

# One-Pot *o*-Nitrobenzenesulfonylhydrazide (NBSH) Formation - Diimide Alkene Reduction Protocol

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## Supporting Information

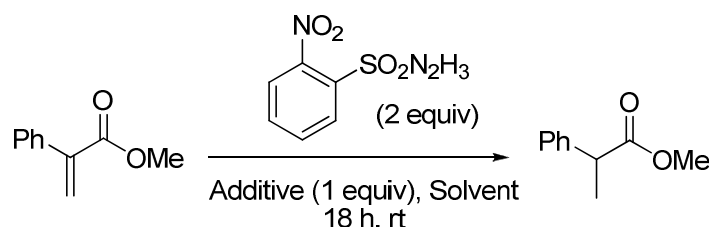
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### *I. General.*

Reactions were carried out using dry solvents under an inert atmosphere of nitrogen. All reaction flasks were dried overnight in an oven at 200 °C prior to use. Acetonitrile was dried by passing through anhydrous alumina columns. All reagents were purchased from commercial suppliers and used without further purification. 2-Nitrobenzenesulfonyl hydrazide was prepared according to the procedure published by Myers.<sup>1</sup> 2-Methyl phenyl acrylate was prepared according to the procedure reported by Davies.<sup>2</sup> Chemical shifts are reported in parts per million relative to tetramethylsilane (TMS) ( $\delta = 0.00$ ). Mass spectroscopy was performed using electrospray ionisation (ESI) in positive ionisation mode. Infra-red spectroscopy was performed with KBr plates.

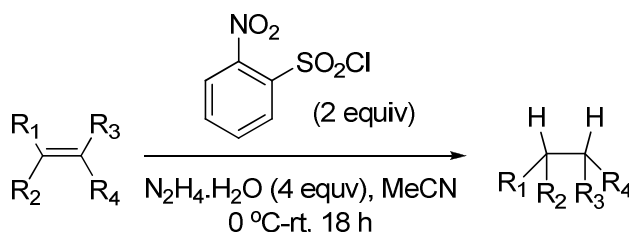
## II. Diimide Hydrogenations

**General Procedure A** for the Hydrogenation of Methyl-2-phenyl acrylate using 2-Nitrobenzenesulfonylhydrazine as a diimide precursor.



2-Nitrobenzenesulfonylhydrazide (434 mg, 2 mmol) and additive (1 mmol) were dissolved in solvent (5 cm<sup>3</sup>) and allowed to stir for 10 mins under N<sub>2</sub>. Methyl-2-phenyl acrylate (162mg, 1 mmol) in solvent (1 cm<sup>3</sup>) was slowly added by syringe over the course of 1 minute. The solution was allowed to stir for 18 hrs. After which time the orange solution was treated with H<sub>2</sub>O (5 cm<sup>3</sup>), the product was extracted with EtOAc (3 × 5 cm<sup>3</sup>) and the combined organic extracts were washed with NaHCO<sub>3</sub> (sat) (10 cm<sup>3</sup>) and brine (sat) (10 cm<sup>3</sup>). The combined organic extracts were then dried over MgSO<sub>4</sub> and filtered. Solvent was removed *in vacuo* to give the methyl-2-phenylpropanoate as a crude oil.

**General Procedure B** for the One Pot Synthesis of NBSH-Alkene Hydrogenation.



The 2-nitrobenzenesulfonyl chloride (442 mg, 2 mmol) and the alkene (1 mmol) were dissolved in dry MeCN (5 cm<sup>3</sup> / mmol of alkene) and cooled to 0 °C. Once cold the hydrazine hydrate (194 μl, 4 mmol) was slowly added down to side of the reaction flask (over a period of 1 min) to the vigorously stirred solution of the alkene and 2-nitrobenzenesulfonyl chloride. The resulting white suspension was slowly allowed to

warm to room temperature and stirred vigorously for a further 18 hours. The product was worked up by various methods:

**Work Up Method I:** After this time the orange suspension was quenched by addition of H<sub>2</sub>O (5 cm<sup>3</sup>) product was extracted with EtOAc (4 × 5 cm<sup>3</sup>), the combined organic extracts were then washed with saturated NaHCO<sub>3</sub> (10 cm<sup>3</sup>) and brine (sat) (10 cm<sup>3</sup>). The combined organic extracts were then dried over MgSO<sub>4</sub> and filtered. Solvent was removed *in vacuo* to give the desired crude product.

**Work Up Method II:** After this time the orange suspension was quenched by addition of H<sub>2</sub>O (5 cm<sup>3</sup>) product was extracted with pentane (4 × 5 cm<sup>3</sup>), the combined organics were then dried over MgSO<sub>4</sub> and filtered. Solvent was removed *in vacuo* to give the crude product.

**Work Up Method III:** After this time the orange suspension was filtered, and the filtrate washed with EtOAc (10 cm<sup>3</sup>), the organics were then dried over Na<sub>2</sub>SO<sub>4</sub>. Solvent was then removed *in vacuo* to give the crude product.

Percentage conversions are determined using equation 1, using appropriate integrations of appropriate starting material peaks (if present) and product peaks in the <sup>1</sup>H NMR of crude reaction mixtures using the following equation:

$$Conv = \left[ \frac{\int H_P}{(\int H_P + \int H_{SM})} \right] \times 100$$

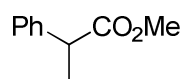
Equation 1

Data labels annotated upon crude <sup>1</sup>H NMR are as follows:

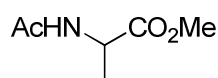
**Red:** Product protons used for conversion calculation labelled H<sub>p</sub>.

**Green:** Starting material protons used for conversion calculations labelled H<sub>SM</sub>.

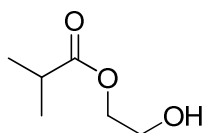
**Blue:** Residual NBSH carried through work up.

**Methyl-2-phenylpropanoate 6.**<sup>3</sup>

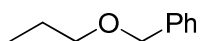
The title compound was obtained using general procedure **B** and work up method **I** for 18 hours using methyl-2-phenyl acrylate (162 mg, 1 mmol). <sup>1</sup>H NMR indicated 100% conversion of the starting material, the identity of the title compound was confirmed by comparison with previously published spectral data in the literature.<sup>3</sup>

**Methyl-2-acetamidopropanoate 8.**

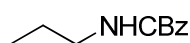
The title compound was obtained using general procedure **B** and work up method **I** for 42 hours using methyl-2-acetamidoacrylate (143 mg, 1 mmol). <sup>1</sup>H NMR indicated 78% conversion of the starting material to the desired compound, the identity of which was confirmed by comparison with commercially available material.

**2-Hydroxy ethyl isobutyrate 9.**<sup>4</sup>

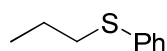
The title compound was obtained using general procedure **B** and work up method **I** for 42 hours using 2-hydroxy ethyl methyl acrylate (130 mg, 1 mmol). <sup>1</sup>H NMR indicated 100% conversion of the starting material to the desired compound, the identity of which was confirmed by comparison with published spectral data in the literature.<sup>4</sup>

**Propyl benzylether 10.**

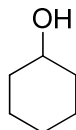
The title compound was prepared using general procedure **B** and work up method **I** for 18 hours using allyl benzyl ether (148 mg, 1mmol). <sup>1</sup>H NMR indicated 99% conversion of the starting material to the desired product, the structure of which was confirmed by comparison with an authentic commercially available source.

**Benzyl propylcarbamate 11.**<sup>5</sup>

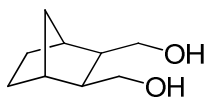
The title compound was prepared using general procedure **B** and work up method **I** for 18 hours using benzyl allylcarbamate (190 mg, 1 mmol). <sup>1</sup>H NMR indicated 100% conversion of the starting material to the desired product, the structure of which was confirmed by comparison with previously recorded literature data for the title compound.<sup>5</sup>

**Phenylpropylsulfide 12.**<sup>5</sup>

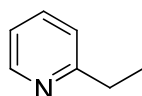
The title compound was prepared using general procedure **B** and work up method **I** for 18 hours using allyl phenyl sulphide (150 mg, 1 mmol). <sup>1</sup>H NMR indicated 98% conversion of the starting material to the desired product, the structure of which was confirmed by comparison with previously reported spectral data from the literature.<sup>5</sup>

**Cyclohexanol 13.**

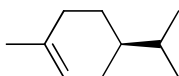
The title compound was obtained using general procedure **B** and work up method **I** for 18 hours using 2-cyclohexen-1-ol (98 mg, 1mmol). <sup>1</sup>H NMR indicated 46% conversion of the starting material to the desired product, the structure of which has confirmed by comparison with an authentic commercially available source.

**2,3-Norbornanedimethanol 14.**<sup>5</sup>

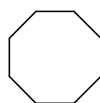
The title compound was obtained using general procedure **B** and work up method **I** for 18 hours using 5-norborene-2-exo-3-exo-dimethanol (154 mg, 1mmol). <sup>1</sup>H NMR indicated 100% conversion of the starting material to the desired product, the structure of which was confirmed by comparison with previously published spectral data.<sup>5</sup>

**2-Ethylpyridine 15.**

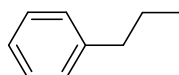
The title compound was obtained using general procedure **B** and work up method **I** for 18 hours using 2-vinyl pyridine (105 mg, 1 mmol).  $^1\text{H}$  NMR indicated 100% of the starting material to the desired product, the structure of which was confirmed by comparison with authentic commercial material.

**(*R*)-4-Isopropyl-1-methylcyclohex-1-ene 16.**

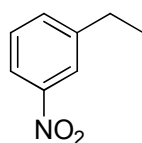
The title compound was obtained using general procedure **B** and work up method **I** for 42 hours using (*R*)-(+)-limonene (136 mg, 1mmol).  $^1\text{H}$  NMR indicated 72% of the starting material to the desired product, the structure of which was confirmed by comparison with an authentic commercial material.

**Cyclooctane 17.**

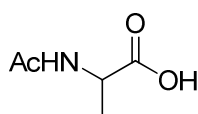
The title compound was obtained using general procedure **B** and work up method **II** for 18 hours *cis*-cyclooctane (110 mg, 1mmol).  $^1\text{H}$  NMR indicated 100% conversion of the starting material to the desired product, the structure of which was confirmed by comparison with authentic commercial material.

**Propylbenzene 18.**

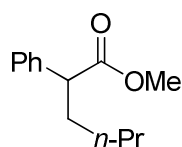
The title compound was obtained using general procedure **B** and work up method **II** for 18 hours using *trans*- $\beta$ -methyl styrene (118 mg, 1 mmol).  $^1\text{H}$  NMR indicated 61% conversion of the starting material to the desired product, the structure of which was confirmed by comparison with authentic material from a commercial supplier.

**3-Ethylnitrobenzene 19.**

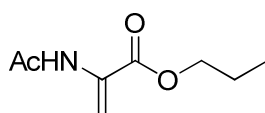
The title compound was obtained using general procedure **B** and work up method **I** for 18 hours using 3-nitro-styrene (149 mg, 1 mmol).  $^1\text{H}$  NMR indicated 100% conversion of the starting material to the desired product, the structure of which was confirmed by comparison with commercially available material.

**2-Acetamidopropanoic acid 20.**

The title compound was obtained using general procedure **B** and work up method **III** for 18 hours using 2-acetamido acrylic acid (129 mg, 1 mmol).  $^1\text{H}$  NMR indicated 87% conversion of the starting material to the desired product, the structure of which was confirmed by comparison with authentic sample from a commercial supplier.

**Methyl 2-Phenylhexanoate 21.<sup>6</sup>**

The title compound was obtained using general procedure **B** and work up method **I** for 18 hours using methyl-phenyl-but-2-enoate (2:1 mixture of isomers) (204 mg, 1mmol).  $^1\text{H}$  NMR indicated 8% conversion of the starting material to the desired product, the structure of which was confirmed by comparison with previously reported spectral data.<sup>6</sup>

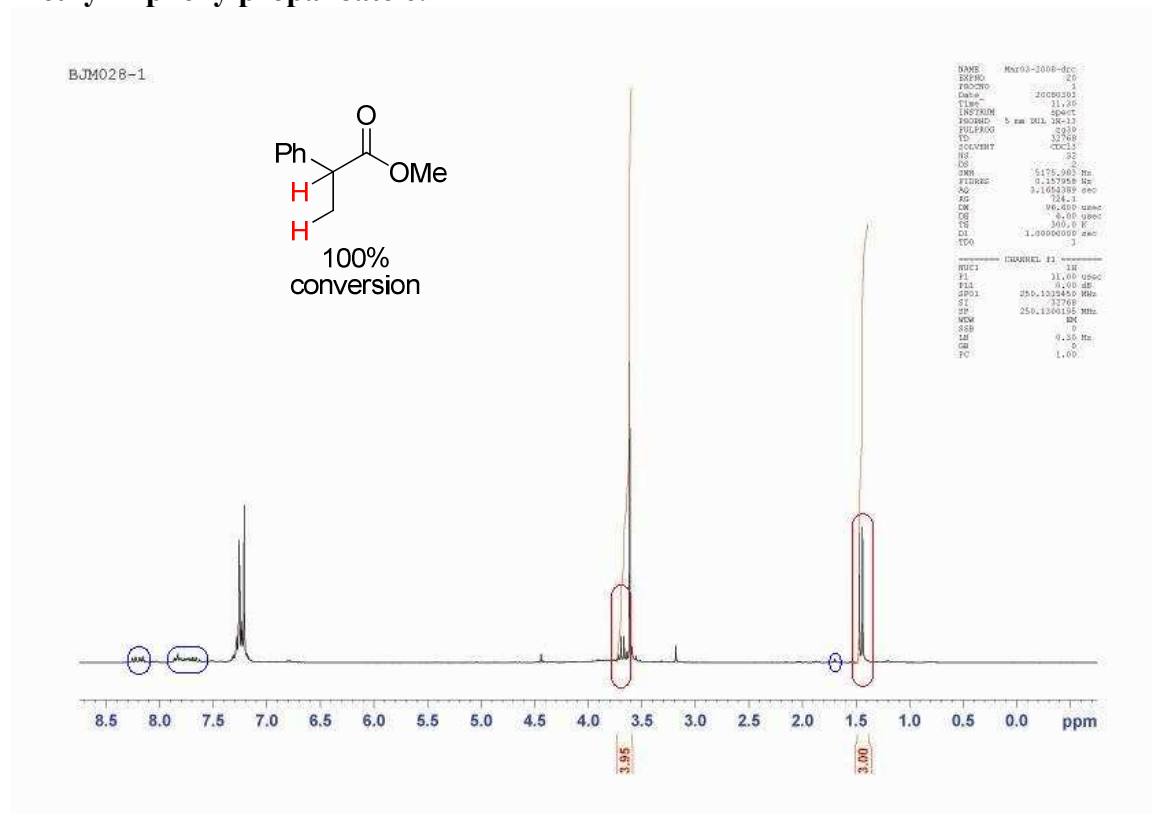
**2-Propyl-acetamidoacrylate 22.**

The title compound was obtained using general procedure **B** and work up method **II** for 18 hours using 2-allyl-acetamidoacrylate (169 mg, 1mmol). Product was purified via column chromatography eluting with 25% EtOAc : petrol (40:60) to give the title

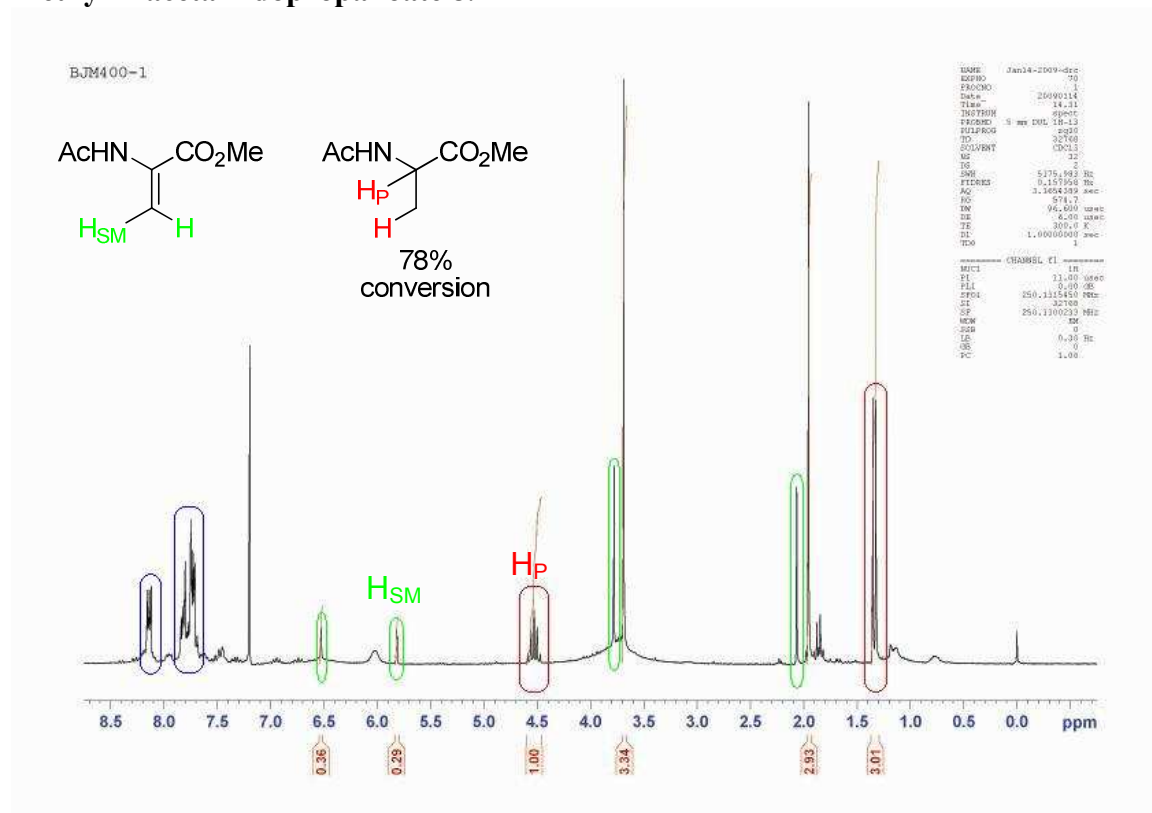
compound as a clear oil (147 mg, 86%).  $\nu_{\max}$  (film)/ $\text{cm}^{-1}$  2970, 2881, 1719, 1674, 1634, 1509;  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  0.96 (3H, t,  $J=7.7$  Hz), 1.71 (2H, qt,  $J=7.7, 6.7$  Hz), 2.10 (3H, s), 4.17 (2H, t,  $J=6.7$  Hz), 5.85 (1H, d,  $J=1.4$  Hz), 6.55 (1H, s), 7.74 (1H, br s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  10.5, 22.1, 24.9, 67.9, 108.3, 131.3, 164.4, 168.9;  $m/z$  (ESI) 194.0781 (95%,  $[\text{M}-\text{Na}]^+$   $\text{C}_8\text{H}_{13}\text{NO}_3\text{Na}$  requires 194.0793).



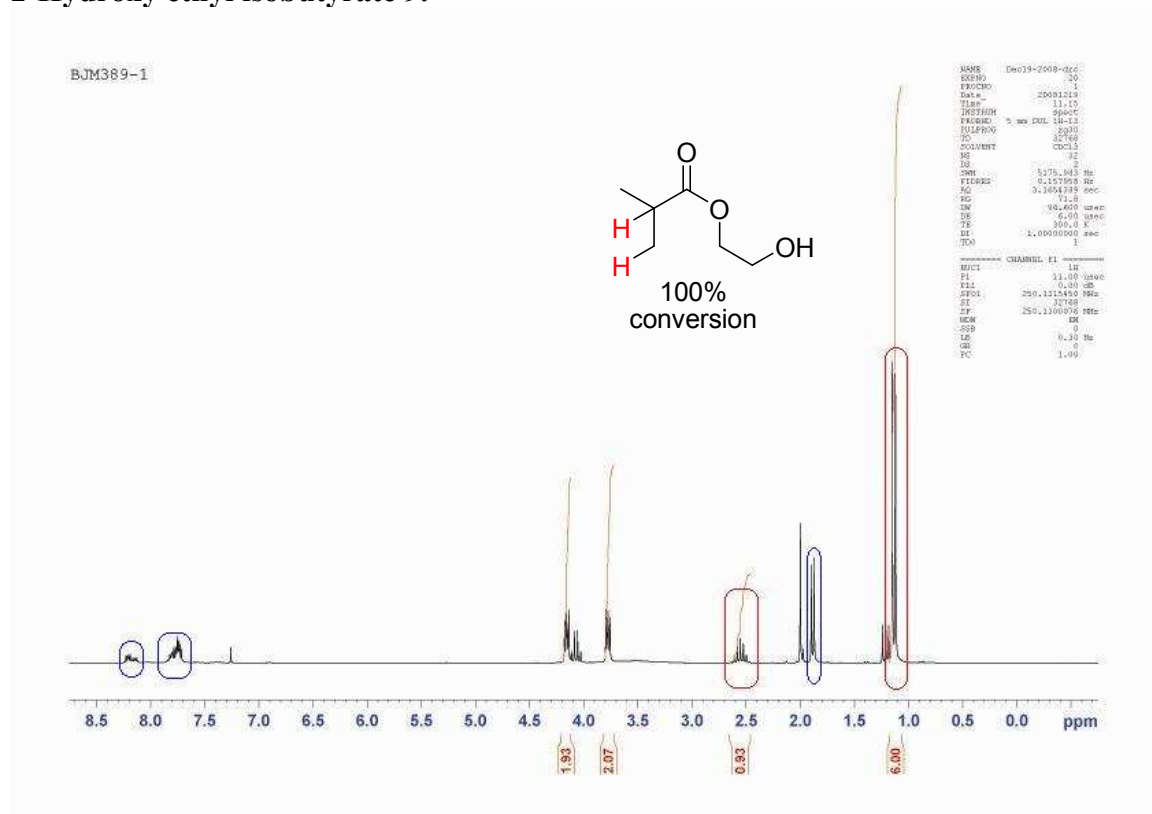
## Methyl-2-phenylpropanoate 6.



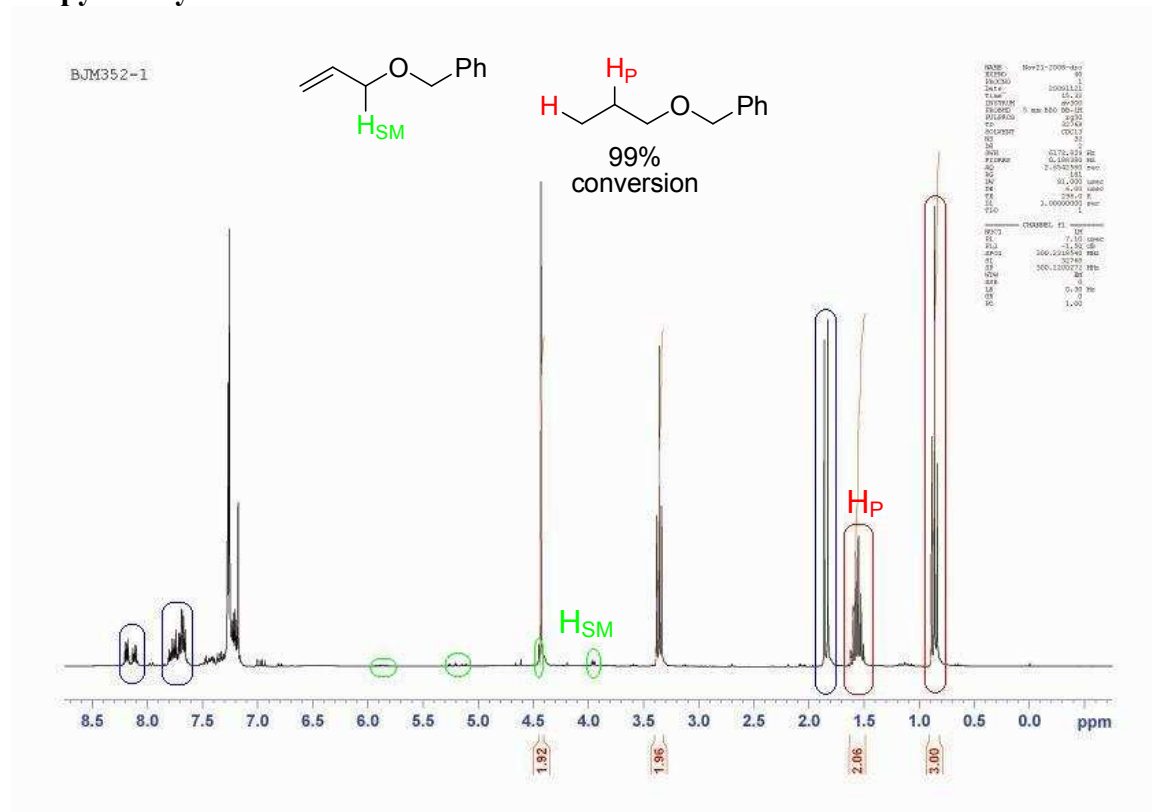
## Methyl-2-acetamidopropanoate 8.



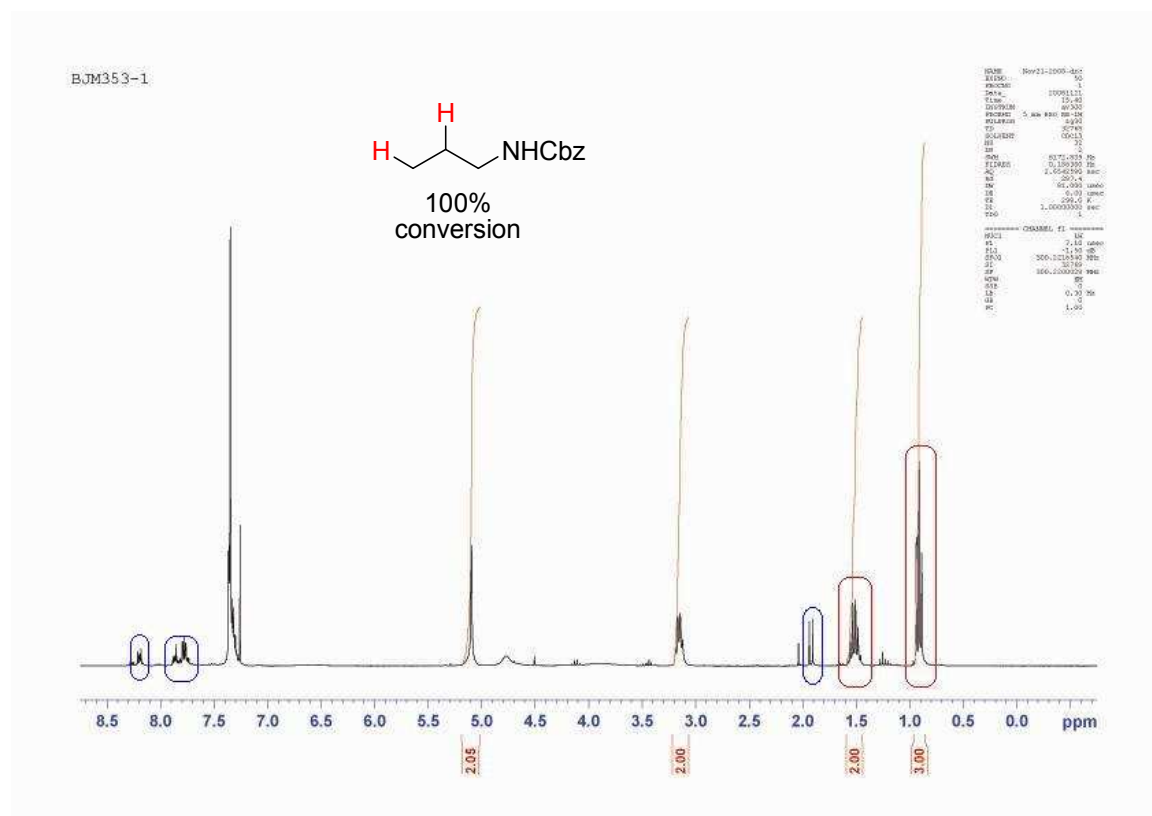
## 2-Hydroxy ethyl isobutyrate 9.



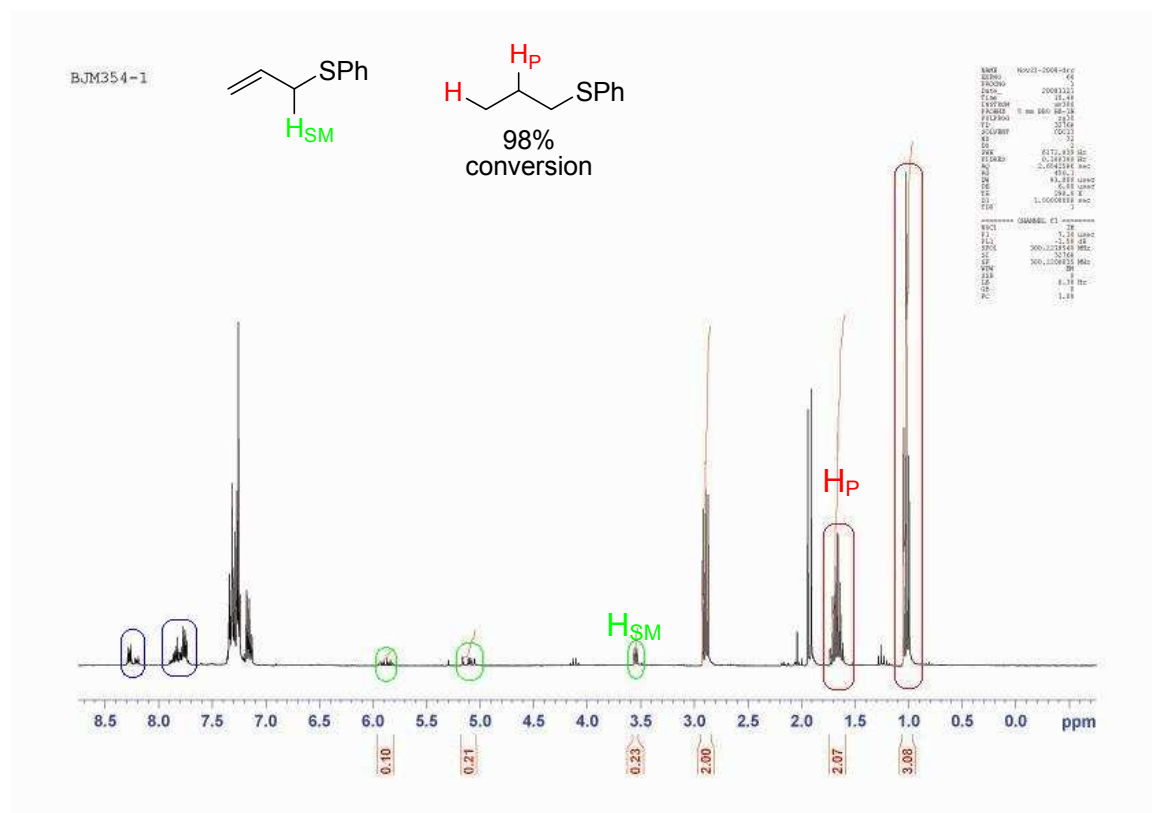
## Propyl benzylether 10.



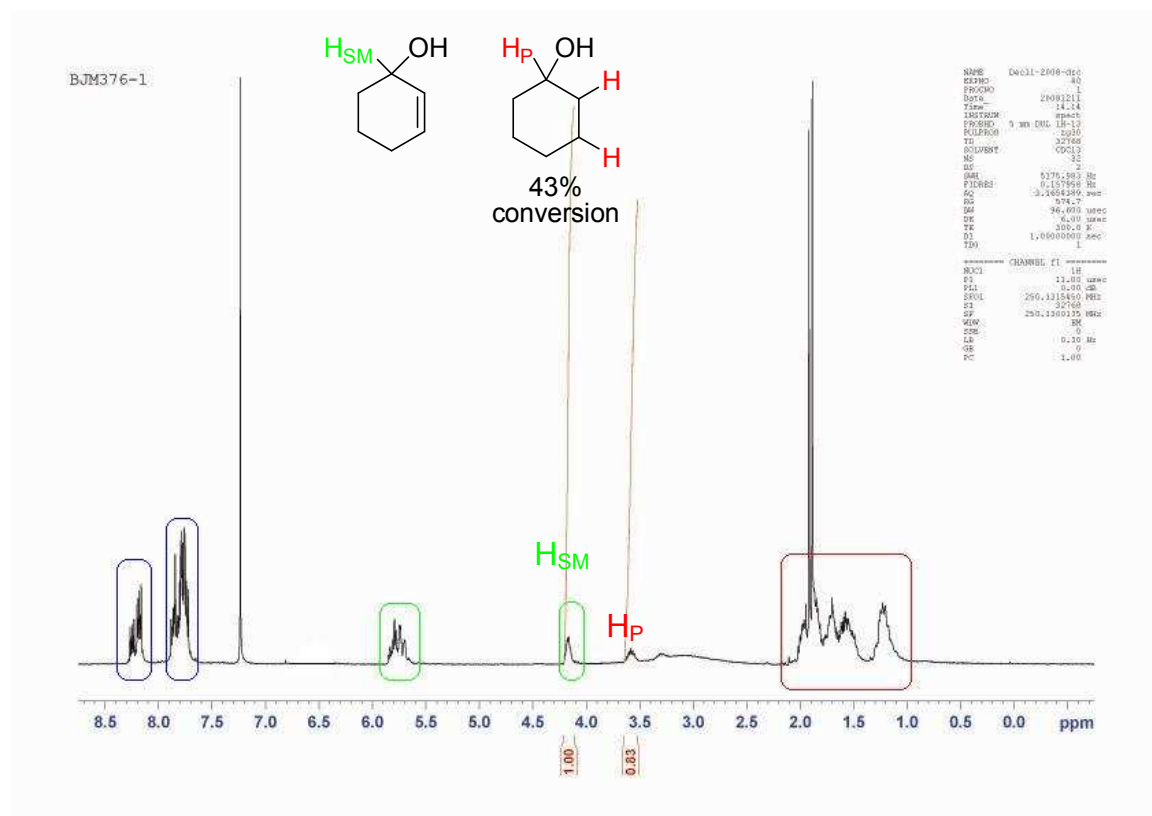
## Benzyl propylcarbamate 11.



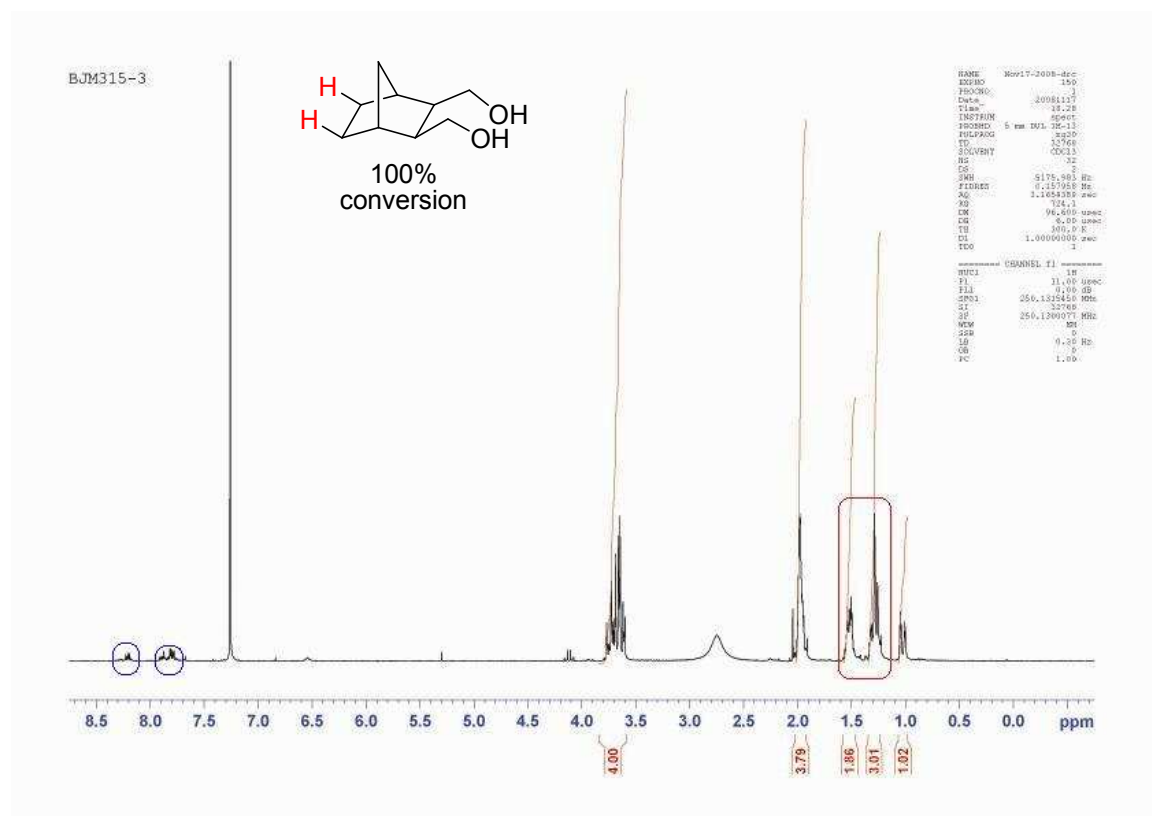
## Phenylpropylsulfide 12.



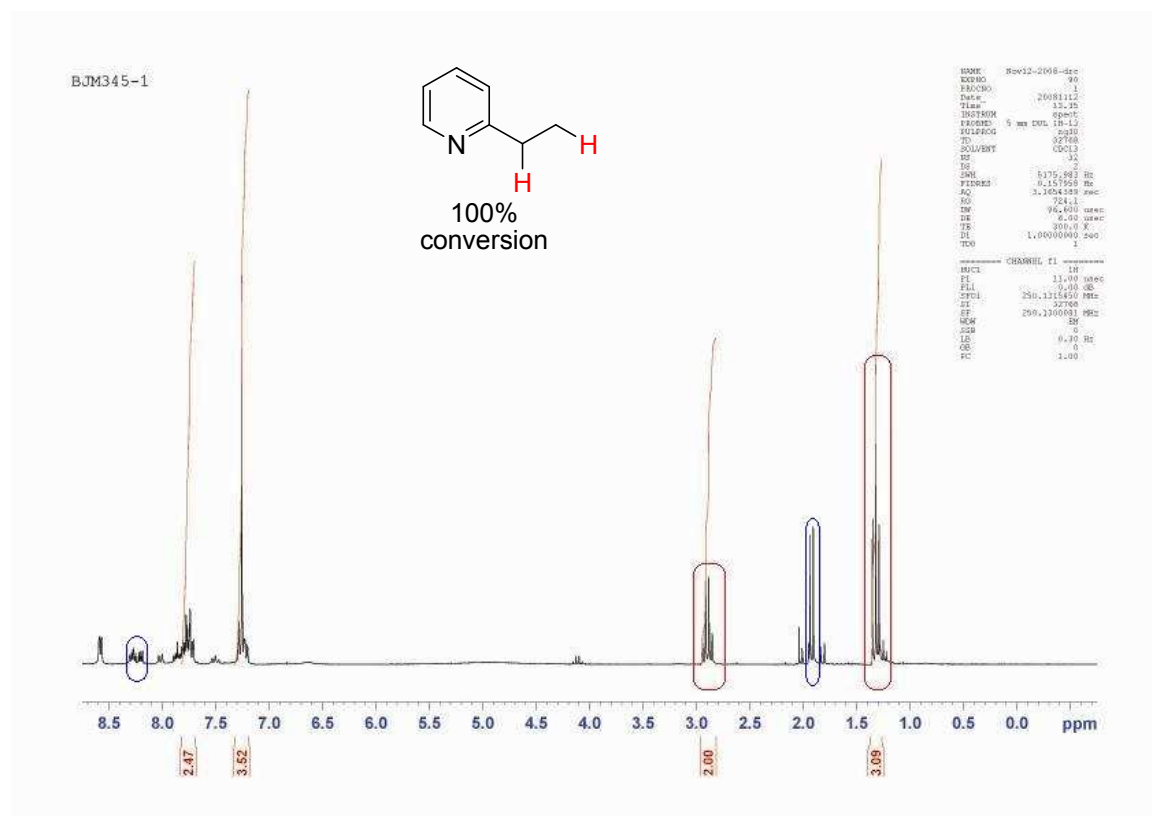
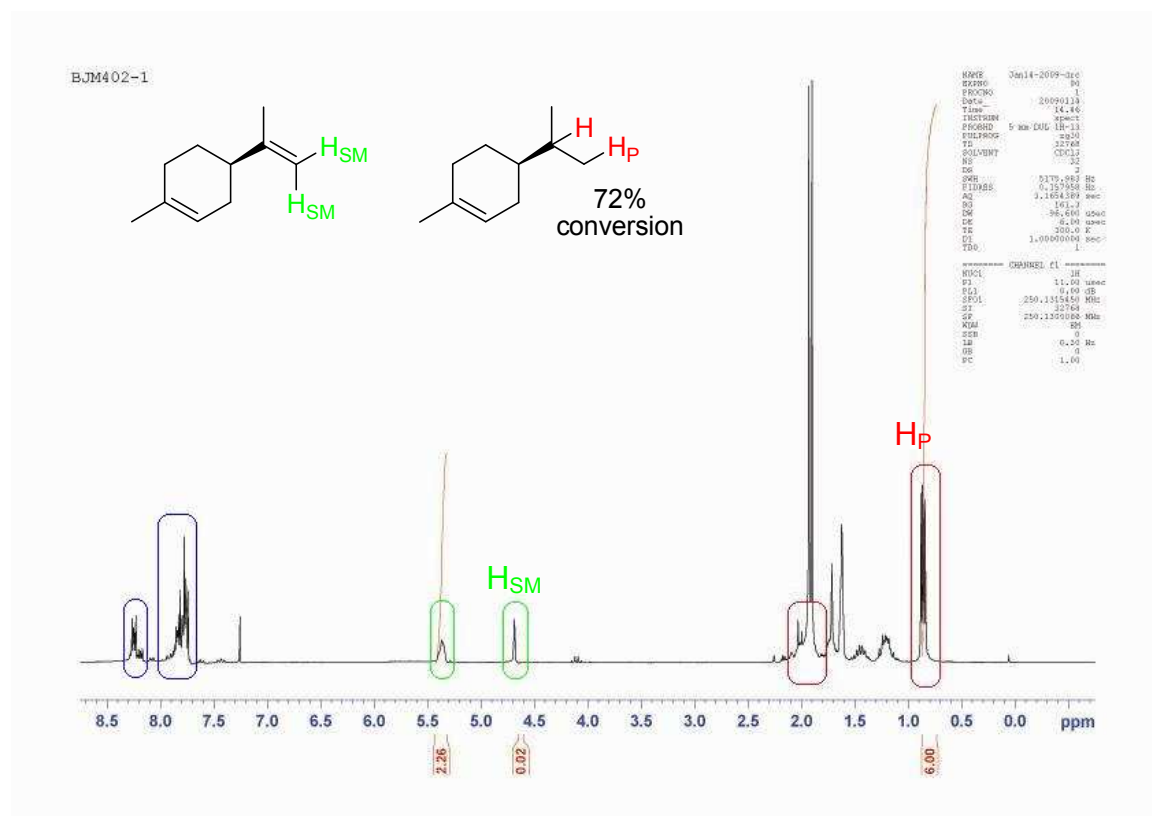
## Cyclohexanol 13.



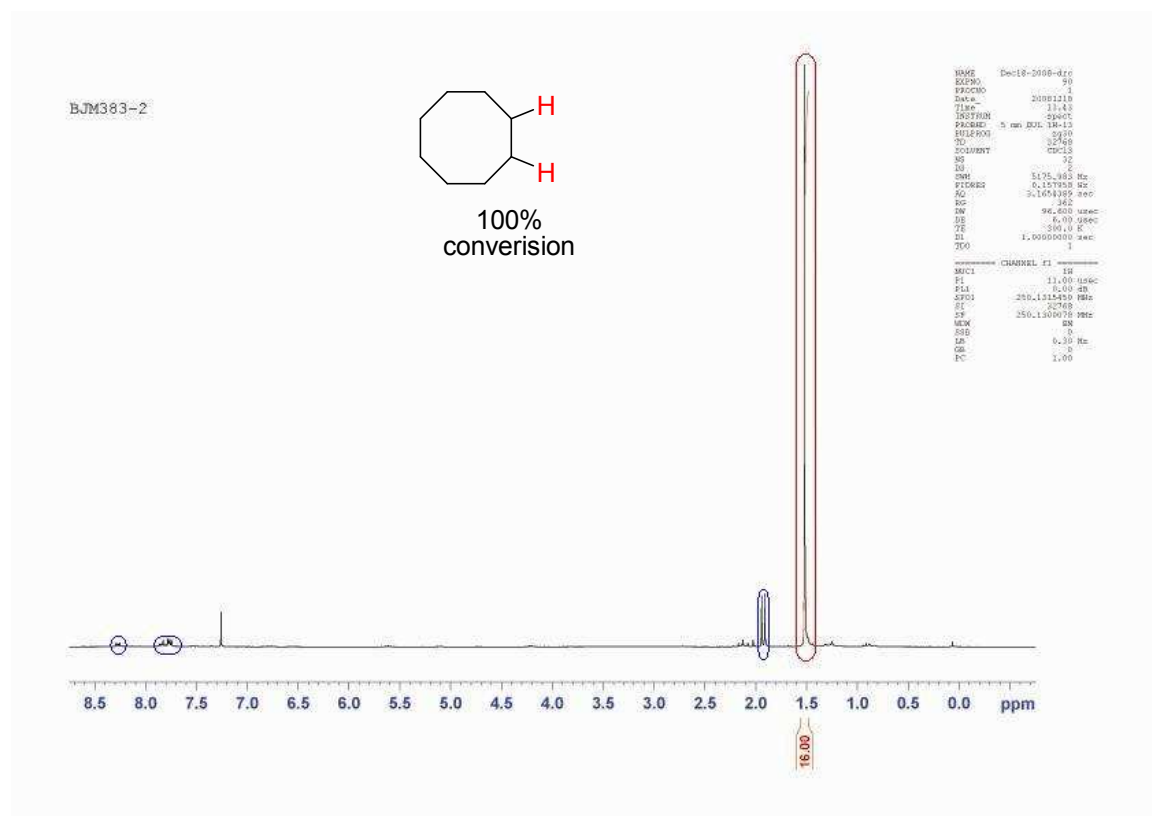
## 2,3-Norbornanedimethanol 14.



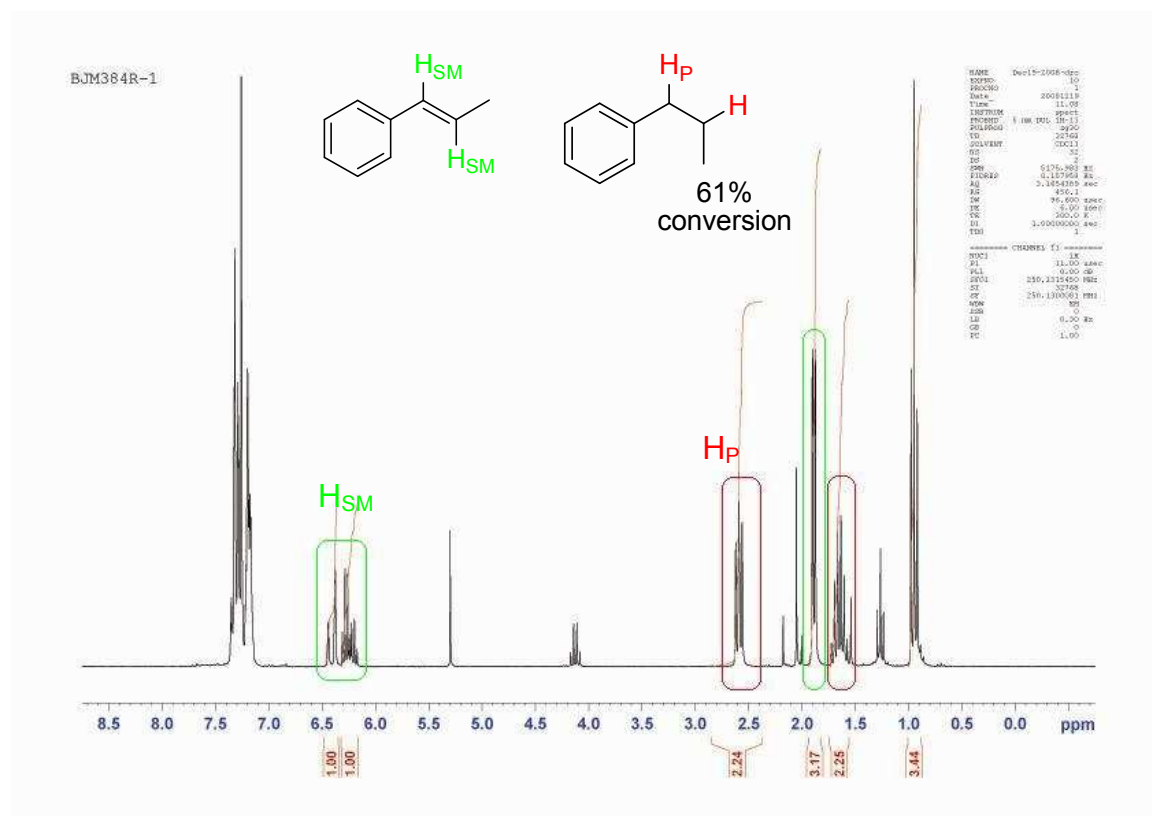
## 2-Ethyl pyridine 15.

*(R)*-4-Isopropyl-1-methylcyclohex-1-ene 16.

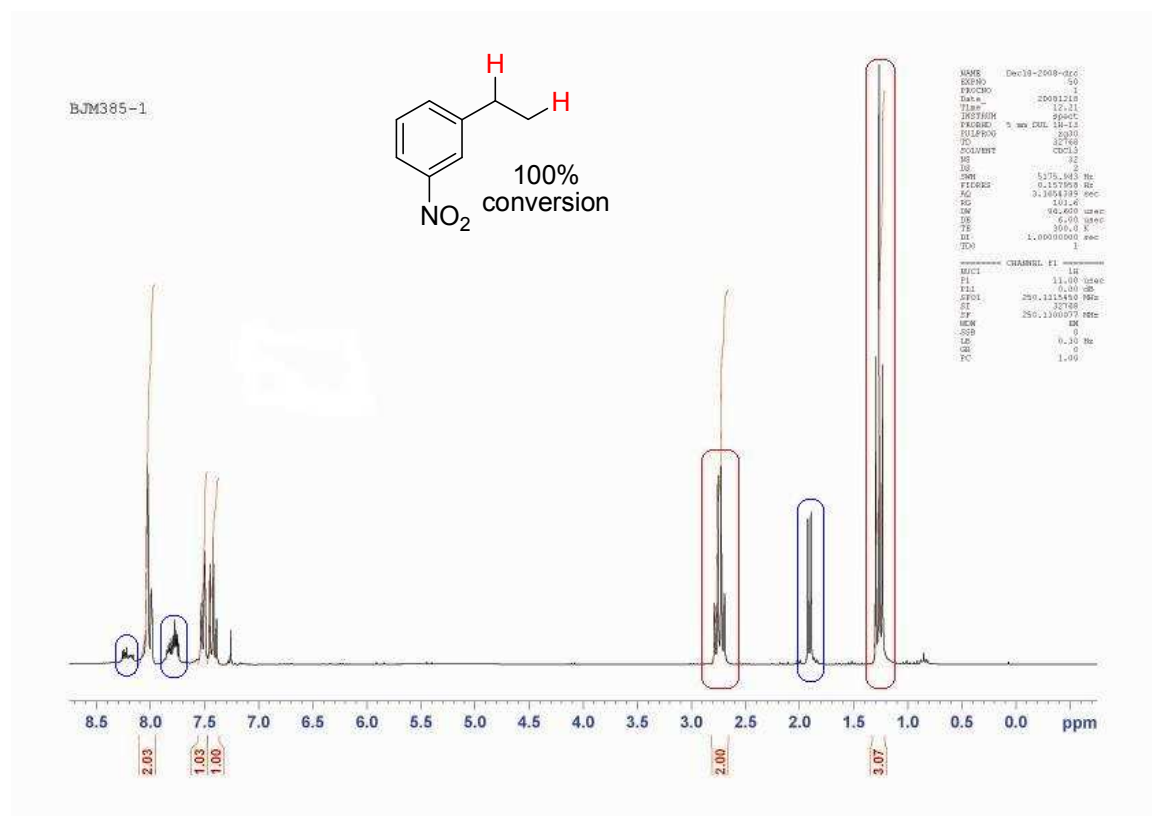
## Cyclooctane 17.



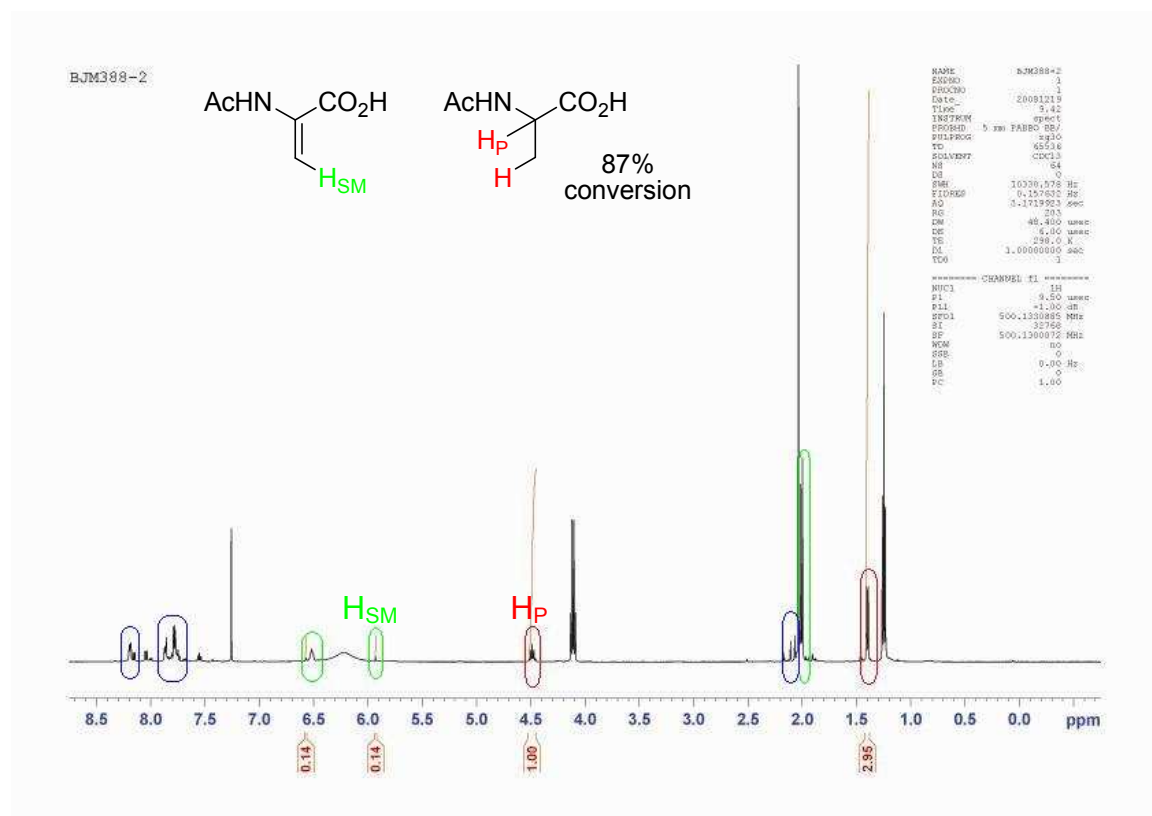
## Propylbenzene 18.



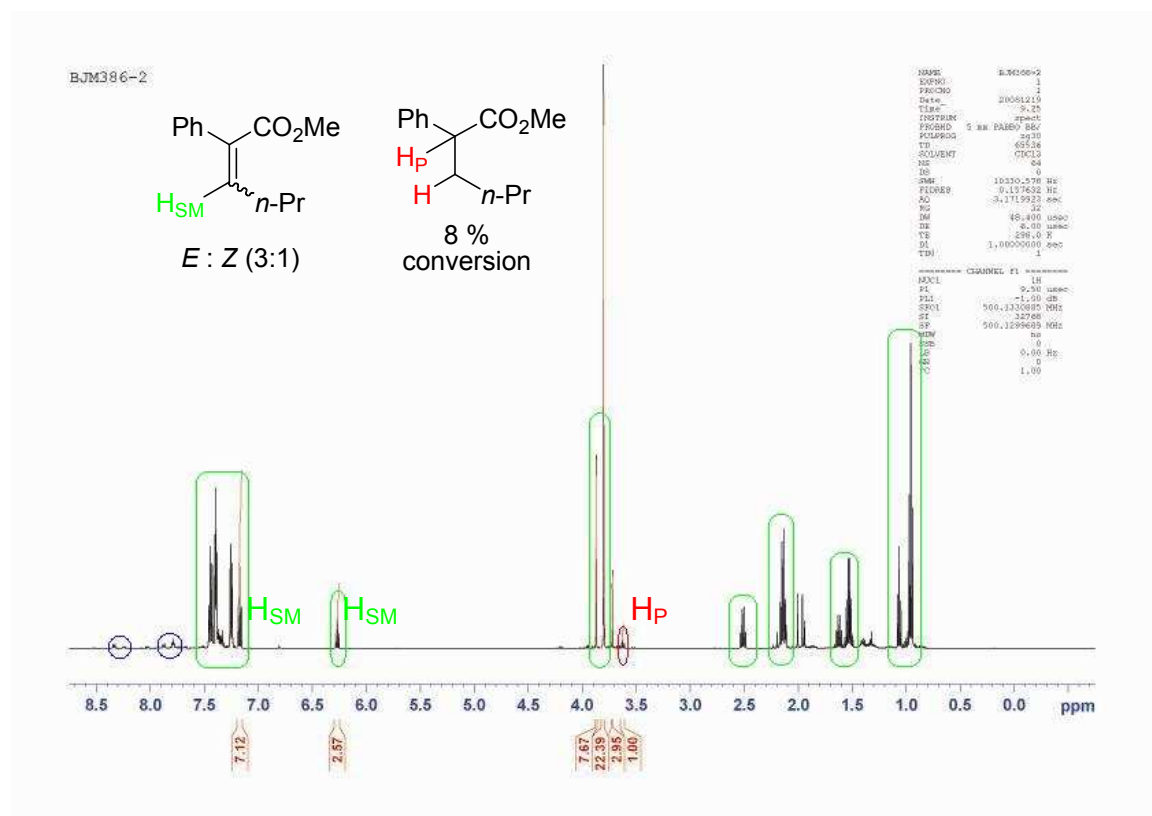
## 2-Ethyl-nitrobenzene 19.



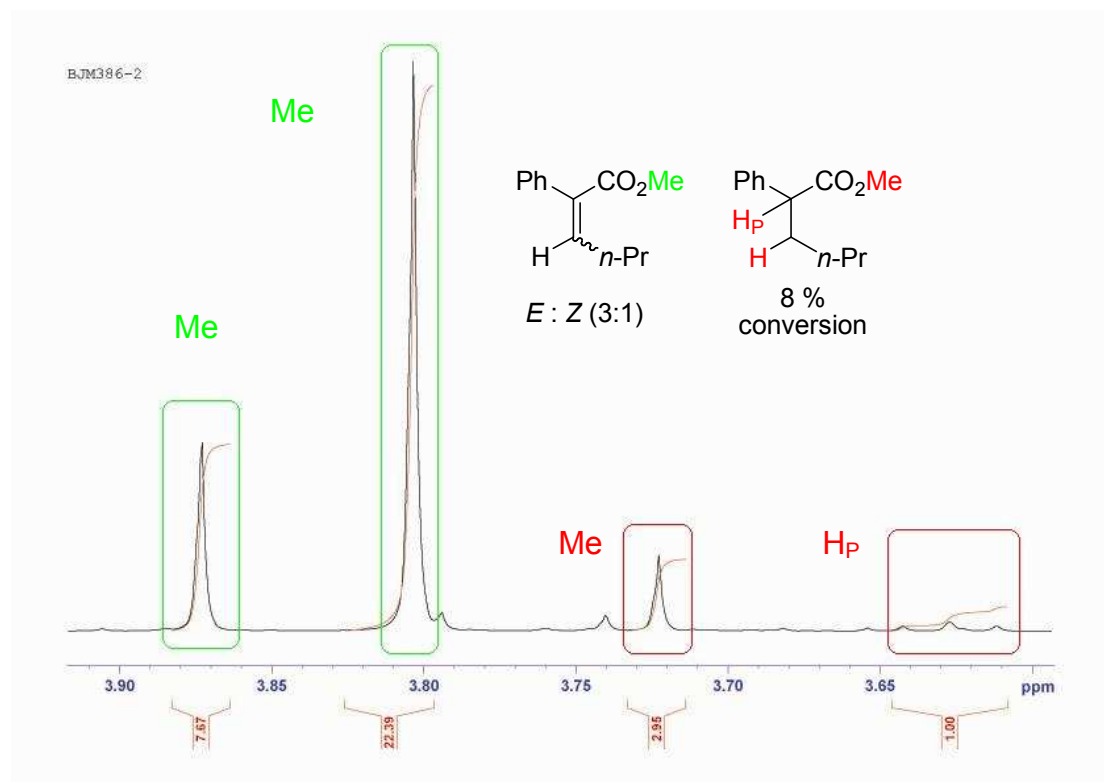
## 2-Acetamidopropanoic acid 20.



## Methyl 2-Phenylhexanoate 21.

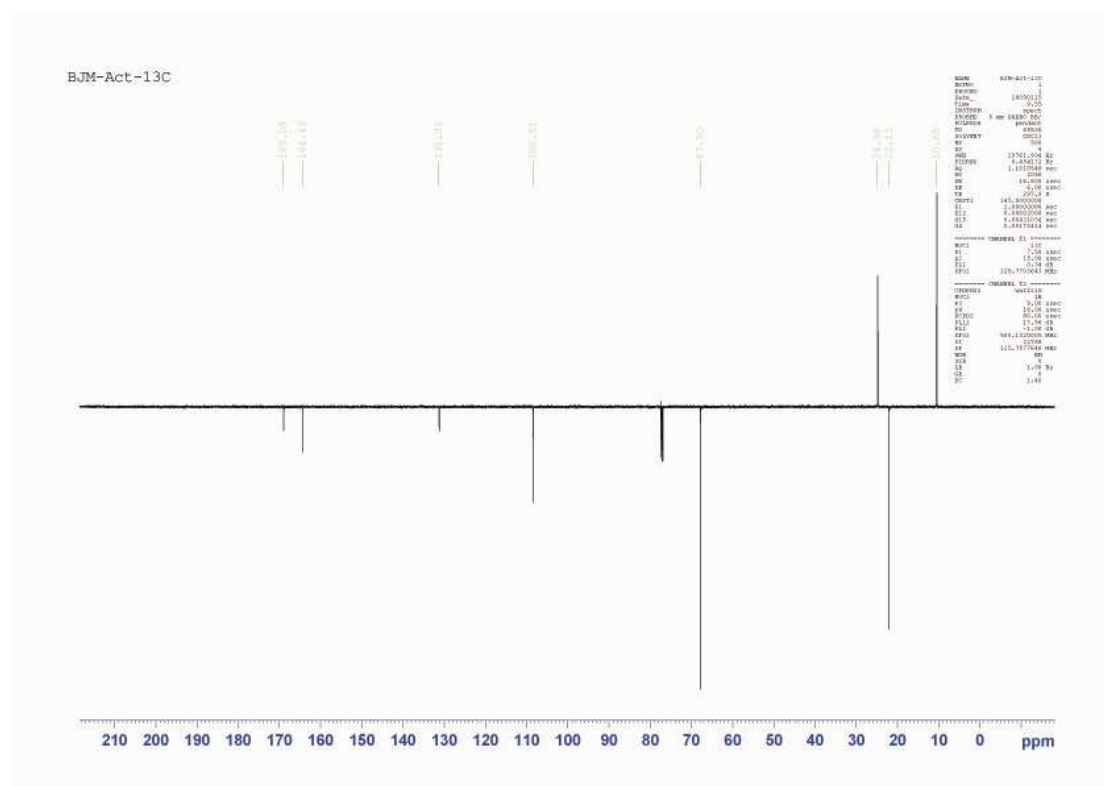
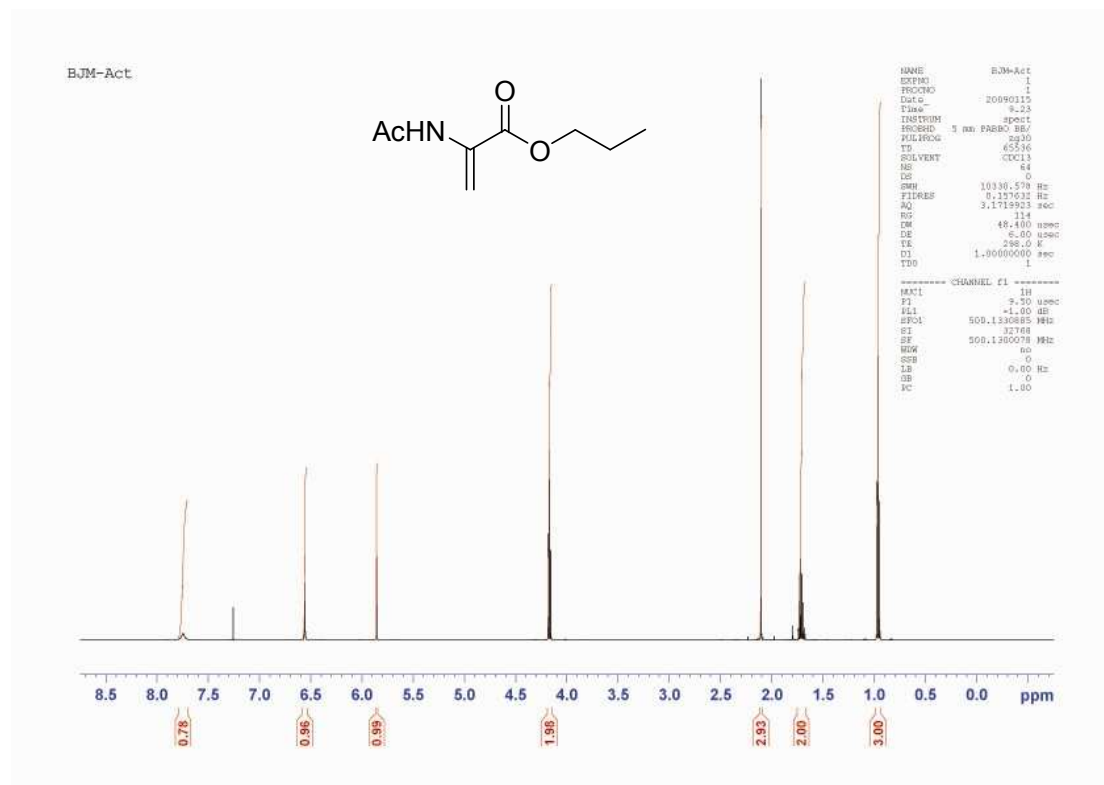


(See Expansion for clearer image)





## 2-Propyl-acetamidoacrylate 22.



**References**

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- (2) Beddow, J. E.; Davies, S. G.; Ling, K. B.; Roberts, P. M; Russell, A. J.; Smith, A. D., Thomson, J. E. *Org. Biomol. Chem.* **2007**, *5*, 2812.
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- (6) Liu, C; He, C; Shi, W; Chen, M; Lei, A. *Org. Lett.* **2007**, *9*, 5601.