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PhI(OAc)₂-Mediated Aminoacyloxylation of β , γ -Unsaturated Hydrazones Using Togni Reagent II as an Acyloxyl Precursor

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1 General remark

¹H NMR and ¹³C NMR spectra were recorded on 400MHz and 100MHz in CDCl₃ (BRUKER 400M or JNM-ECS 400M). All chemical shifts were given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; copies of their ¹H NMR and ¹³C NMR spectra are provided. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. Unless otherwise noted, commercially available reagents and solvents were used without further purification.The β , γ -unsaturated hydrazones **1a-1z** were synthesized from the corresponding ketone derivatives according to literature procedures.¹⁻⁶



2 Figure S1. AcOCF₃ were detected by HRMS as followed

3 General procedure for acyloxyl-substituted pyridazines



In a sealed tube, 25 mL over-dried Schlenk tube charged with a stir bar, β , γ -unsaturated hydrazone **1** (0.2 mmol), Togni-II (0.24 mmol) and iodobenzene diacetate (0.40 mmol) was added MeCN (2.0 mL). The resulting mixture was allowed to stir at -10 °C for 12 hours (monitored by TLC). After completion, solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate (5/1) as eluent to afford pure products **2**.



In a sealed tube, 25 mL over-dried Schlenk tube charged with a stir bar, β , γ -unsaturated hydrazone **1a** (0.2 mmol), **4** (0.24 mmol) and iodobenzene diacetate (0.40 mmol) was added MeCN (2.0 mL). The resulting mixture was allowed to stir at -10 °C for 12 hours (monitored by TLC). After completion, solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate (5/1) as eluent to afford pure products **2** in 51% yield.



In a sealed tube, 25 mL over-dried Schlenk tube charged with a stir bar, β , γ -unsaturated hydrazone **1f** (0.2 mmol), Togni-II (0.24 mmol), *p*-toluic acid (0.24 mmol) and iodobenzene diacetate (0.40 mmol) was added MeCN (2.0 mL). The resulting mixture was allowed to stir at -10 °C for 12 hours (monitored by TLC). After completion, solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate (5/1) as eluent to afford pure products **2f**, **5** and **6** in 42%, 0% and <5% yield,

respectively.

4 The data of products



4-Methyl-6-(p-tolyl)-2-tosyl-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2a)

Yellow solid (61.3 mg, 74% yield). melting point: 182-184 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.83 (dd, J = 7.5, 1.9 Hz, 1H), 7.75 (dd, J = 20.0, 7.5 Hz, 4H), 7.69 (d, J = 1.9 Hz, 1H), 7.43 (td, J = 7.5, 2.0 Hz, 1H), 7.35 (d, J = 6.8 Hz, 2H), 7.32-7.26 (m, 2H), 7.22 (dd, J = 7.5, 2.0 Hz, 1H), 3.63 (d, J = 8.4 Hz, 1H), 3.38 (d, J = 12.4 Hz, 1H), 2.60 (d, J = 12.4 Hz, 1H), 2.42 (s, 3H), 2.35 (d, J = 12.0 Hz, 1H), 2.30 (s, 3H), 1.57 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 166.2, 157.8, 141.7, 141.2, 140.8, 137.9, 135.1, 134.8, 132.3, 130.8, 129.7, 129.3, 128.6, 127.9, 127.3, 97.4, 83.5, 54.4, 36.6, 26.3, 21.6, 21.4; HRMS calcd for C₂₆H₂₆IN₂O₄S [M+H]⁺ 589.0652; found: 589.0559.



4-Methyl-6-phenyl-2-tosyl-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2b)

Yellow solid (54.1 mg, 71% yield). melting point: 177-179 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.98-7.90 (m, 2H), 7.83 (dd, J = 7.5, 1.9 Hz, 1H), 7.77 (d, J = 7.5 Hz, 2H), 7.70 (dd, J = 7.5, 1.9 Hz, 1H), 7.48 (dq, J = 9.4, 4.8 Hz, 3H), 7.38-7.30 (m, 3H), 7.21 (td, J = 7.5, 2.0 Hz, 1H), 3.63 (d, J = 12.0 Hz, 1H), 3.35 (d, J = 12.4 Hz, 1H), 2.60 (d, J = 12.3 Hz, 1H), 2.42 (s, 3H), 2.17 (d, J = 12.0 Hz, 1H), 1.51 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 166.2, 157.7, 141.7, 139.4, 137.9, 136.1, 135.9, 132.3, 130.8, 129.8, 129.6, 129.3, 128.4, 127.9, 126.9, 96.3, 83.6, 53.7, 35.5, 26.4, 20.3; HRMS calcd for C₂₅H₂₄IN₂O₄S [M+H]⁺ 575.0496; found: 575.0492.



4-Methyl-6-(4-nitrophenyl)-2-tosyl-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2c)

Yellow solid (48.8 mg, 67% yield). melting point: 189-191 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.35 (ddd, J = 6.8, 4.8, 1.8 Hz, 2H), 8.10 (ddd, J = 9.5, 8.0, 2.3 Hz, 2H), 7.81 (ddd, J = 14.4, 7.8, 4.2 Hz, 3H), 7.70 (dd, J = 7.5, 1.9 Hz, 1H), 7.40-7.30 (m, 3H), 7.12 (dd, J = 7.5, 1.9 Hz, 1H), 3.74 (s, 1H), 3.46 (s, 1H), 2.65 (s, 1H), 2.35 (d, J = 14.4 Hz, 4H), 1.58 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 165.8, 157.3, 146.0, 141.7, 141.2, 138.7, 137.9, 134.8, 132.3, 130.8, 129.3, 128.6, 127.9, 127.6, 125.0, 97.4, 83.5, 55.2, 35.5, 25.3, 22.0; HRMS calcd for C₂₅H₂₃IN₃O₆S [M+H]⁺ 620.0347; found: 620.0341.



6-(4-Methoxyphenyl)-4-methyl-2-tosyl-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2d) Yellow solid (51.8 mg, 75% yield). melting point: 211-213 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.03 (d, J = 7.5 Hz, 2H), 7.83 (dd, J = 7.5, 1.9 Hz, 1H), 7.73 (ddd, J = 9.4, 7.9, 4.2 Hz, 3H), 7.40-7.30 (m, 3H), 7.24-7.16 (m, 1H), 7.07 (d, J = 7.5 Hz, 2H), 3.80 (s, 3H), 3.63 (d, J = 12.4 Hz, 1H), 3.35 (d, J = 12.4 Hz, 1H), 2.60 (d, J = 12.4 Hz, 1H), 2.47 (s, 3H), 2.35 (d, J = 12.4 Hz, 1H), 1.55 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 166.7, 160.3, 157.8, 141.7, 141.2, 137.9, 134.8, 132.7, 132.3, 130.8, 129.3, 128.6, 127.9, 127.8, 114.3, 97.6, 83.7, 55.3, 54.4, 36.6, 26.3, 21.6; HRMS calcd for C₂₆H₂₆IN₂O₅S [M+H]⁺ 605.0602; found: 605.0606.



6-(4-Chlorophenyl)-4-methyl-2-tosyl-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2e) Yellow solid (61.7 mg, 70% yield). melting point: 168-170 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.83 (dd, J = 7.5, 1.9 Hz, 1H), 7.80-7.75 (m, 3H), 7.70 (dd, J = 7.4, 1.9 Hz, 2H), 7.54 (ddd, J = 13.1, 7.5, 1.9 Hz, 1H), 7.40-7.32 (m, 3H), 7.21 (td, J = 7.5, 2.0 Hz, 1H), 3.72 (d, J = 12.4 Hz, 1H), 3.38 (d, J = 12.4 Hz, 1H), 2.60 (d, J = 12.4 Hz, 1H), 2.40 (s, 3H), 2.35 (d, J = 12.4 Hz, 1H), 1.50 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 165.5, 158.2, 141.7, 141.2, 137.9, 135.9, 135.6, 134.8, 132.3, 130.8, 129.23, 129.2, 128.6, 127.9, 127.5, 971, 82.4, 53.9, 36.6, 25.3, 19.9; HRMS calcd for C₂₅H₂₃ClIN₂O₄S [M+H]⁺ 609.0106; found: 609.0101.



6-(4-Bromophenyl)-4-methyl-2-tosyl-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2f) Yellow solid (81.4 mg, 66% yield). melting point: 189-191 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.83 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.77 (d, *J* = 6.7 Hz, 1H), 7.70 (td, *J* = 5.6, 2.8 Hz, 4H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.35 (dt, *J* = 7.3, 5.1 Hz, 3H), 7.20 (dd, *J* = 7.5, 2.0 Hz, 1H), 3.72 (d, *J* = 12.3 Hz, 1H), 3.49 (d, *J* = 12.4 Hz, 1H), 2.74 (d, *J* = 12.4 Hz, 1H), 2.48 (s, 3H), 2.35 (d, *J* = 12.4 Hz, 1H), 1.54 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 165.5, 157.5, 141.5, 140.6, 137.9, 135.2, 134.78, 132.3, 130.8, 129.3, 128.6, 127.9, 127.8, 126.5, 97.0, 84.3, 53.9, 36.6, 26.1, 21.1; HRMS calcd for C₂₅H₂₃BrIN₂O₄S [M+H]⁺ 652.9601; found: 652.9606.



4-Methyl-6-(naphthalen-2-yl)-2-tosyl-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2g) Yellow solid (53.5 mg, 60% yield). melting point: 253-255 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.48 (s, 1H), 8.12 (d, J = 6.6 Hz, 1H), 7.89-7.80 (m, 3H), 7.77 (d, J = 7.5 Hz, 3H), 7.70 (dd, J =7.5, 1.9 Hz, 1H), 7.53-7.45 (m, 2H), 7.40-7.29 (m, 3H), 7.20 (dd, J = 7.5, 2.1 Hz, 1H), 3.63 (d, J =12.4 Hz, 1H), 3.34 (d, J = 12.4 Hz, 1H), 2.60 (d, J = 12.4 Hz, 1H), 2.42 (s, 3H), 2.35 (d, J = 12.4Hz, 1H), 1.57 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 165.6, 158.6, 141.7, 141.2, 136.9, 134.8, 134.2, 133.8, 132.3, 131.0, 130.8, 129.3, 129.1, 128.9, 128.6, 127.9, 127.8, 127.0, 126.1, 124.7, 96.3, 83.2, 55.2, 35.5, 27.1, 21.3; HRMS calcd for C₂₉H₂₆IN₂O₄S [M+H]⁺ 625.0652; found: 625.0657.



tert-Butyl2-(5-((2-iodobenzoyl)oxy)-5-methyl-1-tosyl-1,4,5,6-tetrahydropyridazin-3-yl)-1H-indole-1-carboxylate (2h)

Yellow solid (27.8 mg, 57% yield). melting point: 157-159 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.22 (d, J = 7.5 Hz, 1H), 8.00 (d, J = 7.5 Hz, 1H), 7.83 (dd, J = 7.5, 1.9 Hz, 1H), 7.77 (d, J = 7.5 Hz, 2H), 7.70 (dd, J = 7.5, 1.9 Hz, 1H), 7.44 (td, J = 7.5, 1.4 Hz, 1H), 7.35 (dt, J = 7.3, 5.1 Hz, 3H), 7.21 (td, J = 7.5, 2.0 Hz, 1H), 6.98-6.86 (m, 1H), 6.23 (s, 1H), 3.63 (d, J = 12.4 Hz, 1H), 3.38 (d, J = 12.4 Hz, 1H), 2.60 (d, J = 12.4 Hz, 1H), 2.42 (s, 3H), 2.35 (d, J = 12.4 Hz, 1H), 1.61 (s, 9H), 1.57 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 166.2, 159.9, 151.9, 141.7, 141.2, 140.6, 137.9, 137.9, 136.4, 134.8, 132.3, 130.8, 130.1, 129.3, 128.6, 127.9, 124.2, 123.2, 121.0, 115.3, 110.8, 97.6, 83.3, 83.1, 54.4, 35.1, 27.9, 26.3, 21.6; HRMS calcd for C₃₂H₃₃IN₃O₆S [M+H]⁺ 714.1129; found: 714.1120.



6-(Furan-2-yl)-4-methyl-2-tosyl-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2i) Yellow solid (53.6 mg, 72% yield). melting point: 128-130 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.83 (dd, J = 7.5, 1.9 Hz, 1H), 7.77 (d, J = 7.5 Hz, 2H), 7.70 (dd, J = 7.5, 1.9 Hz, 1H), 7.40-7.33 (m, 3H), 7.20 (dd, J = 7.5, 2.0 Hz, 2H), 6.45 (dd, J = 7.5, 1.3 Hz, 1H), 6.21 (t, J = 7.5 Hz, 1H), 3.59 (d, J = 12.4 Hz, 1H), 3.42 (d, J = 12.4 Hz, 1H), 2.60 (d, J = 12.4 Hz, 1H), 2.40-2.30 (m, 4H), 1.55 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 167.0, 156.8, 147., 145.1, 141.7, 141.2, 137.9, 134.8, 132.3, 130.8, 129.3, 128.4, 127.9, 115.8, 112.5, 97.4, 84.3, 53.3, 35.5, 26.6, 20.7; HRMS calcd for C₂₃H₂₂IN₂O₅S [M+H]⁺ 565.0289; found: 565.0284.



4-Methyl-6-(thiophen-2-yl)-2-tosyl-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2j)

Yellow solid (54.9 mg, 76% yield). melting point: 144-146 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.91 (dd, J = 7.4, 2.0 Hz, 1H), 7.77 (d, J = 7.5 Hz, 2H), 7.70 (dd, J = 7.4, 1.9 Hz, 1H), 7.57 (dd, J = 6.1, 2.9 Hz, 1H), 7.38-7.28 (m, 3H), 7.24-7.17 (m, 1H), 7.13-7.06 (m, 2H), 3.78 (d, J = 12.4 Hz, 1H), 3.33 (d, J = 12.4 Hz, 1H), 2.65 (d, J = 12.4 Hz, 1H), 2.40-2.30 (m, 4H), 1.57 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 165.8, 152.3, 144.0, 141.7, 141.2, 137.9, 134.8, 132.3, 130.8, 130.3, 129.3, 127.9, 127.3, 126.0, 125.6, 98.3, 83.3, 54.6, 37.3, 25.2, 20.9; HRMS calcd for C₂₃H₂₂IN₂O₄S₂ [M+H]⁺ 581.0060; found: 581.0053.



6-Ethyl-4-methyl-2-tosyl-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2k)

Yellow solid (53.8 mg, 69% yield). melting point: 131-133 °C. ¹H NMR (400 MHz, CDCl₃, ppm):

δ 7.83 (dd, J = 7.4, 2.0 Hz, 1H), 7.77 (dd, J = 7.5, 1.9 Hz, 1H), 7.68 (ddd, J = 12.9, 7.5, 1.9 Hz, 2H), 7.35 (ddd, J = 7.4, 4.7, 2.2 Hz, 2H), 7.31-7.27 (m, 1H), 7.24 (d, J = 1.9 Hz, 1H), 3.77 (d, J = 12.4 Hz, 1H), 3.38 (d, J = 12.4 Hz, 1H), 2.60 (d, J = 12.4 Hz, 1H), 2.42 (s, 3H), 2.35-2.29 (m, 2H), 2.15 (d, J = 8.0 Hz, 1H), 1.56 (s, 3H), 0.84 (t, J = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 166.8, 159.0, 141.7, 141.2, 137.9, 134.8, 132.3, 130.8, 129.3, 128.4, 125.0, 98.8, 81.7, 54.5, 40.8, 30.5, 25.9, 22.5, 8.8; HRMS calcd for C₂₁H₂₄IN₂O₄S [M+H]⁺ 527.0496; found: 527.0491.



6-(tert-Butyl)-4-methyl-2-tosyl-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (21)

Yellow solid (6.1 mg, 63% yield). melting point: 147-149 °C.¹H NMR (400 MHz, CDCl₃, ppm): δ 7.83 (dd, J = 7.5, 1.9 Hz, 1H), 7.77 (d, J = 7.5 Hz, 2H), 7.70 (dd, J = 7.5, 1.9 Hz, 1H), 7.35 (dt, J =7.3, 5.1 Hz, 3H), 7.21 (td, J = 7.5, 2.0 Hz, 1H), 3.63 (d, J = 12.4 Hz, 1H), 3.38 (d, J = 12.4 Hz, 1H), 2.60 (d, J = 12.4 Hz, 1H), 2.42 (s, 3H), 2.35 (d, J = 12.4 Hz, 1H), 1.57 (s, 3H), 1.25 (s, 9H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 166.2, 164.1, 141.7, 141.2, 137.9, 134.8, 132.3, 130.8, 129.3, 128.6, 126.2, 97.4, 82.9, 54.4, 38.0, 37.8, 27.7, 26.3, 21.6; HRMS calcd for C₂₃H₂₈IN₂O₄S [M+H]⁺ 555.0809; found: 555.0814.



6-Cyclopentyl-4-methyl-2-tosyl-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2m)

Yellow solid (42.8 mg, 70% yield). melting point: 162-164 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.94 (dd, J = 7.5, 1.9 Hz, 1H), 7.77 (d, J = 7.4 Hz, 2H), 7.66 (dd, J = 7.5, 2.0 Hz, 1H), 7.35 (td, J= 7.4, 2.0 Hz, 3H), 7.21 (td, J = 7.5, 2.0 Hz, 1H), 3.63 (d, J = 12.4 Hz, 1H), 3.38 (d, J = 12.4 Hz, 1H), 2.60 (d, J = 12.4 Hz, 1H), 2.51 (s, 3H), 2.35 (d, J = 12.4 Hz, 1H), 2.00 (dd, J = 12.5, 6.5 Hz, 1H), 1.85-1.39 (m, 11H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 173.6, 166.5, 141.7, 141.3, 137.9, 134.8, 132.3, 130.8, 129.3, 127.9, 125.8, 97.4, 82.2, 54.4, 40.2, 37.2, 31.9, 26.3, 25.9, 21.6; HRMS calcd for C₂₄H₂₈IN₂O₄S [M+H]⁺ 567.0809; found: 567.0817.



6-Cyclohexyl-4-methyl-2-tosyl-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2n)

Yellow solid (55.1 mg, 72% yield). melting point: 156-158 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.83 (d, J = 7.4 Hz, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.75-7.66 (m, 2H), 7.35 (dt, J = 7.5, 3.7 Hz, 2H), 7.25 (s, 1H), 7.21 (t, J = 7.5 Hz, 1H), 3.63 (d, J = 12.4 Hz, 1H), 3.38 (d, J = 12.4 Hz, 1H), 2.60 (d, J = 12.4 Hz, 1H), 2.42 (s, 3H), 2.35 (d, J = 12.4 Hz, 1H), 1.91-1.72 (m, 5H), 1.70-1.61 (m, 1H), 1.57 (s, 3H), 1.55-1.49 (m, 2H), 1.49-1.41 (m, 2H), 1.39-1.28 (m, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 169.9, 165.8, 141.7, 141.2, 137.9, 134.8, 132.3, 130.8, 129.3, 128.4, 127.9, 97.1, 81.7, 54.4, 42.9, 37.2, 29.3, 27.3, 26.3, 24.7, 20.5; HRMS calcd for C₂₅H₃₀IN₂O₄S [M+H]⁺ 581.0965; found: 581.0971.



4-Methyl-2-(phenylsulfonyl)-6-(*p*-tolyl)-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (20) Yellow solid (55.0 mg, 72% yield). melting point: 196-198 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.83 (ddd, *J* = 7.5, 3.9, 2.0 Hz, 3H), 7.71 (dd, *J* = 11.7, 4.7 Hz, 3H), 7.65-7.58 (m, 1H), 7.54 (t, *J* = 7.3 Hz, 2H), 7.35 (td, *J* = 7.5, 2.0 Hz, 1H), 7.29 (s, 1H), 7.25-7.18 (m, 2H), 3.63 (d, *J* = 12.4 Hz, 1H), 3.38 (d, *J* = 12.4 Hz, 1H), 2.60 (d, *J* = 12.4 Hz, 1H), 2.35 (d, *J* = 12.4 Hz, 1H), 2.13 (s, 3H), 1.64 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 166.3, 157.3, 141.2, 140.4, 138.0, 136.7, 134.8, 133.8, 132.3, 130.8, 129.4, 129.3, 128.6, 127.9, 127.3, 98.0, 83.4, 54.6, 36.7, 26.1, 20.5; HRMS calcd for C₂₅H₂₄IN₂O₄S [M+H]⁺ 575.0496; found: 575.0491.



4-Methyl-2-((2-nitrophenyl)sulfonyl)-6-(*p*-tolyl)-2,3,4,5-tetrahydropyridazin-4-yl 2iodobenzoate (2p)

Yellow solid (56.4 mg, 64% yield). melting point: 223-225 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.37 (ddd, J = 19.7, 7.5, 2.0 Hz, 2H), 8.14 (td, J = 7.5, 2.0 Hz, 1H), 7.92-7.76 (m, 3H), 7.76-7.65 (m, 2H), 7.35 (td, J = 7.5, 2.0 Hz, 1H), 7.30-7.27 (m, 2H), 7.21 (td, J = 7.5, 2.0 Hz, 1H), 3.63 (d, J = 12.4 Hz, 1H), 3.42 (d, J = 12.4 Hz, 1H), 2.60 (d, J = 12.4 Hz, 1H), 2.35 (d, J = 10.9 Hz, 4H), 1.54 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 165.6, 158.0, 149.4, 141.2, 140.8, 135.1, 134.8, 133.8, 133.3, 133.0, 132.3, 130.8, 129.4, 129.4, 127.9, 127.3, 125.7, 97.8, 84.5, 53.8, 37.3, 26.2, 21.8; HRMS calcd for C₂₅H₂₃IN₃O₆S [M+H]⁺ 620.0347; found: 620.0352.





Yellow solid (64.4 mg, 71% yield). melting point: 217-219 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.92-7.79 (m, 2H), 7.71 (dd, J = 11.7, 4.7 Hz, 3H), 7.62 (d, J = 4.1 Hz, 2H), 7.35 (td, J = 7.5, 2.0 Hz, 1H), 7.28 (d, J = 7.8 Hz, 2H), 7.23-7.16 (m, 2H), 3.72 (d, J = 12.4 Hz, 1H), 3.38 (d, J = 12.4 Hz, 1H), 2.72 (d, J = 12.4 Hz, 1H), 2.36 (s, 1H), 2.33 (s, 3H), 1.56 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 166.3, 157.7, 141.6, 141.2, 139.0, 135.1, 134.8, 133.8, 132.3, 131.3, 131.2, 130.8, 130.0, 129.4, 129.0, 127.9, 127.3, 97.1, 84.3, 54.8, 35.8, 25.5, 20.1; HRMS calcd for C₂₅H₂₃ClIN₂O₄S [M+H]⁺609.0106; found: 609.0112.



2-((4-Chlorophenyl)sulfonyl)-4-methyl-6-(*p*-tolyl)-2,3,4,5-tetrahydropyridazin-4-yl 2iodobenzoate (2r)

Yellow solid (55.1 mg, 73% yield). melting point: 201-203 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.91-7.78 (m, 3H), 7.77-7.66 (m, 2H), 7.61 (dd, J = 7.0, 3.1 Hz, 3H), 7.35 (td, J = 7.5, 2.0 Hz, 1H), 7.30-7.27 (m, 2H), 7.21 (td, J = 7.5, 2.0 Hz, 1H), 3.63 (d, J = 12.4 Hz, 1H), 3.48 (d, J = 12.4 Hz, 1H), 2.61 (d, J = 12.4 Hz, 1H), 2.35 (d, J = 12.4 Hz, 1H), 2.30 (s, 3H), 1.55 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 165.3, 157.9, 141.2, 140.8, 140.6, 138.0, 135.5, 134.8, 132.3, 130.8, 130.7, 129.8, 129.4, 127.9, 127.3, 98.1, 83.8, 53.8, 35.5, 26.2, 20.9; HRMS calcd for C₂₅H₂₃ClIN₂O₄S [M+H]⁺ 609.0106; found: 609.0100.



2-((4-Bromophenyl)sulfonyl)-4-methyl-6-(*p*-tolyl)-2,3,4,5-tetrahydropyridazin-4-yl 2iodobenzoate (2s)

Yellow solid (51.3 mg, 71% yield). melting point: 231-233 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.95-7.82 (m, 5H), 7.74-7.65 (m, 3H), 7.35 (td, *J* = 7.5, 2.0 Hz, 1H), 7.31-7.27 (m, 2H), 7.21 (td, *J* = 7.5, 2.0 Hz, 1H), 3.72 (d, *J* = 12.4 Hz, 1H), 3.38 (d, *J* = 12.4 Hz, 1H), 2.53 (d, *J* = 12.3 Hz, 1H), 2.35 (d, *J* = 12.3 Hz, 1H), 2.30 (s, 3H), 1.56 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 167.0, 157.9, 141.5, 141.2, 138.2, 135.1, 134.8, 132.7, 132.3, 130.8, 130.1, 129.4, 129.2, 127.9, 127.3, 96.3, 83.9, 53.5, 36.7, 27.4, 22.3; HRMS calcd for C₂₅H₂₃BrIN₂O₄S [M+H]⁺ 652.9601; found: 652.9609.



4-Methyl-2-(naphthalen-1-ylsulfonyl)-6-(*p*-tolyl)-2,3,4,5-tetrahydropyridazin-4-yl 2iodobenzoate (2t)

Yellow solid (55.1 mg, 66% yield). melting point: 304-306 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.72 (d, J = 7.3 Hz, 1H), 8.23 (d, J = 7.5 Hz, 2H), 7.93-7.79 (m, 2H), 7.71 (dd, J = 11.7, 4.7 Hz, 3H), 7.53-7.43 (m, 2H), 7.40 (td, J = 7.4, 1.5 Hz, 1H), 7.28 (dd, J = 10.1, 4.6 Hz, 3H), 7.24-7.14 (m, 1H), 3.77 (d, J = 12.4 Hz, 1H), 3.38 (d, J = 12.4 Hz, 1H), 2.60 (d, J = 12.4 Hz, 1H), 2.35 (d, J = 12.4 Hz, 1H), 2.23 (s, 3H), 1.58 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 166.2, 157.8, 141.2, 140.8, 136.3, 135.4, 135.1, 134.8, 132.3, 130.8, 130.3, 130.3, 130.0, 129.4, 129.1, 127.9, 127.3, 127.0, 125.7, 122.9, 97.4, 83.5, 54.4, 36.6, 26.3, 21.4; HRMS calcd for C₂₉H₂₆IN₂O₄S [M+H]⁺ 625.0652; found: 625.0659.



2-(Benzylsulfonyl)-4-methyl-6-(*p*-tolyl)-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2u) Yellow solid (36.6 mg, 66% yield). melting point: 178-180 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.83 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.71 (dd, *J* = 11.7, 4.7 Hz, 3H), 7.47-7.31 (m, 5H), 7.31-7.26 (m, 2H), 7.25-7.16 (m, 2H), 4.68 (d, *J* = 3.4 Hz, 2H), 3.16 (d, *J* = 12.4 Hz, 1H), 2.87 (d, *J* = 12.3 Hz, 1H), 2.60 (d, *J* = 12.4 Hz, 1H), 2.39 (d, *J* = 12.4 Hz, 1H), 2.30 (s, 3H), 1.54 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 166.2, 163.2, 141.2, 140.0, 134.8, 133.9, 132.5, 132.3, 130.8, 130.8, 129.5, 129.3, 128.2, 127.9, 125.6, 98.7, 83.2, 57.0, 55.7, 35.8, 25.9, 20.5; HRMS calcd for C₂₆H₂₆IN₂O₄S [M+H]⁺ 589.0652; found: 589.0658.



2-(Butylsulfonyl)-4-methyl-6-(*p***-tolyl)-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2v)** Yellow solid (70.2 mg, 53% yield). melting point: 181-183 °C.¹H NMR (400 MHz, CDCl₃, ppm): δ 7.83 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.71-7.67 (m, 1H), 7.35 (td, *J* = 7.5, 2.0 Hz, 1H), 7.31-7.27 (m, 2H), 7.21 (td, *J* = 7.5, 2.0 Hz, 1H), 3.38 (ddd, *J* = 24.0, 12.0, 7.8 Hz, 3H), 2.87 (d, *J* = 12.4 Hz, 1H), 2.57 (d, *J* = 12.3 Hz, 1H), 2.35 (d, *J* = 12.4 Hz, 1H), 2.30 (s, 3H), 1.87-1.77 (m, 1H), 1.71-1.58 (m, 1H), 1.58 (d, *J* = 8.0 Hz, 3H), 1.50 (dt, *J* = 15.4, 7.7 Hz, 2H), 0.91 (t, *J* = 7.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 166.5, 164.5, 141.2, 140.8, 135.1, 134.8, 132.3, 130.8, 129.4, 127.9, 127.3, 96.5, 82.7, 57.4, 52.1, 36.9, 26.3, 25.1, 21.1, 20.8, 13.2; HRMS calcd for C₂₃H₂₈IN₂O₄S [M+H]⁺ 555.0809; found: 555.0814.



2-(Cyclohexylsulfonyl)-4-methyl-6-(*p*-tolyl)-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2w)

Yellow solid (53.8 mg, 59% yield). melting point: 179-181 °C.¹H NMR (400 MHz, CDCl₃, ppm): δ 7.83 (d, J = 7.4 Hz, 1H), 7.71 (t, J = 7.7 Hz, 3H), 7.29 (t, J = 6.9 Hz, 3H), 7.21 (t, J = 7.4 Hz, 1H), 3.12 (d, J = 12.4 Hz, 1H), 2.90-2.75 (m, 2H), 2.60 (d, J = 12.4 Hz, 1H), 2.35 (d, J = 12.4 Hz, 1H), 2.32 (d, J = 13.4 Hz, 3H), 2.09 (dt, J = 13.2, 6.7 Hz, 2H), 1.83 (dd, J = 13.0, 6.7 Hz, 2H), 1.75-1.61 (m, 2H), 1.57 (s, 3H), 1.51-1.27 (m, 4H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 167.3, 162.6, 141.2, 140.8, 135.1, 134.8, 132.3, 130.8, 129.4, 127.9, 127.3, 97.4, 83.5, 57.1, 55.9, 36.6, 26.3, 26.0, 24.4, 24.3, 21.4; HRMS calcd for C₂₅H₃₀IN₂O₄S [M+H]⁺ 581.0965; found: 581.0970.



4,5,5-Trimethyl-6-(*p*-tolyl)-2-tosyl-2,3,4,5-tetrahydropyridazin-4-yl 2-iodobenzoate (2x) Yellow solid (43.2 mg, 75% yield). melting point: 168-170 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.89-7.79 (m, 2H), 7.77 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.71 (dd, *J* = 11.7, 4.7 Hz, 3H), 7.46-7.32 (m, 2H), 7.30 (d, *J* = 7.1 Hz, 3H), 7.21 (d, *J* = 2.0 Hz, 1H), 3.63 (d, *J* = 12.4 Hz, 1H), 3.38 (d, *J* = 12.4 Hz, 1H), 2.38 (s, 3H), 2.30 (s, 3H), 1.52 (s, 3H), 1.13 (s, 3H), 0.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 166.6, 163.2, 141.7, 141.5, 141.2, 137.9, 134.8, 132.3, 131.9, 130.8, 129.3, 128.4, 127.9, 127.4, 97.4, 80.2, 49.6, 48.3, 23.0, 22.1, 21.4, 20.1; HRMS calcd for C₂₈H₃₀IN₂O₄S [M+H]⁺ 617.0965; found: 617.0960.



10-Methyl-6-(p-tolyl)-8-tosyl-7,8-diazaspiro[4.5]dec-6-en-10-yl 2-iodobenzoate (2y)

Yellow solid (43.8 mg, 73% yield). melting point: 160-162 °C.¹H NMR (400 MHz, CDCl₃, ppm): δ 7.83 (dd, J = 7.5, 1.9 Hz, 1H), 7.78-7.60 (m, 5H), 7.34 (td, J = 7.5, 4.6 Hz, 3H), 7.31-7.26 (m, 2H), 7.21 (d, J = 2.0 Hz, 1H), 3.63 (d, J = 12.4 Hz, 1H), 3.38 (d, J = 12.4 Hz, 1H), 2.42 (s, 3H), 2.30 (s, 3H), 1.62 (dd, J = 6.4, 3.8 Hz, 7H), 1.53 (d, J = 4.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 167.7, 163.2, 141.7, 141.5, 141.2, 137.9, 134.8, 132.3, 132.0, 130.8, 129.6, 129.3, 128.6, 127.9, 127.6, 96.5, 53.9, 50.0, 36.1, 24.6, 22.1, 21.6, 20.1; HRMS calcd for C₃₀H₃₂IN₂O₄S [M+H]⁺ 643.1122; found: 643.1128.



5-Methyl-1-(*p*-tolyl)-3-tosyl-2,3-diazaspiro[5.5]undec-1-en-5-yl 2-iodobenzoate (2z)

Yellow solid (48.8 mg, 70% yield). melting point: 173-175 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.83 (dd, J = 7.5, 1.9 Hz, 1H), 7.79-7.75 (m, 1H), 7.71 (dd, J = 11.8, 4.6 Hz, 4H), 7.40-7.32 (m, 4H), 7.29 (d, J = 0.9 Hz, 1H), 7.21 (td, J = 7.5, 2.0 Hz, 1H), 3.63 (d, J = 12.4 Hz, 1H), 3.38 (d, J = 12.4 Hz, 1H), 2.42 (s, 3H), 2.30 (s, 3H), 1.83-1.58 (m, 4H), 1.54-1.30 (m, 9H); ¹³C NMR (100 MHz, CDCl₃, ppm): 166.6, 165.8, 141.7, 141.5, 141.2, 137.9, 134.8, 132.3, 132.0, 130.8, 129.4, 129.3, 128.6, 127.9, 127.6, 96.3, 79.5, 50.8, 43.0, 31.8, 25.1, 22.1, 21.9, 21.4, 20.5; HRMS calcd for C₃₁H₃₄IN₂O₄S [M+H]⁺ 657.1278; found: 657.1270.



(*E*)-4-methyl-*N*'-(3-methyl-1-tosylbut-3-en-1-ylidene)-*N*-((2,2,6,6-tetramethylpiperidin-1yl)oxy)benzenesulfonohydrazide (3)

Yellow solid (48.8 mg, 70% yield). melting point: 156-158 °C. ¹H NMR (400 MHz, CDCl₃, ppm): 7.81-7.66 (m, 4H), 7.40 (s, 1H), 7.30 (d, *J* = 7.1 Hz, 3H), 4.85 (d, *J* = 8.0 Hz, 2H), 2.80 (s, 2H), 2.42 (s, 3H), 2.25 (s, 3H), 1.84 (d, *J* = 1.3 Hz, 3H), 1.59 (q, *J* = 7.0 Hz, 3H), 1.43 (t, *J* = 7.0 Hz, 4H), 0.92 (s, 12H); ¹³C NMR (100 MHz, CDCl₃, ppm): 164.4, 144.2, 141.7, 140.8, 139.0, 135.6, 129.3, 129.3, 127.7, 127.0, 114.4, 58.6, 43.2, 39.1, 28.6, 22.7, 21.6, 21.4, 17.5; HRMS calcd for C₂₁H₃₃N₃O₃S⁺ [M+H]⁺ 407.2237; found: 407.2235.



(Z)-4-(4-bromophenyl)-2-methyl-4-(2-tosylhydrazono)butan-2-yl 4-methylbenzoate (6)

Yellow solid (5.4 mg, 5% yield). melting point: 139-141 °C. ¹H NMR (400 MHz, CDCl₃, ppm): 10.50 (s, 1H), 7.88 (d, J = 7.4 Hz, 2H), 7.73 (dd, J = 11.5, 7.6 Hz, 4H), 7.64 (d, J = 7.6 Hz, 2H), 7.39 (d, J = 6.7 Hz, 2H), 7.19 (d, J = 6.9 Hz, 2H), 2.47 (s, 2H), 2.42 (s, 3H), 2.30 (s, 3H), 1.52 (s, 6H); ¹³C NMR (100 MHz, CDCl₃, ppm): 163.6, 157.3, 144.6, 143.0, 136.5, 136.2, 132.0, 129.6, 129.5, 129.4, 128.0, 127.6, 127.0, 83.5, 40.3, 27.0, 21.4, 20.5; HRMS calcd for C₂₆H₂₈BrN₂O₄S ⁺ [M+H]⁺ 543.0948; found: 543.0946.

5 X-ray of 2a Crystallography details

Compound **2a** was dissolved in MeOH and cold *n*-hexane was added, leaving to slow evaporation overnight to yield colorless needle. A suitable crystal was selected and mounted on a X-ray with Mo radiation (a = 8.3871(11), b = 16.0084(17), c = 19.7110(19)) for cell determination and subsequent data collection at 296 K. Using SHELXL-2014, the structure was solved with the ShelXT11 structure solution program using Intrinsic Phasing and refined with the ShelXL12 refinement package using Least Squares minimisation. The solved structure of **2a** has been deposited in The Cambridge Crystallographic Data Centre (CCDC: 2271511)



ORTEP view with ellipsoids (at the 50% probability level)

Bond precision:		C-C = 0.0114 A			Wavelength=1.54178	
Cell:	a=8.3871(11)	b=16.008	84(17)	c=19.7110((19)	
	alpha=90	beta=10	6.856(3)	gamma=90		
Temperature:	293 K					
		Calculated			Reported	
Volume		2532.8(5)			2532.8(5)	
Space group		P 21/c			P2(1)/n	
Hall group		-P 2ybc			?	
Moiety formu	la	C25 H22 C1 I N2	04 S		?	
Sum formula		C25 H22 C1 I N2	04 S		C25 H22 C1 I N2 04 S	
Mr		608.86			608.86	
Dx,g cm-3		1.597			1.597	
Z		4			4	
Mu (mm-1)		11.961			11.961	
F000		1216.0			1216.0	
F000'		1220.67				
h,k,lmax		9, 18, 23			9, 18, 23	
Nref		4412			4410	
Tmin, Tmax		0. 512, 0. 620			0. 305, 0. 646	
Tmin'		0.201				
Correction m SCAN	ethod= # Repo	orted T Limits: T	min=0.305 Tmax	a=0.646 Abs	Corr = MULTI-	
Data complet	eness= 1.000		Theta(max) = 6	6.050		
R(reflections)= 0.0628(2505) wR2(reflections)= 0.1209(4410)						
S = 1.018		Npar= 309				

6 Refrence

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7 Copies of NMR Spectra

¹H NMR of **2a** (400 MHz, CDCl₃):



¹³C NMR of **2a** (100 MHz, CDCl₃):



¹H NMR of **2b** (400 MHz, CDCl₃):



¹³C NMR of **2b** (100 MHz, CDCl₃):



¹H NMR of **2c** (400 MHz, CDCl₃):



¹³C NMR of **2c** (100 MHz, CDCl₃):



¹H NMR of **2d** (400 MHz, CDCl₃):



¹³C NMR of **2d** (100 MHz, CDCl₃):



¹H NMR of **2e** (400 MHz, CDCl₃):



¹³C NMR of **2e** (100 MHz, CDCl₃):



¹H NMR of **2f** (400 MHz, CDCl₃):



¹³C NMR of **2f** (100 MHz, CDCl₃):



¹H NMR of **2g** (400 MHz, CDCl₃):



¹³C NMR of **2g** (100 MHz, CDCl₃):



¹H NMR of **2h** (400 MHz, CDCl₃):



¹³C NMR of **2h** (100 MHz, CDCl₃):



¹H NMR of **2i** (400 MHz, CDCl₃):



¹³C NMR of **2i** (100 MHz, CDCl₃):



¹H NMR of **2j** (400 MHz, CDCl₃):



¹³C NMR of **2j** (100 MHz, CDCl₃):



¹H NMR of **2k** (400 MHz, CDCl₃):



¹³C NMR of **2k** (100 MHz, CDCl₃):



¹H NMR of **2l** (400 MHz, CDCl₃):



¹³C NMR of **2l** (100 MHz, CDCl₃):



¹H NMR of **2m** (400 MHz, CDCl₃):



¹³C NMR of **2m** (100 MHz, CDCl₃):



¹H NMR of **2n** (400 MHz, CDCl₃):



¹³C NMR of **2n** (100 MHz, CDCl₃):



¹H NMR of **20** (400 MHz, CDCl₃):



¹³C NMR of **20** (100 MHz, CDCl₃):



¹H NMR of **2p** (400 MHz, CDCl₃):



¹³C NMR of **2p** (100 MHz, CDCl₃):





¹³C NMR of **2q** (100 MHz, CDCl₃):



¹H NMR of **2r** (400 MHz, CDCl₃):



¹³C NMR of **2r** (100 MHz, CDCl₃):

-165.27-157.86141.17132.541732.3771732.377-98.13-98.13-98.13-53.84-53.84-53.84-35.49-35.49





¹³C NMR of **2s** (100 MHz, CDCl₃):





¹H NMR of **2t** (400 MHz, CDCl₃):



¹³C NMR of **2t** (100 MHz, CDCl₃):



¹H NMR of **2u** (400 MHz, CDCl₃):



¹³C NMR of **2u** (100 MHz, CDCl₃):



¹H NMR of **2v** (400 MHz, CDCl₃):



¹³C NMR of **2v** (100 MHz, CDCl₃):





¹³C NMR of **2w** (100 MHz, CDCl₃):



¹H NMR of **2x** (400 MHz, CDCl₃):



¹³C NMR of **2x** (100 MHz, CDCl₃):



¹H NMR of **2y** (400 MHz, CDCl₃):



¹³C NMR of **2**y (100 MHz, CDCl₃):



¹H NMR of **2z** (400 MHz, CDCl₃):



¹³C NMR of **2z** (100 MHz, CDCl₃):



¹H NMR of **3** (400 MHz, CDCl₃):



¹³C NMR of **3** (100 MHz, CDCl₃):



¹H NMR of **6** (400 MHz, CDCl₃):



¹³C NMR of **6** (100 MHz, CDCl₃):

