Ionic liquid supported tin reagents for Stille cross coupling reactions

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Supplemental Information

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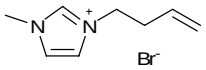
Experimental

1. General

All moisture-sensitive reactions were carried out in oven-dried glassware (100°C) under N_2. Commercially available reagents and solvents were purified and dried, when necessary, by standard methods just prior to use. IR spectra were scanned on a Nicolet Avatar 370 DTGS FTIR spectrophotometer. Melting points were recorded using a Leica DMLS microscope equipped with a heating system and are uncorrected. Melting points for the ionic liquids were recorded on a TA Instruments Q100 DSC Differential Scanning Calorimeter. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) or a Bruker DPX-200 (200 MHz) spectrometer. Chemical shifts are reported in ppm. TMS was used as the internal standard for $CDCl_3$, DSS was used for D_2O. Data are reported as follows: chemical shift, multiplicity (bs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, ps = pseudo quartet, quin = quintet, sex = sextet, sep = septet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) with complete proton decoupling. Elemental analyses were obtained from the Service de Microanalyse, CNRS ICSN, Gif-sur-Yvette. High-resolution mass measurements were performed at the CRMPO, Rennes. Analytical thin layer chromatography was performed on pre-coated silica gel 60-F_{254} plates. For preparative chromatography silica gel 60 (230-400 mesh) was used.

2. Synthesis of Ionic Liquids

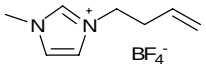
1-But-3-enyl-3-methyl-1*H*-imidazolium bromide (2a)



In a 100 mL round-bottom flask, 1-methylimidazole (**1**) (1.03 g, 12.5 mmol) was mixed with 4-bromobutene (2.00 g, 15.0 mmol) and stirred over night at 40°C. After cooling to ambient temperature, the residue was extracted thoroughly 2-3 times (50 ml each) with diethyl ether to remove traces of starting materials. A clear yellow viscous oily liquid of 1-but-3-enyl-3-methyl-1*H*-imidazolium bromide (**2b**) was obtained (2.64 g, 12.1 mmol, 97%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 2.70 (pq, ^3J = 6.8 Hz, 2H, 2'-H), 4.11 (s, 3H, NCH_3), 4.47 (t, ^3J = 6.8 Hz, 2H, 1'-H), 5.09–5.11 (m, 1H, 4'-H_a), 5.14 (bs, 1H, 4'-H_b), 5.77–5.87 (m, 1H, 3'-H), 7.46 (s, 1H, 4-H, 4-H/5-H), 7.49 (s, 1H, 4-H, 4-H/5-H), 10.40 (s, 1H, 2-H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 34.3 (CH_2), 36.7 (NCH_3), 49.1 (CH_2), 119.6 (C-4'), 122.4 (CH), 122.6 (CH), 132.3 (CH), 137.2 (C-2); **^{1}H NMR** (200 MHz, D_2O): δ [ppm] = 2.61 (pq, ^3J = 6.7

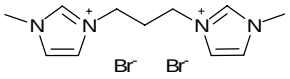
Hz, 2H, 2'-H), 3.87 (s, 3H, NCH_3), 4.28 (t, ^3J = 6.7 Hz, 2H, 1'-H), 5.00–5.12 (m, 2H, 4'-H), 5.70–5.91 (m, 1H, 3'-H), 7.41 (s, 1H, 4-H/5-H), 7.47 (s, 1H, 4-H/5-H), 8.69 (s, 1H, 2-H); **IR** (neat): 3138, 3061, 2980, 2852, 1639, 1568, 1437, 1338, 1165, 997, 924, 825, 752 cm^{-1}.

1-But-3-enyl-3-methyl-1*H*-imidazolium tetrafluoroborate (3a)



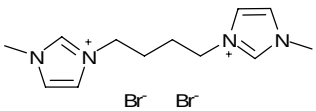
The ionic liquid **2b** (1.93 g, 8.89 mmol) was dissolved in acetone (10 ml) and stirred with $NaBF_4$ (1.0 g, 9.11 mmol) at room temperature for 24 h to exchange the anion. The reaction mixture was filtered off to remove precipitated KBr and excess $NaBF_4$. The acetone was evaporated on rotary evaporator under reduced pressure and the product was vacuum dried to give **3b** in 98% yield (2.09 g, 8.80 mmol). **^{1}H NMR** (200 MHz, D_2O): δ [ppm] = 2.62 (pq, ^3J = 6.7 Hz, 2H, 2'-H), 3.88 (s, 3H, NCH_3), 4.29 (t, ^3J = 6.7 Hz, 2H, 1'-H), 5.01–5.13 (m, 2H, 4'-H), 5.71–5.92 (m, 1H, 3'-H), 7.42 (s, 1H, 4-H/5-H), 7.48 (s, 1H, 4-H/5-H), 8.71 (s, 1H, 2-H).

3-Methyl-1-[3-(3-methyl-1*H*-imidazolium-1-yl)propyl]-1*H*-imidazolium dibromide (2b)[1]



In a 100 mL round-bottom flask, 1-methylimidazole (**1**) (5.0 g, 60.9 mmol) was mixed with 1,3-dibromopropane (12.3 g, 60.9 mmol) and stirred for 3 hours at 50°C. After cooling to ambient temperature, the residue was extracted thoroughly with diethyl ether (20 mL) and with ethyl acetate (2 × 20 mL) to remove traces of starting materials. A yellow waxy solid of the ionic liquid **2c** was obtained (8.34 g, 29.4 mmol, 96%). **^{1}H NMR** (200 MHz, D_2O): δ [ppm] = 2.41–2.62 (m, 2H, CH_2), 3.94 (s, 6H, 2 × NCH_3), 4.40 (t, ^3J = 7.3 Hz, 4H, 2 × CH_2), 7.51 (s, 2H, 2 × 4-H/5-H), 7.58 (s, 2H, 2 × 4-H/5-H), 8.86 (s, 2H, 2 × 2-H).

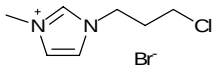
3-Methyl-1-[4-(3-methyl-1*H*-imidazolium-1-yl)butyl]-1*H*-imidazolium dibromide (2c)[2]



In a 100 mL round-bottom flask, 1-methylimidazole (**1**) (5.15 g, 62.7 mmol) was mixed with 1,4-dibromobutane (13.54 g, 62.7 mmol) and stirred over night at 50°C. After cooling to ambient temperature, the residue was extracted thoroughly 3 times with ethyl acetate (20 mL) to remove traces of starting materials. A brownish waxy solid of the ionic liquid **2d** was obtained (11.58 g, 30.5 mmol, 97%). **^{1}H NMR** (200 MHz, D_2O): δ [ppm] = 1.83–2.08 (m,

4H, 2 × CH_2), 3.89 (s, 6H, 2 × CH_3), 4.25 (m, 4H, 2 × CH_2), 7.44 (s, 2H, 2 × 4-H/5-H), 7.49 (s, 2H, 2 × 4-H/5-H), 8.74 (s, 2H, 2 × 2-H).

1-(3-chloropropyl)-1*H*-imidazolium bromide (2d)[3]



1-methylimidazole (**1**) (1.00 g, 12.2 mmol) was mixed with 1-bromo-3-chloropropane (1.90 g, 12.2 mmol) and stirred over night at 50°C. The mixture was cooled to room temperature and then extracted thoroughly 3 times with ethyl ether (10 mL) to remove traces of starting materials. The product **2e** was obtained as colorless viscous oil (2.86 g, 11.9 mmol, 98%). **^{1}H NMR** (200 MHz, D_2O): δ [ppm] = 2.30–2.62 (m, 2H, 3'-H), 3.63 (t, ^3J = 6.7 Hz, 2H, 1'-H), 3.92 (s, 3H, NCH_3), 4.32–4.45 (m, 2H, 2'-H), 7.49–7.54 (m, 2H, 4-H, 5-H), 8.81 (s, 1H, 2-H); **^{1}H NMR** (200 MHz, acetone-d_6): δ [ppm] = 2.48–2.57 (m, 2H, 3'-H), 3.76-3.84 (m, 2H, 2'-H), 4.13 (s, 3H, NCH_3), 4.63–4.72 (m, 2H, 1'-H), 7.83–7.99 (m, 2H, 4-H, 5-H), 10.19 (bs, 1H, 2-H); **IR** (neat): 3402, 3142, 3066, 2955, 1633, 1572, 1454, 1427, 1167, 829, 754 cm^{-1}.

3. Synthesis of organo tin compounds

Dibutyldiphenyltin[4]

To a solution of Bu_2SnCl_2 (5.00 g, 16.46 mmol) in THF (15 mL), the Grignard reagent solution of PhMgBr (3 mol/L, 36.00 mmol, 12 mL) was added dropwise over a period of 1 h. The solution was refluxed for an additional hour and the excess of Grignard reagent was hydrolyzed with HCl (5 mL, 0.1 M). The aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with H_2O (3 × 10 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product was purified by column chromatography (petroleum ether) to yield Bu_2SnPh_2 (5.04 g, 79 %). **^{1}H NMR** (200 MHz, $CDCl_3$): δ [ppm] = 0.87 (t, 6H, ^3J = 7.2 Hz, CH_3), 1.11–1.74 (m, 12H, CH_2), 7.31–7.61 (m, 10H, H_{aryl}); **IR** (neat): 3063, 2955, 2922, 2870, 2850, 1462, 1427, 1375, 1074, 1022, 997, 725, 696, 656 cm^{-1}.

Dibutylphenyltin chloride[4]

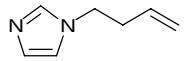
Dibutyldiphenyltin (3.70 g, 9.55 mmol) was diluted in Et_2O (15 mL). A solution of HCl (5.40 mL at 1.95 mol/L in Et_2O) was diluted in Et_2O (15 mL) and then added dropwise at 0–5°C over a period of 30 min. The mixture was stirred for an additional hour at room temperature, and H_2O (20 mL) was poured in. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield $Bu_2SnPhCl$ as colorless oil (2.92 g, 8.45 mmol, 88%). **^{1}H NMR** (200 MHz, $CDCl_3$): δ [ppm] = 0.92 (t, 6H, ^3J = 7.3 Hz,

CH_3), 1.25–1.78 (m, 12H, CH_2), 7.31–7.62 (m, 5H, H_{aryl}); **IR** (neat): 3066, 2956, 2922, 2870, 2852, 1464, 1429, 1377, 1074, 997, 876, 727, 696, 669 cm^{-1}.

Dibutylphenyltin hydride[4]

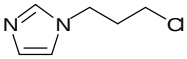
Dibutylphenyltin chloride (2.90 g, 8.39 mmol) was dissolved in Et_2O (90 mL). The flask was purged with N_2 and a solution of $NaBH_4$ (1.60 g, 42.00 mmol) dissolved in H_2O (20 mL) was added dropwise at 0–8°C over a period of 45 min. The mixture was stirred for additional 45 min at room temperature. Then, the organic phase was washed with H_2O (2 × 50 mL), dried over $MgSO_4$, filtered, and concentrated under vacuum to yield $PhBu_2SnH$ as a colorless oil (2.39 g) which was again dissolved in Et_2O (20 mL), filtered, and concentrated to remove precipitated salts (1.91 g, 73%). **^{1}H NMR** (200 MHz, $CDCl_3$): δ [ppm] = 0.91 (t, 6H, ^3J = 7.3 Hz, CH_3), 1.30–1.83 (m, 12H, CH_2), 5.28 (bs, 1H, Sn-H), 7.30–7.67 (m, 5H, H_{aryl}); **IR** (neat): 3063, 2955, 2918, 2870, 2850, 1819 (Sn-H), 1464, 1427, 1375, 1074, 864, 727, 696, 673 cm^{-1}.

Synthesis of 1-(But-3-enyl)-1*H*-imidazole (5a)[5]



To a solution of imidazole (**4a**) (0.51 g, 7.4 mmol) in THF (15 mL) sodium hydride (0.300 g, 7.4 mmol, 60% in oil) was added at 0°C. The mixture was stirred for an additional 1 h at room temperature, then 4-bromobut-1-ene (1.00 g, 7.4 mmol) was added to this solution and stirred for 24 h. Dichloromethane was added (60 mL) and the organic phase was washed with H_2O (20 mL), brine (10 mL), dried over $MgSO_4$, and filtered. Then the solvent was evaporated under reduced pressure. The crude product was finally purified by column chromatography on silica gel (CH_2Cl_2:MeOH: Et_2O = 90:5:5) to obtain the product **5a** as a yellow liquid (0.50 g, 4.1 mmol, 55%). **^{1}H NMR** (200 MHz, $CDCl_3$): δ [ppm] = 2.52 (q, ^3J = 6.7 Hz, 2H, 2'-H), 4.00 (t, ^3J = 6.7 Hz, 2H, 1'-H), 5.00–5.08 (m, 1H, 4'$_\alpha$-H), 5.12 (bs, 1H, 4'$_\beta$-H), 5.63–5.84 (m, 1H, 3'-H), 6.92 (s, 1H, 4-H/5-H), 7.05 (s, 1H, 4-H/5-H), 7.47 (s, 1H, 2-H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 35.3 (CH_2), 46.4 (CH_2), 118.1 (CH_2), 118.7 (CH), 129.3 (CH), 133.5 (CH), 137.0 (CH); **IR** (neat): 3111, 2937, 1641, 1508, 1456, 1439, 1360, 1282, 1228, 1107, 1078, 1036, 995, 914, 816, 737, 663 cm^{-1}.

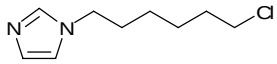
1-(3-chloropropanyl)-1*H*-imidazole (5b)[3,6]



To a solution of sodium hydride (95%, 1.23 g, 51.3 mmol) in THF (30 mL), a solution of imidazole (**4a**) (3.00 g, 44.1 mmol) in THF (40 mL) was added slowly at 0°C. The mixture

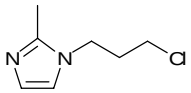
was stirred for 45 min at room temperature. 1-Bromo-3-chloropropane (6.94 g, 4.4 ml, 44.1 mmol) was added slowly to the reaction mixture, which was further on stirred for 2 days. Then the mixture was filtered, and the filtrate was evaporated under reduced pressure to yield **5b** (5.24 g, 36.2 mmol, 82%), which was not purified further. **^{1}H NMR** (200 MHz, $CDCl_3$): δ [ppm] = 2.14–2.31 (m, 2H, 2'-H), 3.48 (t, ^3J = 6.0 Hz, 2H, 3'-H), 4.17 (t, ^3J = 6.4 Hz, 2H, 1'-H), 6.94 (s, 1H, 4-H/5-H), 7.08 (s, 1H, 4-H/5-H), 7.53 (s, 1H, 2-H); **IR** (neat): 2970, 2929, 1699, 1508, 1448, 1362, 1300, 1228, 1217, 1178, 1146, 916, 816, 739, 662 cm^{-1}.

1-(6-chlorohexyl)-1*H*-imidazole (5c)[7]



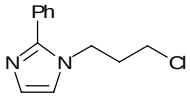
To a solution of sodium hydride (95%, 0.41 g, 16.2 mmol) in THF (20 mL), a solution of imidazole (**4a**) (1.00 g, 14.7 mmol) in THF (30 mL) was added slowly at 0°C. The mixture was stirred for 45 min at room temperature. 1-Bromo-6-chlorohexane (2.93 g, 2.2 ml, 14.7 mmol) was added slowly to the reaction mixture, which was further on stirred for 4 days. Then the mixture was filtered, and the filtrate was evaporated under reduced pressure to yield **5c** (2.64 g, 14.2 mmol, 96%), which was not purified further. **^{1}H NMR** (200 MHz, $CDCl_3$): δ [ppm] = 1.27–1.55 (m, 4H, 2 × CH_2), 1.69–1.87 (m, 4H, 2 × CH_2), 3.52 (t, ^3J = 6.5 Hz, 2H, 6'-H), 3.94 (t, ^3J = 7.0 Hz, 2H, 1'-H), 6.90 (s, 1H, 4-H/5-H), 7.06 (s, 1H, 4-H/5-H), 7.46 (s, 1H, 2-H); **IR** (neat): 2933, 2858, 1506, 1450, 1282, 1228, 1109, 1076, 1030, 906, 816, 733, 663, 646, 625 cm^{-1}; **MS** (EI) for $C_9H_{15}ClN_2$: 187 $[M+H]^+$, 159, 137, 124, 96, 82, 55, 39; **MS** (CI, CH_3CN) for $C_9H_{15}ClN_2$: 187 $[M+H]^+$.

1-(3-chloropropanyl)-1*H*-2-methylimidazole (5d)[8]



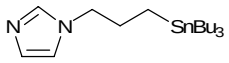
According to the previous described procedure preparing **5a**, 2-methylimidazole (**4b**) (2.00 g, 24.4 mmol) and 1-bromo-3-chloropropane (3.84 g, 2.4 ml, 24.4 mmol) afforded after purification by chromatography on silica gel (CH_2Cl_2:MeOH:Et_2O = 90:5:5) **5d** as a pale yellow liquid (2.80 g, 17.7 mmol, 73%, R_f = 0.2). **^{1}H NMR** (200 MHz, $CDCl_3$): δ [ppm] = 2.17 (m, 2H, 2'-H), 2.41 (s, 3H, CH_3), 3.50 (t, ^3J = 5.9 Hz, 2H, 3'-H), 4.05 (t, ^3J = 6.6 Hz, 2H, 1'-H), 6.85 (s, 1H, 4-H/5-H), 6.93 (s, 1H, 4-H/5-H); **IR** (neat): 3103, 2951, 2928, 1524, 1498, 1421, 1363, 1275, 1147, 1078, 982, 729, 675, 663 cm^{-1}.

1-(3-chloropropanyl)-1*H*-2-phenylimidazole (5e)[9,10]



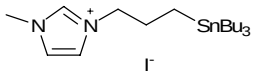
According to the previous described procedure preparing **5a**, 2-phenylimidazole (**4c**) (1.80 g, 12.5 mmol) and 1-bromo-3-chloropropane (1.97 g, 1.2 ml, 12.5 mmol) afforded after purification by chromatography on silica gel (CH_2Cl_2:MeOH:Et_2O = 90:5:5) **5e** as a yellow liquid (1.79 g, 8.1 mmol, 65%, R_f = 0.2). **^{1}H NMR** (200 MHz, $CDCl_3$): δ [ppm] = 2.14 (m, 2H, 2'-H), 3.45 (t, ^3J = 6.1 Hz, 2H, 3'-H), 4.23 (t, ^3J = 6.9 Hz, 2H, 1'-H), 7.05 (s, 1H, 4-H/5-H), 7.12 (s, 1H, 4-H/5-H), 7.45 (m, 3H, H_{aryl}), 7.58 (m, 2H, H_{aryl}); **IR** (neat): 3103, 3063, 2958, 1498, 1471, 1443, 1416, 1273, 1124, 1074, 1018, 914, 770, 696, 642 cm^{-1}.

Synthesis of 1-[3-(tributylstannyl)propyl]-1*H*-imidazole (6a)



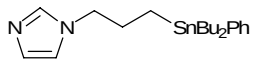
To a solution of lithium diisopropylamide (3.60 mmol) in dry THF (20 mL), tributyltin hydride (1.00 g, 3.44 mmol) was slowly added at -78°C. The resulting mixture was stirred for 1 h at -50°C and subsequently added to a solution of 1-(3-chloropropanyl)-1*H*-imidazole (**5b**) (0.45 g, 3.44 mmol) in dry THF (10 mL) at -50°C. Then the mixture was allowed to warm up to room temperature and stirred for 18 h. Water was slowly added and the mixture was stirred for additional 15 min at room temperature. To this mixture CH_2Cl_2 (50 mL) was added and the organic phase was successively washed with H_2O (2 × 20 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude product (1.28 g) was then purified by column chromatography (silica gel: 20 g, solvent: CH_2Cl_2, CH_2Cl_2/MeOH 98:2, to CH_2Cl_2/MeOH/ether 96:2:2) to yield the product **6a** as an oily colorless liquid (0.741 g, 1.86 mmol, 54%, R_f (CH_2Cl_2/MeOH = 98:2) = 0.1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 0.66–0.70 (m, 2H, CH_2), 0.81–0.90 (m, 15H, CH_2, CH_3), 1.24–1.49 (m, 12H, CH_2), 1.87–1.95 (m, 2H, 2'-H), 3.88 (t, ^3J = 7.1 Hz, 2H, 1'-H), 6.90 (s, 1H, 4-H/5-H), 7.06 (s, 1H, 4-H/5-H), 7.47 (s, 1H, 2-H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 5.1 (C-3'), 8.7 (C-1''), 13.7 (C-4''), 27.3 (C-3''), 28.9 (C-2'), 29.2 (C-2''), 50.9 (C-1'), 118.7 (C-4), 129.4 (C-5), 137.2 (C-2); **IR** (neat): 2953, 2922, 2870, 2850, 1504, 1460, 1375, 1279, 1227, 1109, 1074, 1034, 960, 906, 806, 727, 662 cm^{-1}; **HRMS** calculated for $C_{18}H_{37}N_2{}^{120}Sn$ $[M+H]^+$ 401.19787, found 401.1981 (1 ppm).

1-[3-(tributylstannyl)propyl]-3-methylimidazolium iodide (7a)



In a dried pressure reaction tube, 1-[3-(tributylstannyl)propyl]-1*H*-imidazole (**6a**) (160 mg, 0.40 mmol) was dissolved in methyl iodine (1 mL) and stirred over night at 40°C. The mixture was cooled down to room temperature and the excess methyl iodine was evaporated under reduced pressure. A clear yellow viscous liquid of 1-[3-(tributylstannyl)propyl]-3-methylimidazolium iodide (**7a**) was obtained (216 mg, 0.39 mmol, 99%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 0.65–0.70 (m, 2H, CH_2), 0.84–0.91 (m, 15H, CH_2, CH_3), 1.27–1.49 (m, 12H, CH_2), 2.00–2.04 (m, 2H, 2'-H), 4.15 (s, 3H, NCH_3), 4.27 (t, ^{3}J = 7.2 Hz, 2H, 1'-H), 7.27 (s, 1H, 4-H/5-H), 7.44 (s, 1H, 4-H/5-H), 10.14 (s, 1H, 2-H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 4.5 (C-3'), 8.8 (C-1''), 13.7 (CH_3, C-4''), 27.3 (C-3''), 28.2 (C-2'), 29.1 (C-2''), 37.1 (NCH_3), 53.8 (C-1'), 121.7 (C-4), 123.8 (C-5), 136.9 (C-2); **IR** (neat): 3074, 2953, 2922, 2848, 1570, 1456, 1375, 1167, 1072, 1016, 864, 746, 665, 619, 503 cm^{-1}; **HRMS** calculated for $C_{19}H_{39}N_2{}^{120}Sn$ [C^+] 415.21352, found 415.2140 (1 ppm).

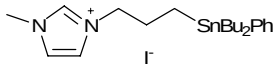
Synthesis of 1-{3-[dibutyl(phenyl)stannyl]propyl}-1*H*-imidazole (6b)



To a solution of lithium diisopropylamide (4.5 mmol) in dry THF (20 mL), dibutylphenyltin hydride (1.37 g, 4.4 mmol) was slowly added at -78°C. The resulting mixture was stirred for 1 h at -50°C and subsequently added to a solution of 1-(3-chloropropanyl)-1*H*-imidazole (**5b**) (0.60 g, 4.1 mmol) in dry THF (15 mL) at -50°C. Then the mixture was allowed to warm up to room temperature and stirred for 18 h. Water was slowly added and the mixture was stirred for additional 15 min at room temperature. To this mixture CH_2Cl_2 (50 mL) was added and the organic phase was successively washed with H_2O (2 × 20 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude product (1.78 g) was then purified by column chromatography (silica gel: 20 g, solvent: CH_2Cl_2, CH_2Cl_2/MeOH 98:2, CH_2Cl_2/MeOH/ether 96:2:2) to yield the liquid product **6b** as a mixture with the starting material **5b** (1.70 g, 67% product, 33% starting material). The mixture was directly used in the next reaction step. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 0.88 (t, ^{3}J = 7.3 Hz, 6H, 4''-H), 1.01–2.00 (m, 16H, CH_2), 3.86 (t, ^{3}J = 7.2 Hz, 2H, 1'-H), 6.84 (s, 1H, 4-H/5-H), 7.04 (s, 1H, 4-H/5-H), 7.28–7.42 (m, 6H, 2-H, H_{aryl}); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 5.8 (C-3'), 9.4 (C-1''), 13.6 (C-4''), 27.3 (C-2''), 28.7 (C-2'), 29.0 (C-3''), 50.6 (C-1'), 118.7 (CH), 128.2 (CH), 128.3 (CH), 129.3 (CH), 136.3 (CH), 137.1 (CH), 140.6 (C_{quart});

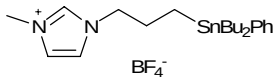
IR (neat): 2955, 2924, 2870, 2850, 1504, 1462, 1427, 1375, 1281, 1227, 1107, 1074, 906, 808, 725, 698, 662 cm^{-1}; **HRMS** calculated for $C_{20}H_{32}N_2Na^{120}Sn$ $[M+Na]^+$ 443.14852, found 443.1482 (1 ppm).

1-{3-[dibutyl(phenyl)stannyl]propyl}-3-methyl-1*H*-imidazolium iodide (7b)



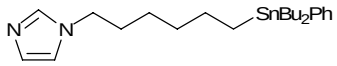
In a dried pressure reaction tube, crude 1-{3-[dibutyl(phenyl)stannyl]propyl}-1*H*-imidazole (**6b**) (1.68 g) was dissolved in methyl iodine (1 mL) and stirred over night at 45°C. The mixture was cooled down to room temperature and the excess methyl iodine was evaporated under reduced pressure. A CH_2Cl_2/ethyl acetate/ether mixture was added and the organic phase was washed with water to remove the ionic liquid side product received from the starting material still existing in the last step, then separated, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield **7b** (0.99 g, 1.8 mmol, 44%, two steps, mp -53.4°C*) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 0.89 (t, ^3J = 7.2 Hz, 6H, 4''-H), 1.11–1.57 (m, 14H, CH_2), 2.03–2.11 (m, 2H, 2'-H), 4.09 (s, 3H, NCH_3), 4.23 (t, ^3J = 7.2 Hz, 2H, 1'-H), 7.04 (m, 1H, 4-H/5-H), 7.30 (m, 1H, 4-H/5-H), 7.33–7.44 (m, 5H, H_{aryl}), 10.11 (s, 1H, 2-H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 5.4 (C-3'), 9.5 (C-1''), 13.7 (C-4''), 27.3 (C-2''), 28.1 (C-2'), 29.0 (C-3''), 37.1 (NCH_3), 53.3 (C-1'), 121.7 (C-4), 123.7 (C-5), 128.4 (C-3'''), 128.5 (C-4'''), 136.5 (C-2'''), 136.8 (C-2), 140.4 (C-1'''); **IR** (neat): 3061, 2953, 2922, 2868, 2850, 1568, 1456, 1425, 1375, 1167, 1072, 1020, 864, 727, 700, 656, 617 cm^{-1}; **HRMS** calculated for $C_{21}H_{35}N_2{}^{120}Sn$ $[C^+]$ 435.18222, found 435.1825 (1 ppm).

1-{3-[dibutyl(phenyl)stannyl]propyl}-3-methyl-1*H*-imidazolium tetrafluoroborate (8b)



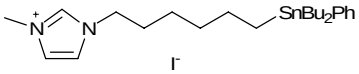
The ionic liquid **7b** (0.93 g, 1.66 mmol) was dissolved in acetone (20 ml) and stirred with $NaBF_4$ (1.3 g, 11.8 mmol) at room temperature for 24 h to exchange the anion. The reaction mixture was filtered off to remove precipitated KBr and excess $NaBF_4$. The acetone was evaporated and the product was dried under vacuum to give **8b** as a colorless liquid (0.86 g, 1.65 mmol, 99%). **^{1}H NMR** (200 MHz, $CDCl_3$): δ [ppm] = 0.89 (t, ^3J = 7.2 Hz, 6H, 4''-H), 1.09–1.60 (m, 14H, CH_2), 1.86–2.12 (m, 2H, 2'-H, CH_2), 4.07 (s, 3H, NCH_3), 4.22 (t, ^3J = 7.3 Hz, 2H, 1'-H), 7.02 (s, 1H, 4-H/5-H), 7.25 (s, 1H, 4-H/5-H), 7.32–7.46 (m, 5H, H_{aryl}), 10.05 (s, 1H, 2-H).

1-{6-[dibutyl(phenyl)stannyl]hexyl}-1*H*-imidazole (6c)



To a solution of lithium diisopropylamide (11.1 mmol) in dry THF (40 mL), dibutylphenyltin hydride (3.45 g, 11.1 mmol) was slowly added at -78°C. The resulting mixture was stirred for 1 h at -50°C and subsequently added to a solution of 1-(6-chlorohexanyl)-1*H*-imidazole (**5c**) (1.57 g, 8.5 mmol) in dry THF (20 mL) at -50°C. Then the mixture was allowed to warm up to room temperature and stirred for 18 h. Water was slowly added and the mixture was stirred for additional 15 min at room temperature. To this mixture CH_2Cl_2 (100 mL) was added and the organic phase was successively washed with H_2O (20 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude product (4.69 g) was then purified by column chromatography (silica gel with solvent: CH_2Cl_2 to CH_2Cl_2/MeOH (98:2) to CH_2Cl_2/MeOH/ether (96:2:2)) to yield the pure product **6c** as a colorless oil (2.86 g, 6.2 mmol, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 0.88 (t, ^3J = 7.2 Hz, 6H, 4''-H), 0.89–1.07 (m, 5H, CH_2), 1.27–1.37 (m, 8H), 1.50–1.57 (m, 5H), 1.64 (bs, 2H, CH_2), 1.68–1.75 (m, 2H, CH_2), 3.87 (t, ^3J = 7.2 Hz, 2H, 1'-H), 6.87 (s, 1H, 4-H/5-H), 7.05 (s, 1H, 4-H/5-H), 7.29–7.45 (m, 6H, 2-H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 9.5 (CH_2), 9.6 (CH_2), 13.7 (CH_3), 26.0 (CH_2), 26.6 (CH_2), 27.4 (CH_2), 29.1 (CH_2), 31.0 (CH_2), 33.7 (CH_2), 47.0 (CH_2), 118.8 (CH), 128.0 (CH), 128.1 (C_{quart}), 129.3 (CH), 136.5 (CH), 137.1 (CH), 141.8 (C-2); **IR** (neat): 2955, 2922, 2850, 1504, 1462, 1427, 1282, 1228, 1074, 808, 725, 698, 662 cm^{-1}.

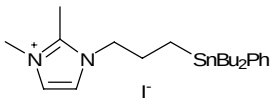
1-{6-[dibutyl(phenyl)stannyl]hexyl}-3-methyl-1*H*-imidazolium iodide (7c)



In a dried pressure reaction tube, crude 1-{3-[dibutyl(phenyl)stannyl]propyl}-1*H*-imidazole (**6c**) (1.02 g, 2.2 mmol) was dissolved in methyl iodine (0.5 mL) and stirred over night at 40°C. The mixture was cooled down to room temperature and the excess methyl iodine was evaporated under reduced pressure to yield **7c** (1.33 g, 2.2 mmol, 99%, mp -64.7°C*) as a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 0.88 (t, ^3J = 7.2 Hz, 6H, 4''-H,), 0.98–1.57 (m, 20H, CH_2), 1.83–1.90 (m, 2H, CH_2), 4.11 (s, 3H, NCH_3), 4.25 (t, ^3J = 7.5 Hz, 2H, 1'-H), 7.20 (s, 1H, 4-H, 5-H), 7.29–7.46 (m, 6H, 4-H/5-H, H_{aryl}), 10.17 (s, 1H, 2-H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 9.4 (CH_2), 9.5 (CH_2), 13.6 (CH_3), 25.6 (CH_2), 26.5 (CH_2), 27.3 (CH_2), 29.0 (CH_2), 30.1 (CH_2), 33.5 (CH_2), 37.1 (NCH_3), 50.1 (NCH_2), 121.8 (CH), 123.6 (CH), 128.0 (CH), 136.4 (CH), 136.8 (CH), 136.8 (CH), 141.7 (C_{quart}); **IR** (neat):

3061, 2953, 2922, 2848, 1568, 1462, 1427, 1375, 1165, 1072, 862, 727, 700, 656 cm^{-1}; **HRMS** calculated for $C_{24}H_{41}N_2{}^{120}Sn$ [C^+] 477.22917, found 477.2296 (1 ppm).

1-{3-[dibutyl(phenyl)stannyl]propyl}-2-methyl-1*H*-imidazole (6d) and
1-{3-[dibutyl(phenyl)stannyl]propyl}-2,3-dimethyl-1*H*-imidazolium iodide (7d)

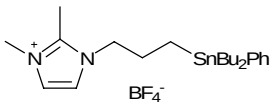


To a solution of lithium diisopropylamide (4.5 mmol) in dry THF (50 mL), dibutylphenyltin hydride (4.14 g, 13.3 mmol) was slowly added at -78°C. The resulting mixture was stirred for 1 h at -50°C and subsequently added to a solution of 1-(3-chloropropanyl)-1*H*-2-methylimidazole (**5d**) (2.11 g, 13.3 mmol) in dry THF (30 mL) at -50°C. Then the mixture was allowed to warm up to room temperature and stirred for 18 h. Water was slowly added and the mixture was stirred for additional 15 min at room temperature. To this mixture CH_2Cl_2 (50 mL) was added and the organic phase was successively washed with H_2O (20 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude product of **6d** was directly used in the next reaction step. **^{1}H NMR** (200 MHz, $CDCl_3$): δ [ppm] = 0.89 (t, ^3J = 7.2 Hz, 6H, CH_3), 1.04–2.00 (m, 16H, CH_2), 2.32 (s, 3H, CH_3), 3.76 (t, ^3J = 7.2 Hz, 2H, 1'-H), 6.75 (s, 1H, 4-H/5-H), 6.89 (s, 1H, 4-H/5-H), 7.31–7.44 (m, 5H, H_{aryl}); **IR** (neat): 3061, 2955, 2924, 2850, 1498, 1462, 1425, 1375, 1275, 1146, 1072, 982, 862, 725, 700, 673 cm^{-1}.

In a dried pressure reaction tube, the crude product **6d** was mixed with methyl iodine (1 mL) and stirred over night at room temperature. CH_2Cl_2 was added and the organic phase was washed with water, separated and concentrated under reduced pressure. The crude product was than dissolved in Et_2O and again washed with water to remove the ionic liquid side product received from the starting material still existing in the last step. Then the organic phase was separated, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield 1-{3-[dibutyl(phenyl)stannyl]propyl}-2,3-dimethyl-1*H*-imidazolium iodide (**7d**) (2.4 g, 4.2 mmol, 32%, two steps, mp 105.5°C*) as a viscous yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 0.89 (t, ^3J = 7.3 Hz, 6H, 4''-H), 0.93–1.57 (m, 14H, CH_2), 1.95–2.03 (m, 2H, 2'-H), 2.68 (s, 3H, CH_3), 3.97 (s, 3H, NCH_3), 4.07 (t, ^3J = 7.3 Hz, 2H, 1'-H), 7.17 (d, ^3J = 2.1 Hz, 1H, 4-H/5-H), 7.32–7.44 (m, 5H, H_{aryl}), 7.56 (d, ^3J = 2.1 Hz, 1H, 4-H/5-H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 5.6 (C-3'), 9.6 (C-1''), 11.6 (CH_3), 13.7 (CH_3), 27.3 (CH_2), 27.4 (CH_2), 28.9 (CH_2), 36.8 (NCH_3), 52.3 (C-1'), 120.9 (C-4), 123.0 (C-5), 128.4 (CH), 128.5 (CH), 136.4 (CH), 140.3 (C_{quart}), 143.6 (C-2); **IR** (neat): 3074, 2953, 2920, 2862, 2850,

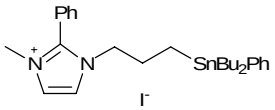
1587, 1537, 1462, 1425, 1375, 1340, 1277, 1246, 1144, 1072, 997, 864, 764, 727, 698, 667, 656 cm^{-1}; **HRMS** calculated for $C_{22}H_{37}N_2{}^{120}Sn$ [C^+] 449.19787, found 449.1993 (3 ppm).

1-{3-[dibutyl(phenyl)stannyl]propyl}-2,3-dimethyl-1*H*-imidazolium tetrafluoroborate (8d)



Using method 2 of the general procedures for preparing the tetrafluoroborates, **8d** was achieved as a colorless solid (1.65 g, 3.1 mmol, 74 %, mp 74.8°C*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 0.89 (t, ^3J = 7.3 Hz, 6H, CH_3), 0.93–1.12 (m, 14H), 1.95–2.03 (m, 2H, 2'-H), 2.67 (s, 3H, CH_3), 3.96 (s, 3H, NCH_3), 4.06 (t, ^3J = 7.5 Hz, 2H, 1'-H), 7.17 (d, ^3J = 2.1 Hz, 1H), 7.32–7.44 (m, 5H, H_{aryl}), 7.56 (d, ^3J = 2.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 7.7 (C-1_{Bu}), 9.6 (C-3'), 11.4 (CH_3), 13.8 (C-4_{Bu}), 29.1 (C-3_{Bu}), 23.8 (C-2'), 27.6 (C-2_{Bu}), 36.4 (NCH_3), 52.2 (C-1'), 120.1 (CH), 122.9 (CH), 128.5 (CH), 136.6 (CH), 140.3 (C_{quart}), 143.6 (C-2); **IR** (neat): 3061, 2953, 2918, 2850, 1587, 1537, 1458, 1425, 1375, 1340, 1246, 1144, 1072, 762, 727, 700, 665 cm^{-1}.

1-{3-[dibutyl(phenyl)stannyl]propyl}-2-phenyl-1*H*-imidazole (6e) and
1-{3-[dibutyl(phenyl)stannyl]propyl}-3-methyl-2-phenyl-1*H*-imidazolium iodide (7e)



Using the procedure for the preparation of **7d**, 1-(3-chloropropanyl)-1*H*-2-phenylimidazole (**5e**) (1.60 g, 7.3 mmol) afforded **7e** as a pale yellow solid (2.03 g, 3.2 mmol, 44%, two steps, mp 110.8°C*).

6e: **^{1}H NMR** (200 MHz, $CDCl_3$): δ [ppm] = 0.87 (t, ^3J = 7.2 Hz, 6H, CH_3), 1.01–1.97 (m, 16H, CH_2), 3.95 (t, ^3J = 7.3 Hz, 2H, 1'-H), 6.94 (s, 1H, 4-H/5-H), 7.12 (s, 1H, 4-H/5-H), 7.26–7.57 (m, 10H, H_{aryl}); **IR** (neat): 3061, 2955, 2924, 2852, 1462, 1416, 1375, 1271, 1144, 1072, 1018, 914, 864, 771, 727, 696, 596 cm^{-1}.

7e: **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 0.77–0.82 (m, 2H, CH_2), 0.87 (t, ^3J = 7.3 Hz, 6H, CH_3), 0.93–1.52 (m, 12H, CH_2), 1.86–1.94 (m, 2H, CH_2), 3.86 (s, 3H, NCH_3), 4.01 (t, ^3J = 7.3 Hz, 2H, CH_2), 7.31–7.36 (m, 5H, H_{aryl}), 7.58 (d, ^3J = 2.0 Hz, 1H), 7.62–7.73 (m, 5H, H_{aryl}), 8.00 (d, ^3J = 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 5.5 (C-3'), 9.4 (C-1''), 13.6 (CH_3), 27.2 (CH_2), 27.7 (CH_2), 28.9 (CH_2), 36.9 (NCH_3), 52.6 (C-1'), 120.7 (C_{quart}), 121.9 (CH), 124.2 (CH), 128.3 (CH), 128.4 (CH), 130.0 (CH), 130.6 (CH), 132.9 (CH), 136.3

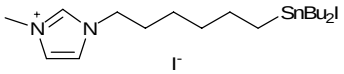
(CH), 140.3 (C_{quart}), 144.4 (C-2); **IR** (neat): 3059, 2953, 2920, 2848, 1579, 1506, 1443, 1427, 1250, 1074, 1018, 997, 960, 798, 773, 725, 696, 669 cm^{-1}; **HRMS** calculated for $C_{27}H_{39}N_2{}^{120}Sn$ [C^+] 511.21352, found 511.2152 (3 ppm).

4. Stille cross coupling reactions

Representative procedure

To a thick walled Pyrex tube containing the ionic liquid supported tin compound **7c** (247 mg, 0.41 mmol) was added $Pd_2dba_3{\cdot}CHCl_3$ (21 mg, 5 mol%). The reaction tube was closed, and heated for 15 min at 35°C. After the mixture was cooled to ambient temperature, iodobenzene (46 µL, 84 mg, 0.41 mmol) was added, and the sealed tube was heated at 35°C for 16 h. Upon cooling, the reaction was checked by GC; therefore a small amount of pentane was added and used for analysis. When complete (GC > 98%), pentane (10 mL) was added to the mixture and stirred for 30 min. The stirring was stopped and the organic phase was separated. This was done 3 times, and then the organic phases were collected, filtered, and concentrated. The resulting crude product was purified by flash chromatography (silica gel; 90/10 pentane/EtOAc) to afford the product biphenyl (267 mg, 39 mmol, 95%).

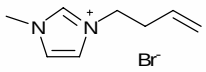
1-{6-[dibutyl(iodo)stannyl]hexyl}-3-methyl-1*H*-imidazolium iodide (9c)



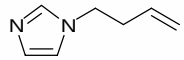
^{1}H NMR (200 MHz, $CDCl_3$): δ [ppm] = 0.92 (t, ^3J = 7.2 Hz, 6H, 4''-H, 2 × CH_3), 1.27–2.04 (m, 22H, CH_2), 4.12 (s, 3H, NCH_3), 4.34 (t, ^3J = 7.5 Hz, 2H, 1'-H), 7.40 (s, 1H, 4-H/5-H), 7.42 (s, 1H, 4-H/5-H), 10.13 (s, 1H, 2-H).

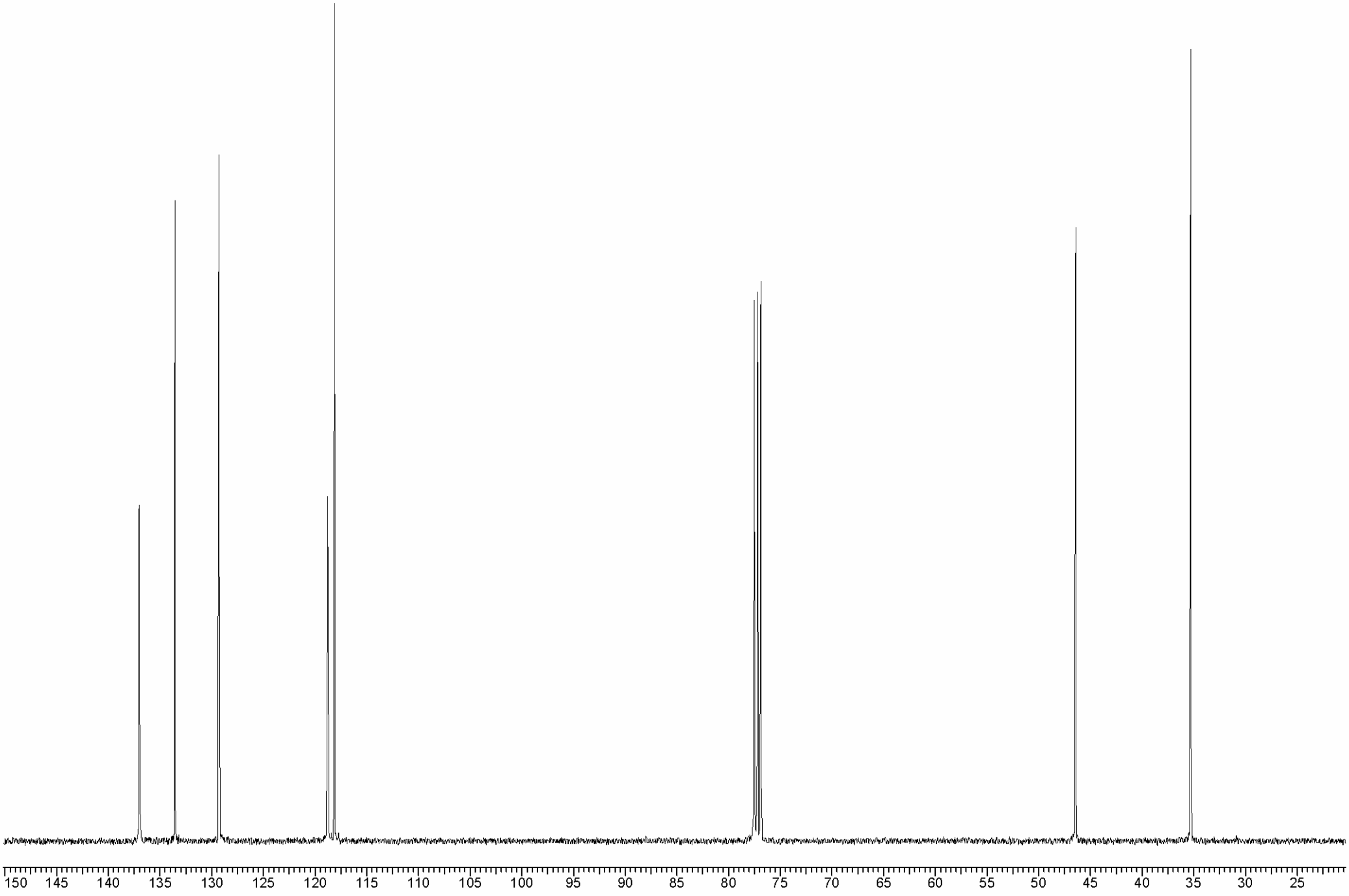
5. Spectra for Compounds

1-But-3-enyl-3-methyl-1*H*-imidazolium bromide (2a)



1-(But-3-enyl)-1*H*-imidazole (5a)

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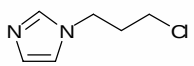
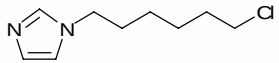
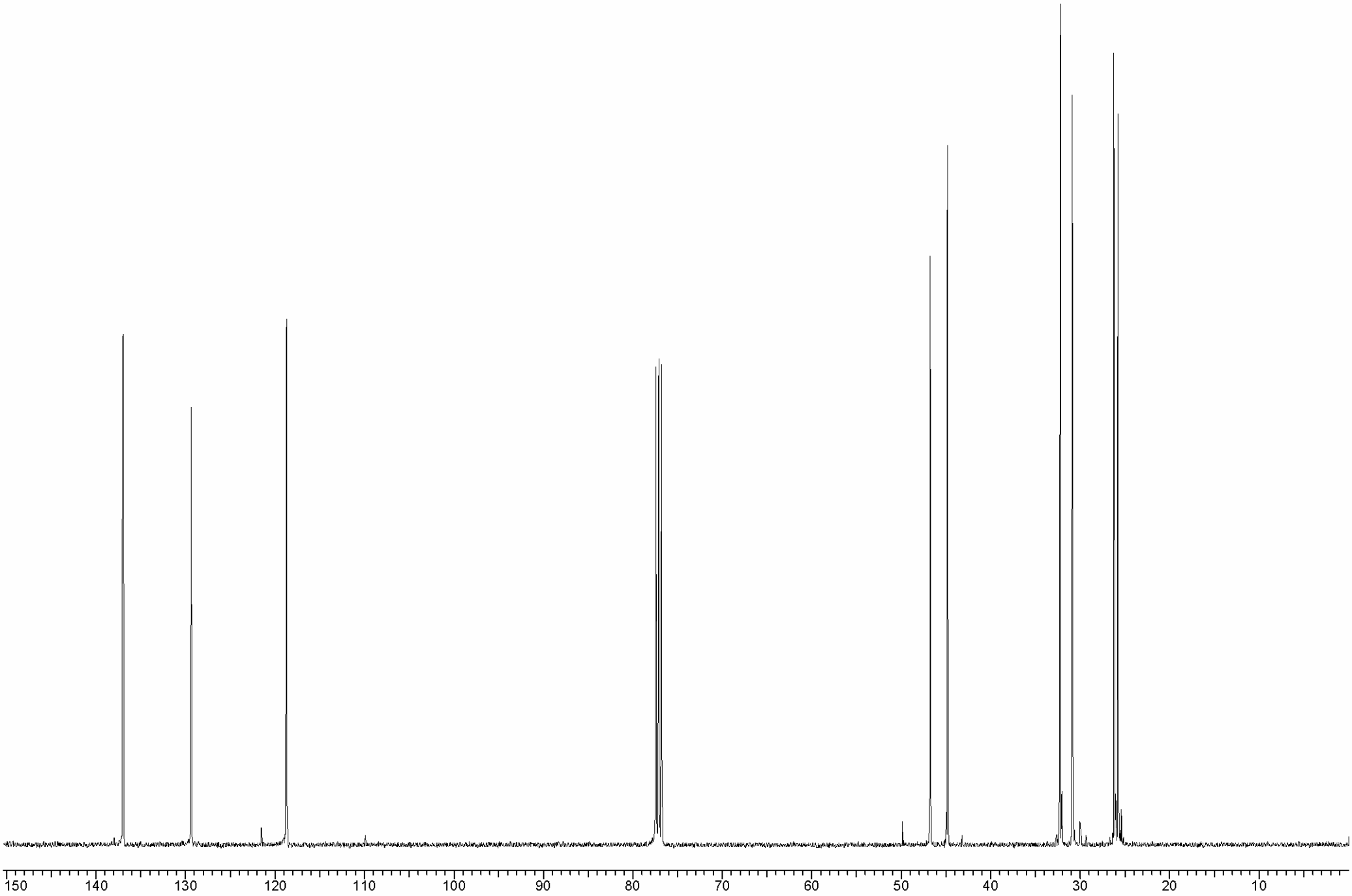
1-(3-chloropropanyl)-1H-imidazole (5b)[3,6]



1-(6-chlorohexyl)-1*H*-imidazole (5c)[7]

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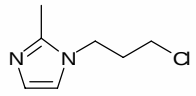
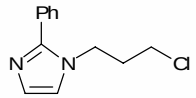
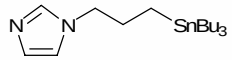
1-(3-chloropropanyl)-1*H*-2-methylimidazole (5d)[8]

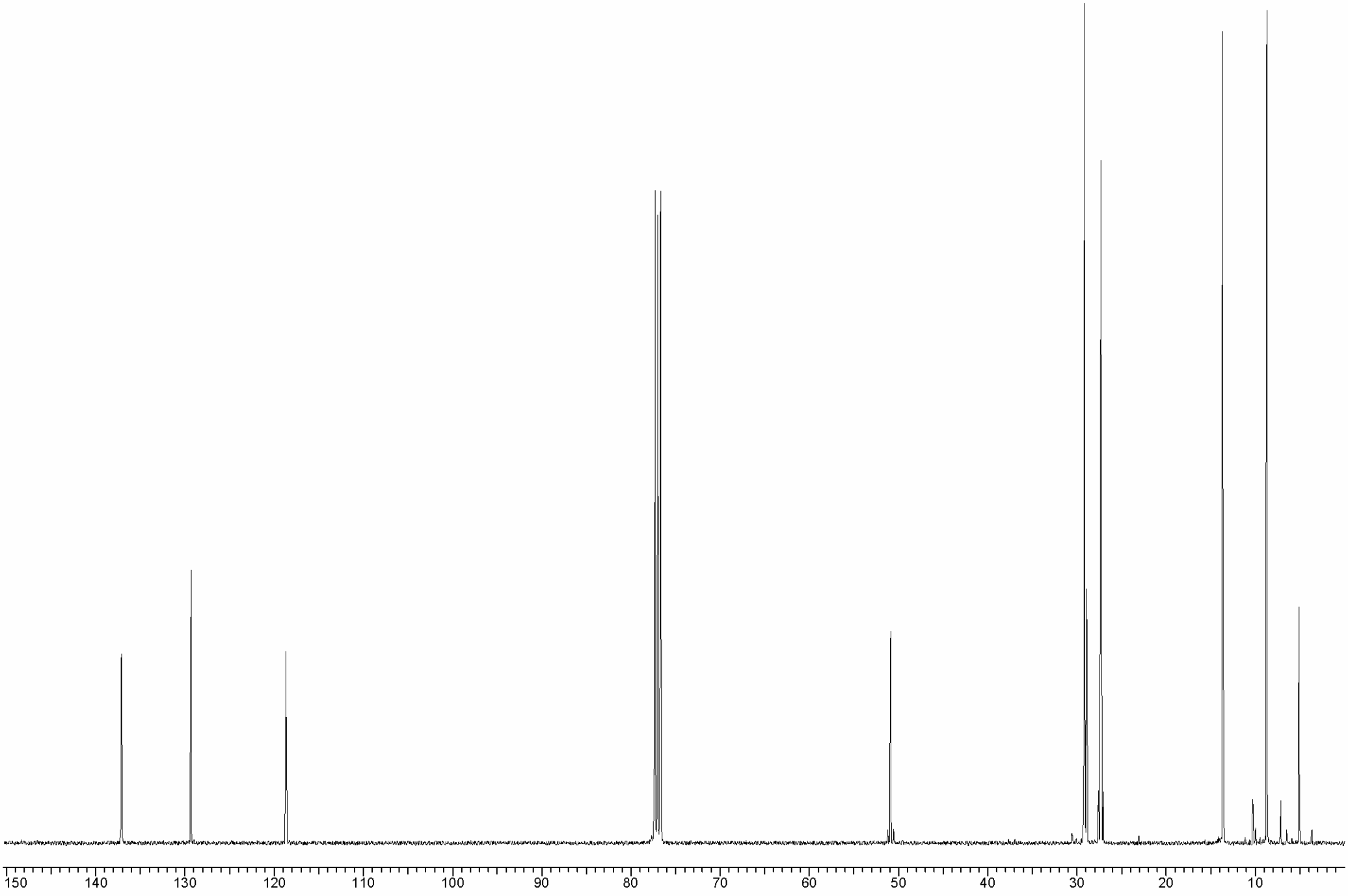


1-(3-chloropropanyl)-1*H*-2-phenylimidazole (5e)[9,10]



1-[3-(tributylstannyl)propyl]-1*H*-imidazole (6a)

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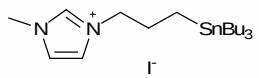
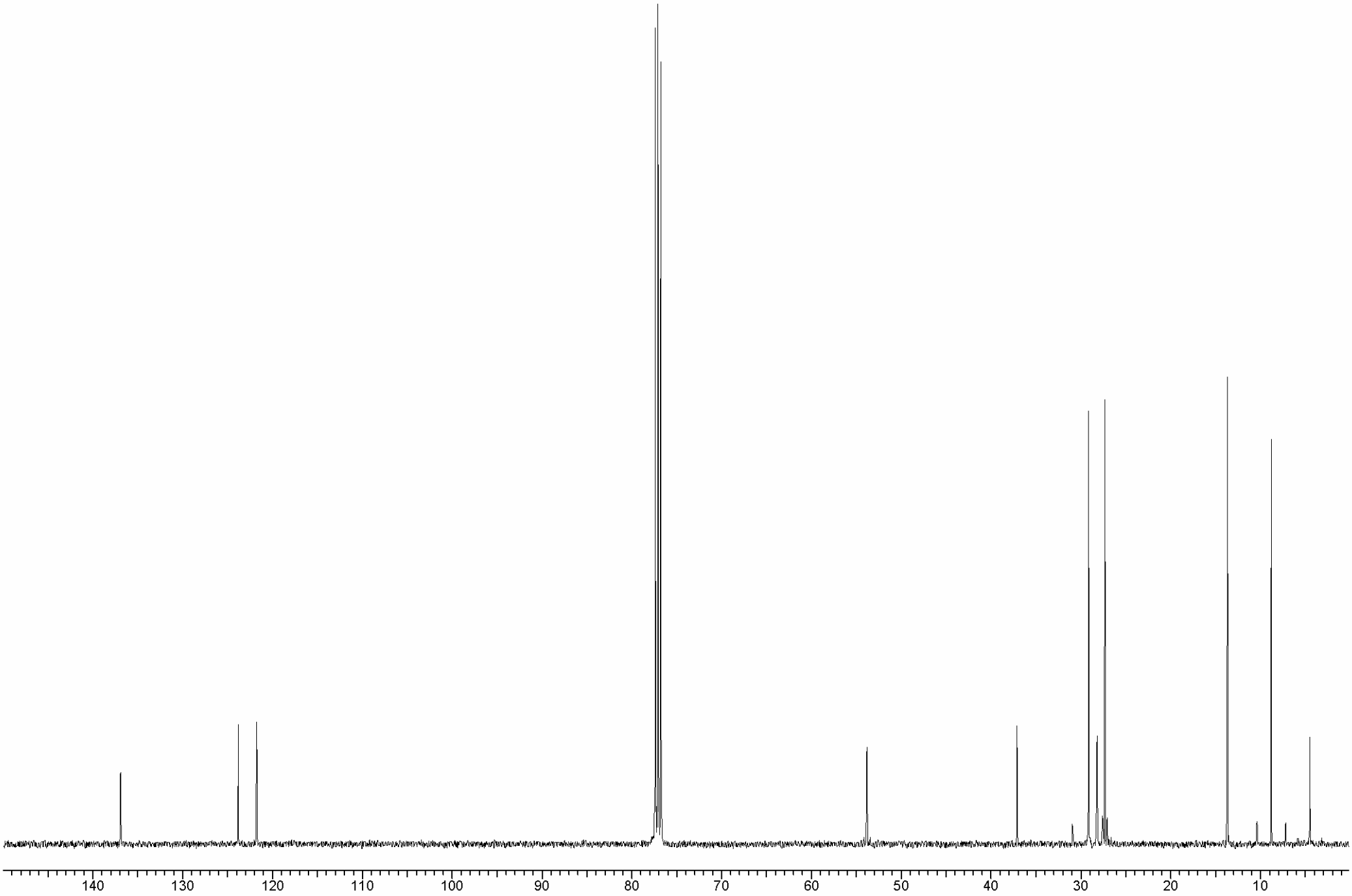
Wavenumber (cm-1)

1-[3-(tributylstannyl)propyl]-3-methylimidazolium iodide (7a)

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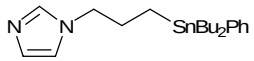
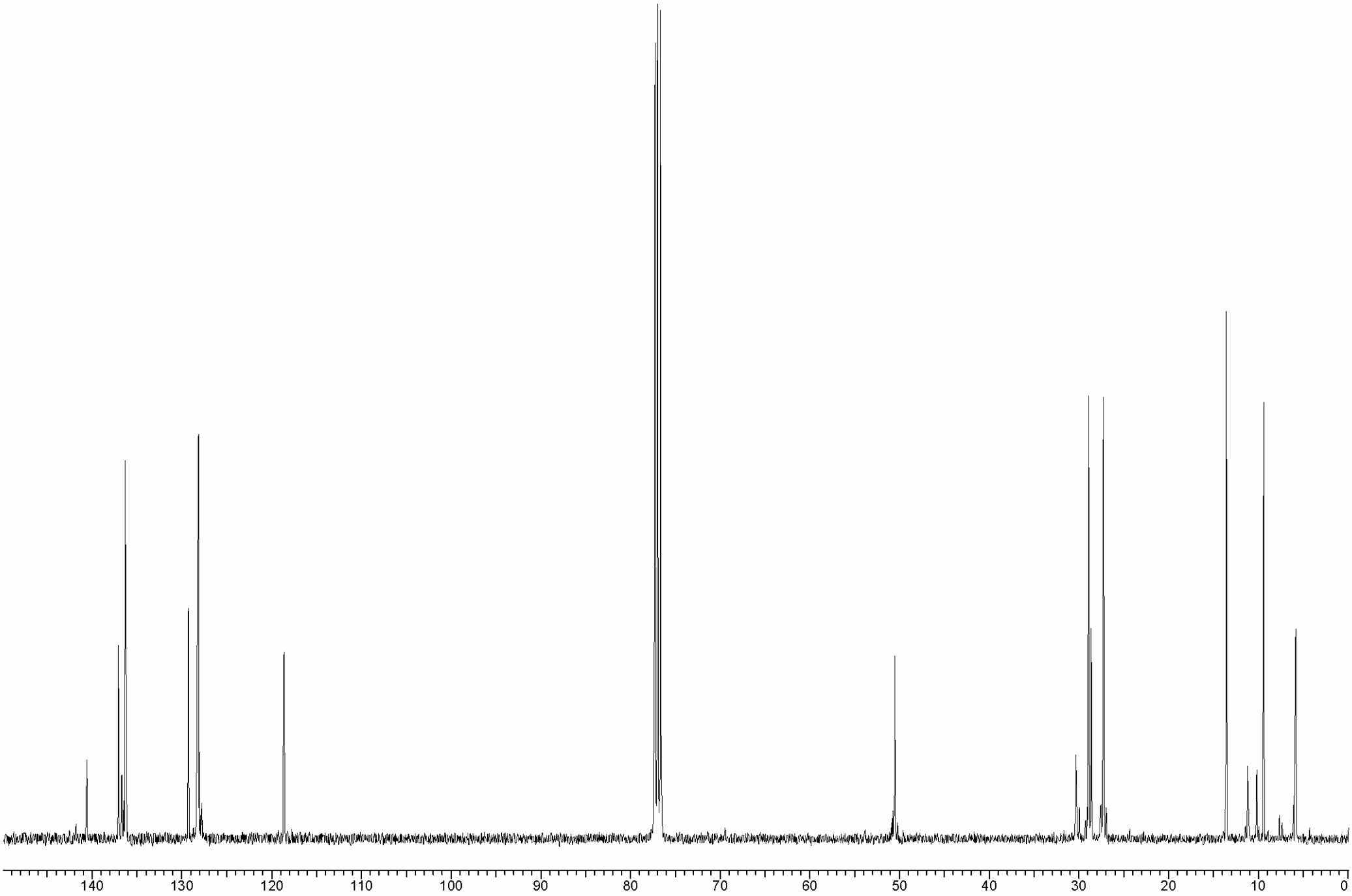
Wavenumber (cm-1)

1-{3-[dibutyl(phenyl)stannyl]propyl}-1*H*-imidazole (6b)

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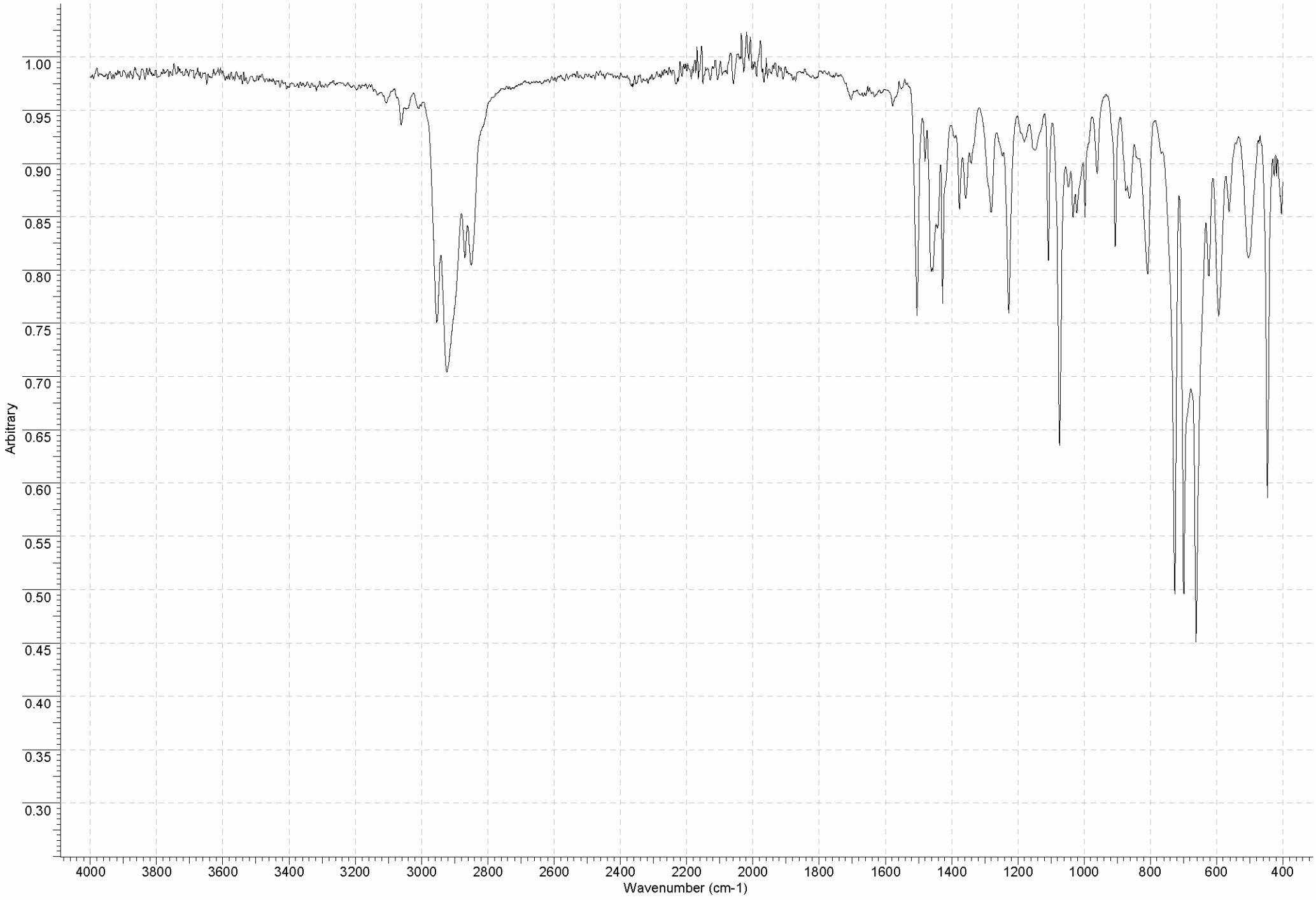
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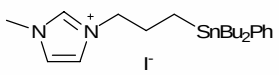
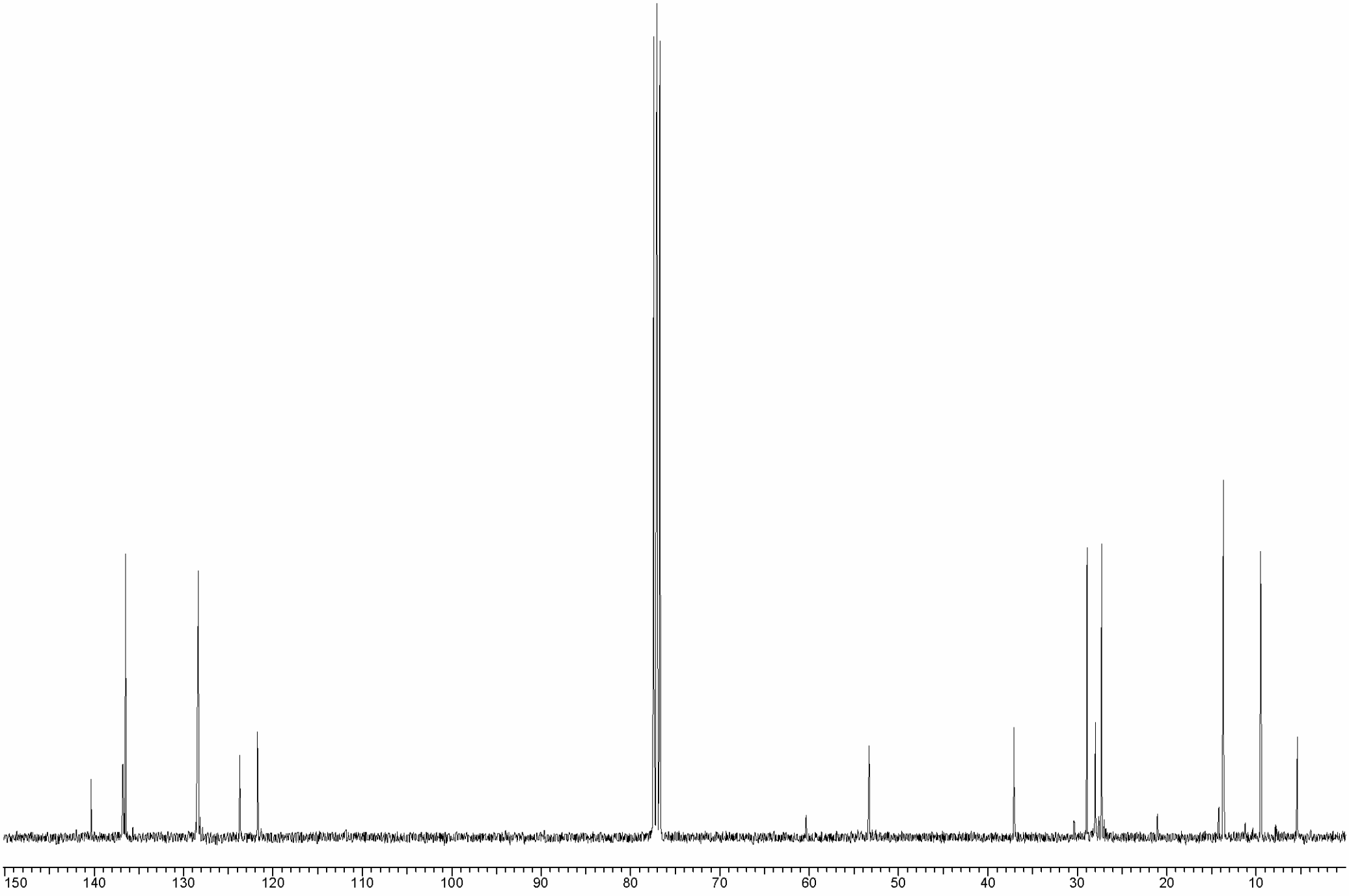
Wavenumber (cm-1)

1-{3-[dibutyl(phenyl)stannyl]propyl}-3-methyl-1*H*-imidazolium iodide (7b)

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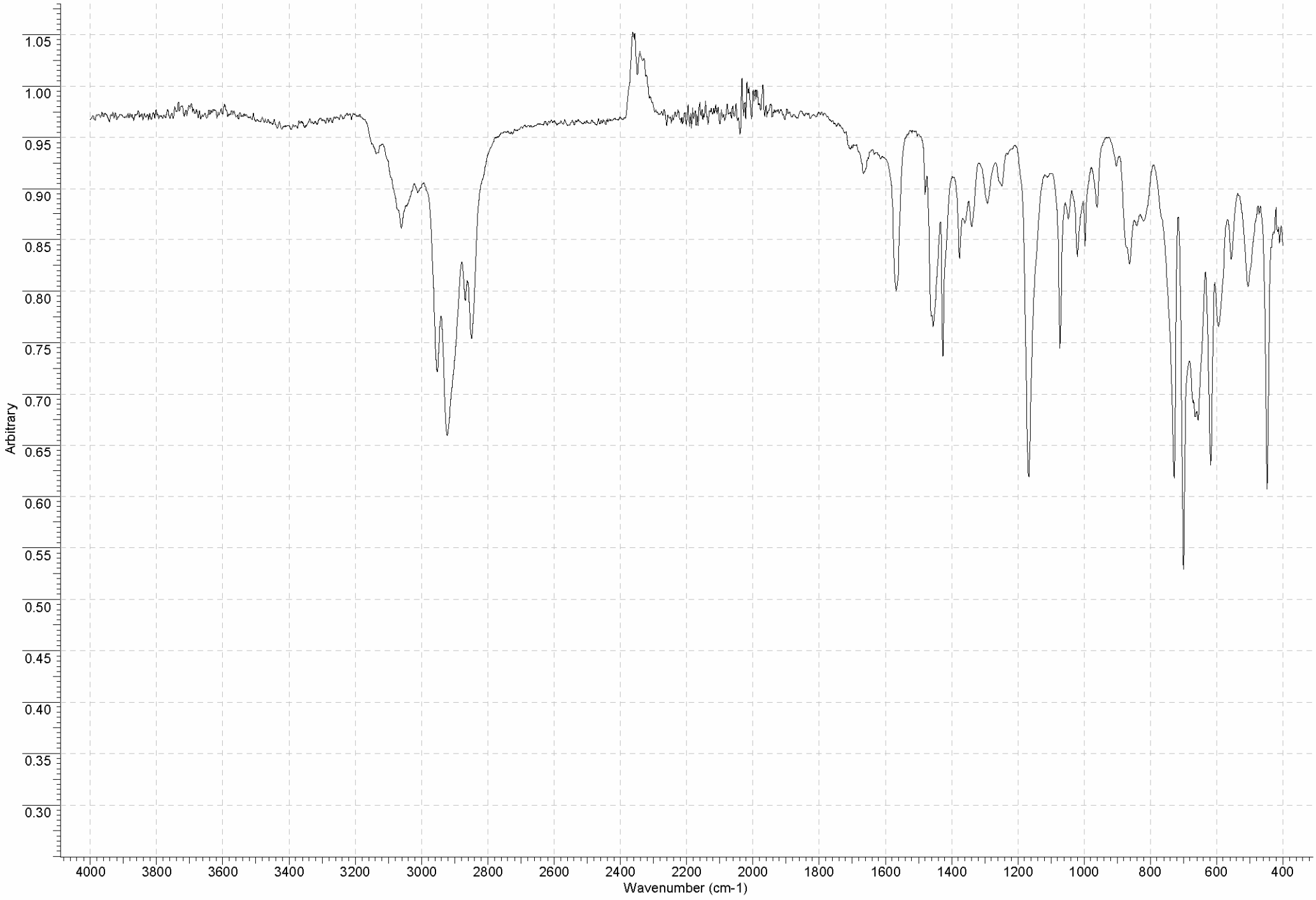
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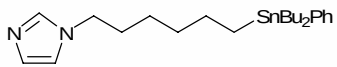
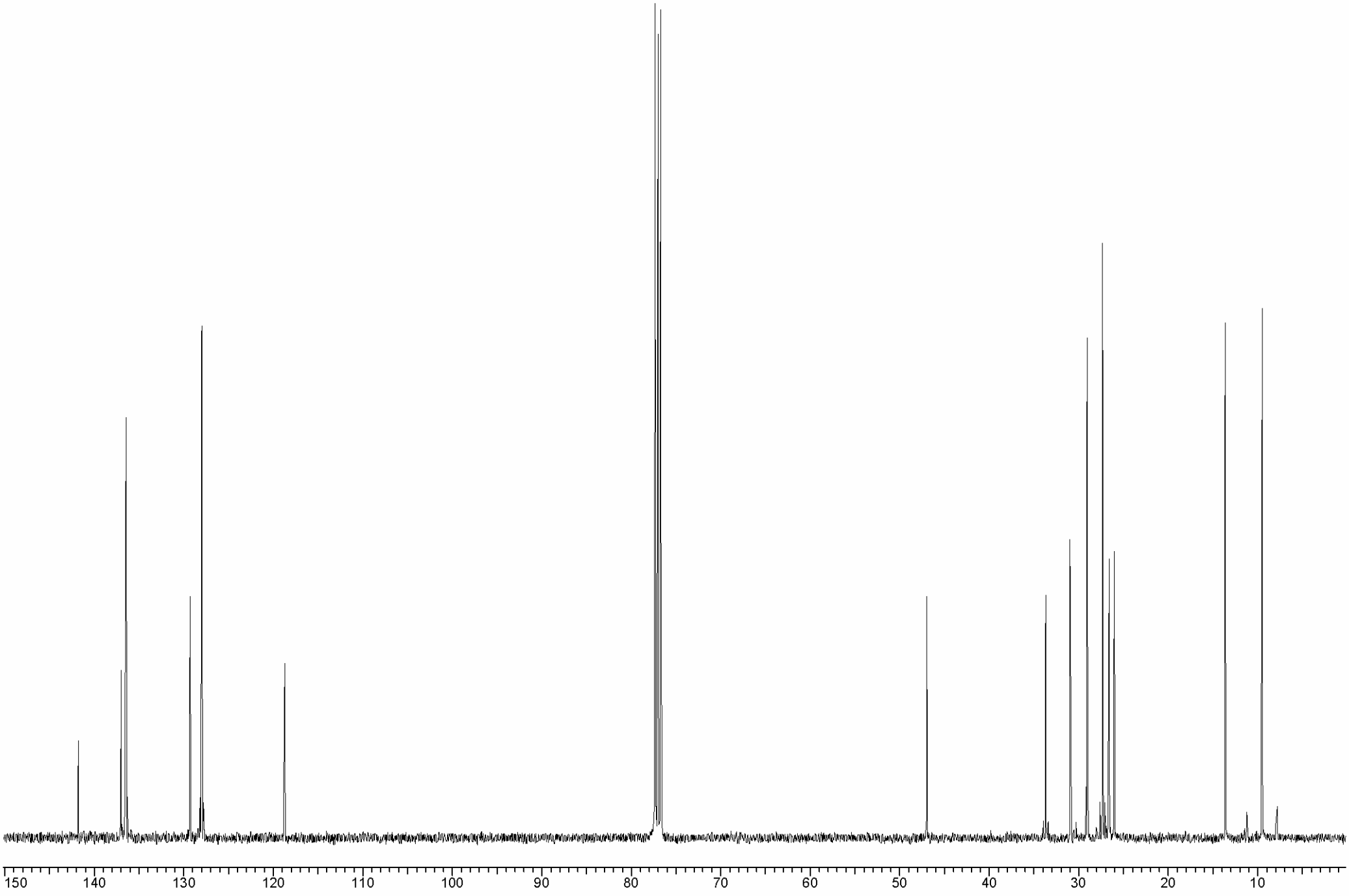
Wavenumber (cm-1)

1-{6-[dibutyl(phenyl)stannyl]hexyl}-1*H*-imidazole (6c)

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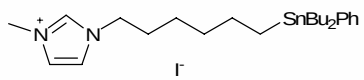
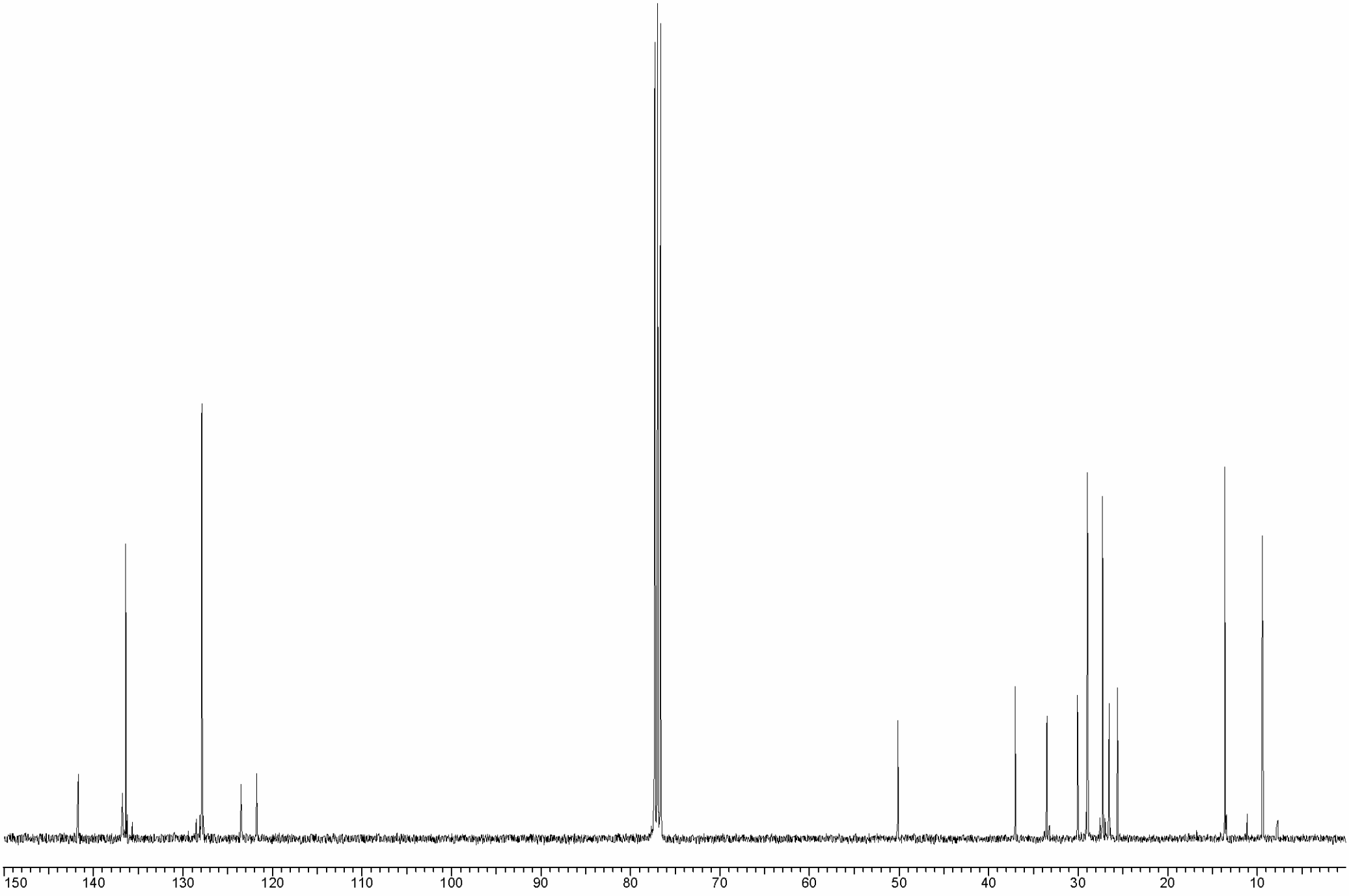
Wavenumber (cm-1)

1-{6-[dibutyl(phenyl)stannyl]hexyl}-3-methyl-1*H*-imidazolium iodide (7c)

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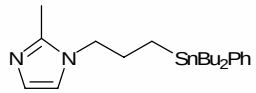
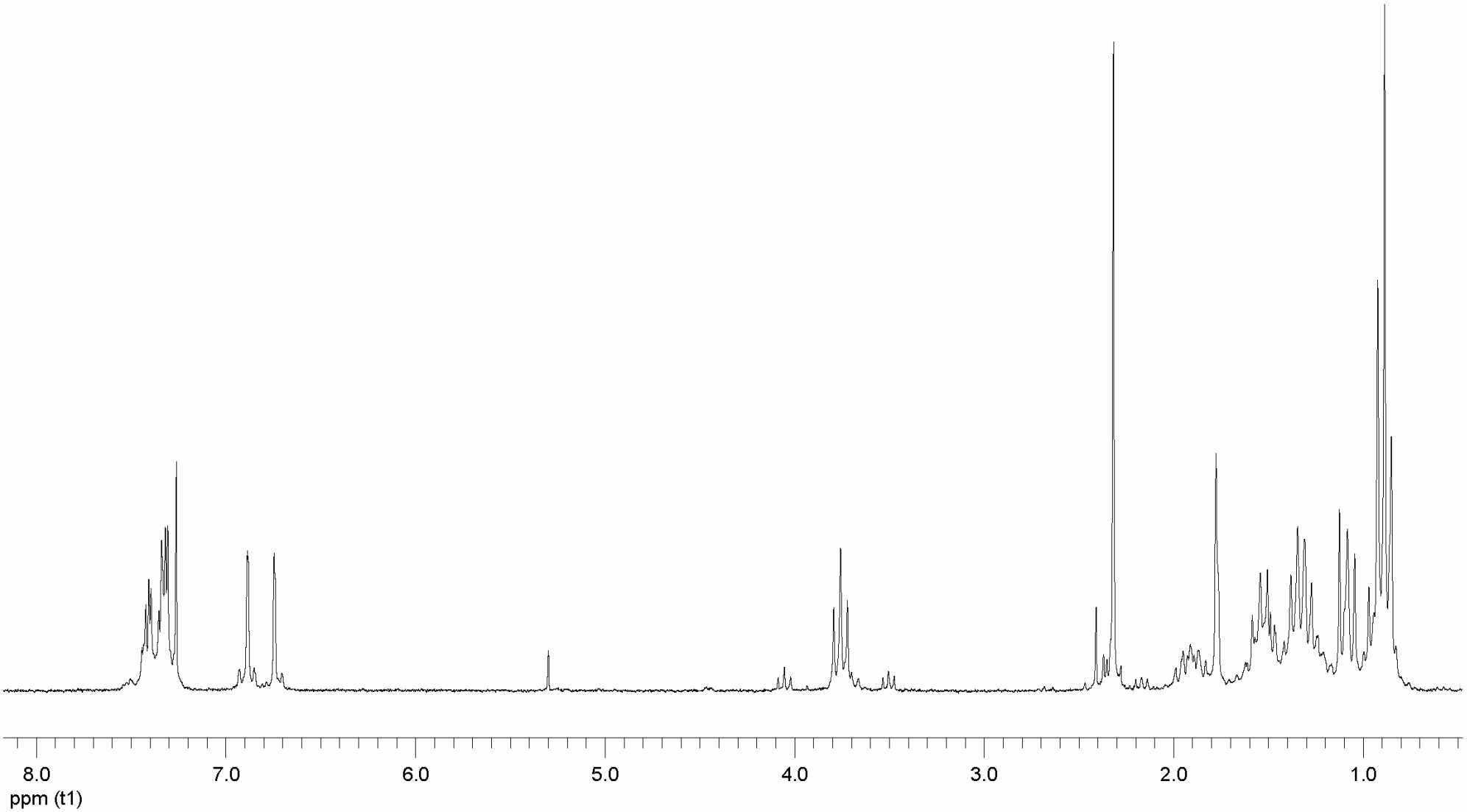
Wavenumber (cm-1)

1-{3-[dibutyl(phenyl)stannyl]propyl}-2-methyl-1*H*-imidazole (6d)



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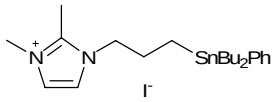
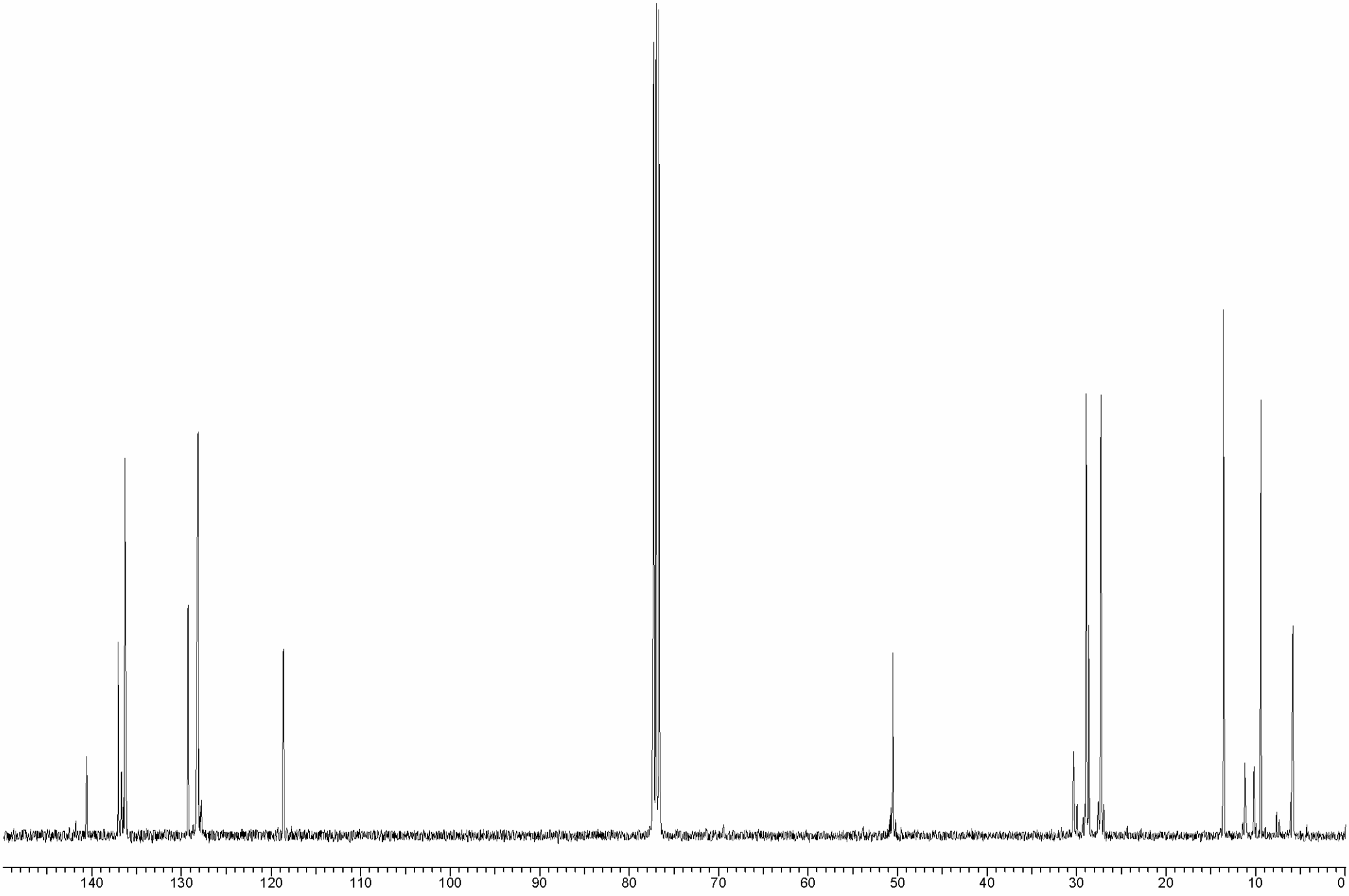
Wavenumber (cm-1)

1-{3-[dibutyl(phenyl)stannyl]propyl}-2,3-dimethyl-1*H*-imidazolium iodide (7d)

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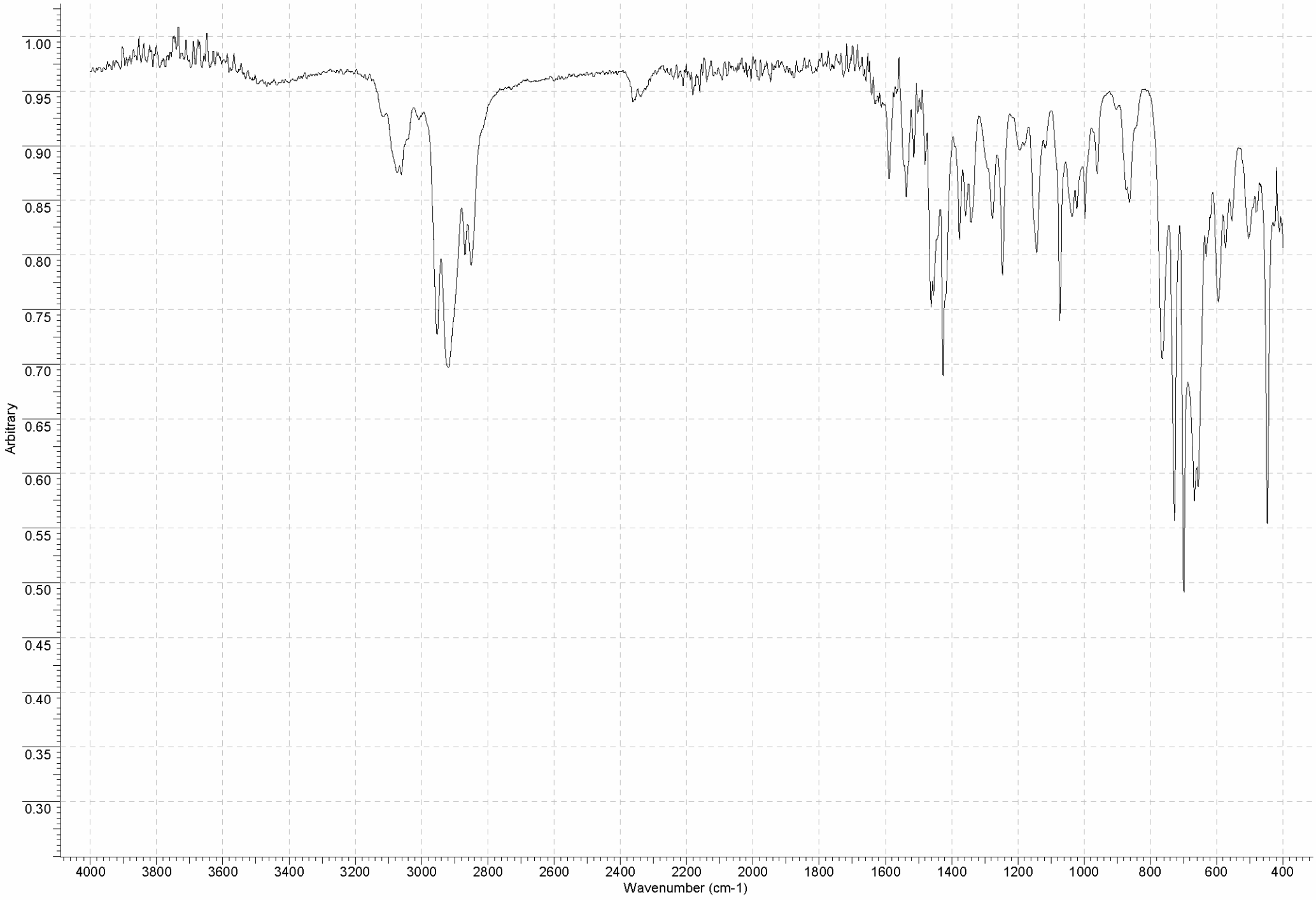
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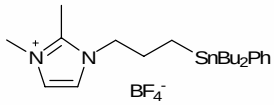
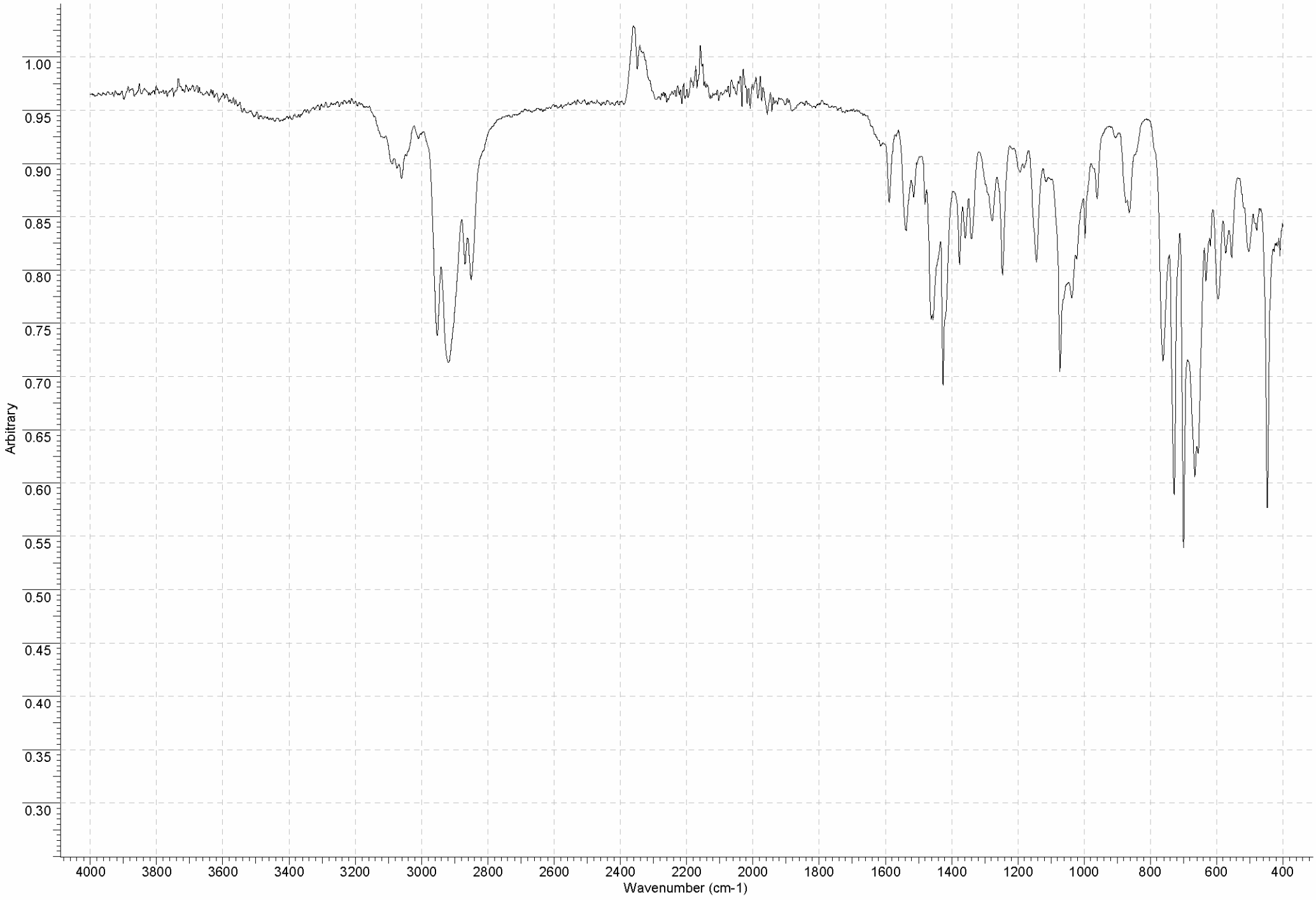
Wavenumber (cm-1)

1-{3-[dibutyl(phenyl)stannyl]propyl}-2,3-dimethyl-1*H*-imidazolium tetrafluoroborate (8d)

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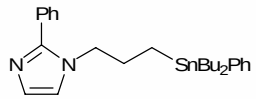
Wavenumber (cm-1)

1-{3-[dibutyl(phenyl)stannyl]propyl}-2-phenyl-1*H*-imidazole (6e)

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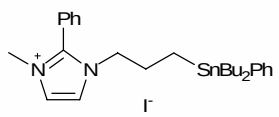
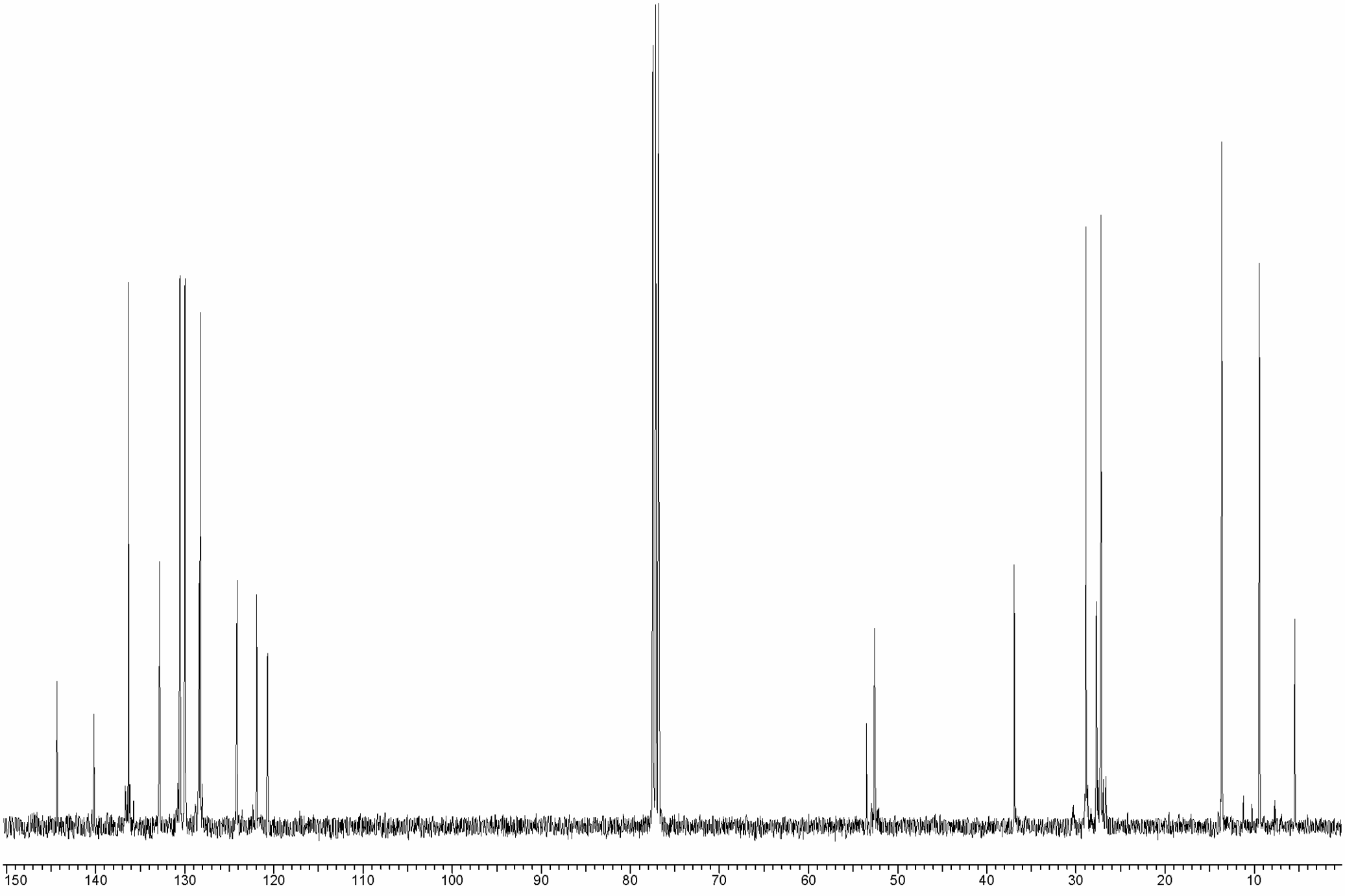
Wavenumber (cm-1)

1-{3-[dibutyl(phenyl)stannyl]propyl}-3-methyl-2-phenyl-1*H*-imidazolium iodide (7e)

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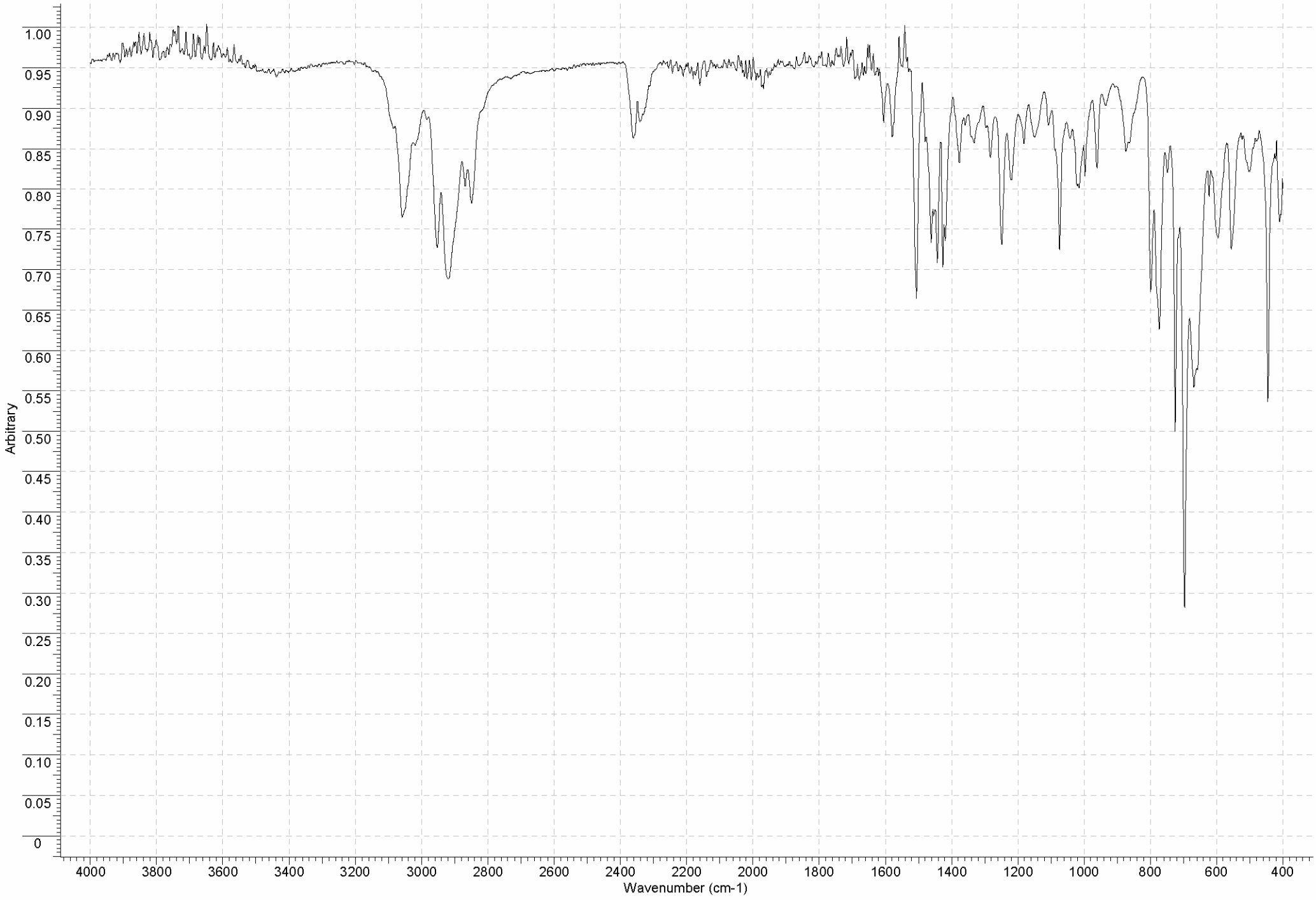
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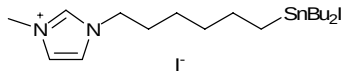
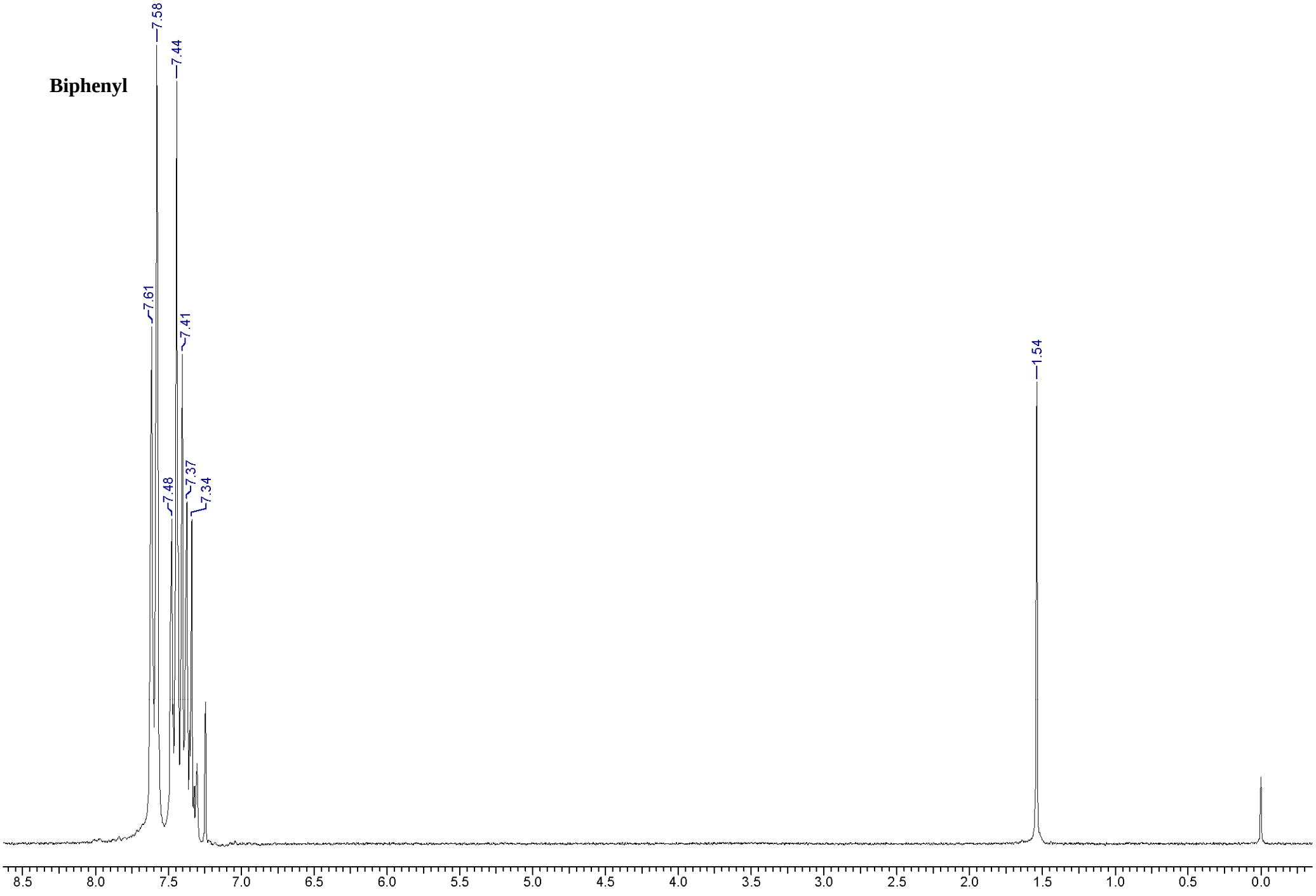
Wavenumber (cm-1)

1-{6-[dibutyl(iodo)stannyl]hexyl}-3-methyl-1*H*-imidazolium iodide (9c)



Biphenyl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6. References

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