Supporting Information

A Base-Free Copper-Assisted Synthesis of *C*₂-Symmetric Spirotelluranes and Biaryls Based on Divergent Stoichiometry of Na₂Te

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Material and Methods

All reactions were accomplished in oven-dried glassware with magnetic stirring bar. Elemental tellurium (200 mesh size), sodium metal, lithium triethyl borohydride (1.0 M in THF), copper iodide, copper bromide, 2-iodobenzoic acid, benzoic acids, anilines and solvents were used without further purification as purchased unless otherwise specified (Aldrich, TCI, Alfa aeser). All NMR experiments were performed on Bruker 400/500/700 MHz spectrometer in CDCl₃/ DMSO-d₆ solvents to record respective ¹H, ¹³C and ¹²⁵Te spectra. Solvents and chemical shifts are reported in ppm. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), td (triplet of doublet) and m (multiplet). High resolution mass spectra were recorded on quadrupole-time of flight Bruker MicroTOF-Q II mass spectrometer equipped with an electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) condition. X-Ray single crystal structure data for 1b, 1d, 1k, 1n, 1q, 1r, 2o, 2r, and 2t were collected on a Bruker D8 VENTURE diffractometer equipped with CMOS Photon 100 detector and MoK α ($\lambda = 0.71073$ Å) radiation was used, computed with Bruker APEX2. Absorption studies were performed on Agilent Carry 100 UV-Visible Spectrophotometer. Purification is done by column chromatography, loaded with silica gel (60-120 mesh size) purchased from RANKEM Pvt. Ltd. India. Progress of the reactions was monitores by thin layer chromatography (TLC) using Merck silica gel (60 F254) plates visualized by UV irradiation (254 nm). Melting points of the compounds were determined with an electro-thermal melting point apparatus in the capillary tubes. Starting material amides were prepared from corresponding benzoyl chlorides.¹

General Experimental Details

A typical synthetic procedure of 2-halo-benzamides: 2-Halobenzoyl chlorides were prepared (Scheme S1) by following reported procedure¹ from respective 2-halobenzoic acids upon reflux with the thionyl chloride and were used for the preparation of amide without any further characterization. The freshly prepared 2-halo-benzoylchloride (1.0 equiv, 10.0 mmol) was dissolved in 10 mL of dry CH₂Cl₂ in a single neck 100 mL round bottom flask under N₂ atmosphere and flask cooled to 0 °C. for 10 minutes. In another single neck 50 mL round bottomed flask, aniline 1.1 mL (1.2 equiv, 12 mmol) was added in 10 mL dry CH₂Cl₂. After this 1.7 mL (1.2 equiv, 12 mmol) of triethyl amine (TEA) was also added to it. This resulting solution is then added drop wise via a syringe to the solution of the 2-halobenzoyl chloride over a period of 30 min at 0 °C. The resulted reaction mixture was brought to room temperature slowly and stirred for an additional hour. The reaction mixture was concentrated under vacuo and residue was washed with 10% aqueous HCl followed by the 200 mL distilled water, followed by the washing of 10% NaHCO₃ solution. The obtained solid compound was dried under high vacuum.

Scheme S1. Preparation of 2-halobenzamides



x = Br,I R = H, 5-OMe, 4,5-*di*-OMe, 3-Me

R¹= Aryl, benzyl



2-Bromo-N-phenylbenzamide^{2a} (Substrate for 1a and 2a)

Off white solid, yield: 2.71 g (98%). ¹H NMR (500 MHz, CDCl₃) δ 7.86 (s, 1H), 7.61 (dd, *J* = 16.2, 7.5 Hz, 4H), 7.37 (dd, *J* = 13.1, 7.0 Hz, 3H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 165.6, 137.8, 137.6, 133.5, 131.6, 129.7, 129.1, 127.7, 124.9, 120.2, 119.3.



2-Bromo-N-(p-tolyl)benzamide^{2a} (Substrate for 1b and 2h)

White solid, yield: 2.84 g (98%). ¹H NMR (500 MHz, CDCl₃) δ 7.73 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H) 2.34 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.5, 137.9, 135.0, 134.6, 133.5, 131.5, 129.8, 129.6, 127.7, 120.2, 119.3, 20.9.



2-Bromo-N-(4-methoxyphenyl)benzamide^{2b} (Substrate for 1c and 2i)

Off white solid, yield: 2.97 g (97%). ¹H NMR (500 MHz, CDCl₃) δ 7.69 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.4, 156.8, 137.9, 133.5, 131.5, 130.6, 129.8, 127.7, 122.0, 119.3, 114.3, 55.5.



2-Bromo-N-(4-chlorophenyl)benzamide^{2b} (Substrate for 1d)

White solid, yield: 2.85 g (92%). ¹H NMR (700 MHz, DMSO-*d*₆) δ 10.65 (s, 1H), 7.80 – 7.74 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 6.5 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 8.5 Hz, 3H). ¹³C NMR (176 MHz, DMSO-*d*₆) δ 166.4, 139.3, 138.4, 133.2, 131.8, 129.3, 129.2, 128.2, 127.9, 121.6, 119.4.



2-Bromo-*N*-(m-tolyl)benzamide (Substrate for 1e and 2e)

Off white solid, yield: 2.76 g (96%).¹H NMR (400 MHz, DMSO-*d*₆) δ 10.40 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.60 (s, 1H), 7.52 (ddd, *J* = 14.7, 10.7, 4.5 Hz, 3H), 7.42 (td, *J* = 7.8, 1.9 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 2.31 (s, 3H). ¹³C NMR (176 MHz, DMSO-*d*₆) δ 166.2, 139.7, 139.4, 138.4, 133.2, 131.6, 129.3, 129.1, 128.2, 125.0, 120.5, 119.5, 117.3, 21.7. HRMS (ESI) m/z calculated for C₁₄H₁₂BrNO [M+H]⁺ 290.0175, found 290.0150.



2-Bromo-N-(3,4-dimethylphenyl)benzamide (Substrate for 1f and 2l)

Off white solid, yield: 2.95 g (97%). ¹H NMR (500 MHz, CDCl₃) δ 7.89 (d, J = 7.4 Hz, 1H), 7.53 – 7.37 (m, 4H), 7.34 (dd, J = 8.0, 1.6 Hz, 1H), 7.12 (d, J = 7.0 Hz, 2H), 2.27 (s, 3H), 2.25 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 167.1, 142.3, 140.0, 137.4, 135.3, 133.3, 131.4, 130.1, 128.5, 128.3, 121.4, 117.7, 92.4, 19.9, 19.3. HRMS (ESI) m/z calculated for C₁₅H₁₄BrNO [M+H]⁺ 326.0151, found 326.0130.



2-Bromo-5-methoxy-N-phenylbenzamide^{2c} (Substrate for 1g)

Pale yellow solid, yield: 2.97 g (97%).¹H NMR (500 MHz, CDCl₃) δ 7.83 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.17 (dd, *J* = 10.5, 4.8 Hz, 2H), 6.86 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.81 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.3, 159.1, 138.3, 137.5, 134.3, 129.1, 124.9, 120.1, 118.3, 114.9, 109.3, 55.7.



2-Bromo-5-methoxy-N-(p-tolyl)benzamide^{2c} (Substrate for 1h)

Pale yellow solid, yield: 3.04 g (95%). ¹H NMR (500 MHz, CDCl₃) δ 7.79 (s, 1H), 7.51 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.8 Hz, 1H), 7.19 – 7.12 (m, 3H), 6.85 (dd, J = 8.8, 3.1 Hz, 1H), 3.80 (s, 3H), 2.34 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.2, 159.1, 138.4, 135.0, 134.6, 134.3, 129.6, 120.2, 118.3, 114.8, 109.4, 55.7, 20.9.



2-Bromo-N-(3,4-dimethylphenyl)-5-methoxybenzamide (Substrate for 1i)

Off white solid, yield: 3.17 g (95%). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (s, 1H), 7.47 (d, J = 8.8 Hz, 1H), 7.43 (s, 1H), 7.35 (dd, J = 8.0, 1.7 Hz, 1H), 7.18 (d, J = 2.9 Hz, 1H), 7.12 (d, J = 8.1 Hz, 1H), 6.85 (dd, J = 8.8, 2.9 Hz, 1H), 3.81 (s, 3H), 2.27 (s, 3H), 2.25 (s, 3H). ¹³C NMR (176 MHz, CDCl₃) δ 165.2, 159.0, 138.5, 137.4, 135.2, 134.3, 133.3, 130.1, 121.4, 118.2,

117.6, 114.8, 109.4, 55.7, 19.9, 19.3. HRMS (ESI) m/z calculated for C₁₆H₁₆BrNO₂ [M+H]⁺ 334.0437, found 334.0422.



2-Bromo-5-methoxy-N-(2-methoxyphenyl)benzamide (Substrate for 1j)

White solid, yield: 3.26 g (97%). ¹H NMR (500 MHz, CDCl₃) δ 8.54 (d, *J* = 7.8 Hz, 1H), 8.38 (s, 1H), 7.51 (d, *J* = 8.7 Hz, 1H), 7.21 (s, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.86 (m, 1H), 3.88 (s, 3H), 3.82 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.1, 159.0, 148.2, 138.8, 134.4, 127.4, 124.3, 121.2, 120.0, 118.0, 114.9, 110.1, 109.5, 55.8, 55.7. HRMS (ESI) m/z calculated for C₁₅H₁₄BrNO₃ [M+H]⁺ 336.0230, found 334.0236.



2-Bromo-5-methoxy-N-(4-methoxyphenyl)benzamide^{2c} (Substrate for 1k)

Off white solid, yield: 3.29 g (98%).¹H NMR (400 MHz, DMSO- d_6) δ 10.31 (s, 1H), 7.63 (d, J = 7.0 Hz, 2H), 7.58 (d, J = 8.7 Hz, 1H), 7.12 (s, 1H), 7.04 – 6.97 (m, 1H), 6.93 (d, J = 7.5 Hz, 2H), 3.81 (s, 3H), 3.74 (s, 3H). ¹³C NMR (176 MHz, DMSO- d_6) δ 165.5, 159.0, 156.0, 140.5, 134.0, 132.6, 121.6, 117.5, 114.7, 114.3, 109.7, 56.2, 55.7.



2-Bromo-4,5-dimethoxy-N-(p-tolyl)benzamide^{2b} (Substrate for 11)

White solid, yield: 3.43 g (98%). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (s, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.26 (s, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.00 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.34 (s,

3H). ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 151.1, 148.5, 135.1, 134.4, 129.6, 129.3, 120.1, 115.8, 113.1, 109.8, 56.3, 56.2, 20.9.

2-Bromo-4,5-dimethoxy-N-(4-methoxyphenyl)benzamide (Substrate for 1m or 2k)

Pale yellow solid, yield: 3.48 g (95%). ¹H NMR (500 MHz, CDCl₃) δ 7.92 (s, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.28 (s, 1H), 7.02 (s, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 3.81 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 164.7, 156.8, 151.1, 148.6, 130.8, 129.2, 121.8, 115.8, 114.3, 113.1, 109.8, 56.3, 56.2, 55.5. HRMS (ESI) m/z calculated for C₁₆H₁₆BrNO₄ [M+H]⁺ 366.0335, found 366.0329.



2-Bromo-N-(quinolin-8-yl)benzamide^{2d} (Substrate for 1n or 2q)

Off white solid, yield: 3.14 g (96%). ¹H NMR (500 MHz, CDCl₃) δ 10.29 (s, 1H), 8.95 (d, *J* = 7.2 Hz, 1H), 8.79 (d, *J* = 3.3 Hz, 1H), 8.18 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.46 (m, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 165.9, 148.4, 138.6, 138.3, 136.4, 134.3, 133.7, 131.5, 129.6, 128.0, 127.7, 127.4, 122.2, 121.7, 119.7, 116.9.



2-Bromo-5-methoxy-N-(quinolin-8-yl)benzamide (Substrate for 10 or 2r)

Pale yellow solid, yield: 3.35 g (94%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.28 (s, 1H), 8.91 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.73 (d, *J* = 7.4 Hz, 1H), 8.47 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.72 – 7.60 (m, 3H), 7.32 (d, *J* = 2.9 Hz, 1H), 7.08 (dd, *J* = 8.8, 3.0 Hz, 1H), 3.84 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.7, 159.0, 148.4, 139.0, 138.6, 136.3, 134.5, 134.3, 128.0, 127.4, 122.2, 121.7, 118.0, 116.9, 114.8, 109.8, 55.7. HRMS (ESI) m/z calcd for C₁₇H₁₃BrN₂O₂ [M+H]⁺ 357.0233, found 357.0201.



2-Bromo-4,5-dimethoxy-N-(quinolin-8-yl)benzamide (Substrate for 1p or 2s)

White solid, yield: 3.64 g (94%). ¹H NMR (400 MHz, CDCl₃) δ 10.49 (s, 1H), 8.92 (d, *J* = 7.2 Hz, 1H), 8.80 (d, *J* = 1.6 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.55 (dd, *J* = 14.8, 7.9 Hz, 2H), 7.44 (dd, *J* = 7.7, 3.8 Hz, 1H), 7.31 (s, 1H), 7.08 (s, 1H), 3.92 (s, 6H). ¹³C NMR (176 MHz, CDCl₃) δ 165.4, 165.4, 151.0, 151.00, 148.5, 148.4, 138.7, 136.3, 134.5, 130.0, 128.0, 127.4, 122.0, 121.7, 116.8, 116.0, 112.8, 110.4, 56.4, 56.2. HRMS (ESI) m/z calcd for C₁₈H₁₅BrN₂O₃ [M+H]⁺ 387.0339, found 387.0338.



2-Bromo-*N*-(o-tolyl)benzamide^{2a} (Substrate for 2b)

White solid, yield: 2.84 g (98%). ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.28 (m, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 2.35 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.6, 138.0, 135.4, 133.6, 131.6, 130.7, 130.0, 129.6, 127.8, 126.9, 125.7, 123.2, 119.1, 18.1. ¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J*

= 17.5, 7.8 Hz, 2H), 7.59 (s, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.26 (d, *J* = 7.4 Hz, 1H), 2.38 (s, 3H).



2-Bromo-N-(2-methoxyphenyl)benzamide^{2b} (Substrate for 2c)

White solid, yield: 2.95 g (96%). ¹H NMR (500 MHz, CDCl₃) δ 7.70 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.44 – 7.36 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 3.83 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.5, 160.3, 138.7, 137.8, 133.5, 131.7, 129.8, 127.8, 119.2, 112.1, 110.8, 105.7, 55.4.



2-Bromo-N-(3-methoxyphenyl)benzamide^{2b} (Substrate for 2f)

White solid, yield: 2.96 g (97%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.46 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 6.70 (d, *J* = 7.0 Hz, 1H), 3.75 (s, 3H). ¹³C NMR (176 MHz, DMSO-*d*₆) δ 166.3, 156.0, 140.6, 139.6, 133.2, 131.6, 130.1, 129.3, 128.2, 119.4, 112.3, 109.7, 105.8, 55.5.



2-Bromo-N-(3-nitrophenyl)benzamide^{3a} (Substrate for 2g)

Light yellow solid, yield: 2.86 g (89%). ¹H NMR (500 MHz, CDCl₃) δ 8.49 (s, 1H), 8.33 (s, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.99 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 8.1 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 166.1, 148.6, 138.7, 136.8, 133.6, 132.1, 130.0, 129.8, 127.8, 125.9, 119.4, 119.3, 114.9.



2-Bromo-N-(4-bromophenyl)benzamide^{3b} (Substrate for 2j)

Light brown solid, yield: 3.19 g (90%). ¹H NMR (400 MHz, DMSO- d_6) δ 10.62 (s, 1H), 7.77 – 7.67 (m, 3H), 7.57 (dd, J = 12.7, 5.1 Hz, 3H), 7.51 (t, J = 7.4 Hz, 1H), 7.44 (td, J = 7.7, 1.7Hz, 1H). ¹³C NMR (176 MHz, DMSO- d_6) δ 166.4, 139.3, 138.8, 133.2, 132.1, 131.8, 129.3, 128.2, 121.9, 119.4, 115.9.



2-Bromo-*N***-(3,4-dimethoxyphenyl)benzamide**^{3c} (Substrate for **2m**)

White solid, yield: 3.26 g (97%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.50 (s, 1H), 7.95 (d, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.23 – 7.05 (m, 3H), 7.00 (d, *J* = 6.5 Hz, 2H), 3.82 (s, 3H), 3.82 (s, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 165.9, 158.9, 151.1, 140.0, 134.1, 127.2, 125.9, 123.5, 120.7, 117.5, 115.1, 112.0, 109.7, 56.2, 56.1.



2-Bromo-*N*-(naphthalen-1-yl)benzamide (Substrate for 2o)

Light pink solid, yield: 3.0 g (92%). ¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, J = 7.4 Hz, 1H), 8.10 (s, 1H), 8.00 (d, J = 7.7 Hz, 1H), 7.90 (d, J = 7.3 Hz, 1H), 7.77 (t, J = 7.0 Hz, 2H), 7.69 (d, J = 7.9 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.46 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 166.2, 137.9, 134.2, 133.6, 132.0, 131.8, 130.2, 128.8, 127.9, 127.2, 126.5, 126.3, 126.1, 125.8, 121.0, 120.8, 119.2. HRMS (ESI) m/z calcd for C₁₇H₁₂BrNO [M+Na]⁺ 347.9994, found 347.9978.



N-Benzyl-2-bromo-5-methoxybenzamide^{3d} (Substrate for 2p)

Light yellow solid, yield: 2.98 g (93%). ¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, *J* = 8.8 Hz, 1H), 7.36 (dt, *J* = 14.9, 7.4 Hz, 4H), 7.29 (t, *J* = 7.0 Hz, 1H), 7.12 (d, *J* = 3.0 Hz, 1H), 6.81 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.38 (s, 1H), 4.64 (d, *J* = 5.7 Hz, 2H), 3.79 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 167.2, 159.0, 138.2, 137.6, 134.2, 128.8, 128.0, 127.7, 117.9, 114.9, 109.4, 55.7, 44.3.



2-Iodo-3-methyl-*N***-phenylbenzamide**^{3e} (Substrate for **2t**)

White solid, yield: 0.98 g (97%) (reaction was performed at 3 mmol scale). ¹H NMR (500 MHz, CDCl₃) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 3H), 7.31 (d, *J* = 4.3 Hz, 2H), 7.25 (d, *J* = 6.5 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 2.52 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 168.2, 143.8, 143.1, 137.6, 130.8, 129.2, 128.3, 125.2, 124.9, 120.1, 99.2, 29.2.

A typical synthetic procedure. of spirodiazatellurane:

Scheme S2. Preparation of spirodiazatellurane



Synthesis of spirodiazatellurane

Under an argon atmosphere, 230 mg (0.6 equiv, 1.8 mmol) of well grinded tellurium powder and dry THF (5 mL) were taken in a single neck 50 mL of round bottom flask. The fresh small Na-pieces 83 mg (1.2 equiv, 3.6 mmol) was added cautiously with stirring to black suspension of tellurium in THF. Further, naphthalene 46 mg (0.36 mmol, 0.2 equiv. w.r.t. Te powder) was added to it.of. After this, reaction mixture was allowed to stir at room temperature for another 12 h. During this time, the colour of the reaction mixture changes from brown to off-white or gray. Next, THF was evaporated under vacuum followed by heating the reaction mixture to 70 °C under nitrogen. The reaction mixture was then cooled to room temperature and 0.83 g dry powder of 2-halo-*N*-arylbenzamides (1.0 equiv, 3.0 mmol) was added followed by the addition of HMPA (5.0 mL). The resulted reaction mixture was stirred for 10 minutes, then 431 mg (3.0 mmol) of CuBr was added and then resulted reaction mixture was stirred at 110 °C for 36-48 h (Scheme S2). The advance of the reaction was monitored by taking the aliquot of reaction mixture by using TLC at regular period of time. Reaction mixture was then added to 400 mL of brine and stirred vigorously for 3-4 h. Residue was filtered out and washed with distilled water. Crude product was dried under vacuum. The resultant selenides were purified by flash column chromatography using petroleum ether/ethyl acetate (8:2) as eluent.⁴



2,2'-Diphenyl-1 λ^{4} **-1,1'-spirobi[benzo**[*d*][**1,2]tellurazole]-3,3'(2H,2'H)-dione 1a**:^{5a} Off white solid, yield: 466 mg (60%), m.p.: 155-157 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.04 (d, *J* = 6.6 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 4H), 7.74 – 7.62 (m, 6H), 7.43 (t, *J* = 7.5 Hz, 4H), 7.18 (t, *J* = 7.2 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 167.4, 141.6, 138.3, 134.1, 132.7, 130.8, 129.8, 129.7, 127.9, 125.2, 124.3; ¹²⁵Te NMR (126 MHz, CDCl₃) δ 741.5; HRMS (ESI) m/z calculated for C₂₆H₁₈N₂O₂Te [M+H]⁺ 521.0505, found 521.0481.



2,2'-Di-p-tolyl-1\lambda^4-1,1'-spirobi[benzo[*d***][1,2]tellurazole]-3,3'(2H,2'H)-dione 1b: White solid, yield: 491 mg (60%), m.p.: 240-241 °C. ¹H NMR (500 MHz, CDCl₃) \delta 8.22 (d,** *J* **= 6.3 Hz, 2H), 7.79 (d,** *J* **= 6.9 Hz, 2H), 7.61 (dd,** *J* **= 12.6, 7.5 Hz, 4H), 7.55 (d,** *J* **= 7.2 Hz, 4H), 7.21 (d,** *J* **= 7.1 Hz, 4H), 2.34 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) \delta 167.3, 138.9, 138.4, 134.9, 133.9, 132.6, 130.7, 130.3, 129.7, 127.9, 124.1, 21.0.; ¹²⁵Te NMR (126 MHz, CDCl₃) \delta 736.5; HRMS (ESI) m/z calculated for C₂₈H₂₂N₂O₂Te [M+H]⁺ 549.0822, found 549.0818.**



2,2'-Bis(4-methoxyphenyl)-1 λ^4 -1,1'-spirobi[benzo[*d*][1,2]tellurazole]-3,3'(2H,2'H)-dione 1c: Light brown solid, yield: 529 mg (61%), m.p.: 238-239 °C.¹H NMR (700 MHz, DMSO*d*₆) δ 8.01 (d, *J* = 6.6 Hz, 2H), 7.76 – 7.61 (m, 10H), 7.00 (d, *J* = 8.6 Hz, 4H), 3.78 (s, 6H). ¹³C NMR (176 MHz, DMSO-*d*₆) δ 167.9, 156.4, 138.8, 136.1, 133.9, 133.2, 132.0, 129.7, 129.2, 126.3, 114.6, 55.7. ¹²⁵Te NMR (126 MHz, DMSO-*d*₆) δ 788.6. HRMS (ESI) m/z calculated for C₂₈H₂₂N₂O₄Te [M+H]⁺ 581.0717, found 581.0742.



2,2'-Bis(4-chlorophenyl)-1\lambda^4-1,1'-spirobi[benzo[*d***][1,2]tellurazole]-3,3'(2H,2'H)-dione 1d**: White solid, yield: 308 mg (35%), m.p.: 233-234 °C. ¹H NMR (700 MHz, DMSO-*d*₆) δ 8.05 (d, *J* = 6.6 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 4H), 7.69 (dd, *J* = 14.8, 7.2 Hz, 4H), 7.65 (d, *J* = 7.1 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 4H). ¹³C NMR (176 MHz, DMSO-*d*₆) δ 168.4, 142.2, 138.3, 134.2, 133.2, 132.2, 130.0, 129.2, 129.0, 128.4, 126.6. ¹²⁵Te NMR (126 MHz, CDCl₃) δ 746.5; HRMS (ESI) m/z calculated for C₂₆H₁₆Cl₂N₂O₂Te [M+H]⁺ 588.9706, found 588.9728.



2,2'-Di-m-tolyl-1λ⁴**-1,1'-spirobi[benzo**[*d*][**1,2]tellurazole]-3,3'(2H,2'H)-dione 1e**: Off white solid, yield: 491 mg (60%), m.p.: 248-250 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.25 (dd, *J* = 7.3, 1.2 Hz, 2H), 7.82 (d, *J* = 7.4 Hz, 2H), 7.66 (t, *J* = 6.9 Hz, 2H), 7.62 (td, *J* = 7.5, 1.4 Hz, 2H), 7.52 (s, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 2H), 2.38 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 167.4, 141.5, 139.8, 138.4, 134.0, 132.7, 130.8, 129.7,

129.6, 128.0, 126.1, 124.9, 121.3, 21.6. ¹²⁵TeNMR (126 MHz, DMSO- d_6) δ 735.9. HRMS (ESI) m/z calculated for C₂₈H₂₂N₂O₂Te [M+H]⁺ 549.0818, found 549.0829.



2,2'-Bis(3,4-dimethylphenyl)-1 λ^4 -1,1'-spirobi[benzo[*d*][1,2]tellurazole]-3,3'(2H,2'H)dione 1f: Off white solid, yield: 516 mg (60%), m.p.: 210-212 °C. ¹H NMR (500 MHz, DMSO d_6) δ 8.01 (m, 2H), 7.69 – 7.60 (m, 10H), 7.17 (d, *J* = 8.1 Hz, 2H), 2.25 (s, 6H), 2.23 (s, 6H); ¹³C NMR (126 MHz, DMSO- d_6) δ 167.9, 141.0, 139.0, 137.1, 133.7, 133.1, 132.2, 132.0, 130.3, 129.7, 129.2, 125.7, 122.1, 20.0, 19.3; ¹²⁵Te NMR (126 MHz, DMSO- d_6) δ 789.9; HRMS (APCI) m/z calculated for C₃₀H₂₆N₂O₂Te [M+H]⁺ 577.1132, found 577.1160.



5,5'-Dimethoxy-2,2'-diphenyl-1 λ^4 **-1,1'-spirobi**[benzo[*d*][**1,2**]tellurazole]-**3,3'(2H,2'H)dione 1g**: Yellowish brown solid, yield: 598 mg (69%), m.p.: 202-203 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.82 (d, *J* = 8.0 Hz, 4H), 7.57 – 7.51 (m, 4H), 7.42 (t, *J* = 7.8 Hz, 4H), 7.26 (dd, *J* = 8.6, 2.5 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 2H), 3.82 (s, 6H). ¹³C NMR (176 MHz, DMSO-*d*₆) δ 167.7, 162.7, 143.3, 140.8, 130.6, 129.4, 124.9, 124.5, 123.0, 120.1, 114.5, 56.1. ¹²⁵Te NMR (126 MHz, DMSO-*d*₆) δ 791.2. HRMS (ESI) m/z calculated for C₃₀H₂₆N₂O₄Te [M+H]⁺ 609.1030, found 609.1008.



5,5'-Dimethoxy-2,2'-di-p-tolyl-1λ⁴**-1,1'-spirobi[benzo**[*d*][1,2]tellurazole]-3,3'(2H,2'H)**dione 1h**: Off white solid, yield: 590 mg (65%), m.p.: 230-232 °C. ¹H NMR (500 MHz,

Hz, 6H), 3.81 (s, 6H), 2.32 (s, 6H). ¹³C NMR (126 MHz, DMSO- d_6) δ 167.5, 162.7, 140.9, 140.7, 133.5, 130.7, 129.9, 124.7, 122.8, 120.0, 114.4, 56.1, 21.0. ¹²⁵Te NMR (126 MHz, DMSO- d_6) δ 785.3. HRMS (ESI) m/z calculated for C₃₀H₂₆N₂O₄Te [M+H]⁺ 609.1030, found 609.1008.

DMSO- d_6) δ 7.72 (d, J = 8.3 Hz, 4H), 7.51 (dd, J = 5.6, 2.9 Hz, 4H), 7.23 (dd, J = 11.4, 5.5



2,2'-Bis(3,4-dimethylphenyl)-5,5'-dimethoxy-1 λ^4 **-1,1'-spirobi[benzo**[*d*][**1,2]tellurazole]-3,3'(2H,2'H)-dione 1i**: Yellowish brown solid, yield: 618 mg (65%), m.p.: 252-255 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 2.6 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.47 (s, 2H), 7.36 (m, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.09 (dd, *J* = 8.7, 2.7 Hz, 2H), 3.85 (s, 6H), 2.28 (s, 6H), 2.25 (s, 6H).¹³C NMR (126 MHz, CDCl₃) δ 167.1, 163.6, 140.6, 139.3, 138.0, 133.6, 130.9, 130.7, 125.3, 121.5, 121.1, 117.6, 114.5, 55.9, 20.1, 19.3. ¹²⁵Te NMR (126 MHz, CDCl₃) δ 739.3. HRMS (ESI) m/z calculated for C₃₂H₃₀N₂O₄Te [M+H]⁺ 637.1343, found 637.1366.



5,5'-Dimethoxy-2,2'-bis(2-methoxyphenyl)- $1\lambda^4$ -1,1'-spirobi[benzo[d][1,2]tellurazole]-

3,3'(2H,2'H)-dione 1j: Off white solid, yield: 631 mg (66%), m.p.: 238-240 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.81 (dd, *J* = 26.7, 8.1 Hz, 4H), 7.47 (s, 2H), 7.22 (dd, *J* = 14.0, 7.5 Hz, 4H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 2H), 3.81 (s, 6H), 3.80 (s, 6H). ¹³C NMR (176 MHz, DMSO-*d*₆) δ 168.6, 162.5, 153.0, 139.5, 131.9, 130.8, 127.9, 126.0, 123.9, 121.2, 120.1, 113.9, 112.5, 56.1, 55.9. ¹²⁵Te NMR (126 MHz, DMSO-*d*₆) δ 810.9. HRMS (ESI) m/z calculated for C₃₀H₂₆N₂O₆Te [M+H]⁺ 641.0928, found 641.0912.



5,5'-Dimethoxy-2,2'-bis(4-methoxyphenyl)-1 λ^4 -1,1'-spirobi[benzo[*d*][1,2]tellurazole]-3,3'(2H,2'H)-dione 1k: Off white solid, yield: 650 mg (68%), m.p.: 225-227 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.72 (d, *J* = 8.6 Hz, 4H), 7.56 – 7.49 (m, 4H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 4H), 3.81 (s, 6H), 3.78 (s, 6H). ¹³C NMR (176 MHz, DMSO-*d*₆) δ 167.5, 162.7, 156.3, 140.8, 136.1, 130.6, 126.1, 122.9, 119.9, 114.6, 114.3, 56.1, 55.7. ¹²⁵Te NMR (126 MHz, DMSO-*d*₆) δ 782.4. HRMS (ESI) m/z calculated for C₃₀H₂₆N₂O₆Te [M+H]⁺ 641.0928, found 641.0931.



5,5',6,6'-Tetramethoxy-2,2'-di-p-tolyl- $1\lambda^4$ -1,1'-spirobi[benzo[d][1,2]tellurazole]-

3,3'(2H,2'H)-dione 11: Yellowish white solid, yield: 659 mg (66%), m.p.: 171-173 °C. ¹H NMR (500 MHz, DMSO- d_6) δ 7.68 (d, J = 8.2 Hz, 4H), 7.51 (s, 2H), 7.24 (d, J = 8.2 Hz, 4H),

7.05 (s, 2H), 3.83 (s, 6H), 3.58 (s, 6H), 2.32 (s, 6H). ¹³C NMR (126 MHz, DMSO- d_6) δ 167.3, 153.0, 152.0, 140.8, 133.4, 132.4, 129.9, 125.1, 122.9, 111.9, 111.7, 56.4, 56.3, 21.0. ¹²⁵Te NMR (126 MHz, CDCl₃) δ 719.2. HRMS (ESI) m/z calculated for C₃₂H₃₀N₂O₆Te [M+H]⁺ 669.1242, found 669.1267.



5,5',6,6'-Tetramethoxy-2,2'-bis(4-methoxyphenyl)- $1\lambda^4$ -1,1'-

spirobi[**benzo**[*d*][1,2]**tellurazole**]-3,3'(2H,2'H)-dione 1m: Off white solid, yield: 712 mg (68%), m.p.: 230-231 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 4.7 Hz, 4H), 7.59 (s, 2H), 7.04 (s, 2H), 6.91 (d, *J* = 8.8 Hz, 4H), 3.86 (s, 6H), 3.78 (s, 6H), 3.69 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 156.8, 153.6, 152.7, 134.8, 132.1, 125.4, 117.9, 114.9, 112.1, 111.4, 56.6, 56.4, 55.5. ¹²⁵Te NMR (126 MHz, CDCl₃) δ 718.7. HRMS (APCI) m/z calculated for C₃₂H₃₀N₂O₈Te [M+H]⁺ 701.1140, found 701.1121.



2,2'-Di(quinolin-8-yl)-1\lambda^4-1,1'-spirobi[benzo[*d***][1,2]tellurazole]-3,3'(2H,2'H)-dione 1n: Yellowish white, yield: 697 mg (75%), m.p.: 237-238 °C. ¹H NMR (400 MHz, DMSO-***d***₆) \delta 9.13 (t,** *J* **= 4.4 Hz, 2H), 8.61 (d,** *J* **= 4.0 Hz, 2H), 8.44 (d,** *J* **= 8.2 Hz, 2H), 8.09 (t,** *J* **= 9.0 Hz, 2H), 7.75 (d,** *J* **= 4.4 Hz, 4H), 7.62 (d,** *J* **= 7.6 Hz, 2H), 7.56 (t,** *J* **= 7.3 Hz, 2H), 7.52 – 7.45 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) \delta 171.0, 145.4, 141.4, 139.9, 138.9, 137.1, 136.6, 133.1,** 130.5, 129.4, 129.2, 128.8, 128.3, 123.1, 121.6, 121.1; ¹²⁵Te NMR (126 MHz, CDCl₃) δ 865.6; HRMS (ESI) m/z calculated for C₃₂H₂₀N₄O₂Te [M+H]⁺ 623.0724, found 623.0706.



5,5'-Dimethoxy-2,2'-di(quinolin-8-yl)- $1\lambda^4$ -1,1'-spirobi[benzo[d][1,2]tellurazole]-

3,3'(2H,2'H)-dione 1o: Yellowish white, yield: 744 mg (73%), m.p.: 235-237 °C. ¹H NMR (500 MHz, CDCl₃) δ 9.31 (d, *J* = 7.9 Hz, 2H), 8.39 (d, *J* = 3.1 Hz, 2H), 8.19 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 2.5 Hz, 2H), 7.74 (t, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.31 (dd, *J* = 8.2, 4.3 Hz, 2H), 6.88 (dd, *J* = 8.6, 2.5 Hz, 2H), 3.86 (s, 6H).¹³C NMR (176 MHz, CDCl₃) δ 170.8, 161.9, 145.4, 141.4, 140.0, 138.5, 137.1, 130.8, 129.7, 129.2, 128.3, 123.0, 121.5, 121.1, 120.8, 112.2, 55.6. ¹²⁵Te NMR (126 MHz, CDCl₃) δ 870.0. HRMS (ESI) m/z calculated for C₃₄H₂₄N₄O₄Te [M+H]⁺ 683.0935, found 683.0967.



5,5',6,6'-Tetramethoxy-2,2'-di(quinolin-8-yl)-1λ⁴**-1,1'-spirobi[benzo**[*d*]**[1,2]tellurazole]-3,3'(2H,2'H)-dione 1p**: Yellowish white, yield: 810 mg (73%), m.p.: 242-243 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.23 (d, *J* = 7.8 Hz, 2H), 8.42 (d, *J* = 3.1 Hz, 2H), 8.16 (d, *J* = 8.1 Hz, 2H), 7.76 (s, 2H), 7.69 (t, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.29 (dd, *J* = 8.1, 4.2 Hz, 2H), 7.10 (s, 2H), 3.95 (s, 6H), 3.39 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 170.9, 153.3, 151.3, 145.5, 141.6, 139.9, 137.1, 129.1, 128.3, 122.8, 121.4, 121.2, 110.9, 110.7, 56.2, 56.0.¹²⁵Te NMR (126 MHz, CDCl₃) δ 855.6. HRMS (APCI) m/z calculated for C₃₆H₂₈N₄O₆Te [M+H]⁺ 743.1147, found 701.1147.

Synthesis of spirodioxytellurane (1q and 1r)

Spirotelluranes **1q** and **1r** were prepared from corresponding 2-iodobenzoyl alcohol (0.73 g, 3 mmol) and 2-bromo-5-methoxy-benzoic acid (0.7 g, 3.0 mmol) respectively; by using the same methodology as mentioned above for preparation of spirotellurane **1a-1p**.



3H,3'H-1 λ ⁴**-1,1'-Spirobi[benzo**[*c*][**1,2**]**oxatellurole**] **1q**:^{5b} Creamy White solid, yield: 366 mg (72%), m.p.: 171-173 °C (171 °C)^{5b}. ¹H NMR (500 MHz, CDCl₃) δ 7.87 (dd, J = 8.2, 6.2 Hz, 2H), 7.39 (dtt, J = 10.5, 7.1, 3.7 Hz, 4H), 7.25 (d, J = 7.3 Hz, 2H), 5.45 – 5.37 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 148.1, 131.1, 130.7, 128.5, 128.0, 124.1, 72.1.¹²⁵Te NMR (126 MHz, CDCl₃) δ 768.6. HRMS (ESI) m/z calculated for C₁₄H₁₂O₂Te [M+H]⁺ 342.9973, found 342.9952.



5,5'-Dimethoxy-3H,3'H-1\lambda^4-1,1'-spirobi[benzo[*c***][1,2]oxatellurole]-3,3'-dione 1r: Light brown solid, yield: 513 mg (80%), m.p.: 242-245 °C. ¹H NMR (500 MHz, CDCl₃) \delta 7.58 (d,** *J* **= 8.8 Hz, 2H), 7.53 (d,** *J* **= 3.1 Hz, 2H), 6.95 (dd,** *J* **= 8.8, 3.0 Hz, 2H), 3.84 (s, 6H). ¹³C NMR (176 MHz, DMSO-***d***₆) \delta 170.8, 162.9, 135.0, 131.0, 129.3, 122.0, 114.5, 56.3. ¹²⁵Te NMR (126** MHz, CDCl₃) δ 1013.7. HRMS (APCI) m/z calculated for C₁₆H₁₂O₆Te 430.9769 [M+H]⁺ 430.9770, found 430.9778.

Chart S1: Substrates failed to provide spirotelluranes

Electron withdrawing groups in benzamide/ acid ring



Electron withdrawing groups in aniline ring



Table S1a. Optimization for the synthesis of biaryls



Entry	X	Te source	Cu-salt	Base	Solvent	Yield of
		(equiv)	(equiv)	(equiv)		$2a^{a}$
1	Br	_	CuBr (1.0)	_	HMPA	_
2	Br	Te powder (3.0)	_	_	HMPA	_
3	Br	Na ₂ Te (3.0)	_	_	HMPA	_
4	Br	Na ₂ Te (3.0)	CuBr (1.0)	-	HMPA	95% (93%) ^b
5	Br	Na ₂ Te (3.0)	CuI (1.0)	-	HMPA	70%
6	Br	Na ₂ Te (3.0)	CuBr ₂ (1.0)	_	HMPA	75%
7	Ι	Na ₂ Te (3.0)	CuBr (1.0)	-	HMPA	66%
8	Br	—	CuBr (1.0)	Na ^t OBu (3.0)	HMPA	30%°
9	Br	Na ₂ Te (3.0)	CuBr (0.2)	Mg (3.0)	HMPA	25%
10	Br	—	CuBr (1.0)	Mg (3.0)	DMF	_
11	Br	Na ₂ Te (0.2)	CuBr (1.0)	Mg (3.0)	DMF	80%
12	Н	Na ₂ Te (0.2)	CuBr (1.0)	Mg (3.0)	DMF	_
13	Н	Na ₂ Te (3.0)	CuBr (1.0)	Mg (3.0)	DMF	_
14	Н	Na ₂ Te (3.0)	CuBr (1.0)	_	HMPA	_

^aNMR yields, reaction time 16 h. ^bIsolated yield. ^cReaction time 24 h.

$R^{1} \xrightarrow{[l]}{} N$					
Entry	R ¹	Ar	Spirotellurane	Yield of biaryl 1,1 - diamides	
1	-H		1a	2a (none)	
2	-H	Me	1f	2I (none)	
3	-OMe	OMe	1k	2n (none)	
4	-H		1n	2q (none)	

Table S1b. Control experiment for the synthesis of biaryls from respective spirotelluranes

Also, we were curious to know whether the biaryl 1,1'-diamides formed from spirotelluranes under the copper mediated optimized reaction conditions. The reaction spirotellurane **1a** (21 mg, 0.04 mmol) with CuBr (6 mg, 0. 04 mmol) was carried out in HMPA (2 mL) under the argon atmosphere at 110 °C (entry 1, Table S1b). Even after 48h no conversion to corresponding biaryl 1,1'-diamide **2a** was noticed. Similarly, the reaction of the synthesized spirotelluranes **1f**, **1k**, and **1n** with copper(I) bromide failed to afford respective biaryls (entries 2-4, Table S1b).

A typical synthetic procedure of biaryl 1,1'-diamides

Scheme S3. Preparation of C-C coupled biaryls



Synthesis of biaryl 1,1'-diamides

Under argon atmosphere, 383 mg (3 equiv, 3 mmol) of well grinded tellurium powder and dry THF (5 mL) were taken in a single neck 50 mL of round bottom flask. The fresh small Napieces 140 mg (6 equiv, 6 mmol) was added cautiously with stirring to that black suspension of tellurium in THF, and followed by addition of 78 mg (0.2 equiv, 0.6 mmol) of naphthalene. After this, reaction mixture was allowed to stir at room temperature for another 12 h. During this time, the colour of the reaction mixture changes from brown to off-white or gray. Next, THF was evaporated under vacuum followed by heating the reaction mixture to 70 °C under nitrogen. The reaction mixture was then cooled to room temperature and 277 mg dry powder of 2-halo-N-arylbenzamides (1.0 equiv, 1.0 mmol) was added followed by the addition of HMPA (5.0 mL). After this, 144 mg (1.0 mmol) of CuBr was added and then resulted reaction mixture was stirred at 110 °C for 16 h (Scheme S3). The advance of the reaction was monitored by taking aliquot of reaction mixture by using TLC at regular period of time. Reaction mixture was then added to 200 mL of brine and stirred vigorously for 3-4 h. Residue was filtered out and washed with distilled water. Crude product was dried under vacuum. The resultant Biaryl 1,1'-diamide 2a were purified by flash column chromatography using petroleum ether/ethyl acetate (8:2) as eluent.



 N^2 , $N^{2'}$ -Diphenyl-[1,1'-biphenyl]-2,2'-dicarboxamide 2a:^{6a,6c} Off white solid, yield: 182 mg (93%), m.p.: 227-228 °C (228-229 °C).^{6a 1}H NMR (500 MHz, CDCl₃) δ 9.04 (s, 2H), 7.67 (d, J = 6.9 Hz, 2H), 7.43 (d, J = 8.0 Hz, 4H), 7.41 – 7.34 (m, 4H), 7.26 – 7.23 (m, 4H), 7.15 (d, J = 7.0 Hz, 2H), 7.07 (t, J = 7.4 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 168.4, 139.1, 137.9, 136.1, 130.2, 129.8, 128.9, 128.1, 127.2, 124.5, 120.0. HRMS (ESI) m/z calculated for C₂₆H₂₀N₂O₂ [M+Na]⁺415.1417, found 415.1415.



 N^2 , $N^{2'}$ -**Di-o-tolyl-[1,1'-biphenyl]-2,2'-dicarboxamide 2b**:^{6a,6c} Off white solid, yield: 191 mg (91%), m.p.: 230-233 °C (230-232 °C).^{6a 1}H NMR (500 MHz, CDCl₃) δ 8.45 (s, 2H), 7.65 (m, 2H), 7.48 – 7.43 (m, 4H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.28 (m, 2H), 7.12 (t, *J* = 6.6 Hz, 4H), 7.05 (t, *J* = 7.3 Hz, 2H), 2.06 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 168.4, 139.2, 136.4, 135.4, 131.0, 130.5, 130.1, 129.9, 128.1, 127.4, 126.5, 125.8, 124.1, 17.9. HRMS (ESI) m/z calculated for C₂₈H₂₄N₂O₂ [M+H]⁺421.1911, found 421.1897.



 N^2 , $N^{2'}$ -Bis(2-methoxyphenyl)-[1,1'-biphenyl]-2,2'-dicarboxamide 2c: Off white solid, yield: 208 mg (92%), m.p.: 200-202 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.54 (s, 2H), 7.84 (d, *J* = 7.3 Hz, 2H), 7.74 (s, 2H), 7.47 (s, 4H), 7.20 (s, 2H), 7.04 (d, *J* = 7.3 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.86 (t, *J* = 6.8 Hz, 2H), 3.68 (s, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.7, 150.5, 139.6, 136.6, 130.2, 129.8, 128.3, 128.1, 127.5, 125.3, 122.3, 120.6, 111.6, 55.9. HRMS (ESI) m/z calculated for C₂₈H₂₄N₂O₄ [M-H]⁺ 451.1652, found 451.1625.



4,4'-Dimethoxy-*N*₂,*N*₂'-bis(2-methoxyphenyl)-[1,1'-biphenyl]-2,2'-dicarboxamide 2d: Off white solid, yield: 237 mg (93%), m.p.: 118-120 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.67 (s, 2H), 8.32 (m, 2H), 7.29 (d, *J* = 2.5 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.00 (td, *J* = 7.9, 1.5 Hz, 2H), 6.96 – 6.86 (m, 4H), 6.77 (d, *J* = 7.5 Hz, 2H), 3.84 (s, 6H), 3.74 – 3.62 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 167.1, 158.9, 148.4, 137.4, 131.8, 131.1, 127.7, 123.9, 120.8, 120.1, 115.9, 113.2, 109.9, 55.5, 55.4. HRMS (ESI) m/z calculated for C₃₀H₂₈N₂O₆ [M+H]⁺ 513.2020, found 513.1997.



*N*²,*N*²'-**Di-m-tolyl-[1,1'-biphenyl]-2,2'-dicarboxamide 2e**:^{6a,6c} Yellowish white solid, yield: 187 mg (89%), m.p.: 207-209 °C (208-210 °C).^{6a 1}H NMR (500 MHz, DMSO-*d*₆) δ 10.54 (s, 2H), 7.71 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.49 (dd, *J* = 9.0, 5.4 Hz, 4H), 7.37 (s, 2H), 7.25 – 7.18 (m, 4H), 7.14 (t, J = 7.8 Hz, 2H), 6.87 (d, J = 7.4 Hz, 2H), 2.24 (s, 6H). ¹³C NMR (126 MHz, DMSO- d_6) δ 168.3, 139.1, 139.0, 138.4, 136.7, 130.3, 129.8, 129.0, 128.3, 128.1, 125.1, 120.4, 117.2, 21.6. HRMS (ESI) m/z calculated for C₂₈H₂₄N₂O₂ [M+H]⁺ 421.1911 found, 421.1904.



*N*²,*N*²'-**Bis**(3-methoxyphenyl)-[1,1'-biphenyl]-2,2'-dicarboxamide 2f: White solid, yield: 199 mg (88%), m.p.:162-164 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.57 (s, 2H), 7.68 (m, 2H), 7.51 – 7.44 (m, 4H), 7.20 – 7.16 (m, 4H), 7.14 (d, *J* = 4.5 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.64 (dd, *J* = 8.2, 2.1 Hz, 2H), 3.71 (d, *J* = 14.3 Hz, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 168.4, 159.9, 140.1, 139.1, 136.6, 130.4, 130.1, 129.8, 128.4, 128.1, 112.2, 109.6, 105.9, 55.5.



 N^2 , N^2 '-Bis(3-nitrophenyl)-[1,1'-biphenyl]-2,2'-dicarboxamide 2g:⁷ Light yellow solid, yield: 180 mg (75%), m.p.: 190-191 °C (190-191°C).⁷ ¹H NMR (400 MHz, CDCl₃) δ 9.27 (s, 2H), 8.30 (s, 2H), 7.92 (d, J = 7.6 Hz, 2H), 7.82 (d, J = 7.5 Hz, 2H), 7.71 (s, 2H), 7.43 (s, 6H), 7.19 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 168.9, 148.5, 138.8, 130.8, 129.9, 129.8, 128.5, 127.3, 125.6, 119.2, 114.7. HRMS (ESI) m/z calculated for C₂₆H₁₈N₄O₆ [M+Na]⁺ 505.1119, found 505.1120.



 N^2 , N^2 '-Di-p-tolyl-[1,1'-biphenyl]-2,2'-dicarboxamide 2h:^{6c} White solid, yield: 185 mg (88%), m.p.: 175-177 °C (177-179 °C).^{6c 1}H NMR (500 MHz, DMSO-*d*₆) δ 10.54 (s, 2H), 7.68 (d, *J* = 5.6 Hz, 2H), 7.45 (t, *J* = 15.8 Hz, 4H), 7.35 (d, *J* = 7.7 Hz, 4H), 7.16 (t, *J* = 12.0 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 4H), 2.25 (s, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 168.2, 139.1, 136.7, 136.5, 133.3, 130.2, 129.7, 129.6, 128.3, 128.0, 119.9, 20.9. HRMS (ESI) m/z calculated for C₂₈H₂₄N₂O₂ [M+H]⁺ 421.1911, found 421.1944.



 N^2 , N^2 '-Bis(4-methoxyphenyl)-[1,1'-biphenyl]-2,2'-dicarboxamide 2i:^{6a} Off white solid, yield: 196 mg (87%), m.p.: 121-124 °C (120-122 °C).^{6a 1}H NMR (500 MHz, CDCl₃) δ 8.93 (s, 2H), 7.65 (d, J = 6.8 Hz, 2H), 7.42 – 7.34 (m, 4H), 7.30 (d, J = 8.9 Hz, 4H), 7.15 (d, J = 6.7 Hz, 2H), 6.77 (d, J = 8.9 Hz, 4H), 3.75 (s, 6H). ¹³C NMR (126 MHz, DMSO d_6) δ 167.9, 156.1, 139.1, 136.8, 132.2, 130.1, 129.7, 128.3, 128.0, 121.5, 114.3, 55.6. HRMS (ESI) m/z calculated for C₂₈H₂₄N₂O₄ [M+Na]⁺ 475.1628, found 475.1629.



 N^2 , N^2 '-Bis(4-bromophenyl)-[1,1'-biphenyl]-2,2'-dicarboxamide 2j:^{6c} Yellowish white solid, yield: 205 mg (75%), m.p.: 182-184 °C (182-183 °C).^{6c 1}H NMR (500 MHz, DMSO-*d*₆) δ 10.67 (s, 2H), 7.69 (m, 2H), 7.53 – 7.47 (m, 4H), 7.44 (s, 8H), 7.21 (m, 2H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 168.4, 139.1, 138.4, 136.3, 132.0, 130.5, 130.0, 128.3, 128.1, 121.7, 116.0. HRMS (ESI) m/z calculated for C₂₆H₁₈Br₂N₂O₂ [M+H]⁺ 548.9808, found 548.9808.



4,4',5,5'-Tetramethoxy- N^2 , N^2 '-bis(4-methoxyphenyl)-[1,1'-biphenyl]-2,2'-dicarboxamide **2k**: Yellowish white solid, yield: 263 mg (92%), m.p.: 168-170 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.27 (s, 2H), 7.40 (d, *J* = 8.9 Hz, 4H), 7.24 (s, 2H), 6.86 (d, *J* = 8.9 Hz, 4H), 6.73 (s, 2H), 3.85 (s, 6H), 3.71 (s, 6H), 3.69 (s, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.8, 156.0, 149.5, 148.2, 132.4, 131.9, 129.4, 121.4, 114.3, 113.5, 111.4, 56.2, 56.2, 55.6. HRMS (ESI) m/z calculated for C₃₂H₃₂N₂O₈ [M+H]⁺ 573.2231, found 573.2220.



 N^2 , N^2 '-Bis(3,4-dimethylphenyl)-[1,1'-biphenyl]-2,2'-dicarboxamide 2l: Off white solid, yield: 192 mg (86%), m.p.: 190-191 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.43 (s, 2H), 7.67 (d, *J* = 6.6 Hz, 2H), 7.52 – 7.41 (m, 4H), 7.26 (s, 2H), 7.14 (dd, *J* = 20.3, 7.2 Hz, 4H), 7.00 (d, *J* = 8.1 Hz, 2H), 2.14 (s, 12H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 168.1, 139.1, 136.8, 136.8, 136.8, 132.2, 130.2, 130.0, 129.7, 128.3, 128.0, 121.1, 117.5, 20.1, 19.2. HRMS (ESI) m/z calculated for C₃₀H₂₈N₂O₂ [M+Na]⁺ 471.2043, found 471.2054.



*N*²,*N*²-**Bis**(**3,4-dimethoxyphenyl**)-[**1,1**'-**biphenyl**]-**2,2**'-**dicarboxamide 2m**:⁷ Off white solid, yield: 222 mg (87%), m.p.: 225-228 °C (226-228 °C).⁷ ¹H NMR (500 MHz, CDCl₃) δ 8.02 (s, 2H), 7.85 (d, *J* = 7.5 Hz, 4H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.44 (dd, *J* = 13.3, 5.5 Hz, 6H), 7.01 (dt, *J* = 9.7, 4.9 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.85 (d, *J* = 1.5 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 165.8, 149.1, 146.1, 134.9, 131.7, 131.6, 128.7, 127.0, 112.4, 111.3, 105.3, 56.1, 55.9.



4,4'-Dimethoxy-*N*²-(**3-methoxyphenyl**)-*N*²'-(**4-methoxyphenyl**)-[**1,1'-biphenyl**]-**2,2'dicarboxamide 2n**: Off white solid, yield: 232 mg (91%), m.p.: 230-240 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.49 (s, 2H), 7.40 (dd, *J* = 6.7, 2.0 Hz, 4H), 7.19 (s, 2H), 7.09 (m, 2H),

7.01 (dd, J = 8.4, 2.5 Hz, 2H), 6.85 (d, J = 8.9 Hz, 4H), 3.82 (s, 6H), 3.70 (s, 6H).¹³C NMR (126 MHz, DMSO-*d*₆) δ 167.8, 158.8, 156.1, 138.2, 132.2, 131.5, 130.9, 121.5, 115.6, 114.4, 113.2, 55.8, 55.6. HRMS (APCI) m/z calculated for C₃₀H₂₈N₂O₆ [M+Na]⁺ 535.1840, found 535.1868.



 N^2 , N^2 -Di(naphthalen-1-yl)-[1,1'-biphenyl]-2,2'-dicarboxamide 20:⁷ Pinkish white solid, yield: 221 mg (90%), m.p.: 253-255 °C (254-256 °C).⁷ ¹H NMR (500 MHz, CDCl₃) δ 10.81 (s, 2H), 8.98 (d, J = 7.3 Hz, 2H), 8.86 (d, J = 3.3 Hz, 2H), 8.21 (d, J = 8.2 Hz, 2H), 8.06 (d, J = 8.3 Hz, 2H), 7.95 (m, 2H), 7.61 (dt, J = 15.7, 8.0 Hz, 4H), 7.50 (dd, J = 8.2, 4.1 Hz, 2H), 7.38 – 7.36 (m, 4H). ¹³C NMR (176 MHz, CDCl₃) δ 169.3, 139.4, 136.3, 134.0, 132.2, 130.3, 130.0, 128.4, 128.3, 127.9, 127.5, 126.4, 126.2, 126.0, 125.5, 121.8, 121.6. HRMS (ESI) m/z calculated for C₃₄H₂₄N₂O₂ [M+H]⁺ 493.1911, found 493.1888.



 N^2 , N^2 '-Dibenzyl-4,4'-dimethoxy-[1,1'-biphenyl]-2,2'-dicarboxamide 2p: Pale yellow solid, yield: 206 mg (86%), m.p.: 133-135 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.06 (s, 2H), 7.19 (s, 6H), 7.00 (d, *J* = 9.3 Hz, 6H), 6.88 (s, 4H), 4.26 (s, 4H), 3.84 (s, 6H). ¹³C NMR (101 MHz,

DMSO-*d*₆) δ 169.6, 158.8, 139.1, 138.2, 131.5, 131, 128.5, 127.2, 127.1, 115.1, 113.0, 55.8, 42.8. HRMS (ESI) m/z calculated for C₃₀H₂₈N₂O₄ [M+H]⁺481.2122 found 481.2105.



 N^2 , $N^{2'}$ -Di(quinolin-8-yl)-[1,1'-biphenyl]-2,2'-dicarboxamide2q:^{2d,6b} Off white solid, yield: 210 mg (85%), m.p.: 212-214 °C (211-213 °C).^{2d 1}H NMR (500 MHz, CDCl₃) δ 10.36 (s, 2H), 8.69 (d, *J* = 7.3 Hz, 2H), 8.46 (m, 2H), 7.95 (m, 2H), 7.86 (d, *J* = 7.4 Hz, 2H), 7.46 (d, *J* = 4.1 Hz, 4H), 7.42 (dt, *J* = 12.0, 4.3 Hz, 2H), 7.30 (m, 2H), 7.25 (dd, *J* = 8.0, 3.8 Hz, 4H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 166.9, 148.8, 139.7, 138.0, 136.7, 136.4, 134.5, 131.1, 131, 128.4, 128.2, 127.8, 127.1, 122.4, 122.3, 116.2. HRMS (ESI) m/z calculated for C₃₂H₂₂N₄O₂ [M+H]⁺ 495.1816, found 495.1805.



4,4'-Dimethoxy-*N*², *N*²'-**di**(**quinolin-8-yl**)-**[1,1'-biphenyl]-2,2'-dicarboxamide 2r**: Off white solid, yield: 235 mg (85%), m.p.: 180-185 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.21 (s, 2H), 8.60 – 8.46 (m, 4H), 8.27 (d, *J* = 8.2 Hz, 2H), 7.50 (dd, *J* = 13.0, 5.9 Hz, 4H), 7.44 – 7.36 (m, 4H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.09 (dd, *J* = 8.5, 2.5 Hz, 2H), 3.79 (s, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 166.5, 159.1, 148.7, 138.1, 137.6, 136.7, 134.5, 132.9, 131.1, 127.8, 127.8, 122.4,

122.3, 116.5, 116.3, 113.9, 55.9. HRMS (ESI) m/z calculated for $C_{34}H_{26}N_4O_4$ [M+H]⁺ 555.2027, found 555.2012.



4,4',5,5'-Tetramethoxy-*N*²,*N*^{2'}-**di**(**quinolin-8-yl**)-**[1,1'-biphenyl]**-**2,2'-dicarboxamide 2s**: White solid, yield: 258 mg (84%), m.p.: 170-173 °C.¹H NMR (500 MHz, DMSO-*d*₆) δ 10.01 (s, 2H), 8.61 (d, *J* = 7.5 Hz, 2H), 8.49 (s, 2H), 8.31 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.54 – 7.47 (m, 4H), 7.43 (s, 2H), 7.03 (s, 2H), 3.76 (s, 6H), 3.75 (s, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 166.0, 150.9, 148.8, 148.6, 138.1, 136.8, 134.9, 131.8, 128.5, 127.9, 127.4, 122.4, 122.1, 116.1, 114.7, 112.7, 56.3, 56.1. HRMS (ESI) m/z calculated for C₃₆H₃₀N₄O₆ [M+H]⁺ 615.2238, found 615.2246.



6,6'-Dimethyl-*N*²,*N*²'-**diphenyl-[1,1'-biphenyl]-2,2'-dicarboxamide 2t**: White solid, yield: 180 mg (86%), m.p.: 220-222 °C. ¹H NMR (500 MHz, CDCl₃) δ 9.16 (s, 2H), 7.52 (t, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 4H), 7.35 (dd, *J* = 10.3, 7.0 Hz, 4H), 7.28 (dd, *J* = 10.7, 4.9 Hz, 4H), 7.09 (t, *J* = 7.4 Hz, 2H), 1.99 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 169.0, 138.0, 136.9, 136.6, 136.4, 132.5, 128.9, 128.1, 124.8, 124.4, 120.1, 20.2. HRMS (APCI) m/z calculated for C₂₈H₂₄N₂O₂ [M+H]⁺ 421.1911, found 421.1883.

GPx like antioxidant property

Peroxide decomposing antioxidant activity as a mimic for glutathione peroxidase (GPx) selenoenzyme was evaluated by thiol peroxidase assay by following eq. 1 (*vide infra*).^{8a} In the thiol peroxidase assay, the oxidation of benzenethiol to diphenyl disulfide (PhSSPh) by H_2O_2 in the presence of various spirodiazatellurane catalysts **1k**, **1m**, **1n**, **1o**, and **1p** were monitored by UV-Visible spectrophotometry at 305 nm at 25 °C (Figure S1).



Figure S1. A model plot of absorbance *vs* time (sec). The initial concentration of benzenethiol, catalyst **1n** (0.1 mM) and H_2O_2 were fixed to 3.75 mM.

The tested spirotelluranes show the H₂O₂ decomposing activity. Chalcogen-bonded spirotelluranes **1n-1p** catalysed thiol oxidation reaction at faster reduction rate ($v_o = 80.2\pm3.0$, 78.1±2, and 78.3±1.7 µMmin⁻¹, respectively) as compared to standards Ph₂Se₂,^{8b} ebselen^{8c} ($v_o = 24.1\pm2$ and 22.3±2.1 µMmin⁻¹) and the tested spirotelluranes **1k** and **1m** ($v_o = 28.2\pm1.8$ and 27.8±1.6, µMmin⁻¹), respectively (Table S2).
entry	catalyst structure	catalyst (mM)	rate ($v_o = \mu \text{Mmin}^{-1}$)
1	Se ^{Se}	Ph ₂ Se ₂	24.1±2 ^{8b}
2		Ebselen	22.3±2.1 ^{8c}
3	MeO MeO MeO MeO MeO MeO MeO MeO	1k	28.3±1.8
4	MeO MeO MeO MeO MeO MeO MeO MeO MeO MeO	1m	27.8±1.6
5		1n	80.2±3
б		10	78.1±2
7		1p	78.3±1.7

Table S2. Thiol peroxidase like activity of spirodiazatellurane

Assay condition: The reactions were carried out in methanol at 25 °C and monitored by UV-Visible spectrophotometer at 305 nm. Catalyst (0.01 mM), PhSH (1.0 mM) and H_2O_2 (3.75 mM) respectively.^{3,4} All experiments have been repeated triplicate.

Catalytic nitro-Michael reaction

Table S3. Optimization table

	MeO N H H	Catalyst DCE, rt, tim NO ₂	$\xrightarrow{\text{NeO}} \overset{\text{Ph}}{\underset{H}{\overset{NO_2}{}}}$	
entry	catalyst	catalyst	time	%yield
		load		
1		10 mol%	48 h	30
2	1n	20 mol%	24 h	50
3	1n	20 mol%	48 h	91
4	MeO OMe	20 mol%	48 h	20
	Meo ome 1k			
5	Meo Meo Meo Meo Meo Meo Meo Meo Meo Meo	20 mol%	48 h	21
6	none	_	48 h	

Nitro-Michael reaction between 5-methoxy indole and trans- β -nitrostyrene was firstly tried with 10 mol% of 8-aminoquinoline derived spirodiazatellurane **1n** in dry dichloroethane and yielded 30% after 48 h (entry 1, Table S3). Further, the increase in the catalytic load from 10 to 20 mol% lead to increase the yield to 50%, after 24 h (entry 2, Table S3). When the reaction was continued to 48h; an almost quantitative conversion (91%) was observed for **3** (entry 3, Table S3). Spirodiazatellurane **1k** and **1m** also catalysed the above reaction, albeit only 20-

21% yields were noticed (entries 4 and 5, Table S3). However, conversion to **3** was observed for uncatalyzed reactions (entry 6, Table S3).

General experimental procedure



A dry capped reaction vial containing a magnetic stir bar was charged with trans- β -nitrostyrene (15 mg, 0.1 mmol) and catalyst (13mg, 0.02 mmol) in dry dichloroethane (2 mL). Next, 5-methoxy indole (23 mg, 0.15 mmol) was added in one portion as a solid and allowed to stir for 48 h at room temperature. The reaction was immediately purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (8:2) as eluent.



5-Methoxy-3-(2-nitro-1-phenylethyl)-1H-indole 3:⁹ White solid, yield: 27 mg (91%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.89 (s, 1H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 2.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.72 (dd, *J* = 8.7, 2.1 Hz, 1H), 5.45 – 5.13 (m, 2H), 5.03 (d, *J* = 8.2 Hz, 1H), 3.72 (s, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 153.6, 141.2, 131.7, 128.9, 128.3, 127.3, 126.8, 123.4, 113.7, 112.6, 111.8, 100.9, 79.5, 55.8, 41.1. HRMS (ESI) m/z calculated for C₁₇H₁₆N₂O₃ 297.1234 [M+H]⁺ found, 297.1234.



5-Methyl-3-(2-nitro-1-phenylethyl)-1H-indole 4:⁹ White solid, yield: 21 mg (76%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.91 (s, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 2.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 3H), 7.25 – 7.18 (m, 2H), 6.89 (d, *J* = 8.2 Hz, 1H), 5.37 – 5.21 (m, 2H), 5.01 (t, *J* = 8.2 Hz, 1H), 2.33 (s, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 141.2, 135.0, 128.9, 128.3, 127.6, 127.3, 126.7, 126.7, 123.4, 122.8, 118.3, 113.3, 111.7, 79.7, 41.1, 21.7. HRMS (ESI) m/z calculated for C₁₇H₁₆N₂O₂ 281.1285 [M+H]⁺ found, 281.1291.



5-Methoxy-2-methyl-3-(2-nitro-1-phenylethyl)-1H-indole 5:¹⁰ Yellow oil, yield: 26 mg (85%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.78 (s, 1H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 8.7 Hz, 1H), 6.90 (s, 1H), 6.64 (d, *J* = 8.7 Hz, 1H), 5.52 (dd, *J* = 12.9, 7.3 Hz, 1H), 5.33 (dd, *J* = 12.8, 9.3 Hz, 1H), 5.06 (t, *J* = 8.2 Hz, 1H), 3.69 (s, 3H), 2.38 (s, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 153.4, 140.8, 134.2, 130.9, 128.8, 127.8, 127.3, 127.0, 111.7, 109.8, 108.4, 101.5, 78.3, 55.8, 12.2. HRMS (ESI) m/z calculated for C₁₈H₁₈N₂O₃ [M+H]⁺ 311.1390, found 311.1400.



3-(2-Nitro-1-phenylethyl)-1H-indole 6:⁹ Light yellow oil, yield: 18 mg (70%), ¹H NMR (500 MHz, DMSO-*d*₆) δ 11.04 (s, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.43 (d, *J* = 2.2 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 5.39 – 5.26 (m, 2H), 5.05 (t, *J* = 8.2 Hz, 1H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 141.2, 136.6, 128.9, 128.3, 127.3, 126.4, 122.7, 121.8, 119.1, 118.9, 113.9, 112.0, 79.6, 41.1.



¹H NMR spectra of 2-bromo-*N*-phenylbenzamide (Substrate for **1a** and **2a**)





¹H NMR spectra of 2-bromo-*N*-(p-tolyl)benzamide (Substrate for **1b** and **2h**)



¹³C NMR spectra of 2-bromo-*N*-(p-tolyl)benzamide (Substrate for **1b** and **2h**)



¹H NMR spectra of 2-bromo-*N*-(4-methoxyphenyl)benzamide (Substrate for **1c** and **2i**)



¹³C NMR spectra of 2-bromo-*N*-(4-methoxyphenyl)benzamide (Substrate for **1c** and **2i**)



¹H NMR spectra of 2-bromo-*N*-(4-chlorophenyl)benzamide (Substrate for **1d**)



¹³C NMR spectra of 2-bromo-*N*-(4-chlorophenyl)benzamide (Substrate for 1d)



¹H NMR spectra of 2-bromo-*N*-(m-tolyl)benzamide (Substrate for **1e** and **2e**)



¹³C NMR spectra of 2-bromo-*N*-(m-tolyl)benzamide (Substrate for **1e** and **2e**)

HRMS spectra of 2-bromo-N-(m-tolyl)benzamide (Substrate for 1e and 2e)

Display Report Analysis Info Acquisition Date 3/29/2022 1:21:52 PM Analysis Name D:\Data\NEW USER DATA 2022\March-2022\29march\Prof.S.Kumar-MB-2E-R_1-A,6_01_11580.d Method hrlcms-20 sept.m Operator RUCHI Prof.S.Kumar-MB-2E-R micrOTOF-Q II 10330 Sample Name Instrument Comment Acquisition Parameter Positive 4500 V -500 V 1.2 Bar 200 °C 6.0 l/min Source Type ESI Ion Polarity Set Nebulizer Focus Scan Begin Set Capillary Set End Plate Offset Set Dry Heater Active 50 m/z Set Dry Gas Set Divert Valve Scan End 3000 m/z Set Collision Cell RF 130.0 Vpp Waste Intens. Prof.S.Kumar-MB-2E-R_1-A,6_01_11580.d: TIC +All MS x10⁷ 2 1 Intens. Prof.S.Kumar-MB-2E-R_1-A,6_01_11580.d: UV Chromatogram, 200-400 nm [mAU] x105 N 3 2 Br 1 0 4 Time [min] 1 2 ż 5 300 200 220 240 260 280 320 340 360 Wavelength [nm] Intens. UV, 3.6-3.7min #(2123-2213), [mAU] 2000 1000 Intens. +MS, 3.6-3.7min #(215-222) x10⁶ 292.0126 2 182.9446 1 603.0094 0 600 700 100 400 500 200 m/z 300 Intens. +MS, 3.6-3.7min #(215-222) x106 292.0126 290.0150 2 291.0216 293.0196 1 290,1993 292,1971 0 2500 C14H12BrNO, M+nH ,290.02 290.0175 292.0155 2000 1500 1000 500 291.0208 293.0188 0 290.5 291.0 291.5 292.5 293.0 293.5 m/z 290.0 292.0

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¹H NMR spectra of 2-bromo-*N*-(3,4-dimethylphenyl)benzamide (Substrate for **1f** and **2l**)



¹³C NMR spectra of 2-bromo-*N*-(3,4-dimethylphenyl)benzamide (Substrate for **1f** and **2l**)

HRMS spectra of 2-bromo-*N*-(3,4-dimethylphenyl)benzamide (Substrate for **1f** and **2l**)

Display Report Analysis Info Acquisition Date 3/29/2022 1:29:04 PM Analysis Name D:\Data\NEW USER DATA 2022\March-2022\29march\Prof.S.Kumar-MB-2L-R_1-A,7_01_11581.d Method hrlcms-20 sept.m RUCHI Operator Sample Name Prof.S.Kumar-MB-2L-R Instrument micrOTOF-Q II 10330 Comment Acquisition Parameter Source Type ESI Ion Polarity Positive Set Nebulizer 1.2 Bar Focus Scan Begin Scan End Set Capillary Set End Plate Offset 4500 V -500 V 200 °C 6.0 l/min Active Set Dry Heater Set Dry Gas Set Divert Valve 50 m/z 3000 m/z Set Collision Cell RF 130.0 Vpp Waste Intens. Prof.S.Kumar-MB-2L-R_1-A,7_01_11581.d: TIC +All MS x10⁷ 2 1 Intens. Prof.S.Kumar-MB-2L-R_1-A,7_01_11581.d: UV Chromatogram, 200-400 nm [mAU] x105 2 0 1 2 3 4 5 Time [min] 200 220 240 260 280 300 320 340 360 Wavelength [nm] Intens UV, 3.6min #2111, [mAU] Me С 2000 1000 Me Intens. +MS, 3.6min #212 Br x10⁶ 328.0112 1.0 0.5 182.9423 148.0754 441.2947475.3242 0.0 50 100 150 200 250 300 350 400 450 500 m/z Intens. +MS. 3.6min #212 x106 328.0112 326.0130 1.0 0.5 327.0158 329.0143 330.0164 0.0 C15H14BrNO, M+nNa ,326.02 326.0151 328.0131 2000 1500 1000 500 327.0184 329.0164 330.0198 \cap 0 325.5 326.0 326.5 327.0 327.5 328.0 328.5 329.0 329.5 330.0 m/z Bruker Compass DataAnalysis 4.0 3/29/2022 2:49:23 PM Page 1 of 1 printed:



¹H NMR spectra of 2-bromo-5-methoxy-*N*-phenylbenzamide (Substrate for **1g**)

Peak at 1.66 ppm is corresponding to water associated in CDCl₃



¹³C NMR spectra of 2-bromo-5-methoxy-*N*-phenylbenzamide (Substrate for **1g**)



¹H NMR spectra of 2-bromo-5-methoxy-*N*-(p-tolyl)benzamide (Substrate for **1h**)



¹³C NMR spectra of 2-bromo-5-methoxy-*N*-(p-tolyl)benzamide (Substrate for **1h**)



¹H NMR spectra of 2-bromo-*N*-(3,4-dimethylphenyl)-5-methoxybenzamide (Substrate for **1i**)



¹³C NMR spectra of 2-bromo-*N*-(3,4-dimethylphenyl)-5-methoxybenzamide (Substrate for **1i**)

HRMS spectra of 2-bromo-N-(3,4-dimethylphenyl)-5-methoxybenzamide (Substrate for 1i)





Peak at 1.66 ppm is corresponding to water associated in CDCl₃



¹³C NMR spectra of 2-bromo-5-methoxy-*N*-(2-methoxyphenyl)benzamide (Substrate for **1j**)

HRMS spectra of 2-bromo-5-methoxy-N-(2-methoxyphenyl)benzamide (Substrate for 1j)





¹H NMR spectra of 2-bromo-5-methoxy-*N*-(4-methoxyphenyl)benzamide (Substrate for **1**k)



¹³C NMR spectra of 2-bromo-5-methoxy-*N*-(4-methoxyphenyl)benzamide (Substrate for **1k**)



¹H NMR spectra of 2-bromo-4,5-dimethoxy-*N*-(p-tolyl)benzamide (Substrate for **1**l)



¹³C NMR spectra of 2-bromo-4,5-dimethoxy-*N*-(p-tolyl)benzamide (Substrate for **1**l)

10.011 Spectrometer Frequency 12 Spectral Width 13 Lowest Frequency ø 00 7 σ u 4 ω Ν -16 Spectral Size 15 Acquired Size 14 Nudeus 10 Modification Relaxation Delay Date Date Time Pulse Width Scans Title Acquisition Acquisition Number of Temperature Solvent Spectrometer Parameter 9.5 spect 32768 65536 500.13 CDCl3 298.0 Sangit-MB-2s(500MHz) 10000.0 3.2768 12.0000 1.0000 16 9.0 보 -1925.0 2022-02-11T23:00:34 2022-01-21T19:40:05 Value 8.5 0.8 ----7.92 8.0 <7.56 7.55 7.5 ----7.92 7.9 1.00-= ----7.28 __7.02 ←6.92 ←6.90 7.8 1.00-≖ 2.00-≖ 7.0 7.7 6.5 7.6 <7.56 7.55 7.5 6.0 7.4 OMe 0 5.5 7.3 ----7.28 MeO N H 5.0 f1 (ppm) 7.2 7.1 f1 (ppm) MeO Br 4.5 7.0 ---7.02 $\leq_{6.90}^{6.92}$ 6.9 4.0 3.00 3.00 3.00 3.91 3.89 3.81 6.8 ω.5 4.1 4.0 3.0 3.9 3.91
3.89 2.5 3.8 -3.81 3.7 2.0 1.5 1.0 0.5 0.0

¹H NMR spectra of 2-bromo-4,5-dimethoxy-*N*-(4-methoxyphenyl)benzamide (Substrate for **1m** or **2k**)

¹³C NMR spectra of 2-bromo-4,5-dimethoxy-*N*-(4-methoxyphenyl)benzamide (Substrate for 1m or 2k)



HRMS spectra of 2-bromo-4,5-dimethoxy-N-(4-methoxyphenyl)benzamide (Substrate for 1m

or **2k**)





¹H NMR spectra of 2-bromo-*N*-(quinolin-8-yl)benzamide (Substrate for **1n** or **2q**)


13 C NMR spectra of 2-bromo-*N*-(quinolin-8-yl)benzamide (Substrate for **1n** or **2q**)



π NIVIR spectra of 2-biointo-5-methoxy- <i>i</i> v-(quintointi-6-yi)benzamine (Substrate for 10 of 2	¹ H NMR st	pectra of 2-bromo-	5-methoxy-N	N-(quinolin-8-	vl)benzamide	(Substrate for	: 10 or 2
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¹³C NMR spectra of 2-bromo-5-methoxy-*N*-(quinolin-8-yl)benzamide (Substrate for **10** or **2r**)

HRMS spectra of 2-bromo-5-methoxy-N-(quinolin-8-yl)benzamide (Substrate for 10 or 2r)



S76



¹H NMR of 2-bromo-4,5-dimethoxy-*N*-(quinolin-8-yl)benzamide (Substrate for **1p** or **2s**)



¹³C NMR of 2-bromo-4,5-dimethoxy-*N*-(quinolin-8-yl)benzamide (Substrate for **1p** or **2s**)

HRMS spectra of 2-bromo-4,5-dimethoxy-N-(quinolin-8-yl)benzamide (Substrate for 1p or 2s)



S79



¹H NMR of 2-bromo-*N*-(o-tolyl)benzamide (Substrate for **2b**)







¹H NMR of 2-bromo-*N*-(2-methoxyphenyl)benzamide (Substrate for **2c**)



 13 C NMR of 2-bromo-*N*-(2-methoxyphenyl)benzamide (Substrate for **2c**)



¹H NMR spectra of 2-bromo-*N*-(3-methoxyphenyl)benzamide (Substrate for **2f**)



13 C NMR spectra of 2-bromo-*N*-(3-methoxyphenyl)benzamide (Substrate for **2f**)



¹H NMR spectra of 2-bromo-*N*-(3-nitrophenyl)benzamide (Substrate for **2g**)



13 C NMR spectra of 2-bromo-*N*-(3-nitrophenyl)benzamide (Substrate for **2g**)



¹H NMR spectra of 2-bromo-*N*-(4-bromophenyl)benzamide (Substrate for **2j**)



13 C NMR spectra of 2-bromo-*N*-(4-bromophenyl)benzamide (Substrate for **2j**)



¹H NMR spectra of 2-bromo-*N*-(3,4-dimethoxyphenyl)benzamide (Substrate for **2m**)



¹³C NMR spectra of 2-bromo-*N*-(3,4-dimethoxyphenyl)benzamide (Substrate for **2m**)



¹H NMR spectra of 2-bromo-*N*-(naphthalen-1-yl)benzamide (Substrate for **2o**)





HRMS spectra of 2-bromo-N-(naphthalen-1-yl)benzamide (Substrate for 20)



S94



¹H NMR spectra of *N*-benzyl-2-bromo-5-methoxybenzamide (Substrate for **2p**)



¹³C NMR spectra of *N*-benzyl-2-bromo-5-methoxybenzamide (Substrate for **2p**)



¹H NMR spectra of 2-iodo-3-methyl-*N*-phenylbenzamide (Substrate for **2t**)



¹³C NMR spectra of 2-iodo-3-methyl-*N*-phenylbenzamide (Substrate for **2t**)

¹H NMR spectra of **1a**



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively

¹³C NMR spectra of **1a**





HRMS spectra of 1a



S102

¹H NMR spectra of **1b**



Peaks at 2.51 and 3.33 correspond to DMSO- d_6 residual peak and water respectively. Peaks at 0.86 and 1.26 correspond to grease.



¹²⁵Te NMR spectra of **1b**

16 15	4	ы	12		Ħ	5	9	00	7	σ	S	4	ω	Ν	н.	
Acquired Size Spectral Size	Frequency Nudeus	Lowest	Spectral Width	Frequency	Spectrometer	Modification Date	Acquisition Date	Acquisition Time	Pulse Width	Relaxation Delay	Number of Scans	Temperature	Solvent	Spectrometer	Title	Parameter
32768 65536		75148.8	39062.5		126.24	2018-07-09T22:43:22	2018-07-09T22:43:21	0.8389	8.9000	2,0000	1200	298.2	CDCl3	spect	Sangit-MBH-25	Value







HRMS spectra of 1b



$^1\mathrm{H}$ NMR spectra of 1c



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively

¹³C NMR spectra of **1c**


¹²⁵Te NMR spectra of **1c**



S109

HRMS spectra of 1c



¹H NMR spectra of **1d**



Peaks at 2.51 and 3.33 correspond to DMSO- d_6 residual peak and water respectively. Peaks at 0.88 and 1.27 correspond to grease.

13 C NMR spectra of **1d**



^{125}Te NMR spectra of 1d



HRMS spectra of 1d



¹H NMR spectra of **1e**



¹³C NMR spectra of **1e**



¹²⁵Te NMR spectra of **1e**



HRMS spectra of 1e



¹H NMR spectra of 1f



Peaks at 2.51 and 3.33 correspond to DMSO- d_6 residual peak and water respectively. Peaks at 0.88 and 1.27 correspond to grease.





_																	
1	5	5	4	t	13	Ħ	5	9	00	7	σ	S	4	ω	Ν	<u>н</u>	
abern al alce	Spectral Size	Acquired Size	Nudeus	Lowest Frequency	Spectral Width	Spectrometer Frequency	Modification Date	Acquisition Date	Acquisition Time	Pulse Width	Relaxation Delay	Number of Scans	Temperature	Solvent	Spectrometer	Title	Parameter
0000	65536	32768		-1277.4	166666.7	126.24	2021-04-06T05:39:32	2021-04-06T08:02:01	0.1966	8.9000	2.0000	1000	298.2	DMSO	spect	Sangit-MB-02-448-Te-R	Value



----789.89



700 650 f1 (ppm)

• -



HRMS spectra of 1f



¹H NMR spectra of **1g**



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively.

¹³C NMR spectra of **1g**



¹²⁵Te NMR spectra of **1g**



HRMS spectra of 1g



S126

^1H NMR spectra of 1h



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively.

¹³C NMR spectra of **1h**



¹²⁵Te NMR spectra of **1h**



S129

HRMS spectra of 1h



¹H NMR spectra of **1i**



S131



¹³C NMR spectra of **1i**

¹²⁵Te NMR spectra of **1i**



S133



¹H NMR spectra of 1j



Peaks at 2.51 and 3.33 correspond to DMSO-*d*₆ residual peak and water respectively.







¹²⁵Te NMR spectra of **1j**



¹H NMR spectra of **1k**



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively.

¹³C NMR spectra of **1k**



¹²⁵Te NMR spectra of **1k**



HRMS spectra of 1k



¹H NMR spectra of **1**l



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively.

¹³C NMR spectra of **11**








S146

¹H NMR spectra of 1m



S147



¹²⁵Te NMR spectra of **1m**



HRMS spectra of 1m



¹H NMR spectra of **1n**



Peak at 3.33 and 2.50 ppm correspond to DMSO- d_6 and water residual peak respectively.

¹³C NMR spectra of **1n**



¹²⁵Te NMR spectra of **1n**



HRMS spectra of 1n



¹H NMR spectra of **10**



Peaks at 7.26 and 1.56 correspond to CDCl₃ residual and water.



¹³C NMR spectra of **10**

10 Modific 11 Spectri 12 Spectri 13 Lowest 14 Nudeu 14 Nudeu	10 Modific 11 Spectro 12 Spectro 13 Lowest 14 Nudeu	10 Modine 11 Spectra 12 Spectra 13 Lowest	10 Modine 11 Spectra 12 Spectra	10 Modine 11 Spectro	TO MODING		9 Acquisi	8 Acquisi	7 Pulse V	6 Relaxa	5 Numbe	4 Temper	3 Solven	2 Spectro	1 Title		
iuon i iine ation Date ation Date al Width I: Frequency s s	ition Date ation Date ometer Frequency al Width t Frequency s	ition Date ation Date ometer Frequency al Width t Frequency	ition Time ation Date ometer Frequency al Width	ition Date ation Date ometer Frequency	ition Date ation Date	tion Date	UOU LIME		Vidth	tion Delay	r of Scans	rature	Ŧ	ometer		Parameter	
0.2097 2021-09-11T07:11:16 2021-09-11T12:16:21 126.24 156250.0 22867.0 32768	0.2097 2021-09-11T07:11:16 2021-09-11T12:16:21 126.24 156250.0 22867.0	0.2097 2021-09-11T07:11:16 2021-09-11T12:16:21 126.24 156250.0 22867.0	0.2097 2021-09-11T07:11:16 2021-09-11T12:16:21 126.24 156250.0	0.2097 2021-09-11T07;11:16 2021-09-11T12:16:21 126.24	0.2097 2021-09-11T07:11:16 2021-09-11T12:16:21	0.2097 2021-09-11T07:11:16	0.2097		8.9000	2.0000	10000	298.2	CDCl3	spect	Sangit-MB-02-546-Te	Value	





¹²⁵Te NMR spectra of **10**



HRMS spectra of 10



¹H NMR spectra of **1p**









¹²⁵Te NMR spectra of **1p**

HRMS spectra of 1p



¹H NMR spectra of $\mathbf{1q}$





¹²⁵Te NMR spectra of **1q**



HRMS spectra of 1q



^1H NMR spectra of 1r



Traces of grease peak at 0.86 and 1.26 ppm.

^{13}C NMR spectra of 1r











S169

HRMS spectra of 1r



¹H NMR spectra of **2a**



Peaks at 7.26 and 1.56 correspond to $CDCl_3$ residual peak and water respectively. Peaks at 0.86 and 1.26 correspond to grease.

¹³C NMR spectra of **2a**



HRMS spectra of 2a



¹H NMR spectra of **2b**



S174



HRMS spectra of 2b



S176

¹H NMR spectra of **2c**



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively.





HRMS spectra of 2c



¹H NMR spectra of **2d**



Peaks at 0.86 and 1.26 correspond to grease and pentane.


Peaks at 13.3, 21.7 and 33.5 correspond to grease and pentane.

HRMS spectra of 2d



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Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively

¹³C NMR of **2e**



HRMS spectra of 2e



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1 H NMR of **2f**



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively

 13 C NMR of **2f**



¹H NMR spectra of **2g**



¹³C NMR spectra of **2g**



HRMS spectra of 2g



¹H NMR spectra of **2h**



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively

¹³C NMR spectra of **2h**



HRMS spectra of 2h



¹H NMR spectra of 2i



¹³C NMR of spectra of 2i



HRMS of spectra of 2i



¹H NMR spectra of **2j**





HRMS spectra of 2j



¹H NMR spectra of **2k**



¹³C NMR spectra of **2k**



HRMS spectra of 2k



¹H NMR spectra of **2**l



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively







¹H NMR spectra of **2m**



¹³C NMR spectra of **2m**



¹H NMR spectra of **2n**



¹³C NMR spectra of **2n**



HRMS spectra of 2n



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¹H NMR spectra of **20**



Peaks at 7.26 and 1.5 correspond to CDCl3 residual peak and water respectively



¹³C NMR spectra of **20**

HRMS spectra of 20



¹H NMR spectra of **2p**



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively



HRMS spectra of 2p


¹H NMR spectra of **2q**





¹³C NMR spectra of **2q**

HRMS spectra of 2q



¹H NMR spectra of **2r**



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively

^{13}C NMR spectra of 2r



HRMS spectra of 2r



¹H NMR of **2s**



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively

¹³C NMR of **2s**



HRMS spectra of 2s



¹H NMR spectra of **2t**







HRMS spectra of 2t



¹H NMR spectra of **3**



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively.

¹³C NMR spectra of **3**



HRMS specta of 3



¹H NMR spectra of **4**



Peaks at 2.51 and 3.33 correspond to DMSO- d_6 residual peak and water respectively. Peaks at 0.88 and 1.27 correspond to grease

¹³C NMR spectra of **4**



HRMS specta of 4



¹H NMR spectra of **5**



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively



HRMS spectra of 5



¹H NMR spectra of **6**



Peaks at 2.51 and 3.33 correspond to DMSO-d₆ residual peak and water respectively



Crystallographic details:

Parameters	1b	1d	1k
Emperical form	$C_{29}H_{24}Cl_2N_2O_2Te$	C14H9Cl2NOTe0.5	$C_{34}H_{26}D_{12}N_2O_8S_2$
			Те
Formula weight	631.00	341.92	806.46
Temperature/K	140(2)	140(2)	140(2)
Crystal System	triclinic	orthorhombic	monoclinic
Space group	P-1	Pbcn	C2/c
a/Å	9.0873(12)	14.5391(13)	22.1733(16)
b/Å	9.2550(11)	14.2888(13)	12.0567(8)
c/Å	15.856(2)	12.0108(12)	27.174(2)
α/ ^o	79.731(5)	90	90
β/ ^o	85.169(5)	90	110.649(3)
$\gamma/^{\rm o}$	88.589(5)	90	90
Volume/Å ³	1307.5(3)	2495.2(4)	6798.0(9)
Ζ	2	8	8
μ/mm^{-1}	1.372	1.653	1.052
F(000)	628	1344	3232
Radiation	Mo Ka $\lambda = 0.71073$ Å	Mo Ka $\lambda = 0.71073$	Mo Ka λ =
		Å	0.71073 Å
2Θ range for data	2.249-30.558	3.392-30.083	1.976-29.583
collection/°			
Index ranges	-12<= <i>h</i> <=12,-	-16<=h<=20,-	-30<=h<=30,-
	11<=k<=13, -	20<=k<=19,-	16<=k<=16,
	22<= <i>l</i> <=22	16<=l<=16	-37<=l<=37
Reflection collected	33537	40257	75251
Independent reflections	7852	3648	9532
Data/restrains/paramete	7852 / 0 / 331	3648 / 0 / 168	9532 /294 /445
rs			
Goodness-of-fit on F^2	1.068	1.105	1.035

Table S4. Crystal data of spirodiazatellurane 1b, 1d and 1k



 Table S5. List of selected bond length (Å) and bond angles (°) of spirodiazatellurane 1b, 1d

 and 1k

Atom	1b	1d	1k
C-Te	2.103(3)	2.104(2)	2.096(3)
C´-Te	2.115(3)	2.104(2)	2.096(3)
N-Te	2.163(2)	2.2178(18)	2.214(2)
N´-Te	2.197(2)	2.2178(18)	2.214(2)
C-Te-C´	98.14(10)	101.18(13)	97.76(10)
C-Te-N´	91.86(10)	90.91 (8)	90.25(9)
C´-Te-N´	78.22(9)	78.22(8)	77.99(9)
C-Te-N	77.87(10)	78.22(8)	78.54(9)
C´-Te-N	91.45(9)	90.91(8)	91.05(9)
N-Te-N´	164.36(9)	162.95(11)	163.21(8)

Parameters	1n
Emperical form	$C_{33}H_{24}Cl_2N_4O_3Te$
Formula weight	723.06
Temperature/K	140(2)
Crystal System	triclinic
Space group	P-1
a/Å	11.0974(8)
b/Å	11.6191(7)
c/Å	11.6886(6)
α/ ^o	81.846(3)
β/ ^o	70.846(2)
$\gamma/^{o}$	81.139(2)
Volume/Å ³	1399.98(15)
Z	2
μ/mm^{-1}	1.298
F(000)	720
Radiation	Mo Ka $\lambda = 0.71073$ Å
2Θ range for data collection/°	2.443-28.708
Index ranges	-14<=h<=12,-14<=k<=14, -15<=l<=15
Reflection collected	37477
Independent reflections	7163
Data/restrains/parameters	7163 / 0 / 391
Goodness-of-fit on F^2	1.035
Final R indexes $[I \ge 2\sigma(I)]$	R1 = 0.0283, $wR2 = 0.0640$
Final R indexes [all data]	R1 = 0.0340, wR2 = 0.0676
R _{int}	0.0573
CCDC	2157186

 Table S6. Crystal data of spirodiazatellurane 1n



Table S7. List of	selected bond	length (Å)	and bond	angles (°)) of s	pirodiazatellurane	1n
LUDIC D7. LISt OI	Selected Johna	iongui (11)	una oona		01.0	phouluZutenuluite	

Atom	1n
C-Te	2.128(2)
C'-Te	2.112(2)
N-Te	2.2298(18)
N´-Te	2.2213(18)
N(008)Te(01)	2.620(2)
C-Te-C´	91.18(8)
C-Te-N′	89.64(7)
C´-Te-N´	76.59(8)
C-Te-N	77.80(17)
C'-Te-N	89.14(8)
N-Te-N´	160.85(7)

$\label{eq:stable} Table ~S8.~Crystal~data~of~spirobenzyloxytellurane~1q~and~spirobenoxytellurane~1r$

Parameters	1q	1r
Emperical form	C ₇ H ₅ OTe _{0.5}	$C_{16}H_{12}O_6Te$
Formula weight	168.91	427.86
Temperature/K	296(2)	140(2)
Crystal System	monoclinic	orthorhombic
Space group	C2/c	Pca2 ₁
a/Å	20.507(4)	19.2430(14)

b/Å	4.8515(8)	4.7234(3)
c/Å	14.046(2)	15.8545(12)
α/ ^o	90	90
β/°	118.957(8)	90
$\gamma/^{o}$	90	90
Volume/Å ³	1222.8(4)	1441.05(18)
Z	8	4
μ/mm^{-1}	2.418	2.095
F(000)	648.0	832
Radiation	Mo Ka $\lambda = 0.71073$ Å	Mo Ka $\lambda = 0.71073$ Å
2Θ range for data collection/°	8.258-57.336	4.952-55.848
Index ranges	-27<=h<=26,-4<=k<=6, -	-25<=h<=25,-6<=k<=6,-
	18<= <i>l</i> <=18	20<=l<=20
Reflection collected	4171	14409
Independent reflections	1563	3399
Data/restrains/parameters	1563 / 0 / 79	3399 / 1 / 196
Goodness-of-fit on F^2	1.069	1.023
Final R indexes $[I \ge 2\sigma(I)]$	R1 = 0.0316, wR2 = 0.0717	R1 = 0.0515, wR2 = 0.1028
Final R indexes [all data]	R1 = 0.0369, wR2 = 0.0749	R1 = 0.0821, wR2 = 0.1149
R _{int}	0.0254	0.0764
Flack parameter	_	0.49(3)
CCDC	2157182	2157187



Table S9. List of selected bond length (Å) and bond angles (°) of 1q and 1r

Atom	1q	1r
C-Te	2.128(3)	2.084(5)
C´-Te	2.112(19)	2.075(6)
O-Te	2.2298(2)	2.089(8)
O´-Te	2.2213(2)	2.102(8)
C-Te-C´	97.9(6)	97.2(3)
C-Te-O´	89.74(10)	88.1(3)
C´-Te-O´	80.0(4)	79.8(3)
C-Te-O	79.96(10)	79.4(3)
C´-Te-O	89.7(5)	87.4(3)
O-Te-O´	164.35(15)	160.9(3)

 Table S10. Crystal data of C-C coupled biaryl 1,1'-diamide 20, 2r and 2t

Parameters	20	2r	2t
Emperical form	$C_{68}H_{48}N_4O_4$	$C_{34}H_{26}N_4O_4$	$C_{28}H_{24}N_2O_2$
Formula weight	985.10	554.59	420.49
Temperature/K	140(2)	140(2)	140(2)
Crystal System	monoclinic	triclinic	monoclinic
Space group	Pna2 ₁	P-1	C2/c
a/Å	8.8678(11)	7.2109(3)	29.849(6)
b/Å	34.130(4)	13.1523(5)	8.7958(18)
c/Å	8.4805(9)	14.1608(6)	17.216(4)

α / ^o	90	79.21(10)	90
β/°	90	83.65(2)	97.164(9)
$\gamma/^{o}$	90	85.01(10)	90
Volume/Å ³	2566.7(5)	1308.18(9)	4484.6(16)
Z	2	2	8
μ/mm^{-1}	0.080	0.094	0.079
F(000)	1032.0	580.0	1776.0
Radiation	Mo Ka $\lambda = 0.71073$ Å	Mo Ka $\lambda = 0.71073$ Å	Mo Ka $\lambda =$ 0.71073 Å
2Θ range for data collection/°	4.746-51.378	5.698-57.398	4.77-50.05
Index ranges	-10<= <i>h</i> <=10,- 41<= <i>k</i> <=41, -10<= <i>l</i> <=9	-9<=h<=9,- 17<=k<=17, 19<=l<=19	-34<=h<=35,- 10<=k<=10,- 20<=l<=20
Reflection collected	22557	20958	29735
Independent reflections	4528	6689	3968
Data/restrains/parameters	4528 / 1 / 343	6689 / 0 / 381	3968 /0./ 291
Goodness-of-fit on F^2	1.059	1.011	1.000
Final R indexes $[I \ge 2\sigma(I)]$	R1 = 0.0461, wR2 = 0.0964	R1 = 0.0517, wR2 = 0.1041	R1 = 0.0621, wR2 = 0.1185
Final R indexes [all data]	R1 = 0.0556, wR2 = 0.1035	R1 = 0.0822, wR2 = 0.1164	R1 = 0.1563, wR2 = 0.1582
R _{int}	0.0990	0.0445	0.1953
Flack parameter CCDC	-2.8(10) 2157183	 2157188	 2157190





Additionally, Crystal structure of 20 suggests that it possesses atropisomerism and crystalize in chiral space group $Pna2_1$, and only one enantiomer is observed.

 Table S11. List of selected bond length (Å) and tortion angles (°) of C-C coupled biaryl 1,1'

 diamide 20, 2r and 2t

Atom	20	2r	2t
C-C′	1.497(4)	1.494(2)	1.51(5)
N-HO-C	2.01(0)		1.85(3)
C ^{····} -C-C [·] -C ^{··}	78.3(4)	-62.60(2)	89.8(4)

Computational Details:

The DFT calculations were carried out using Gaussian 09 package by without optimization. The geometrical coordinations were extracted from respective crystal structure and the calculation perform in the level of B3PW91. The basis sets defz-tzvp used for tellurium and 6- $311+g^{**}$ used for C, H, N, and O. The AIM analysis performed by using the wave function file generated from Gaussian 09 and the bond topological properties of electron density ($\rho_{(r)}$), Laplacian electron density ($\nabla^2 \rho_{(r)}$), Total energy density ($H\rho_{(r)}$) were analysed by using bond critical points (bcp) of respective bonds.

 Table S12. AIM analysis of spirodizatellurane 1n was used without further optimization, the

 coordinates of the crystal 1n were directly used.

Bond	Bond length Å		ρ (r) a.u.	$\nabla^2 \rho(\mathbf{r})$ a.u.	$H\rho$ (r) a.u.
	Expt.	Calc.			
Te01-N006	2.231(2)	2.2292	0.086	0.131	-0.026
Te01-N007	2.221(2)	2.2212	0.087	0.133	-0.027
Te01-N008	2.620(2)	2.6171	0.040	0.084	-0.0032
Te01-N1	3.145(2)	3.1459	0.015	0.040	-0.00066

The quantum theory of atoms in molecules (AIM) analysis afforded low electron density value $(\rho_{(r)} = 0.04 \text{ a.u.}; 0.04 \text{ x } 6.748 = 0.26992 \text{ eÅ}^{-3})$ at bond critical point (bcp) of the Te01···N008 bond (Table S12, Figure S2).¹¹ Thes e parameter is suggesting that one of the quinoline nitrogen (N008) atom is strongly interacting with Te (01). Also the most significant parameter Laplasian electron density ($\nabla^2 \rho_{(r)}$), Total energy density ($H\rho_{(r)}$) values are strongly supporting for strong Te01···N008 intramolecualr interaction.



Figure S2. Bond topological diagram of 1n with bond critical points (bcp).

Energy: -1609.10949524

Te	0.009568000	-0.229141000	-0.326128000
0	-3.591688000	-2.226658000	-1.435172000
0	2.993758000	-0.976021000	2.646001000
Ν	-2.127758000	-0.514697000	-0.891670000
Ν	-1.476493000	1.818126000	0.344511000
Ν	1.995294000	-0.565918000	0.610518000
Ν	2.126076000	2.088012000	-0.107098000
С	-0.020136000	-2.259882000	-0.961198000
С	1.078988000	-3.102864000	-1.023666000
Η	1.935600000	-2.803017000	-0.743368000
С	0.904043000	-4.396231000	-1.504134000
Η	1.649392000	-4.983480000	-1.553288000
С	-0.339332000	-4.837322000	-1.911268000
Н	-0.441499000	-5.719708000	-2.248470000
С	-1.439623000	-3.999955000	-1.830025000
Н	-2.297603000	-4.309152000	-2.094409000
С	-1.276313000	-2.698660000	-1.357011000
С	-2.457559000	-1.793668000	-1.241966000

С	-3.104660000	0.506661000	-0.816999000
С	-4.382671000	0.421929000	-1.342440000
Н	-4.659535000	-0.379703000	-1.770218000
С	-5.281382000	1.507575000	-1.253821000
Н	-6.154735000	1.415739000	-1.616248000
С	-4.926255000	2.685775000	-0.660546000
Н	-5.546766000	3.403994000	-0.611198000
С	-3.632590000	2.827376000	-0.123527000
С	-2.724443000	1.733186000	-0.187714000
С	-1.087190000	2.943512000	0.907746000
Η	-0.213849000	2.985889000	1.279922000
С	-1.904538000	4.085543000	0.983635000
Н	-1.584009000	4.885225000	1.382619000
С	-3.163065000	4.019863000	0.473708000
Н	-3.730402000	4.781129000	0.518168000
С	-0.471364000	-0.795207000	1.651544000
С	-1.759709000	-0.882697000	2.148086000
Η	-2.498769000	-0.608005000	1.617124000
С	-1.960785000	-1.376774000	3.429846000
Η	-2.840022000	-1.425323000	3.785234000
С	-0.884819000	-1.798828000	4.191923000
Н	-1.032197000	-2.166693000	5.055473000
С	0.407089000	-1.687227000	3.700908000
Η	1.143782000	-1.966818000	4.231299000
С	0.621406000	-1.165115000	2.427298000
С	2.000139000	-0.911930000	1.903591000
С	3.184298000	-0.067835000	0.013300000
С	4.281815000	-0.864153000	-0.194889000
Η	4.257523000	-1.775672000	0.069734000
С	5.451491000	-0.342223000	-0.800713000
Н	6.206957000	-0.903840000	-0.926668000
С	5.501826000	0.958752000	-1.203411000
Η	6.287228000	1.296340000	-1.618483000
С	4.387470000	1.809571000	-1.006752000

С	3.215981000	1.305658000	-0.376747000
С	2.178507000	3.350858000	-0.477566000
Η	1.424853000	3.900986000	-0.298131000
С	3.284669000	3.934851000	-1.121775000
Η	3.265168000	4.851698000	-1.371323000
С	4.378971000	3.176282000	-1.383999000
Η	5.133419000	3.557582000	-1.818062000

Reference:

1. N. G. Kundu and M. W. Khan, Tetrahedron, 2000, 56, 4777.

(a) H. Liu, W. Han, C. Li, Z. Ma, R. Li, X. Zheng, H. Fu and H. Chen, *Eur. J. Org. Chem*;
 2016, 389; (b) L. Yadav, M. K. Tiwari, B. R. S. Shyamlal and S. Chaudhary, *J. Org. Chem.*,
 2020, **85**, 8121; (c) P. Cheng, J. Zhou, Z. Qing, W. Kang, S. Liu, W. Liu and H. Xie, *Bioorg. Med. Chem. Lett.*, 2014, **24**, 2712; (d) L. Grigorjeva and O. Daugulis, *Org. Lett.*, 2015, **17**,
 1204.

3. (a) T. Sakai, Y. Matsumoto, M. Ishikawa, K. Sugita, Y. Hashimoto, N. Wakai, A. Kitao, E. Morishita, C. Toyoshima, T. Hayashi and T. Akiyama, *Bioorg. Med. Chem.*, 2015, **23**, 328; (b) Y-Y. Zhu, H-P. Yi, C. Li, X-K. Jiang and Z-T. Li, *Cryst. Growth Des.*, 2008, 8, 1294; (c) S. Mkrtchyan, M. Jakubczyk, S. Lanka, M. Pittelkow and V. O. Iaroshenko, *Molecules*, 2021, 26, 2957; (d) T. Furuta, Y. Kitamura, A. Hashimoto, S. Fujii, K. Tanaka and T. Kan, *Org. Lett.*, 2007, **9**, 183; (e) B. S. Bhakuni, A. Kumar, S. J. Balkrishna, J. A. Sheikh, S. Konar and S. Kumar, *Org. Lett.*, 2012, **14**, 2838.

4. R. Kadu, M. Batabyal, H. Kadyan, A. L. Koner and S. Kumar, *Dalton Trans.*, 2019, 48, 7249.

5. (a) B. K. Sarma, D. Manna, M. Minoura and G. Mugesh, *J. Am. Chem. Soc.*, 2010, **132**, 5364; (b) Y. Takaguchi and N. Furukawa, *Chem. Lett.*, 1996, 365.

6. (a) S. Goswami, A. K. Adak, R. Mukherjee, S. Jana, S. Dey and J. F. Gallagher, *Tetrahedron*, 2005, 61, 4289; (b) M. Wang, Y. Hu, Z. Jiang, H. C. Shen and X. Sun, *Org. Biomol. Chem.*, 2016, 14, 4239; (c) G. Shen, Y. Wang, X. Zhao, X. Huangfu, Y. Tian, T. Zhang and B. Yang, *Synlett*, 2017, 28, 2030.

7. F. Dong, J-Q. Liu, and X-S. Wang, Res. Chem. Intermed., 2018, 44, 5271

(a) G. Mugesh, A. Panda, S. Kumar, S. D. Apte, H. B. Singh and R. J. Butcher, *Organometallics*, 2002, **21**, 884; (b) V. Rathore, A. Upadhyay and S. Kumar, *Org. Lett.*, 2018, **20**, 6274; (c) A. Upadhyay, B. S. Bhakuni, R. Meena and S. Kumar, *Chem. Asian J.*, 2021, **16**, 966.

9. C. Li, Y. Pan, Y. Feng, Y-M. He, Y. Liu and Q-H. Fan, Org. Lett., 2020, 22, 6452.

10. M. De Rosa and A. Soriente, Tetrahedron, 2010, 66, 2981.

11. R. Deka, A. Sarkar, R. J. Butcher, P. C. Junk, D. R. Turner, G. B. Deacon and H. B. Singh, *Organometallics*, 2020, **39**, 334.