

Electronic Supplementary Information

Electrochemical Synthesis of Organochalcogenides in Aqueous Medium

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1. General Remarks

1.1. Materials

Tetrahydrofuran (THF) and ethyl acetate were previously purified in agreement with the literature.¹ Tellurium, selenium and sulfur powder ($\geq 99.5\%$) were purchased from Aldrich and used as received. All other commercially available reagents and solvents were used as received. Reactions were monitored by gas chromatography. The products were characterized by GC/MS and NMR. The isolated product rate, mono- and dichalcogen, was determined by gas chromatography.

1.2. Instrumentation

Controlled-current electrolyses were carried out using Autolab PGSTAT 30 potentiostat/galvanostat or a DC power source, in a two compartment electrochemical cell (Figure 1). Isolated products were determined by GC (Varian CP-3380; Chrompack CP-SPL5CB capillary column 30 m; initial temperature 60 °C then increased to 220°C at 10°C min⁻¹), GC/MS (Agilent 5975C), ¹H NMR (400 MHz) and ¹³C NMR data (100 MHz) were recorded in CDCl₃. The chemical shifts are reported as delta (δ) units in parts per million (ppm) relative to the solvent residual peak as the internal reference. Coupling constants (J) for all spectra are reported in Hertz (Hz). ¹²⁵Te NMR (95 MHz) was obtained using diphenylditellane as external reference (δ 422.0), spectral window equal to 64.4 kHz, acquisition time equal to 0.64 s, 64 repetitions, RF pulse of 45° and line broadening equal to 5.0 Hz.

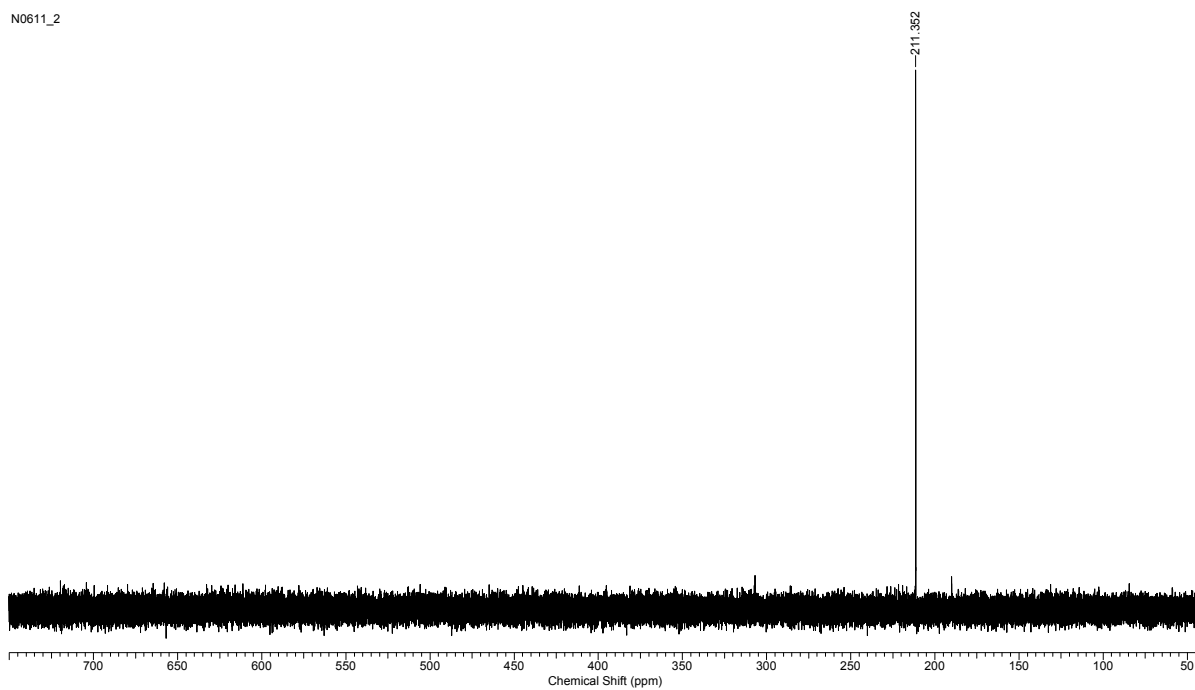
¹ D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, Pergamon, Oxford, **1980**.

1.3. Representative Procedure for the Synthesis of dicyclopentyltellane (2j)

Tellurium powder (0.5 mmol, 63.8 mg) and 0.2 mol L⁻¹ NaOH solution (25 mL) were added to the electrochemical cell (Figure 1). A stainless steel grid cathode and anode were used as electrodes with the anodic compartment separated by Nafion[®]. The system was subjected to constant current (I = -70 mA) electrolysis, under intense argon atmosphere. After the consumption of the Te⁰, the solution becomes purple, and then colorless, which determines the end point of the electroreduction.² 20 mL of co-solvent (THF) was added and the current maintained till the solution (H₂O/THF) becomes colorless again. The current was stopped and bromocyclopentane (150 mg, 102 μL, 1.0 mmol) dissolved in THF (5 mL) (deaerated with argon) was added via syringe to the electrochemical cell. The reaction was stirred for 12 hours at room temperature under argon. After this period the reaction was diluted with ethyl acetate (20 mL) and washed with water (2 x 30 mL). The organic layer was separated, dried over NaSO₄ and filtered. The solvent was removed under reduced pressure to yield 96.3 mg (72%) of the title compound without the need of further purification. ¹H NMR (400 MHz, CDCl₃) δ 3.55 (qui, J = 6.5 Hz, 2H); 2.06-1.98 (m, 8H); 1.75-1.57 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 38.0; 25.4; 17.9; ¹²⁵Te NMR (95 MHz, CDCl₃). δ 211.4. C₁₀H₁₈Te: LRMS (EI) m/z (rel. int.) 268 ([M⁺], 7), 199 (C₅H₁₀Te, 7), 41 (C₃H₅, 28).

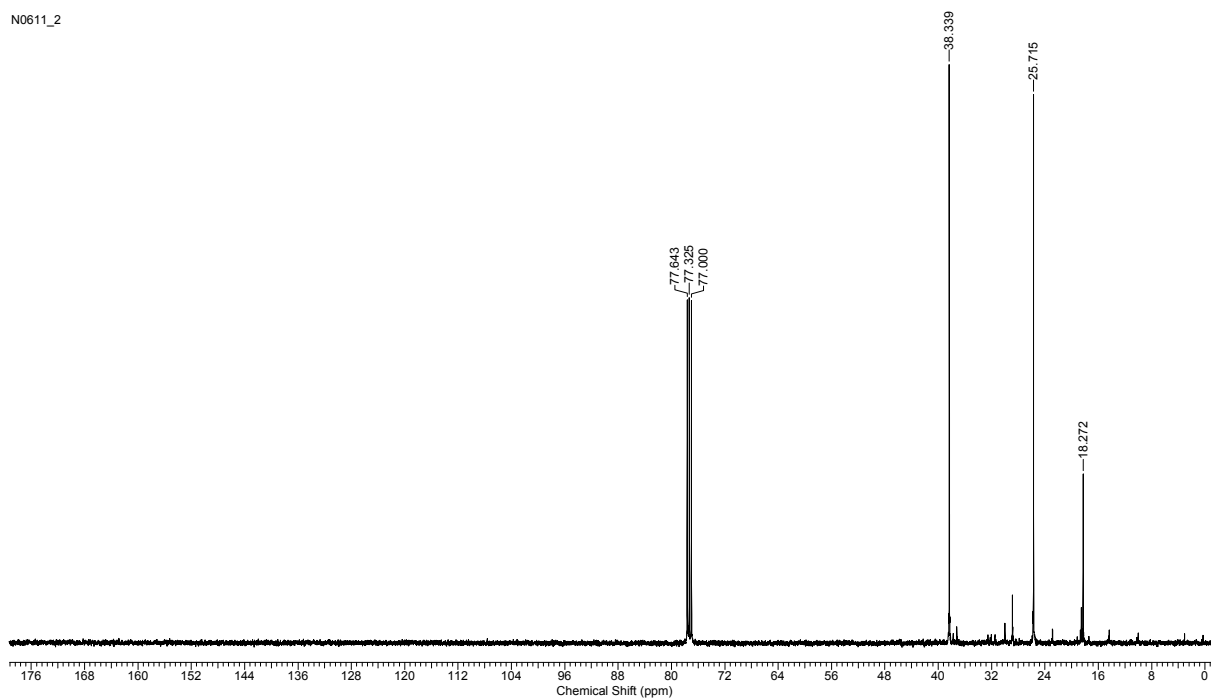
² (a) R. T. Ribeiro, J. M. M. Dias, G. A. G. Pereira, D. V. Freitas, P. E. Cabral Filho, R. A. Raelle, A. Fontes, M. Navarro and B. S. Santos, *Green Chem.* 2013, **15**, 1061-1066 (b) D. V. Freitas, J. M. M. Dias, S. G. B. Passos, G. C. S. de Souza, E. T. Neto and M. Navarro, *Green Chem.*, 2014, **16**, 3247-3254.

N0611_2

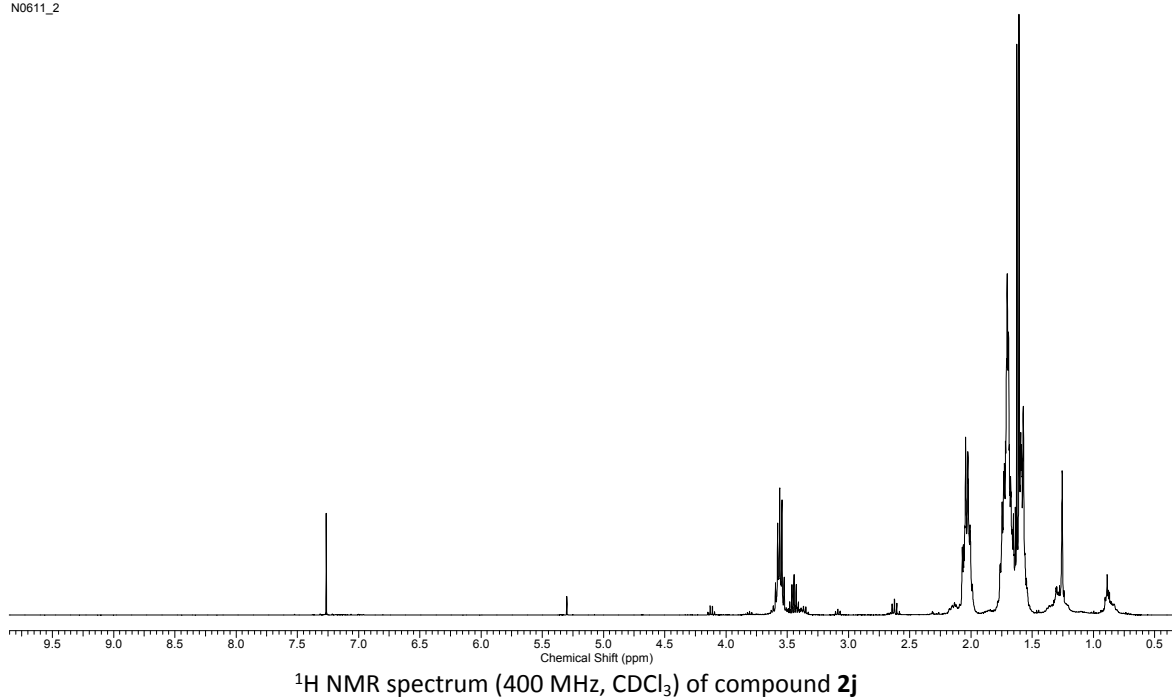


^{125}Te NMR spectrum (95 MHz, CDCl_3) of compound **2j**

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^{13}C NMR spectrum (100 MHz, CDCl_3) of compound **2j**



1.4 Characterization of products

Dipentyltellane (2a) [71475-88-2] C₁₀H₂₂Te: LRMS (EI) *m/z* (rel. int.) 272 ([M⁺], 26), 270 ([M⁺] - 2, 24), 268 ([M⁺] - 4, 16), 202 (C₅H₁₂Te⁺, 15), 200 ([C₅H₁₂Te⁺] - 2, 15), 71 (C₅H₁₁⁺, 99), 43 (C₃H₇⁺, 100). The data match to the previously described compound.³

Dipentylselenide (2b) [14835-67-7] C₁₀H₂₂Se: LRMS (EI) *m/z* (rel. int.) 222 ([M⁺], 46), 220 ([M⁺] - 2, 23), 152 (C₅H₁₂Se⁺, 55), 71 (C₅H₁₁⁺, 100), 43 (C₃H₇⁺, 82). The data match to the previously described compound.⁴

Dipentyldiselenide (3b) [52056-07-2] C₁₀H₂₂Se₂: LRMS (EI) *m/z* (rel. int.) 302 ([M⁺], 18), 300 ([M⁺] - 2, 17), 232 (C₅H₁₂Se₂⁺, 19), 230 ([C₅H₁₂Se₂⁺] - 2, 17), 71 (C₅H₁₁⁺, 92), 43 (C₃H₇⁺, 100). The data match to the previously described compound.⁴

Dipentylsulfide (2c) [872-10-6] C₁₀H₂₂S: LRMS (EI) *m/z* (rel. int.) 174 ([M⁺], 51), 103 (C₅H₁₁S⁺, 86), 71 (C₅H₁₁⁺, 100), 43 (C₃H₇⁺, 40). The data match to the previously described compound.⁵

Dipentyldisulfide (3c) [112-51-6] C₁₀H₂₂S₂: LRMS (EI) *m/z* (rel. int.) 206 ([M⁺], 67), 136 (C₅H₁₂S₂⁺, 51), 103 (C₅H₁₁S⁺, 21), 71 (C₅H₁₁⁺, 75), 43 (C₃H₇⁺, 100). The data match to the previously described compound.⁶

³ P. Lue; B-C. Chen; X-W. Yu; J. Chen and X-J. Zhou; *Synth. Commun.* 1986, **16**, 1849-1854.

⁴ J. A. Gladysz, J. L. Hornby and J. E. Garbe. *J. Org. Chem.*, 1978, **43**, 1204-1208.

⁵ G-P. Lu and C. Cai; *Green Chem. Lett. Rev.* 2012, **5**, 481-485.

Dihexyltellane (2d) [158734-99-7] C₁₂H₂₆Te, LRMS (EI) *m/z* (rel. int.) 300 ([M⁺], 18), 298 ([M⁺] - 2, 16), 296 ([M⁺] - 4, 10), 216 (C₆H₁₄Te⁺, 11), 85 (C₆H₁₃⁺, 62), 43 (C₃H₇⁺, 100). The data match to the previously described compound.⁷

Dihexylselenide (2e) [7732-99-2] C₁₂H₂₆Se, LRMS (EI) *m/z* (rel. int.) 250 ([M⁺], 60), 248 ([M⁺] - 2, 30), 165 (C₆H₁₃Se⁺, 71), 85 (C₆H₁₃⁺, 93), 43 (C₃H₇⁺, 100). The data match to the previously described compound.⁸

Dihexyldiselenide (3e) [52056-08-3] C₁₂H₂₆Se₂, LRMS (EI) *m/z* (rel. int.) 330 ([M⁺], 15), 328 ([M⁺] - 2, 13), 245 (C₆H₁₄Se₂⁺, 16), 85 (C₆H₁₃⁺, 66), 43 (C₃H₇⁺, 100). The data match to the previously described compound.⁹

Dihexylsulfide (2f) [6294-31-1] C₁₂H₂₆S, LRMS (EI) *m/z* (rel. int.) 202 ([M⁺], 35), 117 (C₆H₁₃S⁺, 100), 85 (C₆H₁₃⁺, 55), 59 (C₄H₉⁺, 38), 43 (C₃H₇⁺, 35). The data match to the previously described compound.¹⁰

Dihexyldisulfide (3f) [10496-15-8] C₁₂H₂₆S₂, LRMS (EI) *m/z* (rel. int.) 234 ([M⁺], 56), 150 (C₆H₁₄S₂⁺, 47), 117 (C₆H₁₃S⁺, 21), 85 (C₆H₁₃⁺, 53), 43 (C₃H₇⁺, 100). The data match to the previously described compound.¹¹

Dicyclopentylselenide (2k) [136397-83-6] C₁₀H₁₈Se, LRMS (EI) *m/z* (rel. int.) 218 ([M⁺], 13), 149 (C₅H₁₀Se⁺, 15), 69 (C₅H₉⁺, 100), 41 (C₃H₅⁺, 26). The data match to the previously described compound.¹²

Dicyclopentylselenide (3k) [62212-26-4] C₁₀H₁₈Se₂, LRMS (EI) *m/z* (rel. int.) 298 ([M⁺], 10), 296 ([M⁺] - 2, 9), 230 (C₅H₁₀Se₂⁺, 11), 228 ([C₅H₁₀Se₂⁺] - 2, 10), 69 (C₅H₉⁺, 100), 41 (C₃H₅⁺, 33). The data match to the previously described compound.¹³

Dicyclopentylsulfide (2l) [1126-65-4] C₁₀H₁₈S, LRMS (EI) *m/z* (rel. int.) 170 ([M⁺], 26), 101 (C₅H₉S⁺, 73), 69 (C₅H₉⁺, 100), 41 (C₃H₅⁺, 76). The data match to the previously described compound.¹⁴

⁶ A. Baker; M. Graz, R. Saunders; G.J.S. Evans; S. Kaul and T. Wirth. *J. Flow Chem.* 2013, **3**, 118–121.

⁷ T.S. Butcher; F. Zhou and Michael R. Detty. *J. Org. Chem.* 1998, **63**, 169-176.

⁸ A. Krief and M. Derock; *Tetrahedron Lett.* 2002, **43**, 3083–3086.

⁹ Z-Z. Huang; F-Y. Liu; J-X; Du and X. Huang. *Oppi Briefs*, 1995, **27**, 492-494.

¹⁰ N. Sidiq, M.A. Bhat, K.Z. Khan and M.A. Khuroo. *Heteroatom Chem.*, 2012, **23**, 373-376.

¹¹ D. Chauhan, P. Kumar, C. Joshi, N. Labhsetwar, S. K. Gangulya and S. L. Jain. *New J. Chem.*, 2015, **39**, 6193-6200.

¹² M. Sekiguchi, H. Tanaka, N. Takami, A. Ogawa,; I. Ryu and N. Sonoda. *Heteroatom Chem.*, 1991, **2**, 427-430.

¹³ Y. Nishiyama, S. Hamanaka, A. Ogawa, S. Murai and N. Sonoda. *Synth. Commun.*, 1986, **16**, 1059-1066.

¹⁴ I. Akhrem, A. Orlinikov and Sergei Vitt. *Inorg. Chim. Acta* 1998, **280**, 355-359.

Dicyclopentyldisulfide (3l) [4485-78-3] C₁₀H₁₈S₂, LRMS (EI) *m/z* (rel. int.) 202 ([M⁺], 24), 134 (C₅H₁₀S₂⁺, 39), 69 (C₅H₉⁺, 100), 41 (C₃H₅⁺, 27). The data match to the previously described compound.¹⁵

Dibenzyltellane (2m) [62654-03-9] C₁₄H₁₄Te, LRMS (EI) *m/z* (rel. int.) 312 ([M⁺], 5), 310 ([M⁺] - 2, 4), 308 ([M⁺] - 4, 2), 91 (C₇H₇⁺, 100), 65 (C₅H₅⁺, 12). The data match to the previously described compound.¹⁶

Dibenzylselenide (2n) [1842-38-2] C₁₄H₁₄Se, LRMS (EI) *m/z* (rel. int.) 262 ([M⁺], 19), 260 ([M⁺] - 2, 9), 91 (C₇H₇⁺, 100), 65 (C₅H₅⁺, 15). The data match to the previously described compound.¹⁷

Dibenzylsulfide (2o) [538-74-9] C₁₄H₁₄S, LRMS (EI) *m/z* (rel. int.) 214 ([M⁺], 41), 123 (C₇H₇S⁺, 35), 91 (C₇H₇⁺, 100), 65 (C₅H₅⁺, 11). The data match to the previously described compound. The data match to the previously described compound.¹⁸

Dibenzylsulfide (3o) [150-60-7] C₁₄H₁₄S₂, LRMS (EI) *m/z* (rel. int.) 246 ([M⁺], 5), 181 (C₉H₉S₂⁺, 7), 91 (C₇H₇⁺, 100), 65 (C₅H₅⁺, 12).¹⁵

¹⁵ M. Abbasi, M. R. Mohammadizadeh, H. Moosavi and N.G. Saeedia, *Synlett*, 2015, **26**, 1185–1190.

¹⁶ H.K. Spencer and M.P. Cava. *J. Org. Chem.*, 1977, **42**, 2937-2939.

¹⁷ V.P. Reddy, A.V. Kumar and K.R. Rao. *J. Org. Chem.* 2010, **75**, 8720–8723.

¹⁸ B.W. Yoo, B.R. Yu and C.M. Yoon. *J. Sulfur Chem.*, 2015, **36**, 358–363.