**Electronic supplementary materials** *Mendeleev Commun.*, 2016, **26**, 500–501

# HUSY zeolite promoted hydrophenylation of alkynes conjugated with electron-withdrawing substituents

**Dmitry S. Ryabukhin and Aleksander V. Vasilyev**

List of contents

I. Characteristics of zeolite CBV-720……S2
II. Experimental section……S3
III. Copies of $^{1}H$ and $^{13}C$ NMR spectra of new compounds……..S5
IV. References.....S7

## I. Characteristics of zeolite HUSY (CBV-720)

**Table S1** Characteristics of zeolite HUSY [CBV-720 from manufacturer Zeolyst Int. (http://www.zeolyst.com)].

| Zeolyst Products | $SiO_2/Al_2O_3$ Mole Ratio | Nominal Cation Form | $Na_2O$ Weight % | Unit Cell Size, Å | Surface Area, $m^2/g$ |
|---|---|---|---|---|---|
| CBV 720 | 30 | Hydrogen | 0.03 | 24.28 | 780 |

**Table S2** Physicochemical properties of zeolite CBV-720 (lit.[S1]).

| Catalyst | Unit cell formula | Bulk Si/Al ratio | Crystals size (μm) | Porosity ($cm^3g^{-1}$) | |
|---|---|---|---|---|---|
| | | | | $v_{micro}$ | $v_{meso}$ |
| CBV-720 | $Na_{0.3}H_{11.0}Al_{11.3}Si_{181}O_{384}$, 7.3 EFAL | 13 | 0.5 | 0.317 | 0.190 |

**Table S3** Zeolite sample acidities measured by pyridine desorption between 150 and 450°C (lit.[S1]).

| Acidity (μmol $g^{-1}$): T (°C) | CBV-720 | |
|---|---|---|
| | Brønsted acid sites | Lewis acid sites |
| 150 | 271 | 101 |
| 250 | 220 | 69 |
| 350 | 75 | 46 |
| 450 | 13 | 26 |

## II. Experimental section

### II.1. General

The NMR spectra of compounds solutions in $CDCl_3$ were recorded on a Bruker AM-500 spectrometer at 25°C (at 500, and 125 MHz for $^1H$, and $^{13}C$ NMR spectra, respectively). The residual proton-solvent peak $CDCl_3$ (δ 7.26 ppm) for $^1H$ NMR spectra, and the carbon signal of $CDCl_3$ (δ 77.0 ppm) for $^{13}C$ NMR spectra were used as references. HRMS was carried out at an instrument Bruker MicroTOF (ESI). The preparative reactions were monitored by thin-layer chromatography carried out on silica gel plates (Silufol UV-254) using UV light for detection. Column chromatography was performed on silica gel Chemapol 40/100 (0.04e0.10 mm) with hexanes/ethyl acetate mixture elution.

### II.2. Transformation of acetylenes 1a-g with zeolites into 2a-g.

Phenyl 2,2-diphenylethenyl sulfone (**2a**). Oily compound (lit.[S2] mp 101.5-103.0 °C). $^1H$ HMR (500 MHz, $CDCl_3$): 7.02 s (1H, =CH), 7.07 d ($2H_{arom.}$, *J* 7.4 Hz), 7.20 d ($2H_{arom.}$, *J* 8.0 Hz), 7.27-7.35 m ($8H_{arom.}$), 7.48 t ($1H_{arom.}$, *J* 7.4 Hz), 7.57 d ($2H_{arom.}$, *J* 8.0 Hz). MS ($I_{rel.}$,%): 320 $M^+$ (35), 255 (5), 195 (8), 178 (100).

Diethyl (2,2-diphenylethenyl)phosphonate (**2b**). Oily compound (lit.[S2]). $^1H$ NMR (500 MHz, $CDCl_3$): 1.08-1.11 m (6H, 2Me), 3.78-3.80 m (4H, $2CH_2$), 6.18 s (1H), 6.96-7.45 m ($10H_{arom.}$). MS ($I_{rel.}$,%): 316 $M^+$ (21), 207 (45), 191 (8), 178 (100).

4,4-Diphenylbut-3-en-2-one (**2c**). Oily compound (lit.[S3]). $^1H$ NMR (500 MHz, $CDCl_3$): 1.86 (s, 3H, Me), 6.56 (s, 1H, =CH–), 7.18-7.43 (m, $10H_{arom.}$). MS ($I_{rel.}$,%): 222 $M^+$ (73), 221 (100), 207 (62), 178 (81).

*E/Z*-4-(2-Methylphenyl)-4-phenylbut-3-en-2-ones (**2d**) were obtained as oily mixture of isomers with ratio *E/Z* = 0.08/1.

For *Z*-isomer $^1H$ NMR (500 MHz, $CDCl_3$, from spectrum of mixture isomers): 1.75 s (3H, Me), 2.08 s (3H, Me), 6.73 s (1H, =CH-), 7.11-7.35 m ($10H_{arom.}$). $^{13}C$ NMR(125 MHz, $CDCl_3$): 19.6, 29.8, 125.9, 127.4, 127.8, 128.5, 128.6, 129.3, 129.5, 130.4, 135.7, 138.3, 139.4, 153.5, 199.5 MS ($I_{rel.}$,%): 236 $M^+$ (15), 221 (100), 203 (5), 192 (18), 178 (20).

For *E*-isomer $^1H$ NMR (500 MHz, $CDCl_3$, from spectrum of mixture isomers): 1.75 s (3H, Me), 2.02 s (3H, Me), 6.20 s (1H, =CH-), 7.11-7.35 m ($10H_{arom.}$). MS ($I_{rel.}$,%): 236 $M^+$ (8), 221 (100), 203 (3), 192 (12), 178 (18).

HRMS (for the mixture of *E*/Z-isomers): calcd. for $C_{17}H_{17}O$ [M+H] 237.1274; found 237.1283.

Methyl 3,3-diphenylpropenoate (**2e**). Oily compound (lit.[S4]). $^{1}$H NMR (500 MHz, $CDCl_3$): 3.61 s (3H, OMe), 6.38 s (1H, =CH-), 7.20–7.45 m ($10H_{arom.}$). MS ($I_{rel.}$,%): 238 $M^+$ (88), 207 (92), 178 (100), 165 (8), 152 (15).

Methyl *E/Z*-3-(4-chlorophenyl)-3-phenylpropenoates (**2f**) (lit.[S5]) were obtained as oily mixture of isomers with ratio *E/Z* = 0.8/1.

For *Z*-isomer $^{1}$H NMR (500 MHz, $CDCl_3$, from spectrum of mixture isomers): 3.64 s (3H, MeO), 6.38 s (1H, =CH-), 7.16-7.41 m ($9H_{arom.}$). MS ($I_{rel.}$,%): 272 $M^+$ (78), 241 (100), 213 (31), 178 (82), 165 (10).

For *E*-isomer $^{1}$H NMR (500 MHz, $CDCl_3$, from spectrum of mixture isomers): 3.62 s (3H, MeO), 6.35 s (1H, =CH-), 7.16-7.41 m ($9H_{arom.}$). MS ($I_{rel.}$,%): 272 $M^+$ (81), 241 (100), 213 (25), 178 (85), 165 (12).

Methyl *E/Z*-3-(2-fluorophenyl)-3-phenylpropenoates (**2g**) were obtained as oily mixture of isomers with ratio *E/Z* = 0.13/1.

For *Z*-isomer $^{1}$H NMR (500 MHz, $CDCl_3$): 3.64 s (3H, MeO), 6.52 s (1H, =CH-), 7.12-7.38 m ($9H_{arom.}$). $^{13}$C NMR (125 MHz, $CDCl_3$): 51.3, 115.5, 118.7, 123.7, 127.6, 128.5, 129.6, 129.9, 130.7, 139.5, 150.3, 158.5, 160.5, 165.8. MS ($I_{rel.}$,%): 256 $M^+$ (95), 237 (20), 225 (100), 196 (82), 176 (40).

For *E*-isomer $^{1}$H NMR (500 MHz, $CDCl_3$, from spectrum of mixture isomers): 3.63 s (3H, MeO), 6.34 s (1H, =CH-), 7.16-7.41 m ($9H_{arom.}$). MS ($I_{rel.}$,%): 256 $M^+$ (95), 237 (22), 225 (100), 196 (79), 176 (35). HRMS (for the mixture of E-/Z-isomers): calcd. for $C_{16}H_{14}FO_2$ [M+H] 257.0972; found 257.0970.

## III. Copies of $^{1}H$ and $^{13}C$ NMR spectra of new compounds

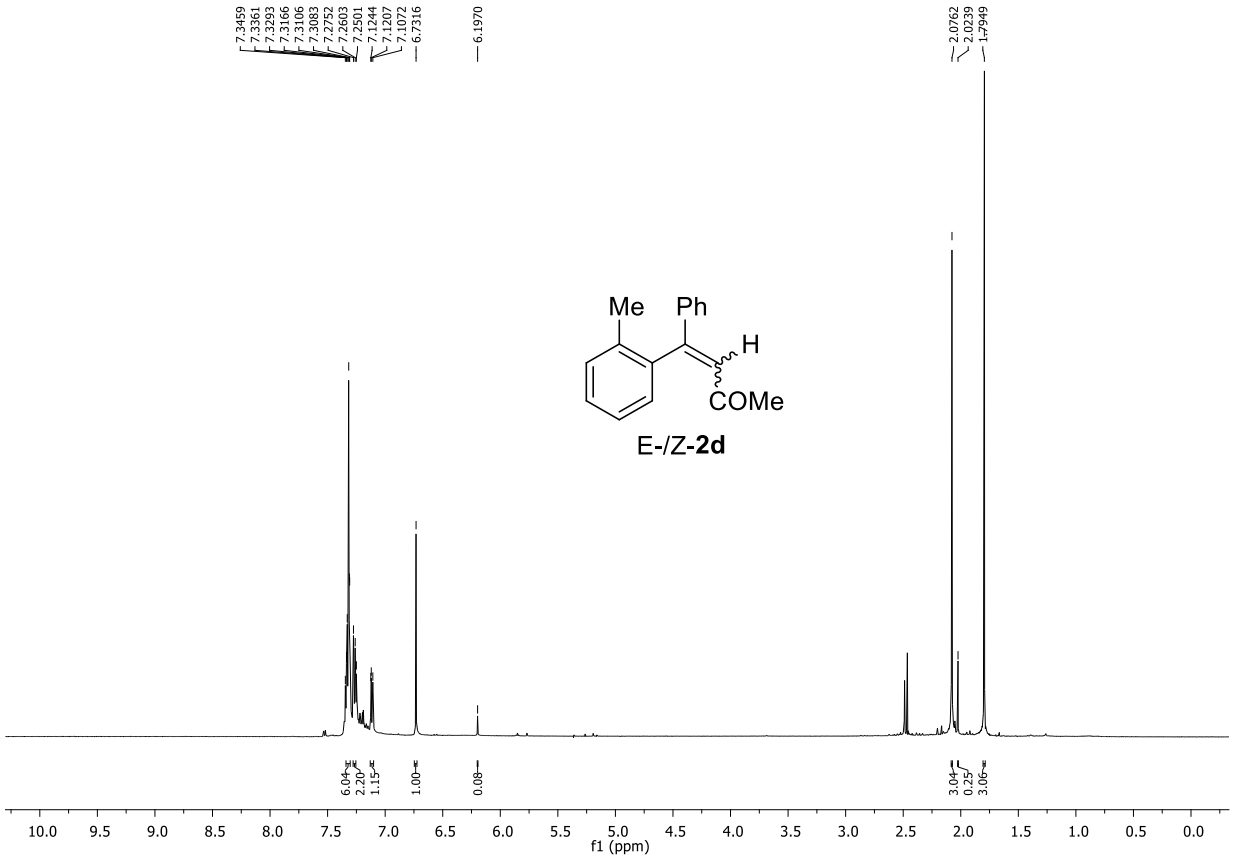


**Figure S1** $^{1}H$ NMR spectrum of mixture of compounds *E/Z*-**2d** (500 MHz, $CDCl_3$).

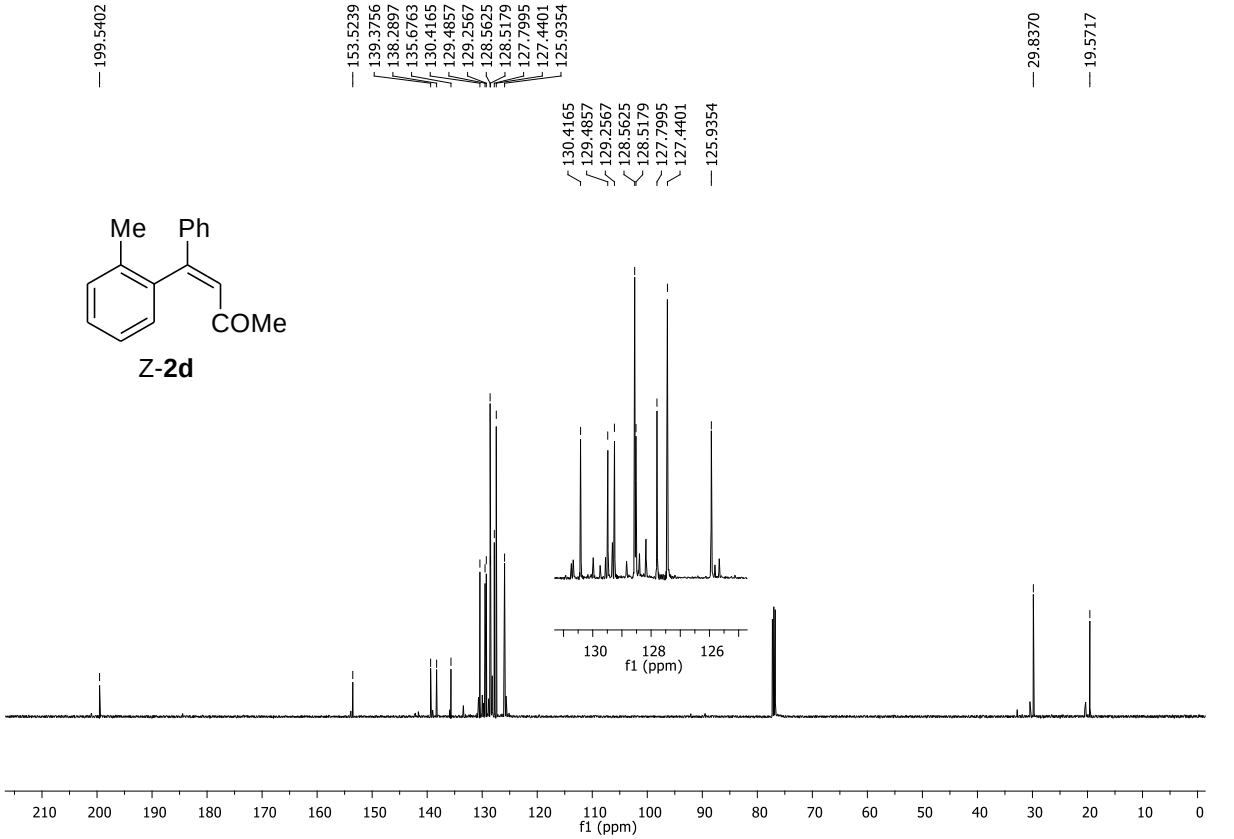


**Figure S2** $^{13}C$ NMR spectrum of compound *Z*-**2d** (125 MHz, $CDCl_3$).

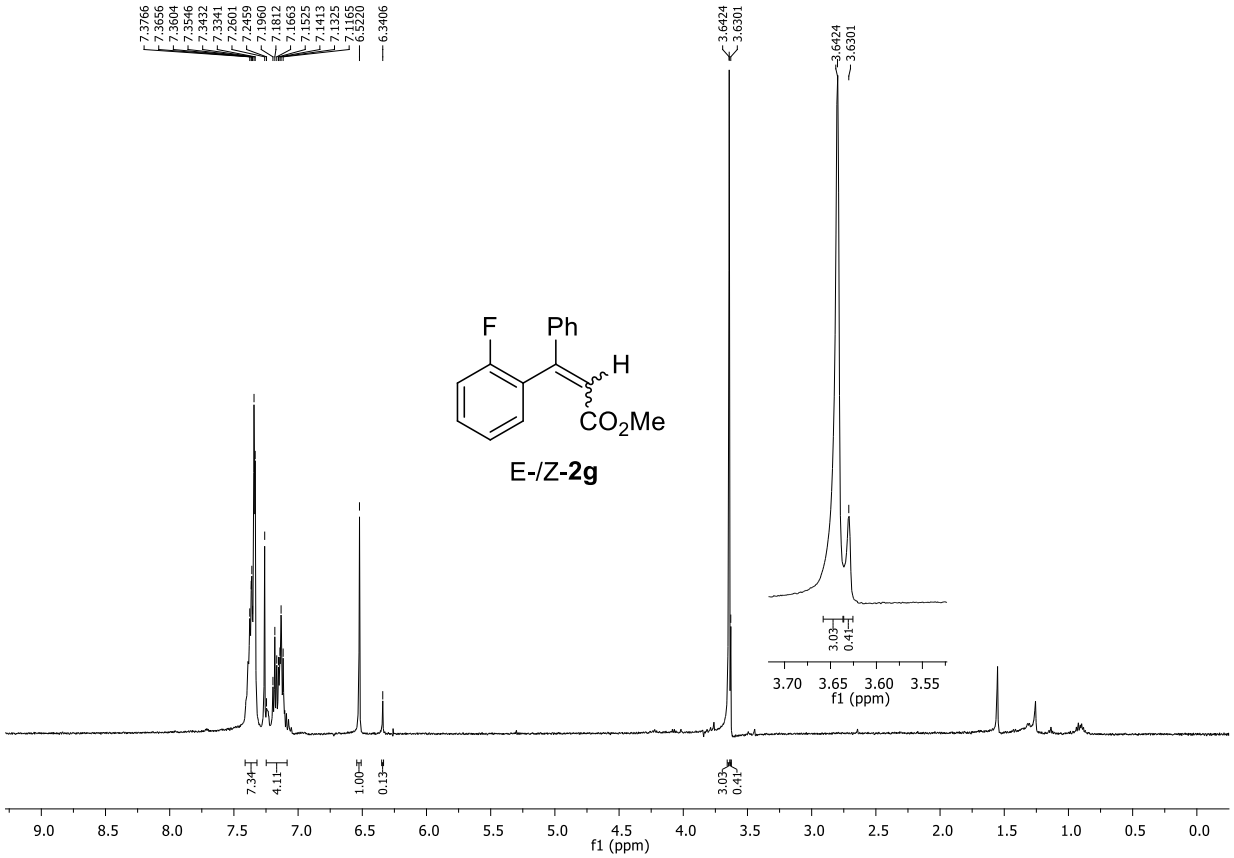


**Figure S3** $^{1}$H NMR spectrum of mixture of compounds *E/Z*-**2g** (500 MHz, $CDCl_3$).

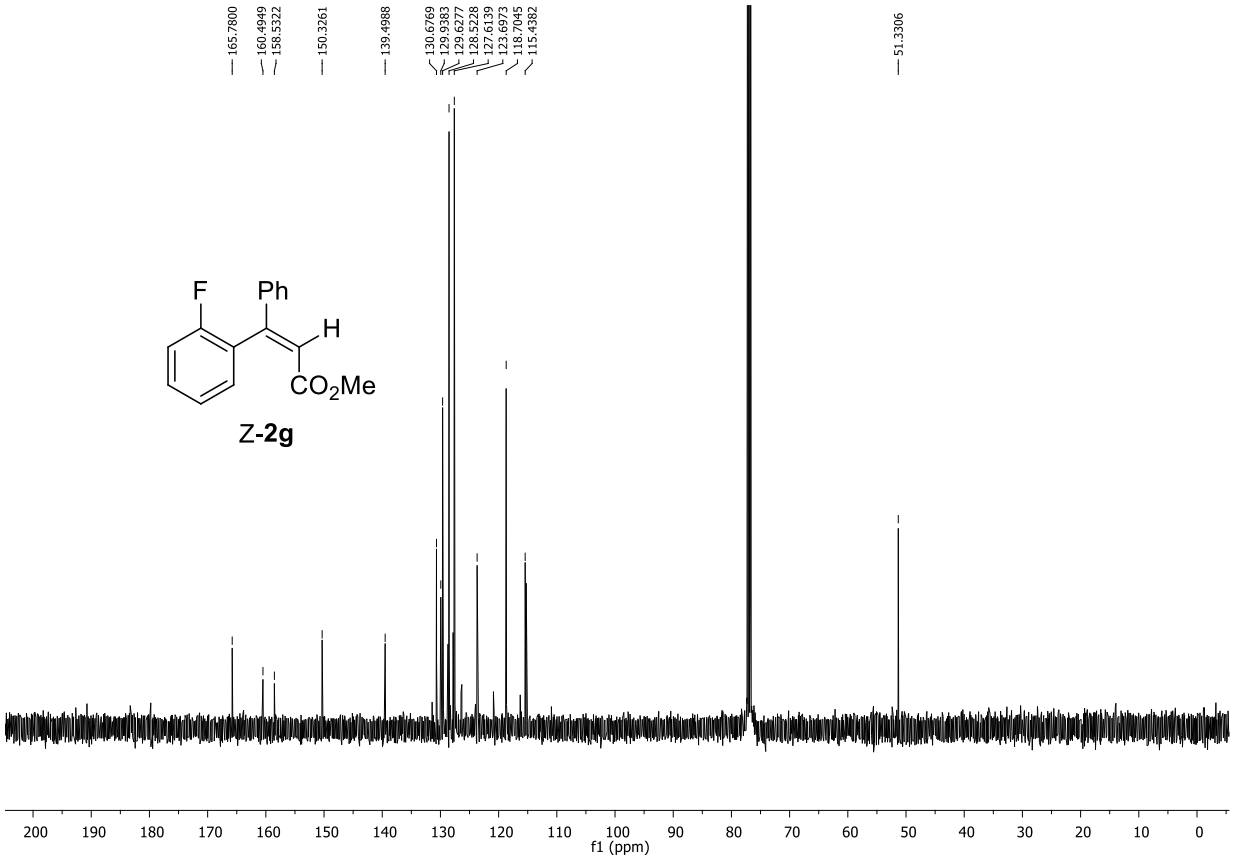


**Figure S4** $^{13}$C NMR spectrum of compound *Z*-**2g** (125 MHz, $CDCl_3$).

## IV. References

S1. N. Fonseca, F. Lemos, S. Laforge, P. Magnoux and F. Ramoa Ribeiro, *React. Kinet. Mech. Catal.*, 2010, **100**, 249.

S2. G. A. Russell, P. Ngoviwatchai, H. Tashtoush and J. Hershberger, *Organometallics*, 1987, **6**, 1414.

S3. A. O. Shchukin and A. V. Vasilyev, *Appl. Catal., A*, 2008, **336**, 140.

S4. P. Yu. Savechenkov, A. P. Rudenko, A. V. Vasil'ev and G. K. Fukin, *Russ. J. Org. Chem.*, 2005, **41**, 1316.

S5. J. C. Pastre and C. R. D. Correia, *Adv. Synth. Catal*., 2009, **351**, 1217.