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Graphical Abstract

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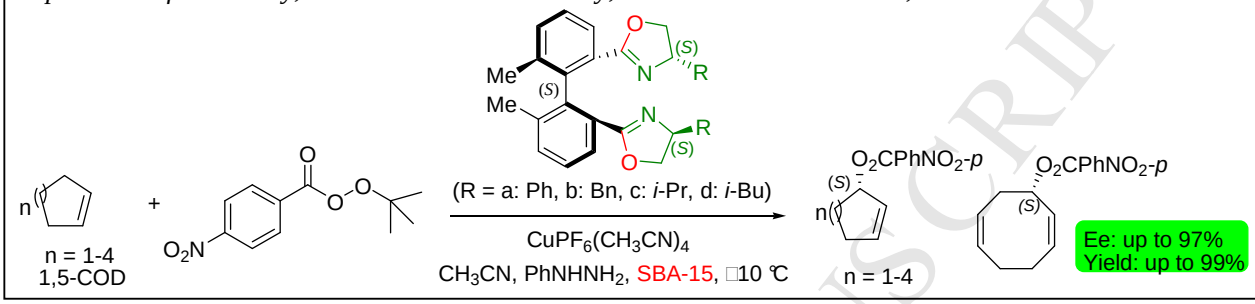

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ABSTRACT

A series of chiral bi-*o*-tolyl bisoxazoline ligands **1** and **2** were conveniently synthesized on a gram scale from inexpensive and commercially available 3-methyl benzoic acid in eight steps. The catalytic and induced asymmetric effects of the chiral copper (I) complexes of these ligands on the asymmetric allylic oxidation of cycloolefins were investigated in the presence of various nano-sized additives. When SBA-15 mesoporous silica was used in conjunction with these ligands very highly enantioselectivities (up to 97% *ee*) and excellent yields (up to 99%) of the corresponding chiral allylic esters were obtained in a reasonably short period of time.

1. Introduction

The copper-catalyzed allylic oxidation of olefins with peresters has been the subject of numerous synthetic investigations. This reaction provides access to chiral allylic alcohols that are key intermediates in natural product synthesis.[1] Chiral C_2-symmetric bisoxazolines (Box's) are one of the most effective and popular classes of chiral ligands used for various metal-catalyzed asymmetric processes,[2] such as allylic oxidation.[3] Among these various ligands, the enantioselectivity of the chiral biarylbisoxazolines can often be enhanced by a synergistic effect of matched chiralities on the oxazoline ring and the biaryl backbone.

The first synthesis of chiral biarylbisoxazoline ligands and chiral copper-bi-*o*-tolyl bisoxazoline complexes was reported by Corey for a highly selective interamolecular cyclopropanation reaction leading to (–)-sirenin.[4] Andrus et al. used bi-*o*-tolyl bisoxazoline ligands in the copper-catalyzed allylic oxidation of cyclohexene and cyclopentene, and the corresponding *S*-allylbenzoates were obtained in up to 73% *ee* and 78% yield in 5 days.[3e,j] Recently we reported improvements in the results of this reaction in terms of enantioselectivity, yield and reactivity by using chiral biphenylbisoxazoline ligands in the presence of mesoporous SBA-15.[3z] Herein, we report a substantial improvement in the efficiency of bi-*o*-tolyl bisoxazoline ligands in asymmetric allylic oxidation of cycloolefins by utilizing mesoporous SBA-15 in comparison to the earlier report.[3e, j]

We discovered that the chiral copper (I) complexes of these ligands allowed the reactions to gain much higher rates, yields and enantiomeric excesses for numerous cycloolefins in the presence of mesoporous SBA-15. Furthermore, a new method was developed for the synthesis of a series of chiral bi-*o*-tolyl bisoxazoline ligands with modifications to the previously reported procedure.[3e,j]

2. Results and discussion

Our study commenced with the synthesis of a series of chiral bi-*o*-tolyl bisoxazoline ligands **1** and **2** on a gram scale from inexpensive and commercially available 3-methyl benzoic acid **3** in eight steps with excellent enantiomeric excess (Scheme 1). The synthesis started with the preparation of 3-methyl-2-nitro benzoic acid **4** by nitration of *m*-toluic acid **3** with fuming nitric acid.[5a] Next, esterification of **4** by two methods, CH_3OH/H_2SO_4 or $CH_3OH/SOCl_2$, afforded methyl ester **5** in quantitative yield. Methyl 2- amino-3-methyl benzoate **6** was obtained by reduction of methyl 3-methyl-2-nitro benzoate **5** with Pd-C/H_2 resulting in the formation of the amino group.[5b] Various reducing agents such as Fe/HCl, Fe/HOAc, Sn/HCl,[5a] Pd-C/NH_2NH_2 and Pd-C/H_2 were trialled, with Pd-C/H_2 being the reagent of choice. Next, diazotization of **6** with a $NaNO_2$/HCl mixture followed by

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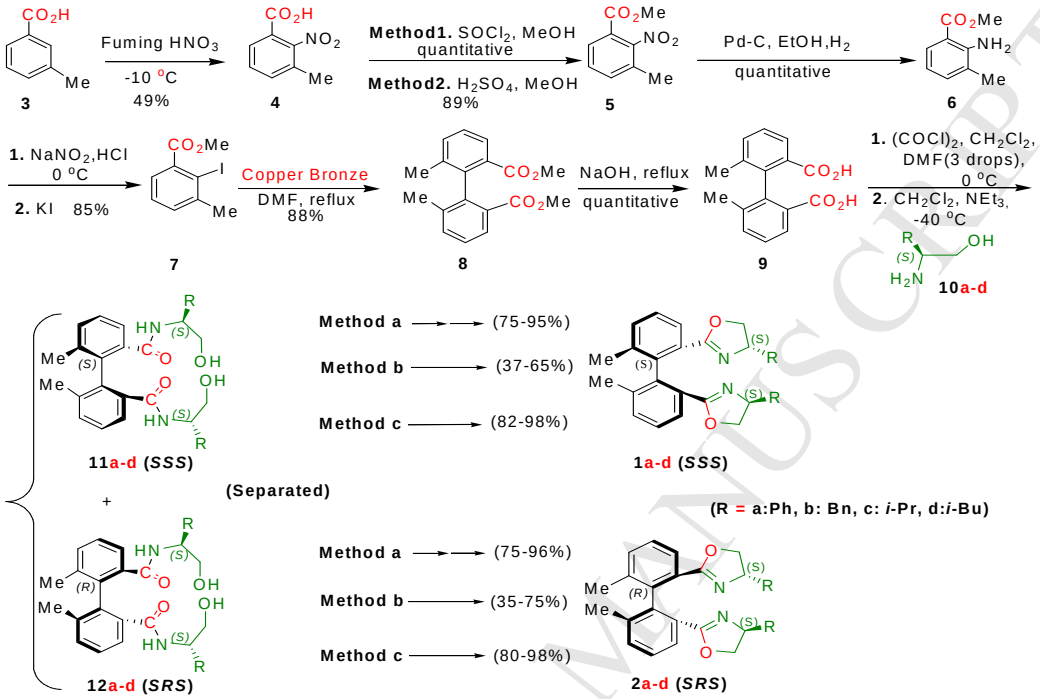
reaction with KI provided methyl 2-iodo-3-methylbenzoate **7**.[5a,c] Ullmann coupling of methyl ester **7** in the presence of activated copper bronze led to symmetrical bitoluyl diester **8**.[5a,3j] Hydrolysis of bitolyl diester **8** with NaOH gave bitolyl diacid **9** that was then treated with oxalyl chloride in the presence of a catalytic amount of DMF, forming the required diacid chloride. The treatment of diacid chloride with four individual *S*-amino alcohols **10a-d** resulted in the formation of *S*,a*S*,*S* and *S*,a*R*,*S* bishydroxylamides **11a-d** and **12a-d** before the final cyclization



Scheme 1. Synthesis of chiral ligands **1** and **2**

step. The diastereoisomers **11** and **12** were readily separated using column chromatography.[3j] The structures of the bishydroxylamide precursors **11** and **12** were assigned from elemental and spectroscopic analyses, including ^{1}H NMR, ^{13}C NMR, and mass spectral data. The absolute configuration of chiral diamide **11d** was determined by single-crystal X-ray analysis as *S*,a*S*,*S* (Figure 1).[6a-c]

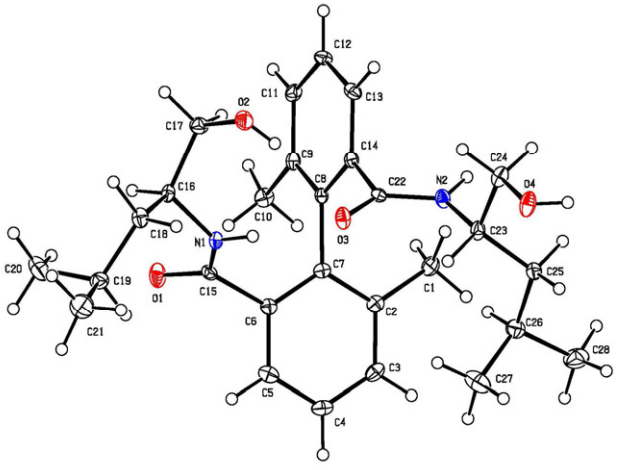


Figure 1. ORTEP diagram of bishydroxylamide precursor **11d**. Thermal ellipsoids are at the 30% probability level.

To improve the cyclization step, we sought to use three different activating agents, forming the required bi-*o*-tolyl bisoxazoline ligands **1** and **2** in high yields (Scheme 1). Activating the bishydroxylamides **11** and **12** with *p*-TsCl; in the presence of DMAP and Et_3N (method **c**) induced the cyclization step at room temperature to a higher yield in a shorter period of time compared to method **a**, the Andrus procedure,[3e,j] and method **b**, which uses $Ph_3P/CCl_4/Et_3N$ as a cyclization reagent (see the Experimental section for more details).[3r,s] Treatment of 1.1 equivalent of **1b** with 1 equivalent of $CuCl_2$ in dichloromethane and *n*-hexane afforded suitable crystals for single-crystal X-ray analysis. The absolute configuration of the diastereoisomer **1b** was also determined to be *S*,a*S*,*S* (Figure 2).[7,6c]

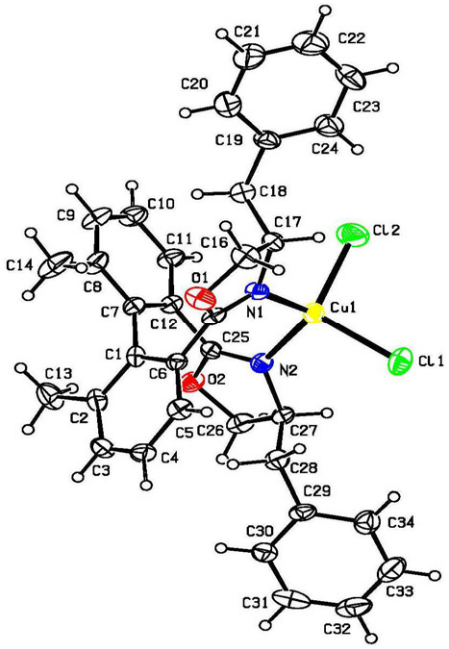


Figure 2. ORTEP diagram of copper (I)-bi-*o*-tolyl-bisoxazoline complex **1b**. The solvent molecules ($CHCl_3$) have been omitted for clarity. Thermal ellipsoids are at the 30% probability level.

Both crystal structures of **1b** and **11d** confirmed that the chiral centers remained unchanged without any racemization over the course of the reaction (Figures 1 & 2).

Encouraged by the efficient and high yielding protocol for the synthesis of ligands **1a-d** and **2a-d,** we sought to investigate the effect of these ligands in conjunction with various nano-sized

additives in the copper-catalyzed allylic oxidations of cycloolefins. In a typical experimental procedure, the reactions were carried out by using cyclohexene as a substrate in the presence of various ligands **1-2** (10 mol%) and $[Cu(CH_3CN)_4]PF_6$ (10 mol%) as a catalyst at different temperatures in acetonitrile. The reactions were monitored by TLC for the consumption of perester and were stopped at the given time. A series of results is

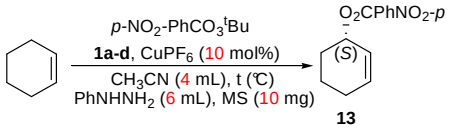


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Table 1: Effect of catalyst on enantioselectivity, yield and reactivity at different temperatures

Entry	Catalyst	T (°C)	Time (h)	Yield (%)	ee (%)
1	**1a**	Reflux	0.25	70	21
2	**1a**	40	2	65	35
3	**1a**	25	3.5	92	60
4	**1a**	10	43	68	68
5	**1a**	0	101	70	72
6	**1a**	–10	200	85	80
7	**1a**	–16	350	69	82
8	**1a**	–20	415	68	82
9	**2a**	–10	200	85	30
10	**1b**	–10	190	80	70
11	**2b**	–10	220	76	20
12	**1c**	–10	185	80	43
13	**2c**	–10	200	63	12
14	**1d**	–10	168	78	17
15	**2d**	–10	176	76	5

summarized in Table 1.

The temperature dependency on both yield and enantiomeric excess of the products was also investigated. A decrease in the reaction temperature from –10 to –20 °C did not lead to a favorable *ee* and decreased the reaction yield substantially, while the enantioselectivity dropped dramatically as the temperature increased from –10 to 40 °C (entries 1-8, Table 1). The stereocontrol induction observed for the (*S*,a*S*,*S*)-ligands **1** was much better than that for the related (*S*,a*R*,*S*)-ligands **2**. The phenyl or benzyl substituted oxazolines **1a** and **1b** resulted in considerably higher enantioselectivities in comparison to the other two ligands **1c** and **1d**, carrying alkyl substitutions (entries 6 and 10 vs. 12, 14). The highest enantioselectivities and yields were achieved by employing ligand **1a** at –10 °C (entry 6).

Considering ligand **1a** to be the ligand of choice, we next examined the effects of solvent, copper salts and molecular sieves (MS) in the reaction at –10 °C to achieve optimal reaction conditions. A series of results is summarized in Table 2.

Table 2: Effect of solvents, MS and counter anions on the reaction

Entry	Cu salt (10 mol%)	Solvent	Time (h)	Yield (%)	ee (%)
1[a]	$CuPF_6$	CH_3CN	215	66	46
2	$CuPF_6$	CH_3CN	200	85	80
3	CuOTf	CH_3CN	215	90	63
4	CuCl	CH_3CN	420	58	29
5	CuI	CH_3CN	275	54	28
6	$CuPF_6$	Acetone	210	87	66
7	$CuPF_6$	CH_2Cl_2	300	55	37

a) In the absence of MS.

It was observed that the reaction rate, yield and *ee* values of the products were generally improved when $CuPF_6$ salts and molecular sieves were used simultaneously (entry 2 vs. entry 1). The effect of various Cu salts was also investigated and in all cases, $CuPF_6$ proved to be the best copper source (Table 2), while other Cu salts such as CuOTf, CuCl and CuI led to *ee* values that were decreased by 17-52% and to longer reaction times (entry 2 versus entries 3-5). Three different solvents were examined under various conditions, and the best results were obtained in MeCN (entry 2 versus entries 6-7).

The effects of catalyst loading were also investigated, and the results are summarized in Table 3. The best results were obtained when 10 mol % catalyst loading was used. Changing the catalyst loading to lower or higher amounts led to sharp decreases in the reaction results (Table 3).

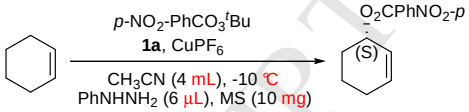

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Table 3: Effect of catalyst loading on the reaction

Entry	Catalyst (mol%)	Time (h)	Yield (%)	ee (%)
1	1	452	22	18
2	2.5	305	42	28
3	5	285	48	48
4	10	200	85	80
5	15	220	54	62
6	20	175	45	56

Although the use of molecular sieves led to formation of the desired product **13** in good yield and enantioselectivity, a longer reaction time was required. Therefore, further optimization of the reaction conditions could be achieved by exploring the effect of various additives in this reaction. For this purpose, we prepared and examined activated silica gel,[8] mesoporous MCM-41[9] and SBA-15 silica,[10] nanocrystalline MgO[11], CuO[12] and TiO_2[13]. A series of results is presented in Table 4; as can be seen from these data, the reaction is generally faster in the presence of these nanoparticles than when molecular sieves were used. Much to our surprise, mesoporous SBA-15 (10 mg/mmol) showed the greatest effect among these additives. The enantioselectivity of the reaction markedly improved (up to 93%), and the reaction was completed in only 36 h, providing the chiral allylic ester **13** in quantitative yield (entry 3 versus entry 1).

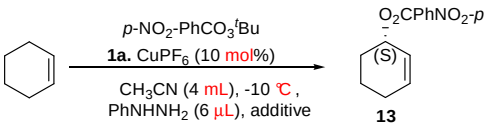

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Table 4: Effects of additive on the reaction

Entry	Additive (10 mg)	Time (h)	Yield (%)	ee (%)
1	Ms	200	85	80
2	Activated silica gel	225	65	62
3	SBA-15	36	96	93
4	MCM-41	68	85	65
5	Nano MgO	48	90	83
6	Nano TiO_2	45	86	77
7	Nano CuO	41	90	79

In a similarly reported reaction with using the same ligands and without any mesoporous materials, the experiment leads to only 73% *ee* and 78% yield of products in 5 days.[3j] Similarly, when the reaction has performed with chiral biphenyl-bisoxazoline ligands in the presence of mesoporous SBA-15, yield of the reaction remarkable improved (99%) but enantioselectivity of products and reactivity of the reaction slightly increased (81% *ee* in 72 h).[3z] Mesoporous MCM-41 silica also exhibited higher yields and reactivity, yet the enantioselectivity values decreased considerably in contrast to those for MS (compare entry 4 with entry 1). It was also found that utilizing metal oxide additives resulted in comparable

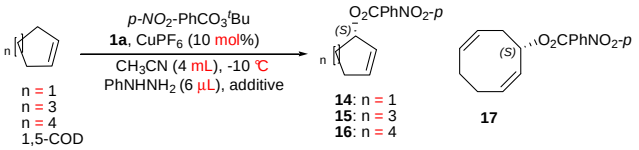

Table 5: Additive effect on other cycloolefins

Entry		1	2	3	4[a]	5	6
Additive (10mg)		SBA 15	Activated silica gel	MCM-41	Nano MgO	Nano TiO_2	Nano CuO
Time (h)		100	200	120	85	95	76
Yield (%)	**14**	90	70	90	92	88	75
ee (%)		81	54	71	73	70	74
Time (h)		80	205	110	78	66	88
Yield (%)	**15**	94	70	88	84	85	92
ee (%)		93	73	85	76	77	86
Time (h)		150	200	165	90	112	85
Yield (%)	**16**	84	62	70	76	74	80
ee (%)		70	39	64	53	66	68
Time (h)		46	180	88	66	70	82
Yield (%)	**17**	95	73	90	96	97	99
ee (%)		97	74	85	84	87	92

a) 2.5 mg Nano MgO

enantioselectivity with higher rates and better yields in comparison to when MS were used (entries 5-7).

The drastic effect of these additives in the allylic oxidation of cyclohexene encouraged us to examine this effect on other substrates. We extended the reaction to several cycloolefins and in all cases, allylic esters **14-17** were obtained in high yields and *ees*; the best results were achieved in the presence of SBA-15 (10 mg) (Table 5).

The SBA-15 was recycled and reused at least three times without a significant loss of efficiency. The XRD, SEM and IR results clearly demonstrated that the mesoporous structure of SBA-15 was preserved after three uses (See SEM image in Supplementary Material). To demonstrate the effect of the mesoporous structure on catalytic activity, we carried out the reaction in the presence of activated silica gel (amorphous system) under similar reaction conditions. As shown by the results in Table 4 and Table 5, a drastic attenuation in values was observed in terms of yields, enantioselectivities and reactivities. The temperature dependency and effect of various ligands **1** on yield, enantiomeric excess and reactivity of the reaction were also investigated in optimized condition for each of above mentioned cycloolefins. (See Table 6 in Supplementary Material for details) In most of cases, the best results were obtained with ligand **1a** at –10 °C.

Conclusions

In conclusion, a series of chiral bi-*o*-tolyl bisoxazoline ligands **1** and **2** were conveniently synthesized on a gram scale from inexpensive and commercially available 3-methyl benzoic acid in eight steps with modifications to an earlier reported procedure. The catalytic potential of these ligands for copper-catalyzed allylic oxidations of cycloolefins was investigated by utilizing numerous nano-sized additives. By optimizing the reaction conditions in the presence of SBA-15, and chiral bi-*o*-tolyl bisoxazoline ligands **1**, allylic benzoates were obtained in up to 97% *ee* and 99% yield in a reasonably short period of time. The obtained results in this work clearly show significant improvement in efficiency of bi-*o*-tolyl bisoxazoline ligands in asymmetric allylic oxidation reaction of cycloolefins, especially for cyclohexene, cycloheptene and 1,5-cyclooctadiene, by utilizing mesoporous SBA-15 as an additive. To the best of our knowledge, *ees*, yields and rates achieved in this work are superior for the allylic oxidation of cycloolefins in comparison with earlier report. Efforts to extend the utility of the mesoporous compounds in other asymmetric transformations are still in progress in our laboratory.

3. Experimental

3.1. General

Melting points were measured on an Elecrtothermal 9100 apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 341 polarimeter at 589 nm. ^1H and ^{13}C NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 and 75.47 MHz in $CDCl_3$, DMSO-d_6 and acetone-d_6 using TMS (δ = 0.0 ppm) as internal standard. IR spectra were recorded on a Bomen FT-IR-MB-series instrument. Enantiomeric excess (*ee*) of the allylic esters **13-17** were determined by HPLC analysis using EC 250/4.6 Nucleocel Alpha S column. All reactions were performed under an atmosphere of dry, oxygen-free nitrogen. All reagents and starting materials were purchased from Aldrich, Merck and Fluka. Olefins were distilled from calcium hydride before use. All solvents were of reagent grade and were dried and distilled immediately before use as follows: acetonitrile and acetone from P_2O_5, methylene chloride from calcium hydride. Column chromatography was performed using silica gel 60 (230±400 mesh) eluting with ethyl acetate: *n*-hexane. TLC was performed using silica gel 60 F_{256} plates with visualization by UV.

3.2. The procedure for synthesis of 2,2′-bitolyl bisoxazoline ligands 1 and 2:

Step 1: *Synthesis of 3-methyl-2-nitro benzoic acid* (**4**):[5a] 2-Toluic acid (1 g, 7.35 mmol) was added slowly with stirring to fuming nitric acid (4 mL) in –10°C, then the mixture was stirred at this temperature for 1 h. TLC analysis of the reaction (*n*-hexane /EtOH) confirmed the formation of a new compound. After the reaction was judged to be completed, the mixture was filtered and precipitated solid was washed with cold water. Compound **4** (0.66 g, 50 %) was obtained after drying, m.p. 217- 219 ºC (lit. 217- 219 ºC)[5a]; δ_H (300 MHz acetone-d_6) 2.33 (3H, s, Me), 7.60 (1H, t, *J* 7.7 Hz, Ph), 7.70 (1H, d, *J* 7.6 Hz, Ph), 7.94 (1H, d, *J* 7.6 Hz, Ph), 10.15 (1H, br s, CO_2H); δ_C (75 MHz DMSO-d_6) 16.7, 124.1, 129.0, 130.3, 131.0, 136.1, 150.5, 165.1.

Step 2: Synthesis of methyl 3-methyl-2-nitrobenzoate (**5**):[14a,b]

Method 1: *H_2SO_4/CH_3OH*: Concentrated sulfuric acid (1 mL) was added to a solution of 2-nitro-3-toluicacid (1 g, 5.49 mmol) in methanol (4 mL) and the reaction mixture was stirred and heated to reflux for 5 h. After completion of the reaction (was determined by TLC analysis), the crystalline product was filtered and washed with cold water and dried (0.95 g, 89%).

Method 2: $CH_3OH/SOCl_2$: 2-Nitro-3-toluic acid (1 g, 5.49 mmol) was placed in a round bottom flask (25 mL) containing methanol (4 mL). The reaction solution was cooled to 0 ºC and thionyl chloride (1 mL, 13.83 mmol) was added to the reaction flask. The solution was allowed to warm slowly to r.t. and was stirred for 10 h. After completion of the reaction (was determined by TLC analysis), aqueous sodium hydrogen carbonate (5 mL, 5%) was added and the crystalline product was collected and washed with cold water and then dried. The product **5** was afforded as a white solid (1.05 g, 99%); m.p. 73-74 ºC (lit.[14b] 72-73 ºC); δ_H (300 MHz $CDCl_3$) 2.35 (3H , s, Me), 3.88 (3H, s, CO_2Me) 7.63 (1H, t, *J* 7.7 Hz, Ph), 7.73 (1H, d, *J* 7.6 Hz, Ph), 7.90(1H, d, *J* 7.6 Hz, Ph); δ_C (75 MHz $CDCl_3$) 16.8, 53.5, 122.9, 129.0, 130.7, 131.2, 136.6, 150.2, 164.3.

Step 3: Synthesis of methyl 2-amino-3-methyl benzoate (**6**) *using Pd-C/H_2 reagent.*[5b, 14c]

Methyl 3-methyl-2-nitro benzoate (1 g, 5.2 mmol) was dissolved in ethanol (40 mL) and then 10% palladium on charcoal (0.1 g)

was added to the reaction mixture and stirred at r.t. for 10 h. Then the mixture was filtrated, and evaporation of solvent under reduced pressure afforded the light yellow oil product. (0.85 g, 99%); δ_H (300 MHz $CDCl_3$) 2.18 (3H, s, Me), 3.88 (3H , s, CO_2Me), 5.84 (2H, br s, NH_2), 6.61 (1H, t, *J* 7.7 Hz, Ph), 7.22 (1H, d, *J* 7.3 Hz, Ph), 7.79 (1H, d, *J* 7.7 Hz, Ph); δ_C (75 MHz $CDCl_3$) 17.4, 51.5, 110.1, 115.6, 123.0, 129.1, 134.9, 149.0, 169.0.

Step 4: Synthesis of methyl 2-iodo-3-methyl benzoate (**7**):[5a,c]

A suspension of compound **6** (1 g, 6 mmol) in a mixture of HCl (2.2 mL, %37) and ice was stirred for 15 min at 0 °C. Then a solution of $NaNO_2$ (0.4 g, 6 mmol) in cold water (3 mL) was added slowly at 0 °C to the reaction mixture. Then the mixture was stirred until it became homogeneous. Another round- bottom flask was charged with potassium iodide (3.46 g, 20 mmol) and water (8 mL). The freshly prepared solution containing the diazonium salt was added to this mixture by funnel at 0 °C. The solution was allowed to warm slowly to r.t. and stirred for further 20 h. The product was extracted with diethyl ether (3 × 8 mL), the organic layer was washed with sodium thiosulfate (5 mL) and the solvent was evaporated to afford compound **7** (1.41 g, 85%); δ_H (300 MHz $CDCl_3$) 2.52 (3H, s, Me), 3.92 (3H, s, CO_2Me), 7.25-7.38 (3H, m, Ph); δ_C (75 MHz $CDCl_3$) 29.7, 52.6, 100.0, 127.1, 127.8, 131.8, 138.4, 143.4, 168.8.

Step 5: Synthesis of bitoluyl diester (**8**):[5a,3j]

To a solution of compound **7** (1 g, 3.7 mmol) in *N*,*N*-dimethyl formamide (3.3 mL) was added activated copper bronze powder (0.55 g) with stirring. The reaction was then slowly refluxed under inert atmosphere. It was stopped after 5 h and cool to r.t. and the copper was filtered off and washed with methylene chloride (3 × 5 mL). Then organic layer was washed with HCl (1M, 2mL), aqueous potassium hydrogen carbonate (3 mL) and brine (3 mL) and then dried over $MgSO_4$. The solvent was evaporated to afford a crude residue. Purification using column chromatography (5-20% EtOAc/hexane), produced dimethyl 6,6-dimethylbiphenyl-2,2 dicarboxylate **8** (0.97 g, 88%) as a light yellow oil. δ_H (300 MHz $CDCl_3$) 1.92 (6H, s, Me), 3.57 (6H, s, CO_2Me), 7.31-7.37 (2H, t, *J* 7.6 Hz, Ph), 7.45 (2H, d, *J* 7.5 Hz, Ph), 7.87 (2H, d, *J* 7.7 Hz, Ph).

Step 6: Synthesis of bitoluyl diacid (**9**):[5a,3j]

Compound **8** (0.4 g, 1.34 mmol) was added to NaOH (0.92 g, 2.3 mmol) in water (2.88 mL). The reaction mixture was refluxed for 4.5 h. The solution was cooled to r.t. and then acidified by the addition of HCl (4 M) until pH = 3 achieved. The mixture was filtered and the residue was washed with cold water and dried at room temperature. The pure product **9** (0.35 g, 96%) as a light yellow crystal was achieved by recrystallization from ethanol. m.p. 234-236 ºC; δ_H (300 MHz DMSO-d_6) 1.80 (6H, s, Me), 7.30 (2H, t, *J* 7.6 Hz, Ph), 7.44 (2H, d, *J* 7.5 Hz , Ph), 7.71 (2H, d, *J* 7.6 Hz, Ph), 12.23 (2H, br s, CO_2H); δ_C (75 MHz DMSO-d_6) 20.2, 127.1, 127.7, 131.0, 133.3, 136.4, 141.1, 168.6.

Step 7: Typical procedure for the synthesis of bishydroxylamide (**11a-d** *and* **12a-d**):[3j]

To a solution of diacid **9** (0.8 g, 3.0 mmol) in anhydrous methylene chloride (10 mL) were added oxalyl chloride (1.25 mL, 12 mmol) and then DMF (3 drops) at 0 °C. The reaction mixture was stirred for 8 h at r.t. under N_2. Then the solvent was removed under reduced pressure to afford the acyl chloride as a light yellow solid (0.91 g, 99%). This solid residue was then dissolved in anhydrous methylene chloride (10 mL) and cooled to –40 °C and slowly added to a stirred solution of (*S*)-phenyl glycinol (0.9 g, 6.5 mmol) and Et_3N (1 mL) in anhydrous methylene chloride (15 mL) over 30 min. The solution was allowed to warm slowly to r.t. with stirring overnight under N_2. TLC analysis of the reaction (90%/10% EtOAc/*n*-hexan) confirmed the formation of two compounds **11a** and **12a**. The mixture was extracted with ethyl acetate (3 × 5 mL); the organic layer was washed with saturated brine (5 mL), dried over magnesium sulfate, and concentrated. Two diastereomers **11a** and **12a** (1.37 g, 90%) as white solid were separated by flash chromatography (55-95% EtOAc/*n*-hexanes). Compounds **11b-d** and **12b-d** were synthesized in the similar method. The total yields for compounds **11b**/**12b**, **11c**/**12c**, and **11d**/**12d** were 95% (1.53 g), 85% (1.12 g) and 99% (1.39 g) respectively.

(S,S,S)-6,6'-Dimethyl-biphenyl-2,2'-dicarboxylic acid bis-[(2-hydroxy-1-phenyl-ethyl)-amide] (**11a**):[3j] m.p. 133-136 °C; R_f (100% EtOAc) 0.42; δ_H (300 MHz $CDCl_3$) 1.97 (6H, s, Me), 2.74 (2H, br s, OH), 3.46-3.59 (4H, m, C<u>H</u>$_2$OH), 4.95-5.02 (2H, m, C<u>H</u>Ph), 7.08-7.38 (16, m, Ph), 7.79 (2H, d, *J* 7.7 Hz, NH); δ_C (75 MHz $CDCl_3$) 20.0, 56.1, 66.1, 124.7, 126.7, 127.4, 128.1, 128.9, 131.8, 136.0, 136.6, 137.1, 138.4, 169.6.

(S,R,S)-6, 6' -Dimethyl-biphenyl-2, 2'-dicarboxylic acid bis-[(2-hydroxy-1-phenyl-ethyl)-amide] (**12a**):[3j] m.p. 105-107 °C; R_f (100% EtOAc) 0.34; δ_H (300 MHz $CDCl_3$) 1.87 (6H, s, Me), 2.94 (2H, OH), 3.6-3.65 (4H, m, C<u>H</u>$_2$OH), 4.78-4.84 (2H, m, C<u>H</u>Ph), 6.88-6.90 (4H, m, Ph), 7.08-7.34 (12, m, Ph), 7.80 (2H, d, *J* 7.1 Hz, NH); δ_C (75 MHz $CDCl_3$) 19.6, 56.8, 66.5, 125.1, 126.2, 127.1, 128.0, 128.7, 132.1, 136.1, 136.4, 136.9, 138.2, 170.5.

(S,S,S)-6,6-Dimethyl-biphenyl-2,2-dicarboxylic acid bis-[(2-hydroxy-1-benzyl-ethyl)-amide] (**11b**):[3j] m.p. 126-128 °C; R_f (100% EtOAc) 0.44; δ_H (300 MHz, $CDCl_3$) 1.90 (6H, s, Me), 2.45 (2H, br s, OH), 2.65-2.79 (4H, m, CHC<u>H</u>$_2$Ph), 3.28-3.31 (2H, m, C<u>H</u>$_2$OH), 3.37-3.41 (2H, m, C<u>H</u>$_2$OH), 4.09-4.14 (2H, m, C<u>H</u>CH$_2$Ph), 7.16-7.29 (16H, m, Ph), 7.47 (2H, d, *J* 8.0 Hz, NH); δ_C (75 MHz, $CDCl_3$) 20.0, 36.7, 52.9, 63.4, 124.3, 126.5, 128.0, 128.5, 129.2, 131.7, 136.2, 137.0, 137.1, 137.8, 170.9.

(S,R,S)-6,6-Dimethyl-biphenyl-2,2-dicarboxylic acid bis-[(2-hydroxy-1-benzyl-ethyl)-amide] (**12b**):[3j] m.p. 113-115 °C; R_f (100% EtOAc) 0.35; δ_H (300 MHz $CDCl_3$) 1.96 (6H , s, Me), 2.44-2.60 (4H, m, CHC<u>H</u>$_2$Ph), 3.36 (2H, dd, *J* 11.3, 3.0 Hz, C<u>H</u>$_2$OH), 3.53 (2H, dd, *J* 11.3, 3.0 Hz, C<u>H</u>$_2$OH), 4.40 (2H, m, C<u>H</u>CH$_2$Ph), 7.18-7.31 (16H, m, Ph), 7.47 (2H, d, *J* 7.9 Hz, NH); δ_C (75 MHz $CDCl_3$) 20.0, 36.4, 53.0, 63.5, 125.2, 126.5, 128.1, 128.5, 129.1, 132.1, 136.1, 136.4, 136.5, 137.7, 170.5.

(S,S,S)-6,6'-Dimethyl-biphenyl-2,2'-dicarboxylic acid bis-[(2-hydroxy-1-i-propyl-ethyl)-amide] (**11c**):[3j] m.p. 129 °C; R_f (100% EtOAc) 0.41; δ_H (300 MHz $CDCl_3$) 0.83-0.85 (6H, d, *J* 6.9 Hz, CH<u>Me</u>$_2$), 0.86-0.88 (6H, d, *J* 6.9 Hz, CH<u>Me</u>$_2$), 1.71-1.82 (2H, m, C<u>H</u>Me$_2$), 2.02 (6H, s, Ph<u>Me</u>), 2.18 (2H, br s, OH), 3.32-3.38 (2H, m, C<u>H</u>$_2$OH), 3.44-3.48 (2H, m, NHC<u>H</u>), 3.68-370 (2H, m, C<u>H</u>$_2$OH), 7.29-7.38 (8H, m, Ph and NH); δ_C (75 MHz $CDCl_3$) 18.9, 19.7, 20.5, 29.3, 56.1, 63.7, 124.1, 127.9, 131.1, 136.3, 136.7, 137.4, 171.8.

(S,R,S)-6,6'-Dimethyl-biphenyl-2,2'-dicarboxylic acid bis-[(2-hydroxy-1-i-propyl-ethyl)-amide] (**12c**):[3j] m.p. 58-60 °C; R_f (100% EtOAc) 0.3; δ_H (300 MHz $CDCl_3$) 0.80-0.82 (12H, d, *J* 6.8 Hz, CH<u>Me</u>$_2$), 1.71-1.78 (2H, m, C<u>H</u>Me$_2$), 2.00 (6H, s, Ph<u>Me</u>), 2.61 (2H, br s, OH), 3.32-3.40 (4H, m, C<u>H</u>$_2$OH), 3.64 (2H, m, NHC<u>H</u>), 7.06-7.33 (6H, m, Ph), 7.51-7.54 (2H, d, *J* 8.2 Hz, NH); δ_C (75 MHz, $CDCl_3$) 18.7, 19.4, 20.2, 28.9, 57.0, 63.4, 124.4, 127.9, 131.6, 136.3, 137.0, 137.1, 171.4.

(S,S,S)-6,6'-Dimethyl-biphenyl-2,2'-dicarboxylic acid bis-[(2-hydroxy-1-i-butyl-ethyl)-amide] (**11d**): m.p. 57-60 °C; **[**Found: C, 71.71; H, 8.57; N, 6.03. $C_{28}H_{40}N_2O_4$ requires C, 71.76; H, 8.60; N, 5.98%**];** R_f (100% EtOAc) 0.50; ν_{max} (KBr) 3380, 3226,1647, 1560, 1460 cm^{-1}; δ_H (300 MHz $CDCl_3$) 0.75 (6H, d, *J* 6.4 Hz, CH<u>Me</u>$_2$), 0.81 (6H, d, *J* 6.4 Hz, CH<u>Me</u>$_2$), 1.12-1.16 (m, 2H, C<u>H</u>$_2$CHMe$_2$), 1.20- 1.25 (2H, m, C<u>H</u>$_2$CHMe$_2$), 1.39-1.41 (2H, m, C<u>H</u>Me$_2$), 1.93 (6H, s, Ph<u>Me</u>), 3.18-3.27 (4H, m, C<u>H</u>$_2$OH), 3.86 (2H, m, NHC<u>H</u>), 7.27 (6H, m, Ph), 7.61 (2H, d, *J* 8.2 Hz, NH); δ_C

(75 MHz $CDCl_3$) 20.1, 22.0, 23.1, 24.7, 39.6, 49.8, 65.3, 124.3, 127.8, 131.4, 136.1, 136.8, 137.1, 171.1; *m/z* (%): 470 (5.5, M+2), 438(35.5), 352 (40), 209(100), 165(17), 55(13).

(S,R,S)-6,6'-Dimethyl-biphenyl-2,2'-dicarboxylic acid bis-[(2-hydroxy-1-i-butyl-ethyl)-amide] (**12d**): m.p. 66-71 °C; **[**Found: C, 71.70; H, 8.55; N, 6.05. $C_{28}H_{40}N_2O_4$ requires C, 71.76; H, 8.60; N, 5.98%**];** R_f (100% EtOAc) 0.35; ν_{max} (KBr) 3400, 3200, 1637, 1550, 1434 cm^{-1}; δ_H (300 MHz $CDCl_3$) 0.80 (6H, d, *J* 5.9 Hz, CH$\underline{Me}_2$), 0.82 (6H, d, *J* 5.9 Hz, CH$\underline{Me}_2$), 1.14-1.17 (4H, m, C$\underline{H}_2$CHMe_2), 1.23-1.27 (2H, m, C$\underline{H}$Me_2), 1.93 (6H, s, Ph$\underline{Me}$), 3.40-3.45 (2H, dd, *J* 11.1, 5.6, Hz C$\underline{H}_2$OH), 3.51-3.56 (2H, dd, *J* 11.1, 3.4 Hz, C$\underline{H}_2$OH), 3.89-4.11 (2H, m, NHC$\underline{H}$), 7.34-7.38 (6H, m, Ph), 7.44-7.47 (2H, m, NH); δ_C (75 MHz $CDCl_3$) 20.3, 22.2, 23.1, 24.7, 39.8, 49.6, 65.3, 124.3, 127.8, 131.4, 136.3, 136.8, 137.3, 171.0; *m/z* (%): 470 (5.5, M+2), 438(35.5), 352 (40), 209 (100), 165 (17), 55 (13).

Step 8: Cyclization of diamides were performed in three methods:

Method a: Cyclization procedures of bishydroxylamides **11a-d** and **12a-d** were performed according to Andrus procedure.[3e, j]

Method b:[3r,s] A solution of diamide **11a** or **12a** (236 mg, 0.5 mmol), triphenylphosphane (0.14 g, 5.2 mmol), triethylamine (69 µL, 0.44 mmol) and tetrachloromethane (50 µL, 0.44 mmol) in dry acetonitrile (3 mL) was stirred over nigh at room temperature for 19 h. After being concentrated in vacuum, the residue was dissolved in CH_2Cl_2 (5 mL), washed with water (3 mL), dried over anhydrous magnesium sulfate and then concentrated in vacuum. The residue was purified by silica gel column chromatography (5:30% EtOAc/*n*-hexanes) to afford light yellow products **1a** (76 mg, 65%) or **2a** (71 mg, 60%). Compounds **1b-d** and **2b-d** were synthesized in the similar method.

Method c:[3k, 3w-y] A flame–dried round–bottom flask with a stirrer bar was charged with diamide **11a** or **12a** (1.77 g, 3.5 mmol), *p*-(dimethylamino) pyridine (0.043 g, 0.3 mmol) and CH_2Cl_2 (10 mL) under N_2. The flask was placed in ice and triethylamine (2.1 mL, 15.4 mmol) and a solution of *p*-toluensulfonyl chloride (1.34 g, 7 mmol) in CH_2Cl_2 (4 mL) was added to the reaction mixture. The light yellow clear solution was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and washing with saturated aqueous NH_4Cl (10 mL), two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 8 mL). The extracted organic layers were combined and washed with saturated aqueous $NaHCO_3$ (10 mL), dried over Na_2SO_4 and concentrated. The light yellow oil **1a** achieved and purified by column chromatography (5-25% EtOAc/*n*-hexanes) to afford pure light yellow products **1a** (1.58 g, 96 %) and **2a** (1.48 mg, 90%). Compounds **1b-d** or **2b-d** were synthesized in the similar method.

(S,S,S)-2,2'-Bi-o-tolyl-1,1'-diphenylbis(oxazoline) (**1a**):[3j] R_f (70:30; *n*-hexane/EtOAc) 0.49; δ_H (300 MHz $CDCl_3$) 2.04 (6H , s, Me), 3.86 (2H, t, *J* 8.3 Hz, OCH_2), 4.39 (2H, dd, *J* 10.1, 8.3 Hz, OCH_2), 5.15 (2H, dd, *J* 10.1, 8.3 Hz, C$\underline{H}_2$Ph), 7.07-7.42 (14, m, Ph), 7.88 (2H, dd, *J* 7.6 Hz, Ph); δ_C (75 MHz $CDCl_3$) 20.3, 69.8, 74.6, 126.7, 126.9, 127.2, 127.4, 127.6, 128.4, 132.1, 136.9, 140.0, 142.7, 165.6.

(S,R,S)-2,2'-Bi-o-tolyl-1,1'-diphenylbis(oxazoline) (**2a**):[3j] R_f (70:30; *n*-hexane/EtOAc) 0.38; δ_H (300 MHz, $CDCl_3$) 2.07 (6H, s, Me), 3.77 (2H, t, *J* 8.4 Hz, OCH_2), 4.43 (2H, dd, *J* 9.3 Hz, OCH_2) 5.16 (2H, dd, *J* 9.3, 8.4 Hz, C$\underline{H}_2$Ph), 6.91-7.75 (14H, m, Ph), 7.75 (2H, d, *J* 7.3 Hz, Ph). δ_C (75 MHz $CDCl_3$) 20.3, 69.8, 74.7, 125.4, 126.6, 126.9, 127.2, 127.8, 128.0, 128.4, 128.7, 132.0, 137.5, 165.8.

(S,S,S)-2,2'-Bi-o-tolyl-1,1'-dibenzylbis(oxazoline) (**1b**):[3j] R_f (72:28; *n*-hexane/EtOAc) 0.46; δ_H (300 MHz $CDCl_3$) 1.99 (6H , s, MePh), 2.46 (2H, dd, *J* 13.8, 8.9 Hz, C$\underline{H}_2$Ph), 2.98 (2H, dd, *J* 13.8, 5.1 Hz, C$\underline{H}_2$Ph), 3.73 (2H, t, *J* 8.9 Hz, OCH_2), 3.93 (2H, t, *J* 8.9 Hz, OCH_2), 4.26-4.31 (2H, m, NCH) , 7.12-7.38 (14H, m, Ph), 7.72 (2H, d, *J* 7.3 Hz, Ph). δ_C (75 MHz $CDCl_3$) 20.2, 41.5, 67.8, 71.7, 126.2, 126.8, 126.9, 127.8, 128.4, 129.2, 131.9, 136.8, 138.4, 139.8, 164.7.

(S,R,S)-2,2'-Bi-o-tolyl-1,1'-dibenzylbis(oxazoline) (**2b**):[3j] R_f (72:28; *n*-hexane/EtOAc) 0.37; δ_H (300 MHz $CDCl_3$) 2.01 (6H , s, MePh), 2.46 (2H, dd, *J* 13.7, 8.9 Hz, C$\underline{H}_2$Ph), 2.98 (2H, dd, *J* 13.7, 5.1 Hz, C$\underline{H}_2$Ph), 3.71 (2H, t, *J* 8.9 Hz, OCH_2), 3.96 (2H, t, *J* 8.9 Hz, OCH_2), 4.26-4.31 (2H, m, NCH), 7.02-7.37 (14H, m, Ph), 7.64 (2H, d, *J* 7.4Hz, Ph); δ_C (75 MHz $CDCl_3$) 20.2, 41.4, 67.8, 71.6, 126.2, 126.7, 126.9, 127.8, 128.3, 129.1, 131.7, 137.4, 138.4, 139.5, 164.6.

(S,S,S)-2,2'-Bi-o-tolyl-1,1'-di i-propyl bisoxazoline (**1c**):[3j] R_f (68:32; *n*-hexane/EtOAc) 0.34; δ_H (300 MHz $CDCl_3$) 0.69-71 (12H, s, CH$\underline{Me}_2$), 1.43-1.52 (2H, m, C$\underline{H}$Me_2), 1.99 (6H, s, MePh), 3.61-3.67 (2H, t, *J* 7.8 Hz, OCH_2), 3.77-3.85 (2H, dd, *J* 16.5, 7.4 Hz, NCH), 4.00-4.06 (t, *J* 7.8 Hz, 2H, OCH_2), 7.23-7.32 (m, 4H, Ph), 7.61-7.64 (d, *J* 7.36 Hz, 2H, Ph); δ_C (100 MHz $CDCl_3$) 18.1, 18.6, 19.4, 20.2, 32.6, 68.9, 72.4, 126.6, 126.8, 127.9, 131.5, 137.3, 139.6, 164.1,

(S,R,S)-2,2'-Bi-o-tolyl-1,1'-di i-propyl bisoxazoline (**2c**):[3j] R_f (68:32; *n*-hexane/EtOAc) 0.21; δ_H (300 MHz $CDCl_3$) 0.69-72 (12H, s, CH$\underline{Me}_2$), 1.43-1.52 (2H, m, C$\underline{H}$Me_2), 2.00 (6H, s, MePh), 3.62-3.67 (2H, t, *J* 7.9 Hz, OCH_2), 3.77-3.86 (2H, m, NCH), 4.00-4.06 (2H, m, OCH_2), 7.23-7.33 (4H, m, Ph),7.61-7.64 (2H, s, Ph); δ_C (75 MHz $CDCl_3$) 18.6, 19.0, 20.6, 36.5, 70.1, 74.9, 124.2, 126.9, 128.2, 129.6, 136.1, 140.5, 164.3.

(S,S,S)-2,2'-Bi-o-tolyl-1,1'-di i-butyl bisoxazoline (**1d**): [Found: C, 77.79; H, 8.35; N, 6.44. $C_{28}H_{36}N_2O_2$ requires C, 77.74; H, 8.39; N, 6.48%] R_f (65:35; *n*-hexane/EtOAc) 0.35; ν_{max} (KBr) 3417, 3060, 1647, 1542 cm^{-1}; δ_H (300 MHz $CDCl_3$) 0.80-0.87(m, 12H, CH$\underline{Me}_2$), 0.98-1.03(2H, m, C$\underline{H}$Me_2), 1.18-1.36 (2H, m, C$\underline{H}_2$CHMe_2), 1.47-1.52 (2H, m, C$\underline{H}_2$CHMe_2), 2.01(6H, s, MePh), 3.50 (2H, t, *J* 6.4 Hz, NCH), 4.00-4.10 (4H, m, OCH_2), 7.14-7.37 (4H, m, Ph), 7.57-7.60 (2H, d, *J* 7.4 Hz, Ph); δ_C (75 MHz, $CDCl_3$) 20.9, 22.6, 22.9, 25.6, 45.8, 65.3, 73.2, 126.8, 127.6, 128.5, 131.7, 140.9, 164.3; *m/z* (%) 433 (100, M+1), 418(35), 306 (42), 234 (29), 91(9), 55(23).

(S,R,S)-2,2'-Bi-o-tolyl-1,1'-di i-butyl bisoxazoline (**2d**): [Found: C, 77.77; H, 8.36; N, 6.46. $C_{28}H_{36}N_2O_2$ requires C, 77.74; H, 8.39; N, 6.48%]; R_f (65:35; *n*-hexane/EtOAc) 0.21; ν_{max} (KBr) 3406, 3060, 1655, 1625 cm^{-1}; δ_H (300 MHz $CDCl_3$) 0.80 (6H, d, *J* 6.6 Hz, CH$\underline{Me}_2$), 0.83 (6H, d, *J* 6.6 Hz, CH$\underline{Me}_2$), 1.15-1.32 (2H, m, C$\underline{H}_2$CHMe_2), 1.45-1.55 (2H, m, C$\underline{H}_2$CHMe_2), 2.00 (6H, s, MePh), 3.50 (2H, t, *J* 6.4 Hz, NCH), 3.97-4.14 (4H, m, OCH_2), 7.23-7.36 (4H, m, Ph), 7.58 (2H, d, *J* 6.8 Hz, Ph); δ_C (62 MHz $CDCl_3$) 22.5, 22.7, 22.9, 25.2, 45.2, 64.9, 73.2, 125.9, 127.0, 128.7, 129.6, 130.0, 141.0, 165.3; *m/z* (%): 433 (100, M+1), 418(35), 306 (42), 234 (29), 91(9), 55(23).

Synthesis of tert-butyl 4-nitrobenzoperoxoate:[3k]

p-Nitrobenzoyl chloride (3.2 g, 17.2 mmol) was dissolved in a round bottom flask (100 mL) containing CH_2Cl_2 (35 mL). The solution was cooled to –20 °C and stirred under nitrogen for 15 min. Pyridine (1.7 mL, 20.0 mmol) was added and the reaction mixture was stirred for 10 min. Then, *tert*-butyl hydroperoxide (3.5 mL, 20.0 mmol) was added dropwise to the reaction at –20 °C, and was stirred for 4 h. Then the reaction solution was diluted with CH_2Cl_2 (20 mL), and washed with water (10 mL). The organic layer was separated, dried over $MgSO_4$, and evaporated to obtained crude yellow solid product. Purification using flash chromatography (*n*-hexane/EtOAc; 90:10) afforded the light yellow solid product. (3.9 g, 98%). m.p. 75-78 °C; δ_H (300 MHz $CDCl_3$) 1.45 (9H, s, Me), 8.14-8.35 (4H, m, Ph).

3.3. General Procedure for enantioselective allylic oxidation of cycloolefin using tert-butyl 4-nitrobenzoperoxoate:[3k]

To a flame-dried round bottom flask (25 mL), a light yellow solution of the bisoxazoline ligand **1** (0.065 mmol) and copper copper salt (0.55 mmol) were stirred in CH_3CN (4 mL) and stirred for 3 h at ambient temperature. In this case, TLC analysis indicated the formation of a single spot (R_f = 0.0 in 50% EtOAc/ hexanes). After addition of phenyl hydrazine (6 µl, 0.06 mmol) colour of the solution was changed from blue-green to red. Then, 4 Å molecular sieves, MCM-41 or SBA-15 (or other nano particles) (10 mg) were added. After a few min, cycloolefin (5 mmol) was added. The reaction mixture was cooled to –10 °C and then *tert*-butyl *p*-nitrobenzoperoxoate (0.203 g, 0.85 mmol) was added dropwise to the reaction solution under nitrogen atmosphere. The mixture was kept at –10 °C until TLC showed to complete disappearance of perester. The reaction mixture was dissolved in %10 NH_4OH, extracted with EtOAc (3 × 5 mL) and dried over $MgSO_4$. Removal of solvent in vacuo afforded a yellow residue that was chromatographed over silica gel to provide the pure white solid product (yield up to 99%), and recovered bisoxazoline ligand in 85-92% yield.

Cyclohex-2-en-1-yl 4-nitrobenzoate (**13**):[3k] m.p. 68-71°C (lit.[3k] 75-76 ºC); R_f (*n*-hexane/EtOAc; 90: 10) 0.64; $[\alpha]_{20}^{D}$ –146.2 (*c* 1.0, $CHCl_3$); δ_H (300 MHz $CDCl_3$) 1.76-2.14 (6H, m, CH_2), 5.54 (1H, m, OCH), 5.84 (1H, d, *J* 9.8 Hz, CH=), 6.04 (1H d, *J* 9.8 Hz, CH=), 8.21-8.31 (4H, m, Ph); δ_C (300 MHz $CDCl_3$) 18.8, 25.0, 28.2, 69.8, 123.4, 125.0, 130.7, 133.6, 136.2; The enantiomeric excess was determined by chiral HPLC (EC 250/4.6 Nucleocel Alpha S column, *iso*-propyl alcohol/hexane; 99.5:0.5; flow rate 0.5 ml/min; t_R = 29.0 min (R), 31.5 min (S), (maximum *ee* = 93% (*S*)).

Cyclopent-2-en-1-yl 4-nitrobenzoate (**14**):[3k] m.p. 77-79 °C (lit.[3k] 81- 83 ºC); R_f (90: 10, *n*-Hexane/EtOAc) 0.57; $[\alpha]_{20}^{D}$ –159.3 (*c* 1.0, $CHCl_3$); δ_H (300 MHz $CDCl_3$) 1.97-2.04 (1H, m, C<u>H</u>$_2$), 2.38-2.50 (2H, m, C<u>H</u>$_2$), 2.59-2.63 (1 H, m, C<u>H</u>$_2$), 5.98 (2H, m, OCH and CH=), 6.22 (1H, m, CH=), 8.20 (d, 2H, *J* 8.5 Hz, Ph), 8.28 (d, 2H, *J* 8.5 Hz, Ph); The enantiomeric excess was determined by chiral HPLC (EC 250/4.6 Nucleocel Alpha S column, *iso*-propyl alcohol/hexane; 99.5:0.5; flow rate 0.4 ml/min; t_R = 35.1 min (R), 36.7 min (S), (maximum *ee* = 80% (*S*)).

Cyclohept-2-en-1-yl 4-nitrobenzoate (**15**):[3k] m.p. 72-75 °C; R_f (*n*-Hexane/EtOAc; 90: 10) 0.57; $[\alpha]_{20}^{D}$ –83.7 (*c* 1.0, $CHCl_3$); δ_H (300 MHz $CDCl_3$) 1.66-1.72 (4H, m, CH_2), 2.02-2.12 (2H, m, CH_2), 2.07-2.40 (2H, m, CH_2), 5.58-5.64 (1H, m, OCH), 5.75-5.82 (1H, m, CH=), 5.92-5.98 (1H, m, CH=), 8.22-8.28 (4H, m, Ph); The enantiomeric excess was determined by chiral HPLC (EC 250/4.6 Nucleocel Alpha S column, *iso*-propyl alcohol/ hexane; 99.5:0.5; flow rate 0.4 ml/min; t_R = 25.9 min (R), 27.9 min (S), (maximum *ee* = 92% (*S*)).

Cyclooct-2-en-1-yl 4-nitrobenzoate (**16**):[3t] m.p. 71-74 °C; R_f (*n*-Hexane/EtOAc; 90: 10) 0.67; $[\alpha]_{20}^{D}$ –39.4 (*c* 1.0, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 1.46-1.72 (7H, m, CH_2), 2.07-2.40 (3H, m, CH_2), 5.60-5.66 (1H, m, OCH), 5.73-5.82 (1H, m, CH=), 5.92-5.96 (1H, m, CH=), 8.22-8.32 (4H, m, Ph); The enantiomeric excess was determined by chiral HPLC (EC 250/4.6 Nucleocel Alpha S column, *iso*-propyl alcohol/hexanes; 99.5:0.5; flow rate 0.4 ml/min; t_R = 24.4 min (R), 27.0 min (S), (maximum *ee* = 75% (*S*)).

Cycloocta-2,6-dien-1-yl 4-nitrobenzoate (**17**):[3k] m.p. 74-76 °C (lit.[3k] 78- 80 ºC); R_f (*n*-Hexane/ EtOAc; 90: 10) 0.62; $[\alpha]_{20}^{D}$ – 27.5 (*c* 1.0, $CHCl_3$); δ_H (300 MHz $CDCl_3$) 2.21-2.41 (2H, m, CH_2), 2.54-2.68 (2H, m, CH_2), 2.85-2.95 (2H, m, OCHC<u>H</u>$_2$), 5.57-5.84 (4H, m, CH=), 6.17-6.26 (1H, m, OCH), 8.23 (2H, d, *J* 8.5 Hz, Ph), 8.30 (2H, d, *J* 8.5 Hz, Ph); The enantiomeric excess was determined by chiral HPLC (EC 250/4.6 Nucleocel Alpha S column, *iso*-propyl alcohol/hexanes, 99.5:0.5; flow rate 0.4 ml/min; t_R = 38.2 min (R), 40.4 min (S), (maximum *ee* = 97% (*S*)).

Acknowledgements

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Supplementary Material

Supplementary data (including the IR, mass, ^1H, ^{13}C NMR data of all compounds and Table 6) associated with this article can be found in the online version.

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6. (a) X-ray data for **11d**: $C_{28}H_{40}N_2O_4$, M = 468.62, orthorhombic system, space group $P2_12_12_1$, a = 10.513(2), b = 11.084(2), c = 22.700(5) Å; V = 2645.1(9) Å^3, Z = 4, Dcalcd = 1.177 g cm^{-3}, μ (Mo-Kα) = 0.078 mm^{-1}, crystal dimension of 0.3×0.2×0.2 mm. The X-ray diffraction measurement was made on a STOE IPDS-II diffractometer with graphite monochromated Mo-Kα radiation. The structure was solved by using SHELXS. The data reduction and structure refinement were carried out with SHELXL using the X-STEP32 crystallographic software package.(b) The non-hydrogen atoms were refined anisotropically by full matrix least-squares on F^2 values to final R_1 = 0.0721, wR_2 = 0.1114 and S = 1.064 with 329 parameters using 6923 independent reflection (θ range = 2.57-29.15º). Hydrogen atoms attached to oxygen and nitrogen were found in a difference Fourier map and refined isotropically. All other hydrogen atoms were added in idealized positions. The crystallographic information file has been deposited with the Cambridge Data Centre, CCDC 910508. (c). *X-STEP32 Version 1.07b*, *Crystallographic Package*; Stoe & Cie GmbH: Darmstadt, Germany, 2000.
7. (a) X-ray data for **1b**: $C_{35}H_{33}Cl_5CuN_2O_2$, M = 468.62, monoclinic system, space group $P2_1$, a = 8.2046(16), b = 17.053(3), c = 13.365(3) Å; β = 102.38(3)º ; V = 1826.5(7) Å^3, Z = 2, Dcalcd = 1.372 g cm^{-3}, μ (Mo-Kα) = 0.996 mm^{-1}, crystal dimension of 0.25×0.25×0.11 mm. The X-ray diffraction measurement was made on a STOE IPDS-II diffractometer with graphite monochromated Mo-Kα radiation. The structure was solved by using SHELXS. The data reduction and structure refinement were carried out with SHELXL using the X-STEP32 crystallographic software package.(b) The non-hydrogen atoms were refined anisotropically by full matrix least-squares on F^2 values to final R_1 = 0.0639, wR_2 = 0.1189 and S = 0.930 with 408 parameters using 8414 independent reflections (θ range = 1.96-29.22º). All hydrogen atoms were added in idealized positions. The crystallographic information file has been deposited with the Cambridge Data Centre, CCDC 910507.
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A significant improvement in enantioselectivity, yield and reactivity for the copper-bi-*o*-tolyl bisoxazoline-catalyzed asymmetric allylic oxidation of cyclic olefins using recoverable SBA-15 mesoporous silica material

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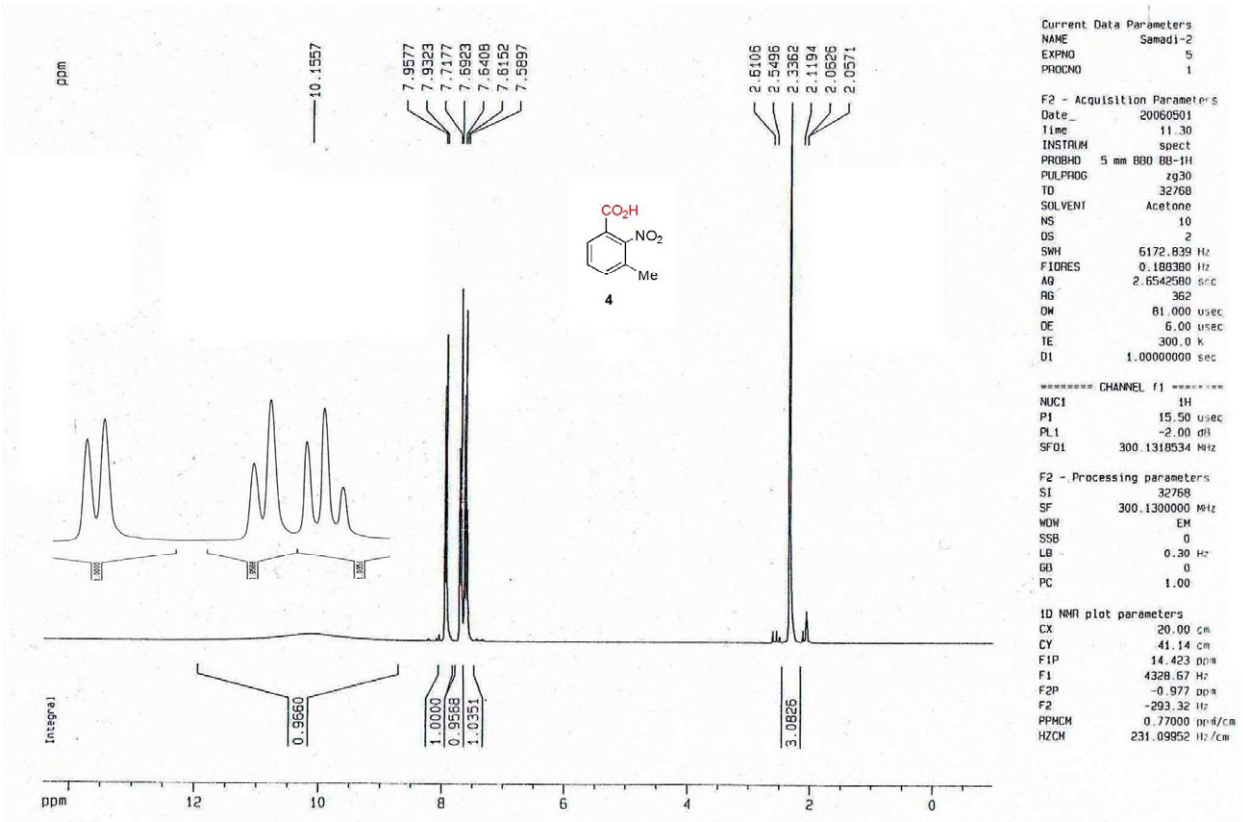
Supplementary Material

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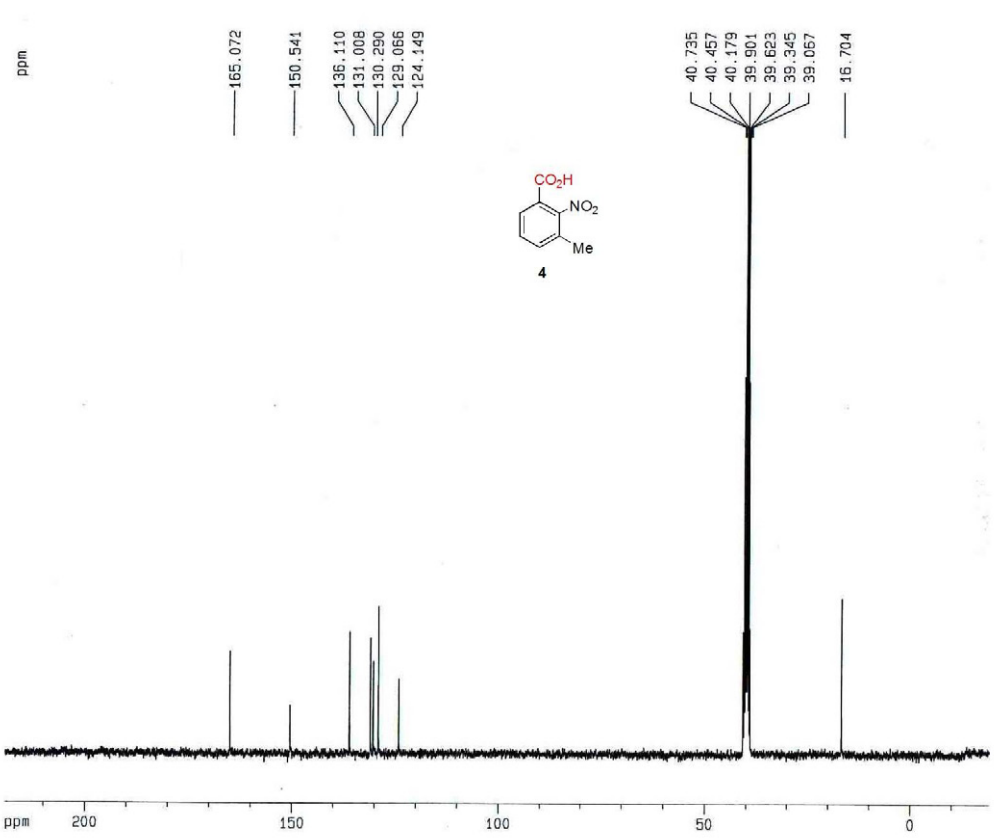


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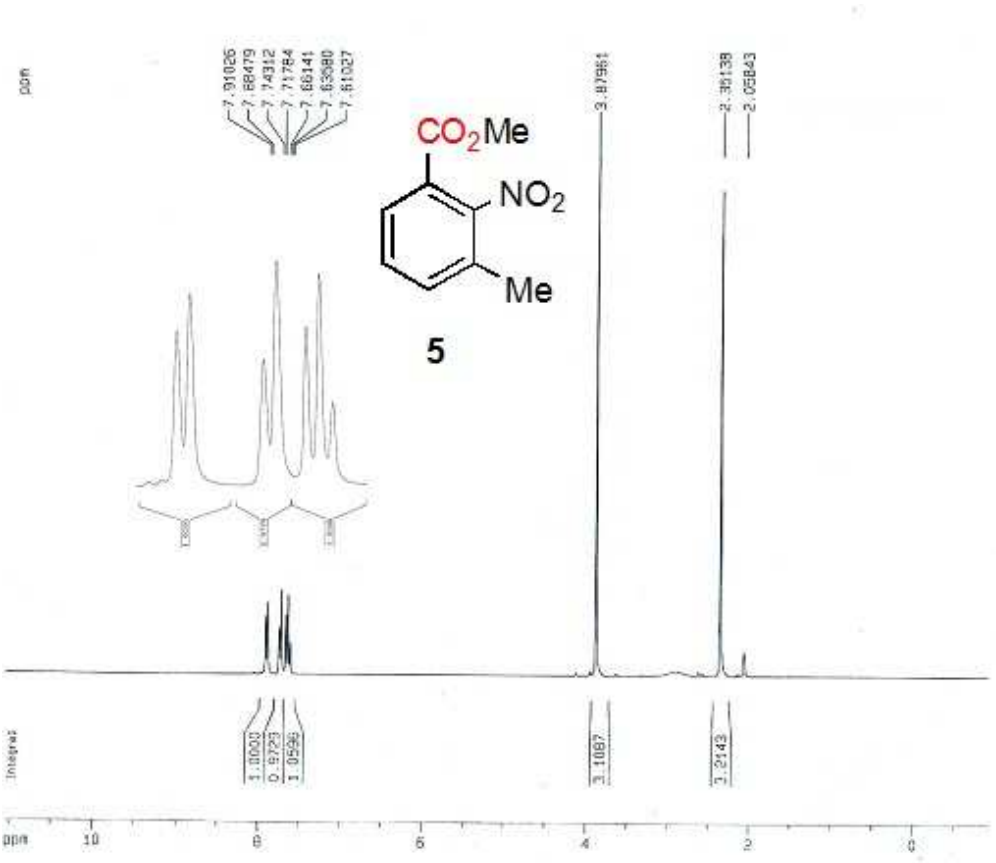


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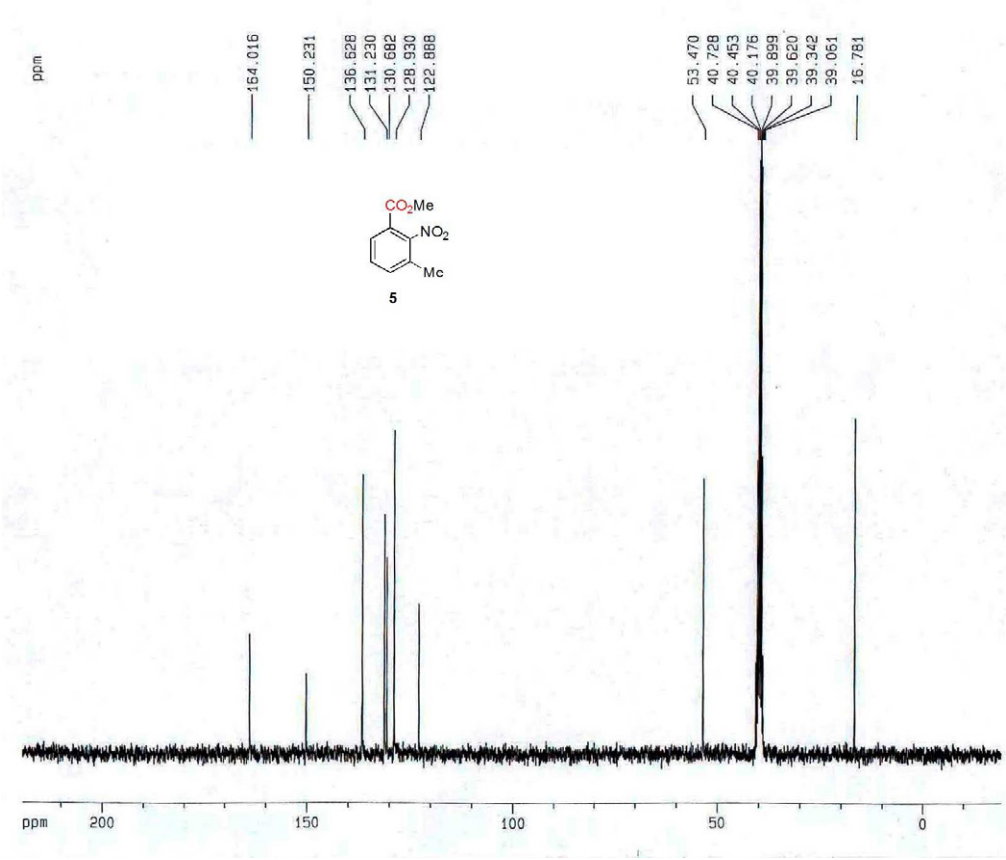


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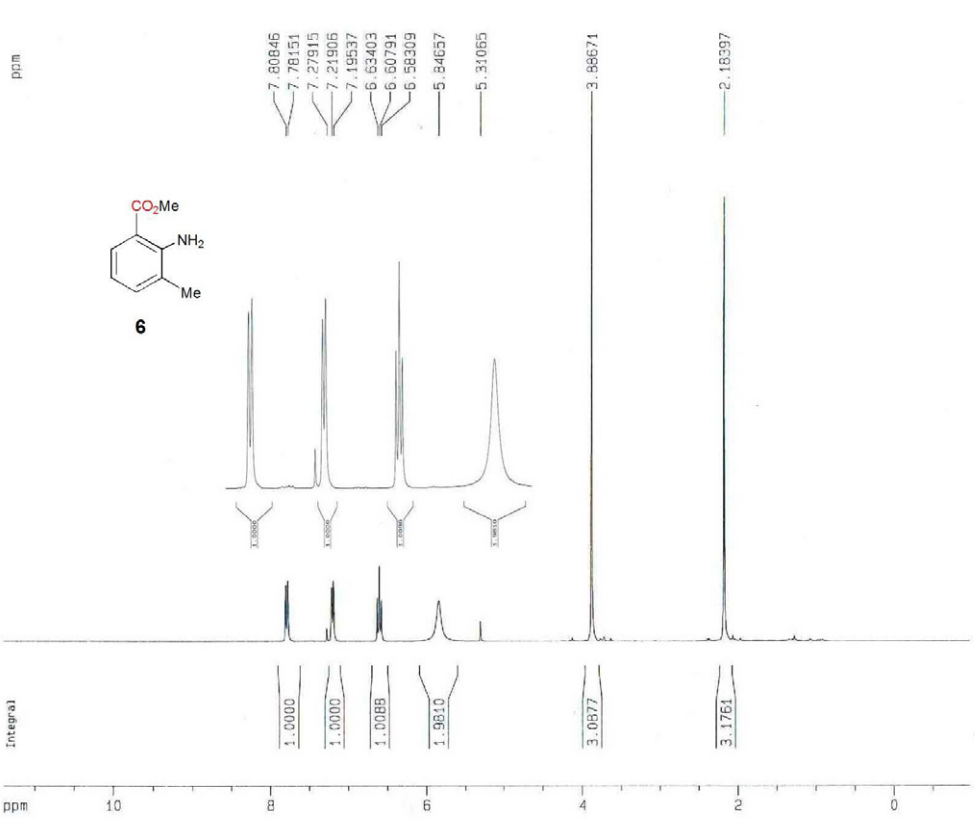


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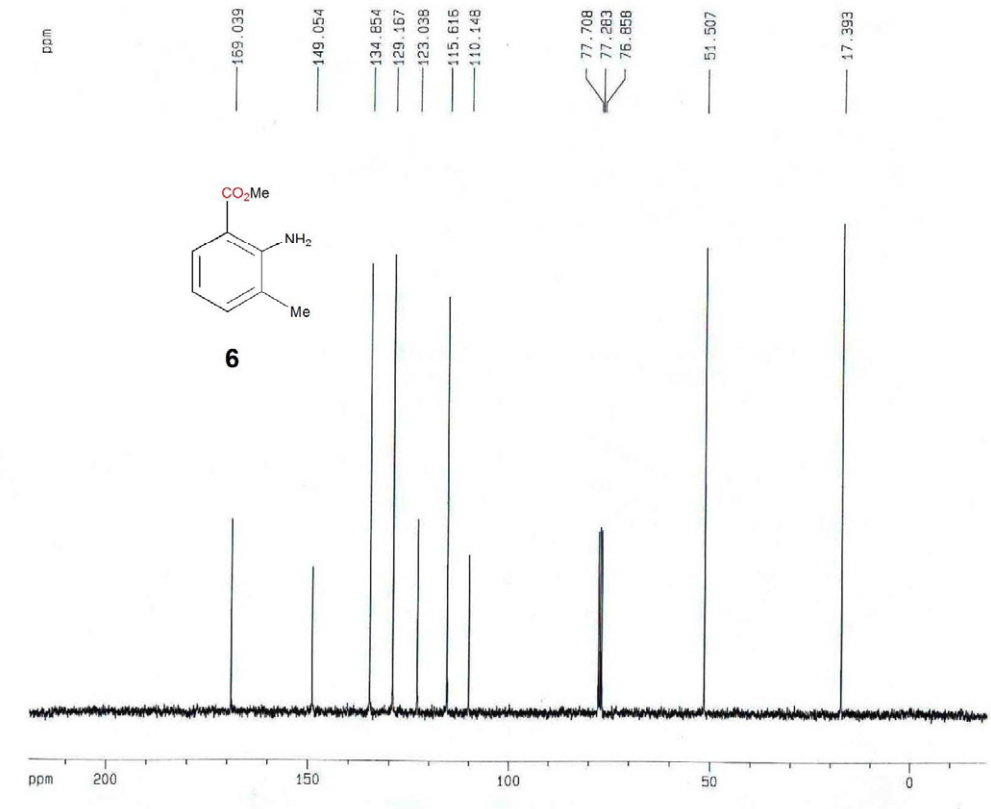
NUC1                      1H
P1                    15.50 usec
PL1                   -2.00 dB
SFO1             300.1327012 MHz

F2 - Processing parameters
SI                      32768
SF                300.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                      20.00 cm
CY                      10.93 cm
F1P                     11.408 ppm
F1                    3423.74 Hz
F2P                    -0.970 ppm
F2                   -290.99 Hz
PPMCM                 0.61885 ppm/cm
HZCM                185.73621 Hz/cm
```




```
Current Data Parameters
NAME                  Nazari
EXPNO                    156
PROCNO                     1

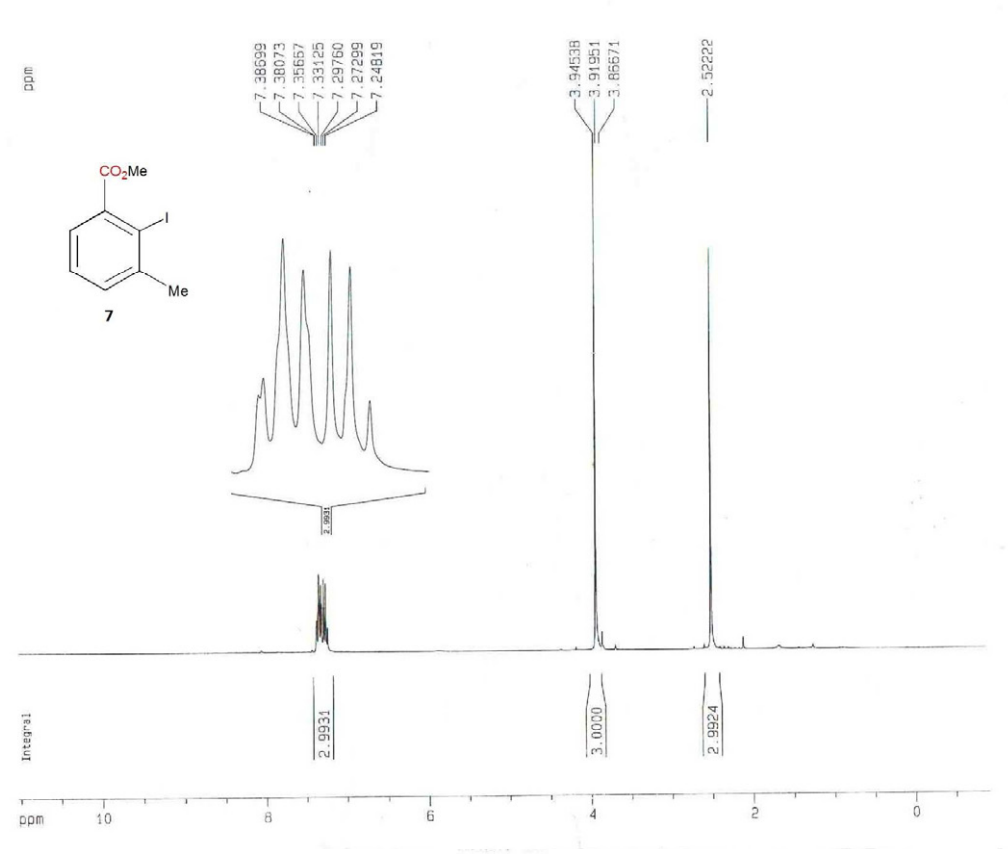
F2 - Acquisition Parameters
Date_               20100914
Time                    16.52
INSTRUM                 spect
PROBHD   5 mm BBO BB-1H
PULPROG                 zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         70
DS                          2
SWH               17985.611 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                       2048
DW                   27.800 usec
DE                    6.00 usec
TE                   300.0 K
D1                2.00000000 sec
d11               0.03000000 sec
d12               0.00002000 sec

-------- CHANNEL f1 --------
NUC1                      13C
P1                    8.75 usec
PL1                   -2.00 dB
SFO1             75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                 87.00 usec
PL2                   -2.00 dB
PL12                  12.00 dB
PL13                  18.00 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                      65536
SF                75.4677490 MHz
WDW                        EM
SSB                         0
LB                       2.00 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                      20.00 cm
CY                      10.24 cm
F1P                     219.155 ppm
F1                    16539.10 Hz
F2P                   -19.167 ppm
F2                   -1446.51 Hz
PPMCM                 11.91609 ppm/cm
HZCM                899.28058 Hz/cm
```



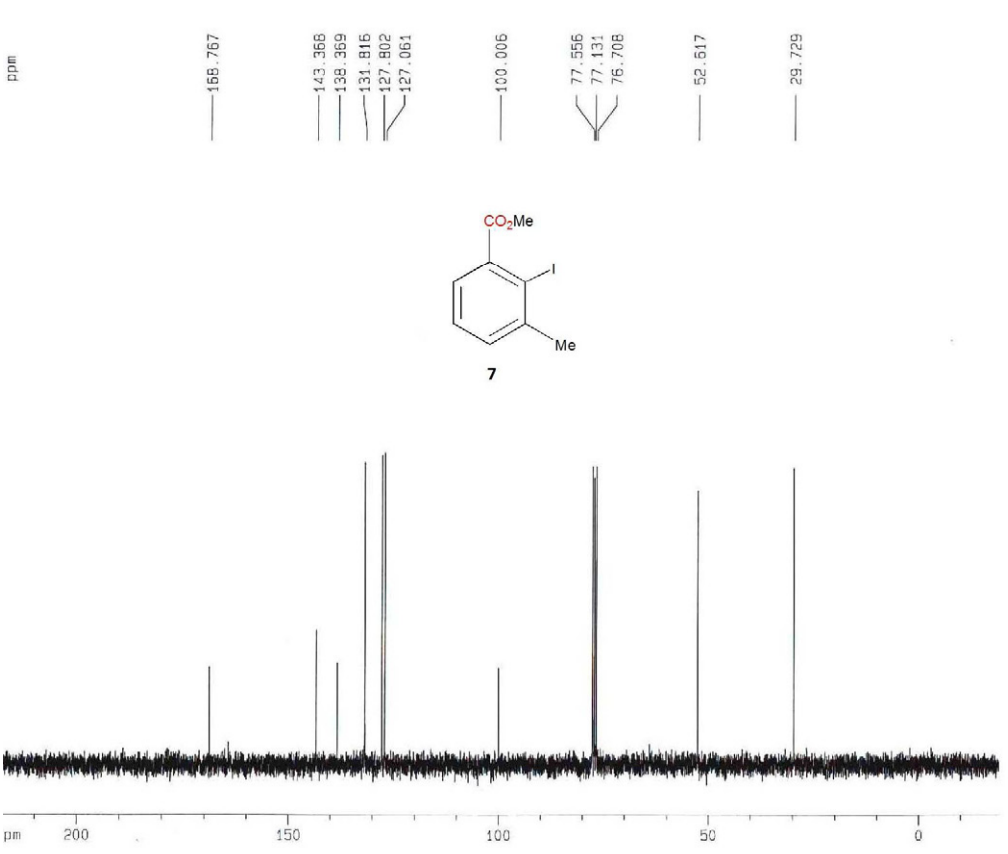

```
Current Data Parameters
NAME                  Samadi-2
EXPNO                       17
PROCNO                       1

F2 - Acquisition Parameters
Date_               20060809
Time                   11.00
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        10
DS                         2
SWH                7485.030 Hz
FIDRES             0.228425 Hz
AQ                 2.1889524 sec
RG                       362
DW                  66.800 usec
DE                   6.00 usec
TE                   300.0 K
D1                 2.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     15.50 usec
PL1                    -2.00 dB
SFO1             300.1327012 MHz

F2 - Processing parameters
SI                     32768
SF               300.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     20.00 cm
CY                     10.95 cm
F1P                   11.037 ppm
F1                  3312.57 Hz
F2P                  -0.908 ppm
F2                  -272.46 Hz
PPMCM                0.59725 ppm/cm
HZCM               179.25163 Hz/cm
```




```
Current Data Parameters
NAME                    Nazari
EXPNO                       74
PROCNO                       1

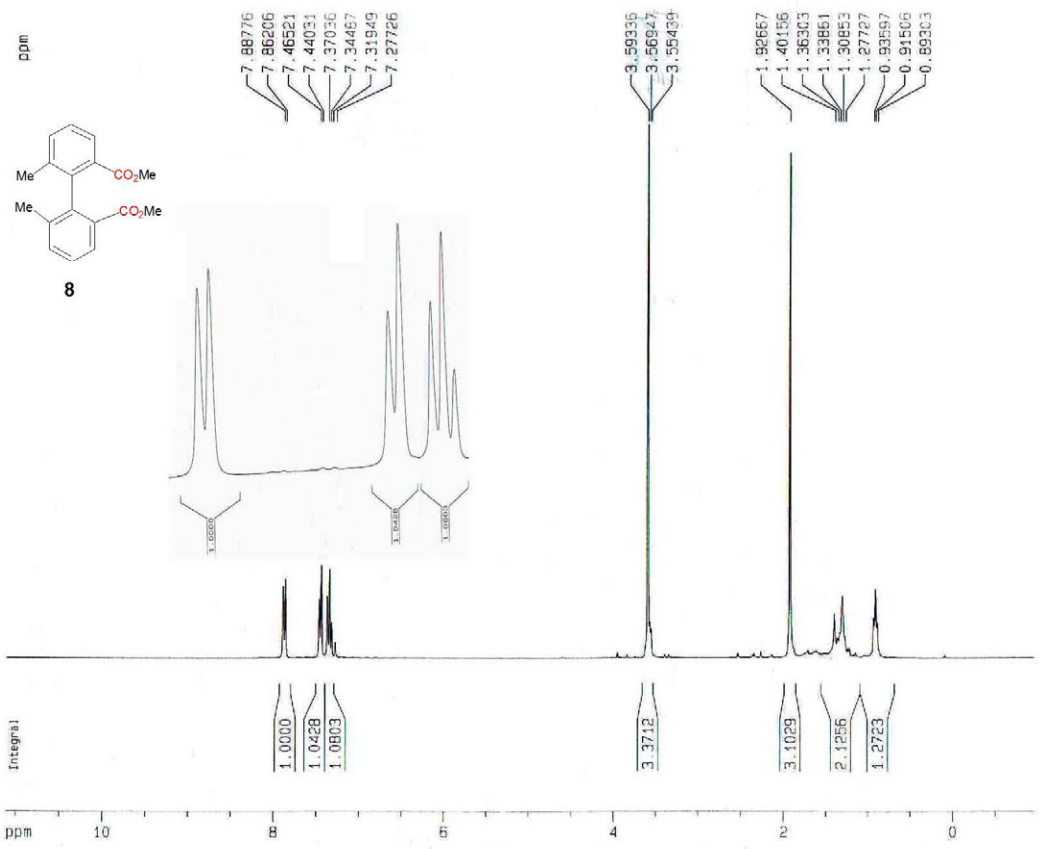
F2 - Acquisition Parameters
Date_               20100511
Time                    4.55
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        33
DS                         2
SWH               17985.611 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                      2048
DW                  27.800 usec
DE                   6.00 usec
TE                   300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
D12                0.00002000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                      8.75 usec
PL1                    -2.00 dB
SFO1             75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                  87.00 usec
PL2                    -2.00 dB
PL12                   12.00 dB
PL13                   18.00 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                     65536
SF               75.4677490 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                     20.00 cm
CY                      6.25 cm
F1P                  219.155 ppm
F1                  16539.11 Hz
F2P                  -19.167 ppm
F2                  -1446.51 Hz
PPMCM               11.91609 ppm/cm
HZCM               899.28058 Hz/cm
```



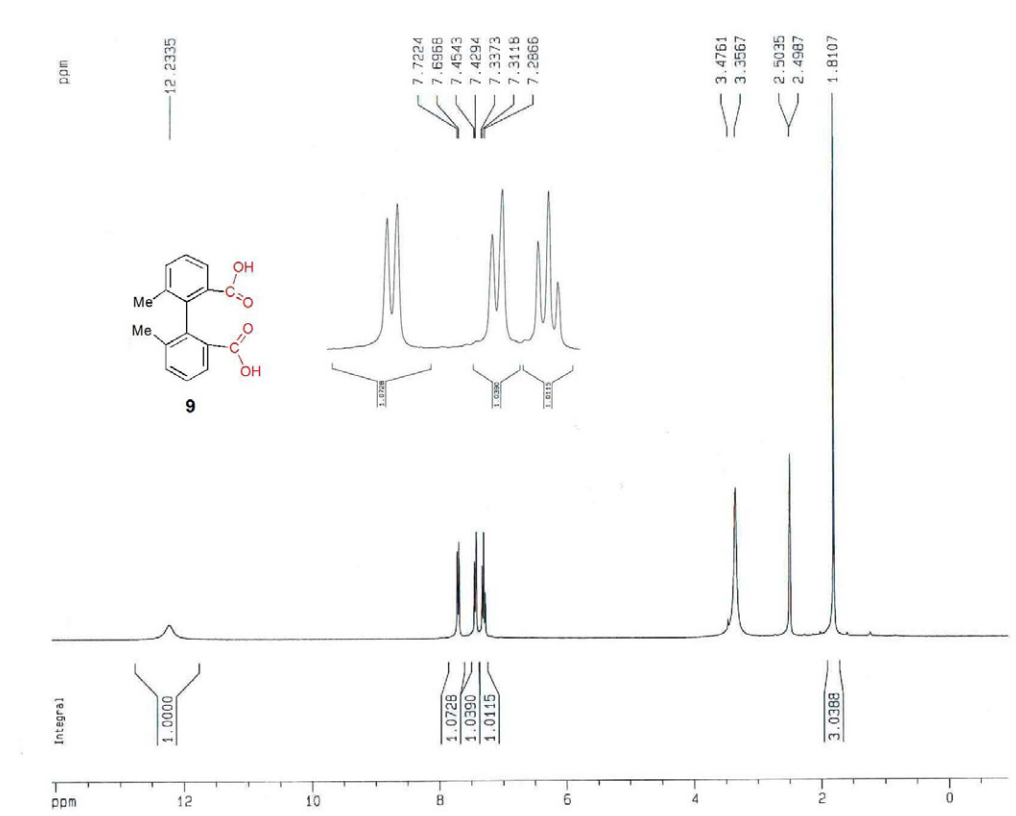

```
Current Data Parameters
NAME                  Samadi-2
EXPNO                       26
PROCNO                       1

F2 - Acquisition Parameters
Date_               20061119
Time                   14.18
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        10
DS                         2
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                 2.6542580 sec
RG                       362
DW                  81.000 usec
DE                   6.00 usec
TE                   300.0 K
D1                1.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      15.50 usec
PL1                     -2.00 dB
SFO1               300.1318534 MHz

F2 - Processing parameters
SI                     32768
SF                 300.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     20.00 cm
CY                     10.45 cm
F1P                   11.114 ppm
F1                  3335.52 Hz
F2P                   -0.952 ppm
F2                  -285.68 Hz
PPMCM                0.60327 ppm/cm
HZCM               181.05978 Hz/cm
```



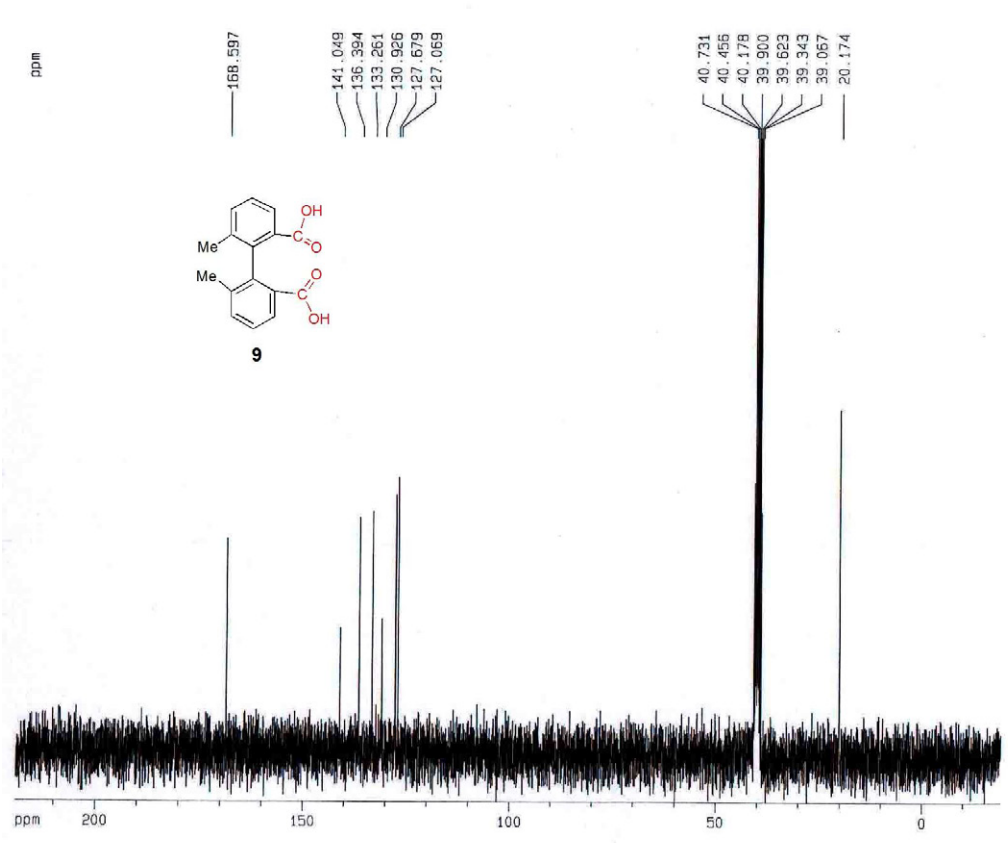

```
Current Data Parameters
NAME                  Samadi-2
EXPNO                       28
PROCNO                       1

F2 - Acquisition Parameters
Date_               20061220
Time                   13.02
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG                 zg30
TD                     32768
SOLVENT                DMSO
NS                        10
DS                         2
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                 2.6542580 sec
RG                       362
DW                  81.000 usec
DE                   6.00 usec
TE                   300.0 K
D1                1.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      15.50 usec
PL1                     -2.00 dB
SFO1               300.1318534 MHz

F2 - Processing parameters
SI                     32768
SF                 300.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     20.00 cm
CY                     11.35 cm
F1P                   14.066 ppm
F1                  4221.72 Hz
F2P                   -0.926 ppm
F2                  -278.04 Hz
PPMCM                0.74963 ppm/cm
HZCM               224.98776 Hz/cm
```




```
Current Data Parameters
NAME                  Nazari
EXPNO                     87
PROCNO                     1

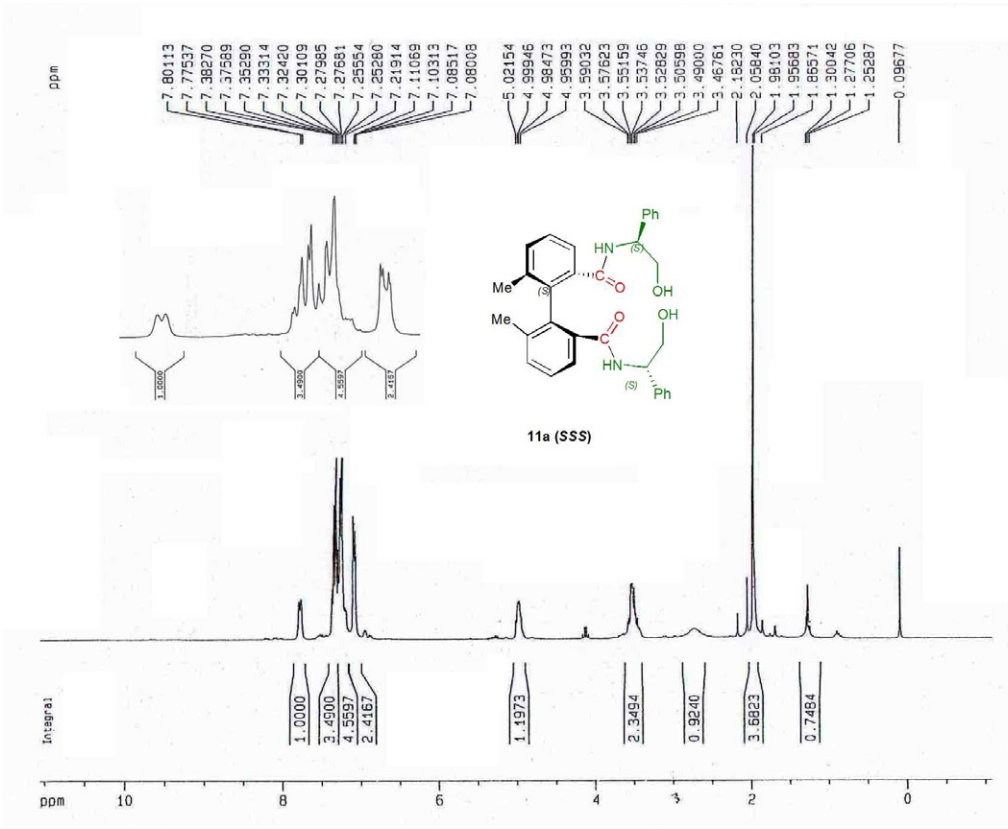
F2 - Acquisition Parameters
Date_              20100611
Time                   3.22
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        79
DS                         2
SWH               17985.611 Hz
FIDRES            0.274439 Hz
AQ                1.8219508 sec
RG                      2048
DW                 27.800 usec
DE                  6.00 usec
TE                  300.0 K
D1                2.00000000 sec
d11               0.03000000 sec
d12               0.00002000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                     8.75 usec
PL1                   -2.00 dB
SFO1              75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                 87.00 usec
PL2                   -2.00 dB
PL12                  12.00 dB
PL13                  18.00 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                        65536
SF                75.4677490 MHz
WDW                       EM
SSB                        0
LB                     1.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                    20.00 cm
CY                    35.98 cm
F1P                 219.155 ppm
F1                16539.10 Hz
F2P                 -19.167 ppm
F2                -1446.51 Hz
PPMCM              11.91609 ppm/cm
HZCM              899.28058 Hz/cm
```



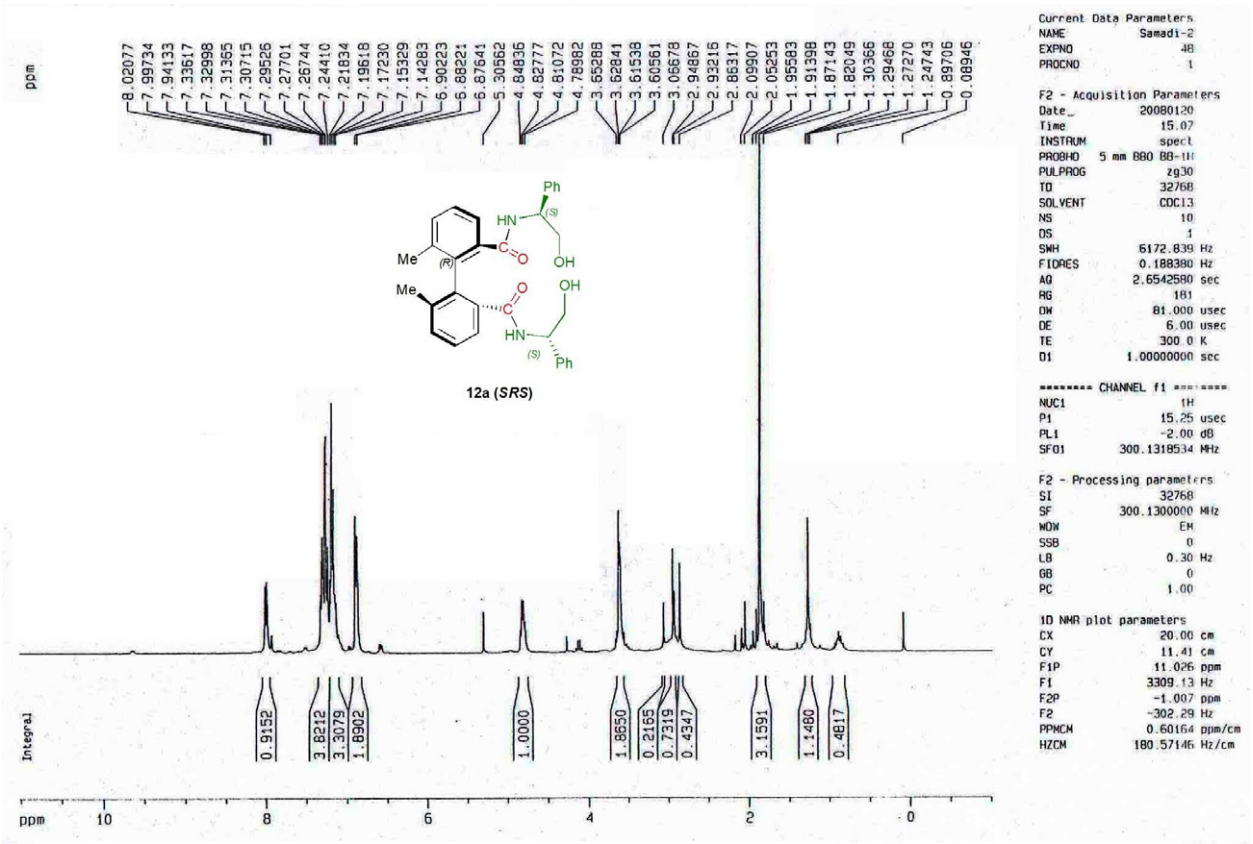

```
Current Data Parameters
NAME                 Samadi-2
EXPNO                      29
PROCNO                      1

F2 - Acquisition Parameters
Date_              20061227
Time                  14.47
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                    32768
SOLVENT               CDCl3
NS                       10
DS                        2
SWH               6172.839 Hz
FIDRES            0.188380 Hz
AQ                2.6542580 sec
RG                      362
DW                 81.000 usec
DE                  6.00 usec
TE                  300.0 K
D1                1.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                    15.50 usec
PL1                   -2.00 dB
SFO1             300.1318534 MHz

F2 - Processing parameters
SI                        32768
SF                300.1300000 MHz
WDW                       EM
SSB                        0
LB                     0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                    20.00 cm
CY                    10.51 cm
F1P                 11.060 ppm
F1                3319.48 Hz
F2P                 -1.075 ppm
F2                -322.50 Hz
PPMCM              0.60673 ppm/cm
HZCM              182.09877 Hz/cm
```



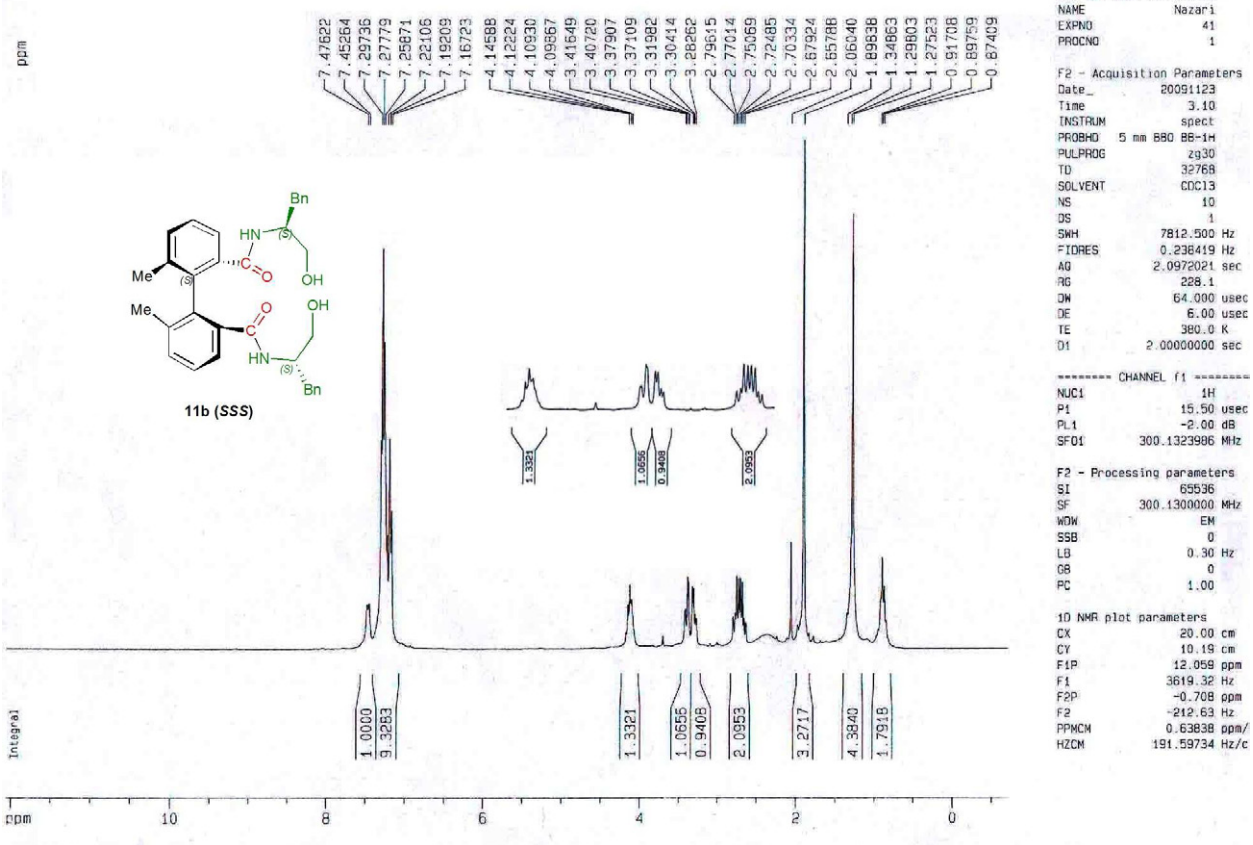

```
Current Data Parameters
NAME                  Samadi-2
EXPNO                       48
PROCNO                       1

F2 - Acquisition Parameters
Date_               20080120
Time                    15.07
INSTRUM                 spect
PROBHD   5 mm BBO BB-1H
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                         10
DS                          1
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                 2.6542580 sec
RG                        181
DW                   81.000 usec
DE                    6.00 usec
TE                   300.0 K
D1                 1.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      15.25 usec
PL1                     -2.00 dB
SFO1               300.1318534 MHz

F2 - Processing parameters
SI                         32768
SF                 300.1300000 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00

1D NMR plot parameters
CX                         20.00 cm
CY                         11.41 cm
F1P                     11.026 ppm
F1                      3309.13 Hz
F2P                     -1.007 ppm
F2                      -302.29 Hz
PPMCM                  0.60164 ppm/cm
HZCM                 180.57146 Hz/cm
```



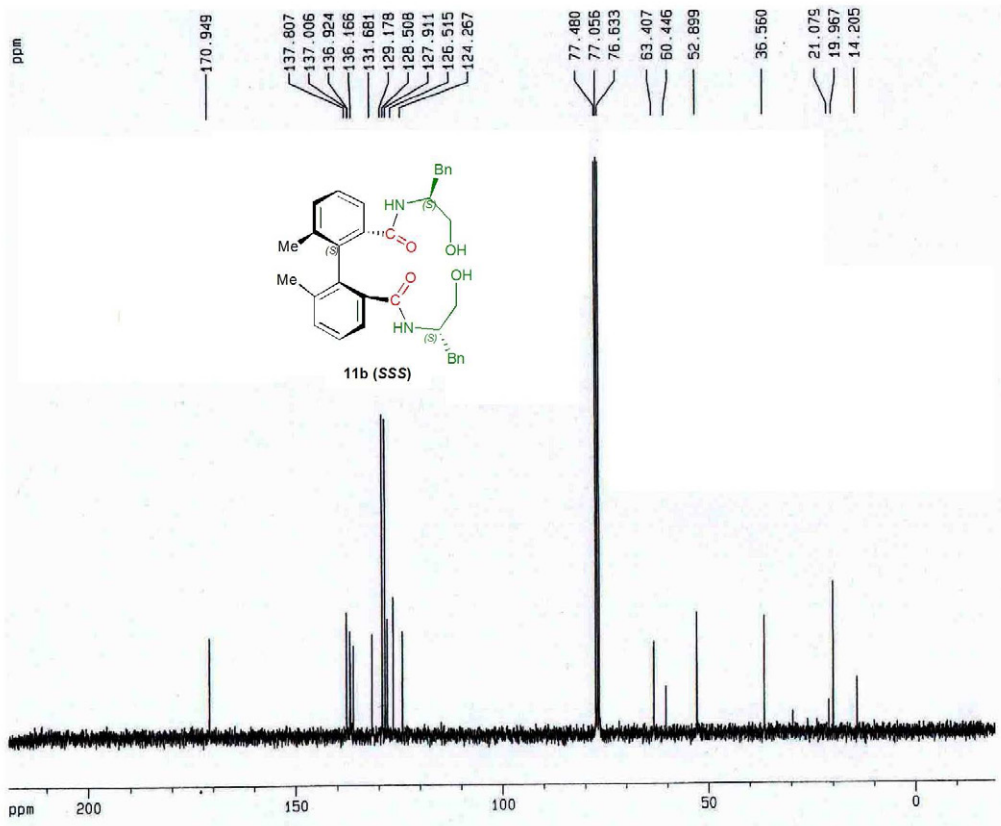

```
Current Data Parameters
NAME                  Nazari
EXPNO                      41
PROCNO                      1

F2 - Acquisition Parameters
Date_               20091123
Time                    3.10
INSTRUM                 spect
PROBHD   5 mm BBO BB-1H
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                         10
DS                          1
SWH                7812.500 Hz
FIDRES             0.238419 Hz
AQ                 2.0972021 sec
RG                      228.1
DW                   64.000 usec
DE                    6.00 usec
TE                   300.0 K
D1                 2.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      15.50 usec
PL1                     -2.00 dB
SFO1               300.1323986 MHz

F2 - Processing parameters
SI                         65536
SF                 300.1300000 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00

1D NMR plot parameters
CX                         20.00 cm
CY                         10.19 cm
F1P                     12.059 ppm
F1                      3619.32 Hz
F2P                     -0.708 ppm
F2                      -212.63 Hz
PPMCM                  0.63838 ppm/
HZCM                 191.59734 Hz/c
```




```
Current Data Parameters
NAME                  Nazari
EXPNO                     81
PROCNO                     1

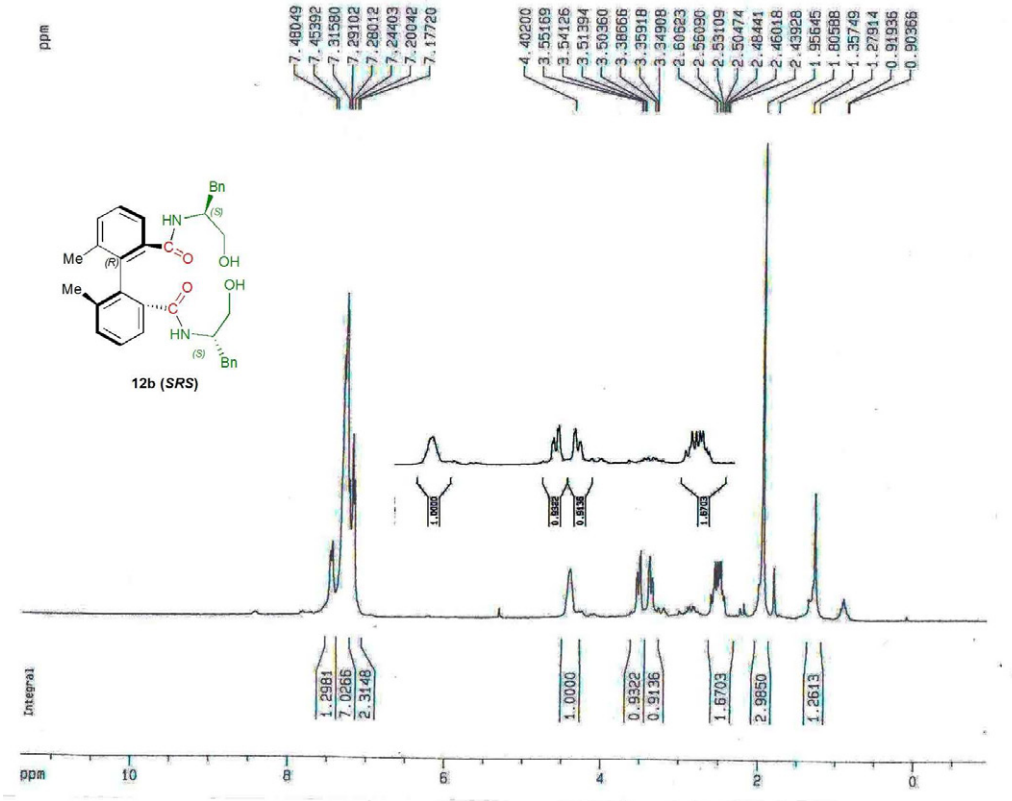
F2 - Acquisition Parameters
Date_              20100608
Time                  23.14
INSTRUN               spect
PROBHD  5 mm BBO BB-1H
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      303
DS                        2
SWH               17985.611 Hz
FIDRES            0.274439 Hz
AQ                1.8219508 sec
RG                     2048
DW                  27.800 usec
DE                   6.00 usec
TE                  300.0 K
D1                2.00000000 sec
d11               0.03000000 sec
d12               0.00002000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                   8.75 usec
PL1                  -2.00 dB
SFO1             75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2               87.00 usec
PL2                  -2.00 dB
PL12                 12.00 dB
PL13                 18.00 dB
SFO2            300.1312005 MHz

F2 - Processing parameters
SI                    65536
SF               75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
CY                   11.80 cm
F1P                219.155 ppm
F1                16539.10 Hz
F2P                -19.167 ppm
F2                -1446.51 Hz
PPMCM             11.91609 ppm/cm
HZCM              899.28058 Hz/cm
```



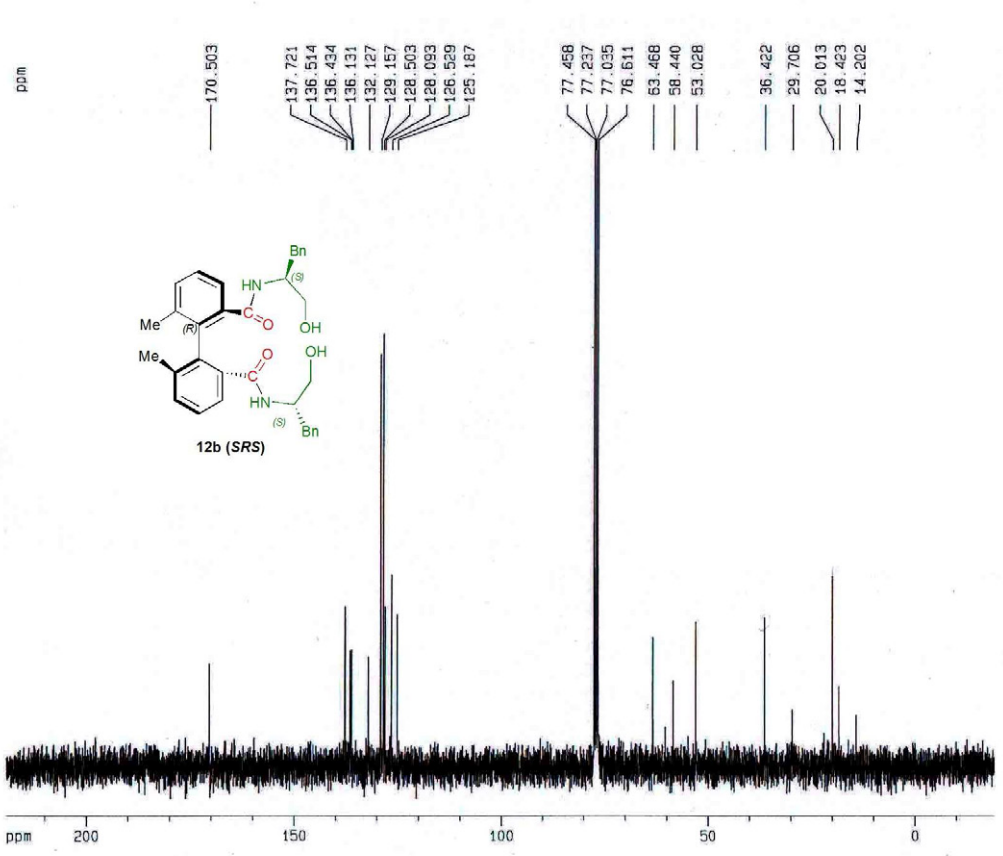

```
Current Data Parameters
NAME                  Nazari
EXPNO                    179
PROCNO                     1

F2 - Acquisition Parameters
Date_              20101019
Time                  14.25
INSTRUN               spect
PROBHD  5 mm BBO BB-1H
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       10
DS                        1
SWH                7812.500 Hz
FIDRES            0.238419 Hz
AQ                2.0972021 sec
RG                     228.1
DW                  64.000 usec
DE                   6.00 usec
TE                  300.0 K
D1                2.00000000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                   15.50 usec
PL1                  -2.00 dB
SFO1            300.1323986 MHz

F2 - Processing parameters
SI                    65536
SF              300.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
CY                    9.85 cm
F1P                11.386 ppm
F1                3417.18 Hz
F2P                -0.930 ppm
F2                -279.06 Hz
PPMCM             0.61577 ppm/cm
HZCM              184.81183 Hz/cm
```




```
Current Data Parameters
NAME                  Nazari
EXPNO                     79
PROCNO                     1

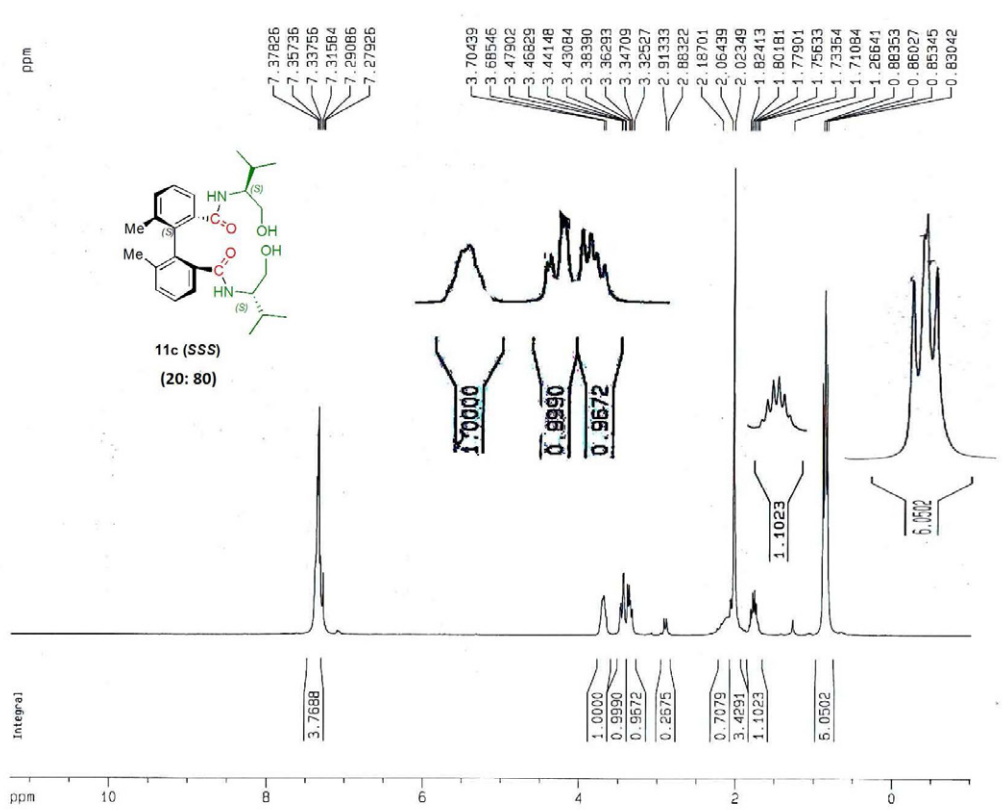
F2 - Acquisition Parameters
Date_               20100608
Time                   22.47
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG                zgpg30
TD                      65536
SOLVENT                CDCl3
NS                        437
DS                          2
SWH                 17985.611 Hz
FIDRES              0.274439 Hz
AQ                  1.8219508 sec
RG                       2048
DW                     27.800 usec
DE                      6.00 usec
TE                     300.0 K
D1                  2.00000000 sec
d11                 0.03000000 sec
d12                 0.00002000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                      8.75 usec
PL1                     -2.00 dB
SF01                75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  87.00 usec
PL2                     -2.00 dB
PL12                    12.00 dB
PL13                    18.00 dB
SF02               300.1312005 MHz

F2 - Processing parameters
SI                      65536
SF                  75.4677490 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                     20.00 cm
CY                     31.92 cm
F1P                  219.155 ppm
F1                  16539.10 Hz
F2P                  -19.167 ppm
F2                  -1446.51 Hz
PPMCM               11.91609 ppm/cm
HZCM                899.28058 Hz/cm
```



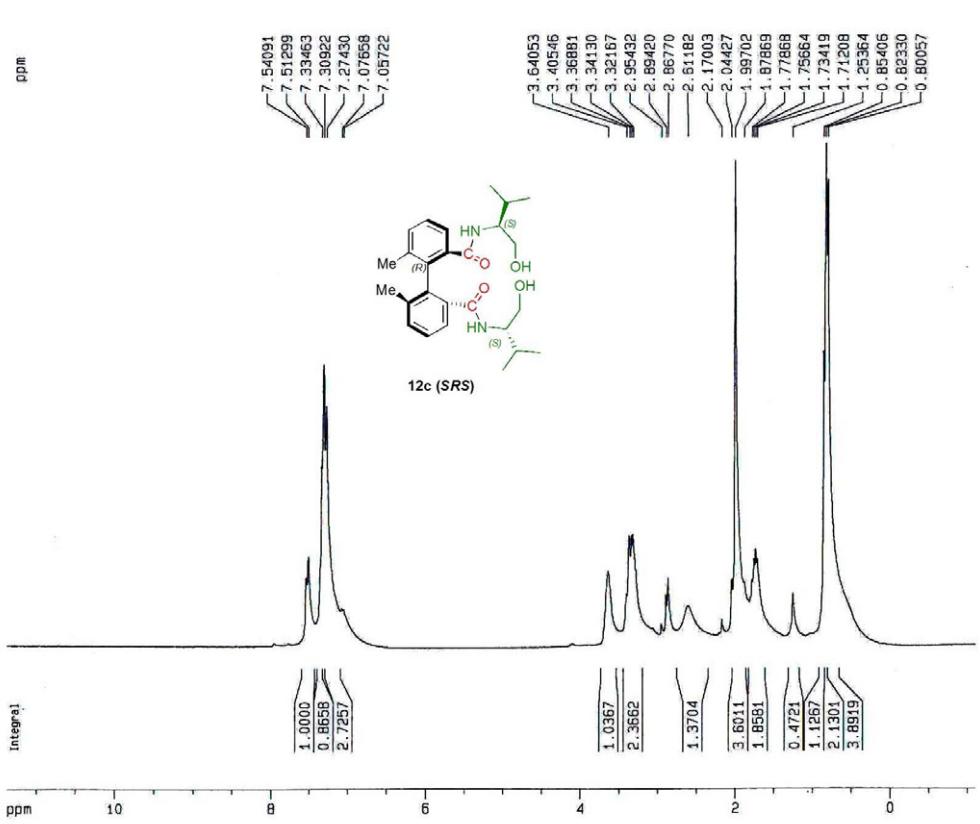

```
Current Data Parameters
NAME                  Samadi
EXPNO                    889
PROCNO                     1

F2 - Acquisition Parameters
Date_               20120311
Time                   13.33
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                      32768
SOLVENT                CDCl3
NS                         10
DS                          1
SWH                 7812.500 Hz
FIDRES              0.238419 Hz
AQ                  2.0972021 sec
RG                       45.3
DW                     64.000 usec
DE                      6.00 usec
TE                     380.0 K
D1                  2.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      15.50 usec
PL1                     -2.00 dB
SF01               300.1323986 MHz

F2 - Processing parameters
SI                      65536
SF                  300.1300000 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                     20.00 cm
CY                      9.73 cm
F1P                  11.246 ppm
F1                   3375.18 Hz
F2P                  -1.013 ppm
F2                   -303.97 Hz
PPMCM                0.81292 ppm/cm
HZCM                183.95712 Hz/cm
```



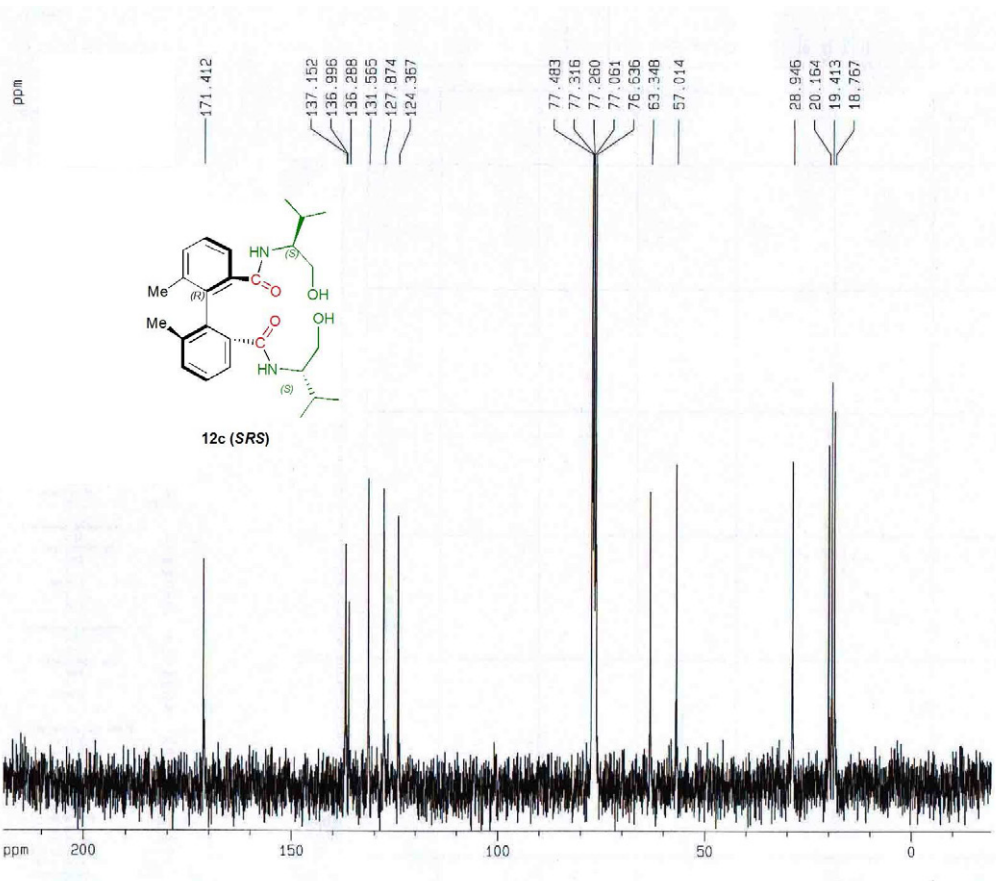
Current Data Parameters
NAME Arvinnejad
EXPNO 349
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110921
Time 7.44
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 10
DS 1
SWH 7812.500 Hz
FIDRES 0.238419 Hz
AQ 2.0972021 sec
RG 32
DW 64.000 usec
DE 6.00 usec
TE 380.0 K
D1 2.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 19.60 usec
PL1 -2.00 dB
SFO1 300.1323986 MHz

F2 - Processing parameters
SI 65536
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 10.37 cm
F1P 11.375 ppm
F1 3413.85 Hz
F2P -1.093 ppm
F2 -328.03 Hz
PPMCM 0.62338 ppm/cm
HZCM 187.09389 Hz/cm



Current Data Parameters
NAME Arvinnejad
EXPNO 350
PROCNO 1

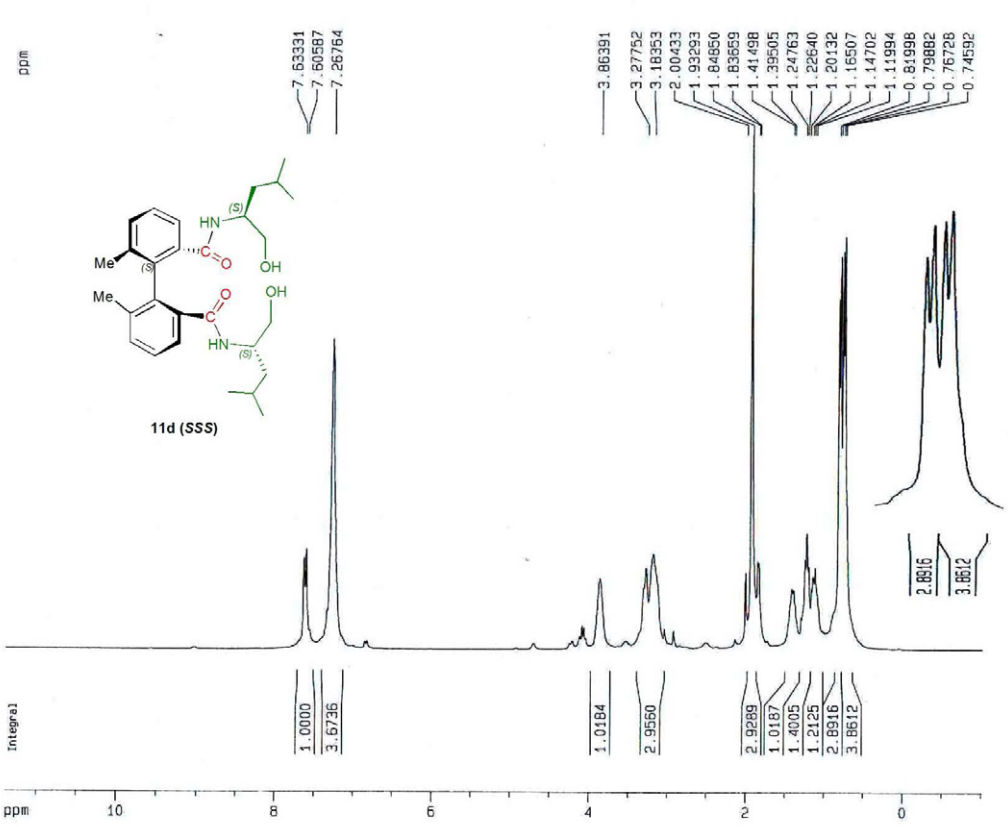
F2 - Acquisition Parameters
Date_ 20110921
Time 7.51
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 158
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 2048
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 12.60 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 87.00 usec
PL2 -2.00 dB
PL12 12.00 dB
PL13 18.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 65536
SF 75.4677490 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 0.20

1D NMR plot parameters
CX 20.00 cm
CY 20.73 cm
F1P 219.155 ppm
F1 16539.10 Hz
F2P -19.167 ppm
F2 -1446.51 Hz
PPMCM 11.91609 ppm/cm
HZCM 899.28058 Hz/cm



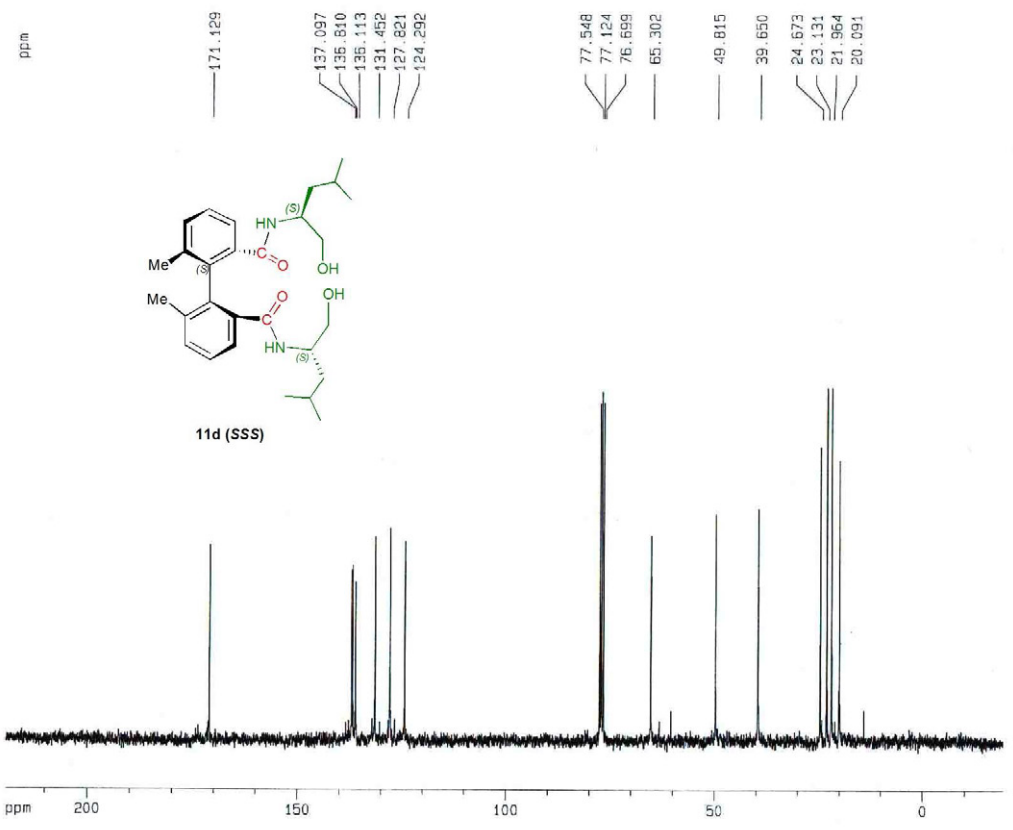

```
Current Data Parameters
NAME                  Samadi
EXPNO                    807
PROCNO                     1

F2 - Acquisition Parameters
Date_               20110916
Time                    9.44
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    32768
SOLVENT                DMSO
NS                       10
DS                        1
SWH                7812.500 Hz
FIDRES             0.238419 Hz
AQ                 2.0972021 sec
RG                      20.2
DW                   64.000 usec
DE                    6.00 usec
TE                   380.0 K
D1                2.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                   19.60 usec
PL1                   -2.00 dB
SFO1           300.1323986 MHz

F2 - Processing parameters
SI                        65536
SF                300.1300000 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                        20.00 cm
CY                        10.97 cm
F1P                       11.397 ppm
F1                      3420.60 Hz
F2P                      -1.013 ppm
F2                       -303.97 Hz
PPMCM                  0.62049 ppm/cm
HZCM                 186.22820 Hz/cm
```

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Current Data Parameters
NAME                  Samadi
EXPNO                    808
PROCNO                     1

F2 - Acquisition Parameters
Date_               20110916
Time                    9.45
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                    65536
SOLVENT             CDCl3
NS                      158
DS                        2
SWH               17985.611 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                     2048
DW                   27.800 usec
DE                    6.00 usec
TE                   300.0 K
D1                2.00000000 sec
d11               0.03000000 sec
d12               0.00002000 sec

======== CHANNEL f1 ========
NUC1                     13C
P1                   12.60 usec
PL1                   -2.00 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                87.00 usec
PL2                   -2.00 dB
PL12                  12.00 dB
PL13                  18.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                        65536
SF                75.4677490 MHz
WDW                          EM
SSB                           0
LB                         2.00 Hz
GB                            0
PC                         0.20

1D NMR plot parameters
CX                        20.00 cm
CY                         7.12 cm
F1P                     219.155 ppm
F1                    16539.11 Hz
F2P                     -19.167 ppm
F2                     -1446.51 Hz
PPMCM                 11.91609 ppm/cm
HZCM                899.28058 Hz/cm
```
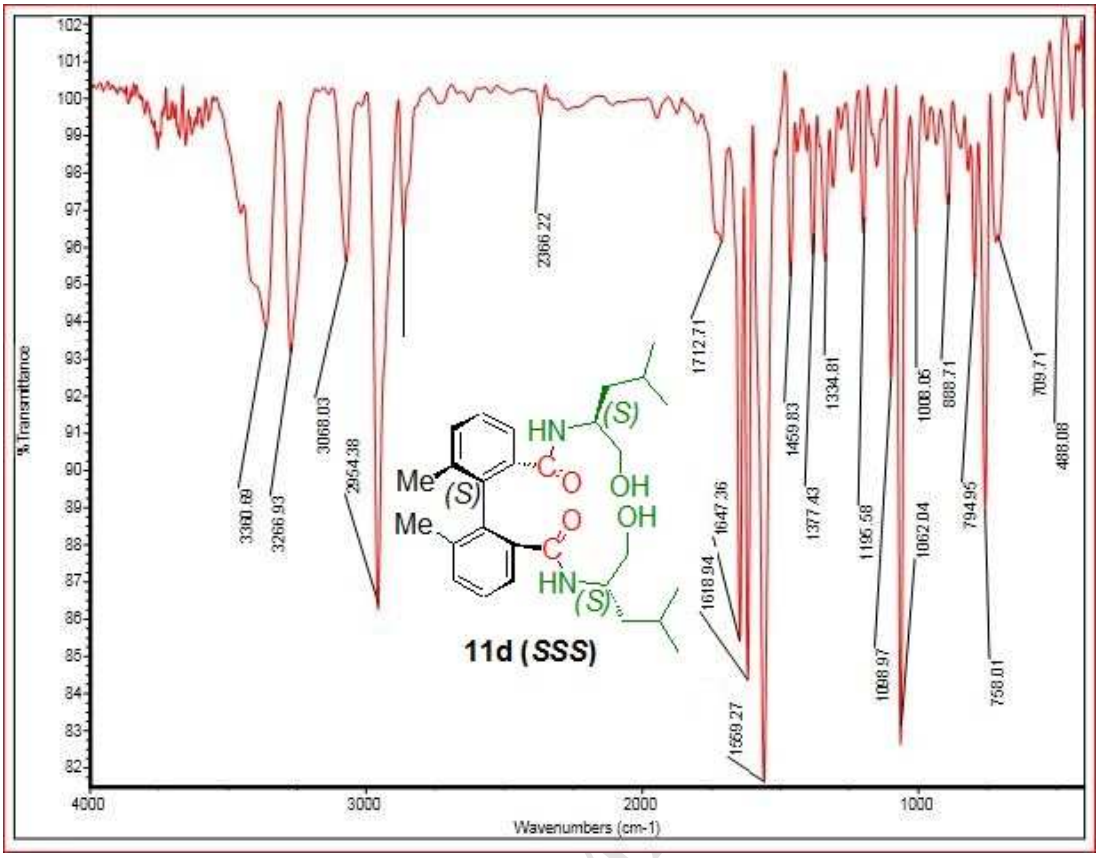
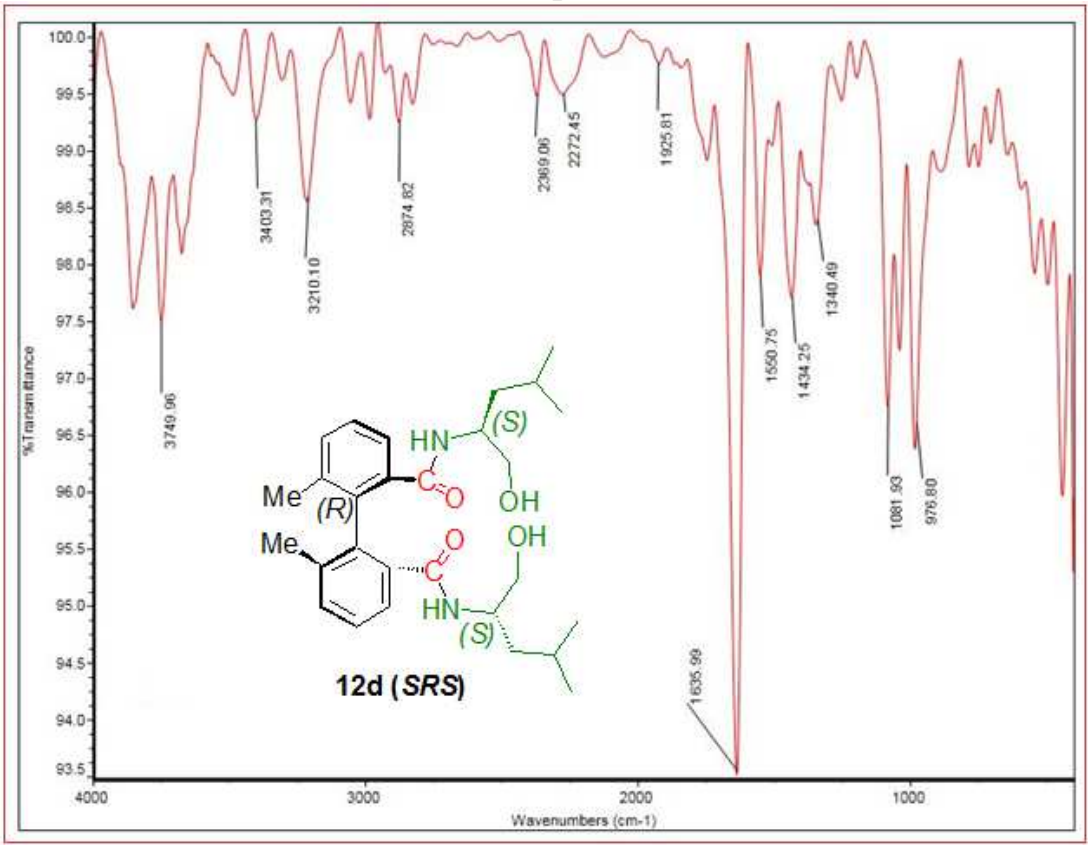
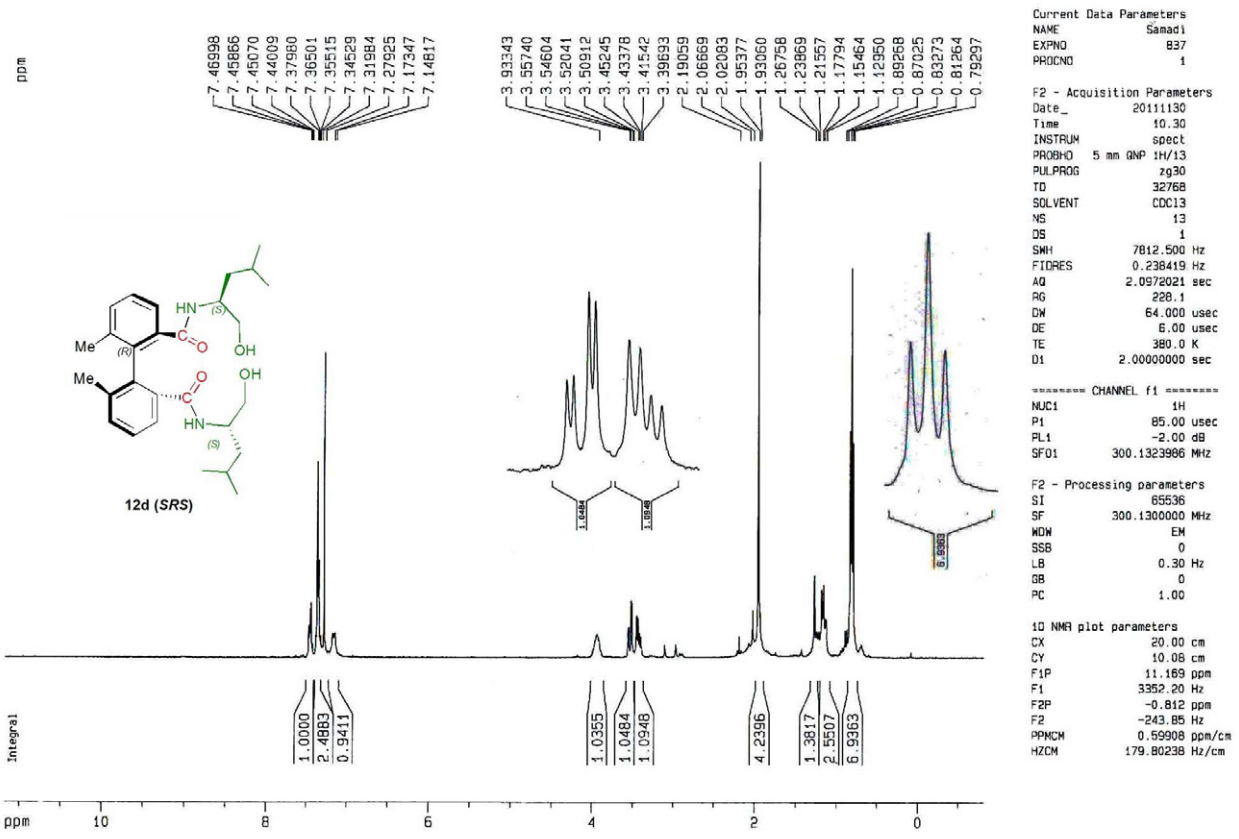
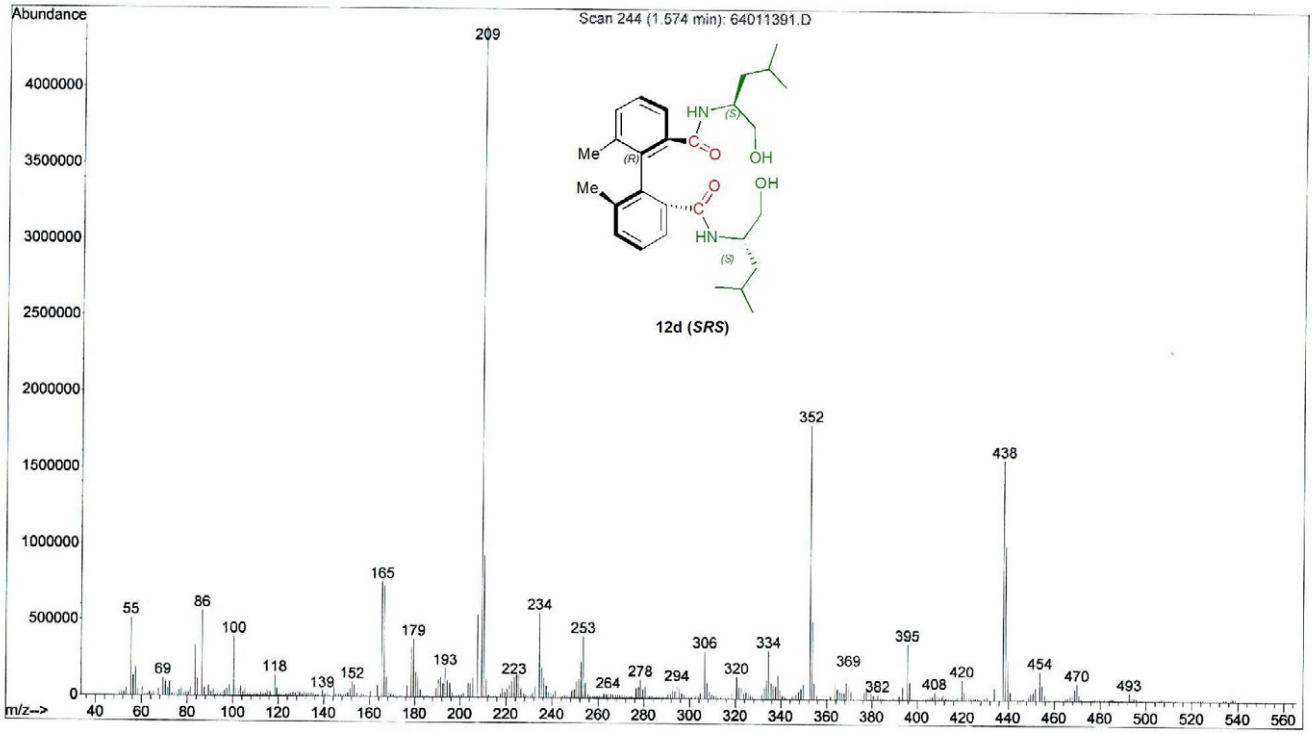
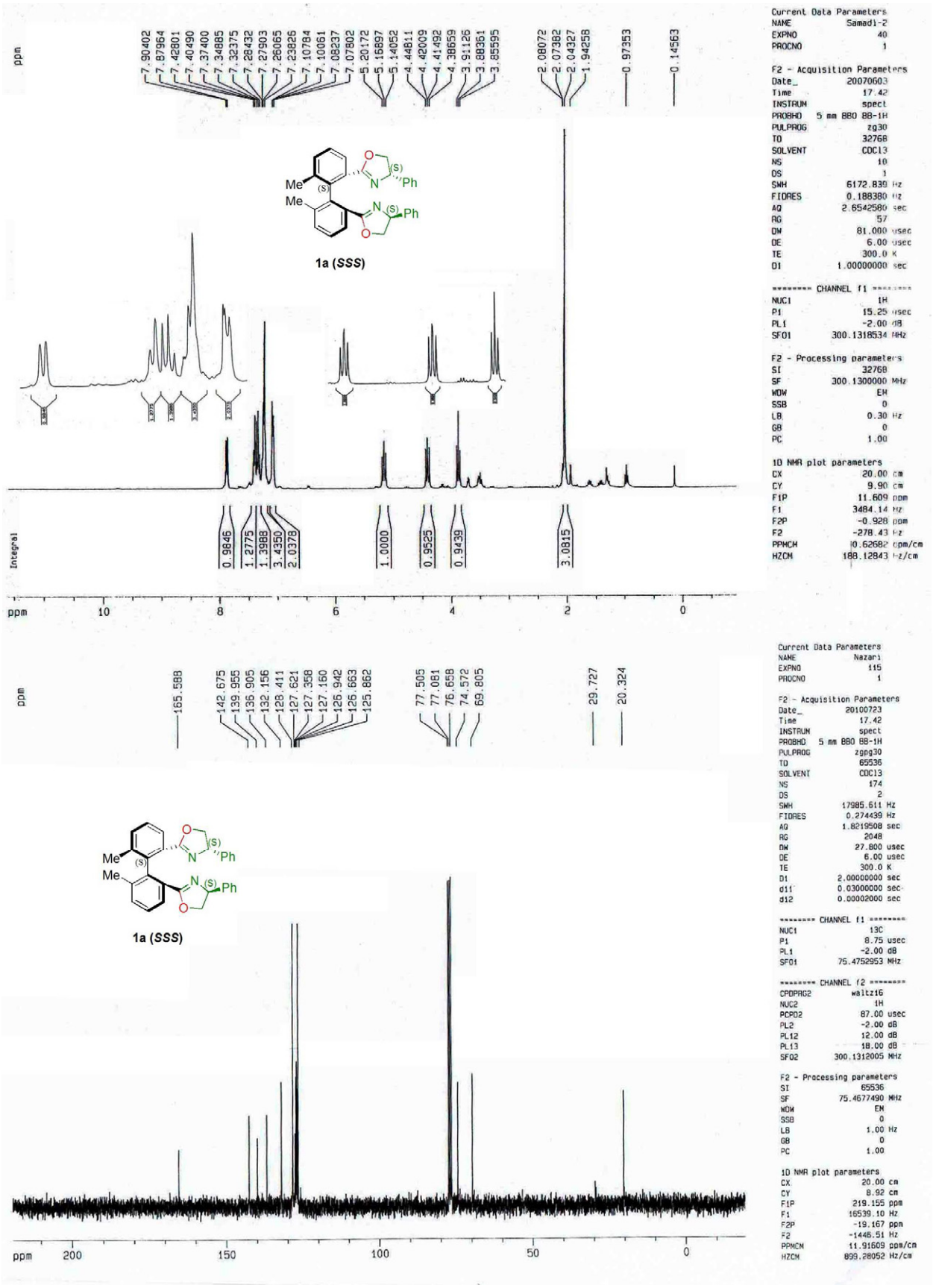
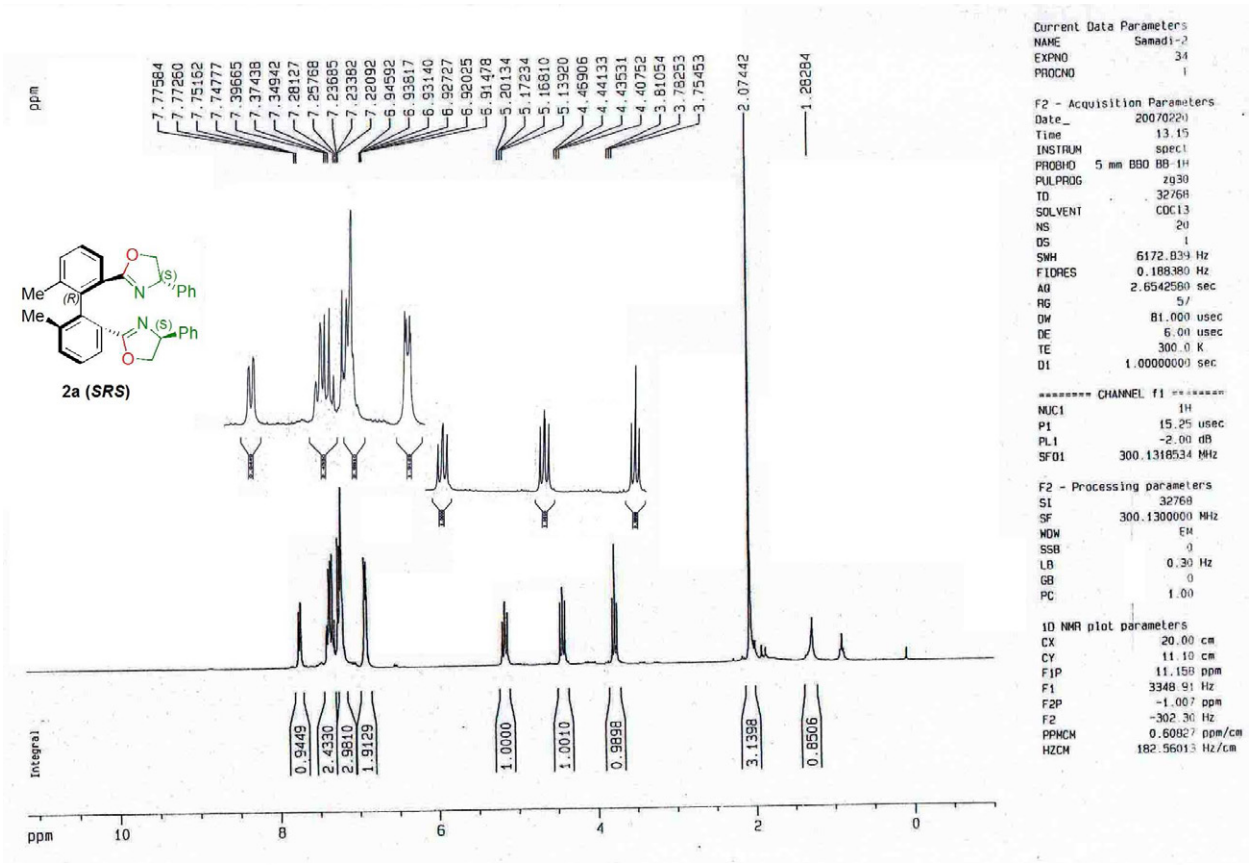


%Transmittance
Wavenumbers (cm-1)
3380.69
3266.93
3068.03
2954.38
2366.22
1712.71
1647.36
1618.94
1569.27
1459.83
1377.43
1334.81
1195.58
1088.97
1062.04
1008.05
888.71
794.95
758.01
709.71
488.08
HN
(S)
OH
Me
(S)
O
C
11d (SSS)

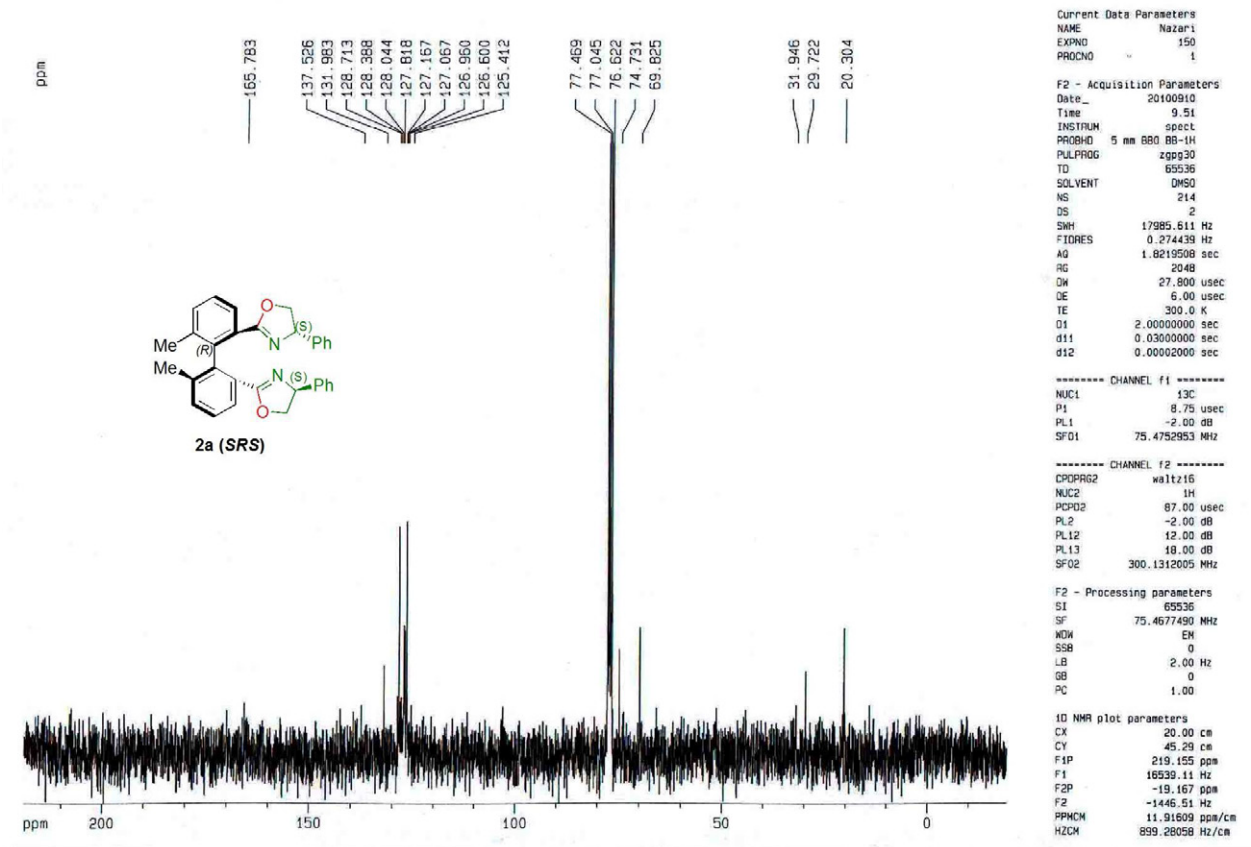

%Transmittance
Wavenumbers (cm-1)
3749.96
3403.31
3210.10
2874.82
2369.06
2272.45
1925.81
1635.99
1550.75
1434.25
1340.49
1081.93
976.80
HN
(S)
OH
Me
(R)
Me
O
C
12d (SRS)

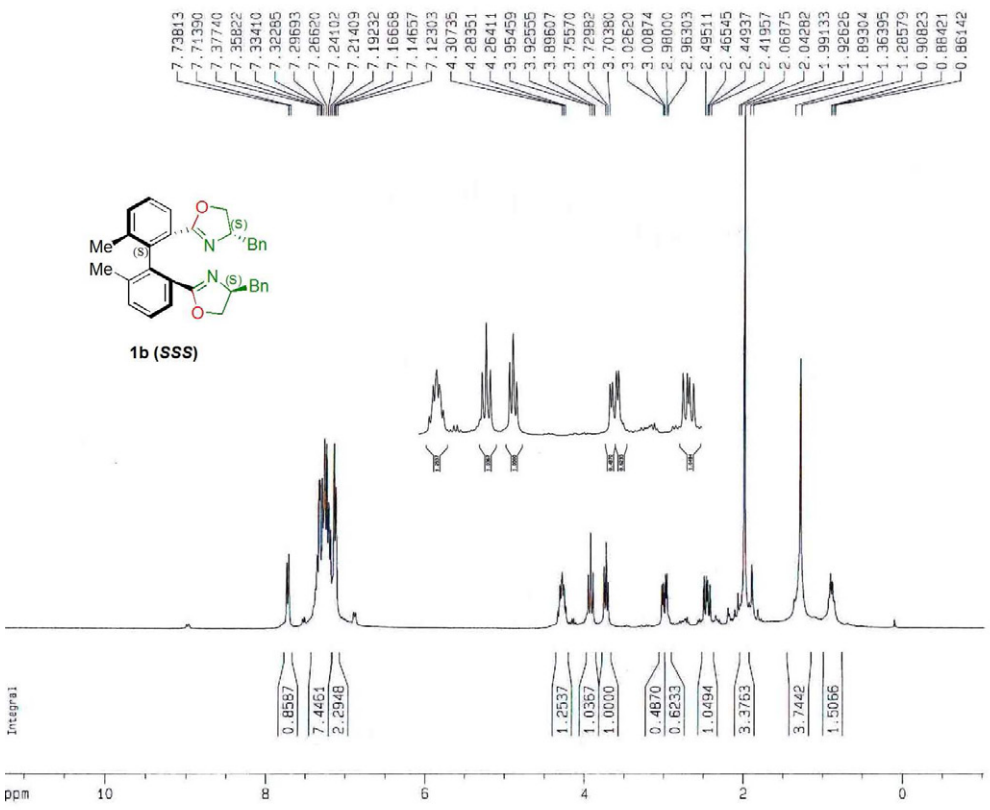

ppm
7.46998
7.45866
7.45070
7.44009
7.37980
7.36501
7.35515
7.34529
7.31984
7.27925
7.17347
7.14817
3.93343
3.55740
3.54604
3.52041
3.50912
3.45245
3.43378
3.41542
3.39693
2.19059
2.06669
2.02083
1.95377
1.93060
1.26758
1.23869
1.21557
1.17794
1.15464
1.12950
0.89268
0.87025
0.83273
0.81264
0.79297
12d (SRS)
Integral
1.0000
2.4883
0.9411
1.0355
1.0484
1.0948
4.2396
1.3817
2.5507
6.9363
ppm
Current Data Parameters
NAME Samadi
EXPNO 837
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111130
Time 10.30
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 13
DS 1
SWH 7812.500 Hz
FIDRES 0.238419 Hz
AQ 2.0972021 sec
RG 228.1
DW 64.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 85.00 usec
PL1 -2.00 dB
SF01 300.1323986 MHz
F2 - Processing parameters
SI 65536
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 10.08 cm
F1P 11.169 ppm
F1 3352.20 Hz
F2P -0.812 ppm
F2 -243.85 Hz
PPMCM 0.59908 ppm/cm
HZCM 179.80238 Hz/cm


Abundance
Scan 244 (1.574 min): 64011391.D
12d (SRS)
m/z-->
209
352
438
165
55
86
100
179
234
253
306
334
395
69
118
139
152
193
223
264
278
294
320
369
382
408
420
454
470
493

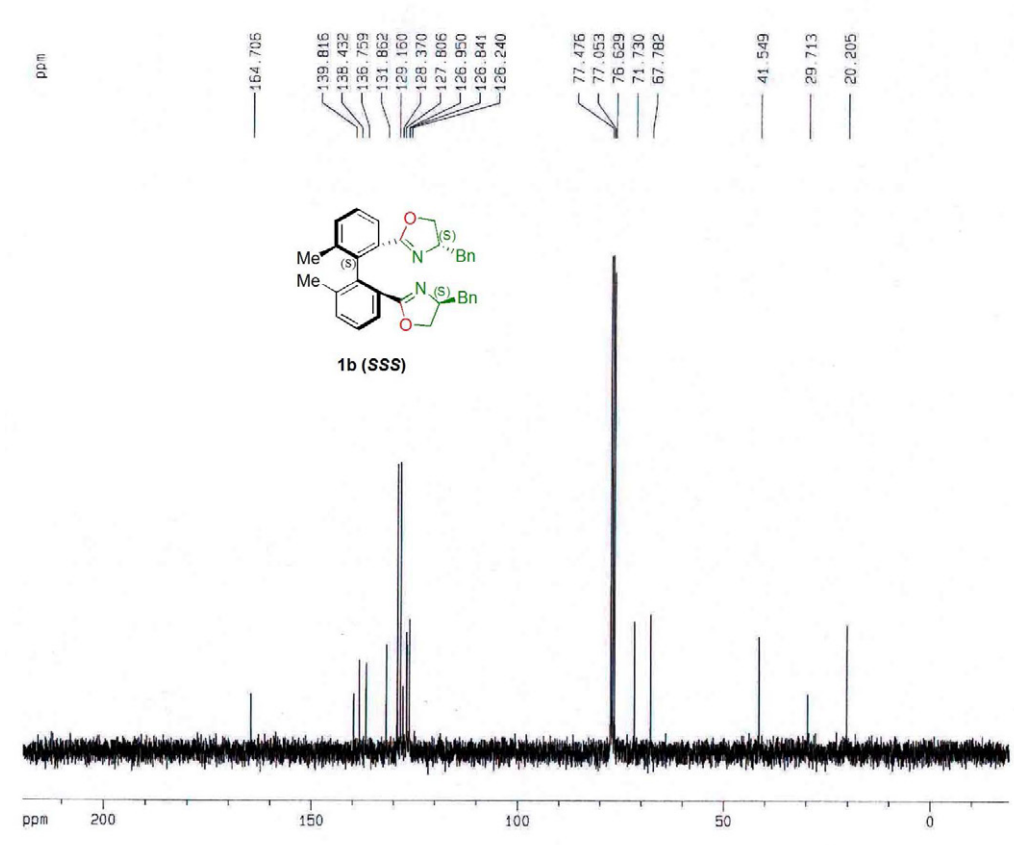

ppm
7.90402
7.87964
7.42801
7.40490
7.37400
7.34885
7.32375
7.28432
7.27903
7.26065
7.23826
7.10784
7.10061
7.08237
7.07802
5.20172
5.16897
5.14052
4.44811
4.42009
4.41492
4.38659
3.91126
3.88361
3.85595
2.08072
2.07382
2.04327
1.94258
0.97353
0.14563
Me
(S)
Me
N
(S)
Ph
O
N
(S)
Ph
O
1a (SSS)
Integral
0.9846
1.2775
1.3988
3.4350
2.0378
1.0000
0.9525
0.9439
3.0815
ppm
10
8
6
4
2
0
Current Data Parameters
NAME Samadi-2
EXPNO 40
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070603
Time 17.42
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 10
DS 1
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 57
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 15.25 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 9.90 cm
F1P 11.609 ppm
F1 3484.14 Hz
F2P -0.928 ppm
F2 -278.43 Hz
PPMCM 10.62682 ppm/cm
HZCM 188.12843 Hz/cm
ppm
165.588
142.675
139.955
136.905
132.156
128.411
127.621
127.358
127.160
126.942
126.663
125.862
77.505
77.081
76.658
74.572
69.805
29.727
20.324
Me
(S)
Me
N
(S)
Ph
O
N
(S)
Ph
O
1a (SSS)
ppm
200
150
100
50
0
Current Data Parameters
NAME Nazari
EXPNO 115
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100723
Time 17.42
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 174
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 2048
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 87.00 usec
PL2 -2.00 dB
PL12 12.00 dB
PL13 18.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 65536
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 8.92 cm
F1P 219.155 ppm
F1 16539.10 Hz
F2P -19.167 ppm
F2 -1446.51 Hz
PPMCM 11.91609 ppm/cm
HZCM 899.28052 Hz/cm


ppm
7.77584
7.77260
7.75162
7.74777
7.39665
7.37438
7.34942
7.28127
7.25768
7.23685
7.23382
7.22092
6.94592
6.93817
6.93140
6.92727
6.92025
6.91478
5.20134
5.17234
5.16810
5.13920
4.46906
4.44133
4.43531
4.40752
3.81054
3.78253
3.75453
2.07442
1.28284
Me
Me
(R)
(S)
Ph
(S)
Ph
2a (SRS)
Integral
0.9449
2.4330
2.9810
1.9129
1.0000
1.0010
0.9898
3.1398
0.8506
ppm
10
8
6
4
2
0
Current Data Parameters
NAME Samadi-2
EXPNO 34
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070220
Time 13.15
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 20
DS 1
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 57
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 15.25 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 11.10 cm
F1P 11.158 ppm
F1 3348.91 Hz
F2P -1.007 ppm
F2 -302.30 Hz
PPMCM 0.60827 ppm/cm
HZCM 182.56013 Hz/cm

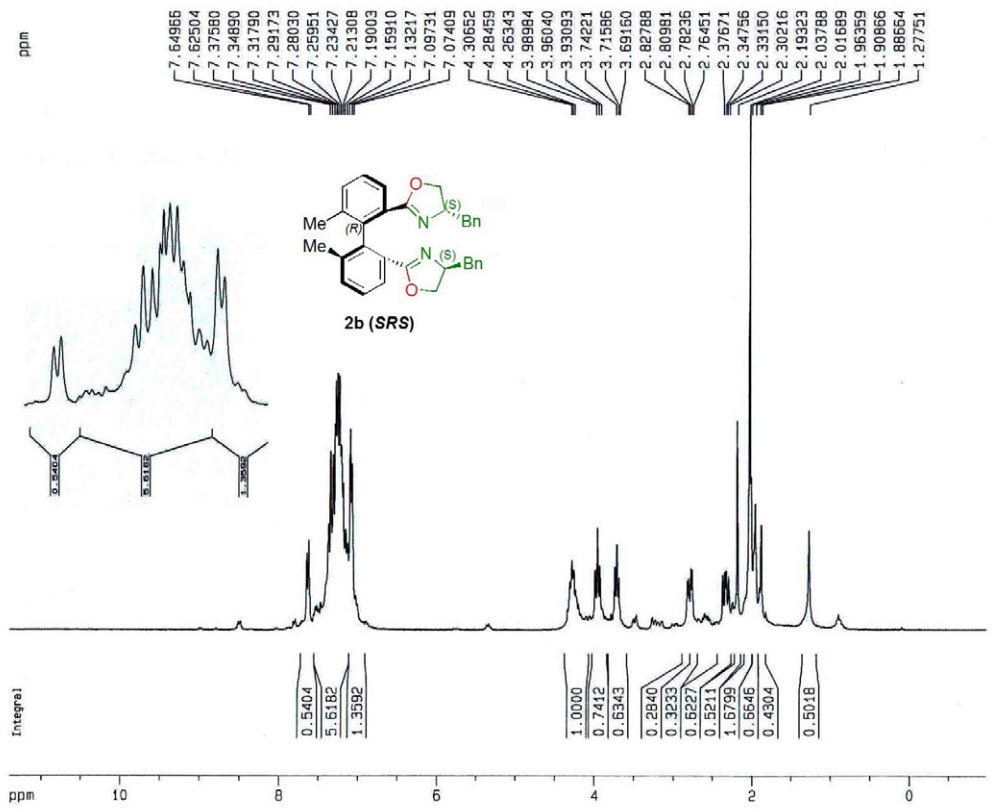

ppm
165.783
137.526
131.983
128.713
128.388
128.044
127.818
127.167
127.067
126.960
126.600
125.412
77.469
77.045
76.622
74.731
69.825
31.946
29.722
20.304
Me
Me
(R)
(S)
Ph
(S)
Ph
2a (SRS)
ppm
200
150
100
50
0
Current Data Parameters
NAME Nazari
EXPNO 150
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100910
Time 9.51
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 214
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 2048
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 87.00 usec
PL2 -2.00 dB
PL12 12.00 dB
PL13 18.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 65536
SF 75.4677490 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 45.29 cm
F1P 219.155 ppm
F1 16539.11 Hz
F2P -19.167 ppm
F2 -1446.51 Hz
PPMCM 11.91609 ppm/cm
HZCM 899.28058 Hz/cm



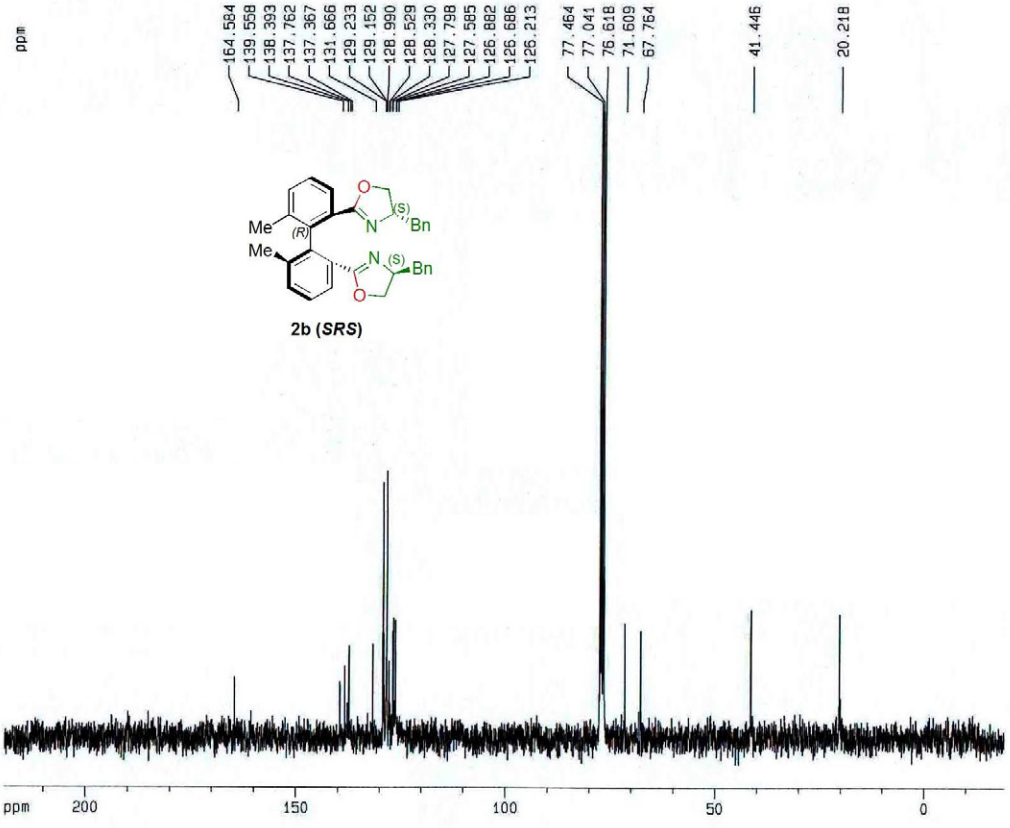

```
Current Data Parameters
NAME                  Nazari
EXPNO                     56
PROCNO                     1

F2 - Acquisition Parameters
Date_               20100104
Time                    3.41
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    32768
SOLVENT                CDCl3
NS                        10
DS                         1
SWH                7812.500 Hz
FIDRES             0.238419 Hz
AQ                 2.0972021 sec
RG                     228.1
DW                  64.000 usec
DE                   6.00 usec
TE                   380.0 K
D1                2.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      15.50 usec
PL1                     -2.00 dB
SFO1              300.1323986 MHz

F2 - Processing parameters
SI                        65536
SF                300.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     20.00 cm
CY                     10.85 cm
F1P                   11.246 ppm
F1                  3375.18 Hz
F2P                   -1.019 ppm
F2                  -305.71 Hz
PPMCM                0.61322 ppm/cm
HZCM               184.04446 Hz/cm
```



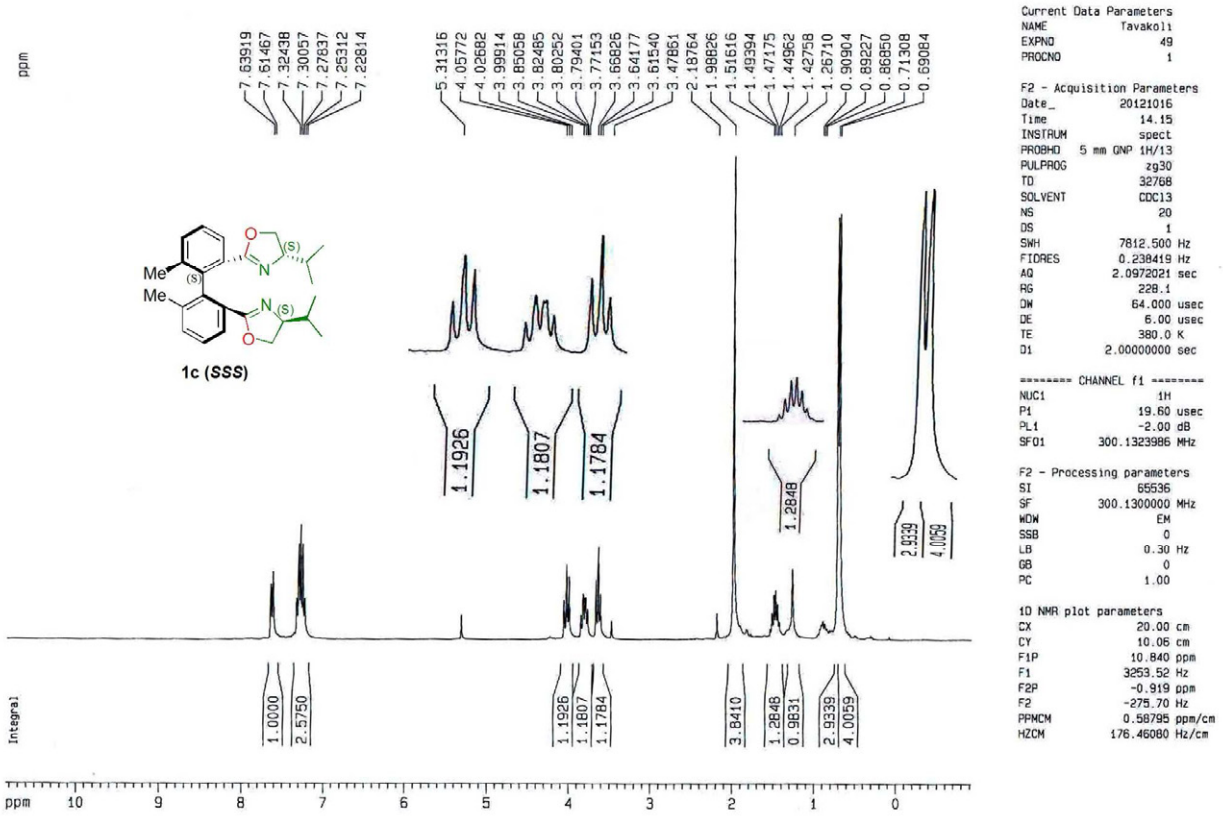

```
Current Data Parameters
NAME                  Nazari
EXPNO                     57
PROCNO                     1

F2 - Acquisition Parameters
Date_               20100104
Time                    3.46
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                    65536
SOLVENT                DMSO
NS                       143
DS                         2
SWH               17985.611 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                      2048
DW                  27.800 usec
DE                   6.00 usec
TE                   300.0 K
D1                2.00000000 sec
D11               0.03000000 sec
D12               0.00002000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                      8.75 usec
PL1                     -2.00 dB
SFO1              75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  87.00 usec
PL2                     -2.00 dB
PL12                    12.00 dB
PL13                    18.00 dB
SFO2              300.1312005 MHz

F2 - Processing parameters
SI                        65536
SF                75.4677490 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                     20.00 cm
CY                     10.19 cm
F1P                  219.155 ppm
F1                  16539.11 Hz
F2P                  -19.167 ppm
F2                  -1446.51 Hz
PPMCM               11.91609 ppm/cm
HZCM               899.28058 Hz/cm
```



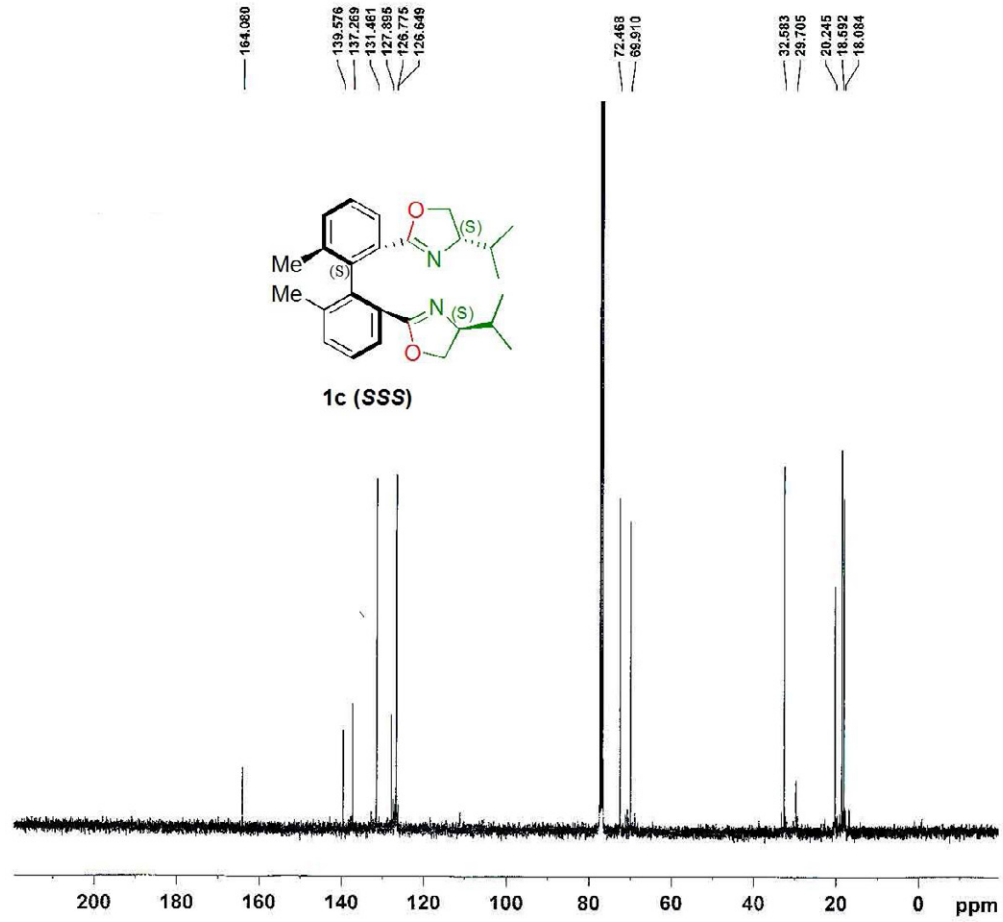

```
Current Data Parameters
NAME                  Nazari
EXPNO                    181
PROCNO                     1

F2 - Acquisition Parameters
Date_              20101019
Time                  14.44
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       10
DS                        1
SWH               7812.500 Hz
FIDRES            0.238419 Hz
AQ                2.0972021 sec
RG                    228.1
DW                   64.000 usec
DE                    6.00 usec
TE                   380.0 K
D1                2.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     15.50 usec
PL1                    -2.00 dB
SFO1             300.1323986 MHz

F2 - Processing parameters
SI                        65536
SF                300.1300000 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                        20.00 cm
CY                        10.63 cm
F1P                      11.397 ppm
F1                     3420.60 Hz
F2P                     -0.975 ppm
F2                     -292.61 Hz
PPMCM                  0.61860 ppm/cm
HZCM                 185.66045 Hz/cm
```



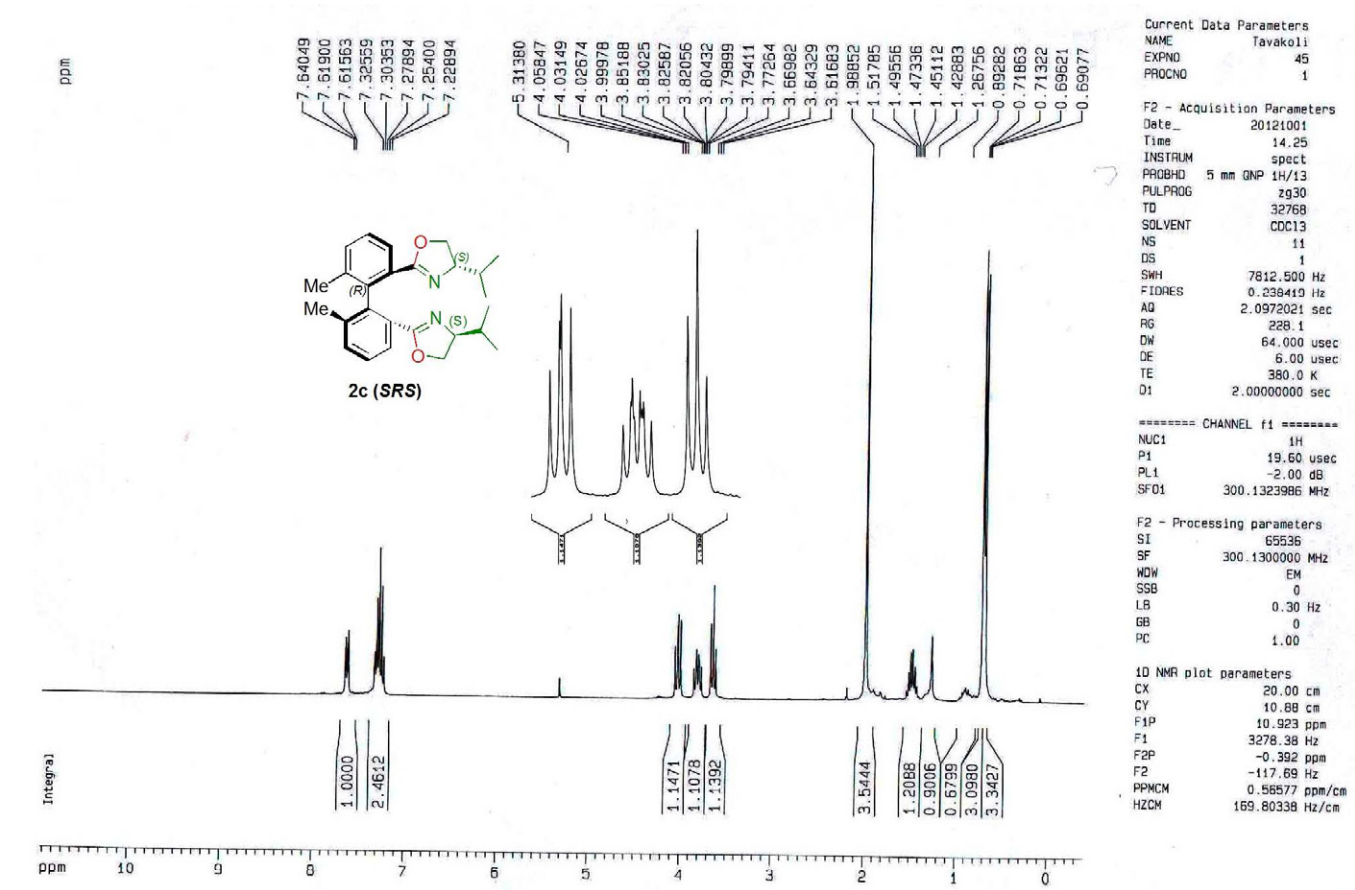

```
Current Data Parameters
NAME                  Nazari
EXPNO                    182
PROCNO                     1

F2 - Acquisition Parameters
Date_              20101019
Time                  14.47
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      548
DS                        2
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ                1.8219508 sec
RG                   9195.2
DW                   27.800 usec
DE                    6.00 usec
TE                   300.0 K
D1                2.00000000 sec
d11               0.03000000 sec
d12               0.00002000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                     8.75 usec
PL1                    -2.00 dB
SFO1             75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                  87.00 usec
PL2                    -2.00 dB
PL12                   12.00 dB
PL13                   18.00 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                        65536
SF                75.4677490 MHz
WDW                          EM
SSB                           0
LB                         2.00 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                        20.00 cm
CY                        31.03 cm
F1P                     219.155 ppm
F1                    16539.10 Hz
F2P                    -19.167 ppm
F2                    -1446.51 Hz
PPMCM                 11.91609 ppm/cm
HZCM                899.28058 Hz/cm
```

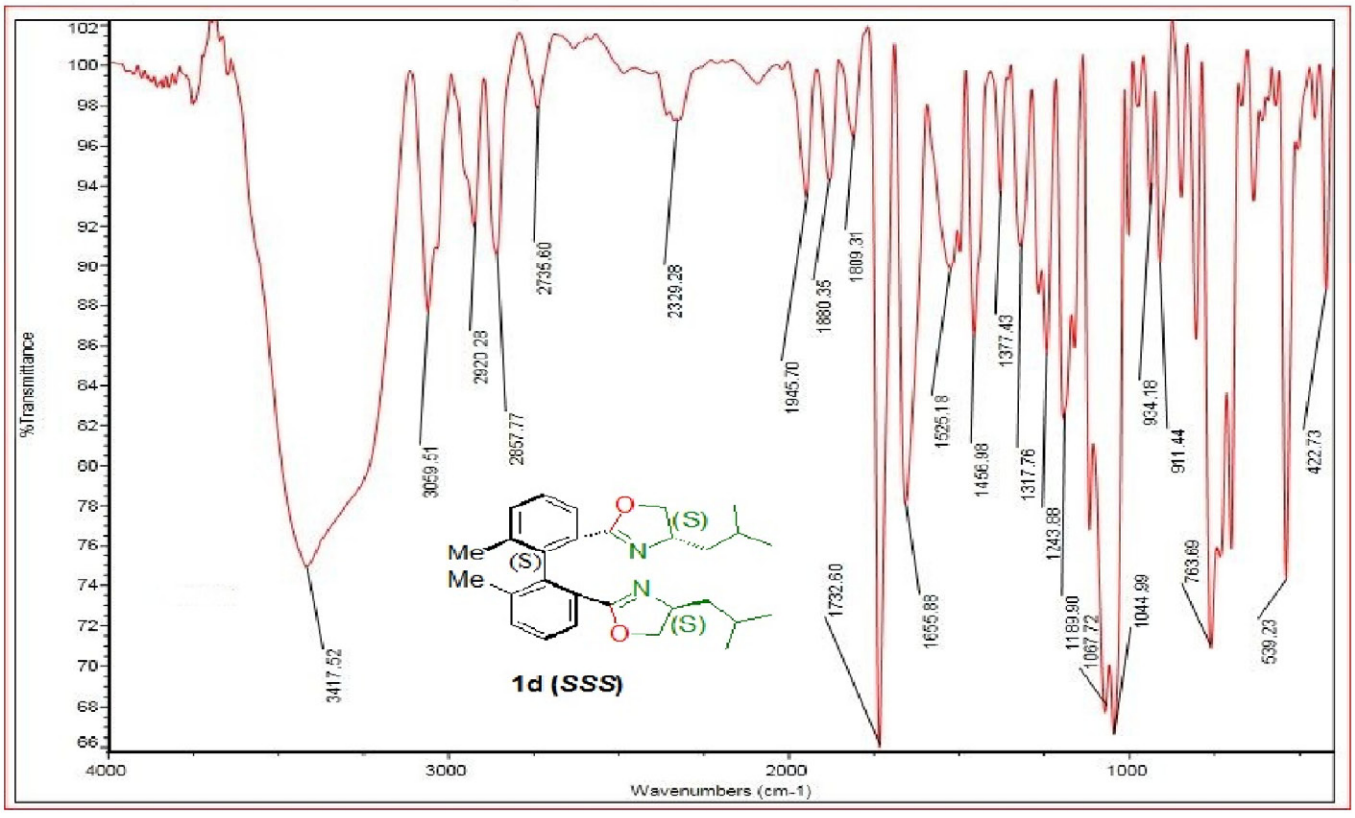


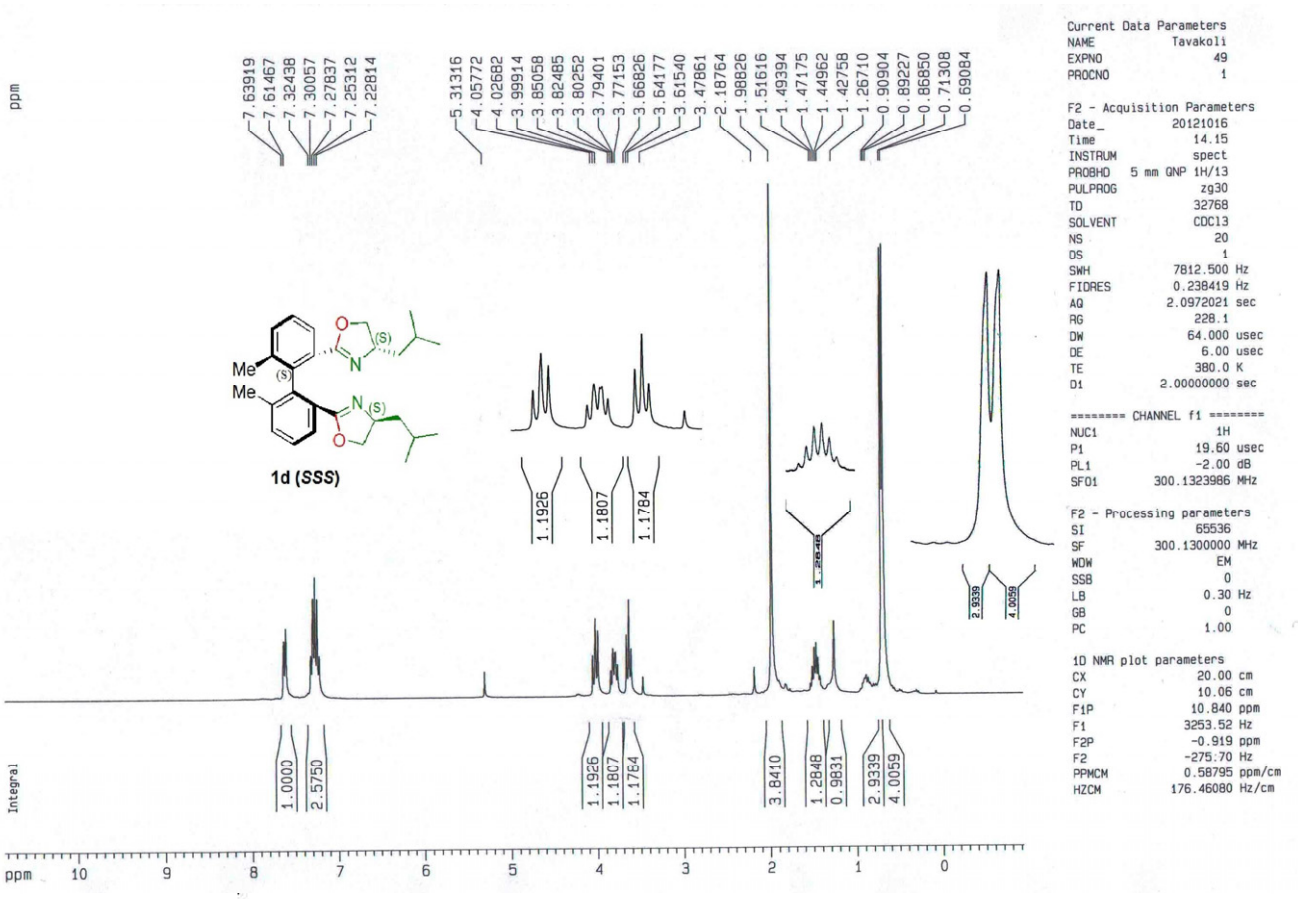

```
Current Data Parameters
NAME                  Tavakoli
EXPNO                       49
PROCNO                       1

F2 - Acquisition Parameters
Date_               20121016
Time                     14.15
INSTRUM                  spect
PROBHD     5 mm QNP 1H/13
PULPROG                  zg30
TD                      32768
SOLVENT                  CDCl3
NS                          20
DS                           1
SWH                 7812.500 Hz
FIDRES                 0.238419 Hz
AQ                  2.0972021 sec
RG                       228.1
DW                      64.000 usec
DE                       6.00 usec
TE                      380.0 K
D1                  2.00000000 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                       19.60 usec
PL1                      -2.00 dB
SFO1                300.1323986 MHz

F2 - Processing parameters
SI                          65536
SF                  300.1300000 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                       20.00 cm
CY                       10.06 cm
F1P                     10.840 ppm
F1                     3253.52 Hz
F2P                     -0.919 ppm
F2                     -275.70 Hz
PPMCM                  0.58795 ppm/cm
HZCM                 176.46080 Hz/cm
```



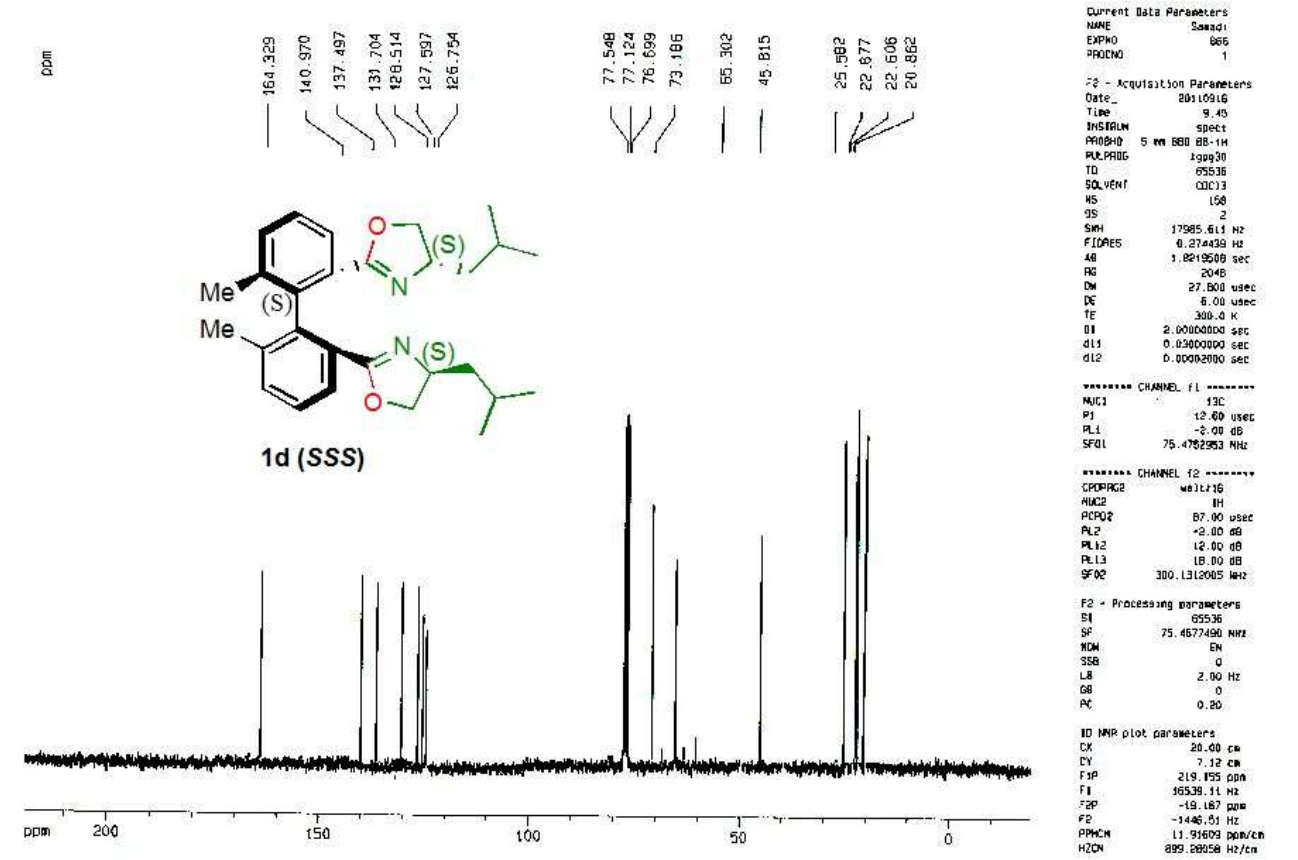

```
NAME   Mehrasbi-Ebrahim YSF2 13C
EXPNO                        1
PROCNO                       1
Date_               20121200
Time                     9.06
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zgpg
TD                      65536
SOLVENT                  CDCl3
NS                        2048
DS                           0
SWH                24038.461 Hz
FIDRES                 0.366798 Hz
AQ                  1.3631988 sec
RG                         203
DW                      20.800 usec
DE                       6.50 usec
TE                      299.3 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        13C
P1                       7.60 usec
PL1                     -2.00 dB
PL1W                58.92832510 W
SFO1               100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                    85.00 usec
PL2                      0.00 dB
PL12                    16.00 dB
PL13                    16.00 dB
PL2W                11.30348873 W
PL12W               0.28393001 W
PL13W               0.28393081 W
SFO2               400.1316005 MHz
SI                       32768
SF                 100.6127690 MHz
WDW                         EM
SSB                          0
LB                       1.00 Hz
GB                           0
PC                        1.40
```


ppm
7.64049
7.61900
7.61563
7.32559
7.30353
7.27894
7.25400
7.22894
5.31380
4.05847
4.03149
4.02674
3.99978
3.85188
3.83025
3.82587
3.82056
3.80432
3.79899
3.79411
3.77264
3.66982
3.64329
3.61683
1.98852
1.51785
1.49556
1.47336
1.45112
1.42883
1.26756
0.89282
0.71863
0.71322
0.69621
0.69077
Me
(R)
Me
N
(S)
O
2c (SRS)
Integral
1.0000
2.4612
1.1471
1.1078
1.1392
3.5444
1.2088
0.9006
0.6799
3.0980
3.3427
ppm
Current Data Parameters
NAME Tavakoli
EXPNO 45
PROCNO 1
F2 - Acquisition Parameters
Date_ 20121001
Time 14.25
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 11
DS 1
SWH 7812.500 Hz
FIDRES 0.238419 Hz
AQ 2.0972021 sec
RG 228.1
DW 64.000 usec
DE 6.00 usec
TE 380.0 K
D1 2.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 19.60 usec
PL1 -2.00 dB
SFO1 300.1323986 MHz
F2 - Processing parameters
SI 65536
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 10.88 cm
F1P 10.923 ppm
F1 3278.38 Hz
F2P -0.392 ppm
F2 -117.69 Hz
PPMCM 0.56577 ppm/cm
HZCM 169.80338 Hz/cm

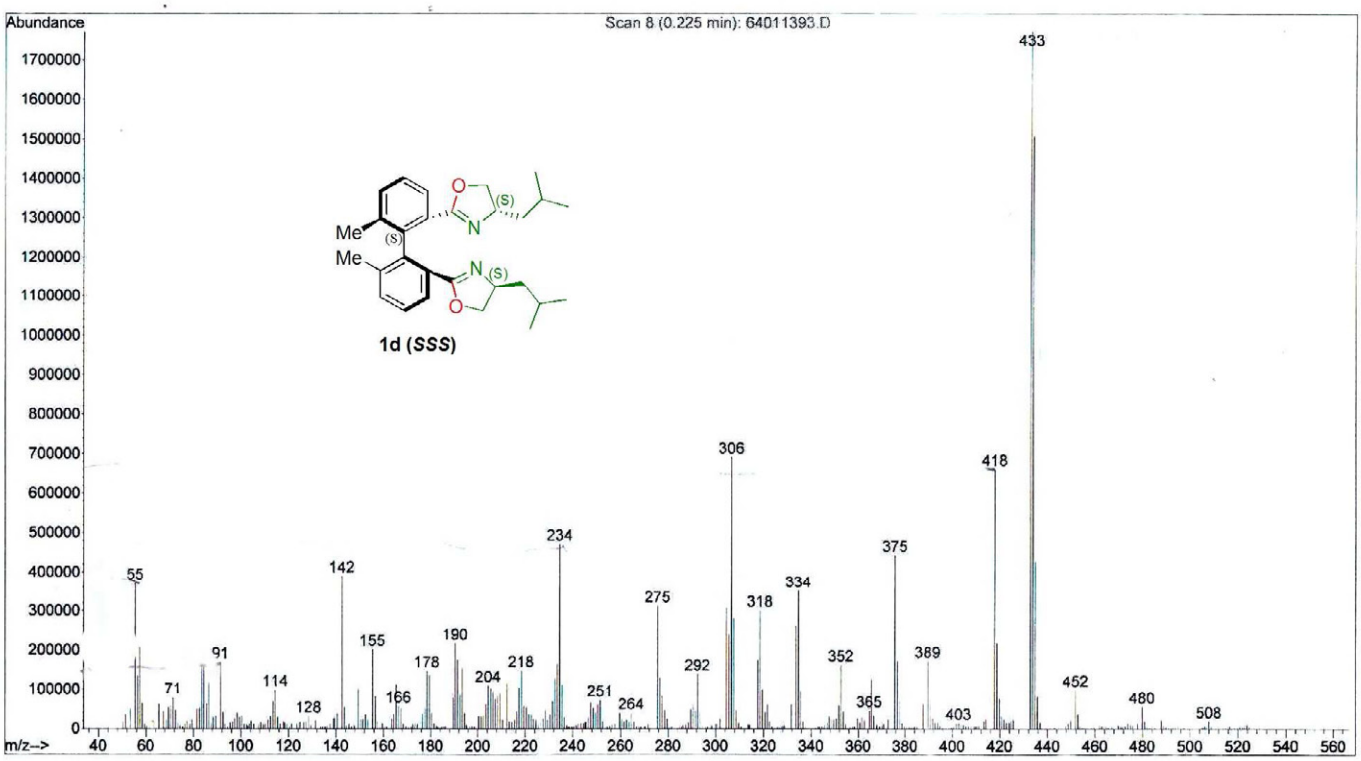

%Transmittance
Wavenumbers (cm-1)
3417.52
3059.51
2923.23
2857.77
2735.60
2329.28
1945.70
1880.35
1809.31
1732.60
1655.88
1525.18
1456.98
1377.43
1317.76
1243.88
1189.90
1067.72
1044.99
934.18
911.44
763.69
539.23
422.73
Me
(S)
Me
N
(S)
O
1d (SSS)

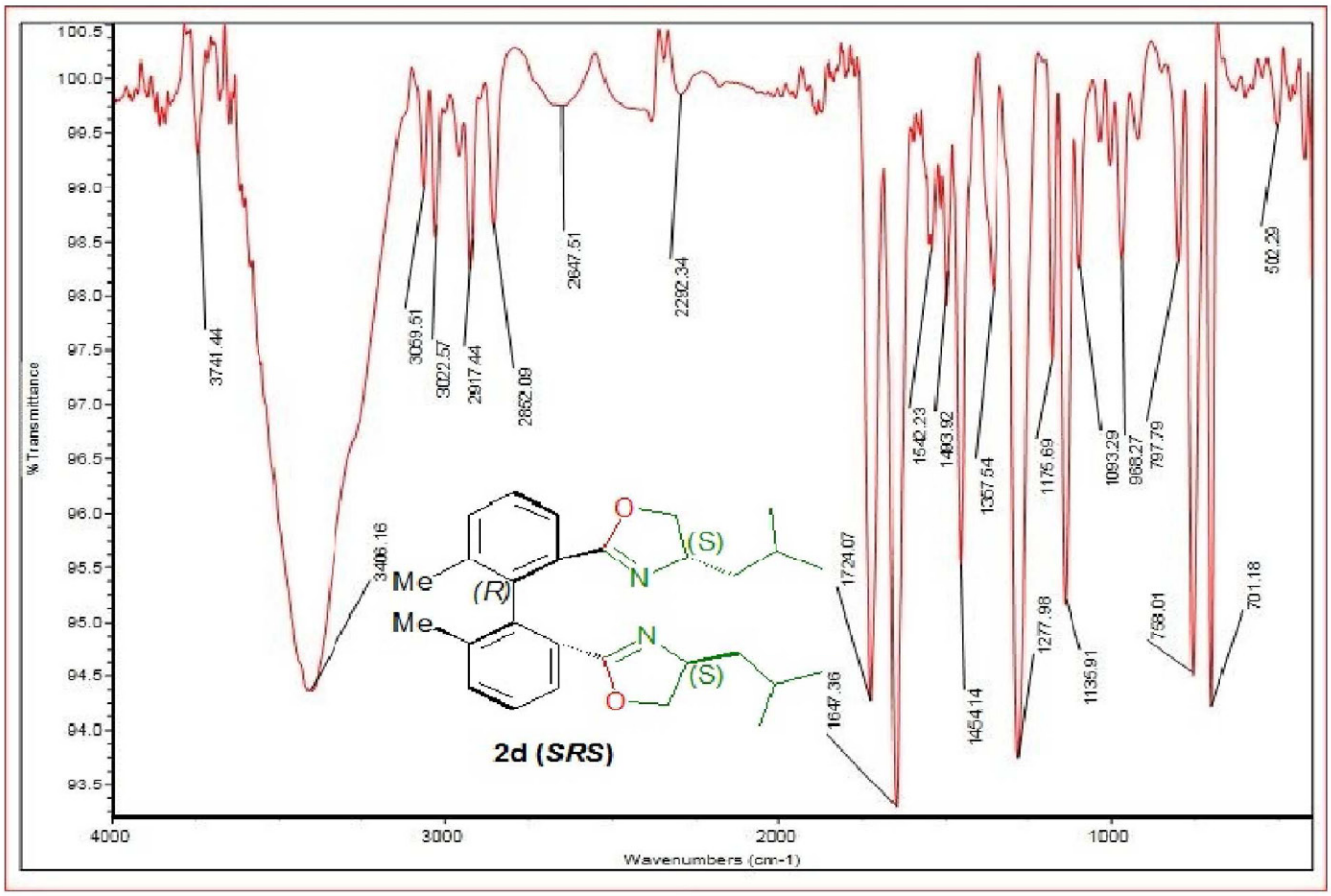


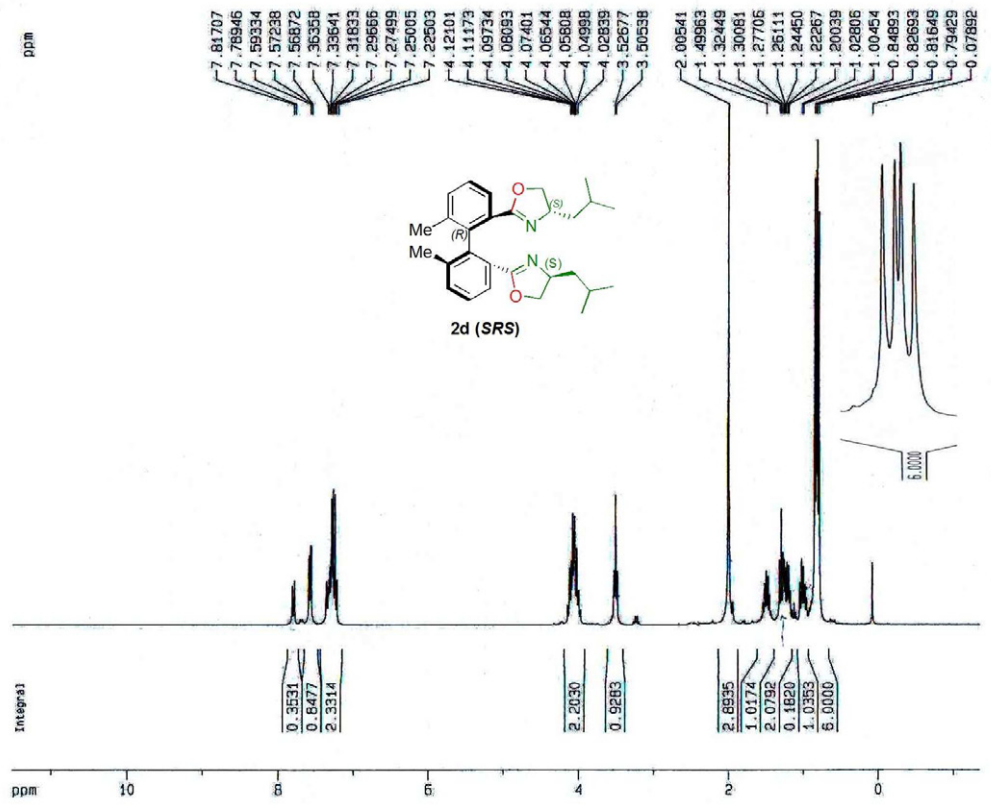

```
Current Data Parameters
NAME                  Tavakoli
EXPNO                       49
PROCNO                       1

F2 - Acquisition Parameters
Date_               20121016
Time                   14.15
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG                zg30
TD                    32768
SOLVENT                CDCl3
NS                        20
DS                         1
SWH                7812.500 Hz
FIDRES             0.238419 Hz
AQ                 2.0972021 sec
RG                     228.1
DW                    64.000 usec
DE                     6.00 usec
TE                    300.0 K
D1                 2.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                     19.60 usec
PL1                    -2.00 dB
SFO1             300.1323986 MHz

F2 - Processing parameters
SI                        65536
SF               300.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     20.00 cm
CY                     10.06 cm
F1P                   10.840 ppm
F1                   3253.52 Hz
F2P                   -0.919 ppm
F2                   -275.70 Hz
PPMCM                 0.58795 ppm/cm
HZCM                176.46080 Hz/cm
```



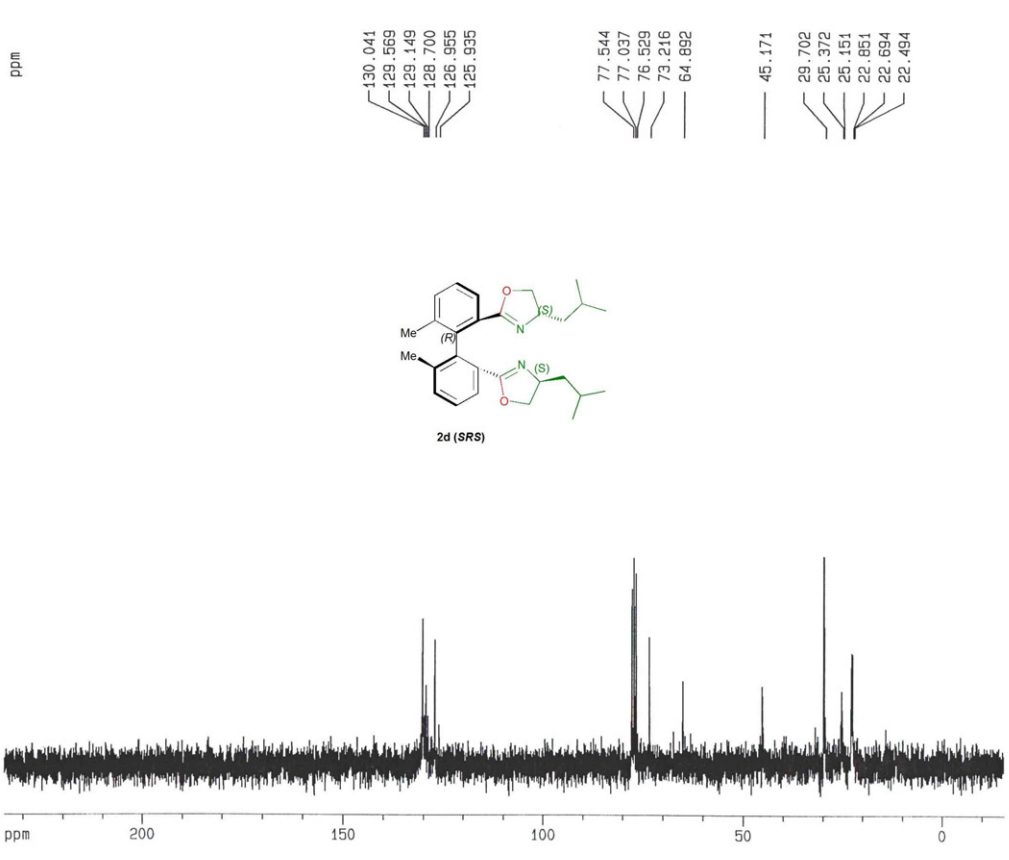

```
Current Data Parameters
NAME                  Samadi
EXPNO                    666
PROCNO                     1

F2 - Acquisition Parameters
Date_               20110916
Time                    9.45
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      158
DS                        2
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ                1.8219508 sec
RG                     2048
DW                   27.800 usec
DE                    6.00 usec
TE                   300.0 K
D1                2.00000000 sec
D11               0.03000000 sec
D12               0.00002000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                     12.60 usec
PL1                    -2.00 dB
SFO1             75.4782953 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                       1H
PCPD2                  87.00 usec
PL2                    +2.00 dB
PL12                   12.00 dB
PL13                   18.00 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                        65536
SF               75.4677490 MHz
WDW                       EM
SSB                        0
LB                      2.00 Hz
GB                         0
PC                      1.20

1D NMR plot parameters
CX                     20.00 cm
CY                      7.12 cm
F1P                  219.155 ppm
F1                  16539.11 Hz
F2P                  -19.187 ppm
F2                  -1446.61 Hz
PPMCM                11.91609 ppm/cm
HZCM                899.28058 Hz/cm
```


Abundance
Scan 8 (0.225 min): 64011393.D
m/z-->
1d (SSS)

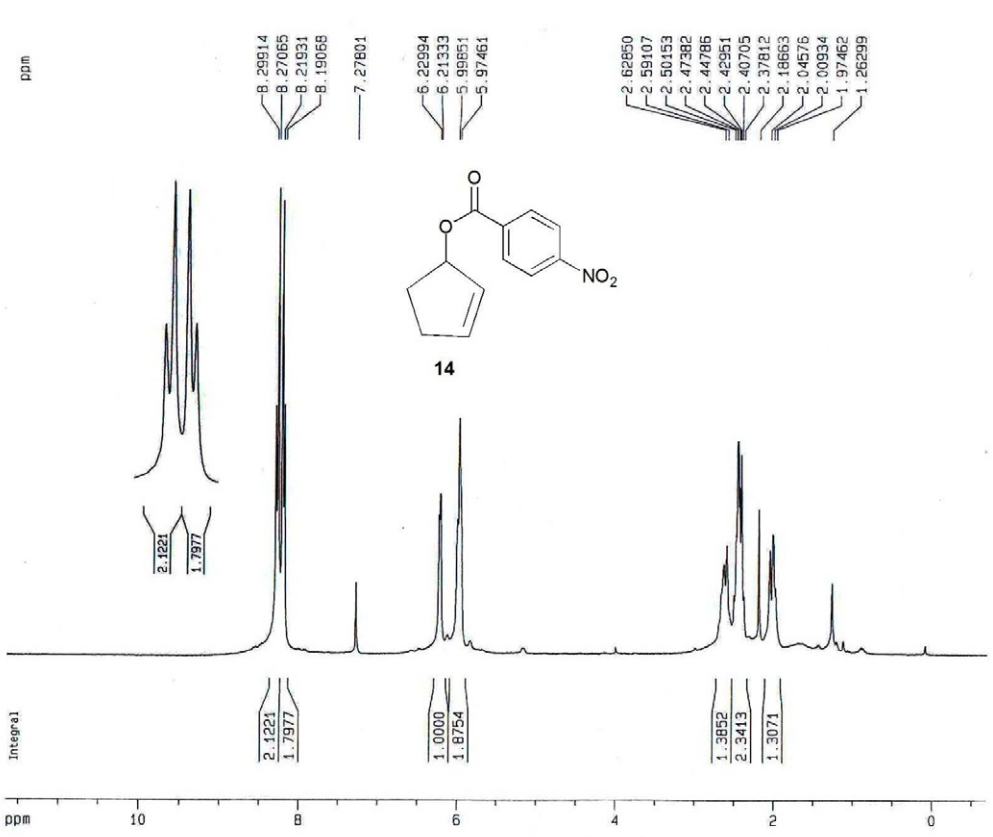

%Transmittance
Wavenumbers (cm-1)
2d (SRS)



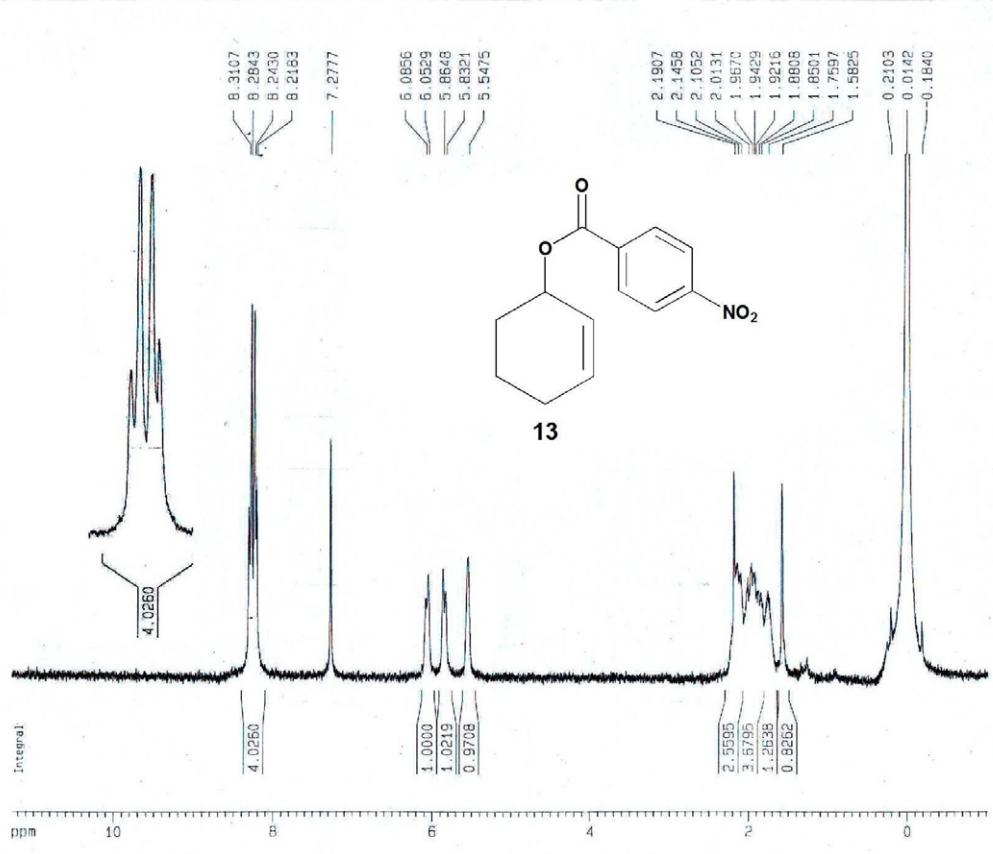

```
Current Data Parameters
NAME                  Tavakoli
EXPNO                       14
PROCNO                       1

F2 - Acquisition Parameters
Date_               20120204
Time                   17.02
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    32768
SOLVENT                CDCl3
NS                        10
DS                         1
SWH                 7812.500 Hz
FIDRES              0.238419 Hz
AQ                  2.0972021 sec
RG                      228.1
DW                     64.000 usec
DE                      6.00 usec
TE                     300.0 K
D1                  2.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      19.60 usec
PL1                     -2.00 dB
SFO1              300.1323986 MHz

F2 - Processing parameters
SI                        65536
SF                300.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     20.00 cm
CY                     13.81 cm
F1P                   11.511 ppm
F1                  3454.66 Hz
F2P                  -1.353 ppm
F2                  -406.16 Hz
PPMCM               0.64319 ppm/cm
HZCM              193.04141 Hz/cm
```



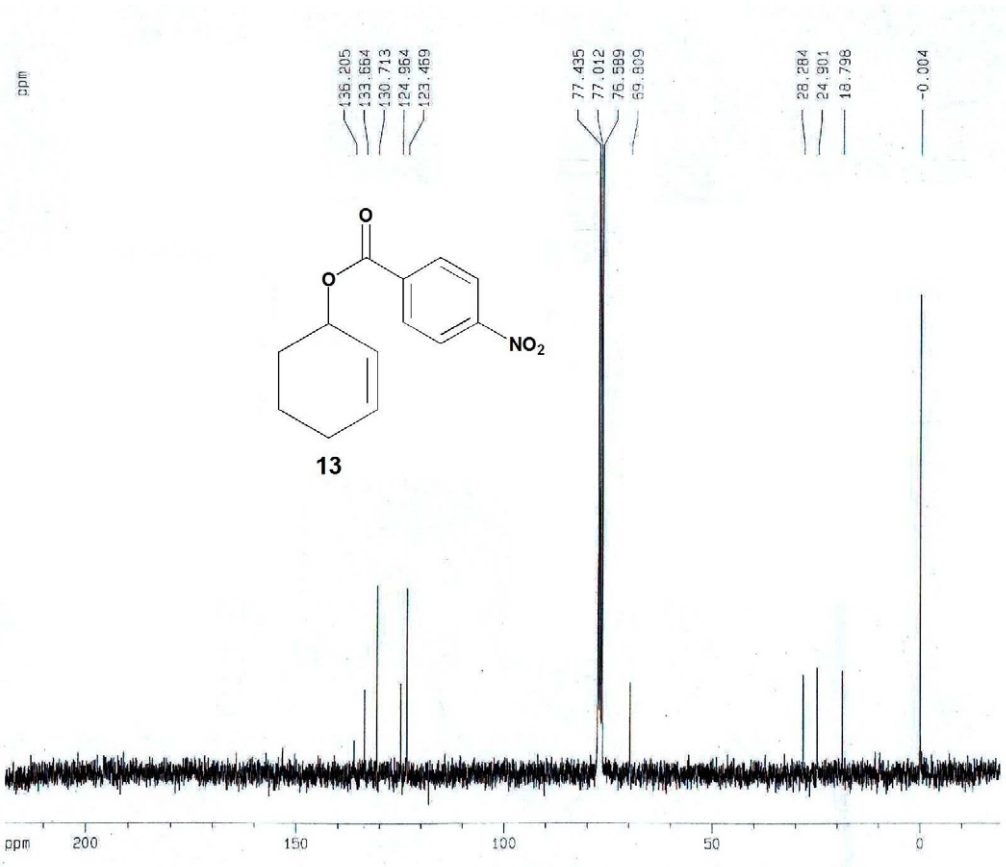

```
Current Data Parameters
NAME                  UBehesti
EXPNO                      195
PROCNO                       1

F2 - Acquisition Parameters
Date_               20120724
Time                   12.59
INSTRUM                spect
PROBHD   5 mm QNP 1H/1
PULPROG                zgpg
TD                    62890
SOLVENT                CDCl3
NS                       353
DS                         4
SWH                15723.271 Hz
FIDRES              0.250012 Hz
AQ                  1.9999520 sec
RG                     14596.5
DW                     31.800 usec
DE                      6.00 usec
TE                     300.0 K
D1                  2.00000000 sec
D11                 0.03000000 sec
D12                 0.00002000 sec

========== CHANNEL f1 =======
NUC1                       13C
P1                      6.50 usec
PL1                     -6.00 dB
SFO1              62.9021320 MHz

========== CHANNEL f2 =======
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2                     -4.00 dB
PL12                    15.00 dB
PL13                    18.00 dB
SFO2             250.1310005 MHz

F2 - Processing parameters
SI                        32768
SF                62.8952401 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                     20.00 cm
F1P                   234.573 ppm
F1                  14753.53 Hz
F2P                  -15.418 ppm
F2                   -969.74 Hz
PPMCM               12.49957 ppm/cm
HZCM               786.16351 Hz/cm
```



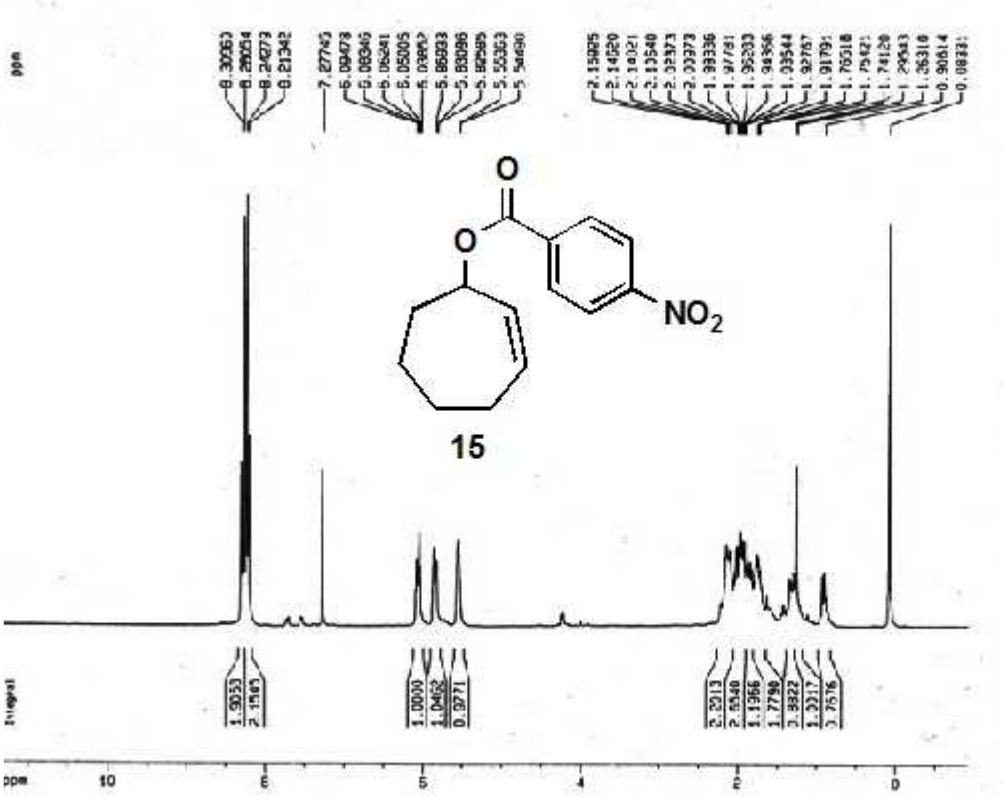

```
Current Data Parameters
NAME                  Samadi
EXPNO                    841
PROCNO                     1

F2 - Acquisition Parameters
Date_               20111220
Time                   15.32
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       10
DS                        1
SWH                7812.500 Hz
FIDRES             0.238419 Hz
AQ                 2.0972021 sec
RG                     228.1
DW                    64.000 usec
DE                     6.00 usec
TE                    380.0 K
D1                 2.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     15.50 usec
PL1                    -2.00 dB
SFO1             300.1323986 MHz

F2 - Processing parameters
SI                        65536
SF               300.1300000 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                        20.00 cm
CY                         9.52 cm
F1P                       11.652 ppm
F1                      3497.25 Hz
F2P                       -0.697 ppm
F2                      -209.25 Hz
PPMCM                  0.61748 ppm/cm
HZCM                 185.32494 Hz/cm
```



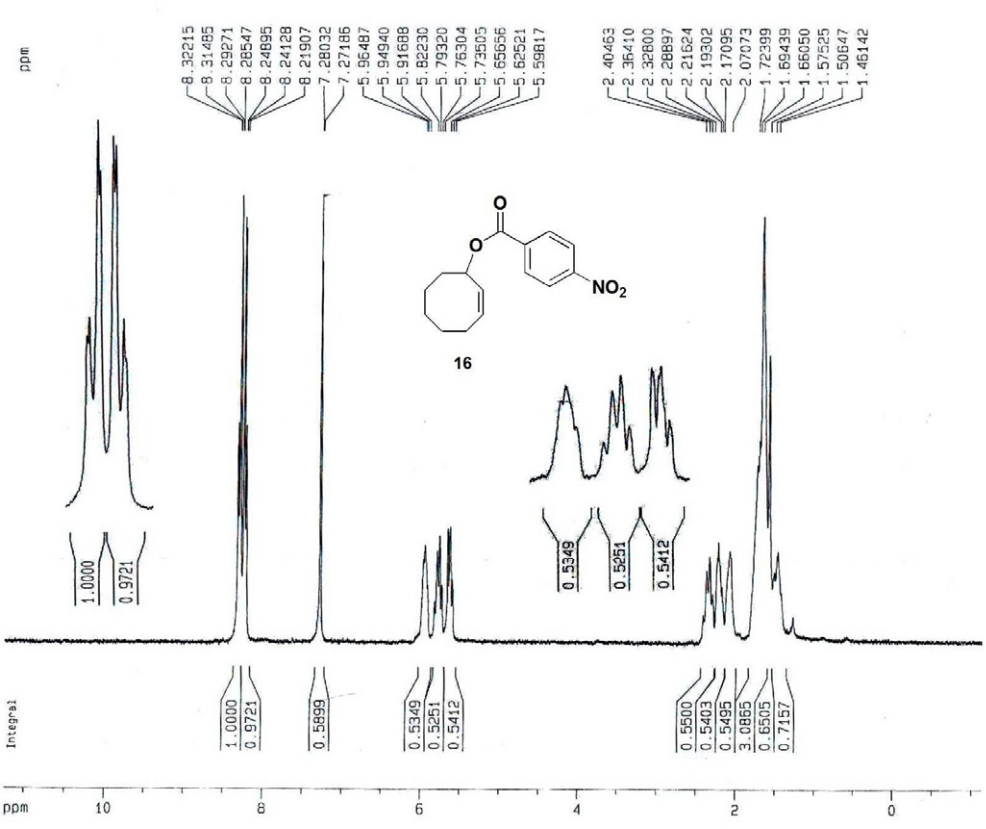

```
Current Data Parameters
NAME                  Arvinnejad
EXPNO                        331
PROCNO                         1

F2 - Acquisition Parameters
Date_               20110805
Time                   23.54
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       64
DS                        1
SWH                7812.500 Hz
FIDRES             0.238419 Hz
AQ                 2.0972021 sec
RG                     228.1
DW                    64.000 usec
DE                     6.00 usec
TE                    380.0 K
D1                 2.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     15.50 usec
PL1                    -2.00 dB
SFO1             300.1323986 MHz

F2 - Processing parameters
SI                        65536
SF               300.1300000 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                        20.00 cm
CY                       127.59 cm
F1P                       11.283 ppm
F1                      3386.40 Hz
F2P                       -1.021 ppm
F2                      -306.58 Hz
PPMCM                  0.61523 ppm/cm
HZCM                 184.64893 Hz/cm
```




```
Current Data Parameters
NAME            Arvinnejad
EXPNO                  332
PROCNO                   1

F2 - Acquisition Parameters
Date_          20110806
Time               0.08
INSTRUM            spect
PROBHD  5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT            CDCl3
NS                   694
DS                     2
SWH            17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                  2048
DW                27.800 usec
DE                 6.00 usec
TE                300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                12.60 usec
PL1                -2.00 dB
SF01          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             87.00 usec
PL2                -2.00 dB
PL12               12.00 dB
PL13               18.00 dB
SF02         300.1312005 MHz

F2 - Processing parameters
SI                 65536
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  0.20

1D NMR plot parameters
CX                 20.00 cm
CY                 21.85 cm
F1P              219.155 ppm
F1             16539.11 Hz
F2P              -19.167 ppm
F2             -1446.51 Hz
PPMCM           11.91609 ppm/cm
HZCM           899.28058 Hz/cm
```




```
Current Data Parameters
NAME            Ganedi-2
EXPNO                  45
PROCNO                  1

F2 - Acquisition Parameters
Date_          20071202
Time               10.48
INSTRUM            spect
PROBHD  5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            6172.839 Hz
FIDRES         0.188380 Hz
AQ             2.6542080 sec
RG                   181
DW                81.000 usec
DE                 6.00 usec
TE                300.3 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                15.25 usec
PL1                0.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF            300.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                  9.10 cm
F1P              11.267 ppm
F1             3308.64 Hz
F2P              -0.926 ppm
F2             -238.63 Hz
PPMCM          0.61225 ppm/cm
HZCM           180.78384 Hz/cm
```



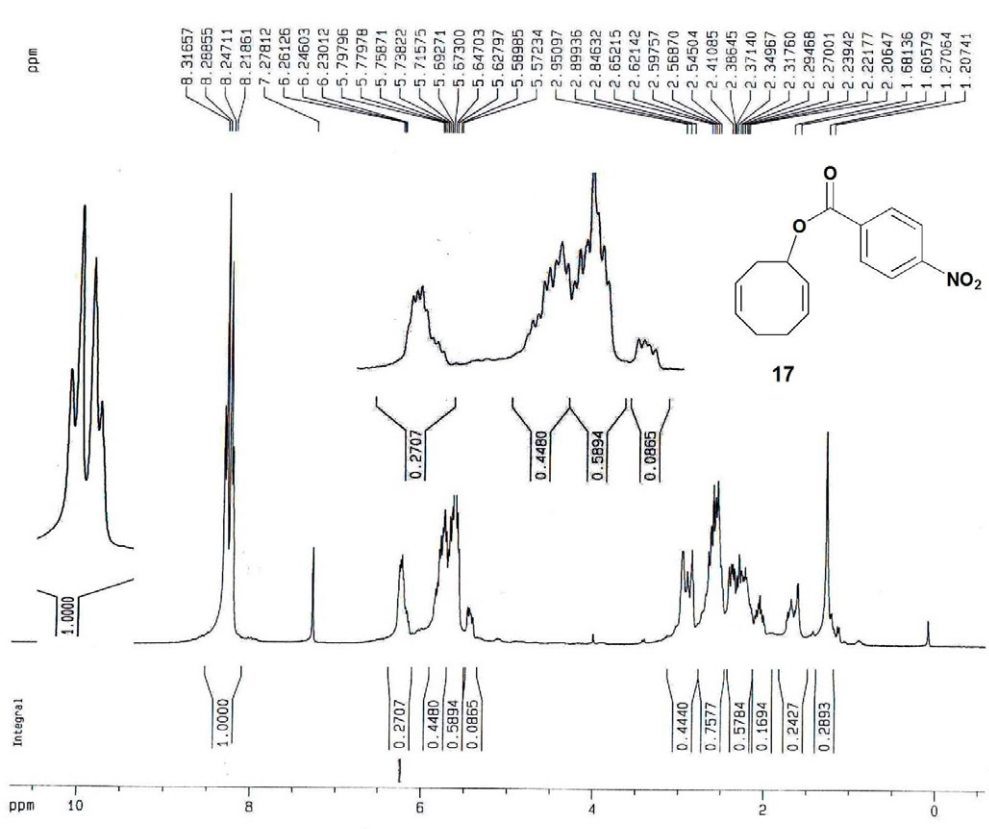
Current Data Parameters
NAME Samadi
EXPNO 856
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120116
Time 10.58
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 10
DS 1
SWH 7812.500 Hz
FIDRES 0.238419 Hz
AQ 2.0972021 sec
RG 45.3
DW 64.000 usec
DE 6.00 usec
TE 380.0 K
D1 2.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 15.50 usec
PL1 -2.00 dB
SFO1 300.1323986 MHz

F2 - Processing parameters
SI 65536
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 9.27 cm
F1P 11.246 ppm
F1 3375.18 Hz
F2P -1.134 ppm
F2 -340.25 Hz
PPMCM 0.61897 ppm/cm
HZCM 185.77138 Hz/cm



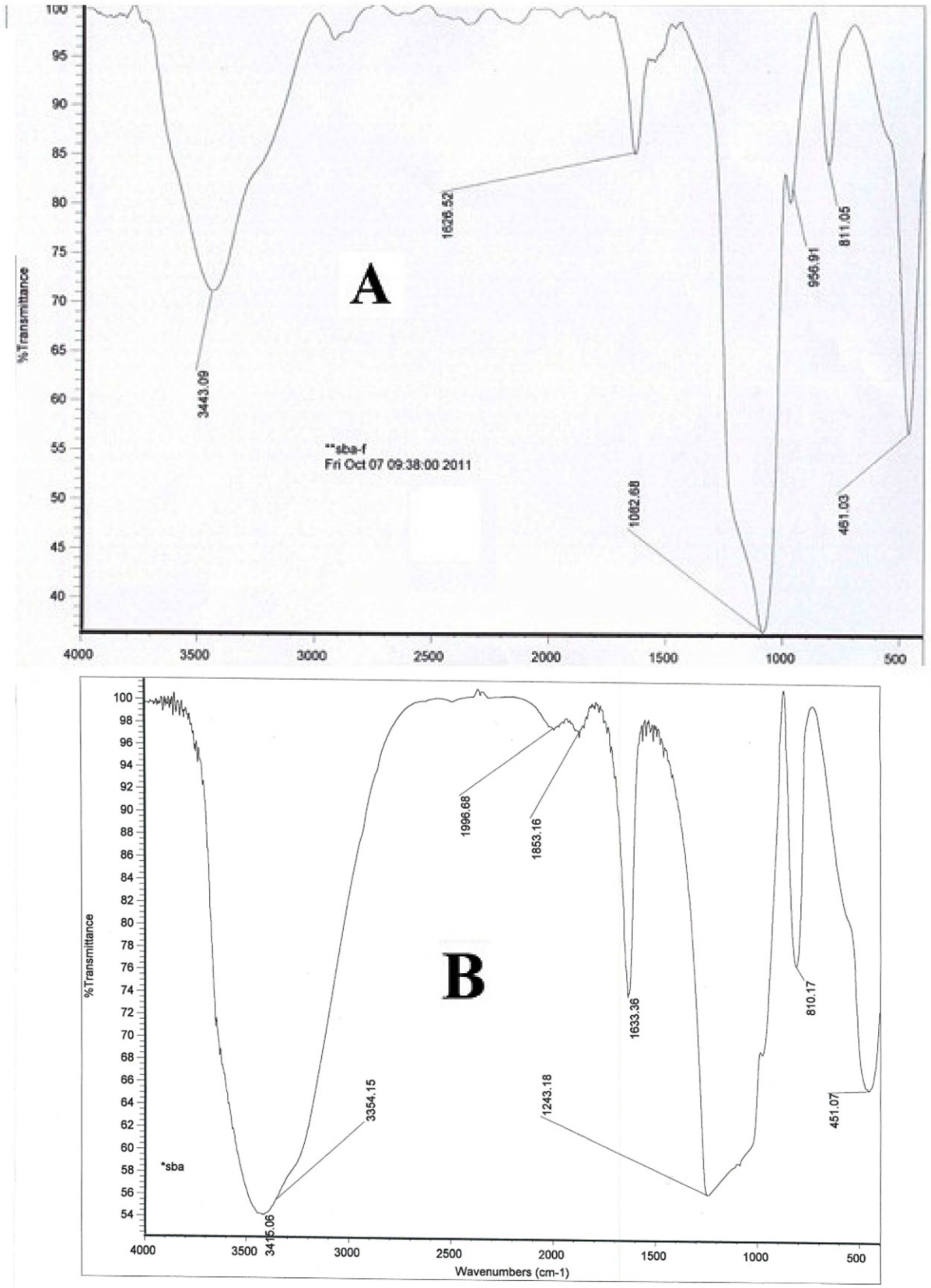
Current Data Parameters
NAME Samadi
EXPNO 840
PROCNO 1

F2 - Acquisition Parameters
Date_ 20111220
Time 15.13
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 10
DS 1
SWH 7812.500 Hz
FIDRES 0.238419 Hz
AQ 2.0972021 sec
RG 228.1
DW 64.000 usec
DE 6.00 usec
TE 380.0 K
D1 2.00000000 sec

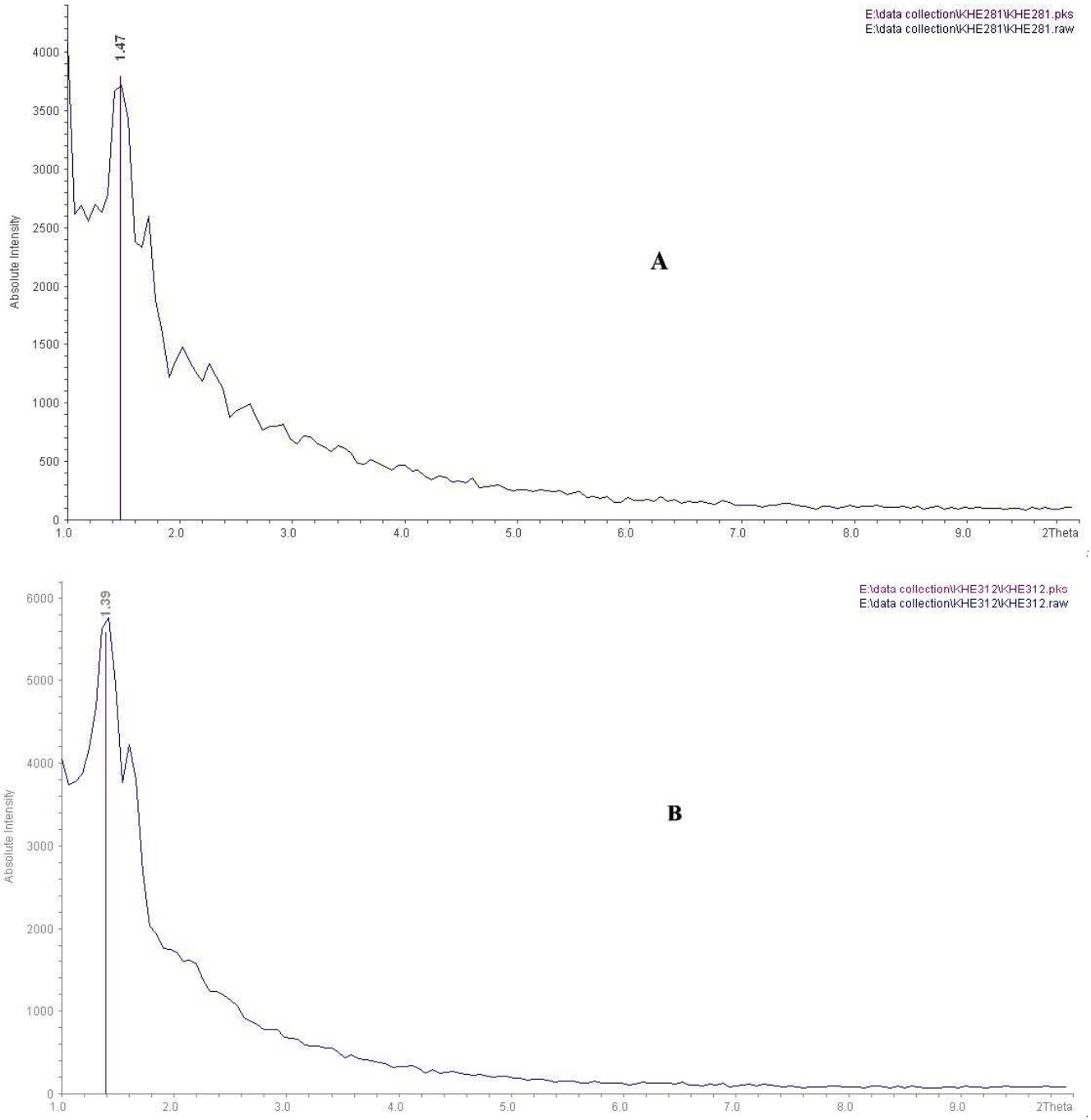
======== CHANNEL f1 ========
NUC1 1H
P1 19.60 usec
PL1 -2.00 dB
SFO1 300.1323986 MHz

F2 - Processing parameters
SI 65536
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

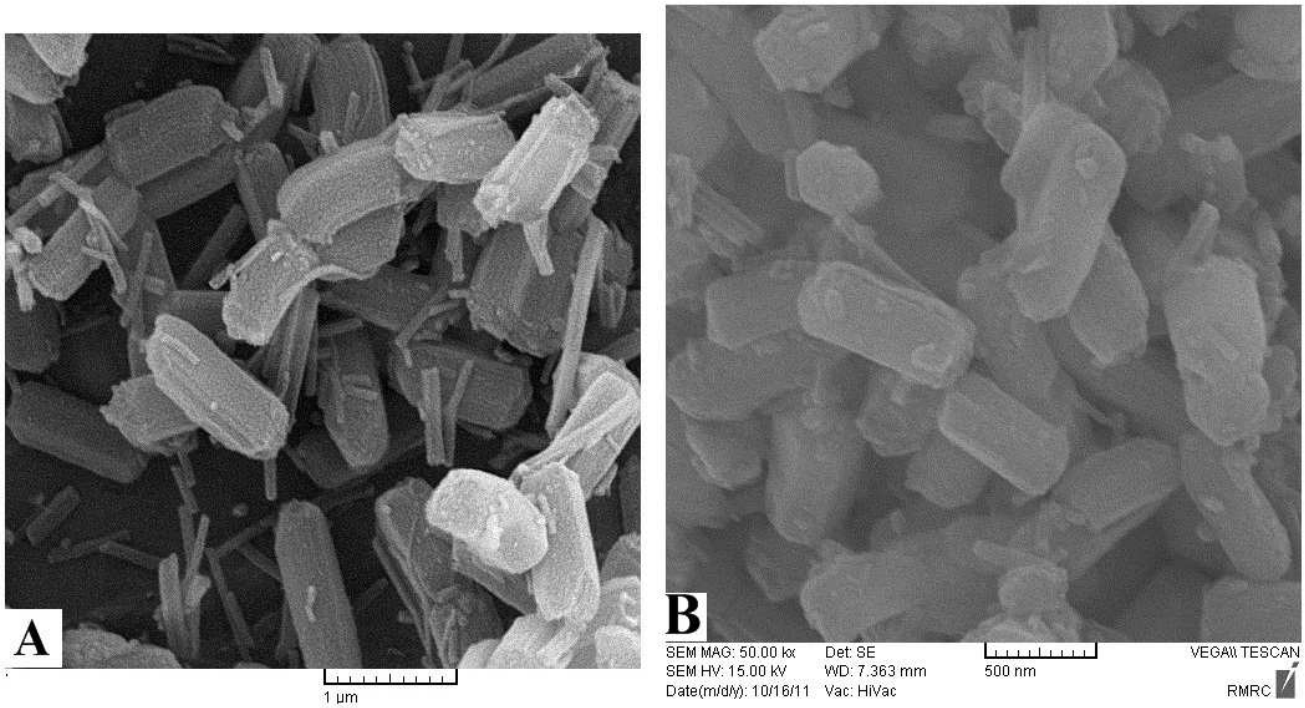
1D NMR plot parameters
CX 20.00 cm
CY 9.23 cm
F1P 10.760 ppm
F1 3229.46 Hz
F2P -0.589 ppm
F2 -176.81 Hz
PPMCM 0.55747 ppm/cm
HZCM 170.31363 Hz/cm



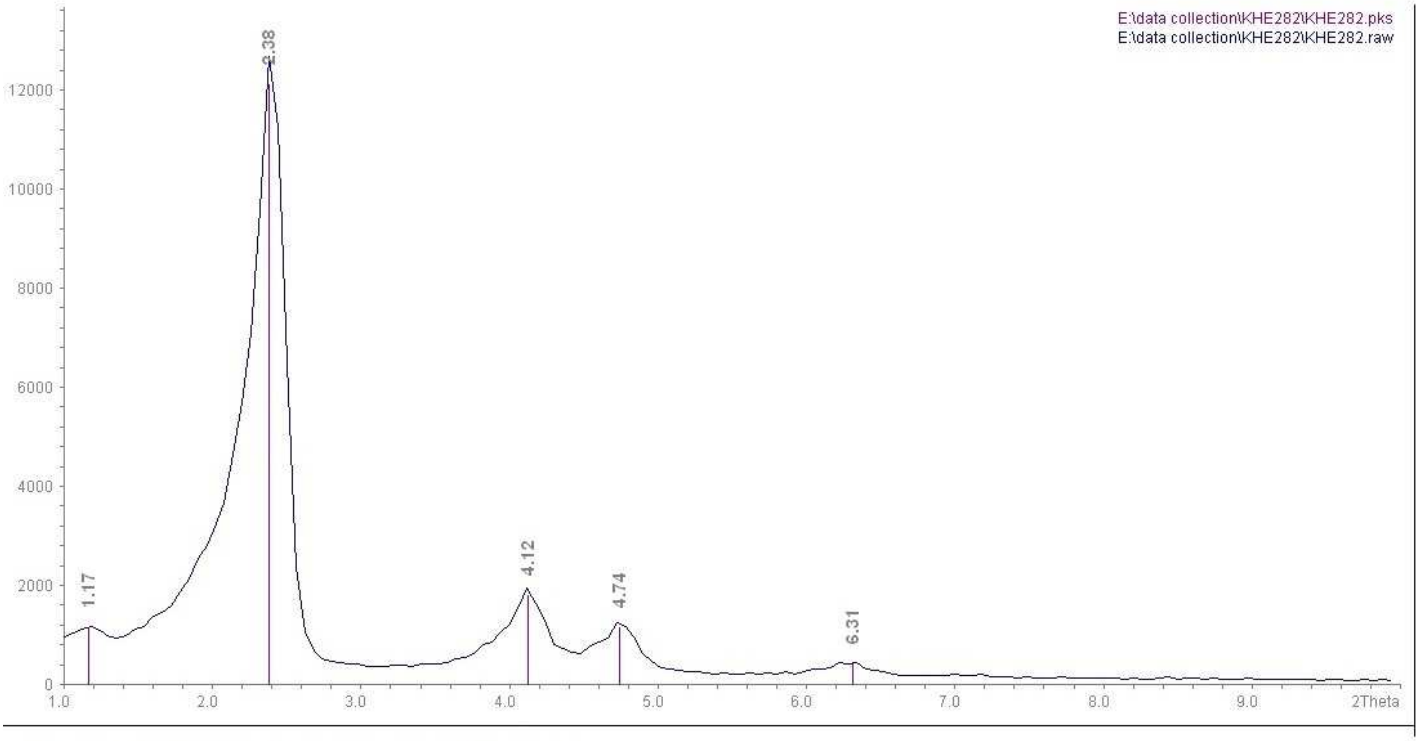
IR Spectrum of mesoporous SBA-15 before (A)and after (B) using in the asymmetric allylic oxidation



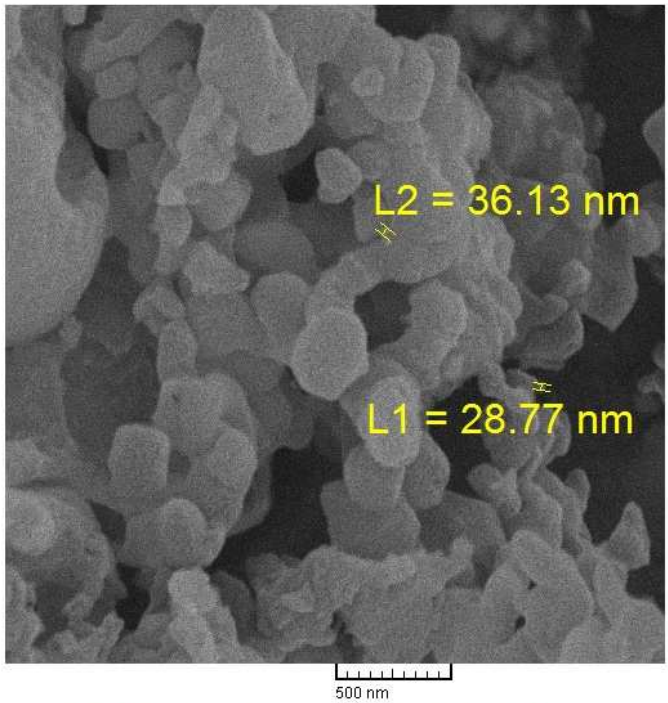
X-ray scattering of mesoporous SBA-15 before (A) and after (B) using in allylic oxidation reaction



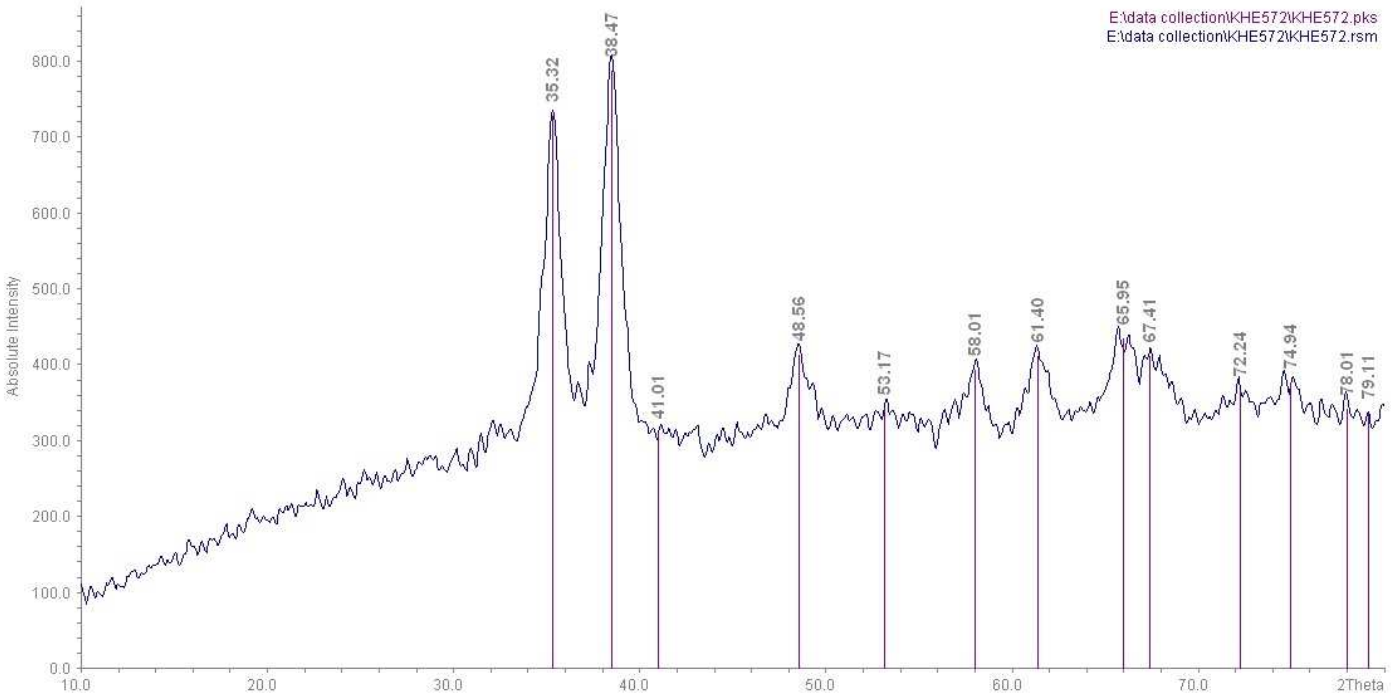
SEM image of mesoporous SBA-15 before (A) and after (B) using in allylic oxidation reaction



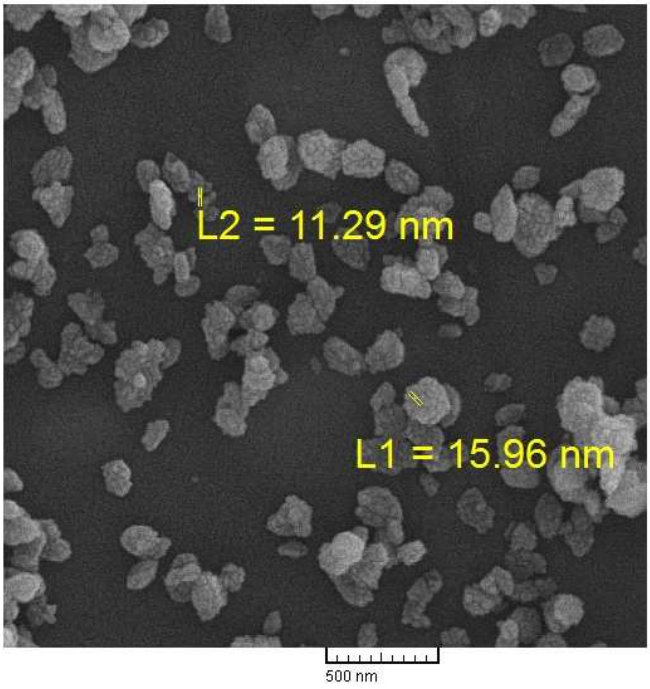
X-ray scattering of mesoporous MCM-41



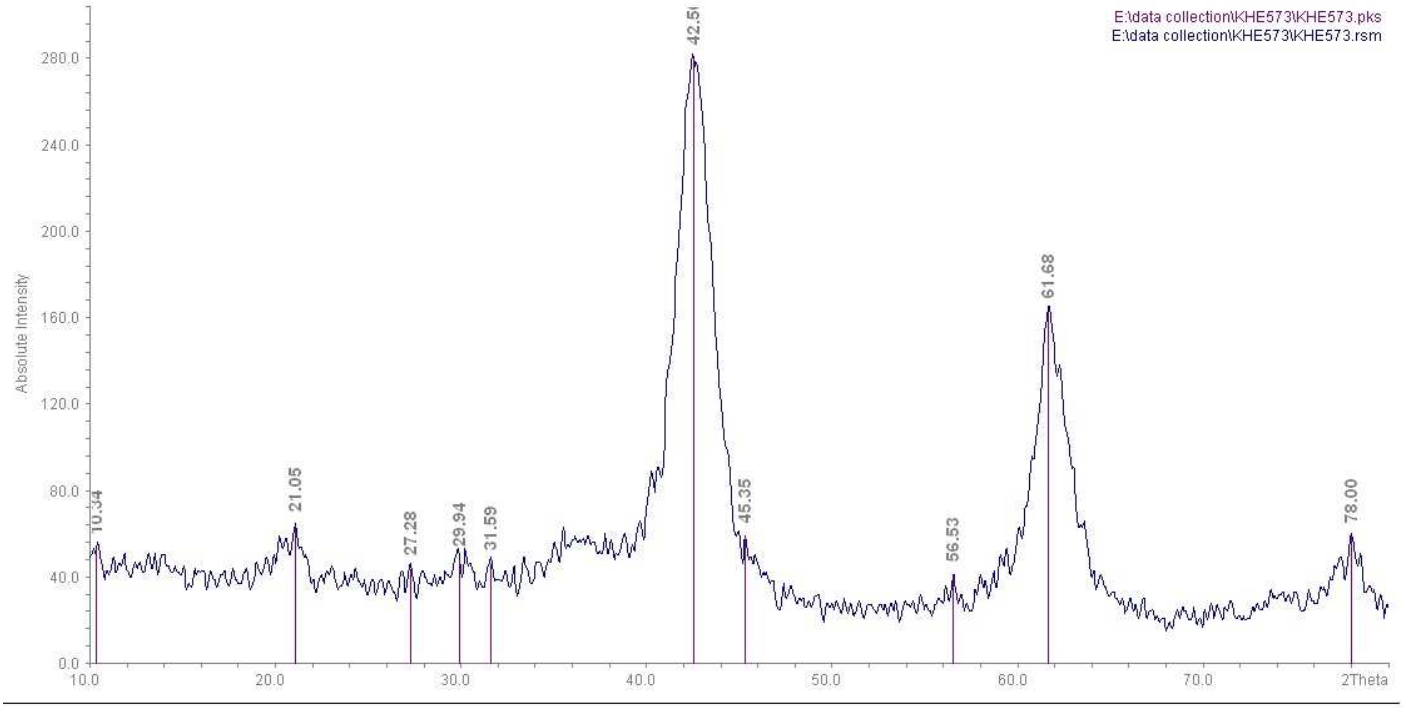
SEM image of mesoporous MCM-41



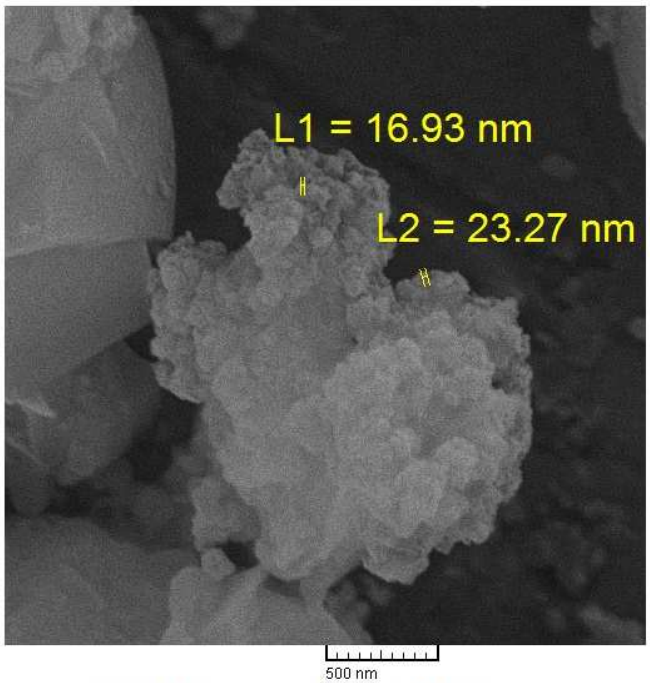
X-ray scattering of nanoCuO



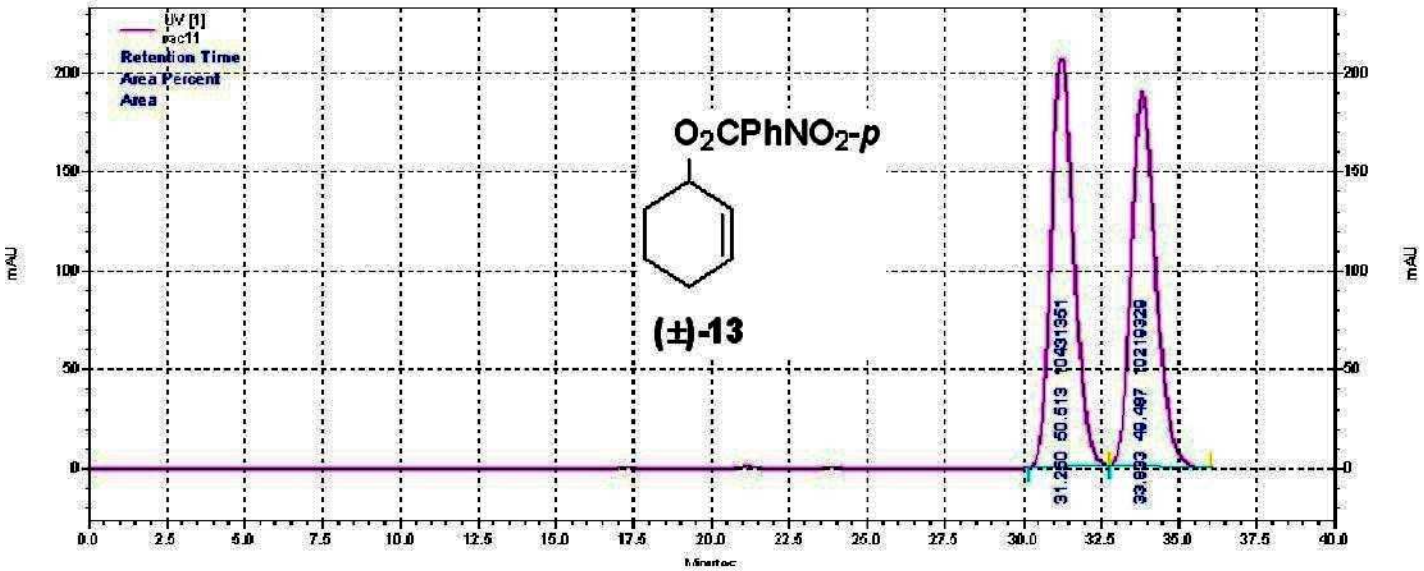
SEM image of nano CuO

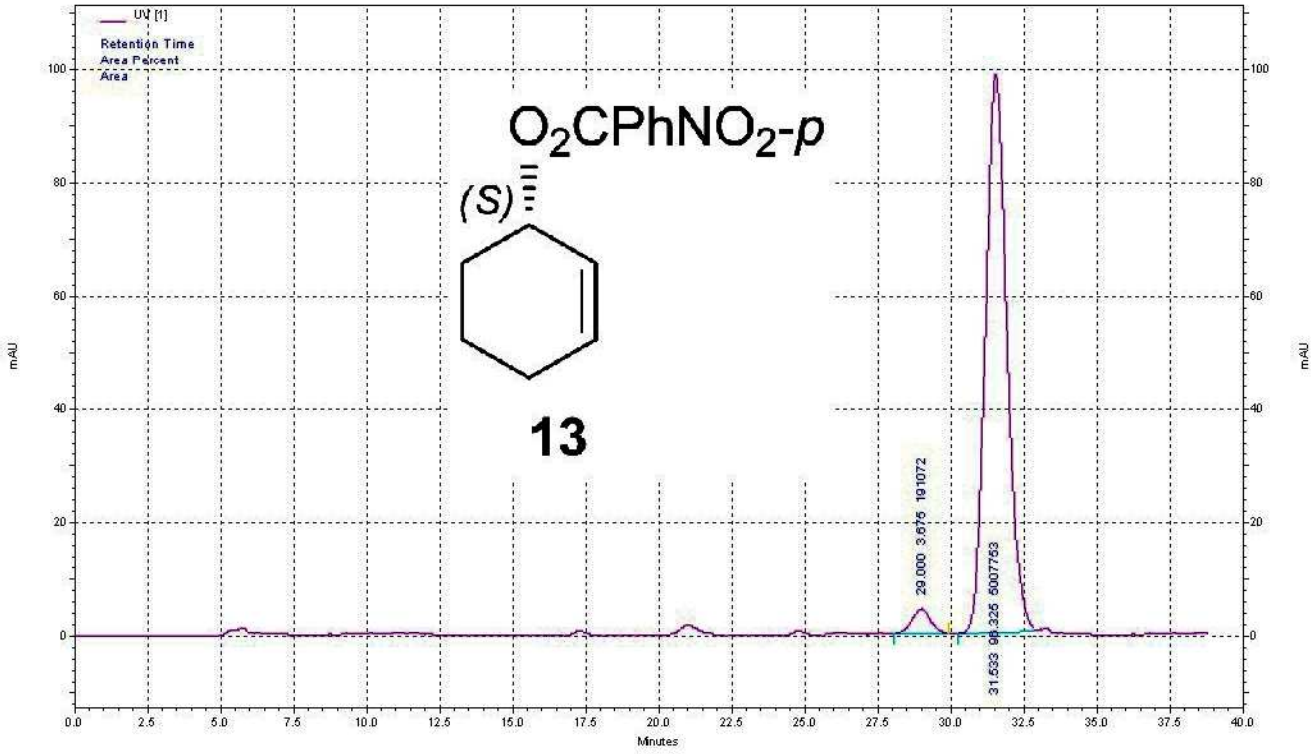


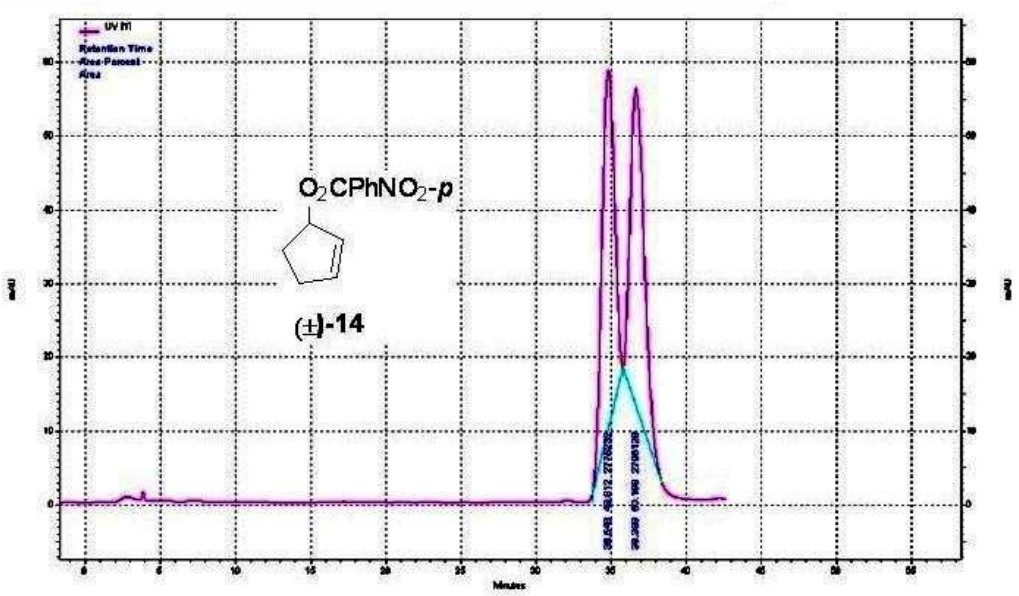
X-ray scattering of nanoMgO



SEM image of nano MgO


UV [1]
pac11
Retention Time
Area Percent
Area
O2CPhNO2-p
(±)-13
mAU
Minutes


UV [1]
Retention Time
Area Percent
Area
O2CPhNO2-p
(S)
13
mAU
Minutes


UV nm
Retention Time
Area Percent
Area
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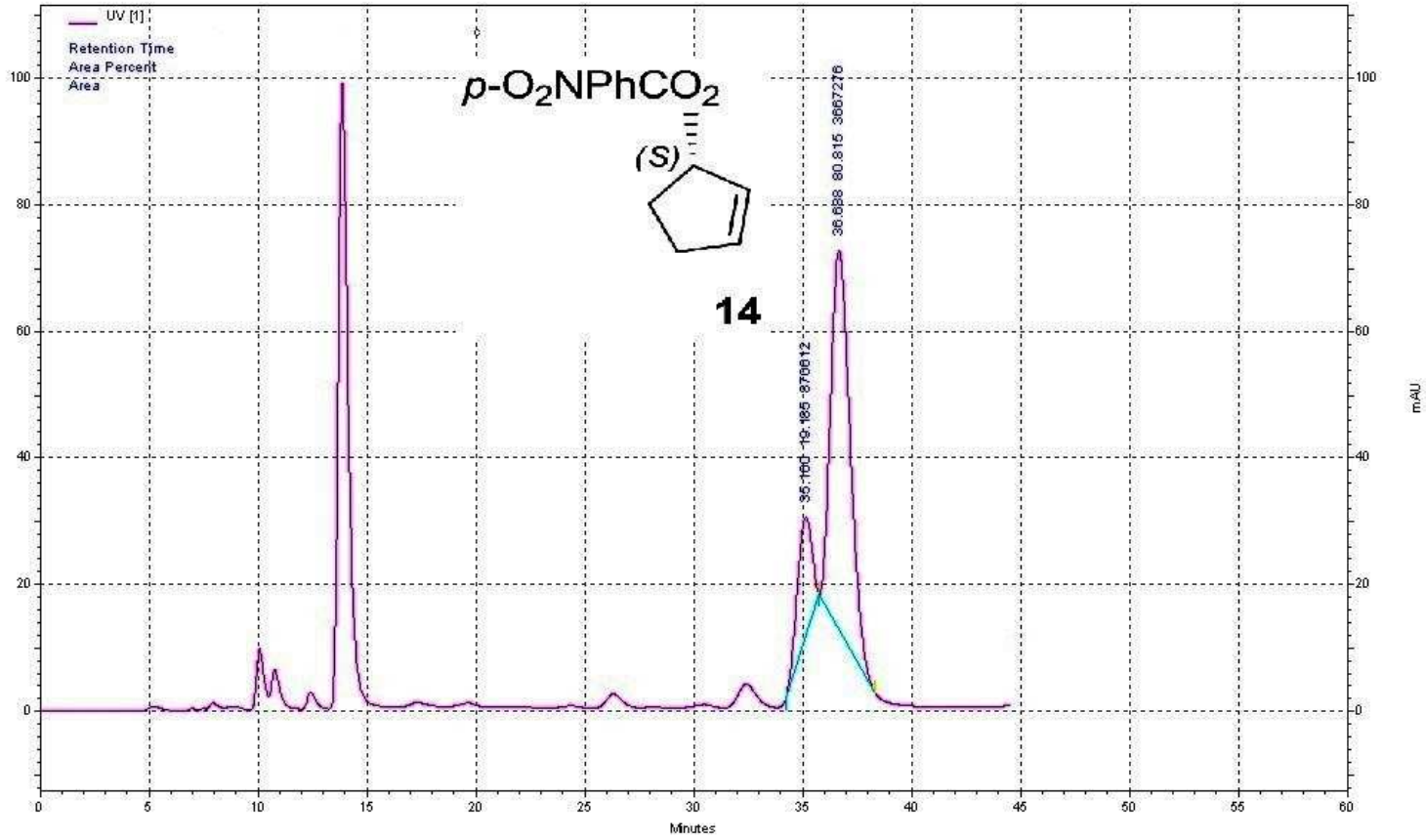
(±)-14
Minutes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Area Percent
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(S)
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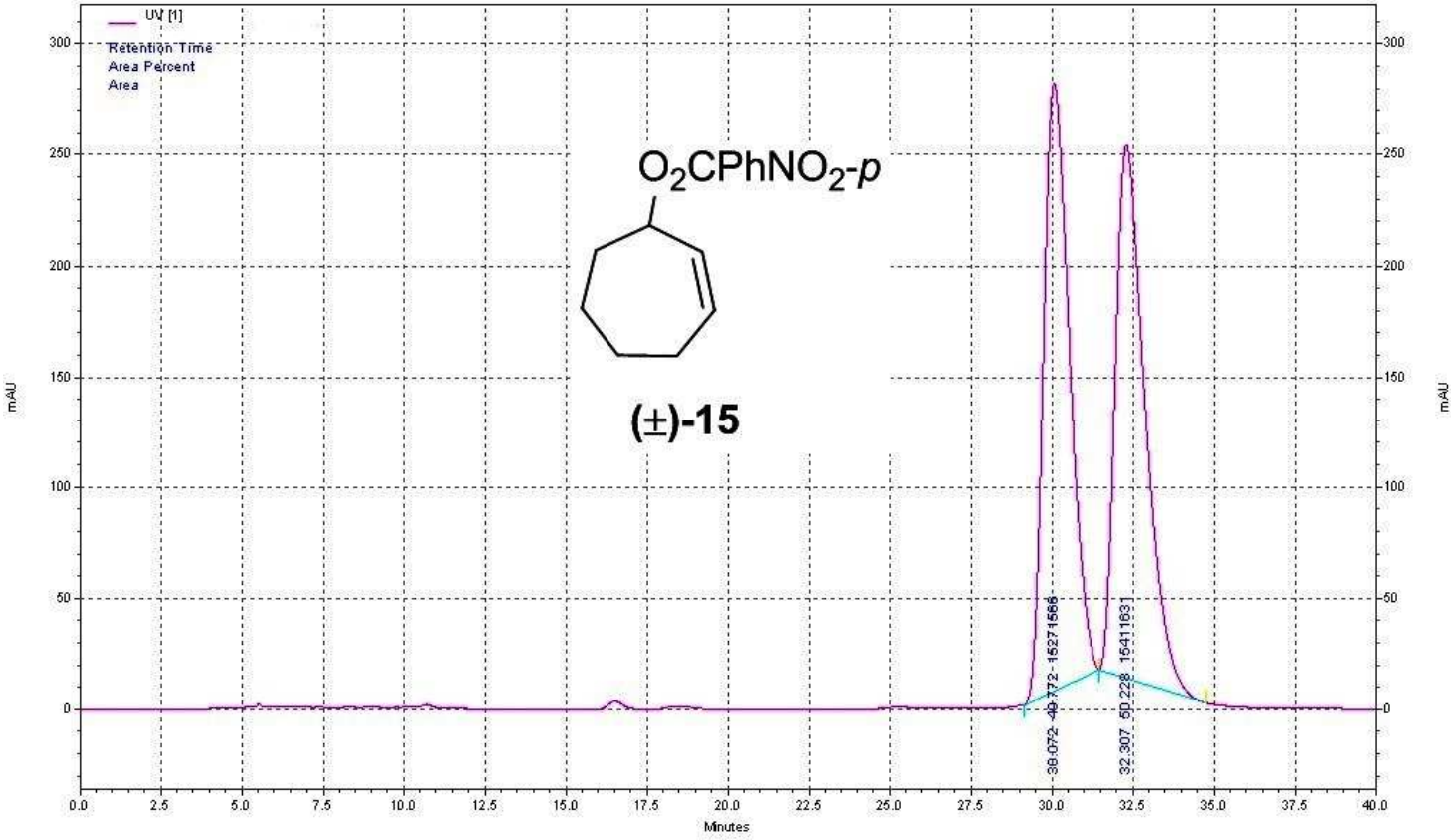
Minutes
mAU


UV [1]
Retention Time
Area Percent
Area
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(±)-15
mAU
Minutes
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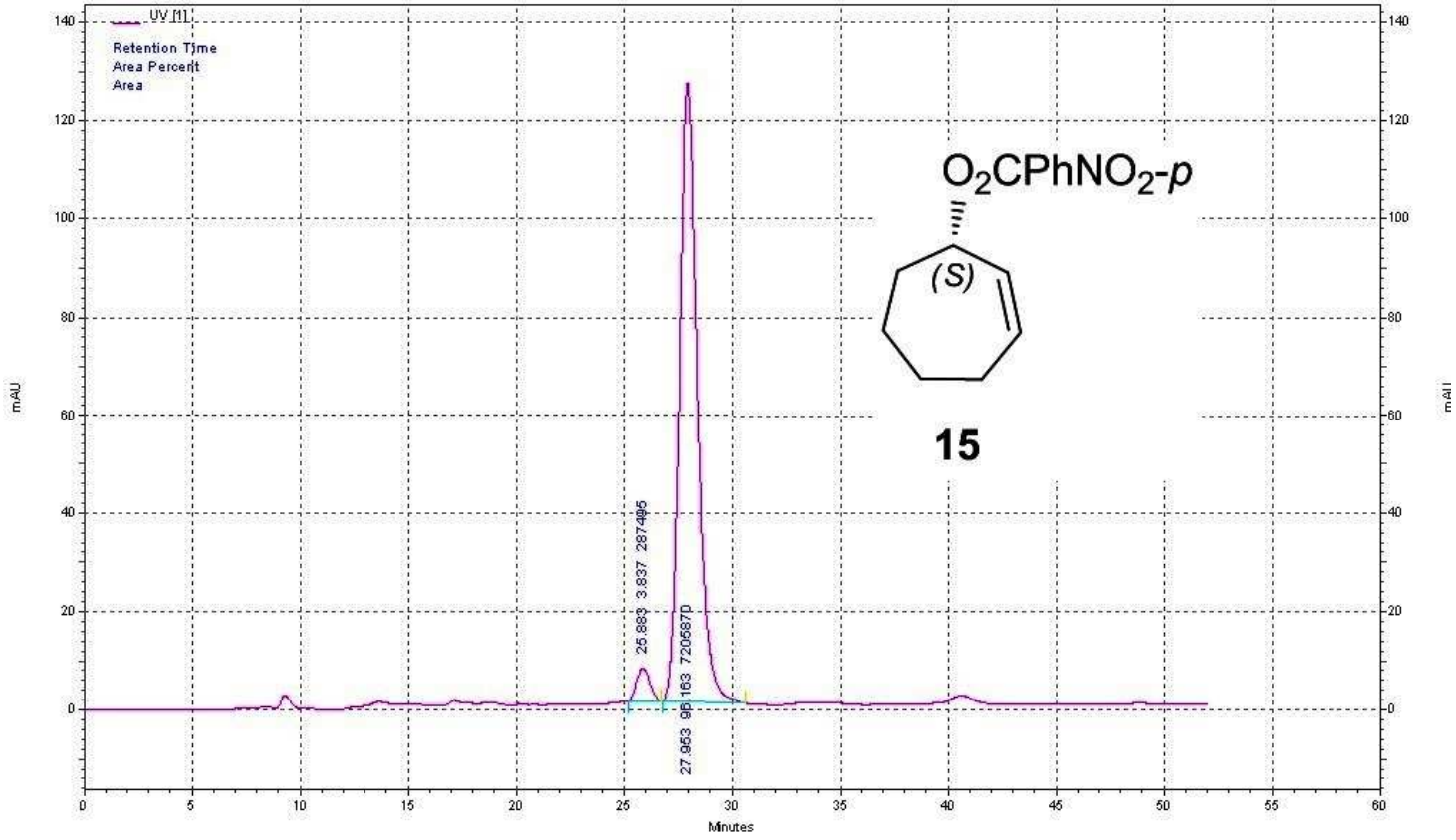
32.307 50.228 1541163


UV [1]
Retention Time
Area Percent
Area
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(S)
15
mAU
Minutes
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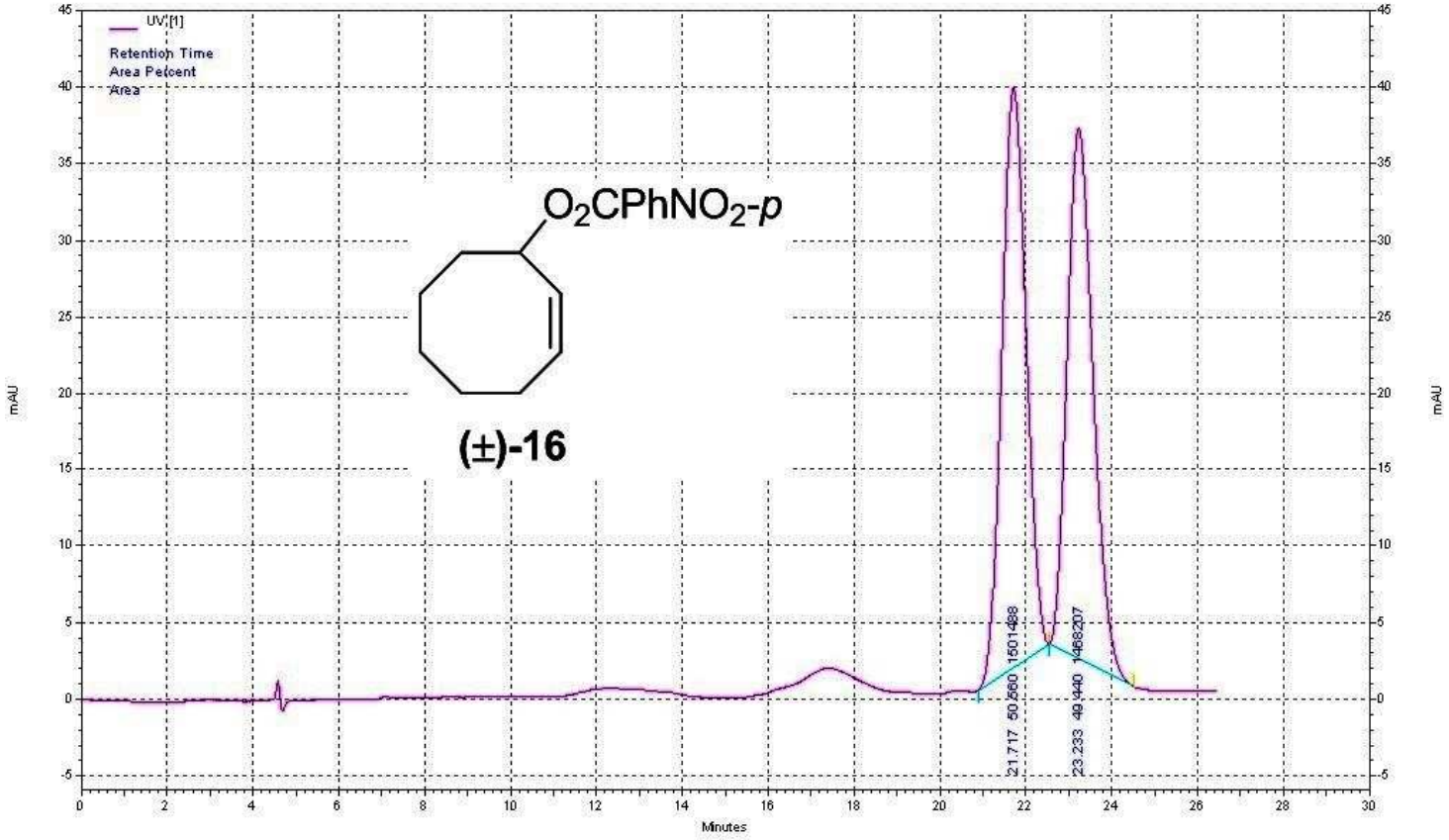
UV [1]
Retention Time
Area Percent
Area
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(±)-16
mAU
Minutes
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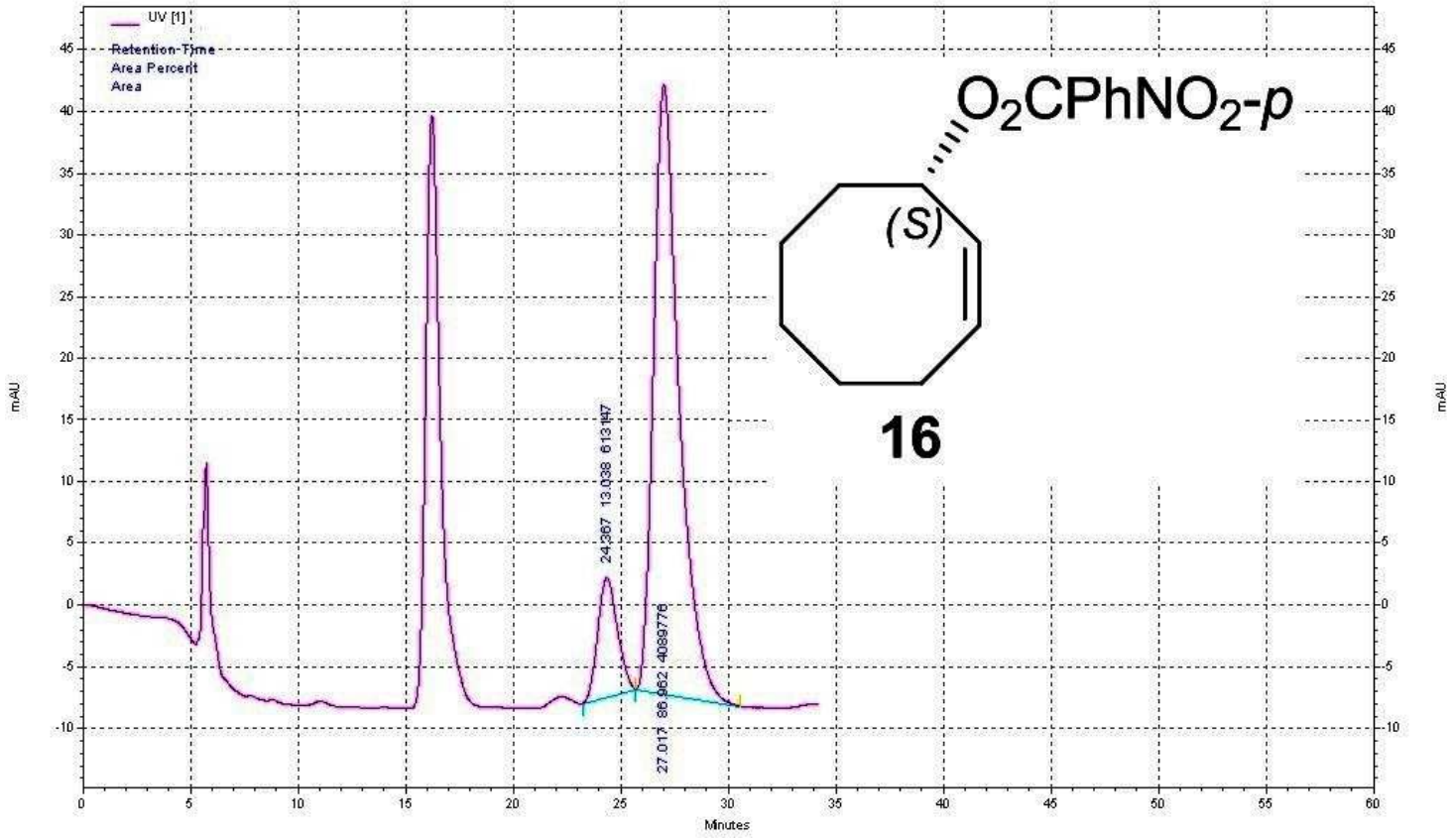
UV [1]
Retention Time
Area Percent
Area
O2CPhNO2-p
(S)
16
mAU
Minutes
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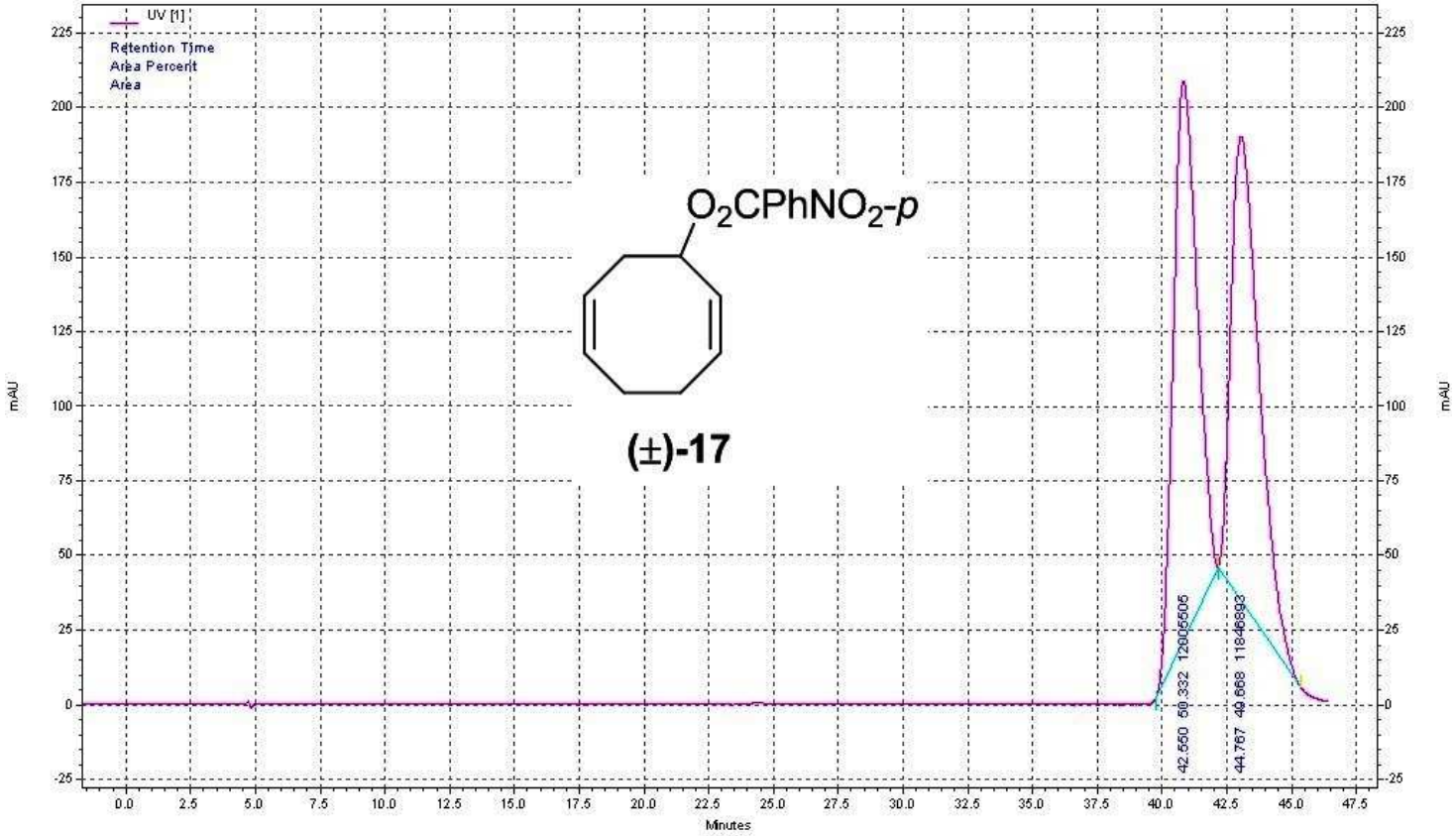
27.017 86.962 4089776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Retention Time
Area Percent
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(±)-17
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Minutes
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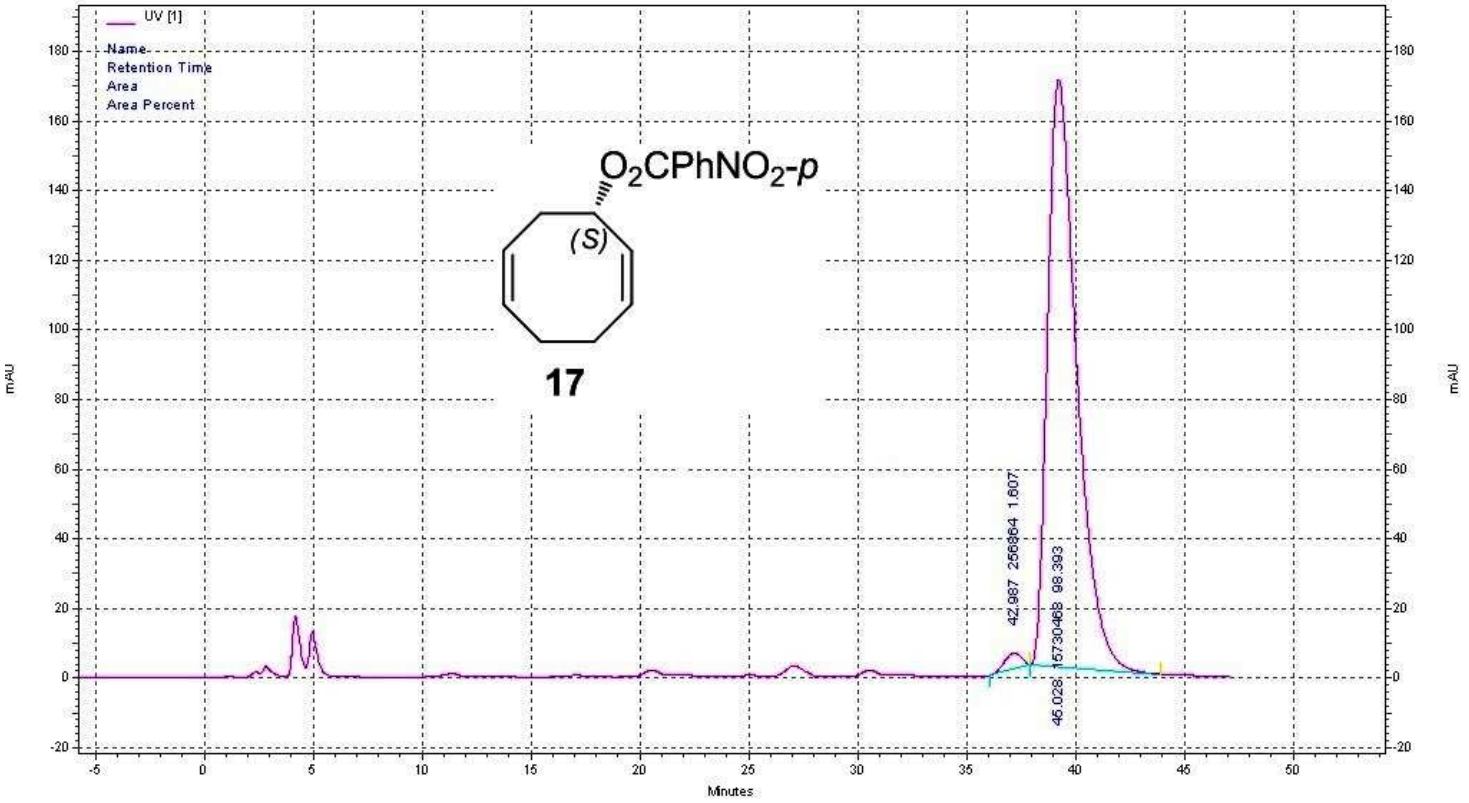
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Name
Retention Time
Area
Area Percent
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(S)
17
mAU
Minutes
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45.028 15730468 98.393

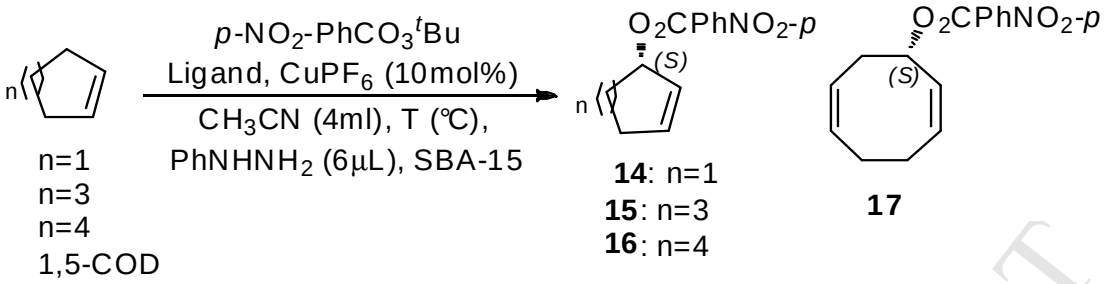

Table 6: Effect of ligand and temperature on other cycloolefins

Entry	Ligand	T (°C)	Time (h)	Yield (%)	Ee (%)	Time (h)	Yield (%)	Ee (%)	Time (h)	Yield (%)	Ee (%)	Time (h)	Yield (%)	Ee (%)
				14			**15**			**16**			**17**	
1	**1a**	25	4	95	56	8	99	43	10	94	30	1.5	99	62
2	**1a**	10	17	92	62	21	96	50	26	91	44	12	99	78
3	**1a**	0	36	90	67	44	92	60	61	88	53	30	98	85
4	**1a**	-10	100	90	81	80	94	93	150	84	70	46	95	97
5	**1b**	25	5	99	57	6	99	54	10	98	30	2	99	64
6	**1b**	10	18	94	65	17	94	61	52	93	42	10.5	95	73
7	**1b**	0	34	90	70	40	93	66	56	91	60	25	90	83
8	**1b**	-10	80	99	75	92	87	71	109	86	72	60	99	95
9	**1c**	25	6	97	14	11	95	8	17	85	2	4.5	90	9
10	**1c**	10	17	90	22	18	88	12	21	85	15	11	85	16
11	**1c**	0	32	88	24	36	81	21	55	60	20	38	85	34
12	**1c**	-10	95	84	39	110	79	28	140	32	20	90	80	37
13	**1d**	25	8	92	7	9	96	5	12	86	0	3.5	95	12
14	**1d**	10	13	88	18	20	92	11	28	63	3	14	90	21
15	**1d**	0	34	81	19	41	70	22	52	78	7	42	92	27
16	**1d**	-10	109	82	32	145	58	22	160	48	17	100	87	38