Supporting Information

**tert-Butyl nitrite mediated nitrogen transfer reactions: Synthesis of benzotriazoles and azides at room temperature**

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Supporting Information

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[1] General information:

All reactions were performed in round bottom flask under open air condition at room temperature (~27-29 °C). Solvents and chemicals were purchased from commercial sources and used without further purification. The reagent tert-butyl nitrite was purchased from Alfa Aesar, Thermo Fisher Scientific. Thin layer chromatography was performed using pre-coated plates contained from E. Merck (TLC silica gel 60 F254). TLC plates were visualized by exposure to ultraviolet light (UV) with 254 nm wavelength lamp, then, further analyzed in iodine (I₂) chamber. The column chromatography was performed on silica gel (60-120 mesh) using a mixture of ethyl acetate and hexane as an eluent. The NMR spectra were recorded on Bruker Avance 500 MHz NMR spectrometer using CDCl₃ & DMSO-d₆. Mass spectra (HRMS) were measured on water’s Quattro Micro V 4.1. The IR, ¹H NMR and ¹³C NMR of the products were compared with literature reports.

o-Phenylenediamine derivatives (1a-1m) were purchased from Alfa Aesar. N-sulfonyl/acyl o-Phenylenediamines (1n-1w) were synthesized through the literature procedure.¹ N-boc protected o-phenylenediamine (1x) was prepared using literature procedure.²

[2] Experimental procedures

2.1 Synthesis of TMS and TBS protected o-phenylenediamines

\[
\begin{align*}
\text{ benzaldehyde } & \quad \text{NaBH₄/MeOH} \quad \text{NaBH₄/MeOH} \quad \text{I₂/HMDS} \quad \text{CH₂Cl₂} \\
& \quad \text{OH} \quad \text{OH} \\
& \quad \text{OTMS} \\
& \uparrow \text{TBSCI} \text{Imidazole} \text{CH₂Cl₂} \\
& \quad \text{OTBS} \\
& \quad 1y \\
& \quad 1z
\end{align*}
\]
A.] Reduction of ketone: 2-Amino-4-benzoylaniline (10 mmol, 2.10 g) was stirred in methanol at room temperature and then cooled to 0 °C to which sodium borohydride (15 mmol, 567 mg) was added portion wise. Further the reaction was allowed to stir for 4 h at room temperature. Methanol was evaporated, diluted with water and extracted with ethyl acetate. Ethyl acetate layer was dried over sodium sulfate and evaporated to get the desired alcohol quantitatively.

B.] Synthesis of 1y: TMS protection was performed using literature procedure developed by B. Karimi and B. Golshani. The alcohol (2.33 mmol, 500 mg) and iodine (0.233 mmol, 30 mg) was stirred in CH₂Cl₂ to which hexamethyldisilazane (HMDS) (1.86 mmol, 300 mg) in 5 mL of CH₂Cl₂ was added dropwise within 5 minutes. This reaction was allowed to stir for 30 min at room temperature after which finely powered Na₂S₂O₃ (approx. 500 mg) was added, the mixture was allowed to stir for additional 30 minutes. Then, the reaction mixture was filtered, concentrated and subjected for silica gel (60-120 mesh) column chromatography purification (SiO₂: ethyl acetate/hexane) to obtain the corresponding protected diammine (1y). The title compound was obtained as yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (70:30), R_f = 0.40; Yield 88% (586 mg); 1H NMR (500 MHz, CDCl₃) δ = 7.44–7.39 (m, 2H), 7.38–7.33 (m, 2H), 7.30–7.25 (m, 1H), 6.76–6.72 (m, 1H), 6.69 (d, J = 1.9 Hz, 1H), 6.64 (d, J = 7.9 Hz, 1H), 5.72 (s, 1H), 3.28 (s, 4H), 0.16 (s, 9H). 13C NMR (125 MHz, CDCl₃) δ = 145.1, 136.8, 134.4, 133.6, 127.9, 126.9, 126.2, 118.5, 116.1, 115.0, 76.1, 0.09. HRMS: Calc. for C₉H₂₅N₂O₅Si [M+H]+: 287.1580, Obser.: 287.1571.

C.] Synthesis of 1z: TBS protection was performed using literature procedure described by Dahal et al. The alcohol (2.33 mmol, 500 mg) was stirred in CH₂Cl₂ to which tert-butyl dimethylsilyl chloride (TBSCI), (2.80 mmol, 350 mg) and Imidazole (2.30 mmol, 190 mg) was added simultaneously. This reaction was allowed to stir for 1 h at room temperature; the reaction mixture was diluted with brine solution and then extracted through ethyl acetate. The organic layer was dried over anhydrous sodium sulphate (Na₂SO₄), concentrated and subjected for silica gel (60-120 mesh) column chromatography purification (SiO₂: ethyl acetate/hexane) to obtain the corresponding protected diammine (1z). The title compound was obtained as a viscous brown liquid. The residue was purified by column chromatography in silica gel eluting
with hexane: EtOAc (70:30), R_{f} = 0.33; Yield 78% (597 mg); {^1}H NMR (500 MHz, CDCl_{3}) δ = 7.37 (dd, J = 4.1, 3.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.23–7.20 (m, 1H), 6.73–6.71 (m, 1H), 6.67 (d, J = 1.9 Hz, 1H), 6.62 (d, J = 7.9 Hz, 1H), 5.66 (s, 1H), 3.19 (s, 4H), 0.95 (s, 9H), 0.01 (d, J = 6.3 Hz, 6H). 
{^{13}}C NMR (125 MHz, CDCl_{3}) δ = 145.7, 137.4, 134.4, 133.4, 127.9, 126.5, 126.1, 118.3, 116.2, 114.9, 76.3, 25.8, 18.2, -4.8, -4.7. HRMS: Calc. for C_{19}H_{29}N_{2}Si [M+H]^+: 329.2049, Obsr.: 329.2040.

2.2 Synthesis of benzotriazoles:

2.2.1 Reactions using tert-butyl nitrite in acetonitrile:

The substituted ortho-phenylenediamine (1a-1z) (1 mmol) was stirred in acetonitrile (5 mL) at room temperature to which 2 equiv. of tert-butyl nitrite (TBN) was added. The progress of the reaction was monitored by TLC. After completion, acetonitrile was evaporated and then, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulphate (Na_{2}SO_{4}), concentrated and subjected for silica gel (60-120 mesh) column chromatography purification (SiO_{2}: ethyl acetate/hexane) to obtain the corresponding benzotriazole (2a-2z).

2.2.2 Reactions with sodium nitrite and acetic acid:

For these reactions, procedure was adopted from previous report described by Wang et al.\textsuperscript{5}: 1 mmol ortho-phenylenediamine (1x or 1y or 1z) was stirred in acetic acid (2 mL) and subsequently, aqueous solution of sodium nitrite (1M, 5 mL) was added and the mixture was stirred at 70 °C for 1 h.
2.2.3 One-pot procedure for the synthesis of benzotriazoles:

A.] Using tert-butyl nitrite in dichloromethane:

\[
\text{NH}_2 \text{NH}_2 \xrightarrow{TBN (3 equiv.)} \xrightarrow{\text{CH}_2\text{Cl}_2, 2 \text{h}, \text{RT}} \xrightarrow{\text{quantitative}} \xrightarrow{(\text{Boc})_2\text{O}} \xrightarrow{\text{or}} \xrightarrow{Tf_2\text{O}} \]

2x: \( R = \text{Boc}, 91\% \)
2ab: \( R = \text{Tf}, 75\% \)

The ortho-phenylenediamine (1a) (108 mg, 1 mmol) was stirred in dichloromethane (3 mL) at room temperature to which 3 equiv. of tert-butyl nitrite (TBN) was added. After 2 h, Boc (or) triflic anhydride (5 equiv.) was added to the same reaction mixture at room temperature. The reaction was allowed to stir for 3 h more. After then, dichloromethane was evaporated and subjected for silica gel (60-120 mesh) column chromatography purification (SiO\(_2\): ethyl acetate/hexane) to obtain the corresponding Boc and Tf protected benzotriazole (2x or 2ab).

B.] Reactions with sodium nitrite and acetic acid:

\[
\text{NH}_2 \text{NH}_2 \xrightarrow{\text{Aq. NaNO}_2} \xrightarrow{\text{Acetic Acid}} \xrightarrow{\text{quantitative}} \xrightarrow{(\text{Boc})_2\text{O}} \xrightarrow{\text{or}} \xrightarrow{Tf_2\text{O}}
\]

2x: \( R = \text{Boc}, 0\% \)
2ab: \( R = \text{Tf}, 0\% \)

For these reactions, procedure was adopted from previous report described by Wang et al.\(^5\) 1 mmol of ortho-phenylenediamine (1a) was stirred in acetic acid (2 mL) and subsequently, aqueous solution of sodium nitrite (1M, 5 mL) was added and the mixture was stirred at 70 °C for 1 h. After that, the reaction mixture was cooled to room temperature after which Boc or triflic anhydride (5 equiv.) was added. The reaction was monitored through thin layer chromatography (TLC). Benzotriazole was remained intact. The desired products were not observed.
2.3 Conversion of sulfonyl hydrazines into sulfonyl azides using tert-butyl nitrite.

![Chemical structure](image)

The substituted sulfonyl hydrazines (3a-3n) (1 mmol) was stirred in acetonitrile (5 mL) at room temperature to which 2 equiv. of tert-butyl nitrite (TBN) was added. The progress of the reaction was monitored by TLC. After completion, acetonitrile was evaporated and then, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulphate (Na₂SO₄), concentrated and subjected for silica gel (60-120 mesh) column chromatography purification (SiO₂: ethyl acetate/hexane) to obtain the desired products (4a-4n).

2.4 Conversion of benzene acyl hydrazines into acyl azide using tert-butyl nitrite.

![Chemical structure](image)

The substituted carbonyl hydrazines (5a-5g) (1 mmol) was stirred in acetonitrile (5 mL) at room temperature to which 3 equiv. of tert-butyl nitrite (TBN) was added. The progress of the reaction was monitored by TLC. After completion, acetonitrile was evaporated and then, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulphate (Na₂SO₄), concentrated and subjected for silica gel (60-120 mesh) column chromatography purification (SiO₂: ethyl acetate/hexane) to obtain the desired products (6a-6g).
2.5 Experimental procedure for the triazole formation with the sulfonyl azides:

The substituted sulfonyl hydrazines (benzene sulfonyl hydrazine and 4-methyl benzenesulfonyl hydrazine) (1 mmol) was stirred in acetonitrile (5 mL) at room temperature to which 2 equiv. of tert-butyl nitrite (TBN) was added. The progress of the reaction was monitored by TLC. Along with it, a mixture of CuSO$_4$. 5H$_2$O (0.03 mmol, 7 mg), sodium ascorbate (0.12 mmol, 23 mg) and DABCO (0.06 mmol, 0.006 mg) in H$_2$O (2 mL) was stirred vigorously in round bottom flask and added to the formed respective sulfonyl azide followed by acetic acid (0.06 mmol) and phenyl acetylene (1 mmol, 102 mg). After consumption of the starting material, acetonitrile was evaporated further, diluted with ethyl acetate (10 mL) and aqueous ammonium chloride solution (5 mL). The aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined organic layer were dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. The obtained crude product was subjected for silica gel (60-120 mesh) column chromatography purification (SiO$_2$: ethyl acetate/hexane) to obtain the desired product (7a and 7b).

2.6 Experimental procedure for the coupling of boronic acids with the sulfonyl azides:
The substituted sulfonyl hydrazines (benzene sulfonyl hydrazine and 4-methyl benzenesulfonyl hydrazine) (1 mmol) was stirred in acetonitrile (5 mL) at room temperature to which 2 equiv. of tert-butyl nitrite (TBN) was added. The progress of the reaction was monitored by TLC. After the formation of desired product, the substituted arylboronic acid (1.2 mmol) and CuCl (10 mol %) were dissolved in methanol (5 mL) and then added to the flask. The reaction mixture was stirred at room temperature in an open flask. After completion of the reaction, the solvent was evaporated and the obtained crude product was subjected for silica gel (60-120 mesh) column chromatography purification (SiO₂: ethyl acetate/hexane) to obtain the desired product (8a-8c).


[3.1] 1,2,3-Benzo[d]triazole (2a)

The title compound was obtained as a white solid. M.p. 97 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), Rf = 0.65; Yield 96% (114 mg); IR (neat): 1726, 1376, 1190, 750 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ = 13.60 (s, 1H), 7.99-7.90 (m, 2H), 7.40 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ = 138.8, 126.0, 114.9.

[3.2] 5-Methyl-1H-benzo[d][1,2,3]triazole (2b)

The title compound was obtained as a white solid. M.p. 135 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), Rf = 0.66; Yield 93% (123 mg); IR (neat): 2340, 1734, 1380, 1225, 1062 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ = 14.23 (s, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.62 (s, 1H), 7.19 (d, J = 8.4 Hz, 1H), 2.43 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ = 138.6, 138.0, 136.7, 127.8, 115.2, 112.9, 21.6.

[3.3] 4,5-Dimethyl-1H-benzo[d][1,2,3]triazole (2c)

The title compound was obtained as a pale yellow solid. M.p. 154 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), Rf = 0.63; Yield 97% (142 mg); IR (neat): 2344, 1734, 1380, 1220, 1062 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ = ...
5,6-Dimethyl-1H-benzo[d][1,2,3]triazole (2d) \(\delta = 7.50 \ (d, J = 31.6 \text{ Hz}, 1\text{H}), 7.16 \ (d, J = 8.3 \text{ Hz}, 1\text{H}), 2.57 \ (s, 3\text{H}), 2.30 \ (d, J = 44.5 \text{ Hz}, 3\text{H}). \) \(^{13}\text{C} \text{NMR (125 MHz, CDCl}_3 \text{ & DMSO-d}_6 \delta = 132.05, 127.59, 111.70, 18.29, 13.39. \)

[3.4] 5,6-Dimethyl-1H-benzo[d][1,2,3]triazole (2d)\(^8\)

The title compound was obtained as a brown solid. M.p. 156 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), \(R_f = 0.62; \) Yield 95% (140 mg); IR (neat): 2340, 1734, 1376, 1222, 1062 cm\(^{-1}\). \(^1\text{H} \text{NMR (500 MHz, DMSO-d}_6 \delta = 143.4, 136.9, 132.8, 131.8, 117.6, 109.9, 20.0. \)

[3.5] 4,6-Dimethyl-1H-benzo[d][1,2,3]triazole (2e)

The title compound was obtained as a brown solid. M.p. 158 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), \(R_f = 0.60; \) Yield 95% (140 mg); IR (neat): 2344, 1740, 1390, 1225, 1062 cm\(^{-1}\). \(^1\text{H} \text{NMR (500 MHz, DMSO-d}_6 \delta = 15.41 \ (s, 1\text{H}), 7.60 \ (d, J = 99.7 \text{ Hz}, 2\text{H}), 2.32 \ (s, 3\text{H}), 2.29 \ (s, 3\text{H}). \)\(^{13}\text{C}\ NMR (125 MHz, DMSO-d}_6 \delta = 143.4, 136.9, 132.8, 131.8, 117.6, 109.9, 20.0. \)

[3.6] 5-Bromo-1H-benzo[d][1,2,3]triazole (2f)\(^7\)

The title compound was obtained as a brown solid. M.p. 154 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), \(R_f = 0.67; \) Yield 94% (183 mg); IR (neat): 2334, 1730, 1380, 1225, 1062 cm\(^{-1}\). \(^1\text{H} \text{NMR (500 MHz, DMSO-d}_6 \delta = 15.90 \ (s, 1\text{H}), 8.15 \ (s, 1\text{H}), 7.86 \ (s, 1\text{H}), 7.50 \ (s, 1\text{H}). \)\(^{13}\text{C}\ NMR (125 MHz, DMSO-d}_6 \delta = 138.6, 130.7, 128.8, 128.4, 118.1. \)

[3.7] 5-Chloro-1H-benzo[d][1,2,3]triazole (2g)\(^6\)

The title compound was obtained as a white solid. M.p. 157 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), \(R_f = 0.65; \) Yield 97% (148 mg); IR (neat):
5-Fluoro-1H-benzo[d][1,2,3]triazole (2h)

δ = 138.1, 130.2, 125.9, 116.8, 114.1, 79.1.

The title compound was obtained as a pale yellow solid. M.p. 148 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), Rf = 0.66; Yield 95% (130 mg); IR (neat): 2336, 1732, 13076, 1220, 1062, 745 cm\(^{-1}\). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) δ = 15.89 (s, 1H), 8.01 (s, 2H), 7.45 (s, 1H). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)) δ = 138.1, 130.2, 125.9, 116.8, 114.1, 79.1.

5-Nitro-1H-benzo[d][1,2,3]triazole (2i)

The title compound was obtained as a yellow solid. M.p. 214 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), Rf = 0.43; Yield 97% (159 mg); IR (neat): 2340, 1740, 1374, 1225, 1062 cm\(^{-1}\). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) δ = 16.18 (s, 1H), 8.37 (s, 1H), 8.06 (d, J = 8.6 Hz, 1H), 7.68 (d, J = 8.6 Hz, 1H). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)) δ = 144.5, 140.4, 138.7, 120.9, 128.4, 116.5.

5,6-Dichloro-1H-benzo[d][1,2,3]triazole (2j)

The title compound was obtained as a brown solid. M.p. 267 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), Rf = 0.55; Yield 96% (178 mg); IR (neat): 2340, 1734, 1384, 1215, 1062 cm\(^{-1}\). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) δ = 16.03 (s, 1H), 8.28 (s, 2H). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)) δ = 138.4, 128.4, 116.5.
[3.11] (1H-Benzoo[d][1,2,3]triazol-6-yl)(phenyl) methanone (2k)

The title compound was obtained as a yellow solid. M.p. 115 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.60; Yield 94% (209 mg); IR (neat): 2347, 1730, 1390, 1225, 1060 cm\(^{-1}\). \(^1\)H NMR (500 MHz, DMSO-d\(_6\)) \(\delta = 16.08\) (s, 1H), 8.23 (s, 1H), 7.97 (d, \(J = 5.5\) Hz, 1H), 7.82 (d, \(J = 7.5\) Hz, 1H), 7.74 (d, \(J = 7.2\) Hz, 2H), 7.62 (t, \(J = 6.9\) Hz, 1H), 7.51 (t, \(J = 7.2\) Hz, 2H). \(^{13}\)C NMR (125 MHz, DMSO-d\(_6\)) \(\delta = 195.6, 137.6, 137.3, 134.0, 133.0, 130.1, 128.9, 127.1, 120.5, 114.0\). HRMS: Calc. for C\(_{13}\)H\(_{10}\)N\(_3\)O [M+H]\(^+\): 224.0824, Obsr.: 224.0810.

[3.12] 5-(Trifluoromethyl)-1H-benzo[d][1,2,3]triazole (2l)

The title compound was obtained as a brown solid. M.p. 130 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.65; Yield 93% (171 mg); IR (neat): 2340, 1730, 1378, 1222, 1062 cm\(^{-1}\). \(^1\)H NMR (500 MHz, DMSO-d\(_6\)) \(\delta = 16.15\) (s, 1H), 8.37 (s, 1H), 8.06 (d, \(J = 8.5\) Hz, 1H), 7.68 (d, \(J = 8.5\) Hz, 1H). \(^{13}\)C NMR (125 MHz, DMSO-d\(_6\)) \(\delta = 139.8, 138.4, 127.5, 125.9, 125.7, 125.4, 125.2, 123.2, 122.1, 121.1, 115.3, 114.6\). HRMS: Calc. for C\(_7\)H\(_5\)F\(_3\)N\(_3\) [M+H]\(^+\): 188.0436, Obsr.: 188.0430.

[3.13] 5-(Tert-butyl)-1H-benzo[d][1,2,3]triazole (2m)

The title compound was obtained as a pale yellow solid. M.p. 92 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.55; Yield 94% (165 mg); IR (neat): 2350, 1734, 1410, 1225, 1060 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 12.11\) (s, 1H), 7.89-7.87 (m, 2H), 7.51 (d, \(J = 8.7\) Hz, 1H), 1.36 (s, 9H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 150.0, 138.3, 124.9, 114.8, 109.6, 35.1, 31.3\).
[3.14] 1-(Phenylsulfonyl)-1H-benzo[d][1,2,3]triazole (2n)\textsuperscript{11}

\[
\begin{align*}
\text{O} & \quad \text{S} \\
\text{N} & \quad \text{N} \\
\text{2n}
\end{align*}
\]

The title compound was obtained as a white solid. M.p. 110 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), $R_f = 0.66$; Yield 96% (248 mg); IR (neat): 3128, 2950, 2209, 1620, 1389, 1182, 956, 893, 747 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) $\delta$ = 8.13 (dd, $J$ = 20.3, 7.3 Hz, 4H), 7.68 (dd, $J$ = 14.0, 6.9 Hz, 2H), 7.56 (t, $J$ = 7.0 Hz, 2H), 7.51 (t, $J$ = 7.3 Hz, 1H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) $\delta$ = 145.4, 137.1, 135.1, 131.6, 129.6, 127.9, 125.8, 120.6, 112.0.

[3.15] 1-Tosyl-1H-benzo[d][1,2,3]triazole (2o)\textsuperscript{11}

\[
\begin{align*}
\text{O} & \quad \text{S} \\
\text{N} & \quad \text{N} \\
\text{2o}
\end{align*}
\]

The title compound was obtained as a white solid. M.p. 132 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), $R_f = 0.66$; Yield 93% (241 mg); IR (neat): 3123, 2950, 2237, 1620, 1387, 1182, 946, 903, 737 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) $\delta$ = 8.13 (d, $J$ = 8.4 Hz, 1H), 8.10 (d, $J$ = 8.3 Hz, 1H), 8.02 (d, $J$ = 8.1 Hz, 2H), 7.68 (t, $J$ = 7.7 Hz, 1H), 7.50 (t, $J$ = 7.7 Hz, 1H), 7.34 (d, $J$ = 8.1 Hz, 2H), 2.42 (s, 3H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) $\delta$ = 146.7, 145.4, 134.0, 131.6, 130.2, 130.1, 128.0, 125.7, 120.5, 112.0, 21.7.

[3.16] 1-((4-Bromophenyl)sulfonyl)-1H-benzo[d][1,2,3]triazole (2p)

\[
\begin{align*}
\text{O} & \quad \text{S} \\
\text{N} & \quad \text{N} \\
\text{2p}
\end{align*}
\]

The title compound was obtained as a white solid. M.p. 148 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), $R_f = 0.62$; Yield 90% (302 mg); IR (neat): 3123, 2950, 2237, 1620, 1387, 1182, 946, 903, 737 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) $\delta$ = 8.09 (dd, $J$ = 8.3, 2.6 Hz, 2H), 7.97 (d, $J$ = 8.6 Hz, 2H), 7.68 (t, $J$ = 6.8 Hz, 3H), 7.50 (t, $J$ = 7.7 Hz, 1H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) $\delta$ = 145.4, 135.8, 133.0, 131.4, 130.8, 130.5, 129.2, 126.0, 120.7, 111.8. HRMS: Calc. for C\textsubscript{12}H\textsubscript{9}BrN\textsubscript{3}O\textsubscript{2}S [M+H]\textsuperscript{+}: 337.9599,
The title compound was obtained as a white solid. M.p. 180 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), \( R_f = 0.60 \); Yield 89% (259 mg); IR (neat): 3160, 2872, 2360, 1525, 1391, 1225, 941, 739 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 8.37 \) (dd, \( J = 23.1, 8.6 \) Hz, 4H), 8.12 (d, \( J = 8.3 \) Hz, 2H), 7.74 (t, \( J = 7.6 \) Hz, 1H), 7.55 (t, \( J = 7.6 \) Hz, 1H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \( \delta = 151.3, 145.4, 142.2, 131.4, 130.9, 129.3, 126.4, 124.8, 120.9, 111.7, \) HRMS: Calc. for C\(_{12}\)H\(_9\)N\(_4\)O\(_4\)S [M+H]\(^+\): 305.0345, Obsr.: 305.0334.

The title compound was obtained as a white solid. M.p. 102 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), \( R_f = 0.55 \); Yield 84% (275 mg); IR (neat): 3089, 2970, 2330, 1618, 1431, 1334, 1067, 970 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 8.25 \) (s, 1H), 8.19 (d, \( J = 7.8 \) Hz, 1H), 8.11 (dd, \( J = 6.5, 3.0 \) Hz, 2H), 7.70 (dd, \( J = 6.5, 2.9 \) Hz, 3H), 7.58 (t, \( J = 7.8 \) Hz, 1H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \( \delta = 144.3, 134.0, 131.1, 130.9, 130.5, 129.3, 127.6, 124.5, 123.1, 122.4, 114.0. \) HRMS: Calc. for C\(_{13}\)H\(_9\)F\(_3\)N\(_3\)O\(_2\)S [M+H]\(^+\): 328.0368, Obsr.: 328.0338.

The title compound was obtained as a white solid. M.p. 121 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), \( R_f = 0.64 \); Yield 85% (256 mg); IR (neat): 3130, 2852, 2320, 1575, 1391, 1080, 945, 770 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 8.10 \) (t, \( J = 7.3 \) Hz, 2H), 7.65 (t, \( J = 7.7 \) Hz, 1H), 7.48 (t, \( J = 7.7 \) Hz, 1H), 7.01 (s, 2H), 2.67 (s, 6H), 2.31 (s, 3H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \( \delta = 145.5, 144.7, 141.5, 132.4, 131.9, 131.4, 129.8,
125.4, 120.3, 112.2, 22.9, 21.0.

[3.20] (1H-Benzod[1,2,3]triazol-1-yl)(phenyl)methanone (2t)

The title compound was obtained as a white solid. M.p. 112 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), \( R_f = 0.66 \); Yield 95% (212 mg); IR (neat): 3164, 3050, 2940, 2345, 1730, 1060, 878 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 8.38 \) (d, \( J = 8.3 \) Hz, 1H), 8.21 (d, \( J = 8.0 \) Hz, 2H), 8.16 (d, \( J = 8.3 \) Hz, 1H), 7.73–7.66 (m, 2H), 7.60–7.51 (m, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta = 166.6, 145.6, 133.6, 132.2, 131.6, 131.4, 130.3, 128.3, 126.2, 120.1, 114.7. \) HRMS: Calc. for C\(_{13}\)H\(_9\)N\(_3\)O [M+H]\(^+\): 224.0824, Obsr.: 224.0802.

[3.21] (1H-Benzod[1,2,3]triazol-1-yl)(4-methoxyphenyl)methanone (2u)

The title compound was obtained as a white solid. M.p. 111 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), \( R_f = 0.66 \); Yield 92% (233 mg); IR (neat): 3164, 2919, 2334, 1709, 1605, 1440, 1361, 1226, 980, 748 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 8.39 \) (d, \( J = 8.3 \) Hz, 1H), 8.32 (d, \( J = 8.8 \) Hz, 2H), 8.18 (d, \( J = 8.2 \) Hz, 1H), 7.71 (t, \( J = 7.6 \) Hz, 1H), 7.55 (t, \( J = 7.6 \) Hz, 1H), 7.08 (d, \( J = 8.8 \) Hz, 2H), 3.95 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta = 165.6, 164.1, 145.6, 134.3, 132.5, 130.1, 126.0, 123.4, 120.0, 114.8, 113.8, 55.5.

[3.22] (1H-Benzod[1,2,3]triazol-1-yl)(4-nitrophenyl)methanone (2v)

The title compound was obtained as a white solid. M.p. 193 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), \( R_f = 0.66 \); Yield 90% (241 mg); IR (neat): 3281, 2899, 2358, 1702, 1514, 1342, 1267, 1097, 773, 741 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 8.43 \) (d, \( J = 11.6 \) Hz, 5H), 8.23 (d, \( J = 7.8 \) Hz, 1H), 7.80 (d, \( J = 7.0 \) Hz, 1H), 7.64 (d, \( J = 7.2 \) Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta = 164.9, 150.4, 145.8, 136.8, 132.6, 131.9, 131.0, 130.3, 128.3, 128.2, 126.2, 120.1, 114.7, 113.8, 55.5.

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[3.23] (1H-Benzod[1,2,3]triazol-1-yl)(2-fluorophenyl)methanone (2w)

The title compound was obtained as a white solid. M.p. 115 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), Rf = 0.58; Yield 88% (212 mg); IR (neat): 3164, 3079, 2919, 2340, 1709, 1605, 1449, 1361, 1219, 940, 728 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ = 8.41 (d, J = 8.2 Hz, 1H), 8.18 (d, J = 8.3 Hz, 1H), 7.81 (t, J = 7.1 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.67 (dd, J = 13.4, 7.5 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 18.3 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ = 164.0, 159.2, 146.0, 134.4, 131.3, 131.1, 130.4, 126.4, 124.1, 120.1, 116.4, 116.2, 114.2. HRMS: Calc. for C₁₃H₁₃FN₃O [M+H]⁺: 242.0730, Obser.: 242.0694.

[3.24] tert-Butyl 1H-benzo[d][1,2,3]triazole-1-carboxylate (2x)

The title compound was obtained as a yellow solid. M.p. 62 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), Rf = 0.58; Yield 95% (208 mg); IR (neat): 3160, 3050, 2943, 2335, 1730, 1220, 1070, 840 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ = 8.07 (d, J = 8.3 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.61–7.55 (m, 1H), 7.46–7.40 (m, 1H), 1.73 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ = 147.1, 145.7, 131.5, 129.7, 125.3, 120.1, 113.4, 86.8, 27.9.

[3.25] 6-(Phenyl((trimethylsilyl)oxy)methyl)-1H-benzo[d][1,2,3]triazole (2y)

The title compound was obtained as colorless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), Rf = 0.38; Yield 90% (267 mg); ¹H NMR (500 MHz, CDCl₃) δ = 7.97 (s, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.41–7.25 (m, 6H), 5.94 (s, 1H), 0.11 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ = 144.1, 143.7, 128.3, 127.4, 126.6, 125.4, 76.3, 0.09. HRMS: Calc. for C₁₆H₂₀N₃OSi
[3.26] 6-(((tert-Butyldimethylsilyloxy)(phenyl)methyl)-1H-benzo[d][1,2,3]triazole (2z)

The title compound was obtained as yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), Rf = 0.40; Yield 93% (316 mg); 1H NMR (500 MHz, CDCl3) δ = 8.01 (s, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.39 (dd, J = 13.3, 8.0 Hz, 3H), 7.29 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 5.92 (s, 1H), 0.92 (s, 9H), -0.01 (d, J = 1.0 Hz, 6H). 13C NMR (125 MHz, CDCl3) δ = 144.5, 144.0, 139.2, 128.3, 127.2, 126.3, 125.2, 115.1, 76.5, 25.7, 18.2, -4.8 (d, J = 1.8 Hz). HRMS: Calc. for C15H26N3OSi [M+H]+: 340.1845, Obsr.: 340.1840.

[3.27] (1H-Benzod[1,2,3]triazol-6-yl)(phenyl)methanol (2aa)

The title compound was obtained as a brown liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), Rf = 0.58; Yield 69% (155 mg); IR (neat): 3140, 3040, 2860, 2400, 2347, 1630, 1390, 1225, 1060 cm⁻¹. 1H NMR (500 MHz, DMSO-d6) δ = 15.66 (s, 1H), 8.32–7.47 (m, 3H), 7.44 (d, J = 7.4 Hz, 2H), 7.31 (dd, J = 10.6, 4.7 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 6.13 (s, 1H), 5.92 (d, J = 2.8 Hz, 1H). 13C NMR (125 MHz, DMSO-d6) δ = 145.3, 143.5, 133.0, 128.8, 128.2, 126.9, 126.4, 123.0, 118.3, 115.3, 110.6, 107.4, 79.2, 74.1. HRMS: Calc. for C13H12N3O [M+H]+: 226.0980, Obsr.: 226.0978.

[3.28] 1-((Trifluoromethyl)sulfonyl)-1H-benzo[d][1,2,3]triazole (2ab)

The title compound was obtained as a yellow solid. M.p. 62 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), Rf = 0.62; Yield 75% (188 mg); IR (neat): 3080, 2968, 2332, 1618, 1401, 1334, 1070, 960 cm⁻¹. 1H NMR (500 MHz, CDCl3) δ = 8.23 (dt, J = 8.3, 0.8 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.80–7.77 (m, 1H), 7.65–7.62 (m, 1H). 13C NMR (125 MHz, CDCl3) δ = 145.4, 131.9, 127.2, 121.4, 120.4, 117.8, 111.7. 19F NMR (471 MHz, CDCl3) δ = -74.6.

[3.29] Benzenesulfonyl azide (4a)

The title compound was obtained as white solid. M.p. 153-155 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), RF = 0.59; Yield: 95% (173 mg); IR (neat): 3068, 2128, 1574, 1475, 1298, 1170, 1068, 1024, 1001 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ = 7.93 (d, J = 8.0 Hz, 2H), 7.71 (t, J = 7.3 Hz, 1H), 7.59 (t, J = 7.1 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ = 138.2, 134.7, 129.6, 127.3.

[3.30] 4-Methoxy Benzenesulfonyl azide (4b)

The title compound was obtained as pale yellow solid. M.p. 55 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), RF = 0.60; Yield: 97% (206 mg); IR (neat): 2949, 2832, 2129, 1577, 1497, 1442, 1369, 1351, 1319, 1272, 1088, 1021 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ = 7.91 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 3.93 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ = 164.5, 129.8, 129.7, 114.7, 55.8.

[3.31] 4-Methyl Benzenesulfonyl azide (4c)

The title compound was obtained as white solid. M.p. 22 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), RF = 0.55; Yield: 94% (185 mg); IR (neat): 2943, 2829, 2123, 1565, 1489, 1349, 1309, 1261, 1078, 1019 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ = 7.79 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ = 146.1, 135.3, 130.2, 127.4, 21.6.
[3.32] 4-(Tert-butyl)benzenesulfonyl azide (4d)

The title compound was obtained as a pale yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), RF = 0.52; Yield 82% (196 mg); IR (neat): 3060, 2900, 2869, 2123, 1593, 1404, 1365, 1297, 1110, 1079, 1010 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ = 7.90 (d, J = 8.7 Hz, 2H), 7.64 (d, J = 8.7 Hz, 2H), 1.39 (s, 4H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) δ = 159.0, 135.4, 127.3, 126.6, 30.9.

[3.33] 4-Bromobenzenesulfonyl azide (4e)

The title compound was obtained as white solid. M.p. 53-53.5 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), RF = 0.52; Yield 92% (239 mg); IR (neat): 2832, 2821, 2120, 1562, 1480, 1355, 1342, 1300, 1069, 1011 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ = 7.84 (d, J = 8.7 Hz, 2H), 7.78 (d, J = 8.7 Hz, 2H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) δ = 137.3, 133.0, 130.2, 128.8.

[3.34] 4-Cyano Benzenesulfonyl azide (4f)

The title compound was obtained as a white solid. M.p. 82 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), RF = 0.54; Yield 85% (177 mg); IR (neat): 2968, 2832, 2122, 1565, 1489, 1329, 1262, 1078, 1001 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ = 8.10 (d, J = 8.3 Hz, 2H), 7.95 (d, J = 8.3 Hz, 2H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) δ = 142.1, 133.4, 128.0, 118.4, 116.6.

[3.35] 4-Nitro Benzenesulfonyl azide (4g)

The title compound was obtained as a white solid. M.p. 100-101 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), RF = 0.55; Yield 90% (205 mg); IR (neat): 3100, 2132, 1531, 1463, 1398, 1372, 1343, 1307, 1172, 1068, 1011 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ = 8.49 (d, J = 9.2 Hz, 2H), 8.19 (d, J = 9.2 Hz, 2H). (125 MHz, CDCl\(_3\)) δ = 151.2, 143.7, 128.8, 124.9.
3-(Trifluoromethyl)benzenesulfonyl azide (4h)

The title compound was obtained as white solid. M.p. 30 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.56; Yield 89% (223 mg); IR (neat): 3100, 2850, 2129, 1531, 1463, 1398, 1362, 1323, 1307, 1172, 1068, 745 cm^{-1}. ^{1}H NMR (500 MHz, CDCl_3) δ = 8.24 (s, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.82 (t, J = 7.9 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ = 139.6, 132.9, 132.6, 132.3, 132.1, 131.4, 131.4, 131.3, 131.3, 130.6, 130.6, 126.0, 124.6, 124.5, 124.5, 124.5, 123.8, 121.7, 119.5. HRMS: Calc. for C_6H_4F_3N_3O_4S [M+H]^+: 229.0032, Obser.:228.0953.

2,4,6-Trimethylbenzenesulfonyl azide (4i)

The title compound was obtained as white solid. M.p. 30 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.56; Yield 89% (223 mg); IR (neat): 3100, 2850, 2129, 1531, 1463, 1398, 1362, 1323, 1307, 1172, 1068, 745 cm^{-1}. ^{1}H NMR (500 MHz, CDCl_3) δ = 8.24 (s, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.82 (t, J = 7.9 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ = 139.6, 132.9, 132.6, 132.3, 132.1, 131.4, 131.4, 131.3, 131.3, 130.6, 130.6, 126.0, 124.6, 124.5, 124.5, 124.5, 123.8, 121.7, 119.5. HRMS: Calc. for C_7H_4F_3N_3O_2S [M+H]^+: 252.0055, Obser.:252.0014.

2,4,6-Triisopropylbenzenesulfonyl azide (4j)

The title compound was obtained as yellow solid. M.p. 79-80 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.60; Yield 88% (198 mg); IR (neat): 2960, 2922, 1451, 1352, 1117, 1101, 1156, 1042, 1031 cm^{-1}. ^{1}H NMR (500 MHz, CDCl_3) δ = 7.04 (s, 2H), 4.08 (m, 2H), 3.03–2.68 (s, 6H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ = 144.5, 139.9, 133.1, 132.1, 22.7, 21.0.

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[3.39] Naphthalene-2-sulfonyl azide (4k)\textsuperscript{16}

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\text{\includegraphics[width=0.2\textwidth]{4k.png}}
\]

The title compound was obtained as yellow solid. M.p. 53 °C. The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), \( R_f = 0.60 \); Yield 82% (191 mg); IR (neat) 3053, 2132, 1589, 1450, 1368, 1232, 1160, 1130, 1071, 1011 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\))  \( \delta = 8.59 \) (d, \( J = 8.6 \) Hz, 1H), 8.37 (d, \( J = 7.3 \) Hz, 1H), 8.21 (d, \( J = 8.2 \) Hz, 1H), 8.01 (d, \( J = 8.2 \) Hz, 1H), 7.77 (t, \( J = 7.5 \) Hz, 1H), 7.69 (t, \( J = 7.5 \) Hz, 1H), 7.62 (t, \( J = 7.8 \) Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\))  \( \delta = 136.2, 134.2, 133.4, 130.0, 129.0, 128.0, 127.5, 124.3, 123.9. \)

[3.40] 1-Methyl-1H-pyrazole-4-sulfonil azide (4l)\textsuperscript{16}

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\text{\includegraphics[width=0.2\textwidth]{4l.png}}
\]

The title compound was obtained as pale yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), \( R_f = 0.65 \); Yield 89% (166 mg); IR (neat): 3053, 2132, 1589, 1450, 1368, 1262, 1140, 1071, 1011 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\))  \( \delta = 7.99 \) (s, 1H), 7.92 (s, 1H), 4.02 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\))  \( \delta = 139.0, 132.7, 120.3, 39.9. \)

[3.41] Butane-1-sulfonyl azide (4m)\textsuperscript{18}

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\text{\includegraphics[width=0.2\textwidth]{4m.png}}
\]

The title compound was obtained as pale yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), \( R_f = 0.60 \); Yield 81% (132 mg); \(^1\)H NMR (500 MHz, CDCl\(_3\))  \( \delta = 3.32–3.29 \) (m, 2H), 1.90–1.87 (m, 2H), 1.49 (d, \( J = 7.3 \) Hz, 2H), 0.96 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\))  \( \delta = 55.60, 25.17, 21.15, 13.30. \)
[3.42] Octane-1-sulfonyl azide (4n)\textsuperscript{19}

The title compound was obtained as a yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), \( R_f = 0.62 \); Yield 82\% (180 mg); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 3.30-3.27 \) (m, 2H), 1.88 (s, 2H), 1.43 (s, 2H), 1.27 (d, \( J = 12.1 \) Hz, 8H), 0.86 (s, 3H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \( \delta = 55.84, 31.54, 28.76, 27.82, 23.24, 22.46, 13.90 \).

[3.43] Benzoyl azide (6a)\textsuperscript{20}

The title compound was obtained as a white solid. M.p. 32 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), \( R_f = 0.67 \); Yield 87\% (128 mg); IR (neat): 3053, 2867, 2173, 2168, 2127, 1695, 1682, 1599, and 1453 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 8.03 \) (d, \( J = 7.3 \) Hz, 2H), 7.62 (t, \( J = 7.4 \) Hz, 1H), 7.46 (t, \( J = 7.8 \) Hz, 2H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \( \delta = 172.5, 134.3, 130.6, 129.4, 128.6 \).

[3.44] 4-Methoxybenzoyl azide (6b)\textsuperscript{20}

The title compound was obtained as a white solid. M.p. 69-70 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), \( R_f = 0.66 \); Yield 80\% (141 mg); IR (neat): 3011, 2983, 2179, 2143, 1677, 1584, 1500 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 7.98 \) (d, \( J = 8.4 \) Hz, 2H), 6.92 (d, \( J = 8.5 \) Hz, 2H), 3.87 (s, 3H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \( \delta = 171.8, 164.8, 131.9, 125.7, 123.4, 114.9, 114.1, 55.7 \).

[3.45] 4-Nitrobenzoyl azide (6c)\textsuperscript{20}

The title compound was obtained as a white solid. M.p. 71-72 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), \( R_f = 0.66 \); Yield 84\% (161 mg); IR (neat): 3108, 3091, 2181, 2180, 2123, 1746, 1678, 1687, 1545 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 8.30 \) (d, \( J = 8.8 \) Hz, 2H), 8.20 (d, \( J = 8.8 \) Hz, 2H).
13C NMR (125 MHz, CDCl₃) δ = 170.8, 151.2, 135.6, 130.5, 123.7.

[3.46] Benzyl carbonazidate (6d)

The title compound was obtained as a white solid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), Rf = 0.66; Yield 81% (143 mg); IR (neat): 3100, 2970, 2181, 2170, 2123, 1746, 1678, 1587, 1080 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ = 7.40 (s, 5H), 5.25 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ = 157.4, 134.3, 128.8, 128.7, 128.5, 70.0. HRMS: Calc. for C₁₀H₇N₃O₂ [M+H]^+: 178.0617 Obsr.: 178.0568.

[3.47] Isonicotinoyl azide (6e)

The title compound was obtained as an orange solid. M.p. 45-46 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), Rf = 0.66; Yield 85% (125 mg); IR (neat): 3100, 2970, 2181, 2170, 2123, 1746, 1678, 1587, 1080 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ = 8.77 (d, J = 5.7 Hz, 1H), 7.78 (d, J = 5.4 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ = 171.4, 150.7, 137.3, 122.1. HRMS: Calc. for C₈H₄N₃O [M+H]^+: 149.0465 Obsr.: 149.0398.

[3.48] Pentanoyl azide (6f)

The title compound was obtained as yellow oil. Pentanoyl azide was found very unstable, hence could not be isolated. However, a complete conversion of pentanoyl hydrazide into pentanoyl azide was observed in TLC.

[3.49] Hexanoyl azide (6g)

The title compound was obtained as yellow oil. Hexanoyl azide was found very unstable, hence could not be isolated. However, a complete conversion of hexanoyl hydrazide into hexanoyl azide was observed in TLC.

[3.50] 4-Phenyl-1-(phenylsulfonyl)-1H-1,2,3-triazole (7a)

The title compound was obtained as a white solid. M.p. 109 °C. The
residue was purified by column chromatography in silica gel eluting
with hexane: EtOAc (85:15), $R_f = 0.43$; Yield 81% (230 mg); IR (neat):
2955, 1367, 1173, 1092. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 7.3$
Hz, 2H), 7.59 (s, 1H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 2H),
7.24 (t, $J = 7.9$ Hz, 2H), 7.16-7.09 (m, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$
138.8, 136.4, 132.9, 129.2, 128.9, 127.1, 121.4.

[3.51] 4-Phenyl-1-tosyl-1H-1,2,3-triazole (7b)$^{23}$

The title compound was obtained as a white solid. M.p. 89 °C. The
residue was purified by column chromatography in silica gel eluting
with hexane: EtOAc (85:15), $R_f = 0.42$; Yield 83% (248 mg); IR (neat):
3037, 1336, 1170, 1105. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.74 (s, 1H),
7.70 (d, $J = 8.3$ Hz, 2H), 7.33-7.28 (m, 2H), 7.22 (d, $J = 8.0$ Hz, 2H),
7.02-6.98 (m, 2H), 2.36 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 144.1,

[3.52] N-Phenylbenzenesulfonamide (8a)$^{24}$

The title compound was obtained as a white solid. M.p. 104 °C. The
residue was purified by column chromatography in silica gel eluting
with hexane: EtOAc (80:20), $R_f = 0.38$; Yield 85% (198 mg); IR (neat):
3186, 1355, 1167. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.74 (s, 1H), 7.70 (d, $J$
= 8.3 Hz, 2H), 7.33-7.28 (m, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.02-6.98 (m,
2H), 2.36 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 144.1, 135.7, 135.3,

[3.53] 4-Methoxy-N-(p-tolyl)benzenesulfonamide (8b)$^{25}$

The title compound was obtained as a white solid. M.p. °C. The
residue was purified by column chromatography in silica gel eluting
with hexane: EtOAc (85:15), $R_f = 0.43$; Yield 80% (221 mg); IR (neat):
3189, 1346, 1169. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.74 (s, 1H), 7.70 (d, $J$
= 8.3 Hz, 2H), 7.33-7.28 (m, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.02-6.98
(m, 2H), 2.36 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 144.1, 135.7, 135.3,

[3.54] 4-Bromo-N-(p-tolyl)benzenesulfonamide (8c)\(^\text{25}\)

The title compound was obtained as a white solid. M.p. 147.5 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), R\(_f\) = 0.66; Yield 84% (272 mg); IR (neat): 3184, 1344, 1165. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.74 (s, 1H), 7.70 (d, \(J = 8.3\) Hz, 2H), 7.33-7.28 (m, 2H), 7.22 (d, \(J = 8.0\) Hz, 2H), 7.02–6.98 (m, 2H), 2.36 (s, 3H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 144.1, 135.7, 135.3, 132.2, 129.7, 127.1, 122.7, 118.2, 21.4.

4) References

[5] $^1$H and $^{13}$C NMR spectra of product:

*Figure 5.1* $^1$H and $^{13}$C NMR of product 1y in CDCl$_3$. 
Figure 5.2 $^1$H and $^{13}$C NMR of product 1z in CDCl$_3$. 
Figure 5.3 $^1$H and $^{13}$C NMR of product 2a in CDCl$_3$. 
Figure 5.4 $^1$H and $^{13}$C NMR of product 2b in CDCl$_3$. 

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Figure 5.5 $^1$H and $^{13}$C NMR of product 2c in CDCl$_3$ and DMSO-d$_6$. 
Figure 5.6 $^1$H and $^{13}$C NMR of product 2d in DMSO-$d_6$. 
Figure 5.7 $^1$H and $^{13}$C NMR of product 2e in CDCl$_3$ and DMSO-d$_6$. 
Figure 5.8 $^1$H and $^{13}$C NMR of product 2f in DMSO-$d_6$. 
Figure 5.9 $^1$H and $^{13}$C NMR of product 2g in DMSO-d$_6$. 
Figure 5.10 $^1$H and $^{13}$C NMR of product 2h in DMSO-d$_6$. 
Figure 5.11 $^1$H and $^{13}$C NMR of product 2i in DMSO-d$_6$. 
Figure 5.12 $^1$H and $^{13}$C NMR of product 2j in DMSO-d$_6$. 
Figure 5.13 $^1$H and $^{13}$C NMR of product 2k in DMSO-$d_6$. 
Figure 5.14 $^1$H and $^{13}$C NMR of product 2I in DMSO-d$_6$. 
Figure 5.15 $^1$H and $^{13}$C NMR of product 2m in CDCl₃.
Figure 5.16: $^1$H and $^{13}$C NMR of product 2n in CDCl$_3$. 
Figure 5.17 $^1$H and $^{13}$C NMR of product $2o$ in CDCl$_3$. 
Figure 5.18 $^1$H and $^{13}$C NMR of product 2p in CDCl$_3$. 
Figure 5.19 $^1$H and $^{13}$C NMR of product 2q in CDCl$_3$. 
Figure 5.20 $^1$H and $^{13}$C NMR of product 2r in CDCl$_3$. 
Figure 5.21 $^1$H and $^{13}$C NMR of product 2s in CDCl$_3$. 
Figure 5.22 $^1$H and $^{13}$C NMR of product 2t in CDCl$_3$. 
Figure 5.23 $^1$H and $^{13}$C NMR of product 2u in CDCl$_3$. 
Figure 5.24 $^1$H and $^{13}$C NMR of product 2v in CDCl$_3$. 
Figure 5.25 $^1$H and $^{13}$C NMR of product 2w in CDCl$_3$. 
Figure 5.26 $^1$H and $^{13}$C NMR of product 2x in CDCl$_3$. 
Figure 5.27 $^1$H and $^{13}$C NMR of product 2y in CDCl$_3$. 
Figure 5.28 $^1$H and $^{13}$C NMR of product 2z in CDCl$_3$. 
Figure 5.29 $^1$H and $^{13}$C NMR of product 2aa in DMSO-d$_6$. 
Figure 5.30 $^1$H and $^{13}$C NMR of product 2ab in CDCl$_3$. 
Figure 5.31 $^{19}$F NMR of product 2ab in CDCl$_3$.
Figure 5.32 $^1$H and $^{13}$C NMR of product 4a in CDCl$_3$. 
Figure 5.33 $^1$H and $^{13}$C NMR of product 4b in CDCl$_3$. 
Figure 5.34 $^1$H and $^{13}$C NMR of product 4c in CDCl$_3$. 
Figure 5.35 $^1$H and $^{13}$C NMR of product 4d in CDCl$_3$. 
Figure 5.36 $^1$H and $^{13}$C NMR of product 4e in CDCl$_3$. 
Figure 5.37 $^1$H and $^{13}$C NMR of product 4f in CDCl$_3$. 
Figure 5.38 $^1$H and $^{13}$C NMR of product 4g in CDCl$_3$. 
Figure 5.39 $^1$H and $^{13}$C NMR of product 4h in CDCl$_3$. 
Figure 5.40 $^1$H and $^{13}$C NMR of product 4i in CDCl$_3$. 
Figure 5.41 $^1$H and $^{13}$C NMR of product 4j in CDCl$_3$. 
Figure 5.42 $^1$H and $^{13}$C NMR of product 4k in CDCl$_3$. 
Figure 5.43 $^1$H and $^{13}$C NMR of product 4l in CDCl$_3$. 
Figure 5.44 $^1$H and $^{13}$C NMR of product 4m in CDCl$_3$. 
Figure 5.45 $^1$H and $^{13}$C NMR of product 4n in CDCl$_3$. 
Figure 5.46 $^1$H and $^{13}$C NMR of product 6a in CDCl$_3$. 

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Figure 5.47 $^1$H and $^{13}$C NMR of product 6b in CDCl$_3$. 
Figure 5.48 $^1$H and $^{13}$C NMR of product 6c in CDCl$_3$. 
Figure 5.49 $^1$H and $^{13}$C NMR of product 6d in CDCl$_3$. 
Figure 5.50 $^1$H and $^{13}$C NMR of product 6e in CDCl$_3$. 
Figure 5.51 $^1$H and $^{13}$C NMR of product 7a in CDCl$_3$. 
Figure 5.52 $^1$H and $^{13}$C NMR of product 7b in CDCl$_3$. 
Figure 5.53 $^1$H and $^{13}$C NMR of product 8a in CDCl$_3$. 
Figure 5.54 $^1$H and $^{13}$C NMR of product 8b in CDCl$_3$. 
Figure 5.55 $^1$H and $^{13}$C NMR of product 8c in CDCl$_3$. 