Synthesis of Symmetrical and Unsymmetrical Tellurides via Silver Catalysis

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General Information: The reactions were monitored by TLC carried out on Merck silica gel (60 F_{254}) by using UV light as visualizing agent and 5% vanillin in 10% H_2SO_4 and heat as developing agents. Baker silica gel (particle size 0.040-0.063 mm) was used for flash chromatography. Proton and carbon-13 nuclear magnetic resonance spectra (¹H NMR) were acquired using a Bruker Fourier 300 spectrometer (300 MHz for ¹H NMR and 75 MHz for ¹³C NMR). All NMR spectra were recorded in CDCl₃ solutions. Chemical shifts are reported in ppm, referenced to tetramethylsilane (TMS) as the internal reference in the ¹H NMR spectra or referenced to the solvent peak in the ¹³C NMR spectra. Coupling constants (*J*) are reported in Hertz. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), q (quartet), quint (quintet), sex (sextet) and m (multiplet). Low-resolution mass spectra were obtained with a Shimadzu GC-MS-QP2010 mass spectrometer. High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics micrOTOF-Q II instrument.

General Procedure for Silver(I)-Catalyzed Synthesis of Diaryl Tellurides 3a-u: To a 5 mL Schlenk tube equipped with a small magnetic stirring bar were added the appropriate diorganoyl ditelluride **1a-h** (0.2 mmol), the appropriate aryl boronic acid **2a-n** (0.4 mmol), AgNO₃ (0.04 mmol, 10 mol%) and 1,4-dioxane (0.8 mL). The resulting mixture was stirred at 100 °C for 6 h. After that, the reaction mixture was cooled to room temperature, and was quenched using water (5 mL). The mixture was then extracted using ethyl acetate (10 mL) and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous MgSO₄ and concentrated under vacuum to yield the crude product, which was purified by flash chromatography on silica gel using hexane or a mixture of hexane/ethyl acetate as eluent. Spectral data for the products prepared are listed below.

Spectral data of the products

^{Te} Ome Phenyl(4-methoxyphenyl)telluride¹ (3a):

Yield: 0.117 g (93%); Yellow solid; mp 57-59 °C; ¹H NMR (CDCl₃, 300 MHz): δ 7.72 (dt, *J* = 8.8, 2.8 Hz, 2H), 7.61 - 7.50 (m, 2H), 7.27 - 7.08 (m, 3H), 6.78 (dd, *J* = 8.8, 2.8 Hz, 2H), 3.77 (s, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 159.9, 141.15, 136.3, 129.3, 127.2, 115.9, 115.5, 103.1, 55.1. MS *m/z* (relative intensity): 314 (M⁺, 24), 312 (22), 184 (100), 169 (62), 141 (37), 115 (18), 92 (11), 77 (44), 51 (26).

Mathematical Chlorophenyl(4-methoxyphenyl)telluride (3b):

Yield: 0.124 g (89%); Yellow oil; ¹H NMR (CDCl₃, 300 MHz): δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 160.1, 141.3, 137.5, 133.6, 129.4, 115.6, 113.6, 102.9, 55.1. MS *m*/*z* (relative intensity): 348 (M⁺, 31), 346 (28), 218 (100), 203 (45), 175 (20), 75 (11), 63 (12). HRMS calculated for C₁₃H₁₁ClOTe [M]⁺: 347.9561, Found: 347.9545.

Br OMe 4-bromophenyl(4-methoxyphenyl)telluride (3c):

Yield: 0.122 g (78%); Yellow solid; mp 42-43°C; ¹H NMR (CDCl₃, 300 MHz): δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 160.1, 141.4, 139.7, 137.7, 132.3, 121.7, 115.6, 102.8, 55.1. MS *m*/*z* (relative intensity): 392 (M⁺, 36), 388 (12), 264 (99), 262 (100), 249 (47), 247 (49), 237 (18), 221 (25), 140 (18), 92 (19), 77 (26), 63 (42), 50 (40). HRMS calculated for C₁₃H₁₁BrOTe [M]⁺: 391.9056, Found: 391.9045.

Meo OMe Bis(4-methoxyphenyl)telluride¹ (3d):

Yield: 0.122 g (89%); Yellow solid; mp 46-48 °C; ¹H NMR (CDCl₃, 300 MHz): δ 7.61 (d, J = 8.8 Hz, 4H), 6.74 (d, J = 8.9 Hz, 4H), 3.74 (s, 6H). ¹³C NMR (CDCl₃, 75 MHz): δ

¹ D. Alves, J. M. Pena, A. S. Vieira, G. V. Botteselle, R. C. Guadagnin and H. A. Stefani, *J. Braz. Chem. Soc.*, 2009, **20**, 988.

159.1, 139.6, 115.3, 104.2, 55.0. MS *m/z* (relative intensity): 344 (M⁺, 28), 340 (17), 214 (100), 199 (94), 171 (30), 128 (15), 107 (7), 77 (10), 63 (17).

Me OMe 4-Methylphenyl(4-methoxyphenyl)telluride¹ (3e):

Yield: 0.122 g (93%); Yellow oil; ¹H NMR (CDCl₃, 300 MHz): δ 7.68 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.00 (d, J = 8.1 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 2.31 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 159.7, 140.5, 137.3, 137.1, 130.2, 115.3, 111.3, 103.5. MS *m*/*z* (relative intensity): 328 (M⁺, 32), 296 (52), 237 (46), 198 (100), 183 (63), 155 (29), 91 (19), 65 (21).

Me Naphthalen-2-yl(4-methoxyphenyl)telluride (3f):

Yield: 0.105 g (72%); Yellow solid; mp 80-83 °C; ¹H NMR (CDCl₃, 300 MHz): δ 8.07 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 3H), 7.71 - 7.59 (m, 1H), 7.59 (s, 2H), 7.48 - 7.34 (m, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 159.9, 141.0, 135.8, 134.2, 133.4, 132.3, 128.4, 127.7, 127.2, 126.2, 126.0, 115.5, 113.3, 103.3, 55.1. MS *m/z* (relative intensity): 364 (M⁺, 21), 234 (100), 219 (61), 191 (30), 127 (35), 77 (19), 63 (13). HRMS calculated for C₁₇H₁₄OTe [M]⁺: 364.0107, Found: 364.0118.

Me Te OMe Mesityl(4-methoxyphenyl)telluride¹ (3g):

Yield: 0.105 g (74%); Yellow solid; mp 31-32 °C; ¹H NMR (CDCl₃, 300 MHz): δ 7.35 (dt, *J* = 8.8, 2.9 Hz, 2H), 6.96 (s, 2H), 6.69 (dt, *J* = 8.8, 2.9 Hz, 2H), 3.73 (s, 3H), 2.53 (s, 6H), 2.28 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 159.0, 145.1, 139.0, 137.2, 127.5, 118.8, 115.3, 104.6, 55.1, 29.7, 29.4, 21.0. MS *m/z* (relative intensity): 356 (M⁺, 100), 354 (92), 248 (52), 244 (30), 237 (12), 226 (81), 214 (17), 211 (46), 199 (15), 195 (19), 119 (58), 115 (22), 103 (18), 91 (52), 77 (40), 63 (22), 51 (15), 41 (24).

^{____} OMe Butyl(4-methoxyphenyl)telluride (3h):

Yield: 0.075 g (64%); Yellow oil; ¹H NMR (CDCl₃, 300 MHz): δ 7.67 (dt, J = 8.8, 2.9 Hz, 2H), 6.75 (dt, J = 8.8, 2.9 Hz, 2H), 3.79 (s, 3H), 2.82 (t, J = 7.3 Hz, 2H), 1.73 (quint,

J = 7.3 Hz, 2H), 1.37 (sex, J = 7.3 Hz, 2H), 0.88 (t, J = 7.3 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 159.5, 140.8, 115.0, 100.5, 55.1, 33.8, 24.9, 13.4, 8.7. MS *m*/*z* (relative intensity): 294 (M⁺, 23), 290 (13), 237 (15), 222 (7), 108 (100), 92 (7), 63 (12), 57 (14), 41 (25). HRMS calculated for C₁₁H₁₆OTe [M]⁺: 294.0263, Found: 294.0263.

Diphenyl telluride¹ (3i):

Yield: 0.104 g (92%); Yellow oil; ¹H NMR (CDCl₃, 300 MHz): δ 7.76 - 7.63 (m, 4H), 7.34 - 7.14 (m, 6H). ¹³C NMR (CDCl₃, 75 MHz): δ 137.9, 129.5, 127.8, 114.6. MS *m/z* (relative intensity): 284 (M⁺, 23), 280 (15), 206 (10), 154 (100), 77 (85), 51 (49). HRMS calculated for C₁₂H₁₀Te [M]⁺: 283.9845, Found: 283.9842.

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^{^/}^{Me} Phenyl(4-methylphenyl)telluride¹ (3j):

Yield: 0.118 g (99%); Yellow oil; ¹H NMR (CDCl₃, 300 MHz): δ 7.73 - 7.52 (m, 3H), 7.29 - 7.09 (m, 3H), 7.02 (d, *J* = 7.6 Hz, 2H), 2.32 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 138.7, 138.0, 137.2, 130.4, 129.3, 127.4, 115.2, 110.2, 21.2. MS *m/z* (relative intensity): 298 (M⁺, 27), 168 (100), 153 (21), 91 (51), 77 (35), 65 (32), 51 (29).

^CBr Phenyl(4-bromophenyl)telluride (3k):

Yield: 0.090 g (62%); Yellow solid; mp 59-61 °C; ¹H NMR (CDCl₃, 300 MHz): δ 7.70 - 7.67 (m, 2H), 7.52 - 7.48 (m, 2H), 7.34 - 7.27 (m, 3H), 7.25 - 7.19 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz): δ 139.3, 138.2, 132.6, 129.6, 128.1, 122.5, 114.2, 113.2. MS *m/z* (relative intensity): 362 (M⁺, 21), 232 (79), 207 (11), 152 (37), 77 (100), 51 (69). HRMS calculated for C₁₂H₉BrTe [M]⁺: 361.8950, Found: 361.8941.

C^IPhenyl(4-chlorophenyl)telluride (3l):

Yield: 0.104 g (82%); Yellow oil; ¹H NMR (CDCl₃, 300 MHz): δ 7.73 - 7.63 (m, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.35 - 7.09 (m, 5H). ¹³C NMR (CDCl₃, 75 MHz): δ 139.1, 138.1, 134.2, 129.7, 129.6, 128.1, 114.4, 112.3. MS *m*/*z* (relative intensity): 318 (M⁺, 44), 316 (37), 188 (100), 153 (18), 111 (12), 77 (57), 51 (55). HRMS calculated for C₁₂H₉ClTe [M]⁺: 317.9455, Found: 317.9453.

Phenyl(2-methoxyphenyl)telluride (3m):

Yield: 0.093 g (74%); Yellow solid; mp 50-53 °C; ¹H NMR (CDCl₃, 300 MHz): δ 7.88 (d, J = 6.7 Hz, 2H), 7.42 - 7.34 (m, 1H), 7.33 - 7.21 (m, 2H), 7.22 - 7.09 (m, 1H), 6.93 (dd, J = 7.6, 1.6 Hz, 1H), 6.81 - 6.65 (m, 2H), 3.83 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 157.9, 141.1, 133.3, 129.5, 128.5, 128.00, 122.3, 111.9, 109.5, 107.6, 55.7. MS *m/z* (relative intensity): 314 (M⁺, 17), 184 (48), 169 (36), 141 (26), 107 (23), 92 (10), 77 (100), 51 (43). HRMS calculated for C₁₃H₁₃O₂Te [M + OH]⁺: 330.9978, Found: 330.9985.

Phenyl(2-methylphenyl)telluride (3n):

Yield: 0.083 g (70%); Yellow oil; ¹H NMR (CDCl₃, 300 MHz): δ 7.74 - 7.64 (m, 2H), 7.48 - 7.44 (m, 1H), 7.34 - 7.24 (m, 1H), 7.27 - 7.15 (m, 4H), 2.40 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 141.8, 138.6, 137.3, 129.6, 129.3, 128.0, 128.0, 126.7, 119.2, 113.9, 26.0. MS *m*/*z* (relative intensity): 298 (M⁺, 41), 296 (38), 167 (92), 153 (43), 91 (100), 77 (53), 65 (67), 51 (58). HRMS calculated for C₁₃H₁₂Te [M]⁺: 298.0001, Found: 297.9999.

Phenyl(2-bromophenyl)telluride (30):

Yield: 0.041 g (28%); Yellow oil; ¹H NMR (CDCl₃, 300 MHz): δ 7.96 - 7.91 (m, 2H), 7.49 - 7.31 (m, 4H), 7.05 - 6.95 (m, 2H), 6.89 - 6.85 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 141.2, 134.3, 132.0, 130.0, 129.2, 128.0, 127.8, 126.9, 123.9, 114.6. MS *m/z* (relative intensity): 362 (M⁺, 12), 234 (18), 207 (13), 152 (33), 77 (100), 51 (85), 44 (43), 40 (51). HRMS calculated for C₁₂H₉BrTe [M]⁺: 361.8950, Found: 361.8940.

Phenyl(2-chlorophenyl)telluride (3p):

Yield: 0.036 g (28%); Yellow oil; ¹H NMR (CDCl₃, 300 MHz): δ 7.94 - 7.91 (m, 2H), 7.48 - 7.43 (m, 1H), 7.37 - 7.29 (m, 3H), 7.14 - 7.08 (m, 1H), 6.96 - 6.93 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz): δ 141.3, 136.4, 134.2, 130.0, 129.2, 128.7, 128.0, 127.4, 120.5, 113.2. MS *m/z* (relative intensity): 318 (M⁺, 27), 316 (23), 188 (100), 152 (30), 111 (10),
77 (99), 51 (77). HRMS calculated for C₁₂H₉ClTe [M]⁺: 317.9455, Found: 317.9432.

Phenyl(3-trifluoromethylphenyl)telluride² (3q):

Yield: 0.093 g (66%); Yellow oil; ¹H NMR (CDCl₃, 300 MHz): δ 7.89 (s, 1H), 7.82 - 7.70 (m, 3H), 7.40 - 7.17 (m, 5H). ¹³C NMR (CDCl₃, 75 MHz): δ 140.4, 138.8, 133.6 (q, $J_{C-F} = 3$ Hz), 131.4 (q, $J_{C-F} = 32$ Hz), 129.8, 125.5, 128.5, 124.4 (q, $J_{C-F} = 3$ Hz), 123.6 (q, $J_{C-F} = 272$ Hz), 115.8, 113.7. MS *m*/*z* (relative intensity): 352 (M⁺, 15), 222 (88), 203 (10), 153 (16), 145 (17), 126 (20), 95 (11), 77 (100), 51 (72), 40 (16).

Phenyl(naphthalen-2-yl)telluride (3r):

Yield: 0.107 g (80%); Yellow solid; mp 39-42 °C; ¹H NMR (CDCl₃, 300 MHz): δ 8.23 (s, 1H), 7.82 - 7.76 (m, 1H), 7.74 - 7.63 (m, 5H), 7.49 - 7.42 (m, 2H), 7.32 - 7.16 (m, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 137.8, 134.7, 134.3, 132.6, 129.5 (2C), 128.6, 127.8, 127.7, 127.4, 126.4, 126.3, 114.8, 111.9.MS *m/z* (relative intensity): 334 (M⁺, 12), 204 (100), 127 (59), 101 (10), 77 (48), 51 (33). HRMS calculated for C₁₆H₁₂Te [M]⁺: 334.0001, Found: 333.9999.

Phenyl(3-acetylphenyl)telluride (3s):

Yield: 0.068 g (52%); Yellow oil; ¹H NMR (CDCl₃, 300 MHz): δ 8.40 - 8.05 (m, 2H), 7.89 - 7.77 (m, 2H), 7.77 - 7.69 (m, 2H), 7.35 - 7.17 (m, 2H), 2.53 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 197.5, 141.8, 138.5, 137.8, 137.1, 129.6, 129.5, 128.2, 127.5, 115.5, 114.0, 26.6. MS *m/z* (relative intensity): 326 (M⁺, 14), 207 (13), 181 (56), 153 (31), 77 (96), 51 (60, 43 (100), 40 (13). HRMS calculated for C₁₄H₁₂OTe [M]⁺: 325.9950, Found: 325.9948.

² S. Roy, T. Chatterjee and S. M. Islam, *Tetradedron Lett.*, 2015, 56, 779.

Phenyl(3-bromophenyl)telluride (3t):

Yield: 0.090 g (62%); Yellow oil; ¹H NMR (CDCl₃, 300 MHz): δ 7.83 - 7.66 (m, 3H), 7.53 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.43 - 7.16 (m, 4H), 7.03 (t, *J* = 7.8 Hz, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 139.4, 138.6, 135.7, 130.7, 130.7, 129.7, 128.3, 123.3, 116.7, 113.9. MS *m*/*z* (relative intensity): 362 (M⁺, 16), 234 (52), 152 (33), 77 (100), 51 (63). HRMS calculated for C₁₂H₉BrTe [M]⁺: 361.8950, Found: 361.8932.

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^Ls⁷Phenyl(3-thienyl)telluride³ (3u):

Yield: 0.101 g (87%); Yellow oil; ¹H NMR (CDCl₃, 300 MHz): δ 7.47 - 7.44 (m, 3H), 7.14 - 7.05 (m, 5H). ¹³C NMR (CDCl₃, 75 MHz): δ 136.7, 136.3, 134.4, 129.3, 127.4, 127.1, 115.2, 103.8. MS *m/z* (relative intensity): 290 (M⁺, 28), 288 (27), 160 (100), 128 (13), 115 (17), 77 (47), 51 (30).

High Resolution Mass Spectrometry Experiments

The experiments were performed using a Bruker Daltonics micrOTOF-Q II instrument equipped with an ESI source operating in positive mode or negative mode. For mechanistic investigation, aliquots were taken directly from the reaction mixture, immediately solubilized MeCN/MeOH (1:1) and inject in the ESI source at a constant flow rate of 180 μ L/min. The Acquisition parameters were: capillary: 4000 V, end plate offset: - 500 V, nebulizer: 0.4 bar, dry gas: 4.0 L min⁻¹, and dry heater: 180 °C. The collision cell energy was set to 5.0 eV. The spectra analysis and simulate pattern were performed using Bruker Compass Data Analysis 4.3 software package.

³ D. Kundu, N. Mukherjee and B. C. Ranu, *RSC Adv.*, 2013, **3**, 117.



Figure S1. HRMS spectrum (ESI+) collected by direct infusion of diphenyl telluride (0.1 mmol) and equimolar amount of silver(I) nitrate (0.1 mmol) in 1,4-dioxane (400 µL).



Figure S2. Isotope pattern for the positive ion with m/z 518.7929 (A) and the simulated isotope pattern for the formula C₁₂H₁₀Te₂Ag (B).



Figure S3. MS² spectrum (50 eV) of the precursor ion m/z 18 leading to formation of the fragments confirming the structural identity of the intermediate **A**. The m/z showed in parentheses correspond to the calculated m/z of most intense peak among the isotopic peaks.



Figure S4. MS² spectrum (50 eV) of the precursor ion m/z 438 leading to formation of the fragments the fragments which confirm the structural identity of the intermediate **C**. The m/z showed in parentheses correspond to the calculated m/z of most intense peak among the isotopic peaks.



Figure S5. Isotope pattern for the positive ion with m/z 438.9092 (A) and the simulated isotope pattern for the adduct with formula C₁₃H₁₂O₂TeAg (B).

SELECTED SPECTRA



gure S5. ¹H NMR (300 MHz) spectrum for compound 3a in CDCl₃.



Figure S6. ¹³C NMR (75 MHz) spectrum for compound 3a in CDCl₃.



Figure S8. ¹³C NMR (75 MHz) spectrum for compound 3b in CDCl₃.



Figure S10. ¹³C NMR (75 MHz) spectrum for compound 3c in CDCl₃.



Figure S12. ¹³C NMR (75 MHz) spectrum for compound 3d in CDCl₃.



Figure S13. ¹H NMR (300 MHz) spectrum for compound 3e in CDCl₃.



Figure S14. ¹³C NMR (75 MHz) spectrum for compound 3e in CDCl₃.



Figure S16. ¹³C NMR (75 MHz) spectrum for compound 3f in CDCl₃.



Figure S18. ¹³C NMR (75 MHz) spectrum for compound 3g in CDCl₃.







Figure S21. ¹H NMR (300 MHz) spectrum for compound 3i in CDCl₃.





Figure S24. ¹³C NMR (75 MHz) spectrum for compound 3j in CDCl₃.



ure S25. ¹H NMR (300 MHz) spectrum for compound 3k in CDCl₃.



Figure S26. ¹³C NMR (75 MHz) spectrum for compound 3k in CDCl₃.



Figure S27. ¹H NMR (300 MHz) spectrum for compound 3I in CDCl₃.



Figure S28. ¹³C NMR (75 MHz) spectrum for compound 31 in CDCl₃.



Figure S29. ¹H NMR (300 MHz) spectrum for compound 3m in CDCl₃.



igure S30. ¹³C NMR (75 MHz) spectrum for compound 3m in CDCl₃.



gure S31. ¹H NMR (300 MHz) spectrum for compound 3n in CDCl₃.







Figure S34. ¹³C NMR (75 MHz) spectrum for compound 30 in CDCl₃.





Figure S36. ¹³C NMR (75 MHz) spectrum for compound 3p in CDCl₃.



Figure S37. ¹H NMR (300 MHz) spectrum for compound 3q in CDCl₃.









Figure S42. ¹³C NMR (75 MHz) spectrum for compound 3s in CDCl₃.



Figure S43. ¹H NMR (300 MHz) spectrum for compound 3t in CDCl₃.





Figure S45. ¹H NMR (300 MHz) spectrum for compound 3u in CDCl₃.



Figure S46. ¹³C NMR (75 MHz) spectrum for compound 3u in CDCl₃.