Supporting Information

Radical Amination with Trimethylstannylated Benzophenone Imine

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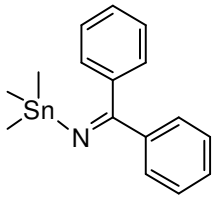
1. General Informations

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in heat-gun-dried glassware under an argon atmosphere and were performed using standard Schlenk techniques.
Thin Layer Chromatography (TLC) was carried out on *Merck* silica gel 60 F_{254} plates; detection by UV or dipping into a solution of $NaHCO_3$ (5.0 g), $KMnO_4$ (1.5 g) and H_2O (200 mL) followed by heating.
Flash chromatography (FC) was carried out on *Merck* or *Fluka* silica gel 60 (40-63 µm) with an argon pressure of about 0.3-0.4 bar.
Melting points (uncorrected) were determined on a *SMP 10 apparatus* (*Stuart Scientific*).
IR spectra were recorded on a *FT-IR Varian 3100 Excalibur Series* equipped with a *MKII Golden Gate Single Reflexion ATR* unit.
^{1}H and ^{13}C NMR spectra were recorded on a *Bruker DPX 300* or a *Varian 600 unity plus* spectrometer at 300.0 K. Chemical shifts δ (ppm) were referenced to the solvent residual peak or the TMS peak as an internal standard.
ESI-MS (*m/z*) was performed using a *Bruker MicroTof*.
Elemental analyses were performed on a *Vario EL III* (*Elementaranalysensysteme GmbH*).
Gas Chromatography (GC) was performed on a *Hewlett Packard 6890* chromatograph with a *HP-5* column (30 m x 0.32 mm, film thickness 0.25 µm), the detection was carried out by flame ionization. The carrier gas was H_2. The injection volume was 1 µL.
Data sets of X-Ray structures were collected with a *Nonius* KappaCCD diffractometer; programs used: data collection COLLECT (Nonius B. V., 1998), data reduction Denzo-SMN,[1] absorbtion correction Denzo,[2] stucture solution SHELXS-97,[3] structure refinement SHELXL-97,[4] graphics SCHAKAL.[5]
All solvents for extraction and flash chromatography were distilled before use. Diethyl ether was distilled from potassium/sodium alloy (both *Merck*, in paraffin oil). Heptane (*Aldrich*, 99+%) was distilled from calcium hydride (*Acros*, 93%) under argon. Toluene (*Acros*, extra dry), dimethylformamide (*Acros*, extra dry), methanol (*Acros*, extra dry), 1,2-dimethoxyethane (*Aldrich*, reagent+™ ≥ 99%) were used as received.
The following chemicals were purchased and used as received: phenyllithium (*Aldrich*, 2.0 M solution in dibutylether), benzonitrile (*Fluka*, > 99% (GC)), trimethyltinchloride (*Aldrich*, 1.0 M solution in tetrahydrofuran), iodine (*Acros*, 99.5% extra pure resublimed), triphenylphosphine (*Acros*, 99%), imidazole (*Sigma*), 5-(*tert*-butyldimethylsilyl-oxy)-1-pentanol (*Aldrich*, 90%), cyclohexene (*Aldrich*, 99% (GC)), sodium borohydride (*Merck*, fine granula for synthesis), *N*-iodosuccinimide (*Aldrich*), di-*tert*-butylperoxide (*Merck*, for synthesis), *tert*-butyldimethylsilylchloride (*Merck*), 5-hexen-1-ol (*Merck*, for synthesis), D-glucal (*Aldrich*, 96%), iodomethane (*Acros*, 99%), methyllithium (*Acros*, 1.6 M solution in diethylether).
Cyclohexyliodide (*Aldrich*, 98%), 5-iodopentane (*Aldrich*, 98%) and *tert*-butyliodide (*Acros*) were distilled under reduced pressure before use and stored under argon.

2. Procedures

A) Amination Reagent

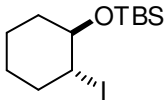
N-Trimethylstannyl benzophenone imine (3)



Prepared according to a literature procedure[6] using phenyllithium (23 mL, 40 mmol, 1.0 equiv), benzonitrile (4.1 mL, 40 mmol, 1.0 equiv) and trimethyltinchloride (40 mL, 40 mmol, 1.0 equiv) in Et_2O (64 mL). Purification by distillation (p = 2.7 mbar, bp = 153 °C) provided the product **3** as yellow oil which solidified upon standing (12.25 g, 35.50 mmol, 89%), stored under inert atmosphere. **^{1}H NMR (300 MHz, C_6D_6)**: δ = 0.08 (t, 9H, J = 28.2 Hz, Sn-C*H*$_3$), 7.12-7.17 (m, 6H, C*H*), 7.48-7.51 (m, 4H, C*H*). **^{13}C NMR (75 MHz, C_6D_6):** δ = -7.9 (3×*C*H$_3$), 125.5 (4×*C*H), 125.9 (4×*C*H), 126.5 (2×*C*H), 140.8 (2×*C*), 174.4 (*C*).

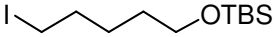
B) Iodides

***trans-tert*-Butyl-(2-iodo-cyclohexyloxy)-dimethyl-silane**



The unprotected alcohol was prepared according to a literature procedure[7] using cyclohexene (1.2 mL, 12 mmol, 1.0 equiv), *N*-iodosuccinimide (4.1 g, 18 mmol, 1.5 equiv) in a mixture of DME/H_2O (2/1, 12 mL). The isolated alcohol (2.0 g, 9.0 mmol, 1.0 equiv) and imidazole (1.2 g, 18 mmol, 2.0 equiv) were stirred in DMF (20 mL). After 15 minutes, *tert*-butyldimethylsilylchloride (2.0 g, 13 mmol, 1.5 equiv) was added to the mixture which was stirred over night under argon. After adding H_2O, the reaction mixture was extracted with AcOEt (3×15 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. Removal of the solvents *in vacuo* and purification by flash chromatography (pentane) yielded the desired product as colorless oil (2.35 g, 6.91 mmol, 77%). The physical data were in agreement with those reported in the literature.[8]

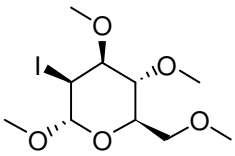
***tert*-Butyl-(5-iodo-pentyloxy)-dimethyl-silane**



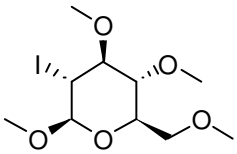
Triphenylphosphine (2.9 g, 11 mmol, 1.1 equiv), imidazole (2.8 g, 11 mmol, 1.1 equiv) and 5-(*tert*-butyldimethylsilyloxy)-1-pentanol (2.5 mL, 10 mmol, 1.0 equiv) were added to a solution of iodine (2.8 g, 11 mmol, 1.1 equiv) in toluene (56 mL). After stirring 1 h at room temperature, the solvents were removed *in vacuo*. The iodide was purified by flash chromatography (pentane/TBME: 80/20) and was obtained as colorless oil (2.4 g, 7.2 mmol, 72%). The physical data were in agreement with those reported in the literature.[9]

(2*S*,3*S*,4*S*,5*R*,6*R*)-3-Iodo-2,4,5-trimethoxy-6-methoxymethyl-tetrahydro-pyran (major isomer) and (2*R*,3*R*,4*S*,5*R*,6*R*)-3-iodo-2,4,5-trimethoxy-6-methoxymethyl-tetrahydro-pyran (minor isomer)

Prepared according to a literature procedure[10] using (2*R*,3*S*,4*R*)-3,4-dimethoxy-2-methoxymethyl-3,4-dihydro-2*H*-pyran[11] (1.1 g, 5.9 mmol, 1.0 equiv), iodine (0.74 g, 2.9 mmol, 0.5 equiv) and 0.40 g of hydrogen peroxide (30% aq., 3.5 mmol, 0.6 equiv) in MeOH (59 mL). Purification by flash chromatography provided the two diastereoisomers as white solids: major (1.33 g, 3.84 mmol, 66%), minor (0.51 g, 1.74 mmol, 25%).



Major isomer: **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 2.88 (dd, 1H, J = 4.2 Hz, J = 8.7 Hz, ICHC*H*(OCH_3)CH), 3.35 (s, 3H, CH_3), 3.39 (s, 3H, CH_3), 3.38-3.42 (m, 1H, CHC*H*(OCH_3)CH), 3.43 (s, 3H, CH_3), 3.51 (s, 3H, CH_3), 3.57-3.63 (m, 2H, CH_2), 3.65-3.70 (m, 1H, OC*H*CH_2), 4.45 (dd, 1H, J = 1.0 Hz, J = 4.2 Hz, C*H*I), 5.06-5.09 (m, 1H, OC*H*OCH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 32.6 (*C*HI), 55.2 (*C*H_3), 56.6 (*C*H_3), 59.5 (*C*H_3), 61.0 (*C*H_3), 71.6 (*C*H_2), 71.8 (*C*HCH_2), 77.8 (CH*C*H(OCH_3)CH), 78.7 (ICH*C*H(OCH_3)CH), 102.6 (O*C*HOCH_3). **HRMS (ESI)**: calcd for $[C_{10}H_{19}IO_5Na]^+$: *m/z* = 369.0175; found: *m/z* = 369.0169. **Elem. anal.** in % calcd for $C_{10}H_{19}IO_5$: C 34.70, H 5.53; found: C 34.79, H 5.60. **IR (neat)**: 2982*w*, 2929*m*, 2911*m*, 2831*m*, 1450*m*, 1378*w*, 1345*w*, 1326*w*, 1294*m*, 1268*m*, 1241*w*, 1188*m*, 1168*w*, 1125*s*, 1105*s*, 1055*s*, 1005*s*, 986*m*, 960*m*, 686*s*, 633*s* cm^{-1}. **Mp** = 33 °C.



Minor isomer: **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 3.21 (dd, 1H, J = 9.0 Hz, J = 9.8 Hz, ICHC*H*(OCH_3)CH), 3.29-3.36 (m, 2H, CHC*H*(OCH_3)C*H*CH_2), 3.41 (s, 3H, CH_3), 3.52 (s, 3H, CH_3), 3.54 (s, 3H, CH_3), 3.60 (d, 1H, J = 4.2 Hz, CH_2), 3.64 (d, 1H, J = 2.0 Hz, CH_2), 3.67 (s, 3H, CH_3), 3.72 (dd, 1H, J = 9.0 Hz, J = 10.8 Hz, C*H*I), 4.38 (d, 1H, J = 9.0 Hz, OC*H*OCH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 32.6 (*C*HI), 57.5 (*C*H_3), 59.5 (*C*H_3), 60.6 (*C*H_3), 60.9 (*C*H_3), 71.0 (*C*H_2), 75.0 (*C*HCH_2), 81.3 (ICH*C*H(OCH_3)CH), 87.7 (CH*C*H(OCH_3)CH), 104.3 (O*C*HOCH_3). **HRMS (ESI)**: calcd for $[C_{10}H_{19}IO_5Na]^+$: *m/z* = 369.0175; found: *m/z* = 369.0169, $[2(C_{10}H_{19}IO_5)Na]^+$: *m/z* = 715.0452; found: *m/z* = 715.0436. **IR (neat)**: 3001*w*, 2983*w*, 2934*m*, 2882*m*, 2839*m*, 2813*w*, 1447*m*, 1380*m*, 1315*m*, 1251*m*, 1221*w*, 1185*w*, 1166*w*, 1138*s*, 1102*s*, 1072*s*, 1036*s*, 1009*s*, 987*s*, 939*m*, 889*m*, 737*s*, 677*s* cm^{-1}. **Mp** = 65 °C.

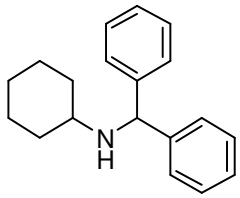
C) Final products

General Procedure (A) for radical amination with imine 3:

A mixture of **3** (2.0 equiv), the corresponding iodide (1.0 equiv) and the initiator di-*tert*-butylperoxide (DTBP) (0.25 equiv) in dry heptane (c = 0.5 mol/L) were placed in a sealed tube under argon. The resulting yellow mixture was heated at 140 °C (oil bath temperature) for 24 h. The reaction mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure to afford the crude imine **5**.

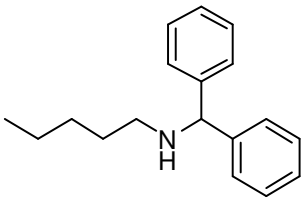
General Procedure (B) for reduction:
$NaBH_4$ (6.0 equiv) was added to a solution of the crude imine (1.0 equiv) in dry MeOH (c = 0.38 mol/L) under argon. The mixture was heated at reflux under argon for 8 h. After cooling to room temperature, a solution of NaOH (2N aq.) was added to the solution which was then extracted three times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography afforded the desired amine **6**.

N-Benzhydryl-cyclohexyl-amine (6a)



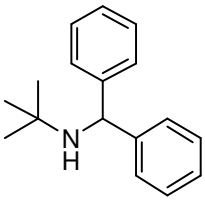
Prepared according to general procedure A with **3** (0.28 g, 0.80 mmol), cyclohexyliodide (52 µL, 0.40 mmol) and DTBP (18 µL, 0.10 mmol), followed by general procedure B with $NaBH_4$ (91 mg, 2.4 mmol). After flash chromatography (pentane/AcOEt: 98/2-95/5), the product was obtained as colorless oil (88.8 mg, 0.337 mmol, 84%). The physical data were in agreement with those reported in the literature.[12]

N-Benzhydryl-pentyl-amine (6b)



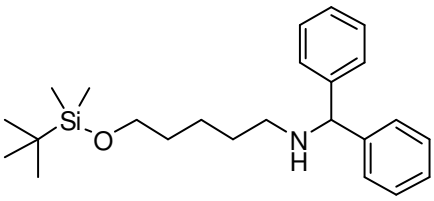
Prepared according to general procedure A with **3** (0.47 g, 1.4 mmol), iodopentane (90 µL, 0.69 mmol) and DTBP (32 µL, 0.17 mmol), followed by general procedure B with $NaBH_4$ (0.157 g, 4.14 mmol). After flash chromatography (pentane/AcOEt: 98/2-95/5), the product was obtained as colorless oil (152 mg, 0.601 mmol, 87%).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86-0.91 (m, 3H, C*H*$_3$), 1.28-1.36 (m, 4H, C*H*$_2$), 1.48-1.57 (m, 2H, C*H*$_2$), 2.57 (t, 2H, J = 7.0 Hz, C*H*$_2$NH), 4.82 (s, 1H, C*H*Ph$_2$), 7.14-7.23 (m, 2H, C*H*), 7.24-7.33 (m, 4H, C*H*), 7.36-7.45 (m, 4H, C*H*). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 14.2 (*C*H$_3$), 22.7 (*C*H$_2$), 29.7 (*C*H$_2$), 30.1 (*C*H$_2$), 48.4 (*C*H$_2$), 67.8 (*C*H), 127.0 (2×*C*H), 127.4 (4×*C*H), 128.5 (4×*C*H), 144.5 (2×*C*). **HRMS (ESI)**: calcd for $[C_{24}H_{23}NH]^+$: *m/z* = 254.1909; found: *m/z* = 254.1903. **Elem. anal.** in % calcd for $C_{24}H_{23}N$: C 85.32, H 9.15, N 5.53; found: C 85.31, H 9.32, N 5.42. **IR (neat)**: 3062*w*, 3026*w*, 2956*m*, 2927*m*, 2857*w*, 1492*m*, 1452*m*, 1341*w*, 1276*w*, 1189*w*, 1112*w*, 1028*m*, 921*w*, 833*w*, 743*s*, 696*s*, 643*m*, 602*m*, 571*m*, 505*m* cm^{-1}. **GC**: rt = 14.49 min.

N-Benzhydryl-*tert*-butyl-amine (6c)



Prepared according to general procedure A with **3** (572 µL, 2.30 mmol, in solution in heptane c = 4.1 mol/L), *tert*-butyliodide (216 mg, 1.20 mmol) and DTBP (55 µL, 0.30 mmol), followed by general procedure B with $NaBH_4$ (272 mg, 7.20 mmol). After flash chromatography (pentane/Et_2O: 95/5-80/20), the product was obtained as colorless oil (181 mg, 0.755 mmol, 63%). The physical data were in agreement with those reported in the literature.[13]

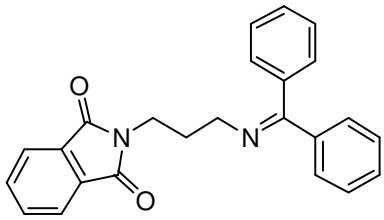
N-Benzhydryl-[5-(*tert*-butyl-dimethyl-silyloxy)-pentyl]-amine (6d)



Prepared according to general procedure A with **3** (0.49 mL, 2.0 mmol, in solution in heptane c = 4.1 mol/L), *tert*-butyl-(5-iodo-pentyloxy)-dimethyl-silane (0.34 g, 1.0 mmol) and DTBP (46 µL, 0.25 mmol), followed by general procedure B with $NaBH_4$ (0.23 g, 6.00 mmol). After flash chromatography (pentane/AcOEt: 98/2-95/5), the product was obtained as colorless oil (278 mg, 0.725 mmol, 73%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.08 (s, 6H, SiC*H*$_3$), 0.93 (s, 9H, SiCC*H*$_3$), 1.35-1.47 (m, 2H, CH_2C*H*$_2$), 1.48-1.65 (m, 4H, C*H*$_2$C*H*$_2$), 2.61 (t, 2H, J = 7.0 Hz, C*H*$_2$NH), 3.63 (t, 2H, J = 7.0 Hz, OC*H*$_2$), 4.85 (s, 1H, C*H*Ph_2), 7.17-7.26 (m, 2H, C*H*), 7.28-7-36 (m, 4H, C*H*), 7.39-7.47 (m, 4H, C*H*). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = -5.1 (2×*C*H_3), 18.5 (*C*), 23.7 (*C*H_2), 26.1 (3×*C*H_3), 30.2 (*C*H_2), 32.9 (*C*H_2), 48.4 (*C*H_2), 63.3 (*C*H_2), 67.7 (*C*H), 127.0 (2×*C*H), 127.4 (4×*C*H), 128.6 (4×*C*H), 144.4 (2×*C*). **HRMS (ESI)**: calcd for $[C_{24}H_{37}NOSiH]^+$: *m/z* = 384.2723; found: *m/z* = 384.2726. **Elem. anal.** in % calcd for $C_{24}H_{37}NOSi$: C 75.14, H 9.72, N 3.65; found: C 75.06, H 9.99, N 3.58. **IR (neat)**: 3063*w*, 3026*w*, 2929*m*, 2898*w*, 2856*m*, 1493*m*, 1453*m*, 1388*w*, 1361*w*, 1254*m*, 1095*s*, 1029*m*, 1006*m*, 833*s*, 774*s*, 743*s*, 699*s*, 662*m*, 602*m*, 573*m*, 531*w* cm^{-1}. **GC**: rt = 19.35 min.

2-[3-(Benzhydrylidene-amino)-propyl]-isoindole-1,3-dione (5f)



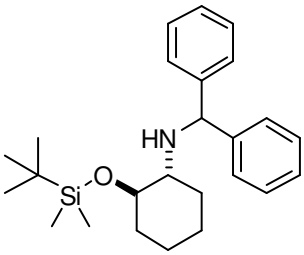
Prepared according to general procedure A with **3** (292 µL, 1.48 mmol, in solution in heptane c = 5.06 mol/L), 2-(3-iodopropyl)-1H-isoindolone-1,3(2H)-dione[14] (0.23 g, 0.74 mmol) and DTBP (34 µL, 0.19 mmol). After flash chromatography (pentane/AcOEt/Et_3N: 95/5/0.01-85/5/0.01), the product was obtained as yellow oil (209 mg, 0.568 mmol, 77%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02-2.13 (m, 2H, CH_2C*H*$_2$$CH_2$), 3.42 (t, 2H, J = 6.8 Hz, C*H*$_2$), 3.81 (t, 2H, J = 6.8 Hz, C*H*$_2$), 7.10-7.17 (m, 2H, C*H*), 7.20-7.27 (m, 2H, C*H*), 7.28-7.35 (m, 2H, C*H*), 7.36-7.48 (m, 2H, C*H*), 7.49-7.58 (m, 2H, C*H*), 7.61-7.69 (m, 2H, C*H*), 7.74-7.83 (m, 2H, C*H*). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 30.0 (*C*H_2), 36.8

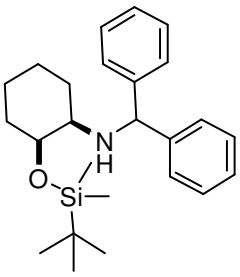
(CH_2), 51.5 (CH_2), 123.1 (2×*C*H), 127.8 (2×*C*H), 128.0 (2×*C*H), 128.3 (3×*C*H), 128.5 (2×*C*H), 129.9 (*C*H), 132.4 (2×*C*), 133.8 (2×*C*H), 136.9 (*C*), 139.7 (*C*), 168.5 (*C*), 168.7 (C). **HRMS (ESI)**: calcd for $[C_{24}H_{20}N_2O_2H]^+$: *m/z* = 369.1603; found: *m/z* = 369.1598. **Elem. anal.** in % calcd for $C_{24}H_{20}N_2O_2$: C 78.24, H 5.47, N 7.60; found: C 78.28, H, 5.80, N 7.21. **IR (neat)**: 3057*w*, 3026*w*, 2934*w*, 2859*w*, 1771*m*, 1706*s*, 1618*m*, 1576*w*, 1467*w*, 1444*m*, 1394*s*, 1367*m*, 1315*m*, 1289*m*, 1130*w*, 1074*m*, 1028*m*, 961*m*, 889*w*, 780*m*, 767*m*, 718*s*, 694*s*, 641*m* cm^{-1}. **GC**: rt = 22.80 min.

***trans*-Benzhydryl-[2-(*tert*-butyl-dimethyl-silyloxy)-cyclohexyl]-amine and *cis*-benzhydryl-[2-(*tert*-butyl-dimethyl-silyloxy)-cyclohexyl]-amine (6e)**

Prepared according to general procedure A with **3** (283 µL, 1.37 mmol, in solution in heptane c = 4.82 mol/L), *trans-tert*-butyl-(2-iodo-cyclohexyloxy)-dimethyl-silane (0.23 g, 0.68 mmol) and DTBP (31 µL, 0.17 mmol), followed by general procedure B with $NaBH_4$ (154 mg, 4.08 mmol). After flash chromatography (pentane/AcOEt: 98/2-95/5), two separated isomers were obtained as colorless oils (48%): *trans* (71.0 mg, 0.179 mmol, 26%), *cis* (58.8 mg, 0.149 mmol, 22%).



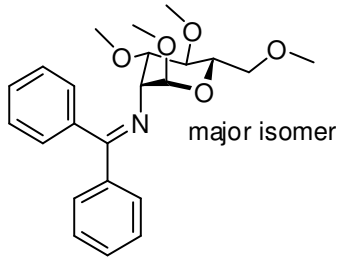
Trans: **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 0.06 (s, 3H, SiCH_3), 0.08 (s, 3H, SiCH_3), 0.88 (s, 9H, CCH_3), 0.98-1.16 (m, 2H, CH_2CH_2), 1.20-1.34 (m, 2H, CH_2CH_2), 1.54-1.64 (m, 2H, CH_2CH_2), 1.81-1.93 (m, 2H, CH_2CH_2), 2.36-2.48, (m, 1H, C*H*NH), 3.45-3.65 (m, 1H, C*H*OTBS), 4.94 (s, 1H, Ph_2CH), 7.14-7.22 (m, 2H, C*H*), 7.22-7.25 (m, 1H, C*H*), 7.25-7.26 (m, 1H, C*H*), 7.27-7.33 (m, 4H, C*H*), 7.34-7.42 (m, 2H, C*H*). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = -4.4 (CH_3), -3.9 (CH_3), 18.1 (*C*), 24.1 (CH_2), 24.4 (CH_2), 26.0 (3×CH_3), 30.1 (CH_2), 34.4 (CH_2), 61.1 (*C*H), 64.1 (*C*H), 75.5 (*C*H), 126.7 (*C*H), 126.9 (*C*H), 127.4 (2×*C*H), 127.6 (2×*C*H), 128.4 (2×*C*H), 128.6 (2×*C*H). **HRMS (ESI)**: calcd for $[C_{25}H_{37}NOSiH]^+$: *m/z* = 396.2723; found: *m/z* = 396.2717. **Elem. anal.** in % calcd for $C_{25}H_{37}NOSi$: C 75.89, H 9.43, N 3.54; found: C 76.31, H 9.37, N 3.60. **IR (neat)**: 3062*w*, 3026*w*, 2928*m*, 2856*m*, 1493*m*, 1451*m*, 1361*w*, 1251*m*, 1083*s*, 1028*m*, 1005*m*, 939*w*, 876*s*, 831*s*, 774*s*, 744*s*, 697*s*, 666*m*, 594*m* cm^{-1}. **GC**: rt = 18.82 min.

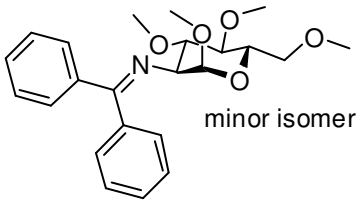


Cis: **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 0.04 (s, 3H, SiCH_3), 0.08 (s, 3H, SiCH_3), 0.85 (s, 9H, CCH_3), 1.05-1.35 (m, 4H, CH_2CH_2), 1.45-1.80 (m, 4H, CH_2CH_2), 2.25-2.50 (m, 1H, C*H*NH), 3.95-4.10 (m, 1H, C*H*OTBS), 4.98 (s, 1H, Ph_2CH), 7.12-7.23 (m, 2H, C*H*), 7.23-7.35 (m, 4H, C*H*), 7.35-7.50 (m, 4H, C*H*). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = -4.6 (CH_3), -4.2 (CH_3), 18.3 (*C*), 21.1 (CH_2), 24.0 (CH_2), 26.0 (3×CH_3), 27.8 (CH_2), 32.7 (CH_2), 56.4 (*C*H), 63.5 (*C*H), 70.4 (*C*H), 126.8 (*C*H), 126.9 (*C*H), 127.4 (2×*C*H), 127.6 (2×*C*H), 128.4 (2×*C*H), 128.5 (2×*C*H), 144.9 (*C*), 145.5 (*C*). **HRMS (ESI)**: calcd for $[C_{25}H_{37}NOSiH]^+$: *m/z* = 396.2723; found: *m/z* = 396.2717. **Elem. anal.** in % calcd for $C_{25}H_{37}NOSi$: C 75.89, H 9.43, N 3.54; found: C 75.59, H 9.56, N 3.28. **IR (neat)**: 3061*w*, 3026*w*, 2929*s*, 2894*w*, 2855*m*, 1492*m*, 1452*m*, 1375*w*, 1251*m*, 1124*w*, 1078*m*, 1065*m*, 1020*s*, 916*m*, 835*s*, 774*s*, 744*s*, 702*s*, 633*s*, 596*s*, 551*s*, 537*s* cm^{-1}. **GC**: rt = 18.68 min.

Benzhydrylidene-((2*S*,3*S*,4*R*,5*S*,6*R*)-2,4,5-trimethoxy-6-methoxymethyl-tetrahydro-pyran-3-yl)-amine (major isomer) and benzhydrylidene-((2*S*,3*R*,4*R*,5*S*,6*R*)-2,4,5-trimethoxy-6-methoxymethyl-tetrahydro-pyran-3-yl)-amine (minor isomer) (5h)

Prepared according to general procedure A with **3** (230 µL, 1.09 mmol, in solution in heptane c = 4.73 mol/L), (2*S*,3*S*,4*S*,5*R*,6*R*)-3-iodo-2,4,5,6-tetramethoxy-tetrahydro-pyran (0.19 g, 0.54 mmol) and DTBP (25 µL, 0.14 mmol). After flash chromatography (pentane/AcOEt/Et_3N: 95/5/0.01-80/20/0.01), the two diastereoisomers were obtained as brown oils (82.6 mg, 0.207 mmol, 38%, 66/34).

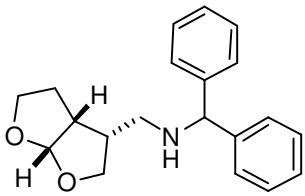




^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.12 (dd, 1H, J = 9.5 Hz, CHC*H*(OCH_3)CH, minor), 3.23 (s, 3H, C*H*$_3$, major), 3.31 (s, 3H, C*H*$_3$, major), 3.37 (s, 3H, C*H*$_3$, minor), 3.40 (s, 3H, C*H*$_3$, minor), 3.50 (s, 3H, C*H*$_3$, major), 3.52 (s, 3H, C*H*$_3$, minor), 3.54 (s, 3H, C*H*$_3$, minor), 3.56 (s, 3H, C*H*$_3$, major), 3.55-3.58 (m, 3H, NCHC*H*(OCH_3)CH (major), C*H*$_2$ (minor)), 3.62 (dd, 1H, J = 3.7 Hz, J = 9.5 Hz, NC*H*, minor), 3.68-3.72 (m, 1H, C*H*$_2$, major), 3.73-3.74 (m, 1H, C*H*CH_2, major), 3.77 (m, 1H, C*H*CH_2, minor), 3.78 (dd, 1H, J = 4.5 Hz, C*H*$_2$, major), 3.93 (dd, 1H, J = 4.3 Hz, NCHC*H*(OCH_3), minor), 3.94 (d, 1H, J = 4.5 Hz, CHC*H*(OCH_3)CH, major), 3.96-3.98 (m, 1H, NC*H*, major), 4.43 (d, 1H, J = 3.7 Hz, OC*H*(OCH_3), minor), 4.51 (d, 1H, J = 1.4 Hz, OC*H*(OCH_3), major), 7.12-7.20, 7.23-7.27, 7.27-7.30, 7.30-7.36, 7.37-7.50, 7.54-7.61, 7.62-7.69 (all m, 20H, *aromatic*-C*H*): **^{13}C NMR (150 MHz, $CDCl_3$)**: δ = 54.8 (*C*H_3, major), 55.3 (*C*H_3, minor), 58.0 (*C*H_3, major), 59.3 (*C*H_3, minor), 59.5 (*C*H_3, major), 60.5 (*C*H_3, minor), 60.7 (*C*H_3, minor), 60.7 (*C*H_3, major), 62.8 (*C*H, major), 67.2 (*C*H, minor), 70.2 (*C*H, minor), 71.3 (*C*H_2, minor), 72.4 (*C*H, major), 72.4 (*C*H_2, major), 76.9 (*C*H, major), 79.2 (*C*H, minor), 82.5 (*C*H, major), 83.9 (*C*H, minor), 100.8 (*C*H, minor), 101.8 (*C*H, major), 127.8 (2×*C*H, major), 128.0 (2×*C*H, minor), 128.0 (2×*C*H, minor), 128.0 (*C*H, minor), 128.3 (2×*C*H, minor), 128.3 (*C*H, major), 128.4 (*C*H, minor), 128.5 (2×*C*H, major), 128.6 (*C*H, major), 128.6 (*C*H, major), 128.8 (*C*H, major), 128.9 (*C*H, major), 130.1 (*C*H, minor), 130.1 (*C*H, major), 130.3 (*C*H, minor), 136.8 (*C*, minor), 136.8 (*C*, major), 139.8 (*C*, major), 140.0 (*C*, minor), 169.8 (*C*, major), 170.9 (*C*, minor). **HRMS (ESI)**: calcd for $[C_{23}H_{29}NO_5H]^+$: *m/z* = 400.2124; found: *m/z* = 400.2118, $[C_{23}H_{29}NO_5Na]^+$: *m/z* = 422.1943; found: *m/z* = 422.1938. **Elem. anal.** in % calcd for $C_{22}H_{29}NO_5$: C 69.15, H 7.32, N, 3.51; found: C 69.09, H 7.31, N 3.40. **IR (neat)**: 3058*w*, 2928*m*, 2833*m*, 1625*m*, 1577*w*, 1446*m*, 1373*w*, 1316*m*, 1278*m*, 1188*m*, 1108*s*, 1065*s*, 1048*s*, 1029*s*, 1000*w*, 960*m*, 917*w*, 810*w*, 781*m*, 696*s*, 639*m* cm^{-1}. **GC**: rt = 19.17 min (minor), 19.27 min (major).

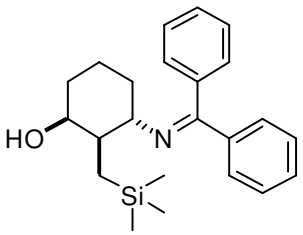
***cis-endo*-Benzhydryl-[1-(hexahydro-furo[2,3-*b*]furan-3-yl)methyl]-amine (major isomer) and *cis-exo*-benzhydryl-[1-(hexahydro-furo[2,3-*b*]furan-3-yl)methyl]-amine (minor isomer) (8)**

Prepared according to general procedure A with **3** (450 µL, 1.94 mmol, in solution in heptane c = 4.31 mol/L), *trans*-3-iodo-2-(2-propenyloxy)tetrahydrofuran (**7**)[15] (0.25 g, 0.97 mmol) and DTBP (44 µL, 0.24 mmol), followed by general procedure B with $NaBH_4$ (220 mg, 5.82 mmol). After flash chromatography (pentane/AcOEt: 98/2-60/40), the product was obtained as yellow oil (145.6 mg, 0.4709 mmol, 49%) as a mixture of isomers (7.3:1).



Major isomer: **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 1.45-1.65 (m, 2H, C*H*$_2$), 1.75-1.87 (m, 1H, C*H*), 2.45-2.72 (m, 2H, C*H*$_2$), 2.80-2.95 (m, 1H, C*H*), 3.47 (dd, 1H, J = 8.5 Hz, J = 11.0 Hz, C*H*$_2$), 3.77-3.87 (m, 2H, C*H*$_2$), 4.03 (dd, 1H, J = 7.3 Hz, J = 8.5 Hz, C*H*$_2$), 4.79 (s, 1H, C*H*Ph$_2$), 5.74 (d, 1H, J = 5.0 Hz, OC*H*O), 7.18-7.25 (m, 2H, C*H*), 7.26-7.35 (m, 4H, C*H*), 7.35-7.42(m, 4H, C*H*). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 25.3 (*C*H$_2$), 43.1 (*C*H), 44.8 (*C*H), 46.8 (*C*H$_2$), 68.2 (*C*H), 69.3 (*C*H$_2$), 71.8 (*C*H$_2$), 110.0 (*C*H), 127.3 (2×*C*H), 127.3 (2×*C*H), 127.4 (2×*C*H), 128.7 (4×*C*H), 144.0 (*C*), 144.1 (*C*). **HRMS (ESI)**: calcd for $[C_{20}H_{23}NO_2H]^+$: *m/z* = 310.1807; found: *m/z* = 310.1802, $[C_{20}H_{23}NO_2Na]^+$: *m/z* = 332.1626; found: *m/z* = 332.1621, $[2(C_{20}H_{23}NO_2)Na]^+$: *m/z* = 641.3355; found: *m/z* = 641.3355. **Elem. anal.** in % calcd for $C_{20}H_{23}NO_2$: C 77.64, H 7.49, N 4.53; found: C 77.20, H 7.48, N 4.45. **IR (neat)**: 3059*w*, 2954*m*, 2936*m*, 2858*m*, 1598*w*, 1492*m*, 1453*m*, 1341*w*, 1311*w*, 1278*m*, 1265*m*, 1188*w*, 1119*m*, 1081*m*, 1001*s*, 945*m*, 923*s*, 907*m*, 867*m*, 748*s*, 699*s*, 648*m*, 639*m* cm^{-1}. **GC**: rt = 19.79 min.

***cis-trans*-3-(Benzhydrylidene-amino)-2-trimethylsilylmethyl-cyclohexanol (10)**

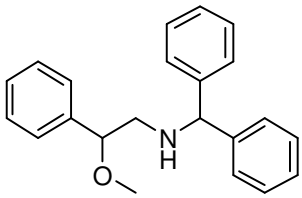


Prepared according to general procedure A with **3** (104 µL, 0.530 mmol, in solution in heptane c = 5.06 mol/L), (2-cyclohexen-1-yloxy)(iodomethyl)-dimethylsilane (**9**)[14] (78 mg, 0.26 mmol) and DTBP (12 µL, 0.070 mmol). After heating 24 h at 140 °C, methyllithium (0.33 mL, 0.53 mmol, 2.0 equiv.) was added to the mixture which was then stirred at room temperature over night. The solvent was removed *in vacuo* and the alcohol was obtained as a single isomer by flash chromatography (pentane/AcOEt/Et_3N: 98/2/0.01-90/10/0.01) as yellow solid (34.2 mg, 93.6 µmol, 36%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 9H, SiC*H*$_3$), 0.45 (dd, 1H, J = 10.6 Hz, J = 14.8 Hz, C*H*$_2$-Si(CH$_3$)$_3$), 0.50 (dd, 1H, J = 4.2 Hz, J = 14.8 Hz, C*H*$_2$-Si(CH$_3$)$_3$), 1.04-1.16 (m, 1H, C*H*$_2$), 1.45-1.68 (m, 5H, 2C*H*$_2$, C*H*-CH$_2$Si(CH$_3$)$_3$, O*H*), 1.71-1.85 (m, 1H, C*H*$_2$), 1.87-2.00 (m, 1H, C*H*$_2$), 3.25-3.37 (m, 1H, C*H*N=CPh$_2$), 4.00-4.13 (m, 1H, C*H*-OH), 7.12-7.15 (m, 2H, C*H*), 7.28-7.38 (m, 3H, C*H*), 7.38-7.49 (m, 3H, C*H*), 7.58-7.61 (m, 2H, C*H*). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = -0.5 (3×*C*H$_3$), 16.0 (*C*H$_2$), 18.8 (*C*H$_2$), 32.7 (*C*H$_2$), 32.8 (*C*H$_2$), 44.1 (*C*H), 62.6 (*C*H), 69.6 (*C*H), 127.8 (2×*C*H), 128.1 (2×*C*H),

128.2 (*C*H), 128.5 (2×*C*H), 128.6 (2×*C*H), 129.8(*C*H), 137.6 (*C*), 140.5 (*C*), 166.8 (*C*). **HRMS (ESI)**: calcd for $[C_{23}H_{31}NOSiH]^+$: *m/z* = 366.2253; found: *m/z* = 366.2248, $[C_{23}H_{31}NOSiNa]^+$: *m/z* = 388.2073; found: *m/z* = 388.2063. **Elem. anal.** in % calcd for $C_{23}H_{31}NOSi$: C 75.56, H 8.55, N 3.83; found: C 75.15, H, 8.62, N 3.72. **IR (neat)**: 3275*m*, 3057*w*, 2946*w*, 2927*m*, 2875*w*, 1617*m*, 1600*w*, 1578*w*, 1445*m*, 1417*w*, 1317*w*, 1289*m*, 1247*m*, 1225*w*, 1194*w*, 1148*m*, 1095*w*, 1053*w*, 991*m*, 922*m*, 895*m*, 854*s*, 834*s*, 770*m*, 729*m*, 697*s*, 642*m* cm^{-1}. **GC**: rt = 18.82 min. **Mp** = 140 °C.

N-Benzhydryl-(2-methoxy-2-phenyl-ethyl)-amine (6g)

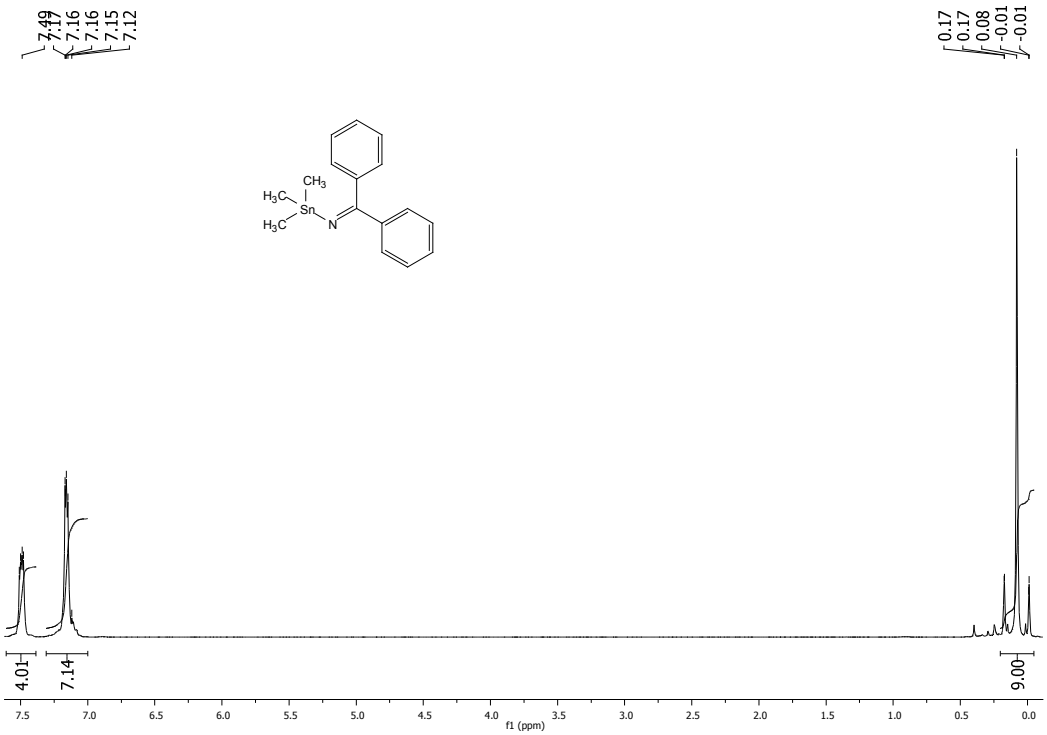


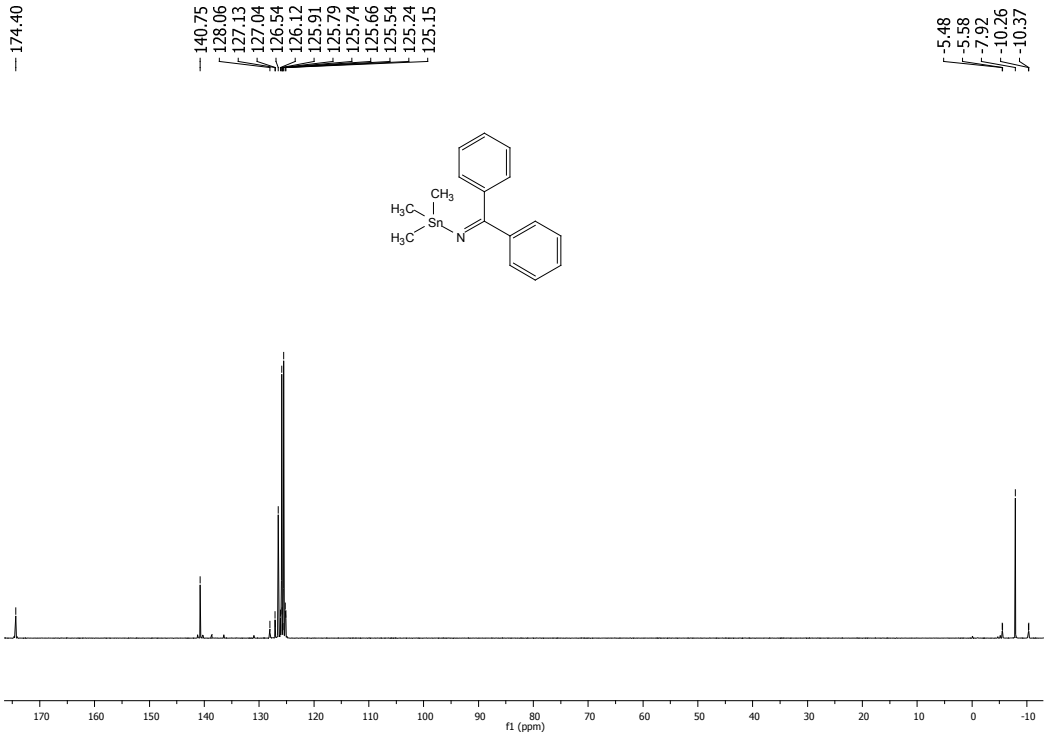
Prepared according to general procedure A with **3** (363 µL, 1.56 mmol, in solution in heptane c = 4.31 mol/L), (2-iodo-1-methoxy-ethyl)-benzene[10] (0.21 g, 0.78 mmol) and DTBP (36 µL, 0.20 mmol), followed by general procedure B with $NaBH_4$ (177 mg, 4.68 mmol). After flash chromatography (pentane/AcOEt: 98/2-90/10), the product was obtained as yellow oil (124.3 mg, 0.3916 mmol, 50%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.70 (dd, 1H, J = 3.8 Hz, J = 12.5 Hz, CH_2), 2.85 (dd, 1H, J = 9.0 Hz, J = 12.5 Hz, CH_2), 3.25 (s, 3H, OCH_3), 4.38 (dd, 1H, J = 3.8 Hz, J = 9.0 Hz, C*H*OCH_3), 4.84 (s, 1H, C*H*Ph_2), 7.16-7.23 (m, 2H, C*H*), 7.24-7.33 (m, 9H, C*H*), 7.34-7.43 (m, 4H, C*H*). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 55.3 (CH_2), 56.9 (CH_3), 67.6 (*C*H), 83.4 (*C*H), 126.9 (2×*C*H), 127.1 (*C*H), 127.1 (*C*H), 127.4 (*C*H), 127.5 (3×*C*H), 127.9 (*C*H), 128.5 (2×*C*H), 128.6 (2×*C*H), 128.6 (2×*C*H), 140.6 (*C*), 144.0 (*C*), 144.3 (*C*). **HRMS (ESI)**: calcd for $[C_{22}H_{23}NOH]^+$: *m/z* = 318.1858; found: *m/z* = 318.1852. **IR (neat)**: 3061*w*, 3026*w*, 2928*w*, 2823*w*, 1600*w*, 1492*m*, 1452*m*, 1354*w*, 1304*w*, 1240*w*, 1183*w*, 1103*m*, 1065*w*, 1028*m*, 915*w*, 890*w*, 840*w*, 760*m*, 744*m*, 698*s*, 644*m*, 621*m*, 605*m* cm^{-1}. **GC**: rt = 18.24 min.

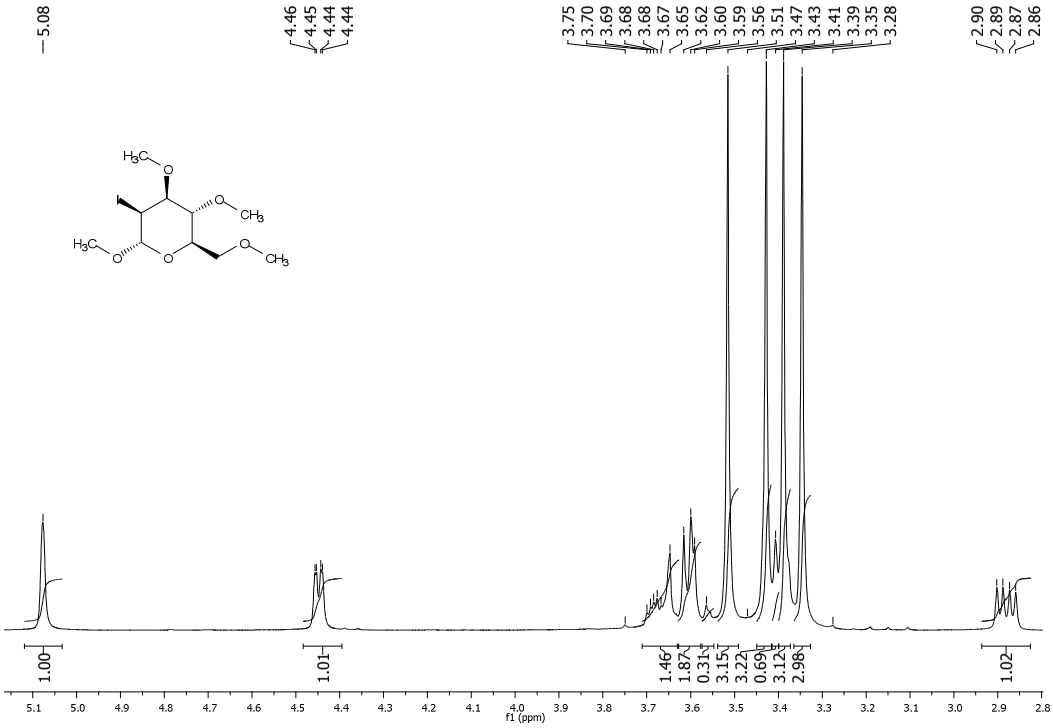
3. Spectral Data

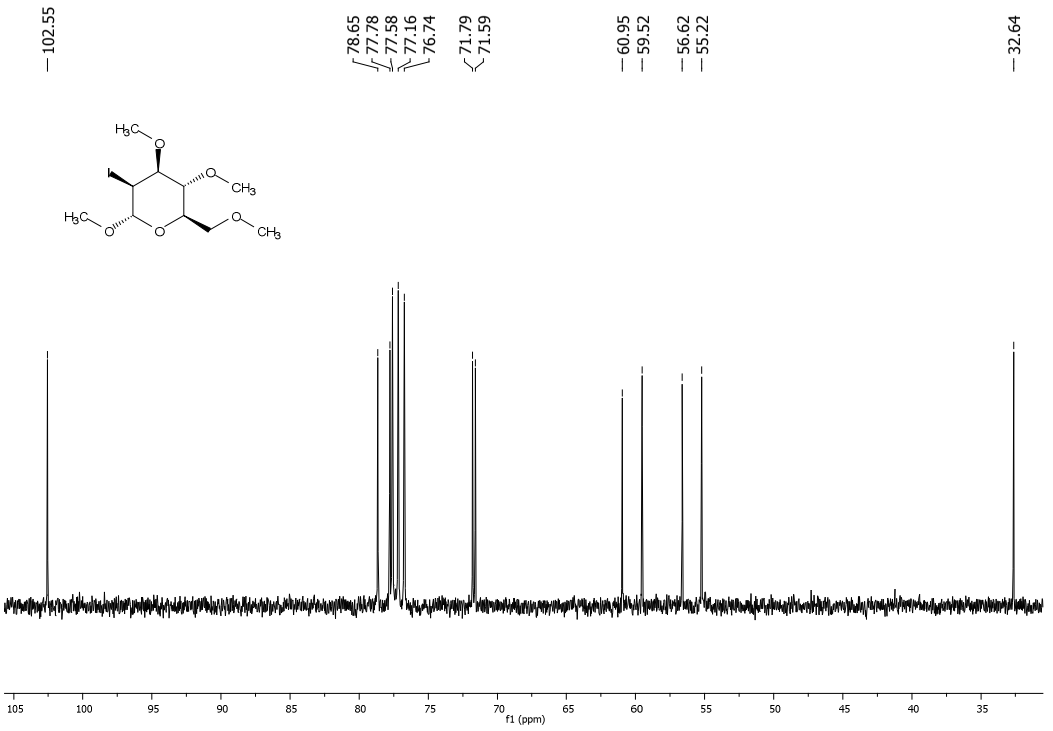
N-Trimethylstannyl benzophenone imine (3)



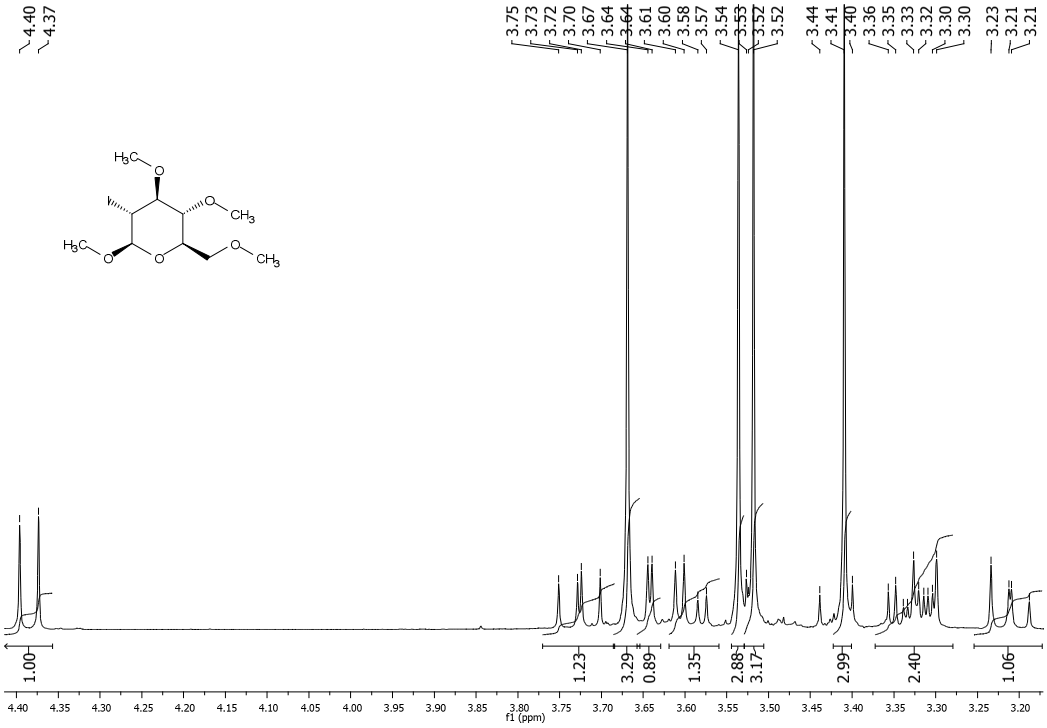


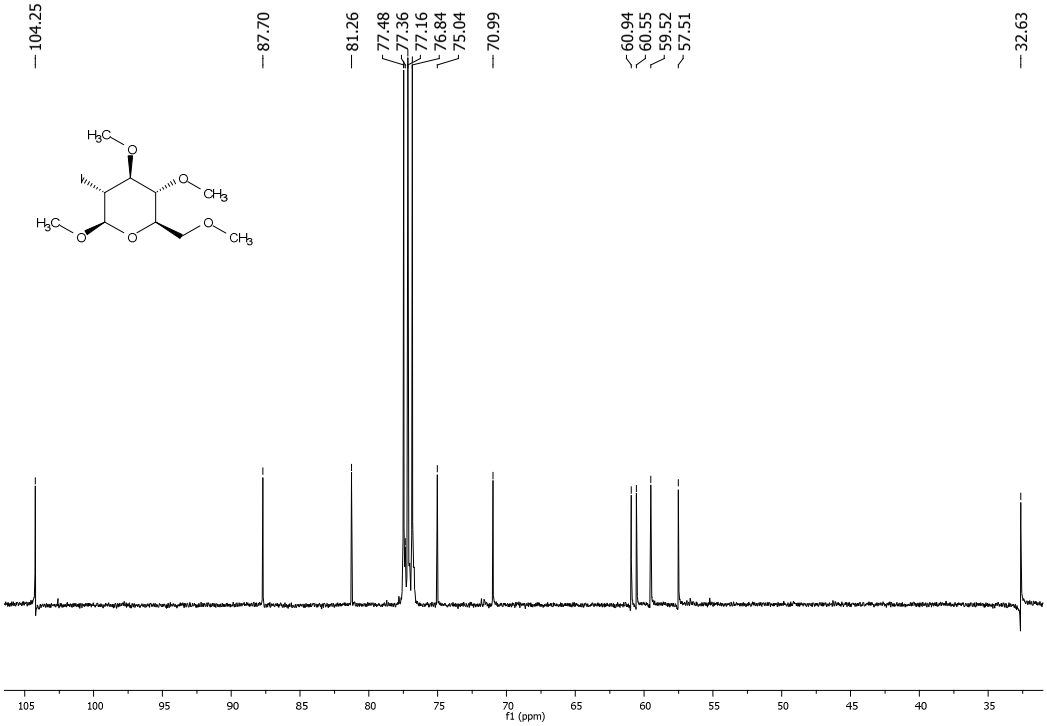
(2*S*,3*S*,4*S*,5*R*,6*R*)-3-Iodo-2,4,5-trimethoxy-6-methoxymethyl-tetrahydro-pyran (major isomer)



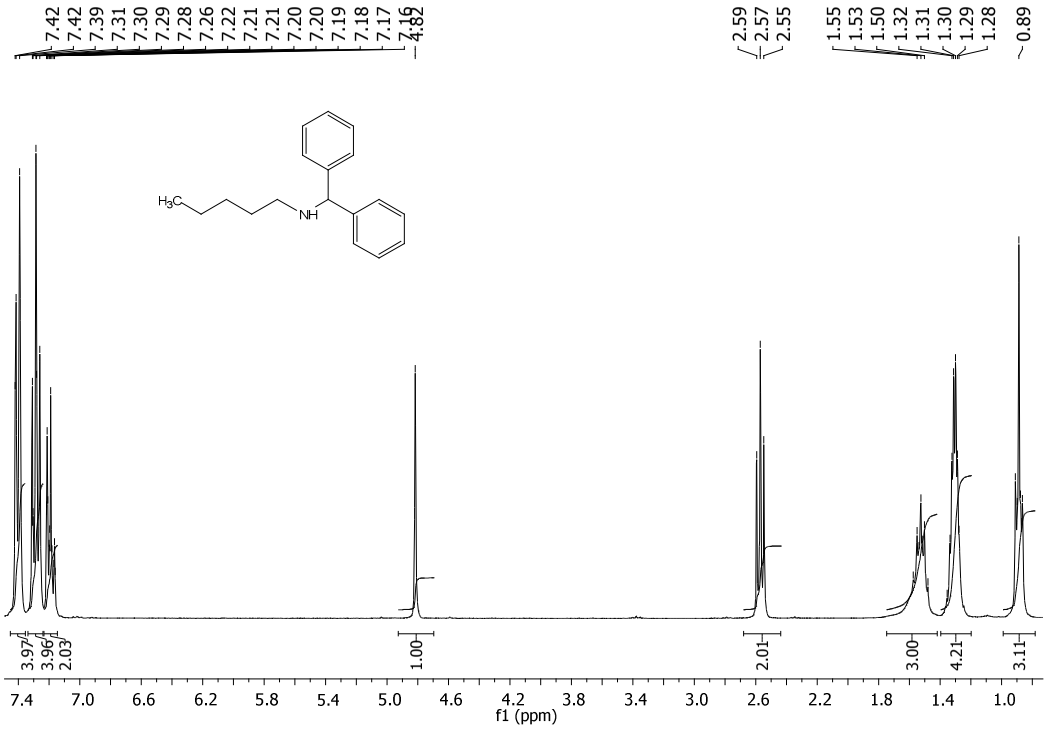


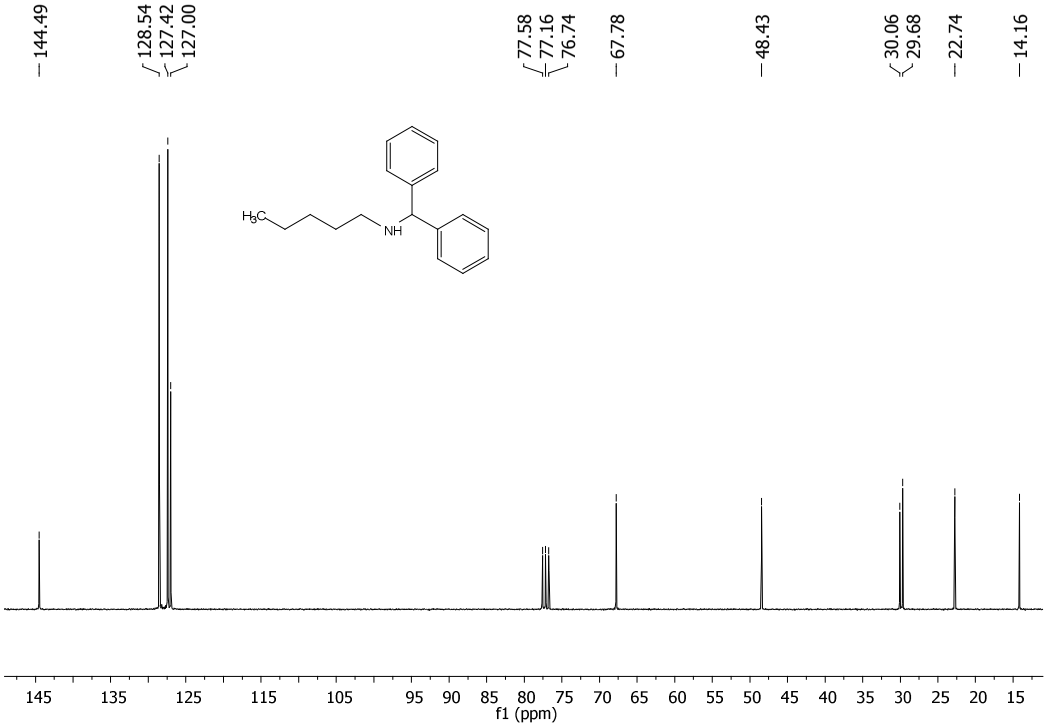
(2*R*,3*R*,4*S*,5*R*,6*R*)-3-iodo-2,4,5-trimethoxy-6-methoxymethyl-tetrahydro-pyran (minor isomer)



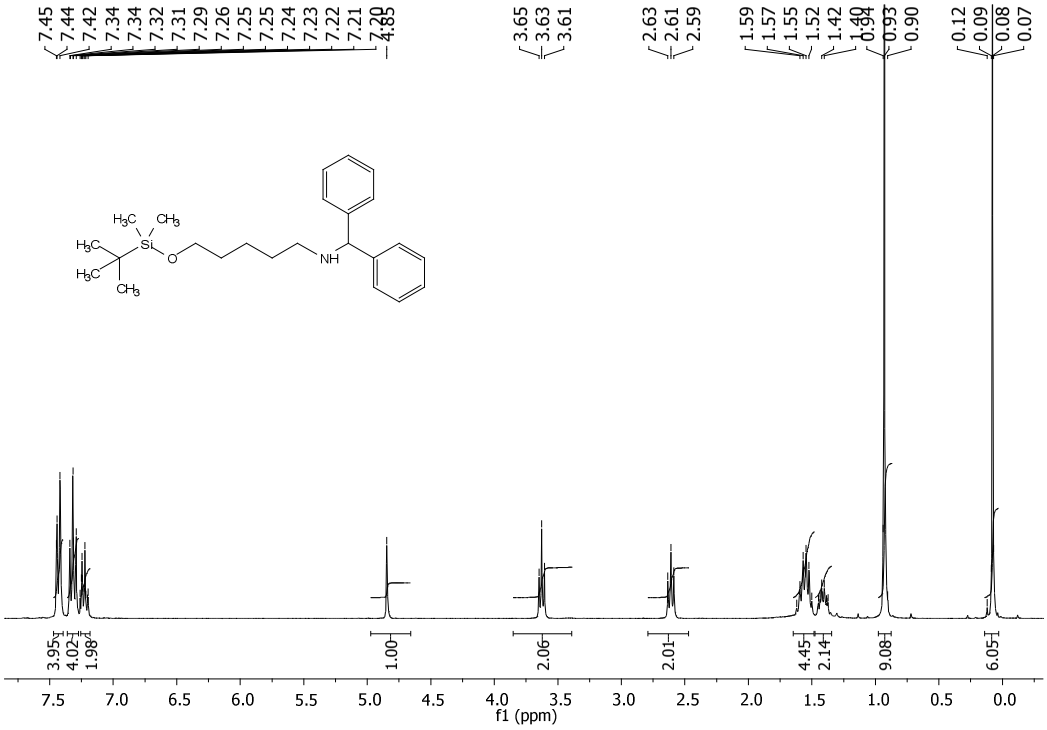


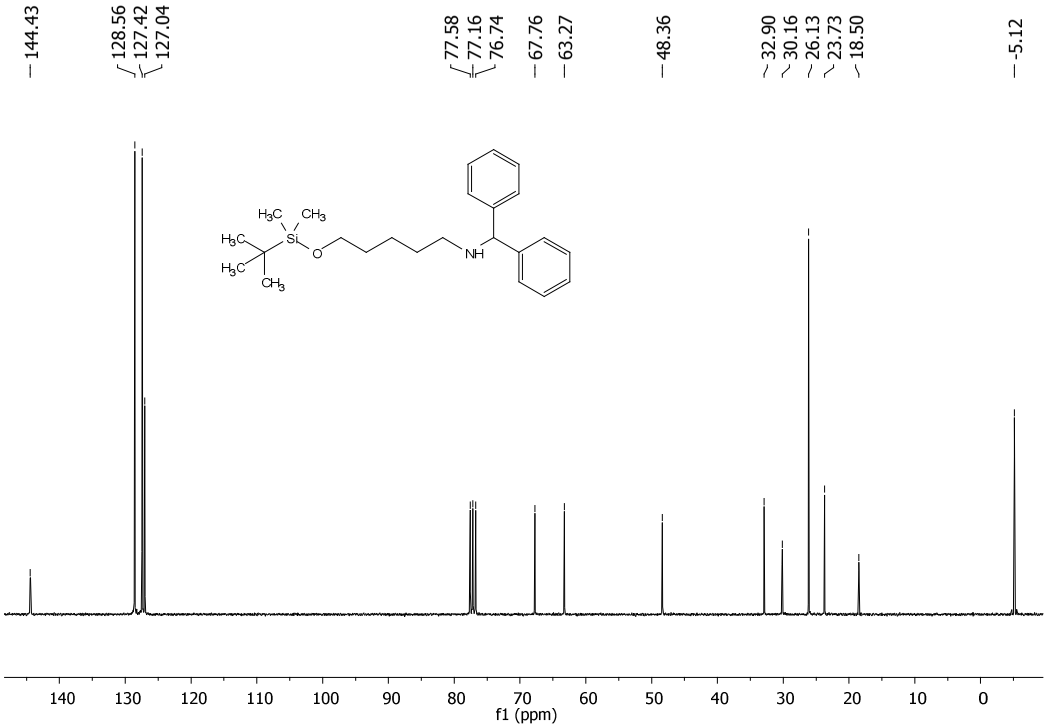
N-Benzhydryl-pentyl-amine (6b)



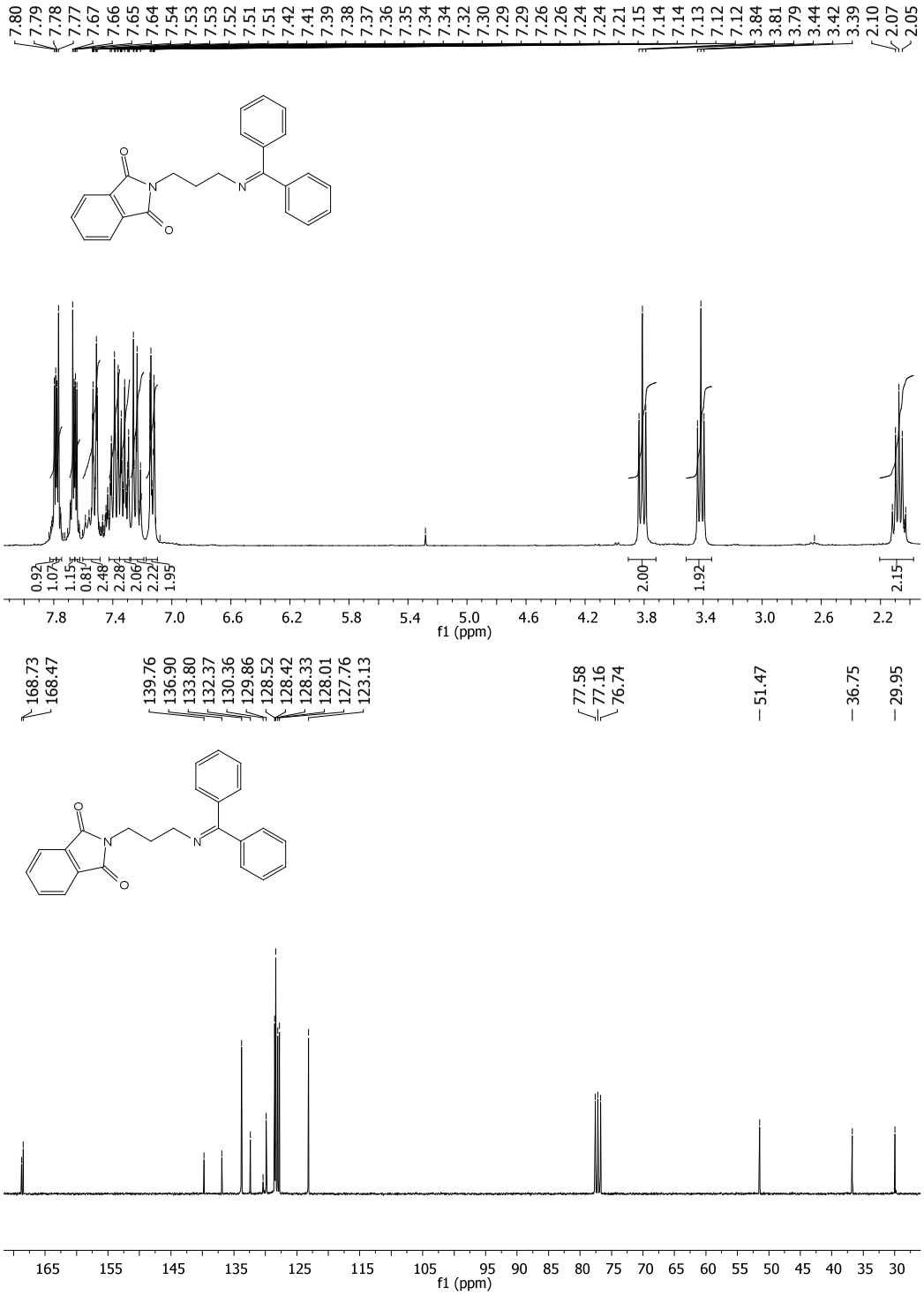


N-Benzhydryl-[5-(*tert*-butyl-dimethyl-silyloxy)-pentyl]-amine (6d)

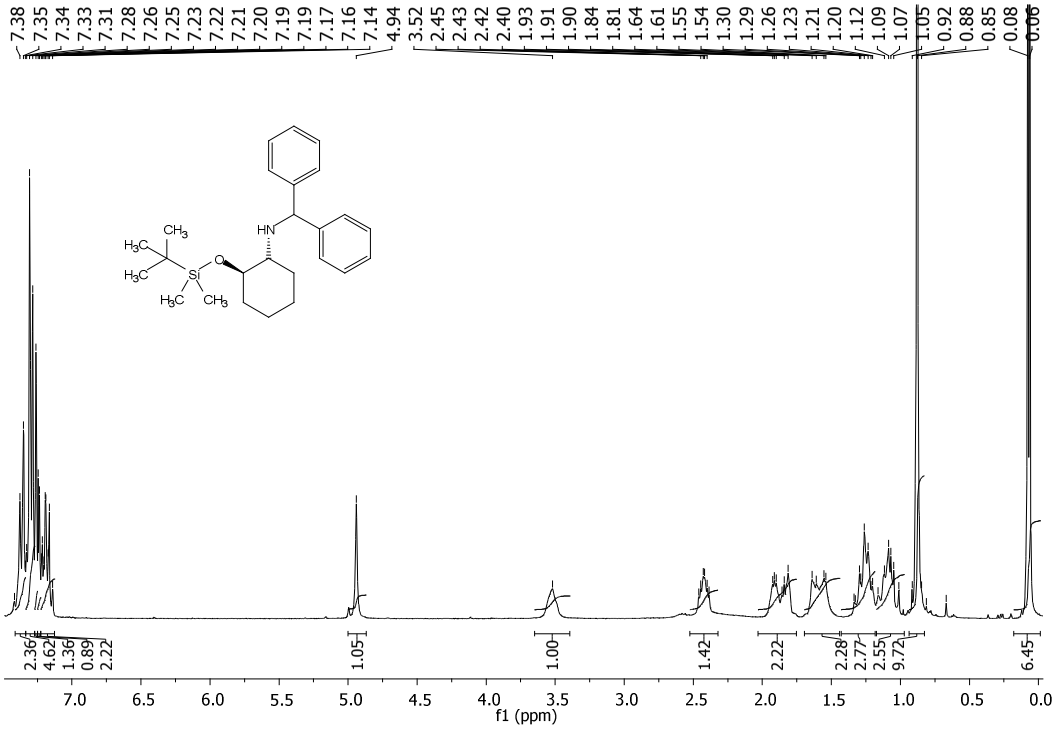


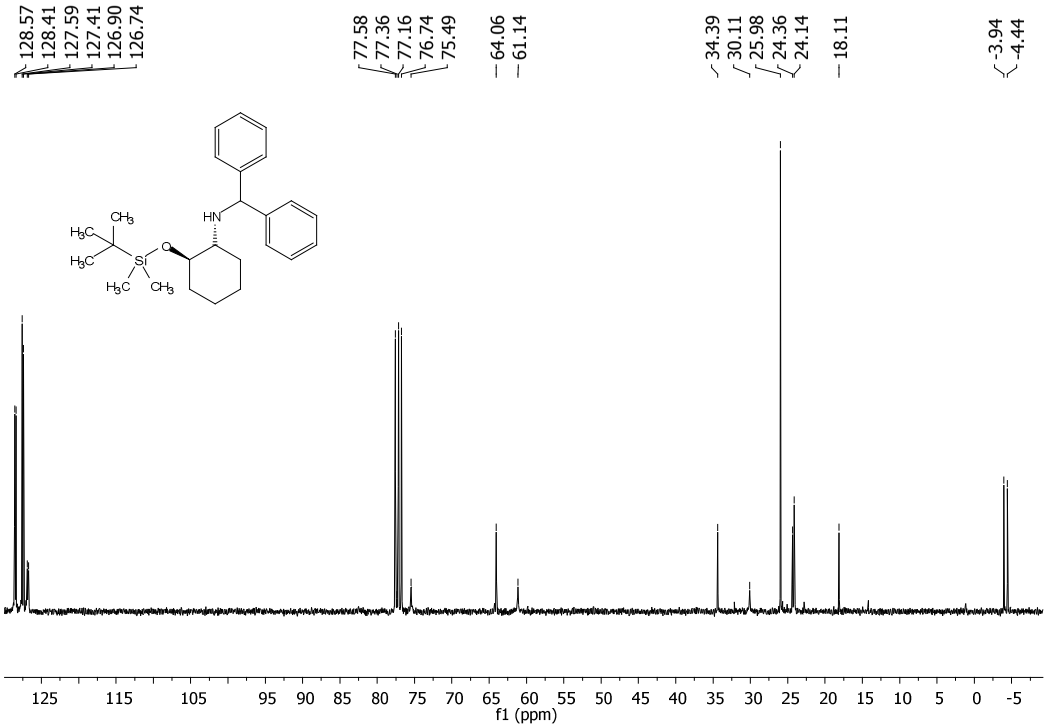


2-[3-(Benzhydrylidene-amino)-propyl]-isoindole-1,3-dione (5f)

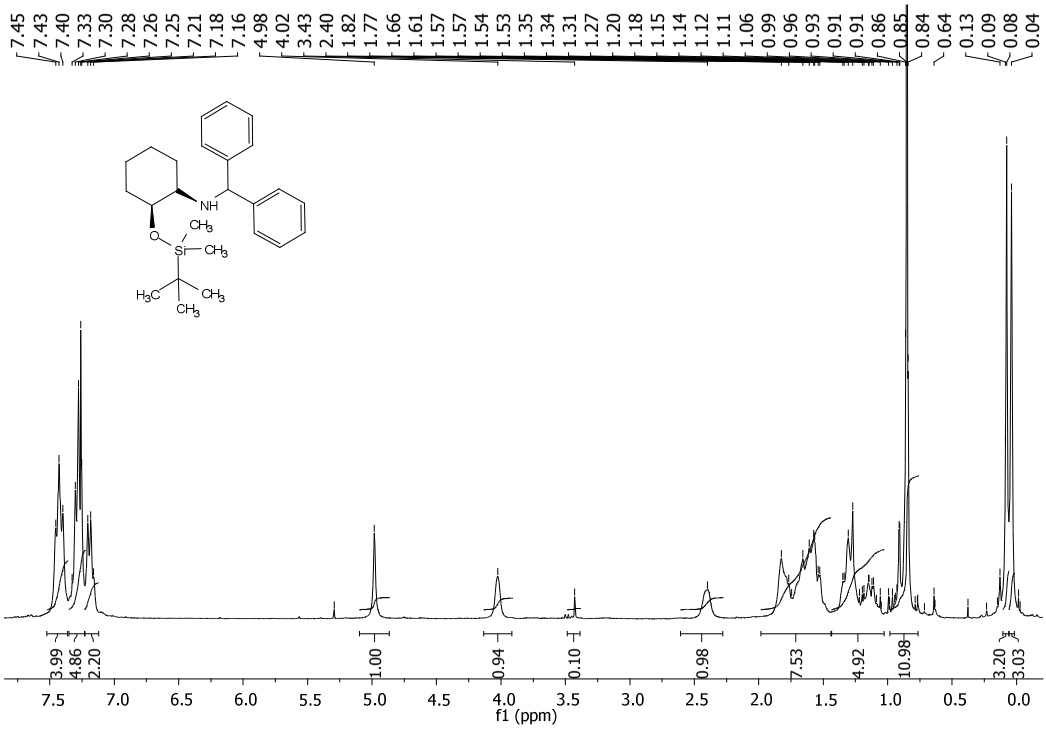


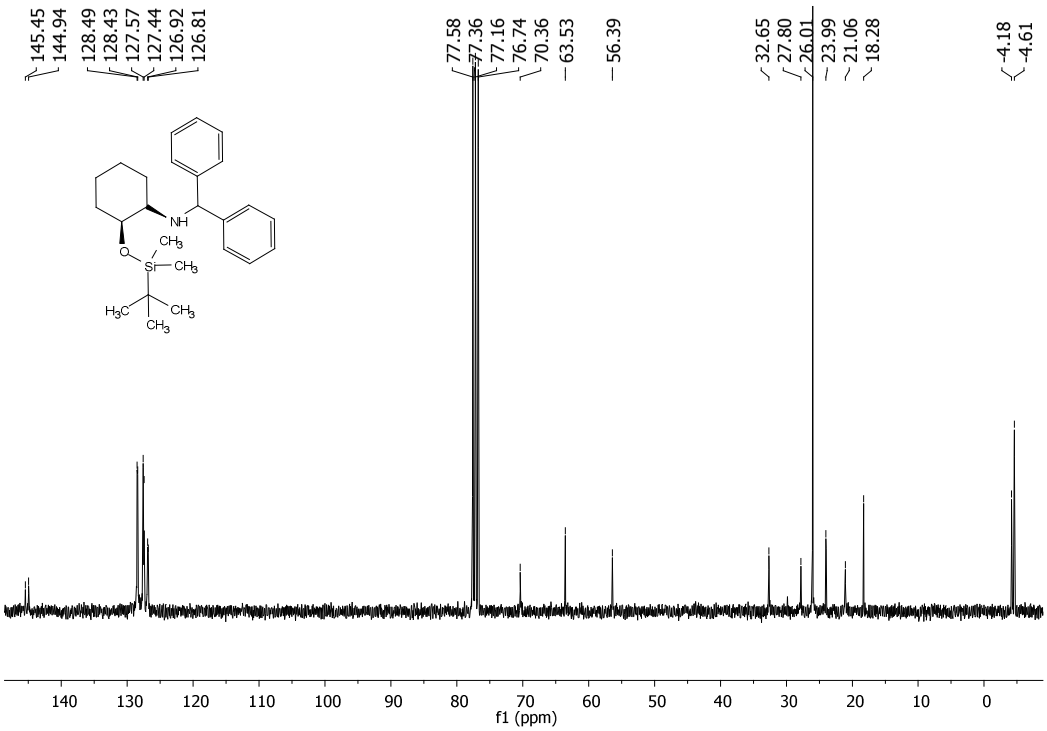
trans-Benzhydryl-[2-(*tert*-butyl-dimethyl-silyloxy)-cyclohexyl]-amine (6e)



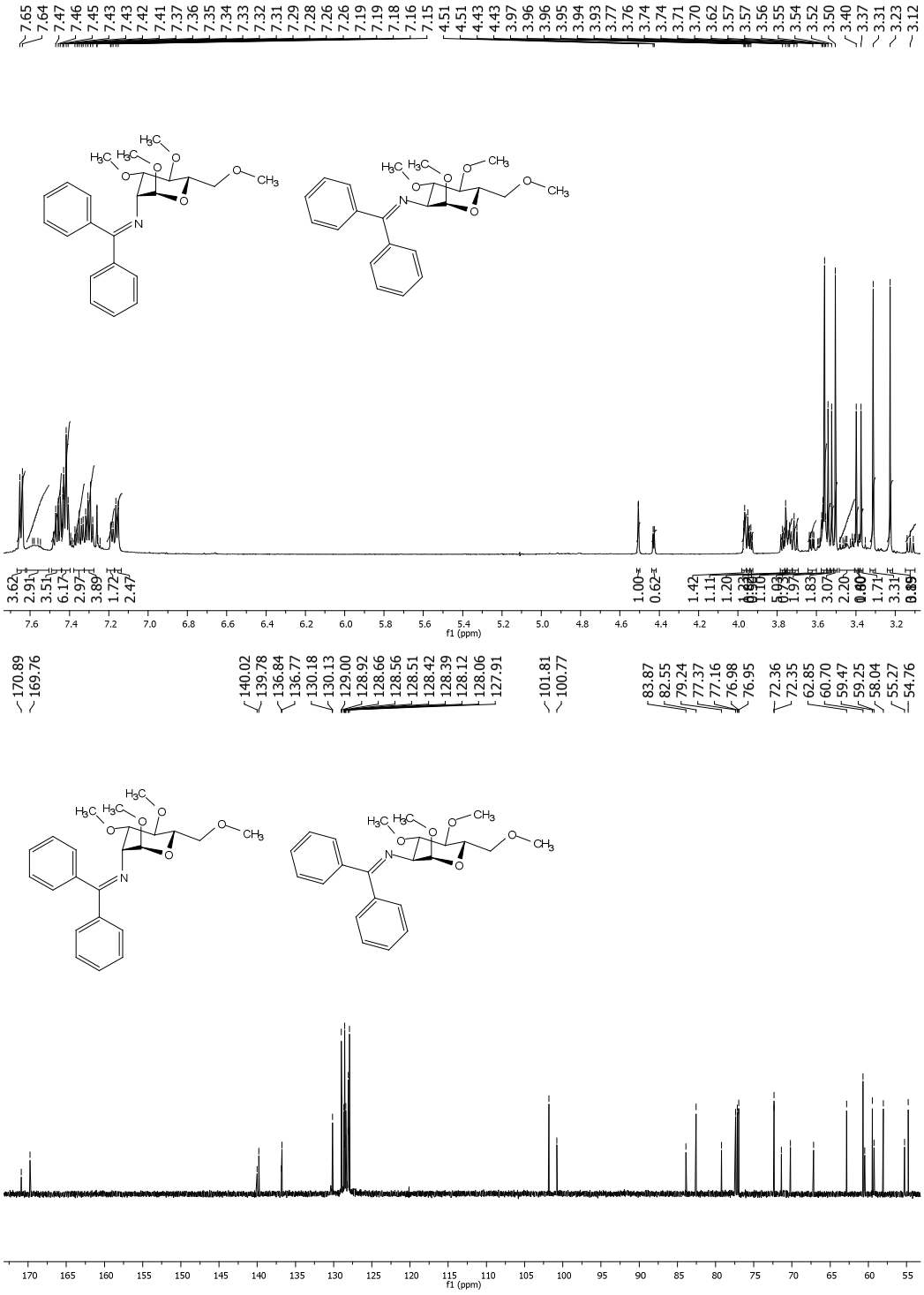


cis-Benzhydryl-[2-(*tert*-butyl-dimethyl-silyloxy)-cyclohexyl]-amine (6e)

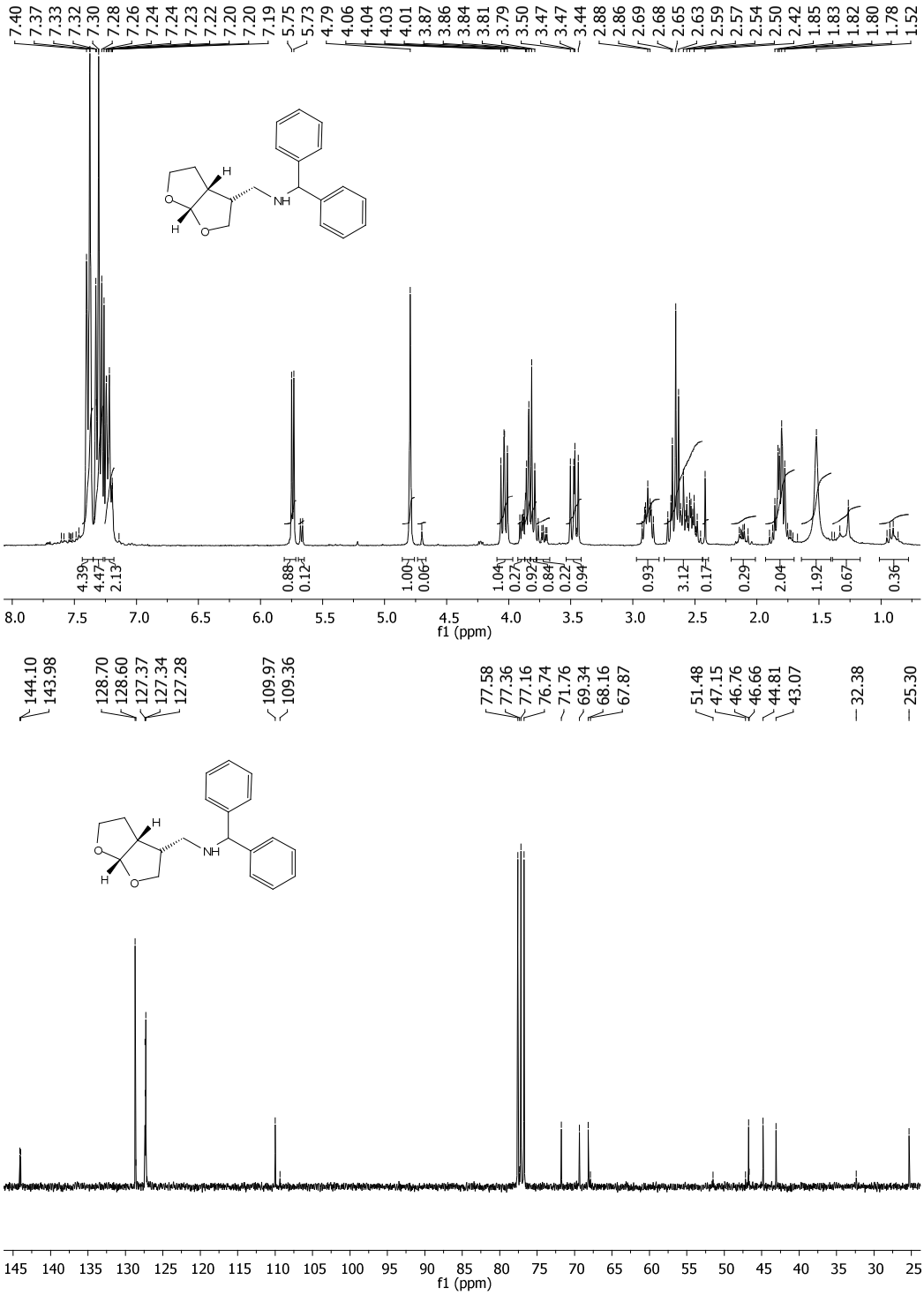




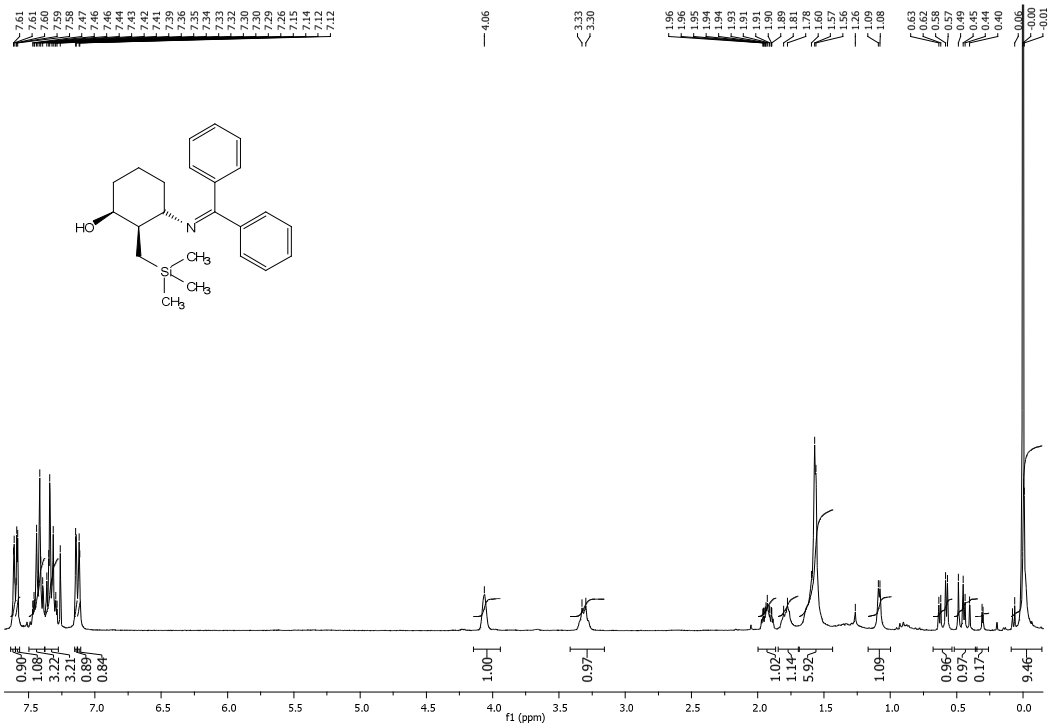
Benzhydrylidene-((2*S*,3*S*,4*R*,5*S*,6*R*)-2,4,5-trimethoxy-6-methoxymethyl-tetrahydro-pyran-3-yl)-amine (major isomer) and benzhydrylidene-((2*S*,3*R*,4*R*,5*S*,6*R*)-2,4,5-trimethoxy-6-methoxymethyl-tetrahydro-pyran-3-yl)-amine (minor isomer) (5h)

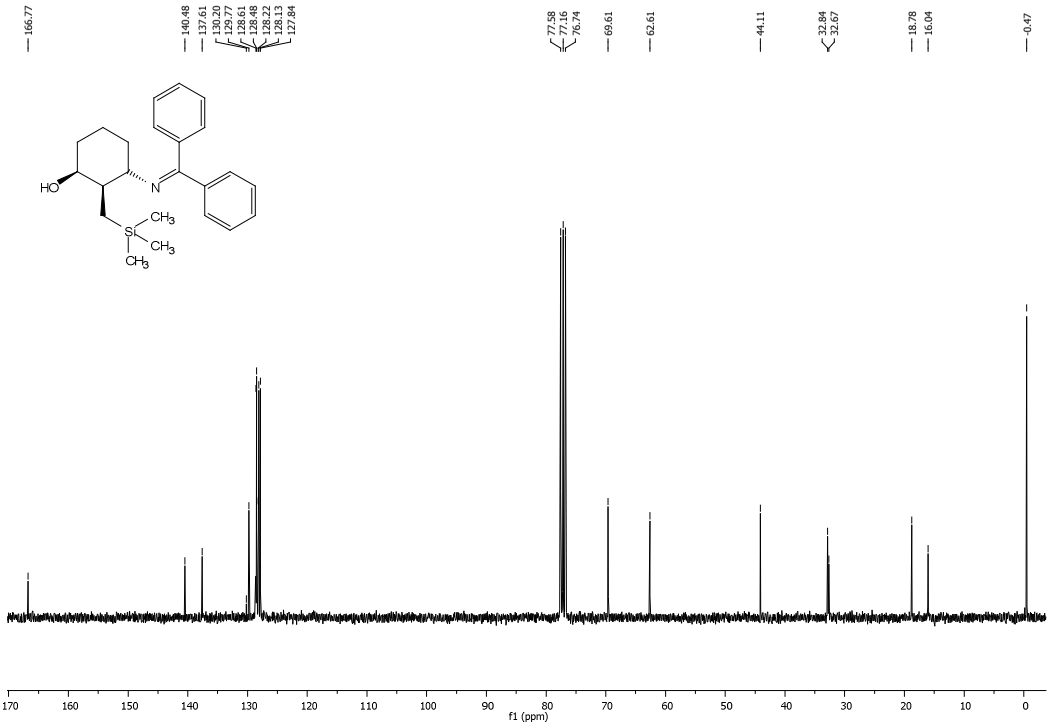


***Cis-endo*-Benzhydryl-[1-(hexahydro-furo[2,3-*b*]furan-3-yl)methyl]-amine (8)**

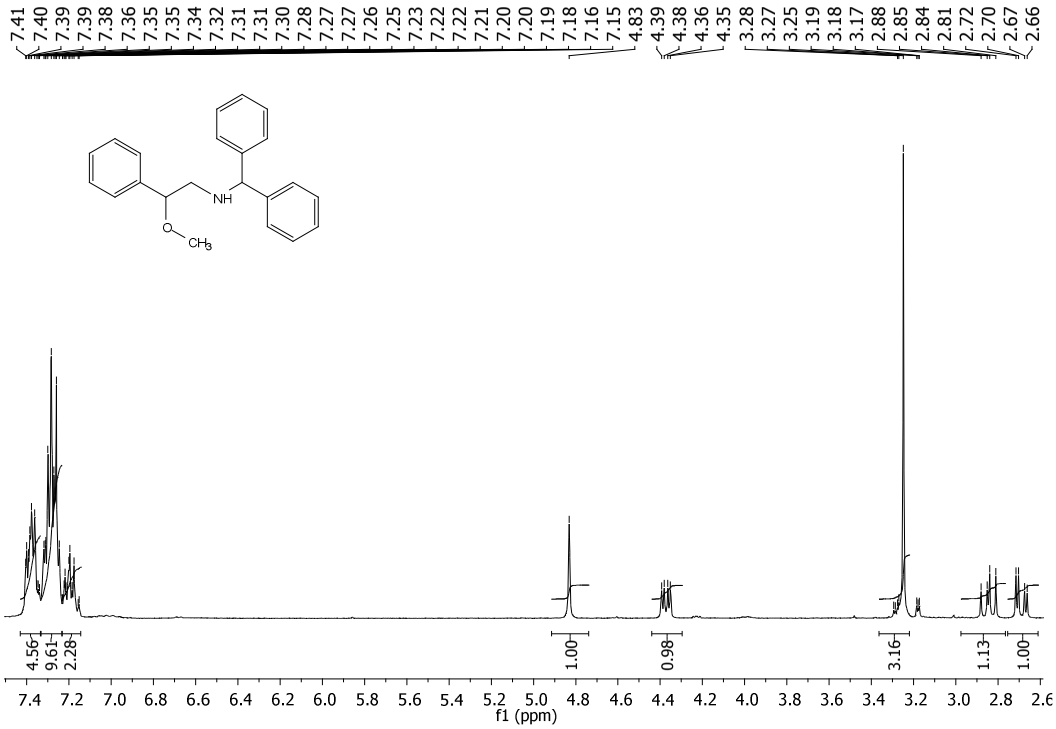


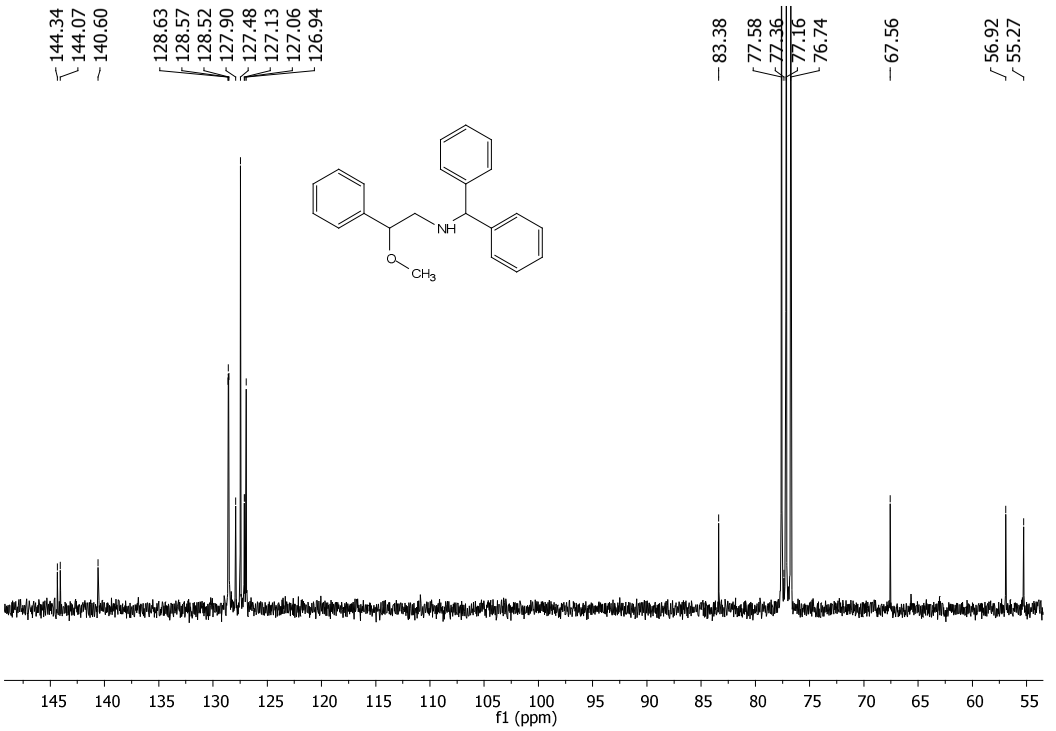
cis-trans-3-(Benzhydrylidene-amino)-2-trimethylsilylmethyl-cyclohexanol (10)





N-Benzhydryl-(2-methoxy-2-phenyl-ethyl)-amine (6g)





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