–Supporting Information for–

Polarity Reversal Catalysis in Radical Reductions of Halides by N-Heterocyclic Carbene Boranes

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Table of Contents

General Remarks: All reagents were purchased commercially and used without further purification unless stated otherwise. Reaction mixtures were stirred with a magnetic stirrer and reaction progress was monitored by TLC with 0.25 mm E. Merck precoated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040–0.063 mm) supplied by Sorbent Technologies or by CombiFlash system (Teledyne ISCO). NMR spectra were taken on a Bruker WH-300, a Bruker AvanceTM 400 NMR, and a Bruker AvanceTM 500 NMR spectrometer. Spectra were recorded at room temperature in the indicated deuteriated solvents, and chemical shifts were reported in parts per million (ppm) downfield relative to TMS using the residual solvent proton resonance of $CDCl_3$ (^1H = 7.27 ppm, ^{13}C =77.0 ppm) or C_6D_6 (^1H = 7.16 ppm, ^{13}C =128.0 ppm) as the internal standard. The ^{11}B chemical shift are given relative to BF_3•OEt_2 (^{11}B = 0 ppm). In reporting spectral data, the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets. The resonances of hydrogen atoms connected to the boron atom are not usually observed in ^1H NMR spectra because of quadrupole broadening.[1] Infrared spectra were taken on a Mattson Genesis Series FTIR using thin film on NaCl plate. Peaks are reported in wave numbers (cm^{-1}). High resolution mass spectra (HRMS) were obtained on a Q-Tof Ultima API, Micromass UK Limited instrument by electrospray ionization (ESI).

Compounds **1**[2], **6**[3], **8a**[4], **8b**[4], **10a**[5], **10b**[6], **14a**[7], **19**[8], **21**,[19] **23a**[9], **23b**[10] have been prepared according to the literature procedures. Their spectroscopic data were consistent with those previous reported.

Caution: Radical initiators (AIBN, DTBP, TBHN) are high energy compounds that should be handled with appropriate precautions.

Experimental Procedures and Compound Characterization:

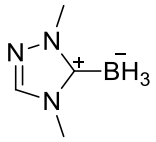
General Procedure for Triethylborane-initiated Free Radical Reactions: Triethylborane (1 M solution in hexane, 0.05 mmol) was added to a solution of diMe-Imd-BH_3 **1** (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.45 mL). Thiophenol or *tert*-dodecanethiol (11.0 mg, 0.1 mmol or 20.2 mg, 0.1 mmol) was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and triethylborane. The septum was pierced with a needle to admit ambient air. The colorless solution was stirred for 1-5 h. Then the solvent was evaporated and the crude product was purified by flash column chromatography.

General Procedure for TBHN-initiated Free Radical Reactions: TBHN (3.5 mg, 0.02 mmol) was added to a solution of diMe-Imd-BH_3 **1** (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.45 mL). Thiophenol or *tert*-dodecanethiol (11.0 mg, 0.1 mmol or 20.2 mg, 0.1 mmol) was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and TBHN. The colorless solution was charged to a sealed tube and heated in oil bath at 80 °C for 2 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography.

General Procedure for DTBP-initiated Free Radical Reactions: DTBP (2.9 mg, 0.02 mmol) was added to a solution of diMe-Imd-BH_3 **1** (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.45 mL). Thiophenol or *tert*-dodecanethiol (11.0 mg, 0.1 mmol or 20.2 mg, 0.1 mmol)

was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and DTBP. The colorless solution was charged to a NMR tube and irradiated with GE-275W sunlamp at 60 °C for 1-7 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography.

General Procedure for Free Radical Reactions with DiMe-Tri-BH_3, 2: TBHN (3.5 mg, 0.02 mmol) was added to a solution of diMe-Tri-BH_3 **2** (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.45 mL). Thiophenol (11.0 mg, 0.1 mmol) was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and TBHN. The colorless solution was charged to a sealed tube and heated in oil bath at 80 °C for 2 h. The mixture was cooled to room temperature, then ether and water (20 mL, respectively) were added to the mixture, and the organic layer was extracted with water (2 × 20 mL). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in *vacuo* to get the product.



2,4-Dimethyl-1,2,4-triazol-3-ylideneborane (diMe-Tri-BH_3, 2): The preparation this compound followed literature procedures[11] with some revisions: A mixture of 1,2,4-triazole (10.0 g, 0.145 mol), iodomethane (61.8 g, 0.435 mol), and potassium carbonate (30.0 g, 0.217 mol) in acetonitrile (80 mL) and methanol (20 mL) was heated at 40 °C for 3 days. The white mixture was filtered with a Buckner funnel, and the white solid was washed with CH_2Cl_2. The filtrate was concentrated to give 2,4-dimethyl-1,2,4-triazolium iodide (white solid, 32.8 g,

100%) . A solution of NaHMDS (1 M in THF, 110 mL, 0.11 mol) was added to a suspension of an imidazolium salt (22.5 g, 0.1 mol) in THF (100 mL) and CH_2Cl_2 (50 mL) at –78 °C under argon. After stirring of the reaction mixture for 1 h at –78 °C, a solution of BH_3-THF (1 M in THF, 110 mL, 0.11 mol) was added. The resulting mixture was warmed from –78 °C to rt and stirred for 2 days. The residue was dried in *vacuo* and purified by flash column chromatography (silica gel) to give the title compound (4.4 g, 40%) as a white solid, mp 60–62 ˚C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.88 (s, 1 H), 3.97 (s, 3 H), 3.77 (s, 3 H), 1.03 (q, $J_{B\text{-}H}$ = 88 Hz, 3 H); ^{11}B NMR ($CDCl_3$, 96.3 MHz) δ –37.8 (q, $J_{B\text{-}H}$ = 88 Hz). These data are consistent with the previously reported characterization.[11] Crystals of pure diMe-Tri-BH_3 were obtained by vaporizing the solvent (CH_2Cl_2) of the solution of the complex.

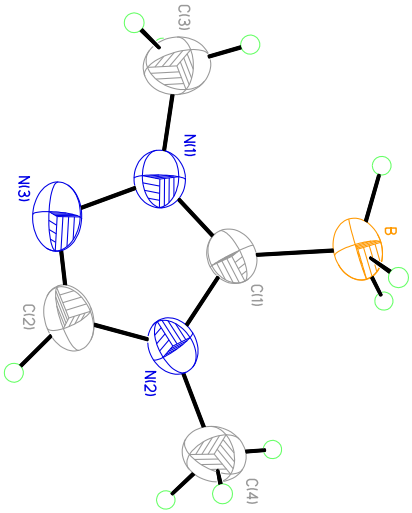
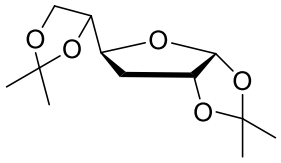
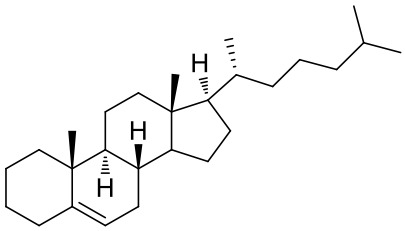


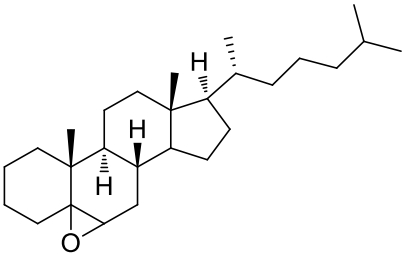
Figure S1. ORTEP plot of diMe-Tri-BH_3 **3**.



Di-*O*-isopropylidene glucofuranose (7): General conditions were used to yield the title compound as a colorless oil: ^{1}H NMR (C_6D_6, 400 MHz): δ 5.58 (d, *J* = 3.6 Hz, 1H), 4.31–4.26 (m, 1H), 4.20–4.18 (m, 1H), 3.91–3.89 (m, 2H), 3.82–3.81 (m, 1H), 2.18 (dd, *J* = 4.4, 9.2 Hz, 1H), 1.45 (s, 3H), 1.37 (s, 3H), 1.26 (s, 3H), 1.13 (s, 3H). These data are consistent with the previously reported characterization.[12]

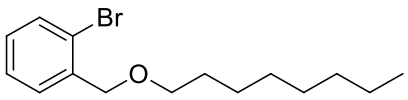


Cholest-5-ene (9): General conditions were used to yield the title compound as a white solid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.29–5.27 (m, 1H), 2.28–2.20 (m, 1H), 2.00–1.99 (m, 3H), 1.85–1.82 (m, 2H), 1.75–1.72 (m, 1H), 1.62–0.93 (m, 26H), 0.92, (d, *J* = 6.4 Hz, 3H), 0.87 (dd, *J* = 6.8, 4.8 Hz, 6H), 0.68 (s, 3H). These data are consistent with the previously reported characterization.[13]

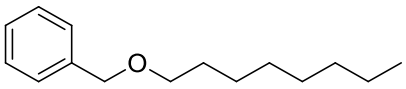


5,6-Epoxycholestane (11): General conditions were used to yield the title compound (two isomers 6:1) as a white solid: ^{1}H NMR ($CDCl_3$, 300 MHz) 5α,6α-epoxycholestane δ 2.88 (d, *J*

=4.5 Hz, 1H), 0.61 (s, 3H); 5β,6β-epoxycholestane δ 3.01 (m, 1H), 0.63 (s, 3H); overlapping signals: δ 2.15–0.85 (m, 42H). These data are consistent with the previously reported characterization.[14]

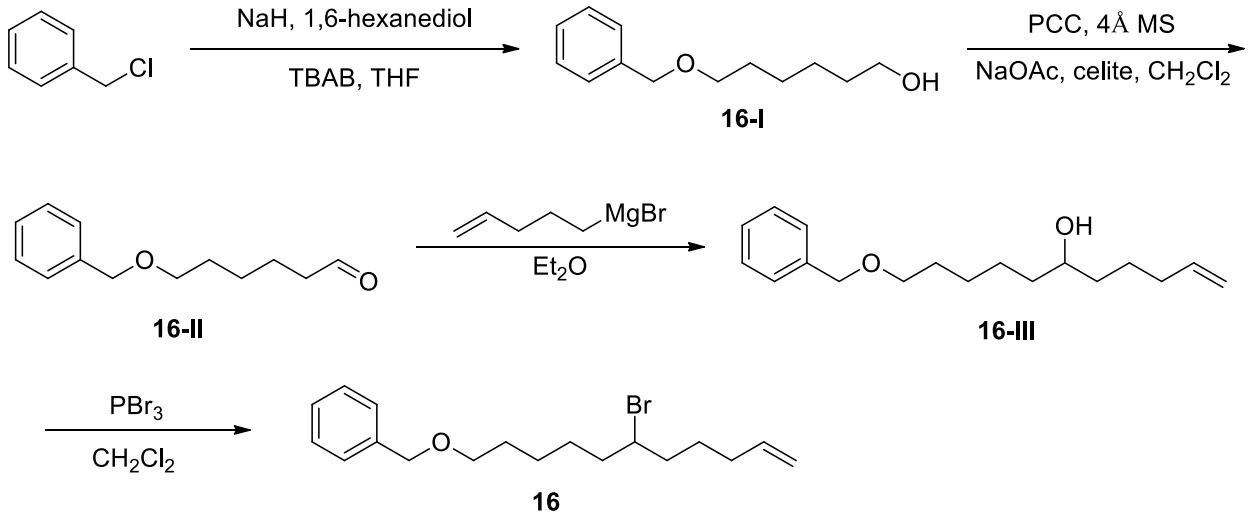


1-Bromo-2-((octyloxy)methyl)benzene (14b): Sodium hydride (60%, 0.43 g, 10.7 mmol) was added to a solution of 1-bromooctane (2.1 g, 10.7 mmol) and 2-bromobenzyl alcohol (1.0 g, 5.3 mmol) in DMF (10 mL). The mixture was heated at 70 °C for 2 h. The mixture was cooled to room temperature, then and quenched by water (30 mL) and diethyl ether (70 mL). The organic layer was extracted with water, and washed with brine, dried over $MgSO_4$ and concentrated in *vacuo*. The crude product was purified by flash column chromatography to give the title compound (1.5 g, 94%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.49 (m, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H), 4.58 (s, 2H), 3.56 (t, J = 6.8 Hz, 2H), 1.71–1.60 (m, 2H), 1.43–1.31 (m, 10H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 132.4, 128.9, 128.7, 127.3, 122.6, 72.0, 71.0, 31.8, 29.7, 29.4, 29.2, 26.2, 22.6, 14.1; FTIR (thin film, CH_2Cl_2, cm^{-1}) 3065, 2926, 2855, 1570, 1466, 1357, 1104, 749; HRMS (ESI) *m/z* (M^+ + H) calculated for $C_{15}H_{23}{}^{79}BrO$ 299.1011, found 299.1023.



((Octyloxy)methyl)benzene (15): General conditions were used to yield the title compound as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35–7.26 (m, 5H), 4.50 (s, 2H), 3.46 (t, J = 6.7 Hz,

2H), 1.70–1.59 (m, 2H), 1.43–1.30 (m, 2H), 1.30–1.15 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H). These data are consistent with the previously reported characterization.[7]



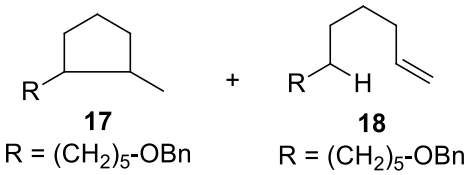
6-(Benzyloxy)hexan-1-ol (16-I): Sodium hydride (60%, 0.96 g, 24.0 mmol) was added to the gray mixture of 1,6-hexanediol (2.36 g, 20.0 mmol), benzyl chloride (3.04 g, 24.0 mmol), and tetrabutylammonium bromide (1.60 g, 5.0 mmol) in THF (30 mL). The white mixture was refluxed for 2 h. The mixture was cooled to room temperature, and then quenched by water (30 mL) and diethyl ether (50 mL). The organic layer was extracted with water, and washed with brine, dried over $MgSO_4$ and concentrated in *vacuo*. The crude product was purified by flash column chromatography to give the title compound (2.40 g, 57%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 –7.29 (m, 5H), 4.51 (s, 2H), 3.65 (t, J = 6.4 Hz, 2H), 3.48 (t, J = 6.8 Hz, 2H), 1.68–1.58 (m, 4H), 1.55–1.39 (m, 4H). These ^{1}H NMR data are consistent with the previously reported characterization.[15]

6-(Benzyloxy)hexanal (16-II): CH_2Cl_2 solution (20 mL) of 6-(benzyloxy)hexan-1-ol **16-I** (2.37 g, 11.4 mmol) was added to the organge mixture of PCC (pyridinium chlorochromate, 4.90 g, 22.8 mmol), 4 Å MS (2.40 g), sodium acetate (0.56 g, 6.84 mmol), and celite (2.40 g) in 70 mL of CH_2Cl_2. The browm mixture was stirred at rt for 2 h, and celite (30 g) and diethyl ether (100 mL) were added. The brown mixture was filtered through a plug of silica gel, and concentrate in *vacuo*. The crude product was purified by flash column chromatography to give the title compound (1.55 g, 66%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76 (t, J = 1.5 Hz, 1H), 7.35–7.27 (m, 5H), 4.50 (s, 2H), 3.47 (t, J = 6.3 Hz, 2H), 2.43 (td, J = 7.5, 1.8 Hz, 2H), 1.68–1.61 (m, 4H), 1.45–1.39 (m, 2H). These ^{1}H NMR data are consistent with the previously reported characterization.[16]

11-(Benzyloxy)undec-1-en-6-ol (16-III): 1,2-Dibromoethane (0.36 g, 1.9 mmol) was added to the mixture of Mg turnings (0.27 g, 10.9 mmol) in ethyl ether (0.8 mL) to activate the Mg turnings. After the generation of bubbles was ceased, the solution of 5-bromo-1-pentene (1.27 g, 8.4 mmol) in ethyl ether (13 mL) was added slowly over 30 min. The Grignard reagent was stirred at rt for 2 h, and then the Grignard reagent was added to a solution of 6-(benzyloxy)hexanal (**16-II**, 1.46 g, 7.0 mmol) in THF (5 mL) at –78 °C slowly. The white mixture was stirred at –78 °C to 0 °C for 3 h, and then saturated NH_4Cl (aq) (10 mL) was added to the white mixture to quench the excess Grignard reagent. The biphase system was partitioned between ethyl ether (70 mL) and saturated NH_4Cl (aq) (30 mL). The organic layer was washed with water (30 mL), brine (30 mL), dried with $MgSO_4$, and concentrated to give title compound (0.82 g, 56%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.28 (m, 5H), 5.82 (ddt, J = 17.2, 10.3, 6.6 Hz, 1H), 5.06–4.94 (m, 2H), 4.51 (s, 2H), 3.60 (m, 1H), 3.48 (t, J = 6.6 Hz, 2H),

2.10–2.05 (m, 2H), 1.67–1.30 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.6, 128.3, 127.6, 127.5, 114.6, 72.8, 71.7, 70.3, 37.4, 36.8, 33.7, 29.7, 26.2, 25.4, 24.9; FTIR (thin film, CH_2Cl_2, cm^{-1}) 3405, 2933, 2858, 1640, 1454, 1363, 1101, 910, 736; HRMS (ESI) *m/z* (M^+ + Na) calculated for $C_{18}H_{28}O_2Na$ 299.1987, found 299.2008.

(((6-Bromoundec-10-en-1-yl)oxy)methyl)benzene (16): Phosphorus tribromide (0.73 g, 2.72 mmol) was added to a CH_2Cl_2 solution of 11-(benzyloxy)undec-1-en-6-ol (**16-III**, 0.50 g, 1.81 mmol) at 0 °C. The colorless solution was stirred at 0 °C for 1 h, and then diluted with ethyl ether (70mL) and washed saturated $NaHCO_3$ (aq)(x4). The organic layer was dried with $MgSO_4$, and concentrated to give a colorless oil. The crude product was purified by flash column chromatography to give the title compound (0.13 g, 21%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.28 (m, 5H), 5.82 (ddt, *J* = 17.2, 10.3, 6.6 Hz, 1H), 5.05–4.96 (m, 2H), 4.50 (s, 2H), 4.05–4.00 (m, 1H), 3.47 (t, *J* = 6.6 Hz, 2H), 2.12–2.03 (m, 2H), 1.85–1.25 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 138.2, 128.3, 127.5, 127.4, 114.9, 72.8, 70.2, 58.3, 39.0, 38.4, 33.0, 29.5, 27.3, 26.7, 25.6; FTIR (thin film, CH_2Cl_2, cm^{-1}) 3053, 2937, 2860, 2305, 1640, 1454, 1363, 1265, 1100, 739, 704; HRMS (ESI) m/z (M^+ – H) calculated for $C_{18}H_{26}{}^{79}BrO$ 337.1167, found 337.1199.

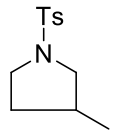


17
R = $(CH_2)_5$-OBn

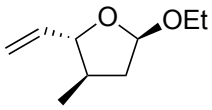
18
R = $(CH_2)_5$-OBn

(((5-(2-methylcyclopentyl)pentyl)oxy)methyl)benzene (17) and ((undec-10-en-1-yloxy)methyl)benzene (18): General conditions were used to yield the title compounds of a 5:1 mixture of (((5-(2-methylcyclopentyl)pentyl)oxy)methyl)benzene (two stereoisomers) and

((undec-10-en-1-yloxy)methyl)benzene as a colorless oil: ^{1}H NMR (C_6D_6, 400 MHz) : major isomer of (((5-(2-methylcyclopentyl)pentyl)oxy)methyl)benzene: δ 0.79 (d, *J* = 6.8 Hz, 3H); minor isomer: δ 0.98 (d, *J* = 6.8 Hz, 3H); ((undec-10-en-1-yloxy)methyl)benzene: δ 5.84–5.73 (m, 1H), 5.07–4.94 (m, 2H); overlapping signals: δ 7.34–7.32 (m, 2H), 7.21–7.17 (m, 2H), 7.12–7.08 (m, 1H), 4.37 (s, 2H), 3.35 (t, *J* = 6.4 Hz, 2H), 1.97–1.05 (m, 16H). These data are consistent with the previously reported characterization.[11,17]

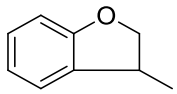


3-Methyl-1-tosylpyrrolidine (20): General conditions were used to yield the title compound as a white solid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.45–3.41 (m, 1H), 3.38–3.32 (m, 1H), 3.26–3.19 (m, 1H), 2.76 (t, *J* = 8.0 Hz, 1H), 2.44 (s, 3H), 2.12 (dq, *J* = 9.7, 7.3 Hz, 1H), 1.95–1.86 (m, 1H), 1.35 (dq, *J* = 9.7, 6.5 Hz, 1H), 0.92 (d, *J* = 6.5 Hz, 3H). These data are consistent with the previously reported characterization.[18]

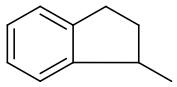


5-Ethoxy-3-methyl-2-vinyltetrahydrofuran (22): General conditions were used to yield the title compound (as two diastereoisomers, 9:1) as a colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) (2S,3R,5R)-5-ethoxy-3-methyl-2-vinyltetrahydrofuran: δ 5.77 (ddd, *J* = 7.5, 10.2, 17.4 Hz, 1H), 5.32–5.15 (m, 3H), 3.95 (t, *J* = 8.4 Hz, 2H), 3.80 (dq, *J* = 7.2, 10.2 Hz, 1H), 3.45 (dq, *J* = 7.2, 10.2 Hz, 1H), 2.41 (ddd, *J* = 5.7, 8.7, 13.8 Hz, 1H), 1.91–1.77 (m, 1H), 1.57–1.49 (m, 1H), 1.22

(t, *J* = 7.2 Hz, 3H), 1.04 (d, J = 6.6 Hz, 3H). These data are consistent with the previously reported characterization.[19]



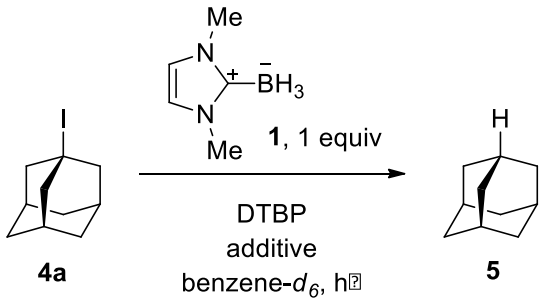
3-Methyl-2,3-dihydrobenzofuran (24): General conditions were used to yield the title compound as a colorless oil: ^{1}H NMR (C_6D_6, 400 MHz): δ 7.02–6.97 (m, 1H), 6.94–6.86 (m, 1H), 6.81–6.80 (m, 1H), 6.79–6.77 (m, 1H), 4.24 (t, *J* = 8.8 Hz, 1H), 3.70 (t, *J* = 7.8 Hz, 1H), 3.06–2.96 (m, 1H), 0.89 (d, *J* = 6.8 Hz, 3H). These data are consistent with the previously reported characterization.[9]



1-Methylindane (25): General conditions were used to yield the title compound as a colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.24–7.15 (m. 4H), 3.23–3.16 (m, 1H), 2.92–2.86 (m, 2H), 2.35–2.28 (m, 1H), 1.65–1.57 (m, 1H), 1.29 (d, *J* = 7.0 Hz, 3H). These data are consistent with the previously reported characterization.[20]

Additional Preparative Experiments:

Table S1. Reduction of Ad-I **4a** with diMe-Imd-BH_3 **1** with other additives and initiators.



Entry	additive (5 mol%)	time	conversion of **4a**	yield of **5**[a]
1[b]	PhSH	1 h	99%	99%
2	PhSeH	2 h	32%	-
3	2,4,6-trimethylphenol **S1**	1 h	20%	-
4	TBC[c] **S2**	3 h	47%	-
5[d]	PhSH	3 h	88%	84%

[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [b] data are from entry 8 in Table 1; [c] 4-*tert*-butylcatechol; [d] initiator source: black light (15W and peak wavelength at 357 nm).

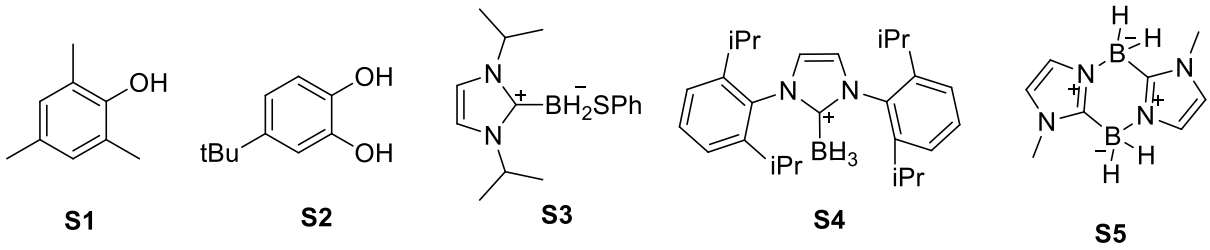
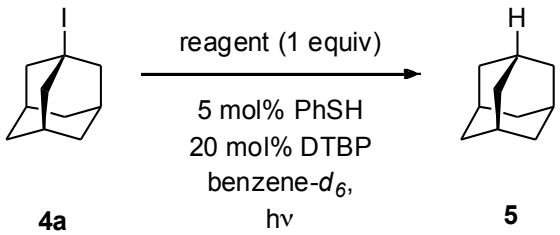


Figure S2. Structure used in Table S1 and S2.

Table S2. Reduction of Ad-I **4a** with other borane sources with 5% PhSH.

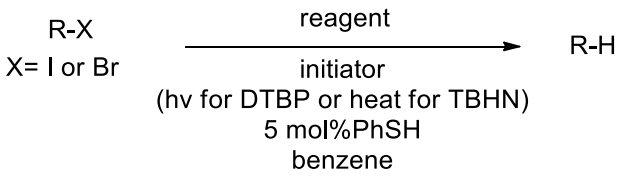


4a **5**

Entry	reagent	time	conversion of **4a**	yield of **5**[a]
1[b]	diMe-Imd-BH_3 **1**	1 h	99%	99%
2	diMe-Imd-BH_3 **1**[c]	1 h	50%	50%
3	dipp-Imd-BH_3 **S4**	1 h	99%	86%
4[d]	diMe-Tri-BH_3 **2**	1 h	99%	77%[e]
5	Dimer **S5**	1 h	0%	-
6	Me_3N-BH_3	12 h	17%	-
7	pyridine-BH_3[f]	12 h	89%	75%
8[d]	pyridine-BH_3[f]	12 h	64%	64%
9	Ph_3P-BH_3	4 h	0%	-
10[d]	Bu_4NBH_3CN[f]	2 h	99%	~20%
11	Bu_4NBH_3CN[g]	3 h	99%	93%

[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [b] data are from entry 8 in Table 1; [c] 0.5 equiv used; [d] 20 mol% TBHN under thermal conditions; [e] isolated yield after aqueous extraction; [f] 2 equiv; [g] 5 equiv.

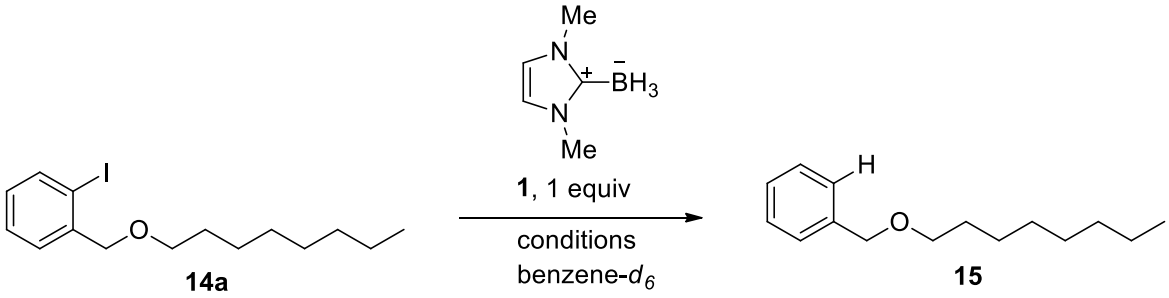
Table S3. Additional reductions with Bu_4NBH_3CN and pyridine-BH_3.



Entry	R-X	reagent	initiator (20 mol%)	time	conversion	yield[a]
1	**4b**	Bu_4NBH_3CN[b]	DTBP	2 h	~20%	-
2	**4b**	Bu_4NBH_3CN[c]	TBHN	2 h	17%	-
3	**14a**	Bu_4NBH_3CN[b]	DTBP	7 h	99%	56%
4	**14a**	Bu_4NBH_3CN[c]	TBHN	2 h	99%	~25%
5	**4b**	pyridine-BH_3[d]	DTBP	8 h	0%	-
6	**14a**	pyridine-BH_3[d]	DTBP	8 h	72%	72%
7	**14b**	pyridine-BH_3[d]	DTBP	8 h	0%	-

a) NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [b)] 5 equiv; [c)] 2 equiv; [d)] 3 equiv.

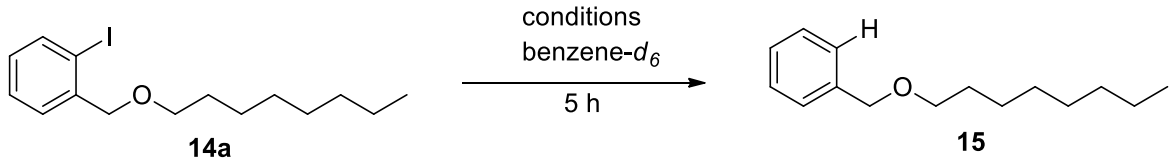
Table S4. Reduction of aryl iodide **14a** with diMe-Imd-BH_3 **1** with and without thiol sources.



Entry	initiator	equiv	PhSH	time	conversion of **14a**	yield of **15**[a]
1	Et_3B	0.5	none	7 h	0%	0%
2	Et_3B	0.5	5 mol%	3 h	61%	61%
3	TBHN	0.2	none	3 h	62%	28%
4[b]	TBHN	0.2	5 mol%	3 h	99%	86%
5	DTBP	0.2	none	7 h	87%	39%
6[b]	DTBP	0.2	5 mol%	7 h	92%	86%
7	AIBN	0.2	none	2 h	58%	15%
8	AIBN	0.2	5 mol%	2 h	61%	24%

[a)] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [b)] data are from Table 2.

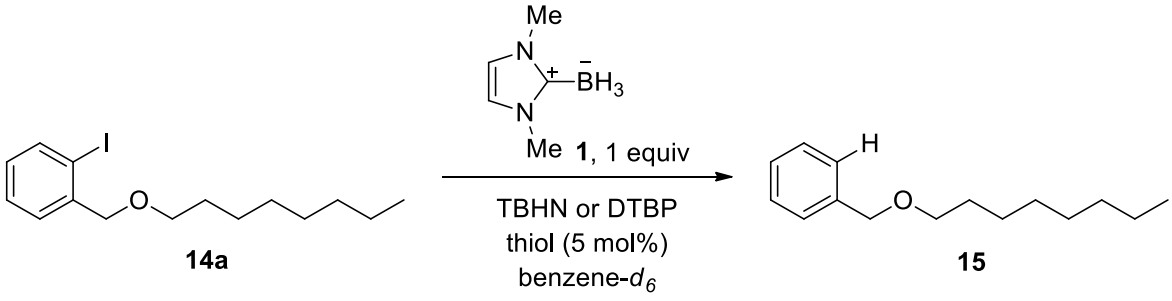
Table S5. Additional control experiments.



Entry	conditions	conversion of **14a**	yield of **15**[a]
1	Et_3B (0.5 equiv), 5% PhSH, rt	0%	0%
2	TBHN (0.1 equiv), 5% PhSH, 80 °C	19%	0%
3	DTBP (0.1 equiv), 5% PhSH, hυ	4%	4%
4	diMe-Imd-BH_3 **1** (1 equiv), 5% PhSH, 80 °C	19%	9%

[a)] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard.

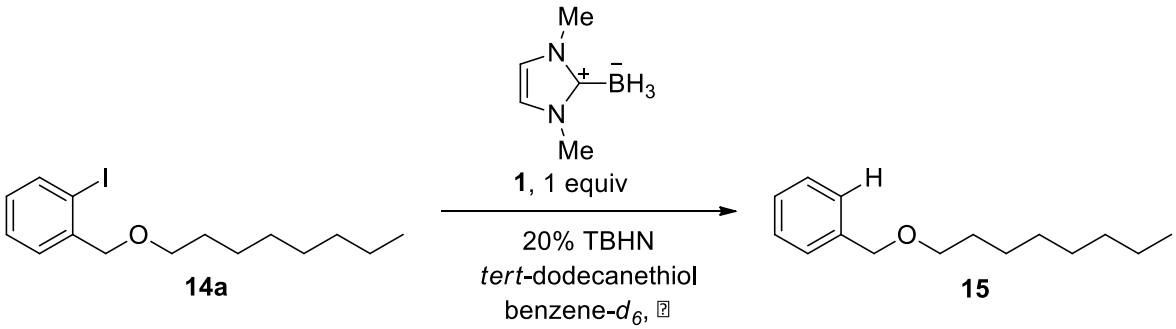
Table S6. TBHN- or DTBP-initiated reduction of **14a** with different thiol sources.



Entry	initiator (0.2 equiv)	thiol (5 mol%)	time	conversion of **14a**	yield of **15**[a]
1	TBHN	thiophenol	3 h	99%	92%
2	TBHN	1-pentadecanethiol	3 h	72%	60%
3	TBHN	*tert*-dodecanethiol	3 h	99%	96%
4	DTBP	thiophenol	6 h	81%	76%
5	DTBP	1-pentadecanethiol	6 h	88%	64%
6	DTBP	*tert*-dodecanethiol	6 h	95%	89%

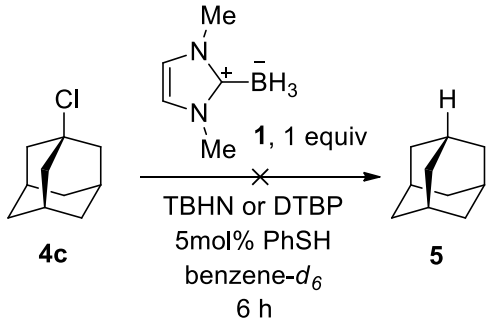
[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard.

Table S7. TBHN-initiated reduction of **14a** with different amounts of *t*-dodecanethiol.



Entry	*tert*-dodecanethiol (mol%)	conversion of **14a**	yield of **15**[a]
1	0.5%	58%	44%
2	1%	66%	53%
3	2%	83%	70%
4	5%	99%	87%
5	10%	99%	86%
6	20%	99%	82%

[a)] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard.



Reductions of adamantyl chloride under TBHN or DTBP conditions: The TBHN- or DTBP-initiated reactions between 1-chloroadamantane **4c** (Ad-Cl) and **1** (1 equiv) with 5mol% PhSH gave only 5% conversion of **5** after 6 h.

Mechanistic Studies

Laser Flash Photolysis Experiments: Nanosecond laser flash photolysis (LFP) experiments were carried out using a Q-switched nanosecond Nd/YAG laser (λ_{exc} = 355 nm, 9 ns pulses; energy reduced down to 10 mJ) from Continuum (Powerlite 9010) and an analyzing system consisting of a pulsed xenon lamp, a monochromator, a fast photomultiplier and a transient digitizer.[21]

ESR spin trapping experiments: ESR spin trapping experiments were carried out using a X-Band spectrometer (MS 200 Magnettech) as presented in reference.[22] The radicals generated under the light irradiation (Xe-Hg lamp (Hamamatsu, L8252, 150 W; λ>310 nm) were trapped by phenyl-N-tbutylnitrone (PBN). The ESR spectra simulations were carried out with the PEST WINSIM program.[23]

Calculations

OPTIMIZED STRUCTURES: UB3LYP/6-31+G* LEVEL (GAUSSIAN 03)[1]

[1] Gaussian 03, Revision B-2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003. b) J.B. Foresman, A. Frisch, in *Exploring Chemistry with Electronic Structure Methods*. Second Edition, Gaussian. Inc. 1996.

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References:

1. Hermanek, S. *Chem. Rev.* **1992**, *92*, 325-362.

2. Walton, J. C.; Brahmi, M. M.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Chu, Q.; Ueng, S.-H.; Solovyev, A.; Curran, D. P. *J. Am. Chem. Soc.* **2010**, *132*, 2350-2358.

3. Kunz, H.; Schmidt, P. *Annalen der Chemie* **1982**, 1245-1260.

4. Sun, Q.; Cai, S.; Peterson, B. R. *Org. Lett.* **2009**, *11*, 567-570.

5. Medeiros, M. R.; Schacherer, L. N.; Spiegel, D. A.; Wood, J. L. *Org. Lett.* **2007**, *9*, 4427-4429.

6. Linskeseder, M.; Zbiral, E. *Annalen der Chemie* **1978**, 1076-1088.

7. Chu, Q.; Makhlouf Brahmi, M.; Solovyev, A.; Ueng, S.-H.; Curran, D. P.; Malacria, M.; Fensterbank, L.; Lacôte, E. *Chem. Eur. J.* **2009**, *15*, 12937-12940.

8. Ohmiya, H.; Wakabayashi, K.; Yorimitsu, H.; Oshima, K. *Tetrahedron* **2006**, *62*, 2207-2213.

9. Kurono, N.; Honda, E.; Komatsu, F.; Orito, K.; Tokuda, M. *Tetrahedron* **2004**, *60*, 1791-1801.

10. Trivedi, R.; Tunge, J. A. *Org. Lett.* **2009**, *11*, 5650-5652.

11. Ueng, S. H.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Curran, D. P. *Org. Lett.* **2010**, *12* (13), 3002-3005.

12. Ueng, S.-H.; Makhlouf Brahmi, M.; Derat, E. t.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Curran, D. P. *J. Am. Chem. Soc.* **2008**, *130*, 10082-10083.

13. Yasuda, H.; Uenoyama, Y.; Nobuta, O.; Kobayashi, S.; Ryu, I. *Tetrahedron Lett.* **2008**, *49*, 367-370.

14. Yates, P.; Stiver, S. *Can. J. Chem.* **1987**, *65*, 2203-2216.

15. Shimojo, M.; Matsumoto, K.; Hatanaka, M. *Tetrahedron* **2000**, *56*, 9281-9288.

16. Narayan, R. S.; Borhan, B. *J. Org. Chem.* **2006**, *71*, 1416-1429.

17. Cryle, M. J.; Matovic, N. J.; De Voss, J. J. *Org. Lett.* **2003**, *5*, 3341-3344.

18. Tang, J.; Shinokubo, H.; Oshima, K. *Tetrahedron* **1999**, *55*, 1893-1904.

19. Villar, F.; Equey, O.; Renaud, P. *Org. Lett.* **2000**, *2*, 1061–1064.

20. Bailey, W. F.; Mealy, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 6787-6788.

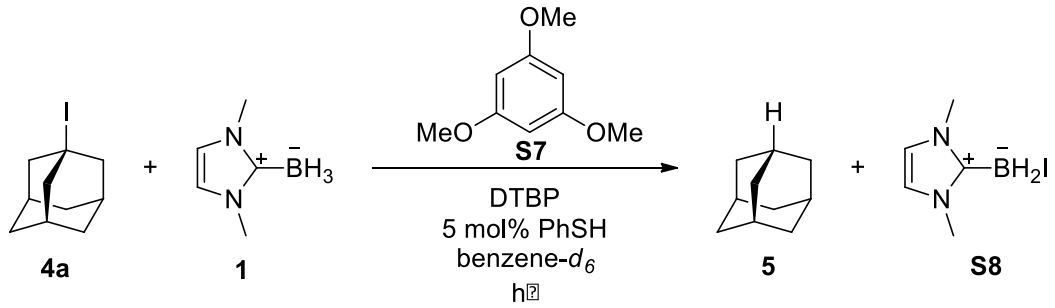
21. Lalevée, J.; Allonas, X.; Fouassier, J. P. *J. Am. Chem. Soc.* **2002**, *124*, 9613-9621.

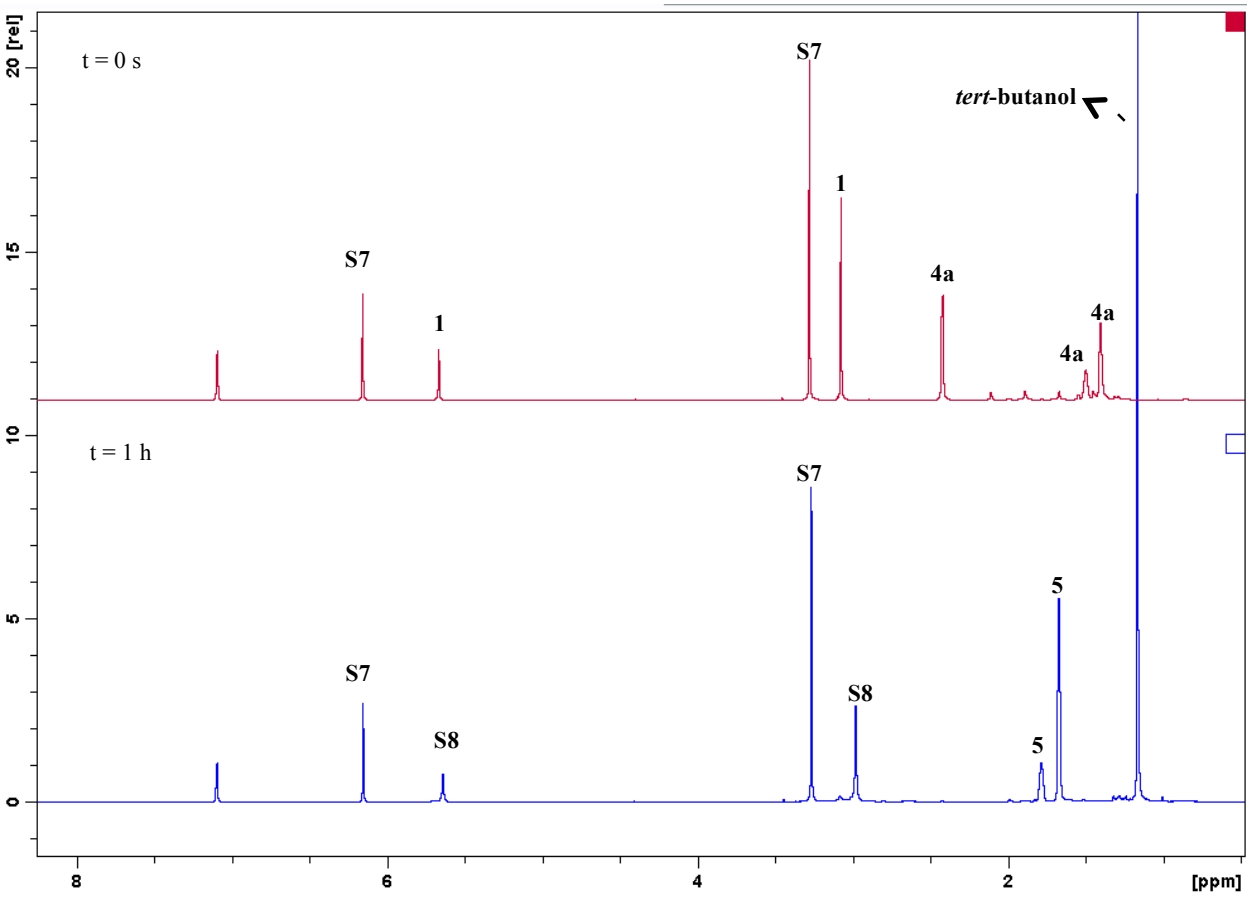
22. Criqui, A.; Lalevée, J.; Allonas, X.; Fouassier, J. P. *Macromol. Chem. Phys.* **2008**, *2009*, 2223-2231.

23. Duling, D. R. *J. Magn. Reson., Ser. B* **1994**, *104*, 105-112.

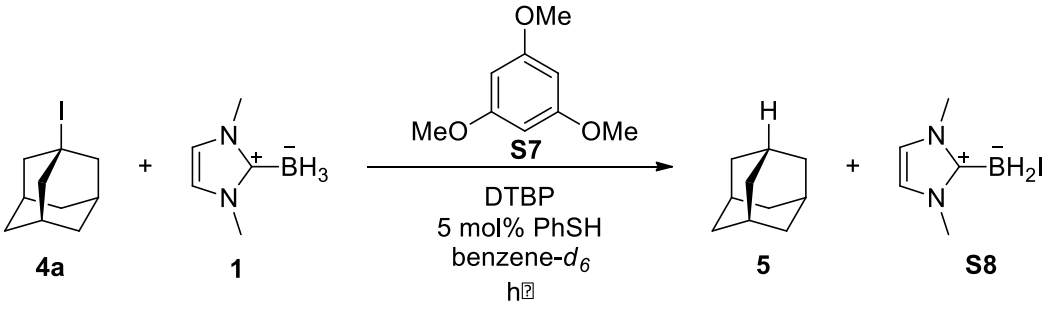
Typical Results for Reactions Followed by NMR Spectroscopy

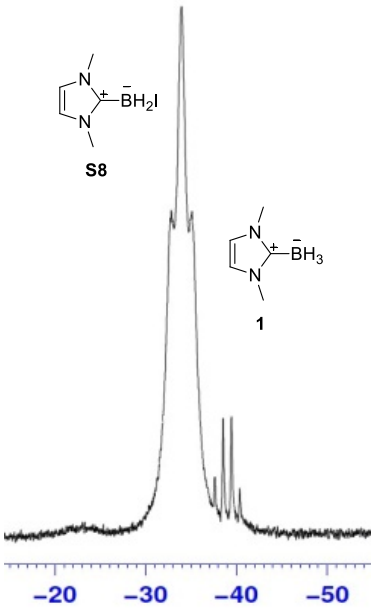
^{1}H spectra for the DTBP-initiated reduction of Ad-I:



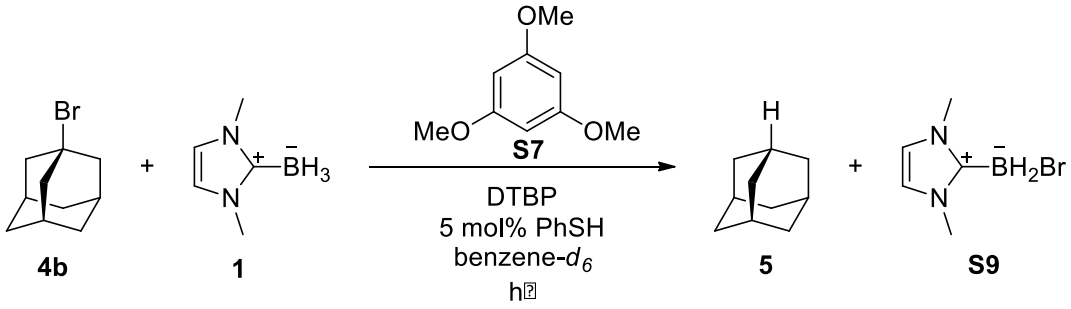


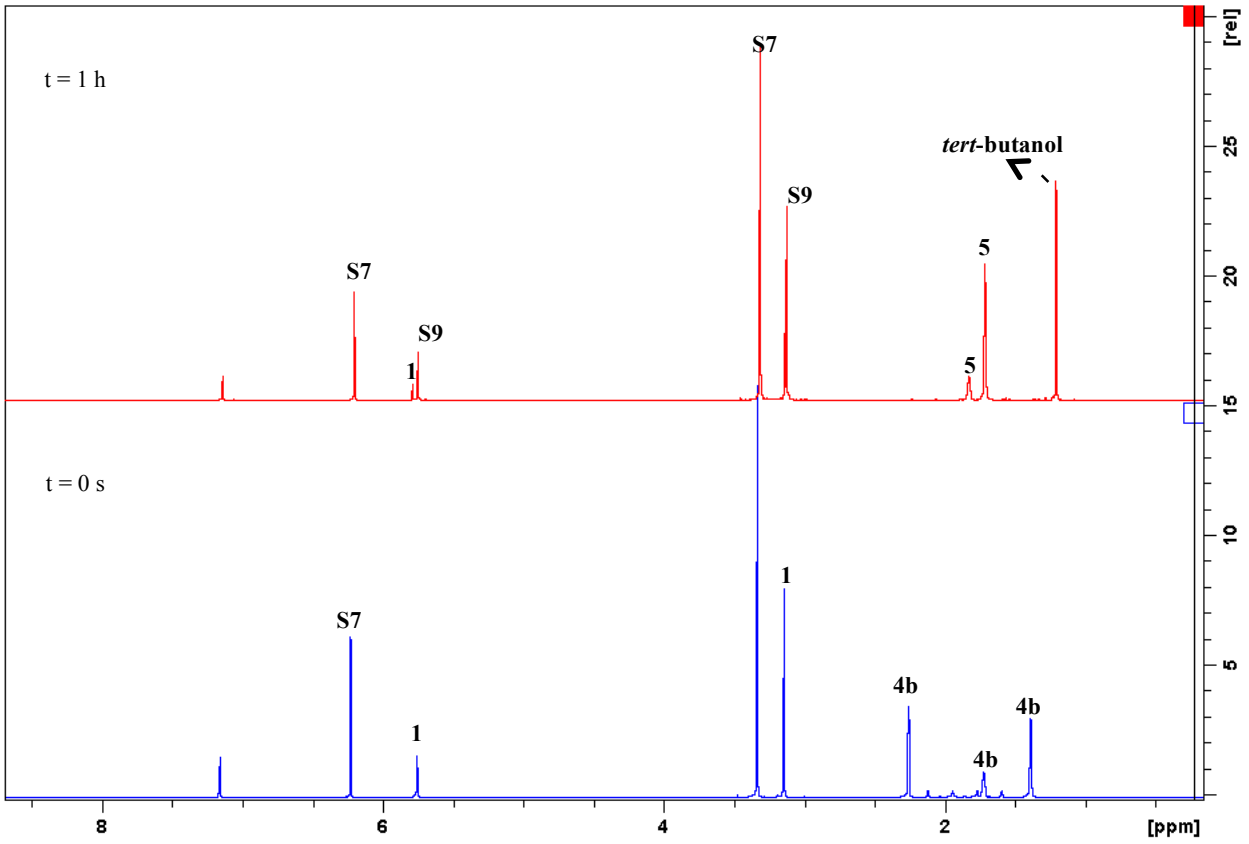
^{11}B NMR spectra for the DTBP-initiated reduction of Ad-I:



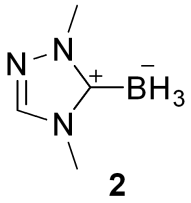


^{1}H spectra for the DTBP-initiated reduction of Ad-Br:



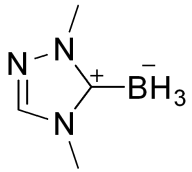


XP-72-92, part I, wash, 1H, CDCl3, 301B, 4/18/2011



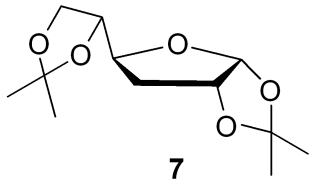
2

XP-72-92, part I, wash, 11B, CDCl3, 301B, 4/18/2011

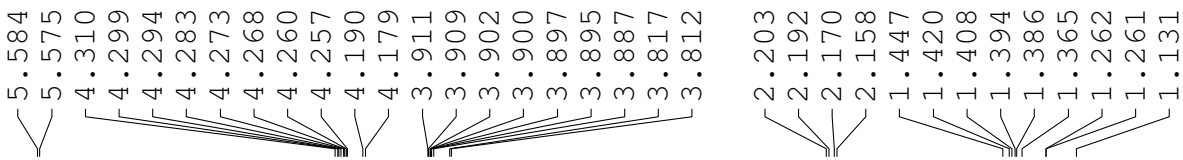


2

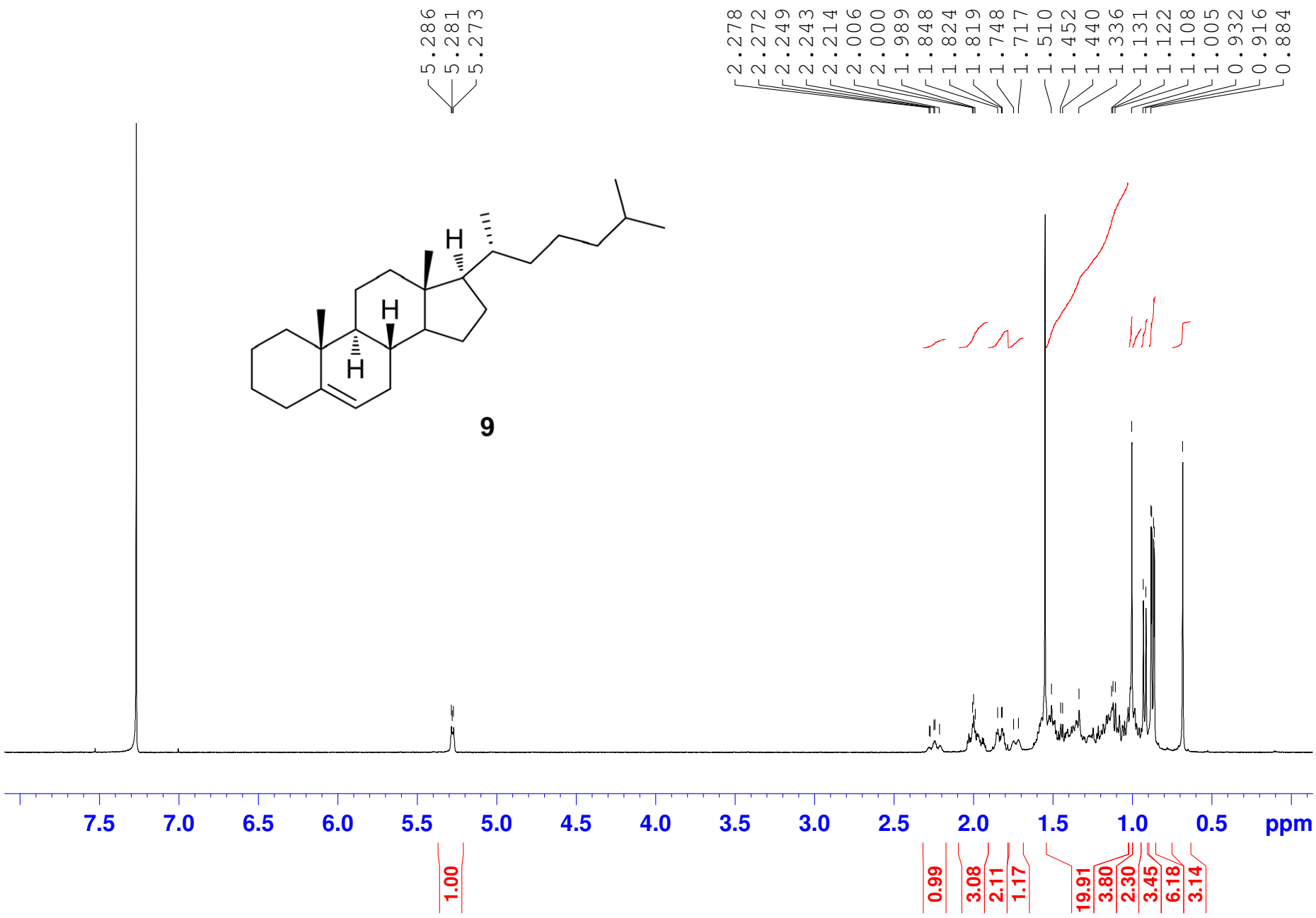
XP-59-82-purified, 1H, C6D6, 400B, 11/22/2010



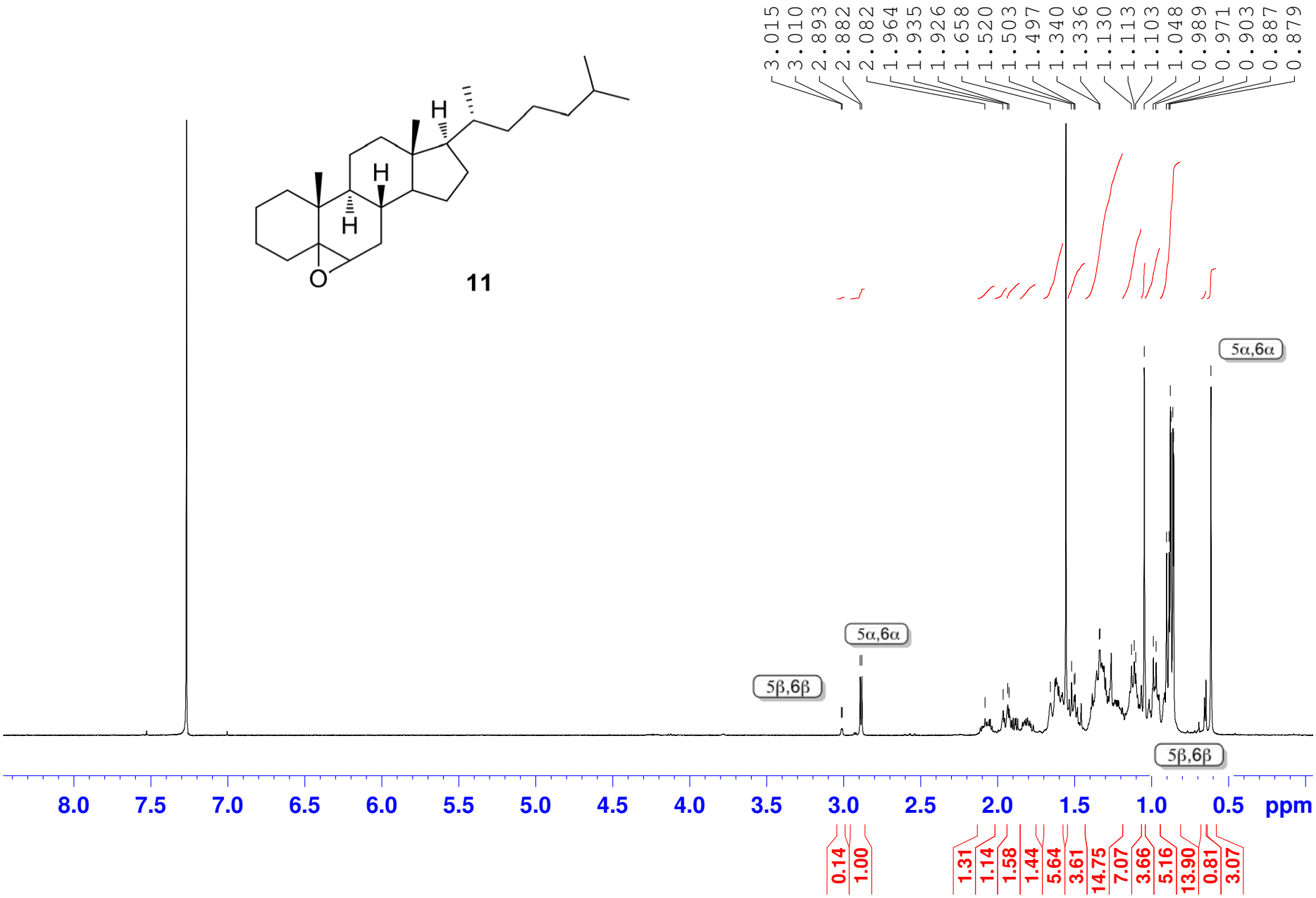
7

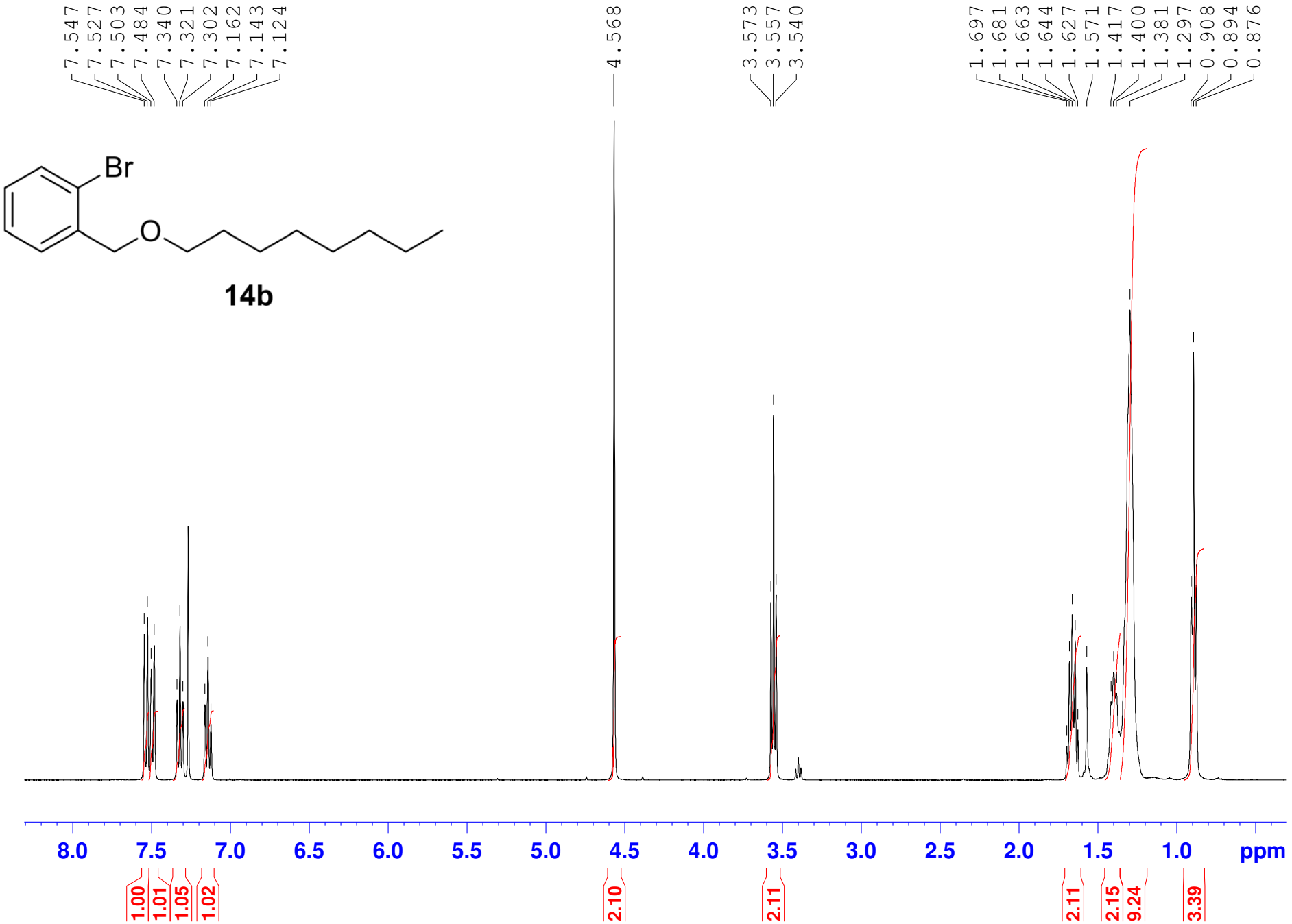


XP-66-86, 1H, CDCl3, 400A, 1/31/2011
PROTON CDCl3 C:\Bruker\TOPSPIN curran 12



XP-66-89, 1H, CDCl3, 400A, 2/3/2011
PROTON CDCl3 C:\Bruker\TOPSPIN curran 2

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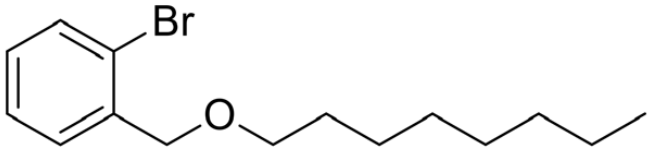
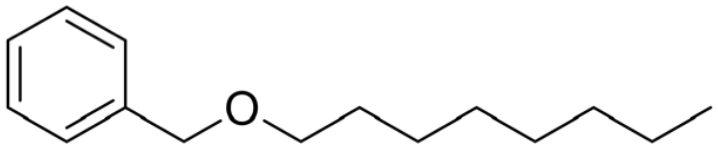
7.503
7.484
7.340
7.321
7.302
7.162
7.143
7.124
4.568
3.573
3.557
3.540
1.697
1.681
1.663
1.644
1.627
1.571
1.417
1.400
1.381
1.297
0.908
0.894
0.876
Br
O
14b
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.01
1.05
1.02
2.10
2.11
2.11
2.15
9.24
3.39

XP octyl 1-bromobenzyl ether, 400B, CDCl3, 5/14/2011

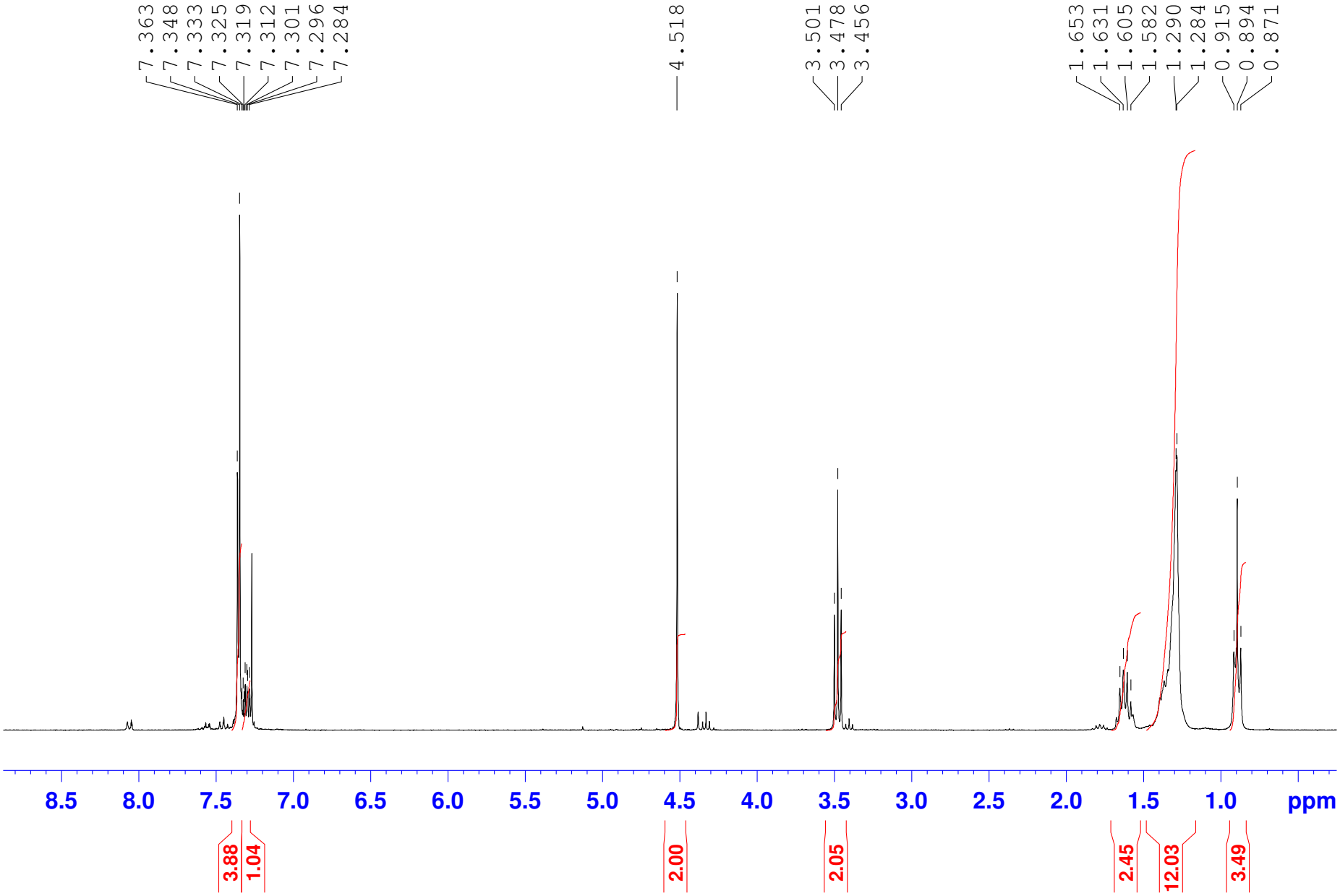


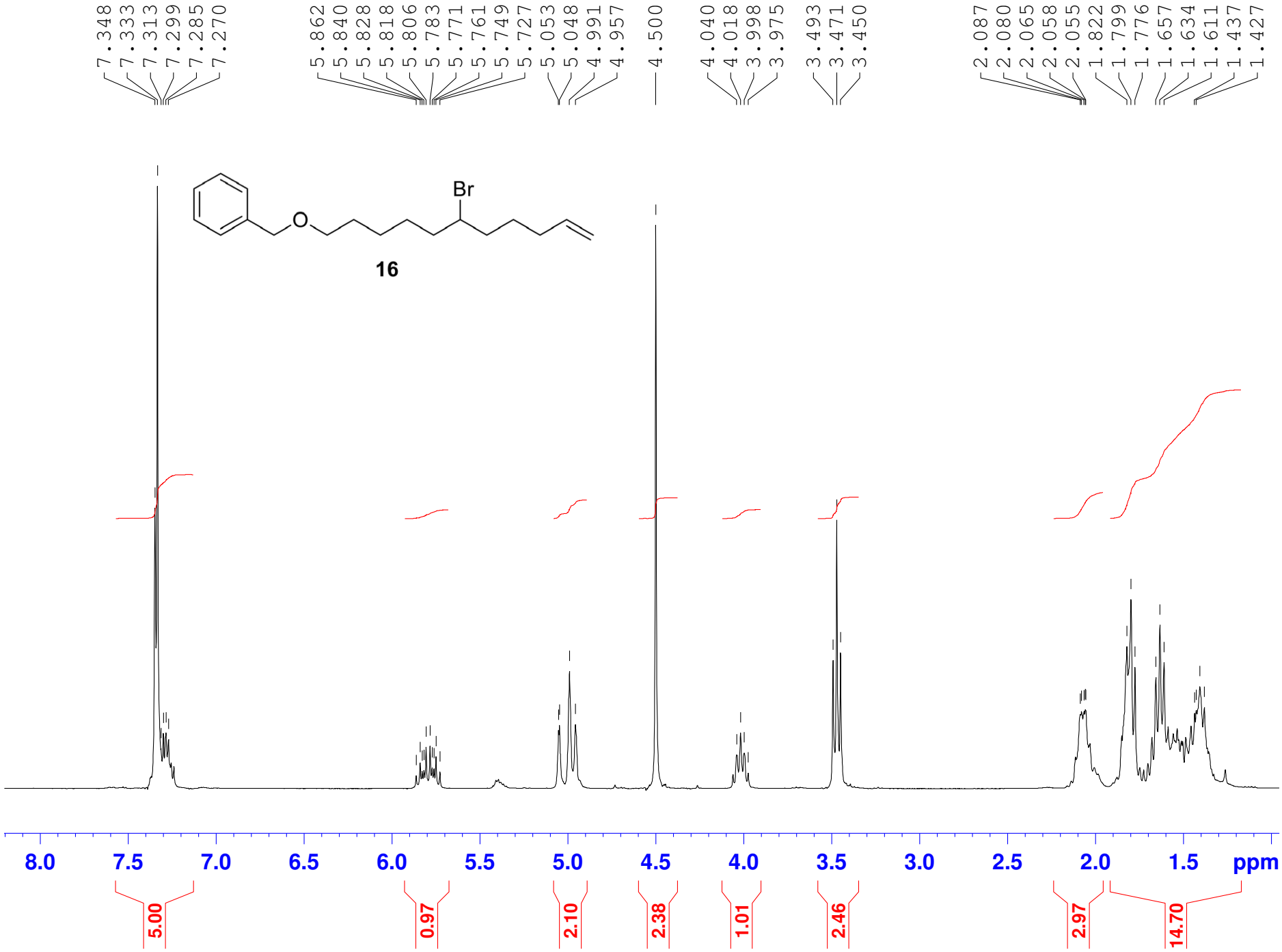
14b

XP-80-65, 1H, pdt, CDCl3, 301B, 11/14/2011



15

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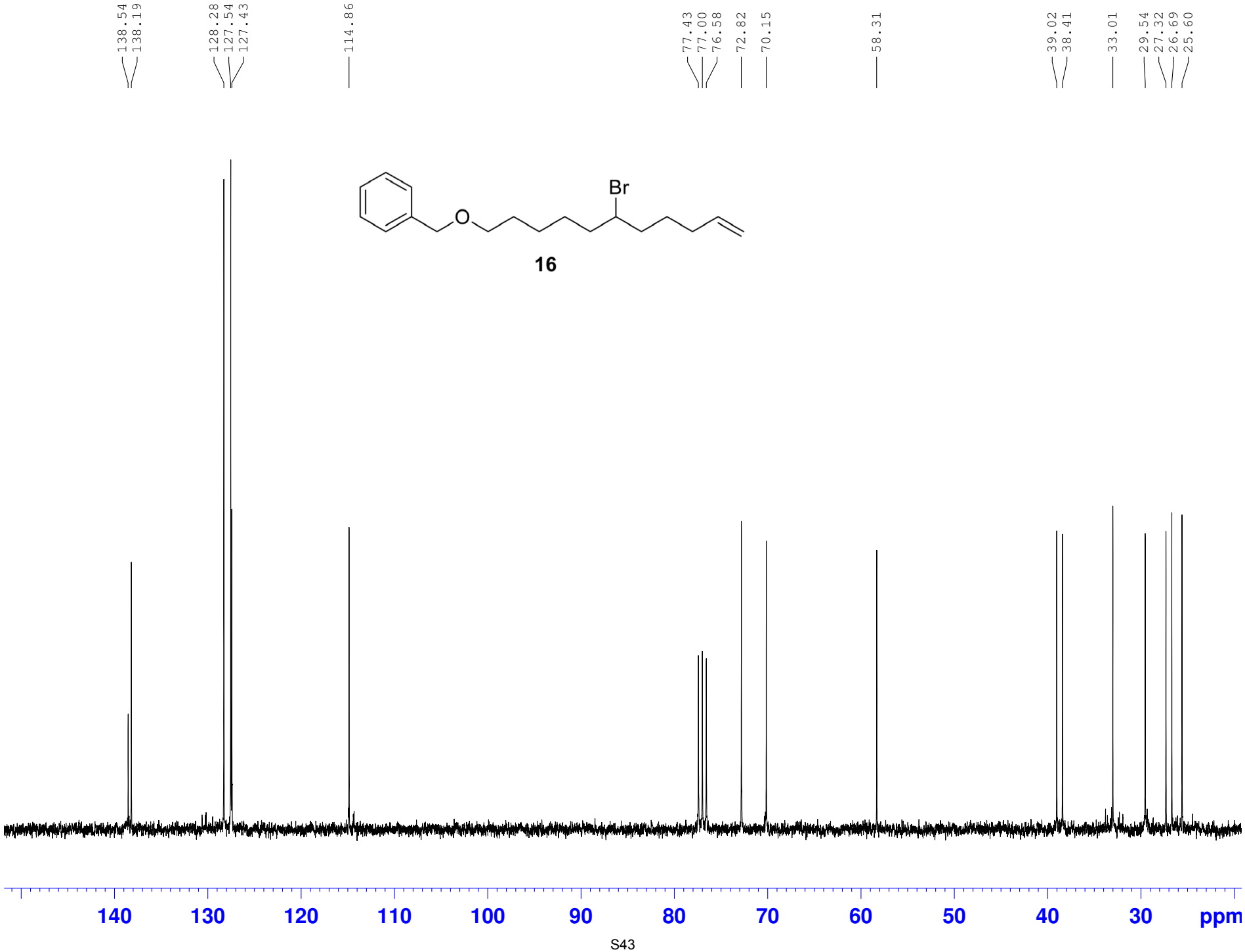
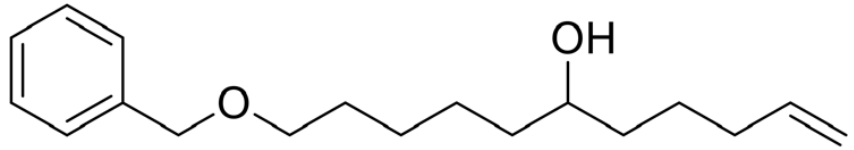
7.333
7.313
7.299
7.285
7.270
5.862
5.840
5.828
5.818
5.806
5.783
5.771
5.761
5.749
5.727
5.053
5.048
4.991
4.957
4.500
4.040
4.018
3.998
3.975
3.493
3.471
3.450
2.087
2.080
2.065
2.058
2.055
1.822
1.799
1.776
1.657
1.634
1.611
1.437
1.427
Br
O
16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
5.00
0.97
2.10
2.38
1.01
2.46
2.97
14.70

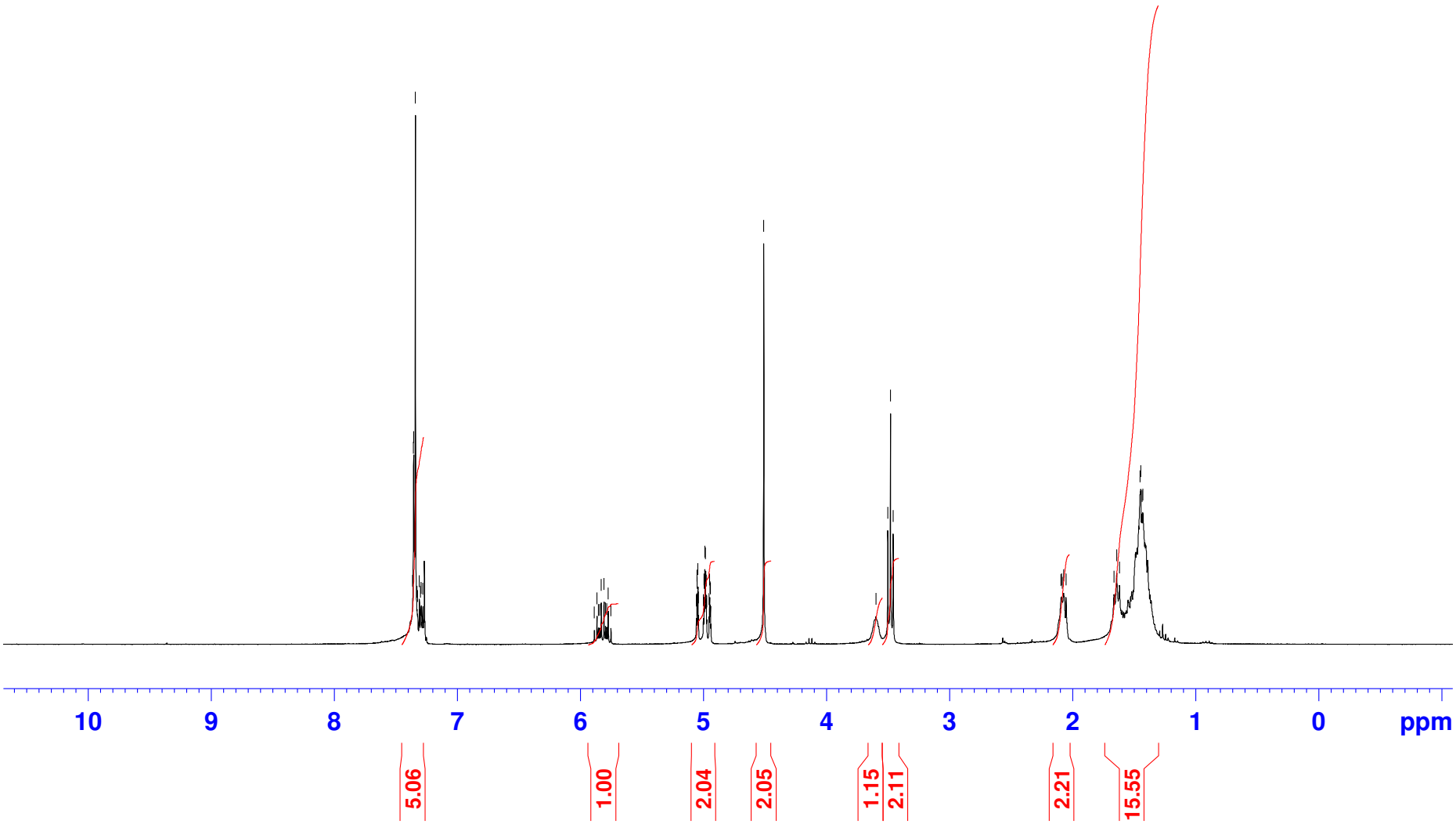

138.54
138.19
128.28
127.54
127.43
114.86
77.43
77.00
76.58
72.82
70.15
58.31
39.02
38.41
33.01
29.54
27.32
26.69
25.60
Br
O
16
140
130
120
110
100
90
80
70
60
50
40
30
ppm



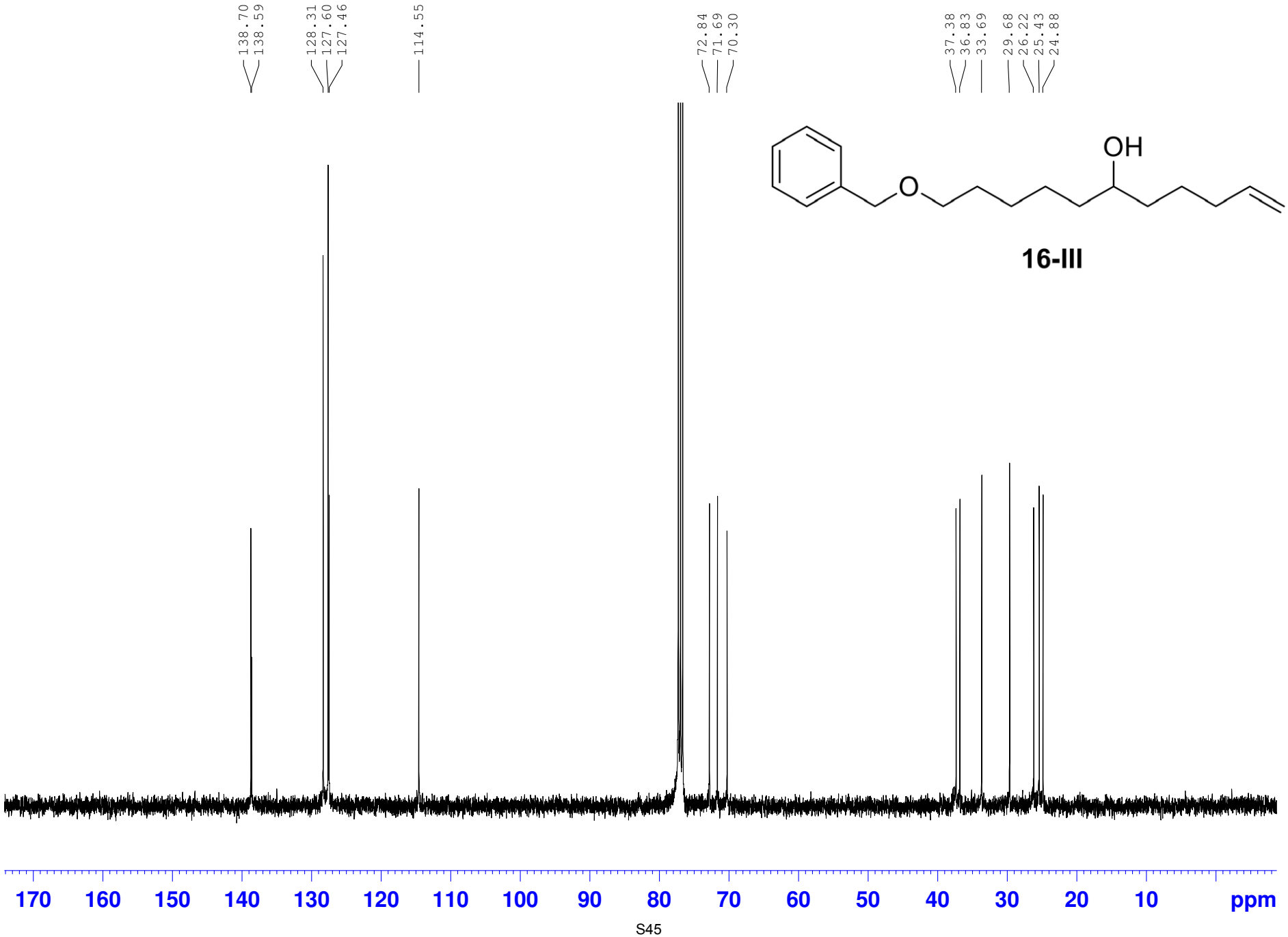
XP 11-(benzyloxy)undec-1-en-6-ol, CDCl3, 301B, 5/12/20

16-III

7.365 7.358 7.356 7.342 7.329 7.324 7.310 7.300 7.295 7.282 5.888 5.866 5.854 5.844 5.832 5.809 5.797 5.787 5.775 5.753 5.059 5.053 5.052 5.047 5.041 5.002 4.996 4.995 4.989 4.985 4.982 4.978 4.974 4.955 4.951 4.947 4.944 4.512 3.599 3.503 3.481 3.459 2.096 2.091 2.085 2.074 2.054 1.665 1.642 1.620 1.453 1.447 1.436 1.430



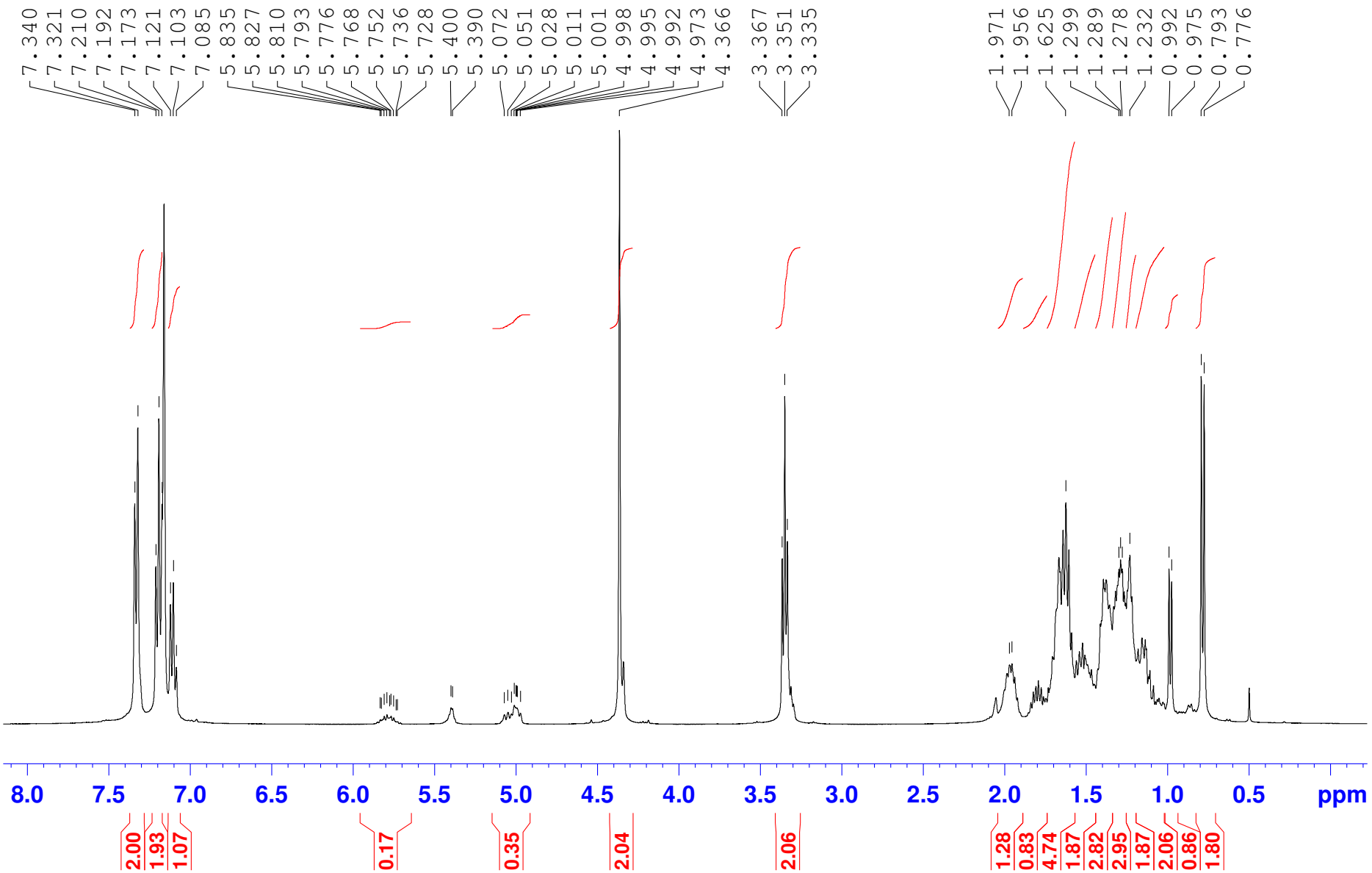
XP 11-(benzyloxy)undec-1-en-6-ol, 400B, CDCl3, 5/14/2011

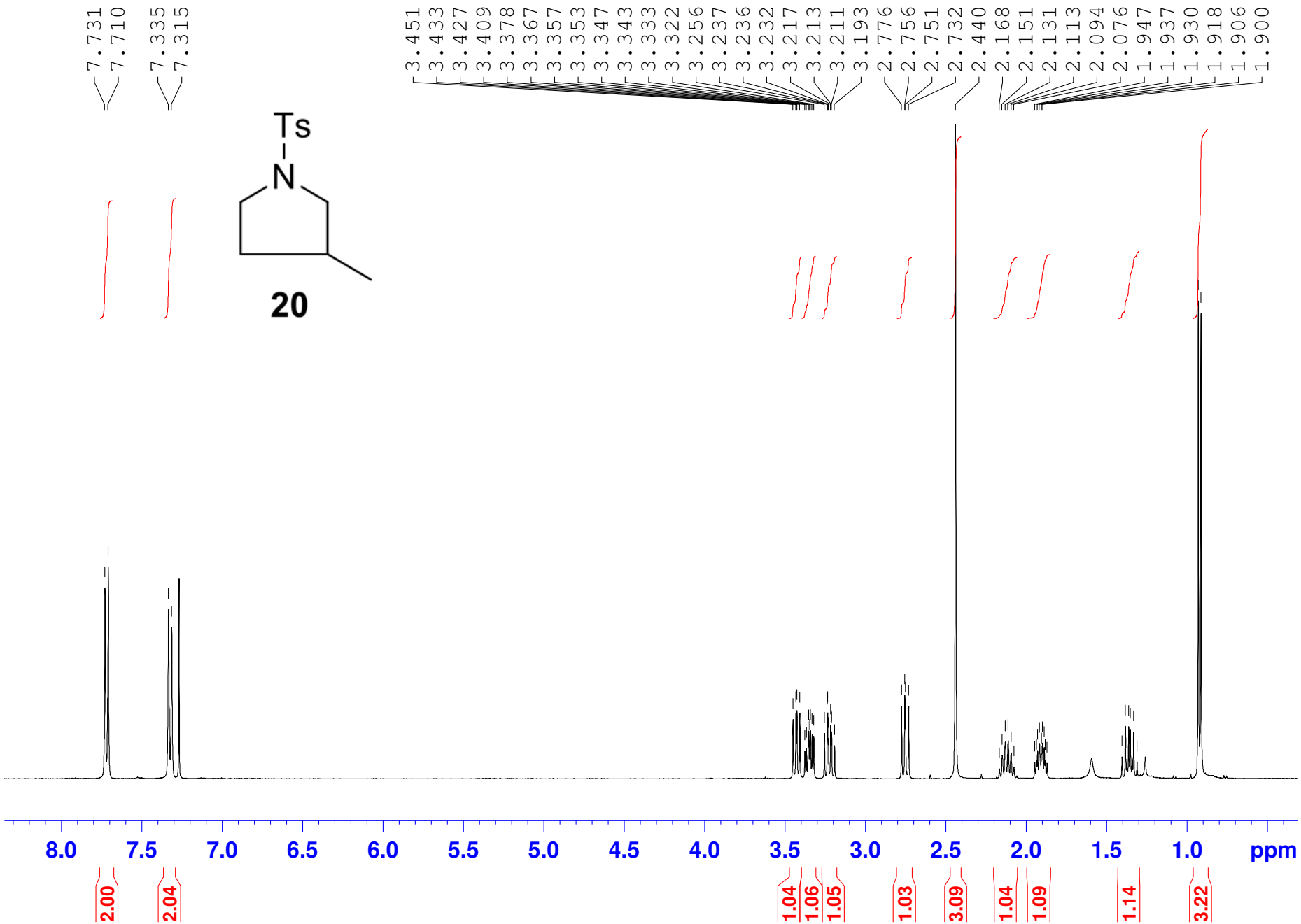


XP-66-64, 13-14, 1H, C6D6, 400A, 1/6/2010
PROTON C6D6 C:\Bruker\TOPSPIN wipf 21

17
R = $(CH_2)_5$-OBn

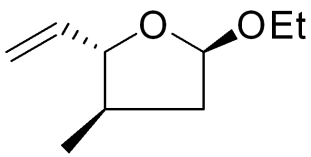
18
R = $(CH_2)_5$-OBn




7.731
7.710
7.335
7.315
3.451
3.433
3.427
3.409
3.378
3.367
3.357
3.353
3.347
3.343
3.333
3.322
3.256
3.237
3.236
3.232
3.217
3.213
3.211
3.193
2.776
2.756
2.751
2.732
2.440
2.168
2.151
2.131
2.113
2.094
2.076
1.947
1.937
1.930
1.918
1.906
1.900
Ts
N
20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
2.04
1.04
1.06
1.05
1.03
3.09
1.04
1.09
1.14
3.22

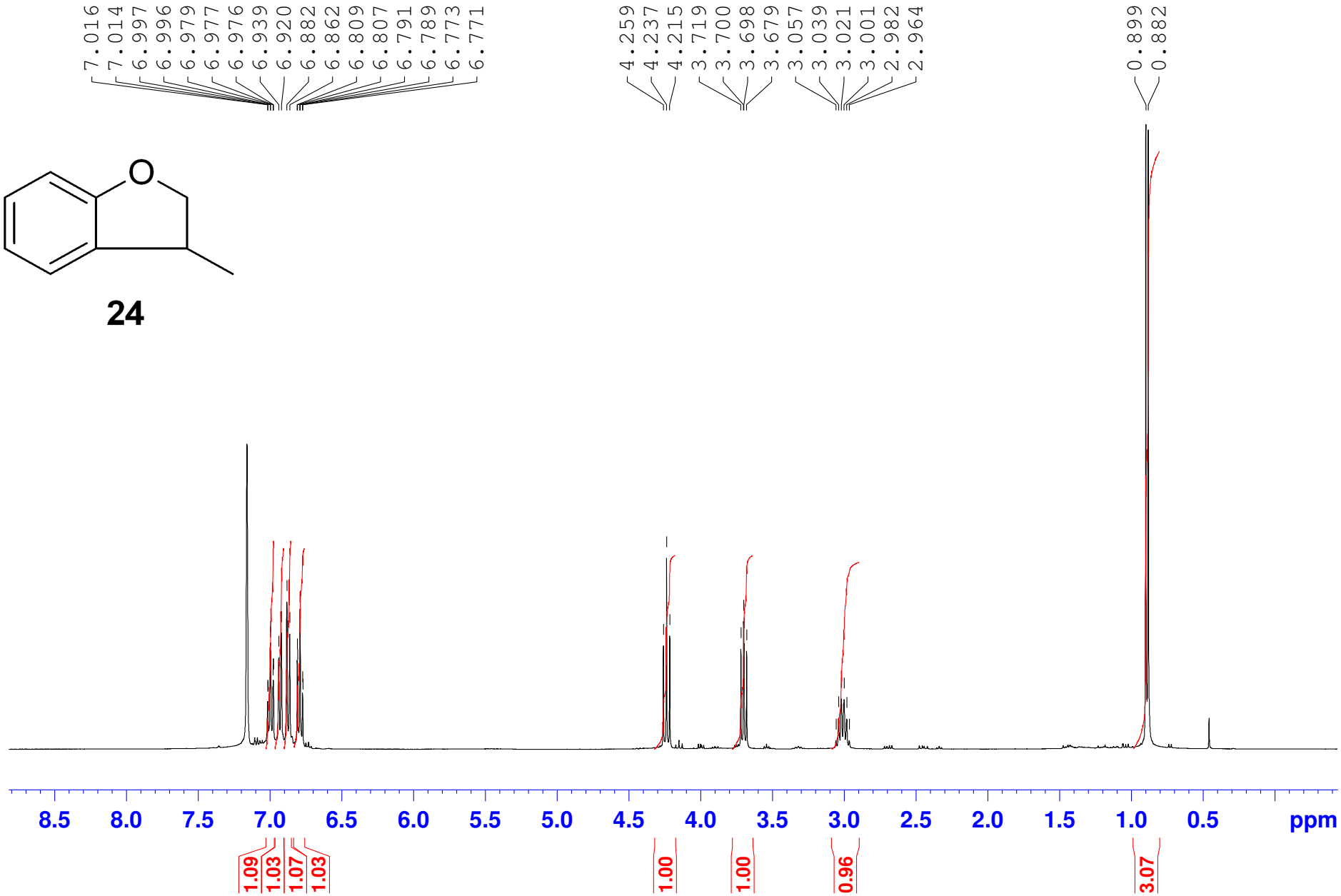
XP-98-58, 1H, CDCl3, m1, 301B, 2/22/2012

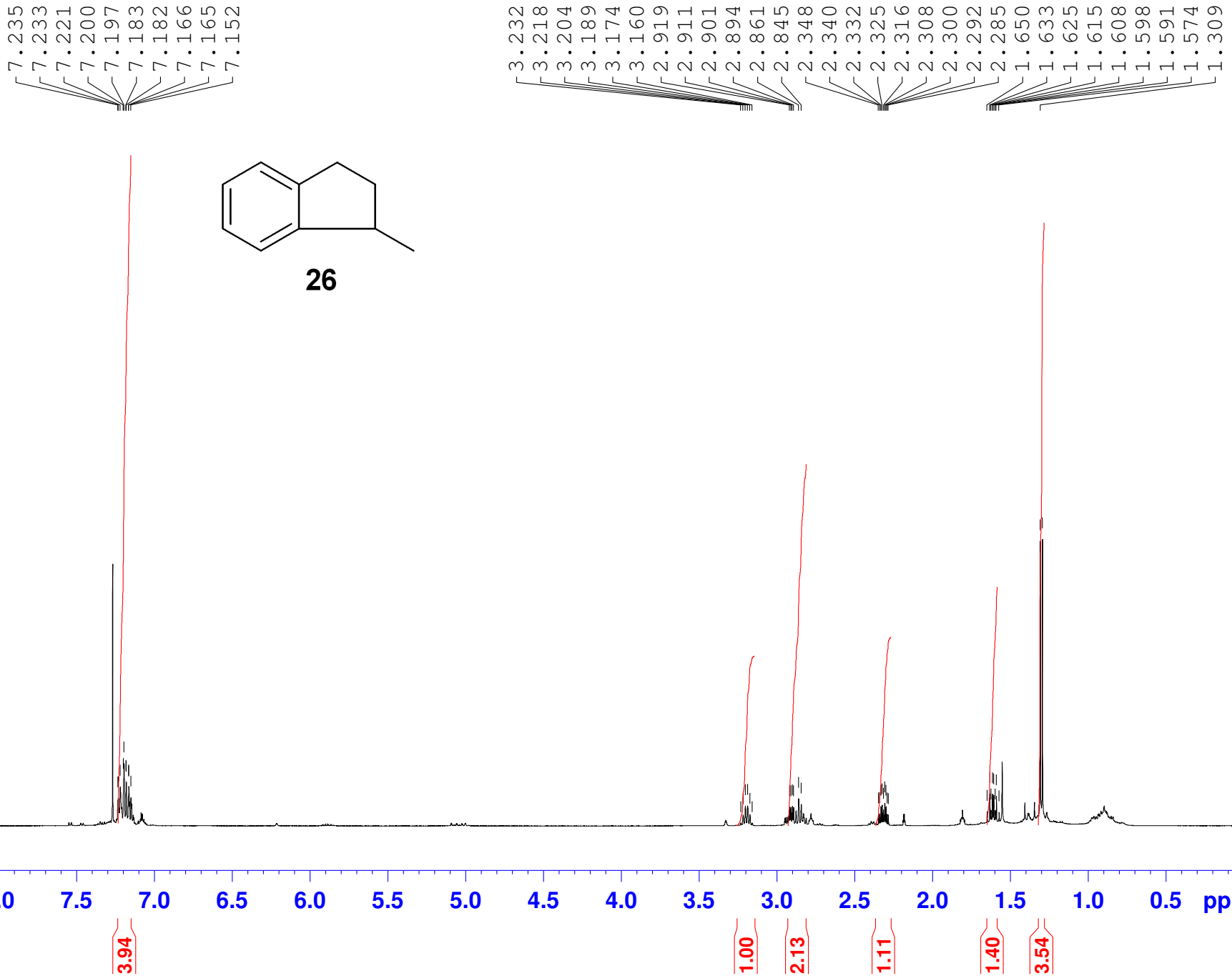
5.846 5.821 5.812 5.788 5.764 5.755 5.730 5.320 5.263 5.260 5.211 5.208 5.176 5.163 5.156 5.144 3.978 3.950 3.923 3.834 3.825 3.810 3.802 3.786 3.778 3.755 3.495 3.487 3.472 3.463 3.448 3.440 2.460 2.441 2.431 2.416 2.412 2.397 2.387 2.368 1.879 1.857 1.849 1.827 1.565 1.547 1.534 1.521 1.503 1.491 1.239 1.215 1.192 1.054 1.032



22

XP-66-63-13, 1H, C6D6, 400A, 1/6/2010
PROTON C6D6 C:\Bruker\TOPSPIN curran 12

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7.221
7.200
7.197
7.183
7.182
7.166
7.165
7.152
3.232
3.218
3.204
3.189
3.174
3.160
2.919
2.911
2.901
2.894
2.861
2.845
2.348
2.340
2.332
2.325
2.316
2.308
2.300
2.292
2.285
1.650
1.633
1.625
1.615
1.608
1.598
1.591
1.574
1.309
26
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.94
1.00
2.13
1.11
1.40
3.54