

Supporting Information

Aminoboranes as "Compatible" Iminium Ion Generators in Aminative C-C Bond Formations

Michinori Suginome,* Lars Uehlin, and Masahiro Murakami*

*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of
Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

Contents

General

Preparation of amino boranes

Aminative alkylation of aldehydes

General

All reactions were performed in a drybox or using Schlenk technique under a nitrogen atmosphere with magnetic stirring. ^1H NMR spectra were recorded on a Varian Mercury-400 (400 MHz) or Varian GEMINI-2000 (300 MHz) spectrometer using CDCl_3 or C_6D_6 as a solvent. ^{13}C NMR spectra were recorded on a Varian GEMINI-2000 spectrometer at 75 MHz with CDCl_3 as solvent. Chemical shifts of the ^{13}C NMR spectra were recorded relative to CDCl_3 (77.0 ppm). ^{11}B NMR spectra were recorded on a Varian GEMINI-2000 spectrometer at 1288 MHz with C_6D_6 as solvent. Chemical shifts of the ^{11}B NMR spectra were recorded relative to $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0 ppm). High resolution mass (FAB) spectra were recorded on a JEOL JMS-700 spectrometer.

Anhydrous solvents were purchased from Kanto Chemical Co., aldehydes and ketones dried over CaH_2 prior to distillation. Bis(diamino)chloroboranes were synthesized

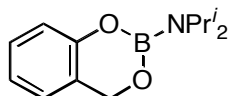
according to the literature.¹

Preparation of amino boranes

N,N-bis(diethylamino)(isopropoxy)borane (2)

n-Butyllithium (1.6 M of in hexane, 84 mmol) was added at 0 °C to diisopropylamine (12 mL, 84 mmol) in THF (100 mL). After stirring for 15 min, the reaction was cooled to -78 °C and isopropanol (6.4 mL, 84 mmol) was added. Stirring was continued for 30 min, then bis(diethylamino)chloroborane (12 g, 84 mmol) was added and the mixture allowed to warm up to room temperature. The solvent was removed in vacuo, the residue extracted with pentane (100 mL) and the desired compound purified by distillation (30-35 °C, 0.5 mbar). Yield: 15.3 g (83 %) colorless oil. ¹H NMR (C₆D₆) δ 0.97 (t, *J* = 7.6 Hz, 12H), 1.14 (d, *J* = 8.4 Hz, 6H), 2.90 (q, *J* = 7.6 Hz, 8H), 4.08 (h, *J* = 8.0 Hz, 1H); ¹³C NMR (C₆D₆) δ 15.1 (4C), 25.3 (2C), 40.3 (4C), 65.3. ¹¹B NMR (C₆D₆) δ 24.89.

N,N-diisopropyl-4H-benzo[d][1,3,2]dioxaborinin-2-amine (6)



Saligenin (1.45 g, 11.7 mmol) was dried by azeotropic distillation of toluene (15 mL). Cyclohexane (20 mL) was added, the mixture cooled in an ice bath and chlorobis(diisopropylamino)borane (2.88g, 11.7 mmol) was added. The mixture was allowed to warm up to room temperature and subsequently heated to 120 °C overnight. Removal of the formed lithium chloride by filtration followed by evaporation of the solvent in vacuo and Kugelrohr distillation of the remaining oil (90°C, 1 mbar) yielded 2.0 g of colorless product (73 %). ¹H NMR (C₆D₆) δ 1.16 (d, *J* = 8.8 Hz, 6H), 3.58 (h, *J* = 8.0 Hz, 2H), 4.60 (s, 2H), 6.47 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 6.68 (dt, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 6.90 (m, 2H) 7.77 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 2H); ¹³C NMR (C₆D₆) δ 23.1 (4C), 44.1 (2C), 62.6, 117.5, 121.6, 123.8, 124.7, 128.4, 15.2; ¹¹B NMR (C₆D₆) δ 19.84.

Three-Component Mannich Reactions Using Aldehyde, Silyl Ketene Acetal, and Amino Boranes

General procedure A Including Extractive Workup with Acid-Treatment

¹Chavant, P. Y.; Vaultier M.; *J. Organomet. Chem.* **1993**; 455; 37-46; Gerrard, W.; Lappert, M. F.; Pearce, C.A. *J.Chem Soc.* **1957**; 381-386

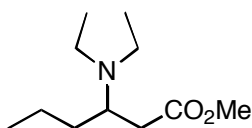
To a solution of aminoborane (**1—6**, 0.125 mmol) in *N*-methylpyrrolidinone (0.25 mL) were added 2-piperidinone (10% w/w solution in NMP, 25 mg, 0.025 mmol), aldehyde (0.25 mmol), and silyl ketene acetal (0.125 mmol) at room temperature with stirring. The mixture was stirred at room temperature for 2 h. To the reaction mixture were added ice water and *tert*-butyl methyl ether (15 mL) with stirring. Basic material was extracted from the organic phase three times with 5 ml 0.5 N hydrochloric acid. The combined acid layers were kept at 0 °C, washed with 10 ml *tert*-butyl methyl ether and the pH brought to 8 by addition of conc. ammonia solution. Organic materials were extracted with *tert*-butyl methyl ether three times and the combined organic layer was washed with 10 ml water. Evaporation left the crude products that showed purities of > 90% and were purified by column chromatography on silica gel (eluent: ethyl acetate/hexane). The reaction scale could be increased at least to a 4.4 mmol scale for the reaction shown as entry 5 in Table 2.

General procedure B: Non-Acidic Workup

Reactions were performed according to the procedure same as the general procedure A shown above. The reaction mixture was then diluted with ether (15 mL) and washed with ice-water three times. The organic layer was dried over K₂CO₃ and evaporated under vacuum. The crude material was purified by chromatography on silica gel using ethyl acetate/hexane mixture as an eluent.

The product shown as entries 1-6 in Table 1 and entry 1 in Table3 has been reported in the literature. (e.g., Saidi et al. *J. Chem. Soc. Perkin Trans. I* **1997**, 1983.) CAS registry No.: 193820-05-2.

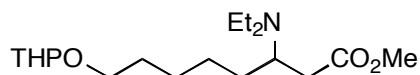
Methyl 3-(diethylamino)-hexanoate (Table 2, entry 1)



General Procedure A. Yield (0.125 mmol scale): 24 mg (96%). ¹H NMR (CDCl₃) δ 0.86 (t, J = 6.9 Hz, 3H), 0.96 (t, J = 6.9 Hz, 6H), 1.12-1.50 (m, 4H), 2.14-2.21 (m, 1H), 2.25-2.48 (m, 5H), 3.10 (quintet, J = 6.9 Hz, 1H), 3.62 (s, 3H); ¹³C NMR (CDCl₃) δ 14.1, 14.6, 20.1,

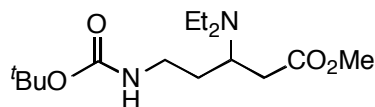
33.3, 36.0, 43.3, 51.4, 56.6, 173.7; IR (neat) 2965, 1740 cm^{-1} . Anal. Calcd. for $\text{C}_{11}\text{H}_{23}\text{NO}_2$: C, 65.63; H, 11.52; N, 6.96. Found: C, 65.54; H, 11.34; N, 6.76.

Methyl 3-(diethylamino)-8-(tetrahydro-2H-pyran-2-yloxy)octanoate (Table 2, entry 2; Table 3, entry 7)



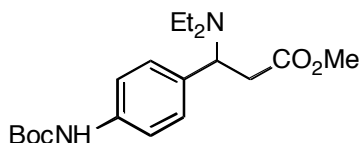
General Procedure B. Yield (0.125 mmol scale): 40 mg (Table 2, 98%) and 30 mg (Table 3, 73%). ^1H NMR (CDCl_3) δ 0.96 (t, J = 6.9 Hz, 6H), 1.19-1.82 (m, 9H), 2.15 (dd, J = 14.1 Hz, J = 6.9 Hz, 2H), 2.26-2.46 (m, 5H), 3.08 (quin, J = 6.9 Hz, 1H), 3.31-3.38 (m, 1H), 3.43-3.50 (m, 1H), 3.62 (s, 3H), 3.65-3.73 (m, 1H), 3.80-3.87 (m, 1H), 4.54 (brs, 1H); ^{13}C NMR (CDCl_3) δ 14.9 (2C), 19.9, 25.7, 26.6, 27.1, 30.0, 31.0, 31.3, 36.2, 43.5 (2C), 51.6, 57.1, 62.5, 67.8, 99.0, 173.9; IR (neat) 2939, 1740 cm^{-1} . Anal. Calcd. for $\text{C}_{18}\text{H}_{35}\text{NO}_4$: C, 65.62; H, 10.71; N, 4.25. Found: C, 65.51; H, 10.39; N, 3.76.

Methyl 5-(tert-butoxycarbonylamino)-3-(diethylamino)pentanoate (Table 2, entry 3)



General Procedure B. Yield (0.125 mmol scale): 24 mg (64%). ^1H NMR (CDCl_3) δ 1.03 (t, J = 7.2 Hz, 6H), 1.40 (s, 9H), 1.44-1.50 (m, 2H), 1.60-1.69 (m, 2H), 2.12 (dd, J = 17.7 Hz, J = 9.7 Hz, 1H), 2.20-2.31 (m, 2H), 2.48-2.60 (m, 3H), 3.01-3.10 (m, 1H), 3.12-3.23 (m, 1H), 3.26-3.39 (m, 1H), 3.64 (s, 3H), 5.76 (s (br), 1H); ^{13}C NMR (CDCl_3) δ 14.4 (2C), 28.7 (3C), 31.2, 34.3, 39.8, 43.4 (2C), 51.9, 56.8, 156.2, 173.5; IR (neat) 3368, 2974, 1720 cm^{-1} . Anal. Calcd. for $\text{C}_{15}\text{H}_{30}\text{N}_2\text{O}_4$: C, 59.57; H, 10.00; N, 9.26. Found: C, 59.27; H, 9.75; N, 9.21.

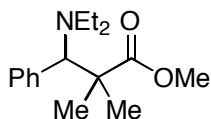
Methyl 3-(4-((tert-butoxycarbonyl)amino)phenyl)-3-(diethylamino)propanoate (Table 2, entry 4; Table 3, entry 8)



General Procedure B. Yield (0.125 mmol scale): 41 mg (Table 2, 64%) and 43 mg (Table 3, 98%). ^1H NMR (CDCl_3) δ 0.98 (t, J = 6.9 Hz, 6H), 1.49 (s, 9H), 2.20-2.31 (m, 2H), 2.46-2.53 (m, 2H), 2.63 (dd, J = 14.4 Hz, J = 8.1 Hz, 1H), 2.90 (dd, J = 14.4 Hz, J = 7.2 Hz, 1H),

4.23 (t, $J = 7.5$ Hz, 1H), 6.45 (s (br), 1H), 7.17 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 13.6 (2C), 28.6 (3C), 37.7, 43.4 (2C), 51.8, 60.0, 118.3 (2C), 129.0 (2C), 134.6, 137.5, 152.9, 172.7; IR (neat) 3343, 2974, 1732 cm^{-1} . HRMS (FAB) Calcd. for $\text{C}_{19}\text{H}_{30}\text{N}_2\text{O}_4 \cdot \text{H}^+$ (MH^+): 351.2278. Found: 351.2283.

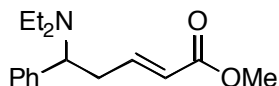
Methyl 3-(diethylamino)-2,2-dimethyl-3-phenylpropanoate (Table 2, entry 5)



General Procedure A. Yield (4.4 mmol scale): 0.93 g (81%); (0.125 mmol scale): 29 mg (88%). ^1H NMR (CDCl_3) δ 0.94 (t, $J = 7.2$ Hz, 6H), 1.04 (s, 3H), 1.32 (s, 3H), 2.34 (dq, $J = 13.2$ Hz, $J = 6.6$ Hz, 2H), 2.64 (dq, $J = 13.2$ Hz, $J = 4.2$ Hz, 2H), 3.60 (s, 3H), 4.02 (s, 1H), 7.23-7.30 (m, 5H); ^{13}C NMR (CDCl_3) δ 13.2 (2C), 21.9, 25.8, 44.9 (2C), 47.5, 51.6, 70.9, 126.9, 127.5 (2C), 130.4 (2C), 138.1, 178.4; IR (neat) 2970, 1740 cm^{-1} . HRMS for $\text{C}_{16}\text{H}_{25}\text{O}_2\text{N} \cdot \text{H}^+$: Calcd.: 264.1964. Found: 264.1964.

The product shown as entry 6 in Table 2 has been reported in the literature. See for example, Suginome, Lars, Murakami *Org. Lett.* **2004**, 6, 1167. CAS registry No.: 83188-04-9

Methyl (E)-5-(diethylamino)-5-phenylpent-2-enoate (eq 2)



General Procedure A. Yield (0.125 mmol scale): 32 mg (98%). ^1H NMR (CDCl_3) δ 0.99 (t, $J = 6.9$ Hz, 6H), 2.34 (dq, $J = 12.9$ Hz, $J = 6.9$ Hz, 2H), 2.54-2.66 (m, 2H), 3.45 (m, 3H), 2.72-2.83 (m, 1H), 3.66 (s, 3H), 3.80 (dd, $J = 11.2$ Hz, $J = 6.0$ Hz, 1H), 5.77 (dt, $J = 15.6$ Hz, $J = 1.5$ Hz, 1H), 6.87 (dt, $J = 15.6$ Hz, $J = 4.2$ Hz, 1H), 7.24-7.32 (m, 5H); ^{13}C NMR (CDCl_3) δ 13.1 (2C), 5.6, 43.3 (2C), 51.6, 63.6, 122.3, 127.3, 128.3 (2C), 128.6 (2C), 140.5, 147.5, 167.0; IR (neat) 2971, 1725, 1655 cm^{-1} . Anal. Calcd. for $\text{C}_{16}\text{H}_{23}\text{NO}_2$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.41; H, 8.73; N, 5.41.

Three-Component Mannich Reactions Using Aldehyde, *sec*-Amine, Silyl Ketene Acetal with Amino Boranes

General procedure A Including Extractive Workup with Acid-Treatment

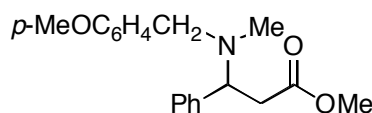
To a solution of diisopropylaminoborane (**11** or **12**, 0.125 mmol) in NMP (0.25 ml) were

added 2-piperidinone (0.025 mmol), aldehyde (0.19 mmol), and *sec*-amine (0.125 mmol). To the mixture was added the nucleophile (0.13 mmol); the mixture was stirred at room temperature for 1–3 h. To the reaction mixture were added ice water and *tert*-butyl methyl ether (15 mL) with stirring. Basic material was extracted from the organic phase three times with 5 ml 0.5 N hydrochloric acid. The combined acid layers were kept at 0 °C, washed with 10 ml *tert*-butyl methyl ether and the pH brought to 8 by addition of conc. ammonia solution. Organic materials were extracted with *tert*-butyl methyl ether three times and the combined organic layer was washed with 10 ml water. Evaporation left the crude products that showed purities of > 90% and were purified by column chromatography on silica gel (eluent: ethyl acetate/hexane).

General procedure B: Non-Acidic Workup

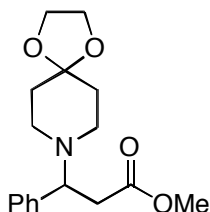
Reactions were performed according to the procedure same as the general procedure A shown above. The reaction mixture was then diluted with ether (15 mL) and washed with ice-water three times. The organic layer was dried over K₂CO₃ and evaporated under vacuum. The crude material was purified by chromatography on silica gel using ethyl acetate/hexane mixture as an eluent.

Methyl 3-[(4-methoxybenzyl)(methyl)amino]-3-phenylpropanoate (Table 3, entry 2)



General Procedure A. Yield (0.125 mmol scale): 28 mg (71%). ¹H NMR (CDCl₃) δ 2.07 (s, 3H), 2.72 (dd, *J* = 14.7 Hz, *J* = 7.2 Hz, 1H), 3.06 (dd, *J* = 14.7 Hz, *J* = 8.1 Hz, 2H), 3.24 (d, *J* = 13.2 Hz, 1H), 3.47 (d, *J* = 13.2 Hz, 1H), 3.63 (s, 3H), 3.78 (s, 3H), 4.42 (t, *J* = 7.5 Hz, 1H), 6.82 (dd, *J* = 6.3 Hz, *J* = 1.8 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.25–7.37 (m, 5H); ¹³C NMR (CDCl₃) δ = 37.6, 37.8, 51.9, 55.5, 58.0, 64.4, 113.8 (2C), 127.6, 128.3 (2C), 128.6 (2C), 130.0 (2C), 131.7, 138.4, 158.8, 172.6; IR (neat) 2951, 1740, 1512, 1246 cm⁻¹. Anal. Calcd. for C₁₉H₂₃NO₃: C, 72.82; H, 7.40; N, 4.47. Found: C, 72.76; H, 7.47; N, 4.53.

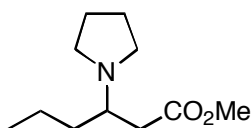
Methyl 3-(1,4-Dioxo-8-azaspiro[4,5]dec-8-yl)-3-phenylpropanoate (Table 3, entry 3)



General Procedure B. Yield (0.125 mmol scale): 32 mg (84%). ^1H NMR (CDCl_3) δ 1.66 (t, $J = 5.4$ Hz, 4H), 2.40-2.47 (m, 2H), 2.48-2.58 (m, 2H), 2.68 (dd, $J = 19.6, 10.0$ Hz, 1H), 2.98 (dd, $J = 19.6, 10.0$ Hz, 1H), 3.59 (s, 3H), 3.86 (s, 4H), 4.06 (t, $J = 7.8$ Hz, 1H), 7.20-7.33 (m, 5H); ^{13}C NMR (CDCl_3) δ 35.5 (2C), 38.3, 47.9 (2C), 51.8, 64.4 (2C), 65.7, 107.4, 127.6, 128.4 (4C), 138.8, 172.5; IR (neat) 2953, 1740 cm^{-1} . Anal. Calcd. for $\text{C}_{17}\text{H}_{23}\text{NO}_4$: C, 66.86; H, 7.59; N, 4.59. Found: C, 66.66; H, 7.66; N, 4.51.

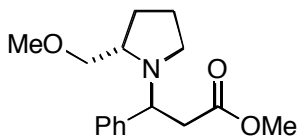
The product shown as entry 4 in Table 3 has been reported in the literature. See for example, Pacheco et al. *Bull. Chim. Soc. Fr.* **1962**, 1379. CAS registry No.: 7032-65-7.

Methyl 3-(pyrrolidin-1-yl)hexanoate (Table 3, entry 5)



General Procedure A. Yield (0.125 mmol scale): 23 mg (94%). ^1H NMR (CDCl_3) δ 0.87 (dt, $J = 6.9$ Hz, 3H), 1.28-1.52 (m, 4H), 1.67-1.74 (m, 4H), 2.32 (dd, $J = 14.7$ Hz, $J = 6.9$ Hz, 1H), 2.49-2.56 (m, 4H), 3.64 (s, 3H); ^{13}C NMR (CDCl_3) δ 14.5, 19.2, 23.7 (2C), 35.4, 36.7, 49.8 (2C), 51.7, 59.0, 173.7; IR (neat) 2959, 1740, 1458, 1437 cm^{-1} . Anal. Calcd. for $\text{C}_{11}\text{H}_{21}\text{NO}_2$: C, 66.29; H, 10.62; N, 7.03. Found: C, 66.29; H, 10.37; N, 7.00.

Methyl 3-((S)-2-methoxymethylpyrrolidino)-3-phenylpropanoate (Table 3, entry 6)

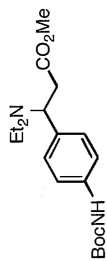


General Procedure A. Yield (0.40 mmol scale): 105 mg (88%). $[\alpha]_{\text{D}}^{25} = -42.2$ (c 0.832, CHCl_3). ^1H NMR (CDCl_3) δ 0.60-0.80 (m, 4H), 2.45-2.55 (m, 1H), 2.75-3.02 (m, 6H), 3.15 (s, 3H), 3.51 (s, 3H), 4.20 (dd, $J = 9.0, 5.4$ Hz, 1H), 7.19-7.36 (m, 5H); ^{13}C NMR (CDCl_3) δ 23.6, 28.6, 37.6, 50.8, 51.5, 58.8, 59.7, 63.1, 76.1, 127.3, 128.1, 128.2, 141.5, 172.3; IR (neat) 2951, 1735 cm^{-1} . HRMS Calcd. for $\text{C}_{16}\text{H}_{23}\text{NO}_3 \cdot \text{H}^+$ (MH^+): 278.1751.

Found: 278.1759.

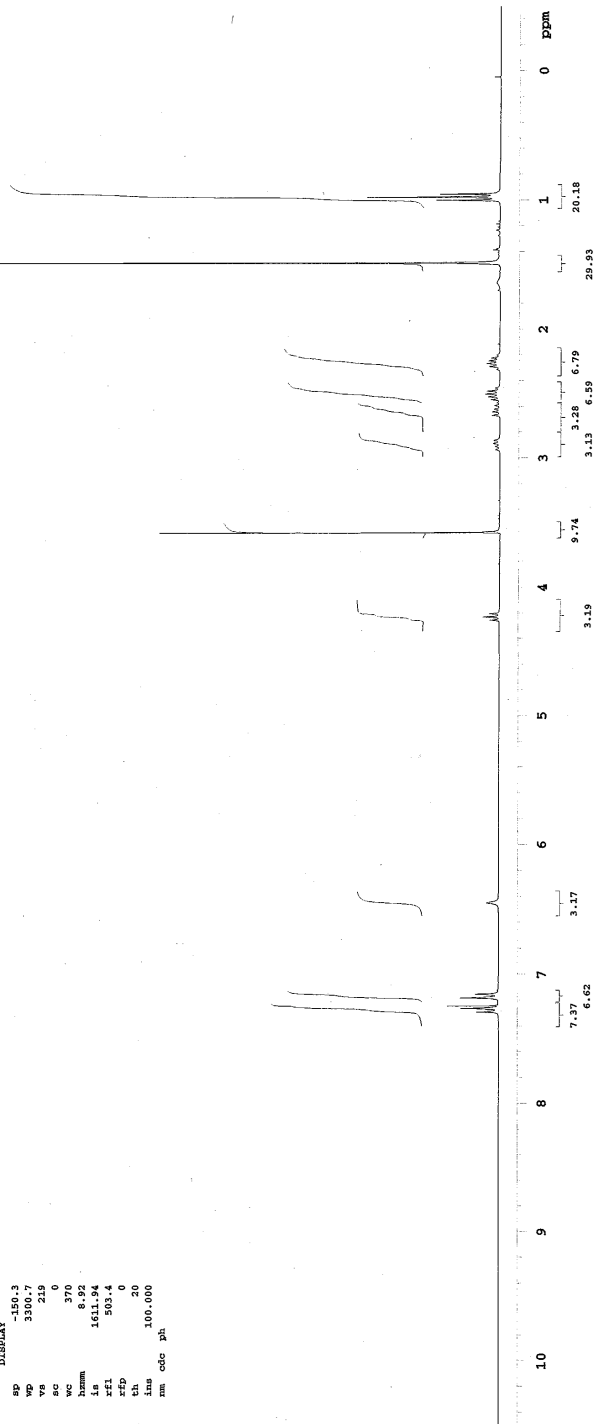
Reaction of Aminoborane **5 and Benzaldehyde in DMF-*d*₇.**

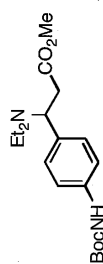
Aminoborane **5** (24 mg, 0.125 mmol) and benzaldehyde (13 mg, 0.125 mmol) were dissolved in freshly distilled DMF-*d*₇ (0.70 mL) at room temperature. The mixture was subjected to ¹H NMR analyses after 10 min (55% conv.), 3 h (64% conv.), and 14 h (64% conv.). The ¹H and ¹³C NMR charts (after 14 h) are shown at the end of the Supporting Information.



STANDARD IN ORBITER

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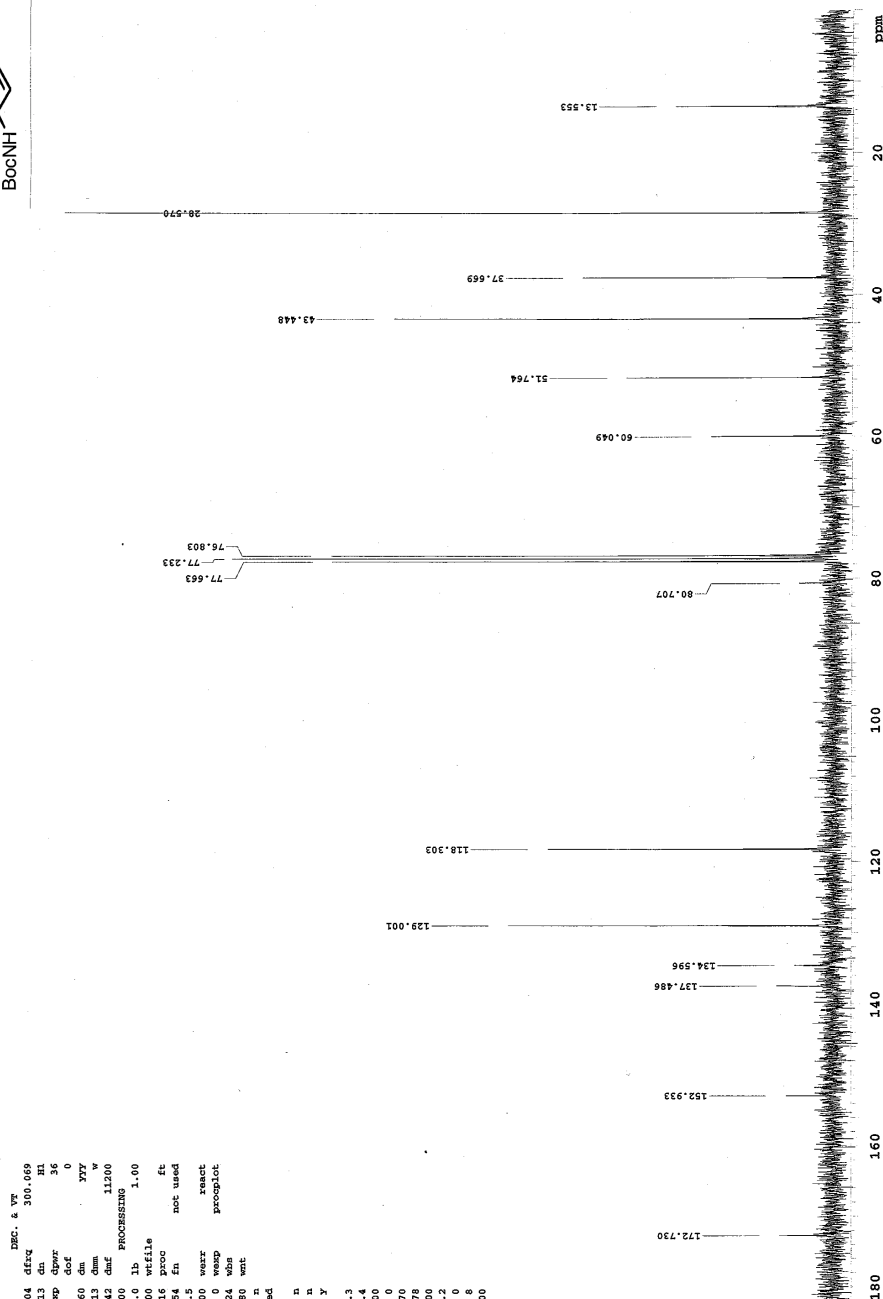




13C NMR

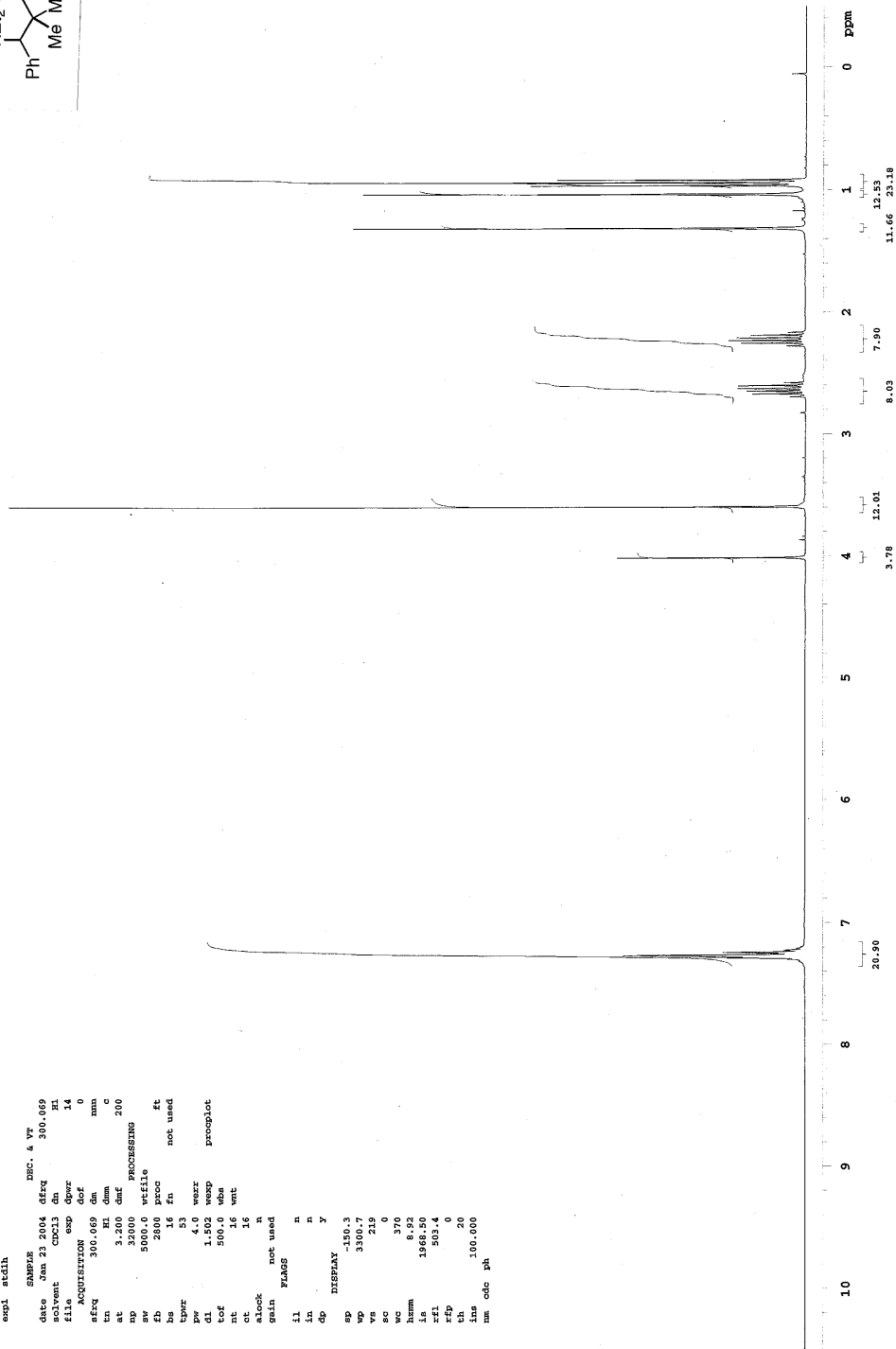
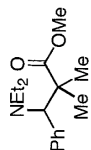
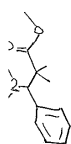
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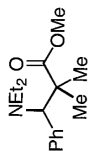
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STANDARD IN OBSERVE

expl stldh
 SMPXZ DEC. & VT
 date Jan 23 2004 dfrq 300.099
 solvent CDCl₃ Refr 1.4
 filia 14
 ACQUISITION exp Def 0
 afreq 300.069 dm mm
 tn H1 dm c
 at 3.200 dm 200
 ap 3200 dm PROCESSING
 fb 1000.0 stflls
 fb 2000 proc
 ba 16 fn not used
 tpr 53
 pr 4.0 warr
 dl 1.502 warr
 df 5000 dm
 nt 16 wnt
 ct 16
 alook n
 gain not used
 FLAG8 n
 in n
 in n
 qp y
 DISPLAY
 ap -150.3
 wp 3300.7
 wpc 210
 wco 0
 wcc 370
 humm 8.92
 la 1968.50
 rfi 503.4
 rfp 20
 th 20
 las 100.000
 um cdc ph





exp1 std13c

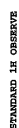
SAMPLE		DATE		TIME		LOC.		ELEV.		WIND		TEMP.		HUMID.		PRESS.		VISIB.		CLOUDS		MOON		STARS		PLANETS		COMETS		METEORS		AURORA		OTHER		REMARKS																																																																																																																																																																			
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(isolated).

16-731
- 4/dane1

(85)



Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

"varian2"

Relax. delay 1.502 sec

Pulse 45.0 degrees

Acq. time 3.200 sec

Width 5000.0 Hz
12 repetitions

RESERVE H1, 300.067236

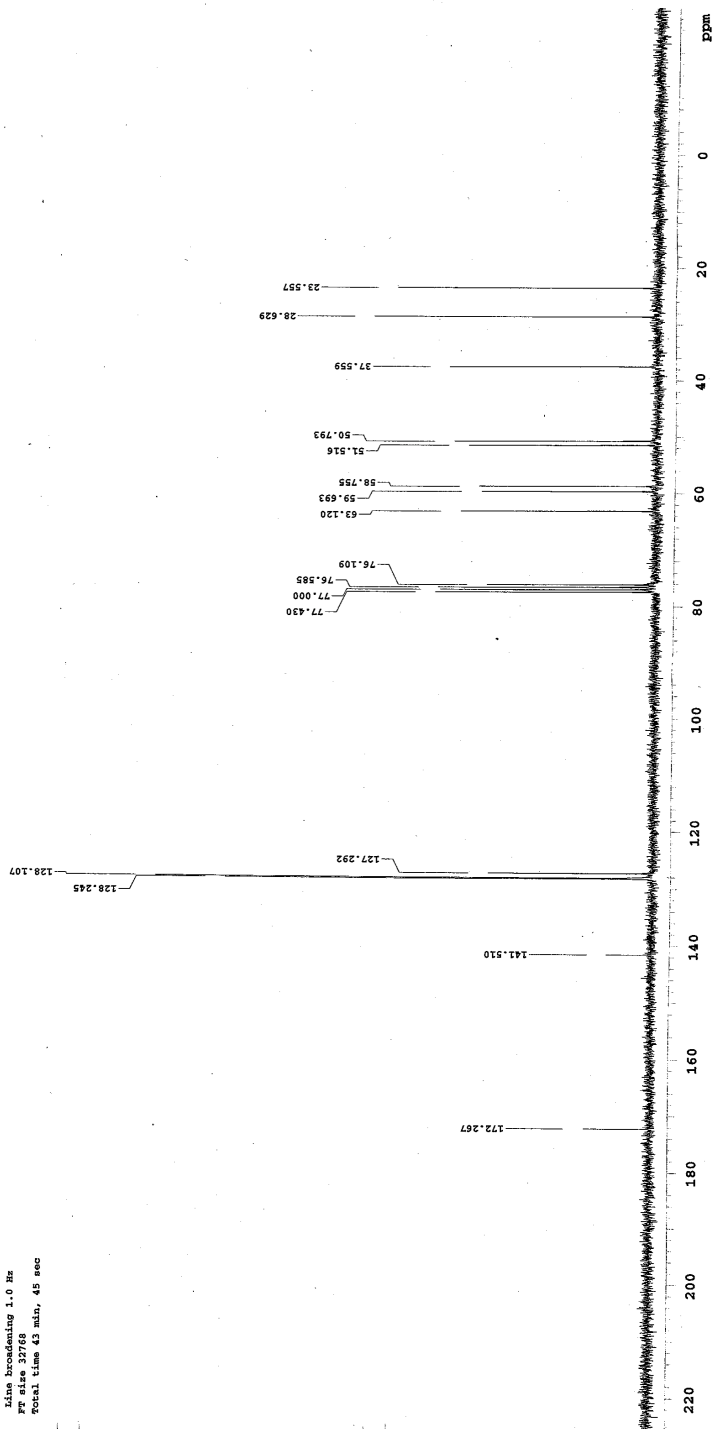
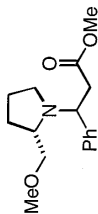
DATA PROCESSING

AT size 32768

total time 1 min, 24 sec

13C OBSERVE

Pulse sequence: zgpg30
Solvent: CDCl3
Ambient temperature
GEMINI-300WB "variant2"
Relax. delay 1.158 sec
Pulse 45.0 degree
Acq. time 0.042 sec
Pulch 1300.000 Hz
SIS repetitions
OBSERVE C13, 75.4515675 MHz
DECOUPLE H1, 300.0687135 MHz
Power 36 dB
continuously on
Waltz-16 decoupled
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 43 min, 45 sec



Mon May 24 14:22:01 2004
 PEAK 52
 MXINT 77.6265945
 RESOL 0.7926643 HZ
 RESOL 0.0078863 PPM
 EXREF 30.1000004 PPM
 OBS -30438.89 HZ
 ABOBS 100535.5000000 KHZ
 NGAIN 1
 COMNT

NO.	PPM	INT (%)	FREQ (HZ)	POSITION	BAR GRAPH
1	193.59226	19.21092	19460.913	4750	++
2	172.57025	4.01611	17347.670	7416	
3	162.98970	37.56280	16384.583	8631	+++++
4	162.89508	3.96657	16375.071	8643	
5	162.69795	38.75281	16355.254	8668	+++++
6	162.40620	38.51586	16325.926	8705	+++++
7	153.81919	2.78271	15462.714	9794	
8	153.07798	34.02372	15388.204	9888	+++++
9	139.10536	4.43208	13963.603	11660	
10	137.40215	3.31138	13912.397	11676	
11	135.99858	9.74168	13671.293	12054	+
12	135.17851	18.36908	13588.856	12158	++
13	132.98642	22.53567	13368.495	12436	+++
14	130.34487	22.04331	13102.953	12771	+++
15	130.13197	30.79151	13081.551	12798	++++
16	129.84022	37.03117	13052.222	12835	+++++
17	129.25671	14.28017	12993.565	12809	++
18	129.20151	9.07663	12988.016	12816	+
19	128.70474	10.25448	12938.078	12979	++
20	128.41299	3.16941	12908.750	13016	
21	128.33414	13.24935	12900.823	13026	++
22	128.28683	16.74634	12896.067	13032	++
23	128.20009	6.59509	12887.348	13043	+
24	127.80583	3.34294	12847.715	13093	
25	117.76794	100.00000	11838.653	14366	+++++
26	108.17182	29.92378	10875.980	15593	+++
27	80.78623	2.96333	8121.057	19056	
28	77.97909	2.99737	7838.868	19412	
29	43.22890	2.93089	4345.597	23819	
30	42.92138	3.71348	4314.683	23858	
31	42.40884	9.42002	4263.160	23923	+
32	42.03035	10.44497	4225.112	23971	++
33	35.84044	4.58389	3602.870	24756	
34	35.63543	13.76119	3582.261	24782	++
35	35.42253	27.35017	3560.859	24809	++++
36	35.21751	32.21557	3540.250	24835	++++
37	35.00461	26.44776	3518.848	24862	++++
38	34.79859	13.70075	3498.238	24888	++
39	34.59458	4.51729	3477.629	24914	
40	30.73082	5.63362	3089.224	25404	+
41	30.67562	3.11917	3083.675	25411	
42	30.51792	16.75507	3067.822	25431	+++
43	30.31290	33.52541	3047.212	25457	+++++
44	30.10000	38.73856	3025.810	25484	+++++
45	29.89498	33.54642	3005.201	25510	+++++
46	29.68208	16.59271	2983.799	25537	++
47	29.47707	5.73689	2963.190	25563	+
48	13.20196	4.94059	1327.131	27627	
49	12.51595	7.65861	1258.169	27714	+
50	12.48441	11.96421	1254.998	27718	++
51	12.05880	14.03343	1212.194	27772	++
52	12.02706	6.55259	1208.024	27776	+

¹³C NMR:

