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Supporting Information

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[Supporting Information]

Platinum(II)-Catalyzed Reaction of γ,δ-Ynones with Alkenes for the Construction of 8-Oxabicyclo[3.2.1]octane Skeletons: Generation of Platinum-Containing Carbonyl Ylides from Acyclic Precursors

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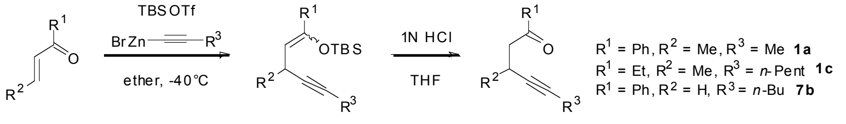
General. All operations were performed under an argon atmosphere. ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker DRX-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) or a JEOL Lambda-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) or a Lambda-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) or a AL-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) or a AL-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) spectrometer using $CHCl_3$ (^{1}H, δ = 7.26) and $CDCl_3$ (^{13}C, δ = 77.0) as an internal standard. IR spectra were recorded on an FT/IR-460 plus (JASCO Co., Ltd.) spectrometer. Flash column chromatography was conducted on silica gel (Kanto 60 N) and preparative thin-layer chromatography (PTLC) was carried out on silica gel (Wako gel B-5F). GPC system (LC–918 or LC-908, Japan Analytical Industry Co. Ltd.) was used for further purification. High resolution mass analyses were performed on a JEOL JMS-700 mass spectrometer operating at 70 eV. Elemental analyses were performed on a Perkin-Elmer 2400 instrument. THF was dried by passing through a column of activated alumina (A-2, Purify) followed by a column of Q-5 scavenger (Engelhard), and all other solvents were distilled according to the usual procedures and stored over molecular sieves. MS4A were heated by heat-gun under reduced pressure just before use.

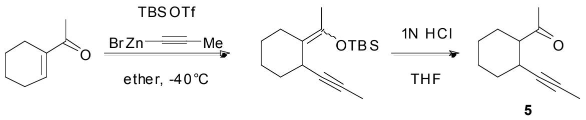
Preparation of acyclic γ,δ-ynones

Compounds **1b**[1] and **7a**[2] are known compounds and their spectral data are in good agreement with those of the literature.

1a, **1c**, **5**, and **7b** were prepared by conjugate addition of an alkynylzinc bromide to an α,β-enone according to the literature procedure.[3]

A 1 M THF solution of zinc bromide was prepared by heating a THF (63.9 mL) suspension of zinc (16.7 g, 255 mmol) and 1,2-dibromoethane (12.0 g, 63.9 mmol) at 90 °C for 2 hours.





Preparation of 3-methyl-1-phenyl-hex-4-yn-1-one (1a):

A mixture of 1 M THF solution (2.74 mL, 2.74 mmol) of zinc bromide and ether (5 mL) was cooled to -40 °C. A 0.5 M THF solution (5.48 mL, 2.74 mmol) of 1-propynylmagnesium bromide was added to the mixture, and the reaction mixture was stirred at room temperature for 10 min. To this solution of 1-propynylzinc bromide were added successively an ether solution (5 mL) of 1-phenyl-but-2-en-1-one (320 mg, 2.19 mmol) and TBSOTf (0.63 mL, 2.74 mmol) at -40 °C. After the mixture was stirred at room temperature for 10 min, saturated $NaHCO_3$ aq. and ether were added. The organic layer was washed with brine and dried over $MgSO_4$. After evaporation of the solvent, 1N hydrochloric acid and THF were added to the crude mixture. After the mixture was stirred at room temperature for one day, saturated $NaHCO_3$ aqueous solution was added to neutralize the mixture. The mixture was extracted with ethyl acetate (three times), and the combined organic layer was dried over $MgSO_4$ and evaporated. The residue was purified by silicagel flash chromatography (hexane:ethyl acetate = 95 : 5) to give 3-methyl-1-phenyl-hex-4-yn-1-one (**1a**).

3-methyl-1-phenyl-hex-4-yn-1-one (1a)

IR (neat) 3061, 2971, 1687, 1449, 1280, 755, 690 cm^{-1};

^{1}H NMR ($CDCl_3$) (300 MHz): δ = 1.23 (3H, d, *J* = 6.8 Hz), 1.75 (3H, d, *J* = 2.2 Hz), 2.98 (1H, dd, *J* = 15.6, 6.8 Hz), 3.04-3.18 (1H, m), 3.22 (1H, dd, *J* = 15.8, 6.1 Hz), 7.46 (2H, t, *J* = 7.1 Hz), 7.56 (1H, t, *J* = 7.6 Hz), 7.97 (2H, d, *J* = 7.3 Hz);

^{13}C NMR ($CDCl_3$) (75 MHz): δ = 3.5, 21.3, 21.9, 45.8, 76.0, 82.9, 128.1, 128.5, 133.0, 137.0, 198.2;

Anal. Calcd for $C_{13}H_{14}O$: C, 83.84; H, 7.58%. Found: C, 83.61; H, 7.73%.

Preparation of 5-methyldodec-6-yn-3-one (1c):

To an ether solution (20 mL) of 1-heptyne (490 mg, 5.0 mmol) were added successively a 1.46 M hexane solution (4.28 mL, 6.25 mmol) of *n*-butyllithium and a 1.0 M THF solution (6.25 mL, 6.25 mmol) of zinc bromide at -40 °C. The reaction mixture was stirred at room temperature for 10 min. To this solution of 1-heptynylzinc bromide were added successively an ether solution (5 mL) of hex-4-en-3-one (predominantly trans, 489 mg, 5.0 mmol) and TBSOTf (1.44 mL, 6.25 mmol) at -40 °C. After the mixture was stirred at room temperature for 10 min, saturated $NaHCO_3$ aq. was added followed by dilution with ether. The organic layer was washed with brine and dried.

After evaporation of the solvent, 1N hydrochloric acid (10 mL) and THF (10 mL) were added to the crude mixture. After the mixture was stirred at room temperature for 3 hours, saturated $NaHCO_3$ aqueous solution was added to neutralize the mixture. The mixture was extracted with ethyl acetate three times , and the combined organic layer was dried over $MgSO_4$, and evaporated. The residue was purified by silicagel flash chromatography twice (hexane:ethyl acetate = 9 : 1 and then toluene only) to give 5-methyldodec-6-yn-3-one (**1c**) (517 mg, 2.66 mmol) in 53% yield.

5-methyldodec-6-yn-3-one (1c)
IR (neat) 2960, 2933, 1716, 1459, 1119 cm^{-1};
^1H NMR ($CDCl_3$) (400 MHz): δ = 0.89 (3H, t, J = 7.2 Hz), 1.06 (3H, t, J = 7.2 Hz), 1.15 (3H, d, J = 6.8 Hz), 1.23-1.40 (4H, m), 1.45 (2H, quint, J = 6.8 Hz), 2.11 (2H, t, J = 7.2 Hz), 2.38-2.54 (3H, m), 2.60 (1H, dd, J = 15.6, 7.6 Hz), 2.93 (1H, sext, J = 7.2 Hz);
^{13}C NMR ($CDCl_3$) (100 MHz): δ = 7.7, 14.0, 18.7, 21.5, 22.1, 22.2, 28.8, 31.1, 36.6, 49.7, 80.8, 83.4, 209.5;
Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41%. Found: C, 80.12; H, 11.25%.

Preparation of 1-phenylnon-4-yn-1-one (7b):

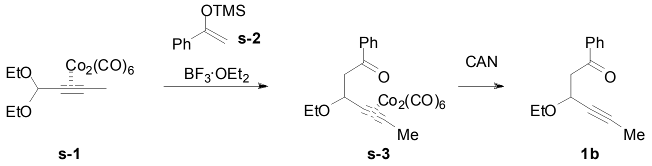
7b was prepared by the similar method for **1c**.

1-phenylnon-4-yn-1-one (7b)
IR (neat) 2957, 2931, 1686, 1449, 1204, 743, 690 cm^{-1};
^1H NMR ($CDCl_3$) (300 MHz): δ = 0.89 (3H, t, J = 7.1 Hz), 1.30-1.53 (4H, m), 2.08-2.20 (2H, m), 2.55-2.67 (2H, m), 3.19 (2H, t, J = 7.7 Hz), 7.47 (2H, t, J = 7.1 Hz), 7.57 (1H, t, J = 7.5 Hz), 7.97 (2H, d, J = 7.1 Hz);
^{13}C NMR ($CDCl_3$) (75 MHz): δ = 13.6, 13.8, 18.4, 21.9, 31.1, 38.3, 78.7, 80.9, 128.0, 128.6, 133.1, 136.7, 198.4;
Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H 8.47%. Found: C, 84.01; H, 8.61%.

Preparation of 1-acetyl-2-(1-propynyl)cyclohexane (5):

A mixture of 1 M THF solution (5.0 mL, 5.0 mmol) of zinc bromide and ether (12 mL) was cooled to -40 °C. A 0.5 M THF solution (10.0 mL, 5.0 mmol) of 1-propynylmagnesium bromide was added to the mixture, and the reaction mixture was stirred at room temperature for 10 min. To this solution of 1-propynylzinc bromide were added successively an ether solution (8 mL) of 1-acetyl-1-cyclohexene (497 mg, 4.0 mmol) and TBSOTf (1.15 mL, 5.0 mmol) at -40 °C. After the mixture was stirred at 0 °C for 2 h, saturated $NaHCO_3$ aq. and ether were added. The organic layer was washed with brine and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by silica gel flash chromatography (hexane : ethyl acetate = 9 : 1) to give silyl enol dether. 1N hydrochloric acid and THF were added to the silyl enol ether. After the mixture was stirred at room temperature for 1 h 30 min, saturated $NaHCO_3$ aqueous solution was added to neutralize the mixture. The mixture was extracted with ethyl acetate (three times), and the combined organic layer was dried over $MgSO_4$ and evaporated. The residue was purified by silica gel flash chromatography (hexane:ethyl acetate = 9 : 1) to give 1-acetyl-2-(1-propynyl)cyclohexane (**5**) containing a small amount of impurity. Further purification was done by GPC to give **5** in 10% yield (65 mg).

1-acetyl-2-(1-propynyl)cyclohexane (5):
IR (neat) 2933, 2857, 1709, 1446, 1352, 1171 cm^{-1};
^1H NMR ($CDCl_3$) (300 MHz): δ = 1.10-1.26 (1H, m), 1.43-1.93 (7H, m), 1.77 (3H, s), 2.17 (3H, s), 2.24-2.34 (1H, m), 3.12-3.21 (1H, m);
^{13}C NMR ($CDCl_3$) (125 MHz): δ = 3.4, 21.4, 23.1, 25.1, 27.7, 29.9, 31.8, 53.8, 78.2, 79.1, 209.8;
HRMS Calcd for $C_{11}H_{16}O$, M^+ 164.12012. Found m/z 164.1185.

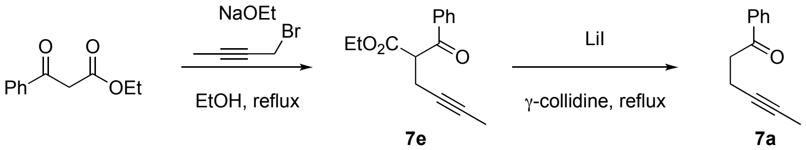


Preparation of 3-ethoxy-1-phenylhex-4-yn-1-one (1b):

3-Ethoxy-1-phenylhex-4-yn-1-one (**1b**) was prepared by using the Nicholas Reaction.[4]
Complex (**s-1**) was prepared according to the literature.[4]
To a CH_2Cl_2 solution (40 mL) of acetophenone TMS enol ether **s-2** (385 mg, 2.0 mmol) and the alkyne-$Co_2(CO)_6$ complex **s-1** was added boron trifluoride diethyl etherate (858 mg, 2.0 mmol) at 0 °C under Ar atmosphere. After the mixture was stirred for 25 min, the mixture was quenched with cold $NaHCO_3$ aq. and washed twice with brine. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was filtered through a short plug of silica gel, and then purified by flash chromatography (toluene only) to give **s-3** (932 mg) in 47% yield.

(s-3)
IR (neat) 2090, 2048, 2019, 1687, 1091, 517 cm^{-1};
^1H NMR ($CDCl_3$) (400 MHz): δ = 1.16 (3H, t, J = 7.2 Hz), 2.66 (3H, s), 3.19 (1H, dd, J = 16.8, 4.0 Hz), 3.60 (1H, dd, J = 16.8, 8.0 Hz), 3.66-3.82 (2H, m), 5.19 (1H, dd, J = 7.6, 4.4 Hz), 7.48 (2H, t, J = 7.2 Hz), 7.58 (1H, t, J = 7.2 Hz), 7.97 (2H, d, J = 7.6 Hz);
^{13}C NMR ($CDCl_3$) (125 MHz): δ = 15.1, 21.0, 46.6, 66.4, 75.6, 93.3, 98.8, 128.1, 128.7, 133.3, 137.0, 197.3, 199.8;
Anal. Calcd for $C_{20}H_{16}Co_2O_8$: C, 47.83; H, 3.21%. Found: C, 47.68; H, 3.44%.

s-3 (120.5 mg, 0.24 mmol) dissolved in 13 mL of dry acetone containing 65 μL of dry NEt$_3$ was treated with ceric ammonium nitrate (395 mg, 0.72 mmol) portionwise at 0 °C under anhydrous conditions with vigorous stirring until CO evolution ceased and the reaction mixture turned from dark red to orange. Solvent was removed under reduced pressure and the residue was quenched with 15 mL of cold 5 M NaHCO$_3$. After the mixture was stirred for 5 min, crude products were extracted with ether four times, and the combined extract was washed twice with brine, dried over anhydrous Na$_2$SO$_4$, and evaporated. The residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate=9:1) to give 3-ethoxy-1-phenylhex-4-yn-1-one (**1b**) (38 mg) in 73 % yield. The spectral data were consistent with those of the literature.[1]



Preparation of ethyl 2-(but-2-yn-1-yl)-3-oxo-3-phenylpropanoate (7e), 1-phenylhex-4-yn-1-one (7a):

(**7a**) and (**7e**) were prepared according to the literature.[5]

An ethanol (10 mL) solution of ethyl benzoylacetate (4.82 g, 25.1 mmol) was added dropwise to an ethanol solution (28 mL) of sodium ethoxide (1.71 g, 25.1 mmol) and the mixture was heated to reflux temperature. An ethanol solution (10 mL) of 1-bromo-2-butyne (4.07 g, 30.6 mmol) was then added and refluxing was continued for 5 hours. After cooling to room temperature, water was added to the reaction mixture. Organic materials were extracted with ethyl acetate. Combined organic layer was washed with water and with brine and then dried over magnesium sulphate. Evaporation of the solvent gave a crude mixture (6.33 g).

The crude mixture (1.50 g) was purified by flash chromatography (hexane : ethyl acetate = 8 : 2) to give (**7e**) (1.27 g).

(**7e**)

IR (neat) 2981, 2921, 1739, 1687, 1236, 690 cm^{-1};

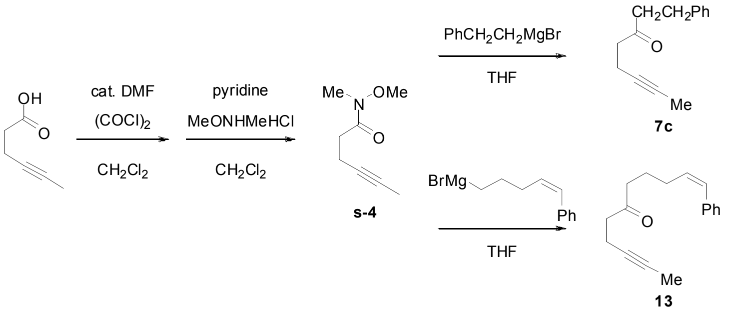
^{1}H NMR (CDCl$_3$) (300 MHz): δ = 1.17 (3H, t, J = 7.2 Hz), 1.69 (3H, t, J = 2.4 Hz), 2.72-2.93 (2H, m), 4.15 (2H, q, J = 7.2 Hz), 4.51 (1H, t, J = 7.5 Hz), 7.48 (2H, t, J = 7.2 Hz), 7.59 (1H, t, J = 7.5 Hz), 8.00-8.05 (2H, m);

^{13}C NMR (CDCl$_3$) (75 MHz): δ = 3.4, 13.9, 18.8, 53.8, 61.6, 75.3, 77.8, 128.7, 128.8, 133.6, 136.1, 168.6, 193.8;

Anal. Calcd for C$_{15}$H$_{16}$O$_3$: C, 73.75; H, 6.60%. Found: C, 73.46; H, 6.59%.

A mixture of lithium iodide (2.66 g, 19.8 mmol) and 2,4,6-trimethylpyridine (γ-collidine) (27.5 mL) was heated to reflux temperature. As soon as all the lithium iodide had dissolved, the above crude mixture (4.83 g) of β-keto ester in γ-collidine (20 mL) was added to the boiling solution. The mixture was refluxed for 19 h, cooled and poured into a mixture of 6 N hydrochloric acid (40 mL), diethyl ether (40 mL), and ice (20 g). The residue in the flask was dissolved in a mixture of 6 N hydrochloric acid and dichloromethane, and was added to the above mixture. The aqueous layer was extracted twice with ether. The combined organic layers were washed once with 6 N hydrochloric acid, once with 2N sodium carbonate solution and twice with brine. The solution was dried over magnesium sulfate and the solvent was evaporated. The crude mixture was purified by recrystallization from *n*-hexane to give 1-phenylhex-4-yn-1-one (**7a**) (1.23 g).

The spectral data were consistent with those of the literature.[2]



Preparation of 1-phenyloct-6-yn-3-one (7c) and (1Z)-1-phenylundec-1-en-9-yn-6-one (13):

(4*Z*)-1-Bromo-5-phenylpent-4-ene was prepared according to the literature.[6]

(4*Z*)-1-Bromo-5-phenylpent-4-ene

IR (neat) 3009, 1493, 1446, 1244, 768, 699 cm^{-1};

^{1}H NMR (CDCl$_3$) (400 MHz): δ = 1.99 (2H, quint, J = 6.8 Hz), 2.47 (2H, dq, J = 1.2, 7.2 Hz), 3.40 (2H, t, J = 6.8 Hz), 5.60 (1H, dt, J = 11.6, 7.2 Hz), 6.46 (1H, d, J = 12.0 Hz), 7.18-7.34 (5H, m);

^{13}C NMR (CDCl$_3$) (100 MHz): δ = 27.3, 33.0, 33.1, 126.6, 128.1, 128.6, 130.1, 130.4, 137.2;

Anal. Calcd for C$_{11}$H$_{13}$Br: C, 58.69; H, 5.82%. Found: C, 58.39; H, 6.04%.

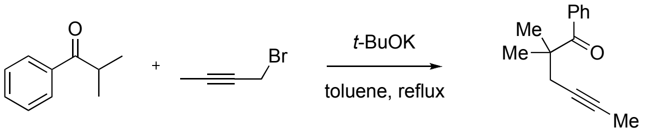
(COCl)$_2$ (4.02 mL, 46.1 mmol) was added to a dichloromethane solution (78 mL) of hex-4-ynoic acid (2.87 g, 25.6 mmol) containing a catalytic amount of *N*,*N*-dimethylformamide at 0 °C. After the resulting mixture was stirred overnight, the solvent was removed under reduced pressure, and then dichloromethane (128 mL) was added. To this CH$_2$Cl$_2$ solution of acyl chloride was added *N*,*O*-dimethylhydroxylamine hydrochloride (3.02 g, 31.0 mmol) followed by pyridine (6.21 mL, 76.8 mmol). After the mixture was stirred at 0 °C for 1 h, aqueous $CuSO_4$ was added, and the products were extracted with ethyl acetate, and dried over $MgSO_4$. Evaporation gave a crude mixture which was purified by flash chromatography (hexane : ethyl acetate = 3 : 1) to give the Weinreb amide **s-4** (2.96 g, 19.1 mmol) in 75% yield.

(s-4)
IR (neat) 2921, 1667, 1421, 1387, 989 cm^{-1};
^{1}H NMR ($CDCl_3$) (400 MHz): δ = 1.72 (3H, t, *J* = 2.8 Hz), 2.36-2.43 (2H, m), 2.58 (2H, t, *J* = 8.0 Hz), 3.13 (3H, s), 3.65 (3H, s);
^{13}C NMR ($CDCl_3$) (100 MHz): δ = 3.4, 14.1, 31.6, 32.1, 61.1, 75.8, 77.9, 172.6;
Anal. Calcd for $C_8H_{13}O_2N$: C, 61.91; H, 8.44; N, 9.03%. Found: C, 61.69; H, 8.17; N, 8.75%.

To a THF solution (10 mL) of **s-4** (1.00 g, 4.44 mmol) was added 0.493 M ether solution (9.0 mL, 4.44 mmol) of (*4Z*)-5-phenylpent-4-enylmagnesium bromide at 0 °C, and the mixture was stirred at 0 °C for 2 h. To the reaction mixture was added saturated NH_4Cl solution, and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was subjected to SiO_2 column chromatography with hexane-EtOAc (9 : 1) as an eluent to afford acyclic ynone **13** (707 mg, 2.94 mmol) in 66 % yield.

(1*Z*)-1-phenylundec-1-en-9-yn-6-one (13)
IR (neat) 2920, 1715, 1494, 1098, 700 cm^{-1};
^{1}H NMR ($CDCl_3$) (400 MHz): δ = 1.70-1.80 (5H, m), 2.30-2.39 (4H, m), 2.43 (2H, t, *J* = 7.6 Hz), 2.55 (2H, t, *J* = 7.6 Hz), 5.62 (1H, dt, *J* = 11.6, 7.2 Hz), 6.45 (1H, d, *J* = 11.6 Hz), 7.19-7.35 (5H, m);
^{13}C NMR ($CDCl_3$) (100 MHz): δ = 3.5, 13.4, 23.8, 27.9, 42.0, 42.1, 76.0, 77.7, 126.5, 128.1, 128.6, 129.6, 131.7, 137.4, 208.8;
Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39%. Found: C, 84.74; H, 8.62%.

7c was prepared by the similar method for **13**.
1-phenyloct-6-yn-3-one (7c)
IR (neat) 2920, 1715, 1496, 1370, 1092, 700 cm^{-1};
^{1}H NMR ($CDCl_3$) (500 MHz): δ = 1.74 (3H, t, *J* = 2.6 Hz), 2.36-2.41 (2H, m), 2.58 (2H, t, *J* = 7.6 Hz), 2.75 (2H, t, *J* = 7.4 Hz), 2.91 (2H, t, *J* = 7.9 Hz), 7.16-7.21 (3H, m), 7.28 (2H, t, *J* = 7.7 Hz);
^{13}C NMR ($CDCl_3$) (125 MHz): δ = 3.4, 13.3, 29.6, 42.1, 44.3, 76.1, 77.6, 126.1, 128.3, 128.5, 141.0, 208.2;
Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05%. Found: C, 83.75; H, 8.26%.



7d

Preparation of 2,2-dimethyl-1-phenylhex-4-yn-1-one (7d):

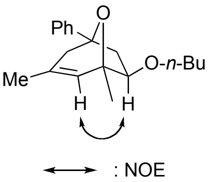
To a toluene solution (40 mL) of isobutyrophenone (589 mg, 4.00 mmol) and 1-bromo-2-butyne (1.05 mL, 12.0 mmol) was added potassium *tert*-butoxide (1.33 g, 12.0 mmol), and the resulting mixture was refluxed for ca. 48 h. Then, 1N HCl solution was added to the mixture, and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. Solvent was removed under reduced pressure to give a mixture of **7d** and isobutyrophenone which was separated by Kugelrohr. Further purification was done by GPC.

2,2-dimethyl-1-phenylhex-4-yn-1-one (7d)
IR (neat) 2969, 2921, 1677, 1468, 962, 702 cm^{-1};
^{1}H NMR ($CDCl_3$) (300 MHz): δ = 1.39 (6H, s), 1.76 (3H, t, *J* = 2.6 Hz), 2.51 (2H, q, *J* = 2.6 Hz), 7.36-7.50 (3H, m), 7.61-7.68 (2H, m);
^{13}C NMR ($CDCl_3$) (75 MHz): δ = 3.5, 25.3, 30.4, 47.7, 75.9, 78.1, 127.4, 128.0, 130.7, 138.9, 208.3;
Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05%. Found: C, 83.73; H, 8.12%.

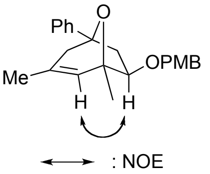
General procedure for platinum-catalyzed reaction of acyclic γ,δ-ynone with alkenes:

Alkene (0.5-1.0 mmol) was added to a mixture of acyclic γ,δ-ynone (0.1 mmol) , platinum(II) chloride (0.01 mmol) and MS4A (100 mg per 1mL of toluene) in toluene (1.0 mL) at room temperature, and then the mixture was stirred at room temperature. After disappearance of the γ,δ-ynone was confirmed by TLC, the reaction was quenched with saturated aq. $NaHCO_3$ and the reaction mixture was filtered through a short pad of Celite®. Organic layer was extracted with ethyl acetate three times and the combined organic layer was washed with brine, then dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silicagal chromatography to afford a 8-oxabicyclo[3.2.1]octane derivative.

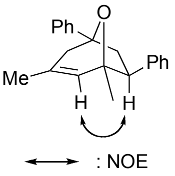
The stereochemistry of the products was determined by measurement of NOE spectra. Observed important correlations were shown in the compound figures.



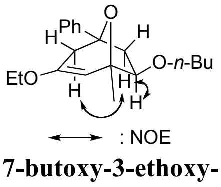
7-butoxy-1,3-dimethyl-5-phenyl-8-oxa-bicyclo[3.2.1]oct-2-ene (2a)
IR (neat) 2931, 1670, 1447, 1360, 1088, 902, 700 cm^{-1};
^{1}H NMR (CDCl$_3$) (500 MHz): δ = 0.88 (3H, t, J = 7.4 Hz), 1.30-1.38 (2H, m), 1.45 (3H, s), 1.46-1.53 (2H, m), 1.68 (3H, s), 2.06 (1H, d, J = 17.4 Hz), 2.09 (1H, d, J = 13.6 Hz), 2.43-2.51 (2H, m), 3.28 (1H, dt, J = 9.4, 6.6 Hz), 3.39 (1H, dt, J = 9.4, 6.5 Hz), 3.71 (1H, dd, J = 6.5, 1.0 Hz), 5.54 (1H, s), 7.23 (1H, t, J = 7.4 Hz), 7.33 (2H, t, J = 7.9 Hz), 7.47 (2H, d, J = 8.1 Hz);
^{13}C NMR (CDCl$_3$) (125 MHz): δ = 13.9, 18.7, 19.4, 22.2, 31.9, 44.6, 47.2, 69.0, 81.5, 82.2, 86.0, 124.5, 126.6, 128.0, 128.1, 132.8, 147.0;
Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15%. Found: C, 79.45; H, 9.35%.



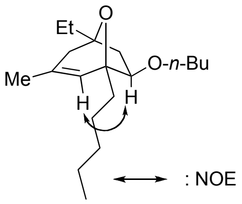
7-(4-methoxyphenylmethoxy)-1,3-dimethyl-5-phenyl-8-oxa-bicyclo[3.2.1]oct-2-ene (2b)
IR (neat) 2932, 1613, 1513, 1247 cm^{-1};
^{1}H NMR (CDCl$_3$) (500 MHz): δ = 1.49 (3H, s), 1.66 (3H, s), 2.06 (1H, d, J = 17.1 Hz), 2.17 (1H, d, J = 13.5 Hz), 2.45-2.51 (2H, m), 3.80 (3H, s), 3.80-3.82 (1H, m), 4.32 (1H, d, J = 12.0 Hz), 4.47 (1H, d, J = 12.0 Hz), 5.51 (1H, s), 6.86 (2H, d, J = 8.7 Hz), 7.20-7.26 (3H, m), 7.34 (2H, t, J = 7.9 Hz), 7.49 (2H, d, J = 7.1 Hz);
^{13}C NMR (CDCl$_3$) (125 MHz): δ = 18.9, 22.2, 44.5, 47.2, 55.2, 70.3, 81.5, 82.1, 84.7, 113.7, 124.4, 126.6, 127.8, 128.2, 129.0, 130.7, 133.0, 146.6, 159.0;
Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.83; H, 7.48%. Found: C, 78.59; H, 7.51%.



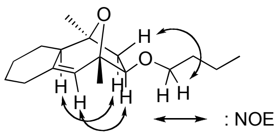
1,3-dimethyl-5,7-diphenyl-8-oxa-bicyclo[3.2.1]oct-2-ene (2c)
IR (KBr) 2898, 1493, 1447, 1094, 767, 708 cm^{-1};
^{1}H NMR (CDCl$_3$) (500 MHz): δ = 0.98 (3H, s), 1.72 (3H, s), 2.22 (1H, d, J = 16.6 Hz), 2.33 (1H, dt, J = 13.3, 1.8 Hz), 2.49 (1H, d, J = 17.0 Hz), 2.90 (1H, dd, J = 13.2, 9.1 Hz), 3.38 (1H, dd, J = 9.1, 2.3 Hz), 5.72 (1H, s), 7.06 (2H, d, J = 6.9 Hz), 7.14 (1H, t, J = 7.2 Hz), 7.19 (2H, t, J = 7.4 Hz), 7.29 (1H, t, J = 7.4 Hz), 7.40 (2H, d, J = 7.5 Hz), 7.56 (2H, d, J = 8.2 Hz);
^{13}C NMR (CDCl$_3$) (125 MHz): δ = 21.4, 22.1, 46.8, 48.0, 57.9, 82.0, 82.2, 124.2, 126.1, 126.5, 128.0, 128.2, 128.5, 131.1, 131.2, 144.1, 146.9;
Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64%. Found: C, 86.72; H, 7.69%.



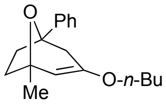
7-butoxy-3-ethoxy-1-methyl-5-phenyl-8-oxa-bicyclo[3.2.1]oct-2-ene (2d)
IR (neat) 2931, 1718, 1658, 1604, 1447, 1297, 1099 cm^{-1};
^{1}H NMR (CDCl$_3$) (500 MHz): δ = 0.89 (3H, t, J = 7.4 Hz), 1.30 (3H, t, J = 7.0 Hz), 1.30-1.40 (2H, m), 1.50 (3H, s), 1.43-1.56 (2H, m), 2.07 (1H, d, J = 13.5 Hz), 2.25 (1H, d, J = 16.3 Hz), 2.54 (1H, dd, J = 13.6, 6.4 Hz), 2.62 (1H, d, J = 16.3 Hz), 3.29 (1H, dt, J = 9.4, 6.6 Hz), 3.39 (1H, dt, J = 9.4, 6.6 Hz), 3.70-3.79 (3H, m), 4.71 (1H, s), 7.23 (1H, t, J = 6.2 Hz), 7.33 (2H, t, J = 7.9 Hz), 7.47 (2H, d, J = 8.1 Hz);
^{13}C NMR (CDCl$_3$) (125 MHz): δ = 13.9, 14.5, 19.4, 19.6, 31.9, 42.0, 47.1, 62.2, 68.9, 81.4, 81.8, 87.0, 100.9, 124.5, 126.7, 128.2, 146.2, 153.6;
Anal. Calcd for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92%. Found: C, 75.94; H, 9.22%.



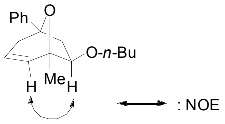
7-butoxy-5-ethyl-3-methyl-1-pentyl-8-oxa-bicyclo[3.2.1]oct-2-ene (2e)
IR (neat) 2959, 2930, 2871, 1462, 1093 cm^{-1};
^{1}H NMR ($CDCl_3$) (500 MHz): δ = 0.85 (6H, m), 0.95 (3H, t, J = 7.5 Hz), 1.24-1.45 (8H, m), 1.45-1.58 (2H, m), 1.63 (3H, s), 1.60-1.80 (6H, m), 1.94 (1H, dd, J = 13.4, 6.4 Hz), 2.21 (1H, dd, J = 17.0 Hz), 3.21 (1H, dt, J = 9.2, 6.6 Hz), 3.42 (1H, dt, J = 9.3, 6.3 Hz), 3.60 (1H, d, J = 6.1 Hz), 5.51 (1H, s);
^{13}C NMR ($CDCl_3$) (125 MHz): δ = 8.6, 13.9, 14.1, 19.5, 22.5, 22.6, 23.7, 31.9, 32.3, 32.7, 33.2, 41.9, 43.0, 68.6, 81.0, 84.3, 85.3, 126.2, 133.3;
Anal. Calcd for $C_{19}H_{34}O_2$: C, 77.50; H, 11.64%. Found: C, 77.29; H, 11.86%.



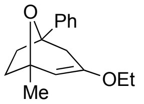
4-butoxy-3,6-dimethyl-12-oxatricyclo[5.4.0.1^{3,6}]undec-1-ene (6)
IR (neat) 2931, 2857, 1444, 1376, 1092 cm^{-1};
^{1}H NMR ($CDCl_3$) (500 MHz): δ = 0.90 (3H, t, J = 7.4 Hz), 1.30 (3H, s), 1.32 (3H, s), 1.23-1.47 (5H, m), 1.48-1.58 (2H, m), 1.74 (1H, d, J = 13.5 Hz), 1.76-1.90 (4H, m), 2.05 (1H, dd, J = 13.5, 6.6 Hz), 2.09-2.14 (1H, m), 3.28 (1H, dt, J = 9.4, 6.7 Hz), 3.42 (1H, dt, J = 9.4, 6.5 Hz), 3.55 (1H, d, J = 6.0 Hz), 5.37 (1H, s);
^{13}C NMR ($CDCl_3$) (125 MHz): δ = 13.9, 18.8, 19.4, 23.8, 26.4, 28.8, 29.3, 31.9, 35.4, 47.7, 49.7, 69.1, 79.5, 81.8, 86.5, 124.5, 141.0;
Anal. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67%. Found: C, 77.32; H, 10.64%.



3-butoxy-1-methyl-5-phenyl-8-oxa-bicyclo[3.2.1]oct-2-ene (8a)
IR (neat) 2959, 2931, 1722, 1656, 1604, 1447, 1364, 1305 cm^{-1};
^{1}H NMR ($CDCl_3$) (500 MHz): δ = 0.94 (3H, t, J = 7.4 Hz), 1.41 (2H, sext, J = 7.3 Hz), 1.53 (3H, s), 1.65 (2H, quint, J = 6.6 Hz), 1.79-1.86 (1H, m), 2.06-2.13 (2H, m), 2.27-2.34 (1H, m), 2.34 (1H, d, J = 16.2 Hz), 2.63 (1H, d, J = 16.1 Hz), 3.60-3.72 (2H, m), 4.80 (1H, s), 7.23 (1H, t, J = 7.3 Hz), 7.34 (2H, t, J = 8.0 Hz), 7.45 (2H, d, J = 8.1 Hz);
^{13}C NMR ($CDCl_3$) (125 MHz): δ = 13.8, 19.4, 24.6, 31.1, 38.9, 43.2, 43.6, 66.5, 79.3, 82.6, 102.0, 124.2, 126.6, 128.2, 146.9, 153.0;
Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88%. Found: C, 79.47; H, 9.16%.

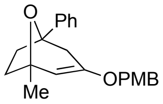


7-butoxy-1-methyl-5-phenyl-8-oxa-bicyclo[3.2.1]oct-2-ene (9a)
IR (neat) 2958, 2932, 1100, 1017, 699 cm^{-1};
^{1}H NMR ($CDCl_3$) (400 MHz): δ = 0.89 (3H, t, J = 7.6 Hz), 1.35 (2H, sextet, J = 7.2 Hz), 1.47 (3H, s), 1.45-1.60 (2H, m), 2.12 (1H, d, J = 13.6 Hz), 2.21 (1H, dd, J = 17.6, 4.0 Hz), 2.50-2.58 (2H, m), 3.26-3.34 (1H, m), 3.37-3.45 (1H, m), 3.76 (1H, d, J = 6.4 Hz), 5.74 (1H, dt, J = 9.2, 2.0 Hz), 5.84 (1H, d, J = 10.4 Hz), 7.23 (1H, t, J = 7.2 Hz), 7.33 (2H, t, J = 7.6 Hz), 7.47 (2H, d, J = 7.6 Hz);
^{13}C NMR ($CDCl_3$) (100 MHz): δ = 13.9, 18.6, 19.4, 31.9, 39.8, 47.5, 69.1, 81.7, 82.5, 86.0, 124.4, 124.8, 126.5, 128.1, 134.0, 146.6;
Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88%. Found: C, 79.13; H, 9.06%.

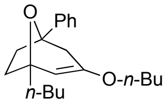


3-ethoxy-1-methyl-5-phenyl-8-oxa-bicyclo[3.2.1]oct-2-ene (8b)
IR (neat) 2975, 2929, 1656, 1372, 1209, 1173, 700 cm^{-1};

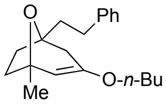
^{1}H NMR (CDCl$_3$) (500 MHz): δ = 1.30 (3H, t, *J* = 12.4 Hz), 1.53 (3H, s), 1.79-1.86 (1H, m), 2.06-2.13 (2H, m), 2.27-2.32 (1H, m), 2.35 (1H, d, *J* = 16.0 Hz), 2.64 (1H, d, *J* = 16.1 Hz), 3.67-3.79 (2H, m), 4.80 (1H, s), 7.24 (1H, t, *J* = 7.4 Hz), 7.34 (2H, t, *J* = 7.9 Hz), 7.45 (2H, d, *J* = 8.2 Hz);
^{13}C NMR (CDCl$_3$) (125 MHz): δ = 14.5, 24.6, 38.9, 43.2, 43.6, 62.2, 79.2, 82.6, 102.1, 124.2., 126.6, 128.2, 146. 8, 152.8;
Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25%. Found: C, 78.42; H, 8.19%.



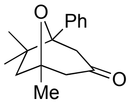
3-(4-methoxyphenylmethoxy)-1-methyl-5-phenyl-8-oxa-bicyclo[3.2.1]oct-2-ene (8c)
IR (KBr) 2930, 1652, 1613, 1515, 1361, 1303, 1253, 1168 cm^{-1};
^{1}H NMR (CDCl$_3$) (500 MHz): δ = 1.56 (3H, s), 1.81-1.88 (1H, m), 2.08-2.15 (2H, m), 2.28-2.36 (1H, m), 2.41 (1H, d, *J* = 16.2 Hz), 2.69 (1H, d, *J* = 16.2 Hz), 3.81 (3H, s), 4.65 (1H, d, *J* = 10.9 Hz), 4.69 (1H, t, *J* = 10.9 Hz), 4.94 (1H, s), 6.89 (2H, d, *J* = 8.7 Hz), 7.24 (1H, t, *J* = 7.5 Hz), 7.28 (2H, d, *J* = 8.6 Hz), 7.34 (2H, t, *J* = 7.5 Hz), 7.45 (2H, d, *J* = 7.1 Hz);
^{13}C NMR (CDCl$_3$) (125 MHz): δ = 24.6, 38.9, 43.2, 43.6, 55.3, 68.7, 79.3, 82.6, 102.8, 113.9, 124.2, 126.6, 128.2, 129.1, 129.3, 146.7, 153.0, 159.4;
Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19%. Found: C, 78.77; H, 7.37%.



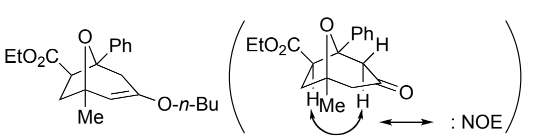
3-butoxy-1-butyl-5-phenyl-8-oxa-bicyclo[3.2.1]oct-2-ene (8d)
IR (neat) 2957, 1655, 1364, 700 cm^{-1};
^{1}H NMR (CDCl$_3$) (500 MHz): δ = 0.92-0.98 (6H, m), 1.36-1.46 (4H, m), 1.46-1.56 (2H, m), 1.66 (2H, quint, *J* = 6.6 Hz), 1.76-1.88 (3H, m), 1.97-2.09 (2H, m), 2.29 (1H, dt, *J* = 12.4, 8.5 Hz), 2.35 (1H, d, *J* = 16.1 Hz), 2.63 (1H, d, *J* = 16.1 Hz), 3.64 (1H, dt, *J* = 9.3, 6.7 Hz), 3.71 (1H, dt, *J* = 9.3, 6.7 Hz), 4.82 (1H, s), 7.23 (1H, tt, *J* = 7.3, 1.2 Hz), 7.33 (2H, t, *J* = 7.9 Hz), 7.44 (2H, d, *J* = 8.1 Hz);
^{13}C NMR (CDCl$_3$) (125 MHz): δ = 13.9, 14.1, 19.4, 23.4, 26.7, 31.1, 37.9, 38.5, 41.2, 43.8, 66.5, 81.8, 82.2, 101.1, 124.2, 126.5, 128.1, 147.1, 153.0;
Anal. Calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62%. Found: C, 79.99; H, 9.49%.



3-butoxy-1-methyl-5-phenethyl-8-oxa-bicyclo[3.2.1]oct-2-ene (8e)
IR (neat) 2929, 1655, 1604, 1496, 1456, 1364 cm^{-1};
^{1}H NMR (CDCl$_3$) (500 MHz): δ = 0.94 (3H, t, *J* = 7.4 Hz), 1.37-1.46 (2H, m), 1.44 (3H, s), 1.61-1.69 (2H, m), 1.69-1.78 (1H, m), 1.81-1.90 (2H, m), 1.93-2.06 (4H, m), 2.51 (1H, d, *J* = 16.0 Hz), 2.73 (2H, dd, *J* = 9.6, 7.8 Hz), 3.58-3.69 (2H, m), 4.73 (1H, s), 7.15-7.25 (3H, m), 7.25-7.30 (2H, m);
^{13}C NMR (CDCl$_3$) (125 MHz): δ = 13.9, 19.4, 24.6, 30.3, 31.1, 35.2, 41.6, 42.0, 43.1, 66.4, 78.8, 81.5, 102.1, 125.7, 128.3, 128.3, 142.4, 153.1;
Anal. Calcd for $C_{20}H_{28}O_2$: C, 79.96; H, 9.39%. Found: C, 79.73; H, 9.29%.

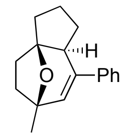


1,6,6-trimethyl-5-phenyl-8-oxa-bicyclo[3.2.1]octan-3-one (8f)
IR (KBr) 2963, 1709, 1307, 769, 713 cm^{-1};
^{1}H NMR (CDCl$_3$) (500 MHz): δ = 0.62 (3H, s), 1.16 (3H, s), 1.55 (3H, s), 1.76-1.82 (2H, m), 2.37 (1H, dd, *J* = 15.0, 1.5 Hz), 2.44 (1H, d, *J* = 16.0 Hz), 2.52 (1H, d, *J* = 15.0 Hz), 3.14 (1H, dd, *J* = 16.0, 1.5 Hz), 7.24-7.37 (5H, m);
^{13}C NMR (CDCl$_3$) (125 MHz): δ = 24.1, 27.3, 29.9, 46.9, 50.5, 52.8, 54.8, 78.3, 87.9, 127.0, 128.0, 142.2, 208.5;
Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25%. Found: C, 78.45; H, 8.53%.



ethyl 3-butoxy-1-methyl-5-phenyl-8-oxa-bicyclo[3.2.1]oct-2-ene-6-carboxylate (8h)
IR (neat) 2959, 2934, 1735, 1657, 1179, 699 cm^{-1};

^{1}H NMR ($CDCl_3$) (400 MHz): δ = 0.81 (3H, t, *J* = 7.2 Hz), 0.94 (3H, t, *J* = 7.2 Hz), 1.41 (2H, sext, *J* = 7.6 Hz), 1.57-1.70 (2H, m), 1.59 (3H, s), 2.25-2.35 (2H, m), 2.63-2.73 (2H, m), 3.27-3.41 (2H, m), 3.52-3.73 (3H, m), 4.82 (1H, s), 7.18-7.32 (3H, m), 7.45 (2H, d, *J* = 6.8 Hz);
^{13}C NMR ($CDCl_3$) (125 MHz): δ = 13.6, 13.8, 19.3, 24.4, 31.0, 43.2, 47.4, 55.7, 60.2, 66.6, 79.1, 85.1, 101.8, 125.3, 127.2, 127.5, 141.8, 152.5, 172.9;
Anal. Calcd for $C_{21}H_{28}O_4$: C, 73.23; H, 8.19%. Found: C, 73.11; H, 8.25%.



4-methyl-2-phenyl-11-oxatricyclo[5.3.0.1^{4,7}]dec-2-ene (14)
IR (neat) 2964, 2868, 1121, 757, 694 cm^{-1};
^{1}H NMR ($CDCl_3$) (500 MHz): δ = 1.49 (3H, s), 1.51-1.57 (1H, m), 1.67-1.77 (2H, m), 1.85-1.95 (2H, m), 1.95-2.10 (5H, m), 2.46-2.52 (1H, m), 6.13 (1H, d, *J* = 1.4 Hz), 7.22-7.26 (1H, m), 7.32 (2H, t, *J* = 7.8 Hz), 7.38-7.42 (2H, m);
^{13}C NMR ($CDCl_3$) (125 MHz): δ =22.8, 24.0, 31.3, 33.9, 36.1, 40.4, 49.0, 79.3, 89.2, 125.6, 127.2, 128.3, 131.4, 137.4, 139.6;
Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39%. Found: C, 84.73; H, 8.42.

Reference

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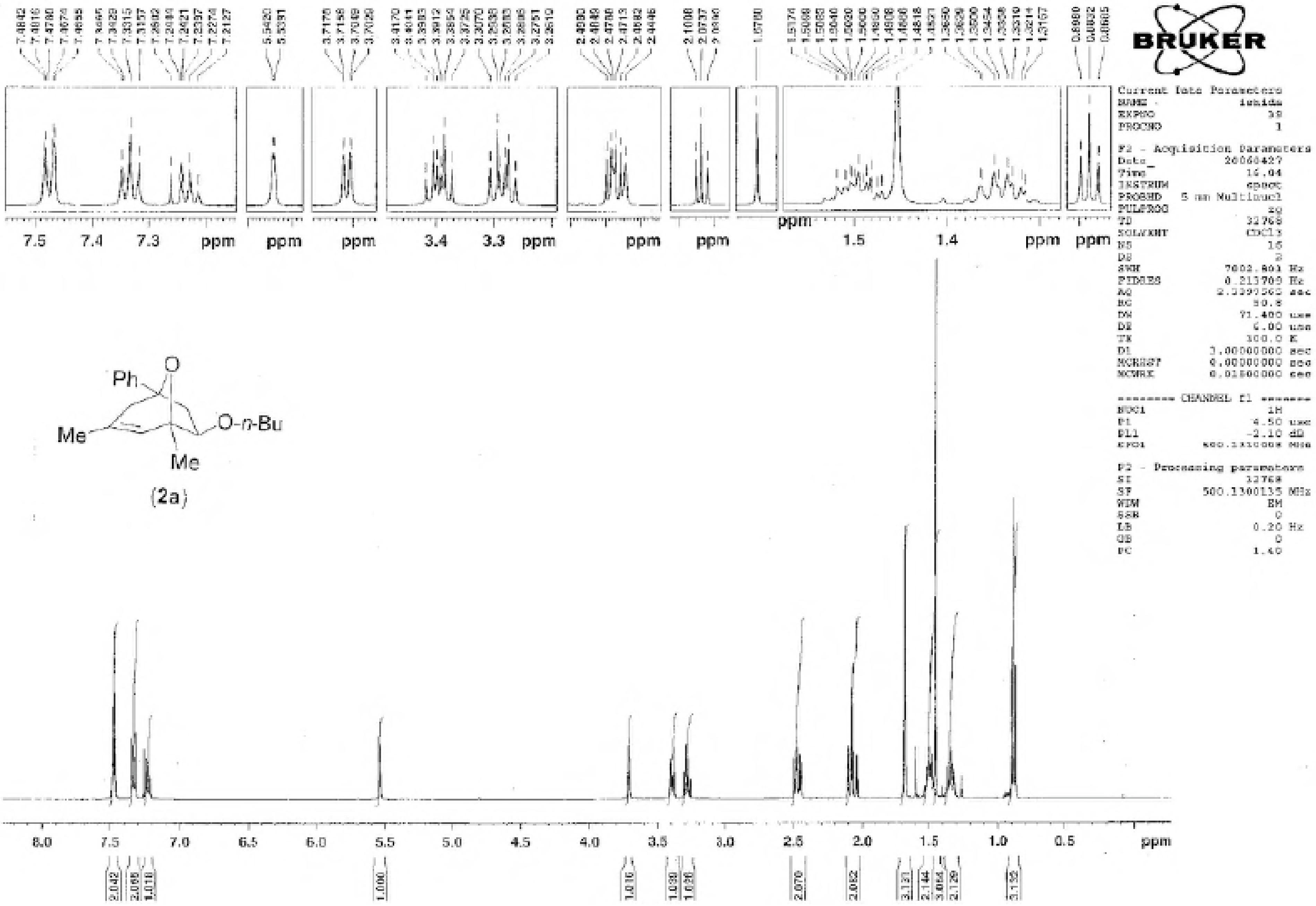

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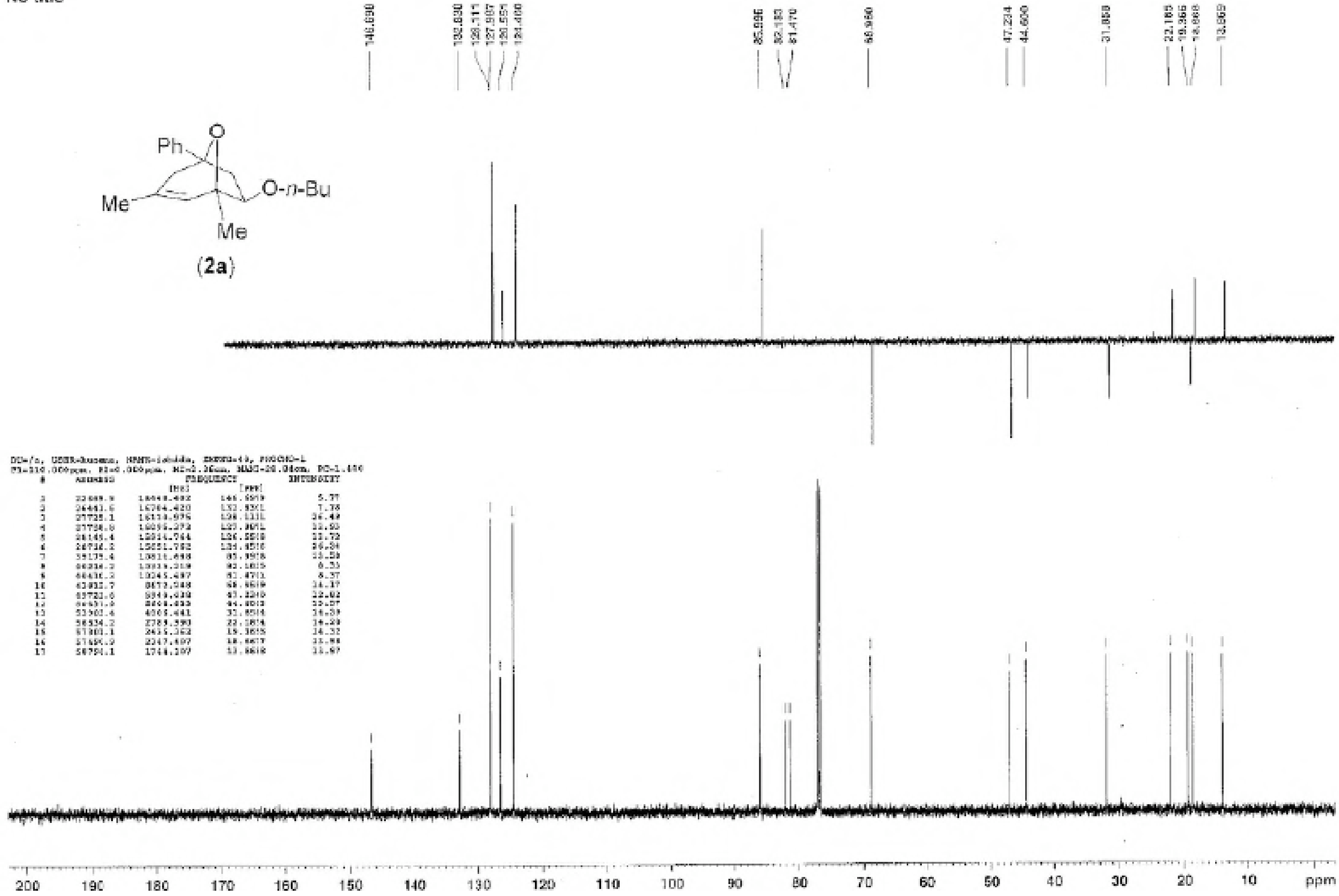
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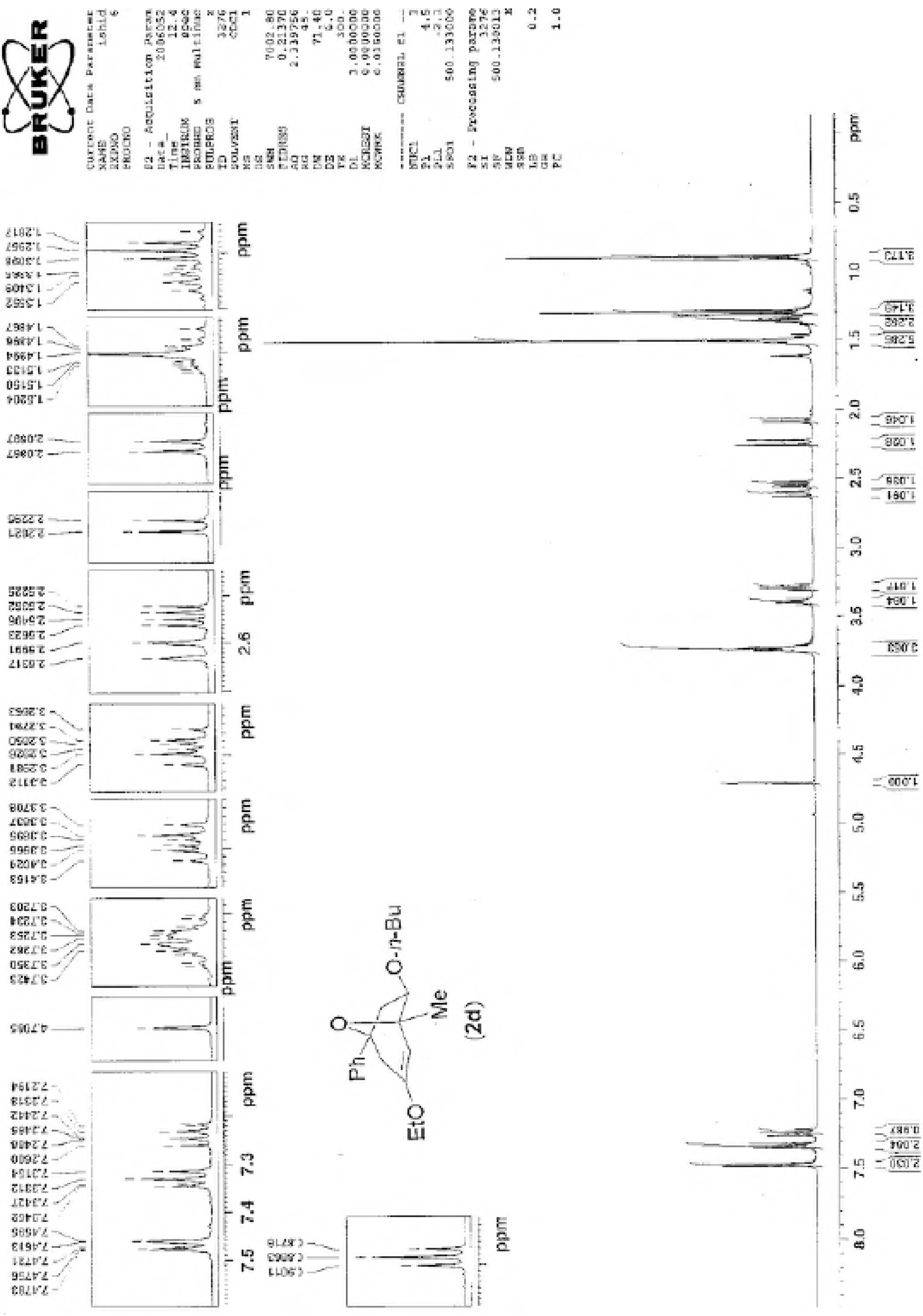
127.987
126.551
124.400
85.996
82.183
81.470
68.960
47.234
44.600
31.858
22.185
19.366
18.868
13.869
Ph
O
Me
O-n-Bu
Me
(2a)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


BRUKER
Current Data Parameters
F2 - Acquisition Parameters
SOLVENT CDCl3
SF 500.130013
EtO
Ph
O
O-n-Bu
Me
(2d)
ppm
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1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
3.173
3.140
2.202
5.285
1.046
1.088
1.026
1.061
1.017
1.064
3.053
1.000
0.987
2.064
2.030
7.4783
7.4756
7.4731
7.4613
7.4585
7.4402
7.3427
7.3312
7.3164
7.2600
7.2408
7.2486
7.2442
7.2318
7.2194
4.7065
3.7425
3.7350
3.7282
3.7253
3.7234
3.7203
3.4153
3.4029
3.3966
3.3895
3.3837
3.3708
3.3112
3.2981
3.2926
3.2850
3.2791
3.2663
2.6317
2.5991
2.5623
2.5406
2.5082
2.2825
2.2621
2.2295
2.0867
2.0587
1.6204
1.5150
1.5133
1.4994
1.4896
1.4867
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1.3365
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1.2957
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0.9011
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0.8718

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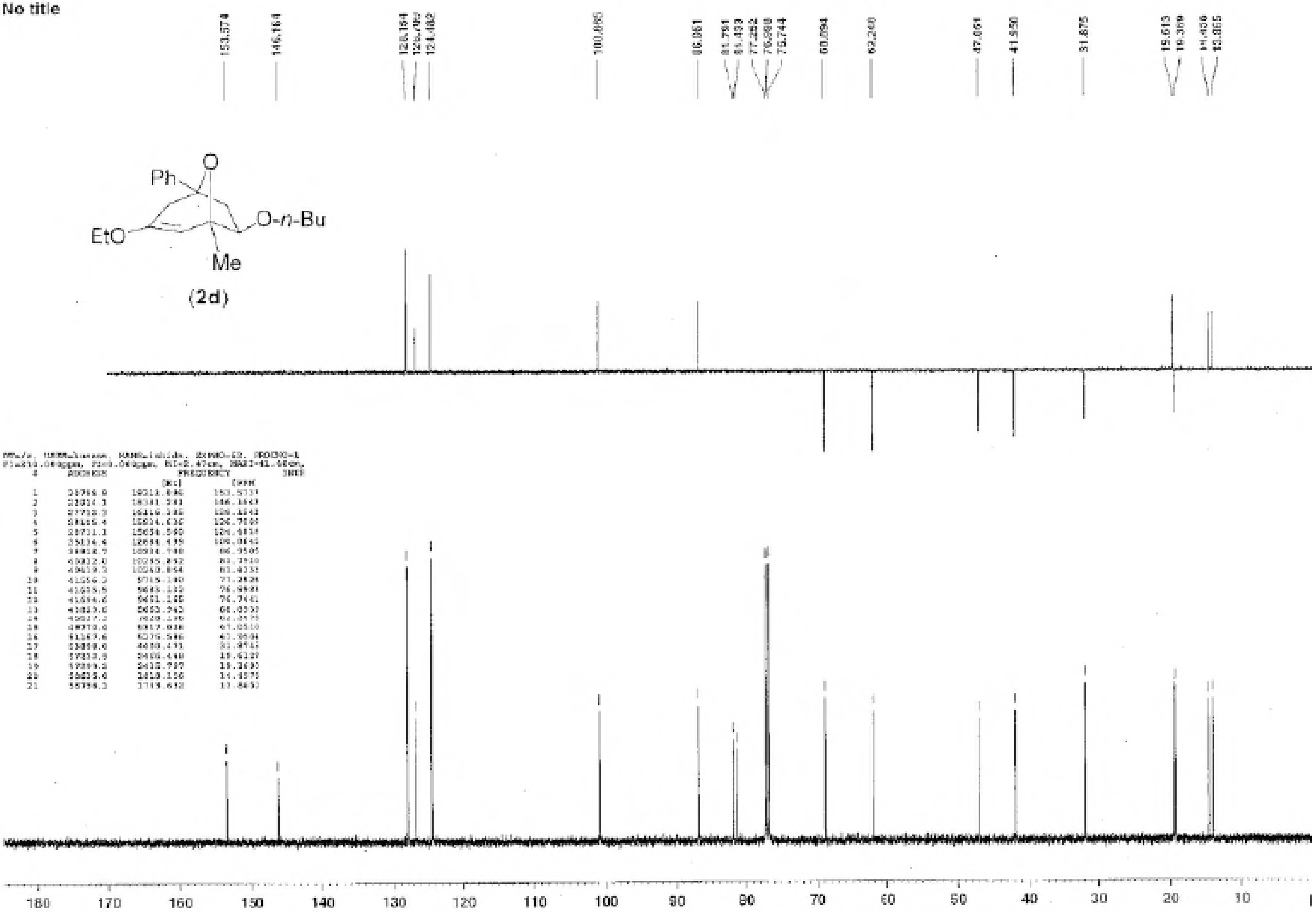
(2d)

153.574
146.164
128.164
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124.482
100.865
86.351
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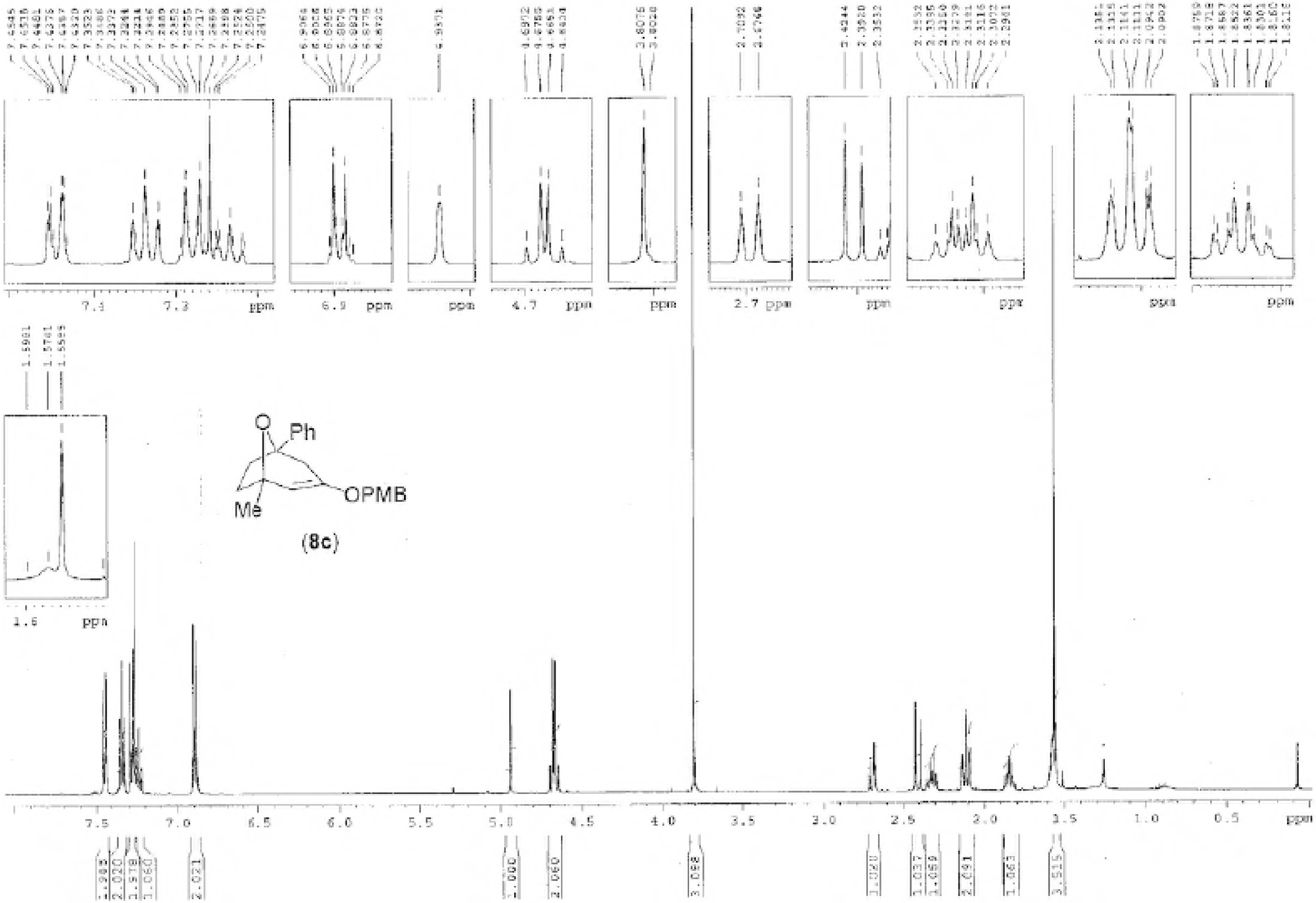
81.433
77.262
76.880
75.744
68.894
62.240
47.061
41.950
31.875
19.613
19.369
14.456
13.865
Ph
O
EtO
O-n-Bu
Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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7.4518
7.4461
7.4375
7.4397
7.4320
7.3523
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7.3372
7.3244
7.3214
7.2946
7.2889
7.2852
7.2755
7.2717
7.2669
7.2598
7.2524
7.2500
7.2475
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6.9028
6.8965
6.8876
6.8833
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6.8720
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2.3930
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2.3632
2.3395
2.3350
2.3279
2.3181
2.3116
2.3072
2.2961
2.1381
2.1335
2.1141
2.1111
2.0942
2.0902
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1.8522
1.8361
1.8301
1.8160
1.8116
1.5901
1.5741
1.5569
7.4
7.3
6.9
4.7
2.7
1.6
ppm
O
Ph
OPMB
Me
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.983
2.020
1.978
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2.060
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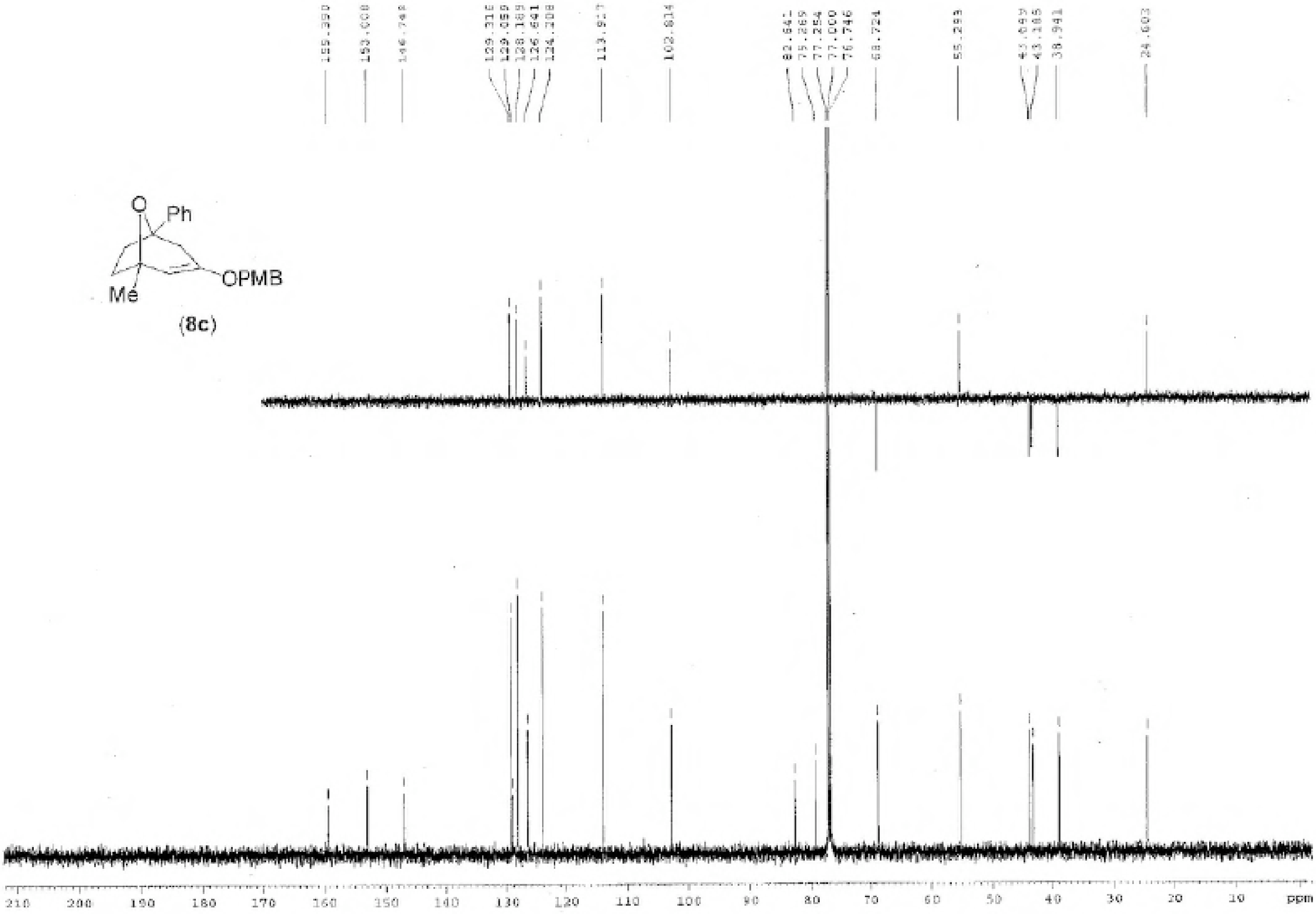
1.059
2.091
1.063
3.515

(8c)


(8c)
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146.748
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129.059
128.189
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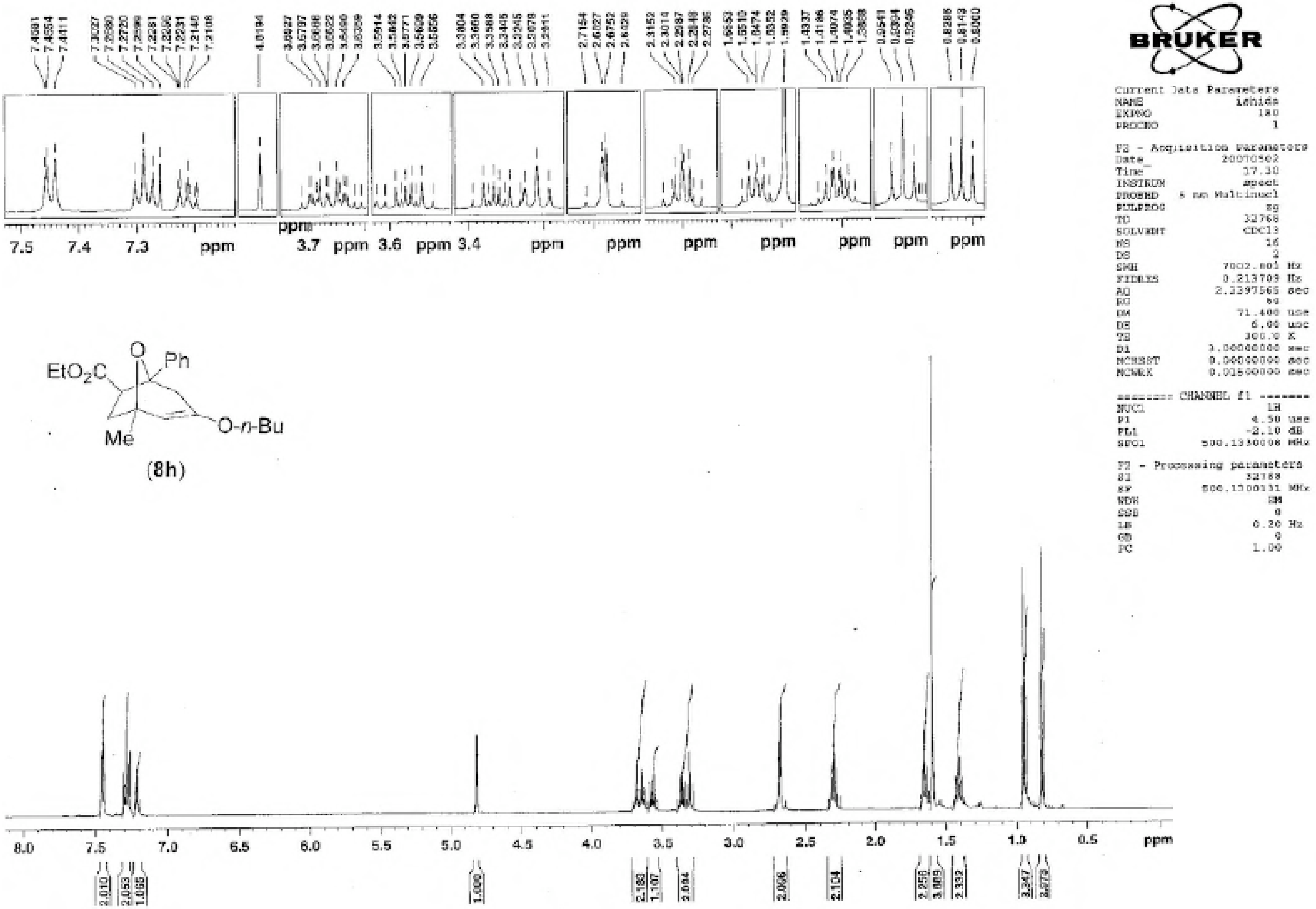
124.208
113.917
102.814
82.641
79.269
77.254
77.000
76.746
68.724
55.293
43.699
43.185
38.941
24.603
O
Ph
OPMB
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



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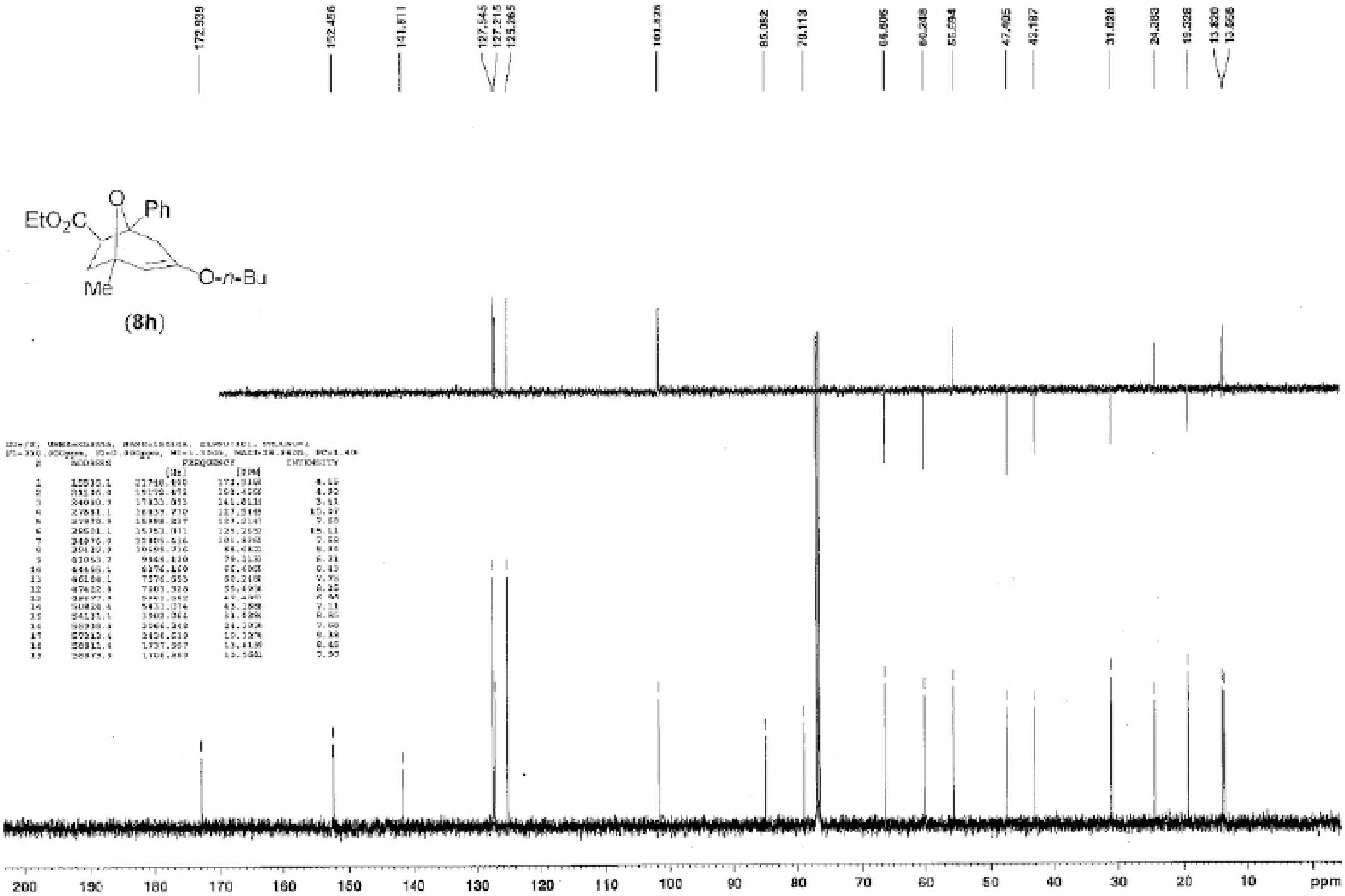
Current Data Parameters
NAME                 ishida
EXPNO                   180
PROCNO                    1

F2 - Acquisition Parameters
Date_              20070502
Time                  17.30
INSTRUM               spect
PROBHD   5 mm Multinucl
PULPROG                  zg
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                7002.801 Hz
FIDRES             0.213709 Hz
AQ                2.3397565 sec
RG                       64
DW                   71.400 usec
DE                     6.00 usec
TE                    300.0 K
D1               3.00000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                     4.50 usec
PL1                   -2.10 dB
SFO1            500.1330008 MHz

F2 - Processing parameters
SI                    32768
SF              500.1300131 MHz
WDW                      EM
SSB                       0
LB                     0.20 Hz
GB                        0
PC                     1.00
```

No title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127.545
127.215
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101.826
85.052
79.113
66.606
60.248
55.594
47.605
43.187
31.028
24.383
19.328
13.820
13.668
EtO2C
O
Ph
Me
O-n-Bu
(8h)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm