

# Chemical Communication

Supplementary Information for

**Ligand-free nickel-catalyzed semihydrogenation of alkynes with  
sodium borohydride: a highly efficient and selective process for  
*cis*-alkenes under ambient conditions**

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# Supplementary Information

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## Experimental Details

### General

Chemical reactants were purchased from J&K Scientific Ltd. and Aladdin Reagent Co. Ltd. and used without further purification.

The NMR spectra were measured with a Bruker spectrometer using a reference compound, for example, tetramethylsilane for  $^1\text{H}$  and  $^{13}\text{C}$ NMR and borontrifluoride-ether complex for  $^{11}\text{B}$  NMR. The *in-situ* IR spectra were performed on a Nicolet iS10 spectrometer configured with a flexible infrared fiber-optic probe. Transmission electron microscopy (TEM) images were obtained with a FEI Tecnai G2 F20 S-TWIN instrument at a voltage of 200 kV. Reaction mixtures were analyzed by Agilent 7820A gas chromatography by using a 30 m HP-5 capillary column and the product were identified using gas chromatography–mass spectrometry (GC–MS) on an Agilent 7890-5977a spectrometer.

### **Typical procedure of the Ni(0)-catalyzed semihydrogenation of alkynes**

To a vial containing alkyne (1.0 mmol) in the solvent (8 mL), 50  $\mu$ L of methanol solution containing  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (20 mg/mL) were added at room temperature. The solution was then stirred vigorously using a magnetic stirrer. After 10 minutes, a certain amount of borohydrides or ammonia borane was added, and the color of solution immediately turned to black or brown. The reaction was monitored by TLC and GC, and when the reaction was complete, the methanol was removed under reduced pressure. The crude products were purified by column chromatography on silica gel to withhold the catalyst and inorganic salts.

The crude products of alkynes were identified using GC–MS and the *cis-trans* isomerism was determined by NMR.

### **Two-steps procedure of the semihydrogenation of DPA**

To a vial containing methanol (8 mL), 50  $\mu$ L of methanol solution containing  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (20 mg/mL) were added at room temperature. The solution was then stirred vigorously using a magnetic stirrer. After 10 minutes, sodium borohydride (15 mg, 0.39 mmol) was added and then the color of solution turned to black immediately, suggesting that the formation of Ni nanoparticles. DPA (178 mg, 1.0 mmol) and sodium borohydride (61 mg, 1.61 mmol) were added to the reaction mixture and the reaction was monitored by TLC and GC.

**Table S1** Influence of ratio of Ni and DPA on the selectivity for *cis*-stilbene<sup>a</sup>

Substrate	Ratio of Ni and DPA (mol%)	Time (min)	Conversion (%)	Z/E/alkane (%)
DPA	0.2	5	72	93/6/1
		10	100	89/8/3
DPA	0.4	5	98	94/5/1
DPA	0.8	3	100	92/5/3
		5	100	76/11/13
DPA	2	5	100	54/17/29
DPA	8	5	100	3/9/88

<sup>a</sup>**Reaction conditions:** DPA (178 mg, 1.0 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (0.4 mol%), methanol (8 mL), NaBH<sub>4</sub> (78 mg), at room temperature, in air atmosphere.

**Table S2** Comparison of TOF for the semihydrogenation of DPA to *cis*-stilbene with different reported catalysts

Catalyst	Hydrogen source	Temp. (°C)	TOF <sup>a</sup> (h <sup>-1</sup> )	Reference
Lindlar catalyst	1 atm H <sub>2</sub>	r. t.	380	S1
Pd <sup>0</sup> -AmP-HSNs	1 atm H <sub>2</sub>	r. t.	106	S1
Pd(OAc) <sub>2</sub> PPh <sub>2</sub> Et/SiO <sub>2</sub>	1.03 MPa syngas	70	10.4	S2
Pd-PEI-HAS	0.1 MPa H <sub>2</sub>	r. t.	3027	S3
Pd/SBA-gt-PEI	0.1 MPa H <sub>2</sub>	r. t.	2598	S3
Pd@Ag-0.20	1 atm H <sub>2</sub>	r. t.	75	S4
Pd(OAc) <sub>2</sub>	DMF/KOH	145	8.25	S5
Au/TiO <sub>2</sub>	NH <sub>3</sub> BH <sub>3</sub>	25	190	S6
Nanoporous Au	HCOOH	70	5	S7
Ni/gallium nanoalloys	0.5 MPa H <sub>2</sub>	120	139	S8
NiBr <sub>2</sub>	Zn/HCOOH	120	0.59	S9
(P-P)Ni(2-C, C-alkyne)	NH <sub>3</sub> BH <sub>3</sub>	80	2.78	S10
(P-P)Ni(2-C, C-alkyne)	NaBH <sub>4</sub>	80	2.4	S10
Fe <sub>2</sub> (CO) <sub>9</sub> source [Fe]	PhSiH <sub>3</sub>	100	0.5	S11
[(PPh <sub>3</sub> )CuCl] <sub>4</sub>	5 atm H <sub>2</sub> and <i>i</i> -PrOH	100	16.5	S12
POPs-[V]	1.38 MPa H <sub>2</sub>	60	4	S13
POPs-[Cr]	1.38 MPa H <sub>2</sub>	60	0.6	S13
Ni catalyst	NaBH <sub>4</sub>	r. t.	2940	This work

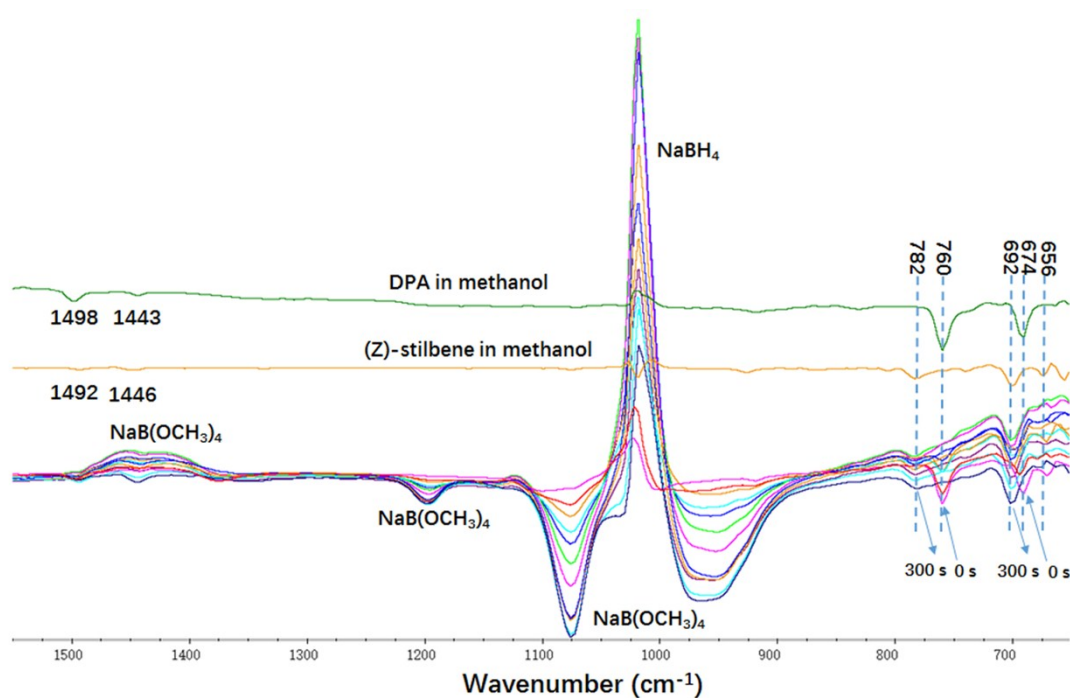
<sup>a</sup>TOF = mol of consumed DPA/(mol of metal × time)

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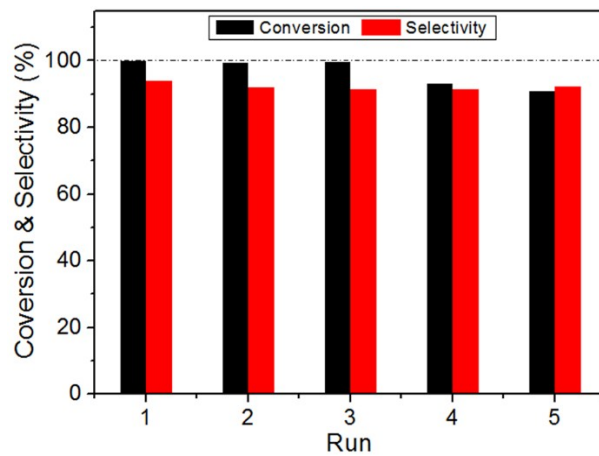
## The *in-situ* IR monitoring of the semihydrogenation of DPA

The *in-situ* IR spectra of DPA and *cis*-stilbene were measured with a methanol background. Before the reaction, the background in the mixture of methanol (8 mL), NiCl<sub>2</sub>·6H<sub>2</sub>O in methanol (50 μL, 20 mg/mL), was collected and then DPA (178 mg, 1.0 mmol) was added and the results were shown in Fig. S1. In the absence of NaBH<sub>4</sub> (0 s), the spectrum of solution was consistent with the spectra of DPA. After the addition of NaBH<sub>4</sub> (76 mg), the absorption peaks of DPA (mainly at 674, 760, 1443 and 1498 cm<sup>-1</sup>) were weakened markedly compared with the pure DPA, whilst the absorption peaks of *cis*-stilbene appeared at 656, 692 and 782 cm<sup>-1</sup>. When the reaction was completed (300 seconds), the characteristic peaks of DPA disappeared. The peaks of NaBH<sub>4</sub> at about 1010-1030 cm<sup>-1</sup> decreased along with the increasing of peaks at about 1200, 1080 and 960-980 cm<sup>-1</sup>, thus exhibiting the generation of NaB(OCH<sub>3</sub>)<sub>4</sub>, as demonstrated by <sup>11</sup>B NMR.



**Fig. S1** The *in-situ* IR spectra of the semihydrogenation of DPA.

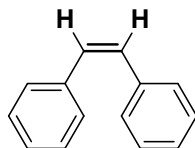




**Fig. S2** Influence of cycle number on the conversion and selectivity in the semihydrogenation of DPA within 20 minutes.

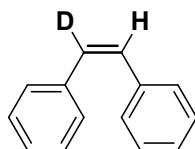
## NMR spectra data of products

### *cis*-Stilbene<sup>S14</sup>



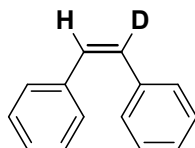
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 7.18-7.11 (m, 10H), 6.53 (s, 2H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): 137.3, 130.3, 128.9, 128.2, 127.1.

### Monodeuterated *cis*-stilbene using NaBD<sub>4</sub><sup>S15</sup>



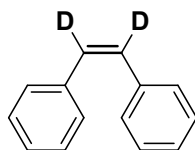
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 7.25-7.16 (m, 10H), 6.59 (s, 1H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): 137.3, 137.2, 130.2, 129.0, 128.3, 127.2.

### Monodeuterated *cis*-stilbene using CH<sub>3</sub>OD<sup>S15</sup>



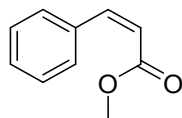
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): 7.27-7.20 (m, 10H), 6.64 (s, 1H); <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>): 136.8, 136.7, 129.0, 128.4, 128.3, 127.2.

**Dideuterated *cis*-stilbene using NaBD<sub>4</sub> and CH<sub>3</sub>OD<sup>S16</sup>**



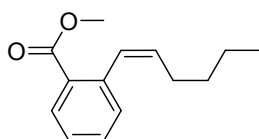
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): 7.27-7.20 (m, 10H); <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>): 136.7, 128.5, 128.3, 127.2.

***cis*-Methyl 3-phenylacrylate<sup>S17</sup>**



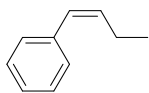
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): 7.62 (d, 2H), 7.40-7.35 (m, 3H), 7.03 (d, *J*=12.6 Hz, 1H), 6.03 (d, *J* = 12.6 Hz, 1H), 3.66 (s, 3H); <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>): 166.1, 142.3, 134.5, 129.6, 129.0, 128.0, 119.2, 51.1.

***cis*-methyl-2-(hex-1-en-1-yl) benzoate<sup>S18</sup>**



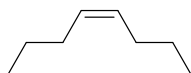
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): 7.83 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 11.6 Hz, 1H), 5.65 (td, *J*<sub>1</sub> = 11.6 Hz, *J*<sub>2</sub> = 7.4 Hz, 1H), 3.78 (s, 3H), 2.07-2.03 (m, 2H), 1.33-1.28 (m, 2H), 1.24-1.17 (m, 2H), 0.76 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>): 166.9, 137.8, 131.9, 131.5, 130.3, 129.8, 129.2, 128.2, 126.8, 51.8, 31.2, 27.4, 21.6, 13.5.

**cis-but-1-ene-1-yl-benzene**<sup>S18</sup>



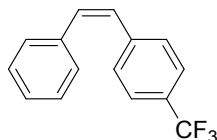
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): 7.38-7.27 (m, 5H), 6.38 (d, *J* = 12.0 Hz, 1H), 5.64 (td, *J*<sub>1</sub> = 11.4 Hz, *J*<sub>2</sub> = 7.2 Hz, 1H), 2.93 (q, 3H), 1.02 (t, 3H); <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>): 137.1, 134.2, 128.5, 128.4, 128.2, 128.1, 126.6, 125.7, 21.5, 14.2.

**cis-4-octene**<sup>S19</sup>



<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 5.35 (t, 2H, *J* = 7.2 Hz), 2.05 (m, 4H), 1.39 (m, 4H), 0.91 (t, 6H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): 130.5, 30.3, 23.2, 14.1.

**cis-1-styryl-4-(trifluoromethyl)benzene**<sup>S20</sup>



<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): 7.57 (d, 2H), 7.40 (d, 2H), 7.27-7.19 (m, 5H), 6.78 (d, 1H, *J* = 12.6 Hz), 6.68 (d, 1H, *J* = 11.4 Hz); <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>): 141.0, 136.2, 132.2, 129.1, 128.5, 128.4, 128.4, 127.6, 125.1 (*J*<sub>1</sub> = 3.8 Hz, *J*<sub>2</sub> = 3.5 Hz), 123.2.

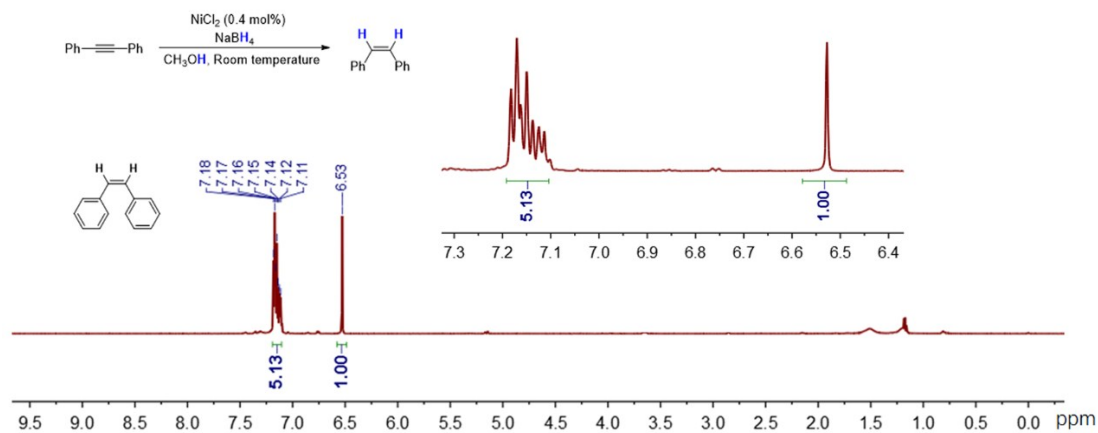
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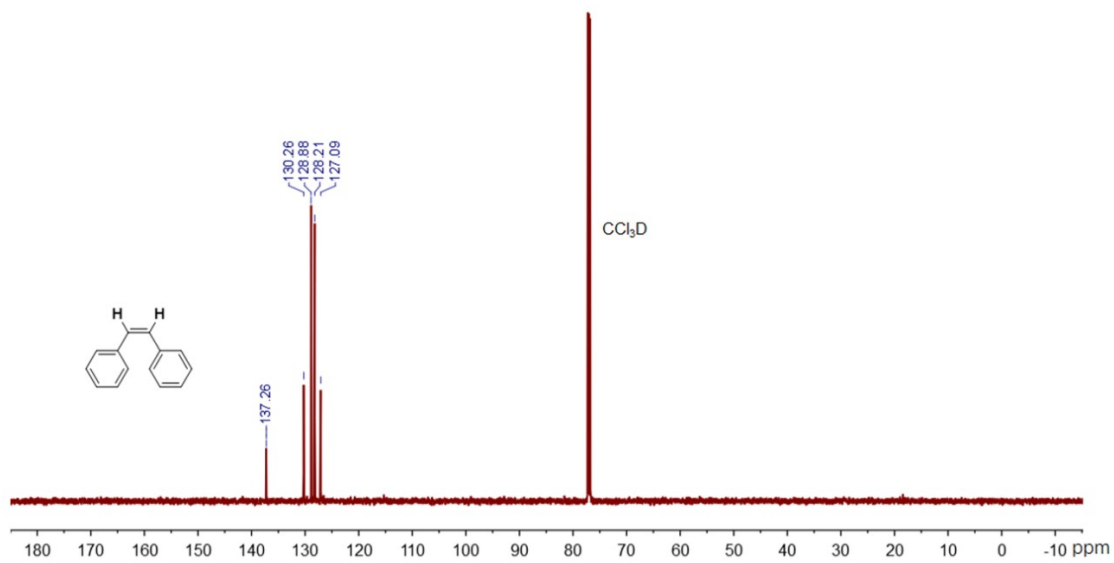
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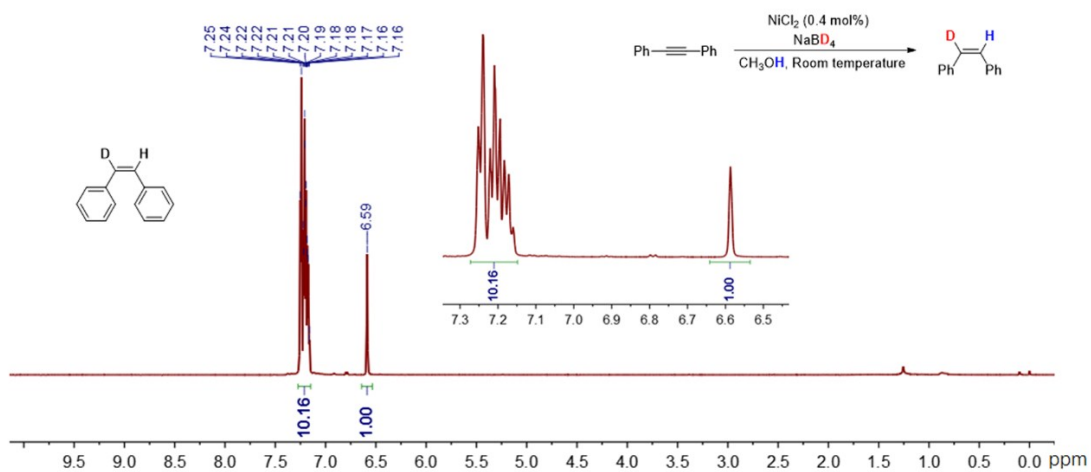
## $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of products



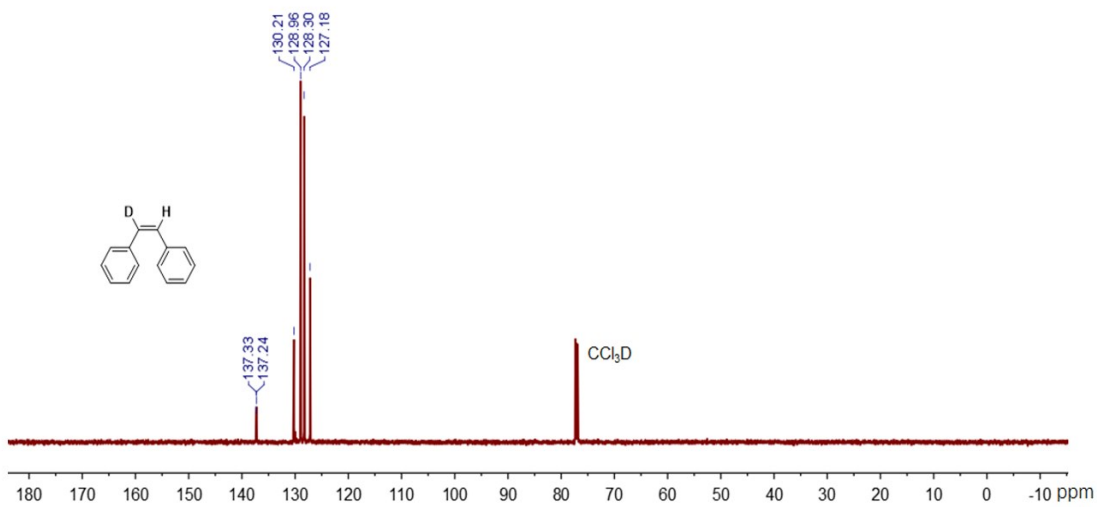
## $^1\text{H}$ NMR of monodeuterated *cis*-stilbene using $\text{NaBH}_4$ and $\text{CH}_3\text{OH}$ in $\text{CDCl}_3$



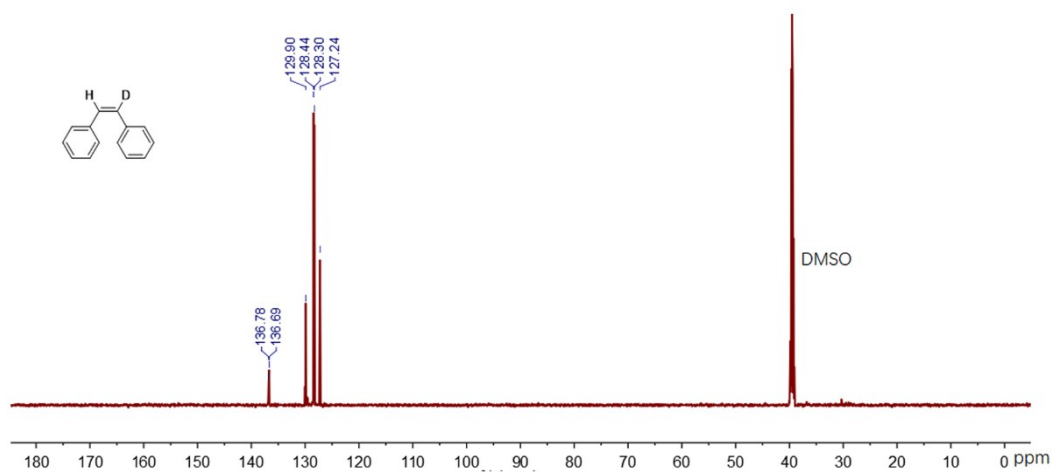
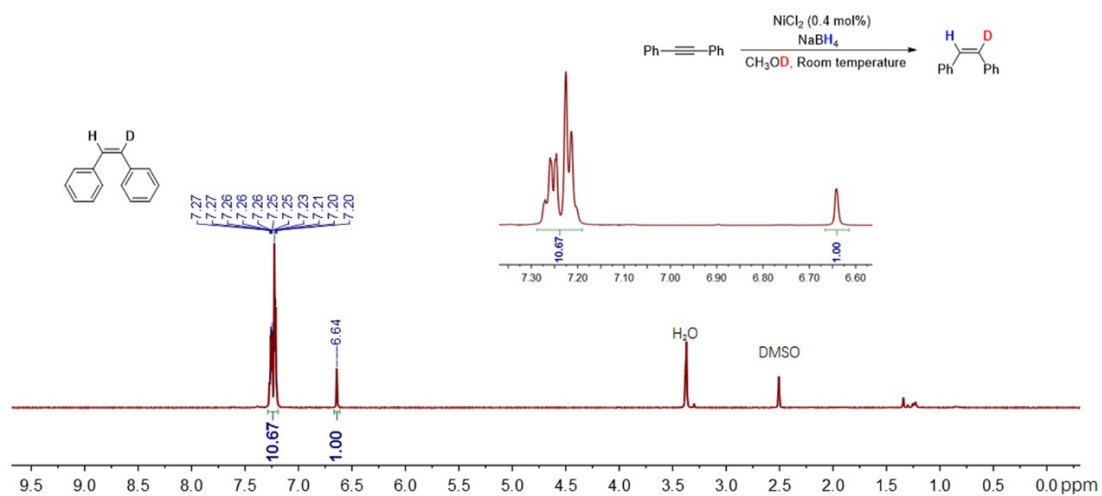
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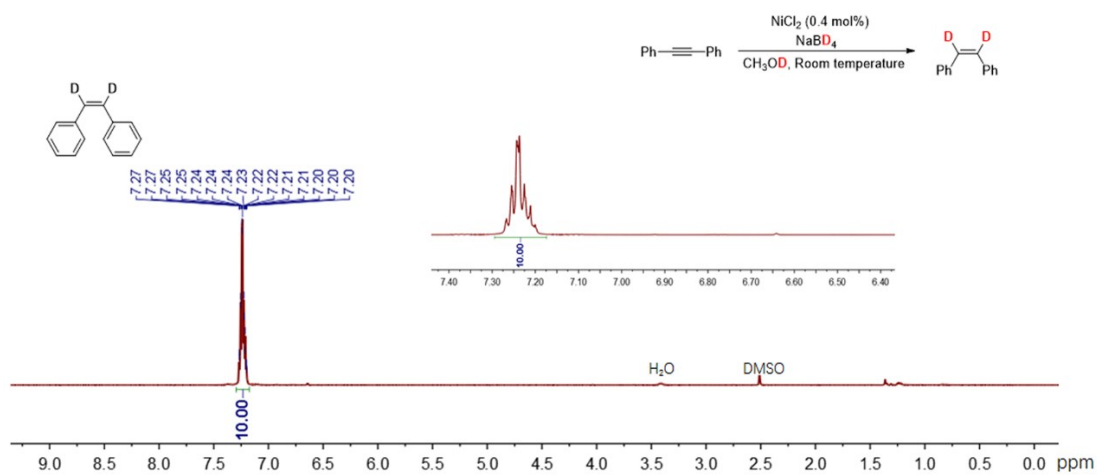
**<sup>1</sup>H NMR of monodeuterated *cis*-stilbene using NaBD<sub>4</sub> and CH<sub>3</sub>OH in CDCl<sub>3</sub>**



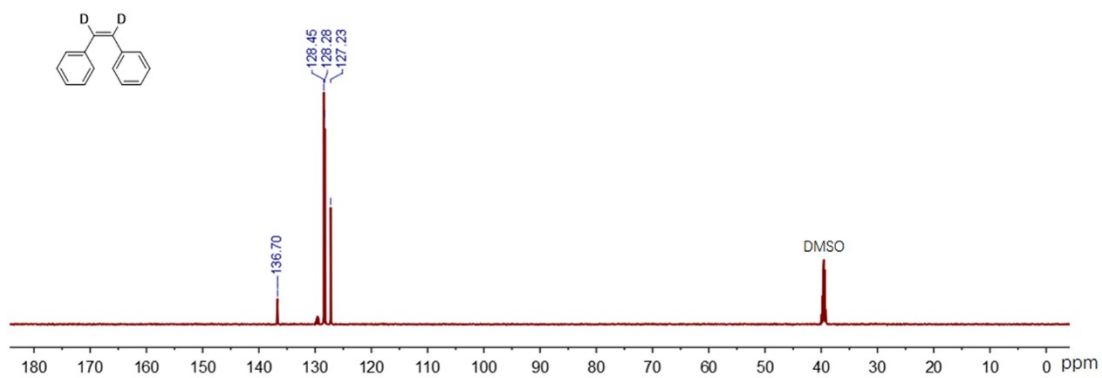
**<sup>13</sup>C NMR of monodeuterated *cis*-stilbene using NaBD<sub>4</sub> and CH<sub>3</sub>OH in CDCl<sub>3</sub>**



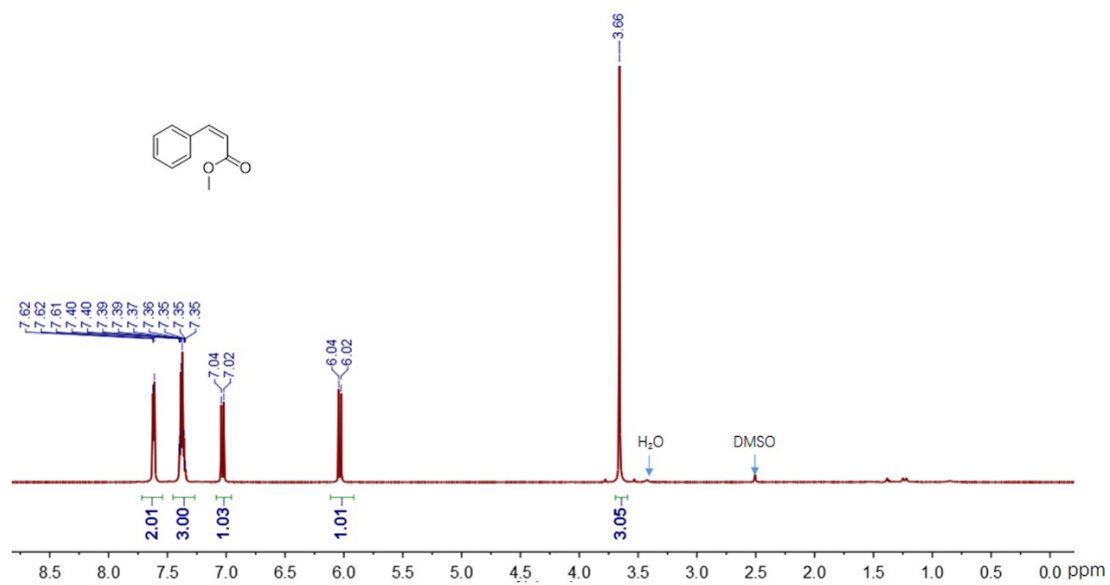




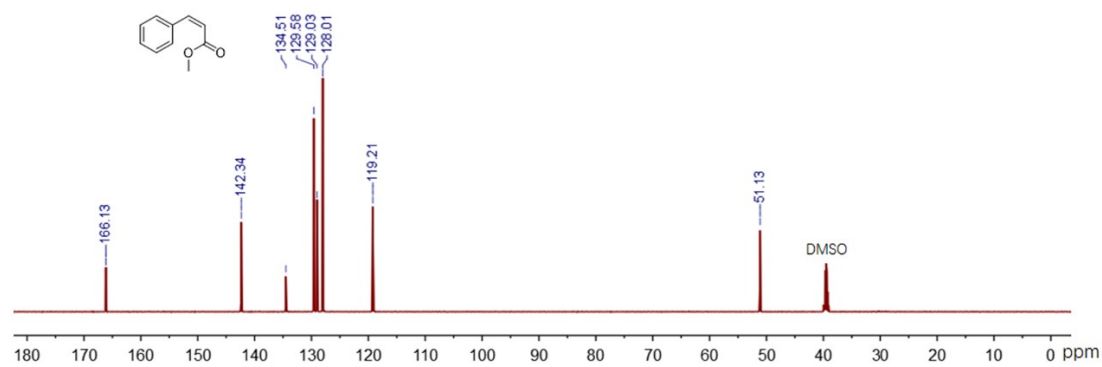
**<sup>1</sup>H NMR of dideuterated *cis*-stilbene using NaBD<sub>4</sub> and CH<sub>3</sub>OD in DMSO-*d*<sub>6</sub>**



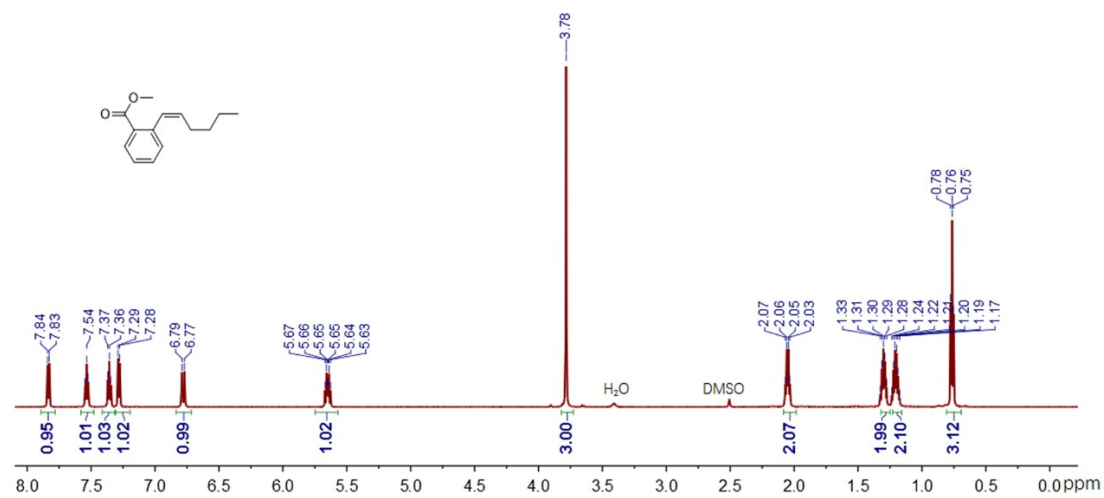
**<sup>13</sup>C NMR of dideuterated *cis*-stilbene using NaBD<sub>4</sub> and CH<sub>3</sub>OD in DMSO-*d*<sub>6</sub>**



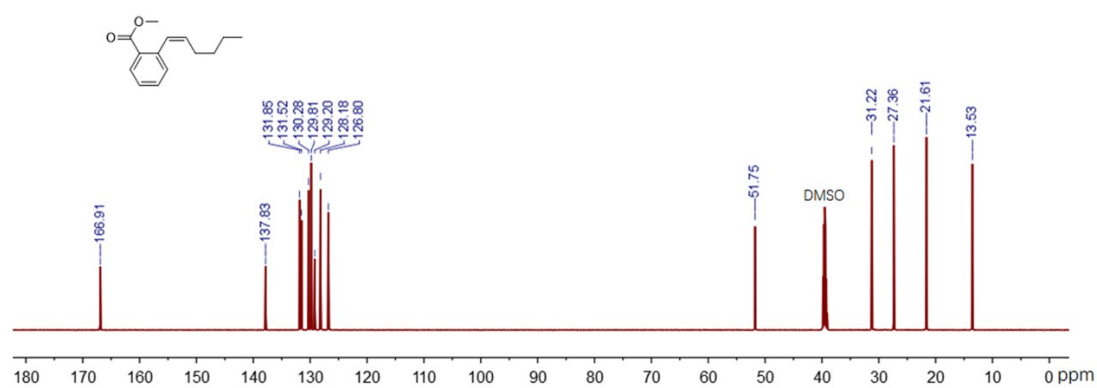
**<sup>1</sup>H NMR of *cis*-methyl 3-phenylacrylate in DMSO-*d*<sub>6</sub>**



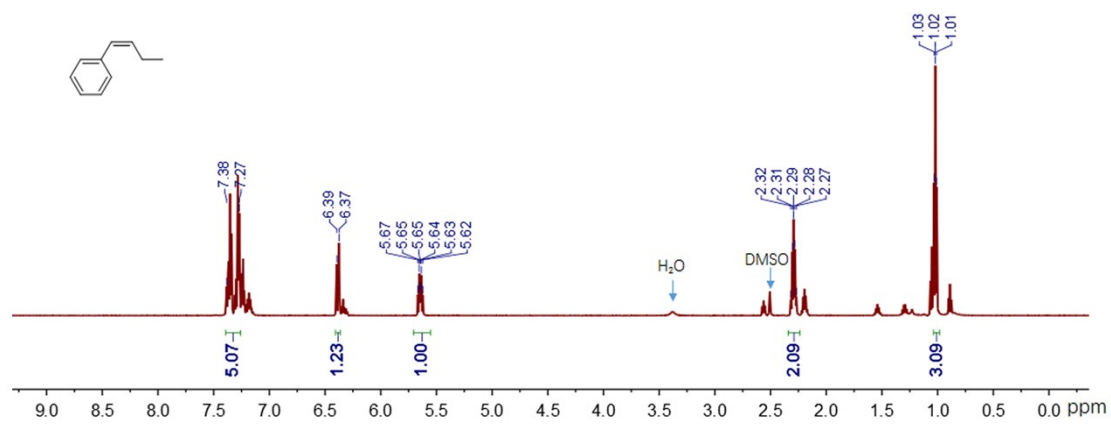
**<sup>13</sup>C NMR of *cis*-methyl 3-phenylacrylate in DMSO-*d*<sub>6</sub>**



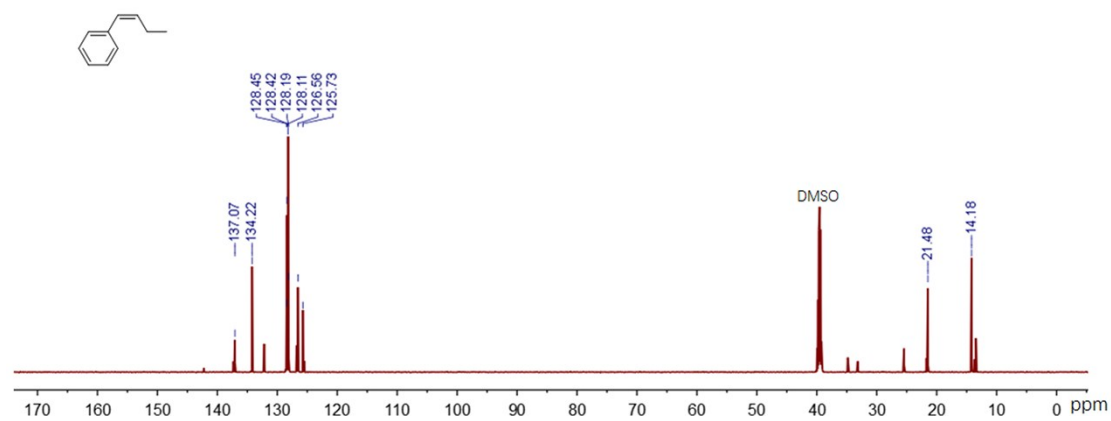
**<sup>1</sup>H NMR of *cis*-methyl-2-(hex-1-en-1-yl) benzoate in DMSO-*d*<sub>6</sub>**



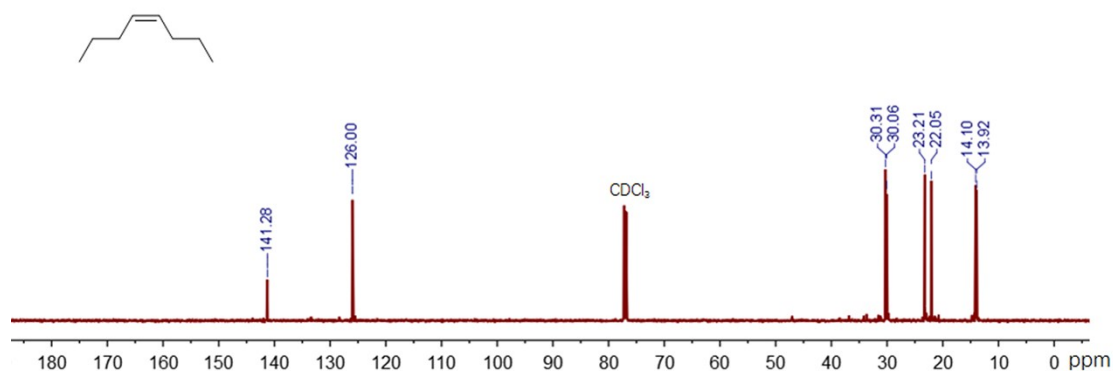
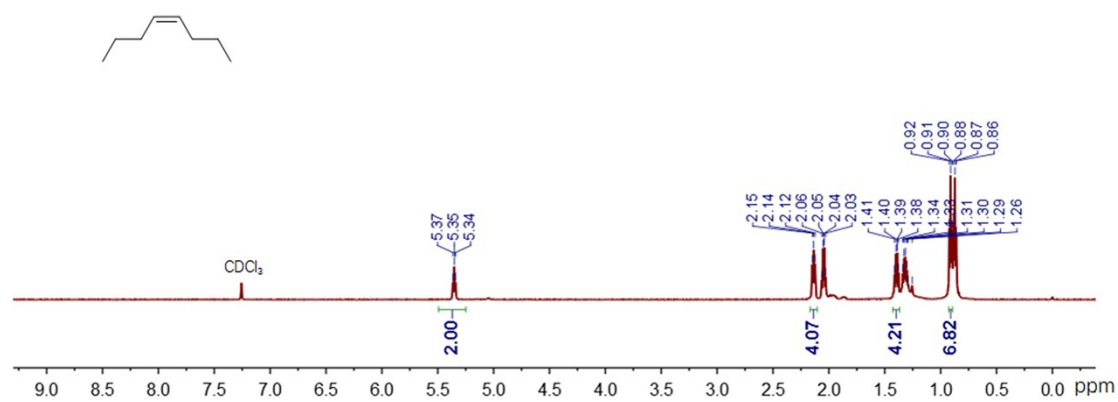
**<sup>13</sup>C NMR of *cis*-methyl-2-(hex-1-en-1-yl) benzoate in DMSO-*d*<sub>6</sub>**

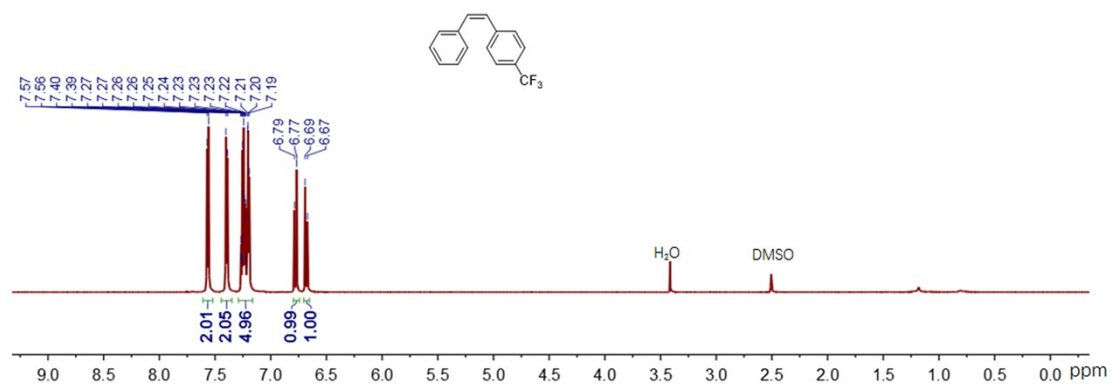


<sup>1</sup>H NMR of *cis*-But-1-ene-1-yl-benzene in DMSO-*d*<sub>6</sub>

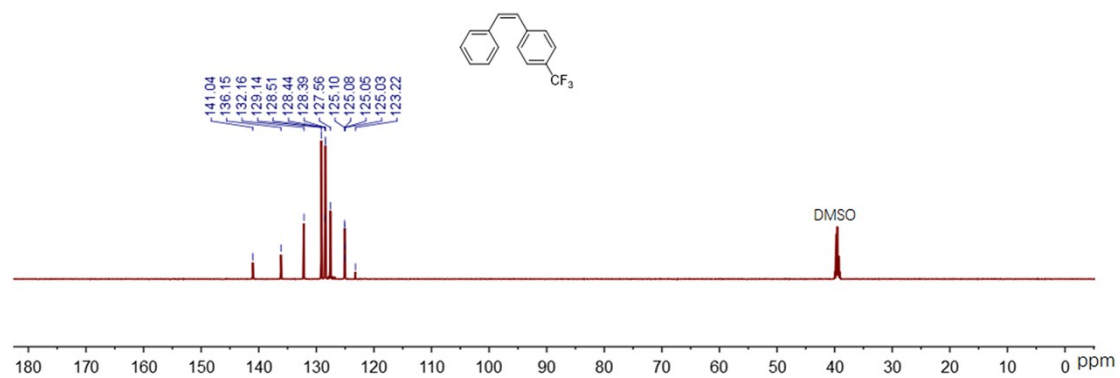


<sup>13</sup>C NMR of *cis*-But-1-ene-1-yl-benzene in DMSO-*d*<sub>6</sub>



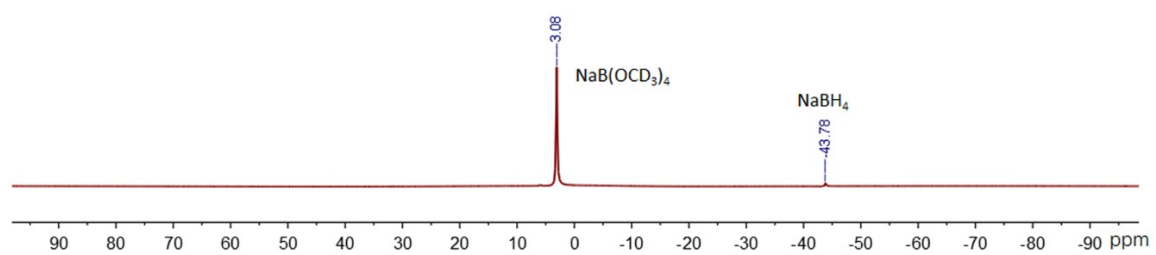


**<sup>1</sup>H NMR of *cis*-1-styryl-4-(trifluoromethyl)benzene in DMSO-*d*<sub>6</sub>**



**<sup>13</sup>C NMR of *cis*-1-styryl-4-(trifluoromethyl)benzene in DMSO-*d*<sub>6</sub>**

## Direct $^{11}\text{B}$ NMR in $\text{CD}_3\text{OD}$



## Direct $^{11}\text{B}$ NMR of liquid phase from the semihydrogenation of DPA using $\text{CD}_3\text{OD}$ as solvent