             11
```



3-bu-NH reflux 30min F1(main)

C:\Documents and Settings\Owner\ƒƒfXfNfgfbfv\Nishino_Lab\kumabe-NMR data\3-Bu-NH\reflux\30MIN_NON.ALS

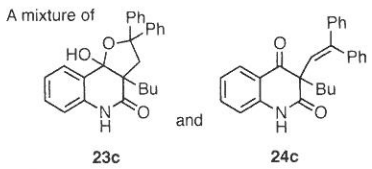
```
DFILE  30MIN_NON.ALS
COMNT  3-bu-NH reflux 30min F1(main)
DATIM  Wed Jun 12 15:43:02 2002
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           21.0 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             11
```



3-bu-NH reflux 30min F1(main)

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Bu-NH\reflux\30MIN_BCM.ALS

```
DFILE   30MIN_BCM.ALS
COMNT   3-bu-NH reflux 30min F1(main)
DATIM   Wed Jun 12 15:33:27 2002
OBNUC   13C
EXMOD   BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS          100
ACQTM        1.6056 sec
PD           1.3940 sec
PW1            4.20 usec
IRNUC   1H
CTEMP         22.1 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            23
```

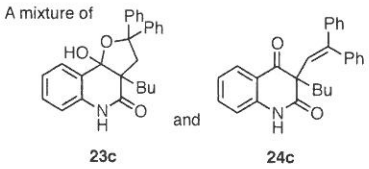


23c **24c**

3-bu-NH reflux 30min F1(main)

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Bu-NH\reflux\30MIN_DEPT.ALS

```
DFILE   30MIN_DEPT.ALS
COMNT   3-bu-NH reflux 30min F1(main)
DATIM   Wed Jun 12 15:39:39 2002
OBNUC   13C
EXMOD   DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS          100
ACQTM        1.6056 sec
PD           1.3940 sec
PW1            8.50 usec
IRNUC   1H
CTEMP         21.6 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            24
```



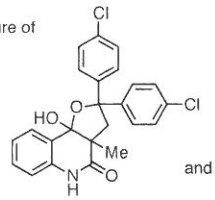
23c **24c**

3-Me NH ClPh reflux

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Me-NH\ClPh\REFLUX1NON_E1.ALS

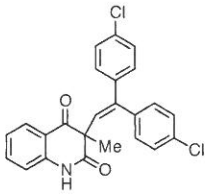
```
DFILE  REFLUX1NON_E1.ALS
COMNT  3-Me NH ClPh reflux
DATIM  Fri Apr 25 10:32:07 2003
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6020.40 Hz
SCANS            16
ACQTM         5.4428 sec
PD            1.5539 sec
PW1             5.25 usec
IRNUC  1H
CTEMP           22.7 c
SLVNT  DMSO
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             14
```

A mixture of



23d

and

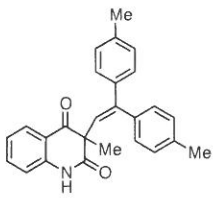


24d

3-Me MePh reflux main

C:\Documents and Settings\Owner\ƒfƒXƒNƒgƒbƒv\Nishino_Lab\kumabe-NMR data\3-Me-NH\MePh\reflux_F1_NON.als

```
DFILE  reflux_F1_NON.als
COMNT  3-Me MePh reflux main
DATIM  Thu Mar 13 12:31:26 2003
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6013.20 Hz
SCANS            16
ACQTM         5.4493 sec
PD            1.5510 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           21.7 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             10
```

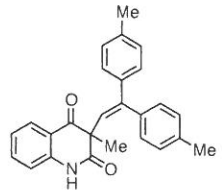


24e

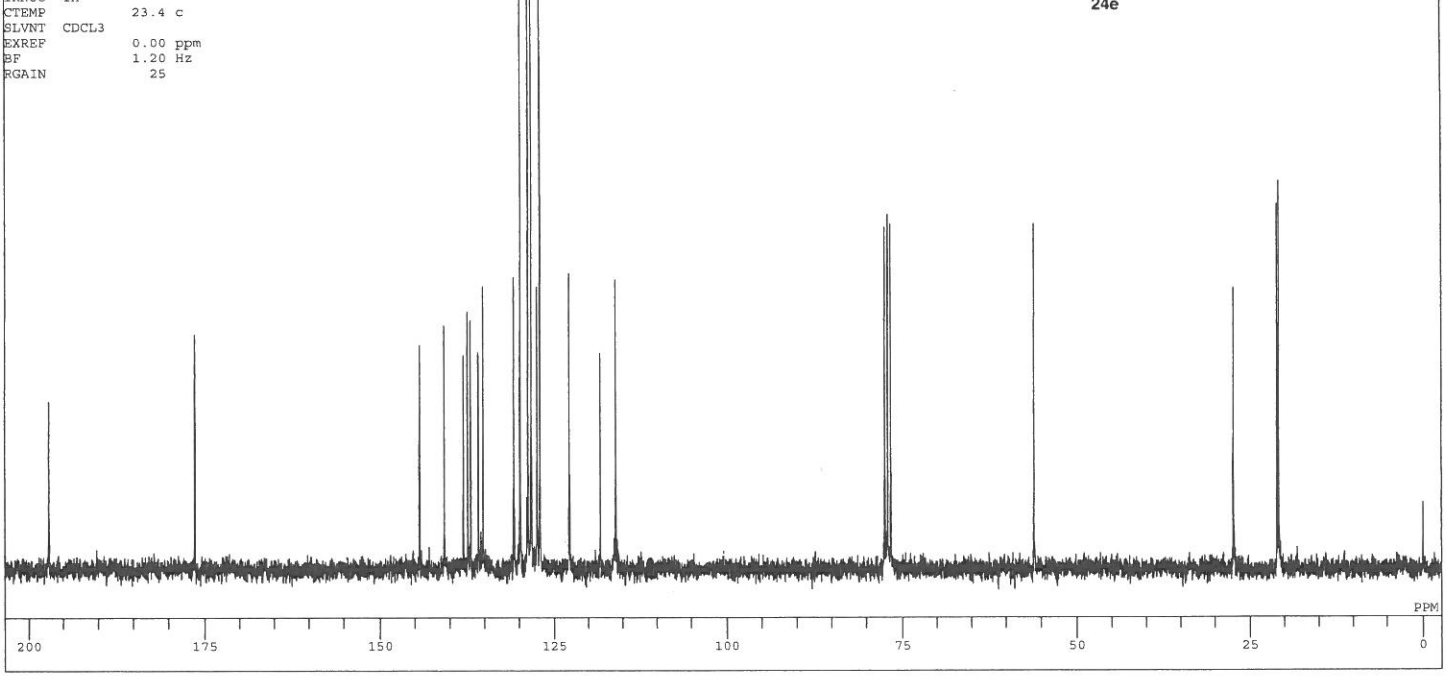
3-Me MePh reflux main

C:\Documents and Settings\Owner\ƒƒfXfNfgfbfv\Nishino_Lab\kumabe-NMR data\3-Me-NH\MePh\reflux_F1_BCM.als

```
DFILE  reflux_F1_BCM.als
COMNT  3-Me MePh reflux main
DATIM  Thu Mar 13 12:21:25 2003
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             4.20 usec
IRNUC  1H
CTEMP           23.4 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              1.20 Hz
RGAIN             25
```



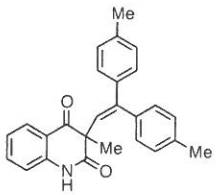
24e



3-Me MePh reflux main

C:\Documents and Settings\Owner\ƒƒfXfNfgfbfv\Nishino_Lab\kumabe-NMR data\3-Me-NH\MePh\reflux_F1_DEPT.als

```
DFILE  reflux_F1_DEPT.als
COMNT  3-Me MePh reflux main
DATIM  Thu Mar 13 12:28:27 2003
OBNUC  13C
EXMOD  DEPT
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20408.10 Hz
SCANS           100
ACQTM         1.6056 sec
PD            1.3940 sec
PW1             8.50 usec
IRNUC  1H
CTEMP           22.4 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              1.20 Hz
RGAIN             24
```



24e