Supporting Information

Solid Phase Synthesis of Functionalized Indazoles using Triazenes – Scope and Limitations

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General experimental section

¹H NMR spectra were recorded on a BRUKER 300 (300 MHz) or a BRUKER AM 400 (400 MHz) and a BRUKER AM 500 (500 MHz) spectrometers. Chemical shifts are given in parts per million (δ /ppm), downfield from tetramethylsilane (TMS) and are referenced to chloroform (7.26 ppm), acetone (2.09) or dimethylsulfoxide (2.49) as internal standards. All coupling constants are absolute values and J values are expressed in Hertz (Hz). The description of signals include: s = singlet, br. s = broad singlet, d = doublet, bd = broad doublet, t = triplet, dd = doublet of doublets, dt doublet of triplets, m = multiplet. The spectra were analyzed according to first order. **¹³C NMR** spectra were recorded on Bruker 300 (75 MHz), Bruker AM 400 (100 MHz) and Bruker AM 500 (125 MHz) spectrometers. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to CDCl₃ (77.4 ppm), acetone[d₆] (30.6 ppm) or dimethylsulfoxide[d₆] (39.5) as internal standard.

MS (EI) (electron impact mass spectrometry): Finnigan MAT 90 (70 eV). The molecular fragments are quoted as the relation between mass and charge (m/z), the intensities as a percentage value relative to the intensity of the base signal (100%). The abbreviation [M⁺] refers to the molecule ion.

IR (infrared spectroscopy): ATR spectra were recorded by diamond crystal on Bruker ALPHA-IR.

Routine monitoring of reactions were performed using silica gel coated aluminium plates (Merck, silica gel 60, F254) which were analyzed under UV-light at 254 nm and/or dipped into a solution of molybdate phosphate (5% phosphor molybdic acid in ethanol, dipping solution) and heated with a heat gun. Solvent mixtures are understood as volume/volume. Solid materials were powdered. Solvents, reagents and chemicals were purchased from SigmaAldrich, Alfa Aesar, ABCR and VWR. Solvents, reagents and chemicals were used as purchased unless stated otherwise. Merrifield resin was purchased from Polymer Laboratories (PL-CMS resin 0.94 mmol/g, 75–150 μ m, CMS 191).

In order to get the molecular mass of the resin and to calculate the elemental analysis the following calculation has to be performed:

$$\text{molar mass}_{\text{new}} = \frac{1000}{\text{Loading}_{\text{old}}} - (\text{molar mass}_{\text{sub}} - \text{molar mass}_{\text{add}})$$

Formula 1: Formula for the calculation of the molar mass of a modified resin. The *molar mass_{sub}* is the molecular mass of the fragment being substituted (e.g. Cl in case of Merrifield resin), while *molar mass_{add}* is the molecular mass of the fragment being added.

General procedures

GP1: General synthetic procedure for the synthesis of amino-polystyrene resins. Merrifield resin (1 equiv.) was suspended in DMF (15 mL/1.0 g). The corresponding amine (6 equiv.) and potassium iodide (1.1 equiv.) were added to the mixture. The resulting mixture was shaken overnight at 80 °C, the resin was filtered off, was washed sequentially with water, methanol, acetone, dichloromethane and was dried in vacuo.

GP2: General synthetic procedure for the synthesis of triazene resins T1 (3a-h). A solution of the corresponding amine (3 equiv.) and $\text{BF}_3 \cdot \text{OEt}_2$ (5 equiv.) in anhydrous THF was prepared and cooled to -20 °C. After 10 minutes, isoamyl nitrite (5 equiv.) was added and the reaction was stirred for 2 hours at -20 °C. The diazonium salt was obtained as solid which was dissolved in acetonitrile and added to the resin **2** (1 equiv.), diluted in a mixture of THF/pyridine (9:1). The resulting mixture was shaken overnight at room temperature. The resin was filtered off, washed sequentially with tetrahydrofuran, methanol, acetone, dichloromethane and was dried under high vacuum.

GP3: General synthetic procedure for the reduction of immobilized nitriles. Resin **3** (1 equiv.) was suspended in anhydrous THF (10 mL/1.0 g) and was cooled to 0 °C. Lithium aluminium hydride (2 equiv., 1 M in LiAlH_4) was added and the resulting mixture was shaken overnight at 70 °C. The resin was filtered off and washed with a Na/K tartrate solution, and sequentially with methanol, acetone, dichloromethane, and dried under high vacuum.

GP4: General synthetic procedure for acid chloride coupling. Resin **4** (1 equiv.) was suspended in anhydrous THF (10 mL/1.0 g) and triethylamine (3 equiv.) was added. The corresponding chloride acid (2.5 equiv.) was added to the mixture. The reaction was shaken overnight at room temperature. The resin was filtered off and washed with water, *N,N*-dimethylformamide, methanol, acetone and dichloromethane, and dried under high vacuum.

GP5: General synthetic procedure for acid coupling (4). Resin **4** (1 equiv.) was suspended in chloroform (10 mL/1.0 g). A mixture of the corresponding acid (3 equiv.), DCC (3 equiv.) and DMAP (1.5 equiv.) was stirred for 1 hour at room temperature and was added to the resin. The mixture was shaken overnight at room temperature. The resin was filtered off and washed with water, methanol, acetone and dichloromethane, and dried under high vacuum.

GP6: Synthetic procedure for Suzuki coupling reaction. Catalytic amounts of $\text{Pd}(\text{PPh}_3)_4$ (0.1 equiv.) were added to a suspension of the resin **7r** (1 equiv.) under nitrogen atmosphere in DMF. The slurry was stirred for 5 min, and then the 2-methylphenylboronic acid (2 equiv.) and 2 M Na_2CO_3 (2.5

equiv.) were added. The mixture was shaken 12 h at 85 °C and then cooled to room temperature, diluted with 25% NH₄OAc solution and stirred for an additional 5 min before being filtered. The resin was washed with water, *N,N*-dimethylformamide, water, methanol and dried under high vacuum.

GP7: General synthetic procedure for indazole/triazine derivatives. Resin **7** or **12** (1 equiv.) was suspended in abs. dichloromethane under a nitrogen atmosphere. Trifluoroacetic acid (2.1 equiv.) was added and the reaction was shaken overnight at room temperature. The mixture was filtered and the solvent was removed by evaporation. The crude material was purified as given in the analysis of single compounds to obtain the corresponding product.

Synthesis and analysis of single compounds

Resins

N,N-Isopropylpolystyrylmethylamine (**2**)

According to GP1, 12.0 g of Merrifield resin (0.94 mmol/g) have been converted to 12.09 g of resin **2** in 81% yield.

IR (cm⁻¹): ν = 3024, 2919, 2847, 1600, 1491, 1450, 1362, 1027, 905, 754, 695, 536. **Anal. calcd. for C₁₅₆H₁₅₆N:** C 91.38, H 7.96, N 0.67; found: C 90.04, H 7.90, N 0.66. Loading: 0.7557 mmol/g.

N,N-Benzylpolystyrylmethylamine (Supplemental material -1)

According to GP1, 5.00 g of the starting material (Merrifield resin, 0.94 mmol/g) have been converted to 5.28 g of resin **Sup. Mat. -1** in 83% yield.

IR (cm⁻¹): ν = 3015, 2912, 2826, 1585, 1499, 1473, 1328, 1018, 914, 754, 699, 529, 407. **Anal. calcd. for C₁₅₈H₁₅₈N:** C 91.54, H 7.78, N 0.68; found: C 90.20, H 7.61, N 0.65. Loading: 0.7399 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-3-(trifluoromethyl)benzonitrile (**3a**)

According to GP2, 4.73 g of starting material **2** have been converted to 5.14 g of resin **3a** in 63% yield. **IR (cm⁻¹):** ν = 3024, 2920, 2847, 1600, 1492, 1451, 1390, 1317, 1231, 1137, 1027, 753, 695, 537. **Anal. calcd. for C₁₈₃H₁₈₃F₃N₄:** C 88.08, H 7.39, N 2.25; found C 83.83, H 7.30, N 1.68. Loading: 0.4379 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-3,5-dichlorobenzonitrile (3b)

According to GP2, 856.0 mg of starting material **2** have been converted to 915.5 mg of resin **3b** in 47% yield. **IR (cm⁻¹):** ν = 3024, 2915, 1600, 1492, 1450, 1393, 1229, 1173, 1066, 1027, 754, 695, 538. **Anal. calcd. for C₂₉₈H₂₉₈Cl₂N₄:** C 89.33, H 7.50, N 1.40; found C 85.64, H 7.68, N 1.25. Loading: 0.3320 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-3,5-dibromobenzonitrile (3c)

According to GP2, 725.0 mg of starting material **2** have been converted to 795.0 mg of resin **3c** in 44% yield. **IR (cm⁻¹):** ν = 3024, 2917, 1600, 1492, 1450, 1390, 1227, 1027, 906, 754, 695, 533. **Anal. calcd. for C₂₉₇H₂₉₇Br₂N₄:** C 87.38, H 7.33, N 1.37; found C 82.51, H 7.33, N 0.98. Loading: 0.3069 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-3-chlorobenzonitrile (3d)

According to GP2, 1.00 g of starting material **2** have been converted to 1.05 g of resin **3d** in 42% yield. **IR (cm⁻¹):** ν = 3024, 2916, 1600, 1492, 1450, 1390, 1229, 1172, 1065, 1027, 905, 843, 748, 695, 535. **Anal. calcd. for C₂₀₆H₂₀₇ClN₄:** C 89.18, H 7.52, N 2.02; found C 83.59, H 7.27, N 1.57. Loading: 0.3022 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)benzonitrile (3e)

According to GP2, 4.00 g of starting material **2** have been converted to 4.23 g of resin **3e** in 59% yield. **IR (cm⁻¹):** ν = 3433, 3024, 2919, 1610, 1492, 1360, 1261, 1165, 1065, 1027, 817, 751, 695, 530, 458. **Anal. calcd. for C₁₇₆H₁₇₈N₄:** C 89.98, H 7.64, N 2.38; found C 85.60, H 7.30, N 2.08. Loading: 0.4216 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-4-chlorobenzonitrile (3f)

According to GP2, 4.00 g of starting material **2** have been converted to 4.30 g of resin **3f** in 61% yield. **IR (cm⁻¹):** ν = 3023, 2917, 1583, 1492, 1450, 1387, 1231, 1172, 1065, 1027, 904, 814, 752, 695, 535, 420. **Anal. calcd. for C₁₇₆H₁₇₆ClN₄:** C 88.68, H 7.48, N 2.35; found C 84.52, H 7.17, N 2.27. Loading: 0.4265 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-5-fluorobenzonitrile (3g)

According to GP2, 2.02 g of starting material **2** have been converted to 2.14 g of resin **3g** in 55% yield. **IR (cm⁻¹):** ν = 3023, 2914, 1600, 1491, 1449, 1390, 1257, 1169, 1062, 1027, 904, 827, 753, 695, 535. **Anal. calcd. for C₁₈₀H₁₈₁FN₄:** C 89.36, H 7.54, N 2.32; found C 85.42, H 7.33, N 2.10. Loading: 0.3941 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-5-chlorobenzonitrile (3h)

According to GP2, 900.0 mg of starting material **2** have been converted to 965.0 mg of resin **3h** in 58% yield. **IR (cm⁻¹):** ν = 3024, 2919, 1580, 1492, 1452, 1368, 1220, 1168, 1065, 1027, 910, 817, 751, 695, 530, 420. **Anal. calcd. for C₁₈₁H₁₈₂ClN₄:** C 88.77, H 7.49, N 2.29; found C 85.48, H 7.20, N 1.80. Loading: 0.4113 mmol/g.

2-(3-Benzylpolystyrylmethyl-1-triazen-1-yl)-4-chlorobenzonitrile (Supplemental material -2)

According to GP2, 4.00 g of **Sup. Mat. -1** have been converted to 4.30 g of resin **Sup. Mat. 2** in 62% yield. **IR (cm⁻¹):** ν = 3015, 2912, 1799, 1585, 1499, 1480, 1328, 1245, 1191, 1048, 1019, 914, 753, 699, 528, 409. **Anal. calcd. for C₁₇₃H₁₇₀ClN₄:** C 88.77, H 7.32, N 2.39; found C 86.85, H 7.18, N 2.19. Loading: 0.4265 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-3-(trifluoromethyl)benzylamine (4a)

According to GP3, 4.99 g of starting material **3a** have been converted to 5.01 g of resin **4a** in 100% yield. **IR (cm⁻¹):** ν = 3427, 3058, 3023, 2919, 2848, 1645, 1600, 1492, 1450, 1374, 1153, 1116, 1075, 1027, 979, 904, 749, 695, 589, 532. **Anal. calcd. for C₁₉₃H₁₉₇F₃N₄:** C 88.15, H 7.55, N 2.13; found C 76.67, H 6.89, N 1.96. Loading: 0.4357 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-3,5-dichlorobenzylamine (4b)

According to GP3, 800.0 mg of starting material **3b** have been converted to 803.7 mg of resin **4b** in 100% yield. **IR (cm⁻¹):** ν = 3406, 3023, 2918, 1598, 1492, 1450, 1366, 1125, 1067, 1026, 746, 695, 532. **Anal. calcd. for C₃₄₄H₃₄₅Cl₂N₄:** C 89.70, H 7.55, N 1.22; found C 75.25, H 7.25, N 0.84. Loading: 0.3305 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-3,5-dibromobenzylamine (4c)

According to GP3, 700.0 mg of starting material **3c** have been converted to 702.6 mg of resin **4c** in 100% yield. **IR (cm⁻¹):** ν = 3441, 3024, 2918, 1600, 1492, 1451, 1367, 1167, 1068, 1027, 904, 747, 695, 533. **Anal. calcd. for C₄₀₅H₄₀₅Br₂N₄:** C 88.66, H 7.51, N 0.99; found C 75.23, H 7.25, N 0.76. Loading: 0.3057 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-3-chlorobenzylamine (4d)

According to GP3, 800.0 mg of starting material **3d** have been converted to 803.4 mg of resin **4d** in 100% yield. **IR (cm⁻¹):** ν = 3423, 3024, 2921, 1600, 1492, 1450, 1363, 1170, 1066, 1026, 905, 747, 695, 532. **Anal. calcd. for C₂₄₁H₂₄₆ClN₄:** C 89.34, H 7.73, N 1.65; found C 77.16, H 7.19, N 1.26. Loading: 0.3008 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)benzylamine (4e)

According to GP3, 4.20 g of starting material **3e** have been converted to 4.22 g of resin **4e** in 39% yield. **IR (cm⁻¹):** ν = 3433, 3025, 2919, 1610, 1490, 1363, 1261, 1165, 1065, 1027, 817, 751, 695, 540, 450. **Anal. calcd. for C₂₁₇H₂₂₃N₄:** C 90.27, H 7.79, N 1.94; found C 87.40, H 7.22, N 1.78. Loading: 0.4198 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-4-chlorobenzylamine (4f)

According to GP3, 4.10 g of starting material **3f** have been converted to 4.12 g of resin **4f** in 100% yield. **IR (cm⁻¹):** ν = 3384, 3024, 2920, 1590, 1492, 1367, 1112, 1065, 994, 919, 746, 694, 666, 530. **Anal. calcd. for C₂₁₉H₂₂₄ClN₄:** C 89.24, H 7.66, N 1.90; found C 86.81, H 7.18, N 1.59. Loading: 0.4242 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-5-fluorobenzylamine (4g)

According to GP3, 1.90 g of starting material **3g** have been converted to 1.91 mg of resin **4g** in 100% yield. **IR (cm⁻¹):** ν = 3433, 3024, 2919, 1600, 1492, 1450, 1363, 1261, 1165, 1065, 1027, 817, 751, 695, 530, 456. **Anal. calcd. for C₂₉₁H₂₉₆FN₄:** C 90.35, H 7.71, N 1.45; found C 87.30, H 7.30, N 1.17. Loading: 0.3921 mmol/g.

2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-5-chlorobenzylamine (4h)

According to GP3, 890.0 mg of starting material **3h** have been converted to 895.0 mg of resin **4h** in 30% yield. **IR (cm⁻¹):** ν = 3386, 3024, 2920, 1580, 1492, 1376, 1115, 1065, 994, 920, 750, 695, 665, 530. **Anal. calcd. for C₂₆₄H₂₆₉ClN₄:** C 89.74, H 7.67, N 1.59; found C 80.03, H 7.44, N 0.92. Loading: 0.4091 mmol/g.

2-(3-Benzylpolystyrylmethyl-1-triazen-1-yl)-4-chlorobenzylamine (Supplemental material -3)

According to GP3, 1.00 g of **Sup. Mat. -2** have been converted to 1.004 g of resin **Sup. Mat. -3** in 100% yield. **IR (cm⁻¹):** ν = 3301, 3032, 2912, 1585, 1480, 1328, 1191, 1048, 1019, 914, 753, 699, 528, 409. **Anal. calcd. for C₂₁₇H₂₁₈ClN₄:** C 89.33, H 7.53, N 1.92; found C 87.79, H 7.28, N 1.62. Loading: 0.4248 mmol/g.

N-(2-(3-Isopropyl-3-polystyryl-1-triazen-1-yl)-3-(trifluoromethyl)benzyl)benzamide (7a)

According to GP4, 720.0 mg of starting material **4a** have been converted to 723.0 mg of resin **7a** in 70% yield.

¹⁹F Gel-NMR (376 MHz, CDCl₃, ppm), δ = -57.5. **IR (cm⁻¹):** ν = 3433, 3024, 2921, 1636, 1600, 1508, 1491, 1449, 1316, 1126, 1026, 753, 695, 528. **Anal. calcd. for C₁₇₁H₁₇₂F₃N₄O:** C 87.17, H 7.36, N 2.38; found C 84.33, H 6.80, N 2.12. Loading: 0.3061 mmol/g.

2,6-Difluoro-N-(2-(3-isopropyl-3-polystyryl-1-triazen-1-yl)-3-(trifluoromethyl)benzyl)benzamide (7b)

According to GP4, 900.0 mg of starting material **4a** have been converted to 940.5 mg of resin **7b** in 73% yield.

¹⁹F Gel-NMR (376 MHz, CDCl₃, ppm), δ = -57.7 (CF₃), -111.8 (C_{ar}-F), -112.8 (C_{ar}-F). **IR (cm⁻¹):** ν = 3424, 3024, 2920, 1624, 1600, 1492, 1466, 1451, 1317, 1233, 1126, 1026, 1003, 906, 754, 695, 530. **Anal. calcd. for C₂₁₄H₂₁₃F₅N₄O:** C 87.07, H 7.27, N 1.90; found C 73.88, H 6.62, N 1.23. Loading: 0.3044 mmol/g.

4-Methoxy-N-(2-(3-isopropyl-3-polystyryl-1-triazen-1-yl)-3-(trifluoromethyl)benzyl)benzamide (7c)

According to GP4, 1.00 g of starting material **4a** have been converted to 1.044 g of resin **7c** in 75% yield.

¹⁹F Gel-NMR (376 MHz, CDCl₃, ppm), δ = -57.5. **IR (cm⁻¹):** ν = 3409, 3024, 2918, 1602, 1492, 1450, 1316, 1251, 1126, 1027, 839, 753, 695, 532, 405. **Anal. calcd. for C₂₀₆H₂₀₆F₃N₄O₂:** C 87.46, H 7.41, N 1.98;

found C 74.35, H 6.84, N 1.20. Loading: 0.3130 mmol/g.

***N*-(2-(3-Isopropyl-3-polystyryl-1-triazen-1-yl)-3-(trifluoromethyl)benzyl)-3-methylbutyramide (7d)**

According to GP4, 900.0 mg of starting material **4a** have been converted to 924.5 mg of resin **7d** in 73% yield.

¹⁹F Gel-NMR (376 MHz, CDCl₃, ppm), $\delta = -57.6$. **IR** (cm⁻¹): $\nu = 3448, 3024, 2921, 1643, 1600, 1492, 1450, 1366, 1316, 1126, 1027, 905, 753, 695, 531$. **Anal. calcd. for** C₂₀₈H₂₁₅F₃N₄O: C 87.84, H 7.62, N 1.97; found

C 79.53, H 7.18, N 1.25. Loading: 0.3096 mmol/g.

***N*-(2-(3-Isopropyl-3-polystyryl-1-triazen-1-yl)-3-(trifluoromethyl)benzyl)-3-butyramide (7e)**

According to GP4, 500.0 mg of starting material **4a** have been converted to 512.0 mg of resin **7e** in 77% yield.

IR (cm⁻¹): $\nu = 3446, 3024, 2921, 1645, 1600, 1492, 1450, 1316, 1127, 1026, 905, 754, 695, 532$. **Anal. calcd. for** C₂₀₅H₂₁₁F₃N₄O: C 87.81, H 7.59, N 2.00; found C 79.82, H 7.22, N 1.18. Loading: 0.3277 mmol/g.

***N*-(2-(3-Isopropyl-3-polystyryl-1-triazen-1-yl)-3-(trifluoromethyl)benzyl)thiophene-2-carboxamide (7f)**

According to GP4, 500.0 mg of starting material **4a** have been converted to 527.0 mg of resin **7f** in 70% yield.

¹⁹F Gel-NMR (376 MHz, CDCl₃, ppm), $\delta = -57.6$. **IR** (cm⁻¹): $\nu = 3420, 3024, 2921, 1648, 1600, 1488, 1450, 1368, 1320, 1127, 1026, 908, 754, 695, 532$. **Anal. calcd. for** C₂₀₉H₂₁₀F₃N₄OS: C 87.07, H 7.34, N 1.94, S

1.11; found: C 83.80, H 6.87, N 1.75, S 1.02. Loading: 0.2950 mmol/g.

***N*-(2-(3-Isopropyl-3-polystyryl-1-triazen-1-yl)-3-(trifluoromethyl)benzyl)-3-methyl-2-butenamide (7g)**

According to GP4, 880.0 mg of starting material **4a** have been converted to 902.0 mg of resin **7g** in 69% yield.

¹⁹F Gel-NMR (376 MHz, CDCl₃, ppm), $\delta = -57.7$. **IR** (cm⁻¹): $\nu = 3425, 3024, 2920, 1646, 1600, 1492, 1450, 1366, 1316, 1126, 1027, 904, 753, 695, 533$. **Anal. calcd. for** C₂₀₉H₂₁₄F₃N₄O: C 87.93, H 7.56, N 1.96; found

C 74.42, H 7.11, N 1.54. Loading: 0.2976 mmol/g.

***N*-(2-(3-Isopropyl-3-polystyryl-1-triazen-1-yl)-3-(trifluoromethyl)benzyl)-2-phenylacetamide (7h)**

According to GP4, 600.0 mg of starting material **4a** have been converted to 622.0 mg of resin **7h** in 71% yield.

^{19}F Gel-NMR (376 MHz, CDCl_3 , ppm), $\delta = -57.7$. **IR** (cm^{-1}): $\nu = 3459$, 3059, 3024, 2920, 1600, 1492, 1450, 1316, 1126, 1028, 905, 754, 695, 533, 430. **Anal. calcd. for $\text{C}_{210}\text{H}_{212}\text{F}_3\text{N}_4\text{O}$** : C 88.04, H 7.46, N 1.96;

found C 75.49, H 6.85, N 1.53. Loading: 0.2968 mmol/g.

N-(2-(3-Isopropyl-3-polystyryl-1-triazene-1-yl)-3-(trifluoromethyl)benzyl)isonicotinamide (**7i**)

According to GP5, 800.0 mg of starting material **4a** have been converted to 833.5 mg of resin **7i** in 80% yield.

IR (cm^{-1}): $\nu = 3401$, 3058, 3024, 2919, 1638, 1600, 1492, 1450, 1316, 1222, 1126, 1025, 906, 753, 695, 530. **Anal. calcd. for $\text{C}_{206}\text{H}_{207}\text{F}_3\text{N}_5\text{O}$** : C 87.56, H 7.38, N 2.48; found C 79.53, H 7.18, N 1.25. Loading: 0.3346

mmol/g.

N-(2-(3-Isopropyl-3-polystyryl-1-triazene-1-yl)-3,5-dichlorobenzyl)benzamide (**7j**)

According to GP4, 725.0 mg of starting material **4b** have been converted to 742.0 mg of resin **7j** in 69% yield.

IR (cm^{-1}): $\nu = 3417$, 3024, 2917, 1634, 1600, 1492, 1450, 1269, 1175, 1067, 1026, 750, 695, 532, 400. **Anal. calcd. for $\text{C}_{379}\text{H}_{380}\text{Cl}_2\text{N}_4\text{O}$** : C 89.64, H 7.54, N 1.10; found C 77.60, H 6.75, N 0.91. Loading: 0.2227 mmol/g.

N-(2-(3-Isopropyl-3-polystyryl-1-triazene-1-yl)-3,5-dibromobenzyl)benzamide (**7k**)

According to GP4, 540.0 mg of starting material **4c** have been converted to 556.0 mg of resin **7k** in 69% yield.

IR (cm^{-1}): $\nu = 3417$, 3023, 2920, 1636, 1600, 1491, 1450, 1269, 1175, 1067, 1026, 905, 750, 695, 533. **Anal. calcd. for $\text{C}_{439}\text{H}_{440}\text{Br}_2\text{N}_4\text{O}$** : C 88.65, H 7.46, N 0.94; found C 76.51, H 7.01, N 0.74. Loading: 0.2790 mmol/g.

N-(2-(3-Isopropyl-3-polystyryl-1-triazene-1-yl)-3-chlorobenzyl)benzamide (**7l**)

According to GP3, 700.0 mg of starting material **4d** have been converted to 716.0 mg of resin **7l** in 73% yield.

IR (cm^{-1}): $\nu = 3433$, 3058, 3024, 2920, 1651, 1600, 1512, 1492, 1450, 1366, 1269, 1175, 1067, 1026, 962, 905, 752, 695, 527, 404. **Anal. calcd. for $\text{C}_{305}\text{H}_{307}\text{ClN}_4\text{O}$** : C 89.78, H 7.58, N 1.37; found: C 80.09, H 6.89, N 1.25.

Loading: 0.2118 mmol/g.

***N*-(2-(3-Isopropyl-3-polystyryl-1-triazen-1-yl)-3-(trifluoromethyl)benzyl)acetamide (7m)**

According to GP4, 1.00 g of starting material **4a** have been converted to 1.015 g of resin **7m** in 79% yield.

^{19}F Gel-NMR (376 MHz, CDCl_3 , ppm), $\delta = -57.5$. **IR** (cm^{-1}): $\nu = 3424, 3024, 2920, 1647, 1600, 1492, 1450, 1367, 1317, 1126, 1026, 905, 753, 695, 532, 403$. **Anal. calcd. for $\text{C}_{229}\text{H}_{233}\text{F}_3\text{N}_4\text{O}$** : C 88.32, H 7.54, N 1.80; found C 78.80,

H 7.06, N 1.40. Loading: 0.3393 mmol/g.

***N*-(2-(3-Isopropyl-3-polystyryl-1-triazen-1-yl)benzyl)benzamide (7n)**

According to GP4, 2.00 g of starting material **4e** have been converted to 2.07 g of resin **7n** in 74% yield.

IR (cm^{-1}): $\nu = 3438, 3024, 2921, 1640, 1600, 1508, 1488, 1449, 1320, 1128, 1050, 753, 695, 528$. **Anal. calcd. for $\text{C}_{230}\text{H}_{233}\text{N}_4\text{O}$** : C 90.00, H 7.65, N 1.83; found C 87.77, H 7.32, N 1.29. Loading: 0.3049 mmol/g.

***N*-(2-(3-Isopropyl-3-polystyryl-1-triazen-1-yl)-4-chlorobenzyl)benzamide (7o)**

According to GP4, 1.00 g of starting material **4f** have been converted to 1.06 g of resin **7o** in 72% yield.

IR (cm^{-1}): $\nu = 3377, 3024, 2917, 1666, 1600, 1512, 1491, 1450, 1388, 1270, 1171, 1068, 1027, 905, 752, 695, 534, 403$. **Anal. calcd. for $\text{C}_{236}\text{H}_{238}\text{ClN}_4\text{O}$** : C 89.08, H 7.54, N 1.76; found C 79.75, H 6.92, N 1.59.

Loading: 0.2799 mmol/g.

***N*-(2-(3-Isopropyl-3-polystyryl-1-triazen-1-yl)-5-fluorobenzyl)benzamide (7p)**

According to GP4, 950.0 mg of starting material **4g** have been converted to 978.0 mg of resin **7p** in 72% yield.

IR (cm^{-1}): $\nu = 3433, 3023, 2921, 1663, 1600, 1509, 1491, 1450, 1365, 1268, 1166, 1066, 1026, 952, 820, 750, 695, 530$. **Anal. calcd. for $\text{C}_{308}\text{H}_{310}\text{FN}_4\text{O}$** : C 90.17, H 7.62, N 1.37; found C 87.18, H 7.12, N 1.11. Loading: 0.2780 mmol/g.

***N*-(2-(3-Isopropyl-3-polystyryl-1-triazen-1-yl)-5-chlorobenzyl)benzamide (7q)**

According to GP4, 850.0 mg of starting material **4h** have been converted to 876.0 mg of resin **7q** in 72% yield.

IR (cm⁻¹): ν = 3374, 3025, 2912, 1660, 1600, 1510, 1491, 1448, 1388, 1258, 1170, 1068, 1027, 905, 752, 695, 530, 420. **Anal. calcd. for C₂₈₆H₂₈₈ClN₄O:** C 89.62, H 7.57, N 1.46; found C 79.77, H 7.32, N 1.09. Loading: 0.2818 mmol/g.

***N*-(2-(3-Benzylpolystyryl-1-triazen-1-yl)-4-chlorobenzyl)benzamide (Supplemental material -4)**

According to GP4, 980.0 mg of **Sup. Mat. -3** have been converted to 1.012 g of resin **Sup. Mat. -4** in 74% yield.

IR (cm⁻¹): ν = 3278, 3082, 2912, 1866, 1690, 1585, 1499, 1480, 1328, 1245, 1191, 1048, 1019, 914, 753, 699, 528, 409. **Anal. calcd. for C₂₂₂H₂₂₀ClN₄O:** C 89.01, H 7.40, N 1.87; found C 86.92, H 7.02, N 1.68.

Loading: 0.3040 mmol/g.

4-Iodo-*N*-(2-(3-Isopropyl-3-polystyryl-1-triazen-1-yl)-3-(trifluoromethyl)benzyl)benzamide (7r)

According to GP5, 1.00 g of starting material **4a** have been converted to 1.08 g of resin **7r** in 81% yield.

IR (cm⁻¹): ν = 3425, 3024, 2921, 2848, 1583, 1492, 1450, 1389, 1316, 1269, 1127, 1084, 1027, 1006, 838, 748, 695, 533. **Anal. calcd. for C₂₀₆H₂₀₆F₃IN₄O:** C 84.22, H 7.07 N 1.91; found C 68.35 H 6.17, N 1.47. Loading: 0.3262 mmol/g.

***N*-(2-(3-Isopropyl-3-polystyryl-1-triazen-1-yl)-3-(trifluoromethyl)benzyl)-2'-methyl-[1,1'-biphenyl]-4-carboxamide (12).**

According to GP6, 900.0 mg of starting material **7r** have been converted to 893.0 mg of resin **12** in 69% yield.

¹⁹F Gel-NMR (376 MHz, CDCl₃, ppm), δ = -57.5. **IR (cm⁻¹):** ν = 3442, 3024, 2921, 1664, 1600, 1492, 1450, 1316, 1271, 1126, 1026, 854, 750, 695, 533. **Anal. calcd. for C₂₀₆H₂₀₆F₃N₄O:** C 88.02, H 7.39, N 1.99; found C 80.53, H 7.18, N 1.25. Loading:

0.2256 mmol/g.

Products cleaved from the solid support

***N*-(7-(Trifluoromethyl)-1*H*-indazol-3-yl)benzamide (8a)**

Synthesis according to GP7. Reagents: resin **7a** (0.214 mmol, 700.0 mg), trifluoroacetic acid (0.450 mmol, 51.3 mg, 0.034 mL). Purification: ethyl acetate/cyclohexane (1:2). Yield: white solid (20.0 mg, 31%). R_f (cyclohexane/ethyl, 2:1) = 0.46. ^1H NMR (400 MHz, DMSO- d_6 , ppm), δ = 13.40 (s, 1 H), 11.00 (s, 1 H), 8.10 (d, J = 7.7 Hz, 2 H), 8.07 (d, J = 7.7 Hz, 1 H), 7.79 (d, J = 7.7 Hz, 1 H), 7.65 (t, J = 7.7 Hz, 1 H), 7.57 (t, J = 7.3 Hz, 2 H), 7.28 (t, J = 7.7 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO- d_6 , ppm), δ = 165.8, 141.1, 135.6 (q, J = 5.0 Hz), 133.4, 132.0, 128.4 (2 C), 127.9 (2 C), 127.1, 124.4 (q, J = 4.5 Hz), 124.0 (q, J = 271.3 Hz), 119.2, 118.8, 111.5 (q, J = 35.1 Hz). ^{19}F NMR (376 MHz, CDCl_3 , ppm), δ = -60.8. EI (m/z, 70 eV, 190 $^\circ\text{C}$): 305 (70) $[\text{M}]^+$, 105 (100), 77 (20). HRMS ($\text{C}_{15}\text{H}_{10}\text{F}_3\text{N}_3\text{O}$) $[\text{M}]$: calc. 305.0772, found. 305.0770. IR (ATR, ν): 3257.4, 1652.4, 1603.8, 1549.5, 1508.7, 1465.6, 1421.7, 1325.2, 1274.1, 1216.6, 1150.2, 1112.7, 1088.5, 1053.8, 928.6, 907.8, 805.3, 785.6, 752.9, 716.6, 690.2, 655.5, 598.3, 563.6, 545.3, 403.1 cm^{-1} .

2,6-Difluoro-*N*-(7-(trifluoromethyl)-1*H*-indazol-3-yl)benzamide (8b)

Synthesis according to GP7. Reagents: resin **7b** (0.274 mmol, 900.0 mg), trifluoroacetic acid (0.575 mmol, 65.6 mg, 0.044 mL). Purification: ethyl acetate/cyclohexane (1:2). Yield: white solid (28.0 mg, 30%). R_f (cyclohexane/ethyl acetate, 2:1) = 0.48. ^1H NMR (400 MHz, DMSO- d_6 , ppm), δ = 6.88 (d, J = 7.8 Hz, 1 H), 6.46 (d, J = 7.8 Hz, 1 H), 6.29 (tt, J = 8.1, 6.5 Hz, 1 H), 6.02 (t, J = 7.8 Hz, 1 H), 5.86 (t, J = 8.1 Hz, 2 H). ^{13}C NMR (100 MHz, DMSO- d_6 , ppm), δ = 160.0, 159.3 (dd, J = 250.5, 7.1 Hz, 2 C), 139.5, 135.7 (m), 131.8, 125.6, 124.2 (q, J = 4.7 Hz), 123.7 (q, J = 270.3 Hz), 119.0, 117.7, 113.9 (t, J = 21.7 Hz), 112.3 (q, J = 33.5 Hz), 111.2 (dd, J = 19.8, 5.4 Hz, 2 C). ^{19}F NMR (376 MHz, CDCl_3 , ppm), δ = -62.0 (CF₃), -112.7 (C_{arom}-F). EI (m/z, 70 eV, 190 $^\circ\text{C}$): 341 (15) $[\text{M}]^+$, 141 (100), 113 (15). HRMS ($\text{C}_{15}\text{H}_8\text{F}_5\text{N}_3\text{O}$) $[\text{M}]$: calcd. 341.0582, found 341.0581. IR (ATR, ν): 3258.3, 2919.6, 1668.5, 1622.5, 1556.6, 1466.8, 1421.4, 1325.4, 1235.6, 1112.4, 1089.2, 1054.5, 1009.3, 929.1, 911.7, 800.7, 694.6, 654.6, 590.5, 455.5 cm^{-1} .

4-Methoxy-*N*-(7-(trifluoromethyl)-1*H*-indazol-3-yl)benzamide (8c)

Synthesis according to GP7. Reagents: resin **7c** (0.313 mmol, 1.0 g), trifluoroacetic acid (0.657 mmol, 74.9 mg, 0.050 mL). Purification: precipitated with diethyl ether. Yield: white solid (31.0 mg, 30%). R_f (cyclohexane/ethyl acetate, 1:1) = 0.73. ^1H NMR (400 MHz, DMSO- d_6 , ppm), δ = 13.36 (s, 1 H), 10.84 (s, 1 H), 8.09 (d, J = 8.8 Hz, 2 H), 8.04 (d, J = 7.3 Hz, 1 H), 7.78 (d, J = 7.3 Hz, 1 H), 7.26 (t, J = 7.3 Hz, 1 H), 7.09 (d, J = 8.7 Hz, 2 H), 3.87

(s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6 , ppm), δ = 165.2, 162.2, 141.4, 135.6 (m), 129.9 (2 C), 127.2, 124.3 (q, J = 4.8 Hz), 124.0 (q, J = 280.0 Hz), 119.1, 118.9, 113.7 (2 C), 111.4 (q, J = 33.4 Hz), 55.4. ^{19}F NMR (376 MHz, CDCl_3 , ppm), δ = -60.8. EI (m/z, 70 eV, 190 °C): 335 (40) $[\text{M}]^+$, 169 (15), 135 (100), 69 (25). HRMS ($\text{C}_{16}\text{H}_{12}\text{F}_3\text{N}_3\text{O}_2$) $[\text{M}]$: calcd. 335.0882, found 335.0881. IR (ATR, ν): 3402.1, 1738.3, 1709.8, 1672.7, 1625.2, 1604.0, 1556.0, 1512.2, 1458.9, 1374.7, 1350.6, 1316.9, 1263.5, 1210.9, 1145.3, 1112.0, 1072.4, 1032.1, 940.6, 853.1, 796.4, 758.3, 745.4, 727.1, 628.7, 600.2, 520.0 cm^{-1} .

3-Methyl-*N*-(7-(trifluoromethyl)-1*H*-indazol-3-yl)butyramide (8d)

Synthesis according to GP7. Reagents: resin **7d** (0.279 mmol, 900.0 mg), trifluoroacetic acid (0.585 mmol, 66.7 mg, 0.045 mL). Purification: ethyl acetate/cyclohexane (1:1). Yield: white solid (24.0 mg, 30%). R_f (cyclohexane/ethyl acetate, 1:1) = 0.66. ^1H NMR (400 MHz, DMSO- d_6 , ppm), δ = 12.15 (s, 1 H), 10.52 (s, 1 H), 8.08 (d, J = 7.3 Hz, 1 H), 7.74 (d, J = 7.3 Hz, 1 H), 7.24 (t, J = 7.3 Hz, 1 H), 2.31 (d, J = 7.1 Hz, 2 H), 2.17-2.12 (m, 1 H), 0.99 (d, J = 6.6 Hz, 6 H). ^{13}C NMR (400 MHz, DMSO- d_6 , ppm), δ = 171.0, 141.1, 135.4 (q, J = 5.2 Hz), 127.4, 124.3 (q, J = 4.2 Hz), 124.0 (q, J = 271.3 Hz), 118.9, 118.2, 111.3 (q, J = 33.3 Hz), 44.4, 25.6, 22.3 (2 C). ^{19}F NMR (376 MHz, CDCl_3 , ppm), δ = -60.7. EI (m/z, 70 eV, 190 °C): 285 (20) $[\text{M}]^+$, 201 (100), 181 (15), 57 (15). HRMS ($\text{C}_{13}\text{H}_{14}\text{F}_3\text{N}_3\text{O}$) $[\text{M}]$: calcd. 285.1089, found 285.1089. IR (ATR, ν): 3269.1, 2960.1, 1664.0, 1603.5, 1551.4, 1508.7, 1452.1, 1422.2, 1370.0, 1320.3, 1269.1, 1218.7, 1117.6, 1083.7, 1049.2, 978.6, 927.1, 861.8, 798.4, 727.8, 687.8, 599.3, 578.0, 556.3 cm^{-1} .

N-(7-(Trifluoromethyl)-1*H*-indazol-3-yl)butyramide (8e)

Synthesis according to GP7. Reagents: resin **7e** (0.164 mmol, 500.0 mg), trifluoroacetic acid (0.344 mmol, 34.2 mg, 0.026 mL). Purification: ethyl acetate/cyclohexane (1:2). Yield: white solid (15.0 mg, 34%). R_f (cyclohexane/ethyl acetate, 2:1) = 0.43. ^1H NMR (400 MHz, acetone- d_6 , ppm), δ = 12.16 (s, 1 H), 9.51 (s, 1 H), 8.17 (d, J = 7.3 Hz, 1 H), 7.60 (d, J = 7.3 Hz, 1 H), 7.12 (t, J = 7.3 Hz, 1 H), 2.38 (t, J = 7.3 Hz, 2 H), 1.64 (hp, J = 7.2 Hz, 2 H), 0.88 (t, J = 7.4 Hz, 3 H). ^{19}F NMR (376 MHz, CDCl_3 , ppm), δ = -60.9. ^{13}C NMR (100 MHz, acetone- d_6 , ppm), δ = 172.0, 142.8, 137.1 (m), 129.3, 125.3 (q, J = 4.8 Hz), 125.2 (q, J = 270.4 Hz), 119.7, 119.2, 112.9 (q, J = 34.5 Hz), 38.5, 19.6, 14.0. EI (m/z, 70 eV, 190 °C): 271 (20) $[\text{M}]^+$, 201 (100), 181 (15), 69 (12). HRMS ($\text{C}_{12}\text{H}_{12}\text{F}_3\text{N}_3\text{O}$) $[\text{M}]$: calcd. 271.0927; found 271.0927. IR (ATR, ν): 3267.4, 2959.8, 1661.5, 1603.3, 1550.8, 1508.5, 1451.8, 1421.6, 1369.7, 1309.4, 1230.8, 1116.6, 1084.1, 1049.4, 978.3, 926.3, 861.5, 799.2, 727.4, 686.7, 596.5, 577.7, 542.3 cm^{-1} .

***N*-(7-(Trifluoromethyl)-1*H*-indazol-3-yl)thiophene-2-carboxamide (8f)**

Synthesis according to GP7. Reagents: resin **7f** (0.148 mmol, 500.0 mg), trifluoroacetic acid (0.310 mmol, 35.3 mg, 0.024 mL). Purification: ethyl acetate/cyclohexane (1:2). Yield: white solid (14.0 mg, 30%). R_f (cyclohexane/ethyl acetate, 2:1) = 0.67. ^1H NMR (400 MHz, acetone- d_6 , ppm), δ = 8.17 (d, J = 7.2 Hz, 1 H), 8.01 (dd, J = 3.8, 1.1 Hz, 1 H), 7.71 (dd, J = 5.0, 1.1 Hz, 1 H), 7.64 (t, J = 7.2 Hz, 1 H), 7.18 (t, J = 7.2 Hz, 1 H), 7.12 (dd, J = 5.0, 3.8 Hz, 1 H). ^{13}C NMR (100 MHz, Acetone- d_6 , ppm), δ = 161.0, 142.2, 140.1, 137.2 (q, J = 4.5 Hz), 132.7, 130.3, 128.9, 128.8, 125.5 (q, J = 4.8 Hz), 125.3 (q, J = 270.4 Hz), 120.2, 119.6, 113.0 (q, J = 31.4 Hz). ^{19}F NMR (376 MHz, CDCl_3 , ppm), δ = -60.8. EI (m/z, 70 eV, 190 °C): 311 (35) $[\text{M}]^+$, 111 (100), 69 (15). HRMS ($\text{C}_{13}\text{H}_8\text{F}_3\text{N}_3\text{OS}$) $[\text{M}]$: calcd. 311.0335, found 311.0336. IR (ATR, ν): 3271.2, 1644.7, 1601.8, 1550.0, 1508.1, 1457.9, 1416.1, 1356.7, 1320.3, 1286.3, 1269.2, 1214.5, 1150.7, 1113.5, 1087.1, 1054.1, 927.4, 887.6, 851.9, 804.8, 764.3, 751.8, 717.9, 695.1, 654.4, 596.8, 552.1 cm^{-1} .

3-Methyl-*N*-(7-(trifluoromethyl)-1*H*-indazol-3-yl)-2-butenamide (8g)

Synthesis according to GP7. Reagents: resin **7g** (0.253 mmol, 850.0 mg), trifluoroacetic acid (0.531 mmol, 60.6 mg, 0.041 mL). Purification: ethyl acetate/cyclohexane (1:2). Yield: white solid (22.0 mg, 31%). R_f (cyclohexane/ethyl acetate, 2:1) = 0.53. ^1H NMR (400 MHz, Acetone- d_6 , ppm), δ = 12.26 (s, 1 H), 9.56 (s, 1 H), 8.38 (d, J = 7.8 Hz, 1 H), 7.73 (d, J = 7.8 Hz, 1 H), 7.26 (t, J = 7.8 Hz, 1 H), 6.12 (hp, J = 1.4 Hz, 1 H), 2.26 (d, J = 1.4 Hz, 3 H), 1.93 (d, J = 1.4 Hz, 3 H); ^{13}C NMR (100 MHz, Acetone- d_6 , ppm), δ = 167.3, 155.1, 141.9, 137.0 (m), 127.3, 125.3 (q, J = 270.2 Hz), 125.2 (q, J = 4.7 Hz), 119.9, 119.2, 118.1, 113.3, 27.1, 19.8. ^{19}F NMR (376 MHz, CDCl_3 , ppm), δ = -60.9. EI (m/z, 70 eV, 190 °C): 283 (30) $[\text{M}]^+$, 201 (45), 83 (100), 55 (22). HRMS ($\text{C}_{13}\text{H}_{12}\text{F}_3\text{N}_3\text{O}$) $[\text{M}]$: calcd. 283.0927, found 283.0929. IR (ATR, ν): 3277.4, 2923.6, 1662.5, 1645.7, 1601.6, 1546.3, 1505.6, 1453.0, 1421.8, 1317.3, 1271.5, 1245.5, 1213.2, 1151.4, 1112.2, 1088.8, 1051.5, 995.5, 926.5, 871.0, 842.9, 797.5, 747.1, 727.1, 692.7, 650.7, 596.7, 554.5, 463.2 cm^{-1} .

2-Phenyl-*N*-(7-(trifluoromethyl)-1*H*-indazol-3-yl)acetamide (8h)

Synthesis according to GP7. Reagents: resin **7h** (0.148 mmol, 500.0 mg), trifluoroacetic acid (0.312 mmol, 35.5 mg, 0.024 mL). Purification: ethyl acetate/cyclohexane (1:2). Yield: white solid (16.0 mg, 34%). R_f (cyclohexane/ethyl acetate, 2:1) = 0.53. ^1H NMR (400 MHz, Acetone- d_6 , ppm), δ = 12.32 (s, 1H), 9.86 (s, 1 H), 8.18 (d, J = 7.4 Hz, 1 H), 7.71 (d, J = 7.4 Hz, 1 H), 7.46 (d, J = 7.3 Hz, 2 H), 7.35 (t, J = 7.4 Hz, 2 H), 7.28 (t, J = 7.4 Hz, 1 H), 7.23 (t, J = 7.5 Hz, 1 H), 3.85 (s, 2 H); ^{13}C NMR (100 MHz, Acetone- d_6 , ppm), δ = 169.9, 141.4, 136.2 (q, J = 4.2 Hz), 135.7, 129.2 (2 C), 128.4 (2 C), 127.7, 126.7, 124.4 (q, J = 4.5 Hz), 124.3 (q, J = 270.4 Hz), 119.0, 118.2, 112.1 (q, J = 32.8 Hz), 42.6.

^{19}F NMR (376 MHz, CDCl_3 , ppm), $\delta = -60.9$. EI (m/z, 70 eV, 190 °C): 319 (60) $[\text{M}]^+$, 201 (100), 181 (12), 91 (70). HRMS ($\text{C}_{16}\text{H}_{12}\text{F}_3\text{N}_3\text{O}$) $[\text{M}]$: calcd. 319.0927, found 319.0928. IR (ATR, ν): 3273.5, 3030.8, 2925.1, 2400.6, 1665.9, 1614.0, 1593.9, 1524.3, 1498.8, 1453.8, 1429.6, 1391.6, 1338.8, 1306.0, 1220.0, 1184.4, 1152.8, 1116.9, 1103.0, 1049.5, 957.3, 902.8, 848.5, 806.8, 791.1, 748.7, 702.8, 637.4, 623.0, 597.5, 534.5, 490.6, 473.8 cm^{-1} .

N-(7-(Trifluoromethyl)-1*H*-indazol-3-yl)isonicotinamide (8i)

Synthesis according to GP7. Reagents: resin **7i** (0.268 mmol, 800.0 mg), trifluoroacetic acid (0.562 mmol, 64.1 mg, 0.043 mL). Purification: methanol/dichloromethane (1:30). Yield: white solid (24.0 mg, 29%). R_f (dichloromethane/methanol, 30:1) = 0.61. ^1H NMR (400 MHz, DMSO-d_6 , ppm), $\delta = 13.49$ (s, 1 H), 11.34 (s, 1 H), 8.85 (br. s, 2 H), 8.10 (d, $J = 7.6$ Hz, 1 H), 8.01 (d, $J = 4.6$ Hz, 2 H), 7.80 (d, $J = 7.6$ Hz, 1 H), 7.29 (t, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6 , ppm), $\delta = 164.3$, 150.2 (2 C), 140.7, 140.4, 135.6 (m), 127.0, 124.5 (q, $J = 4.9$ Hz), 123.9 (q, $J = 271.1$ Hz), 121.9 (2 C), 119.4, 118.5, 111.6 (q, $J = 33.7$ Hz). ^{19}F NMR (376 MHz, acetone- d_6 , ppm), $\delta = -61.4$. EI (m/z, 70 eV, 190 °C): 306 (50) $[\text{M}]^+$, 106 (100), 78 (60), 69 (18). HRMS ($\text{C}_{14}\text{H}_9\text{F}_3\text{N}_4\text{O}$) $[\text{M}]$: calcd. 306.0849, found 306.0848. IR (ATR, ν): 3272.9, 2913.0, 1657.3, 1600.0, 1551.4, 1508.1, 1467.8, 1421.7, 1356.3, 1321.5, 1281.2, 1214.2, 1164.7, 1107.5, 1085.1, 1046.6, 999.7, 921.0, 862.9, 845.8, 806.6, 786.1, 755.4, 740.4, 725.9, 655.3, 624.7, 595.6, 563.3, 502.8 cm^{-1} .

N-(5,7-Dichloro-1*H*-indazol-3-yl)benzamide (8j)

Synthesis according to GP7. Reagents: resin **7j** (0.134 mmol, 600.0 mg), trifluoroacetic acid (0.281 mmol, 32.0 mg, 0.021 mL). Purification: ethyl acetate/cyclohexane (1:2). Yield: white solid (12.0 mg, 29%). R_f (cyclohexane/ethyl acetate, 2:1) = 0.42. ^1H NMR (400 MHz, CDCl_3 , ppm) $\delta = 12.40$ (s, 1H), 9.97 (s, 1 H), 7.94 (d, $J = 7.6$ Hz, 2 H), 7.87 (d, $J = 1.5$ Hz, 1 H), 7.54 (t, $J = 7.2$ Hz, 1 H), 7.48-7.44 (m, 2 H), 7.31 (d, $J = 1.7$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm), $\delta = 166.7$, 140.1, 137.9, 133.2, 132.3, 128.6 (2 C), 127.6 (2 C), 126.8, 125.5, 120.7, 117.9, 116.4. EI (m/z, 70 eV, 190 °C): 305/307/308 (20/15/6) $[\text{M}]^+$, 105 (100), 77 (40), 69 (12). HRMS ($\text{C}_{14}\text{H}_9\text{Cl}_2\text{N}_3\text{O}$) $[\text{M}]$: calcd. 305.0117, found 305.0116. IR (ATR, ν): 3251.8, 2417.6, 1648.0, 1576.7, 1541.7, 1513.7, 1478.9, 1447.6, 1414.6, 1387.8, 1322.0, 1125.5, 1058.5, 1013.5, 931.7, 905.9, 867.4, 850.5, 788.5, 738.3, 710.6, 690.5, 666.4, 625.4, 602.7, 559.5, 510.6, 483.6, 410.4 cm^{-1} .

N-(5,7-Dibromo-1*H*-indazol-3-yl)benzamide (8k)

Synthesis according to GP7. Reagents: resin **7k** (0.145 mmol, 520.0 mg), trifluoroacetic acid (0.305 mmol, 34.7 mg, 0.023 mL). Purification: ethyl acetate/cyclohexane (1:2). Yield: white solid (15.0 mg, 26%). R_f

(cyclohexane/ethyl acetate, 2:1) = 0.33. ^1H NMR (300 MHz, Acetone- d_6 , ppm), δ = 12.38 (s, 1 H), 9.98 (s, 1 H), 8.15 (d, J = 1.6 Hz, 1 H), 8.04 (d, J = 7.3 Hz, 2 H), 7.62 (d, J = 1.6 Hz, 1 H), 7.57-7.47 (m, 2 H), 7.44 (t, J = 7.3 Hz, 1 H). EI (m/z , 70 eV, 190 $^\circ\text{C}$): 393/395/397 (7/13/3) $[\text{M}]^+$, 201 (100), 181 (15), 57 (15). HRMS ($\text{C}_{14}\text{H}_9\text{Br}_2\text{N}_3\text{O}$) $[\text{M}]$: calcd. 392.9107, found 392.9105. IR (ATR, ν): 3239.3, 2915.7, 2847.8, 1739.4, 1572.4, 1532.6, 1448.6, 1377.9, 1323.3, 1260.9, 1099.8, 919.9, 851.6, 788.7, 692.6, 658.2, 614.8, 590.7, 405.9 cm^{-1} .

***N*-(7-Chloro-1*H*-indazol-3-yl)benzamide (8l)**

Synthesis according to GP7. Reagents: resin **7l** (0.095 mmol, 450.0 mg), trifluoroacetic acid (0.200 mmol, 22.8 mg, 0.015 mL). Purification: ethyl acetate/cyclohexane (1:2). Yield: white solid (7.7 mg, 30%). R_f (cyclohexane/ethyl acetate, 2:1) = 0.35. ^1H NMR (500 MHz, Acetone- d_6 , ppm), δ = 12.24 (s, 1 H), 9.90 (s, 1 H), 8.04 (d, J = 7.4 Hz, 2 H), 7.83 (d, J = 7.8 Hz, 1 H), 7.57-7.37 (m, 3 H), 7.32 (t, J = 7.8 Hz, 1 H), 7.00 (t, J = 7.8 Hz, 1 H); ^{13}C NMR (125 MHz, Acetone- d_6 , ppm), δ = 165.7, 141.2, 138.4, 133.5, 132.0, 128.5 (2 C), 128.0 (2 C), 125.8, 121.1, 120.7, 119.0, 114.8. EI (m/z , 70 eV, 140 $^\circ\text{C}$): 271/273 (27/9) $[\text{M}]^+$, 131 (7), 105 (100). EI-HRMS (m/z) for $\text{C}_{14}\text{H}_{10}\text{ClN}_3\text{O}$: calcd. 271.0507; found 271.0508. IR (ATR, ν): 3259, 2925, 1651, 1579, 1541, 1450, 1413, 1341, 1272, 1103, 922, 906, 853, 781, 692, 630, 613, 576, 537, 472 cm^{-1} .

1-(8-(Trifluoromethyl)benzo[d][1,2,3]triazin-3(4*H*)-yl)ethanone (9)

Synthesis according to GP7. Reagents: resin **7m** (0.305 mmol, 900.0 mg), trifluoroacetic acid (0.641 mmol, 73.1 mg, 0.049 mL). Purification: ethyl acetate/cyclohexane (1:1). Yield: white solid (21.0 mg, 28%). R_f (cyclohexane/ethyl acetate, 1:1) = 0.71. ^1H NMR (300 MHz, CDCl_3 , ppm), δ = 7.78 (d, J = 7.7 Hz, 1 H), 7.58 (t, J = 7.7 Hz, 1 H), 7.36 (d, J = 7.7 Hz, 1 H), 4.89 (s, 2 H), 2.67 (s, 3 H). ^{13}C NMR (75 MHz, CDCl_3 , ppm), δ = 173.7, 132.8 (q, J = 5.0 Hz), 131.7, 130.0, 126.9, 126.8, 121.6 (q, J = 271.0 Hz), 120.1, 38.2, 21.5. ^{19}F NMR (376 MHz, CDCl_3 , ppm), δ = -58.4. EI (m/z , 70 eV, 190 $^\circ\text{C}$): 243 (25) $[\text{M}]^+$, 200 (100), 172 (48), 145 (50), 127 (25), 96 (25). HRMS ($\text{C}_{10}\text{H}_8\text{F}_3\text{N}_3\text{O}$) $[\text{M}]$: calc. 243.0619, found. 243.0618. IR (ATR, ν): 2920, 1691, 1597, 1497, 1478, 1447, 1379, 1324, 1300, 1199, 1119, 961, 919, 864, 807, 762, 730, 699, 634, 589, 550, 527, 442 cm^{-1} .

***N*-(2-Hydroxybenzyl)benzamide (10a)**

Synthesis according to GP7. Reagents: resin **7n** (0.610 mmol, 2.0 g), trifluoroacetic acid (1.281 mmol, 146.0 mg, 0.098 mL). Purification: ethyl acetate/cyclohexane (1:2). Yield: white solid (39.0 mg, 28%). R_f (cyclohexane/ethyl acetate, 2:1) = 0.49. ^1H NMR (300 MHz, CDCl_3 , ppm), δ = 9.55 (s, 1 H), 7.77 (d, J = 7.5 Hz, 2 H), 7.56-7.47 (m, 2 H), 7.40 (t, J = 7.5 Hz, 2

H), 7.27-7.20 (m, 2 H), 7.16 (dd, $J = 7.5, 1.5$ Hz, 1 H), 6.84 (td, $J = 7.4, 1.1$ Hz, 1 H), 4.57 (d, $J = 6.5$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3 , ppm), $\delta = 169.1, 156.1, 133.9, 131.3, 128.9, 128.2, 128.9, 128.2, 128.1, 126.8, 124.4, 119.1, 115.1, 39.0$. EI (m/z, 70 eV, 190 °C): 227 (40) $[\text{M}]^+$, 210 (30), 105 (100), 77 (48). HRMS ($\text{C}_{14}\text{H}_{13}\text{NO}_2$) $[\text{M}]$: calcd. 227.0941, found 227.0941. IR (ATR, ν): 3335.4, 2584.2, 1600.8, 1584.5, 1551.4, 1487.1, 1439.2, 1348.8, 1311.0, 1256.2, 1227.8, 1180.8, 1109.1, 1030.1, 937.9, 819.5, 797.5, 751.3, 728.0, 705.6, 687.2, 633.9, 575.4, 519.6 cm^{-1} .

N-(4-Chloro-2-hydroxybenzyl)benzamide (10b)

Procedure 1:

Synthesis according to GP7. Reagents: resin **7o** (0.263 mmol, 940.0 mg), trifluoroacetic acid (0.552 mmol, 63.0 mg, 0.042 mL). Purification: ethyl acetate/cyclohexane (1:2). Yield: white solid (23.0 mg, 33%).

Procedure 2:

Synthesis according to GP7. Reagents: resin **sup. Mat. -4** (0.298 mmol, 980.0 mg), trifluoroacetic acid (0.626 mmol, 71.3 mg, 0.018 mL). Yield: white solid (23.0 mg, 30%).

R_f (cyclohexane/ethyl acetate, 2:1) = 0.49. ^1H NMR (300 MHz, CDCl_3 , ppm), $\delta = 9.87$ (s, 1 H), 7.79 (d, $J = 7.4$ Hz, 2 H), 7.56 (t, $J = 7.4$ Hz, 1 H), 7.46 (t, $J = 7.4$ Hz, 2 H), 7.07 (d, $J = 8.1$ Hz, 1 H), 6.99 (d, $J = 2.0$ Hz, 1 H), 6.93 (s, 1 H), 6.82 (dd, $J = 8.1, 2.0$ Hz, 1 H), 4.53 (d, $J = 6.6$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3 , ppm), $\delta = 170.0, 157.1, 135.4, 132.7, 132.6, 131.7, 128.9$ (2 C), 127.2 (2 C), 122.7, 119.9, 118.5, 40.6. EI (m/z, 70 eV, 190 °C): 261/263 (43/15) $[\text{M}]^+$, 105 (100), 77 (45), 69 (20). HRMS ($\text{C}_{14}\text{H}_{12}\text{ClNO}_2$) $[\text{M}]$: calcd. 261.0551, found 261.0550. IR (ATR, ν): 3326.8, 2536.2, 1622.9, 1600.0, 1551.2, 1487.0, 1382.6, 1312.9, 1274.8, 1227.8, 1180.8, 1081.4, 1028.9, 1011.3, 965.4, 934.3, 909.5, 865.3, 830.1, 809.4, 790.4, 716.4, 691.7, 638.0, 596.8, 568.5, 544.1, 501.8, 473.5, 421.9 cm^{-1} .

N-(3-Fluorobenzyl)benzamide (11a)

Synthesis according to GP7. Reagents: resin **7p** (0.250 mmol, 900.0 mg), trifluoroacetic acid (0.525 mmol, 59.9 mg, 0.040 mL). Purification: ethyl acetate/cyclohexane (1:2). Yield: white solid (17.0 mg, 30%). R_f (cyclohexane/ethyl acetate, 2:1) = 0.54. ^1H NMR (300 MHz, CDCl_3 , ppm), $\delta = 7.73$ (d, $J = 7.0$ Hz, 2 H), 7.48-7.40 (m, 1 H), 7.36 (t, $J = 7.0$ Hz, 2 H), 7.30-7.15 (m, 1 H), 7.05 (d, $J = 7.6$ Hz, 1 H), 6.98 (d, $J = 9.5$ Hz, 1 H), 6.90 (m, 1 H), 6.46 (s, 1H, 1 H), 4.57 (d, $J = 5.8$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3 , ppm) δ 168.1,

166.1 (d, $J = 212.1$ Hz), 140.8, 134.1, 131.7, 130.3, 128.6 (2 C), 127.0 (2 C), 123.3, 114.6 (d, $J = 21.1$ Hz), 114.5 (d, $J = 21.8$ Hz), 43.5. EI (m/z, 70 eV): 229 (22), 219 (28), 212 (1). HRMS ($\text{C}_{14}\text{H}_{12}\text{FNO}$) $[\text{M}]$: calcd. 229.0903, found 229.0905. IR (ATR, ν): 3271.5, 2922.5, 1636.2, 1613.7, 1589.2, 1546.2, 1487.5, 1445.4, 1414.9, 1355.0, 1312.9, 1247.9, 1127.0, 1074.8, 1027.5, 993.8, 912.3, 869.0, 805.6, 777.6, 744.2, 695.5, 620.6, 525.6, 458.8, 438.4, 411.6 cm^{-1} .

***N*-(3-Chlorobenzyl)benzamide (11b)**

Synthesis according to GP7. Reagents: resin **7q** (0.240 mmol, 850.0 mg), trifluoroacetic acid (0.503 mmol, 57.3 mg, 0.038 mL). Purification: ethyl acetate/cyclohexane (1:2). Yield: white solid (20.0 mg, 34%). R_f (cyclohexane/ethyl acetate, 2:1) = 0.60. ^1H NMR (300 MHz, CDCl_3 , ppm), δ = 7.73 (d, J = 8.4 Hz, 2 H), 7.44 (t, J = 8.4 Hz, 1 H), 7.37 (t, J = 8.4 Hz, 2 H), 7.27–7.20 (m, 4 H), 4.56 (d, J = 5.8 Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3 , ppm), δ = 167.5, 140.4, 134.8, 134.2, 131.9, 130.2, 128.8 (2 C), 128.1 (2 C), 128.0, 127.1, 126.1, 43.6. EI (m/z, 70 eV, 190 °C): 245/247 (43/15) $[\text{M}]^+$, 105 (100), 77 (55). HRMS ($\text{C}_{14}\text{H}_{12}\text{ClNO}$) $[\text{M}]$: calcd. 245.0607, found 245.0607. IR (ATR, ν): 3284.7, 2920.9, 1636.6, 1596.7, 1543.0, 1474.0, 1414.8, 1352.1, 1312.4, 1255.5, 1194.7, 1094.1, 1076.2, 1026.3, 1312.4, 1255.5, 1194.7, 1094.1, 1076.2, 1026.3, 988.7, 882.4, 844.6, 805.2, 775.8, 694.4, 683.1, 614.9, 524.0, 452.4, 429.3, 415.8 cm^{-1} .

***N*-[7-(Trifluoromethyl)-1*H*-indazol-3-yl]-(2'-methyl-1,1'-biphenyl)-4-carboxamide (13)**

Synthesis according to GP7. Reagents: resin **12** (0.113 mmol, 500.0 mg), trifluoroacetic acid (0.237 mmol, 27.0 mg, 0.018 mL). Purification: ethyl acetate/cyclohexane (1:2). Yield: white solid (16.0 mg, 36%). R_f (cyclohexane/ethyl acetate, 2:1) = 0.59. ^1H NMR (400 MHz, DMSO-d_6 , ppm), δ = 13.41 (s, 1 H), 11.06 (s, 1 H), 8.18 (d, J = 8.3 Hz, 2 H), 8.09 (d, J = 7.2 Hz, 1 H), 7.79 (d, J = 7.2 Hz, 1 H), 7.54 (d, J = 8.3 Hz, 2 H), 7.37–7.25 (m, 5 H), 2.29 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6 , ppm), δ = 165.5, 144.9, 141.1, 140.3, 135.6 (q, J = 4.2 Hz), 134.7, 131.9, 130.5, 129.4, 129.1 (2 C), 128.0 (2 C), 127.8, 127.1, 126.1, 124.4 (q, J = 4.8 Hz), 124.0 (q, J = 271.2 Hz), 119.2, 118.8, 111.5 (q, J = 33.5 Hz), 20.1. ^{19}F NMR (376 MHz, CDCl_3 , ppm), δ = –57.9. EI (m/z, 70 eV, 190 °C): 395 (35) $[\text{M}]^+$, 195 (100), 165 (15), 152 (20). HRMS ($\text{C}_{22}\text{H}_{16}\text{F}_3\text{N}_3\text{O}$) $[\text{M}]$: calcd. 395.1242, found 395.1240. IR (ATR, ν): 3270.9, 1650.9, 1547.9, 1508.0, 1456.5, 1421.5, 1352.2, 1321.8, 1271.0, 1215.8, 1152.5, 1111.3, 1086.2, 1049.7, 1023.8, 993.5, 928.5, 905.3, 849.1, 825.8, 803.3, 788.6, 754.33, 726.3, 697.8, 651.7, 596.8, 446.7 cm^{-1} .

Spectra of cleaved products

Compound 8A

Compound 8B

Compound 8C

Compound 8D

Compound 8E

Compound 8F

Compound 8G

¹H NMR spectrum of compound 10a in CDCl₃. The x-axis represents the chemical shift in ppm, ranging from 0 to 15. The y-axis represents the intensity, ranging from -100 to 1300. The spectrum shows several peaks with corresponding integration values:

- Peak at ~12.5 ppm: Integration 0.86
- Peak at ~10.0 ppm: Integration 0.80
- Peak at ~8.1 ppm: Integration 1.00
- Peak at ~7.8 ppm: Integration 1.00
- Peak at ~7.5 ppm: Integration 6.54
- Peak at ~3.9 ppm: Integration 2.02
- Peak at ~2.9 ppm: Integration 9.00
- Peak at ~2.1 ppm: Integration 5.00

Compound 8I

Compound 8J

Compound 8K

Compound 8L

Compound 9

Compound 10a

Compound 10b

Compound 11a

Compound 11b

Compound 13