Supplementary Material (ESI) for Chemical Communications

Aldehyde Allylation with Allylboronates Providing α-Addition Products

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Electronic Supplementary Information

Experimental

General

NMR spectra were recorded on a JEOL ECX-600 or ECX-500 spectrometer, operating at 600 MHz or 500 MHz for ^{1}H and 150 MHz or 125 MHz for ^{13}C NMR in $CDCl_3$ unless otherwise noted. Tetramethylsilane (TMS) served as the internal standard (δ = 0) for ^{1}H NMR and $CDCl_3$ was used as the internal standard (δ = 77.0) for ^{13}C NMR. IR spectra were measured using a JASCO FT/IR-610 spectrometer. High Resolution Mass Spectra (HRMS) were recorded using a JEOL JMS-T100TD (DART) spectrometer or Brucker Daltonics BioTOF II spectrometer (ESI). Preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F from Wako Pure Chemical Industries, Ltd. Deionized water from a MILLIPORE MilliQ machine (Gradient A 10) was used as solvent without further treatment. All organic solvents used were commercially available dry solvents, which were distilled appropriately under an argon atmosphere or were stored over molecular sieves prior to use. All aldehydes in this study were commercially available and were distilled prior to use. α-Substituted allylboronates **2a–d** were prepared by slightly modified procedures of reported methods.[1] Zinc hydroxide (99.9%, powder) was purchased from Soekawa Chemicals Co. Ltd.

Typical Experimental Procedure for Allylation Reaction in Aqueous Media (Table 2, entry 1):

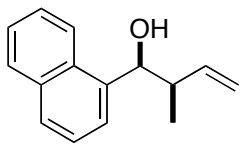
To a 30 mL-round-bottomed flask with magnetic stirring bar were added zinc hydroxide

(2.0 mg, 0.02 mmol) and 2,9-dimethyl-1,10-phenanthroline (**3c**, 5.0 mg, 0.024 mmol). After addition of water (3.2 mL) and acetonitrile (12.8 mL), the mixture was stirred for 30 min at room temperature. To the mixture were added successively benzaldehyde (**1a**; 41 μL, 0.4 mmol) and α-methyl-substituted allylboronate (**2a**; 97 μL, 0.48 mmol). The reaction mixture was further stirred at room temperature for 1 h, before adding an aqueous sat. $NaHCO_3$ solution. The aqueous phase was extracted with ethyl acetate (three times), washed with brine, and the combined organic layers were dried (Na_2SO_4). After filtration and concentration *in vacuo*, the regio- and diastereoselectivities were determined by ^{1}H NMR analysis of the crude sample, which was then purified by preparative thin-layer chromatography (*n*-hexane/ethyl acetate = 4:1) to afford the corresponding homoallylic alcohol **4a** (83% yield, α/γ = >98/<2, *syn*/*anti* = 94/6).

Analytical Data for Homoallylic Alcohols 4a–n

Homoallylic alcohols **4a**,[2] **4b**,[3] **4c**,[2] **4d**,[2] **4e**,[3] **4f**,[2] **4h**,[13] **4i**,[5] **4k**,[6] **4l**,[4] **4m**,[7] **4n**,[8] (1*S*,2*R*)-**4a**,[9] and **11**[10] are literature-known; obtained analytical data for these compounds were in full agreement with reported data. Products **4g** and **4j** are new compounds; analytical data are as follows.

4g:



IR (neat): 778, 1217, 1511, 1597, 1639, 3429 cm^{-1}.

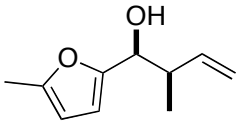
^{1}H NMR *syn*: 0.97 (d, 3H, *J* = 6.8 Hz), 2.12 (s, 1H), 2.77-2.81 (m, 1H), 5.08 (dd, 2H, *J*

= 10.3, 17.4 Hz), 5.42 (d, 1H, *J* = 4.5 Hz), 5.94 (ddd, 1H, *J* = 6.8, 10.3, 17.4 Hz), 7.41-7.49 (m, 3H), 7.61 (d, 1H, *J* = 6.8 Hz), 7.74 (d, 1H, *J* = 8.5 Hz), 7.84 (dd, 1H, *J* = 7.4, 8.2 Hz), 7.99 (d, 1H, *J* = 8.5 Hz).

^{13}C NMR *syn*: 12.8, 43.1, 73.3, 115.0, 123.0, 123.9, 125.2, 125.2, 125.3, 125.8, 127.7, 128.9, 133.6, 138.3, 141.2.

HRMS: $C_{15}H_{16}O$; calc: 195.11738 $(M–OH)^+$; found: 195.11757.

4j:



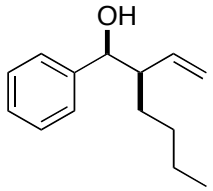
IR (neat): 786, 915, 1018, 1220, 1564, 1640, 3413 cm^{-1}.

^{1}H NMR *syn*: 1.08 (d, 3H, *J* = 6.8 Hz), 1.99 (d, 1H, *J* = 5.7 Hz), 2.27 (s, 3H), 2.65-2.73 (m, 1H), 4.48 (dd, 1H, *J* = 4.0, 7.9 Hz), 5.08 (ddd, 2H, *J* = 1.7, 10.2, 17.6 Hz), 5.77 (ddd, 1H, *J* = 7.4, 10.2, 17.6 Hz), 5.89-5.91 (m, 1H), 6.09 (d, 1H, *J* = 2.8 Hz). *anti*: 0.94 (d, 3H, *J* = 6.8 Hz), 2.09 (d, 1H, *J* = 4.0 Hz), 2.29 (s, 3H), 2.65-2.73 (m, 1H), 4.33 (dd, 1H, *J* = 5.9, 5.9 Hz), 5.21 (ddd, 2H, *J* = 1.7, 10.1, 17.9 Hz), 5.81 (ddd, 1H, *J* = 7.8, 10.1, 17.9 Hz), 5.89-5.91 (m, 1H), 6.13 (d, 1H, *J* = 3.4 Hz).

^{13}C NMR *syn*: 13.5, 15.1, 42.9, 71.4, 105.9, 107.7, 115.7, 139.8, 151.5, 152.9. *anti*: 13.6, 16.4, 43.5, 71.4, 105.9, 108.3, 117.0, 140.3, 151.8, 153.4.

HRMS: $C_{10}H_{14}O_2$; calc: 149.09664 $(M–OH)^+$; found: 149.09604.

4m: (NMR data were partially reported[7])



IR (neat): 702, 762, 915, 1039, 1454, 1604, 1640, 2860, 3069, 3417 cm^{-1}.

^{1}H NMR *syn*: 0.85 (d, 3H, *J* = 7.1 Hz), 1.11-1.33 (m, 5H), 1.53-1.58 (m, 1H), 2.17-2.20 (m, 1H), 2.35-2.41 (m, 1H), 4.59 (dd, 1H, *J* = 5.1, 5.1 Hz), 5.01 (ddd, 2H, *J* = 1.7, 10.6, 18.4 Hz), 5.49 (ddd, 1H, *J* = 9.5, 10.6, 18.4 Hz), 7.22-7.34 (m, 5H). *anti*: 0.79 (d, 3H, *J* = 6.8 Hz), 1.11 (m, 5H),1.70-1.74 (m, 1H), 2.17-2.20 (m, 1H), 2.24-2.30 (m, 1H), 4.37 (dd, 1H, *J* = 2.3, 7.4 Hz), 5.22 (ddd, 2H, *J* = 1.7, 10.1, 18.4 Hz), 5.64 (ddd, 1H, *J* = 8.9, 10.1, 18.4 Hz), 7.22-7.34 (m, 5H).

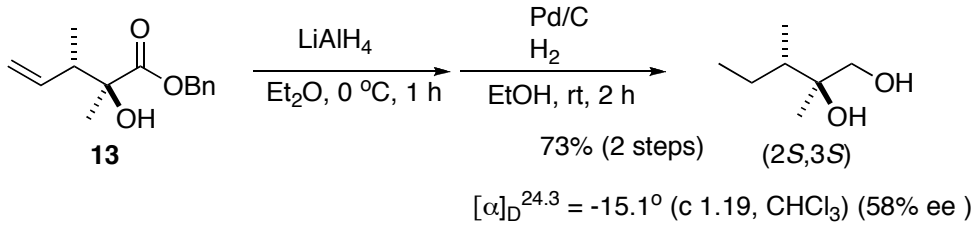
^{13}C NMR *syn*: 13.9, 22.6, 29.3, 29.4, 51.4, 76.8, 117.2, 126.7, 127.3, 127.9, 138.6, 142.5. (*Anti*-adduct was reported.[7b])

HRMS: $C_{14}H_{20}O$; calc: 187.14868 $(M–OH)^{+}$; found: 187.14779.

Determination of the Absolute Configuration of Compound 13[10]

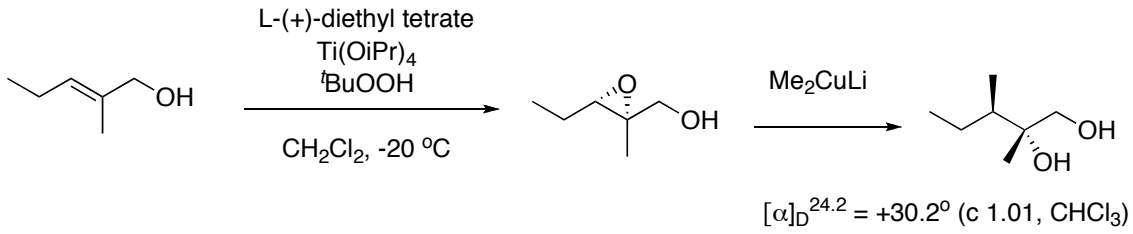
We converted compound **13** into 2,3-dimethylpentane-1,2-diol according to the same procedure as shown in Ref. 11 (Scheme S–1).

Scheme S-1



(2*R*,3*R*)-2,3-Dimethylpentane-1,2-diol was independently synthesized according to the same procedure as shown in Ref. 12 (Scheme S–2). Compared with the value of the optical rotation, we determined the absolute configuration of **13** to be 2*S*,3*S*.

Scheme S-2



$[\alpha]_D^{24.2}$ = +30.2° (c 1.01, $CHCl_3$)

(2*S*,3*S*)-**13**: $[\alpha]_D^{23.4}$ +0.564 (c = 1.35, $CHCl_3$) (58% *ee*)

(2*S*,3*S*)-2,3-dimethylpentane-1,2-diol: $[\alpha]_D^{24.3}$ –15.1 (c = 1.19, $CHCl_3$) (58% *ee*)

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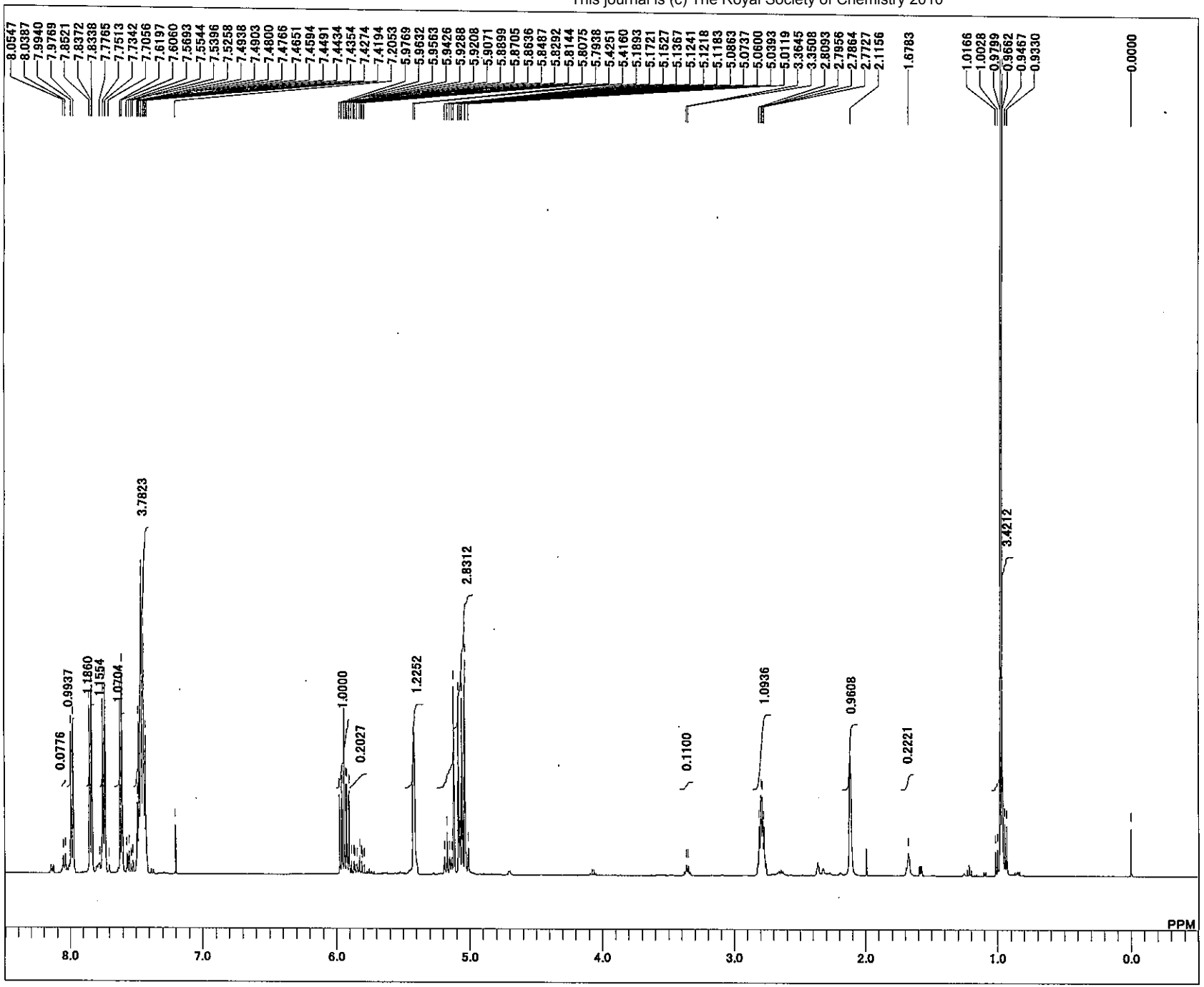

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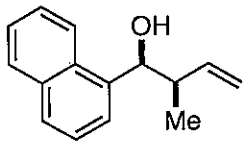

4g

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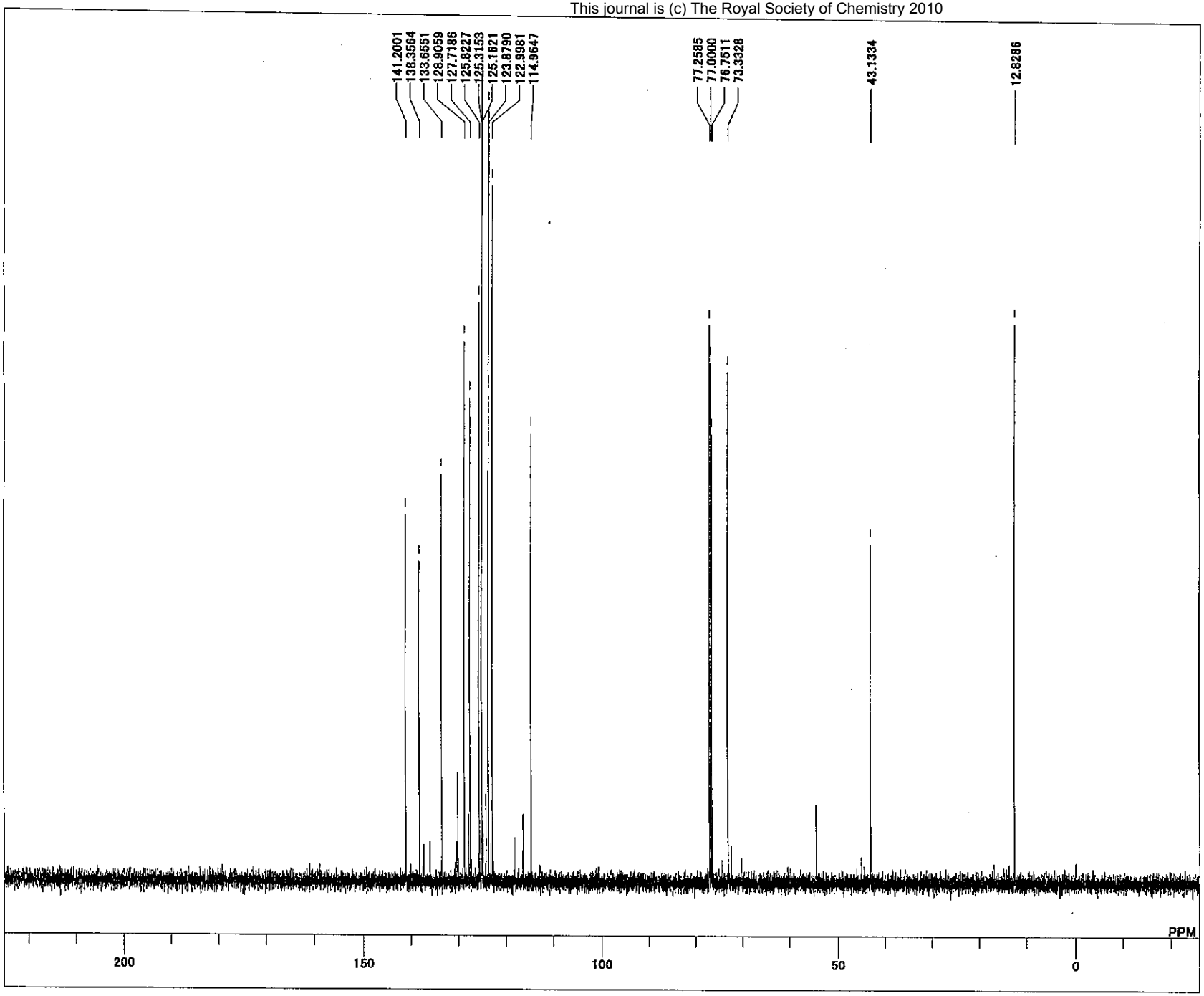

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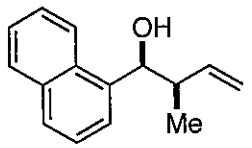

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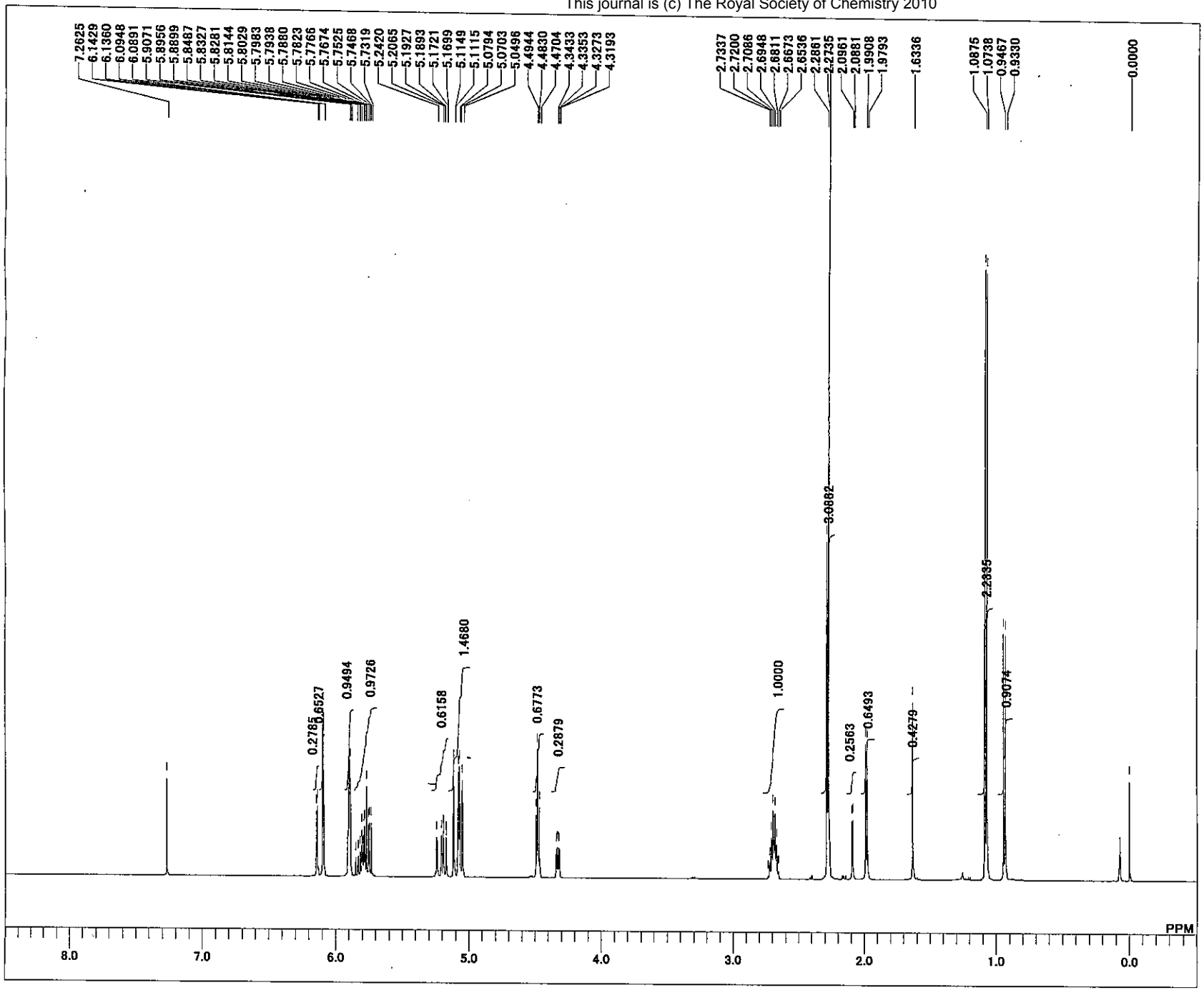

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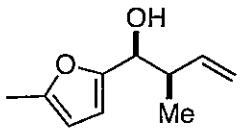

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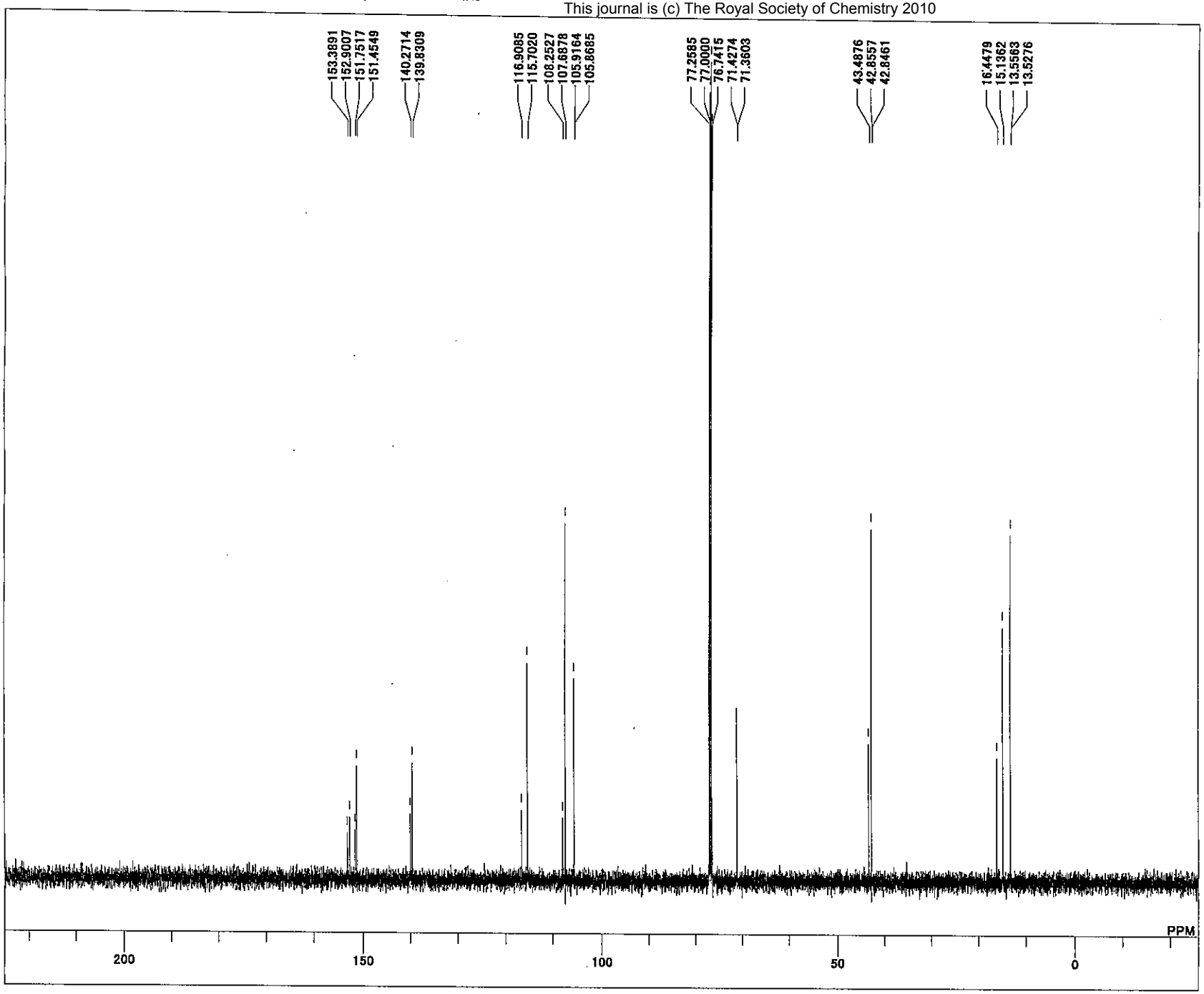

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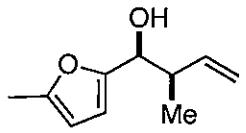

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