Supplementary Material (ESI) for Organic & Biomolecular Chemistry

SUPPORTING INFORMATION

Radical reductions of alkyl halides bearing electron withdrawing groups with N-heterocyclic carbene boranes

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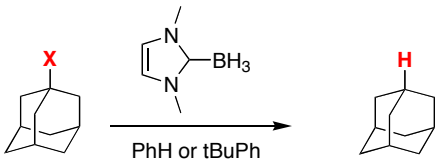
General Remarks: Chemicals and solvents were purchased from commercial suppliers and used as received. The benzene used for AIBN-initiated free radical reactions was deoxygenated by passing a gentle stream of argon through for 20 min before use. All flash column chromatography was performed with 230–400 mesh silica gel purchased from Sorbent Technologies as the stationary phase. Proton (^{1}H), carbon (^{13}C), and boron (^{11}B) nuclear magnetic resonance spectra were measured on a Bruker Avance 300 instrument at 300 MHz, 75 MHz, and 96.3 MHz, and Bruker Avance spectrometer fitted with a BBFO probehead at 400, 100, and 128.4 MHz, respectively. The chemical shifts in spectra were measured in parts per million (ppm) on the delta (δ) scale relative to the resonance of the solvent peak ($CDCl_3$ signal as reference, ^{1}H = 7.26 ppm, ^{13}C = 77.0 ppm). ^{11}B chemical shifts are given relative to BF_3•OEt_2 (^{11}B = 0 ppm). Unless noted, NMR spectra were recorded in $CDCl_3$ at 300 K. The resonance of the carbene carbon center connected to boron could not be observed because of the quadrupole broadening. The following abbreviations were used to describe coupling: s = singlet; d = doublet; t = triplet; q = quartet; br = broad; m = multiplet. Infrared (IR) spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer as thin films (CH_2Cl_2) on NaCl plates and Bruker Tensor 27 ATR diamant PIKE spectrometer. Low and high resolution mass spectra were obtained on a Micromass Inc. Autospec instrument with E-B-E geometry and also recorded by Structure et fonction de molecules bioactives (UMR 7613) of Université Pierre et Marie Curie (electrospray source).

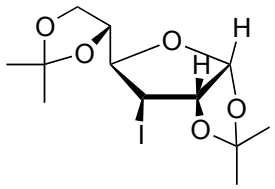
Table S1. Pilot reductions of adamantyl halides with **3**



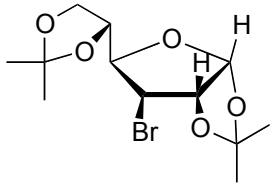
entry	X	conditions	time	solvent	[RX]	T °C	GC yield (%)
1	I	Et_3B/O_2 (1 equiv)	2 h	benzene (1 mL)	0.1 M	rt	21%
2	I	Et_3B/O_2 (6 equiv)	2 h	benzene (1 mL)	0.1 M	rt	32% (25% SM)
3	I	AIBN (1 equiv)	2 h	benzene (1 mL)	0.1 M	80°C	31% (15% SM)
4	I	ACCN (1 equiv)	2 h	benzene (1 mL)	0.1 M	110°C	64% (14% SM)
5	I	ACCN (1 equiv)	2 h	toluene (4 mL)	0.025 M	110°C	53% (20% SM) Pressure tube
6	I	–	2 h	toluene-d_8 (0.5 mL)	0.1 M	110°C	9% (80% SM)
7	Br	Et_3B/O_2 (1 equiv)	2 h	benzene (1 mL)	0.1M	rt	9%
8	Br	Et_3B/O_2 (6 equiv)	2 h	benzene (1 mL)	0.1 M	rt	12% (82% SM)
9	Br	AIBN (1 equiv)	2 h	benzene (1 mL)	0.1M	80°C	2% (98% SM)
10	Br	ACCN (1 equiv)	2 h	toluene (4 mL)	0.025 M	110°C	48% (50% SM) pressure tube
11	Br	ACCN (1 equiv)	2 h	benzene (1 mL)	0.1 M	80°C	12% (88% SM)
12	Br	ACCN (1 equiv)	2 h	benzene (1 mL)	0.1 M	80°C	27% (78% SM)
13	Br	tBuOOtBu hν	2 h	benzene (0.1 mL) *tert*-butylbenzene (0.5 mL)	0.08 M	~60 °C	60% (NMR tube)
14	Br	No tBuOOtBu	2 h	benzene (0.1 mL) *tert*-butylbenzene (0.5 mL)	0.08 M	~60 °C	0%

ACCN is 1,1'-azobis(cyclohexane-1-carbonitrile)

Dr. Julien Monot also contributed to these results.



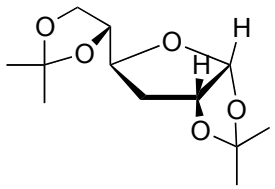
1,2:5,6-Di-*O*-isopropylidene-3-iodo-α-D-glucofuranose (5a): Iodine (0.58 g, 2.28 mmol) was added to the solution of diacetone-α-D-glucose (0.5 g, 1.9 mmol), triphenylphosphine (0.6 g, 2.28 mmol), and imidazole (0.26 g, 3.8 mmol) in of toluene (12 mL). The brown mixture was reflux for 3 h, and followed by the addition of sat'd $NaHCO_{3\ (aq)}$ (10 mL). The byphase system was partitioned between ethyl ether (70 mL) and sat'd $NaHCO_{3\ (aq)}$ solution (30 mL). The org. layer was washed with sat'd $Na_2S_2O_{3\ (aq)}$ (30 mL), water (30 mL) and brine (30 mL), dried ($MgSO_4$), and concentrated to give a yellow oil. The yellow oil was purified by flash chromatography (SiO_2, elution with hexane : ethyl acetate = 85 : 15) to give the desired iodide **5a** as a white solid (0.38 g, 54 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.82 (d, *J* = 3.6 Hz, 1H), 4.61 (t, *J* = 4.1 Hz, 1H), 4.40–4.23 (m, 2H), 4.20–4.04 (m, 2H), 3.77 (dd, *J* = 9.9, 4.5 Hz, 1H), 1.56 (s, 3H), 1.50 (s, 3H), 1.38 (s, 6H). Data correspond to those reported in the literature.[1]



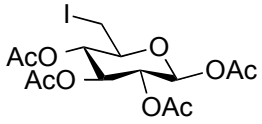
1,2:5,6-Di-*O*-isopropylidene-3-bromo-α-D-glucofuranose (5b): Carbon tetra-bromide (0.76 g, 2.28 mmol) was added to the solution of diacetone-α-D-glucose (0.5 g, 1.9 mmol), triphenylphosphine (0.6 g, 2.28 mmol), and imidazole (0.26 g, 3.8 mmol) in toluene (12 mL). The brown mixture was reflux for 3 h, and followed by the addition of sat'd $NaHCO_{3\ (aq)}$ (10 mL). The byphase system was partitioned between ethyl ether (70 mL) and 30 mL of sat'd $NaHCO_{3\ (aq)}$ solution. The org. layer was

[1] Kunz, H.; Schmidt, P. *Liebigs Ann. Chem*. **1982**, 1245–1260.

washed with sat'd $Na_2S_2O_{3\ (aq)}$ (30 mL), water (30 mL) and brine (30 mL), dried ($MgSO_4$), and concentrated to give a yellow oil. The yellow oil was purified by flash chromatography (SiO_2, elution with hexane : ethyl acetate = 8 : 2) to give the desired iodide **5b** as a white solid (0.17 g, 28 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.75 (d, *J* = 3.6 Hz, 1H), 4.62 (t, *J* = 4.1 Hz, 1H), 4.35–4.23 (m, 1H), 4.15 (dd, *J* = 9.6, 3.3 Hz), 4.11–3.95 (m, 2H), 3.83 (dd, *J* = 9.9, 4,5 Hz, 1H), 1.51 (s, 3H), 1.41 (s, 3H), 1.32 (s, 6H). Data correspond to those reported in the literature.[2]



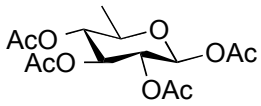
1,2:5,6-Di-*O*-isopropylidene-3-deoxy-α-D-glucofuranose (6): This was prepared by the conditions listed in Table 1 with 0.1 mmol of starting halides **5a** and **5b**; product **6** was isolated (hexane : ethyl acetate = 85 : 15, 10.0–19.3 mg, 41–79 %) as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.81 (d, *J* = 3.7 Hz, 1H), 4.75 (t, *J* = 4.2 Hz, 1H), 4.23–4.03 (m, 3H), 3.87–3.75 (m, 1H), 2.18 (dd, *J* = 13.6, 4.2 Hz, 1H), 1.76 (ddd, *J* = 13.6, 9.6, 4.2 Hz, 1H), 1.50 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H). Data correspond to those reported in the literature.[1]



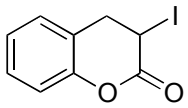
1,2,3,4-Tetra-*O*-acetyl-6-iodo-β-D-glucopyranose (9): This was prepared following the procedure that described the synthesis of **5a** with 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose (0.2 g, 0.57 mmol). The crude product was purified by flash chromatography (SiO_2, elution with hexane : ethyl acetate = 7 : 3) to give iodide **9** as a white solid (0.187 g, 72 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.75 (d, *J* = 8.1 Hz, 1H),

[2] Hodosi, G.; Podányi, B.; Kuszmann, J. *Carbohydrate Res.* **1992**, *230*, 327–342.

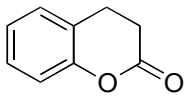
5.26 (t, *J* = 9.3 Hz, 1H), 5.13 (dd, *J* = 9.3, 8.1 Hz, 1H), 4.99 (t, *J* = 9.3 Hz, 1H), 3.65–3.51 (m, 1H), 3.33 (dd, *J* = 11.1, 3.0 Hz, 1H), 3.16 (dd, *J* = 11.1, 6.3 Hz, 1H), 2.13 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H). Data correspond to those reported in the literature.[3]



1,2,3,4-Tetra-*O*-acetyl-6-deoxy-β-D-glucopyranose (10): This was prepared by the conditions listed in Table 2 with 0.1 mmol of starting halides **9**; product **10** was isolated (hexane : ethyl acetate = 7 : 3, 22.2–23.6 mg, 67–71 %) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.68 (d, *J* = 8.1 Hz, 1H), 5.19 (t, *J* = 9.5 Hz, 1H), 5.09 (t, *J* = 9.0 Hz, 1H), 4.84 (t, *J* = 9.5 Hz, 1H), 3.78–3.63 (m, 1H), 2.14 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 3H). Data correspond to those reported in the literature.[4]



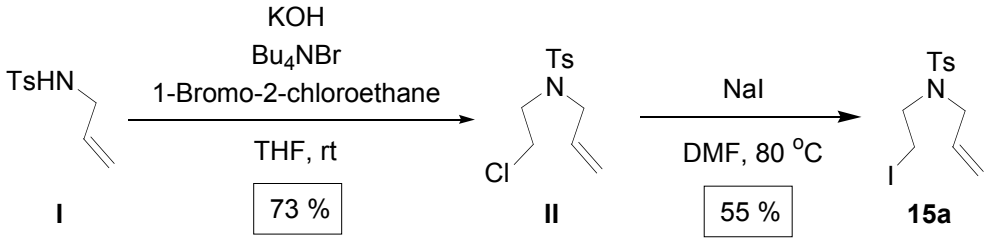
3-Iodo-3,4-dihydrocoumarin (11): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42–7.32 (m, 1H), 7.25–7.15 (m, 2H), 7.15–7.08 (m, 1H), 4.95 (dd, *J* = 4.5, 3.0 Hz, 1H), 3.49 (dd, *J* = 17.4, 4.5 Hz, 1H), 3.11 (dd, *J* = 17.4, 3 Hz, 1H). Data correspond to those reported in the literature.[5]



3,4-Dihydrocoumarin (12): A solution of 3-iodo-3,4-dihydrocoumarin **11** (27.4 mg,

[3] Kaszynski, P.; McMurdie, N. D.; Michl, J. *J. Org. Chem.* **1991**, *56*, 307–316.
[4] Zercher, C. K.; Fedor, L. R. *Carbohydrate Res.* **1987**, *165*, 299–305.
[5] Murakata, M.; Jono, T.; Shoji, T.; Moriy, A.; Shirai, Y. *Tetrahedron: Asymm.* **2008**, *19*, 2479–2483.

0.1 mmol) and dimethylimidazolylidene borane **3** (11.0 mg, 0.1 mmol) in of benzene-d_6 (1 mL) was placed in a NMR tube, and the reaction progress was monitored by ^{1}H NMR spectroscopy until the conversion of the starting material was complete. 1,3,5-Trimethoxybenzene (11.8 mg, 0.07 mmol) was added to the reaction solution as the internal standard, and the yield was determined by ^{1}H NMR spectroscopy analysis (70 %). The resulting product was purified by flash chromatography (SiO_2, pentane : ethyl ether = 8 : 2) to give **12** as a colorless oil (8.9 mg, 60 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.32–7.15 (m, 2H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 3.01 (dd, *J* = 7.5, 6.9 Hz, 2H), 2.79 (dd, *J* = 6.9, 5.4 Hz, 2H), Data correspond to those reported in the literature.[6]



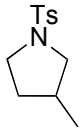
***N*-Allyl-*N*-(2-chloro-ethyl)-4-methyl-benzenesulfonamide (II)**: Tetrabutyl-ammonium bromide (0.6 mmol) was added to a solution of **I** (6.0 mmol), potassium hydroxide (9.0 mmol), and 1-bromo-2-chloroethane (9.0 mmol) in THF (30 mL). The white mixture was stirred at room temperature for 16 h, and then partitioned between ethyl ether (100 mL) and water (40 mL). The organic layer was washed with water (40 mL), brine (40 mL), dried ($MgSO_4$), and concentrated. The crude product was purified by flash chromatography (SiO_2, ethyl acetate : pentane = 1 : 9 then 2 : 8) to afford the chloride **II** as a colorless oil (1.2 g, 73 %). IR (neat, cm^{-1}) ν_{max} 2930, 1710, 1598, 1451, 1340, 1156, 1091; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.75–5.57 (m, 1H), 5.25–5.12 (m, 2H), 3.83 (d, *J* = 7.5 Hz,

[6] Hwu, J. R.; Wein, Y. S.; Leu, Y.-J. *J. Org. Chem.* **1996**, *61*, 1493–1499.

2H), 3.62 (t, J = 7.4 Hz, 2H), 3.37 (t, J = 7.4 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.4, 137.0, 133.5, 130.5, 127.9, 120.3, 52.8, 49.5, 42.4, 22.2; HRMS calcd. for $C_{12}H_{16}O_2NClNaS$ ($[M+Na]^+$) 296.0482, found 296.0483.

***N*-Allyl-*N*-(2-iodo-ethyl)-4-methyl-benzenesulfonamide (15a)**: Sodium iodide (15 mmol) was added to a solution of chloride **II** (3.0 mmol) in DMF (7 mL). The colorless solution was stirred at 80 ^{o}C for 16 h, and then cooled to room temperature. The white resulting mixture was partitioned between ethyl ether (100 mL) and water (40 mL). The organic layer was washed with water (40 mL), brine (40 mL), dried ($MgSO_4$), and concentrated. The crude product was purified by flash chromatography (SiO_2, ethyl acetate : pentane = 1 : 9) to afford the iodide **15a** as a colorless oil (0.6 g, 55 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76–7.65 (m, 2H), 7.32 (d, J = 8.5 Hz, 2H), 5.76–5.60 (m, 1H), 5.27–5.12 (m, 2H), 3.85–3.73 (m, 2H), 3.50–3.35 (m, 2H), 3.30–3.15 (m, 2H), 2.44 (s, 3H). Data correspond to those reported in the literature.[7]

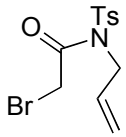
***N*-Allyl-*N*-(2-bromo-ethyl)-4-methyl-benzenesulfonamide (15b)**: Bromide **15b** was prepared following established procedures.[8,9] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 5.76–5.60 (m, 1H), 5.26–5.13 (m, 2H), 3.81 (d, J = 6.6 Hz, 2H), 3.50–3.35 (m, 4H), 2.43 (s, 3H). Data correspond to those reported in the literature.[9]



3-Methyl-1-(toluene-4-sulfonyl)-pyrrolidine (16): This was prepared by the

[7] Ohmiya, H.; Wakabayashi, K.; Yorimitsu, H.; Oshima, K. *Tetrahedron* **2006**, *62*, 2207–2213.
[8] Miyata, O.; Ozawa, Y.; Ninomiya, I.; Naito, T. *Tetrahedron* **2000**, *56*, 6199–6208.
[9] Rai, K. M. L.; Hassner, A. *Heterocycles* **1990**, *30*, 817.

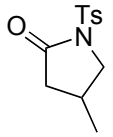
conditions listed in Table 2 with 0.1 mmol of corresponding substrate; product **16** was isolated (pentane : ethyl acetate = 9 : 1 then 8 : 2) as a colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 3.42 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.38–3.30 (m, 1H), 3.28–3.15 (m, 1H), 2.74 (dd, *J* = 9.6, 7.9 Hz, 1H), 2.43 (s, 3H), 2.16–2.05 (m, 1H), 1.95–1.80 (m, 1H), 1.42–1.28 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 3H). Data correspond to those reported in the literature.[10]



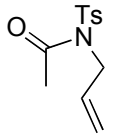
***N*-Allyl-*N*-(2-bromo-acetyl)-4-methyl-benzenesulfonamide (17)**: NaH (60 % in mineral oil) (92 mg, 2.31 mmol) was added to the solution of **I** (0.325 g, 1.54 mmol) in THF (10 mL) at room temperature in one portion, before the addition of bromoacetyl bromide (0.37 g, 1.85 mmol). The yellow mixture was stirred at room temperature for 18 h, and then the yellow reaction mixture was partitioned between of ethyl ether (70 mL) and water (30 mL). The org. layer was washed with water (30 mL), brine (30 mL), dried ($MgSO_4$), and concentrated to give a yellow oil. The yellow oil was purified by flash chromatography (SiO_2, ethyl acetate : pentane = 1 : 9) to give the desired product **17** as a colorless oil (0.25 g, 49 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 5.95–5.75 (m, 1H), 5.33–5.18 (m, 2H), 4.46 (d, *J* = 6.6 Hz, 2H), 4.23 (s, 2H), 2.46 (s, 3H). Data correspond to those reported in the literature.[11]

[10] Tang, J.; Shinokubo, H.; Oshima, K. *Tetrahedron* **1999**, *55*, 1893–1904.

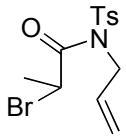
[11] Ozaki, S.; Matsushita, H.; Ohmori, H. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2339–2344.



4-Methyl-1-(toluene-4-sulfonyl)-pyrrolidin-2-one (18): This was prepared by the conditions listed in Table 2 with 0.1 mmol of **17**; product **18** was isolated (hexane : ethyl acetate = 9 : 1 then 7 : 3, 2.8–10.6 mg, 11–42 %) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.03 (dd, *J* = 9.9, 7.2 Hz, 1H), 3.41 (dd, *J* = 9.9, 6.3 Hz, 1H), 2.57 (dd, *J* = 16.6, 8.1 Hz, 1H), 2.52–2.38 (m overlapped with s at 2.44, 4H), 2.06 (dd, *J* = 16.6, 7.2 Hz, 1H), 1.09 (d, *J* = 6.6 Hz, 3H). Data correspond to those reported in the literature.[11]

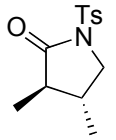


***N*-Acetyl-*N*-allyl-4-methyl-benzenesulfonamide (19)**: This was prepared by the conditions listed in Table 2 with 0.1 mmol of **17**; product **19** was isolated (hexane : ethyl acetate = 9 : 1 then 7 : 3, 6.8–14.7 mg, 27–58 %) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.98–5.80 (m, 1H), 5.33–5.20 (m, 2H), 4.46 (dt, *J* = 5.7, 1.5 Hz, 2H), 2.44 (s, 3H), 2.29 (s, 3H). Data correspond to those reported in the literature.[11]

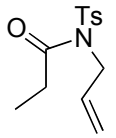


***N*-Allyl-*N*-(2-bromo-propionyl)-4-methyl-benzenesulfonamide (20)**: This was prepared following the procedure described the synthesis of **17** with **I (**1.54 mmol) and of 2-bromopropionyl bromide (1.85 mmol). The crude product was purified by flash chromatography (SiO_2, ethyl acetate : pentane = 15 : 85) to give the desired product **20** as a white solid (0.38 g, 71 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.87 (d, *J* =

8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.00–5.83 (m, 1H), 5.33–5.20 (m, 2H), 4.86 (q, *J* = 6.6 Hz, 1H), 4.70 (dd, *J* = 17.4, 4.2 Hz, 1H), 4.41 (dd, *J* = 17.4, 5.4 Hz, 1H), 2.45 (s, 3H), 1.74 (d, *J* = 6.6 Hz, 3H). Data correspond to those reported in the literature.[12]



***trans*-3,4-Dimethyl-1-(toluene-4-sulfonyl)-pyrrolidin-2-one (*trans*-21)**: This was prepared by the conditions listed in Table 2 with 0.1 mmol of **20**; product **21** was isolated (hexane : ethyl acetate = 9 : 1 then 7 : 3, 6.8–14.7 mg, 36–44 %) as a colorless oil. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 3.98 (dd, *J* = 9.3, 7.5 Hz, 1H), 3.28 (t, *J* = 9.6 Hz, 1H), 2.40 (s, 3H), 2.22–2.10 (m, 1H), 2.03–1.85 (m, 1H), 1.03 (d, *J* = 6.3 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H). Data correspond to those reported in the literature.[12]



***N*-Allyl-4-methyl-*N*-propionyl-benzenesulfonamide (22)**: Following corresponding conditions with 0.1 mmol of **20**, a mixture of compounds **22**, **I**, and rest of the AIBN was isolated (hexane : ethyl acetate = 9 : 1 then 7 : 3) as a colorless oil. The percent yield of amide **22** was determined by ^{1}H NMR spectroscopy analysis as 17–28 %. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.98–5.82 (m, 1H), 5.33–5.20 (m, 2H), 4.48 (d, *J* = 8.4 Hz, 2H), 2.56 (q, *J* = 7.3 Hz, 2H), 2.45 (s, 3H), 1.04 (t, *J* = 7.3 Hz, 3H). Data correspond to those reported in the literature.[12]

[12] Ozaki, S.; Matsushita, H.; Emoto, M.; Ohmori, H. *Chem. Pharm. Bull.* **1995**, *43*, 32–36.

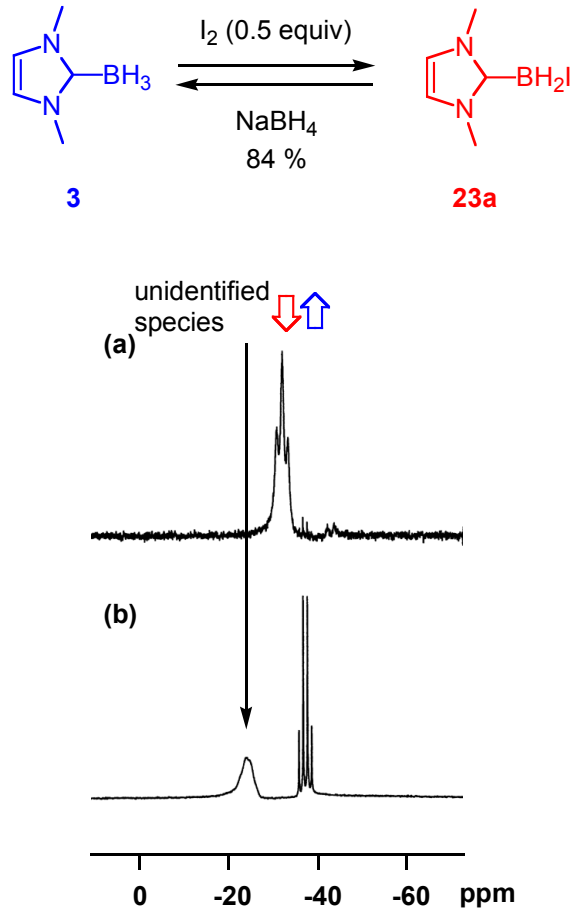


Figure S1. Partial ^{11}B NMR spectra [96.3 MHz, Benzene-d_6, 298 K] displaying (a-b) the formation of the 1,3-dimethylimidazol-2-ylidene borane **3** from monoiodide intermediate **23a** under the treatment with $NaBH_4$ over time—(a) 0 min, (b) 30 min, after addition of 2 equiv of $NaBH_4$.

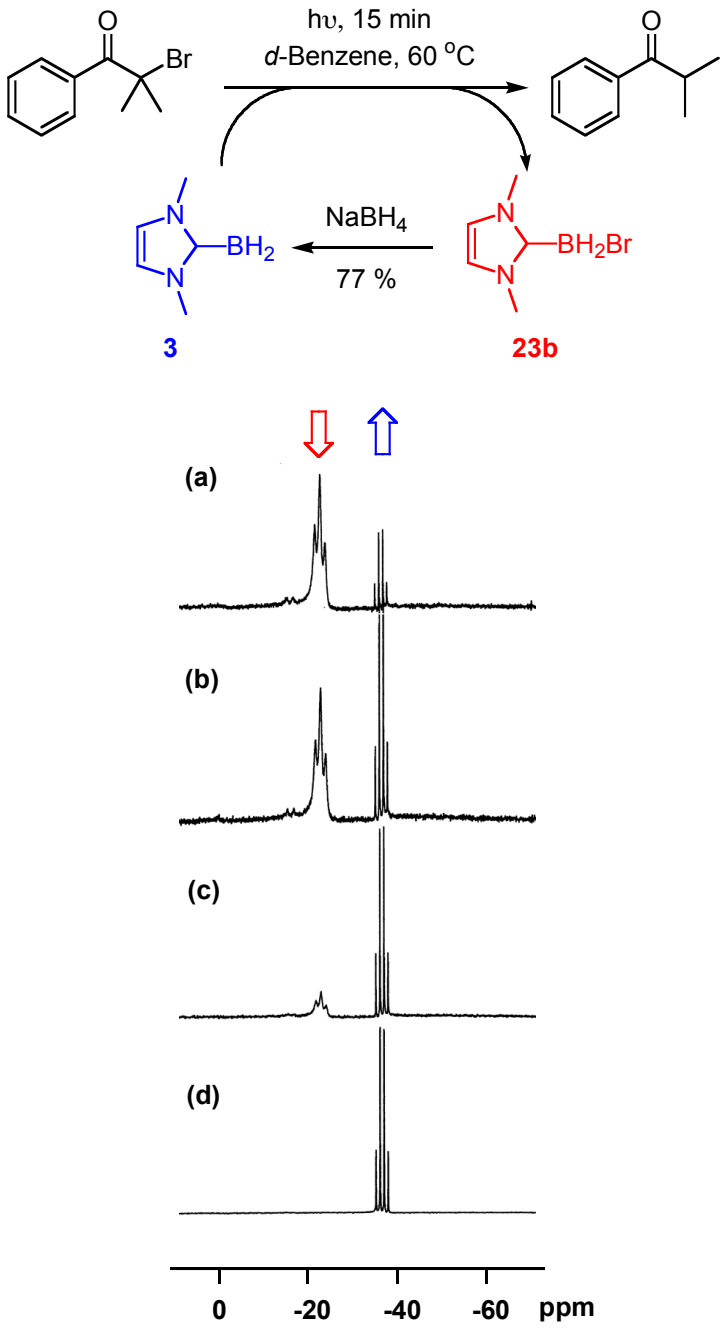
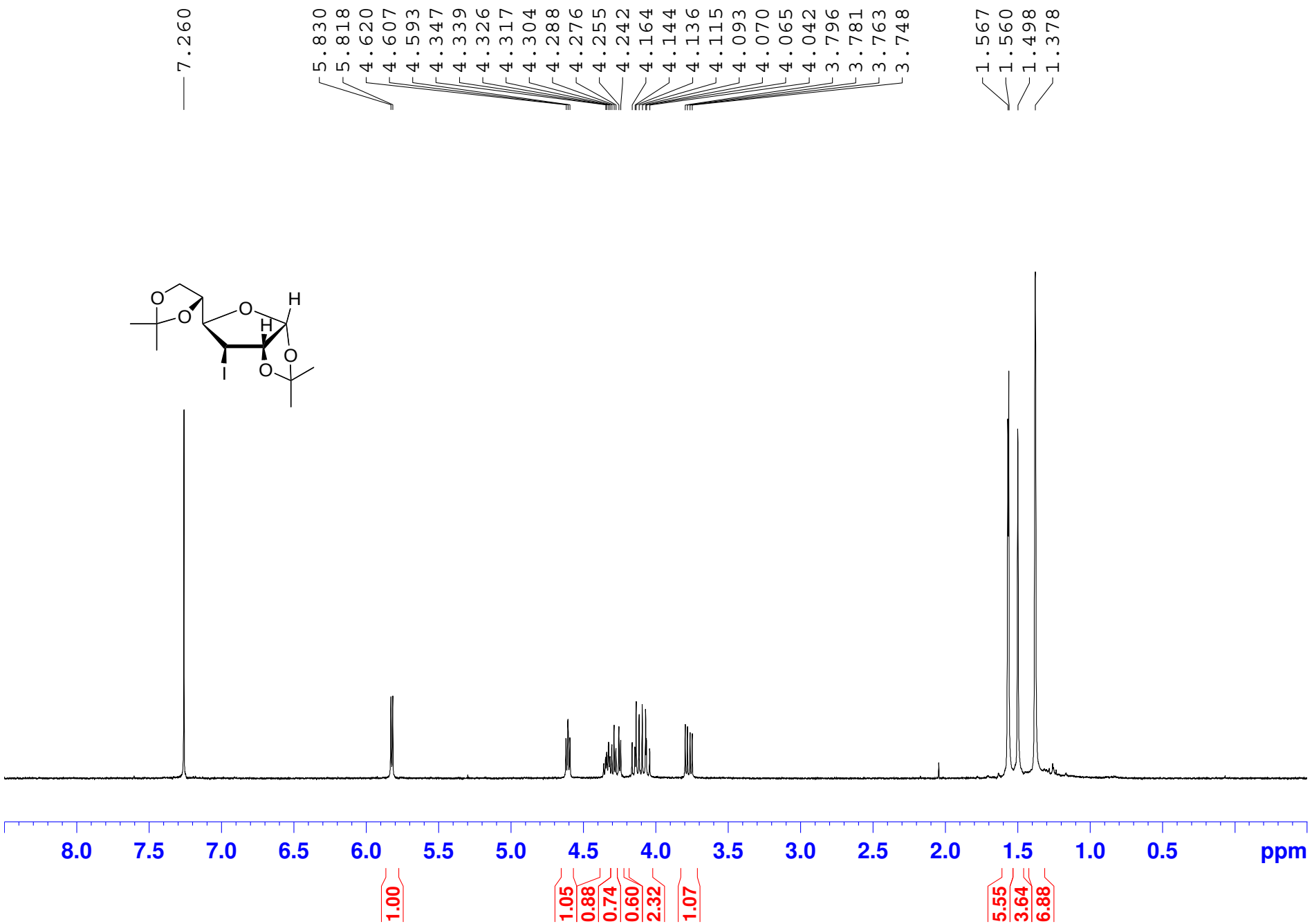
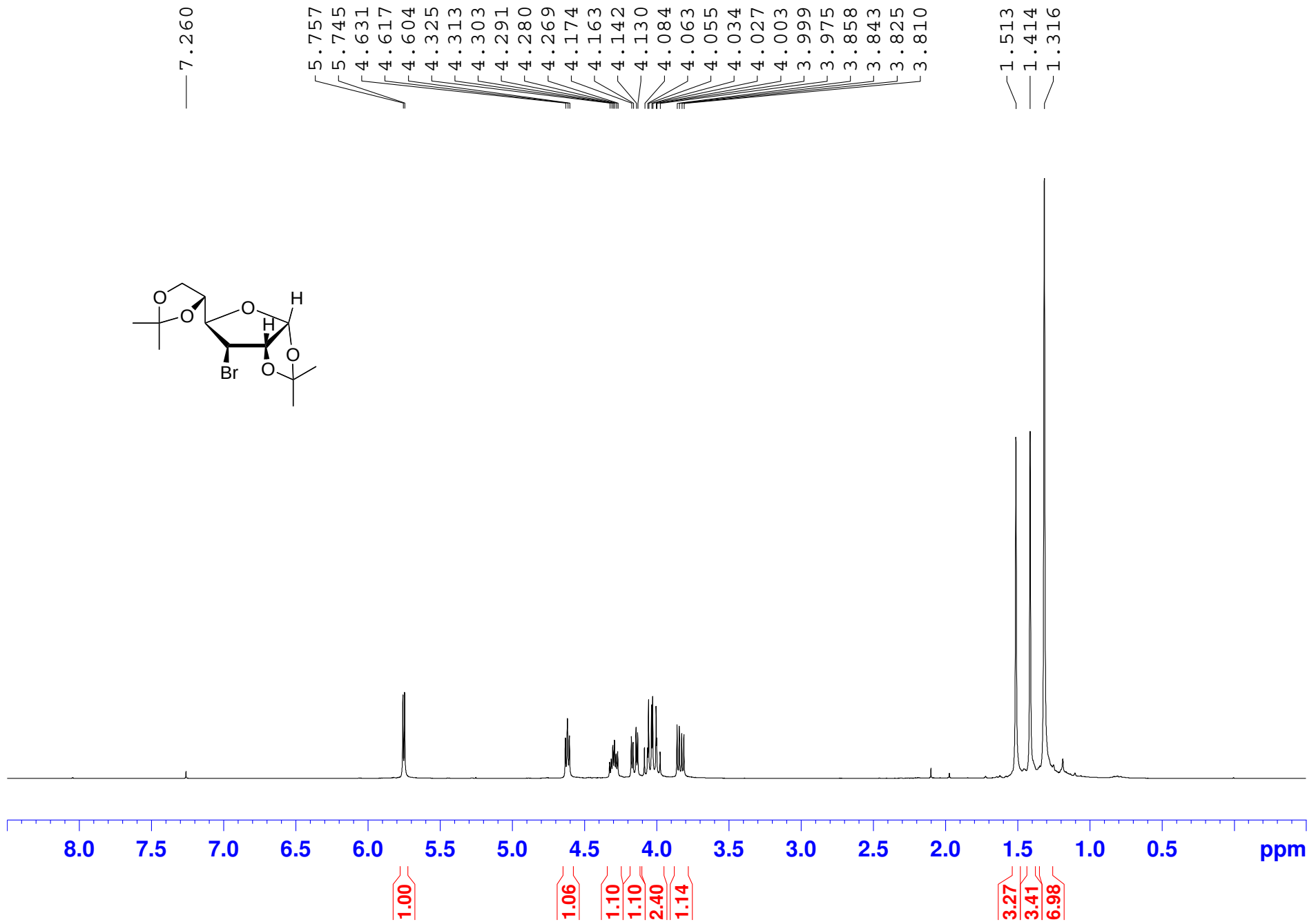


Figure S2. Partial ^{11}B NMR spectra [96.3 MHz, Benzene-d_6, 298 K] displaying (a-d) the formation of the 1,3-dimethylimidazol-2-ylidene borane **3** from monobromide intermediate **23b** under the treatment with $NaBH_4$ over time and the loading scale of $NaBH_4$—(a) 0 min, after irradiation for 15 min (b) 10 min, 0.5 equiv of $NaBH_4$ (c) 20 min, 1.5 equiv of $NaBH_4$, and (d) 180 min, 2 equiv of $NaBH_4$.

shu2099b, 08-19-09, 301b



shu2100a, 08-20-09, 301b



shu20140a, 06-25-09, 301b

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4.144
4.130
4.126
4.114
4.112
4.103
4.086
4.071
4.065
3.845
3.831
3.823
3.816
3.806
3.798
3.777
2.205
2.192
2.160
2.146
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1.789
1.772
1.760
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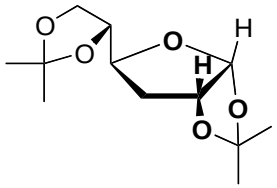

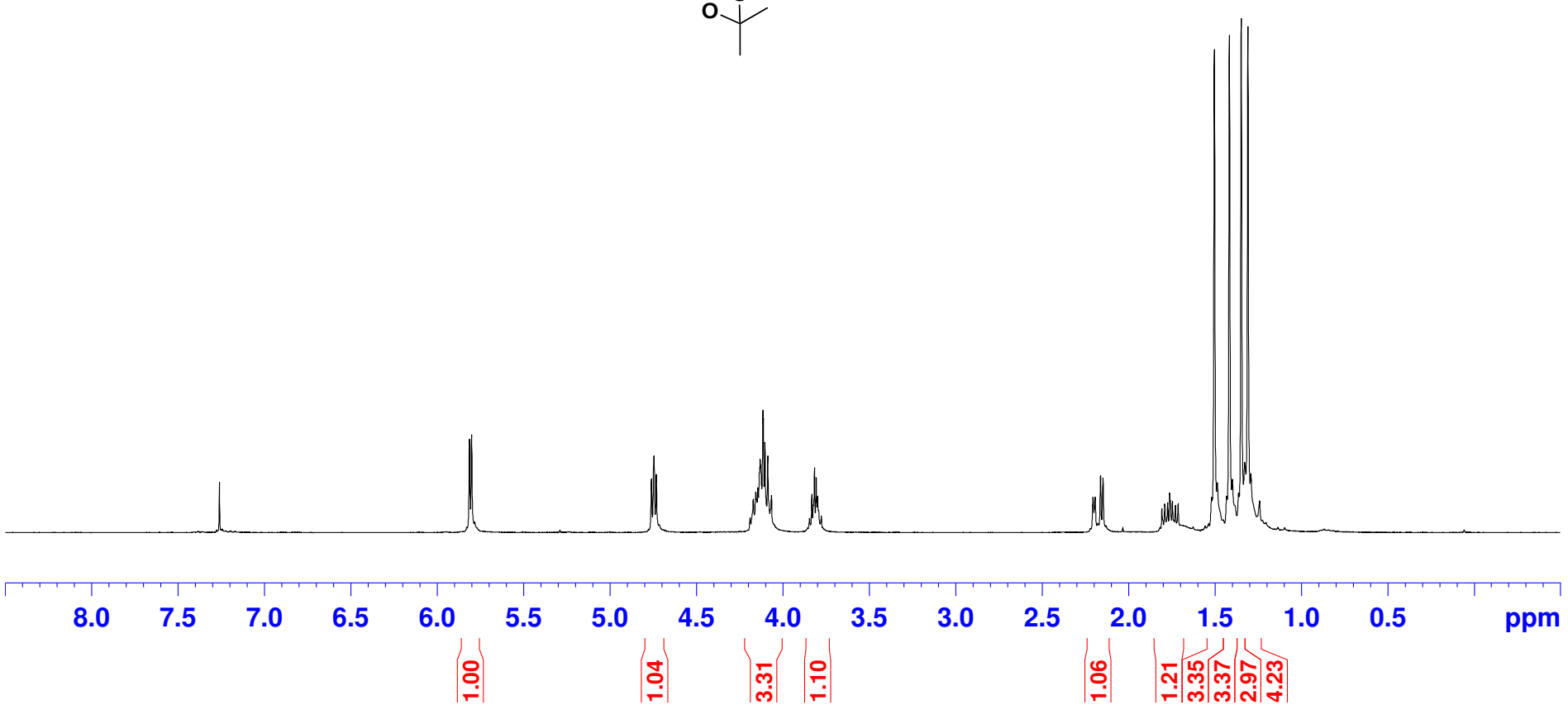

shu3 05ar, e1-0e-09, s01a

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5.102
5.019
4.988
4.957
3.597
3.587
3.576
3.566
3.555
3.544
3.534
3.349
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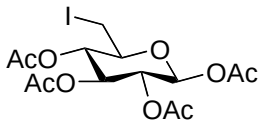

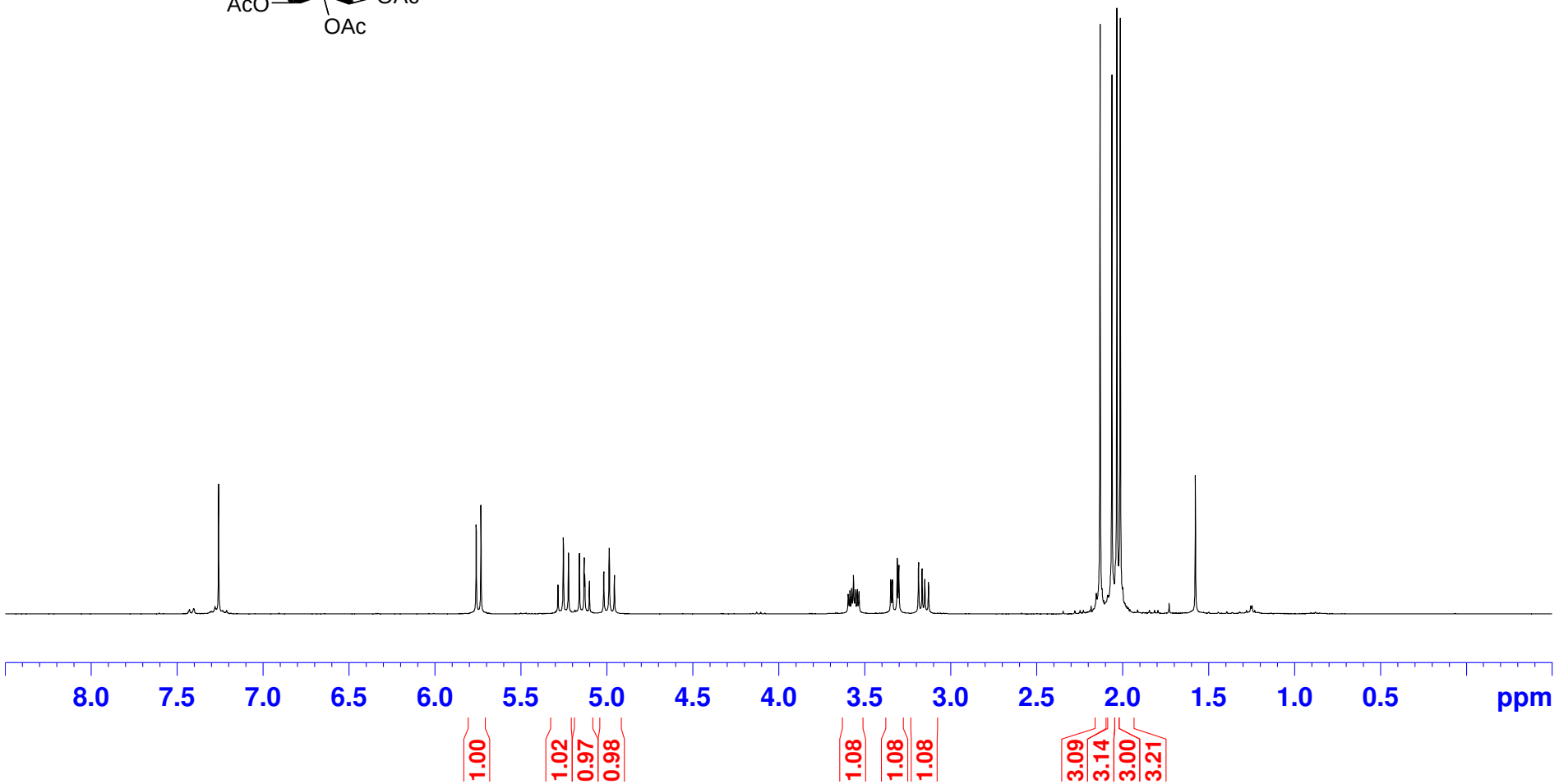

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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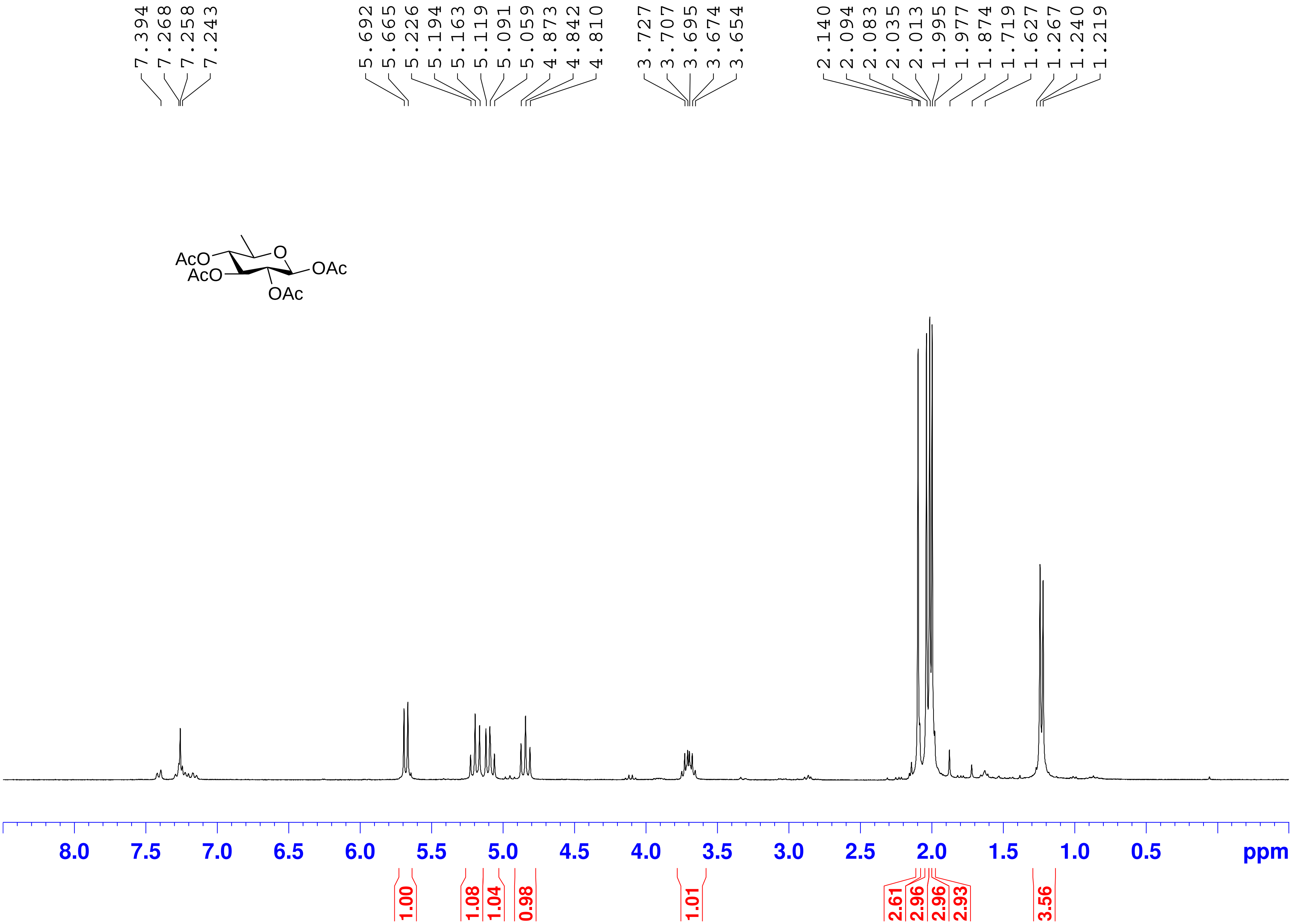
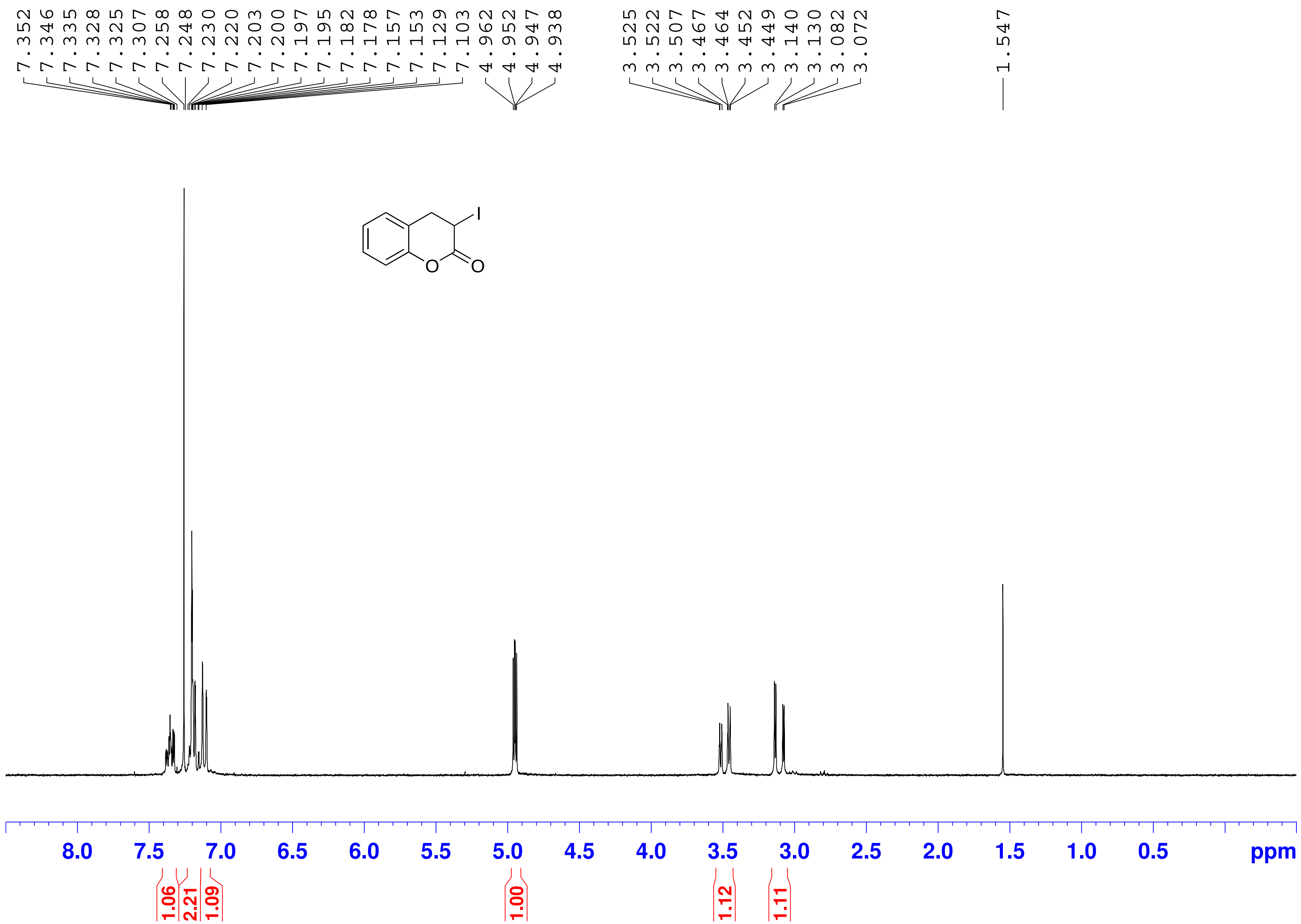


Supplementary Material (ESI) for Organic & Biomolecular Chemistry



shu3094ar, 12-02-09, s01a

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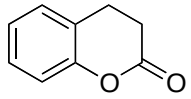
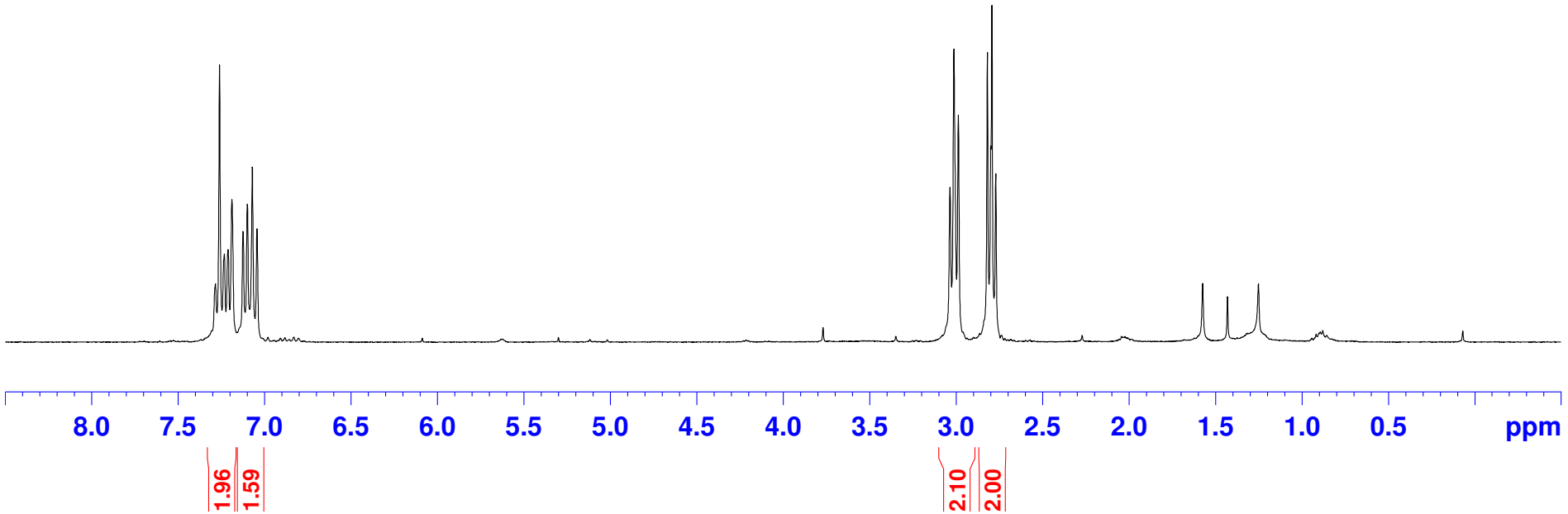
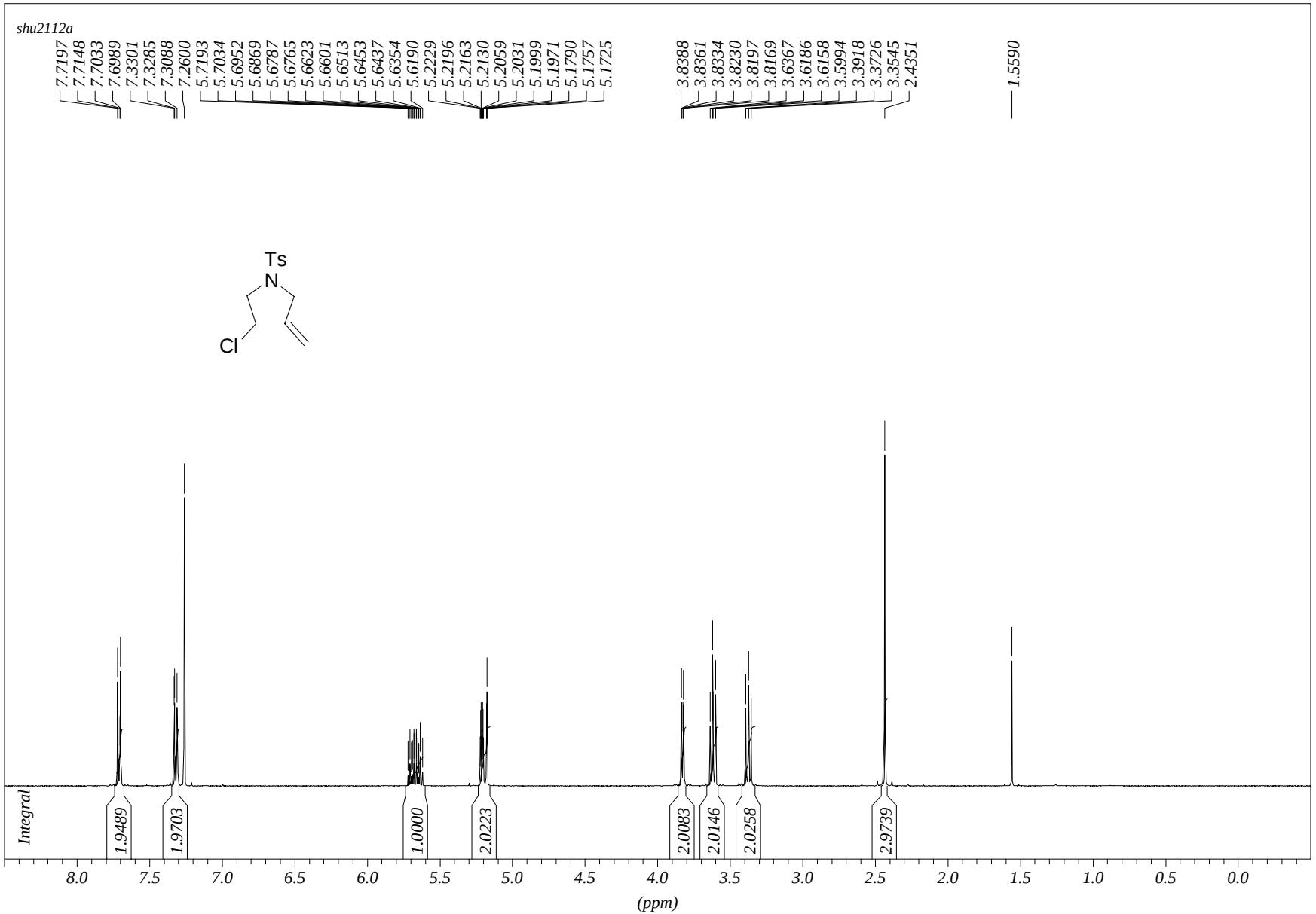
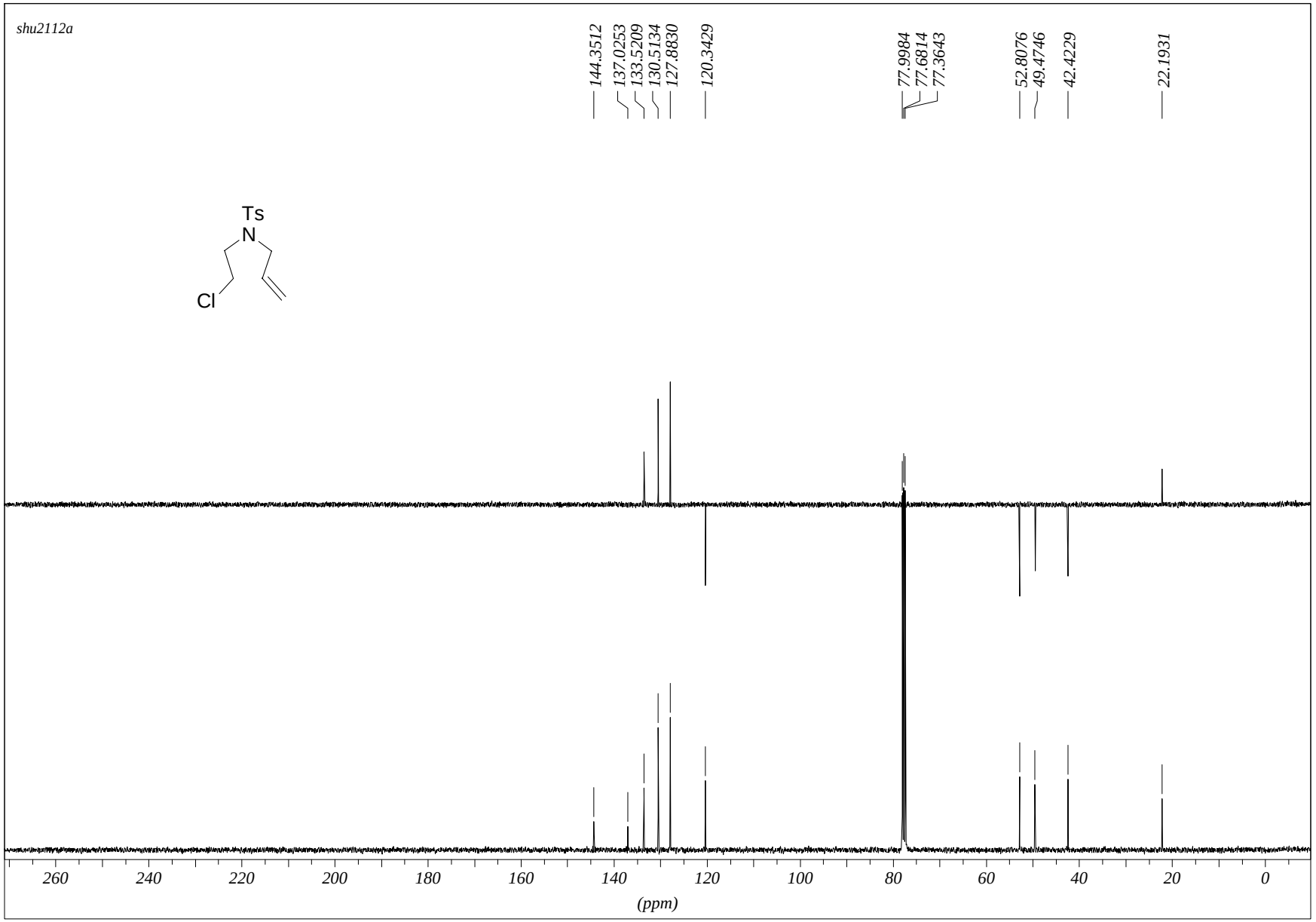
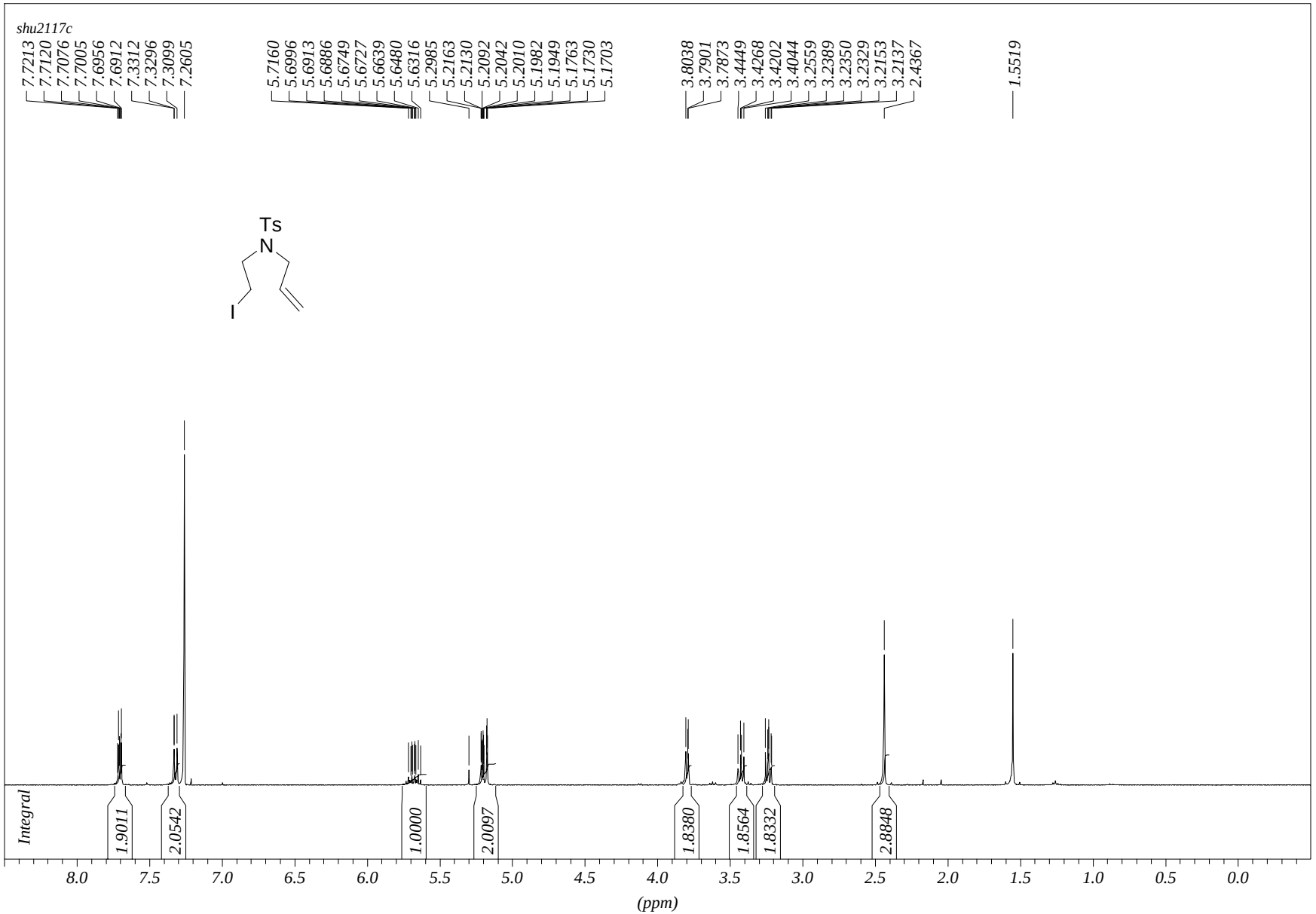
1.252







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5.6996
5.6913
5.6886
5.6749
5.6727
5.6639
5.6480
5.6316
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5.2163
5.2130
5.2092
5.2042
5.2010
5.1982
5.1949
5.1763
5.1730
5.1703
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3.7901
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3.4202
3.4044
3.2559
3.2389
3.2350
3.2329
3.2153
3.2137
2.4367
1.5519
Ts
N
I
Integral
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1.0000
2.0097
1.8380
1.8564
1.8332
2.8848
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7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
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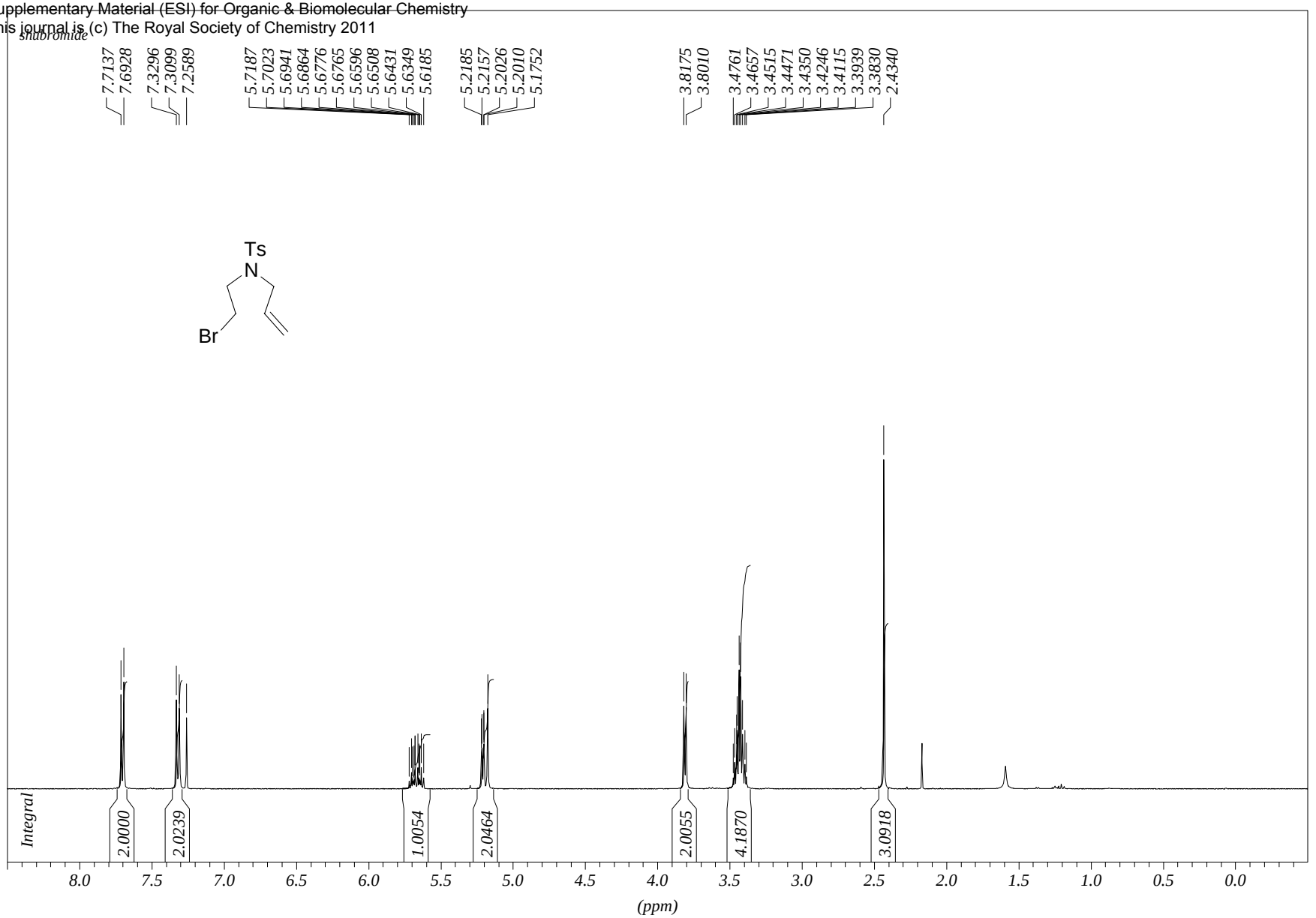
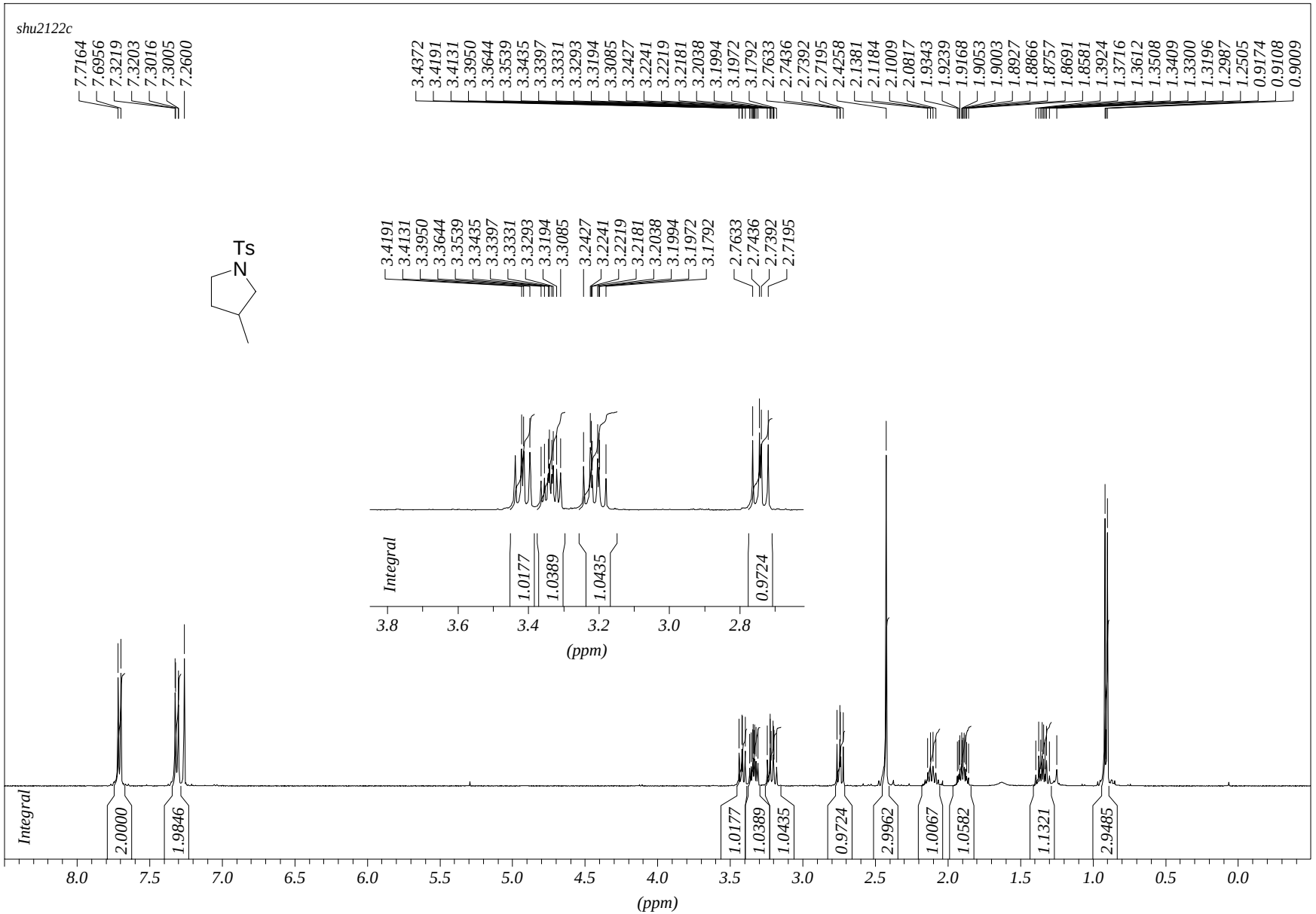
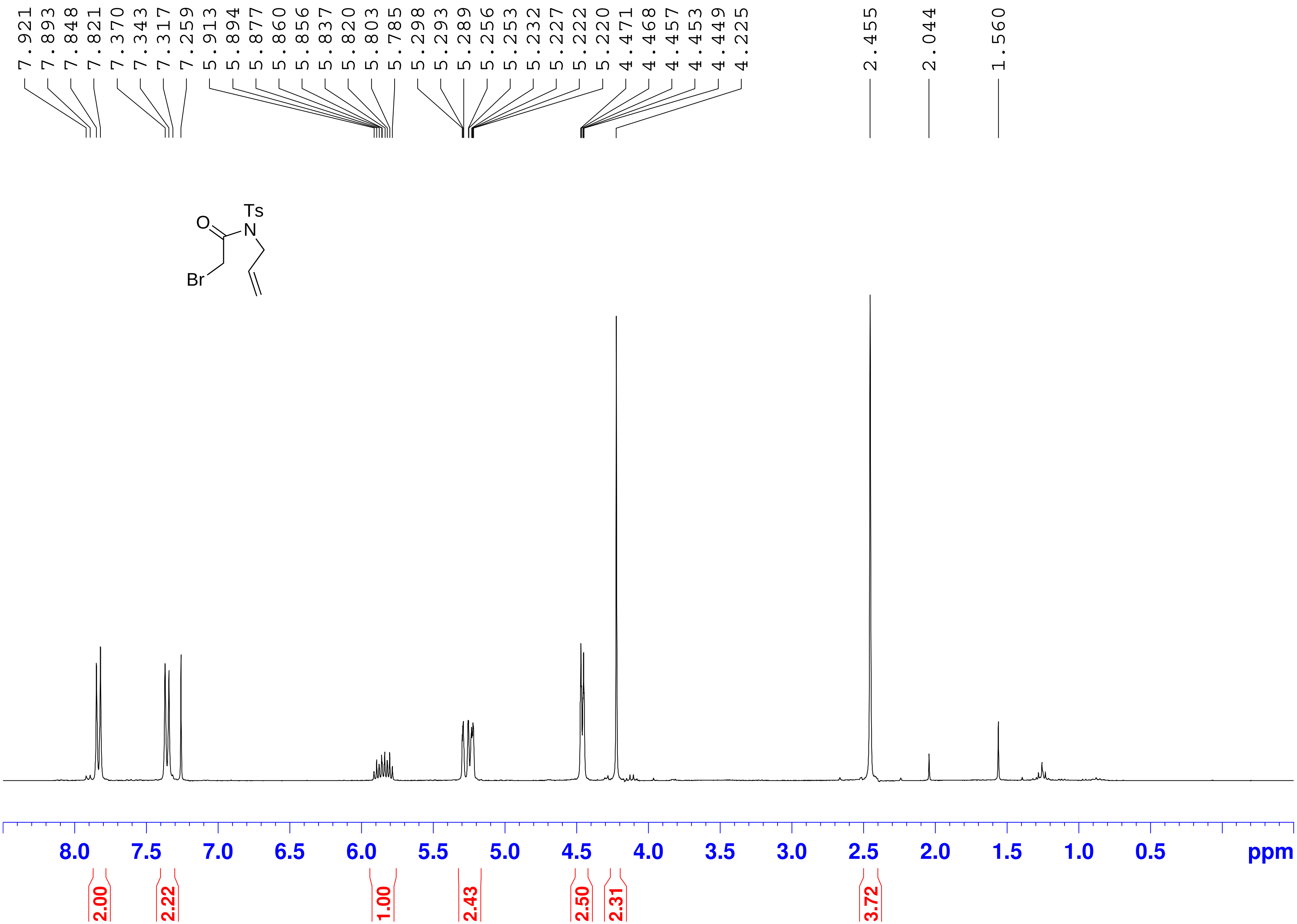
(ppm)




shu2122c
Ts
N
Integral
(ppm)



shu310409, 12-09-09, 501

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7.319
7.260

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4.030
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3.629
3.437
3.416
3.404
3.383
2.607
2.580
2.551
2.525
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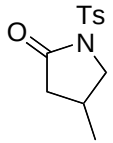

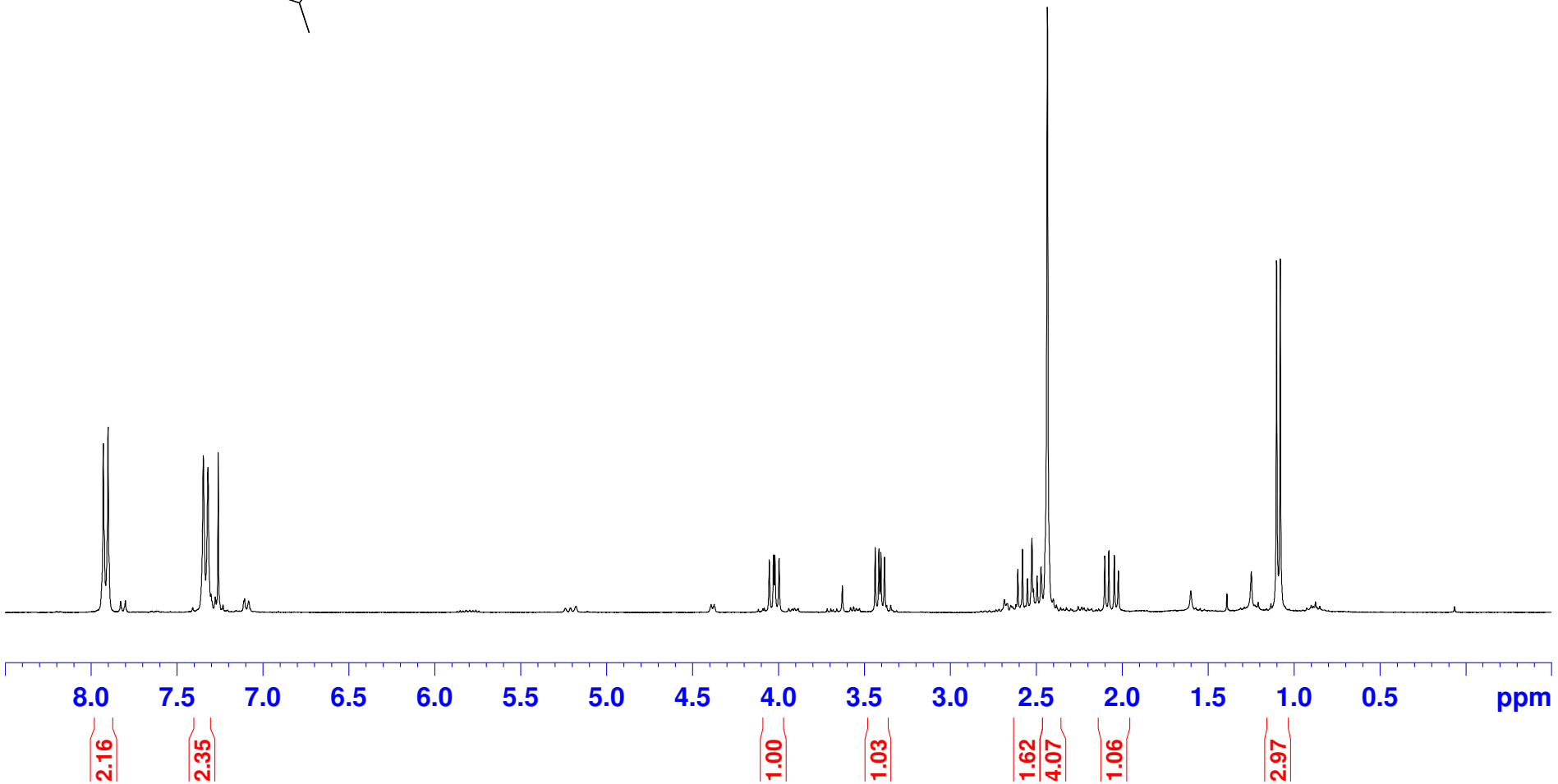

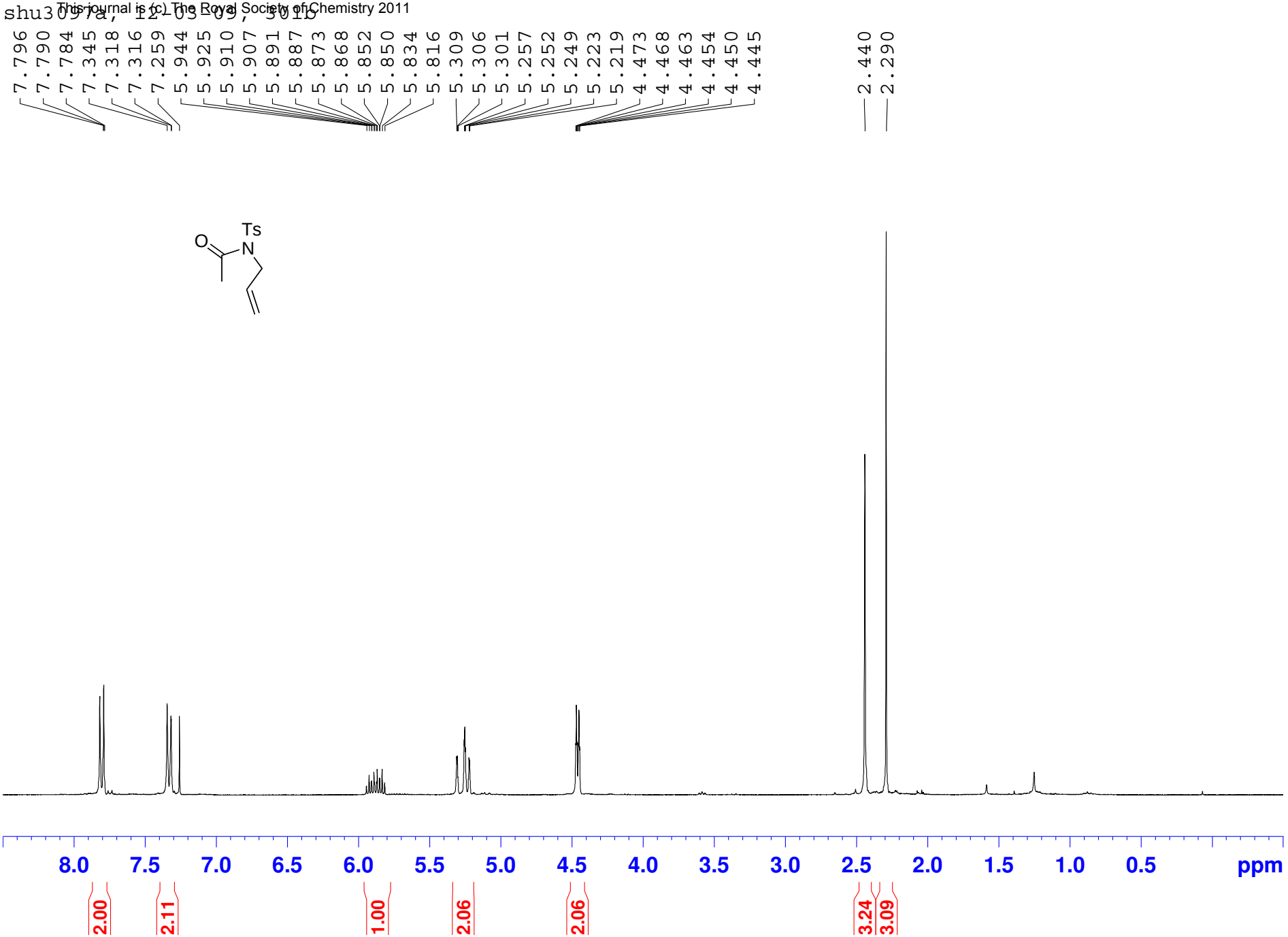

shu3044c, 11-12-09, 301a

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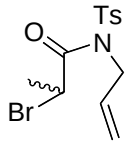

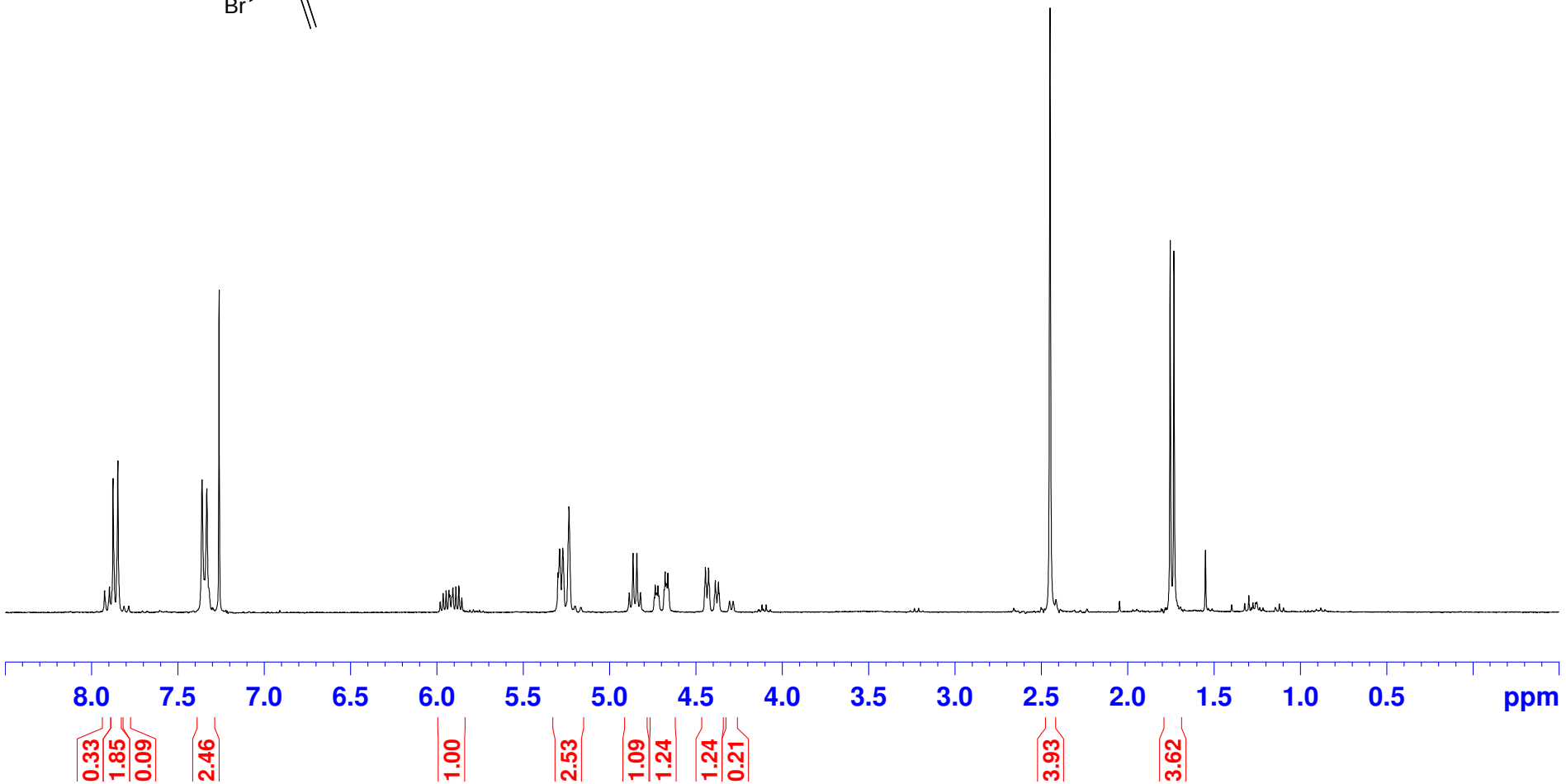

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0.33 1.85 0.09 2.46 1.00 2.53 1.09 1.24 1.24 0.21 3.93 3.62