

Supporting Information

Ethylaluminum as Ethylene Source for the Mizoroki-Heck-type Reaction. Rhodium-catalyzed Preparation of Stilbene Derivatives

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Experimental Section

General

All the reactions were carried out under nitrogen atmosphere. ^1H NMR (300 MHz) spectra were measured on Varian Gemini 300 as a CDCl_3 solution unless noted. The chemical shifts were expressed in ppm with CHCl_3 (7.26 ppm for ^1H) as internal standards. High resolution mass spectra (HRMS) were measured by JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F254) were used. Arylmagnesium bromide was prepared from the corresponding arylbromide and magnesium turning in THF. Rhodium catalyst, $[\text{RhCl}(\text{cod})]_2$ was prepared according to the literature procedures.¹ Arylmagnesium bromide was prepared from arylbromide with magnesium turning. Other chemicals were purchased and used without further purification. For the solvent of the rhodium-catalyzed reaction anhydrous THF purchased from Kanto Chemical Co. Ltd. was employed. Diisopropyl ketone was dried over molecular sieves (3Å) and stored overnight prior to use.

General procedure for the rhodium-catalyzed reaction of aryl(diethyl)aluminum: To a 20 mL of Schlenk tube equipped with a magnetic stirring bar was added 1.05 M diethylaluminum chloride as a hexane solution (0.5 mmol, 0.48 mL). To the solution was slowly added a THF solution of arylmagnesium bromide (1.0 M, 0.5 mmol, 0.5 mL) dropwise at 0 °C. The reaction was allowed to warm to room temperature and stirring was continued for 3 h. To the resulting white suspension were added diisopropylketone (2.5 mmol, 0.31 mL) and $[\text{RhCl}(\text{cod})]_2$ (0.0125 mmol, 6.1 mg) and the mixture was stirred at 60 °C for 24 h. After cooling to room temperature the reaction mixture was quenched with water (CAUTION: Gas evolution occurs.). To the solution was added 1.0 M hydrochloric acid (1.0 mL) and the solution was poured into the mixture of diethyl ether/water to result in separation into two phases. Aqueous was extracted with diethyl ether twice and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by column chromatography on silica gel.

(E)-Stilbene (2a)², ^1H NMR (300 MHz, CDCl_3) δ 7.12 (s, 2H), 7.23-7.30 (m, 2H), 7.32-7.43 (m, 4H), 7.49-7.56 (m, 4H); HRMS (DART-ESI+) Calcd for $\text{C}_{14}\text{H}_{13}$ $[\text{M}+\text{H}]^+$: 181.1017; found: m/z 181.1017.

(E)-1,2-Bis(4-methylphenyl)ethene (2b)², ^1H NMR (300 MHz, CDCl_3) δ 2.36 (s, 6H), 7.04 (s, 2H), 7.16 (d, $J = 8.0$ Hz, 4H), 7.40 (d, $J = 8.0$ Hz, 4H); HRMS (DART-ESI+)

Calcd for C₁₆H₁₇ [M+H]⁺: 209.1330; found: m/z 209.1327.

(E)-1,2-Bis(2-methylphenyl)ethene (2c)³, ¹H NMR (300 MHz, CDCl₃) δ 2.43 (s, 6H), 7.13-7.28 (m, 8H), 7.60 (d, *J* = 6.4 Hz, 2H).

(E)-1,2-Bis(3,5-dimethylphenyl)ethene (2d)⁴, ¹H NMR (300 MHz, CDCl₃) δ 2.34 (s, 12H), 6.91 (s, 2H), 7.03 (s, 2H), 7.14 (s, 4H).

(E)-1,2-Bis(2-phenylphenyl)ethene (2e)⁴, ¹H NMR (300 MHz, CDCl₃) δ 7.05 (s, 2H), 7.23-7.32 (m, 6H), 7.39-7.51 (m, 12H).

(E)-1,2-Bis(4-methoxyphenyl)ethene (2f)², ¹H NMR (300 MHz, CDCl₃) δ 3.83 (s, 6H), 6.89 (d, *J* = 8.7 Hz, 4H), 6.93 (s, 2H), 7.43 (d, *J* = 8.7 Hz, 4H); HRMS (DART-ESI+) Calcd for C₁₆H₁₇O₂ [M+H]⁺: 241.1229; found: m/z 241.1226.

(E)-1,2-Bis(4-fluorophenyl)ethene (2g)⁵, ¹H NMR (300 MHz, CDCl₃) δ 6.98 (s, 2H), 7.05 (t, *J* = 8.7 Hz, 4H), 7.41-7.51 (m, 4H).

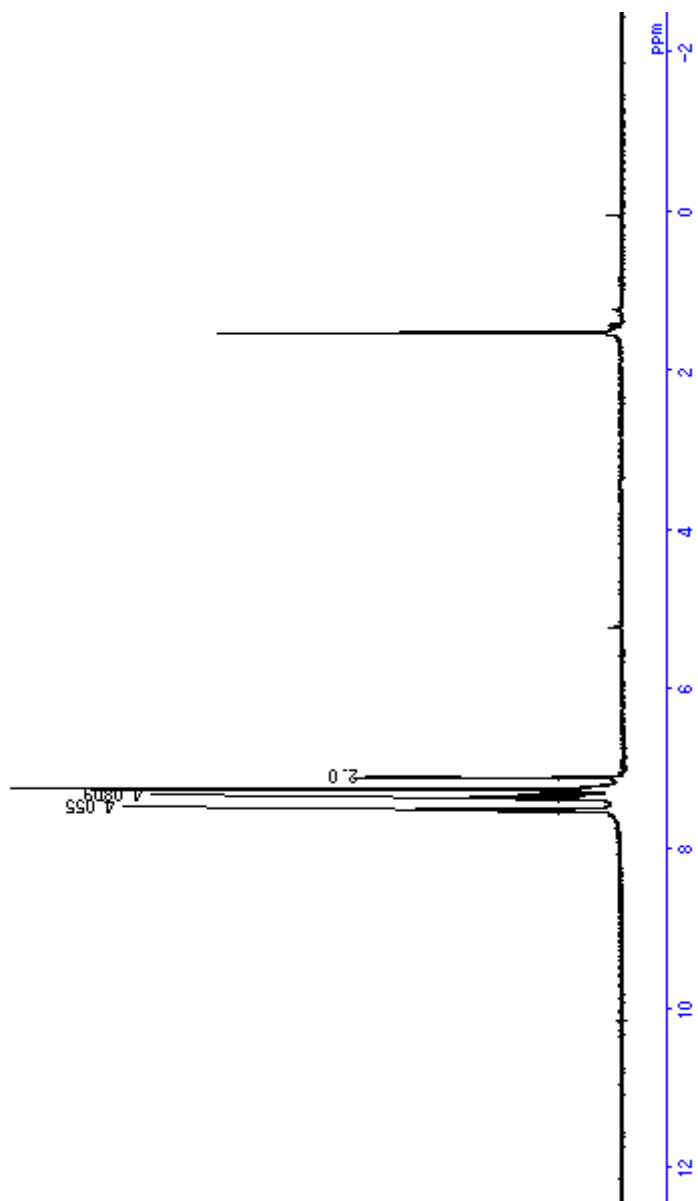
(E)-1,2-Bis(1-naphthyl)ethene (2h)⁶, ¹H NMR (300 MHz, CDCl₃) δ 7.52-7.57 (m, 6H), 7.84-7.93 (m, 6H), 7.92 (s, 2H), 8.27 (m, 2H).

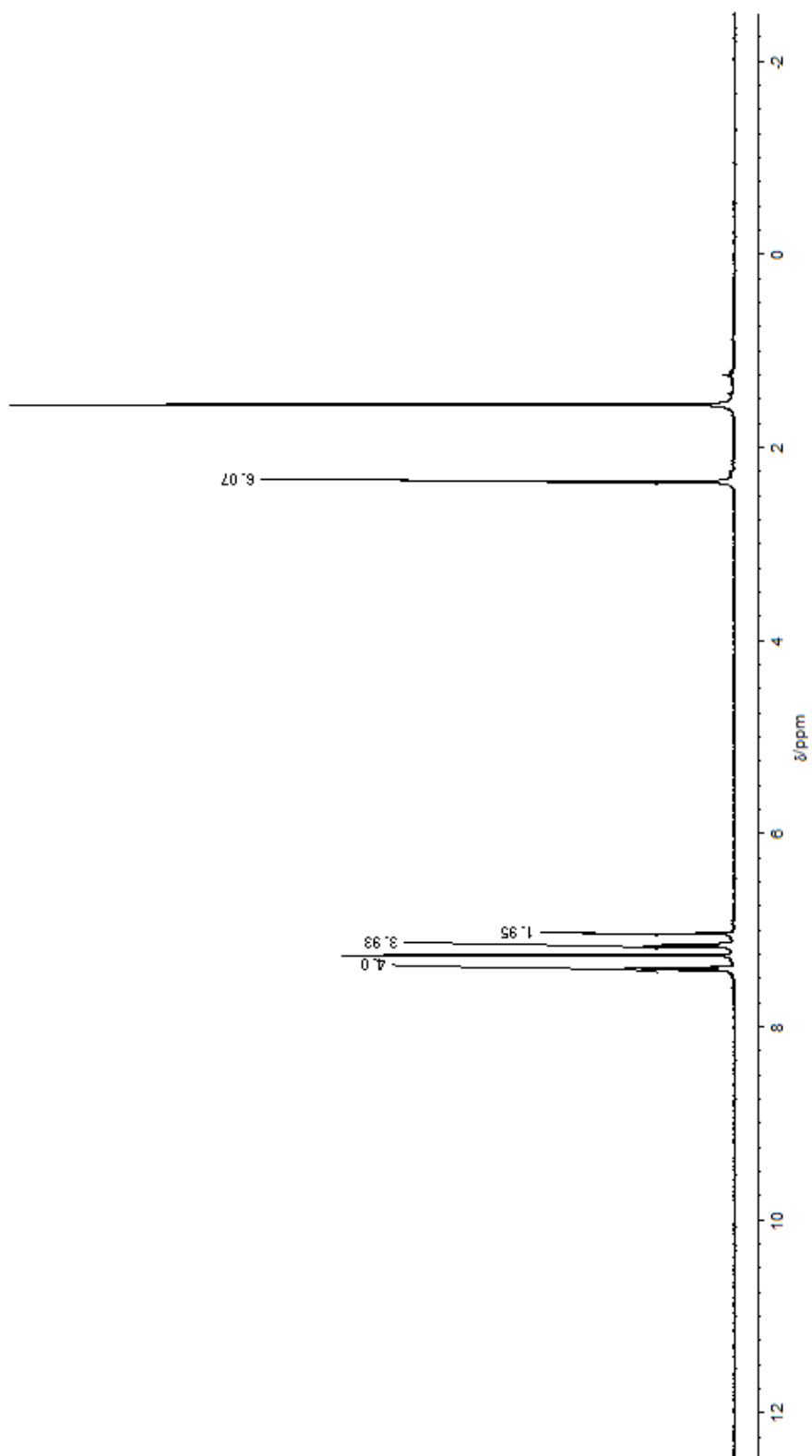
(E)-1-(4-Methylphenyl)-2-phenylethene (2i)², ¹H NMR (300 MHz, CDCl₃) δ 2.36 (s, 3H), 7.08 (br, 1H x 2), 7.17 (d, *J* = 8.0 Hz, 2H), 7.21-7.29 (m, 1H), 7.35 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.51 (m, 2H)

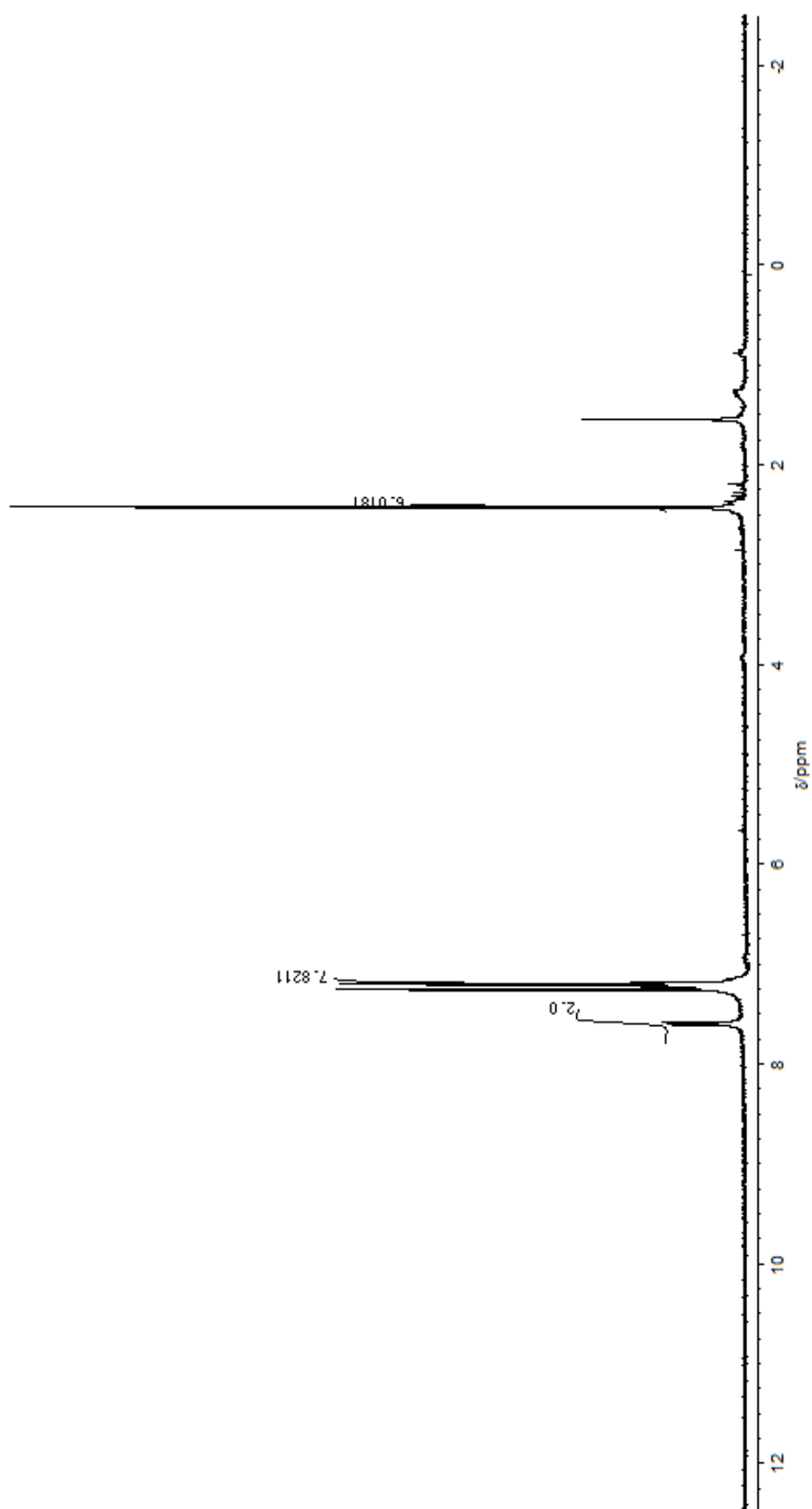
General procedure for the rhodium-catalyzed reaction of ethyl Grignard reagent and aryl Grignard reagent in the presence of aluminum chloride: To a 20 mL of Schlenk tube equipped with a magnetic stirring bar were added aluminum chloride (0.5 mmol, 66.7 mg), ethyl magnesium bromide (0.97 M, 1.0 mmol, 1.03 mL) and arylmagnesium bromide (1.0 M, 0.5 mmol, 0.5 mL) successively at 0 °C. To the solution were added diisopropylketone (2.5 mmol, 0.31 mL) and [RhCl(cod)]₂ (0.0125 mmol, 6.1 mg) and stirred at 60 °C for 24 h. After cooling to room temperature the reaction mixture was quenched with water (CAUTION: Gas evolution occurs.). To the solution was added 1.0 M hydrochloric acid (1.0 mL) and the solution was poured into the mixture of diethyl ether/water to result in separation into two phases. Aqueous was extracted with diethyl ether twice and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by column chromatography on silica gel.

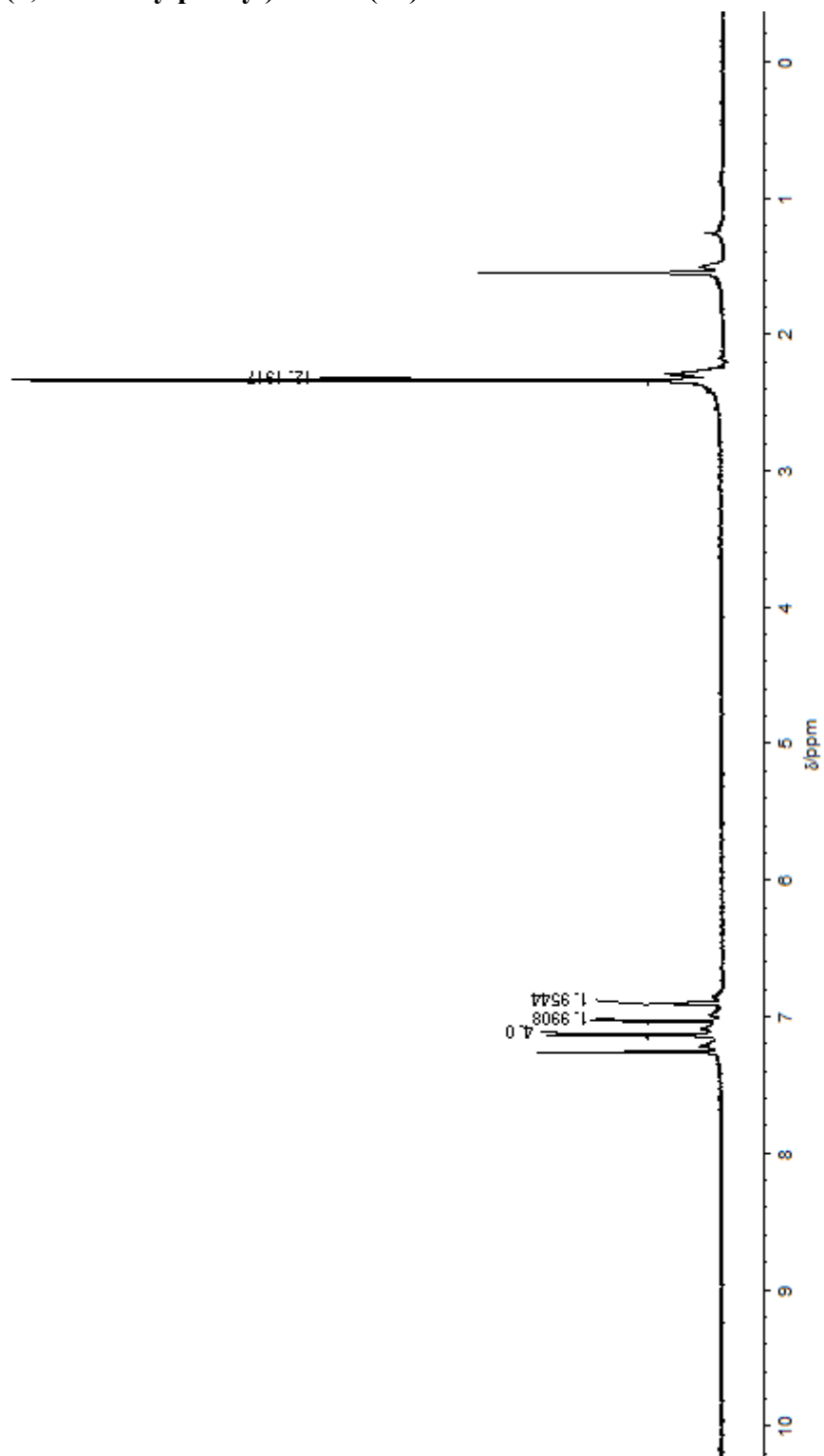
References

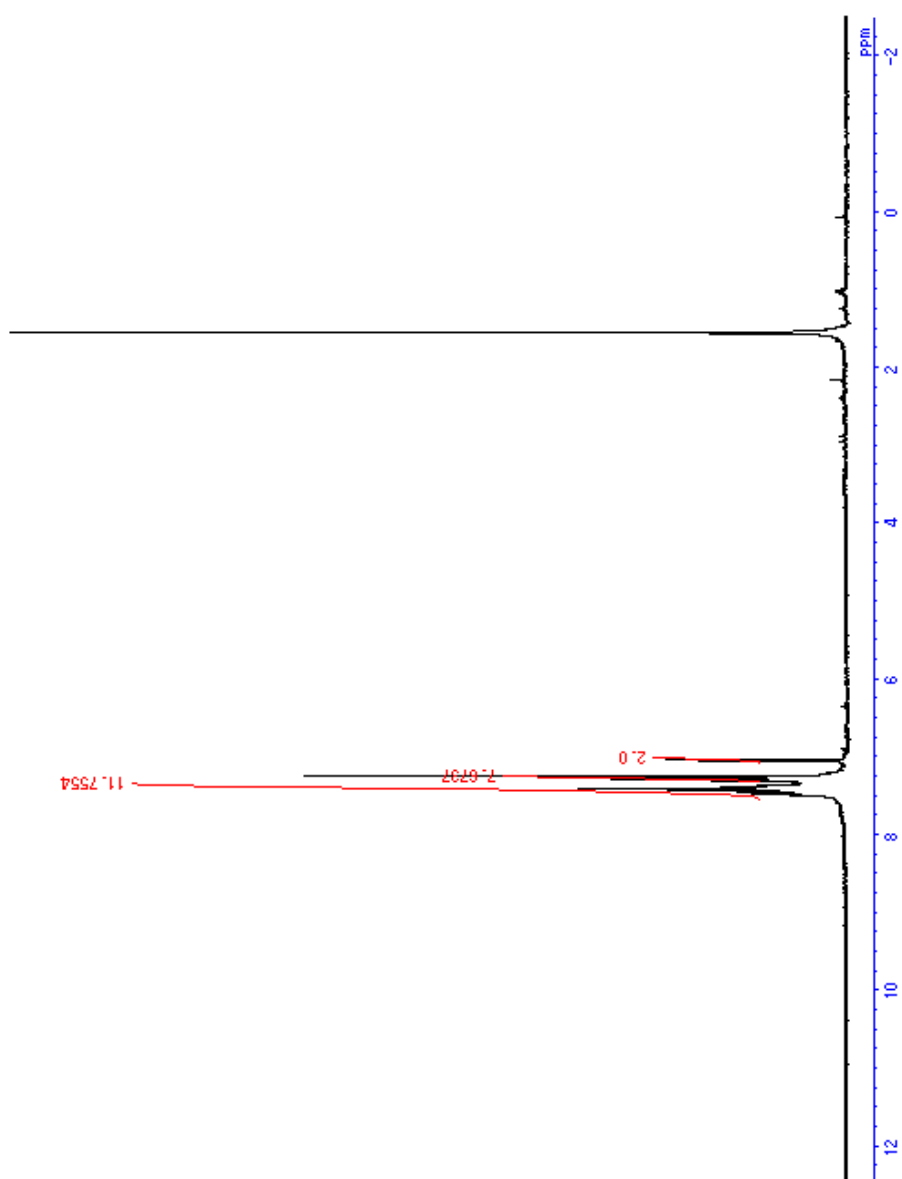
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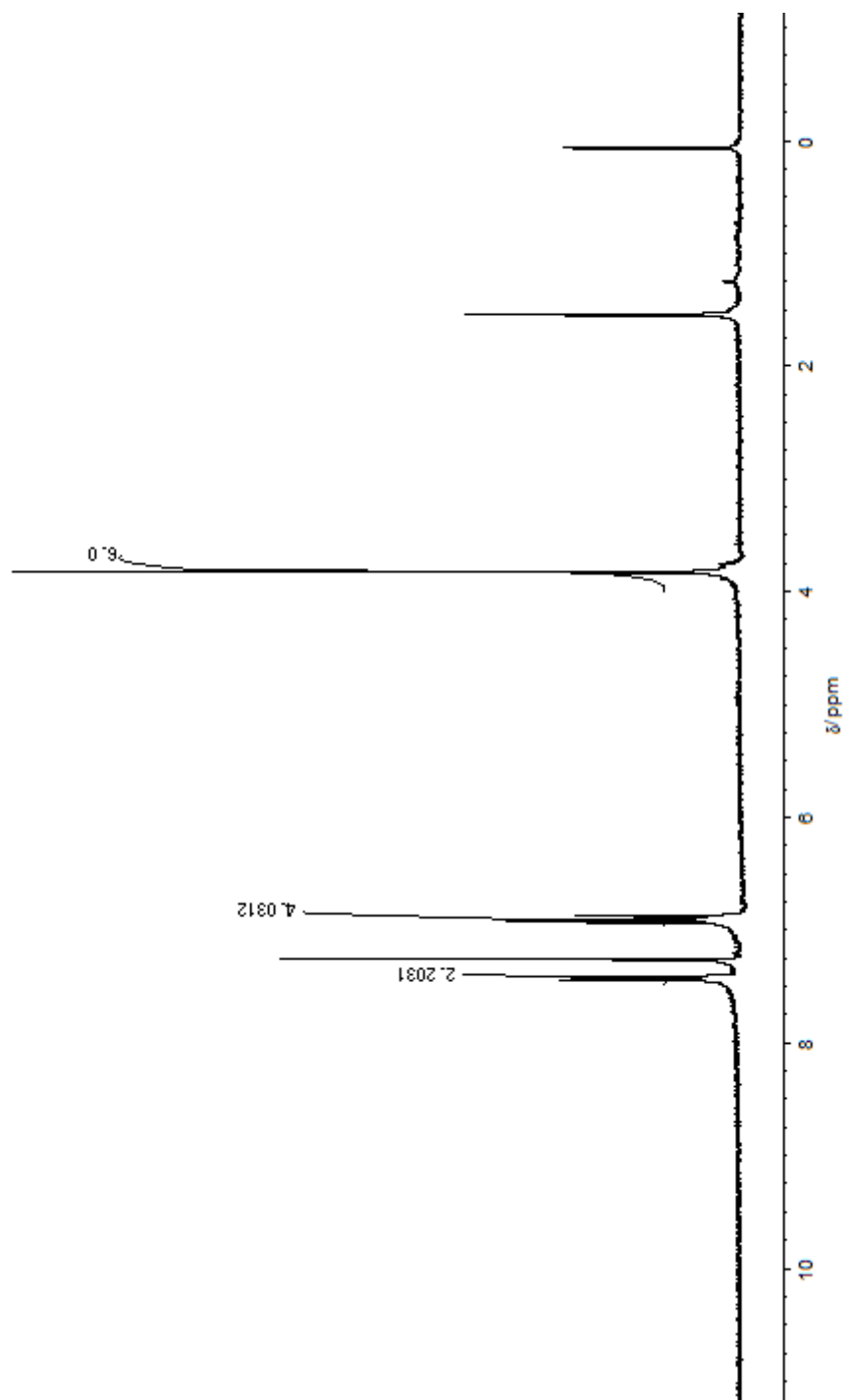
(E)-Stilbene (2a)²

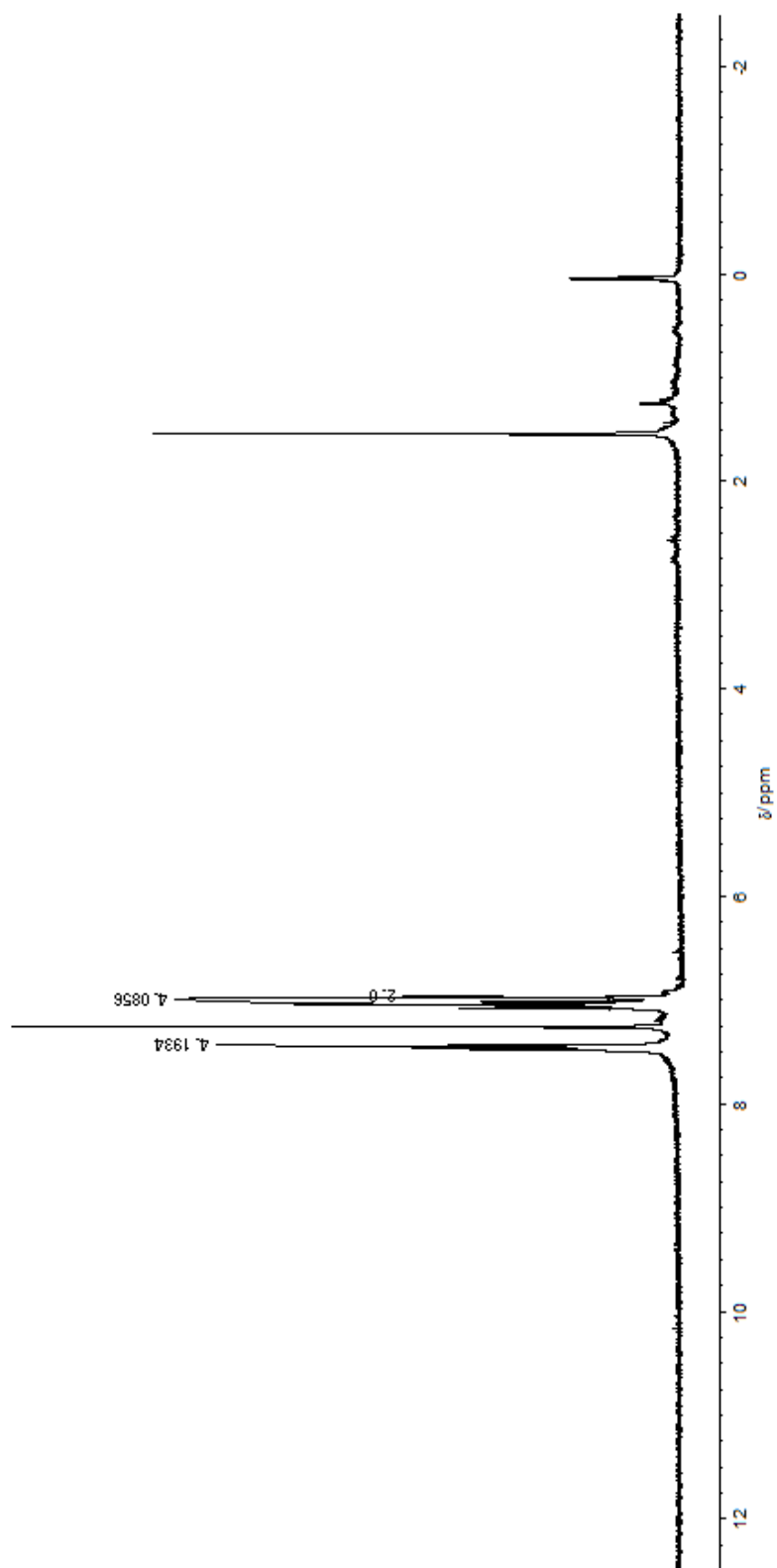
(E)-1,2-Bis(4-methylphenyl)ethene (2b)²

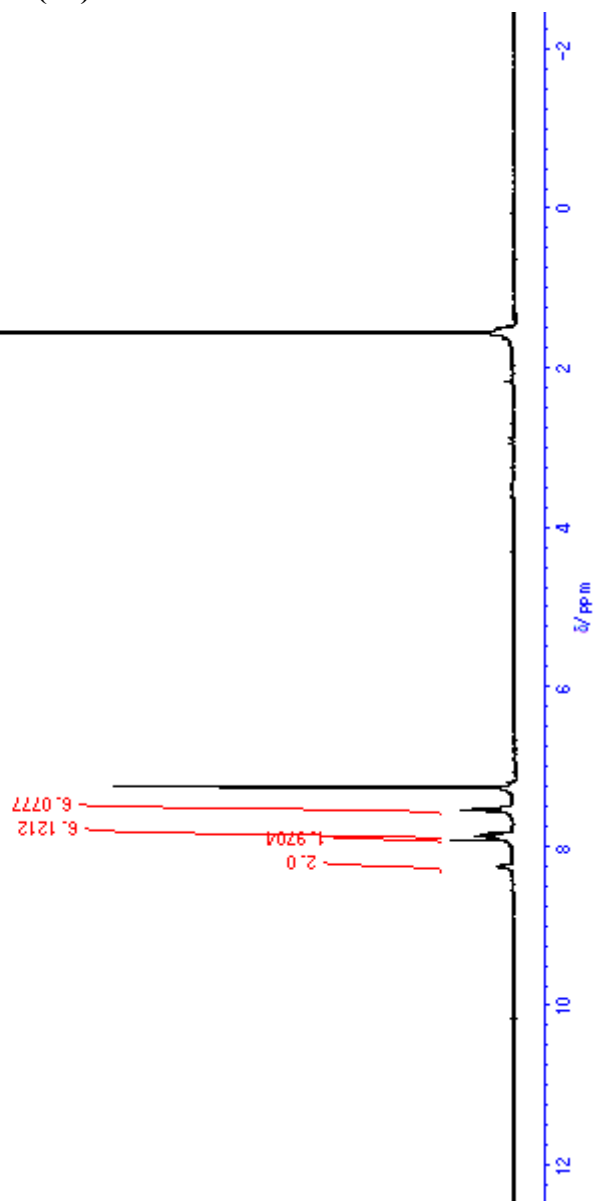
(E)-1,2-Bis(2-methylphenyl)ethene (2c)³

(E)-1,2-Bis(3,5-dimethylphenyl)ethene (2d)

(E)-1,2-Bis(2-phenylphenyl)ethene (2e)

(E)-1,2-Bis(4-methoxyphenyl)ethene (2f)

(E)-1,2-Bis(4-fluorophenyl)ethene (2g)

(E)-1,2-Bis(1-naphthyl)ethene (2h)

(E)-1-(4-Methylphenyl)-2-phenylethene (2i)⁷