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## Supporting Information

### A New and Mild System for the Generation of Nonstabilized Carbonyl Ylides: Synthetically Practical Use in Reactions with Electron-Deficient Dipolarophiles

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#### Experimental Section

Boiling points listed in the section for compound data were determined with Kugelrohr distillation apparatus.  $^1\text{H}$  NMR spectra at 270 MHz and  $^{13}\text{C}$  NMR spectra at 67.7 MHz were determined on a JEOL JNM-EX270 instrument with tetramethylsilane ( $\delta = 0.00$  ppm) or chloroform ( $^1\text{H}$ , 7.26 ppm;  $^{13}\text{C}$ , 77.0 ppm) as an internal standard. Infrared spectra were measured with a Shimadzu IR-460 spectrophotometer. Mass spectra were measured (by EI method) on a Shimadzu GCMS-QP2000, QP5000 and JEOL JMS-GCMATE instruments. Microanalyses were performed by the Analysis Center of University of Tsukuba.

**Solvents and Reagents.** Unless otherwise specified, the following solvents and reagents (reagent grade) were used without further purification: lithium bromide, manganese dibromide, calcium chloride, and sodium iodide (Kishida Chemical Co., Ltd.); benzophenone, hydrochloric acid, chlorosulfonic acid, sodium hydride (60% dispersion in mineral oil), naphthalene, *p*-toluenesulfonamide, sodium hydroxide, potassium hydroxide, ammonium chloride, magnesium sulfate, and iodine (Wako Pure Chemical Industries, Ltd.); manganese, lead chloride, paraformaldehyde, ethyl acetate, and *n*-hexane (Kanto Chemical Co., Inc.); lithium wire (Aldrich Chemical Co., Ltd.). Methyl iodide was distilled under nitrogen atmosphere and stored over molecular sieves (4A). Heptanal was dried over  $\text{CaCl}_2$  and purified by fractional distillation. 3-Buten-1-ol, 3-phenylpropyl bromide, benzaldehyde, benzyl bromide, allyl alcohol, methanol, ethanol, *cis*-2-butene-1,4-diol, propargyl alcohol, trimethyl orthoformate, tetramethylurea, and

dimethyl sulfoxide were distilled over  $\text{CaH}_2$  under nitrogen atmosphere. Tetrahydrofuran and diethyl ether were dried and distilled from benzophenone and sodium immediately before use under nitrogen atmosphere.

**Preparation of Bis(chloromethyl) Ether (1a).**<sup>1</sup> *Caution! Very high carcinogenic activity has been reported for bis(chloromethyl) ether.* (Hazard Note, *Org. Syntheses*, 1973, *Coll. Vol. 5*, 218.)

A 300 mL three-necked round-bottom flask, containing a magnetic stirring bar, finely divided paraformaldehyde (48.0 g, 1.60 mol), and conc. HCl (33.6 mL, excess) was fitted with a thermometer, a dropping funnel, a condenser, and a three-way stopcock connected with a nitrogen-balloon and a NaOH solution through a bubbler. Chlorosulfonic acid (90.4 mL, 1.32 mol) was added from a dropping funnel during 6 h at the temperature below 10 °C, and the mixture was stirred for further 6 h. Water layer was separated from the resultant two-phase mixture using a separating funnel and an organic layer was washed twice with ice water and then with a chilled 40% NaOH solution (50 mL). After drying over KOH pellet, the crude product was purified by distillation (104 °C/750 mmHg; 42%, 38.5 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.56 (s, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  76.9 ( $\text{CH}_2 \times 2$ ).

**Preparation of 1-Chloroethyl Chloromethyl Ether (1b).** This compound was prepared by chlorination<sup>2</sup> of ethyl 1-chloromethyl ether<sup>3</sup>.

**Preparation of Ethyl 1-Chloromethyl Ether.** In a 50 mL two-necked round-bottom flask, containing a magnetic stirring bar fitted with a rubber septum with two Teflon-tubes as an inlet and an outlet of HCl gas and a NaOH solution through a bubbler, *s*-trioxane (25.6 g, 284 mmol) and ethanol (39.3 g, 852 mmol) were set. The weight of this apparatus including reagents was measured. Through the tube, HCl gas was introduced to the mixture at 0 °C. After 20 min, a colorless water layer (lower layer) was appeared. To avoid direct bubbling into this water layer, a position of the end of the HCl-inlet was adjusted to an organic layer (upper layer). Bubbling was continued until the weight of incorporated HCl reached to 121% (37.6 g, 1.03 mol) to theoretical amounts. After the removal of a water layer, an organic layer was dried over  $\text{K}_2\text{CO}_3$  (15 g, 15 min) in cooling the outside of the flask with an ice water to give 55.1 g of a crude mixture. Pure  $\alpha$ -chloromethyl ethyl ether was obtained by fractional distillation (62 °C/432 mmHg; 43.8 g, 54% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.24 (t,  $J = 7.3$  Hz, 3H), 3.73 (q,  $J = 7.3$  Hz, 2H), 5.49 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.3 ( $\text{CH}_3$ ), 66.0 ( $\text{CH}_2$ ), 82.9 (CH).

**Preparation of 1-Chloroethyl Chloromethyl Ether (1b).** A 50 mL two-necked round-bottom flask, containing a magnetic stirring bar was fitted with a rubber septum with two Teflon-tubes as an inlet and an outlet of  $\text{Cl}_2$  gas. To this apparatus,  $\alpha$ -chloromethyl ethyl ether (10.3 g, 109 mmol) was introduced. At -50 °C, bubbling of  $\text{Cl}_2$  was started under irradiation of light (tungsten lump), and the reaction temperature was maintained between -40 - -50 °C for 4 h. Excess  $\text{Cl}_2$  gas and other volatiles were removed at 0 °C by an aspirator and a pump, respectively.

Pure  $\alpha$ -chloroethyl  $\alpha'$ -chloromethyl ether was obtained by fractional distillation (52 °C/221 mmHg; 11.5 g, 82% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.80 (d,  $J$  = 5.6 Hz, 3H), 5.49 (d,  $J$  = 6.2 Hz, 1H), 5.61 (d,  $J$  = 6.2 Hz, 1H), 5.96 (q,  $J$  = 5.6 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25.8 ( $\text{CH}_3$ ), 77.1 ( $\text{CH}_2$ ), 89.0 (CH).

Dipolarophiles **2a-2d** were prepared from commercially available alcohols and halides by ordinary Williamson synthesis.

**3-Butenyl 3-Phenylpropyl Ether (2a).**  $R_f$  = 0.28 (hexane/ethyl acetate = 10:1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.90 (m, 2H), 2.35 (dt,  $J$  = 6.9, 6.6, 1.3 Hz, 2H), 2.70 (t,  $J$  = 7.6 Hz, 2H), 3.44 (t,  $J$  = 6.6 Hz, 2H), 3.48 (t,  $J$  = 6.9 Hz, 2H), 5.08 (m, 2H), 5.85 (ddt,  $J$  = 17.2, 10.2, 6.9 Hz, 1H), 7.15-7.31 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  31.2 ( $\text{CH}_2$ ), 32.3 ( $\text{CH}_2$ ), 34.2 ( $\text{CH}_2$ ), 69.9 ( $\text{CH}_2$ ), 70.1 ( $\text{CH}_2$ ), 116.3 ( $\text{CH}_2$ ), 125.7 (CH), 128.3 (CH x 2), 128.5 (CH x 2), 135.4 (CH), 142.0 (quart.); IR (neat film) 3066 (w), 3060 (m), 2947 (s), 2930 (s), 1640 (w), 1490 (w), 1444 (m), 1363 (m), 1115 (s), 1038 (w), 987 (m), 909 (m), 745 (m), 697 (s)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (% relative intensity) 190 ( $\text{M}^+$ , 0.4), 149 (1), 131 (4), 118 (99), 105 (22), 91 (100), 77 (21), 65 (38), 55 (48), 45 (48), 41 (59).

**Allyl Benzyl Ether (2b).** A 100 mL two-necked round-bottom flask containing NaH (60% in oil, 2.4 g, ca. 60 mmol), was fitted with a rubber septum and a reflux condenser with a three-way stopcock connected to a balloon filled with nitrogen. The apparatus was purged with nitrogen. Mineral oil was washed with dry ether (10 mL x 3) and a small amount of ether was removed by a pump. Ether (50 mL) was introduced to the flask and allyl alcohol (2.9 g, 50 mmol) was slowly added to the suspension at 0 °C. The resultant mixture was stirred for 1 h at rt. Benzyl bromide (8.6 g, 50 mmol) and tetramethylurea (TMU, 5.0 mL) were slowly added. After stirring for 8 h at rt, the mixture was poured into saturated aqueous  $\text{NH}_4\text{Cl}$ . Extraction with ether (40 mL x 3), drying over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporation gave a crude mixture. Pure ether was obtained by chromatography on silica gel (hexane/ethyl acetate = 5:1) and distillation (95%, 7.1 g, 47.9 mmol). bp 80 °C/2.0 mmHg.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.04 (ddd,  $J$  = 5.6, 1.7, 1.3 Hz, 2H), 4.45 (s, 2H), 5.21 (m, 1H), 5.32 (ddt,  $J$  = 17.2, 3.3, 1.7 Hz, 1H), 5.96 (ddt,  $J$  = 17.2, 10.6, 5.6 Hz, 1H), 7.15-7.34 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  71.1 ( $\text{CH}_2$ ), 72.1 ( $\text{CH}_2$ ), 117.1 ( $\text{CH}_2$ ), 127.6 (CH), 127.7 (CH x 2), 128.4 (CH x 2), 134.7 (CH), 138.3 (quart.); IR (neat film) 3070 (m), 2920 (s), 1495 (w), 1452 (m), 1421 (w), 1387 (w), 1358 (m), 1262 (w), 1203 (w), 1090 (s), 1028 (m), 989 (m), 924 (s), 736 (s), 696 (s)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (% relative intensity) 148 ( $\text{M}^+$ , 0.39), 147 (2), 107 (19), 105 (17), 91 (100), 77 (18), 65 (23), 51 (22), 41 (36). Anal. Calcd for  $\text{C}_{10}\text{H}_{12}\text{O}$ : C, 81.04; H, 8.16. Found: C, 80.60; H, 8.15.

**(Z)-1,4-Dimethoxy-2-butene (2c).** 45% (1.0 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.29 (s, 6H), 3.96 (dd,  $J$  = 4.7, 1.0 Hz, 4H), 5.67 (dt,  $J$  = 4.7, 1.0 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  58.0 ( $\text{CH}_3$ )

x 2), 68.1 (CH<sub>2</sub> x 2), 129.3 (CH x 2). Anal. Calcd for C<sub>6</sub>H<sub>12</sub>O<sub>2</sub>: C, 62.04; H, 10.41. Found: C, 61.95; H, 10.55.

**Propargyl Benzyl Ether (2d).** 99% (14.5 g): bp 80 °C/2.0 mmHg. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.48 (t, *J* = 2.0 Hz, 1H), 4.19 (d, *J* = 2.0 Hz, 2H), 4.60 (s, 2H), 7.24-7.47 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 57.1 (CH<sub>2</sub>), 71.5 (CH<sub>2</sub>), 74.6 (quart.), 77.5 (CH), 127.9 (CH), 128.1 (CH x 2), 128.5 (CH x 2), 137.3 (quart.); IR (neat film) 3295 (s), 3070 (m), 2950 (s), 2115 (w), 1734 (w), 1495 (m), 1452 (s), 1355 (s), 1262 (m), 1206 (m), 1087 (s), 1027 (s), 936 (m), 912 (m), 740 (s), 696 (s) cm<sup>-1</sup>; mass spectrum *m/z* (% relative intensity) 146 (M<sup>+</sup>, 3), 145 (8), 116 (62), 105 (48), 92 (63), 91 (100), 79 (62), 77 (71), 65 (37), 51 (55). Anal. Calcd for C<sub>10</sub>H<sub>10</sub>O: C, 82.16; H, 6.90. Found: C, 82.16; H, 6.95.

**3-Phenylpropyl Acrylate (2e).** This compound was prepared by alcoholysis of methyl acrylate.<sup>4</sup> bp 100 °C/0.6 mmHg; *R<sub>f</sub>* = 0.15 (hexane/ethyl acetate = 30:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.02 (m, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 4.19 (t, *J* = 6.6 Hz, 2H), 5.48 (dd, *J* = 10.2, 1.7 Hz, 1H), 6.14 (dd, *J* = 17.2, 10.2 Hz, 1H), 6.43 (dd, *J* = 17.2, 1.7 Hz, 1H), 7.18-7.32 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 30.2 (CH<sub>2</sub>), 32.2 (CH<sub>2</sub>), 63.9 (CH<sub>2</sub>), 126.0 (CH), 124.4 (CH x 5), 130.6 (CH<sub>2</sub>), 141.2 (quart.), 160.2 (quart.); IR (neat film) 3015 (w), 1726 (s), 1624 (w), 1491 (w), 1445 (w), 1407 (s), 1387 (w), 1296 (m), 1273 (s), 1189 (s), 1056 (m), 1017 (w), 979 (m), 810 (m), 747 (m), 698 (m), 660 (w) cm<sup>-1</sup>; mass spectrum *m/z* (% relative intensity) 190 (M<sup>+</sup>, 0.07), 118 (99), 117 (100), 105 (10), 91 (50), 77 (13), 65 (17), 55 (60), 51 (14), 41 (10). Anal. Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>: C, 75.76; H, 7.42. Found: C, 75.75; H, 7.50.

Aldehydes **2f-h** were commercially available.

***N*-Benzylidenetosylamide (2i).**<sup>5</sup> A 500 mL two-necked round-bottom flask was fitted with a rubber septum and a three-way stopcock connected to a balloon filled with nitrogen. The apparatus was purged with nitrogen. CeCl<sub>3</sub> 7H<sub>2</sub>O (20.5 g, 55 mmol), benzaldehyde (50 mmol), trimethyl orthoformate (53.1 g, 500 mmol, 54.7 mL) and methanol (125 mL) were introduced to the flask and the mixture was stirred at rt for 12 h. The mixture was poured into the saturated NaHCO<sub>3</sub> solution (500 mL) at 0 °C, and an organic layer was separated. Organics were extracted from water layer with ether (150 mL x 3), and the combined organic layer was washed with saturated NaHCO<sub>3</sub> (500 mL x 3) and brine (500 mL). After drying over MgSO<sub>4</sub>, and evaporation of solvents a crude product was obtained. After distillation, pure benzaldehyde dimethyl acetal was obtained. A 50 mL three-necked round-bottom flask was fitted with a rubber septum, distillation apparatus and a three-way stopcock connected to a balloon filled with nitrogen. *p*-Toluenesulfonamide (3.4 g, 20 mmol) was placed in the flask and the apparatus was purged with nitrogen. Benzaldehyde dimethyl acetal prepared above was added, and the mixture was heated to 170 °C. During this operation, most of produced methanol was distilled off, and finally the

apparatus was connected to a pump and methanol was thoroughly removed under reduced pressure. After cooling the flask, the residue was recrystallized from ethyl acetate-hexane. (100%) mp 107.0-107.5 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.44 (s, 3H), 7.33-7.94 (m, 9H), 9.03 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.7 ( $\text{CH}_3$ ), 128.1 ( $\text{CH} \times 2$ ), 129.2 ( $\text{CH} \times 2$ ), 129.8 ( $\text{CH} \times 2$ ), 131.3 ( $\text{CH} \times 2$ ), 132.4 (quart.), 134.9 (CH), 135.2 (quart.), 144.6 (quart.), 170.1 (CH); IR (KBr disk) 1596 (m), 1573 (m), 1318 (m), 1296 (m), 1156 (s), 1087 (m), 816 (m), 782 (m), 756 (m), 670 (m), 555 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (% relative intensity) 259 ( $\text{M}^+$ , 10), 207 (41), 155 (38), 104 (14), 92 (13), 91 (100), 77 (15), 65 (32), 51 (21).

**1,4-Dimethoxy-2-butyne (2j).**  $R_f = 0.27$  (hexane/ethyl acetate = 15:1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.33 (s, 6H), 4.09 (s, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  57.5 ( $\text{CH}_3 \times 2$ ), 59.7 ( $\text{CH}_2 \times 2$ ), 82.2 (quart.  $\times 2$ ); IR (neat film) 2980 (s), 1464 (m), 1378 (m), 1353 (s), 1280 (w), 1189 (s), 1118 (s), 1002 (w), 950 (w), 906 (s), 659 (w)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (% relative intensity) 114 ( $\text{M}^+$ , 0.7), 99 (31), 83 (9), 71 (66), 69 (42), 55 (29), 45 (100), 41 (93).

**Reaction of Bis(chloromethyl) Ether (1a) with Dipolarophiles (Conditions A: Mn-PbCl<sub>2</sub>, in Table 1). General Procedure.** A 20 mL two-necked round-bottom flask containing manganese (330 mg, 6.0 mmol) was fitted with a rubber septum and an air-cooling column with a three-way stopcock connected to a balloon filled with argon. Under reduced pressure this flask was heated and after cooled down, argon was again introduced. PbCl<sub>2</sub> (34 mg, 0.12 mmol) and THF (1.0 mL) were added and the mixture was stirred at rt for 1 h. A dipolarophile **2** (0.5 mmol), NaI (600 mg, 4.0 mmol) and bis(chloromethyl) ether **1a** (230 mg, 2.0 mmol) were successively added and the mixture was stirred for 4 h. Water was added and organics were extracted with ethyl acetate (20 mL  $\times$  3). After drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>, evaporation of solvents, and purification by means of column chromatography on silica gel (hexane/ethyl acetate), a pure cycloadduct **3** was obtained.

**Reaction of Bis(chloromethyl) Ether (1a) with Dipolarophiles (Conditions B: Rieke Manganese, in Table 1).** A 50 mL two-necked round-bottom flask was fitted with a rubber septum and an air-cooling column with a three-way stopcock connected to a balloon filled with argon. Under reduced pressure this flask was heated and after cooled down, argon was again introduced. Naphthalene (667 mg, 5.2 mmol), lithium (wire, 35 mg, 5.0 mmol) and THF (2.5 mL) were introduced to the flask, and the mixture was stirred at rt for 2 h. Another 50 mL two-necked round-bottom flask fitted with a rubber septum and an air-cooling column with a three-way stopcock connected to a balloon filled with argon was dried in the same way as above. MnBr<sub>2</sub> (538 mg, 2.5 mmol) and LiBr (435 mg, 5.0 mmol) were introduced to the flask, and the flask was dried with a heating-gun under a reduced pressure. THF (2.5 mL) was added to the flask and the resultant mixture was added to the flask containing lithium naphthalenide. The mixture was stirred at rt for 30 min. A dipolarophile (0.5 mmol) and bis(chloromethyl) ether **1a**

(345 mg, 03.0 mmol) were added to a refluxing mixture of Rieke manganese prepared above. The resultant mixture was stirred for 2 h. Water was added and organics were extracted with ethyl acetate (20 mL x 3). After drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>, evaporation of solvents, and purification by means of column chromatography on silica gel (hexane/ethyl acetate), a pure cycloadduct **3** was obtained.

### Reaction of 1-Chloroethyl Chloromethyl Ether (**1b**) with Dipolarophiles.

A reaction of **1b** with 1,4-dimethoxy-2-butyne (**2j**), equation 3 was carried out using **1b** (460 mg, 4.0 mmol), **2j** (57 mg, 0.5 mmol), Mn (660 mg, 12.0 mmol), PbCl<sub>2</sub> (68 mg, 0.24 mmol), and NaI (30 mg, 0.2 mmol) in THF (2 mL) at rt for 12 h, in the same manner as in the reactions conducted under conditions A. Similar conditions were used in the reaction with 1,4-dimethoxy-2-butene (**2c**).

Reactions of **1b** with benzophenoneone (**2h**) and benzaldehyde (**2g**), reactions mentioned in reference 13 were carried out using **1b** (230 mg, 2.0 mmol), dipolarophile (**2h** or **2g**) (0.5 mmol), Mn (330 mg, 6.0 mmol), PbCl<sub>2</sub> (34 mg, 0.12 mmol), and NaI (30 mg, 0.2 mmol) in THF (1 mL) at rt for 8 h, in the same manner as in the reactions conducted under conditions A.

**3-(2'-Phenylpropyloxyethyl)tetrahydrofuran (3a).** 76% (89 mg). bp 160 °C/0.5 mmHg; *R<sub>f</sub>* = 0.23 (hexane/ethyl acetate = 5:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.55 (dq, *J* = 12.2, 7.9 Hz, 1H), 1.68 (q, *J* = 6.6 Hz, 2H), 1.90 (m, 2H), 2.06 (dtd, *J* = 12.2, 7.3, 4.6 Hz, 1H), 2.31 (sept, *J* = 7.4 Hz, 1H), 2.69 (dd, *J* = 8.3, 7.3 Hz, 2H), 3.32-3.54 (m, 5H), 3.76 (m, 1H), 3.85 (td, *J* = 7.9, 4.6 Hz, 1H), 3.93 (dd, *J* = 7.9, 7.6 Hz, 1H), 7.2-7.4 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 31.6 (CH<sub>2</sub>), 32.7 (CH<sub>2</sub>), 32.8 (CH<sub>2</sub>), 33.6 (CH<sub>2</sub>), 36.9 (CH), 68.1 (CH<sub>2</sub>), 70.1 (CH<sub>2</sub>), 70.4 (CH<sub>2</sub>), 73.7 (CH<sub>2</sub>), 126.1 (CH), 128.6 (CH x 2), 128.7 (CH x 2), 142.3 (quart.); IR (neat film) 2845 (m), 1493 (w), 1475 (w), 1448 (w), 1371 (w), 1116 (m), 744 (w), 697 (m) cm<sup>-1</sup>; mass spectrum *m/z* (% relative intensity) 234 (M<sup>+</sup>, 1), 207 (1), 118 (100), 91 (31), 70 (20), 65 (8). Anal. Calcd for C<sub>15</sub>H<sub>22</sub>O<sub>2</sub>: C, 76.88; H, 9.46. Found: C, 76.86; H, 9.66.

**3-Benzyloxymethyltetrahydrofuran (3b).** 93% (89 mg). bp 150 °C/0.8 mmHg; *R<sub>f</sub>* = 0.21 (hexane/ethyl acetate = 10:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.61 (m, 1H), 2.02 (m, 1H), 2.57 (m, 1H), 3.40 (dd, *J* = 8.9, 7.9 Hz, 1H), 3.45 (dd, *J* = 8.9, 6.6 Hz, 1H), 3.60 (dd, *J* = 8.6, 5.3 Hz, 1H), 3.71 (dd, *J* = 8.6, 7.3 Hz, 1H), 3.78 (m, 1H), 3.86 (dd, *J* = 8.6, 7.3 Hz, 1H), 4.53 (s, 2H), 7.29-7.37 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 29.6 (CH<sub>2</sub>), 39.7 (CH), 68.2 (CH<sub>2</sub>), 71.5 (CH<sub>2</sub>), 72.9 (CH<sub>2</sub>), 73.6 (CH<sub>2</sub>), 128.1 (CH x 3), 128.8 (CH x 2), 138.7 (quart.); IR (neat film) 1495 (w), 1450 (w), 1303 (w), 1205 (w), 1098 (s), 911 (w), 737 (m), 697 (m) cm<sup>-1</sup>; mass spectrum *m/z* (% relative intensity) 192 (M<sup>+</sup>, 3), 191 (2), 145 (5), 120 (12), 107 (11), 71 (26), 65 (38), 55 (45), 41 (74). Anal. Calcd for C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>: C, 74.96; H, 8.39. Found: C, 74.77; H, 8.37.

**(3S\*,4R\*)-Di(methoxymethyl)tetrahydrofuran (3c).**<sup>6</sup> 63% (54 mg). bp 100 °C/0.5 mmHg;  $R_f$  = 0.12 (hexane/ethyl acetate = 10:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.56 (m, 2H), 3.21-3.36 (m, 2H), 3.33 (s, 6H), 3.46 (dd,  $J$  = 9.2, 6.0 Hz, 2H), 3.65 (dd,  $J$  = 8.6, 5.6 Hz, 2H), 3.90 (dd,  $J$  = 8.6, 7.3 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 41.3 (CH x 2), 59.1 (CH<sub>3</sub> x 2), 71.3 (CH<sub>2</sub> x 2), 71.4 (CH<sub>2</sub> x 2); IR (neat film) 2870 (s), 1683 (w), 1475 (w), 1454 (w), 1392 (w), 1217 (w), 1193 (m), 1104 (s), 1058 (m), 947 (m), 908 (m), 748 (w) cm<sup>-1</sup>; mass spectrum  $m/z$  (% relative intensity) 110 (2), 96 (22), 83 (14), 71 (13), 67 (12), 55 (19), 45 (100). Anal. Calcd for C<sub>8</sub>H<sub>16</sub>O<sub>3</sub>: C, 59.98; H, 10.07. Found: C, 59.90; H, 10.04.

**3-Benzylloxymethyl-2,5-dihydrofuran (3d).**<sup>6</sup> 81% (77 mg). bp 120 °C/0.5 mmHg;  $R_f$  = 0.29 (hexane/ethyl acetate = 10:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.07 (d,  $J$  = 0.7 Hz, 2H), 4.46 (s, 2H), 4.59 (m, 4H), 5.73 (brs, 1H), 7.19-7.33 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 65.6 (CH<sub>2</sub>), 72.4 (CH<sub>2</sub>), 75.6 (CH<sub>2</sub>), 75.8 (CH<sub>2</sub>), 122.8 (CH), 127.7 (CH), 127.8 (CH x 2), 128.5 (CH x 2), 137.6 (quart.), 137.9 (quart.); IR (neat film) 2845 (s), 1451 (w), 1363 (w), 1198 (w), 1091 (m), 1065 (s), 1023 (w), 893 (w), 799 (w), 738 (w), 695 (m) cm<sup>-1</sup>; mass spectrum  $m/z$  (% relative intensity) 190 (M<sup>+</sup>, 0.04), 99 (25), 91 (100), 84 (57), 69 (49), 41 (32). Anal. Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>: C, 75.69; H, 7.41. Found: C, 75.63; H, 7.37.

**3-(3'-Phenylpropyloxycarbonyl)tetrahydrofuran (3e).** 85% (234 mg). bp 130 °C/0.5 mmHg;  $R_f$  = 0.09 (hexane/ethyl acetate = 10:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.98 (tt,  $J$  = 8.3, 6.6 Hz, 2H), 2.20 (m, 2H), 2.69 (t,  $J$  = 7.6 Hz, 2H), 3.08 (tt,  $J$  = 7.6, 8.3 Hz, 1H), 3.80-3.98 (m, 4H), 4.13 (t,  $J$  = 6.6 Hz, 2H), 7.21-7.32 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 29.5 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>), 32.2 (CH<sub>2</sub>), 43.9 (CH), 64.2 (CH<sub>2</sub>), 68.3 (CH<sub>2</sub>), 70.3 (CH<sub>2</sub>), 126.1 (CH), 128.4 (CH x 2), 128.5 (CH x 2), 141.0 (quart.), 173.8 (quart.); IR (neat film) 2940 (m), 1734 (s), 1469 (m), 1346 (m), 1258 (m), 1175 (s), 1067 (m), 1019 (m), 914 (m), 699 (m), 695 (m) cm<sup>-1</sup>; mass spectrum  $m/z$  (% relative intensity) 207 (1), 163 (1), 118 (100), 91 (38), 69 (17), 65 (11), 41 (47).

**4-Hexyl-1,3-dioxolane (3f).** 79% (62 mg). bp 100 °C/2.0 mmHg;  $R_f$  = 0.48 (hexane/ethyl acetate = 40:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.89 (t,  $J$  = 6.4 Hz, 3H), 1.17-1.58 (m, 9H), 1.58-1.76 (m, 1H), 3.35 (m, 1H), 3.91 (m, 2H), 4.80 (s, 1H), 4.95 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 14.0 (CH<sub>3</sub>), 22.5 (CH<sub>2</sub>), 25.8 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 33.0 (CH<sub>2</sub>), 69.6 (CH<sub>2</sub>), 76.3 (CH), 94.8 (CH<sub>2</sub>); IR (neat film) 2925 (s), 1455 (m), 1376 (w), 1153 (m), 1091 (s), 1008 (m), 930 (s), 890 (w), 843 (w), 722 (w), 659 (m) cm<sup>-1</sup>; mass spectrum  $m/z$  (% relative intensity) 157 (M<sup>+</sup>-1, 3), 126 (2), 97 (5), 82 (8), 73 (61), 55 (20), 44 (100). Anal. Calcd for C<sub>9</sub>H<sub>18</sub>O<sub>2</sub>: C, 68.31; H, 11.47. Found: C, 68.15; H, 11.92.

**4-Phenyl-1,3-dioxolane (3g).** 78% (59 mg). bp 100 °C/0.6 mmHg;  $R_f$  = 0.39 (hexane/ethyl acetate = 40:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.70 (dd,  $J$  = 8.3, 6.9 Hz, 1H), 4.26 (dd,  $J$  =



8.3, 6.6 Hz, 1H), 5.00 (dd,  $J = 6.9, 6.6$  Hz, 1H), 5.10 (s, 1H), 5.27 (s, 1H), 7.28-7.40 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  71.9 ( $\text{CH}_2$ ), 77.6 (CH), 96.0 ( $\text{CH}_2$ ), 126.1 (CH x 2), 128.1 (CH), 128.6 (CH x 2), 139.4 (quart.); IR (neat film) 3015 (w), 2855 (m), 1490 (m), 1446 (m), 1367 (w), 1306 (w), 1205 (w), 1154 (s), 1088 (s), 1014 (s), 944 (s), 923 (s), 757 (s), 716 (s), 659 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (% relative intensity) 150 ( $\text{M}^+$ , 6), 120 (40), 104 (25), 91 (46), 77 (13), 65 (10), 44 (100). Anal. Calcd for  $\text{C}_9\text{H}_{10}\text{O}_2$ : C, 71.98; H, 6.71. Found: C, 71.65; H, 6.84.

**4,4-Diphenyl-1,3-dioxolane (3h).** 98% (111 mg).  $R_f = 0.19$  (hexane/ethyl acetate = 40:1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.42 (s, 2H), 5.21 (s, 2H), 7.24-7.43 (m, 10H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  75.8 ( $\text{CH}_2$ ), 85.6 (quart.), 95.3 ( $\text{CH}_2$ ), 126.2 (CH x 4), 127.5 (CH x 2), 128.4 (CH x 4), 143.0 (quart. x 2); IR (neat film) 3015 (w), 2860 (m), 1590 (w), 1488 (m), 1467 (w), 1260 (m), 1156 (m), 1080 (s), 1049 (s), 970 (m), 946 (s), 873 (w), 743 (s), 700 (s), 662 (m), 610 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (% relative intensity) 226 ( $\text{M}^+$ , 11), 195 (100), 180 (19), 165 (59), 139 (6), 119 (8), 105 (67), 91 (41), 77 (36), 65 (20), 44 (75).

***N*-Tosyl-4-phenyl-1,3-oxazolizine (3i).** 73% (111 mg).  $R_f = 0.10$  (hexane/ethyl acetate = 10:1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.44 (s, 3H), 3.70 (dd,  $J = 8.9, 6.3$  Hz, 1H), 4.07 (dd,  $J = 8.9, 7.3$  Hz, 1H), 4.75 (brt,  $J = 6.8$  Hz, 1H), 4.82 (d,  $J = 6.3$  Hz, 1H), 5.30 (d,  $J = 6.3$  Hz, 1H), 7.18-7.39 (m, 7H), 7.72 (d,  $J = 8.3$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.6 ( $\text{CH}_3$ ), 61.5 (CH), 74.3 ( $\text{CH}_2$ ), 81.7 ( $\text{CH}_2$ ), 126.4 (CH x 2), 127.9 (CH x 2), 128.0 (CH), 128.8 (CH x 2), 129.9 (CH x 2), 134.5 (quart.), 138.8 (quart.), 144.2 (quart.); IR (KBr disk) 1584 (w), 1487 (w), 1443 (w), 1351 (s), 1304 (w), 1162 (s), 1104 (m), 1057 (m), 985 (w), 930 (m), 819 (m), 757 (m), 663 (m), 542 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (% relative intensity) 303 ( $\text{M}^+ - 1$ , 2), 148 (8), 118 (100), 91 (86), 77 (6), 65 (24). Anal. Calcd for  $\text{C}_{16}\text{H}_{17}\text{O}_3\text{NS}$ : C, 63.34; H, 5.65; N, 4.62. Found: C, 63.37; H, 5.70; N, 4.43.

**2-Methyl-3,4-di(methoxymethyl)-2,5-dihydrofuran (3j).** 83% (71 mg). bp 80  $^\circ\text{C}/0.5$  mmHg;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.29 (d,  $J = 6.3$  Hz, 3H), 3.30 (s, 3H), 3.31 (s, 3H), 3.93-4.11 (m, 4H), 4.54 (m, 1H; coalescing to td,  $J = 12.5, 6.5$  Hz by irr. at 4.07), 4.57 (m, 1H; coalescing to td,  $J = 12.5, 5.3$  Hz by irr. at 4.07), 4.85 (m, 1H; coalescing to q,  $J = 6.3$  Hz by irr. at 4.07, 4.57);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.3 ( $\text{CH}_3$ ), 58.2 ( $\text{CH}_3$  x 2), 65.5 ( $\text{CH}_2$ ), 66.0 ( $\text{CH}_2$ ), 75.6 ( $\text{CH}_2$ ), 83.7 (CH), 136.2 (quart.), 133.4 (quart.); IR (neat film) 2060 (s), 1445 (m), 1385 (m), 1347 (m), 1281 (w), 1246 (w), 1193 (s), 1092 (s), 1035 (s), 94 (m), 890 (m), 858 (m), 660 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (% relative intensity) 172 ( $\text{M}^+$ , 0.05), 157 (2), 140 (2), 127 (14), 110 (1), 95 (12), 81 (28), 67 (5), 45 (100). Anal. Calcd for  $\text{C}_9\text{H}_{16}\text{O}_3$ : C, 62.77; H, 9.36. Found: C, 62.67; H, 9.38.

**4-Benzylloxymethyl-2-methyl-2,5-dihydrofuran (3k) and 3-**

**Benzyloxymethyl-2-methyl-2,5-dihydrofuran (3k').<sup>6</sup>**

78% (80 mg). bp 120 °C/0.5 mmHg;  $R_f$  = 0.22 (hexane/ethyl acetate = 10:1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) (as a mixture of **3k**/**3k'** = 50/50 after chromatographic isolation)  $\delta$  1.28 (d,  $J$  = 6.3 Hz, 3H x 0.5), 1.30 (d,  $J$  = 6.3 Hz, 3H x 0.5), 4.09 (brs, 2H x 0.5; **3k**), 4.12 (brs, 2H x 0.5; **3k'**), 4.53 (s, 2H), 4.56-4.75 (m, 2H), 4.86-5.40 (m, 1H), 5.70 (m, 1H x 0.5; **3k'**), 5.79 (m, 1H x 0.5; **3k**), 7.17-7.45 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) (as a mixture of **3k**/**3k'** = 50/50)  $\delta$  20.4 ( $\text{CH}_3$ ), 21.6 ( $\text{CH}_3$ ), 65.4 ( $\text{CH}_2$ ), 65.5 ( $\text{CH}_2$ ), 72.3 ( $\text{CH}_2$ ), 73.9 ( $\text{CH}_2$ ), 74.8 ( $\text{CH}_2$ ), 81.6 (CH), 82.3 (CH), 122.8 (CH), 127.6 (CH), 128.3 (CH), 137.2 (quart.), 137.8 (quart.), 140.9 (quart.); IR (neat film) (as a mixture of **3k** and **3k'**) 2850 (s), 1495 (w), 1449 (m), 1366 (m), 1342 (m), 1199 (m), 1081 (s), 1044 (s), 824 (w), 737 (s), 695 (s)  $\text{cm}^{-1}$ ; mass spectrum (as a mixture of **3k** and **3k'**)  $m/z$  (% relative intensity) 189 ( $\text{M}^+$ -Me, 0.5), 129 (1), 113 (3), 98 (14), 91 (100), 83 (23), 65 (33), 51 (20), 43 (85). The assignment of the regioisomers was done by the NOE experiment. Anal. Calcd. for  $\text{C}_{13}\text{H}_{16}\text{O}_2$ : C, 76.44; H, 7.90. Found (for a mixture of **3k** and **3k'**): C, 76.13; H, 8.01.

**2(R\*)-Methyl-4(R\*)-phenyl-1,3-dioxolane [2(R\*)-4(R\*)-3I] and 5(R\*)-Methyl-4(R\*)-phenyl-1,3-dioxolane [5(R\*)-4(R\*)-3I'].**

86% (71 mg). bp 90 °C/1.0 mmHg;  $R_f$  = 0.29 (hexane/ethyl acetate = 30:1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) (as a mixture of **3I**/**3I'** = 50/50 after chromatographic isolation)  $\delta$  1.37 (d,  $J$  = 5.9 Hz, 3H x 0.5; **3I'**), 1.47 (d,  $J$  = 4.9 Hz, 3H x 0.5; **3I**), 3.70 (dd,  $J$  = 8.3, 7.9 Hz, 1H x 0.5; **3I**), 3.82 (dq,  $J$  = 7.6, 5.9 Hz, 1H x 0.5; **3I'**), 4.40 (d,  $J$  = 7.6 Hz, 1H x 0.5; **3I'**), 4.43 (dd,  $J$  = 8.3, 6.3 Hz, 1H x 0.5; **3I**), 5.08 (dd,  $J$  = 7.9, 6.3 Hz, 1H x 0.5; **3I**), 5.24 (s, 1H x 0.5; **3I'**), 5.25 (s, 1H x 0.5; **3I'**), 5.39 (q,  $J$  = 4.9 Hz, 1H x 0.5; **3I**), 7.19-7.46 (m, 5H); mass spectrum (as a mixture of three isomers)  $m/z$  (% relative intensity) the first isomer 164 ( $\text{M}^+$ , 0.3), 149 (3), 134 (15), 120 (29), 104 (25), 91 (20), 77 (17), 58 (100), 51 (21), 43 (75); the second isomer 163 (0.2), 149 (3), 134 (13), 120 (25), 104 (24), 91 (20), 77 (20), 58 (100), 43 (78); the third isomer 164 ( $\text{M}^+$ , 3), 120 (92), 105 (9), 91 (51), 77 (24), 58 (100), 51 (29), 43 (67). Anal. Calcd. for  $\text{C}_{10}\text{H}_{12}\text{O}_2$ : C, 73.15; H, 7.37. Found (for a mixture of **3I** and **3I'**): C, 73.08; H, 7.41.

**4,4-Diphenyl-2-methyl-1,3-dioxolane (3m) and 4,4-Diphenyl-5-methyl-1,3-dioxolane (3m').**

78% (94 mg). bp 130 °C/0.5 mmHg;  $R_f$  = 0.21 (hexane/ethyl acetate = 20:1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) (for the major isomer **3m**)  $\delta$  1.56 (d,  $J$  = 4.6 Hz, 3H), 4.50 (s, 2H), 5.31 (q,  $J$  = 4.6 Hz, 1H), 7.21-7.59 (m, 10H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) (for the major isomer **3m**)  $\delta$  20.2 ( $\text{CH}_3$ ), 76.7 ( $\text{CH}_2$ ), 86.0 (quart.), 102.1 (CH), 126.2 (CH x 2), 126.3 (CH x 2), 127.5 (CH), 127.6 (CH), 128.3 (CH x 2), 128.4 (CH x 2), 143.3 (quart.), 144.4 (quart.); IR (neat film) (as a mixture of **3m** and **3m'**) 3050 (m), 2925 (m), 1590 (w), 1489 (m), 1444 (m), 1407 (m), 1258 (w), 1148 (s), 1113 (s), 1080 (s), 1040 (m), 994 (s), 889 (m), 748 (s), 699 (s), 661 (w)  $\text{cm}^{-1}$ ; mass

spectrum (for major isomer **3m**)  $m/z$  (% relative intensity) 240 ( $M^+$ , 3), 210 (45), 195 (68), 183 (14), 165 (27), 119 (9), 105 (62), 82 (30), 77 (37), 58 (100), 43 (68). Anal. Calcd for  $C_{16}H_{16}O_2$ : C, 79.97; H, 6.71. Found: C, 80.07; H, 6.75.

## References

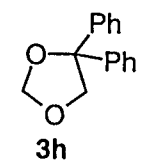
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- (2) Hall, G. E.; Ubertini, F. M. *J. Org. Chem.* **1950**, *15*, 715-719.
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- (6) (a) Hojo, M.; Aihara, H.; Hosomi, A. *J. Am. Chem. Soc.*, **1996**, *118*, 3533-3534. (b) Hojo, M.; Aihara, H.; Ito, H.; Hosomi, A. *Tetrahedron Lett.*, **1996**, *37*, 9241-9244.

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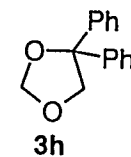
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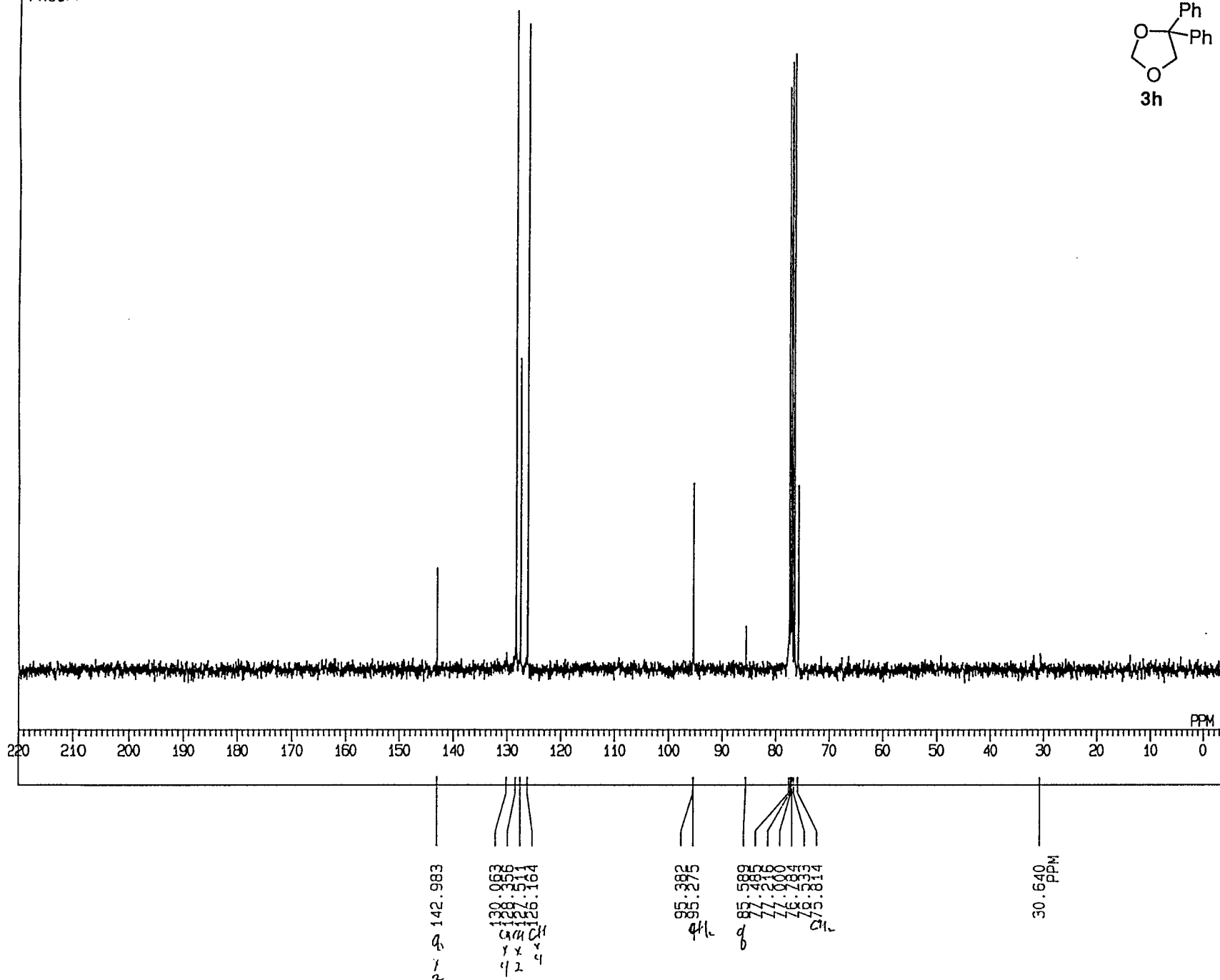
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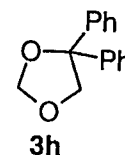
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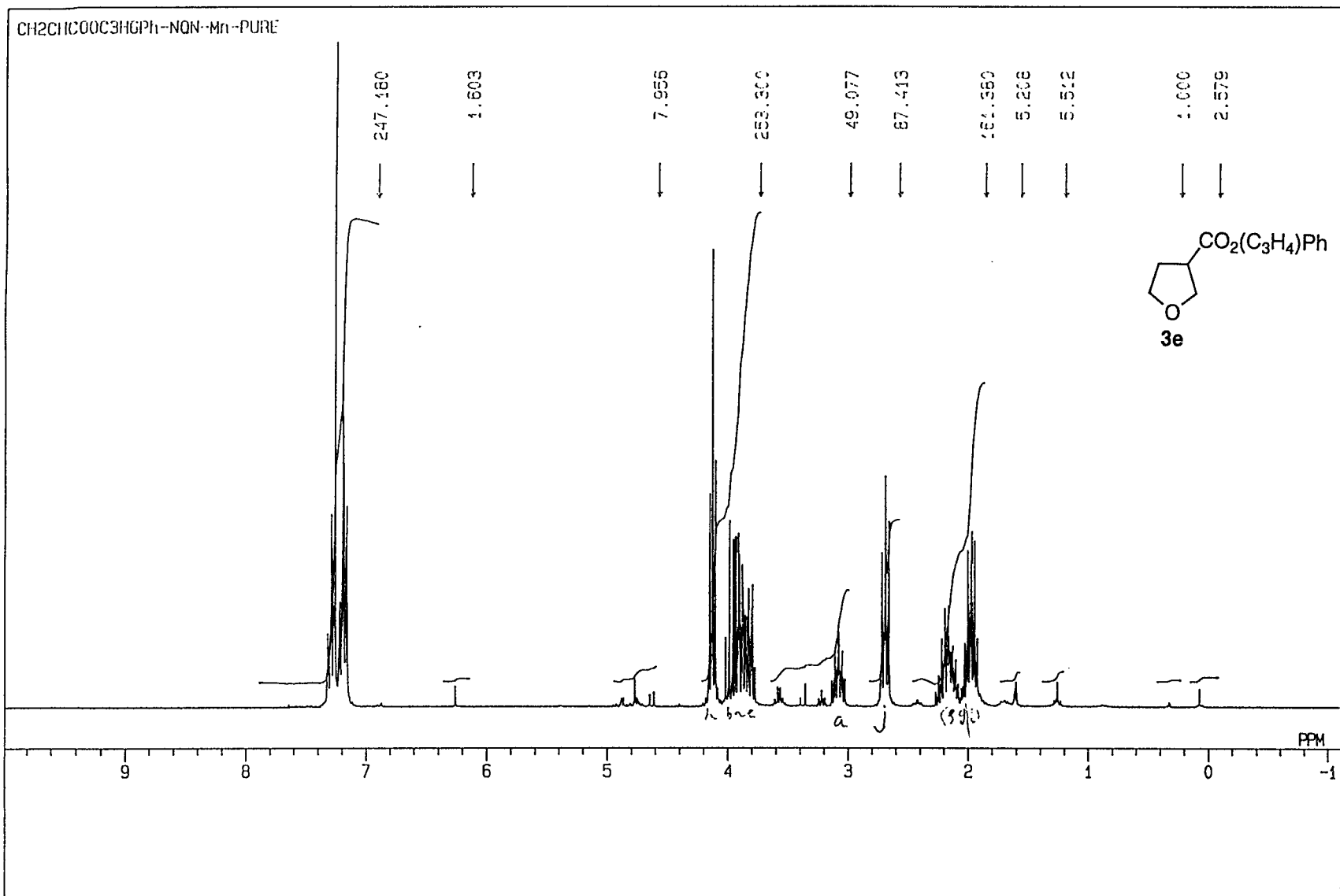
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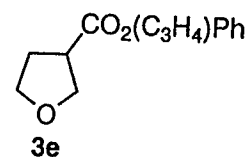
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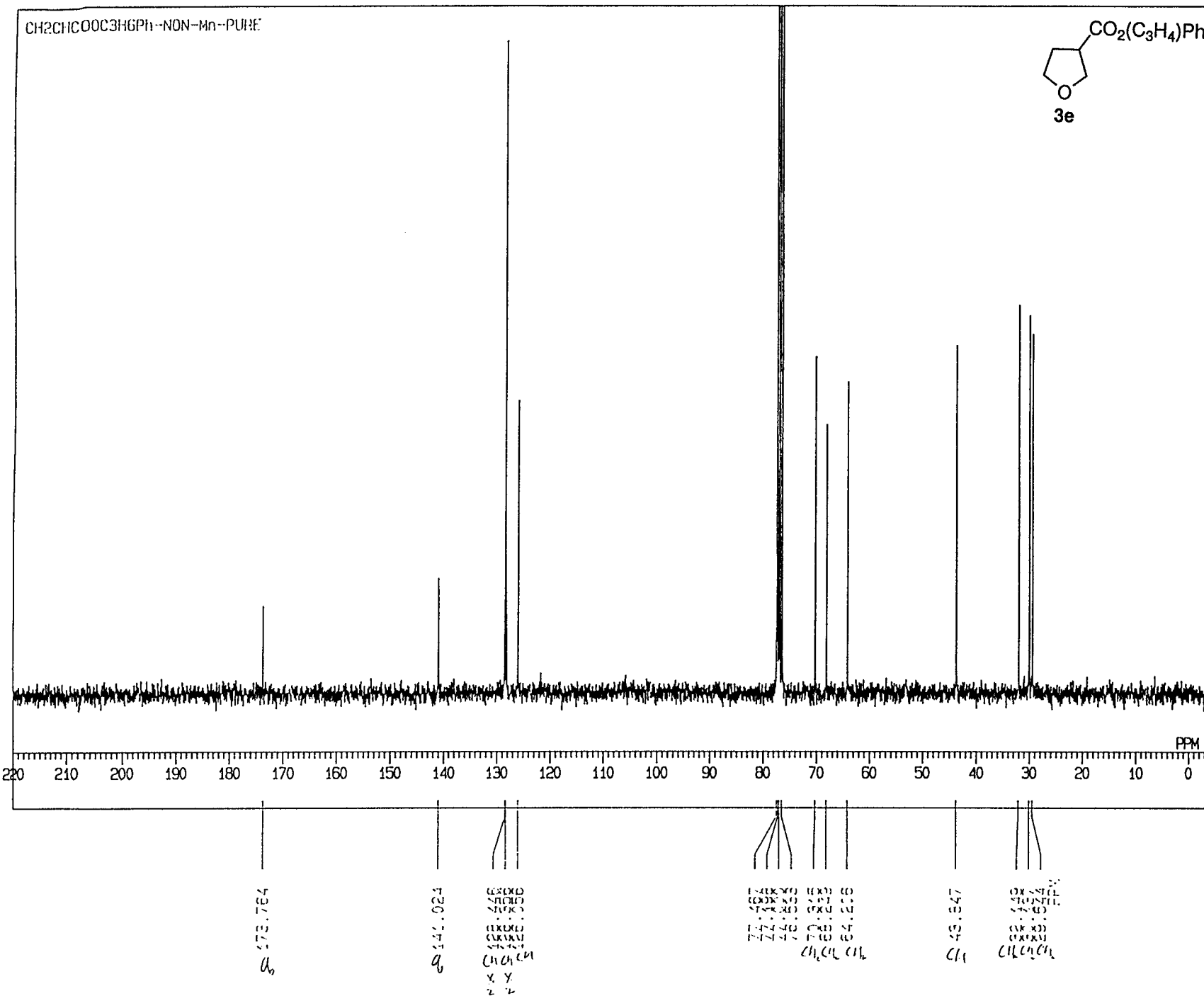


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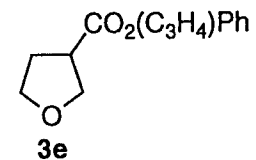
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 OBFIN 5200.0 Hz  
 PW1 8.6 us  
 PW2 19.8 us  
 PW3 29.7 us  
 PI1 3.846 ms  
 PI2 1.000 ms  
 PI3 1.000 ms  
 LOOP1 1  
 POINT 32768  
 SPO 32768  
 SCANS 412  
 DUMMY 1  
 FREQU 20000.0 Hz  
 ACQTM 0.819 sec  
 PD 2.181 sec  
 RGAIN 24  
 BF 1.50 Hz  
 EXMOD DEPT  
 FNUC 1H  
 FFR 270.05 MHz  
 FSET 112.00 kHz  
 FFIN 5800.0 Hz  
 FRRPW 50 us  
 FRATN 511  
 CSPED 15 Hz  
 CTEMP 26.9 c  
 XF 14945.3400 Hz  
 XS -643.9004 Hz  
 OPERATOR : \_\_\_\_\_

POOR QUALITY ORIGINAL

