# *N*-Triflylthiophosphoramide Catalyzed Enantioselective Mukaiyama Aldol Reaction of Aldehydes with Silyl Enol Ethers of Ketones

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## 1. General Procedures

All reactions were carried out in oven- or flame-dried glassware under an atmosphere of dry argon unless otherwise noted. Except as otherwise indicated, all reactions were magnetically stirred and monitored by analytical thin layer chromatography (TLC) using Whatman pre-coated silica gel glass plates (0.25 mm) with F254 indicator or Merck pre-coated silica gel plates with F254 indicator. Visualization was accomplished by UV light (254 nm), with combination of potassium permanganate and/or phosphomolybdic acid solution as an indicator. Flash column chromatography was performed according to the method of Still using silica gel 60 (mesh 230-400) supplied by Silicycle. Yields refer to chromatographically and spectrographically pure compounds, unless otherwise noted.

Commercial grade reagents and solvents were used without further purification except as indicated below. Toluene (anhydrous, 99.8 %, 18 L in Pure-Pac$^{TM}$), dichloromethane (anhydrous, 99.9%, 18L in Pure-Pac$^{TM}$), hexanes (anhydrous, 99.9%, 18L in Pure-Pac$^{TM}$), and THF (anhydrous, 99.9%, 18L in Pure-Pac$^{TM}$) purchased from Aldrich were purified by M. BRAUN solvent purification system (A2 Alumina).

$^{1}$H NMR, $^{13}$C NMR, $^{19}$F NMR and $^{31}$P NMR spectra were recorded on a Bruker Avance 500 (500 MHz $^{1}$H, 125 MHz $^{13}$C, 471 MHz $^{19}$F, 202 MHz $^{31}$P). Tetramethylsilane was used as an internal standard for $^{1}$H NMR (δ: 0.0 ppm), $CDCl_3$ for $^{13}$C NMR (δ: 77.0 ppm), $CFCl_3$ for $^{19}$F NMR (δ: 0.0 ppm) as an external standard, and $H_3PO_4$ for $^{31}$P NMR (δ: 0.0 ppm) as an external standard. The proton spectra are reported as follows δ (position of proton, multiplicity, coupling constant *J*, number of protons). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), h (septet), m (multiplet) and br (broad). High performance liquid chromatography (HPLC) was performed on a Varian ProStar Series equipped with a variable wavelength detector using chiral stationary columns (0.46 cm x 25 cm) from Daicel. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter.

## 2. Synthesis of Chiral Brønsted Acids (1-3)

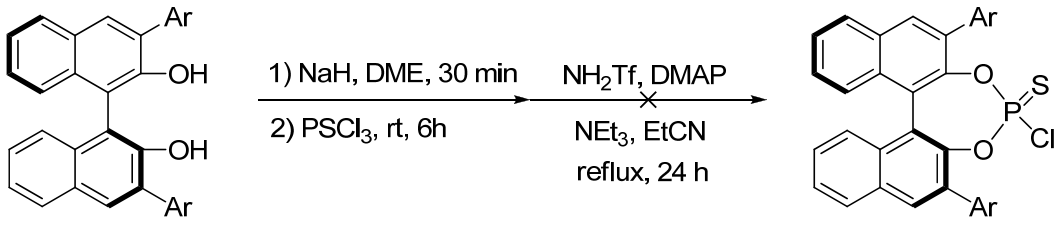
All *N*-triflylphosphoramide **1**,[1] *N*-trflylthiophosphoramides **2a-2d**,[2] and *N*-triflylselenophosphoramide **3**[2] were synthesized following the reported procedure.

### Synthesis of *N*-triflylthiosphosphoramide 2e

(*S*)-3,3'-Bis-(2,6-diisopropyl-4-(9-anthryl)-phenyl)-2,2'-dihydroxy-1,1'-dinaphthyl[3]

This compound was synthesized following the reported procedure and $^{1}$H NMR was in agreement with the literature. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 1.16 (d, *J* = 7.0 Hz, 6H), 1.22 (d, *J* = 6.5 Hz, 6H), 1.26 (d, *J* =7. 0 Hz, 6H), 1.31 (d, *J* = 6.5 Hz, 6H), 2.93-2.98 (m, 2H), 3.10-3.14 (m, 2H), 5.22 (s, 2H), 7.37-7.55 (m, 18H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 8.04-8.13 (m,8H), 8.55 (s, 2H).

Preparation of **2e** via thiophosphorylation followed by amidation sequence:

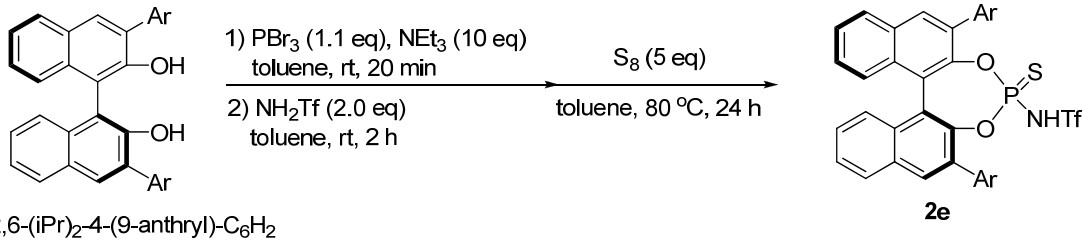



Ar = 2,6-(iPr)$_2$-4-(9-anthryl)-C$_6$H$_2$

Initial trial to synthesize *N*-triflylthiophosphoramide **2e** carrying very bulky 2,6-(*i*-Pr)$_2$-4-(9-anthryl)-phenyl group at the 3,3'-position of the binaphthyl scaffold was conducted by the same method for the previous synthesis of *N*-triflylthiosphosphoramide.[2] However, amidation between the resulting thiophosphoryl chloride and $NH_2Tf$ was very slow presumably due to steric effect of the bulky substituent at the 3,3'-position of the binaphthyl backbone and the thiophosphoryl chloride was obtained as a major product. Thus, we needed to develop other synthetic routes to synthesize thiosphosphoramide **2e**.

Preparation of **2e** via phosphorylation, amidation followed by oxidation**:**

In order to overcome the low reactivity in the amidation stop between the resulting thiophosphoryl chloride and $NH_2Tf$, we chose an alternative method: phosphorylation, amdiation, followed by oxidation as shown the above scheme.




Ar = 2,6-(iPr)$_2$-4-(9-anthryl)-C$_6$H$_2$

**2e**

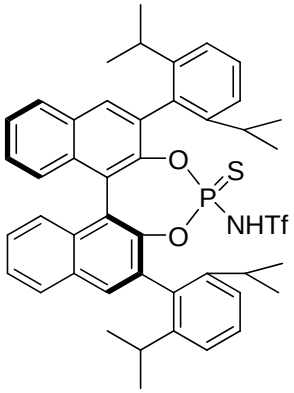
The procedure was as shown below: To a solution of (*S*)-3,3'-bis-(2,6-diisopropyl-4-(9-anthryl)-phenyl)-2,2'-dihydroxy-1,1'-dinaphthyl (0.582 g; 0,606 mmol; 1.0 eq) and $NEt_3$ (0.613 g; 6.06 mmol; 10 eq) was added $PBr_3$ (0.180 g; 0.667 mmol; 1.1 eq) dropwise. The reaction mixture was stirred for 20 min and monitored by $^{31}P$ NMR. After complete consumption of the starting material, $NH_2Tf$ (0.181 g; 1.21 mmol; 2.0 eq) was added to the reaction mixture and the reaction mixture was allowed to stir for additional 2 h. After complete comsumption of the resulting phosphoryl bromide, element sulfur was added to the reaction mixture and the reaction mixture was stirred for 24 h at 80 $^oC$. After 24 h, the reaction mixture was cooled to room temperature, quenched with $NaHCO_3$ (aq), extracted with ether (50 mL x 3), dried over $Na_2SO_4$, and concentrated. After purification by column chromatography on silica gel

(hexanes/EtOAc, 2/1), the product was re-dissolved in $Et_2O$ was washed with 4 N HCl (aq) twice, dried over anhydrous $Na_2SO_4$, and concentrated in vacuo. Foam-like pale brown solid was obtained in 65 % yield.

$^1$H NMR ($CDCl_3$, 500 MHz) δ: 0.97 (d, *J* = 6.7 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 1.16 (d, *J* = 6.7 Hz, 3H), 1.24 (d, *J* = 6.7 Hz, 2H), 1.29 (d, *J* = 6.4 Hz, 6H), 1.42-1.46 (m, 6H), 2.80-2.85 (m, 1H), 2.92-2.97 (m, 1H), 3.00-3.05 (m, 1H), 3.16-3.21 (m, 1H), 5.32 (s, 1H), 7.28-7.34 (m, 4H), 7.39-7.48 (m, 12H), 7.63 (t, *J* = 7.0 Hz, 2H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 8.03-8.11 (m, 6H), 8.24-8.27 (d, *J* = 17.0 Hz, 2H), 8.51-8.53 (d, *J* = 15.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 22.5, 23.3, 23.7, 23.8, 25.6, 25.8, 27.8, 30.8, 31.2,31.3, 31.9, 117.8, 120.5 (q, *J* = 60 Hz), 122.2, 122.8 (2C), 125.0, 125.1, 125.2, 125.3, 125.4 (2C), 125.5, 125.9, 126.4, 126.7 (2C), 126.8, 126.9, 127.0, 127.1 (2C), 127.2, 127.3, 127.4, 127.5, 126.6, 127.7, 128.1, 128.3, 128.5, 128.6, 128.7, 130.0, 130.2 (2C), 130.4, 130.8, 131.2, 131.4, 131.5, 131.6, 131.7, 132.3, 132,4 (2C). 133.2, 133.8, 134.3, 137.4, 138.4, 139.1, 139.9, 144.9, 145.0, 146.2, 146.4, 146.6, 147.4, 148.2, 149.3; $^{19}$F NMR ($CDCl_3$, 471 MHz) δ:-78.88; $^{31}$P NMR (202 MHz, $CDCl_3$) δ: 52.7; $[\alpha]_D^{27}$ = +36.9 (*c* 1.2, $CHCl_3$); MS (APCI) Exact mass calcd for $C_{73}H_{61}F_3NO_4PS_2$ (M-1): 1166.3 Found: 1166.2.

Other *N*-triflylthiophophoramides **2a** and **2d** were prepared by the same method for the synthesis of **2e**.

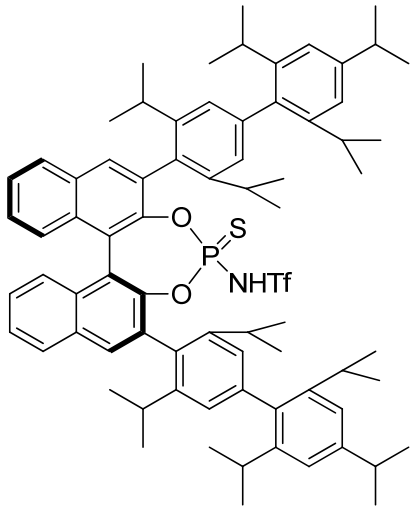
(*S*)-{3,3'-bis-(2,6-diisopropylphenyl)-1,1'-binaphthalen-2,2'-yl}-*N*-triflylthiophosphoramide **(2a)**




$^1$H NMR ($CDCl_3$, 500 MHz) δ: 0.82-0.83 (d, *J* = 6.8 Hz, 3H), 0.87-0.88 (d, *J* = 6.7 Hz, 3H), 1.16-1.27 (m, 12H), 1.30-1.35 (m, 6H), 2.66-2.72 (h, *J* = 7.0 Hz, 1H), 2.77-2.83 (h, *J* = 7.0 Hz, 1H), 2.95-3.00 (h, *J* = 7.0 Hz, 1H), 3.03-3.08 (h, *J* = 7.0 Hz, 1H), 7.08-7.09 (d, *J* = 8.0 Hz, 1H), 7.14-7.15 (d, *J* = 9.0 Hz, 1H), 7.18-7.20 (d, *J* = 8.0 Hz, 2H), 7.23-7.34 (m, 6H), 7.46-7.50 (m, 2H), 7.85 (s, 1H), 7.91-7.93 (m, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 21.2, 21.7, 23.6, 23.8, 25.1, 25.6, 27.0, 27.5, 29.8, 30.8, 30.9, 31.1, 117.8, 118.5 (q, *J* = 132 Hz), 121.9, 122.3 (2C), 122.6, 123.3, 123.7, 125.6, 125.7, 126.3, 126.4, 127.3, 128.3, 128.4 (2C), 128.5, 130.8, 130.9, 131.6, 132.3, 132.8, 132.9, 133.0, 134.4, 135.4, 145.6, 145.7, 147.1,

147.2, 148.3, 148.4, 148.7, 149.1; $^{19}$F NMR ($CDCl_3$, 471 MHz) δ:-78.84; $^{31}$P NMR (202 MHz, $CDCl_3$) δ: 64.2; $[\alpha]_D^{27}$ = +31.2 (*c* 1.0, $CHCl_3$); MS (APCI) Exact mass calcd for $C_{45}H_{45}F_3NO_4PS_2$ (M-1): 814.2 Found: 814.1.

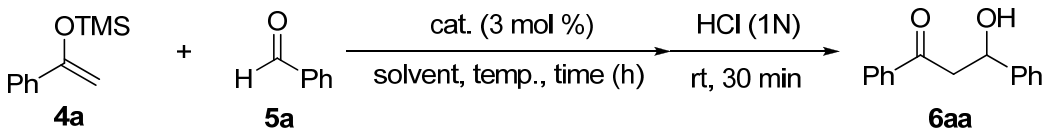
(*S*)-{3,3'-bis-(2,6-diisopropyl-4-(2,4,6-triisopropylphenyl)-phenyl)-1,1'-binaphthalen-2,2'-yl}-*N*-triflyl-thiophosphoramide **(2d)**




$^1$H NMR ($CDCl_3$, 500 MHz) δ: 0.76-0.77 (d, *J* = 7.0 Hz, 3H), 0.86-0.88 (d, *J* = 6.5 Hz, 3H), 1.00-1.02 (d, *J* = 7.0 Hz, 3H), 1.05-1.22 (m, 36H), 1.30-1.34 (m, 15H), 2.60-2.66 (h, *J* = 7.0 Hz, 2H), 2.70-2.78 (m, 3H), 2.92-2.98 (m, 3H), 3.04-3.10 (h, *J* = 7.0 Hz, 1H), 3.29-3.32 (h, *J* = 7.0 Hz, 1H), 7.03-7.05 (d, *J* = 9.5 Hz, 4H), 7.09-7.12 (m, 5H), 7.16 (s, 1H), 7.26-7.28 (m, 2H), 7.47-7.50 (t, *J* = 7.0 Hz, 2H), 7.86 (s, 1H), 7.93-7.96 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 22.2, 23.7, 24.0, 24.1, 24.2 (3C), 24.4, 24.5, 24.6 (2C), 25.0, 26.6, 27.2, 30.4, 30.5 (3C), 30.6, 30.7, 30.8, 30.9 (2C), 34.4, 119.3 (q, *J* = 272 Hz), 120.8, 120.9, 122.2 (2C), 123.3 (2C), 123.4 (2C), 124.2, 124.3, 124.9, 125.6, 125.6 (2C), 126.4 (2C), 127.1, 127.2, 128.2, 128.3, 130.8, 131.1, 131.6 (2C), 132.4 (2C), 132.8, 133.1, 133.2, 137.8, 137.9, 140.6, 146.5, 146.6, 146.8, 146.9, 147.5, 147.6, 147.7, 147.8, 147.9, 148.1; $^{19}$F NMR ($CDCl_3$, 471 MHz) δ:-78.50; $^{31}$P NMR (202 MHz, $CDCl_3$) δ: 62.0; $[\alpha]_D^{27}$ = +36.4 (*c* 1.0, $CHCl_3$); MS (APCI) Exact mass calcd for $C_{75}H_{89}F_3NO_4PS_2$ (M-1): 1218.59 Found: 1218.58.

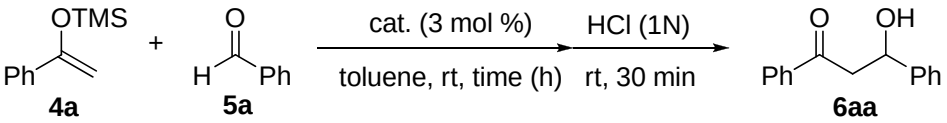
## 3. Catalytic Asymmetric Mukaiyama Aldol Reactions of Aldehydes and Silyl Enol Ethers of Ketones

### 3-1. Optimization of Reaction Condition




**General Procedures:** To a solution of benaldehyde **5a** (0.10 mmol; 10.6 mg; 1.0 eq) and chiral Brønsted source (0.03 eq) was added silyl enol ether of acetophenone **4a** (0.11 mmol; 21.1 mg; 1.1 eq) dropwise. The reaction mixture was monitored by TLC. When benzaldehyde **5a** was completely consumed, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with ether. The resulting aldol product was dissolved in ether and treated with 1 N HCl to deprotect the silyl ether. After the deprotection was over, the reaction mixture was extracted with ether. The organic layer was combined, washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated. The residue was purified by flash column chromatography (EtOAc/hexanes, 1/5) on silica gel. Enantiomeric ratio (e.r.) was determined by HPLC with a chiral OD-H column.

#### 3-1-1. Reactivity Comparison



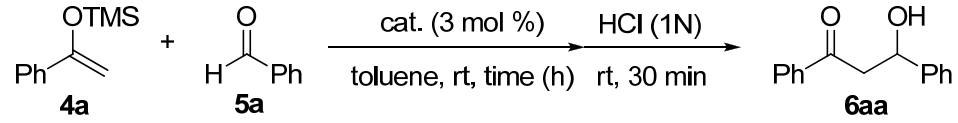

| entry | cat. | time (h) | yield (%)[a] | er[b] |
|---|---|---|---|---|
| 1 | **1** | 48 | N, R. | N. D. |
| 2 | **2b** | 1 | 96 | 56.5:43.5 |
| 3 | **3** | 1 | 93 | 55:45 |

[a] Isolation yield after column chromatography separation.
[b] Enantiomeric ratio (er) was determined using chiral HPLC using a chiral OD-H column.

The reactivities of oxo-, thio-, and seleno-phosphoramides **1-3** were compared in enantioselective Mukaiyama aldol reaction of benzaldehyde **5a** with silyl enol ether of acetophenone **4a**. Unlike the previous protonation reaction,[2] the reactivities of these acids showed dramatic difference in Mukaiyama aldol reaction. Thio- and seleno-phosphoramides **2b** and **3** afforded the desired aldol product **6aa** in excellent yields, whereas oxophosphoramide **1** did not give any product. In addition, thiophosphoramide

**2b** gave slightly better enantioselectivity than selenophosphoramide **3**. Thus, thiophosphoramide **2** was chosen for the further investigation of enantioselective Mukaiyama aldol reaction.

### 3-1-2. Effect of Substituents at 3,3'-Position of Binaphthyl Backbone

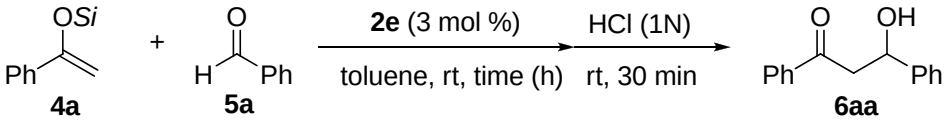



| entry | cat. | time (h) | yield (%)[a] | er[b] |
|---|---|---|---|---|
| 1 | **2a** | 1 | 94 | 54:46 |
| 2 | **2b** | 1 | 96 | 57:43 |
| 3 | **2c** | 1 | 93 | 57:43 |
| 4 | **2d** | 1 | 94 | 65:35 |
| 5 | **2e** | 1 | 96 | 67:33 |

[a] Isolation yield after column chromatography separation.
[b] Enantiomeric ratio (er) was determined using chiral HPLC using a chiral OD-H column.

We tried to optimize the catalyst structure. Although all the thiophosphoramides **2a-e** provided the aldol product **6aa**, the enantioselectivities highly depended on the size of the aryl substituents at the 3,3'-position of the binaphthyl backbone. Particularly, the enantioselectivity increased with the size of *para*-substituent at the aryl substituent at the 3,3'-position of the binaphthyl backbone.[2-5] Thiophosphoramide **2e** carrying bulky 9-anthryl substituent at the *para*-position of the aryl substituent gave the aldol product in 67:33 er.

### 3-1-3. Effect of Size of Silyl Groups

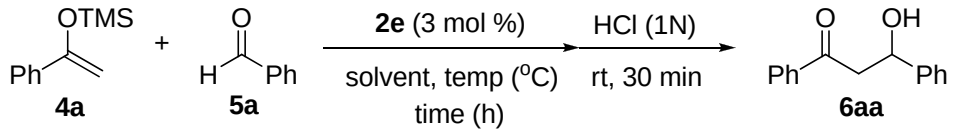



| entry | *Si* | time (h) | yield (%)[a] | er[b] |
|---|---|---|---|---|
| 1 | **TMS** | 1 | 94 | 67:34 |
| 2[c] | **TBS** | 2 | 96 | 56:14 |
| 3 | **PMDS** | 2 | 93 | 64:36 |
| 4[d] | **TIPS** | 4 | 87 | 59:41 |

[a] Isolation yield after column chromatography separation.
[b] Enantiomeric ratio (er) was determined using chiral HPLC using a chiral OD-H column.
[c] Deprotection of the aldol product was carried out at room temperature for 3 h.
[d] TBAF was used for removal of the TIPS ether of the aldol adduct.

We further investigated the effect of size of silyl groups on enantioselectivity. Although reactivity did not show significant dependence on the silyl groups, enantioselectivity exhibited strong dependence on the size of the silyl group. As the size of silyl group increased, the enantioselectivity decreased: Among silyl groups tested, TMS silyl enol ether of acetophenone gave the best enantioselectivity, and thus we chose the TMS group for the future investigation.

**3-1-4. Further optimization**



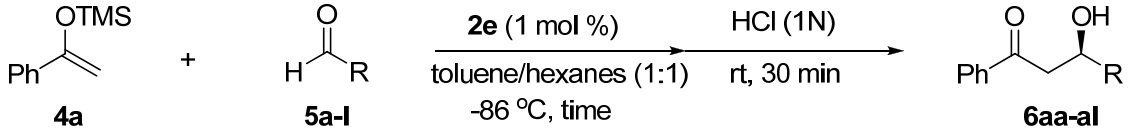

| entry | solvent | temp (°C) | time (h) | yield (%)[a] | er[b] |
|---|---|---|---|---|---|
| 1 | toluene | rt | 1 | 94 | 67:34 |
| 2 | toluene | -78 | 6 | 93 | 87:13 |
| 3 | $CH_2Cl_2$ | -78 | 4 | 95 | 62:38 |
| 4 | hexanes | -78 | 8 | N. R. | N. D. |
| 5 | toluene | -86 | 12 | 94 | 89:11 |
| 6 | toluene/hexanes | -86 | 12 | 97 | 92:8 |
| 7[c] | toluene/hexanes | -86 | 12 | 96 | 92:8 |

[a] Isolation yield after column chromatography.
[b] Enantiomeric ratio (er) was determined by HPLC using a chiral OD-H column.
[c] 1 mol % of catalyst was used.

Then, we attempted to optimize the reaction conditions, such as temperature and solvent. The enantioselectivity highly depended on the temperature. Enantioselectivity increased from 67:33 to 87:13 er when reaction was carried out at -78 °C (entry 2). Then, we screened solvent. Dichloromethane gave significantly lower enantioselectivity (62:38 er vs 87:13 er), although it increased the reactivity (4 h vs 6 h) (entry 3). The reaction did not proceed at all in hexanes presumably poor solubility of catalyst **2e** (entry 4). Then we tried to increase the enantioselectivity further by decreasing reaction temperature. The enantioselectivity could be improved to 89:11 er at -86 °C (entry 5). It could further increase up to 92:8 er

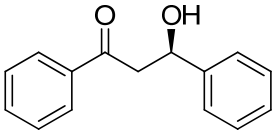
in the 1:1 mixture of toluene and hexanes (entry 6). To our delight, the catalyst loading could be decreased to 1 mol % without any loss of enantioselectivity (entry 7).

### 3-2. Enantioselective Mukaiyama Aldol Reaction of Aldehydes with Silyl Enol Ether of Acetophenone

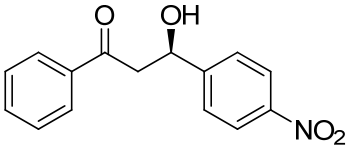



**General procedure:** To a solution of aldehyde (0.10 mmol; 1.0 eq) in toluene/hexanes (1:1 (v/v), 0.5 mL) was added chiral Brønsted acid **2e** (1.2 mg; 0.001 mmol; 0.01 eq) in toluene/hexanes (1:1 (v/v), 0.5 mL) at room temperature. The mixture was stirred for 30 min at room temperature and them cooled to -86 $^{o}$C. Silyl enol ether of acetophenone **4a** (0.11 mmol; 21.1 mg; 1.1 eq) was added dropwise to the reaction mixture at -86 $^{o}$C and the reaction mixture was monitored by TLC. When the aldehyde was completely consumed, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with ether. The resulting aldol product was dissolved in ether and treated with 1 N HCl to deprotect the silyl ether. After deprotection was over, the reaction mixture was extracted with ether. The organic layer was combined, washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated. The residue was purified by flash column chromatography (EtOAc/hexanes, 1/5) on silica gel. Enantiomeric ratio (e.r.) was determined by HPLC with a chiral column.

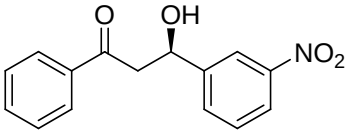
#### 3-2-1. Characterization of Compounds 6aa-6al



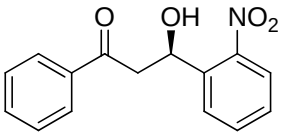

The product (**6aa**)[6] was obtained as a white solid in 95 % yield and 92:8 er. $^1$H NMR ($CDCl_3$, 500 MHz) δ: 3.38-3.39 (d, *J* = 8.0 Hz, 2H), 3.59 (d, *J* = 3.0 Hz, 1H), 5.34-5.37 (td, *J* = 6.0 Hz, 2.0 Hz, 1H), 7.29-7.32 (t, *J* = 7.5 Hz, 1H), 7.37-7.40 (t, *J* = 8.0 Hz, 2H), 7.44-7.48 (m, 4H), 7.57-7.61 (t, *J* = 8.0 Hz, 1H), 7.95-7.97 (d, *J* = 9.0 Hz, 2H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 47.5, 70.2, 125.9, 127.8, 128.3, 128.7, 128.8, 133.8, 136.7, 143.1. 200.3. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes:2-propanol = 90:10, flow rate = 1.0 mL/min, λ= 254 nm), $t_r$(major, *R*) = 11.3 min., $t_r$(minor, *S*) = 10.5 min. $[\alpha]_D^{27}$ = +60.8 (*c* 1.0, $CHCl_3$) (Lit. $[\alpha]_D^{20}$ = +60 (*c* 0.83, $CHCl_3$) for (*R*) enantiomer (85:15 er)).



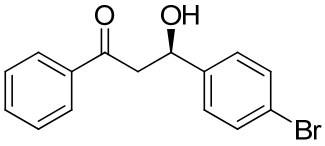

The product (**6ab**)[6] was obtained as a white solid in 94 % yield and 96:4 er. $^1$H NMR ($CDCl_3$, 500 MHz) δ: 3.31-3.43 (m, 2H), 3.87 (d, *J* = 3.0 Hz, 1H), 5.44-5.47 (dt, *J* = 9.0, 3.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.61-7.63 (m, 3H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 2H), 8.22 (dt, *J* = 8.0, 2.0 Hz, 2H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 47.1, 69.3, 123.9, 126.7, 128.3, 128.9, 134.1, 136.3, 147.4, 150.4, 199.6. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel AD-H column equipped with an AD-H guard column (hexanes:2-propanol = 80:20, flow rate = 1.0 mL/min, λ= 254 nm), $t_r$(major, *R*) = 13.7 min., $t_r$(minor, *S*) = 11.3 min. $[\alpha]_D^{27}$ = +52.3 (*c* 1.0, $CHCl_3$) (Lit. $[\alpha]_D^{20}$ = +27 (*c* 2.88, $CHCl_3$) for (*R*) enantiomer (73:27 er)).



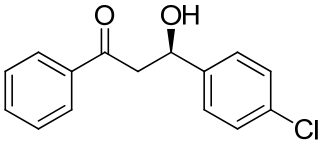

The product (**6ac**)[6] was obtained as a white solid in 96 % yield and 94:6 er. $^1$H NMR ($CDCl_3$, 500 MHz) δ: 3.34-3.47 (m, 3H), 3.85 (d, *J* = 2.5 Hz, 1H), 5.45 (d, *J* = 9.0 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 6.8 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 2H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.33 (s, 1H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 47.1, 69.2, 121.0, 122.7, 128.3, 129.0, 129.7, 132.1, 134.1, 136.3, 145.2, 148.6, 199.7. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel AS-H column equipped with an AS-H guard column (hexanes:2-propanol = 90:10, flow rate = 1.0 mL/min, λ= 254 nm), $t_r$(major, *R*) = 35.7 min., $t_r$(minor, *S*) = 27.9 min.. $[\alpha]_D^{27}$ = +60.2 (*c* 1.0, $CHCl_3$).



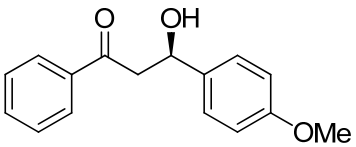

The product (**6ad**)[7] was obtained as a white solid in 91 % yield and 94:6 er. $^1$H NMR ($CDCl_3$, 500 MHz) δ: 3.18-3.24 (dd, *J* = 18, 9.6 Hz, 1H), 3.69-3.73 (dd, *J* = 15 Hz, 2.5 Hz, 1H), 4.00 (d, *J* = 3.0 Hz, 1H), 5.85-5.87 (dt, *J* = 7.5 Hz, 3.0 Hz, 1H), 7.45-7.49 (m, 3H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.96-8.00 (m, 4H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 46.6, 66.1, 124.6, 128.4, 128.5, 128.6, 128.9, 134.0, 136.5, 138.7, 147.4, 200.1. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel AS-H column equipped with an AS-H guard column (hexanes:2-propanol = 90:10, flow rate = 1.0 mL/min, λ= 254 nm), $t_r$(major, *R*) = 36.1 min., $t_r$(minor, *S*) = 28.6 min.. $[\alpha]_D^{27}$ = -58.0 (*c* 1.0, $CHCl_3$).



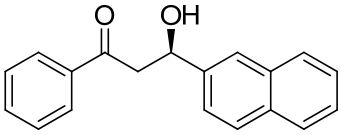

The product (**6ae**)[8] was obtained as a white solid in 92 % yield and 91:9 er. $^1$H NMR ($CDCl_3$, 500 MHz) δ: 3.33-3.35 (m, 2H), 5.30-5.32 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.31-7.33 (d, *J* = 8.0 Hz, 2H), 7.46-7.52 (m, 4H), 7.58-7.61 (t, *J* = 8.0 Hz, 1H), 7.93-7.96 (dd, J = 8.5 Hz, 1.5 Hz, 2H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 47.3, 69.5, 121.5, 127.6, 128.3, 128.9, 131.7, 133.9, 136.5, 142.1. 200.0. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes:2-propanol = 90:10, flow rate = 1.0 mL/min, λ= 254 nm), $t_r$(major, *R*) = 16.2 min., $t_r$(minor, *S*) = 13.7 min.. $[\alpha]_D^{27}$ = +41.1 (*c* 1.0, $CHCl_3$).



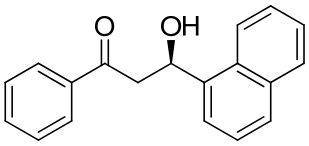

The product (**6af**)[6] was obtained as a white solid in 93 % yield and 90:10 er. $^1$H NMR ($CDCl_3$, 500 MHz) δ: 3.33-3.37 (m, 2H), 5.32-5.34 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.35-7.40 (m, 4H), 7.46-7.49 (t, *J* = 7.5 Hz, 2H), 7.59-7.62 (t, *J* = 7.5 Hz, 1H), 7.94-7.96 (d, *J* = 8.0 Hz, 2H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 47.4, 69.5, 127.3, 128.3, 128.8, 128.9, 133.5, 133.9, 136.5, 141.5. 200.1. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel AD-H column equipped with an AD-H guard column (hexanes:2-propanol = 90:10, flow rate = 1.0 mL/min, λ= 254 nm), $t_r$(major, *R*) = 18.4 min., $t_r$(minor, *S*) = 15.1 min.. $[\alpha]_D^{27}$ = +47.3 (*c* 1.0, $CHCl_3$).



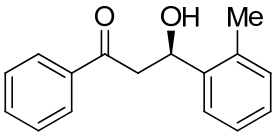

The product (**6ag**)[8] was obtained as colorless oil in 96 % yield and 92:8 er. $^1$H NMR ($CDCl_3$, 500 MHz) δ: 3.36-3.38 (m, 2H), 3.51 (d, *J* = 3.0 Hz, 1H), 3.82 (s, 3H), 5.30 (m, 1H), 6.91-6.93 (d, *J* = 8.0 Hz, 2H), 7.36-7.38 (d, *J* = 8.0 Hz, 2H), 7.45-7.49 (t, *J* = 8.0 Hz, 2H), 7.58-7.60 (t, *J* = 7.5 Hz, 1H), 7.95-7.97 (dd, *J* = 8.0 Hz, 1.0 Hz, 2H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 47.5, 55.4, 69.8, 114.1, 127.2, 128.3, 128.8, 133.7, 135.3, 136.7, 159.2, 200.4. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes:2-propanol = 90:10, flow rate = 1.0 mL/min, λ= 254 nm), $t_r$(major, *R*) = 21.3 min., $t_r$(minor, *S*) = 17.0 min.. $[\alpha]_D^{27}$ = +50.6 (*c* 1.0, $CHCl_3$).



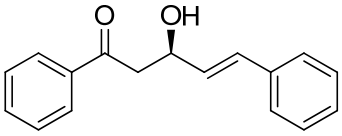
The product (**6ah**)[6] was obtained as a white solid in 94 % yield and 90:10 er. $^{1}$H NMR ($CDCl_3$, 500 MHz) δ: 3.42-3.49 (m, 2H), 3.73 (d, *J* = 2.5 Hz, 1H), 5.52-5.55 (m, 1H), 7.46-7.53 (m, 4H), 7.54-7.56 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 7.59-7.62 (t, *J* = 7.5 Hz, 1H), 7.84-7.88 (m, 3H), 7.92 (s, 1H), 7.97-7.99 (dd, *J* = 8.5 Hz, 1.0 Hz, 2H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 47.5, 70.3, 124.0, 124.6, 126.1, 126.4, 127.8, 128.2, 128.3, 128.5, 128.9, 133.1, 133.5, 133.9, 136.9, 140.4, 200.3. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes:2-propanol = 95:5, flow rate = 1.0 mL/min, λ= 225 nm), $t_r$(major, *R*) = 55.8 min., $t_r$(minor, *S*) = 52.3 min.. $[\alpha]_D^{27}$ = +48.4 (*c* 1.0, $CHCl_3$).



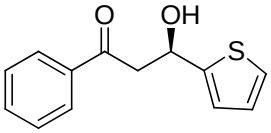
The product (**6ai**)[6] was obtained as a white solid in 95 % yield and 81:19 er. $^{1}$H NMR ($CDCl_3$, 500 MHz) δ: 3.45-3.51 (dd, J = 18.0 Hz, 9.5 Hz, 1H), 3.56-3.60 (dd, J = 18.0 Hz, 2.0 Hz, 1H), 3.71 (d, J = 3.0 Hz, 1H), 6.15-6.17 (m, 1H), 7.45-7.48 (t, J = 8.5 Hz, 2H), 7.50-7.55 (m, 3H), 7.57-7.61 (t, J = 7.5 Hz, 1H), 7.80-7.83 (t, J = 8.0 Hz, 2H), 7.90-7.92 (m, 1H), 7.96-7.98 (dt, 7.0 Hz, 1.5 Hz, 2H), 8.04-8.06 (d, 9.0 Hz, 1H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 46.9, 66.9, 122.9, 123.3, 125.7, 125.8, 126.4, 128.2, 128.3, 128.9, 129.2, 130.0, 133.8, 133.9, 136.6, 138.6, 200.5. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes:2-propanol = 90:10, flow rate = 1.0 mL/min, λ= 254 nm), $t_r$(major, R) = 16.4 min., $t_r$(minor, S) = 12.9 min.. $[\alpha]_D^{27}$ = +84.5 (*c* 1.0, $CHCl_3$).



The product (**6aj**) was obtained as colorless oil in 97 % yield and 84:16 er. $^{1}$H NMR ($CDCl_3$, 500 MHz) δ: 2.36 (s, 3H), 3.32-3.34 (m, 2H), 3.53(d, *J* = 3.0 Hz, 1H), 5.567-5.60 (m, 1H), 7.17 (d, *J* = 7.0 Hz, 1H), 7.21 (td, *J* = 7.0 Hz, 1.0 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.46-7.49 (t, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 2H), 7.96-7.98 (dt, *J* = 7.0 Hz, 1.0 Hz, 2H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 19.2, 46.2, 66.6, 125.6, 126.5, 127.5, 128.3, 128.8, 130.5, 133.8, 134.2, 136.7, 141.1, 200.3. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes:2-propanol = 95:5, flow rate = 1.0 mL/min, λ= 254 nm), $t_r$(major) = 19.4 min., $t_r$(minor) = 15.1 min.. $[\alpha]_D^{27}$ = +60.9 (*c* 0.68, $CHCl_3$).

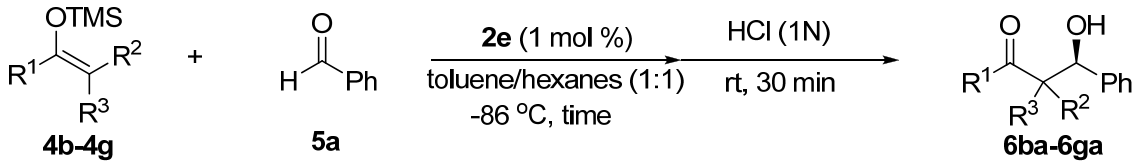


The product (**6ak**)[9] was obtained as pale green oil in 87 % yield and 86:14 er. $^1$H NMR ($CDCl_3$, 500 MHz) δ: 3.28-3.31 (m, 2H), 3.38 (d, *J* = 3.5 Hz, 1H), 4.96 (br, 1H), 6.30-6.35 (dd, *J* = 16.0 Hz, 6.0 Hz, 1H), 6.70-6.74 (d, *J* = 16.0 Hz, 1H), 7.25 (t, *J* = 7.0 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1Hz), 7.97-7.99 (d, *J* = 7.0 Hz, 2H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 45.3, 68.8, 126.7, 127.9, 128.3, 128.7, 128.9, 130.4, 130.6, 133.8, 136.7, 137.8, 200.3. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel IC column equipped with an IC guard column (hexanes:2-propanol = 99:1, flow rate = 1.0 mL/min, λ= 254 nm), $t_r$(major, *R*) = 44.1 min., $t_r$(minor, *S*) = 38.4 min.. $[\alpha]_D^{27}$ = +17.8 (*c* 1.0, $CHCl_3$).



The product (**6al**)[6] was obtained as colorless oil in 92 % yield and 85:15 er. $^1$H NMR ($CDCl_3$, 500 MHz) δ: 3.17-3.21 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 3.63-3.68 (dd, *J* = 16.0 Hz, 8.5 Hz, 1H), 5.66-5.69 (dd, *J* = 8.5 Hz, 4.5 Hz, 1H), 6.93-6.97 (m, 2H), 7.21-7.22 (dd, *J* = 5.0 Hz, 1.0 Hz, 1h), 7.46 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 2H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 47.3, 66.6, 123.7, 124.9, 126.9, 128.3, 128.9, 133.9, 136.6, 146.8, 199.8. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel AS column equipped with an AS guard column (hexanes:2-propanol = 90:10, flow rate = 1.0 mL/min, λ= 254 nm), $t_r$(major, *R*) = 19.4 min., $t_r$(minor, *S*) = 15.7 min.. $[\alpha]_D^{27}$ = +24.0 (*c* 1.0, $CHCl_3$).

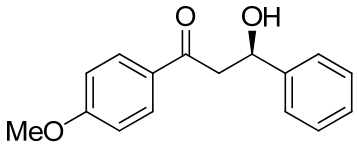
**3-3. Enantioselective Mukaiyama Aldol Reaction of Benzaldehyde with Silyl Enol Ethers of Ketones**



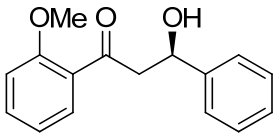

**General Procedures:** To a solution of benzaldehyde **5a** (0.10 mmol; 10.6 mg, 1.0 eq) in toluene/hexanes (1:1(v/v); 0.5 mL) was added chiral Brønsted acid **2e** (1.2 mg; 0.001 mmol; 0.01 eq) in toluene/hexanes (1:1(v/v); 0.5 mL). The mixture was stirred for 30 min at -86 °C. Silyl enol ether of

acetophenone (0.11 mmol; 21.1 mg; 1.1 eq) was added dropwise to the reaction mixture and the reaction mixture was monitored by TLC. When the aldehyde was completely consumed, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with ether. The resulting aldol product was dissolved in ether and treated with 1 N HCl to deprotect the silyl ether. After deprotection was over, the reaction mixture was extracted with ether. The organic layer was combined, washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated. The residue was purified by flash column chromatography (EtOAc/hexanes, 1/5) on silica gel. Enantiomeric ratio (e.r.) was determined by HPLC with a chiral column.

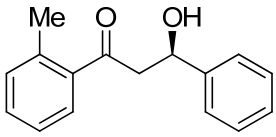
3-3-1. Characterization of Compounds **6ba-6ga**



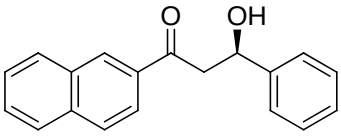

The product (**6ba**)[11] was obtained as a white solid in 97 % yield and 92:8 er. $^1$H NMR ($CDCl_3$, 500 MHz) δ: 3.29-3.34 (m, 2H), 3.76 (br, 1H), 3.89 (s, 3H), 5.31-5.34 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.93 (dt, *J* = 9.5 Hz, 2.5 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.92 (dt, *J* = 9.5, 2.5 Hz, 2H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 47.1, 55.7, 70.3, 114.0, 125.9, 127.8, 128.7, 129.8, 130.6, 143.2, 164.1, 198.9. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel IB column equipped with an IB guard column (hexanes:2-propanol = 95:5, flow rate = 1.0 mL/min, λ= 254 nm), $t_r$(major) = 24.8 min., $t_r$(minor) = 28.0 min.. $[\alpha]_D^{27}$ = +39.7 (*c* 1.0, $CHCl_3$).



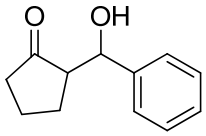

The product (**6ca**)[12] was obtained as colorless oil in 98 % yield and 90:10 er. $^1$H NMR ($CDCl_3$, 500 MHz) δ: 3.32-3.38 (dd, *J* = 18.0 Hz, 9.5 Hz, 1H), 3.44-3.48 (m, 1H), 3.66 (d, *J* = 2.5 Hz, 1H), 3.87 (s, 3H), 5.28-5.30 (d, *J* = 9.5 Hz, 1H), 6.95-6.97 (d, *J* = 8.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 7.28 (tt, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.42-7.43 (d, *J* = 7.0 Hz, 2H), 7.49 (td, *J* = 7.5 Hz, 2.0 Hz, 1H), 7.76-7.78 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 52.6, 55.7, 70.5, 111.7, 120.9, 126.0, 127.5, 127.6, 128.6, 130.6, 134.4, 143.3, 159.1, 202.4. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes:2-propanol = 95:5, flow rate = 1.0 mL/min, λ= 254 nm), $t_r$(major, *R*) = 33.7 min., $t_r$(minor, *S*) = 27.2 min.. $[\alpha]_D^{27}$ = +45.5 (*c* 1.0, $CHCl_3$).



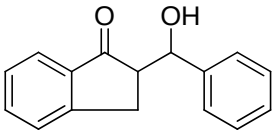

The product (**6da**) was obtained as colorless oil in 98 % yield and 92:8 er. $^{1}$H NMR ($CDCl_3$, 500 MHz) δ: 2.53 (s, 3H), 3.25-3.35 (m, 2H), 3.57 (d, *J* = 3.0 Hz, 1H), 5.31 (d, *J* = 8.5 Hz, 1H), 7.22-7.30 (m, 3H), 7.34-7.42 (m, 5H), 7.62 (d, *J* = 8.0 Hz, 1H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 21.7, 50.0, 70.5, 125.9 (2C), 127.8, 128.7, 129.1, 132.0, 132.3, 137.2, 138.8, 143.1, 204.0. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes:2-propanol = 95:5, flow rate = 1.0 mL/min, λ= 254 nm), $t_r$(major, *R*) = 18.5 min., $t_r$(minor, *S*) = 15.9 min.. $[\alpha]_D^{27}$ = +54.2 (*c* 1.0, $CHCl_3$).




The product (**6ea**)[6] was obtained as a white solid in 94 % yield and 92:8 er. $^{1}$H NMR ($CDCl_3$, 500 MHz) δ: 3.46-3.53 (m, 2H), 3.65 (br, 1H), 5.41 (t, *J* = 6.0 Hz, 1H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.88-7.97 (m, 3H), 8.05 (dd, J = 8.5 Hz, 1.5 Hz, 1H), 8.45 (s, 1H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 47.6, 70.3, 123.7, 125.9, 127.1, 127.9, 128.0, 128.8, 128.9, 129.8, 130.4, 132.6, 134.0, 135.9, 143.1, 200.3. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes:2-propanol = 85:15, flow rate = 0.8 mL/min, λ= 254 nm), $t_r$(major, *R*) = 22.3 min., $t_r$(minor, *S*) = 15.1 min.. $[\alpha]_D^{27}$ = +59.2 (*c* 1.0, $CHCl_3$) (Lit. $[\alpha]_D^{20}$ = +45 (*c* 4.0, $CHCl_3$) for (*R*) enantiomer (79:21 er)).




The product (**6fa**)[10] was obtained as a white solid in 86 % yield and 16:1 dr (*syn:anti*) and 95:5 er (for *syn*) and 97:4 er (for *anti*). $^{1}$H NMR ($CDCl_3$, 500 MHz) δ: 1.68-2.38 (m, 14H), 4.65 (d, J = 9.0 Hz, 1H), 5.23 (s, 1H), 7.18-7.29 (m, 10H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 20.3, 20.4, 26.9 (anti), 29.6 (anti), 38.7 (anti), 39.1, 71.5, 75.2 (anti), 125.5, 126.5 (anti), 127.3, 127.9 (anti), 128.3, 128.4 (anti), 142.6, 220.4. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes:2-propanol = 95:5, flow rate = 1.0 mL/min, λ= 220 nm), $t_r$(*syn*-major) = 13.8 min., $t_r$(*syn*-minor) = 10.8 min, $t_r$(*anti*-major) = 15.4 min., $t_r$(*anti*-minor) = 19.2 min..



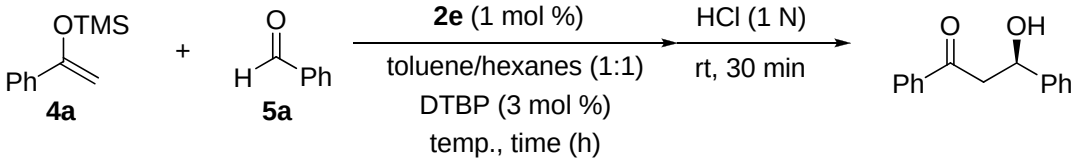

The product (**6ha**)[10] was obtained as colorless oil in 93 % yield 1.7:1 dr (syn:anti) and 76:24 er (for *syn*) and 73:27 er (for *anti*). $^1$H NMR ($CDCl_3$, 500 MHz) δ: 2.33(d, *J* = 4.0 Hz, 1H), 2.61-2.65 (m, 1H), 2.81-3.00 (m, 3H), 3.18-3.22 (dd, *J* = 17.0 Hz, 4.0 Hz, 1H), 4.72 (d, J = 10.0 Hz, 1H), 5.53 (br, 1H), 7.20-7.38 (m, 14H), 7.49-7.56 (m, 2H), 7.69-7.74 (m, 2H).; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 26.9, 30.1, 53.3, 54.9, 72.3, 75.9, 124.0, 124.4, 125.7, 126.7, 126.8, 127.2, 127.5, 127.6, 127.9, 128.5, 128.7, 128.8, 135.2, 135.7, 136.4, 137.2, 141.5, 142.7, 154.2, 154.9, 207.4, 209.9. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel AS-H column equipped with an AS-H guard column (hexanes:2-propanol = 90:10, flow rate = 1.0 mL/min, λ= 240 nm), $t_r$(*syn*-major) = 22.3 min., $t_r$(*syn*-minor) = 18.5 min., $t_r$(*anti*-major) = 26.3 min., $t_r$(*anti*-minor) = 28.3 min..

## 4. Mechanistic Studies

### 4-1. Effect of 2,6-di(*t*-butyl)pyridine (DTBP)

In order to distinguish whether the actual catalyst for the Mukaiyama aldol reaction is Brønsted acid or silylated Brønsted acid, Mukaiyama aldol reaction was conducted in the presence of 2,6-di(*t*-butyl)pyridine (DTBP), which is known to inhibit any potential Brønsted acid catalysis.[13]

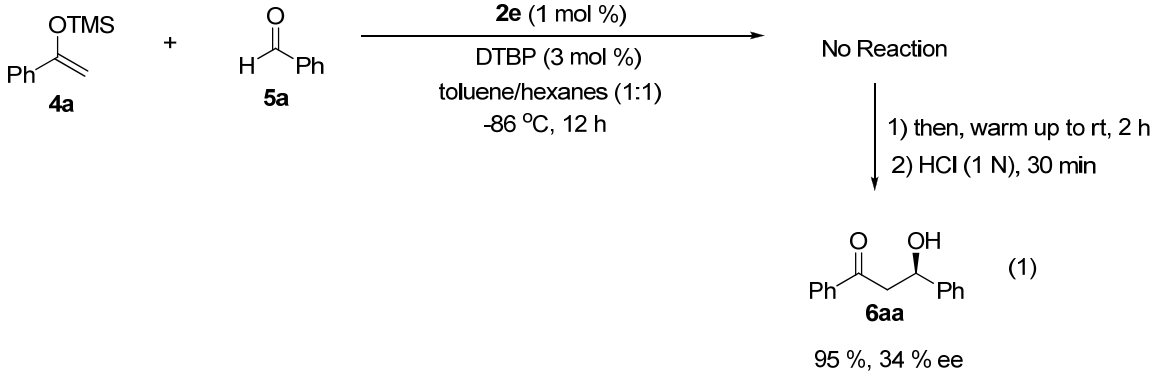
**General Procedures:** To a solution of benaldehyde **5a** (0.10 mmol; 10.6 mg; 1.0 eq) and Brønsted acid **2e** (0.001 mmol; 1.2 mg; 0.01 eq) in toluene/hexanes (1:1(v/v), 1 mL) was added a solution of DTBP (0.003 mmol; 0.57 mg; 0.03 eq). The mixture was allowed to stir for 1 h at room temperature and the reaction mixture was adjusted to the reaction temperature (either room temperature or -86 $^{o}$C). Silyl enol ether **4a** (0.11 mmol; 21.1 mg; 1.1 eq) was added dropwise to the reaction mixture. The reaction mixture was monitored by TLC. When **5a** was completely consumed, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with ether. The resulting aldol product was dissolved in ether and treated with 1 N HCl to deprotect the silyl ether. After the deprotection was over, the reaction mixture was extracted with ether. The organic layer was combined, washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated. The residue was purified by flash column chromatography (EtOAc/hexanes, 1/5) on silica gel. Enantiomeric ratio (e.r.) was determined by HPLC with a chiral OD-H column.




| entry | DTBP | temp. ($^{o}$C) | time (h) | yield (%)[a] | er[b] |
|---|---|---|---|---|---|
| 1 | **-** | rt | 2 | 96 | 67:33 |
| 2 | **3 mol %** | rt | 2 | 95 | 67:33 |
| 3 | **-** | -86 | 12 | 93 | 92:8 |
| 4 | **3 mol %** | -86 | 12 | N. R. | N. D. |

[a] Isolation yield after column chromatography.
[b] Enantiomeric ratio (er) was determined by HPLC using a chiral OD-H column.

At room temperature, DTBP has no effect on Mukaiyama aldol reaction in terms of reactivity as well as enantioselectivity (entries 1 and 2). However, at low temperature DTBP had a dramatic effect on the Mukaiyama aldol reaction (entries 3 and 4). DTBP completely inhibited Mukaiyama aldol reaction at low temperature (entry 4). Furthermore, when the reaction mixture at low temperature (from entry 4) was warmed up to room temperature, the aldol reaction proceeded again with the same yield and enantioselectivity of the reaction at room temperature with DTBP (eq. 1).



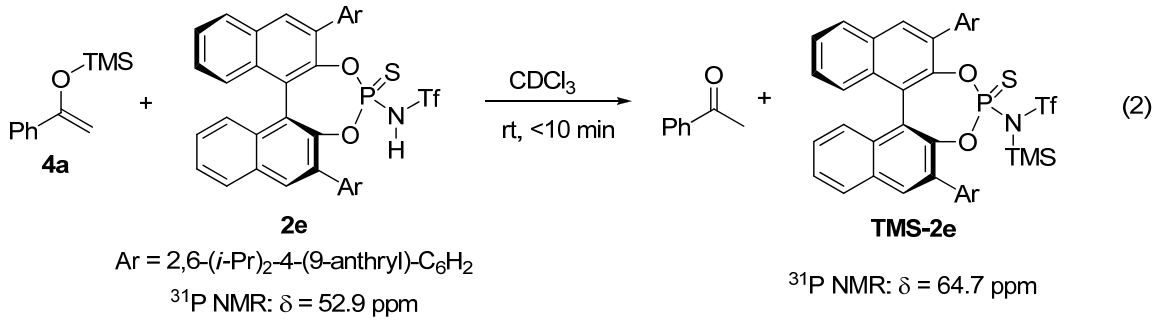

These results suggest that the aldol reaction predominantly proceeds through the silylated Brønsted acid at room temperature (Lewis acid pathway), whereas the aldol reaction proceeds via Brønsted acid activation of carbonyl compounds (Brønsted acid pathway).

### 4-2. Mukaiyama aldol reaction with the silylated Brønsted acid

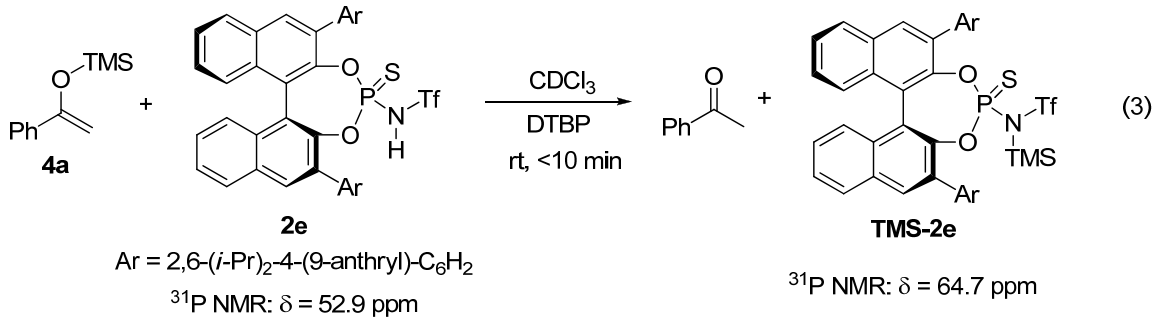
#### 4-2-1. Generation of the silylated Brønsted acid

To a solution of silyl enol ether **4a** in chloroform-*d* was added a solution of Brønsted acid **2e** in chloroform-*d* and the reaction was monitored by $^{1}$H NMR. As soon as **2e** was added, the vinyl peaks (δ =

4.43, 4.93 ppm) from the silyl enol ether disappeared and a new methyl peak from acetophenone was observed at δ = 2.60 ppm. In addition, the TMS peak (δ = 0.25 ppm) from **4a** disappeared and two new peaks were observed at 0.15 and 0.07 ppm. Furthermore, a new signal from the silylated Brønsted acid was observed in $^{31}$P NMR.



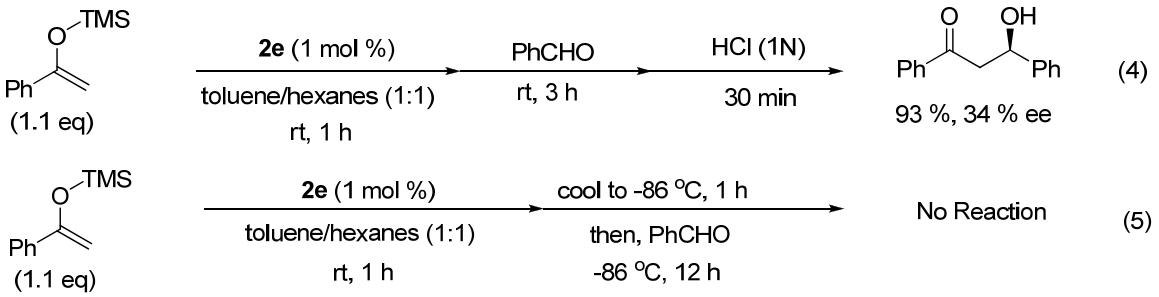

Furthermore, we examined the effect of DTBP on the protodesilylation between silyl enol ether **4a** and thiophosphoramide **2e**. It was turned out that DTBP has no effect on the protodesilylation (eq. 3).



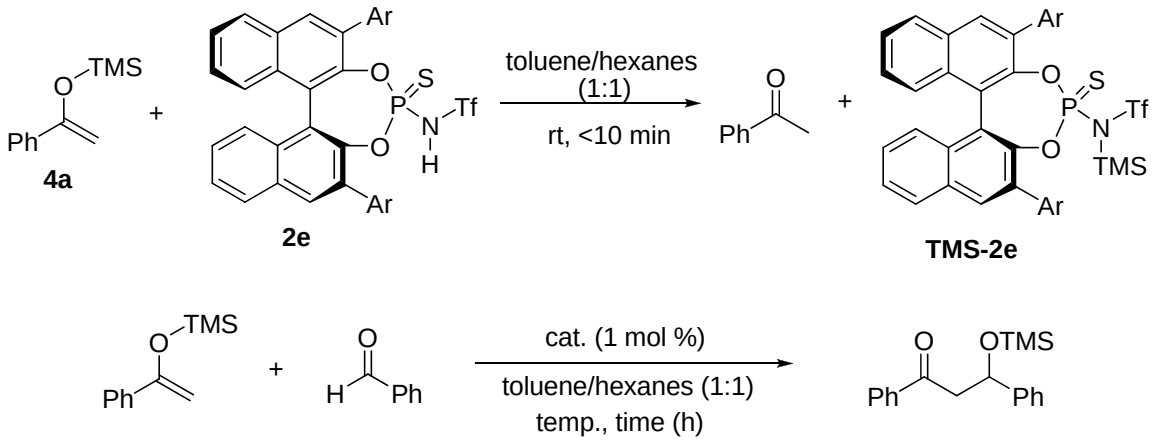

**4-2-2. Mukaiyama aldol Reaction with Silylated Brønsted Acid**

From the above reaction, the silyl enol ether **4a** rapidly silylates Brønsted acid **2e**. Based on this observation, we could generate the silylated Brønsted acid **TMS-2e** and apply this pre-silylated catalyst to Mukaiyama aldol reaction to further examine the reaction mechanism.

At room temperature, the desired aldol product was obtained in same yield and enantioselectivity at the standard room temperature reaction (eq. 4). However, at low temperature, the silylated Brønsted acid could not catalyze Mukaiyama aldol reaction (eq. 5).




These results are summarized in the table as shown below.




| entry | cat. | temp. ($^{o}$C) | time (h) | yield (%)[a] | er[b] |
|---|---|---|---|---|---|
| 1 | **2e** | rt | 2 | 96 | 67:33 |
| 2 | **TMS-2e** | rt | 3 | 93 | 67:33 |
| 3 | **2e** | -86 | 12 | 93 | 92:8 |
| 4 | **TMS-2e** | -86 | 12 | N. R. | N. D. |

[a] Isolation yield after column chromatography separation.
[b] Enantiomeric ratio (ER) was determined using chiral HPLC after deprotection of silyl ether.

This result also supported that two different reaction pathways are operative depending on reaction temperature, and that Lewis acid catalyzed pathway would be operative at room temperature and Brønsted acid catalyzed pathway would be in effect at low temperature.

**5. References**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13. Usage of this base to differentiate reaction pathway between Lewis acid and Brønsted acid catalysis, see: (a) Cheon, C. H.; Yamamoto, H. *Tetrahedron Lett.* **2009**, *50*, 3555. (b) Hara, K.; Akiyama, R.; Sawamura, M. *Org. Lett.* **2005**, *7*, 5621. (c) Mathieu, B.; Ghosez, L. *Tetrahedron* **2002**, *58*, 8219. (d) Zamfir, A.; Tsogoeva, S. B. *Org. Lett.* **2010**, *12*, 188. (e) García-García, P.; Lay, F.; García-García, P.; Babalakos, C.; List, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 4363.

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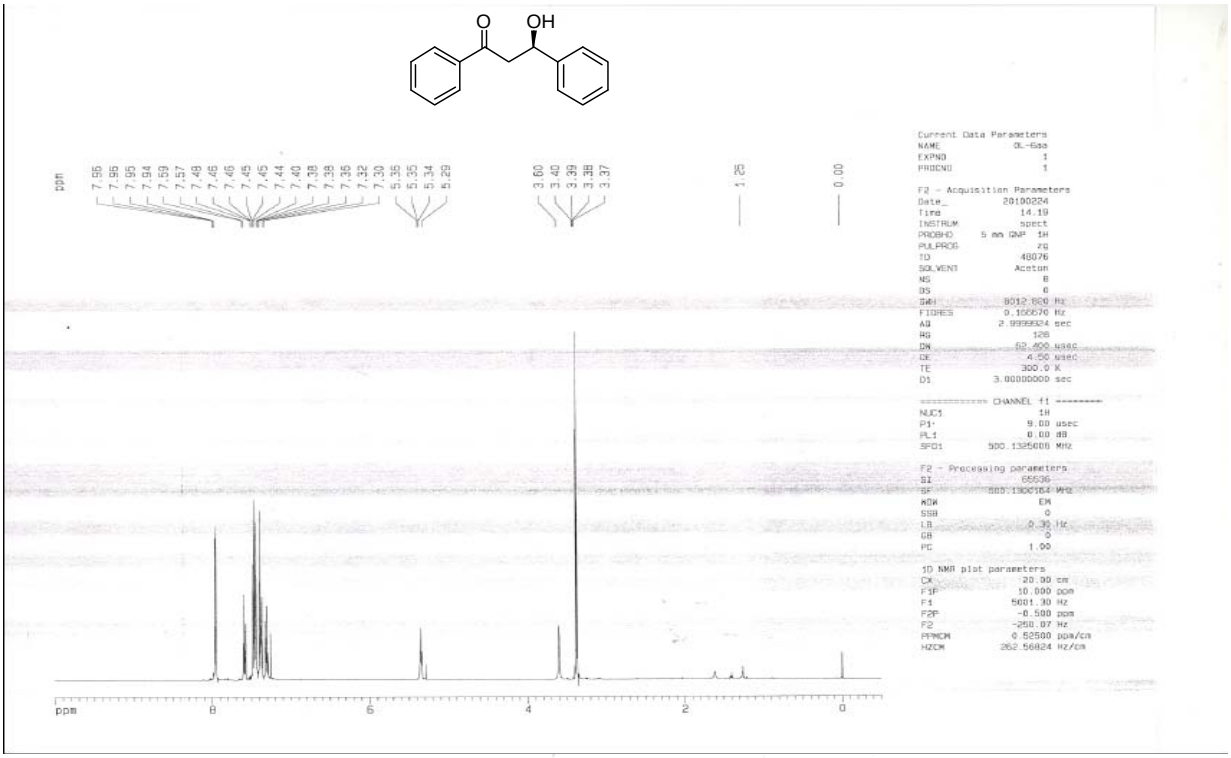
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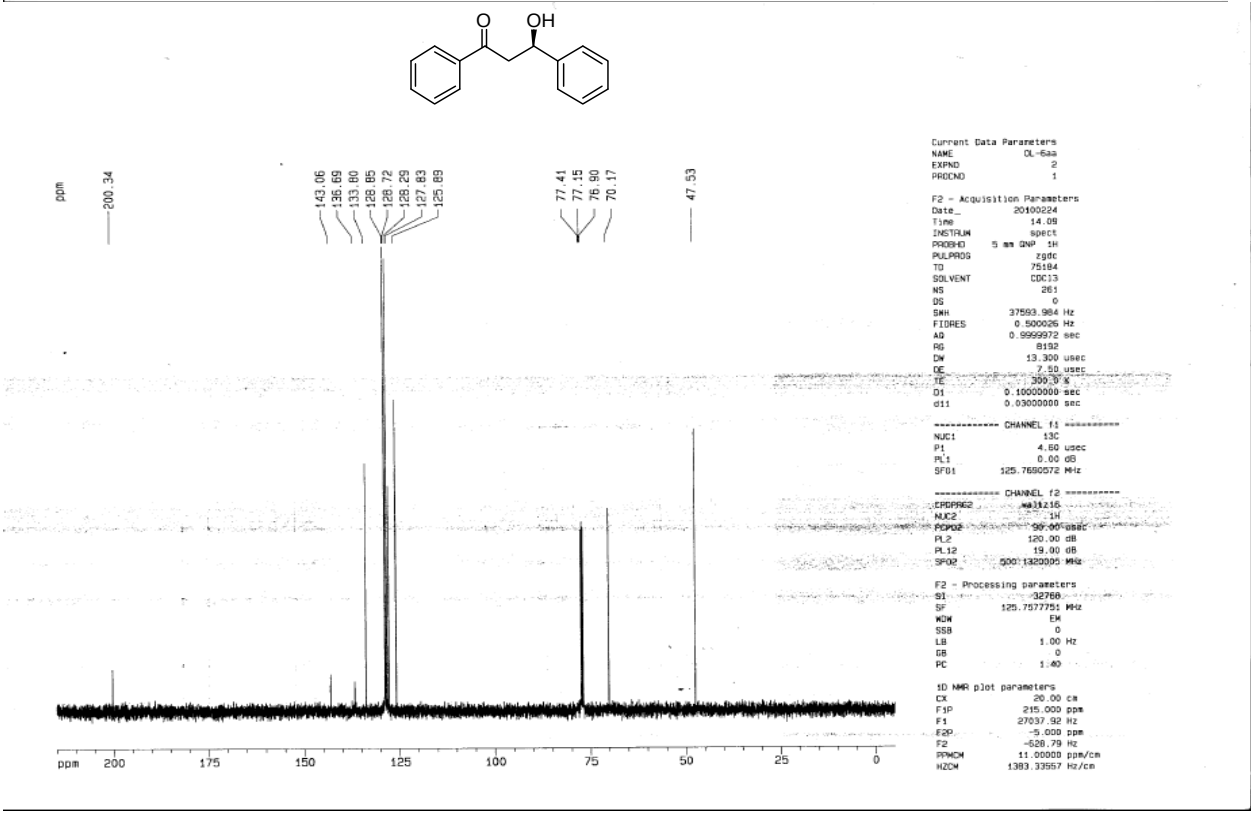
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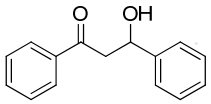


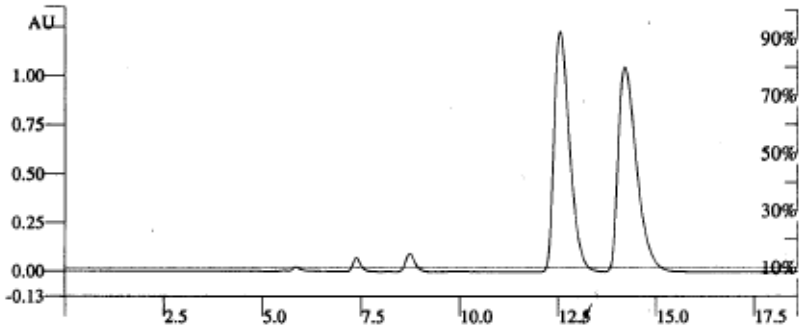


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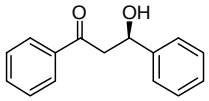


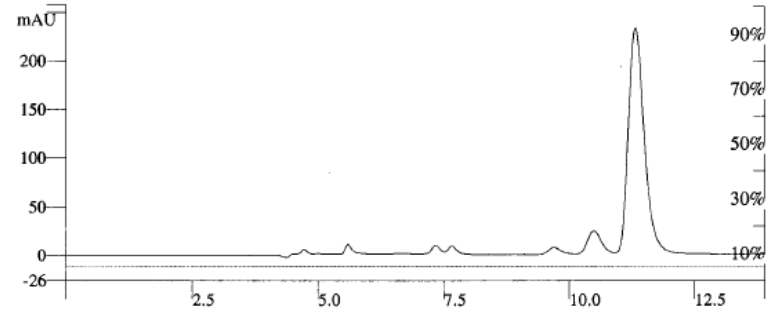


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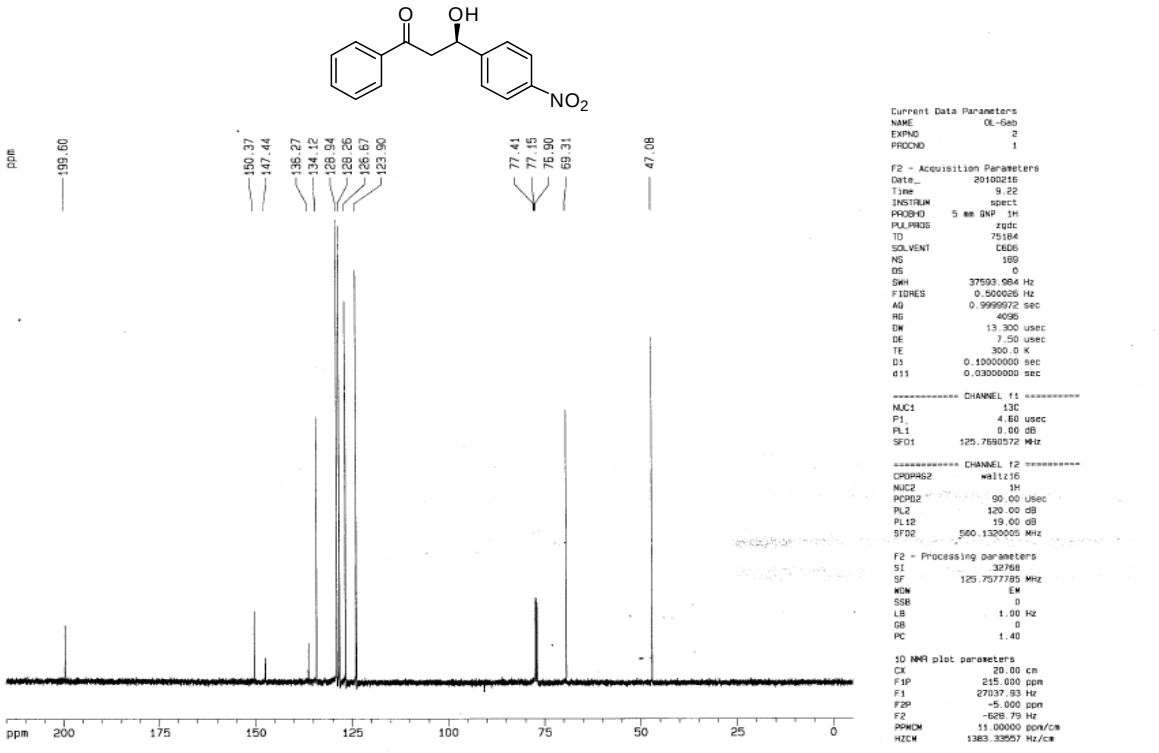
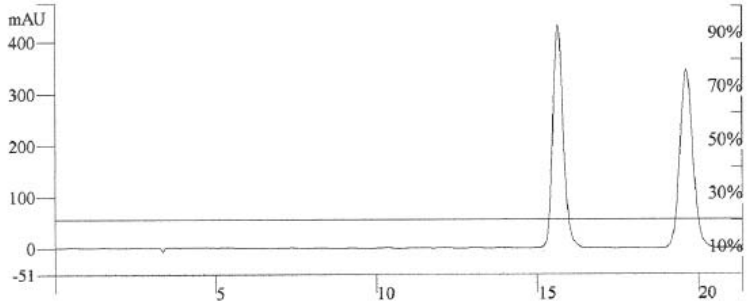
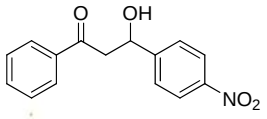
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56824 Hz/cm


O
OH
NO2
ppm
199.60
150.37
147.44
136.27
134.12
128.94
128.26
126.67
123.90
77.41
77.15
76.90
69.31
47.08
ppm
200
175
150
125
100
75
50
25
0
Current Data Parameters
NAME 0L-6ab
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100216
Time 9.22
INSTRUM spect
PROBHD 5 mm BNP 1H
PULPROG zgdc
TD 75184
SOLVENT DMSO
NS 189
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 4096
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SFO1 125.7690572 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577785 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 27037.93 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 11.00000 ppm/cm
HZCM 1383.33557 Hz/cm

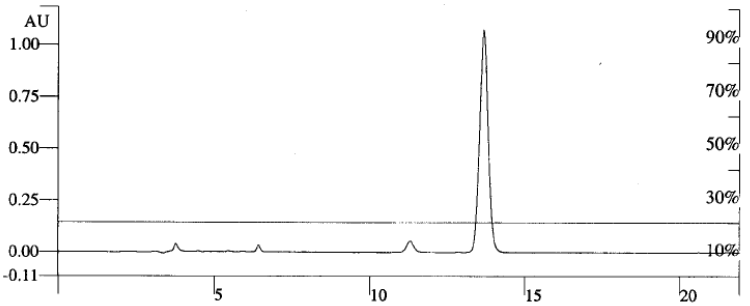
| | | | |
|---|---|---|---|
| Data File: | c:\star\8-28-09 10;13;19 pm -1.run | Run Mode: | Analysis |
| Sample ID: | 224-rac | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 08/28/09 10:13:19 PM | Run Time (min): | 21.387 |

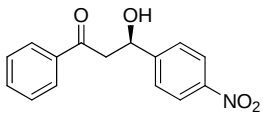



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 49.8687 | 15.613 | 0.000 | 49946512 | 0.00 | BB | 20.5 |
| 2 | 50.1313 | 19.613 | 0.000 | 50209460 | 0.00 | BB | 26.1 |
| | **100.0000** | | **0.000** | **100155968** | | | |

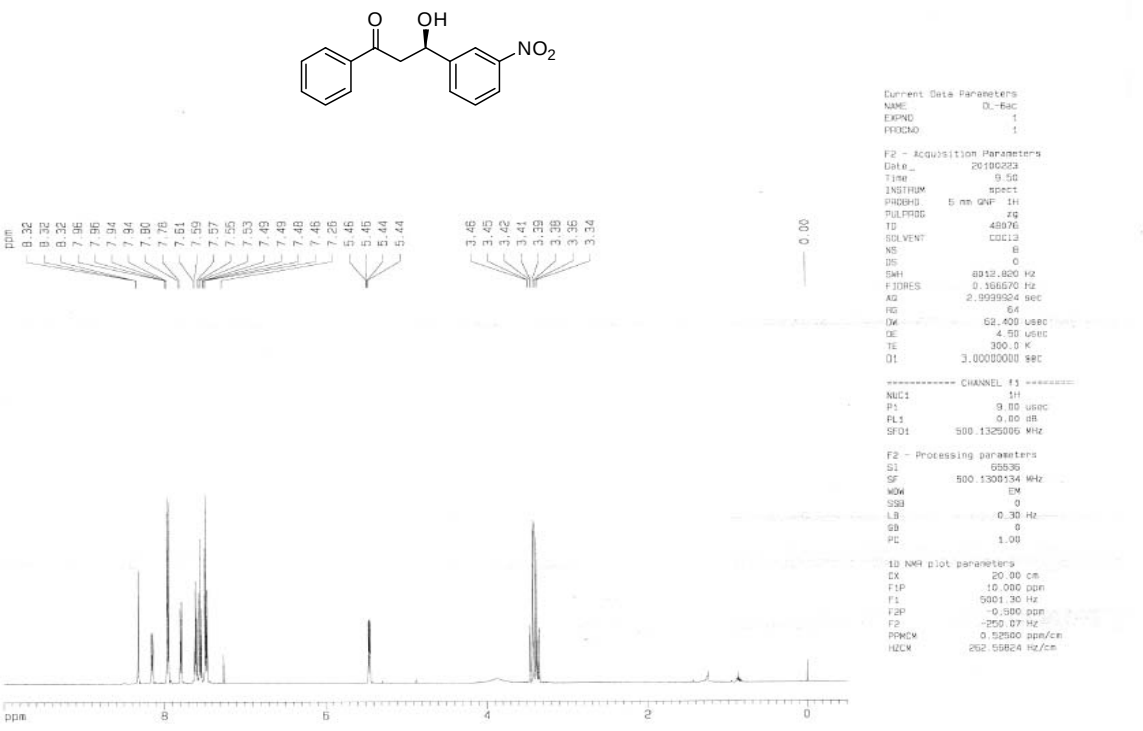
| | | | |
|---|---|---|---|
| Data File: | c:\star\9-28-09 6;48;33 pm -1.run | Run Mode: | Analysis |
| Sample ID: | 15-289-4-NO2 | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 09/28/09 06:48:32 PM | Run Time (min): | 21.947 |

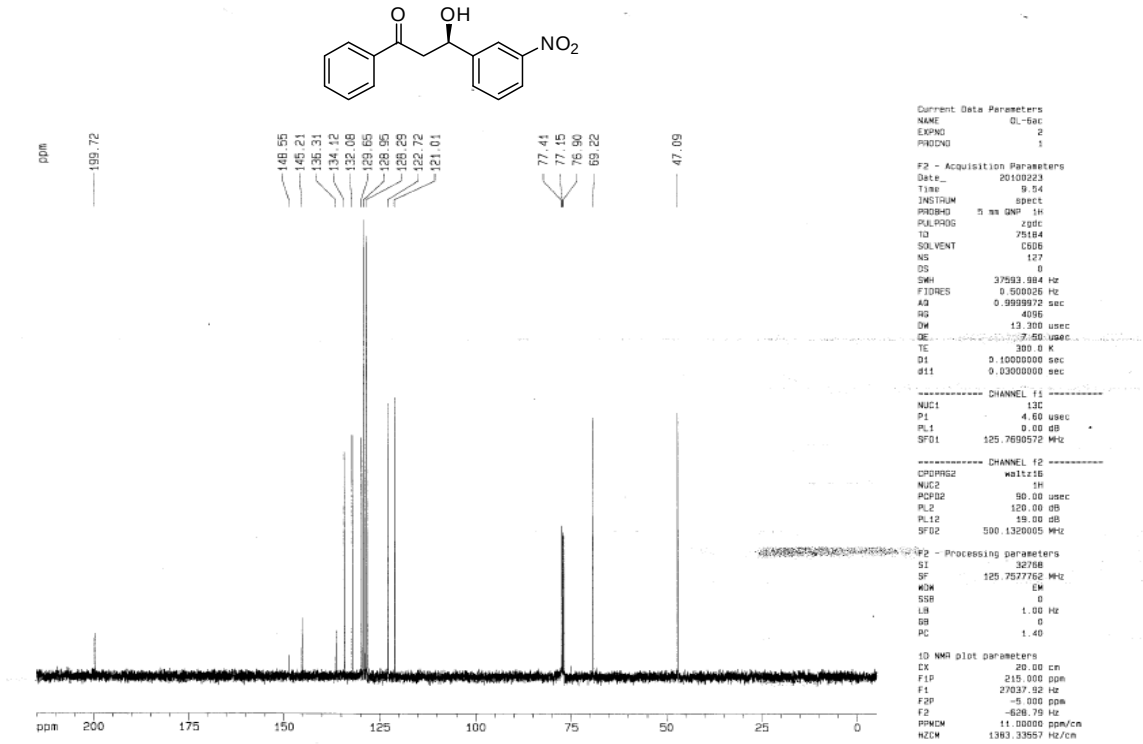



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 3.8600 | 11.293 | 0.000 | 4275139 | 0.00 | BB | 14.3 |
| 2 | 96.1400 | 13.667 | 0.000 | 106479424 | 0.00 | BB | 17.9 |
| | **100.0000** | | **0.000** | **110754560** | | | |

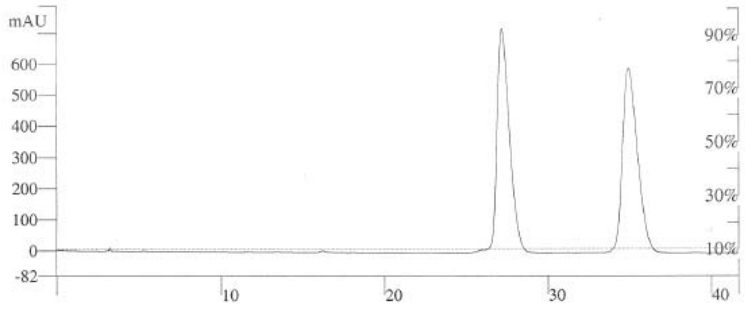
6ac:

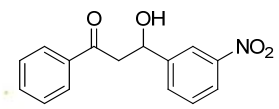

O
OH
NO2
ppm
8.32
8.32
8.32
7.96
7.96
7.94
7.94
7.80
7.78
7.61
7.59
7.57
7.55
7.53
7.49
7.49
7.48
7.46
7.26
5.46
5.45
5.44
5.44
3.46
3.45
3.42
3.41
3.39
3.38
3.36
3.34
0.00
Current Data Parameters
NAME 6L-6ac
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100223
Time 9.50
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 48976
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 64
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.80 usec
PL1 0.00 dB
SFO1 500.1325006 MHz
F2 - Processing parameters
SI 65536
SF 500.1300134 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.55824 Hz/cm
ppm
8
6
4
2
0


O
OH
NO2
ppm
199.72
148.55
145.21
136.31
134.12
132.08
129.65
128.95
128.29
122.72
121.01
77.41
77.15
76.90
69.22
47.09
Current Data Parameters
NAME 6L-6ac
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100223
Time 9.54
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 75184
SOLVENT C6D6
NS 127
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 4096
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SFO1 125.7690572 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577762 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 27037.92 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 11.00000 ppm/cm
HZCM 1383.33557 Hz/cm
ppm
200
175
150
125
100
75
50
25
0

| | | | |
|---|---|---|---|
| Data File: | c:\star\3-4-10 4;05;56 pm -1.run | Run Mode: | Analysis |
| Sample ID: | Manual Sample | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 03/04/10 04:05:56 PM | Run Time (min): | 41.680 |

Injection Method: c:\star\cheol hong\mukaiyama

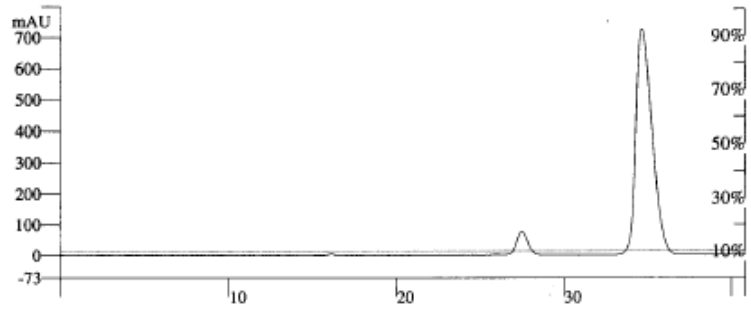


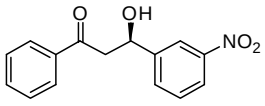




| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 49.4437 | 27.133 | 0.000 | 190876240 | 0.00 | BB | 48.2 |
| 2 | 50.5563 | 34.893 | 0.000 | 195171344 | 0.00 | BB | 59.6 |
| | **100.0000** | | **0.000** | **386047584** | | | |

| | | | |
|---|---|---|---|
| Data File: | c:\star\3-4-10 4;49;29 pm -1.run | Run Mode: | Analysis |
| Sample ID: | Manual Sample | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 03/04/10 04:49:29 PM | Run Time (min): | 40.880 |

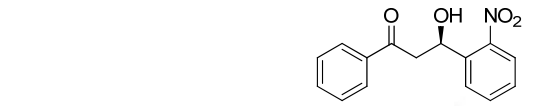
Injection Method: c:\star\cheol hong\mukaiyama

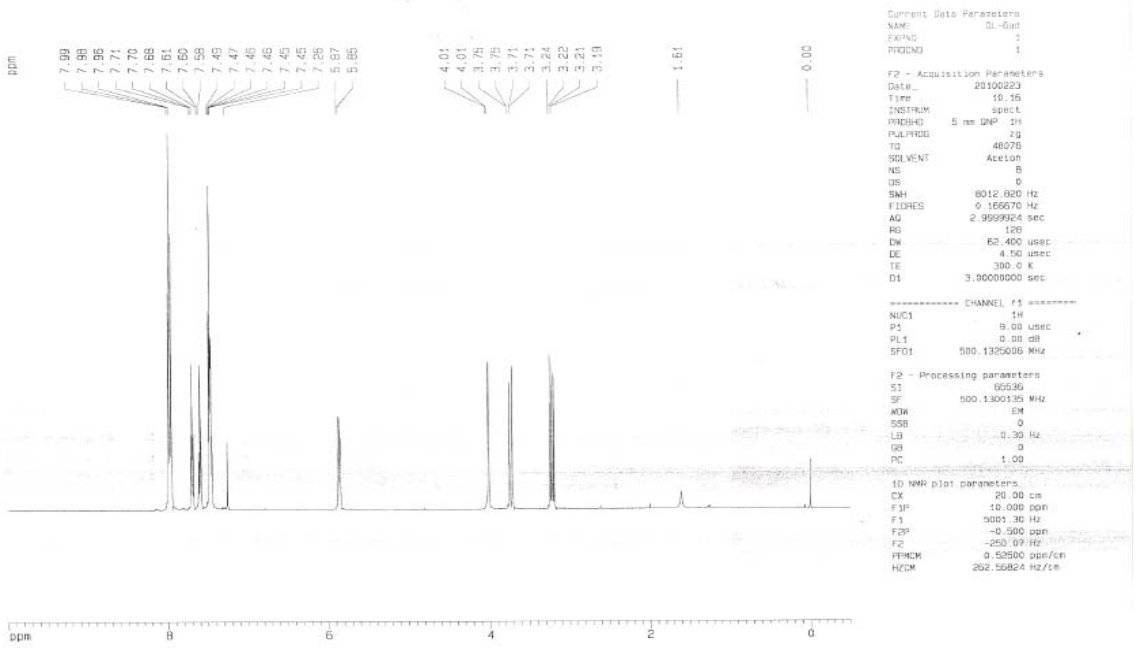


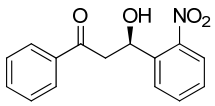



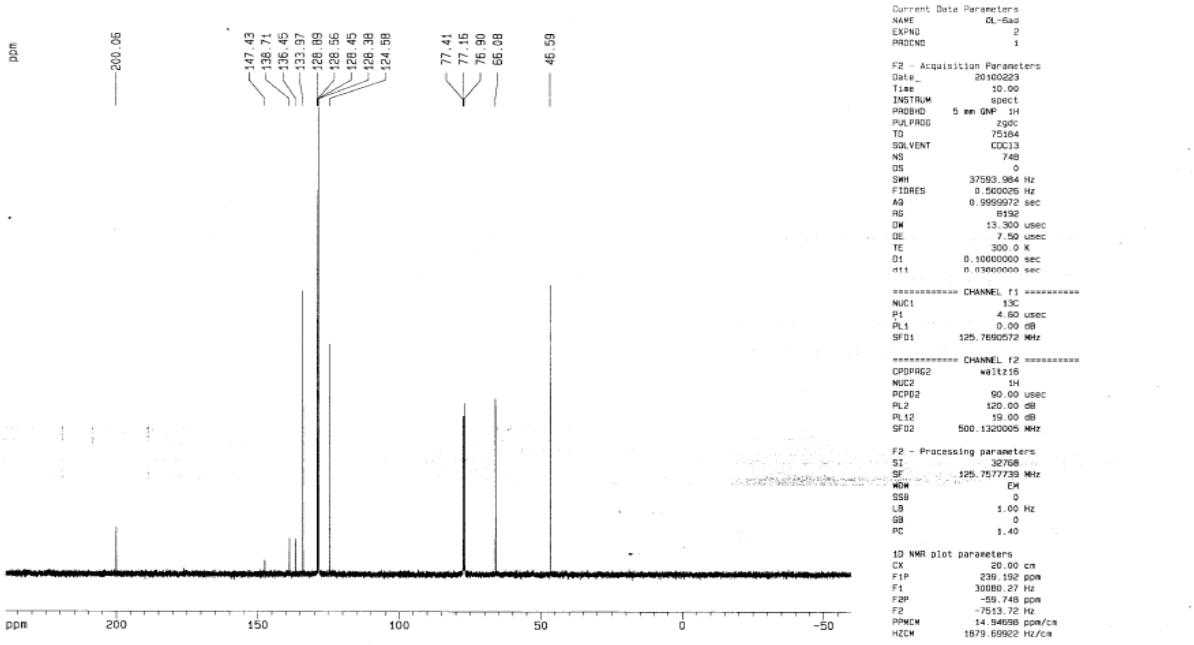

| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 5.8391 | 27.480 | 0.000 | 15666151 | 0.00 | BB | 40.9 |
| 2 | 94.1609 | 34.680 | 0.000 | 252632192 | 0.00 | BB | 63.5 |
| | **100.0000** | | **0.000** | **268298336** | | | |

6ad:


O
OH
NO2

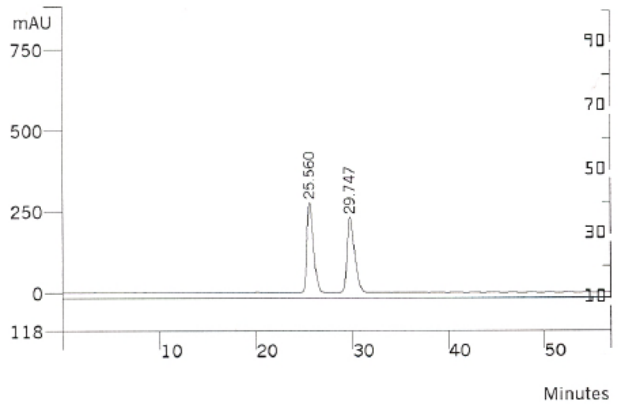

ppm
7.99
7.98
7.96
7.71
7.70
7.68
7.61
7.60
7.59
7.45
7.47
7.45
7.45
7.45
7.45
7.26
5.67
5.65
4.01
4.01
3.75
3.75
3.71
3.71
3.24
3.22
3.21
3.19
1.61
0.00
Current Data Parameters
NAME DL-6ad
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100223
Time 10.16
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 48076
SOLVENT Aceton
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166570 Hz
AQ 2.9999924 sec
RG 128
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1325006 MHz
F2 - Processing parameters
SI 65536
SF 500.1300135 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56824 Hz/cm
ppm
8
6
4
2
0


O
OH
NO2

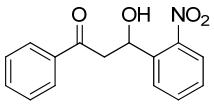

ppm
200.06
147.43
138.71
136.45
133.97
128.89
128.56
128.45
128.38
124.98
77.41
77.16
76.90
66.08
46.59
Current Data Parameters
NAME DL-6ad
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100223
Time 10.09
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 75184
SOLVENT CDCl3
NS 748
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 8192
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SFO1 125.7690572 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577739 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 239.192 ppm
F1 30080.27 Hz
F2P -59.748 ppm
F2 -7513.72 Hz
PPMCM 14.94698 ppm/cm
HZCM 1879.69922 Hz/cm
ppm
200
150
100
50
0
-50

| | |
|---|---|
| Data File: | c:\star\data\11-10-092;05;48 pm.run |
| Channel: | 1 = 210.00 nm RESULTS |
| Sample ID: | 6ad-2-NO2 |
| Injection Method: | c:\star\cheol hong\inst_2.mth |
| Injection Date/Time (Inj): | 11/10/09 02:05:48 PM |
| Instrument (Inj): | PDA |
| Workstation: | |
| Verification Tolerance: | N/A |

| | |
|---|---|
| Operator (Calc): | |
| Calc Date: | 11/10/09 03:02:52 PM |
| Times Calculated: | 1 |
| Calculation Method: | Analysis |
| Instrument (Calc): | PDA |
| Run Mode: | |
| Peak Measurement: | Peak Area |
| Calculation Type: | Percent |
| Calibration Level: | N/A |

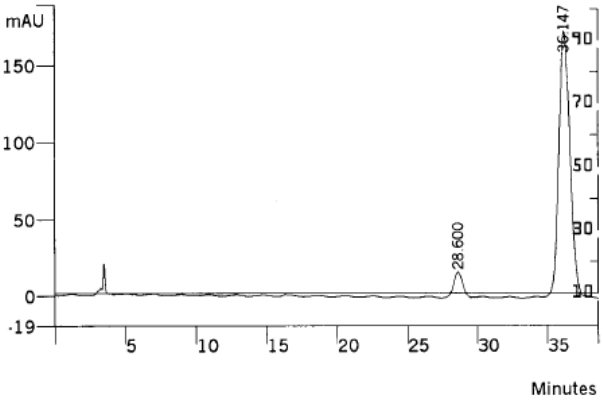



| Peak No | Result () | Ret. Time (min) |
|---|---|---|
| 1 | 50.1682 | 25.560 |
| 2 | 49.8318 | 29.747 |
| | **100.0000** | |

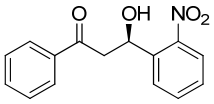



| | |
|---|---|
| Data File: | c:\star\data\11-10-093;12;20 pm.run |
| Channel: | 1 = 210.00 nm RESULTS |
| Sample ID: | Manual Sample |
| Injection Method: | c:\star\cheol hong\inst_2.mth |
| Injection Date/Time (Inj): | 11/10/09 03:12:20 PM |
| Instrument (Inj): | PDA |
| Workstation: | |
| Verification Tolerance: | N/A |

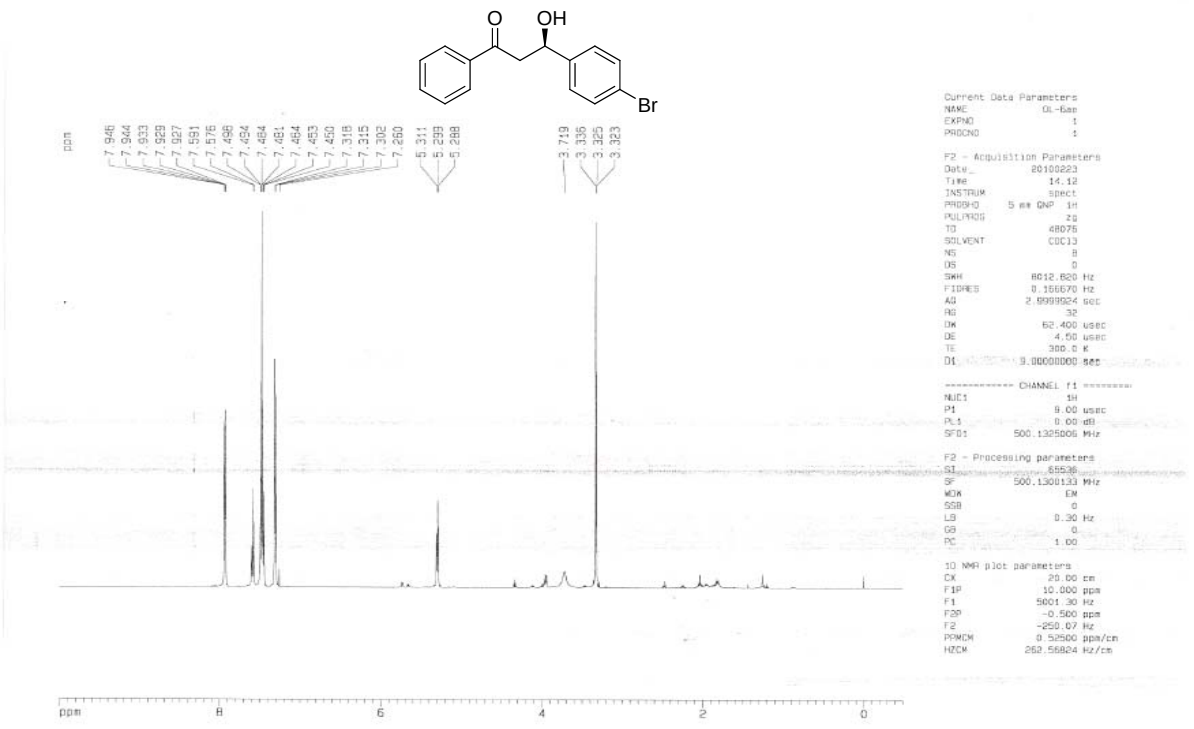
| | |
|---|---|
| Operator (Calc): | |
| Calc Date: | 11/10/09 03:47:55 PM |
| Times Calculated: | 1 |
| Calculation Method: | Analysis |
| Instrument (Calc): | PDA |
| Run Mode: | |
| Peak Measurement: | Peak Area |
| Calculation Type: | Percent |
| Calibration Level: | N/A |

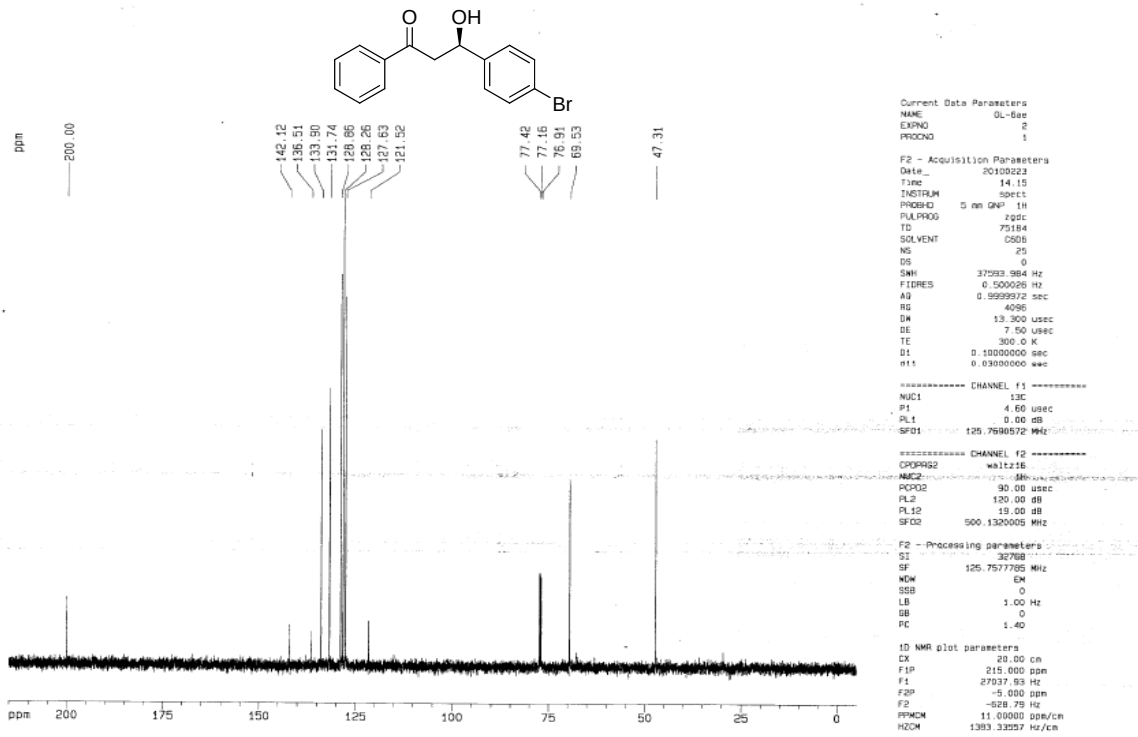



| Peak No | Result () | Ret. Time (min) |
|---|---|---|
| 1 | 4.6069 | 28.600 |
| 2 | 95.3931 | 36.147 |
| | **100.0000** | |

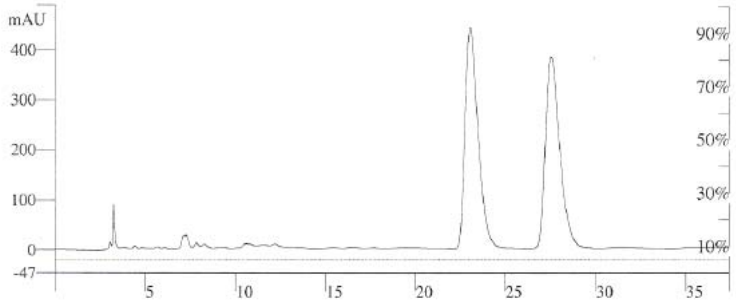


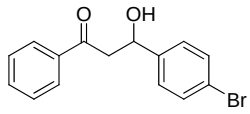
6ae:


O
OH
Br
ppm
7.946
7.944
7.933
7.929
7.927
7.591
7.576
7.498
7.484
7.481
7.464
7.453
7.450
7.315
7.315
7.302
7.260
5.311
5.299
5.288
3.719
3.336
3.325
3.323
Current Data Parameters
NAME OL-6ae
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100223
Time 14.12
INSTRUM spect
PROBHD 5 mm CNP 1H
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 32
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 9.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1325006 MHz
F2 - Processing parameters
SI 65536
SF 500.1300133 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56824 Hz/cm
ppm
8
6
4
2
0


O
OH
Br
ppm
200.00
142.12
136.51
133.90
131.74
128.86
128.26
127.63
121.52
77.42
77.16
76.91
69.53
47.31
Current Data Parameters
NAME OL-6ae
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100223
Time 14.15
INSTRUM spect
PROBHD 5 mm CNP 1H
PULPROG zgdc
TD 75184
SOLVENT CDCl3
NS 25
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 4096
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
D11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SFO1 125.7690572 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577785 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 27037.93 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 11.00000 ppm/cm
HZCM 1383.33357 Hz/cm
ppm
200
175
150
125
100
75
50
25
0

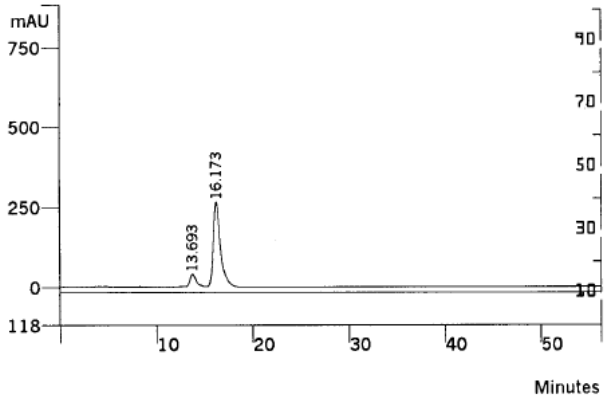
| | | | |
|---|---|---|---|
| Data File: | c:\star\9-9-09 11;08;05 am -1.run | Run Mode: | Analysis |
| Sample ID: | 4-BrPh-rac | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 09/09/09 11:08:05 AM | Run Time (min): | 37.467 |



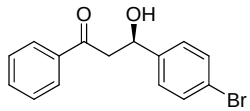




| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 51.4481 | 23.027 | 0.000 | 115483192 | 0.00 | BB | 46.8 |
| 2 | 48.5519 | 27.480 | 0.000 | 108982136 | 0.00 | BB | 50.7 |
| | **100.0000** | | **0.000** | **224465328** | | | |

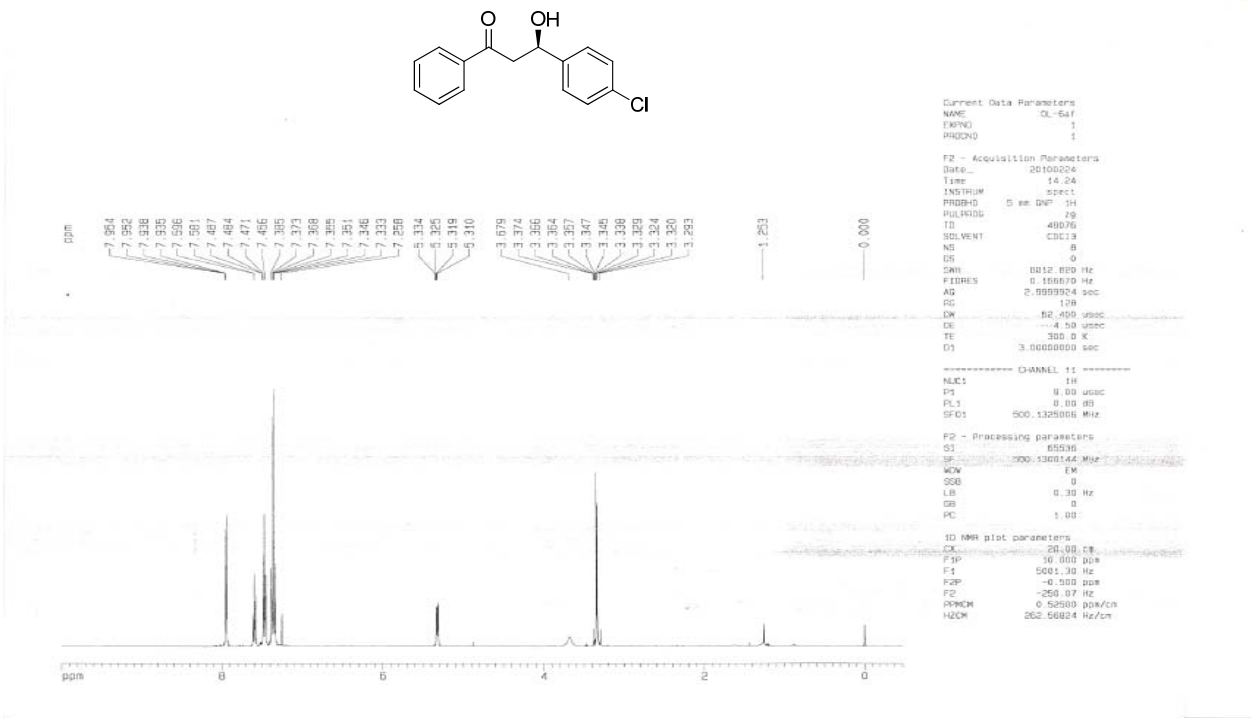
| | | | |
|---|---|---|---|
| Data File: | c:\star\data\11-10-094;21;15 pm.run | Operator (Calc): | |
| Channel: | 1 = 210.00 nm RESULTS | Calc Date: | 11/10/09 05:17:39 PM |
| Sample ID: | 6ae-4-Br | Times Calculated: | 1 |
| Operator (Inj): | | Calculation Method: | Analysis |
| Injection Method: | c:\star\cheol hong\inst_2.mth | Instrument (Calc): | PDA |
| Injection Date: | 11/10/09 04:21:15 PM | Run Mode: | |
| Instrument (Inj): | PDA | Peak Measurement: | Peak Area |
| Workstation: | | Calculation Type: | Percent |
| Verification Tolerance: | N/A | Calibration Level: | N/A |

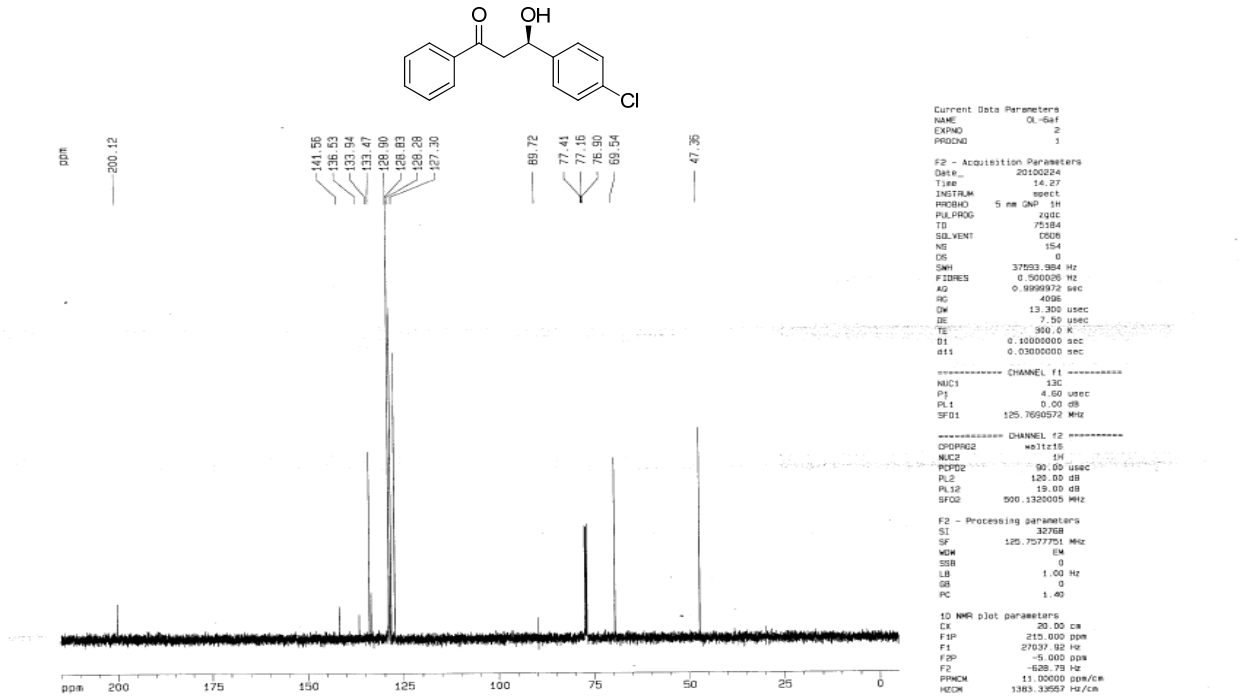



| Peak No | Result () | Ret. Time (min) |
|---|---|---|
| 1 | 9.2309 | 13.693 |
| 2 | 90.7691 | 16.173 |
| | **100.0000** | |

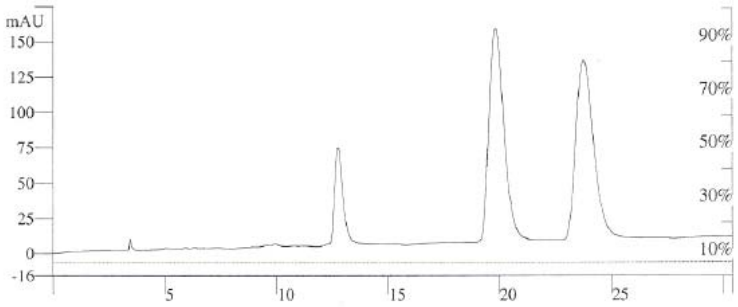


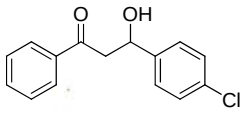
6af:


O
OH
Cl
ppm
7.954
7.952
7.938
7.935
7.596
7.581
7.487
7.484
7.471
7.456
7.385
7.373
7.368
7.365
7.351
7.346
7.333
7.258
5.334
5.325
5.319
5.310
3.679
3.374
3.366
3.364
3.357
3.347
3.345
3.338
3.329
3.324
3.320
3.293
1.253
0.000
Current Data Parameters
NAME OL-6af
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100224
Time 14.24
INSTRUM spect
PROBHD 5 mm DNP 1H
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 128
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1325006 MHz
F2 - Processing parameters
SI 65536
SF 500.1300144 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56824 Hz/cm
ppm
8
6
4
2
0


O
OH
Cl
ppm
200.12
141.56
136.53
133.94
133.47
128.90
128.83
128.28
127.30
89.72
77.41
77.16
76.90
69.54
47.36
Current Data Parameters
NAME OL-6af
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100224
Time 14.27
INSTRUM spect
PROBHD 5 mm DNP 1H
PULPROG zgpg
TD 75184
SOLVENT DSO
NS 154
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 4096
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SFO1 125.7690572 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577751 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 27037.92 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 11.00000 ppm/cm
HZCM 1383.33557 Hz/cm
ppm
200
175
150
125
100
75
50
25
0

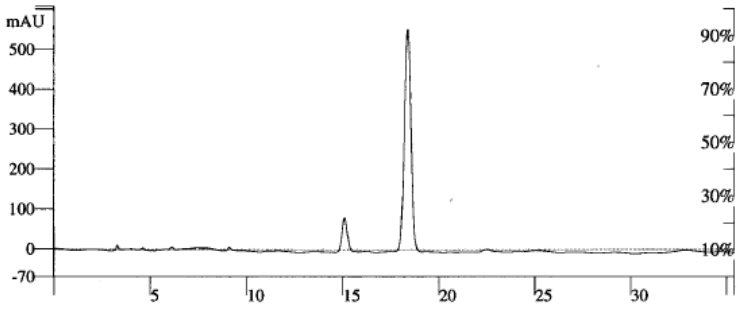
| | | | |
|---|---|---|---|
| Data File: | c:\star\11-12-09 11;44;49 am -1.run | Run Mode: | Analysis |
| Sample ID: | 6af-4-Cl | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 11/12/09 11:44:49 AM | Run Time (min): | 30.453 |

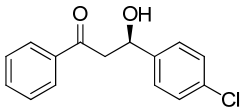



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 49.9526 | 19.827 | 0.000 | 36017396 | 0.00 | BB | 43.9 |
| 2 | 50.0474 | 23.720 | 0.000 | 36085760 | 0.00 | BB | 52.1 |
| | **100.0000** | | **0.000** | **72103152** | | | |

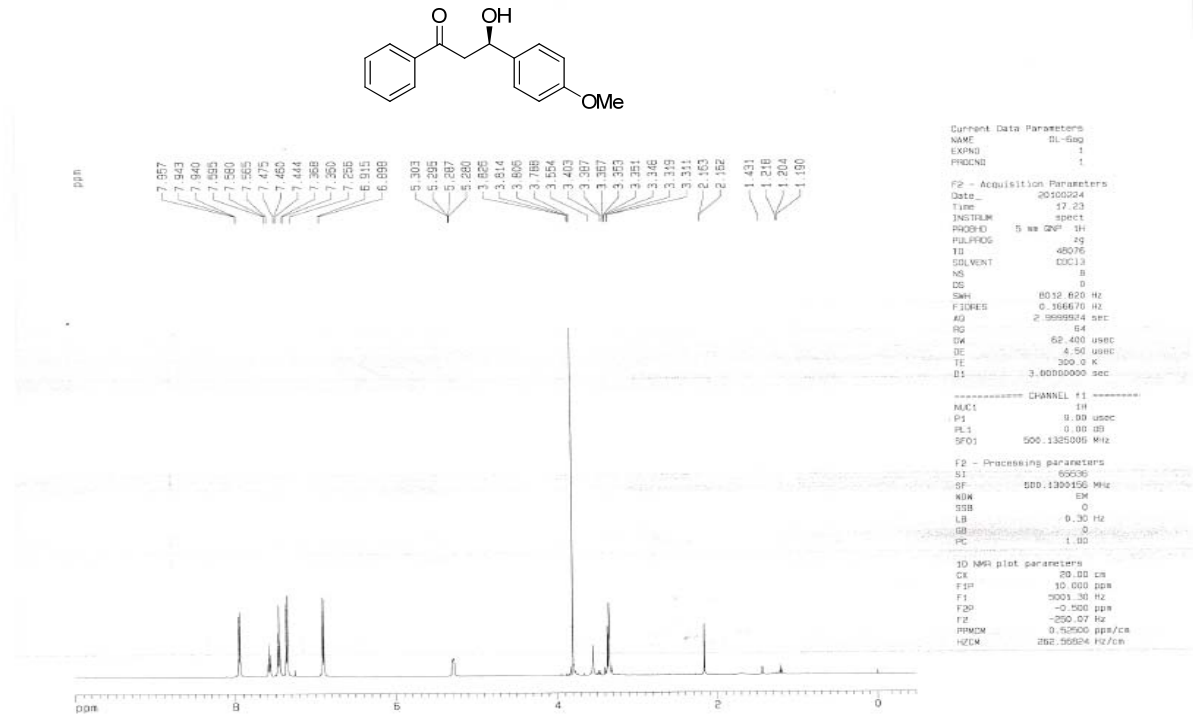
| | | | |
|---|---|---|---|
| Data File: | c:\star\9-9-09 2;57;59 pm -1.run | Run Mode: | Analysis |
| Sample ID: | 15-242-4-ClPh | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 09/09/09 02:57:59 PM | Run Time (min): | 35.440 |

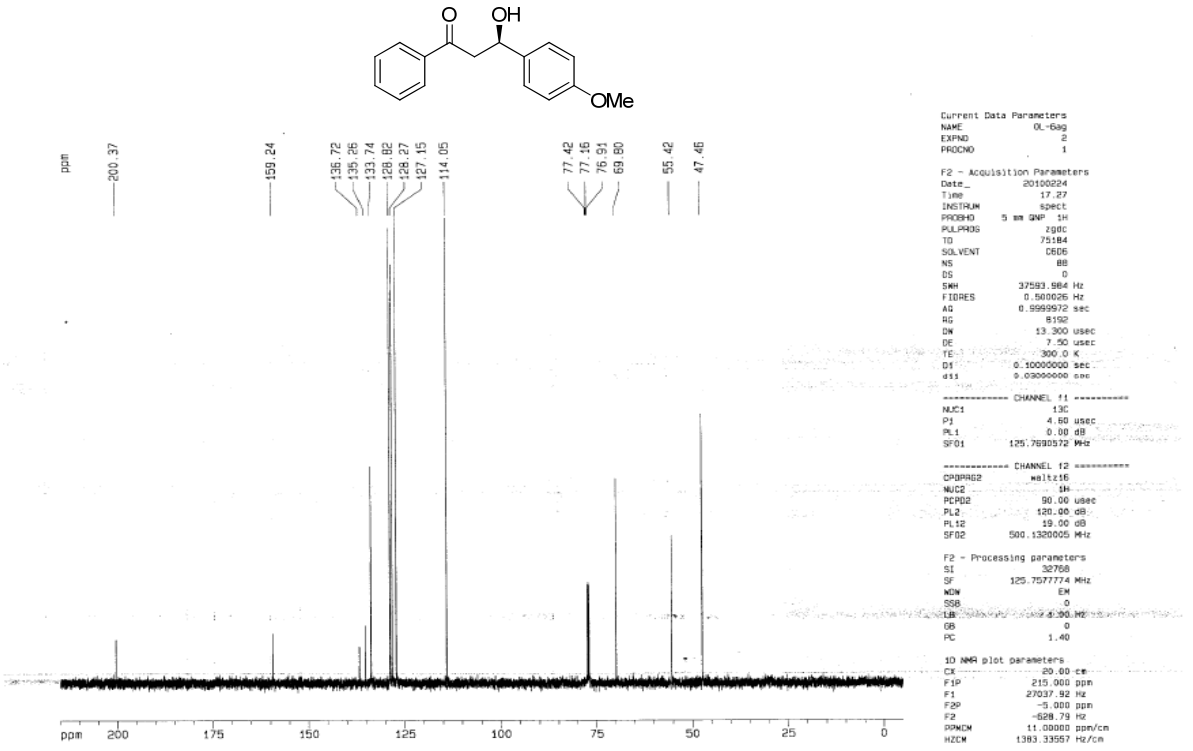



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 10.2628 | 15.080 | 0.000 | 7807594 | 0.00 | BB | 17.1 |
| 2 | 89.7372 | 18.360 | 0.000 | 68268896 | 0.00 | BB | 22.2 |
| | **100.0000** | | **0.000** | **76076488** | | | |

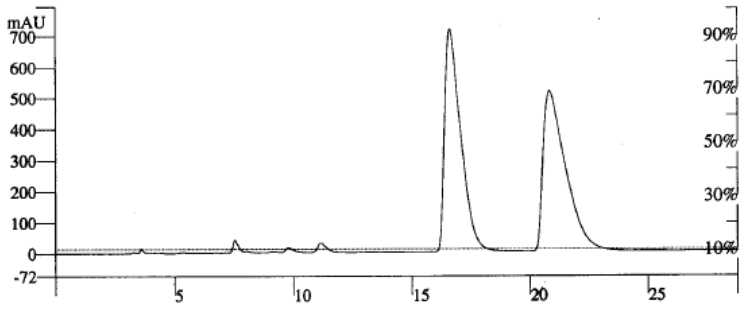
6ag:

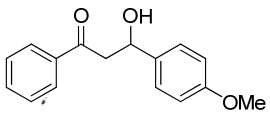

O
OH
OMe
ppm
7.957
7.943
7.940
7.595
7.580
7.565
7.475
7.460
7.444
7.368
7.360
7.256
6.915
6.898
5.303
5.295
5.287
5.280
3.825
3.814
3.805
3.788
3.554
3.403
3.387
3.367
3.353
3.351
3.346
3.319
3.311
2.163
2.162
1.431
1.218
1.204
1.190
Current Data Parameters
NAME 0L-6ag
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100224
Time 17.23
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 2.9999524 sec
RG 64
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 8.00 usec
PL1 0.00 dB
SF01 500.1325005 MHz
F2 - Processing parameters
SI 65536
SF 500.1300156 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.62500 ppm/cm
HZCM 262.56524 Hz/cm
ppm
8
6
4
2
0


O
OH
OMe
ppm
200.37
159.24
136.72
135.26
133.74
128.82
128.27
127.15
114.05
77.42
77.16
76.91
69.80
55.42
47.46
Current Data Parameters
NAME 0L-6ag
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100224
Time 17.27
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 75184
SOLVENT C6D6
NS 88
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 8192
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SF01 125.7690572 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SF02 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577774 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 27037.92 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 11.00000 ppm/cm
HZCM 1383.33557 Hz/cm
ppm
200
175
150
125
100
75
50
25
0

| | | | |
|---|---|---|---|
| Data File: | c:\star\3-3-10 12;06;16 am -1.run | Run Mode: | Analysis |
| Sample ID: | Manual Sample | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 03/03/10 12:06:16 AM | Run Time (min): | 28.800 |

Injection Method: c:\star\cheol hong\mukaiyama

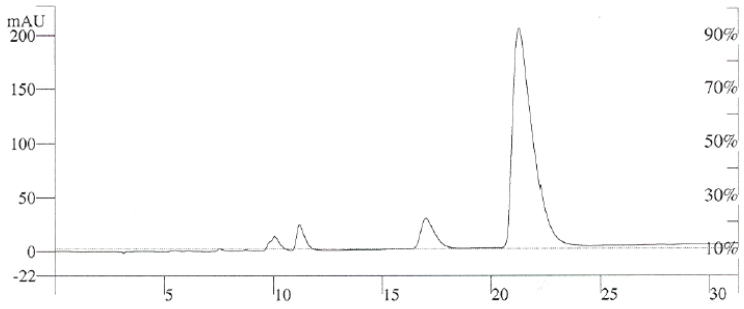


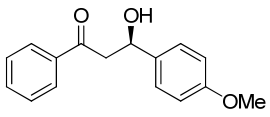




| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 49.7038 | 16.600 | 0.000 | 172814992 | 0.00 | BB | 44.1 |
| 2 | 50.2962 | 20.813 | 0.000 | 174874832 | 0.00 | BB | 61.4 |
| | **100.0000** | | **0.000** | **347689824** | | | |

| | | | |
|---|---|---|---|
| Data File: | c:\star\3-2-10 11;29;15 pm -1.run | Run Mode: | Analysis |
| Sample ID: | Manual Sample | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 03/02/10 11:29:15 PM | Run Time (min): | 31.360 |

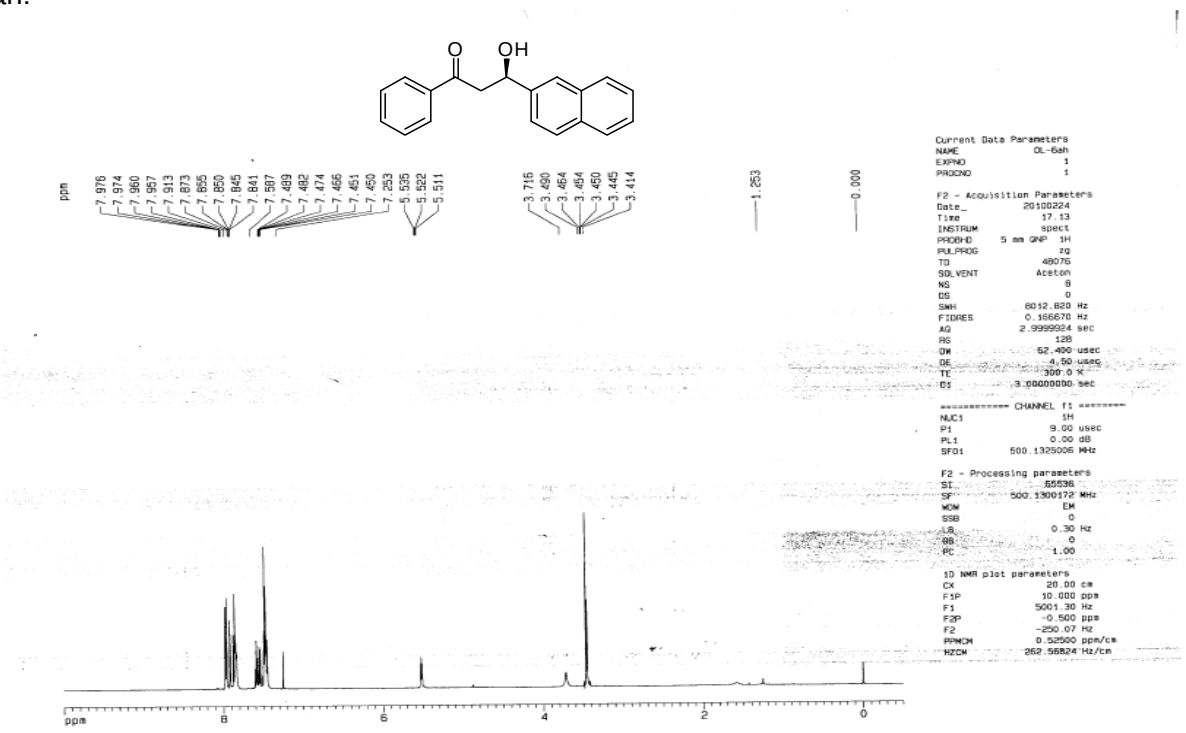
Injection Method: c:\star\cheol hong\mukaiyama

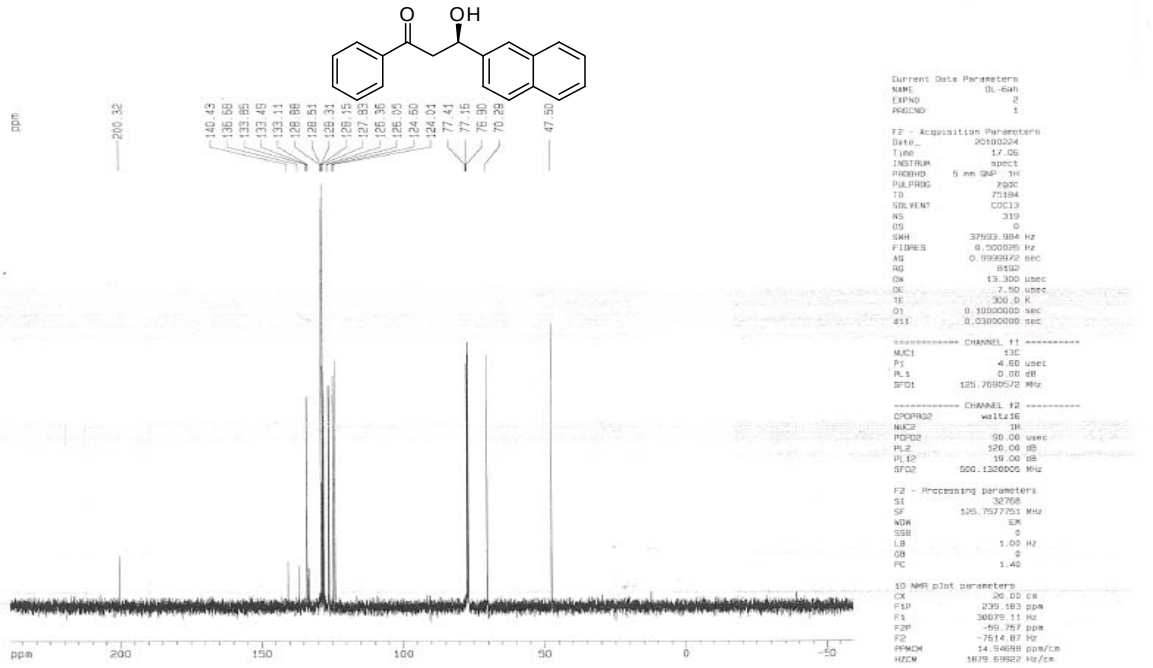


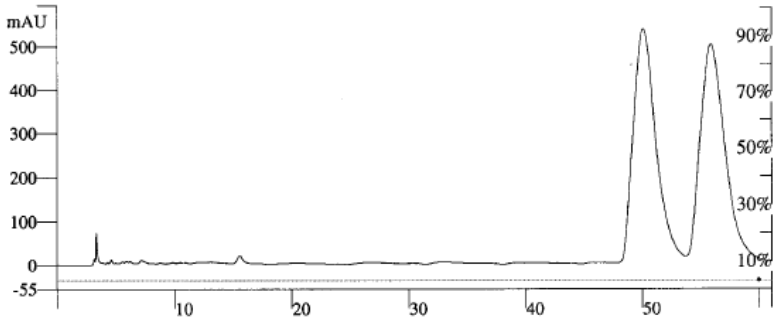

| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 7.7459 | 17.000 | 0.000 | 5500550 | 0.00 | BB | 38.5 |
| 2 | 92.2541 | 21.267 | 0.000 | 65511700 | 0.00 | BB | 58.1 |
| | **100.0000** | | **0.000** | **71012248** | | | |

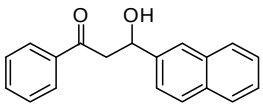
6ah:


O
OH
ppm
7.976
7.974
7.960
7.957
7.913
7.873
7.865
7.850
7.845
7.841
7.597
7.489
7.482
7.474
7.466
7.451
7.450
7.253
5.535
5.522
5.511
3.716
3.490
3.464
3.454
3.450
3.445
3.414
1.253
0.000
Current Data Parameters
NAME OL-6ah
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100224
Time 17.13
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 48076
SOLVENT Aceton
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 2.9999994 sec
RG 128
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1325006 MHz
F2 - Processing parameters
SI 65536
SF 500.1300172 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.58824 Hz/cm
ppm
8
6
4
2
0


O
OH
ppm
200.32
140.43
136.66
133.85
133.45
133.11
128.88
128.51
128.31
126.15
127.83
126.36
126.05
124.60
124.01
77.41
77.16
76.90
70.29
47.50
Current Data Parameters
NAME OL-6ah
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100224
Time 17.06
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 75184
SOLVENT CDCl3
NS 319
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 8192
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SFO1 125.7680572 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577751 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 239.183 ppm
F1 30079.11 Hz
F2P -59.757 ppm
F2 -7514.87 Hz
PPMCM 14.54698 ppm/cm
HZCM 5879.69922 Hz/cm
ppm
200
150
100
50
0
-50

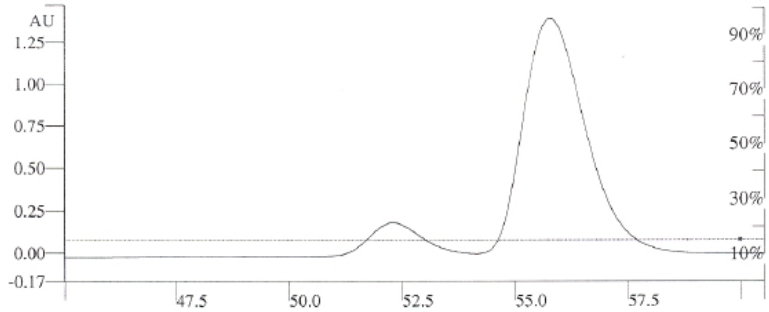
| | | | |
|---|---|---|---|
| Data File: | c:\star\11-12-09 4;30;59 pm -1.run | Run Mode: | Analysis |
| Sample ID: | 6ah-2naphthyl | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 11/12/09 04:30:59 PM | Run Time (min): | 61.120 |

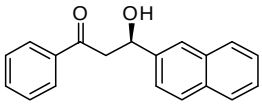



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 49.7408 | 50.067 | 0.000 | 356369888 | 0.00 | BB | 123.2 |
| 2 | 50.2592 | 55.853 | 0.000 | 360083392 | 0.00 | BB | 134.8 |
| | **100.0000** | | **0.000** | **716453248** | | | |

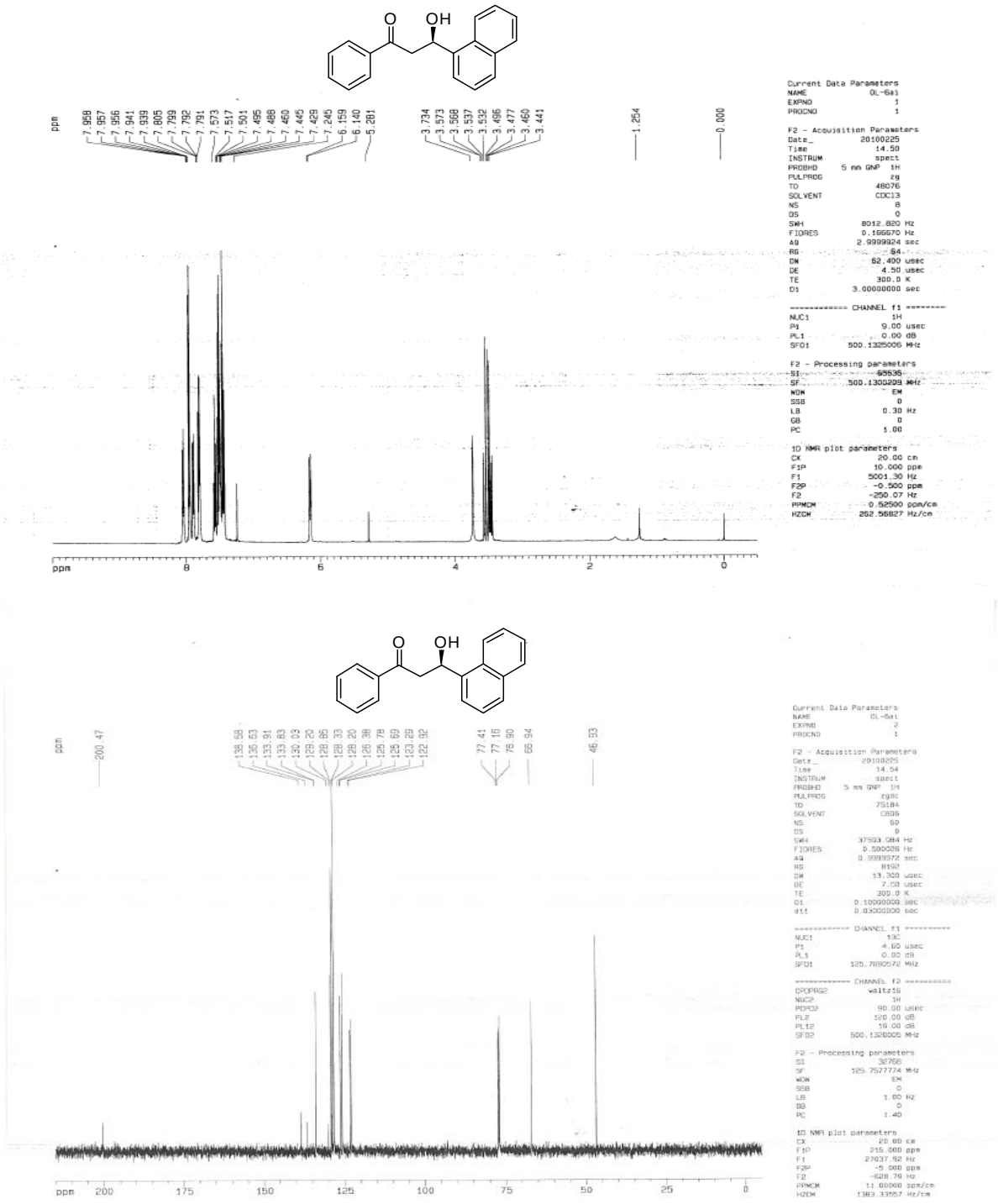
| | | | |
|---|---|---|---|
| Data File: | c:\star\10-14-09 1;22;03 pm -1.run | Run Mode: | Analysis |
| Sample ID: | 16-17-2-naphthyl | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 10/14/09 01:22:03 PM | Run Time (min): | 60.533 |



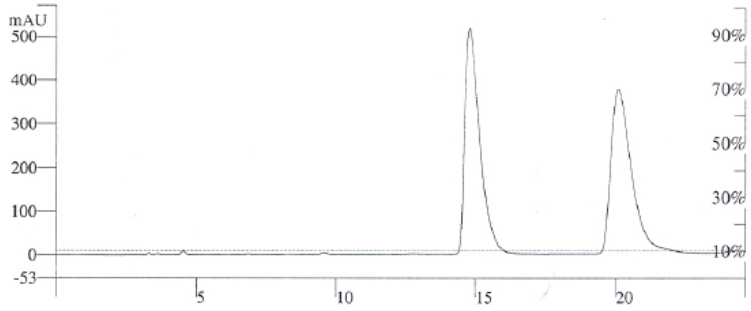

| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 9.9545 | 52.280 | 0.000 | 75602712 | 0.00 | BB | 75.9 |
| 2 | 90.0455 | 55.773 | 0.000 | 683883072 | 0.00 | BB | 88.6 |
| | **100.0000** | | **0.000** | **759485760** | | | |

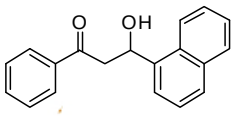
6ai:


O
OH
ppm
7.958
7.957
7.956
7.941
7.939
7.805
7.799
7.792
7.791
7.573
7.517
7.501
7.495
7.488
7.450
7.445
7.429
7.245
6.159
6.140
5.281
3.734
3.573
3.568
3.537
3.532
3.496
3.477
3.460
3.441
1.254
0.000
Current Data Parameters
NAME 0L-6ai
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100225
Time 14.50
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 64
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1325006 MHz
F2 - Processing parameters
SI 65536
SF 500.1300299 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56827 Hz/cm
ppm
8
6
4
2
0
O
OH
ppm
200.47
138.58
135.63
133.91
133.83
130.03
128.20
128.85
128.33
128.20
126.38
125.78
125.69
123.89
122.92
77.41
77.15
76.90
66.94
46.93
Current Data Parameters
NAME 0L-6ai
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100225
Time 14.54
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg
TD 75184
SOLVENT CDCl3
NS 60
DS 8
SWH 37593.084 Hz
FIDRES 0.500026 Hz
AQ 0.9999872 sec
RG 8192
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SFO1 125.7695672 MHz
CHANNEL f2
DPOPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577774 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 27037.92 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 11.00000 ppm/cm
HZCM 1383.33557 Hz/cm
ppm
200
175
150
125
100
75
50
25
0

| | | | |
|---|---|---|---|
| Data File: | c:\star\3-3-10 8;57;50 am -1.run | Run Mode: | Analysis |
| Sample ID: | Manual Sample | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 03/03/10 08:57:50 AM | Run Time (min): | 24.693 |

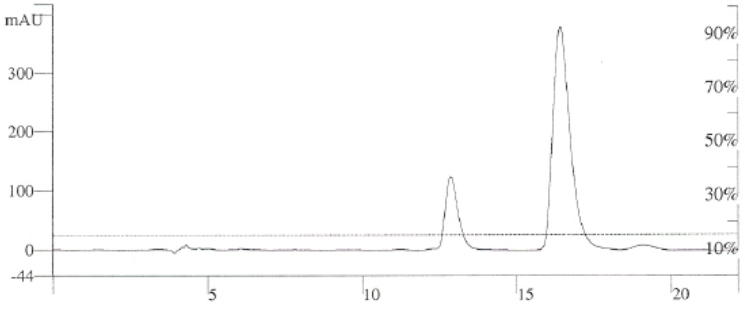
Injection Method: c:\star\cheol hong\mukaiyama

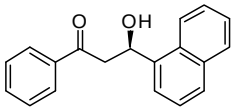



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 50.2628 | 14.787 | 0.000 | 98443992 | 0.00 | BB | 33.6 |
| 2 | 49.7372 | 20.093 | 0.000 | 97414728 | 0.00 | BB | 45.8 |
| | **100.0000** | | **0.000** | **195858720** | | | |

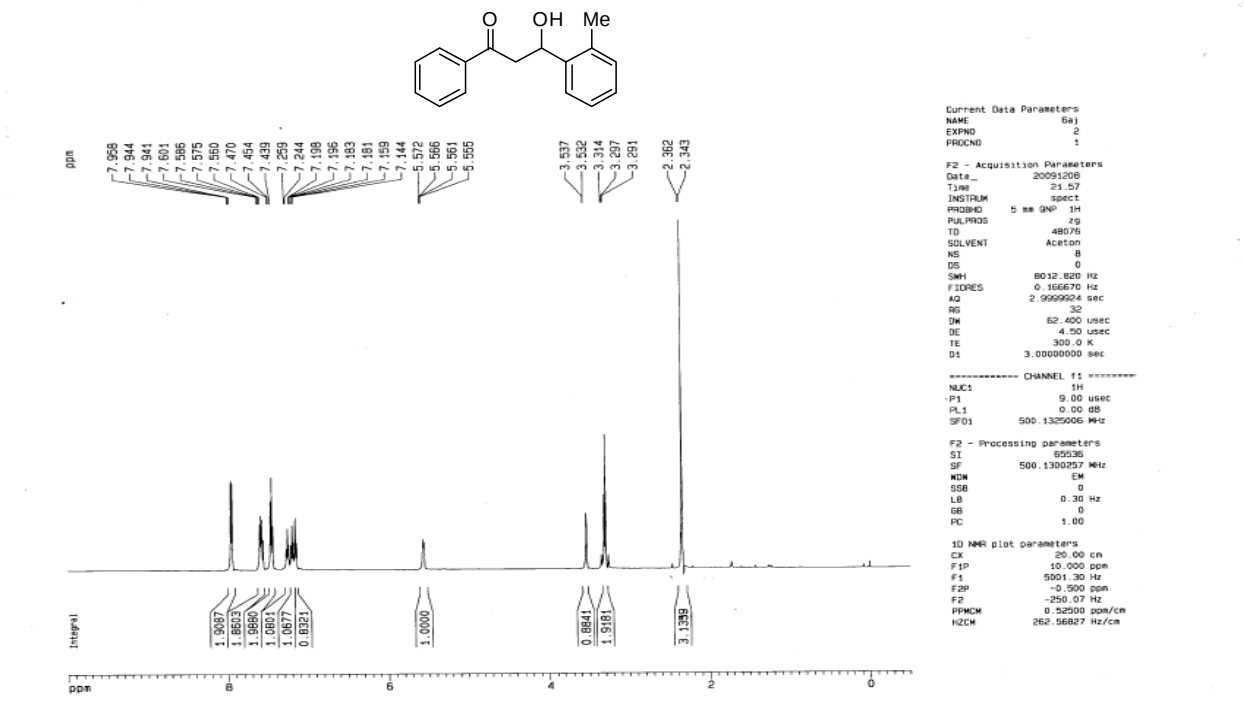
| | | | |
|---|---|---|---|
| Data File: | c:\star\10-20-09 5;21;04 pm -1.run | Run Mode: | Analysis |
| Sample ID: | 16-41-tol/hxs(1:1) | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 10/20/09 05:21:04 PM | Run Time (min): | 22.187 |

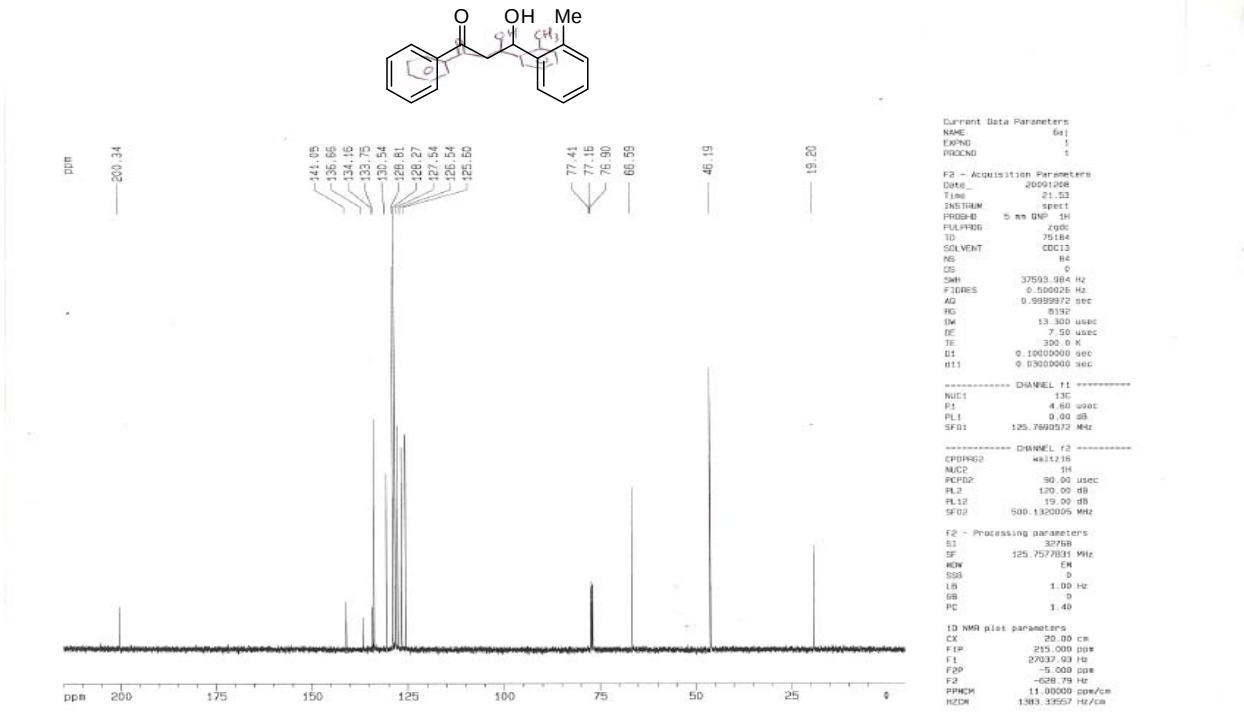


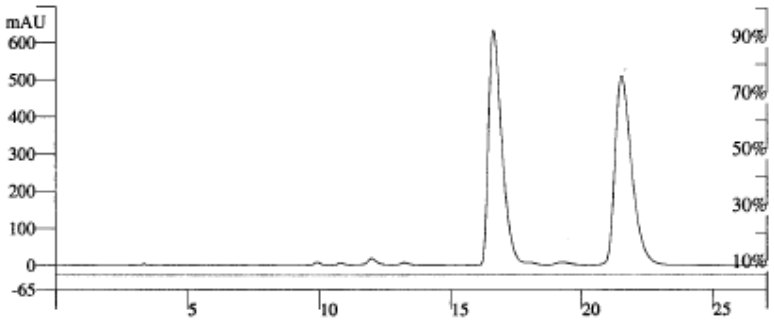

| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 18.9378 | 12.867 | 0.000 | 17839408 | 0.00 | BB | 26.3 |
| 2 | 81.0622 | 16.387 | 0.000 | 76360552 | 0.00 | BB | 35.6 |
| | **100.0000** | | **0.000** | **94199960** | | | |

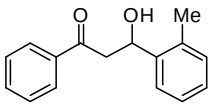
6aj:


O
OH
Me
ppm
7.958
7.944
7.941
7.601
7.586
7.575
7.560
7.470
7.454
7.439
7.259
7.244
7.198
7.196
7.183
7.181
7.159
7.144
5.572
5.566
5.561
5.555
3.537
3.532
3.314
3.297
3.291
2.362
2.343
Integral
1.9087
1.8603
1.9860
1.0801
1.0677
0.8321
1.0000
0.8841
1.9181
3.1399
ppm
8
6
4
2
0
Current Data Parameters
NAME 6aj
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091208
Time 21.57
INSTRUM spect
PROBHD 5 mm GNP 1H
PULPROG zg
TD 48076
SOLVENT Aceton
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 32
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SF01 500.1325006 MHz
F2 - Processing parameters
SI 65536
SF 500.1300257 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56827 Hz/cm


O
OH
Me
ppm
200.34
141.05
136.66
134.16
133.75
130.54
128.81
128.27
127.54
126.54
125.50
77.41
77.16
76.90
66.59
46.19
19.20
ppm
200
175
150
125
100
75
50
25
0
Current Data Parameters
NAME 6aj
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091208
Time 21.53
INSTRUM spect
PROBHD 5 mm GNP 1H
PULPROG zgdc
TD 75184
SOLVENT CDCl3
NS 64
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9999872 sec
RG 8192
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SF01 125.7690572 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SF02 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577831 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 27037.93 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 11.00000 ppm/cm
HZCM 1383.33557 Hz/cm

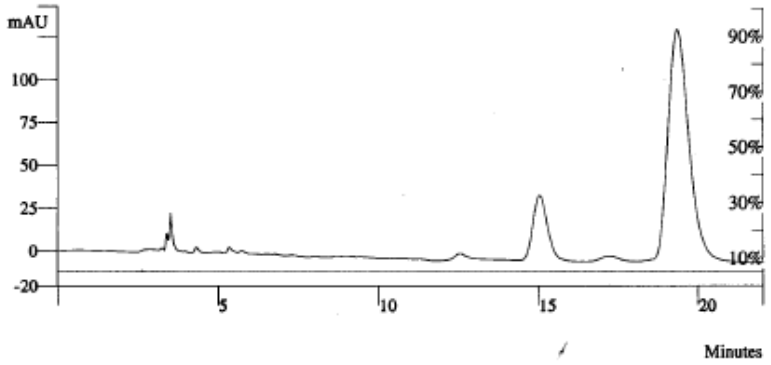
| | | | |
|---|---|---|---|
| Data File: | c:\star\9-10-09 3;48;57 pm -1.run | Run Mode: | Analysis |
| Sample ID: | 2-MePh-rac, 15-248 | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 09/10/09 03:48:57 PM | Run Time (min): | 27.093 |

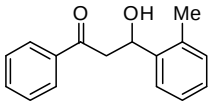



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 49.6295 | 16.627 | 0.000 | 113052048 | 0.00 | BB | 32.5 |
| 2 | 50.3705 | 21.533 | 0.000 | 114739976 | 0.00 | BB | 40.2 |
| | **100.0000** | | **0.000** | **227792032** | | | |

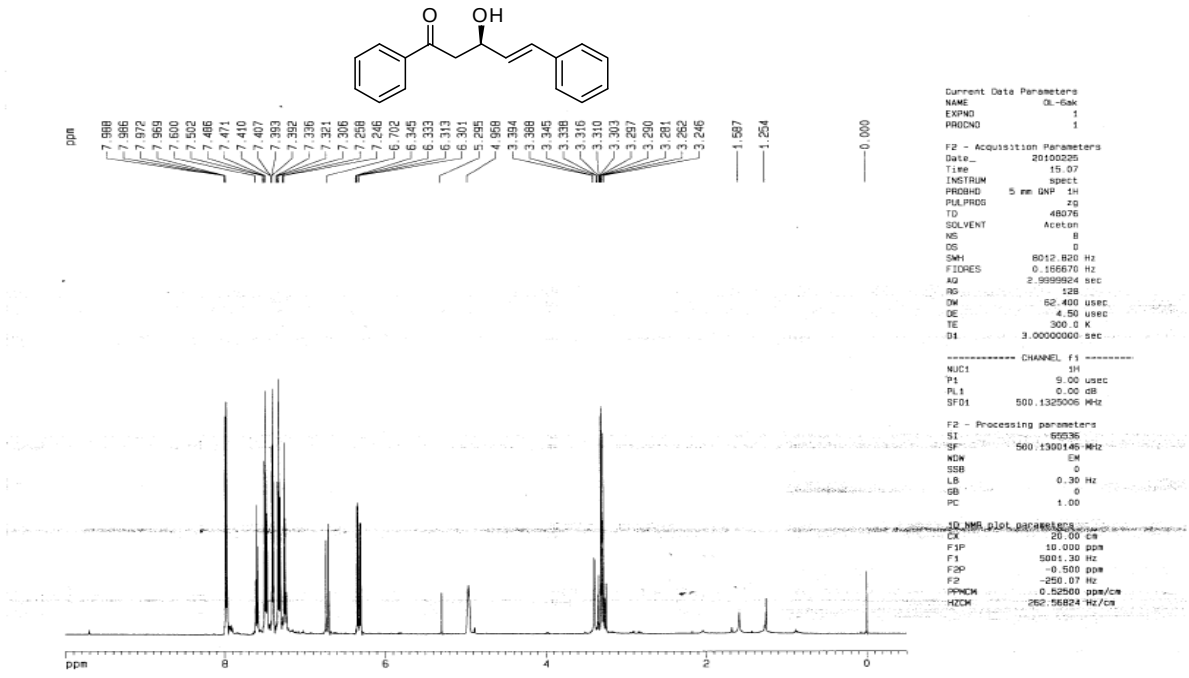
| | | | |
|---|---|---|---|
| Data File: | c:\star\10-20-09 9;51;25 am -1.run | Run Mode: | Analysis |
| Sample ID: | 16-40-tol/hex(1:1) | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 10/20/09 09:51:25 AM | Run Time (min): | 22.053 |




| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 16.2120 | 15.027 | 0.000 | 6045745 | 0.00 | BB | 29.3 |
| 2 | 83.7880 | 19.347 | 0.000 | 31246108 | 0.00 | BB | 41.7 |
| | **100.0000** | | **0.000** | **37291852** | | | |

6ak:


O
OH
ppm
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7.986
7.972
7.969
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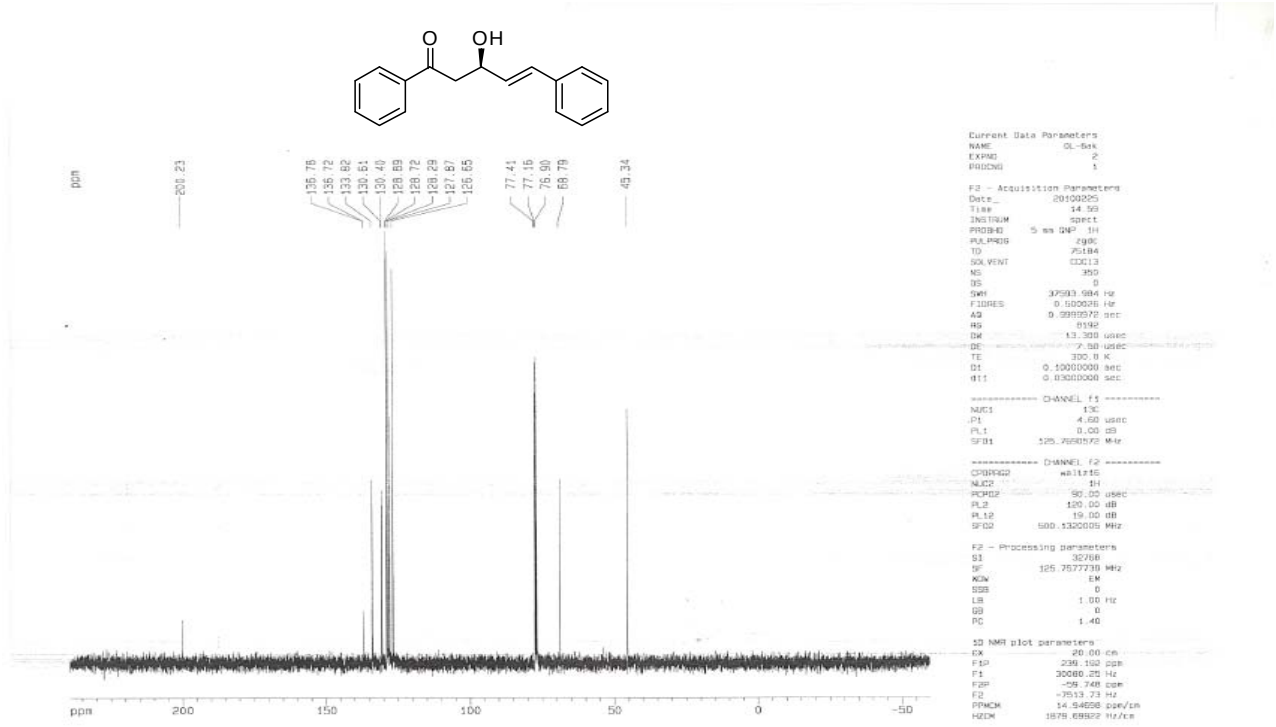
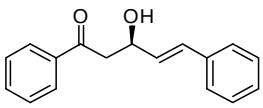
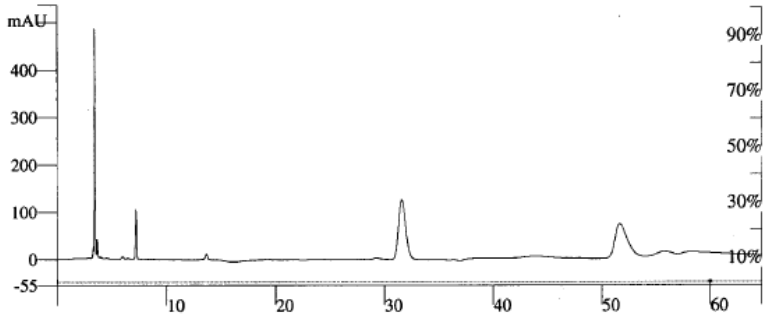
7.502
7.486
7.471
7.410
7.407
7.393
7.392
7.336
7.321
7.306
7.258
7.246
6.702
6.345
6.333
6.313
6.301
5.295
4.958
3.394
3.388
3.345
3.338
3.316
3.310
3.303
3.297
3.290
3.281
3.262
3.246
1.587
1.254
0.000
Current Data Parameters
NAME OL-6ak
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100225
Time 15.07
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 48076
SOLVENT Aceton
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 128
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SF01 500.1325006 MHz
F2 - Processing parameters
SI 65536
SF 500.1300145 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56824 Hz/cm
ppm
8
6
4
2
0

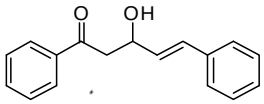

O
OH
ppm
208.23
136.76
136.72
133.82
130.61
130.40
128.89
128.72
128.29
127.87
126.65
77.41
77.16
76.90
68.79
45.34
Current Data Parameters
NAME OL-6ak
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100225
Time 14.59
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg
TD 75184
SOLVENT CDCl3
NS 350
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9988572 sec
RG 8192
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SF01 125.7685578 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SF02 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577738 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 236.192 ppm
F1 30680.25 Hz
F2P -59.748 ppm
F2 -7513.73 Hz
PPMCM 14.54658 ppm/cm
HZCM 1879.69922 Hz/cm
ppm
200
150
100
50
0
-50


O
OH

| | | | |
|---|---|---|---|
| Data File: | c:\star\3-3-10 12;06;18 pm -1.run | Run Mode: | Analysis |
| Sample ID: | Manual Sample | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 03/03/10 12:06:18 PM | Run Time (min): | 64.773 |

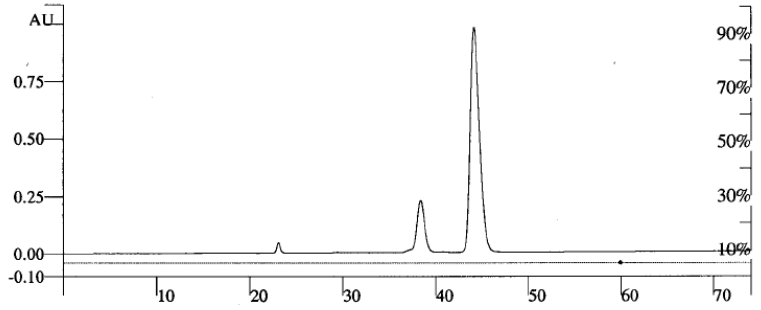
Injection Method: c:\star\cheol hong\mukaiyama

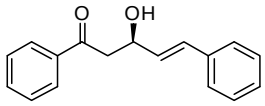



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 50.1852 | 31.560 | 0.000 | 28737336 | 0.00 | BB | 41.9 |
| 2 | 49.8148 | 51.640 | 0.000 | 28525232 | 0.00 | BB | 74.6 |
| | **100.0000** | | **0.000** | **57262568** | | | |

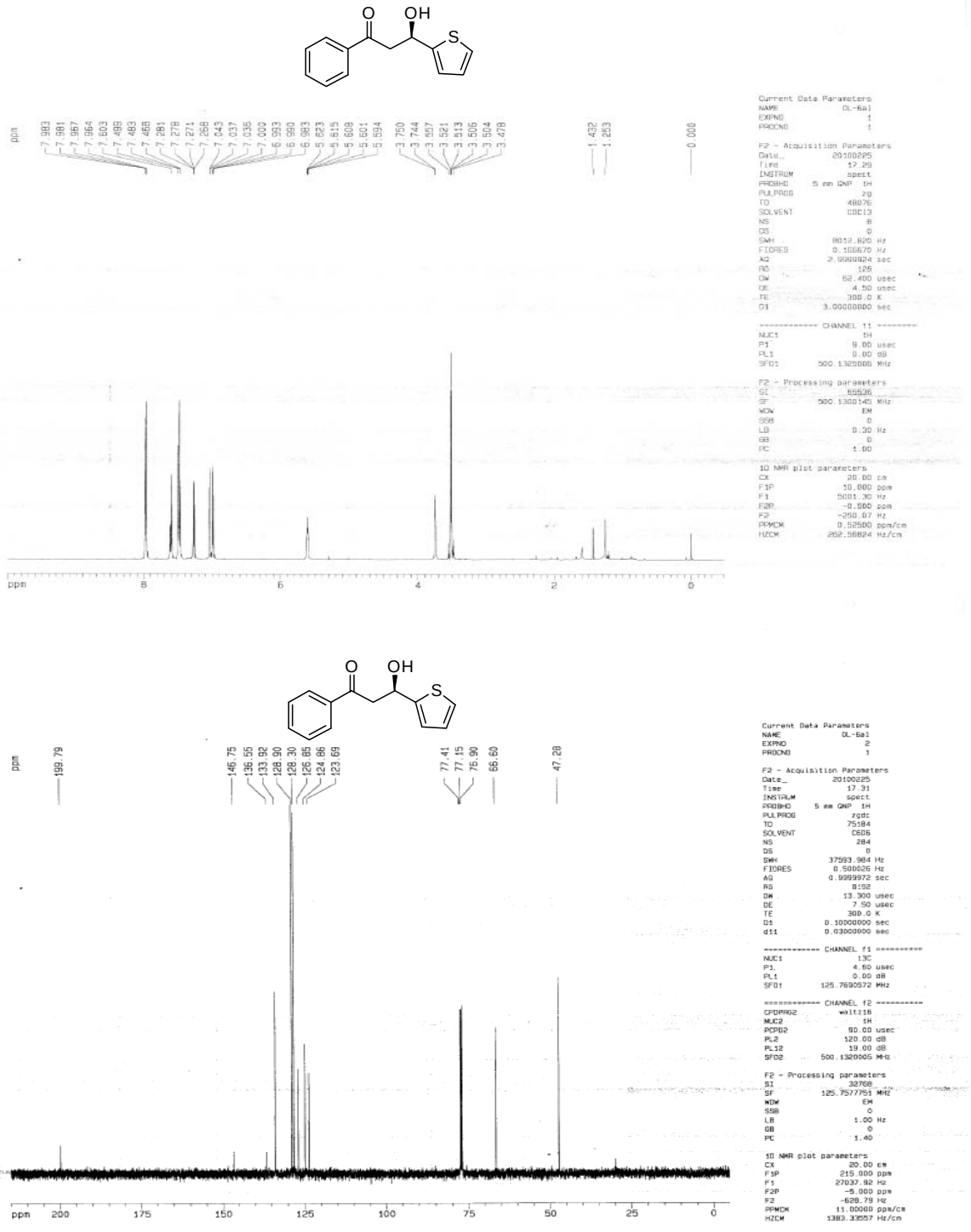
| | | | |
|---|---|---|---|
| Data File: | c:\star\11-13-09 11;48;05 am -1.run | Run Mode: | Analysis |
| Sample ID: | 6ak-cinnamovl | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 11/13/09 11:48:05 AM | Run Time (min): | 74.107 |



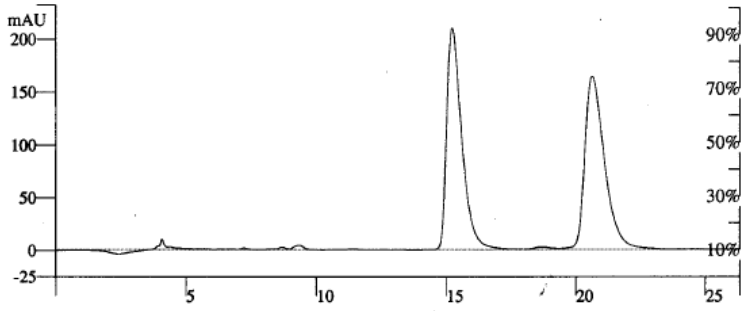

| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 13.9294 | 38.360 | 0.000 | 55779180 | 0.00 | BB | 48.4 |
| 2 | 86.0706 | 44.093 | 0.000 | 344662816 | 0.00 | BB | 63.9 |
| | **100.0000** | | **0.000** | **400441984** | | | |

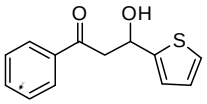
6al:


O
OH
S
ppm
7.983
7.981
7.967
7.964
7.603
7.498
7.483
7.458
7.281
7.278
7.271
7.268
7.043
7.037
7.036
7.000
6.993
6.990
6.983
5.623
5.615
5.608
5.601
5.594
3.750
3.744
3.557
3.521
3.513
3.506
3.504
3.478
1.432
1.253
0.000
Current Data Parameters
NAME DL-6al
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100225
Time 17.29
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 128
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1320000 MHz
F2 - Processing parameters
SI 65536
SF 500.1300140 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.660 ppm
F2 -258.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56824 Hz/cm
ppm
8
6
4
2
0
O
OH
S
ppm
199.79
146.75
136.55
133.92
128.90
128.30
126.85
124.86
123.69
77.41
77.15
76.90
66.60
47.28
Current Data Parameters
NAME DL-6al
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100225
Time 17.31
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 75184
SOLVENT CDCl3
NS 284
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9999872 sec
RG 8192
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SFO1 125.7690572 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577751 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 27037.92 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 11.00000 ppm/cm
HZCM 1383.33557 Hz/cm
ppm
200
175
150
125
100
75
50
25
0

| | | | |
|---|---|---|---|
| Data File: | c:\star\3-3-10 3;12;47 pm -1.run | Run Mode: | Analysis |
| Sample ID: | Manual Sample | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 03/03/10 03:12:47 PM | Run Time (min): | 26.347 |

Injection Method: c:\star\cheol hong\mukaiyama

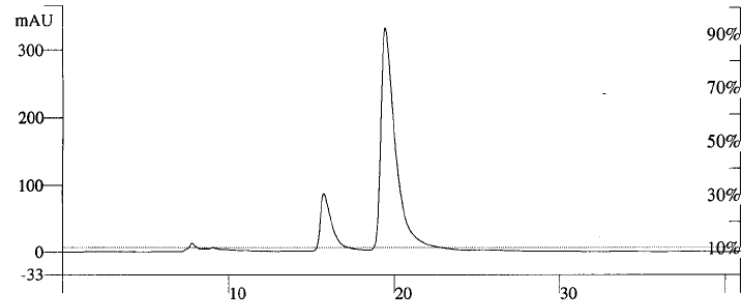


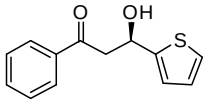




| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 50.1517 | 15.213 | 0.000 | 43247828 | 0.00 | BB | 36.6 |
| 2 | 49.8483 | 20.627 | 0.000 | 42986264 | 0.00 | BB | 47.3 |
| | **100.0000** | | **0.000** | **86234096** | | | |

| | | | |
|---|---|---|---|
| Data File: | c:\star\10-5-09 9;00;21 pm -1.run | Run Mode: | Analysis |
| Sample ID: | Manual Sample | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 10/05/09 09:00:21 PM | Run Time (min): | 40.933 |

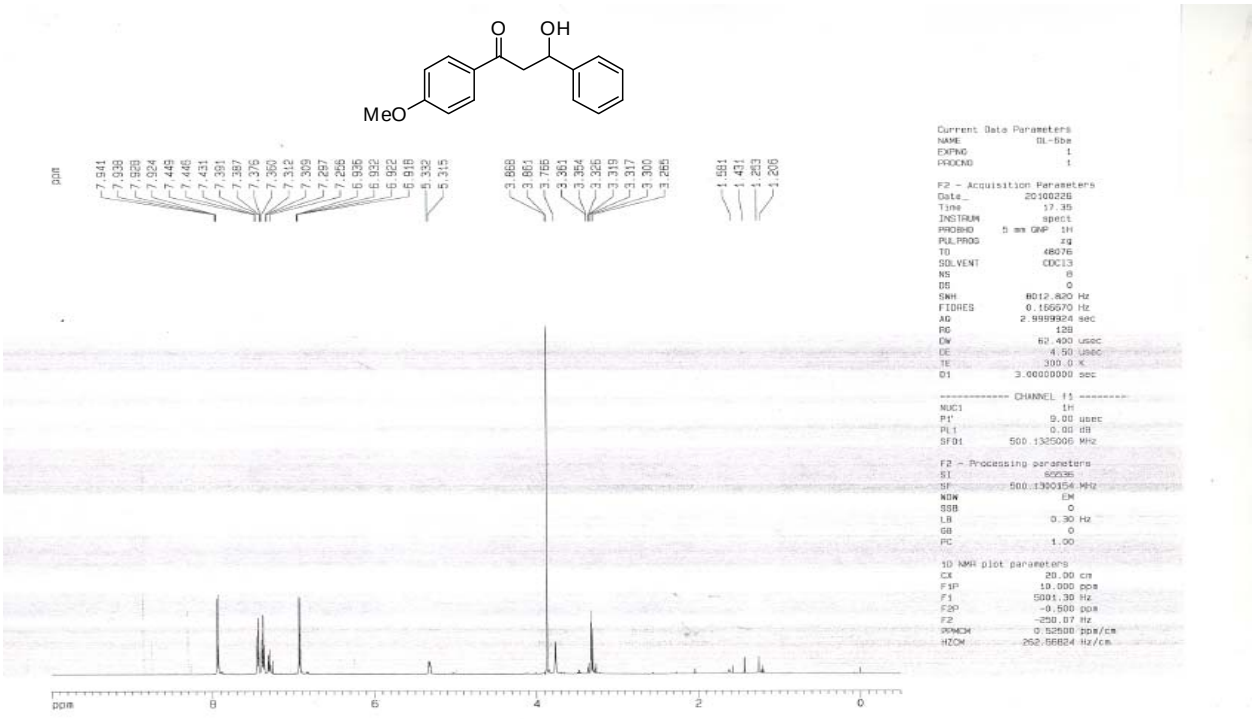
Injection Method: c:\star\cheol hong\mukaiyama

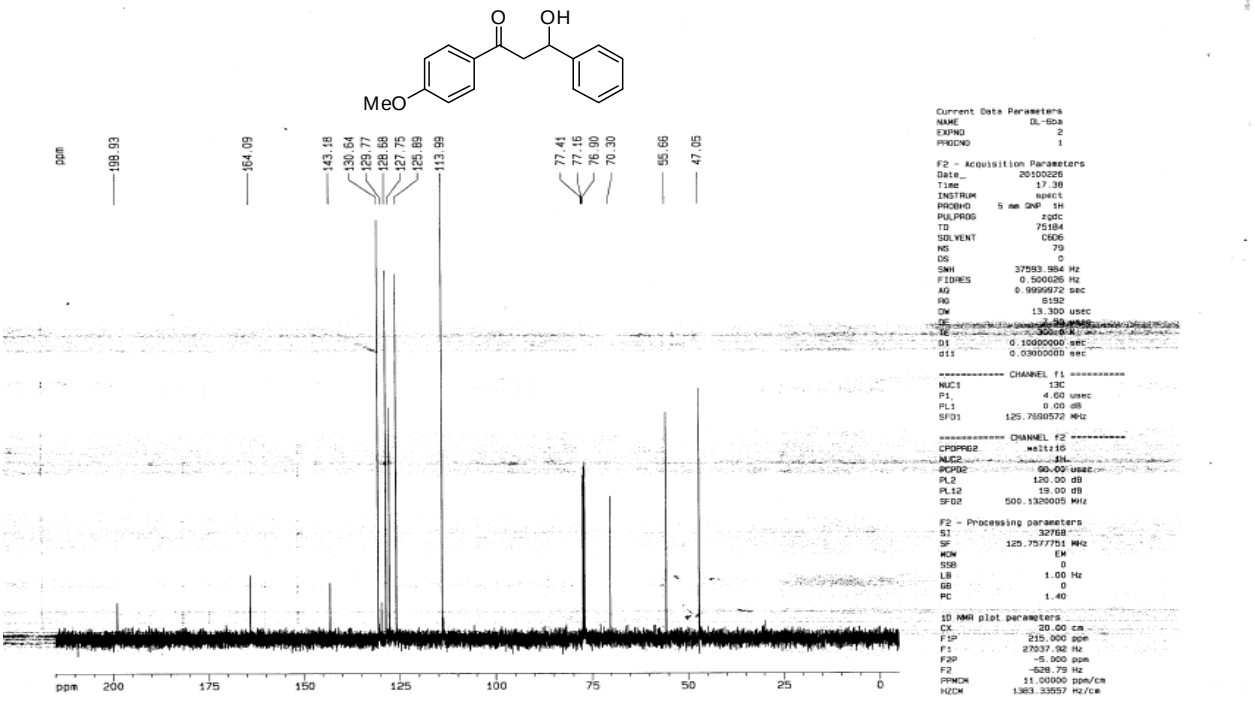



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 15.0669 | 15.720 | 0.000 | 18674750 | 0.00 | BB | 41.4 |
| 2 | 84.9331 | 19.427 | 0.000 | 105270680 | 0.00 | BB | 51.9 |
| | **100.0000** | | **0.000** | **123945432** | | | |

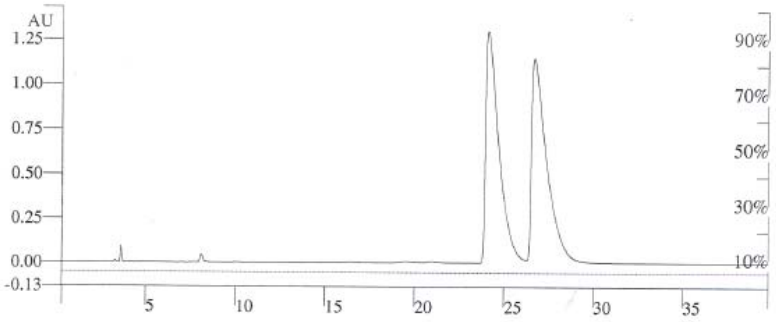
6ba:

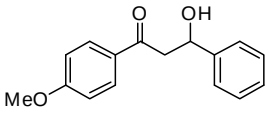

O
OH
MeO
ppm
7.941
7.938
7.928
7.924
7.445
7.431
7.391
7.387
7.376
7.360
7.312
7.309
7.297
7.266
6.936
6.932
6.922
6.918
5.332
5.315
3.868
3.861
3.766
3.361
3.354
3.326
3.319
3.317
3.300
3.265
1.581
1.431
1.263
1.206
Current Data Parameters
NAME DL-6ba
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100226
Time 17.35
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166570 Hz
AQ 2.9999924 sec
RG 128
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1325006 MHz
F2 - Processing parameters
SI 65536
SF 500.1300154 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56824 Hz/cm
ppm
8
6
4
2
0


O
OH
MeO
ppm
198.93
164.09
143.18
130.64
129.77
128.68
127.75
125.89
113.99
77.41
77.15
76.90
70.30
55.66
47.05
Current Data Parameters
NAME DL-6ba
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100226
Time 17.38
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 75184
SOLVENT CDCl3
NS 79
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 8192
DW 13.300 usec
D1 0.10000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SFO1 125.7690572 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577751 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 27037.92 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 11.00000 ppm/cm
HZCM 1383.33557 Hz/cm
ppm
200
175
150
125
100
75
50
25
0

| | | | |
|---|---|---|---|
| Data File: | c:\star\3-4-10 11;38;03 am -1.run | Run Mode: | Analysis |
| Sample ID: | Manual Sample | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 03/04/10 11:38:03 AM | Run Time (min): | 115.387 |

Injection Method: c:\star\cheol hong\mukaiyama

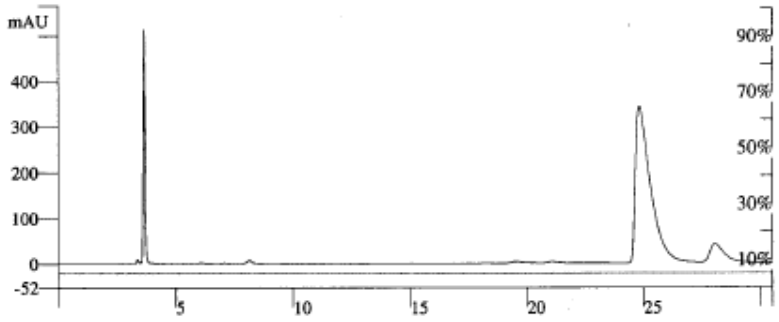


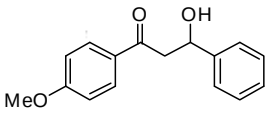




| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 49.8773 | 24.093 | 0.000 | 336204224 | 0.00 | BB | 46.0 |
| 2 | 50.1227 | 26.653 | 0.000 | 337858688 | 0.00 | BB | 51.2 |
| | **100.0000** | | **0.000** | **674062912** | | | |

| | | | |
|---|---|---|---|
| Data File: | c:\star\3-4-10 1;56;05 pm -1.run | Run Mode: | Analysis |
| Sample ID: | Manual Sample | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 03/04/10 01:56:05 PM | Run Time (min): | 30.533 |

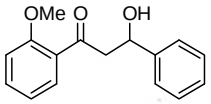
Injection Method: c:\star\cheol hong\mukaiyama

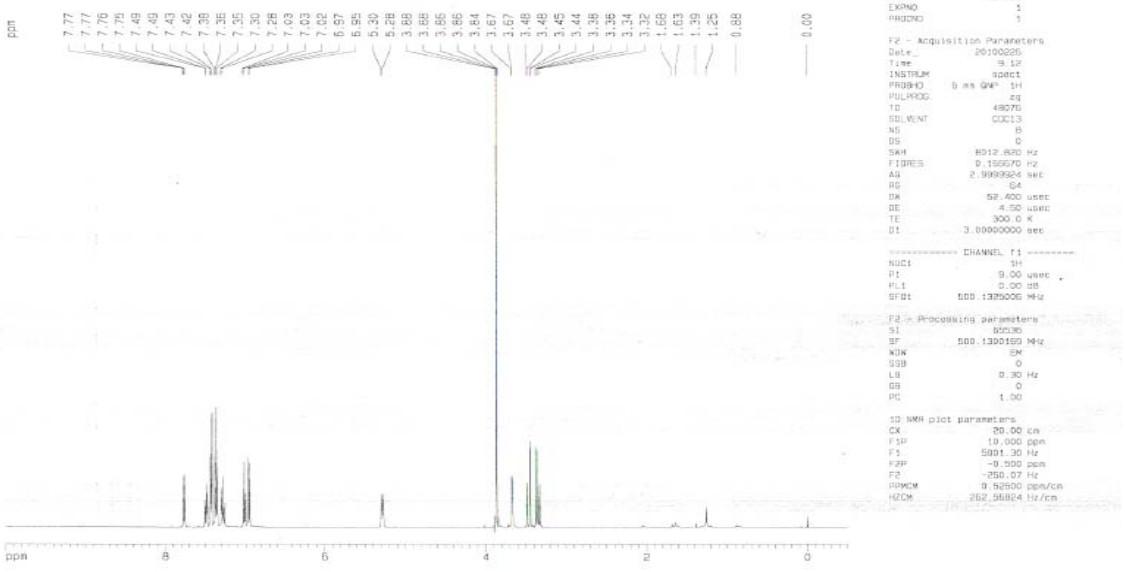



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 91.9505 | 24.813 | 0.000 | 79332808 | 0.00 | BB | 40.0 |
| 2 | 8.0495 | 28.040 | 0.000 | 6944919 | 0.00 | BB | 35.5 |
| | **100.0000** | | **0.000** | **86277728** | | | |

6ca:



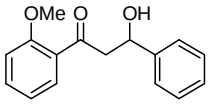

Current Data Parameters
NAME DL-6ca
EXPNO 1
PROCNO 1

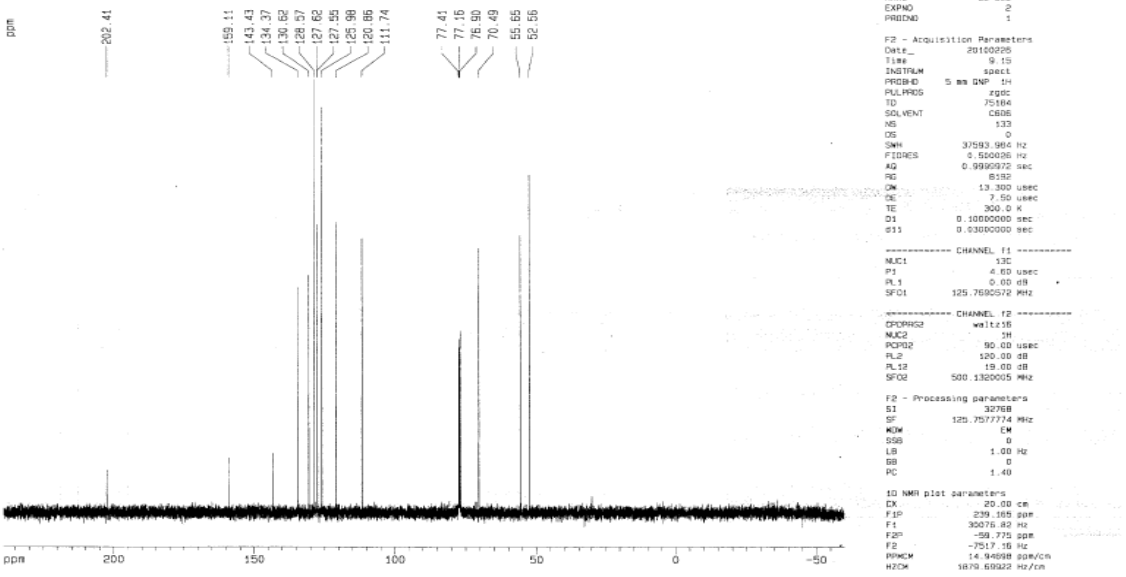
F2 - Acquisition Parameters
Date_ 20100225
Time 9.12
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166970 Hz
AQ 2.9999924 sec
RG 64
DW 52.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec

CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1325006 MHz

F2 - Processing parameters
SI 65536
SF 500.1300169 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56824 Hz/cm




Current Data Parameters
NAME DL-6ca
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100225
Time 9.15
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 75164
SOLVENT CDCl3
NS 133
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 8192
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec

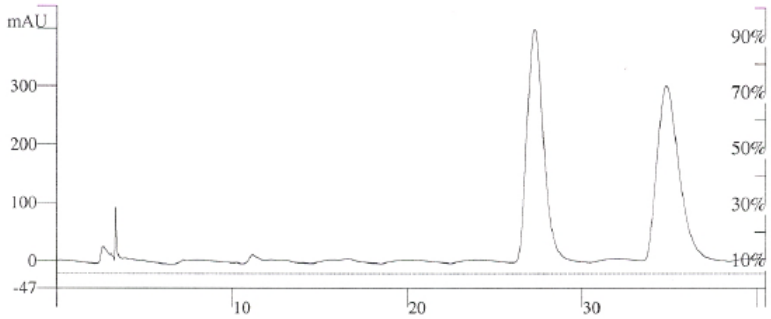
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SFO1 125.7690572 MHz

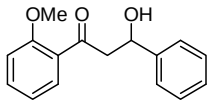
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7577774 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 239.165 ppm
F1 30076.82 Hz
F2P -59.775 ppm
F2 -7517.16 Hz
PPMCM 14.94698 ppm/cm
HZCM 1879.60922 Hz/cm

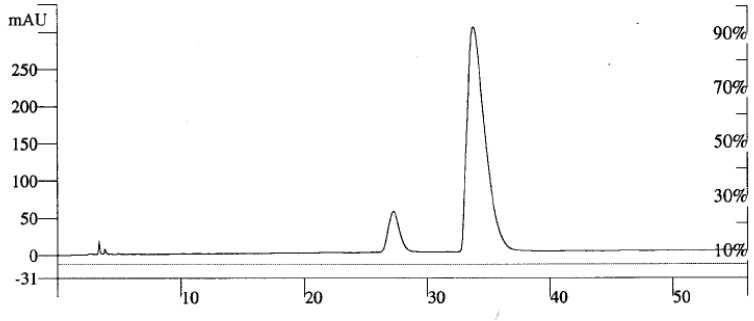
| | | | |
|---|---|---|---|
| Data File: | c:\star\11-17-09 10;52;59 am -1.run | Run Mode: | Analysis |
| Sample ID: | 16-115-racemic | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 11/17/09 10:52:59 AM | Run Time (min): | 40.533 |

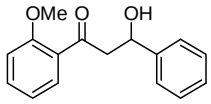



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 49.9770 | 27.240 | 0.000 | 134677360 | 0.00 | BB | 61.2 |
| 2 | 50.0230 | 34.787 | 0.000 | 134801456 | 0.00 | BB | 81.6 |
| | **100.0000** | | **0.000** | **269478816** | | | |

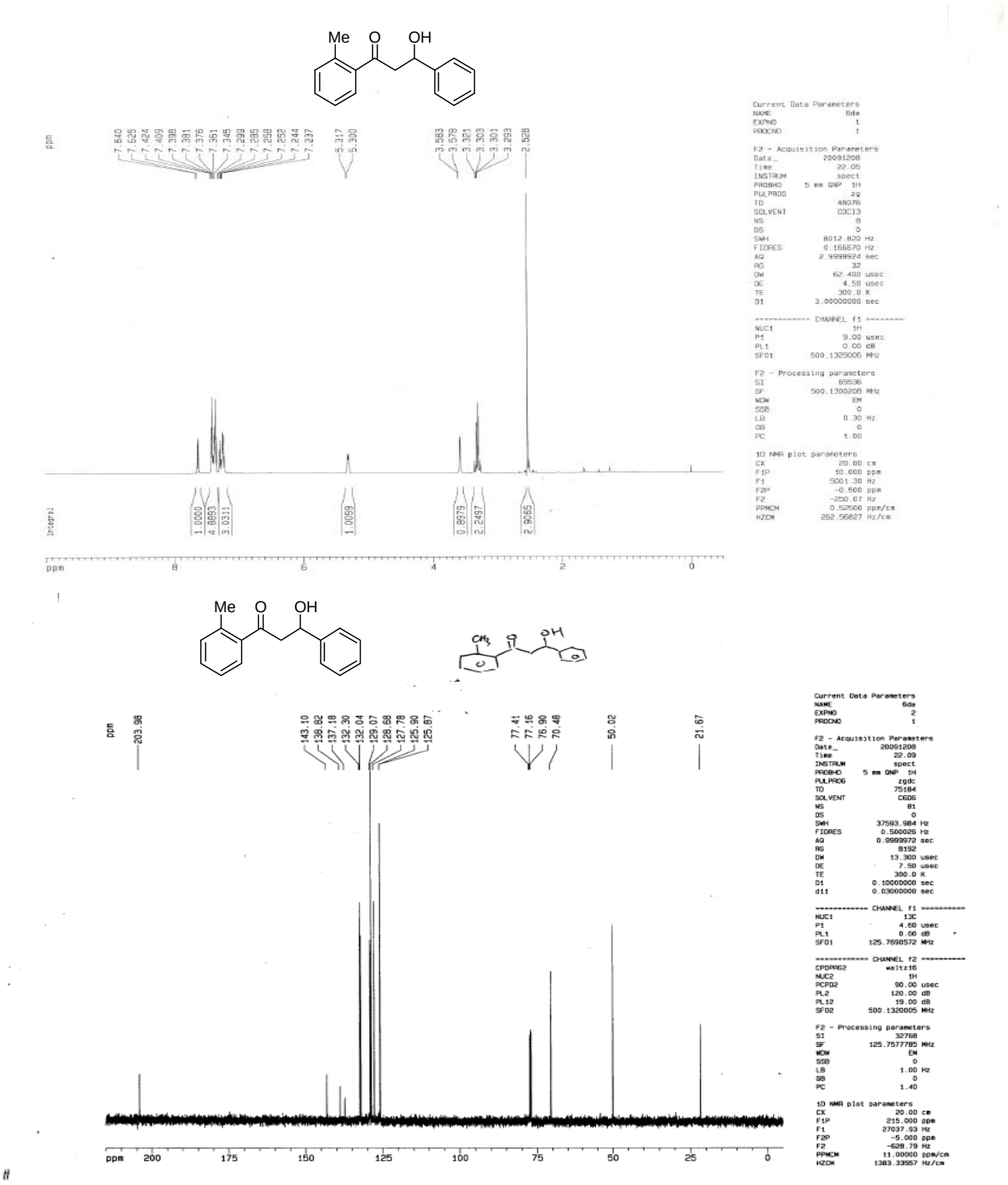
| | | | |
|---|---|---|---|
| Data File: | c:\star\11-17-09 12;54;18 pm -1.run | Run Mode: | Analysis |
| Sample ID: | 16-117-2-OMe | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 11/17/09 12:54:18 PM | Run Time (min): | 56.133 |



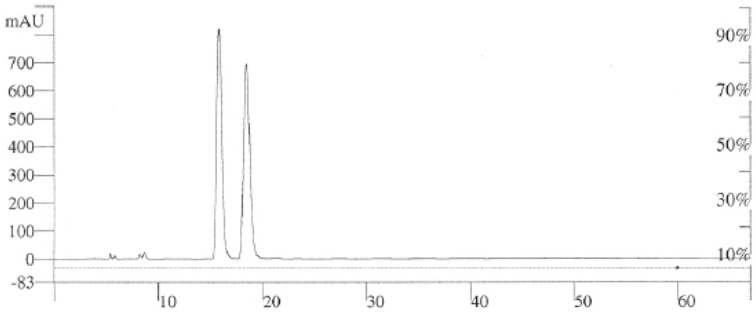



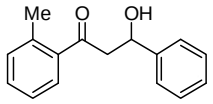

| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 10.0771 | 27.240 | 0.000 | 17373392 | 0.00 | BB | 59.2 |
| 2 | 89.9229 | 33.720 | 0.000 | 155031200 | 0.00 | BB | 92.6 |
| | **100.0000** | | **0.000** | **172404592** | | | |

6da:


Me O OH
7.640 7.625 7.424 7.409 7.398 7.381 7.376 7.361 7.345 7.299 7.285 7.258 7.252 7.244 7.237
5.317 5.300
3.583 3.579 3.324 3.303 3.301 3.293
2.528
Integral
1.0000 4.8883 3.0311 1.0099 0.8979 2.2497 2.9055
ppm
Current Data Parameters
NAME 6da
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091208
Time 22.05
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 32
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1325006 MHz
F2 - Processing parameters
SI 65536
SF 500.1300208 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56827 Hz/cm
Me O OH
ppm
203.98
143.10 138.82 137.18 132.30 132.04 129.07 128.68 127.78 125.90 125.67
77.41 77.16 76.90 70.48
50.02
21.67
Current Data Parameters
NAME 6da
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091208
Time 22.09
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 75184
SOLVENT CDCl3
NS 81
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 8192
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SFO1 125.7690572 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577785 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 27037.93 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 11.00000 ppm/cm
HZCM 1383.33557 Hz/cm

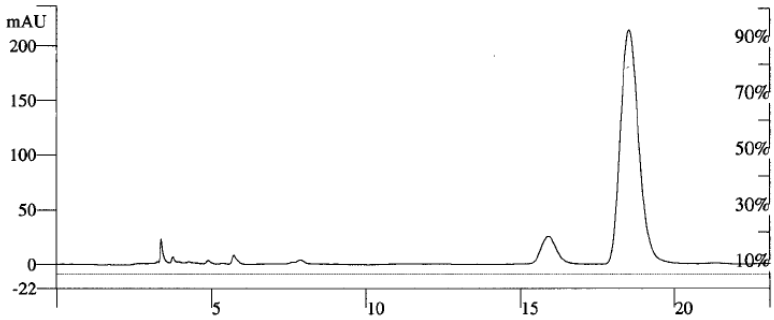
| | | | |
|---|---|---|---|
| Data File: | c:\star\11-23-09 3;54;28 pm -1.run | Run Mode: | Analysis |
| Sample ID: | 16-129-racemic | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 11/23/09 03:54:28 PM | Run Time (min): | 67.067 |

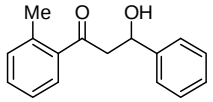



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 49.8665 | 15.773 | 0.000 | 146396576 | 0.00 | BB | 32.6 |
| 2 | 50.1335 | 18.413 | 0.000 | 147180448 | 0.00 | BB | 38.7 |
| | **100.0000** | | **0.000** | **293577024** | | | |

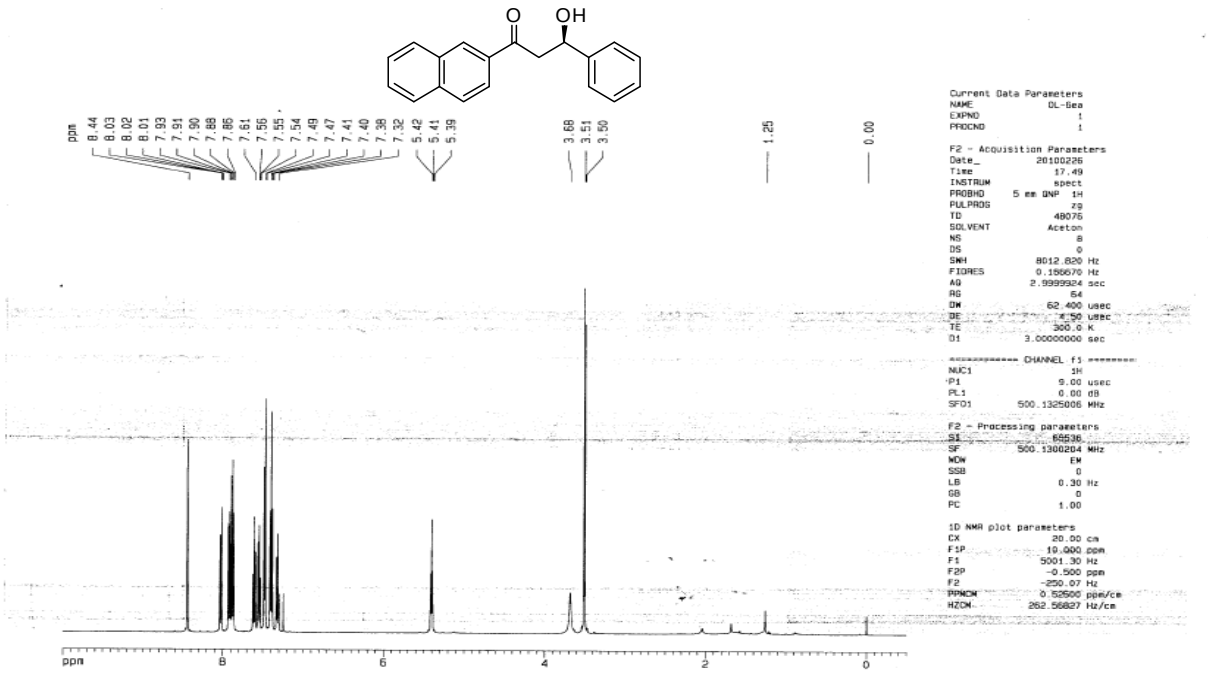
| | | | |
|---|---|---|---|
| Data File: | c:\star\11-23-09 7;24;55 pm -1.run | Run Mode: | Analysis |
| Sample ID: | 16-131-tol/hxs (1:1) | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 11/23/09 07:24:55 PM | Run Time (min): | 23.120 |

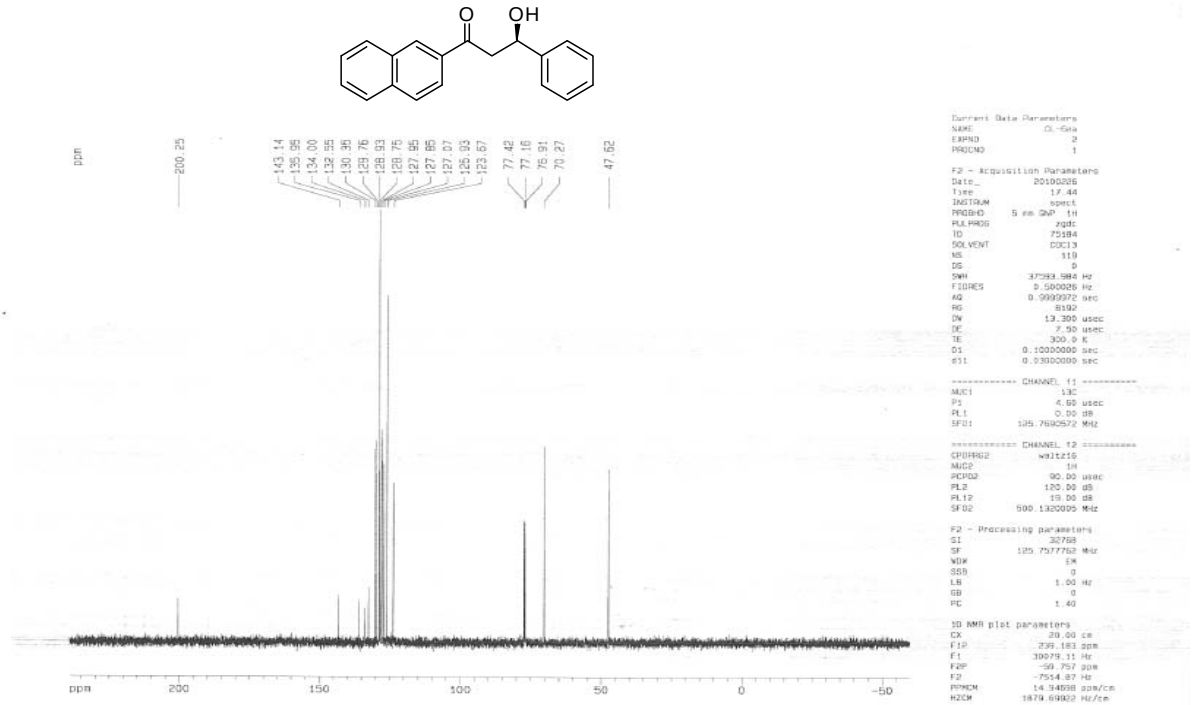



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 8.2273 | 15.907 | 0.000 | 4063493 | 0.00 | BB | 32.0 |
| 2 | 91.7727 | 18.520 | 0.000 | 45326956 | 0.00 | BB | 38.5 |
| | **100.0000** | | **0.000** | **49390448** | | | |

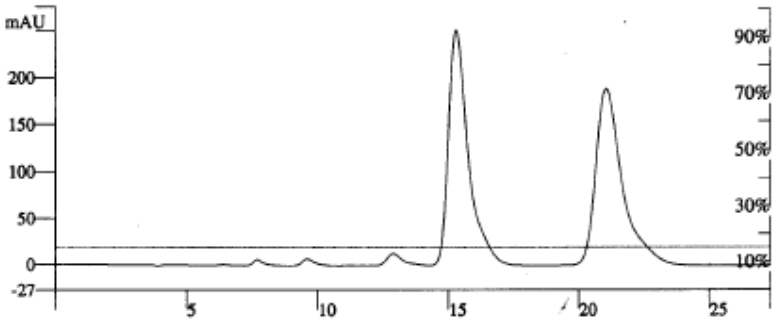
6ea:

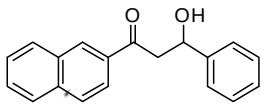

O
OH
ppm
8.44
8.03
8.02
8.01
7.93
7.91
7.90
7.88
7.85
7.61
7.56
7.55
7.54
7.49
7.47
7.41
7.40
7.38
7.32
5.42
5.41
5.39
3.68
3.51
3.50
1.25
0.00
Current Data Parameters
NAME DL-6ea
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100226
Time 17.49
INSTRUM spect
PROBHD 5 mm BNP 1H
PULPROG zg
TD 48076
SOLVENT Aceton
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 64
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1325006 MHz
F2 - Processing parameters
SI 65536
SF 500.1300204 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56827 Hz/cm
ppm
8
6
4
2
0


O
OH
ppm
200.25
143.14
135.95
134.00
132.55
130.35
128.76
128.53
128.75
127.95
127.85
127.07
126.93
123.67
77.42
77.16
76.91
70.27
47.62
Current Data Parameters
NAME DL-6ea
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100226
Time 17.44
INSTRUM spect
PROBHD 5 mm BNP 1H
PULPROG zgdc
TD 75184
SOLVENT CDCl3
NS 119
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9999872 sec
RG 8192
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SFO1 125.7690572 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577762 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 239.183 ppm
F1 30079.11 Hz
F2P -59.757 ppm
F2 -7514.87 Hz
PPMCM 14.94698 ppm/cm
HZCM 1879.89902 Hz/cm
ppm
200
150
100
50
0
-50

| | | | |
|---|---|---|---|
| Data File: | c:\star\3-4-10 7;57;45 am -1.run | Run Mode: | Analysis |
| Sample ID: | Manual Sample | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 03/04/10 07:57:45 AM | Run Time (min): | 27.360 |

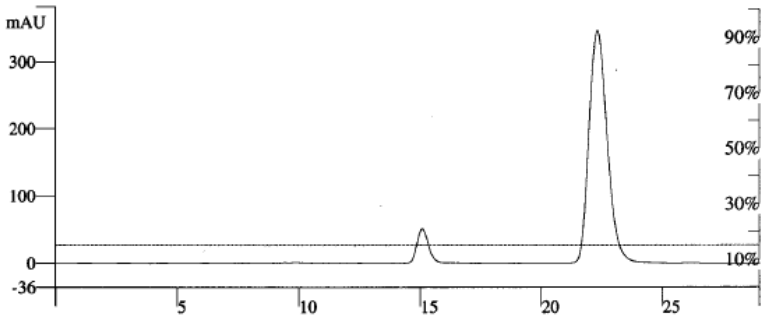
Injection Method: c:\star\cheol hong\mukaiyama

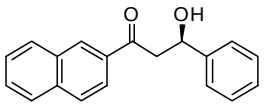



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 49.7333 | 15.293 | 0.000 | 68451536 | 0.00 | BB | 45.1 |
| 2 | 50.2667 | 21.053 | 0.000 | 69185736 | 0.00 | BB | 60.5 |
| | **100.0000** | | **0.000** | **137637280** | | | |

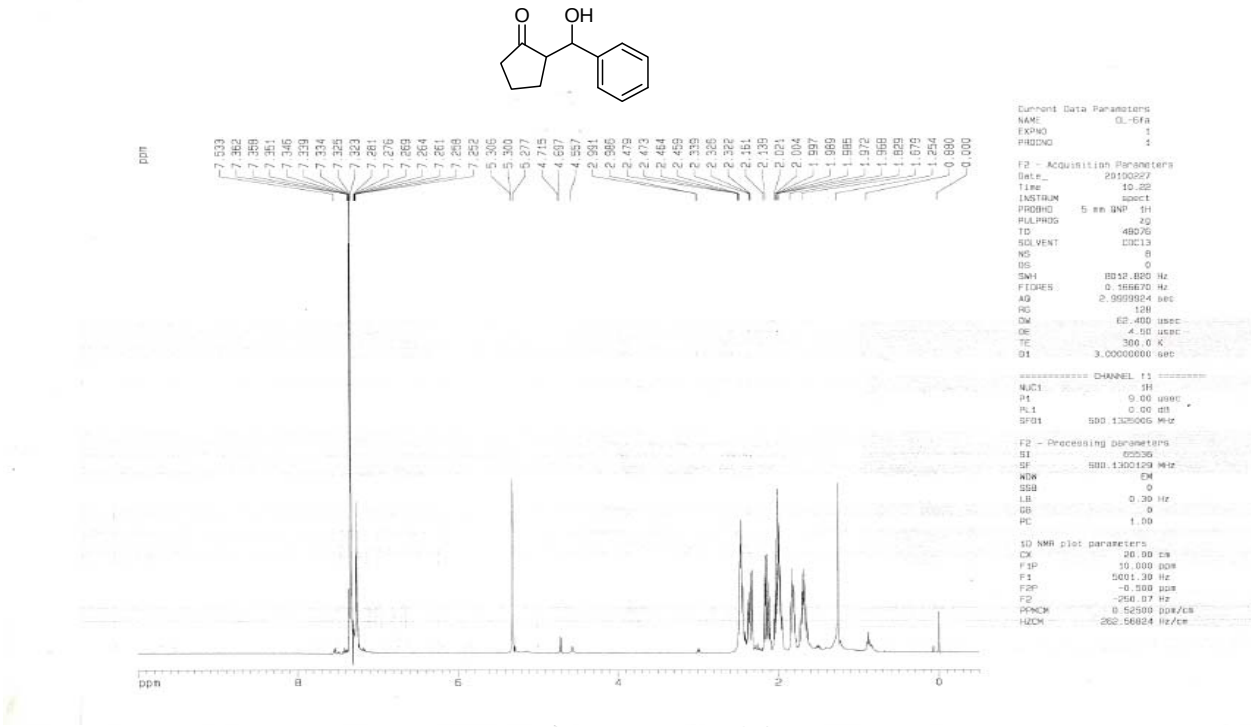
| | | | |
|---|---|---|---|
| Data File: | c:\star\10-27-09 4;47;21 pm -1.run | Run Mode: | Analysis |
| Sample ID: | 16-59-2-naphthyl | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 10/27/09 04:47:21 PM | Run Time (min): | 29.040 |

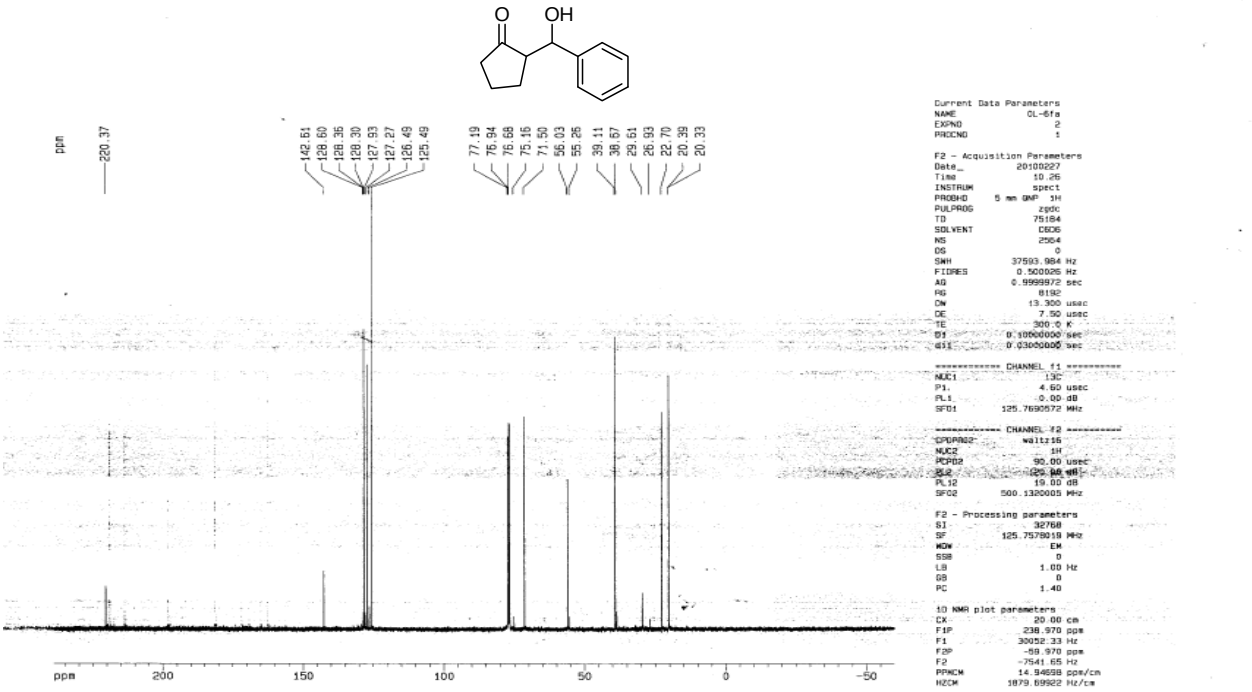


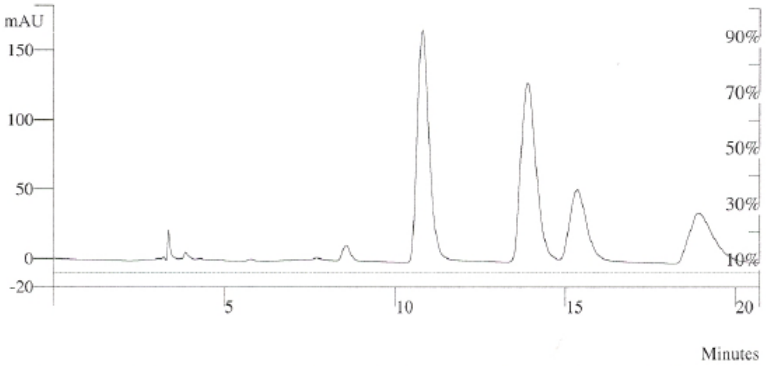

| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 8.1914 | 15.080 | 0.000 | 8223395 | 0.00 | BB | 30.2 |
| 2 | 91.8086 | 22.307 | 0.000 | 92167080 | 0.00 | BB | 48.5 |
| | **100.0000** | | **0.000** | **100390472** | | | |

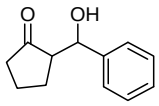
6fa:





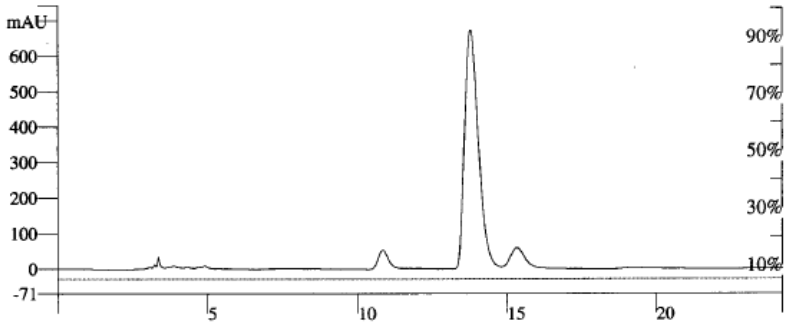
| | | | |
|---|---|---|---|
| Data File: | c:\star\11-24-09 9;52;00 pm -1.run | Run Mode: | Analysis |
| Sample ID: | 6fa-rac-ODH-5 % | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 11/24/09 09:52:00 PM | Run Time (min): | 20.747 |

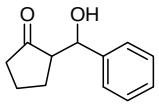



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 35.2100 | 10.787 | 0.000 | 20668720 | 0.00 | BB | 22.5 |
| 2 | 34.4850 | 13.880 | 0.000 | 20243118 | 0.00 | BB | 29.1 |
| 3 | 14.6824 | 15.347 | 0.000 | 8618765 | 0.00 | BB | 31.3 |
| 4 | 15.6226 | 18.920 | 0.000 | 9170630 | 0.00 | BB | 46.8 |
| | **100.0000** | | **0.000** | **58701232** | | | |

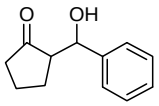
| | | | |
|---|---|---|---|
| Data File: | c:\star\11-25-09 12;09;43 pm -1.run | Run Mode: | Analysis |
| Sample ID: | 6ga-syn-enantio | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 11/25/09 12:09:43 PM | Run Time (min): | 24.267 |

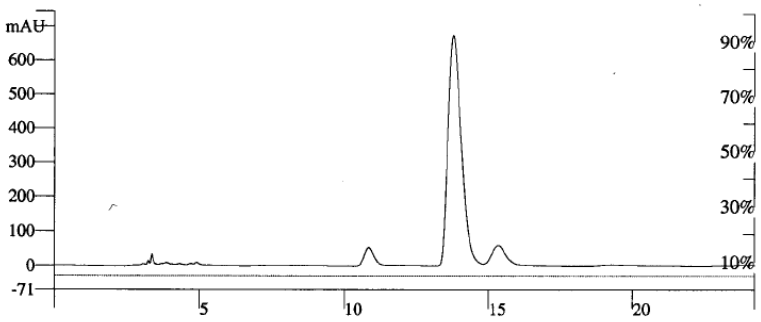



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 4.9890 | 10.840 | 0.000 | 5774900 | 0.00 | BB | 21.4 |
| 2 | 95.0110 | 13.773 | 0.000 | 109977640 | 0.00 | BB | 30.0 |
| | **100.0000** | | **0.000** | **115752544** | | | |

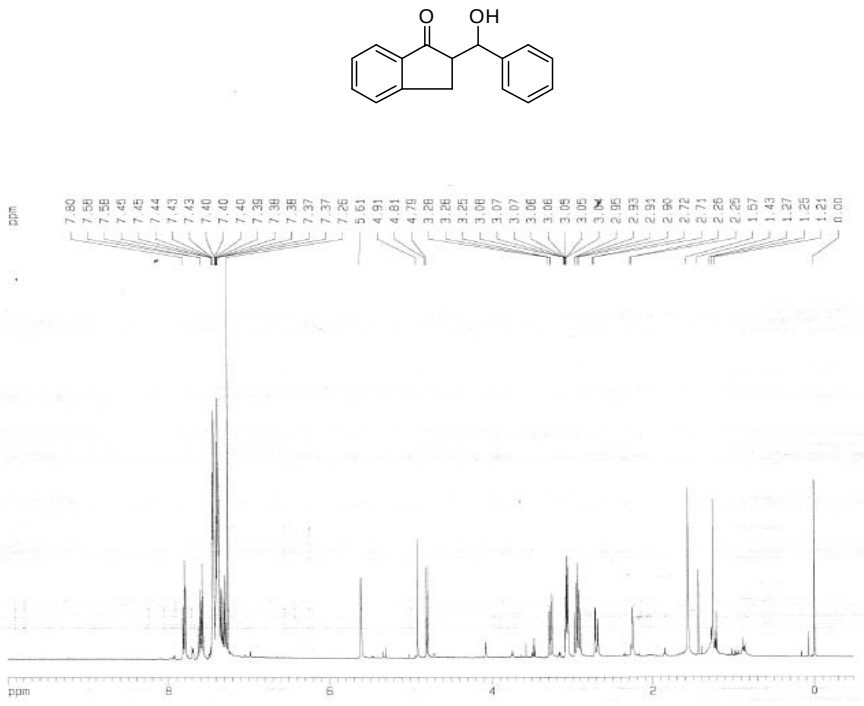
| | | | |
|---|---|---|---|
| Data File: | c:\star\11-25-09 12;09;43 pm -1.run | Run Mode: | Analysis |
| Sample ID: | 6fa-anti-enantio | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 11/25/09 12:09:43 PM | Run Time (min): | 24.267 |

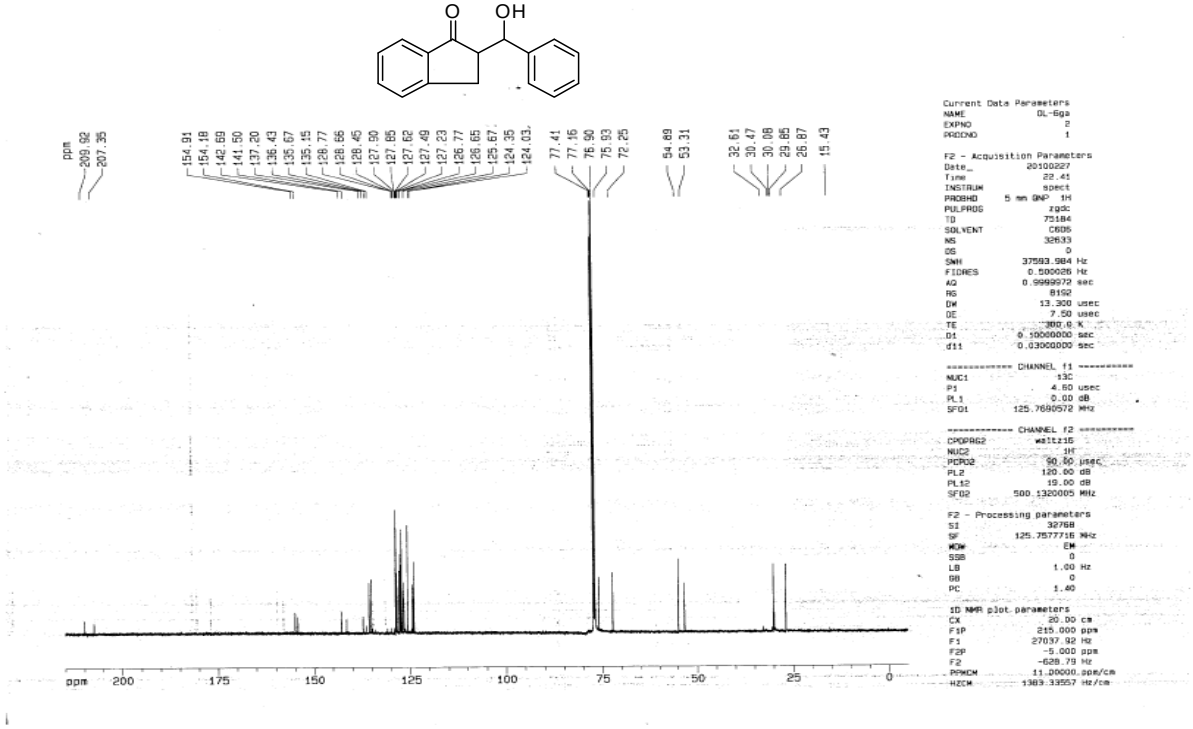


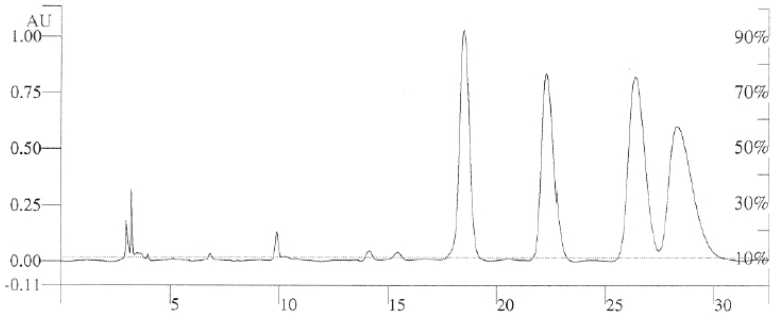

| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 97.2143 | 15.347 | 0.000 | 9149424 | 0.00 | BB | 30.1 |
| 2 | 2.7857 | 19.293 | 0.000 | 262178 | 0.00 | BB | 30.2 |
| | **100.0000** | | **0.000** | **9411602** | | | |

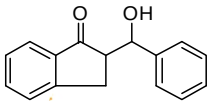
6ga:


O
OH
ppm
7.80 7.58 7.58 7.45 7.45 7.44 7.43 7.43 7.40 7.40 7.40 7.39 7.38 7.38 7.37 7.37 7.26 5.61 4.91 4.81 4.79 3.26 3.26 3.25 3.08 3.07 3.07 3.06 3.06 3.05 3.05 2.95 2.93 2.91 2.90 2.72 2.71 2.26 2.25 1.57 1.43 1.27 1.25 1.21 0.00
ppm 8 6 4 2 0
Current Data Parameters
NAME DL-6ga
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100227
Time 22.33
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 85
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 256
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1325006 MHz
F2 - Processing parameters
SI 65536
SF 500.1300130 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56824 Hz/cm


O
OH
ppm
209.92 207.35
154.91 154.18 142.69 141.50 137.20 136.43 135.67 135.15 128.77 128.66 128.45 127.90 127.85 127.62 127.49 127.23 126.77 126.65 125.67 124.35 124.03
77.41 77.16 76.90 75.93 72.25
54.89 53.31
32.61 30.47 30.08 29.85 26.87 15.43
ppm 200 175 150 125 100 75 50 25 0
Current Data Parameters
NAME DL-6ga
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100227
Time 22.41
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 75184
SOLVENT CDCl3
NS 32633
DS 0
SWH 37593.984 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 8192
DW 13.300 usec
DE 7.50 usec
TE 300.0 K
D1 0.50000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 4.60 usec
PL1 0.00 dB
SFO1 125.7680572 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.90 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577716 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 27037.92 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 11.00000 ppm/cm
HZCM 1383.33557 Hz/cm

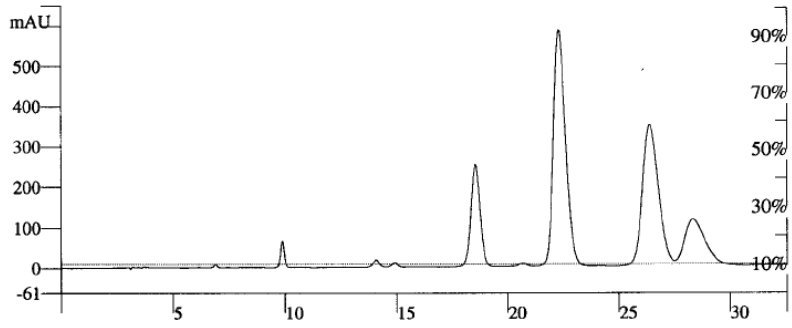
| | | | |
|---|---|---|---|
| Data File: | c:\star\12-5-09 4;49;34 pm -1.run | Run Mode: | Analysis |
| Sample ID: | Manual Sample | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 12/05/09 04:49:34 PM | Run Time (min): | 32.560 |

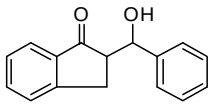



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 22.5196 | 18.493 | 0.000 | 169327232 | 0.00 | BB | 29.8 |
| 2 | 22.4038 | 22.307 | 0.000 | 168456208 | 0.00 | BB | 37.0 |
| 3 | 27.7007 | 26.360 | 0.000 | 208283808 | 0.00 | BB | 50.6 |
| 4 | 27.3759 | 28.307 | 0.000 | 205841600 | 0.00 | BB | 67.5 |
| | **100.0000** | | **0.000** | **751908800** | | | |

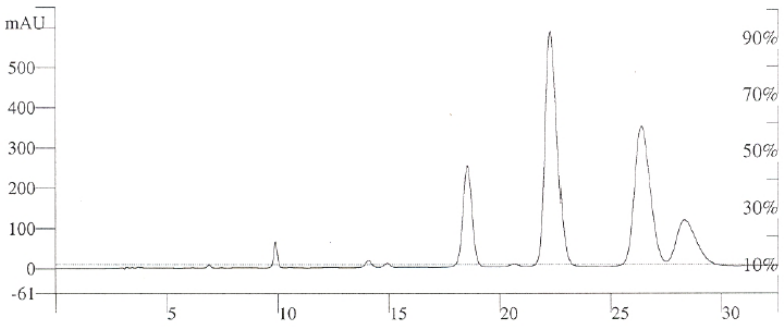
| | | | |
|---|---|---|---|
| Data File: | c:\star\12-7-09 10;24;51 am -1.run | Run Mode: | Analysis |
| Sample ID: | Manual Sample | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 12/07/09 10:24:51 AM | Run Time (min): | 32.587 |

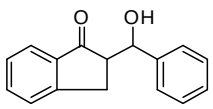



| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 72.4779 | 26.360 | 0.000 | 84845432 | 0.00 | BB | 46.5 |
| 2 | 27.5221 | 28.333 | 0.000 | 32218360 | 0.00 | BB | 55.0 |
| | **100.0000** | | **0.000** | **117063792** | | | |

| | | | |
|---|---|---|---|
| Data File: | c:\star\12-7-09 10;24;51 am -1.run | Run Mode: | Analysis |
| Sample ID: | 6ga-anti | Peak Measurement: | Peak Area |
| Operator (Inj): | | Calibration Level: | N/A |
| Injection Date: | 12/07/09 10:24:51 AM | Run Time (min): | 32.587 |




| Peak No | Result () | Ret Time (min) | Time Offset (min) | Peak Area (counts) | Rel Ret Time | Sep. Code | Width 1/2 (sec) |
|---|---|---|---|---|---|---|---|
| 1 | 24.1207 | 18.547 | 0.000 | 35788020 | 0.00 | BB | 26.3 |
| 2 | 75.8793 | 22.280 | 0.000 | 112582392 | 0.00 | BB | 34.9 |
| | **100.0000** | | **0.000** | **148370416** | | | |