Electronic Supplementary Information

Mild and Efficient Capture and Functionalisation of CO_2 using Silver(I) Oxide and Application to ^{13}C-labelled Dialkyl Carbonates

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Experimental

General Experimental

Chemicals, solvents and reagents were purchased from commercial sources and used without further purification. PE refers to petroleum ether, bp 40-60 °C. Anhydrous solvents were used where indicated. Glassware for dry reactions was dried either by heating in an oven at 120 °C for at least 1 h, or heating with a hot air gun for 5 min. The glassware was then allowed to cool under a stream of N_2. $CO_{2(g)}$ was generated by allowing commercially available dry ice ($CO_{2(S)}$) to sublime at room temperature in a stoppered flask fitted with an empty balloon. The balloon would gradually fill with CO_2 gas which was used directly in the CO_2 reactions. In the ^{13}C incorporation experiments, $CO_{2(g)}$ was generated by the addition of 3M $HCl_{(aq)}$ to $NaHCO_{3(s)}$. $^{13}CO_{2(g)}$ was generated from $NaH^{13}CO_3$ (isotopic enrichment 99% ^{13}C – see Certificate of Analysis pS71), obtained from CK Gas Products Ltd.

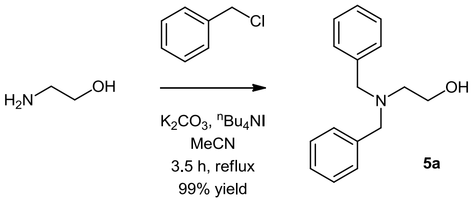
TLCs were carried out on Merck Aluminium backed TLC plates Silica Gel 60 F254 and viewed using UV light of wavelength 254 nm and then stained with potassium permanganate. Merck Silica Gel (0.040-0.063 mm) was used for column chromatography. Compounds were loaded as an oil, CH_2Cl_2 solution or dry loaded by adsorption onto silica.

Melting points were obtained using a Reichert-Jung heated-stage microscope. Infrared spectra were recorded on a Perkin-Elmer Spectrum RXI FT-IR system and reported as cm^{-1}.

NMR spectra were obtained on Varian Mercury VX (400 MHz) or Bruker Avance III (500 or 400 MHz) spectrometers. The chemical shifts are recorded in parts per million (ppm) with reference to tetramethylsilane. The coupling constants *J* are quoted to the nearest 0.5 Hz and are not corrected.

Mass spectra and high resolution mass spectra were obtained on a micrOTOF^{TM} from Bruker Daltonics (Bremen, Germany) coupled with an electrospray source (ESI-TOF) using an autosampler in an Agilent 1100 LC system. Data was processed using external calibration with the Bruker Daltonics software, DataAnalysis^{TM} as part of the overall hardware control software, Compass 1.1^{TM}.

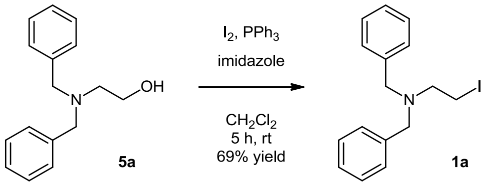
N,*N*-Dibenzyl-2-aminoethanol (5a)



^{n}Bu$_4$NI (1.11 g, 3 mmol, 30 mol%) was added to a rapidly stirred suspension of ethanolamine (604 µL, 10 mmol), benzyl chloride (2.5 mL, 22 mmol, 2.2 equiv.) and K_2CO_3 (4.15 g, 30 mmol, 3 equiv.) in MeCN (30 mL) open to the air. The mixture was heated at reflux for 3.5 h, cooled to room temperature and the solvent removed under reduced pressure. H_2O (30 mL) was added to the residue and the product extracted with EtOAc (4 × 30 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude mixture was purified by column chromatography [silica, PE:EtOAc gradient from 100:0 to 20:80] to afford the alcohol **5a** (2.4 g, 99% yield) as a white solid.

R$_f$ [PE:EtOAc 80:20] 0.30;
Mp 42-44 °C (from PE/EtOAc); Lit.[1] 38 °C (from pentane/EtOAc);
IR ν_{max} (liquid film) 3321 (OH) and 1600 (C=C);
^{1}H NMR δ_H (400 MHz; $CDCl_3$) 7.35-7.26 (10 H, m, Ph), 3.64 (4 H, s, $PhCH_2N$), 3.59 (2 H, t, J = 5.5 Hz, NCH_2CH_2OH), 2.68 (2 H, t, J = 5.5 Hz, NCH_2CH_2OH) and 2.65-2.50 (1 H, m, OH);
^{13}C NMR δ_C (100 MHz; $CDCl_3$) 138.7 (Ph), 129.0 (Ph), 128.4 (Ph), 127.2 (Ph), 58.5 (NCH_2CH_2OH), 58.2 ($PhCH_2N$) and 54.8 (NCH_2CH_2OH);
MS *m/z* (+ESI) 264 (1%, MNa^+) and 242 (100%, MH^+);
HRMS *m/z* (+ESI) Found 242.1546 (MH^+) and 264.1368 (MNa^+). $C_{16}H_{20}NO$ (MH^+) requires 242.1545 and $C_{16}H_{19}NNaO$ (MNa^+) requires 264.1364.
Consistent with the spectroscopic data previously reported.[1, 2]

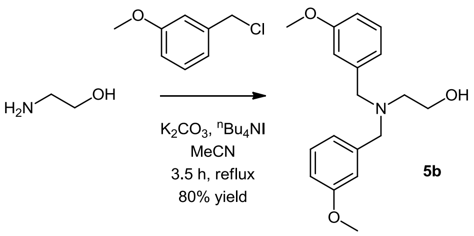
N,*N*-Dibenzylamino-2-iodoethane (1a)



Iodine (858 mg, 3.38 mmol, 1.1 equiv.) was added to a rapidly stirred solution of the alcohol **5a** (743 mg, 3.08 mmol), PPh_3 (887 mg, 3.38 mmol, 1.1 equiv.) and imidazole (230 mg, 3.38 mmol, 1.1 equiv.) in CH_2Cl_2 (20 mL) under a N_2 atmosphere. After 5 h of stirring at room temperature, the solvent was removed under reduced pressure. EtOAc (30 mL) and saturated aqueous $NaHCO_3$ solution (40 mL) were added, the layers separated and the aqueous layer extracted with EtOAc (2 × 30 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude mixture was purified by column chromatography [silica, PE:EtOAc gradient from 100:0 to 30:70] to afford the alkyl iodide **1a** (744 mg, 69% yield) as a clear brown oil.

R_f [PE:EtOAc 70:30] 0.80.
IR ν_{max} (liquid film) 2925 (CH) and 1602 (C=C);
^{1}H NMR δ_H (400 MHz; $CDCl_3$) 7.38 (4 H, t, J = 7.5 Hz, Ph), 7.34-7.28 (4 H, m, Ph), 7.27-7.21 (2 H, m, Ph), 3.63 (4 H, s, $PhCH_2N$), 3.16 (2 H, t, J = 7.5 Hz, NCH_2CH_2I) and 2.83 (2 H, t, J = 7.5 Hz, NCH_2CH_2I);
^{13}C NMR δ_C (100 MHz; $CDCl_3$) 139.0 (Ph), 128.8 (Ph), 128.3 (Ph), 127.1 (Ph), 58.1 ($PhCH_2N$), 56.1 (NCH_2CH_2I) and 4.0 (NCH_2CH_2I);
MS *m/z* (+ESI) 352 (11%, MH^+) and 224 (100%, M^+-I);
HRMS *m/z* (+ESI) Found 352.0561 (MH^+). $C_{16}H_{19}IN$ (MH^+) requires 352.0562.
Consistent with the spectroscopic data previously reported.[2]

N,*N*-bis-(3-Methoxybenzyl)-2-aminoethanol (5b)



^{n}Bu$_4$NI (554 mg, 1.5 mmol, 30 mol%) was added to a rapidly stirred suspension of ethanolamine (302 µL, 5 mmol), 3-methoxybenzyl chloride (1.6 mL, 11 mmol, 2.2 equiv.) and K_2CO_3 (2.07 g, 15 mmol, 3 equiv.) in MeCN (30 mL) open to the air. The mixture was heated at reflux for 3.5 h, cooled to room temperature and the solvent removed under reduced pressure. H_2O (30 mL) was added to the residue and the product extracted with EtOAc (4 × 30 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude mixture was purified by column chromatography [silica, PE:EtOAc gradient from 100:0 to 20:80] to afford the alcohol **5b** (1.2 g, 80% yield) as a colourless oil.

R_f [PE:EtOAc 50:50] 0.60;

IR ν_{max} (liquid film) 3451 (OH), 2943 (C-H), 1600 (C=C) and 1049 (C-O);

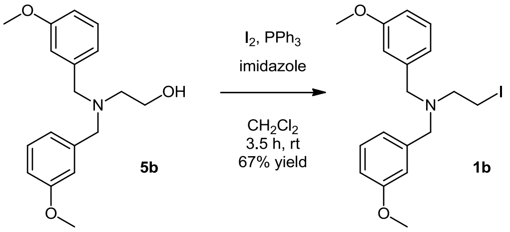
^{1}H NMR δ_H (400 MHz; $CDCl_3$) 7.24 (2 H, t, *J* = 8.0 Hz, Ar), 6.91 (2 H, br.d, *J* = 7.5 Hz, Ar), 6.87 (2 H, t, *J* = 1.5 Hz, Ar), 6.79 (2 H, ddd, *J* = 8.5, 2.5 and 1.0 Hz, Ar), 3.80 (6 H, s, ArOCH_3), 3.60 (4 H, s, ArCH_2N), 3.59 (2 H, t, *J* = 5.0 Hz, NCH$_2$CH_2OH) and 2.68 (2 H, t, *J* = 5.0 Hz, NCH_2CH$_2$OH);

^{13}C NMR δ_C (100 MHz; $CDCl_3$) 159.7 (Ar), 140.4 (Ar), 129.4 (Ar), 121.2 (Ar), 114.6 (Ar), 112.4 (Ar), 58.6 (NCH$_2$*C*H$_2$OH), 58.2 (Ar*C*H$_2$N), 55.1 (ArO*C*H$_3$) and 54.9 (N*C*H$_2$CH$_2$OH);

MS *m/z* (+ESI) 324 (13%, MNa$^+$) and 302 (100%, MH$^+$);

HRMS *m/z* (+ESI) Found 324.1554 (MNa$^+$) and 302.1748 (MH$^+$). $C_{18}H_{23}NNaO_3$ (MNa$^+$) requires 324.1576 and $C_{18}H_{24}NO_3$ (MH$^+$) requires 302.1756.

N,*N*-bis-(3-Methoxybenzyl)amino-2-iodoethane (1b)



Iodine (558 mg, 2.2 mmol, 1.1 equiv.) was added to a rapidly stirred solution of the alcohol **5b** (602 mg, 2 mmol), PPh_3 (577 mg, 2.2 mmol, 1.1 equiv.) and imidazole (150 mg, 2.2 mmol, 1.1 equiv.) in CH_2Cl_2 (8 mL) open to the air. After 3.5 h of stirring at room temperature, the solvent was removed under reduced pressure. EtOAc (30 mL) and saturated aqueous $NaHCO_3$ solution (40 mL) were added, the layers separated and the aqueous layer extracted with EtOAc (2 × 30 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude mixture was purified by column chromatography [silica, PE:EtOAc gradient from 100:0 to 30:70] to afford the alkyl iodide **1b** (550 mg, 67% yield) as a clear brown oil.

$\mathbf{R_f}$ [PE:EtOAc 70:30] 0.80;

IR ν_{max} (liquid film) 2939 (C-H), 1600 (C=C) and 1050 (C-O);

^{1}H NMR δ_H (400 MHz; $CDCl_3$) 7.22 (2 H, t, *J* = 8.0 Hz, Ar), 7.01 (2 H, br.s, Ar), 6.95 (2 H, d, *J* = 7.5 Hz, Ar), 6.79 (2 H, dd, *J* = 8.0 and 2.5 Hz, Ar), 3.82 (6 H, s, $ArOCH_3$), 3.61 (4 H, s, $ArCH_2N$), 3.20 (2 H, t, *J* = 7.5 Hz, NCH_2CH_2I) and 2.83 (2 H, t, *J* = 7.5 Hz, NCH_2CH_2I);

^{13}C NMR δ_C (100 MHz; $CDCl_3$) 159.6 (Ar), 140.7 (Ar), 129.2 (Ar), 121.0 (Ar), 114.2 (Ar), 112.6 (Ar), 58.0 ($ArCH_2N$), 55.9 (NCH_2CH_2I), 55.2 ($ArOCH_3$) and 4.30 (NCH_2CH_2I);

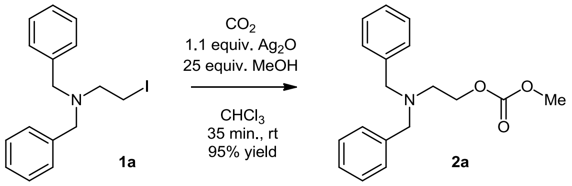
MS *m/z* (+ESI) 316 (100%, $M^+{-}I{+}MeOH$; **3b**+H^+), 284 (58%, $M^+{-}I$);

HRMS *m/z* (+ESI) Found 284.1646 ($M^+{-}I$). $C_{18}H_{22}NO_2$ ($M^+{-}I$) requires 284.1651.

CO_2 capture and functionalisation
Table 1

Entry 1, Table 1

2-*N*,*N*-Dibenzylaminoethyl methyl carbonate (2a)

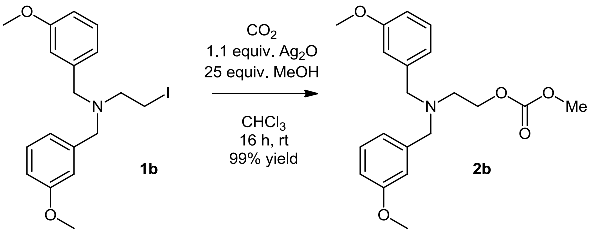


N,*N*-Dibenzylamino-2-iodoethane **1a** (50 mg, 0.14 mmol) was dissolved in $CHCl_3$ (2 mL) and CO_2 (1 balloon) was bubbled through. MeOH (0.14 mL, 3.5 mmol, 25 equiv.) was added, followed by Ag_2O (37 mg, 0.16 mmol, 1.1 equiv.) and the reaction vigorously stirred under an atmosphere of CO_2 at room temperature for 35 mins. The reaction mixture was filtered through a cotton wool and silica plug and washed with $CHCl_3$ (10 mL) and EtOAc (10 mL). The solvent was removed under reduced pressure to give, without the need for further purification, the unsymmetrical carbonate **2a** (40 mg, 95% yield) as a colourless oil.

R_f [PE:EtOAc 80:20] 0.51;
IR ν_{max} (liquid film) 2955 (CH), 1747 (C=O) and 1602 (C=C);
^{1}H NMR δ_H (400 MHz; $CDCl_3$) 7.36 (4 H, d, J = 7.0 Hz, Ph), 7.30 (4 H, t, J = 7.0 Hz, Ph), 7.23 (2 H, t, J = 7.0 Hz, Ph), 4.20 (2 H, t, J = 6.0 Hz, NCH_2CH_2O), 3.75 (3 H, s, OCO_2CH_3), 3.65 (4 H, s, $PhCH_2N$) and 2.76 (2 H, t, J = 6.0 Hz, NCH_2CH_2O);
^{13}C NMR δ_C (100 MHz; $CDCl_3$) 155.7 (C=O), 139.2 (Ph), 128.7 (Ph), 128.2 (Ph), 127.0 (Ph), 66.0 (NCH_2CH_2O), 58.7 ($PhCH_2N$), 54.7 (OCO_2CH_3) and 51.6 (NCH_2CH_2O);
MS *m/z* (+ESI) 322 (2%, MNa^+) and 300 (100%, MH^+);
HRMS *m/z* (+ESI) Found 322.1419 (MNa^+) and 300.1597 (MH^+). $C_{18}H_{21}NNaO_3$ (MNa^+) requires 322.1419 and $C_{18}H_{22}NO_3$ (MH^+) requires 300.1600.

Entry 2, Table 1

2-*N*,*N*-bis-(3-Methoxybenzyl)aminoethyl methyl carbonate (2b)



N,*N*-bis-(3-Methoxybenzyl)amino-2-iodoethane **1b** (44 mg, 0.11 mmol) was dissolved in $CHCl_3$ (2 mL) and CO_2 (1 balloon) was bubbled through. MeOH (0.11 mL, 2.72 mmol, 25 equiv.) was added, followed by Ag_2O (27 mg, 0.12 mmol, 1.1 equiv.) and the reaction vigorously stirred under an atmosphere of CO_2 at room temperature for 16 h. The reaction mixture was filtered through a cotton wool and silica plug and washed with $CHCl_3$ (10 mL) and EtOAc (10 mL). The solvent was removed under reduced pressure to give, without the need for further purification, the unsymmetrical carbonate **2b** (38 mg, 99% yield) as a pale yellow oil.

R_f [PE:EtOAc 70:30] 0.63;

IR ν_{max} (liquid film) 2834 (CH), 1749 (C=O), 1600 (C=C) and 1047 (CO);

^{1}H NMR δ_H (400 MHz; $CDCl_3$) 7.23 (2 H, t, J = 8.0 Hz, Ar), 6.98 (2 H, br.s, Ar), 6.95 (2 H, d, J = 7.5 Hz, Ar), 6.79 (2 H, dd, J = 8.0 and 2.5 Hz, Ar), 4.24 (2 H, t, J = 6.0 Hz, NCH_2CH_2O), 3.82 (6 H, s, $ArOCH_3$), 3.77 (3 H, s, OCO_2CH_3), 3.65 (4 H, s, $ArCH_2N$) and 2.79 (2 H, t, J = 6.0 Hz, NCH_2CH_2O);

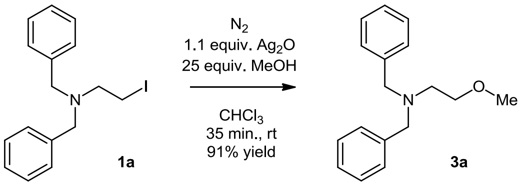
^{13}C NMR δ_C (100 MHz; $CDCl_3$) 159.7 (Ar), 155.7 (C=O), 140.9 (Ar), 129.2 (Ar), 121.0 (Ar), 114.0 (Ar), 112.5 (Ar), 65.9 (NCH_2CH_2O), 58.6 ($ArCH_2N$), 55.1 ($ArOCH_3$), 54.7 (OCO_2CH_3) and 51.7 (NCH_2CH_2O);

MS *m/z* (+ESI) 360 (100%, MH^+);

HRMS *m/z* (+ESI) Found 360.1805 (MH^+). $C_{20}H_{26}NO_5$ (MH^+) requires 360.1811.

Entry 3, Table 1

N,*N*-Dibenzylamino-2-methoxyethane (3a)



Ag_2O (41 mg, 0.18 mmol, 1.1 equiv.) was added in one portion to a rapidly stirred solution of *N*,*N*-dibenzylamino-2-iodoethane **1a** (57 mg, 0.16 mmol) and MeOH (0.16 mL, 4 mmol, 25 equiv.) in $CHCl_3$ (2 mL) under a N_2 atmosphere at room temperature. After 35 min. the reaction mixture was filtered through a cotton wool and silica plug and washed with $CHCl_3$ (10 mL) and EtOAc (10 mL). The solvent was removed under reduced pressure to give, without the need for purification, the ether **3a** (37 mg, 91% yield) as a colourless oil.

R_f [PE:EtOAc 70:30] 0.53;

IR ν_{max} (liquid film) 2923 (CH) and 1601 (C=C);

^{1}H NMR δ_H (400 MHz; $CDCl_3$) 7.38 (4 H, d, *J* = 8.0 Hz, Ph), 7.30 (4 H, t, *J* = 8.0 Hz, Ph), 7.25-7.21 (2 H, m, Ph), 3.65 (4 H, s, $PhCH_2N$), 3.49 (2 H, t, *J* = 6.5 Hz, NCH_2CH_2OMe), 3.28 (3 H, s, NCH_2CH_2OMe) and 2.66 (2 H, t, *J* = 6.5 Hz, NCH_2CH_2OMe);

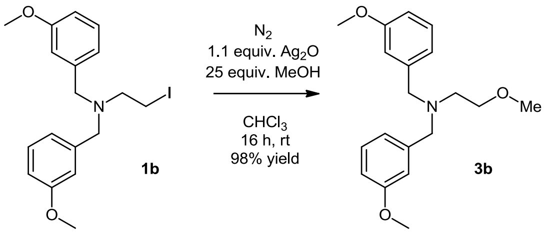
^{13}C NMR δ_C (100 MHz; $CDCl_3$) 139.7 (Ph), 128.8 (Ph), 128.2 (Ph), 126.8 (Ph), 71.5 (NCH_2CH_2OMe), 58.9 ($PhCH_2N$), 58.7 (NCH_2CH_2OMe) and 52.7 (NCH_2CH_2OMe);

MS *m/z* (+ESI) 256 (100%, MH^+);

HRMS *m/z* (+ESI) Found 256.1691 (MH^+). $C_{17}H_{22}NO$ (MH^+) requires 256.1701.

Entry 4, Table 1

N,*N*-bis-(3-Methoxybenzyl)amino-2-methoxyethane (3b)



Ag_2O (49 mg, 0.21 mmol, 1.1 equiv.) was added in one portion to a rapidly stirred solution of *N*,*N*-bis-(3-methoxybenzyl)amino-2-iodoethane **1b** (80 mg, 0.19 mmol) and MeOH (0.2 mL, 4.94 mmol, 25 equiv.) in $CHCl_3$ (3 mL) under a N_2 atmosphere at room temperature. After for 16 h. the reaction mixture was filtered through a cotton wool and silica plug and washed with $CHCl_3$ (10 mL) and EtOAc (10 mL). The solvent was removed under reduced pressure to give, without the need for further purification, the ether **3b** (60 mg, 98% yield) as a pale yellow oil.

R_f [PE:EtOAc 70:30] 0.66;

IR ν_{max} (liquid film) 2833 (CH), 1600 (C=C) and 1048 (CO);

^{1}H NMR δ_H (400 MHz; $CDCl_3$) 7.21 (2 H, t, $J = 8.0$ Hz, Ar), 6.98 (2 H, d, $J = 2.5$ Hz, Ar), 6.95 (2 H, d, $J = 8.0$ Hz, Ar), 6.78 (2 H, dd, $J = 8.0$ and 2.5 Hz, Ar), 3.81 (6 H, s, ArO*Me*), 3.63 (4 H, s, ArC*H*$_2$N), 3.50 (2 H, t, $J = 6.0$ Hz, NCH_2CH_2OMe) with *H*$_2$ on the second carbon, 3.29 (3 H, s, NCH_2CH_2O*Me*) and 2.69 (2 H, t, $J = 6.0$ Hz, NC*H*$_2$CH$_2$OMe);

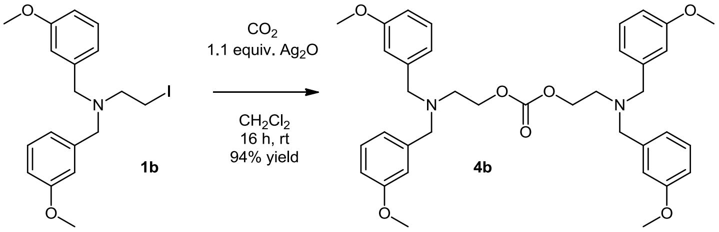
^{13}C NMR δ_C (100 MHz; $CDCl_3$) 159.6 (Ar), 141.5 (Ar), 129.1 (Ar), 121.0 (Ar), 114.2 (Ar), 112.3 (Ar), 71.5 (NCH$_2$*C*H$_2$OMe), 58.8 (Ar*C*H$_2$N), 58.7 (NCH$_2$CH$_2$O*Me*), 55.1 (ArO*Me*) and 52.8 (N*C*H$_2$CH$_2$OMe);

MS *m/z* (+ESI) 338 (1%, MNa^+) and 316 (100%, MH^+);

HRMS *m/z* (+ESI) Found 338.1718 (MNa^+) and 316.1891 (MH^+). $C_{19}H_{25}NNaO_3$ (MNa^+) requires 338.1732 and $C_{19}H_{26}NO_3$ (MH^+) requires 316.1913.

Entry 5, Table 1

Bis-[2-*N*,*N*-bis-(3-Methoxybenzyl)aminoethyl] carbonate (4b)



A solution of *N*,*N*-bis-(3-methoxybenzyl)amino-2-iodoethane **1b** (133 mg, 0.32 mmol) in CH_2Cl_2 (2 mL) was vigorously stirred under an atmosphere of CO_2 (balloon) at room temperature for 2 h before Ag_2O (81 mg, 0.35 mmol, 1.1 equiv.) was added in one portion and the reaction stirred for a further 16 h under an atmosphere of CO_2. The reaction mixture was filtered through a pad of Celite®, washed with CH_2Cl_2 (10 mL) and the solvent removed under reduced pressure to give, without the need for further purification, the symmetrical carbonate **4b** (95 mg, 94% yield) as a clear yellow oil.

R_f [PE:EtOAc 70:30] 0.40;

IR ν_{max} (liquid film) 3054 (CH), 1744 (C=O), 1601 (C=C) and 1264 (CO);

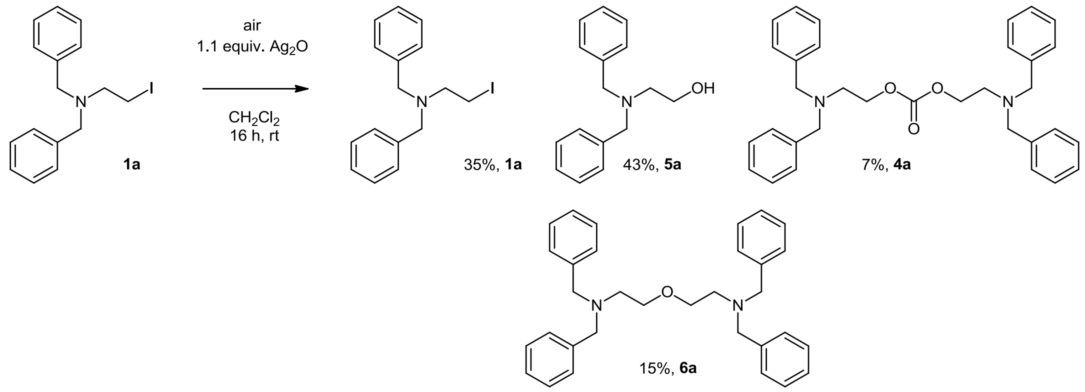
^{1}H NMR δ_H (400 MHz; $CDCl_3$) 7.20 (4 H, t, *J* = 8.0 Hz, Ar), 6.95 (4 H, br.s, Ar), 6.93 (4 H, d, *J* = 8.0 Hz, Ar), 6.77 (4 H, dd, *J* = 8.0 and 2.0 Hz, Ar), 4.20 (4 H, t, *J* = 6.5 Hz, NCH_2CH_2O), 3.79 (12 H, s, ArO*Me*), 3.63 (8 H, s, $ArCH_2N$) and 2.77 (4 H, t, *J* = 6.5 Hz, NCH_2CH_2O);

^{13}C NMR δ_C (100 MHz; $CDCl_3$) 159.7 (Ar), 155.1 (C=O), 140.9 (Ar), 129.2 (Ar), 121.0 (Ar), 114.0 (Ar), 112.5 (Ar), 65.8 (NCH_2CH_2O), 58.6 ($ArCH_2N$), 55.1 (ArO*Me*) and 51.6 (NCH_2CH_2O);

MS *m/z* (+ESI) 651 (100%, MNa^+);

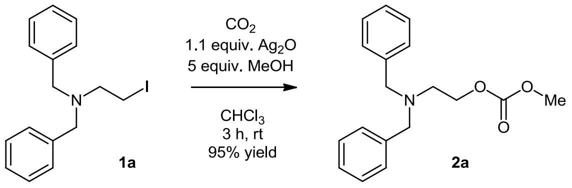
HRMS *m/z* (+ESI) Found 651.3028 (MNa^+). $C_{37}H_{44}N_2NaO_7$ (MNa^+) requires 651.3046.

Entry 6, Table 1



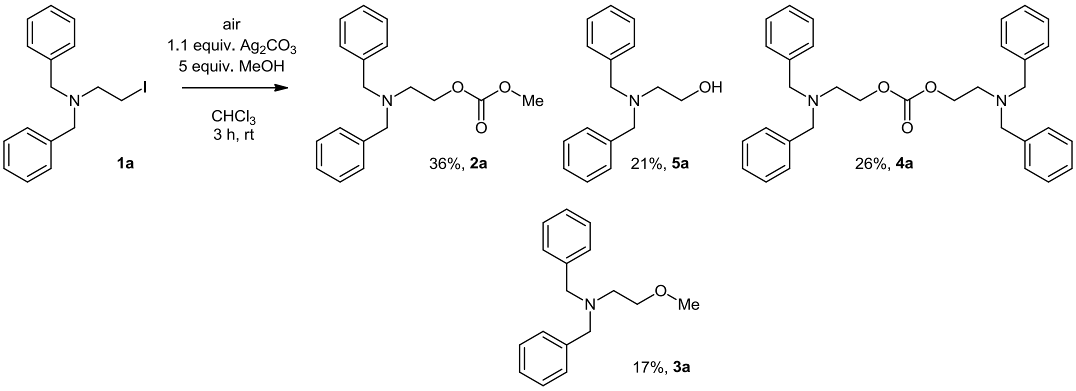
Ag_2O (67 mg, 0.29 mmol, 1.1 equiv.) was added in one portion to a rapidly stirred solution of *N*,*N*-dibenzylamino-2-iodoethane **1a** (92 mg, 0.26 mmol) in CH_2Cl_2 (2 mL) at room temperature open to the air. After 16 h. the reaction mixture was filtered through a pad of Celite® and washed with $CHCl_3$ (10 mL) and the solvent removed under reduced pressure to give a colourless oil. ^1H NMR of this material showed unreacted starting material **1a** (35%), the symmetrical carbonate **4a** (7%), the alcohol **5a** (43%) and the symmetrical ether **6a** (15%).

Entry 7, Table 1



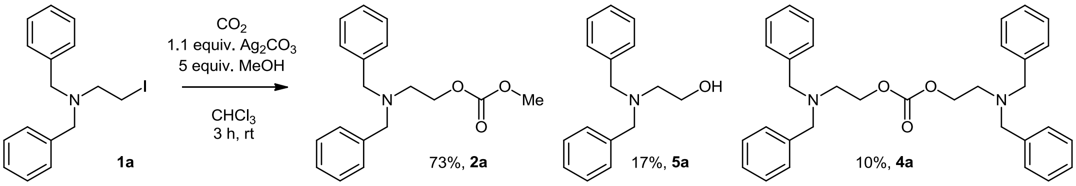
N,*N*-Dibenzylamino-2-iodoethane **1a** (196 mg, 0.56 mmol) was dissolved in $CHCl_3$ (5 mL) and CO_2 was bubbled through. MeOH (0.11 mL, 2.80 mmol, 5 equiv.) was added, followed by Ag_2O (144 mg, 0.62 mmol, 1.1 equiv.) and the reaction vigorously stirred under an atmosphere of CO_2 at room temperature for 3 h. The reaction mixture was filtered through a pad of Celite®, washed with $CHCl_3$ (10 mL) and the solvent removed under reduced pressure to give, without the need for further purification, the unsymmetrical carbonate **2a** (158 mg, 95% yield) as a clear pale yellow oil, consistent with the spectroscopic data previous reported for carbonate **2a**.

Entry 8, Table 1



Ag_2CO_3 (83 mg, 0.30 mmol, 1.1 equiv.) was added in one portion to a rapidly stirred solution of *N*,*N*-dibenzylamino-2-iodoethane **1a** (96 mg, 0.27 mmol) and MeOH (0.05 mL, 1.35 mmol, 5 equiv.) in $CHCl_3$ (2.5 mL) at room temperature open to the air and stirred for 3 h. The reaction mixture was filtered through a pad of Celite® and washed with $CHCl_3$ (10 mL) and the solvent removed under reduced pressure to give a colourless oil. ^1H NMR of this material showed the unsymmetrical carbonate **2a** (36%), the ether **3a** (17%), the symmetrical carbonate **4a** (26%) and the alcohol **5a** (21%).

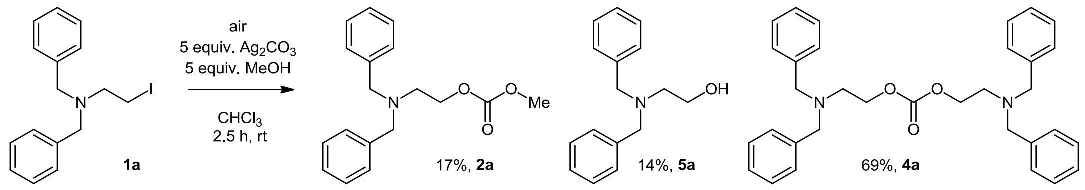
Entry 9, Table 1



N,*N*-Dibenzylamino-2-iodoethane **1a** (160 mg, 0.46 mmol) was dissolved in $CHCl_3$ (4 mL) and CO_2 was bubbled through. MeOH (0.09 mL, 2.30 mmol, 5 equiv.) was added, followed by Ag_2CO_3 (141 mg, 0.51 mmol, 1.1 equiv.) and the reaction vigorously stirred under an atmosphere of CO_2 at room temperature for 3 h. The reaction mixture was filtered through a pad of Celite® and washed with $CHCl_3$ (10 mL) and the solvent removed under reduced pressure to give a clear yellow oil. ^1H NMR of this material showed the unsymmetrical carbonate **2a** (73%), the alcohol **5a** (17%) and the symmetrical carbonate **4a** (10%).

Entry 10, Table 1

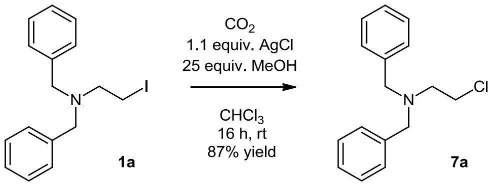
Bis-(2-*N*,*N*-Dibenzylaminoethyl) carbonate (4a)



Using 5 equivalents of Ag_2CO_3 as reported by Teranishi *et al.*,[3,4] Ag_2CO_3 (938 mg, 3.40 mmol, 5 equiv.) was added in one portion to a rapidly stirred solution of *N*,*N*-dibenzylamino-2-iodoethane **1a** (237 mg, 0.68 mmol) and MeOH (0.14 mL, 3.40 mmol, 5 equiv.) in $CHCl_3$ (9 mL) open to the atmosphere at room temperature. The flask was covered in foil[5] and after 2.5 h. the reaction mixture was filtered through a pad of Celite® and washed with $CHCl_3$ (10 mL). The solvent was removed under reduced pressure to give a pale yellow oil. ^1H NMR of this material showed the unsymmetrical carbonate **2a** (17%), the alcohol **5a** (14%) and the symmetrical carbonate **4a** (69%).

Entry 11, Table 1

N,*N*-Dibenzylamino-2-chloroethane (7a)



N,*N*-Dibenzylamino-2-iodoethane **1a** (135 mg, 0.38 mmol) was dissolved in $CHCl_3$ (4 mL) and CO_2 was bubbled through. MeOH (0.39 mL, 9.62 mmol, 25 equiv.) was added followed by AgCl (62 mg, 0.43 mmol, 1.1 equiv.) and the reaction vigorously stirred under a CO_2 atmosphere at room temperature for 16 h. The resulting cloudy pale yellow mixture was filtered through a pad of Celite®, washed with $CHCl_3$ (10 mL) and the solvent removed under reduced pressure to give, without the need for further purification, the alkyl chloride **7a** (87 mg, 87% yield) as a clear yellow oil.

R_f [PE:EtOAc 80:20] 0.55;

IR ν_{max} (liquid film) 3003 (CH) and 1601 (C=C);

^{1}H NMR δ_H (400 MHz; $CDCl_3$) 7.37 (4 H, d, J = 7.0 Hz, Ph), 7.31 (4 H, t, J = 8.0 Hz, Ph), 7.24 (2 H, t, J = 7.0 Hz, Ph), 3.65 (4 H, s, $PhCH_2N$), 3.48 (2 H, t, J = 7.0 Hz, NCH_2CH_2Cl) and 2.83 (2 H, t, J = 7.0 Hz, NCH_2CH_2Cl);

^{13}C NMR δ_C (100 MHz; $CDCl_3$) 139.4 (Ph), 129.0 (Ph), 128.6 (Ph), 127.4 (Ph), 59.0 ($PhCH_2N$), 55.6 (NCH_2CH_2Cl) and 42.1 (NCH_2CH_2Cl);

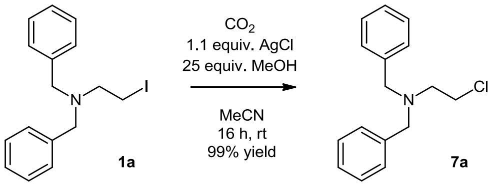
MS *m/z* (+ESI) 260 (100%, MH^+) and 224 (12%, M^+−Cl);

HRMS *m/z* (+ESI) Found 260.1185 (MH^+). $C_{16}H_{19}ClN$ (MH^+) requires 260.1206.

Consistent with the spectroscopic data previously reported for the alkyl chloride **7a**.[6]

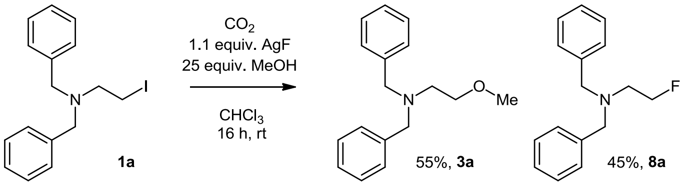
Entry 12, Table 1

N,*N*-Dibenzylamino-2-chloroethane (7a)



N,*N*-Dibenzylamino-2-iodoethane **1a** (82 mg, 0.23 mmol) was dissolved in MeCN (2 mL) and CO_2 was bubbled through. MeOH (0.24 mL, 5.75 mmol, 25 equiv.) was added followed by AgCl (36 mg, 0.25 mmol, 1.1 equiv.) and the reaction vigorously stirred under a CO_2 atmosphere at room temperature for 16 h. The resulting cloudy pale yellow mixture was filtered through a pad of Celite®, washed with EtOAc (10 mL) and the solvent removed under reduced pressure to give, without the need for further purification, the alkyl chloride **7a** (60 mg, 99% yield) as a clear yellow oil.

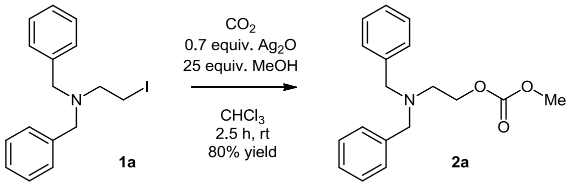
Entry 13, Table 1



N,*N*-Dibenzylamino-2-iodoethane **1a** (65 mg, 0.19 mmol) was dissolved in $CHCl_3$ (3 mL) and CO_2 was bubbled through. MeOH (0.19 mL, 4.63 mmol, 25 equiv.) was added followed by AgF (27 mg, 0.21 mmol, 1.1 equiv.) and the reaction vigorously stirred under a CO_2 atmosphere at room temperature for 16 h. The reaction mixture was filtered through a pad of silica and washed with EtOAc (10 mL) and $CHCl_3$ (10 mL). The solvent was removed under reduced pressure to give a pale orange oil. ^1H NMR of this material showed the methyl ether **3a** (55%) and the alkyl fluoride **8a** (45%), which were consistent with the spectroscopic data previously reported in this study for the methyl ether **3a** and with the alkyl fluoride **8a** described previously.[7]

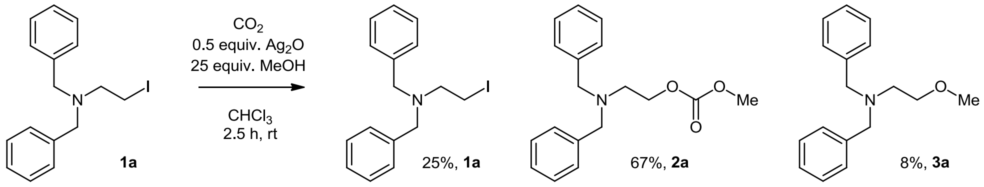
Investigation of the Ag_2O loading
Table 2

Entry 2, Table 2



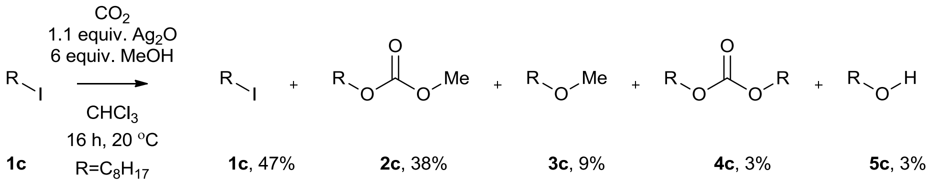
N,*N*-Dibenzylamino-2-iodoethane **1a** (74 mg, 0.21 mmol) was dissolved in $CHCl_3$ (3 mL) and CO_2 was bubbled through. MeOH (0.21 mL, 5.25 mmol, 25 equiv.) was added, followed by Ag_2O (35 mg, 0.15 mmol, 0.7 equiv.) and the reaction vigorously stirred under an atmosphere of CO_2 at room temperature for 2.5 h. The reaction mixture was filtered through a cotton wool plug and washed with EtOAc (10 mL). The solvent was removed under reduced pressure to give, without the need for further purification, the unsymmetrical carbonate **2a** (50 mg, 80% yield) as a colourless oil.

Entry 3, Table 2



N,*N*-Dibenzylamino-2-iodoethane **1a** (74 mg, 0.21 mmol) was dissolved in $CHCl_3$ (3 mL) and CO_2 was bubbled through. MeOH (0.21 mL, 5.25 mmol, 25 equiv.) was added, followed by Ag_2O (25 mg, 0.11 mmol, 0.5 equiv.) and the reaction vigorously stirred under an atmosphere of CO_2 at room temperature for 2.5 h. The reaction mixture was filtered through a cotton wool plug and washed with EtOAc (10 mL). The solvent was removed under reduced pressure to give a colourless oil. ^{1}H NMR of this material showed unreacted starting material **1a** (25%), the unsymmetrical carbonate **2a** (67%) and the methyl ether **3a** (8%).

Scheme 4



1-Iodooctane **1c** (0.36 mL, 2 mmol, 1eq.) was dissolved in $CHCl_3$ (15 mL) and CO_2 was bubbled through. MeOH (0.49 mL, 12 mmol, 6 eq.) was added followed by Ag_2O (510 mg, 2.2 mmol, 1.1 eq.) and the reaction vigorously stirred under a CO_2 atmosphere at room temperature for 16 h. Na_2SO_4 was added and the reaction mixture filtered through a pad of Celite® and washed with $CHCl_3$ (20 mL). The solvent removed under reduced pressure to afford a colourless oil. ^{1}H NMR of this material showed unreacted starting material **1c** (47%), the unsymmetrical carbonate **2c** (38%), the unsymmetrical ether **3c** (9%), the symmetrical carbonate **4c** (3%) and octanol **5c** (3%). Assignments were made with the spectroscopic data previously reported for the unsymmetrical **2c**[8-10] and symmetrical **4c**[9,10] carbonates.

Experimental References

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4. K. Teranishi, H. Nakao, A. Komoda and M. Hisamatsu, *Synthesis*, 1995, 176.
5. R. L. Baumes, C. L. Bayonove, R. E. Cordonnier, Y. Z. Gunata, R. Wylde and A. Heitz, *Carbohydr. Res.*, 1989, **189**, 331-340.
6. S. Andrews, S. J. Burgess, D. Skaalrud, J. X. Kelly and D. H. Peyton, *J. Med. Chem.*, 2010, **53**, 916-919.
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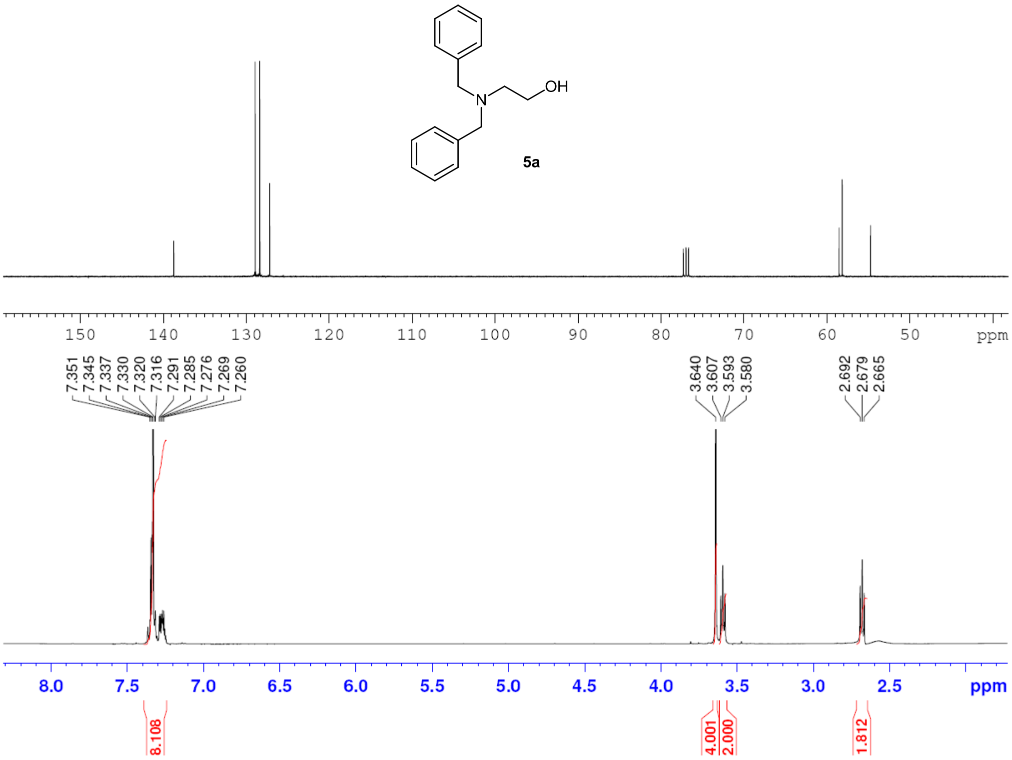
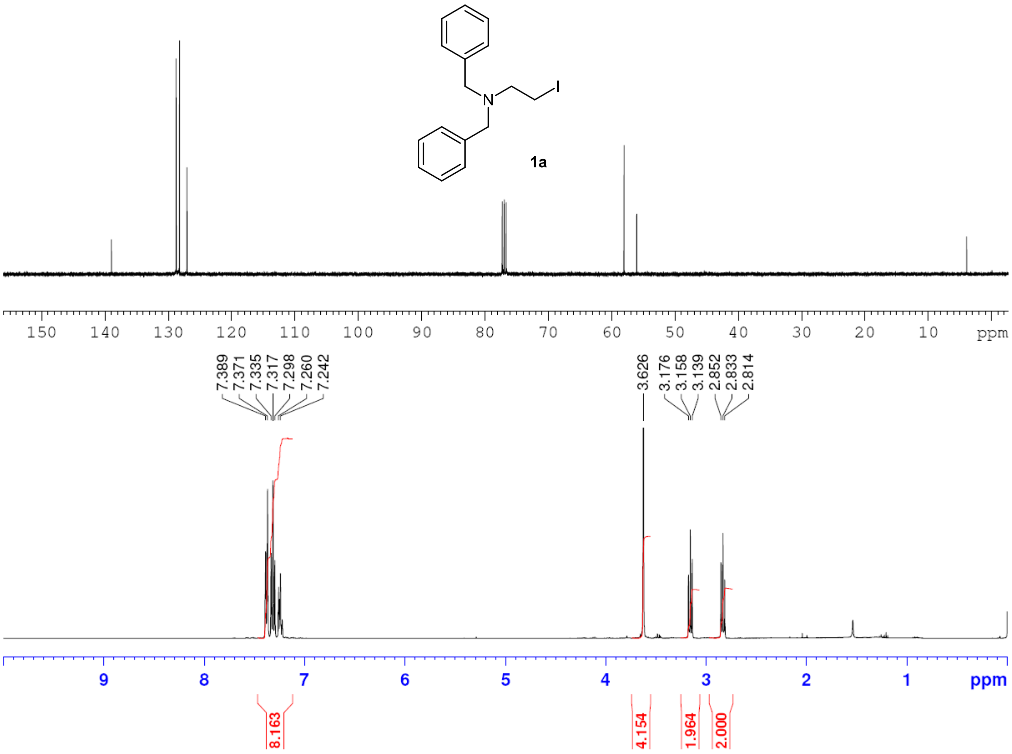
10. P. Tundo, C. R. McElroy and F. Aricò, *Synlett*, 2010, 1567-1571.

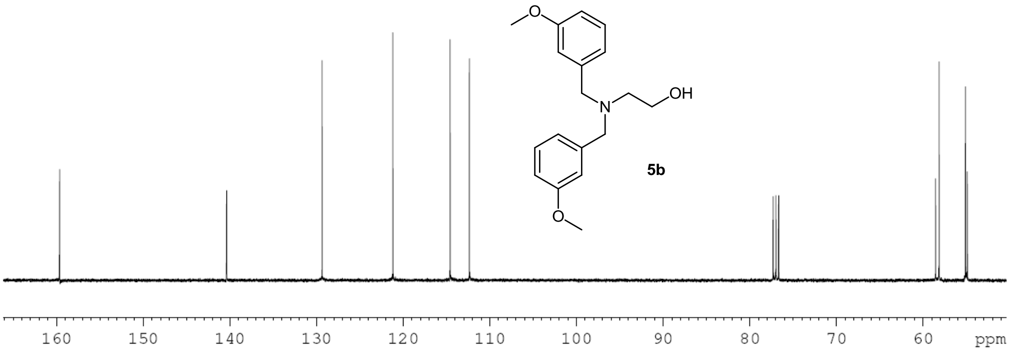
N,*N*-Dibenzyl-2-aminoethanol (5a)

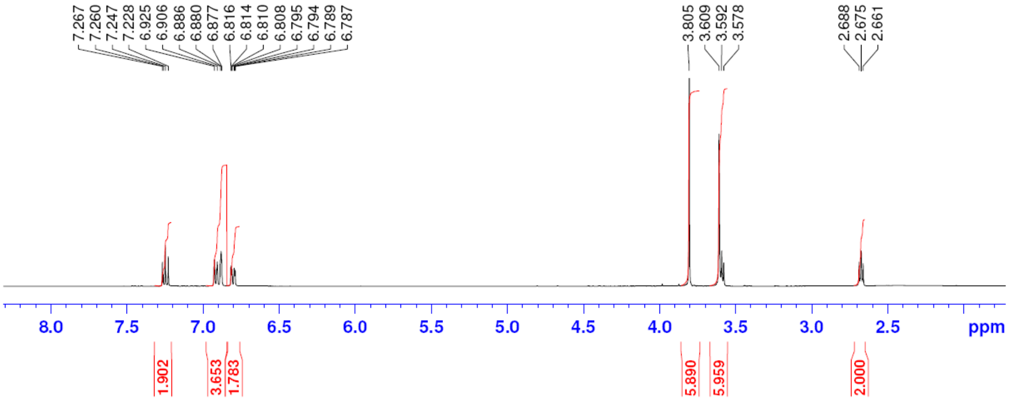


N,*N*-Dibenzylamino-2-iodoethane (1a)

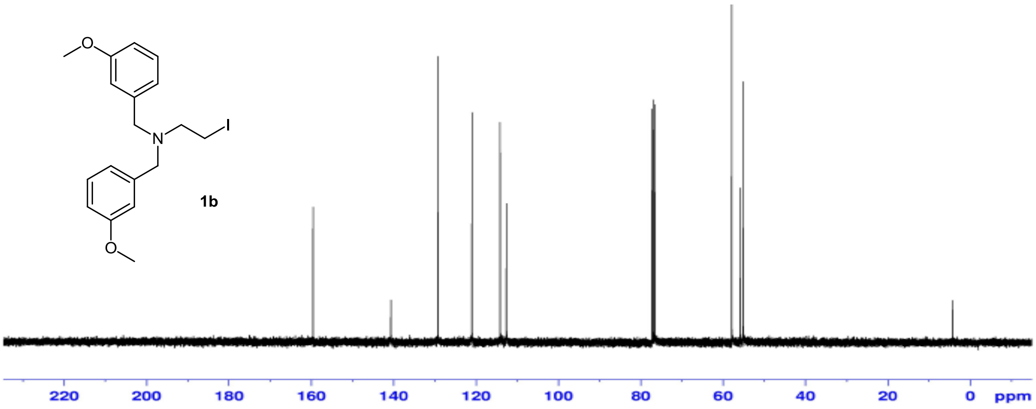


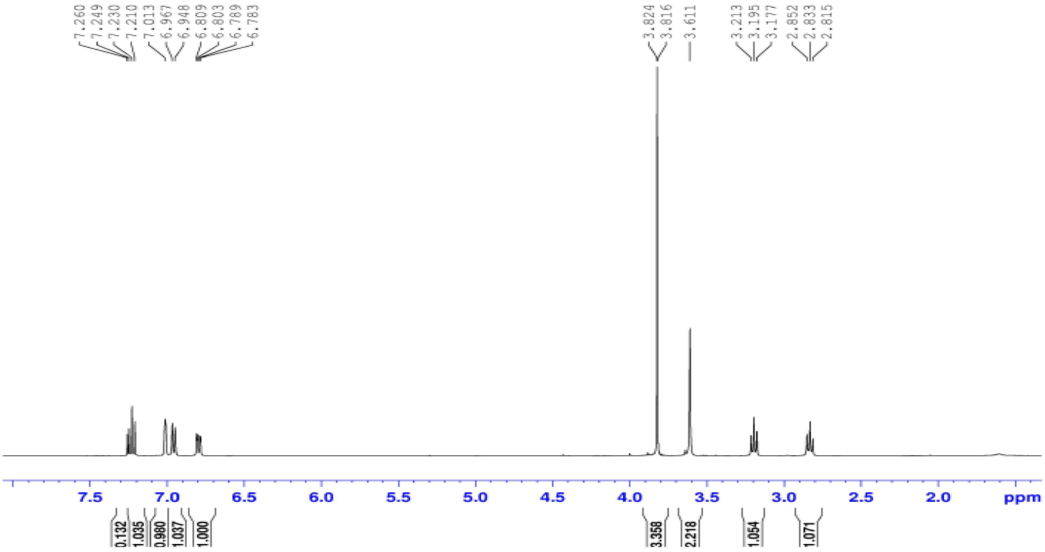
N,*N*-bis-(3-Methoxybenzyl)-2-aminoethanol (5b)





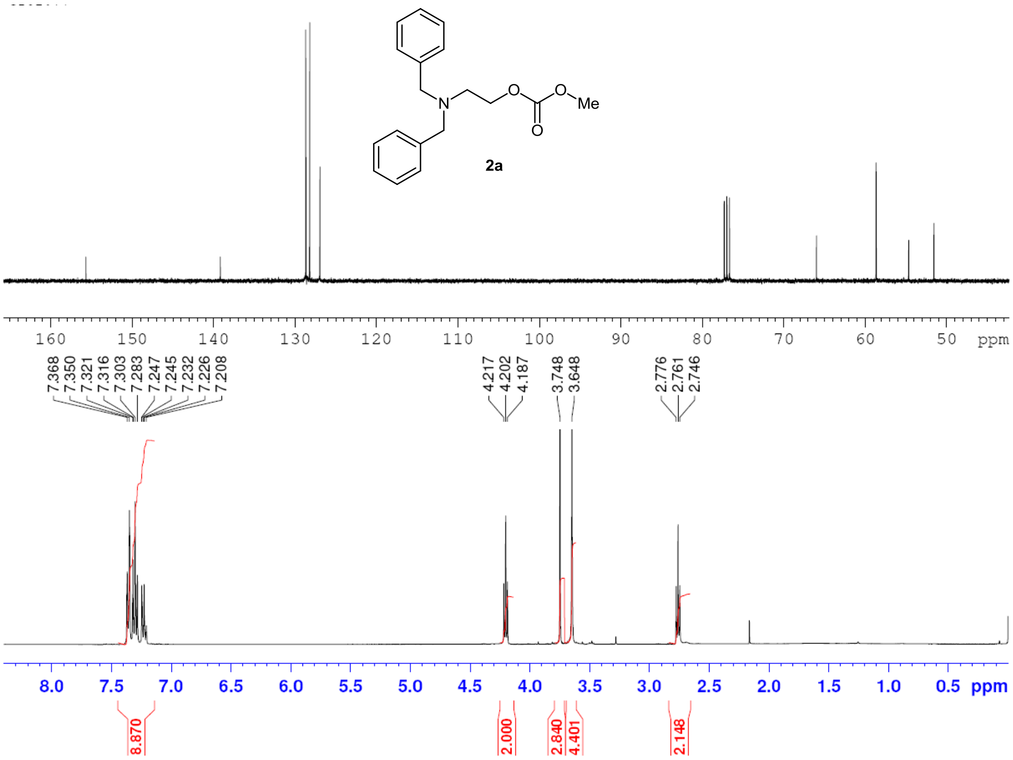
N,*N*-bis-(3-Methoxybenzyl)amino-2-iodoethane (1b)





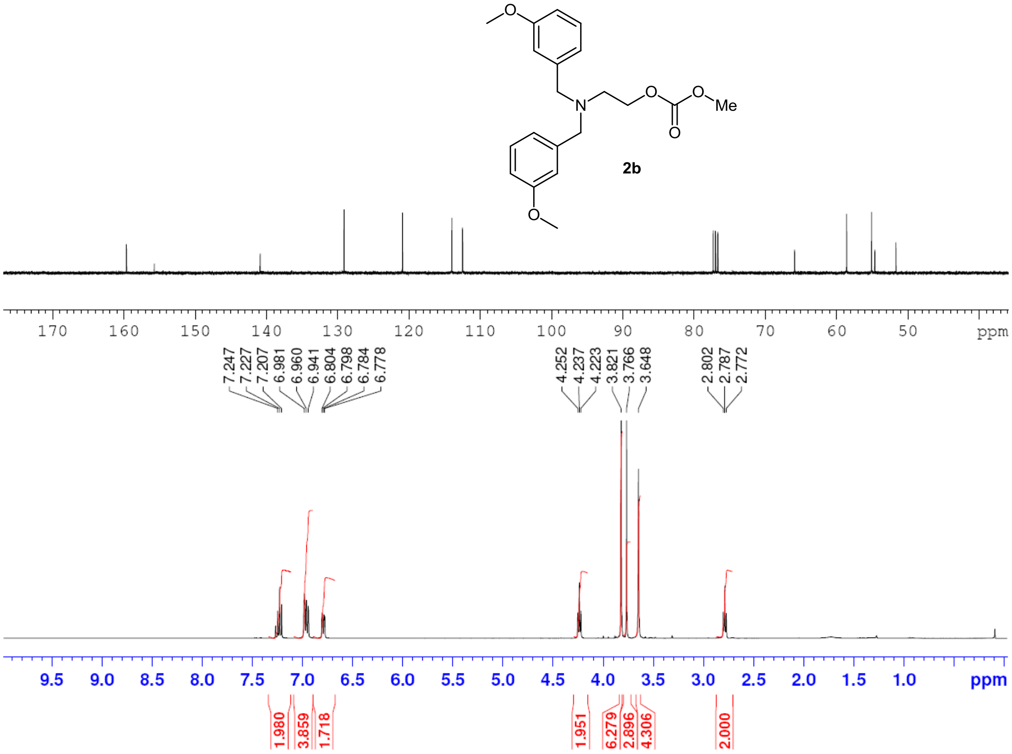
Entry 1, Table 1

2-*N*,*N*-Dibenzylaminoethyl methyl carbonate (2a)



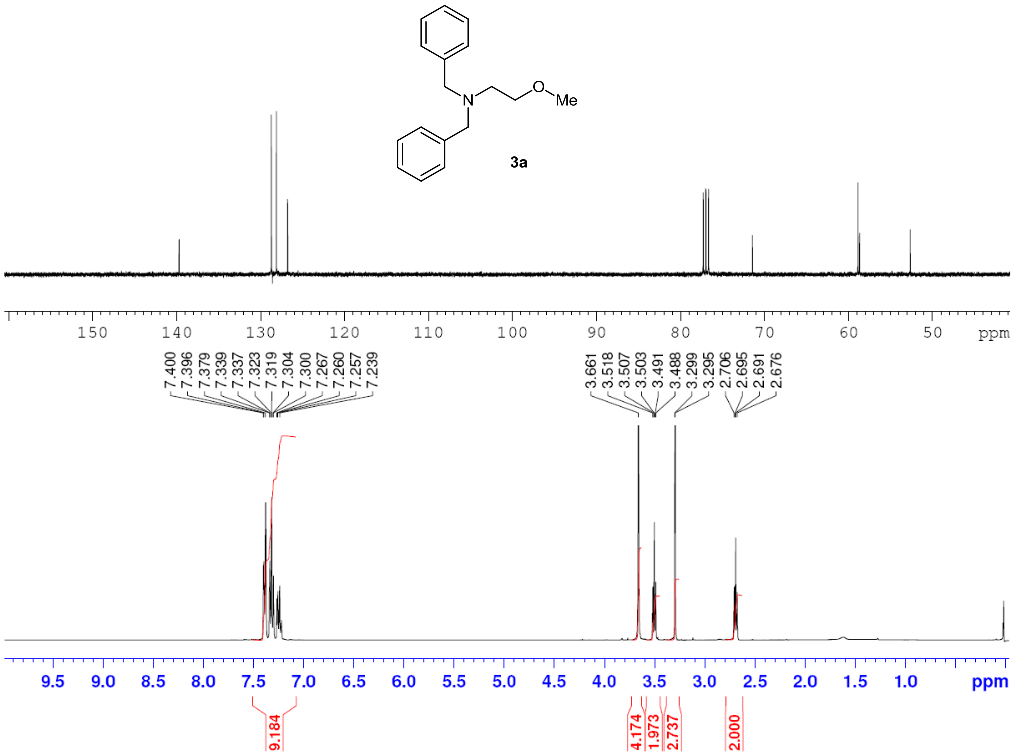
Entry 2, Table 1

2-*N*,*N*-bis-(3-Methoxybenzyl)aminoethyl methyl carbonate (2b)



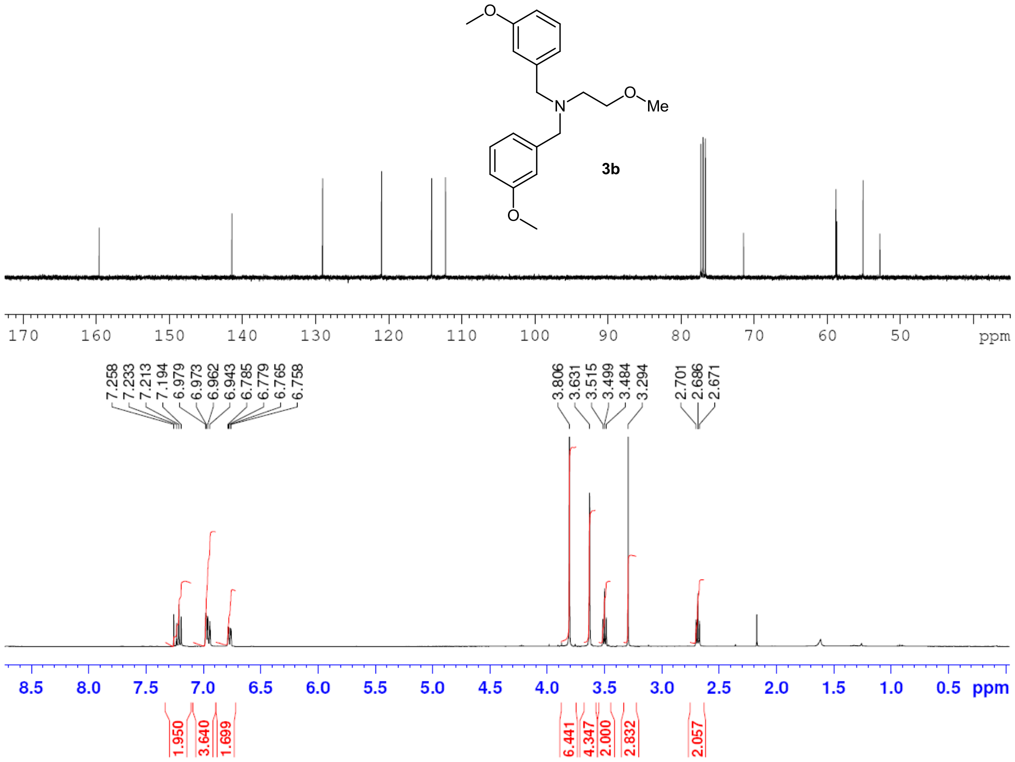
Entry 3, Table 1

N,*N*-Dibenzylamino-2-methoxyethane (3a)



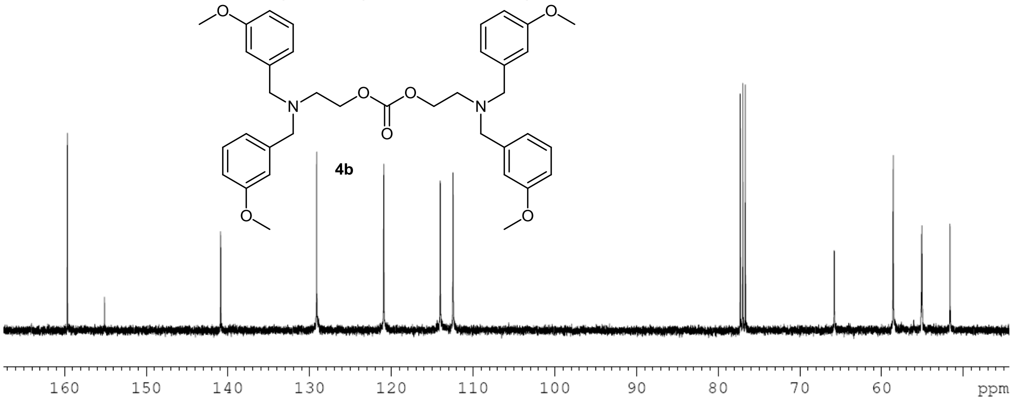
Entry 4, Table 1

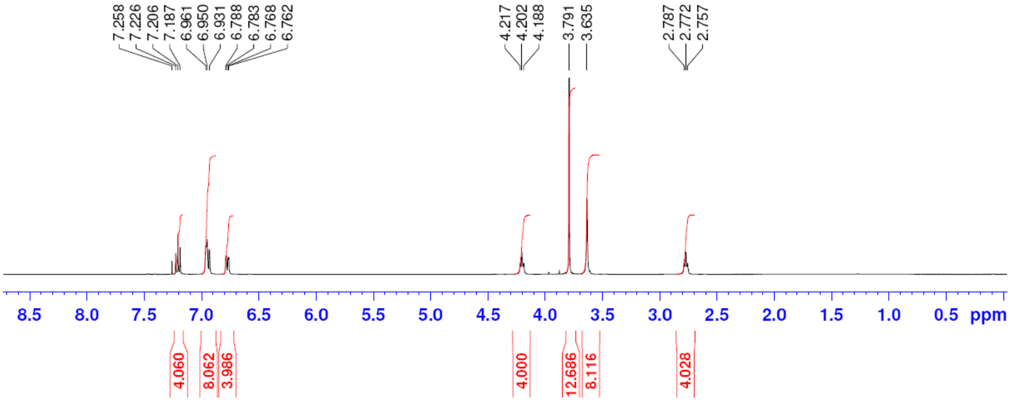
N,*N*-bis-(3-Methoxybenzyl)amino-2-methoxyethane (3b)



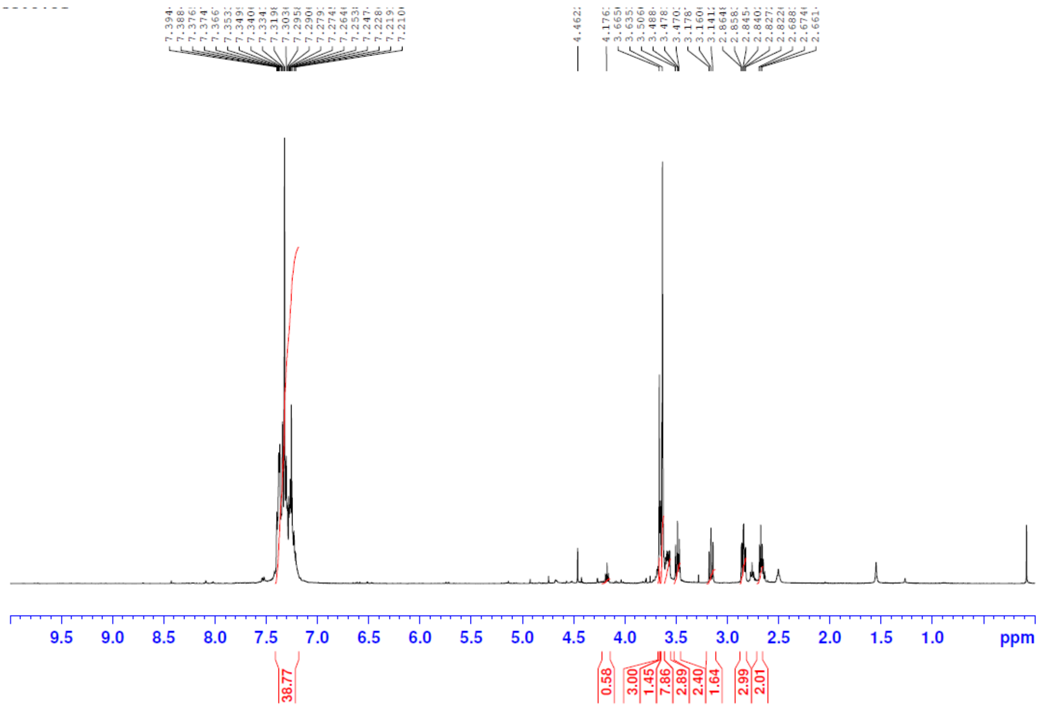
Entry 5, Table 1

Bis-[2-*N*,*N*-bis-(3-Methoxybenzyl)aminoethyl] carbonate (4b)





Entry 6, Table 1



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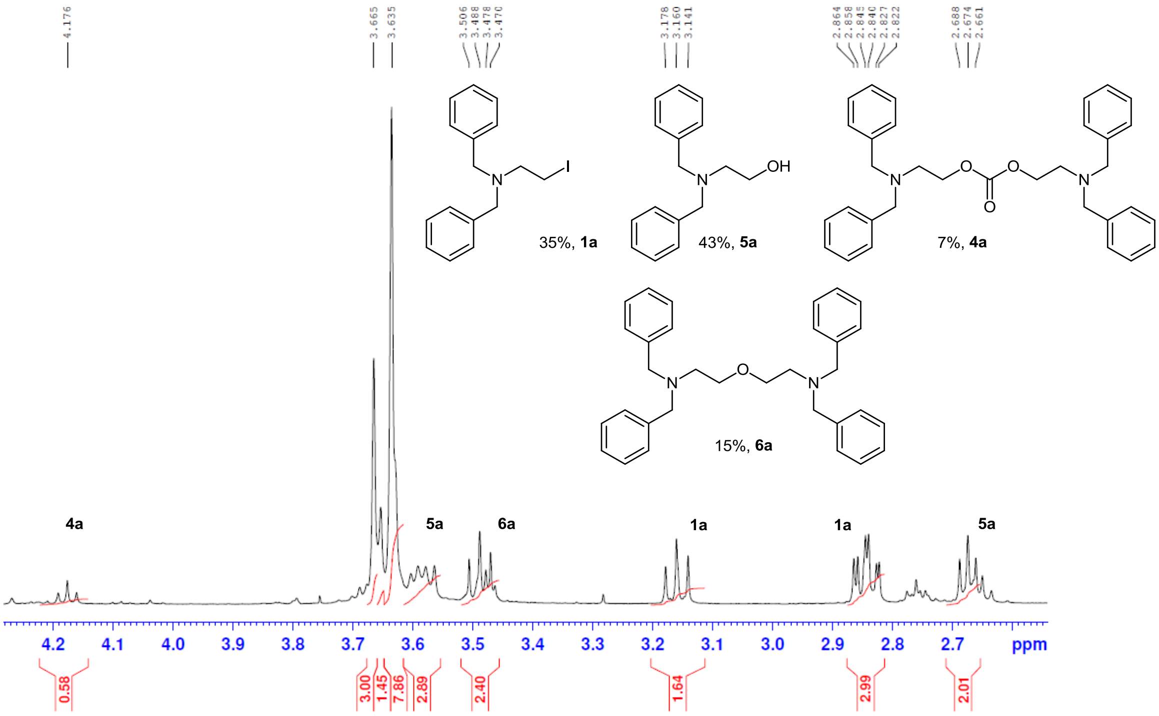
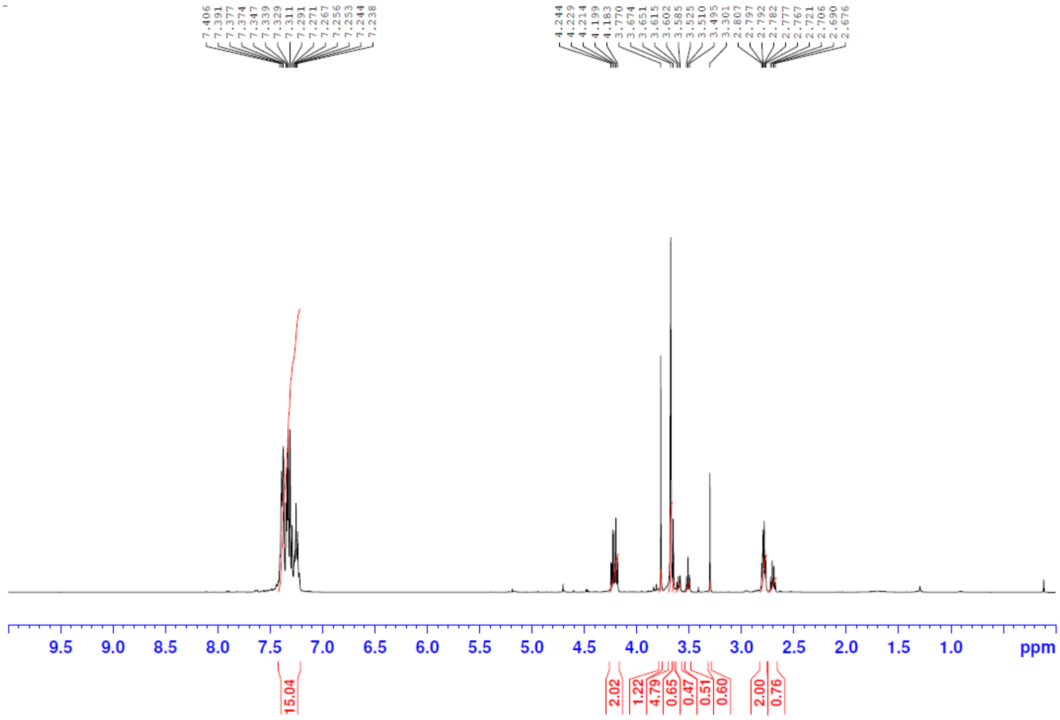


Entry 8, Table 1



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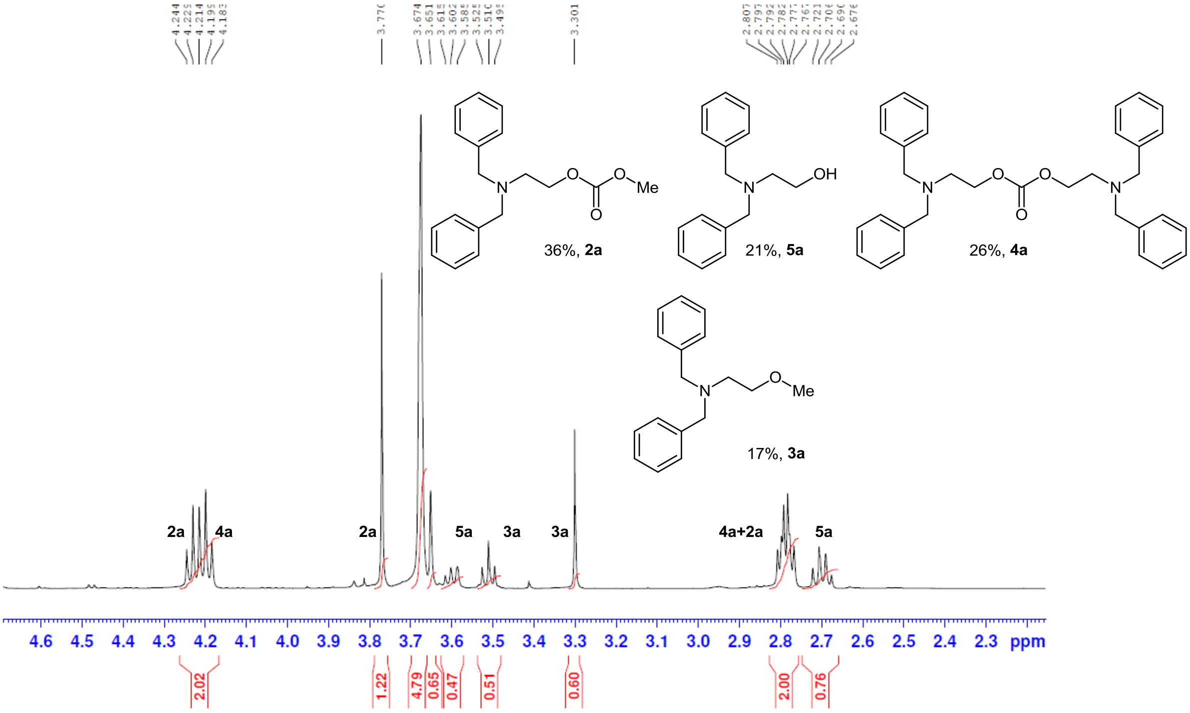
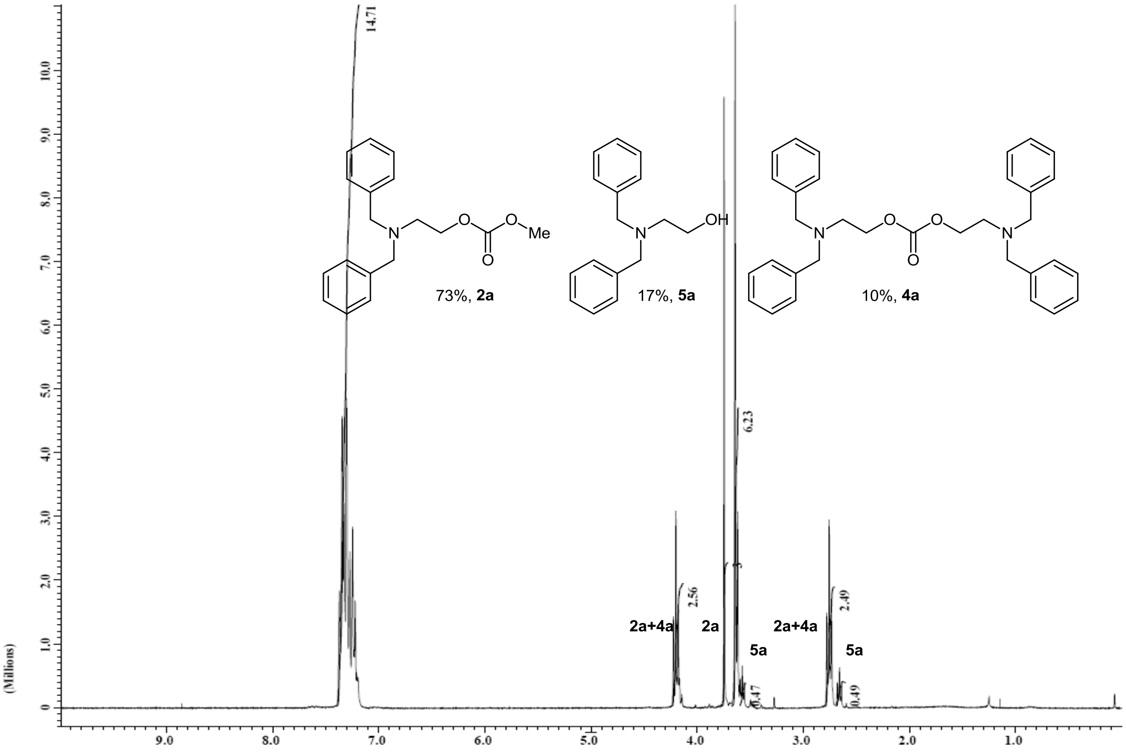
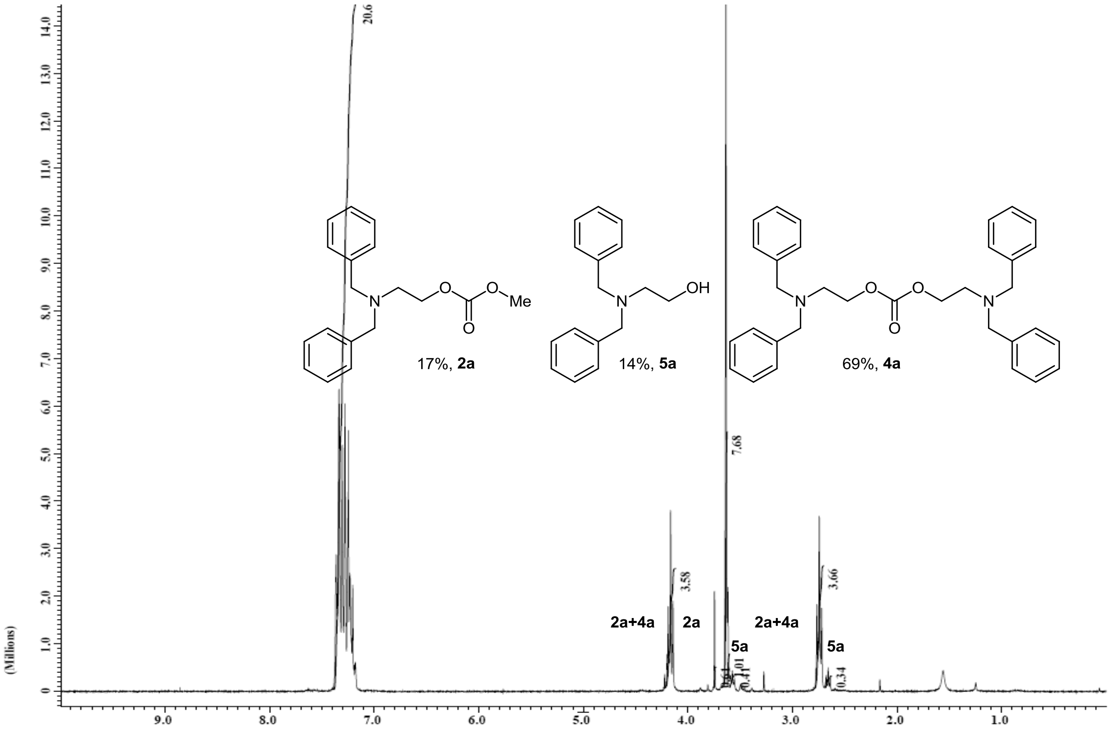


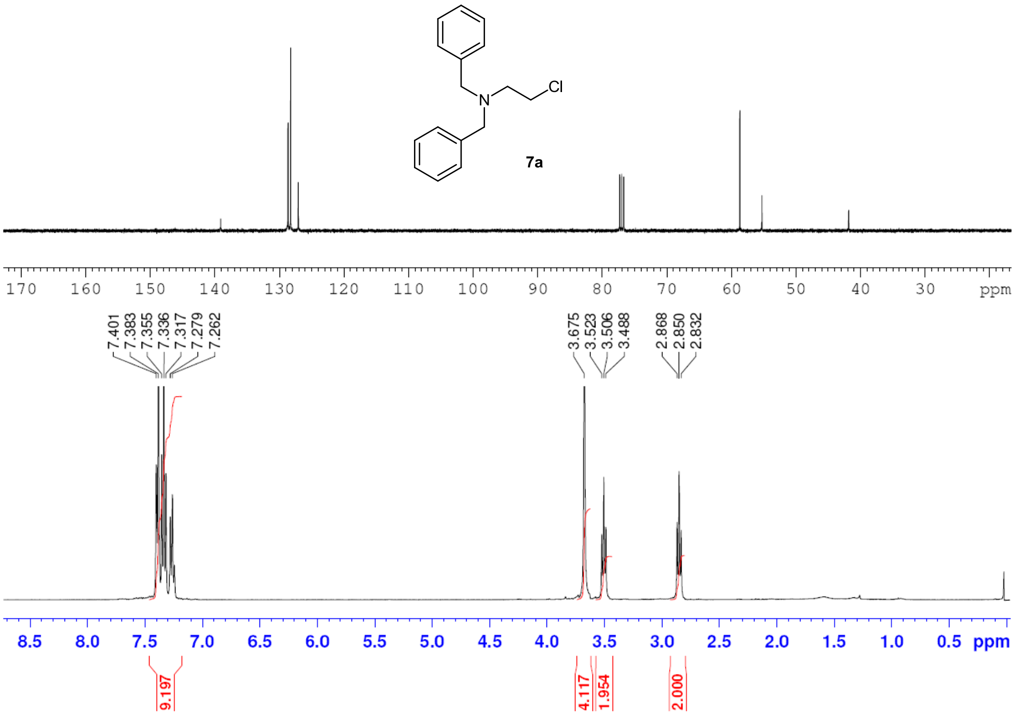
Entry 9, Table 1



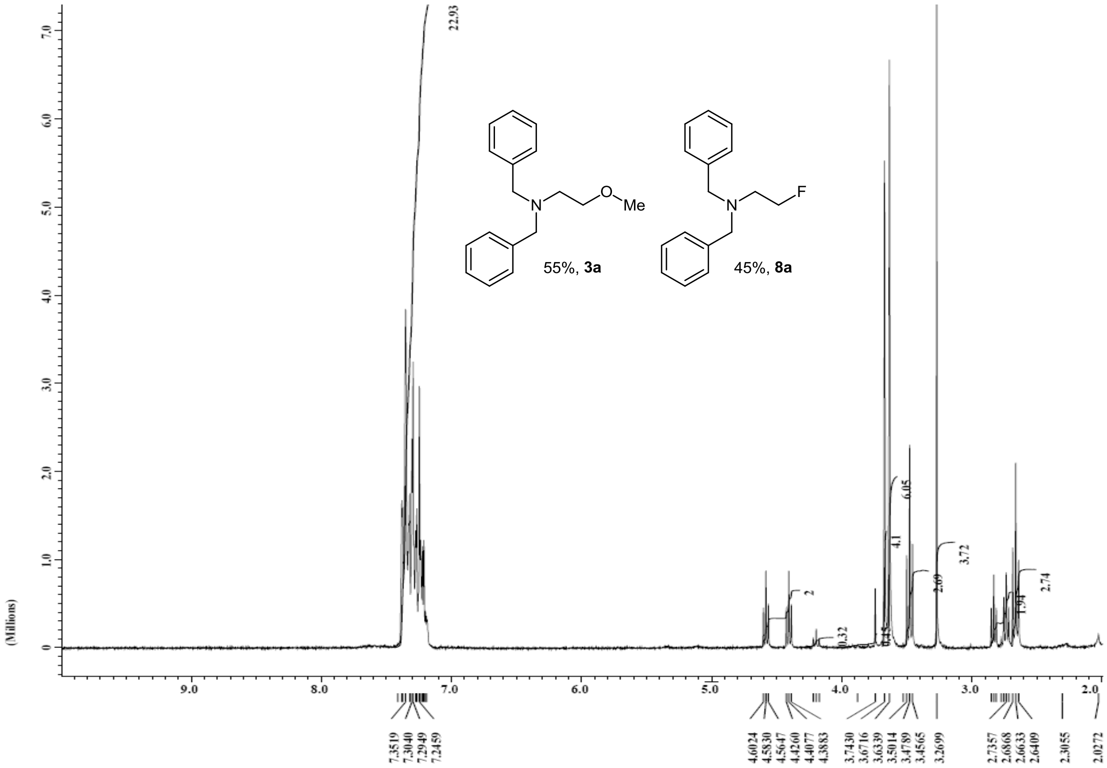
Entry 10, Table 1



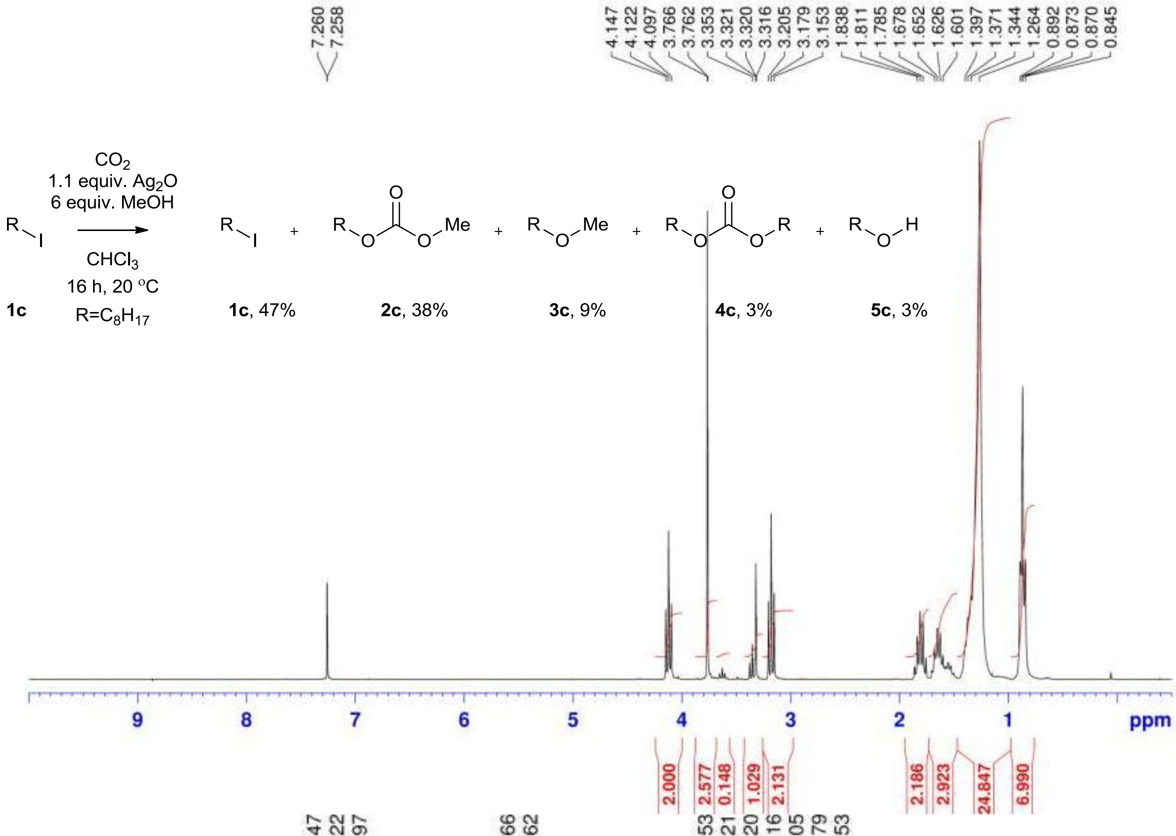
N,*N*-Dibenzylamino-2-chloroethane (7a)



Entry 13, Table 1



Scheme 4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6 equiv. MeOH
CHCl3
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R=C8H17
1c
1c, 47%
2c, 38%
3c, 9%
4c, 3%
5c, 3%
7.260
7.258
4.147
4.122
4.097
3.766
3.762
3.353
3.321
3.320
3.316
3.205
3.179
3.153
1.838
1.811
1.785
1.678
1.652
1.626
1.601
1.397
1.371
1.344
1.264
0.892
0.873
0.870
0.845
9
8
7
6
5
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3
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ppm
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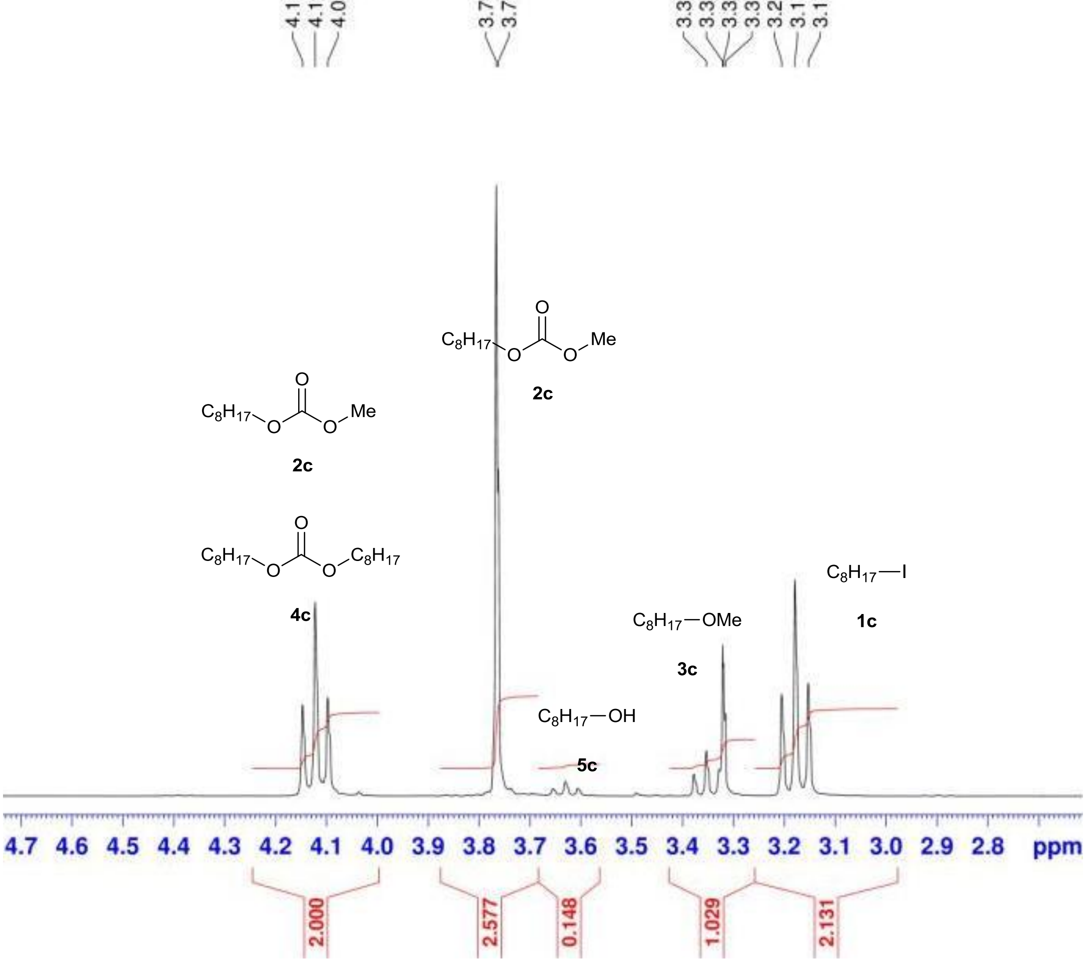
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2c
2c
4c
C8H17—OH
5c
C8H17—OMe
3c
C8H17—I
1c
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
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3.5
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ppm
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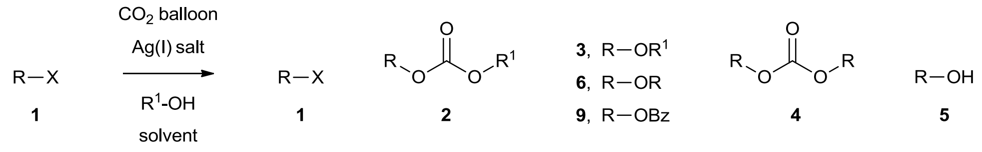
Synthetic Procedure for the Optimisation Study (Table 3)

Table 3. Optimisation of the Ag-mediated capture and functionalisation of CO_2 with alkyl halides.[a]

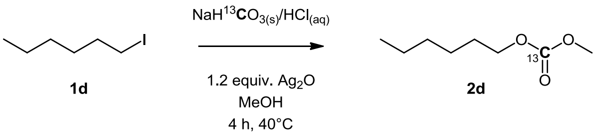


Entry	R-X 1	R^1-OH (equiv.)	Ag_2O (equiv.)	*T* (°C)	Time (h)	solvent	R-X 1	$ROCO_2R^1$ 2	R-O-R' 3 (6/9)[b]	$ROCO_2R$ 4	R-OH 5
1	Oct-I	BnOH (1.5)	1.5	20	18	$CHCl_3$	56	22	9	4	9
2	Oct-I	BnOH (1.5)	1.5	45	20	$CHCl_3$	31	25	25	5	14
3	Oct-I	BnOH (1.5)	1.1	50	20	$CHCl_3$	76	8	5	2	9
4	Oct-I	BnOH (5)	1.1	50	20	$CHCl_3$	20	35	22	3	20
5	Oct-I	BnOH (5)	1.5	45	20	$CHCl_3$	14	36	24	4	22
6	Oct-I	MeOH (5)	1.1	45	16	$CHCl_3$	32	42	10	4	12
7	Oct-I	EtOH (5)	1.1	45	16	$CHCl_3$	59	24	7	2	8
8	Oct-I	iPrOH (5)	1.5	45	16	$CHCl_3$	16	44	13 (**3**), 2 (**6**)	10	15
9	Oct-I	BnOH (1.5)	1.5	20	18	PhMe	69	17	4	2	8
10	Oct-I	BnOH (1.5)	1.5	45	18	PhMe	51	19	11	3	16
11	Oct-I	BnOH (1.5)	1.5	100	18	PhMe	-	11	48 (**3**), 2 (**6**), 10 (**9**)	2	27
12	Oct-I	BnOH (5)	1.5	100	18	PhMe	-	10	47 (**3**), 11 (**9**)	1	31
13[c]	Oct-I	BnOH (1.5)	1.5	100	18	PhMe	6	-	71 (**3**), 2 (**6**), 14 (**9**)	-	7
14	Oct-I	BnOH (1.5)	1.5	20	18	MeCN	7	15	3 (**3**), 2 (**6**)	7	66
15	Oct-I	BnOH (1.5)	1.5	45	18	MeCN	3	19	5 (**3**), 1 (**6**)	6	66
16	Oct-I	BnOH (20)	1.5	20	20	neat	-	55	44	1	-
17	Oct-I	BnOH (20)	1.5	45	4	neat	-	43	40	1	16
18[d]	Oct-I	MeOH(123)	1.1	40	4	neat	-	72	7	2	19
19	Oct-I	iPrOH (30)	1.5	45	5	neat	-	72	13	4	11
20	Oct-I	iPrOH (30)	1.5	45	20	neat	-	75	12	4	9
21	Oct-I	iPrOH (30)	0.5	45	5	neat	45	37	10	2	6
22	Oct-I	iPrOH (30)	0.5	45	20	neat	31	37	23	2	7
23	Hex-Br	iPrOH (30)	1.5	45	20	neat	4	27	4	3	62
24	Hex-Br	BnOH (20)	1.5	45	20	neat	12	12	21 (**3**), 1 (**9**)	1	53
25	Hex-Br	BnOH (20)	2	45	16	neat	10	14	22	1	53
26	Hex-Cl	iPrOH (30)	2	45	16	neat	100	-	-	-	-
27	Oct-I	iPrOH (30)	1.5Ag_2CO_3	45	20	neat	15	35	12 (**3**), 4 (**6**)	21	13
28[c]	Oct-I	iPrOH (30)	1.5Ag_2CO_3	45	20	neat	28	6	31 (**3**), 3 (**6**)	7	25
29	Hex-I	BnOH (20)	3 AgCl	45	20	neat	100	-	-	-	-
30	Hex-I	BnOH (20)	3 $AgNO_3$	45	20	neat	-	-	54 (**3**), 46 (**9**)	-	-
31	Hex-I	BnOH (20)	2.5 AgI	45	16	neat	100	-	-	-	-
			+ 1.0 Ag_2O	45	5	neat	-	40	41	2	17

[a] The ratios are expressed as % and were obtained from ^1H NMR of the crude reaction mixture after it had been filtered through Celite® and the solvent removed under reduced pressure. All experiments were conducted with 1 mmol of R-X under an atmosphere of CO_2 generated from the sublimation of dry ice, except where indicated. [b] All values are of the unsymmetrical ether **3**, unless otherwise stated. [c] Reaction conducted under an atmosphere of N_2. [d] Reaction conducted with 3 mmol Oct-I in 15 mL MeOH.

A balloon filled with $CO_{2(g)}$, generated by the sublimation of commercially available dry ice, was bubbled through a rapidly stirred suspension of the alkyl halide (1mmol), Ag(I) salt and an alcohol in a solvent (if any) at room temperature in a sealed tube. The reaction was then sealed, thus maintaining a $CO_{2(g)}$ atmosphere, and heated at the required temperature for the times shown in Table 3 above. The reaction mixture was filtered through Celite®, washed with $CHCl_3$ and the solvent carefully evaporated under reduced pressure. ^1H NMR was performed of the crude reaction mixture and the ratio of products calculated from integration of indicative signals.

Synthetic Procedures for ^{13}C-labelled experiments (Table 4, Scheme 5)



The desired mixture of $NaHCO_{3(s)}$ was accurately weighted and placed in a sealed 5 mL round-bottomed flask, fitted with a cannula which was positioned in the air-space *above* the reaction mixture. The other end of the cannula was positioned *in* the reaction mixture of a separate and sealed round-bottomed flask which contained a rapidly stirred suspension of the alkyl iodide, Ag_2O and MeOH at room temperature. This flask was also fitted with an empty balloon to act as a reservoir of the $CO_{2(g)}$ produced. The addition of 3M $HCl_{(aq)}$ to the first flask containing the $NaHCO_{3(s)}$ generated $CO_{2(g)}$ which passed through the cannula and into the reaction mixture in the second flask and into the balloon reservoir. Once the bubbling had ceased and no more $NaHCO_{3(s)}$ was evident, the cannula was removed from the reaction mixture in the second flask and the reaction heated to 40 ^{o}C for 4 hours under the balloon filled with CO_2. The reaction was filtered through filter paper and cotton wool, washed with MeOH and the solvent carefully removed under reduced pressure to afford carbonate **2d**.

Entry 1, Table 4. Measured ratio **100:0** $NaH^{12}CO_3$:$NaH^{13}CO_3$

Following the general procedure, CO_2 generated by the addition of 3M HCl to $NaH^{12}CO_3$ (571 mg, 6.80 mmol, 5 eq.) was bubbled through a rapidly stirred mixture of 1-iodohexane (287 mg, 1.36 mmol, 1 eq.) and Ag_2O (377 mg, 1.63 mmol, 1.2 eq.) in MeOH (2.5 mL) to give the carbonate **2d** (137 mg, 63% yield) as a colourless oil.

^{1}H NMR δ_H (400 MHz; $CDCl_3$) 4.12 (2 H, t, J = 6.5 Hz, CH_2OCO_2Me), 3.76 (3 H, s, CH_2OCO_2Me), 1.64 (2 H, quintet, J = 7.0 Hz, $CH_2CH_2OCO_2$), 1.40-1.24 (6 H, m, $CH_3(CH_2)_3$) and 0.86 (3 H, t, J = 7.0 Hz, $CH_3(CH_2)_3$);

^{13}C NMR δ_C (100 MHz; $CDCl_3$) 155.84 (C=O), 68.21 (CH_2OCO_2Me), 54.57 (CH_2OCO_2Me), 31.33 ($CH_3(CH_2)_3$), 28.56 ($CH_2CH_2OCO_2$), 25.29 ($CH_3(CH_2)_3$), 22.46 ($CH_3(CH_2)_3$) and 13.93 ($CH_3(CH_2)_3$);

MS *m/z* (+ESI) 184.1 (10%, MNa^+) and 183.1 (100%, MNa^+);

HRMS *m/z* (+ESI) Found 183.1035 (MNa^+). $C_8H_{16}NaO_3$ (MNa^+) requires 183.0997.

Entry 2, Table 4. Measured ratio **75:25** $NaH^{12}CO_3$:$NaH^{13}CO_3$

Following the general procedure, CO_2 generated by the addition of 3M HCl to a mixture of 75% $NaH^{12}CO_3$ (428.4 mg, 5.10 mmol, 3.75 eq.) and 25% $NaH^{13}CO_3$ (144.5 mg, 1.70 mmol, 1.25 eq.) was bubbled through a rapidly stirred mixture of 1-iodohexane (288 mg, 1.36 mmol, 1 eq.) and Ag_2O (378 mg, 1.63 mmol, 1.2 eq.) in MeOH (2.5 mL) to give the carbonate **2d** (148 mg, 68% yield) as a colourless oil.

Entry 3, Table 4. Measured ratio **50:50** $NaH^{12}CO_3$:$NaH^{13}CO_3$

Following the general procedure, CO_2 generated by the addition of 3M HCl to a mixture of 50% $NaH^{12}CO_3$ (286 mg, 3.40 mmol, 2.50 eq.) and 50% $NaH^{13}CO_3$ (289 mg, 3.40 mmol, 2.50 eq.) was bubbled through a rapidly stirred mixture of 1-iodohexane (287 mg, 1.36 mmol, 1 eq.) and Ag_2O (378 mg, 1.63 mmol, 1.2 eq.) in MeOH (2.5 mL) to give the carbonate **2d** (148 mg, 68% yield) as a colourless oil.

Entry 4, Table 4. Measured ratio **25:75** $NaH^{12}CO_3$:$NaH^{13}CO_3$

Following the general procedure, CO_2 generated by the addition of 3M HCl to a mixture of 25% $NaH^{12}CO_3$ (143 mg, 1.70 mmol, 1.25 eq.) and 75% $NaH^{13}CO_3$ (435 mg, 5.12 mmol, 3.76 eq.) was bubbled through a rapidly stirred mixture of 1-iodohexane (288 mg, 1.36 mmol, 1 eq.) and Ag_2O (378 mg, 1.63 mmol, 1.2 eq.) in MeOH (2.5 mL) to give the carbonate **2d** (153 mg, 70% yield) as a colourless oil.

Entry 5, Table 4. Measured ratio **0:100** $NaH^{12}CO_3$:$NaH^{13}CO_3$

Following the general procedure, CO_2 generated by the addition of 3M HCl to $NaH^{13}CO_3$ (425 mg, 5 mmol, 5 eq.) was bubbled through a rapidly stirred mixture of 1-iodohexane (212 mg, 1 mmol, 1 eq.) and Ag_2O (278 mg, 1.2 mmol, 1.2 eq.) in MeOH (2 mL) to give the carbonate **2d** (96 mg, 60% yield) as a colourless oil.

^{1}H NMR δ_H (400 MHz; $CDCl_3$) 4.12 (2 H, tt, *J* = 6.5 and 1.5 Hz, $CH_2O^{13}CO_2Me$), 3.76 (3 H, t, *J* = 2.0 Hz, $CH_2O^{13}CO_2Me$), 1.72-1.61 (2 H, m, $CH_2CH_2O^{13}CO_2$), 1.40-1.24 (6 H, m, $CH_3(CH_2)_3$) and 0.88 (3 H, t, *J* = 7.0 Hz, $CH_3(CH_2)_3$);

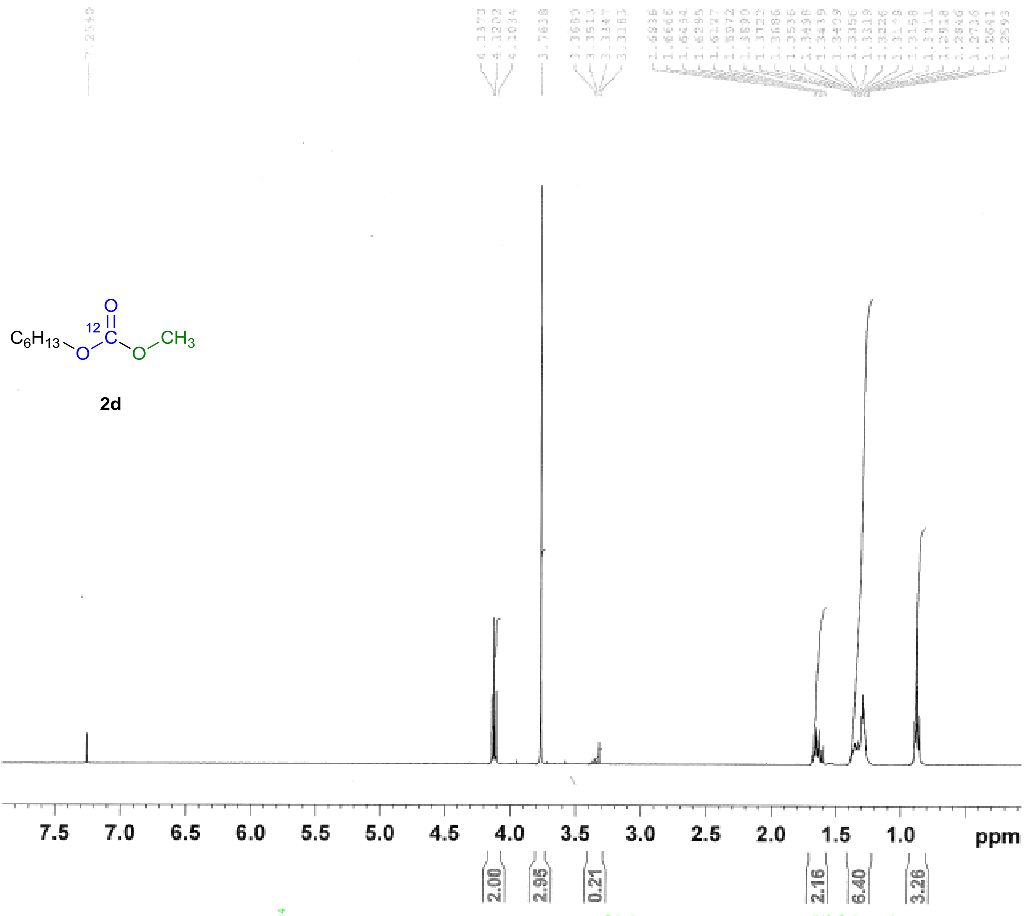
^{13}C NMR δ_C (100 MHz; $CDCl_3$) 155.82 ($^{13}C{=}O$), 68.16 (d, *J* = 1.5 Hz, $CH_2O^{13}CO_2Me$), 54.48 (d, *J* = 1.5 Hz, $CH_2O^{13}CO_2Me$), 31.30 ($CH_3(CH_2)_3$), 28.55 (d, *J* = 2.5 Hz, $CH_2CH_2O^{13}CO_2$), 25.26 ($CH_3(CH_2)_3$), 22.41 ($CH_3(CH_2)_3$) and 13.86 ($CH_3(CH_2)_3$);

MS *m/z* (+ESI) 185.1 (7.6%, MNa^+), 184.1 (100%, MNa^+) and 183.1 (3.0%, MNa^+);

HRMS *m/z* (+ESI) Found 184.1025 (MNa^+). $C_7{}^{13}CH_{16}NaO_3$ (MNa^+) requires 184.1031.

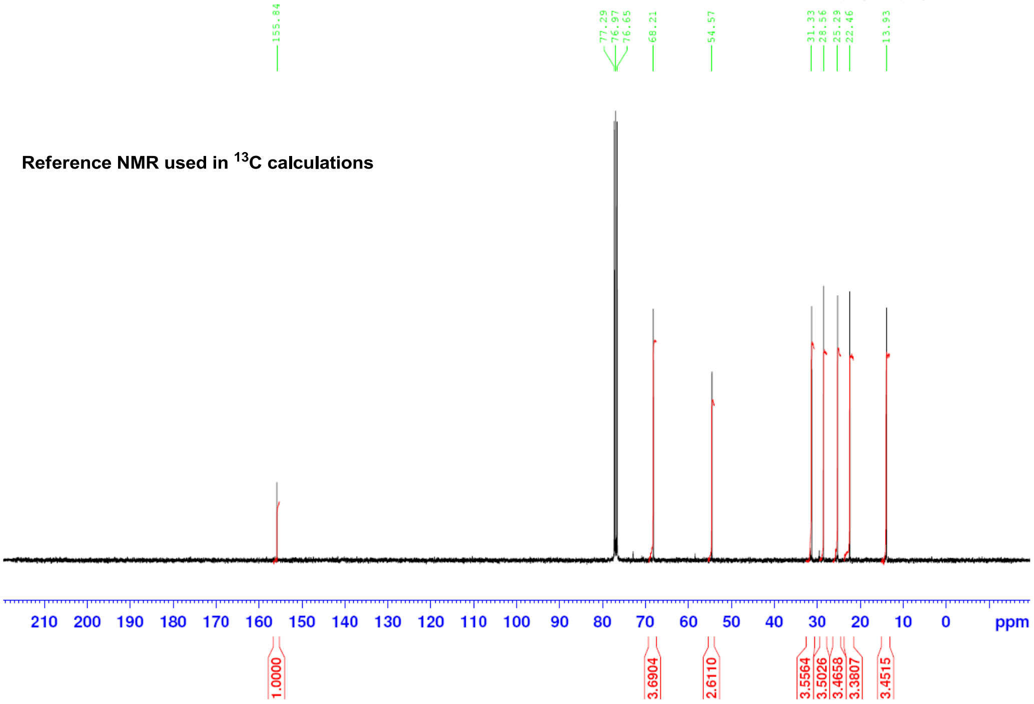
NMR Spectra for the ^{13}C-labelled CO_2 experiments

Measured ratio 100:0 $NaH^{12}CO_3$:$NaH^{13}CO_3$
Entry 1, Table 4

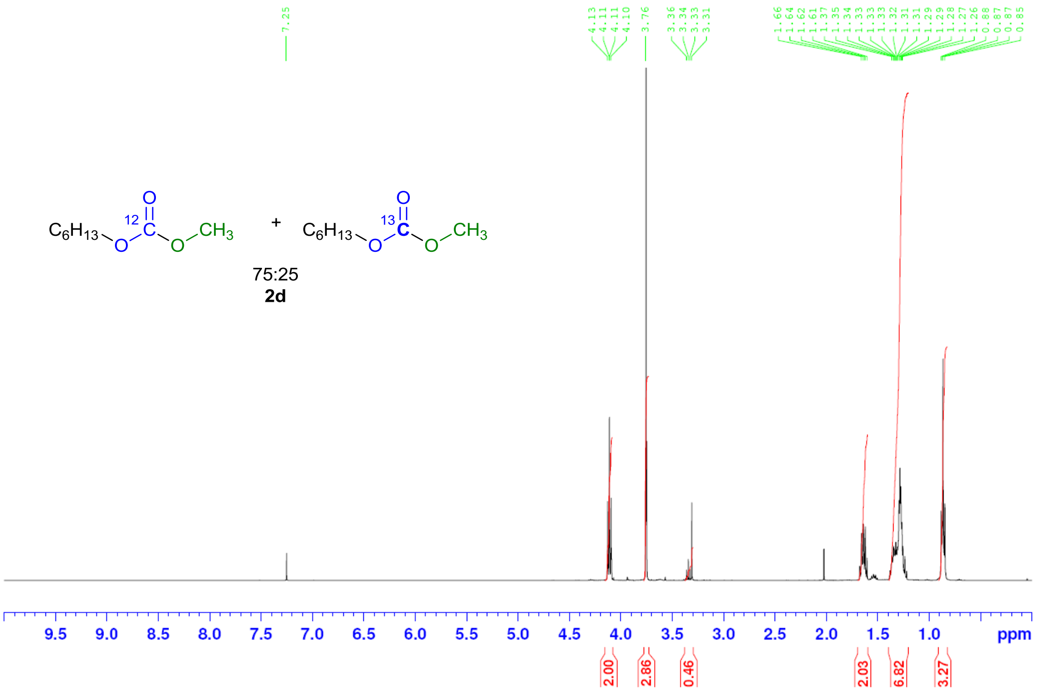


2d

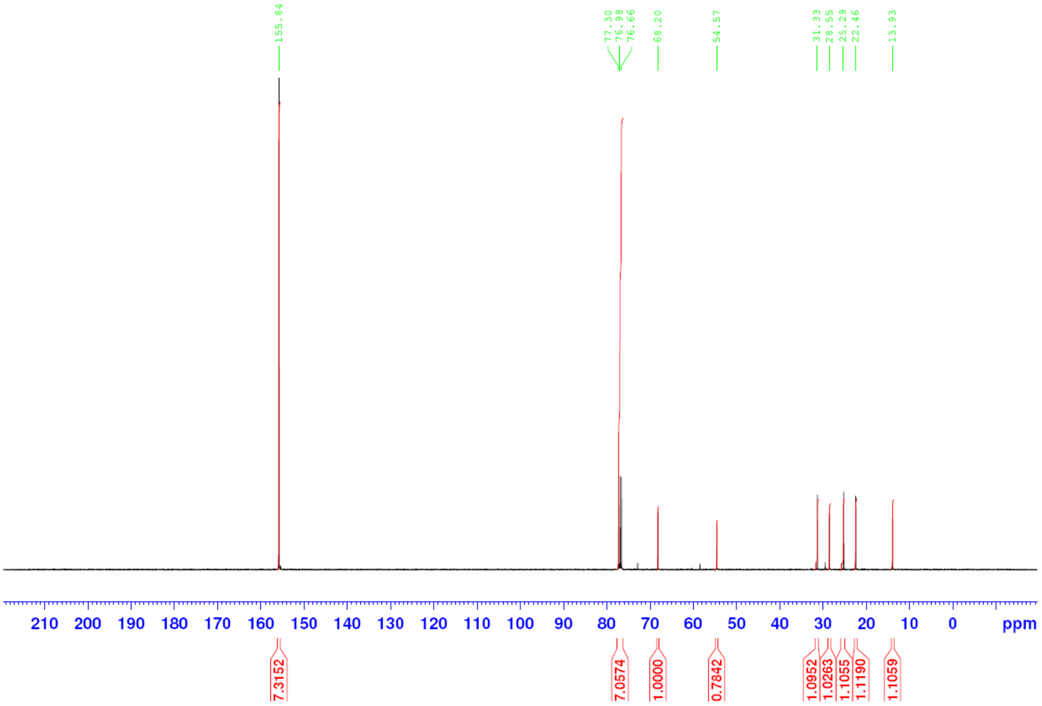
Reference NMR used in ^{13}C calculations



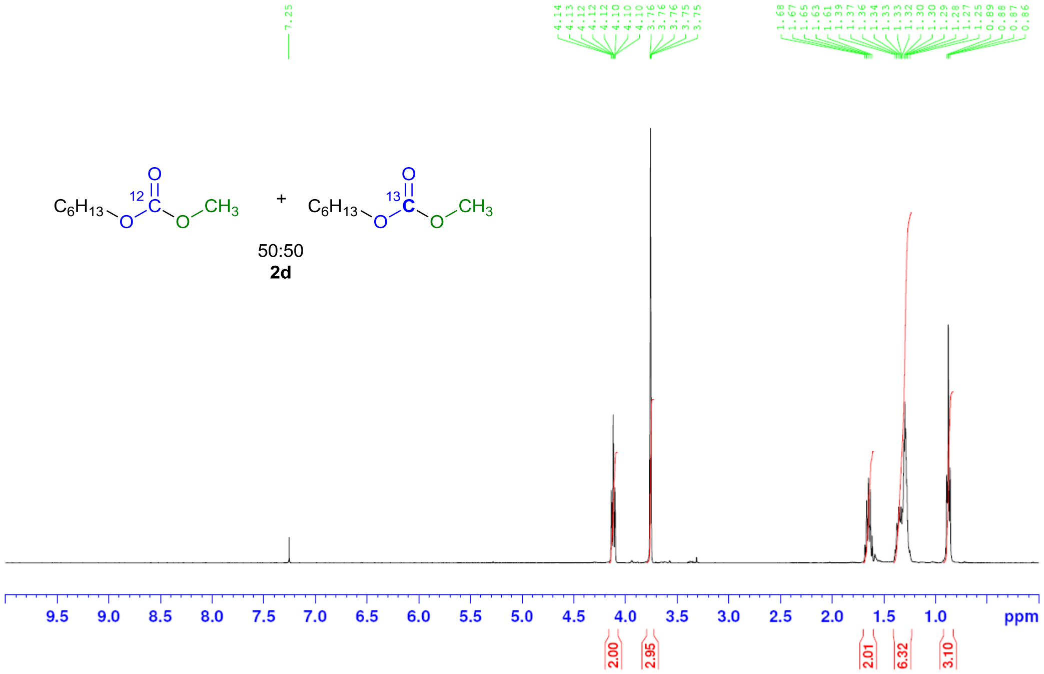
Measured ratio 75:25 $NaH^{12}CO_3$:$NaH^{13}CO_3$
Entry 2, Table 4

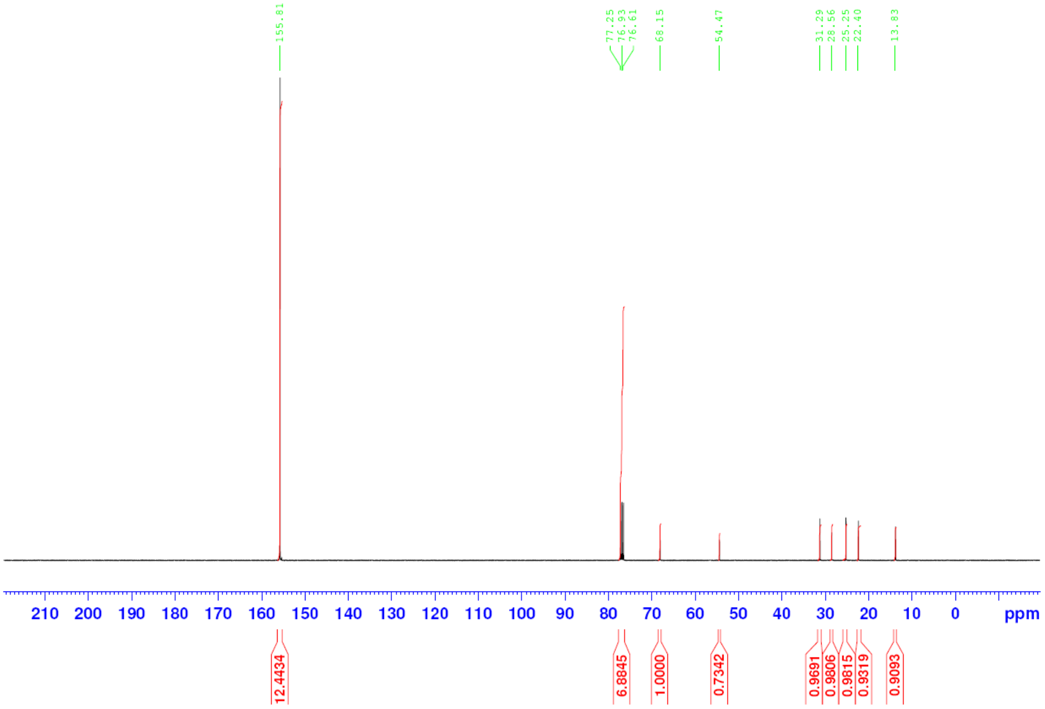


75:25
2d

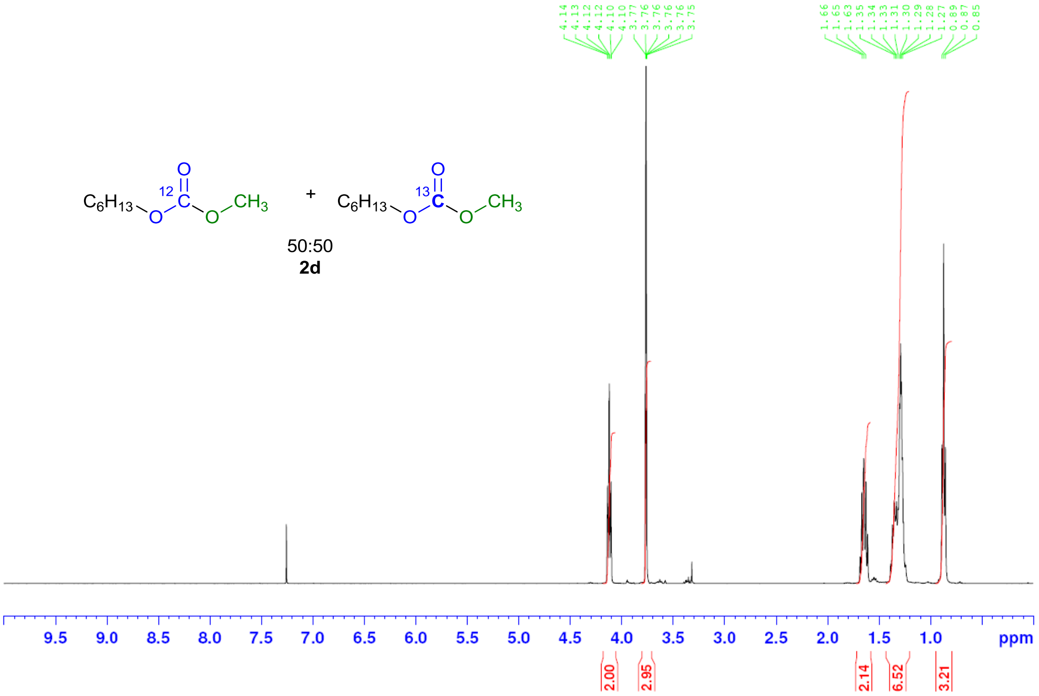


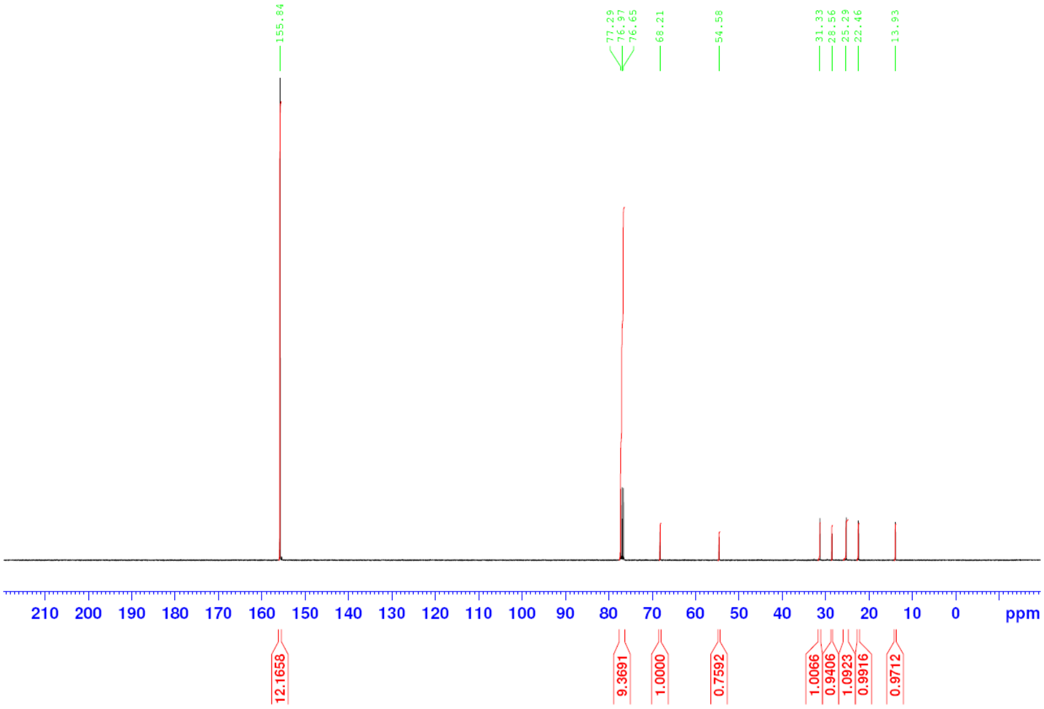
Measured ratio 50:50 NaH^{12}CO$_3$:NaH^{13}CO$_3$
Entry 3, Table 4



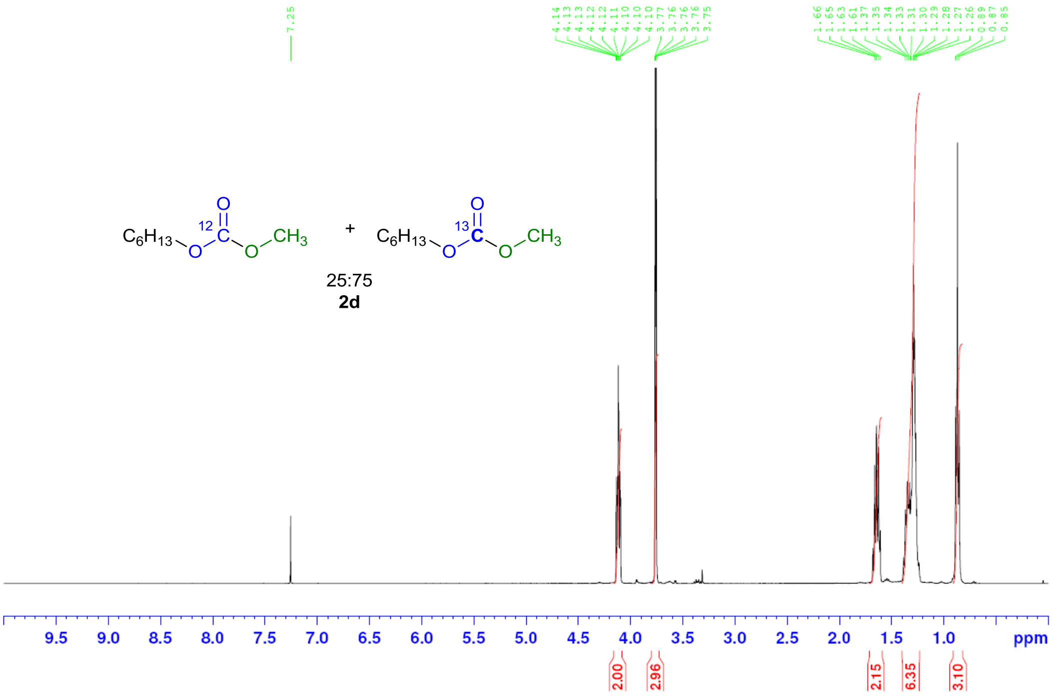


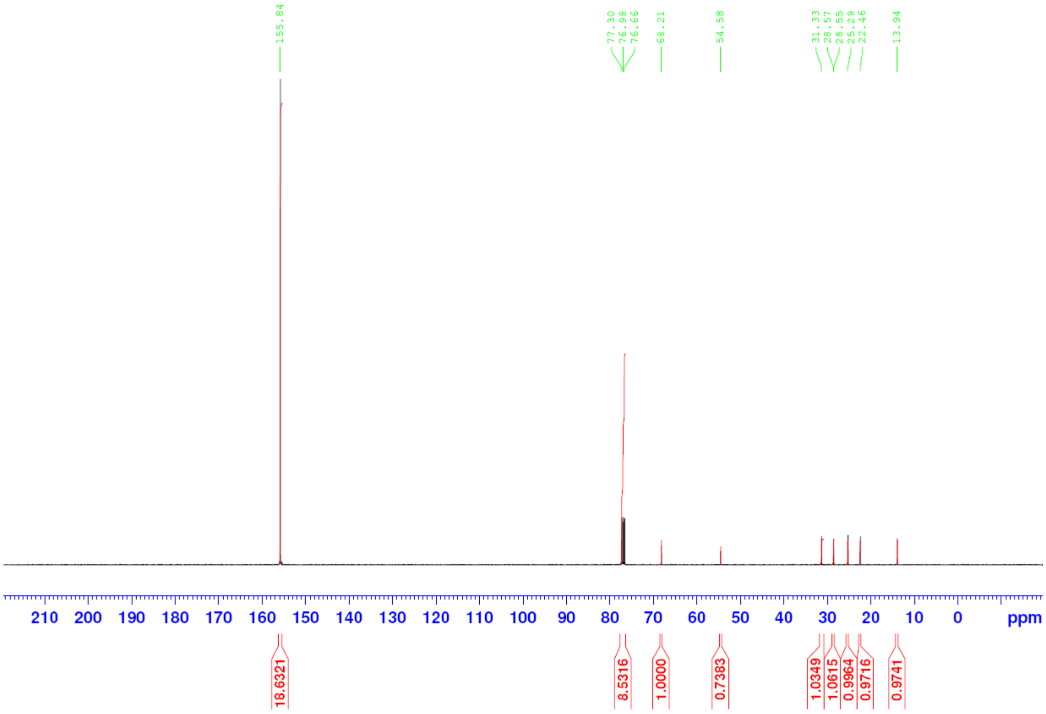
Measured ratio 50:50 $NaH^{12}CO_3$:$NaH^{13}CO_3$
As Entry 3, Table 4, but purged with N_2 before CO_2 generation



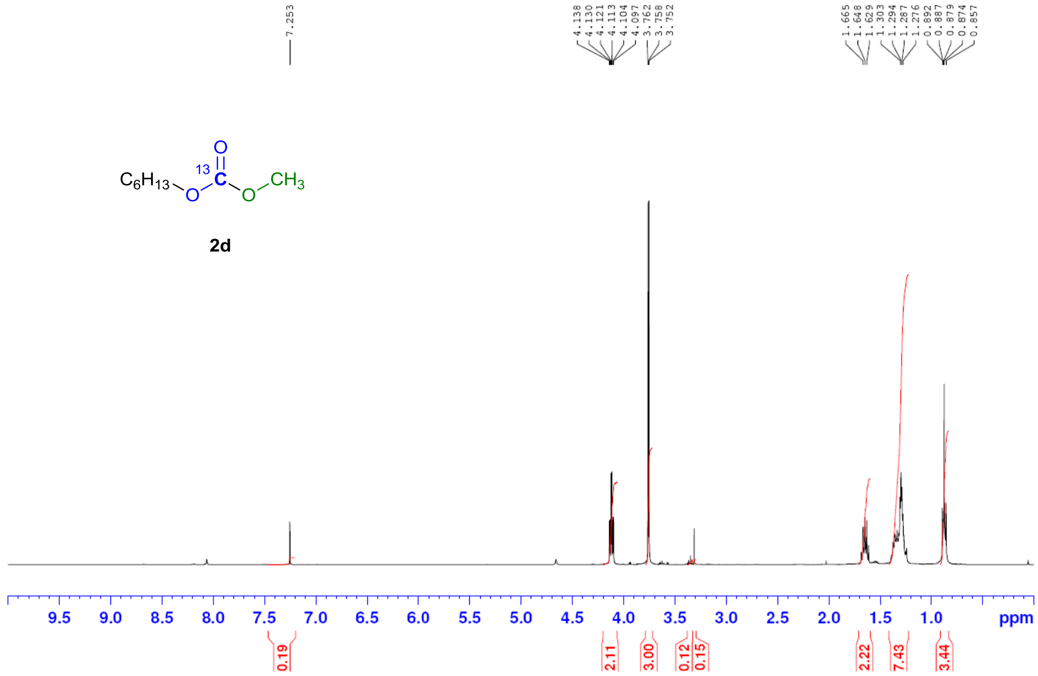


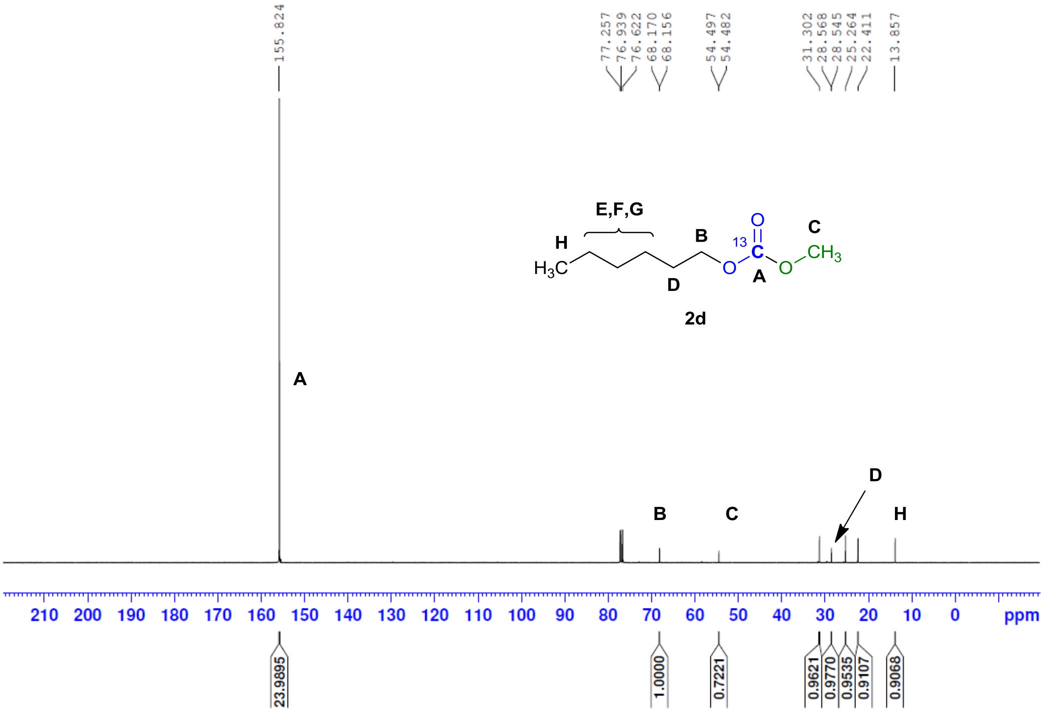
Measured ratio 25:75 NaH^{12}CO$_3$:NaH^{13}CO$_3$
Entry 4, Table 4



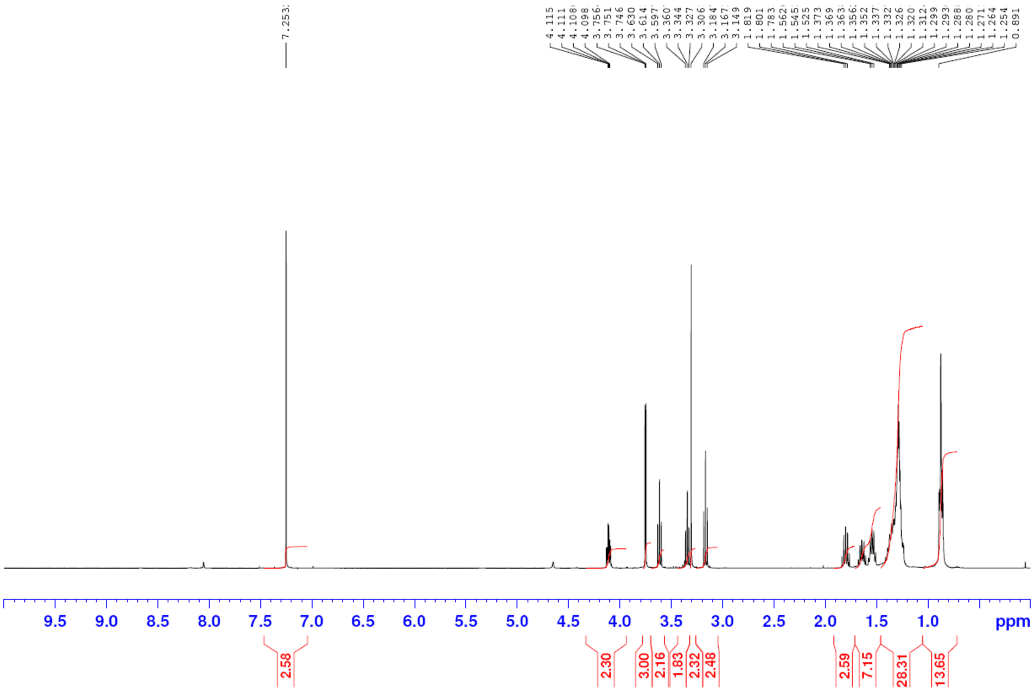


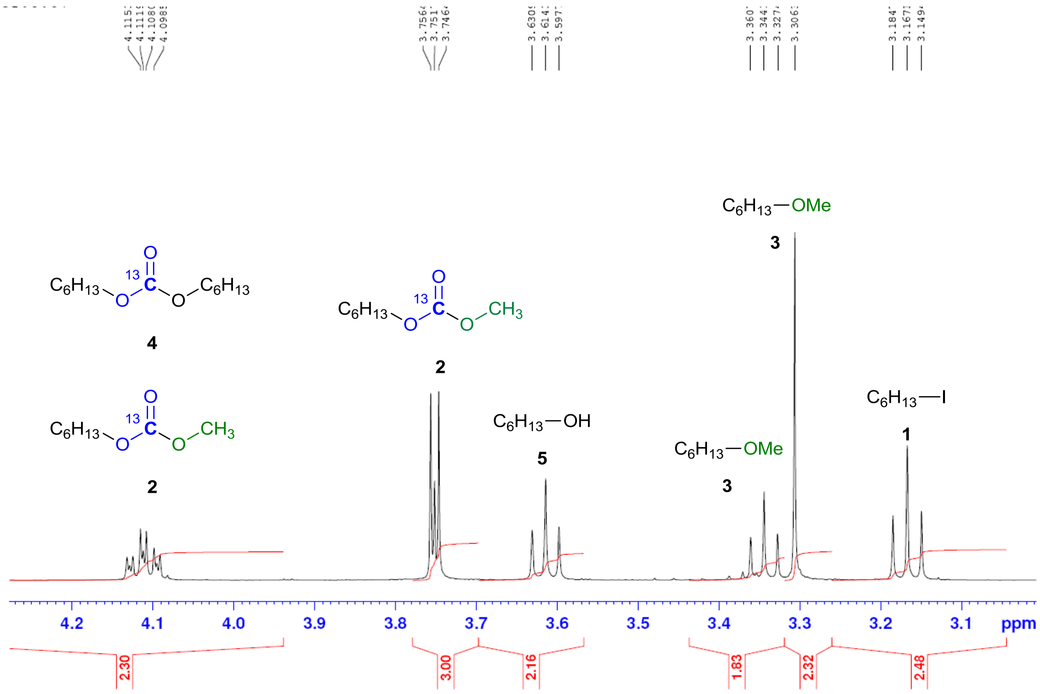
Measured ratio 0:100 NaH^{12}CO$_3$:NaH^{13}CO$_3$
Entry 5, Table 4



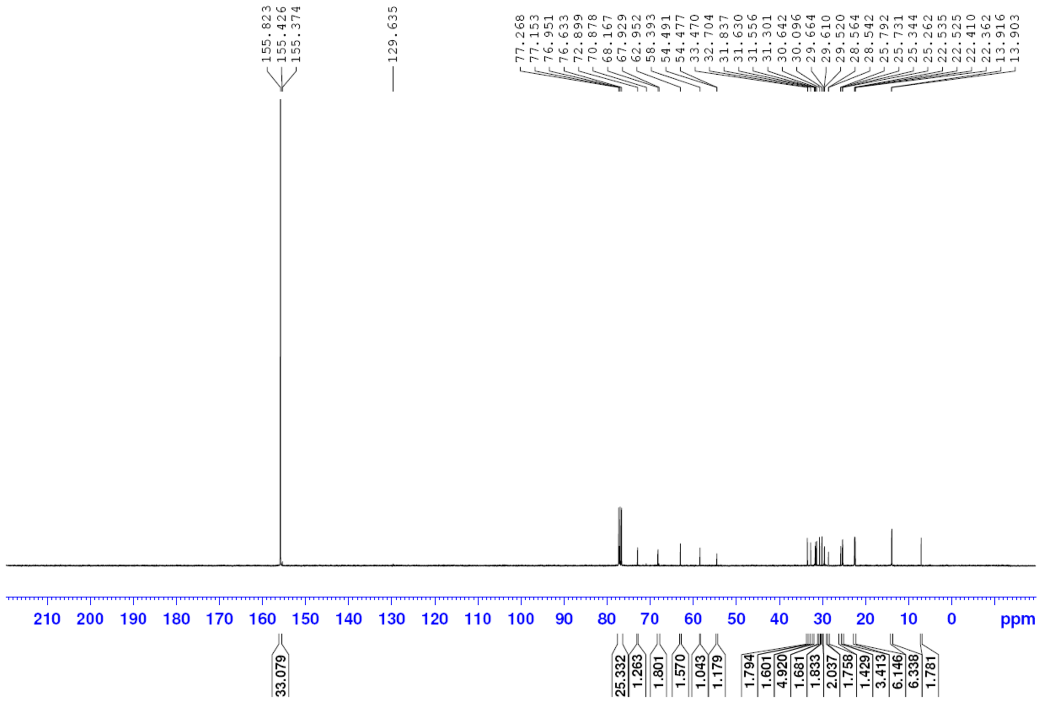


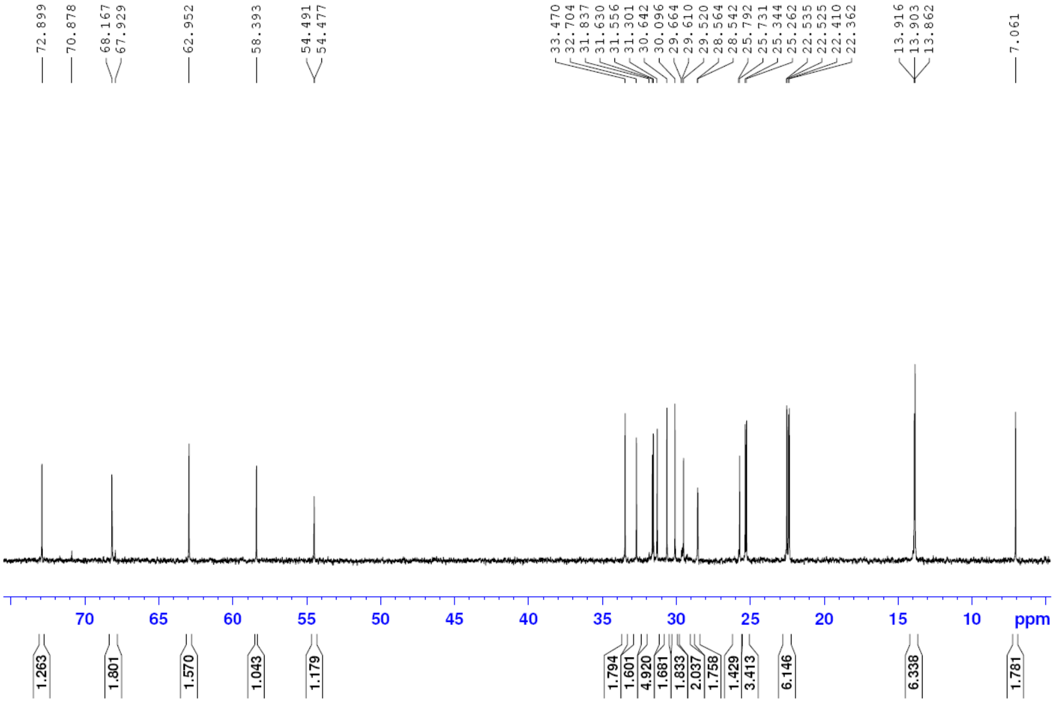
Measured ratio 0:100 $NaH^{12}CO_3$:$NaH^{13}CO_3$
As Entry 5, Table 4, but with Ag_2CO_3





Measured ratio 0:100 NaH^{12}CO$_3$:NaH^{13}CO$_3$
As Entry 5, Table 4, but with Ag$_2$CO$_3$





Isotopic labelling experiments
Determination of ratios by ^{13}C NMR

Simultaneous equations: **x** is the proportion of the integral corresponding to the ^{12}C compound and **y** is the proportion of the integral corresponding to the ^{13}C compound.

Standard 100 MHz ^{13}C NMR experiments were performed, with 1024 scans. Owing to different relaxation times, the integral of the C=O peak differs to the integrals of the remaining peaks, although each peak represents a single carbon. The difference in the integrals was determined from the non-labelled compound (“reference ^{13}C NMR”, page S6), which was incorporated in the equations below as the “integration factor”.

In addition, the C=O signal for the ^{13}C compound **y** will be 100% abundant, so in order to make a direct comparison with the C=O signal for the ^{12}C compound **x**, we must use a conversion factor to take into account the natural abundance of ^{13}C which is 1.11%. Therefore, the C=O peak for compound **y** will be magnified by a factor of 100/1.11. For all other C signals, **x** + **y** will simply equal the integral of that peak.

Measured ratio 75:25 $NaH^{12}CO_3$:$NaH^{13}CO_3$

Entry 2, Table 4

Comparison of C=O peak at 155.8 ppm integral 7.3152 with 68.2 ppm integral 1.0000
Integration factor = 3.6904

1) $x + y = 1.0000$
2) $x + (100y/1.11) = 7.3152 \times 3.6904$

Rearranging Eq. 1 to $y = 1.0000 – x$ and substituting into Eq. 2 gives:

3) $x + (100(1 – x)/1.11) = 26.9960$, becomes
4) $90.0901 – 89.0901x = 26.9960$, becomes
5) $89.0901x = 63.0941$,
6) $x = 0.7082$

From Eq. 1, $x + y = 1.0000$; $x = 0.7082$ and $y = 0.2918$, ^{12}C = 70.8% and ^{13}C = 29.2%

Comparison of C=O peak at 155.8 ppm integral 7.3152 with 54.57 ppm integral 0.7842
Integration factor = 2.6110

1) $x + y = 0.7842$
2) $x + (100y/1.11) = 7.3152 \times 2.6110$

Rearranging Eq. 1 to $y = 0.7842 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.7842 – x)/1.11) = 19.1000$, becomes
4) $70.6486 – 89.0901x = 19.1000$, becomes
5) $89.0901x = 51.5487$,
6) $x = 0.5786$

From Eq. 1, $x + y = 0.7842$, $x = 0.5786$ and $y = 0.2056$, ^{12}C = 73.8% and ^{13}C = 26.2%

Comparison of C=O peak at 155.8 ppm integral 7.3152 with 31.3 ppm integral 1.0952
Integration factor = 3.5564

1) $x + y = 1.0952$
2) $x + (100y/1.11) = 7.3152 \times 3.5564$

Rearranging Eq. 1 to $y = 1.0952 - x$ and substituting into Eq. 2 gives:

3) $x + (100(1.0952 - x)/1.11) = 26.0158$, becomes
4) $98.6667 - 89.0901x = 26.0158$, becomes
5) $89.0901x = 72.6509$,
6) $x = 0.815$

From Eq. 1, $x + y = 1.0952$; $x = 0.8155$ and $y = 0.2797$, $^{12}C = 74.5\%$ and $^{13}C = 25.5\%$

Comparison of C=O peak at 155.8 ppm integral 7.3152 with 28.6 ppm integral 1.0263
Integration factor = 3.5026

1) $x + y = 1.0263$
2) $x + (100y/1.11) = 7.3152 \times 3.5026$

Rearranging Eq. 1 to $y = 1.0263 - x$ and substituting into Eq. 2 gives:

3) $x + (100(1.0263 - x)/1.11) = 25.6222$, becomes
4) $92.4595 - 89.0901x = 25.6222$, becomes
5) $89.0901x = 66.8372$,
6) $x = 0.7502$

From Eq. 1, $x + y = 1.0263$; $x = 0.7502$ and $y = 0.2761$, $^{12}C = 73.1\%$ and $^{13}C = 26.9\%$

Comparison of C=O peak at 155.8 ppm integral 7.3152 with 25.3 ppm integral 1.1055
Integration factor = 3.4658

1) $x + y = 1.1055$
2) $x + (100y/1.11) = 7.3152 \times 3.4658$

Rearranging Eq. 1 to $y = 1.1055 - x$ and substituting into Eq. 2 gives:

3) $x + (100(1.1055 - x)/1.11) = 25.3530$, becomes
4) $99.5946 - 89.0901x = 25.3530$, becomes
5) $89.0901x = 74.2416$,
6) $x = 0.8333$

From Eq. 1, $x + y = 1.1055$; $x = 0.8333$ and $y = 0.2722$, $^{12}C = 75.4\%$ and $^{13}C = 24.6\%$

Comparison of C=O peak at 155.8 ppm integral 7.3152 with 22.5 ppm integral 1.1190
Integration factor = 3.3807

1) $x + y = 1.1190$
2) $x + (100y/1.11) = 7.3152 \times 3.3807$

Rearranging Eq. 1 to $y = 1.1190 – x$ and substituting into Eq. 2 gives:

3) $x + (100(1.1190 – x)/1.11) = 24.7305$, becomes
4) $100.8108 – 89.0901x = 24.7305$, becomes
5) $89.0901x = 76.0803$,
6) $x = 0.854$

From Eq. 1, $x + y = 1.1190$; $x = 0.8540$ and $y = 0.2650$, $^{12}C = 76.3\%$ and $^{13}C = 23.7\%$

Comparison of C=O peak at 155.8 ppm integral 7.3152 with 13.9 ppm integral 1.1059
Integration factor = 3.4515

1) $x + y = 1.1059$
2) $x + (100y/1.11) = 7.3152 \times 3.4515$

Rearranging Eq. 1 to $y = 1.1059 – x$ and substituting into Eq. 2 gives:

3) $x + (100(1.1059 – x)/1.11) = 25.2484$, becomes
4) $99.6306 – 89.0901x = 25.2484$, becomes
5) $89.0901x = 74.3822$,
6) $x = 0.8349$

From Eq. 1, $x + y = 1.1059$; $x = 0.8349$ and $y = 0.2710$, $^{12}C = 75.5\%$ and $^{13}C = 24.5\%$

Average of the 7 peaks and using population Standard deviation

$$\frac{70.8 + 73.8 + 74.5 + 73.1 + 75.4 + 76.3 + 75.5}{7} = \mathbf{74.2 \pm 1.7}$$

$^{12}C = 74.2 \pm 1.7\%$ and $^{13}C = 25.8 \pm 1.7\%$

Measured ratio 50:50 $NaH^{12}CO_3$:$NaH^{13}CO_3$

Entry 3, Table 4

Comparison of C=O peak at 155.8 ppm integral 12.4434 with 68.2 ppm integral 1.0000

Integration factor = 3.6904

1) $x + y = 1.0000$
2) $x + (100y/1.11) = 12.4434 \times 3.6904$

Rearranging Eq. 1 to $y = 1.0000 – x$ and substituting into Eq. 2 gives:

3) $x + (100(1 – x)/1.11) = 45.9211$, becomes
4) $90.0901 – 89.0901x = 45.9211$, becomes
5) $89.0901x = 44.1690$,
6) $x = 0.4958$

From Eq. 1, $x + y = 1.0000$; $x = 0.4958$ and $y = 0.5042$, $^{12}C = 49.6\%$ and $^{13}C = 50.4\%$

Comparison of C=O peak at 155.8 ppm integral 12.4434 with 54.57 ppm integral 0.7342

Integration factor = 2.6110

1) $x + y = 0.7342$
2) $x + (100y/1.11) = 12.4434 \times 2.6110$

Rearranging Eq. 1 to $y = 0.7342 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.7342 – x)/1.11) = 32.4897$, becomes
4) $66.1444 – 89.0901x = 32.4897$, becomes
5) $89.0901x = 33.6544$,
6) $x = 0.3778$

From Eq. 1, $x + y = 0.7342$, $x = 0.3778$ and $y = 0.3564$, $^{12}C = 51.5\%$ and $^{13}C = 48.5\%$

Comparison of C=O peak at 155.8 ppm integral 12.4434 with 31.3 ppm integral 0.9691

Integration factor = 3.5564

1) $x + y = 0.9691$
2) $x + (100y/1.11) = 12.4434 \times 3.5564$

Rearranging Eq. 1 to $y = 0.9691 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.9691 – x)/1.11) = 44.2537$, becomes
4) $87.3063 – 89.0901x = 44.2537$, becomes
5) $89.0901x = 43.0526$,
6) $x = 0.4832$

From Eq. 1, $x + y = 0.9691$; $x = 0.4832$ and $y = 0.4859$, $^{12}C = 49.9\%$ and $^{13}C = 50.1\%$

Comparison of C=O peak at 155.8 ppm integral 12.4434 with 28.6 ppm integral 0.9806
Integration factor = 3.5026

1) $x + y = 0.9806$
2) $x + (100y/1.11) = 12.4434 \times 3.5026$

Rearranging Eq. 1 to $y = 0.9806 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.9806 – x)/1.11) = 43.5843$, becomes
4) $88.3423 – 89.0901x = 43.5843$, becomes
5) $89.0901x = 44.7581$,
6) $x = 0.5024$

From Eq. 1, $x + y = 0.9806$; $x = 0.5024$ and $y = 0.4782$, ^{12}C = 51.2% and ^{13}C = 48.8%

Comparison of C=O peak at 155.8 ppm integral 12.4434 with 25.3 ppm integral 0.9815
Integration factor = 3.4658

1) $x + y = 0.9815$
2) $x + (100y/1.11) = 12.4434 \times 3.4658$

Rearranging Eq. 1 to $y = 0.9815 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.9815 – x)/1.11) = 43.1263$, becomes
4) $88.4234 – 89.0901x = 43.1263$, becomes
5) $89.0901x = 45.2971$,
6) $x = 0.5084$

From Eq. 1, $x + y = 0.9815$; $x = 0.5084$ and $y = 0.4731$, ^{12}C = 51.8% and ^{13}C = 48.2%

Comparison of C=O peak at 155.8 ppm integral 12.4434 with 22.5 ppm integral 0.9319
Integration factor = 3.3807

1) $x + y = 0.9319$
2) $x + (100y/1.11) = 12.4434 \times 3.3807$

Rearranging Eq. 1 to $y = 0.9319 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.9319 – x)/1.11) = 42.0674$, becomes
4) $83.9550 – 89.0901x = 42.0674$, becomes
5) $89.0901x = 41.8876$,
6) $x = 0.4702$

From Eq. 1, $x + y = 0.9319$; $x = 0.4702$ and $y = 0.4617$, ^{12}C = 50.5% and ^{13}C = 49.5%

Comparison of C=O peak at 155.8 ppm integral 12.4434 with 13.9 ppm integral 0.9093
Integration factor = 3.4515

1) $x + y = 0.9093$
2) $x + (100y/1.11) = 12.4434 \times 3.4515$

Rearranging Eq. 1 to $y = 0.9093 - x$ and substituting into Eq. 2 gives:

3) $x + (100(0.9093 - x)/1.11) = 42.9484$, becomes
4) $81.9189 - 89.0901x = 42.9484$, becomes
5) $89.0901x = 38.9705$,
6) $x = 0.4374$

From Eq. 1, $x + y = 0.9093$; $x = 0.4374$ and $y = 0.4719$, $\underline{^{12}\text{C} = 48.1\% \text{ and } ^{13}\text{C} = 51.9\%}$

Average of the 7 peaks and using population Standard deviation

$$\frac{49.6 + 51.5 + 49.9 + 51.2 + 51.8 + 50.5 + 48.1}{7} = \mathbf{50.4 \pm 1.2}$$

$\underline{\underline{\mathbf{^{12}C = 50.4 \pm 1.2\% \text{ and } ^{13}C = 49.6 \pm 1.2\%}}}$

Measured ratio 25:75 $NaH^{12}CO_3$:$NaH^{13}CO_3$

Entry 4, Table 4

Comparison of C=O peak at 155.8 ppm integral 18.6321 with 68.2 ppm integral 1.0000

Integration factor = 3.6904

1) $x + y = 1.0000$
2) $x + (100y/1.11) = 18.6321 \times 3.6904$

Rearranging Eq. 1 to $y = 1.0000 – x$ and substituting into Eq. 2 gives:

3) $x + (100(1 – x)/1.11) = 68.7599$, becomes
4) $90.0901 – 89.0901x = 68.7599$, becomes
5) $89.0901x = 21.3302$,
6) $x = 0.2394$

From Eq. 1, $x + y = 1.0000$; $x = 0.2394$ and $y = 0.7606$, $^{12}C = 23.9\%$ and $^{13}C = 76.1\%$

Comparison of C=O peak at 155.8 ppm integral 18.6321 with 54.57 ppm integral 0.7383

Integration factor = 2.6110

1) $x + y = 0.7383$
2) $x + (100y/1.11) = 18.6321 \times 2.6110$

Rearranging Eq. 1 to $y = 0.7383 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.7383 – x)/1.11) = 48.6484$, becomes
4) $66.5135 – 89.0901x = 48.6484$, becomes
5) $89.0901x = 17.8651$,
6) $x = 0.2005$

From Eq. 1, $x + y = 0.7383$, $x = 0.2005$ and $y = 0.5378$, $^{12}C = 27.2\%$ and $^{13}C = 72.8\%$

Comparison of C=O peak at 155.8 ppm integral 18.6321 with 31.3 ppm integral 1.0349

Integration factor = 3.5564

1) $x + y = 1.0349$
2) $x + (100y/1.11) = 18.6321 \times 3.5564$

Rearranging Eq. 1 to $y = 1.0349 – x$ and substituting into Eq. 2 gives:

3) $x + (100(1.0349 – x)/1.11) = 66.2632$, becomes
4) $93.2342 – 89.0901x = 66.2632$, becomes
5) $89.0901x = 26.9710$,
6) $x = 0.3027$

From Eq. 1, $x + y = 1.0349$; $x = 0.3027$ and $y = 0.7322$, $^{12}C = 29.3\%$ and $^{13}C = 70.7\%$

Comparison of C=O peak at 155.8 ppm integral 18.6321 with 28.6 ppm integral 1.0615
Integration factor = 3.5026

1) $x + y = 1.0615$
2) $x + (100y/1.11) = 18.6321 \times 3.5026$

Rearranging Eq. 1 to $y = 1.0615 – x$ and substituting into Eq. 2 gives:

3) $x + (100(1.0615 – x)/1.11) = 65.2608$, becomes
4) $95.6306 – 89.0901x = 65.2608$, becomes
5) $89.0901x = 30.3698$,
6) $x = 0.3409$

From Eq. 1, $x + y = 1.0615$; $x = 0.3409$ and $y = 0.7206$, $^{12}C = 32.1\%$ and $^{13}C = 67.9\%$

Comparison of C=O peak at 155.8 ppm integral 18.6321 with 25.3 ppm integral 0.9964
Integration factor = 3.4658

1) $x + y = 0.9964$
2) $x + (100y/1.11) = 18.6321 \times 3.4658$

Rearranging Eq. 1 to $y = 0.9964 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.9964 – x)/1.11) = 64.5751$, becomes
4) $89.7658 – 89.0901x = 64.5751$, becomes
5) $89.0901x = 25.1906$,
6) $x = 0.2828$

From Eq. 1, $x + y = 0.9964$; $x = 0.2828$ and $y = 0.7136$, $^{12}C = 28.4\%$ and $^{13}C = 71.6\%$

Comparison of C=O peak at 155.8 ppm integral 18.6321 with 22.5 ppm integral 0.9716
Integration factor = 3.3807

1) $x + y = 0.9716$
2) $x + (100y/1.11) = 18.6321 \times 3.3807$

Rearranging Eq. 1 to $y = 0.9716 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.9716 – x)/1.11) = 62.9895$, becomes
4) $87.5315 – 89.0901x = 62.9895$, becomes
5) $89.0901x = 24.5420$,
6) $x = 0.2755$

From Eq. 1, $x + y = 0.9716$; $x = 0.2755$ and $y = 0.6961$, $^{12}C = 28.4\%$ and $^{13}C = 71.6\%$

Comparison of C=O peak at 155.8 ppm integral 18.6321 with 13.9 ppm integral 0.9741
Integration factor = 3.4515

1) $x + y = 0.9741$
2) $x + (100y/1.11) = 18.6321 \times 3.4515$

Rearranging Eq. 1 to $y = 0.9741 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.9741 – x)/1.11) = 64.3087$, becomes
4) $87.7568 – 89.0901x = 64.3087$, becomes
5) $89.0901x = 23.4481$,
6) $x = 0.2632$

From Eq. 1, $x + y = 0.9741$; $x = 0.2632$ and $y = 0.7109$, $\underline{{}^{12}C = 27.0\% \text{ and } {}^{13}C = 73.0\%}$

Average of the 7 peaks and using population Standard deviation

$$\frac{23.9 + 27.2 + 29.3 + 32.1 + 28.4 + 28.4 + 27.0}{7} = \mathbf{28.0 \pm 2.3}$$

$$\underline{\underline{\mathbf{{}^{12}C = 28.0 \pm 2.3\% \text{ and } {}^{13}C = 72.0 \pm 2.3\%}}}$$

Measured ratio 0:100 $NaH^{12}CO_3$:$NaH^{13}CO_3$

Entry 4, Table 4

Comparison of C=O peak at 155.8 ppm integral 23.9895 with 68.2 ppm integral 1.0000
Integration factor = 3.6904

1) $x + y = 1.0000$
2) $x + (100y/1.11) = 23.9895 \times 3.6904$

Rearranging Eq. 1 to $y = 1.0000 – x$ and substituting into Eq. 2 gives:

3) $x + (100(1 – x)/1.11) = 88.5309$, becomes
4) $90.0901 – 89.0901x = 88.5309$, becomes
5) $89.0901x = 1.5592$,
6) $x = 0.0175$

From Eq. 1, $x + y = 1.0000$; $x = 0.0175$ and $y = 0.9825$, $^{12}C = 1.75\%$ and $^{13}C = 98.25\%$

Comparison of C=O peak at 155.8 ppm integral 23.9895 with 54.5 ppm integral 0.7221
Integration factor = 2.6110

1) $x + y = 0.7221$
2) $x + (100y/1.11) = 23.9895 \times 2.6110$

Rearranging Eq. 1 to $y = 0.7221 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.7221 – x)/1.11) = 62.6366$, becomes
4) $66.0541 – 89.0901x = 62.6366$, becomes
5) $89.0901x = 2.4175$,
6) $x = 0.0271$

From Eq. 1, $x + y = 0.7221$, $x = 0.0271$ and $y = 0.6950$, $^{12}C = 3.8\%$ and $^{13}C = 96.2\%$

Comparison of C=O peak at 155.8 ppm integral 23.9895 with 31.3 ppm integral 0.9621
Integration factor = 3.5564

1) $x + y = 0.9621$
2) $x + (100y/1.11) = 23.9895 \times 3.5564$

Rearranging Eq. 1 to $y = 0.9621 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.9621 – x)/1.11) = 85.3163$, becomes
4) $86.6757 – 89.0901x = 66.2632$, becomes
5) $89.0901x = 1.3594$,
6) $x = 0.0153$

From Eq. 1, $x + y = 0.9621$; $x = 0.0153$ and $y = 0.9468$, $^{12}C = 1.6\%$ and $^{13}C = 98.4\%$

Comparison of C=O peak at 155.8 ppm integral 23.9895 with 28.6 ppm integral 0.9770
Integration factor = 3.5026

1) $x + y = 0.9770$
2) $x + (100y/1.11) = 23.9895 \times 3.5026$

Rearranging Eq. 1 to $y = 0.9770 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.9770 – x)/1.11) = 84.0256$, becomes
4) $88.0180 – 89.0901x = 84.0256$, becomes
5) $89.0901x = 3.9924$,
6) $x = 0.0448$

From Eq. 1, $x + y = 0.9770$; $x = 0.0448$ and $y = 0.9322$, <u>^{12}C = 4.6% and ^{13}C = 95.4%</u>

Comparison of C=O peak at 155.8 ppm integral 23.9895 with 25.3 ppm integral 0.9535
Integration factor = 3.4658

1) $x + y = 0.9535$
2) $x + (100y/1.11) = 23.9895 \times 3.4658$

Rearranging Eq. 1 to $y = 0.9535 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.9535 – x)/1.11) = 83.1428$, becomes
4) $85.9009 – 89.0901x = 83.1428$, becomes
5) $89.0901x = 2.7581$,
6) $x = 0.0310$

From Eq. 1, $x + y = 0.9535$; $x = 0.0310$ and $y = 0.9225$, <u>^{12}C = 3.2% and ^{13}C = 96.8%</u>

Comparison of C=O peak at 155.8 ppm integral 23.9895 with 22.4 ppm integral 0.9107
Integration factor = 3.3807

1) $x + y = 0.9107$
2) $x + (100y/1.11) = 23.9895 \times 3.3807$

Rearranging Eq. 1 to $y = 0.9107 – x$ and substituting into Eq. 2 gives:

3) $x + (100(0.9107 – x)/1.11) = 81.1013$, becomes
4) $82.0450 – 89.0901x = 81.1013$, becomes
5) $89.0901x = 0.9437$,
6) $x = 0.0106$

From Eq. 1, $x + y = 0.9107$; $x = 0.0106$ and $y = 0.9001$, <u>^{12}C = 1.2% and ^{13}C = 98.8%</u>

Comparison of C=O peak at 155.8 ppm integral 23.9895 with 13.9 ppm integral 0.9068
Integration factor = 3.4515

1) $x + y = 0.9068$
2) $x + (100y/1.11) = 23.9895 \times 3.4515$

Rearranging Eq. 1 to $y = 0.9068 - x$ and substituting into Eq. 2 gives:

3) $x + (100(0.9068 - x)/1.11) = 82.7998$, becomes
4) $81.6937 - 89.0901x = 82.7998$, becomes
5) $89.0901x = -1.1061$,
6) $x = -0.0124$

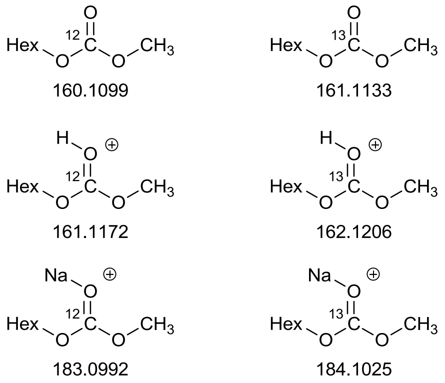
From Eq. 1, $x + y = 0.9068$; $x = -0.0124$ and $y = 0.9192$, $\underline{{}^{12}C = -1.4\%\text{ and }{}^{13}C = 101.4\%}$

Average of the 7 peaks and using population Standard deviation

$$\frac{1.75 + 3.8 + 1.6 + 4.6 + 3.2 + 1.2 - 1.4}{7} = \mathbf{2.1 \pm 1.8}$$

$\underline{\underline{\mathbf{{}^{12}C = 2.1 \pm 1.8\%\text{ and }{}^{13}C = 97.9 \pm 1.8\%}}}$

Isotopic labelling experiments
Determination of ratios by High Resolution Mass Spectroscopy



x **y**

m/z of 100% ^{12}C compound **x** shows the MNa$^+$ ion at 183.1035 (39 090, 91.26%) and 184.1067 (3 746, 8.74%), due to natural abundance of ^{13}C present in this compound. Using this background reading, the ratios of the mixtures are calculated below.

The proportion of the peak at 184.1 due to the natural abundance of ^{13}C is (3 746/39 090) of the peak at 183.09.

x is the proportion of the integral corresponding to the ^{12}C compound and **y** is the proportion of the integral corresponding to the ^{13}C compound.

The table below shows the exact mass found and the integration of each peak corresponding to ^{12}C and ^{13}C.

Entry	**Ratio NaH^{12}CO$_3$:NaH^{13}CO$_3$**	**MNa$^+$ ^{12}C (x)^a**	**Integration**	**MNa$^+$ ^{13}C (y)^a**	**Integration**
1	100:0	183.1035	39090	184.1067	3746
2	75:25	183.0977	159796	184.1013	72738
3	50:50	183.1026	43599	184.1056	48240
4	25:75	183.0990	16043	184.1018	42118
5	0:100	183.0973	24203	184.1008	800762

[a] Source Type: ESI+

The calculations below show how the ratio of isotopes was determined using theses integrals to give the values quoted as Table 4 in the paper (and reproduced below)

Table 4. ^{13}C-labelled CO_2 experiments.[a]

Entry	Yield (%)[b]	Measured ratio[c]		Observed ratio ^{13}C NMR[d]		Observed ratio HRMS[e]	
		^{12}C	^{13}C	^{12}C	^{13}C	^{12}C	^{13}C
1	63	100	0	100	0	100	0
2	68	75	25	74.2±1.7	25.8±1.7	73.6	26.4
3	68	50	50	50.4±1.2	49.6±1.2	49.7	50.3
4	70	25	75	28.0±2.3	72.0±2.3	28.3	71.7
5	60	0	100	2.1±1.8	97.9±1.8	2.9	97.1

[a] All reactions were performed by adding 3M $HCl_{(aq)}$ to $NaHCO_3$ (5 equiv.) and passing the CO_2 gas generated through a rapidly stirred suspension of Hex-I (1 equiv.) and Ag_2O (1.2 equiv.) in MeOH. The reaction was then rapidly stirred at 40 °C for 4h. [b] Yield of **2d** after filtration and careful evaporation under reduced pressure. [c] Ratio of the $NaH^{12}CO_3$ (99% ^{12}C) and $NaH^{13}CO_3$ (99% ^{13}C). [d] Average of ratios obtained from a comparison of the C=O peak with each of the aliphatic carbon signals (seven calculations). [e] Ratio based on MNa^+ (ESI+). [d] and [e] see below for calculations.

Measured ratio 75:25 $NaH^{12}CO_3$:$NaH^{13}CO_3$

Entry 2, Table 4

MNa^+ 183.0977, integration 159 796 (is solely due to compound x)
MNa^+ 184.1013, integration 72 738 (is due to the natural abundance of ^{13}C in compound x plus compound y), therefore

1) $x = 159\ 796$
2) $(3\ 746/39\ 090)x + y = 72\ 738$

substituting Eq. 1 into Eq. 2 gives:

3) $(3\ 746/39\ 090) \times 159\ 796 + y = 72\ 738$, becomes
4) $y = 57\ 424.728$

From Eq. 1 x = 159 796 and Eq. 4 y = 57 424.728, **^{12}C = 73.6% and ^{13}C = 26.4%**

Measured ratio 50:50 $NaH^{12}CO_3$:$NaH^{13}CO_3$

Entry 3, Table 4

MNa^+ 183.1026, integration 43 599 (is solely due to compound x)
MNa^+ 184.1056, integration 48 240 (is due to the natural abundance of ^{13}C in compound x plus compound y), therefore

1) $x = 43\ 599$
2) $(3\ 746/39\ 090)x + y = 48\ 240$

substituting Eq. 1 into Eq. 2 gives:

3) $(3\ 746/39\ 090) \times 43\ 599 + y = 48\ 240$, becomes
4) $y = 44\ 061.902$

From Eq. 1 x = 43 599 and Eq. 4 y = 44 061.902, **^{12}C = 49.7% and ^{13}C = 50.3%**

Measured ratio 25:75 NaH^{12}CO$_3$:NaH^{13}CO$_3$

Entry 4, Table 4

MNa$^+$ 183.0990, integration 16 043 (is solely due to compound x)
MNa$^+$ 184.1018, integration 42 118 (is due to the natural abundance of ^{13}C in compound x plus compound y), therefore

1) x = 16 043
2) (3 746/39 090)x + y = 42 118

substituting Eq. 1 into Eq. 2 gives:

3) (3 746/39 090) × 16 043 + y = 42 118, becomes
4) y = 40 580.597

From Eq. 1 x = 16 043 and Eq. 4 y = 40 580.597, **^{12}C = 28.3% and ^{13}C = 71.7%**

Measured ratio 0:100 NaH^{12}CO$_3$:NaH^{13}CO$_3$

Entry 5, Table 4

MNa$^+$ 183.0973, integration 24 203 (is solely due to compound x)
MNa$^+$ 184.1008, integration 800 762 (is due to the natural abundance of ^{13}C in compound x plus compound y), therefore

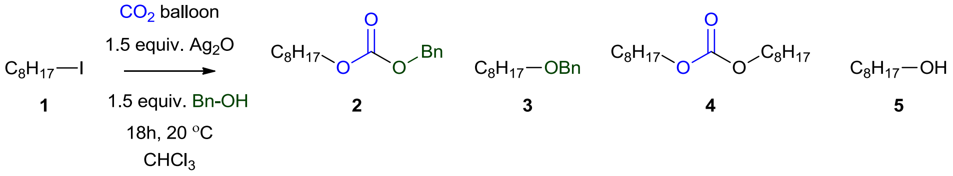
1) x = 24 203
2) (3 746/39 090)x + y = 800 762

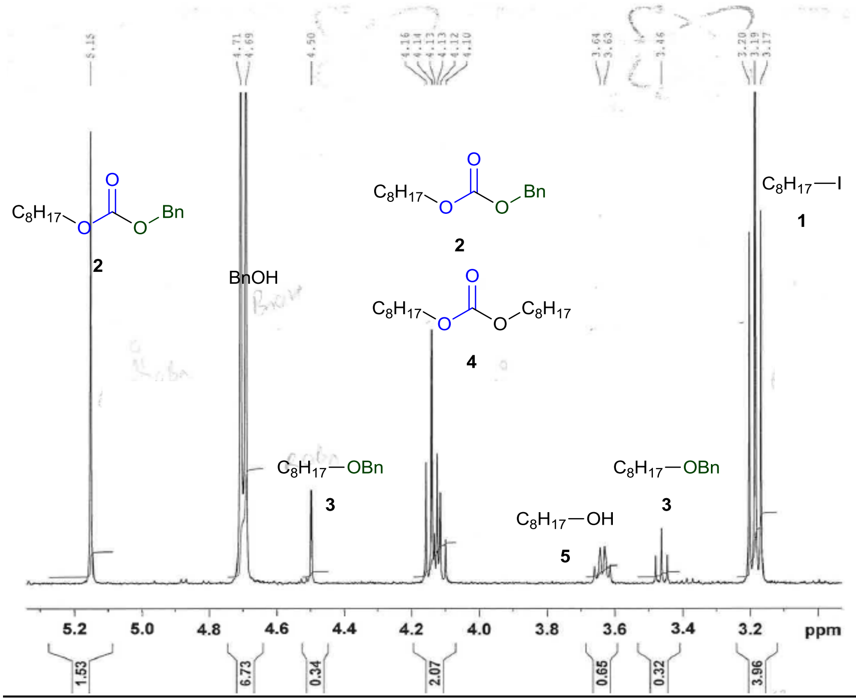
substituting Eq. 1 into Eq. 2 gives:

3) (3 746/39 090) × 24 203 + y = 800 762, becomes
4) y = 798 442.623

From Eq. 1 x = 24 203 and Eq. 4 y = 798 442.623, **^{12}C = 2.9% and ^{13}C = 97.1%**

^{1}H NMR Spectra from optimisation study, Table 3, Entry 1





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FIDRES                 0.125483 Hz
AQ                    3.9846387 sec
RG                          256
DW                       60.800 usec
DE                        17.24 usec
TE                        298.0 K
D1                   1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
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PL1                        0.00 dB
PL1W                 9.74611950 W
SFO1                400.0424704 MHz
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WDW                          EM
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PC                         1.00
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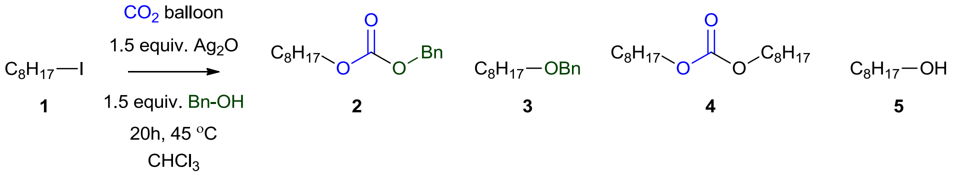
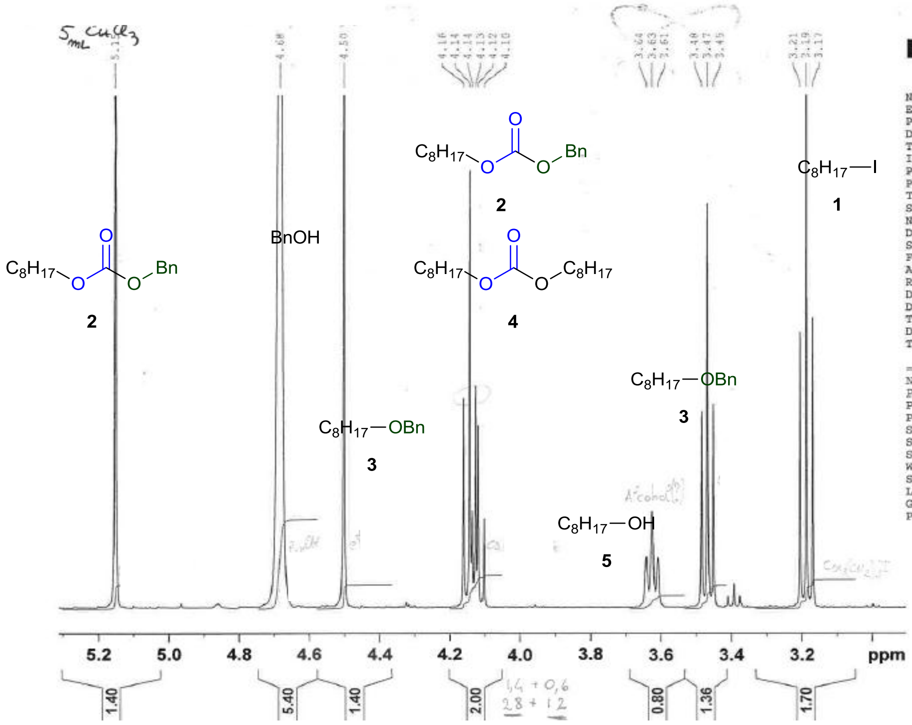
Table 3, Entry 2





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PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8223.685 Hz
FIDRES                 0.125483 Hz
AQ                    3.9846387 sec
RG                           57
DW                       60.800 usec
DE                        17.24 usec
TE                        298.0 K
D1                   1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        13.00 usec
PL1                        0.00 dB
PL1W                 9.74611950 W
SFO1                400.0424704 MHz
SI                        65536
SF                  400.0400148 MHz
WDW                          EM
SSB                           0
LB                         0.20 Hz
GB                            0
PC                         1.00
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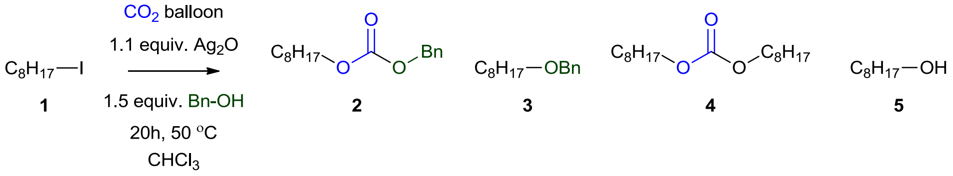
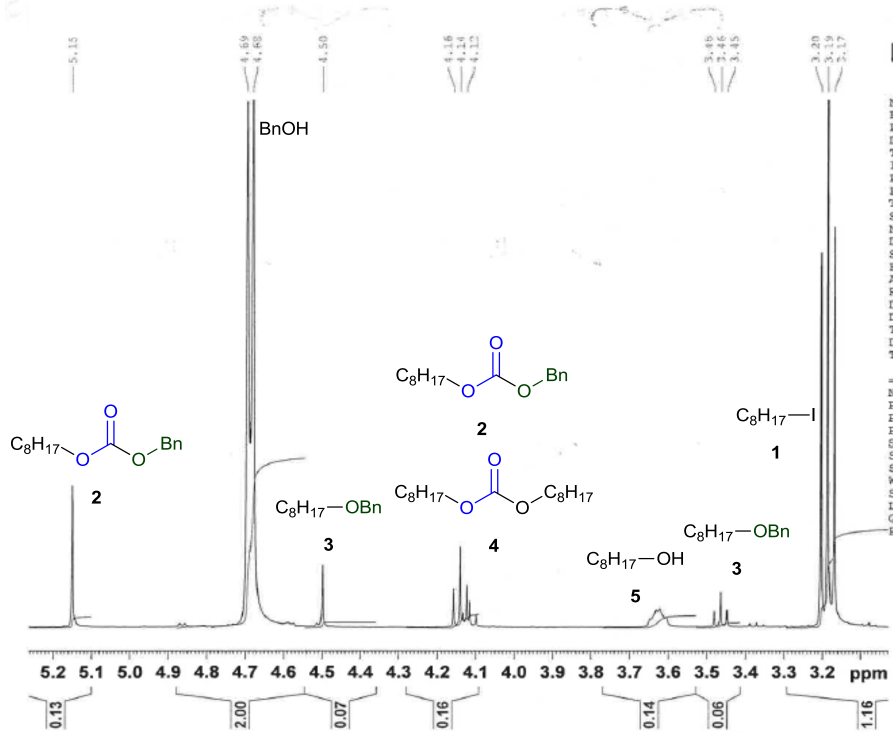
Table 3, Entry 3





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PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ               3.9846387 sec
RG                      80.6
DW                    60.800 usec
DE                     17.24 usec
TE                     298.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.00 usec
PL1                     0.00 dB
PL1W              9.74611950 W
SFO1             400.0424704 MHz
SI                     65536
SF               400.0400148 MHz
WDW                       EM
SSB                        0
LB                      0.20 Hz
GB                         0
PC                      1.00
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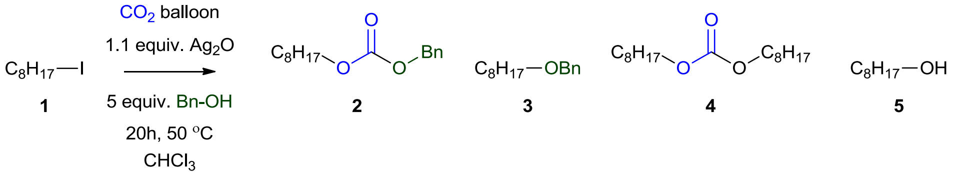
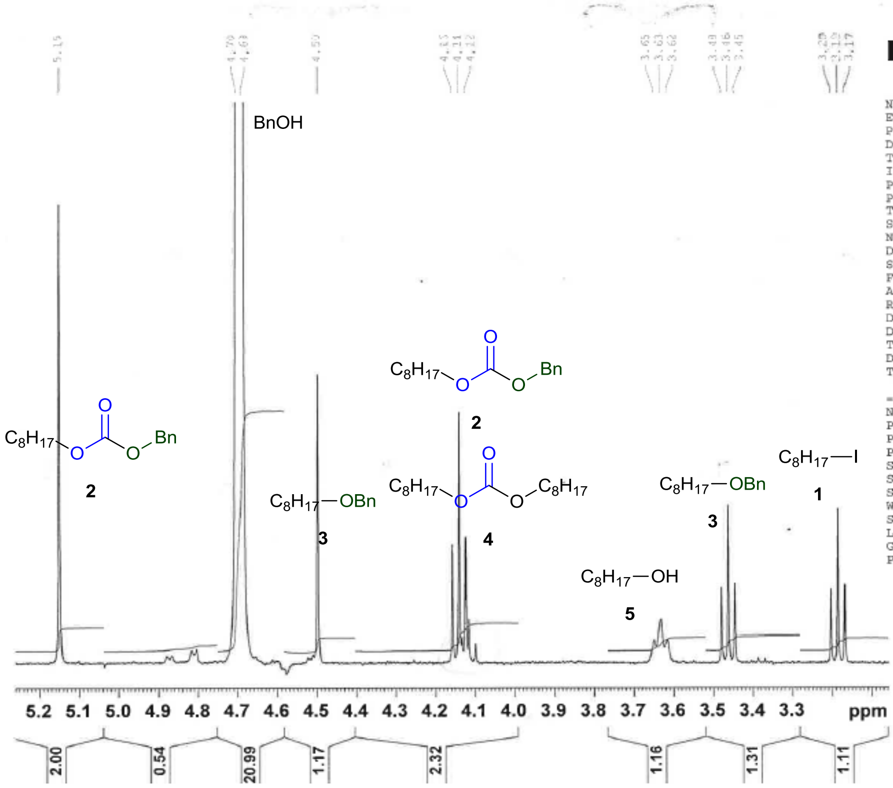
Table 3, Entry 4





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PROCNO                     1
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Time                   14.00
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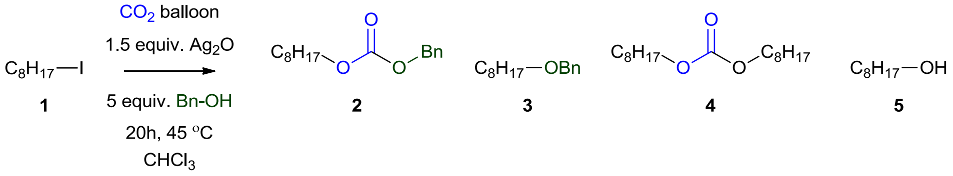
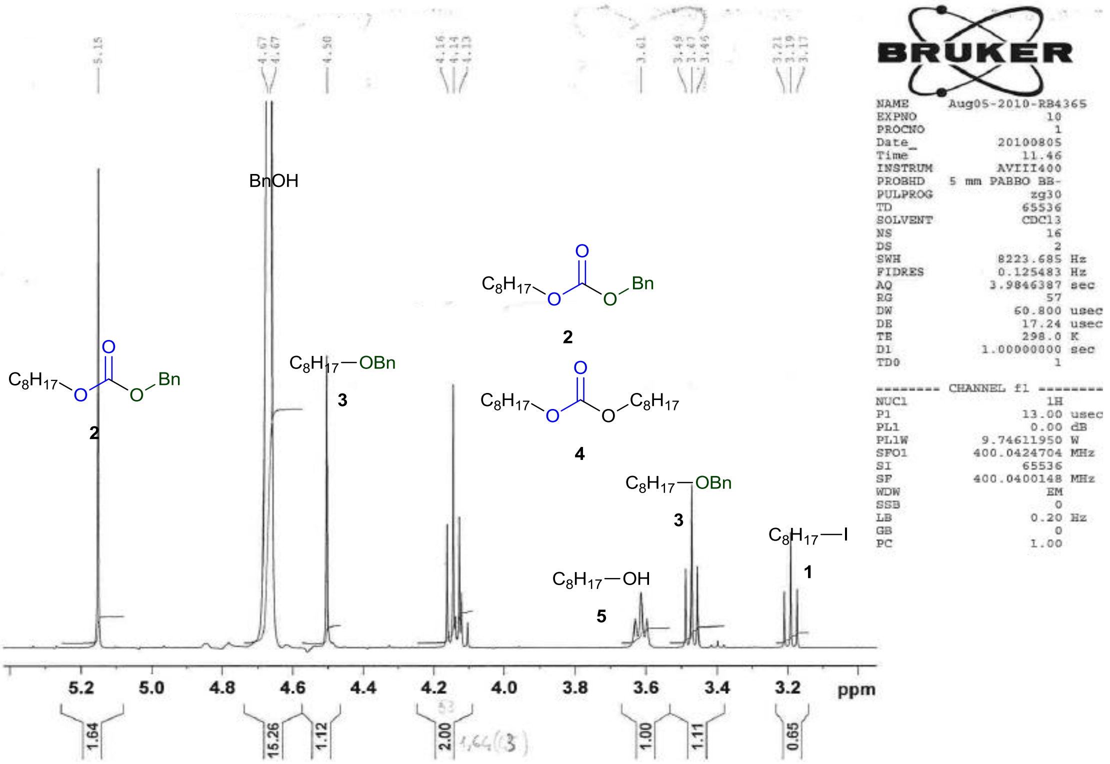
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ               3.9846387 sec
RG                       256
DW                    60.800 usec
DE                     17.24 usec
TE                     298.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.00 usec
PL1                     0.00 dB
PL1W              9.74611950 W
SFO1             400.0424704 MHz
SI                     65536
SF               400.0400148 MHz
WDW                       EM
SSB                        0
LB                      0.20 Hz
GB                         0
PC                      1.00
```

Table 3, Entry 5





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PROCNO                    1
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INSTRUM            AVIII400
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                3.9846387 sec
RG                       57
DW                   60.800 usec
DE                    17.24 usec
TE                    298.0 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    13.00 usec
PL1                    0.00 dB
PL1W             9.74611950 W
SFO1            400.0424704 MHz
SI                    65536
SF              400.0400148 MHz
WDW                      EM
SSB                       0
LB                     0.20 Hz
GB                        0
PC                     1.00
```
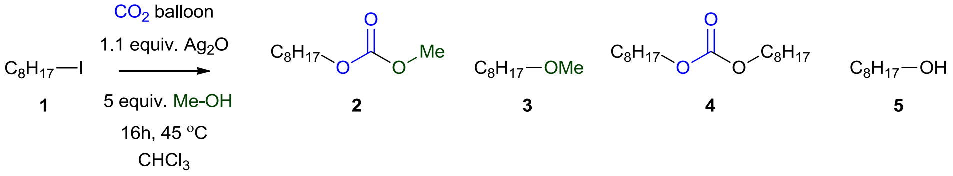
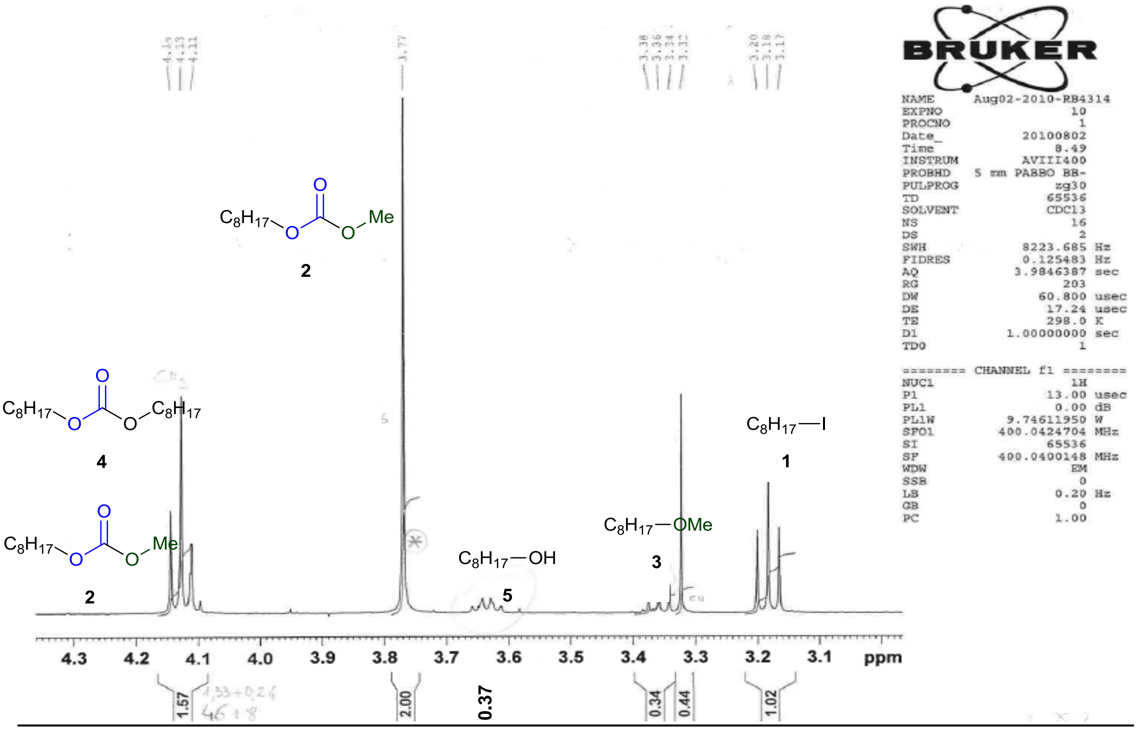
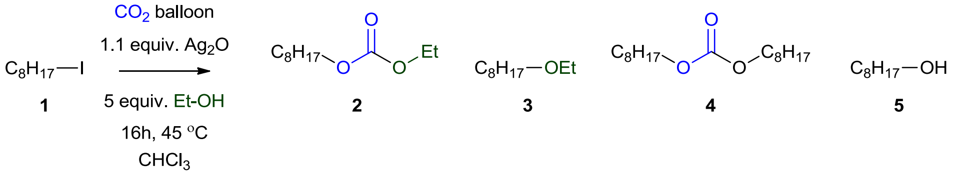

Table 3, Entry 6

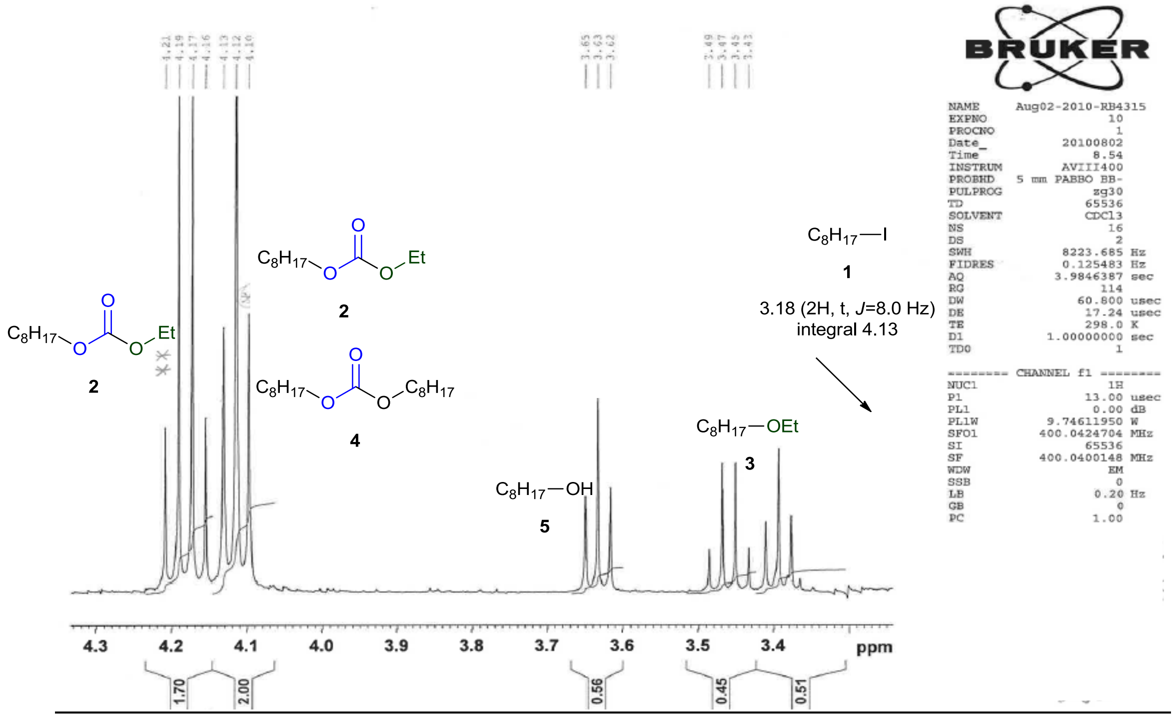




```
NAME      Aug02-2010-RB4314
EXPNO                    10
PROCNO                    1
Date_              20100802
Time                   8.49
INSTRUM            AVIII400
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                3.9846387 sec
RG                      203
DW                   60.800 usec
DE                    17.24 usec
TE                    298.0 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    13.00 usec
PL1                    0.00 dB
PL1W             9.74611950 W
SFO1            400.0424704 MHz
SI                    65536
SF              400.0400148 MHz
WDW                      EM
SSB                       0
LB                     0.20 Hz
GB                        0
PC                     1.00
```

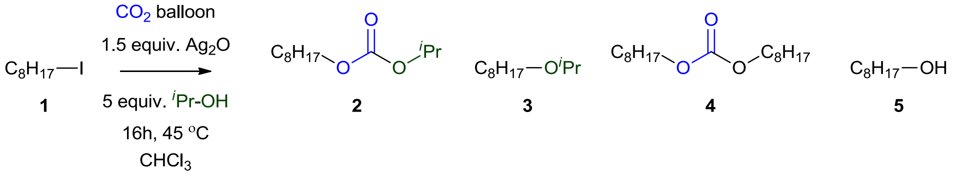
Table 3, Entry 7

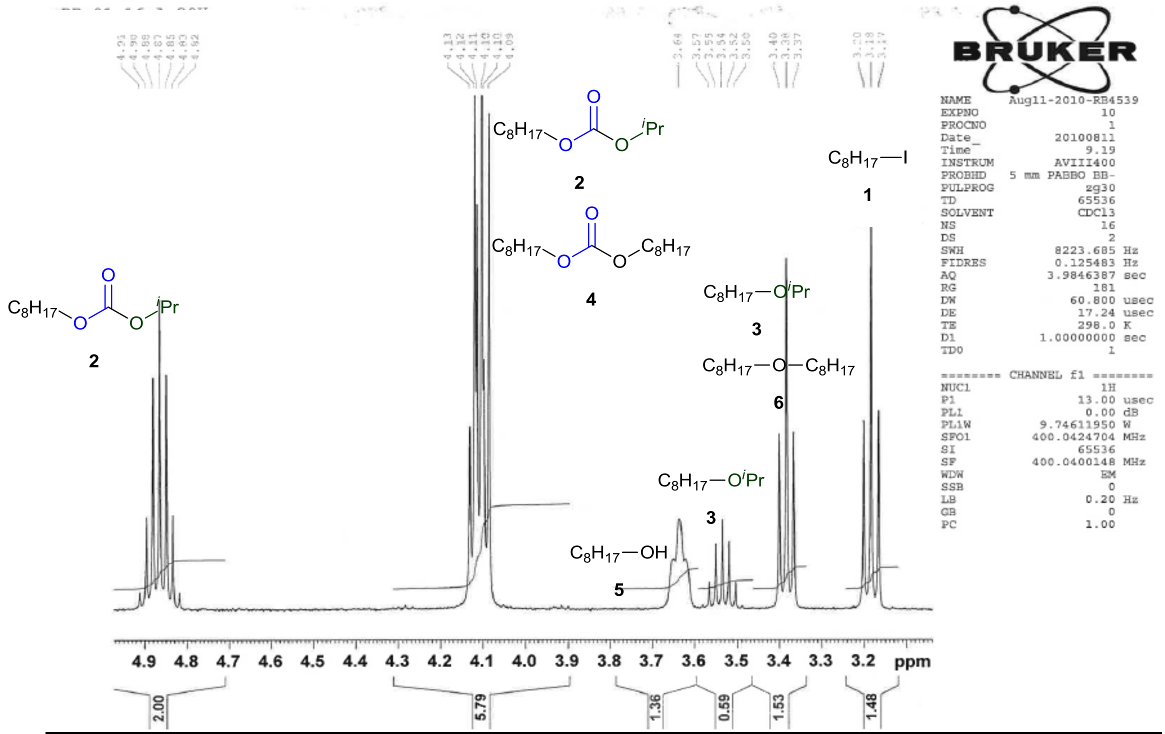




```
NAME        Aug02-2010-RB4315
EXPNO                      10
PROCNO                      1
Date_                20100802
Time                     8.54
INSTRUM              AVIII400
PROBHD      5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                  3.9846387 sec
RG                        114
DW                     60.800 usec
DE                      17.24 usec
TE                      298.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.00 usec
PL1                      0.00 dB
PL1W               9.74611950 W
SFO1             400.0424704 MHz
SI                      65536
SF               400.0400148 MHz
WDW                        EM
SSB                         0
LB                       0.20 Hz
GB                          0
PC                       1.00
```

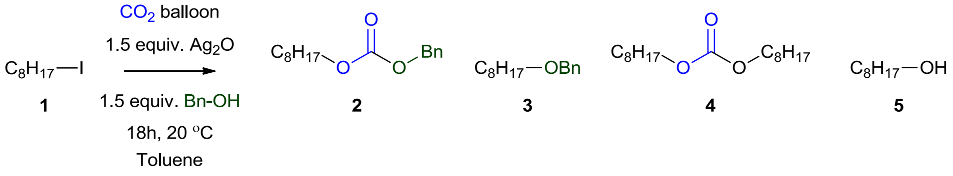
Table 3, Entry 8

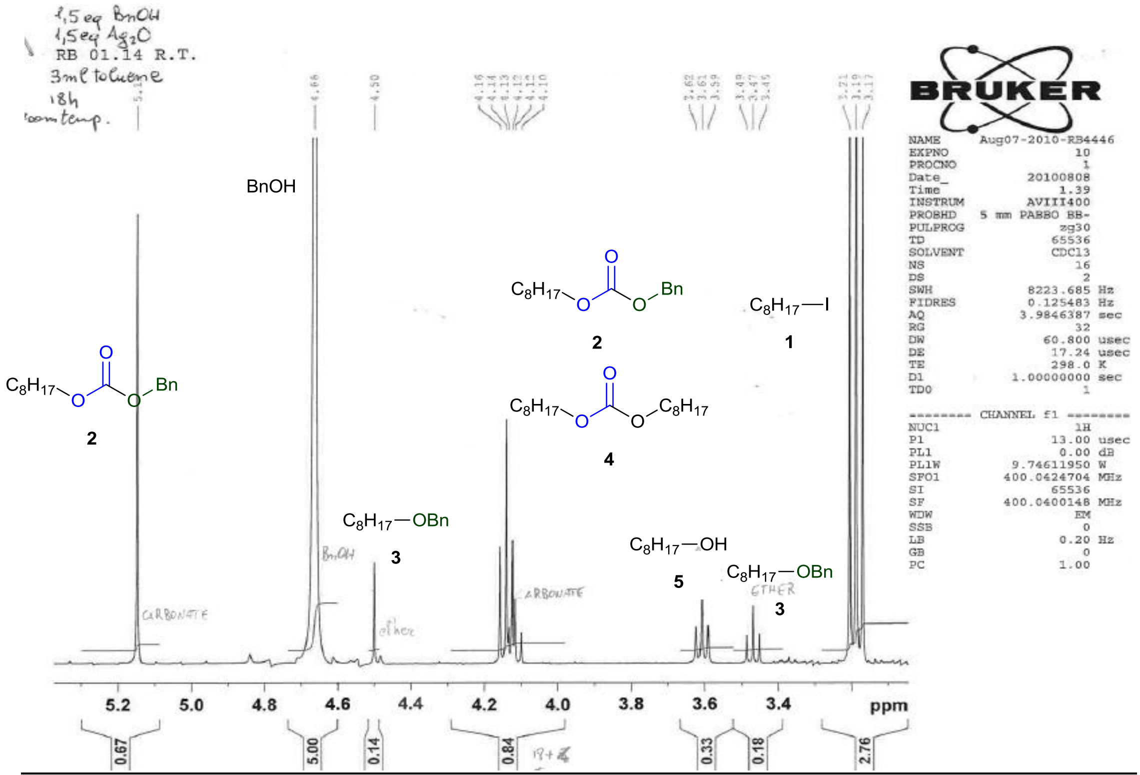




```
NAME        Aug11-2010-RB4539
EXPNO                      10
PROCNO                      1
Date_                20100811
Time                     9.19
INSTRUM              AVIII400
PROBHD      5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                  3.9846387 sec
RG                        181
DW                     60.800 usec
DE                      17.24 usec
TE                      298.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.00 usec
PL1                      0.00 dB
PL1W               9.74611950 W
SFO1             400.0424704 MHz
SI                      65536
SF               400.0400148 MHz
WDW                        EM
SSB                         0
LB                       0.20 Hz
GB                          0
PC                       1.00
```

Table 3, Entry 9

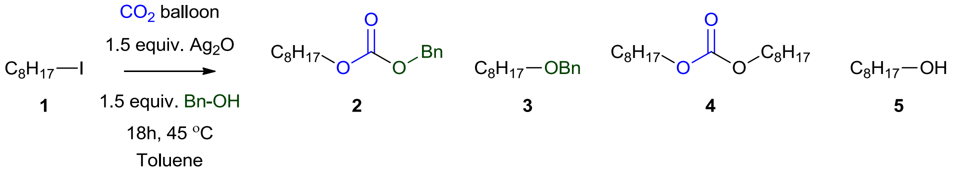


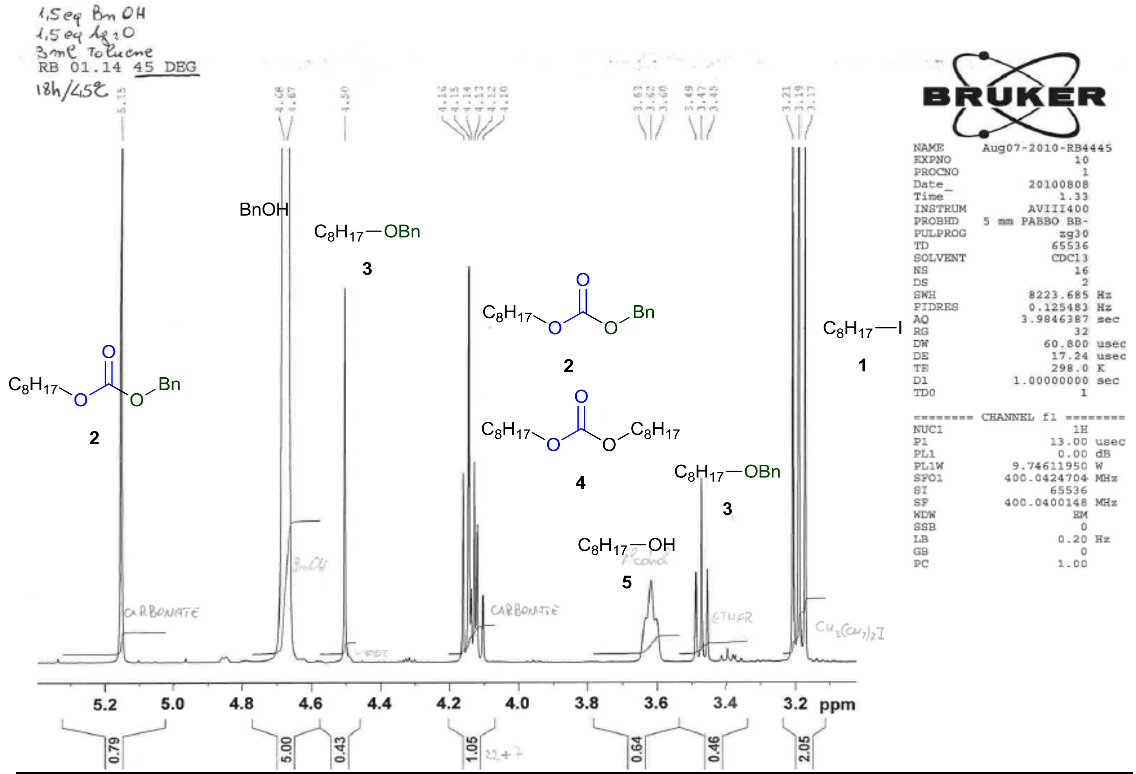


1,5 eq BnOH
1,5eq Ag2O
RB 01.14 R.T.
3ml toluene
18h
room temp.

```
NAME          Aug07-2010-RB4446
EXPNO                        10
PROCNO                        1
Date_                  20100808
Time                       1.39
INSTRUM                AVIII400
PROBHD         5 mm PABBO BB-
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8223.685 Hz
FIDRES                 0.125483 Hz
AQ                    3.9846387 sec
RG                           32
DW                       60.800 usec
DE                        17.24 usec
TE                        298.0 K
D1                   1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        13.00 usec
PL1                        0.00 dB
PL1W                 9.74611950 W
SFO1                400.0424704 MHz
SI                        65536
SF                  400.0400148 MHz
WDW                          EM
SSB                           0
LB                         0.20 Hz
GB                            0
PC                         1.00
```

Table 3, Entry 10

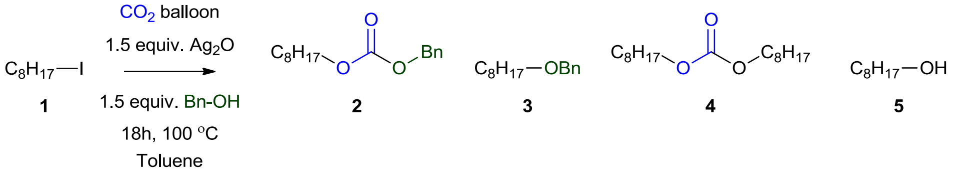


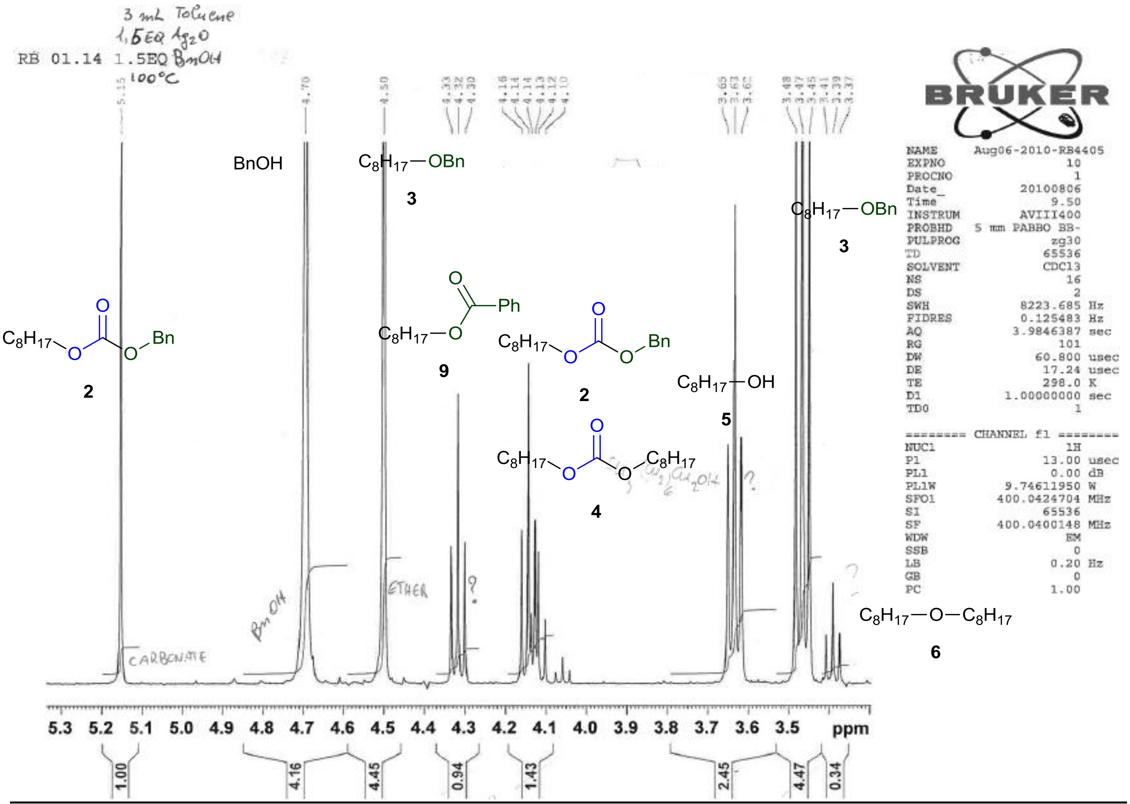


1,5eq BnOH
1,5 eq Ag2O
3ml Toluene
RB 01.14 45 DEG
18h/45C

```
NAME          Aug07-2010-RB4445
EXPNO                        10
PROCNO                        1
Date_                  20100808
Time                       1.33
INSTRUM                AVIII400
PROBHD         5 mm PABBO BB-
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8223.685 Hz
FIDRES                 0.125483 Hz
AQ                    3.9846387 sec
RG                           32
DW                       60.800 usec
DE                        17.24 usec
TE                        298.0 K
D1                   1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        13.00 usec
PL1                        0.00 dB
PL1W                 9.74611950 W
SFO1                400.0424704 MHz
SI                        65536
SF                  400.0400148 MHz
WDW                          EM
SSB                           0
LB                         0.20 Hz
GB                            0
PC                         1.00
```

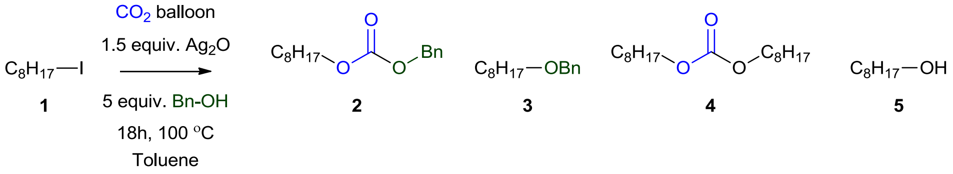
Table 3, Entry 11

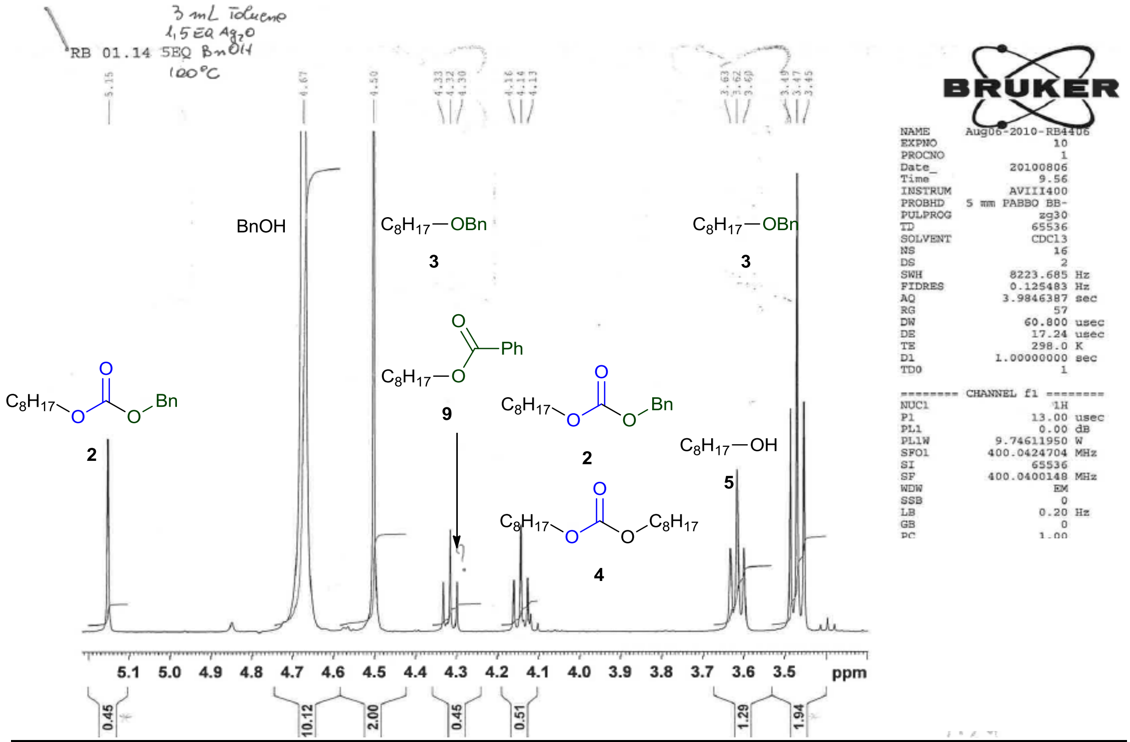




```
NAME        Aug06-2010-RB4405
EXPNO                      10
PROCNO                      1
Date_                20100806
Time                     9.50
INSTRUM              AVIII400
PROBHD   5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                  3.9846387 sec
RG                        101
DW                     60.800 usec
DE                      17.24 usec
TE                      298.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.00 usec
PL1                      0.00 dB
PL1W               9.74611950 W
SFO1              400.0424704 MHz
SI                      65536
SF                400.0400148 MHz
WDW                        EM
SSB                         0
LB                       0.20 Hz
GB                          0
PC                       1.00
```

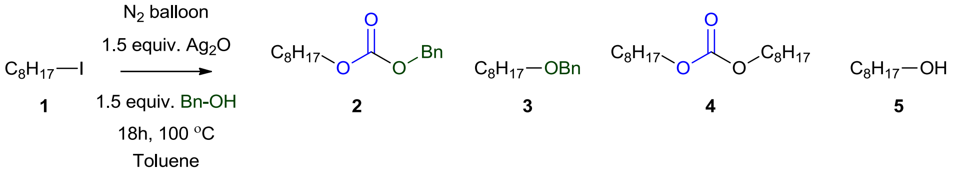
Table 3, Entry 12

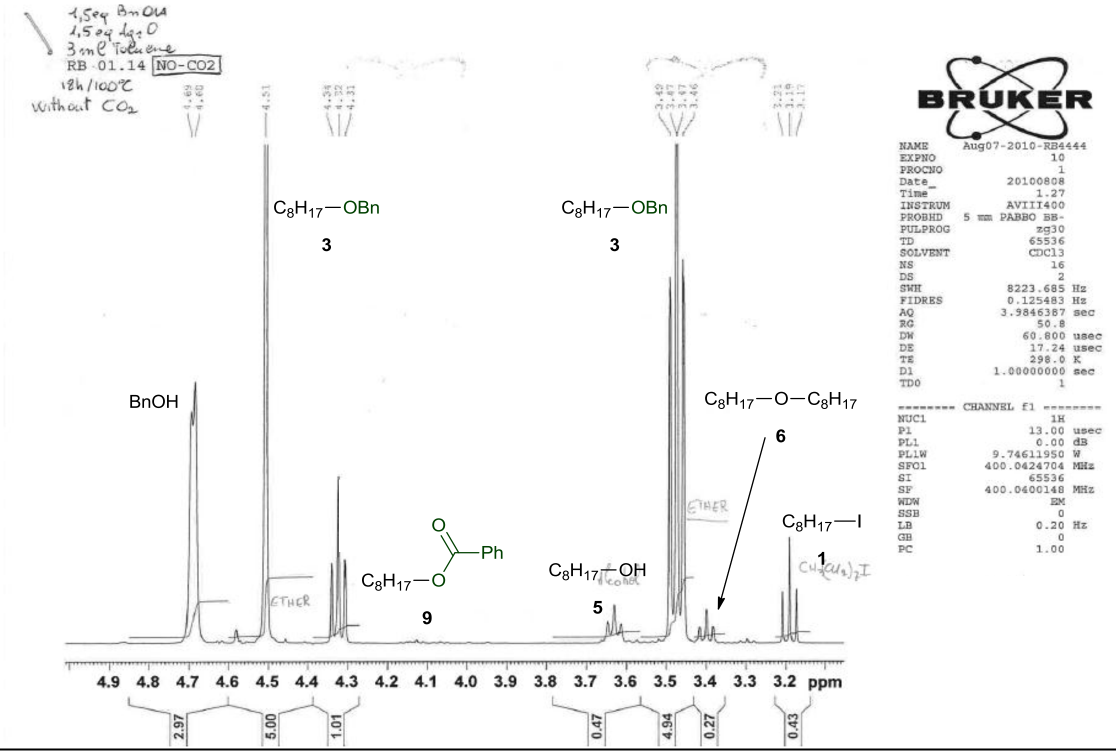




```
NAME        Aug06-2010-RB4406
EXPNO                      10
PROCNO                      1
Date_                20100806
Time                     9.56
INSTRUM              AVIII400
PROBHD   5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                  3.9846387 sec
RG                         57
DW                     60.800 usec
DE                      17.24 usec
TE                      298.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.00 usec
PL1                      0.00 dB
PL1W               9.74611950 W
SFO1              400.0424704 MHz
SI                      65536
SF                400.0400148 MHz
WDW                        EM
SSB                         0
LB                       0.20 Hz
GB                          0
PC                       1.00
```

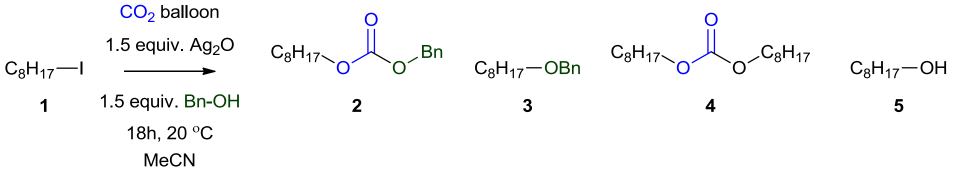
Table 3, Entry 13

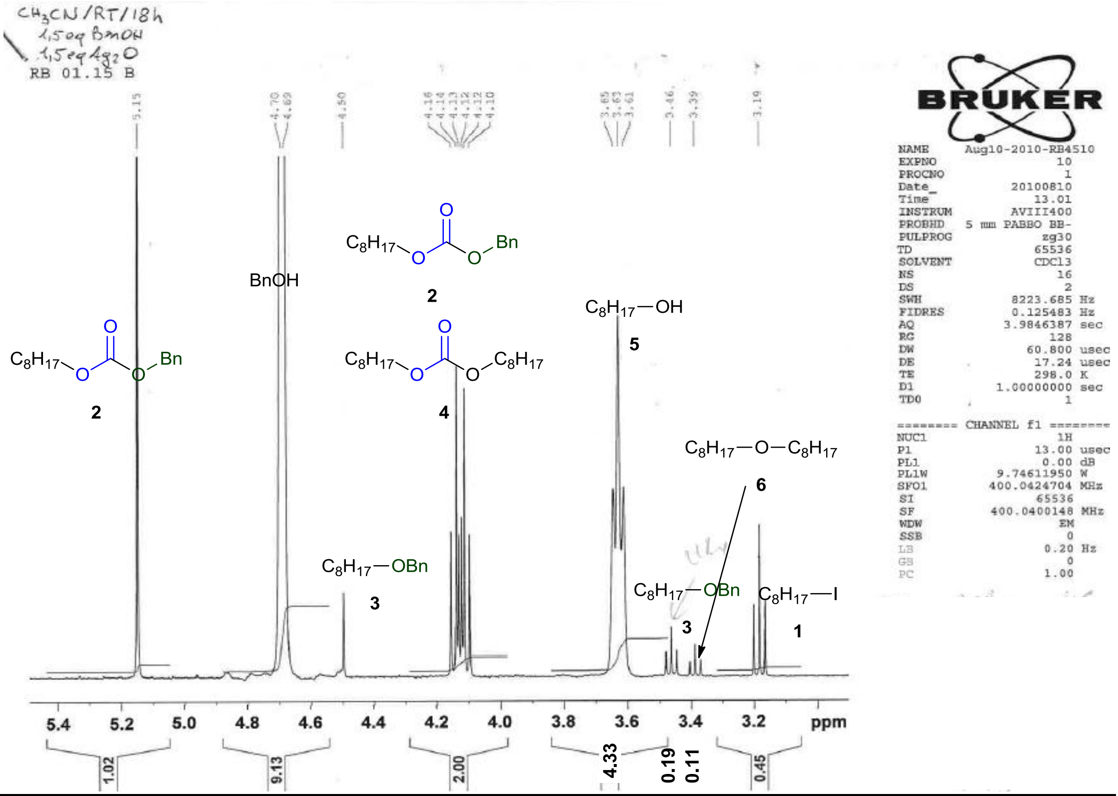




```
NAME       Aug07-2010-RB4444
EXPNO                     10
PROCNO                     1
Date_               20100808
Time                    1.27
INSTRUM             AVIII400
PROBHD      5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                 3.9846387 sec
RG                      50.8
DW                    60.800 usec
DE                     17.24 usec
TE                     298.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.00 usec
PL1                     0.00 dB
PL1W              9.74611950 W
SFO1             400.0424704 MHz
SI                     65536
SF               400.0400148 MHz
WDW                       EM
SSB                        0
LB                      0.20 Hz
GB                         0
PC                      1.00
```

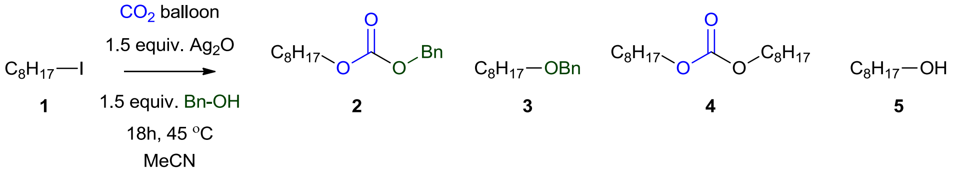
Table 3, Entry 14

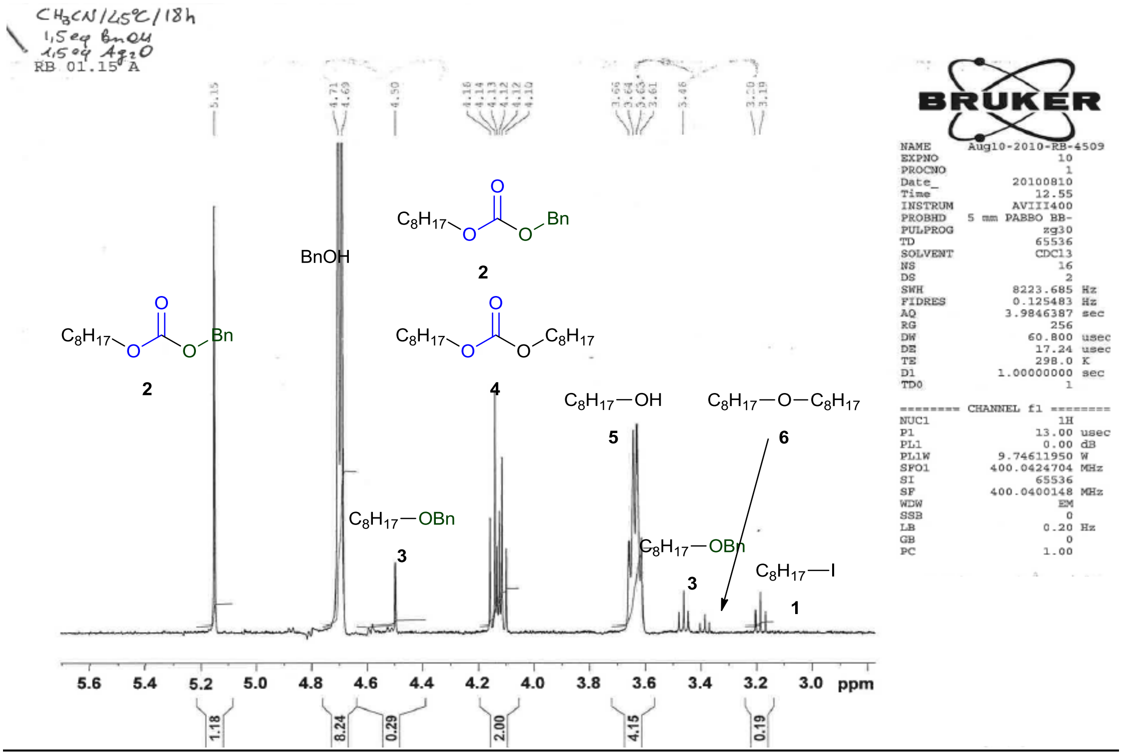




```
NAME       Aug10-2010-RB4510
EXPNO                     10
PROCNO                     1
Date_               20100810
Time                   13.01
INSTRUM             AVIII400
PROBHD      5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                 3.9846387 sec
RG                       128
DW                    60.800 usec
DE                     17.24 usec
TE                     298.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.00 usec
PL1                     0.00 dB
PL1W              9.74611950 W
SFO1             400.0424704 MHz
SI                     65536
SF               400.0400148 MHz
WDW                       EM
SSB                        0
LB                      0.20 Hz
GB                         0
PC                      1.00
```

Table 3, Entry 15

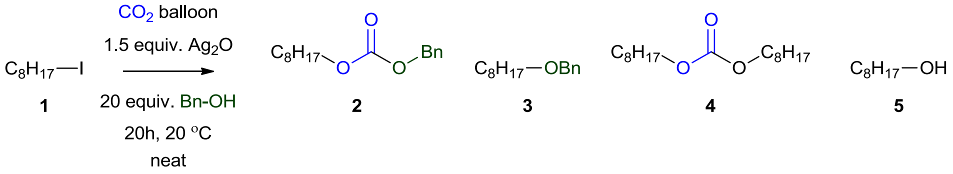


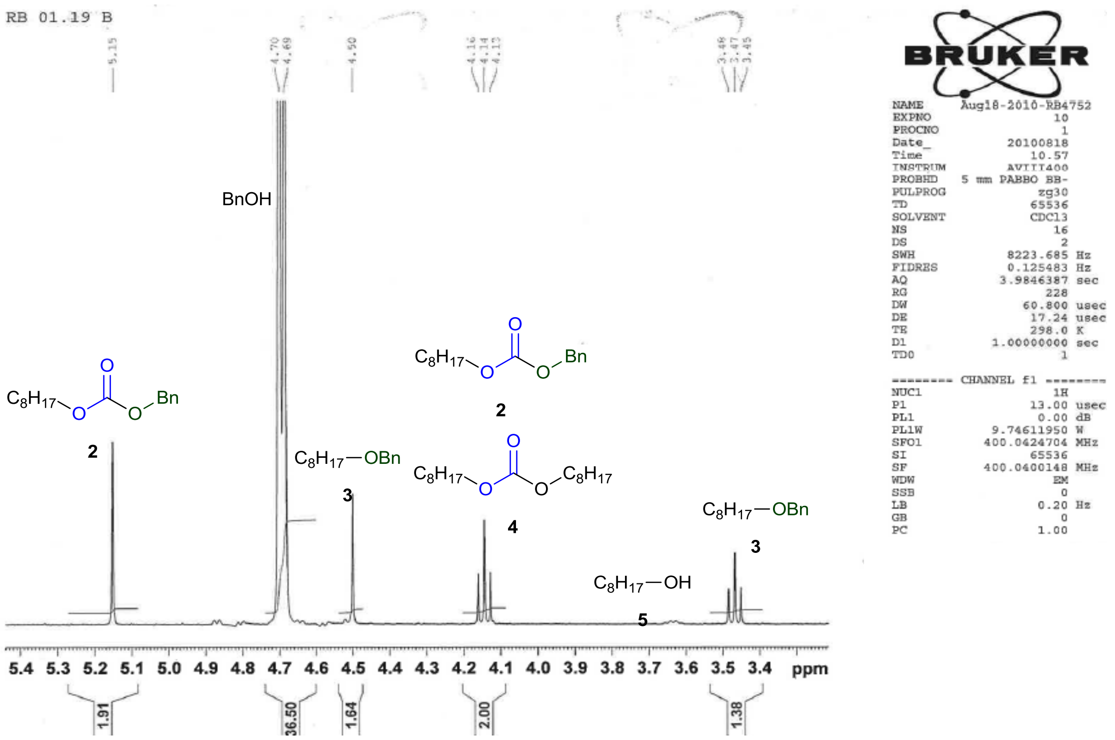


CH_3CN/45°C/18h
1,5eq BnOH
1,5eq Ag_2O

```
NAME        Aug10-2010-RB-4509
EXPNO                      10
PROCNO                      1
Date_                20100810
Time                    12.55
INSTRUM              AVIII400
PROBHD      5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                  3.9846387 sec
RG                        256
DW                     60.800 usec
DE                      17.24 usec
TE                      298.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.00 usec
PL1                      0.00 dB
PL1W               9.74611950 W
SFO1              400.0424704 MHz
SI                      65536
SF                400.0400148 MHz
WDW                        EM
SSB                         0
LB                       0.20 Hz
GB                          0
PC                       1.00
```

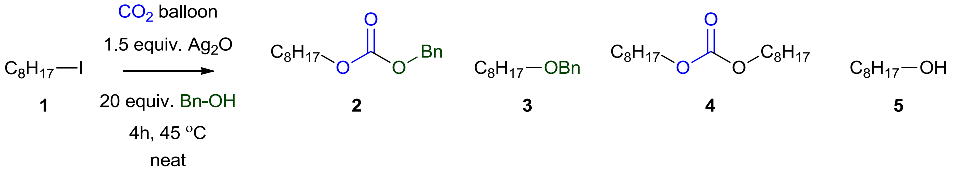
Table 3, Entry 16

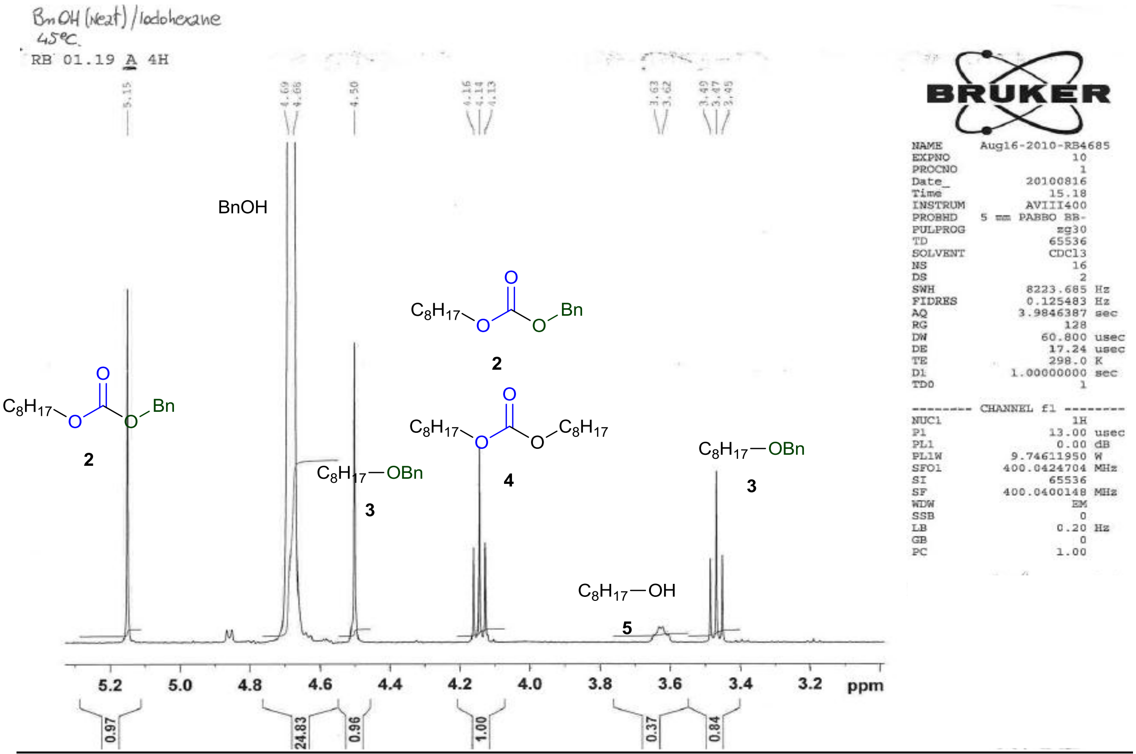




```
NAME        Aug18-2010-RB4752
EXPNO                      10
PROCNO                      1
Date_                20100818
Time                    10.57
INSTRUM              AVIII400
PROBHD      5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                  3.9846387 sec
RG                        228
DW                     60.800 usec
DE                      17.24 usec
TE                      298.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.00 usec
PL1                      0.00 dB
PL1W               9.74611950 W
SFO1              400.0424704 MHz
SI                      65536
SF                400.0400148 MHz
WDW                        EM
SSB                         0
LB                       0.20 Hz
GB                          0
PC                       1.00
```

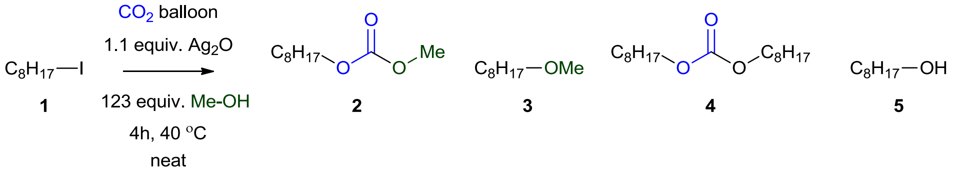
Table 3, Entry 17

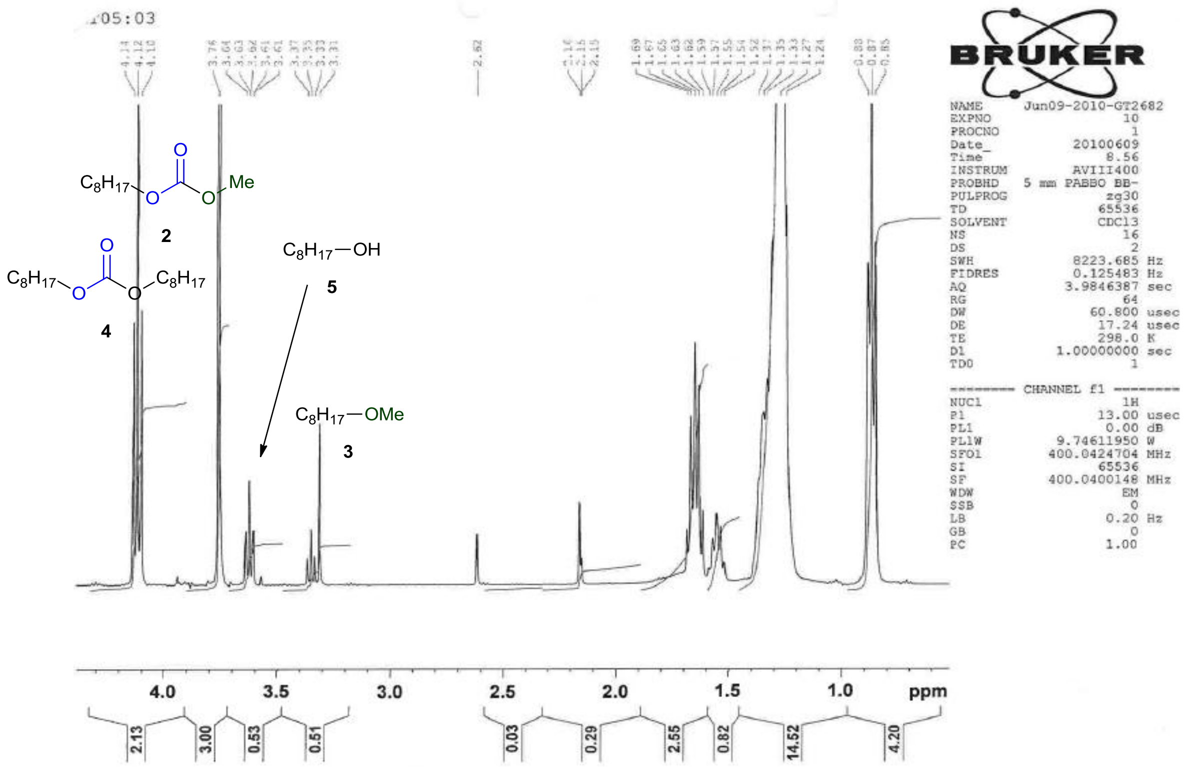



BnOH (Neat) / Iodohexane
45°C.
RB 01.19 A 4H

```
NAME       Aug16-2010-RB4685
EXPNO                     10
PROCNO                     1
Date_               20100816
Time                   15.18
INSTRUM             AVIII400
PROBHD      5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                 3.9846387 sec
RG                       128
DW                    60.800 usec
DE                     17.24 usec
TE                     298.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.00 usec
PL1                     0.00 dB
PL1W              9.74611950 W
SFO1             400.0424704 MHz
SI                     65536
SF               400.0400148 MHz
WDW                       EM
SSB                        0
LB                      0.20 Hz
GB                         0
PC                      1.00
```

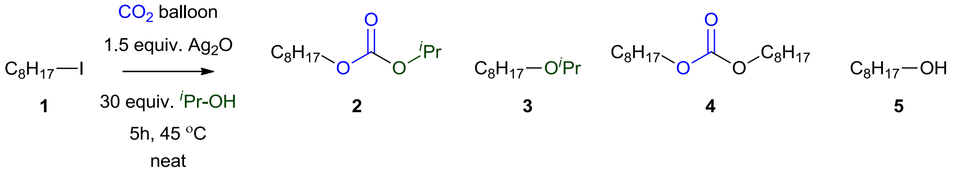
Table 3, Entry 18




:05:03

```
NAME       Jun09-2010-GT2682
EXPNO                     10
PROCNO                     1
Date_               20100609
Time                    8.56
INSTRUM             AVIII400
PROBHD      5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                 3.9846387 sec
RG                        64
DW                    60.800 usec
DE                     17.24 usec
TE                     298.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.00 usec
PL1                     0.00 dB
PL1W              9.74611950 W
SFO1             400.0424704 MHz
SI                     65536
SF               400.0400148 MHz
WDW                       EM
SSB                        0
LB                      0.20 Hz
GB                         0
PC                      1.00
```

Table 3, Entry 19



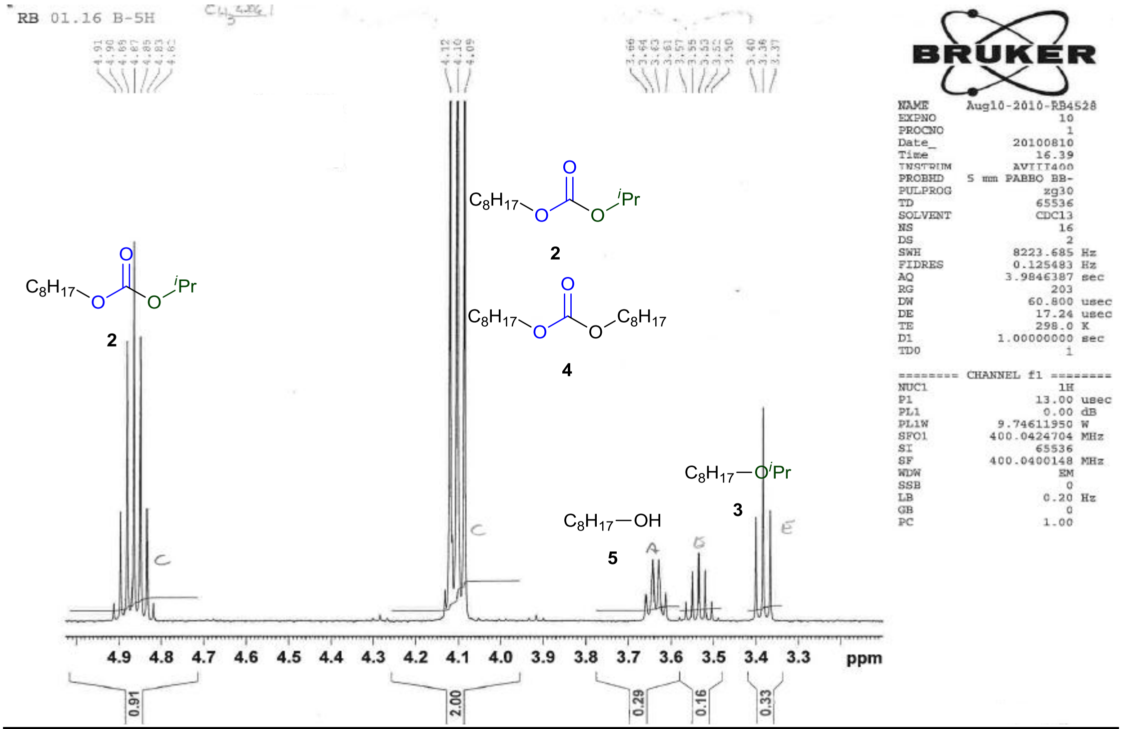
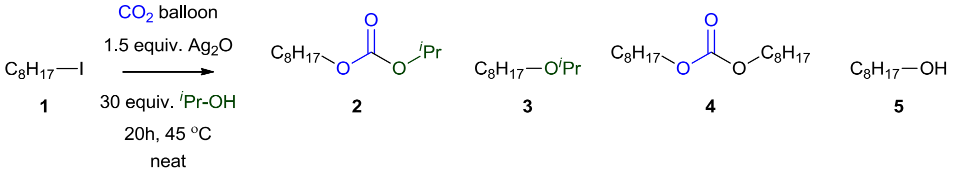


Table 3, Entry 20



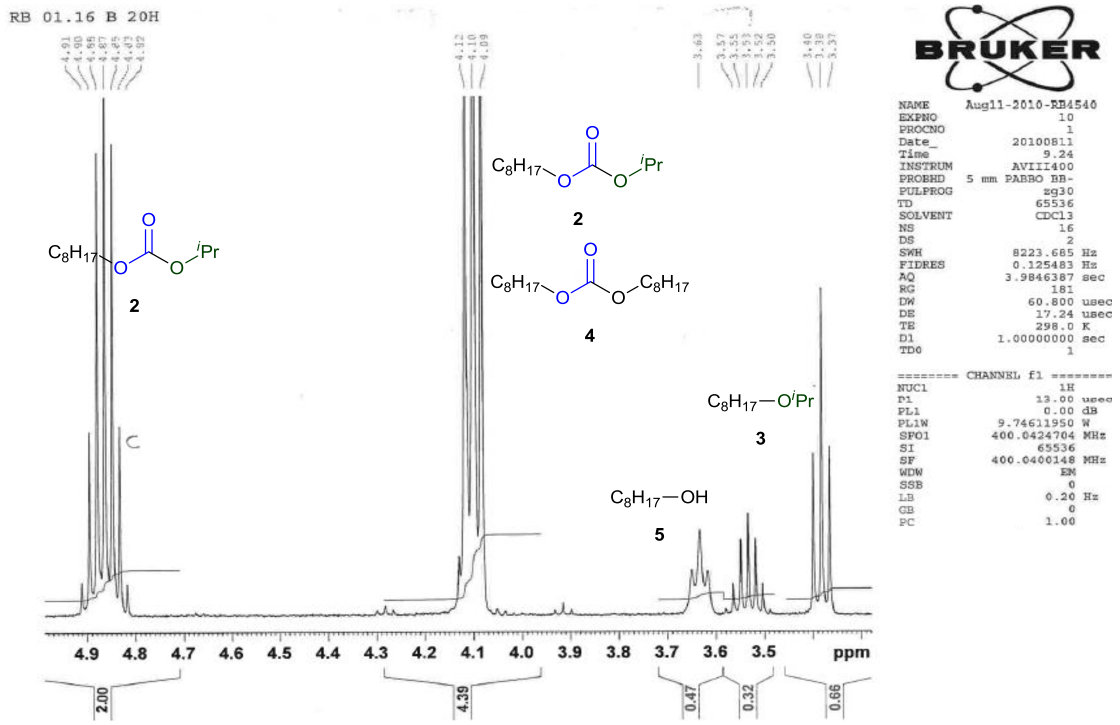
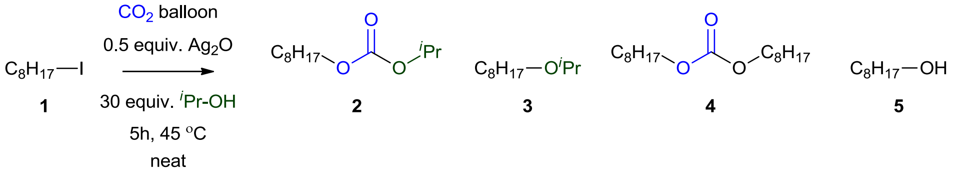
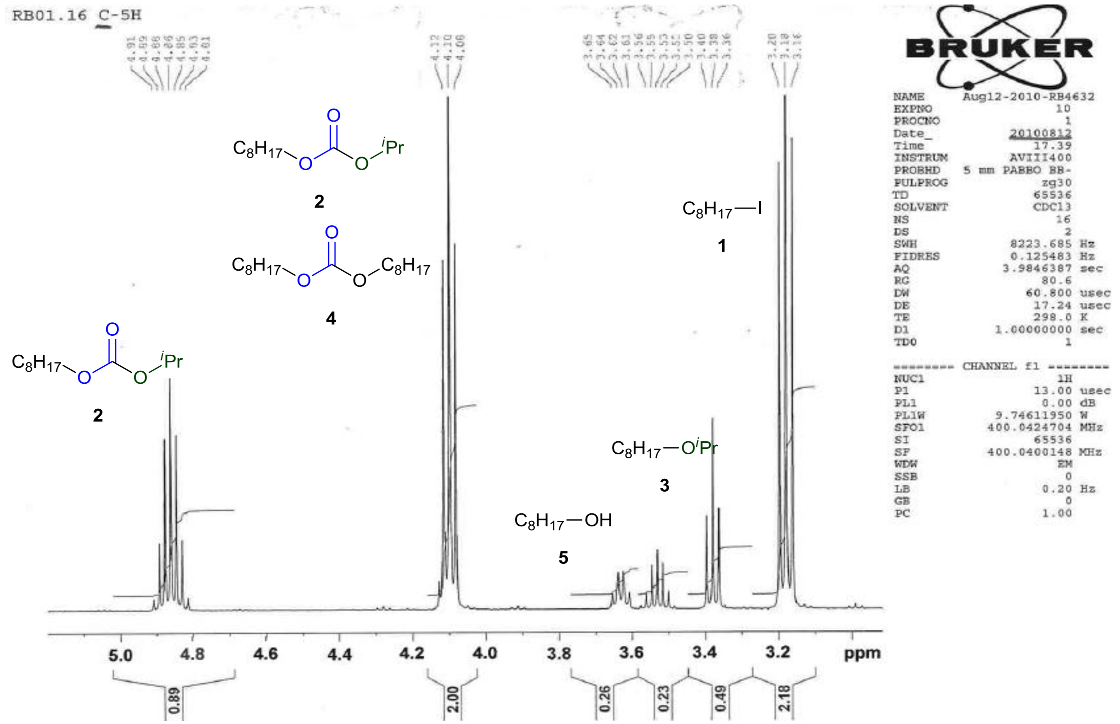


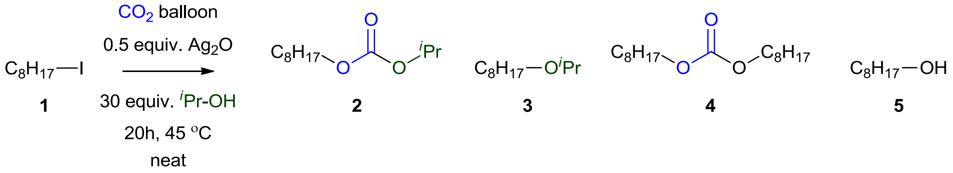
Table 3, Entry 21



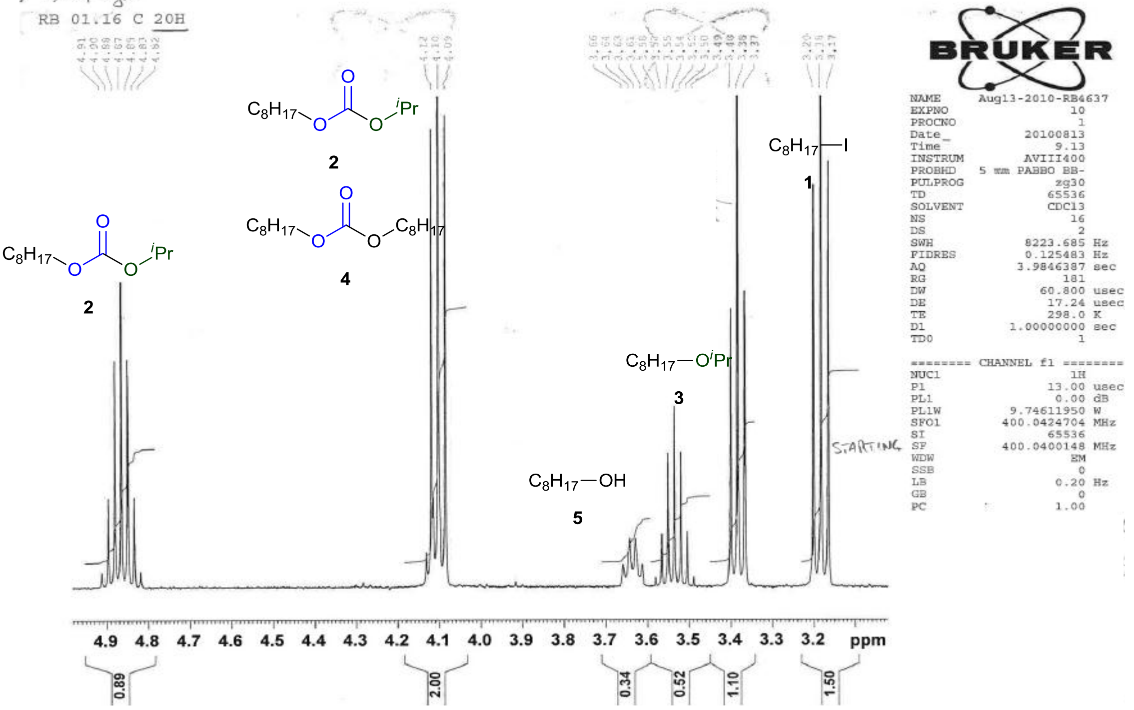


```
NAME        Aug12-2010-RB4632
EXPNO                      10
PROCNO                      1
Date_                20100812
Time                    17.39
INSTRUM              AVIII400
PROBHD       5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                  3.9846387 sec
RG                       80.6
DW                     60.800 usec
DE                      17.24 usec
TE                      298.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.00 usec
PL1                      0.00 dB
PL1W               9.74611950 W
SFO1              400.0424704 MHz
SI                      65536
SF                400.0400148 MHz
WDW                        EM
SSB                         0
LB                       0.20 Hz
GB                          0
PC                       1.00
```

Table 3, Entry 22

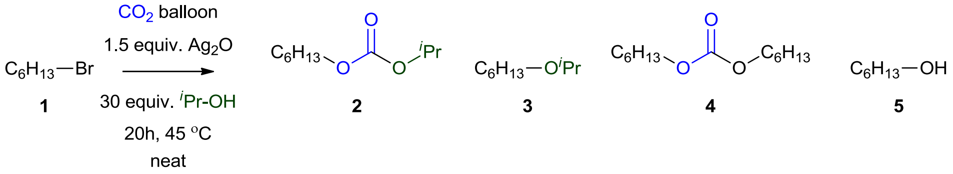


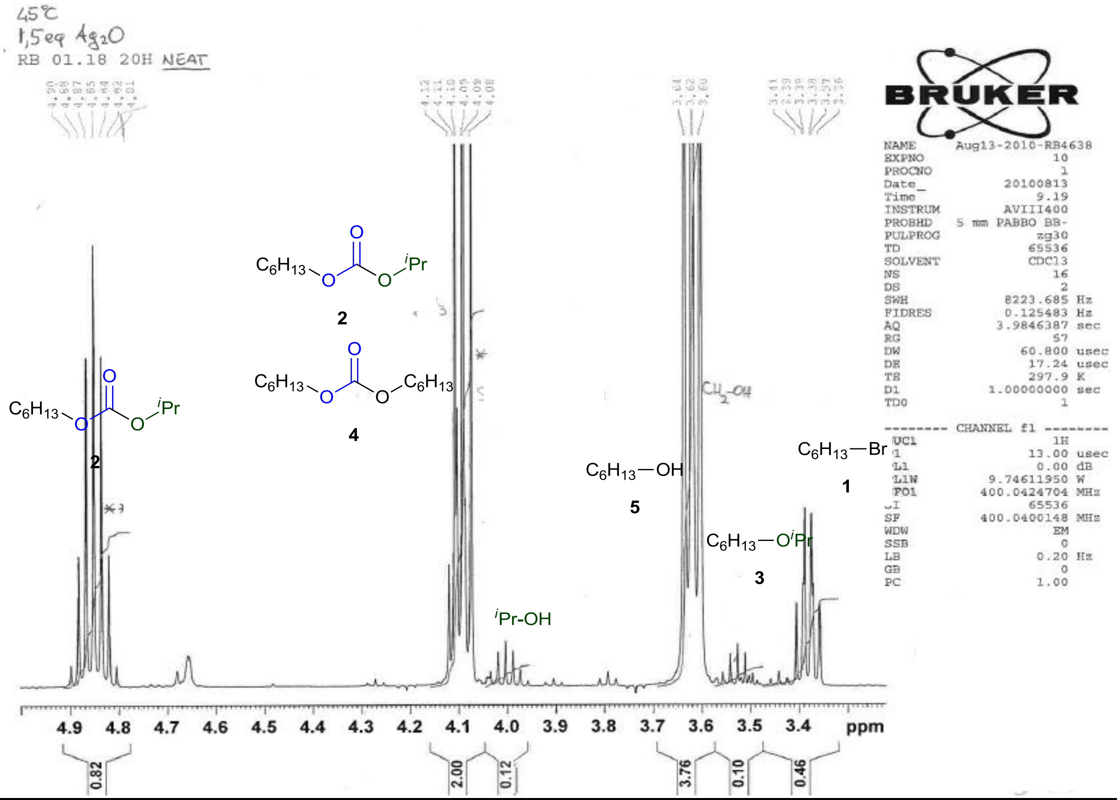
45°C NEAT
0,5 eq Ag_2O



```
NAME        Aug13-2010-RB4637
EXPNO                      10
PROCNO                      1
Date_                20100813
Time                     9.13
INSTRUM              AVIII400
PROBHD       5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                  3.9846387 sec
RG                        181
DW                     60.800 usec
DE                      17.24 usec
TE                      298.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.00 usec
PL1                      0.00 dB
PL1W               9.74611950 W
SFO1              400.0424704 MHz
SI                      65536
SF                400.0400148 MHz
WDW                        EM
SSB                         0
LB                       0.20 Hz
GB                          0
PC                       1.00
```

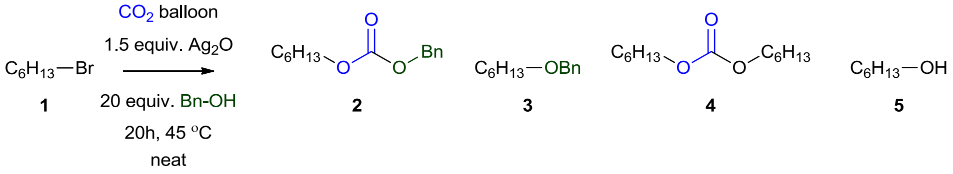
Table 3, Entry 23

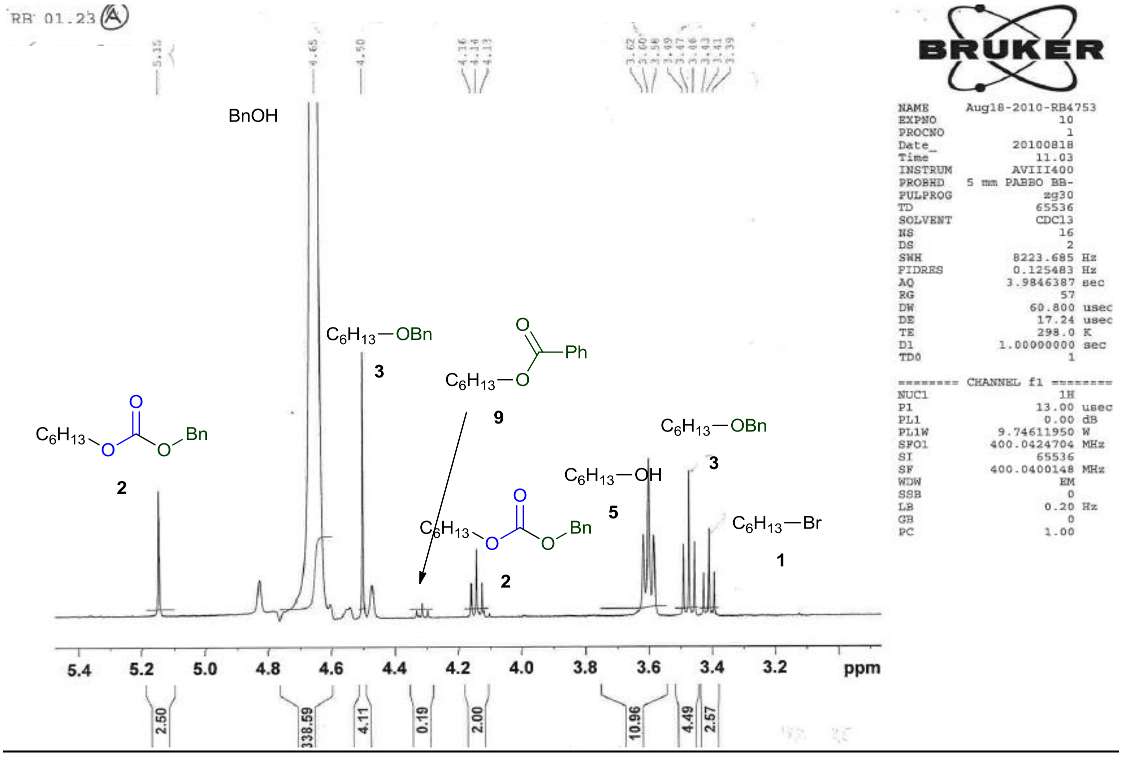




```
NAME       Aug13-2010-RB4638
EXPNO                     10
PROCNO                     1
Date_               20100813
Time                    9.19
INSTRUM             AVIII400
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                 3.9846387 sec
RG                        57
DW                    60.800 usec
DE                     17.24 usec
TE                     297.9 K
D1                1.00000000 sec
TD0                        1

-------- CHANNEL f1 --------
UC1                       1H
1                      13.00 usec
L1                      0.00 dB
L1W               9.74611950 W
FO1              400.0424704 MHz
I                      65536
SF               400.0400148 MHz
WDW                       EM
SSB                        0
LB                      0.20 Hz
GB                         0
PC                      1.00
```

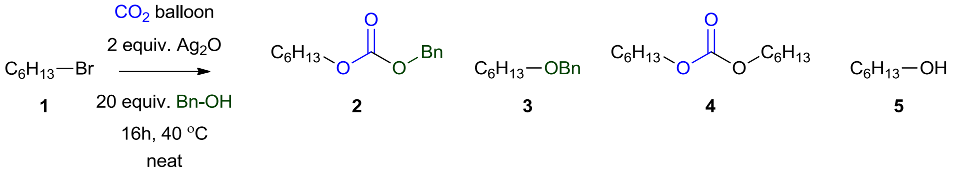
Table 3, Entry 24





```
NAME       Aug18-2010-RB4753
EXPNO                     10
PROCNO                     1
Date_               20100818
Time                   11.03
INSTRUM             AVIII400
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                 3.9846387 sec
RG                        57
DW                    60.800 usec
DE                     17.24 usec
TE                     298.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.00 usec
PL1                     0.00 dB
PL1W              9.74611950 W
SFO1             400.0424704 MHz
SI                     65536
SF               400.0400148 MHz
WDW                       EM
SSB                        0
LB                      0.20 Hz
GB                         0
PC                      1.00
```

Table 3, Entry 25



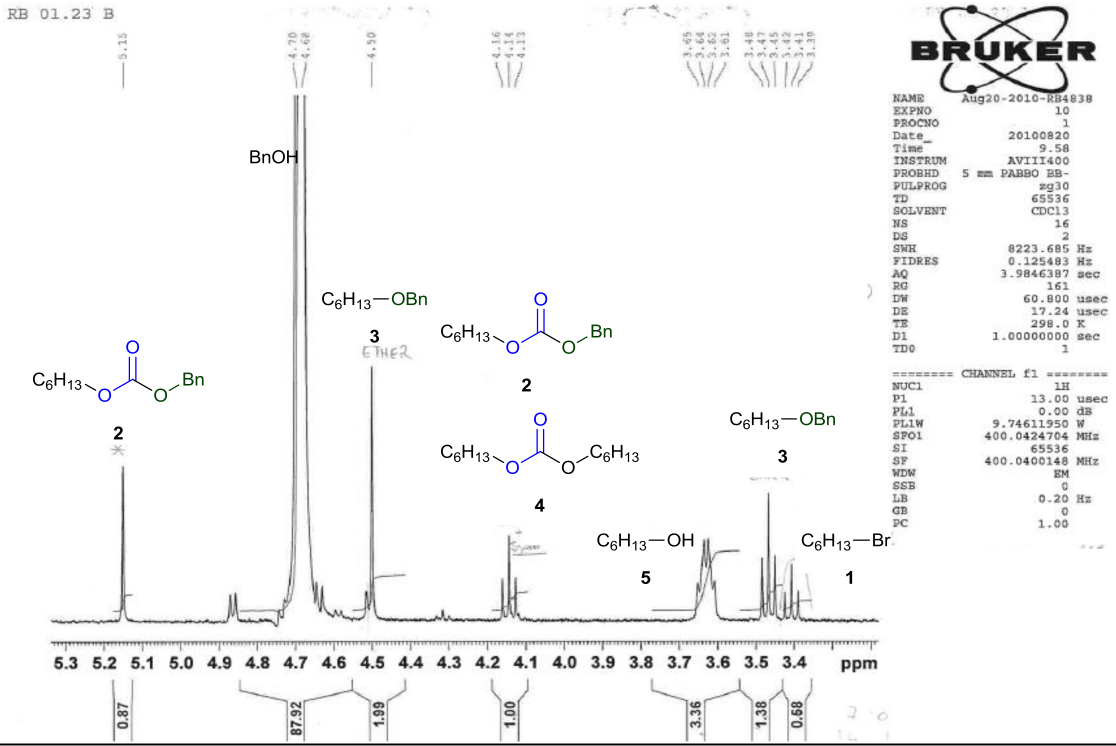
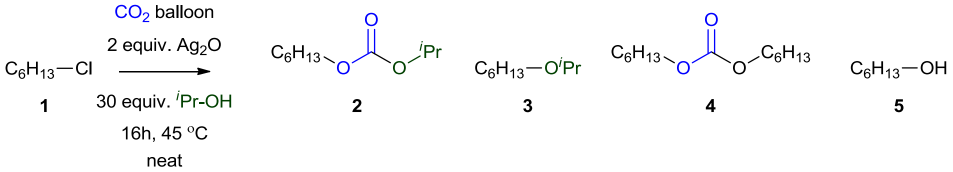


Table 3, Entry 26



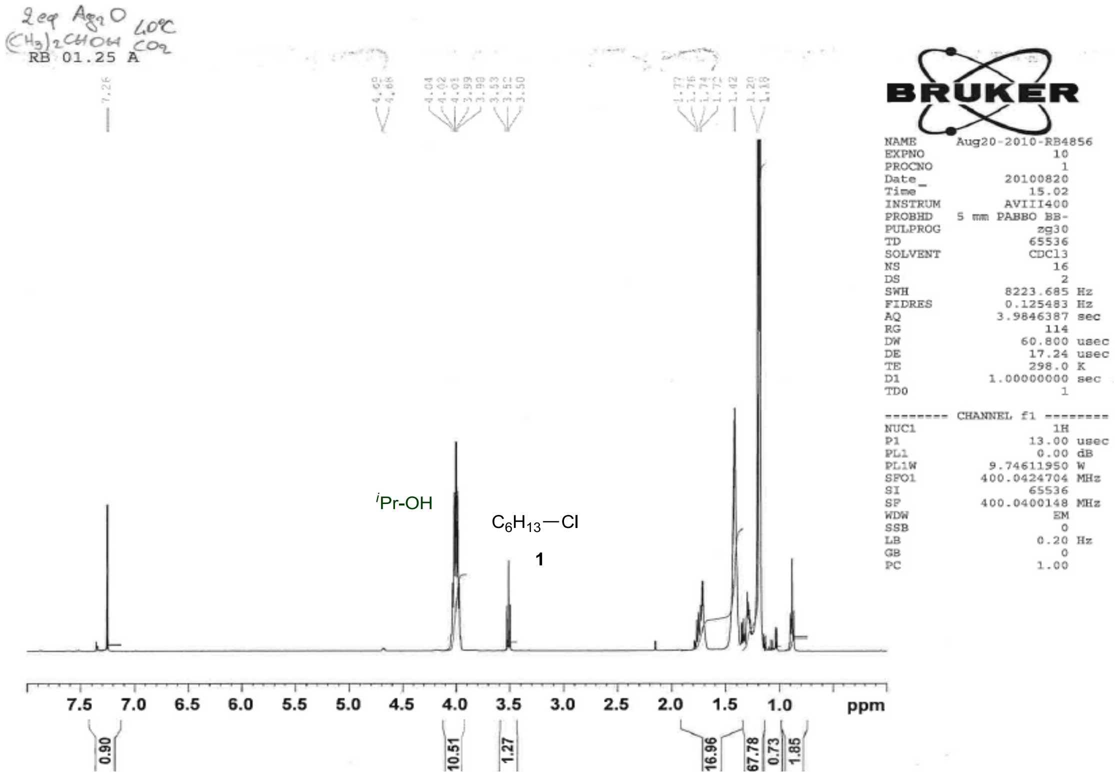
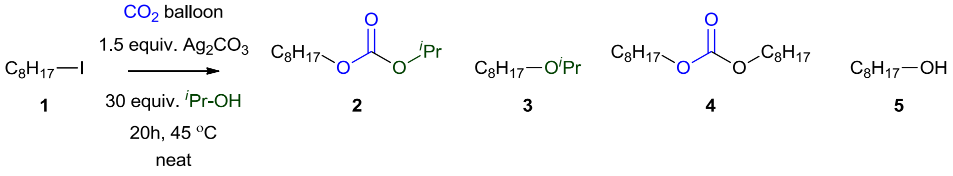


Table 3, Entry 27



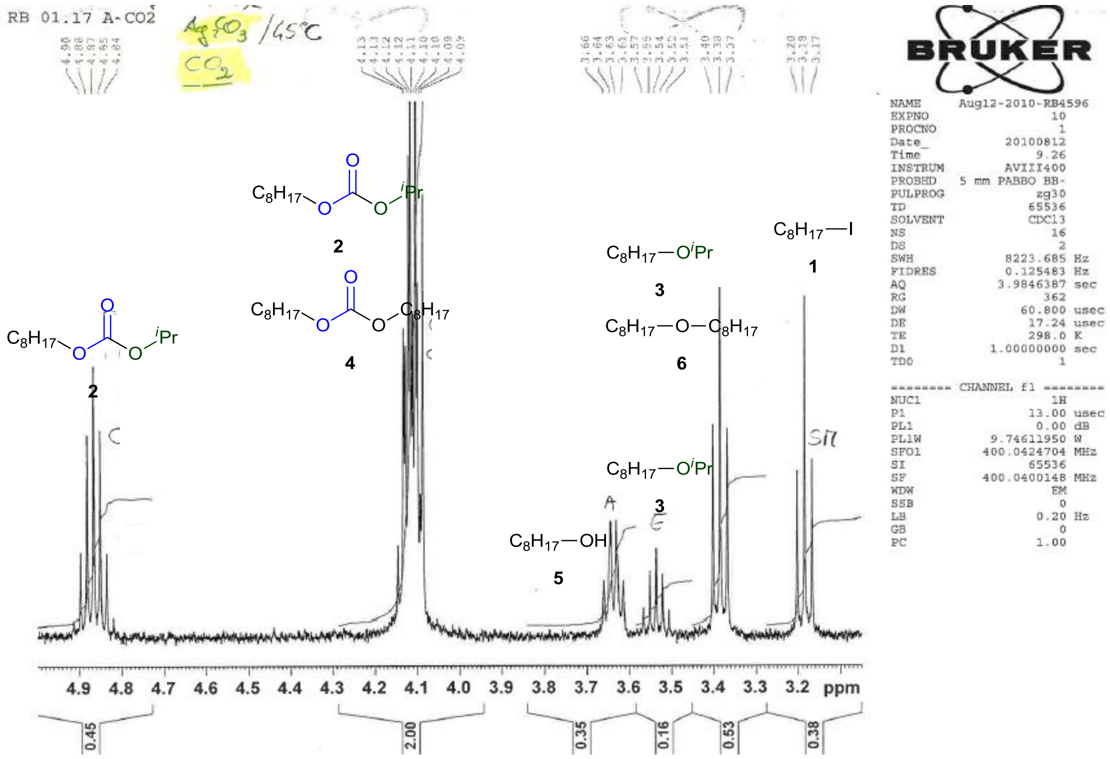
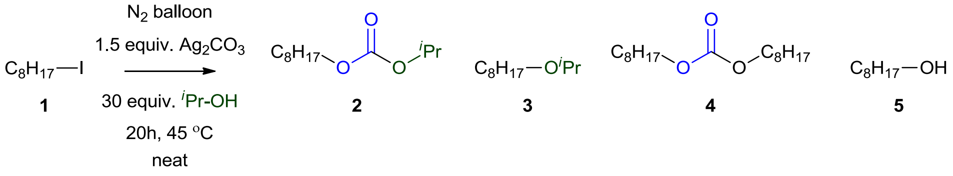


Table 3, Entry 28



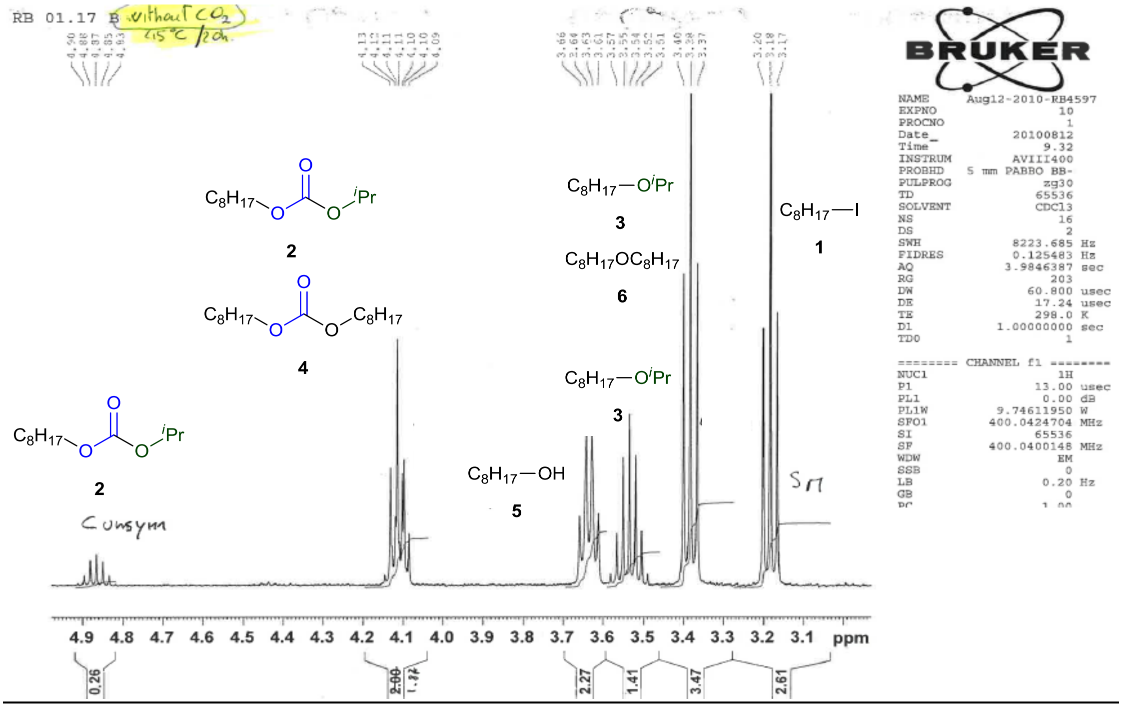
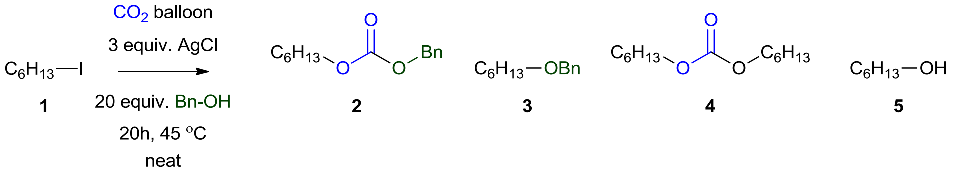
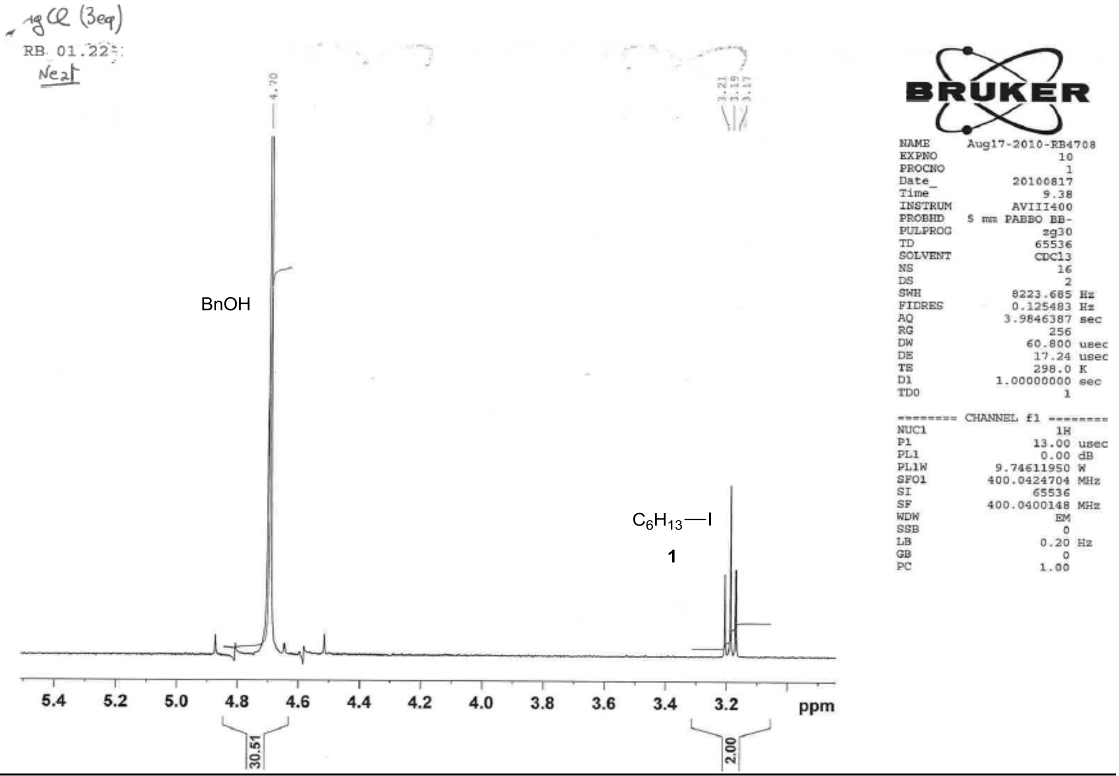


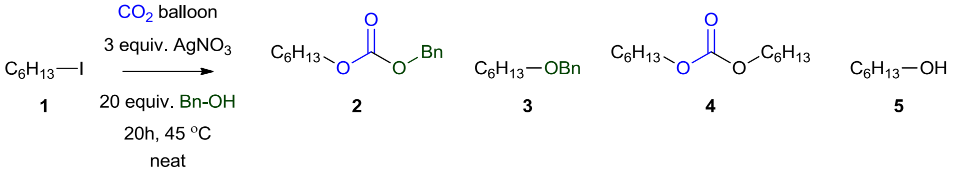
Table 3, Entry 29

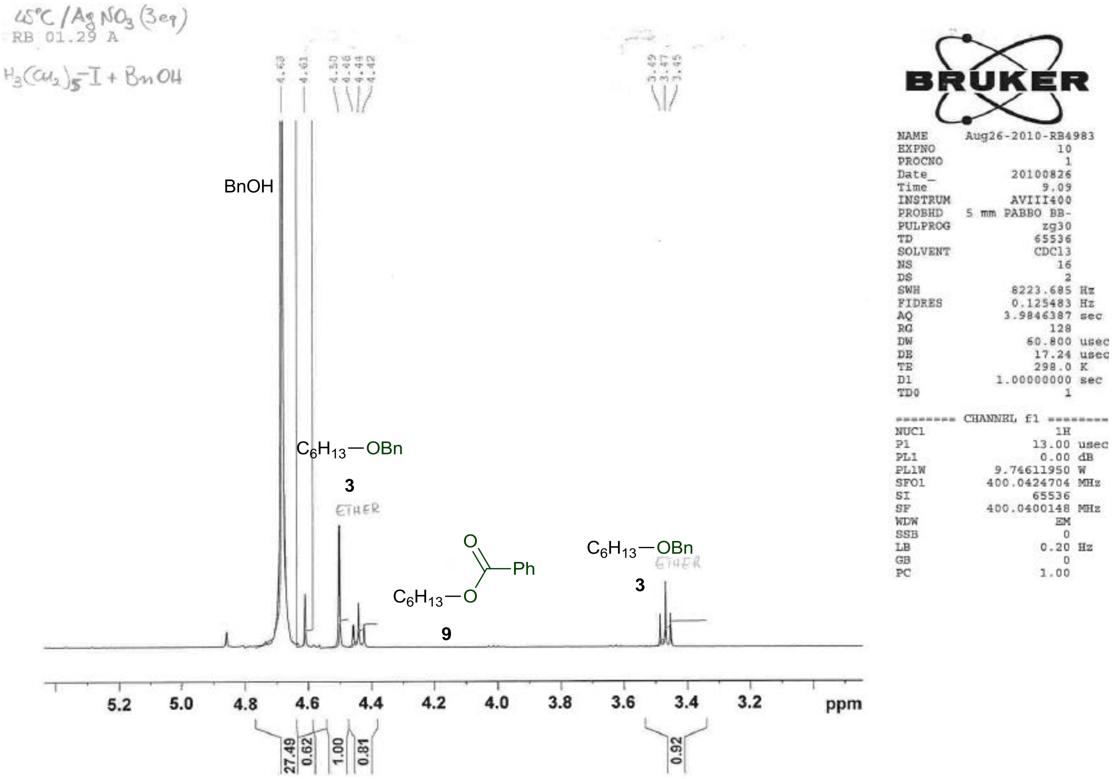




```
NAME        Aug17-2010-RB4708
EXPNO                      10
PROCNO                      1
Date_                20100817
Time                     9.38
INSTRUM              AVIII400
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                  3.9846387 sec
RG                        256
DW                     60.800 usec
DE                      17.24 usec
TE                      298.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.00 usec
PL1                      0.00 dB
PL1W               9.74611950 W
SFO1              400.0424704 MHz
SI                      65536
SF                400.0400148 MHz
WDW                        EM
SSB                         0
LB                       0.20 Hz
GB                          0
PC                       1.00
```

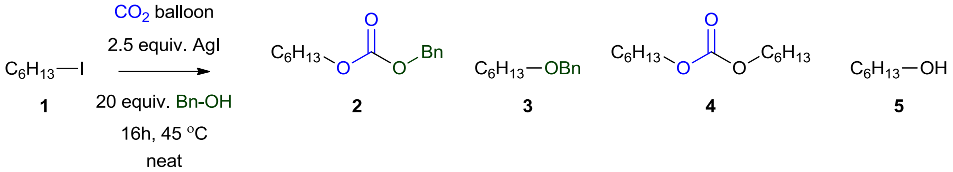
Table 3, Entry 30

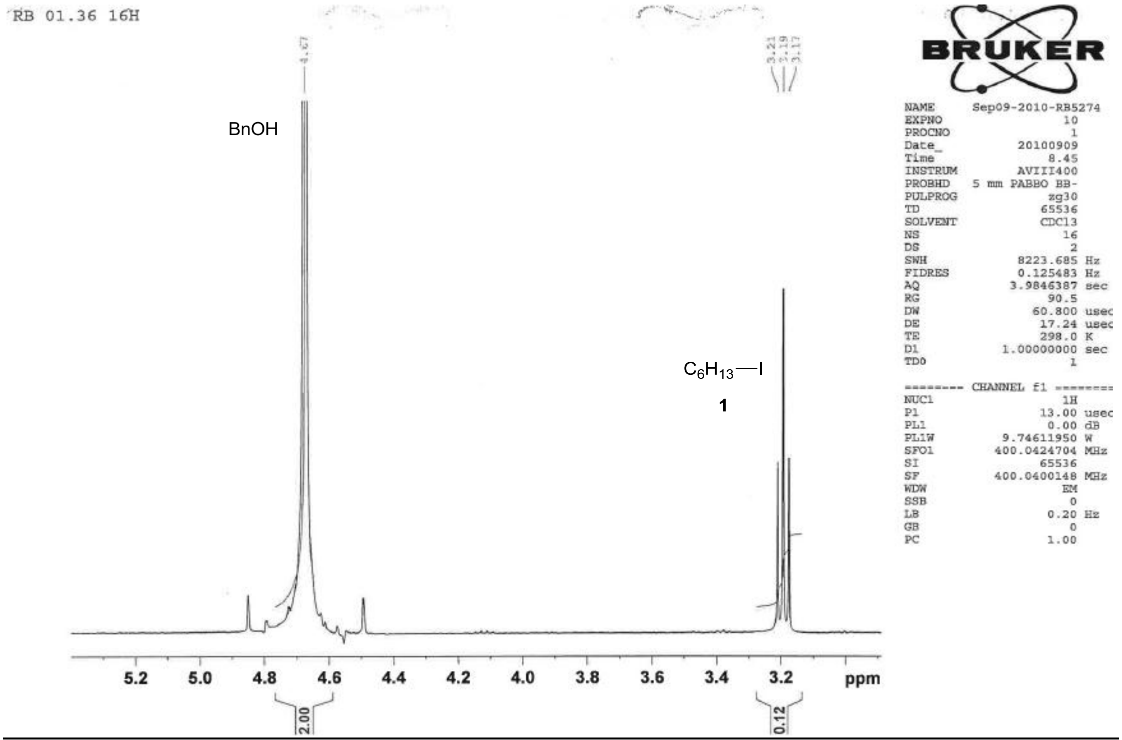




```
NAME        Aug26-2010-RB4983
EXPNO                      10
PROCNO                      1
Date_                20100826
Time                     9.09
INSTRUM              AVIII400
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                  3.9846387 sec
RG                        128
DW                     60.800 usec
DE                      17.24 usec
TE                      298.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.00 usec
PL1                      0.00 dB
PL1W               9.74611950 W
SFO1              400.0424704 MHz
SI                      65536
SF                400.0400148 MHz
WDW                        EM
SSB                         0
LB                       0.20 Hz
GB                          0
PC                       1.00
```

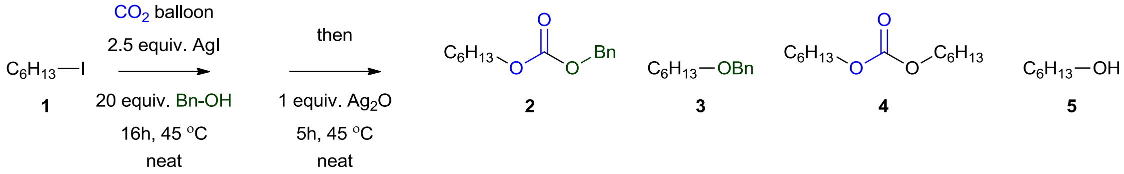
Table 3, Entry 31

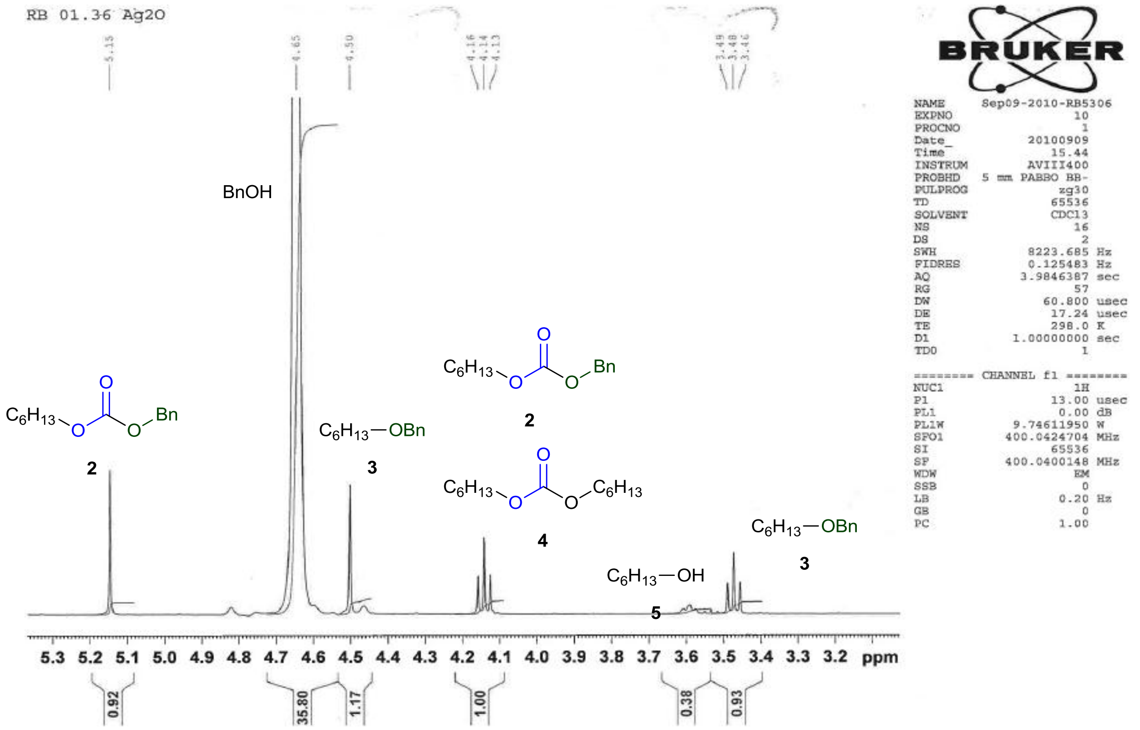




```
NAME       Sep09-2010-RB5274
EXPNO                     10
PROCNO                     1
Date_               20100909
Time                    8.45
INSTRUM             AVIII400
PROBHD      5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                 3.9846387 sec
RG                      90.5
DW                    60.800 usec
DE                     17.24 usec
TE                     298.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.00 usec
PL1                     0.00 dB
PL1W              9.74611950 W
SFO1             400.0424704 MHz
SI                     65536
SF               400.0400148 MHz
WDW                       EM
SSB                        0
LB                      0.20 Hz
GB                         0
PC                      1.00
```

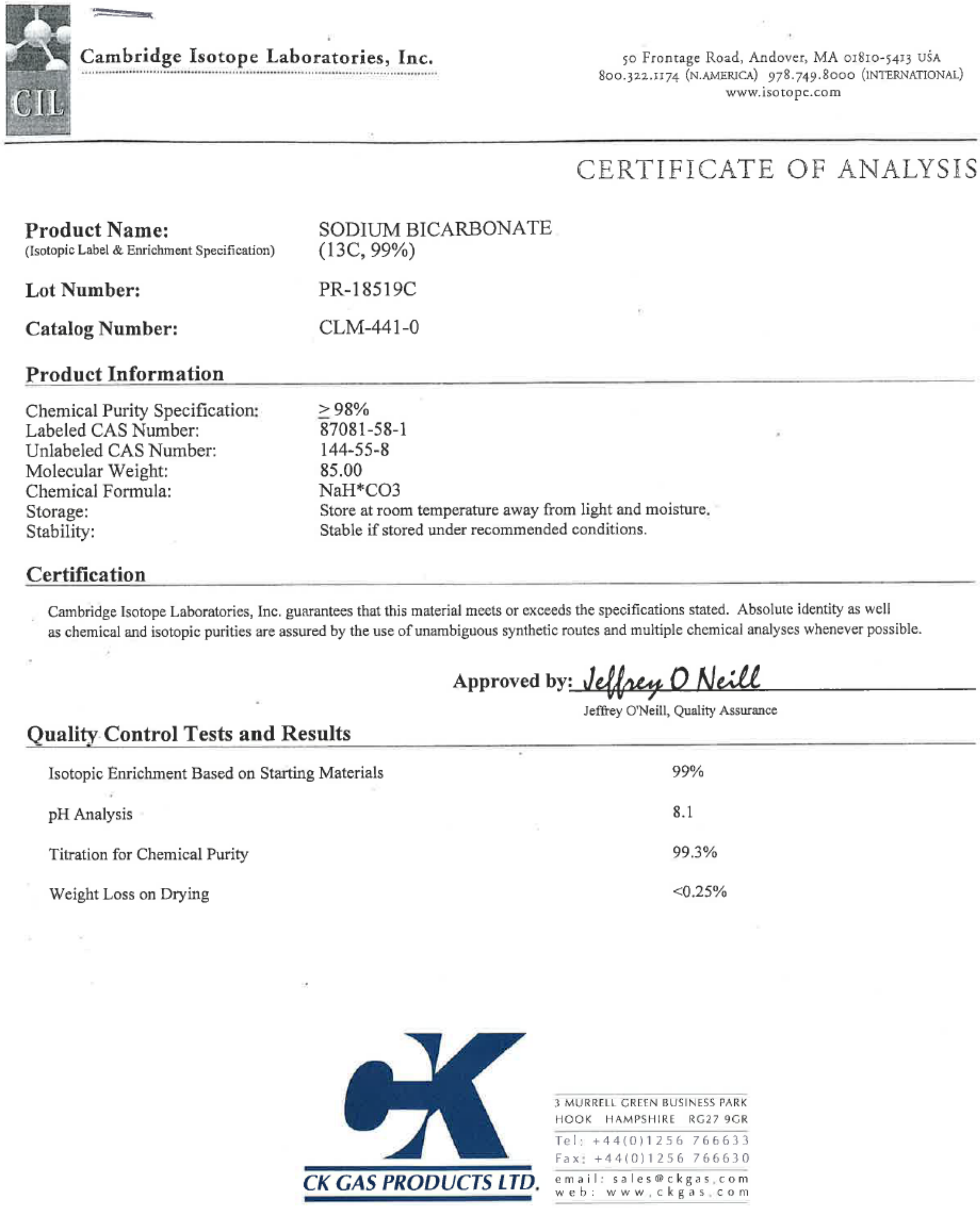
Table 3, Entry 31 – continued





```
NAME       Sep09-2010-RB5306
EXPNO                     10
PROCNO                     1
Date_               20100909
Time                   15.44
INSTRUM             AVIII400
PROBHD      5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                 3.9846387 sec
RG                        57
DW                    60.800 usec
DE                     17.24 usec
TE                     298.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.00 usec
PL1                     0.00 dB
PL1W              9.74611950 W
SFO1             400.0424704 MHz
SI                     65536
SF               400.0400148 MHz
WDW                       EM
SSB                        0
LB                      0.20 Hz
GB                         0
PC                      1.00
```

Certificate of Analysis of $NaH^{13}CO_3$



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www.isotopc.com

CERTIFICATE OF ANALYSIS

Product Name: (Isotopic Label & Enrichment Specification)	SODIUM BICARBONATE (13C, 99%)
Lot Number:	PR-18519C
Catalog Number:	CLM-441-0

Product Information

Chemical Purity Specification:	≥ 98%
Labeled CAS Number:	87081-58-1
Unlabeled CAS Number:	144-55-8
Molecular Weight:	85.00
Chemical Formula:	NaH*CO3
Storage:	Store at room temperature away from light and moisture.
Stability:	Stable if stored under recommended conditions.

Certification

Cambridge Isotope Laboratories, Inc. guarantees that this material meets or exceeds the specifications stated. Absolute identity as well as chemical and isotopic purities are assured by the use of unambiguous synthetic routes and multiple chemical analyses whenever possible.

Approved by: Jeffrey O Neill

Jeffrey O'Neill, Quality Assurance

Quality Control Tests and Results

Isotopic Enrichment Based on Starting Materials	99%
pH Analysis	8.1
Titration for Chemical Purity	99.3%
Weight Loss on Drying	<0.25%

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