Supporting Information

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

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General experimental section

$^1$H 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. $^{13}$C 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 CDCl$_3$ (77.4 ppm), acetone[d$_6$] (30.6 ppm) or dimethylsulfoxide[d$_6$] (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 µm, 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:

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

Formula 1: Formula for the calculation of the molar mass of a modified resin. The \text{molar\ mass}_{\text{sub}} is the molecular mass of the fragment being substituted (e.g. Cl in case of Merrifield resin), while \text{molar\ mass}_{\text{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 BF$_3$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 Pd(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$_2$CO$_3$ (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-Isopropylpolystyrilmethylamine (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-Benzylpolystyrilmethylamine (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-polystyrilmethyl-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\(^{-1}\)): \(\nu = 3024, 2915, 1600, 1492, 1450, 1393, 1229, 1173, 1066, 1027, 754, 695, 538\). Anal. calcd. for C\(_{298}\)H\(_{298}\)Cl\(_2\)N\(_4\): 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\(^{-1}\)): \(\nu = 3024, 2917, 1600, 1492, 1450, 1390, 1227, 1027, 906, 754, 695, 533\). Anal. calcd. for C\(_{297}\)H\(_{297}\)Br\(_2\)N\(_4\): 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\(^{-1}\)): \(\nu = 3024, 2916, 1600, 1492, 1450, 1390, 1229, 1172, 1065, 1027, 905, 843, 748, 695, 535\). Anal. calcd. for C\(_{206}\)H\(_{207}\)ClN\(_4\): 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\(^{-1}\)): \(\nu = 3433, 3024, 2919, 1610, 1492, 1360, 1261, 1165, 1065, 1027, 817, 751, 695, 530, 458\). Anal. calcd. for C\(_{176}\)H\(_{178}\)N\(_4\): 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\(^{-1}\)): \(\nu = 3023, 2917, 1583, 1492, 1450, 1387, 1231, 1172, 1065, 1027, 904, 814, 752, 695, 535, 420\). Anal. calcd. for C\(_{176}\)H\(_{176}\)ClN\(_4\): 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$^{-1}$): $\nu = 3441, 3024, 2918, 1600, 1492, 1451, 1367, 1167, 1068, 1027, 904, 747, 695, 533$. Anal. calcd. for C$_{405}$H$_{405}$Br$_2$N$_4$: 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$^{-1}$): $\nu = 3423, 3024, 2921, 1600, 1492, 1450, 1363, 1170, 1066, 1026, 905, 747, 695, 532$. Anal. calcd. for C$_{241}$H$_{246}$ClN$_4$: 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$^{-1}$): $\nu = 3433, 3025, 2919, 1610, 1490, 1363, 1261, 1165, 1065, 1027, 817, 751, 695, 540, 450$. Anal. calcd. for C$_{217}$H$_{223}$N$_4$: 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$^{-1}$): $\nu = 3384, 3024, 2920, 1590, 1492, 1367, 1112, 1065, 994, 919, 746, 694, 666, 530$. Anal. calcd. for C$_{219}$H$_{224}$ClN$_4$: 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$^{-1}$): $\nu = 3433, 3024, 2919, 1600, 1492, 1450, 1363, 1261, 1165, 1065, 1027, 817, 751, 695, 530, 456$. Anal. calcd. for C$_{291}$H$_{296}$FN$_4$: 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\(^{-1}\))**: \(\nu = 3386, 3024, 2920, 1580, 1492, 1376, 1115, 1065, 994, 920, 750, 695, 665, 530.\) **Anal. calcd. for C\(_{264}\)H\(_{269}\)ClN\(_4\):** C 89.74, H 7.67, N 1.59; found C 80.03, H 7.44, N 0.92. Loading: 0.4091 mmol/g.

![Structure of 2-(3-Isopropyl-3-polystyrylmethyl-1-triazen-1-yl)-5-chlorobenzylamine](image)

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\(^{-1}\))**: \(\nu = 3301, 3032, 2912, 1585, 1480, 1328, 1191, 1048, 1019, 914, 753, 699, 528, 409.\) **Anal. calcd. for C\(_{217}\)H\(_{218}\)ClN\(_4\):** C 89.33, H 7.53, N 1.92; found C 87.79, H 7.28, N 1.62. Loading: 0.4248 mmol/g.

![Structure of 2-(3-Benzylpolystyrylmethyl-1-triazen-1-yl)-4-chlorobenzylamine](image)

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. **\(^{19}\)F Gel-NMR (376 MHz, CDCl\(_3\), ppm), \(\delta = -57.5.\)** **IR (cm\(^{-1}\))**: \(\nu = 3433, 3024, 2921, 1636, 1600, 1508, 1491, 1449, 1316, 1126, 1026, 753, 695, 528.\) **Anal. calcd. for C\(_{171}\)H\(_{172}\)F\(_3\)N\(_4\)O: C 87.17, H 7.36, N 2.38; found C 84.33, H 6.80, N 2.12. Loading: 0.3061 mmol/g.

![Structure of N-(2-(3-Isopropyl-3-polystyryl-1-triazen-1-yl)-3-(trifluoromethyl)benzyl)benzamide](image)

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. **\(^{19}\)F Gel-NMR (376 MHz, CDCl\(_3\), ppm), \(\delta = -57.7 (\text{CF3}), -111.8 (\text{C}_{\text{ar}}-\text{F}), -112.8 (\text{C}_{\text{ar}}-\text{F}).\)** **IR (cm\(^{-1}\))**: \(\nu = 3424, 3024, 2920, 1624, 1600, 1492, 1466, 1451, 1317, 1233, 1126, 1026, 1003, 906, 754, 695, 530.\) **Anal. calcd. for C\(_{214}\)H\(_{213}\)F\(_5\)N\(_4\)O: C 87.07, H 7.27, N 1.90; found C 73.88, H 6.62, N 1.23. Loading: 0.3044 mmol/g.

![Structure of 2,6-Difluoro-N-(2-(3-isopropyl-3-polystyryl-1-triazen-1-yl)-3-(trifluoromethyl)benzyl)benzamide](image)

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. **\(^{19}\)F Gel-NMR (376 MHz, CDCl\(_3\), ppm), \(\delta = -57.5.\)** **IR (cm\(^{-1}\))**: \(\nu = 3409, 3024, 2918, 1602, 1492, 1450, 1316, 1251, 1126, 1027, 839, 753, 695,
Anal. calcd. for C_{206}H_{206}F_{3}N_{4}O_{2}: C 87.46, H 7.41, N 1.98; found C 74.35, H 6.84, N 1.20.

Loading: 0.3130 mmol/g.

\( N-(2-(3-\text{Isopropyl}-3-\text{polystyryl}-1-\text{triazen-1-yl})-3-(\text{trifluoromethyl})\text{benzyl})-3-\text{methylbutyramide} \) (7d)

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

\(^{19}\text{F Gel-NMR} \) \((376 \text{ MHz, CDCl}_3, \text{ppm}), \delta = -57.6. \ \text{IR (cm}^{-1})\): \( \nu = 3448, 3024, 2921, 1643, 1600, 1492, 1450, 1366, 1316, 1126, 1027, 905, 753, 695, 531. \ \text{Anal. calcd. for C}_{208}H_{215}F_{3}N_{4}O: C 87.84, H 7.62, N 1.97; found C 79.53, H 7.18, N 1.25. \)

Loading: 0.3096 mmol/g.

\( N-(2-(3-\text{Isopropyl}-3-\text{polystyryl}-1-\text{triazen-1-yl})-3-(\text{trifluoromethyl})\text{benzyl})-3-\text{butyramide} (7e) \)

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

\text{IR (cm}^{-1})\): \( \nu = 3446, 3024, 2921, 1645, 1600, 1492, 1450, 1316, 1127, 1026, 905, 754, 695, 532. \ \text{Anal. calcd. for C}_{208}H_{211}F_{3}N_{4}O: C 87.81, H 7.59, N 2.00; found C 79.82, H 7.22, N 1.18. \)

Loading: 0.3277 mmol/g.

\( N-(2-(3-\text{Isopropyl}-3-\text{polystyryl}-1-\text{triazen-1-yl})-3-(\text{trifluoromethyl})\text{benzyl})\text{thiophene-2-carboxamide} (7f) \)

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

\(^{19}\text{F Gel-NMR} \) \((376 \text{ MHz, CDCl}_3, \text{ppm}), \delta = -57.6. \ \text{IR (cm}^{-1})\): \( \nu = 3420, 3024, 2921, 1648, 1600, 1488, 1450, 1368, 1320, 1127, 1026, 908, 754, 695, 532. \ \text{Anal. calcd. for C}_{209}H_{210}F_{3}N_{4}O_{S: C 87.07, H 7.34, N 1.94, S 1.11; found: C 83.80, H 6.87, N 1.75, S 1.02. \) \)

Loading: 0.2950 mmol/g.

\( N-(2-(3-\text{Isopropyl}-3-\text{polystyryl}-1-\text{triazen-1-yl})-3-(\text{trifluoromethyl})\text{benzyl})-3-\text{methyl-2-butenamide} (7g) \)

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

\(^{19}\text{F Gel-NMR} \) \((376 \text{ MHz, CDCl}_3, \text{ppm}), \delta = -57.7. \ \text{IR (cm}^{-1})\): \( \nu = 3425, 3024, 2920, 1646, 1600, 1492, 1450, 1366, 1316, 1126, 1027, 904, 753, 695, 533. \ \text{Anal. calcd. for C}_{209}H_{214}F_{3}N_{4}O: C 87.93, H 7.56, N 1.96; found C 74.42, H 7.11, N 1.54. \)

Loading: 0.2976 mmol/g.

\( N-(2-(3-\text{Isopropyl}-3-\text{polystyryl}-1-\text{triazen-1-yl})-3-(\text{trifluoromethyl})\text{benzyl})-2-\text{phenylacetamide} (7h) \)
According to GP4, 600.0 mg of starting material 4a have been converted to 622.0 mg of resin 7h in 71% yield.

\[ \text{\textsuperscript{19}F Gel-NMR (376 MHz, CDCl}_3, \delta = -57.7. \text{ IR (cm\textsuperscript{-1})}: \nu = 3459, 3059, 2920, 1600, 1492, 1450, 1316, 1126, 1028, 905, 754, 695, 533, 430. Anal. calcd. for C\textsubscript{210}H\textsubscript{212}F\textsubscript{3}N\textsubscript{4}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.}

\( \text{N-}(2-(3-\text{Isopropyl}-3-\text{polystyryl}-1\text{-triazen-1-yl})-3-(\text{trifluoromethyl})\text{benzyl})\text{isonicotinamide (7i)} \)

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

\[ \text{IR (cm\textsuperscript{-1})}: \nu = 3401, 3058, 3024, 2919, 1638, 1600, 1492, 1450, 1316, 1222, 1126, 1025, 906, 753, 695, 530. Anal. calcd. for C\textsubscript{206}H\textsubscript{207}F\textsubscript{3}N\textsubscript{5}O: C 87.56, H 7.38, N 2.48; found C 79.53, H 7.18, N 1.25. Loading: 0.3346 mmol/g. \]

\( \text{N-}(2-(3-\text{Isopropyl}-3-\text{polystyryl}-1\text{-triazen-1-yl})-3,5\text{-dichlorobenzyl})\text{benzamide (7j)} \)

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

\[ \text{IR (cm\textsuperscript{-1})}: \nu = 3417, 3024, 2917, 1634, 1600, 1492, 1450, 1269, 1175, 1067, 1026, 750, 695, 532, 400. Anal. calcd. for C\textsubscript{379}H\textsubscript{380}Cl\textsubscript{2}N\textsubscript{4}O: C 89.64, H 7.54, N 1.10; found C 77.60, H 6.75, N 0.91. Loading: 0.2227 mmol/g. \]

\( \text{N-}(2-(3-\text{Isopropyl}-3-\text{polystyryl}-1\text{-triazen-1-yl})-3,5\text{-dibromobenzyl})\text{benzamide (7k)} \)

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

\[ \text{IR (cm\textsuperscript{-1})}: \nu = 3417, 3023, 2920, 1636, 1600, 1491, 1450, 1269, 1175, 1067, 1026, 905, 750, 695, 533. \text{ Anal. calcd. for C\textsubscript{439}H\textsubscript{440}Br\textsubscript{2}N\textsubscript{4}O: C 88.65, H 7.46, N 0.94; found C 76.51, H 7.01, N 0.74. Loading: 0.2790 mmol/g.} \]

\( \text{N-}(2-(3-\text{Isopropyl}-3-\text{polystyryl}-1\text{-triazen-1-yl})-3\text{-chlorobenzyl})\text{benzamide (7l)} \)

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

\[ \text{IR (cm\textsuperscript{-1})}: \nu = 3433, 3058, 3024, 2920, 1651, 1600, 1512, 1492, 1450, 1366, 1269, 1175, 1067, 1026, 962, 905, 752, 695, 527, 404. \text{ Anal. calcd. for C\textsubscript{305}H\textsubscript{307}Cl\textsubscript{4}N\textsubscript{4}O: C 89.78, H 7.58, N 1.37; found: C 80.09, H 6.89, N 1.25. Loading: 0.2118 mmol/g.} \]
**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.

\[ ^{19}F \text{ Gel-NMR (376 MHz, CDCl}_3, \text{ ppm), } \delta = -57.5. \]

**IR (cm\(^{-1}\)):** \(\nu = 3424, 3024, 2920, 1647, 1600, 1492, 1450, 1367, 1317, 1126, 1026, 905, 753, 695, 532, 403. \)

**Anal. calcd. for C\(_{229}\)H\(_{233}\)F\(_3\)N\(_4\)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 C\(_{230}\)H\(_{233}\)N\(_4\)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 C\(_{236}\)H\(_{238}\)ClN\(_4\)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 C\(_{308}\)H\(_{310}\)F\(_2\)N\(_4\)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, 1448, 1388, 1258, 1170, 1068, 1027, 905, 752, 695, 530, 420. Anal. calcd. for C_{286}H_{288}ClIN_4O: C 89.62, H 1.46; found C 79.77, H 7.32, N 1.09.

Loading: 0.2818 mmol/g.

N-(2-(3-Benzylpolystyril-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 C_{222}H_{220}ClIN_4O: C 89.01, H 1.87; found C 86.92, H 7.02, N 1.68.

Loading: 0.3040 mmol/g.

4-Iodo-N-(2-(3-Isopropyl-3-polystyril-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 C_{206}H_{206}F_3IN_4O: 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-polystyril-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.

^{19}F 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 C_{206}H_{206}F_3IN_4O: 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)-1H-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%). Rf (cyclohexane/ethyl, 2:1) = 0.46. 1H NMR (400 MHz, DMSO-d6, 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); 13C NMR (100 MHz, DMSO-d6, 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). 19F NMR (376 MHz, CDCl3, ppm), δ = –60.8. EI (m/z, 70 eV, 190 °C): 305 (70) [M]+, 105 (100), 77 (20). HRMS (C15H10F3N3O) [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)-1H-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%). Rf (cyclohexane/ethyl acetate, 2:1) = 0.48. 1H NMR (400 MHz, DMSO-d6, 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). 13C NMR (100 MHz, DMSO-d6, 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). 19F NMR (376 MHz, CDCl3, ppm), δ = –62.0 (CF3), –112.7 (C arom-F). EI (m/z, 70 eV, 190 °C): 341 (15) [M]+, 141 (100), 113 (15). HRMS (C15H10F5N3O) [M]: calc. 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, 455.3 cm⁻¹.

**4-Methoxy-N-(7-(trifluoromethyl)-1H-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%). Rf (cyclohexane/ethyl acetate, 1:1) = 0.73. 1H NMR (400 MHz, DMSO-d6, 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), $\delta$ = 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), $\delta$ = –60.8. EI (m/z, 70 eV, 190 °C): 335 (40) [M]$^+$, 169 (15), 135 (100), 69 (25). HRMS (C$_{16}$H$_{12}$F$_3$N$_3$O$_2$) [M]: calcd. 335.0882, found 335.0881. IR (ATR, $\nu$): 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, 758.3, 745.4, 727.1, 628.7, 600.2, 520.0 cm$^{-1}$.

3-Methyl-N-(7-(trifluoromethyl)-1H-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. $^1$H NMR (400 MHz, DMSO-$d_6$, ppm), $\delta$ = 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), $\delta$ = 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), $\delta$ = –60.7. EI (m/z, 70 eV, 190 °C): 285 (20) [M]$^+$, 201 (100), 181 (15), 57 (15). HRMS (C$_{13}$H$_{14}$F$_3$N$_3$O) [M]: calcd. 285.1089, found 285.1089. IR (ATR, $\nu$): 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)-1H-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. $^1$H NMR (400 MHz, acetone-$d_6$, ppm), $\delta$ = 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). $^{13}$C NMR (100 MHz, acetone-$d_6$, ppm), $\delta$ = 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) [M]$^+$, 201 (100), 181 (15), 69 (12). HRMS (C$_{13}$H$_{12}$F$_3$N$_3$O) [M]: calcd. 271.0927; found 271.0927. IR (ATR, $\nu$): 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)-1H-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\textsubscript{f} (cyclohexane/ethyl acetate, 2:1) = 0.67. \textsuperscript{1}H NMR (400 MHz, acetone-d\textsubscript{6}, ppm), δ = 8.17 (d, J = 7.2 Hz, 1 H), 8.01 (dd, J = 4.5 Hz, 1 H), 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). \textsuperscript{13}C NMR (100 MHz, Acetone-d\textsubscript{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). \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}, ppm), δ = –60.8. EI (m/z, 70 eV, 190 °C): 311 (35) [M]+, 111 (100), 69 (15). HRMS (C\textsubscript{13}H\textsubscript{8}F\textsubscript{3}N\textsubscript{3}O) [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, 1150.7, 1087.1, 1054.1, 927.4, 887.6, 851.9, 804.8, 764.3, 751.8, 717.9, 695.1, 654.9, 596.8, 552.1 cm\textsuperscript{-1}.

**3-Methyl-N-(7-(trifluoromethyl)-1H-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\textsubscript{f} (cyclohexane/ethyl acetate, 2:1) = 0.53. \textsuperscript{1}H NMR (400 MHz, Acetone-d\textsubscript{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). \textsuperscript{13}C NMR (100 MHz, Acetone-d\textsubscript{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. \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}, ppm), δ = –60.9. EI (m/z, 70 eV, 190 °C): 283 (30) [M]+, 201 (45), 83 (100), 55 (22). HRMS (C\textsubscript{13}H\textsubscript{12}F\textsubscript{3}N\textsubscript{3}O) [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\textsuperscript{-1}.

**2-Phenyl-N-(7-(trifluoromethyl)-1H-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\textsubscript{f} (cyclohexane/ethyl acetate, 2:1) = 0.53. \textsuperscript{1}H NMR (400 MHz, Acetone-d\textsubscript{6}, ppm), δ = 12.32 (s, 1 H), 9.86 (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). \textsuperscript{13}C NMR (100 MHz, Acetone-d\textsubscript{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.
**19F NMR** (376 MHz, CDCl$_3$, ppm), $\delta = -60.9$. EI (m/z, 70 eV, 190 °C): 319 (60) [M]$^+$, 201 (100), 181 (12), 91 (70). HRMS (C$_{16}$H$_2$F$_3$N$_3$O) [M]: calced. 319.0927, found 319.0928. IR (ATR, $\nu$): 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)-1H-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. $^1$H 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, 1 H); $^{13}$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) [M]$^+$, 106 (100), 78 (60), 69 (18). HRMS (C$_{14}$H$_9$F$_3$N$_4$O) [M]: calcd. 306.0849, found 306.0848. IR (ATR, $\nu$): 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-1H-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. $^1$H 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), $\delta = 166.7, 140.1, 137.9, 133.2, 132.3, 128.6 (2 C), 127.6 (2 C), 126.8, 125.5, 120.7, 117.9, 116.4. EI (m/z, 70 eV, 190 °C): 305/307/308 (20/15/6) [M]$^+$, 105 (100), 77 (40), 69 (12). HRMS (C$_{14}$H$_9$Cl$_2$N$_3$O) [M]: calcd. 305.0117, found 305.0116. IR (ATR, $\nu$): 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-1H-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%).
(cyclohexane/ethyl acetate, 2:1) = 0.33. \(^1\)H NMR (300 MHz, Acetone-\(d_6\), ppm), \(\delta = 12.38\) (s, 1 H), 9.98 (s, 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 °C): 393/395/397 (7/13/3) [M]\(^+\), 201 (100), 181 (15), 57 (15). HRMS (C\(_{14}\)H\(_{10}\)Br\(_2\)N\(_3\)O) [M]: calcd. 392.9107, found 392.9105. IR (ATR, \(\nu\)):

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. \(^1\)H NMR (500 MHz, Acetone-\(d_6\), ppm), \(\delta = 12.24\) (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), \(\delta = 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 °C): 271/273 (27/9) [M]\(^+\), 131 (7), 105 (100). EI-HRMS (\(m/z\)) for C\(_{14}\)H\(_{10}\)ClN\(_3\)O: calcd. 271.0507; found 271.0508. IR (ATR, \(\nu\)):

3259, 2925, 1651, 1579, 1541, 1450, 1413, 1341, 1272, 1103, 922, 906, 853, 781, 692, 630, 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. \(^1\)H NMR (300 MHz, CDCl\(_3\), ppm), \(\delta = 7.78\) (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), \(\delta = 173.7, 132.8 (q, J = 5.0\) 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), \(\delta = -58.4\). EI (m/z, 70 eV, 190 °C): 243 (25) [M]\(^+\), 200 (100), 172 (48), 145 (50), 127 (25), 96 (25). HRMS (C\(_{10}\)H\(_{8}\)F\(_3\)N\(_3\)O) [M]: calcld. 243.0619, found 243.0618. IR (ATR, \(\nu\)):

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. \(^1\)H NMR (300 MHz, CDCl\(_3\), ppm), \(\delta = 9.55\) (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, 128.1, 126.8, 124.4, 119.1, 115.1, 39.0. EI (m/z, 70 eV, 190 °C): 227 (40) [M$^+$], 210 (30), 105 (100), 77 (48). HRMS (C$_{14}$H$_{13}$NO$_2$) [M]: calcd. 227.0941, found 227.0941. IR (ATR, $\nu$): 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, 0.042 mL). Yield: white solid (23.0 mg, 30%).

R$_f$ (cyclohexane/ethyl acetate, 2:1) = 0.49. $^1$H 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, 2 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) [M$^+$], 105 (100), 77 (45), 69 (20). HRMS (C$_{14}$H$_{12}$ClNO$_2$) [M]: calcd. 261.0551, found 261.0550. IR (ATR, $\nu$): 3271.5, 2922.5, 1636.2, 1613.7, 1589.2, 1546.2, 1487.5, 1445.4, 1414.9, 1355.0, 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 (0.626 mmol, 71.3 mg, 0.018 mL). Yield: white solid (23.0 mg, 30%).

R$_f$ (cyclohexane/ethyl acetate, 2:1) = 0.54. $^1$H 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) $\delta = 168.1$, 166.1 (d, $J = 21.2$ 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 (C$_{14}$H$_{12}$FNO) [M]: calcd. 229.0903, found 229.0905. IR (ATR, $\nu$): 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, CDCl₃, 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); 13C NMR (75 MHz, CDCl₃, 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) [M]+, 105 (100), 77 (55). HRMS (C₁₄H₁₂ClNO) [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, 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)-1H-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-d₆, 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); 13C NMR (100 MHz, DMSO-d₆, 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. 19F NMR (376 MHz, CDCl₃, ppm), δ = −57.9. EI (m/z, 70 eV, 190 °C): 395 (35) [M]+, 195 (100), 165 (15), 152 (20). HRMS (C₂₂H₁₆F₃N₃O) [M]: calcd. 395.1242, found 395.1240. IR (ATR, ν): 3270.9, 2920.9, 1636.6, 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
Compound 8J
Compound 8K
Compound 8L
Compound 9

[Graph showing a spectrum with peaks at specific chemical shifts and normalized intensity values.]
Compound 10a
Compound 10b
Compound 11a
Compound 11b
Compound 13