Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Catalysis Science & Technology

E-Selective Semi-hydrogenation of Alkynes via a Sulfur-radical Mediation over Cyclodextrin-modified Nickel Nanocatalyst

*Yatao Su,[a, ‡] Xiu Wang,[a, ‡] Qianwen Lin,[a] Qi Shen,[a] Shuangwen Xu,[a] Liping Fang,[a] Xin Wen[a,]**

[a]Key Laboratory of Chemical Biology of Hebei Province, College of Chemistry and Materials Science, Hebei University, Baoding 071002, China.

‡ These authors contributed equally to this work.

* Corresponding author: E-mail address: wenxin767@hotmail.com

Supplementary Materials

Table of contents

Synthesis of CH-SH

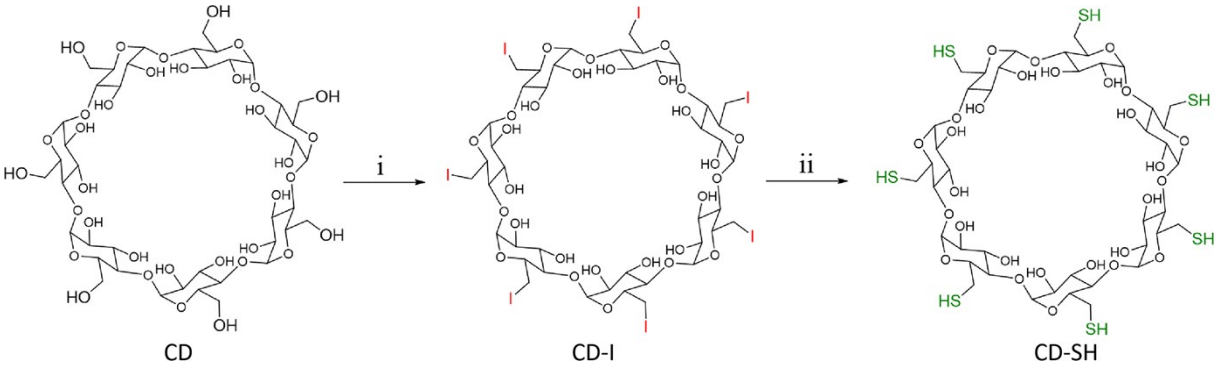


Fig. S1 Synthesis of heptakis-(6-mercapto-6-deoxy)-β-cyclodextrin (CD-SH).

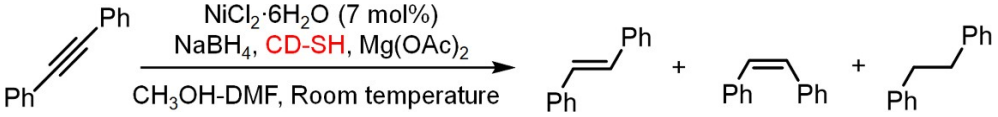
Heptakis-(6-mercapto-6-deoxy)-β-cyclodextrin (CD-SH) was synthesized in two steps (Fig. S1).

(i) Synthesis of CD-I: β-cyclodextrin (CD) was recrystallized three times in distilled water (12.0 g CD, 24 mL water) and vacuum dried at 120 °C for 24 h. Triphenylphosphine (40.1 g, 153 mmol) and I_2 (40.5 g, 160 mmol) were dissolved in dried DMF (120 mL and 40 mL), respectively. Subsequently, I_2 solution was added dropwise to the triphenylphosphine solution under stirring. CD (10.2 g) was added to the dark brown solution. The mixture was then heated to 70 °C under a nitrogen atmosphere and stirred for 18 hours. After completed, half of the volume of DMF in the reaction system was removed by vacuum distillation. A solution of sodium methoxide (17.0 mg, 90 mL) was slowly added to the concentrated reaction mixture with cooling in an ice bath, and the pH was adjusted to 9 by NaOH aqueous solution (1.0 M). After stirring for another hour, a large amount of yellow solids were produced, and the color of the solution was turned to brick red. When the reaction mixture was poured into a large amount of methanol (400 mL), more precipitate was formed. The yellow solids were separated by filtration, washed with methanol several times until the color of precipitate was white, and dried under vacuum to give white solids (CD-I).

(ii) Synthesis of CD-SH: In a 250-mL three-necked flask with a dropping funnel, CD-I (0.965 g) and thiourea (0.301 g) in DMF (10 mL) was placed under a nitrogen atmosphere. The reaction mixture was raised to 70 °C and stirred for 19 h. Most DMF was removed by vacuum distillation to obtain yellow oily substance. Water (50 mL) and sodium hydroxide (0.26 g) were added and then refluxed for 1 h under a nitrogen atmosphere. The reaction solution was cooled to room temperature and acidified with $KHSO_4$ solution. The precipitate was separated by filtration, washed with distilled water several times, and dried under vacuum below 35 °C for several days to obtain white solid powder (CD-SH).

Optimization of reaction conditions

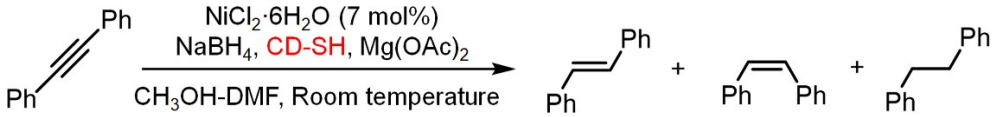
Table S1 Screening of ligands for the semi-hydrogenation of DPA to *E*-stilbene



Entry	Ligand[a]	Conv. (%)	*E*/*Z*/alkane (%)
1	α-CD-SH	>99	68/26/6
2	CD-SH	>99	82/7/11
3	γ-CD-SH	>99	65/24/11
4	1-octanethiol	>99	53/47/0
5	1-dodecanethiol	>99	50/48/2
6	1-octadecanethiol	>99	53/43/4

Reaction conditions: DPA (1 mmol), $NiCl_2·6H_2O$ (7 mol%), $NaBH_4$ (4 equiv.), ligand (3 mol%), $Mg(OAc)_2$ (4 equiv.), CH_3OH (0.35 mL), DMF (8 mL), room temperature, 1 h. [a] α-CD-SH, CD-SH and γ-CD-SH refer to heptakis-(6-mercapto-6-deoxy)-α-cyclodextrin, heptakis-(6-mercapto-6-deoxy)-β-cyclodextrin and heptakis-(6-mercapto-6-deoxy)-γ-cyclodextrin, respectively.

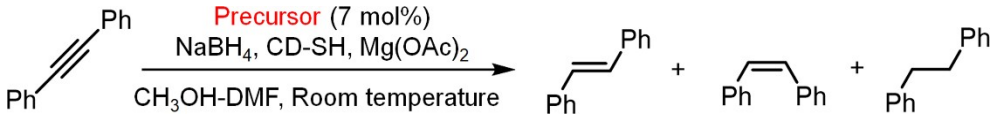
Table S2 Screening of the amount of CD-SH for the semi-hydrogenation of DPA to *E*-stilbene



Entry	CD-SH (mol%)	Conv. (%)	*E*/*Z*/alkane (%)
1	0	>99	36/54/10
2	1	>99	66/25/9
3	2	>99	78/9/13
4	3	>99	82/7/11
5	4	>99	78/8/14
6	5	>99	77/7/16

Reaction conditions: DPA (1 mmol), $NiCl_2·6H_2O$ (7 mol%), $NaBH_4$ (4 equiv.), CD-SH, $Mg(OAc)_2$ (4 equiv.), CH_3OH (0.35 mL), DMF (8 mL), room temperature, 1 h.

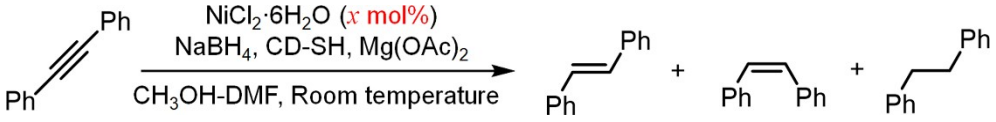
Table S3 Screening of catalyst precursors for the semi-hydrogenation of DPA to *E*-stilbene



Entry	Catalyst precursor	Conv. (%)	*E*/*Z*/alkane (%)
1	$NiCl_2$	>99	82/7/11
2	$Ni(OAc)_2$	>99	80/8/12
3	$Ni(C_5H_7O_2)_2$	>99	76/10/14
4	NiI_2	>99	42/54/4
5	$Pd(OAc)_2$	39	0/99/1
6	$Co(OAc)_2$	>99	24/57/19

Reaction conditions: DPA (1 mmol), catalyst precursor (7 mol%), $NaBH_4$ (4 equiv.), CD-SH (3 mol%), $Mg(OAc)_2$ (4 equiv.), CH_3OH (0.35 mL), DMF (8 mL), room temperature, 1 h.

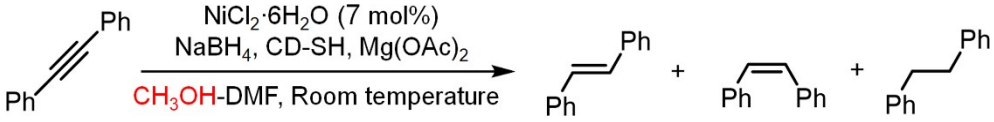
Table S4 Screening of the amount of $NiCl_2 \cdot 6H_2O$ for the semi-hydrogenation of DPA to *E*-stilbene



Entry	Amount of $NiCl_2 \cdot 6H_2O$ (mol%)	Conv. (%)	*E*/*Z*/alkane (%)
1	0	0	0/0/0
2	5	>99	69/16/15
3	6	>99	73/14/13
4	7	>99	82/7/11
5	8	>99	75/9/16

Reaction conditions: DPA (1 mmol), $NiCl_2 \cdot 6H_2O$, $NaBH_4$ (4 equiv.), CD-SH (3 mol%), $Mg(OAc)_2$ (4 equiv.), CH_3OH (0.35 mL), DMF (8 mL), room temperature, 1 h.

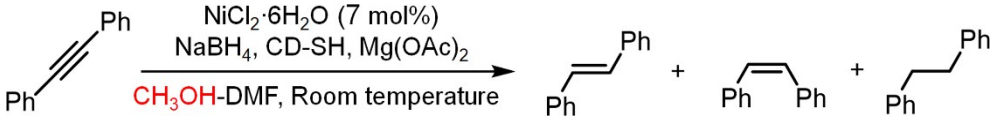
Table S5 Screening of protic solvent for the semi-hydrogenation of DPA to *E*-stilbene



Entry	Protic solvent	Conv. (%)	*E*/*Z*/alkane (%)
1	CH_3OH	>99	82/7/11
2	C_2H_5OH	>99	64/27/9
3	H_2O	>99	46/50/4

Reaction conditions: DPA (1 mmol), $NiCl_2·6H_2O$ (7 mol%), $NaBH_4$ (4 equiv.), CD-SH (3 mol%), $Mg(OAc)_2$ (4 equiv.), protic solvent (0.35 mL), DMF (8 mL), room temperature, 1 h.

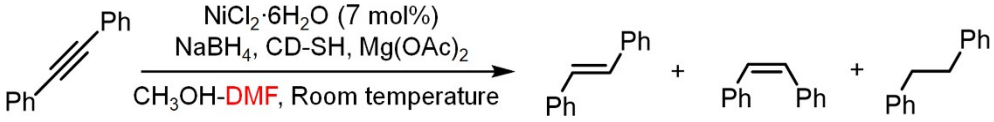
Table S6 Screening of the amount of methanol for the semi-hydrogenation of DPA to *E*-stilbene



Entry	CH_3OH volume (mL)	Conv. (%)	*E*/*Z*/alkane (%)
1	0	98	52/36/12
2	0.10	>99	63/29/8
3	0.20	>99	75/15/10
4	0.30	>99	79/8/13
5	0.35	>99	82/7/11
6	0.40	>99	81/5/14

Reaction conditions: DPA (1 mmol), $NiCl_2·6H_2O$ (7 mol%), $NaBH_4$ (4 equiv.), CD-SH (3 mol%), $Mg(OAc)_2$ (4 equiv.), CH_3OH, DMF (8 mL), room temperature, 1 h.

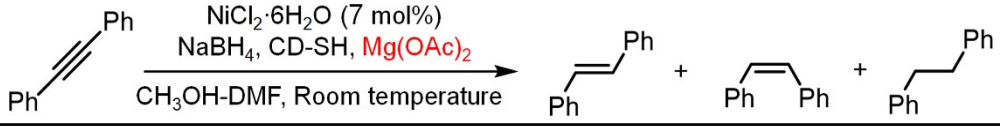
Table S7 Screening of solvent for the semi-hydrogenation of DPA to *E*-stilbene



Entry	Solvent	Conv. (%)	*E*/*Z*/alkane (%)
1	DMF	>99	82/7/11
2	*N,N*-dimethylacetamide (DMAc)	>99	73/7/20
3	tetrahydrofuran THF	84	48/50/2
4	CH_2Cl_2	22	72/21/7
5	1,4-dioxane	61	9/87/4
6	acetone	10	32/64/4
7	acetonitrile	>99	31/60/9

Reaction conditions: DPA (1 mmol), $NiCl_2·6H_2O$ (7 mol%), $NaBH_4$ (4 equiv.), CD-SH (3 mol%), $Mg(OAc)_2$ (4 equiv.), CH_3OH (0.35 mL), solvent (8 mL), room temperature, 1 h.

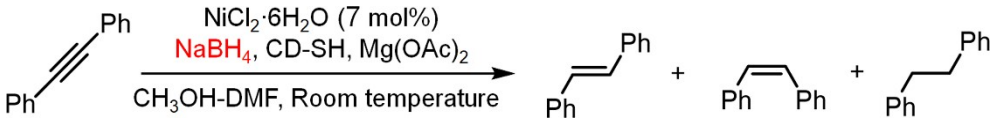
Table S8 Screening of the amount of $Mg(OAc)_2$ for the semi-hydrogenation of DPA to *E*-stilbene



Entry	$Mg(OAc)_2$ (equiv.)	Conv. (%)	*E*/*Z*/alkane (%)
1	0	>99	52/38/10
2	3	>99	74/16/10
3	4	>99	82/7/11
4	5	>99	72/15/13
5	6	>99	71/17/12

Reaction conditions: DPA (1 mmol), $NiCl_2·6H_2O$ (7 mol%), $NaBH_4$ (4 equiv.), CD-SH (3 mol%), $Mg(OAc)_2$, CH_3OH (0.35 mL), DMF (8 mL), room temperature, 1 h.

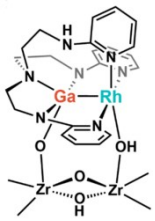
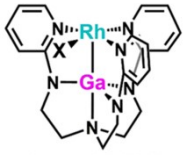
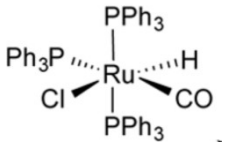
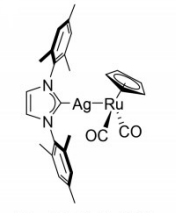
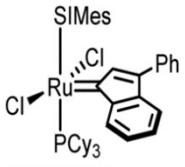
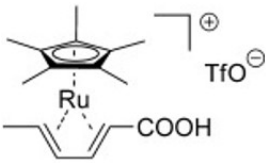
Table S9 Screening of the amount of $NaBH_4$ for the semi-hydrogenation of DPA to *E*-stilbene

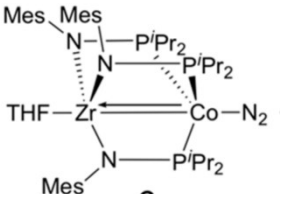
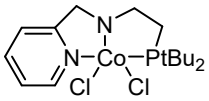
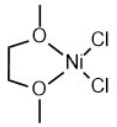
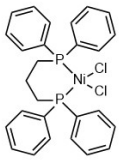
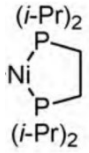
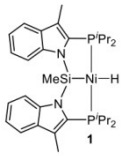
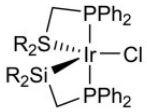


Entry	$NaBH_4$ (equiv.)	Conv. (%)	*E*/*Z*/alkane (%)
1	0	0	0/0/0
2	2	>99	44/49/7
3	3	>99	47/46/7
4	4	>99	82/7/11
5	5	>99	74/11/15
6	NH_3BH_3 (8 equiv.)	53	28/68/4

Reaction conditions: DPA (1 mmol), $NiCl_2·6H_2O$ (7 mol%), $NaBH_4$, CD-SH (3 mol%), $Mg(OAc)_2$ (4 equiv.), CH_3OH (0.35 mL), DMF (8 mL), room temperature, 1 h.

Table S10 Comparison of TOF for the semihydrogenation of DPA to *E*-stilbene with different reported catalysts

Catalyst	Hydrogen source	Temp. (°C)	TOF[a] (h^{-1})	Reference
	H_2 (4.84 bar)	100	6.2	S1
 (py$_3$tren)GaRhX *X = Me, OPh*	H_2 (5 bar)	100	6.1	S2
	H_2 (10 equiv.)	45	2.2	S3
	H_2 (1 atm)	150	0.19	S4
	NaH	80	2.02	S5
	H_2 (10 bar)	25	0.71	S6
$Cl_2Pd(PPh_3)_2$	H_2 (1 atm)	25	0.8	S7
	H_2 (4 atm)	30	4.64	S8

	H_2 (1 atm)	60	1.86	S9
	NH_3BH_3	50	2.28	S10
NiI_2	H_2 (15 bar)	100	0.97	S11
	HCOOH	120	0.59	S12
	H_3PO_2	80	8.1	S13
	$NaBH_4$	80	1.1	S14
	H_2 (1 atm)	25	24.0	S15
	H_2 (30 bar)	60	6.2	S16
	H_2 (1 atm)	25	9.9	S17
$NiCl_2 \cdot 6H_2O$ + CD-SH	**$NaBH_4$**	**Room temperture**	**11.8**	**This work**

[a]TOF = mol of yield *E*-stilbene/(mol of metal × time)

References:

[S1] S. P. Desai, J. Ye, T. Islamoglu, O. K. Farha and C. C. Lu, *Organometallics*, 2019, **38**, 3466-3473.

[S2] S. P. Desai, J. Ye, J. Zheng, M. S. Ferrandon, T. E. Webber, A. E. Platero-Prats, J. Duan, P. Garcia-Holley, D. M. Camaioni, K. W. Chapman, M. Delferro, O. K. Farha, J. L. Fulton, L. Gagliardi, J. A. Lercher, R. L. Penn, A. Stein and C. C. Lu, *J. Am. Chem. Soc*., 2018, **140**, 15309-15318.

[S3] K. T. Neumann, S. Klimczyk, M. N. Burhardt, B. Bang-Andersen, T. Skrydstrup and A. T. Lindhardt, *ACS Catal*., 2016, **6**, 4710-4714.

[S4] Y. Zhang, M. K. Karunananda, H. C. Yu, K. J. Clark, W. Williams, N. P. Mankad and D. H. Ess, *ACS Catal*., 2019, **9**, 2657-2663.

[S5] R. Kusy and K. Grela, *Org. Lett*., 2016, **18,** 6196-6199.

[S6] K. Radkowski, B. Sundararaju and A. Fürstner, *Angew. Chem*., 2013, **125**, 373-378.

[S7] R. Maazaoui, R. Abderrahim, F. Chemla, F. Ferreira, A. Perez-Luna and O. Jackowski, *Org. Lett*., 2018, **20**, 7544-7549.

[S8] K. Tokmic and A. R. Fout, *J. Am. Chem. Soc*., 2016, **138**, 13700 -13705.

[S9] K. M. Gramigna, D. A. Dickie, B. M. Foxman and C. M. Thomas, *ACS Catal*., 2019, **9**, 3153-3164.

[S10] S. Fu, N.Y. Chen, X. Liu, Z. Shao, S. P. Luo and Q. Liu, *J. Am. Chem. Soc*., 2016, **138**, 8588 -8594.

[S11] N. O. Thiel, B. Kaewmee, T. T. Ngoc and J. F. eichert, *Chem.-Eur. J*., 2020, **26**, 1597-1603.

[S12] E. Richmond and J. Moran, *J. Org. Chem*., 2015, **80**, 6922 -6929.

[S13] T. Chen, J. Xiao, Y. Zhou, S. Yin and L.-B. Han, *J. Organomet. Chem*., 2014, **794**, 51-54.

[S14] R. Barrios-Francisco and J. J. García, *Appl. Catal. A: Gen*., 2010, **385**, 108-113.

[S15] D. J. Hale, M. J. Ferguson and L. Turculet, *ACS Catal*., 2022, **12**, 146−155.

[S16] R. A. Farrar-Tobar, S. Weber, Z. Csendes, A. Ammaturo, S. Fleissner, H. Hoffmann, L. F. Veiros and K. Kirchner, *ACS Catal*., 2022, **12**, 2253−2260.

[S17] J. Shen, R. Usui and Y. Sunada, *Eur. J. Org. Chem.*, 2022, **2022**, e202101563.

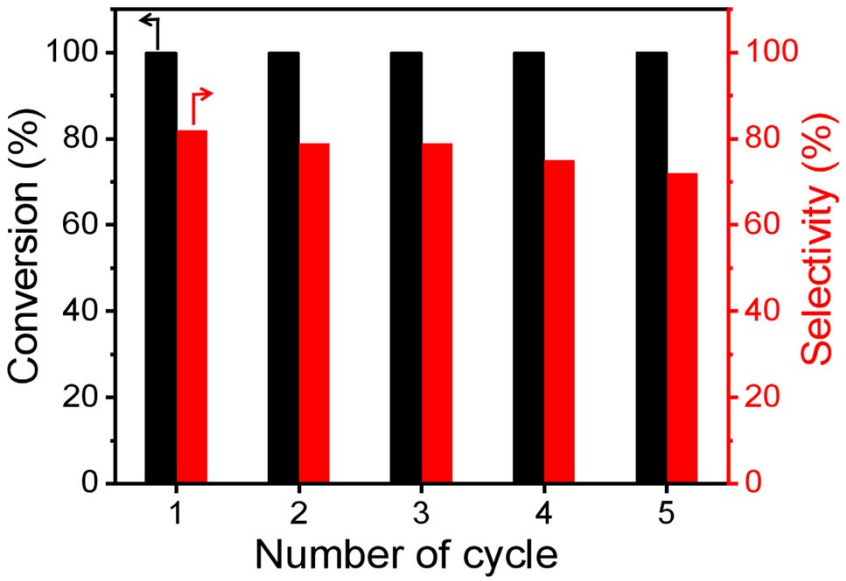
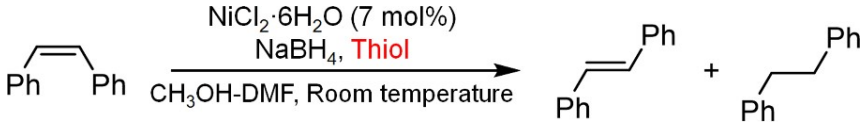
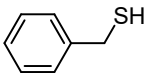
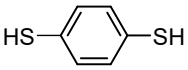
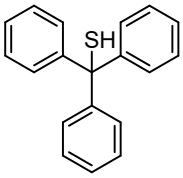
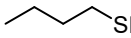
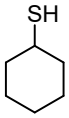


Fig. S2 Reusability of CD-SH modified nickel nanocatalyst in the semi-hydrogenation of DPA to *E*-stilbene with sodium borohydride.

Table S11 Effect of thiols on the *Z*-to-*E* isomerization of stilbene.

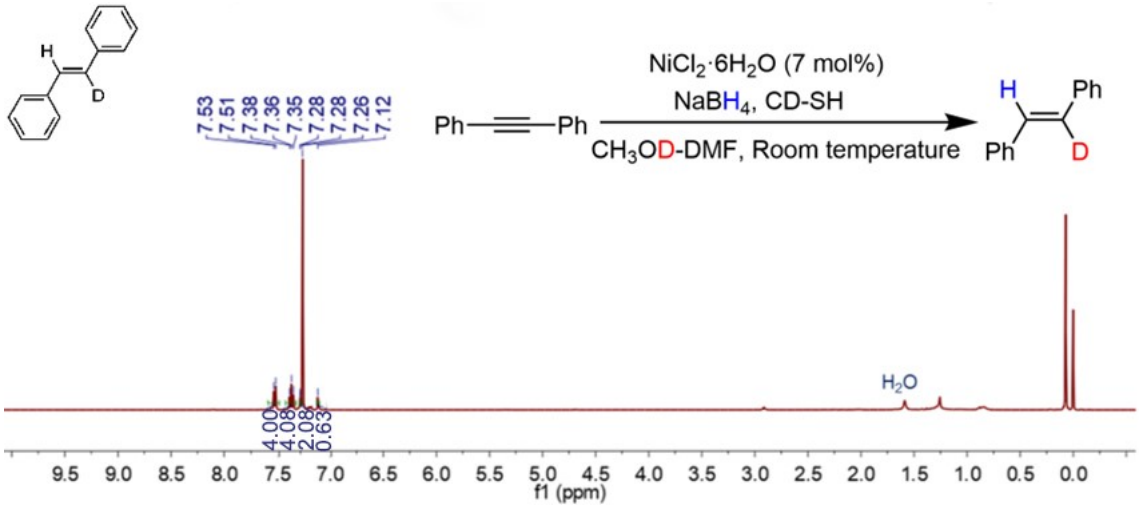


Entry	Catalyst precursor	Solvent	Additives	Conv. (%)	*E*/alkane (%)
1	$NiCl_2·6H_2O$	CH_3OH/DMF	-	8	63/35
2	$NiCl_2·6H_2O$	CH_3OH/DMF		8	80/20
3	$NiCl_2·6H_2O$	CH_3OH/DMF		31	24/76
4	$NiCl_2·6H_2O$	CH_3OH/DMF		0	0
5	$NiCl_2·6H_2O$	CH_3OH/DMF		10	23/77
6	$NiCl_2·6H_2O$	CH_3OH/DMF	$CH_3(CH_2)_{17}SH$	43	100/0
7	$NiCl_2·6H_2O$	CH_3OH/DMF		45	90/10
8	$NiCl_2·6H_2O$	CH_3OH/DMF	CD-SH	93	94/6

Reaction conditions: *Z*-stilbene (1 mmol), $NiCl_2·6H_2O$ (7 mol%), thiol (3 mol%), CH_3OH (0.35 mL), DMF (8 mL), $NaBH_4$ (4 equiv.), room temperature, 1 h.

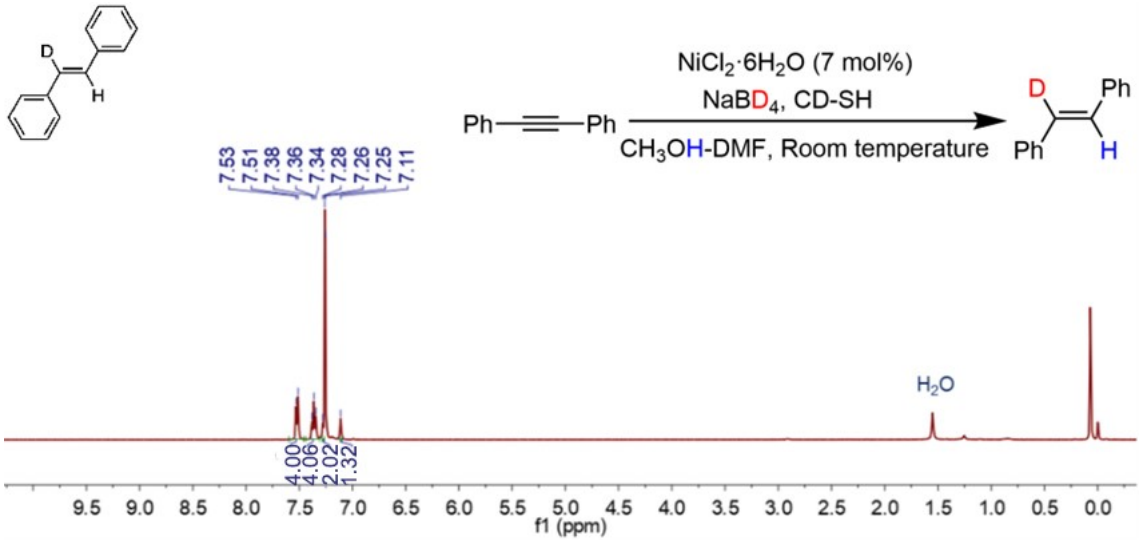
NMR spectra data of products

^{1}H NMR of monodeuterated *trans*-stilbene using $NaBH_4$ and CH_3OD in $CDCl_3$



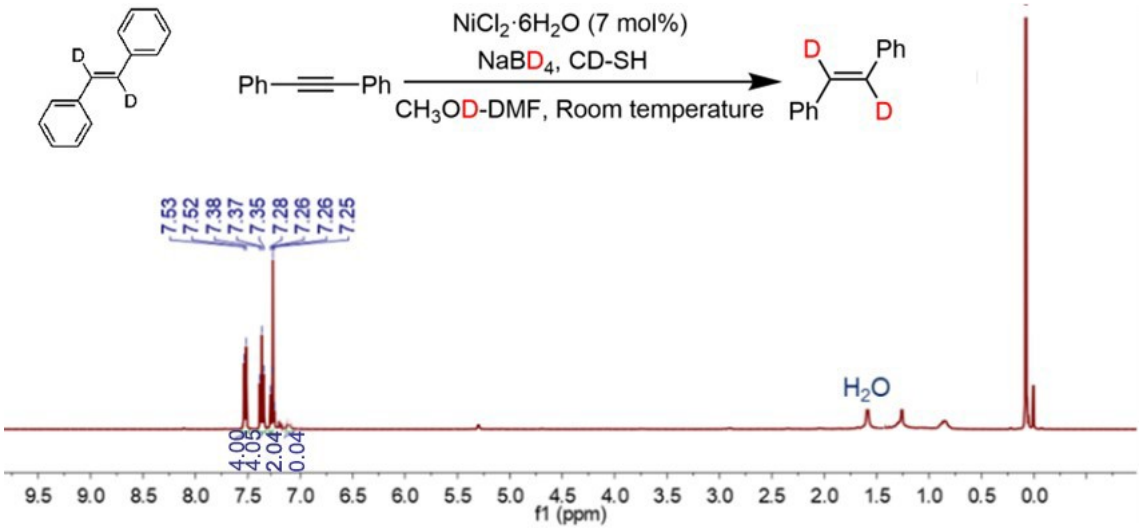
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.6 Hz, 4H), 7.37 (t, J = 7.5 Hz, 4H), 7.28 (s, 2H), 7.12 (s, 1H).

^{1}H NMR of monodeuterated *trans*-stilbene using $NaBD_4$ and CH_3OH in $CDCl_3$



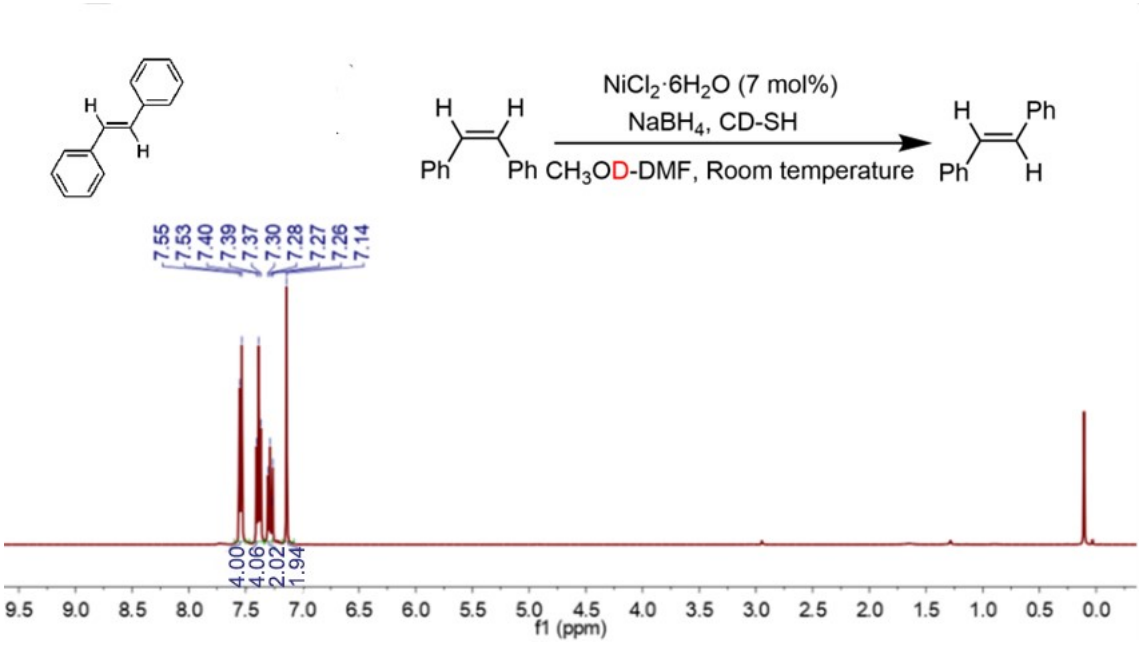
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.4 Hz, 4H), 7.37 (t, J = 6.9 Hz, 4H), 7.28 (s, 2H), 7.12 (s, 1H).

^{1}H NMR of dideuterated *trans*-stilbene using $NaBD_4$ and CH_3OD in $CDCl_3$



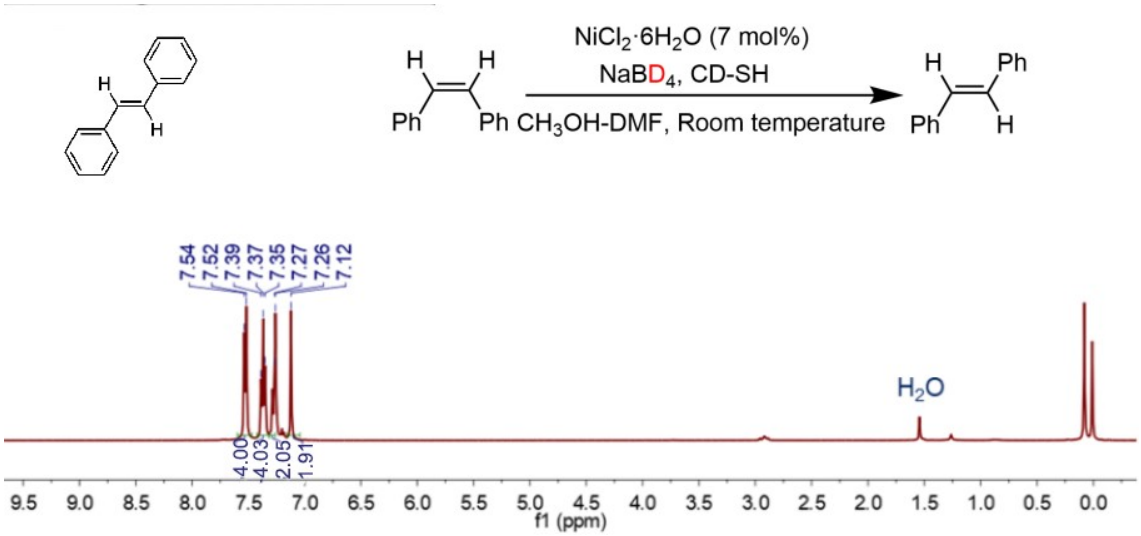
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.7 Hz, 4H), 7.36 (s, 4H), 7.29 (s, 2H).

^{1}H NMR of *trans*-stilbene using $NaBH_4$ and CH_3OD in $CDCl_3$



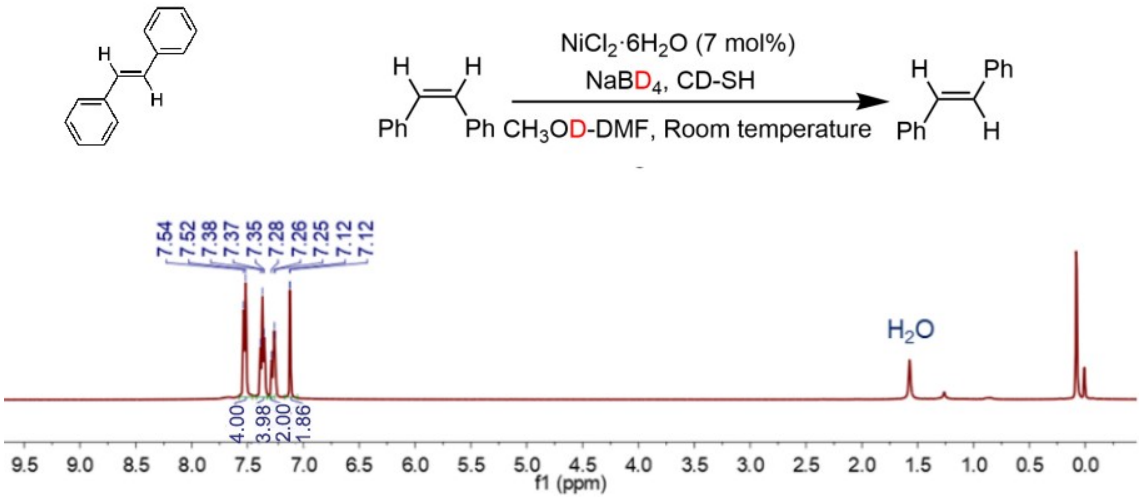
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.5 Hz, 4H), 7.39 (t, J = 7.6 Hz, 4H), 7.28 (t, J = 7.4 Hz, 2H), 7.14 (s, 2H).

^{1}H NMR of *trans*-stilbene using $NaBD_4$ and CH_3OH in $CDCl_3$



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.7 Hz, 4H), 7.37 (t, *J* = 7.5 Hz, 4H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.12 (s, 2H).

^{1}H NMR of *trans*-stilbene using $NaBD_4$ and CH_3OD in $CDCl_3$



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.4 Hz, 4H), 7.38 (t, *J* = 7.0 Hz, 4H), 7.28 (dd, *J* = 6.3, 4.8 Hz, 2H), 7.13 (d, *J* = 1.4 Hz, 2H).