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Supporting Information

Ruthenium Complex-Catalyzed *anti*-Markovnikov Hydration of Terminal Alkynes

Toshiaki Suzuki,[†] Makoto Tokunaga,[‡] and Yasuo Wakatsuki[†,*]

RIKEN (The Institute of Physical and Chemical Research), Wako-shi, Saitama 351-0198, Japan

PRESTO, Japan Science and Technology Corporation (JST)

General. GLC analyses were carried out on gas chromatographs equipped with a glass capillary column (J & W, NO. 122-1032; DB-1, 0.32 mm id × 30 m). NMR spectra were recorded on a JEOL EX-270 instrument (FT, 270 MHz (^{1}H), 67.8 Hz (^{13}C)). IR spectra were recorded using a PERKIN ELMER Spectrum RX FT-IR System. GC/MS studies were conducted on a HP-5971A with 70-eV electron impact ionization with HP-5890 (GC) equipped with a capillary column (J & W, NO. 122-1032; DB-1, 0.32 mm id × 30 m).

Materials. $RuCpCl(PPh_3)_2$,[1] RuCpCl(dppm),[2] RuCpCl(dppe),[2] RuCpCl(dppp),[3] RuCpCl(dppb),[3] RuCpCl(dmpm),[4,5] RuCpCl(depe),[4,5] RuCpCl(dppbts),[4,5] $RuCpCl(PMePh_2)_2$,[6] $RuCpCl(PMe_2Ph)_2$,[6] and $RuCpCl(PMe_3)_2$[6] were synthesized as described in the literature.

All solvents and organic reagents except benzyl 3-butynyl ether and 3-butynyl benzoate were commercially available and only degassed before use without further purification. Benzyl 3-butynyl ether was synthesized by the reaction of 3-butyn-1-ol with benzyl bromide in the presence of K_2CO_3 in acetonitrile. 3-Butynyl benzoate was prepared by the reaction of 3-butyn-1-ol with benzoyl chloride in pyridine.

General Procedure of Hydration of 1-alkyne. All reactions were carried out under an argon atmosphere. 1-Alkyne (1.0 mmol) was added to a mixture of ruthenium catalyst (1.0–10.0 mol %), H_2O (0.75 mL), and 2-propanol (2.5 mL) in a 16-mL screw-capped vial. The reaction mixture was stirred for 12–36 h in the oil bath adjusted to 100–130 °C, then diethyl ether (5.0 mL) was added, and the solution was dried with Na_2SO_4. After concentration, the products were isolated by Kugelrohr distillation. All products have been reported. Decane-1,10-dial, 4-(Benzyloxy)butanal, 4-oxobutyl benzoate, and 6-oxohexanenitrile were characterized by GC/MS, ^1H and ^{13}C NMR, and IR spectra (see below) and fully consisted with those in the literature.[7–10] The spectral data of the other aldehyde were fully consistent with those of a commercially available authentic sample.

Decane-1,10-dial.[7] [45037-67-0] Colorless liquid, bp 85–90 °C/4.0 mmHg (Kugelrohr). MS(*m/z*): 170 (M^+). IR spectrum (neat) 2930, 2856, 2826, 2722, 1725, 1466,

1462, 1410, 1392 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 9.76 (t, 2H, 2 × CHO, J = 1.8 Hz), 2.43 (td, 4H, 2 × CH_2CHO, J = 7.3, 1.8 Hz), 1.63 (m, 4H, 2 × CH_2), 1.32 (br, 8H, 4 × CH_2). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 202.4 (2 × CHO), 43.7 (2 × CH_2), 29.03 (2 × CH_2), 28.97 (2 × CH_2), 21.9 (2 × CH_2).

4-(Benzyloxy)butanal.[8] [5470-84-8] Colorless liquid, bp 75–80 °C/3.0 mmHg (Kugelrohr). MS(*m/z*): 178 (M^+). IR spectrum (neat): 3064, 3030, 2933 2859, 2725, 1723, 1496, 1454, 1362, 1206, 1101, 1028, 739, 699 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 9.76 (t, 1H, CHO, J = 1.6 Hz), 7.4–7.2 (m, 5H, Ph), 4.48 (s, 2H, PhCH_2), 3.49 (t, 2H, OCH_2, J = 6.1 Hz), 2.53 (td, 2H, CH_2CHO, J = 7.1, 1.6 Hz), 1.93 (m, 2H, CH_2). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 202.0 (CHO), 138.0 (Ph), 128.2 (Ph), 127.4 (Ph), 72.8 (CH_2), 69.1 (CH_2), 40.9 (CH_2), 22.6 (CH_2).

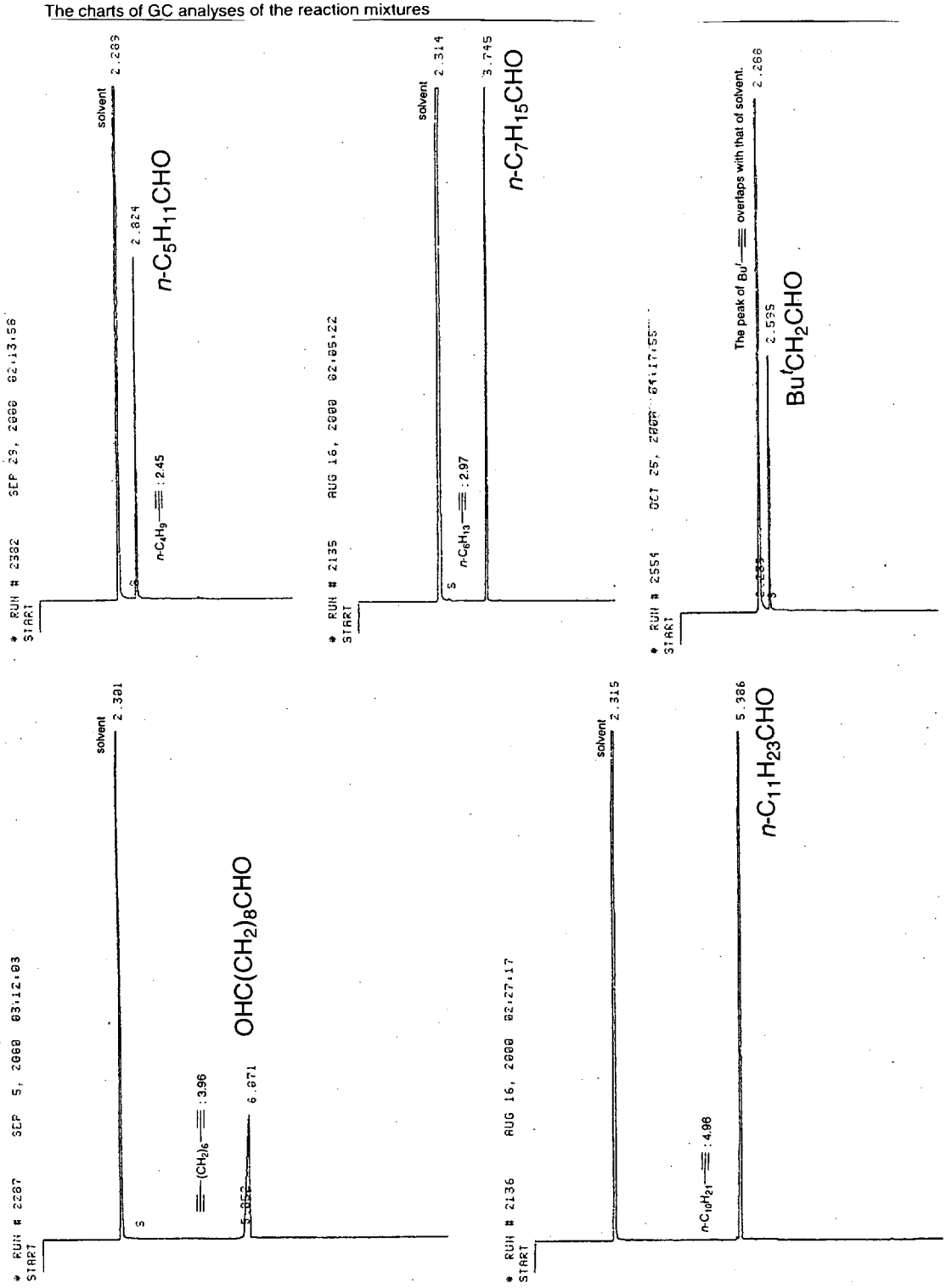
4-Oxobutyl benzoate.[9] [22927-31-7] Colorless liquid, bp 100–105 °C/4.0 mmHg (Kugelrohr). MS(*m/z*): 192 (M^+). IR spectrum (neat): 3064, 2966 2901, 2834, 2730, 1720, 1452, 1316, 1276, 1177, 1119, 1071, 1027, 712 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 9.84 (t, 1H, CHO, J = 1.3 Hz), 8.03 (m, 2H, Ph), 7.57 (m, 1H, Ph), 7.44 (m, 2H, Ph), 4.37 (t, 2H, CO_2CH_2, J = 6.3 Hz), 2.65 (td, 2H, CH_2CHO, J = 7.2, 1.3 Hz), 2.13 (m, 2H, CH_2). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 200.9 (CHO), 166.2 (CO_2), 132.8 (Ph), 129.9 (Ph), 129.3 (Ph),

128.2 (Ph), 63.9 (CH_2), 40.5 (CH_2), 21.5 (CH_2).

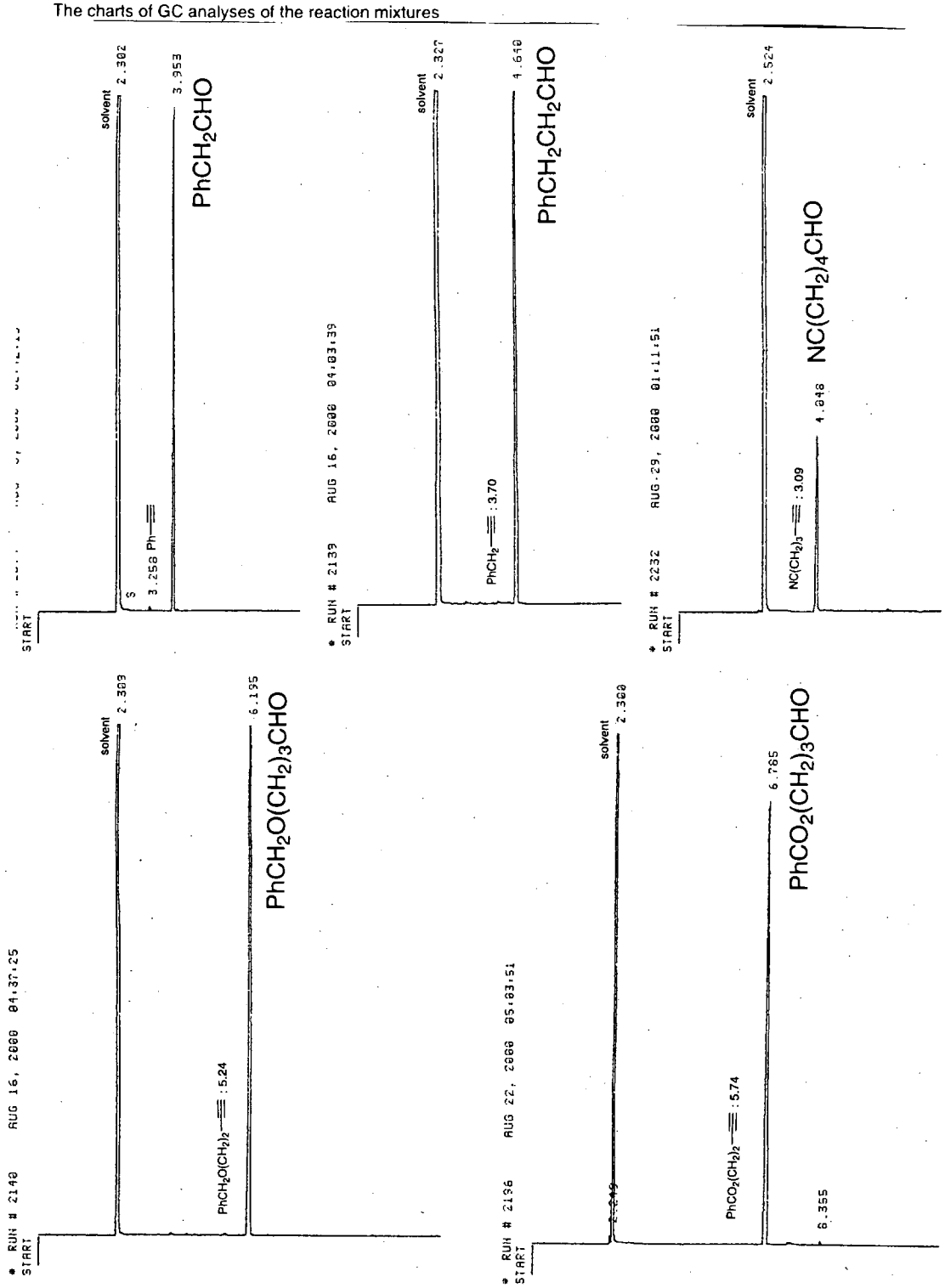
6-Oxohexanenitrile.[10] [3523-02-2] Colorless liquid, bp 75–80 °C/4.0 mmHg (Kugelrohr). MS(*m/z*): 111 (M^+). IR spectrum (neat): 2944, 2874, 2836, 2733, 2245, 1722, 1461, 1426, 1413, 1393, 1354, 1080 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 9.78 (t, 1H, CHO, J = 1.4 Hz), 2.54 (t, 2H, CH_2, J = 6.8 Hz), 2.39 (t, 2H, CH_2, J = 6.8 Hz), 1.75 (m, 4H, 2 × CH_2). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 200.9 (CHO), 119.1 (CN), 42.8 (CH_2), 24.8 (CH_2), 21.0 (CH_2), 17.1 (CH_2).

RuCpCl(CO)(PPh_3).[11] [32613-25-5] 1-Octyne (110 mg, 1.0 mmol) was added to a mixture of RuCpCl(PPh_3)$_2$ (218 mg, 0.30 mmol), H_2O (0.75 mL), and 2-propanol (2.5 mL). The reaction mixture was stirred at 100 °C for 15 h. After cooling to room temperature, yellow precipitate was separated by filtration, washed with 2-propanol/hexane, and dried under vacuum to give RuCpCl(CO)(PPh_3) (96 mg, 65%), the spectral data of which were fully consistent with those in the literature.[11] IR spectrum (KBr): 1959, 1481, 1434, 1096, 751, 695, 530 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.56–7.38 (m, 15H, Ph), 4.88 (s, 5H, Cp). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 203.3 (d, CO, J = 22.1 Hz), 134.5 (d, *ipso*-C of Ph, J = 48.8 Hz), 133.4 (d, Ph, J = 10.7 Hz), 130.2 (d, *p*-C of Ph, J = 2.3 Hz), 128.2 (d, Ph, J = 9.9 Hz), 85.8 (d, Cp, J = 2.3 Hz).

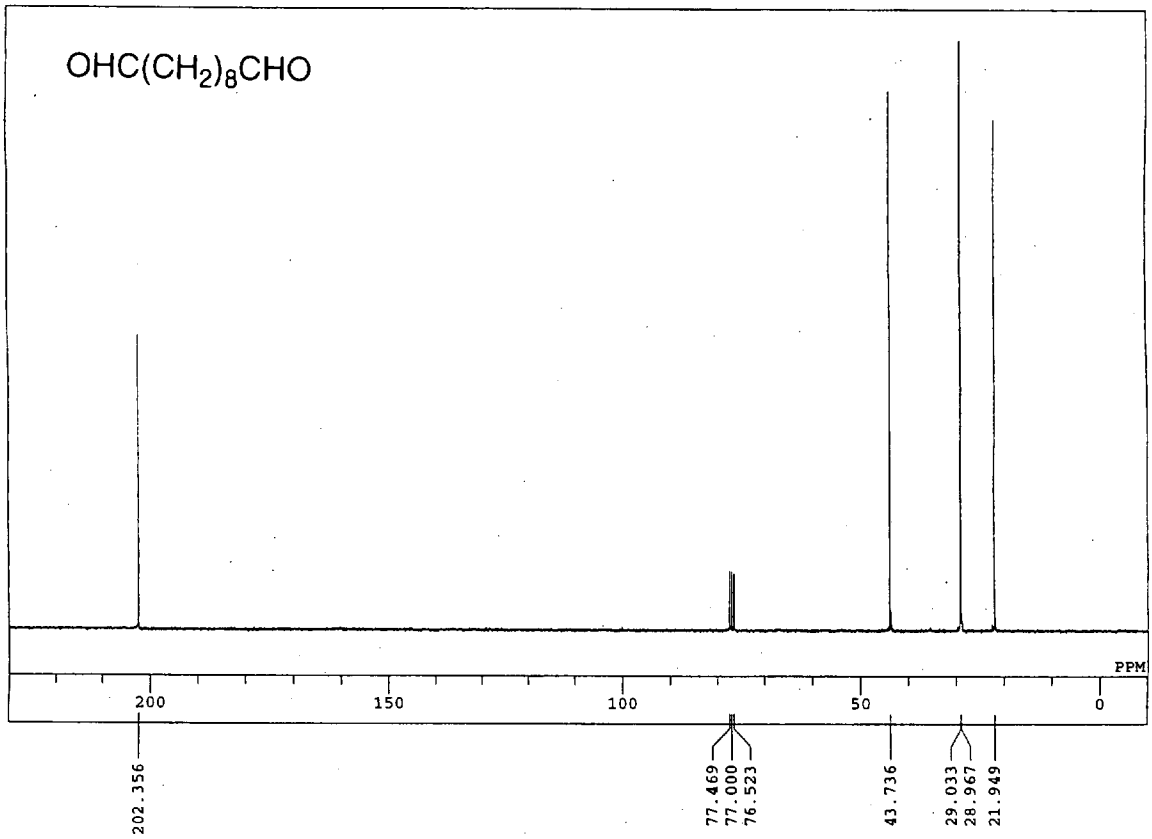
The charts of GC analyses of the reaction mixtures

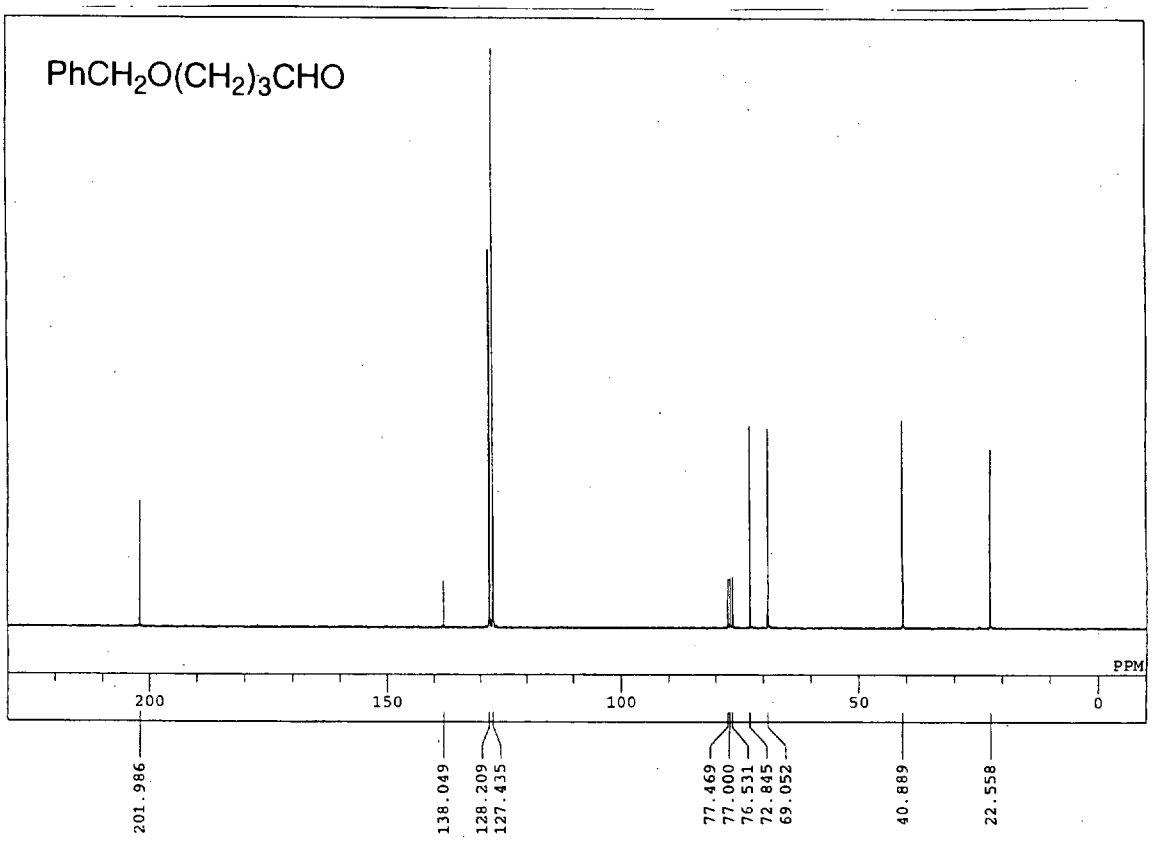


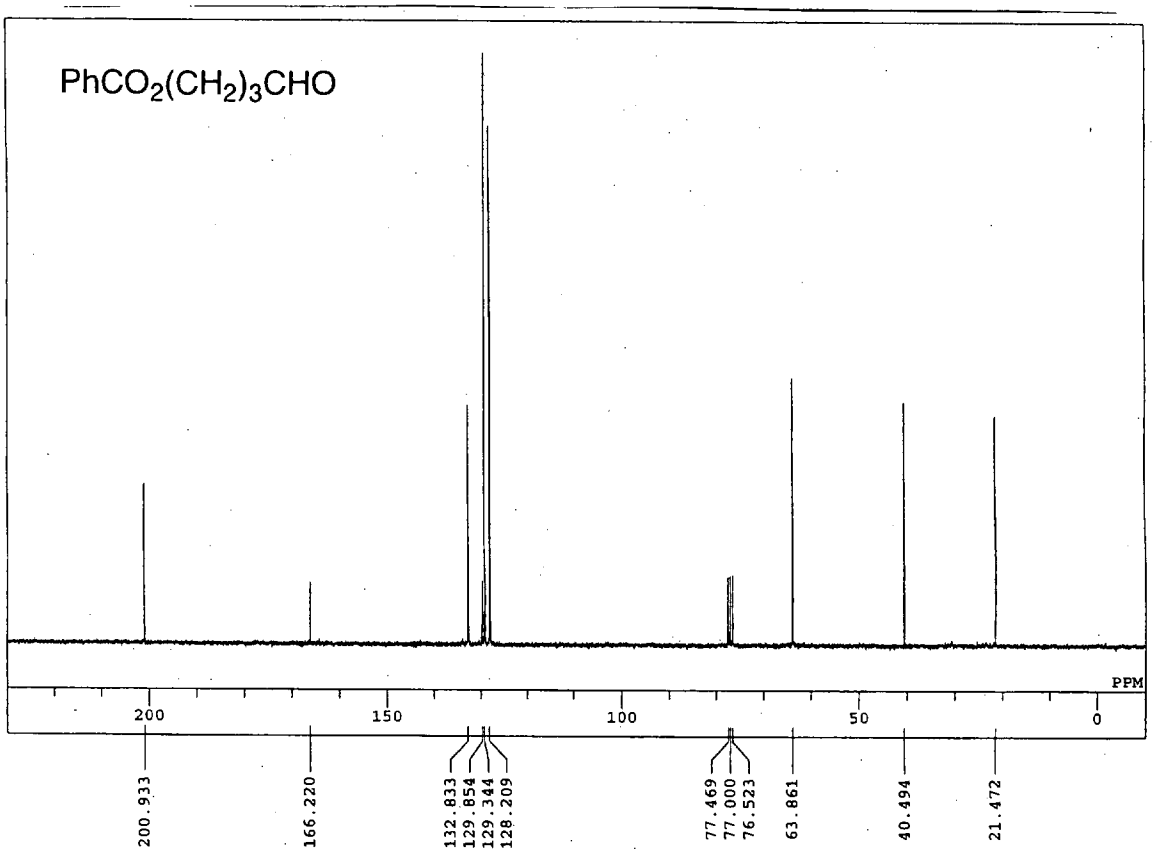
The charts of GC analyses of the reaction mixtures



^{13}C NMR spectra of some obtained aldehyde.






PhCO2(CH2)3CHO
PPM
200
150
100
50
0
200.933
166.220
132.833
129.854
129.344
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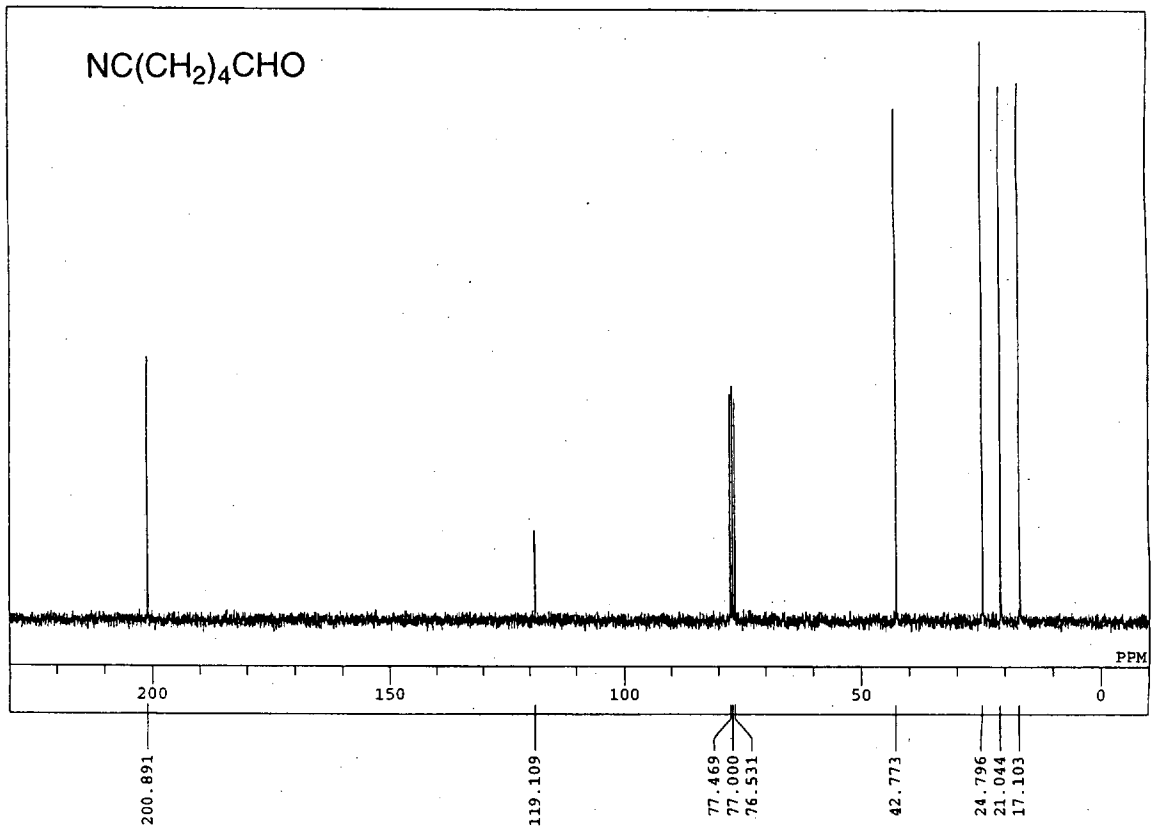
77.469
77.000
76.523
63.861
40.494
21.472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PPM
200
150
100
50
0
200.891
119.109
77.469
77.000
76.531
42.773
24.796
21.044
17.103

References and Notes

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(3) The complex, RuCpCl(dppp) or ruCpCl(dppb), was synthesized by a procedure similar to that for RuCpCl(dppm).[2]

(4) The complex, RuCpCl(dmpm), RuCpCl(depe), or RuCpCl(dppbts), was synthesized by a procedure similar to that for RuCpCl(dppe) from RuCpCl(cod)[5] and phosphine.

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